Supporting Information

Enantioselective Tail-to-Head Cyclizations Catalyzed by Dual-Hydrogen-Bond Donors

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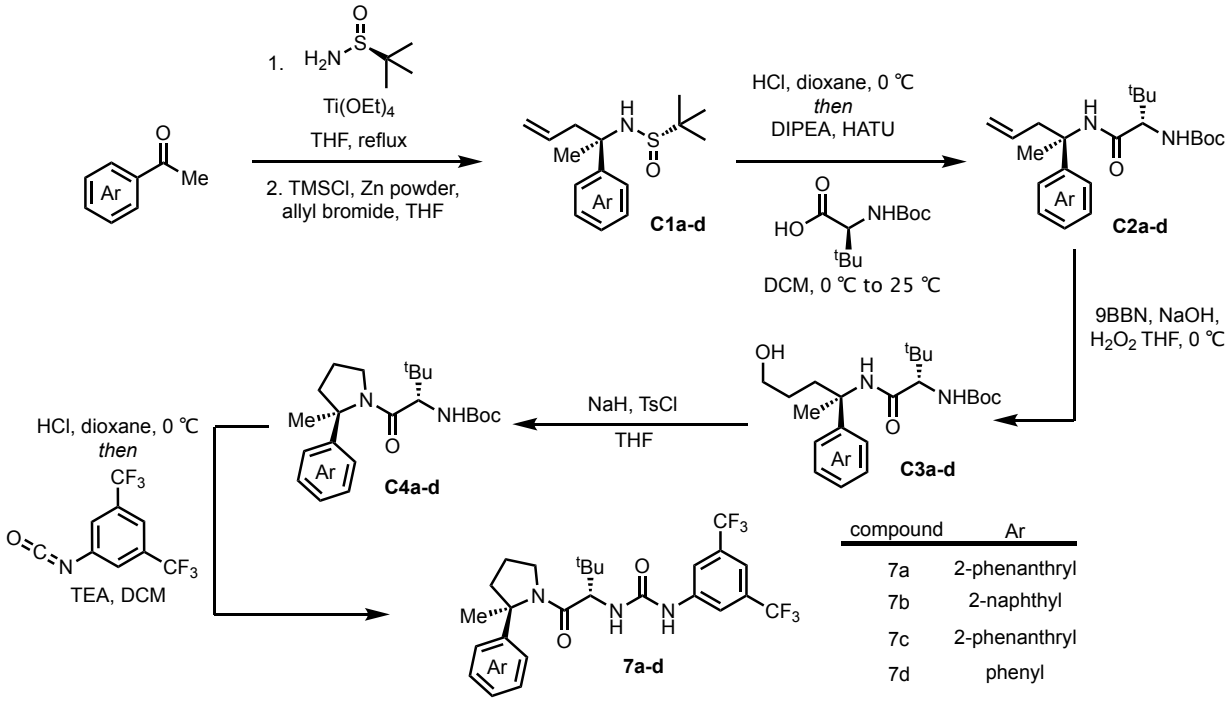
1. General Information

All reactions were performed in flame dried vials or round bottom flasks unless otherwise noted. The vials and flasks were fitted with rubber septa, and reactions were conducted under an atmosphere of nitrogen. Stainless steel syringes and cannulae were used to transfer air and moisture sensitive liquids. Column chromatography was performed on a Biotage Isolera automated purification system using silica gel 60 (230-400 mesh) from EM Science. Dimethylated silica gel (dimethylsilan derivative) was purchased from EM Science used as received. Commercial chemical reagents were purchased from Sigma Aldrich, Alfa Aesar, Strem, or TCI, and used as received. Anhydrous solvents (benzene, dichloromethane, diethyl ether, N,N-dimethylformamide, tetrahydrofuran, and toluene) were dried by passage through activated alumina columns using a solvent purification system. Proton nuclear magnetic resonance (^{1}H NMR), fluorine nuclear magnetic resonance (^{19}F NMR), and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Inova-500 (500 MHz) or Inova-600 (600 MHz) spectrometers. Proton, fluorine, and carbon chemical shifts are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton in the NMR solvent ($CHCl_3$ = δ 7.27; CH_2Cl_2 = δ 5.32; CyH = δ 1.44) or the carbon resonances of the NMR solvent ($CDCl_3$ = δ 77.0) respectively. NMR data are represented as follows: chemical shift, multiplicity (br. = broad signal, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant in Hertz (Hz), integration. Infrared (IR) spectra were collected on a Bruker Optics Tensor 27 FTIR spectrometer from a thin film sample. Optical rotations were measured using a 1.0 mL cell with a 5 cm path length on a Jasco DIP 370 digital polarimeter. Gas chromatography (GC) analysis was performed on an Agilent 7890A series GC system outfitted with a commercially available cyclosil-B 30m column. High-performance liquid chromatography (HPLC) analysis was performed using an Agilent 1200 series quaternary HPLC system with commercially available ChiralPak and ChiralCel columns, or a Waters Prep-C18 SunFire column (for preparative HPLC). High-resolution mass spectrometry was measured at the Small Molecule Mass Spectrometry Facility at Harvard University within the Faculty of Arts and Sciences using an Agilent 6210 TOF LC/MS spectrometer or a Waters Quattro micro GC/MS/MS spectrometer. All curve fitting presented in this report was carried out using Microsoft Excel. NMR spectra were processed with the Mnova (Mestrelab Research). Computations were performed with Gaussian '16, and computed structures were rendered with CYLview or VMD (for NCI plots).

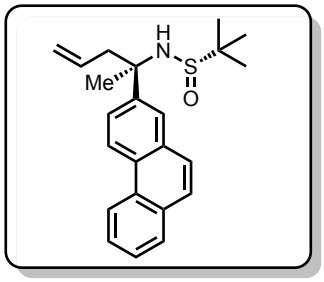
Abbreviations used:
Boc – tert–butyloxycarbonyl, n-BuLi – n-butyllithium, DCM – dichloromethane, DIPEA – N,N-diisopropylethylamine, DIBAL-H – diisobutylaluminium hydride, DMF – N,N-dimethylformamide, e.e. – enantiomeric excess, Et_2O – diethyl ether, EtOAc – ethyl acetate, HATU – 1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxide hexafluorophosphate, Hexafluorophosphate Azabenzotriazole Tetramethyl Uronium, IPA – isopropyl alcohol, ITC – isothermal titration calorimetry, LDA – lithium diisopropylamide, Ms – methanesulfonyl, NEt_3 – triethylamine, THF – tetrahydrofuran, TLC – thin layer chromatography, 9BBN – 9-borabicyclo[3.3.1]nonane

2. Synthesis and Characterization of Catalysts 7a-7d and Intermediates



Scheme S1. General synthesis of catalysts **7a-7d**. The synthesis of catalyst **7a** is described below as an example.

(*S*)-2-methyl-*N*-((*R*)-2-(phenanthren-2-yl)pent-4-en-2-yl)propane-2-sulfinamide (C1a)



To a flame-dried round bottom flask was added 2-acetylphenanthrene (9.08 mmol, 2.0 g, 1.0 eq.) and anhydrous THF (9 mL). Following additions of titanium ethoxide (19.98 mmol, 4.14 mL, 2.2 eq.) and (S)-Ellman sulfinamide (10.0 mmol, 1.21 g, 1.1 eq.) the mixture was brought to reflux (85 °C) for 12 hours. After this time, the crude reaction was passed through a short silica plug eluting with warm EtOAc (this was critical to ensure the Ellman ketimine was soluble). The eluent was concentrated *in vacuo* and the residue was taken in anhydrous THF (40 mL) and transferred to a flame-dried round bottomed flask. In a separate flame-dried round bottomed flask was added zinc powder (9.98 mmol, 0.65 g, 1.1 eq.) and anhydrous THF (50 mL). Chlorotrimethylsilane (TMSCl) (0.45 mmol, 157 μL, 0.05 eq.) was added, followed by allyl bromide (9.98 mmol, 868 μL, 1.1 eq.) and the mixture was stirred for 1 hr. before being transferred via cannula to the flask containing the ketimine in 40 mL of THF. The ensuing reaction was allowed to proceed for 24 hr. after which point it was quenched with sat. aq. NH_4Cl (45 mL) and extracted (3X 40 mL) with EtOAc. The organic layers were combined, washed (2X 40 mL) with brine, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 40% EtOAc in hexanes (v/v) to provide product **C1a** in 58% yield (1.93 g) as a white solid.

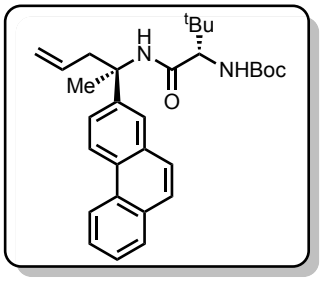
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 8.5, 2.8 Hz, 2H), 7.92 (m, 2H), 7.76 (dd, *J* = 8.9, 2.3 Hz, 3H), 7.68 (ddd, *J* = 8.4, 7.0, 1.5 Hz, 1H), 7.62 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 5.63 (ddt, *J* = 17.4, 10.1, 7.3 Hz, 1H), 5.23 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.16 (dd, *J* = 10.2, 2.1 Hz, 1H), 3.88 (m, 1H), 2.82 (d, *J* = 7.3 Hz, 2H), 1.95 (s, 3H), 1.28 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 143.5, 133.1, 132.1, 131.7, 130.0, 129.2, 128.6, 127.2, 127.1, 126.7, 126.6, 126.2, 125.3, 122.8, 122.6, 120.5, 60.1, 56.3, 49.3, 27.8, 22.9

HR-MS: (ESI) calcd. for $C_{23}H_{27}NOS$ 366.1886 [M + H^+], found 366.1887

$[a]_D^{22} = +95.2$ (c =1.0, $CDCl_3$)

***tert*-butyl ((*S*)-3,3-dimethyl-1-oxo-1-(((*R*)-2-(phenanthren-2-yl)pent-4-en-2-yl)amino)butan-2-yl)carbamate (C2a)**



To a flame-dried round bottom flask was added compound **C1a** (5.03 mmol, 1.84 g, 1.0 eq.) and methanol (11.2 mL). The flask was cooled to 0 °C and HCl solution was added (35 mmol, 8.9 mL of a 4 M solution in 1,4 dioxane, 7.0 eq.). The ensuing reaction was allowed to take place for 1 hr. at 0 °C, after which the reaction was seen to be complete by TLC analysis. The solvent was vaporized under reduced pressure, and the resulting residue was taken in DCM (20 mL) and cooled to 0 °C. DIPEA (25.15 mmol, 4.4 mL, 5.0 eq.) was added, followed by HATU (7.55 mmol, 2.87 g, 1.5 eq.) and N-Boc-tert leucine (6.04 mmol, 1.39 g, 1.2 eq.). The reaction was allowed to stir for 24 hours, gradually warming to room temperature before being quenched with sat. aq. NH_4Cl (70 mL) and extracted with EtOAc (3X 70mL). The organic layers were combined, washed with brine (70 mL), filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 35% Et_2O in hexanes (v/v) to provide product **C2a** in quantitative yield (2.40 g) as a white solid.

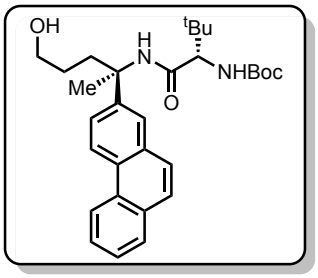
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 11.5, 8.5 Hz, 2H), 7.88 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.64 (m, 5H), 6.13 (s, 1H), 5.65 (ddt, *J* = 17.3, 10.1, 7.3 Hz, 1H), 5.19 (m, 3H), 3.85 (d, *J* = 9.5 Hz, 1H), 2.83 (dd, *J* = 13.9, 7.5 Hz, 1H), 2.64 (dd, *J* = 13.8, 7.2 Hz, 1H), 1.93 (s, 3H), 1.49 (s, 9H), 1.04 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.0, 156.1, 143.4, 133.0, 132.0, 131.9, 130.1, 129.0, 128.5, 127.2, 126.9, 126.5, 126.3, 124.8, 124.0, 122.9, 122.6, 119.9, 79.7, 62.8, 58.0, 47.9, 34.4, 28.4, 26.7, 25.1

HR-MS (ESI): calcd. for $C_{30}H_{38}N_2O_3$ 475.2955 [M + H^+], found 475.2958

$[a]_D^{22} = +28.2$ (c =1.0, $CDCl_3$)

***tert*-butyl ((*S*)-1-(((*R*)-5-hydroxy-2-(phenanthren-2-yl)pentan-2-yl)amino)-3,3-dimethyl-1-oxobutan-2-yl)carbamate (C3a)**



A flame-dried round bottom flask was charged with compound **C2a** (1.21 mmol, 0.576 g, 1.0 eq.) and anhydrous THF (6 mL) before being cooled to 0 °C. A solution of 9BBN (1.27 mmol, 0.4 M in Hexanes, 3.2 mL, 1.05 eq.) was added, and the ensuing hydroboration was allowed to proceed for 3 hr. at this temperature. After this point, aqueous sodium hydroxide (2 M, 6 mL, 10 eq.) was added dropwise to the reaction mixture, followed by dropwise addition of aqueous hydrogen peroxide solution (50 wt. %, 1.2 mL, 17 eq.). After 2 hours, the reaction was allowed to warm to room temperature and was diluted in Et_2O (50 mL) and brine (30 mL). The organic layer was removed and the aqueous layer was extracted with Et_2O (2X 50 mL). The organic layers were combined, washed with brine (70 mL), filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 10 to 75% Et_2O in hexanes (v/v) to provide product **C3a** in 56% yield (0.37 g) as a white solid.

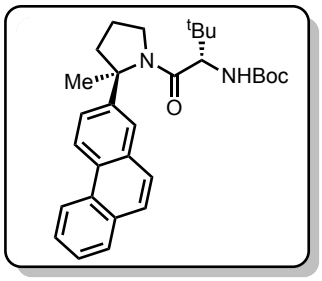
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 14.9, 8.5 Hz, 2H), 7.88 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.81 (d, *J* = 2.2 Hz, 1H), 7.71 (m, 2H), 7.64 (m, 2H), 7.59 (m, 1H), 6.78 (s, 1H), 5.20 (d, *J* = 9.6 Hz, 1H), 3.83 (d, *J* = 9.5 Hz, 1H), 3.63 (m, 2H), 2.18 (m, 1H), 2.05 (t, *J* = 11.6 Hz, 1H), 1.93 (d, *J* = 2.1 Hz, 3H), 1.73 (br, 1H), 1.50 (s, 9H), 1.06 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.1, 156.3, 143.5, 132.0, 131.9, 130.1, 128.9, 128.5, 127.3, 126.9, 126.5, 126.3, 124.9, 124.2, 122.8, 122.6, 79.8, 62.8, 62.5, 58.6, 39.9, 34.2, 28.4, 26.8, 26.7, 25.0

HR-MS (ESI): calcd. for $C_{30}H_{40}N_2O_4$ 493.3061 [M + H^+], found 493.3062

$[a]_D^{22} = +1.2$ (c =1.0, $CDCl_3$)

***tert*-butyl ((*S*)-3,3-dimethyl-1-((*R*)-2-methyl-2-(phenanthren-2-yl)pyrrolidin-1-yl)-1-oxobutan-2-yl)carbamate (C4a)**



A flame-dried round bottom flask was charged with sodium hydride (60 wt.% in mineral oil, 1.27 mmol, 0.051 g, 4.0 eq.) and THF (1 mL). The flask was cooled to 0 °C before a solution of compound **C3a** (0.32 mmol, 0.15 g, 1.0 eq.) in THF (2 mL) was added dropwise. The reaction was allowed to stir for 30 min. at this temperature before a solution of tosyl chloride (0.38 mmol, 0.072 g, 1.2 eq.) in THF (500 µL) was added. The ensuing reaction was allowed to proceed for 24 hours, gradually warming to room temperature. After this time, the reaction was diluted in Et_2O (15 mL) and brine (15 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (2X 15 mL). The organic layers were combined, washed with brine (10 mL), filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 30% Et_2O in hexanes (v/v) to provide product **C4a** in 94% yield (0.143 g) as a white solid.

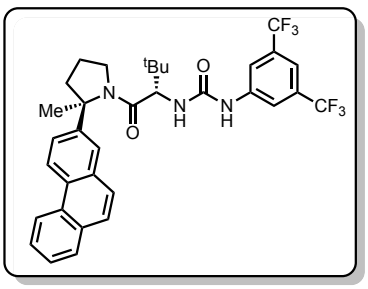
^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 23.5, 8.5 Hz, 2H), 7.87 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.70 (m, 3H), 7.61 (m, 2H), 7.49 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 4.43 (dd, *J* = 10.0, 1.3 Hz, 1H), 4.34 (dt, *J* = 10.1, 6.3 Hz, 1H), 3.91 (dt, *J* = 10.0, 7.5 Hz, 1H), 2.15 (td, *J* = 7.3, 6.9, 2.2 Hz, 2H), 2.05 (d, *J* = 1.1 Hz, 3H), 1.95 (m, 2H), 1.56 (s, 9H), 1.07 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.1, 156.4, 144.6, 131.9, 131.9, 130.2, 128.6, 128.4, 127.3, 126.7, 126.4, 126.1, 124.2, 123.8, 122.7, 122.5, 79.5, 67.3, 58.9, 50.1, 44.6, 34.9, 28.5, 26.5, 25.2, 22.6

HR-MS (ESI): calcd. for $C_{30}H_{38}N_2O_3$ 475.2955 [M + H^+], found 475.2955

$[a]_D^{22} = +56.4$ (c =1.0, $CDCl_3$)

1-(3,5-bis(trifluoromethyl)phenyl)-3-((*S*)-3,3-dimethyl-1-((*R*)-2-methyl-2-(phenanthren-2-yl)pyrrolidin-1-yl)-1-oxobutan-2-yl)urea (7a)



To a flame-dried 20 mL scintillation vial was added compound **C4a** (0.29 mmol, 0.139 g, 1.0 eq) dissolved in 500 µL of DCM. This solution was cooled to 0 °C before HCl solution (4 M in 1,4-dioxane, 1.45 mL, 20 eq.) was added dropwise over the course of 5 min. Following complete addition of HCl, the vial was allowed to stir at 0 °C for 2 hr. after which point Et_2O (5 mL) was added followed by the careful addition of sat. aq. $NaHCO_3$ (5 mL). The organic layer was removed and the aqueous layer was extracted with Et_2O (2X 15 mL). The organic layers were combined, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was dissolved in anhydrous DCM (1 mL) and to this solution was added triethylamine (0.87 mmol, 120 µL, 3.0 eq.) and 3,5-bis(trifluoromethyl)phenyl isocyanate (0.32 mmol, 55 µL, 1.1 eq.). The mixture was

allowed to stir for 12 hrs., after which point the reaction was diluted in DCM (20 mL) and brine (15 mL). The organic layer was separated and the aqueous layer was extracted with DCM (2X 15 mL). The organic layers were combined, washed with brine (10 mL), filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 30% Et_2O in hexanes (v/v) to provide product **7a** in 75% yield (0.137 g) as a white solid.

^{1}H NMR: (600 MHz, $CDCl_3$) δ 8.38 (dd, *J* = 26.6, 8.3 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.53 (m, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.42 (s, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 4.73 (d, *J* = 9.7 Hz, 1H), 4.32 (dt, *J* = 10.1, 6.5 Hz, 1H), 3.95 (dt, *J* = 10.0, 7.4 Hz, 1H), 2.15 (t, *J* = 6.8 Hz, 2H), 2.04 (s, 3H), 1.97 (p, *J* = 7.7, 7.2 Hz, 2H), 1.08 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.9, 155.8, 143.5, 140.3, 132.3, 132.0, 131.8, 131.7, 131.5, 129.7, 128.5, 128.4, 126.9, 126.7, 126.5, 126.3, 124.1, 123.4, 122.6, 122.1, 122.0, 119.0, 115.8, 67.7, 58.6, 50.5, 44.4, 35.1, 26.6, 25.0, 22.7

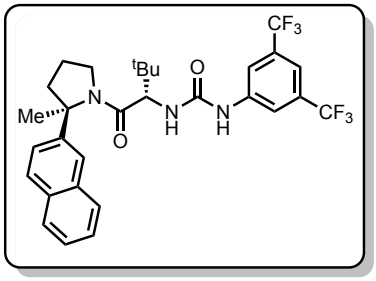
^{19}F NMR: (471 MHz, $CDCl_3$) δ -62.97 (s, 6F)

HR-MS (ESI): calcd. for $C_{34}H_{33}F_6N_3O_2$ 630.2550 [M + H^+], found 630.2543

$[a]_D^{22} = +12.6$ (c =1.0, $CDCl_3$)

Catalysts **7a-7d** were synthesized as described above for catalyst **7a**:

1-(3,5-bis(trifluoromethyl)phenyl)-3-((*S*)-3,3-dimethyl-1-((*R*)-2-methyl-2-(naphthalen-2-yl)pyrrolidin-1-yl)-1-oxobutan-2-yl)urea (7b)



^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.17 (br, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 4H), 7.40 (m, 2H), 7.29 (m, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.16 (dd, *J* = 8.6, 2.0 Hz, 1H), 4.77 (d, *J* = 9.8 Hz, 1H), 4.31 (ddd, *J* = 10.3, 7.3, 4.9 Hz, 1H), 3.94 (dt, *J* = 10.2, 7.5 Hz, 1H), 2.11 (dd, *J* = 7.8, 5.8 Hz, 2H), 2.00 (s, 3H), 1.92 (m, 2H), 1.10 (s, 9H)

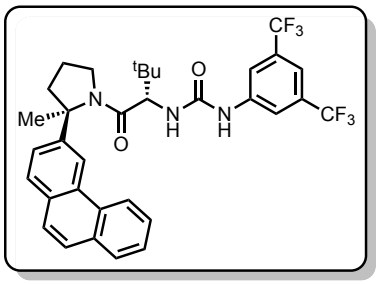
^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.9, 155.8, 142.3, 140.2, 132.8, 132.3, 132.0, 131.8, 131.7, 131.5, 127.8, 127.6, 127.1, 126.4, 125.8, 125.5, 124.2, 123.1, 123.0, 122.0, 119.1, 115.8, 67.8, 58.5, 50.5, 44.2, 35.1, 26.5, 25.1, 22.6

^{19}F NMR: (471 MHz, $CDCl_3$) δ -62.92 (s, 6F)

HR-MS (ESI): calcd. for $C_{30}H_{31}F_6N_3O_2$ 580.2393 [M + H^+], found 580.2371

$[a]_D^{22} = +9.4$ (c =1.0, $CDCl_3$)

1-(3,5-bis(trifluoromethyl)phenyl)-3-((*S*)-3,3-dimethyl-1-((*R*)-2-methyl-2-(phenanthren-3-yl)pyrrolidin-1-yl)-1-oxobutan-2-yl)urea (7c)



^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.3 Hz, 1H), 8.26 (s, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.56 (p, *J* = 8.3, 7.9 Hz, 2H), 7.43 (m, 3H), 7.36 (s, 1H), 7.29 (m, 3H), 4.85 (d, *J* = 9.6 Hz, 1H), 4.34 (ddd, *J* = 11.4, 7.8, 4.5 Hz, 1H), 3.99 (dt, *J* = 9.9, 7.6 Hz, 1H), 2.19 (t, *J* = 7.3 Hz, 2H), 2.09 (s, 3H), 1.94 (m, 2H), 1.08 (s, 9H)

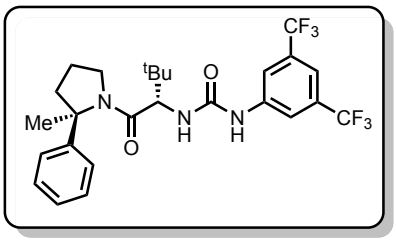
^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.7, 155.4, 143.0, 140.3, 132.3, 132.0, 131.8, 131.5, 130.1, 129.9, 129.4, 128.5, 128.5, 126.7, 126.3, 126.3, 126.2, 126.0, 124.1, 123.4, 122.1, 122.0, 118.6, 118.0, 115.6, 68.1, 58.3, 50.5, 44.5, 35.6, 26.5, 25.4, 22.6

