Supporting information for

VCD spectroscopy distinguishes the enamine and iminium ion of a 1,1'-binaphthyl azepine

Tino P. Golub[a], Taichi Kano[b], Keiji Maruoka[c] and Christian Merten[a],*

a) Ruhr Universität Bochum
Fakultät für Chemie und Biochemie, Organische Chemie II
Universitätsstraße 150
44801 Bochum, Germany
christian.merten@ruhr-uni-bochum.de
www.mertenlab.de

b) Tokyo University of Agriculture and Technology
Department of Applied Chemistry
Graduate School of Engineering
2-24-16 Nakacho, Koganei 184-8588, Japan

c) Kyoto University
Graduate School of Pharmaceutical Sciences
Sakyo, Kyoto 606-8501, Japan

1. Experimental and computational details

Materials. Catalyst **1** and its iminium salt were prepared according to literature procedures.[1, 2]

IR and VCD spectroscopy. The IR and VCD spectra were recorded on a Bruker Vertex FT-IR spectrometer equipped with a PMA 50 module for VCD measurements. Samples were held in a transmission cell with BaF2 windows and 100 μm path length. Concentration are given in the main text. Spectra were recorded at room temperature with 4 cm^{-1} spectral resolution by accumulating 32 scans for the IR and ~32000 scans (4 hours accumulation time) for VCD. Baseline correction of the VCD spectra was done by subtraction of the spectra of the solvent recorded under identical conditions.

NMR spectroscopy. ^{1}H-NMR reaction monitoring was carried out on a 300 MHz Bruker Avance III NMR spectrometer. Concentrations of **1** was 0.5 M with equimolar CH_2Br_2 as internal standard. Reaction monitoring was carried out at room temperature. Spectra analysis and quantification was carried out using MestReNova 14.

Computational details. Details on the conformational analysis can be found in the SI. All geometry optimizations and frequency calculations were carried out at B3LYP/6-31G+(2d,p) level of theory using the Gaussian 09 Rev. E software package.[3] Solvent effects were taken into account implicitly by using the integral equation formalism of the polarizable continuum model (IEFPCM) [4, 5] of chloroform or DMSO. Explicit solvation of **1** with DMSO-d_6 was considered by placing a solvent molecule with its oxygen near the N-H group and re-optimizing the geometry prior to spectra calculations. Relative energy differences and Boltzmann populations generally refer to the zero-point corrected energies of the conformers (ΔE_{ZPC}). Note that we regularly find ΔE_{ZPC}-derived populations to better explain the experimental signatures than Gibbs Free energies (for a detailed discussion see References [6-9], for instance). Vibrational line broadening was simulated by assigning a Lorentzian band shape with half-width at half-height of 6 cm-1 to the calculated dipole and rotational strength. The calculated frequencies were scaled by 0.98 to account for anharmonic effects not captured by the harmonic approximation employed in the frequency calculations. Figures were prepared using CYLview.[10]

