

Supporting Information:

From Humorous Post to Detailed Quantum-Chemical Study:

Isocyanate Synthesis Revisited

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1 Computation details

All calculations were carried out using the quantum-chemical package Orca 5^{S1} and solvation effects were accounted for using conductor-like polarizable continuum model (CPCM),^{S2,S3} unless otherwise specified in the sections. Geometry optimizations were performed out without symmetry constraints using the DFT functionals B3LYP,^{S4-S6} PBE,^{S7} PBE0,^{S8} r²SCAN,^{S9} ω B97X.^{S10} Dispersion corrections used were D3(BJ)^{S11} and D4.^{S12,S13} Analytical frequency calculations were performed to confirm the nature of the stationary points.

Based on the DFT geometries, the accurate single-point energies of the structures were obtained using the DLPNO-CCSD(T) level of theory,^{S14} including the CPCM-based results.^{S15} The basis sets used were 6-31G,^{S16} def2-TZVP, def2-TZVPP,^{S17} and cc-pVQZ.^{S18} With DLPNO-CCSD(T) calculations, a complete basis set (CBS) extrapolation scheme CBS(3/4) based on cc-pVTZ and cc-pVQZ basis sets was applied.^{S19-S21}

2 Conversion of phenyl nitrile oxide

2.1 The SO₂-catalyzed conversion

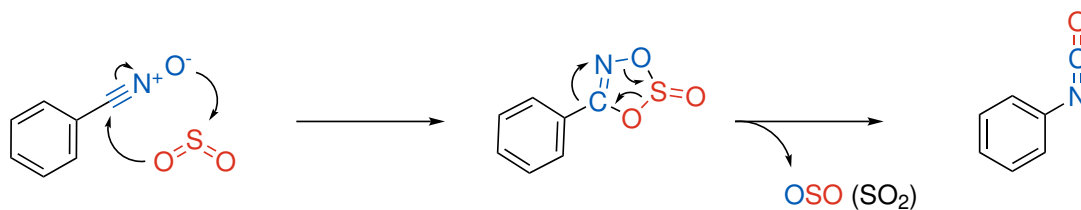
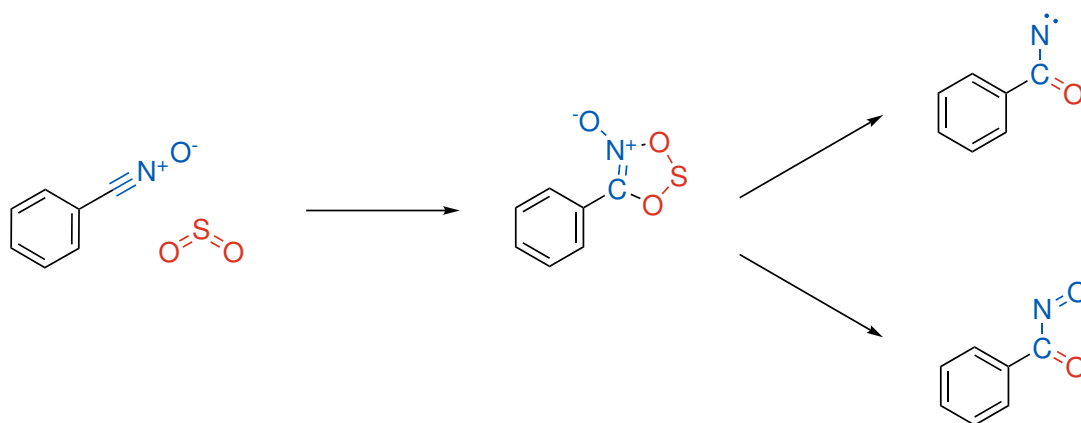
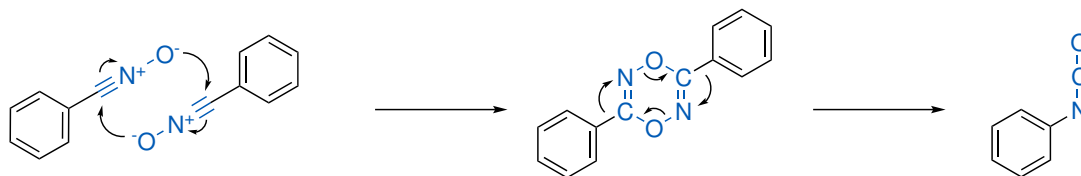


Figure S1 Reaction of the phenyl nitrile oxide with sulfur dioxide.



(a) The SO₂-catalyzed conversion.



(b) Reaction of the phenyl nitrile oxide with phenyl nitrile oxide.

Figure S2 Alternative reaction pathways.

2.1.1 Initial screening

Metadynamics simulations

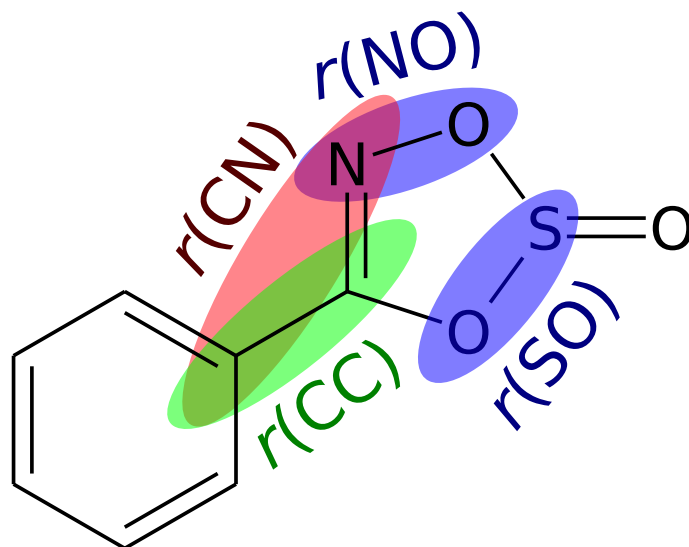


Figure S3 Definition of the internal coordinates of the intermediate, used to define the collective variable (CV).

To produce the TS2 in the dynamics, we used bond-breaking Bohmian metadynamics (BBBMTD) simulations.^{S22} We used the PyRAMD^{S23,S24} software with forces at the B3LYP-D3(BJ)/6-31G level of theory, obtained from the ORCA 5 package. The following settings were applied:

- time step was 1 fs;
- total duration of the trajectories was 5 ps;
- update period of the bias potential was 10 fs;
- bias potential width was $\sigma = 0.05 \text{ \AA}$;
- initial velocities were sampled from 300 K Maxwell-Boltzmann distribution;
- initial structure was the equilibrium structure at the B3LYP-D3(BJ)/6-31G level of theory;
- Berendsen thermostat with a relaxation time of 100 fs was used to force the temperature to be 300 K.

The collective variables were defined as

$$\text{CV} = c_{\text{CN}} \cdot r(\text{CN}) + c_{\text{CC}} \cdot r(\text{CC}) + c_{\text{NO}} \cdot r(\text{NO}) + c_{\text{SO}} \cdot r(\text{SO}) ,$$

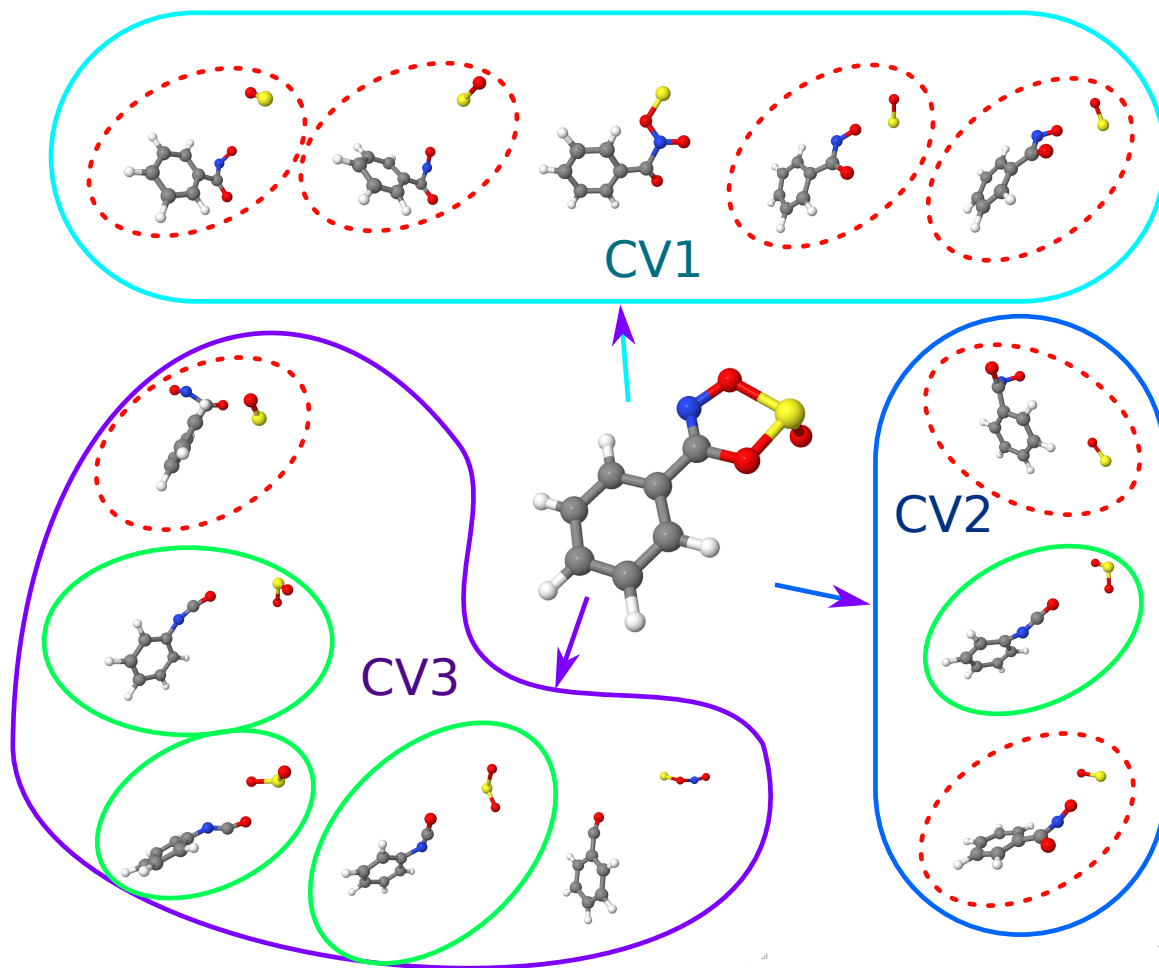


Figure S4 Products of the BBBMTD simulations with various CVs. The green solid ellipses indicated the desired product of the reaction ($\text{Ph-NCO} + \text{SO}_2$), whether the dashed red ellipses indicate the N-oxobenzamide production ($\text{Ph-CO-N=O} + \text{SO}$)

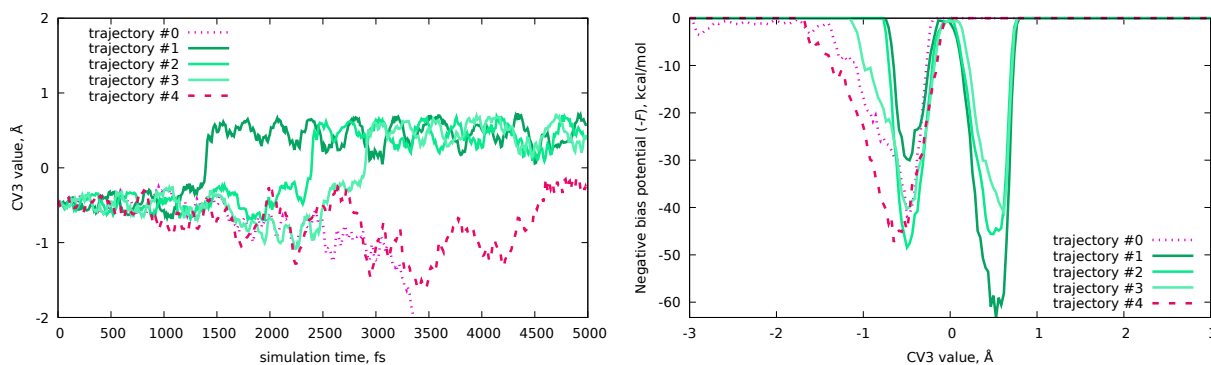


Figure S5 Left: values of the CV3 during the BBBMTD simulations for five trajectories in the third batch of simulations. Right: the resulting negative bias potential from these simulations. The green solid lines indicate the trajectories of the desired reaction and the red dashed ones – of the undesired products.

where the definition of four interatomic distances $r(\text{CN})$, $r(\text{CC})$, $r(\text{NO})$, and $r(\text{SO})$ is given in Figure S3, and c_{XY} are the coefficients for distances $r(XY)$. Three different CVs were tested, with consecutive lowering of the weights for $r(\text{NO})$ and $r(\text{SO})$ distances.

- CV1 had parameters $c_{\text{CN}} = -0.25$, $c_{\text{CC}} = +0.25$, $c_{\text{NO}} = +0.25$, and $c_{\text{SO}} = +0.25$. The bias potential height, in this case, was 0.3 kcal/mol.

- CV2 had parameters $c_{\text{CN}} = -0.5$, $c_{\text{CC}} = +0.5$, $c_{\text{NO}} = +0.1$, and $c_{\text{SO}} = +0.1$. The bias potential height, in this case, was 0.8 kcal/mol.
- CV3 had parameters $c_{\text{CN}} = -0.5$, $c_{\text{CC}} = +0.5$, $c_{\text{NO}} = +0.1$, and $c_{\text{SO}} = +0.1$. The bias potential height, in this case, was 0.8 kcal/mol.

In each case, five trajectories were initiated. In the CV2 case, two of them crashed. The resulting structures are given in Figure S4. The desired product yields increase as we decrease $r(\text{NO})$ and $r(\text{SO})$ contributions to the CV, which makes CV3 the most efficient reaction coordinate of all tested. The resulting CV3 trajectories and the bias potentials are given in Figure S5.

Reaction pathway calculations *Reaction pathway*

Table S1 Energy profile of the SO_2 -catalyzed conversion. The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-13.8	-12.7	-40.3	-1.1	-63.9	-55.2
	$E + \Delta\text{ZPE}$, kcal/mol	0.0	-12.8	-11.7	-37.9	-1.2	-62.7	-54.7
	$E + \Delta G$, kcal/mol	0.0	-1.3	0.5	-24.9	11.0	-51.8	-54.6

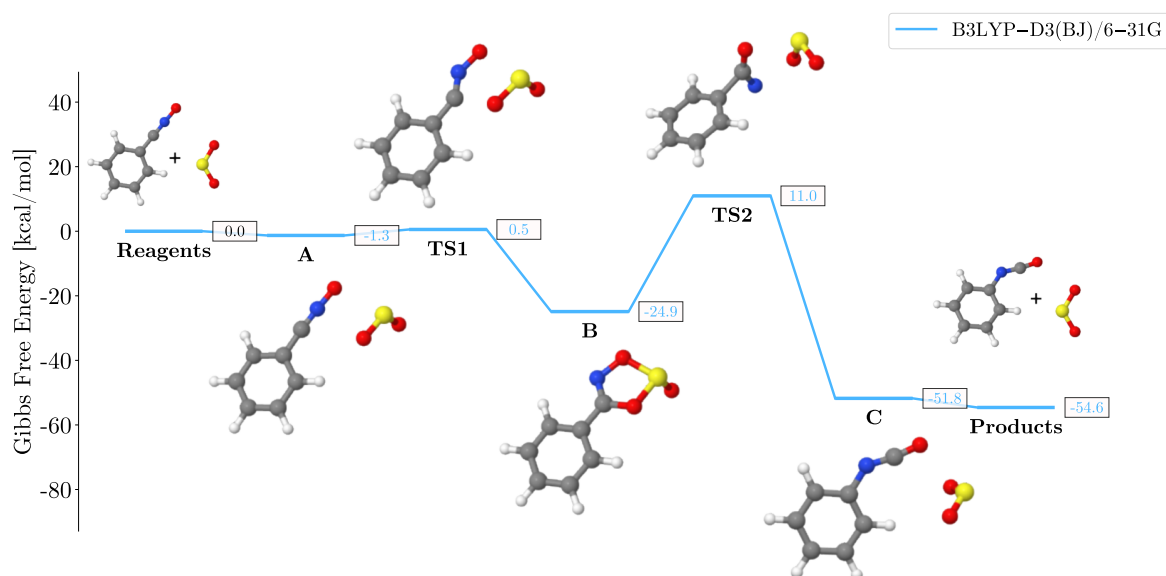


Figure S6 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. B3LYP-D3(BJ)/6-31G electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S2 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.082735	-0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	-1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	-0.505698	0.592333
C	1.800258	-1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	-1.150542	0.096505	0.259821
H	-0.255928	-2.222203	0.354837
H	3.745041	-0.664438	0.685138
H	2.193632	-2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S3 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.083522	0.068703	-0.140480
C	0.675208	1.225864	-0.315973
C	0.500636	-1.081616	0.405449
C	2.034406	1.228211	0.060630
C	2.625463	0.070936	0.613934
C	1.850263	-1.076393	0.780503
H	0.230057	2.120195	-0.737311
C	2.837489	2.390159	-0.106465
H	-1.129118	0.064097	-0.428267
H	-0.094856	-1.978540	0.538945
H	3.668155	0.105474	0.906628
H	2.300554	-1.966974	1.205049
N	3.521914	3.326509	-0.256243
O	4.392121	4.247197	-0.311625
O	5.152471	1.858660	1.391347
S	6.246697	2.999476	1.015233
O	7.280662	2.514544	-0.123953

Table S4 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

TS1 at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.100035	-0.013477	-0.020613
C	0.791744	1.030049	-0.262819
C	0.355936	-1.218065	0.531465
C	2.158733	0.861295	0.049685
C	2.620374	-0.349093	0.603514
C	1.711789	-1.380758	0.841266
H	0.446503	1.965341	-0.689057

C	3.079445	1.921564	-0.196977
H	-1.150012	0.113029	-0.260797
H	-0.343870	-2.025417	0.719101
H	3.672383	-0.448811	0.836635
H	2.063243	-2.313080	1.269165
N	3.479377	2.961680	-0.614367
O	4.405065	3.832921	-0.749381
O	5.032561	1.439439	0.792926
S	6.191213	2.489252	0.262806
O	6.959950	1.931131	-1.041855

Table S5 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

B ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.053471	0.075389	-0.108728
C	1.052831	1.036600	-0.247192
C	0.346957	-1.171179	0.461536
C	2.361738	0.752768	0.186618
C	2.656765	-0.497089	0.755988
C	1.647946	-1.453388	0.892116
H	0.837164	2.002447	-0.688820
C	3.407823	1.761713	0.044035
H	-0.953535	0.296333	-0.445710
H	-0.434422	-1.916402	0.567900
H	3.666884	-0.707868	1.084480
H	1.878398	-2.417198	1.333073
N	3.217077	2.933592	-0.479589
O	4.370590	3.743610	-0.492799
O	4.677438	1.419534	0.517898
S	5.930804	2.712320	0.014739
O	6.656471	2.225820	-1.324845

Table S6 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.217146	-0.005995	-0.491781
C	1.303771	0.868271	-0.524373
C	0.226287	-1.101424	0.385009
C	2.402395	0.607338	0.309133
C	2.412132	-0.465553	1.213228
C	1.318338	-1.331682	1.235139
H	1.315685	1.732478	-1.177719
C	3.795421	1.341414	-0.022100
H	-0.637730	0.171010	-1.134432
H	-0.626704	-1.771002	0.414787
H	3.259727	-0.608855	1.872633
H	1.308801	-2.173176	1.918522
N	3.392574	2.160794	0.867297

O	5.205147	3.425237	0.668495
O	4.685083	1.035101	-0.856817
S	6.092573	3.022235	-0.653510
O	5.703757	3.890810	-1.952809

Table S7 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.313454	0.119052	1.713104
C	2.156653	0.756292	0.801138
C	0.484346	-0.932687	1.302966
C	2.161501	0.328123	-0.537421
C	1.337386	-0.725296	-0.958503
C	0.500658	-1.352395	-0.032417
C	3.790904	1.748376	-1.851788
N	2.989396	0.952560	-1.468477
O	6.868578	3.896521	0.174491
O	4.597663	2.522891	-2.321809
S	5.323967	4.189202	-0.166904
O	4.301658	3.273255	0.682161
H	2.807099	1.569998	1.101485
H	1.305911	0.446666	2.747294
H	-0.167911	-1.421687	2.018626
H	1.361564	-1.037781	-1.995758
H	-0.137326	-2.168191	-0.355285

Table S8 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235
H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

Table S9 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

3

Sulfur dioxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

S	0.000000	0.000000	0.464422
O	0.000000	1.351922	-0.413795
O	0.000000	-1.351922	-0.413795

Alternative reaction pathways (a)

While species of the main discussed pathway (Figure 4/Figure 5 of main text) have "classical" structures and "normal" electronic structures, among species on alternative pathways there are few with less intuitive structure that are more demanding to a description of their electronic structure. We performed extensive study with different approaches that are not always consistent. In particular r²SCAN-3c and B3LYP/6-31G even demonstrate qualitatively different mechanisms that are consistent just on the point that alternative reactions (that imminently results in alternative products) are not going. Herewith we present (Fig S7) results obtained with B3LYP/6-31G. We would like to point out that relative energy of some species (i.e., with monocoordinated sulfur) being quite robust with respect to different functionals demonstrate strong artificial overstabilisation with small basis sets.

Table S10 Relative energy of B2 vs R with different DFT functionals and basis sets (all calculations are UKS singpoints performed on r²SCAN-3c geometry)

Functional/basis set	Energy of B2 vs R, (S7) kcal/mol
B3LYP-D3BJ/6-31G	-58.5
TPSS-D3BJ/6-31G	-57.7
B3LYP-D3BJ/6-311G*	+14.1
r ² SCAN-3c	+20.0
B3LYP-D3BJ/def2-TZVP	+37.5
TPSS-D3BJ/def2-TZVP	+35.5

Keeping that in mind we recommend to take values on following figure cautiously.

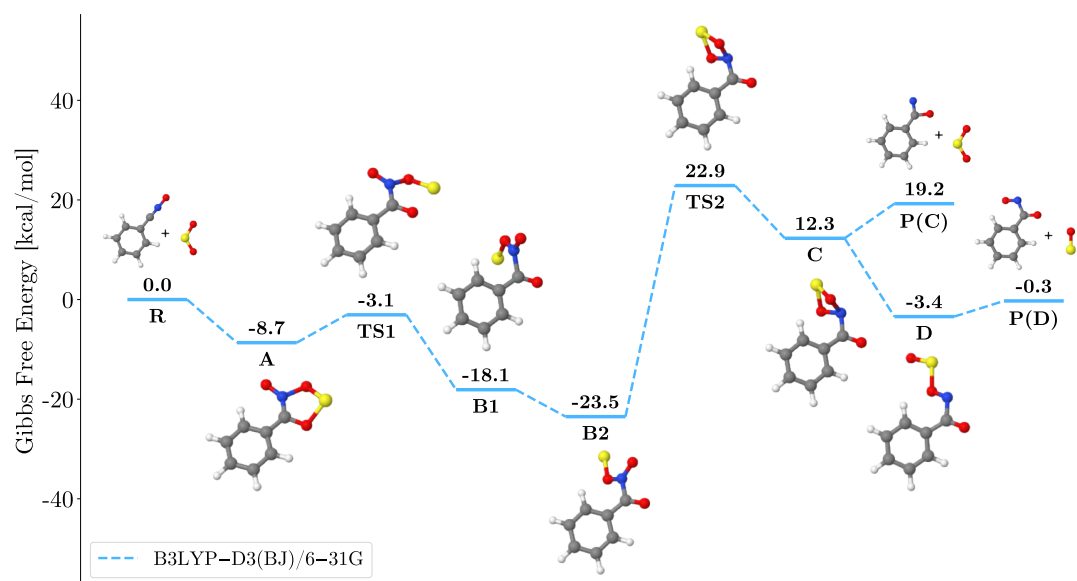


Figure S7 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide (alternative reaction pathways (a)). B3LYP-D3(BJ)/6-31G electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Wiberg bond analysis (Fig. S8) was performed with Multiwfn software,^{S25} following images were generated by code of D.Tikhonov that is available from <https://habr.com/ru/articles/600093/> (make_tikz_picture_bond_orders.py)

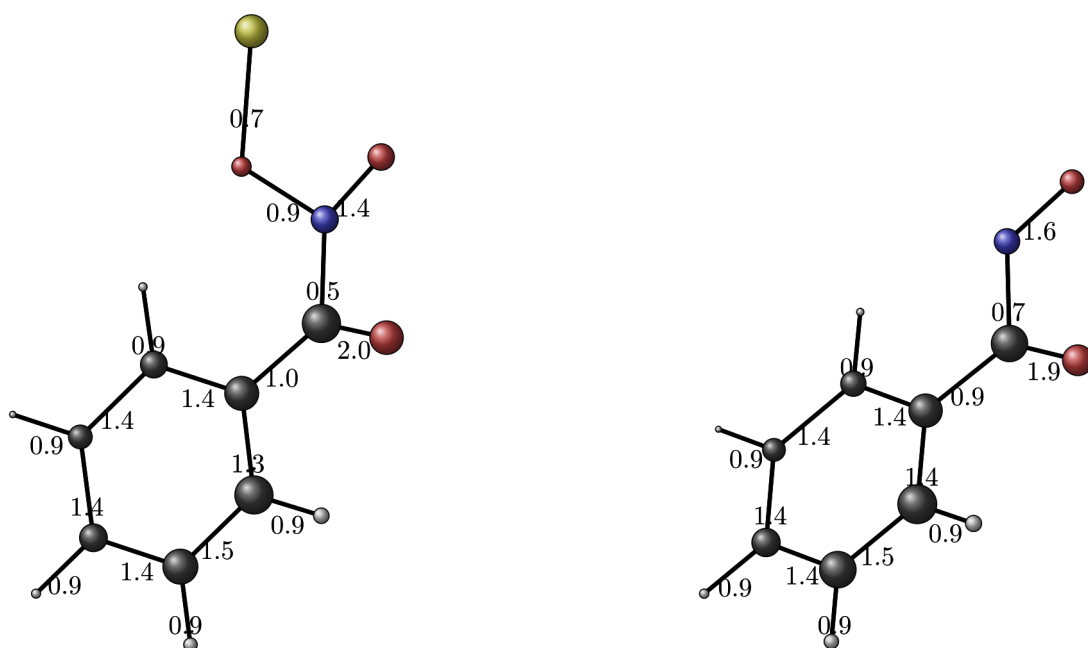


Figure S8 Wiberg bond order for B2 (left) and P(D) (right)

Table S11 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.082735	-0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	-1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	-0.505698	0.592333
C	1.800258	-1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	-1.150542	0.096505	0.259821
H	-0.255928	-2.222203	0.354837
H	3.745041	-0.664438	0.685138
H	2.193632	-2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S12 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.398673	0.285616	-0.084095
C	1.421253	1.200118	-0.339074
C	0.685971	-0.966831	0.471165
C	2.754749	0.858882	-0.031520
C	3.042502	-0.403600	0.529704
C	2.010384	-1.306982	0.775200
H	1.197581	2.167813	-0.768157
C	3.859144	1.770621	-0.289296
H	-0.625222	0.553753	-0.321065
H	-0.115027	-1.672007	0.666626
H	4.068327	-0.658812	0.762566
H	2.238601	-2.275881	1.206167
N	3.718594	3.009702	-0.707982
O	2.744945	3.746775	-1.014973
O	5.182008	3.644491	-1.051503
S	6.266983	2.743954	0.055764
O	5.141735	1.275204	-0.110829

Table S13 Cartesian coordinates of the transition state between pre-intermediate and post-intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

TS1 at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.411175	0.278150	-0.203347
C	1.449262	1.202744	-0.328758
C	0.647601	-0.985431	0.350389
C	2.744770	0.857214	0.102966
C	2.979013	-0.415730	0.667960

C	1.935260	-1.329853	0.783444
H	1.259499	2.180520	-0.751008
C	3.901608	1.747130	-0.035101
H	-0.584460	0.548049	-0.537823
H	-0.166569	-1.695731	0.449605
H	3.978845	-0.666153	1.000058
H	2.122115	-2.306682	1.215911
N	3.743133	3.038419	-0.485416
O	2.707648	3.733813	-0.690239
O	4.937152	3.390894	-1.378044
S	6.433239	2.824942	-0.596647
O	5.100008	1.317838	0.242445

Table S14 Cartesian coordinates of the post-intermediate (B1) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

B1 ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.702331	0.299501	-0.618122
C	1.772833	1.180326	-0.478193
C	0.736632	-0.952203	0.011878
C	2.883844	0.805988	0.299511
C	2.919534	-0.453587	0.930286
C	1.844807	-1.327581	0.784418
H	1.752068	2.140191	-0.981432
C	4.028127	1.682021	0.483787
H	-0.153546	0.583477	-1.219489
H	-0.098622	-1.635133	-0.101055
H	3.786934	-0.723699	1.521484
H	1.867903	-2.297229	1.268723
N	3.796827	3.148356	-0.096072
O	3.394933	4.055993	0.650976
O	4.142566	3.412293	-1.359563
S	4.781436	2.006812	-2.372522
O	5.042266	1.537715	1.140435

Table S15 Cartesian coordinates of the pre-intermediate (B2) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

B2 ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.649806	0.347137	-0.563650
C	1.620917	1.302964	-0.264446
C	0.822741	-0.985077	-0.169333
C	2.780105	0.922688	0.441861
C	2.941022	-0.419463	0.851832
C	1.970409	-1.366787	0.540216
H	1.476328	2.327915	-0.574852
C	3.832490	1.845861	0.860913
H	-0.241776	0.643139	-1.104640
H	0.065086	-1.723198	-0.410531
H	3.830513	-0.694010	1.406658

H	2.103704	-2.397884	0.847613
N	3.876115	3.220381	0.208178
O	4.358497	4.219378	0.766081
O	3.501033	3.225574	-1.112299
S	3.670885	4.758202	-2.038866
O	4.691924	1.658418	1.713831

Table S16 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.742988	0.462666	-0.568205
C	1.788571	1.346092	-0.298601
C	0.809411	-0.864081	-0.124867
C	2.904462	0.901218	0.434636
C	2.964231	-0.432676	0.887497
C	1.920977	-1.310712	0.604145
H	1.733794	2.369799	-0.641380
C	4.009655	1.787717	0.814636
H	-0.120332	0.807574	-1.126216
H	-0.002430	-1.549093	-0.346377
H	3.828676	-0.754048	1.457020
H	1.969403	-2.337652	0.949117
N	4.176826	3.074419	0.038671
O	3.234280	4.020810	0.434670
O	3.949191	3.041650	-1.461104
S	3.198203	4.781312	-1.507348
O	4.848583	1.575571	1.685108

Table S17 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.748435	0.446389	-0.611005
C	1.795148	1.338801	-0.373314
C	0.799954	-0.857271	-0.105098
C	2.909684	0.927152	0.385228
C	2.949592	-0.388228	0.898648
C	1.904544	-1.273505	0.652293
H	1.740901	2.343209	-0.758243
C	4.057050	1.783923	0.713917
H	-0.108269	0.770976	-1.191345
H	-0.016030	-1.546340	-0.297354
H	3.809793	-0.690120	1.484624
H	1.946196	-2.282992	1.046474
N	4.279593	3.131189	0.081939
O	3.017179	4.005641	0.383603
O	3.953617	3.025284	-1.441474
S	3.227836	4.736485	-1.318607
O	4.947929	1.485148	1.514663

Table S18 Cartesian coordinates of the post-intermediate (D) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

D ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.726197	0.829250	0.556157
C	1.559116	1.476108	-0.359015
C	1.112543	-0.390461	1.123060
C	2.795381	0.901292	-0.713612
C	3.186184	-0.317732	-0.121908
C	2.346458	-0.962381	0.783216
H	1.247403	2.419970	-0.783510
C	3.765295	1.520259	-1.639149
H	-0.222935	1.279083	0.825957
H	0.458317	-0.891140	1.829187
H	4.147586	-0.739208	-0.391026
H	2.649324	-1.906074	1.223675
N	3.402230	2.579168	-2.574732
O	2.123261	2.578593	-2.871235
O	-0.111695	3.581074	-4.234908
S	1.477579	3.894816	-4.135141
O	4.969034	1.209697	-1.691009

Table S19 Cartesian coordinates of the product C (P(C)) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

P(C) ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.737343	0.446120	-0.608554
C	1.776550	1.337569	-0.344066
C	0.800469	-0.867506	-0.122230
C	2.882167	0.909059	0.410892
C	2.947121	-0.406115	0.898397
C	1.903412	-1.292758	0.629646
H	1.737998	2.357075	-0.714611
C	3.972986	1.810843	0.700878
H	-0.118693	0.770216	-1.189978
H	-0.009960	-1.558413	-0.329713
H	3.810200	-0.715272	1.478446
H	1.947808	-2.309836	1.003080
N	4.321134	3.027780	0.464128
O	5.103367	1.595061	1.410204

Table S20 Cartesian coordinates of the product D (P(D)) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

15

P(D) ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.712744	0.765462	0.550544
C	1.537926	1.397208	-0.381585
C	1.134394	-0.411519	1.180246

C	2.797403	0.846012	-0.688854
C	3.218753	-0.336713	-0.046427
C	2.389392	-0.962001	0.880959
H	1.201409	2.304189	-0.866045
C	3.719882	1.456697	-1.652181
H	-0.257083	1.190412	0.784455
H	0.489000	-0.898178	1.904113
H	4.193238	-0.742798	-0.293010
H	2.714730	-1.873023	1.371285
N	3.345217	2.764087	-2.318132
O	2.302943	2.702826	-2.997050
O	4.844385	1.042115	-1.954713

Table S21 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

3

Sulfur dioxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

S	0.000000	0.000000	0.464422
O	0.000000	1.351922	-0.413795
O	0.000000	-1.351922	-0.413795

Table S22 Cartesian coordinates of the sulfur oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

2

Sulfur oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

S	0.000000	-0.011110	0.471639
O	0.000000	1.363032	-0.421012

Alternative reaction pathways (b)

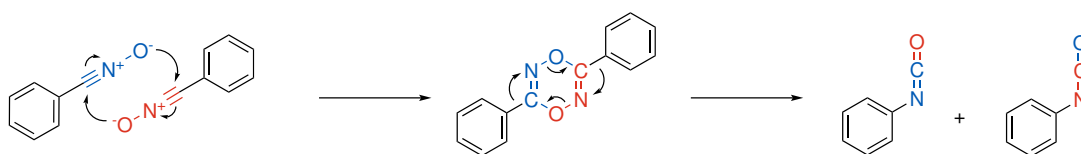


Figure S9 Reaction of the phenyl nitrile oxide with phenyl nitrile oxide (alternative reaction pathways (b)).

Table S23 Energy profile of the autocatalyzed conversion (alternative reaction pathways (b)). The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagent	B	TS2
Gas phase	E , kcal/mol	0.0	-45.0	10.8
	$E + \Delta ZPE$, kcal/mol	0.0	-42.0	10.4
	$E + \Delta G$, kcal/mol	0.0	-26.9	24.3

Table S24 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.082735	-0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	-1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	-0.505698	0.592333
C	1.800258	-1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	-1.150542	0.096505	0.259821
H	-0.255928	-2.222203	0.354837
H	3.745041	-0.664438	0.685138
H	2.193632	-2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S25 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

28

B ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.645467	-0.398530	-0.792458
C	1.930777	0.133179	-0.918262
C	0.095213	-0.617502	0.475705
C	2.672704	0.442979	0.234541
C	2.122367	0.215832	1.510299
C	0.835597	-0.308032	1.625378
H	2.367249	0.310810	-1.893045
C	4.022063	0.998476	0.104704
H	0.074146	-0.639150	-1.682586
H	-0.903860	-1.030557	0.569703
H	2.710317	0.448068	2.390478
H	0.411634	-0.482595	2.608441
N	4.618808	1.565875	1.111643
O	6.049338	1.913174	0.746370
O	4.599224	0.876121	-1.152409
N	5.466264	2.057885	-1.543095
C	6.187386	2.440953	-0.530513
C	7.210164	3.479726	-0.675687
C	7.735462	4.108935	0.466068
C	7.667609	3.844915	-1.956043
C	8.709137	5.100041	0.324110
C	8.635001	4.839993	-2.087659
C	9.158414	5.468766	-0.949190
H	7.376950	3.816571	1.444998
H	7.263015	3.342646	-2.826834
H	9.114240	5.584948	1.205764
H	8.986826	5.120900	-3.074527
H	9.915005	6.239383	-1.055492

Table S26 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.437474	0.168402	-0.736901
C	1.552131	0.971575	-0.517064
C	0.173570	-0.913092	0.121694
C	2.411323	0.658520	0.554579
C	2.140690	-0.404176	1.436711
C	1.018595	-1.198338	1.204867
H	1.777379	1.819516	-1.153188
C	3.990518	1.133631	0.419986
H	-0.231294	0.382523	-1.562497
H	-0.701347	-1.530688	-0.051050
H	2.806050	-0.588871	2.271826
H	0.796279	-2.028765	1.864879
N	3.430795	1.949226	1.182416
O	5.922750	2.600526	1.170974
O	4.921949	0.615848	-0.289260
N	5.969484	1.667226	-0.992289
C	6.348161	2.546743	-0.034109
C	7.357669	3.536665	-0.543687
C	7.766205	4.542943	0.343390
C	7.893708	3.489204	-1.841976
C	8.702975	5.496381	-0.063095
C	8.828723	4.446087	-2.244225
C	9.235468	5.451092	-1.357019
H	7.337454	4.552813	1.338533
H	7.581067	2.707435	-2.524433
H	9.016860	6.272655	0.627695
H	9.242221	4.406830	-3.247122
H	9.963486	6.192236	-1.672309

Table S27 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235
H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

2.1.2 r²SCAN-3c

Table S28 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-7.3	0.7	-24.2	1.6	-62.5	-58.2
	$E + \Delta ZPE$, kcal/mol	0.0	-6.4	1.5	-21.7	2.1	-61.4	-57.6
	$E + \Delta G$, kcal/mol	0.0	4.5	14.1	-8.5	14.8	-50.9	-57.3
Benzene	E , kcal/mol	0.0	-6.2	1.7	-22.8	1.3	-60.5	-57.6
	$E + \Delta ZPE$, kcal/mol	0.0	-5.4	2.5	-20.3	1.8	-59.6	-57.1
	$E + \Delta G$, kcal/mol	0.0	6.1	15.0	-7.3	14.4	-47.8	-56.9
Toluene	E , kcal/mol	0.0	-6.1	1.7	-22.7	1.3	-60.7	-57.6
	$E + \Delta ZPE$, kcal/mol	0.0	-5.3	2.5	-20.3	1.7	-59.7	-57.0
	$E + \Delta G$, kcal/mol	0.0	5.5	15.0	-7.3	14.3	-49.3	-56.9

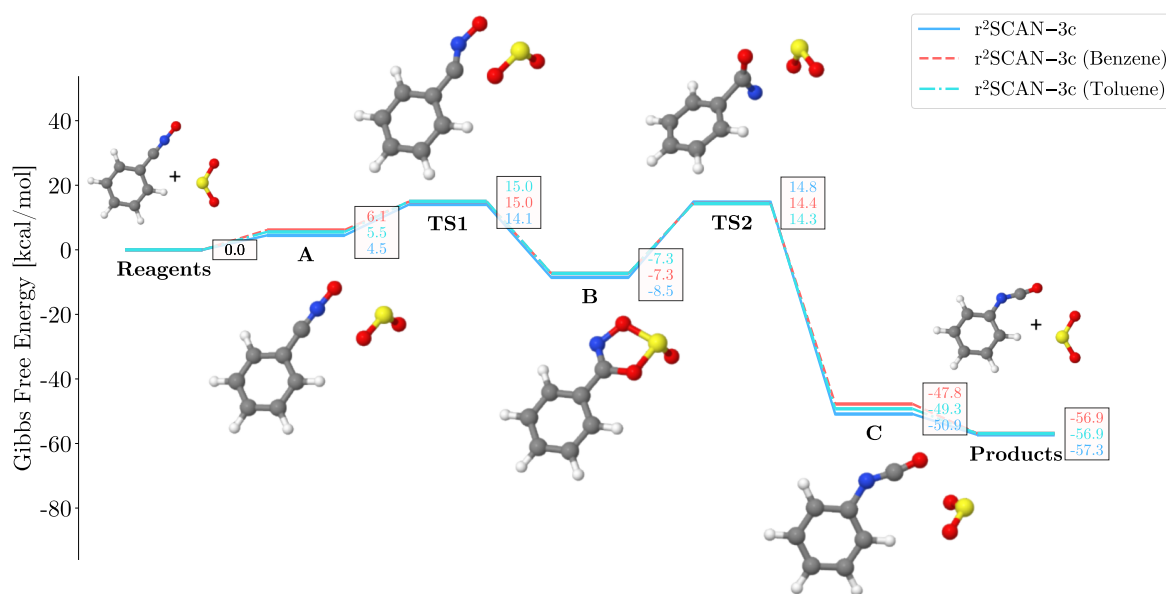


Figure S10 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S29 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−6.6	7.0	−25.1	7.7	−64.5	−60.9
	$E + \Delta ZPE$, kcal/mol	0.0	−5.8	7.9	−22.7	8.1	−63.4	−60.3
	$E + \Delta G$, kcal/mol	0.0	5.2	20.4	−9.5	20.8	−52.9	−60.0
Benzene	E , kcal/mol	0.0	−5.2	7.9	−23.4	8.0	−62.8	−60.0
	$E + \Delta ZPE$, kcal/mol	0.0	−4.4	8.8	−21.0	8.4	−61.9	−59.4
	$E + \Delta G$, kcal/mol	0.0	7.1	21.2	−8.0	21.0	−50.1	−59.3

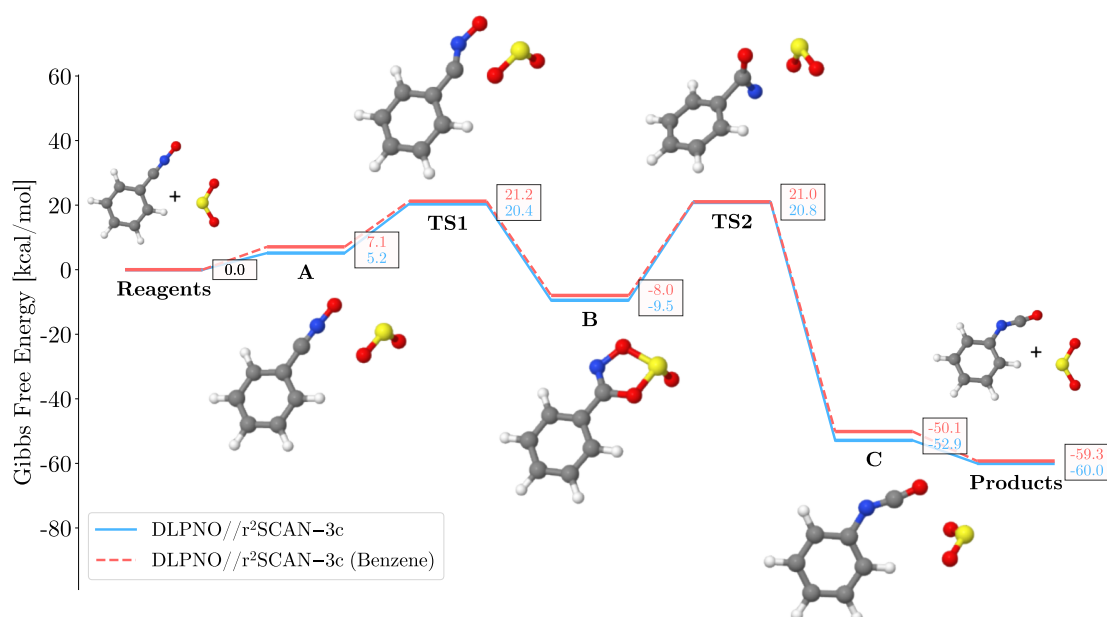


Figure S11 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S30 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021

H	-0.248893	-2.210375	0.356466
H	3.744529	-0.661291	0.684203
H	2.194048	-2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

14

Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	-0.070011	-0.064477	0.353451
C	0.790463	1.022328	0.417736
C	0.430226	-1.364123	0.407122
C	2.174624	0.809409	0.537228
C	2.677066	-0.502349	0.591715
C	1.802309	-1.577563	0.526116
H	0.406907	2.036617	0.376609
C	3.061424	1.912690	0.602594
H	-1.138734	0.104487	0.260883
H	-0.248747	-2.210021	0.356343
H	3.746414	-0.661821	0.684516
H	2.194673	-2.589276	0.568175
N	3.800741	2.809808	0.648216
O	4.568944	3.742590	0.695297

14

Phenyl nitrile oxide ES at r2SCAN-3c in the toluene

C	-0.070195	-0.064536	0.353500
C	0.790307	1.022414	0.417688
C	0.430123	-1.364253	0.407164
C	2.174569	0.809494	0.537186
C	2.677148	-0.502310	0.591616
C	1.802345	-1.577637	0.526068
H	0.406579	2.036686	0.376353
C	3.061402	1.912838	0.602611
H	-1.138948	0.104420	0.260887
H	-0.248817	-2.210221	0.356493
H	3.746538	-0.661870	0.684321
H	2.194812	-2.589346	0.568284
N	3.800970	2.809881	0.648319
O	4.569466	3.742742	0.695511

Table S31 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

A ES at r2SCAN-3c in the gas phase

C	-0.082811	0.057737	-0.195501
C	0.678572	1.207382	-0.345952
C	0.472590	-1.083616	0.377910
C	2.015118	1.214209	0.083303
C	2.576750	0.063577	0.662489
C	1.798962	-1.075809	0.804019
H	0.253281	2.100489	-0.791763

C	2.812738	2.375391	-0.059093
H	-1.116301	0.053044	-0.528024
H	-0.128947	-1.980166	0.492753
H	3.610157	0.087042	0.991722
H	2.232506	-1.965072	1.251316
N	3.517916	3.292624	-0.156450
O	4.291297	4.225637	-0.230768
O	5.490193	1.954256	1.474011
S	6.410209	2.978855	0.934471
O	7.176368	2.610922	-0.267042

17

A ES at r2SCAN-3c in the benzene

C	-0.098478	0.075217	-0.179121
C	0.688832	1.207622	-0.331034
C	0.435791	-1.084170	0.379906
C	2.030571	1.175628	0.082119
C	2.571438	0.007851	0.646278
C	1.767410	-1.113537	0.790222
H	0.280764	2.114545	-0.765087
C	2.852392	2.319571	-0.062897
H	-1.135826	0.098473	-0.498970
H	-0.186768	-1.966257	0.495974
H	3.609083	-0.000512	0.963225
H	2.183867	-2.016515	1.226279
N	3.537910	3.247102	-0.186938
O	4.302063	4.191163	-0.281933
O	5.548879	2.035035	1.508755
S	6.413146	3.096718	0.948320
O	7.207527	2.728568	-0.237698

17

A ES at r2SCAN-3c in the toluene

C	-0.105237	0.081302	-0.162096
C	0.686306	1.209846	-0.320883
C	0.430166	-1.083062	0.385815
C	2.033640	1.168405	0.073431
C	2.575544	-0.004145	0.626689
C	1.767118	-1.121450	0.778153
H	0.277747	2.120731	-0.746157
C	2.859964	2.307961	-0.080077
H	-1.146810	0.111381	-0.467454
H	-0.195841	-1.961991	0.507534
H	3.617400	-0.018998	0.929587
H	2.184162	-2.028216	1.205786
N	3.545369	3.234009	-0.216788
O	4.311076	4.175865	-0.322296
O	5.534504	2.055354	1.521360
S	6.402394	3.120434	0.973088
O	7.231097	2.749073	-0.188290

Table S32 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

TS1 at r2SCAN-3c in the gas phase

C	-2.412483	-0.743353	-0.358515
C	-1.541814	0.326389	-0.492368
C	-1.962370	-1.958609	0.154071
C	-0.193869	0.169107	-0.125463
C	0.260877	-1.052165	0.391117
C	-0.629900	-2.106483	0.530034
H	-1.884208	1.279249	-0.882437
C	0.707384	1.256600	-0.276040
H	-3.451978	-0.625180	-0.648891
H	-2.652737	-2.789516	0.262611
H	1.300722	-1.149793	0.680886
H	-0.279340	-3.051814	0.932451
N	0.989253	2.293962	-0.816539
O	1.854938	3.190330	-0.769989
O	2.234904	1.217785	1.076953
S	3.350598	2.163475	0.649248
O	4.310024	1.580017	-0.307126

17

TS1 at r2SCAN-3c in the benzene

C	-2.428861	-0.707308	-0.255795
C	-1.548203	0.350219	-0.424960
C	-1.962206	-1.949095	0.172928
C	-0.178019	0.148282	-0.185107
C	0.293605	-1.099820	0.248985
C	-0.605352	-2.140428	0.428306
H	-1.899816	1.324836	-0.747633
C	0.733970	1.219750	-0.371046
H	-3.486822	-0.559140	-0.449659
H	-2.659811	-2.769656	0.311970
H	1.352335	-1.231338	0.444397
H	-0.245432	-3.107347	0.765997
N	1.094461	2.181695	-0.999519
O	1.960381	3.086118	-0.916005
O	2.062019	1.367359	1.162364
S	3.217422	2.284336	0.777564
O	4.300329	1.601539	0.037215

17

TS1 at r2SCAN-3c in the toluene

C	-0.049597	0.083098	0.143627
C	0.872665	1.077947	-0.143066
C	0.380602	-1.176710	0.558306
C	2.245400	0.793629	-0.036505
C	2.680882	-0.472881	0.381797
C	1.742073	-1.449181	0.680515
H	0.550626	2.065881	-0.456105

C	3.196408	1.801326	-0.344011
H	-1.110630	0.294984	0.052863
H	-0.348547	-1.947297	0.790382
H	3.743773	-0.668516	0.472638
H	2.074497	-2.429554	1.007591
N	3.529175	2.747877	-1.009932
O	4.454388	3.594799	-1.042893
O	4.731384	1.840607	0.991743
S	5.878968	2.689278	0.456475
O	6.802332	1.951714	-0.432727

Table S33 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

B ES at r2SCAN-3c in the gas phase

C	0.080939	0.089224	-0.096399
C	1.066144	1.053886	-0.232948
C	0.385478	-1.156396	0.451921
C	2.376079	0.771880	0.177857
C	2.682517	-0.476726	0.727737
C	1.684674	-1.434602	0.862630
H	0.836295	2.026532	-0.655234
C	3.415652	1.785966	0.033438
H	-0.932833	0.309274	-0.416954
H	-0.391430	-1.907685	0.558059
H	3.697373	-0.694535	1.041986
H	1.926110	-2.403472	1.288971
N	3.256906	2.904650	-0.577358
O	4.445167	3.648731	-0.498639
O	4.639541	1.525509	0.594044
S	5.786763	2.670401	-0.001825
O	6.419025	2.084363	-1.186585

17

B ES at r2SCAN-3c in the benzene

C	0.078195	0.089546	-0.092368
C	1.062165	1.056086	-0.230811
C	0.386751	-1.157066	0.452920
C	2.374364	0.773976	0.174381
C	2.685088	-0.475537	0.721578
C	1.688357	-1.434813	0.858832
H	0.824731	2.028870	-0.648954
C	3.414042	1.787993	0.027912
H	-0.937207	0.309420	-0.408133
H	-0.389060	-1.909400	0.561027
H	3.700715	-0.695189	1.032600
H	1.932618	-2.403927	1.283239
N	3.262095	2.901333	-0.596076
O	4.452824	3.647551	-0.508558
O	4.632341	1.533822	0.600813
S	5.785871	2.671954	0.010926

O	6.420509	2.072379	-1.168628
17			
B ES at r2SCAN-3c in the toluene			
C	0.076733	0.090099	-0.089334
C	1.060716	1.056594	-0.229883
C	0.386440	-1.156953	0.454518
C	2.373944	0.773677	0.171663
C	2.685845	-0.476308	0.717470
C	1.689115	-1.435455	0.856894
H	0.822151	2.029920	-0.646184
C	3.413537	1.787562	0.024122
H	-0.939587	0.310525	-0.401843
H	-0.389396	-1.909009	0.564625
H	3.702277	-0.696288	1.025774
H	1.934246	-2.404867	1.280169
N	3.263829	2.897684	-0.606414
O	4.453234	3.646073	-0.515623
O	4.629245	1.536946	0.604015
S	5.784520	2.674805	0.017101
O	6.427551	2.071996	-1.156373

Table S34 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17			
TS2 at r2SCAN-3c in the gas phase			
C	-2.418875	-0.444954	0.161002
C	-1.429819	0.493735	-0.095209
C	-2.071626	-1.770899	0.416499
C	-0.095579	0.087663	-0.053622
C	0.265507	-1.242846	0.165406
C	-0.735013	-2.169490	0.418041
H	-1.672385	1.527869	-0.316790
C	1.019063	1.158141	-0.099213
H	-3.462466	-0.146751	0.146942
H	-2.851028	-2.504369	0.600590
H	1.312393	-1.528134	0.144560
H	-0.475109	-3.207076	0.602691
N	1.094145	1.082448	-1.354248
O	2.480081	2.569269	-1.487510
O	1.535101	1.742441	0.883493
S	3.237708	2.688426	-0.179329
O	4.267902	1.664527	0.046697

17			
TS2 at r2SCAN-3c in the benzene			
C	-2.420321	-0.442347	0.161879
C	-1.432787	0.496571	-0.101286
C	-2.070595	-1.767113	0.423443
C	-0.097699	0.088433	-0.060929
C	0.266998	-1.242656	0.159328

C	-0.733111	-2.166690	0.422625
H	-1.677814	1.530028	-0.324096
C	1.014185	1.151722	-0.113681
H	-3.464167	-0.144849	0.149314
H	-2.849074	-2.500016	0.614394
H	1.313681	-1.529706	0.138827
H	-0.472519	-3.202850	0.614448
N	1.087394	1.109453	-1.370133
O	2.484562	2.585513	-1.472830
O	1.558547	1.720207	0.869952
S	3.230876	2.673799	-0.151943
O	4.261842	1.640498	0.040689

17

TS2 at r2SCAN-3c in the toluene

C	0.277619	0.023264	-0.519592
C	1.378168	0.865450	-0.578792
C	0.263057	-1.044581	0.379301
C	2.470615	0.592840	0.249222
C	2.455919	-0.447682	1.181179
C	1.346345	-1.279974	1.226413
H	1.409371	1.711335	-1.258340
C	3.776327	1.375423	0.024013
H	-0.576158	0.206249	-1.164552
H	-0.608823	-1.690195	0.431000
H	3.304505	-0.598783	1.840694
H	1.319130	-2.104311	1.932151
N	3.489855	2.241768	0.892342
O	5.257635	3.224499	0.694644
O	4.682884	1.103429	-0.808295
S	5.859989	2.927921	-0.669434
O	5.267965	3.690348	-1.781253

Table S35 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

C ES at r2SCAN-3c in the gas phase

C	1.310066	0.426727	1.559844
C	2.028091	1.066344	0.558720
C	0.746689	-0.827709	1.337184
C	2.180810	0.439352	-0.681413
C	1.622998	-0.817891	-0.911862
C	0.906821	-1.445058	0.100371
C	3.443695	2.093093	-1.935511
N	2.894861	1.044427	-1.721078
O	5.639362	1.870188	0.212307
O	4.013979	3.066527	-2.268286
S	5.643295	3.340225	0.279248
O	4.478474	3.988388	0.903331
H	2.477883	2.039689	0.732694
H	1.192967	0.913950	2.523347

H	0.187290	-1.321638	2.125524
H	1.755874	-1.288090	-1.880653
H	0.472345	-2.423627	-0.080864

17

C ES at r2SCAN-3c in the benzene

C	1.371045	0.153756	1.625695
C	2.168426	0.741401	0.651548
C	0.523454	-0.904965	1.304581
C	2.113768	0.258448	-0.659557
C	1.266960	-0.799917	-0.990957
C	0.475323	-1.377114	-0.004508
C	3.740872	1.660504	-1.819678
N	2.897130	0.817953	-1.674151
O	6.802189	3.886226	0.104555
O	4.568167	2.447103	-2.106976
S	5.396144	4.314764	0.099925
O	4.472686	3.586790	0.987323
H	2.826483	1.569930	0.896959
H	1.413763	0.529083	2.644081
H	-0.096586	-1.358210	2.071958
H	1.238579	-1.159592	-2.014535
H	-0.182902	-2.201261	-0.263359

17

C ES at r2SCAN-3c in the toluene

C	1.443892	0.316900	1.591300
C	2.181383	0.926049	0.583928
C	0.719419	-0.846008	1.335070
C	2.189435	0.360965	-0.695226
C	1.471768	-0.805958	-0.959987
C	0.738133	-1.403365	0.059022
C	3.546527	1.940777	-1.959104
N	2.914796	0.941191	-1.742057
O	5.761325	2.229967	0.461820
O	4.175364	2.872653	-2.306585
S	5.564551	3.681896	0.319811
O	4.275781	4.225783	0.778147
H	2.758043	1.825161	0.781044
H	1.438214	0.755735	2.584920
H	0.145311	-1.315944	2.127786
H	1.493429	-1.230343	-1.958685
H	0.178131	-2.310559	-0.148303

Table S36 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117

C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671
H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

14

Phenyl isocyanate ES at r2SCAN-3c in the benzene

C	1.803887	-0.429972	0.365559
C	2.885572	0.376270	0.029182
C	1.991774	-1.778532	0.656905
C	4.166973	-0.174601	-0.015655
C	4.364734	-1.528186	0.275871
C	3.274615	-2.321533	0.610396
H	2.750503	1.428595	-0.199560
C	6.426998	0.559017	-0.497533
H	0.807741	0.001398	0.399657
H	1.144299	-2.404447	0.919050
H	5.366178	-1.948342	0.238437
H	3.430633	-3.372559	0.836012
N	5.233036	0.665626	-0.359073
O	7.586657	0.597866	-0.668250

14

Phenyl isocyanate ES at r2SCAN-3c in the toluene

C	1.803689	-0.429986	0.365651
C	2.885466	0.376431	0.029319
C	1.991701	-1.778679	0.656884
C	4.166954	-0.174452	-0.015502
C	4.364871	-1.528121	0.275880
C	3.274656	-2.321629	0.610346
H	2.750372	1.428767	-0.199540
C	6.427154	0.559075	-0.497608
H	0.807522	0.001463	0.399577
H	1.144171	-2.404632	0.918882
H	5.366326	-1.948350	0.238406
H	3.430621	-3.372683	0.836002
N	5.233232	0.665759	-0.358683
O	7.586866	0.597639	-0.668613

Table S37 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030

0	0.000000	1.259580	-0.373599
0	0.000000	-1.259580	-0.373599

3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
0	0.000000	1.256012	-0.376224
0	0.000000	-1.256011	-0.376224

3

Sulfur dioxide ES at r2SCAN-3c in the toluene

S	0.000000	0.000000	0.389228
0	0.000000	1.256198	-0.376198
0	0.000000	-1.256198	-0.376198

2.1.3 r²SCAN-D4/TZ2P

The calculations were performed in Amsterdam Density Functional (ADF) module of Amsterdam Modeling Suite (AMS). The r²SCAN functional with the charge dependent London-dispersion correction (D4) using all-electron TZ2P Slater Type orbitals basis set. The chemistry of solution was studied with the Conductor like Screening Model (COSMO) of solvation. Hessians were calculated numerically. The Climbing Image Nudge Elastic Band (CI-NEB) method was used as implemented in AMS driver to find transition state (TS) geometries.

Table S38 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−7.0	1.5	−23.1	2.6	−61.5	−57.6
	<i>E</i> + ΔZPE, kcal/mol	0.0	−6.2	2.5	−20.6	3.0	−60.5	−57.0
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.1	15.0	−7.1	15.8	−50.1	−56.6
Benzene	<i>E</i> , kcal/mol	0.0	−5.1	3.6	−21.1	3.2	−59.2	−57.0
	<i>E</i> + ΔZPE, kcal/mol	0.0	−4.2	4.5	−18.6	3.7	−58.3	−56.5
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.0	16.8	−5.4	16.4	−50.0	−56.3
Toluene	<i>E</i> , kcal/mol	0.0	−5.0	3.7	−21.0	3.2	−59.1	−57.0
	<i>E</i> + ΔZPE, kcal/mol	0.0	−4.1	4.6	−18.5	3.7	−58.1	−56.5
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.1	16.6	−5.3	16.4	−48.9	−56.3

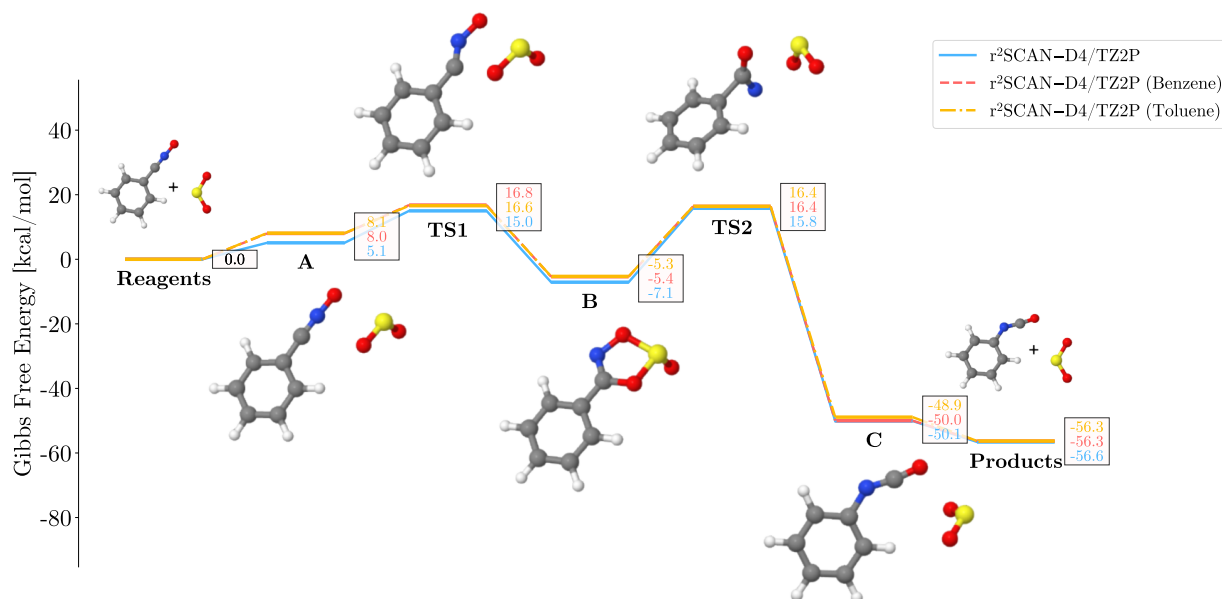


Figure S12 Calculated PES for reaction of the phenyl nitrile sulfide with sulfur dioxide. r²SCAN-D4/TZ2P electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S39 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase

C	-0.065871	-0.064027	0.353992
C	0.794778	1.019397	0.416967
C	0.431014	-1.362130	0.408214
C	2.177293	0.809106	0.536322
C	2.674280	-0.502511	0.590531
C	1.800587	-1.575288	0.526212
H	0.414111	2.032083	0.375427
C	3.062288	1.909009	0.601136
H	-1.131896	0.106712	0.262067
H	-0.247122	-2.205347	0.358399
H	3.741201	-0.661935	0.682240
H	2.192079	-2.584751	0.568388
N	3.796392	2.807299	0.648148
O	4.557163	3.740682	0.697948

14

Phenyl nitrile oxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	-0.066081	-0.062800	0.353994
C	0.795028	1.020817	0.416902
C	0.431445	-1.361196	0.408302
C	2.176683	0.806744	0.536113
C	2.675975	-0.503654	0.590609
C	1.801247	-1.576149	0.526305
H	0.414954	2.033610	0.375385
C	3.062596	1.906660	0.600822
H	-1.131980	0.108000	0.262126
H	-0.247079	-2.204114	0.358523
H	3.742737	-0.663395	0.682303
H	2.191877	-2.585818	0.568474
N	3.793013	2.804911	0.647955
O	4.555881	3.744685	0.698181

14

Phenyl nitrile oxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	-0.066087	-0.062770	0.353993
C	0.795026	1.020849	0.416907
C	0.431463	-1.361167	0.408300
C	2.176659	0.806682	0.536116
C	2.676015	-0.503683	0.590614
C	1.801265	-1.576167	0.526308
H	0.414952	2.033638	0.375391
C	3.062591	1.906607	0.600816
H	-1.131981	0.108028	0.262122
H	-0.247068	-2.204078	0.358517
H	3.742770	-0.663444	0.682310

H	2.191874	-2.585838	0.568475
N	3.792939	2.804854	0.647945
O	4.555878	3.744787	0.698177

Table S40 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

17			
A ES at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase			
C	-0.128815	0.135255	-0.038080
C	0.706181	1.218951	-0.251775
C	0.389057	-1.068050	0.429946
C	2.079400	1.097316	0.006050
C	2.601390	-0.114590	0.481151
C	1.750735	-1.187981	0.688142
H	0.312911	2.160072	-0.614584
C	2.941121	2.196328	-0.205930
H	-1.189403	0.231413	-0.236804
H	-0.269708	-1.911978	0.595181
H	3.661503	-0.190413	0.686361
H	2.153984	-2.124177	1.054937
N	3.625521	3.108403	-0.403335
O	4.386304	4.043629	-0.557651
O	5.406214	2.281970	1.611254
S	6.283686	3.316175	1.100394
O	7.298513	2.924173	0.152142

17			
A ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene			
C	-0.137721	0.191406	0.056045
C	0.749852	1.229130	-0.174303
C	0.330798	-1.060029	0.444764
C	2.126622	1.009447	-0.016796
C	2.599012	-0.250326	0.377498
C	1.696057	-1.276140	0.604982
H	0.395909	2.206565	-0.475776
C	3.035815	2.063962	-0.258236
H	-1.200441	0.361248	-0.067139
H	-0.369298	-1.866983	0.623974
H	3.662755	-0.406887	0.501136
H	2.060452	-2.249864	0.908738
N	3.718222	2.957393	-0.529221
O	4.479778	3.884350	-0.750656
O	5.351774	2.600805	1.759257
S	6.199685	3.603013	1.142783
O	7.309322	3.119408	0.350348

17			
A ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene			
C	-0.135509	0.205792	0.089926
C	0.760597	1.233680	-0.150886
C	0.324928	-1.056291	0.453014

C	2.137567	0.993020	-0.030277
C	2.601841	-0.277296	0.339086
C	1.690513	-1.293049	0.577679
H	0.413421	2.219390	-0.432577
C	3.054552	2.037312	-0.285517
H	-1.198422	0.391599	-0.005108
H	-0.381771	-1.855628	0.640181
H	3.665980	-0.450180	0.434413
H	2.048467	-2.275061	0.861725
N	3.746645	2.918785	-0.570737
O	4.514682	3.836937	-0.806482
O	5.298730	2.687734	1.796204
S	6.163712	3.659918	1.155963
O	7.302667	3.139837	0.430792

Table S41 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

17

TS1 at r²SCAN-D4/TZ2P (ADF/AMS) in the gas phase

C	0.070998	0.214452	-0.131247
C	0.947658	1.280632	-0.226439
C	0.503697	-1.010037	0.369267
C	2.283351	1.113968	0.175029
C	2.720392	-0.116273	0.678816
C	1.824278	-1.168926	0.773866
H	0.620091	2.238533	-0.609731
C	3.182010	2.204627	0.063094
H	-0.958185	0.342200	-0.444825
H	-0.190396	-1.838280	0.445374
H	3.750290	-0.221473	0.990758
H	2.161374	-2.121108	1.165058
N	3.434257	3.282582	-0.400491
O	4.330686	4.154935	-0.308560
O	4.787582	2.098425	1.297118
S	5.835595	3.067971	0.857049
O	6.704921	2.594270	-0.196733

17

TS1 at r²SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	0.060922	0.228042	-0.085750
C	0.940917	1.290294	-0.198190
C	0.503463	-1.005234	0.384628
C	2.289265	1.106204	0.150044
C	2.736475	-0.132728	0.624007
C	1.836611	-1.179653	0.741403
H	0.606656	2.255135	-0.556876
C	3.192214	2.188661	0.008491
H	-0.977843	0.365820	-0.360518
H	-0.193522	-1.829457	0.476029
H	3.776002	-0.251938	0.896921
H	2.179565	-2.138501	1.110062

N	3.480515	3.228772	-0.516260
O	4.379165	4.106653	-0.402615
O	4.709631	2.174405	1.350730
S	5.777061	3.128103	0.920656
O	6.711502	2.581920	-0.045361

17

TS1 at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	-2.411150	-0.718444	-0.344611
C	-1.529599	0.342077	-0.460932
C	-1.968695	-1.952511	0.123742
C	-0.180094	0.155330	-0.118816
C	0.267062	-1.084414	0.353176
C	-0.634242	-2.129621	0.474529
H	-1.863480	1.307742	-0.817737
C	0.723486	1.236758	-0.263273
H	-3.450875	-0.578661	-0.614635
H	-2.666829	-2.775405	0.218238
H	1.307519	-1.205646	0.621786
H	-0.291649	-3.089184	0.841636
N	1.013124	2.274502	-0.791956
O	1.909477	3.154829	-0.676742
O	2.232894	1.233268	1.088868
S	3.299430	2.188919	0.661125
O	4.243621	1.640462	-0.294397

Table S42 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

17

B ES at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase

C	0.087992	0.085338	-0.106885
C	1.068963	1.051779	-0.248290
C	0.395510	-1.152693	0.452039
C	2.376231	0.779027	0.171032
C	2.684827	-0.463300	0.729929
C	1.692916	-1.423666	0.867417
H	0.838130	2.018047	-0.677841
C	3.413865	1.790092	0.032491
H	-0.923962	0.296917	-0.431096
H	-0.377104	-1.904537	0.562219
H	3.697717	-0.669978	1.048203
H	1.936475	-2.386570	1.300096
N	3.267788	2.921780	-0.550325
O	4.483744	3.633733	-0.432918
O	4.637983	1.521785	0.580599
S	5.760033	2.633828	-0.017246
O	6.333286	2.065417	-1.208724

17

B ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	0.089765	0.084124	-0.112211

C	1.069860	1.052468	-0.249595
C	0.397652	-1.153440	0.448514
C	2.376346	0.781675	0.174429
C	2.685400	-0.460313	0.734868
C	1.694237	-1.422208	0.869513
H	0.835128	2.017517	-0.679550
C	3.413920	1.792782	0.038305
H	-0.921148	0.294071	-0.440305
H	-0.374009	-1.906610	0.555665
H	3.696498	-0.667227	1.058409
H	1.937666	-2.384190	1.304074
N	3.268776	2.927448	-0.540591
O	4.491735	3.635678	-0.423793
O	4.639397	1.519436	0.576666
S	5.763994	2.628326	-0.017868
O	6.309179	2.057459	-1.225831

17

B ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	0.089747	0.084117	-0.112250
C	1.069919	1.052346	-0.249928
C	0.397602	-1.153370	0.448686
C	2.376445	0.781499	0.173974
C	2.685467	-0.460434	0.734592
C	1.694216	-1.422188	0.869592
H	0.835125	2.017354	-0.679936
C	3.414063	1.792558	0.037872
H	-0.921199	0.294116	-0.440190
H	-0.374134	-1.906411	0.556159
H	3.696541	-0.667360	1.058195
H	1.937576	-2.384059	1.304427
N	3.268932	2.927429	-0.540696
O	4.491854	3.635840	-0.422984
O	4.639395	1.519200	0.576459
S	5.764064	2.628373	-0.017376
O	6.308781	2.057986	-1.225897

Table S43 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

17

TS2 at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase

C	0.024996	0.188908	0.264790
C	1.011436	1.121082	-0.015077
C	0.373469	-1.129385	0.545583
C	2.344910	0.717004	0.025385
C	2.705933	-0.609068	0.263238
C	1.708019	-1.528555	0.541176
H	0.767607	2.148950	-0.251242
C	3.453339	1.788177	0.004894
H	-1.016213	0.487043	0.254002
H	-0.402481	-1.855882	0.755806

H	3.749942	-0.895094	0.243460
H	1.968545	-2.559806	0.745780
N	3.536789	1.732078	-1.244212
O	4.916583	3.236761	-1.292280
O	3.964411	2.358502	0.994160
S	5.631447	3.303161	0.005703
O	6.635669	2.293123	0.229533

17

TS2 at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	0.027204	0.190678	0.264612
C	1.013976	1.122487	-0.013617
C	0.375239	-1.128466	0.544629
C	2.347505	0.714858	0.032081
C	2.709220	-0.612944	0.266327
C	1.709611	-1.530429	0.542554
H	0.770164	2.150510	-0.248102
C	3.451518	1.778366	-0.003488
H	-1.013523	0.489403	0.252330
H	-0.401710	-1.854589	0.751541
H	3.752160	-0.902201	0.248404
H	1.968314	-2.561908	0.746778
N	3.544687	1.735526	-1.252644
O	4.911607	3.238150	-1.291944
O	3.978573	2.359599	0.978397
S	5.609681	3.309559	0.020276
O	6.620173	2.298400	0.232566

17

TS2 at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	0.027304	0.190496	0.265125
C	1.013908	1.122429	-0.013211
C	0.375529	-1.128688	0.544788
C	2.347499	0.714830	0.032114
C	2.709398	-0.613023	0.265979
C	1.709924	-1.530606	0.542294
H	0.769885	2.150468	-0.247393
C	3.451286	1.778273	-0.003938
H	-1.013434	0.489156	0.253211
H	-0.401318	-1.854897	0.751732
H	3.752323	-0.902312	0.247658
H	1.968742	-2.562097	0.746244
N	3.544951	1.735392	-1.253063
O	4.911492	3.237940	-1.292238
O	3.978484	2.360044	0.977732
S	5.608701	3.310150	0.020553
O	6.619726	2.299446	0.233113

Table S44 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

17

C ES at r2SCAN-3c in the gas phase

C	1.512841	0.000815	1.678275
C	2.352111	0.563967	0.728869
C	0.510150	-0.886110	1.299800
C	2.183848	0.227118	-0.615824
C	1.179101	-0.656597	-1.003444
C	0.346718	-1.210177	-0.042146
C	3.976309	1.445870	-1.733618
N	3.001189	0.763285	-1.604852
O	6.504875	4.283271	0.270379
O	4.916761	2.095597	-2.000837
S	5.128143	4.420609	-0.127520
O	4.121693	3.703611	0.619287
H	3.125901	1.267801	1.013459
H	1.643064	0.260958	2.722186
H	-0.141799	-1.320476	2.047725
H	1.068368	-0.897063	-2.053170
H	-0.433779	-1.897583	-0.345666

17

C ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	1.421162	0.104565	1.643906
C	2.237789	0.677393	0.680431
C	0.512995	-0.892390	1.299526
C	2.140872	0.243367	-0.643619
C	1.232383	-0.751581	-0.997297
C	0.422222	-1.315751	-0.021743
C	3.839146	1.565638	-1.785311
N	2.940386	0.787852	-1.643001
O	6.682283	4.124115	0.165843
O	4.714938	2.295586	-2.065282
S	5.266021	4.358703	0.033335
O	4.375415	3.564056	0.847025
H	2.943170	1.457903	0.939018
H	1.496103	0.441402	2.671187
H	-0.121594	-1.334479	2.057794
H	1.174949	-1.071091	-2.030129
H	-0.282748	-2.090392	-0.298783

17

C ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	1.501536	0.039387	1.657787
C	2.345607	0.575908	0.697252
C	0.505288	-0.863838	1.298356
C	2.187094	0.202018	-0.639267
C	1.190763	-0.698969	-1.007470
C	0.354922	-1.229527	-0.034581
C	3.943386	1.458844	-1.752139
N	3.009473	0.717142	-1.636962
O	6.531165	4.250033	0.218574
O	4.851078	2.159467	-2.001777
S	5.126170	4.446172	-0.039516

O	4.186164	3.679997	0.745577
H	3.119134	1.282933	0.970964
H	1.625477	0.329579	2.694515
H	-0.150432	-1.278401	2.054184
H	1.087007	-0.974468	-2.049390
H	-0.418337	-1.931379	-0.323205

Table S45 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase

C	1.808786	-0.429899	0.366398
C	2.888311	0.371823	0.026302
C	1.995134	-1.775826	0.659564
C	4.167495	-0.177581	-0.021337
C	4.362186	-1.529635	0.271433
C	3.274513	-2.319951	0.609900
H	2.761213	1.421793	-0.204805
C	6.418642	0.561303	-0.494319
H	0.816081	0.002782	0.402227
H	1.149502	-2.398111	0.925040
H	5.361392	-1.948941	0.231359
H	3.428944	-3.368442	0.836682
N	5.225910	0.656507	-0.364934
O	7.575483	0.604780	-0.652512

14

Phenyl isocyanate ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

C	1.807966	-0.429450	0.366368
C	2.888027	0.372654	0.026061
C	1.994950	-1.775823	0.659618
C	4.166815	-0.178034	-0.021186
C	4.363083	-1.529819	0.271221
C	3.274894	-2.320287	0.609881
H	2.758997	1.422576	-0.204729
C	6.418789	0.560699	-0.494286
H	0.815277	0.003199	0.402293
H	1.149346	-2.398238	0.925251
H	5.362124	-1.948910	0.231164
H	3.429474	-3.368725	0.836709
N	5.227082	0.656092	-0.364920
O	7.576770	0.604667	-0.652449

14

Phenyl isocyanate ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

C	1.807956	-0.429432	0.366368
C	2.888053	0.372645	0.026046
C	1.994918	-1.775816	0.659632
C	4.166817	-0.178110	-0.021194
C	4.363072	-1.529896	0.271212
C	3.274854	-2.320329	0.609890

H	2.759009	1.422570	-0.204734
C	6.418834	0.560788	-0.494310
H	0.815284	0.003249	0.402305
H	1.149298	-2.398207	0.925276
H	5.362088	-1.949033	0.231171
H	3.429413	-3.368763	0.836737
N	5.227149	0.655970	-0.364943
O	7.576848	0.604967	-0.652459

Table S46 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-D4/TZ2P level of theory in the gas phase and benzene, toluene, which was treated with COSMO continuum solvent model.

3

Sulfur dioxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the gas phase

S	0.000000	-0.000000	0.365891
O	0.000000	1.241344	-0.364529
O	0.000000	-1.241344	-0.364529

3

Sulfur dioxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the benzene

S	0.000000	0.000000	0.374334
O	0.000000	1.236222	-0.368750
O	0.000000	-1.236222	-0.368751

3

Sulfur dioxide ES at r2SCAN-D4/TZ2P (ADF/AMS) in the toluene

S	0.000000	0.000000	0.374615
O	0.000000	1.236053	-0.368891
O	0.000000	-1.236053	-0.368891

2.1.4 DSD-BLYP-D3(BJ)/def2-TZVP

Table S47 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Benzene	E , kcal/mol	0.0	-5.3	8.1	-18.4	10.0	-61.8	-58.5
	$E + \Delta ZPE$, kcal/mol	0.0	-4.4	9.3	-15.4	10.8	-60.6	-58.0
	$E + \Delta G$, kcal/mol	0.0	6.9	22.3	-1.8	23.9	-49.7	-57.8

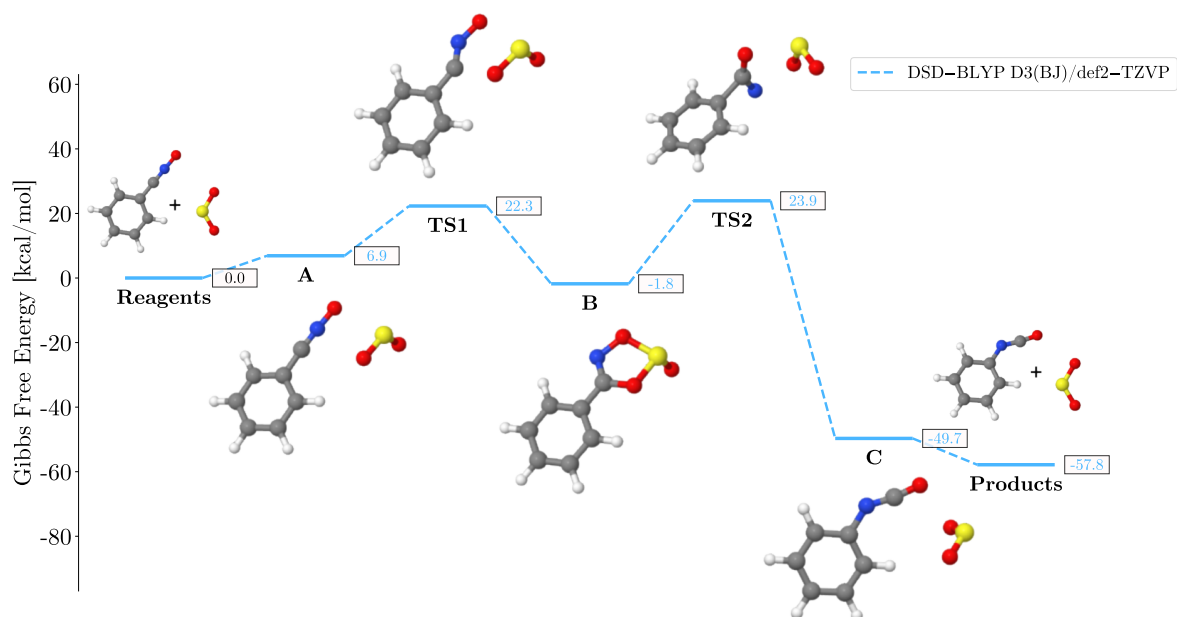


Figure S13 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DSD-BLYP-D3(BJ)/def2-TZVP electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S48 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	-0.077854	-0.051165	0.353064
C	0.796100	1.025194	0.416858
C	0.407286	-1.354949	0.406279
C	2.172432	0.795048	0.535331
C	2.661135	-0.516056	0.588987
C	1.775511	-1.582976	0.524027
H	0.425525	2.039967	0.375694
C	3.074272	1.897691	0.601298
H	-1.140096	0.129599	0.261486

H	-0.278525	-2.189555	0.356417
H	3.724692	-0.686723	0.680681
H	2.155073	-2.594718	0.565947
N	3.795607	2.811761	0.647544
O	4.544722	3.760832	0.698808

Table S49 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

A ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	-0.030460	-0.016822	-0.455190
C	0.726856	1.145483	-0.497081
C	0.350974	-1.074140	0.366128
C	1.876457	1.245669	0.293750
C	2.265378	0.183646	1.119295
C	1.497040	-0.971332	1.150082
H	0.439835	1.970842	-1.133471
C	2.670869	2.428261	0.263186
H	-0.918643	-0.097158	-1.066543
H	-0.242912	-1.977409	0.394051
H	3.160982	0.273487	1.717812
H	1.795062	-1.792786	1.786955
N	3.341032	3.376789	0.288050
O	4.093761	4.334542	0.315719
O	5.569886	1.777348	1.201279
S	6.360407	2.898897	0.737943
O	6.817035	2.870919	-0.631486

Table S50 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS1 at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	-2.223641	-0.814571	-0.678463
C	-1.363192	0.271954	-0.646056
C	-1.909189	-1.979777	0.016836
C	-0.183737	0.188542	0.106046
C	0.136708	-0.977845	0.806546
C	-0.731042	-2.059453	0.753674
H	-1.590674	1.178639	-1.188927
C	0.695543	1.313196	0.146614
H	-3.136851	-0.754365	-1.254060
H	-2.581204	-2.826277	-0.019314
H	1.056517	-1.027918	1.369702
H	-0.486195	-2.966210	1.289036
N	0.837978	2.503088	0.008773
O	1.844229	3.283527	0.009036
O	2.537233	0.846803	0.584335
S	3.444840	1.931281	0.080551
O	3.771366	1.821767	-1.326849

Table S51 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

B ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	0.086929	0.099552	-0.063562
C	1.062730	1.073543	-0.211649
C	0.415939	-1.150806	0.456875
C	2.380883	0.791467	0.160554
C	2.713073	-0.459235	0.683705
C	1.726934	-1.427164	0.829509
H	0.813268	2.048439	-0.606171
C	3.416606	1.806795	-0.000995
H	-0.933452	0.315995	-0.348455
H	-0.349570	-1.905986	0.573112
H	3.734126	-0.670540	0.966372
H	1.984851	-2.396562	1.232925
N	3.300741	2.864886	-0.715463
O	4.504905	3.612674	-0.562467
O	4.596855	1.625038	0.659061
S	5.738345	2.688433	0.039751
O	6.405517	2.002961	-1.037260

Table S52 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS2 at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	0.309159	0.018104	-0.529111
C	1.417977	0.847846	-0.586187
C	0.276143	-1.038635	0.380625
C	2.498541	0.575622	0.255136
C	2.466453	-0.454988	1.194567
C	1.347566	-1.274209	1.240372
H	1.464814	1.682412	-1.272109
C	3.805673	1.352645	0.026234
H	-0.533187	0.200585	-1.181483
H	-0.596995	-1.675394	0.427817
H	3.304245	-0.606579	1.860614
H	1.304084	-2.086373	1.952325
N	3.513851	2.206832	0.897925
O	5.207895	3.209654	0.675712
O	4.714484	1.118358	-0.808655
S	5.777150	2.953088	-0.676830
O	5.135346	3.667472	-1.755491

Table S53 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

C ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	0.615498	-1.407227	0.025878
C	1.373357	-0.814803	-0.977131
C	0.619002	-0.881011	1.313821
C	2.137434	0.311181	-0.683754
C	2.149926	0.847051	0.604416
C	1.388253	0.244251	1.597266
H	1.380304	-1.212623	-1.982217
C	3.613932	1.820765	-1.917028
H	0.021295	-2.281549	-0.202394
H	0.027712	-1.343972	2.091778
H	2.751318	1.719994	0.819817
H	1.396672	0.659242	2.596085
N	2.888303	0.886453	-1.715097
O	4.332085	2.694782	-2.241276
O	4.222809	3.799719	0.847242
S	5.502401	4.024206	0.215126
O	6.514149	3.004750	0.346899

Table S54 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

C	1.807349	-0.418347	0.362889
C	2.894477	0.379686	0.026607
C	1.988320	-1.766422	0.655272
C	4.170051	-0.176891	-0.016702
C	4.360387	-1.528087	0.275277
C	3.266714	-2.316030	0.610159
H	2.767906	1.428499	-0.202706
C	6.434740	0.567988	-0.500218
H	0.817964	0.017057	0.395268
H	1.141082	-2.385313	0.916250
H	5.355422	-1.951733	0.238892
H	3.416013	-3.363191	0.835913
N	5.241268	0.655933	-0.359436
O	7.594236	0.616830	-0.670463

Table S55 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the DSD-BLYP-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at DSD-BLYP-D3(BJ)/def2-TZVP in the benzene

S	-5.390605	0.283878	0.000000
O	-5.503789	-1.154869	0.000000
O	-4.072007	0.870989	0.000000

2.1.5 ω B97X-D3(BJ)/def2-TZVP

Table S56 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Benzene	E , kcal/mol	0.0	-6.5	5.8	-28.2	6.1	-64.3	-60.8
	$E + \Delta ZPE$, kcal/mol	0.0	-5.6	6.7	-25.4	6.4	-63.6	-60.6
	$E + \Delta G$, kcal/mol	0.0	5.0	18.6	-12.4	18.8	-52.9	-60.6
Toluene	E , kcal/mol	0.0	-6.4	5.8	-28.1	6.1	-64.2	-60.8
	$E + \Delta ZPE$, kcal/mol	0.0	-5.6	6.8	-25.3	6.4	-63.5	-60.5
	$E + \Delta G$, kcal/mol	0.0	5.0	18.7	-12.3	18.9	-52.8	-60.5

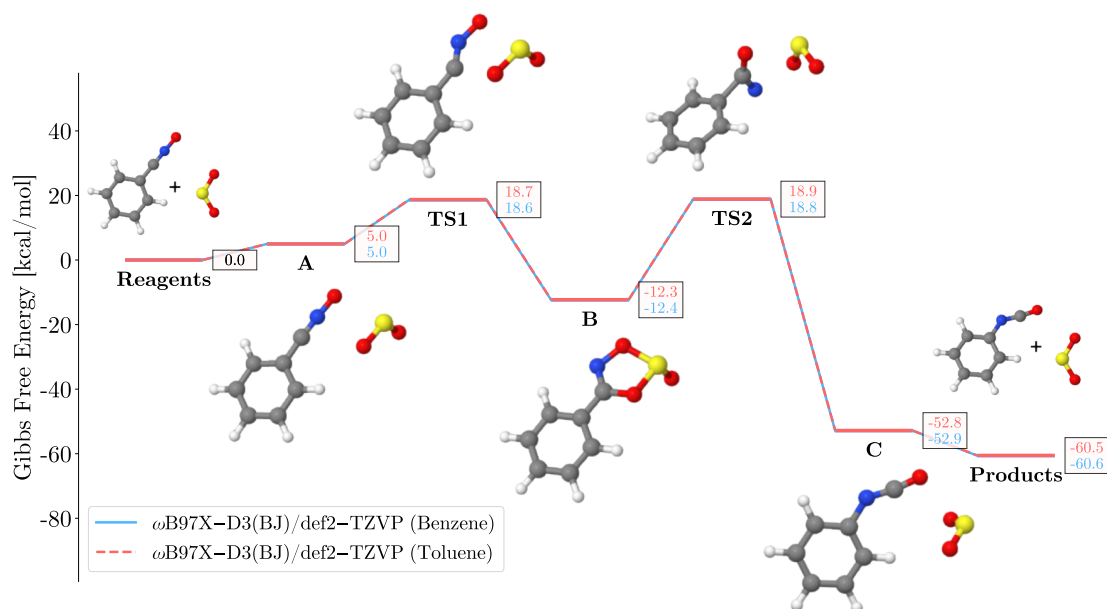


Figure S14 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. ω B97X-D3(BJ)/def2-TZVP electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S57 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-0.067240	-0.063982	0.353909
C	0.797006	1.018735	0.417913
C	0.431386	-1.361016	0.407597
C	2.170887	0.797533	0.536479
C	2.674086	-0.504119	0.590930
C	1.799752	-1.578707	0.525912

H	0.417864	2.033014	0.376538
C	3.071455	1.915930	0.602265
H	-1.133940	0.106124	0.261623
H	-0.248356	-2.204390	0.357279
H	3.741831	-0.663912	0.683323
H	2.188598	-2.589810	0.568143
N	3.795700	2.809513	0.647480
O	4.557272	3.753387	0.696608

14

Phenyl nitrile oxide ES at wB97X-D3(BJ)/def2-TZVP in the toluene

C	-0.067271	-0.063931	0.353907
C	0.796974	1.018811	0.417912
C	0.431412	-1.360977	0.407597
C	2.170830	0.797432	0.536477
C	2.674176	-0.504167	0.590939
C	1.799798	-1.578743	0.525914
H	0.417847	2.033102	0.376538
C	3.071420	1.915838	0.602258
H	-1.133975	0.106156	0.261619
H	-0.248343	-2.204350	0.357279
H	3.741926	-0.663951	0.683335
H	2.188608	-2.589862	0.568146
N	3.795567	2.809377	0.647469
O	4.557330	3.753564	0.696611

Table S58 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

17

A ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	-0.088153	0.083302	-0.175334
C	0.703109	1.211903	-0.326154
C	0.448603	-1.078709	0.368790
C	2.039435	1.167405	0.074049
C	2.583961	0.003793	0.621232
C	1.781036	-1.117252	0.765716
H	0.296498	2.122843	-0.749242
C	2.876761	2.324719	-0.073429
H	-1.126917	0.111221	-0.483927
H	-0.174821	-1.958437	0.484126
H	3.623443	-0.009168	0.927042
H	2.197422	-2.023757	1.189791
N	3.559737	3.241380	-0.172592
O	4.328155	4.192087	-0.244565
O	5.569513	2.224355	1.682030
S	6.409722	3.088813	0.900317
O	6.981097	2.532002	-0.290451

17

A ES at wB97X-D3(BJ)/def2-TZVP in the toluene

C	-0.088433	0.082421	-0.171679

C	0.698338	1.214444	-0.320696
C	0.454073	-1.079597	0.366793
C	2.036127	1.172911	0.074940
C	2.586369	0.009431	0.616707
C	1.787819	-1.114898	0.759682
H	0.287160	2.125544	-0.739012
C	2.869904	2.332991	-0.070943
H	-1.128243	0.107752	-0.476974
H	-0.165955	-1.961864	0.481087
H	3.626753	-0.000427	0.919644
H	2.208641	-2.021300	1.179582
N	3.559394	3.243620	-0.179710
O	4.337135	4.185994	-0.264786
O	5.557401	2.236881	1.696773
S	6.406844	3.081541	0.903454
O	6.975273	2.501056	-0.277461

Table S59 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

17

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	0.001819	0.147820	0.348652
C	0.929448	1.103411	-0.033272
C	0.415514	-1.153415	0.615692
C	2.271210	0.736041	-0.158984
C	2.692527	-0.567617	0.114690
C	1.756040	-1.511015	0.502123
H	0.629132	2.123920	-0.239091
C	3.237149	1.714297	-0.553814
H	-1.043308	0.418128	0.443543
H	-0.313917	-1.896439	0.919031
H	3.742409	-0.821377	0.027878
H	2.069432	-2.525918	0.716704
N	3.804243	2.416154	-1.326187
O	4.764773	3.259501	-1.252696
O	4.294643	2.354114	1.086629
S	5.541534	2.976515	0.581480
O	6.581749	2.022881	0.278319

17

TS1 at ω B97X-D3(BJ)/def2-TZVP in the toluene

C	0.003289	0.149803	0.352696
C	0.931387	1.104048	-0.031356
C	0.415653	-1.152273	0.617953
C	2.272211	0.734376	-0.160870
C	2.692252	-0.570159	0.110964
C	1.755260	-1.512176	0.500476
H	0.632244	2.125151	-0.235960
C	3.238614	1.711141	-0.557452
H	-1.041144	0.421717	0.450539
H	-0.314179	-1.894237	0.922929

H	3.741427	-0.825746	0.020886
H	2.067499	-2.527731	0.713644
N	3.809489	2.408288	-1.331377
O	4.769817	3.252492	-1.257150
O	4.286956	2.363564	1.084645
S	5.536099	2.982519	0.580807
O	6.577527	2.026224	0.289325

Table S60 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

17

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	0.077556	0.095455	-0.072870
C	1.057325	1.064497	-0.215115
C	0.400026	-1.152900	0.452331
C	2.368942	0.780050	0.168476
C	2.693891	-0.467689	0.695888
C	1.705469	-1.432744	0.835809
H	0.814918	2.040859	-0.617372
C	3.411919	1.800719	0.008648
H	-0.942242	0.314320	-0.368416
H	-0.370402	-1.908023	0.563659
H	3.714451	-0.681842	0.988507
H	1.957769	-2.404884	1.243754
N	3.295668	2.864835	-0.685318
O	4.498673	3.600389	-0.537866
O	4.599701	1.611546	0.649116
S	5.725869	2.672672	0.028584
O	6.364868	1.999739	-1.067116

17

B ES at ω B97X-D3(BJ)/def2-TZVP in the toluene

C	0.077417	0.095496	-0.072615
C	1.057129	1.064615	-0.214933
C	0.400076	-1.152926	0.452367
C	2.368855	0.780134	0.168342
C	2.694003	-0.467664	0.695580
C	1.705630	-1.432774	0.835585
H	0.814407	2.041020	-0.616913
C	3.411803	1.800768	0.008339
H	-0.942462	0.314367	-0.367889
H	-0.370300	-1.908097	0.563765
H	3.714607	-0.681899	0.988005
H	1.958047	-2.404942	1.243398
N	3.295980	2.864479	-0.686390
O	4.498955	3.600211	-0.538659
O	4.599303	1.612053	0.649451
S	5.725733	2.672814	0.029268
O	6.365218	1.999345	-1.066002

Table S61 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

17

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	0.280347	0.026232	-0.517243
C	1.383839	0.861545	-0.580039
C	0.266596	-1.038213	0.381227
C	2.471404	0.592731	0.248096
C	2.458797	-0.448095	1.172514
C	1.347810	-1.275902	1.225056
H	1.416388	1.704377	-1.260615
C	3.781139	1.380743	0.021590
H	-0.573296	0.209699	-1.159014
H	-0.603662	-1.683330	0.432390
H	3.307888	-0.601662	1.827973
H	1.319501	-2.098167	1.930242
N	3.484235	2.229980	0.896373
O	5.255011	3.221806	0.662220
O	4.692402	1.141961	-0.798608
S	5.834371	2.925714	-0.658165
O	5.251631	3.647580	-1.753294

17

TS2 at ω B97X-D3(BJ)/def2-TZVP in the toluene

C	0.279730	0.026094	-0.516937
C	1.382854	0.861854	-0.580157
C	0.266870	-1.038525	0.381391
C	2.470927	0.593188	0.247478
C	2.459189	-0.447779	1.171896
C	1.348574	-1.276017	1.224727
H	1.414704	1.704823	-1.260607
C	3.779973	1.381719	0.021425
H	-0.574319	0.209339	-1.158229
H	-0.603137	-1.683959	0.432884
H	3.308644	-0.601175	1.826942
H	1.320886	-2.098433	1.929760
N	3.482689	2.231317	0.895603
O	5.254080	3.222148	0.662497
O	4.692635	1.143407	-0.797835
S	5.835031	2.923335	-0.656806
O	5.255074	3.645665	-1.753332

Table S62 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

17

C ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.382405	0.185872	1.621559
C	2.150777	0.794404	0.639010
C	0.577320	-0.905527	1.313399

C	2.108809	0.298672	-0.662071
C	1.305442	-0.790006	-0.981354
C	0.541304	-1.389511	0.011072
C	3.696871	1.731598	-1.859605
N	2.873216	0.885008	-1.685031
O	6.692816	3.469293	0.264651
O	4.504031	2.532021	-2.148140
S	5.463525	4.186593	0.123222
O	4.327043	3.718464	0.860074
H	2.775178	1.649300	0.873323
H	1.414531	0.570582	2.634970
H	-0.020484	-1.375939	2.085950
H	1.287742	-1.156697	-2.000895
H	-0.085025	-2.239227	-0.237230

