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Computational Study of the Mechanism of the [(Salen)Cr + DMAP]- Catalyzed Formation of Cyclic Carbonates from CO_2 to Epoxide

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S1. Computational details

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 7.8[S1] suite of *ab initio* quantum chemistry programs. Geometry optimizations were performed using the B3LYP[S2-S5] functional and the 6-31G** basis set. 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, cc-pVTZ(-f) that includes a double set of polarization functions. For Cr, a modified version of LACVP[S6,S7] was used, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with triple-ζ quality.[S8] 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 = 9.08 for dichloromethane. Solvation energies were evaluated using a self-consistent reaction field (SCRF) approach based on accurate numerical solutions of the Poisson-Boltzmann equation.[S9-S11] For all continuum models, the solvation energies are subject to empirical parameterization of the atomic radii that are used to generate the solute surface. We employed the standard set[S12] 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:

$$G(\text{Sol}) = G(\text{gas}) + G^{\text{solv}} \quad (1)$$

$$G(\text{gas}) = H(\text{gas}) - TS(\text{gas}) \quad (2)$$

$$H(\text{gas}) = E(\text{SCF}) + ZPE \quad (3)$$

$$\Delta G(\text{Sol}) = \sum G(\text{Sol}) \text{ for products} - \sum G(\text{Sol}) \text{ for reactants} \quad (4)$$

where *G*(gas) is the free energy of the molecule in gas phase; G^{solv} is the free energy of solvation as computed using the continuum solvation model; *H*(gas) is the enthalpy in gas phase; *T* is the temperature (353.15 K); *S*(gas) is the entropy in gas phase; *E*(SCF) is the self-consistent field energy, i.e., the "raw" electronic energy as computed from the 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)[S13] method, followed by a quadratic synchronous transit (QST)[S14] search 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 eigenvector that is most similar to the tangent of this curve. In the relative energy diagram, the ΔG(Sol) values have been corrected for excess concentration of epoxide and dissolved CO_2. To decrease the computational cost, the *tert*-Bu groups of the salen ligand 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 metal complex. As the (salen)$Cr^{III}Cl$ complex can potentially be in both doublet and quartet spin states, we initially performed several calculations on both of these spin states. In all cases, the quartet configuration was observed to give the lowest ground state energy, and was used in all calculations (both ground-state and transtion state). All the free energy values have benn corrected for the effect of excess concenration of substartes compared to the catalyst.

S2. Correction factors for the free energy calculations

In our experimental conditions, the epoxide concentration (used as a solvent) was 1500 times higher than that of Cr-catalyst. To take this difference in concentrations into account, a correction factor of 5.12 kcal mol^{-1} (at 80 ^oC) has been included in the computation. To get this correction factor we used the equation $\Delta G = -RT\ln K$ where K is the concentration ratio of substrate to the catalyst. Similarly, CO_2 pressure was 100 psi under experimental condition, the dissolved CO_2 concentration in dichloromethane was approximately 85 times.[S15] So the correction factor included was 3.09 kcal mol^{-1}.

S3. Results of geometry optimizations concerning bimetallic mechanism

Several attempts were made to geometrically optimize the structure where one (Salen)$Cr^{III}Cl$ is acting as a nucleophile to attack another (Salen)$Cr^{III}Cl$- activated epoxide to probe the bimetallic mechanism for epoxide ring opening. These calculations did not converge after many itirations and often led to chemically unreasonable structures. When the geometry optimizations were performed keeping the C–Cl distance costrained to a resonable value to promote the epoxide ring opening, we found that the chloride ligand detached completely from the chromium(III) center. When the starting guess geometry was varied to contain a closed epoxide ring with a properly aligned Cr–Cl bond to facilitate the ring opening, the geometry optimization did not produce a ring opened product.