2. NMR spectra of enamine 2

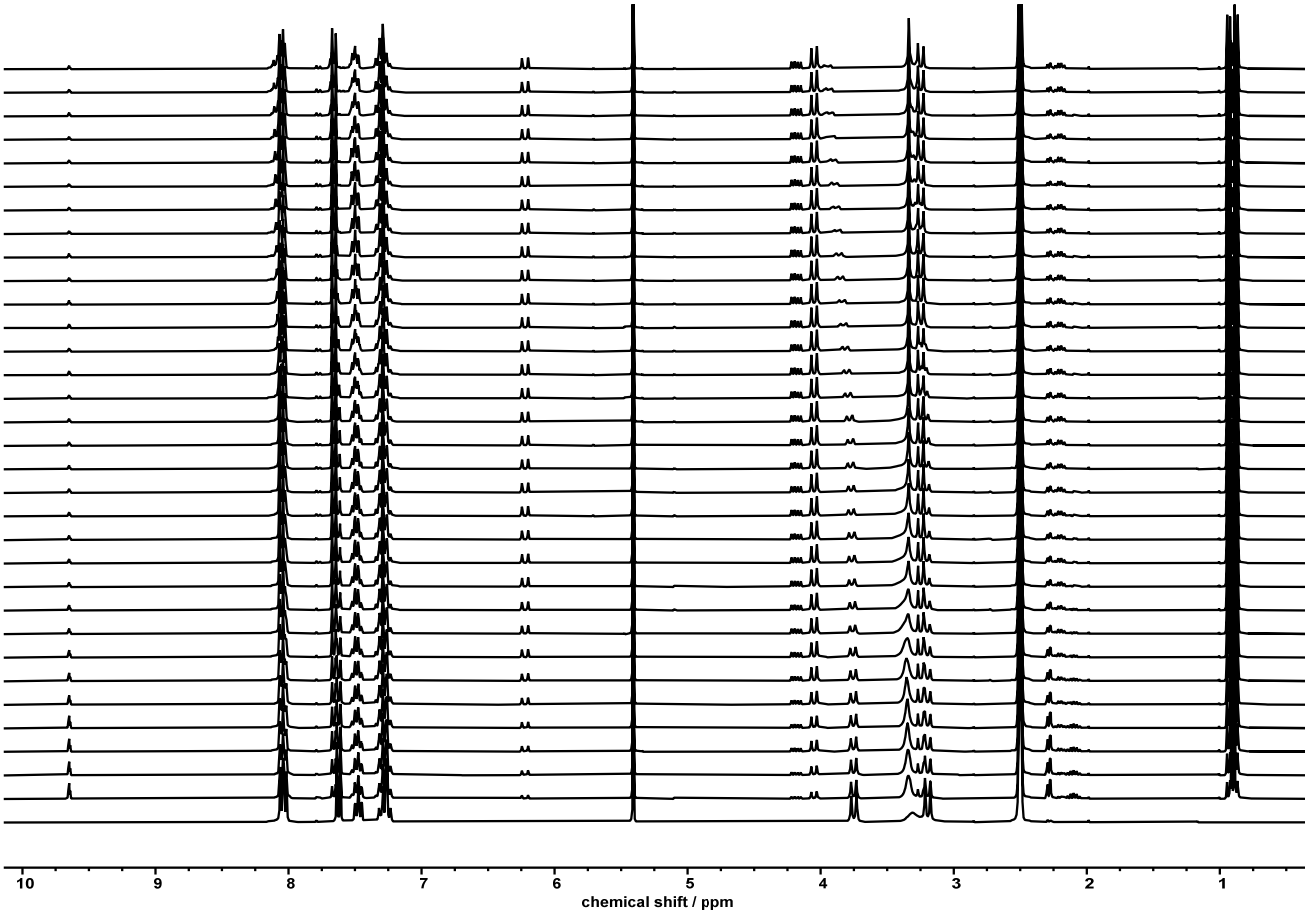


Figure S1. Reaction monitoring of enamine formation: catalyst **1** + 1 eq of isovaleraldehyde + 1 eq CH_2Br_2 as reference (^{1}H-NMR, 300 MHz, DMSO-d_6)

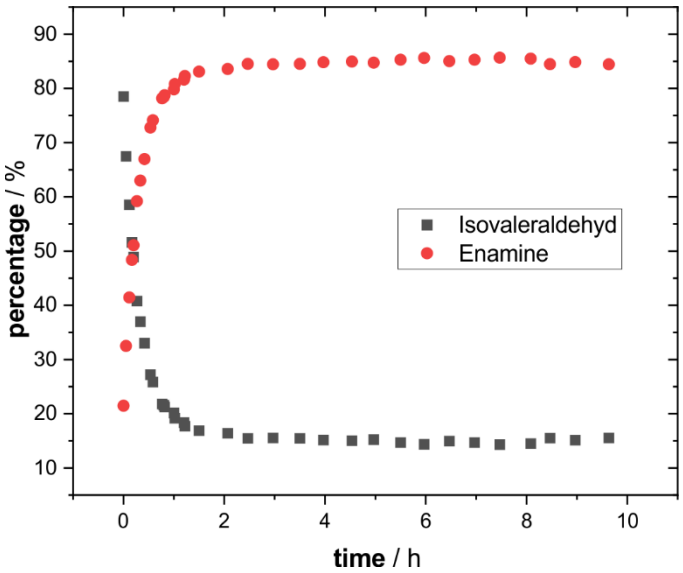


Figure S2. Integrals of aldehyde (~9.6 ppm) and enamine (~6.2 ppm) normalized to reference CH_2Br_2.