^{19}F NMR: (471 MHz, $CDCl_3$) δ -62.93 (s, 6F)

HR-MS (ESI): calcd. for $C_{34}H_{33}F_6N_3O_2$ 630.2550 [M + H^+], found 630.2554

$[a]_D^{22} = +64.2$ (c =1.0, $CDCl_3$)

1-(3,5-bis(trifluoromethyl)phenyl)-3-((*S*)-3,3-dimethyl-1-((*R*)-2-methyl-2-phenylpyrrolidin-1-yl)-1-oxobutan-2-yl)urea (7d)



^{1}H NMR: (500 MHz, $CDCl_3$) δ 8.01 (br, 1H), 7.66 (s, 2H), 7.46 (s, 1H), 7.03 (m, 4H), 6.96 (m, 1H), 6.15 (br, 1H), 4.76 (d, J = 9.6 Hz, 1H), 4.20 (ddd, J = 11.6, 7.6, 4.3 Hz, 1H), 3.90 (dt, J = 9.7, 7.6 Hz, 1H), 2.07 (m, 2H), 1.91 (s, 3H), 1.89 (td, J = 24.3, 21.8, 10.8 Hz, 2H), 1.10 (s, 9H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 170.7, 155.4, 145.0, 140.5, 132.3, 132.0, 131.8, 131.5, 127.9, 126.1, 124.5, 124.3, 122.1, 119.5, 115.8, 67.69, 67.67, 58.3, 50.5, 44.5, 35.5, 26.6, 25.1, 22.4

^{19}F NMR: (500 MHz, $CDCl_3$) δ -63.00 (s, 6F)

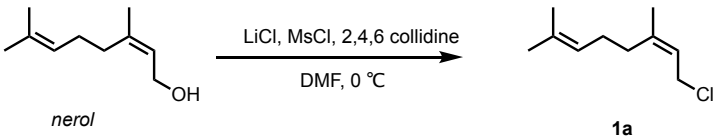
HR-MS (ESI): calcd. for $C_{26}H_{29}F_6N_3O_2$ 530.2237 [M + H^+], found 530.2236

$[a]_D^{22} = +7.8$ (c =1.0, $CDCl_3$)

Catalyst **6** was synthesized as described in the literature. Characterization data were found to be in accord with those previously published.[1]

3. Synthesis and Characterization of Substrates 1a-1i, 1b-d_1, Z-1b, and Intermediates

Synthesis and characterization of substrate 1a (neryl chloride)



nerol **1a**

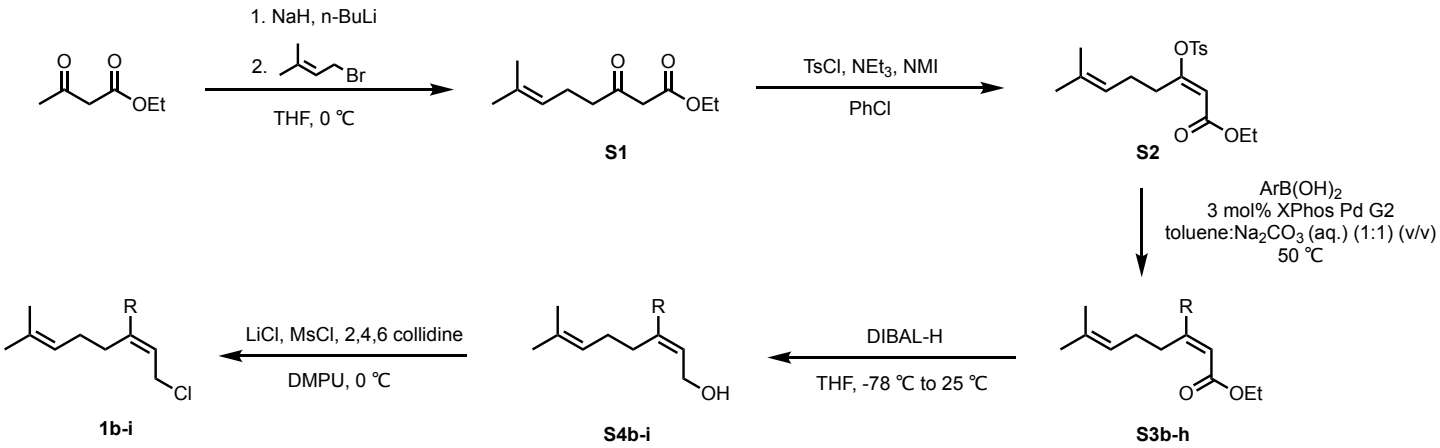
To a flame-dried round bottom flask was added nerol (4.0 mmol, 1.0 eq.), anhydrous lithium chloride (48.0 mmol, 12.0 eq.), and 2,4,6 collidine (6.0 mmol, 1.5 eq.) in anhydrous DMF (27 mL). The reaction vessel was cooled to 0 °C before methanesulfonyl chloride (MsCl) (8.8 mmol, 2.2 eq.) was added slowly to the stirring solution. Following addition of MsCl, the reaction flask was maintained at 0 °C for 60 min. before being diluted in hexanes (100 mL) and transferred to a separatory funnel. The organic layer was washed with sat. aq. ammonium chloride (50 mL), sat. aq. sodium bicarbonate (50 mL), and brine (50 mL). The organic layer was filtered over Na_2SO_4, and concentrated *in vacuo.* The resulting residue was purified via flash column chromatography using methylated silica gel eluting with 100% hexanes to afford product **1a** in 66% yield (0.46 g). NMR spectral data were found to be in agreement with literature values.[2]

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.46 (t, J = 8.0 Hz, 1H), 5.12 (m, 1H), 4.09 (d, J = 8.0 Hz, 2H), 2.13 (m, 4H), 1.78 (s, 3H), 1.70 (s, 3H), 1.63 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.7, 132.4, 123.5, 121.1, 41.0, 31.9, 26.5, 25.7, 23.5, 17.7

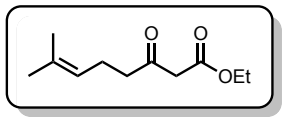
HR-MS (EI): calcd. for $C_{10}H_{17}Cl$ 172.1013 [M^+•], found 172.1012

Geranyl chloride was purchased from commercial sources and was used as received without further purification.



Scheme S2. General synthesis of compounds **1b-1i** and **d1-1b**. The synthesis of compound **1b** is used as the example below.

ethyl 7-methyl-3-oxooct-6-enoate (S1)



To a flame-dried round bottom flask was added solid NaH (60 wt.% in mineral oil, 27.5 mmol, 1.10 g, 1.1 eq.) and anhydrous THF (25 mL). The flask was cooled to 0 °C before ethyl acetoacetate (25 mmol, 3.18 mL, 1.0 eq) was added carefully over 5 min (caution: vigorous gas evolution). Following addition of ethyl acetoacetate, the mixture was stirred for 5 min. before n-BuLi solution (2.5 M in hexanes, 26.25 mmol, 10.5 mL, 1.05 eq.) was added dropwise. After 10 minutes, prenyl bromide (27.5 mmol, 3.17 mL, 1.1 eq.) was added and the ensuing reaction was allowed to take place at 0 °C for 30 minutes before being quenched with brine (25 mL) and extracted (3X 40 mL) with diethyl ether. The organic layers were combined, washed with brine (25 mL), filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 10% Et_2O in hexanes (v/v) to provide product **S1** in 53% yield (2.63 g).

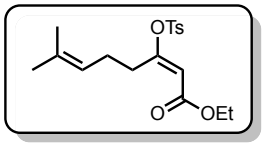
^{1}H NMR: (500 MHz, $CDCl_3$) δ (major tautomer) 5.05 (t, *J* = 7.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.42 (s, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.26 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ (major tautomer) 202.6, 167.2, 133.1, 122.2, 61.3, 49.4, 43.0, 25.6, 22.2, 17.6, 14.1

IR (thin film): υ_{max} 2977, 2914, 1742, 1715, 1647, 1367, 1235, 1177, 1079 cm^{-1}

HR-MS (ESI): calcd. for $C_{11}H_{18}O_3$ 199.1329 [M + H^+], found 199.1329

ethyl (*E*)-7-methyl-3-(tosyloxy)octa-2,6-dienoate (S2)



Compound **S2** was synthesized according to a modified literature procedure.[3] To a flame-dried round bottom flask was added compound **S1** (13.27 mmol, 2.63 g, 1.0 eq.), triethylamine (19.9 mmol, 2.75 mL, 1.5 eq.), and N-methyl imidazole (19.9 mmol, 1.58 mL, 1.5 eq.) in 30 mL of chlorobenzene. Tosyl chloride (17.25 mmol, 3.28 g, 1.3 eq.) was added in three portions over 20 min. and following addition of the final portion, the mixture was allowed to stir for 4 hours at room temperature before being quenched with brine (30 mL) and extracted (3X 30 mL) with ethyl acetate. The organic layers were combined, washed (2X 20 mL) with brine, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 60% dichloromethane in hexanes (v/v) to afford product **S2** in 71% yield (3.30 g) as a light-yellow oil. ^{1}H NMR analysis of the crude reaction mixture revealed product **S2** was formed in an 11:1 E:Z ratio; the minor Z isomer was found to be readily separable by conventional flash chromatography.

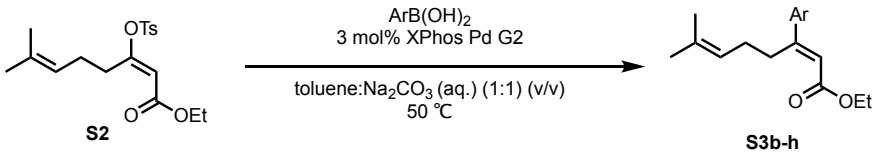
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 33.1 Hz, 2H), 5.80 (s, 1H), 5.01 (tdq, *J* = 7.2, 5.8, 1.4 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.71 (m, 2H), 2.47 (s, 3H), 2.13 (m, 2H), 1.56 (s, 3H), 1.64 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 165.4, 165.2, 145.7, 133.2, 133.0, 129.9, 128.2, 122.1, 110.0, 60.4, 31.5, 25.6, 25.1, 21.7, 17.6, 14.1

IR (thin film): υ_{max} 2979.43, 2926.71, 1719.49, 1649.04, 1370.78, 1179.23, 1157.96 cm^{-1}

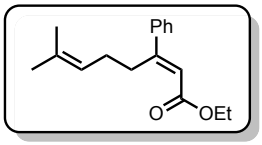
HR-MS (ESI): calcd. for $C_{18}H_{24}O_5S$ 353.1417 [M + H^+], found 353.1419

General procedure for synthesis of β-aryl esters S3b-h and Z-S3b



All β-aryl esters (**S3b-h** and **Z-S3b**) were synthesized according to the following procedure. Compound **S3b** (Ar = Ph) is used as the example. To a flame-dried round-bottom flask was added compound **S2** (6.5 mmol, 1.0 eq.) and phenyl boronic acid (7.8 mmol, 1.2 eq.) in anhydrous toluene (19 mL). A saturated aqueous solution of Na_2CO_3 sparged with N_2 was added (19 mL), followed by solid XPhos Pd G2 catalyst (0.2 mmol, 0.03 eq.). The reaction vessel was heated to 50 °C and allowed to stir for 12 hours before being quenched with brine (50 mL) and extracted (3X 50 mL) with ethyl acetate. The organic layers were combined, washed (2X 50 mL) with brine, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 5% Et_2O in Hexanes (v/v) to afford product **S3b** in 85% yield (1.43 g) as a clear light yellow oil.

ethyl (*E*)-7-methyl-3-phenylocta-2,6-dienoate (S3b)



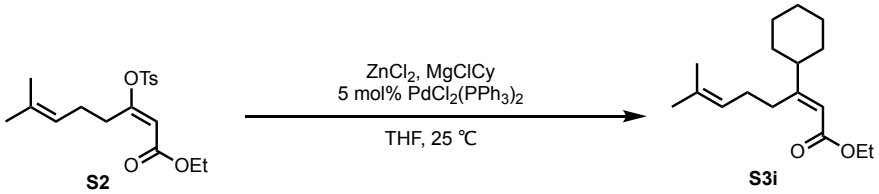
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.38 (m, 3H), 6.04 (s, 1H), 5.15 (ddt, *J* = 7.3, 5.8, 3.0, 1.5 Hz, 1H), 4.23 (q, *J* = 7.2, 2H), 3.13 (t, *J* = 7.8Hz, 2H), 2.13 (q, *J* = 7.6 Hz, 2H), 1.66 (s, 3H), 1.53 (s, 3H), 1.33 (t, *J* = 7.1Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.5, 160.0, 141.4, 132.2, 128.8, 128.5, 126.7, 123.6, 117.6, 59.8, 31.1, 27.6, 25.7, 17.6, 14.4

IR (thin film): υ_{max} 2977.75, 2928.16, 1712.02, 1623.76, 1163.45 cm^{-1}

HR-MS (ESI): calcd. for $C_{17}H_{22}O_2$ 259.1693 [M + H^+], found 259.1695

ethyl (*E*)-3-cyclohexyl-7-methylocta-2,6-dienoate (S3i)



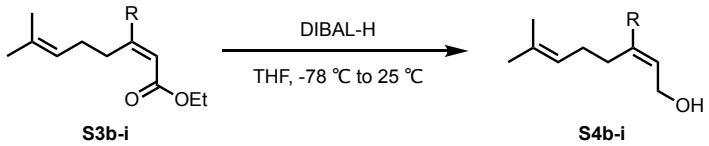
To a flame-dried round bottom flask was added $ZnCl_2$ solution (1 M in THF, 10.25 mL, 1.6 eq.) and anhydrous THF (10 mL). A solution of cyclohexyl magnesium chloride (2 M in Et_2O, 4.8 mL, 1.5 eq.) was added slowly over the course of 10 minutes. Following complete addition of the Grignard reagent, the mixture was allowed to stir for 40 minutes, after which point a solution of compound **S2** (9.61 mmol, 1.0 eq.) and $PdCl_2(PPh_3)_2$ (0.32 mmol, 0.05 eq.) in THF (10 mL) was added dropwise. The ensuing reaction was allowed to proceed for 12 hours at room temperature after which it was quenched with brine (50 mL) and diluted in Et_2O (50 mL). The organic layer was separated, and the aqueous layer was extracted (2X 50 mL) with Et_2O. The combined organic layers were dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 5% Et_2O in Hexanes (v/v) to afford product **S3i** in 65% yield (1.11 g) as a colorless oil.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.61 (s, 1H), 5.17 (tt, *J* = 7.6, 1.8 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.59 (m, 2H), 2.13 (q, *J* = 7.8 Hz, 2H), 1.98 (tt, *J* = 11.4, 3.0 Hz, 1H), 1.80 (m, 4H), 1.69 (s, 3H), 1.62 (s, 3H) 1.28 (m, 5H), 1.17 (m, 4H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 168.9, 166.9, 131.8, 124.1, 113.8, 59.4, 47.0, 32.2, 32.2, 27.8, 26.6, 26.2, 25.7, 17.7, 14.3

HR-MS (EI): calcd. for $C_{17}H_{28}O_2$ 264.2089 [$M^{+\bullet}$], found 264.2079

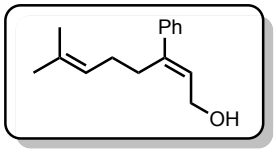
General procedure for synthesis of allylic alcohols S4b-i and Z-S4b



S3b-i **S4b-i**

All allylic alcohols (**S4b-i** and **Z-S4b**) were synthesized according to the following procedure. Synthesis of compound **S4b** (R = Ph) is used as the example. To a flame-dried round-bottom flask was added compound **S3b** (5.36 mmol, 1.0 eq.) in anhydrous THF (10 mL). The reaction vessel was cooled to -78 °C before diisobutyl aluminum hydride (DIBAL-H) (16 mmol, 16 mL, 1 M in THF, 3.0 eq.) was added slowly to the stirring solution. Following addition of DIBAL-H, the reaction flask was maintained at -78 °C for 1 hour before warming to 25 °C for an additional hour. The reaction flask was then cooled to 0 °C and slowly quenched with sat. aq. sodium potassium tartrate (10 mL). After one hour of stirring, the reaction was transferred to a separatory funnel and extracted (3X 50 mL) with ethyl acetate. The organic layers were combined, washed (2X 50 mL) with brine, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 40% Et_2O in hexanes (v/v) to afford product **S4b** in 82% yield (0.95 g).

(*E*)-7-methyl-3-phenylocta-2,6-dien-1-ol (S4b)



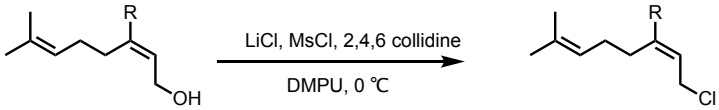
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.36 (m, 3H), 7.28 (m, 2H), 5.90 (t, *J* = 7.0 Hz, 1H), 5.11 (tdt, *J* = 7.3, 2.7, 1.5 Hz, 1H), 4.31 (dd, *J* = 6.9, 5.6 Hz, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 2.02 (q, *J* = 7.5 Hz, 2H), 1.68 (1, 3H), 1.51 (s, 3H), 1.45 (t, *J* = 5.7 Hz, 1H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 142.9, 142.0, 132.6, 128.3, 127.2, 127.1, 126.5, 123.6, 59.6, 30.0, 27.1, 25.6, 17.7

IR (thin film): υ_{max} 3316.61, 2964.92, 2856.66, 1492.93, 929.60, 697.17 cm^{-1}

HR-MS (EI): calcd. for $C_{15}H_{20}O$ 216.1509 [$M^{+\bullet}$], found 216.1511

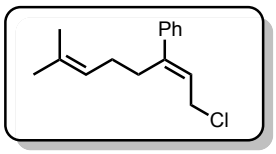
General procedure for synthesis of allylic chlorides 1b-1i, d1-1b, and Z-1b



S4b-i **1b-1i**

All allylic chlorides **1b-i** and **Z-1b** were synthesized according to the following procedure. Synthesis of compound **1b** (Ar = Ph) is used as the example. To a flame-dried 20 mL scintillation vial was added compound **S4b** (2.12 mmol, 1.0 eq.), anhydrous lithium chloride (25.5 mmol, 12.0 eq.), and 2,4,6 collidine (3.19 mmol, 1.5 eq.) in anhydrous DMPU (5.0 mL). The reaction vessel was cooled to 0 °C before methanesulfonyl chloride (MsCl) (4.67 mmol, 2.2 eq.) was added slowly to the stirring solution. Following addition of MsCl, the reaction flask was maintained at 0 °C for 40 min. before being diluted in hexanes (20 mL) and transferred to a separatory funnel. The organic layer was subsequently washed with sat. aq. ammonium chloride (15 mL), sat. aq. sodium bicarbonate (15 mL), and brine (15 mL) before being filtered over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using dimethylated silica gel eluting with pure hexanes to afford product **1b** in 52% yield (0.26 g).

(*E*)-(1-chloro-7-methylocta-2,6-dien-3-yl)benzene (1b)



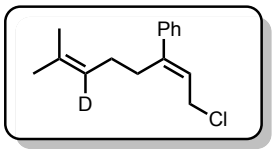
Conducted on 2.12 mmol scale; yield: 52% (0.26 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.35 (m, 5H), 5.89 (t, *J* = 8.0, 1H), 5.11 (t, *J* = 8.7 Hz, 1H), 4.27 (d, *J* = 8.1Hz, 2H), 2.60 (m, 2H), 2.06 (q, *J* = 7.6 Hz, 2H), 1.68 (s, 3H), 1.53 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.4, 141.5, 132.6, 128.3, 127.6, 126.6, 123.5, 123.2, 41.1, 30.0, 27.2, 25.7, 17.7

HR-MS (EI): calcd. for $C_{15}H_{19}Cl$ 234.1175 [$M^{+\bullet}$], found 234.1164

(E)-(1-chloro-7-methylocta-2,6-dien-3-yl-6-d)benzene (1b-*d*$_1$) – 83% deuterium incorporation

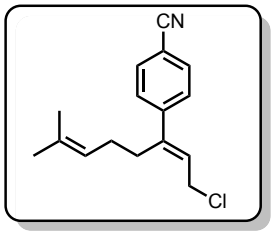


Deuterated substrate **1b**-*d*$_1$ was prepared analogously to **1b** following the general procedure for substrate synthesis (S7) with the following modification: deuterated (d1) prenyl bromide (prepared according to a previously reported procedure from Poulter[4]) was used during the alkylation of ethyl acetoacetate.

The deoxychlorination was conducted on 1.31 mmol scale; yield: 67% (0.16 g)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 5.88 (t, *J* = 8.1 Hz, 1H), 5.11 (ddt, *J* = 7.3, 5.9, 1.5 Hz, 0.17 H – residual protio material), 4.26 (d, *J* = 8.1 Hz, 2H), 2.62 – 2.57 (m, 2H), 2.05 (t, *J* = 7.7 Hz, 2H), 1.67 (s, 3H), 1.51 (s, 3H).

(*E*)-4-(1-chloro-7-methylocta-2,6-dien-3-yl)benzonitrile (1c)



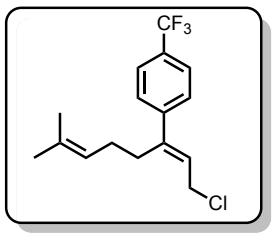
Conducted on 0.70 mmol scale; yield: 39% (0.070 g)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.94 (td, *J* = 8.0, 1.6 Hz, 1H), 5.06 (tdt, *J* = 7.3, 3.0, 1.5 Hz, 1H), 4.25 (dd, *J* = 8.0, 1.7 Hz, 2H), 2.60 (td, *J* = 7.6, 1.6 Hz, 2H), 2.04 (q, *J* = 7.3 Hz, 2H), 1.66 (s, 3H), 1.50 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 146.2, 143.7, 133.1, 132.2, 127.3, 126.2, 122.6, 118.8, 111.2, 40.3, 29.7, 27.0, 25.6, 17.7

HR-MS (EI): calcd. for $C_{16}H_{18}ClN$ 259.1122 [$M^{+\bullet}$], found 259.1125

(*E*)-1-(1-chloro-7-methylocta-2,6-dien-3-yl)-4-(trifluoromethyl)benzene (1d)



Conducted on 0.95 mmol scale; yield: 33% (0.095 g)

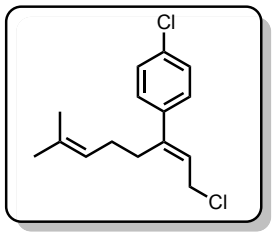
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.47 (m, 2H), 5.92 (td, *J* = 8.0, 1.8 Hz, 1H), 5.08 (tdq, *J* = 7.3, 3.0, 1.5 Hz, 1H), 4.26 (dd, *J* = 8.0, 1.9 Hz, 2H), 2.61 (ddd, *J* = 8.1, 6.8, 1.8 Hz, 2H), 2.04 (q, *J* = 7.6 Hz, 2H), 1.67 (s, 3H), 1.51 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.2, 144.2, 132.9, 129.8, 126.9, 125.4, 125.3, 125.3, 122.8, 40.5, 29.9, 27.0, 25.6, 17.7

^{19}F NMR: (500 MHz, $CDCl_3$) δ -62.53 (s, 3F)

HR-MS (EI): calcd. for $C_{16}H_{18}ClF_3$ 302.1044 [$M^{+\bullet}$], found 302.1042

(*E*)-1-chloro-4-(1-chloro-7-methylocta-2,6-dien-3-yl)benzene (1e)



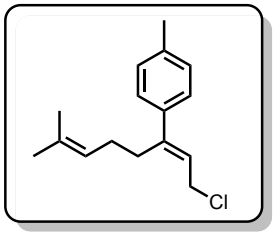
Conducted on 0.70 mmol scale; yield: 46% (0.088 g)

^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.27 (m, 4H), 5.83 (t, *J* = 8.0 Hz, 1H), 5.05 (ddq, *J* = 8.8, 5.8, 1.4 Hz, 1H), 4.21 (dd, *J* = 8.0, 1.1 Hz, 2H), 2.54 (t, *J* = 7.7 Hz, 2H), 2.00 (q, *J* = 7.5 Hz, 2H), 1.64 (d, *J* = 1.3 Hz, 3H), 1.48 (s, 3H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.3, 139.9, 133.5, 132.8, 128.5, 127.9, 124.0, 123.0, 40.8, 30.0, 27.0, 25.7, 17.7

HR-MS (EI): calcd. for $C_{15}H_{18}Cl_2$ 268.0780 [$M^{+\bullet}$], found 268.0777

(*E*)-1-(1-chloro-7-methylocta-2,6-dien-3-yl)-4-methylbenzene (1f)



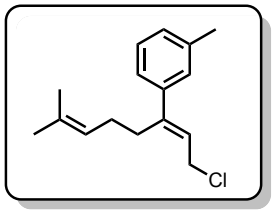
Conducted on 0.40 mmol scale; yield: 54% (0.054 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.28 (m, 2H), 7.15 (m, 2H), 5.87 (td, *J* = 8.1, 1.7 Hz, 1H), 5.12 (ddq, *J* = 8.9, 5.9, 1.6 Hz, 1H), 4.26 (m, 2H), 2.58 (ddd, *J* = 8.0, 6.8, 1.7 Hz, 2H), 2.36 (s, 3H), 2.06 (m, 2H), 1.68 (s, 3H), 1.54 (s, 3H).