S4. Recation profile on electronic surface

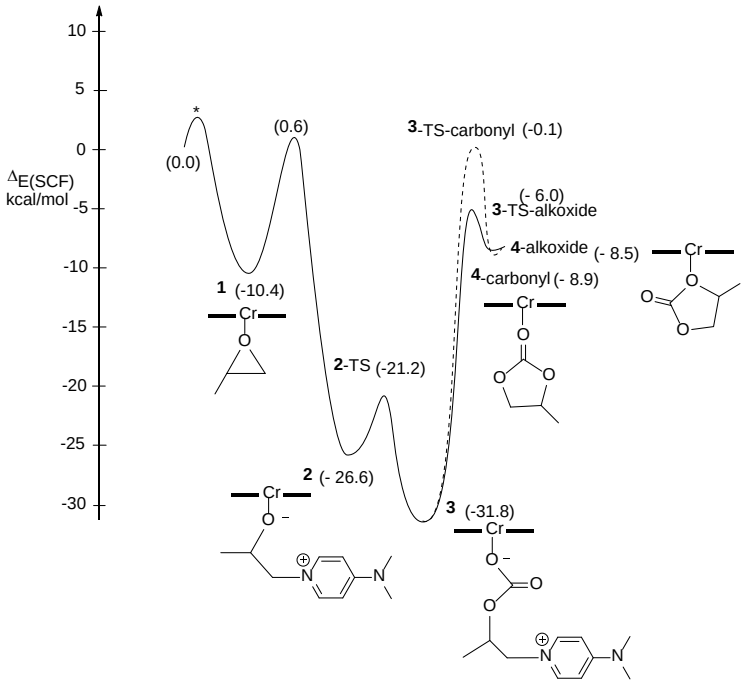

Figure S1. Reaction profile for cyclic carbonate formation from CO_2 and epoxide on the electronic surface.

S5. Relative energy of 3-TS, for t-Bu salen backbone

During the review process of the manuscript one reviewer suggested us to check the validity of your truncated model of salen ligand. To accomplish this goal, his/her suggestion was to install at least two t-Bu groups to the ortho positions of the phenolic group in salen ligand and compare the corresponding transition state energy for the truncated model we used. To comply with the reviewer's suggestion we re-optimized the catalyst structure and **3-TS** after installing two t-Bu salen groups at the suggested position. The computed energy from the modified calculations appeared to be 31.7 kcal mol^{-1} which is in the same bulk part of the enrgy for truncated model (33.6 kcal mol^{-1}). From this calculation we can conclude that our simplified model after t-Bu groups truncation from the salen backbone is a reliable model for this mechanistic investigation.

S6. Explanation for free energy discrepency in case of 3-TS

At 80 °C, there is enough thermal energy for the molecules to overcome an energy barrier of ~30 kcal mol^{-1}. There is a 3.5 kcal mol^{-1} difference between the energy available at 80 ^{o}C and our computed **3-TS** energy. This slight discrepancy in energy can be easily explained when we consider the fundamental limitations of the computational methodology currently available to the community: it cannot properly account for the entropic component in transition state calculations. During the nucleophilic attack in a S_N2 reaction, such as that occurring when **3** is converted to **4**, the leaving group departs from the electrophilic metal center and the reaction gains some translational entropy. For an ensemble of molecular transition states, the C–N bond cleavage in the transition state **3-TS** may happen considerably earlier before the C–O bond formation (a late TS). Under such a scenario, the computational methodology cannot properly compensate for the electronic energy loss by the gain of translational entropy associated with the process. This stems from the fact that we cannot execute our calculations on free energy surface; instead, the calculations must be carried out on electronic surface and then projected the transition state onto free energy surface. In this manner the entropy gain from the departure of the leaving group cannot be accounted for, leading to an artificially high energy barrier. As the upper limit of translational entropy for a multiatomic species is ~10 kcal mol^{-1}, as derived from statistical mechanical considerations, the 3.5 kcal mol^{-1} higher-than-expected energy barrier in our computational model can easily be explained.