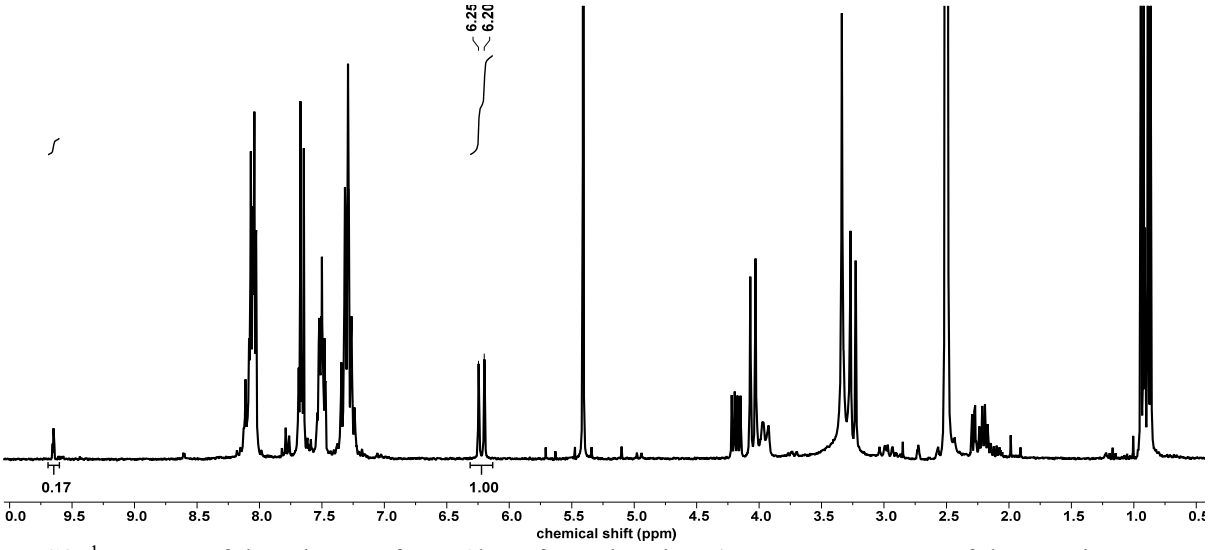


Figure S3. ^{1}H-NMR of the mixture after ~ 9hrs of reaction time (top-most spectrum of the reaction monitoring plot in Figure S1)

3. Conformational analysis of 2 and 3

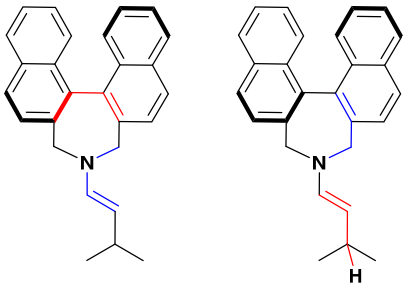


Table S1. Geometries, relative energies (zero-point corrected ΔE_{ZPC} and Gibbs Free energy ΔG_{298K} in kcal/mol) ad corresponding Boltzmann populations χ (in percentage) of the optimized conformations of **2** obtained at B3LYP/6-31G+(2d,p)/IEFPCM(DMSO) level of theory.

	C=C-C=C	C=C-C-N	C-N-C=C	N-C=C-C	C=C-C(CH$_3$)$_2$-H	ΔE_{ZPC}	ΔG_{298K}	$\chi(\Delta E)$	$\chi(\Delta G)$
AzE_c1	54.2	-70.5	8.6	E	3.5	0.00	0.00	78.8	80.7
AzE_c2	54.1	-70.7	8.6	E	-117.1	1.28	1.46	8.7	6.6
AzE_c3	54.1	-70.6	8.4	E	123.3	1.29	1.46	8.6	6.5
AzE_c4	54.2	-72.1	-154.2	E	-2.7	1.86	1.57	3.2	5.4
AzE_c5	54.2	-72.1	-153.4	E	-122.8	3.19	3.19	0.3	0.3
AzE_c6	54.1	-72.2	-154.5	E	117.5	3.20	3.18	0.3	0.3
AzE_c7	53.8	-71.4	7.8	Z	-14.8	5.35	5.20	0.0	0.0
AzE_c8	54.0	-73.2	161.9	Z	-4.0	5.41	5.28	0.0	0.0
AzE_c9	53.9	-72.1	-163.8	Z	37.8	7.13	6.82	0.0	0.0
AzE_c10	54.0	-73.2	155.6	Z	-140.9	9.30	9.42	0.0	0.0
AzE_c11	54.0	-73.8	128.2	Z	178.7	10.11	9.81	0.0	0.0
AzE_c12	53.5	-72.2	24.6	Z	174.6	11.14	10.66	0.0	0.0

