Supporting Information

Ring expansion of bicyclic methyleneaziridines via concerted, near-barrierless [2,3]-Stevens rearrangements of aziridinium ylides

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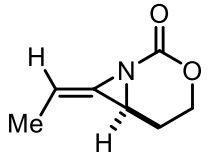
I. General Information

All glassware was either oven-dried overnight at 130 °C or flame-dried under a stream of dry nitrogen prior to use. Unless otherwise specified, reagents were used as obtained from the vendor without further purification. Tetrahydrofuran, deuterated tetrahydrofuran, and toluene were vacuum transferred from purple Na/benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and freshly distilled prior to use. All other solvents were purified in accordance with "Purification of Laboratory Chemicals".[1a] Air- and moisture-sensitive reactions were performed either in an MBraun LabStar glovebox under an atmosphere of nitrogen or using standard Schlenk techniques under an atmosphere of nitrogen. Analytical thin layer chromatography (TLC) was performed utilizing pre-coated silica gel 60 F_{254} plates containing a fluorescent indicator, while preparative chromatography was performed using SilicaFlash P60 silica gel (230-400 mesh) via Still's method.[1b] The mobile phases for column chromatography varied depending on substrate as hexanes/ether, hexanes/ethyl acetate, or benzene/ethyl acetate were used. Columns were typically run using a gradient method, beginning with 100% of the less polar eluent and gradually increasing the polarity with the other solvent. For reactions producing products without a UV signature, ceric ammonium molybdate was employed to visualize the reaction products.

^{1}H NMR and ^{13}C NMR spectra were obtained using Bruker-300, Varian Inova-500, Varian Unity-500 or Varian Inova-600 NMR spectrometers. For ^{1}H NMR, chemical shifts are reported relative to residual protiated solvent peaks (δ 7.26, 2.49, 7.15 and 4.80 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6 and CD_3OD respectively). ^{13}C NMR spectra were measured at either 125 MHz or 150 MHz on the same instruments noted above for recording ^{1}H NMR spectra. Chemical shifts were again reported in accordance to residual protiated solvent peaks (δ 77.1, 39.5, 128.0 and 49.0 ppm for $CDCl_3$, $(CD_3)_2SO$, C_6D_6, and CD_3OD, respectively). Accurate mass measurements were acquired at the University of Wisconsin, Madison using a Micromass LCT (electrospray ionization, time-of-flight analyzer or electron impact methods). The NMR and Mass Spectrometry facilities are funded by the NSF (CHE-9974839, CHE-9304546, CHE-9208463, CHE-9629688) and the University of Wisconsin, as well as the NIH (RR08389-01).

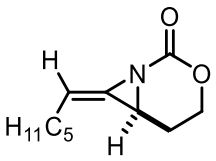
II. Preparation of Substrates

Diazo compounds (**2a-d**) and homoallenic carbamate precursors to **1a-b** were synthesized according to the reported literature procedures.[2] The methylene aziridines **1-b** were prepared as previously described; the NMR data is given below for convenience.[2]



1a

Following the general literature procedure[2] (2.5 mmol scale), compound **1a** was isolated as a clear oil (30%, >19:1 *E/Z*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.56 (q, *J* = 7.0 Hz, 1H), 4.54 (ddd, *J* = 11.8, 10.8, 2.1 Hz, 1H), 4.37 (ddd, *J* = 10.8, 3.9, 2.5 Hz, 1H), 3.43 (dd, *J* = 7.6, 6.1 Hz, 1H), 2.37 (ddt, *J* = 14.5, 6.2, 2.3 Hz, 1H), 1.80 (d, *J* = 7.0 Hz, 3H), 1.63 (dddd, *J* = 14.5, 12.2, 8.6, 3.9, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 126.1, 98.0, 69.0, 39.4, 24.1, 13.4.



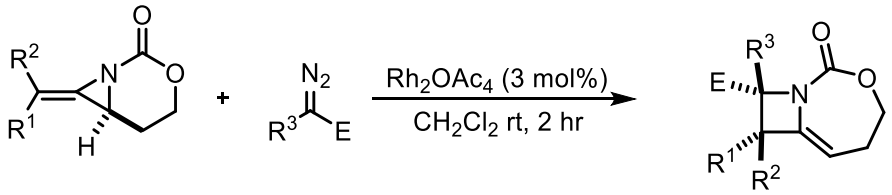
1b

Following the general literature procedure[2] (10 mmol scale), compound **1b** was isolated as a clear oil (51%, >19:1 *E/Z*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (t, *J* = 7.0 Hz, 1H), 4.55 (ddd, *J* = 12.0, 10.9, 2.1 Hz, 1H), 4.37 (ddd, *J* = 10.8, 3.9, 2.6 Hz, 1H), 3.43 (dd, *J* = 8.5, 6.3 Hz, 1H), 2.37 (ddt, *J* = 14.6, 6.2, 2.4 Hz, 1H), 2.16 (m, 2H), 1.62 (dddd, *J* = 14.4, 12.2, 8.4, 3.9 Hz, 1H), 1.44 (m, 2H), 1.30 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 125.5, 103.3, 68.9, 39.5, 31.4, 28.9, 28.3, 24.3, 22.5, 14.1.

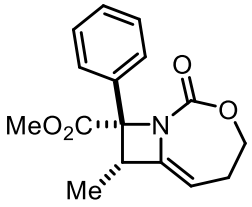
The enantioenriched methylene aziridine (*S*)-**1b** was prepared using the literature procedure[2] starting with the (*S*)-1-octyn-3-ol to give the product in 99:1 *er*.

III. General Procedure for Azetidine Synthesis.

The general procedure has previously been reported, but is indicated here for convenience.[3] Spectroscopic data is also included for the purposes of comparison.

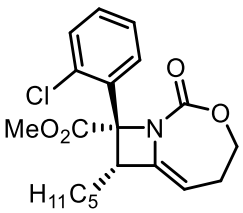


A flame-dried, roundbottom flask was placed under nitrogen and charged with Rh_2OAc_4 (0.03 equiv, where the catalyst loading can be decreased upon scale-up), followed by a solution of the methylene aziridine (0.1 mmol, typically 0.1 mM - ~1 mL). To this mixture was added a solution of the diazo compound (1.2-4 equivalents, brought to 0.1 mM in CH_2Cl_2) dropwise over 2 h using a syringe pump. The conversion was checked by TLC after the addition and once the reaction was completed, the mixture was concentrated and loaded directly onto silica for column chromatography. *Note: The R_f differences between the aziridine and azetidine can be quite small – we recommend using a 2:1 ether/hexanes eluent for the TLC analysis.*



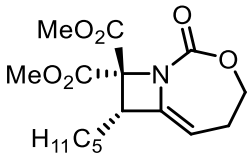
3aa

The general procedure was followed to yield compound **3aa** as a white solid (73%, >19:1 *dr*) after column chromatography (0 to 12.5% EtOAc/benzene, 2.5% increments). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (m, 2H), 7.36 (m, 2H), 7.32 (m, 1H), 4.89 (dt, *J* = 5.2, 2.4 Hz, 1H), 4.43 (m, 2H), 3.80 (s, 3H), 3.49 (m, 1H), 2.66 (m, 1H), 2.33 (m, 1H), 1.33 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.8, 156.5, 143.6, 138.9, 128.2, 128.1, 126.6, 99.6, 76.1, 68.2, 52.8, 46.1, 28.3, 13.5. HRMS (ESI) *m/z* calculated for $C_{16}H_{17}NO_4[M+Na]^+$ 310.1050, found 310.1048.



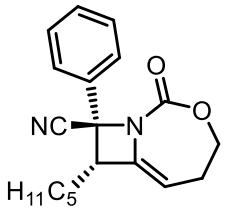
3bb

Following the general procedure, column chromatography (0 to 10% EtOAc/benzene, 2% increments) yielded compound **3bb** as an off-white solid (84%, >19:1 *dr*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.27 (m, 2H), 4.99 (d, *J* = 6.3 Hz, 1H), 4.46 (m, 2H), 3.77 (s, 3H), 3.18 (m, 1H), 2.71 (m, 1H), 2.32 (m, 1H), 2.01 (m, 2H), 1.47 (m, 1H), 1.33 (m, 5H), 0.90 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 156.8, 144.0, 137.0, 132.9, 130.5, 129.3, 127.9, 126.8, 100.0, 75.2, 68.2, 52.8, 50.5, 31.8, 30.7, 28.5, 28.4, 22.7, 14.1. HRMS (ESI) *m/z* calculated for $C_{20}H_{24}ClNO_4[M+H]^+$ 378.1467, found 378.1463.



3bc

In contrast to the general procedure, the phenyl iodonium ylide was used for this reaction. The ylide was added in two portions (4.0 equiv) to a solution of the methylene aziridine and the rhodium catalyst. The reaction was stirred until consumption of the starting material was noted by TLC. The crude mixture was concentrated and purified by column chromatography (0 to 10% EtOAc/benzene, 2.5% increments) to deliver compound **3bc** as a clear oil (44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.91 (m, 1H), 4.41 (m, 2H), 3.85 (s, 3H), 3.85 (s, 3H), 3.49 (m, 1H), 2.47 (m, 2H), 1.70 (m, 1H), 1.54 (m, 1H), 1.40 (m, 1H), 1.30 (m, 5H), 0.89 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 165.9, 155.2, 142.1, 100.6, 72.5, 68.1, 53.5, 53.1, 47.2, 31.7, 29.0, 28.2, 26.7, 22.5, 14.1. HRMS (ESI) *m/z* calculated for $C_{16}H_{23}NO_6[M+H]^+$ 326.1598, found 326.1593.



3bd

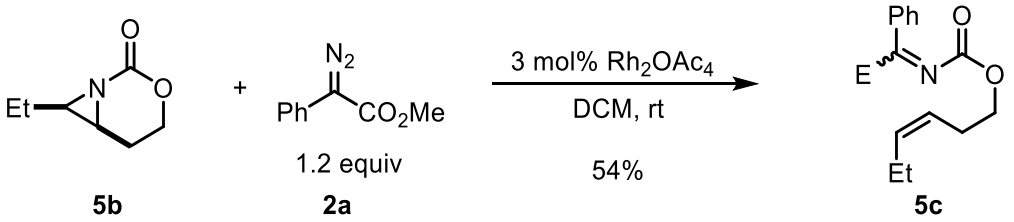
Following the general procedure at 0.05 mmol scale with 2 equiv of diazonitrile (used and kept as a 0.1 M stock solution), column chromatography (0 to 10% EtOAc/benzene, 2.5% increments) yielded compound **3bd** as a clear oil (12.1 mg, 78%, 18:1 *dr*, 99:1 *er*). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.46 (m, 5H), 5.03 (ddd, *J* = 5.2, 3.0, 1.8 Hz, 1H), 4.50 (m, 2H), 3.66 (m,

1H), 2.67 (m, 1H), 2.44 (m, 1H), 1.00-1.23 (m, 8H), 0.77 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 141.3, 131.0, 129.6, 128.8, 126.1, 118.4, 102.3, 68.1, 64.2, 51.5, 31.3, 29.1, 28.3, 26.1, 22.2, 13.8. HRMS (ESI) *m/z* calculated for $C_{19}H_{22}N_2O_2[M+H]^+$ 311.1754, found 311.1748.

IV. Bicyclic Aziridine Experiments.

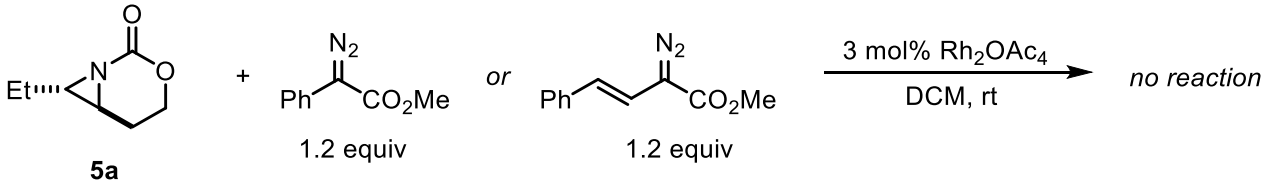
5a **5b**

Bicyclic aziridines **5a** and **5b** were synthesized according to the literature procedure.[2]



5b **2a** **5c**

Following the same general procedure as with the methyleneaziridines, column chromatography (0 to 10% EtOAc/hexanes, 2% increments) yielded **5c** as a clear oil (15.5 mg, 54%) as a single stereoisomer at the imine and alkene – *comparison of alkene peaks to the corresponding homoallylic alcohol showed that the cis olefin was formed, the stereochemistry at the imine is unknown*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.1 ppm, 2H), 7.56 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 5.53 (m, 1H), 5.36 (m, 1H), 4.24 (t, *J* = 7.1 ppm, 2H), 3.94 (s, 3H), 2.48 (q, *J* = 7.4 Hz, 2H), 2.07 (app pentet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 162.9, 161.8, 135.0, 133.2, 132.0, 129.3, 128.7, 123.1, 66.7, 53.1, 26.7, 20.7, 14.2. HRMS (ESI) *m/z* calculated for $C_{16}H_{19}NO_4[M+H]^+$ 290.1387, found 290.1381.

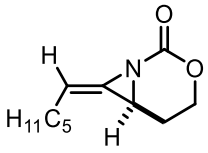


5a

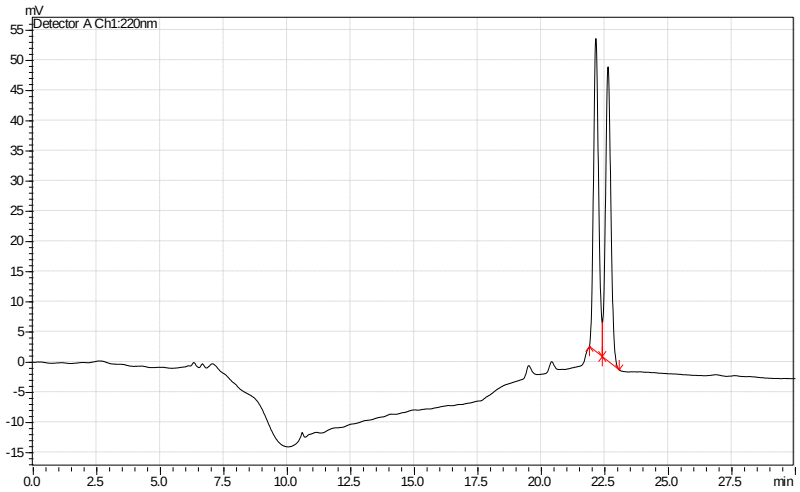
V. Preparation of enantioenriched substrates and azetidines.

Enantioenriched methylene aziridine **1b** was synthesized as described,[2] starting from the enantioenriched propargyl alcohol. HPLC conditions - chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel OJ-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 ^{o}C; Solvent: 5:95 *i*PrOH:hexane and increasing to 30:70 *i*PrOH:hexane over 10 minutes. The eluent composition was held at this composition for another 20 minutes to complete the analysis. This method of analysis was used for both substrates.isocratic 1.00%

*i*PrOH in hexanes; Detector: UV @ 220 nm:\

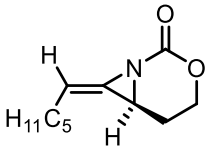


1b - racemic

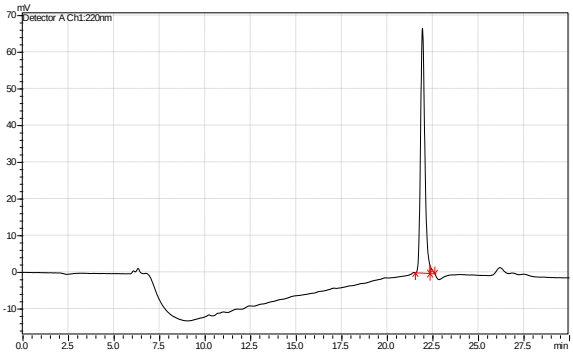


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	22.142	717567	51807	21.892	22.4	50.1029
2	22.621	714620	48750	22.4	23.067	49.8971

Figure S1. Chiral HPLC of racemic **1b**.

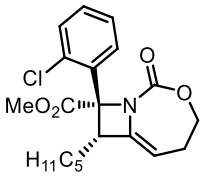


(*S*) - **1b** - 99:1 *er*

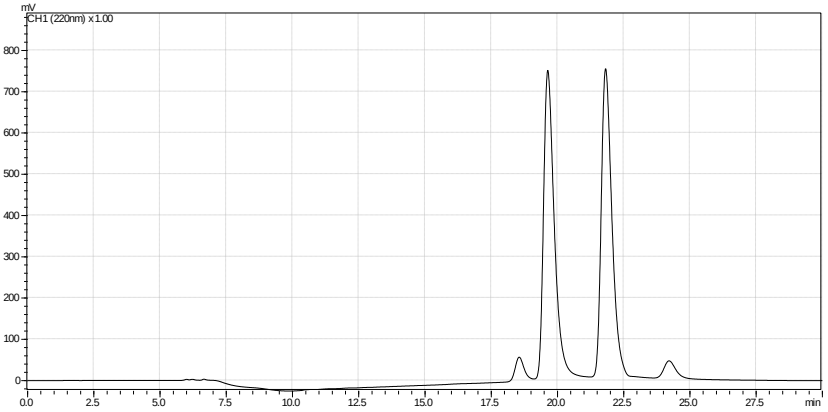


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	21.922	1092588	66792	21.542	22.342	98.6571
2	22.35	14872	2066	22.342	22.608	1.3429

Figure S2. Chiral HPLC of enantioenriched (*S*)-**1b**.

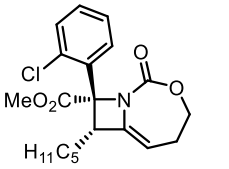


3bb - racemic

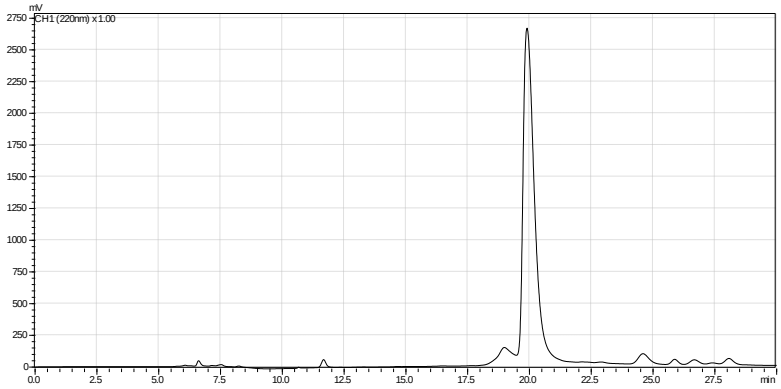


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	19.631	23402904	764917	19.117	21.250	49.0291
2	21.813	24329780	766403	21.250	24.210	50.9709

Figure S3. Chiral HPLC of racemic **3bb**.

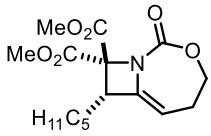


(*S*,*S*) - **3bb** - >99:1 *er*
(after recrystallization)

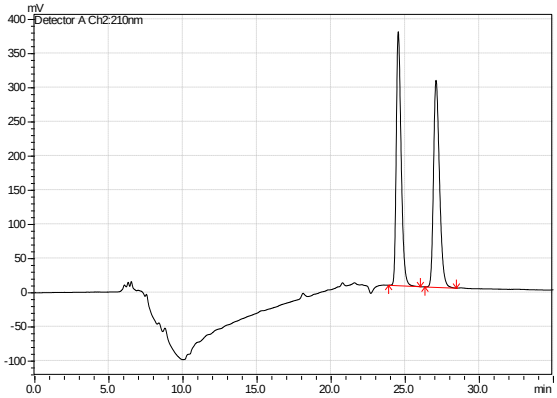


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	19.896	89149438	2671601	19.467	22.124	99.9462
2	22.124	300072	12579	21.925	23.358	0.0538

Figure S4. Chiral HPLC of enantioenriched (*S*,*S*)-**3bb**.

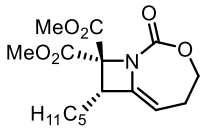


3bc - racemic

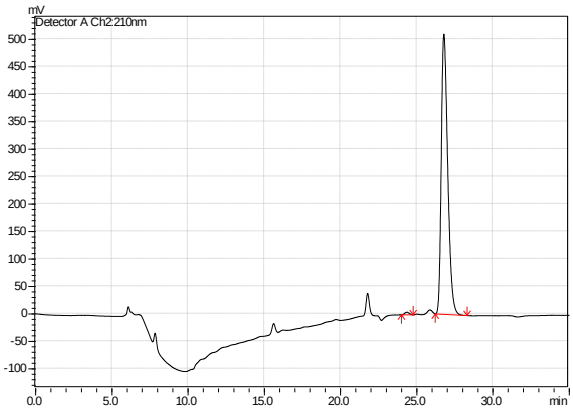


Peak#	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	24.522	11286864	490386	23.900	26.317	50.0890
2	27.074	11246732	399632	26.358	28.458	49.9110

Figure S5. Chiral HPLC of racemic **3bc**.

