[Electronic Supporting Information to accompany]

[(salcen)Cr^{III} + Lewis Base]-Catalyzed Synthesis of *N*-aryl-substituted Oxazolidinones from Epoxides and Aryl Isocyanates

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S1. General information

^{1}H and ^{13}C NMR spectra were recorded on either a Varian Inova 500 (499.773 MHz for ^{1}H, 125.669 MHz for ^{13}C) or a Mercury 400 (400.178 MHz for ^{1}H, 100 MHz for ^{13}C) spectrometer. ^{1}H NMR data are reported as follows: chemical shift (multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, and m = multiplet), and integration). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS, δ scale) with the solvent resonances as internal standards. IR data were collected on a Nicolet 5PC FT-IR spectrometer with PC-IR software. Flash column chromatography was carried out with 230-400 mesh silica gel, purchased from Bodman Industries.

Reaction yields were determined using GC analyses, which were carried out on a Hewlett-Packard 6890 instrument equipped with an FID detector and an HP7683 series autosampler and injector and analyzed using HP ChemStation software. The column was a 30 m HP-5 (crosslinked 5% Ph Me siloxane) capillary column with a 0.32 mm inner diameter and a 0.25 μm film thickness. The temperature program for all determinations of reaction yield was as follows: Inlet pressure = 15.0 psi; column flow = 1.3 mL/min; initial temp = 50 °C; initial time = 2 min; rate = 10 °C/min; final temp = 275 °C; final time = 8 min. All reported reaction yields were determined by GC through the use of experimentally measured response ratios versus an internal standard (1,2,4,5-tetramethylbenzene, TMB). Retention times for various components of the reaction mixture were determined by injecting a pure sample of each component of the reaction mixture.

S2. Materials

Toluene, CH_2Cl_2, ether, and THF were purified using a Dow-Grubbs solvent purification system[S1] installed by Glass Contours (now JC Meyer Solvent Systems, Laguna Beach, CA, USA), collected under argon, degassed under vacuum, and stored under nitrogen in a Strauss flask prior to use. Dioxane, propylene oxide, styrene oxide, epichlorohydrin, 1,2-epoxy-3-phenoxypropane, and hexene oxide were distilled over calcium hydride, collected under nitrogen, and saturated with nitrogen prior to use. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used without further purification. All other reagents were purchased from the Aldrich Chemical Company and used without further purification, unless otherwise noted. The Cr^{III}(salcen) catalyst (salcen = *N*,*N'*-*bis*(3,5-di-*tert*-butylsalicylidene)-1,2-*trans*-diaminocyclohexane) was synthesized according to a literature procedure.[S2]

S3. Representative procedure for reaction of epoxides and isocyanates

All reactions were setup under a dry nitrogen atmosphere in a glove box; however, they were removed from the glovebox and sampled for GC analysis on the bench top. In a typical reaction, Cr^{III}(salcen) complex **1** (15 mg, 2.37 × 10^{-5} mol) and PPh_3O (13.2 mg, 4.74 × 10^{-5} mol) were weighed into a 1.8 mL vial equipped with a magnetic stir bar. To this vial was added an aliquot (0.790 mL) of a CH_2Cl_2 stock solution containing propylene oxide, PhNCO, and TMB [CH_2Cl_2 (2.965 mL), TMB (53.0 mg, 3.95 x 10^{-4} mol), propylene oxide (554 uL, 7.92 × 10^{-3} mol), PhNCO (430 uL, 3.96 × 10^{-3} mol)]. The reaction was then stirred and aliquots (20 uL) were taken at the appropriate times to determine the reaction progress. These aliquots were passed through a 2 cm plug of silica in a disposable Pasteur pipet using ether (10 mL) as an eluent, then analyzed by GC to determine the yield of the oxazolidinone product.

Analytically pure samples of the oxazolidinone products, which were characterized and used to make the GC calibration curves, were obtained from scaled-up versions of the reaction and purified via flash column chromatography using hexanes:ether (1:1 v/v) eluent. Analytical data was available from the literature for 5-methyl-3-phenyl-1,3-dioxazolidin-2-one,[S3] 5-chloromethyl-3-phenyl-1,3-dioxazolidin-2-one,[S4] 3,5-diphenyl-1,3-dioxazolidin-2-one,[S5] 3,4-diphenyl-1,3-dioxazolidin-2-one,[S5] 3-phenyl-5-(phenoxymethyl)-1,3-oxazolidin-2-one,[S4] 5-Butyl-3-phenyl-1,3-oxazolidin-2-one.[S6] Analytical data for the remaining few compounds have not been reported earlier and are reported in section S7.