17

C ES at ω B97X-D3(BJ)/def2-TZVP in the toluene

C	1.382912	0.185353	1.621635
C	2.151255	0.793910	0.639036
C	0.577348	-0.905743	1.313480
C	2.108829	0.298410	-0.662125
C	1.304841	-0.789806	-0.981504
C	0.540543	-1.389184	0.010944
C	3.697488	1.730488	-1.859867
N	2.873664	0.884169	-1.685065
O	6.692771	3.470958	0.265558
O	4.504889	2.530572	-2.148662
S	5.463361	4.187971	0.123351
O	4.326780	3.719759	0.860025
H	2.775111	1.649055	0.873509
H	1.415632	0.569882	2.635094
H	-0.020301	-1.376253	2.086084
H	1.286691	-1.156169	-2.001147
H	-0.086314	-2.238473	-0.237444

Table S63 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.805533	-0.431675	0.366187
C	2.886072	0.372845	0.029283
C	1.994676	-1.777507	0.657026
C	4.162974	-0.175754	-0.016059
C	4.361971	-1.524004	0.274079
C	3.274996	-2.318660	0.609612
H	2.752390	1.423557	-0.199687
C	6.425013	0.565116	-0.498057
H	0.810496	-0.001884	0.400745
H	1.148873	-2.402861	0.919566
H	5.362002	-1.942504	0.236016
H	3.431464	-3.367863	0.835112

N	5.236122	0.664809	-0.360823
O	7.581018	0.586986	-0.662000

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the toluene

C	1.805518	-0.431625	0.366176
C	2.886169	0.372808	0.029281
C	1.994561	-1.777494	0.657034
C	4.162998	-0.175990	-0.016002
C	4.361957	-1.524250	0.274146
C	3.274862	-2.318793	0.609664
H	2.752514	1.423535	-0.199694
C	6.425142	0.565351	-0.498135
H	0.810518	-0.001733	0.400703
H	1.148690	-2.402775	0.919563
H	5.361958	-1.942820	0.236106
H	3.431223	-3.368015	0.835180
N	5.236305	0.664458	-0.360764
O	7.581186	0.587942	-0.662258

Table S64 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene and toluene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

S	0.000000	0.000000	0.369442
O	0.000000	1.227167	-0.366305
O	0.000000	-1.227167	-0.366305

3

Sulfur dioxide ES at ω B97X-D3(BJ)/def2-TZVP in the toluene

S	0.000000	0.000000	0.369679
O	0.000000	1.227027	-0.366423
O	0.000000	-1.227027	-0.366423

2.1.6 ω B97X-D3(BJ)/def2-TZVPPD

Table S65 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−7.0	9.3	−28.9	10.1	−65.7	−61.6
	$E + \Delta ZPE$, kcal/mol	0.0	−6.2	10.3	−26.0	10.4	−64.9	−61.4
	$E + \Delta G$, kcal/mol	0.0	4.6	22.7	−13.0	22.8	−54.0	−61.3
Benzene	E , kcal/mol	0.0	−5.6	10.6	−26.8	10.6	−63.3	−60.4
	$E + \Delta ZPE$, kcal/mol	0.0	−4.8	11.5	−24.0	10.9	−62.5	−60.1
	$E + \Delta G$, kcal/mol	0.0	5.8	23.9	−11.0	23.4	−52.5	−60.1
Toluene	E , kcal/mol	0.0	−5.5	10.3	−26.7	10.6	−63.2	−60.3
	$E + \Delta ZPE$, kcal/mol	0.0	−4.7	11.2	−23.9	11.0	−62.5	−60.1
	$E + \Delta G$, kcal/mol	0.0	5.9	23.2	−10.9	23.4	−51.8	−60.1

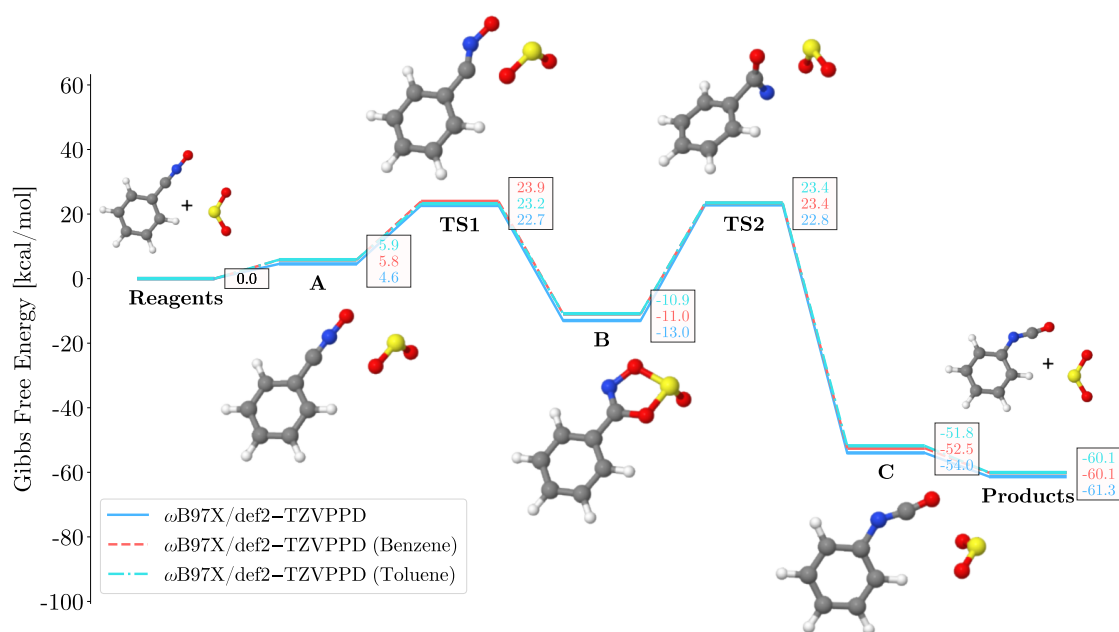


Figure S15 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. ω B97X-D3(BJ)/def2-TZVPPD electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S66 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-6.7	6.1	-26.6	7.5	-64.6	-60.8
	$E + \Delta ZPE$, kcal/mol	0.0	-5.8	7.0	-23.8	7.8	-63.9	-60.6
	$E + \Delta G$, kcal/mol	0.0	4.9	19.4	-10.7	20.3	-53.0	-60.6
Benzene	E , kcal/mol	0.0	-5.3	6.9	-24.8	7.7	-62.7	-59.8
	$E + \Delta ZPE$, kcal/mol	0.0	-4.5	7.8	-22.0	8.1	-62.0	-59.6
	$E + \Delta G$, kcal/mol	0.0	6.0	20.3	-9.0	20.5	-52.0	-59.6
Toluene	E , kcal/mol	0.0	-5.3	7.1	-24.7	7.8	-62.5	-59.8
	$E + \Delta ZPE$, kcal/mol	0.0	-4.5	8.0	-21.9	8.1	-61.9	-59.6
	$E + \Delta G$, kcal/mol	0.0	6.1	20.1	-8.9	20.6	-51.1	-59.6

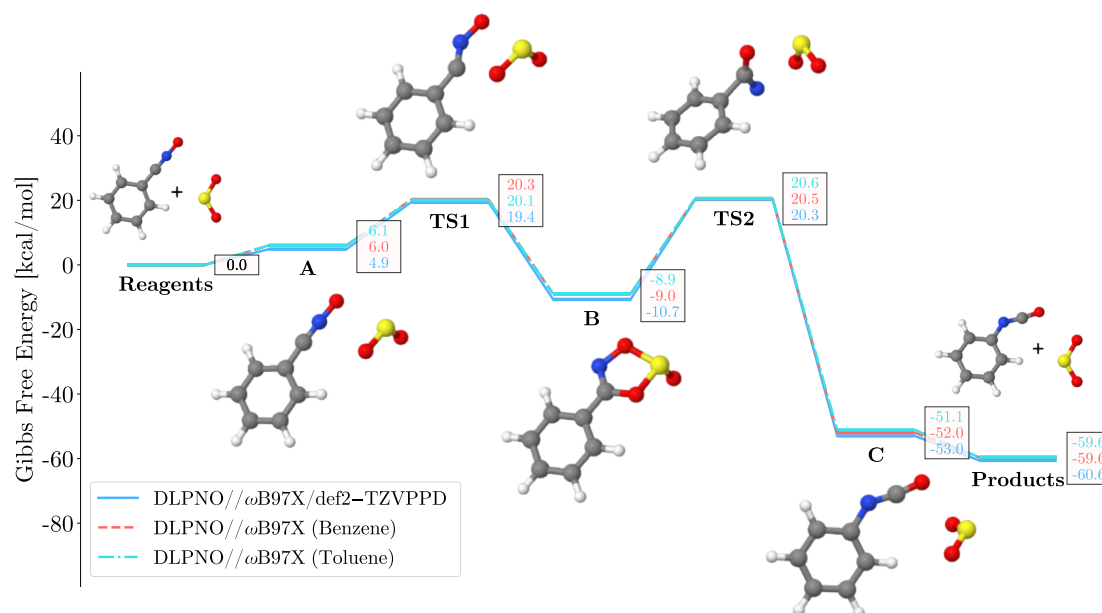


Figure S16 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVPPD electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S67 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVPPD in the gas phase

C	-0.069843	-0.067991	0.353422
C	0.790375	1.017460	0.418376
C	0.432247	-1.363054	0.406796
C	2.165537	0.805125	0.537226
C	2.669822	-0.496251	0.591947

C	1.800917	-1.574268	0.525874
H	0.407102	2.029378	0.377124
C	3.065962	1.922412	0.602831
H	-1.136399	0.098411	0.261289
H	-0.243459	-2.208527	0.355826
H	3.737493	-0.651374	0.684436
H	2.194714	-2.582669	0.567649
N	3.804112	2.806899	0.648006
O	4.577719	3.732748	0.695197

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVPPD in the benzene

C	-0.070609	-0.066948	0.353329
C	0.789507	1.019109	0.418347
C	0.432830	-1.362251	0.406765
C	2.164089	0.802979	0.537160
C	2.671720	-0.497077	0.592118
C	1.801979	-1.574975	0.525894
H	0.406558	2.031298	0.377174
C	3.065127	1.920579	0.602721
H	-1.137257	0.099108	0.261156
H	-0.243081	-2.207760	0.355859
H	3.739538	-0.651880	0.684692
H	2.195235	-2.583628	0.567759
N	3.801330	2.803756	0.647769
O	4.579336	3.735991	0.695258

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVPPD in the toluene

C	-0.070640	-0.066899	0.353325
C	0.789470	1.019181	0.418344
C	0.432858	-1.362210	0.406764
C	2.164026	0.802878	0.537155
C	2.671806	-0.497120	0.592124
C	1.802026	-1.575006	0.525895
H	0.406536	2.031383	0.377175
C	3.065087	1.920486	0.602715
H	-1.137291	0.099143	0.261151
H	-0.243063	-2.207720	0.355863
H	3.739629	-0.651914	0.684701
H	2.195254	-2.583672	0.567764
N	3.801196	2.803611	0.647759
O	4.579406	3.736158	0.695264

Table S68 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

A ES at ω B97X-D3(BJ)/def2-TZVPPD in the gas phase

C	-2.580893	-0.865170	-0.338911
C	-1.824640	0.276362	-0.556931
C	-1.980624	-2.016232	0.158099

C	-0.459299	0.257882	-0.271956
C	0.147633	-0.895116	0.231173
C	-0.619634	-2.029720	0.441415
H	-2.282734	1.178537	-0.942615
C	0.354157	1.423070	-0.480483
H	-3.641993	-0.855651	-0.556545
H	-2.575893	-2.905766	0.327044
H	1.206204	-0.882455	0.457685
H	-0.152591	-2.926441	0.830141
N	1.095723	2.290785	-0.610050
O	1.915316	3.187954	-0.706869
O	2.854059	1.130044	1.353715
S	3.826778	2.053260	0.839132
O	4.718431	1.578658	-0.174043

17

A ES at wB97X-D3(BJ)/def2-TZVPPD in the benzene

C	-2.589712	-0.849372	-0.324640
C	-1.811963	0.277657	-0.544374
C	-2.008550	-2.016110	0.160280
C	-0.444133	0.225673	-0.274277
C	0.144734	-0.942750	0.214590
C	-0.644591	-2.061774	0.428759
H	-2.253746	1.192188	-0.919984
C	0.387594	1.377271	-0.486397
H	-3.652579	-0.816324	-0.531353
H	-2.621298	-2.893540	0.330667
H	1.206799	-0.959213	0.424550
H	-0.193252	-2.970795	0.807524
N	1.114701	2.253234	-0.628345
O	1.928258	3.162450	-0.737212
O	2.885008	1.216920	1.395340
S	3.826873	2.150035	0.842417
O	4.725858	1.654449	-0.157544

17

A ES at wB97X-D3(BJ)/def2-TZVPPD in the toluene

C	-2.590373	-0.848565	-0.323805
C	-1.811502	0.277671	-0.543731
C	-2.010215	-2.016118	0.160460
C	-0.443539	0.223907	-0.274528
C	0.144369	-0.945322	0.213564
C	-0.646113	-2.063495	0.428036
H	-2.252469	1.192822	-0.918791
C	0.389269	1.374680	-0.486830
H	-3.653329	-0.814243	-0.529848
H	-2.623875	-2.892881	0.331024
H	1.206598	-0.963248	0.422617
H	-0.195573	-2.973133	0.806276
N	1.115795	2.250947	-0.629431
O	1.929142	3.160686	-0.738868
O	2.887285	1.220664	1.396841

S	3.827028	2.155380	0.843006
O	4.727499	1.660250	-0.155993

Table S69 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

TS1 at ω B97X-D3(BJ)/def2-TZVPPD in the gas phase

C	-2.406439	-0.747293	-0.364552
C	-1.544220	0.329430	-0.489115
C	-1.940575	-1.960543	0.130230
C	-0.203819	0.175642	-0.125325
C	0.270067	-1.037674	0.370694
C	-0.608132	-2.102544	0.499317
H	-1.894251	1.281769	-0.869222
C	0.689129	1.291730	-0.273675
H	-3.446386	-0.637215	-0.649236
H	-2.621418	-2.798401	0.230847
H	1.309336	-1.123577	0.659240
H	-0.249321	-3.047659	0.889813
N	1.031556	2.311520	-0.770567
O	1.975215	3.147233	-0.624801
O	2.202702	1.229464	1.100047
S	3.275913	2.137534	0.627484
O	4.160643	1.550583	-0.341178

17

TS1 at ω B97X-D3(BJ)/def2-TZVPPD in the benzene

C	-2.413366	-0.738345	-0.341285
C	-1.545324	0.332339	-0.480521
C	-1.947036	-1.956456	0.142825
C	-0.198896	0.163485	-0.143917
C	0.276439	-1.054881	0.340027
C	-0.608223	-2.112097	0.485777
H	-1.894718	1.288508	-0.851722
C	0.698159	1.271846	-0.309949
H	-3.457763	-0.619835	-0.605779
H	-2.633059	-2.788631	0.255986
H	1.320728	-1.153402	0.606520
H	-0.250583	-3.060875	0.868387
N	1.054302	2.279610	-0.821664
O	1.997406	3.121831	-0.647734
O	2.177663	1.250019	1.106430
S	3.241757	2.181750	0.659184
O	4.182516	1.595133	-0.262565

17

TS1 at ω B97X-D3(BJ)/def2-TZVPPD in the toluene

C	-2.411351	-0.669203	-0.103502
C	-1.527634	0.370544	-0.344165
C	-1.926073	-1.935691	0.206296
C	-0.154717	0.120984	-0.286640

C	0.337999	-1.147524	0.029038
C	-0.556401	-2.175230	0.274780
H	-1.885135	1.366190	-0.578643
C	0.769286	1.185264	-0.529659
H	-3.479145	-0.490468	-0.150378
H	-2.622370	-2.744091	0.400512
H	1.408131	-1.307025	0.087951
H	-0.187534	-3.163825	0.521452
N	1.341556	1.987188	-1.191961
O	2.241253	2.872131	-0.976307
O	1.691414	1.703088	1.230253
S	2.924370	2.443103	0.871118
O	4.036351	1.584567	0.539857

Table S70 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

B ES at ω B97X-D3(BJ)/def2-TZVPPD in the gas phase

C	0.078263	0.093315	-0.076191
C	1.056312	1.064011	-0.215330
C	0.400978	-1.154366	0.449320
C	2.366492	0.782863	0.173511
C	2.690923	-0.463482	0.702546
C	1.704667	-1.430808	0.838298
H	0.817570	2.039318	-0.620274
C	3.410271	1.803419	0.015158
H	-0.940044	0.309277	-0.376240
H	-0.367356	-1.911066	0.556502
H	3.710270	-0.672651	0.999838
H	1.957640	-2.401699	1.246809
N	3.290243	2.873610	-0.667217
O	4.498090	3.599878	-0.530277
O	4.603589	1.601294	0.641959
S	5.729790	2.664866	0.015288
O	6.366704	1.999220	-1.082998

17

B ES at ω B97X-D3(BJ)/def2-TZVPPD in the benzene

C	0.075956	0.093838	-0.072611
C	1.053222	1.065642	-0.213974
C	0.401858	-1.154562	0.450572
C	2.365217	0.783926	0.169782
C	2.693284	-0.463073	0.696788
C	1.707620	-1.431023	0.835185
H	0.808069	2.041168	-0.614836
C	3.408425	1.803957	0.009317
H	-0.943651	0.309968	-0.368279
H	-0.365789	-1.911773	0.559942
H	3.713310	-0.674193	0.990870
H	1.962603	-2.401981	1.242453
N	3.295910	2.869202	-0.683588

O	4.503752	3.598079	-0.539566
O	4.597197	1.608415	0.646421
S	5.727597	2.666149	0.028556
O	6.369819	1.993264	-1.066329

17

B ES at wB97X-D3(BJ)/def2-TZVPPD in the toluene

C	0.075844	0.093870	-0.072419
C	1.053062	1.065735	-0.213877
C	0.401919	-1.154575	0.450605
C	2.365148	0.783989	0.169622
C	2.693399	-0.463044	0.696512
C	1.707776	-1.431033	0.835008
H	0.807612	2.041291	-0.614503
C	3.408326	1.803989	0.009048
H	-0.943833	0.310004	-0.367850
H	-0.365688	-1.911818	0.560072
H	3.713463	-0.674235	0.990437
H	1.962860	-2.402005	1.242189
N	3.296194	2.868928	-0.684474
O	4.504013	3.597954	-0.540125
O	4.596852	1.608820	0.646707
S	5.727472	2.666224	0.029196
O	6.369983	1.992905	-1.065447

Table S71 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

TS2 at wB97X-D3(BJ)/def2-TZVPPD in the gas phase

C	-2.421408	-0.461803	0.149158
C	-1.452570	0.499655	-0.097131
C	-2.043568	-1.774669	0.410429
C	-0.114795	0.125399	-0.054759
C	0.275725	-1.190753	0.175746
C	-0.700529	-2.141556	0.422812
H	-1.719796	1.526080	-0.317794
C	0.995302	1.209849	-0.095676
H	-3.470210	-0.190308	0.127284
H	-2.804745	-2.524537	0.595448
H	1.328154	-1.449491	0.166033
H	-0.417146	-3.169993	0.613235
N	1.050634	1.156052	-1.349796
O	2.516781	2.585125	-1.436751
O	1.548948	1.765302	0.868690
S	3.275389	2.575931	-0.180292
O	4.153832	1.459718	0.003362

17

TS2 at wB97X-D3(BJ)/def2-TZVPPD in the benzene

C	-2.417870	-0.451950	0.159040
C	-1.443016	0.501290	-0.093736

C	-2.048828	-1.769197	0.416144
C	-0.107352	0.112146	-0.058640
C	0.275154	-1.209017	0.165297
C	-0.708883	-2.150243	0.418181
H	-1.702748	1.530883	-0.309535
C	1.001868	1.185897	-0.114646
H	-3.464388	-0.171265	0.145554
H	-2.815718	-2.512245	0.605561
H	1.324917	-1.478599	0.148038
H	-0.434451	-3.181722	0.605169
N	1.065998	1.128693	-1.366368
O	2.519785	2.570440	-1.446372
O	1.564564	1.764503	0.839060
S	3.233340	2.604646	-0.159559
O	4.157627	1.525741	0.046812

17

TS2 at wB97X-D3(BJ)/def2-TZVPPD in the toluene

C	-2.418703	-0.453666	0.159337
C	-1.446630	0.502347	-0.093709
C	-2.045850	-1.769883	0.416414
C	-0.109908	0.116631	-0.059298
C	0.276457	-1.203582	0.164327
C	-0.704835	-2.147369	0.417952
H	-1.709274	1.531254	-0.309305
C	0.997312	1.191764	-0.115979
H	-3.466009	-0.175940	0.146205
H	-2.810600	-2.515028	0.606234
H	1.326975	-1.470244	0.146409
H	-0.427496	-3.178052	0.605018
N	1.061904	1.134047	-1.367517
O	2.525968	2.565894	-1.446185
O	1.562517	1.769425	0.837294
S	3.236616	2.594631	-0.157440
O	4.151554	1.507770	0.050243

Table S72 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

17

C ES at wB97X-D3(BJ)/def2-TZVPPD in the gas phase

C	0.660078	-1.408584	0.049533
C	1.366004	-0.792779	-0.974634
C	0.690086	-0.885197	1.335928
C	2.106581	0.351649	-0.703891
C	2.139921	0.887528	0.581207
C	1.429760	0.262653	1.595949
H	1.353795	-1.189495	-1.981957
C	3.601145	1.835328	-1.942229
H	0.084795	-2.302499	-0.160705
H	0.139117	-1.369072	2.133420
H	2.714817	1.784517	0.779608

H	1.456272	0.678213	2.596338
N	2.818868	0.950002	-1.757683
O	4.372308	2.667891	-2.233648
O	4.205083	4.016499	0.725501
S	5.550185	3.923809	0.244197
O	6.306683	2.754434	0.565969

17

C ES at ω B97X-D3(BJ)/def2-TZVPPD in the benzene

C	1.375619	0.196116	1.619130
C	2.138348	0.809499	0.635218
C	0.585611	-0.907276	1.314299
C	2.105094	0.307428	-0.663663
C	1.319022	-0.794896	-0.978748
C	0.561294	-1.400033	0.015111
C	3.676704	1.752966	-1.869244
N	2.858880	0.901858	-1.689919
O	6.670658	3.356018	0.278975
O	4.476808	2.558936	-2.162734
S	5.496473	4.159345	0.131991
O	4.323716	3.779297	0.862121
H	2.757191	1.667939	0.868563
H	1.399928	0.585745	2.630238
H	-0.008611	-1.380539	2.087038
H	1.309930	-1.167561	-1.995561
H	-0.051162	-2.259942	-0.229909

17

C ES at ω B97X-D3(BJ)/def2-TZVPPD in the toluene

C	0.702897	-1.411234	0.056967
C	1.408427	-0.796010	-0.968727
C	0.716312	-0.874165	1.338691
C	2.131108	0.361366	-0.703395
C	2.150492	0.909523	0.577082
C	1.440631	0.285583	1.593444
H	1.407596	-1.203387	-1.972098
C	3.588926	1.868846	-1.962485
H	0.140831	-2.314635	-0.149007
H	0.164700	-1.356702	2.136774
H	2.715697	1.813758	0.771192
H	1.454650	0.710824	2.590190
N	2.838085	0.961785	-1.759967
O	4.327823	2.724892	-2.272063
O	4.277788	4.222545	0.753831
S	5.562051	3.804227	0.278566
O	5.967487	2.457682	0.543906

Table S73 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVPPD in the gas phase

C	1.805766	-0.432976	0.365173
C	2.884892	0.373858	0.032140
C	1.996091	-1.778513	0.653871
C	4.163510	-0.170587	-0.012270
C	4.362366	-1.518912	0.276635
C	3.276952	-2.316486	0.608531
H	2.750898	1.423772	-0.195804
C	6.422724	0.560907	-0.499887
H	0.810422	-0.005775	0.398242
H	1.151520	-2.405285	0.913408
H	5.362480	-1.935738	0.241287
H	3.435111	-3.364743	0.833420
N	5.234213	0.672596	-0.353789
O	7.576654	0.568481	-0.669958

14

Phenyl isocyanate ES at wB97X-D3(BJ)/def2-TZVPPD in the benzene

C	1.805461	-0.431880	0.364626
C	2.887416	0.372969	0.032697
C	1.993207	-1.778325	0.653543
C	4.164309	-0.176101	-0.009822
C	4.362034	-1.524708	0.279322
C	3.273619	-2.319687	0.609965
H	2.754423	1.423272	-0.195282
C	6.425738	0.566925	-0.502630
H	0.810989	-0.002302	0.396378
H	1.146848	-2.403479	0.911965
H	5.361324	-1.943450	0.244940
H	3.429160	-3.368417	0.835021
N	5.238732	0.664464	-0.350955
O	7.580339	0.591319	-0.678768

14

Phenyl isocyanate ES at wB97X-D3(BJ)/def2-TZVPPD in the toluene

C	1.805453	-0.431827	0.364603
C	2.887542	0.372917	0.032718
C	1.993070	-1.778312	0.653534
C	4.164350	-0.176375	-0.009717
C	4.362009	-1.524995	0.279439
C	3.273452	-2.319842	0.610032
H	2.754608	1.423239	-0.195266
C	6.425883	0.567226	-0.502754
H	0.811025	-0.002131	0.396297
H	1.146625	-2.403381	0.911913
H	5.361258	-1.943835	0.245098
H	3.428863	-3.368593	0.835099
N	5.238950	0.664052	-0.350830
O	7.580511	0.592458	-0.679166

Table S74 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, toluene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at wB97X-D3(BJ)/def2-TZVPPD in the gas phase

S	0.000000	0.000000	0.361410
O	0.000000	1.232737	-0.362289
O	0.000000	-1.232737	-0.362289

3

Sulfur dioxide ES at wB97X-D3(BJ)/def2-TZVPPD in the benzene

S	0.000000	0.000000	0.366756
O	0.000000	1.229586	-0.364962
O	0.000000	-1.229586	-0.364962

3

Sulfur dioxide ES at wB97X-D3(BJ)/def2-TZVPPD in the toluene

S	0.000000	0.000000	0.367000
O	0.000000	1.229442	-0.365084
O	0.000000	-1.229442	-0.365084

2.1.7 PBE0-D3(BJ)/def2-TZVPPD

Table S75 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−7.0	9.3	−28.9	10.1	−65.7	−61.6
	$E + \Delta ZPE$, kcal/mol	0.0	−6.2	10.3	−26.0	10.4	−64.9	−61.4
	$E + \Delta G$, kcal/mol	0.0	4.6	22.7	−13.0	22.8	−54.0	−61.3
Benzene	E , kcal/mol	0.0	−5.6	10.6	−26.8	10.6	−63.3	−60.4
	$E + \Delta ZPE$, kcal/mol	0.0	−4.8	11.5	−24.0	10.9	−62.5	−60.1
	$E + \Delta G$, kcal/mol	0.0	5.8	23.9	−11.0	23.4	−52.5	−60.1

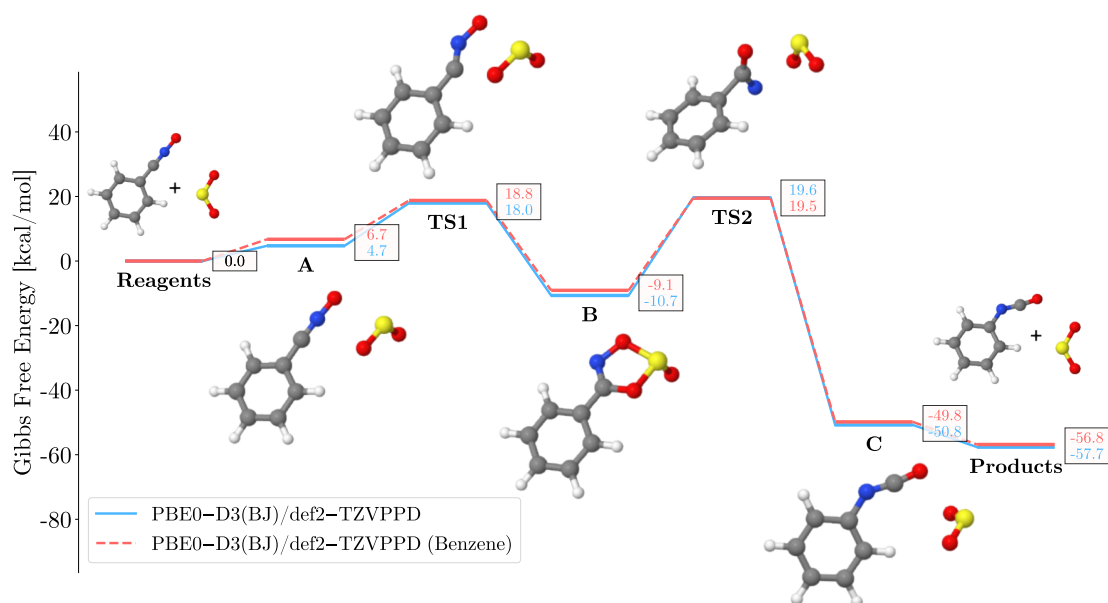


Figure S17 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. PBE0-D3(BJ)/def2-TZVPPD electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S76 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-6.8	6.1	-26.5	7.3	-64.7	-60.8
	$E + \Delta ZPE$, kcal/mol	0.0	-6.0	7.0	-23.8	7.6	-63.9	-60.5
	$E + \Delta G$, kcal/mol	0.0	4.6	19.2	-10.7	20.1	-53.6	-60.4
Benzene	E , kcal/mol	0.0	-5.3	7.2	-24.8	7.6	-62.6	-59.8
	$E + \Delta ZPE$, kcal/mol	0.0	-4.5	8.0	-22.1	7.9	-61.9	-59.5
	$E + \Delta G$, kcal/mol	0.0	6.9	20.1	-9.1	20.5	-52.5	-59.5

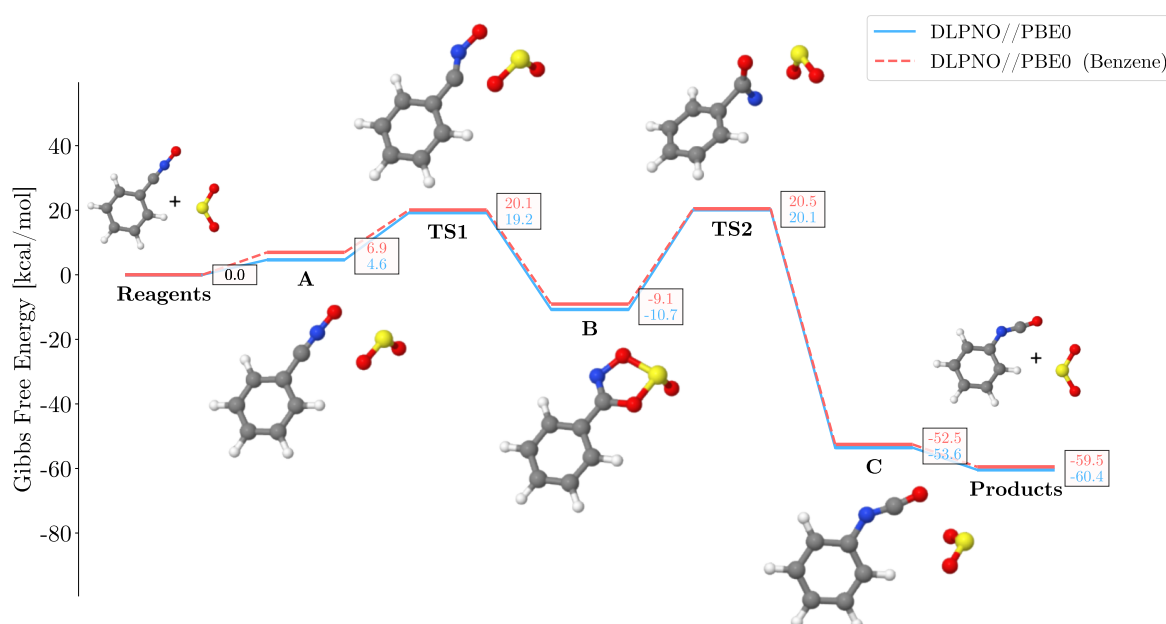


Figure S18 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//PBE0-D3(BJ)/def2-TZVPPD electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S77 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	-0.065526	-0.066395	0.353702
C	0.791745	1.017446	0.417681
C	0.434841	-1.359906	0.407543
C	2.169040	0.809928	0.536581
C	2.669481	-0.494428	0.591096
C	1.801752	-1.569402	0.525931
H	0.407165	2.028140	0.376363
C	3.059018	1.914425	0.602284
H	-1.131520	0.100093	0.261898

H	-0.240338	-2.204906	0.357349
H	3.736311	-0.650728	0.683368
H	2.195790	-2.577087	0.567982
N	3.800108	2.801416	0.648336
O	4.568432	3.719704	0.695887

14

Phenyl nitrile oxide ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	-0.066308	-0.065504	0.353627
C	0.790907	1.019010	0.417659
C	0.435327	-1.359273	0.407514
C	2.167689	0.808125	0.536526
C	2.671219	-0.495023	0.591263
C	1.802743	-1.570042	0.525960
H	0.406477	2.029945	0.376367
C	3.058313	1.913032	0.602188
H	-1.132426	0.100695	0.261775
H	-0.240031	-2.204375	0.357358
H	3.738232	-0.651041	0.683604
H	2.196443	-2.577946	0.568079
N	3.797900	2.798754	0.648131
O	4.569816	3.721943	0.695948

Table S78 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

A ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	-0.085541	0.035325	-0.230491
C	0.656863	1.196112	-0.355208
C	0.474920	-1.094154	0.349532
C	1.974594	1.223608	0.105313
C	2.539108	0.088295	0.694194
C	1.783734	-1.063982	0.811122
H	0.227482	2.080062	-0.808434
C	2.771558	2.392595	-0.019875
H	-1.106484	0.011805	-0.590060
H	-0.109876	-2.000871	0.441529
H	3.560880	0.129512	1.048980
H	2.221217	-1.944267	1.264804
N	3.510074	3.274827	-0.092770
O	4.308111	4.180441	-0.153459
O	5.626924	1.944245	1.439664
S	6.456763	2.982375	0.890305
O	7.198277	2.680574	-0.297744

17

A ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	0.035792	0.009595	-0.481330
C	0.826576	1.144832	-0.462092
C	0.400972	-1.110067	0.254738
C	1.994522	1.155207	0.304288

C	2.364199	0.029241	1.045137
C	1.563399	-1.098143	1.014627
H	0.551191	2.021134	-1.034339
C	2.824246	2.307136	0.331684
H	-0.869319	-0.001784	-1.075384
H	-0.221062	-1.996325	0.234108
H	3.275679	0.049167	1.628260
H	1.850153	-1.972375	1.585364
N	3.511246	3.229990	0.375811
O	4.272454	4.174887	0.417846
O	6.036639	1.774541	0.758617
S	6.594623	3.070499	0.476605
O	6.997290	3.328966	-0.876539

Table S79 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17
TS1 at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	-2.389091	-0.759706	-0.417558
C	-1.534650	0.321807	-0.516009
C	-1.939023	-1.962343	0.111671
C	-0.210085	0.189440	-0.087038
C	0.245652	-1.016345	0.444880
C	-0.625995	-2.086060	0.542068
H	-1.876385	1.264174	-0.923557
C	0.674795	1.297350	-0.199635
H	-3.414073	-0.661884	-0.752098
H	-2.615641	-2.803977	0.190583
H	1.270950	-1.089785	0.778177
H	-0.275406	-3.022266	0.957252
N	0.973608	2.359606	-0.645781
O	1.911731	3.183397	-0.543054
O	2.291814	1.130864	1.012883
S	3.338200	2.077496	0.552763
O	4.173597	1.578233	-0.505549

17
TS1 at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	-2.401188	-0.749779	-0.385237
C	-1.542780	0.327653	-0.499143
C	-1.944558	-1.959004	0.124502
C	-0.207090	0.179671	-0.109684
C	0.255827	-1.032577	0.402723
C	-0.620965	-2.096045	0.519643
H	-1.889127	1.275439	-0.890172
C	0.682840	1.279564	-0.247503
H	-3.434189	-0.643506	-0.691625
H	-2.624869	-2.796563	0.216285
H	1.288944	-1.119327	0.708014
H	-0.266825	-3.036826	0.921358
N	1.000924	2.324005	-0.721192

O	1.941110	3.151689	-0.592944
O	2.253049	1.165571	1.033141
S	3.300040	2.124842	0.601923
O	4.208857	1.605191	-0.390089

Table S80 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

B ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	0.084281	0.094525	-0.078724
C	1.058865	1.064653	-0.216421
C	0.405880	-1.150998	0.447388
C	2.368584	0.787345	0.174925
C	2.690605	-0.458468	0.705994
C	1.707077	-1.424600	0.839290
H	0.820178	2.038995	-0.622386
C	3.404821	1.798049	0.019540
H	-0.933021	0.309201	-0.380823
H	-0.361309	-1.908081	0.552645
H	3.709174	-0.665961	1.005093
H	1.960490	-2.394369	1.248454
N	3.284172	2.876825	-0.650092
O	4.482929	3.591428	-0.529500
O	4.599468	1.586383	0.631043
S	5.725478	2.651499	0.014335
O	6.366727	2.000576	-1.090062

17

B ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	0.082013	0.094865	-0.075466
C	1.055575	1.066409	-0.214980
C	0.406992	-1.151348	0.448276
C	2.367096	0.788835	0.171609
C	2.692898	-0.457575	0.700726
C	1.710184	-1.424635	0.836278
H	0.810080	2.040884	-0.616876
C	3.402923	1.799072	0.014088
H	-0.936593	0.309443	-0.373494
H	-0.359353	-1.909210	0.555313
H	3.712101	-0.666818	0.996989
H	1.965772	-2.394447	1.244232
N	3.289640	2.873181	-0.665747
O	4.489263	3.589774	-0.537894
O	4.593264	1.593185	0.635470
S	5.723594	2.652022	0.026672
O	6.368952	1.993363	-1.074498

Table S81 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS2 at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	-2.408088	-0.442440	0.151837
C	-1.422914	0.495481	-0.099995
C	-2.058229	-1.761180	0.413079
C	-0.090853	0.096647	-0.059127
C	0.269419	-1.229410	0.167652
C	-0.724907	-2.155348	0.420487
H	-1.668805	1.524942	-0.324549
C	1.022649	1.160501	-0.092401
H	-3.449831	-0.149364	0.132240
H	-2.833683	-2.494038	0.599315
H	1.313822	-1.513044	0.152306
H	-0.463899	-3.188426	0.610823
N	1.053032	1.099131	-1.341640
O	2.463829	2.572629	-1.441217
O	1.586671	1.726504	0.862195
S	3.207517	2.635458	-0.170853
O	4.204271	1.621956	0.019 847

17

TS2 at PBD3(BJ)/def2-TZD in the benzene

C	-2.400665	-0.424869	0.164203
C	-1.398989	0.491977	-0.097376
C	-2.074558	-1.751205	0.422013
C	-0.073824	0.063308	-0.065507
C	0.263212	-1.271739	0.152462
C	-0.749406	-2.175161	0.414659
H	-1.625496	1.527021	-0.317662
C	1.042885	1.110979	-0.115369
H	-3.436135	-0.109713	0.155202
H	-2.863522	-2.467364	0.617065
H	1.300740	-1.579445	0.127177
H	-0.509832	-3.213931	0.602290
N	1.078508	1.062012	-1.363857
O	2.454290	2.558526	-1.446627
O	1.616606	1.696283	0.830931
S	3.143432	2.698010	-0.146967
O	4.232755	1.785313	0.067365

Table S82 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

C ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	1.375012	0.176292	1.620120
C	2.181944	0.749377	0.652740
C	0.527673	-0.875361	1.299836
C	2.135657	0.263192	-0.651765
C	1.292499	-0.791507	-0.979255
C	0.492375	-1.357267	-0.000079
C	3.725042	1.677119	-1.861386

N	2.925025	0.817331	-1.651990
O	6.742033	3.928317	0.163459
O	4.510459	2.484406	-2.180180
S	5.340278	4.208497	0.137851
O	4.470245	3.422225	0.963479
H	2.853885	1.561658	0.899226
H	1.412130	0.556572	2.633528
H	-0.100469	-1.318758	2.061995
H	1.274626	-1.157015	-1.997586
H	-0.162913	-2.180179	-0.257091

17

C ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	1.356676	0.292434	1.598870
C	2.087320	0.899069	0.591314
C	0.630870	-0.864204	1.345501
C	2.097536	0.334114	-0.682034
C	1.367844	-0.819336	-0.945179
C	0.637352	-1.413850	0.071503
C	3.640050	1.741959	-1.967622
N	2.827870	0.906149	-1.716389
O	6.647268	3.214409	0.529006
O	4.432368	2.525003	-2.328433
S	5.516285	4.022415	0.185595
O	4.243134	3.671560	0.743324
H	2.643753	1.808437	0.778772
H	1.353833	0.731334	2.589200
H	0.061055	-1.332880	2.138036
H	1.382783	-1.239262	-1.942617
H	0.069506	-2.312452	-0.135944

Table S83 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

C	1.812616	-0.430795	0.363535
C	2.896425	0.365719	0.032698
C	1.991006	-1.775293	0.653581
C	4.171884	-0.185899	-0.009452
C	4.356624	-1.535764	0.281938
C	3.266124	-2.321982	0.611484
H	2.770310	1.415813	-0.196118
C	6.425071	0.578995	-0.504854
H	0.821530	0.004653	0.393982
H	1.141737	-2.394951	0.911783
H	5.352788	-1.960255	0.249052
H	3.415933	-3.370618	0.837273
N	5.237570	0.638633	-0.346148
O	7.573982	0.642344	-0.687753

14

Phenyl isocyanate ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

C	1.812514	-0.429590	0.363142
C	2.898883	0.364954	0.032779
C	1.988536	-1.774957	0.653624
C	4.172612	-0.191263	-0.007844
C	4.356446	-1.541368	0.283733
C	3.263152	-2.325015	0.612705
H	2.773758	1.415414	-0.196189
C	6.427302	0.584523	-0.506767
H	0.822283	0.008177	0.392703
H	1.137609	-2.392924	0.911350
H	5.351948	-1.967457	0.251298
H	3.410466	-3.374089	0.838797
N	5.241739	0.630480	-0.344312
O	7.576350	0.663715	-0.694020

Table S84 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the PBE0-D3(BJ)/def2-TZVPPD level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at PBE0-D3(BJ)/def2-TZVPPD in the gas phase

S	0.000000	0.000000	0.361403
O	0.000000	1.234494	-0.362285
O	0.000000	-1.234494	-0.362285

3

Sulfur dioxide ES at PBE0-D3(BJ)/def2-TZVPPD in the benzene

S	0.000000	0.000000	0.366517
O	0.000000	1.231378	-0.364842
O	0.000000	-1.231378	-0.364842

2.1.8 MP2/(aug)-cc-pVTZ

Geometries were obtained at the MP2/(aug)-cc-pVTZ level of theory^{S26} and verified to be minimum energy structures by vibrational analysis. The calculations used the (aug)-cc-pVTZ basis set,^{S18,S27} where the augmented functions were only affixed to the oxygen and sulfur atoms. All MP2 calculations were carried out using the Firefly 8.2.0 computational package,^{S28} partially based on the GAMESS US code.^{S29}

Table S85 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−6.8	7.1	−17.9	15.9	−60.9	−56.5
	$E + \Delta ZPE$, kcal/mol	0.0	−5.9	8.6	−14.7	17.1	−59.6	−55.7
	$E + \Delta G$, kcal/mol	0.0	2.9	20.6	−2.0	29.4	−52.5	−56.1
Benzene	E , kcal/mol	0.0	−6.1	7.4	−17.1	15.2	−59.8	−56.1
	$E + \Delta ZPE$, kcal/mol	0.0	−5.2	8.9	−14.0	16.4	−58.6	−55.4
	$E + \Delta G$, kcal/mol	0.0	3.6	20.9	−1.3	28.7	−51.5	−55.8

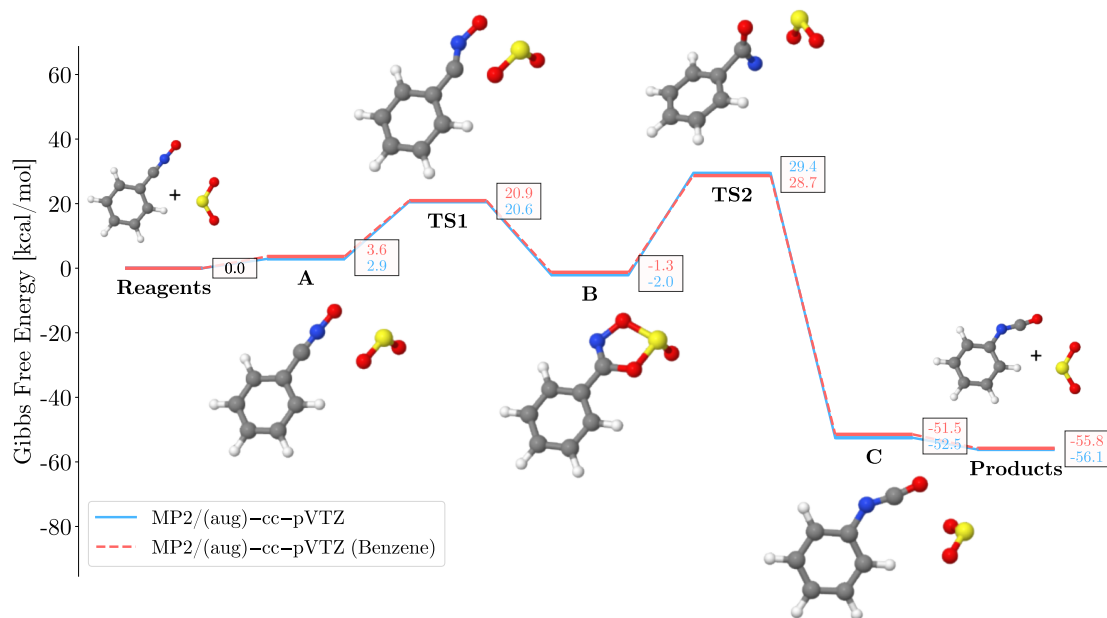


Figure S19 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. MP2/(aug)-cc-pVTZ electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S86 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-6.8	6.0	-27.5	7.6	-65.1	-61.1
	$E + \Delta ZPE$, kcal/mol	0.0	-5.9	7.5	-24.3	8.7	-63.8	-60.4
	$E + \Delta G$, kcal/mol	0.0	3.0	19.5	-11.6	21.0	-56.7	-60.8
Benzene	E , kcal/mol	0.0	-5.3	7.2	-25.7	7.6	-63.0	-60.1
	$E + \Delta ZPE$, kcal/mol	0.0	-4.4	8.7	-22.6	8.8	-61.7	-59.4
	$E + \Delta G$, kcal/mol	0.0	4.4	20.7	-9.9	21.1	-54.6	-59.8

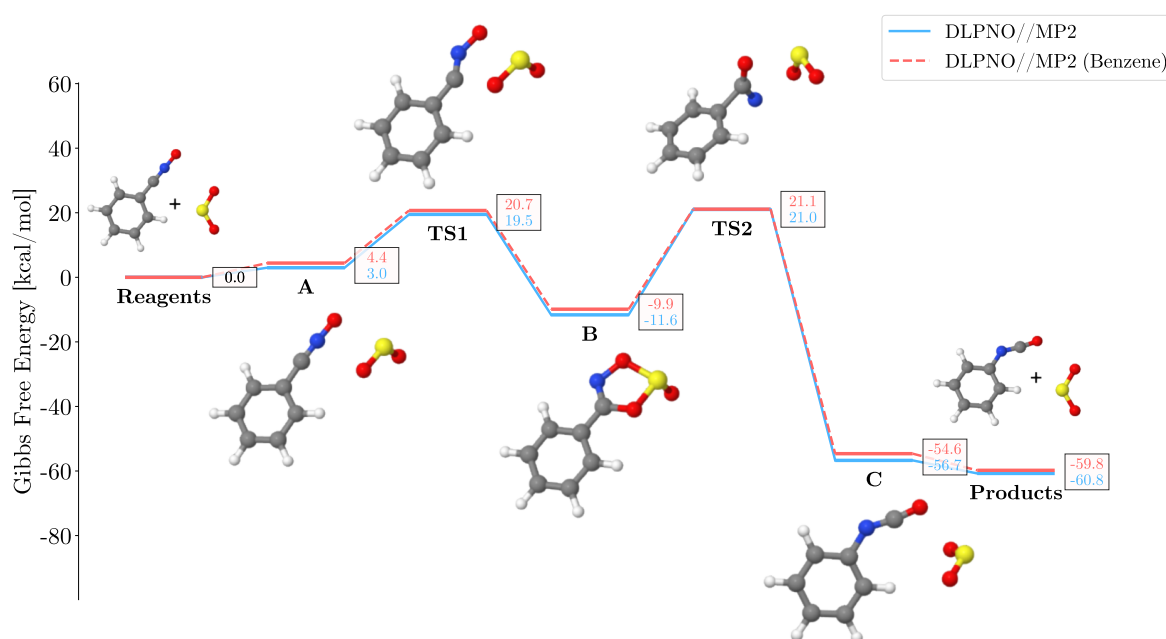


Figure S20 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//MP2/(aug)-cc-pVTZ electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S87 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at MP2/(aug)-cc-pVTZ in the gas phase

C	-0.072962	-0.069905	0.353326
C	0.788905	1.019011	0.418068
C	0.426138	-1.370198	0.406563
C	2.170361	0.807955	0.537486
C	2.673349	-0.500352	0.591788
C	1.799030	-1.579282	0.525849
H	0.406994	2.029360	0.377128
C	3.058784	1.918536	0.603073
H	-1.136972	0.098836	0.260974

H	-0.248754	-2.213033	0.355554
H	3.738795	-0.657303	0.684327
H	2.192272	-2.585627	0.567761
N	3.817246	2.822465	0.647970
O	4.583112	3.747837	0.696128

14

Phenyl nitrile oxide ES at MP2/(aug)-cc-pVTZ in the benzene

C	-0.073480	-0.068877	0.353456
C	0.787658	1.020972	0.418149
C	0.427112	-1.368900	0.406692
C	2.167710	0.804791	0.537313
C	2.675256	-0.501071	0.591833
C	1.800049	-1.579534	0.525873
H	0.406027	2.030987	0.376878
C	3.058501	1.915914	0.602228
H	-1.136910	0.098885	0.260904
H	-0.247316	-2.211174	0.355746
H	3.740385	-0.657453	0.684427
H	2.192523	-2.585402	0.567907
N	3.814084	2.818866	0.647938
O	4.584700	3.750296	0.696651

Table S88 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

A ES at MP2/(aug)-cc-pVTZ in the gas phase

C	-2.555405	-0.892098	-0.434508
C	-1.803161	0.265705	-0.600272
C	-1.981559	-2.032449	0.124680
C	-0.460705	0.278113	-0.199700
C	0.122443	-0.865622	0.365178
C	-0.645144	-2.013929	0.521730
H	-2.241469	1.153735	-1.033413
C	0.330049	1.452320	-0.359234
H	-3.591599	-0.902549	-0.742892
H	-2.571801	-2.929278	0.250714
H	1.158364	-0.833869	0.672026
H	-0.196770	-2.896547	0.956380
N	1.068546	2.362154	-0.468178
O	1.848873	3.283336	-0.552907
O	2.912308	0.994672	1.206005
S	3.898855	1.972156	0.728269
O	4.708175	1.604150	-0.433877

17

A ES at MP2/(aug)-cc-pVTZ in the benzene

C	-2.556969	-0.873249	-0.445082
C	-1.770293	0.263631	-0.594115
C	-2.023045	-2.033315	0.114037
C	-0.433633	0.229866	-0.176257

C	0.110623	-0.931761	0.389152
C	-0.692284	-2.058028	0.529664
H	-2.175905	1.167004	-1.025819
C	0.392305	1.382157	-0.321121
H	-3.588212	-0.851537	-0.766081
H	-2.640713	-2.912205	0.226130
H	1.143279	-0.934325	0.707721
H	-0.277382	-2.955476	0.965350
N	1.074106	2.329320	-0.459837
O	1.833746	3.275100	-0.558782
O	2.982196	1.074071	1.202374
S	3.907931	2.094006	0.691286
O	4.714251	1.734741	-0.478621

Table S89 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS1 at MP2/(aug)-cc-pVTZ in the gas phase

C	-2.337708	-0.758182	-0.511428
C	-1.467521	0.323341	-0.542568
C	-1.935497	-1.970693	0.049395
C	-0.179311	0.183372	-0.003817
C	0.231048	-1.030383	0.560465
C	-0.654611	-2.102229	0.582052
H	-1.766707	1.267753	-0.975183
C	0.722693	1.292001	-0.031582
H	-3.330547	-0.654282	-0.926122
H	-2.618302	-2.808517	0.069553
H	1.227704	-1.115727	0.966172
H	-0.341701	-3.041724	1.015215
N	0.870640	2.439192	-0.402534
O	1.799332	3.289956	-0.337809
O	2.339798	1.003605	0.884591
S	3.378642	2.026887	0.423628
O	4.062048	1.655631	-0.820025

17

TS1 at MP2/(aug)-cc-pVTZ in the benzene

C	-2.365425	-0.747956	-0.451892
C	-1.495679	0.332776	-0.513498
C	-1.937835	-1.968714	0.071666
C	-0.181301	0.178570	-0.045854
C	0.255956	-1.042478	0.481875
C	-0.631458	-2.111650	0.535930
H	-1.815140	1.283766	-0.915564
C	0.721297	1.284035	-0.110477
H	-3.378138	-0.635910	-0.811193
H	-2.621443	-2.803952	0.117506
H	1.271132	-1.137064	0.835917
H	-0.300244	-3.056833	0.940684
N	0.913248	2.395352	-0.561838

O	1.842695	3.251910	-0.469996
O	2.260207	1.082913	0.969491
S	3.329821	2.079750	0.533704
O	4.132307	1.615488	-0.606460

Table S90 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

B ES at MP2/(aug)-cc-pVTZ in the gas phase

C	0.091988	0.087630	-0.114896
C	1.076544	1.058707	-0.241998
C	0.394517	-1.155886	0.441665
C	2.379231	0.777998	0.186635
C	2.688921	-0.465510	0.744082
C	1.691195	-1.427784	0.870565
H	0.853124	2.026458	-0.668562
C	3.418396	1.791688	0.048794
H	-0.914157	0.300535	-0.448063
H	-0.376730	-1.907141	0.539089
H	3.698676	-0.671671	1.068353
H	1.928601	-2.390055	1.302138
N	3.260984	2.921678	-0.548273
O	4.475089	3.641714	-0.431794
O	4.644145	1.530288	0.600983
S	5.758550	2.635013	-0.035278
O	6.305323	2.043337	-1.242740

17

B ES at MP2/(aug)-cc-pVTZ in the benzene

C	0.080651	0.092932	-0.086307
C	1.059555	1.069017	-0.220361
C	0.399150	-1.157278	0.446008
C	2.371724	0.784687	0.176013
C	2.697882	-0.464917	0.711018
C	1.705520	-1.431900	0.843876
H	0.820925	2.042928	-0.623575
C	3.407022	1.799097	0.024218
H	-0.932855	0.308029	-0.392590
H	-0.368088	-1.910536	0.550874
H	3.714465	-0.673467	1.010754
H	1.954396	-2.398975	1.256248
N	3.278827	2.886760	-0.654142
O	4.484433	3.624552	-0.513526
O	4.605612	1.585790	0.654503
S	5.744169	2.652854	0.015259
O	6.351007	1.987426	-1.127572

Table S91 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS2 at MP2/(aug)-cc-pVTZ in the gas phase

C	-2.408535	-0.439324	0.146052
C	-1.421826	0.508652	-0.096736
C	-2.055758	-1.765593	0.401308
C	-0.084820	0.106421	-0.052392
C	0.283988	-1.223577	0.167061
C	-0.715536	-2.157573	0.408887
H	-1.665151	1.539242	-0.313149
C	1.024940	1.183673	-0.050521
H	-3.449725	-0.150110	0.124773
H	-2.828757	-2.499212	0.583737
H	1.329259	-1.499323	0.152691
H	-0.454160	-3.190505	0.590320
N	1.089781	1.100197	-1.298536
O	2.404638	2.463600	-1.496480
O	1.564869	1.782179	0.913576
S	3.186287	2.632041	-0.211695
O	4.200506	1.609210	0.031102

17

TS2 at MP2/(aug)-cc-pVTZ in the benzene

C	-2.405363	-0.433134	0.149318
C	-1.415427	0.510714	-0.094593
C	-2.057378	-1.761557	0.402999
C	-0.079670	0.099462	-0.048990
C	0.285758	-1.233658	0.166102
C	-0.718847	-2.161515	0.408680
H	-1.654368	1.542459	-0.308711
C	1.026915	1.166094	-0.062911
H	-3.444886	-0.139570	0.129290
H	-2.833361	-2.491404	0.584990
H	1.329042	-1.515447	0.150461
H	-0.463304	-3.195747	0.588337
N	1.094236	1.089411	-1.309780
O	2.402333	2.462584	-1.496404
O	1.582280	1.779254	0.892035
S	3.158015	2.643309	-0.194966
O	4.194026	1.638743	0.044142

Table S92 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

C ES at MP2/(aug)-cc-pVTZ in the gas phase

C	0.624474	-1.403385	0.032301
C	1.380293	-0.795386	-0.965021
C	0.620430	-0.884922	1.325630
C	2.134255	0.337352	-0.661176
C	2.138736	0.865954	0.632198
C	1.378159	0.247630	1.619615
H	1.396510	-1.183433	-1.973347

C	3.634676	1.837904	-1.898725
H	0.040164	-2.281999	-0.203060
H	0.032418	-1.359470	2.098370
H	2.730869	1.743895	0.852662
H	1.380471	0.654506	2.621349
N	2.881672	0.921578	-1.686145
O	4.381279	2.690526	-2.242445
O	4.191281	3.726902	0.790929
S	5.490124	4.016416	0.177229
O	6.559682	3.030830	0.332535

17

C ES at MP2/(aug)-cc-pVTZ in the benzene

C	0.574136	-1.406951	0.022982
C	1.336392	-0.803159	-0.972765
C	0.580602	-0.897953	1.320467
C	2.108865	0.314607	-0.660068
C	2.124300	0.833776	0.636878
C	1.356194	0.220914	1.622063
H	1.343566	-1.184787	-1.983759
C	3.659476	1.781314	-1.880298
H	-0.023277	-2.275050	-0.216555
H	-0.013094	-1.369451	2.090296
H	2.731337	1.700235	0.861740
H	1.367030	0.621276	2.626080
N	2.865904	0.898242	-1.680032
O	4.442579	2.606859	-2.213813
O	4.317541	3.581238	0.860513
S	5.473717	4.123721	0.141399
O	6.750229	3.420066	0.277772

Table S93 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at MP2/(aug)-cc-pVTZ in the gas phase

C	1.801522	-0.430215	0.365577
C	2.886149	0.374085	0.030386
C	1.989336	-1.779794	0.656959
C	4.166641	-0.176575	-0.014001
C	4.362535	-1.529138	0.276892
C	3.271522	-2.324484	0.611494
H	2.758447	1.422538	-0.198067
C	6.429964	0.562592	-0.500322
H	0.810038	-0.000529	0.398514
H	1.145090	-2.402280	0.917163
H	5.360219	-1.945969	0.239402
H	3.425738	-3.370716	0.836563
N	5.230907	0.662917	-0.355252
O	7.595489	0.608168	-0.674309

14

Phenyl isocyanate ES at MP2/(aug)-cc-pVTZ in the benzene

C	1.801633	-0.429011	0.365810
C	2.888158	0.373014	0.029699
C	1.986812	-1.779319	0.657505
C	4.166456	-0.182926	-0.013219
C	4.361717	-1.535344	0.278302
C	3.267926	-2.327757	0.612533
H	2.761169	1.421462	-0.199569
C	6.433526	0.569084	-0.501937
H	0.811487	0.003218	0.399243
H	1.140779	-2.399196	0.917449
H	5.358524	-1.953889	0.241803
H	3.419692	-3.374080	0.837251
N	5.235683	0.652277	-0.354788
O	7.600036	0.633066	-0.679084

Table S94 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the MP2/(aug)-cc-pVTZ level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at MP2/(aug)-cc-pVTZ in the gas phase

S	0.000000	0.000001	0.375718
O	0.000000	1.259626	-0.369442
O	0.000000	-1.259628	-0.369443

3

Sulfur dioxide ES at MP2/(aug)-cc-pVTZ in the benzene

S	0.000000	0.000001	0.380442
O	0.000000	1.256005	-0.371804
O	0.000000	-1.256007	-0.371805

2.1.9 Reference calculation

Geometry optimizations were carried out without symmetry constraints using the r²SCAN-3c composite method,^{S30} tight optimization and SCF convergence criteria, default “DEFGRID3” integration grid, and conductor-like polarizable continuum solvation model (CPCM)^{S31} as implemented in ORCA 5.0.4 program code. Analytical frequency calculations were performed to confirm the nature of the stationary points.

The domain-based local pair natural orbital coupled-cluster theory with single-, double-, and perturbative triple excitations (DLPNO-CCSD(T))^{S32} electronic energies were obtained using the iterative full LMP2 guess, improved perturbative triples correction (T1),^{S33} and CPCM solvation. The T_{CutPNO} cutoffs were varied (10^{-6} and 10^{-7}), while the other DLPNO thresholds corresponded to the default “TightPNO” option. The resulting correlation energies were extrapolated to the complete PNO space (CPS).^{S34,S35}

The zeroth-order regular approximation (ZORA) Hamiltonian^{S36} was used in DLPNO-CCSD(T) computations together with the relativistically recontracted Karlsruhe basis set ZORA-def2-nZVPP (n = T, Q)^{S37} and corresponding auxiliary basis set for correlated methods def2-nZVPP/C (n = T, Q).^{S38} The SCF step was converged with the “VeryTightSCF” option employing the RI-JK approximation with the automatically-constructed exchange-fitting auxiliary basis set^{S39} of the largest size (“AutoAuxSize 3”) and maximal angular momentum (“AutoAuxLmax true”). Both the HF component and correlation energy of CPS quality were extrapolated to the complete basis set limit (CBS)^{S40} using the following exponents: $\alpha = 7.88$, $\beta = 2.97$. The resulting total electronic energies are reported in Table S96 as E .

Table S95 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Benzene	E , kcal/mol	0.0	−6.2	1.6	−22.8	1.3	−60.6	−57.6
	$E + \Delta\text{ZPE}$, kcal/mol	0.0	−5.4	2.5	−20.4	1.8	−59.6	−57.1
	$E + \Delta G$, kcal/mol	0.0	5.5	15.0	−7.3	14.4	−49.2	−56.9

Table S96 Energy profile of the SO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T1)/CBS(ZORA-def2-TZVPP/ZORA-def2-QZVPP)//r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Benzene	E , kcal/mol	0.0	−5.2	7.7	−22.5	7.6	−62.4	−59.6
	$E + \Delta ZPE$, kcal/mol	0.0	−4.4	8.6	−20.2	8.0	−61.4	−59.1
	$E + \Delta G$, kcal/mol	0.0	6.5	21.0	−7.1	20.6	−51.0	−59.0

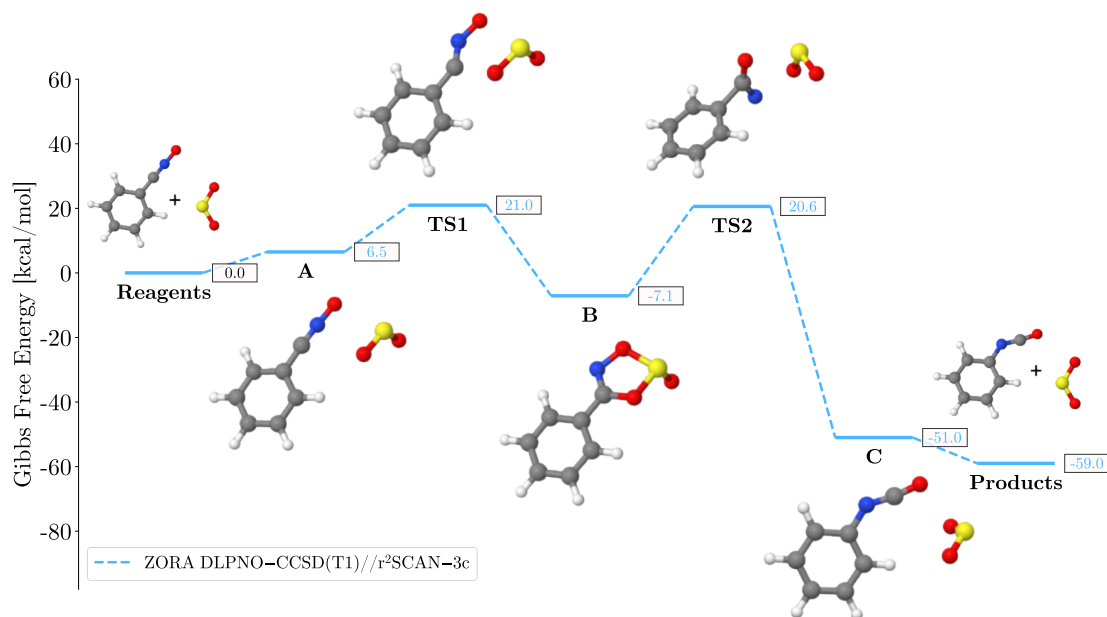


Figure S21 Calculated PES for reaction of the phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T1)/CBS(ZORA-def2-TZVPP/ZORA-def2-QZVPP)//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S97 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	−0.068393	−0.062884	0.354178
C	0.794489	1.022222	0.415874
C	0.429061	−1.363651	0.408976
C	2.178524	0.806596	0.534356
C	2.678111	−0.506218	0.589554
C	1.800912	−1.579717	0.526497
H	0.413054	2.037315	0.373590
C	3.067024	1.908633	0.597661
H	−1.136856	0.108458	0.262566
H	−0.251782	−2.208178	0.360199
H	3.747262	−0.667995	0.681112
H	2.191314	−2.592190	0.569521

N	3.797374	2.812935	0.649184
O	4.556203	3.752974	0.702725

Table S98 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

A ES at r2SCAN-3c in the benzene

C	-0.088055	0.068068	-0.213306
C	0.699727	1.202382	-0.347377
C	0.433092	-1.086779	0.367451
C	2.028705	1.177035	0.106333
C	2.556215	0.013988	0.692398
C	1.751902	-1.109533	0.817820
H	0.302188	2.105681	-0.798499
C	2.850331	2.323203	-0.021942
H	-1.115377	0.086006	-0.564450
H	-0.189779	-1.970461	0.469107
H	3.584246	0.010463	1.039470
H	2.158150	-2.008986	1.270536
N	3.527095	3.258622	-0.136622
O	4.284870	4.208756	-0.222258
O	5.598067	2.005339	1.463789
S	6.438625	3.083806	0.899527
O	7.188593	2.748903	-0.324578

Table S99 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS1 at r2SCAN-3c in the benzene

C	-2.427866	-0.710026	-0.267251
C	-1.546943	0.347817	-0.433007
C	-1.963742	-1.949858	0.170299
C	-0.178448	0.148501	-0.180408
C	0.290775	-1.097758	0.261654
C	-0.608838	-2.138604	0.437570
H	-1.896997	1.320815	-0.762319
C	0.732941	1.221259	-0.362602
H	-3.484300	-0.563554	-0.470695
H	-2.661752	-2.770495	0.306910
H	1.347953	-1.227628	0.466121
H	-0.250598	-3.103790	0.782084
N	1.081460	2.195984	-0.978095
O	1.945476	3.101643	-0.891897
O	2.084943	1.343152	1.152921
S	3.230639	2.272693	0.769264
O	4.305296	1.609849	-0.000545

Table S100 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

B ES at r2SCAN-3c in the benzene

C	0.075660	0.090774	-0.086153
C	1.059115	1.057724	-0.227323
C	0.386815	-1.157029	0.454978
C	2.373304	0.774234	0.170620
C	2.686658	-0.476541	0.713893
C	1.690406	-1.436010	0.854063
H	0.819647	2.031914	-0.641051
C	3.412263	1.788118	0.021576
H	-0.941474	0.311592	-0.395716
H	-0.388680	-1.909336	0.565738
H	3.703910	-0.696607	1.019372
H	1.936513	-2.406070	1.275265
N	3.265556	2.893563	-0.617569
O	4.453277	3.643785	-0.525433
O	4.625519	1.542830	0.610442
S	5.782798	2.676806	0.021887
O	6.433107	2.067250	-1.143890

Table S101 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS2 at r2SCAN-3c in the benzene

C	-2.418344	-0.438062	0.166963
C	-1.426794	0.496390	-0.096744
C	-2.074763	-1.765671	0.423495
C	-0.093438	0.081567	-0.059812
C	0.265031	-1.251688	0.157109
C	-0.739318	-2.171946	0.418705
H	-1.667461	1.531707	-0.315946
C	1.020657	1.142224	-0.116579
H	-3.460705	-0.135135	0.158489
H	-2.856621	-2.495240	0.613470
H	1.310267	-1.543709	0.133333
H	-0.483505	-3.210182	0.605805
N	1.101238	1.090131	-1.372497
O	2.484424	2.576401	-1.481823
O	1.555591	1.724550	0.864455
S	3.219189	2.691520	-0.156089
O	4.264550	1.677138	0.057666

Table S102 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

C ES at r2SCAN-3c in the benzene

C	0.669504	-1.415214	0.048939
C	1.403293	-0.815692	-0.968740
C	0.666479	-0.871708	1.330939
C	2.138472	0.338295	-0.695969

C	2.142861	0.892194	0.588150
C	1.404763	0.281007	1.593852
H	1.413697	-1.230070	-1.971796
C	3.578345	1.868551	-1.930725
H	0.097220	-2.313331	-0.164256
H	0.092490	-1.343404	2.122683
H	2.720486	1.790318	0.788412
H	1.408652	0.711028	2.591327
N	2.867801	0.917930	-1.740389
O	4.282304	2.754062	-2.255236
O	4.211807	3.973656	0.829646
S	5.563113	3.932188	0.245581
O	6.334205	2.695086	0.440481

Table S103 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-3c in the benzene

C	1.803763	-0.430017	0.365803
C	2.885355	0.376359	0.029076
C	1.991773	-1.778658	0.657172
C	4.166947	-0.174357	-0.016014
C	4.364767	-1.528053	0.275498
C	3.274686	-2.321524	0.610340
H	2.750294	1.428662	-0.199899
C	6.427049	0.558767	-0.498303
H	0.807577	0.001366	0.399944
H	1.144290	-2.404527	0.919457
H	5.366218	-1.948274	0.237790
H	3.430754	-3.372545	0.836072
N	5.233062	0.665820	-0.359236
O	7.587058	0.597581	-0.666705

Table S104 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.776227	0.642566	0.000000
O	2.243738	0.542269	0.000000
O	0.191813	1.992428	0.000000

2.2 The SeO₂-catalyzed conversion

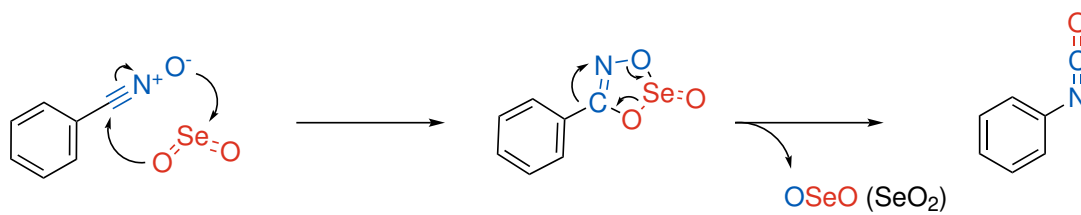


Figure S22 Reaction of the phenyl nitrile oxide with selenium dioxide.

2.2.1 r²SCAN-3c

Table S105 Energy profile of the SeO₂-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-10.2	-7.1	-40.4	-6.6	-64.1	-58.2
	$E + \Delta ZPE$, kcal/mol	0.0	-9.3	-6.3	-38.1	-6.3	-62.9	-57.6
	$E + \Delta G$, kcal/mol	0.0	2.4	6.5	-24.7	6.6	-51.4	-57.3
Benzene	E , kcal/mol	0.0	-9.0	-5.9	-38.6	-7.1	-62.2	-57.6
	$E + \Delta ZPE$, kcal/mol	0.0	-8.0	-5.1	-36.3	-6.8	-61.0	-57.0
	$E + \Delta G$, kcal/mol	0.0	3.4	7.5	-23.0	6.0	-49.8	-56.8

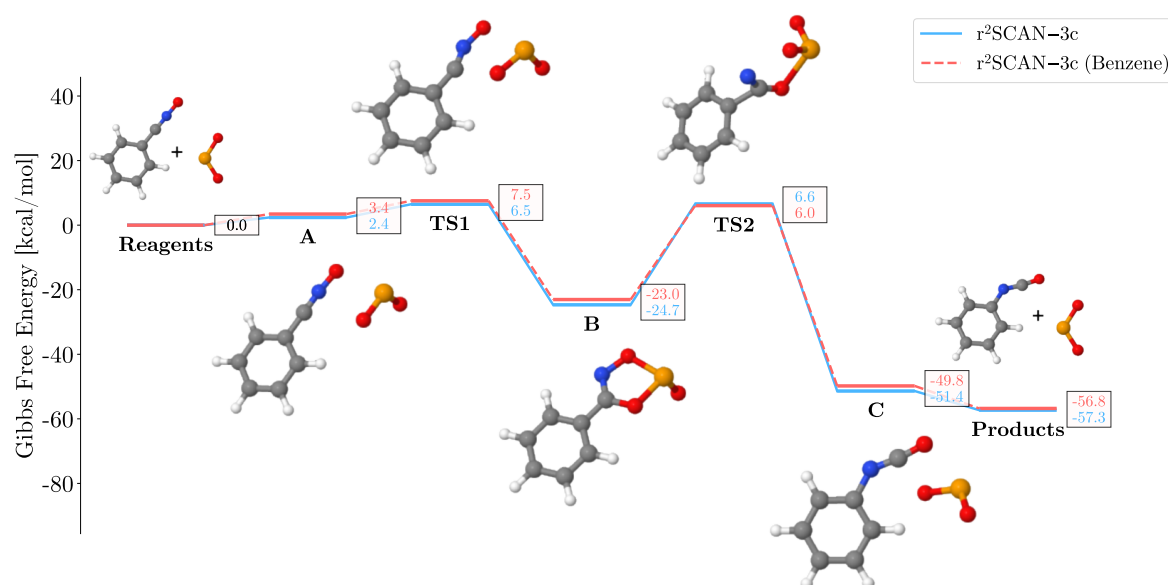


Figure S23 Calculated PES for reaction of the phenyl nitrile oxide with selenium dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S106 Energy profile of the SeO₂-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−10.0	−4.5	−43.3	−2.9	−66.2	−60.9
	<i>E</i> + Δ <i>ZPE</i> , kcal/mol	0.0	−9.1	−3.7	−40.9	−2.7	−65.0	−60.3
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	2.6	9.0	−27.5	10.2	−53.5	−60.0
Benzene	<i>E</i> , kcal/mol	0.0	−8.5	−3.2	−41.3	−3.1	−63.9	−60.0
	<i>E</i> + Δ <i>ZPE</i> , kcal/mol	0.0	−7.6	−2.4	−39.0	−2.8	−62.7	−59.3
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	3.9	10.2	−25.8	10.0	−51.5	−59.2

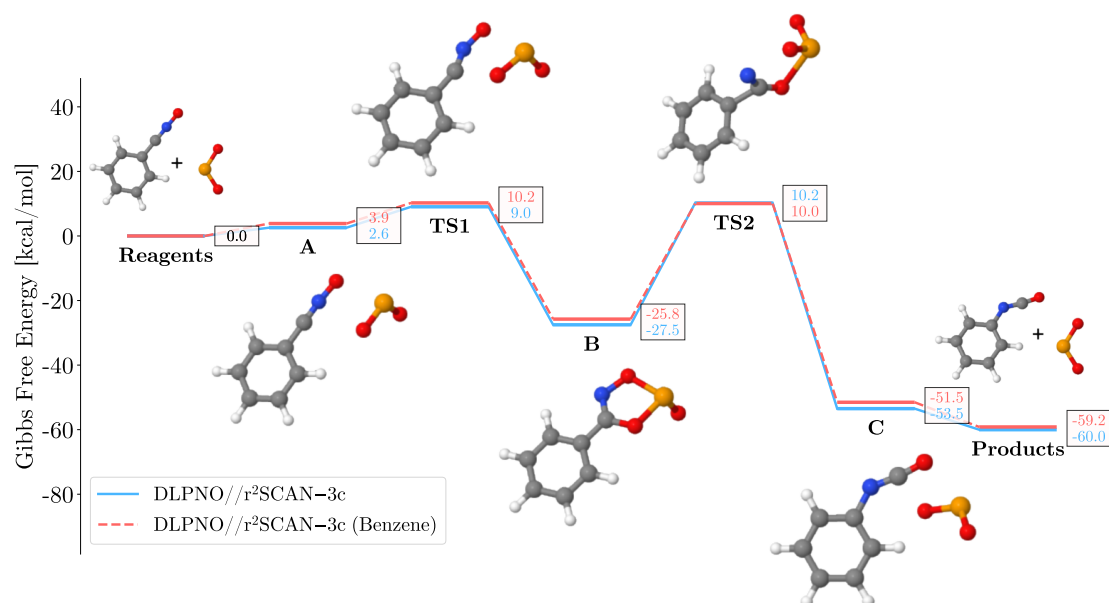


Figure S24 Calculated PES for reaction of the phenyl nitrile oxide with selenium dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S107 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021

H	-0.248893	-2.210375	0.356466
H	3.744529	-0.661291	0.684203
H	2.194048	-2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

14

Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	-0.070011	-0.064477	0.353451
C	0.790463	1.022328	0.417736
C	0.430226	-1.364123	0.407122
C	2.174624	0.809409	0.537228
C	2.677066	-0.502349	0.591715
C	1.802309	-1.577563	0.526116
H	0.406907	2.036617	0.376609
C	3.061424	1.912690	0.602594
H	-1.138734	0.104487	0.260883
H	-0.248747	-2.210021	0.356343
H	3.746414	-0.661821	0.684516
H	2.194673	-2.589276	0.568175
N	3.800741	2.809808	0.648216
O	4.568944	3.742590	0.695297

Table S108 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

A ES at r2SCAN-3c in the gas phase

C	-0.066963	0.057546	-0.215227
C	0.693954	1.209133	-0.350662
C	0.481377	-1.082779	0.367699
C	2.022055	1.215768	0.104045
C	2.578137	0.067838	0.692905
C	1.799562	-1.073103	0.818577
H	0.275493	2.101755	-0.803944
C	2.822678	2.376208	-0.022532
H	-1.094073	0.050143	-0.566890
H	-0.120242	-1.980842	0.470275
H	3.606161	0.097052	1.038694
H	2.226636	-1.962035	1.272621
N	3.509732	3.304938	-0.123427
O	4.296340	4.234651	-0.181932
O	5.392782	1.883764	1.492266
Se	6.394017	3.038090	0.920398
O	7.190954	2.578374	-0.415466

17

A ES at r2SCAN-3c in the benzene

C	-0.082897	0.073002	-0.201853
C	0.702655	1.208004	-0.341687
C	0.445030	-1.081970	0.372639
C	2.035124	1.179700	0.100048

C	2.571294	0.017761	0.680200
C	1.767905	-1.105622	0.811034
H	0.300949	2.111998	-0.787627
C	2.858672	2.323375	-0.031045
H	-1.113480	0.090497	-0.543107
H	-0.176600	-1.966006	0.478855
H	3.602738	0.018484	1.017000
H	2.178214	-2.005669	1.258743
N	3.532848	3.257789	-0.153272
O	4.315042	4.196131	-0.225031
O	5.459927	1.941996	1.513870
Se	6.390795	3.151928	0.936227
O	7.220383	2.705102	-0.387594

Table S109 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS1 at r2SCAN-3c in the gas phase

C	-0.086875	0.032877	0.062698
C	0.814276	1.054586	-0.192496
C	0.362657	-1.203581	0.522579
C	2.187499	0.825862	0.000682
C	2.642743	-0.416314	0.465775
C	1.723139	-1.421898	0.724890
H	0.474331	2.022847	-0.545185
C	3.120806	1.858500	-0.269358
H	-1.147653	0.204687	-0.092269
H	-0.350367	-1.996817	0.725878
H	3.705306	-0.561448	0.623109
H	2.072293	-2.383925	1.086996
N	3.494661	2.850673	-0.803921
O	4.380274	3.711860	-0.916080
O	4.912913	1.654848	1.011046
Se	6.100143	2.648757	0.411885
O	6.968254	1.915487	-0.745532

17

TS1 at r2SCAN-3c in the benzene

C	-0.083757	0.079105	0.192928
C	0.826422	1.076164	-0.123323
C	0.363451	-1.185941	0.571979
C	2.201574	0.788448	-0.080214
C	2.654843	-0.483013	0.304751
C	1.728663	-1.462114	0.630742
H	0.492427	2.067774	-0.411063
C	3.142430	1.794009	-0.409004
H	-1.147558	0.292247	0.151933
H	-0.355814	-1.958836	0.826290
H	3.720995	-0.676364	0.350824
H	2.073154	-2.446625	0.931738
N	3.578438	2.698365	-1.044976

O	4.473394	3.562875	-1.135645
O	4.737491	1.862419	1.120356
Se	5.962288	2.826156	0.547059
O	7.005956	1.962334	-0.353677

Table S110 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

B ES at r2SCAN-3c in the gas phase

C	0.065767	0.087486	-0.085369
C	1.054386	1.049065	-0.222283
C	0.366940	-1.161749	0.456629
C	2.365406	0.761820	0.181587
C	2.667653	-0.490412	0.725600
C	1.666906	-1.445808	0.860547
H	0.826209	2.024018	-0.639841
C	3.412642	1.773424	0.037859
H	-0.948526	0.313243	-0.400668
H	-0.412494	-1.910412	0.563207
H	3.682806	-0.713358	1.034942
H	1.907029	-2.417326	1.281837
N	3.235455	2.883711	-0.584505
O	4.366230	3.685734	-0.567152
O	4.624504	1.495187	0.607510
Se	5.879458	2.746601	0.052889
O	6.614028	2.115776	-1.232088

17

B ES at r2SCAN-3c in the benzene

C	0.063975	0.088079	-0.081851
C	1.051917	1.051008	-0.220896
C	0.368380	-1.162071	0.457684
C	2.365012	0.763462	0.177639
C	2.670681	-0.489649	0.719497
C	1.670541	-1.446019	0.857100
H	0.816576	2.026105	-0.634492
C	3.412759	1.774859	0.032393
H	-0.951802	0.314071	-0.392493
H	-0.410382	-1.911301	0.566506
H	3.686348	-0.714821	1.026123
H	1.912950	-2.417669	1.277033
N	3.241239	2.880297	-0.601988
O	4.374441	3.684851	-0.576471
O	4.618503	1.502767	0.613755
Se	5.878957	2.750204	0.068143
O	6.604305	2.102828	-1.216984

Table S111 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS2 at r2SCAN-3c in the gas phase

C	0.267023	0.045203	-0.488730
C	1.368089	0.886626	-0.528989
C	0.252221	-1.042727	0.385060
C	2.461221	0.598376	0.293186
C	2.445277	-0.466509	1.197435
C	1.335583	-1.297944	1.225903
H	1.401947	1.750297	-1.185344
C	3.811613	1.334064	0.010831
H	-0.588102	0.243721	-1.127178
H	-0.619610	-1.689313	0.421932
H	3.294173	-0.628408	1.853640
H	1.306664	-2.137511	1.913329
N	3.464916	2.147471	0.896258
O	5.268611	3.284823	0.730165
O	4.683431	1.037992	-0.834596
Se	5.956603	2.950841	-0.743822
O	5.264738	3.779999	-1.948376

17

TS2 at r2SCAN-3c in the benzene

C	0.259206	0.042000	-0.484706
C	1.355251	0.889122	-0.532426
C	0.256755	-1.046947	0.389500
C	2.456423	0.600415	0.281525
C	2.453212	-0.463913	1.189155
C	1.347355	-1.299822	1.223218
H	1.379435	1.752653	-1.189664
C	3.788089	1.350527	0.010310
H	-0.601416	0.236702	-1.116891
H	-0.612682	-1.696481	0.433060
H	3.307646	-0.625211	1.838613
H	1.326592	-2.140450	1.909604
N	3.456147	2.168039	0.897605
O	5.269296	3.288214	0.731258
O	4.673818	1.072072	-0.836331
Se	5.964385	2.910409	-0.732839
O	5.294890	3.759672	-1.940290

Table S112 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

C ES at r2SCAN-3c in the gas phase

C	1.334073	0.411408	1.575561
C	2.070092	1.046716	0.584902
C	0.734997	-0.823083	1.333366
C	2.202306	0.432978	-0.664288
C	1.611398	-0.805086	-0.915014
C	0.877342	-1.427030	0.087654
C	3.478428	2.079398	-1.924024

N	2.934677	1.034638	-1.692969
O	5.658540	1.792495	0.192842
O	4.047545	3.052565	-2.268453
Se	5.634638	3.414676	0.195302
O	4.316647	4.034919	0.910763
H	2.552339	2.001659	0.773728
H	1.232314	0.885796	2.547164
H	0.162273	-1.312883	2.114794
H	1.732163	-1.263940	-1.890809
H	0.415726	-2.390328	-0.107616

17

C ES at r2SCAN-3c in the benzene

C	1.292827	0.413438	1.567074
C	2.021558	1.057989	0.576220
C	0.729570	-0.839888	1.330997
C	2.183531	0.435547	-0.665652
C	1.627812	-0.820220	-0.910463
C	0.900338	-1.451897	0.092069
C	3.443899	2.101362	-1.909821
N	2.911407	1.046932	-1.693335
O	5.609760	1.763817	0.196739
O	4.000538	3.084951	-2.243665
Se	5.732138	3.382632	0.161700
O	4.504432	4.118410	0.926841
H	2.472415	2.029576	0.758583
H	1.167664	0.894915	2.532604
H	0.162037	-1.337226	2.111656
H	1.769275	-1.286395	-1.880279
H	0.466300	-2.429043	-0.098364

Table S113 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117
C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671
H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

14

Phenyl isocyanate ES at r2SCAN-3c in the benzene

C	1.803887	-0.429972	0.365559
C	2.885572	0.376270	0.029182
C	1.991774	-1.778532	0.656905
C	4.166973	-0.174601	-0.015655
C	4.364734	-1.528186	0.275871
C	3.274615	-2.321533	0.610396
H	2.750503	1.428595	-0.199560
C	6.426998	0.559017	-0.497533
H	0.807741	0.001398	0.399657
H	1.144299	-2.404447	0.919050
H	5.366178	-1.948342	0.238437
H	3.430633	-3.372559	0.836012
N	5.233036	0.665626	-0.359073
O	7.586657	0.597866	-0.668250

Table S114 Cartesian coordinates of the selenium dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

Selenium dioxide ES at r2SCAN-3c in the gas phase

Se	0.000000	0.000000	0.463500
O	0.000000	1.362452	-0.413334
O	0.000000	-1.362451	-0.413334

3

Selenium dioxide ES at r2SCAN-3c in the benzene

Se	0.000000	0.000000	0.472594
O	0.000000	1.354840	-0.417881
O	0.000000	-1.354840	-0.417881

2.3 The SO₃-catalyzed conversion

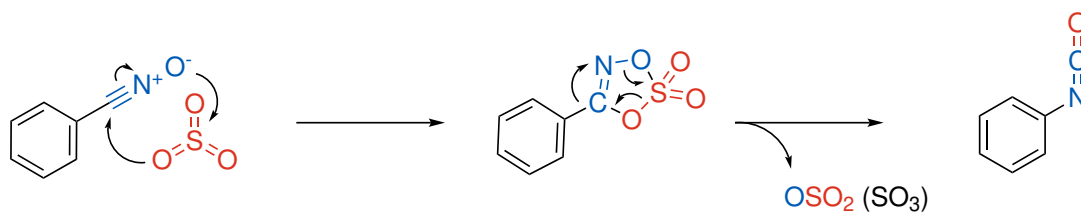


Figure S25 Reaction of the phenyl nitrile oxide with sulfur trioxide.

2.3.1 r²SCAN-3c

Table S115 Energy profile of the SO₃-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−9.8	0.4	−32.1	−2.9	−63.7	−58.2
	<i>E</i> + ΔZPE, kcal/mol	0.0	−9.0	1.2	−29.7	−2.4	−62.6	−57.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.2	14.0	−15.6	10.8	−49.8	−57.3
CH ₂ Cl ₂	<i>E</i> , kcal/mol	0.0	−10.8	−3.2	−29.7	−7.4	−61.3	−57.1
	<i>E</i> + ΔZPE, kcal/mol	0.0	−9.8	−2.3	−27.3	−6.6	−60.3	−56.5
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	3.0	11.8	−13.8	6.8	−47.2	−56.4

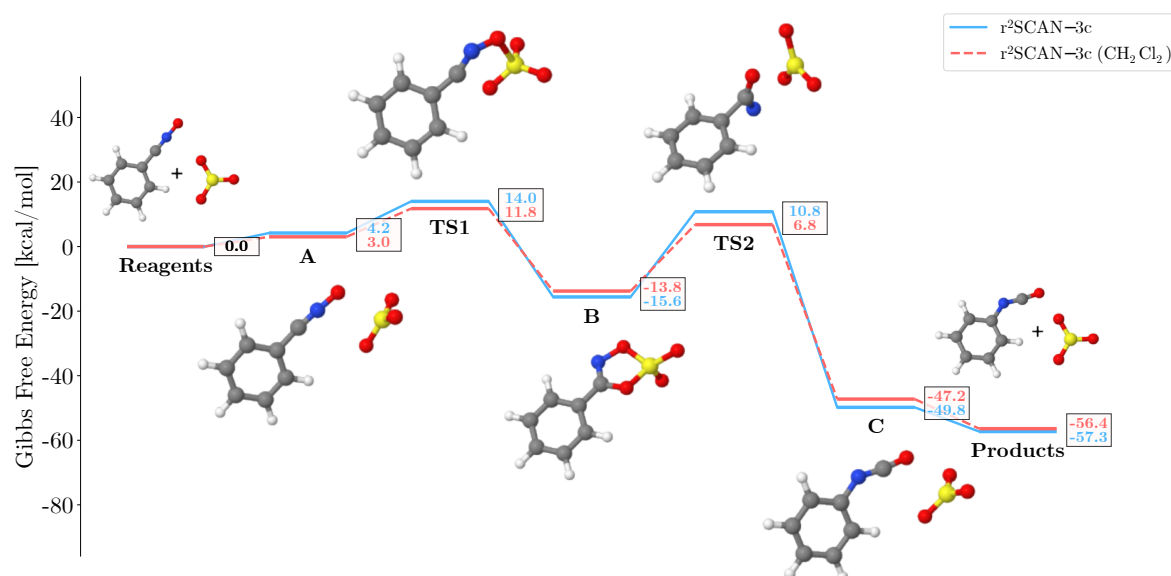


Figure S26 Calculated PES for reaction of the phenyl nitrile oxide with sulfur trioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S116 Energy profile of the SO₃-catalyzed conversion. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−11.0	−0.3	−38.9	−1.5	−66.9	−60.9
	<i>E</i> + ΔZPE, kcal/mol	0.0	−10.1	0.6	−36.4	−1.0	−65.8	−60.3
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	3.0	13.3	−22.3	12.2	−52.9	−60.0
CH ₂ Cl ₂	<i>E</i> , kcal/mol	0.0	−12.7	−5.6	−36.1	−7.2	−63.3	−59.2
	<i>E</i> + ΔZPE, kcal/mol	0.0	−11.6	−4.8	−33.7	−6.5	−62.2	−58.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	1.2	9.3	−20.2	6.9	−49.2	−58.5

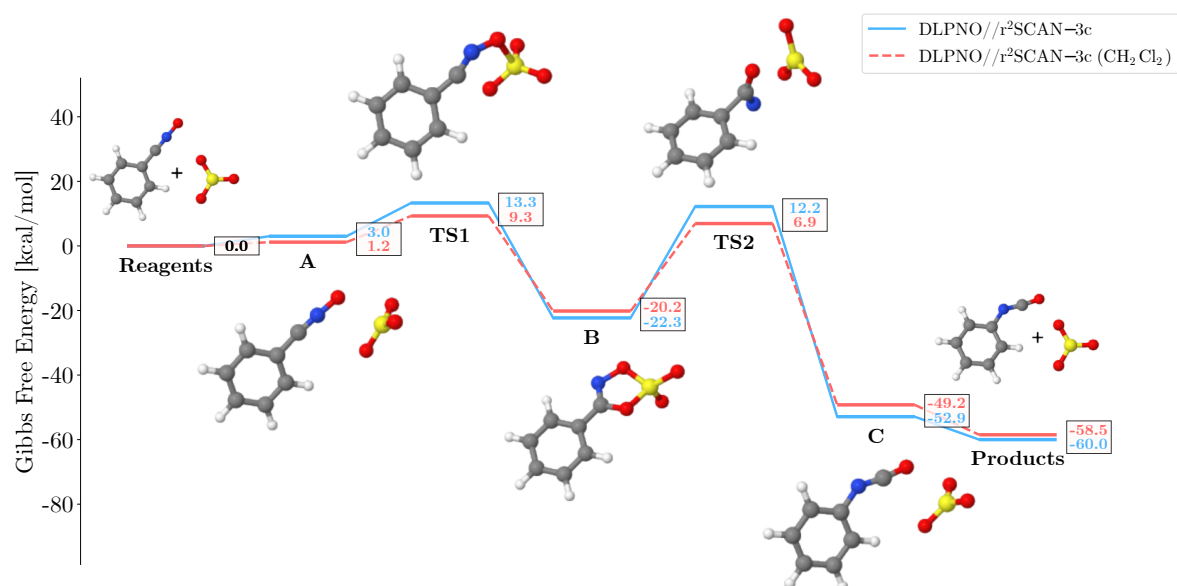


Figure S27 Calculated PES for reaction of the phenyl nitrile oxide with sulfur trioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S117 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065297	0.353512
C	0.791195	1.020771	0.417689
C	0.429900	−1.364571	0.407188
C	2.175756	0.811020	0.537191
C	2.675333	−0.501768	0.591475
C	1.801407	−1.576849	0.526092
H	0.407660	2.034876	0.376569
C	3.061915	1.913795	0.602642
H	−1.137826	0.103842	0.261021

H	-0.248893	-2.210375	0.356466
H	3.744528	-0.661290	0.684203
H	2.194049	-2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567887	3.740538	0.695396

14

Phenyl nitrile oxide ES at r2SCAN-3c in the dichloromethane

C	-0.070498	-0.063822	0.353411
C	0.789991	1.023429	0.417734
C	0.430525	-1.363669	0.407108
C	2.173825	0.808060	0.537210
C	2.678342	-0.502931	0.591855
C	1.802930	-1.578083	0.526139
H	0.406422	2.037851	0.376609
C	3.061060	1.911663	0.602530
H	-1.139294	0.105010	0.260804
H	-0.248611	-2.209594	0.356318
H	3.747781	-0.662498	0.684702
H	2.194968	-2.589983	0.568214
N	3.799234	2.808203	0.648057
O	4.569624	3.744664	0.695309

Table S118 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

18

A ES at r2SCAN-3c in the gas phase

C	0.706219	0.115308	-0.930521
C	1.756663	0.926097	-0.528359
C	0.193124	-0.852408	-0.069558
C	2.299478	0.760844	0.756869
C	1.786231	-0.214878	1.624579
C	0.733820	-1.014295	1.203770
H	2.167378	1.683500	-1.188032
C	3.372281	1.593010	1.157616
H	0.285291	0.240477	-1.923308
H	-0.630056	-1.482445	-0.392236
H	2.214755	-0.334770	2.614028
H	0.333936	-1.769072	1.873687
N	4.230709	2.333263	1.396062
O	5.140699	3.114280	1.629148
O	7.007194	3.407953	-0.580423
S	5.761184	4.149954	-0.446625
O	4.560585	3.654171	-1.119073
O	5.766793	5.495976	0.106794

18

A ES at r2SCAN-3c in the dichloromethane

C	0.277172	0.030200	-0.735376
C	1.155618	1.077645	-0.504689
C	0.320862	-1.111570	0.064059

C	2.084904	0.970282	0.544186
C	2.133223	-0.178690	1.351851
C	1.245795	-1.214306	1.102689
H	1.134747	1.972098	-1.118573
C	2.983770	2.031946	0.788735
H	-0.444720	0.104043	-1.542683
H	-0.370722	-1.927510	-0.124089
H	2.858814	-0.244192	2.155811
H	1.275428	-2.106110	1.720885
N	3.700434	2.912202	1.004011
O	4.482510	3.850486	1.220814
O	6.778899	2.353812	0.849880
S	6.353119	3.569441	0.157233
O	5.783269	3.439974	-1.183764
O	6.897489	4.856330	0.579459

Table S119 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

18

TS1 at r2SCAN-3c in the gas phase

C	-2.241342	-1.091671	-1.021291
C	-1.448939	0.034060	-0.871608
C	-2.068323	-2.184915	-0.173203
C	-0.495032	0.069445	0.161308
C	-0.316527	-1.035358	1.012093
C	-1.105772	-2.159032	0.835512
H	-1.555212	0.889007	-1.530941
C	0.325435	1.202351	0.319531
H	-2.988571	-1.124645	-1.807673
H	-2.686289	-3.068418	-0.303484
H	0.444957	-0.994676	1.783474
H	-0.973735	-3.018714	1.484541
N	0.576019	2.351196	0.557205
O	1.633744	3.067330	0.491299
O	2.320667	0.621817	-0.141473
S	3.122357	1.897021	-0.178641
O	3.348965	2.474261	-1.499471
O	4.107601	2.070939	0.882822

18

TS1 at r2SCAN-3c in the dichloromethane

C	-2.097619	-1.111494	-1.098948
C	-1.286249	-0.008803	-0.902283
C	-2.070188	-2.169216	-0.187477
C	-0.450486	0.028997	0.232926
C	-0.412584	-1.043931	1.146844
C	-1.232752	-2.136369	0.929625
H	-1.285317	0.823600	-1.598434
C	0.386626	1.133097	0.431195
H	-2.752800	-1.153386	-1.963080
H	-2.709207	-3.032240	-0.351098

H	0.250478	-0.996647	2.004445
H	-1.222307	-2.967424	1.627421
N	0.652208	2.239106	0.840785
O	1.752762	2.933414	0.712128
O	2.213654	0.716614	-0.475542
S	3.006774	1.992612	-0.342665
O	3.086367	2.818427	-1.548896
O	4.170641	1.933644	0.543054

Table S120 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

18

B ES at r2SCAN-3c in the gas phase

C	0.096958	0.131333	-0.048134
C	1.102108	1.066291	-0.233858
C	0.386956	-1.113592	0.509748
C	2.415774	0.754341	0.141739
C	2.708887	-0.493753	0.700431
C	1.690850	-1.421910	0.882044
H	0.883670	2.036820	-0.666987
C	3.473421	1.738124	-0.049859
H	-0.920444	0.373091	-0.339761
H	-0.405769	-1.841782	0.652962
H	3.725872	-0.734439	0.990442
H	1.919800	-2.390014	1.316546
N	3.283465	2.909215	-0.555053
O	4.502123	3.617319	-0.590047
O	4.735292	1.387431	0.336014
S	5.782905	2.661460	-0.055490
O	6.608736	2.246148	-1.168632
O	6.338239	3.198354	1.167670

18

B ES at r2SCAN-3c in the dichloromethane

C	0.083414	0.155397	0.012938
C	1.089198	1.087888	-0.188432
C	0.386281	-1.107541	0.523584
C	2.415102	0.750711	0.119248
C	2.721993	-0.514987	0.632491
C	1.702663	-1.438273	0.832654
H	0.854541	2.074963	-0.573728
C	3.473920	1.725484	-0.096847
H	-0.944076	0.415918	-0.222203
H	-0.407166	-1.831886	0.683161
H	3.747860	-0.776589	0.869456
H	1.940116	-2.419978	1.230970
N	3.323867	2.834292	-0.739659
O	4.545239	3.554893	-0.734611
O	4.706021	1.438372	0.423959
S	5.767225	2.671931	-0.000222

0	6.700922	2.166208	-0.986362
0	6.221721	3.337633	1.203378

Table S121 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

18			
TS2 at r2SCAN-3c in the gas phase			
C	-2.412473	-0.426320	0.187718
C	-1.414346	0.496185	-0.079230
C	-2.079019	-1.760817	0.424210
C	-0.081205	0.065919	-0.066618
C	0.260314	-1.279774	0.126947
C	-0.749612	-2.187956	0.394223
H	-1.640281	1.537018	-0.286986
C	1.036703	1.104714	-0.113546
H	-3.451647	-0.113779	0.197386
H	-2.867511	-2.482431	0.617344
H	1.301640	-1.582011	0.079407
H	-0.508890	-3.232322	0.564775
N	1.066976	1.047191	-1.365182
O	2.552447	2.613993	-1.415518
O	1.617473	1.683096	0.847558
S	3.161665	2.658489	-0.045261
O	4.221225	1.701588	0.239448
O	3.111712	3.936833	0.646247

18			
TS2 at r2SCAN-3c in the dichloromethane			
C	-2.394184	-0.388232	0.223704
C	-1.381892	0.515455	-0.043050
C	-2.086408	-1.736375	0.429755
C	-0.055187	0.049062	-0.051822
C	0.260708	-1.312548	0.107023
C	-0.767039	-2.197858	0.373042
H	-1.587674	1.565493	-0.225024
C	1.060706	1.041412	-0.158954
H	-3.425736	-0.053015	0.256172
H	-2.889574	-2.443040	0.618092
H	1.293461	-1.640594	0.039771
H	-0.551089	-3.250896	0.521300
N	1.115430	1.033599	-1.410782
O	2.610395	2.505900	-1.441308
O	1.698052	1.642294	0.785899
S	3.080448	2.641019	-0.013742
O	4.253049	1.852716	0.351977
O	2.891703	3.955226	0.590870

Table S122 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

18

C ES at r2SCAN-3c in the gas phase

C	1.208350	0.249210	1.605465
C	2.065216	0.819237	0.673503
C	0.446715	-0.869652	1.276441
C	2.155801	0.256410	-0.602595
C	1.398070	-0.863872	-0.941912
C	0.545094	-1.421525	0.002682
C	3.783789	1.690159	-1.745819
N	3.006547	0.796921	-1.570114
O	6.787586	3.944039	-0.383603
O	4.566483	2.517172	-2.057730
S	5.382616	4.211067	-0.125630
O	4.656194	3.392135	0.838217
H	2.663732	1.690015	0.923445
H	1.137554	0.684777	2.597691
H	-0.220463	-1.309218	2.011224
H	1.484998	-1.283733	-1.938548
H	-0.045398	-2.293796	-0.260755
O	4.717257	5.338903	-0.757070

18

C ES at r2SCAN-3c in the dichloromethane

C	1.465940	-0.239460	1.782549
C	2.396701	0.361142	0.944168
C	0.389480	-0.949045	1.251346
C	2.239979	0.245431	-0.440140
C	1.165887	-0.459430	-0.982986
C	0.244196	-1.056515	-0.129624
C	4.186367	1.438838	-1.322294
N	3.150244	0.842551	-1.319500
O	6.428481	4.356333	0.026649
O	5.198802	2.034020	-1.468624
S	5.110495	4.488261	-0.574008
O	3.922345	4.160443	0.202658
H	3.237328	0.917171	1.349440
H	1.583682	-0.150726	2.858655
H	-0.333681	-1.415637	1.913428
H	1.063452	-0.534221	-2.060911
H	-0.592450	-1.607209	-0.549365
O	4.969848	5.051506	-1.907980

Table S123 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804374	-0.430950	0.365941
C	2.883883	0.376434	0.028869
C	1.993876	-1.778576	0.657116
C	4.166459	-0.170762	-0.017343
C	4.364437	-1.524100	0.274057

C	3.276740	-2.319149	0.609373
H	2.748758	1.428424	-0.199958
C	6.424810	0.555113	-0.495671
H	0.807665	-0.001293	0.400931
H	1.147686	-2.405515	0.920014
H	5.366570	-1.942505	0.235881
H	3.434435	-3.369792	0.834893
N	5.229817	0.670827	-0.360749
O	7.584091	0.582445	-0.662355

14

Phenyl isocyanate ES at r2SCAN-3c in the dichloromethane

C	1.803641	-0.429232	0.365280
C	2.886988	0.375929	0.029372
C	1.990133	-1.778424	0.656809
C	4.167441	-0.177778	-0.014443
C	4.364744	-1.531542	0.277198
C	3.272786	-2.323395	0.611191
H	2.752194	1.428518	-0.199358
C	6.428760	0.562331	-0.498949
H	0.807965	0.003538	0.398725
H	1.141638	-2.403438	0.918468
H	5.365634	-1.953169	0.240328
H	3.427415	-3.374713	0.836926
N	5.235610	0.661135	-0.357784
O	7.588651	0.610841	-0.672761

Table S124 Cartesian coordinates of the sulfur trioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and dichloromethane, which was treated with CPCM continuum solvent model.