^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.3, 138.5, 137.4, 132.5, 129.0, 126.4, 123.3, 122.7, 41.2, 30.0, 27.2, 25.7, 21.1, 17.7

HR-MS (EI): calcd. for $C_{16}H_{21}Cl$ 248.1326 [$M^{+\bullet}$], found 248.1323

(*E*)-1-(1-chloro-7-methylocta-2,6-dien-3-yl)-3-methylbenzene (1g)



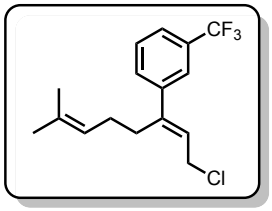
Conducted on 0.70 mmol scale; yield: 54% (0.094 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.5 Hz, 1H), 7.18 (m, 2H), 7.11 (dd, *J* = 7.4, 1.8 Hz, 1H), 5.87 (t, *J* = 8.0 Hz, 1H), 5.13 (tp, *J* = 7.2, 1.4 Hz, 1H), 4.27 (d, *J* = 8.1 Hz, 2H), 2.59 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.37 (s, 3H), 2.06 (q, *J* = 7.6 Hz, 2H), 1.69 (s, 3H), 1.54 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 145.6, 141.5, 137.9, 132.5, 128.4, 128.2, 127.4, 123.7, 123.3, 123.3, 41.1, 30.1, 27.2, 25.7, 21.5, 17.7

HR-MS (EI): calcd. for $C_{16}H_{21}Cl$ 248.1326 [$M^{+\bullet}$], found 248.1327

(*E*)-1-(1-chloro-7-methylocta-2,6-dien-3-yl)-3-(trifluoromethyl)benzene (1h)



Conducted on 0.70 mmol scale; yield: 56% (0.12 g)

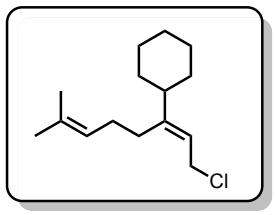
^{1}H NMR: (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.55 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 5.92 (t, *J* = 8.0 Hz, 1H), 5.09 (tp, *J* = 7.4, 1.5 Hz, 1H), 4.26 (d, *J* = 8.0 Hz, 2H), 2.62 (m, 2H), 2.06 (q, *J* = 7.5 Hz, 2H), 1.67 (s, 3H), 1.51 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.2, 142.4, 132.9, 130.9, 129.9, 128.8, 125.2, 125.1, 124.3, 123.4, 122.8, 40.5, 29.9, 27.0, 25.6, 17.6

^{19}F NMR: (500 MHz, $CDCl_3$) δ -62.64 (s, 3F)

HR-MS (EI): calcd. for $C_{16}H_{18}ClF_3$ 302.1044 [$M^{+\bullet}$], found 302.1047

(*E*)-(1-chloro-7-methylocta-2,6-dien-3-yl)cyclohexane (1i)

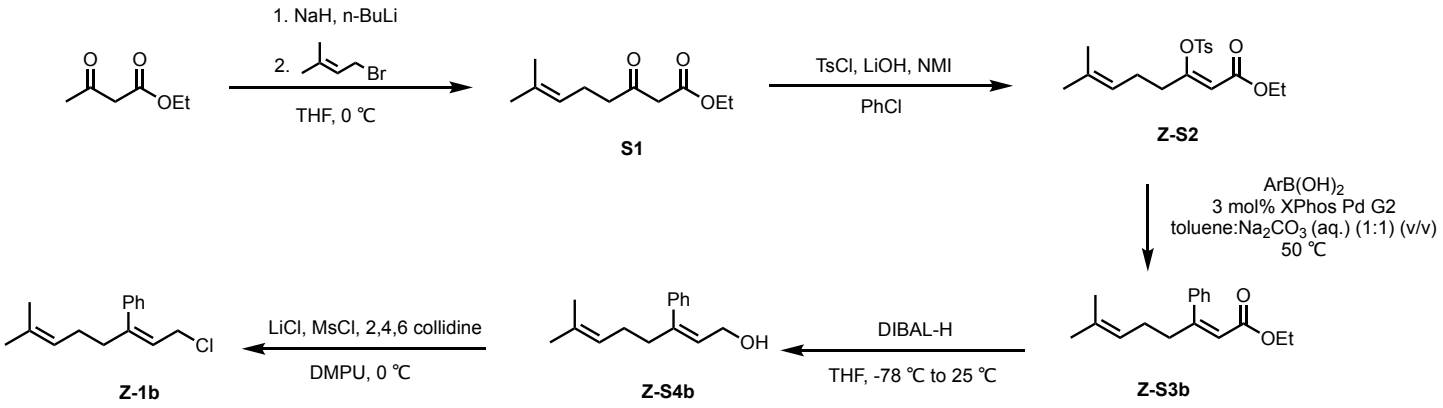


Conducted on 0.70 mmol scale; yield: 30% (0.050 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ 5.40 (t, *J* = 8.0 Hz, 1H), 5.12 (m, 1H), 4.12 (d, *J* = 8.1, 2H), 2.10 (m, 4H), 1.89 (m, 1H), 1.76 (m, 5H), 1.70 (s, 3H), 1.62 (s, 3H), 1.27 (m, 2H), 1.17 (m, 3H)

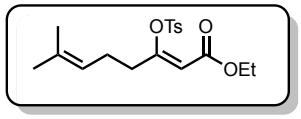
^{13}C NMR: (126 MHz, $CDCl_3$) δ 151.4, 132.1, 123.8, 119.1, 45.0, 41.4, 32.4, 30.1, 28.0, 26.8, 26.3, 25.7, 17.7

HR-MS (EI): calcd. for $C_{15}H_{25}Cl$ 240.1639 [$M^{+\bullet}$], found 240.1638



Scheme S3. Synthesis of compound **Z-1b**

ethyl (*Z*)-7-methyl-3-(tosyloxy)octa-2,6-dienoate (Z-S2)



Z-S2 was synthesized according to a modified literature procedure.[3] To a flame-dried round bottom flask was added compound **S1** (8.73 mmol, 1.73 g, 1.0 eq.), lithium hydroxide (13.09 mmol, 0.313 g, 1.5 eq.), and N-methyl imidazole (13.09 mmol, 1.04 mL, 1.5 eq.) in 20 mL of chlorobenzene. The reaction flask was cooled to 0 °C before tosyl chloride (13.09 mmol, 2.50 g, 1.5 eq.) was added in three portions over 20 minutes. Following addition of the final portion, the mixture was allowed to stir for 24 hours warming to room temperature. After this time, full consumption of the **S1** was observed by TLC and the reaction was quenched with brine (30 mL) and extracted (3X 30 mL) with ethyl acetate. The organic layers were combined, washed (2X 20 mL) with brine, filtered over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash column chromatography using a gradient of 0 to 60% dichloromethane in hexanes (v/v) to afford product **Z-S2** in 51% yield (1.57 g) as a light-yellow oil.

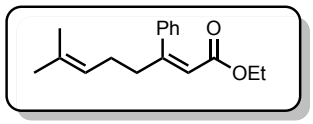
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.53 (s, 1H), 5.00 (tq, *J* = 7.1, 1.4 Hz, 1H), 4.07 (q, *J* = 7.2, 2H), 2.46 (s, 3H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.18 (q, *J* = 7.5 Hz, 2H), 1.67 (s, 3H), 1.56 (s, 3H), 1.22 (t, *J* = 7.1, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 163.0, 159.4, 145.3, 133.6, 133.6, 129.6, 128.3, 121.6, 110.6, 60.4, 35.2, 25.6, 24.9, 21.7, 17.7, 14.0

HR-MS (ESI): calcd. for $C_{18}H_{24}O_5S$ 353.1417 [M + H^+], found 353.1416

The general procedures for synthesis of **1b-1i** were used to synthesize **Z-1b** from **Z-S2**

ethyl (*Z*)-7-methyl-3-phenylocta-2,6-dienoate (Z-S3b)



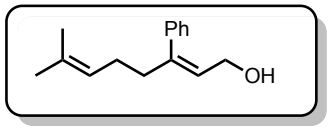
Conducted on 4.45 mmol scale; yield: 91% (1.05 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ7.34 (m, 3H), 7.17 (dd, *J* = 6.9, 1.5 Hz, 2H), 5.90 (s, 1H), 5.08 (ddt, *J* = 8.5, 6.9, 1.5 Hz, 1H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.48 (dd, *J* = 8.9, 7.0 Hz, 2H), 2.09 (q, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.54 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 166.0, 159.2, 140.1, 132.6, 127.8, 127.5, 127.1, 122.8, 117.4, 59.7, 40.4, 25.9, 25.6, 17.7, 13.9

HR-MS (ESI): calcd. for $C_{17}H_{22}O_2$ 259.1693 [M + H^+], found 259.1693

(*Z*)-7-methyl-3-phenylocta-2,6-dien-1-ol (Z-S4b)



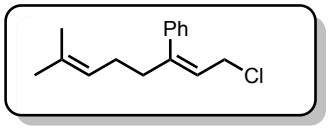
Conducted on 4.07 mmol scale; yield: 93% (0.82 g)

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.35 (td, *J* = 7.8, 7.3, 1.6 Hz, 2H), 7.28 (m, 1H), 7.14 (dt, *J* = 6.5, 1.5 Hz, 2H), 5.71 (t, *J* = 6.9 Hz, 1H), 5.10 (ddt, *J* = 7.0, 5.5, 1.5 Hz, 1H), 4.06 (d, *J* = 6.9 Hz, 2H), 2.42 (m, 2H), 2.04 (q, *J* = 7.5 Hz, 2H), 1.68 (s, 3H), 1.54 (s, 3H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 144.5, 140.0, 131.9, 128.1, 128.1, 127.0, 125.6, 123.6, 60.3, 39.0, 26.6, 25.7, 17.7

HR-MS (ESI): calcd. for $C_{15}H_{20}O$ 217.1542 [M + H^+], found 217.1544

(*Z*)-(1-chloro-7-methylocta-2,6-dien-3-yl)benzene (Z-1b)



Conducted on 0.92 mmol scale; yield: 69% (0.150 g); synthesized as a 30:1 mixture of Z:E.

^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.3, 7.1 Hz, 2H), 7.31 (m, 1H), 7.20 (dd, *J* = 8.0, 1.6 Hz, 2H), 5.71 (td, *J* = 8.0, 1.4 Hz, 1H), 5.08 (tq, *J* = 6.9, 1.5 Hz, 1H), 3.98 (d, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 7.7 Hz, 2H), 2.03 (q, *J* = 7.6 Hz, 2H), 1.68 (s, 3H), 1.53 (s, 3H)

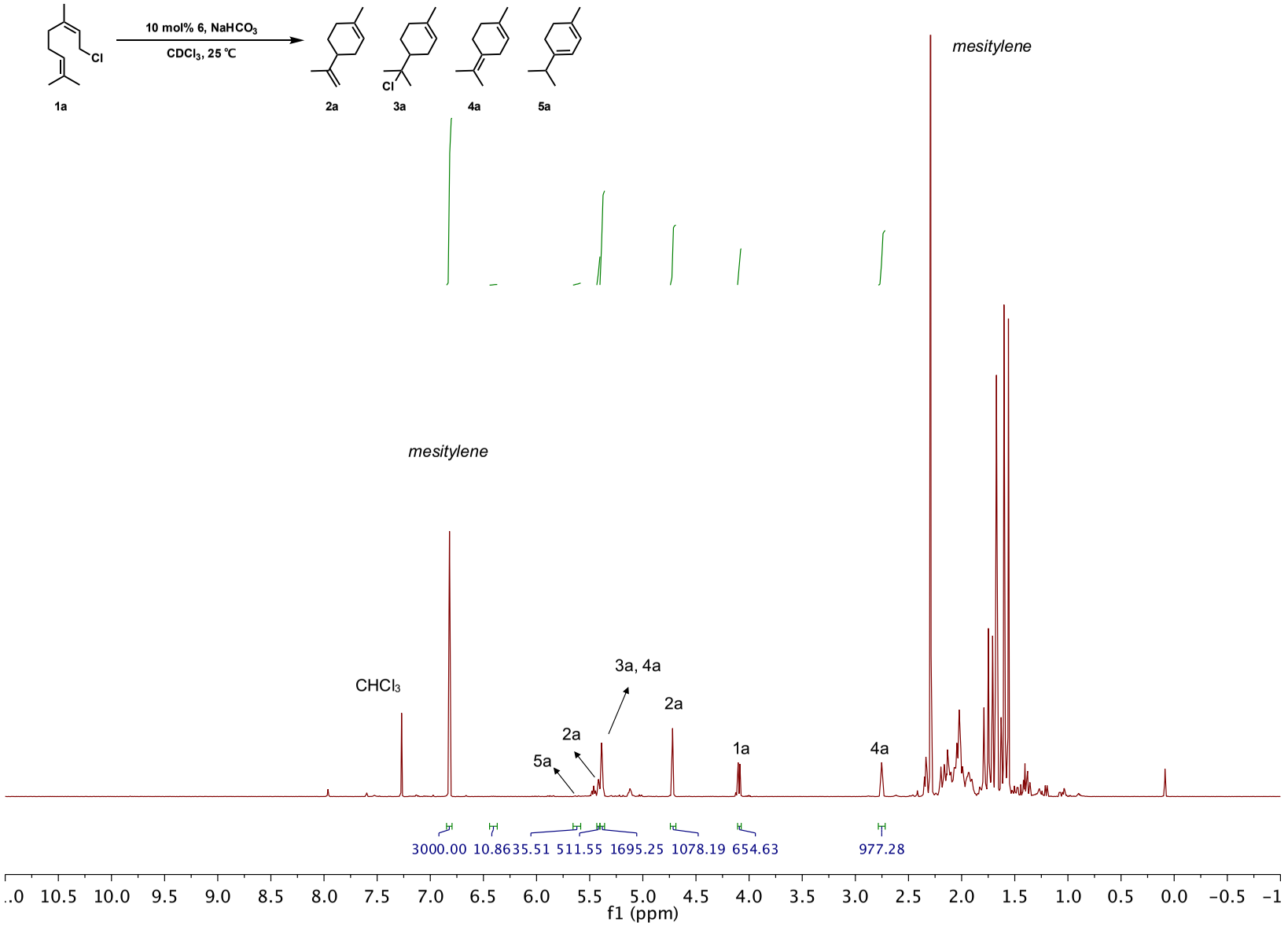
^{13}C NMR: (126 MHz, $CDCl_3$) δ 146.67, 139.16, 132.10, 128.28, 128.03, 127.37, 123.36, 122.40, 42.36, 38.97, 26.34, 25.65, 17.71

HR-MS (EI): calcd. for $C_{15}H_{19}Cl$ 234.1170 [$M^{+\bullet}$], found 234.1173

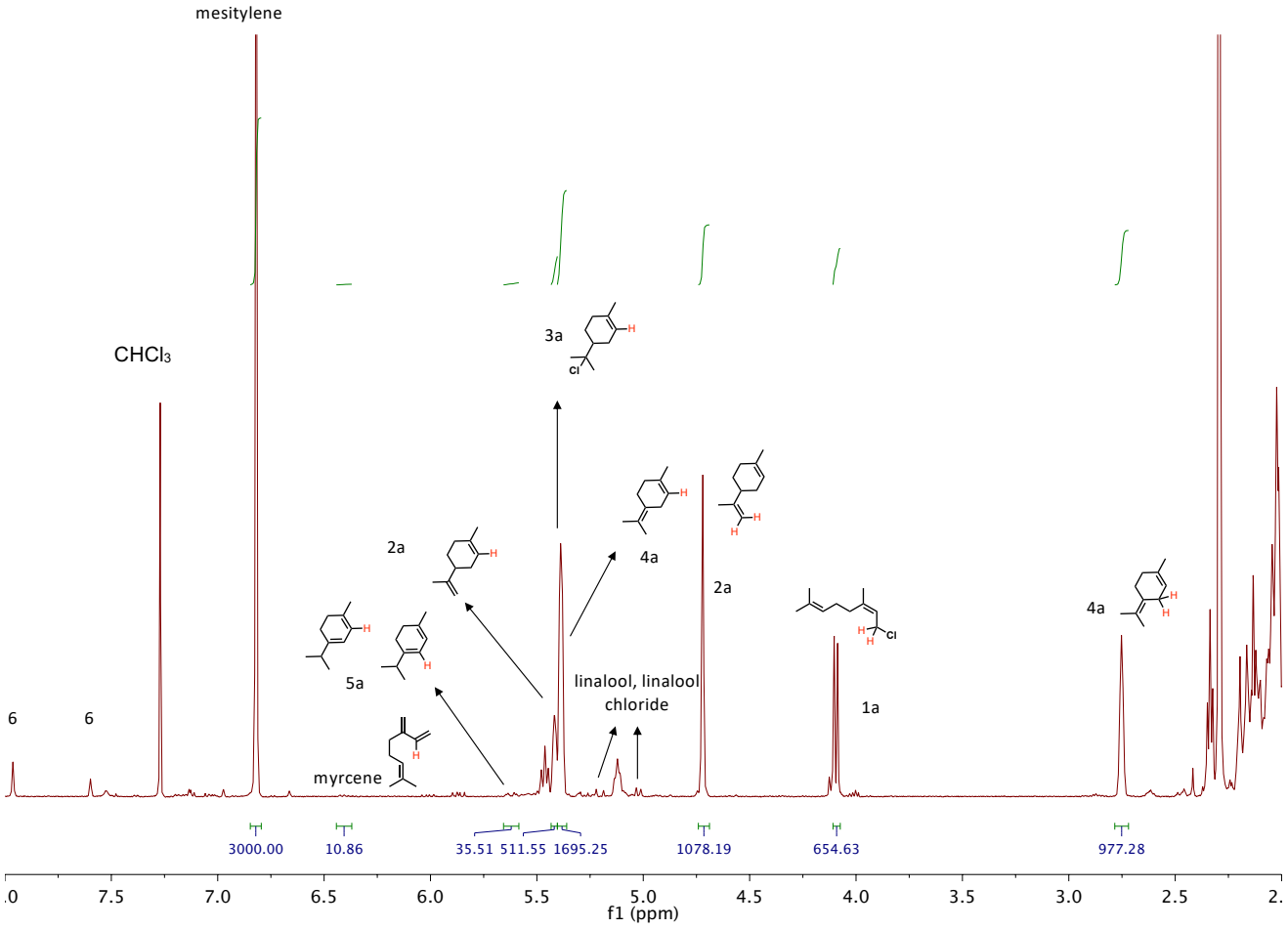
4. Cyclization of Neryl and Geranyl Chlorides with 6

Geranyl chloride was purchased from Sigma Aldrich and used as received; neryl chloride (**1a**) was synthesized as described in section 3. Experiments were carried out using 0.2 mmol of either geranyl or neryl chloride, a 10 mol% (0.02 mmol) loading of bis-aryl urea hydrogen bond donor catalyst **6**, 1.5 eq. of sodium bicarbonate (0.3 mmol), and 2.0 mL of $CDCl_3$ (0.1 M) at room temperature for 24 hours. A stock solution (1.0 mL) of geranyl chloride or **1a** in $CDCl_3$ was added to a stirring 1.0 mL solution of **6**, sodium bicarbonate, and mesitylene internal standard (10 μL) in $CDCl_3$ to initiate reactions. Reactions were carried out in sealed oven-dried screw-cap vials under air. After 24 hours, 700 μL aliquots of each reaction were analyzed by ^{1}H NMR. Product distributions and conversions were assessed from crude ^{1}H NMR reaction mixtures against mesitylene internal standard. The identities of the products in these experiments were determined by comparing crude ^{1}H NMR spectra of the catalyzed reactions with ^{1}H NMR spectra of authentic samples of limonene, α-terpinene, terpinolene, myrcene, and terpinyl chloride (synthesized according to a literature procedure[5]). Note: urea catalyst **6** is only partially soluble in deuterochloroform at these concentrations. Note: the commercial geranyl chloride used in this study contained a small (< 2%) impurity of linalool chloride and synthesized **1a** contained small impurities of linalool chloride (< 2%) and linalool (< 2%).

crude reaction of 1a, ($CDCl_3$, 600 MHz)

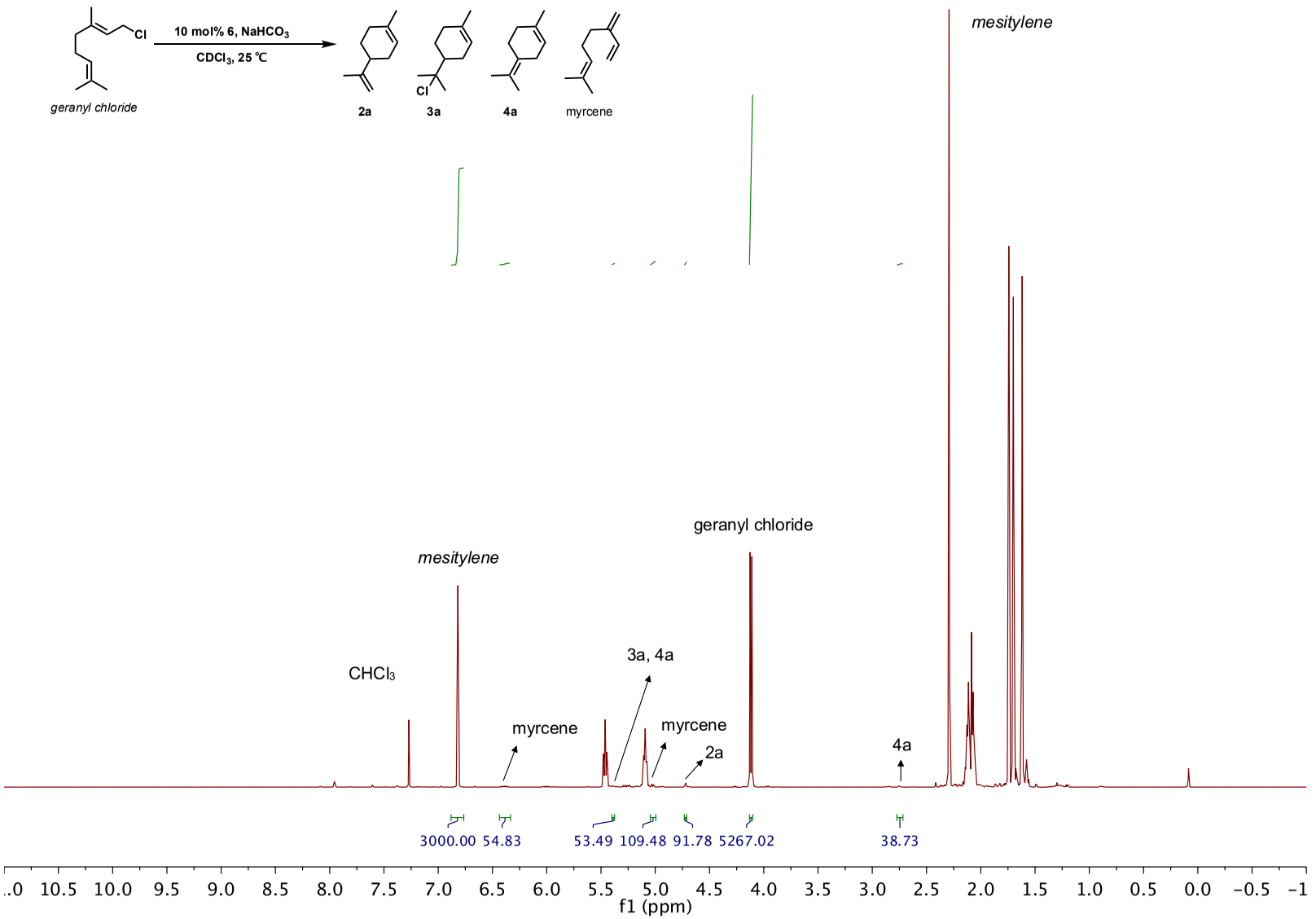


crude reaction of 1a, ($CDCl_3$, 600 MHz)