S7. Coordinates and vibrational frequencies of calculated structures

Table S1. Cartesian coordinates of all structures investigated

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1			
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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
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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
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H	1.152249288	-4.347834918	-3.830855556
H	4.356695605	-0.769169342	0.150368196
H	-1.226721291	-4.297840524	-7.435959136
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H	0.152308346	-5.537636734	-5.759913081
C	-0.557383473	-0.686137614	-0.511643083
O	-0.270556250	0.108041649	-1.646502228
C	0.194623975	-1.987313836	-0.300746694
H	1.272296597	-1.830974438	-0.374025997
H	-0.054998188	-2.393319578	0.687032305
H	-0.090820301	-2.712002869	-1.065292121
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H	-2.077588637	-0.197980269	4.826505835
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C	1.267481958	0.001478637	4.200800824
C	0.104252960	-0.172882495	4.992456691
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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
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H	1.316706998	-0.699273780	8.057309150
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H	2.028224811	0.442527758	6.907551223

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2

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H	1.639098959	1.550907151	1.908503026
C	1.493275465	0.846166211	1.078214110
C	2.501638059	1.111559139	-0.046636505
H	3.521544629	0.853821930	0.269711813
N	0.155842532	0.940608759	0.509931959
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C	-3.071650251	2.386118615	1.415591614
O	-1.913837864	0.116986450	-1.249576024
Cr	0.057292611	0.069991376	-1.339496383
O	0.247779978	-0.760971492	-3.102366740
C	1.287650931	-0.799256688	-3.877524256
C	2.614814044	-0.392388046	-3.490605174
C	3.680266854	-0.505176469	-4.413880555
C	3.497505104	-0.996314165	-5.691643403
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C	1.136724577	-1.298555468	-5.203894607
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C	2.921933807	0.165951210	-2.201441088
N	2.092235539	0.344729546	-1.228953724
H	0.136171307	-1.592327546	-5.507290343
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C	-2.469644838	-2.383420784	-3.179615621
C	-2.158905873	-3.208082162	-4.286479715
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H	-2.174263649	-2.030601828	-1.089097452
H	-1.208372425	-5.128543176	-4.769228467
H	-2.974677586	-1.434661864	-3.284493444

Cl	0.033084091	2.277964338	-2.316932020
C	0.560069119	-2.889452145	-0.295188556
H	-0.235112404	-4.968689159	-0.293850200
H	0.971153858	-3.077819956	0.721418616
C	1.685810823	-3.213749031	-1.291153084
H	2.080252621	-4.225856371	-1.130040141
H	1.346972875	-3.122057644	-2.325794759
H	2.505691106	-2.505878742	-1.152900163
N	-2.498802794	-2.860905731	-5.553962320
C	-2.139694764	-3.722343731	-6.674865509
H	-1.051917432	-3.838498075	-6.764501707
H	-2.589916313	-4.717522129	-6.575482920
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C	-3.093777135	-1.546354527	-5.806018637
H	-3.195097519	-1.403367713	-6.881230460
H	-4.089976038	-1.467226743	-5.354884901
H	-2.462855583	-0.745078825	-5.406548252