4

Sulfur trioxide ES at r2SCAN-3c in the gas phase

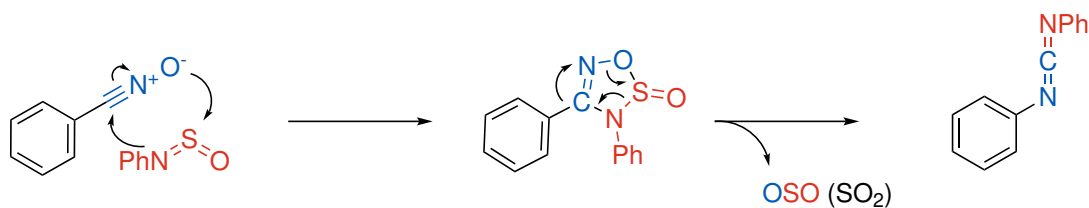
S	0.043509	0.008011	0.341438
O	-0.017613	1.262956	-0.393788
O	-0.016087	-1.257993	-0.374677
O	0.164367	0.019064	1.792150

4

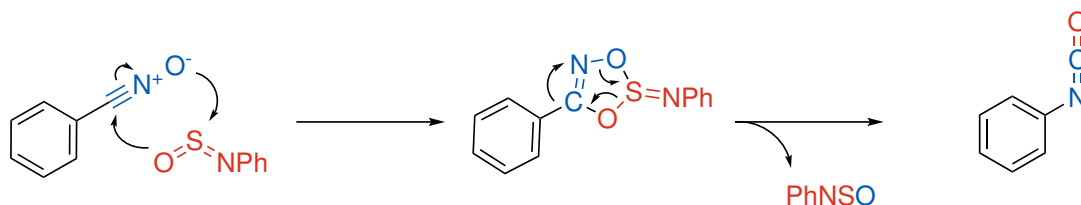
Sulfur trioxide ES at r2SCAN-3c in the dichloromethane

S	0.043866	0.008016	0.341487
O	-0.017691	1.262132	-0.393406
O	-0.016168	-1.257167	-0.374290
O	0.164169	0.019057	1.791332

2.4 The PhNSO-catalyzed conversion



(a) Preparative synthesis of diphenylcarbodiimide.



(b) Alternative hypothetical isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst.

Figure S28 Two reactions of the phenyl nitrile oxide with N-silfinylaniline.

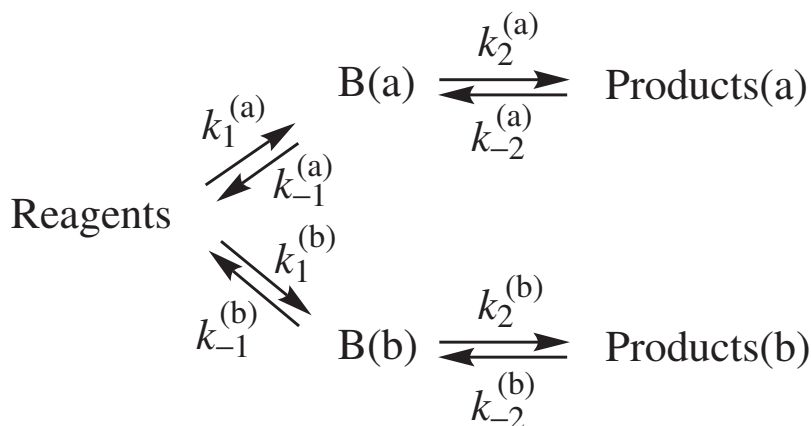
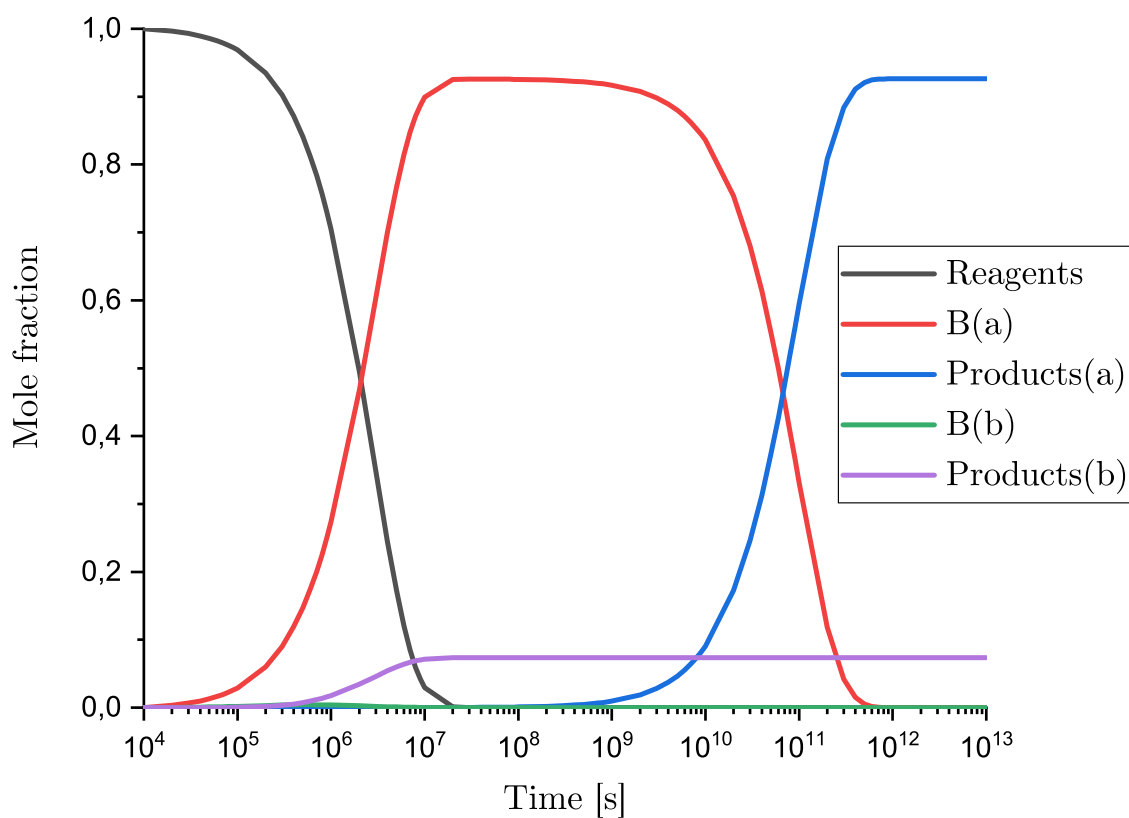


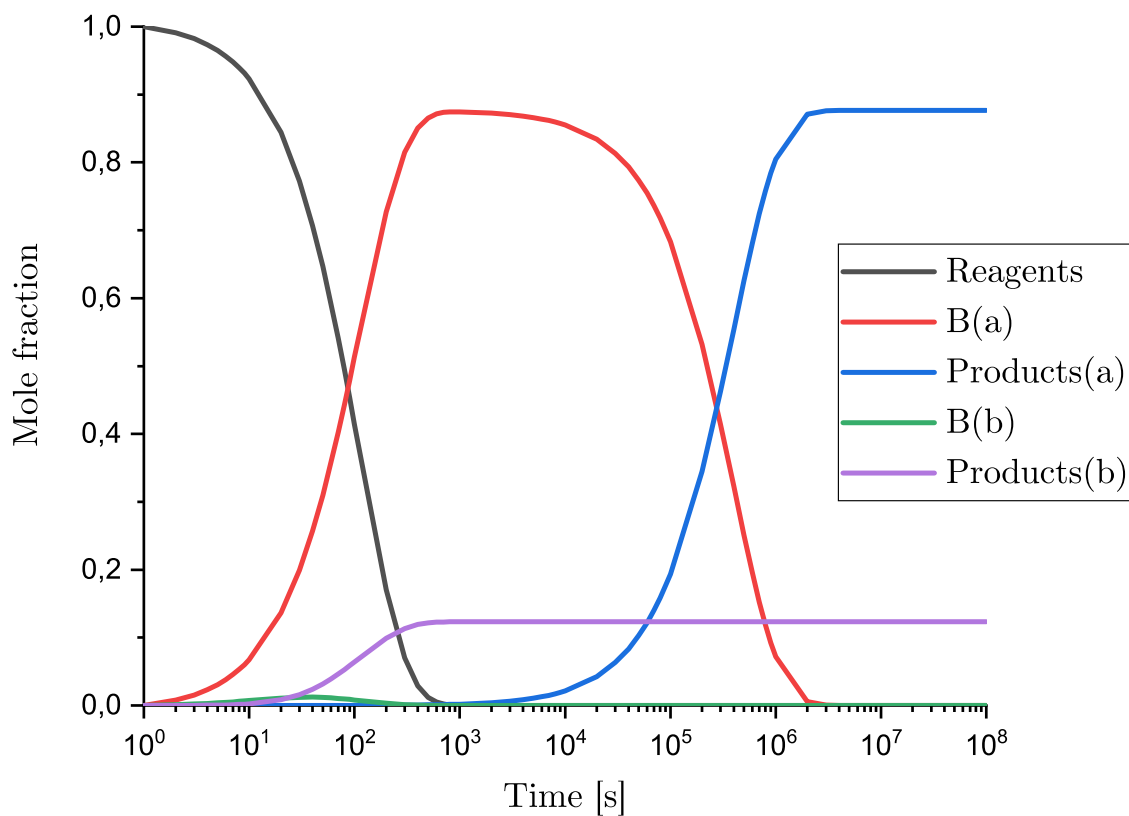
Figure S29 Kinetic scheme of the reactions shown in the figure S28a, S28b.

Table S125 Eyring's rate constants (at 298.15 K and 383 K, s^{-1}) of the diphenylcarbodiimide formation (a) and PhNSO-catalyzed conversion (b). The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVP level of theory in benzene, which was treated with CPCM continuum solvent model.

		$k_1^{(i)}$	$k_{-1}^{(i)}$	$k_2^{(i)}$	$k_{-2}^{(i)}$
298.15 K	Reaction pathway (a)	$3.3 \cdot 10^{-7}$	$6.4 \cdot 10^{-22}$	$1.0 \cdot 10^{-11}$	$3.7 \cdot 10^{-30}$
	Reaction pathway (b)	$2.6 \cdot 10^{-8}$	$1.9 \cdot 10^{-9}$	$5.0 \cdot 10^{-6}$	$8.3 \cdot 10^{-43}$
383 K	Reaction pathway (a)	$7.8 \cdot 10^{-3}$	$2.8 \cdot 10^{-14}$	$2.5 \cdot 10^{-6}$	$1.1 \cdot 10^{-20}$
	Reaction pathway (b)	$1.1 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$6.5 \cdot 10^{-2}$	$1.5 \cdot 10^{-30}$



(a) Kinetic curve at 298.15 K.



(b) Kinetic curve at 383 K.

Figure S30 Kinetic curve of the reactions shown in the figure S28a, S28b.

2.4.1 r²SCAN-3c

Preparative synthesis of diphenylcarbodiimide (a)

Table S126 Energy profile of the diphenylcarbodiimide formation (a). The calculations were done at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	<i>E</i> , kcal/mol	0.0	−6.1	7.7	−28.0	−2.4	−50.9	−45.1
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.7	8.0	−25.6	−2.1	−50.2	−45.1
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.0	22.2	−10.6	11.9	−38.3	−44.0
Benzene	<i>E</i> , kcal/mol	0.0	−6.2	7.6	−28.0	−0.5	−51.2	−45.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.7	7.9	−25.6	−0.4	−50.5	−45.2
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.0	22.1	−10.7	13.7	−38.3	−44.1

Table S127 Energy profile of the diphenylcarbodiimide formation (a). The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the THF, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	<i>E</i> , kcal/mol	0.0	−5.9	12.0	−36.5	−3.7	−57.3	−53.6
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.4	12.3	−34.1	−3.5	−56.6	−53.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.3	26.5	−19.2	10.6	−44.6	−52.5

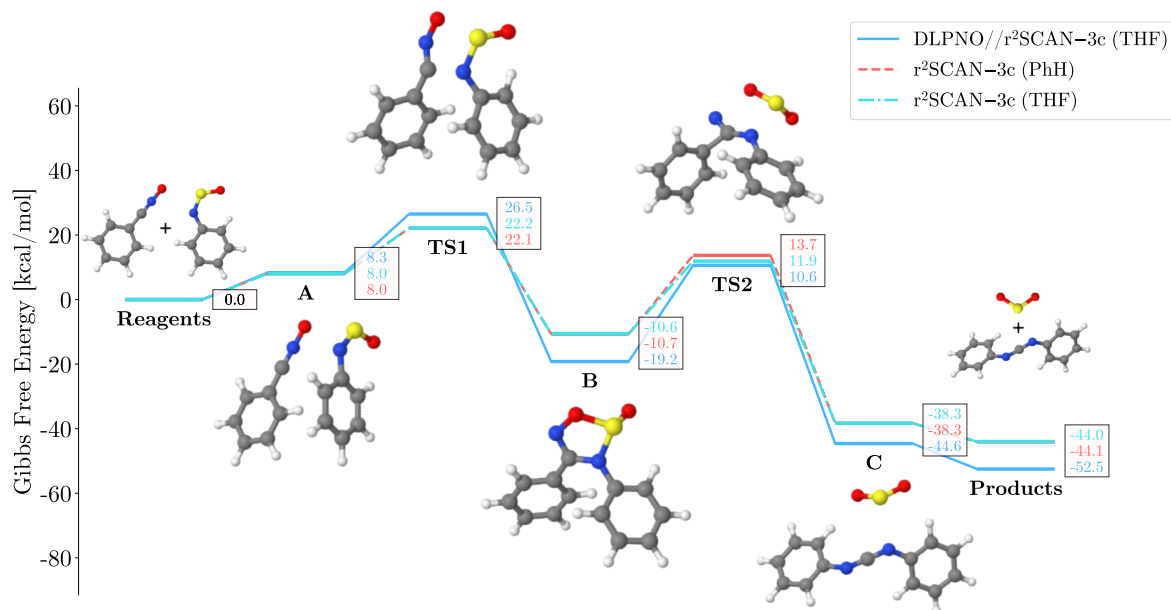


Figure S31 Calculated PES for diphenylcarbodiimide formation.

DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S128 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the THF

C	-3.962793	0.525220	0.401535
C	-2.973591	1.457302	0.119894
C	-3.686749	-0.839317	0.330520
C	-1.687150	1.018667	-0.238244
C	-1.409698	-0.357629	-0.310310
C	-2.411205	-1.275272	-0.025258
H	-3.181753	2.521084	0.173407
C	-0.669901	1.962578	-0.526669
H	-4.955899	0.866627	0.678274
H	-4.465574	-1.562953	0.552228
H	-0.414656	-0.690372	-0.587880
H	-2.194287	-2.337932	-0.081405
N	0.185697	2.713940	-0.759616
O	1.071165	3.507743	-0.999497

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Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	-3.962339	0.524622	0.401367
C	-2.972965	1.456040	0.119882
C	-3.687276	-0.839712	0.330501
C	-1.685883	1.019444	-0.238384
C	-1.410736	-0.357268	-0.309876
C	-2.411875	-1.274886	-0.025113
H	-3.180964	2.519755	0.173430
C	-0.669083	1.963252	-0.526674
H	-4.955246	0.866526	0.677996
H	-4.466082	-1.563223	0.552086
H	-0.415786	-0.690022	-0.587357
H	-2.194717	-2.337439	-0.081340
N	0.186910	2.715814	-0.759792
O	1.069648	3.506785	-0.999746

Table S129 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

N-silfinylaniline ES at r2SCAN-3c in the THF

N	2.491797	1.260873	1.420096
S	3.086367	2.642435	1.022946
O	3.541161	2.888607	-0.390153
C	2.273277	0.107680	0.679595
C	2.568620	-0.039858	-0.691751
C	1.712675	-0.970609	1.391574
C	2.301215	-1.247974	-1.318511
C	1.452866	-2.170172	0.749020
C	1.746140	-2.312711	-0.607524

H	2.999382	0.783878	-1.246764
H	1.491805	-0.839070	2.446495
H	2.528170	-1.362174	-2.374586
H	1.020769	-2.997605	1.304012
H	1.542149	-3.252989	-1.111427

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N-silfinylaniline ES at r2SCAN-3c in the benzene

N	2.493943	1.259691	1.423430
S	3.085395	2.640880	1.018345
O	3.531247	2.884283	-0.395872
C	2.274799	0.107455	0.681342
C	2.570858	-0.039778	-0.689618
C	1.712984	-0.970914	1.391452
C	2.302805	-1.247398	-1.316988
C	1.452111	-2.169574	0.748206
C	1.746091	-2.311783	-0.607855
H	3.003054	0.784690	-1.242508
H	1.492277	-0.838060	2.446079
H	2.530758	-1.360927	-2.372875
H	1.018618	-2.996786	1.302374
H	1.541453	-3.251467	-1.112487

Table S130 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

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A ES at r2SCAN-3c in the THF

C	-2.916951	-0.216823	0.974673
C	-2.128082	0.905599	0.768604
C	-2.979729	-1.219979	0.008530
C	-1.390855	1.026233	-0.421843
C	-1.457091	0.017342	-1.396491
C	-2.250729	-1.098776	-1.173114
H	-2.068878	1.688953	1.517443
C	-0.567337	2.159062	-0.631998
H	-3.484498	-0.310379	1.895859
H	-3.597600	-2.097224	0.176881
H	-0.880794	0.115904	-2.310670
H	-2.296896	-1.880925	-1.925200
N	0.141113	3.062660	-0.808590
O	0.887261	4.005815	-0.980249
N	2.205159	1.568821	1.248294
S	3.167073	2.672862	0.720458
O	3.940262	2.446538	-0.549724
C	1.884621	0.314796	0.742994
C	2.327028	-0.194520	-0.494945
C	1.041011	-0.467086	1.554607
C	1.928744	-1.463149	-0.890098
C	0.658063	-1.734512	1.146487
C	1.101331	-2.236968	-0.075938
H	2.968548	0.403782	-1.129540

H	0.699851	-0.055207	2.499597
H	2.267522	-1.854283	-1.845291
H	0.005388	-2.330210	1.777807
H	0.796465	-3.228326	-0.398544

28

A ES at r2SCAN-3c in the benzene

C	-2.936769	-0.224989	0.963428
C	-2.165750	0.913454	0.780307
C	-2.955891	-1.225601	-0.006680
C	-1.401229	1.054930	-0.390340
C	-1.423897	0.047438	-1.368365
C	-2.200215	-1.084801	-1.168766
H	-2.140867	1.695401	1.532360
C	-0.594665	2.203439	-0.576187
H	-3.525815	-0.332554	1.869432
H	-3.560913	-2.115037	0.142724
H	-0.826041	0.160441	-2.266724
H	-2.211877	-1.864572	-1.924557
N	0.104066	3.116733	-0.747381
O	0.839563	4.065273	-0.907471
N	2.207202	1.574118	1.185494
S	3.173098	2.659683	0.625376
O	3.935370	2.396758	-0.641241
C	1.883615	0.309809	0.706937
C	2.334653	-0.234325	-0.512417
C	1.031668	-0.449034	1.531296
C	1.937387	-1.513370	-0.875491
C	0.648863	-1.726037	1.154873
C	1.101769	-2.263324	-0.048891
H	2.985476	0.344278	-1.155721
H	0.686029	-0.010327	2.462304
H	2.286396	-1.931738	-1.815386
H	-0.010349	-2.302741	1.796920
H	0.799124	-3.263304	-0.345832

Table S131 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS1 at r2SCAN-3c in the THF

C	-2.938080	-0.003399	1.118628
C	-2.005008	1.012722	0.967961
C	-3.158554	-0.909499	0.082196
C	-1.294331	1.125827	-0.235761
C	-1.507315	0.206446	-1.275060
C	-2.446420	-0.801901	-1.111959
H	-1.813668	1.717578	1.771139
C	-0.277058	2.119659	-0.360728
H	-3.493028	-0.092128	2.047652
H	-3.886549	-1.706020	0.206542
H	-0.933604	0.292841	-2.192399

H	-2.618036	-1.512017	-1.915361
N	0.116422	3.088113	-0.971044
O	1.115303	3.830969	-1.020508
N	1.358918	1.604255	0.809377
S	2.537727	2.688911	0.600986
O	3.757167	2.204854	-0.124968
C	1.533010	0.229670	0.477679
C	2.035228	-0.206718	-0.753284
C	1.074808	-0.698596	1.417520
C	2.087975	-1.569050	-1.027059
C	1.139895	-2.058178	1.135595
C	1.646383	-2.497201	-0.086185
H	2.354961	0.515700	-1.496055
H	0.667570	-0.341440	2.358662
H	2.471981	-1.906117	-1.985720
H	0.785437	-2.775686	1.870103
H	1.688865	-3.559596	-0.307951

28

TS1 at r2SCAN-3c in the benzene

C	-2.939061	-0.001328	1.126626
C	-2.008446	1.016224	0.971798
C	-3.153619	-0.914950	0.096215
C	-1.293765	1.124983	-0.229456
C	-1.501617	0.197665	-1.261905
C	-2.437697	-0.812690	-1.095510
H	-1.820667	1.726957	1.770511
C	-0.276778	2.120258	-0.355127
H	-3.496890	-0.085231	2.054358
H	-3.879437	-1.712904	0.223432
H	-0.923624	0.278671	-2.176876
H	-2.603213	-1.529225	-1.894371
N	0.112260	3.088860	-0.968382
O	1.103677	3.836093	-1.024263
N	1.365068	1.605988	0.807269
S	2.545080	2.691511	0.590484
O	3.757667	2.208564	-0.142028
C	1.535848	0.232523	0.472466
C	2.059690	-0.205592	-0.749042
C	1.051621	-0.695939	1.399062
C	2.105109	-1.567337	-1.025695
C	1.108665	-2.054669	1.114146
C	1.635055	-2.494449	-0.098409
H	2.408614	0.515533	-1.479315
H	0.630495	-0.336992	2.333212
H	2.509072	-1.904960	-1.975876
H	0.733654	-2.771149	1.839295
H	1.673238	-3.556418	-0.322619

Table S132 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

B ES at r2SCAN-3c in the THF

C	-3.556085	0.589601	0.704006
C	-2.372067	1.296481	0.876323
C	-3.666704	-0.355153	-0.314222
C	-1.291829	1.060559	0.019632
C	-1.401960	0.112069	-1.003122
C	-2.589512	-0.590174	-1.166654
H	-2.273664	2.023908	1.676105
C	-0.052048	1.832370	0.187563
H	-4.392760	0.772069	1.371909
H	-4.591844	-0.909574	-0.442981
H	-0.566978	-0.065174	-1.674510
H	-2.674711	-1.321549	-1.964842
N	-0.091760	3.088166	0.495994
O	1.239386	3.579259	0.603437
N	1.197002	1.285836	-0.048004
S	2.419156	2.537700	-0.099970
O	2.612283	2.943557	-1.512829
C	1.567529	-0.083939	0.071635
C	2.423729	-0.643151	-0.876320
C	1.091088	-0.843145	1.141127
C	2.808300	-1.974233	-0.745352
C	1.458473	-2.179681	1.242565
C	2.320476	-2.746843	0.305442
H	2.771675	-0.045404	-1.714089
H	0.439889	-0.388292	1.881741
H	3.478725	-2.411135	-1.479458
H	1.081820	-2.775279	2.068906
H	2.612391	-3.788850	0.395968

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B ES at r2SCAN-3c in the benzene

C	-3.570075	0.616661	0.701253
C	-2.382816	1.318109	0.870002
C	-3.679476	-0.346344	-0.299451
C	-1.296817	1.059518	0.027437
C	-1.406756	0.093446	-0.978292
C	-2.597511	-0.603730	-1.138364
H	-2.285769	2.063569	1.652996
C	-0.054287	1.827474	0.192658
H	-4.411301	0.818793	1.357584
H	-4.607523	-0.896303	-0.425733
H	-0.568150	-0.101355	-1.639985
H	-2.681457	-1.348516	-1.924092
N	-0.091592	3.082928	0.499609
O	1.235231	3.575384	0.597342
N	1.195088	1.279915	-0.047337
S	2.417696	2.535840	-0.108260
O	2.613771	2.930207	-1.521421
C	1.569706	-0.086441	0.067743
C	2.451035	-0.631837	-0.865944

C	1.075721	-0.862042	1.117804
C	2.842728	-1.960909	-0.739509
C	1.450657	-2.196416	1.213836
C	2.337654	-2.748134	0.291561
H	2.812683	-0.022815	-1.689701
H	0.403490	-0.420328	1.847256
H	3.533000	-2.384952	-1.462599
H	1.059670	-2.803053	2.025276
H	2.635402	-3.788669	0.378332

Table S133 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS2 at r²SCAN-3c in the THF

C	1.552868	1.227644	-2.472556
C	1.556847	1.255136	-1.088867
C	0.414112	1.629934	-3.177085
C	0.385205	1.651320	-0.426342
C	-0.752125	2.086410	-1.120479
C	-0.732487	2.057124	-2.506079
H	2.431778	0.966155	-0.514863
C	0.297980	1.435116	1.078495
H	2.441497	0.909423	-3.008420
H	0.428442	1.625388	-4.263071
H	-1.622108	2.430452	-0.570246
H	-1.604345	2.381441	-3.065218
N	0.649515	2.624814	1.250325
O	0.472227	2.236309	3.491083
N	0.023686	0.352976	1.766205
S	0.468841	0.734262	3.708041
O	1.826841	0.144579	3.862166
C	-0.333659	-0.898296	1.227918
C	0.514974	-1.993328	1.417072
C	-1.544223	-1.047155	0.543204
C	0.148181	-3.235694	0.912741
C	-1.885860	-2.289147	0.020162
C	-1.045445	-3.384895	0.208060
H	1.451085	-1.857970	1.949989
H	-2.206329	-0.193272	0.432122
H	0.804616	-4.088503	1.059246
H	-2.820148	-2.404251	-0.521632
H	-1.321963	-4.355974	-0.191972

28

TS2 at r²SCAN-3c in the benzene

C	1.514852	1.243822	-2.479938
C	1.521533	1.257960	-1.095797
C	0.381488	1.668585	-3.178748
C	0.359088	1.664131	-0.425308
C	-0.772455	2.118494	-1.114085
C	-0.756232	2.105567	-2.500376

H	2.393624	0.953548	-0.525660
C	0.276052	1.422709	1.081654
H	2.398447	0.919102	-3.020232
H	0.393359	1.674028	-4.264707
H	-1.633969	2.472954	-0.557338
H	-1.623944	2.450199	-3.053865
N	0.623588	2.615013	1.247654
O	0.526096	2.233878	3.485124
N	0.030623	0.330253	1.757286
S	0.572683	0.741699	3.727143
O	1.940509	0.172168	3.814655
C	-0.325879	-0.917382	1.222205
C	0.465980	-2.033807	1.511840
C	-1.481306	-1.055200	0.444481
C	0.100717	-3.279252	1.015729
C	-1.818013	-2.301563	-0.070295
C	-1.033381	-3.416233	0.217252
H	1.358110	-1.910431	2.118184
H	-2.108121	-0.188465	0.257341
H	0.714031	-4.146182	1.243533
H	-2.709321	-2.404928	-0.682407
H	-1.308162	-4.390665	-0.175323

Table S134 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

C ES at r2SCAN-3c in the THF

C	1.698711	2.240894	-2.601550
C	1.042197	1.631262	-1.541306
C	1.146849	3.361648	-3.223595
C	-0.179931	2.151203	-1.100513
C	-0.737925	3.271385	-1.717120
C	-0.069593	3.872859	-2.778500
H	1.468866	0.761098	-1.048435
C	-0.645860	0.596178	0.647543
H	2.648500	1.840048	-2.943851
H	1.666365	3.833810	-4.052058
H	-1.686553	3.659677	-1.359389
H	-0.502954	4.745417	-3.258474
N	-0.887085	1.576238	-0.027656
O	1.617777	1.969803	2.174924
N	-0.450101	-0.255678	1.508994
S	1.704155	0.636267	2.807640
O	2.663694	-0.307840	2.197700
C	-0.696824	-1.643707	1.472188
C	-0.592634	-2.353216	2.669065
C	-1.018020	-2.303688	0.281729
C	-0.819315	-3.725430	2.674176
C	-1.243597	-3.674381	0.301434
C	-1.145705	-4.389957	1.494341
H	-0.341864	-1.825535	3.584511

H	-1.085752	-1.743194	-0.647356
H	-0.739781	-4.276456	3.606704
H	-1.493363	-4.187047	-0.623141
H	-1.320258	-5.461658	1.501994

28

C ES at r2SCAN-3c in the benzene

C	1.774331	2.324266	-2.470221
C	1.100891	1.709525	-1.424080
C	1.178704	3.368632	-3.177582
C	-0.183672	2.147072	-1.083667
C	-0.784302	3.193051	-1.783962
C	-0.098994	3.799381	-2.831129
H	1.565561	0.904251	-0.860710
C	-0.671642	0.595281	0.661742
H	2.773337	1.988312	-2.732570
H	1.712491	3.845696	-3.993943
H	-1.780085	3.519020	-1.500500
H	-0.566618	4.613813	-3.376500
N	-0.911279	1.564192	-0.029103
O	1.660019	1.962990	2.164672
N	-0.482456	-0.253501	1.528402
S	1.832468	0.585539	2.667660
O	2.697918	-0.300592	1.864021
C	-0.727873	-1.640930	1.483549
C	-0.569071	-2.364611	2.665827
C	-1.103772	-2.289334	0.303088
C	-0.792867	-3.736777	2.666247
C	-1.326150	-3.660184	0.317428
C	-1.172087	-4.388899	1.495861
H	-0.277226	-1.845279	3.573722
H	-1.216243	-1.718644	-0.615299
H	-0.669378	-4.298202	3.587617
H	-1.617652	-4.163217	-0.600096
H	-1.344352	-5.460853	1.499526

Table S135 Cartesian coordinates of the diphenylcarbodiimide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

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Diphenylcarbodiimide ES at r2SCAN-3c in the THF

C	1.792237	2.315139	-2.409178
C	1.048711	1.675063	-1.425555
C	1.258293	3.398615	-3.106745
C	-0.244612	2.124186	-1.134570
C	-0.784263	3.207242	-1.830811
C	-0.029856	3.840141	-2.813455
H	1.462458	0.829470	-0.881495
C	-0.776212	0.579748	0.589154
H	2.795699	1.963975	-2.633192
H	1.844329	3.894156	-3.875016
H	-1.789170	3.543401	-1.593730

H	-0.453205	4.683114	-3.352156
N	-1.045104	1.517173	-0.146277
N	-0.583620	-0.235562	1.478287
C	-0.772896	-1.631668	1.457915
C	-0.489556	-2.341258	2.626421
C	-1.227282	-2.305922	0.318534
C	-0.662877	-3.721289	2.654131
C	-1.396322	-3.684324	0.358549
C	-1.115578	-4.397755	1.523752
H	-0.137571	-1.803837	3.501829
H	-1.444063	-1.748145	-0.589275
H	-0.441910	-4.269458	3.565545
H	-1.748924	-4.204986	-0.527463
H	-1.249105	-5.475157	1.548448

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Diphenylcarbodiimide ES at r2SCAN-3c in the benzene

C	1.806214	2.334535	-2.391780
C	1.061449	1.690862	-1.412013
C	1.264730	3.405211	-3.102180
C	-0.241159	2.122649	-1.137335
C	-0.787682	3.193460	-1.846627
C	-0.032179	3.830127	-2.825225
H	1.481197	0.855898	-0.856402
C	-0.775016	0.575986	0.583323
H	2.816998	1.996619	-2.602448
H	1.851805	3.904024	-3.867355
H	-1.799409	3.515915	-1.620833
H	-0.461334	4.663575	-3.373871
N	-1.042512	1.512109	-0.153862
N	-0.582542	-0.240087	1.471389
C	-0.774970	-1.634387	1.454264
C	-0.470391	-2.345561	2.616203
C	-1.254360	-2.307806	0.324842
C	-0.646283	-3.724646	2.646962
C	-1.425995	-3.685381	0.367731
C	-1.123267	-4.399735	1.526251
H	-0.100052	-1.807768	3.483489
H	-1.489519	-1.748342	-0.577238
H	-0.408530	-4.273669	3.553522
H	-1.798467	-4.204868	-0.510699
H	-1.259125	-5.476656	1.553540

Table S136 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at r2SCAN-3c in the THF

O	1.658937	1.961697	2.167002
S	1.834981	0.587346	2.662908
O	2.696487	-0.301106	1.866443

3

Sulfur dioxide ES at r2SCAN-3c in the benzene

O	1.657103	1.963370	2.168818
S	1.836594	0.588485	2.659869
O	2.696708	-0.303918	1.867665

Isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst (b)

Table S137 Energy profile of the PhNSO-catalyzed conversion (b). The calculations were done at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	<i>E</i> , kcal/mol	0.0	−6.1	9.6	−13.9	4.0	−62.4	−57.1
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.7	9.8	−12.2	3.8	−61.5	−56.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.9	23.3	2.1	17.5	−48.8	−56.5
Benzene	<i>E</i> , kcal/mol	0.0	−6.2	8.8	−14.9	4.3	−63.4	−57.6
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.8	9.0	−13.1	4.1	−62.5	−57.0
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	22.8	1.2	17.8	−50.2	−56.9

Table S138 Energy profile of the PhNSO-catalyzed conversion (b). The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the THF, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	<i>E</i> , kcal/mol	0.0	−6.0	16.5	−14.3	10.2	−64.4	−59.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.6	16.7	−12.5	10.0	−63.6	−58.7
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	7.0	30.3	1.8	23.7	−50.9	−58.6

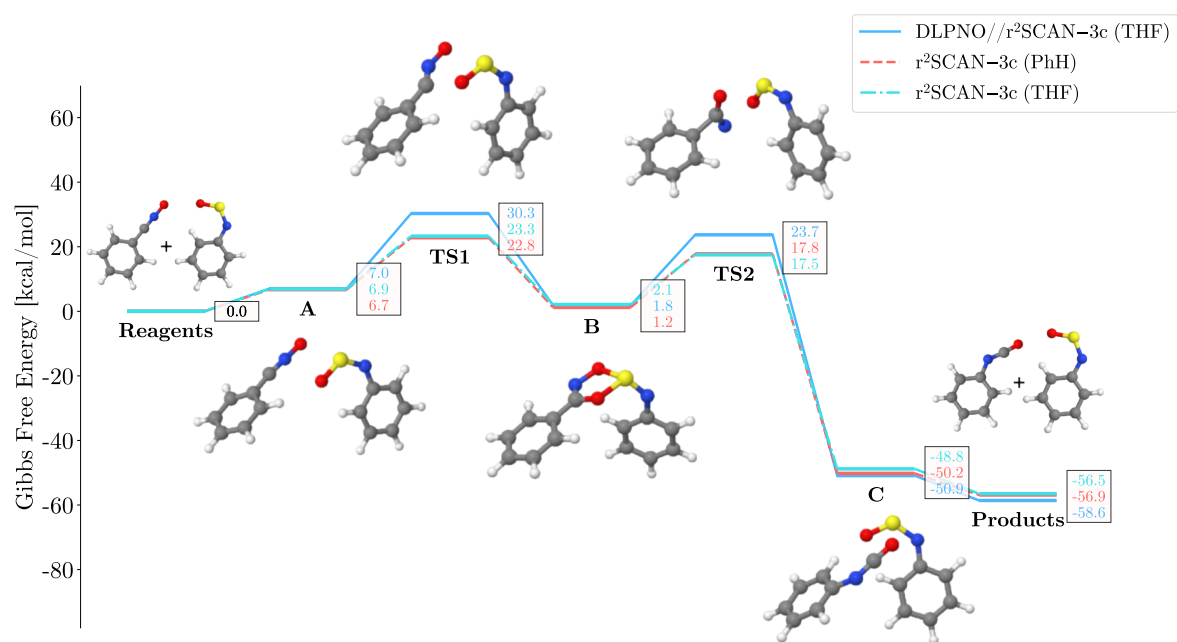


Figure S32 Calculated PES for isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S139 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the THF

C	-3.962793	0.525220	0.401535
C	-2.973591	1.457302	0.119894
C	-3.686749	-0.839317	0.330520
C	-1.687150	1.018667	-0.238244
C	-1.409698	-0.357629	-0.310310
C	-2.411205	-1.275272	-0.025258
H	-3.181753	2.521084	0.173407
C	-0.669901	1.962578	-0.526669
H	-4.955899	0.866627	0.678274
H	-4.465574	-1.562953	0.552228
H	-0.414656	-0.690372	-0.587880
H	-2.194287	-2.337932	-0.081405
N	0.185697	2.713940	-0.759616
O	1.071165	3.507743	-0.999497

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Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	-3.962339	0.524622	0.401367
C	-2.972965	1.456040	0.119882
C	-3.687276	-0.839712	0.330501
C	-1.685883	1.019444	-0.238384
C	-1.410736	-0.357268	-0.309876
C	-2.411875	-1.274886	-0.025113
H	-3.180964	2.519755	0.173430
C	-0.669083	1.963252	-0.526674
H	-4.955246	0.866526	0.677996
H	-4.466082	-1.563223	0.552086
H	-0.415786	-0.690022	-0.587357
H	-2.194717	-2.337439	-0.081340
N	0.186910	2.715814	-0.759792
O	1.069648	3.506785	-0.999746

Table S140 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

N-silfinylaniline ES at r2SCAN-3c in the THF

N	2.491797	1.260873	1.420096
S	3.086367	2.642435	1.022946
O	3.541161	2.888607	-0.390153
C	2.273277	0.107680	0.679595
C	2.568620	-0.039858	-0.691751
C	1.712675	-0.970609	1.391574
C	2.301215	-1.247974	-1.318511
C	1.452866	-2.170172	0.749020
C	1.746140	-2.312711	-0.607524
H	2.999382	0.783878	-1.246764
H	1.491805	-0.839070	2.446495
H	2.528170	-1.362174	-2.374586
H	1.020769	-2.997605	1.304012

H	1.542149	-3.252989	-1.111427

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N-silfinylaniline ES at r2SCAN-3c in the benzene

N	2.493943	1.259691	1.423430
S	3.085395	2.640880	1.018345
O	3.531247	2.884283	-0.395872
C	2.274799	0.107455	0.681342
C	2.570858	-0.039778	-0.689618
C	1.712984	-0.970914	1.391452
C	2.302805	-1.247398	-1.316988
C	1.452111	-2.169574	0.748206
C	1.746091	-2.311783	-0.607855
H	3.003054	0.784690	-1.242508
H	1.492277	-0.838060	2.446079
H	2.530758	-1.360927	-2.372875
H	1.018618	-2.996786	1.302374
H	1.541453	-3.251467	-1.112487

Table S141 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

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A ES at r2SCAN-3c in the THF

C	-2.179893	-0.739704	-1.241978
C	-1.779468	0.440305	-0.631905
C	-2.369965	-1.894788	-0.485713
C	-1.564179	0.463892	0.755652
C	-1.756731	-0.700172	1.519106
C	-2.158905	-1.870599	0.892289
H	-1.622995	1.342213	-1.214678
C	-1.135837	1.658916	1.383655
H	-2.339717	-0.758734	-2.316063
H	-2.681767	-2.815322	-0.970555
H	-1.583621	-0.673359	2.590193
H	-2.306090	-2.770314	1.482487
N	-0.780717	2.639905	1.895024
O	-0.389768	3.659170	2.427649
O	2.286395	1.452296	2.995075
S	2.522558	2.501717	1.942247
N	2.331305	2.143425	0.440583
C	1.977806	0.955355	-0.185524
C	1.850480	1.024678	-1.586340
C	1.522274	-0.107576	-2.313802
C	1.318784	-1.322658	-1.659870
C	1.442192	-1.398003	-0.272914
C	1.765365	-0.273912	0.471933
H	2.018070	1.978602	-2.077363
H	1.424642	-0.045877	-3.393772
H	1.059461	-2.210137	-2.229885
H	1.276315	-2.343589	0.235139
H	1.854007	-0.335730	1.549330

A ES at r2SCAN-3c in the benzene

C	-2.337880	-0.947781	-1.078975
C	-1.930951	0.320754	-0.690883
C	-2.371794	-1.990147	-0.155068
C	-1.549509	0.550588	0.640548
C	-1.583925	-0.501116	1.572420
C	-1.995977	-1.762029	1.167835
H	-1.896397	1.136214	-1.406020
C	-1.112113	1.834999	1.045975
H	-2.628176	-1.124097	-2.110548
H	-2.691781	-2.980527	-0.465367
H	-1.276727	-0.316240	2.596586
H	-2.020974	-2.573344	1.889432
N	-0.716663	2.862174	1.421154
O	-0.301968	3.929765	1.814181
O	1.626411	0.964743	3.129585
S	2.337492	2.021848	2.331615
N	2.485196	1.852101	0.792685
C	2.068245	0.827829	-0.049115
C	2.071618	1.128772	-1.423660
C	1.686363	0.170228	-2.347409
C	1.317880	-1.104801	-1.918829
C	1.329668	-1.413677	-0.559649
C	1.688606	-0.459429	0.380267
H	2.376292	2.122613	-1.736920
H	1.682358	0.412634	-3.406110
H	1.022093	-1.857729	-2.643615
H	1.039558	-2.405754	-0.226439
H	1.683055	-0.698591	1.436324

Table S142 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

TS1 at r2SCAN-3c in the THF

C	-3.179059	-1.173154	-0.456229
C	-2.510922	0.006512	-0.162668
C	-3.157507	-2.238033	0.443981
C	-1.829463	0.130289	1.060896
C	-1.810030	-0.939104	1.968210
C	-2.469999	-2.118444	1.650350
H	-2.508534	0.834824	-0.864067
C	-1.137975	1.342424	1.358155
H	-3.710215	-1.265959	-1.398952
H	-3.674406	-3.162274	0.202977
H	-1.276076	-0.838188	2.906677
H	-2.451867	-2.947291	2.351674
N	-1.093681	2.533019	1.128495
O	-0.306378	3.487174	1.326616
O	0.453263	0.999497	2.391893

S	1.583035	2.044737	2.160791
N	2.482001	1.882950	0.908581
C	2.405931	1.044520	-0.196999
C	3.220230	1.395127	-1.289822
C	3.218515	0.620060	-2.439803
C	2.418377	-0.519492	-2.517436
C	1.622091	-0.881268	-1.430552
C	1.607498	-0.113821	-0.274734
H	3.839256	2.284106	-1.215001
H	3.845651	0.904576	-3.279829
H	2.419205	-1.126268	-3.418129
H	1.005476	-1.774462	-1.482365
H	0.995581	-0.412059	0.567289

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TS1 at r2SCAN-3c in the benzene

C	-3.285751	-1.152792	-0.407168
C	-2.608229	0.025065	-0.130249
C	-3.200699	-2.237338	0.464936
C	-1.849371	0.128406	1.048813
C	-1.765808	-0.961209	1.927635
C	-2.437829	-2.138068	1.626276
H	-2.656533	0.869215	-0.810530
C	-1.151267	1.340244	1.330744
H	-3.875887	-1.228272	-1.315726
H	-3.726903	-3.159574	0.237246
H	-1.173066	-0.875632	2.831382
H	-2.369440	-2.981506	2.306789
N	-1.104723	2.527321	1.085816
O	-0.330559	3.488317	1.273812
O	0.441132	1.011374	2.373504
S	1.562755	2.065535	2.141643
N	2.476640	1.899498	0.901587
C	2.422033	1.051683	-0.196606
C	3.263922	1.387384	-1.272834
C	3.285384	0.602531	-2.415443
C	2.479751	-0.531995	-2.503444
C	1.654606	-0.878409	-1.433745
C	1.617638	-0.101599	-0.285038
H	3.885267	2.273657	-1.188898
H	3.934492	0.875907	-3.242310
H	2.498169	-1.146117	-3.398875
H	1.031676	-1.766640	-1.493400
H	0.982600	-0.386986	0.544082

Table S143 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

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B ES at r2SCAN-3c in the THF

C	-4.021821	-1.164323	0.385275
C	-3.193325	-0.051818	0.403027

C	-3.653061	-2.329034	1.059841
C	-1.976779	-0.100572	1.097990
C	-1.608481	-1.266841	1.777650
C	-2.447755	-2.375759	1.754479
H	-3.484066	0.856346	-0.115095
C	-1.088870	1.065205	1.113138
H	-4.964058	-1.122360	-0.153261
H	-4.307272	-3.196000	1.044890
H	-0.667270	-1.306141	2.315802
H	-2.156279	-3.279259	2.281908
N	-1.257786	2.082134	0.333817
O	-0.259076	3.027699	0.557176
O	-0.039667	1.047351	1.953670
S	1.096544	2.439142	1.585357
N	2.330866	1.987842	0.812825
C	2.527680	1.217356	-0.341553
C	3.864832	0.977982	-0.689779
C	4.164537	0.220319	-1.813336
C	3.139851	-0.304746	-2.599087
C	1.811103	-0.063115	-2.254738
C	1.495976	0.693902	-1.133214
H	4.652928	1.391736	-0.068032
H	5.202529	0.038094	-2.075831
H	3.375288	-0.898685	-3.477168
H	1.008037	-0.466441	-2.864855
H	0.455392	0.879987	-0.890898

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B ES at r2SCAN-3c in the benzene

C	-3.997593	-1.179281	0.360580
C	-3.168145	-0.068023	0.378985
C	-3.646713	-2.333014	1.062383
C	-1.968523	-0.106494	1.102854
C	-1.617800	-1.261848	1.808951
C	-2.458012	-2.369775	1.784712
H	-3.442089	0.832508	-0.160903
C	-1.081734	1.059694	1.121077
H	-4.926743	-1.145367	-0.200667
H	-4.301724	-3.199263	1.046445
H	-0.689404	-1.291554	2.369237
H	-2.180384	-3.264908	2.333304
N	-1.254541	2.079687	0.347522
O	-0.258013	3.024555	0.571495
O	-0.029984	1.039474	1.959812
S	1.100119	2.433477	1.590466
N	2.333408	1.985558	0.813849
C	2.523661	1.219747	-0.344478
C	3.858530	0.961965	-0.687152
C	4.153272	0.207589	-1.813775
C	3.125549	-0.295486	-2.609219
C	1.799308	-0.034767	-2.271130
C	1.488980	0.718867	-1.146271

H	4.647909	1.359971	-0.057132
H	5.189752	0.010954	-2.071553
H	3.356822	-0.886663	-3.490164
H	0.993705	-0.420053	-2.889351
H	0.450388	0.922447	-0.909875

Table S144 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS2 at r2SCAN-3c in the THF

C	-4.471569	-0.845454	-0.681923
C	-3.554073	0.156082	-0.975235
C	-4.096207	-1.922539	0.121171
C	-2.273557	0.076533	-0.426613
C	-1.875048	-1.011661	0.351915
C	-2.802392	-2.006073	0.636857
H	-3.823068	0.995993	-1.608788
C	-1.320775	1.299214	-0.546239
H	-5.476467	-0.792949	-1.090096
H	-4.813397	-2.709457	0.336384
H	-0.859629	-1.063127	0.734124
H	-2.513324	-2.853074	1.251883
N	-0.777916	0.875359	-1.620301
O	0.430906	2.314996	-2.031812
O	-1.268622	2.245960	0.254326
S	0.927151	3.179451	-0.844132
N	1.998380	2.608052	0.110115
C	2.576849	1.360855	0.263794
C	2.374201	0.269486	-0.606047
C	3.017972	-0.930203	-0.348859
C	3.858706	-1.064234	0.757945
C	4.065663	0.015852	1.616649
C	3.433641	1.224004	1.373908
H	1.721519	0.369915	-1.463885
H	2.864339	-1.771926	-1.017791
H	4.355003	-2.011305	0.948726
H	4.721667	-0.087598	2.475743
H	3.580047	2.077846	2.028180

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TS2 at r2SCAN-3c in the benzene

C	-4.480477	-0.841750	-0.702349
C	-3.554231	0.152622	-0.991389
C	-4.120099	-1.915780	0.110757
C	-2.280463	0.069286	-0.429873
C	-1.897003	-1.015820	0.359219
C	-2.832473	-2.003227	0.640188
H	-3.809215	0.989969	-1.633597
C	-1.319137	1.288918	-0.543427
H	-5.480499	-0.786195	-1.121787
H	-4.843986	-2.697188	0.323369

H	-0.885675	-1.069301	0.751259
H	-2.554791	-2.848149	1.263193
N	-0.784158	0.854767	-1.615417
O	0.435866	2.303025	-2.014681
O	-1.262121	2.231704	0.259507
S	0.903805	3.162664	-0.815971
N	1.984758	2.604233	0.135581
C	2.577548	1.360665	0.276844
C	2.367872	0.266255	-0.586574
C	3.027695	-0.927612	-0.340378
C	3.892926	-1.053300	0.747385
C	4.106166	0.029766	1.600039
C	3.456504	1.231021	1.369409
H	1.695335	0.358239	-1.429976
H	2.866761	-1.771107	-1.005395
H	4.402644	-1.995112	0.928393
H	4.780442	-0.065708	2.445854
H	3.606007	2.087116	2.019819

Table S145 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

C ES at r2SCAN-3c in the THF

C	-2.583018	-0.989307	-1.358457
C	-2.077785	0.076504	-0.624105
C	-2.652873	-2.264715	-0.798929
C	-1.636965	-0.140194	0.684940
C	-1.711152	-1.410592	1.255885
C	-2.218087	-2.468656	0.508660
H	-2.012169	1.070046	-1.059483
C	-0.791084	2.050665	1.278451
H	-2.921646	-0.820632	-2.376863
H	-3.046633	-3.093630	-1.379420
H	-1.361637	-1.559897	2.272839
H	-2.271091	-3.458392	0.953071
N	-1.096081	0.897140	1.454114
O	0.220803	2.969567	-2.415345
O	-0.454961	3.175266	1.253655
S	1.347676	3.639517	-1.677768
N	2.206856	2.820010	-0.673354
C	2.118347	1.486127	-0.293982
C	1.436808	0.490810	-1.022801
C	1.433311	-0.814322	-0.554026
C	2.075449	-1.142994	0.639245
C	2.749695	-0.159589	1.364014
C	2.787123	1.144510	0.896846
H	0.927955	0.743318	-1.944645
H	0.909785	-1.581483	-1.117644
H	2.051646	-2.166020	1.003320
H	3.254203	-0.414847	2.291253
H	3.315527	1.921790	1.440527

C ES at r2SCAN-3c in the benzene

C	-2.542780	-0.945869	-1.453374
C	-2.047850	0.101870	-0.687175
C	-2.694947	-2.217361	-0.902044
C	-1.699175	-0.129520	0.647071
C	-1.855475	-1.396639	1.209050
C	-2.352203	-2.435928	0.429937
H	-1.913283	1.090556	-1.117302
C	-0.798543	2.022624	1.297404
H	-2.809602	-0.765530	-2.490888
H	-3.081820	-3.031427	-1.507483
H	-1.578631	-1.555985	2.246450
H	-2.470801	-3.422513	0.868552
N	-1.173530	0.886219	1.452384
O	-0.081672	2.827927	-2.161386
O	-0.406268	3.128541	1.299737
S	1.140092	3.539447	-1.651080
N	2.162136	2.774609	-0.762829
C	2.139722	1.459746	-0.312321
C	1.385201	0.427020	-0.901994
C	1.450986	-0.853687	-0.373764
C	2.238803	-1.120732	0.744543
C	2.989118	-0.100239	1.329876
C	2.955693	1.179202	0.799301
H	0.762063	0.631856	-1.763486
H	0.865949	-1.647617	-0.829457
H	2.270502	-2.124368	1.158330
H	3.607780	-0.307520	2.198001
H	3.538534	1.985319	1.233948

Table S146 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

Phenyl isocyanate ES at r2SCAN-3c in the THF

C	-2.537397	-0.947740	-1.456098
C	-2.005941	0.090121	-0.700043
C	-2.719344	-2.211264	-0.895483
C	-1.653374	-0.142896	0.633231
C	-1.832147	-1.404533	1.202345
C	-2.365273	-2.433549	0.433091
H	-1.862146	1.076174	-1.133562
C	-0.826220	2.035064	1.310420
H	-2.810717	-0.765777	-2.491629
H	-3.135012	-3.017462	-1.492392
H	-1.553060	-1.567372	2.238668
H	-2.503833	-3.414767	0.877854
N	-1.114104	0.870836	1.435885
O	-0.504845	3.163627	1.329885

14

Phenyl isocyanate ES at r2SCAN-3c in the benzene

C	-2.536633	-0.946768	-1.454849
C	-2.005395	0.089841	-0.697769
C	-2.719005	-2.210324	-0.895686
C	-1.652811	-0.142922	0.635525
C	-1.832524	-1.405294	1.202391
C	-2.365349	-2.433255	0.432484
H	-1.861237	1.076206	-1.130371
C	-0.827129	2.033976	1.308291
H	-2.809737	-0.763895	-2.490177
H	-3.134447	-3.015948	-1.493250
H	-1.553518	-1.567639	2.238621
H	-2.504273	-3.414758	0.876254
N	-1.113982	0.869067	1.439135
O	-0.507373	3.162172	1.321573

2.4.2 PBE/ Λ 01

A fast DFT code implemented in the PRIRODA software^{S41,S42} and employing a PBE functional^{S7} with full-electron basis Λ 01^{S43,S44} similar to the cc-pVDZ basis set was chosen for preliminary calculations. In this case, additional post-optimization corrections were used: Grimme's D3(BJ) dispersion correction^{S11,S45} implemented in the dft-d3 software (<https://www.chemiebn.uni-bonn.de/pctc/mulliken-center/software/dft-d3/dft-d3>) and Minenkov's SPT-V solvation correction.^{S46}

Preparative synthesis of diphenylcarbodiimide (a)

Table S147 Energy profile of the diphenylcarbodiimide formation (a). The calculations were done at the PBE/ Λ 01 level of theory in the gas phase and benzene, which was treated with Minenkov's SPT-V continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	-5.2	7.0	-24.4	5.8	-48.5	-41.6
	$E + \Delta ZPE$, kcal/mol	0.0	-4.9	7.1	-22.5	5.5	-47.8	-41.6
	$E + \Delta G$, kcal/mol	0.0	3.9	20.0	-8.4	18.3	-38.4	-41.7
Benzene	E , kcal/mol	0.0	-5.1	7.5	-24.6	4.8	-49.5	-42.1
	$E + \Delta ZPE$, kcal/mol	0.0	-4.8	7.6	-22.6	4.5	-48.8	-42.2
	$E + \Delta G$, kcal/mol	0.0	4.0	20.5	-8.6	17.3	-39.4	-42.3

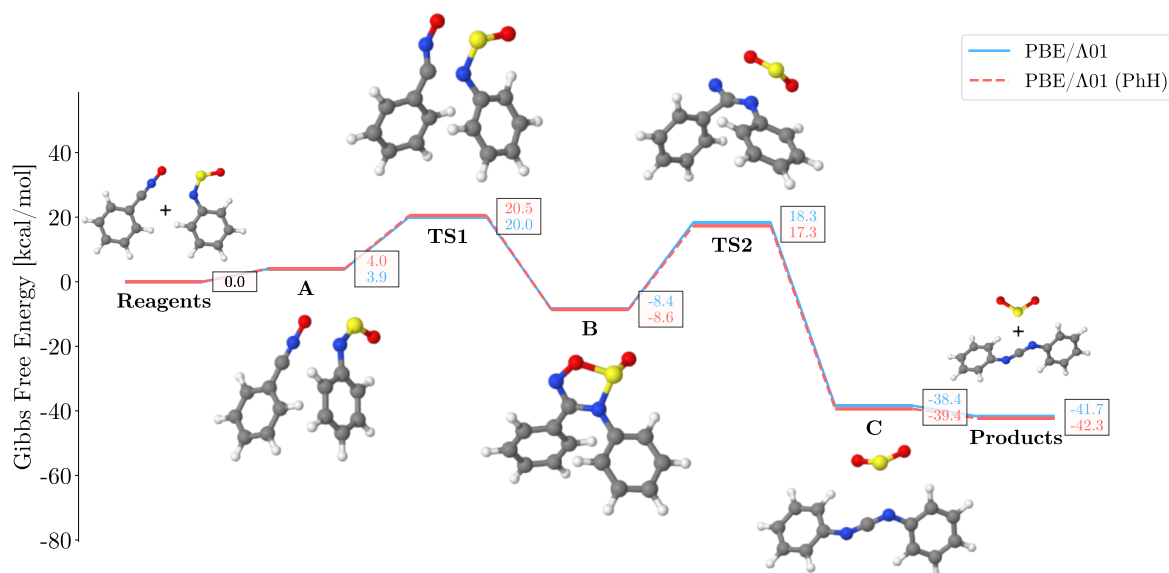


Figure S33 Calculated PES for diphenylcarbodiimide formation. PBE/ Λ 01 electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S148 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

14

Phenyl nitrile oxide ES at PBE in the gas phase

C	-1.768415	-0.011425	0.492630
C	-0.770324	0.917880	0.211915
C	-1.500286	-1.381938	0.421911
C	0.523535	0.481706	-0.147219
C	0.786575	-0.903665	-0.216540
C	-0.221278	-1.821560	0.066877
H	-0.976503	1.988981	0.266237
C	1.546621	1.423873	-0.435142
H	-2.766244	0.338149	0.769633
H	-2.287469	-2.106832	0.643348
H	1.786550	-1.243769	-0.494209
H	-0.005777	-2.891567	0.009959
N	2.392541	2.204742	-0.672734
O	3.260475	3.005423	-0.916666

Table S149 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

14

N-silfinylaniline ES at PBE in the gas phase

N	0.296764	1.805829	1.340979
S	0.894936	3.178666	0.898655
O	1.340803	3.418545	-0.518306
C	0.074130	0.646080	0.605437
C	0.373264	0.501040	-0.769676
C	-0.489504	-0.441161	1.308587
C	0.108846	-0.707168	-1.408110
C	-0.748112	-1.642186	0.657204
C	-0.450049	-1.779532	-0.703303
H	0.808392	1.345827	-1.305386
H	-0.712964	-0.308809	2.369801
H	0.341238	-0.815602	-2.470762
H	-1.184402	-2.477888	1.210179
H	-0.653342	-2.723639	-1.215299

Table S150 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

A ES at PBE in the gas phase

C	-4.229857	0.446824	-0.023055
C	-3.325527	1.501877	0.065926
C	-3.771994	-0.867810	-0.155145
C	-1.937749	1.249108	0.022635
C	-1.480677	-0.080008	-0.110574
C	-2.397978	-1.123929	-0.197955
H	-3.678688	2.530176	0.169051
C	-1.007713	2.319553	0.111780

H	-5.302588	0.653124	0.010942
H	-4.486195	-1.692028	-0.224661
H	-0.407490	-0.279852	-0.143170
H	-2.033107	-2.149006	-0.300711
N	-0.185117	3.155632	0.174172
O	0.650802	4.025916	0.240765
N	2.957650	1.290721	0.986388
S	3.467749	2.555112	0.225453
O	3.651393	2.538082	-1.266190
C	2.591504	0.039376	0.496635
C	2.601919	-0.322005	-0.871260
C	2.183417	-0.912677	1.456498
C	2.211010	-1.604208	-1.249878
C	1.798202	-2.190736	1.064018
C	1.810114	-2.541890	-0.290933
H	2.920283	0.417243	-1.607613
H	2.180772	-0.614751	2.507670
H	2.221723	-1.877602	-2.308364
H	1.487204	-2.919264	1.817197
H	1.510937	-3.546978	-0.599620

Table S151 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the PBE/A01 level of theory in the gas phase.

28

TS1 at PBE in the gas phase

C	-3.451069	0.386914	1.017377
C	-2.410006	1.305770	0.915012
C	-3.486318	-0.730945	0.177021
C	-1.398135	1.121923	-0.049867
C	-1.434348	-0.011489	-0.885263
C	-2.477130	-0.928246	-0.769634
H	-2.369289	2.178698	1.570365
C	-0.325253	2.071303	-0.146910
H	-4.239039	0.541423	1.758662
H	-4.303570	-1.451813	0.262416
H	-0.640038	-0.162091	-1.619055
H	-2.501976	-1.802842	-1.424050
N	-0.065318	3.215385	-0.482662
O	0.888155	4.013920	-0.438294
N	1.508545	1.477665	0.665714
S	2.629794	2.629945	0.402486
O	3.683714	2.355386	-0.629605
C	1.702764	0.118609	0.294966
C	2.371657	-0.307462	-0.868942
C	1.159661	-0.842985	1.166844
C	2.497681	-1.671893	-1.135020
C	1.293514	-2.202183	0.891493
C	1.962106	-2.622923	-0.262004
H	2.802565	0.435816	-1.539130
H	0.639247	-0.497744	2.063286
H	3.024477	-1.993777	-2.037454

H	0.871420	-2.937285	1.581703
H	2.066186	-3.689079	-0.479455

Table S152 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

B ES at PBE in the gas phase

C	-3.651367	0.723218	0.672065
C	-2.438002	1.387365	0.839173
C	-3.774909	-0.285406	-0.288438
C	-1.331900	1.050545	0.040071
C	-1.461102	0.039609	-0.926109
C	-2.678473	-0.621915	-1.086459
H	-2.328602	2.178338	1.584301
C	-0.072276	1.799169	0.208603
H	-4.505854	0.992327	1.298122
H	-4.726338	-0.808246	-0.415652
H	-0.610973	-0.220735	-1.560153
H	-2.771109	-1.403570	-1.844582
N	-0.105194	3.060952	0.514351
O	1.210910	3.566318	0.598554
N	1.185936	1.251014	-0.026755
S	2.425999	2.519483	-0.110105
O	2.653622	2.904581	-1.522160
C	1.586144	-0.108549	0.068563
C	2.514198	-0.615666	-0.853651
C	1.094267	-0.932528	1.092319
C	2.954593	-1.935369	-0.740130
C	1.518718	-2.257781	1.176035
C	2.453663	-2.762946	0.267309
H	2.876472	0.027404	-1.659861
H	0.381420	-0.529758	1.815134
H	3.683318	-2.321556	-1.457233
H	1.126191	-2.896931	1.971002
H	2.790647	-3.799367	0.345687

Table S153 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

TS2 at PBE in the gas phase

C	1.514871	1.397571	-2.533809
C	1.517930	1.365819	-1.144319
C	0.372444	1.823612	-3.225873
C	0.350326	1.734236	-0.447521
C	-0.791685	2.181598	-1.137420
C	-0.775257	2.217971	-2.529211
H	2.402350	1.056933	-0.583156
C	0.254029	1.375878	1.057510
H	2.411526	1.104493	-3.084873
H	0.383960	1.861809	-4.318072

H	-1.665146	2.508236	-0.569196
H	-1.655559	2.566777	-3.074225
N	0.582896	2.583723	1.221839
O	0.650921	2.245581	3.427400
N	0.068303	0.256570	1.697533
S	0.735788	0.774748	3.762236
O	2.087308	0.166603	3.830719
C	-0.319524	-0.989906	1.203112
C	0.374661	-2.132521	1.645469
C	-1.410667	-1.143216	0.326626
C	-0.014679	-3.397655	1.211210
C	-1.772501	-2.412800	-0.122126
C	-1.082409	-3.545159	0.319875
H	1.217969	-2.002867	2.328508
H	-1.971937	-0.262195	0.007327
H	0.529244	-4.277672	1.564392
H	-2.615428	-2.519259	-0.810210
H	-1.379736	-4.538911	-0.023746

Table S154 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the PBE/A01 level of theory in the gas phase.

28

C ES at PBE in the gas phase

C	1.944704	2.880319	-2.324875
C	1.323179	2.171704	-1.298254
C	1.184574	3.559499	-3.282585
C	-0.079851	2.141587	-1.229818
C	-0.845011	2.837449	-2.176635
C	-0.210426	3.536054	-3.203041
H	1.911662	1.662024	-0.530632
C	-0.483693	0.499611	0.495375
H	3.036421	2.904807	-2.373463
H	1.679946	4.112625	-4.084294
H	-1.934175	2.814326	-2.096474
H	-0.811582	4.070155	-3.943227
N	-0.754010	1.460555	-0.204684
O	2.524641	1.332346	1.927717
N	-0.270995	-0.361868	1.351297
S	1.712602	0.818728	3.055689
O	2.197276	-0.382906	3.773885
C	-0.663806	-1.715901	1.381871
C	-0.107495	-2.547255	2.364256
C	-1.602514	-2.236275	0.475137
C	-0.485856	-3.888329	2.431687
C	-1.972840	-3.577153	0.553407
C	-1.417353	-4.409601	1.530504
H	0.623780	-2.133680	3.062026
H	-2.039058	-1.582306	-0.285214
H	-0.045404	-4.530887	3.198295
H	-2.703571	-3.975139	-0.155648
H	-1.711142	-5.460492	1.587700

Table S155 Cartesian coordinates of the diphenylcarbodiimide equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

25

Diphenylcarbodiimide ES at PBE in the gas phase

C	2.136567	2.596156	-2.112961
C	1.415749	1.901274	-1.143942
C	1.531349	3.619276	-2.850271
C	0.069406	2.227090	-0.902353
C	-0.535932	3.255015	-1.641119
C	0.193853	3.944181	-2.608965
H	1.888256	1.103093	-0.564333
C	-0.467441	0.614622	0.794237
H	3.183017	2.336130	-2.293830
H	2.101766	4.160734	-3.608852
H	-1.581607	3.498839	-1.439833
H	-0.287598	4.743138	-3.178838
N	-0.704116	1.568092	0.061602
N	-0.318501	-0.223746	1.675613
C	-0.541635	-1.606209	1.704696
C	-0.185785	-2.305631	2.867887
C	-1.110019	-2.303618	0.624082
C	-0.392658	-3.682280	2.947322
C	-1.313090	-3.679193	0.713460
C	-0.955973	-4.375665	1.872808
H	0.251553	-1.749540	3.700293
H	-1.391638	-1.756898	-0.280399
H	-0.111771	-4.217319	3.858212
H	-1.755992	-4.213132	-0.131602
H	-1.117758	-5.454410	1.937086

Table S156 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

3

Sulfur dioxide ES at PBE in the gas phase

O	-0.416979	1.229528	-0.055984
S	-0.221550	-0.157068	0.417722
O	0.638530	-1.072459	-0.361738

Isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst (b)

Table S157 Energy profile of the PhNSO-catalyzed conversion (b). The calculations were done at the PBE/ Λ 01 level of theory in the gas phase and benzene, which was treated with Minenkov's SPT-V continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−5.9	5.7	−15.9	5.7	−60.8	−55.1
	$E + \Delta ZPE$, kcal/mol	0.0	−5.5	5.9	−14.4	5.3	−59.9	−54.6
	$E + \Delta G$, kcal/mol	0.0	3.2	18.6	−0.8	18.0	−51.4	−54.0
Benzene	E , kcal/mol	0.0	−4.8	6.0	−15.3	6.8	−60.7	−55.5
	$E + \Delta ZPE$, kcal/mol	0.0	−4.4	6.1	−13.8	6.4	−59.8	−55.0
	$E + \Delta G$, kcal/mol	0.0	4.3	18.8	−0.2	19.1	−51.4	−54.4

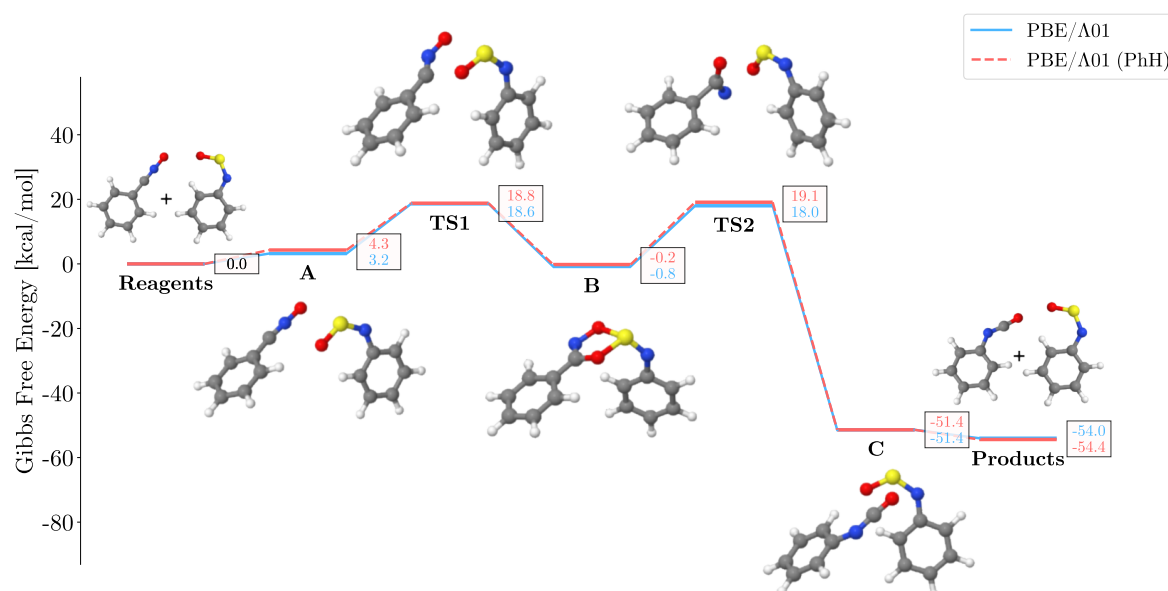


Figure S34 Calculated PES for isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst. PBE/ Λ 01 electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S158 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

14

Phenyl nitrile oxide ES at PBE in the gas phase

C	−1.768415	−0.011425	0.492630
C	−0.770324	0.917880	0.211915
C	−1.500286	−1.381938	0.421911
C	0.523535	0.481706	−0.147219
C	0.786575	−0.903665	−0.216540
C	−0.221278	−1.821560	0.066877
H	−0.976503	1.988981	0.266237

C	1.546621	1.423873	-0.435142
H	-2.766244	0.338149	0.769633
H	-2.287469	-2.106832	0.643348
H	1.786550	-1.243769	-0.494209
H	-0.005777	-2.891567	0.009959
N	2.392541	2.204742	-0.672734
O	3.260475	3.005423	-0.916666

Table S159 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the PBE/Å01 level of theory in the gas phase.

14

N-silfinylaniline ES at PBE in the gas phase

N	0.296764	1.805829	1.340979
S	0.894936	3.178666	0.898655
O	1.340803	3.418545	-0.518306
C	0.074130	0.646080	0.605437
C	0.373264	0.501040	-0.769676
C	-0.489504	-0.441161	1.308587
C	0.108846	-0.707168	-1.408110
C	-0.748112	-1.642186	0.657204
C	-0.450049	-1.779532	-0.703303
H	0.808392	1.345827	-1.305386
H	-0.712964	-0.308809	2.369801
H	0.341238	-0.815602	-2.470762
H	-1.184402	-2.477888	1.210179
H	-0.653342	-2.723639	-1.215299

Table S160 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the PBE/Å01 level of theory in the gas phase.

28

A ES at PBE in the gas phase

C	-4.921805	-1.357802	0.744482
C	-4.315275	-0.118230	0.555369
C	-4.205004	-2.415714	1.311748
C	-2.971708	0.074491	0.936556
C	-2.249911	-0.996387	1.509000
C	-2.871549	-2.228836	1.691161
H	-4.870537	0.711923	0.113249
C	-2.334341	1.332476	0.753666
H	-5.963847	-1.499006	0.446640
H	-4.685829	-3.386111	1.458658
H	-1.209010	-0.834222	1.798604
H	-2.308204	-3.053412	2.135592
N	-1.608470	2.255662	0.709543
O	-0.893120	3.227630	0.646064
O	0.850560	0.505096	1.780028
S	1.709183	1.745550	1.779934
N	2.793504	1.971796	0.683776
C	3.146033	1.195724	-0.415286
C	4.183499	1.700135	-1.229466

C	4.604586	0.994018	-2.351085
C	3.999672	-0.224262	-2.680167
C	2.970263	-0.731655	-1.879046
C	2.538997	-0.036293	-0.753015
H	4.638112	2.654152	-0.952635
H	5.408006	1.393637	-2.975048
H	4.330159	-0.778805	-3.562201
H	2.497632	-1.682903	-2.137297
H	1.738404	-0.418650	-0.118825

Table S161 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

TS1 at PBE in the gas phase

C	-4.105486	-1.061205	0.174481
C	-3.322491	0.083672	0.280192
C	-3.722871	-2.245325	0.814417
C	-2.134208	0.055606	1.043095
C	-1.752918	-1.136750	1.688018
C	-2.546520	-2.275750	1.567724
H	-3.615052	1.009296	-0.220110
C	-1.331654	1.233630	1.157236
H	-5.024104	-1.029380	-0.416879
H	-4.342043	-3.141305	0.725198
H	-0.835257	-1.146063	2.277533
H	-2.242623	-3.196449	2.072090
N	-1.284399	2.420460	0.883970
O	-0.512789	3.392027	0.997946
O	0.352285	0.930725	2.076392
S	1.403130	2.078727	1.891164
N	2.451688	1.992926	0.750961
C	2.638903	1.136295	-0.323185
C	3.682175	1.464463	-1.216912
C	3.952068	0.655058	-2.315485
C	3.191638	-0.496559	-2.545810
C	2.158104	-0.831405	-1.663782
C	1.876400	-0.030109	-0.560924
H	4.264475	2.367618	-1.020352
H	4.761412	0.923499	-2.999429
H	3.403469	-1.131569	-3.409643
H	1.561797	-1.730935	-1.838441
H	1.074871	-0.291199	0.130534

Table S162 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

B ES at PBE in the gas phase

C	-4.014834	-1.218639	0.353408
C	-3.161119	-0.119609	0.355948
C	-3.718304	-2.345802	1.129105

C	-1.992117	-0.139664	1.137722
C	-1.697960	-1.269520	1.917043
C	-2.560111	-2.366502	1.909208
H	-3.383075	0.767489	-0.241296
C	-1.088074	1.019141	1.145178
H	-4.922001	-1.196984	-0.255912
H	-4.392809	-3.205952	1.125415
H	-0.790182	-1.277509	2.523295
H	-2.324378	-3.243325	2.517595
N	-1.253908	2.031833	0.351399
O	-0.263025	2.988703	0.568334
O	-0.040714	1.005555	1.995611
S	1.108252	2.388186	1.592789
N	2.348243	1.948089	0.809598
C	2.555163	1.219481	-0.369591
C	3.896925	0.942195	-0.692935
C	4.209306	0.225284	-1.844727
C	3.190094	-0.221662	-2.690848
C	1.856655	0.057511	-2.375996
C	1.530626	0.772963	-1.225334
H	4.678499	1.300795	-0.019315
H	5.254685	0.014091	-2.083615
H	3.433699	-0.785032	-3.594994
H	1.055467	-0.285071	-3.035773
H	0.484999	0.993953	-1.001312

Table S163 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

TS2 at PBE in the gas phase

C	-4.605505	-0.801016	-0.780018
C	-3.626925	0.154475	-1.050708
C	-4.310925	-1.889746	0.047754
C	-2.362475	0.022364	-0.463340
C	-2.049720	-1.079646	0.344002
C	-3.035626	-2.028910	0.607519
H	-3.831539	1.002855	-1.707286
C	-1.356709	1.238389	-0.516032
H	-5.598462	-0.703065	-1.225737
H	-5.077410	-2.642680	0.248738
H	-1.046131	-1.176913	0.764023
H	-2.806814	-2.886961	1.244435
N	-0.853530	0.763970	-1.587443
O	0.434754	2.214695	-1.948232
O	-1.279265	2.159853	0.307076
S	0.845789	3.066251	-0.722290
N	1.972448	2.577703	0.224814
C	2.645657	1.368104	0.340337
C	2.407283	0.235607	-0.472398
C	3.149935	-0.924083	-0.269401
C	4.131693	-0.980817	0.726931
C	4.371455	0.137053	1.533656

C	3.635251	1.301820	1.345715
H	1.637873	0.280268	-1.244526
H	2.961785	-1.796876	-0.900155
H	4.709548	-1.896817	0.874425
H	5.135615	0.097350	2.314011
H	3.801953	2.186771	1.964129

Table S164 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

28

C ES at PBE in the gas phase

C	-2.881417	-1.135140	-1.700637
C	-2.354108	-0.179090	-0.833540
C	-3.593060	-2.232874	-1.206532
C	-2.541163	-0.323248	0.551877
C	-3.253948	-1.423176	1.051322
C	-3.775852	-2.371161	0.171825
H	-1.793126	0.677657	-1.217845
C	-1.406002	1.639455	1.468942
H	-2.733606	-1.017191	-2.777429
H	-4.003927	-2.976381	-1.893861
H	-3.390543	-1.518720	2.130806
H	-4.331170	-3.224660	0.569276
N	-2.034450	0.603482	1.463174
O	-0.125157	2.267503	-1.745910
O	-0.806357	2.643122	1.621379
S	0.922534	3.284289	-1.368727
N	2.226161	2.867520	-0.623504
C	2.657801	1.623948	-0.176122
C	1.953369	0.413383	-0.373394
C	2.478021	-0.777999	0.118657
C	3.696664	-0.789135	0.807133
C	4.399682	0.404920	1.004062
C	3.887994	1.602501	0.516860
H	1.006081	0.434853	-0.912992
H	1.928757	-1.710406	-0.034992
H	4.098890	-1.730268	1.190681
H	5.351462	0.398779	1.541129
H	4.416473	2.548034	0.658361

Table S165 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the PBE/ Λ 01 level of theory in the gas phase.