Relative energies referenced to E_{zpc}(c1) = -1098.338939 hartree and G(c1)=-1098.391084 hartree

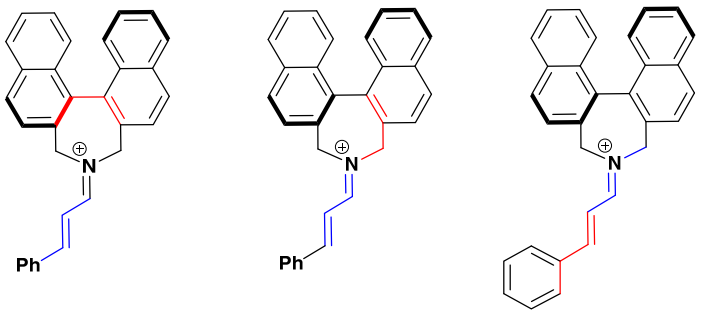


Table S2. Geometries, relative energies (zero-point corrected ΔE_{ZPC} and Gibbs Free energy ΔG_{298K} in kcal/mol) ad corresponding Boltzmann populations χ (in percentage) of the optimized conformations of **3** obtained at B3LYP/6-31G+(2d,p)/IEFPCM(DMSO) level of theory.

	C=C-C=C	C=C-C-N	C-N=C-C	N=C-C=C	C-C=C-C_{Ar}	C=C-C_{Ar}-C_{Ar}	ΔE_{ZPC}	ΔG_{298K}	$\chi(\Delta E)$	$\chi(\Delta G)$
AzI_c1	54.0	-72.5	177.2	179.6	179.4	-179.0	0.00	0.00	100.0	99.9
AzI_c2	53.9	-72.3	-176.3	-174.0	11.4	-150.1	5.28	4.42	0.0	0.1
AzI_c3	53.7	-72.8	175.2	-24.5	-176.2	174.1	5.99	5.64	0.0	0.0
AzI_c4	53.9	-71.3	-173.7	34.1	175.3	-172.9	8.51	8.33	0.0	0.0
AzI_c5	53.9	-71.9	-177.8	-44.9	-9.9	-23.6	11.03	11.22	0.0	0.0
AzI_c6	53.9	-68.1	2.6	54.0	7.0	-156.0	13.25	13.22	0.0	0.0

Relative energies referenced to E_{zpc}(c1) = -1249.988727 hartree and G(c1)= -1250.043312 hartree