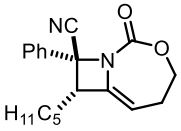


(*S*) - **3bc** - 99:1 *er*

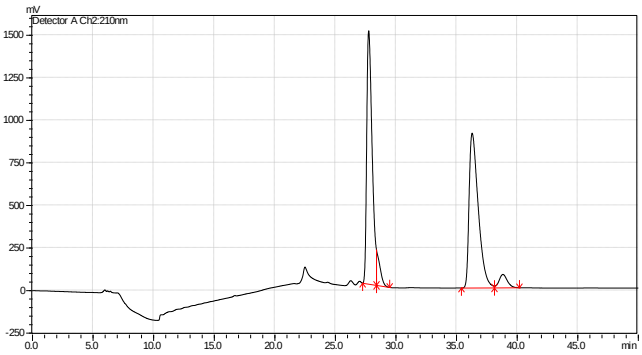


Peak#	Ret. Time.	Area	Height	Peak Start	Peak End	Area%
1	24.343	135432	6530	23.717	24.775	0.6797
2	26.764	19789846	673297	26.192	28.483	99.3203

Figure S6. Chiral HPLC of enantioenriched (*S*)-**3bc**.



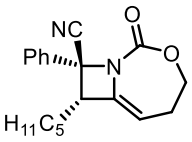
3bd - racemic



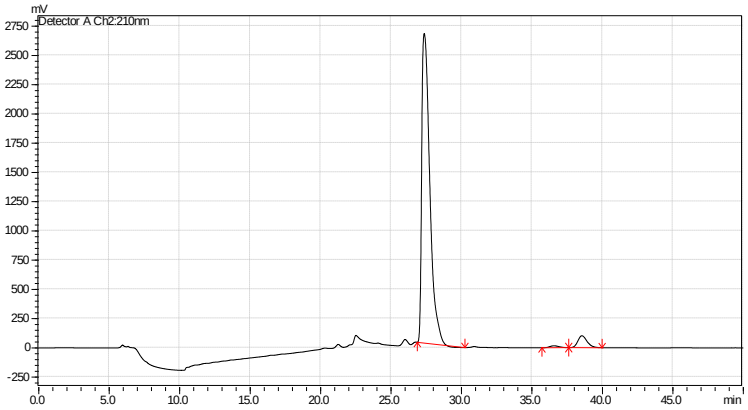
Peak #	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	27.742	40033013	1277911	27.242	28.392	45.3596
2	28.400	3577494	179964	28.392	29.500	4.0535
3	36.280	41251230	782678	35.400	38.117	46.7399
4	38.814	3395312	71033	38.117	40.433	3.8471

Peaks 2 and 4 are likely the minor diastereomer observed.

Figure S7. Chiral HPLC of racemic **3bd**.



(*R,S*) - **3bd** - 99:1 *er*



Peak #	Ret. Time	Area	Height	Peak Start	Peak End	Area%
1	27.346	933505	2440058	26.858	30.358	94.9912
2	36.550	694088	14590	35.700	37.592	0.7063
3	38.539	422822	91440	37.592	40.233	4.3025

Figure S8. Chiral HPLC of enantioenriched (*R,S*)-**3bd**.

VI. Computational Studies.

Computational details.

All the calculations reported in this paper were performed with the Gaussian 09 suite of programs.[4] Electron correlation was partially taken into account using the hybrid functional usually denoted as B3LYP[5] in conjunction with the D3 dispersion correction suggested by Grimme et al.[6] using the standard double-ζ quality def2-SVP[7] basis set for all atoms. The SMD continuum model was used to model the effects of the solvent (CH_2Cl_2). This level is denoted SMD(CH_2Cl_2)-B3LYP-D3/def2-SVP. Geometries were fully optimized in solution without any geometry or symmetry constraints. Reactants, intermediates, and products were characterized by frequency calculations,[8] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their

associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[9] Frequency calculations were also used to determine the difference between the potential (E) and Gibbs (G) energies, G −E, which contains the zero-point, thermal, and entropy energies. Potential energies were refined, E_{sol}, by means of single point (SP) calculations at the same level with a larger basis set, def2-TZVPP,[7] where all elements were described with a triple-ζ + polarization quality basis set. This level is denoted SMD(CH_2Cl_2)-B3LYP-D3/def2-TZVPP//SMD(CH_2Cl_2)-B3LYP-D3/def2-SVP. The ΔG and $\Delta G^{\ddagger}$ values given in the text were obtained from the Gibbs energy in solution, G_{sol}, which was calculated by adding the thermochemistry corrections, G − E, to the refined SP energies, E_{sol}, i.e., $G_{sol} = E_{sol} + G - E$. Cartesian coordinates (in Å) and energies (in a.u.) of all the stationary points discussed in the text are given below. All calculations were performed at the SCM(dichloromethane)-B3LYP- D3/ /def2-SVP level.

Compound 1a

```
 Sum of electronic and zero-point Energies=          -476.823207
 Sum of electronic and thermal Energies=             -476.814066
 Sum of electronic and thermal Enthalpies=           -476.813122
 Sum of electronic and thermal Free Energies=        -476.857914

C       -0.265268000      0.744952000      1.126063000
N        0.325089000     -0.627475000      0.924022000
C        1.402222000     -0.846608000      0.024351000
O        1.882458000      0.219059000     -0.641506000
C        1.014828000      1.344806000     -0.914204000
H        0.250705000      1.023694000     -1.640999000
H        1.654820000      2.096030000     -1.393881000
C        0.379672000      1.876826000      0.358345000
H       -0.360750000      2.652836000      0.106811000
H        1.151116000      2.341663000      0.993082000
O        1.909470000     -1.929807000     -0.102198000
C       -0.976789000     -0.334068000      0.458162000
C       -1.980314000     -0.856550000     -0.236519000
H       -1.860583000     -1.879343000     -0.612835000
C       -3.263200000     -0.136384000     -0.532637000
H       -4.129817000     -0.687455000     -0.126572000
H       -3.272061000      0.878781000     -0.106382000
H       -3.428719000     -0.052527000     -1.621242000
H       -0.482671000      0.946792000      2.182129000
```

Compound 2a-Rh_2

```
 Sum of electronic and zero-point Energies=         -1632.164985
 Sum of electronic and thermal Energies=            -1632.132471
 Sum of electronic and thermal Enthalpies=          -1632.131527
 Sum of electronic and thermal Free Energies=       -1632.231461

Rh       0.008249000      0.065877000      0.118611000
C       -1.922217000      0.567005000      0.308009000
C       -2.116022000      2.026343000      0.493777000
O       -2.032408000      2.583361000      1.566915000
O       -2.341297000      2.635413000     -0.671620000
C       -2.293143000      4.069345000     -0.675523000
H       -1.299791000      4.419937000     -0.356624000
H       -2.485036000      4.377057000     -1.710993000
H       -3.059290000      4.491066000     -0.007434000
C       -3.083230000     -0.261636000      0.217799000
C       -2.977063000     -1.637866000     -0.137895000
C       -4.115812000     -2.426568000     -0.249501000
C       -5.380280000     -1.877120000      0.004352000
C       -5.512859000     -0.526284000      0.362872000
C       -4.384267000      0.275064000      0.459301000
H       -4.495785000      1.325288000      0.737792000
H       -6.501879000     -0.105982000      0.559001000
H       -6.271855000     -2.504134000     -0.080303000
H       -4.025051000     -3.477167000     -0.534822000
H       -1.995072000     -2.058034000     -0.338683000
Rh       2.376849000     -0.526047000     -0.234241000
O        1.968128000     -2.317818000      0.708455000
C        0.804827000     -2.550867000      1.138633000
O       -0.189822000     -1.756227000      1.052317000
O        2.771984000      0.341666000      1.590606000
C        1.825077000      0.835426000      2.266118000
O        0.602863000      0.872795000      1.910399000
O        1.804472000     -1.358751000     -2.034699000
C        0.591331000     -1.334964000     -2.379719000
O       -0.359399000     -0.821182000     -1.702469000
O        2.601372000      1.312122000     -1.143232000
C        1.618701000      2.101919000     -1.214332000
O        0.437635000      1.854518000     -0.805418000
C        1.839583000      3.469234000     -1.807231000
H        1.847654000      4.207744000     -0.988480000
H        2.796830000      3.514990000     -2.342141000
H        1.008932000      3.726708000     -2.480248000
C        0.213037000     -1.930692000     -3.710462000
H        0.056499000     -1.108990000     -4.429049000
H        1.010142000     -2.585797000     -4.084961000
H       -0.733541000     -2.482963000     -3.622358000
C        2.137773000      1.413179000      3.621798000
H        3.221448000      1.504347000      3.769331000
H        1.650301000      2.392804000      3.733291000
H        1.719407000      0.745128000      4.392433000
C        0.542598000     -3.862505000      1.831091000
H        1.399349000     -4.539972000      1.726290000
H        0.356074000     -3.669515000      2.899987000
H       -0.365193000     -4.326120000      1.416762000
```

TS1

```
 Sum of electronic and zero-point Energies=         -2109.007940
 Sum of electronic and thermal Energies=            -2108.965760
 Sum of electronic and thermal Enthalpies=          -2108.964816
 Sum of electronic and thermal Free Energies=       -2109.084315

Rh       0.793925000      0.095547000      0.214943000
C       -1.008631000      0.394823000      1.135822000
C       -1.172131000     -0.525804000      2.298414000
O       -1.048703000     -0.119349000      3.438064000
O       -1.324204000     -1.811205000      1.984844000
C       -1.415120000     -2.724463000      3.079738000
H       -0.482794000     -2.726740000      3.665146000
H       -2.256069000     -2.462381000      3.740111000
H       -1.582129000     -3.713684000      2.634776000
C       -1.759733000      1.635142000      1.123650000
C       -2.821458000      1.880502000      2.037977000
C       -3.528158000      3.076421000      2.006337000
C       -3.207429000      4.062004000      1.059302000
C       -2.179794000      3.837497000      0.138834000
C       -1.467978000      2.638708000      0.164036000
H       -0.678738000      2.464058000     -0.560758000
H       -1.934697000      4.597720000     -0.606917000
H       -3.765120000      5.002343000      1.040616000
H       -4.337320000      3.247455000      2.720772000
H       -3.090340000      1.117332000      2.764605000
N       -2.728766000     -0.708509000     -0.235638000
C       -2.334821000     -1.199627000     -1.605212000
C       -3.087010000      0.024838000     -1.389394000
C       -3.727727000      1.138367000     -1.724115000
H       -4.182030000      1.720142000     -0.914978000
C       -3.843091000      1.659005000     -3.123818000
H       -3.392298000      2.664687000     -3.195712000
H       -3.340875000      1.003595000     -3.851636000
H       -4.899959000      1.766736000     -3.423875000
H       -1.256367000     -1.117371000     -1.752364000
C       -2.976214000     -2.490879000     -2.056898000
C       -4.334251000     -2.661681000     -1.403987000
O       -4.259069000     -2.486034000      0.033135000
C       -3.727140000     -1.367801000      0.541619000
O       -4.051898000     -0.963508000      1.627087000
H       -5.064567000     -1.935257000     -1.796153000
H       -4.735194000     -3.672094000     -1.550631000
H       -3.088491000     -2.505625000     -3.152629000
H       -2.315330000     -3.325940000     -1.775979000
Rh       3.030583000     -0.181862000     -0.807688000
O        3.697420000     -0.751958000      1.063329000
C        2.877359000     -0.854324000      2.019478000
O        1.629426000     -0.612111000      1.956339000
O        3.383025000      1.795823000     -0.334049000
C        2.522517000      2.447619000      0.320839000
O        1.396734000      1.999977000      0.713850000
O        2.507395000     -2.137816000     -1.207599000
C        1.348826000     -2.544333000     -0.908774000
O        0.431679000     -1.845512000     -0.371362000
O        2.184840000      0.402827000     -2.603225000
C        0.971408000      0.743452000     -2.638914000
O        0.175491000      0.753339000     -1.642794000
C        2.839566000      3.870490000      0.703049000
H        3.050689000      3.905611000      1.784529000
H        3.714742000      4.238642000      0.152516000
H        1.966129000      4.511887000      0.514732000
C        3.419564000     -1.252775000      3.368243000
H        4.248768000     -1.964379000      3.253610000
H        3.812542000     -0.346626000      3.860025000
H        2.627425000     -1.672963000      4.001628000
C        0.375013000      1.144116000     -3.963686000
H        1.159983000      1.410242000     -4.683299000
H       -0.196944000      0.288900000     -4.361138000
H       -0.326172000      1.979752000     -3.827797000
```

C	1.021953000	-3.991619000	-1.175213000
H	1.563468000	-4.352420000	-2.060341000
H	1.351003000	-4.585524000	-0.305972000
H	-0.061041000	-4.128242000	-1.294813000

TS1-iso

Sum of electronic and zero-point Energies= -2109.002511
Sum of electronic and thermal Energies= -2108.960323
Sum of electronic and thermal Enthalpies= -2108.959378
Sum of electronic and thermal Free Energies= -2109.078677

Rh	-0.750706000	0.182199000	0.055454000
C	1.042772000	0.946447000	0.687885000
C	1.209343000	0.735692000	2.160968000
O	1.567609000	-0.270593000	2.723582000
O	0.769440000	1.832380000	2.809569000
C	0.561814000	1.694747000	4.218937000
H	-0.088988000	0.834134000	4.431932000
H	1.520682000	1.560069000	4.743721000
H	0.080293000	2.623826000	4.549858000
C	1.762104000	2.016456000	0.029940000
C	1.602607000	2.228295000	-1.365118000
C	2.282191000	3.253746000	-2.014076000
C	3.125816000	4.106965000	-1.289378000
C	3.299368000	3.919487000	0.087512000
C	2.640624000	2.880866000	0.738194000
H	2.799251000	2.735395000	1.804867000
H	3.962905000	4.579355000	0.651640000
H	3.652630000	4.917718000	-1.799924000
H	2.152800000	3.396752000	-3.089796000
H	0.951083000	1.561470000	-1.925416000
N	2.764430000	-0.746040000	0.115152000
C	2.408871000	-1.727669000	-0.973042000
C	2.731794000	-2.139449000	0.382073000
C	3.000675000	-2.998395000	1.355418000
H	3.300054000	-2.578477000	2.321238000
C	2.891074000	-4.486882000	1.219332000
H	2.181103000	-4.898548000	1.957583000
H	2.553515000	-4.784764000	0.214661000
H	3.862491000	-4.975064000	1.413506000
H	1.350419000	-1.647946000	-1.229246000
C	3.363240000	-1.812183000	-2.139631000
C	4.776038000	-1.482562000	-1.696979000
O	4.823545000	-0.250468000	-0.935336000
C	4.036533000	-0.105202000	0.141535000
O	4.371489000	0.585042000	1.067293000
H	5.197378000	-2.285015000	-1.069369000
H	5.445328000	-1.320951000	-2.551075000
H	3.342125000	-2.817721000	-2.589063000
H	3.029913000	-1.095062000	-2.906823000
Rh	-2.994868000	-0.604543000	-0.621015000
O	-3.413712000	1.345439000	-1.146374000
C	-2.537221000	2.242478000	-0.989665000
O	-1.365323000	2.061768000	-0.525702000
O	-3.615682000	-0.223787000	1.308235000
C	-2.784739000	0.207047000	2.156238000
O	-1.561630000	0.472348000	1.926536000
O	-2.223700000	-0.952828000	-2.502600000
C	-1.011969000	-0.698839000	-2.737892000
O	-0.182153000	-0.217025000	-1.896695000
O	-2.392705000	-2.496264000	-0.036442000
C	-1.226170000	-2.668212000	0.418913000
O	-0.345401000	-1.761145000	0.564496000
C	-3.249854000	0.409741000	3.575423000
H	-4.345998000	0.409322000	3.632041000
H	-2.857519000	-0.415057000	4.192901000
H	-2.843236000	1.349738000	3.975362000
C	-2.903529000	3.660357000	-1.346094000
H	-2.028039000	4.193511000	-1.741954000
H	-3.729186000	3.678304000	-2.069735000

H	-3.228562000	4.176959000	-0.427410000
C	-0.809695000	-4.064332000	0.805187000
H	-0.112321000	-4.449409000	0.043749000
H	-0.274150000	-4.044178000	1.764715000
H	-1.680723000	-4.729506000	0.863933000
C	-0.463092000	-1.019271000	-4.103894000
H	0.093483000	-1.969343000	-4.039560000
H	-1.274169000	-1.132980000	-4.834703000
H	0.241479000	-0.239641000	-4.426671000

TS1'

Sum of electronic and zero-point Energies= -2108.995990
Sum of electronic and thermal Energies= -2108.954321
Sum of electronic and thermal Enthalpies= -2108.953377
Sum of electronic and thermal Free Energies= -2109.071323

Rh	0.959139000	0.015964000	-0.025881000
C	-1.078589000	0.425469000	-0.545134000
C	-1.459635000	-0.579348000	-1.589693000
O	-1.377071000	-0.324479000	-2.775594000
O	-1.765103000	-1.793348000	-1.125810000
C	-1.941437000	-2.821788000	-2.104366000
H	-1.017551000	-2.951070000	-2.686500000
H	-2.169062000	-3.736202000	-1.543052000
H	-2.777917000	-2.582278000	-2.774855000
C	-1.584039000	1.797227000	-0.719879000
C	-1.128301000	2.821787000	0.142926000
C	-1.608687000	4.125613000	0.030223000
C	-2.547444000	4.450199000	-0.956507000
C	-3.009592000	3.453243000	-1.823960000
C	-2.544547000	2.143743000	-1.705619000
H	-2.921994000	1.383403000	-2.386497000
H	-3.742904000	3.696558000	-2.597380000
H	-2.915908000	5.475265000	-1.050988000
H	-1.242072000	4.897459000	0.712237000
H	-0.392439000	2.575693000	0.905855000
N	-4.235368000	-0.441869000	-0.280288000
C	-4.536753000	0.738927000	0.614628000
C	-3.342288000	-0.082785000	0.697542000
C	-2.163741000	-0.386617000	1.299823000
H	-1.705210000	-1.355612000	1.110780000
H	-4.499966000	1.690480000	0.072919000
C	-5.659757000	0.535172000	1.606573000
C	-5.817165000	-0.949457000	1.898948000
O	-5.951519000	-1.723194000	0.677614000
C	-5.028763000	-1.632132000	-0.287586000
O	-4.919511000	-2.469485000	-1.138871000
H	-4.955564000	-1.345171000	2.461600000
H	-6.729188000	-1.157921000	2.471097000
H	-5.457271000	1.076502000	2.544266000
H	-6.592332000	0.935463000	1.179014000
Rh	3.357844000	-0.426069000	0.335345000
O	3.742432000	1.053577000	-1.047719000
C	2.781339000	1.690389000	-1.568274000
O	1.546649000	1.487265000	-1.338373000
O	3.261506000	-1.812426000	-1.181152000
C	2.163595000	-1.995365000	-1.781319000
O	1.076552000	-1.387655000	-1.531736000
O	3.333602000	0.985912000	1.833162000
C	2.251885000	1.570591000	2.115454000
O	1.132052000	1.358419000	1.547778000
O	2.790432000	-1.867434000	1.699895000
C	1.562997000	-2.088995000	1.906548000
O	0.597695000	-1.495200000	1.328770000
C	1.206919000	-3.118266000	2.948523000
H	1.902341000	-3.967868000	2.894722000
H	1.317758000	-2.655386000	3.943562000
H	0.170156000	-3.459185000	2.831253000
C	2.266822000	2.625998000	3.190540000
H	2.089048000	3.607845000	2.721891000

H	1.451720000	2.446710000	3.907145000
H	3.234067000	2.643941000	3.708985000
C	2.116688000	-3.042613000	-2.864646000
H	1.411090000	-2.744666000	-3.652096000
H	3.116871000	-3.209382000	-3.286766000
H	1.760892000	-3.988193000	-2.422878000
C	3.111448000	2.813637000	-2.517382000
H	2.384973000	2.847474000	-3.341391000
H	3.042973000	3.764941000	-1.964111000
H	4.131691000	2.704992000	-2.908989000
C	-1.737662000	0.371475000	2.522412000
H	-2.070177000	-0.174673000	3.423216000
H	-0.646516000	0.456227000	2.566352000
H	-2.175682000	1.380249000	2.554366000

INT1

Sum of electronic and zero-point Energies= -2109.026072
Sum of electronic and thermal Energies= -2108.984040
Sum of electronic and thermal Enthalpies= -2108.983096
Sum of electronic and thermal Free Energies= -2109.101594

