Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

An asymmetric pericyclic cascade approach to 3-alkyl-3-aryloxindoles; generality, applications and mechanistic investigations

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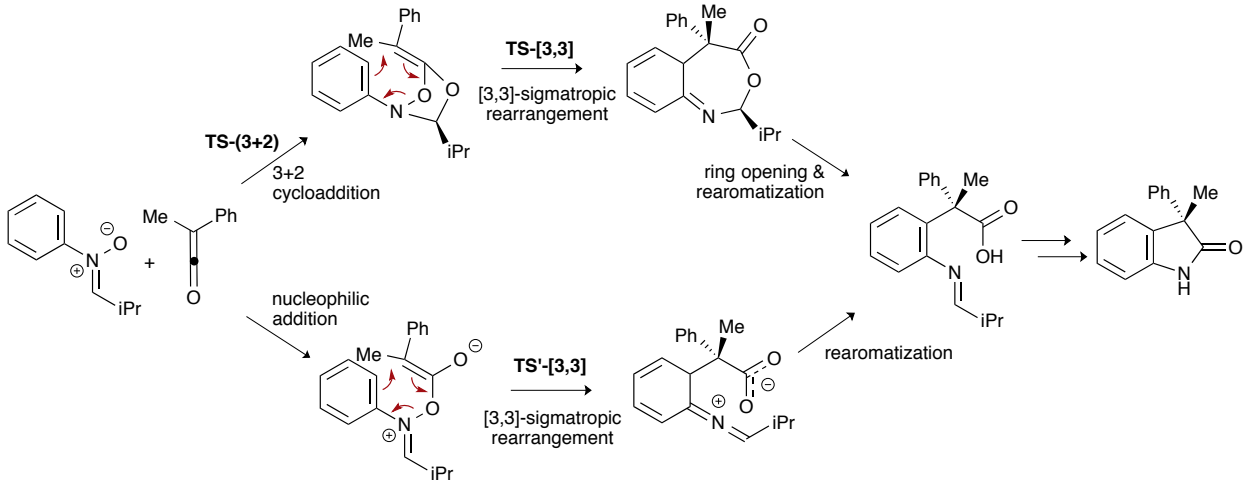
I. COMPUTATIONAL METHODOLOGY

All calculations were carried out using *Gaussian 09*, Rev. D01 (Reference 32). [1] The possible reaction pathways for the formation of the key imino acid intermediates in the reaction of model *N*-phenylnitrone with methylphenylketene (Scheme S1) were explored using the B3LYP/6-31G(d) and MP2/6-31G(d) optimizations in the gas phase and in a dielectric continuum representing THF as the solvent. The solvent effects were treated using the Integral-Equation-Formalism Polarizable Continuum Model (IEF-PCM) [2] with radii and non-electrostatic terms for the SMD solvation model [3] as implemented in *Gaussian 09*. The harmonic vibrational frequency calculations at the same level of theory were used to characterize all located stationary points on the potential energy surface as minima or saddle points, and to calculate zero-point vibrational energies as well as corrections to enthalpy and free energy at 298.15 K. The quasi-harmonic approximation described by Cramer and Truhlar [4] was used to correct the entropic contributions of the low-frequency vibrations below 100 cm^{-1} by setting these frequencies to a value of 100 cm^{-1}. The energies of the B3LYP/6-31G(d) and MP2/6-31G(d) optimized geometries were further refined with M06-2X/6-311+G(d,p)(THF) and SCS-MP2/6-31G(d)(THF) single-point calculations, respectively. The free energies of the species in solution were calculated by adding the correction to Gibbs free energy from unscaled harmonic frequencies computed for 1 mol/L solute at 298.15 K to the predicted energy in solution including all computed corrections. The intrinsic reaction coordinate (IRC) method [5] was used to follow the minimum energy paths.

Scheme S1. Possible Reaction Pathways in the Reaction of Model *N*-Phenylnitrone with Methylphenylketene



[1]. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2009.

[2]. a) M. Cossi, V. Barone, R. Cammi, J. Tomasi *Chem. Phys. Lett.* **1996**, *255*, 327-335; b) E. Cancès, B. Mennucci, J. Tomasi *J. Chem. Phys.* **1997**, *107*, 3032-3041. c) J. Tomasi, B. Mennucci, R. Cammi *Chem. Rev.* **2005**, *105*, 2999-3093.

[3]. A. V. Marenich, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. B* **2009**, *113*, 6378-6396.

[4]. R. F. Ribeiro, A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B*, **2011**, *115*, 14556-14562.

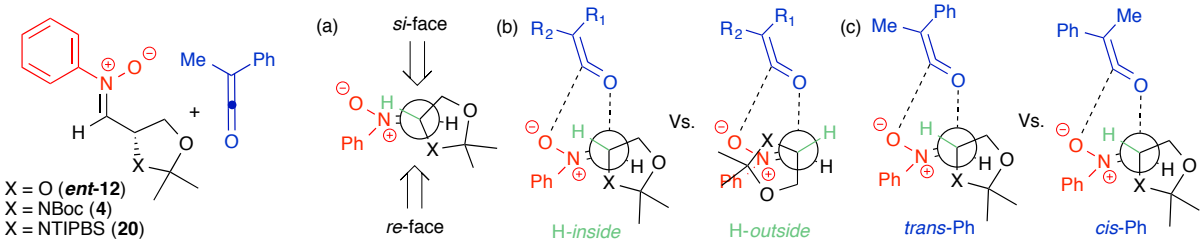
[5]. a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154-2161; b) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523-5527.

As shown in Figure S1, B3LYP and MP2 optimizations using the 6-31G(d) basis set yield geometrically very similar 3+2 cycloaddition transition structures, but the hetero-[3,3]-rearrangement transition structures differ significantly; B3LYP gives a highly asynchronous rearrangement transition structure with a long forming C-C bond, predicting almost no bonding between the interacting orbitals compared with the 0.2-0.6 Å shorter critical distances in the MP2 optimized geometry. The tendency of B3LYP to give highly asynchronous and dissociative transition states for hetero-[3,3]-rearrangements has previously been reported. [6]

According to the proposed mechanism, the stereochemical outcome of the reaction is determined at the 3+2 cycloaddition step of the pericyclic cascade by two factors: The facial selectivity of nitrone, and the direction of attack on the ketene. In order to understand the role of the *N*-substituent of the chiral auxiliary in determining the enantioselectivity of the reaction, the competing stereoisomeric 3+2 cycloaddition transition structures for nitrones **4**, *ent*-**12**, and **20** were studied in detail. Because of the markedly large number of conformational degrees of freedom of the nitrones under investigation, *re*- and *si*-face attack of ketene to the single-crystal X-ray structures of nitrones **4** and **20** were initially considered (Scheme S2a), and the rotamers of the chiral auxiliary (H-*inside* and H-*outside*) were additionally evaluated (Scheme S2b). The direction of attack on the ketene (*trans*-Ph and *cis*-Ph) was also taken into account for each transition state (Scheme S2c). As B3LYP and MP2 optimized 3+2 cycloaddition transition structures agree well, the calculations were carried out at the M06-2X/6-311+G(d,p)(THF)//B3LYP/6-31G(d) level to avoid the excessively high computational cost of MP2 calculations for these real systems, which comprise 49-90 atoms. The located stereoisomeric transition structures were given in Figures S2-S4 and the differences in their activation free energy were used to compute the enantiomeric product populations using the Boltzmann distribution:

$$p_i = \frac{e^{\frac{-\Delta\Delta G_i^{\ddagger}}{RT}}}{\sum e^{\frac{-\Delta\Delta G^{\ddagger}}{RT}}}$$

Scheme S2. Considerations for Building Stereoisomeric 3+2 Cycloaddition Transition Structures for Nitrones **4**, ***ent*-12**, and **20**.



The π-π interactions displayed in the X-ray structure of nitrone **20** (Figure 5, main text) suggest that dispersion interactions are important in determining the selectivity at the cycloaddition step. In order to test the reliability of B3LYP geometries, stereoisomeric 3+2 transition states were optimized using dispersion-corrected density functional theory (B3LYP-D) and the optimized geometries are given in Figure S5.

For the distortion-interaction analysis of the cycloaddition TSs, single-point energies of the nitrone and the ketene fragments in the transition structures were evaluated using M06-2X/6-311+G(d,p)(THF).

[6]. N. Celebi-Olcum, B. W. Boal, A. D. Huters, N. K. Garg, K. N. Houk *J. Am. Chem. Soc.* **2011**, *133*, 5752-5755.

II. COMPARISON OF B3LYP AND MP2 GEOMETRIES

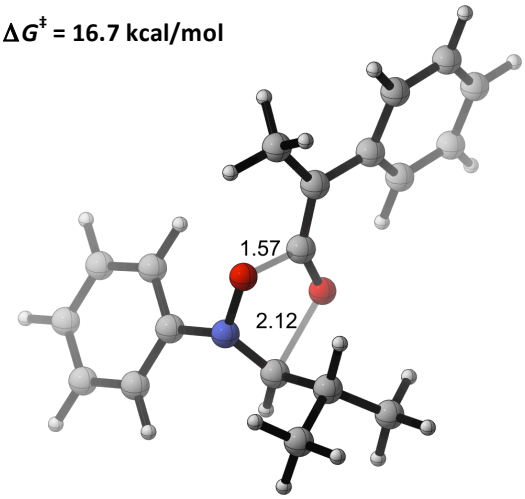
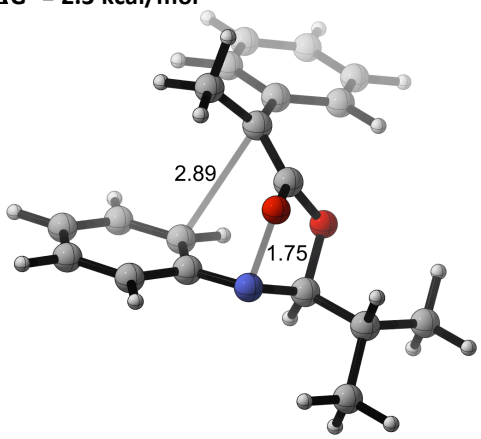
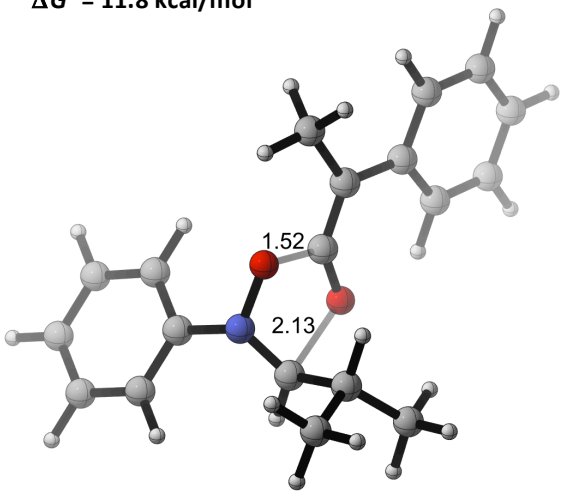
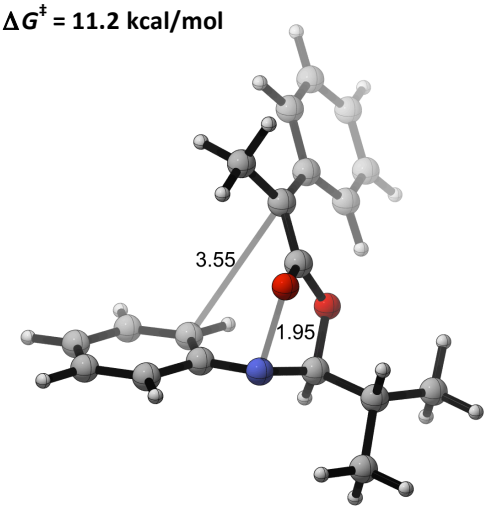
	TS-(3+2)	TS-[3,3]
SCS-MP2/6-31G(d)(THF)//MP2/6-31G(d)(THF)	$\Delta G^{\ddagger}$ = 16.7 kcal/mol 	$\Delta G^{\ddagger}$ = 2.3 kcal/mol 
M06-2X/6-311+G(d,p)(THF)//B3LYP/6-31G(d)	$\Delta G^{\ddagger}$ = 11.8 kcal/mol 	$\Delta G^{\ddagger}$ = 11.2 kcal/mol 