4. VCD of catalyst 1

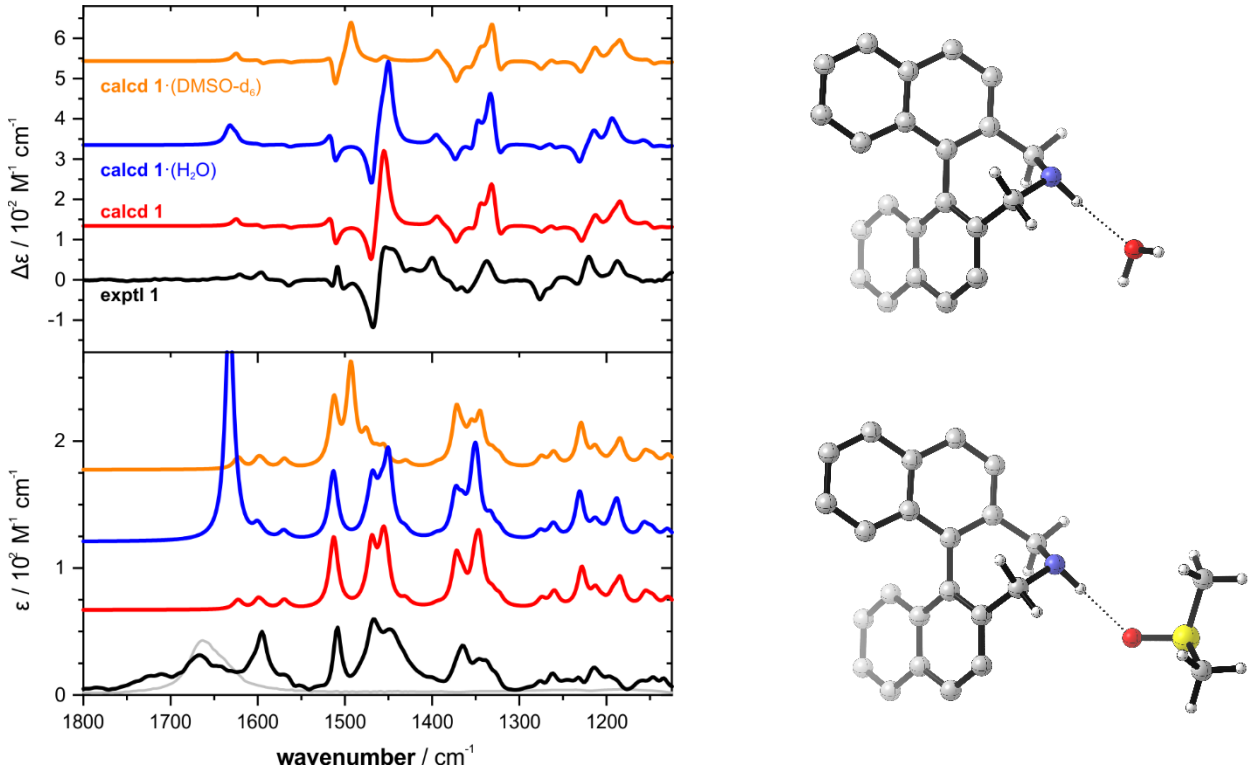


Figure S4. IR and VCD spectra of 1 and different clusters as discussed in the main text.

5. VCD of catalyst 2

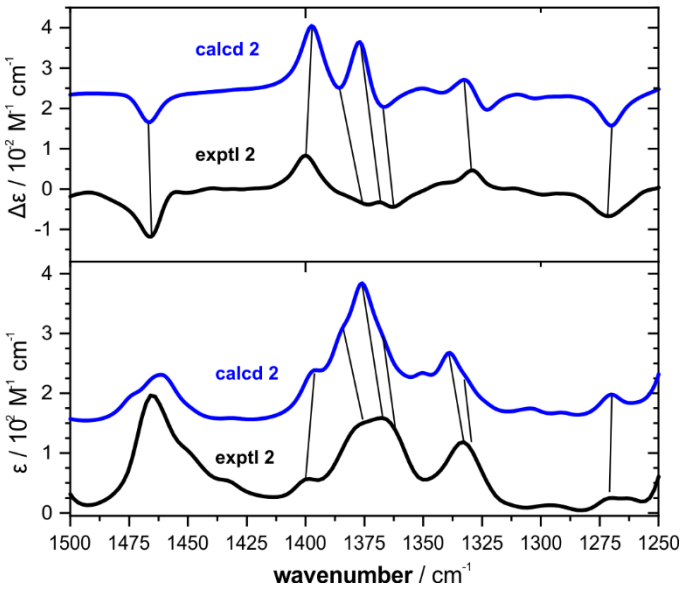


Figure S5. Detailed IR and VCD spectra assignment of **2**

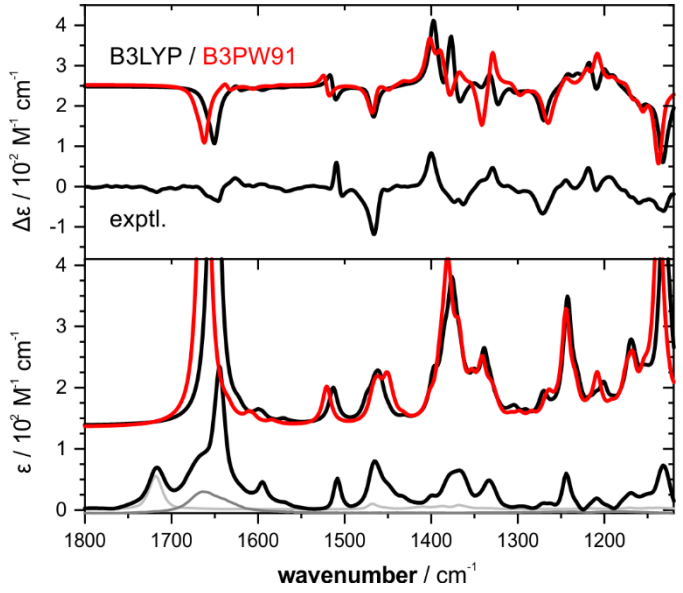


Figure S6. Comparison of the computed IR and VCD spectra of **2** obtained using the B3LYP and B3PW91 functionals.