Rh	-0.694981000	0.003610000	-0.149957000
C	1.557108000	0.292810000	-0.763933000
C	1.481928000	-0.360991000	-2.090458000
O	1.179458000	0.159063000	-3.143730000
O	1.761241000	-1.694270000	-2.005110000
C	1.634401000	-2.443036000	-3.210793000
H	0.604105000	-2.393443000	-3.595535000
H	2.322307000	-2.067538000	-3.984947000
H	1.888507000	-3.480899000	-2.957139000
C	1.893363000	1.765090000	-0.718870000
C	2.452003000	2.454269000	-1.812504000
C	2.761447000	3.814747000	-1.728158000
C	2.537944000	4.523125000	-0.542873000
C	1.986547000	3.853738000	0.554326000
C	1.658444000	2.498918000	0.461191000
H	1.182980000	2.002730000	1.305238000
H	1.790288000	4.393306000	1.485490000
H	2.785616000	5.586346000	-0.477515000
H	3.192357000	4.321659000	-2.596487000
H	2.648524000	1.919781000	-2.738982000
N	2.576984000	-0.495652000	0.072559000
C	2.123620000	-1.600407000	1.073426000
C	2.705166000	-0.373749000	1.531630000
C	3.270164000	0.461771000	2.384782000
H	3.715881000	1.377317000	1.985309000
C	3.295175000	0.238416000	3.862321000
H	2.749901000	1.049910000	4.373785000
H	2.842653000	-0.722759000	4.147088000
H	4.332311000	0.269445000	4.236319000
H	1.037491000	-1.689681000	1.058099000
C	2.887889000	-2.891716000	0.993098000
C	4.367535000	-2.619296000	0.889325000
O	4.649193000	-1.714619000	-0.209507000
C	3.893202000	-0.718438000	-0.623028000
O	4.220296000	0.003802000	-1.514734000
H	4.762635000	-2.158362000	1.806967000
H	4.947191000	-3.522952000	0.664644000
H	2.681060000	-3.480605000	1.900687000
H	2.522503000	-3.460618000	0.125023000
Rh	-3.030782000	-0.202827000	0.588113000
O	-3.559749000	-0.417867000	-1.385586000
C	-2.654520000	-0.397963000	-2.274215000
O	-1.413338000	-0.250924000	-2.064462000
O	-3.197819000	1.836303000	0.411536000
C	-2.195807000	2.503696000	0.013494000
O	-1.065497000	2.022489000	-0.301441000
O	-2.724461000	-2.245256000	0.710335000
C	-1.605172000	-2.731161000	0.388004000
O	-0.588748000	-2.059132000	0.017209000

O	-2.345835000	0.030399000	2.526656000
C	-1.111679000	0.195693000	2.737956000
O	-0.206765000	0.223625000	1.843838000
C	-2.336277000	4.003218000	-0.052830000
H	-1.642298000	4.423693000	-0.792830000
H	-3.372396000	4.285853000	-0.284409000
H	-2.077684000	4.418303000	0.935979000
C	-3.099025000	-0.557342000	-3.706574000
H	-2.237517000	-0.576401000	-4.385739000
H	-3.683919000	-1.484563000	-3.808629000
H	-3.761673000	0.281896000	-3.971497000
C	-0.645610000	0.392590000	4.158362000
H	-1.464516000	0.230442000	4.870529000
H	0.186829000	-0.294351000	4.371831000
H	-0.262351000	1.419969000	4.267738000
C	-1.446371000	-4.230151000	0.407075000
H	-2.250185000	-4.704191000	0.985139000
H	-1.489406000	-4.596908000	-0.631888000
H	-0.463426000	-4.504928000	0.816254000

INT1-iso

Sum of electronic and zero-point Energies= -2109.029771
Sum of electronic and thermal Energies= -2108.987939
Sum of electronic and thermal Enthalpies= -2108.986995
Sum of electronic and thermal Free Energies= -2109.103835

Rh	-0.612800000	-0.028016000	0.038511000
C	1.609978000	0.453411000	0.613077000
C	1.543927000	0.278361000	2.091606000
O	1.989011000	-0.682596000	2.696298000
O	0.878413000	1.255801000	2.726371000
C	0.602890000	1.040697000	4.108815000
H	0.090523000	0.080159000	4.256117000
H	1.529998000	1.050285000	4.704230000
H	-0.048751000	1.867668000	4.420936000
C	1.888907000	1.799285000	-0.005908000
C	2.199635000	1.890234000	-1.380432000
C	2.474406000	3.113157000	-1.997714000
C	2.441060000	4.301581000	-1.263961000
C	2.128308000	4.235261000	0.097625000
C	1.860509000	3.011564000	0.715057000
H	1.621156000	2.997525000	1.773846000
H	2.097376000	5.150019000	0.696893000
H	2.652980000	5.260904000	-1.743567000
H	2.706266000	3.131158000	-3.066582000
H	2.186450000	1.003380000	-2.005845000
N	2.639013000	-0.539562000	0.115899000
C	2.395264000	-1.351496000	-1.204510000
C	2.366165000	-1.987540000	0.077358000
C	2.327046000	-3.004745000	0.917107000
H	2.458922000	-2.781160000	1.977110000
C	2.073149000	-4.410862000	0.483354000
H	1.149250000	-4.786271000	0.954604000
H	1.972806000	-4.504627000	-0.607207000
H	2.891069000	-5.068078000	0.824412000
H	1.444629000	-1.055958000	-1.657422000
C	3.594000000	-1.459636000	-2.108330000
C	4.836797000	-1.750512000	-1.299183000
O	5.017061000	-0.767122000	-0.246868000
C	4.061500000	-0.164968000	0.434216000
O	4.283749000	0.653730000	1.271629000
H	4.793428000	-2.741879000	-0.824885000
H	5.749300000	-1.683483000	-1.904089000
H	3.417242000	-2.282898000	-2.818487000
H	3.708608000	-0.531315000	-2.688375000
Rh	-2.984667000	-0.255360000	-0.556858000
O	-3.220669000	1.740601000	-0.107325000
C	-2.210045000	2.405872000	0.270314000
O	-1.036102000	1.948633000	0.411700000
O	-3.341277000	-0.738220000	1.414779000
C	-2.378364000	-0.770911000	2.236616000

O	-1.162133000	-0.537488000	1.960216000
O	-2.461653000	0.256465000	-2.489970000
C	-1.246416000	0.460329000	-2.772008000
O	-0.273970000	0.384360000	-1.953797000
O	-2.611557000	-2.236513000	-0.983843000
C	-1.445335000	-2.701279000	-0.828931000
O	-0.435181000	-2.048565000	-0.420956000
C	-2.691685000	-1.084504000	3.678503000
H	-2.607293000	-0.155506000	4.265613000
H	-3.708616000	-1.484392000	3.782672000
H	-1.956580000	-1.798747000	4.077043000
C	-2.402655000	3.863689000	0.605511000
H	-1.598974000	4.459065000	0.147665000
H	-3.384585000	4.221539000	0.269862000
H	-2.324562000	3.988090000	1.698042000
C	-1.230214000	-4.163810000	-1.130574000
H	-2.084175000	-4.580152000	-1.680072000
H	-0.303292000	-4.297666000	-1.706073000
H	-1.114247000	-4.707985000	-0.179510000
C	-0.893614000	0.845849000	-4.185983000
H	-1.770598000	0.793281000	-4.843404000
H	-0.494880000	1.873185000	-4.182208000
H	-0.097314000	0.185821000	-4.562602000

TS2

Sum of electronic and zero-point Energies= -2109.007725
Sum of electronic and thermal Energies= -2108.965960
Sum of electronic and thermal Enthalpies= -2108.965016
Sum of electronic and thermal Free Energies= -2109.081642

Rh	-0.633162000	0.080062000	-0.149703000
C	1.645700000	0.303904000	-0.749688000
C	1.418145000	-0.167329000	-2.142485000
O	1.252094000	0.546375000	-3.111470000
O	1.371150000	-1.518796000	-2.228096000
C	1.091953000	-2.055057000	-3.514444000
H	0.108167000	-1.715288000	-3.871186000
H	1.861132000	-1.758279000	-4.245682000
H	1.091546000	-3.147660000	-3.399752000
C	2.111112000	1.746715000	-0.615334000
C	3.022610000	2.283794000	-1.545565000
C	3.522376000	3.581490000	-1.400619000
C	3.130176000	4.374179000	-0.316447000
C	2.233420000	3.850958000	0.620232000
C	1.728899000	2.555006000	0.468950000
H	1.030486000	2.159276000	1.203089000
H	1.917694000	4.455990000	1.475209000
H	3.521350000	5.389230000	-0.203187000
H	4.229026000	3.972052000	-2.138794000
H	3.349778000	1.672349000	-2.384798000
N	2.507200000	-0.616043000	-0.014076000
C	1.813991000	-1.773326000	1.689841000
C	2.581356000	-0.586523000	1.434390000
C	3.163356000	0.337966000	2.202488000
H	3.708832000	1.142362000	1.703449000
C	3.094344000	0.352102000	3.691131000
H	2.616458000	1.286996000	4.030519000
H	2.530352000	-0.501375000	4.096098000
H	4.107644000	0.341205000	4.127771000
H	0.798257000	-1.700655000	2.083272000
C	2.349463000	-3.098769000	1.339182000
C	3.818100000	-3.072500000	0.971565000
O	4.133126000	-2.347644000	-0.232140000
C	3.602759000	-1.220571000	-0.710592000
O	4.050817000	-0.741828000	-1.720487000
H	4.411175000	-2.641333000	1.793420000
H	4.181388000	-4.090154000	0.778975000
H	2.214188000	-3.750950000	2.225268000
H	1.717081000	-3.556133000	0.556620000
Rh	-2.979145000	-0.130633000	0.551823000

O	-3.472019000	-0.471925000	-1.409903000
C	-2.549788000	-0.503286000	-2.279544000
O	-1.316583000	-0.318173000	-2.053847000
O	-3.169831000	1.895112000	0.246253000
C	-2.177948000	2.551460000	-0.194587000
O	-1.029340000	2.075047000	-0.447780000
O	-2.624297000	-2.156974000	0.788017000
C	-1.475367000	-2.625669000	0.548767000
O	-0.465659000	-1.948890000	0.170174000
O	-2.360996000	0.246857000	2.485275000
C	-1.140357000	0.479615000	2.712684000
O	-0.208197000	0.446647000	1.845707000
C	-2.372579000	4.019968000	-0.473043000
H	-3.238983000	4.412198000	0.075596000
H	-1.461646000	4.577936000	-0.213645000
H	-2.548898000	4.149613000	-1.553962000
C	-2.940222000	-0.821270000	-3.700724000
H	-2.272132000	-0.307093000	-4.404816000
H	-2.835065000	-1.907946000	-3.857475000
H	-3.986531000	-0.543978000	-3.886714000
C	-0.733446000	0.846647000	4.117044000
H	-1.559706000	0.689333000	4.821757000
H	0.145952000	0.260843000	4.420863000
H	-0.441173000	1.909443000	4.130490000
C	-1.255961000	-4.102564000	0.762575000
H	-2.212997000	-4.639673000	0.788023000
H	-0.607846000	-4.511185000	-0.025534000
H	-0.746804000	-4.247232000	1.730002000

TS2-iso

Sum of electronic and zero-point Energies=	-2109.007936
Sum of electronic and thermal Energies=	-2108.966422
Sum of electronic and thermal Enthalpies=	-2108.965478
Sum of electronic and thermal Free Energies=	-2109.081307

Rh	-0.604356000	-0.007794000	0.114893000
C	1.698354000	0.481266000	0.804730000
C	1.468332000	0.390898000	2.273455000
O	1.795123000	-0.548153000	2.980258000
O	0.818328000	1.450441000	2.788572000
C	0.423694000	1.350722000	4.154070000
H	-0.209560000	0.466131000	4.309274000
H	1.299470000	1.290093000	4.819675000
H	-0.146303000	2.263533000	4.373035000
C	1.932128000	1.786835000	0.105941000
C	2.244463000	1.770379000	-1.271823000
C	2.490935000	2.941445000	-1.989976000
C	2.439824000	4.185573000	-1.354262000
C	2.139792000	4.224693000	0.011990000
C	1.889455000	3.052999000	0.727812000
H	1.660330000	3.123036000	1.786734000
H	2.103439000	5.184762000	0.535382000
H	2.633129000	5.106578000	-1.910833000
H	2.720934000	2.877345000	-3.057650000
H	2.254065000	0.822325000	-1.800992000
N	2.649858000	-0.514698000	0.365854000
C	2.146512000	-2.011567000	-1.190917000
C	2.326330000	-1.927186000	0.230064000
C	2.262496000	-2.843245000	1.202271000
H	2.473993000	-2.497904000	2.215457000
C	1.923110000	-4.274678000	0.979282000
H	1.088375000	-4.572734000	1.633992000
H	1.656807000	-4.495174000	-0.064822000
H	2.780687000	-4.912690000	1.258322000
H	1.152143000	-2.157883000	-1.623910000
C	3.304533000	-1.806427000	-2.075871000
C	4.633797000	-1.869178000	-1.345461000
O	4.882178000	-0.815409000	-0.396405000
C	4.027662000	-0.153786000	0.394007000
O	4.437395000	0.735940000	1.092765000

H	4.727004000	-2.831070000	-0.816886000
H	5.460070000	-1.789469000	-2.064031000
H	3.278542000	-2.615000000	-2.834204000
H	3.189645000	-0.880764000	-2.674503000
Rh	-2.888815000	-0.248966000	-0.749413000
O	-2.989842000	1.797172000	-0.902681000
C	-1.991816000	2.484888000	-0.529831000
O	-0.912383000	2.017708000	-0.058341000
O	-3.543681000	-0.139651000	1.198636000
C	-2.698457000	-0.049026000	2.138642000
O	-1.439636000	0.016546000	1.995981000
O	-2.073620000	-0.333347000	-2.643743000
C	-0.822257000	-0.240279000	-2.791467000
O	0.023182000	-0.121236000	-1.847293000
O	-2.672070000	-2.283042000	-0.549757000
C	-1.586827000	-2.762199000	-0.109429000
O	-0.561308000	-2.089163000	0.220348000
C	-3.216036000	-0.020315000	3.554949000
H	-2.821526000	-0.892668000	4.099532000
H	-2.842633000	0.881983000	4.062492000
H	-4.313119000	-0.035982000	3.575781000
C	-2.068249000	3.984437000	-0.662004000
H	-1.823699000	4.450290000	0.304655000
H	-1.306138000	4.315694000	-1.385254000
H	-3.063122000	4.304682000	-0.996840000
C	-1.497164000	-4.261175000	0.032085000
H	-2.442873000	-4.737185000	-0.255694000
H	-0.682360000	-4.641697000	-0.601943000
H	-1.250779000	-4.516741000	1.073474000
C	-0.259970000	-0.271927000	-4.189367000
H	0.427796000	-1.126713000	-4.288758000
H	-1.059385000	-0.351566000	-4.936702000
H	0.325567000	0.644539000	-4.362445000

INT2

Sum of electronic and zero-point Energies=	-974.528145
Sum of electronic and thermal Energies=	-974.508736
Sum of electronic and thermal Enthalpies=	-974.507791
Sum of electronic and thermal Free Energies=	-974.575790

C	-0.462812000	-0.696617000	0.229597000
C	-0.119311000	-2.064378000	0.422001000
O	-0.867202000	-3.005550000	0.677491000
O	1.247491000	-2.280930000	0.282730000
C	1.683487000	-3.624024000	0.438838000
H	1.458232000	-4.009109000	1.447169000
H	1.208197000	-4.292266000	-0.297617000
H	2.771337000	-3.619339000	0.280917000
C	-1.812172000	-0.196520000	0.035529000
C	-2.088907000	0.951044000	-0.751784000
C	-3.388401000	1.434807000	-0.917412000
C	-4.475870000	0.785756000	-0.322460000
C	-4.228934000	-0.366372000	0.437000000
C	-2.932952000	-0.848288000	0.618608000
H	-2.764243000	-1.747477000	1.210058000
H	-5.063059000	-0.898251000	0.905441000
H	-5.493786000	1.161352000	-0.455446000
H	-3.551495000	2.322535000	-1.536348000
H	-1.277420000	1.452343000	-1.280591000
N	0.667840000	0.178666000	-0.073254000
C	1.724600000	0.359512000	1.083436000
C	0.842228000	1.422531000	0.706514000
C	0.412086000	2.673448000	0.690668000
H	-0.340070000	2.962060000	-0.047123000
C	0.898544000	3.714236000	1.648126000
H	0.051361000	4.122419000	2.224952000
H	1.647182000	3.319921000	2.350871000
H	1.339650000	4.559793000	1.093231000
H	1.455212000	-0.285656000	1.923028000
C	3.159381000	0.323822000	0.635515000

C	3.329761000	1.088426000	-0.657138000
O	2.431219000	0.586224000	-1.680317000
C	1.209202000	0.133520000	-1.477185000
O	0.522464000	-0.302446000	-2.348431000
H	3.128247000	2.162688000	-0.530289000
H	4.334250000	0.962633000	-1.078919000
H	3.787611000	0.778460000	1.418029000
H	3.462556000	-0.726562000	0.514503000

INT2-iso

Sum of electronic and zero-point Energies= -974.528339
Sum of electronic and thermal Energies= -974.509005
Sum of electronic and thermal Enthalpies= -974.508060
Sum of electronic and thermal Free Energies= -974.575898

C	-0.522985000	0.495458000	0.051837000
C	-0.423928000	1.888654000	-0.238214000
O	0.611220000	2.483994000	-0.552527000
O	-1.608832000	2.567205000	-0.155069000
C	-1.566455000	3.945997000	-0.496682000
H	-0.900626000	4.513211000	0.174785000
H	-1.218699000	4.098012000	-1.531844000
H	-2.595141000	4.319886000	-0.395818000
C	-1.697893000	-0.345265000	0.205113000
C	-2.934739000	0.154332000	0.703453000
C	-4.045017000	-0.671450000	0.864791000
C	-3.989534000	-2.037408000	0.551691000
C	-2.786786000	-2.554231000	0.062341000
C	-1.670145000	-1.732084000	-0.110588000
H	-0.770804000	-2.186805000	-0.527714000
H	-2.711644000	-3.613328000	-0.202565000
H	-4.863694000	-2.679660000	0.685665000
H	-4.972479000	-0.240165000	1.254350000
H	-3.008353000	1.207191000	0.968838000
N	0.758543000	-0.179919000	-0.128582000
C	1.247660000	-1.149077000	1.010317000
C	1.818463000	0.154213000	0.845954000
C	2.711589000	1.114615000	1.020094000
H	2.657948000	1.963130000	0.334667000
C	3.730811000	1.102798000	2.113743000
H	3.591605000	1.977497000	2.772032000
H	3.681268000	0.190472000	2.726763000
H	4.744818000	1.189348000	1.687342000
H	0.443845000	-1.308421000	1.735938000
C	1.981311000	-2.369644000	0.518034000
C	2.919061000	-2.001523000	-0.612274000
O	2.211383000	-1.321034000	-1.682268000
C	1.168049000	-0.524051000	-1.533662000
O	0.544951000	-0.085924000	-2.449258000
H	3.731504000	-1.342965000	-0.272193000
H	3.355833000	-2.889696000	-1.085134000
H	2.563238000	-2.787870000	1.354640000
H	1.255044000	-3.132334000	0.197625000

TS3

Sum of electronic and zero-point Energies= -974.523629
Sum of electronic and thermal Energies= -974.504172
Sum of electronic and thermal Enthalpies= -974.503228
Sum of electronic and thermal Free Energies= -974.572015

C	0.489959000	0.661295000	-0.107443000
C	0.099301000	1.992076000	0.330101000
O	0.835592000	2.943968000	0.544396000
O	-1.247892000	2.066356000	0.543472000
C	-1.746140000	3.330468000	0.972741000
H	-1.260523000	3.654795000	1.906681000
H	-1.576467000	4.101944000	0.204253000
H	-2.824215000	3.199979000	1.135745000
C	1.876384000	0.220465000	-0.142440000

C	2.266268000	-0.802290000	-1.044102000
C	3.583332000	-1.251852000	-1.103103000
C	4.562202000	-0.686857000	-0.273740000
C	4.200431000	0.337855000	0.609997000
C	2.882075000	0.787866000	0.678792000
H	2.616867000	1.586049000	1.371432000
H	4.955521000	0.789236000	1.259802000
H	5.597213000	-1.034930000	-0.323263000
H	3.854649000	-2.038591000	-1.812644000
H	1.517007000	-1.226418000	-1.716550000
N	-0.524742000	-0.224884000	-0.434862000
C	-2.004123000	-0.756037000	1.288282000
C	-0.874147000	-1.284916000	0.583509000
C	-0.153790000	-2.402695000	0.729007000
H	0.677465000	-2.583510000	0.044742000
C	-0.419364000	-3.437026000	1.773608000
H	0.488068000	-3.617592000	2.375682000
H	-1.241911000	-3.147238000	2.445692000
H	-0.678486000	-4.402952000	1.304998000
H	-1.860998000	-0.197548000	2.219726000
C	-3.331715000	-0.712399000	0.631384000
C	-3.299175000	-1.353760000	-0.739891000
O	-2.524545000	-0.592131000	-1.686654000
C	-1.385606000	0.094250000	-1.508181000
O	-1.072607000	0.925920000	-2.325535000
H	-2.906511000	-2.381701000	-0.689400000
H	-4.304304000	-1.390783000	-1.180810000
H	-4.078880000	-1.238603000	1.260691000
H	-3.701026000	0.330490000	0.560695000