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C	-0.351249603	-0.577360731	1.597060600
O	0.821673419	0.516183866	3.879800102
H	6.136536369	1.647249635	1.248524485
C	5.277522725	1.039173585	1.561735948
C	5.725682971	-0.126586658	2.457307780
H	6.031342070	0.243431199	3.442941081
N	4.567007905	0.481665989	0.411881574
C	4.714474486	0.948242639	-0.779606298
C	4.025411365	0.473648266	-1.955719760
C	2.989284873	-0.517286969	-1.901167918
C	2.360382630	-0.865907528	-3.123182316
C	2.737393309	-0.291531171	-4.324956208
C	3.757871035	0.674327913	-4.377697540
C	4.378631670	1.045056819	-3.197835124
O	2.571322767	-1.076925418	-0.792919821
Cr	3.499154550	-1.177516581	0.897949260
O	2.529539800	-2.712655387	1.597760108
C	2.553363621	-3.225698065	2.801862573
C	3.449453068	-2.797596302	3.837693687
C	3.381655282	-3.403929531	5.112032032
C	2.475022931	-4.407755347	5.400824899
C	1.609228908	-4.841509017	4.382218111
C	1.649271919	-4.272940981	3.120610349
H	1.575065896	-1.614599457	-3.080104145
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N	4.621139636	-1.082343375	2.568628102
H	0.986647611	-4.622069698	2.333731606
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H	4.051595285	1.119765721	-5.322804148
H	2.438154169	-4.854840251	6.388831574
H	4.573342923	1.656494053	2.127268861
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H	4.068230636	-3.056805809	5.881502028
H	0.896340292	-5.637917606	4.583681565
H	5.168236318	1.794059879	-3.213542789
H	2.237125873	-0.595716412	-5.241892988
H	-1.205434623	0.006741924	1.942851160
N	-0.852594925	-1.480240050	0.519410890
C	-0.056648161	-2.482865978	0.062600628
C	-2.042296153	-1.252773052	-0.088166285
C	-0.435521483	-3.270889276	-0.996680963
C	-2.477170431	-1.999346248	-1.154896784
C	-1.668068370	-3.053825969	-1.665405432
H	0.893309622	-2.628170300	0.580183885
H	-2.633405403	-0.438147226	0.313406592
H	0.253988226	-4.043802323	-1.307542821

H	-3.435713835	-1.755125303	-1.591925020
Cl	5.197279815	-2.508556530	-0.058507644
C	0.822757388	0.326003983	1.084699240
H	-0.002070791	-1.197140665	2.419907553
H	0.993974525	0.057677989	0.038325324
C	0.444459643	1.814421086	1.117507866
H	-0.419354815	2.005791769	0.467439667
H	0.198577561	2.146228899	2.128769264
H	1.282533876	2.409628941	0.743919773
C	1.960389557	0.653328845	3.511582959
O	2.025176332	0.063623812	1.772768391
N	-2.048549434	-3.801618141	-2.731977629
C	-3.302884125	-3.515926118	-3.421747359
H	-3.451598476	-4.253233200	-4.209863126
H	-4.156179576	-3.581531185	-2.737062941
H	-3.298032431	-2.518755031	-3.880083839
C	-1.152145938	-4.829190658	-3.261187948
H	-0.943311679	-5.599376291	-2.510194767
H	-1.628138893	-5.309961918	-4.115305774
H	-0.199578713	-4.400722397	-3.594772560

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C	-1.368181432	0.476370365	0.705150940
O	0.266531323	0.143045267	3.164329254
H	6.479018337	-0.515736809	3.191313023
C	5.407837554	-0.686285312	3.019107565
C	5.044968569	-2.165641155	3.211760326
H	5.142012199	-2.460163857	4.265223436
N	5.006151662	-0.295228147	1.669922320
C	5.684215494	0.548739665	0.972226521
C	5.310567897	1.072361460	-0.316068563
C	4.046215514	0.792652185	-0.940793886
C	3.795100865	1.431011345	-2.186208123
C	4.721340638	2.268960378	-2.779988061
C	5.960652566	2.532848143	-2.168909350
C	6.230291034	1.938145481	-0.950924989
O	3.125497213	0.019460040	-0.434490304
Cr	3.261903373	-1.190230856	1.094914216
O	1.546868680	-2.085898443	0.854159122
C	0.970004408	-2.973093488	1.618502744
C	1.548207249	-3.523198099	2.813767948
C	0.818113351	-4.459731132	3.578982036
C	-0.445991538	-4.884902387	3.213911999
C	-1.005348348	-4.369357397	2.031893305
C	-0.320096051	-3.449955188	1.257310633
H	2.837503391	1.237982156	-2.661090362
C	2.872628463	-3.192038615	3.275067674
N	3.683230017	-2.361347369	2.718305240
H	-0.752229171	-3.068068639	0.337348103
O	2.380243509	0.103395200	2.354859372
H	6.683544787	3.191627574	-2.638830085
H	-0.988143336	-5.603590229	3.819664138
H	4.833387119	-0.079147178	3.729645963
H	5.714480492	-2.785078501	2.603197676
H	3.208817798	-3.723276969	4.174190479
H	6.628302175	0.925770902	1.385344653
H	1.279948256	-4.852868869	4.482836473
H	-1.992786737	-4.699930860	1.716060533
H	7.177445439	2.133738576	-0.451387847
H	4.483250593	2.731853202	-3.735250565
H	-2.413061252	0.788062338	0.626361884
N	-1.029918889	-0.197094397	-0.582889232
C	0.256875241	-0.305576032	-1.008585583
C	-2.002589294	-0.845124626	-1.277637150
C	0.599685492	-1.070593543	-2.093043310
C	-1.727688002	-1.623884496	-2.371901230
C	-0.377819423	-1.809739512	-2.800893980