6. Cartesian coordinates

Structure of 1

C	-1.22314800	1.59737800	-0.88355200
C	-0.72574800	0.50301400	-0.18047500
C	-1.62418800	-0.53877000	0.23300300
C	-2.99713300	-0.48271300	-0.17778800
C	-3.44617800	0.61910300	-0.95000300
C	-2.58508800	1.64064000	-1.27023600
H	-0.20528700	-1.65443300	1.43621000
C	-1.22731600	-1.61219200	1.07983200
C	-3.88932100	-1.51583700	0.22004200
H	-4.48526900	0.65381500	-1.26391300
H	-2.94278900	2.49707700	-1.83411400
C	-3.46343800	-2.55059700	1.02007200
C	-2.11967900	-2.58840400	1.46373900
H	-4.92260900	-1.46384700	-0.11097800
H	-4.15519600	-3.33011300	1.32279500
H	-1.79142200	-3.39199400	2.11544900
C	2.59242200	1.60846900	1.28820100
C	3.44453000	0.58097700	0.96345200
C	2.98744900	-0.51124900	0.18184900
C	1.61503500	-0.55171800	-0.23238000
C	0.72559000	0.49591600	0.18654000
C	1.23033700	1.58188700	0.89817500
H	4.90432700	-1.50856200	0.11221700
H	2.95793200	2.45710600	1.85952500
H	4.48278300	0.60253300	1.28162500
C	3.87135000	-1.54919300	-0.22142500
C	1.21053800	-1.61596600	-1.08703200
C	2.09503900	-2.59758500	-1.47574800
C	3.43818800	-2.57478300	-1.02950900
H	0.18886000	-1.64694200	-1.44571700
H	1.76074700	-3.39394300	-2.13327700
H	4.12363700	-3.35832600	-1.33614500
C	-0.30980100	2.75866600	-1.20317000
H	0.61805500	2.37280100	-1.65181900
H	-0.78013800	3.41607200	-1.94020300
C	0.32813000	2.76237400	1.20068500
H	-0.59589100	2.41028400	1.67104800
H	0.81194000	3.43831700	1.91045500
N	-0.03721400	3.56325800	0.00946700
H	0.72539900	4.20084700	-0.20505200

Lowest energy conformer of 2

C	0.10556100	-1.64276000	-0.51457800
C	1.06691600	-0.75509200	-0.03942000
C	2.42330000	-1.20212700	0.12028000
C	2.78226400	-2.52041200	-0.31520200
C	1.78227700	-3.36871700	-0.85506700
C	0.47727900	-2.94625900	-0.92691900
H	3.17516100	0.57212700	1.11726000
C	3.43072800	-0.41097900	0.74158000
C	4.12507800	-2.96456800	-0.17002000
H	2.05860500	-4.36482000	-1.18780200
H	-0.28879500	-3.61301500	-1.31104600
C	5.07745800	-2.16164200	0.41311400
C	4.71882000	-0.87639800	0.88558800
H	4.38160900	-3.96100100	-0.51804700
H	6.09789700	-2.51376400	0.52472400
H	5.46510200	-0.25399200	1.36914600
C	-0.81954000	1.98758800	1.77501200
C	-0.25020000	3.14099400	1.29264100
C	0.74465200	3.08369300	0.28272900
C	1.18270700	1.80621400	-0.19969200
C	0.62967800	0.61284400	0.37781700
C	-0.39304600	0.71662100	1.31703000
H	0.95938200	5.22793000	0.10728400
H	-1.60407600	2.04048300	2.52422000
H	-0.57147800	4.11080900	1.66104300
C	1.29324800	4.26906700	-0.27869100
C	2.11857900	1.78558200	-1.27202800
C	2.61778600	2.95180300	-1.80812400
C	2.21309900	4.20938100	-1.29975600
H	2.43473800	0.83310900	-1.67990400