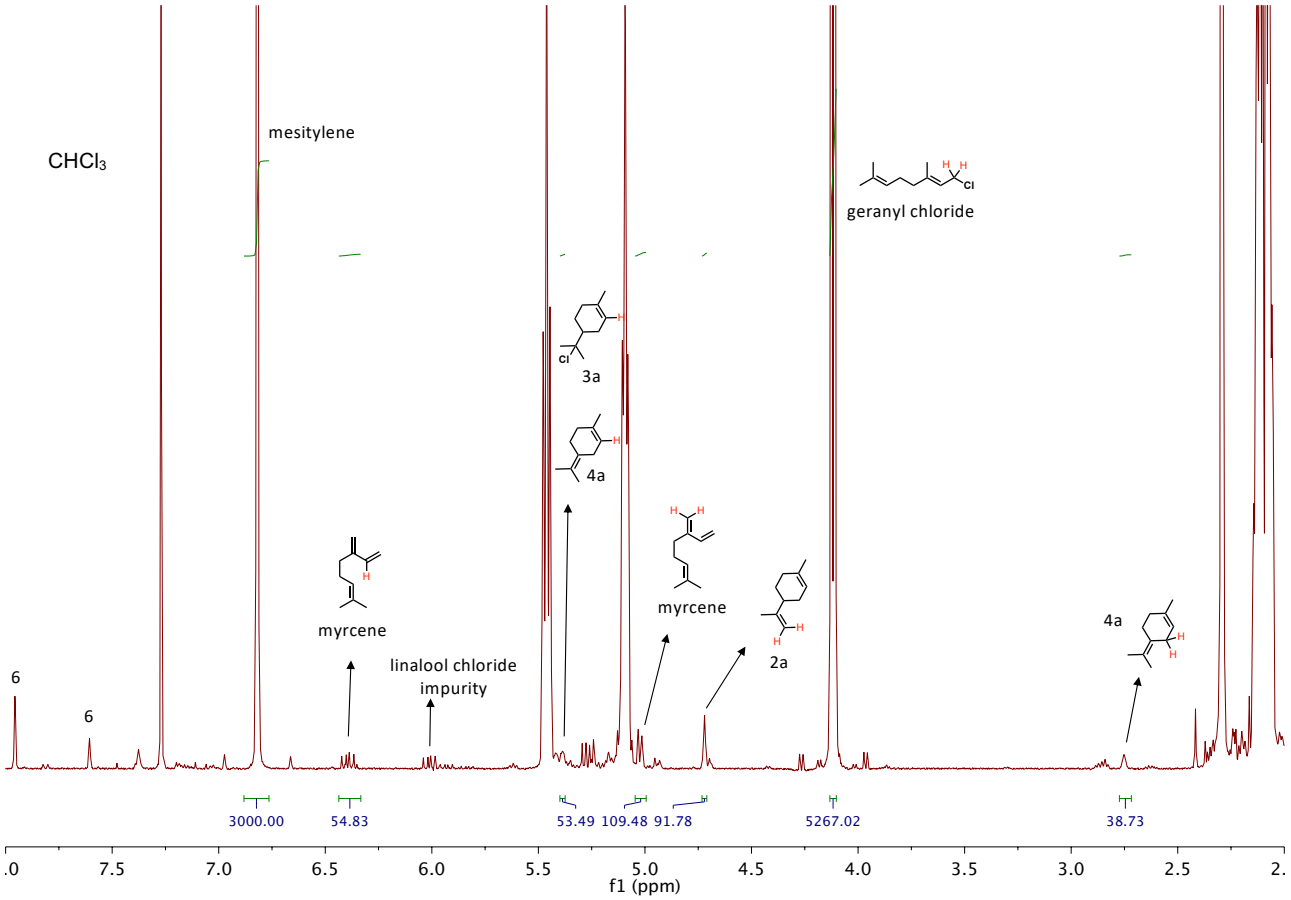


Mesitylene (M)	2a (M)	3a (M)	4a (M)	5a (M)	Myrcene (M)	1a (M)	PDT (M)
0.035764269	0.019276941	0.04314959	0.01747085	0.00064376	0.000393407	0.01194527	0.08093454
Sample	2a (%)	3a (%)	4a (%)	5a (%)	Myrcene (%)	Conv. (%)	Yield (%)
1a	19.28	43.15	17.47	0.64	0.39	88.05	80.93

crude reaction of geranyl chloride, ($CDCl_3$, 600 MHz)



crude reaction of geranyl chloride, ($CDCl_3$, 600 MHz)

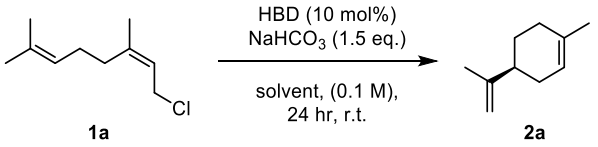


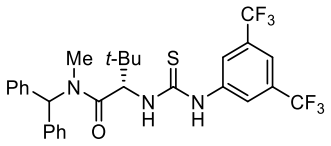
Mesitylene (M)	2a (M)	3a (M)	4a (M)	5a (M)	Myrcene (M)	G-Cl (M)	PDT (M)
0.035764269	0.001627274	0.00121599	0.00067952	0	0.001967035	0.09416732	0.005489815
Sample	2a (%)	3a (%)	4a (%)	5a (%)	Myrcene (%)	Conv. (%)	Yield (%)
Geranyl Cl	1.63	1.22	0.68	0.00	1.97	5.83	5.49

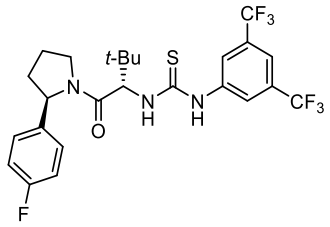
5. Optimization of Catalyst Structure and Reaction Conditions for Enantioselective Cyclization Reactions

5.1 Optimization with 1a

General procedure for reaction optimization with 1a: To an oven-dried 0.5-dram vial equipped with a magnetic stir-bar was added $NaHCO_3$ (6.3 mg, 0.075 mmol, 1.5 eq.) and catalyst (0.005 mmol, 0.1 eq.). Then the indicated solvent (0.5 mL, 0.1 M) was added followed by **1a** (8.6 mg, 0.05 mmol, 1 eq.). The reaction vial was capped and was stirred vigorously at room temperature. After 24 hours, the reaction was diluted with 5 mL of hexanes, filtered through a plug of cotton and subjected to chiral GC analysis to determine enantiomeric excess.







solvent	e.e. of **2a** (%)
CH_2Cl_2	34
benzene	31
Et_2O	26
cyclohexane	27

solvent	e.e. of **2a** (%)
CH_2Cl_2	17
benzene	-14
Et_2O	-10
cyclohexane	-21

Figure S1. Representative solvent screening data for neryl chloride**.** All reactions were run according to the general procedure for reaction optimization with **1a**.

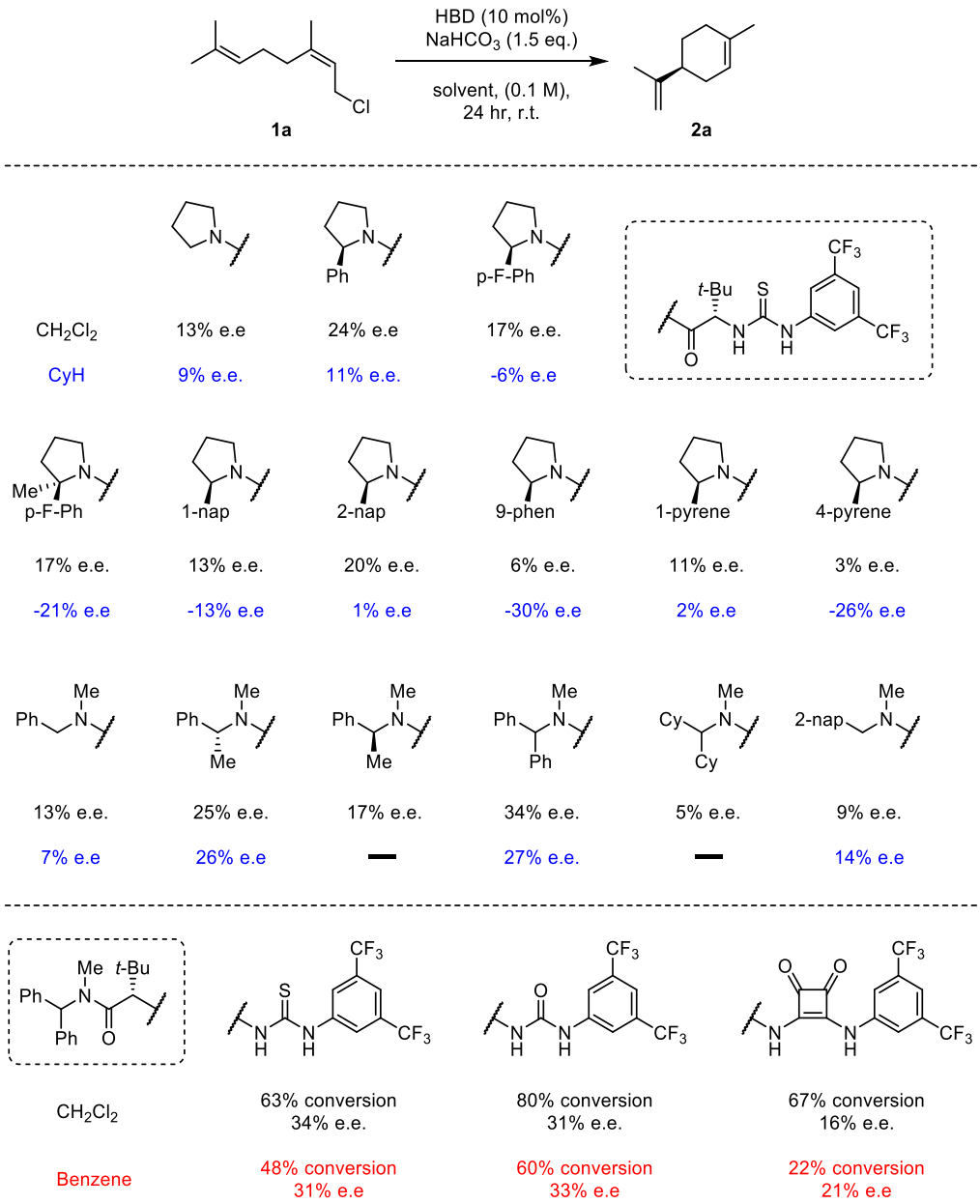


Figure S2. Representative catalyst screening data for neryl chloride (3,5-bis(trifluoromethyl)phenyl aniline-*t*-leucine catalysts). All reactions were run according to the general procedure for reaction optimization with **1a**. Approximate conversion was determined with crude NMR analysis of the reaction by comparing the sum of all products to unreacted starting material (no internal standard was used).

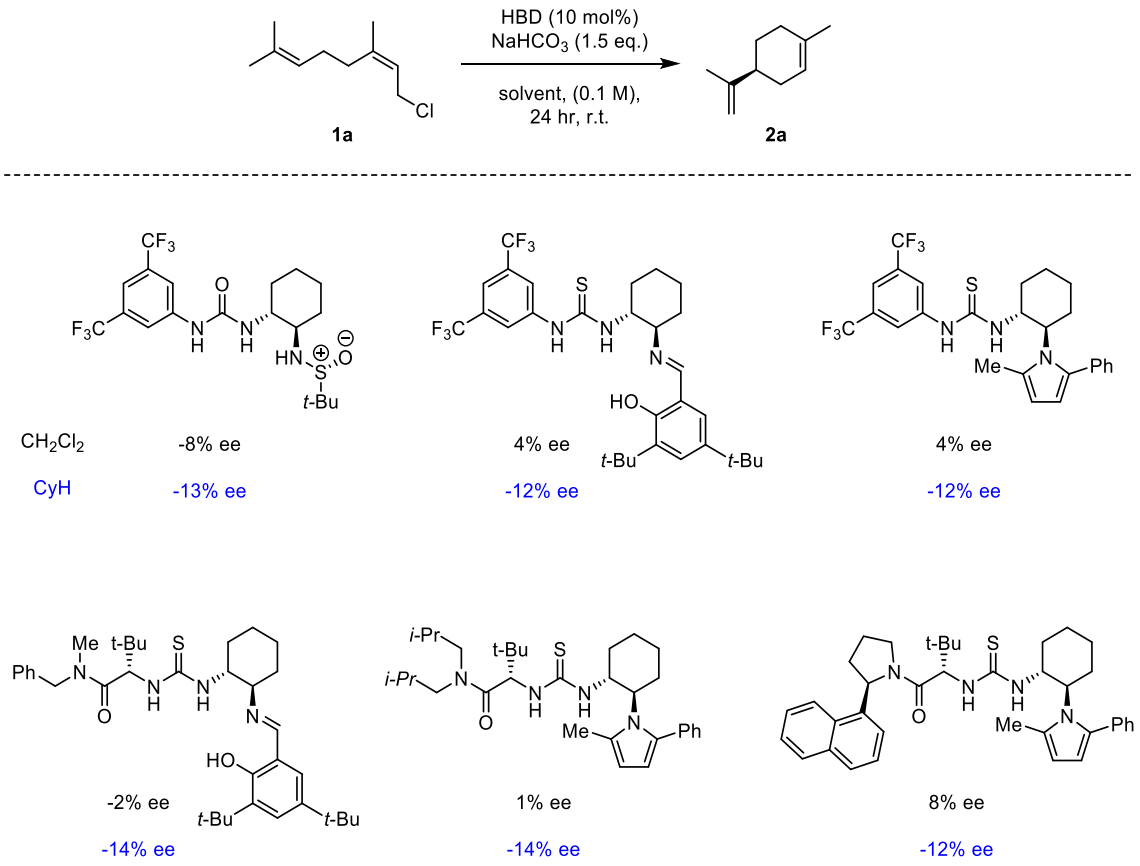
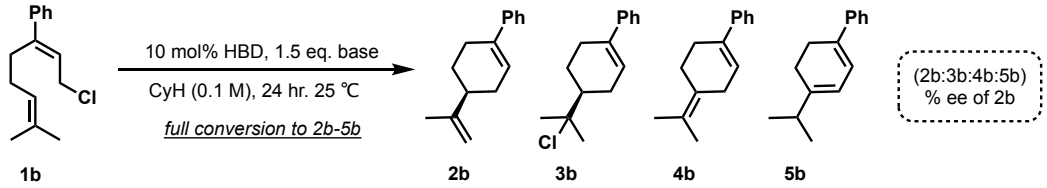


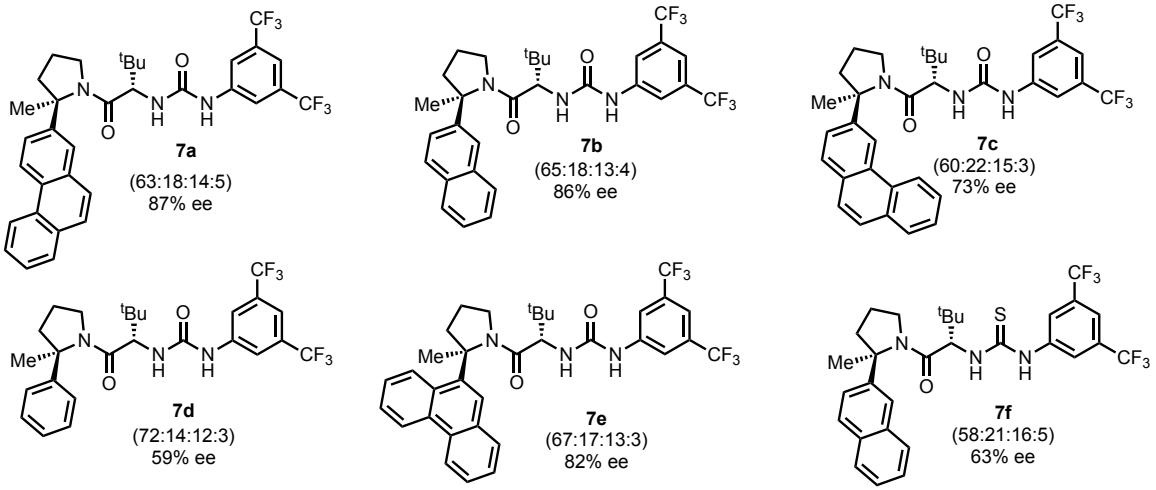
Figure S3. Representative catalyst screening data for neryl chloride (catalysts with a cyclohexane diamine fragment). All reactions were run according to the general procedure for reaction optimization with **1a**.

5.2 Optimization with 1b and 1d

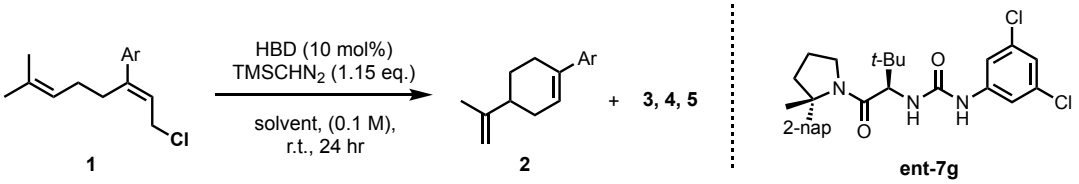
General procedure for reaction optimization with 1b and 1d: All optimization-scale experiments were carried out using 0.05 mmol of substrate **1b** or **1d**, a 10 mol% (0.005 mmol) loading of hydrogen bond donor catalyst, base (typically 1.5 equiv., 0.075 mmol), and 500 μL of solvent (0.1 M) at room temperature for 24 hours. A stock solution (250 μL) of HBD catalyst in the desired solvent was added to a 250 μL solution of **1** and base to initiate reactions. All reactions were carried out in sealed oven-dried screw-cap vials under air. In all cases, reactions were determined to have proceeded to full conversion of substrates **1**, resulting exclusively in products **2-5**. Product distributions were assessed from crude ^{1}H NMR spectra. Enantiomeric excess (e.e.) values were determined using an Agilent 7890A series GC system outfitted with a commercially available cyclosil-β 30m column. Method for **1b**: 150 °C isocratic, 7psi, t_r(major): 28.7 min. t_r(minor): 29.4 min. Method for **1d**: 120 °C to 200 °C at 0.5 °C/min, 7psi, t_r(major): 61.9 min. t_r(minor): 63.0 min.



screen of chiral hydrogen bond donors



screen of solvents

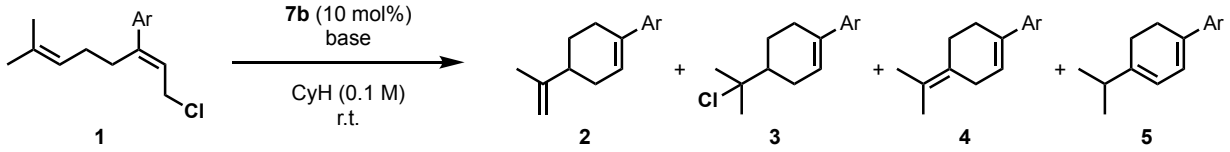


entry	substrate	HBD	solvent	conversion	e.e. of **2** (%)
1[#]	**1d**	**7b**	cyclohexane	complete	91
2	**1d**	**7b**	toluene	complete	87
3	**1d**	**7b**	dichloromethane	complete	78
4	**1b**	**ent-7g**	cyclohexane	complete	-84
5[†]	**1b**	**ent-7g**	cyclohexane	complete	-84
6[†]	**1b**	**ent-7g**	benzene	complete	-77
7[†]	**1b**	**ent-7g**	toluene	complete	-81
8[†]	**1b**	**ent-7g**	Et_2O	50%	ND
9[†]	**1b**	**ent-7g**	*t*-BuOMe	47%	ND

- 1.5 eq. $NaHCO_3$ was used in place of $TMSCHN_2$; † - an ethereal solution of $TMSCHN_2$ (2.0 M) was used

Figure S4. Representative catalyst and solvent optimization data for **1b** and **1d**. All reactions were run according to the general procedure for reaction optimization.

screen of bases



entry	substrate	base	loading (equiv.)	time (hr)	conversion	e.e. of 2	[2_x]:[3_x]:[4_x]:[5_x]
1	**1b**	$NaHCO_3$	1.5	24	complete	86	68 : 19 : 9 : 4
2#,†	**1b**	$TMSCHN_2$	1.15	36	complete	-85	68: 17 : 11 : 4
3#	**1b**	2,2,6,6-tetramethylpiperidine	1.5	22	7%	ND	ND
4#	**1b**	triethylamine	1.5	22	8%	ND	ND
5#	**1b**	pyridine	1.5	22	13%	ND	ND
6#	**1b**	2,6-di-t-butyl-4-methylpyridine	1.5	22	11%	ND	ND
7	**1d**	$NaHCO_3$	1.5	36	complete	91	70 : 13 : 13 : 4
8	**1d**	$NaHCO_3$	1.1	36	complete	91	70 : 13 : 13 : 4
9	**1d**	$NaHCO_3$	3	36	complete	91	70 : 13 : 13 : 4
10	**1d**	Na_2CO_3	1.5	36	complete	91	71 : 13 : 12 : 4
11	**1d**	K_2CO_3	1.5	36	complete	91	72 : 12 : 12 : 4
12	**1d**	Cs_2CO_3	1.5	36	complete	91	71 : 12 : 13 : 4

- **ent-7b** was used; † - a 5 mol% loading of urea was used.

Figure S5. Representative base optimization data for **1b** and **1d**. All reactions were run according to the general procedure for reaction optimization.