H	1.018507248	0.224468495	-0.452628661
H	-3.015183827	-0.719213393	-0.912060030
H	1.655336842	-1.121724676	-2.319966686
H	-2.556646786	-2.098165483	-2.879961591
Cl	4.460003062	-2.761024051	-0.246425417
C	-0.494511536	1.698689126	1.035005827
H	-1.272243506	-0.255853948	1.511111144
H	-0.410525772	2.313053250	0.129222360
C	-1.130120101	2.547598746	2.139214015
H	-2.082056880	2.971040338	1.798265151
H	-1.288464144	1.955934127	3.040875046
H	-0.455897333	3.374065999	2.379701379
C	1.149588858	0.452422954	2.372699187
O	0.863482829	1.336331426	1.308265880
N	-0.046994157	-2.642032453	-3.815595527
C	-1.082433359	-3.324276042	-4.583505694
H	-0.610476043	-4.024735231	-5.271703108
H	-1.747284696	-3.897661607	-3.928022058
H	-1.689194283	-2.621894250	-5.170341055
C	1.359783205	-2.804726324	-4.195182337
H	1.972429477	-3.054226510	-3.323453066
H	1.438597222	-3.621937009	-4.911896475
H	1.763095174	-1.895611048	-4.658398378

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C	0.041714262	-0.066883705	-0.040745791
O	0.018696385	-0.018272097	1.921149795
O	1.834120232	-0.015774300	3.284510933
H	-1.435632562	-0.734814240	6.201760477
C	-0.725570185	-0.876172094	5.375875063
C	-0.795747115	-2.309976587	4.828496089
H	-1.751383969	-2.489877976	4.317641417
N	0.650706692	-0.613411886	5.794027501
C	0.922112715	0.184995720	6.773728106
C	2.232705548	0.592153413	7.189967332
C	3.429693841	0.198837714	6.492978199
C	4.661900487	0.717866943	6.980454372
C	4.710191562	1.557831957	8.074451670
C	3.536399769	1.939811034	8.757046541
C	2.325061663	1.457385680	8.307696834
O	3.452632276	-0.569566867	5.447031533
Cr	2.038209089	-1.586714359	4.657790996
O	3.087491195	-2.496180478	3.291248793
C	2.686144236	-3.031743737	2.186603887
C	1.311877856	-3.354542288	1.882211964
C	0.986986168	-3.946132723	0.638781113
C	1.948642913	-4.214270876	-0.319130912
C	3.295351503	-3.906633510	-0.024314906
C	3.653095866	-3.341607880	1.182288014
H	5.562421180	0.421771692	6.452213393
C	0.235624147	-3.118087999	2.810712849
N	0.341238445	-2.490998382	3.929907649
H	4.687194277	-3.106664348	1.413276031
H	3.586515560	2.601136681	9.616326304
H	1.679930189	-4.688352469	-1.258868912
H	-0.981141115	-0.179846347	4.566825484
H	-0.685414724	-3.022395527	5.653553260
H	-0.748979427	-3.504448588	2.517160717
H	0.084540945	0.612521093	7.339477876
H	-0.055043256	-4.200945289	0.448426363
H	4.068520063	-4.124934809	-0.758133001
H	1.404276268	1.742423790	8.814153544
H	5.673254708	1.931428506	8.415146790
H	-0.976208575	0.291019534	-0.003255555
N	-0.090092604	-0.250357897	-1.999035381
C	0.627560962	-1.193678113	-2.634819432
C	-0.908441734	0.520525809	-2.732638531