14

Phenyl isocyanate ES at PBE in the gas phase

C	-0.584135	-0.338059	-1.558012
C	-0.052390	0.706122	-0.803676
C	-0.764396	-1.603619	-0.991592
C	0.306367	0.487456	0.537105
C	0.126125	-0.781501	1.106495
C	-0.406788	-1.818499	0.341826

H	0.088917	1.696172	-1.245623
C	1.143984	2.670533	1.240427
H	-0.860592	-0.159238	-2.600433
H	-1.181988	-2.418017	-1.588337
H	0.409426	-0.936837	2.149786
H	-0.543521	-2.803935	0.794468
N	0.841726	1.499710	1.332434
O	1.477265	3.799713	1.285132

2.4.3 ω B97X-D3(BJ)/def2-TZVP

Preparative synthesis of diphenylcarbodiimide (a)

Table S166 Energy profile of the diphenylcarbodiimide formation (a). The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	E , kcal/mol	0.0	-6.5	11.2	-41.9	-5.3	-59.0	-53.5
	$E + \Delta ZPE$, kcal/mol	0.0	-5.8	11.6	-39.1	-4.9	-58.5	-53.7
	$E + \Delta G$, kcal/mol	0.0	7.3	26.4	-23.7	9.7	-45.8	-52.3
Benzene	E , kcal/mol	0.0	-6.6	11.2	-42.0	-3.2	-59.4	-53.7
	$E + \Delta ZPE$, kcal/mol	0.0	-6.0	11.5	-39.3	-3.0	-59.0	-54.0
	$E + \Delta G$, kcal/mol	0.0	7.0	26.0	-24.3	11.3	-46.1	-52.9

Table S167 Energy profile of the diphenylcarbodiimide formation (a). The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	E , kcal/mol	0.0	-6.0	11.5	-37.9	-4.4	-58.0	-53.8
	$E + \Delta ZPE$, kcal/mol	0.0	-5.3	11.9	-35.1	-4.1	-57.4	-54.1
	$E + \Delta G$, kcal/mol	0.0	7.8	26.7	-19.7	10.6	-44.7	-52.6
Benzene	E , kcal/mol	0.0	-5.9	11.6	-37.8	-2.1	-58.4	-53.9
	$E + \Delta ZPE$, kcal/mol	0.0	-5.3	11.9	-35.0	-1.9	-58.0	-54.2
	$E + \Delta G$, kcal/mol	0.0	7.6	26.3	-20.0	12.4	-45.2	-53.2

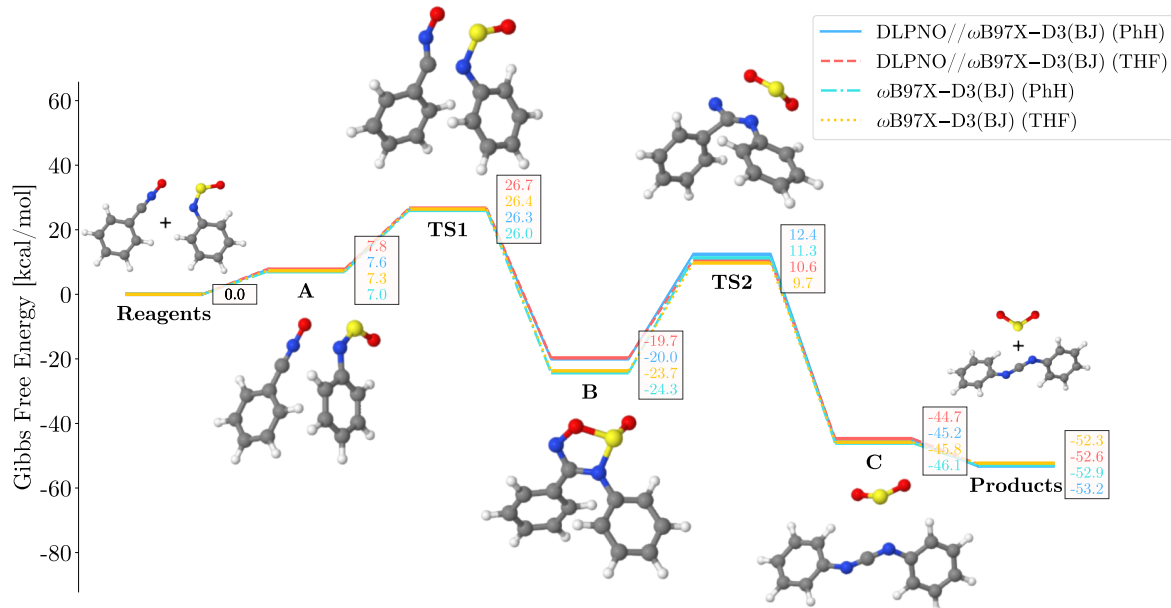


Figure S35 Calculated PES for diphenylcarbodiimide formation. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVP electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S168 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-3.957852	0.526933	0.399867
C	-2.964392	1.451751	0.114744
C	-3.685288	-0.835577	0.332408
C	-1.690275	1.003395	-0.241027
C	-1.413708	-0.363670	-0.312708
C	-2.415840	-1.278297	-0.024398
H	-3.165966	2.515342	0.165506
C	-0.654539	1.957472	-0.530213
H	-4.947824	0.871591	0.676460
H	-4.464951	-1.554759	0.558151
H	-0.421092	-0.698391	-0.590721
H	-2.204010	-2.340231	-0.077468
N	0.174843	2.721677	-0.754117
O	1.054501	3.532453	-0.989504

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-3.957483	0.526117	0.399740
C	-2.963920	1.450589	0.114834
C	-3.685829	-0.836065	0.332376
C	-1.689097	1.004692	-0.241084
C	-1.414850	-0.362830	-0.312264

C	-2.416450	-1.277747	-0.024262
H	-3.165870	2.514010	0.165794
C	-0.653277	1.958342	-0.530193
H	-4.947335	0.871119	0.676223
H	-4.465430	-1.555235	0.557928
H	-0.422337	-0.697631	-0.590072
H	-2.204091	-2.339539	-0.077445
N	0.176938	2.723448	-0.755159
O	1.052637	3.530418	-0.989438

Table S169 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

N-silfinylaniline ES at ω B97X-D3(BJ)/def2-TZVP in the THF

N	2.270966	1.377872	1.310510
S	3.109613	2.591514	1.032028
O	3.967658	2.631195	-0.143490
C	2.147370	0.153349	0.622929
C	2.418186	0.006044	-0.739927
C	1.696942	-0.936303	1.370203
C	2.238304	-1.233483	-1.339832
C	1.541624	-2.174128	0.765627
C	1.809269	-2.324498	-0.591760
H	2.756428	0.852512	-1.321791
H	1.478699	-0.795207	2.422584
H	2.439168	-1.346978	-2.399499
H	1.202374	-3.020743	1.352048
H	1.679792	-3.290835	-1.066605

14

N-silfinylaniline ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	2.526968	1.275581	1.405877
S	3.078274	2.616790	1.017267
O	3.479587	2.876857	-0.357808
C	2.285135	0.099500	0.673051
C	2.573978	-0.044946	-0.687798
C	1.725332	-0.964211	1.385056
C	2.299148	-1.251137	-1.317872
C	1.454548	-2.162670	0.745325
C	1.741170	-2.308347	-0.608724
H	3.007415	0.776923	-1.239604
H	1.510707	-0.829147	2.438835
H	2.523845	-1.363251	-2.372782
H	1.020250	-2.985233	1.302409
H	1.530036	-3.246399	-1.110210

Table S170 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

A ES at wB97X-D3(BJ)/def2-TZVP in the THF

C	-3.671740	0.361578	0.712502
C	-2.752236	1.356810	0.417874
C	-3.450244	-0.943582	0.282758
C	-1.604897	1.034906	-0.310734
C	-1.379723	-0.272161	-0.745338
C	-2.307306	-1.257886	-0.444825
H	-2.912515	2.376501	0.747783
C	-0.631784	2.051273	-0.598642
H	-4.562717	0.604980	1.280262
H	-4.171613	-1.718697	0.517409
H	-0.479557	-0.507897	-1.299249
H	-2.132789	-2.275895	-0.774373
N	0.169585	2.844223	-0.817921
O	1.040294	3.675470	-1.030341
N	2.098858	1.489131	1.211444
S	3.021108	2.635112	0.903177
O	4.022099	2.497804	-0.144036
C	1.985966	0.214289	0.617517
C	2.394178	-0.060190	-0.690144
C	1.401885	-0.789047	1.391866
C	2.224420	-1.339210	-1.204484
C	1.252848	-2.066818	0.874398
C	1.662880	-2.345259	-0.425464
H	2.830238	0.721388	-1.297029
H	1.073453	-0.551106	2.397184
H	2.536358	-1.549068	-2.221730
H	0.804355	-2.844109	1.483018
H	1.538595	-3.342539	-0.832882

28

A ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	-3.966835	0.520783	0.402211
C	-2.983455	1.455459	0.115944
C	-3.680075	-0.838761	0.335300
C	-1.706510	1.019793	-0.244289
C	-1.416596	-0.343885	-0.319255
C	-2.407623	-1.268046	-0.024943
H	-3.195297	2.516866	0.168750
C	-0.672106	1.974854	-0.531209
H	-4.960008	0.854688	0.680323
H	-4.451707	-1.565705	0.563837
H	-0.422858	-0.667942	-0.600371
H	-2.183083	-2.327455	-0.076611
N	0.184294	2.707222	-0.758081
O	1.105465	3.471818	-0.984627
N	2.193595	1.415803	1.276766
S	3.101004	2.582350	0.994466
O	4.102165	2.479368	-0.051408
C	2.107826	0.173386	0.612936
C	2.368960	0.025967	-0.751044

C	1.694605	-0.924149	1.367868
C	2.221737	-1.220928	-1.343960
C	1.572550	-2.170120	0.770519
C	1.834503	-2.321921	-0.587233
H	2.673517	0.881692	-1.338854
H	1.475017	-0.783195	2.419891
H	2.418246	-1.331582	-2.404694
H	1.260525	-3.022241	1.364075
H	1.732143	-3.294119	-1.056304

Table S171 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS1 at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-2.966914	0.046451	1.087525
C	-2.046596	1.069589	0.925585
C	-3.108911	-0.922741	0.098477
C	-1.275830	1.117084	-0.237780
C	-1.409288	0.141719	-1.228268
C	-2.334391	-0.875649	-1.056606
H	-1.910897	1.824055	1.691655
C	-0.270333	2.132117	-0.375822
H	-3.570603	0.000198	1.986454
H	-3.827002	-1.724617	0.231078
H	-0.786608	0.186365	-2.113397
H	-2.446172	-1.636768	-1.820063
N	0.173006	3.114168	-0.886182
O	1.238017	3.791436	-0.798966
N	1.374485	1.606686	0.817968
S	2.478320	2.686133	0.586039
O	3.612918	2.281263	-0.234154
C	1.524767	0.227939	0.469385
C	2.008589	-0.203454	-0.764453
C	1.064040	-0.702080	1.398824
C	2.039301	-1.562665	-1.053743
C	1.095297	-2.057626	1.101994
C	1.583332	-2.492306	-0.126169
H	2.341900	0.520001	-1.496650
H	0.671764	-0.347880	2.345328
H	2.414734	-1.893445	-2.016167
H	0.730800	-2.775070	1.829271
H	1.602276	-3.550905	-0.361165

28

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.934523	-0.014159	1.081489
C	-2.033877	1.030333	0.949704
C	-3.057818	-0.957060	0.065642
C	-1.264612	1.128130	-0.210840
C	-1.380292	0.178689	-1.227701
C	-2.284367	-0.861402	-1.086360

H	-1.912069	1.764495	1.737401
C	-0.277705	2.165210	-0.321973
H	-3.537609	-0.097806	1.978106
H	-3.760116	-1.776252	0.174417
H	-0.757238	0.260184	-2.109752
H	-2.379570	-1.602675	-1.871166
N	0.130445	3.184405	-0.784642
O	1.180226	3.877164	-0.706761
N	1.432608	1.619167	0.788161
S	2.538096	2.681394	0.488216
O	3.570969	2.284721	-0.456574
C	1.537799	0.234334	0.454872
C	2.020419	-0.237853	-0.764946
C	1.039960	-0.665506	1.396135
C	2.010734	-1.603208	-1.026002
C	1.028735	-2.025976	1.125928
C	1.514772	-2.500185	-0.088009
H	2.392123	0.458403	-1.503794
H	0.654154	-0.280276	2.332956
H	2.389953	-1.964211	-1.975996
H	0.635156	-2.716830	1.863711
H	1.503647	-3.563231	-0.302223

Table S172 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

B ES at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-3.543351	0.604592	0.680821
C	-2.371549	1.333176	0.833910
C	-3.626503	-0.384151	-0.293206
C	-1.280395	1.070579	0.008289
C	-1.363554	0.081938	-0.971121
C	-2.537428	-0.642703	-1.119325
H	-2.293514	2.099301	1.596412
C	-0.046646	1.865682	0.169277
H	-4.390076	0.806142	1.327361
H	-4.540941	-0.955962	-0.408101
H	-0.517830	-0.116395	-1.618959
H	-2.602282	-1.410539	-1.882059
N	-0.090574	3.135118	0.361989
O	1.253546	3.587692	0.524114
N	1.216625	1.320410	0.095785
S	2.381745	2.542094	-0.035925
O	2.618661	2.801369	-1.443614
C	1.571884	-0.062443	0.139859
C	2.396013	-0.591918	-0.845271
C	1.097805	-0.856241	1.178118
C	2.752738	-1.934222	-0.783908
C	1.437450	-2.201175	1.215237
C	2.269177	-2.740984	0.238588
H	2.742783	0.036385	-1.657375

H	0.465345	-0.421058	1.943434
H	3.398834	-2.350639	-1.548596
H	1.061485	-2.825868	2.017852
H	2.540551	-3.790181	0.276415

28

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-3.553568	0.627435	0.680218
C	-2.379283	1.352822	0.826330
C	-3.636398	-0.378660	-0.275416
C	-1.284142	1.070129	0.012887
C	-1.368082	0.064900	-0.949020
C	-2.544470	-0.656656	-1.090630
H	-2.301536	2.135984	1.571176
C	-0.048255	1.863242	0.170214
H	-4.403331	0.846130	1.317075
H	-4.553067	-0.947800	-0.385223
H	-0.519860	-0.149369	-1.588288
H	-2.609111	-1.437304	-1.840185
N	-0.091782	3.132447	0.357821
O	1.249962	3.585726	0.515753
N	1.216290	1.316632	0.100680
S	2.381424	2.542276	-0.040522
O	2.622835	2.784679	-1.447774
C	1.573773	-0.063511	0.137456
C	2.424003	-0.579883	-0.832953
C	1.079401	-0.872958	1.154378
C	2.785752	-1.920908	-0.777392
C	1.423832	-2.216386	1.184500
C	2.281698	-2.741760	0.223176
H	2.786883	0.059777	-1.629015
H	0.425976	-0.450173	1.908738
H	3.452665	-2.325324	-1.530525
H	1.031109	-2.851557	1.970642
H	2.557281	-3.789928	0.255898

Table S173 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS2 at ω B97X-D3(BJ)/def2-TZVP in the THF

C	1.543423	1.264137	-2.522246
C	1.580193	1.269661	-1.140108
C	0.386763	1.672184	-3.187439
C	0.430415	1.658850	-0.445750
C	-0.721911	2.099298	-1.101134
C	-0.740496	2.091361	-2.485150
H	2.466757	0.969072	-0.594164
C	0.363647	1.415721	1.062040
H	2.414758	0.953489	-3.086213
H	0.369639	1.674665	-4.271914
H	-1.576292	2.431407	-0.523456

H	-1.624821	2.421273	-3.016874
N	0.722385	2.593253	1.237950
O	0.447892	2.177017	3.427001
N	0.053307	0.362871	1.767971
S	0.320687	0.710963	3.616944
O	1.591404	0.043553	3.872352
C	-0.308117	-0.903827	1.233389
C	0.524413	-1.996469	1.454119
C	-1.501941	-1.047696	0.533878
C	0.152030	-3.244181	0.970427
C	-1.855793	-2.295014	0.036039
C	-1.033230	-3.394212	0.258290
H	1.448563	-1.859956	2.002339
H	-2.148070	-0.188624	0.393141
H	0.795314	-4.099765	1.143922
H	-2.783176	-2.409641	-0.514143
H	-1.317742	-4.369390	-0.121210

28

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.503103	1.234320	-2.477638
C	1.519641	1.257995	-1.095193
C	0.363215	1.651104	-3.164246
C	0.368873	1.673586	-0.421170
C	-0.766903	2.118607	-1.097303
C	-0.766103	2.095363	-2.482017
H	2.392923	0.952783	-0.530742
C	0.294808	1.420622	1.092662
H	2.378374	0.903870	-3.023968
H	0.361234	1.640369	-4.248724
H	-1.623306	2.471368	-0.535232
H	-1.637868	2.432094	-3.030093
N	0.654347	2.600794	1.247690
O	0.533518	2.175553	3.455082
N	0.026627	0.354472	1.787596
S	0.530726	0.712905	3.653773
O	1.855079	0.119286	3.716402
C	-0.322040	-0.905779	1.239918
C	0.459618	-2.017764	1.540906
C	-1.453630	-1.034472	0.438731
C	0.103366	-3.259756	1.031482
C	-1.787722	-2.276385	-0.085001
C	-1.013399	-3.391631	0.213694
H	1.334745	-1.898343	2.168124
H	-2.070875	-0.166357	0.238973
H	0.708975	-4.127632	1.268029
H	-2.664829	-2.374060	-0.715435
H	-1.282498	-4.362915	-0.186298

Table S174 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

C ES at wB97X-D3(BJ)/def2-TZVP in the THF

C	1.799170	2.343894	-2.395772
C	1.145329	1.789887	-1.304538
C	1.137235	3.236258	-3.234320
C	-0.181105	2.135955	-1.053742
C	-0.847062	3.031780	-1.881447
C	-0.184681	3.578249	-2.973982
H	1.662032	1.103997	-0.641001
C	-0.601601	0.648854	0.739608
H	2.832061	2.077299	-2.591354
H	1.653102	3.666148	-4.085756
H	-1.877143	3.290095	-1.664043
H	-0.705391	4.274819	-3.621890
N	-0.893120	1.599023	0.049814
O	1.749069	1.968659	2.359923
N	-0.339133	-0.221686	1.556702
S	1.824270	0.668057	2.961154
O	2.742120	-0.269703	2.381504
C	-0.660710	-1.600726	1.460790
C	-0.367509	-2.410373	2.552156
C	-1.239970	-2.143808	0.315577
C	-0.655119	-3.768505	2.496800
C	-1.524444	-3.501260	0.269805
C	-1.231779	-4.318133	1.357800
H	0.080030	-1.972536	3.437017
H	-1.461672	-1.506541	-0.534555
H	-0.426622	-4.398228	3.349694
H	-1.974753	-3.922578	-0.622429
H	-1.452603	-5.378896	1.316486

28

C ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	1.875516	2.553568	-2.385243
C	1.253933	1.960048	-1.295748
C	1.135545	3.297249	-3.298861
C	-0.118996	2.117710	-1.122672
C	-0.864060	2.868413	-2.024552
C	-0.233465	3.452108	-3.115784
H	1.828082	1.392572	-0.571365
C	-0.481851	0.598410	0.667846
H	2.945168	2.435653	-2.519101
H	1.626577	3.758381	-4.148555
H	-1.929590	2.984822	-1.863870
H	-0.815586	4.032556	-3.823129
N	-0.796460	1.542729	-0.018683
O	2.126031	1.744238	2.226462
N	-0.206404	-0.275291	1.478920
S	1.615775	0.896240	3.263260
O	2.373583	-0.275509	3.590411
C	-0.604729	-1.636784	1.401697
C	-0.095007	-2.518093	2.348251

C	-1.483388	-2.090686	0.420193
C	-0.462671	-3.856913	2.307934
C	-1.845815	-3.429453	0.389093
C	-1.337756	-4.317362	1.331571
H	0.589857	-2.151912	3.103381
H	-1.880464	-1.397597	-0.314533
H	-0.061094	-4.542314	3.046275
H	-2.529467	-3.779824	-0.376512
H	-1.623263	-5.362958	1.303315

Table S175 Cartesian coordinates of the diphenylcarbodiimide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

25

Diphenylcarbodiimide ES at ω B97X-D3(BJ)/def2-TZVP in the THF

C	1.764479	2.228563	-2.355149
C	1.008921	1.642671	-1.349238
C	1.246194	3.282380	-3.102106
C	-0.277160	2.114863	-1.089196
C	-0.800404	3.167225	-1.833184
C	-0.036827	3.748362	-2.838067
H	1.412039	0.820333	-0.766866
C	-0.809754	0.644753	0.681330
H	2.764362	1.859059	-2.555880
H	1.840629	3.736659	-3.887066
H	-1.802678	3.519952	-1.617970
H	-0.448383	4.568636	-3.416202
N	-1.094321	1.551288	-0.078070
N	-0.582608	-0.173136	1.553098
C	-0.763490	-1.576709	1.480219
C	-0.467880	-2.327517	2.613010
C	-1.215959	-2.205292	0.320567
C	-0.623711	-3.707966	2.585624
C	-1.368053	-3.584584	0.301784
C	-1.071516	-4.340915	1.431783
H	-0.118578	-1.821654	3.505947
H	-1.444996	-1.615442	-0.561342
H	-0.392594	-4.289962	3.471242
H	-1.718418	-4.070862	-0.602309
H	-1.189692	-5.418643	1.411687

25

Diphenylcarbodiimide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.777459	2.246734	-2.339729
C	1.020141	1.657043	-1.337832
C	1.252902	3.289078	-3.097388
C	-0.274391	2.113210	-1.092139
C	-0.803360	3.154565	-1.847146
C	-0.038166	3.739569	-2.847811
H	1.428389	0.844393	-0.745542
C	-0.809763	0.641255	0.675644
H	2.784049	1.889584	-2.528594

H	1.848753	3.746781	-3.879144
H	-1.811801	3.494610	-1.641593
H	-0.454527	4.551330	-3.434334
N	-1.092772	1.546187	-0.085828
N	-0.583004	-0.177041	1.546759
C	-0.765890	-1.579164	1.476833
C	-0.450501	-2.330903	2.603462
C	-1.241081	-2.207813	0.326538
C	-0.608252	-3.710665	2.578798
C	-1.394955	-3.586584	0.310270
C	-1.078212	-4.343177	1.433987
H	-0.084654	-1.824018	3.488915
H	-1.487616	-1.616898	-0.549850
H	-0.361590	-4.293018	3.459891
H	-1.763421	-4.072345	-0.586796
H	-1.198137	-5.420648	1.416276

Table S176 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

3

Sulfur dioxide ES at ω B97X-D3(BJ)/def2-TZVP in the THF

O	1.665955	1.933402	2.172142
S	1.844007	0.593682	2.645925
O	2.680443	-0.279147	1.878286

3

Sulfur dioxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

O	1.664356	1.934670	2.173830
S	1.845545	0.594768	2.643027
O	2.680504	-0.281501	1.879495

Isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst (b)

Table S177 Energy profile of the PhNSO-catalyzed conversion (b). The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	E , kcal/mol	0.0	-6.9	12.7	-20.9	9.2	-66.0	-59.9
	$E + \Delta ZPE$, kcal/mol	0.0	-6.4	13.2	-18.5	8.9	-65.2	-59.7
	$E + \Delta G$, kcal/mol	0.0	7.7	27.9	-3.3	23.8	-51.9	-59.7
Benzene	E , kcal/mol	0.0	-7.3	12.3	-21.8	8.9	-67.4	-60.8
	$E + \Delta ZPE$, kcal/mol	0.0	-6.8	12.6	-19.6	8.6	-66.6	-60.6
	$E + \Delta G$, kcal/mol	0.0	6.2	26.8	-4.8	22.2	-53.6	-60.6

Table S178 Energy profile of the PhNSO-catalyzed conversion (b). The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C// ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
THF	E , kcal/mol	0.0	-5.9	13.7	-17.8	9.8	-64.5	-59.0
	$E + \Delta ZPE$, kcal/mol	0.0	-5.4	14.1	-15.5	9.6	-63.7	-58.8
	$E + \Delta G$, kcal/mol	0.0	8.7	28.9	-0.2	24.5	-50.3	-58.9
Benzene	E , kcal/mol	0.0	-6.1	13.4	-18.6	9.9	-65.5	-59.8
	$E + \Delta ZPE$, kcal/mol	0.0	-5.6	13.7	-16.3	9.6	-64.7	-59.6
	$E + \Delta G$, kcal/mol	0.0	7.4	27.8	-1.5	23.2	-51.7	-59.6

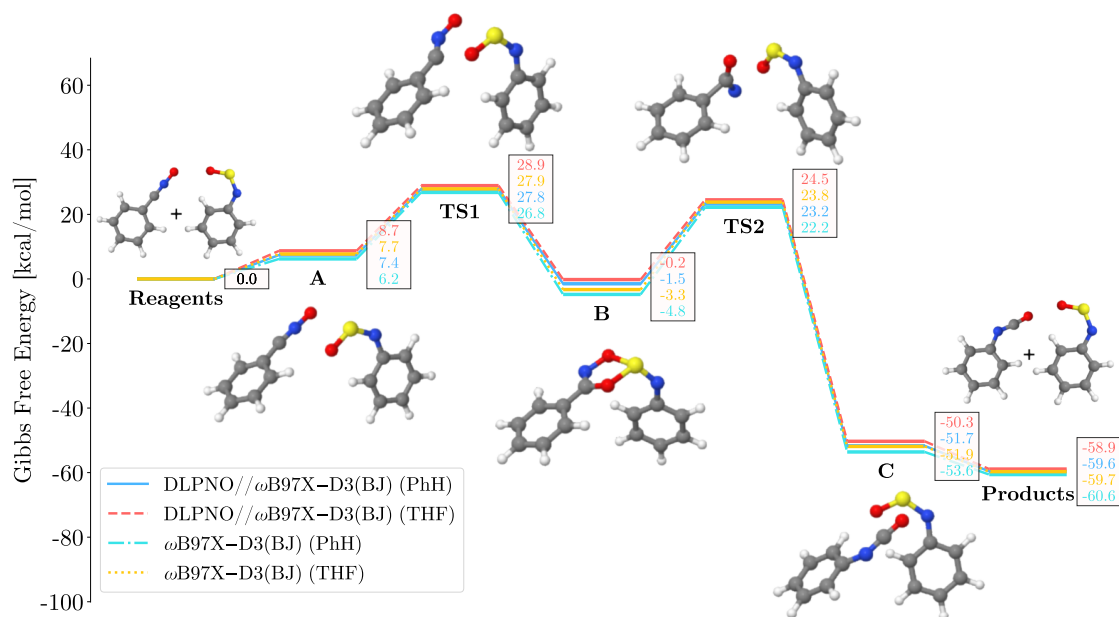


Figure S36 Calculated PES for isomerization of nitrile oxide into isocyanate with silfinylaniline as catalyst. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//ωB97X-D3(BJ)/def2-TZVP electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S179 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ωB97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ωB97X-D3(BJ)/def2-TZVP in the THF

C	-3.957852	0.526933	0.399867
C	-2.964392	1.451751	0.114744
C	-3.685288	-0.835577	0.332408
C	-1.690275	1.003395	-0.241027
C	-1.413708	-0.363670	-0.312708
C	-2.415840	-1.278297	-0.024398
H	-3.165966	2.515342	0.165506
C	-0.654539	1.957472	-0.530213
H	-4.947824	0.871591	0.676460
H	-4.464951	-1.554759	0.558151
H	-0.421092	-0.698391	-0.590721
H	-2.204010	-2.340231	-0.077468
N	0.174843	2.721677	-0.754117
O	1.054501	3.532453	-0.989504

14

Phenyl nitrile oxide ES at ωB97X-D3(BJ)/def2-TZVP in the benzene

C	-3.957483	0.526117	0.399740
C	-2.963920	1.450589	0.114834
C	-3.685829	-0.836065	0.332376
C	-1.689097	1.004692	-0.241084

C	-1.414850	-0.362830	-0.312264
C	-2.416450	-1.277747	-0.024262
H	-3.165870	2.514010	0.165794
C	-0.653277	1.958342	-0.530193
H	-4.947335	0.871119	0.676223
H	-4.465430	-1.555235	0.557928
H	-0.422337	-0.697631	-0.590072
H	-2.204091	-2.339539	-0.077445
N	0.176938	2.723448	-0.755159
O	1.052637	3.530418	-0.989438

Table S180 Cartesian coordinates of the N-silfinylaniline equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

N-silfinylaniline ES at ω B97X-D3(BJ)/def2-TZVP in the THF

N	2.270966	1.377872	1.310510
S	3.109613	2.591514	1.032028
O	3.967658	2.631195	-0.143490
C	2.147370	0.153349	0.622929
C	2.418186	0.006044	-0.739927
C	1.696942	-0.936303	1.370203
C	2.238304	-1.233483	-1.339832
C	1.541624	-2.174128	0.765627
C	1.809269	-2.324498	-0.591760
H	2.756428	0.852512	-1.321791
H	1.478699	-0.795207	2.422584
H	2.439168	-1.346978	-2.399499
H	1.202374	-3.020743	1.352048
H	1.679792	-3.290835	-1.066605

14

N-silfinylaniline ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	2.526968	1.275581	1.405877
S	3.078274	2.616790	1.017267
O	3.479587	2.876857	-0.357808
C	2.285135	0.099500	0.673051
C	2.573978	-0.044946	-0.687798
C	1.725332	-0.964211	1.385056
C	2.299148	-1.251137	-1.317872
C	1.454548	-2.162670	0.745325
C	1.741170	-2.308347	-0.608724
H	3.007415	0.776923	-1.239604
H	1.510707	-0.829147	2.438835
H	2.523845	-1.363251	-2.372782
H	1.020250	-2.985233	1.302409
H	1.530036	-3.246399	-1.110210

Table S181 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

A ES at wB97X-D3(BJ)/def2-TZVP in the THF

C	-2.325288	-1.060708	-1.138833
C	-1.894010	0.212468	-0.797734
C	-2.367128	-2.064657	-0.178328
C	-1.505460	0.473961	0.515769
C	-1.546631	-0.530765	1.485077
C	-1.978815	-1.798928	1.131344
H	-1.846116	0.999705	-1.540527
C	-1.033204	1.780950	0.877456
H	-2.622461	-1.270538	-2.160066
H	-2.701662	-3.059625	-0.451018
H	-1.230187	-0.313170	2.498257
H	-2.008946	-2.583395	1.879084
N	-0.637732	2.811991	1.193622
O	-0.189391	3.895872	1.537859
O	1.426539	1.263968	3.062511
S	2.305270	2.159375	2.324102
N	2.588704	1.890792	0.874655
C	2.113731	0.865712	0.026606
C	1.921427	1.193930	-1.315665
C	1.461209	0.232087	-2.202210
C	1.218896	-1.065056	-1.760787
C	1.432032	-1.394066	-0.428049
C	1.869920	-0.433250	0.473475
H	2.127437	2.206178	-1.644614
H	1.296750	0.494225	-3.241601
H	0.859528	-1.817030	-2.454412
H	1.240844	-2.402899	-0.079820
H	2.024742	-0.687129	1.513844

28

A ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	-2.349325	-1.000033	-1.094990
C	-1.898233	0.266140	-0.754214
C	-2.392946	-2.006774	-0.138091
C	-1.489666	0.519245	0.554619
C	-1.531616	-0.489255	1.519905
C	-1.984903	-1.750211	1.167140
H	-1.848940	1.055600	-1.494487
C	-0.994554	1.817824	0.915178
H	-2.661814	-1.202056	-2.113222
H	-2.744686	-2.995926	-0.410168
H	-1.194968	-0.278060	2.527716
H	-2.016409	-2.536769	1.912651
N	-0.561083	2.834349	1.231879
O	-0.078655	3.896451	1.581807
O	1.393268	1.117746	3.033886
S	2.314718	2.010761	2.347712
N	2.622034	1.779197	0.896285
C	2.125292	0.796231	0.012831
C	1.975136	1.164655	-1.323814

C	1.493970	0.245012	-2.243512
C	1.188356	-1.050784	-1.840766
C	1.358574	-1.421090	-0.512836
C	1.816678	-0.502086	0.420649
H	2.231331	2.175257	-1.620317
H	1.364070	0.539040	-3.279236
H	0.813784	-1.769759	-2.560796
H	1.116279	-2.428410	-0.193565
H	1.934307	-0.786294	1.457756

Table S182 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS1 at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-2.098431	-1.509681	-0.694597
C	-1.363029	-0.389248	-0.341305
C	-3.007926	-2.055496	0.206367
C	-1.557710	0.181471	0.919142
C	-2.461778	-0.369064	1.831038
C	-3.189173	-1.489861	1.466049
H	-0.643032	0.046416	-1.023559
C	-0.792662	1.336228	1.280530
H	-1.961094	-1.959400	-1.671228
H	-3.580538	-2.932798	-0.074515
H	-2.584317	0.083552	2.808026
H	-3.897596	-1.924196	2.161745
N	-0.537756	2.501436	1.222720
O	0.433587	3.210040	1.672540
O	0.720480	0.787565	2.452778
S	1.823598	1.793082	2.313039
N	2.707980	1.625854	1.103227
C	2.352107	0.901403	-0.064418
C	2.034347	1.599562	-1.228315
C	1.727996	0.904083	-2.391901
C	1.743835	-0.486783	-2.405227
C	2.061390	-1.180456	-1.242394
C	2.362382	-0.492591	-0.073204
H	2.030672	2.683737	-1.210150
H	1.480353	1.454202	-3.293539
H	1.509827	-1.026203	-3.316420
H	2.073454	-2.265263	-1.242062
H	2.613036	-1.027591	0.835632

28

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.212357	-1.206892	-0.909426
C	-1.560713	-0.049231	-0.514946
C	-2.771932	-2.048546	0.045542
C	-1.495985	0.266654	0.843245
C	-2.050852	-0.577516	1.806527
C	-2.686929	-1.738858	1.400544

H	-1.091168	0.604305	-1.239832
C	-0.803890	1.458840	1.237674
H	-2.270906	-1.459001	-1.961913
H	-3.274248	-2.957588	-0.267003
H	-1.965820	-0.322973	2.856073
H	-3.118496	-2.404370	2.139077
N	-0.552541	2.619067	1.120156
O	0.388772	3.370117	1.547453
O	0.624531	0.998231	2.540345
S	1.763529	1.947224	2.325430
N	2.630793	1.659461	1.128053
C	2.249381	0.865578	0.017291
C	2.094530	1.480735	-1.223920
C	1.755374	0.722207	-2.337270
C	1.574610	-0.651737	-2.223324
C	1.732416	-1.263328	-0.984777
C	2.065862	-0.511798	0.134635
H	2.243937	2.551635	-1.301546
H	1.637521	1.209166	-3.299523
H	1.314582	-1.242157	-3.095064
H	1.591018	-2.334286	-0.885065
H	2.188981	-0.984939	1.101564

Table S183 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

B ES at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-3.149257	-1.636833	0.166819
C	-2.593143	-0.367496	0.186675
C	-2.599034	-2.653668	0.942891
C	-1.478540	-0.114356	0.987819
C	-0.928859	-1.129207	1.768238
C	-1.491924	-2.398484	1.743192
H	-3.017966	0.429054	-0.412567
C	-0.864424	1.220705	0.989884
H	-4.015806	-1.834731	-0.454035
H	-3.037474	-3.645588	0.923885
H	-0.061630	-0.927336	2.384892
H	-1.062910	-3.188687	2.349069
N	-1.094565	2.127403	0.119311
O	-0.315489	3.253772	0.461376
O	0.035550	1.512108	1.957087
S	0.938166	2.877039	1.493236
N	2.157079	2.425409	0.746154
C	2.109919	1.460204	-0.304600
C	2.158229	0.102655	0.001979
C	2.099208	-0.836130	-1.020537
C	2.005033	-0.425481	-2.345584
C	1.972219	0.932547	-2.645369
C	2.025211	1.878480	-1.629357
H	2.231739	-0.207438	1.038028

H	2.125944	-1.893005	-0.777538
H	1.960364	-1.160286	-3.141762
H	1.901492	1.260459	-3.676947
H	1.990869	2.938889	-1.852239

28

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-3.043846	-1.669253	0.101783
C	-2.480324	-0.403737	0.121857
C	-2.583179	-2.654189	0.971287
C	-1.447966	-0.121573	1.017637
C	-0.986457	-1.105098	1.888953
C	-1.556960	-2.371056	1.863494
H	-2.831072	0.368028	-0.552723
C	-0.829877	1.212033	1.027212
H	-3.845580	-1.890030	-0.593840
H	-3.027138	-3.643612	0.951466
H	-0.182314	-0.880063	2.578552
H	-1.196999	-3.136702	2.541535
N	-1.071933	2.130202	0.173054
O	-0.278960	3.246345	0.511353
O	0.086629	1.488120	1.984650
S	0.992567	2.850030	1.511198
N	2.190852	2.394350	0.735661
C	2.109093	1.449314	-0.330107
C	2.165637	0.086153	-0.052122
C	2.069559	-0.832309	-1.089746
C	1.929322	-0.396241	-2.402152
C	1.888620	0.966953	-2.673990
C	1.978799	1.892500	-1.642728
H	2.274981	-0.243317	0.974724
H	2.103396	-1.893654	-0.868496
H	1.854870	-1.115274	-3.210281
H	1.781555	1.315131	-3.695632
H	1.936727	2.956950	-1.842597

Table S184 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

TS2 at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-4.512036	-0.807218	-0.685605
C	-3.591471	0.194845	-0.958346
C	-4.128081	-1.918847	0.059582
C	-2.299173	0.075694	-0.456287
C	-1.896798	-1.043618	0.267010
C	-2.824671	-2.040046	0.534178
H	-3.868305	1.063408	-1.545245
C	-1.326771	1.279844	-0.569902
H	-5.525921	-0.725992	-1.060469
H	-4.848840	-2.703192	0.263847
H	-0.873392	-1.122712	0.616676

H	-2.529821	-2.914289	1.103358
N	-0.809236	0.874619	-1.662302
O	0.464325	2.300921	-1.958247
O	-1.215319	2.210707	0.230112
S	0.900514	3.123260	-0.791426
N	1.930890	2.578321	0.138005
C	2.568890	1.338987	0.307558
C	2.285814	0.206821	-0.462111
C	2.970119	-0.973727	-0.209475
C	3.932943	-1.032857	0.792797
C	4.214877	0.096983	1.555222
C	3.532776	1.279397	1.317001
H	1.539155	0.246811	-1.241860
H	2.748581	-1.853514	-0.803477
H	4.463738	-1.959821	0.980155
H	4.964266	0.055218	2.337646
H	3.732946	2.169996	1.901605

28

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-4.503451	-0.808489	-0.684659
C	-3.580089	0.189382	-0.962369
C	-4.124354	-1.913929	0.071197
C	-2.290335	0.073054	-0.455269
C	-1.893195	-1.039877	0.279432
C	-2.823231	-2.032546	0.551681
H	-3.851597	1.053114	-1.558398
C	-1.315625	1.278769	-0.572700
H	-5.515681	-0.728872	-1.064183
H	-4.847006	-2.695414	0.279501
H	-0.871192	-1.116370	0.633305
H	-2.531944	-2.902168	1.129653
N	-0.806128	0.861250	-1.662714
O	0.469212	2.300908	-1.960752
O	-1.203078	2.210304	0.224154
S	0.889578	3.119674	-0.788346
N	1.923289	2.580574	0.141978
C	2.561273	1.340173	0.305330
C	2.292944	0.215783	-0.480632
C	2.976932	-0.965749	-0.231138
C	3.925238	-1.034705	0.783542
C	4.193202	0.087379	1.561598
C	3.511605	1.270414	1.326513
H	1.558774	0.263525	-1.271786
H	2.766918	-1.838546	-0.839506
H	4.456161	-1.962219	0.967609
H	4.931735	0.039098	2.353922
H	3.700046	2.155482	1.923039

Table S185 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

28

C ES at wB97X-D3(BJ)/def2-TZVP in the THF

C	-2.457657	-0.953848	-1.433924
C	-1.945565	0.085170	-0.669814
C	-2.665357	-2.209129	-0.869833
C	-1.637472	-0.140744	0.669567
C	-1.849417	-1.387786	1.244927
C	-2.362621	-2.420575	0.470394
H	-1.760922	1.059660	-1.107016
C	-0.665055	1.989215	1.353805
H	-2.690813	-0.781214	-2.479055
H	-3.062535	-3.018044	-1.472877
H	-1.602681	-1.540513	2.289170
H	-2.524120	-3.395060	0.918205
N	-1.089928	0.875601	1.470477
O	-0.190093	2.912581	-1.968464
O	-0.231191	3.075938	1.370150
S	1.079892	3.538985	-1.629492
N	2.124487	2.761498	-0.883233
C	2.103252	1.442137	-0.383143
C	1.417674	0.403029	-1.013176
C	1.457722	-0.872433	-0.465687
C	2.160962	-1.113344	0.708007
C	2.844785	-0.074063	1.333495
C	2.830433	1.198285	0.783327
H	0.859721	0.591513	-1.920316
H	0.917473	-1.677186	-0.951933
H	2.176376	-2.109204	1.137132
H	3.397470	-0.257429	2.248304
H	3.365180	2.016959	1.251002

28

C ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	-2.451242	-0.957896	-1.436740
C	-1.956111	0.090385	-0.674297
C	-2.633144	-2.217165	-0.873654
C	-1.639061	-0.129984	0.663927
C	-1.826313	-1.381661	1.238127
C	-2.322029	-2.423432	0.465148
H	-1.793152	1.068308	-1.112540
C	-0.678606	2.005188	1.346247
H	-2.692524	-0.788486	-2.480507
H	-3.018192	-3.032759	-1.475439
H	-1.573023	-1.528906	2.281414
H	-2.464238	-3.400850	0.913021
N	-1.108278	0.892985	1.465301
O	-0.205735	2.909431	-1.939830
O	-0.241264	3.089666	1.361224
S	1.062726	3.539187	-1.604349
N	2.116923	2.761282	-0.872055
C	2.096695	1.439991	-0.378069
C	1.400209	0.405965	-1.004563

C	1.437904	-0.871052	-0.461260
C	2.150262	-1.118721	0.704977
C	2.845201	-0.085089	1.326820
C	2.832669	1.188664	0.780853
H	0.832295	0.600697	-1.904005
H	0.886081	-1.670470	-0.943132
H	2.163163	-2.115490	1.131874
H	3.404564	-0.274250	2.236288
H	3.374221	2.004462	1.245218

Table S186 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the THF and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the THF

C	-2.537794	-0.949177	-1.454453
C	-2.010349	0.088018	-0.697455
C	-2.715857	-2.210681	-0.895153
C	-1.659822	-0.144213	0.631088
C	-1.835239	-1.401516	1.198586
C	-2.364174	-2.431737	0.431473
H	-1.869685	1.073049	-1.129375
C	-0.821086	2.032864	1.318597
H	-2.810520	-0.768499	-2.488541
H	-3.127057	-3.017391	-1.491555
H	-1.556317	-1.560470	2.233754
H	-2.500250	-3.412060	0.874833
N	-1.120827	0.877157	1.433849
O	-0.494435	3.155115	1.326522

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.536197	-0.946916	-1.452313
C	-2.008010	0.088073	-0.693477
C	-2.715860	-2.208629	-0.895329
C	-1.657773	-0.145108	0.634915
C	-1.835173	-1.403381	1.199377
C	-2.364807	-2.431505	0.430777
H	-1.866164	1.073424	-1.124293
C	-0.823658	2.031058	1.314560
H	-2.808333	-0.764372	-2.486149
H	-3.127671	-3.013988	-1.492902
H	-1.556539	-1.563201	2.234301
H	-2.502192	-3.412286	0.872536
N	-1.118047	0.873502	1.439639
O	-0.502990	3.153790	1.310530

2.5 The N₂O-catalyzed conversion

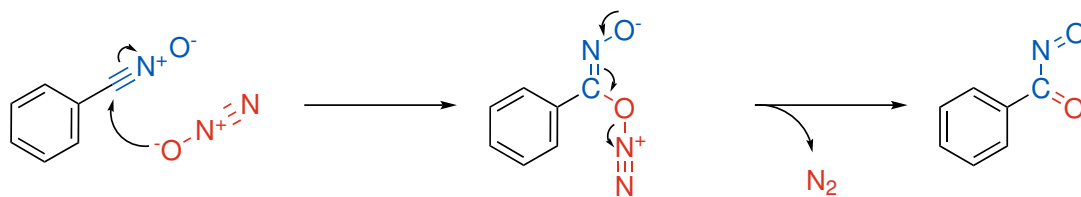


Figure S37 Reaction of the phenyl nitrile sulfide with dinitrogen oxide.

2.5.1 r²SCAN-3c

Table S187 Energy profile of the N₂O-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS	C	Products
Benzene	<i>E</i> , kcal/mol	0.0	−4.9	40.8	−48.4	−47.6
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−4.6	39.5	−49.7	−49.2
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.2	50.3	−41.9	−48.4

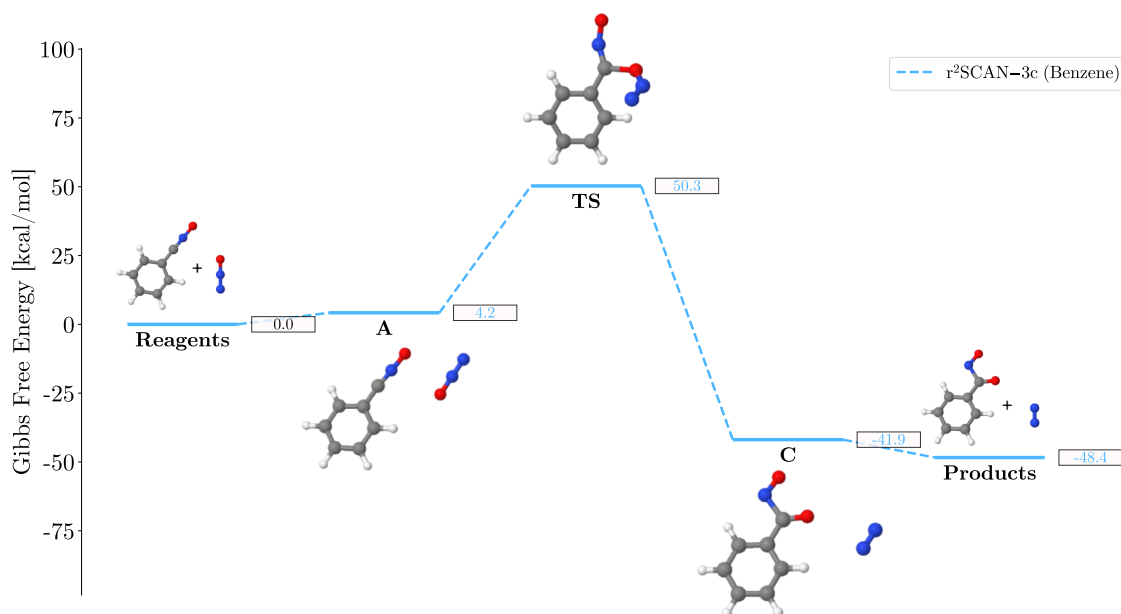


Figure S38 Calculated PES for reaction of the phenyl nitrile oxide with dinitrogen oxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S188 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021
H	−0.248893	−2.210375	0.356466

H	3.744529	-0.661291	0.684203
H	2.194048	-2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

Table S189 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

A ES at r2SCAN-3c in the benzene

C	-2.114391	-0.374461	-2.732624
C	-1.336664	0.757368	-2.933319
C	-1.541842	-1.543969	-2.236357
C	0.035291	0.721399	-2.633509
C	0.611750	-0.459036	-2.132583
C	-0.180780	-1.581235	-1.938252
H	-1.775996	1.671285	-3.319731
C	0.842513	1.868731	-2.833730
H	-3.174570	-0.343077	-2.965608
H	-2.155817	-2.426191	-2.081961
H	1.672293	-0.480538	-1.903332
H	0.267701	-2.491537	-1.551512
N	1.589151	2.750457	-2.964386
O	2.354065	3.678282	-3.105479
N	5.555448	3.305302	-2.162803
N	4.926383	2.371716	-2.172196
O	4.272197	1.387133	-2.179317

Table S190 Cartesian coordinates of the transition state between pre-intermediate and post-intermediate (TS) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

TS at r2SCAN-3c in the benzene

C	-2.138522	-0.604036	0.285099
C	-1.355204	0.473912	-0.097731
C	-1.565270	-1.862781	0.463924
C	0.020068	0.297612	-0.315347
C	0.593418	-0.967771	-0.140451
C	-0.201767	-2.039188	0.248963
H	-1.796466	1.457309	-0.230209
C	0.828219	1.429764	-0.728605
H	-3.202144	-0.460628	0.450888
H	-2.181918	-2.702860	0.769167
H	1.651864	-1.116129	-0.326395
H	0.248953	-3.018239	0.380558
N	0.535468	2.455431	-1.343914
O	0.765871	3.561967	-1.771218
N	2.503050	0.776638	1.902251
N	2.885136	0.991152	0.852374
O	2.409246	1.327849	-0.399352

Table S191 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

C ES at r2SCAN-3c in the benzene

C	-1.690589	-0.413622	-2.533990
C	-1.006725	0.772343	-2.772065
C	-0.995649	-1.557409	-2.151078
C	0.390248	0.809729	-2.625188
C	1.085201	-0.349044	-2.239134
C	0.393551	-1.524177	-2.003746
H	-1.549504	1.662840	-3.064960
C	1.157796	2.028574	-2.876515
H	-2.770041	-0.444444	-2.645786
H	-1.536166	-2.481252	-1.965036
H	2.164555	-0.303902	-2.131494
H	0.930223	-2.419637	-1.705069
N	0.255540	3.262483	-3.342408
O	0.943334	4.178687	-3.666130
N	5.556049	1.508940	-1.599864
N	4.969406	0.626057	-1.329926
O	2.344584	2.183633	-2.755300

Table S192 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

15

Product ES at r2SCAN-3c in the benzene

C	-2.987286	3.431130	-1.064862
C	-1.989137	4.364621	-1.316283
C	-2.659887	2.174223	-0.564028
C	-0.647786	4.032290	-1.062084
C	-0.324816	2.761454	-0.556499
C	-1.327030	1.839850	-0.309969
H	-2.245298	5.342906	-1.704405
C	0.440747	4.976281	-1.313642
H	-4.024487	3.685796	-1.259913
H	-3.444669	1.448639	-0.369224
H	0.716812	2.521194	-0.366446
H	-1.078262	0.857577	0.080372
N	-0.056316	6.377941	-1.906707
O	0.876637	7.076189	-2.148968
O	1.615177	4.805674	-1.119881

Table S193 Cartesian coordinates of the dinitrogen oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

Dinitrogen oxide ES at r2SCAN-3c in the benzene

N	-0.990459	0.000000	-3.399369
N	-0.949237	0.000000	-2.273224
O	-0.906056	0.000000	-1.092947

Table S194 Cartesian coordinates of the nitrogen equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

2

Nitrogen ES at r2SCAN-3c in the benzene

N	-0.989855	0.000000	-3.382856
N	-0.949841	0.000000	-2.289737

2.5.2 B3LYP-D3(BJ)/6-31G

Table S195 Energy profile of the N₂O-catalyzed conversion. The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS	C	Products
Gas phase	E , kcal/mol	0.0	−4.9	30.2	−53.7	−50.9
	$E + \Delta ZPE$, kcal/mol	0.0	−3.6	30.1	−53.0	−50.8
	$E + \Delta G$, kcal/mol	0.0	1.7	36.2	−48.1	−54.0

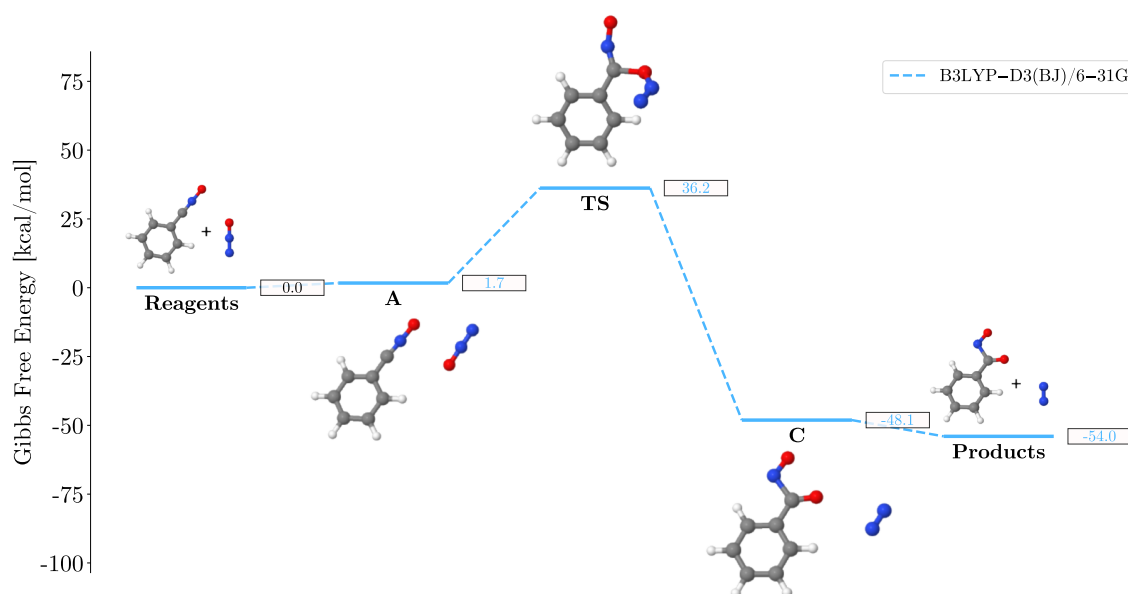


Figure S39 Calculated PES for reaction of the phenyl nitrile oxide with dinitrogen oxide. B3LYP-D3(BJ)/6-31G electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S196 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	−0.082735	−0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	−1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	−0.505698	0.592333
C	1.800258	−1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	−1.150542	0.096505	0.259821
H	−0.255928	−2.222203	0.354837
H	3.745041	−0.664438	0.685138

H	2.193632	-2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S197 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.079098	-0.397300	-2.709776
C	-1.355028	0.773131	-2.940131
C	-1.437504	-1.538125	-2.211904
C	0.028454	0.807632	-2.670249
C	0.674059	-0.344920	-2.168443
C	-0.062751	-1.507396	-1.943360
H	-1.845506	1.659744	-3.325454
C	0.788748	1.991487	-2.895597
H	-3.143313	-0.419654	-2.918647
H	-2.004830	-2.445588	-2.034163
H	1.738019	-0.309261	-1.964268
H	0.435903	-2.390359	-1.558003
N	1.608352	2.825004	-2.996099
O	2.472042	3.727504	-3.107310
N	5.451224	3.002326	-2.232323
N	4.688772	2.151814	-2.135990
O	3.887528	1.227258	-2.026914

Table S198 Cartesian coordinates of the transition state between pre-intermediate and post-intermediate (TS) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

TS at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.307331	-0.772839	-0.127318
C	-1.563836	0.365142	-0.436608
C	-1.677710	-1.899755	0.417487
C	-0.172087	0.383796	-0.200705
C	0.456259	-0.748715	0.345419
C	-0.297994	-1.882981	0.651197
H	-2.049202	1.239146	-0.857825
C	0.591548	1.566829	-0.525242
H	-3.376376	-0.780790	-0.310585
H	-2.259205	-2.783533	0.657326
H	1.521570	-0.733601	0.523370
H	0.193246	-2.753521	1.072041
N	0.440572	2.666581	-1.002424
O	0.480834	3.812428	-1.457092
N	4.054355	-0.070478	0.956275
N	3.605074	0.838641	0.441796
O	2.360285	1.553654	-0.147111

Table S199 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

17

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-1.621716	-0.456276	-2.645605
C	-0.954314	0.748049	-2.874724
C	-0.922884	-1.563637	-2.150000
C	0.427513	0.844668	-2.603973
C	1.126941	-0.275041	-2.104357
C	0.451665	-1.471353	-1.880046
H	-1.485018	1.609575	-3.256899
C	1.164153	2.085124	-2.829800
H	-2.683537	-0.531917	-2.852811
H	-1.445970	-2.497965	-1.973411
H	2.187806	-0.184378	-1.901643
H	0.988443	-2.332225	-1.496496
N	0.262032	3.231820	-3.397690
O	0.906040	4.260154	-3.612059
N	5.325894	1.286783	-1.665286
N	4.560523	0.476508	-1.582987
O	2.360545	2.292240	-2.620898

Table S200 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

15

Product ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.968972	3.352383	-1.271888
C	-1.973488	4.311674	-1.468619
C	-2.639411	2.090927	-0.761950
C	-0.633996	4.003255	-1.151330
C	-0.308659	2.730320	-0.637163
C	-1.307524	1.780673	-0.444043
H	-2.218076	5.289496	-1.861318
C	0.443940	4.970880	-1.343698
H	-3.999314	3.587613	-1.515207
H	-3.416837	1.348957	-0.610916
H	0.726972	2.514295	-0.399602
H	-1.057398	0.802245	-0.048549
N	-0.060013	6.334398	-1.923981
O	0.867321	7.121642	-2.120438
O	1.639793	4.809111	-1.098226

Table S201 Cartesian coordinates of the dinitrogen oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

3

Dinitrogen oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

N	-0.991536	0.000000	-3.429367
N	-0.949554	0.000000	-2.280754
O	-0.904662	0.000000	-1.055420

Table S202 Cartesian coordinates of the nitrogen equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

2

Nitrogen ES at B3LYP-D3(BJ)/6-31G in the gas phase

N	-0.990306	0.000000	-3.395195
N	-0.949389	0.000000	-2.277398

2.6 The O₃-catalyzed conversion

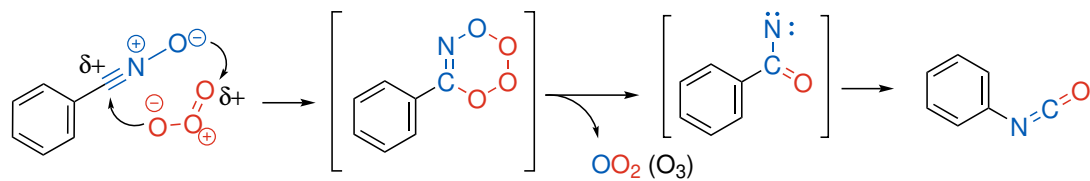


Figure S40 Reaction of the phenyl nitrile sulfide with ozone.

2.6.1 r²SCAN-3c

Table S203 Energy profile of the O₃-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

		R	A	TS1	B	TS2	C	TS3	D	P
Benzene	<i>E</i> , kcal/mol	0.0	−2.6	0.8	−45.0	31.8	15.0	27.8	−61.3	−57.6
	<i>E</i> + ΔZPE, kcal/mol	0.0	−2.0	1.2	−43.8	31.9	15.1	26.7	−60.1	−57.1
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.2	12.6	−32.4	43.9	25.6	37.7	−49.3	−56.9

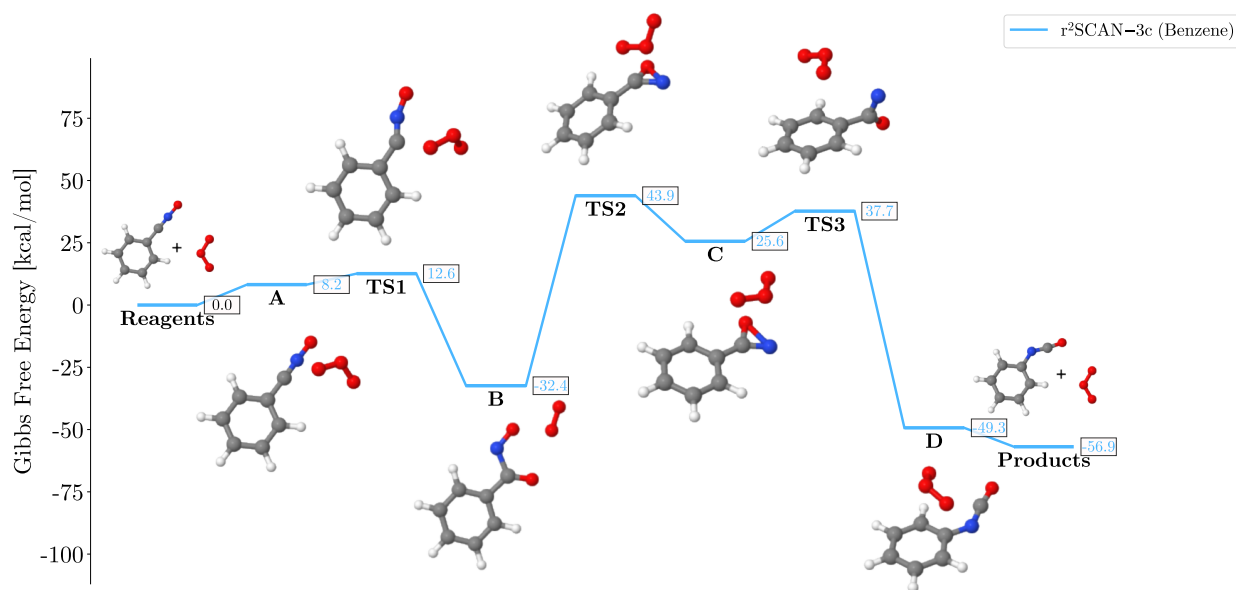


Figure S41 Calculated PES for reaction of the phenyl nitrile oxide with ozone. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

Table S204 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the benzene

C	−0.070011	−0.064477	0.353451
C	0.790463	1.022328	0.417736
C	0.430226	−1.364123	0.407122
C	2.174624	0.809409	0.537228
C	2.677066	−0.502349	0.591715
C	1.802309	−1.577563	0.526116
H	0.406907	2.036617	0.376609
C	3.061424	1.912690	0.602594
H	−1.138734	0.104487	0.260883
H	−0.248747	−2.210021	0.356343
H	3.746414	−0.661821	0.684516

H	2.194673	-2.589276	0.568175
N	3.800741	2.809808	0.648216
O	4.568944	3.742590	0.695297

Table S205 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

A ES at r2SCAN-3c in the benzene

C	0.015007	0.221833	0.164588
C	0.824106	1.313187	-0.115075
C	0.581902	-1.009568	0.489431
C	2.221364	1.165925	-0.076670
C	2.793479	-0.074298	0.254527
C	1.967984	-1.152876	0.534680
H	0.392441	2.276624	-0.365787
C	3.060169	2.269033	-0.359277
H	-1.064483	0.333557	0.131995
H	-0.057862	-1.858711	0.710305
H	3.873534	-0.170248	0.293868
H	2.408723	-2.111117	0.792333
N	3.700607	3.178777	-0.708346
O	4.417352	4.110411	-0.977556
O	4.664489	2.620920	1.793137
O	5.774326	2.959850	1.263261
O	6.435462	2.043202	0.671987

Table S206 Cartesian coordinates of the transition state between pre-intermediate and post-intermediate (TS1) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS1 at r2SCAN-3c in the benzene

C	-2.357635	-0.617570	-0.154955
C	-1.460531	0.395679	-0.456283
C	-1.921693	-1.774821	0.489405
C	-0.106250	0.243459	-0.115527
C	0.334738	-0.918301	0.530742
C	-0.579211	-1.920248	0.829860
H	-1.792777	1.303511	-0.950223
C	0.822617	1.284156	-0.444519
H	-3.404355	-0.501305	-0.419420
H	-2.630392	-2.562839	0.726063
H	1.382854	-1.023979	0.786346
H	-0.238222	-2.821871	1.329483
N	1.008947	2.196186	-1.205687
O	1.575296	3.130764	-1.704582
O	2.184463	1.393140	0.860883
O	3.370539	1.590788	0.296978
O	3.811612	0.603250	-0.398563

Table S207 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

B ES at r2SCAN-3c in the benzene

C	0.053767	0.155176	-0.070104
C	1.174006	0.952206	-0.262798
C	0.172715	-1.076708	0.569934
C	2.427195	0.512088	0.190505
C	2.542343	-0.728785	0.835015
C	1.418337	-1.516705	1.021721
H	1.079939	1.910785	-0.761362
C	3.647059	1.307206	0.015978
H	-0.915832	0.495519	-0.420310
H	-0.706659	-1.696926	0.718086
H	3.518269	-1.055548	1.179942
H	1.507874	-2.477152	1.520162
N	3.396777	2.572745	-0.680027
O	4.332335	3.316396	-0.895875
O	4.769908	1.018467	0.376642
O	6.183637	3.062020	-0.425339
O	6.772730	4.046215	-0.841467

Table S208 Cartesian coordinates of the transition state between intermediate and intermediate (TS2) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS2 at r2SCAN-3c in the benzene

C	-2.061632	-0.625611	-0.646289
C	-1.097786	0.373086	-0.624020
C	-1.943594	-1.727641	0.199440
C	-0.016779	0.254835	0.253746
C	0.110528	-0.847472	1.102379
C	-0.862362	-1.837237	1.073301
H	-1.178694	1.241643	-1.271361
C	0.979046	1.304601	0.294318
H	-2.908007	-0.544566	-1.321191
H	-2.701188	-2.505614	0.179656
H	0.960766	-0.919003	1.774707
H	-0.778773	-2.696371	1.731551
N	1.070849	2.618602	0.151926
O	1.742992	1.777231	1.277665
O	2.441144	0.581828	-0.691347
O	2.539534	1.664882	-1.533525
O	3.703956	1.886807	-1.950955

Table S209 Cartesian coordinates of the intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

C ES at r2SCAN-3c in the benzene

C	0.119327	-2.190854	0.609233
C	0.215594	-1.375841	-0.507080
C	-0.543219	-1.734777	1.750425
C	-0.360351	-0.099485	-0.469478

C	-1.023541	0.363511	0.672458
C	-1.112180	-0.462504	1.783355
H	0.731636	-1.711599	-1.402204
C	-0.254145	0.771616	-1.603859
H	0.561072	-3.182235	0.596813
H	-0.614231	-2.377792	2.622976
H	-1.454173	1.360659	0.678248
H	-1.622060	-0.116036	2.676633
N	0.229748	0.884818	-2.769321
O	-0.668491	2.005845	-1.822080
O	1.972717	1.961317	-0.046250
O	2.184422	2.402738	-1.228987
O	1.637875	3.500618	-1.540883

Table S210 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS3) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

TS3 at r²SCAN-3c in the benzene

C	0.164374	-1.908577	0.561141
C	0.133798	-1.320251	-0.688636
C	-0.356279	-1.224518	1.666867
C	-0.453704	-0.048836	-0.832723
C	-0.940599	0.657182	0.288507
C	-0.910341	0.049669	1.531706
H	0.538529	-1.823715	-1.561157
C	-0.581591	0.558201	-2.183121
H	0.597870	-2.895440	0.689302
H	-0.315249	-1.688241	2.648327
H	-1.362137	1.648988	0.154868
H	-1.298736	0.569949	2.401450
N	0.503259	1.164488	-2.466972
O	-1.563950	0.551915	-2.975411
O	2.294242	1.089687	-0.408558
O	2.088163	2.258343	0.037870
O	1.462352	2.361157	1.136540

Table S211 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

17

C ES at r²SCAN-3c in the benzene

C	2.229814	-0.561318	0.321349
C	2.149582	0.007561	-0.939133
C	1.631102	0.063115	1.415597
C	1.457966	1.219146	-1.110206
C	0.835703	1.840041	-0.012054
C	0.932499	1.257573	1.242278
H	2.617811	-0.457089	-1.800628
C	1.088380	2.834015	-2.850015
H	2.770771	-1.493185	0.454230
H	1.699615	-0.386079	2.401681

H	0.274317	2.757284	-0.161218
H	0.455961	1.738225	2.091407
N	1.376521	1.751234	-2.390109
O	0.833744	3.814091	-3.433691
O	4.050039	2.162482	-0.813971
O	3.784239	2.993984	0.116984
O	2.832575	3.819890	-0.109970

Table S212 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at r2SCAN-3c in the benzene

C	1.803887	-0.429972	0.365559
C	2.885572	0.376270	0.029182
C	1.991774	-1.778532	0.656905
C	4.166973	-0.174601	-0.015655
C	4.364734	-1.528186	0.275871
C	3.274615	-2.321533	0.610396
H	2.750503	1.428595	-0.199560
C	6.426998	0.559017	-0.497533
H	0.807741	0.001398	0.399657
H	1.144299	-2.404447	0.919050
H	5.366178	-1.948342	0.238437
H	3.430633	-3.372559	0.836012
N	5.233036	0.665626	-0.359073
O	7.586657	0.597866	-0.668250

Table S213 Cartesian coordinates of the ozone equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the benzene, which was treated with CPCM continuum solvent model.

3

Ozone ES at r2SCAN-3c in the benzene

O	0.000000	0.000000	0.311840
O	0.000000	1.084427	-0.337504
O	0.000000	-1.084427	-0.337504

2.7 The C₃H₆O-catalyzed conversion

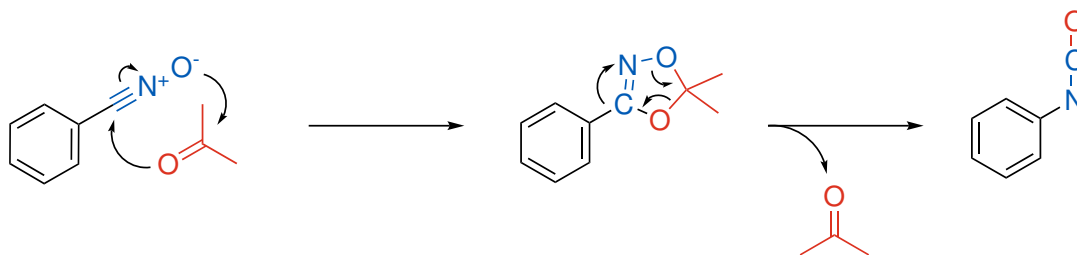


Figure S42 Reaction of the phenyl nitrile oxide with C₃H₆O.

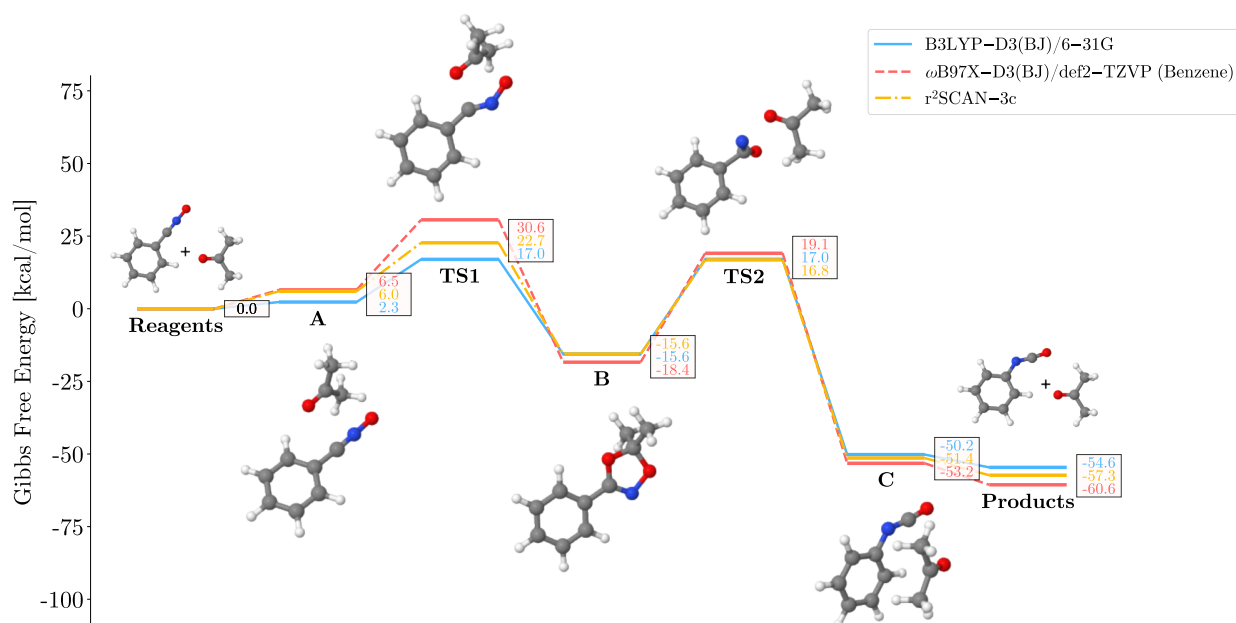


Figure S43 Calculated PES for reaction of the phenyl nitrile sulfide with C₃H₆O. Electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

2.7.1 r²SCAN-3c

Table S214 Energy profile of the C₃H₆O-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−6.6	8.7	−33.8	3.4	−64.3	−58.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−5.8	9.8	−29.8	4.0	−63.0	−57.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.0	22.7	−15.6	16.8	−51.4	−57.3

Table S215 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021
H	−0.248893	−2.210375	0.356466
H	3.744529	−0.661291	0.684203
H	2.194048	−2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

Table S216 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

24

A ES at r2SCAN-3c in the gas phase

N	1.020954	0.965301	1.174800
C	1.445534	0.182829	0.426395
O	−1.805015	0.357746	0.103373
C	−2.179361	1.202781	0.896074
O	0.599153	1.782482	1.960738
C	1.761185	−0.798579	−0.546524
C	−2.527862	0.855302	2.322981
C	−2.330422	2.651561	0.501120
C	0.731113	−1.374570	−1.310608
C	1.044546	−2.334913	−2.261492
C	2.365495	−2.729874	−2.462802
C	3.385360	−2.158744	−1.705353
C	3.092341	−1.196776	−0.749599
H	−2.101159	1.587241	3.015414
H	−3.618804	0.888953	2.439577
H	−2.172524	−0.147361	2.565481

H	-1.525092	3.221980	0.979046
H	-2.256892	2.760659	-0.582090
H	-3.278670	3.062530	0.865042
H	-0.292117	-1.056495	-1.141613
H	0.248129	-2.779213	-2.851198
H	2.600199	-3.482486	-3.209578
H	4.415858	-2.464372	-1.859686
H	3.881276	-0.747219	-0.155405

Table S217 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase.

24

TS1 at r2SCAN-3c in the gas phase

N	0.968658	0.985416	1.211938
C	0.667912	0.216105	0.331042
O	-1.248205	0.739400	0.116569
C	-1.593422	1.480859	1.076349
O	0.395467	1.842684	1.911013
C	1.103101	-0.777654	-0.586294
C	-2.122407	0.858161	2.341659
C	-1.901049	2.930878	0.809718
C	0.175534	-1.420831	-1.418221
C	0.613487	-2.388890	-2.311410
C	1.961458	-2.727469	-2.385493
C	2.882597	-2.087832	-1.557343
C	2.466714	-1.115955	-0.661530
H	-2.020301	1.526745	3.199206
H	-3.189224	0.637102	2.199739
H	-1.605722	-0.083865	2.540618
H	-1.279835	3.301266	-0.007749
H	-2.954418	3.013410	0.508893
H	-1.753035	3.545601	1.700350
H	-0.870069	-1.146223	-1.350425
H	-0.107370	-2.883653	-2.955472
H	2.295798	-3.486331	-3.086273
H	3.935923	-2.346777	-1.611199
H	3.178404	-0.612147	-0.015684

Table S218 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

24

B ES at r2SCAN-3c in the gas phase

N	1.136189	0.943115	1.127089
C	0.411272	0.181296	0.386837
O	-0.933711	0.268626	0.582761
C	-1.099092	1.420795	1.450868
O	0.236118	1.634297	1.970500
C	0.916891	-0.760392	-0.600552
C	-2.030398	1.079530	2.588492
C	-1.526087	2.612601	0.615033

C	0.025720	-1.487153	-1.397069
C	0.513116	-2.390001	-2.335298
C	1.883400	-2.570852	-2.488643
C	2.772395	-1.845123	-1.695215
C	2.297888	-0.945953	-0.753795
H	-2.070735	1.918406	3.288464
H	-3.038248	0.891147	2.207807
H	-1.667359	0.193065	3.113197
H	-1.598968	3.500171	1.249586
H	-0.785680	2.798482	-0.168145
H	-2.499118	2.423012	0.152173
H	-1.042378	-1.341598	-1.276715
H	-0.182620	-2.953296	-2.950119
H	2.261229	-3.276000	-3.223116
H	3.842992	-1.985530	-1.811318
H	2.981842	-0.380928	-0.128923

Table S219 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase.

24

TS2 at r2SCAN-3c in the gas phase

N	0.670178	0.650614	0.475168
C	0.081046	-0.495451	0.463156
O	-0.803531	-1.149578	1.011787
C	-1.237341	1.865635	1.963591
O	-0.053970	1.521702	2.004978
C	0.916747	-1.010900	-0.755294
C	-1.831355	2.495518	3.186752
C	-2.104242	1.668216	0.769558
C	0.334795	-0.997393	-2.022997
C	0.965240	-1.656006	-3.070444
C	2.180115	-2.305803	-2.855657
C	2.767231	-2.296327	-1.592485
C	2.142932	-1.636873	-0.540071
H	-2.157818	3.513826	2.944366
H	-2.727559	1.934607	3.476655
H	-1.113822	2.514613	4.007216
H	-3.004056	2.284895	0.812569
H	-1.528225	1.854802	-0.140774
H	-2.383890	0.604367	0.757671
H	-0.612212	-0.487964	-2.175288
H	0.514170	-1.658346	-4.058552
H	2.674183	-2.813972	-3.678745
H	3.718664	-2.794528	-1.430626
H	2.592721	-1.605655	0.447467

Table S220 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

24

C ES at r2SCAN-3c in the gas phase

N	2.360418	0.700499	0.640960
C	2.626054	0.981013	1.789878
O	2.990249	1.362212	2.832457
C	-0.862546	1.470721	1.321283
O	-0.335350	1.142510	2.366562
C	1.576741	-0.271925	0.017221
C	-1.960733	0.649958	0.687886
C	-0.439258	2.712405	0.571396
C	0.998332	-1.328488	0.729603
C	0.226975	-2.267000	0.058482
C	0.019916	-2.164246	-1.315958
C	0.597851	-1.111732	-2.020089
C	1.376847	-0.167171	-1.361305
H	-2.810834	1.281988	0.407810
H	-1.577131	0.197375	-0.235920
H	-2.281124	-0.142012	1.366401
H	-1.284117	3.407091	0.494477
H	0.393785	3.199068	1.080701
H	-0.149063	2.447999	-0.452430
H	1.141291	-1.392217	1.804058
H	-0.221827	-3.083223	0.617208
H	-0.585878	-2.901381	-1.833707
H	0.446448	-1.024895	-3.092088
H	1.839455	0.653526	-1.900549

Table S221 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

14

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117
C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671
H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

Table S222 Cartesian coordinates of the C₃H₆O equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

10

C3H6O ES at r2SCAN-3c in the gas phase

O	-0.881033	0.630560	0.511027
C	-1.607177	1.374165	1.136669

C	-2.280855	0.940799	2.420976
C	-1.890728	2.788544	0.678217
H	-1.980795	1.599802	3.244275
H	-3.369233	1.032237	2.325793
H	-2.014937	-0.090420	2.657079
H	-1.359837	2.997479	-0.251505
H	-2.968110	2.928386	0.530787
H	-1.583666	3.503774	1.450382

2.7.2 B3LYP-D3(BJ)/6-31G

Table S223 Energy profile of the C₃H₆O-catalyzed conversion. The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−10.7	2.8	−33.1	4.4	−62.9	−55.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−9.8	4.0	−29.4	4.5	−61.6	−54.7
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	2.3	17.0	−15.6	17.0	−50.2	−54.6

Table S224 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	−0.082735	−0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	−1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	−0.505698	0.592333
C	1.800258	−1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	−1.150542	0.096505	0.259821
H	−0.255928	−2.222203	0.354837
H	3.745041	−0.664438	0.685138
H	2.193632	−2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S225 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

24

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

N	1.019606	1.089690	1.243112
C	1.402093	0.288041	0.478936
O	−1.863943	0.287733	−0.112219
C	−2.179658	1.119303	0.760209
O	0.612522	1.954622	2.066199
C	1.706740	−0.716060	−0.485041
C	−2.454330	0.701225	2.184888
C	−2.246717	2.595331	0.449120
C	0.656871	−1.340932	−1.194982
C	0.960452	−2.325482	−2.136206
C	2.289944	−2.694159	−2.378548
C	3.329760	−2.073008	−1.674771
C	3.045935	−1.086896	−0.729938
H	−1.657696	1.101046	2.824511
H	−3.406428	1.111592	2.541096
H	−2.468627	−0.387947	2.260471

H	-1.419820	3.096662	0.967881
H	-2.150003	2.756839	-0.626353
H	-3.183188	3.035829	0.810290
H	-0.365791	-1.040147	-0.996958
H	0.155466	-2.805470	-2.682618
H	2.515407	-3.460889	-3.112526
H	4.359909	-2.356964	-1.861897
H	3.844721	-0.601198	-0.180565

Table S226 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

24			
TS1 at B3LYP-D3(BJ)/6-31G in the gas phase			
N	0.981295	0.970585	1.276728
C	0.732698	0.192542	0.383587
O	-1.268215	0.510308	0.294900
C	-1.620533	1.400344	1.161611
O	0.324479	1.796706	2.025145
C	1.153046	-0.776288	-0.577811
C	-2.241121	0.952884	2.463922
C	-1.845890	2.821372	0.702220
C	0.198671	-1.390556	-1.411769
C	0.613924	-2.336943	-2.349250
C	1.967144	-2.677308	-2.464672
C	2.915414	-2.065313	-1.634237
C	2.518612	-1.117357	-0.692041
H	-2.085671	1.691256	3.253397
H	-3.323301	0.817023	2.323665
H	-1.813100	-0.004227	2.769918
H	-1.165832	3.058490	-0.118960
H	-2.877391	2.925445	0.335747
H	-1.695317	3.532434	1.517281
H	-0.840724	-1.111657	-1.305047
H	-0.121434	-2.809800	-2.991557
H	2.282202	-3.414111	-3.196046
H	3.964752	-2.326597	-1.720816
H	3.246291	-0.639232	-0.045915

Table S227 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

24			
B ES at B3LYP-D3(BJ)/6-31G in the gas phase			
N	1.186454	0.944404	1.126271
C	0.448956	0.202799	0.355806
O	-0.928941	0.355928	0.490200
C	-1.130685	1.487170	1.436039
O	0.246232	1.728486	1.954299
C	0.942449	-0.766068	-0.612742
C	-2.017017	1.035333	2.574500
C	-1.597681	2.700007	0.655659

C	0.037223	-1.486893	-1.409823
C	0.514040	-2.415031	-2.338666
C	1.889999	-2.627284	-2.479335
C	2.793442	-1.907331	-1.684897
C	2.326405	-0.980862	-0.753950
H	-2.096791	1.832628	3.319141
H	-3.017789	0.794009	2.203709
H	-1.584823	0.150802	3.047365
H	-1.682747	3.561081	1.324923
H	-0.872917	2.935795	-0.127981
H	-2.571498	2.505286	0.196144
H	-1.025639	-1.313799	-1.293696
H	-0.187777	-2.970592	-2.951873
H	2.257918	-3.348118	-3.202225
H	3.860642	-2.070314	-1.791904
H	3.015203	-0.419717	-0.133064

Table S228 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

24

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

N	0.695576	0.541752	0.380602
C	0.041615	-0.576695	0.388417
O	-0.888422	-1.232118	0.897695
C	-1.316044	1.926483	2.057752
O	-0.113109	1.576216	2.039226
C	0.976091	-1.030804	-0.839620
C	-1.835043	2.720026	3.228734
C	-2.268274	1.560648	0.957397
C	0.469467	-0.926722	-2.143146
C	1.115692	-1.599192	-3.182614
C	2.271464	-2.348840	-2.919477
C	2.786875	-2.426142	-1.618266
C	2.146517	-1.754849	-0.573306
H	-2.227583	3.684859	2.882979
H	-2.668734	2.183860	3.699945
H	-1.042803	2.884953	3.960221
H	-3.242585	2.038698	1.073292
H	-1.830225	1.829858	-0.009897
H	-2.379694	0.466793	0.959585
H	-0.420238	-0.335878	-2.329179
H	0.727920	-1.533989	-4.193673
H	2.775473	-2.864299	-3.730623
H	3.688078	-2.997412	-1.422887
H	2.537986	-1.787207	0.436844

Table S229 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

24

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

N	2.487921	0.580506	0.805201
C	2.758254	1.006140	1.903979
O	3.150792	1.519408	2.914455
C	-0.910990	1.415560	1.370173
O	-0.165293	1.238642	2.350145
C	1.697682	-0.274426	0.044032
C	-2.218269	0.668851	1.231358
C	-0.536136	2.354280	0.246370
C	0.845063	-1.218251	0.645572
C	0.050588	-2.041108	-0.155706
C	0.096828	-1.934767	-1.551881
C	0.952463	-0.998630	-2.145785
C	1.753684	-0.171099	-1.355121
H	-3.048669	1.361007	1.048093
H	-2.161011	-0.011410	0.371565
H	-2.414026	0.088238	2.134774
H	-1.320446	3.104124	0.086796
H	0.408078	2.851732	0.473265
H	-0.427332	1.788299	-0.687401
H	0.795319	-1.275959	1.726193
H	-0.605139	-2.766461	0.314920
H	-0.522472	-2.576720	-2.169137
H	0.998861	-0.912984	-3.226423
H	2.420751	0.557102	-1.801098

Table S230 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235
H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

Table S231 Cartesian coordinates of the C₃H₆O equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

10

C₃H₆O ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.411267	2.005258	-0.521333
O	-2.411262	2.005258	-1.762783

C	-2.411262	3.295607	0.272220
C	-2.411262	0.714909	0.272220
H	-2.411260	4.149985	-0.406957
H	-2.411259	-0.139468	-0.406958
H	-1.528940	3.346220	0.923137
H	-3.293583	3.346226	0.923138
H	-3.293584	0.664291	0.923137
H	-1.528941	0.664297	0.923138

2.7.3 ω B97X-D3(BJ)/def2-TZVP

Table S232 Energy profile of the C₃H₆O-catalyzed conversion. The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Benzene	<i>E</i> , kcal/mol	0.0	−5.0	16.4	−36.6	6.4	−66.2	−60.8
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−4.5	17.5	−32.6	6.4	−65.1	−60.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.5	30.6	−18.4	19.1	−53.2	−60.6

Table S233 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	−0.067240	−0.063982	0.353909
C	0.797006	1.018735	0.417913
C	0.431386	−1.361016	0.407597
C	2.170887	0.797533	0.536479
C	2.674086	−0.504119	0.590930
C	1.799752	−1.578707	0.525912
H	0.417864	2.033014	0.376538
C	3.071455	1.915930	0.602265
H	−1.133940	0.106124	0.261623
H	−0.248356	−2.204390	0.357279
H	3.741831	−0.663912	0.683323
H	2.188598	−2.589810	0.568143
N	3.795700	2.809513	0.647480
O	4.557272	3.753387	0.696608

Table S234 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

24

A ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	1.046782	0.941236	1.229751
C	1.384634	0.164441	0.453062
O	−1.791455	0.427533	0.015493
C	−2.168297	1.234824	0.841620
O	0.677672	1.763752	2.049216
C	1.725012	−0.821955	−0.535214
C	−2.584143	0.815063	2.228555
C	−2.245689	2.708408	0.531995
C	0.702325	−1.507811	−1.194700
C	1.029939	−2.460786	−2.147796
C	2.362127	−2.728858	−2.443479
C	3.376573	−2.042563	−1.784516
C	3.063796	−1.087633	−0.828805

H	-1.995072	1.365130	2.966064
H	-3.635704	1.071549	2.387394
H	-2.439500	-0.256693	2.358388
H	-1.544766	3.241170	1.179673
H	-1.994805	2.889651	-0.512337
H	-3.248999	3.084525	0.749961
H	-0.329376	-1.283354	-0.952764
H	0.239993	-2.995922	-2.662581
H	2.610896	-3.474928	-3.190160
H	4.415126	-2.251136	-2.015378
H	3.846160	-0.546880	-0.309348

Table S235 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

24

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	0.962480	0.870358	1.306340
C	0.698194	0.138055	0.408074
O	-1.250685	0.546089	0.323685
C	-1.520946	1.427629	1.185922
O	0.338853	1.689841	2.027101
C	1.090722	-0.822982	-0.589138
C	-2.205214	1.012208	2.464847
C	-1.682319	2.859027	0.737142
C	0.128578	-1.593163	-1.240108
C	0.531206	-2.519441	-2.191697
C	1.879205	-2.680966	-2.489034
C	2.835044	-1.909134	-1.836039
C	2.447818	-0.974810	-0.888784
H	-2.061465	1.751757	3.252686
H	-3.278578	0.919992	2.266745
H	-1.827184	0.043194	2.790795
H	-1.538868	3.555406	1.563373
H	-0.974937	3.079123	-0.062582
H	-2.698765	2.984489	0.348432
H	-0.916061	-1.453518	-0.996811
H	-0.214029	-3.119207	-2.701850
H	2.186932	-3.407900	-3.232476
H	3.886834	-2.031490	-2.068804
H	3.183182	-0.364556	-0.377819

Table S236 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

24

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	1.126216	0.938658	1.137830
C	0.411146	0.180679	0.401918
O	-0.922159	0.265575	0.600684
C	-1.092054	1.415774	1.458173

O	0.226981	1.614973	1.985760
C	0.920173	-0.765012	-0.599790
C	-2.046116	1.082905	2.580253
C	-1.506979	2.606091	0.613396
C	0.028896	-1.493509	-1.383855
C	0.512140	-2.392304	-2.327097
C	1.880786	-2.562252	-2.490383
C	2.771096	-1.832115	-1.707085
C	2.295896	-0.936544	-0.762637
H	-2.113877	1.932336	3.262108
H	-3.038451	0.876671	2.175084
H	-1.685538	0.210335	3.125498
H	-1.578201	3.492990	1.245487
H	-0.764270	2.784610	-0.166651
H	-2.477674	2.417485	0.150835
H	-1.037501	-1.355612	-1.253754
H	-0.184098	-2.958978	-2.935320
H	2.256805	-3.263530	-3.227327
H	3.839953	-1.964212	-1.832904
H	2.981487	-0.367295	-0.146323

Table S237 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

24

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	0.658514	0.608395	0.419521
C	0.162626	-0.563186	0.525937
O	-0.597909	-1.270401	1.164556
C	-1.289598	1.880967	1.966029
O	-0.108510	1.558616	1.979301
C	0.982343	-1.022291	-0.746477
C	-1.870580	2.604197	3.144387
C	-2.198812	1.560266	0.819284
C	0.377632	-0.969131	-1.997680
C	0.985039	-1.603528	-3.072581
C	2.192914	-2.270569	-2.891427
C	2.802393	-2.300542	-1.640480
C	2.202206	-1.664176	-0.562697
H	-2.229100	3.584017	2.815712
H	-2.739525	2.048499	3.508198
H	-1.131610	2.716812	3.935523
H	-3.111326	2.154052	0.855473
H	-1.674233	1.706775	-0.124678
H	-2.455009	0.499198	0.899807
H	-0.561405	-0.441115	-2.120738
H	0.520620	-1.573356	-4.051901
H	2.667249	-2.763052	-3.733485
H	3.748919	-2.812570	-1.508282
H	2.667160	-1.667879	0.416696

Table S238 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

24

C ES at ω B97X-D3(BJ)/def2-TZVP in the benzene			
N	2.349924	0.705321	0.649152
C	2.628281	1.001789	1.781776
O	2.983797	1.382804	2.824379
C	-0.881171	1.473264	1.343153
O	-0.414214	1.186898	2.426290
C	1.564404	-0.268756	0.012261
C	-1.958194	0.640809	0.694329
C	-0.406073	2.677305	0.567247
C	0.996014	-1.326541	0.719426
C	0.226291	-2.263872	0.046294
C	0.017834	-2.153519	-1.324605
C	0.586069	-1.094530	-2.022904
C	1.360418	-0.152023	-1.359171
H	-2.818970	1.268875	0.448864
H	-1.574299	0.228528	-0.243646
H	-2.260844	-0.170340	1.354537
H	-1.240283	3.366680	0.408293
H	0.394348	3.183056	1.105248
H	-0.052370	2.363335	-0.418436
H	1.145704	-1.400471	1.790481
H	-0.217762	-3.083864	0.599952
H	-0.584964	-2.889220	-1.844947
H	0.429550	-0.999873	-3.091874
H	1.813010	0.676417	-1.891760

Table S239 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene			
C	1.805533	-0.431675	0.366187
C	2.886072	0.372845	0.029283
C	1.994676	-1.777507	0.657026
C	4.162974	-0.175754	-0.016059
C	4.361971	-1.524004	0.274079
C	3.274996	-2.318660	0.609612
H	2.752390	1.423557	-0.199687
C	6.425013	0.565116	-0.498057
H	0.810496	-0.001884	0.400745
H	1.148873	-2.402861	0.919566
H	5.362002	-1.942504	0.236016
H	3.431464	-3.367863	0.835112
N	5.236122	0.664809	-0.360823
O	7.581018	0.586986	-0.662000

Table S240 Cartesian coordinates of the C₃H₆O equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

10

C3H6O ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.411259	2.005258	-0.526904
O	-2.411268	2.005259	-1.739469
C	-2.411261	3.289041	0.268502
C	-2.411261	0.721476	0.268501
H	-2.411259	4.148362	-0.400564
H	-2.411261	-0.137846	-0.400564
H	-1.531306	3.320465	0.917368
H	-3.291221	3.320464	0.917362
H	-3.291219	0.690053	0.917364
H	-1.531304	0.690052	0.917365

2.8 The C₄H₃F₃O₃-catalyzed conversion

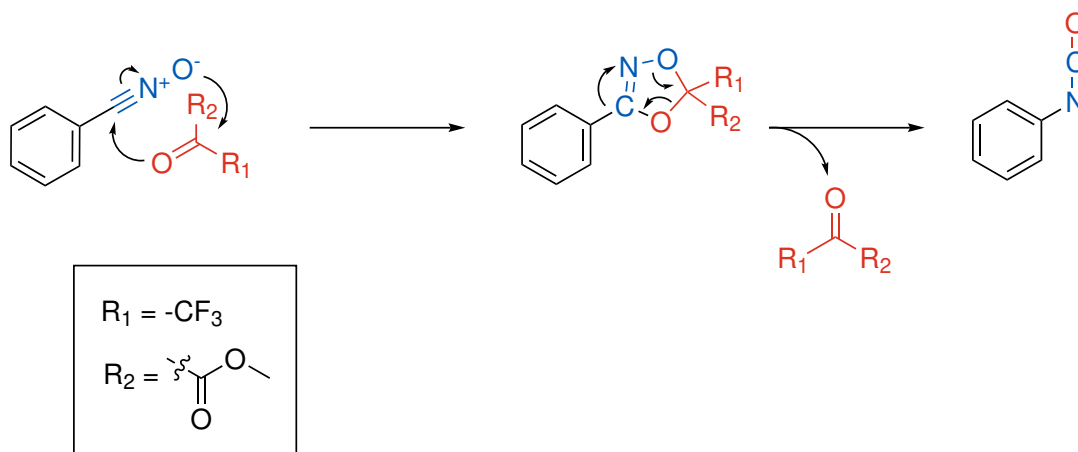


Figure S44 Reaction of the phenyl nitrile oxide with C₄H₃F₃O₃.

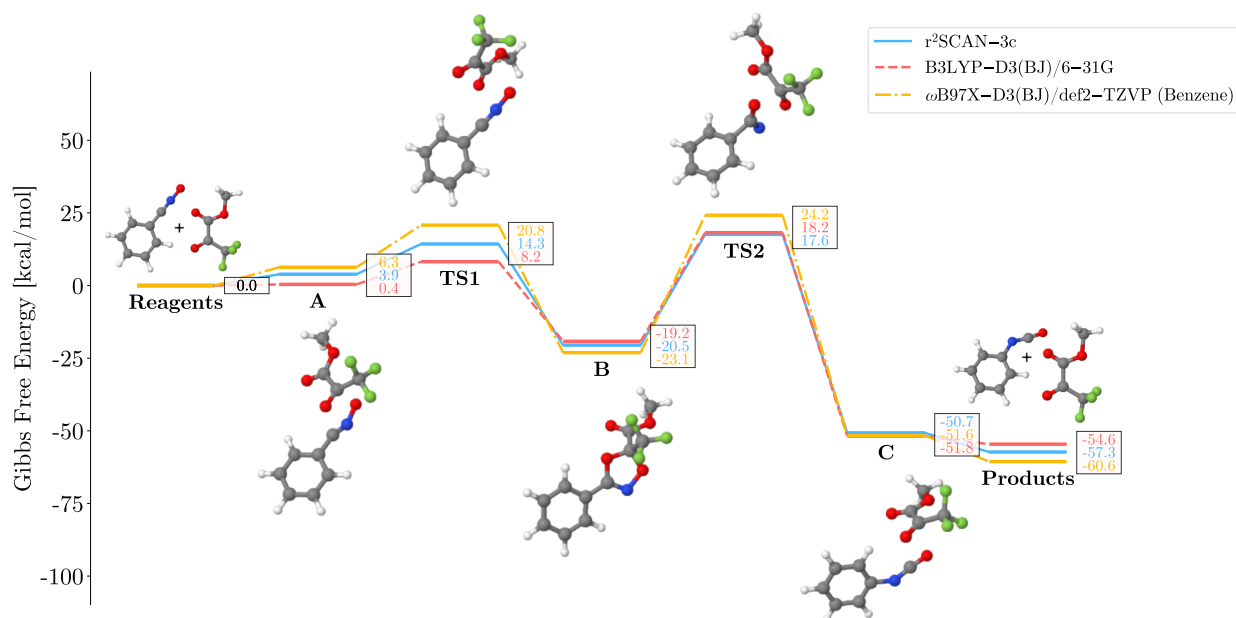


Figure S45 Calculated PES for reaction of the phenyl nitrile sulfide with C₄H₃F₃O₃. Electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

2.8.1 r²SCAN-3c

Table S241 Energy profile of the C₄H₃F₃O₃-catalyzed conversion. The calculations were done at the r²SCAN-3c level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−9.1	−0.2	−37.7	3.5	−64.7	−58.2
	<i>E</i> + ΔZPE, kcal/mol	0.0	−8.4	0.6	−34.7	3.7	−63.6	−57.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	3.9	14.3	−20.5	17.6	−50.7	−57.3

Table S242 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

14

Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021
H	−0.248893	−2.210375	0.356466
H	3.744529	−0.661291	0.684203
H	2.194048	−2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

Table S243 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

27

A ES at r2SCAN-3c in the gas phase

C	1.594957	−0.508832	−0.855779
N	0.884970	−0.021214	−1.634474
O	0.142718	0.527766	−2.423758
C	−1.066140	1.818229	−0.503442
O	−0.181124	1.856182	0.307942
C	2.238497	−1.116121	0.251054
C	1.536687	−1.214377	1.464741
C	2.153838	−1.802294	2.558474
C	3.454976	−2.291310	2.458224
C	4.148194	−2.191304	1.254406
C	3.549048	−1.604960	0.148910
C	−1.373611	3.065836	−1.384222
C	−1.978922	0.580236	−0.588588
O	−1.713739	−0.444270	−0.010352
O	−3.061180	0.810861	−1.330769
C	−3.964856	−0.311654	−1.469605

F	-2.446592	3.696587	-0.844021
F	-1.656292	2.776210	-2.659617
F	-0.338062	3.910830	-1.361077
H	0.525331	-0.824743	1.521125
H	1.614349	-1.878356	3.497748
H	3.929986	-2.749741	3.320330
H	5.162503	-2.570606	1.176555
H	4.082095	-1.520051	-0.792363
H	-4.782996	0.051584	-2.090044
H	-3.446092	-1.144075	-1.951971
H	-4.325460	-0.625878	-0.486753

Table S244 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase.

27

TS1 at r2SCAN-3c in the gas phase

C	1.029349	-0.439051	-0.248791
N	0.766541	-0.511476	-1.417806
O	-0.016730	0.010912	-2.233343
C	-1.059851	1.144617	-0.849650
O	-0.402824	0.935952	0.187445
C	1.798139	-0.801702	0.884520
C	1.172206	-0.884886	2.136998
C	1.924358	-1.232988	3.248475
C	3.284113	-1.507384	3.121059
C	3.903021	-1.424087	1.875125
C	3.172993	-1.059487	0.754925
C	-0.831264	2.481124	-1.587436
C	-2.340586	0.343572	-1.058655
O	-2.552836	-0.685591	-0.467300
O	-3.158958	0.921608	-1.944657
C	-4.386380	0.202648	-2.204594
F	-1.635722	3.424394	-1.035154
F	-1.091417	2.442279	-2.901447
F	0.440793	2.881674	-1.425409
H	0.112759	-0.666782	2.212692
H	1.445447	-1.294576	4.220727
H	3.865430	-1.783461	3.995622
H	4.963843	-1.633574	1.777940
H	3.645733	-0.977819	-0.218316
H	-4.925131	0.805656	-2.934695
H	-4.159822	-0.788444	-2.606310
H	-4.963207	0.096872	-1.281964

Table S245 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

27

B ES at r2SCAN-3c in the gas phase

C	0.827613	-0.165095	-0.197525
N	1.039743	-0.344627	-1.448770

O	-0.051107	0.267524	-2.125304
C	-0.904783	0.841738	-1.129403
O	-0.322947	0.516048	0.110136
C	1.672720	-0.616698	0.893113
C	1.280455	-0.401625	2.218265
C	2.094853	-0.838862	3.255921
C	3.294083	-1.487137	2.980425
C	3.683375	-1.701089	1.658105
C	2.881035	-1.269755	0.614400
C	-0.904609	2.387250	-1.282573
C	-2.301108	0.182462	-1.226557
O	-2.652149	-0.706522	-0.497082
O	-2.985038	0.687595	-2.252675
C	-4.272301	0.068058	-2.498485
F	-1.825126	2.926955	-0.455616
F	-1.175621	2.766778	-2.535523
F	0.300986	2.877591	-0.947919
H	0.342823	0.100758	2.429344
H	1.788871	-0.672067	4.284165
H	3.927805	-1.826773	3.794300
H	4.619783	-2.206348	1.441998
H	3.176324	-1.429830	-0.417418
H	-4.679652	0.588062	-3.364382
H	-4.138274	-0.996359	-2.706394
H	-4.918151	0.192866	-1.625849

Table S246 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase.

27

TS2 at r2SCAN-3c in the gas phase

C	0.724607	0.130614	0.029274
N	1.641344	0.511660	-0.738897
O	0.239491	1.008081	-2.173416
C	-0.853743	1.048489	-1.580879
O	-0.525813	0.123033	0.121876
C	1.742033	-0.437199	1.040234
C	2.153866	0.367951	2.103925
C	2.887873	-0.211084	3.128502
C	3.227151	-1.562560	3.065351
C	2.839339	-2.345385	1.978257
C	2.107316	-1.781176	0.943719
C	-1.278317	2.379428	-0.900490
C	-1.946847	0.072266	-2.067100
O	-1.692288	-1.033432	-2.461913
O	-3.158111	0.635548	-2.019284
C	-4.241590	-0.202305	-2.487885
F	-2.238335	2.242583	0.024469
F	-1.731939	3.218217	-1.859059
F	-0.216419	2.962737	-0.316020
H	1.888408	1.420056	2.117629
H	3.207871	0.393058	3.971614
H	3.813882	-2.006360	3.864280

H	3.122095	-3.392288	1.930974
H	1.807640	-2.359675	0.075900
H	-5.139087	0.407891	-2.393816
H	-4.069103	-0.489639	-3.528287
H	-4.311318	-1.100509	-1.868956

Table S247 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

27

C ES at r2SCAN-3c in the gas phase

C	1.186318	-0.524070	-1.724440
N	2.102391	-0.832131	-1.011791
O	0.024831	1.862578	-0.143456
C	-0.893824	1.862650	-0.912027
O	0.389337	-0.213250	-2.534336
C	2.348785	-1.183889	0.319358
C	1.338007	-1.132806	1.283360
C	1.633602	-1.494865	2.590817
C	2.918375	-1.902373	2.943250
C	3.917627	-1.944948	1.975576
C	3.639617	-1.586074	0.662252
C	-1.147619	3.084501	-1.844729
C	-1.862219	0.659681	-0.972872
O	-1.783950	-0.256379	-0.194561
O	-2.738554	0.786160	-1.965011
C	-3.643116	-0.333117	-2.136499
F	-2.374342	3.593974	-1.600862
F	-1.074713	2.732138	-3.138184
F	-0.243433	4.039520	-1.614620
H	0.342361	-0.801111	1.003971
H	0.849615	-1.454501	3.341383
H	3.139478	-2.182734	3.968486
H	4.922479	-2.258772	2.242122
H	4.408609	-1.613701	-0.102780
H	-4.267489	-0.070927	-2.989236
H	-3.067713	-1.241199	-2.333548
H	-4.244136	-0.467321	-1.233646

Table S248 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

14

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117
C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671

H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

Table S249 Cartesian coordinates of the C₄H₃F₃O₃ equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

13

C4H3F3O3 ES at r2SCAN-3c in the gas phase

O	0.278899	1.087022	-1.978069
C	-0.882506	1.232465	-1.731417
C	-1.383060	2.508738	-0.988938
C	-1.915893	0.148206	-2.116633
O	-1.591626	-0.977483	-2.383873
O	-3.155345	0.645561	-2.121017
C	-4.194594	-0.292643	-2.497965
F	-2.127901	2.158831	0.079776
F	-2.131768	3.272094	-1.807122
F	-0.348859	3.236108	-0.563069
H	-5.121713	0.277965	-2.470716
H	-3.999047	-0.680043	-3.501047
H	-4.220861	-1.121158	-1.785723

2.8.2 B3LYP-D3(BJ)/6-31G

Table S250 Energy profile of the C₄H₃F₃O₃-catalyzed conversion. The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−13.8	−7.3	−37.2	4.1	−65.5	−55.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−12.9	−6.3	−34.3	4.0	−64.3	−54.7
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	0.4	8.2	−19.2	18.2	−51.8	−54.6

Table S251 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	−0.082735	−0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	−1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	−0.505698	0.592333
C	1.800258	−1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	−1.150542	0.096505	0.259821
H	−0.255928	−2.222203	0.354837
H	3.745041	−0.664438	0.685138
H	2.193632	−2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S252 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

27

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.569824	−0.469744	−0.861973
N	0.891434	0.063289	−1.649928
O	0.100629	0.690911	−2.415927
C	−1.051994	1.805969	−0.473554
O	−0.140619	1.842244	0.354221
C	2.216183	−1.093827	0.241119
C	1.585891	−1.034772	1.503908
C	2.202040	−1.635230	2.601448
C	3.430587	−2.292447	2.453578
C	4.051660	−2.351424	1.199305
C	3.451711	−1.753918	0.090542
C	−1.402118	3.053438	−1.291414
C	−1.917707	0.568436	−0.582325
O	−1.624992	−0.492471	−0.023713
O	−3.030768	0.777123	−1.321902
C	−3.910107	−0.384498	−1.548210

F	-2.519866	3.653464	-0.707752
F	-1.695229	2.811750	-2.613185
F	-0.368079	3.964671	-1.241571
H	0.635009	-0.523544	1.592589
H	1.722924	-1.589558	3.573361
H	3.903091	-2.756280	3.313052
H	5.002746	-2.860271	1.086266
H	3.926410	-1.791586	-0.883408
H	-4.727053	0.003668	-2.150877
H	-3.353715	-1.158864	-2.079834
H	-4.264808	-0.771988	-0.591140

Table S253 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

27

TS1 at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.083813	-0.433437	-0.296894
N	0.785590	-0.497281	-1.464149
O	-0.058210	0.068077	-2.269833
C	-1.047589	1.163764	-0.857343
O	-0.341788	0.945550	0.185103
C	1.832943	-0.795960	0.857871
C	1.176938	-0.853067	2.104328
C	1.900535	-1.216582	3.239380
C	3.263347	-1.526079	3.139609
C	3.913218	-1.465888	1.899398
C	3.208144	-1.094724	0.755556
C	-0.860358	2.492066	-1.577231
C	-2.314417	0.365212	-1.018430
O	-2.528643	-0.672779	-0.389611
O	-3.165624	0.911387	-1.924739
C	-4.404801	0.166307	-2.203184
F	-1.690736	3.454096	-1.000093
F	-1.142202	2.460591	-2.925177
F	0.444697	2.930278	-1.429030
H	0.125221	-0.601630	2.154342
H	1.401976	-1.260327	4.201200
H	3.819506	-1.810643	4.026506
H	4.969138	-1.701255	1.825518
H	3.702193	-1.036500	-0.207593
H	-4.930574	0.772681	-2.936486
H	-4.156976	-0.818703	-2.603859
H	-4.985344	0.054844	-1.285160

Table S254 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

27

B ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.877613	-0.192648	-0.211031
N	1.122190	-0.351572	-1.473532

O	-0.030986	0.268522	-2.188952
C	-0.926270	0.821476	-1.165050
O	-0.325556	0.467479	0.094341
C	1.708020	-0.627906	0.896767
C	1.308395	-0.367117	2.218692
C	2.114305	-0.785834	3.279073
C	3.313154	-1.462687	3.027693
C	3.710201	-1.722567	1.708303
C	2.913939	-1.308422	0.642612
C	-0.927965	2.348287	-1.278326
C	-2.280659	0.128885	-1.284839
O	-2.566389	-0.901843	-0.682969
O	-3.065988	0.756400	-2.192844
C	-4.367176	0.130903	-2.497852
F	-1.859445	2.887988	-0.402366
F	-1.215329	2.783655	-2.549865
F	0.319303	2.841403	-0.934090
H	0.377915	0.155534	2.402188
H	1.806138	-0.584371	4.299163
H	3.936585	-1.786490	3.854493
H	4.639213	-2.246936	1.513132
H	3.210922	-1.502905	-0.381486
H	-4.820667	0.790586	-3.233029
H	-4.204377	-0.869413	-2.903262
H	-4.967482	0.070490	-1.588266

Table S255 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

27

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	0.741767	0.194846	0.060726
N	1.687837	0.507522	-0.742987
O	0.261415	1.214415	-2.181550
C	-0.886313	1.208388	-1.659947
O	-0.519073	0.271104	0.184762
C	1.773037	-0.434983	1.053469
C	2.269636	0.355678	2.101174
C	2.983205	-0.265701	3.126834
C	3.218699	-1.647911	3.078450
C	2.747129	-2.419272	2.005716
C	2.033411	-1.811819	0.971620
C	-1.388381	2.479786	-0.966823
C	-1.877533	0.143806	-2.087998
O	-1.546274	-0.983789	-2.445744
O	-3.153412	0.613012	-2.066968
C	-4.212776	-0.327630	-2.472005
F	-2.373474	2.274189	-0.028056
F	-1.894639	3.349775	-1.929437
F	-0.334034	3.124121	-0.339186
H	2.086829	1.423578	2.105049
H	3.364414	0.323663	3.952914
H	3.784203	-2.123429	3.872794

H	2.947279	-3.484097	1.970555
H	1.673034	-2.380035	0.122328
H	-5.131207	0.250917	-2.413113
H	-4.024767	-0.680430	-3.488029
H	-4.230009	-1.175705	-1.784548

Table S256 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G-3c level of theory in the gas phase.