TS3-iso

Sum of electronic and zero-point Energies=	-974.522625
Sum of electronic and thermal Energies=	-974.503313
Sum of electronic and thermal Enthalpies=	-974.502368
Sum of electronic and thermal Free Energies=	-974.570679

C	-0.566233000	0.475381000	-0.298052000
C	-0.756917000	1.927620000	-0.422788000
O	0.017281000	2.683873000	-0.989433000
O	-1.893083000	2.384769000	0.149012000
C	-2.169567000	3.776198000	-0.009335000
H	-1.400117000	4.390229000	0.485272000
H	-2.209958000	4.056568000	-1.073686000
H	-3.145896000	3.950039000	0.462133000
C	-1.587080000	-0.493673000	0.052131000
C	-2.984993000	-0.225493000	-0.014040000
C	-3.921660000	-1.178963000	0.365265000
C	-3.519798000	-2.442506000	0.828889000
C	-2.156415000	-2.738652000	0.884092000
C	-1.207070000	-1.793522000	0.489841000
H	-0.158135000	-2.076412000	0.522212000
H	-1.821738000	-3.722667000	1.224108000
H	-4.263346000	-3.187160000	1.124304000
H	-4.986238000	-0.938487000	0.294549000
H	-3.327118000	0.741775000	-0.374476000
N	0.737400000	0.041679000	-0.474482000
C	1.878793000	-0.763168000	1.396902000
C	1.751222000	0.408821000	0.578567000
C	2.342482000	1.608806000	0.614498000
H	2.092672000	2.321642000	-0.172759000
C	3.322599000	2.023458000	1.661914000
H	3.454903000	1.255586000	2.440033000
H	4.307953000	2.228170000	1.206560000
H	3.001250000	2.965111000	2.139872000
H	1.335059000	-0.859927000	2.342957000
C	2.617226000	-1.935154000	0.858676000
C	3.225455000	-1.645228000	-0.498877000
O	2.240673000	-1.472808000	-1.538464000
C	1.040983000	-0.871139000	-1.507783000
O	0.259125000	-1.085416000	-2.401734000

H	3.870621000	-0.753829000	-0.460932000
H	3.831338000	-2.494040000	-0.843015000
H	3.432971000	-2.208340000	1.559543000
H	1.977844000	-2.840078000	0.810252000

Compound 3aa

Sum of electronic and zero-point Energies= -974.625647
Sum of electronic and thermal Energies= -974.606952
Sum of electronic and thermal Enthalpies= -974.606008
Sum of electronic and thermal Free Energies= -974.672579

C	-0.390853000	0.344798000	-0.253320000
C	-0.328180000	1.657275000	0.550117000
O	-1.292457000	2.302284000	0.882379000
O	0.933955000	2.030880000	0.773577000
C	1.129657000	3.245748000	1.508992000
H	0.647042000	4.092696000	0.998088000
H	0.713974000	3.149750000	2.523561000
H	2.214598000	3.400029000	1.558144000
C	-1.749799000	-0.314744000	-0.148486000
C	-1.928704000	-1.534646000	0.515370000
C	-3.195309000	-2.127418000	0.577493000
C	-4.294166000	-1.507566000	-0.023875000
C	-4.120658000	-0.287980000	-0.689705000
C	-2.857653000	0.304484000	-0.750164000
H	-2.728145000	1.257298000	-1.267673000
H	-4.973830000	0.204368000	-1.164087000
H	-5.282734000	-1.971960000	0.024231000
H	-3.320226000	-3.078919000	1.101265000
H	-1.080961000	-2.024461000	0.995193000
N	0.775686000	-0.520221000	-0.003362000
C	2.589444000	-0.575577000	-1.733294000
C	1.380932000	-0.261846000	-1.260850000
C	0.171224000	0.521328000	-1.737345000
H	-0.453511000	-0.083916000	-2.412060000
C	0.373062000	1.909741000	-2.319850000
H	-0.591225000	2.432627000	-2.420437000
H	1.041001000	2.521887000	-1.697877000
H	0.817797000	1.831887000	-3.324484000
H	2.851518000	-0.226837000	-2.735754000
C	3.591981000	-1.386097000	-0.958140000
C	2.975863000	-2.212455000	0.163664000
O	2.482041000	-1.424219000	1.270243000
C	1.284642000	-0.817482000	1.241553000
O	0.693416000	-0.542315000	2.264015000
H	2.161090000	-2.850747000	-0.216617000
H	3.736794000	-2.861500000	0.617339000
H	4.108622000	-2.087401000	-1.636873000
H	4.383860000	-0.741672000	-0.533097000

Compound 3aa-iso

Sum of electronic and zero-point Energies= -974.620725
Sum of electronic and thermal Energies= -974.601973
Sum of electronic and thermal Enthalpies= -974.601028
Sum of electronic and thermal Free Energies= -974.668453

C	0.266470000	0.284690000	-0.446351000
C	0.376646000	1.823935000	-0.406662000
O	-0.542761000	2.532297000	-0.747187000
O	1.543672000	2.281182000	0.031291000
C	1.685156000	3.706484000	0.123182000
H	1.550721000	4.176733000	-0.862880000
H	0.944730000	4.120771000	0.824287000
H	2.701425000	3.886512000	0.494617000
C	1.459933000	-0.498302000	0.066239000
C	2.729760000	-0.276070000	-0.494733000
C	3.827502000	-1.045063000	-0.104060000
C	3.675492000	-2.053759000	0.854673000
C	2.415195000	-2.287983000	1.410321000

C	1.314237000	-1.519902000	1.014450000
H	0.336235000	-1.729069000	1.448541000
H	2.281867000	-3.075701000	2.156586000
H	4.534866000	-2.654944000	1.163245000
H	4.806761000	-0.855941000	-0.552020000
H	2.860646000	0.506920000	-1.243474000
N	-1.038052000	-0.084717000	0.125190000
C	-2.762076000	-1.155806000	-1.323671000
C	-1.577941000	-0.590853000	-1.074447000
C	-0.321506000	-0.231708000	-1.847995000
H	-0.499535000	0.625678000	-2.513478000
C	0.399710000	-1.347867000	-2.580704000
H	0.576139000	-2.215228000	-1.927711000
H	-0.211061000	-1.679841000	-3.435632000
H	1.370454000	-1.005722000	-2.970735000
H	-2.964603000	-1.503507000	-2.339761000
C	-3.832021000	-1.270332000	-0.270554000
C	-3.823566000	-0.118854000	0.732459000
O	-2.743175000	-0.153244000	1.692319000
C	-1.483288000	0.206615000	1.388874000
O	-0.757859000	0.720745000	2.215456000
H	-3.806583000	0.851964000	0.210072000
H	-4.725421000	-0.157972000	1.358138000
H	-4.824387000	-1.272092000	-0.751758000
H	-3.763116000	-2.224730000	0.284474000

INT2-E

Sum of electronic and zero-point Energies= -971.385789
Sum of electronic and thermal Energies= -971.366705
Sum of electronic and thermal Enthalpies= -971.365761
Sum of electronic and thermal Free Energies= -971.432860

C	0.805768000	0.725182000	-0.351583000
C	2.138414000	0.218677000	-0.525392000
O	3.156424000	0.836286000	-0.783965000
O	2.171226000	-1.156523000	-0.352236000
C	3.449074000	-1.769127000	-0.475281000
H	3.874310000	-1.619225000	-1.481227000
H	4.161195000	-1.367937000	0.264019000
H	3.298330000	-2.842646000	-0.295080000
N	-0.198204000	-0.261710000	0.019317000
C	-0.554638000	-1.345957000	-1.058560000
C	-1.482637000	-0.311564000	-0.707930000
C	-2.657471000	0.292108000	-0.659055000
H	-2.768354000	1.121789000	0.042585000
C	-3.817544000	-0.092554000	-1.519489000
H	-4.132706000	0.765823000	-2.137064000
H	-3.586430000	-0.938713000	-2.183268000
H	-4.681920000	-0.360205000	-0.887843000
H	0.084845000	-1.214362000	-1.935304000
C	-0.682838000	-2.742295000	-0.515847000
C	-1.430926000	-2.730511000	0.798323000
O	-0.797212000	-1.836455000	1.750719000
C	-0.176907000	-0.710172000	1.455808000
O	0.395819000	-0.048383000	2.263612000
H	-2.474779000	-2.405322000	0.675033000
H	-1.419168000	-3.712986000	1.285504000
H	-1.230115000	-3.358908000	-1.246272000
H	0.325436000	-3.164974000	-0.392660000
C	0.523086000	2.113203000	-0.112643000
O	1.249911000	3.067024000	-0.335034000
O	-0.727146000	2.293545000	0.434582000
C	-1.110375000	3.639702000	0.683370000
H	-2.133357000	3.604231000	1.083839000
H	-0.444245000	4.117987000	1.419792000
H	-1.095819000	4.243324000	-0.239017000

TS3-E

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 Sum of electronic and zero-point Energies=           -971.370382
 Sum of electronic and thermal Energies=              -971.350941
 Sum of electronic and thermal Enthalpies=            -971.349997
 Sum of electronic and thermal Free Energies=         -971.419628

C       -0.821769000      0.706809000     -0.024512000
C       -0.362890000      2.013031000     -0.449263000
O       -1.018116000      3.004942000     -0.709509000
O        1.011455000      2.013422000     -0.576326000
C        1.595536000      3.244808000     -0.987459000
H        1.233268000      3.549458000     -1.982737000
H        1.364453000      4.051683000     -0.273455000
H        2.681036000      3.079281000     -1.020777000
N        0.142982000     -0.221875000      0.376057000
C        1.647000000     -0.766667000     -1.200536000
C        0.479694000     -1.309010000     -0.573027000
C       -0.258886000     -2.405305000     -0.780174000
H       -1.132190000     -2.546809000     -0.140441000
C        0.044892000     -3.436813000     -1.812722000
H       -0.836832000     -3.602196000     -2.455522000
H        0.904568000     -3.164310000     -2.444283000
H        0.262736000     -4.406816000     -1.331721000
H        1.591035000     -0.314974000     -2.198358000
C        2.909719000     -0.656975000     -0.449554000
C        2.850487000     -1.358759000      0.890710000
O        1.964353000     -0.715181000      1.825838000
C        0.868222000      0.014933000      1.567262000
O        0.485378000      0.818539000      2.378885000
H        2.542520000     -2.409459000      0.769917000
H        3.833307000     -1.340070000      1.380201000
H        3.712662000     -1.102833000     -1.071058000
H        3.195720000      0.408436000     -0.342828000
C       -2.231137000      0.362660000      0.001820000
O       -3.151942000      1.016253000     -0.455939000
O       -2.456810000     -0.818544000      0.655000000
C       -3.811501000     -1.253467000      0.708092000
H       -4.230340000     -1.398127000     -0.301604000
H       -3.808968000     -2.209493000      1.249386000
H       -4.444595000     -0.527558000      1.243486000
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Compound 3bc'

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 Sum of electronic and zero-point Energies=           -971.469165
 Sum of electronic and thermal Energies=              -971.450512
 Sum of electronic and thermal Enthalpies=            -971.449568
 Sum of electronic and thermal Free Energies=         -971.516105

C        0.706698000      0.100521000      0.441884000
C        1.263778000      1.219011000     -0.447218000
O        2.432625000      1.332706000     -0.728017000
O        0.302185000      2.051733000     -0.835686000
C        0.682923000      3.109128000     -1.728284000
H        1.441327000      3.756517000     -1.263086000
H        1.084312000      2.689907000     -2.663145000
H       -0.231770000      3.679486000     -1.930457000
N       -0.611548000     -0.388638000      0.027132000
C       -2.580070000      0.195418000      1.464023000
C       -1.280016000      0.127398000      1.171607000
C        0.034220000      0.566195000      1.798258000
H        0.351657000     -0.121027000      2.596898000
C        0.190654000      2.002777000      2.266205000
H        1.249915000      2.217390000      2.479546000
H       -0.171414000      2.719878000      1.516961000
H       -0.379284000      2.155044000      3.196109000
H       -2.868928000      0.678141000      2.401427000
C       -3.651613000     -0.367851000      0.570097000
C       -3.143079000     -1.417433000     -0.411585000
O       -2.307325000     -0.881612000     -1.461709000
C       -1.007066000     -0.602389000     -1.278322000
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O	-0.242141000	-0.524909000	-2.213278000
H	-2.597394000	-2.218978000	0.113157000
H	-3.986754000	-1.871594000	-0.948121000
H	-4.434332000	-0.845702000	1.184900000
H	-4.161878000	0.433429000	0.003920000
C	1.789739000	-0.960904000	0.632877000
O	2.605054000	-0.911288000	1.522003000
O	1.711086000	-1.923274000	-0.278554000
C	2.690866000	-2.969867000	-0.202033000
H	2.619676000	-3.497448000	0.761592000
H	2.466208000	-3.655402000	-1.028382000
H	3.705394000	-2.558058000	-0.314373000

Int1-b

Sum of electronic and zero-point Energies= -2110.230923
Sum of electronic and thermal Energies= -2110.188903
Sum of electronic and thermal Enthalpies= -2110.187959
Sum of electronic and thermal Free Energies= -2110.305171

Rh	-0.698807000	-0.054520000	0.010305000
C	1.529231000	-0.499069000	0.539571000
C	1.358972000	-0.555753000	2.016200000
O	1.564655000	0.332436000	2.830320000
O	0.886074000	-1.757476000	2.390913000
C	0.410333000	-1.869726000	3.728843000
H	1.211907000	-1.673278000	4.458529000
H	-0.415569000	-1.163867000	3.902676000
H	0.050162000	-2.901287000	3.838530000
C	2.155765000	-1.776586000	-0.012320000
C	1.653042000	-2.444444000	-1.138142000
C	2.283350000	-3.593752000	-1.629470000
C	3.432821000	-4.093806000	-1.011812000
C	3.951886000	-3.434712000	0.108989000
C	3.317953000	-2.290956000	0.599415000
H	3.727170000	-1.794942000	1.484099000
H	4.848724000	-3.815983000	0.605258000
H	3.922215000	-4.991836000	-1.399031000
H	1.869556000	-4.099041000	-2.506832000
H	0.769267000	-2.049838000	-1.633741000
N	2.503307000	0.635473000	0.127342000
C	3.622459000	1.122770000	1.033475000
C	2.511358000	2.046459000	0.690533000
H	3.511807000	0.689735000	2.026036000
C	5.029702000	1.044670000	0.504514000
C	5.139290000	1.263390000	-0.987362000
O	4.056900000	0.628680000	-1.710771000
C	2.787035000	0.614645000	-1.341034000
O	1.890671000	0.549876000	-2.118130000
H	5.131819000	2.328990000	-1.259264000
H	6.052863000	0.814636000	-1.396136000
H	5.656701000	1.781205000	1.031262000
H	5.410882000	0.045136000	0.762360000
Rh	-3.089856000	0.368355000	-0.429277000
O	-3.420874000	-1.624667000	-0.001017000
C	-2.443152000	-2.368099000	0.308118000
O	-1.230609000	-2.005650000	0.388504000
O	-2.775465000	-0.116349000	-2.402654000
C	-1.620620000	-0.502827000	-2.751856000
O	-0.605882000	-0.566261000	-1.998696000
O	-3.299853000	0.830761000	1.571117000
C	-2.286277000	0.780676000	2.326472000
O	-1.112089000	0.468435000	1.965236000
O	-2.569825000	2.326346000	-0.820802000
C	-1.363343000	2.692879000	-0.718556000
O	-0.385414000	1.949843000	-0.391946000
C	-1.044933000	4.136699000	-1.027702000
H	-1.964801000	4.722635000	-1.149521000
H	-0.426784000	4.567594000	-0.226358000
H	-0.460669000	4.182331000	-1.960944000
C	-2.491417000	1.085861000	3.790131000

H	-1.540311000	1.353020000	4.268737000
H	-3.226879000	1.893701000	3.912777000
H	-2.895081000	0.185553000	4.282593000
C	-1.433231000	-0.962599000	-4.176701000
H	-2.228241000	-0.571173000	-4.825250000
H	-0.444644000	-0.656833000	-4.547327000
H	-1.472999000	-2.064813000	-4.194146000
C	-2.727998000	-3.814871000	0.629953000
H	-3.772982000	-4.071021000	0.413160000
H	-2.049717000	-4.462139000	0.053729000
H	-2.520556000	-3.989282000	1.698243000
H	1.759400000	2.121281000	1.477226000
C	2.547176000	3.234218000	-0.240287000
H	3.289047000	3.121730000	-1.041743000
H	1.562396000	3.288821000	-0.720090000
C	2.832750000	4.513379000	0.548894000
H	3.826944000	4.484265000	1.023887000
H	2.085167000	4.665467000	1.344309000
H	2.800659000	5.389878000	-0.116445000

TS4-b

Sum of electronic and zero-point Energies= -2110.212077
Sum of electronic and thermal Energies= -2110.170342
Sum of electronic and thermal Enthalpies= -2110.169398
Sum of electronic and thermal Free Energies= -2110.289462

Rh	0.899945000	-0.106371000	-0.006379000
C	-2.167924000	0.738161000	0.706259000
C	-1.643584000	0.490879000	2.071925000
O	-1.603132000	-0.604106000	2.607476000
O	-1.248368000	1.610741000	2.700387000
C	-0.579120000	1.432872000	3.947207000
H	-1.245052000	0.970560000	4.692835000
H	0.312427000	0.802085000	3.817857000
H	-0.283168000	2.435637000	4.281548000
C	-2.323951000	2.099604000	0.158577000
C	-1.319183000	3.081731000	0.296542000
C	-1.503272000	4.361401000	-0.225835000
C	-2.689722000	4.697052000	-0.892004000
C	-3.689009000	3.729729000	-1.043136000
C	-3.502804000	2.442750000	-0.535348000
H	-4.285574000	1.694467000	-0.672724000
H	-4.616828000	3.975605000	-1.567031000
H	-2.828962000	5.702511000	-1.298259000
H	-0.708075000	5.104777000	-0.119738000
H	-0.385366000	2.821355000	0.791727000
N	-2.695849000	-0.340789000	0.105632000
C	-5.043660000	-0.743604000	0.287969000
C	-3.913146000	-1.295188000	0.943324000
H	-5.480898000	0.142663000	0.758097000
C	-5.541975000	-1.053709000	-1.078514000
C	-4.633951000	-1.977841000	-1.857020000
O	-3.250133000	-1.563996000	-1.854042000
C	-2.651382000	-0.486479000	-1.309648000
O	-1.946526000	0.210823000	-1.992708000
H	-4.663348000	-2.997003000	-1.446006000
H	-4.939465000	-2.031720000	-2.912990000
H	-6.548263000	-1.518750000	-1.047652000
H	-5.684812000	-0.106284000	-1.633259000
Rh	3.231954000	-0.440164000	-0.455412000
O	3.644079000	0.920940000	1.029473000
C	2.686988000	1.460579000	1.664033000
O	1.455975000	1.238965000	1.450305000
O	3.124405000	1.097195000	-1.817617000
C	2.015263000	1.697310000	-1.981367000
O	0.940573000	1.420876000	-1.371218000
O	3.223109000	-1.946303000	0.939175000
C	2.135140000	-2.243504000	1.525240000
O	1.025905000	-1.659999000	1.340993000
O	2.686490000	-1.783340000	-1.912558000

C	1.452253000	-2.018041000	-2.107638000
O	0.500676000	-1.478148000	-1.469911000
C	1.100562000	-3.025497000	-3.168862000
H	0.017859000	-3.040191000	-3.347080000
H	1.637969000	-2.785874000	-4.098743000
H	1.434471000	-4.022574000	-2.838822000
C	2.161565000	-3.403177000	2.484807000
H	3.138053000	-3.468495000	2.984225000
H	1.352135000	-3.314643000	3.221452000
H	2.009337000	-4.331272000	1.908275000
C	1.959729000	2.800525000	-3.004035000
H	1.210225000	3.549448000	-2.713740000
H	2.946792000	3.264741000	-3.132726000
H	1.650624000	2.363150000	-3.968244000
C	3.032920000	2.404605000	2.783794000
H	4.022192000	2.853395000	2.623378000
H	2.264593000	3.183522000	2.881650000
H	3.060359000	1.828732000	3.724172000
H	-3.805250000	-0.893596000	1.952741000
C	-3.432141000	-2.739619000	0.941032000
H	-3.187704000	-3.094017000	-0.066972000
H	-2.489381000	-2.742488000	1.507548000
C	-4.451251000	-3.671320000	1.599935000
H	-5.393615000	-3.711028000	1.028710000
H	-4.696833000	-3.342606000	2.623763000
H	-4.053460000	-4.697004000	1.665713000