Figure S1. Geometries and activation free energies ($\Delta G^{\ddagger}$ in kcal/mol, relative to separated reactants) of 3+2 cycloaddition and [3,3]-rearrangement transition states. B3LYP and MP2 optimizations using the 6-31G(d) basis set locate geometrically very similar 3+2 cycloaddition transition structures (**TS-(3+2)**). However, the located hetero-[3,3]-rearrangement transition structures (**TS-[3,3]**) have significantly different geometries. B3LYP gives a highly asynchronous—but concerted—rearrangement transition structure with a long forming C-C bond that predicts almost no bonding between the interacting orbitals, whereas the MP2 optimized geometry has 0.2-0.6 Å shorter critical distances compared with the B3LYP geometry also predicting a facile rearrangement. This difference in B3LYP and MP2 geometries has previously been observed in the key hetero-[3,3]-sigmatropic rearrangement of the acid-promoted Fischer indole reaction.[6]

III. ENANTIOMERIC DISTRIBUTIONS

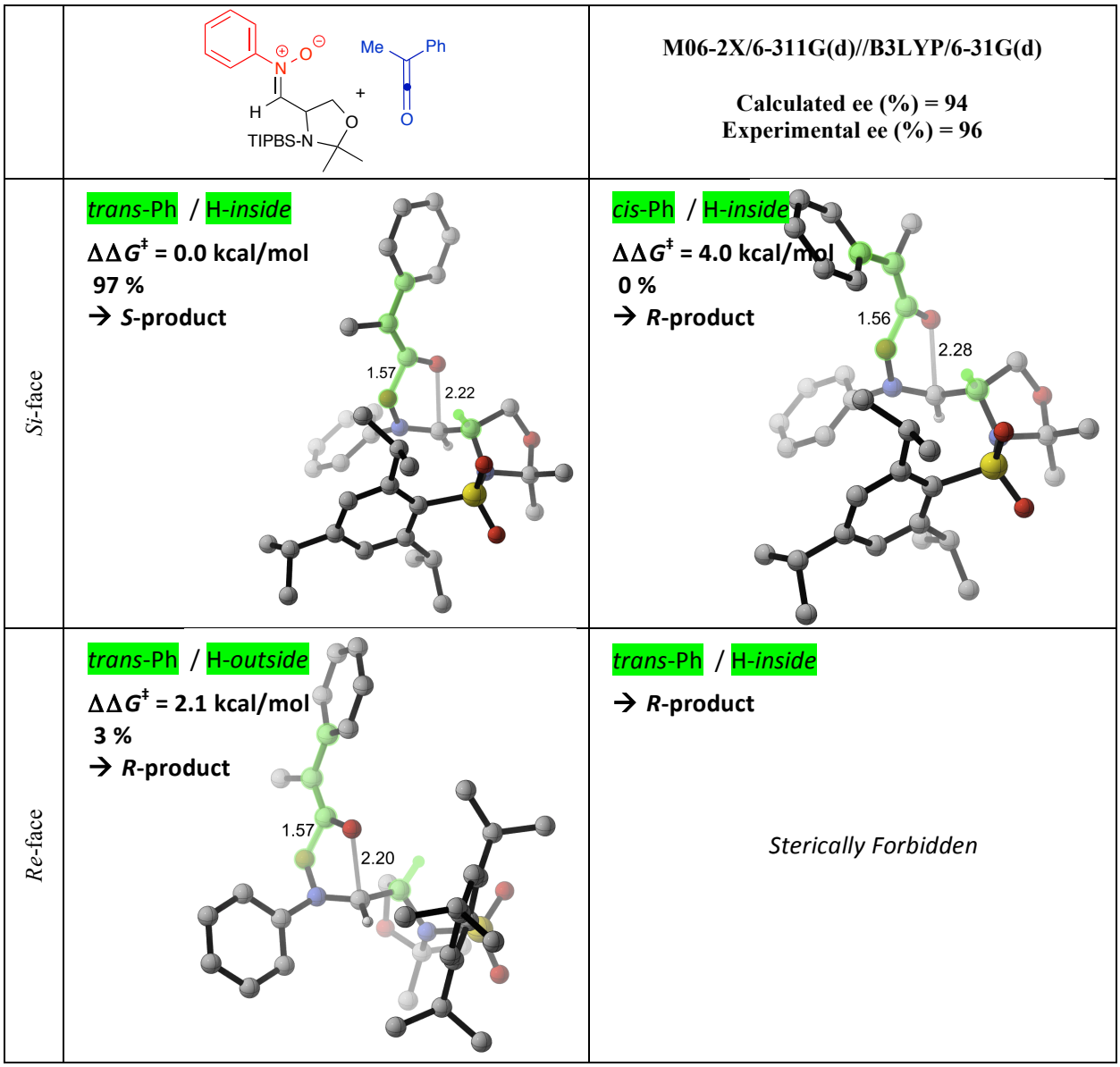
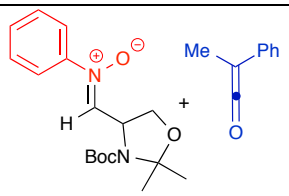


Figure S2. Geometries, relative activation free energies ($\Delta\Delta G^{\ddagger}$ in kcal/mol), and populations of stereoisomeric 3+2 cycloaddition transition states for the reaction of nitrone **20** with methylphenylketene. The hydrogen atoms, except those at the stereocenters, are omitted for clarity. As is represented in the X-ray structure of **20**, the large TIPBS motif sterically blocks the *Re*-face of the nitrone. Only the H-*outside* conformation of the chiral auxiliary allows this approach, which suffers from substantial 1,3-allylic strain, and therefore, is high in energy. Boltzmann populations suggest that the *Re*-face attack contributes 3% to the enantiomeric product distribution. The cycloaddition occurs in the plane of ketene substituents, and the attack of nitrone from the more hindered side of ketene (*cis*-Ph) is found to be significantly destabilizing because of the unfavorable steric interactions of the phenyl group on the ketene with the *N*-protecting group.

<table>
<tr><td></td><td> 
</td><td>M06-2X/6-311G(d)//B3LYP/6-31G(d)

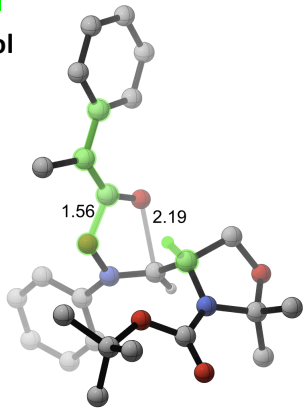
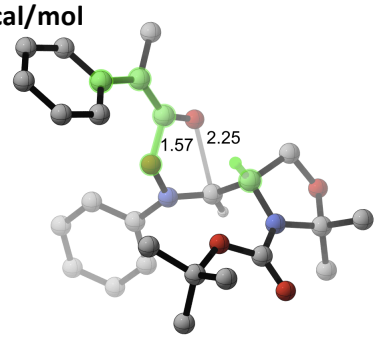
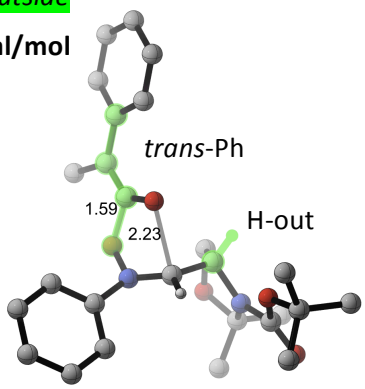
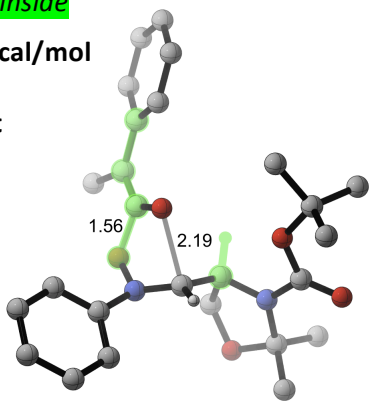
Calculated ee (%) = 82
Experimental ee (%) = 84</td></tr>
<tr><td>Si-face</td><td>trans-Ph / H-inside
ΔΔG‡ = 0.0 kcal/mol
91 %
→ S-product
 
</td><td>cis-Ph / H-inside
ΔΔG‡ = 1.4 kcal/mol
9 %
→ R-product
 
</td></tr>
<tr><td>Re-face</td><td>trans-Ph / H-outside
ΔΔG‡ = 3.8 kcal/mol
0 %
→ R-product
 
</td><td>trans-Ph / H-inside
ΔΔG‡ = 4.7 kcal/mol
0 %
→ R-product
 
</td></tr>
</table>

Figure S3. Geometries, relative activation free energies (ΔΔ$G^{‡}$ in kcal/mol), and populations of stereoisomeric 3+2 cycloaddition transition states in the reaction of nitrone **4** with methylphenylketene. The hydrogen atoms, except those at the stereocenters, are omitted for clarity. Even though the size of the BOC group allows the approach of ketene from the *Re*-face of the nitrone, these transition structures are highly sterically demanding: The H-*outside* conformation of the chiral auxiliary places the ring methylene group to the more demanding *inside* position, and for the H-*inside* conformation, the arrangement of bulky phenyl and *tert*-butyl groups is sterically disfavored. Therefore, the selectivity is determined by the direction of attack on ketene from the *Si*-face. Steric effects of the ketene substituents at the ketene LUMO favor the attack of nitrone from the least hindered side of the ketene (*trans*-Ph).