Table S1. Listing of pKa and references data

Entry	Lewis base	pK_a of the conjugated acid
1	DMAP	9.5[a]
2	Pyridine	5.2[a]
3	4-CF_3-pyridine	~1.9[b]
4	*N*-Me-imidazole	7.4[a]
5	$NEt(^iPr)_2$	11.4[a]
6	pyridine-*N*-oxide	0.8[c]
7	PPh_3	2.7[d]
8	PCy_3	9.7[d]
9	PPh_3O	0[d]
10	PCy_3O	0[d]

[a]http://www.cem.msu.edu/~reusch/OrgPage/basicity.htm. Accessed January 23, 2014. [b]Estimated based on the value measured in the laboratories of Reilly Industries, Inc. for 4-CN-pyridine, as cited in Scriven, E. F. V.; Toomey, J. E., Murugan, *Pyridine and Pyridine Devivatives* In *Kirk-Othmer Encyclopedia of Chemical Technology,* 4th Ed.; Kirk, R. E.; Othmer, D. F.; Kroschwitz, J. I.; Howe-Grant, M., Eds.; Wiley: New York, NY, 1991; Vol. 20, pp 1-33. [c]http://www.scripps.edu/baran/images/grpmtgpdf/Weickgenannt_Jun12.pdf. Accessed January 23, 2014 [d]http://www2.chem.umd.edu/groups/vedernikov/Lecture-2011-608-04-phosphine%20complexes.pdf. Accessed January 23, 2014

S4. Computational details

All calculations were carried out using Density Functional Theory (DFT) as implemented in the Jaguar 7.8 suite[S7] of *ab initio* quantum chemistry programs. Geometry optimizations were performed using the B3LYP functional[S8, 9] and the 6-31G** basis set. Chromium was represented using the Los Alamos LACVP basis[S10, 11] that includes relativistic effective core potentials. The energies of the optimized structures were reevaluated by additional single-point energy calculations of each optimized geometry using Dunning's correlation consistent triple-ζ basis set,[S12] cc-pVTZ(-f) that includes a double set of polarization functions. All stationary points were verified to be minima or transition states by proper vibrational analysis at the double-ζ level.

Solvation calculations were carried out with the 6-31G**/LACVP basis at the optimized gas-phase geometry employing a dielectric constants of ε = 2.38 for toluene. Solvation energies were evaluated using a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson-Boltzmann equation.[S13-15] For all continuum models, the solvation energies are subjected to empirical parameterization of the atomic radii that are used to generate the solute surface. We employed the standard set[S16] of optimized radii in Jaguar for H (1.150 Å), C (1.900

Å), O (1.600 Å), N (1.600 Å) and Cr (1.511Å). Analytical vibrational frequencies within the harmonic approximation were computed with the 6-31G**/LACVP basis set to confirm proper convergence to well-defined minima or saddle points on the potential energy surface. The free energy of a molecule in solution phase, *G*(Sol), is computed as follows

$$G(\text{Sol}) = G(\text{gas}) + G^{\text{solv}} \quad \text{(S1)}$$

$$G(\text{gas}) = H(\text{gas}) - TS(\text{gas}) \quad \text{(S2)}$$

$$H(\text{gas}) = E(\text{SCF}) + ZPE \quad \text{(S3)}$$

$$\Delta G(\text{Sol}) = \sum G(\text{Sol}) \text{ for products} - \sum G(\text{Sol}) \text{ for reactants} \quad \text{(S4)}$$

where *G*(gas) is the free energy of the molecule in the gas phase; G^{solv} is the free energy of solvation as computed using the continuum solvation model; *H*(gas) and *S*(gas) are the enthalpic and entropic components of the molecule in the gas phase, respectively; *T* is the temperature (298.15 K); *E*(SCF) is the self-consistent field energy, i.e., the "raw" electronic energy as computed from the self-consistent field (SCF) procedure; and *ZPE* is the zero-point energy. To locate transition states, the potential energy surface was first explored approximately using the linear synchronous transit (LST) methods followed by a quadratic synchronous transit (QST) searches[S17] that uses the LST transition state as an initial guess. In QST, the initial part of the transition state search is restricted to a circular curve connecting the reactant, initial transition state guess, and the product, followed by a search along the Hessian eigenvectors tangential to this curve. In the relative energy diagram, the Δ*G*(Sol) values have been corrected to account for the excess concentrations of epoxide and aryl isocyanate. To decrease the computational cost, the *tert*-Bu groups of the salen ligand (salen = *N,N'-bis*(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane) were replaced with hydrogens and all the calculations were carried out with this truncated framework. We assume that such a small change in the steric environment would not significantly change the electronic environment of the (salen)$Cr^{III}Cl$ complex. As this complex can potentially be in both doublet and quartet spin configurations, we initially performed several calculations on both of these states. In all cases, the quartet configuration was observed to give the lowest ground-state energy, and was used in all subsequent calculations. The energy of **3-TS** is slightly higher than what we expect at 25 °C, and a plausible explanation for that has been discussed in our previous work. [S18]