C	0.568524340	-1.389672677	-4.000709079
C	-1.035552905	0.404652281	-4.102680341
C	-0.277343131	-0.573746129	-4.798368821
H	1.262600946	-1.820555667	-2.011423528
H	-1.486388650	1.263488769	-2.188385105
H	1.174312275	-2.171979367	-4.438503342
H	-1.716200526	1.067092619	-4.620956408
Cl	2.186178171	-3.304085263	6.238931201
C	1.230304845	0.896208641	0.000648578
H	0.210534539	-1.130979199	0.046662468
H	1.897661646	0.693361084	-0.839810387
C	0.805643637	2.363389340	-0.004191140
H	0.306064281	2.626448139	-0.942608183
H	0.123294408	2.562016570	0.827461542
H	1.685778273	3.001645655	0.106456033
C	1.248678848	0.158853848	2.205607426
O	2.017042482	0.609752556	1.161990203
N	-0.359771004	-0.722081871	-6.149886593
C	-1.249060727	0.134027333	-6.927528040
H	-1.173547434	-0.134797003	-7.980951573
H	-2.295795750	0.014114206	-6.621603869
H	-0.977706153	1.192192360	-6.828536657
C	0.431129749	-1.747311213	-6.824103338
H	1.505656924	-1.596457765	-6.663361594
H	0.166442841	-2.754624918	-6.479270771
H	0.241666889	-1.697056803	-7.896039459

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H	6.913603426	-0.977571305	3.810309487
C	5.840279583	-1.023455815	3.583853943
C	5.427630171	-2.437914797	3.147722618
H	5.477615869	-3.138321929	3.991964101
N	5.469716083	-0.090223469	2.520440571
C	6.174690934	0.961724727	2.263066680
C	5.843635200	1.975384370	1.300450165
C	4.591587936	1.996452912	0.593853993
C	4.363183821	3.086142626	-0.287157233
C	5.304852207	4.082314281	-0.465849562
C	6.531370098	4.060274803	0.226753959
C	6.779632797	3.017675626	1.097120946
O	3.649767550	1.103032443	0.741196469
Cr	3.807766480	-0.671812181	1.471160201
O	2.129262712	-1.336246391	0.838138983
C	1.421151200	-2.342195313	1.262686556
C	1.880017953	-3.315009225	2.218507281
C	1.020476172	-4.368874485	2.614314048
C	-0.259995283	-4.489173639	2.114979622
C	-0.709906104	-3.539664552	1.174789055
C	0.101828676	-2.503214663	0.757388711
H	3.421388127	3.094879920	-0.827077172
C	3.198393655	-3.281361849	2.784314259
N	4.079325174	-2.355321327	2.589347948
H	-0.238580276	-1.773675194	0.029632563
H	7.264417517	4.846311661	0.078283056
H	-0.905796833	-5.301470565	2.432672687
H	5.283710291	-0.750413345	4.490022839
H	6.100366231	-2.785058570	2.355122690
H	3.466433339	-4.124003927	3.433553562
H	7.103962098	1.115859265	2.825284781
H	1.393759639	-5.094975821	3.334257727
H	-1.714634903	-3.624928505	0.767159674
H	7.717880592	2.980573727	1.647449516
H	5.093971191	4.894851019	-1.157257581
Cl	5.127365452	-1.526227666	-0.214538117
C	1.851964451	1.028717610	3.187959728
O	2.706184509	0.166378632	3.250340300
O	1.814592428	2.081735576	4.019274634