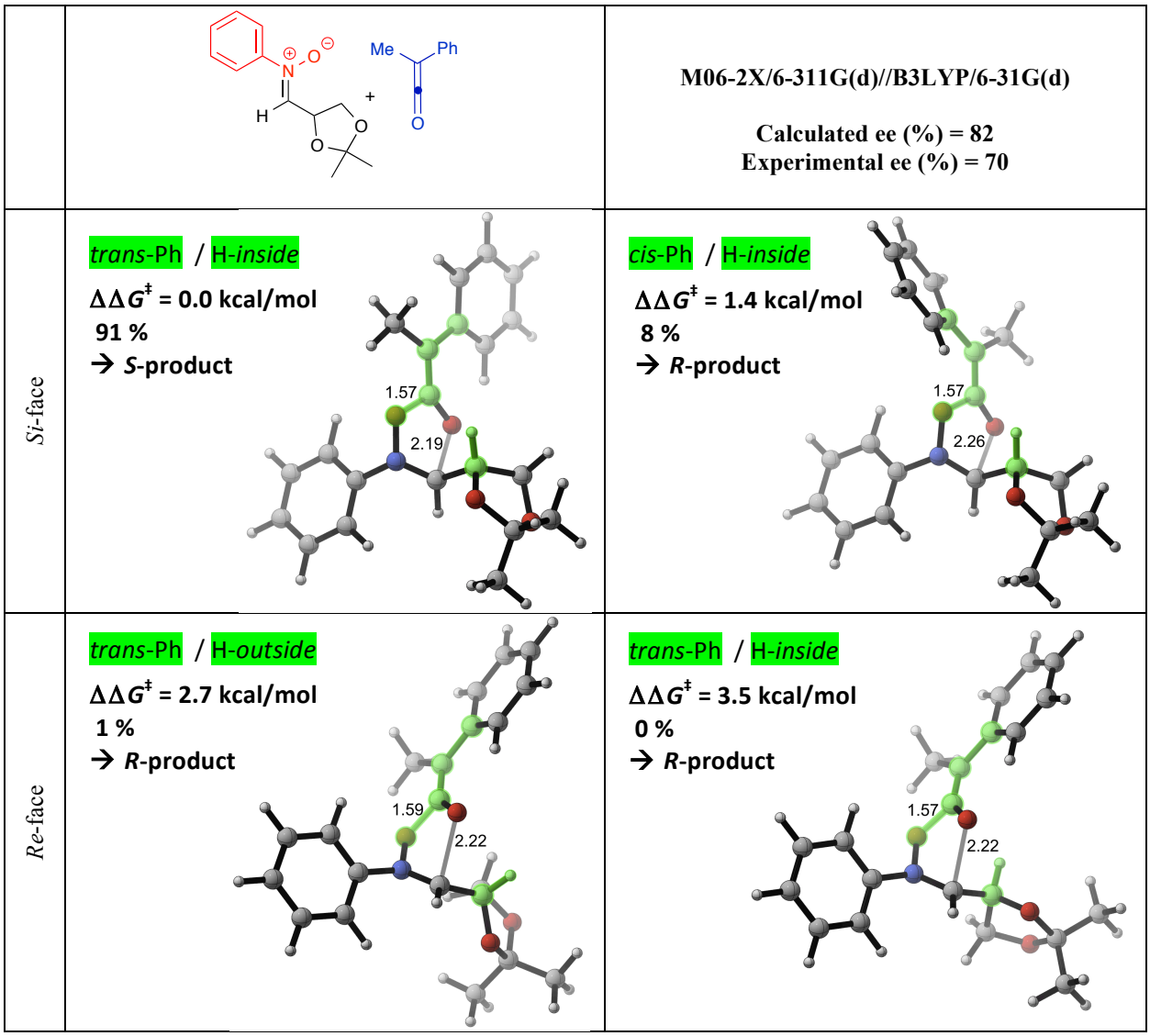
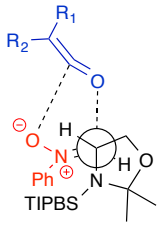
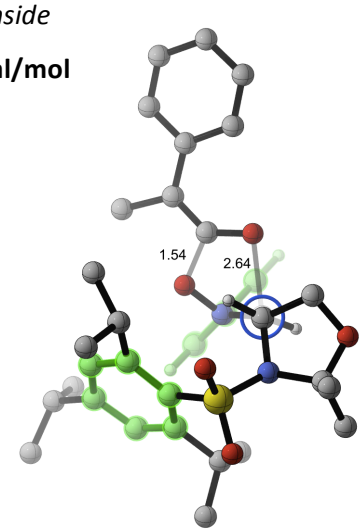
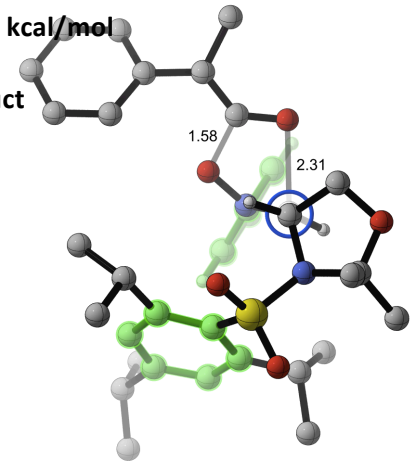
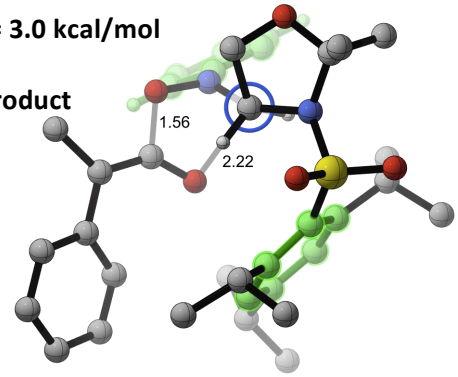


Figure S4. Geometries, relative activation free energies ($\Delta\Delta G^{\ddagger}$ in kcal/mol), and populations of stereoisomeric 3+2 cycloaddition transition states in the reaction of nitrone *ent*-**12** with methylphenylketene. In the absence of steric interactions from the protecting group, *Re*-face attack is sterically allowed both for the H-*outside*, and H-*inside* conformations of the chiral auxiliary. H-*outside* conformation places the C-O bond on the stereocenter *anti* to the forming C-O bond in accord with the Felkin-Anh model for nucleophilic additions, but the 1,3-allylic strain of the *inside* ring methylene group with the nitrone oxygen results in substantial destabilization. H-*inside* conformation for the *Re*-face attack relieves this strain by putting the small hydrogen atom to the *inside* position. The C-C bond on the stereocenter is *anti* to the forming C-O bond at this conformation giving a high energy transition state. For the *Si*-face attack, the cycloaddition occurs with *trans*-phenyl selectivity, which can be explained by the attack of nitrone from the least hindered side in the plane of ketene.

IV. B3LYP-D GEOMETRIES AND ENERGIES

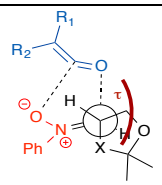
<table>
<tr><td></td><td>  </td><td>M06-2X/6-311G(d)//B3LYP-D/6-31G(d)

Calculated ee (%) = 98
Experimental ee (%) = 96</td></tr>
<tr><td>Si-face</td><td>trans-Ph / H-inside
ΔΔG‡ = 0.0 kcal/mol
99 %
→ S-product
  </td><td>cis-Ph / H-inside
ΔΔG‡ = 4.7 kcal/mol
0 %
→ R-product
  </td></tr>
<tr><td>Re-face</td><td>trans-Ph / H-outside
ΔΔG‡ = 3.0 kcal/mol
1 %
→ R-product
  </td><td>trans-Ph / H-inside
→ R-product

Sterically Forbidden</td></tr>
</table>

Figure S5. Optimized geometries using dispersion-corrected density functional theory, relative activation free energies ($\Delta\Delta G^{\ddagger}$ in kcal/mol), and populations of stereoisomeric 3+2 cycloaddition transition states in the reaction of nitrone **20** with methylphenylketene at the M06-2X/6-311+G(d,p)//B3LYP-D/6-31G(d) level.

V. EFFECT OF ANTIPERIPLANARITY ON STEREOSELECTION

	τ°	$\Delta G^{\ddagger}$ (kcal/mol)
TSE-O	180.7	15.3
TSZ-O	178.9	16.6
TSE-NBOC	177.1	13.3
TSZ-NBOC	174.1	14.7
TSE-NTIPBS	171.1	18.4
TSZ-NTIPBS	160.3	22.1

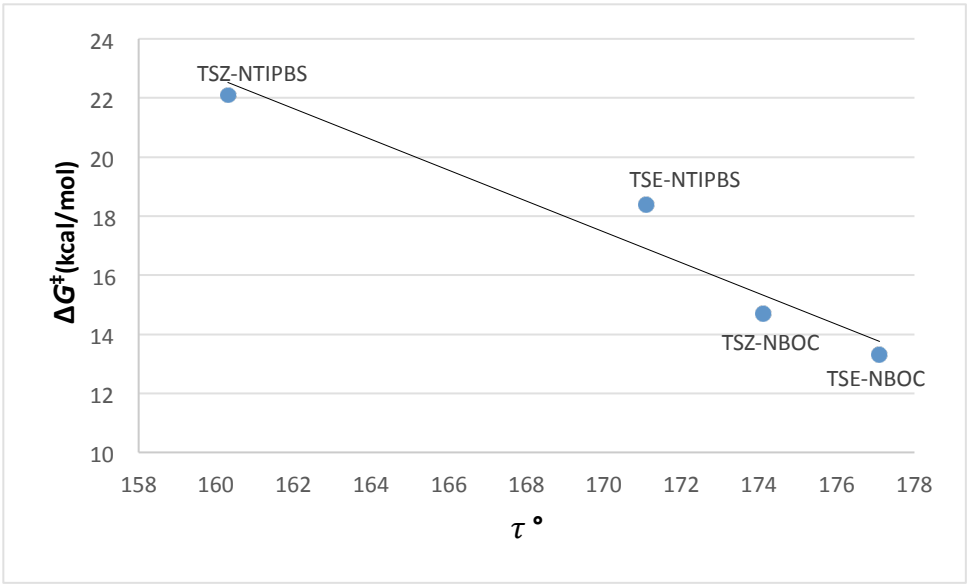


Figure S6. The O-C-C-N dihedral angle (τ) decreases with the increasing size of the *X*-substituent, and the deviations from antiperiplanarity of the C-N bond at the TS with increasing size of the *N*-protecting group shows a good correlation with the activation free energy ($R^2 = 0.94$).

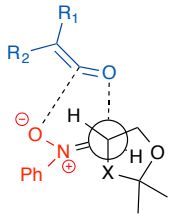
VI. DISTORTION-INTERACTION ANALYSIS

Table S1. Distortion and interaction energies of stereoisomeric 3+2 cycloaddition transition states in the reactions of nitrone ***ent*-12**, **4**, and **20** with methylphenylketene.

	$E_{distortion}$-ketene (kcal/mol)	$E_{distortion}$-nitrone (kcal/mol)	$E_{distortion}$-total (kcal/mol)	$E_{interaction}$ (kcal/mol)
TSE-O	35.6	12.3	47.9	46.6
TSZ-O	33.4	14.5	47.9	48.4
TSE-NBoc	35.8	10.6	46.4	47.8
TSZ-NBoc	33.7	13.1	46.8	49.8
TSE-NTIPBS	37.9	17.4	55.3	48.9
TSZ-NTIPBS	34.5	18.5	53.0	50.9

VII. CARTESIAN COORDINATES OF OPTIMIZED STRUCTURES

ENANTIOSELECTIVITY



TSE-O

3+2-cycloaddition TS for X=O, R_1=Ph, R_2=Me
B3LYP/6-31G(d)

C	-0.78883	3.33855	-0.01526
C	2.36009	0.48685	0.84499
C	1.13936	0.39101	0.24506
C	-1.65208	2.24299	0.05643
O	-0.00589	0.94664	1.15977
C	-1.41112	-0.16096	-0.21291
N	-1.14505	0.95859	0.42949
O	0.68807	-0.05874	-0.83764
C	-1.30575	4.57593	-0.39376
C	-2.66357	4.71930	-0.69037
C	-3.51653	3.61804	-0.59752
C	-3.01739	2.37502	-0.21107
C	3.56590	-0.02453	0.16497
C	4.79792	-0.06651	0.85572
C	3.57143	-0.48819	-1.17139
C	5.95836	-0.55380	0.25614
C	4.73278	-0.97501	-1.76448
C	5.93831	-1.01503	-1.05957
C	2.51713	1.12657	2.20818
C	-1.21101	-1.53181	0.37361
H	2.85483	0.40053	2.96150
H	1.58309	1.55633	2.57003
H	3.26743	1.92865	2.18662
H	4.85311	0.27918	1.88221
H	6.88419	-0.57147	0.82693
H	6.84291	-1.39314	-1.52868
H	4.69540	-1.32064	-2.79540
H	2.65371	-0.45565	-1.74527
H	0.26261	3.21271	0.21298
H	-0.64033	5.43160	-0.46101
H	-3.05713	5.68850	-0.98236
H	-4.57665	3.72721	-0.80656
H	-3.67992	1.52301	-0.09104
H	-2.10251	-0.07399	-1.04562
H	-0.46436	-1.51109	1.16749
O	-2.48040	-1.91216	0.92132
C	-0.94352	-2.60214	-0.69443
H	-0.37357	-3.43732	-0.26640
H	-0.41910	-2.22098	-1.56957
O	-2.25703	-2.99861	-1.07559
C	-3.05634	-2.95820	0.09754
C	-4.47421	-2.57036	-0.29581
H	-5.09630	-2.45647	0.59680
H	-4.91382	-3.34221	-0.93471
H	-4.46412	-1.62514	-0.84574
C	-2.99468	-4.27607	0.87277
H	-3.54714	-4.18717	1.81305
H	-1.95989	-4.53968	1.11026
H	-3.43394	-5.08380	0.27887

TSZ-O

3+2-cycloaddition TS for X=O, R_1=Me, R_2=Ph
B3LYP/6-31G(d)