S5. Correction factors for the free energy calculations

Under our experimental conditions, the epoxide concentration was 33 times that of Cr-catalyst. To account for such a high concentration effect, a correction factor of 2.07 kcal mol^{-1} (at 25 °C by using the equation ΔG =-RTlnK, where K is the ratio of concentrations of the substrate and the catalyst) has been included in the computation. Similarly, to account for the 37 times higher concentration of phenyl isocyanate compared to catalyst, a correction factor of 2.14 kcal mol^{-1} has been applied.

S6. Thermodynamic stability comparison between oxazolidinone and imidazolidinone

Since two products such as oxazolidinone and imidazolidinone were formed in the work reported by Saito and coworkers,[S19] we computed the thermodynamic energies for the above mentioned products. *N*-phenyl-substituted oxazolidinone from phenyl isocyanate and propylene oxide is more stable over *N*-phenyl-imidazolidinone by 19.7 kcal mol^{-1} and this can be understood from the thermodynamic stability of carbonyl functionality over imines.

S7. Characterization data for products

5-Butyl-3-phenyl-1,3-oxazolidin-2-one. IR (CH_2Cl_2, υ_{CO}): 1752 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.95 (t, *J* = 7.2 Hz, 3H), 1.41 (m, 3H), 1.51 (m, 1H), 1.74 (m, 1H), 1.86 (m, 1H), 3.66 (t, *J* = 7.6 Hz, 1H), 4.08 (t, *J* = 7.6 Hz, 1H), 4.64 (m, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 14.1, 22.6, 26.8, 34.9, 50.7, 73.3, 118.3, 124.1, 129.2, 138.6, 155.2. EIMS: m/z 219 (M^+, 42), 132 (68), 119 (100), 104 (51), 77 (79).

5-Benzyl-3-phenyl-1,3-oxazolidinone. IR (CH_2Cl_2, υ_{CO}): 1755 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.02 (dd, *J* = 14 and 6.4 Hz, 1H), 3.23 (dd, *J* = 14 and 6.4 Hz, 1H), 3.74 (t, *J* = 8.6 Hz, 1H), 4.0 (t, *J* = 8.6 Hz, 1H), 4.89 (qt, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.2-7.4 (bm, 7H), 7.48 (d, *J* = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 40.9, 49.8, 73.3, 118.5, 124.2, 127.5, 129.1, 129.2, 129.6, 135.0, 138.4, 154.9. EIMS: m/z 253 (M^+, 95), 208 (45), 117 (67, 91 (100), 77 (75).

5-Methyl-3-(2,6-diisopropylphenyl)-1,3-oxazolidinone. IR (CH_2Cl_2, υ_{CO}): 1753 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.27 (m, 12H), 1.59 (d, *J* = 6 Hz, 2H), 3.0 (m, 2H), 3.42 (dd, *J* = 8.8 and 6.8 Hz, 1H), 3.90 (t, *J* = 8.6 Hz, 1H), 4.88 (m, 1H),

7.21 (d, J = 8 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 21.4, 24.2, 24.3, 24.4, 24.7, 28.8, 28.9, 55.7, 70.6, 124.4, 129.5, 131.5, 147.6, 147.7, 157.4. EIMS: m/z 261 (M^+, 100), 160 (90), 146 (85), 132 (60), 91 (42).

5-Methyl-3-(1-napthyl)-1,3-oxazolidinone. IR (CH_2Cl_2, υ_{CO}): 1754 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (d, J = 6 Hz, 3H), 3.68 (t, J = 7.5 Hz, 1H), 4.16 (t, J = 7.5 Hz, 1H), 4.97 (m, 1H), 7.46-7.61 (m, 4H), 7.86 (d, J = 8 Hz, 1H), 7.91 (t, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$): δ 20.9, 55.9, 71.0, 122.5, 124.7, 125.8, 126.7, 127.1, 128.8, 130.1, 134.2, 139.8, 157.3. EIMS: m/z 227 (M^+, 52), 154 (100), 127 (65).