6. Catalytic Enantioselective Cyclization Reactions

6.1 General procedures

Procedure for Enantioselective Cyclization of Substrate 1a

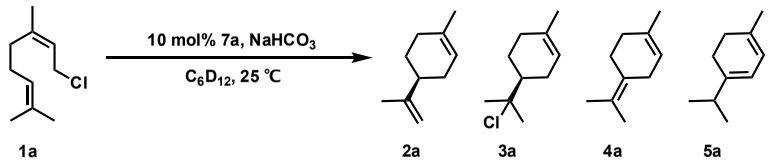
Hydrogen bond donor catalyst **7a** (0.015 mmol, 0.0094 g, 10 mol%) and sodium bicarbonate (0.23 mmol, 0.019 g, 1.5 eq.) were weighed directly into a flame-dried 1 dram vial charged with a magnetic stir bar. Then, 500 μL of deuterocyclohexane were added, followed by 1 mL of a 0.15 M stock solution of substrate **1a** (0.15 mmol) in deuterocyclohexane and 10 μL of mesitylene internal standard. The reaction vial was capped and sealed with electrical tape. The reaction mixture was allowed to stir for 72 hours. After this time, 600 μL of the crude reaction were transferred to a flame-dried NMR tube for analysis by ^{1}H NMR. Yields of products **2a-5a** were determined relative to the mesitylene aromatic CH frequency (6.7 ppm) by ^{1}H NMR. The enantiomeric excess value for limonene product **2a** was determined using an Agilent 7890A series GC system outfitted with a commercially available cyclosil-β 30m column (method: 50 °C to 80 °C at 1 °C/min, 7psi) t_r(major): 22.9 min. t_r(minor): 23.9 min.

General Procedure for Enantioselective Cyclization of Substrates 1b-1i

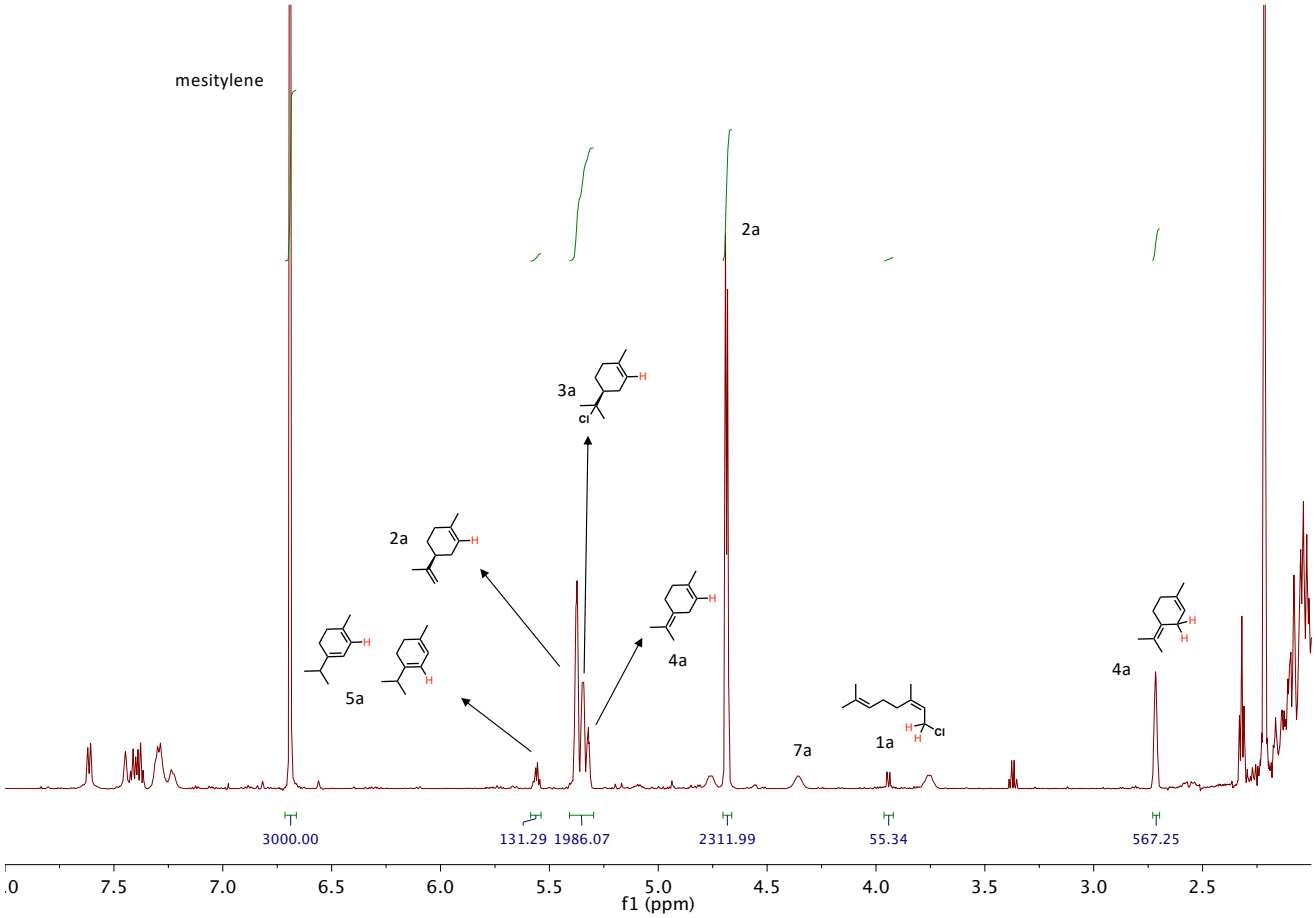
Hydrogen bond donor catalyst **7a** (0.015 mmol, 0.0094 g, 10 mol%) and sodium bicarbonate (0.23 mmol, 0.019 g, 1.5 eq.) were weighed directly into a flame-dried 1 dram vial charged with a magnetic stir bar. Then, 500 μL of anhydrous cyclohexane (CyH) were added, followed by 1 mL of a 0.15 M stock solution of substrate **1b-1i** (0.15 mmol) in CyH. The reaction vial was capped and sealed with electrical tape, and was allowed to stir for the following times: substrates **1b**, **1f**, **1g** (24 hr.), **1d**, **1e**, **1h** (48 hr.), **1a**, **1c**, **1i** (72 hr.). After this time, the crude reaction was transferred to a flame-dried 20 mL vial, concentrated *in vacuo* and resuspended in 1.5 mL of $CDCl_3$ with 10 μL of mesitylene internal standard (substrates **1b-1d**, **1f**, **1g**, and **1i**) or 1.5 mL of a 0.1 M solution of mesitylene in $CDCl_3$ (substrates **1e** and **1h**) for analysis by ^{1}H NMR. In all cases, full conversion of the reactive E isomer of substrates **1b-1i** was observed. Yields of products **2-5** were determined relative to the mesitylene aromatic CH frequency (6.7 ppm) by ^{1}H NMR and are corrected to account for the presence of the unreactive Z isomer of substrates **1b-1i**. Enantiomeric excess values for products **2** and **3** were determined using an Agilent 7890A series GC system outfitted with a commercially available cyclosil-β 30m column.

6.2 NMR analysis & GC traces of reactions involving substrates 1a-1i

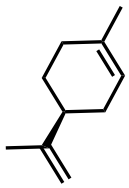
crude reaction of 1a, (C_6D_{12}, 600 MHz)



crude reaction of 1a, (C_6D_{12}, 600 MHz)



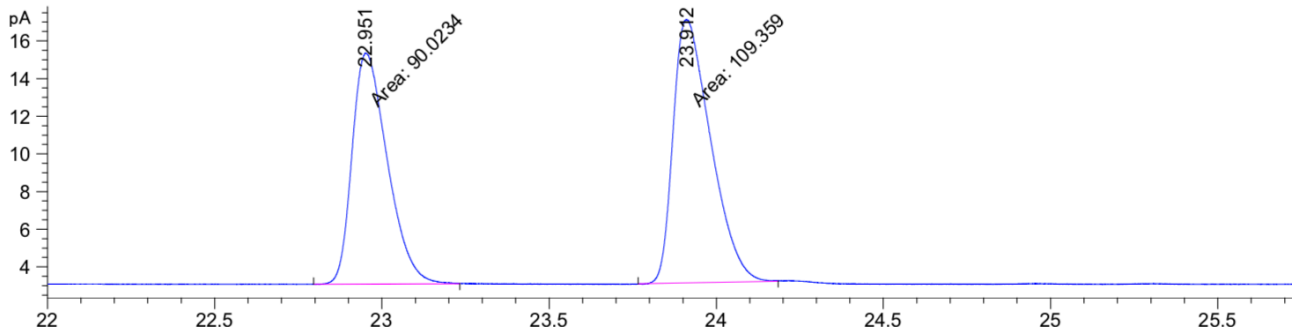
Mesitylene (M)	2a (M)	3a (M)	4a (M)	5a (M)	1a (M)	PDT	Mass Balance
0.047606	0.055032536	0.02482653	0.0134963	0.003142	0.001047332	0.09649736	0.097544694
Sample	2a (%)	3a (%)	4a (%)	5a (%)		Conv. (%)	Yield (%)
1a	55.03	24.83	13.50	3.14		98.95	96.50



2a, 9% ee

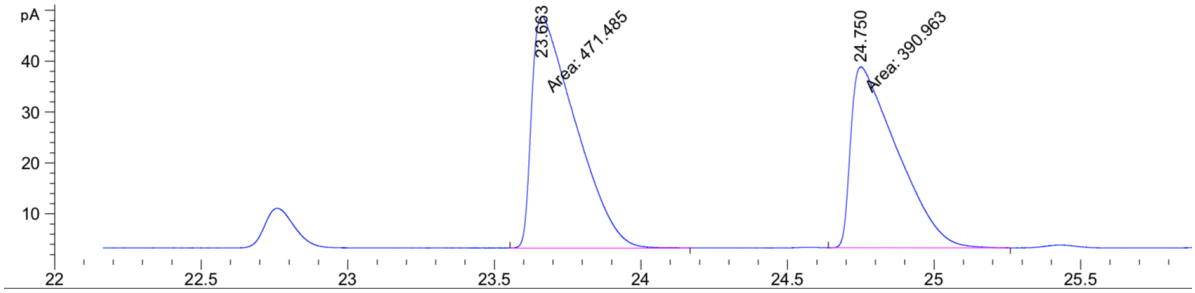
GC (cyclosil-***β***, 30 m)
50 ℃ - 80 ℃, 1 ℃/min, 7 psi

~1:1 mixture of authentic R&S-limonene (-10% ee)



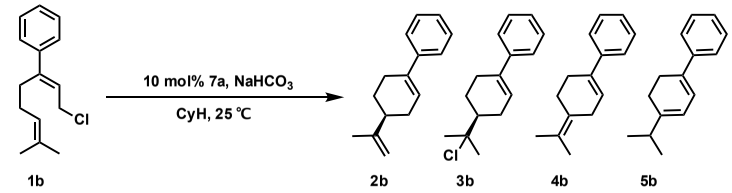
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	22.951	MM	0.1221	90.02339	12.28328	45.15109
2	23.912	MM	0.1303	109.35913	13.98554	54.84891

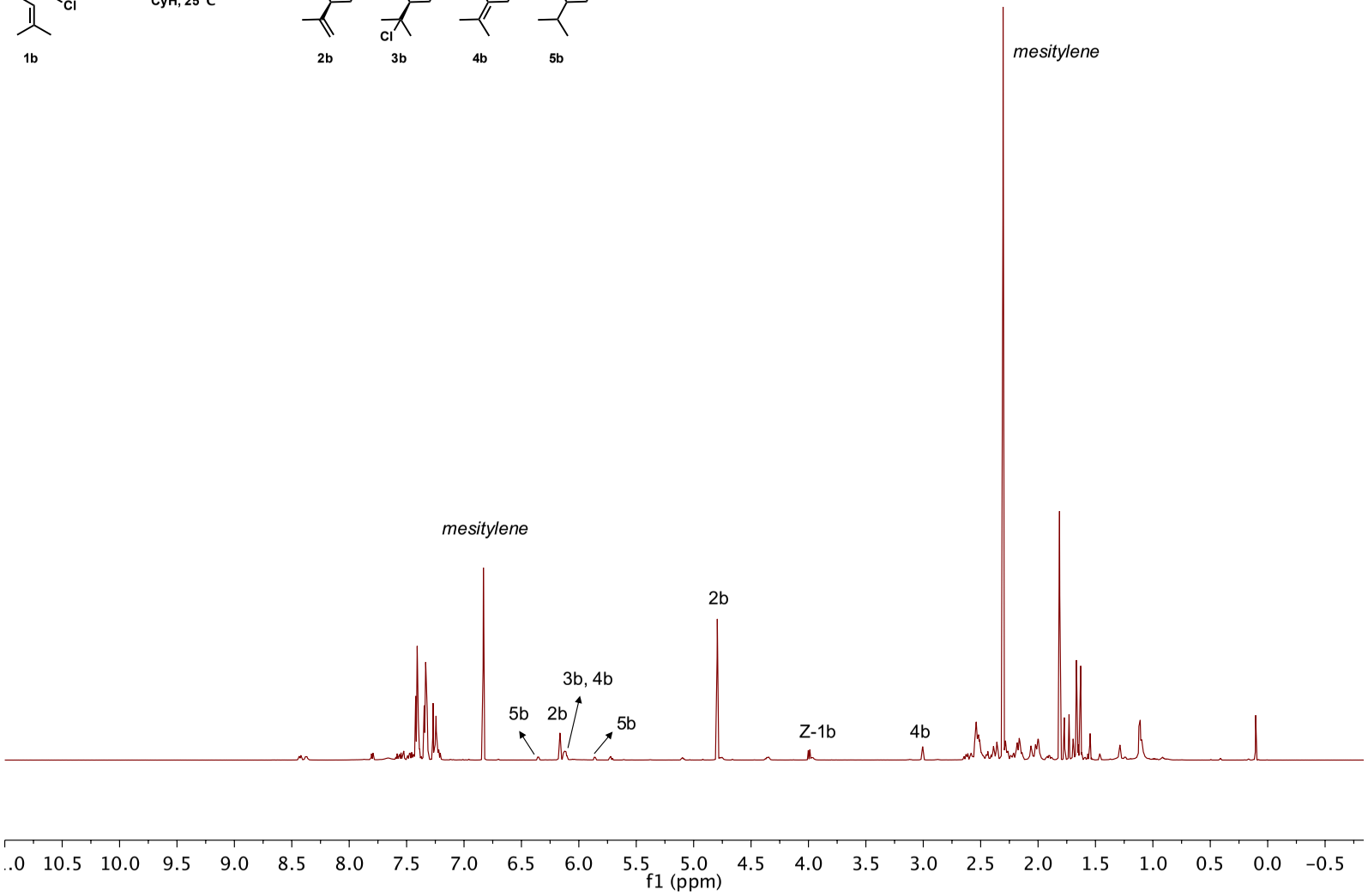
enantioenriched sample



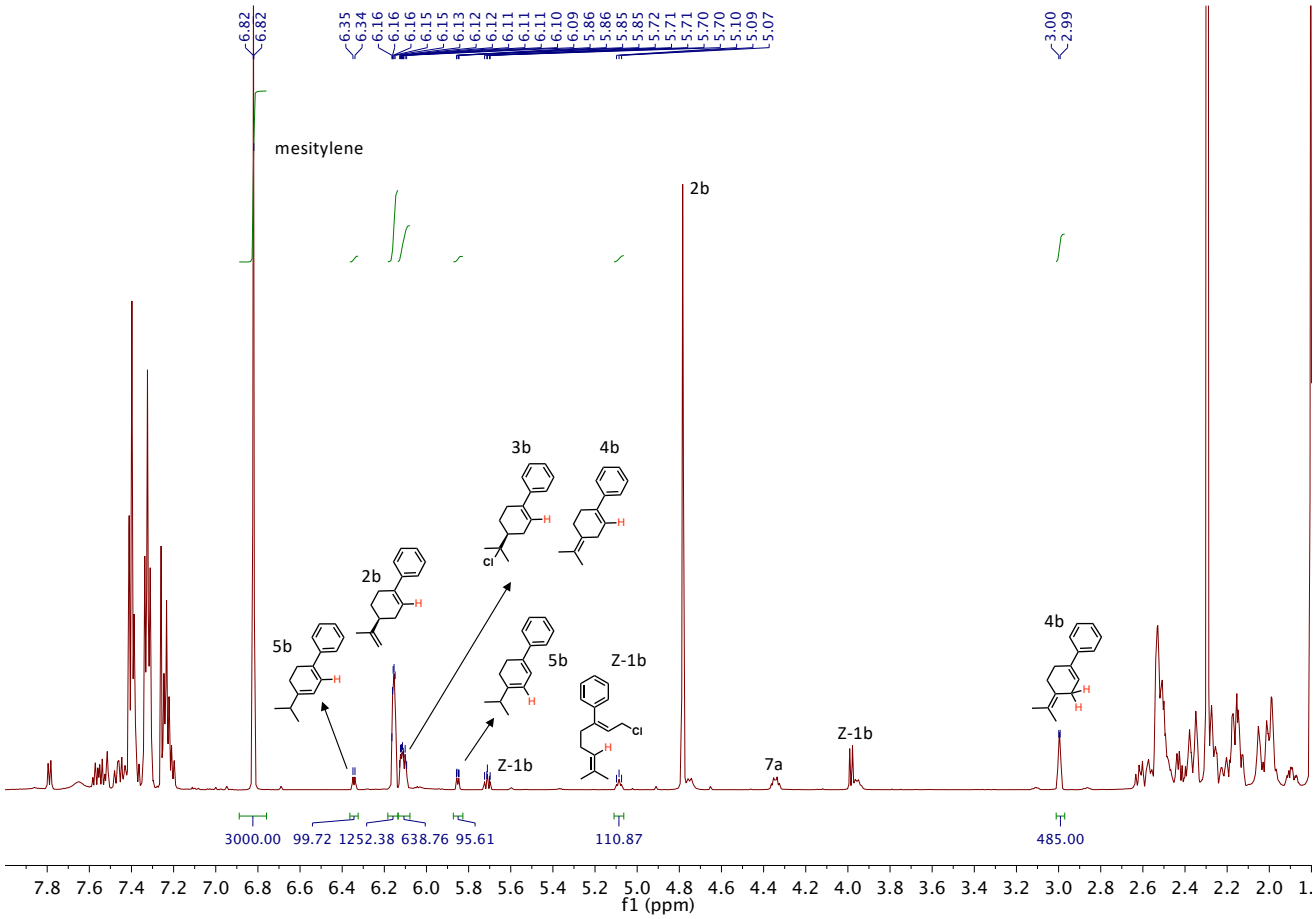
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.663	MM	0.1726	471.48495	45.52736	54.66824
2	24.750	MM	0.1831	390.96268	35.58746	45.33176

crude reaction of 1b, ($CDCl_3$, 600 MHz)

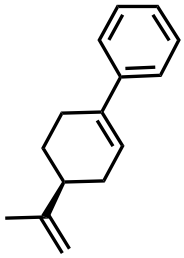




crude reaction of 1b, ($CDCl_3$, 600 MHz)



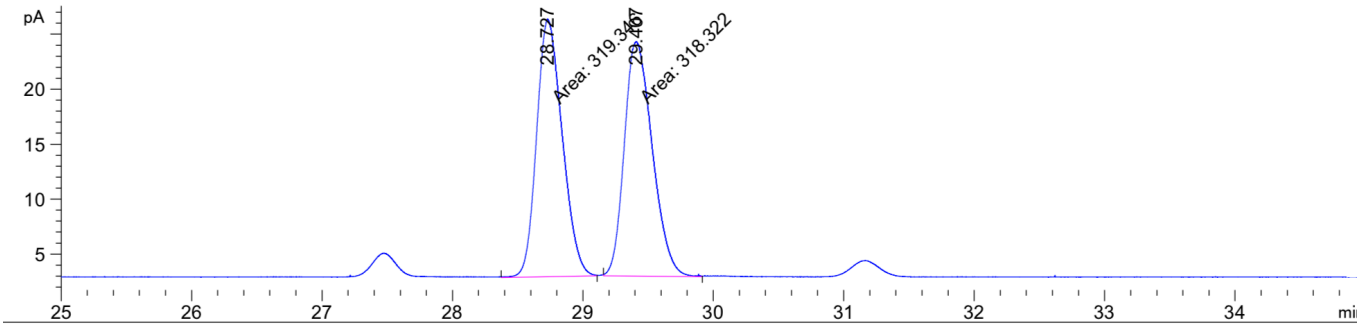
Mesitylene (M)	2b (M)	3b (M)	4b (M)	5b (M)	Z-1b (M)	PDT (M)	Mass Balance
0.047606742	0.059603641	0.01882847	0.01154463	0.00452264	0.005236742	0.09449938	0.099736124
Sample	2b (%)	3b (%)	4b (%)	5b (%)		Conv. (%)	Yield (%)
1b	62.90	19.87	12.18	4.77		100.00	99.72



GC (cyclosil-***β***, 30 m)
150 ℃, isocratic, 40 min, 7 psi

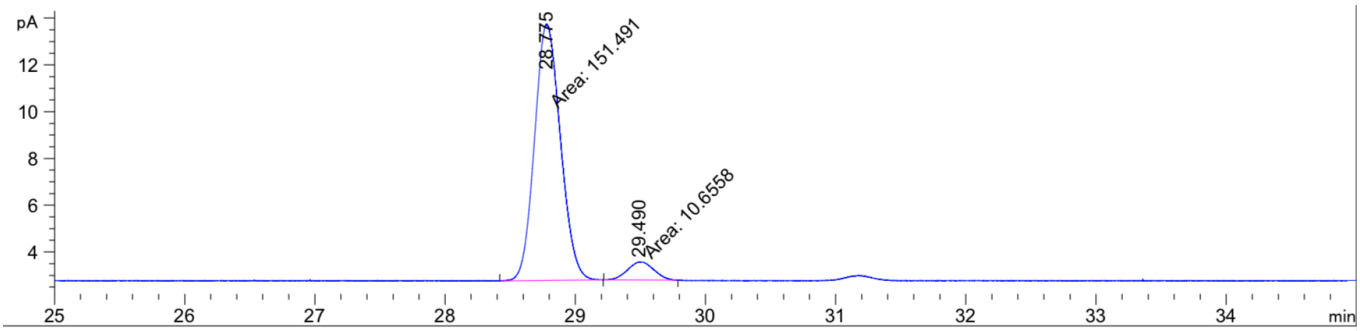
2b, 87% ee

racemic sample

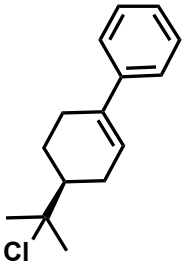


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.727	MM	0.2271	319.34555	23.44049	50.08029
2	29.407	MM	0.2483	318.32153	21.36424	49.91971

enantioenriched sample



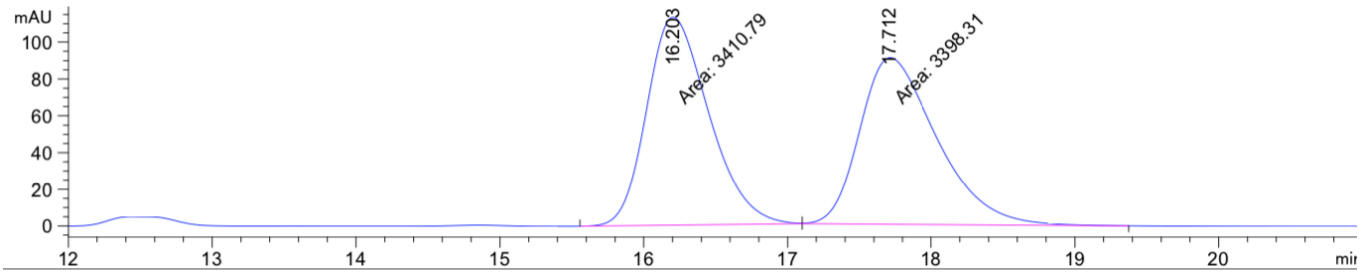
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	28.775	MM	0.2303	151.49139	10.96295	93.42832
2	29.490	MM	0.2324	10.65580	7.64076e-1	6.57168