C	-1.03004	2.75511	0.32359
C	-2.11969	-1.29417	1.09173
C	-0.89448	-0.69696	1.04848
C	0.23855	2.27751	-0.01404
O	-0.62959	0.09596	-0.27553
C	1.53423	0.25100	0.36146
N	0.46414	0.86649	-0.08768
O	0.07324	-0.62827	1.84074
C	-1.22707	4.13226	0.40354
C	-0.17826	5.01796	0.14455
C	1.07802	4.52429	-0.21239
C	1.29061	3.15008	-0.30675
C	-3.17908	-1.20665	0.06898
C	-4.53252	-1.24860	0.47184
C	-2.93506	-1.14361	-1.32135
C	-5.57600	-1.20309	-0.45090
C	-3.97901	-1.09093	-2.24188
C	-5.30933	-1.11798	-1.81777
C	-2.42510	-2.02157	2.38963
C	1.94543	-1.13726	-0.04085
H	-3.04105	-1.42578	3.07999
H	-1.49892	-2.26277	2.91815
H	-2.96915	-2.95460	2.19692
H	-4.77079	-1.30657	1.52946
H	-6.60392	-1.23123	-0.09621
H	-6.12122	-1.08356	-2.53953
H	-3.74808	-1.04534	-3.30393
H	-1.91481	-1.15309	-1.68507
H	-1.83529	2.05699	0.51762
H	-2.20810	4.51289	0.67185
H	-0.34301	6.08962	0.20723
H	1.89114	5.20768	-0.43877
H	2.25052	2.76019	-0.63156
H	2.29557	0.88819	0.80049
H	1.09776	-1.69688	-0.43532
O	2.92872	-0.97122	-1.07211
C	2.70944	-1.87760	1.06678
H	2.60115	-2.96360	0.94517
H	2.39997	-1.59497	2.07189
O	4.05274	-1.45450	0.85721
C	4.23227	-1.32780	-0.54612
C	5.21297	-0.19377	-0.80768
H	5.31458	-0.02249	-1.88329
H	6.19614	-0.44197	-0.39652
H	4.85752	0.72507	-0.33283
C	4.66819	-2.64795	-1.18542
H	4.71325	-2.54311	-2.27362
H	3.95896	-3.44689	-0.95022
H	5.65702	-2.93782	-0.81623

TSE-NBoc

3+2-cycloaddition TS for X=NBoc, R_1=Ph, R_2=Me
B3LYP/6-31G(d)

C	0.49262	3.54961	-0.48433
C	2.93428	0.22995	0.87792
C	1.91644	0.35816	-0.02085
C	-0.47332	2.57893	-0.76000
O	0.64753	1.01357	0.61693
C	-0.45709	0.18268	-1.16548
N	-0.24847	1.21956	-0.37723
O	1.72374	0.05537	-1.22499
C	0.25244	4.86592	-0.87352
C	-0.93497	5.21083	-1.52386
C	-1.89767	4.23244	-1.77850
C	-1.67772	2.91276	-1.38649
C	4.20706	-0.40016	0.47703
C	5.19242	-0.67655	1.45141
C	4.51694	-0.75430	-0.85689
C	6.40380	-1.28083	1.11825
C	5.72753	-1.35857	-1.18365
C	6.68413	-1.62992	-0.20225
C	2.79826	0.74053	2.29660
C	-0.59263	-1.23931	-0.68199
H	2.82952	-0.07916	3.02881
H	1.86217	1.27697	2.45198
H	3.62006	1.42240	2.55467
H	5.01040	-0.42391	2.49035
H	7.13206	-1.47860	1.90171
H	7.62926	-2.09877	-0.46338
H	5.92811	-1.61339	-2.22212
H	3.79903	-0.54281	-1.63942
H	1.41192	3.26861	0.01493
H	1.00253	5.62474	-0.67079
H	-1.11338	6.23981	-1.82189
H	-2.83136	4.49632	-2.26640
H	-2.43996	2.15519	-1.54264
H	-0.87125	0.41046	-2.14304
H	-0.08605	-1.37485	0.27185
N	-2.02469	-1.55467	-0.58459
C	-0.16167	-2.25196	-1.75324
H	0.11639	-3.20235	-1.27790
H	0.66533	-1.90062	-2.36815
O	-1.31685	-2.39072	-2.57482
C	-2.46936	-2.40507	-1.73260
C	-3.61741	-1.77586	-2.51547
H	-4.51140	-1.71854	-1.89179
H	-3.83092	-2.38319	-3.40045
H	-3.34033	-0.77003	-2.84601
C	-2.79479	-3.83132	-1.27299
H	-3.63552	-3.82179	-0.57612
H	-1.93269	-4.28703	-0.77585
H	-3.05513	-4.44109	-2.14355
C	-2.82848	-1.27940	0.49686
O	-3.99991	-1.62067	0.57081
O	-2.13828	-0.58616	1.42652
C	-2.77589	-0.14242	2.68419
C	-3.25493	-1.35697	3.48538
H	-3.61062	-1.02763	4.46815
H	-4.06652	-1.87560	2.97321
H	-2.42786	-2.05794	3.64310

C	-1.62698	0.56598	3.40513
H	-1.24476	1.39722	2.80572
H	-1.97632	0.95701	4.36649
H	-0.80046	-0.12693	3.59063
C	-3.91057	0.83655	2.36784
H	-4.31020	1.24793	3.30143
H	-3.53463	1.67031	1.76429
H	-4.72000	0.34181	1.82839

TSZ-NBoc

3+2-cycloaddition TS for X=NBoc R_1=Me, R_2=Ph
B3LYP/6-31G(d)

C	1.80733	2.79022	0.25290
C	2.82800	-0.72828	-1.78942
C	1.62538	-0.09025	-1.71269
C	0.46915	2.39509	0.18003
O	1.13192	0.16721	-0.24520
C	-0.84947	0.81539	-1.11856
N	0.14493	1.08837	-0.30448
O	0.82217	0.36001	-2.56140
C	2.10364	4.06892	0.72080
C	1.08311	4.93746	1.11538
C	-0.24796	4.52062	1.05438
C	-0.56237	3.24161	0.59807
C	3.69302	-1.11924	-0.66142
C	5.09561	-1.11906	-0.83236
C	3.20949	-1.56129	0.58997
C	5.96057	-1.50710	0.18923
C	4.07529	-1.94152	1.61262
C	5.45901	-1.91643	1.42528
C	3.34382	-0.94094	-3.20251
C	-1.43809	-0.55625	-1.32145
H	4.07998	-0.18244	-3.50866
H	2.52081	-0.89254	-3.92047
H	3.83130	-1.91916	-3.29798
H	5.51606	-0.79739	-1.78028
H	7.03428	-1.48548	0.01638
H	6.13155	-2.22041	2.22311
H	3.66179	-2.27814	2.56102
H	2.14096	-1.62476	0.75394
H	2.58941	2.10655	-0.05420
H	3.14071	4.38664	0.77416
H	1.32496	5.93124	1.48063
H	-1.04503	5.18260	1.37977
H	-1.59215	2.89725	0.59032
H	-1.45751	1.66294	-1.41988
H	-0.74662	-1.32428	-0.97941
N	-2.71587	-0.61114	-0.59649
C	-1.93183	-0.77917	-2.75991
H	-1.96593	-1.85597	-2.97513
H	-1.31647	-0.27848	-3.50457
O	-3.23210	-0.19952	-2.77002
C	-3.87668	-0.51518	-1.53705
C	-4.81096	0.64338	-1.20138
H	-5.29692	0.47134	-0.23948
H	-5.57243	0.73253	-1.98228
H	-4.24822	1.58113	-1.16101
C	-4.62223	-1.85163	-1.63161
H	-5.04987	-2.11503	-0.66177
H	-3.94734	-2.65354	-1.94705
H	-5.42681	-1.76619	-2.36840
C	-2.86539	-0.86363	0.74670
O	-3.95304	-0.95904	1.29631
O	-1.65843	-0.97417	1.34174
C	-1.54531	-1.19891	2.80023
C	-2.21373	-2.52280	3.18341
H	-2.00974	-2.74007	4.23792
H	-3.29330	-2.48130	3.03439
H	-1.80257	-3.34283	2.58451
C	-0.03175	-1.27714	3.00854
H	0.46099	-0.36582	2.65753
H	0.19052	-1.40711	4.07290
H	0.39061	-2.12617	2.46194
C	-2.14005	-0.00277	3.54999
H	-1.96531	-0.12079	4.62510
H	-1.65600	0.92675	3.22972
H	-3.21480	0.07583	3.37745

TSE-NTIPBS

3+2-cycloaddition TS for X=NTIPBS, R_1=Ph,
R_2=Me
B3LYP/6-31G(d)

C	0.49578	-2.56965	-1.86870
C	-3.73522	-1.09922	0.68956
C	-2.84248	-0.46613	-0.11968
C	-0.56166	-1.66800	-1.97998
O	-1.36567	-0.93091	0.12644
C	-0.71618	0.66372	-1.33086
N	-0.67119	-0.60609	-1.00369
O	-2.89691	0.42034	-1.01521
C	0.59052	-3.61257	-2.79026
C	-0.36384	-3.74483	-3.80175
C	-1.42152	-2.83746	-3.89332
C	-1.53293	-1.79211	-2.97614
C	-5.15700	-0.69751	0.69034
C	-6.03557	-1.22586	1.66257
C	-5.71688	0.20185	-0.24633
C	-7.38503	-0.87714	1.69953
C	-7.06490	0.54676	-0.20533
C	-7.91491	0.01273	0.76617
C	-3.30559	-2.22265	1.60746
C	-0.66918	1.81828	-0.36135
H	-3.96830	-3.09065	1.49334
H	-3.33905	-1.93684	2.66885
H	-2.29086	-2.55495	1.38806
H	-5.66047	-1.91496	2.41161
H	-8.02354	-1.30627	2.46863

H	-8.96688	0.28464	0.79338
H	-7.45626	1.24020	-0.94681
H	-5.08255	0.62653	-1.01425
H	1.22678	-2.44830	-1.07627
H	1.41200	-4.31942	-2.71807
H	-0.28513	-4.55843	-4.51729
H	-2.16861	-2.94608	-4.67408
H	-2.35982	-1.09011	-3.00743
H	-0.89872	1.48578	0.65083
N	0.69095	2.41913	-0.47092
C	-1.56836	2.98070	-0.82047
H	-1.86438	3.58672	0.04490
H	-2.45596	2.65176	-1.35428
O	-0.73498	3.70237	-1.71716
C	0.55279	3.80513	-1.12948
C	1.55751	3.97562	-2.25996
H	2.57230	4.03167	-1.86060
H	1.33862	4.90248	-2.79986
H	1.48521	3.13886	-2.96008
C	0.59281	4.98423	-0.14562
H	-0.10212	4.84681	0.68574
H	0.30706	5.88546	-0.69704
H	1.59280	5.12247	0.26745
S	1.72015	2.27563	0.89628
O	2.91001	3.07549	0.57735
O	0.96215	2.62224	2.10562
C	2.21507	0.51869	0.93063
C	3.11866	0.07513	-0.07677
C	1.84672	-0.32372	2.01570
C	3.67347	-1.19992	0.05959
C	2.45714	-1.58556	2.07324
C	3.37707	-2.04128	1.13348
H	4.37850	-1.53411	-0.69527
H	2.20622	-2.23854	2.90215
C	0.87868	0.01148	3.15972
H	0.20420	0.79779	2.83059
C	4.03843	-3.40333	1.29081
H	3.61737	-3.86140	2.19556
C	3.56120	0.88324	-1.30193
C	3.36761	0.10099	-2.61593
H	2.33842	-0.25784	-2.72527
H	4.03156	-0.76747	-2.69232
H	3.59159	0.75426	-3.46732
C	5.02015	1.35579	-1.14877
H	5.13439	1.97265	-0.25384
H	5.31522	1.95512	-2.01847
H	5.71123	0.50711	-1.07795
C	-0.00433	-1.18164	3.57213
H	-0.49485	-1.63472	2.70625
H	-0.78505	-0.82506	4.25334
H	0.55083	-1.96118	4.10647
C	1.65405	0.55740	4.37678
H	0.95491	0.81138	5.18192
H	2.21448	1.45996	4.12027
H	2.35642	-0.19166	4.76330
C	3.72625	-4.34307	0.11093
H	4.17150	-5.33026	0.28011
H	4.13359	-3.95372	-0.82994
H	2.64590	-4.47720	-0.01542
C	5.55877	-3.27035	1.50436
H	6.04924	-2.83657	0.62497
H	6.00736	-4.25412	1.68485
H	5.78405	-2.62921	2.36313
H	2.94276	1.77189	-1.38020
H	-0.45207	0.88954	-2.36051