S8. Additional experimental results

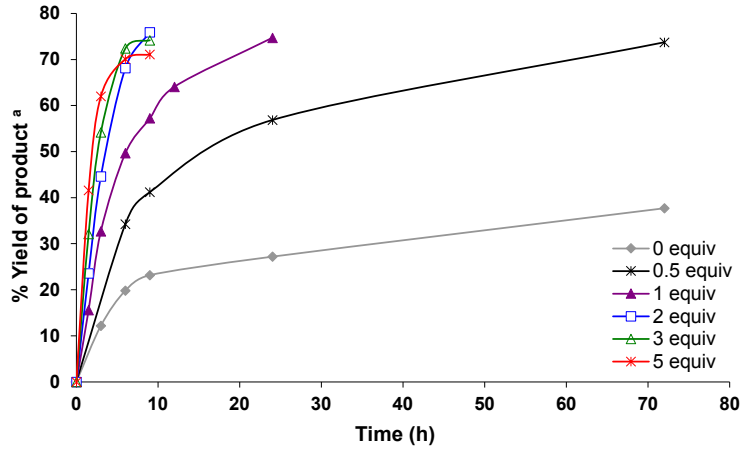

Figure S1. Effect of the Cr^{III}(salcen)/PPh_3O ratio on reaction 2. Reaction conditions: catalyst (1.58 × 10^{-5} mol), PPh_3O (variable concentration), PhNCO (5.27 × 10^{-4} mol), propylene oxide (1.05 × 10^{-3} mol), CH_2Cl_2, rt. [a]Yields are reported relative to PhNCO and determined by GC analysis employing TMB as an internal standard.

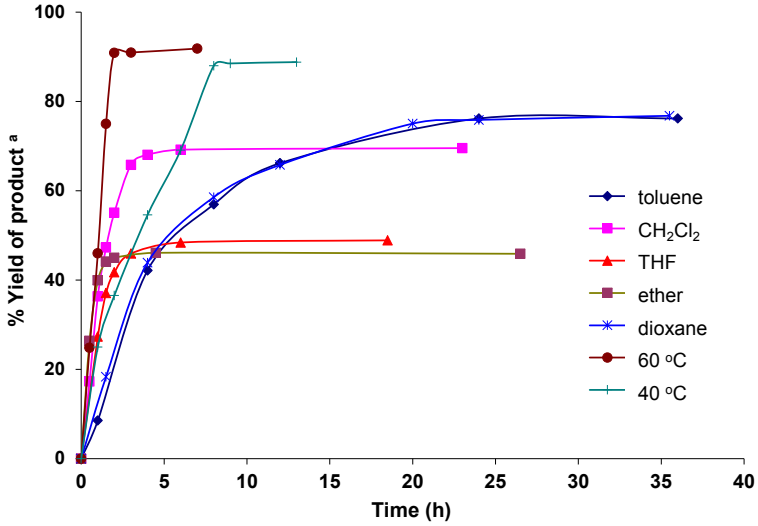

Figure S2. Solvent and temperature effect on reaction 2. Reaction conditions: catalyst (2.37 ×10^{-5} mol), PPh_3O (4.74 × 10^{-5} mol), PhNCO (7.91 × 10^{-3} mol), propylene oxide (1.58 ×10^{-3} mol), rt. Reactions carried out at 40 and 60 °C were run in toluene. [a]Yields are reported relative to PhNCO and determined by GC analysis employing TMB as an internal standard.

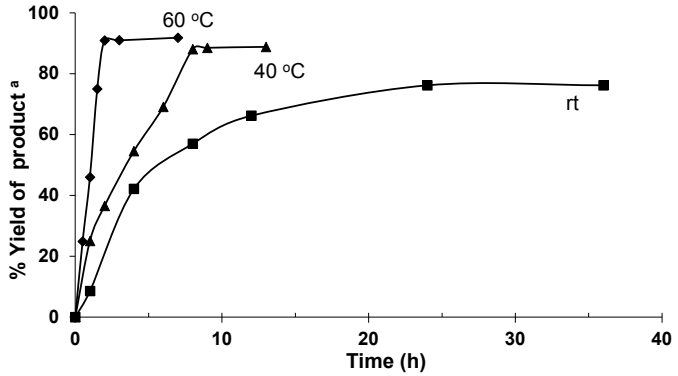

Figure S3. Optimization of temperature effect on reaction 2. Reaction conditions: catalyst (2.37×10^{-5} mol), PPh_3O (4.74×10^{-5} mol), PhNCO (7.91×10^{-3} mol), propylene oxide (1.58×10^{-3} mol). Reactions in toluene were run at 27, 40, and 60 °C. [a]Yields are reported relative to PhNCO and determined by GC analysis employing TMB as an internal standard.