H	3.32511500	2.90697100	-2.63024000
H	2.61986200	5.12112100	-1.72520000
C	-1.34793300	-1.23113100	-0.59381700
H	-1.44084600	-0.28189800	-1.14870600
H	-1.90993900	-1.98324300	-1.15493100
C	-1.10131100	-0.53867500	1.78559500
H	-0.37337900	-1.29641500	2.08949700
H	-1.72993900	-0.32332200	2.65153400
N	-1.96600700	-1.10490300	0.73141700
C	-3.31196400	-0.74948100	0.75877100
H	-3.68250300	-0.57378600	1.76725100
C	-4.16952200	-0.65744200	-0.27590000
H	-3.83007200	-0.81755200	-1.29713700
C	-5.64269300	-0.36902900	-0.10727500
H	-5.83538800	-0.19709800	0.96080800
C	-6.50581100	-1.56564800	-0.55405000
H	-6.33408500	-1.79439200	-1.61357100
H	-6.26646300	-2.46352100	0.02558000
H	-7.57381300	-1.35066600	-0.42767000
C	-6.05393100	0.90265900	-0.87375200
H	-7.12338600	1.11000900	-0.74866600
H	-5.49260800	1.77503800	-0.52268300
H	-5.85953100	0.78868500	-1.94786000

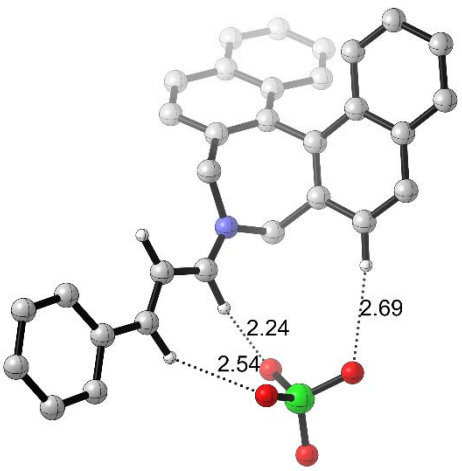
Lowest energy conformer of 3 (charge +1)

C	1.02450000	-1.21715000	-1.24793600
C	1.91946900	-0.72053400	-0.30586200
C	2.80233100	-1.62965100	0.36907300
C	2.81312100	-3.00939000	-0.02161300
C	1.92805900	-3.45385800	-1.03703000
C	1.03734700	-2.58418300	-1.61591100
H	3.62185000	-0.20459000	1.78552100
C	3.64070800	-1.23343900	1.44792800
C	3.69098300	-3.91382300	0.63472200
H	1.94796000	-4.49783000	-1.33379400
H	0.34081200	-2.93854800	-2.36961300
C	4.50424300	-3.48982800	1.65905100
C	4.46633300	-2.13817000	2.07599100
H	3.69780100	-4.95266700	0.31875500
H	5.16663300	-4.18989900	2.15737200
H	5.09252500	-1.81291400	2.90035000
C	0.56034300	2.67128300	0.71804300
C	1.65994300	3.48918700	0.63776800
C	2.90319600	2.98154700	0.18293300
C	3.01514900	1.59298400	-0.15691900
C	1.87341000	0.73796200	0.01116000
C	0.65886800	1.29492300	0.39920300
H	3.93440900	4.87772000	0.30531600
H	-0.39508300	3.07546600	1.03784200
H	1.58302700	4.53998200	0.89902100
C	4.03158700	3.83181700	0.03028700
C	4.25027200	1.13494100	-0.69468400
C	5.31931500	1.98821100	-0.84834600
C	5.21709500	3.34791100	-0.47012100
H	4.34751700	0.09970700	-0.99681800
H	6.24878400	1.61568300	-1.26645700
H	6.07091600	4.00684300	-0.58856900
C	-0.01070500	-0.30007800	-1.85615100
H	0.42862900	0.64726800	-2.17858200
H	-0.49600600	-0.76593300	-2.71317200
C	-0.58641900	0.44218100	0.48761500
H	-0.40770300	-0.46981900	1.06567100
H	-1.38373600	1.00292100	0.97028600
N	-1.06873900	0.01744700	-0.85726000
C	-2.33123400	-0.14587000	-1.15131300
H	-2.52780000	-0.48194700	-2.16624200
C	-3.45279800	0.05451400	-0.30459100
H	-3.31253700	0.35830800	0.72399900
C	-4.70227300	-0.16497400	-0.81194000
H	-4.76853400	-0.47951700	-1.85230900
C	-5.97166500	-0.03489200	-0.13287300
C	-7.14438100	-0.33642400	-0.85670900
C	-6.09184100	0.37486400	1.21286200
C	-8.39558300	-0.23402000	-0.25903400
H	-7.06256100	-0.65331700	-1.89181500
C	-7.34203000	0.47639600	1.80563200
H	-5.20922700	0.61414000	1.79508300