O	0.836228783	1.038198627	2.321619210
C	0.137409824	2.292930386	2.422948348
H	0.438705914	2.921578803	1.580612587
H	-0.934338979	2.091592977	2.374102926
H	-0.682680964	1.566509372	4.980172061
C	-0.375575951	2.616285434	4.932605834
H	0.895782105	3.893256513	3.724296533
H	0.084811916	2.888844990	5.885624057
H	-1.269472319	3.232884348	4.791799966
C	0.597122660	2.844458751	3.787487890

Table S2. Vibratonal frequencies of all species investigated

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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

1504.44 1509.74 1510.40 1515.86 1527.13 1540.53

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

3159.69 3162.34 3167.94 3169.60 3172.33 3178.71

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

70.04 74.33 82.46 92.81 98.47 108.37

116.61 119.78 136.99 146.27 149.70 160.44

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

362.48 368.85 381.09 396.89 404.03 430.64

432.50 437.83 469.46 477.42 479.60 489.79

506.04 509.57 534.93 536.24 559.35 560.04

575.36 588.10 607.16 623.14 630.63 648.19

657.20 674.36 717.51 749.89 752.79 754.56

764.26 765.26 783.99 795.70 802.57 814.73

834.73 839.15 862.30 863.84 868.80 890.53

906.70 915.75 933.33 935.68 949.59 961.81

963.37 968.76 976.94 976.98 980.78 984.79

991.75 1053.15 1056.74 1057.58 1060.11 1076.62

1083.93 1098.11 1113.97 1116.86 1143.03 1146.07

1154.20 1157.50 1160.49 1178.73 1180.03 1197.58

1203.93 1217.36 1230.20 1232.82 1235.81 1248.95

1260.98 1270.52 1273.37 1278.96 1285.54 1314.23

1361.95 1365.13 1368.77 1370.94 1371.41 1375.48

1381.37 1395.28 1400.19 1409.26 1413.51 1426.94

1431.74 1439.39 1460.76 1480.75 1487.08 1489.17

1491.29 1497.08 1499.18 1501.71 1505.38 1507.20

1510.59 1511.39 1517.41 1518.09 1539.30 1544.38

1580.28 1581.63 1583.67 1589.30 1662.92 1664.73

1697.80 1706.48 1718.47 2856.10 3020.99 3024.85

3029.10 3033.60 3039.86 3059.13 3059.80 3069.10

3077.04 3079.62 3088.77 3102.58 3122.44 3139.37

3153.73 3158.83 3159.49 3159.90 3164.09 3168.48

3171.23 3193.07 3197.02 3205.23 3205.84 3232.62

3253.86 3272.24 3278.20

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2-TS

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-254.45 7.95 26.11 37.61 44.83 52.85