INT2-b

Sum of electronic and zero-point Energies= -975.745795
Sum of electronic and thermal Energies= -975.726326
Sum of electronic and thermal Enthalpies= -975.725381
Sum of electronic and thermal Free Energies= -975.793752

C	0.628154000	0.534336000	-0.123104000
C	0.575238000	1.946274000	0.075862000
O	-0.454147000	2.611806000	0.234270000
O	1.796313000	2.564258000	0.063520000
C	1.789103000	3.972242000	0.255770000
H	1.234983000	4.491275000	-0.544221000
H	1.335514000	4.248528000	1.221765000
H	2.841010000	4.290766000	0.239163000
C	1.761530000	-0.369264000	-0.185837000
C	3.070378000	0.054873000	-0.556504000
C	4.134717000	-0.840294000	-0.637632000
C	3.965210000	-2.205172000	-0.362901000
C	2.691964000	-2.648466000	0.005201000
C	1.619702000	-1.757473000	0.095318000
H	0.658380000	-2.162652000	0.412076000
H	2.523925000	-3.704492000	0.237933000
H	4.804723000	-2.901493000	-0.432250000
H	5.119636000	-0.463351000	-0.930808000
H	3.237029000	1.104856000	-0.787315000
N	-0.688799000	-0.081805000	0.014865000
C	-1.269065000	-0.910411000	-1.131956000
C	-1.802329000	0.445895000	-0.904651000
H	-0.529957000	-0.986733000	-1.932793000
C	-1.913889000	-2.217750000	-0.764210000
C	-2.682360000	-2.151600000	0.537110000
O	-1.954540000	-1.439600000	1.571218000
C	-1.087140000	-0.453522000	1.411871000
O	-0.581602000	0.108252000	2.333073000
H	-3.657518000	-1.659853000	0.421617000
H	-2.853146000	-3.151673000	0.954445000
H	-2.598953000	-2.513127000	-1.574263000
H	-1.128559000	-2.986292000	-0.708087000
H	-1.364566000	1.195522000	-1.564257000
C	-3.132850000	0.892671000	-0.344856000
H	-3.425767000	0.339608000	0.556775000
H	-2.989922000	1.936625000	-0.030990000
C	-4.229306000	0.784210000	-1.406594000

H	-4.402185000	-0.262995000	-1.703856000
H	-3.967779000	1.353756000	-2.313239000
H	-5.177797000	1.187344000	-1.019723000

TS5-b

Sum of electronic and zero-point Energies= -975.730210
Sum of electronic and thermal Energies= -975.710488
Sum of electronic and thermal Enthalpies= -975.709544
Sum of electronic and thermal Free Energies= -975.778700

C	0.641612000	0.540081000	0.250896000
C	0.745170000	2.011796000	0.185683000
O	-0.174796000	2.775896000	0.432561000
O	1.951773000	2.456152000	-0.216573000
C	2.115609000	3.873048000	-0.295133000
H	1.410776000	4.312030000	-1.018921000
H	1.953089000	4.347510000	0.685666000
H	3.148230000	4.043358000	-0.626187000
C	1.756665000	-0.379412000	-0.021164000
C	3.095765000	-0.088687000	0.330587000
C	4.118774000	-0.997824000	0.065871000
C	3.844976000	-2.219005000	-0.564037000
C	2.525890000	-2.525896000	-0.913386000
C	1.495788000	-1.626119000	-0.636004000
H	0.474240000	-1.889196000	-0.914168000
H	2.294332000	-3.476002000	-1.402630000
H	4.651689000	-2.926880000	-0.771516000
H	5.143205000	-0.752339000	0.359239000
H	3.328779000	0.851024000	0.829067000
N	-0.605134000	0.078953000	0.437084000
C	-1.870245000	-0.552620000	-1.488093000
C	-1.870648000	0.592834000	-0.652058000
H	-1.180283000	-0.524319000	-2.336701000
C	-2.489701000	-1.870935000	-1.198564000
C	-2.973631000	-1.999592000	0.227614000
O	-1.960099000	-1.758902000	1.224723000
C	-0.846621000	-1.015212000	1.301291000
O	-0.081741000	-1.243916000	2.210047000
H	-3.821601000	-1.329077000	0.423094000
H	-3.311557000	-3.025282000	0.431772000
H	-3.358689000	-2.065398000	-1.860229000
H	-1.767443000	-2.677038000	-1.426936000
H	-1.371766000	1.436032000	-1.134372000
C	-3.001619000	1.124556000	0.218686000
H	-3.272172000	0.420549000	1.016148000
H	-2.598902000	2.015183000	0.722258000
C	-4.236480000	1.484793000	-0.607981000
H	-4.674094000	0.595252000	-1.090284000
H	-3.989292000	2.205981000	-1.404691000
H	-5.011536000	1.941257000	0.028480000

Compound 5c

Sum of electronic and zero-point Energies= -975.781350
Sum of electronic and thermal Energies= -975.760305
Sum of electronic and thermal Enthalpies= -975.759361
Sum of electronic and thermal Free Energies= -975.832745

C	0.614149000	0.324716000	0.594724000
C	0.306014000	1.818095000	0.633818000
O	-0.270374000	2.375839000	1.533296000
O	0.715731000	2.401713000	-0.493635000
C	0.390934000	3.791423000	-0.655870000
H	-0.699435000	3.937852000	-0.624447000
H	0.858961000	4.392894000	0.137982000
H	0.785878000	4.083144000	-1.636571000
C	1.977878000	-0.110777000	0.211598000
C	3.078128000	0.707738000	0.533180000
C	4.376250000	0.299184000	0.225659000
C	4.591460000	-0.920322000	-0.426027000

C	3.503152000	-1.732930000	-0.764609000
C	2.205095000	-1.335660000	-0.443727000
H	1.369012000	-1.975794000	-0.728669000
H	3.665562000	-2.680528000	-1.283835000
H	5.607940000	-1.235634000	-0.675051000
H	5.222900000	0.936532000	0.492166000
H	2.920445000	1.662241000	1.041426000
N	-0.398015000	-0.400856000	0.858619000
C	-2.103647000	0.595828000	-1.488656000
C	-3.007288000	0.843322000	-0.527433000
H	-1.852862000	1.443305000	-2.140301000
C	-1.335321000	-0.641652000	-1.882389000
C	-1.632049000	-2.017869000	-1.292932000
O	-1.154638000	-2.427227000	0.021041000
C	-0.466476000	-1.778810000	0.967825000
O	-0.063304000	-2.380590000	1.937371000
H	-2.717339000	-2.196050000	-1.273643000
H	-1.189225000	-2.769711000	-1.962598000
H	-1.523807000	-0.790436000	-2.962564000
H	-0.254196000	-0.426669000	-1.839484000
H	-3.407249000	1.866783000	-0.502285000
C	-3.563804000	-0.040859000	0.553874000
H	-3.126370000	-1.045914000	0.531216000
H	-3.262858000	0.393819000	1.524851000
C	-5.093659000	-0.142009000	0.501559000
H	-5.429871000	-0.616331000	-0.435854000
H	-5.565231000	0.853999000	0.557441000
H	-5.480352000	-0.741884000	1.341733000

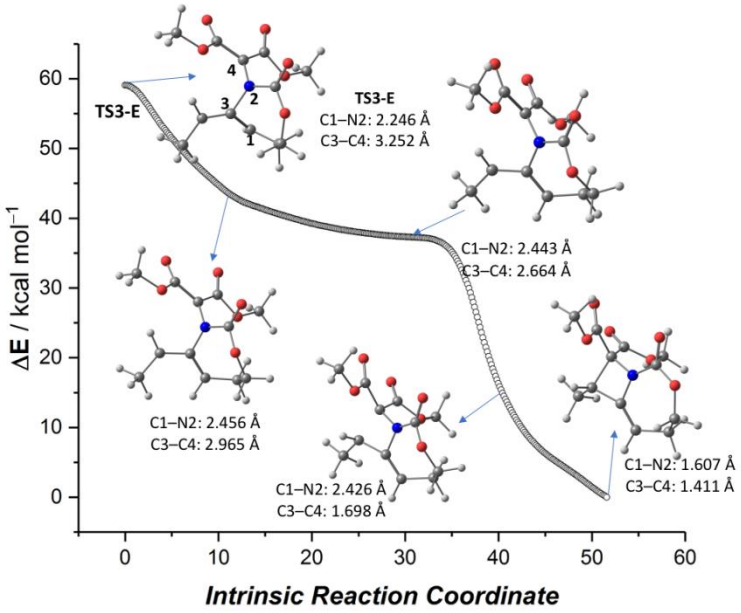
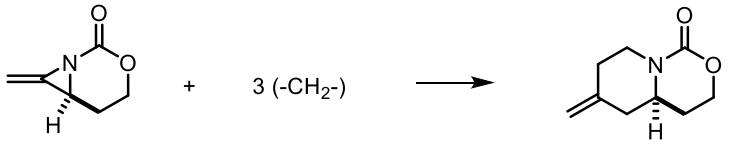


Figure S9. Computed intrinsic reaction coordinate (IRC) at the reference SCM(CH_2Cl_2)-B3LYP-D3/def2-SVP level for the transformation of **TS3-E** into **3bc'.**

VII. Ring Strain Calculations

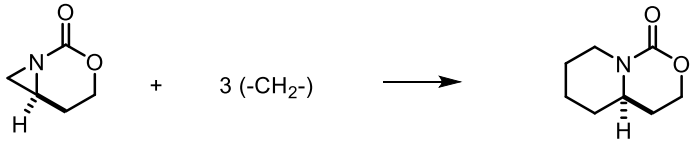
Ring strain energies estimates were preformed via simple, gas-phase DFT calculations (B3LYP/6-311G*) according to Dudev and Lim.[10] Thus, isodesmic equations using the strained molecule of interest plus a number of unstrained CH_2 groups (derived from geometry optimization of n-hexane) were balanced against an unstrained, ring-expanded variant as per equations 1 and 2.



A **B** **C** (1)

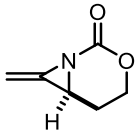
strain energy (B3LYP/6-311G)* = *A* + *B* - *C* = 44.2 kcal/mol

The B3LYP energy of the right side of the equation was subtracted from the combined B3LYP energies of the strained molecule and requisite number of methylene groups yielding an estimate of the additional ring strain present in the aziridines. For the ring expanded piperidine in equation 1, several vinyl isomers were evaluated and the 4-vinyl isomer was chosen as the equatorial vinyl group at the 4 position is the lowest energy isomer (higher energy isomers with interactions between the vinyl group and the carbamate ring thus underestimate the strain associate with **A**).



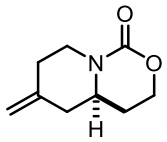
(2)

strain energy (B3LYP/6-311G):* 39.7 kcal/mol



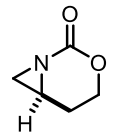
B3LYP energy = -438.079668341

C	0.00000000	0.00000000	0.00000000
N	-0.71214400	-1.32617100	0.06654800
C	-1.97782800	-1.47203100	0.71090000
O	-2.54872200	-0.33266100	1.18352000
C	-1.67789800	0.70510400	1.68741900
H	-1.14863100	0.31904000	2.56312800
H	-2.34854300	1.49854700	2.01192300
C	-0.70593700	1.18509600	0.62004000
H	0.01041700	1.89027100	1.05376400
H	-1.25766600	1.71636400	-0.16140600
O	-2.53795600	-2.52295700	0.77700200
C	0.46870500	-1.12453200	0.79841700
C	1.26990100	-1.69877000	1.67545700
H	1.06854800	-2.69579500	2.05014400
H	2.15766300	-1.18733700	2.02737500
H	0.44420900	0.16398100	-0.97866200



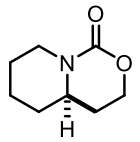
B3LYP energy = -556.115511734

C	0.00000000	0.00000000	0.00000000
N	-0.46854200	1.35623300	-0.32475300
C	-1.76762100	1.73116200	-0.59086900
O	-2.64775400	0.72326800	-0.85635000
C	-2.12285500	-0.57453800	-1.16136300
H	-1.64388000	-0.54833300	-2.14702200
H	-2.99204900	-1.22908900	-1.22228500
C	-1.15567500	-1.00014900	-0.07458600
H	-0.77312200	-2.00802000	-0.26063200
H	-1.69634800	-1.02560800	0.87580500
O	-2.15314500	2.87524900	-0.61379700
C	0.54199100	2.40024900	-0.16504300
C	1.74787800	2.10829900	-1.07438400
C	2.26023300	0.70479600	-0.85588600
C	1.18918800	-0.35946300	-0.91826400
H	0.81950900	-0.45754000	-1.94771400
H	1.59581300	-1.33076800	-0.62104000
C	3.53292900	0.42822100	-0.57567500
H	4.28617500	1.20812300	-0.51703500
H	3.87417500	-0.58863100	-0.40521300
H	1.42417000	2.22724200	-2.11644800
H	2.53734600	2.84283200	-0.89238600
H	0.07818700	3.35352300	-0.40526100
H	0.86603900	2.43735100	0.88366300
H	0.38303800	0.02367900	1.02977300



B3LYP energy = -399.995938255

C	0.00000000	0.00000000	0.00000000
N	1.45731900	0.17145000	-0.00328400
C	2.32538700	-0.91355300	0.27155000
O	1.77015600	-2.16347800	0.29072900
C	0.45726100	-2.28993100	0.87059100
H	0.52421900	-2.06579800	1.94072800
H	0.20195200	-3.34369000	0.76967800
C	-0.55481000	-1.39595800	0.16914000
H	-1.50002600	-1.38748400	0.72219400
H	-0.76446900	-1.80666600	-0.82326400
O	3.50469800	-0.77114700	0.40497700
C	0.67037600	0.75671000	1.09477000
H	0.75154100	0.29543900	2.07498200
H	0.63888500	1.84104500	1.10884000
H	-0.47796000	0.59255700	-0.77612700



B3LYP energy = -518.024518653

C	0.00000000	0.00000000	0.00000000
N	-0.29582200	1.39865300	-0.36109800
C	-1.54387700	1.92753500	-0.60498700
O	-2.53872200	1.03155600	-0.87003400
C	-2.16597500	-0.31584100	-1.18168500
H	-1.67484900	-0.33874100	-2.16126100
H	-3.10462800	-0.86458100	-1.25606800
C	-1.26656600	-0.85697500	-0.08866500
H	-1.00268600	-1.90186700	-0.27653100
H	-1.81709900	-0.82288700	0.85581900
O	-1.79336900	3.10931200	-0.61806000
C	0.83036500	2.32000600	-0.19740400
H	1.12528200	2.34731000	0.86195100
H	0.48519900	3.31538000	-0.46559100
C	2.01007800	1.86824600	-1.06171600
C	2.38157800	0.40811300	-0.77280700
C	1.15788100	-0.51286800	-0.87225600
H	0.82225000	-0.57982900	-1.91410600
H	1.42189800	-1.52744100	-0.55354000
H	3.16659800	0.06874400	-1.45565000
H	2.80168600	0.33558400	0.23904800
H	1.73773600	1.98240400	-2.11718000
H	2.86784300	2.52441000	-0.88102900

H 0.35119300 0.00198400 1.04300700

VIII. Crystallographic Information for (*S*,*S*)-**3bb**.

Data Collection

The deposition number for (*S*,*S*)-**3bb** is CCDC 183870.

A colorless crystal with approximate dimensions 0.064 x 0.048 x 0.027 mm^3 was selected under oil under ambient conditions and attached to the tip of a MiTeGen MicroMount©. The crystal was mounted in a stream of cold nitrogen at 100(1) K and centered in the X-ray beam by using a video camera.

The crystal evaluation and data collection were performed on a Bruker Quazar SMART APEXII diffractometer with Mo K_α (λ = 0.71073 Å) radiation and the diffractometer to crystal distance of 4.96 cm.[11]

The initial cell constants were obtained from three series of ω scans at different starting angles. Each series consisted of 12 frames collected at intervals of 0.5º in a 6º range about ω with the exposure time of 20 seconds per frame. The reflections were successfully indexed by an automated indexing routine built in the APEXII program suite. The final cell constants were calculated from a set of 4481 strong reflections from the actual data collection.

The data were collected by using the full sphere data collection routine to survey the reciprocal space to the extent of a full sphere to a resolution of 0.75 Å. A total of 16434 data were harvested by collecting 4 sets of frames with 0.6º scans in ω and φ with exposure times of 150 sec per frame. These highly redundant datasets were corrected for Lorentz and polarization effects. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements.[12]

Structure Solution and Refinement

The systematic absences in the diffraction data were consistent for the space groups $P2_1$ and $P2_1/m$. The *E*-statistics strongly suggested the non-centrosymmetric space group $P2_1$ that yielded chemically reasonable and computationally stable results of refinement.[13-18]

A successful solution by the direct methods provided most non-hydrogen atoms from the *E*-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The absolute configuration was unambiguously established by anomalous dispersion: C1 – *S*; C2 – *S*.

The final least-squares refinement of 237 parameters against 4616 data resulted in residuals *R* (based on F^2 for $I \geq 2\sigma$) and *wR* (based on F^2 for all data) of 0.0362 and 0.0809, respectively. The final difference Fourier map was featureless.

Summary

Crystal Data for $C_{20}H_{24}ClNO_4$ (M =377.85 g/mol): monoclinic, space group $P2_1$ (no. 4), a = 7.421(3) Å, b = 16.048(6) Å, c = 8.176(3) Å, β = 101.174(11)°, V = 955.3(6) Å^3, Z = 2, T = 100.0 K, μ(MoKα) = 0.225 mm^{-1}, *Dcalc* = 1.314 g/cm^3, 16434 reflections measured (5.076° ≤ 2Θ ≤ 56.632°), 4616 unique (R_{int} = 0.0422, R_{sigma} = 0.0496) which were used in all calculations. The final R_1 was 0.0362 ($I > 2\sigma(I)$) and wR_2 was 0.0809 (all data).

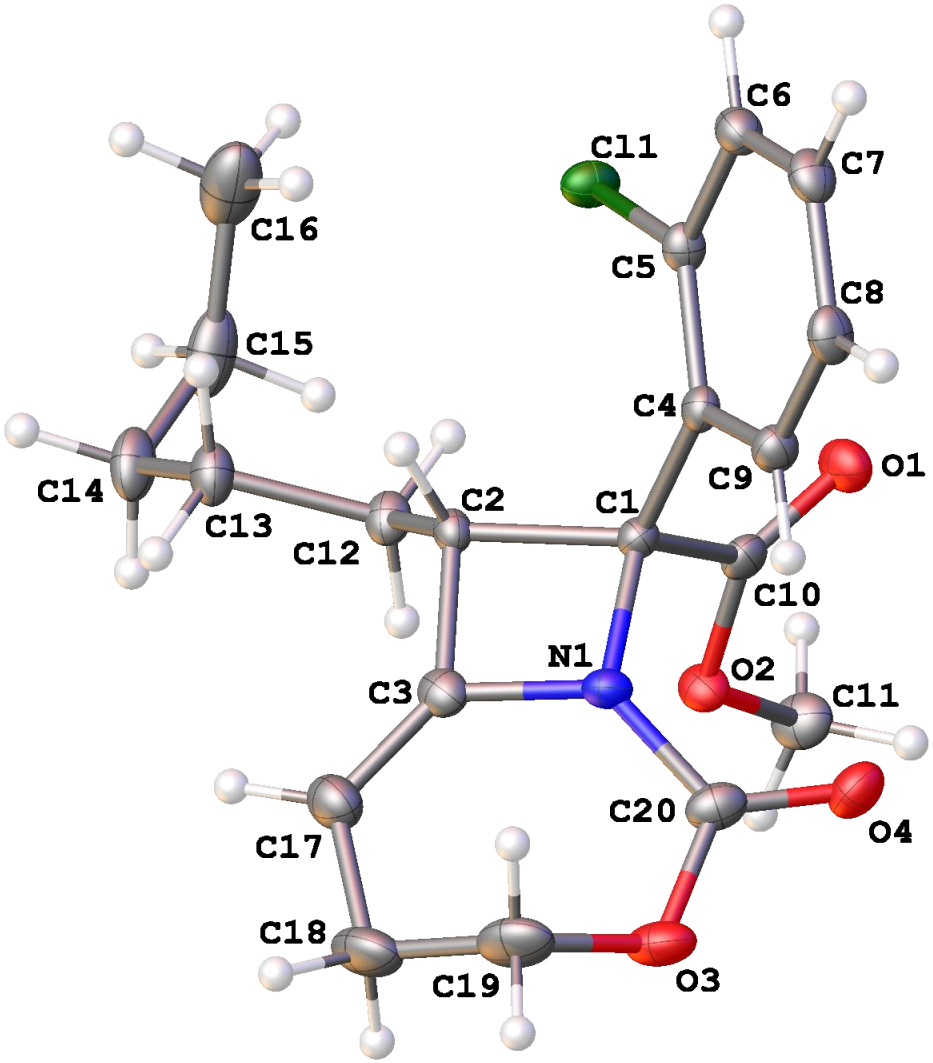


Figure S10. A molecular drawing of (*S*,*S*)-**3bb** shown with 50% probability ellipsoids.