27

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.243615	-0.293123	-1.718559
N	1.956889	-0.816120	-0.914203
O	-0.113319	1.970182	-0.052386
C	-0.946532	1.858493	-0.946205
O	0.583671	0.221937	-2.594650
C	2.284005	-1.172743	0.395127
C	1.434683	-0.821768	1.457974
C	1.793141	-1.181107	2.758301
C	2.979708	-1.884100	3.002617
C	3.815332	-2.231917	1.934714
C	3.472448	-1.878216	0.627682
C	-1.160117	2.989750	-1.958135
C	-1.803267	0.609160	-1.041790
O	-1.576782	-0.399788	-0.371399
O	-2.820771	0.757556	-1.916900
C	-3.691227	-0.413580	-2.142694
F	-2.385082	3.600862	-1.713396
F	-1.149888	2.543262	-3.260801
F	-0.176322	3.945484	-1.821191
H	0.518948	-0.280870	1.253080
H	1.142190	-0.909097	3.582517
H	3.250899	-2.157188	4.016883
H	4.735516	-2.776607	2.117703
H	4.108556	-2.136170	-0.210744
H	-4.422308	-0.073799	-2.871274
H	-3.089926	-1.237600	-2.531165
H	-4.163735	-0.705859	-1.203128

Table S257 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235

H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

Table S258 Cartesian coordinates of the C₄H₃F₃O₃ equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

13

C4H3F3O3 ES at B3LYP-D3(BJ)/6-31G in the gas phase

O	0.334985	1.039913	-1.840694
C	-0.868343	1.213985	-1.690159
C	-1.395775	2.491752	-1.019602
C	-1.869073	0.160585	-2.137468
O	-1.538603	-0.958280	-2.524240
O	-3.141347	0.625822	-2.063195
C	-4.219814	-0.292308	-2.479310
F	-2.159282	2.170393	0.092723
F	-2.174406	3.236923	-1.887748
F	-0.349794	3.284980	-0.603469
H	-5.126787	0.301949	-2.407120
H	-4.038847	-0.630265	-3.501357
H	-4.247188	-1.149787	-1.804175

2.8.3 ω B97X-D3(BJ)/def2-TZVP

Table S259 Energy profile of the $\text{C}_4\text{H}_3\text{F}_3\text{O}_3$ -catalyzed conversion. The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
	E , kcal/mol	0.0	-7.1	6.0	-40.9	9.7	-65.7	-60.8
Benzene	$E + \Delta\text{ZPE}$, kcal/mol	0.0	-6.5	6.6	-37.9	9.7	-65.0	-60.6
	$E + \Delta G$, kcal/mol	0.0	6.3	20.8	-23.1	24.2	-51.6	-60.6

Table S260 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-0.067240	-0.063982	0.353909
C	0.797006	1.018735	0.417913
C	0.431386	-1.361016	0.407597
C	2.170887	0.797533	0.536479
C	2.674086	-0.504119	0.590930
C	1.799752	-1.578707	0.525912
H	0.417864	2.033014	0.376538
C	3.071455	1.915930	0.602265
H	-1.133940	0.106124	0.261623
H	-0.248356	-2.204390	0.357279
H	3.741831	-0.663912	0.683323
H	2.188598	-2.589810	0.568143
N	3.795700	2.809513	0.647480
O	4.557272	3.753387	0.696608

Table S261 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

27

A ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.513331	-0.478665	-0.728803
N	0.874867	0.037158	-1.530446
O	0.162000	0.607504	-2.344706
C	-1.208254	1.824875	-0.426231
O	-0.381154	1.864009	0.433718
C	2.234727	-1.101298	0.345152
C	1.744043	-0.967946	1.645901
C	2.429277	-1.565904	2.692373
C	3.590337	-2.290623	2.444567
C	4.073433	-2.420078	1.146813
C	3.399481	-1.825836	0.090523
C	-1.503532	3.094128	-1.276492
C	-2.064139	0.557357	-0.626284

O	-1.801462	-0.464963	-0.055769
O	-3.077701	0.766675	-1.445971
C	-3.908965	-0.379519	-1.718711
F	-2.647253	3.643284	-0.824503
F	-1.644174	2.852559	-2.577594
F	-0.525126	3.983938	-1.118067
H	0.836569	-0.401419	1.818480
H	2.054462	-1.466053	3.704632
H	4.121470	-2.756805	3.267061
H	4.978496	-2.985472	0.956294
H	3.766224	-1.918135	-0.924917
H	-4.673832	-0.026226	-2.405171
H	-3.306970	-1.164319	-2.176875
H	-4.353069	-0.743686	-0.792300

Table S262 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

27

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.024535	-0.577768	-0.299134
N	0.653811	-0.761734	-1.410957
O	-0.163628	-0.213134	-2.204363
C	-0.877379	1.118737	-1.049261
O	-0.170696	1.053443	-0.025215
C	1.765991	-0.873634	0.888489
C	1.103145	-1.462473	1.968276
C	1.817685	-1.758685	3.117183
C	3.177011	-1.467441	3.184343
C	3.830076	-0.871465	2.110061
C	3.125743	-0.563701	0.957099
C	-0.635340	2.313729	-2.000609
C	-2.272030	0.481662	-0.982732
O	-2.525305	-0.384422	-0.188567
O	-3.112665	0.982027	-1.875984
C	-4.430016	0.399936	-1.888254
F	-1.312348	3.388151	-1.549561
F	-1.014981	2.098199	-3.262945
F	0.664584	2.629414	-2.012291
H	0.043037	-1.674724	1.894292
H	1.316472	-2.218119	3.961099
H	3.732435	-1.704506	4.085266
H	4.887650	-0.643674	2.173674
H	3.614244	-0.093826	0.111866
H	-4.976403	0.935276	-2.660624
H	-4.361815	-0.661792	-2.125930
H	-4.903816	0.530522	-0.915222

Table S263 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

27

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	0.803872	-0.147803	-0.183594
N	1.024593	-0.265508	-1.430636
O	-0.078522	0.333128	-2.085985
C	-0.935267	0.849102	-1.086383
O	-0.361342	0.482330	0.138708
C	1.669596	-0.616360	0.901061
C	1.355143	-0.313041	2.223445
C	2.188658	-0.752100	3.244044
C	3.326637	-1.490289	2.945469
C	3.636753	-1.793634	1.622215
C	2.812391	-1.358263	0.598306
C	-0.954765	2.400178	-1.168111
C	-2.339367	0.211091	-1.215595
O	-2.789344	-0.539745	-0.396900
O	-2.909993	0.577991	-2.349085
C	-4.204549	-0.001684	-2.613680
F	-1.876376	2.891435	-0.325956
F	-1.230084	2.830535	-2.397915
F	0.239080	2.887474	-0.814943
H	0.466540	0.263092	2.450823
H	1.946866	-0.516139	4.274097
H	3.975277	-1.831915	3.744668
H	4.523896	-2.371823	1.389760
H	3.044467	-1.588603	-0.434668
H	-4.503711	0.389748	-3.582316
H	-4.122794	-1.088156	-2.640551
H	-4.908050	0.299857	-1.837577

Table S264 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

27

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	0.685709	0.400648	0.060727
N	1.568358	0.589255	-0.810792
O	0.312576	1.663985	-1.959978
C	-0.825948	1.490302	-1.508759
O	-0.520239	0.662412	0.241592
C	1.634819	-0.383682	0.992442
C	2.296513	0.298693	2.008987
C	2.987489	-0.436951	2.959159
C	3.030044	-1.825799	2.865434
C	2.389475	-2.491328	1.823943
C	1.693522	-1.768372	0.866980
C	-1.572027	2.746290	-0.977534
C	-1.637554	0.273034	-1.996717
O	-1.096764	-0.669906	-2.504976
O	-2.934981	0.407733	-1.780983
C	-3.752079	-0.712951	-2.173759
F	-2.504384	2.497137	-0.059129

F	-2.171457	3.351310	-2.020676
F	-0.693571	3.603355	-0.452878
H	2.257404	1.380749	2.051855
H	3.501137	0.071612	3.766511
H	3.579612	-2.395633	3.606665
H	2.442058	-3.571294	1.751606
H	1.197349	-2.258622	0.037450
H	-4.770934	-0.431786	-1.920331
H	-3.650631	-0.888361	-3.244775
H	-3.445495	-1.601829	-1.622061

Table S265 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

27

C ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.235810	-0.500791	-1.762051
N	2.071386	-0.988879	-1.062611
O	-0.132003	2.154730	-0.062619
C	-1.031137	2.041742	-0.836239
O	0.493207	-0.031766	-2.539888
C	2.331307	-1.274445	0.289644
C	1.482454	-0.816815	1.294332
C	1.773860	-1.121390	2.616502
C	2.899189	-1.872967	2.937621
C	3.740341	-2.321615	1.926151
C	3.460928	-2.023581	0.598883
C	-1.442824	3.234435	-1.746399
C	-1.814548	0.712994	-0.940907
O	-1.660267	-0.162646	-0.135898
O	-2.610515	0.695051	-1.990479
C	-3.329657	-0.536273	-2.213901
F	-2.742127	3.518637	-1.576088
F	-1.230867	2.949856	-3.034928
F	-0.734349	4.315825	-1.433068
H	0.606626	-0.232687	1.037886
H	1.113671	-0.766923	3.400530
H	3.119612	-2.106647	3.973222
H	4.620167	-2.907510	2.168388
H	4.107233	-2.366440	-0.200546
H	-3.919261	-0.367370	-3.110729
H	-2.618167	-1.348814	-2.361032
H	-3.969745	-0.748678	-1.357800

Table S266 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.805533	-0.431675	0.366187
C	2.886072	0.372845	0.029283

C	1.994676	-1.777507	0.657026
C	4.162974	-0.175754	-0.016059
C	4.361971	-1.524004	0.274079
C	3.274996	-2.318660	0.609612
H	2.752390	1.423557	-0.199687
C	6.425013	0.565116	-0.498057
H	0.810496	-0.001884	0.400745
H	1.148873	-2.402861	0.919566
H	5.362002	-1.942504	0.236016
H	3.431464	-3.367863	0.835112
N	5.236122	0.664809	-0.360823
O	7.581018	0.586986	-0.662000

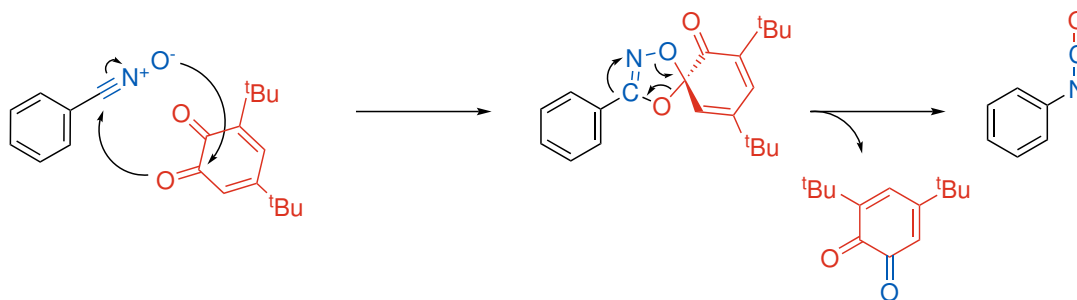
Table S267 Cartesian coordinates of the C₄H₃F₃O₃ equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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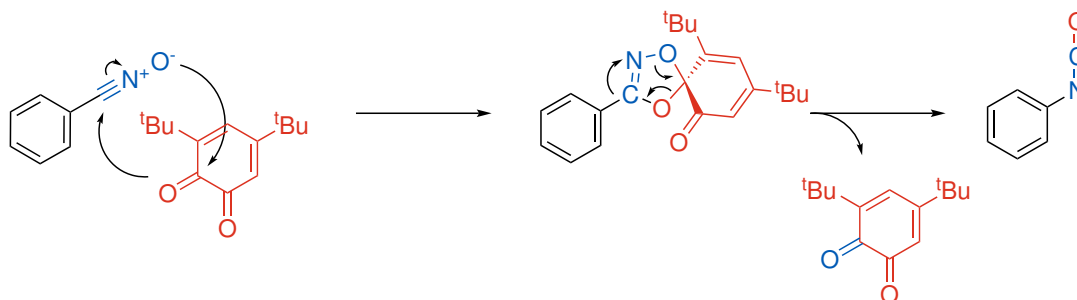
C4H3F3O3 ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

O	0.282518	1.011040	-1.820616
C	-0.883531	1.206201	-1.679131
C	-1.388729	2.517303	-1.010273
C	-1.920296	0.155050	-2.142588
O	-1.579524	-0.926837	-2.526525
O	-3.156230	0.614978	-2.058485
C	-4.192910	-0.297555	-2.479749
F	-2.135513	2.231067	0.065001
F	-2.126370	3.238009	-1.863969
F	-0.358993	3.261539	-0.619419
H	-5.122592	0.256341	-2.382257
H	-4.021498	-0.595906	-3.513808
H	-4.190607	-1.175566	-1.833994

2.9 The C₁₄H₂₀O₂-catalyzed conversion



(a) Reaction of the phenyl nitrile oxide with C₁₄H₂₀O₂.



(b) Reaction of the phenyl nitrile oxide with C₁₄H₂₀O₂.

Figure S46 Two reactions of the phenyl nitrile oxide with C₁₄H₂₀O₂.

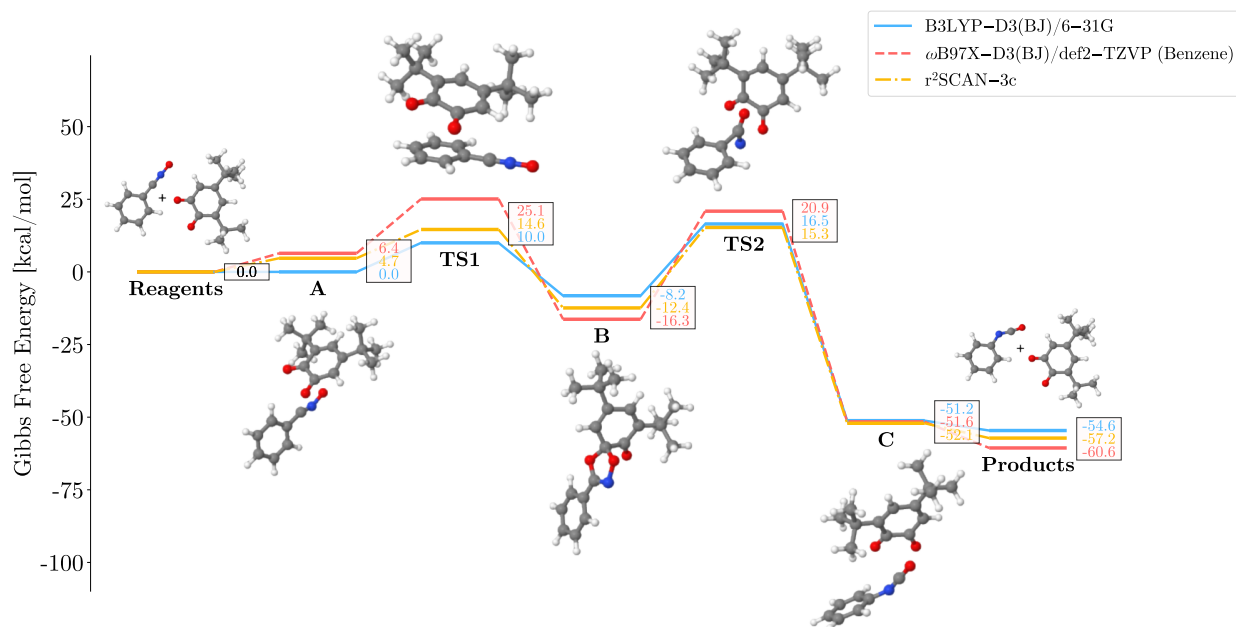


Figure S47 Calculated PES for reaction of the phenyl nitrile sulfide with C₁₄H₂₀O₂ (a). Electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

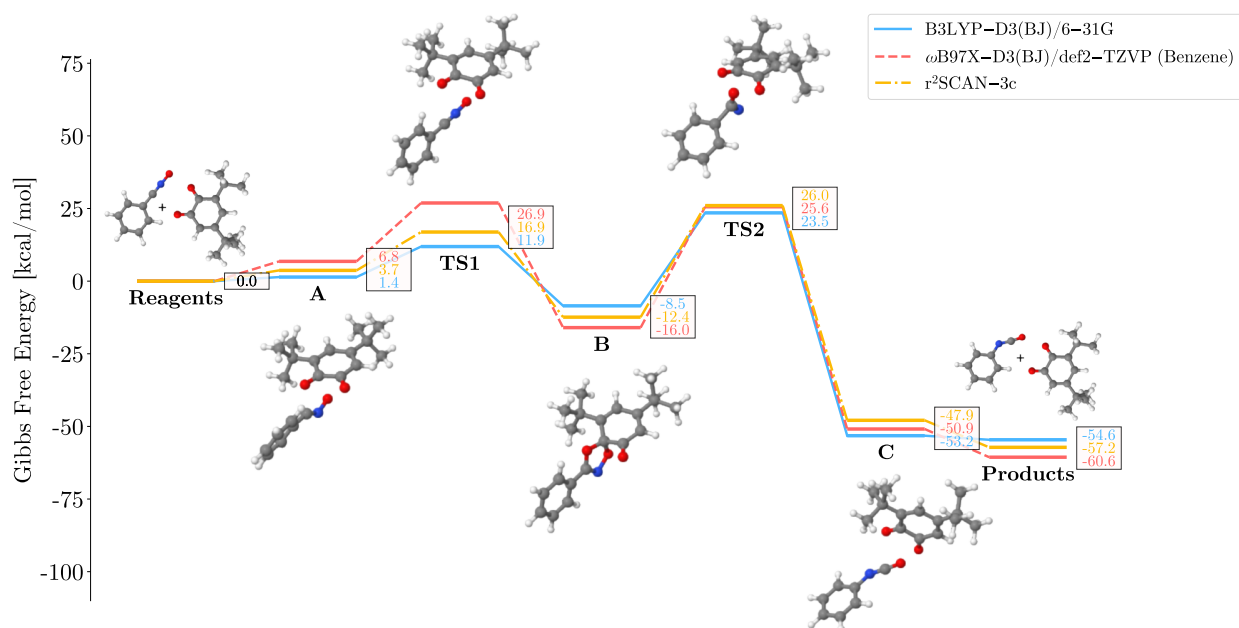


Figure S48 Calculated PES for reaction of the phenyl nitrile sulfide with $C_{14}H_{20}O_2$ (b). Electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

2.9.1 r²SCAN-3c

Reaction pathway (a)

Table S268 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (a). The calculations were done at the r²SCAN-3c level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−9.9	−0.9	−30.7	0.3	−67.6	−58.2
	<i>E</i> + ΔZPE, kcal/mol	0.0	−9.3	−0.3	−28.0	0.3	−66.3	−57.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.7	14.6	−12.4	15.3	−52.1	−57.2

Table S269 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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Phenyl nitrile oxide ES at r2SCAN-3c in the gas phase

C	−0.069210	−0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	−1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	−0.501768	0.591475
C	1.801408	−1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	−1.137826	0.103841	0.261021
H	−0.248893	−2.210375	0.356466
H	3.744529	−0.661291	0.684203
H	2.194048	−2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

Table S270 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

50

A ES at r2SCAN-3c in the gas phase

C	2.174993	1.557104	0.465934
N	1.572183	2.511305	0.178310
O	0.926535	3.496774	−0.090001
C	−0.424114	0.717772	2.283943
O	0.188595	1.029864	3.293700
C	2.982568	0.408216	0.666054
C	3.713136	−0.124606	−0.411235
C	4.488839	−1.257904	−0.222944
C	4.544869	−1.871252	1.027299
C	3.823923	−1.342967	2.094632
C	3.045872	−0.206264	1.926994
C	−0.287324	−0.743196	1.750819
C	−0.852852	−1.046601	0.416351
C	−1.561003	−0.061630	−0.182960

C	-1.790518	1.284390	0.352861
C	-1.256855	1.643070	1.542903
O	0.269776	-1.560043	2.460653
C	-0.637211	-2.424261	-0.199302
C	0.877153	-2.689628	-0.331567
C	-1.283320	-3.502783	0.696079
C	-1.262606	-2.526756	-1.595797
C	-2.626158	2.225998	-0.502184
C	-4.031740	1.614481	-0.681803
C	-2.771120	3.610583	0.136083
C	-1.952684	2.396519	-1.880198
H	3.660817	0.356913	-1.382567
H	5.050487	-1.667385	-1.057324
H	5.149210	-2.762484	1.167464
H	3.855718	-1.823275	3.067651
H	2.464598	0.194189	2.751465
H	-2.006105	-0.265515	-1.149868
H	-1.360921	2.637990	1.960693
H	1.037768	-3.676436	-0.780451
H	1.345952	-1.940410	-0.978895
H	1.377254	-2.666503	0.638479
H	-1.151818	-4.486631	0.231460
H	-2.358200	-3.320266	0.806103
H	-0.827839	-3.522791	1.687129
H	-2.350768	-2.397459	-1.569285
H	-0.836988	-1.792798	-2.289910
H	-1.060644	-3.522347	-2.003389
H	-4.645543	2.285357	-1.292738
H	-4.003810	0.642257	-1.184036
H	-4.525215	1.483449	0.287003
H	-3.381709	4.245717	-0.513576
H	-1.796982	4.093936	0.260951
H	-3.268258	3.556957	1.110622
H	-1.879481	1.453291	-2.430594
H	-2.546224	3.086946	-2.489537
H	-0.947010	2.812404	-1.764883

Table S271 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase.

50

TS1 at r2SCAN-3c in the gas phase

N	0.978205	1.407619	1.138240
C	0.722858	0.523329	0.361040
O	0.478722	2.129348	2.008480
C	1.216400	-0.337943	-0.659372
C	0.328588	-0.892222	-1.590539
C	0.817464	-1.723607	-2.588252
C	2.178806	-2.003949	-2.671070
C	3.060552	-1.449402	-1.745234
C	2.589554	-0.624004	-0.735915
H	-0.725982	-0.655058	-1.513232
H	0.129048	-2.152051	-3.310449

H	2.553926	-2.653850	-3.455925
H	4.122817	-1.666679	-1.805969
H	3.267773	-0.192585	-0.006782
C	-1.641539	0.933986	1.538465
O	-1.114220	0.008202	0.868025
C	-1.825250	2.287071	0.866716
C	-2.361361	3.380859	1.705616
C	-2.816436	3.048851	2.939250
C	-2.751832	1.723869	3.536780
C	-2.140962	0.714190	2.865697
O	-1.530659	2.393060	-0.316912
C	-2.420531	4.793922	1.141430
C	-0.997183	5.230943	0.735370
C	-3.351379	4.830594	-0.089167
C	-2.952312	5.798167	2.171217
C	-3.348929	1.554351	4.928417
C	-2.603266	2.480272	5.911715
C	-4.842281	1.936356	4.887675
C	-3.232386	0.114313	5.438434
H	-3.256999	3.828031	3.550564
H	-2.028222	-0.285299	3.270166
H	-1.026996	6.257637	0.352912
H	-0.323823	5.202859	1.598642
H	-0.589380	4.582173	-0.041816
H	-3.406089	5.855549	-0.474162
H	-4.364736	4.515632	0.184686
H	-2.983847	4.178991	-0.883236
H	-3.984061	5.576332	2.467662
H	-2.326228	5.831152	3.070462
H	-2.947841	6.799024	1.727754
H	-3.014695	2.355587	6.919654
H	-1.536705	2.234322	5.940279
H	-2.699980	3.536122	5.641849
H	-5.283476	1.813848	5.883187
H	-5.387068	1.293373	4.188334
H	-4.995822	2.975613	4.581988
H	-2.187278	-0.200857	5.525297
H	-3.684527	0.042831	6.432790
H	-3.755178	-0.589712	4.782215

Table S272 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

50

B ES at r2SCAN-3c in the gas phase

C	2.688033	0.360082	0.801612
N	2.799211	0.354599	-0.476804
O	1.497942	0.548532	-0.989604
C	0.570374	0.398485	0.146667
O	1.417110	0.520425	1.282195
C	3.780145	0.251163	1.752724
C	5.107474	0.275111	1.303491
C	6.144456	0.169078	2.216232

C	5.873602	0.043942	3.579100
C	4.556430	0.021315	4.025102
C	3.507724	0.121888	3.118471
C	0.049797	-1.054104	0.026878
C	-1.181417	-1.238710	-0.770096
C	-1.951068	-0.141334	-0.952324
C	-1.651168	1.210112	-0.460232
C	-0.454532	1.463586	0.089858
O	0.700177	-1.950667	0.531103
C	-1.555708	-2.631228	-1.264106
C	-0.379432	-3.210885	-2.076086
C	-1.863439	-3.548694	-0.061790
C	-2.792861	-2.594228	-2.169490
C	-2.738200	2.266054	-0.628587
C	-4.012140	1.800887	0.103319
C	-2.316166	3.620271	-0.049990
C	-3.037489	2.449812	-2.129726
H	5.307585	0.377398	0.241870
H	7.172176	0.187080	1.865924
H	6.690593	-0.036313	4.290178
H	4.341933	-0.079678	5.084813
H	2.478643	0.093730	3.459432
H	-2.886762	-0.254410	-1.488596
H	-0.148848	2.440982	0.445919
H	-0.651901	-4.199583	-2.461725
H	-0.141311	-2.565386	-2.928671
H	0.516060	-3.317681	-1.460842
H	-2.157197	-4.540151	-0.425605
H	-2.692048	-3.143353	0.529668
H	-0.992023	-3.659158	0.585351
H	-3.687674	-2.259948	-1.631836
H	-2.640827	-1.943805	-3.038630
H	-2.994706	-3.604190	-2.540213
H	-4.799963	2.554006	-0.008793
H	-4.399260	0.856363	-0.291853
H	-3.816207	1.664802	1.172197
H	-3.130444	4.340988	-0.176324
H	-1.435067	4.021240	-0.561964
H	-2.096278	3.549425	1.020652
H	-3.404753	1.530923	-2.597086
H	-3.808012	3.217436	-2.262207
H	-2.137671	2.767542	-2.666694

Table S273 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase.

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TS2 at r2SCAN-3c in the gas phase

C	2.494127	0.355018	0.624742
N	3.295599	0.545470	-0.340516
O	2.035814	1.313403	-1.668728
C	0.863287	0.937861	-1.480064
O	1.299505	0.357725	0.958785

C	3.681761	-0.058133	1.557477
C	4.278778	0.900180	2.374198
C	5.154881	0.483659	3.368397
C	5.447411	-0.871171	3.517131
C	4.868141	-1.817232	2.672391
C	3.989761	-1.412615	1.675990
C	0.545024	-0.552689	-1.262785
C	-0.807766	-0.879091	-0.739060
C	-1.736433	0.100334	-0.800853
C	-1.488382	1.464623	-1.256463
C	-0.230832	1.864126	-1.576543
O	1.361634	-1.382201	-1.615766
C	-1.102892	-2.292617	-0.259087
C	-1.071377	-3.260824	-1.461963
C	-0.044031	-2.717440	0.778792
C	-2.484795	-2.386152	0.400068
C	-2.683033	2.406913	-1.296102
C	-3.747476	1.820947	-2.247056
C	-3.268447	2.536258	0.125867
C	-2.307868	3.806439	-1.794183
H	4.049048	1.950783	2.227660
H	5.621125	1.216577	4.020021
H	6.143108	-1.190725	4.287614
H	5.113485	-2.869285	2.782533
H	3.540235	-2.125858	0.991899
H	-2.748553	-0.124700	-0.486437
H	0.014385	2.880513	-1.861177
H	-1.307816	-4.274428	-1.117787
H	-1.818251	-2.971391	-2.209573
H	-0.087658	-3.271856	-1.933983
H	-0.291050	-3.714994	1.158763
H	-0.016196	-2.016381	1.618483
H	0.951040	-2.755370	0.331683
H	-2.576801	-1.695883	1.246394
H	-3.295751	-2.185662	-0.309400
H	-2.630738	-3.402532	0.779332
H	-4.609444	2.495677	-2.290901
H	-3.344761	1.711855	-3.259480
H	-4.108201	0.842166	-1.917549
H	-4.111565	3.235610	0.110877
H	-2.514157	2.918713	0.821012
H	-3.635129	1.581923	0.514671
H	-1.886522	3.776754	-2.804565
H	-3.205199	4.432541	-1.825633
H	-1.587021	4.293157	-1.129124

Table S274 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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C ES at r²SCAN-3c in the gas phase

C	-0.100378	0.886228	1.778301
N	1.026391	0.789639	1.357805

O	1.894323	1.655887	-1.914469
C	0.787821	1.187680	-1.700543
O	-1.224053	1.058047	2.070276
C	2.213562	0.153343	1.749893
C	3.311513	0.224167	0.894087
C	4.491897	-0.414743	1.255641
C	4.583724	-1.111393	2.456545
C	3.480822	-1.173299	3.305617
C	2.292763	-0.545423	2.957976
C	0.662289	-0.335402	-1.387050
C	-0.673842	-0.854216	-1.003419
C	-1.710519	0.012683	-1.065023
C	-1.626819	1.424548	-1.450326
C	-0.427332	1.980414	-1.738622
O	1.660184	-1.024787	-1.485356
C	-0.824728	-2.314225	-0.590783
C	-0.425285	-3.228066	-1.768972
C	0.081348	-2.604644	0.624171
C	-2.268642	-2.646735	-0.195413
C	-2.937654	2.198003	-1.509465
C	-3.866320	1.512790	-2.534696
C	-3.605815	2.190837	-0.119680
C	-2.733854	3.653900	-1.940701
H	3.224420	0.754275	-0.049102
H	5.345005	-0.367372	0.585719
H	5.509997	-1.606543	2.731336
H	3.543427	-1.715436	4.244615
H	1.427278	-0.592515	3.613740
H	-2.698919	-0.347291	-0.805079
H	-0.308844	3.023961	-2.008681
H	-0.572592	-4.275529	-1.482224
H	-1.052306	-3.024181	-2.644201
H	0.620493	-3.086699	-2.045695
H	-0.015650	-3.659023	0.906342
H	-0.222677	-1.999231	1.486006
H	1.131294	-2.401189	0.406129
H	-2.613221	-2.033681	0.645635
H	-2.963462	-2.519119	-1.033572
H	-2.320326	-3.694871	0.115999
H	-4.808363	2.067825	-2.601366
H	-3.404481	1.497152	-3.527544
H	-4.107419	0.482799	-2.255197
H	-4.558576	2.729353	-0.172143
H	-2.968217	2.682659	0.620723
H	-3.813525	1.179268	0.240765
H	-2.288638	3.722014	-2.938825
H	-3.703317	4.161095	-1.971628
H	-2.096251	4.197851	-1.236099

Table S275 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117
C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671
H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

Table S276 Cartesian coordinates of the C₁₄H₂₀O₂ equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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C14H20O2 ES at r2SCAN-3c in the gas phase

C	-0.368176	0.689338	2.319446
O	0.165114	0.963466	3.379751
C	-0.182730	-0.747322	1.730985
C	-0.824572	-1.048525	0.426995
C	-1.539958	-0.056053	-0.149973
C	-1.736617	1.292560	0.391623
C	-1.173551	1.639976	1.570444
O	0.474963	-1.547700	2.367060
C	-0.657522	-2.430695	-0.193700
C	0.841419	-2.709399	-0.435184
C	-1.241086	-3.497703	0.756878
C	-1.385414	-2.542684	-1.539110
C	-2.588570	2.244176	-0.437946
C	-3.997831	1.639228	-0.606841
C	-2.728621	3.620718	0.219114
C	-1.933828	2.429687	-1.822495
H	-2.018952	-0.256676	-1.101301
H	-1.283909	2.623743	2.013295
H	0.956893	-3.689764	-0.910782
H	1.272306	-1.955339	-1.103385
H	1.402304	-2.711151	0.500619
H	-1.149279	-4.486378	0.293339
H	-2.303907	-3.308303	0.944519
H	-0.713006	-3.512817	1.711547
H	-2.466049	-2.390246	-1.435456
H	-0.997660	-1.830436	-2.276707
H	-1.233742	-3.548661	-1.942684
H	-4.622495	2.323325	-1.191487
H	-3.980794	0.678467	-1.130323
H	-4.473291	1.487262	0.367734
H	-3.348299	4.263452	-0.414062
H	-1.757257	4.111112	0.341456

H	-3.211387	3.554054	1.199701
H	-1.859627	1.490710	-2.379221
H	-2.534303	3.122871	-2.421650
H	-0.926188	2.846273	-1.721890

Reaction pathway (b)

Table S277 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (b). The calculations were done at the r²SCAN-3c level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
	<i>E</i> , kcal/mol	0.0	-10.4	1.5	-31.1	10.6	-63.7	-58.2
Gas phase	<i>E</i> + Δ ZPE, kcal/mol	0.0	-9.7	2.1	-28.1	10.2	-62.8	-57.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	3.7	16.9	-12.4	26.0	-47.9	-57.2

Table S278 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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Phenyl nitrile oxide ES at r²SCAN-3c in the gas phase

C	-0.069210	-0.065296	0.353512
C	0.791195	1.020773	0.417689
C	0.429899	-1.364572	0.407188
C	2.175757	0.811022	0.537192
C	2.675335	-0.501768	0.591475
C	1.801408	-1.576849	0.526092
H	0.407658	2.034876	0.376569
C	3.061915	1.913794	0.602642
H	-1.137826	0.103841	0.261021
H	-0.248893	-2.210375	0.356466
H	3.744529	-0.661291	0.684203
H	2.194048	-2.588361	0.568126
N	3.802599	2.811967	0.648429
O	4.567886	3.740538	0.695396

Table S279 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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A ES at r²SCAN-3c in the gas phase

C	-1.634025	0.479259	-1.787436
C	-1.320492	1.448125	-0.735777
C	-0.196591	1.465598	0.015883
C	0.826903	0.438511	-0.284568
C	0.490055	-0.632072	-1.363558
C	-0.766564	-0.517271	-2.076507
O	1.300263	-1.522765	-1.574611
O	-0.599087	-1.473065	1.188064
C	-2.974266	0.644133	-2.492089
C	-4.104077	0.510384	-1.449320
C	-3.035510	2.038154	-3.149467

C	-3.191472	-0.412757	-3.579445
C	0.058451	2.480528	1.123281
C	-1.131845	3.429589	1.310608
C	0.290390	1.734557	2.454681
C	1.298095	3.331143	0.774802
O	1.923189	0.384729	0.246551
C	1.506568	-2.508196	1.550577
N	0.469997	-2.012892	1.378650
C	2.829335	-3.015386	1.575651
C	3.222703	-3.953482	2.542277
C	4.524030	-4.434606	2.540279
C	5.435372	-3.988715	1.585887
C	5.042600	-3.056082	0.627839
C	3.746314	-2.562942	0.611567
H	-2.075710	2.201885	-0.546358
H	-0.959147	-1.271023	-2.831763
H	-5.075650	0.602758	-1.947274
H	-4.059271	-0.465280	-0.954660
H	-4.051746	1.284080	-0.677641
H	-3.995013	2.158670	-3.664322
H	-2.233472	2.155487	-3.885829
H	-2.947804	2.848538	-2.419703
H	-3.196978	-1.425285	-3.162991
H	-4.160088	-0.245793	-4.061440
H	-2.419181	-0.358351	-4.353880
H	-0.905683	4.126575	2.123687
H	-1.326689	4.025904	0.411656
H	-2.046413	2.889753	1.581896
H	0.437046	2.464033	3.259347
H	1.173457	1.095048	2.403209
H	-0.575120	1.111832	2.703703
H	1.146887	3.863649	-0.171032
H	1.461922	4.076724	1.561373
H	2.193871	2.713873	0.690694
H	2.505500	-4.295034	3.281587
H	4.828335	-5.161387	3.287437
H	6.452619	-4.368885	1.588983
H	5.753034	-2.708968	-0.116540
H	3.414014	-1.838301	-0.124947

Table S280 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase.

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TS1 at r2SCAN-3c in the gas phase

C	-1.873911	0.467159	-1.639040
C	-1.618058	1.112656	-0.363806
C	-0.501144	0.933615	0.390982
C	0.542968	0.074845	-0.172894
C	0.337441	-0.562442	-1.543293
C	-0.939463	-0.353904	-2.184536
O	1.252128	-1.218602	-2.033930
O	-0.376112	-2.003298	0.562999

C	-3.205889	0.693288	-2.367697
C	-4.145619	1.657352	-1.630186
C	-2.924934	1.274938	-3.766545
C	-3.925204	-0.662945	-2.508527
C	-0.294644	1.601476	1.746287
C	-1.515473	2.433099	2.161076
C	-0.068923	0.519802	2.823609
C	0.924812	2.545525	1.688469
O	1.666439	-0.087984	0.367629
C	1.917474	-1.995007	0.777408
N	0.775658	-2.381870	0.801688
C	3.291964	-2.296962	0.983376
C	3.676574	-3.235879	1.953865
C	5.021205	-3.528714	2.123784
C	5.985229	-2.883607	1.351365
C	5.600156	-1.945341	0.396835
C	4.258864	-1.648445	0.203320
H	-2.390950	1.766370	0.014889
H	-1.085011	-0.855051	-3.136873
H	-5.068343	1.768059	-2.208853
H	-4.423677	1.282129	-0.639331
H	-3.706751	2.654901	-1.517814
H	-3.868750	1.442513	-4.297771
H	-2.312557	0.599330	-4.369911
H	-2.398082	2.232290	-3.691595
H	-4.111356	-1.107705	-1.525251
H	-4.887860	-0.524704	-3.013887
H	-3.333291	-1.373728	-3.091703
H	-1.324747	2.880815	3.141636
H	-1.711417	3.250925	1.458593
H	-2.418413	1.818137	2.247075
H	0.019252	0.997614	3.806006
H	0.845162	-0.047567	2.637196
H	-0.911919	-0.178126	2.851176
H	0.780442	3.316703	0.923445
H	1.045389	3.045721	2.656244
H	1.843254	2.000103	1.465700
H	2.918380	-3.726433	2.555804
H	5.319517	-4.259696	2.869315
H	7.036855	-3.113258	1.494535
H	6.350595	-1.445451	-0.208105
H	3.932745	-0.932645	-0.542757

Table S281 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

50

B ES at r2SCAN-3c in the gas phase

C	-2.033883	0.207197	-1.679470
C	-1.584977	1.003509	-0.533238
C	-0.495939	0.749344	0.215206
C	0.219600	-0.539809	-0.089921
C	-0.004600	-1.118088	-1.512552

C	-1.274007	-0.812861	-2.141184
O	0.841511	-1.849515	-1.997392
O	-0.319898	-1.581450	0.804836
C	-3.353379	0.613881	-2.322287
C	-4.468323	0.508852	-1.260888
C	-3.253797	2.067536	-2.829027
C	-3.725653	-0.284968	-3.505783
C	-0.040977	1.640660	1.366320
C	-1.098111	2.703622	1.700436
C	0.213360	0.816854	2.644771
C	1.254185	2.380335	0.958693
O	1.610277	-0.547697	0.194358
C	1.832952	-1.717506	0.868316
N	0.779568	-2.351797	1.235641
C	3.204634	-2.103220	1.146238
C	3.471682	-3.178772	2.004085
C	4.783379	-3.540881	2.264573
C	5.837619	-2.837137	1.681762
C	5.572595	-1.769234	0.830998
C	4.260763	-1.400202	0.557653
H	-2.188051	1.868108	-0.286662
H	-1.521618	-1.384553	-3.028107
H	-5.428794	0.785871	-1.709264
H	-4.546209	-0.515549	-0.882380
H	-4.294284	1.172517	-0.408505
H	-4.198524	2.355575	-3.303068
H	-2.453734	2.165813	-3.570220
H	-3.059496	2.779757	-2.021854
H	-3.823680	-1.332430	-3.202209
H	-4.688654	0.035859	-3.915571
H	-2.984859	-0.222792	-4.309697
H	-0.746332	3.300568	2.547771
H	-1.269042	3.393591	0.866972
H	-2.053260	2.248232	1.984414
H	0.478475	1.500016	3.459330
H	1.033934	0.105948	2.531113
H	-0.681171	0.259163	2.937380
H	1.089572	2.973209	0.052548
H	1.549884	3.061325	1.765057
H	2.076947	1.687561	0.776060
H	2.644435	-3.716982	2.455207
H	4.988559	-4.375363	2.928487
H	6.863844	-3.124328	1.891290
H	6.390752	-1.222939	0.371332
H	4.047975	-0.578845	-0.117932

Table S282 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase.

50

TS2 at r2SCAN-3c in the gas phase

C	-2.267277	0.236223	-1.562237
C	-1.988780	1.092118	-0.411209

C	-0.973589	0.931338	0.475602
C	-0.064881	-0.188856	0.223191
C	-0.401609	-1.193972	-0.898446
C	-1.492404	-0.847608	-1.793257
O	0.225122	-2.234364	-0.985826
O	0.967364	-0.295422	0.898914
C	-3.451095	0.622225	-2.437659
C	-4.735229	0.615584	-1.582452
C	-3.212597	2.037407	-3.004506
C	-3.641952	-0.345083	-3.609834
C	-0.726259	1.871561	1.653868
C	-1.823756	2.939462	1.749116
C	-0.730037	1.065881	2.970682
C	0.631063	2.590202	1.486398
O	3.523675	0.070996	2.027456
C	3.262636	-0.937458	1.387849
N	2.330225	-1.531372	0.704445
C	4.277564	-2.104427	1.139867
C	4.371986	-3.141050	2.066991
C	5.426215	-4.041904	1.978014
C	6.363545	-3.919747	0.954144
C	6.248453	-2.896003	0.015398
C	5.197688	-1.990992	0.098533
H	-2.656813	1.933113	-0.271043
H	-1.664615	-1.539291	-2.609808
H	-5.593420	0.882593	-2.208621
H	-4.914354	-0.378177	-1.159120
H	-4.691576	1.334246	-0.758541
H	-4.052033	2.319082	-3.649361
H	-2.295058	2.067782	-3.601238
H	-3.132137	2.794210	-2.218264
H	-3.844393	-1.364328	-3.264560
H	-4.497164	-0.023080	-4.212300
H	-2.763852	-0.366660	-4.263847
H	-1.626232	3.569081	2.621650
H	-1.839082	3.595378	0.870827
H	-2.818759	2.497588	1.879751
H	-0.608733	1.754180	3.813914
H	0.088788	0.345297	3.006455
H	-1.679264	0.533650	3.099863
H	0.669379	3.126110	0.531181
H	0.745614	3.325826	2.290277
H	1.474458	1.898605	1.540725
H	3.625975	-3.229005	2.850992
H	5.512141	-4.847316	2.701653
H	7.181447	-4.630854	0.881711
H	6.974593	-2.810006	-0.787766
H	5.089020	-1.192766	-0.629574

Table S283 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

C ES at r2SCAN-3c in the gas phase

C	-2.301688	-0.152754	-1.351104
C	-1.679412	0.710686	-0.343563
C	-0.665155	0.364270	0.480988
C	-0.149494	-1.019568	0.366430
C	-0.754025	-1.934716	-0.744742
C	-1.856370	-1.415806	-1.534102
O	-0.276174	-3.043400	-0.914161
O	0.721714	-1.484288	1.078923
C	-3.431250	0.457889	-2.169880
C	-4.559253	0.911481	-1.220537
C	-2.883408	1.673323	-2.947016
C	-4.019061	-0.534756	-3.177896
C	-0.043425	1.314944	1.496975
C	-0.678569	2.709388	1.434276
C	-0.246229	0.758401	2.921962
C	1.465400	1.460872	1.204462
O	1.498596	-0.288186	-2.074497
C	2.297421	-0.961023	-1.532600
N	3.087043	-1.744284	-1.080090
C	3.943942	-1.865862	0.016076
C	4.177349	-3.137954	0.536150
C	5.033481	-3.285945	1.620171
C	5.661357	-2.177890	2.182069
C	5.428632	-0.911513	1.651820
C	4.575258	-0.748393	0.568218
H	-2.077144	1.716598	-0.274879
H	-2.268631	-2.087600	-2.278722
H	-5.378702	1.342082	-1.806310
H	-4.952809	0.062093	-0.652355
H	-4.227107	1.672285	-0.507765
H	-3.684817	2.113456	-3.550659
H	-2.072912	1.368818	-3.617110
H	-2.499381	2.455366	-2.284960
H	-4.432928	-1.417967	-2.680136
H	-4.830562	-0.052120	-3.731684
H	-3.269443	-0.863408	-3.905015
H	-0.193056	3.355805	2.172216
H	-0.549559	3.175483	0.450474
H	-1.747785	2.683550	1.674392
H	0.183021	1.456047	3.650069
H	0.239255	-0.211155	3.043892
H	-1.313576	0.649383	3.144643
H	1.627441	1.825561	0.183522
H	1.903857	2.184995	1.900630
H	1.986547	0.509387	1.327793
H	3.669653	-3.989349	0.095795
H	5.207196	-4.276368	2.030309
H	6.329502	-2.299725	3.028967
H	5.915768	-0.041648	2.082849
H	4.392880	0.235518	0.145628

Table S284 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

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Phenyl isocyanate ES at r2SCAN-3c in the gas phase

C	1.804373	-0.430949	0.365941
C	2.883883	0.376435	0.028869
C	1.993875	-1.778577	0.657117
C	4.166461	-0.170760	-0.017344
C	4.364439	-1.524100	0.274057
C	3.276740	-2.319150	0.609373
H	2.748757	1.428425	-0.199958
C	6.424809	0.555112	-0.495671
H	0.807664	-0.001294	0.400931
H	1.147685	-2.405516	0.920014
H	5.366571	-1.942506	0.235882
H	3.434435	-3.369793	0.834893
N	5.229817	0.670830	-0.360749
O	7.584090	0.582442	-0.662355

Table S285 Cartesian coordinates of the C₁₄H₂₀O₂ equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase.

36

C14H20O2 ES at r2SCAN-3c in the gas phase

C	-0.368176	0.689338	2.319446
O	0.165114	0.963466	3.379751
C	-0.182730	-0.747322	1.730985
C	-0.824572	-1.048525	0.426995
C	-1.539958	-0.056053	-0.149973
C	-1.736617	1.292560	0.391623
C	-1.173551	1.639976	1.570444
O	0.474963	-1.547700	2.367060
C	-0.657522	-2.430695	-0.193700
C	0.841419	-2.709399	-0.435184
C	-1.241086	-3.497703	0.756878
C	-1.385414	-2.542684	-1.539110
C	-2.588570	2.244176	-0.437946
C	-3.997831	1.639228	-0.606841
C	-2.728621	3.620718	0.219114
C	-1.933828	2.429687	-1.822495
H	-2.018952	-0.256676	-1.101301
H	-1.283909	2.623743	2.013295
H	0.956893	-3.689764	-0.910782
H	1.272306	-1.955339	-1.103385
H	1.402304	-2.711151	0.500619
H	-1.149279	-4.486378	0.293339
H	-2.303907	-3.308303	0.944519
H	-0.713006	-3.512817	1.711547
H	-2.466049	-2.390246	-1.435456
H	-0.997660	-1.830436	-2.276707
H	-1.233742	-3.548661	-1.942684
H	-4.622495	2.323325	-1.191487

H	-3.980794	0.678467	-1.130323
H	-4.473291	1.487262	0.367734
H	-3.348299	4.263452	-0.414062
H	-1.757257	4.111112	0.341456
H	-3.211387	3.554054	1.199701
H	-1.859627	1.490710	-2.379221
H	-2.534303	3.122871	-2.421650
H	-0.926188	2.846273	-1.721890

2.9.2 B3LYP-D3(BJ)/6-31G

Reaction pathway (a)

Table S286 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (a). The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	<i>E</i> , kcal/mol	0.0	−14.8	−5.2	−26.2	2.4	−65.5	−55.2
	<i>E</i> + Δ ZPE, kcal/mol	0.0	−14.0	−4.6	−23.9	2.0	−64.4	−54.7
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	0.0	10.0	−8.2	16.5	−51.2	−54.6

Table S287 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

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Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	−0.082735	−0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	−1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	−0.505698	0.592333
C	1.800258	−1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	−1.150542	0.096505	0.259821
H	−0.255928	−2.222203	0.354837
H	3.745041	−0.664438	0.685138
H	2.193632	−2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S288 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	2.153824	1.557387	0.313564
N	1.526301	2.508171	0.034366
O	0.829391	3.514955	−0.251869
C	−0.343112	0.682455	2.282399
O	0.321848	0.998234	3.295229
C	2.962131	0.408261	0.554324
C	3.669509	−0.183463	−0.516990
C	4.441150	−1.322748	−0.294046
C	4.514756	−1.884057	0.987964
C	3.816831	−1.298015	2.050304
C	3.044473	−0.153676	1.846132
C	−0.232918	−0.756037	1.742102
C	−0.847393	−1.057145	0.431531
C	−1.570158	−0.066330	−0.156397

C	-1.766827	1.284562	0.391701
C	-1.185889	1.623433	1.573676
O	0.377874	-1.598000	2.431177
C	-0.647881	-2.442874	-0.194128
C	0.871247	-2.707334	-0.383055
C	-1.257818	-3.531035	0.731848
C	-1.330699	-2.545407	-1.574533
C	-2.613584	2.254707	-0.435135
C	-4.047972	1.673767	-0.571106
C	-2.697322	3.646914	0.221322
C	-1.977450	2.419671	-1.843342
H	3.603272	0.253837	-1.507122
H	4.980801	-1.775399	-1.119035
H	5.109593	-2.775767	1.155333
H	3.858341	-1.737627	3.040302
H	2.480472	0.280869	2.663055
H	-2.040809	-0.263706	-1.109374
H	-1.259264	2.614512	1.998257
H	1.016333	-3.693965	-0.838816
H	1.316339	-1.955727	-1.044241
H	1.400097	-2.684494	0.570864
H	-1.128769	-4.517057	0.269779
H	-2.331336	-3.358817	0.874497
H	-0.767574	-3.534978	1.706661
H	-2.416003	-2.405952	-1.503578
H	-0.928602	-1.810941	-2.282558
H	-1.150441	-3.542510	-1.989511
H	-4.661622	2.353838	-1.172736
H	-4.052160	0.694937	-1.062937
H	-4.517196	1.564770	0.413069
H	-3.306623	4.307705	-0.404495
H	-1.702043	4.091063	0.318888
H	-3.165628	3.598090	1.211088
H	-1.922910	1.470540	-2.387668
H	-2.589554	3.108017	-2.437497
H	-0.969803	2.835657	-1.752673

Table S289 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

TS1 at B3LYP-D3(BJ)/6-31G in the gas phase

N	1.008300	1.406776	1.148231
C	0.757835	0.508381	0.370514
O	0.420685	2.143026	2.028013
C	1.238504	-0.369465	-0.653029
C	0.324346	-1.061616	-1.468777
C	0.800976	-1.905614	-2.472409
C	2.177612	-2.063485	-2.672888
C	3.086614	-1.370385	-1.862578
C	2.626767	-0.525610	-0.853261
H	-0.734273	-0.920796	-1.299600
H	0.095725	-2.437913	-3.101711

H	2.541204	-2.720571	-3.455952
H	4.153912	-1.489259	-2.016039
H	3.323341	0.013979	-0.221397
C	-1.622395	0.983418	1.521214
O	-1.085094	0.039983	0.822134
C	-1.822541	2.328522	0.864858
C	-2.367243	3.411907	1.710716
C	-2.822218	3.074254	2.949181
C	-2.755523	1.735312	3.531284
C	-2.139461	0.734899	2.839328
O	-1.520250	2.456446	-0.344564
C	-2.412968	4.837770	1.155861
C	-0.976267	5.267520	0.748923
C	-3.346328	4.891591	-0.084976
C	-2.940966	5.841260	2.202876
C	-3.367456	1.536380	4.921589
C	-2.648424	2.467778	5.934954
C	-4.877196	1.894449	4.864360
C	-3.228481	0.081373	5.413325
H	-3.255356	3.846088	3.570384
H	-2.022293	-0.267745	3.226594
H	-0.993918	6.303876	0.390869
H	-0.296989	5.205210	1.606091
H	-0.588925	4.628120	-0.046099
H	-3.380638	5.916889	-0.472928
H	-4.366606	4.594699	0.187144
H	-2.982888	4.229603	-0.872622
H	-3.972252	5.615826	2.500666
H	-2.312189	5.858037	3.100983
H	-2.933912	6.847110	1.769781
H	-3.079995	2.329597	6.933153
H	-1.579832	2.232077	5.982763
H	-2.751846	3.524217	5.667604
H	-5.326009	1.771640	5.856970
H	-5.403081	1.236164	4.163804
H	-5.040321	2.929346	4.546418
H	-2.177109	-0.214517	5.498935
H	-3.686372	-0.015931	6.403518
H	-3.732955	-0.619457	4.738767

Table S290 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

B ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	2.758200	0.399880	0.739301
N	2.913553	0.470097	-0.545077
O	1.556220	0.608229	-1.116313
C	0.585989	0.361713	0.013462
O	1.436271	0.449752	1.197391
C	3.817955	0.304753	1.730383
C	5.165396	0.316155	1.323963
C	6.176952	0.223187	2.278123

C	5.856279	0.120594	3.639152
C	4.516583	0.108419	4.042728
C	3.495909	0.198350	3.093703
C	0.110042	-1.088859	-0.158312
C	-1.209239	-1.298306	-0.780976
C	-2.023305	-0.213076	-0.897366
C	-1.691235	1.154256	-0.464470
C	-0.449464	1.414109	-0.001881
O	0.881627	-2.002181	0.192501
C	-1.614056	-2.710678	-1.219999
C	-0.563344	-3.254494	-2.225905
C	-1.686973	-3.646328	0.017864
C	-2.994078	-2.716608	-1.911855
C	-2.736473	2.281453	-0.599051
C	-4.167200	1.738495	-0.821816
C	-2.752039	3.149698	0.683741
C	-2.345248	3.163585	-1.814753
H	5.400905	0.394864	0.268884
H	7.214911	0.230064	1.962809
H	6.647100	0.048581	4.378783
H	4.265805	0.025236	5.094939
H	2.455433	0.181494	3.393460
H	-3.002982	-0.353978	-1.327763
H	-0.121761	2.399349	0.304571
H	-0.872755	-4.245285	-2.579046
H	-0.481014	-2.591166	-3.094776
H	0.419708	-3.342939	-1.759181
H	-1.968408	-4.656494	-0.303260
H	-2.444173	-3.290171	0.726823
H	-0.722631	-3.697285	0.525840
H	-3.788852	-2.368660	-1.241352
H	-2.998152	-2.092746	-2.813845
H	-3.238652	-3.740763	-2.212441
H	-4.873368	2.575712	-0.821767
H	-4.269212	1.227420	-1.785378
H	-4.465435	1.045995	-0.025991
H	-3.492957	3.950472	0.579614
H	-1.781436	3.618013	0.872462
H	-3.015423	2.545862	1.559162
H	-2.326021	2.571739	-2.737048
H	-3.070063	3.976690	-1.941858
H	-1.351507	3.601024	-1.674383

Table S291 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	2.524861	0.456458	0.639499
N	3.379874	0.621979	-0.308825
O	2.019752	1.329060	-1.806483
C	0.831920	0.949484	-1.591366
O	1.308036	0.495656	0.951708

C	3.734608	-0.036820	1.552866
C	4.347864	0.864135	2.433492
C	5.178323	0.363840	3.439200
C	5.407420	-1.016381	3.536055
C	4.812994	-1.904980	2.627981
C	3.981521	-1.415567	1.618699
C	0.538795	-0.525606	-1.303577
C	-0.805424	-0.864728	-0.777171
C	-1.756196	0.103322	-0.830797
C	-1.529126	1.473720	-1.302683
C	-0.277000	1.870213	-1.663843
O	1.416726	-1.372823	-1.561832
C	-1.062755	-2.276069	-0.241799
C	-0.961314	-3.304115	-1.402586
C	-0.007308	-2.613494	0.847894
C	-2.465654	-2.392123	0.391638
C	-2.734876	2.417650	-1.316769
C	-3.828570	1.826905	-2.247871
C	-3.293053	2.549589	0.127041
C	-2.366288	3.824807	-1.828188
H	4.167492	1.927729	2.330017
H	5.653004	1.044695	4.137405
H	6.061078	-1.399061	4.313096
H	5.008788	-2.969257	2.699748
H	3.525487	-2.074098	0.888199
H	-2.755551	-0.126556	-0.488901
H	-0.042938	2.881805	-1.964748
H	-1.145999	-4.313074	-1.014348
H	-1.711449	-3.091910	-2.174019
H	0.030231	-3.278838	-1.857657
H	-0.242460	-3.588489	1.290609
H	-0.005407	-1.854295	1.635722
H	0.993605	-2.660144	0.414983
H	-2.593690	-1.683607	1.218391
H	-3.261673	-2.222728	-0.343432
H	-2.595761	-3.403464	0.790992
H	-4.701628	2.489508	-2.255046
H	-3.455822	1.737514	-3.274229
H	-4.160611	0.837312	-1.917720
H	-4.148642	3.234704	0.128212
H	-2.527186	2.948679	0.800505
H	-3.631647	1.589040	0.527854
H	-1.966873	3.789484	-2.847735
H	-3.262067	4.454851	-1.839508
H	-1.625405	4.306087	-1.180674

Table S292 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G-3c level of theory in the gas phase.

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C ES at B3LYP-D3(BJ)/6-31G in the gas phase
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symmetry c1

C	0.487247	-0.237568	2.347258
N	1.569422	-0.500211	2.784292
O	1.375252	1.802278	-0.176603
C	0.307067	1.292575	-0.584782
O	-0.648812	-0.028017	1.983595
C	2.964291	-0.497833	2.728442
C	3.633557	0.074901	1.633600
C	5.029900	0.062228	1.616243
C	5.754385	-0.511009	2.669048
C	5.074986	-1.079863	3.752940
C	3.678737	-1.075767	3.787779
C	0.231524	-0.234636	-0.762520
C	-1.058643	-0.828587	-1.168721
C	-2.091973	0.023138	-1.409635
C	-2.030183	1.482804	-1.281029
C	-0.868493	2.076533	-0.890697
O	1.264239	-0.901430	-0.544916
C	-1.182585	-2.352049	-1.273774
C	-0.190955	-2.890103	-2.342260
C	-0.863950	-2.989945	0.107726
C	-2.608823	-2.777922	-1.682255
C	-3.279036	2.341466	-1.558366
C	-4.501076	1.508007	-2.003122
C	-3.655924	3.101983	-0.257954
C	-2.953516	3.363305	-2.679740
H	3.059311	0.507936	0.822677
H	5.552333	0.502655	0.773334
H	6.839196	-0.514964	2.644638
H	5.630334	-1.526065	4.571398
H	3.134734	-1.510547	4.618215
H	-3.041957	-0.393716	-1.704424
H	-0.775560	3.148404	-0.763417
H	-0.296154	-3.978612	-2.421793
H	-0.407817	-2.454355	-3.325104
H	0.840970	-2.659067	-2.072718
H	-1.017582	-4.073890	0.050695
H	-1.524880	-2.583741	0.880847
H	0.171050	-2.800885	0.398954
H	-3.354978	-2.456170	-0.946073
H	-2.887234	-2.376643	-2.664145
H	-2.651739	-3.870222	-1.744522
H	-5.343215	2.181967	-2.192121
H	-4.305033	0.955012	-2.928957
H	-4.813503	0.797729	-1.229482
H	-4.551015	3.711266	-0.429356
H	-2.846991	3.763808	0.065478
H	-3.864525	2.398827	0.555675
H	-2.680985	2.849560	-3.608628
H	-3.831060	3.989817	-2.876781
H	-2.123814	4.018429	-2.397497

Table S293 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235
H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

Table S294 Cartesian coordinates of the C₁₄H₂₀O₂ equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

36

C₁₄H₂₀O₂ ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.382378	0.666700	2.320627
O	0.143821	0.945303	3.417353
C	-0.189622	-0.744104	1.729473
C	-0.827652	-1.049664	0.426691
C	-1.547878	-0.059103	-0.163625
C	-1.744089	1.291941	0.382373
C	-1.179886	1.625512	1.572219
O	0.493955	-1.565768	2.371132
C	-0.650939	-2.441988	-0.192068
C	0.859170	-2.714386	-0.436467
C	-1.226565	-3.517509	0.770088
C	-1.387135	-2.561740	-1.543577
C	-2.595775	2.259695	-0.445372
C	-4.020559	1.664366	-0.611951
C	-2.718611	3.642464	0.225369
C	-1.942932	2.447126	-1.841978
H	-2.022364	-0.260457	-1.114067
H	-1.289187	2.603149	2.021987
H	0.982056	-3.701594	-0.897252
H	1.281565	-1.965297	-1.116978
H	1.417601	-2.695777	0.500765
H	-1.119640	-4.508925	0.314278
H	-2.292871	-3.339892	0.954085
H	-0.697325	-3.514232	1.724490
H	-2.467577	-2.409054	-1.433920
H	-1.004609	-1.846015	-2.281160
H	-1.233344	-3.568165	-1.946279
H	-4.637006	2.346575	-1.208384

H	-4.005942	0.694813	-1.120564
H	-4.499428	1.530723	0.364218
H	-3.334016	4.298008	-0.399744
H	-1.739137	4.117625	0.347921
H	-3.195654	3.571579	1.208988
H	-1.868198	1.504138	-2.393222
H	-2.547791	3.137767	-2.440537
H	-0.935682	2.866754	-1.744605

Reaction pathway (b)

Table S295 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (b). The calculations were done at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

		Reagents	A	TS1	B	TS2	C	Products
	<i>E</i> , kcal/mol	0.0	-12.8	-3.5	-27.1	10.6	-67.7	-55.2
Gas phase	<i>E</i> + Δ ZPE, kcal/mol	0.0	-12.1	-2.7	-24.4	10.0	-66.5	-54.7
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	1.4	11.9	-8.5	23.5	-53.2	-54.6

Table S296 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl nitrile oxide ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.082735	-0.070642	0.352380
C	0.782473	1.021935	0.417554
C	0.421197	-1.376237	0.406103
C	2.173885	0.813079	0.538038
C	2.676680	-0.505698	0.592333
C	1.800258	-1.588890	0.526010
H	0.397050	2.034356	0.376356
C	3.065623	1.920910	0.603643
H	-1.150542	0.096505	0.259821
H	-0.255928	-2.222203	0.354837
H	3.745041	-0.664438	0.685138
H	2.193632	-2.598933	0.567751
N	3.814846	2.824037	0.649439
O	4.614819	3.784519	0.696598

Table S297 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

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A ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-1.601772	0.659146	-1.803843
C	-1.408182	1.447581	-0.584582
C	-0.318207	1.374834	0.226867
C	0.771966	0.463031	-0.177701
C	0.564593	-0.412909	-1.422293
C	-0.647891	-0.233541	-2.189058
O	1.451094	-1.242266	-1.733284

O	-0.642246	-1.664282	0.906812
C	-2.890965	0.811378	-2.634734
C	-3.863994	1.862213	-2.056707
C	-2.514258	1.241524	-4.077277
C	-3.621846	-0.557278	-2.675709
C	-0.181215	2.174539	1.526218
C	-1.444606	3.013003	1.814084
C	0.027209	1.189751	2.711677
C	1.032315	3.138951	1.427760
O	1.860839	0.367794	0.429034
C	1.579819	-2.579749	1.276173
N	0.493554	-2.176249	1.115946
C	2.954085	-2.949548	1.304605
C	3.438014	-3.876495	2.249912
C	4.791946	-4.213004	2.256301
C	5.665811	-3.632154	1.328197
C	5.183038	-2.710858	0.389230
C	3.832492	-2.362398	0.366738
H	-2.209106	2.115585	-0.309501
H	-0.754683	-0.857742	-3.068138
H	-4.747400	1.923718	-2.701091
H	-4.205966	1.592893	-1.051151
H	-3.412415	2.860057	-2.017503
H	-3.421077	1.342530	-4.685071
H	-1.861782	0.505933	-4.557327
H	-1.993641	2.205952	-4.072598
H	-3.873236	-0.892710	-1.663812
H	-4.549450	-0.467721	-3.253231
H	-3.001159	-1.327834	-3.142516
H	-1.305352	3.556892	2.754347
H	-1.632899	3.753551	1.027247
H	-2.333662	2.380455	1.920841
H	0.048450	1.751877	3.652842
H	0.969639	0.649305	2.606771
H	-0.788536	0.460901	2.752807
H	0.897297	3.849279	0.602929
H	1.120978	3.711255	2.359097
H	1.959232	2.584961	1.269535
H	2.754510	-4.320145	2.965379
H	5.165462	-4.925634	2.983980
H	6.718209	-3.896785	1.337671
H	5.860882	-2.261590	-0.328815
H	3.433164	-1.653016	-0.348043

Table S298 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

TS1 at B3LYP-D3(BJ)/6-31G in the gas phase

C	-1.874240	0.483500	-1.652029
C	-1.627721	1.118675	-0.361260
C	-0.511224	0.921559	0.397526
C	0.518335	0.034020	-0.157041

C	0.341966	-0.554390	-1.540950
C	-0.922033	-0.323455	-2.203045
O	1.281899	-1.217489	-2.045509
O	-0.419140	-1.909081	0.567908
C	-3.210518	0.706469	-2.389458
C	-4.159995	1.668307	-1.641647
C	-2.928907	1.299379	-3.794682
C	-3.926456	-0.662855	-2.538345
C	-0.297665	1.579433	1.765385
C	-1.515590	2.433725	2.178923
C	-0.088018	0.481951	2.844487
C	0.948274	2.506086	1.715204
O	1.672154	-0.138680	0.400286
C	1.896893	-2.013589	0.842342
N	0.742637	-2.398146	0.854296
C	3.285718	-2.300947	1.022209
C	3.715793	-3.184618	2.032513
C	5.076040	-3.463016	2.166921
C	6.007353	-2.858591	1.312342
C	5.576256	-1.976314	0.313005
C	4.218924	-1.695399	0.158579
H	-2.397693	1.772204	0.015987
H	-1.054728	-0.806990	-3.163334
H	-5.083473	1.781598	-2.219615
H	-4.432897	1.283468	-0.652689
H	-3.719577	2.664662	-1.520224
H	-3.872302	1.448784	-4.333046
H	-2.297910	0.634122	-4.391709
H	-2.421332	2.267363	-3.713657
H	-4.120467	-1.106973	-1.555812
H	-4.884335	-0.530179	-3.055308
H	-3.319885	-1.368868	-3.113553
H	-1.322223	2.881318	3.159475
H	-1.698229	3.249931	1.470213
H	-2.425900	1.828377	2.259607
H	-0.019644	0.952144	3.832792
H	0.833488	-0.074255	2.664144
H	-0.925794	-0.222477	2.846853
H	0.810099	3.298715	0.970080
H	1.092265	2.979349	2.693963
H	1.847096	1.939625	1.465034
H	2.987186	-3.642045	2.692522
H	5.409763	-4.146211	2.940528
H	7.064476	-3.075721	1.424972
H	6.297865	-1.513142	-0.351221
H	3.853422	-1.031340	-0.613961

Table S299 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

B ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.038794	0.319996	-1.672491

C	-1.668675	0.982312	-0.414680
C	-0.592655	0.663508	0.343883
C	0.187365	-0.545175	-0.088954
C	0.018220	-0.996545	-1.550644
C	-1.213850	-0.621767	-2.208662
O	0.898036	-1.709450	-2.073104
O	-0.306745	-1.735019	0.719340
C	-3.319995	0.742213	-2.417429
C	-4.224783	1.671122	-1.577274
C	-2.911965	1.492094	-3.714628
C	-4.142174	-0.519947	-2.787423
C	-0.203704	1.430743	1.612916
C	-1.326370	2.401796	2.045483
C	0.066762	0.463935	2.796599
C	1.073099	2.273604	1.327121
O	1.602301	-0.511117	0.228631
C	1.910640	-1.751106	0.804354
N	0.895194	-2.497145	1.104823
C	3.310230	-2.056204	1.046582
C	3.663505	-3.201772	1.784022
C	5.007659	-3.488940	2.014406
C	6.005733	-2.639281	1.516857
C	5.654025	-1.501469	0.782026
C	4.309912	-1.207286	0.542871
H	-2.302960	1.791920	-0.092052
H	-1.403838	-1.085233	-3.168951
H	-5.147544	1.870695	-2.132405
H	-4.500375	1.210957	-0.621675
H	-3.749036	2.637409	-1.376038
H	-3.808406	1.808941	-4.260705
H	-2.316570	0.849544	-4.370918
H	-2.318580	2.383357	-3.480476
H	-4.428440	-1.074276	-1.886907
H	-5.055349	-0.224520	-3.316930
H	-3.579420	-1.195831	-3.437688
H	-1.023860	2.906215	2.968998
H	-1.510829	3.177245	1.293466
H	-2.264543	1.870144	2.240681
H	0.264908	1.054263	3.698714
H	0.934674	-0.172057	2.618510
H	-0.796174	-0.181781	2.981794
H	0.888206	2.986518	0.515195
H	1.343762	2.839680	2.226596
H	1.913847	1.636805	1.047794
H	2.881955	-3.849150	2.164796
H	5.278960	-4.372580	2.582156
H	7.051107	-2.865710	1.699936
H	6.425171	-0.846248	0.391121
H	4.025611	-0.337418	-0.036002

Table S300 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

50

TS2 at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.365129	0.270402	-1.600172
C	-2.038690	1.113690	-0.442327
C	-1.008139	0.900960	0.423232
C	-0.150311	-0.266249	0.160141
C	-0.483470	-1.189479	-1.016277
C	-1.605561	-0.824031	-1.865974
O	0.191287	-2.221060	-1.204385
O	0.845894	-0.492539	0.890915
C	-3.570316	0.684053	-2.449722
C	-4.841326	0.693044	-1.556665
C	-3.325603	2.108031	-3.020081
C	-3.805155	-0.281725	-3.628414
C	-0.692822	1.818162	1.613166
C	-1.706193	2.979876	1.699365
C	-0.771270	1.007896	2.937083
C	0.732709	2.423348	1.460321
O	3.425954	0.061430	1.942244
C	3.252133	-1.032531	1.367424
N	2.368633	-1.746755	0.709162
C	4.351773	-2.150384	1.184470
C	4.483104	-3.156252	2.152349
C	5.603467	-3.991263	2.128105
C	6.571664	-3.833540	1.127360
C	6.422044	-2.842513	0.146741
C	5.304916	-2.004265	0.165917
H	-2.675203	1.972640	-0.283949
H	-1.799229	-1.487619	-2.697332
H	-5.708396	0.993205	-2.155823
H	-5.033614	-0.304569	-1.147092
H	-4.752786	1.394780	-0.720959
H	-4.189367	2.415790	-3.620156
H	-2.437907	2.120602	-3.661741
H	-3.185719	2.852065	-2.229119
H	-4.008516	-1.300146	-3.279634
H	-4.671584	0.053242	-4.208201
H	-2.941625	-0.310694	-4.301895
H	-1.457351	3.603295	2.563755
H	-1.671094	3.619500	0.808910
H	-2.733594	2.619227	1.833845
H	-0.587927	1.681272	3.782052
H	-0.018177	0.218680	2.961256
H	-1.765467	0.562473	3.064069
H	0.828609	2.945420	0.500259
H	0.894842	3.156332	2.259466
H	1.514047	1.663320	1.536343
H	3.716161	-3.273775	2.909421
H	5.717352	-4.766730	2.878284
H	7.437652	-4.487410	1.106001
H	7.168982	-2.730918	-0.632203
H	5.170319	-1.238289	-0.589533

Table S301 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G-3c level of theory in the gas phase.

50

C ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-2.065741	-0.114519	-1.330078
C	-1.849094	0.734071	-0.149594
C	-0.892293	0.536342	0.794660
C	-0.016532	-0.641802	0.630430
C	-0.187617	-1.509074	-0.630738
C	-1.263423	-1.189816	-1.547252
O	0.608408	-2.454254	-0.824692
O	0.862932	-0.973560	1.452321
C	-3.196752	0.290795	-2.278780
C	-4.540448	0.291108	-1.499953
C	-2.909144	1.716469	-2.825798
C	-3.324455	-0.673816	-3.474516
C	-0.676435	1.472655	1.988714
C	-1.641276	2.676588	1.944969
C	-0.922100	0.697845	3.312509
C	0.778743	2.018858	1.961903
O	1.592975	0.889205	-1.231948
C	2.580985	0.265020	-0.913103
N	3.611131	-0.267899	-0.622721
C	4.373426	-1.315637	-0.104685
C	3.748946	-2.448863	0.443046
C	4.546042	-3.476265	0.952539
C	5.943117	-3.382920	0.919763
C	6.552423	-2.248665	0.370033
C	5.771450	-1.211020	-0.143515
H	-2.503310	1.589067	-0.053359
H	-1.363404	-1.835399	-2.408934
H	-5.353456	0.590201	-2.171338
H	-4.763531	-0.709391	-1.113038
H	-4.529196	0.988877	-0.656350
H	-3.706755	2.011492	-3.517184
H	-1.956100	1.736983	-3.364882
H	-2.863762	2.463330	-2.026855
H	-3.535993	-1.697001	-3.144834
H	-4.149753	-0.351000	-4.117953
H	-2.411695	-0.685574	-4.080085
H	-1.444528	3.322731	2.806588
H	-1.498165	3.274937	1.037436
H	-2.690607	2.361811	1.997624
H	-0.778574	1.374002	4.163607
H	-0.228046	-0.138766	3.412123
H	-1.948795	0.314203	3.350530
H	0.982335	2.524492	1.012090
H	0.911497	2.739007	2.777769
H	1.502298	1.211930	2.090137
H	2.666892	-2.508415	0.460430
H	4.069752	-4.353983	1.376729
H	6.552197	-4.187620	1.318416

H	7.634203	-2.169920	0.340150
H	6.224617	-0.324842	-0.572417

Table S302 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

14

Phenyl isocyanate ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	1.806997	-0.419592	0.362265
C	2.922676	0.352003	0.030274
C	1.949608	-1.779650	0.662171
C	4.193171	-0.242406	-0.001790
C	4.343102	-1.607584	0.298593
C	3.219814	-2.368147	0.628522
H	2.828883	1.405482	-0.204694
C	6.472869	0.673489	-0.531235
H	0.825828	0.042593	0.386512
H	1.080461	-2.375178	0.919770
H	5.329927	-2.057214	0.271485
H	3.338470	-3.421525	0.859683
N	5.292558	0.545181	-0.335681
O	7.629234	0.923148	-0.754876

Table S303 Cartesian coordinates of the C₁₄H₂₀O₂ equilibrium geometry state (ES) obtained at the B3LYP-D3(BJ)/6-31G level of theory in the gas phase.

36

C₁₄H₂₀O₂ ES at B3LYP-D3(BJ)/6-31G in the gas phase

C	-0.382378	0.666700	2.320627
O	0.143821	0.945303	3.417353
C	-0.189622	-0.744104	1.729473
C	-0.827652	-1.049664	0.426691
C	-1.547878	-0.059103	-0.163625
C	-1.744089	1.291941	0.382373
C	-1.179886	1.625512	1.572219
O	0.493955	-1.565768	2.371132
C	-0.650939	-2.441988	-0.192068
C	0.859170	-2.714386	-0.436467
C	-1.226565	-3.517509	0.770088
C	-1.387135	-2.561740	-1.543577
C	-2.595775	2.259695	-0.445372
C	-4.020559	1.664366	-0.611951
C	-2.718611	3.642464	0.225369
C	-1.942932	2.447126	-1.841978
H	-2.022364	-0.260457	-1.114067
H	-1.289187	2.603149	2.021987
H	0.982056	-3.701594	-0.897252
H	1.281565	-1.965297	-1.116978
H	1.417601	-2.695777	0.500765
H	-1.119640	-4.508925	0.314278
H	-2.292871	-3.339892	0.954085
H	-0.697325	-3.514232	1.724490

H	-2.467577	-2.409054	-1.433920
H	-1.004609	-1.846015	-2.281160
H	-1.233344	-3.568165	-1.946279
H	-4.637006	2.346575	-1.208384
H	-4.005942	0.694813	-1.120564
H	-4.499428	1.530723	0.364218
H	-3.334016	4.298008	-0.399744
H	-1.739137	4.117625	0.347921
H	-3.195654	3.571579	1.208988
H	-1.868198	1.504138	-2.393222
H	-2.547791	3.137767	-2.440537
H	-0.935682	2.866754	-1.744605

2.9.3 ω B97X-D3(BJ)/def2-TZVP

Reaction pathway (a)

Table S304 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (a). The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
Gas phase	E , kcal/mol	0.0	−8.4	10.1	−34.2	6.7	−65.7	−60.8
	$E + \Delta ZPE$, kcal/mol	0.0	−7.8	10.6	−31.4	6.4	−65.1	−60.6
	$E + \Delta G$, kcal/mol	0.0	6.4	25.1	−16.3	20.9	−51.6	−60.6

Table S305 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	−0.067240	−0.063982	0.353909
C	0.797006	1.018735	0.417913
C	0.431386	−1.361016	0.407597
C	2.170887	0.797533	0.536479
C	2.674086	−0.504119	0.590930
C	1.799752	−1.578707	0.525912
H	0.417864	2.033014	0.376538
C	3.071455	1.915930	0.602265
H	−1.133940	0.106124	0.261623
H	−0.248356	−2.204390	0.357279
H	3.741831	−0.663912	0.683323
H	2.188598	−2.589810	0.568143
N	3.795700	2.809513	0.647480
O	4.557272	3.753387	0.696608

Table S306 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

50

A ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.964345	2.805152	0.753688
N	1.562340	3.874997	0.886931
O	1.124060	5.000668	1.022888
C	−0.409603	0.217017	2.503875
O	−0.044654	0.431953	3.638896
C	2.457522	1.464199	0.604112
C	2.656453	0.934054	−0.672655
C	3.131320	−0.361333	−0.807310
C	3.400354	−1.128450	0.321009
C	3.194245	−0.601407	1.590247
C	2.727241	0.696220	1.738308
C	−0.306203	−1.238415	1.956565

C	-0.770093	-1.491668	0.566199
C	-1.207167	-0.431029	-0.128757
C	-1.321315	0.954717	0.373121
C	-0.943087	1.252949	1.624097
O	0.147516	-2.083904	2.690968
C	-0.758461	-2.914326	0.013045
C	0.675207	-3.469118	-0.010541
C	-1.648626	-3.807876	0.895755
C	-1.309805	-2.963548	-1.415467
C	-1.892083	1.980234	-0.596537
C	-3.279850	1.511573	-1.069244
C	-2.046907	3.359580	0.046591
C	-0.945622	2.098941	-1.803116
H	2.440571	1.538208	-1.545816
H	3.289183	-0.774597	-1.797183
H	3.763689	-2.143705	0.210304
H	3.389052	-1.203102	2.470354
H	2.561003	1.113640	2.723738
H	-1.532863	-0.584235	-1.147597
H	-1.007997	2.249246	2.041394
H	0.658591	-4.497231	-0.382609
H	1.304024	-2.873678	-0.676496
H	1.122934	-3.469725	0.982192
H	-1.686052	-4.813870	0.468991
H	-2.669370	-3.416860	0.934490
H	-1.263451	-3.879207	1.911891
H	-2.344687	-2.613664	-1.463284
H	-0.706887	-2.365821	-2.104818
H	-1.290795	-3.997874	-1.766078
H	-3.701861	2.260711	-1.743762
H	-3.240961	0.563720	-1.609190
H	-3.957584	1.395822	-0.219292
H	-2.471843	4.049573	-0.686172
H	-1.091148	3.771832	0.373948
H	-2.722202	3.323992	0.905262
H	-0.804788	1.143301	-2.313093
H	-1.361425	2.806920	-2.524487
H	0.032967	2.468719	-1.488762

Table S307 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

50

TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

N	0.981275	1.345058	1.170179
C	0.756704	0.473184	0.387576
O	0.335028	1.997561	2.027458
C	1.231330	-0.410767	-0.647062
C	0.339941	-0.926706	-1.585947
C	0.816768	-1.761269	-2.586048
C	2.169621	-2.073787	-2.653175
C	3.054606	-1.554953	-1.713486

C	2.591196	-0.725868	-0.704150
H	-0.708850	-0.669436	-1.520036
H	0.127686	-2.165608	-3.318824
H	2.536386	-2.724770	-3.439120
H	4.109398	-1.800322	-1.763922
H	3.269656	-0.318849	0.036389
C	-1.532380	1.014264	1.527340
O	-1.080170	0.079934	0.821181
C	-1.805329	2.352677	0.850416
C	-2.356580	3.432732	1.710168
C	-2.778508	3.083513	2.936392
C	-2.690195	1.739533	3.529350
C	-2.057749	0.763848	2.862619
O	-1.559098	2.463798	-0.333086
C	-2.448261	4.850622	1.157958
C	-1.048414	5.316939	0.720915
C	-3.411358	4.886660	-0.041301
C	-2.967188	5.831172	2.214127
C	-3.319274	1.547497	4.902997
C	-2.642077	2.491701	5.911383
C	-4.818777	1.877697	4.809241
C	-3.165812	0.110670	5.406662
H	-3.218416	3.845819	3.564204
H	-1.929185	-0.238400	3.248692
H	-1.106741	6.343712	0.348943
H	-0.355353	5.298015	1.566511
H	-0.646136	4.685762	-0.070414
H	-3.494022	5.913212	-0.409985
H	-4.408368	4.550434	0.257924
H	-3.058727	4.253765	-0.853902
H	-3.983868	5.585788	2.533322
H	-2.320509	5.853909	3.095637
H	-2.987412	6.836031	1.785737
H	-3.078996	2.341079	6.902137
H	-1.570334	2.285760	5.972680
H	-2.773407	3.542600	5.645807
H	-5.284999	1.758359	5.790907
H	-5.317661	1.204767	4.106740
H	-4.991493	2.904252	4.478831
H	-2.113982	-0.164007	5.518535
H	-3.643547	0.017122	6.384852
H	-3.641164	-0.603543	4.729623

Table S308 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

50

B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	2.651919	0.349789	0.852232
N	2.754334	0.345998	-0.417482
O	1.453848	0.588562	-0.913908
C	0.551292	0.426585	0.200677

O	1.396837	0.539804	1.332410
C	3.756259	0.199263	1.805454
C	5.073702	0.189383	1.344413
C	6.115566	0.042175	2.245350
C	5.849581	-0.092207	3.605677
C	4.538338	-0.080408	4.063281
C	3.488080	0.063207	3.165234
C	0.014501	-1.019491	0.092309
C	-1.172271	-1.195061	-0.786127
C	-1.939485	-0.110810	-0.963975
C	-1.676181	1.231439	-0.394681
C	-0.496847	1.481742	0.171858
O	0.596144	-1.911098	0.665081
C	-1.479899	-2.567599	-1.372752
C	-0.231403	-3.099598	-2.096647
C	-1.894550	-3.536494	-0.252036
C	-2.623366	-2.489509	-2.388388
C	-2.787699	2.263715	-0.528943
C	-4.051190	1.728603	0.164891
C	-2.407777	3.597980	0.115019
C	-3.075011	2.506021	-2.020472
H	5.269944	0.297850	0.284356
H	7.139131	0.033781	1.887714
H	6.667982	-0.206266	4.308271
H	4.329387	-0.186187	5.121938
H	2.462754	0.065210	3.514142
H	-2.838807	-0.205735	-1.556965
H	-0.212569	2.445544	0.572953
H	-0.455322	-4.071079	-2.545414
H	0.071440	-2.416078	-2.895003
H	0.607397	-3.225045	-1.412203
H	-2.139618	-4.510802	-0.684870
H	-2.780515	-3.161359	0.267840
H	-1.094144	-3.669504	0.474764
H	-3.563917	-2.186592	-1.920478
H	-2.394377	-1.790815	-3.197870
H	-2.776158	-3.477968	-2.827816
H	-4.862471	2.454160	0.063182
H	-4.389162	0.785117	-0.269635
H	-3.865488	1.567625	1.230045
H	-3.238513	4.299772	0.008734
H	-1.531159	4.040079	-0.365037
H	-2.198627	3.481009	1.181400
H	-3.410293	1.600558	-2.530297
H	-3.863232	3.256371	-2.123714
H	-2.181004	2.873591	-2.530711

Table S309 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

50

TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

Table S310 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

50

C ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	2.494037	0.402271	0.692075
N	3.283065	0.591100	-0.290436
O	2.030147	1.369468	-1.584939
C	0.864065	0.989711	-1.459465
O	1.304206	0.443983	0.999784
C	3.659700	-0.043075	1.631259
C	4.299136	0.903223	2.423731
C	5.179275	0.474414	3.407981
C	5.424921	-0.885052	3.573881
C	4.798288	-1.822968	2.757819
C	3.916256	-1.402849	1.772412
C	0.554753	-0.513535	-1.313556
C	-0.797435	-0.878587	-0.807779
C	-1.725425	0.086779	-0.833920
C	-1.490337	1.482546	-1.247513
C	-0.249280	1.908170	-1.546737
O	1.385195	-1.304691	-1.690953
C	-1.068084	-2.310380	-0.363975
C	-1.024513	-3.247971	-1.583620
C	-0.009474	-2.742069	0.665823
C	-2.448569	-2.435135	0.287969
C	-2.701189	2.403459	-1.256961
C	-3.755186	1.831465	-2.221223
C	-3.280597	2.474673	0.167127
C	-2.345226	3.820477	-1.710016
H	4.102713	1.958083	2.269585
H	5.679868	1.199964	4.039122
H	6.118244	-1.216409	4.339377
H	5.004677	-2.879634	2.884939
H	3.424377	-2.114822	1.119130
H	-2.732705	-0.151300	-0.524147
H	-0.015988	2.933860	-1.796313
H	-1.249084	-4.269231	-1.262876
H	-1.772632	-2.949796	-2.323438
H	-0.043415	-3.240511	-2.056543
H	-0.240503	-3.751264	1.017168
H	-0.004687	-2.066877	1.524509
H	0.989761	-2.751080	0.231461
H	-2.548850	-1.765879	1.146755
H	-3.254194	-2.221370	-0.419461
H	-2.582163	-3.460537	0.640090
H	-4.631213	2.484771	-2.226929
H	-3.360262	1.778349	-3.239115
H	-4.084831	0.832643	-1.928553
H	-4.138737	3.151437	0.174067

H	-2.534060	2.856211	0.868124
H	-3.619921	1.500884	0.524846
H	-1.926303	3.824247	-2.719372
H	-3.250122	4.432321	-1.717850
H	-1.627693	4.290515	-1.033346

Table S311 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.805533	-0.431675	0.366187
C	2.886072	0.372845	0.029283
C	1.994676	-1.777507	0.657026
C	4.162974	-0.175754	-0.016059
C	4.361971	-1.524004	0.274079
C	3.274996	-2.318660	0.609612
H	2.752390	1.423557	-0.199687
C	6.425013	0.565116	-0.498057
H	0.810496	-0.001884	0.400745
H	1.148873	-2.402861	0.919566
H	5.362002	-1.942504	0.236016
H	3.431464	-3.367863	0.835112
N	5.236122	0.664809	-0.360823
O	7.581018	0.586986	-0.662000

Table S312 Cartesian coordinates of the $C_{14}H_{20}O_2$ equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

36

C14H20O2 ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

O	1.353965	2.511224	-1.656387
C	0.344994	1.847346	-1.570175
C	0.475969	0.340093	-1.204486
C	-0.774990	-0.418555	-0.931062
C	-1.932081	0.228166	-1.134967
C	-2.078517	1.626029	-1.592758
C	-0.993788	2.387731	-1.794923
O	1.585764	-0.136235	-1.170411
C	-0.688077	-1.868718	-0.466856
C	-0.048578	-2.726134	-1.573190
C	0.155359	-1.952977	0.817246
C	-2.074959	-2.442350	-0.160539
C	-3.501260	2.125058	-1.804556
C	-4.184068	1.243607	-2.864831
C	-4.273574	2.031058	-0.477175
C	-3.533815	3.576846	-2.286408
H	-2.856438	-0.303316	-0.958335
H	-1.045378	3.421553	-2.109691
H	-0.013715	-3.770202	-1.249761
H	-0.642430	-2.673523	-2.490122

H	0.966512	-2.400208	-1.795022
H	0.167572	-2.986067	1.175107
H	-0.275640	-1.326270	1.603485
H	1.182915	-1.637856	0.642891
H	-2.582003	-1.876644	0.626147
H	-2.714791	-2.459348	-1.047106
H	-1.962543	-3.471965	0.186414
H	-5.206879	1.594437	-3.023998
H	-3.648952	1.300245	-3.816224
H	-4.234566	0.195802	-2.561877
H	-5.293089	2.396014	-0.625332
H	-3.797345	2.644438	0.292149
H	-4.338670	1.006105	-0.106425
H	-3.008242	3.695362	-3.237000
H	-4.571752	3.883325	-2.435435
H	-3.084601	4.252527	-1.554393

Reaction pathway (b)

Table S313 Energy profile of the C₁₄H₂₀O₂-catalyzed conversion (b). The calculations were done at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
	<i>E</i> , kcal/mol	0.0	-7.7	11.8	-34.3	12.3	-64.9	-60.8
Gas phase	<i>E</i> + Δ ZPE, kcal/mol	0.0	-7.2	12.4	-31.3	11.8	-64.3	-60.6
	<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.8	26.9	-16.0	25.6	-50.9	-60.6

Table S314 Cartesian coordinates of the phenyl nitrile oxide equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl nitrile oxide ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-0.067240	-0.063982	0.353909
C	0.797006	1.018735	0.417913
C	0.431386	-1.361016	0.407597
C	2.170887	0.797533	0.536479
C	2.674086	-0.504119	0.590930
C	1.799752	-1.578707	0.525912
H	0.417864	2.033014	0.376538
C	3.071455	1.915930	0.602265
H	-1.133940	0.106124	0.261623
H	-0.248356	-2.204390	0.357279
H	3.741831	-0.663912	0.683323
H	2.188598	-2.589810	0.568143
N	3.795700	2.809513	0.647480
O	4.557272	3.753387	0.696608

Table S315 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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A ES at wB97X-D3(BJ)/def2-TZVP in the benzene

C	-1.797772	0.528095	-1.967680
C	-1.312076	1.379012	-0.863398
C	-0.100615	1.313376	-0.293307
C	0.849521	0.310999	-0.842242
C	0.353887	-0.610045	-1.990706
C	-1.002347	-0.412281	-2.495806
O	1.113572	-1.446617	-2.427951
O	-0.569744	-1.769378	0.498090
C	-3.231675	0.762807	-2.424957
C	-4.173999	0.489141	-1.238957
C	-3.386796	2.220776	-2.890538
C	-3.626127	-0.158203	-3.581390
C	0.332429	2.190126	0.876790
C	-0.794328	3.126526	1.323025
C	0.707367	1.295501	2.072523
C	1.536156	3.056757	0.466093
O	1.989975	0.170209	-0.460658
C	1.553437	-2.498042	1.251081
N	0.515653	-2.158851	0.894973
C	2.870314	-2.873511	1.683708
C	3.047562	-3.990663	2.501950
C	4.325254	-4.336813	2.914713
C	5.418120	-3.574995	2.514501
C	5.235987	-2.463445	1.698750
C	3.963953	-2.106037	1.277366
H	-2.020147	2.102016	-0.483885
H	-1.312880	-1.071172	-3.295730
H	-5.209576	0.648048	-1.550857
H	-4.070669	-0.543758	-0.897131
H	-3.974887	1.149515	-0.392447
H	-4.413729	2.388301	-3.225491
H	-2.714689	2.432504	-3.726228
H	-3.176195	2.935528	-2.092572
H	-3.567051	-1.210923	-3.295100
H	-4.657525	0.053651	-3.873131
H	-2.989023	0.000470	-4.455010
H	-0.441814	3.729600	2.163064
H	-1.093779	3.810589	0.524398
H	-1.674814	2.570013	1.655398
H	0.951568	1.923649	2.933585
H	1.569700	0.668598	1.848744
H	-0.131108	0.649416	2.345813
H	1.271042	3.706878	-0.372696
H	1.832280	3.690750	1.306609
H	2.390173	2.445949	0.177428
H	2.188194	-4.576284	2.806755
H	4.467952	-5.203556	3.550140
H	6.415895	-3.849669	2.838538
H	6.089164	-1.872105	1.386311
H	3.803268	-1.247468	0.636535

Table S316 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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TS1 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-1.916195	0.478862	-1.698875
C	-1.605305	1.072184	-0.392158
C	-0.477106	0.855194	0.303475
C	0.539637	-0.031426	-0.318989
C	0.304757	-0.533256	-1.743870
C	-1.004928	-0.283941	-2.328692
O	1.199437	-1.127220	-2.316949
O	-0.311644	-1.856850	0.299523
C	-3.284059	0.728620	-2.348023
C	-4.214068	1.584453	-1.480875
C	-3.079195	1.449591	-3.690269
C	-3.970638	-0.625534	-2.591128
C	-0.198772	1.485648	1.664519
C	-1.409065	2.278978	2.169405
C	0.115717	0.394167	2.702740
C	0.990553	2.455593	1.552370
O	1.699219	-0.166816	0.143081
C	1.918430	-2.003382	0.707094
N	0.783354	-2.364952	0.644480
C	3.294756	-2.260537	1.039646
C	3.601383	-3.022793	2.168669
C	4.929188	-3.286039	2.468095
C	5.939921	-2.780119	1.657233
C	5.627129	-2.011138	0.540929
C	4.303191	-1.748748	0.223825
H	-2.355463	1.717831	0.034529
H	-1.184184	-0.723859	-3.302648
H	-5.168216	1.704150	-1.999539
H	-4.416243	1.114195	-0.515013
H	-3.804594	2.582471	-1.304696
H	-4.047850	1.630749	-4.164452
H	-2.469598	0.855677	-4.373587
H	-2.584701	2.413268	-3.541116
H	-4.103451	-1.166817	-1.650694
H	-4.955559	-0.464630	-3.038090
H	-3.387962	-1.254662	-3.266245
H	-1.172285	2.699710	3.149477
H	-1.659026	3.108475	1.502672
H	-2.290827	1.642198	2.280096
H	0.243911	0.858279	3.684627
H	1.032669	-0.140116	2.460562
H	-0.702895	-0.326951	2.765624
H	0.767376	3.254715	0.840027
H	1.179100	2.912974	2.527894
H	1.895745	1.942892	1.230448
H	2.802737	-3.403613	2.794400
H	5.175399	-3.881964	3.339570

H	6.977326	-2.984498	1.898403
H	6.417787	-1.617088	-0.087202
H	4.035113	-1.153927	-0.640303

Table S317 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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B ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.016247	0.231137	-1.717285
C	-1.546553	1.041119	-0.571712
C	-0.467781	0.774604	0.168923
C	0.244293	-0.519765	-0.151966
C	0.063324	-1.009730	-1.610674
C	-1.238836	-0.741436	-2.215983
O	0.946359	-1.643962	-2.144399
O	-0.311981	-1.575051	0.665410
C	-3.380385	0.586809	-2.290092
C	-4.427224	0.453801	-1.170143
C	-3.353480	2.033390	-2.813345
C	-3.782003	-0.338727	-3.440349
C	-0.007532	1.646411	1.335139
C	-1.034683	2.744599	1.637245
C	0.166234	0.807036	2.612327
C	1.320309	2.343170	0.980079
O	1.621185	-0.541697	0.167244
C	1.824787	-1.720933	0.804754
N	0.768683	-2.366992	1.102981
C	3.200503	-2.107142	1.131423
C	3.438355	-3.231467	1.923678
C	4.739591	-3.586229	2.239204
C	5.805626	-2.822176	1.771076
C	5.567259	-1.703446	0.983492
C	4.265324	-1.343820	0.659306
H	-2.140717	1.910514	-0.332505
H	-1.494337	-1.318471	-3.094384
H	-5.415208	0.706530	-1.563589
H	-4.458524	-0.571457	-0.792513
H	-4.219532	1.119309	-0.329883
H	-4.328580	2.283421	-3.239453
H	-2.597999	2.146692	-3.595335
H	-3.140894	2.756168	-2.023444
H	-3.818337	-1.382650	-3.119474
H	-4.776896	-0.059208	-3.794821
H	-3.090358	-0.257789	-4.282480
H	-0.683908	3.329992	2.490095
H	-1.155798	3.429328	0.794137
H	-2.010967	2.325128	1.893480
H	0.424153	1.472634	3.440295
H	0.960495	0.066629	2.524278
H	-0.760004	0.286709	2.865536
H	1.205950	2.942793	0.072860

H	1.603160	3.012365	1.797394
H	2.129230	1.631495	0.826265
H	2.601621	-3.815609	2.287980
H	4.924868	-4.459350	2.854827
H	6.823201	-3.101443	2.021862
H	6.396221	-1.108556	0.616837
H	4.073285	-0.476689	0.039338

Table S318 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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TS2 at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.110353	0.058327	-1.289972
C	-1.921420	1.135608	-0.293385
C	-0.944090	1.202956	0.624572
C	0.052239	0.115614	0.573644
C	-0.337079	-1.176281	-0.184848
C	-1.344943	-1.040126	-1.236607
O	0.154319	-2.227421	0.147662
O	1.148733	0.225402	1.099828
C	-3.219300	0.266408	-2.311065
C	-4.564612	0.412319	-1.579104
C	-2.915977	1.547854	-3.107423
C	-3.322270	-0.904721	-3.289074
C	-0.784222	2.343534	1.624339
C	-2.011595	3.259549	1.603964
C	-0.641848	1.764106	3.042684
C	0.451648	3.189156	1.268574
O	2.407034	-1.702877	2.805420
C	2.839061	-1.543880	1.674057
N	2.620895	-0.861486	0.604267
C	4.059888	-2.305106	1.069123
C	3.842135	-3.472563	0.346560
C	4.927865	-4.246878	-0.042946
C	6.218442	-3.841241	0.279161
C	6.430362	-2.662255	0.988889
C	5.349373	-1.884059	1.379109
H	-2.640676	1.941286	-0.332434
H	-1.474939	-1.893067	-1.888895
H	-5.364375	0.529122	-2.314476
H	-4.777255	-0.476886	-0.980249
H	-4.588364	1.283937	-0.921713
H	-3.704894	1.712746	-3.845437
H	-1.963719	1.457111	-3.636456
H	-2.869462	2.431009	-2.466515
H	-3.575418	-1.835386	-2.775341
H	-4.110319	-0.696354	-4.016041
H	-2.388467	-1.052207	-3.837265
H	-1.889724	4.029243	2.369115
H	-2.127883	3.766396	0.642292
H	-2.929744	2.707315	1.823013

H	-0.567877	2.584127	3.761300
H	0.247932	1.142804	3.143779
H	-1.517243	1.162395	3.303117
H	0.355192	3.602980	0.260922
H	0.532535	4.021671	1.972775
H	1.370394	2.606927	1.319556
H	2.828268	-3.765020	0.097216
H	4.767916	-5.160939	-0.604102
H	7.066256	-4.443423	-0.029784
H	7.439520	-2.347306	1.230509
H	5.498062	-0.960423	1.927684

Table S319 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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C ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	-2.455845	-0.067325	-1.421050
C	-1.956538	0.695650	-0.258347
C	-1.211856	0.208873	0.744699
C	-0.886122	-1.241691	0.698991
C	-1.366243	-2.056549	-0.537502
C	-2.166291	-1.369834	-1.548971
O	-1.065233	-3.227054	-0.610626
O	-0.276942	-1.831758	1.560338
C	-3.287664	0.709067	-2.433377
C	-4.546889	1.247693	-1.732910
C	-2.454480	1.882685	-2.978283
C	-3.721201	-0.164289	-3.612622
C	-0.695075	1.058761	1.900917
C	-1.115481	2.523782	1.749971
C	-1.262967	0.535326	3.231666
C	0.843212	1.006342	1.928476
O	1.333783	-0.777449	-1.225807
C	2.187139	-1.188198	-0.536623
N	2.968295	-1.639574	0.247161
C	4.350386	-1.778555	0.440515
C	4.797457	-2.331211	1.635358
C	6.161312	-2.468969	1.856481
C	7.075365	-2.060752	0.892131
C	6.618745	-1.514811	-0.302618
C	5.258205	-1.370516	-0.534117
H	-2.218237	1.743899	-0.241410
H	-2.496000	-1.971518	-2.385485
H	-5.147835	1.813723	-2.449339
H	-5.155041	0.425330	-1.347131
H	-4.303818	1.912512	-0.901336
H	-3.038194	2.423361	-3.727751
H	-1.538303	1.520000	-3.451282
H	-2.178760	2.593322	-2.196932
H	-4.341610	-1.002532	-3.286348
H	-4.309008	0.438590	-4.308756

H	-2.859372	-0.561336	-4.154459
H	-0.710455	3.096117	2.587671
H	-0.728678	2.963627	0.826613
H	-2.203098	2.636552	1.763357
H	-0.909512	1.167930	4.050730
H	-0.948692	-0.488814	3.425884
H	-2.356215	0.571266	3.222153
H	1.257260	1.380356	0.987649
H	1.213518	1.641308	2.738047
H	1.208118	-0.006444	2.093615
H	4.072828	-2.645499	2.377226
H	6.509426	-2.898550	2.789380
H	8.139558	-2.169110	1.068756
H	7.325163	-1.197292	-1.061745
H	4.895277	-0.944441	-1.463043

Table S320 Cartesian coordinates of the phenyl isocyanate equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

14

Phenyl isocyanate ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

C	1.805533	-0.431675	0.366187
C	2.886072	0.372845	0.029283
C	1.994676	-1.777507	0.657026
C	4.162974	-0.175754	-0.016059
C	4.361971	-1.524004	0.274079
C	3.274996	-2.318660	0.609612
H	2.752390	1.423557	-0.199687
C	6.425013	0.565116	-0.498057
H	0.810496	-0.001884	0.400745
H	1.148873	-2.402861	0.919566
H	5.362002	-1.942504	0.236016
H	3.431464	-3.367863	0.835112
N	5.236122	0.664809	-0.360823
O	7.581018	0.586986	-0.662000

Table S321 Cartesian coordinates of the $C_{14}H_{20}O_2$ equilibrium geometry state (ES) obtained at the ω B97X-D3(BJ)/def2-TZVP level of theory in the benzene, which was treated with CPCM continuum solvent model.