HPLC (Chiralcel OJ-H)
0.5% IPA isocratic, 1 mL/min, 30 min, 254 nm

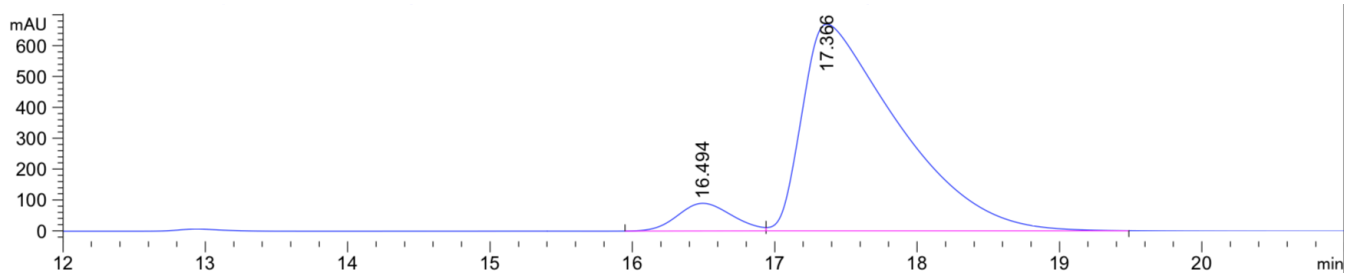
3b, 86% ee

racemic sample



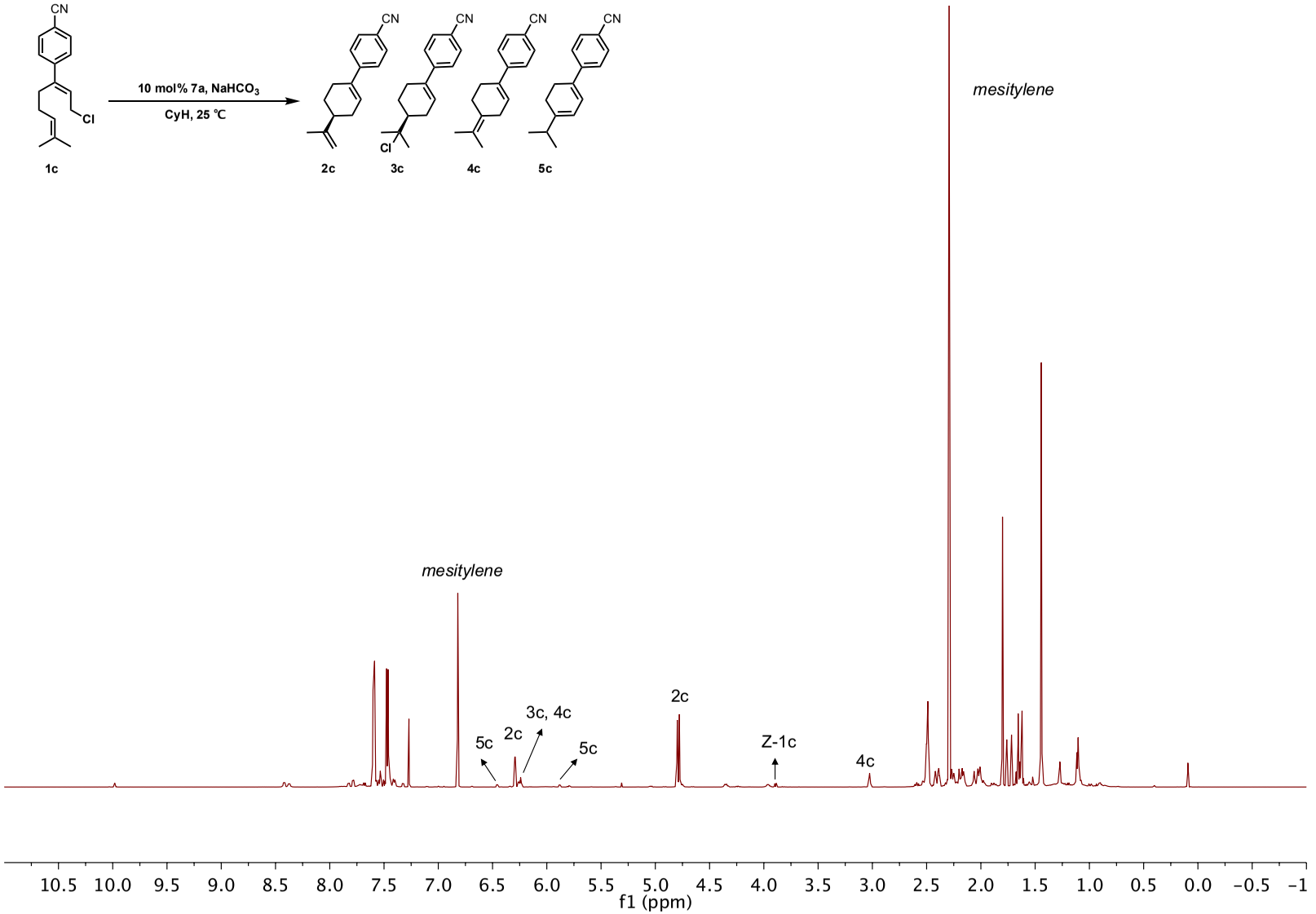
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.203	MM	0.5022	3410.78735	113.19047	50.0916
2	17.712	MM	0.6242	3398.30981	90.73719	49.9084

enantioenriched sample

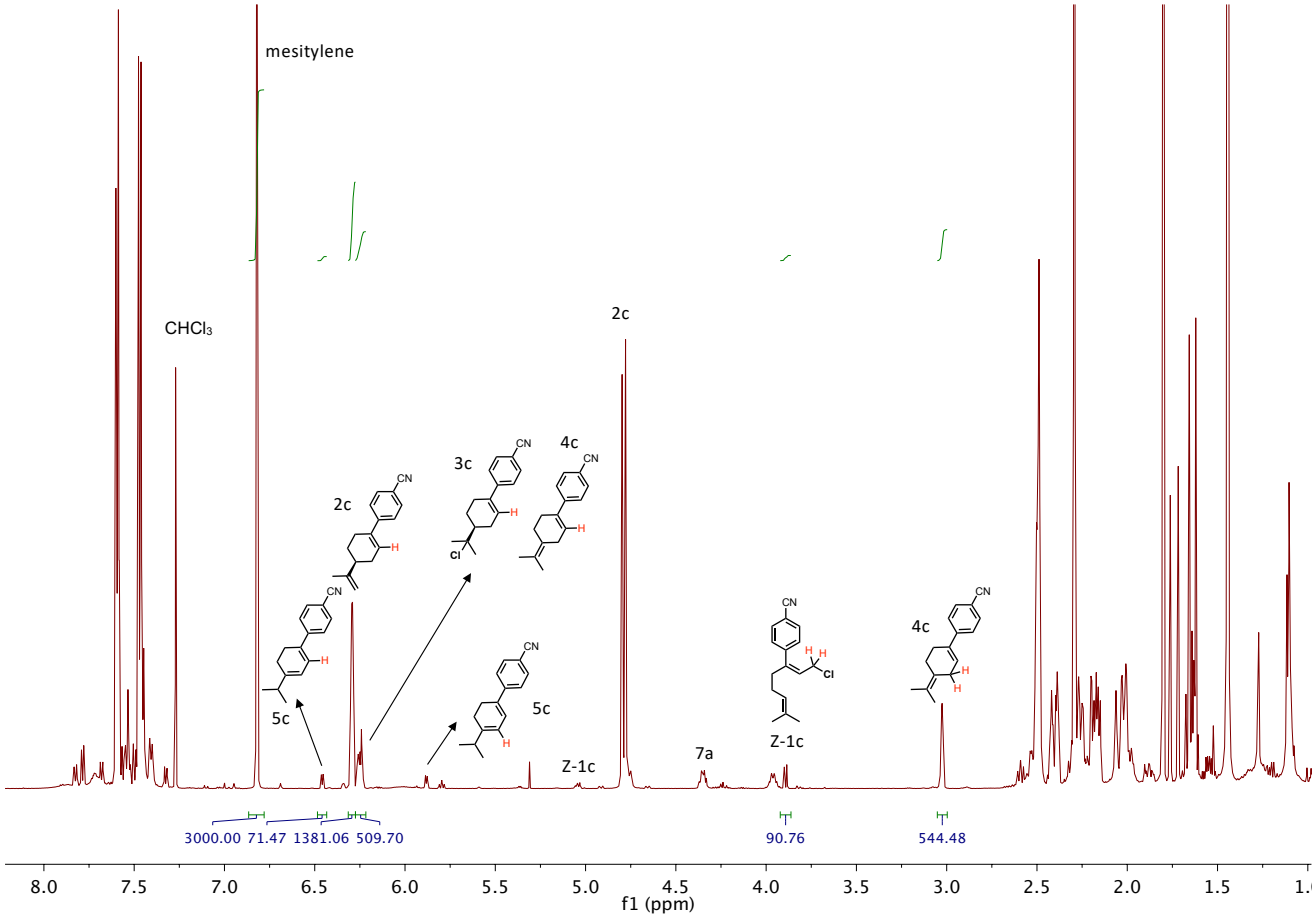


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.494	BV	0.4156	2405.01953	90.04417	7.1006
2	17.366	VB	0.6818	3.14657e4	670.13757	92.8994

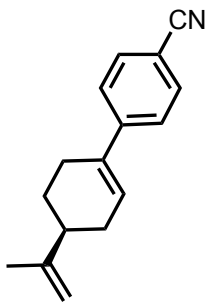
crude reaction of 1c, ($CDCl_3$, 600 MHz)



crude reaction of 1c, ($CDCl_3$, 600 MHz)

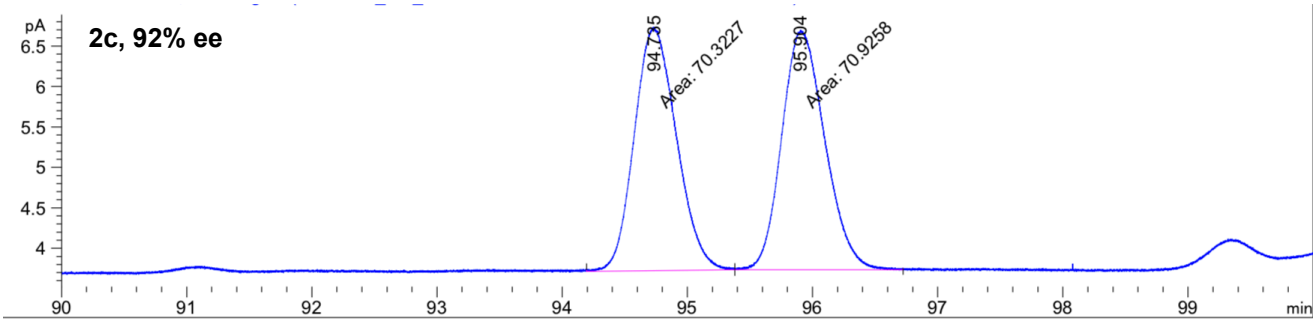


Mesitylene (M)	2c (M)	3c (M)	4c (M)	5c (M)	Z-1c (M)	PDT	Mass Balance
0.047606742	0.065744911	0.0113066	0.01297284	0.00342769	0.002142303	0.09345203	0.095594338
Sample	2c (%)	3c (%)	4c (%)	5c (%)		Conv. (%)	Yield (%)
1c	67.18	11.55	13.26	3.50		100.00	95.50



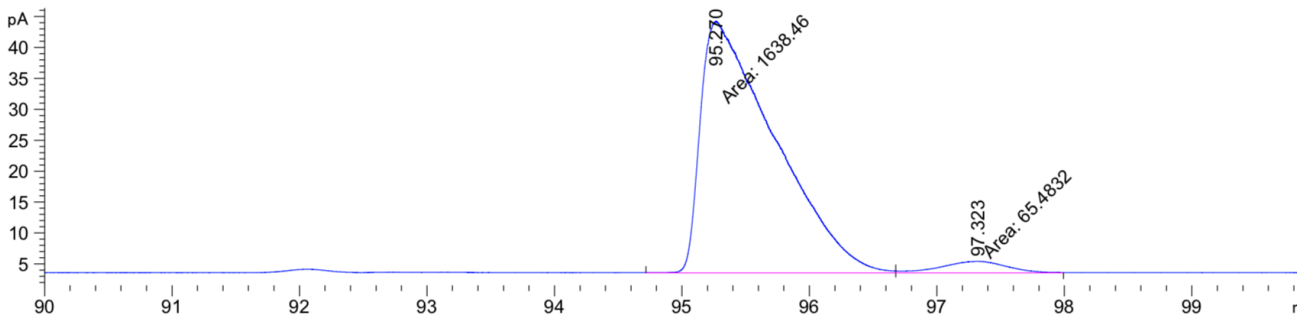
GC (cyclosil-***β***, 30 m)
140 ℃ - 180 ℃, 0.3 ℃/min, 7 psi

racemic sample



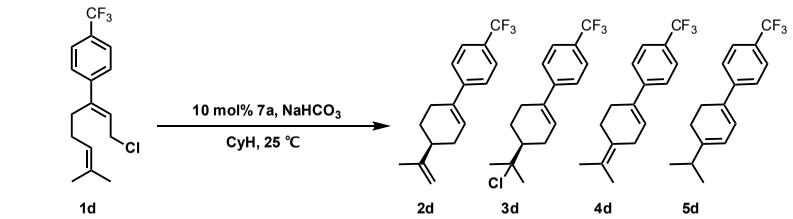
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	94.735	MM	0.3900	70.32269	3.00535	49.78652
2	95.904	MM	0.3989	70.92578	2.96352	50.21348

enantioenriched sample

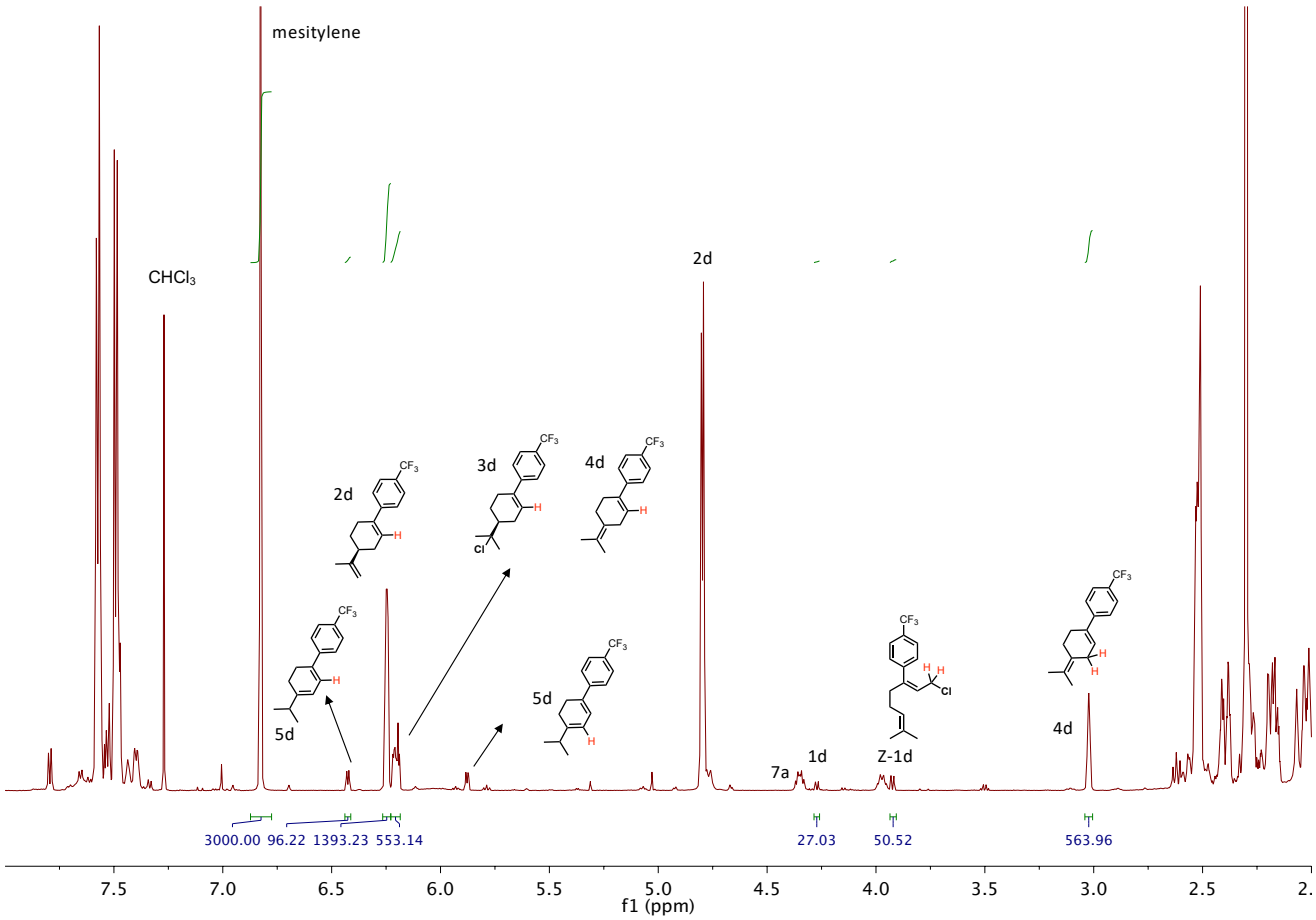


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	95.270	MF	0.6703	1638.46021	40.74041	96.15696
2	97.323	FM	0.5870	65.48323	1.85935	3.84304

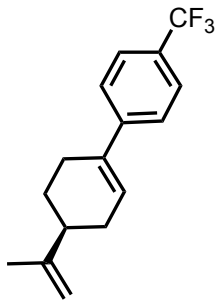
crude reaction of 1d, ($CDCl_3$, 600 MHz)



crude reaction of 1d, ($CDCl_3$, 600 MHz)

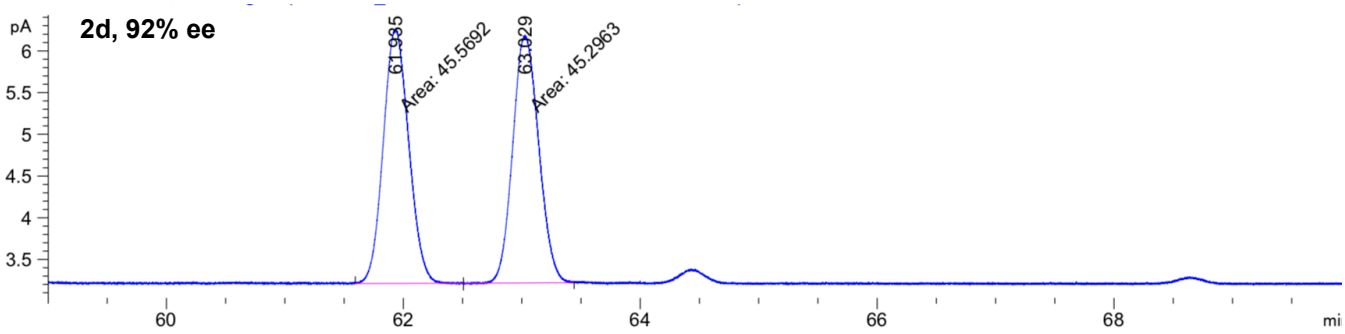


Mesitylene (M)	2d (M)	3d (M)	4d (M)	5d (M)	Z-1d (M)	PDT	Mass Balance
0.047606742	0.066316191	0.01290143	0.0134251	0.00457025	0.001190169	0.09721297	0.09906963
Sample	2d (%)	3d (%)	4d (%)	5d (%)		Conv. (%)	Yield (%)
1d	67.11	13.06	13.59	4.63		99.33	98.38



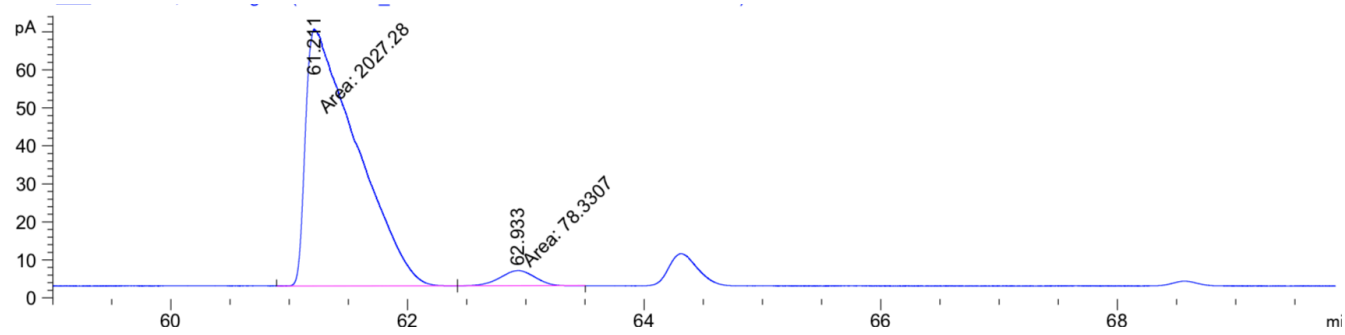
GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

racemic sample



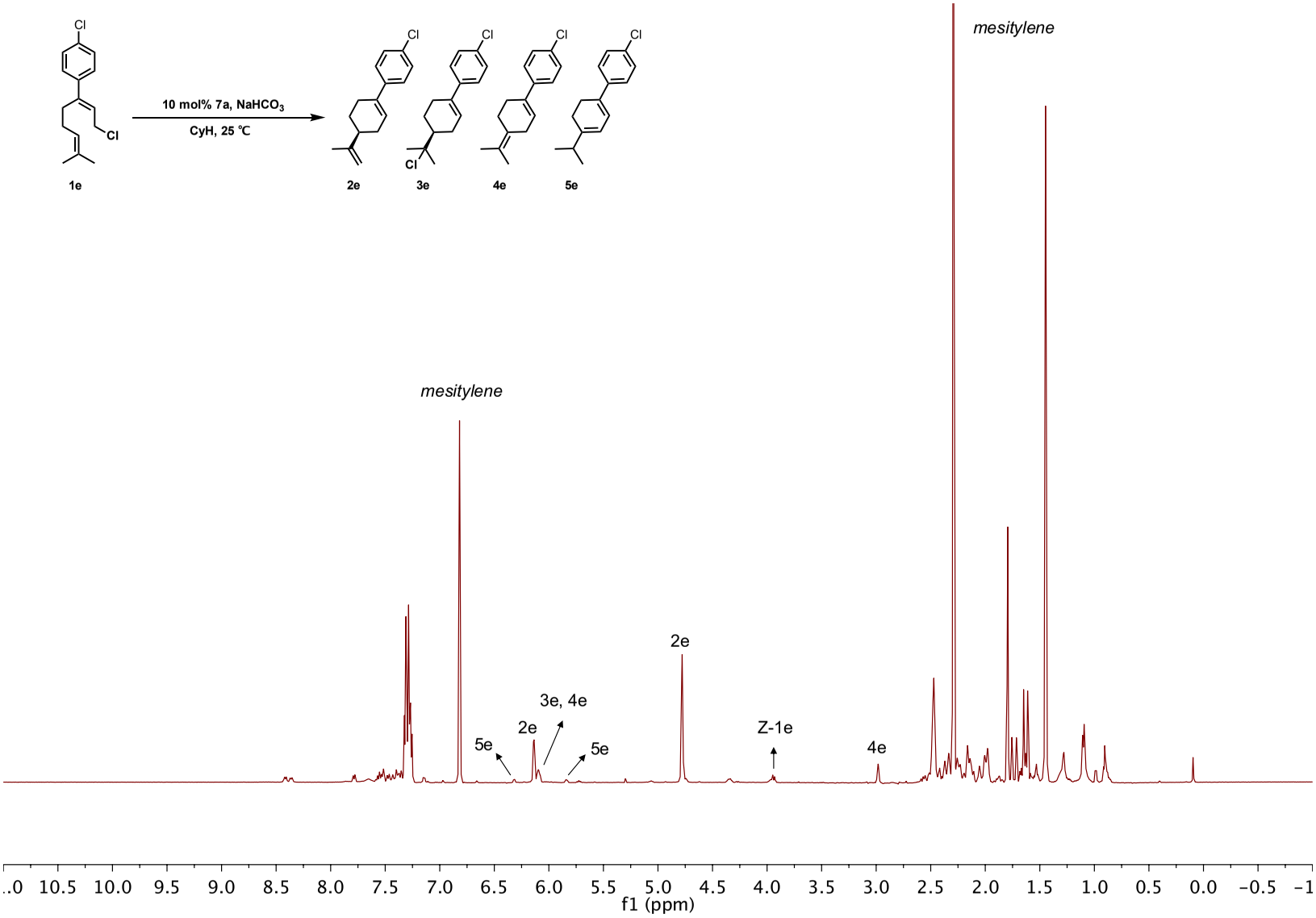
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	61.935	MF	0.2481	45.56916	3.06077	50.15017
2	63.029	FM	0.2550	45.29626	2.96061	49.84983