54.83 65.33 72.90 84.85 86.68 93.97

97.21 102.15 105.96 118.83 127.13 130.34

134.13 147.65 156.65 161.05 176.45 183.33

196.03 201.13 223.21 227.72 235.13 238.62

243.62 264.51 276.31 290.00 302.98 315.76

324.60 335.48 344.61 359.11 364.71 367.81

379.89 394.66 395.73 400.60 422.76 436.29

455.78 464.90 469.68 472.48 488.82 493.36

513.87 539.07 542.56 559.62 559.73 579.51

582.37 593.48 613.30 618.43 638.16 648.92

669.25 669.96 722.39 736.51 739.15 740.26

753.03 754.31 756.68 788.80 799.09 800.63

821.62 834.51 842.81 846.03 847.57 848.15

879.36 895.08 902.52 918.85 920.88 936.33

945.05 949.19 962.25 962.54 963.55 966.36

970.98 1037.07 1043.20 1044.88 1051.70 1061.34

1063.73 1070.21 1091.75 1097.19 1104.87 1111.30

1117.94 1127.36 1132.61 1137.00 1145.30 1148.14

1154.46 1172.84 1190.69 1216.48 1218.73 1220.33

1222.93 1237.43 1243.66 1254.37 1257.73 1262.06

1288.06 1303.93 1324.25 1340.26 1342.43 1348.62

1350.65 1352.65 1358.90 1366.72 1376.19 1379.09

1382.86 1397.35 1404.70 1404.97 1419.98 1426.80
1432.44 1439.82 1451.62 1456.13 1458.67 1463.51
1476.55 1477.14 1482.23 1486.27 1492.31 1494.07
1500.24 1526.01 1575.35 1578.43 1582.95 1583.91
1656.95 1658.62 1696.82 1697.74 1707.05 2143.90
3027.78 3035.10 3036.71 3041.95 3047.90 3077.60
3092.27 3099.49 3103.37 3111.81 3112.51 3113.94
3121.07 3125.20 3133.45 3165.36 3170.60 3173.58
3173.65 3173.98 3176.85 3180.85 3198.83 3201.59
3209.04 3210.74 3213.10 3230.83 3259.00 3259.63

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18.28 23.32 27.70 40.63 41.55 49.09
56.66 70.02 72.56 81.89 85.02 93.78
101.65 104.76 114.93 124.12 133.41 136.04
152.61 157.31 178.92 182.58 192.85 213.46
216.76 227.85 229.30 239.19 244.57 253.90
259.94 268.86 283.38 310.71 316.48 323.17
327.22 334.38 348.61 357.63 371.07 379.45
396.60 399.67 405.84 435.82 439.91 446.54
474.11 474.77 478.29 490.42 508.50 531.51
540.27 554.23 560.84 561.84 572.29 580.79
593.41 613.24 625.95 649.04 658.72 676.34
715.33 728.36 741.88 754.14 755.78 764.08
764.65 801.82 806.42 818.39 819.77 827.99
846.40 863.68 865.49 871.79 877.86 906.96
907.97 915.91 930.23 934.48 935.55 953.64
960.69 968.94 975.67 979.49 983.12 988.68
993.73 1050.71 1058.34 1062.61 1074.51 1075.23
1085.50 1108.63 1109.37 1110.78 1138.30 1144.37
1147.84 1153.25 1155.11 1158.11 1176.00 1179.92
1181.50 1195.39 1216.72 1230.71 1234.21 1237.00
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1303.88 1326.60 1360.39 1366.07 1369.23 1369.86
1379.46 1380.61 1391.79 1395.59 1409.63 1415.64
1421.79 1432.65 1434.94 1438.89 1462.74 1482.85
1487.47 1493.06 1494.11 1497.03 1498.44 1501.21
1505.24 1509.24 1510.92 1511.29 1515.71 1528.25
1537.17 1546.36 1574.71 1584.27 1585.45 1596.84
1661.33 1663.46 1706.87 1709.44 1716.97 1782.45
3025.65 3026.26 3033.23 3038.98 3042.81 3051.87
3065.24 3067.22 3075.94 3081.01 3086.53 3093.79
3109.65 3125.17 3140.79 3158.77 3161.77 3162.30
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3-TS

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-509.93 10.96 18.66 27.89 29.43 31.81
41.83 47.60 56.93 68.47 75.08 85.28
86.65 89.80 94.67 107.90 116.99 123.13
126.47 138.84 148.12 175.70 183.49 190.85
192.17 213.25 222.13 224.34 229.66 244.45
252.28 260.74 265.45 285.39 294.18 317.90
321.50 335.15 340.57 355.08 366.14 375.74
394.65 399.72 400.69 416.30 422.86 441.14
444.60 469.57 473.51 486.52 491.82 534.31
536.35 547.28 559.72 560.28 561.23 575.88
595.86 616.34 625.71 640.22 641.96 653.04
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3150.58 3162.09 3164.24 3174.68 3175.65 3204.51
3205.20 3210.95 3212.22

S8. Author contributions audit. DA, STN, and M-HB conceived the idea of the project. DA completed all the computations under the supervision of M-HB. DA, STN, and M-HB co-authored the manuscript.

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