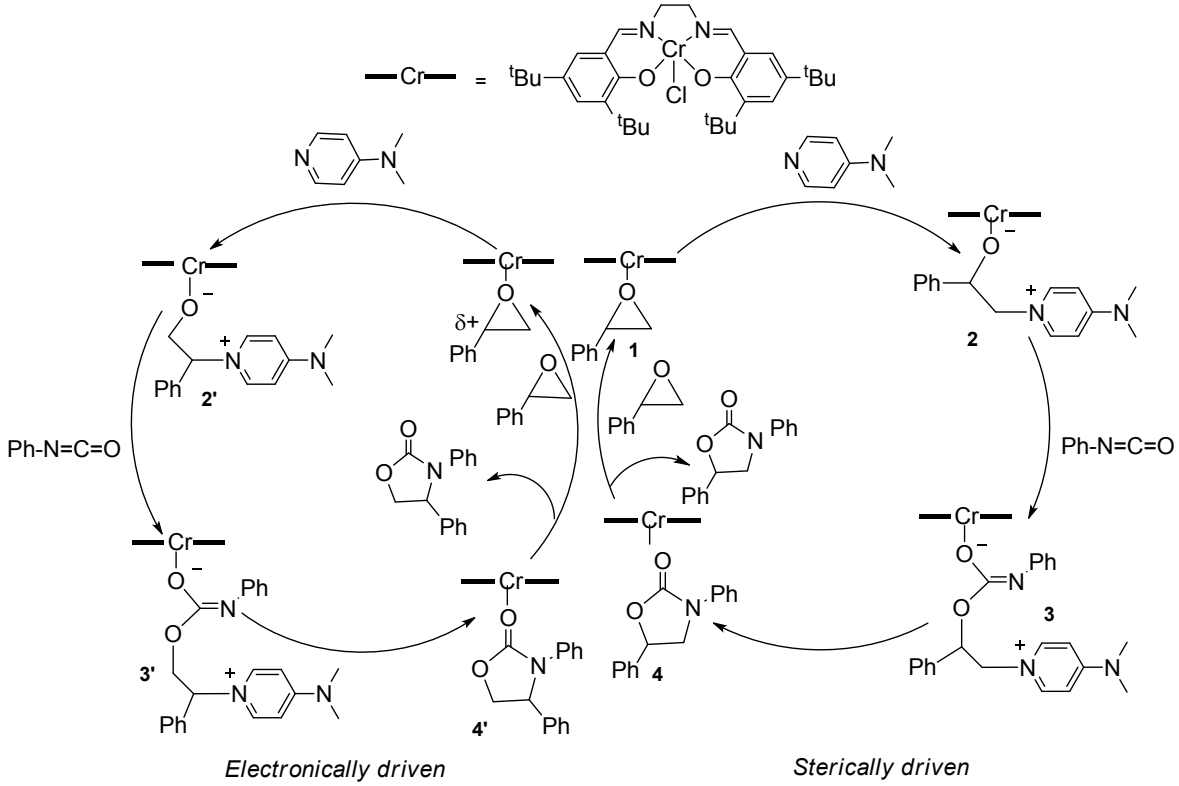

Figure S4. Alternative mode of ring-opening for styrene oxide, which degrades the selectivity of the oxazolidinone product.

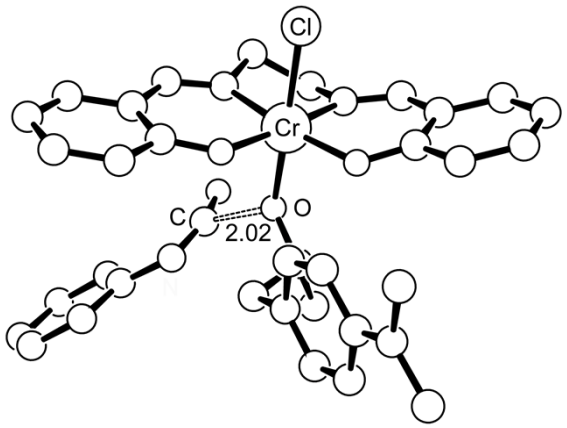

Figure S5. Computationally obtained transition state **2-TS** for the insertion of phenyl isocyanate into the (salen)Cr^{III}-alkoxide bond.