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C14H20O2 ES at ω B97X-D3(BJ)/def2-TZVP in the benzene

O	1.353965	2.511224	-1.656387
C	0.344994	1.847346	-1.570175
C	0.475969	0.340093	-1.204486
C	-0.774990	-0.418555	-0.931062
C	-1.932081	0.228166	-1.134967
C	-2.078517	1.626029	-1.592758
C	-0.993788	2.387731	-1.794923
O	1.585764	-0.136235	-1.170411
C	-0.688077	-1.868718	-0.466856
C	-0.048578	-2.726134	-1.573190

C	0.155359	-1.952977	0.817246
C	-2.074959	-2.442350	-0.160539
C	-3.501260	2.125058	-1.804556
C	-4.184068	1.243607	-2.864831
C	-4.273574	2.031058	-0.477175
C	-3.533815	3.576846	-2.286408
H	-2.856438	-0.303316	-0.958335
H	-1.045378	3.421553	-2.109691
H	-0.013715	-3.770202	-1.249761
H	-0.642430	-2.673523	-2.490122
H	0.966512	-2.400208	-1.795022
H	0.167572	-2.986067	1.175107
H	-0.275640	-1.326270	1.603485
H	1.182915	-1.637856	0.642891
H	-2.582003	-1.876644	0.626147
H	-2.714791	-2.459348	-1.047106
H	-1.962543	-3.471965	0.186414
H	-5.206879	1.594437	-3.023998
H	-3.648952	1.300245	-3.816224
H	-4.234566	0.195802	-2.561877
H	-5.293089	2.396014	-0.625332
H	-3.797345	2.644438	0.292149
H	-4.338670	1.006105	-0.106425
H	-3.008242	3.695362	-3.237000
H	-4.571752	3.883325	-2.435435
H	-3.084601	4.252527	-1.554393

3 The effects of the phenyl substitution

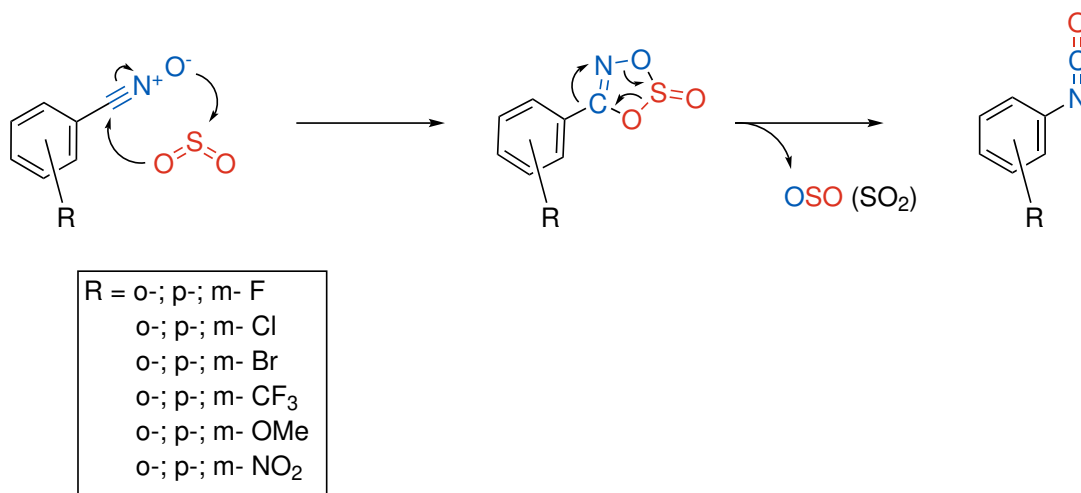


Figure S49 Reaction of the substituted phenyl nitrile oxide with sulfur dioxide.

3.1 –F

Table S322 Energy profile of the SO₂-catalyzed conversion for –F substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
<i>o</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.1	1.2	–22.1	2.7	–56.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.3	2.0	–19.7	3.2	–56.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.9	14.6	–6.4	15.9	–56.0
	Benzene	<i>E</i> , kcal/mol	0.0	–5.9	2.2	–21.1	2.5	–56.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.2	3.0	–18.7	3.0	–55.9
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.8	15.6	–5.6	15.7	–55.7
<i>m</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.0	1.1	–24.2	2.5	–58.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.2	2.0	–21.8	2.8	–58.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.1	14.7	–8.5	15.6	–57.7
	Benzene	<i>E</i> , kcal/mol	0.0	–5.9	2.2	–22.8	2.3	–58.1
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.1	3.1	–20.4	2.7	–57.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.9	15.7	–7.3	15.4	–57.3
<i>p</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.4	0.6	–24.6	1.2	–57.8
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.5	1.4	–22.1	1.7	–57.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.7	14.0	–8.8	14.6	–56.8
	Benzene	<i>E</i> , kcal/mol	0.0	–6.2	1.5	–23.1	1.0	–57.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.4	2.3	–20.7	1.6	–56.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.4	14.8	–7.6	14.3	–56.4

Table S324 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

o-reagent ES at r2SCAN-3c in the gas phase

C	–0.101848	0.018657	0.350296
C	0.810023	1.053443	0.417371
C	0.365749	–1.291480	0.402454
C	2.190188	0.832233	0.536039
C	2.635974	–0.500813	0.586780
C	1.730307	–1.548262	0.520256
F	0.371162	2.321690	0.368084
C	3.082951	1.922162	0.600616
H	–1.158362	0.247484	0.258770
H	–0.341759	–2.112938	0.350491
H	3.700164	–0.689868	0.678715
H	2.090231	–2.571092	0.560344
N	3.763265	2.867101	0.644801
O	4.483124	3.827673	0.693513

14

o-reagent ES at r2SCAN-3c in the benzene

Table S323 Energy profile of the SO₂-catalyzed conversion for –F substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
<i>o</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.5	7.6	–23.0	8.6	–63.6	–59.9
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.7	8.4	–20.6	9.1	–62.6	–59.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.5	21.0	–7.3	21.8	–51.7	–59.1
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	8.7	–21.8	9.0	–62.0	–59.3
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.3	9.6	–19.4	9.5	–61.0	–58.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.6	22.1	–6.3	22.2	–50.3	–58.6
<i>m</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.5	7.4	–25.1	8.4	–65.0	–61.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.6	8.3	–22.7	8.8	–64.0	–60.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	21.0	–9.4	21.6	–53.1	–60.4
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	8.7	–23.4	8.9	–63.1	–60.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.2	9.6	–21.0	9.3	–62.1	–59.9
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.8	22.2	–7.9	21.9	–51.3	–59.7
<i>p</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.7	7.0	–25.5	7.4	–64.7	–60.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.9	7.8	–23.0	7.9	–63.6	–60.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.3	20.5	–9.7	20.7	–53.1	–59.7
	Benzene	<i>E</i> , kcal/mol	0.0	–5.2	8.1	–23.7	7.7	–62.6	–59.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.5	8.9	–21.3	8.3	–61.6	–59.1
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.4	21.4	–8.1	21.0	–51.2	–58.9

C	–0.103417	0.019142	0.350145
C	0.809252	1.052723	0.417520
C	0.365939	–1.290949	0.402318
C	2.188717	0.831205	0.536051
C	2.637663	–0.500889	0.587070
C	1.731260	–1.548126	0.520308
F	0.371446	2.324086	0.368532
C	3.080760	1.922579	0.600346
H	–1.160563	0.246256	0.258439
H	–0.341582	–2.112540	0.350177
H	3.702063	–0.689376	0.679137
H	2.091198	–2.571060	0.560478
N	3.761941	2.864834	0.644492
O	4.486493	3.828106	0.693516

14

m-reagent ES at r2SCAN-3c in the gas phase

C	–0.103120	–0.040136	0.350676
C	0.741911	1.050953	0.412581
C	0.350706	–1.349067	0.401104
C	2.122266	0.817144	0.531514
C	2.608349	–0.500879	0.584963
C	1.721010	–1.565369	0.519303
H	0.342346	2.057505	0.369869
C	3.019073	1.910155	0.597735

F	-1.427893	0.181687	0.236412
H	-0.357547	-2.168686	0.348503
H	3.674844	-0.672553	0.677171
H	2.099497	-2.581910	0.560467
N	3.767845	2.801527	0.645322
O	4.538901	3.722587	0.696259

14

m-reagent ES at r2SCAN-3c in the benzene

C	-0.101702	-0.039664	0.350768
C	0.741300	1.052781	0.412552
C	0.350771	-1.348951	0.401042
C	2.121040	0.815744	0.531514
C	2.609310	-0.501289	0.585130
C	1.721503	-1.566112	0.519288
H	0.342723	2.060114	0.370024
C	3.018384	1.909217	0.597798
F	-1.429264	0.182691	0.236267
H	-0.356716	-2.169694	0.348444
H	3.675967	-0.673065	0.677435
H	2.099514	-2.582865	0.560446
N	3.765678	2.799477	0.645141
O	4.539681	3.724577	0.696032

14

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.099809	-0.071271	0.351026
C	0.772932	1.003800	0.415277
C	0.420881	-1.354996	0.407112
C	2.157559	0.790284	0.534549
C	2.649777	-0.525796	0.588486
C	1.779944	-1.603094	0.524476
H	0.390792	2.018117	0.373921
C	3.047132	1.888942	0.600512
H	-1.170813	0.074071	0.259046
F	-0.425343	-2.401238	0.346099
H	3.717513	-0.693158	0.680848
H	2.141104	-2.625149	0.564403
N	3.787753	2.787211	0.647456
O	4.550709	3.716888	0.697559

14

p-reagent ES at r2SCAN-3c in the benzene

C	-0.100969	-0.070282	0.350875
C	0.771642	1.005248	0.415275
C	0.422682	-1.352825	0.407171
C	2.155699	0.788368	0.534539
C	2.651370	-0.526352	0.588697
C	1.781257	-1.603799	0.524531
H	0.388978	2.019519	0.373949
C	3.045662	1.887564	0.600589
H	-1.172067	0.076072	0.258778

F	-0.425003	-2.401082	0.346019
H	3.719191	-0.693827	0.681112
H	2.143716	-2.625663	0.564602
N	3.785555	2.784095	0.647337
O	4.552415	3.717575	0.697297

Table S325 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-A ES at r2SCAN-3c in the gas phase

C	-0.101254	0.103097	-0.213483
C	0.691466	1.225861	-0.346815
C	0.450065	-1.039518	0.359178
C	2.027147	1.248399	0.073695
C	2.564759	0.083623	0.650468
C	1.776292	-1.047656	0.788561
F	0.177191	2.338706	-0.894932
C	2.810064	2.411778	-0.076474
H	-1.130259	0.135509	-0.555283
H	-0.163381	-1.928187	0.469542
H	3.597911	0.099500	0.980606
H	2.198637	-1.941922	1.234709
N	3.513596	3.329366	-0.179246
O	4.286411	4.259580	-0.255261
O	5.464483	1.975730	1.462646
S	6.402176	2.987597	0.929648
O	7.169286	2.611386	-0.268158

17

o-A ES at r2SCAN-3c in the benzene

C	-0.118963	0.121380	-0.192969
C	0.700751	1.223511	-0.331110
C	0.413024	-1.038857	0.363481
C	2.043263	1.208805	0.066991
C	2.561074	0.027120	0.627295
C	1.745961	-1.084579	0.771360
F	0.207536	2.355608	-0.863532
C	2.849870	2.355212	-0.088417
H	-1.152660	0.181236	-0.517274
H	-0.221279	-1.912326	0.478243
H	3.599445	0.010867	0.940901
H	2.151845	-1.992603	1.205032
N	3.533662	3.283037	-0.219064
O	4.295629	4.224793	-0.316283
O	5.516666	2.060582	1.506440
S	6.403883	3.106059	0.952238
O	7.204883	2.723004	-0.223933

17

m-A ES at r2SCAN-3c in the gas phase

C	-0.080741	0.073303	-0.192616

C	0.653970	1.231852	-0.356798
C	0.447045	-1.077411	0.372624
C	1.990541	1.229955	0.071169
C	2.554027	0.079536	0.648496
C	1.774767	-1.059517	0.791315
H	0.202169	2.109774	-0.803926
C	2.786505	2.391555	-0.073489
F	-1.364807	0.066050	-0.600221
H	-0.175297	-1.959590	0.477471
H	3.587491	0.101781	0.975191
H	2.206795	-1.950067	1.236718
N	3.501079	3.301815	-0.168408
O	4.277910	4.229326	-0.241572
O	5.461084	1.945363	1.469757
S	6.400217	2.955535	0.936849
O	7.161876	2.581570	-0.265011

17

m-A ES at r2SCAN-3c in the benzene

C	-0.090884	0.087966	-0.180201
C	0.665686	1.231812	-0.346023
C	0.413746	-1.078140	0.374213
C	2.005677	1.194579	0.070163
C	2.548705	0.029093	0.636182
C	1.745552	-1.093485	0.781187
H	0.231407	2.123314	-0.784169
C	2.824359	2.340247	-0.075871
F	-1.380771	0.111617	-0.577279
H	-0.226556	-1.947491	0.480954
H	3.585493	0.022681	0.953406
H	2.160788	-1.996116	1.218184
N	3.517493	3.262784	-0.194481
O	4.284707	4.201790	-0.284444
O	5.513237	2.014398	1.500330
S	6.400204	3.060525	0.947187
O	7.185789	2.685257	-0.241788

17

p-A ES at r2SCAN-3c in the gas phase

C	-0.086802	0.039737	-0.191488
C	0.672178	1.189513	-0.341722
C	0.502955	-1.074612	0.386453
C	2.009590	1.211398	0.086115
C	2.579454	0.066080	0.669744
C	1.820571	-1.083271	0.819900
H	0.236352	2.075462	-0.790997
C	2.797433	2.377038	-0.061710
H	-1.121271	-0.002665	-0.514688
F	-0.232721	-2.191857	0.531137
H	3.612441	0.096547	0.999332
H	2.236534	-1.980074	1.266410
N	3.507324	3.290523	-0.160515

O	4.283091	4.221244	-0.235523
O	5.464478	1.938309	1.469201
S	6.396113	2.953689	0.931723
O	7.156180	2.580641	-0.271643

17

p-A ES at r2SCAN-3c in the benzene

C	-0.099826	0.056318	-0.181143
C	0.685834	1.188430	-0.330507
C	0.468523	-1.074150	0.386720
C	2.026532	1.171889	0.088364
C	2.573507	0.010560	0.661384
C	1.787931	-1.121184	0.811490
H	0.268753	2.087517	-0.771488
C	2.838961	2.320567	-0.059287
H	-1.137393	0.042752	-0.497672
F	-0.295166	-2.175375	0.530816
H	3.609255	0.009690	0.983873
H	2.186040	-2.029949	1.250456
N	3.524050	3.248369	-0.183520
O	4.287608	4.192979	-0.276643
O	5.527762	2.012517	1.497428
S	6.399378	3.068378	0.937148
O	7.182152	2.698393	-0.255688

Table S326 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-TS1 at r2SCAN-3c in the gas phase

C	-2.387318	-0.703165	-0.359276
C	-1.488196	0.337214	-0.485078
C	-1.936244	-1.922791	0.136497
C	-0.134930	0.192264	-0.146891
C	0.298898	-1.046652	0.352172
C	-0.599488	-2.091596	0.493395
F	-1.910975	1.519913	-0.954224
C	0.763853	1.278267	-0.284004
H	-3.422617	-0.544787	-0.641959
H	-2.637032	-2.744661	0.244704
H	1.341348	-1.154045	0.629090
H	-0.255785	-3.044167	0.882297
N	1.069435	2.302486	-0.839354
O	1.938544	3.191506	-0.764285
O	2.212215	1.250627	1.125001
S	3.358452	2.178504	0.732682
O	4.351110	1.566513	-0.170226

17

o-TS1 at r2SCAN-3c in the benzene

C	-2.400162	-0.666981	-0.264131
C	-1.484088	0.351905	-0.433623

C	-1.942865	-1.909773	0.165107
C	-0.112908	0.161259	-0.209561
C	0.326325	-1.100892	0.225480
C	-0.586627	-2.125123	0.412018
F	-1.906402	1.558213	-0.841200
C	0.799385	1.229202	-0.379249
H	-3.450444	-0.478000	-0.460161
H	-2.655634	-2.716116	0.308078
H	1.384049	-1.245328	0.417026
H	-0.242229	-3.096791	0.749839
N	1.171457	2.186651	-1.010130
O	2.026757	3.095149	-0.905666
O	2.062873	1.394502	1.191971
S	3.232729	2.308538	0.841094
O	4.339053	1.619014	0.143648

17

m-TS1 at r2SCAN-3c in the gas phase

C	-2.373238	-0.789499	-0.485808
C	-1.529665	0.295265	-0.619957
C	-1.978509	-1.981655	0.104055
C	-0.212436	0.163155	-0.149436
C	0.217136	-1.028311	0.450735
C	-0.673110	-2.086271	0.573596
H	-1.879640	1.212354	-1.079915
C	0.687355	1.255016	-0.285509
F	-3.635413	-0.678494	-0.941611
H	-2.686098	-2.799431	0.188422
H	1.235028	-1.102377	0.812958
H	-0.344791	-3.010027	1.039143
N	0.968725	2.292596	-0.825515
O	1.830994	3.188875	-0.784569
O	2.201642	1.221554	1.076512
S	3.325333	2.159689	0.652400
O	4.285996	1.569371	-0.297490

17

m-TS1 at r2SCAN-3c in the benzene

C	-2.394470	-0.754499	-0.394947
C	-1.542056	0.318270	-0.564626
C	-1.980798	-1.972423	0.124408
C	-0.193841	0.138602	-0.213560
C	0.257297	-1.078992	0.315580
C	-0.643627	-2.121466	0.482606
H	-1.905442	1.259568	-0.961663
C	0.719094	1.213015	-0.388309
F	-3.690086	-0.603444	-0.738504
H	-2.697247	-2.778540	0.244025
H	1.299597	-1.187695	0.591789
H	-0.301869	-3.066346	0.892706
N	1.078231	2.175331	-1.015651
O	1.935028	3.083831	-0.941104

O	2.029418	1.372169	1.158005
S	3.190767	2.285186	0.782420
O	4.279313	1.599243	0.054836

17

p-TS1 at r2SCAN-3c in the gas phase

C	-1.559089	-0.246679	-0.370358
C	-0.733112	0.856028	-0.508845
C	-1.016574	-1.425821	0.121208
C	0.629608	0.756686	-0.179342
C	1.148712	-0.448029	0.319226
C	0.319461	-1.546460	0.474650
H	-1.129535	1.795090	-0.880230
C	1.484293	1.877614	-0.337038
H	-2.612205	-0.202070	-0.626196
F	-1.821489	-2.492632	0.264013
H	2.197675	-0.501635	0.587997
H	0.693187	-2.488754	0.860302
N	1.794811	2.869403	-0.944642
O	2.605560	3.815681	-0.861483
O	2.814591	2.049121	1.197011
S	3.938278	3.008005	0.820987
O	5.034729	2.383193	0.057101

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p-TS1 at r2SCAN-3c in the benzene

C	-1.568313	-0.215875	-0.294551
C	-0.726351	0.870464	-0.463043
C	-1.020505	-1.415782	0.137099
C	0.652420	0.729144	-0.227105
C	1.176005	-0.498056	0.211247
C	0.332640	-1.579868	0.398861
H	-1.122822	1.827028	-0.786886
C	1.517033	1.837994	-0.402625
H	-2.634411	-0.140718	-0.480809
F	-1.841080	-2.466933	0.314359
H	2.239199	-0.586942	0.406536
H	0.707363	-2.539234	0.739386
N	1.885782	2.781033	-1.056279
O	2.686979	3.741505	-0.937752
O	2.685375	2.149322	1.235793
S	3.819590	3.111580	0.900642
O	4.999997	2.454078	0.299485

Table S327 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-B ES at r2SCAN-3c in the gas phase

C	0.041759	0.150393	-0.088139
C	1.029850	1.107751	-0.232405
C	0.374573	-1.095855	0.430302

C	2.361263	0.860696	0.125733
C	2.669245	-0.403440	0.650964
C	1.688136	-1.371448	0.800276
F	0.682368	2.304206	-0.722215
C	3.408679	1.863575	-0.014781
H	-0.972843	0.397681	-0.381811
H	-0.397033	-1.850970	0.544632
H	3.694153	-0.615244	0.933592
H	1.950129	-2.343502	1.204470
N	3.328964	2.948647	-0.698518
O	4.534159	3.655944	-0.582327
O	4.587633	1.602526	0.644092
S	5.809068	2.668978	0.060464
O	6.495789	1.994173	-1.044200

17

o-B ES at r2SCAN-3c in the benzene

C	0.040232	0.151355	-0.087160
C	1.030189	1.105285	-0.233441
C	0.374063	-1.094910	0.432513
C	2.362091	0.859103	0.122326
C	2.671342	-0.405166	0.648228
C	1.688699	-1.371581	0.800161
F	0.683815	2.305187	-0.725748
C	3.408909	1.862293	-0.018589
H	-0.975441	0.397896	-0.378719
H	-0.398150	-1.849088	0.549616
H	3.696076	-0.620130	0.929647
H	1.950416	-2.343559	1.205030
N	3.330841	2.948144	-0.703074
O	4.537603	3.658448	-0.579970
O	4.585567	1.603449	0.641703
S	5.808126	2.670904	0.068693
O	6.491512	1.996480	-1.041085

17

m-B ES at r2SCAN-3c in the gas phase

C	0.076140	0.126087	-0.095733
C	1.045328	1.097054	-0.240667
C	0.340026	-1.128012	0.438395
C	2.350172	0.791531	0.166757
C	2.647757	-0.462554	0.708637
C	1.639935	-1.411350	0.840093
H	0.796892	2.065973	-0.659022
C	3.397721	1.798155	0.024739
F	-1.182961	0.409418	-0.483853
H	-0.461437	-1.853059	0.531995
H	3.660543	-0.691565	1.018747
H	1.870331	-2.385536	1.259556
N	3.247248	2.914241	-0.591856
O	4.436312	3.651846	-0.513808
O	4.615903	1.532322	0.592821

S	5.773754	2.669189	-0.002312
O	6.409106	2.075488	-1.180669

17

m-B ES at r2SCAN-3c in the benzene

C	0.076960	0.125108	-0.094836
C	1.043171	1.098465	-0.241582
C	0.340681	-1.128794	0.438867
C	2.349040	0.793329	0.164532
C	2.648761	-0.460750	0.706360
C	1.641754	-1.410799	0.839501
H	0.789458	2.066984	-0.658282
C	3.396940	1.799783	0.022036
F	-1.185433	0.408654	-0.482699
H	-0.459205	-1.855750	0.534384
H	3.661372	-0.691392	1.016392
H	1.873450	-2.384529	1.259367
N	3.250622	2.916085	-0.596713
O	4.443418	3.653013	-0.513034
O	4.612913	1.533496	0.592053
S	5.774849	2.666677	0.005141
O	6.404018	2.069652	-1.177669

17

p-B ES at r2SCAN-3c in the gas phase

C	0.070725	0.096036	-0.092605
C	1.061758	1.052956	-0.228078
C	0.405642	-1.135475	0.454602
C	2.374558	0.771313	0.176120
C	2.681451	-0.479003	0.723181
C	1.691780	-1.442200	0.866038
H	0.827975	2.025580	-0.647943
C	3.412084	1.784202	0.028835
H	-0.951594	0.290426	-0.398613
F	-0.558330	-2.064704	0.592255
H	3.696785	-0.699702	1.033239
H	1.906698	-2.418518	1.286637
N	3.257147	2.895208	-0.596997
O	4.443513	3.643145	-0.512110
O	4.630596	1.531172	0.604101
S	5.782017	2.671953	0.003874
O	6.423067	2.071641	-1.168506

17

p-B ES at r2SCAN-3c in the benzene

C	0.069199	0.095724	-0.092706
C	1.059348	1.053862	-0.229395
C	0.408277	-1.134273	0.454754
C	2.373085	0.772689	0.173735
C	2.682967	-0.477387	0.721417
C	1.694271	-1.441543	0.865887
H	0.818765	2.025325	-0.648274

C	3.410847	1.785282	0.026231
H	-0.953515	0.290524	-0.397941
F	-0.556451	-2.066323	0.594035
H	3.697896	-0.700019	1.031701
H	1.912241	-2.417041	1.287450
N	3.260343	2.897416	-0.600514
O	4.450695	3.644298	-0.509743
O	4.627800	1.531439	0.602715
S	5.783014	2.668167	0.011407
O	6.417089	2.065890	-1.166730

Table S328 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-TS2 at r2SCAN-3c in the gas phase

C	-0.014056	0.240438	0.217856
C	1.000380	1.158386	0.018580
C	0.327539	-1.091916	0.432143
C	2.343139	0.772266	0.059527
C	2.670995	-0.574250	0.248736
C	1.662368	-1.501541	0.449541
F	0.701081	2.441573	-0.192570
C	3.441207	1.850470	0.049692
H	-1.046525	0.572470	0.194907
H	-0.462510	-1.822307	0.578279
H	3.716592	-0.864785	0.236617
H	1.910213	-2.545705	0.607104
N	3.564882	1.729726	-1.201336
O	4.950316	3.213386	-1.337271
O	3.909284	2.471568	1.030430
S	5.657752	3.394043	-0.009117
O	6.680394	2.385730	0.302352

17

o-TS2 at r2SCAN-3c in the benzene

C	-0.013100	0.251677	0.224212
C	1.007755	1.160353	0.024621
C	0.321701	-1.083672	0.436056
C	2.348833	0.764285	0.063574
C	2.670390	-0.585901	0.247656
C	1.654280	-1.504073	0.450170
F	0.721811	2.449282	-0.184141
C	3.447108	1.830464	0.039543
H	-1.044086	0.589077	0.204088
H	-0.473184	-1.808723	0.582807
H	3.713651	-0.885514	0.233851
H	1.894034	-2.550211	0.607441
N	3.564942	1.735939	-1.214172
O	4.939831	3.220562	-1.336473
O	3.941616	2.449839	1.015723
S	5.637168	3.396994	0.002297

O	6.680300	2.399172	0.288219

17

m-TS2 at r2SCAN-3c in the gas phase

C	-0.044082	0.253580	0.100135
C	0.948173	1.181402	-0.154915
C	0.236917	-1.050192	0.488198
C	2.267090	0.765146	0.027530
C	2.595685	-0.543436	0.383362
C	1.566397	-1.442361	0.627728
H	0.707139	2.189464	-0.473062
C	3.392741	1.833194	0.011988
F	-1.328419	0.621381	-0.048024
H	-0.580889	-1.741563	0.662873
H	3.636801	-0.833642	0.472191
H	1.796776	-2.462221	0.918414
N	3.586037	1.649914	-1.219106
O	5.008166	3.113459	-1.338685
O	3.807215	2.488335	0.993722
S	5.640566	3.341035	0.018805
O	6.623004	2.331784	0.437166

17

m-TS2 at r2SCAN-3c in the benzene

C	-0.040106	0.255099	0.100134
C	0.951973	1.181604	-0.156699
C	0.236613	-1.049628	0.488971
C	2.269877	0.759751	0.029906
C	2.597372	-0.550589	0.384188
C	1.565146	-1.446124	0.629383
H	0.713462	2.191145	-0.473478
C	3.393342	1.818907	0.000280
F	-1.325265	0.626419	-0.048064
H	-0.582114	-1.740322	0.663804
H	3.637441	-0.844990	0.474897
H	1.792415	-2.466309	0.921251
N	3.597920	1.642095	-1.229676
O	5.010707	3.111401	-1.340158
O	3.817945	2.488482	0.974627
S	5.611512	3.355813	0.032608
O	6.611080	2.362524	0.456345

17

p-TS2 at r2SCAN-3c in the gas phase

C	0.325367	0.030454	-0.501864
C	1.431964	0.857520	-0.583322
C	0.340959	-1.002579	0.428902
C	2.533596	0.609118	0.241678
C	2.515488	-0.409496	1.198240
C	1.409872	-1.239284	1.284603
H	1.459756	1.684759	-1.285106
C	3.836181	1.388969	-0.015061

H	-0.545559	0.176010	-1.131620
F	-0.733750	-1.799834	0.513133
H	3.366742	-0.544990	1.857023
H	1.357334	-2.049696	2.003388
N	3.532787	2.253312	0.852639
O	5.279463	3.275629	0.634399
O	4.725555	1.116844	-0.857620
S	5.856106	3.022929	-0.745124
O	5.204619	3.750904	-1.843308

17

p-TS2 at r2SCAN-3c in the benzene

C	0.323756	0.028848	-0.505661
C	1.427219	0.859471	-0.588091
C	0.346163	-1.003677	0.425845
C	2.530423	0.610785	0.236785
C	2.517464	-0.406077	1.197451
C	1.414921	-1.239216	1.282737
H	1.450437	1.685983	-1.291140
C	3.819953	1.400895	-0.005203
H	-0.547509	0.172934	-1.135605
F	-0.726593	-1.804896	0.510887
H	3.369097	-0.541660	1.856060
H	1.366251	-2.050220	2.001410
N	3.523939	2.277654	0.852158
O	5.268486	3.284463	0.633923
O	4.730553	1.136940	-0.837089
S	5.857953	2.989378	-0.736524
O	5.223967	3.718965	-1.846962

Table S329 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-C ES at r2SCAN-3c in the gas phase

C	0.942995	-1.464959	0.047605
C	1.668664	-0.814205	-0.933625
C	0.733399	-0.829277	1.267048
C	2.195436	0.463534	-0.734299
C	1.977625	1.089528	0.497079
C	1.250759	0.444723	1.488165
F	1.872307	-1.422413	-2.115000
C	3.461006	2.100080	-1.991365
H	0.554197	-2.456849	-0.157628
H	0.165678	-1.332399	2.043157
H	2.392302	2.079225	0.665304
H	1.090261	0.942013	2.439279
N	2.913892	1.052578	-1.767322
O	4.028375	3.071334	-2.331207
O	4.281123	4.047660	0.839492
S	5.521188	3.441560	0.327874
O	5.569413	1.972819	0.252662

17

o-C ES at r2SCAN-3c in the benzene

C	0.987491	-1.476685	0.060443
C	1.688895	-0.813767	-0.929673
C	0.760387	-0.831299	1.272535
C	2.175985	0.482308	-0.750148
C	1.938666	1.118309	0.472616
C	1.235539	0.462972	1.474743
F	1.911336	-1.431201	-2.106771
C	3.421807	2.128015	-2.009662
H	0.630279	-2.483821	-0.128937
H	0.211628	-1.342536	2.057091
H	2.317212	2.124963	0.624536
H	1.059459	0.967720	2.419362
N	2.873646	1.077602	-1.795305
O	3.989367	3.099456	-2.345648
O	4.407713	4.099292	0.835972
S	5.590559	3.329082	0.418851
O	5.418651	1.874544	0.267213

17

m-C ES at r2SCAN-3c in the gas phase

C	0.917922	-1.420511	0.087746
C	1.626576	-0.830266	-0.943561
C	0.721887	-0.808586	1.314438
C	2.162268	0.439306	-0.726523
C	1.987514	1.089535	0.499451
C	1.269120	0.457643	1.505121
H	1.759334	-1.340924	-1.890196
C	3.434103	2.074330	-1.984300
F	0.396239	-2.648017	-0.117543
H	0.158655	-1.315406	2.089988
H	2.419544	2.072378	0.658385
H	1.133347	0.960195	2.457797
N	2.873502	1.029401	-1.773604
O	4.007669	3.043313	-2.318177
O	4.379397	3.965639	0.858598
S	5.597575	3.340926	0.318133
O	5.605062	1.874738	0.196050

17

m-C ES at r2SCAN-3c in the benzene

C	0.956364	-1.427194	0.097997
C	1.643592	-0.830273	-0.943728
C	0.747257	-0.810437	1.319790
C	2.145122	0.456236	-0.741846
C	1.954427	1.114893	0.477782
C	1.258408	0.473960	1.494164
H	1.786155	-1.347673	-1.885784
C	3.400950	2.098659	-2.002732
F	0.466906	-2.673650	-0.093688

H	0.201812	-1.323638	2.104265
H	2.353894	2.113587	0.622380
H	1.110527	0.983025	2.441689
N	2.836030	1.053543	-1.799052
O	3.975706	3.066126	-2.336659
O	4.483219	4.011840	0.839683
S	5.661378	3.234663	0.422685
O	5.467966	1.790027	0.214857

17

p-C ES at r2SCAN-3c in the gas phase

C	0.519924	-1.383740	0.026306
C	1.256168	-0.764612	-0.975636
C	0.615656	-0.896805	1.319147
C	2.071977	0.325410	-0.670468
C	2.152591	0.802097	0.641957
C	1.418102	0.185274	1.645204
H	1.204975	-1.121702	-1.998651
C	3.585216	1.805038	-1.887624
H	-0.120166	-2.233193	-0.186284
F	-0.095506	-1.497679	2.296694
H	2.786643	1.652848	0.872589
H	1.464208	0.535657	2.670857
N	2.796471	0.916600	-1.708349
O	4.352323	2.638708	-2.205640
O	4.195443	3.754303	0.831472
S	5.529543	3.950265	0.238281
O	6.515409	2.877491	0.423526

17

p-C ES at r2SCAN-3c in the benzene

C	0.514020	-1.392117	0.026283
C	1.246232	-0.773062	-0.979470
C	0.615337	-0.901389	1.317081
C	2.061683	0.318528	-0.677543
C	2.146176	0.798390	0.633547
C	1.416168	0.182273	1.641194
H	1.190731	-1.133095	-2.001454
C	3.578042	1.793394	-1.891992
H	-0.125662	-2.242769	-0.184164
F	-0.092953	-1.503127	2.300644
H	2.778355	1.651437	0.861597
H	1.465630	0.535570	2.666004
N	2.782628	0.909429	-1.719502
O	4.350911	2.624215	-2.204106
O	4.234541	3.809453	0.866834
S	5.557390	3.976933	0.240846
O	6.529751	2.891899	0.437581

Table S330 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-product ES at r2SCAN-3c in the gas phase

C	1.791152	-0.341164	0.346410
C	2.897022	0.420841	0.016619
C	1.960672	-1.690342	0.640683
C	4.182273	-0.125082	-0.030250
C	4.334598	-1.482890	0.268505
C	3.231670	-2.257690	0.601043
F	2.736633	1.724513	-0.267331
C	6.437334	0.586440	-0.505144
H	0.814946	0.131776	0.368401
H	1.098195	-2.295440	0.900615
H	5.329361	-1.918743	0.235755
H	3.367801	-3.309727	0.830063
N	5.242887	0.705614	-0.370446
O	7.595965	0.609324	-0.670433

14

o-product ES at r2SCAN-3c in the benzene

C	1.790209	-0.340372	0.346176
C	2.898210	0.418358	0.017480
C	1.959294	-1.690382	0.640538
C	4.182962	-0.127749	-0.029109
C	4.335710	-1.485513	0.269680
C	3.230738	-2.258713	0.601639
F	2.740727	1.726038	-0.267574
C	6.437500	0.588762	-0.506121
H	0.813440	0.132422	0.367893
H	1.095457	-2.294096	0.899745
H	5.329913	-1.922760	0.237312
H	3.366175	-3.311021	0.830668
N	5.243666	0.705110	-0.370164
O	7.596508	0.617343	-0.673674

14

m-product ES at r2SCAN-3c in the gas phase

C	1.781277	-0.406842	0.363295
C	2.842701	0.413480	0.024514
C	1.931048	-1.751518	0.659389
C	4.119356	-0.147992	-0.017647
C	4.309121	-1.502974	0.275724
C	3.214704	-2.288783	0.610290
H	2.684890	1.461824	-0.200410
C	6.378945	0.562717	-0.490683
F	0.546612	0.134386	0.407140
H	1.065794	-2.350790	0.919334
H	5.307339	-1.928432	0.239965
H	3.362465	-3.340008	0.837782
N	5.183563	0.688480	-0.359799
O	7.537765	0.581692	-0.652655

14

m-product ES at r2SCAN-3c in the benzene

C	1.782819	-0.407168	0.362984
C	2.843517	0.414266	0.024819
C	1.929462	-1.751818	0.659229
C	4.119444	-0.149866	-0.016285
C	4.309415	-1.504895	0.277113
C	3.213657	-2.290122	0.610973
H	2.686286	1.463158	-0.200107
C	6.379553	0.564294	-0.491754
F	0.545446	0.136759	0.405873
H	1.064266	-2.352084	0.918645
H	5.307199	-1.931599	0.241833
H	3.360421	-3.341599	0.838353
N	5.185145	0.686926	-0.358832
O	7.538950	0.588988	-0.656604

14

p-product ES at r2SCAN-3c in the gas phase

C	1.782295	-0.434769	0.369823
C	2.868750	0.362597	0.033654
C	2.000136	-1.772250	0.654962
C	4.152047	-0.184296	-0.012884
C	4.346198	-1.538377	0.279092
C	3.263911	-2.339886	0.615615
H	2.731582	1.414102	-0.194812
C	6.409826	0.546888	-0.491257
H	0.776910	-0.029878	0.412237
F	0.946758	-2.550172	0.983171
H	5.345986	-1.961479	0.242122
H	3.391837	-3.392274	0.845782
N	5.214479	0.656556	-0.355722
O	7.568926	0.579079	-0.657474

14

p-product ES at r2SCAN-3c in the benzene

C	1.781314	-0.433770	0.369583
C	2.869030	0.363164	0.033949
C	2.001139	-1.770874	0.654124
C	4.151376	-0.186557	-0.011473
C	4.347146	-1.540567	0.280358
C	3.263616	-2.341442	0.616244
H	2.730776	1.414837	-0.194258
C	6.410013	0.547513	-0.491964
H	0.776422	-0.026776	0.411025
F	0.944430	-2.550441	0.982349
H	5.346401	-1.964948	0.243971
H	3.392417	-3.394113	0.846061
N	5.215744	0.654693	-0.354842
O	7.569818	0.585122	-0.660817

Table S331 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

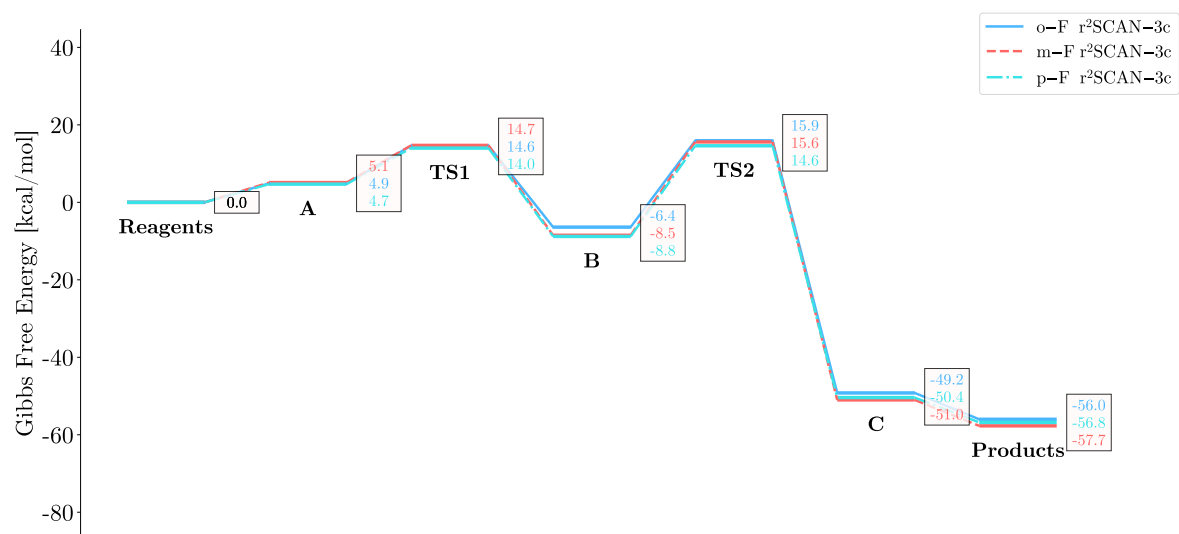
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

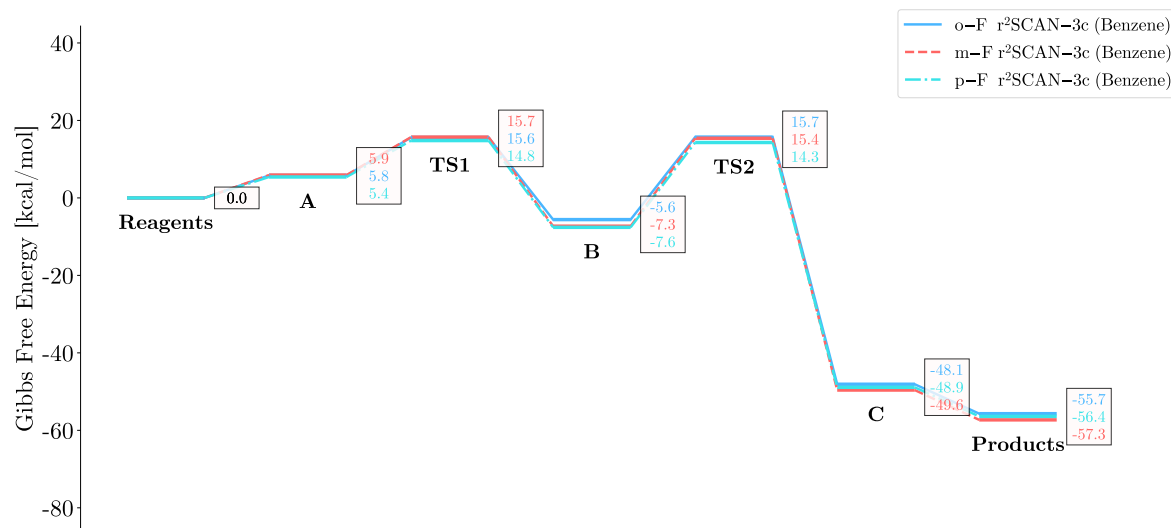
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

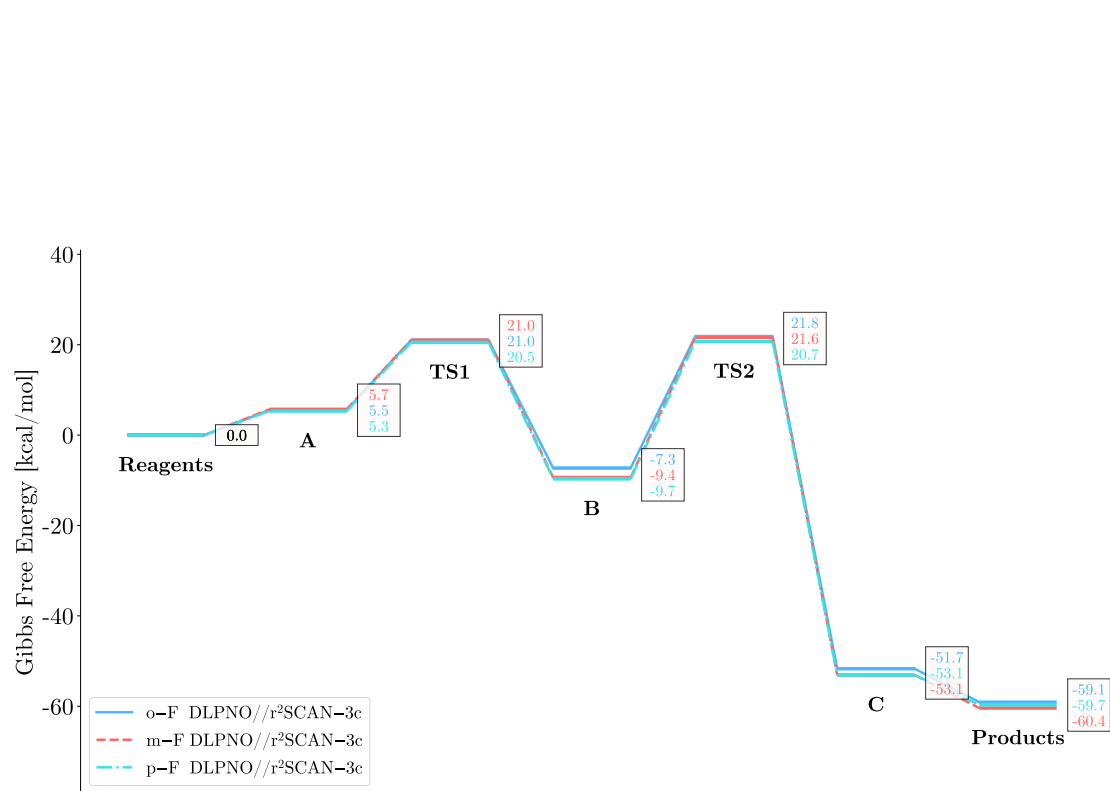


(a) Reaction in the gas phase.

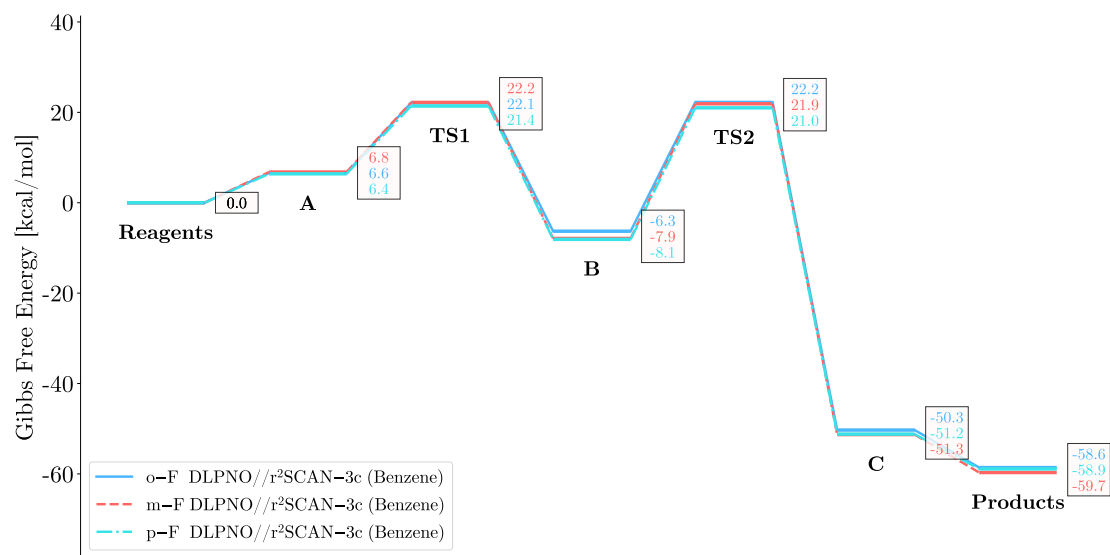


(b) Reaction in the benzene.

Figure S50 Calculated PES for reaction of the -F substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S51 Calculated PES for reaction of the -F substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

3.2 –Cl

Table S332 Energy profile of the SO₂-catalyzed conversion for –Cl substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	2.3	–20.2	2.8	–61.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.4	3.2	–17.9	3.3	–60.6
		<i>E</i> + Δ G, kcal/mol	0.0	4.6	16.0	–4.5	16.2	–48.3
	Benzene	<i>E</i> , kcal/mol	0.0	–6.0	2.7	–19.2	2.6	–60.1
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.2	3.5	–16.8	3.1	–59.2
		<i>E</i> + Δ G, kcal/mol	0.0	6.6	16.3	–3.6	16.0	–47.2
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.0	1.1	–24.2	2.5	–62.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.2	1.9	–21.8	2.9	–61.6
		<i>E</i> + Δ G, kcal/mol	0.0	5.2	14.8	–8.4	15.8	–50.8
	Benzene	<i>E</i> , kcal/mol	0.0	–5.9	2.2	–22.7	2.4	–61.5
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.1	3.0	–20.4	2.8	–60.5
		<i>E</i> + Δ G, kcal/mol	0.0	6.0	15.3	–7.2	15.5	–49.6
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	–2.9	–24.4	1.7	–62.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.4	–2.2	–22.0	2.2	–61.2
		<i>E</i> + Δ G, kcal/mol	0.0	4.7	10.5	–8.6	15.1	–49.0
	Benzene	<i>E</i> , kcal/mol	0.0	–6.0	1.8	–22.9	1.5	–60.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.3	2.7	–20.5	2.0	–59.7
		<i>E</i> + Δ G, kcal/mol	0.0	6.4	15.2	–7.4	14.7	–47.7

Table S334 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

o-reagent ES at r2SCAN-3c in the gas phase

C	–0.065797	–0.063555	0.353772
C	0.799461	1.015964	0.417858
C	0.433388	–1.362803	0.407923
C	2.187377	0.818210	0.537433
C	2.668962	–0.504844	0.590602
C	1.801196	–1.585089	0.526387
H	0.423218	2.032658	0.377034
C	3.065840	1.919659	0.602115
H	–1.133310	0.108575	0.261445
H	–0.241448	–2.211487	0.358048
H	2.199817	–2.592835	0.569167
N	3.799841	2.823044	0.647964
O	4.553268	3.757552	0.696120
Cl	4.381941	–0.784954	0.738865

14

o-reagent ES at r2SCAN-3c in the benzene

Table S333 Energy profile of the SO₂-catalyzed conversion for –Cl substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
<i>o</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–3.8	11.2	–18.8	11.4	–61.7	–57.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–3.0	12.1	–16.4	11.8	–60.7	–57.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	8.0	24.9	–3.0	24.8	–48.4	–56.7
	Benzene	<i>E</i> , kcal/mol	0.0	–5.2	8.8	–20.4	8.9	–62.8	–59.9
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.5	9.7	–18.0	9.4	–61.9	–59.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	7.3	22.4	–4.8	22.2	–49.8	–59.1
<i>m</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.5	7.3	–25.1	8.3	–65.3	–61.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.6	8.2	–22.7	8.7	–64.3	–60.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.8	21.0	–9.4	21.6	–53.5	–60.4
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	8.6	–23.5	8.8	–63.3	–60.5
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.3	9.4	–21.1	9.2	–62.3	–60.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.8	21.7	–7.9	21.9	–51.5	–59.8
<i>p</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.6	7.2	–25.3	7.9	–65.0	–61.0
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.8	8.0	–22.9	8.4	–64.0	–60.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.3	20.7	–9.6	21.2	–51.8	–60.1
	Benzene	<i>E</i> , kcal/mol	0.0	–1.7	8.3	–23.6	8.3	–60.1	–60.1
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–0.9	9.2	–21.2	8.8	–59.2	–59.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	10.7	21.7	–8.0	21.5	–47.2	–59.4

C	–0.056313	–0.054213	0.354598
C	0.818873	1.018055	0.418700
C	0.430522	–1.358847	0.408380
C	2.204150	0.802729	0.538010
C	2.672713	–0.523663	0.590577
C	1.796542	–1.596607	0.526500
H	0.452719	2.038576	0.378094
C	3.095326	1.895462	0.602634
H	–1.122240	0.128148	0.262364
H	–0.252744	–2.200890	0.358373
H	2.183340	–2.609173	0.568721
N	3.774331	2.839220	0.645776
O	4.489965	3.808815	0.693726
Cl	4.386572	–0.817517	0.738279

14

m-reagent ES at r2SCAN-3c in the gas phase

C	–0.087115	–0.046322	0.352097
C	0.769683	1.041048	0.415404
C	0.383676	–1.354498	0.403724
C	2.150891	0.811337	0.534470
C	2.640130	–0.504815	0.588017
C	1.753868	–1.569080	0.522095
H	0.384543	2.053106	0.374039
C	3.042573	1.908159	0.600277

Cl	-1.807575	0.238620	0.203343
H	-0.310524	-2.185833	0.352075
H	3.707094	-0.674980	0.680335
H	2.131600	-2.585998	0.563013
N	3.786563	2.803595	0.646851
O	4.552784	3.728621	0.696139

14

m-reagent ES at r2SCAN-3c in the benzene

C	-0.085554	-0.045843	0.352270
C	0.769168	1.042967	0.415398
C	0.383764	-1.354524	0.403868
C	2.149746	0.809876	0.534374
C	2.641140	-0.505306	0.588057
C	1.754366	-1.569911	0.522157
H	0.385151	2.055775	0.374190
C	3.041777	1.907305	0.600052
Cl	-1.809064	0.239793	0.202941
H	-0.309628	-2.186857	0.352289
H	3.708258	-0.675486	0.680276
H	2.131454	-2.587082	0.563048
N	3.784317	2.801566	0.646585
O	4.553294	3.730688	0.696374

14

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.075777	-0.062160	0.352925
C	0.791026	1.016923	0.417292
C	0.438639	-1.353980	0.408039
C	2.176325	0.811574	0.536660
C	2.671925	-0.502741	0.590757
C	1.806235	-1.582621	0.526487
H	0.401642	2.028553	0.375520
C	3.060887	1.913158	0.601902
H	-1.144797	0.095229	0.260575
H	3.739978	-0.668540	0.683269
H	2.187561	-2.597013	0.567734
N	3.802318	2.810904	0.648331
O	4.566027	3.739231	0.697167
Cl	-0.653775	-2.715710	0.327103

14

p-reagent ES at r2SCAN-3c in the benzene

C	-0.076935	-0.061000	0.352846
C	0.790243	1.018419	0.417370
C	0.440543	-1.351542	0.408142
C	2.174797	0.809261	0.536674
C	2.673682	-0.503601	0.591035
C	1.807489	-1.583762	0.526641
H	0.400441	2.030002	0.375621
C	3.060037	1.911385	0.601800
H	-1.145867	0.097925	0.260403

H	3.741747	-0.669799	0.683572
H	2.190164	-2.597819	0.568016
N	3.799821	2.808180	0.648017
O	4.566154	3.740767	0.696908
Cl	-0.654097	-2.715607	0.326714

Table S335 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-A ES at r2SCAN-3c in the gas phase

C	-0.091443	0.070068	-0.194889
C	0.670571	1.218973	-0.345817
C	0.481790	-1.061155	0.376654
C	2.013208	1.252089	0.071006
C	2.574973	0.098800	0.647191
C	1.810244	-1.046436	0.795957
C	2.800027	2.414477	-0.075978
H	-0.118231	-1.958266	0.493012
H	3.610277	0.134791	0.969073
H	2.252690	-1.931388	1.241615
N	3.519734	3.320745	-0.167614
O	4.302258	4.242874	-0.235828
O	5.457257	1.940791	1.472284
S	6.404941	2.944800	0.941838
O	7.165190	2.565185	-0.259258
H	-1.124866	0.066304	-0.523692
Cl	-0.037211	2.641247	-1.059607

17

o-A ES at r2SCAN-3c in the benzene

C	-0.108386	0.081495	-0.180626
C	0.674141	1.215646	-0.335534
C	0.450990	-1.062615	0.380518
C	2.021923	1.221822	0.065134
C	2.569416	0.056336	0.630412
C	1.784697	-1.074952	0.784410
C	2.826952	2.371285	-0.086497
H	-0.164531	-1.948696	0.500815
H	3.609054	0.068590	0.940203
H	2.215348	-1.969851	1.221886
N	3.536936	3.281842	-0.197852
O	4.314923	4.210899	-0.282419
O	5.508718	2.006492	1.505315
S	6.412071	3.042410	0.959332
O	7.199571	2.659537	-0.225850
H	-1.145785	0.097153	-0.497043
Cl	-0.014630	2.656505	-1.036258

17

m-A ES at r2SCAN-3c in the gas phase

C	-0.067811	0.068589	-0.187767

C	0.678106	1.225882	-0.347697
C	0.476346	-1.078248	0.381689
C	2.014795	1.228392	0.079583
C	2.581912	0.080608	0.657443
C	1.803926	-1.058224	0.800147
H	0.239504	2.111051	-0.793257
C	2.805475	2.393251	-0.067049
Cl	-1.735271	0.055976	-0.716091
H	-0.130880	-1.969557	0.494431
H	3.615626	0.105218	0.983864
H	2.234976	-1.949326	1.245627
N	3.515329	3.307224	-0.162140
O	4.288222	4.237697	-0.235113
O	5.477172	1.947180	1.472113
S	6.414186	2.958840	0.937905
O	7.173020	2.586278	-0.266138

17

m-A ES at r2SCAN-3c in the benzene

C	-0.079404	0.082649	-0.171890
C	0.688379	1.224593	-0.336598
C	0.443148	-1.080215	0.385313
C	2.030095	1.191171	0.074327
C	2.577915	0.028161	0.639437
C	1.776092	-1.093881	0.787566
H	0.266412	2.122978	-0.772142
C	2.843555	2.339694	-0.076761
Cl	-1.755787	0.110719	-0.680614
H	-0.182455	-1.958516	0.501999
H	3.615985	0.023714	0.953162
H	2.191539	-1.996922	1.223684
N	3.533386	3.264358	-0.198292
O	4.297268	4.205399	-0.290545
O	5.523066	2.025622	1.509450
S	6.412366	3.070078	0.956906
O	7.203070	2.691227	-0.227453

17

p-A ES at r2SCAN-3c in the gas phase

C	-0.086392	0.068156	-0.195318
C	0.675740	1.215672	-0.344312
C	0.489570	-1.061405	0.378851
C	2.013506	1.233198	0.080154
C	2.578232	0.083567	0.658451
C	1.814455	-1.062526	0.806418
H	0.239364	2.103012	-0.790438
C	2.804731	2.396422	-0.065019
H	3.611793	0.106273	0.987030
H	2.242895	-1.953847	1.251447
N	3.517525	3.308325	-0.159679
O	4.294556	4.236925	-0.231358
O	5.468879	1.940780	1.468811

S	6.409177	2.950488	0.936126
O	7.166374	2.576975	-0.268763
H	-1.120307	0.047299	-0.521497
Cl	-0.470702	-2.507854	0.565994

17

p-A ES at r2SCAN-3c in the benzene

C	-0.098440	0.082494	-0.184556
C	0.688226	1.213696	-0.333777
C	0.458259	-1.061478	0.380021
C	2.029311	1.195553	0.081146
C	2.573488	0.031497	0.649390
C	1.785357	-1.098330	0.798390
H	0.268928	2.113164	-0.771952
C	2.843409	2.342880	-0.064594
H	3.609731	0.024969	0.970350
H	2.197880	-2.000865	1.236164
N	3.532727	3.268382	-0.183919
O	4.298869	4.209692	-0.272905
O	5.527422	2.011124	1.495759
S	6.411770	3.060185	0.943278
O	7.192606	2.689240	-0.250297
H	-1.135064	0.088123	-0.503383
Cl	-0.535082	-2.488864	0.567782

Table S336 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-TS1 at r2SCAN-3c in the gas phase

C	-2.405260	-0.647450	-0.080249
C	-1.490807	0.366425	-0.308384
C	-1.954330	-1.935583	0.203299
C	-0.112272	0.097019	-0.281511
C	0.324883	-1.209006	0.006894
C	-0.594072	-2.220335	0.250796
H	-1.818055	1.379972	-0.515336
C	0.822775	1.142920	-0.491116
H	-3.468664	-0.434712	-0.113946
H	-2.668056	-2.731820	0.391934
H	-0.241573	-3.222057	0.470674
N	1.322950	1.950766	-1.235271
O	2.159633	2.878124	-1.161754
O	1.687500	1.732123	1.232280
S	2.938771	2.553834	0.938481
O	4.151242	1.753602	0.684656
Cl	2.023277	-1.554865	0.045877

17

o-TS1 at r2SCAN-3c in the benzene

C	-2.399566	-0.635377	-0.041617
C	-1.482898	0.373643	-0.283194

C	-1.952979	-1.931623	0.212533
C	-0.106822	0.088156	-0.295338
C	0.325218	-1.224865	-0.030693
C	-0.594082	-2.232061	0.221527
H	-1.805778	1.392453	-0.471044
C	0.831961	1.125910	-0.517161
H	-3.461598	-0.413180	-0.043759
H	-2.669063	-2.723839	0.409352
H	-0.248275	-3.240622	0.420576
N	1.382482	1.886896	-1.275852
O	2.231763	2.810386	-1.184018
O	1.619763	1.790626	1.211494
S	2.876816	2.612357	0.935568
O	4.105476	1.802036	0.797547
Cl	2.025524	-1.581941	-0.028597

17

m-TS1 at r2SCAN-3c in the gas phase

C	-2.355448	-0.752078	-0.367033
C	-1.500654	0.331189	-0.486428
C	-1.920249	-1.975404	0.135541
C	-0.157932	0.168992	-0.106052
C	0.299229	-1.053868	0.402243
C	-0.590381	-2.111698	0.520120
H	-1.854992	1.280733	-0.870555
C	0.738271	1.264440	-0.234523
Cl	-4.025962	-0.568824	-0.849317
H	-2.615066	-2.803298	0.223664
H	1.336372	-1.151029	0.699650
H	-0.244543	-3.061969	0.914284
N	1.013502	2.311508	-0.759514
O	1.877972	3.205300	-0.710954
O	2.271900	1.197596	1.100751
S	3.390617	2.144404	0.681936
O	4.337365	1.574006	-0.293814

17

m-TS1 at r2SCAN-3c in the benzene

C	-2.361484	-0.738190	-0.321578
C	-1.499434	0.335183	-0.472776
C	-1.925046	-1.967908	0.163735
C	-0.145590	0.150601	-0.145693
C	0.315461	-1.078373	0.345222
C	-0.583051	-2.124089	0.498483
H	-1.853429	1.291608	-0.840460
C	0.759683	1.232958	-0.311226
Cl	-4.049520	-0.531773	-0.739001
H	-2.625976	-2.787658	0.278987
H	1.361893	-1.193312	0.602864
H	-0.236811	-3.079542	0.879471
N	1.074629	2.235969	-0.896831
O	1.935971	3.139219	-0.829398

O	2.177683	1.291394	1.143605
S	3.312449	2.228579	0.747153
O	4.342573	1.595334	-0.102556

17

p-TS1 at r2SCAN-3c in the gas phase

C	-2.434954	-0.701081	-0.250900
C	-1.546695	0.347031	-0.423720
C	-1.951813	-1.935561	0.176471
C	-0.175120	0.145743	-0.194613
C	0.292800	-1.104055	0.238356
C	-0.598507	-2.146812	0.428026
H	-1.904689	1.319576	-0.744922
C	0.738396	1.213743	-0.381434
H	-3.494470	-0.560374	-0.434927
H	1.351282	-1.244212	0.428500
H	-0.248133	-3.116449	0.764300
N	1.106168	2.169391	-1.015945
O	1.966121	3.077663	-0.927426
O	2.039154	1.377345	1.170803
S	3.200045	2.293085	0.798765
O	4.296133	1.606029	0.082907
Cl	-3.075879	-3.252086	0.408534

17

p-TS1 at r2SCAN-3c in the benzene

C	-2.434954	-0.701081	-0.250900
C	-1.546695	0.347031	-0.423720
C	-1.951813	-1.935561	0.176471
C	-0.175120	0.145743	-0.194613
C	0.292800	-1.104055	0.238356
C	-0.598507	-2.146812	0.428026
H	-1.904689	1.319576	-0.744922
C	0.738396	1.213743	-0.381434
H	-3.494470	-0.560374	-0.434927
H	1.351282	-1.244212	0.428500
H	-0.248133	-3.116449	0.764300
N	1.106168	2.169391	-1.015945
O	1.966121	3.077663	-0.927426
O	2.039154	1.377345	1.170803
S	3.200045	2.293085	0.798765
O	4.296133	1.606029	0.082907
Cl	-3.075879	-3.252086	0.408534

Table S337 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-B ES at r2SCAN-3c in the gas phase

C	0.024911	0.083869	0.003586
C	0.968095	1.090386	-0.176334
C	0.415091	-1.165772	0.466462

C	2.324987	0.853421	0.104166
C	2.692079	-0.414219	0.582264
C	1.751976	-1.415701	0.758591
C	3.382642	1.849639	-0.059717
H	-1.016099	0.293219	-0.216461
H	-0.332526	-1.941431	0.601323
H	3.737208	-0.601889	0.801739
H	2.063718	-2.389556	1.121530
N	3.404999	2.804336	-0.916011
O	4.594033	3.530842	-0.770459
O	4.471213	1.706183	0.771535
S	5.769457	2.668470	0.177430
O	6.575577	1.824635	-0.709606
Cl	0.391266	2.639703	-0.723595

17

o-B ES at r2SCAN-3c in the benzene

C	0.022048	0.087019	0.012263
C	0.966798	1.090686	-0.170774
C	0.415289	-1.164939	0.468876
C	2.325090	0.851853	0.098625
C	2.695420	-0.417276	0.570891
C	1.754266	-1.417757	0.750937
C	3.382586	1.847652	-0.070514
H	-1.021088	0.296383	-0.198333
H	-0.332579	-1.939853	0.607067
H	3.741827	-0.608983	0.781937
H	2.067011	-2.393140	1.109146
N	3.416710	2.781824	-0.949492
O	4.601955	3.520362	-0.795358
O	4.455606	1.728110	0.780992
S	5.760200	2.684319	0.193788
O	6.579254	1.822089	-0.666632
Cl	0.388233	2.647788	-0.706976

17

m-B ES at r2SCAN-3c in the gas phase

C	0.087610	0.117147	-0.091390
C	1.066875	1.085031	-0.232523
C	0.368620	-1.136183	0.448516
C	2.372776	0.784852	0.175435
C	2.674721	-0.466659	0.719238
C	1.668626	-1.415915	0.851358
H	0.832080	2.057177	-0.650662
C	3.416624	1.795476	0.031519
Cl	-1.547429	0.479525	-0.598960
H	-0.419752	-1.874254	0.549692
H	3.688242	-0.692672	1.029908
H	1.898441	-2.389787	1.272063
N	3.259663	2.914023	-0.578935
O	4.447370	3.653930	-0.504861
O	4.638268	1.529324	0.590923

S	5.790507	2.672614	-0.006242
O	6.419529	2.085603	-1.191258

17

m-B ES at r2SCAN-3c in the benzene

C	0.087908	0.116639	-0.087905
C	1.063384	1.087648	-0.231370
C	0.369636	-1.137408	0.449039
C	2.371103	0.787202	0.172320
C	2.676265	-0.464823	0.714039
C	1.671571	-1.415939	0.848253
H	0.822781	2.060120	-0.645805
C	3.414853	1.797848	0.026443
Cl	-1.552187	0.479769	-0.590840
H	-0.416656	-1.877510	0.551879
H	3.690142	-0.692753	1.022633
H	1.903801	-2.389778	1.267708
N	3.264321	2.912154	-0.594683
O	4.454556	3.653113	-0.513492
O	4.631691	1.536116	0.595980
S	5.789887	2.672313	0.005861
O	6.419713	2.074519	-1.176240

17

p-B ES at r2SCAN-3c in the gas phase

C	0.076401	0.092107	-0.101805
C	1.066973	1.049627	-0.234168
C	0.396326	-1.146910	0.449897
C	2.377273	0.771272	0.177507
C	2.679607	-0.477640	0.728253
C	1.688934	-1.440297	0.866731
H	0.832294	2.020136	-0.658457
C	3.415503	1.784246	0.034715
H	-0.939255	0.300559	-0.419498
H	3.692299	-0.700205	1.045687
H	1.918078	-2.410911	1.292324
N	3.255461	2.903013	-0.576101
O	4.441911	3.647857	-0.496861
O	4.638343	1.523532	0.596098
S	5.786270	2.670208	-0.000595
O	6.417044	2.084874	-1.185740
Cl	-0.855066	-2.353913	0.622021

17

p-B ES at r2SCAN-3c in the benzene

C	0.072569	0.093327	-0.096175
C	1.061848	1.052637	-0.230552
C	0.399468	-1.145778	0.450616
C	2.374633	0.773473	0.173453
C	2.682459	-0.476467	0.720122
C	1.693596	-1.440948	0.861387
H	0.818442	2.023548	-0.649165

C	3.412728	1.786478	0.027653
H	-0.944735	0.303594	-0.407877
H	3.696184	-0.701453	1.032875
H	1.927893	-2.411811	1.284039
N	3.261349	2.897414	-0.600763
O	4.449225	3.644976	-0.512454
O	4.628681	1.534361	0.605932
S	5.784112	2.671701	0.015345
O	6.421658	2.069357	-1.160557
Cl	-0.851713	-2.356854	0.626130

Table S338 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-TS2 at r2SCAN-3c in the gas phase

C	-2.430135	-0.446071	0.180614
C	-1.441381	0.497046	-0.067019
C	-2.071184	-1.772242	0.401804
C	-0.093990	0.108001	-0.059567
C	0.254648	-1.231575	0.137569
C	-0.734270	-2.169249	0.382328
C	1.020113	1.174118	-0.103391
H	-3.470730	-0.140554	0.191227
H	-2.851419	-2.505400	0.582970
H	1.303082	-1.508842	0.097581
H	-0.468536	-3.208322	0.545589
N	1.142069	1.012862	-1.348696
O	2.544012	2.480708	-1.528049
O	1.490294	1.818834	0.860331
S	3.249229	2.697717	-0.204457
O	4.264461	1.693283	0.142150
Cl	-1.872649	2.151493	-0.347564

17

o-TS2 at r2SCAN-3c in the benzene

C	-2.428535	-0.439552	0.182867
C	-1.434663	0.496830	-0.062331
C	-2.074573	-1.768777	0.401061
C	-0.088107	0.100542	-0.052609
C	0.255869	-1.242148	0.139569
C	-0.739387	-2.173602	0.382146
C	1.023654	1.156705	-0.112500
H	-3.468339	-0.130844	0.194768
H	-2.858911	-2.498284	0.579361
H	1.302732	-1.526472	0.101590
H	-0.479843	-3.214464	0.544068
N	1.150187	1.008685	-1.359034
O	2.537341	2.481052	-1.530567
O	1.508251	1.812787	0.843492
S	3.222986	2.710461	-0.194552
O	4.258265	1.721094	0.144831

Cl	-1.853313	2.157795	-0.338741

17

m-TS2 at r2SCAN-3c in the gas phase

C	0.018449	0.198695	0.204404
C	1.002379	1.145522	-0.038588
C	0.345048	-1.126855	0.484986
C	2.332451	0.733330	0.039280
C	2.691166	-0.592513	0.282881
C	1.682582	-1.514489	0.522227
H	0.753602	2.173838	-0.274857
C	3.448464	1.811986	0.033850
Cl	-1.660163	0.672541	0.135505
H	-0.444943	-1.849473	0.659513
H	3.737638	-0.877759	0.293129
H	1.932744	-2.550114	0.729120
N	3.549415	1.737450	-1.219721
O	4.949341	3.222992	-1.318032
O	3.934809	2.380737	1.035664
S	5.687752	3.333906	-0.000250
O	6.702035	2.299436	0.244708

17

m-TS2 at r2SCAN-3c in the benzene

C	0.022011	0.204255	0.208639
C	1.006869	1.148684	-0.036634
C	0.342682	-1.123498	0.487151
C	2.335472	0.727725	0.040537
C	2.691368	-0.600560	0.280020
C	1.678851	-1.517913	0.520960
H	0.762484	2.179182	-0.269504
C	3.450253	1.797168	0.020113
Cl	-1.656799	0.685590	0.144860
H	-0.448812	-1.844419	0.663184
H	3.736462	-0.891850	0.288837
H	1.924527	-2.554777	0.726759
N	3.561169	1.730804	-1.232774
O	4.951744	3.217454	-1.320729
O	3.947623	2.378053	1.015869
S	5.663181	3.342060	0.014600
O	6.693683	2.321272	0.261931

17

p-TS2 at r2SCAN-3c in the gas phase

C	-2.426450	-0.441898	0.158800
C	-1.433122	0.491512	-0.087788
C	-2.062917	-1.764703	0.408922
C	-0.095598	0.093391	-0.048084
C	0.261111	-1.240665	0.163599
C	-0.729487	-2.175536	0.411017
H	-1.683763	1.524851	-0.303463
C	1.017448	1.160787	-0.087742

H	-3.472541	-0.156988	0.146586
H	1.306646	-1.530765	0.144181
H	-0.479881	-3.214945	0.592778
N	1.078322	1.099062	-1.345935
O	2.473693	2.582094	-1.477222
O	1.549042	1.727683	0.896217
S	3.251542	2.677689	-0.179698
O	4.272515	1.639979	0.021901
Cl	-3.309966	-2.942557	0.705919

17

p-TS2 at r2SCAN-3c in the benzene

C	-2.424141	-0.436926	0.160238
C	-1.428010	0.492436	-0.088711
C	-2.062692	-1.760347	0.412244
C	-0.091567	0.086495	-0.045109
C	0.263108	-1.249283	0.166748
C	-0.731353	-2.179205	0.415992
H	-1.676370	1.526621	-0.303861
C	1.018524	1.144933	-0.103952
H	-3.468801	-0.146268	0.147774
H	1.307275	-1.545138	0.149414
H	-0.484189	-3.218938	0.599924
N	1.091323	1.088467	-1.361443
O	2.473569	2.574323	-1.484247
O	1.560644	1.729344	0.871496
S	3.222035	2.688557	-0.166467
O	4.262301	1.667883	0.040385
Cl	-3.315061	-2.933965	0.709563

Table S339 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-C ES at r2SCAN-3c in the gas phase

C	0.627046	-1.443426	0.009021
C	1.383050	-0.838990	-0.987739
C	0.621442	-0.909240	1.291747
C	2.140672	0.306224	-0.712039
C	2.127073	0.834532	0.583776
C	1.371730	0.228787	1.576304
C	3.613372	1.822199	-1.916356
H	0.029539	-1.385477	2.066746
H	2.715468	1.722623	0.794550
H	1.371403	0.649935	2.576691
N	2.885790	0.884497	-1.729865
O	4.333502	2.694185	-2.236886
O	4.152896	3.817464	0.797309
S	5.498519	4.003997	0.227783
O	6.465617	2.913398	0.407966
H	0.048355	-2.329100	-0.229659
Cl	1.385041	-1.513892	-2.595840

17

o-C ES at r2SCAN-3c in the benzene

C	0.620207	-1.450899	0.009495
C	1.373760	-0.847922	-0.990092
C	0.620291	-0.913062	1.291409
C	2.133812	0.297133	-0.720964
C	2.125302	0.828349	0.573882
C	1.372962	0.225483	1.571000
C	3.603944	1.811482	-1.925065
H	0.030494	-1.387141	2.069491
H	2.714899	1.716927	0.780160
H	1.376167	0.648681	2.570670
N	2.876075	0.872551	-1.743779
O	4.324929	2.684924	-2.239049
O	4.186337	3.873084	0.828195
S	5.526407	4.033258	0.238099
O	6.476501	2.928405	0.432444
H	0.038669	-2.336749	-0.222742
Cl	1.369760	-1.526788	-2.599644

17

m-C ES at r2SCAN-3c in the gas phase

C	0.638187	-1.420701	0.021412
C	1.386393	-0.834208	-0.989636
C	0.617269	-0.905663	1.311809
C	2.133695	0.305329	-0.690820
C	2.131810	0.845718	0.598613
C	1.372496	0.231726	1.584615
H	1.395644	-1.245194	-1.992226
C	3.605722	1.817070	-1.907856
Cl	-0.304434	-2.850094	-0.348278
H	0.025386	-1.384313	2.083299
H	2.718070	1.732686	0.817165
H	1.367031	0.646168	2.588110
N	2.877882	0.877306	-1.723492
O	4.325088	2.688552	-2.230321
O	4.155030	3.821145	0.804170
S	5.500307	4.008401	0.234260
O	6.467513	2.917483	0.411895

17

m-C ES at r2SCAN-3c in the benzene

C	0.971732	-1.407381	0.108219
C	1.654187	-0.797580	-0.934765
C	0.765093	-0.772900	1.326829
C	2.144440	0.495030	-0.742782
C	1.950612	1.159461	0.472322
C	1.263435	0.517239	1.492919
H	1.808332	-1.304597	-1.880349
C	3.400813	2.129982	-2.010795
Cl	0.351928	-3.033069	-0.127949

H	0.228538	-1.273305	2.125087
H	2.339324	2.163587	0.609925
H	1.110973	1.028666	2.438544
N	2.824657	1.090687	-1.806927
O	3.981818	3.092622	-2.346153
O	4.514671	3.972253	0.864123
S	5.685963	3.173175	0.469689
O	5.453196	1.749824	0.173867

17

p-C ES at r2SCAN-3c in the gas phase

C	0.628335	-1.438280	0.017113
C	1.383376	-0.834969	-0.979577
C	0.630945	-0.894290	1.296096
C	2.133835	0.305479	-0.693890
C	2.130334	0.844433	0.596121
C	1.376428	0.242012	1.592869
H	1.395105	-1.244088	-1.984217
C	3.605833	1.820247	-1.908818
H	2.716512	1.731514	0.816685
H	1.368780	0.653665	2.596249
N	2.878808	0.879904	-1.725394
O	4.324920	2.693702	-2.228576
O	4.148751	3.814089	0.807579
S	5.495010	4.001441	0.239854
O	6.460404	2.908564	0.415191
H	0.042233	-2.324922	-0.197872
Cl	-0.319020	-1.652865	2.556607

17

p-C ES at r2SCAN-3c in the benzene

C	0.625917	-1.445582	0.018456
C	1.376605	-0.844720	-0.983842
C	0.635139	-0.895213	1.294531
C	2.127107	0.297530	-0.703816
C	2.128845	0.841842	0.584036
C	1.379728	0.242634	1.587006
H	1.383363	-1.258457	-1.986818
C	3.593602	1.812546	-1.918506
H	2.714380	1.730666	0.799950
H	1.376355	0.658962	2.588719
N	2.868207	0.869427	-1.740872
O	4.312089	2.688494	-2.232628
O	4.178133	3.881468	0.840038
S	5.522445	4.018157	0.253667
O	6.449607	2.893004	0.444135
H	0.039845	-2.333482	-0.192592
Cl	-0.310780	-1.651639	2.564557

Table S340 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

o-product ES at r2SCAN-3c in the gas phase

C	1.800757	-0.429209	0.365980
C	2.885822	0.371360	0.030472
C	1.995100	-1.774201	0.655361
C	4.179914	-0.163491	-0.020114
C	4.359233	-1.520178	0.274149
C	3.276154	-2.318243	0.608875
C	6.435830	0.552617	-0.497122
H	0.809648	0.010212	0.397861
H	1.143559	-2.393996	0.916792
H	5.362834	-1.934467	0.235013
H	3.434460	-3.368267	0.833817
N	5.241461	0.663937	-0.359119
O	7.593853	0.583261	-0.665501
Cl	2.630642	2.057583	-0.330096

14

o-product ES at r2SCAN-3c in the benzene

C	1.799480	-0.428306	0.365572
C	2.887384	0.368799	0.031499
C	1.993315	-1.774084	0.654928
C	4.181025	-0.166432	-0.018330
C	4.360117	-1.523221	0.276048
C	3.274567	-2.319397	0.609636
C	6.437019	0.555805	-0.498920
H	0.807839	0.010447	0.397062
H	1.140766	-2.393161	0.915379
H	5.363002	-1.939264	0.237803
H	3.431416	-3.369781	0.834576
N	5.243558	0.661702	-0.357292
O	7.595067	0.594545	-0.671287
Cl	2.634711	2.059267	-0.330305

14

m-product ES at r2SCAN-3c in the gas phase

C	1.795037	-0.416364	0.363625
C	2.866453	0.398165	0.025713
C	1.961280	-1.764376	0.658154
C	4.144748	-0.159941	-0.017317
C	4.338427	-1.513773	0.274977
C	3.244948	-2.300172	0.609121
H	2.724318	1.448119	-0.201660
C	6.400573	0.558494	-0.493049
Cl	0.189696	0.281397	0.419720
H	1.106459	-2.377639	0.919159
H	5.337487	-1.937818	0.238695
H	3.392187	-3.351613	0.836410
N	5.204994	0.681270	-0.360131
O	7.558971	0.579490	-0.657177

14

m-product ES at r2SCAN-3c in the benzene

C	1.796924	-0.416826	0.363346
C	2.867422	0.399230	0.025920
C	1.959485	-1.765014	0.658026
C	4.144920	-0.161879	-0.015993
C	4.338571	-1.515792	0.276452
C	3.243930	-2.301689	0.609818
H	2.725804	1.449626	-0.201429
C	6.401223	0.560155	-0.494351
Cl	0.188562	0.284290	0.418567
H	1.104995	-2.379462	0.918461
H	5.337180	-1.941075	0.240757
H	3.389767	-3.353405	0.837062
N	5.206625	0.679477	-0.359221
O	7.560173	0.587604	-0.661175

14

p-product ES at r2SCAN-3c in the gas phase

C	1.799305	-0.425943	0.365273
C	2.883754	0.373010	0.029741
C	2.005293	-1.770003	0.652852
C	4.167696	-0.171213	-0.017562
C	4.361211	-1.525043	0.274064
C	3.279487	-2.326174	0.609724
H	2.742898	1.424294	-0.197766
C	6.424009	0.555570	-0.495094
H	0.799376	-0.007896	0.403575
H	5.360332	-1.949942	0.237675
H	3.423669	-3.376908	0.836797
N	5.228268	0.670191	-0.360199
O	7.582548	0.585444	-0.661157
Cl	0.639431	-2.780840	1.076790

14

p-product ES at r2SCAN-3c in the benzene

C	1.798460	-0.424787	0.364856
C	2.885194	0.372796	0.030409
C	2.005494	-1.768620	0.651929
C	4.167808	-0.175268	-0.015198
C	4.361622	-1.529244	0.276525
C	3.277880	-2.329089	0.611074
H	2.743920	1.424285	-0.196887
C	6.425223	0.559119	-0.497341
H	0.799707	-0.003320	0.401397
H	5.359890	-1.956077	0.241235
H	3.422571	-3.380010	0.837855
N	5.230708	0.664674	-0.357458
O	7.583881	0.600118	-0.668498
Cl	0.634920	-2.780029	1.074815

Table S341 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

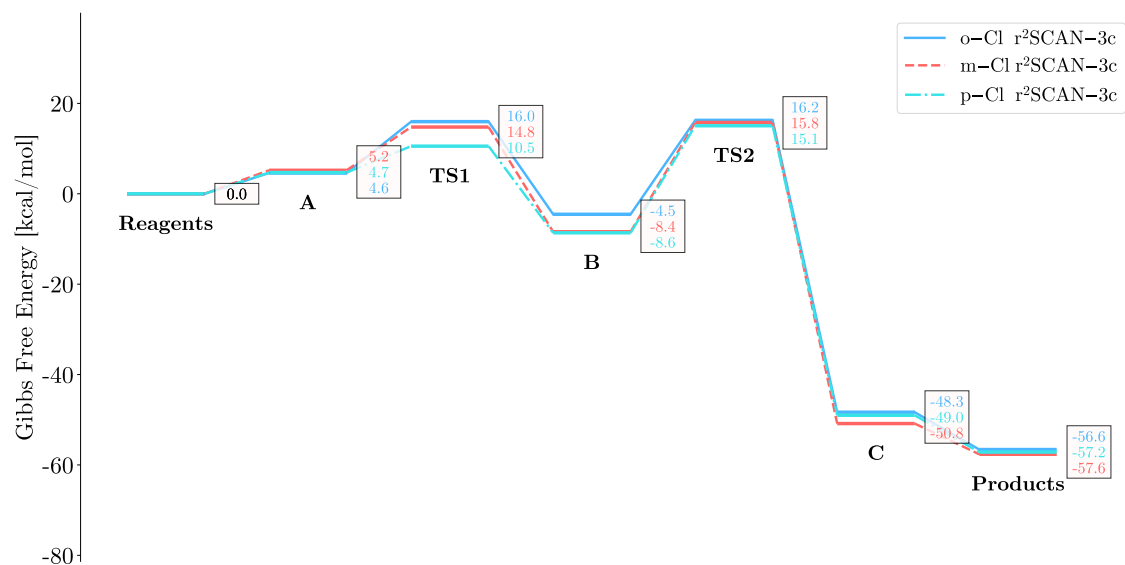
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

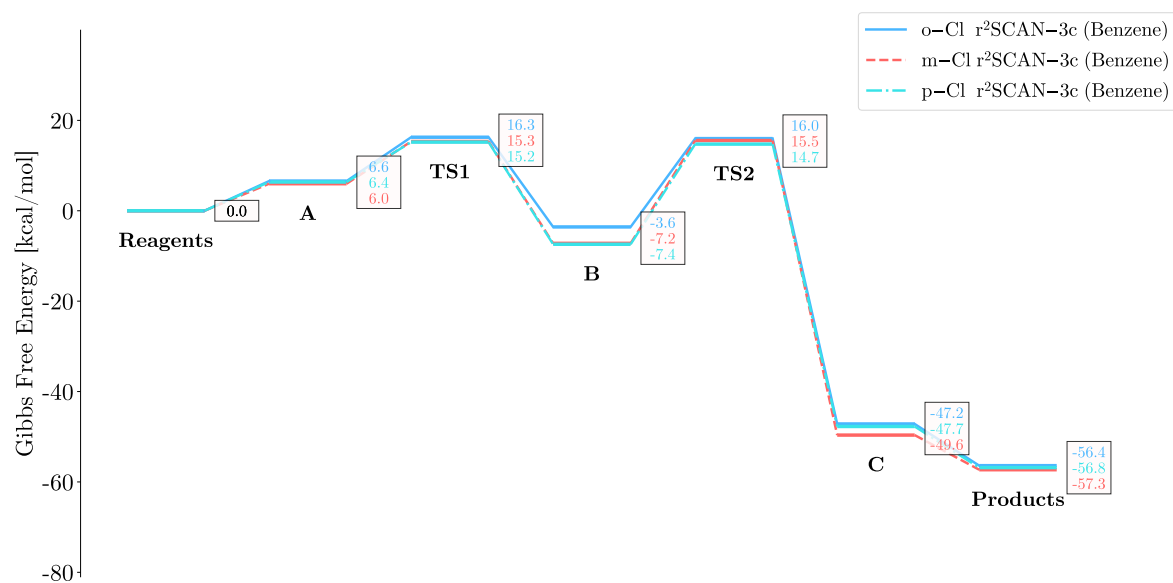
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

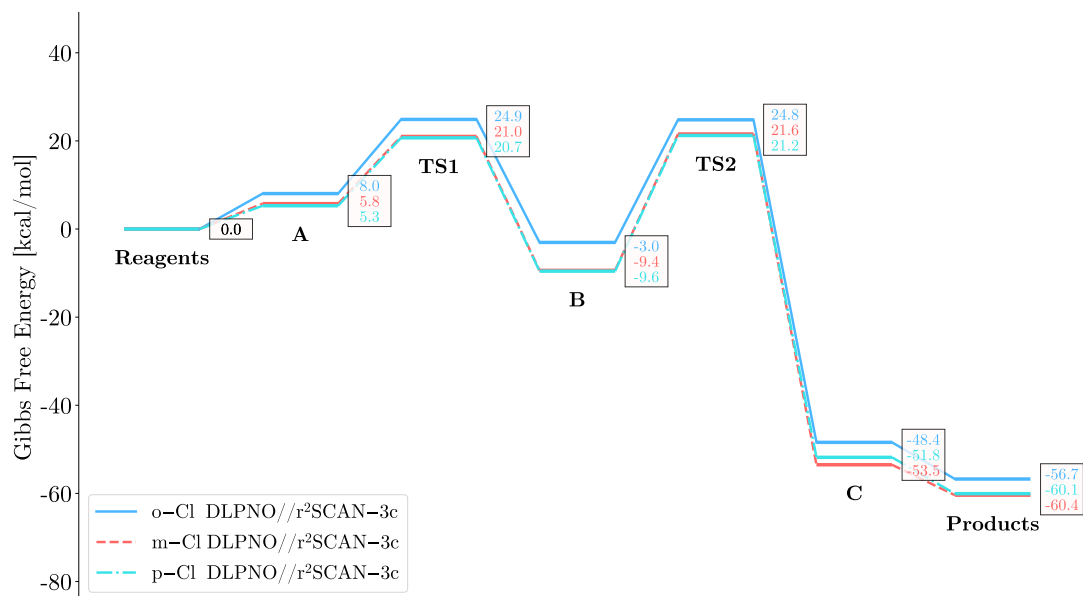


(a) Reaction in the gas phase.

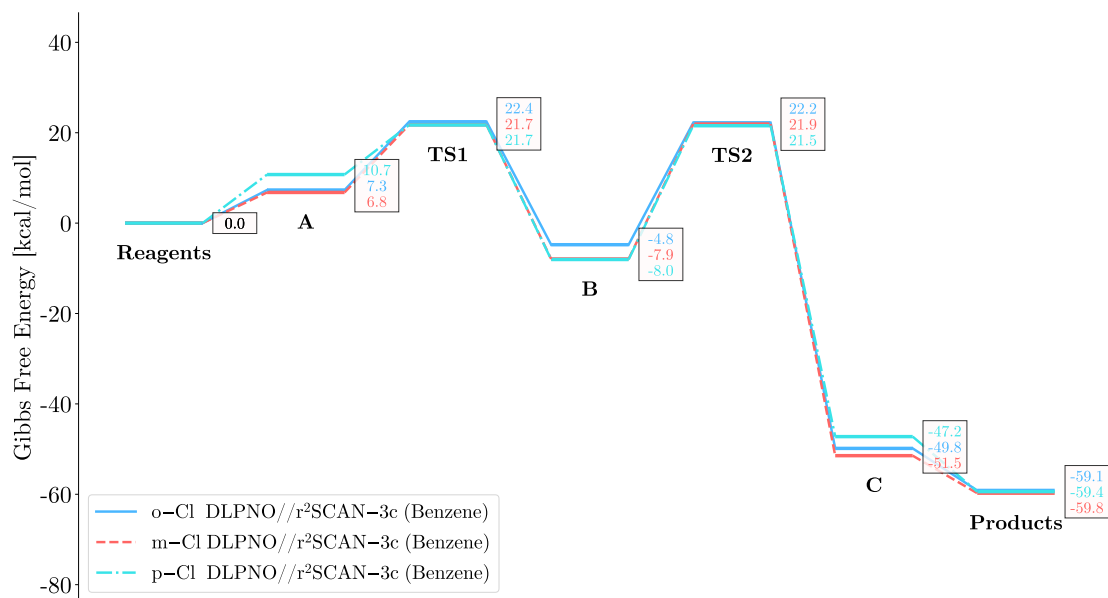


(b) Reaction in the benzene.