C	-8.49612100	0.17258700	1.07272800
H	-9.28868100	-0.46948200	-0.82721700
H	-7.42449100	0.79211800	2.83987600
H	-9.47066200	0.25405200	1.54251800

Lowest energy conformer of 3 with perchlorate

C	-1.33377200	1.12282500	-0.02701200
C	-2.41607600	0.36100300	0.40089000
C	-3.24148200	0.85288700	1.46776500
C	-2.99181100	2.16403500	1.99174300
C	-1.91705000	2.93057300	1.47211900
C	-1.09087300	2.41249900	0.50548000
H	-4.45382900	-0.92958400	1.71451700
C	-4.27241400	0.07791700	2.06861800
C	-3.80830300	2.66155200	3.04328100
H	-1.73999900	3.92562000	1.86865100
H	-0.24653200	2.98741300	0.13715700
C	-4.81088200	1.89199900	3.58507800
C	-5.03391000	0.58189000	3.09885600
H	-3.61459000	3.66118500	3.42079700
H	-5.42371600	2.28032300	4.39204400
H	-5.81035600	-0.03173500	3.54435500
C	-1.74398800	-3.16624000	-0.83106300
C	-2.93139700	-3.52788500	-1.41719700
C	-4.00623800	-2.60639300	-1.49135100
C	-3.85628100	-1.30266400	-0.91392600
C	-2.63441200	-0.97330900	-0.23380000
C	-1.58553900	-1.88780800	-0.24221100
H	-5.31835100	-3.93820200	-2.57638000
H	-0.91422000	-3.86598700	-0.80831000
H	-3.05141400	-4.51477000	-1.85336400
C	-5.21687600	-2.94218900	-2.15569500
C	-4.91784200	-0.37099200	-1.08713800
C	-6.07102700	-0.72057700	-1.75240200
C	-6.23175600	-2.02329900	-2.28113500
H	-4.81100600	0.63380700	-0.69820200
H	-6.86266700	0.01118900	-1.87683300
H	-7.14930600	-2.28773100	-2.79655800
C	-0.36268000	0.55148200	-1.03419100
H	-0.88097600	0.07983000	-1.87276500
H	0.30911600	1.31446800	-1.42499200
C	-0.25150900	-1.54182500	0.37985300
H	-0.37530000	-1.16823700	1.40166700
H	0.37627900	-2.43015700	0.41493900
N	0.47674500	-0.49212000	-0.38444900
C	1.77971800	-0.39566800	-0.41123600
H	2.16833000	0.45202600	-0.97160900
C	2.72017500	-1.26258300	0.21008100
H	2.38773200	-2.11882500	0.78246700
C	4.04586200	-0.96332100	0.08274800
H	4.29779300	-0.06156200	-0.47256200
C	5.17331600	-1.69591100	0.62211400
C	6.46456600	-1.17003400	0.41453300
C	5.04158800	-2.90407400	1.33860100
C	7.58803800	-1.82550000	0.90835600
H	6.57526400	-0.24052200	-0.13488000
C	6.16435900	-3.55651500	1.82876700
H	4.06142100	-3.33534500	1.50857300
C	7.43988200	-3.01940200	1.61600300
H	8.57495800	-1.40748700	0.74240500
H	6.05211800	-4.48567100	2.37724500
H	8.31391700	-3.53398600	2.00163500
Cl	3.06567400	3.19059100	-1.49111300
O	2.36092100	2.20727500	-2.35633400
O	2.06719500	4.00916100	-0.77827900
O	3.92434500	4.04732300	-2.32014200
O	3.88920700	2.44797700	-0.51013400



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