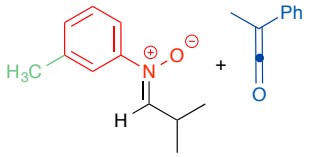
TSZ-NTIPBS

3+2-cycloaddition TS for X=NTIPBS R_1=Me, R_2=Ph
B3LYP/6-31G(d)

C	0.21775	-1.95887	2.15319
C	4.38921	0.93763	0.28744
C	3.13649	1.09694	0.79699
C	1.01499	-0.82168	2.26749
O	2.08672	0.03904	0.32772
C	0.46691	1.31654	1.26242
N	1.02525	0.13276	1.17925
O	2.63969	1.91705	1.61175
C	0.21880	-2.88758	3.19541
C	1.00948	-2.67329	4.32576
C	1.80402	-1.52796	4.42158
C	1.81561	-0.59096	3.38929
C	4.85309	-0.14532	-0.59728
C	6.18517	-0.60244	-0.49308
C	4.05856	-0.73200	-1.60448
C	6.68428	-1.60343	-1.32432
C	4.55592	-1.73748	-2.43041
C	5.87205	-2.18520	-2.29824
C	5.41449	1.93517	0.80057
C	0.25729	2.24867	0.09283
H	6.11034	2.22530	0.00389
H	6.02003	1.53659	1.62865
H	4.92005	2.83597	1.17331
H	6.83750	-0.17438	0.26185
H	7.71458	-1.93151	-1.20598
H	6.25927	-2.96506	-2.94874
H	3.91225	-2.16415	-3.19631
H	3.04611	-0.37756	-1.75345
H	-0.38631	-2.11031	1.26465
H	-0.40041	-3.77666	3.12210
H	1.00700	-3.39969	5.13361
H	2.41847	-1.36199	5.30167
H	2.42292	0.30674	3.43400
H	0.71743	1.82628	-0.80286
N	-1.21457	2.43380	-0.05466
C	0.73501	3.69474	0.34794
H	1.00744	4.16279	-0.60655
H	1.57164	3.74656	1.03877
O	-0.39332	4.32002	0.93845
C	-1.54349	3.91753	0.21697
C	-2.73554	4.06496	1.15187

H	-3.65206	3.73349	0.66021
H	-2.84333	5.11930	1.42606
H	-2.57425	3.48494	2.06447
C	-1.70438	4.76707	-1.05309
H	-0.87009	4.63186	-1.74532
H	-1.74094	5.81772	-0.74835
H	-2.62572	4.51846	-1.58138
S	-1.97900	1.67438	-1.38962
O	-3.35648	2.18440	-1.39308
O	-1.15880	1.88476	-2.58983
C	-2.06018	-0.10542	-0.97560
C	-2.95719	-0.49497	0.05952
C	-1.41314	-1.07491	-1.79053
C	-3.22733	-1.85682	0.21515
C	-1.74916	-2.41902	-1.56675
C	-2.66018	-2.83683	-0.60089
H	-3.92495	-2.15462	0.99200
H	-1.28528	-3.17360	-2.19273
C	-0.41272	-0.81097	-2.92449
H	0.04344	0.16394	-2.77115
C	-3.02191	-4.30841	-0.45716
H	-2.46158	-4.85366	-1.22823
C	-3.67324	0.45492	1.02465
C	-3.42502	0.07122	2.49728
H	-2.35500	-0.00661	2.72100
H	-3.88843	-0.88482	2.76493
H	-3.85581	0.83545	3.15467
C	-5.18117	0.52471	0.71582
H	-5.34900	0.86232	-0.31008
H	-5.67212	1.23207	1.39498
H	-5.66452	-0.45119	0.84476
C	0.73624	-1.83701	-2.96384
H	1.49271	-1.48986	-3.67632
H	1.22016	-1.94632	-1.98811
H	0.41476	-2.82842	-3.30263
C	-1.14005	-0.76540	-4.28439
H	-0.42274	-0.55348	-5.08572
H	-1.90400	0.01590	-4.30156
H	-1.61906	-1.72744	-4.50516
C	-2.59774	-4.87830	0.90968
H	-2.84105	-5.94515	0.97291
H	-3.11419	-4.36995	1.73269
H	-1.51864	-4.76892	1.06625
C	-4.52118	-4.55071	-0.71699
H	-5.14380	-4.05440	0.03666
H	-4.74673	-5.62279	-0.68093
H	-4.81983	-4.17161	-1.70003
H	-3.27306	1.45535	0.89532
H	-0.14717	1.48422	2.14188

REGIOSELECTIVITY



TS for 4-isomer

[3,3]-rearrangement TS
MP2/6-31G(d)

C	-2.83433	-1.55024	0.87435
C	1.07733	-0.05697	1.22832
C	0.07648	0.85964	0.99093
C	-1.97740	-0.67007	0.17409
O	-0.99979	0.97150	1.73971
C	-1.49299	1.61736	-0.44832
H	-1.61393	1.28801	-1.48913
N	-2.16240	0.68705	0.44070
H	-3.61792	-1.12335	1.49624
O	-0.03439	1.56928	-0.17883
C	-2.67488	-2.91912	0.73805
C	-1.64987	-3.43660	-0.07293
H	-1.53919	-4.51502	-0.17695
C	-0.79262	-2.58692	-0.77546
C	-0.93287	-1.19620	-0.61866
H	-3.33672	-3.59926	1.26980
C	2.31339	-0.04221	0.43590
C	3.03946	-1.23579	0.24694
C	2.80805	1.13909	-0.15116
C	4.20057	-1.25109	-0.52597
H	2.69154	-2.16269	0.69527
C	3.97174	1.11956	-0.91985
H	2.28932	2.07869	0.01406
C	4.67111	-0.07428	-1.11532
H	4.74019	-2.18533	-0.66593
H	4.34000	2.04478	-1.35790
H	5.57956	-0.08606	-1.71320
C	0.97557	-0.95686	2.42682
H	1.11108	-2.00124	2.12623
H	1.74746	-0.72393	3.16893
H	-0.00545	-0.86198	2.89440
C	-1.99776	3.03722	-0.26251
H	-1.83969	3.28790	0.79360
C	-1.20319	4.00356	-1.13699
H	-1.56413	5.02752	-0.99622
H	-0.13828	3.97911	-0.89344
H	-1.32026	3.74918	-2.19706
C	-3.48950	3.10496	-0.58088
H	-3.67557	2.81435	-1.62167
H	-4.06465	2.44158	0.06918
H	-3.85925	4.12689	-0.44746
H	-0.29753	-0.53427	-1.20197
C	0.26414	-3.13238	-1.69918
H	0.48126	-4.18045	-1.47249
H	-0.06556	-3.07600	-2.74294

H	1.19251	-2.56000	-1.61339

[3,3]-rearrangement TS
B3LYP /6-31G(d)

C	-3.0923378	-1.6507295	0.8147374
C	1.3496372	-0.0469795	1.3750824
C	0.1859832	0.6670895	1.0911774
C	-2.1295748	-0.8257945	0.1815194
O	-0.8241858	0.7345795	1.8814704
C	-1.4591778	1.4685285	-0.3044406
H	-1.6145018	1.2404265	-1.3662186
N	-2.1864848	0.5138255	0.5017044
H	-3.8008808	-1.1855435	1.4931924
O	-0.0148268	1.3051725	-0.1006126
C	-3.1225718	-3.0119115	0.5573774
C	-2.1962538	-3.5812995	-0.3261816
H	-2.2308768	-4.6501775	-0.5244526
C	-1.2236128	-2.7961665	-0.9645846
C	-1.1882738	-1.4252555	-0.6974626
H	-3.8680438	-3.6401415	1.0371154
C	2.5975042	0.0441845	0.6093664
C	3.7115132	-0.7398115	1.0027804
C	2.7778192	0.8783575	-0.5239466
C	4.9110112	-0.7161255	0.2963294
H	3.6408242	-1.3817665	1.8728104
C	3.9811292	0.9008215	-1.2229886
H	1.9719142	1.5196675	-0.8517536
C	5.0571972	0.1027035	-0.8253036
H	5.7374492	-1.3388955	0.6294464
H	4.0797162	1.5555215	-2.0854076
H	5.9945722	0.1253905	-1.3745416
C	1.3386822	-0.8410605	2.6601474
H	1.6687422	-1.8725725	2.4887664
H	2.0087672	-0.4123225	3.4185514
H	0.3335242	-0.8698735	3.0818814
C	-1.8907428	2.9108615	-0.0045056
H	-1.7429048	3.0697665	1.0703734
C	-1.0336458	3.9187905	-0.7809166
H	-1.3558128	4.9422325	-0.5568546
H	0.0262172	3.8368315	-0.5214026
H	-1.1298668	3.7715075	-1.8650976
C	-3.3805328	3.0905635	-0.3280746
H	-3.5773358	2.9312505	-1.3969466
H	-3.9999848	2.3886875	0.2387824
H	-3.7038498	4.1080105	-0.0795066
H	-0.4471398	-0.8117435	-1.1972106
C	-0.2337798	-3.4277295	-1.9145346
H	0.3751192	-4.1860335	-1.4065296
H	-0.7452228	-3.9311725	-2.7443966
H	0.4450992	-2.6816665	-2.3387426

TS for 6-isomer

[3,3]-rearrangement TS
MP2/6-31G(d)

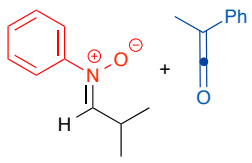
C	-2.94819	-0.85972	0.29378
C	1.10646	-0.50542	1.14220
C	0.41062	0.67656	1.04131
C	-1.83553	-0.12411	-0.17328
O	-0.68777	0.94299	1.72280
C	-0.75578	2.03453	-0.33494
H	-0.84035	1.90882	-1.42258
N	-1.72079	1.17494	0.32983
H	-3.66989	-0.34338	0.92493
O	0.60748	1.57713	0.02254
C	-3.12957	-2.19155	-0.05739
C	-2.15663	-2.81104	-0.87124
H	-2.28903	-3.85371	-1.15836
C	-1.05926	-2.09837	-1.34352
C	-0.86088	-0.76117	-0.97322
C	2.35369	-0.70294	0.39224
C	2.69493	-1.99098	-0.06537
C	3.22122	0.36539	0.09496
C	3.85607	-2.19821	-0.80969
H	2.04492	-2.83503	0.15092
C	4.38258	0.15283	-0.64802
H	2.99341	1.36016	0.46721
C	4.70352	-1.12725	-1.10760
H	4.09794	-3.19910	-1.16094
H	5.04340	0.99027	-0.86156
H	5.61075	-1.29103	-1.68467
C	0.67111	-1.53862	2.14111
H	0.51688	-2.50164	1.64170
H	1.42952	-1.68713	2.91784
H	-0.26753	-1.24522	2.61343
C	-0.93100	3.48935	0.06079
H	-0.85989	3.52680	1.15483
C	0.17708	4.34382	-0.54877
H	0.04765	5.39295	-0.26396
H	1.16368	4.01563	-0.21344
H	0.14918	4.28775	-1.64342
C	-2.30918	3.98112	-0.37468
H	-2.41378	3.91836	-1.46441
H	-3.10506	3.38798	0.08202
H	-2.44754	5.02790	-0.08491
H	-0.02762	-0.20372	-1.38969
C	-4.32616	-2.97226	0.41573
H	-4.93873	-3.29987	-0.43098
H	-4.01781	-3.86900	0.96318
H	-4.95374	-2.36716	1.07574
H	-0.32547	-2.59013	-1.97913

[3,3]-rearrangement TS
B3LYP/6-31G(d)