Figure S52 Calculated PES for reaction of the -Cl substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S53 Calculated PES for reaction of the -Cl substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

3.3 –Br

Table S342 Energy profile of the SO₂-catalyzed conversion for –Br substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	1.8	–19.9	2.8	–57.8
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.4	2.7	–17.6	3.2	–57.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.9	15.5	–4.2	16.1	–57.0
	Benzene	<i>E</i> , kcal/mol	0.0	–6.0	2.9	–18.9	2.6	–57.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.2	3.7	–16.5	3.1	–56.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.0	16.4	–3.2	15.9	–56.7
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.0	1.1	–24.1	2.5	–58.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.2	1.9	–21.7	2.9	–58.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.3	14.9	–8.3	15.9	–57.6
	Benzene	<i>E</i> , kcal/mol	0.0	–5.9	2.2	–22.7	2.4	–58.1
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.1	3.0	–20.4	2.8	–57.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.0	15.7	–7.1	15.6	–57.3
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	1.0	–24.4	1.8	–58.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.3	1.9	–22.0	2.3	–57.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.0	14.5	–8.6	15.1	–57.2
	Benzene	<i>E</i> , kcal/mol	0.0	–6.0	2.0	–22.9	1.7	–57.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.2	2.8	–20.5	2.1	–57.1
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.8	15.4	–7.4	14.8	–56.9

Table S344 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

14

o-reagent ES at r2SCAN-3c in the gas phase

C	–0.111866	–0.049583	0.350175
C	0.752365	1.032945	0.412149
C	0.400576	–1.341950	0.406161
C	2.142775	0.848789	0.530759
C	2.636425	–0.468735	0.585504
C	1.772770	–1.549526	0.523648
Br	0.047136	2.797375	0.336818
C	3.030699	1.943479	0.595387
H	–1.179149	0.119384	0.259012
H	–0.279592	–2.186504	0.357513
H	3.707168	–0.617255	0.677228
H	2.171297	–2.558107	0.567184
N	3.851878	2.768300	0.652941
O	4.678688	3.637378	0.714052

14

o-reagent ES at r2SCAN-3c in the benzene

Table S343 Energy profile of the SO₂-catalyzed conversion for –Br substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
<i>o</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.7	7.9	–21.4	8.3	–64.5	–60.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.9	8.7	–19.1	8.7	–63.5	–60.1
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.5	21.6	–5.7	21.6	–52.6	–59.9
	Benzene	<i>E</i> , kcal/mol	0.0	–5.3	9.1	–20.1	8.7	–62.8	–60.0
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.5	9.9	–17.7	9.1	–61.8	–59.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	22.6	–4.4	22.0	–51.1	–59.3
<i>m</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.6	7.3	–25.1	8.3	–65.2	–61.3
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.7	8.1	–22.7	8.6	–64.1	–60.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.8	21.1	–9.3	21.6	–53.1	–60.3
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	8.6	–23.5	8.7	–63.3	–60.5
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.4	9.5	–21.1	9.1	–62.3	–60.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	22.1	–7.9	21.9	–51.3	–59.8
<i>p</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.6	7.3	–25.3	8.0	–64.9	–61.0
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.7	8.1	–22.8	8.4	–63.8	–60.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.6	20.8	–9.5	21.3	–52.8	–60.1
	Benzene	<i>E</i> , kcal/mol	0.0	–5.2	8.4	–23.6	8.4	–62.9	–60.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.4	9.2	–21.2	8.9	–61.9	–59.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.6	21.8	–8.0	21.6	–51.1	–59.5

C	–0.113309	–0.048990	0.350004
C	0.752201	1.032217	0.412225
C	0.400615	–1.341516	0.406071
C	2.141968	0.847280	0.530689
C	2.638136	–0.469077	0.585714
C	1.773323	–1.549626	0.523693
Br	0.048048	2.800352	0.337194
C	3.030278	1.942819	0.595351
H	–1.181010	0.118473	0.258703
H	–0.279536	–2.186215	0.357357
H	3.708976	–0.617603	0.677544
H	2.171607	–2.558372	0.567346
N	3.849820	2.767007	0.652667
O	4.680053	3.639242	0.713972

14

m-reagent ES at r2SCAN-3c in the gas phase

C	–0.074085	–0.049773	0.353115
C	0.780311	1.038360	0.415845
C	0.395224	–1.357588	0.404814
C	2.162559	0.809095	0.535004
C	2.651914	–0.506814	0.588815
C	1.766213	–1.571484	0.523181
H	0.398140	2.051387	0.374557
C	3.052815	1.906953	0.600600

Br	-1.951441	0.261334	0.191676
H	-0.295825	-2.191334	0.353749
H	3.718952	-0.676672	0.681212
H	2.143785	-2.588529	0.564315
N	3.793555	2.805191	0.647432
O	4.556074	3.732834	0.697567

14

m-reagent ES at r2SCAN-3c in the benzene

C	-0.072753	-0.049375	0.353273
C	0.779506	1.040316	0.415948
C	0.395393	-1.357641	0.404843
C	2.161117	0.807871	0.535073
C	2.652903	-0.506970	0.589003
C	1.766871	-1.572061	0.523227
H	0.398436	2.054077	0.374863
C	3.051565	1.906493	0.600622
Br	-1.953503	0.262097	0.191209
H	-0.294527	-2.192686	0.353660
H	3.720099	-0.676743	0.681386
H	2.143789	-2.589368	0.564258
N	3.791617	2.802928	0.647216
O	4.557676	3.734024	0.697299

14

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.072541	-0.041989	0.353368
C	0.799500	1.033750	0.417934
C	0.437364	-1.334821	0.408207
C	2.183622	0.821660	0.537089
C	2.673808	-0.494403	0.590895
C	1.802880	-1.571074	0.526432
H	0.414147	2.046974	0.376396
C	3.072724	1.919774	0.602428
H	-1.140243	0.123353	0.261150
Br	-0.761653	-2.814696	0.319229
H	3.741081	-0.665472	0.683283
H	2.182790	-2.585860	0.567663
N	3.812622	2.818903	0.648718
O	4.574032	3.748513	0.697980

14

p-reagent ES at r2SCAN-3c in the benzene

C	-0.073838	-0.040990	0.353278
C	0.798206	1.035290	0.418069
C	0.439204	-1.332629	0.408253
C	2.181723	0.819942	0.537211
C	2.675386	-0.494699	0.591254
C	1.804267	-1.571778	0.526583
H	0.411993	2.048314	0.376542
C	3.071227	1.918624	0.602463
H	-1.141509	0.125484	0.260910

Br	-0.761733	-2.815231	0.318681
H	3.742686	-0.666107	0.683699
H	2.185832	-2.586133	0.567893
N	3.810651	2.815771	0.648461
O	4.576035	3.748752	0.697473

Table S345 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-A ES at r2SCAN-3c in the gas phase

C	-0.089524	0.051907	-0.187188
C	0.662965	1.205720	-0.343463
C	0.495328	-1.074234	0.383991
C	2.006813	1.251420	0.065900
C	2.580442	0.103097	0.642265
C	1.825377	-1.047610	0.796761
Br	-0.130481	2.747712	-1.122860
C	2.789523	2.416700	-0.084846
H	-1.124518	0.036572	-0.510164
H	-0.097067	-1.975861	0.504852
H	3.616868	0.148008	0.959607
H	2.277156	-1.928053	1.242199
N	3.532517	3.305116	-0.168354
O	4.325514	4.217675	-0.235264
O	5.464299	1.922034	1.486625
S	6.415438	2.925978	0.962622
O	7.183942	2.546668	-0.233282

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o-A ES at r2SCAN-3c in the benzene

C	-0.101709	0.063765	-0.176439
C	0.671344	1.203413	-0.334072
C	0.467609	-1.075752	0.385681
C	2.019373	1.221820	0.063918
C	2.576985	0.060756	0.630152
C	1.801777	-1.076611	0.787111
Br	-0.099536	2.765379	-1.101539
C	2.821729	2.373676	-0.087399
H	-1.139890	0.066922	-0.490076
H	-0.141232	-1.966234	0.508086
H	3.617009	0.081636	0.938276
H	2.240841	-1.967235	1.225098
N	3.544884	3.274708	-0.192201
O	4.329996	4.197811	-0.272929
O	5.504759	1.988611	1.517600
S	6.417445	3.015938	0.970796
O	7.203204	2.624248	-0.212664

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m-A ES at r2SCAN-3c in the gas phase

C	-0.058076	0.064470	-0.186439

C	0.682792	1.224216	-0.345067
C	0.486478	-1.080270	0.385057
C	2.019149	1.231356	0.085880
C	2.587939	0.085659	0.665927
C	1.813347	-1.055478	0.807559
H	0.245748	2.109151	-0.792347
C	2.806602	2.398307	-0.061259
Br	-1.874286	0.043303	-0.772427
H	-0.115734	-1.974887	0.497334
H	3.620955	0.113366	0.994528
H	2.245995	-1.945065	1.254680
N	3.522229	3.308140	-0.153966
O	4.296856	4.236826	-0.227050
O	5.495148	1.939504	1.465597
S	6.427600	2.957141	0.934814
O	7.181888	2.595090	-0.275270

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m-A ES at r2SCAN-3c in the benzene

C	-0.062799	0.077695	-0.183422
C	0.704093	1.220743	-0.337977
C	0.451689	-1.083489	0.383361
C	2.040137	1.190675	0.094192
C	2.580666	0.029310	0.669136
C	1.778815	-1.093979	0.806530
H	0.290673	2.119220	-0.781244
C	2.853125	2.340492	-0.047533
Br	-1.881670	0.104093	-0.770342
H	-0.171252	-1.964481	0.492638
H	3.614017	0.026369	0.998220
H	2.188986	-1.995892	1.250065
N	3.530630	3.274593	-0.167002
O	4.287383	4.221575	-0.256095
O	5.551063	2.014412	1.480218
S	6.430989	3.065947	0.925830
O	7.198084	2.703548	-0.279025

17

p-A ES at r2SCAN-3c in the gas phase

C	-0.071559	0.069695	-0.191624
C	0.687440	1.219421	-0.346327
C	0.509829	-1.054764	0.385120
C	2.025854	1.241806	0.075210
C	2.595604	0.096158	0.656093
C	1.834933	-1.052095	0.809727
H	0.247472	2.104022	-0.794460
C	2.813373	2.407160	-0.075297
H	-1.105840	0.047714	-0.516185
Br	-0.532950	-2.634792	0.598752
H	3.629766	0.122503	0.982716
H	2.269464	-1.939060	1.257257
N	3.531653	3.314996	-0.168640

O	4.309329	4.242462	-0.241447
O	5.484253	1.953059	1.473149
S	6.420576	2.968772	0.944931
O	7.184701	2.600643	-0.257245

17

p-A ES at r2SCAN-3c in the benzene

C	-0.079307	0.085451	-0.183510
C	0.707068	1.217286	-0.334731
C	0.478043	-1.056101	0.383944
C	2.047756	1.200549	0.081466
C	2.592328	0.038088	0.652026
C	1.804274	-1.092374	0.802921
H	0.287324	2.115600	-0.774979
C	2.860946	2.348455	-0.064897
H	-1.115340	0.093277	-0.503906
Br	-0.605510	-2.612574	0.593603
H	3.628361	0.032190	0.973860
H	2.220035	-1.992085	1.243159
N	3.542485	3.279309	-0.187733
O	4.303874	4.224016	-0.278120
O	5.536641	2.035570	1.496904
S	6.421446	3.082890	0.941685
O	7.203477	2.708153	-0.249962

Table S346 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-TS1 at r2SCAN-3c in the gas phase

C	-2.384390	-0.741241	-0.280420
C	-1.522758	0.333590	-0.448305
C	-1.890020	-1.958557	0.175629
C	-0.146426	0.191105	-0.186093
C	0.331911	-1.047369	0.276618
C	-0.534536	-2.110869	0.457427
Br	-2.231865	1.987459	-1.054643
C	0.775637	1.257648	-0.341114
H	-3.439856	-0.619118	-0.496964
H	-2.574574	-2.789919	0.313159
H	1.390383	-1.137866	0.494139
H	-0.152682	-3.060970	0.816309
N	1.174087	2.200426	-0.978462
O	2.067396	3.066606	-0.900519
O	2.071939	1.343364	1.187451
S	3.286430	2.193825	0.819742
O	4.340594	1.457315	0.096589

17

o-TS1 at r2SCAN-3c in the benzene

C	-2.386674	-0.722612	-0.243931
C	-1.511049	0.337236	-0.428134

C	-1.896660	-1.954113	0.180837
C	-0.128975	0.166158	-0.216670
C	0.344308	-1.085482	0.216382
C	-0.535004	-2.135316	0.414862
Br	-2.206964	2.014712	-0.990123
C	0.801384	1.221496	-0.385757
H	-3.447208	-0.582197	-0.421749
H	-2.591275	-2.774703	0.332741
H	1.407902	-1.200506	0.395899
H	-0.159657	-3.096790	0.749615
N	1.221258	2.144037	-1.039349
O	2.098326	3.031666	-0.929535
O	2.009412	1.404229	1.212723
S	3.218797	2.271742	0.871389
O	4.323350	1.525873	0.231339

17

m-TS1 at r2SCAN-3c in the gas phase

C	-2.353635	-0.817714	-0.374572
C	-1.504035	0.266210	-0.513816
C	-1.924453	-2.020110	0.179342
C	-0.168523	0.126474	-0.097528
C	0.283647	-1.075142	0.462966
C	-0.602102	-2.134030	0.597828
H	-1.851956	1.200517	-0.938740
C	0.723382	1.222620	-0.246417
Br	-4.165169	-0.646521	-0.947295
H	-2.613755	-2.850755	0.282178
H	1.314415	-1.155325	0.786543
H	-0.259961	-3.067909	1.032529
N	0.991358	2.262034	-0.790011
O	1.847780	3.163840	-0.758401
O	2.255697	1.195159	1.096616
S	3.368375	2.140631	0.659816
O	4.320126	1.557309	-0.303207

17

m-TS1 at r2SCAN-3c in the benzene

C	-2.363738	-0.795125	-0.310164
C	-1.503288	0.274097	-0.491050
C	-1.928218	-2.010816	0.208583
C	-0.148735	0.098678	-0.158878
C	0.311991	-1.116000	0.366617
C	-0.585644	-2.157484	0.548436
H	-1.854482	1.221306	-0.884145
C	0.756602	1.175946	-0.352327
Br	-4.205327	-0.582661	-0.770828
H	-2.626480	-2.829121	0.347057
H	1.358633	-1.223320	0.627515
H	-0.239447	-3.102173	0.955595
N	1.088494	2.147621	-0.980233
O	1.934756	3.065935	-0.920872

O	2.100849	1.336157	1.162626
S	3.243084	2.265582	0.769153
O	4.322142	1.598667	0.010743

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p-TS1 at r2SCAN-3c in the gas phase

C	-2.250148	-0.793732	-0.660769
C	-1.382708	0.285463	-0.634818
C	-1.916710	-1.951429	0.036872
C	-0.193026	0.211940	0.109449
C	0.126976	-0.962794	0.804242
C	-0.734223	-2.047842	0.763331
H	-1.621519	1.191383	-1.181945
C	0.685597	1.325662	0.150951
H	-3.173495	-0.740337	-1.226793
Br	-3.105443	-3.437577	-0.010827
H	1.055062	-1.017483	1.361294
H	-0.490398	-2.960795	1.294927
N	0.843678	2.514584	0.047063
O	1.765026	3.353387	0.020336
O	2.625733	0.813218	0.530982
S	3.565364	1.915112	0.054960
O	3.904624	1.851080	-1.378145

17

p-TS1 at r2SCAN-3c in the benzene

C	-2.179173	-0.803778	-0.739847
C	-1.309142	0.271857	-0.667531
C	-1.906027	-1.945372	0.008529
C	-0.185764	0.207118	0.173923
C	0.072008	-0.952534	0.919801
C	-0.787751	-2.035515	0.832398
H	-1.495773	1.166148	-1.252873
C	0.698276	1.312918	0.256558
H	-3.053296	-0.758297	-1.379997
Br	-3.095644	-3.430273	-0.104177
H	0.949472	-1.000182	1.555274
H	-0.593428	-2.937246	1.402303
N	0.866120	2.506278	0.263310
O	1.821605	3.316039	0.203176
O	2.650749	0.748908	0.329122
S	3.545588	1.897044	-0.126134
O	3.706569	1.986729	-1.592725

Table S347 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-B ES at r2SCAN-3c in the gas phase

C	0.026196	0.118579	-0.001251
C	0.971215	1.123583	-0.177659
C	0.415392	-1.136572	0.449446

C	2.327824	0.878726	0.089864
C	2.694491	-0.393028	0.557994
C	1.752600	-1.392860	0.733300
Br	0.324067	2.822495	-0.741379
C	3.395656	1.865021	-0.078585
H	-1.016579	0.329320	-0.210641
H	-0.334557	-1.910282	0.582947
H	3.741007	-0.583868	0.769405
H	2.063114	-2.369980	1.088663
N	3.451807	2.774033	-0.980296
O	4.637036	3.505664	-0.828867
O	4.453458	1.757323	0.795666
S	5.776111	2.687264	0.199515
O	6.607051	1.798693	-0.617993

17

o-B ES at r2SCAN-3c in the benzene

C	0.023928	0.120492	0.003292
C	0.971143	1.122532	-0.175739
C	0.415020	-1.135880	0.451930
C	2.328664	0.877305	0.085414
C	2.696971	-0.395406	0.550999
C	1.753601	-1.393780	0.729775
Br	0.322714	2.827654	-0.733155
C	3.396132	1.862987	-0.086285
H	-1.020239	0.330743	-0.201028
H	-0.335207	-1.908845	0.589113
H	3.743962	-0.590674	0.756832
H	2.064493	-2.371568	1.083243
N	3.459927	2.762420	-0.997894
O	4.642531	3.501788	-0.839982
O	4.445198	1.768433	0.797863
S	5.770723	2.695976	0.211979
O	6.606328	1.799932	-0.596230

17

m-B ES at r2SCAN-3c in the gas phase

C	0.097062	0.112817	-0.084674
C	1.072948	1.082807	-0.226817
C	0.379013	-1.140523	0.452876
C	2.380795	0.783701	0.178389
C	2.684960	-0.467911	0.720291
C	1.680645	-1.418858	0.853399
H	0.839278	2.055917	-0.643094
C	3.422951	1.795654	0.032243
Br	-1.687415	0.506094	-0.637848
H	-0.406061	-1.881557	0.554931
H	3.699463	-0.692971	1.028696
H	1.912458	-2.392977	1.272597
N	3.266103	2.910624	-0.584498
O	4.452135	3.652734	-0.511123
O	4.643803	1.534234	0.596233

S	5.795802	2.675812	-0.003799
O	6.428830	2.083633	-1.183983

17

m-B ES at r2SCAN-3c in the benzene

C	0.098034	0.112014	-0.083617
C	1.070905	1.084548	-0.227376
C	0.379620	-1.141412	0.453193
C	2.379684	0.785487	0.176270
C	2.686021	-0.466198	0.717887
C	1.682562	-1.418305	0.852580
H	0.832629	2.057576	-0.641590
C	3.422042	1.797445	0.029296
Br	-1.690638	0.505162	-0.636095
H	-0.403483	-1.884546	0.557096
H	3.700334	-0.693091	1.026035
H	1.915349	-2.392126	1.271963
N	3.269445	2.911995	-0.590707
O	4.459216	3.653682	-0.511541
O	4.640398	1.536225	0.596139
S	5.796517	2.673642	0.004009
O	6.424134	2.077133	-1.179723

17

p-B ES at r2SCAN-3c in the gas phase

C	0.097291	0.117196	-0.098993
C	1.089437	1.073691	-0.233460
C	0.417605	-1.121063	0.452497
C	2.399845	0.793583	0.176006
C	2.701594	-0.455159	0.726928
C	1.709458	-1.417003	0.867567
H	0.854864	2.044241	-0.657884
C	3.439243	1.805346	0.030503
H	-0.917588	0.329779	-0.416030
Br	-0.949530	-2.436063	0.641692
H	3.714479	-0.679285	1.042916
H	1.941127	-2.386735	1.293535
N	3.279206	2.923472	-0.581140
O	4.465994	3.667161	-0.505378
O	4.662791	1.543882	0.589963
S	5.810790	2.689022	-0.009656
O	6.439265	2.101965	-1.195034

17

p-B ES at r2SCAN-3c in the benzene

C	0.095389	0.117263	-0.098533
C	1.086879	1.075075	-0.233842
C	0.420445	-1.119720	0.452395
C	2.398182	0.795098	0.173880
C	2.703226	-0.453488	0.724684
C	1.712150	-1.416729	0.866846
H	0.845131	2.044603	-0.656723

C	3.438014	1.806679	0.027745
H	-0.919757	0.330794	-0.414527
Br	-0.947620	-2.438546	0.643269
H	3.715740	-0.679799	1.040567
H	1.947412	-2.385624	1.293152
N	3.282494	2.924558	-0.587124
O	4.473195	3.667586	-0.505596
O	4.659248	1.545466	0.590071
S	5.811365	2.686096	-0.001597
O	6.434376	2.094717	-1.190636

Table S348 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-TS2 at r2SCAN-3c in the gas phase

C	-0.013886	0.214386	0.227377
C	0.982326	1.151751	-0.009603
C	0.336475	-1.108785	0.481675
C	2.327471	0.762255	0.043061
C	2.668930	-0.574571	0.273304
C	1.672568	-1.507151	0.506643
Br	0.513371	2.951684	-0.357370
C	3.451480	1.820194	0.013504
H	-1.054853	0.517673	0.204624
H	-0.450093	-1.837461	0.653657
H	3.717825	-0.852942	0.267550
H	1.932500	-2.543473	0.695213
N	3.612792	1.631992	-1.223279
O	5.034219	3.084465	-1.385133
O	3.894842	2.480168	0.979378
S	5.696594	3.322373	-0.043344
O	6.690491	2.316992	0.358213

17

o-TS2 at r2SCAN-3c in the benzene

C	-0.011357	0.217226	0.225505
C	0.988602	1.149448	-0.009201
C	0.335424	-1.108234	0.479075
C	2.333255	0.754082	0.048597
C	2.671773	-0.585041	0.276342
C	1.670158	-1.512698	0.506937
Br	0.531233	2.954576	-0.354808
C	3.453987	1.803545	0.004751
H	-1.052036	0.522123	0.202489
H	-0.454548	-1.833905	0.648279
H	3.719479	-0.868798	0.274805
H	1.925107	-2.550209	0.695799
N	3.625693	1.625267	-1.232115
O	5.027520	3.086182	-1.385547
O	3.906296	2.479008	0.962896
S	5.664122	3.342283	-0.030375

O	6.678342	2.354695	0.372042

17

m-TS2 at r2SCAN-3c in the gas phase

C	0.028272	0.194924	0.208213
C	1.010213	1.142837	-0.034646
C	0.354268	-1.130602	0.486057
C	2.341093	0.730459	0.040274
C	2.700282	-0.595804	0.280737
C	1.692604	-1.518300	0.520653
H	0.764345	2.172120	-0.269405
C	3.456793	1.809551	0.035685
Br	-1.803617	0.711546	0.131254
H	-0.432940	-1.856045	0.660780
H	3.746874	-0.880922	0.288127
H	1.942843	-2.554445	0.725245
N	3.553646	1.738919	-1.218359
O	4.953328	3.226114	-1.316302
O	3.947055	2.374566	1.037692
S	5.695172	3.333698	-0.000115
O	6.712539	2.300614	0.237931

17

m-TS2 at r2SCAN-3c in the benzene

C	0.032300	0.198025	0.209090
C	1.015386	1.143126	-0.037033
C	0.353118	-1.128794	0.489196
C	2.344983	0.723107	0.041236
C	2.701725	-0.604752	0.281620
C	1.690179	-1.522466	0.524094
H	0.773982	2.173958	-0.271197
C	3.458050	1.794374	0.020631
Br	-1.799291	0.721168	0.133104
H	-0.435410	-1.852707	0.665639
H	3.747078	-0.895311	0.289853
H	1.935983	-2.559189	0.730813
N	3.569144	1.725075	-1.231997
O	4.955602	3.217708	-1.322924
O	3.953671	2.378708	1.015166
S	5.664601	3.350269	0.012922
O	6.701668	2.336931	0.263607

17

p-TS2 at r2SCAN-3c in the gas phase

C	0.304020	0.027491	-0.534450
C	1.413826	0.854413	-0.588991
C	0.290535	-1.024782	0.380793
C	2.501918	0.593403	0.247115
C	2.466891	-0.437845	1.187222
C	1.357028	-1.265936	1.244968
H	1.449870	1.690449	-1.280069
C	3.816702	1.367573	0.013701

H	-0.546869	0.200713	-1.183661
Br	-1.237569	-2.150181	0.467947
H	3.306320	-0.587587	1.858179
H	1.312007	-2.080901	1.958548
N	3.505767	2.222273	0.887203
O	5.268072	3.237018	0.702762
O	4.710353	1.093165	-0.821381
S	5.861416	2.998598	-0.671202
O	5.230583	3.744017	-1.769383

17

p-TS2 at r2SCAN-3c in the benzene

C	0.298159	0.028283	-0.534686
C	1.405722	0.857607	-0.593035
C	0.291817	-1.023272	0.382133
C	2.497193	0.594847	0.240041
C	2.468327	-0.434344	1.184398
C	1.360241	-1.264227	1.244656
H	1.436512	1.692532	-1.285956
C	3.799731	1.377610	0.017163
H	-0.553981	0.200857	-1.182630
Br	-1.234733	-2.151230	0.475040
H	3.309883	-0.585645	1.852619
H	1.320713	-2.078850	1.959115
N	3.502428	2.238969	0.888489
O	5.268148	3.235240	0.702338
O	4.707303	1.114621	-0.815281
S	5.870350	2.959609	-0.665182
O	5.263058	3.719274	-1.769921

Table S349 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-C ES at r2SCAN-3c in the gas phase

C	0.933644	-1.425519	0.099134
C	1.609388	-0.773552	-0.924525
C	0.798575	-0.811344	1.338481
C	2.156121	0.498740	-0.722174
C	2.014104	1.105671	0.531570
C	1.339880	0.453880	1.551993
Br	1.786152	-1.624917	-2.616549
C	3.371906	2.177008	-1.975872
H	0.517553	-2.410799	-0.080471
H	0.270430	-1.325569	2.135045
H	2.448390	2.088170	0.691630
H	1.239350	0.937411	2.518615
N	2.826809	1.125897	-1.763245
O	3.933537	3.153090	-2.310447
O	4.415210	3.980981	0.884429
S	5.600260	3.352126	0.278874
O	5.581506	1.888636	0.128345

17

o-C ES at r2SCAN-3c in the benzene

C	0.981617	-1.439120	0.113639
C	1.639044	-0.778364	-0.916145
C	0.814948	-0.807248	1.341138
C	2.136324	0.517305	-0.736114
C	1.962660	1.140646	0.505969
C	1.306618	0.481806	1.534390
Br	1.862962	-1.655463	-2.593498
C	3.316497	2.214540	-1.987230
H	0.604065	-2.443026	-0.048211
H	0.300823	-1.326507	2.143720
H	2.354370	2.143586	0.649366
H	1.180244	0.978867	2.491241
N	2.785735	1.152184	-1.787183
O	3.859080	3.202977	-2.313379
O	4.560281	3.963412	0.951118
S	5.686380	3.240054	0.338714
O	5.491167	1.804263	0.077298

17

m-C ES at r2SCAN-3c in the gas phase

C	0.922084	-1.391275	0.095562
C	1.630649	-0.790892	-0.934310
C	0.735151	-0.767770	1.322315
C	2.167788	0.479722	-0.721489
C	1.997257	1.131076	0.503666
C	1.282289	0.499196	1.510767
H	1.771527	-1.285572	-1.887990
C	3.447833	2.103628	-1.984906
Br	0.184777	-3.131334	-0.190395
H	0.177680	-1.258077	2.111968
H	2.428544	2.114780	0.661174
H	1.147517	1.000103	2.464665
N	2.873968	1.065936	-1.773183
O	4.031251	3.065950	-2.319867
O	4.421102	3.973131	0.853695
S	5.631154	3.319713	0.329335
O	5.599139	1.855379	0.190799

17

m-C ES at r2SCAN-3c in the benzene

C	0.980084	-1.393403	0.112629
C	1.658390	-0.784866	-0.932701
C	0.769590	-0.758312	1.329479
C	2.143003	0.511258	-0.744381
C	1.946102	1.177651	0.469069
C	1.262077	0.535387	1.491488
H	1.816840	-1.290657	-1.878111
C	3.401952	2.143449	-2.011676
Br	0.316205	-3.172056	-0.138434

H	0.236213	-1.256338	2.131125
H	2.330288	2.183876	0.604367
H	1.106973	1.048118	2.436085
N	2.819690	1.106720	-1.810702
O	3.986563	3.104458	-2.344959
O	4.531250	3.953393	0.875447
S	5.696084	3.145860	0.478990
O	5.448411	1.729157	0.164088

17

p-C ES at r2SCAN-3c in the gas phase

C	0.877076	-1.425575	0.065508
C	1.588227	-0.787199	-0.942346
C	0.734273	-0.798426	1.296599
C	2.148645	0.469382	-0.714239
C	2.000108	1.089140	0.529985
C	1.290224	0.452764	1.538329
H	1.712044	-1.259027	-1.911334
C	3.435459	2.110617	-1.953576
H	0.439041	-2.402128	-0.108106
Br	-0.245598	-1.670943	2.685182
H	2.445940	2.062838	0.710285
H	1.172692	0.929010	2.505490
N	2.850679	1.076465	-1.757041
O	4.026783	3.073387	-2.275030
O	4.441539	3.889629	0.913992
S	5.641610	3.240407	0.361495
O	5.597678	1.779440	0.191860

17

p-C ES at r2SCAN-3c in the benzene

C	0.927106	-1.435768	0.078815
C	1.612431	-0.787131	-0.941096
C	0.765415	-0.793451	1.299742
C	2.128578	0.492304	-0.733085
C	1.957306	1.126994	0.501101
C	1.273207	0.481618	1.522171
H	1.749804	-1.271033	-1.902536
C	3.398113	2.140571	-1.976261
H	0.525587	-2.430537	-0.080560
Br	-0.179346	-1.681758	2.707804
H	2.361541	2.121667	0.663590
H	1.139135	0.970999	2.480837
N	2.806751	1.107520	-1.787418
O	3.990565	3.101667	-2.297622
O	4.546941	3.908235	0.910724
S	5.703893	3.097895	0.497613
O	5.449392	1.679992	0.193233

Table S350 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-product ES at r2SCAN-3c in the gas phase

C	1.795517	-0.384861	0.356134
C	2.891330	0.400648	0.022344
C	1.973169	-1.732090	0.648751
C	4.178755	-0.148039	-0.023914
C	4.341098	-1.507033	0.273597
C	3.247640	-2.291075	0.606715
Br	2.632375	2.242554	-0.375335
C	6.446989	0.529530	-0.493212
H	0.808122	0.062615	0.385461
H	1.113515	-2.341154	0.909010
H	5.339526	-1.934025	0.238285
H	3.392841	-3.342552	0.834085
N	5.253754	0.662368	-0.361002
O	7.605878	0.540544	-0.656429

14

o-product ES at r2SCAN-3c in the benzene

C	1.794228	-0.384234	0.355935
C	2.892433	0.398592	0.023111
C	1.971815	-1.732053	0.648529
C	4.179476	-0.150140	-0.022815
C	4.342151	-1.508999	0.274797
C	3.246832	-2.291742	0.607267
Br	2.634516	2.244729	-0.375429
C	6.447569	0.531024	-0.494145
H	0.806321	0.062665	0.385053
H	1.111362	-2.340613	0.908108
H	5.340074	-1.937204	0.239845
H	3.391833	-3.343397	0.834532
N	5.254995	0.662185	-0.360757
O	7.606905	0.546618	-0.659539

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m-product ES at r2SCAN-3c in the gas phase

C	1.806419	-0.422657	0.363865
C	2.875581	0.393819	0.026790
C	1.971207	-1.770078	0.658151
C	4.154958	-0.163874	-0.016403
C	4.348599	-1.517760	0.275313
C	3.256063	-2.305112	0.609046
H	2.735989	1.443923	-0.200769
C	6.409919	0.557012	-0.495101
Br	0.054492	0.336723	0.422211
H	1.119017	-2.386803	0.918792
H	5.347927	-1.941285	0.238708
H	3.403139	-3.356761	0.835889
N	5.214472	0.677501	-0.358698
O	7.567798	0.580591	-0.661553

14

m-product ES at r2SCAN-3c in the benzene

C	1.808162	-0.423020	0.363625
C	2.876607	0.394589	0.026975
C	1.969579	-1.770614	0.658131
C	4.155172	-0.166074	-0.015195
C	4.348962	-1.520010	0.276591
C	3.254972	-2.306593	0.609718
H	2.737913	1.445181	-0.200600
C	6.410452	0.559012	-0.496154
Br	0.053030	0.339778	0.421013
H	1.117637	-2.388329	0.918433
H	5.347704	-1.945012	0.240476
H	3.400608	-3.358520	0.836532
N	5.215914	0.675731	-0.358053
O	7.568869	0.589122	-0.665251

14

p-product ES at r2SCAN-3c in the gas phase

C	1.814899	-0.411698	0.359942
C	2.901131	0.386122	0.024554
C	2.020514	-1.755047	0.647766
C	4.184350	-0.159686	-0.021889
C	4.376136	-1.513580	0.270482
C	3.292936	-2.313729	0.606015
H	2.761258	1.437471	-0.203443
C	6.441414	0.564110	-0.500752
H	0.817014	0.010979	0.396423
Br	0.530338	-2.856692	1.109233
H	5.374709	-1.939973	0.234946
H	3.439435	-3.364002	0.832977
N	5.245886	0.679612	-0.364103
O	7.599619	0.591952	-0.667841

14

p-product ES at r2SCAN-3c in the benzene

C	1.813926	-0.410468	0.359800
C	2.901757	0.386600	0.025033
C	2.021599	-1.753534	0.646953
C	4.184001	-0.162267	-0.020294
C	4.377201	-1.516144	0.272125
C	3.292643	-2.315642	0.606991
H	2.760531	1.438065	-0.202676
C	6.441656	0.565217	-0.501935
H	0.816807	0.014607	0.395127
Br	0.526900	-2.857030	1.107560
H	5.375003	-1.944286	0.237339
H	3.440078	-3.366060	0.833644
N	5.247165	0.677045	-0.363217
O	7.600374	0.599738	-0.672140

Table S351 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

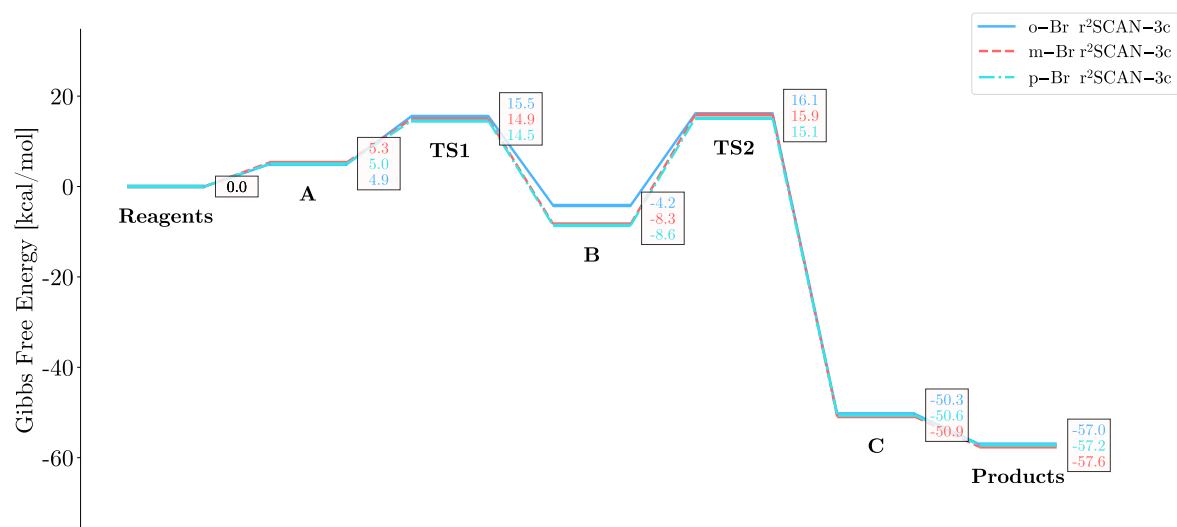
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

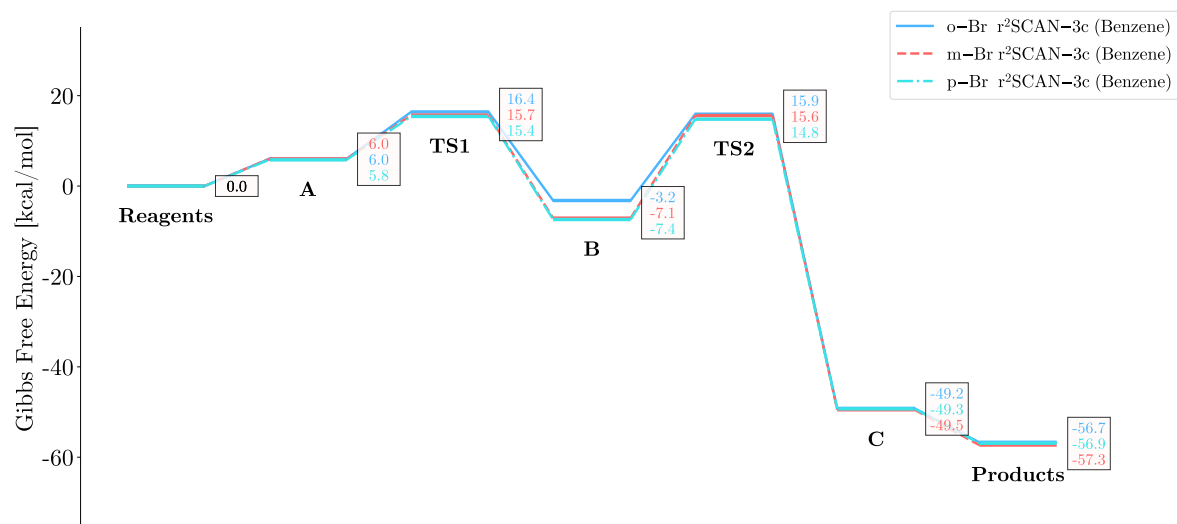
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

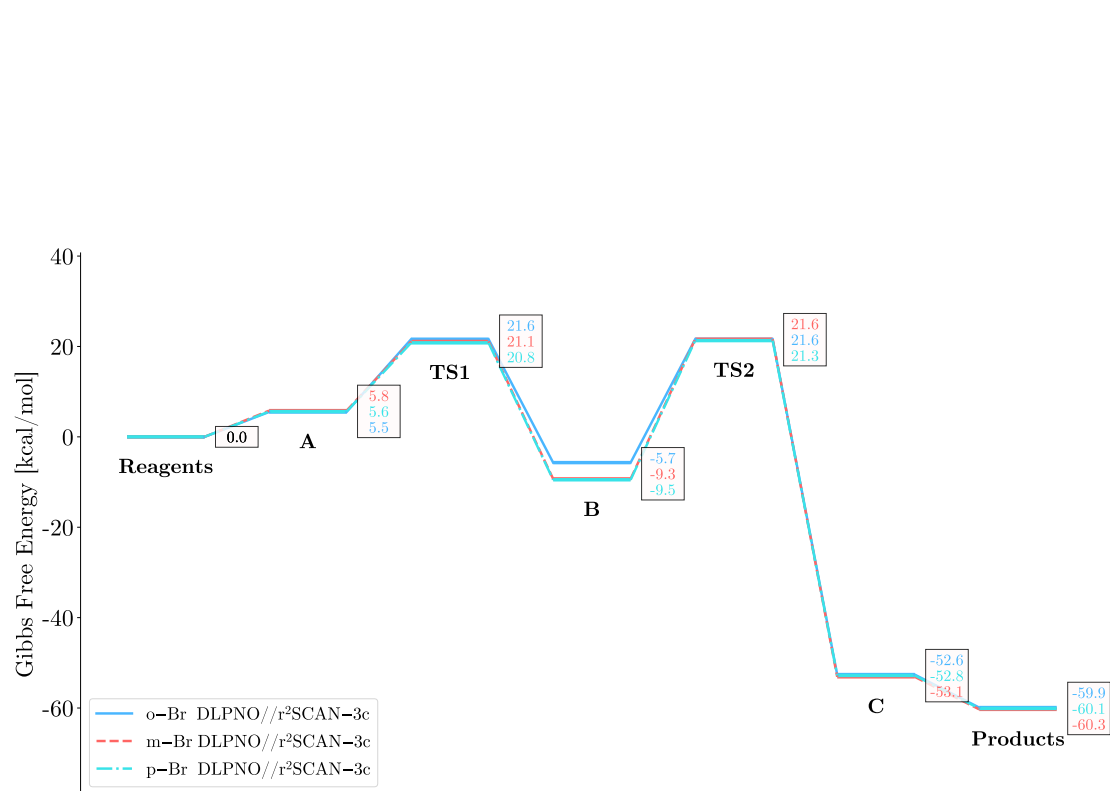


(a) Reaction in the gas phase.

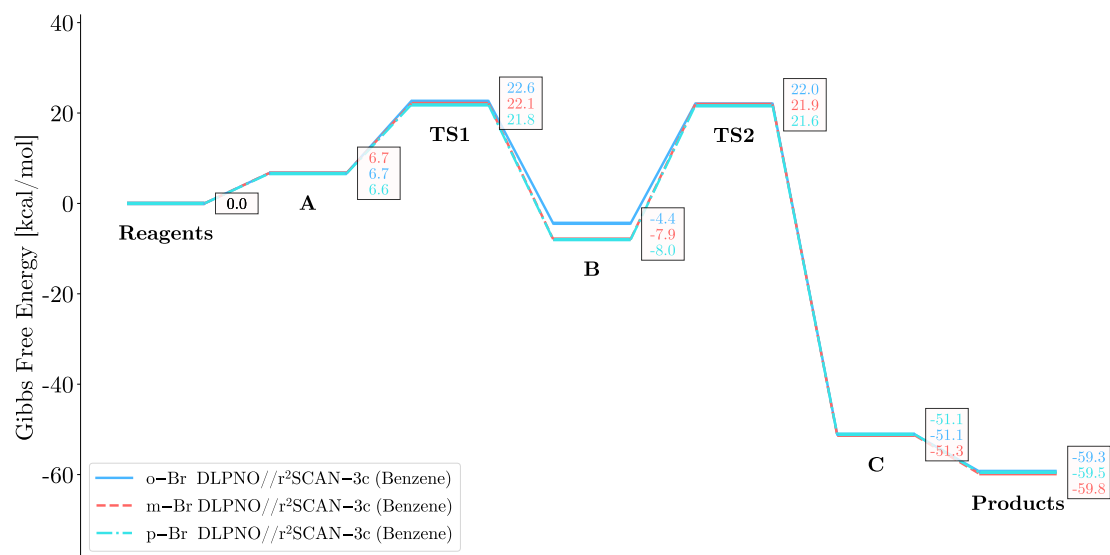


(b) Reaction in the benzene.

Figure S54 Calculated PES for reaction of the -Br substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S55 Calculated PES for reaction of the -Br substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

3.4 –CF₃

Table S352 Energy profile of the SO₂-catalyzed conversion for –CF₃ substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.1	2.2	–19.8	4.1	–63.3	–58.2
		<i>E</i> + ΔZPE, kcal/mol	0.0	–6.4	3.1	–17.4	4.5	–62.1	–57.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	16.0	–3.9	17.6	–50.6	–57.2
	Benzene	<i>E</i> , kcal/mol	0.0	–5.8	3.6	–18.8	3.9	–62.0	–57.9
		<i>E</i> + ΔZPE, kcal/mol	0.0	–5.1	4.5	–16.4	4.4	–60.9	–57.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	17.1	–3.2	17.3	–49.7	–57.1
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	1.2	–24.3	2.7	–63.3	–58.8
		<i>E</i> + ΔZPE, kcal/mol	0.0	–6.3	2.0	–21.9	3.0	–62.3	–58.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.2	14.6	–8.5	15.8	–51.0	–58.1
	Benzene	<i>E</i> , kcal/mol	0.0	–6.0	2.4	–22.8	2.6	–61.8	–58.3
		<i>E</i> + ΔZPE, kcal/mol	0.0	–5.2	3.2	–20.5	2.9	–60.8	–57.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.2	15.6	–7.4	15.5	–49.9	–57.8
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.9	1.2	–24.1	3.1	–63.4	–58.9
		<i>E</i> + ΔZPE, kcal/mol	0.0	–6.1	2.1	–21.6	3.5	–62.2	–58.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.3	15.0	–8.1	16.5	–52.0	–57.8
	Benzene	<i>E</i> , kcal/mol	0.0	–5.8	2.4	–22.6	3.1	–61.9	–58.5
		<i>E</i> + ΔZPE, kcal/mol	0.0	–5.0	3.2	–20.2	3.5	–61.0	–57.9
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.9	16.0	–7.0	16.3	–50.3	–57.7

Table S354 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

17

o-reagent ES at r2SCAN-3c in the gas phase

C	–0.047039	–0.056152	0.363328
C	0.830468	1.017404	0.362308
C	0.432653	–1.355082	0.495885
C	2.212980	0.806570	0.494369
C	2.689827	–0.515916	0.627886
C	1.799422	–1.580691	0.627621
H	0.463692	2.033056	0.259899
C	3.087059	1.916161	0.491666
H	–1.112551	0.124758	0.259949
H	–0.254105	–2.195248	0.497107
H	2.178339	–2.591118	0.730663
N	3.769973	2.859804	0.475733
O	4.476477	3.829575	0.462345
C	4.168631	–0.757192	0.768905
F	4.671870	–0.140712	1.864380
F	4.459348	–2.070060	0.881190
F	4.853735	–0.285987	–0.300012

Table S353 Energy profile of the SO₂-catalyzed conversion for –CF₃ substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
<i>o</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.7	8.4	–21.4	9.4	–65.0	–61.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.9	9.3	–19.0	9.8	–63.9	–60.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.2	22.1	–5.5	22.9	–52.3	–60.5
	Benzene	<i>E</i> , kcal/mol	0.0	–5.2	9.6	–20.2	9.9	–63.4	–60.8
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.5	10.5	–17.9	10.3	–62.3	–60.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	7.4	23.1	–4.6	23.2	–51.1	–60.0
<i>m</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.6	7.4	–25.1	8.5	–65.4	–61.5
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.7	8.2	–22.8	8.8	–64.3	–61.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.8	20.9	–9.3	21.6	–53.1	–60.8
	Benzene	<i>E</i> , kcal/mol	0.0	–5.2	8.7	–23.5	8.9	–63.6	–60.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.4	9.5	–21.2	9.2	–62.6	–60.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.9	21.9	–8.1	21.8	–51.6	–60.2
<i>p</i> -substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.5	7.5	–25.0	8.8	–65.6	–61.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.6	8.3	–22.5	9.2	–64.4	–61.1
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	21.3	–9.0	22.2	–54.2	–60.7
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	8.8	–23.3	9.3	–63.7	–60.9
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.3	9.7	–20.9	9.7	–62.7	–60.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.6	22.4	–7.6	22.5	–52.1	–60.1

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o-reagent ES at r2SCAN-3c in the benzene

C	–0.045941	–0.053784	0.363685
C	0.833000	1.019562	0.362640
C	0.432444	–1.353682	0.496100
C	2.214069	0.803254	0.494548
C	2.690414	–0.519077	0.627715
C	1.799055	–1.583448	0.627710
H	0.467296	2.035688	0.260252
C	3.091439	1.912011	0.491617
H	–1.111261	0.128422	0.260415
H	–0.255749	–2.192802	0.497213
H	2.172536	–2.596079	0.730420
N	3.763343	2.861608	0.474195
O	4.468161	3.838250	0.460103
C	4.167655	–0.760270	0.768934
F	4.673248	–0.145282	1.867092
F	4.463743	–2.071493	0.877787
F	4.857328	–0.283709	–0.297207

17

m-reagent ES at r2SCAN-3c in the gas phase

C	–0.007265	–0.152119	0.358128
C	0.843103	0.945450	0.421859

C	0.492715	-1.449724	0.409294
C	2.224955	0.744553	0.540288
C	2.731758	-0.567301	0.593086
C	1.866627	-1.646754	0.527116
H	0.444612	1.953955	0.382051
C	3.102852	1.852260	0.608331
C	-1.484594	0.107996	0.231862
H	-0.182665	-2.296050	0.358930
H	3.801807	-0.720020	0.685944
H	2.263901	-2.655999	0.568289
N	3.844064	2.749836	0.659209
O	4.604608	3.678188	0.713652
F	-2.208585	-1.029355	0.215049
F	-1.771253	0.787479	-0.904661
F	-1.940192	0.862955	1.260655

17

m-reagent ES at r2SCAN-3c in the benzene

C	-0.006405	-0.151722	0.358371
C	0.843191	0.947028	0.421899
C	0.493076	-1.450097	0.409526
C	2.224159	0.742290	0.540263
C	2.733099	-0.568433	0.593287
C	1.867197	-1.647953	0.527267
H	0.446624	1.956530	0.381912
C	3.102590	1.850658	0.608177
C	-1.482280	0.108163	0.232092
H	-0.180178	-2.298350	0.359197
H	3.803189	-0.721498	0.686075
H	2.263648	-2.657507	0.568329
N	3.840919	2.748242	0.658833
O	4.602861	3.681709	0.713389
F	-2.209997	-1.027116	0.214310
F	-1.772850	0.789460	-0.904578
F	-1.942393	0.863944	1.260733

17

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.080633	-0.059012	0.335764
C	0.785899	1.019971	0.409867
C	0.420261	-1.357410	0.384760
C	2.168476	0.806482	0.537520
C	2.663715	-0.509288	0.589333
C	1.791552	-1.580370	0.513560
H	0.403745	2.034127	0.367798
C	3.056554	1.904739	0.609679
H	-1.146982	0.109635	0.233524
H	3.731149	-0.675165	0.686271
H	2.175456	-2.595113	0.548815
N	3.801009	2.799696	0.661755
O	4.566564	3.723826	0.716348
C	-0.506007	-2.539872	0.341368

F	-1.736038	-2.210987	-0.106871
F	-0.027902	-3.517941	-0.463227
F	-0.663605	-3.089909	1.571899

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p-reagent ES at r2SCAN-3c in the benzene

C	-0.081822	-0.057922	0.335914
C	0.785001	1.021321	0.410106
C	0.421397	-1.355950	0.384644
C	2.166805	0.804354	0.537316
C	2.665243	-0.509836	0.589634
C	1.792791	-1.581238	0.513799
H	0.402372	2.035396	0.368417
C	3.055642	1.903219	0.609190
H	-1.147962	0.113353	0.234891
H	3.732644	-0.675960	0.686928
H	2.178767	-2.595300	0.550924
N	3.798810	2.796877	0.660941
O	4.567243	3.724677	0.715499
C	-0.504394	-2.537413	0.340254
F	-1.736054	-2.212415	-0.107628
F	-0.028770	-3.518570	-0.463992
F	-0.664500	-3.091182	1.571327

Table S355 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-A ES at r2SCAN-3c in the gas phase

C	-0.010441	-0.056116	-0.031991
C	0.717036	1.105542	-0.249343
C	0.595497	-1.163995	0.553268
C	2.075114	1.163254	0.124423
C	2.677313	0.040769	0.714400
C	1.935347	-1.112213	0.923588
C	2.858694	2.322815	-0.075419
H	-1.054306	-0.093441	-0.321948
H	0.017171	-2.067381	0.717934
H	3.722066	0.099226	0.999733
H	2.410042	-1.975356	1.379786
N	3.568002	3.231701	-0.211761
O	4.340350	4.155220	-0.327538
O	5.563957	1.894005	1.390177
S	6.495738	2.901316	0.838317
O	7.243304	2.518936	-0.369312
C	0.073455	2.307841	-0.884161
F	0.114820	3.384125	-0.062703
F	0.706765	2.661332	-2.027988
F	-1.220147	2.088006	-1.192591

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o-A ES at r2SCAN-3c in the benzene

C	-0.025513	-0.054344	-0.030875
C	0.716889	1.097865	-0.246900
C	0.568300	-1.170227	0.553475
C	2.076336	1.138051	0.126833
C	2.665330	0.008220	0.714611
C	1.908861	-1.136203	0.923235
C	2.872327	2.289954	-0.070895
H	-1.070056	-0.081632	-0.319882
H	-0.021404	-2.066354	0.717774
H	3.711138	0.050044	0.999257
H	2.372760	-2.005873	1.378156
N	3.573117	3.202087	-0.221186
O	4.339959	4.132914	-0.349753
O	5.624520	1.945197	1.406104
S	6.503714	2.985103	0.829369
O	7.259045	2.603645	-0.376569
C	0.089128	2.309074	-0.878596
F	0.140236	3.384965	-0.053890
F	0.730397	2.663654	-2.020000
F	-1.205304	2.109447	-1.193392

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m-A ES at r2SCAN-3c in the gas phase

C	0.023688	0.010492	-0.128246
C	0.754925	1.173696	-0.309747
C	0.604190	-1.118005	0.452393
C	2.096610	1.207745	0.100883
C	2.686272	0.076384	0.686884
C	1.932772	-1.076755	0.856021
H	0.301747	2.048734	-0.760421
C	2.867564	2.382977	-0.067121
C	-1.416632	-0.067903	-0.557537
H	0.014709	-2.019775	0.586885
H	3.723127	0.123597	1.002265
H	2.387775	-1.951563	1.309351
N	3.576679	3.297019	-0.168748
O	4.342740	4.231184	-0.251099
O	5.524235	1.970724	1.505838
S	6.471103	2.969374	0.964356
O	7.235082	2.576268	-0.229556
F	-1.875142	1.101883	-1.046645
F	-2.217156	-0.417164	0.477687
F	-1.591877	-1.006160	-1.518734

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m-A ES at r2SCAN-3c in the benzene

C	0.017342	0.008316	-0.124314
C	0.769303	1.158347	-0.307391
C	0.576401	-1.132783	0.454046
C	2.112331	1.162546	0.100198
C	2.681911	0.019777	0.683375
C	1.906819	-1.118936	0.854586

H	0.336005	2.044565	-0.755993
C	2.904748	2.323040	-0.069665
C	-1.423460	-0.042392	-0.551782
H	-0.027975	-2.024732	0.589921
H	3.720779	0.042704	0.995222
H	2.345159	-2.003215	1.305843
N	3.587031	3.253158	-0.192425
O	4.340249	4.201350	-0.289508
O	5.582669	2.045362	1.528644
S	6.468925	3.089206	0.969934
O	7.260933	2.705949	-0.211854
F	-1.865243	1.136709	-1.035066
F	-2.232929	-0.383829	0.480993
F	-1.618588	-0.972391	-1.520053

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p-A ES at r2SCAN-3c in the gas phase

C	-0.075783	0.036137	-0.164737
C	0.677894	1.187111	-0.332860
C	0.496729	-1.087109	0.426489
C	2.015194	1.213297	0.090247
C	2.589625	0.076006	0.684883
C	1.826727	-1.066740	0.847945
H	0.240332	2.068868	-0.788294
C	2.798466	2.380831	-0.069803
H	-1.110561	0.013661	-0.488065
H	3.622964	0.112057	1.012047
H	2.263029	-1.946618	1.310201
N	3.501705	3.299661	-0.170740
O	4.264307	4.236093	-0.252431
O	5.465092	1.948981	1.458200
S	6.416867	2.945318	0.921967
O	7.159338	2.566365	-0.289751
C	-0.294511	-2.356519	0.580017
F	-1.623613	-2.146790	0.472224
F	0.044994	-3.264562	-0.368478
F	-0.071073	-2.941281	1.779160

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p-A ES at r2SCAN-3c in the benzene

C	-0.072738	0.031589	-0.159207
C	0.701945	1.166913	-0.335748
C	0.481924	-1.101058	0.433840
C	2.042155	1.165005	0.080717
C	2.597981	0.019474	0.675210
C	1.814176	-1.108818	0.847273
H	0.278906	2.055526	-0.791569
C	2.845834	2.317545	-0.086838
H	-1.109347	0.031665	-0.478581
H	3.633573	0.031501	0.997279
H	2.239228	-1.994190	1.309066
N	3.523832	3.249004	-0.224048

O	4.275115	4.196927	-0.331948
O	5.516691	2.061600	1.510736
S	6.407543	3.102824	0.954700
O	7.206775	2.716499	-0.221098
C	-0.341288	-2.349094	0.586565
F	-1.666152	-2.087579	0.620952
F	-0.135596	-3.207195	-0.446819
F	-0.032833	-3.023371	1.717741

Table S356 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-TS1 at r2SCAN-3c in the gas phase

C	-2.060554	-0.411110	0.608398
C	-0.957471	0.422580	0.506424
C	-1.935701	-1.769737	0.343536
C	0.289249	-0.097765	0.131154
C	0.407752	-1.475624	-0.156753
C	-0.704355	-2.297071	-0.035166
H	-1.036630	1.485271	0.704377
C	1.381823	0.808347	0.036154
H	-3.019937	0.004632	0.899693
H	-2.796599	-2.425405	0.426292
H	-0.608668	-3.355464	-0.247948
N	2.557526	1.036669	0.172529
O	3.351826	1.978392	-0.005922
O	0.805724	2.578414	-0.704479
S	1.852257	3.654237	-0.416403
O	1.723322	4.275809	0.914873
C	1.732033	-2.061332	-0.578968
F	2.652657	-1.971609	0.408298
F	1.622489	-3.365745	-0.903718
F	2.236066	-1.421714	-1.658580

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o-TS1 at r2SCAN-3c in the benzene

C	-2.291157	-0.525131	0.152209
C	-1.321672	0.416134	-0.162846
C	-1.930846	-1.853366	0.350963
C	0.019633	0.029907	-0.281743
C	0.382643	-1.314920	-0.055061
C	-0.597939	-2.247566	0.246628
H	-1.583587	1.457452	-0.317850
C	0.985184	1.032430	-0.575825
H	-3.328979	-0.219948	0.240267
H	-2.687545	-2.592497	0.594745
H	-0.323911	-3.283477	0.410500
N	1.831334	1.480060	-1.310182
O	2.655936	2.424782	-1.287520
O	1.059037	2.419748	0.867130
S	2.379534	3.186871	0.799750

O	3.496344	2.519954	1.500289
C	1.827997	-1.733831	-0.154600
F	2.619030	-0.980325	0.641956
F	2.006209	-3.020618	0.204692
F	2.295563	-1.603884	-1.419712

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m-TS1 at r2SCAN-3c in the gas phase

C	-2.304148	-0.847088	-0.393828
C	-1.433671	0.219476	-0.575847
C	-1.891935	-2.003645	0.262855
C	-0.118339	0.114778	-0.103764
C	0.305434	-1.048143	0.556825
C	-0.586146	-2.093533	0.736739
H	-1.760953	1.121524	-1.082797
C	0.785935	1.194421	-0.296698
C	-3.712388	-0.704036	-0.908751
H	-2.584982	-2.825632	0.401549
H	1.324970	-1.107287	0.919132
H	-0.259780	-2.992856	1.248889
N	1.052298	2.219179	-0.867381
O	1.915412	3.113473	-0.876093
O	2.336557	1.184241	1.022477
S	3.449992	2.112823	0.550809
O	4.386193	1.502114	-0.409921
F	-4.382732	0.266550	-0.242337
F	-4.421575	-1.843342	-0.783047
F	-3.724892	-0.358763	-2.217558

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m-TS1 at r2SCAN-3c in the benzene

C	-2.251220	-0.811422	-0.418990
C	-1.384188	0.268353	-0.456925
C	-1.909319	-1.985976	0.254775
C	-0.157361	0.173960	0.220767
C	0.192702	-0.999133	0.901635
C	-0.686103	-2.073630	0.907362
H	-1.641387	1.176677	-0.989586
C	0.731921	1.282341	0.207162
C	-3.569843	-0.754421	-1.140348
H	-2.598410	-2.825011	0.266589
H	1.148842	-1.057086	1.408888
H	-0.416196	-2.985409	1.430051
N	0.896023	2.468089	0.085082
O	1.831750	3.290478	-0.002768
O	2.679454	0.747965	0.448321
S	3.600062	1.844278	-0.076554
O	3.844760	1.777435	-1.531820
F	-3.871264	0.487034	-1.572746
F	-4.588662	-1.162682	-0.346897
F	-3.575271	-1.567501	-2.226389

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p-TS1 at r2SCAN-3c in the gas phase

C	-2.396921	-0.764070	-0.375570
C	-1.521452	0.294987	-0.534764
C	-1.967227	-1.937797	0.243856
C	-0.195122	0.173044	-0.084216
C	0.234295	-1.008931	0.533625
C	-0.655576	-2.058961	0.695514
H	-1.848786	1.216342	-1.004309
C	0.706293	1.258571	-0.249020
H	-3.421674	-0.674029	-0.720631
H	1.256641	-1.084386	0.884025
H	-0.328476	-2.973174	1.178924
N	0.962302	2.303167	-0.788811
O	1.827130	3.195164	-0.786668
O	2.284696	1.202846	1.037678
S	3.392928	2.139916	0.572575
O	4.304499	1.556933	-0.427963
C	-2.919293	-3.094910	0.377881
F	-4.192714	-2.678426	0.556477
F	-2.909883	-3.870328	-0.734687
F	-2.601307	-3.892492	1.419656

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p-TS1 at r2SCAN-3c in the benzene

C	-2.442718	-0.695359	-0.183592
C	-1.571631	0.372904	-0.306708
C	-1.956546	-1.950622	0.182924
C	-0.199206	0.176175	-0.074962
C	0.285247	-1.085612	0.295567
C	-0.598755	-2.144507	0.427841
H	-1.937911	1.354639	-0.587148
C	0.698647	1.267842	-0.217434
H	-3.501848	-0.550348	-0.369720
H	1.344953	-1.221140	0.477177
H	-0.227554	-3.122911	0.713530
N	0.941774	2.344098	-0.697063
O	1.819959	3.228859	-0.649043
O	2.319435	1.124068	1.002929
S	3.404709	2.103635	0.573239
O	4.284936	1.592631	-0.497559
C	-2.919768	-3.089659	0.371305
F	-3.976698	-3.004198	-0.467045
F	-2.335940	-4.290142	0.165297
F	-3.420732	-3.106888	1.634035

Table S357 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-B ES at r2SCAN-3c in the gas phase

C	0.054049	0.116083	-0.017781

C	1.000545	1.119323	-0.208080
C	0.434396	-1.139538	0.441018
C	2.354402	0.847381	0.050341
C	2.721505	-0.409605	0.539697
C	1.768412	-1.399380	0.730214
C	3.436101	1.815400	-0.173013
H	-0.990803	0.326927	-0.213344
H	-0.317858	-1.908788	0.584725
H	3.767601	-0.604387	0.753003
H	2.070544	-2.373669	1.101324
N	3.608036	2.490696	-1.245710
O	4.756483	3.286239	-1.108646
O	4.359164	1.934899	0.834037
S	5.746849	2.766094	0.218106
O	6.687150	1.746602	-0.256093
C	0.524528	2.485501	-0.652889
F	1.128066	3.477198	0.040063
F	0.744434	2.702727	-1.964615
F	-0.807231	2.625536	-0.450739

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o-B ES at r2SCAN-3c in the benzene

C	0.050718	0.118031	-0.010939
C	1.000610	1.117305	-0.205910
C	0.431247	-1.139522	0.444179
C	2.355323	0.840502	0.043852
C	2.722975	-0.417703	0.528945
C	1.766630	-1.404390	0.724271
C	3.436981	1.807965	-0.184351
H	-0.995401	0.329401	-0.200068
H	-0.322581	-1.906491	0.591962
H	3.769647	-0.618622	0.734553
H	2.067850	-2.380203	1.092195
N	3.621887	2.461060	-1.269260
O	4.762094	3.274010	-1.127365
O	4.340844	1.957696	0.833226
S	5.730503	2.793310	0.229711
O	6.686004	1.770997	-0.212083
C	0.529973	2.484070	-0.646669
F	1.150676	3.477024	0.032600
F	0.737346	2.700548	-1.964687
F	-0.796953	2.640252	-0.432541

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m-B ES at r2SCAN-3c in the gas phase

C	0.160641	0.090173	0.019319
C	1.145153	1.043170	-0.184342
C	0.453443	-1.119695	0.652763
C	2.449827	0.783611	0.253094
C	2.748694	-0.423132	0.890604
C	1.747755	-1.367827	1.086814
H	0.915553	1.984453	-0.670867

C	3.491460	1.785449	0.047627
C	-1.238943	0.330477	-0.479341
H	-0.330796	-1.853582	0.808822
H	3.760605	-0.619118	1.227684
H	1.981445	-2.304213	1.583049
N	3.337779	2.852302	-0.649641
O	4.518350	3.603487	-0.616363
O	4.705577	1.569692	0.643256
S	5.861379	2.674127	-0.019068
O	6.516080	2.003833	-1.144188
F	-1.490543	1.638203	-0.691301
F	-2.163082	-0.125858	0.397796
F	-1.459548	-0.314919	-1.651446

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m-B ES at r2SCAN-3c in the benzene

C	0.160086	0.090500	0.019869
C	1.142286	1.046275	-0.184797
C	0.455277	-1.121051	0.649763
C	2.448239	0.785988	0.248368
C	2.750719	-0.421753	0.883250
C	1.751386	-1.368265	1.080329
H	0.908319	1.988252	-0.667944
C	3.489761	1.787894	0.040981
C	-1.240139	0.330325	-0.472590
H	-0.325523	-1.858797	0.806222
H	3.763085	-0.619945	1.218027
H	1.987445	-2.305336	1.574103
N	3.344914	2.845801	-0.672768
O	4.527275	3.600252	-0.630078
O	4.696388	1.581902	0.653082
S	5.859576	2.678180	-0.001189
O	6.522233	1.992965	-1.115576
F	-1.494218	1.637082	-0.693453
F	-2.164265	-0.117960	0.410007
F	-1.472016	-0.321675	-1.641337

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p-B ES at r2SCAN-3c in the gas phase

C	1.066480	1.045788	-0.247038
C	0.378639	-1.144928	0.468032
C	2.371111	0.768806	0.179372
C	2.670671	-0.471561	0.752282
C	1.674107	-1.425007	0.895286
H	0.839279	2.011584	-0.685354
C	3.413674	1.779852	0.032767
H	-0.935398	0.302576	-0.435181
H	3.680764	-0.687026	1.081887
H	1.903103	-2.386871	1.342816
N	3.255383	2.892981	-0.587429
O	4.438440	3.636240	-0.519061
O	4.634102	1.522385	0.598586

S	5.786125	2.663308	-0.003860
O	6.420945	2.069105	-1.181761
C	-0.675535	-2.210188	0.596129
F	-1.924432	-1.710843	0.486881
F	-0.537126	-3.156047	-0.366232
F	-0.595342	-2.849790	1.785991
C	0.075613	0.088551	-0.106683

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p-B ES at r2SCAN-3c in the benzene

C	1.059906	1.051590	-0.240700
C	0.379346	-1.143172	0.466591
C	2.367450	0.771753	0.175048
C	2.672831	-0.471463	0.739734
C	1.677837	-1.426420	0.884411
H	0.824055	2.019133	-0.670645
C	3.410514	1.782421	0.025849
H	-0.942451	0.310867	-0.421127
H	3.684526	-0.691023	1.061878
H	1.913417	-2.390532	1.324150
N	3.261898	2.887055	-0.612717
O	4.446794	3.632167	-0.535747
O	4.623465	1.533341	0.609496
S	5.784016	2.663963	0.014223
O	6.427676	2.052167	-1.152693
C	-0.671791	-2.209236	0.598802
F	-1.923460	-1.719666	0.474731
F	-0.524690	-3.169212	-0.351196
F	-0.600642	-2.837755	1.796582
C	0.069904	0.092936	-0.099239

Table S358 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-TS2 at r2SCAN-3c in the gas phase

C	-2.427623	-0.432486	0.191271
C	-1.462635	0.532342	-0.071674
C	-2.054122	-1.751501	0.436527
C	-0.113060	0.153886	-0.059669
C	0.261103	-1.173618	0.151455
C	-0.713023	-2.124009	0.417399
C	1.042976	1.198692	-0.089237
H	-3.474731	-0.151353	0.199558
H	-2.821090	-2.494381	0.632437
H	1.313272	-1.437317	0.114930
H	-0.426879	-3.155594	0.595866
N	1.078861	1.127026	-1.346657
O	2.563991	2.524380	-1.500721
O	1.610495	1.709569	0.896641
S	3.372725	2.574183	-0.222279
O	4.332995	1.477795	-0.035809

C	-1.891757	1.946417	-0.395019
F	-1.072911	2.861956	0.158633
F	-1.909372	2.158894	-1.725725
F	-3.139197	2.191329	0.065691

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o-TS2 at r2SCAN-3c in the benzene

C	-2.428283	-0.430769	0.194267
C	-1.459908	0.529102	-0.068821
C	-2.058028	-1.752318	0.438222
C	-0.110242	0.144640	-0.054760
C	0.260479	-1.185201	0.151413
C	-0.718586	-2.131024	0.417885
C	1.041105	1.182349	-0.099049
H	-3.475378	-0.149166	0.203201
H	-2.828192	-2.492176	0.632974
H	1.311212	-1.455419	0.114230
H	-0.436707	-3.163969	0.594981
N	1.082877	1.120478	-1.356865
O	2.551224	2.526416	-1.505402
O	1.620090	1.708743	0.878292
S	3.340723	2.597267	-0.211821
O	4.325790	1.520162	-0.026925
C	-1.879970	1.944299	-0.390908
F	-1.055577	2.857045	0.166042
F	-1.886618	2.163706	-1.723711
F	-3.125993	2.202046	0.060373

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m-TS2 at r2SCAN-3c in the gas phase

C	0.060985	0.085033	0.083514
C	0.995243	1.066387	-0.210458
C	0.471045	-1.190381	0.479642
C	2.346976	0.752174	-0.069152
C	2.777004	-0.524339	0.290508
C	1.824739	-1.492301	0.581029
H	0.694868	2.055154	-0.537827
C	3.394911	1.895888	-0.137623
C	-1.415478	0.361871	-0.026684
H	-0.274407	-1.950528	0.694367
H	3.839243	-0.739321	0.347068
H	2.137210	-2.488991	0.874753
N	3.541050	1.716519	-1.376057
O	4.849499	3.274944	-1.572918
O	3.808732	2.579602	0.822944
S	5.538798	3.552894	-0.253682
O	6.606304	2.613030	0.113876
F	-1.671393	1.609512	-0.463225
F	-2.028237	0.213391	1.171450
F	-2.010473	-0.502349	-0.881627

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m-TS2 at r2SCAN-3c in the benzene

C	0.064083	0.086700	0.101777
C	0.999371	1.060793	-0.213408
C	0.471082	-1.183313	0.519226
C	2.350068	0.744470	-0.062328
C	2.779978	-0.527372	0.318244
C	1.824887	-1.486978	0.625333
H	0.702471	2.046335	-0.554608
C	3.395305	1.879039	-0.161362
C	-1.408056	0.364472	-0.040458
H	-0.274157	-1.938914	0.750411
H	3.841442	-0.744701	0.383073
H	2.134978	-2.478368	0.938660
N	3.544089	1.694918	-1.398400
O	4.839143	3.256388	-1.607551
O	3.823762	2.585742	0.782381
S	5.507664	3.558641	-0.278991
O	6.591769	2.636112	0.092381
F	-1.668349	1.671927	-0.234344
F	-2.093671	-0.027118	1.059343
F	-1.939237	-0.310583	-1.089480

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p-TS2 at r2SCAN-3c in the gas phase

C	-2.431492	-0.442448	0.152253
C	-1.437539	0.492546	-0.103708
C	-2.078486	-1.764559	0.409715
C	-0.105628	0.087075	-0.064678
C	0.255855	-1.243515	0.157765
C	-0.740744	-2.168956	0.412170
H	-1.683206	1.525380	-0.326376
C	1.017080	1.162013	-0.085599
H	-3.474549	-0.147759	0.137430
H	1.301628	-1.531900	0.139433
H	-0.487093	-3.207861	0.599177
N	1.077770	1.103536	-1.342109
O	2.483223	2.585656	-1.463888
O	1.533687	1.709410	0.911339
S	3.266429	2.674487	-0.171059
O	4.281334	1.631436	0.028352
C	-3.132750	-2.806773	0.682450
F	-4.382026	-2.313201	0.581567
F	-3.030471	-3.840611	-0.184205
F	-2.995901	-3.320359	1.927274

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p-TS2 at r2SCAN-3c in the benzene

C	-2.422079	-0.440213	0.205398
C	-1.431290	0.498194	-0.043881
C	-2.070110	-1.776598	0.390798
C	-0.101490	0.078682	-0.063495
C	0.258319	-1.262340	0.086214

C	-0.737670	-2.192098	0.333219
H	-1.677368	1.541479	-0.211298
C	1.021402	1.144428	-0.087623
H	-3.462215	-0.135221	0.237213
H	1.300036	-1.559054	0.020497
H	-0.483165	-3.238937	0.463673
N	1.064389	1.133590	-1.345638
O	2.462983	2.618023	-1.439537
O	1.568151	1.672988	0.909220
S	3.244011	2.683557	-0.140271
O	4.280227	1.650713	0.013127
C	-3.134531	-2.801779	0.686610
F	-4.360558	-2.391543	0.303750
F	-2.885522	-3.974809	0.063649
F	-3.196401	-3.065464	2.015676

Table S359 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-C ES at r2SCAN-3c in the gas phase

C	0.554131	0.025997	-0.505653
C	1.247824	1.122121	-0.004178
C	1.047964	-1.262334	-0.338064
C	2.459196	0.918725	0.683133
C	2.950510	-0.377282	0.844112
C	2.246612	-1.460042	0.337308
C	3.215995	3.144648	1.381533
H	-0.377439	0.187452	-1.035847
H	0.496668	-2.106302	-0.739257
H	3.893918	-0.512161	1.361892
H	2.643410	-2.462034	0.467256
N	3.246886	1.950285	1.184847
O	3.977430	1.354568	-2.063727
O	3.337129	4.276025	1.639850
S	5.134416	1.733468	-1.236998
O	5.883288	0.648227	-0.582121
C	0.703452	2.507640	-0.196823
F	1.571163	3.303678	-0.873756
F	-0.455297	2.516509	-0.879397
F	0.469735	3.119836	0.995952

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o-C ES at r2SCAN-3c in the benzene

C	0.551013	0.024548	-0.506540
C	1.245966	1.121494	-0.006447
C	1.045380	-1.263853	-0.337181
C	2.457804	0.918938	0.680641
C	2.947093	-0.377115	0.847740
C	2.242958	-1.460856	0.341287
C	3.216086	3.143384	1.389724
H	-0.382063	0.182502	-1.035505

H	0.493730	-2.108510	-0.736638
H	3.885747	-0.514502	1.373917
H	2.637298	-2.463209	0.476929
N	3.242906	1.953088	1.181458
O	3.998454	1.360196	-2.077240
O	3.335447	4.274682	1.655973
S	5.155120	1.741434	-1.249259
O	5.900476	0.647596	-0.603440
C	0.700114	2.505838	-0.197409
F	1.566390	3.305831	-0.874636
F	-0.459400	2.516757	-0.878712
F	0.466472	3.120782	0.995398

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m-C ES at r2SCAN-3c in the gas phase

C	0.925467	-1.353153	0.147060
C	1.632583	-0.745694	-0.881409
C	0.749763	-0.713831	1.373601
C	2.172416	0.524750	-0.676649
C	2.002513	1.177128	0.547034
C	1.291908	0.550940	1.562964
H	1.770930	-1.239878	-1.835705
C	3.484344	2.129091	-1.932775
C	0.331416	-2.722186	-0.036201
H	0.194321	-1.203010	2.167469
H	2.431266	2.163328	0.697853
H	1.161539	1.058648	2.513565
N	2.874088	1.109349	-1.731258
O	4.096043	3.074145	-2.263631
O	4.458721	3.982532	0.919045
S	5.655599	3.237543	0.497335
O	5.509179	1.787780	0.292916
F	0.542142	-3.220288	-1.271936
F	-1.008756	-2.710126	0.170452
F	0.849759	-3.608420	0.849590

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m-C ES at r2SCAN-3c in the benzene

C	0.922927	-1.357913	0.145583
C	1.628476	-0.751079	-0.885167
C	0.742938	-0.717184	1.371246
C	2.161901	0.522429	-0.681884
C	1.987972	1.177431	0.540120
C	1.279584	0.550954	1.557949
H	1.770314	-1.245755	-1.838976
C	3.465454	2.133407	-1.935394
C	0.336021	-2.728996	-0.034552
H	0.189337	-1.204811	2.167726
H	2.409388	2.167314	0.687861
H	1.145919	1.060481	2.507143
N	2.862484	1.108380	-1.737728
O	4.070588	3.083297	-2.264305

O	4.551195	4.038038	0.916506
S	5.714382	3.229125	0.518249
O	5.486091	1.788063	0.320380
F	0.542703	-3.229433	-1.270700
F	-1.004686	-2.728692	0.177154
F	0.862250	-3.616405	0.848109

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p-C ES at r2SCAN-3c in the gas phase

C	0.895654	-1.442113	0.111283
C	1.604419	-0.822634	-0.907963
C	0.709107	-0.787900	1.325688
C	2.132574	0.453072	-0.709574
C	1.946115	1.112680	0.510563
C	1.236846	0.488471	1.522500
H	1.754902	-1.317788	-1.861186
C	3.447242	2.063829	-1.950633
H	0.483912	-2.433643	-0.042443
H	2.361449	2.104522	0.660085
H	1.088258	0.998058	2.469385
N	2.836625	1.041393	-1.759721
O	4.058686	3.011373	-2.272814
O	4.414374	3.881510	0.928334
S	5.611426	3.128581	0.521950
O	5.450864	1.685799	0.281995
C	-0.010776	-1.464398	2.454779
F	-0.788840	-0.599119	3.147622
F	-0.806295	-2.469836	2.027544
F	0.859049	-2.002753	3.349082

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p-C ES at r2SCAN-3c in the benzene

C	0.912895	-1.450506	0.116885
C	1.615741	-0.830962	-0.906873
C	0.712135	-0.784605	1.323433
C	2.122586	0.455550	-0.719818
C	1.922506	1.125757	0.492492
C	1.219753	0.501951	1.509857
H	1.776094	-1.335753	-1.853603
C	3.417087	2.076073	-1.963902
H	0.519310	-2.450575	-0.030096
H	2.318868	2.126718	0.632219
H	1.062802	1.021491	2.450116
N	2.820386	1.044279	-1.775014
O	4.016751	3.030678	-2.285874
O	4.489490	3.884413	0.971816
S	5.658974	3.075345	0.592318
O	5.410388	1.662908	0.258645
C	-0.002112	-1.459775	2.454659
F	-0.786037	-0.598888	3.148253
F	-0.792744	-2.473514	2.036644
F	0.870717	-1.991482	3.354319

Table S360 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

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o-product ES at r2SCAN-3c in the gas phase

C	1.812470	-0.414938	0.384761
C	2.891493	0.390923	0.033692
C	2.000007	-1.761059	0.673101
C	4.179898	-0.163023	-0.029485
C	4.362366	-1.517717	0.261904
C	3.277698	-2.308536	0.610485
C	6.440850	0.528224	-0.529932
H	0.820481	0.019257	0.431372
H	1.150871	-2.378911	0.945659
H	5.362579	-1.938489	0.210838
H	3.434119	-3.359589	0.833983
N	5.248311	0.652229	-0.382570
O	7.596644	0.544675	-0.707704
C	2.682897	1.849464	-0.278721
F	3.390998	2.650859	0.550105
F	3.055315	2.153564	-1.543844
F	1.383909	2.205309	-0.155626

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o-product ES at r2SCAN-3c in the benzene

C	1.810130	-0.415193	0.384634
C	2.891384	0.389273	0.034374
C	1.998040	-1.761560	0.672898
C	4.179715	-0.165626	-0.027956
C	4.362839	-1.519874	0.263666
C	3.276280	-2.309562	0.611417
C	6.440538	0.531764	-0.531951
H	0.817092	0.016944	0.431210
H	1.148369	-2.379266	0.944599
H	5.362526	-1.941840	0.213427
H	3.432019	-3.360770	0.835052
N	5.248791	0.651075	-0.381496
O	7.596462	0.556280	-0.713456
C	2.684593	1.845903	-0.277633
F	3.394191	2.651327	0.550414
F	3.060149	2.154700	-1.543678
F	1.387791	2.208667	-0.157503

17

m-product ES at r2SCAN-3c in the gas phase

C	-0.007265	-0.152119	0.358128
C	0.843103	0.945450	0.421859
C	0.492715	-1.449724	0.409294
C	2.224955	0.744553	0.540288
C	2.731758	-0.567301	0.593086
C	1.866627	-1.646754	0.527116
H	0.444612	1.953955	0.382051

C	3.102852	1.852260	0.608331
C	-1.484594	0.107996	0.231862
H	-0.182665	-2.296050	0.358930
H	3.801807	-0.720020	0.685944
H	2.263901	-2.655999	0.568289
N	3.844064	2.749836	0.659209
O	4.604608	3.678188	0.713652
F	-2.208585	-1.029355	0.215049
F	-1.771253	0.787479	-0.904661
F	-1.940192	0.862955	1.260655

17

m-product ES at r2SCAN-3c in the benzene

C	-0.006405	-0.151722	0.358371
C	0.843191	0.947028	0.421899
C	0.493076	-1.450097	0.409526
C	2.224159	0.742290	0.540263
C	2.733099	-0.568433	0.593287
C	1.867197	-1.647953	0.527267
H	0.446624	1.956530	0.381912
C	3.102590	1.850658	0.608177
C	-1.482280	0.108163	0.232092
H	-0.180178	-2.298350	0.359197
H	3.803189	-0.721498	0.686075
H	2.263648	-2.657507	0.568329
N	3.840919	2.748242	0.658833
O	4.602861	3.681709	0.713389
F	-2.209997	-1.027116	0.214310
F	-1.772850	0.789460	-0.904578
F	-1.942393	0.863944	1.260733

17

p-product ES at r2SCAN-3c in the gas phase

C	1.788277	-0.418749	0.342452
C	2.874206	0.376959	0.003449
C	1.980459	-1.759565	0.658465
C	4.156669	-0.170492	-0.021063
C	4.350195	-1.520891	0.296510
C	3.263741	-2.308357	0.633911
H	2.740084	1.424508	-0.243713
C	6.417289	0.534408	-0.487598
H	0.791784	0.008105	0.361704
H	5.350776	-1.943150	0.277283
H	3.411350	-3.355343	0.881664
N	5.220180	0.663049	-0.366882
O	7.576454	0.549886	-0.640907
C	0.826961	-2.650294	1.015725
F	-0.339001	-1.975930	1.102163
F	0.653824	-3.633997	0.096343
F	1.024607	-3.269077	2.206497

17

p-product ES at r2SCAN-3c in the benzene

C	1.788146	-0.418473	0.341519
C	2.875708	0.375700	0.002771
C	1.980641	-1.759471	0.659021
C	4.157198	-0.174707	-0.019524
C	4.351388	-1.524881	0.299295
C	3.263574	-2.311082	0.636440
H	2.740717	1.423135	-0.245262
C	6.418677	0.538548	-0.489612
H	0.792989	0.011926	0.358371
H	5.351239	-1.948690	0.281201
H	3.412043	-3.358089	0.884393
N	5.222310	0.657679	-0.365553
O	7.578174	0.566693	-0.646714
C	0.826810	-2.647532	1.015078
F	-0.339905	-1.974535	1.107439
F	0.646032	-3.630658	0.093151
F	1.022111	-3.274494	2.203989

Table S361 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

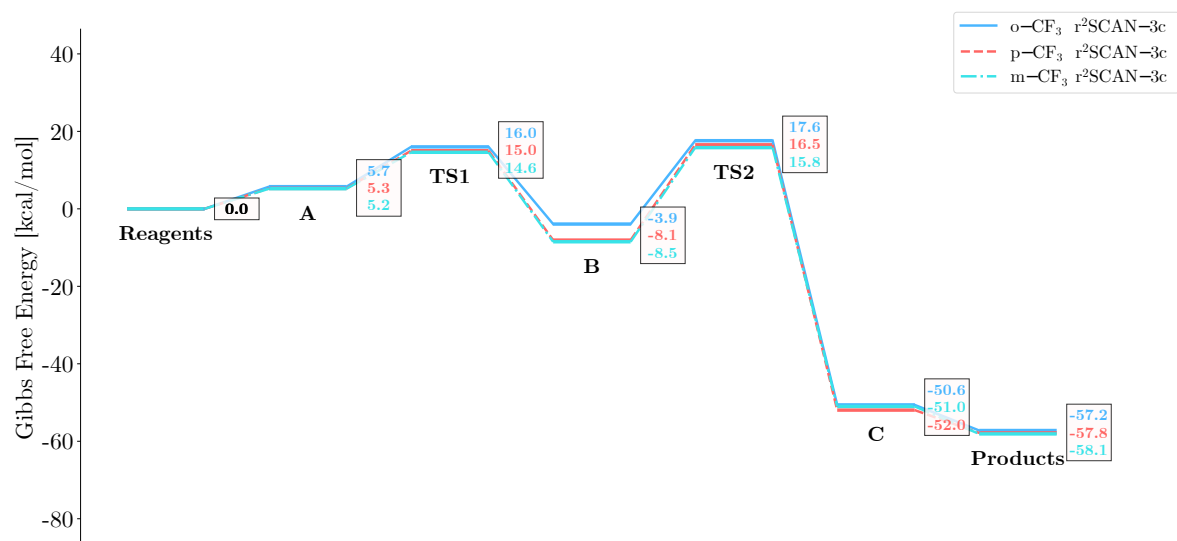
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

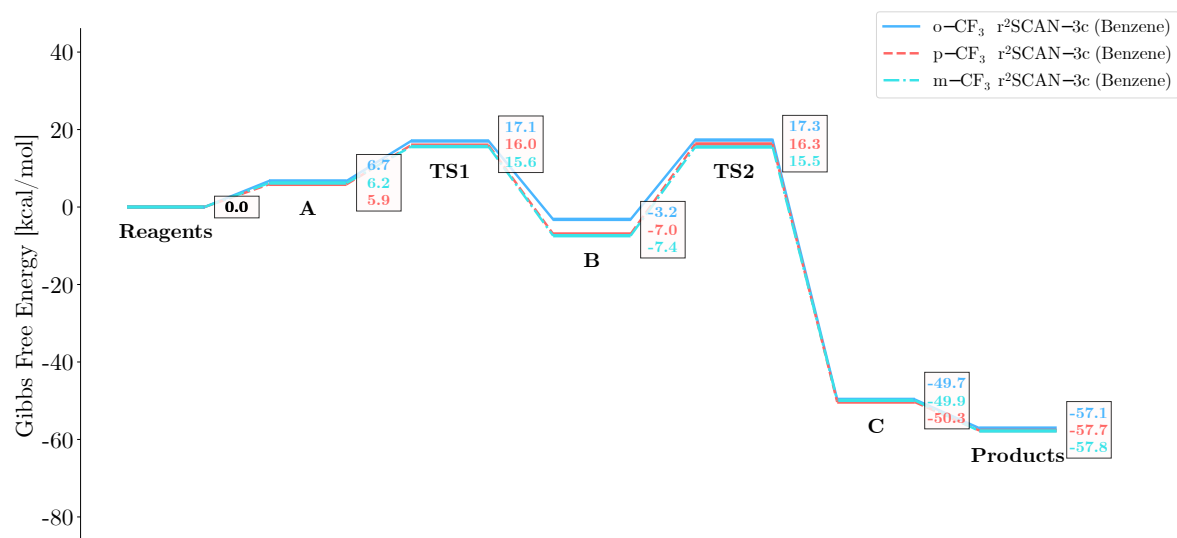
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

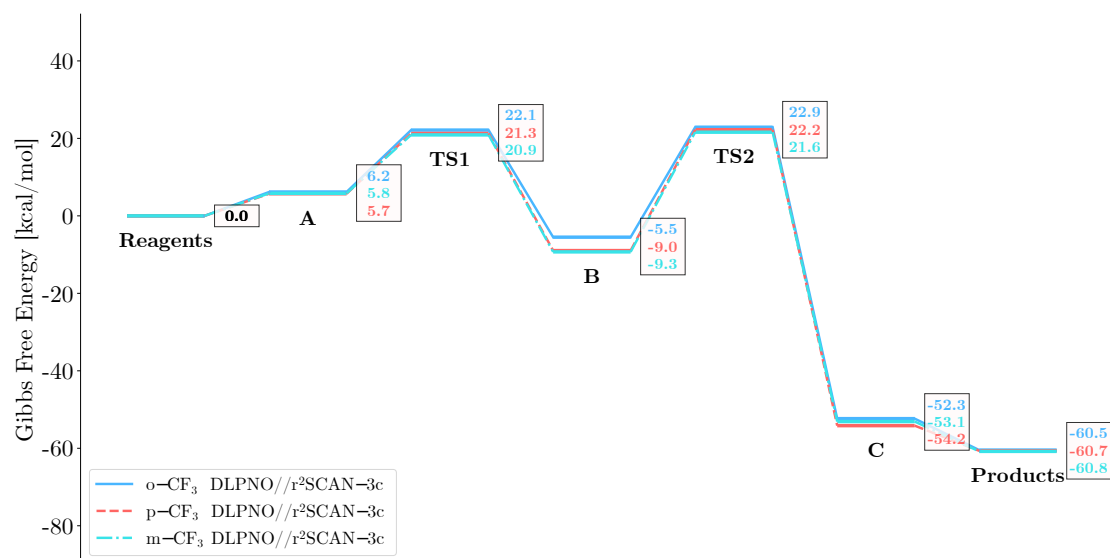


(a) Reaction in the gas phase.

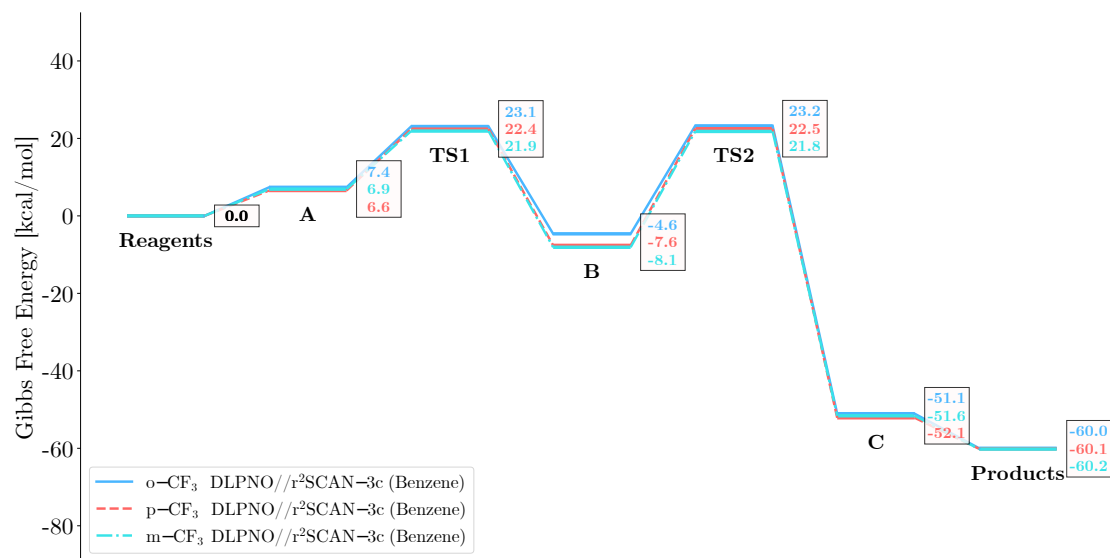


(b) Reaction in the benzene.