Table S1. Crystal data and structure refinement for (*S*,*S*)-**3bb.**

Identification code	Schomaker81
Empirical formula	$C_{20}H_{24}ClNO_4$
Formula weight	377.85
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.421(3)
b/Å	16.048(6)
c/Å	8.176(3)
α/°	90
β/°	101.174(11)
γ/°	90
Volume/Å^3	955.3(6)
Z	2
ρ_{calc}g/cm^3	1.314
μ/mm^{-1}	0.225
F(000)	400.0
Crystal size/mm^3	0.064 × 0.048 × 0.027
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.076 to 56.632
Index ranges	$-9 \leq h \leq 9$, $-21 \leq k \leq 20$, $-10 \leq l \leq 10$
Reflections collected	16434
Independent reflections	4616 [R_{int} = 0.0422, R_{sigma} = 0.0496]
Data/restraints/parameters	4616/1/237
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0362, wR_2 = 0.0774
Final R indexes [all data]	R_1 = 0.0472, wR_2 = 0.0809
Largest diff. peak/hole / e Å^{-3}	0.26/-0.20
Flack parameter	-0.04(3)

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for (*S*,*S*)-**3bb. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.**

Atom	*x*	*y*	*z*	U(eq)
Cl1	3606.3(8)	6441.1(4)	8596.7(7)	20.52(15)
O1	4001(3)	4468.5(11)	9714(2)	23.4(4)
O2	3913(2)	3721.8(11)	7372(2)	18.4(4)
O3	-1179(3)	3003.9(12)	5391(2)	28.1(5)
O4	243(3)	3186.5(12)	8027(2)	25.5(4)
N1	374(3)	4230.5(13)	6182(2)	17.0(4)
C1	1682(3)	4780.9(15)	7268(3)	14.8(5)
C2	2070(3)	5201.9(15)	5604(3)	14.3(5)
C3	779(4)	4548.9(17)	4670(3)	18.9(5)
C4	765(3)	5339.8(16)	8365(3)	15.3(5)
C5	1509(3)	6096.5(16)	9009(3)	16.1(5)
C6	635(4)	6608.2(16)	9981(3)	19.5(6)
C7	-1049(3)	6362.5(19)	10318(3)	20.2(5)
C8	-1833(4)	5618.0(17)	9703(3)	20.0(6)
C9	-933(4)	5119.1(16)	8739(3)	18.5(5)
C10	3313(3)	4312.3(16)	8295(3)	16.9(5)
C11	5400(4)	3214.4(18)	8253(3)	24.5(6)
C12	3979(4)	5251.5(17)	5217(3)	18.7(5)
C13	4001(4)	5861.3(19)	3782(3)	22.8(6)
C14	5847(4)	5935(2)	3241(3)	27.2(7)
C15	7447(4)	6165(2)	4613(4)	34.5(8)
C16	7196(5)	6955(2)	5540(4)	43.7(9)
C17	206(4)	4311.1(18)	3115(3)	26.2(6)
C18	-1188(4)	3630(2)	2619(4)	34.6(7)
C19	-2258(4)	3428(2)	3959(4)	32.4(7)
C20	-148(4)	3455.3(17)	6618(3)	21.3(6)

Table S3. Anisotropic Displacement Parameters ($Å^2×10^3$) for (*S*,*S*)**-3bb. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.**

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	17.0(3)	19.0(3)	26.7(3)	-3.9(3)	7.3(2)	-2.7(3)
O1	25.2(10)	23.6(11)	18.5(9)	-0.2(8)	-2.7(7)	2.7(8)
O2	18.4(9)	17.0(9)	19.3(9)	-0.3(7)	2.3(7)	5.4(7)
O3	28.1(12)	17.9(10)	35.6(11)	-6.4(8)	-0.5(9)	-1.5(9)
O4	26.7(11)	19.6(10)	30(1)	4.8(8)	5.3(8)	-3.2(8)
N1	17.9(11)	14.2(11)	18.2(10)	-3.2(8)	2.1(8)	-1.0(9)
C1	16.5(13)	13.1(12)	14.8(11)	0.3(9)	2.8(9)	-0.7(10)
C2	16.3(12)	14.6(13)	12.2(11)	1.4(9)	2.9(9)	2.5(10)
C3	19.3(13)	17.4(13)	19.0(12)	0.2(10)	1.4(10)	4.8(11)
C4	16.7(13)	15.3(13)	13.6(11)	3.1(9)	2.5(9)	1.3(10)
C5	12.9(12)	19.7(13)	15.6(11)	1.8(9)	2.8(9)	-0.7(10)
C6	22.9(13)	18.9(15)	16.5(11)	-0.6(9)	3.3(9)	1.9(10)
C7	21.1(13)	23.9(14)	17.0(11)	0.4(11)	7.1(9)	5.5(12)
C8	16.5(13)	26.8(16)	18.1(12)	2.7(10)	6.7(10)	-0.3(11)
C9	18.9(14)	18.5(14)	17.9(12)	0.6(10)	3.3(10)	-2.4(11)
C10	17.3(13)	14.3(13)	19.6(12)	1.9(9)	5.0(9)	-2.7(10)
C11	19.7(15)	22.2(15)	29.1(14)	1.7(11)	-1.0(11)	5.3(11)
C12	18.3(13)	19.6(14)	19.0(12)	3.5(10)	5.4(9)	5.2(11)
C13	23.1(15)	27.1(15)	18.8(13)	6.5(10)	5.7(11)	4.2(12)
C14	27.2(16)	34.0(17)	23.9(14)	10.3(12)	13.5(11)	8.4(13)
C15	19.1(15)	50(2)	36.5(16)	22.4(14)	9.8(12)	4.2(13)
C16	35(2)	53(2)	38.5(18)	15.4(16)	-5.9(15)	-17.6(17)
C17	30.5(17)	25.8(16)	20.4(13)	-1.2(11)	0.1(11)	2.3(13)
C18	42.2(19)	27.2(17)	27.8(15)	-8.6(12)	-9.8(13)	0.3(15)
C19	26.5(16)	25.6(17)	38.5(16)	-7.9(13)	-10.2(13)	-3.8(13)
C20	16.5(14)	17.4(14)	30.2(14)	-1.9(11)	4.5(11)	-0.7(11)

Table S4. Bond Lengths for (*S*,*S*)-**3bb.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C5	1.745(3)	C2	C12	1.512(4)
O1	C10	1.200(3)	C3	C17	1.316(3)
O2	C10	1.340(3)	C4	C5	1.394(4)
O2	C11	1.446(3)	C4	C9	1.399(4)
O3	C19	1.453(3)	C5	C6	1.388(3)
O3	C20	1.349(3)	C6	C7	1.388(4)
O4	C20	1.211(3)	C7	C8	1.381(4)
N1	C1	1.476(3)	C8	C9	1.383(3)
N1	C3	1.423(3)	C12	C13	1.530(3)
N1	C20	1.371(4)	C13	C14	1.523(4)
C1	C2	1.595(3)	C14	C15	1.513(4)
C1	C4	1.519(3)	C15	C16	1.507(5)
C1	C10	1.530(3)	C17	C18	1.506(4)
C2	C3	1.522(4)	C18	C19	1.507(5)

Table S5. Bond Angles for (*S*,*S*)-**3bb.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10	O2	C11	115.00(19)	C4	C5	Cl1	120.38(19)
C20	O3	C19	119.5(2)	C6	C5	Cl1	117.1(2)
C3	N1	C1	94.78(19)	C6	C5	C4	122.5(2)
C20	N1	C1	124.9(2)	C5	C6	C7	119.0(2)
C20	N1	C3	132.1(2)	C8	C7	C6	120.4(2)
N1	C1	C2	86.92(16)	C7	C8	C9	119.5(2)
N1	C1	C4	113.0(2)	C8	C9	C4	122.2(2)
N1	C1	C10	113.2(2)	O1	C10	O2	124.5(2)
C4	C1	C2	115.42(19)	O1	C10	C1	124.8(2)
C4	C1	C10	111.30(19)	O2	C10	C1	110.64(19)
C10	C1	C2	115.0(2)	C2	C12	C13	110.1(2)
C3	C2	C1	86.35(17)	C14	C13	C12	114.6(2)
C12	C2	C1	122.2(2)	C15	C14	C13	115.1(2)
C12	C2	C3	117.1(2)	C16	C15	C14	115.0(3)
N1	C3	C2	91.69(18)	C3	C17	C18	123.2(3)
C17	C3	N1	130.7(3)	C17	C18	C19	113.1(2)
C17	C3	C2	137.6(3)	O3	C19	C18	113.6(3)
C5	C4	C1	123.2(2)	O3	C20	N1	116.2(2)
C5	C4	C9	116.5(2)	O4	C20	O3	120.9(3)
C9	C4	C1	120.3(2)	O4	C20	N1	122.9(2)

Table S6. Torsion Angles for (*S*,*S*)-**3bb.**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C5	C6	C7	179.10(18)	C4	C1	C2	C3	-117.8(2)
N1	C1	C2	C3	-3.66(18)	C4	C1	C2	C12	122.3(3)
N1	C1	C2	C12	-123.6(2)	C4	C1	C10	O1	-12.7(3)
N1	C1	C4	C5	-155.4(2)	C4	C1	C10	O2	169.6(2)
N1	C1	C4	C9	22.6(3)	C4	C5	C6	C7	-0.5(4)
N1	C1	C10	O1	-141.4(3)	C5	C4	C9	C8	-0.4(3)
N1	C1	C10	O2	41.0(3)	C5	C6	C7	C8	0.4(4)
N1	C3	C17	C18	4.0(5)	C6	C7	C8	C9	-0.3(4)
C1	N1	C3	C2	-4.1(2)	C7	C8	C9	C4	0.3(4)
C1	N1	C3	C17	174.7(3)	C9	C4	C5	Cl1	-179.09(18)
C1	N1	C20	O3	-172.1(2)	C9	C4	C5	C6	0.5(3)
C1	N1	C20	O4	9.6(4)	C10	C1	C2	C3	110.6(2)
C1	C2	C3	N1	3.79(18)	C10	C1	C2	C12	-9.3(3)
C1	C2	C3	C17	-174.9(3)	C10	C1	C4	C5	75.8(3)
C1	C2	C12	C13	-166.4(2)	C10	C1	C4	C9	-106.1(3)
C1	C4	C5	Cl1	-0.9(3)	C11	O2	C10	O1	5.2(4)
C1	C4	C5	C6	178.6(2)	C11	O2	C10	C1	-177.1(2)
C1	C4	C9	C8	-178.6(2)	C12	C2	C3	N1	128.3(2)
C2	C1	C4	C5	-57.6(3)	C12	C2	C3	C17	-50.4(4)
C2	C1	C4	C9	120.5(2)	C12	C13	C14	C15	-55.6(4)
C2	C1	C10	O1	120.9(3)	C13	C14	C15	C16	-55.4(4)
C2	C1	C10	O2	-56.8(3)	C17	C18	C19	O3	-70.8(3)
C2	C3	C17	C18	-177.7(3)	C19	O3	C20	O4	154.3(3)
C2	C12	C13	C14	-177.8(2)	C19	O3	C20	N1	-24.0(4)
C3	N1	C1	C2	3.92(19)	C20	O3	C19	C18	84.6(3)
C3	N1	C1	C4	120.3(2)	C20	N1	C1	C2	155.4(2)
C3	N1	C1	C10	-112.0(2)	C20	N1	C1	C4	-88.2(3)
C3	N1	C20	O3	-32.0(4)	C20	N1	C1	C10	39.5(3)
C3	N1	C20	O4	149.7(3)	C20	N1	C3	C2	-152.3(3)
C3	C2	C12	C13	89.9(3)	C20	N1	C3	C17	26.6(5)
C3	C17	C18	C19	17.0(4)					

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for (*S*,*S*)-**3bb.**

Atom	*x*	*y*	*z*	U(eq)
H2	1473.19	5762.74	5453.47	17
H6	1181.25	7118.62	10408.87	23
H7	-1665.36	6708.6	10976.59	24
H8	-2982.65	5449.54	9939.88	24
H9	-1487.48	4609.45	8315.91	22
H11A	5805.76	2827.13	7470.58	37
H11B	4975.34	2898.44	9131.3	37
H11C	6427.64	3573.82	8753.18	37
H12A	4365.6	4692.42	4905.85	22
H12B	4857.11	5439.64	6218.35	22
H13A	3066.61	5682.16	2810.87	27
H13B	3638.87	6419.22	4121.94	27
H14A	6123.68	5396.16	2754.89	33
H14B	5737.81	6360.59	2351.04	33
H15A	7669.53	5700.86	5423.73	41
H15B	8557.66	6224.77	4119.8	41
H16A	7018.78	7425.09	4759.02	66
H16B	8288.95	7054.33	6404.45	66
H16C	6117.46	6900.79	6059.17	66
H17	696.41	4582.08	2265.12	31
H18A	-550.19	3121.17	2351.3	42
H18B	-2056.31	3802.83	1598.17	42
H19A	-2747.22	3952.12	4340.41	39
H19B	-3317.55	3072.51	3475.32	39

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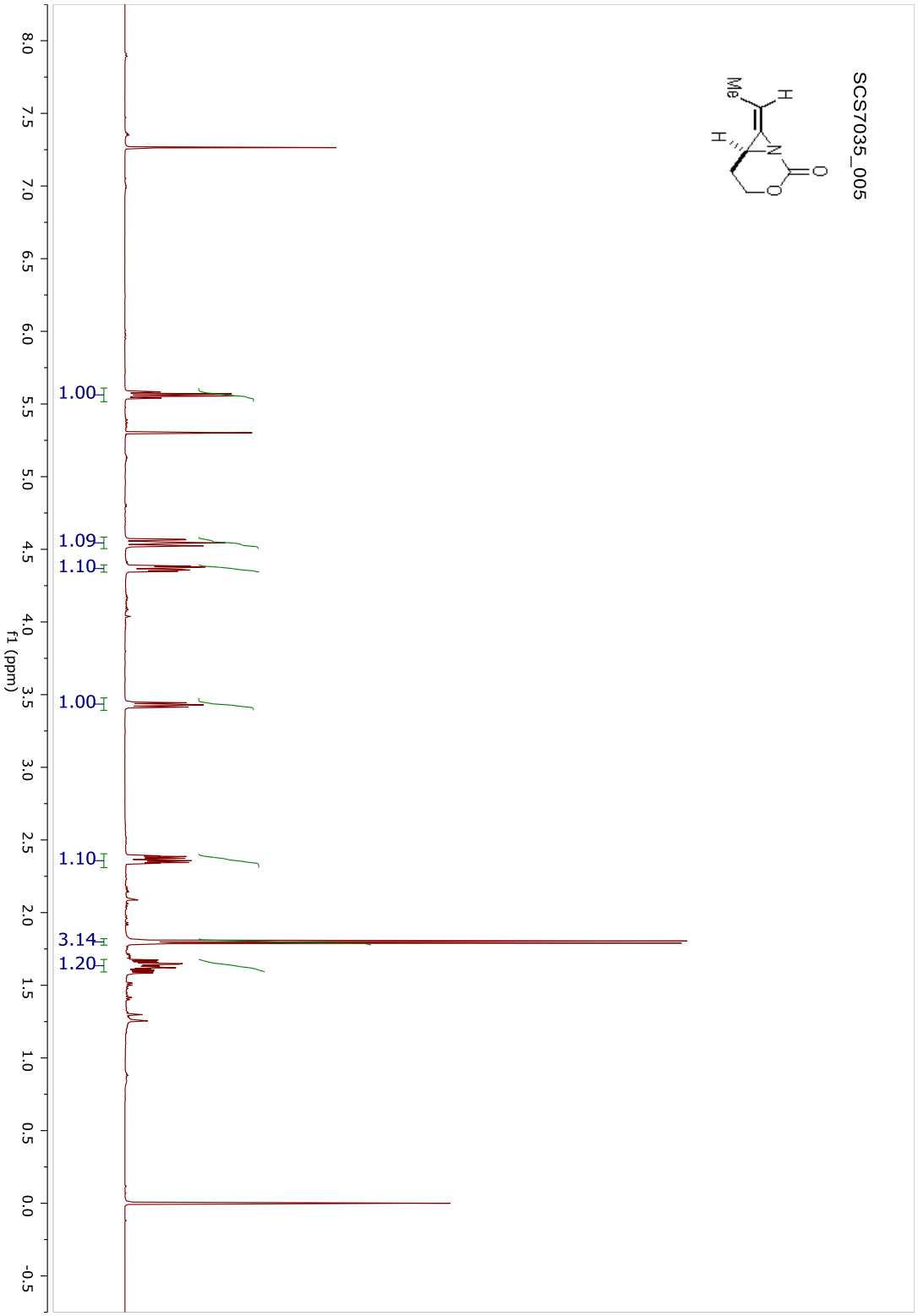
X. NMR Spectra.

^{1}H NMR for Compound 1a.



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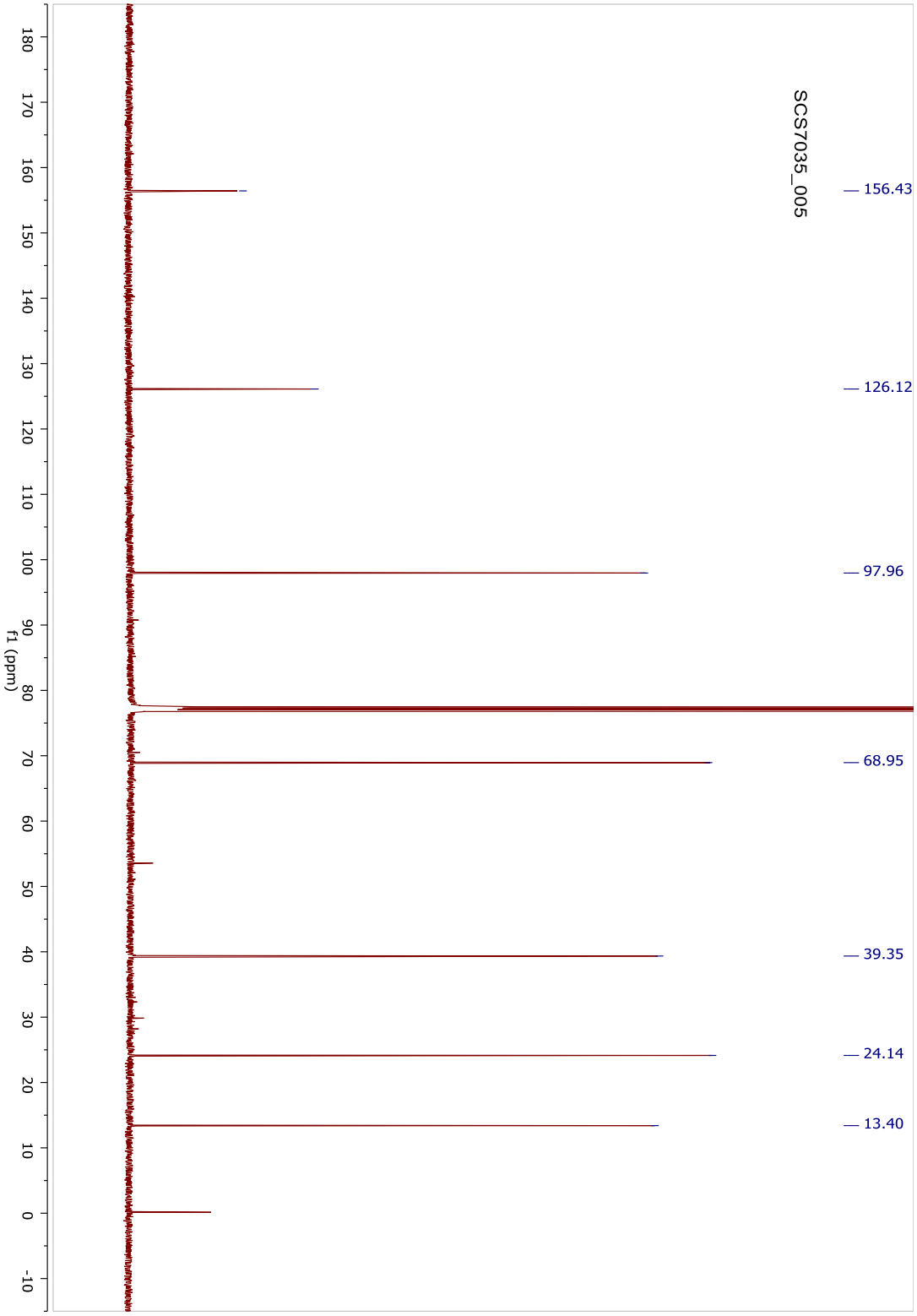