S9. Coordinates and vibrational frequencies of computed structures

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Cr	2.131343645	1.159049714	0.415440414
Cl	3.790534836	2.518120121	1.270986559
N	2.481308896	-0.183161668	1.924450025
C	1.898207399	0.248248872	3.197507061
C	0.569239376	0.956040373	2.899968430
N	0.776592365	1.864358305	1.774526214
C	0.196216222	3.018475717	1.712154601
C	0.276608436	3.932866060	0.609629087
C	0.922964001	3.592227448	-0.627863865
C	0.888491954	4.557914985	-1.666715239
C	0.264353383	5.779532146	-1.494883822
C	-0.370070081	6.112722923	-0.281695050
C	-0.359616876	5.190406460	0.745264989
O	1.496522466	2.440553726	-0.859787108
C	3.250581523	-1.221126513	1.859443551
C	3.983438497	-1.658005056	0.703623520
C	4.767354120	-2.832286248	0.829948228
C	5.517258830	-3.323945164	-0.219349279
C	5.500255645	-2.626377013	-1.443762800
C	4.749830704	-1.476575038	-1.605769099
C	3.960023981	-0.949213577	-0.548115825
O	3.238397206	0.114626889	-0.777087387
H	0.196879070	1.483568738	3.787932534
H	1.749098828	-0.596014442	3.883445133
H	1.384144091	4.302806727	-2.597994650
H	4.742694880	-0.935208426	-2.546432132
H	-0.856069237	7.074883919	-0.158517187
H	6.112028169	-4.223995310	-0.103625221
H	-0.179281343	0.208892220	2.604656993
H	2.592188344	0.961056037	3.658502296
H	3.382653039	-1.825750080	2.765211235
H	-0.425624373	3.333636761	2.558970848
H	4.770810339	-3.347929123	1.788381342
H	6.090812877	-2.995672390	-2.278760164
H	-0.847155164	5.422272229	1.690223770
H	0.266914342	6.496031976	-2.312780274
C	-0.158590744	-0.417249002	-1.510772041
C	0.463450183	-1.490230961	-0.722570289
O	0.435144004	-0.140159072	-0.203787104
C	0.493619701	0.159757102	-2.737627996
H	1.578468142	0.061320118	-2.683831141
H	0.118210970	-0.372309602	-3.619633136
H	0.254243655	1.220050723	-2.839314630
H	-0.148578956	-2.189893743	-0.156494203
H	1.451384430	-1.841472736	-1.007394068
H	-1.244650757	-0.334446402	-1.464615152

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1-TS

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C	-0.071561931	0.534226170	0.154721335
N	-0.036134547	0.332334496	2.213183618
Cr	1.250198520	-0.005498555	-2.998705285
Cl	2.877603011	0.090172581	-4.719295946
N	1.427112206	2.047631440	-2.902625934
C	0.671054881	2.720221757	-3.961421408
C	-0.589539221	1.892940709	-4.252387883
N	-0.197639404	0.491595250	-4.348331902
C	-0.702054182	-0.310373540	-5.224891665
C	-0.418482685	-1.714659412	-5.330703896
C	0.373991226	-2.420710037	-4.359341845
C	0.547130395	-3.817036951	-4.559089400
C	-0.013969992	-4.469346019	-5.640244834
C	-0.791569554	-3.776303463	-6.589572655
C	-0.985044561	-2.419757871	-6.419171549
O	0.904252539	-1.871407701	-3.303543797
C	2.233951190	2.703241189	-2.141312883
C	3.133896098	2.134100126	-1.169682680
C	3.923821380	3.033250321	-0.415905550
C	4.836492699	2.598426689	0.525466469

C	4.984279394	1.212472507	0.727085477
C	4.231982548	0.300261655	0.009538797
C	3.276377600	0.714687851	-0.964219728
O	2.576591836	-0.194057183	-1.573202309
H	-1.085381896	2.243517783	-5.167704596
H	0.411661128	3.751074393	-3.684249617
H	1.152249288	-4.347834918	-3.830855556
H	4.356695605	-0.769169342	0.150368196
H	-1.226721291	-4.297840524	-7.435959136
H	5.434715461	3.307941185	1.088179283
H	-1.290257580	1.992240480	-3.413785831
H	1.302012178	2.740305504	-4.857822819
H	2.272030442	3.796195607	-2.238232506
H	-1.412993300	0.096593938	-5.955103782
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H	5.709498573	0.849391246	1.452360912
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H	0.152308346	-5.537636734	-5.759913081
C	-0.557383473	-0.686137614	-0.511643083
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C	0.194623975	-1.987313836	-0.300746694
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H	-0.090820301	-2.712002869	-1.065292121
H	-0.725065582	1.393863618	0.202864334
H	0.993752357	0.702838689	0.154564758
H	-1.641473943	-0.842880618	-0.414440496
C	-1.134938503	-0.078919301	4.308244807
H	-2.077588637	-0.197980269	4.826505835
C	-1.146548130	0.168795902	2.947618924
C	1.145685328	0.243174339	2.844395401
C	1.267481958	0.001478637	4.200800824
C	0.104252960	-0.172882495	4.992456691
H	-2.090770227	0.241215324	2.412440692
H	2.033625890	0.370613747	2.228263666
H	2.258316459	-0.053659496	4.632554574
N	0.172916443	-0.418442005	6.334605422
C	-1.048857446	-0.593221102	7.109000128
H	-1.680528917	0.304137429	7.080488812
H	-1.641125942	-1.442296855	6.744686021
H	-0.788183699	-0.787972507	8.149432262
C	1.468920373	-0.497571038	6.996859586
H	1.316706998	-0.699273780	8.057309150
H	2.086219433	-1.305390542	6.583867619
H	2.028224811	0.442527758	6.907551223