Figure S56 Calculated PES for reaction of the -CF₃ substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S57 Calculated PES for reaction of the -CF₃ substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

3.5 –OMe

Table S362 Energy profile of the SO₂-catalyzed conversion for –OMe substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

		Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−7.6	0.4	−21.4	0.8	−55.7
		<i>E</i> + ΔZPE, kcal/mol	0.0	−6.8	1.2	−19.1	1.3	−55.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.5	13.9	−5.8	14.1	−55.1
	Benzene	<i>E</i> , kcal/mol	0.0	−6.5	1.1	−20.4	0.1	−58.8
		<i>E</i> + ΔZPE, kcal/mol	0.0	−5.7	2.0	−18.1	0.7	−57.9
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.2	14.5	−4.9	13.5	−54.7
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−7.3	0.7	−24.1	1.6	−58.4
		<i>E</i> + ΔZPE, kcal/mol	0.0	−6.4	1.6	−21.6	2.1	−57.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.0	14.2	−8.4	14.9	−57.4
	Benzene	<i>E</i> , kcal/mol	0.0	−6.2	1.7	−22.7	1.3	−57.8
		<i>E</i> + ΔZPE, kcal/mol	0.0	−5.4	2.6	−20.3	1.8	−57.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	15.2	−7.0	14.5	−57.0
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−7.7	−0.3	−24.8	−0.7	−56.9
		<i>E</i> + ΔZPE, kcal/mol	0.0	−6.8	0.6	−22.3	0.0	−56.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.3	13.2	−9.1	12.8	−56.3
	Benzene	<i>E</i> , kcal/mol	0.0	−6.6	0.2	−23.3	−1.3	−59.8
		<i>E</i> + ΔZPE, kcal/mol	0.0	−5.8	1.1	−20.9	−0.6	−58.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.9	13.6	−7.8	12.1	−55.6

Table S364 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

18

o-reagent ES at r2SCAN-3c in the gas phase

C	0.044493	−0.194655	0.360533
C	0.924840	0.883004	0.424306
C	0.535919	−1.497397	0.417601
C	2.316757	0.645823	0.546699
C	2.783339	−0.673500	0.601957
C	1.899339	−1.741546	0.537944
O	0.561171	2.186175	0.379407
C	3.204138	1.743032	0.611910
H	−1.022572	−0.030581	0.266989
H	−0.163142	−2.326755	0.366829
H	3.851148	−0.841294	0.696486
H	2.274161	−2.758635	0.581973
N	3.745110	2.776079	0.644227
O	4.359343	3.810534	0.684908
C	−0.828728	2.489004	0.268774
H	−0.891330	3.577704	0.254060
H	−1.388179	2.100777	1.129575

Table S363 Energy profile of the SO₂-catalyzed conversion for –OMe substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−6.8	6.3	−22.4	6.6	−62.5	−58.8
		<i>E</i> + ΔZPE, kcal/mol	0.0	−6.0	7.1	−20.0	7.1	−61.5	−58.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.2	19.8	−6.8	19.9	−50.7	−58.2
	Benzene	<i>E</i> , kcal/mol	0.0	−5.6	7.6	−21.1	6.7	−60.8	−58.1
		<i>E</i> + ΔZPE, kcal/mol	0.0	−4.8	8.5	−18.8	7.3	−59.9	−57.6
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.1	20.9	−5.6	20.1	−49.4	−57.5
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−6.5	7.1	−24.9	7.8	−64.9	−61.0
		<i>E</i> + ΔZPE, kcal/mol	0.0	−5.6	8.0	−22.5	8.3	−63.7	−60.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	20.6	−9.2	21.2	−53.0	−60.1
	Benzene	<i>E</i> , kcal/mol	0.0	−5.2	8.3	−23.3	8.2	−62.9	−60.1
		<i>E</i> + ΔZPE, kcal/mol	0.0	−4.3	9.1	−20.9	8.7	−61.9	−59.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	21.8	−7.6	21.4	−51.5	−59.3
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	−6.8	6.1	−25.6	6.0	−63.4	−59.7
		<i>E</i> + ΔZPE, kcal/mol	0.0	−5.9	7.0	−23.2	6.7	−62.3	−59.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.3	19.6	−10.0	19.5	−51.5	−59.1
	Benzene	<i>E</i> , kcal/mol	0.0	−5.4	6.8	−23.9	6.1	−61.4	−58.6
		<i>E</i> + ΔZPE, kcal/mol	0.0	−4.7	7.7	−21.6	6.8	−60.4	−58.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.1	20.2	−8.5	19.5	−49.6	−58.1

H −1.250559 2.085371 −0.660737

18

o-reagent ES at r2SCAN-3c in the benzene

C	0.034123	−0.195274	0.361872
C	0.901145	0.894394	0.424915
C	0.543762	−1.490878	0.418364
C	2.295287	0.671966	0.546104
C	2.782881	−0.641057	0.601349
C	1.911573	−1.719384	0.537646
O	0.521900	2.191738	0.379959
C	3.169982	1.778888	0.609706
H	−1.035079	−0.045096	0.269190
H	−0.144677	−2.329399	0.367973
H	3.852979	−0.795359	0.694790
H	2.298738	−2.732042	0.581036
N	3.830366	2.735961	0.651437
O	4.537122	3.717265	0.698874
C	−0.876856	2.477973	0.264100
H	−0.951561	3.565618	0.248203
H	−1.430110	2.081803	1.124074
H	−1.286325	2.066024	−0.666152

18

m-reagent ES at r2SCAN-3c in the gas phase

C	-0.131100	0.035552	0.350009
C	0.772710	1.096776	0.416412
C	0.327465	-1.283602	0.400365
C	2.141673	0.838957	0.533375
C	2.609688	-0.488100	0.584973
C	1.696065	-1.525090	0.517571
H	0.399378	2.113926	0.376019
C	3.059165	1.916771	0.600377
O	-1.438125	0.394736	0.237064
H	-0.358949	-2.120145	0.350293
H	3.672335	-0.681648	0.676170
H	2.048903	-2.551369	0.556393
N	3.826979	2.791330	0.648777
O	4.619045	3.697200	0.700674
C	-2.407743	-0.647285	0.158765
H	-3.373446	-0.146977	0.074245
H	-2.398679	-1.270433	1.062824
H	-2.245444	-1.277638	-0.725517

18

m-reagent ES at r2SCAN-3c in the benzene

C	-0.132016	0.037930	0.349894
C	0.772471	1.099734	0.416392
C	0.326976	-1.281921	0.400165
C	2.140971	0.838325	0.533134
C	2.611137	-0.487765	0.584522
C	1.695823	-1.524534	0.516950
H	0.402110	2.118443	0.376413
C	3.059122	1.916494	0.600373
O	-1.438661	0.395461	0.237183
H	-0.359961	-2.118176	0.350500
H	3.673956	-0.681660	0.675541
H	2.047693	-2.551266	0.555600
N	3.826975	2.788686	0.649152
O	4.623427	3.697598	0.701793
C	-2.410684	-0.651194	0.158822
H	-3.375983	-0.151074	0.071694
H	-2.399880	-1.270772	1.064294
H	-2.243556	-1.281348	-0.723632

18

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.064332	-0.135408	0.352359
C	0.788644	0.957932	0.415718
C	0.462657	-1.429062	0.409446
C	2.174762	0.785079	0.535989
C	2.690428	-0.525204	0.591862
C	1.846110	-1.613832	0.529220
H	0.379691	1.962074	0.371880
C	3.039192	1.902650	0.600649
H	-1.130403	0.034300	0.259350
O	-0.277389	-2.566245	0.357782

H	3.761426	-0.672246	0.685003
H	2.234495	-2.626277	0.571468
N	3.760674	2.816527	0.646551
O	4.505027	3.764827	0.695807
C	-1.692643	-2.434793	0.237958
H	-2.083807	-3.452750	0.214624
H	-1.967600	-1.917303	-0.690443
H	-2.117010	-1.900599	1.098076

18

p-reagent ES at r2SCAN-3c in the benzene

C	-0.064706	-0.135699	0.351411
C	0.787923	0.957765	0.415069
C	0.464038	-1.429853	0.408849
C	2.174216	0.782457	0.535818
C	2.693316	-0.526469	0.592151
C	1.848565	-1.615302	0.529166
H	0.378143	1.961749	0.371005
C	3.038273	1.900846	0.600719
H	-1.130848	0.033396	0.257948
O	-0.276102	-2.564846	0.357088
H	3.764414	-0.673622	0.685715
H	2.239888	-2.626923	0.571892
N	3.757196	2.814686	0.646810
O	4.503488	3.768633	0.696667
C	-1.696956	-2.432971	0.238167
H	-2.086149	-3.451365	0.214693
H	-1.968535	-1.914161	-0.689379
H	-2.116245	-1.898652	1.099509

Table S365 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

21

o-A ES at r2SCAN-3c in the gas phase

C	-0.071795	-0.083666	-0.137775
C	0.659859	1.089636	-0.307792
C	0.533000	-1.197033	0.441310
C	2.009971	1.133140	0.109844
C	2.599393	0.002216	0.690731
C	1.860627	-1.160155	0.855296
O	0.185484	2.233223	-0.854248
C	2.758107	2.317373	-0.058560
H	-1.107416	-0.140057	-0.451214
H	-0.049698	-2.104652	0.567707
H	3.635785	0.064587	1.005666
H	2.320654	-2.033224	1.305603
N	3.414206	3.265934	-0.187820
O	4.150646	4.228604	-0.286112
O	5.452939	2.045344	1.436108
S	6.309887	3.107542	0.864986
O	7.081498	2.755030	-0.338375

C	-1.173237	2.251766	-1.292827
H	-1.340234	3.254142	-1.688419
H	-1.860633	2.067563	-0.457518
H	-1.343123	1.511788	-2.085211

21

o-A ES at r2SCAN-3c in the benzene

C	-0.092423	-0.086265	-0.130234
C	0.667452	1.069527	-0.303491
C	0.488434	-1.214731	0.443877
C	2.021722	1.076085	0.106862
C	2.586914	-0.070085	0.683022
C	1.820167	-1.213553	0.850727
O	0.219912	2.223356	-0.845511
C	2.794300	2.243548	-0.066480
H	-1.130961	-0.115928	-0.437838
H	-0.116349	-2.107627	0.572487
H	3.626583	-0.038708	0.992146
H	2.260139	-2.099003	1.297166
N	3.421686	3.205108	-0.232374
O	4.137627	4.184719	-0.360644
O	5.518875	2.173392	1.484544
S	6.298036	3.267298	0.863783
O	7.097875	2.901658	-0.320076
C	-1.145170	2.276924	-1.280427
H	-1.285746	3.283317	-1.675304
H	-1.830008	2.110013	-0.440588
H	-1.333144	1.540055	-2.070268

21

m-A ES at r2SCAN-3c in the gas phase

C	-0.189278	0.121175	-0.222161
C	0.606683	1.258977	-0.362105
C	0.340692	-1.040064	0.347132
C	1.934509	1.227823	0.069600
C	2.478735	0.064384	0.644498
C	1.668899	-1.050410	0.772321
H	0.182147	2.152624	-0.805791
C	2.753661	2.375796	-0.067039
O	-1.465704	0.248351	-0.672205
H	-0.262342	-1.932757	0.463602
H	3.510638	0.062118	0.975713
H	2.074596	-1.955690	1.213799
N	3.472660	3.282011	-0.163500
O	4.260663	4.203353	-0.235177
O	5.423406	1.901864	1.451770
S	6.360239	2.911579	0.913585
O	7.113618	2.536527	-0.293940
C	-2.325504	-0.883277	-0.557679
H	-3.284622	-0.569160	-0.971498
H	-2.460285	-1.177087	0.491624
H	-1.941470	-1.735347	-1.133779

21

m-A ES at r2SCAN-3c in the benzene

C	-0.193602	0.114838	-0.219938
C	0.620370	1.241151	-0.357762
C	0.317860	-1.056072	0.348806
C	1.947535	1.185571	0.074841
C	2.473745	0.013325	0.648109
C	1.645580	-1.089096	0.774710
H	0.213110	2.143935	-0.799918
C	2.783099	2.321889	-0.061039
O	-1.466655	0.261115	-0.670089
H	-0.299638	-1.938848	0.464356
H	3.505578	-0.009540	0.979459
H	2.035843	-2.001652	1.215297
N	3.482907	3.239601	-0.175758
O	4.260864	4.173508	-0.261724
O	5.505606	1.968368	1.468102
S	6.370870	3.030810	0.911074
O	7.144296	2.673708	-0.292138
C	-2.345321	-0.863419	-0.560678
H	-3.297513	-0.534319	-0.978166
H	-2.485353	-1.154863	0.487678
H	-1.967242	-1.717223	-1.136452

21

p-A ES at r2SCAN-3c in the gas phase

C	-0.049103	-0.016168	-0.158168
C	0.702859	1.139131	-0.317675
C	0.535770	-1.147169	0.420963
C	2.040590	1.182408	0.094487
C	2.620811	0.038264	0.678113
C	1.873925	-1.109096	0.836861
H	0.251337	2.017654	-0.766939
C	2.816038	2.353121	-0.063411
H	-1.081343	-0.021341	-0.486857
O	-0.104813	-2.324515	0.623414
H	3.656040	0.075902	1.000457
H	2.305965	-1.998243	1.284397
N	3.505560	3.280504	-0.177159
O	4.267912	4.225787	-0.262026
O	5.485610	2.002870	1.474740
S	6.379444	3.042818	0.919493
O	7.159169	2.672653	-0.273212
C	-1.469788	-2.422233	0.218510
H	-1.780727	-3.436837	0.470364
H	-1.575428	-2.265934	-0.862768
H	-2.097316	-1.703140	0.760656

21

p-A ES at r2SCAN-3c in the benzene

C	-0.048715	-0.022836	-0.146590

C	0.724533	1.117715	-0.306219
C	0.520911	-1.171868	0.414854
C	2.069831	1.127055	0.087097
C	2.634811	-0.033536	0.652465
C	1.866142	-1.166533	0.812791
H	0.285411	2.009792	-0.741057
C	2.863478	2.284249	-0.074690
H	-1.085397	-0.003854	-0.460715
O	-0.141719	-2.334975	0.615133
H	3.675159	-0.024967	0.960697
H	2.287533	-2.067506	1.247325
N	3.528028	3.223989	-0.221760
O	4.272900	4.186420	-0.331967
O	5.547645	2.132111	1.540414
S	6.370106	3.210395	0.948428
O	7.191137	2.832617	-0.216940
C	-1.519552	-2.399954	0.226756
H	-1.846814	-3.410194	0.474298
H	-1.632576	-2.230082	-0.850801
H	-2.120344	-1.671600	0.784725

Table S366 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

21

o-TS1 at r2SCAN-3c in the gas phase

C	-1.536522	-0.283571	-0.315153
C	-0.721467	0.836359	-0.476233
C	-0.987367	-1.481239	0.133535
C	0.663383	0.728685	-0.197113
C	1.192362	-0.486381	0.256536
C	0.370007	-1.588645	0.423183
O	-1.143098	2.046088	-0.899261
C	1.504782	1.857239	-0.336593
H	-2.597380	-0.228336	-0.528042
H	-1.637716	-2.341958	0.258801
H	2.251707	-0.531821	0.484388
H	0.784352	-2.526305	0.777318
N	1.828545	2.846354	-0.946225
O	2.639377	3.792526	-0.821564
O	2.772223	2.039632	1.228406
S	3.901440	3.007609	0.886584
O	5.030995	2.384529	0.168571
C	-2.533341	2.213163	-1.183769
H	-2.645524	3.254310	-1.487475
H	-3.144290	2.022158	-0.292710
H	-2.850369	1.555714	-2.002865

21

o-TS1 at r2SCAN-3c in the benzene

C	-1.534426	-0.268796	-0.259264
C	-0.687325	0.817553	-0.486145

C	-1.001759	-1.481153	0.166291
C	0.708782	0.652399	-0.299196
C	1.219995	-0.579114	0.137601
C	0.368546	-1.644734	0.369843
O	-1.087016	2.036947	-0.889555
C	1.577912	1.747273	-0.497718
H	-2.604213	-0.175087	-0.402657
H	-1.676115	-2.313956	0.344548
H	2.290179	-0.669631	0.293762
H	0.764702	-2.596350	0.707364
N	2.037677	2.595160	-1.227510
O	2.816560	3.580135	-1.094618
O	2.445791	2.324824	1.224452
S	3.613828	3.265457	0.934121
O	4.883622	2.561643	0.645695
C	-2.490664	2.258570	-1.092109
H	-2.577047	3.300558	-1.400056
H	-3.048795	2.099238	-0.162329
H	-2.878133	1.605174	-1.882203

21

m-TS1 at r2SCAN-3c in the gas phase

C	-2.413751	-0.784844	-0.460672
C	-1.535810	0.291800	-0.586327
C	-1.974521	-1.986228	0.104649
C	-0.210499	0.149333	-0.164726
C	0.241587	-1.051846	0.404450
C	-0.652913	-2.100251	0.532946
H	-1.890620	1.221858	-1.016474
C	0.688041	1.240743	-0.316472
O	-3.675462	-0.558202	-0.910763
H	-2.644742	-2.829957	0.217409
H	1.268993	-1.134222	0.736462
H	-0.319603	-3.035157	0.972923
N	0.999195	2.249460	-0.893406
O	1.859523	3.151229	-0.843432
O	2.139001	1.279537	1.118698
S	3.276155	2.204351	0.702850
O	4.284721	1.574211	-0.170109
C	-4.623964	-1.617044	-0.792457
H	-5.556180	-1.224950	-1.200976
H	-4.776561	-1.900005	0.257268
H	-4.313530	-2.496359	-1.371832

21

m-TS1 at r2SCAN-3c in the benzene

C	-2.410885	-0.781874	-0.457166
C	-1.520824	0.282464	-0.610012
C	-1.969580	-1.990642	0.092504
C	-0.183873	0.114776	-0.236402
C	0.270837	-1.093770	0.316417
C	-0.635679	-2.127902	0.475966

H	-1.872022	1.221552	-1.024072
C	0.724701	1.192212	-0.416265
O	-3.682797	-0.537032	-0.862209
H	-2.648934	-2.823884	0.228071
H	1.308103	-1.195825	0.612450
H	-0.304093	-3.069062	0.903867
N	1.104133	2.135482	-1.060591
O	1.953839	3.053951	-0.974345
O	1.978881	1.412453	1.172254
S	3.141369	2.328142	0.807476
O	4.263660	1.633105	0.140790
C	-4.643569	-1.588891	-0.717848
H	-5.581481	-1.183424	-1.098649
H	-4.765693	-1.870071	0.335427
H	-4.357034	-2.468300	-1.307653

21

p-TS1 at r2SCAN-3c in the gas phase

C	-1.572985	-0.218385	-0.312003
C	-0.730899	0.871241	-0.468061
C	-1.047615	-1.439494	0.128148
C	0.643648	0.750114	-0.219399
C	1.160692	-0.479835	0.229114
C	0.322906	-1.558471	0.403747
H	-1.132470	1.824100	-0.797508
C	1.505577	1.857918	-0.391217
H	-2.629197	-0.102807	-0.523280
O	-1.778693	-2.560180	0.324668
H	2.220722	-0.560326	0.444302
H	0.702536	-2.513320	0.752023
N	1.874467	2.807860	-1.036034
O	2.680850	3.761949	-0.917531
O	2.707525	2.127798	1.232981
S	3.851269	3.074772	0.889018
O	5.010561	2.415813	0.255393
C	-3.179695	-2.508054	0.049419
H	-3.557387	-3.510139	0.255182
H	-3.366795	-2.254923	-1.001721
H	-3.685016	-1.785633	0.702758

21

p-TS1 at r2SCAN-3c in the benzene

C	-1.543670	-0.211431	-0.276918
C	-0.677932	0.852635	-0.462794
C	-1.027546	-1.464489	0.083714
C	0.707674	0.677677	-0.320797
C	1.215351	-0.583629	0.051024
C	0.357010	-1.640284	0.250242
H	-1.068486	1.829004	-0.731642
C	1.583264	1.769647	-0.501227
H	-2.608021	-0.056761	-0.406224
O	-1.779145	-2.562761	0.297306

H	2.285216	-0.711308	0.180737
H	0.729056	-2.619153	0.535083
N	2.094662	2.596771	-1.222273
O	2.872937	3.582318	-1.058228
O	2.364175	2.392933	1.262393
S	3.545284	3.326665	1.008856
O	4.830607	2.618904	0.812307
C	-3.202628	-2.453403	0.148475
H	-3.595233	-3.447105	0.364689
H	-3.467212	-2.166263	-0.875780
H	-3.615362	-1.729967	0.861057

Table S367 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

21

o-B ES at r2SCAN-3c in the gas phase

C	0.048307	0.064635	-0.078991
C	0.997160	1.074107	-0.255826
C	0.418832	-1.160088	0.465179
C	2.341775	0.841256	0.123680
C	2.682819	-0.400890	0.672068
C	1.734708	-1.398467	0.842577
O	0.712929	2.286725	-0.770941
C	3.379206	1.854276	-0.022161
H	-0.983468	0.229023	-0.364194
H	-0.335137	-1.931473	0.591540
H	3.713046	-0.577941	0.958342
H	2.024658	-2.354597	1.264774
N	3.307089	2.948446	-0.696151
O	4.522046	3.648028	-0.570770
O	4.564614	1.591565	0.635752
S	5.786245	2.647204	0.056212
O	6.465857	1.976259	-1.057262
C	-0.630893	2.565559	-1.159650
H	-0.614917	3.588050	-1.538655
H	-1.314735	2.501810	-0.303354
H	-0.963931	1.885643	-1.954149

21

o-B ES at r2SCAN-3c in the benzene

C	0.048015	0.067087	-0.078680
C	0.997747	1.076022	-0.260701
C	0.419643	-1.156547	0.466559
C	2.343389	0.841348	0.117666
C	2.686317	-0.401451	0.667280
C	1.737484	-1.397197	0.841120
O	0.711852	2.286180	-0.779112
C	3.381176	1.853024	-0.026972
H	-0.984423	0.231935	-0.361446
H	-0.334898	-1.927124	0.596706
H	3.716597	-0.581544	0.952046

H	2.026779	-2.353508	1.263760
N	3.315086	2.947179	-0.704000
O	4.532078	3.648895	-0.567424
O	4.562389	1.592961	0.637364
S	5.788264	2.646079	0.069782
O	6.465828	1.972024	-1.046212
C	-0.640423	2.564905	-1.160521
H	-0.626922	3.586313	-1.541769
H	-1.314438	2.501323	-0.297840
H	-0.975331	1.881222	-1.949587

21

m-B ES at r2SCAN-3c in the gas phase

C	-0.112956	0.265972	-0.130007
C	0.928901	1.183506	-0.253114
C	0.130447	-1.007696	0.396115
C	2.215913	0.824279	0.143422
C	2.471063	-0.448182	0.671431
C	1.422015	-1.346728	0.790558
H	0.724645	2.168688	-0.657923
C	3.302996	1.790124	0.007425
O	-1.329891	0.707963	-0.545919
H	-0.667241	-1.732956	0.502628
H	3.473985	-0.723538	0.974781
H	1.607618	-2.336265	1.197216
N	3.205104	2.913381	-0.606770
O	4.426100	3.601060	-0.514431
O	4.507152	1.472841	0.582869
S	5.713327	2.561757	0.003001
O	6.336177	1.946979	-1.172414
C	-2.432792	-0.189161	-0.444664
H	-3.295297	0.357090	-0.828744
H	-2.618974	-0.476625	0.598652
H	-2.271831	-1.089347	-1.052432

21

m-B ES at r2SCAN-3c in the benzene

C	-0.117254	0.269226	-0.129611
C	0.922516	1.190665	-0.253302
C	0.132865	-1.007844	0.386361
C	2.213376	0.829688	0.130763
C	2.475516	-0.445544	0.649358
C	1.428148	-1.346879	0.769897
H	0.711750	2.179863	-0.645688
C	3.299601	1.795647	-0.010406
O	-1.338064	0.710654	-0.532033
H	-0.662953	-1.735307	0.494428
H	3.480651	-0.723336	0.944007
H	1.618162	-2.338743	1.169046
N	3.222981	2.888024	-0.682004
O	4.439350	3.588577	-0.567413
O	4.481582	1.512572	0.623970

S	5.705462	2.578755	0.046950
O	6.366715	1.911580	-1.080729
C	-2.441587	-0.193888	-0.426607
H	-3.307488	0.354213	-0.799789
H	-2.614600	-0.486986	0.616468
H	-2.280269	-1.087796	-1.041986

21

p-B ES at r2SCAN-3c in the gas phase

C	0.098865	0.034489	-0.066144
C	1.076926	1.005565	-0.210203
C	0.432510	-1.206863	0.489655
C	2.394987	0.758194	0.187142
C	2.718799	-0.487980	0.742588
C	1.748479	-1.459121	0.893197
H	0.820755	1.970067	-0.636544
C	3.411573	1.785603	0.026790
H	-0.913226	0.254485	-0.384022
O	-0.444070	-2.224157	0.679010
H	3.737986	-0.693000	1.051586
H	1.986288	-2.427856	1.320134
N	3.238644	2.894186	-0.601119
O	4.418964	3.659946	-0.518458
O	4.639937	1.552838	0.595044
S	5.768400	2.705054	-0.016545
O	6.407820	2.110059	-1.193946
C	-1.800292	-2.022154	0.282693
H	-2.319327	-2.951265	0.521528
H	-1.875234	-1.828948	-0.795214
H	-2.258419	-1.194673	0.839598

21

p-B ES at r2SCAN-3c in the benzene

C	0.095776	0.036321	-0.062293
C	1.072687	1.008259	-0.207589
C	0.433253	-1.206289	0.490791
C	2.393359	0.761085	0.184973
C	2.720925	-0.485936	0.738434
C	1.751689	-1.458038	0.890848
H	0.808839	1.972498	-0.630203
C	3.409578	1.787371	0.022324
H	-0.917703	0.256046	-0.375990
O	-0.441173	-2.222819	0.680188
H	3.740543	-0.693360	1.044955
H	1.994890	-2.426317	1.316573
N	3.244234	2.892651	-0.615961
O	4.428026	3.659217	-0.524399
O	4.634114	1.558913	0.599930
S	5.768577	2.702847	-0.006602
O	6.405100	2.096529	-1.182822
C	-1.802765	-2.023432	0.281097
H	-2.318160	-2.953771	0.521662

H	-1.872811	-1.831774	-0.796515
H	-2.258618	-1.195531	0.837366

Table S368 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

21

o-TS2 at r2SCAN-3c in the gas phase

C	0.101712	-0.050158	0.009892
C	1.072074	0.929661	-0.211077
C	0.490506	-1.321331	0.420381
C	2.427461	0.602403	0.015124
C	2.802394	-0.685864	0.399713
C	1.831867	-1.648256	0.620472
O	0.828196	2.190045	-0.603597
C	3.470945	1.717432	-0.050799
H	-0.948526	0.165477	-0.146067
H	-0.275143	-2.075554	0.578277
H	3.858253	-0.904684	0.523029
H	2.113646	-2.647789	0.932862
N	3.770581	1.421154	-1.241290
O	5.094900	2.947608	-1.427700
O	3.793805	2.525979	0.859025
S	5.587082	3.367824	-0.053936
O	6.604406	2.488907	0.542603
C	-0.529115	2.579263	-0.828960
H	-0.485749	3.627782	-1.123622
H	-1.123667	2.477342	0.087041
H	-0.976978	1.987940	-1.636881

21

o-TS2 at r2SCAN-3c in the benzene

C	0.101740	-0.048474	0.014026
C	1.076448	0.927953	-0.204939
C	0.487170	-1.322298	0.418316
C	2.431397	0.592298	0.023287
C	2.804437	-0.701070	0.399669
C	1.828813	-1.657843	0.616515
O	0.841221	2.189470	-0.593061
C	3.472918	1.694300	-0.062466
H	-0.947836	0.172689	-0.138968
H	-0.281449	-2.074310	0.572777
H	3.858921	-0.926521	0.524255
H	2.105172	-2.660121	0.925269
N	3.788180	1.414579	-1.253280
O	5.081891	2.945994	-1.429795
O	3.802760	2.522237	0.837980
S	5.539679	3.387947	-0.044851
O	6.579700	2.534163	0.554907
C	-0.519638	2.587640	-0.826503
H	-0.465714	3.631229	-1.135326
H	-1.110434	2.499703	0.092066

H	-0.966726	1.985615	-1.625390

21

m-TS2 at r2SCAN-3c in the gas phase

C	-0.079689	0.285199	0.162880
C	0.952007	1.198958	-0.065312
C	0.227655	-1.048370	0.456678
C	2.264902	0.760487	0.040748
C	2.596804	-0.573026	0.297258
C	1.559576	-1.462028	0.520618
H	0.721106	2.229188	-0.312925
C	3.402448	1.813024	0.048447
O	-1.335848	0.785751	0.062339
H	-0.558419	-1.775397	0.623530
H	3.635466	-0.881800	0.330361
H	1.779990	-2.502524	0.738409
N	3.522130	1.749751	-1.203027
O	4.955148	3.208378	-1.260537
O	3.894561	2.367240	1.059776
S	5.659775	3.293235	0.078689
O	6.661705	2.247214	0.330370
C	-2.429507	-0.112540	0.251880
H	-3.329772	0.488691	0.120753
H	-2.420923	-0.541174	1.262323
H	-2.415714	-0.917198	-0.494509

21

m-TS2 at r2SCAN-3c in the benzene

C	-0.077690	0.286698	0.157836
C	0.956919	1.197055	-0.072306
C	0.226788	-1.049673	0.449178
C	2.268847	0.751113	0.035646
C	2.598708	-0.584795	0.287068
C	1.556998	-1.469129	0.511878
H	0.731450	2.230373	-0.313953
C	3.402301	1.796346	0.031406
O	-1.331131	0.789455	0.061518
H	-0.561441	-1.775010	0.613848
H	3.636097	-0.898938	0.318760
H	1.772958	-2.510760	0.728762
N	3.547822	1.731018	-1.217171
O	4.965961	3.194061	-1.262115
O	3.891558	2.376156	1.036695
S	5.625082	3.312984	0.101877
O	6.645518	2.289271	0.382092
C	-2.430649	-0.107346	0.264098
H	-3.328461	0.497772	0.136014
H	-2.412518	-0.529371	1.276274
H	-2.421717	-0.914221	-0.478655

21

p-TS2 at r2SCAN-3c in the gas phase

C	0.341797	0.009567	-0.504704
C	1.440129	0.832888	-0.598799
C	0.324644	-1.033220	0.438723
C	2.549963	0.600353	0.227390
C	2.519680	-0.405078	1.194426
C	1.416447	-1.237054	1.294629
H	1.464142	1.649660	-1.313189
C	3.829962	1.397169	-0.010017
H	-0.526537	0.150183	-1.139790
O	-0.800796	-1.776372	0.451696
H	3.366965	-0.531696	1.860522
H	1.408490	-2.022974	2.039915
N	3.542899	2.250355	0.876175
O	5.280903	3.267476	0.655649
O	4.725406	1.164595	-0.869137
S	5.835146	3.024057	-0.738138
O	5.177254	3.780650	-1.814361
C	-0.895068	-2.851670	1.389347
H	-1.864222	-3.316422	1.206234
H	-0.855929	-2.480039	2.420631
H	-0.098756	-3.588228	1.226190

21

p-TS2 at r2SCAN-3c in the benzene

C	0.337705	0.008260	-0.511097
C	1.432307	0.835270	-0.606939
C	0.325718	-1.036512	0.433109
C	2.545928	0.601456	0.216378
C	2.520440	-0.403877	1.186972
C	1.420738	-1.238325	1.288206
H	1.450915	1.651256	-1.322714
C	3.808250	1.412125	-0.001499
H	-0.530641	0.148055	-1.146781
O	-0.793489	-1.782118	0.447474
H	3.370221	-0.533300	1.849744
H	1.417331	-2.026414	2.031218
N	3.542217	2.273733	0.883369
O	5.276707	3.261883	0.663684
O	4.720401	1.196959	-0.860495
S	5.836155	2.985219	-0.728558
O	5.197747	3.761971	-1.805726
C	-0.890848	-2.854793	1.398488
H	-1.863976	-3.312473	1.221067
H	-0.843125	-2.470784	2.423680
H	-0.098182	-3.593389	1.233812

Table S369 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

21

o-C ES at r2SCAN-3c in the gas phase

C	0.901331	-1.527941	0.184801

C	1.688832	-0.968051	-0.821188
C	0.645881	-0.812737	1.352577
C	2.215860	0.325888	-0.639439
C	1.955013	1.028679	0.534575
C	1.169691	0.461550	1.531157
O	1.997868	-1.574472	-1.994791
C	3.534777	1.888184	-1.958604
H	0.484284	-2.520803	0.065453
H	0.032084	-1.264600	2.125793
H	2.383945	2.018829	0.659738
H	0.974214	1.016218	2.442926
N	3.002140	0.856252	-1.657702
O	4.109966	2.836670	-2.355886
O	4.272202	4.049167	0.722200
S	5.509635	3.427427	0.221859
O	5.615537	1.963361	0.329529
C	1.493848	-2.889183	-2.211865
H	1.860635	-3.186339	-3.195322
H	0.395794	-2.900535	-2.212885
H	1.869292	-3.590252	-1.454764

21

o-C ES at r2SCAN-3c in the benzene

C	0.916414	-1.533298	0.189855
C	1.683103	-0.958259	-0.824657
C	0.643811	-0.815148	1.352442
C	2.171360	0.352923	-0.655129
C	1.892997	1.059004	0.513162
C	1.128907	0.477408	1.518478
O	2.006585	-1.565894	-1.993015
C	3.462263	1.942808	-1.959975
H	0.529447	-2.539580	0.081350
H	0.046763	-1.278610	2.132154
H	2.288840	2.064636	0.625871
H	0.918863	1.034369	2.425865
N	2.937698	0.898645	-1.683653
O	4.024041	2.905634	-2.340412
O	4.510713	4.083889	0.779837
S	5.621878	3.297244	0.219140
O	5.501965	1.830931	0.294866
C	1.538129	-2.901567	-2.198247
H	1.909362	-3.194618	-3.180977
H	0.441689	-2.941246	-2.192672
H	1.938003	-3.581962	-1.436122

21

m-C ES at r2SCAN-3c in the gas phase

C	0.631491	-1.502996	0.041897
C	1.387472	-0.896532	-0.964274
C	0.611427	-0.964757	1.330018
C	2.118616	0.247273	-0.674311
C	2.113216	0.802926	0.611664

C	1.356906	0.184450	1.593246
H	1.396730	-1.322298	-1.961276
C	3.575890	1.769133	-1.903855
O	-0.050976	-2.617038	-0.341235
H	0.031930	-1.419166	2.124000
H	2.690551	1.696409	0.825227
H	1.343648	0.604362	2.594751
N	2.861179	0.823082	-1.709709
O	4.284859	2.647891	-2.235821
O	4.131200	3.830877	0.779287
S	5.460908	4.011042	0.172629
O	6.448682	2.943010	0.377021
C	-0.836508	-3.281742	0.643928
H	-1.292285	-4.132412	0.134890
H	-1.626314	-2.626706	1.035363
H	-0.214644	-3.644717	1.473171

21

m-C ES at r2SCAN-3c in the benzene

C	0.628187	-1.513450	0.038467
C	1.383090	-0.910443	-0.972256
C	0.612246	-0.971273	1.325841
C	2.116196	0.233389	-0.686353
C	2.114936	0.792969	0.598190
C	1.360146	0.177961	1.584320
H	1.389889	-1.337924	-1.969088
C	3.566492	1.760443	-1.909186
O	-0.056445	-2.627174	-0.338808
H	0.034530	-1.423655	2.122602
H	2.694415	1.686776	0.806000
H	1.349511	0.599995	2.585141
N	2.858447	0.806972	-1.725354
O	4.270096	2.648519	-2.227545
O	4.172792	3.889569	0.831867
S	5.480976	4.046985	0.174062
O	6.469920	2.980906	0.391992
C	-0.849787	-3.285605	0.651894
H	-1.308246	-4.136050	0.145581
H	-1.634294	-2.621952	1.036810
H	-0.229117	-3.644868	1.482433

21

p-C ES at r2SCAN-3c in the gas phase

C	0.892376	-1.448476	0.186306
C	1.681629	-0.852800	-0.793263
C	0.603373	-0.749926	1.359832
C	2.178896	0.432869	-0.612289
C	1.893580	1.130410	0.568671
C	1.112491	0.541533	1.543654
H	1.911988	-1.387813	-1.708776
C	3.469308	2.055640	-1.882331
H	0.514414	-2.449907	0.018503

O	-0.158821	-1.231415	2.380390
H	2.296738	2.128121	0.718135
H	0.884051	1.067047	2.465337
N	2.964075	0.996374	-1.623855
O	4.007132	3.037055	-2.250888
O	4.386142	3.776282	0.933656
S	5.626662	3.454245	0.207391
O	5.995952	2.033836	0.107662
C	-0.681182	-2.549571	2.248613
H	-1.242518	-2.740716	3.164429
H	0.123743	-3.290901	2.154086
H	-1.356118	-2.627602	1.385586

21

p-C ES at r2SCAN-3c in the benzene

C	0.886436	-1.457045	0.175358
C	1.657857	-0.857018	-0.816227
C	0.620348	-0.763457	1.358013
C	2.161750	0.427090	-0.637347
C	1.895625	1.121098	0.550215
C	1.131672	0.528917	1.537438
H	1.869529	-1.389963	-1.737772
C	3.475870	2.038115	-1.897551
H	0.504976	-2.457727	0.010477
O	-0.119067	-1.251358	2.391255
H	2.297164	2.120075	0.695879
H	0.919786	1.054093	2.463687
N	2.933165	0.992813	-1.659021
O	4.043876	3.008656	-2.249486
O	4.725040	4.256848	0.800986
S	5.719526	3.333429	0.229884
O	5.447134	1.892029	0.373972
C	-0.657534	-2.568715	2.256313
H	-1.206753	-2.760120	3.179070
H	0.141003	-3.313133	2.143797
H	-1.343496	-2.630341	1.401910

Table S370 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

18

o-product ES at r2SCAN-3c in the gas phase

C	1.858515	-0.547279	0.386218
C	2.937910	0.268168	0.047125
C	2.060504	-1.895141	0.675462
C	4.232724	-0.287741	0.001074
C	4.417481	-1.637121	0.293104
C	3.335835	-2.443130	0.630138
O	2.849951	1.589028	-0.251436
C	6.482533	0.465605	-0.482537
H	0.855794	-0.138823	0.427516
H	1.208285	-2.514572	0.937459

H	5.422970	-2.047270	0.252292
H	3.494500	-3.492718	0.855004
N	5.288509	0.553022	-0.341038
O	7.641772	0.517955	-0.654023
C	1.559179	2.189615	-0.216654
H	1.713935	3.235771	-0.484472
H	1.117636	2.131443	0.787206
H	0.881407	1.722888	-0.943798

18

o-product ES at r2SCAN-3c in the benzene

C	1.857759	-0.546660	0.386040
C	2.938956	0.267790	0.047444
C	2.059350	-1.894980	0.675267
C	4.232641	-0.291135	0.002431
C	4.418606	-1.640667	0.294450
C	3.335037	-2.445236	0.630963
O	2.851988	1.588467	-0.250938
C	6.484027	0.467893	-0.483864
H	0.855493	-0.136848	0.426688
H	1.206031	-2.513543	0.936703
H	5.423747	-2.051840	0.254043
H	3.492399	-3.495205	0.855988
N	5.290960	0.549697	-0.340288
O	7.643681	0.527763	-0.657941
C	1.556346	2.191982	-0.216733
H	1.713189	3.237593	-0.484399
H	1.117284	2.131474	0.787026
H	0.881947	1.723154	-0.944241

18

m-product ES at r2SCAN-3c in the gas phase

C	1.645209	-0.346474	0.367726
C	2.751619	0.437844	0.032337
C	1.804392	-1.701687	0.664955
C	4.014622	-0.137215	-0.004625
C	4.192743	-1.495624	0.290739
C	3.083397	-2.255882	0.620888
H	2.616676	1.489034	-0.196289
C	6.286900	0.542326	-0.474103
O	0.453361	0.310963	0.375877
H	0.959624	-2.326460	0.927221
H	5.184798	-1.935210	0.259037
H	3.210164	-3.309634	0.851448
N	5.094191	0.685019	-0.345538
O	7.447487	0.544477	-0.634639
C	-0.711807	-0.437616	0.710947
H	-1.542423	0.267939	0.658981
H	-0.645073	-0.846770	1.727793
H	-0.882082	-1.253290	-0.004267

18

m-product ES at r2SCAN-3c in the benzene

C	1.645097	-0.345560	0.367219
C	2.753233	0.438563	0.032204
C	1.802982	-1.701573	0.664528
C	4.015542	-0.139397	-0.003684
C	4.193977	-1.497682	0.291667
C	3.082373	-2.256749	0.621205
H	2.620249	1.490478	-0.196742
C	6.288957	0.544040	-0.475125
O	0.453760	0.311831	0.375171
H	0.957386	-2.325723	0.926242
H	5.185703	-1.938314	0.260295
H	3.207622	-3.310839	0.851854
N	5.097099	0.683148	-0.344928
O	7.450378	0.552002	-0.637705
C	-0.715868	-0.438775	0.711907
H	-1.545556	0.267354	0.659173
H	-0.646205	-0.846762	1.728126
H	-0.882929	-1.254302	-0.002918

18

p-product ES at r2SCAN-3c in the gas phase

6	1.797541	-0.505591	0.383544
6	2.869097	0.315832	0.044324
6	2.021711	-1.852947	0.670037
6	4.162124	-0.193647	-0.011868
6	4.382618	-1.546769	0.276282
6	3.322607	-2.366521	0.613514
1	2.703128	1.364518	-0.179670
6	6.403372	0.585604	-0.498864
1	0.801680	-0.080106	0.418992
8	1.051672	-2.746481	1.012929
1	5.390695	-1.950152	0.233769
1	3.479557	-3.416492	0.839034
7	5.207494	0.670266	-0.357560
8	7.562452	0.641540	-0.670602
6	-0.287827	-2.268625	1.084585
1	-0.896047	-3.128351	1.369925
1	-0.629580	-1.888034	0.112552
1	-0.391783	-1.481634	1.843747

18

p-product ES at r2SCAN-3c in the benzene

C	1.797597	-0.506990	0.384818
C	2.870312	0.313750	0.045828
C	2.021692	-1.855168	0.671201
C	4.162932	-0.198150	-0.009817
C	4.384744	-1.551147	0.278187
C	3.323070	-2.370095	0.615186
H	2.702783	1.362569	-0.177851
C	6.404721	0.590820	-0.501981
H	0.801981	-0.080829	0.420019

O	1.050480	-2.746747	1.013419
H	5.392356	-1.955749	0.236086
H	3.482510	-3.420187	0.840213
N	5.210212	0.665475	-0.356214
O	7.563854	0.659093	-0.678645
C	-0.293614	-2.265489	1.083538
H	-0.901621	-3.125091	1.368748
H	-0.629943	-1.885486	0.110365
H	-0.393555	-1.478169	1.841570

Table S371 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

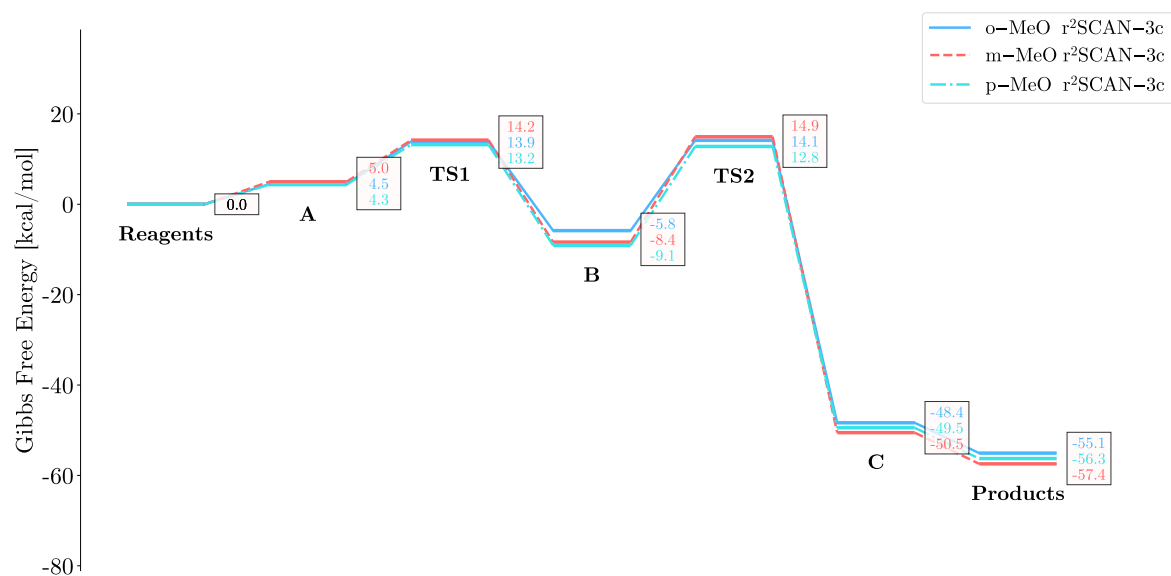
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

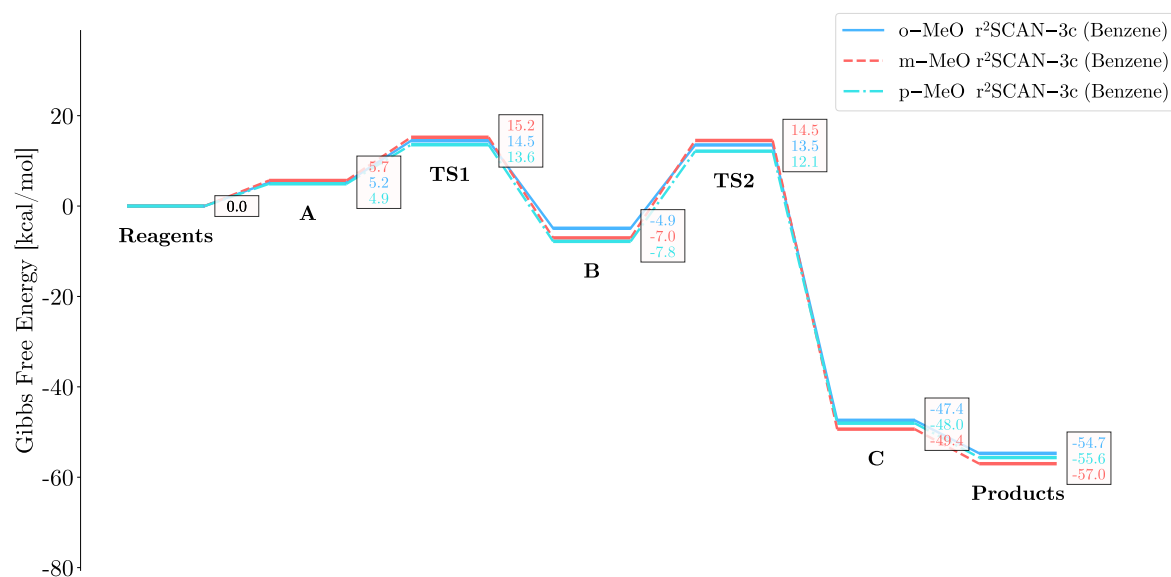
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

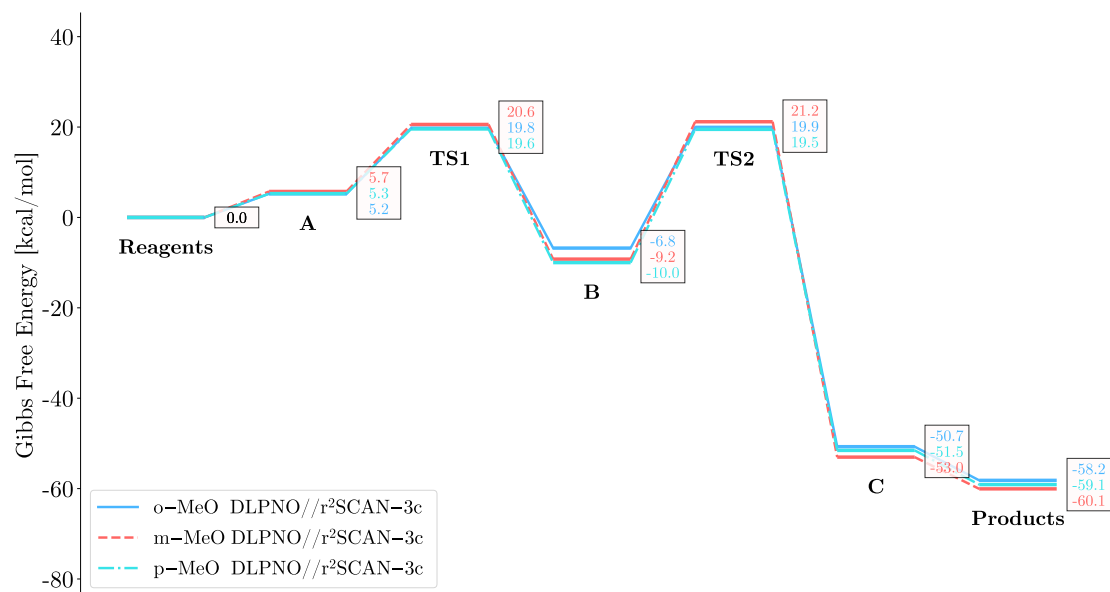


(a) Reaction in the gas phase.

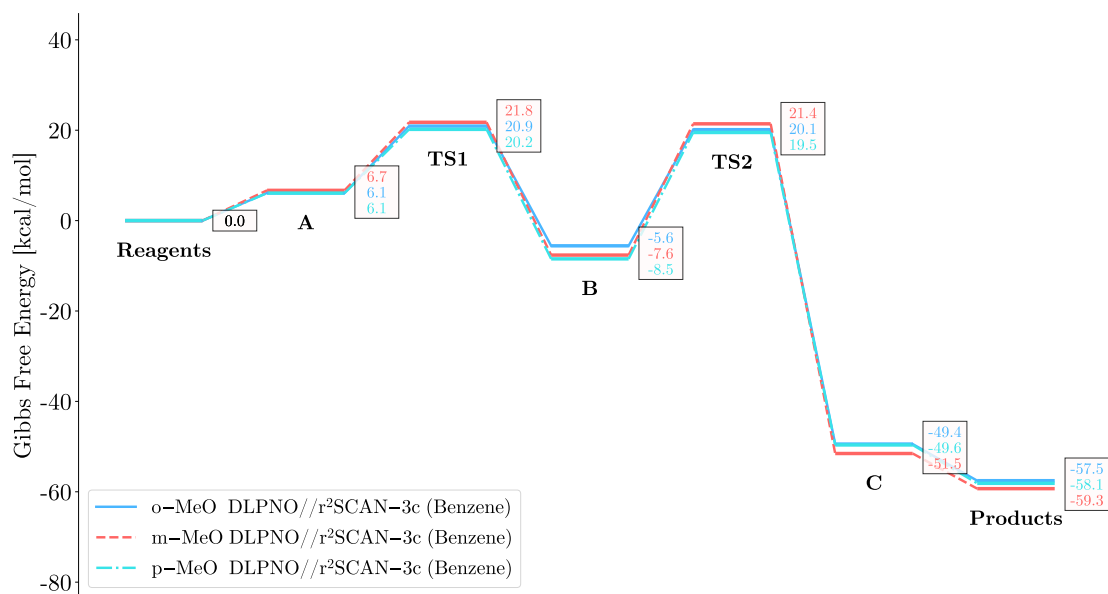


(b) Reaction in the benzene.

Figure S58 Calculated PES for reaction of the -OMe substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S59 Calculated PES for reaction of the -OMe substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

3.6 –NO₂

Table S372 Energy profile of the SO₂-catalyzed conversion for –NO₂ substitution. The calculations were done at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.5	3.6	–20.4	5.0	–63.6	–56.0
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.7	4.4	–18.1	5.3	–62.4	–55.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	4.6	17.2	–4.8	18.0	–51.3	–55.4
	Benzene	<i>E</i> , kcal/mol	0.0	–6.1	4.2	–19.2	4.8	–62.2	–55.8
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.3	5.0	–16.9	5.1	–61.0	–55.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.9	17.8	–3.5	17.9	–50.2	–55.3
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.0	1.4	–24.1	3.3	–63.7	–59.0
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.1	2.2	–21.7	3.6	–62.5	–58.4
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.5	15.2	–8.1	16.7	–51.2	–57.8
	Benzene	<i>E</i> , kcal/mol	0.0	–5.8	2.6	–22.7	3.4	–62.2	–58.6
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.0	3.4	–20.4	3.7	–61.1	–58.0
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.2	16.0	–7.1	16.4	–50.2	–57.7
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.6	1.6	–23.7	4.3	–63.8	–59.3
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.8	2.4	–21.4	4.6	–62.7	–58.7
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.5	15.1	–8.0	17.4	–51.8	–58.3
	Benzene	<i>E</i> , kcal/mol	0.0	–5.4	2.9	–22.3	4.5	–62.6	–58.9
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.7	3.6	–19.9	4.8	–61.5	–58.3
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.2	16.1	–6.7	17.4	–50.6	–58.1

Table S374 Cartesian coordinates of the reagent equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

16

o-reagent ES at r2SCAN-3c in the gas phase

C	–0.067387	–0.217078	0.354601
C	0.756184	0.899752	0.414855
C	0.490361	–1.484765	0.413463
C	2.154338	0.783598	0.534533
C	2.693822	–0.517346	0.592499
C	1.872735	–1.629576	0.532731
N	0.124463	2.227114	0.349910
C	3.029774	1.885508	0.598003
H	–1.136715	–0.070495	0.262246
H	–0.151238	–2.358398	0.366560
H	3.768982	–0.626983	0.684974
H	2.314500	–2.620288	0.579393
N	4.000773	2.531099	0.666127
O	4.945633	3.266821	0.735912
O	–1.095064	2.269016	0.245970
O	0.856429	3.208550	0.403834

Table S373 Energy profile of the SO₂-catalyzed conversion for –NO₂ substitution. The calculations were done at the DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

			Reagents	A	TS1	B	TS2	C	Products
o-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–7.2	8.5	–23.3	9.0	–65.7	–60.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–6.3	9.3	–20.9	9.3	–64.6	–59.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.0	22.1	–7.7	22.0	–53.4	–59.7
	Benzene	<i>E</i> , kcal/mol	0.0	–5.6	9.2	–21.7	9.5	–64.1	–59.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.8	10.0	–19.4	9.8	–63.0	–59.2
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.5	22.8	–6.1	22.6	–52.1	–59.1
m-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.5	7.7	–25.0	9.0	–65.7	–61.7
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.7	8.5	–22.6	9.2	–64.6	–61.1
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.9	21.6	–9.0	22.3	–53.2	–60.5
	Benzene	<i>E</i> , kcal/mol	0.0	–5.1	9.0	–23.4	8.9	–64.0	–61.1
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.3	9.8	–21.1	9.2	–62.9	–60.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.9	22.4	–7.8	21.9	–51.9	–60.2
p-substituted	Gas phase	<i>E</i> , kcal/mol	0.0	–6.4	7.7	–24.8	9.3	–66.0	–62.2
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–5.6	8.4	–22.5	9.6	–64.9	–61.5
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	5.7	21.1	–9.1	22.4	–54.0	–61.2
	Benzene	<i>E</i> , kcal/mol	0.0	–5.0	9.2	–23.1	9.9	–64.3	–61.4
		<i>E</i> + Δ ZPE, kcal/mol	0.0	–4.3	9.9	–20.8	10.2	–63.2	–60.8
		<i>E</i> + Δ <i>G</i> , kcal/mol	0.0	6.7	22.3	–7.6	22.8	–52.4	–60.6

16

o-reagent ES at r2SCAN-3c in the benzene

C	–0.068647	–0.216217	0.355439
C	0.757279	0.899587	0.415757
C	0.488426	–1.484462	0.414608
C	2.155657	0.778033	0.535046
C	2.695006	–0.521409	0.592026
C	1.870596	–1.632536	0.532823
N	0.132765	2.224867	0.351441
C	3.035088	1.878065	0.596838
H	–1.138859	–0.075866	0.263536
H	–0.155062	–2.356812	0.368554
H	3.769999	–0.633496	0.683156
H	2.310237	–2.624176	0.579065
N	3.995319	2.536433	0.663406
O	4.932486	3.288850	0.731273
O	–1.085875	2.277324	0.227272
O	0.863173	3.208344	0.425370

16

m-reagent ES at r2SCAN-3c in the gas phase

C	–0.020246	–0.127132	0.357873
C	0.816760	0.973490	0.419118
C	0.447447	–1.433934	0.409697
C	2.197587	0.756253	0.538425

C	2.690704	-0.560928	0.592818
C	1.818102	-1.637491	0.528312
H	0.406439	1.974609	0.375188
C	3.086503	1.854414	0.604042
N	-1.479440	0.103852	0.231662
H	-0.252391	-2.258455	0.357648
H	3.759464	-0.722670	0.685474
H	2.209697	-2.648709	0.570734
N	3.834552	2.746606	0.651634
O	4.602597	3.667203	0.702553
O	-2.200949	-0.882306	0.179186
O	-1.865616	1.263398	0.188307

16

m-reagent ES at r2SCAN-3c in the benzene

C	-0.021039	-0.126389	0.357157
C	0.815943	0.975315	0.418169
C	0.447594	-1.433726	0.409625
C	2.195299	0.754836	0.537688
C	2.691003	-0.561088	0.592856
C	1.818005	-1.637853	0.528481
H	0.411080	1.978689	0.374545
C	3.084245	1.853986	0.603479
N	-1.476024	0.103845	0.232163
H	-0.247854	-2.262627	0.358320
H	3.759781	-0.722824	0.685921
H	2.208689	-2.649324	0.571374
N	3.831686	2.744158	0.651437
O	4.603058	3.668180	0.703044
O	-2.202599	-0.880048	0.177413
O	-1.867660	1.263071	0.190998

16

p-reagent ES at r2SCAN-3c in the gas phase

C	-0.117464	-0.068087	0.349150
C	0.756954	1.001796	0.414089
C	0.394500	-1.359569	0.404336
C	2.141372	0.776808	0.533948
C	2.631719	-0.541715	0.587972
C	1.756798	-1.611120	0.522704
H	0.382492	2.018740	0.373174
C	3.034342	1.868711	0.600155
H	-1.186545	0.081875	0.256625
N	-0.538015	-2.500180	0.335235
H	3.698768	-0.711658	0.680834
H	2.112142	-2.633953	0.561903
N	3.781189	2.762595	0.647052
O	4.547440	3.683941	0.696327
O	-1.732111	-2.247734	0.234066
O	-0.057513	-3.625610	0.383690

16

p-reagent ES at r2SCAN-3c in the benzene

C	-0.118576	-0.067117	0.349051
C	0.756001	1.002549	0.413845
C	0.395003	-1.358874	0.404689
C	2.139554	0.774005	0.533960
C	2.632821	-0.543092	0.588759
C	1.757813	-1.612331	0.523430
H	0.381173	2.019381	0.372421
C	3.033067	1.866093	0.599737
H	-1.186630	0.088958	0.256006
N	-0.535008	-2.496368	0.335171
H	3.699761	-0.713499	0.681931
H	2.118637	-2.633099	0.563410
N	3.778077	2.759162	0.646366
O	4.546085	3.684437	0.695956
O	-1.732240	-2.249554	0.237443
O	-0.059469	-3.625811	0.379084

Table S375 Cartesian coordinates of the pre-intermediate (A) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

19

o-A ES at r2SCAN-3c in the gas phase

C	0.021905	-0.095590	-0.096478
C	0.707403	1.095729	-0.288140
C	0.677548	-1.174812	0.477468
C	2.055536	1.239118	0.085585
C	2.701055	0.131390	0.666605
C	2.014396	-1.056634	0.856192
N	-0.012221	2.223217	-0.899457
C	2.793334	2.428623	-0.088695
H	-1.016005	-0.155856	-0.401253
H	0.145086	-2.107948	0.629100
H	3.739431	0.236068	0.961589
H	2.529583	-1.899851	1.305782
N	3.606194	3.258196	-0.132314
O	4.436812	4.135735	-0.181236
O	5.506255	1.847463	1.562461
S	6.483895	2.815106	1.017114
O	7.232422	2.391702	-0.176408
O	-1.183719	2.050208	-1.206113
O	0.609581	3.267736	-1.063043

19

o-A ES at r2SCAN-3c in the benzene

C	0.007624	-0.092967	-0.093431
C	0.705216	1.091337	-0.286560
C	0.653751	-1.179226	0.479022
C	2.056470	1.219100	0.084818
C	2.691264	0.105376	0.663041
C	1.992635	-1.076333	0.854540
N	0.000319	2.224221	-0.895299

C	2.808771	2.399774	-0.088673
H	-1.031689	-0.148939	-0.394147
H	0.111283	-2.106459	0.631290
H	3.731997	0.194630	0.954515
H	2.499985	-1.925265	1.302194
N	3.612895	3.235822	-0.139599
O	4.439418	4.121380	-0.193940
O	5.554794	1.876437	1.564115
S	6.495568	2.880885	1.021348
O	7.261927	2.475566	-0.169943
O	-1.175220	2.070382	-1.201328
O	0.631484	3.263879	-1.063204

19

m-A ES at r2SCAN-3c in the gas phase

C	0.018298	-0.007352	-0.127706
C	0.722379	1.170228	-0.312729
C	0.584854	-1.139066	0.444188
C	2.060914	1.211267	0.097489
C	2.657539	0.077867	0.680300
C	1.915118	-1.082203	0.846486
H	0.241052	2.029356	-0.763297
C	2.826362	2.390385	-0.066756
N	-1.398854	-0.056185	-0.559357
H	-0.011969	-2.034876	0.565585
H	3.694484	0.131643	0.994568
H	2.378656	-1.954222	1.296231
N	3.538295	3.302932	-0.162937
O	4.303796	4.235641	-0.241363
O	5.488076	1.948075	1.491696
S	6.445870	2.940262	0.957635
O	7.197106	2.552788	-0.245638
O	-1.870133	0.955475	-1.059321
O	-2.001832	-1.105656	-0.386256

19

m-A ES at r2SCAN-3c in the benzene

C	0.010075	-0.007275	-0.125294
C	0.735279	1.157930	-0.310995
C	0.556140	-1.151156	0.444281
C	2.074836	1.169968	0.096490
C	2.651515	0.025338	0.676362
C	1.887860	-1.121003	0.843907
H	0.275800	2.030411	-0.758579
C	2.860567	2.335550	-0.068255
N	-1.405165	-0.028453	-0.552444
H	-0.052391	-2.038738	0.568812
H	3.690263	0.054768	0.988172
H	2.334737	-2.002503	1.291797
N	3.548634	3.262538	-0.181919
O	4.302604	4.208242	-0.273883
O	5.547202	2.021079	1.515986

S	6.447272	3.054091	0.959444
O	7.221070	2.669382	-0.233363
O	-1.866318	0.994500	-1.041786
O	-2.029971	-1.068309	-0.389914

19

p-A ES at r2SCAN-3c in the gas phase

C	-0.072916	0.032071	-0.172721
C	0.673474	1.185954	-0.335797
C	0.528300	-1.078631	0.407351
C	2.014640	1.217145	0.083566
C	2.602319	0.080257	0.668166
C	1.852969	-1.071931	0.828979
H	0.229278	2.067191	-0.785523
C	2.788539	2.389247	-0.074152
H	-1.108632	-0.019352	-0.486475
N	-0.269759	-2.309554	0.582182
H	3.637457	0.122416	0.988765
H	2.279591	-1.961978	1.276015
N	3.494087	3.307675	-0.168199
O	4.253572	4.244155	-0.244566
O	5.460754	1.945114	1.468315
S	6.420404	2.938510	0.941211
O	7.164356	2.563509	-0.270255
O	-1.433913	-2.284521	0.204347
O	0.285651	-3.272837	1.093373

19

p-A ES at r2SCAN-3c in the benzene

C	-0.071255	0.036646	-0.168052
C	0.695165	1.177721	-0.327185
C	0.511260	-1.087561	0.407106
C	2.036988	1.180557	0.091897
C	2.605573	0.031685	0.670523
C	1.836737	-1.108001	0.827570
H	0.266044	2.068499	-0.772606
C	2.829522	2.340523	-0.060463
H	-1.107528	0.012137	-0.483074
N	-0.306652	-2.301123	0.578256
H	3.641571	0.049063	0.990552
H	2.253872	-2.004271	1.270833
N	3.500633	3.280101	-0.179757
O	4.242839	4.232793	-0.273346
O	5.509272	2.017664	1.482283
S	6.422137	3.042661	0.933040
O	7.179332	2.664575	-0.272156
O	-1.474153	-2.257352	0.208069
O	0.228811	-3.281877	1.081091

Table S376 Cartesian coordinates of the transition state between pre-intermediate and intermediate (TS1) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

19

o-TS1 at r2SCAN-3c in the gas phase

C	-2.069031	-0.946878	0.230258
C	-1.182494	0.057597	-0.118164
C	-1.611664	-2.256931	0.313553
C	0.173941	-0.208039	-0.359525
C	0.621187	-1.532291	-0.236448
C	-0.270710	-2.547825	0.075180
N	-1.710729	1.429335	-0.266062
C	1.118265	0.822028	-0.621687
H	-3.105431	-0.692259	0.419281
H	-2.305514	-3.050880	0.570390
H	1.675050	-1.740991	-0.386331
H	0.087522	-3.569655	0.150283
N	2.060375	1.186536	-1.278490
O	2.937700	2.072397	-1.228831
O	1.216997	2.153140	0.870964
S	2.579951	2.839176	0.895212
O	3.621376	2.100787	1.633993
O	-2.740176	1.696263	0.336687
O	-1.096614	2.188490	-1.000263

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o-TS1 at r2SCAN-3c in the benzene

C	-2.075987	-0.955520	0.220415
C	-1.194384	0.055227	-0.121206
C	-1.606777	-2.261853	0.310557
C	0.166794	-0.201811	-0.352960
C	0.625340	-1.521068	-0.224095
C	-0.261981	-2.542983	0.083896
N	-1.726849	1.421347	-0.268556
C	1.108376	0.829772	-0.616358
H	-3.118355	-0.716266	0.395708
H	-2.296949	-3.060593	0.562402
H	1.681352	-1.722845	-0.368421
H	0.103397	-3.561968	0.162785
N	2.035740	1.209819	-1.285213
O	2.913557	2.102976	-1.218443
O	1.245741	2.138112	0.899029
S	2.607444	2.828340	0.889099
O	3.666134	2.078519	1.597702
O	-2.776728	1.680143	0.303506
O	-1.095864	2.200651	-0.969848

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m-TS1 at r2SCAN-3c in the gas phase

C	-2.313780	-0.829326	-0.387420
C	-1.482327	0.268330	-0.519795
C	-1.893313	-2.028362	0.175545
C	-0.158499	0.148044	-0.073931
C	0.289952	-1.050437	0.501972
C	-0.581025	-2.124260	0.623327

H	-1.852369	1.186497	-0.959518
C	0.729841	1.250912	-0.201734
N	-3.707900	-0.717730	-0.876726
H	-2.588829	-2.854542	0.259462
H	1.314516	-1.115667	0.849086
H	-0.231175	-3.049437	1.069327
N	0.990741	2.299687	-0.730449
O	1.856704	3.189006	-0.711720
O	2.298462	1.164909	1.080613
S	3.415038	2.102060	0.631684
O	4.320714	1.527258	-0.378581
O	-4.040446	0.340544	-1.390843
O	-4.429356	-1.694867	-0.737889

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m-TS1 at r2SCAN-3c in the benzene

C	-2.316311	-0.825849	-0.376407
C	-1.476314	0.262712	-0.533258
C	-1.894474	-2.029602	0.176605
C	-0.140690	0.120479	-0.133521
C	0.311557	-1.083394	0.428768
C	-0.569945	-2.144361	0.582694
H	-1.842328	1.189597	-0.957806
C	0.757587	1.210565	-0.294722
N	-3.724923	-0.691480	-0.806808
H	-2.593170	-2.850540	0.284548
H	1.346187	-1.167505	0.741361
H	-0.220171	-3.073878	1.019403
N	1.056542	2.221482	-0.873852
O	1.912832	3.125888	-0.822321
O	2.195018	1.256691	1.137219
S	3.324805	2.197760	0.733935
O	4.339167	1.575366	-0.140870
O	-4.073226	0.381129	-1.282040
O	-4.455194	-1.662440	-0.660517

19

p-TS1 at r2SCAN-3c in the gas phase

C	-2.394617	-0.771179	-0.461547
C	-1.523578	0.299477	-0.539023
C	-1.944724	-1.966060	0.089650
C	-0.202478	0.158507	-0.073555
C	0.230505	-1.056428	0.478639
C	-0.648230	-2.123399	0.561773
H	-1.849181	1.244865	-0.959157
C	0.692771	1.256301	-0.163279
H	-3.415856	-0.692564	-0.815093
N	-2.880192	-3.106510	0.175910
H	1.249184	-1.145342	0.836157
H	-0.340739	-3.073197	0.982657
N	0.930559	2.341801	-0.627092
O	1.791549	3.232197	-0.590595

O	2.309702	1.105240	1.070587
S	3.410683	2.066309	0.640507
O	4.281189	1.556293	-0.432738
O	-4.014848	-2.936772	-0.250825
O	-2.458690	-4.144210	0.668553

19

p-TS1 at r2SCAN-3c in the benzene

C	-2.396744	-0.767407	-0.454934
C	-1.523143	0.300823	-0.535973
C	-1.944656	-1.965868	0.088143
C	-0.199494	0.151742	-0.080458
C	0.236212	-1.065859	0.463348
C	-0.644371	-2.130838	0.549126
H	-1.850131	1.248461	-0.949849
C	0.695760	1.249590	-0.173443
H	-3.419586	-0.677790	-0.800877
N	-2.880779	-3.100795	0.178622
H	1.257023	-1.162687	0.812665
H	-0.330194	-3.080841	0.964314
N	0.934387	2.335625	-0.634621
O	1.800799	3.224879	-0.581885
O	2.298881	1.103496	1.069491
S	3.393283	2.080926	0.659589
O	4.280051	1.578493	-0.408373
O	-4.026800	-2.925122	-0.218289
O	-2.457489	-4.151499	0.644936

Table S377 Cartesian coordinates of the intermediate (B) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

19

o-B ES at r2SCAN-3c in the gas phase

C	0.132006	0.088327	0.340149
C	1.115313	1.005690	0.001847
C	0.480507	-1.245203	0.515053
C	2.456888	0.633593	-0.132642
C	2.787902	-0.708691	0.059668
C	1.804907	-1.642996	0.364838
N	0.682526	2.384474	-0.301331
C	3.542281	1.590285	-0.390475
H	-0.892818	0.427565	0.438542
H	-0.286009	-1.971997	0.764239
H	3.829153	-1.002342	-0.020863
H	2.080701	-2.683881	0.501390
N	4.464536	1.364424	-1.248602
O	5.384731	2.424345	-1.216519
O	3.617737	2.705306	0.391271
S	5.186807	3.421491	0.191399
O	6.039037	2.904026	1.264127
O	-0.313558	2.798915	0.273758
O	1.331041	2.999569	-1.136702

19

o-B ES at r2SCAN-3c in the benzene

C	0.125252	0.083165	0.326856
C	1.106634	1.004925	-0.006000
C	0.482543	-1.246488	0.516832
C	2.452263	0.639273	-0.127247
C	2.791892	-0.697656	0.079592
C	1.811263	-1.636070	0.385266
N	0.675484	2.379291	-0.312343
C	3.533731	1.601472	-0.385975
H	-0.905562	0.408870	0.406242
H	-0.282087	-1.976581	0.762055
H	3.835190	-0.988170	0.013453
H	2.093129	-2.673663	0.534113
N	4.420662	1.414337	-1.288916
O	5.347724	2.472760	-1.242901
O	3.645933	2.679305	0.442754
S	5.206091	3.402461	0.215889
O	6.097446	2.823979	1.226714
O	-0.351178	2.782595	0.217094
O	1.357279	3.019097	-1.104329

19

m-B ES at r2SCAN-3c in the gas phase

C	0.167418	0.053893	-0.054980
C	1.124777	1.038798	-0.210947
C	0.450426	-1.192338	0.494175
C	2.432260	0.759957	0.199611
C	2.742711	-0.485746	0.755692
C	1.752424	-1.451373	0.899722
H	0.861069	1.997701	-0.640938
C	3.467927	1.778333	0.048033
N	-1.220561	0.342390	-0.489303
H	-0.338923	-1.926860	0.594566
H	3.759288	-0.695733	1.069555
H	2.000479	-2.415875	1.330576
N	3.297100	2.890082	-0.569977
O	4.474544	3.640852	-0.509464
O	4.692004	1.525773	0.605234
S	5.833805	2.678059	-0.004017
O	6.464416	2.088285	-1.185795
O	-1.444892	1.444417	-0.968114
O	-2.050192	-0.544206	-0.338827

19

m-B ES at r2SCAN-3c in the benzene

C	0.166380	0.053901	-0.054644
C	1.123092	1.040463	-0.210876
C	0.450859	-1.192584	0.494781
C	2.430577	0.761483	0.197832
C	2.742963	-0.484211	0.753942

C	1.753232	-1.450391	0.899638
H	0.859218	2.000152	-0.638605
C	3.466584	1.779907	0.044908
N	-1.217577	0.341321	-0.488062
H	-0.334108	-1.931987	0.598526
H	3.759256	-0.696223	1.067641
H	2.001810	-2.414443	1.331010
N	3.299508	2.891342	-0.575952
O	4.480737	3.641743	-0.510437
O	4.688418	1.527214	0.603786
S	5.834148	2.675822	0.002629
O	6.459708	2.082467	-1.182730
O	-1.448437	1.445707	-0.962221
O	-2.050289	-0.545274	-0.346365

19

p-B ES at r2SCAN-3c in the gas phase

C	0.086903	0.113279	-0.101513
C	1.080053	1.065982	-0.236813
C	0.410792	-1.118104	0.459281
C	2.387586	0.779908	0.182783
C	2.690019	-0.466372	0.742736
C	1.695889	-1.423169	0.883802
H	0.854920	2.035491	-0.667648
C	3.430855	1.789625	0.039938
H	-0.930217	0.308614	-0.419241
N	-0.650779	-2.136537	0.607793
H	3.701995	-0.685964	1.063427
H	1.904540	-2.395442	1.313600
N	3.262651	2.916109	-0.553902
O	4.443351	3.654949	-0.497804
O	4.660090	1.519207	0.578051
S	5.804699	2.670890	-0.020561
O	6.417500	2.103201	-1.221920
O	-1.773798	-1.839462	0.222575
O	-0.336709	-3.209816	1.105216

19

p-B ES at r2SCAN-3c in the benzene

C	0.084804	0.113395	-0.102358
C	1.077266	1.066514	-0.238639
C	0.411622	-1.117996	0.458275
C	2.385463	0.780090	0.179169
C	2.690909	-0.466084	0.738473
C	1.697970	-1.423461	0.881331
H	0.845963	2.035295	-0.667830
C	3.429343	1.789848	0.036876
H	-0.931412	0.313783	-0.419606
N	-0.646583	-2.133589	0.609903
H	3.702593	-0.687737	1.058724
H	1.913655	-2.393784	1.311910
N	3.264873	2.916488	-0.558920

O	4.448569	3.654738	-0.497519
O	4.656045	1.519099	0.577559
S	5.804731	2.668420	-0.010158
O	6.415197	2.098725	-1.214399
O	-1.773851	-1.842372	0.227861
O	-0.336819	-3.208982	1.109146

Table S378 Cartesian coordinates of the transition state between intermediate and post-intermediate (TS2) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

19

o-TS2 at r2SCAN-3c in the gas phase

C	0.071103	0.014173	0.114294
C	1.029279	0.993636	-0.083944
C	0.474229	-1.273353	0.455999
C	2.390726	0.702370	0.058341
C	2.785389	-0.603252	0.353982
C	1.827346	-1.582718	0.574763
N	0.572471	2.358319	-0.419688
C	3.500564	1.800263	0.055859
H	-0.975615	0.271937	-0.000334
H	-0.275870	-2.041372	0.616106
H	3.845783	-0.828576	0.404988
H	2.137701	-2.593216	0.820385
N	3.655229	1.590186	-1.179179
O	5.094018	3.032748	-1.366213
O	3.957457	2.416371	1.032623
S	5.790523	3.258446	-0.043503
O	6.771943	2.235230	0.341529
O	-0.541992	2.463067	-0.910470
O	1.333404	3.278644	-0.166394

19

o-TS2 at r2SCAN-3c in the benzene

C	0.069405	0.017270	0.122533
C	1.025934	0.995131	-0.084803
C	0.476831	-1.270372	0.463977
C	2.389724	0.704231	0.055693
C	2.788435	-0.601247	0.346724
C	1.830310	-1.579965	0.575095
N	0.572885	2.356058	-0.422281
C	3.493512	1.795669	0.033406
H	-0.979941	0.270616	0.022588
H	-0.272397	-2.037866	0.630267
H	3.848779	-0.828722	0.392417
H	2.142225	-2.589997	0.820336
N	3.658751	1.590369	-1.200121
O	5.111735	3.036584	-1.360001
O	3.959524	2.422810	1.005858
S	5.779253	3.249431	-0.017376
O	6.753132	2.215025	0.364102
O	-0.541196	2.468922	-0.912668

O	1.336787	3.278954	-0.176598

19

m-TS2 at r2SCAN-3c in the gas phase

C	0.049451	0.069704	0.090536
C	0.963686	1.065809	-0.210588
C	0.440377	-1.201997	0.495302
C	2.312785	0.755980	-0.064682
C	2.744927	-0.519622	0.305291
C	1.798083	-1.491253	0.599406
H	0.635476	2.043834	-0.542130
C	3.363293	1.902786	-0.133393
N	-1.393925	0.368444	-0.042724
H	-0.316479	-1.947167	0.711236
H	3.807889	-0.729986	0.366434
H	2.116068	-2.483566	0.901676
N	3.496550	1.723872	-1.373573
O	4.807766	3.275309	-1.582976
O	3.783578	2.574839	0.829107
S	5.518659	3.552885	-0.275816
O	6.583737	2.607009	0.081304
O	-1.701550	1.495992	-0.401055
O	-2.177601	-0.534523	0.215814

19

m-TS2 at r2SCAN-3c in the benzene

C	0.051898	0.072447	0.091519
C	0.967171	1.066572	-0.211691
C	0.439020	-1.201537	0.494659
C	2.315108	0.750298	-0.062769
C	2.746088	-0.527174	0.305783
C	1.795852	-1.495626	0.598896
H	0.646275	2.047542	-0.542341
C	3.363902	1.888769	-0.145975
N	-1.389984	0.376941	-0.037768
H	-0.315416	-1.949156	0.710570
H	3.808181	-0.741806	0.369577
H	2.110222	-2.489135	0.900614
N	3.506408	1.711839	-1.384807
O	4.811999	3.268005	-1.587521
O	3.792018	2.577760	0.807055
S	5.492315	3.559574	-0.263839
O	6.570507	2.627376	0.098517
O	-1.698532	1.506073	-0.391608
O	-2.180261	-0.520413	0.220298

19

p-TS2 at r2SCAN-3c in the gas phase

C	-0.034279	0.128055	0.062758
C	0.919495	1.086631	-0.241060
C	0.396228	-1.123633	0.488250
C	2.269087	0.769633	-0.081900

C	2.692717	-0.500958	0.311381
C	1.739799	-1.459836	0.615338
H	0.630992	2.072068	-0.590735
C	3.324238	1.913952	-0.155568
H	-1.094276	0.329601	-0.034865
N	-0.624407	-2.153622	0.804048
H	3.752616	-0.720954	0.383761
H	2.018642	-2.456649	0.935279
N	3.488260	1.698046	-1.385127
O	4.793916	3.250393	-1.609272
O	3.712105	2.619989	0.795993
S	5.467363	3.577331	-0.293302
O	6.532050	2.655962	0.122619
O	-1.797869	-1.838310	0.670013
O	-0.220859	-3.245303	1.177338

19

p-TS2 at r2SCAN-3c in the benzene

C	-0.034190	0.131066	0.063990
C	0.920523	1.087637	-0.242931
C	0.396390	-1.120800	0.490054
C	2.269105	0.765074	-0.082734
C	2.694343	-0.506320	0.308313
C	1.739468	-1.461908	0.615451
H	0.631327	2.073512	-0.591246
C	3.324721	1.900980	-0.166137
H	-1.092438	0.341020	-0.033717
N	-0.624223	-2.146884	0.807693
H	3.753476	-0.730603	0.380237
H	2.022988	-2.457361	0.935271
N	3.489267	1.701170	-1.397677
O	4.795710	3.258771	-1.604715
O	3.728630	2.607284	0.783887
S	5.451200	3.577489	-0.275038
O	6.525642	2.657323	0.125513
O	-1.799302	-1.836739	0.667622
O	-0.226819	-3.238318	1.191114

Table S379 Cartesian coordinates of the post-intermediate (C) equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

19

o-C ES at r2SCAN-3c in the gas phase

C	0.608931	-0.013902	-0.477035
C	1.316163	1.086184	0.003542
C	1.060365	-1.298377	-0.233974
C	2.507611	0.914201	0.741276
C	2.954580	-0.397770	0.951138
C	2.242762	-1.486206	0.479423
N	0.769275	2.404958	-0.317715
C	3.283255	3.109348	1.416163
H	-0.296408	0.167264	-1.043572

H	0.497773	-2.147468	-0.607120
H	3.886379	-0.529042	1.490417
H	2.618005	-2.487884	0.664668
N	3.347517	1.904120	1.219073
O	3.584886	1.751483	-2.036645
O	3.476339	4.219899	1.703490
S	4.901751	1.850668	-1.382881
O	5.579445	0.589535	-1.041849
O	-0.102702	2.475794	-1.167707
O	1.207756	3.380097	0.298457

19

o-C ES at r2SCAN-3c in the benzene

C	0.606803	-0.017604	-0.474722
C	1.322213	1.080881	-0.001295
C	1.050397	-1.302634	-0.217731
C	2.511562	0.907513	0.739699
C	2.953463	-0.403465	0.958875
C	2.232135	-1.491617	0.497401
N	0.788433	2.399092	-0.326818
C	3.288060	3.100362	1.431370
H	-0.300468	0.159699	-1.039863
H	0.481008	-2.152202	-0.579456
H	3.883406	-0.538870	1.500811
H	2.598716	-2.494561	0.693108
N	3.353419	1.904242	1.202099
O	3.589950	1.786494	-2.076474
O	3.465095	4.209637	1.739168
S	4.900594	1.883146	-1.408340
O	5.572411	0.613292	-1.084412
O	-0.015656	2.487191	-1.242792
O	1.162143	3.362308	0.348522

19

m-C ES at r2SCAN-3c in the gas phase

C	0.922337	-1.358433	0.165475
C	1.617885	-0.772362	-0.881030
C	0.741237	-0.733837	1.391586
C	2.155064	0.497606	-0.684724
C	1.988124	1.154310	0.540985
C	1.284914	0.534290	1.564907
H	1.738717	-1.291375	-1.823652
C	3.460068	2.102083	-1.940234
N	0.350511	-2.708205	-0.040667
H	0.190097	-1.234461	2.177926
H	2.415514	2.142143	0.684958
H	1.159716	1.047809	2.512895
N	2.850216	1.080260	-1.742912
O	4.070048	3.048453	-2.266998
O	4.430180	3.933367	0.928395
S	5.629835	3.192260	0.507441
O	5.482570	1.744990	0.285954

O	0.522127	-3.234612	-1.131827
O	-0.257830	-3.210547	0.894773

19

m-C ES at r2SCAN-3c in the benzene

C	0.935984	-1.358726	0.168584
C	1.623788	-0.771928	-0.884004
C	0.741185	-0.725003	1.388897
C	2.137928	0.509049	-0.699091
C	1.956417	1.175309	0.519752
C	1.262321	0.554264	1.549656
H	1.757316	-1.295153	-1.822630
C	3.421259	2.124702	-1.955074
N	0.389077	-2.715992	-0.024625
H	0.197694	-1.222349	2.182516
H	2.362527	2.173544	0.653362
H	1.125593	1.075714	2.491681
N	2.824801	1.093259	-1.762338
O	4.018796	3.078897	-2.280057
O	4.539701	3.928592	0.976394
S	5.690278	3.099039	0.583751
O	5.411711	1.691217	0.253885
O	0.569830	-3.255781	-1.109512
O	-0.214875	-3.224912	0.912103

19

p-C ES at r2SCAN-3c in the gas phase

C	0.926279	-1.440680	0.119388
C	1.611120	-0.813713	-0.907695
C	0.755260	-0.767898	1.323566
C	2.119502	0.475541	-0.721929
C	1.936176	1.141455	0.497458
C	1.251501	0.516083	1.524152
H	1.762037	-1.311346	-1.859448
C	3.417497	2.086377	-1.968171
H	0.524873	-2.439985	0.000932
N	0.028158	-1.431629	2.416927
H	2.335398	2.141594	0.633942
H	1.096429	1.009120	2.476520
N	2.795870	1.066713	-1.783392
O	4.031552	3.029664	-2.289376
O	4.408272	3.794858	0.957198
S	5.621557	3.031809	0.625942
O	5.444857	1.633837	0.203015
O	-0.397255	-2.562375	2.210817
O	-0.106616	-0.812624	3.466254

19

p-C ES at r2SCAN-3c in the benzene

C	1.019930	-1.437054	0.143720
C	1.669695	-0.803955	-0.901691
C	0.794789	-0.732790	1.322317

C	2.091001	0.522451	-0.759822
C	1.850981	1.220290	0.432521
C	1.201241	0.589950	1.477902
H	1.860844	-1.327201	-1.832383
C	3.341210	2.150763	-2.017862
H	0.689626	-2.464951	0.054229
N	0.109234	-1.401269	2.431763
H	2.176183	2.251165	0.531889
H	1.006582	1.111708	2.407394
N	2.739027	1.117079	-1.835875
O	3.944409	3.099330	-2.339075
O	4.506323	3.650792	1.055636
S	5.596589	2.677476	0.885524
O	5.282793	1.449508	0.136408
O	-0.242838	-2.566318	2.270846
O	-0.075149	-0.760174	3.462659

Table S380 Cartesian coordinates of the product equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

16

o-product ES at r2SCAN-3c in the gas phase

C	1.827958	-0.587427	0.311926
C	2.915271	0.228478	0.021078
C	2.023646	-1.935711	0.563445
C	4.224724	-0.276265	0.009106
C	4.403089	-1.637578	0.290314
C	3.316827	-2.456493	0.552011
N	2.635710	1.642158	-0.281923
C	6.499052	0.440595	-0.333706
H	0.838333	-0.145053	0.326042
H	1.173630	-2.576611	0.771690
H	5.413029	-2.037140	0.304346
H	3.482720	-3.509879	0.756381
N	5.303092	0.557769	-0.211552
O	7.659174	0.469767	-0.475199
O	3.353325	2.204548	-1.095584
O	1.678022	2.149475	0.290706

16

o-product ES at r2SCAN-3c in the benzene

C	1.825386	-0.587189	0.311625
C	2.914846	0.227051	0.019016
C	2.022063	-1.934906	0.564745
C	4.224606	-0.278953	0.005176
C	4.403474	-1.639020	0.289082
C	3.315833	-2.456010	0.553574
N	2.638965	1.637314	-0.280158
C	6.499634	0.442700	-0.332974
H	0.833426	-0.149781	0.319985
H	1.171847	-2.575710	0.772876
H	5.412799	-2.039926	0.303233

H	3.481302	-3.509193	0.759588
N	5.303254	0.555842	-0.218338
O	7.660923	0.480000	-0.468728
O	3.347907	2.203091	-1.102112
O	1.691339	2.155321	0.302490

16

m-product ES at r2SCAN-3c in the gas phase

C	1.854805	-0.500414	0.375274
C	2.911875	0.329835	0.035842
C	2.016982	-1.846924	0.669767
C	4.191996	-0.218719	-0.009827
C	4.386296	-1.574884	0.282356
C	3.302538	-2.374969	0.618271
H	2.744073	1.376060	-0.187140
C	6.445815	0.495708	-0.484278
N	0.493464	0.081940	0.424303
H	1.157615	-2.451681	0.929142
H	5.388219	-1.993368	0.243913
H	3.462323	-3.424763	0.842888
N	5.249447	0.622619	-0.352009
O	7.603162	0.512798	-0.646991
O	0.377114	1.270923	0.160314
O	-0.427593	-0.664990	0.726015

16

m-product ES at r2SCAN-3c in the benzene

C	1.854122	-0.500082	0.375576
C	2.912974	0.329993	0.036885
C	2.015156	-1.847686	0.669663
C	4.191516	-0.221300	-0.007767
C	4.385723	-1.577708	0.284166
C	3.300369	-2.376709	0.618891
H	2.751123	1.377122	-0.186578
C	6.445243	0.498942	-0.485792
N	0.497686	0.081833	0.423307
H	1.158497	-2.457279	0.928689
H	5.386825	-1.998017	0.246380
H	3.458390	-3.426845	0.842992
N	5.249836	0.620263	-0.349989
O	7.602846	0.525075	-0.652399
O	0.376680	1.271371	0.156690
O	-0.428858	-0.659803	0.727125

16

p-product ES at r2SCAN-3c in the gas phase

C	1.773300	-0.420480	0.367644
C	2.857913	0.372844	0.033862
C	1.983554	-1.764051	0.654471
C	4.140798	-0.182092	-0.010618
C	4.334332	-1.539242	0.281767
C	3.251920	-2.333539	0.615673

H	2.727398	1.424858	-0.195139
C	6.396801	0.521143	-0.484047
H	0.769848	-0.014008	0.408737
N	0.832231	-2.609341	1.009651
H	5.333802	-1.962748	0.245153
H	3.375492	-3.385215	0.845718
N	5.199867	0.653124	-0.351461
O	7.553011	0.536578	-0.648377
O	-0.272753	-2.080519	1.033200
O	1.051397	-3.788833	1.259365

16

p-product ES at r2SCAN-3c in the benzene

C	1.772864	-0.419432	0.368653
C	2.858257	0.372534	0.035862
C	1.983105	-1.764239	0.655704
C	4.140574	-0.185067	-0.007384
C	4.335304	-1.542128	0.286356
C	3.252273	-2.335306	0.619055
H	2.726781	1.424481	-0.193489
C	6.395579	0.521735	-0.487947
H	0.771839	-0.006889	0.406732
N	0.834730	-2.606370	1.005606
H	5.334072	-1.967016	0.251115
H	3.381067	-3.386441	0.848325
N	5.199672	0.649418	-0.349632
O	7.551487	0.544714	-0.657962
O	-0.274497	-2.081661	1.031053
O	1.045805	-3.789853	1.253552

Table S381 Cartesian coordinates of the sulfur dioxide equilibrium geometry state (ES) obtained at the r²SCAN-3c level of theory in the gas phase and benzene, which was treated with CPCM continuum solvent model.

3

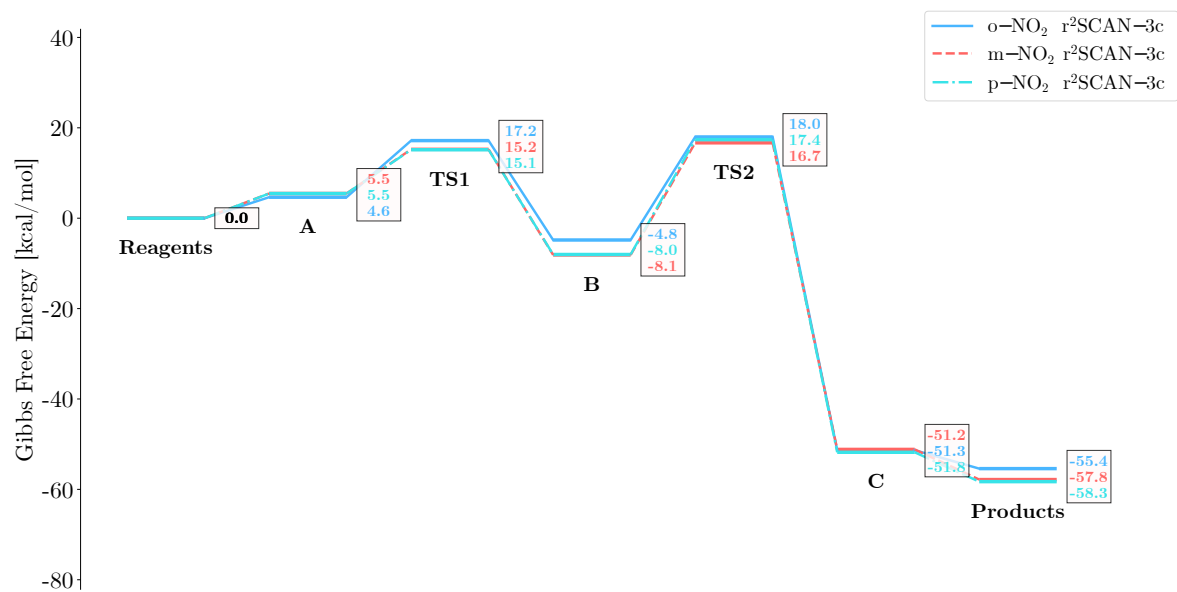
Sulfur dioxide ES at r2SCAN-3c in the gas phase

S	0.000000	0.000000	0.384030
O	0.000000	1.259580	-0.373599
O	0.000000	-1.259580	-0.373599

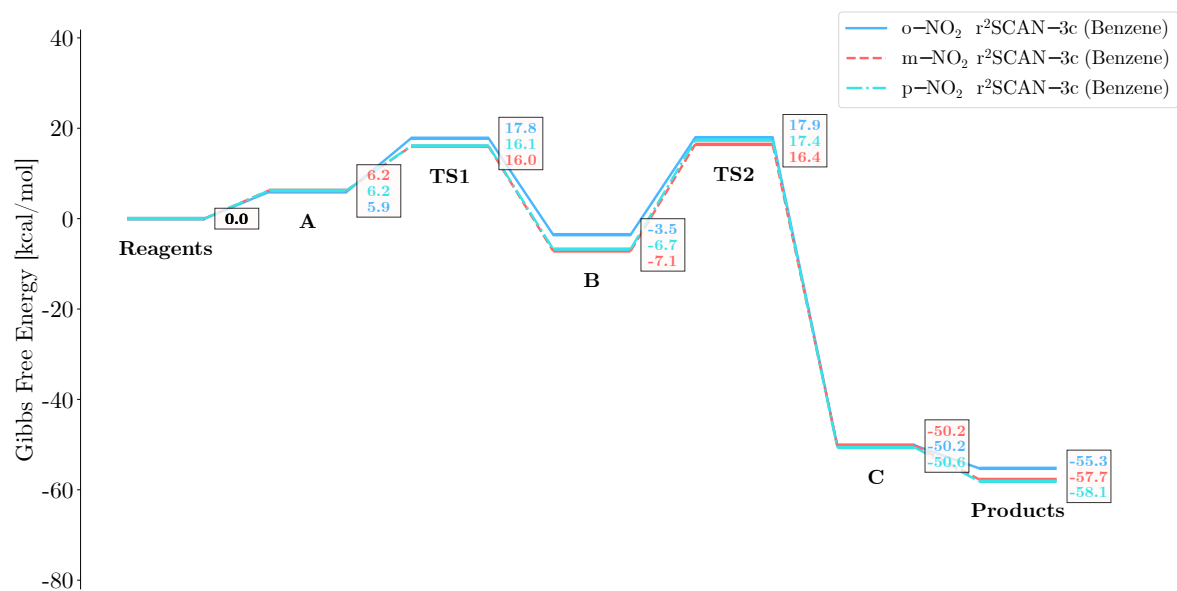
3

Sulfur dioxide ES at r2SCAN-3c in the benzene

S	0.000000	0.000000	0.389280
O	0.000000	1.256012	-0.376224
O	0.000000	-1.256011	-0.376224

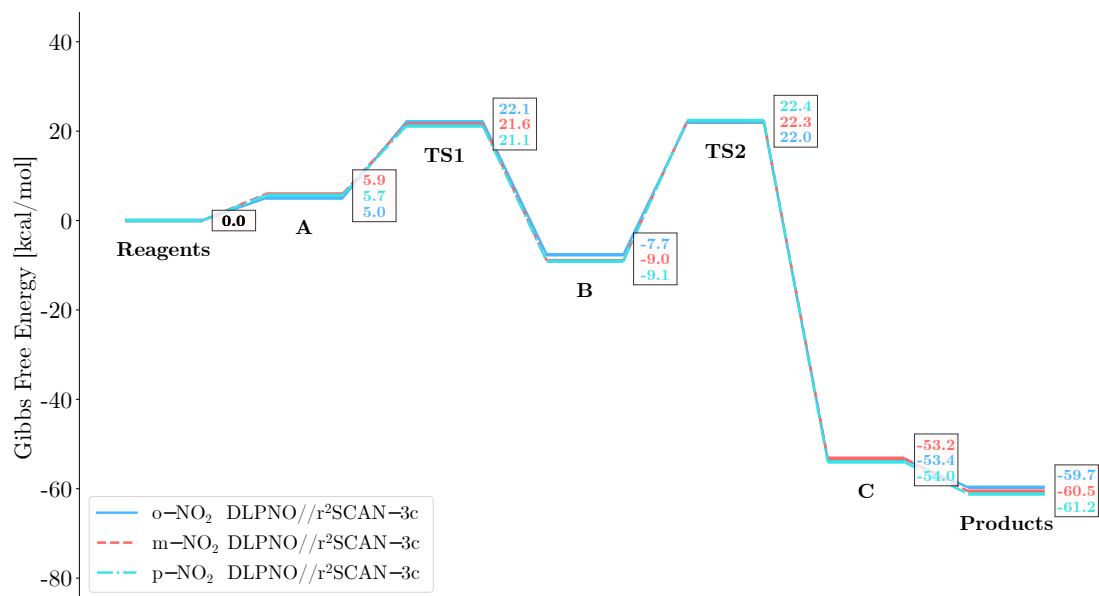


(a) Reaction in the gas phase.

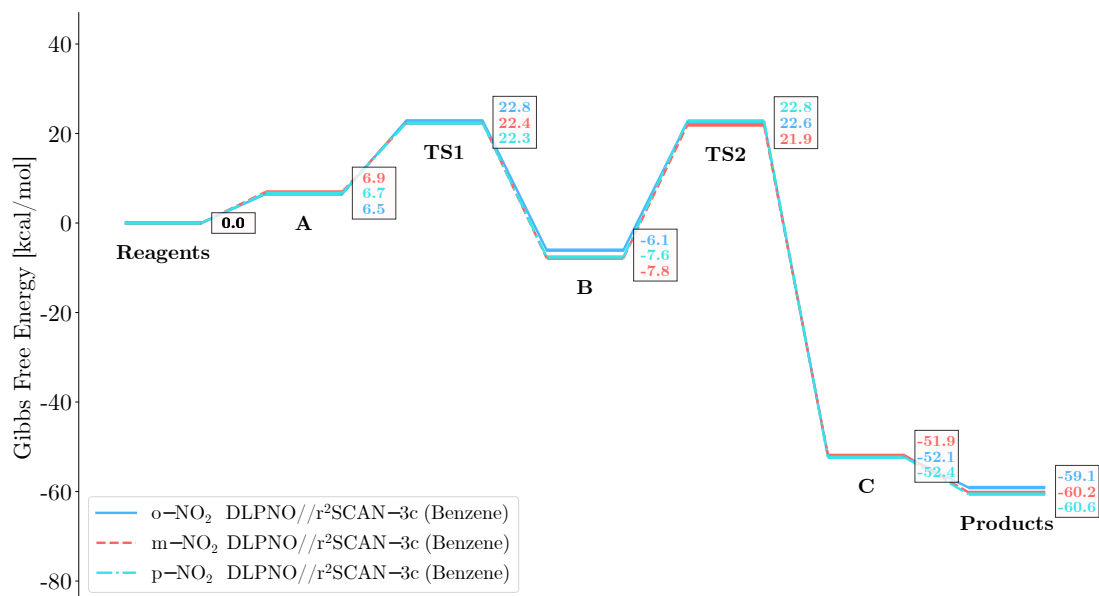


(b) Reaction in the benzene.

Figure S60 Calculated PES for reaction of the -NO₂ substituted phenyl nitrile oxide with sulfur dioxide. r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).



(a) Reaction in the gas phase.



(b) Reaction in the benzene.

Figure S61 Calculated PES for reaction of the -NO₂ substituted phenyl nitrile oxide with sulfur dioxide. DLPNO-CCSD(T)/CBS(3/4)/cc-pVQZ/C//r²SCAN-3c electronic energies corrected for the Gibbs free energy (298.15 K) are in kcal/mol and are relative to the starting molecules (reagents).

4 Reaction coordinate scans

4.1 Intrinsic reaction coordinate

The IRC plots for the reactions $A \rightarrow B$ and $B \rightarrow C$ were generated by employing the PBE/L1 technique within the Priroda software.^{S41,S42}

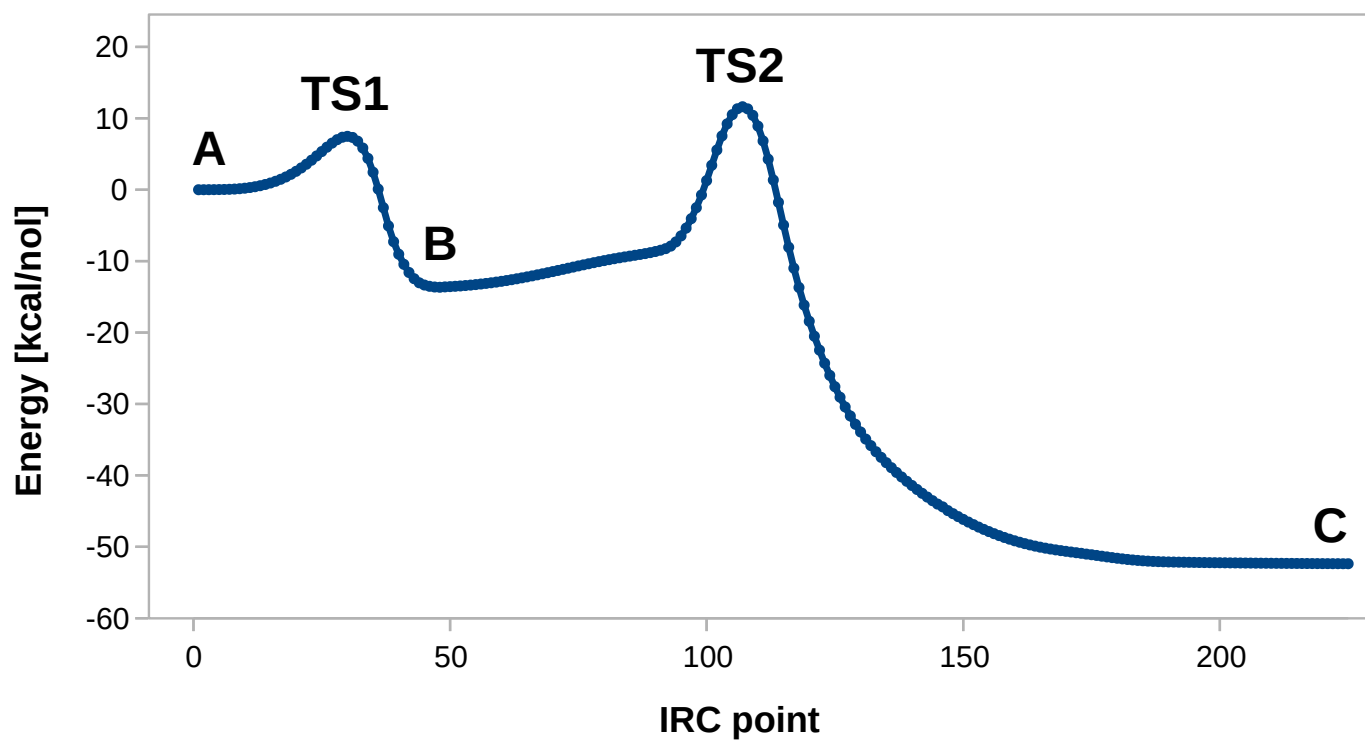


Figure S62 Calculated IRC for the conversion of phenyl nitrile oxide.

5 Internal rotation of the intermediate

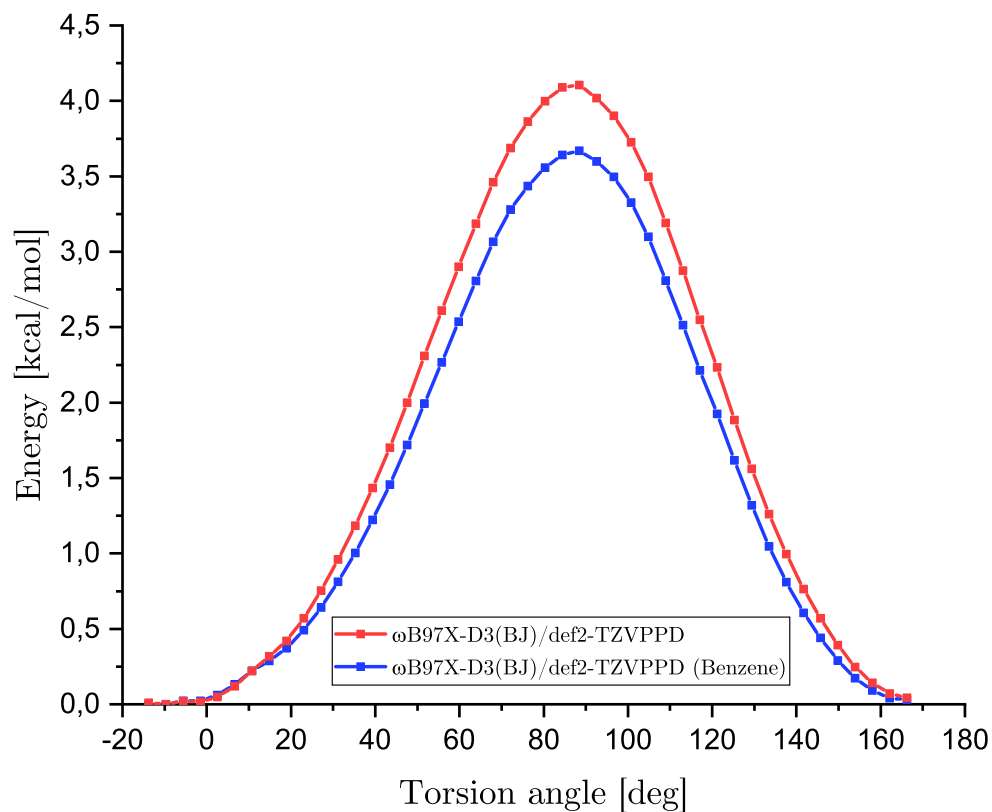
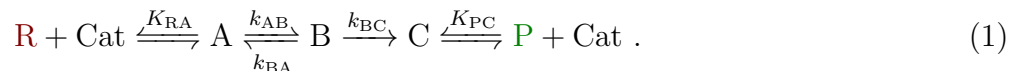


Figure S63 Calculated geometry-relaxed potential energy scans for rotation of intermediate around the C–C single bond. The calculations were done at the ω B97X-D3(BJ)/def2-TZVPPD level of theory in the gas phase (red) and benzene (blue), which was treated with CPCM continuum solvent model.

6 Derivation of the effective barrier of the reaction

We will represent the kinetics, given by the scheme of the type given, e.g., in Figure S6, as follows:



Here, the “R” is the reagent, “P” the product, “Cat” is the catalyst (SO₂, SeO₂, etc.), “A” is the pre-reactive complex, “B” is the intermediate, and “C” is the post-reactive complex. The notation corresponds to that used in Figure S6, etc. The concentration of the component “X” we will denote as [X].

Here we are making the following assumptions.

- The reactant, catalyst, and pre-reactive complex are in the equilibrium $\text{R} + \text{Cat} \rightleftharpoons \text{A}$ described by the equilibrium constant K_{RA} . In this case, the concentration of “A” at each point in time is

$$[\text{A}] = K_{\text{RA}}[\text{R}] \cdot [\text{Cat}] . \quad (2)$$

- The product, catalyst, and pre-reactive complex are in the equilibrium $\text{P} + \text{Cat} \rightleftharpoons \text{C}$ described by the equilibrium constant K_{PC} . Therefore, the concentration of the “C” at each point in time is given as

$$[\text{C}] = K_{\text{PC}}[\text{P}] \cdot [\text{Cat}] . \quad (3)$$

- The concentration of the catalyst we will take as fixed at each point of time:

$$\frac{d[\text{Cat}]}{dt} = 0 . \quad (4)$$

- The barrier for the reverse reaction $\text{C} \rightarrow \text{B}$ is considered to be the largest one. Thus, we assume that the rate constant of this reaction is negligible, and we do not include this reaction in scheme 1.
- We apply the steady state approximation^{S47} for the intermediate “B”, which means that

$$\frac{d[\text{B}]}{dt} = 0 . \quad (5)$$

Taking said above into account, we write the kinetic equations for reaction scheme 1 as follows:

$$\begin{cases} \frac{d[B]}{dt} = k_{AB}[A] - (k_{BA} + k_{BC})[B] = 0, \\ \frac{d[C]}{dt} = k_{BC}[B] . \end{cases} \quad (6)$$

This gives us

$$\frac{d[C]}{dt} = \frac{k_{AB} \cdot k_{BC}}{(k_{BA} + k_{BC})} \cdot [A]$$

Now, from here and Equations 2, 3, and 4, we get an effective first-order reaction kinetics equation with an effective rate constant k_{eff} :

$$\frac{d[P]}{dt} = \overbrace{\frac{k_{AB} \cdot k_{BC}}{(k_{BA} + k_{BC})}}^{k_{\text{eff}}} \cdot \frac{K_{RA}}{K_{PC}} \cdot [R] = k_{\text{eff}}[R] . \quad (7)$$

We take the first-order reaction constants k_{XY} to be given by the Eyring–Polanyi equation^{S47}

$$k_{XY} = \frac{k_B T}{h} \exp \left(-\frac{\Delta G_{XY}^\ddagger}{k_B T} \right) , \quad (8)$$

where $k_B = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant, T is the absolute temperature, $h = 6.63 \times 10^{-34}$ J·s is the Planck constant, and $\Delta G_{XY}^\ddagger$ is the Gibbs free energy barrier for going from state X to state Y . The ratio of the equilibrium constants we will take as^{S47}

$$\frac{K_{RA}}{K_{PC}} = \exp \left(\frac{\Delta G_{PC} - \Delta G_{RA}}{k_B T} \right) , \quad (9)$$

where ΔG_{PC} is the Gibbs free energy of the reaction $P + \text{Cat} \rightarrow C$ and ΔG_{RA} is the Gibbs free energy of the reaction $R + \text{Cat} \rightarrow A$.

Using Equations 8 and 9 we can rewrite the effective rate constant k_{eff} from Equation 7 as

$$k_{\text{eff}} = \frac{k_B T}{h} \cdot \frac{\exp \left(-\frac{\Delta G_{AB}^\ddagger}{k_B T} \right)}{\left(\exp \left(\frac{\Delta G_{BC}^\ddagger - \Delta G_{BA}^\ddagger}{k_B T} \right) + 1 \right)} \cdot \exp \left(\frac{\Delta G_{PC} - \Delta G_{RA}}{k_B T} \right) .$$

Assuming that we can effectively represent this rate constant using Eyring–Polanyi equation (Equation 8) with an effective Gibbs free energy barrier $\Delta G_{\text{eff}}^\ddagger$ as

$$k_{\text{eff}} = \frac{k_B T}{h} \exp \left(-\frac{\Delta G_{\text{eff}}^\ddagger}{k_B T} \right) ,$$

we get the resulting equation for the $\Delta G_{\text{eff}}^\ddagger$ in the following form:

$$\Delta G_{\text{eff}}^\ddagger = \Delta G_{\text{AB}}^\ddagger + \Delta G_{\text{RA}} - \Delta G_{\text{PC}} + k_{\text{B}}T \ln \left(1 + \exp \left(\frac{\Delta G_{\text{BC}}^\ddagger - \Delta G_{\text{BA}}^\ddagger}{k_{\text{B}}T} \right) \right) \quad (10)$$

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