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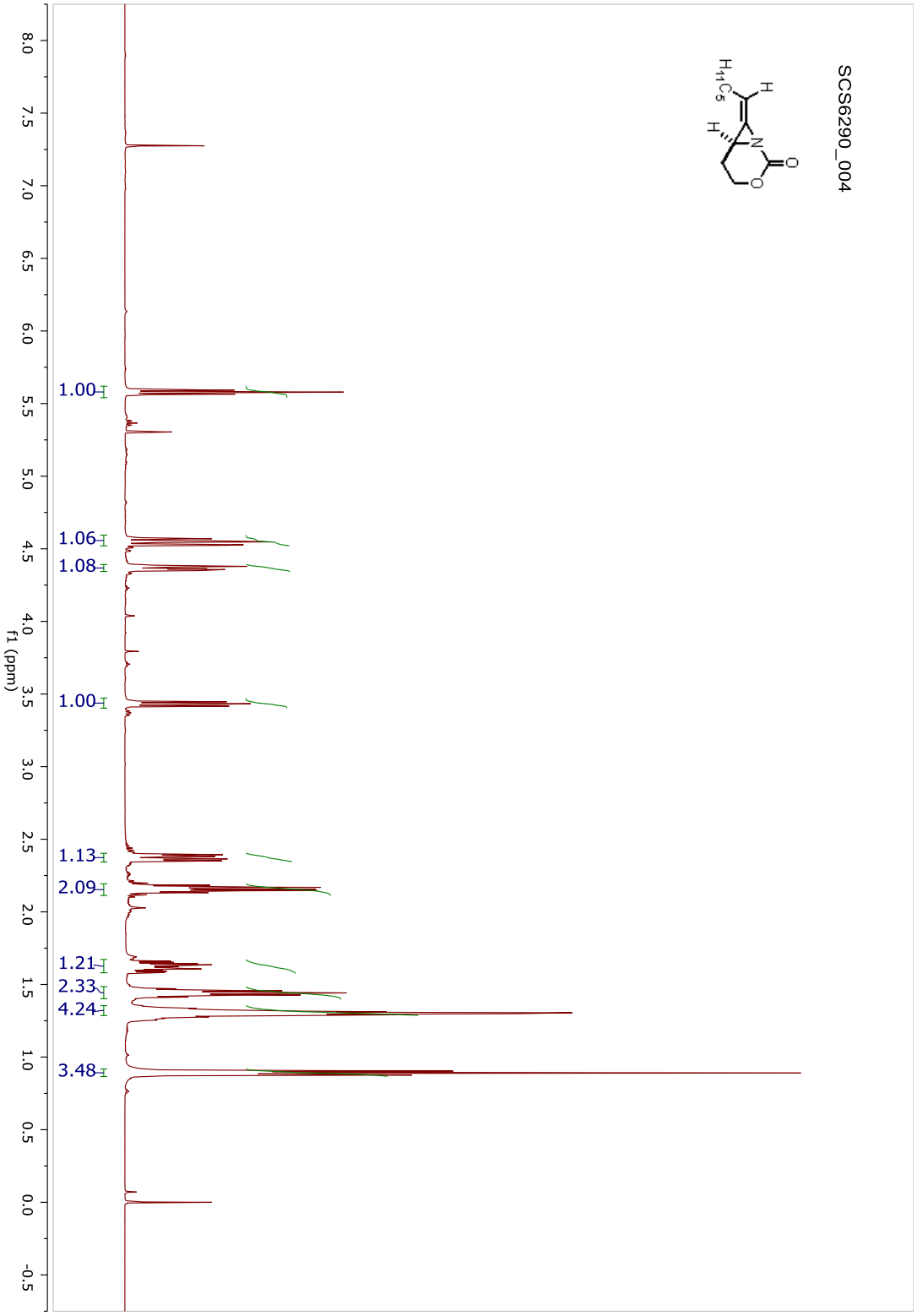

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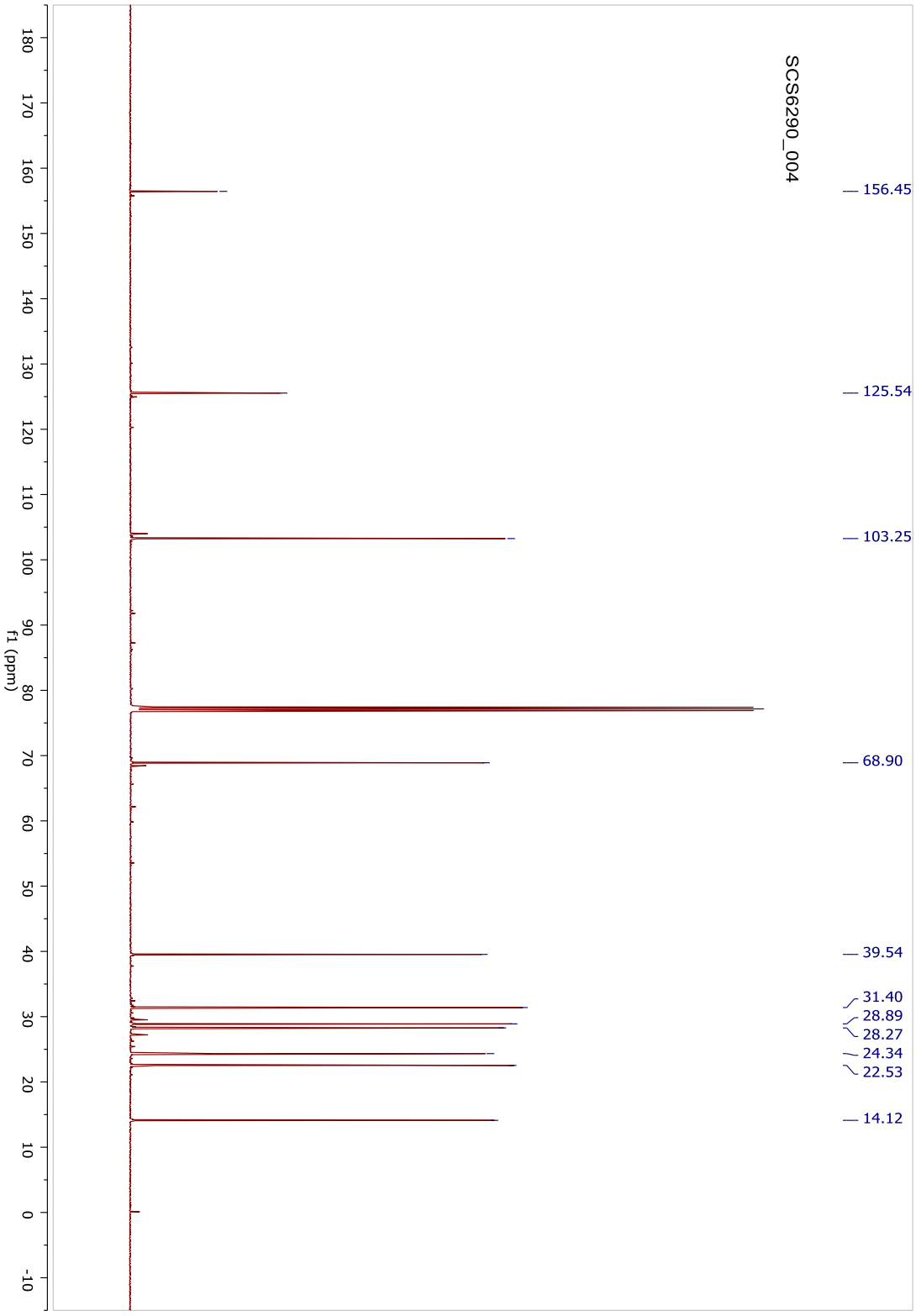

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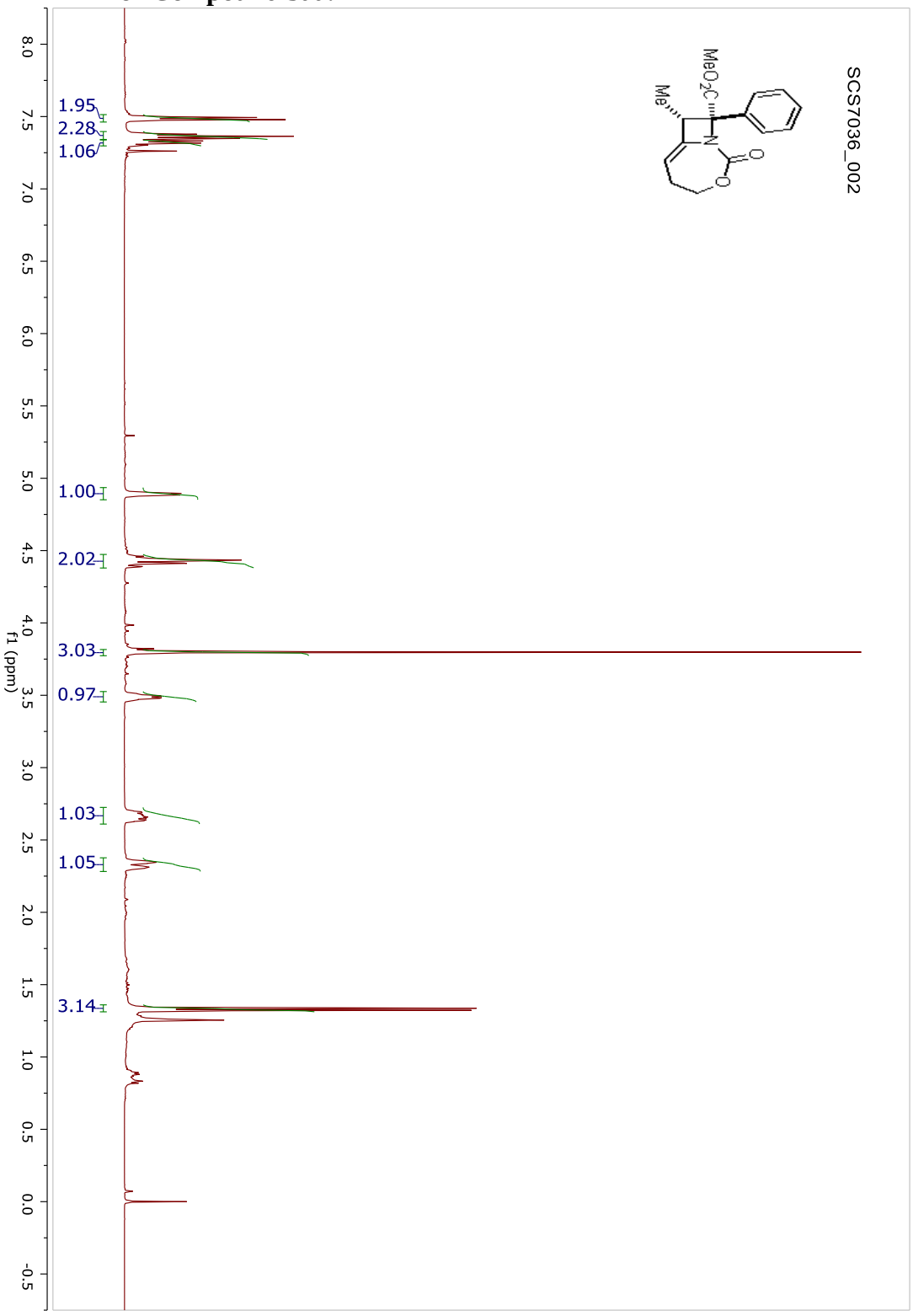

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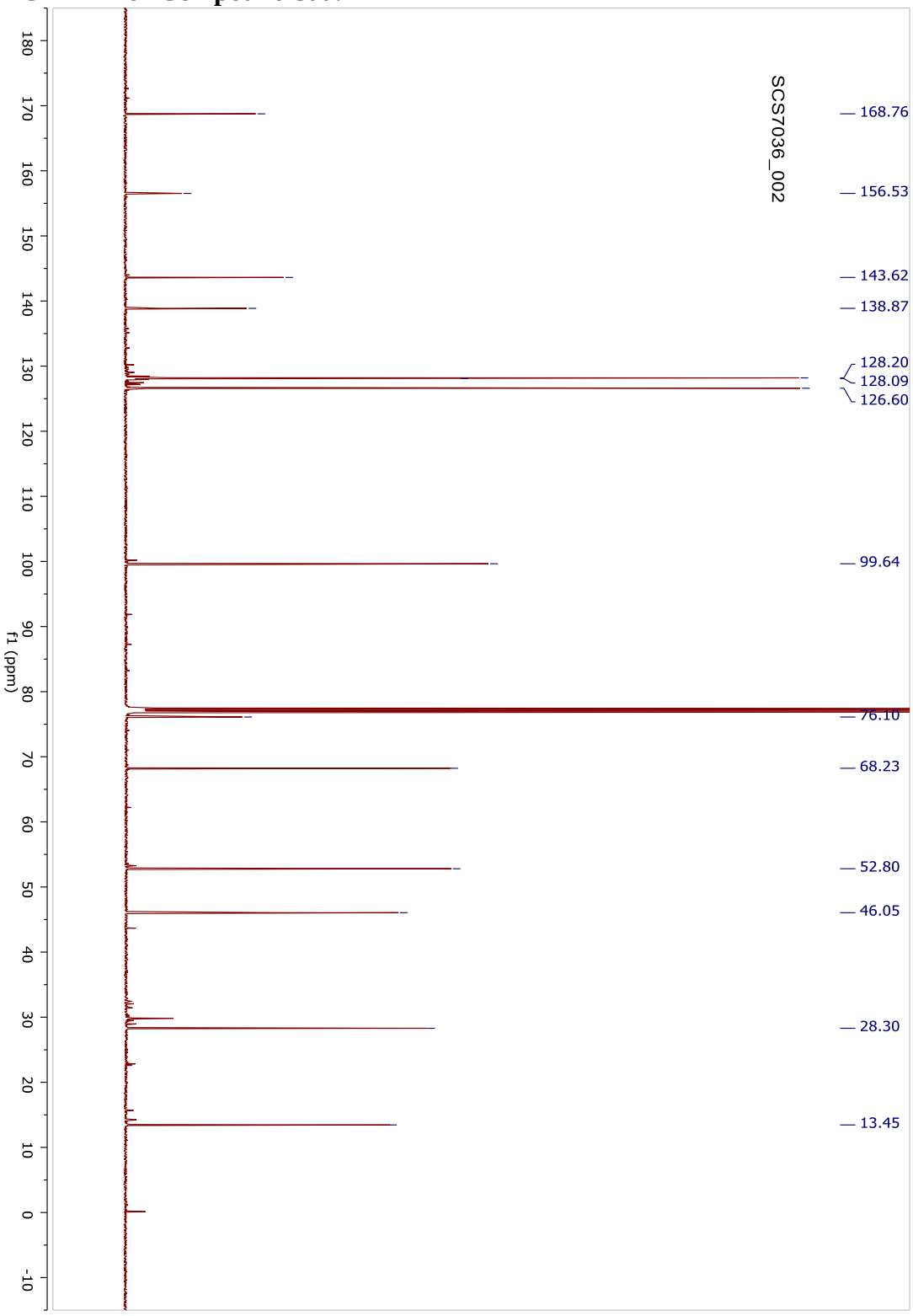

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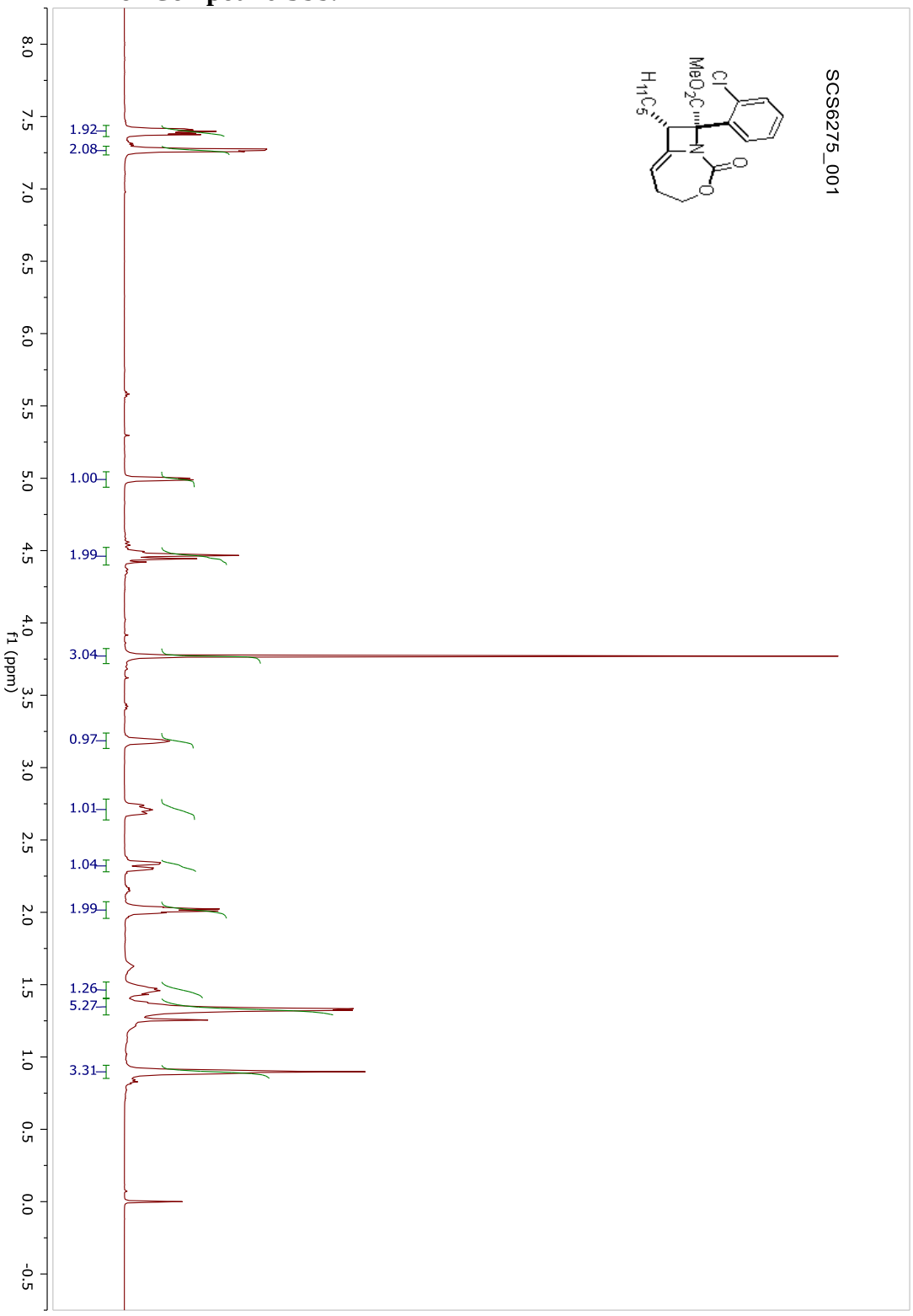