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H	1.639098959	1.550907151	1.908503026
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N	0.155842532	0.940608759	0.509931959
C	-0.813628948	1.528809649	1.118848262
C	-2.173591276	1.604725700	0.653771436
C	-2.648357984	0.896001409	-0.504910204
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C	-4.406143073	2.506992660	1.080066237
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Cr	0.057292611	0.069991376	-1.339496383
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C	2.614814044	-0.392388046	-3.490605174
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C	2.320209204	-0.777128126	-3.157858236
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C	2.319922356	-4.673550358	-0.611069490
C	3.495628628	-5.381458946	-0.275053583
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C	1.581597558	-4.963349598	1.689903068
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H	-3.924004963	-4.952936306	4.248003864

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N	-0.709172318	-3.859218005	-1.763664362
C	-1.962294731	-3.877533520	-1.472774672
C	-2.510814070	-3.763559961	-0.144150201
C	-1.718236360	-3.435253433	1.008264568
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C	-3.765975392	-3.564375173	2.351113972
C	-4.538275949	-3.867909143	1.217945494
C	-3.901968011	-3.958346452	-0.006224388
O	-0.433545422	-3.170519885	0.974343051
C	3.177021773	-4.402820802	-2.096667870
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O	2.403149111	-3.694800441	0.676323955
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H	1.568885832	-4.727709785	-4.103908838
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H	-0.777659441	0.874052523	6.944010844
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C	-1.173698937	0.061853213	-0.914094349
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C	-2.218709265	0.059898520	-3.109986574
C	-3.454659722	0.386137999	-2.546303512
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H	-2.129323344	-0.063722611	-4.186865464
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N	-0.251176290	-1.582424655	7.973392484
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H	1.061946917	-3.243147727	8.024677765
H	0.051556352	-3.027454574	9.455026986
C	-0.736134644	-0.636876599	8.970854098
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C	-2.945664438	4.461557522	4.294775266
O	-2.224650512	2.175240389	1.497913331
Cr	-0.319928847	2.011834049	1.178983772
O	-0.452977862	1.078493410	-0.486495401
C	0.464316736	0.440058808	-1.154481438
C	1.854188566	0.392440330	-0.785104122
C	2.766205521	-0.340995590	-1.583204917
C	2.361340513	-1.022041090	-2.712219116
C	1.001036901	-0.972228337	-3.078459024
C	0.082756813	-0.262993391	-2.329665462
H	-4.702762594	2.738428264	1.306892499
C	2.381501889	1.084621454	0.355233993
N	1.695368559	1.764784157	1.215264372
H	-0.964071470	-0.221941647	-2.611817442
H	-4.857897019	5.322122050	4.763027856
H	3.074974764	-1.579819853	-3.310025979
H	1.436496660	1.511572433	3.963387094
H	2.455191538	3.563983707	1.933511609
H	3.468928451	1.029821217	0.488859407
H	-0.458664992	3.868578937	4.704021260
H	3.812890663	-0.357456096	-1.284807844
H	0.666148163	-1.499531390	-3.968777263
H	-2.436977682	4.937725956	5.130982018
H	-5.989148406	4.203201966	2.837291004
Cl	-0.064445559	4.123469530	0.268070758
O	-1.315455365	0.103852667	4.228887107
C	-1.356683117	-0.318221893	2.943087062
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H	-2.864390393	0.196491090	5.571471762
H	-0.928519893	-1.039481849	6.595471758
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H	-1.129696312	-2.338295412	5.400877907
H	-4.174807074	-0.696737189	3.796247987
H	-3.478714954	-2.279137386	4.214186613
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H	-2.845854309	0.202805044	0.492283771
C	-2.813727991	-1.703314520	1.499795289
C	-3.044708045	-3.079246072	1.402518958
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C	-3.492868693	-3.621364551	0.199948189
H	-4.044003365	-3.214622074	-1.843807076
C	-3.698252438	-2.792181752	-0.904639289
C	-3.458378690	-1.421838515	-0.799149521
H	-3.620136694	-0.772401864	-1.654408830