C	-3.1210013	-0.9158601	0.2488128
C	1.5211267	-0.6275521	1.1221848
C	0.6014587	0.4063679	0.9573878

C	-1.9476683	-0.2735441	-0.2258412
O	-0.4066743	0.5998159	1.7304648
C	-0.7006333	1.8211079	-0.3051942
H	-0.8427403	1.8073479	-1.3925202
N	-1.6884783	0.9673779	0.3178558
H	-3.7196163	-0.3860741	0.9848718
O	0.6441627	1.2688979	-0.1019682
C	-3.5059663	-2.1698011	-0.2065642
C	-2.6893223	-2.8074371	-1.1637682
H	-2.9749483	-3.7886771	-1.5362052
C	-1.5285023	-2.2004781	-1.6412222
C	-1.1377443	-0.9454491	-1.1758592
C	2.8036107	-0.7262561	0.4160728
C	3.6417817	-1.8443951	0.6540988
C	3.2811457	0.2406269	-0.5051112
C	4.8573797	-2.0026561	-0.0060152
H	3.3387577	-2.6061471	1.3624778
C	4.4997517	0.0791119	-1.1580052
H	2.6962547	1.1279649	-0.7027812
C	5.2975237	-1.0434781	-0.9203742
H	5.4653987	-2.8797071	0.2012628
H	4.8319297	0.8439959	-1.8556992
H	6.2482337	-1.1638521	-1.4328032
C	1.2166487	-1.6171681	2.2225878
H	1.2745157	-2.6470631	1.8503708
H	1.9248187	-1.5387831	3.0592958
H	0.2134937	-1.4533481	2.6169618
C	-0.7863283	3.2606509	0.2194998
H	-0.6889993	3.2089049	1.3106928
C	0.3478807	4.1268459	-0.3431192
H	0.2612827	5.1538729	0.0301438
H	1.3320517	3.7468599	-0.0526532
H	0.3101027	4.1687869	-1.4401112
C	-2.1579493	3.8578879	-0.1247272
H	-2.2972493	3.9308139	-1.2118892
H	-2.9722933	3.2489299	0.2802708
H	-2.2497383	4.8685219	0.2894948
H	-0.2408893	-0.4787641	-1.5653582
C	-4.7613313	-2.8404601	0.2963248
H	-5.4540333	-3.0566801	-0.5267252
H	-4.5329853	-3.7976181	0.7819138
H	-5.2862573	-2.2117931	1.0221968
H	-0.9179623	-2.7116481	-2.3807262

MECHANISM



nitrone

MP2/6-31G(d)

C	3.26796	0.75636	-0.47944
C	1.41310	-1.10607	0.49626
C	1.91547	1.09218	-0.43619
C	3.69876	-0.49849	-0.03614
C	2.77275	-1.42344	0.45276
C	1.00615	0.14523	0.03342
N	-0.39654	0.52600	0.05905
C	-1.32245	-0.35228	-0.30213
O	-0.64671	1.73081	0.40909
H	-0.97218	-1.32547	-0.62748
H	0.69061	-1.80737	0.90475
H	3.10792	-2.39101	0.81818
H	4.75571	-0.75169	-0.06500
H	3.98820	1.47921	-0.85468
H	1.55529	2.06356	-0.75977
C	-2.75769	0.04068	-0.25175
H	-2.82504	1.05472	-0.67107
C	-3.24842	0.11131	1.20031
H	-2.62317	0.79899	1.77582
H	-4.28336	0.46865	1.23782
H	-3.20929	-0.87845	1.66719
C	-3.60541	-0.91460	-1.08702
H	-4.65587	-0.60708	-1.06910
H	-3.27526	-0.93300	-2.13058
H	-3.54694	-1.93445	-0.69115

B3LYP/6-31G(d)

C	3.6603564	0.9556870	-0.4253866
C	1.7985104	-0.9371310	0.4568844
C	2.3060914	1.2832100	-0.3919186
C	4.0902814	-0.3112540	-0.0197486
C	3.1586774	-1.2514230	0.4251534
C	1.3834204	0.3261430	0.0319654
N	-0.0244156	0.7102210	0.0453674
C	-0.9563326	-0.1608210	-0.2566626
O	-0.2686366	1.9442710	0.3367434
H	-0.6304926	-1.1562640	-0.5320926
H	1.0794544	-1.6584080	0.8312484
H	3.4875544	-2.2303900	0.7624704
H	5.1476274	-0.5602930	-0.0400666
H	4.3811604	1.6938080	-0.7660156
H	1.9499684	2.2640840	-0.6841046
C	-2.4028776	0.2239400	-0.2274196
H	-2.4713196	1.2286140	-0.6675976
C	-2.9150036	0.3292890	1.2254494
H	-2.3056996	1.0382740	1.7941574
H	-3.9537806	0.6808550	1.2377494
H	-2.8798676	-0.6447360	1.7284434
C	-3.2434436	-0.7542550	-1.0577676
H	-4.2965676	-0.4511910	-1.0562586
H	-2.9054616	-0.7901960	-2.1002876
H	-3.1892026	-1.7720330	-0.6503046

ketene

MP2/6-31G(d)

C	-2.22165	-0.59982	0.00005
C	-1.36175	0.41402	0.00005
O	-2.99337	-1.49720	0.00006
C	-1.92662	1.81826	0.00005
H	-3.02032	1.80010	0.00009
H	-1.59850	2.36802	0.88806
H	-1.59857	2.36801	-0.88800
C	0.08571	0.14201	0.00001
C	0.99888	1.21080	-0.00007
C	0.59745	-1.17097	0.00005
C	2.37544	0.97145	-0.00011
H	0.64027	2.23658	-0.00010
C	1.97030	-1.40370	0.00001
H	-0.08330	-2.02182	0.00011
C	2.87050	-0.33309	-0.00007
H	3.06262	1.81510	-0.00016
H	2.33840	-2.42752	0.00004
H	3.94236	-0.51620	-0.00010

B3LYP/6-31G(d)

C	-2.4580803	-0.8836078	0.0000299
C	-1.5910803	0.1172002	0.0000449
O	-3.2390713	-1.7608188	0.0000229
C	-2.1605563	1.5269252	0.0000659
H	-3.2545583	1.5154852	0.0001069
H	-1.8319323	2.0800742	0.8883239
H	-1.8320033	2.0800802	-0.8882151
C	-0.1375863	-0.1489428	0.0000179
C	0.7763977	0.9201152	-0.0000761
C	0.3791707	-1.4613128	0.0000619
C	2.1531047	0.6826422	-0.0001161
H	0.4163517	1.9439652	-0.0001211
C	1.7509367	-1.6919078	0.0000209
H	-0.3008463	-2.3108238	0.0001329
C	2.6507337	-0.6202068	-0.0000691
H	2.8374417	1.5274762	-0.0001871
H	2.1196207	-2.7145508	0.0000579
H	3.7219567	-0.8017918	-0.0001021

TS-(3+2)

[3+2]-cycloaddition TS
MP2/6-31G(d)

C	-2.08199	-1.89376	0.00410
C	1.56158	-0.49214	0.89218
C	0.48591	0.11480	0.30418
C	-2.61042	-0.60119	0.02454
O	-0.74756	0.16193	1.27368
C	-1.58214	1.57316	-0.25051
H	-2.22735	1.67375	-1.12470
N	-1.79877	0.49015	0.46835
H	-1.05966	-2.07913	0.31886
O	0.24064	0.65190	-0.81221
C	-2.89716	-2.93217	-0.44742
C	-4.21013	-2.68121	-0.85734
H	-4.83619	-3.49934	-1.20424
C	-4.72073	-1.38096	-0.81483
H	-5.74714	-1.18529	-1.11457
C	-3.92618	-0.32961	-0.35661
H	-4.32109	0.68072	-0.28056
H	-2.50122	-3.94414	-0.47775
C	2.84798	-0.53544	0.18587
C	4.02772	-0.86730	0.89021
C	2.98122	-0.28838	-1.20052
C	5.26839	-0.92829	0.25339
H	3.98445	-1.06329	1.95788
C	4.22350	-0.34422	-1.83105
H	2.09850	-0.04420	-1.78195
C	5.37866	-0.66947	-1.11411
H	6.15359	-1.18264	0.83404
H	4.28499	-0.14764	-2.90029
H	6.34511	-0.71628	-1.61118
C	1.48168	-1.03765	2.29701
H	1.95055	-2.02664	2.35662
H	1.99232	-0.39548	3.02687
H	0.44599	-1.14328	2.62306
C	-0.95314	2.80914	0.30102
H	-0.16317	2.53327	1.00362
C	-0.37080	3.66056	-0.82278
H	0.04971	4.58105	-0.40710
H	0.41962	3.11847	-1.34546
H	-1.14727	3.93878	-1.54410
C	-2.05467	3.56203	1.06473
H	-2.89424	3.80776	0.40550
H	-2.43018	2.96740	1.90266
H	-1.64590	4.49798	1.45848

[3+2]-cycloaddition TS
B3LYP/6-31G(d)

C	-2.2056536	-2.1675515	0.0436587
C	1.6463994	-0.6570875	0.8493517
C	0.5340374	-0.1251595	0.2523827
C	-2.6344286	-0.8386815	-0.0115183
O	-0.6882636	-0.1352075	1.1579757
C	-1.5443696	1.3215395	-0.3283463
H	-2.1718476	1.4154025	-1.2123613
N	-1.7604586	0.2237405	0.3872347
H	-1.2041856	-2.4066485	0.3806327
O	0.2981804	0.3982285	-0.8722423
C	-3.0840466	-3.1764525	-0.3511643
C	-4.3724496	-2.8663085	-0.7930933
H	-5.0497136	-3.6592545	-1.0970003
C	-4.7913726	-1.5344025	-0.8302643
H	-5.7973606	-1.2849385	-1.1551333

C	-3.9302116	-0.5147325	-0.4266583
H	-4.2644196	0.5180735	-0.4164963
H	-2.7536526	-4.2105685	-0.3157673
C	2.9418994	-0.6855085	0.1498237
C	4.0939804	-1.1692805	0.8169697
C	3.1273364	-0.2510435	-1.1869463
C	5.3430864	-1.2080795	0.1970677
H	4.0180114	-1.5172655	1.8414087
C	4.3774904	-0.2902195	-1.7997883
H	2.2741234	0.1155385	-1.7438213
C	5.5008664	-0.7684565	-1.1181293
H	6.1987974	-1.5866485	0.7523207
H	4.4725064	0.0531045	-2.8280673
H	6.4734084	-0.8000885	-1.6025443
C	1.5692414	-1.2495025	2.2419487
H	1.9020574	-2.2972145	2.2563287
H	2.2089554	-0.7092165	2.9547317
H	0.5543634	-1.2253815	2.6405017
C	-0.9535486	2.5844385	0.2282507
H	-0.1833666	2.3387415	0.9635587
C	-0.3447186	3.4419825	-0.8877293
H	0.0391874	4.3780905	-0.4686883
H	0.4792224	2.9175255	-1.3781793
H	-1.0955226	3.6968985	-1.6465313
C	-2.0968086	3.3346955	0.9521817
H	-2.9177566	3.5751825	0.2659527
H	-2.5004166	2.7454225	1.7821597
H	-1.7085776	4.2762925	1.3560317

int-1

cycloadduct
MP2/6-31G(d)

C	-2.14803	-1.88456	0.18194
C	1.46132	-0.69419	1.00063
C	0.32567	-0.03679	0.68656
C	-2.54151	-0.54794	0.07481
O	-0.77048	0.00774	1.54626
C	-1.15235	1.43268	-0.13567
H	-1.69760	1.54291	-1.07746
N	-1.87258	0.52915	0.76188
H	-1.28508	-2.16375	0.77656
O	0.06585	0.69230	-0.43204
C	-2.88415	-2.86514	-0.49003
C	-4.00264	-2.52429	-1.25186
H	-4.56748	-3.29484	-1.77057
C	-4.39529	-1.18491	-1.33826
H	-5.27526	-0.90813	-1.91436
C	-3.67918	-0.19681	-0.66460
H	-4.00132	0.84196	-0.70176
H	-2.57640	-3.90533	-0.40985
C	2.66595	-0.58512	0.16004
C	3.93764	-0.64408	0.76255
C	2.60407	-0.46636	-1.24258
C	5.10138	-0.56003	-0.00310
H	4.01966	-0.74115	1.84244
C	3.76964	-0.37353	-2.00389
H	1.63878	-0.45653	-1.73946
C	5.02466	-0.42178	-1.39099
H	6.07138	-0.60193	0.48837
H	3.69571	-0.28368	-3.08591
H	5.93152	-0.35551	-1.98789
C	1.51879	-1.47086	2.29245
H	2.05518	-2.41382	2.14541
H	2.03454	-0.91687	3.08577
H	0.51399	-1.70111	2.65621
C	-0.84006	2.77438	0.50279
H	-0.32092	2.57353	1.44873
C	0.07796	3.58149	-0.41155
H	0.30139	4.55260	0.04082
H	1.02182	3.06015	-0.58969
H	-0.40491	3.76309	-1.37876
C	-2.14134	3.51776	0.79190
H	-2.68980	3.71174	-0.13744
H	-2.78660	2.94407	1.46211
H	-1.92755	4.48277	1.26181

cycloadduct
B3LYP/6-31G(d)