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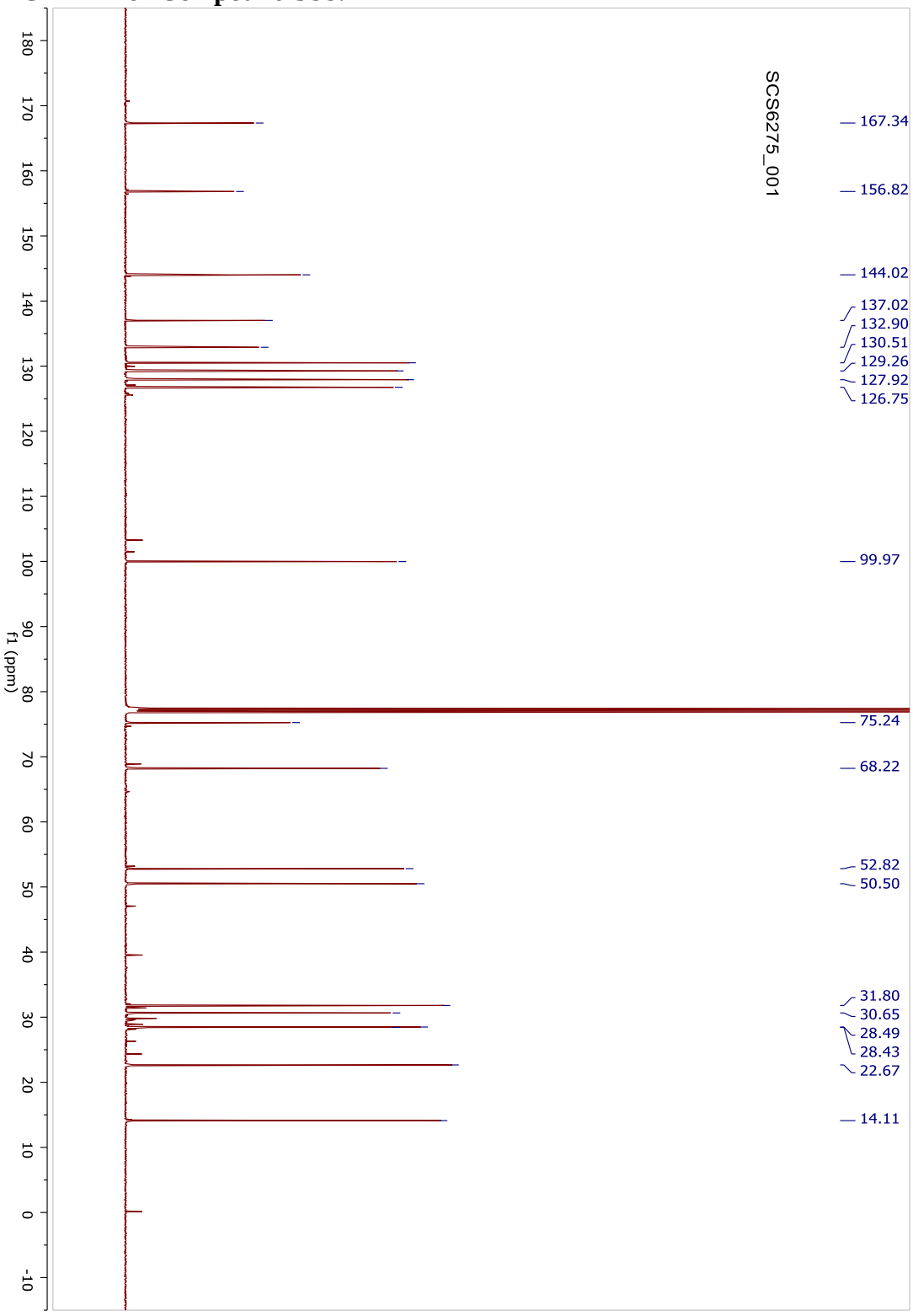

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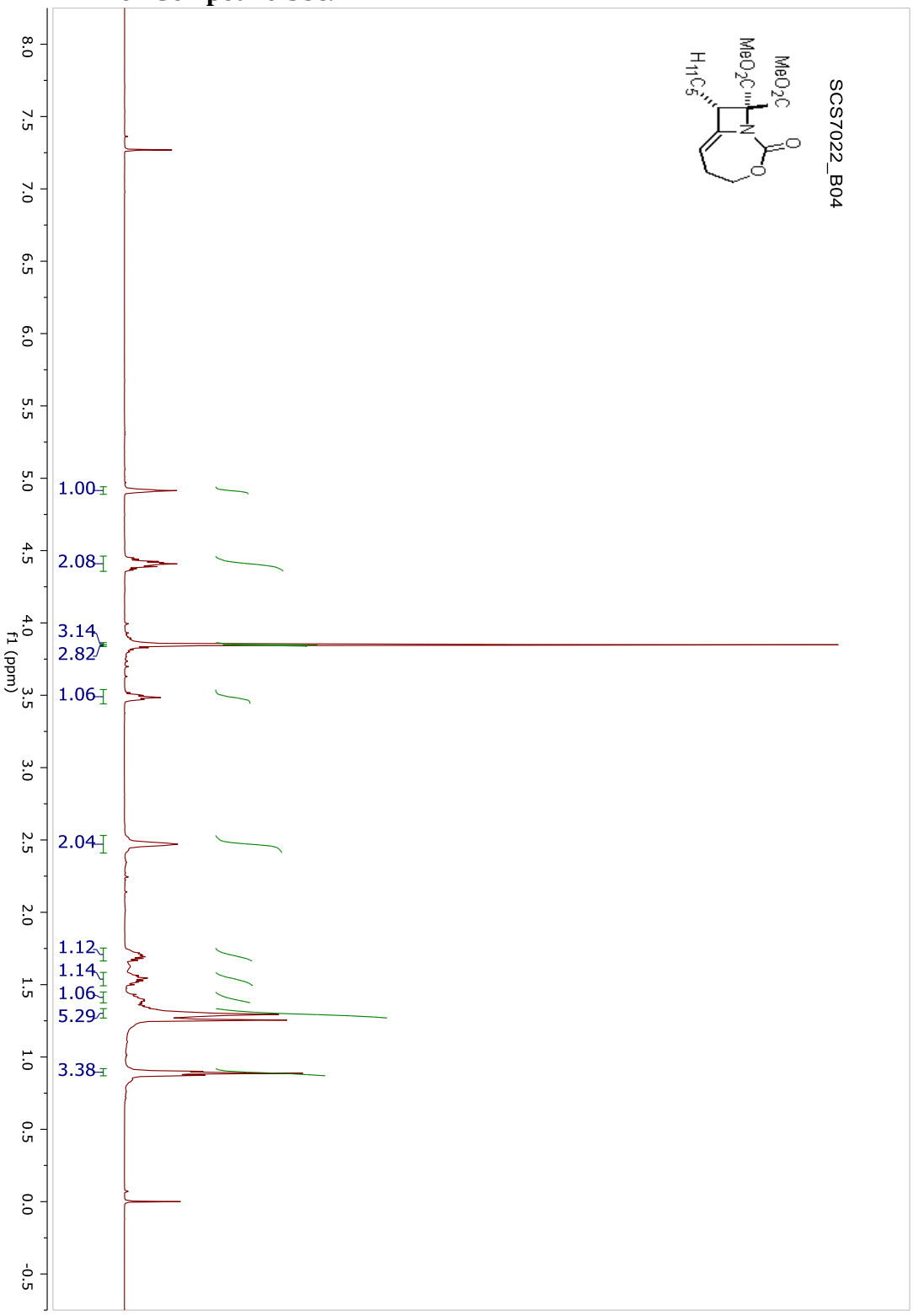

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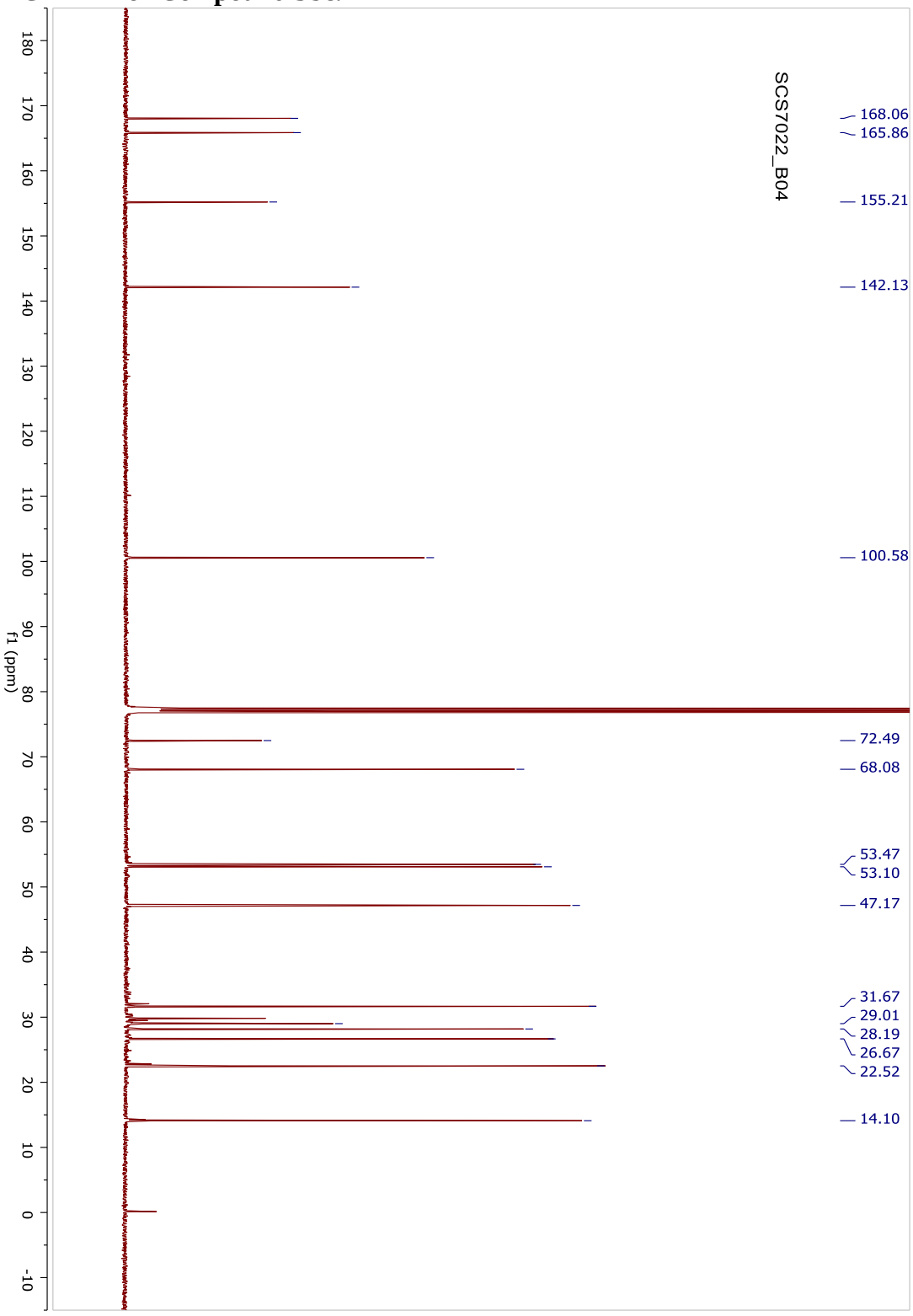

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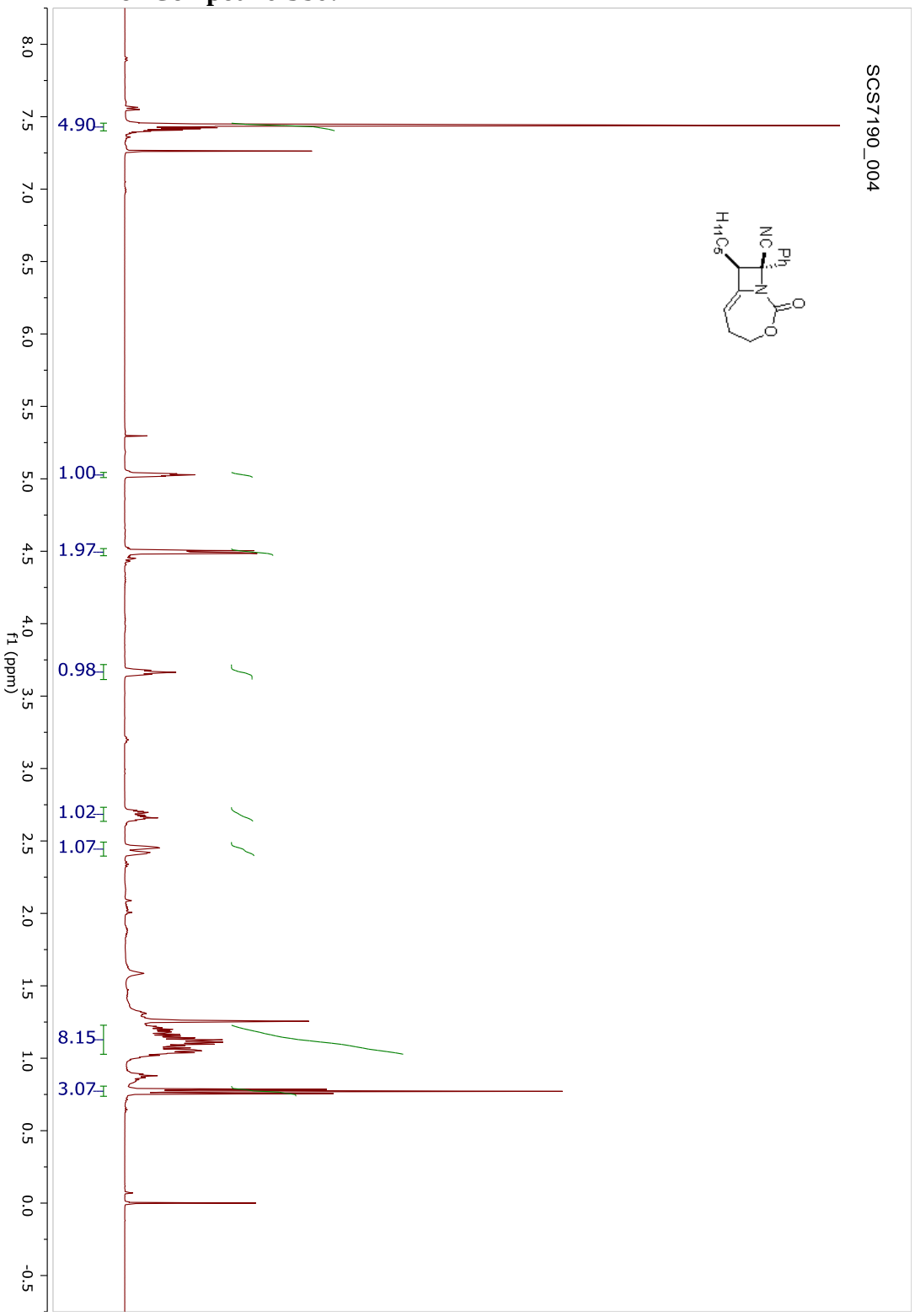

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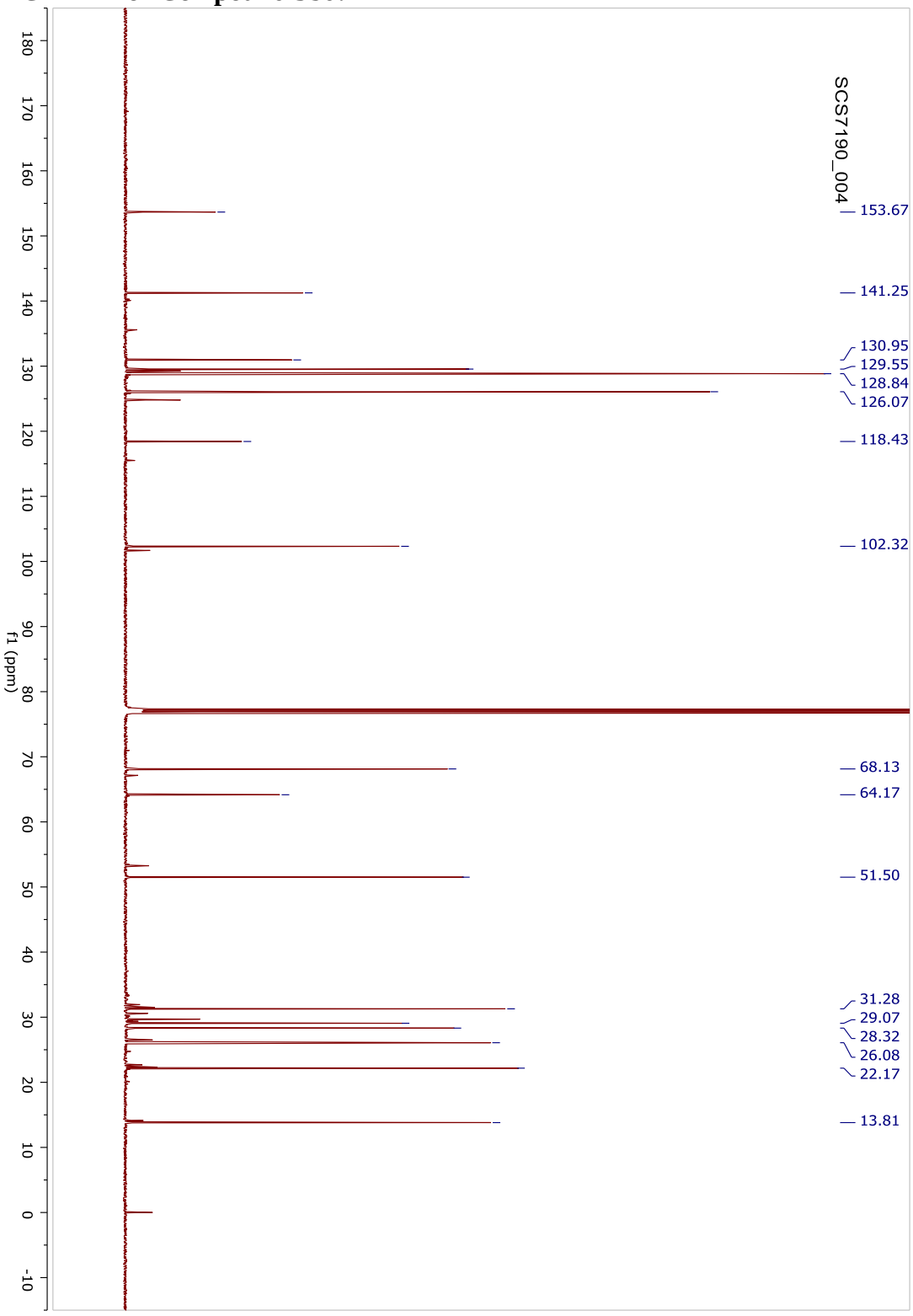
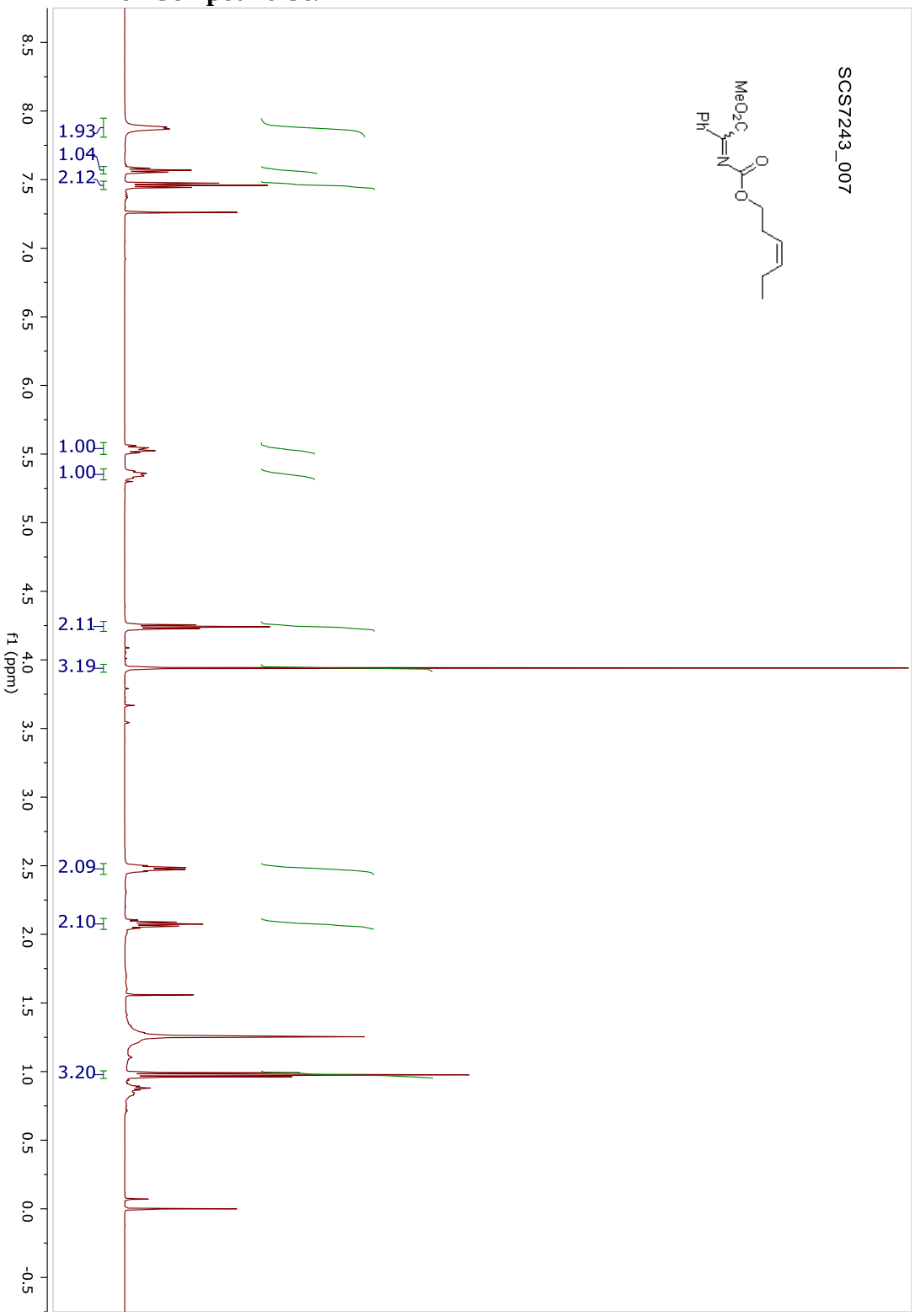


^{1}H NMR for Compound 5c.



^{13}C NMR for Compound 5c.