Vibrational frequencies (cm^{-1}) of computed structures

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1

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30.19	44.50	54.49	61.51	71.89	84.09
93.29	102.86	116.89	136.95	146.14	161.21
174.39	184.03	192.68	211.29	224.77	234.51
249.75	262.42	295.50	320.27	330.94	340.68
352.95	363.83	370.48	382.49	391.03	398.30
427.04	443.70	470.05	477.19	487.95	534.38
558.90	560.11	579.51	597.70	618.91	627.66
645.87	656.37	743.17	756.19	757.30	768.98
769.27	803.22	810.41	840.85	868.38	873.64
874.43	907.74	916.05	917.40	941.11	942.27
961.95	973.35	990.44	991.35	991.92	997.06
1053.26	1054.06	1056.57	1073.76	1105.14	1109.92
1132.86	1156.33	1159.14	1161.23	1180.20	1181.05
1181.72	1203.67	1234.15	1235.76	1240.37	1267.73
1277.65	1285.50	1303.48	1357.55	1366.02	1369.49
1379.32	1395.42	1396.68	1414.36	1429.55	1436.98
1448.23	1479.24	1488.24	1489.89	1495.61	1498.39
1506.88	1508.28	1510.92	1533.95	1579.17	1582.07
1662.02	1664.62	1689.29	1699.65	3024.38	3033.88
3055.44	3069.78	3070.68	3072.95	3092.29	3125.26
3135.28	3139.60	3165.36	3165.47	3173.72	3178.69
3179.62	3207.48	3208.18	3213.09	3213.68	3227.51

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1-TS

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-443.83	15.47	22.93	25.48	29.74	41.37
45.83	64.79	71.87	74.62	76.32	84.40
86.27	92.87	101.82	116.21	129.56	146.21
163.55	179.56	191.13	192.49	196.02	199.46
215.21	227.16	233.32	247.31	256.46	263.23
276.95	288.46	299.08	320.92	328.74	336.90
352.44	356.03	367.24	375.06	395.13	396.69

400.40 411.81 419.04 440.30 470.21 476.96
481.14 487.35 491.24 535.29 543.63 559.45
559.92 560.60 579.52 593.48 615.65 626.04
647.53 656.71 675.85 743.71 754.39 756.41
765.33 765.56 771.71 795.22 807.58 830.06
833.79 843.63 867.75 870.08 871.05 901.18
907.73 916.62 935.21 937.10 947.84 959.76
971.42 972.39 982.91 984.97 986.58 992.85
999.67 1013.08 1052.11 1053.71 1056.23 1073.79
1085.23 1086.08 1103.16 1111.95 1125.40 1143.63
1148.07 1153.51 1153.68 1157.40 1165.26 1178.57
1179.46 1186.49 1210.37 1228.25 1232.89 1234.91
1236.42 1257.92 1268.90 1274.89 1278.23 1285.18
1302.93 1358.88 1361.28 1367.65 1370.04 1379.55
1384.00 1397.34 1398.78 1400.40 1419.16 1430.18
1433.25 1437.99 1459.06 1461.26 1480.47 1486.41
1491.04 1493.33 1494.63 1498.88 1501.77 1504.31
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1575.82 1578.63 1580.40 1595.84 1661.21 1664.73
1672.37 1701.74 1710.75 3009.22 3018.98 3023.02
3025.95 3030.35 3048.30 3057.73 3064.47 3071.25
3071.95 3074.90 3091.60 3136.69 3150.57 3159.62
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3181.39 3202.02 3204.04 3207.58 3209.79 3217.00
3239.90 3241.47 3343.59

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22.52 26.66 31.08 39.68 48.57 53.64
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178.28 190.61 197.95 200.75 209.17 224.60
237.81 245.73 253.70 268.89 276.33 282.95
309.95 322.85 331.01 336.41 348.39 357.90
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963.37 968.76 976.94 976.98 980.78 984.79
991.75 1053.15 1056.74 1057.58 1060.11 1076.62
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2-TS

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833.23 851.41 851.59 861.77 864.07 865.06
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3-TS

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3244.51 3245.04 3327.90

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S10. Author's contribution audit

RLP and STN conceived the idea for the project. RLP and RLL carried out all the experiments. DA carried out all the computations. RLP, DA, and STN wrote the manuscript with inputs from all the coauthors. M-HB and STN managed the project.

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