C	-2.2958589	-2.1223687	0.3212267
C	1.5647051	-0.8370587	0.9488807
C	0.4130831	-0.2047657	0.6378177
C	-2.5661569	-0.7685617	0.0965647
O	-0.6995439	-0.2308147	1.4683167
C	-1.1277099	1.2267363	-0.1903113
H	-1.6538139	1.2831103	-1.1446193
N	-1.8039629	0.2868013	0.7063187
H	-1.4559699	-2.4166607	0.9381977
O	0.1435731	0.5651323	-0.4428013
C	-3.1177979	-3.0948127	-0.2540873
C	-4.2053049	-2.7334167	-1.0492573
H	-4.8388789	-3.4955817	-1.4938573
C	-4.4769399	-1.3786377	-1.2595523
H	-5.3271919	-1.0787997	-1.8663313
C	-3.6724289	-0.3976497	-0.6833343
H	-3.9079399	0.6528503	-0.8275733
H	-2.8963679	-4.1439127	-0.0763983
C	2.8016221	-0.7281907	0.1447697
C	4.0256901	-1.1665737	0.6966447
C	2.8410981	-0.2257957	-1.1761973
C	5.2200841	-1.0934017	-0.0201453
H	4.0516691	-1.5638187	1.7056077
C	4.0369331	-0.1531777	-1.8883373
H	1.9278151	0.0995883	-1.6571973
C	5.2379171	-0.5836097	-1.3189323
H	6.1410181	-1.4377697	0.4445057
H	4.0251111	0.2371253	-2.9033573
H	6.1677051	-0.5266307	-1.8787633

C	1.5926631	-1.6653557	2.2179437
H	2.0058591	-2.6639257	2.0291047
H	2.2132961	-1.2011257	2.9962877
H	0.5926651	-1.7919947	2.6383747
C	-0.9255069	2.6140603	0.4282097
H	-0.4285039	2.4711143	1.3968487
C	-0.0267829	3.4780313	-0.4666503
H	0.1168891	4.4656073	-0.0145053
H	0.9594191	3.0256493	-0.6085713
H	-0.4790339	3.6276613	-1.4558953
C	-2.2853089	3.2834423	0.6693657
H	-2.8215659	3.4457123	-0.2751113
H	-2.9210689	2.6797363	1.3249867
H	-2.1451779	4.2620513	1.1418137

TS-[3,3]

[3,3]-rearrangement TS
MP2/6-31G(d)

C	2.13998	2.57802	0.14708
C	-1.05088	0.14186	1.18367
C	0.16223	-0.49259	1.04510
C	1.57739	1.35152	-0.27362
O	1.26066	-0.11843	1.67175
C	1.81218	-1.05473	-0.39043
H	1.77028	-0.93563	-1.48136
N	2.19840	0.20320	0.22406
H	3.05435	2.54892	0.73565
O	0.43044	-1.38298	0.03422
C	1.54381	3.77794	-0.20741
C	0.35633	3.78086	-0.96049
H	-0.10663	4.72492	-1.23937
C	-0.20118	2.57765	-1.38583
H	-1.11295	2.57894	-1.97951
C	0.37534	1.35405	-1.01811
H	-0.04423	0.42770	-1.39874
H	1.98577	4.71885	0.11215
C	-2.24349	-0.37401	0.49928
C	-3.24191	0.52067	0.06608
C	-2.42033	-1.74815	0.24825
C	-4.36626	0.05688	-0.61664
H	-3.13539	1.58685	0.24935
C	-3.54834	-2.20755	-0.43167
H	-1.68032	-2.45813	0.60658
C	-4.52398	-1.30854	-0.87053
H	-5.12150	0.76460	-0.95185
H	-3.67002	-3.27382	-0.61016
H	-5.40353	-1.66937	-1.39886
C	-1.18754	1.27116	2.16372
H	-1.57980	2.16130	1.65923
H	-1.88230	1.01540	2.97147
H	-0.21837	1.52412	2.59615
C	2.75159	-2.18125	0.00052
H	2.76529	-2.20946	1.09706
C	2.23560	-3.51398	-0.53454
H	2.91723	-4.32447	-0.25702
H	1.24519	-3.74601	-0.13617
H	2.16992	-3.49101	-1.62880
C	4.15800	-1.88587	-0.51510
H	4.16301	-1.82789	-1.61005
H	4.53640	-0.94040	-0.11868
H	4.84593	-2.68467	-0.21935

[3,3]-rearrangement TS
B3LYP/6-31G(d)

C	-3.1271441	-1.9409353	0.3821697
C	1.3544149	-0.5181793	1.1310397
C	0.1996029	0.2474187	0.9652607
C	-2.1512341	-1.0475963	-0.1313373
O	-0.8032381	0.2089677	1.7653427
C	-1.4384701	1.2791987	-0.2809403
H	-1.6020541	1.2103047	-1.3634593
N	-2.1807751	0.2310747	0.3829097
H	-3.8223951	-1.5611513	1.1249327
O	0.0039019	1.0621317	-0.1130343
C	-3.1917541	-3.2520743	-0.0599413
C	-2.2807771	-3.7125363	-1.0235193
H	-2.3335851	-4.7401883	-1.3723343
C	-1.3082191	-2.8509903	-1.5358443
H	-0.6047421	-3.2094893	-2.2823083
C	-1.2255271	-1.5320233	-1.0929543
H	-0.4737091	-0.8720613	-1.5095233
H	-3.9496181	-3.9223683	0.3359667
C	2.6119949	-0.3058753	0.4060567
C	3.7460439	-1.0867383	0.7450327
C	2.7834859	0.6428897	-0.6349683
C	4.9584459	-0.9487003	0.0747047
H	3.6820729	-1.8141243	1.5456427
C	3.9987359	0.7773637	-1.2994723
H	1.9594139	1.2814337	-0.9198373
C	5.0963479	-0.0166973	-0.9558973
H	5.8012139	-1.5710783	0.3647767
H	4.0892159	1.5161647	-2.0919823
H	6.0431779	0.0945207	-1.4774303
C	1.3289209	-1.5089643	2.2708237
H	1.6847329	-2.4924573	1.9414057
H	1.9707609	-1.1985573	3.1073607
H	0.3147289	-1.6212143	2.6556627
C	-1.8397871	2.6714647	0.2252077
H	-1.6927311	2.6703397	1.3120277
C	-0.9577191	3.7614437	-0.3979233
H	-1.2678641	4.7501897	-0.0406243
H	0.0974399	3.6266957	-0.1416213
H	-1.0426101	3.7640827	-1.4930693
C	-3.3238671	2.9279357	-0.0716483
H	-3.5178431	2.9293287	-1.1528503
H	-3.9619131	2.1654767	0.3858067

H	-3.6270761	3.9055757	0.3203887

int-2

rearranged product
MP2/6-31G(d)

C	1.43493	2.96029	0.11749
C	-0.68045	0.13050	0.58133
C	0.34262	-1.00033	0.67844
C	1.22285	1.56571	-0.25198
O	0.53329	-1.66808	1.67629
C	2.28285	-0.56989	-0.64978
H	2.48484	-0.63335	-1.72901
N	2.28679	0.81741	-0.26464
H	2.43995	3.23618	0.42858
O	0.99114	-1.25366	-0.51488
C	0.44295	3.87952	0.01901
C	-0.88855	3.51013	-0.43323
H	-1.63556	4.29049	-0.55884
C	-1.18810	2.22434	-0.71213
H	-2.18417	1.94916	-1.05314
C	-0.20117	1.10773	-0.54858
H	-0.18671	0.52437	-1.47799
H	0.64119	4.91793	0.27672
C	-2.01535	-0.49537	0.17647
C	-3.20397	-0.20721	0.86267
C	-2.07208	-1.35722	-0.93367
C	-4.41583	-0.77168	0.45389
H	-3.19797	0.45385	1.72385
C	-3.28263	-1.92238	-1.33610
H	-1.16417	-1.59986	-1.48065
C	-4.46190	-1.62919	-0.64619
H	-5.32680	-0.53564	0.99994
H	-3.30315	-2.59313	-2.19245
H	-5.40563	-2.06906	-0.96033
C	-0.73047	0.83637	1.93696
H	-1.38290	1.71148	1.89579
H	-1.09496	0.15494	2.70836
H	0.27143	1.16699	2.22595
C	3.36967	-1.32317	0.12128
H	3.16885	-1.17048	1.18953
C	3.32072	-2.81640	-0.18614
H	4.13744	-3.33336	0.32817
H	2.37589	-3.25569	0.13755
H	3.43560	-2.99354	-1.26210
C	4.73938	-0.73628	-0.21501
H	4.95105	-0.84569	-1.28535
H	4.79350	0.32413	0.03895
H	5.52243	-1.26662	0.33658

rearranged product
B3LYP/6-31G(d)

C	1.3045865	3.0006170	-0.0064988
C	-0.8590975	0.0968140	0.5643362
C	0.1298765	-1.0866290	0.6161302
C	1.0728575	1.5852800	-0.2944558
O	0.1920525	-1.8572620	1.5447482
C	2.1424895	-0.5565680	-0.6554298
H	2.3587915	-0.6576720	-1.7275078
N	2.1200225	0.8329170	-0.3275028
H	2.3239645	3.2787920	0.2450232
O	0.8579095	-1.2696220	-0.5255868
C	0.3182785	3.9206750	-0.0908678
C	-1.0391225	3.5474140	-0.4600058
H	-1.7854995	4.3303780	-0.5649538
C	-1.3619775	2.2604550	-0.6699328
H	-2.3770335	1.9846010	-0.9412738
C	-0.3761795	1.1274750	-0.5386828
H	-0.3824425	0.5792170	-1.4882448
H	0.5351745	4.9677300	0.1057662
C	-2.2267035	-0.4989960	0.1580012
C	-3.3898585	-0.2725420	0.9065122
C	-2.3276705	-1.2876140	-1.0014128
C	-4.6163305	-0.8095460	0.5048782
H	-3.3531025	0.3265000	1.8094922
C	-3.5501265	-1.8277160	-1.4001178
H	-1.4423215	-1.4919610	-1.5968608
C	-4.7031345	-1.5880960	-0.6490748
H	-5.5044105	-0.6158160	1.1009752
H	-3.5991675	-2.4375720	-2.2984748
H	-5.6570735	-2.0061910	-0.9592298
C	-0.8808625	0.7518340	1.9569822
H	-1.5454645	1.6196540	1.9754902
H	-1.2116335	0.0370930	2.7137562
H	0.1225795	1.0892200	2.2342902
C	3.2414725	-1.2868480	0.1506012
H	3.0310375	-1.1089750	1.2142792
C	3.2226585	-2.7975270	-0.1098118
H	4.0362635	-3.2850550	0.4401822
H	2.2790165	-3.2473500	0.2080332
H	3.3651745	-3.0178210	-1.1764348
C	4.6181465	-0.6903620	-0.1778338
H	4.8668825	-0.8357640	-1.2378018
H	4.6536605	0.3817460	0.0333732
H	5.3963175	-1.1849080	0.4151452

TS'-[3,3]

Heterolytic cleavage TS
(proposed [3,3]-rearrangement TS for pathway B)
MP2/6-31G(d)

C	-2.8081426	-1.7940502	0.6206647
C	1.5235174	-0.4351702	0.5832247
C	0.5953874	0.4511798	0.0026247
C	-1.9749326	-0.9999202	-0.1816253
O	-0.4238126	0.6716198	0.9168447

C	-2.6135226	1.3525098	-0.1007653
H	-3.5319226	1.1263498	-0.6525753
N	-1.8428526	0.3615598	0.1281347
H	-3.4017126	-1.3344102	1.4074547
O	0.5804174	1.0676998	-1.0976253
C	-2.8656626	-3.1600502	0.3634647
C	-2.0674526	-3.7239702	-0.6417053
H	-2.1130526	-4.7938502	-0.8298853
C	-1.2303226	-2.9171002	-1.4143053
H	-0.6177126	-3.3589502	-2.1962353
C	-1.1529126	-1.5411402	-1.1806653
H	-0.5316126	-0.8829602	-1.7807753
H	-3.5192526	-3.7921802	0.9592847
C	2.9262874	-0.3987502	0.1673747
C	3.9200774	-1.0339602	0.9500047
C	3.3549174	0.2324198	-1.0257753
C	5.2625474	-1.0283102	0.5722447
H	3.6482874	-1.5245902	1.8800547
C	4.6994074	0.2413098	-1.3951953
H	2.6116874	0.7232798	-1.6439253
C	5.6630474	-0.3933802	-0.6062253
H	5.9985474	-1.5235802	1.2031347
H	4.9943174	0.7372898	-2.3185153
H	6.7098374	-0.3899002	-0.9024253
C	1.1499174	-1.3324502	1.7357047
H	1.5427174	-2.3422602	1.5654547
H	1.5570074	-0.9889302	2.6962447
H	0.0675374	-1.4027102	1.8390947
C	-2.3274026	2.7594698	0.2853547
H	-1.5293526	2.7556398	1.0301647
C	-1.8274726	3.4849798	-0.9732653
H	-1.6169326	4.5297198	-0.7235253
H	-0.9138926	3.0057298	-1.3331553
H	-2.5851126	3.4674598	-1.7641853
C	-3.5916626	3.4022098	0.8566547
H	-4.3999326	3.4015598	0.1177647
H	-3.9391426	2.8800498	1.7532847
H	-3.3796826	4.4405398	1.1281247

Heterolytic cleavage TS
(proposed [3,3]-rearrangement TS for pathway B)
B3LYP/6-31G(d)

C	-3.1286512	-1.7922819	0.5679870
C	1.6939228	-0.4759049	0.6008020
C	0.6613528	0.2452551	-0.0480000
C	-2.1611002	-1.1356569	-0.2069360
O	-0.3762312	0.4383781	0.8507240
C	-2.5471322	1.2501871	-0.1229530
H	-3.5067372	1.0945191	-0.6251930
N	-1.8436602	0.2077311	0.0782310
H	-3.6400532	-1.2544489	1.3605990
O	0.6025418	0.7722491	-1.1763840
C	-3.4132362	-3.1292609	0.3022640
C	-2.7282062	-3.8074519	-0.7117070
H	-2.9517082	-4.8516369	-0.9110310
C	-1.7564342	-3.1456359	-1.4667630
H	-1.2270262	-3.6717919	-2.2558490
C	-1.4577782	-1.8065759	-1.2182130
H	-0.7154712	-1.2701789	-1.7988550
H	-4.1689392	-3.6429619	0.8895530
C	3.0902468	-0.2872929	0.2072490
C	4.1365178	-0.8737609	0.9666510
C	3.4823818	0.4709321	-0.9287180
C	5.4753918	-0.7208949	0.6121320
H	3.9010488	-1.4538789	1.8522370
C	4.8221608	0.6248611	-1.2713770
H	2.7083478	0.9274181	-1.5325280
C	5.8340448	0.0300771	-0.5097760
H	6.2442158	-1.1896609	1.2225640
H	5.0803208	1.2140741	-2.1489970
H	6.8786748	0.1490111	-0.7858310
C	1.4030438	-1.3602299	1.7919510
H	1.8711268	-2.3468879	1.6686250
H	1.7911328	-0.9510499	2.7378960
H	0.3313928	-1.5121509	1.9203360
C	-2.1653772	2.6511251	0.2330630
H	-1.3133122	2.6145821	0.9137570
C	-1.7309352	3.3659761	-1.0662290
H	-1.4671682	4.4032181	-0.8315680
H	-0.8594192	2.8642271	-1.4962800
H	-2.5392422	3.3800061	-1.8072490
C	-3.3553602	3.3533171	0.9079480
H	-4.2263012	3.3929621	0.2426040
H	-3.6526502	2.8476891	1.8334400
H	-3.0757362	4.3817971	1.1598220

***E*-imine**

MP2/6-31G(d)

H	-3.22707	-3.07642	-2.45611
H	-2.13591	3.27429	-1.97071
H	-2.26808	-0.83317	-1.96908
H	-0.53922	2.57584	-1.63427
C	-1.33452	3.20781	-1.22658
H	-0.92946	4.21360	-1.07540
C	-3.15497	-2.73115	-1.42697
C	-2.62487	-1.46653	-1.15936
H	-3.23981	1.18442	-0.86087
H	-3.99375	-4.53626	-0.59222
C	-2.41600	1.27037	-0.13416
H	-3.81009	3.61856	-0.00374
C	-3.58103	-3.55271	-0.38077
C	-1.86784	2.64358	0.09274
C	-2.52280	-1.01847	0.16544
C	-2.95668	3.54596	0.67933
N	-1.95737	0.24259	0.49118
H	-2.56711	4.55590	0.84348
H	-1.04467	2.55256	0.81095
C	-3.46504	-3.10949	0.94124

C	-2.91903	-1.85636	1.21702
H	-3.31664	3.15763	1.63720
H	-3.78601	-3.74928	1.76038
H	-2.81123	-1.50458	2.24077

B3LYP/6-31G(d)

C	3.1215966	-1.9562826	-1.0081386
C	2.9027586	-0.9605606	-0.0421066
C	2.5718696	1.3443184	-0.0395346
H	3.4939256	1.4669854	0.5505854
N	2.1785416	0.1923354	-0.4280226
H	2.7522076	-1.7968396	-2.0176206
C	3.8172406	-3.1178116	-0.6776636
C	4.2780536	-3.3176656	0.6276054
H	4.8086736	-4.2298666	0.8867464
C	4.0371696	-2.3436686	1.5992864
H	4.3748486	-2.4980516	2.6210804
C	3.3554406	-1.1704906	1.2711914
H	3.1452456	-0.4271386	2.0351354
H	3.9923466	-3.8737716	-1.4389876
C	1.8296296	2.6106144	-0.3657776
H	0.9372826	2.3319414	-0.9378096
C	1.3912486	3.3117424	0.9340344
H	0.8530836	4.2380544	0.7004444
H	0.7277956	2.6724674	1.5263504
H	2.2572416	3.5761064	1.5545274
C	2.7146936	3.5326674	-1.2248876
H	3.6311566	3.8144244	-0.6908926
H	3.0061896	3.0476844	-2.1636646
H	2.1749326	4.4541674	-1.4725366

acetolactone

MP2/6-31G(d)

C	1.84403	-0.14671	0.35968
C	1.00782	0.23423	-0.76781
O	1.40043	1.32918	-0.11640
O	0.32407	-0.02894	-1.72985
C	3.28527	-0.41348	0.13763
C	4.20660	-0.28568	1.18862
C	3.73695	-0.78228	-1.13927
C	5.56203	-0.52143	0.95894
H	3.87292	0.00219	2.18218
C	5.09400	-1.01735	-1.36201
H	3.02556	-0.89853	-1.95428
C	6.00899	-0.88608	-0.31447
H	6.27224	-0.41654	1.77572
H	5.43542	-1.30761	-2.35278
H	7.06658	-1.07046	-0.48819
C	1.20128	-0.52303	1.66210
H	1.33820	-1.59514	1.83504
H	1.65586	0.02306	2.49371
H	0.13098	-0.30407	1.64193

B3LYP/6-31G(d)

O	-1.7881414	1.3527164	-0.0550566
H	-6.1654424	-0.0738346	2.1852764
H	-3.7497654	0.3476994	1.9506124
C	-5.6538284	-0.3737736	1.2750994
C	-4.2893994	-0.1317896	1.1387624
C	-1.4417814	0.4879564	0.8739384
H	-7.4225214	-1.2023806	0.3570034
C	-6.3587734	-1.0088656	0.2486894
C	-3.6079074	-0.5136466	-0.0306466
H	-1.7499574	-0.6606586	-2.2501956
C	-2.1519054	-0.2476156	-0.1706586
C	-5.6907774	-1.3995336	-0.9132036
O	-0.8667654	0.5107884	1.9312664
C	-4.3250744	-1.1529526	-1.0544016
H	-6.2320314	-1.8957946	-1.7138856
H	-3.8218024	-1.4613956	-1.9644816
H	-0.3034564	-0.5853926	-1.2151176
C	-1.3484334	-0.9024446	-1.2605956
H	-1.3854094	-1.9904456	-1.1317486

VIII. ABSOLUTE ENERGIES AND CORRECTIONS

ENANTIOSELECTIVITY

Table S2. Absolute energies (in Hartrees) and calculated corrections (at 298.15 K) at the M06-2X/6-311+G(d,p)(THF)//B3LYP/6-31G(d) level for enantioselectivity determining transition structures.

	E(B3LYP/6-31G(d))[a]	*H*corr[a]	*G*corr[a] (1 atm)	*G*quasi[a,b] (1 atm)	*G*quasi[a,b,c] (1 M)	*E*(M06-2X/6-311+G(d,p))[a,b,c,d]
TSE-O	-1169.615191	0.426623	0.347549	0.354045	0.357063	-1169.476212
TSZ-O	-1169.611224	0.426400	0.346934	0.353573	0.356589	-1169.473440
TSE-NBoc	-1495.584468	0.575123	0.477373	0.486594	0.489612	-1495.406605
TSZ-NBoc	-1495.580284	0.574953	0.477191	0.486292	0.489310	-1495.404090
TSE-NTIPBS	-2283.170448	0.806440	0.682198	0.695196	0.698214	-2282.921314
TSZ-NTIPS	-2283.163564	0.806075	0.681298	0.694681	0.697699	-2282.914483

[a] Values are given in Hartrees [b] quasi-harmonic correction to Gibbs Free Energy [c] for 1 mol/L solute [d] include solvation corrections.

REGIOSELECTIVITY

Table S3. Absolute energies (in Hartrees) and calculated corrections (at 298.15 K) at the SCS-MP2/6-31G(d)(THF)//MP2/6-31G(d)(THF) level for regioselectivity determining transition structures.

	E(MP2/6-31G(d))[a]	*H*corr[a]	*G*corr[a] (1 atm)	*G*quasi[a,b] (1 atm)	*G*quasi[a,b,c] (1 M)	*E*(SCS-MP2)[a,b,c,d]
TS for 4-isomer	-977.956538	0.411938	0.339562	0.342565	0.345584	-977.509203
TS for 6-isomer	-977.955741	0.411679	0.337598	0.341908	0.344927	-977.509401

[a] Values are given in Hartrees [b] quasi-harmonic correction to Gibbs Free Energy [c] for 1 mol/L solute [d] include solvation corrections.

MECHANISM

Table S4. Absolute energies (in Hartrees) and calculated corrections (at 298.15 K) at the SCS-MP2/6-31G(d)(THF)//MP2/6-31G(d)(THF) level for the stationary points on the competing pathways in the reaction of the model *N*-phenylnitrone (R=iPr) with methylphenylketene.

	E(MP2/6-31G(d))[a]	*H*corr[a]	*G*corr[a] (1 atm)	*G*quasi[a,b] (1 atm)	*G*quasi[a,b,c] (1 M)	*E*(SCS-MP2)[a,b,c,d]
nitrone	-517.121434	0.226156	0.176273	0.177042	0.180044	-516.893695
ketene	-421.631438	0.153714	0.108643	0.109844	0.112872	-421.475521
TS-(3+2)	-938.757752	0.381771	0.310889	0.314819	0.317837	-938.342527
Int-1	-938.794740	0.383931	0.312776	0.317141	0.320159	-938.383215
TS-[3,3]	-938.783685	0.381584	0.311944	0.315397	0.318415	-938.365627
Int-2	-938.841700	0.384796	0.316492	0.319445	0.322464	-938.430497
TS'-[3,3]	-938.741665	0.380948	0.308047	0.312677	0.315695	-938.328109
imine	-442.141673	0.220574	0.171626	0.172926	0.175944	-441.929191
acetolactone	-496.675611	0.159508	0.113909	0.114776	0.117794	-496.504519

[a] Values are given in Hartrees [b] quasi-harmonic correction to Gibbs Free Energy [c] for 1 mol/L solute [d] include solvation corrections.

IX. **FULL CITATION FOR REF. 33**

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