enantioenriched sample

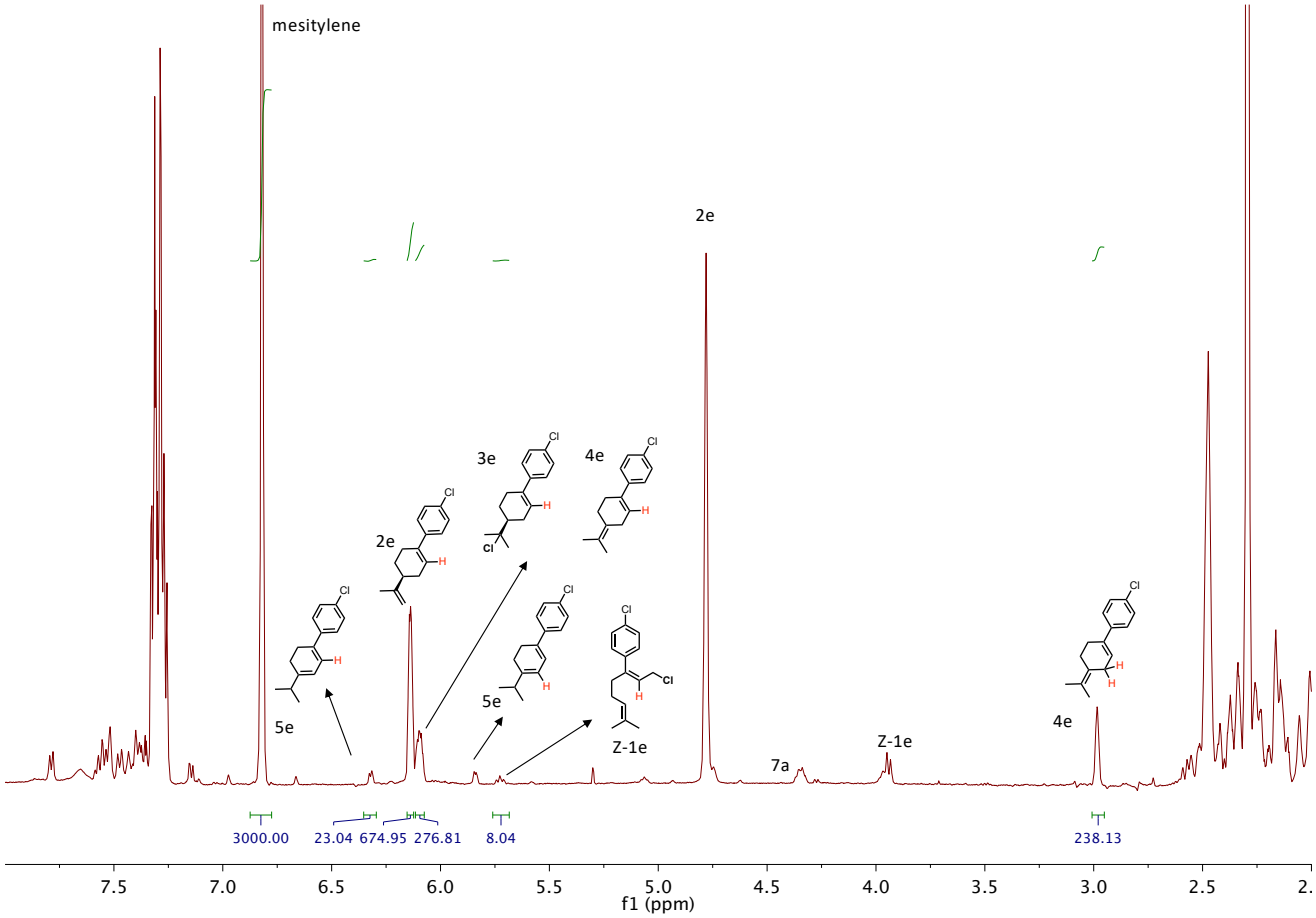


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	61.211	MF	0.4992	2027.28235	67.69080	96.27991
2	62.933	FM	0.3302	78.33067	3.95343	3.72009

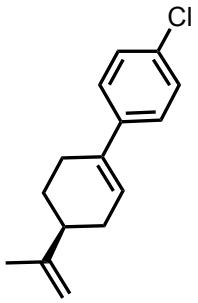
crude reaction of 1e, ($CDCl_3$, 600 MHz)



crude reaction of 1e, ($CDCl_3$, 600 MHz)



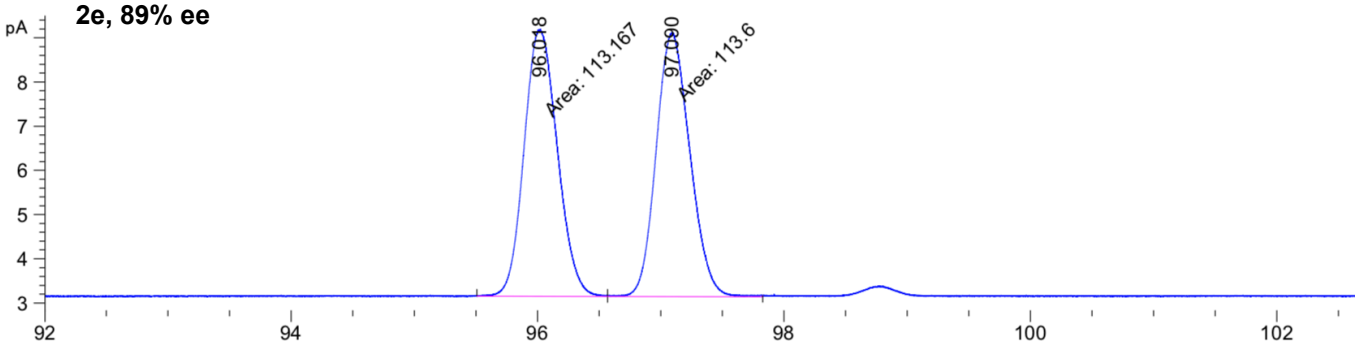
Mesitylene (M)	2e (M)	3e (M)	4e (M)	5e (M)	Z-1e (M)	PDT	Mass Balance
0.1	0.0675	0.0158	0.0119	0.0023	0.0008	0.0975	0.0983
Sample	2e (%)	3e (%)	4e (%)	5e (%)		Conv. (%)	Yield (%)
1e	68.04	15.93	12.00	2.32		100.00	98.29



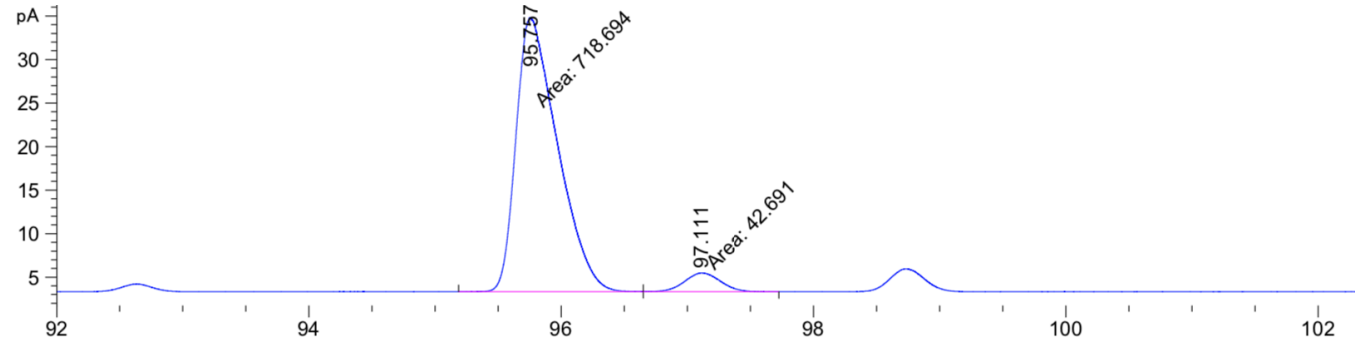
GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

racemic sample

2e, 89% ee

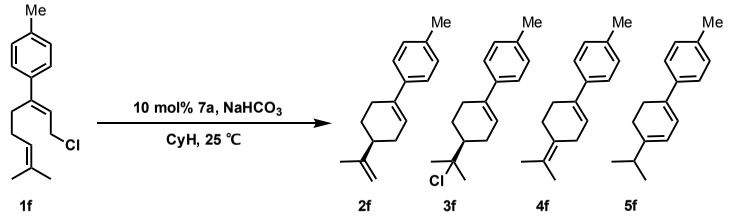


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	96.018	MF	0.3126	113.16673	6.03448	49.90439
2	97.090	FM	0.3163	113.60035	5.98659	50.09561

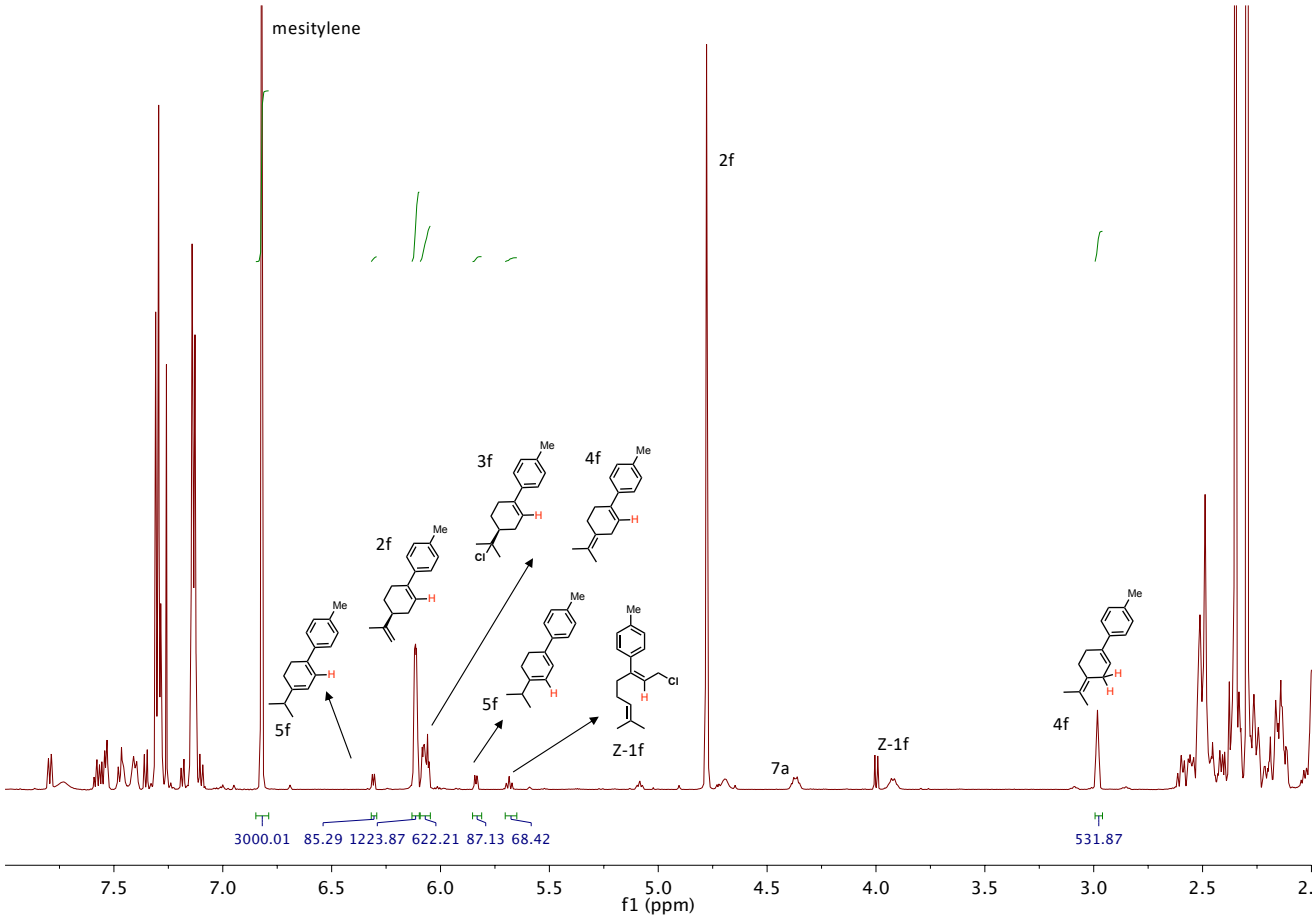


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	95.757	MM	0.3805	718.69391	31.48136	94.39298
2	97.111	MM	0.3305	42.69099	2.15310	5.60702

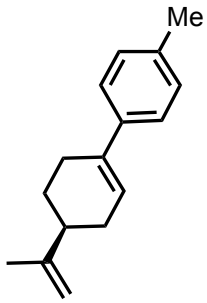
crude reaction of 1f, ($CDCl_3$, 600 MHz)



crude reaction of 1f, ($CDCl_3$, 600 MHz)



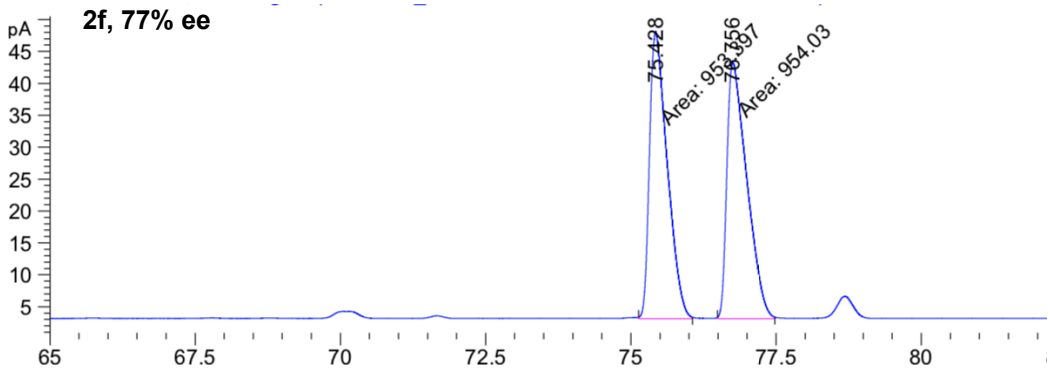
Mesitylene (M)	2f (M)	3f (M)	4f (M)	5f (M)	Z-1f (M)	PDT	Mass Balance
0.047606742	0.058270652	0.01635292	0.01325848	0.00414179	0.003237258	0.09202383	0.09526109
Sample	2f (%)	3f (%)	4f (%)	5f (%)		Conv. (%)	Yield (%)
1f	60.22	16.90	13.70	4.28		100.00	95.10



GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

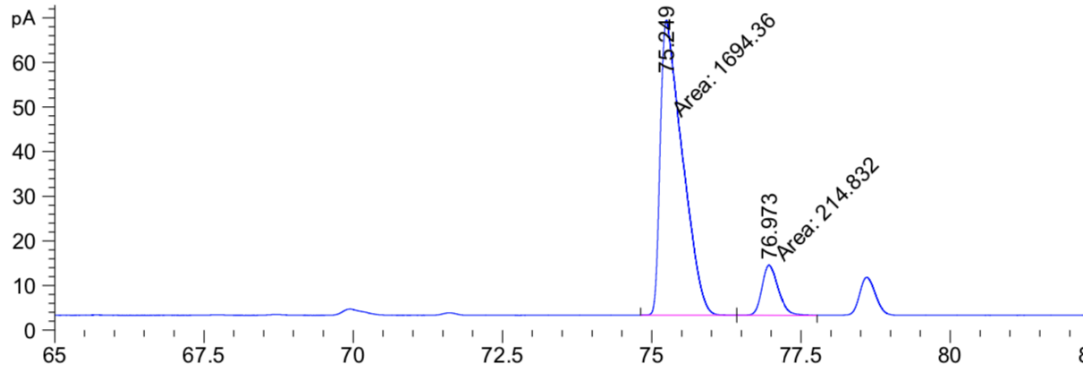
racemic sample

2f, 77% ee



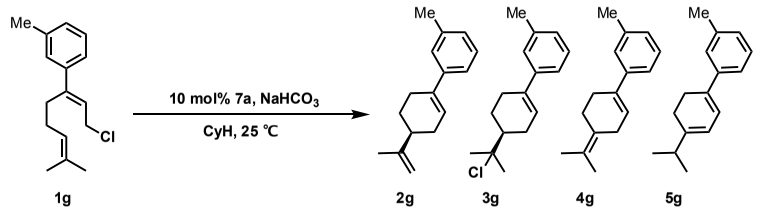
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	75.428	MM	0.3524	953.39685	45.08876	49.98341
2	76.756	MM	0.3960	954.02991	40.14808	50.01659

enantioenriched sample

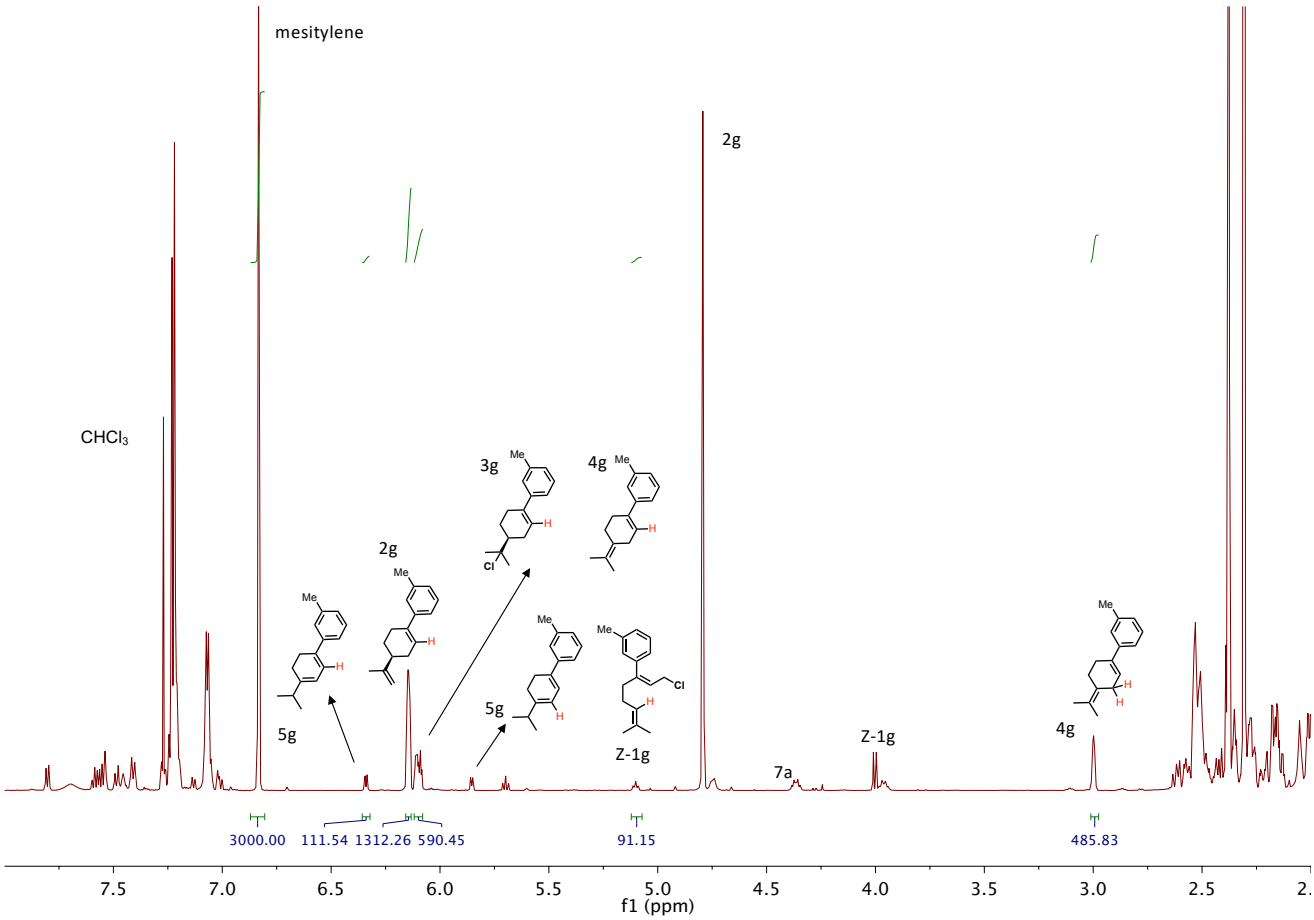


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	75.249	MF	0.4273	1694.35828	66.08471	88.74747
2	76.973	FM	0.3172	214.83226	11.28682	11.25253

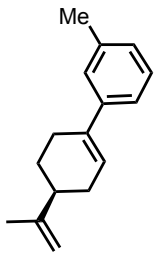
crude reaction of 1g, ($CDCl_3$, 600 MHz)



crude reaction of 1g, ($CDCl_3$, 600 MHz)



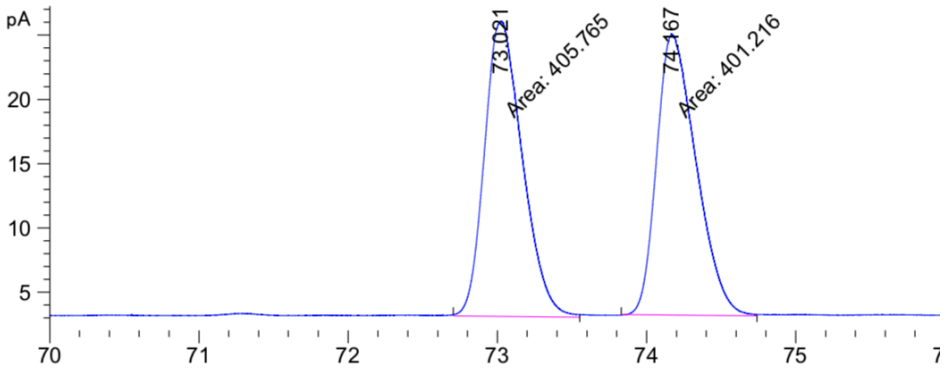
Mesitylene (M)	2g (M)	3g (M)	4g (M)	5g (M)	Z-1g (M)	PDT	Mass Balance
0.047606742	0.062460045	0.01651954	0.01156844	0.00528435	0.004332214	0.09583237	0.100164585
Sample	2g (%)	3g (%)	4g (%)	5g (%)		Conv. (%)	Yield (%)
1g	65.29	17.27	12.09	5.52		100.00	100.17



GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

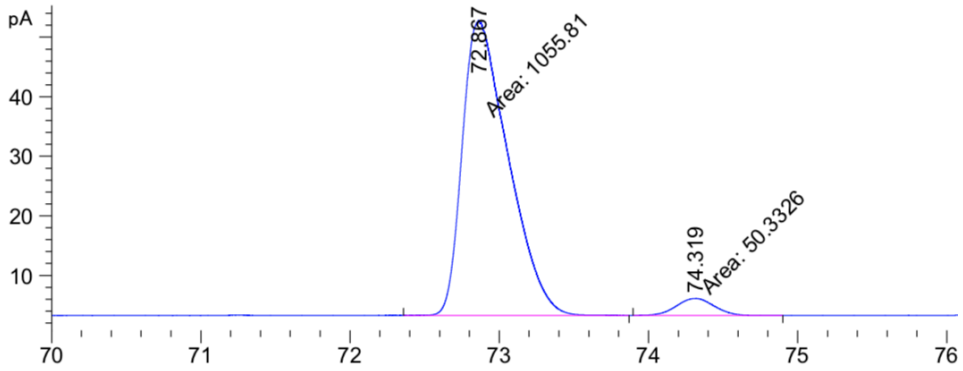
2g, 91% ee

racemic sample



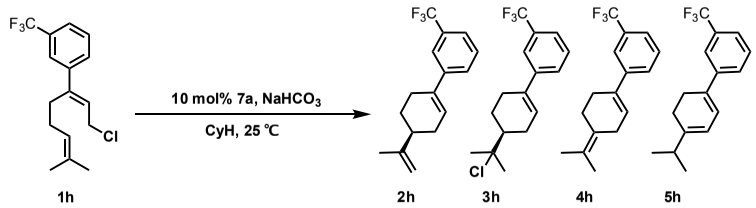
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	73.021	MM	0.2940	405.76456	22.99967	50.28182
2	74.167	MM	0.3056	401.21613	21.88286	49.71818

enantioenriched sample

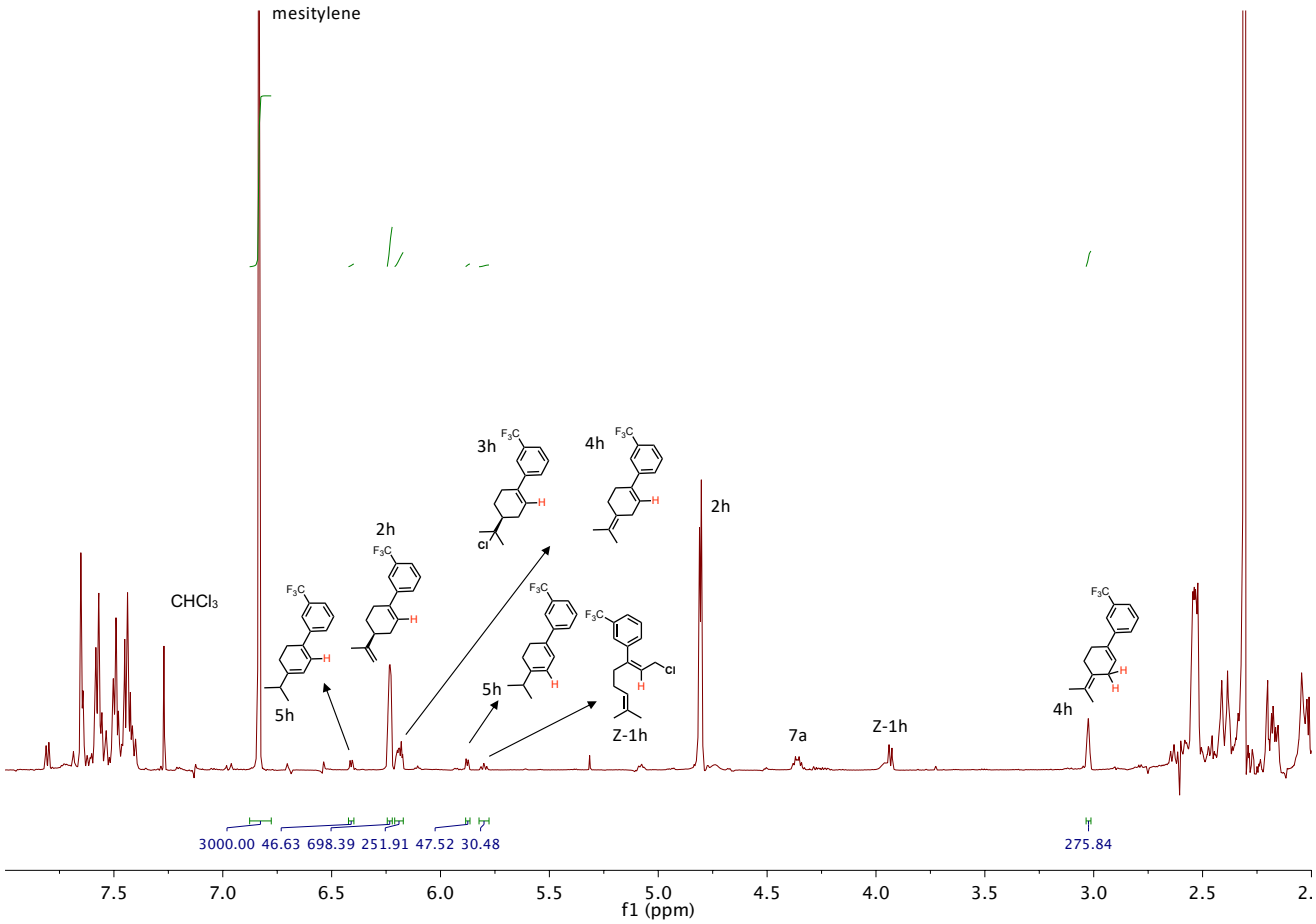


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	72.867	MM	0.3560	1055.81421	49.43515	95.44974
2	74.319	MM	0.2923	50.33256	2.87015	4.55026

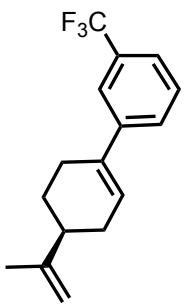
crude reaction of 1h, ($CDCl_3$, 600 MHz)



crude reaction of 1h, ($CDCl_3$, 600 MHz)



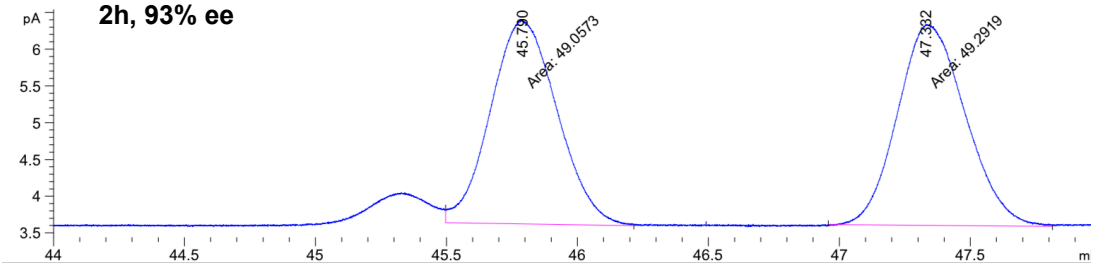
Mesitylene (M)	2h (M)	3h (M)	4h (M)	5h (M)	Z-1h (M)	PDT	Mass Balance
0.1	0.0698	0.0113	0.0138	0.0046	0.003	0.0995	0.1025
Sample	2h (%)	3h (%)	4h (%)	5h (%)		Conv. (%)	Yield (%)
1h	71.96	11.65	14.23	4.74		100.00	102.58



GC (cyclosil-***β***, 30 m)
120 ℃ - 180 ℃, 0.2 ℃/min, 14 psi

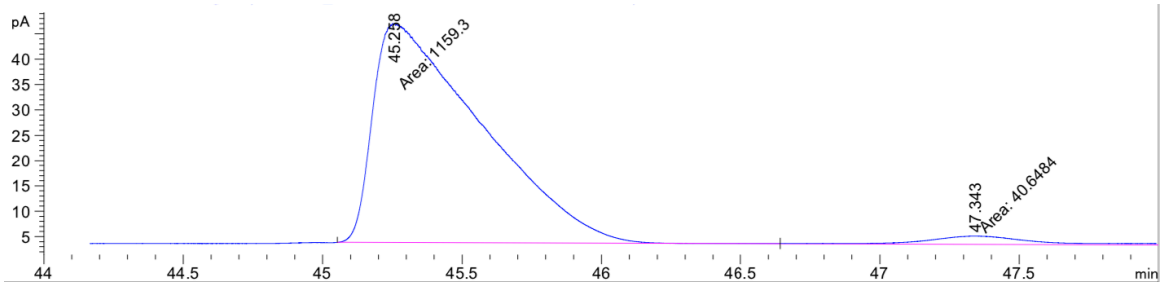
racemic sample

2h, 93% ee

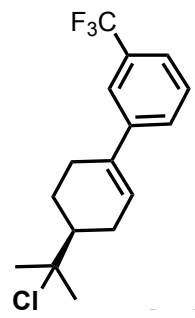


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.790	MM	0.2946	49.05734	2.77573	49.88074
2	47.332	MM	0.3004	49.29193	2.73524	50.11926

enantioenriched sample



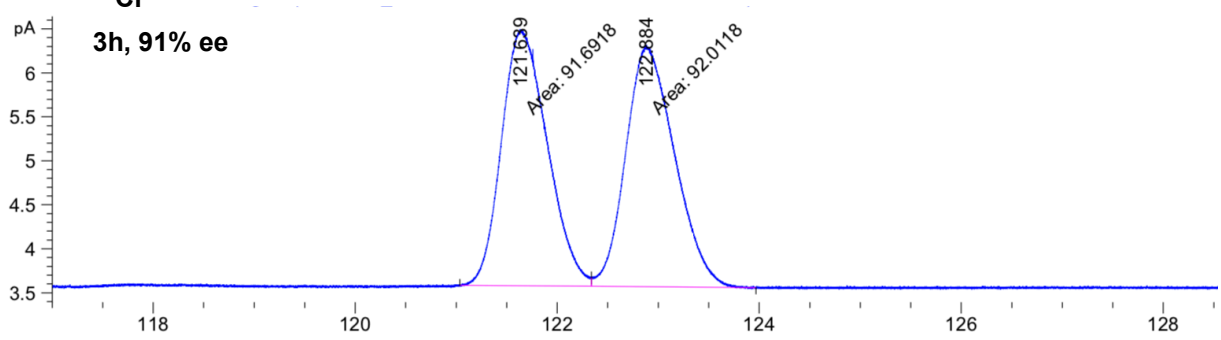
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	45.258	MF	0.4473	1159.29749	43.19694	96.61248
2	47.343	FM	0.4203	40.64842	1.61187	3.38752



GC (cyclosil-***β***, 30 m)
120 ℃ - 180 ℃, 0.2 ℃/min, 14 psi

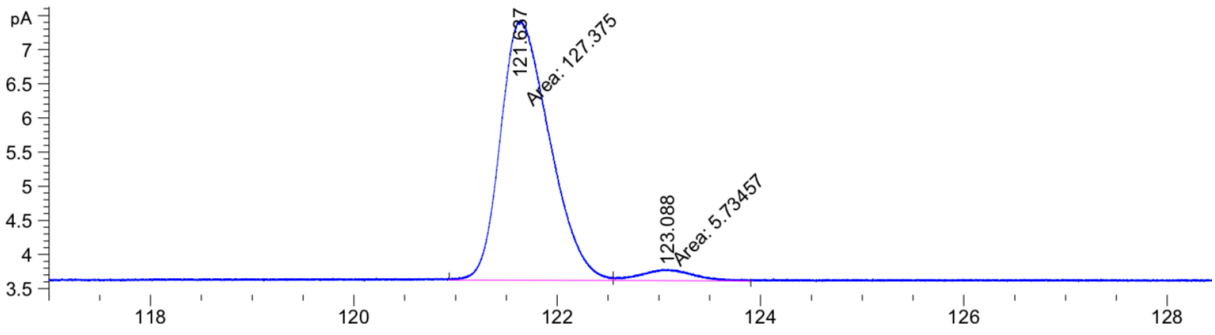
3h, 91% ee

racemic sample



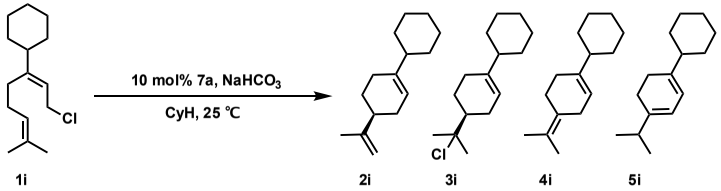
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	121.639	MF	0.5254	91.69181	2.90887	49.91289
2	122.884	FM	0.5584	92.01185	2.74629	50.08711

enantioenriched sample

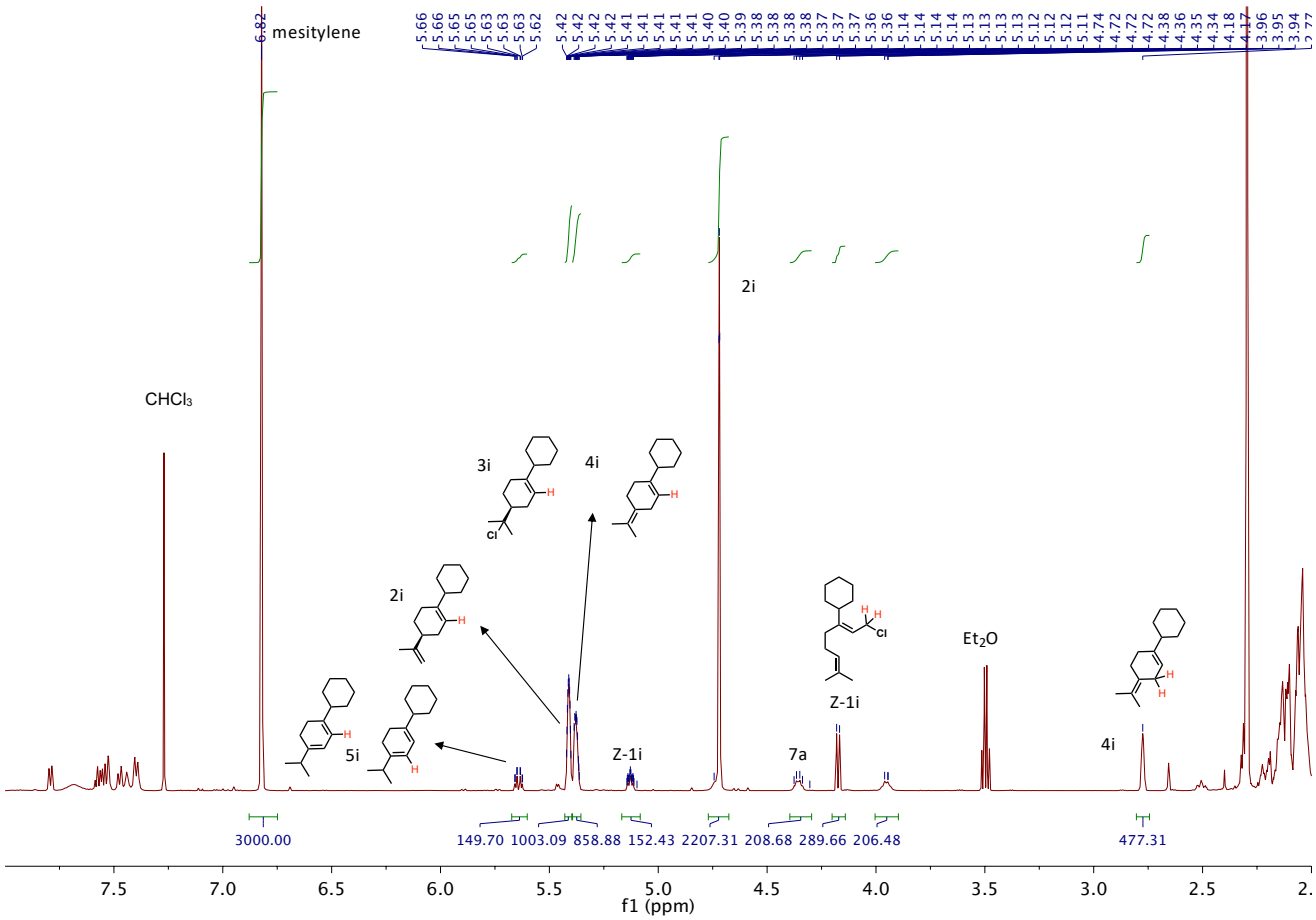


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	121.637	MF	0.5585	127.37526	3.80091	95.69185
2	123.088	FM	0.5680	5.73457	1.68276e-1	4.30815

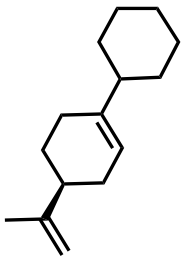
crude reaction of 1i, ($CDCl_3$, 600 MHz)



crude reaction of 1i, ($CDCl_3$, 600 MHz)



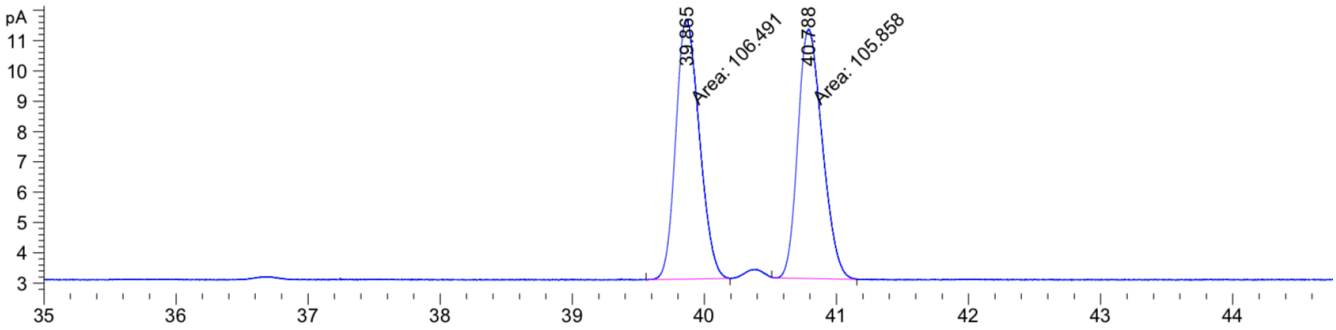
Mes	2i (M)	3i (M)	4i (M)	5i (M)	Z-1i (M)	PDT	Mass Balance
0.047606742	0.047749562	0.02953998	0.01135421	0.00357051	0.006855371	0.09221426	0.09906963
Sample	2i (%)	3i (%)	4i (%)	5i (%)		Conv. (%)	Yield (%)
1i	51.26	31.71	12.19	3.83		100.00	99.00



GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

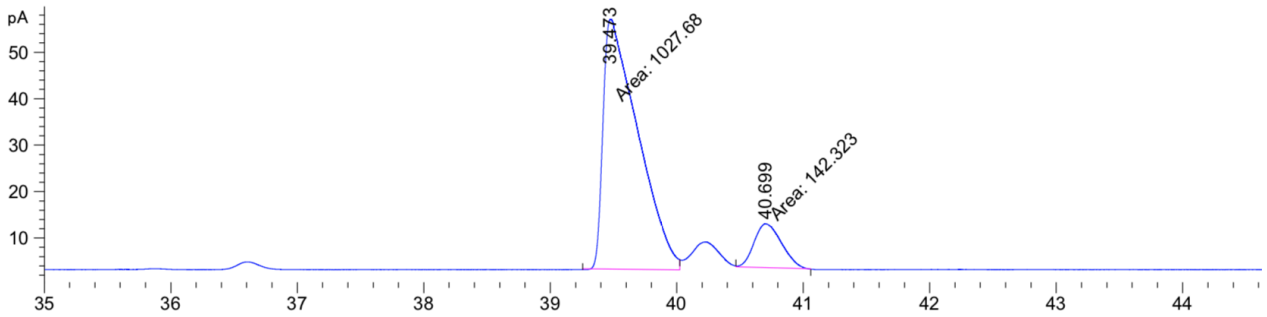
2i, 76% ee

racemic sample

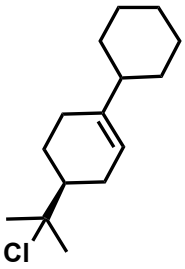


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.865	MM	0.2070	106.49110	8.57230	50.14896
2	40.788	MM	0.2145	105.85844	8.22679	49.85104

enantioenriched sample



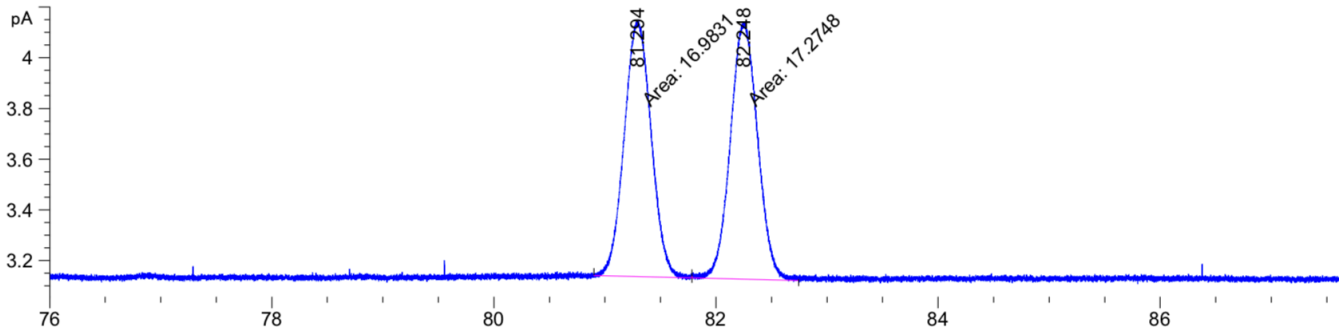
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	39.473	MM	0.3184	1027.68005	53.79232	87.83566
2	40.699	MM	0.2515	142.32312	9.43091	12.16434



GC (cyclosil-***β***, 30 m)
120 ℃ - 200 ℃, 0.5 ℃/min, 7 psi

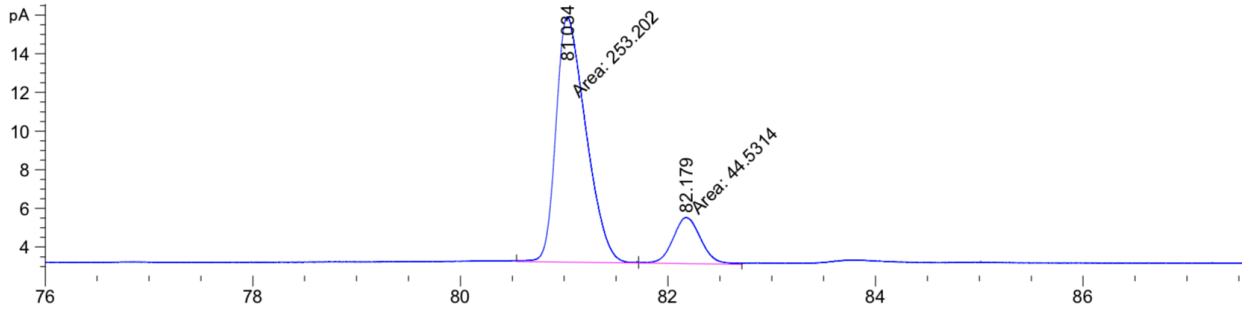
3i, 70% ee

racemic sample



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	81.294	MF	0.2819	16.98306	1.00422	49.57426
2	82.248	FM	0.2848	17.27476	1.01092	50.42574

enantioenriched sample

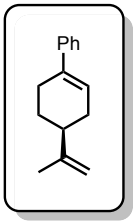


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	81.034	MF	0.3325	253.20250	12.69217	85.04322
2	82.179	FM	0.3099	44.53142	2.39520	14.95678

6.3 Isolation and characterization of compounds 2b-5b

Hydrogen bond donor catalyst **7a** (0.015 mmol, 0.0094 g, 10 mol%) and sodium bicarbonate (0.23 mmol, 0.019 g, 1.5 eq.) were weighed directly into a flame-dried 1 dram vial charged with a magnetic stir bar. Then, 500 μL of anhydrous cyclohexane (CyH) were added, followed by 1 mL of a 0.15 M stock solution of substrate **1b** (0.15 mmol) in CyH. The reaction vial was capped and sealed with electrical tape, and was allowed to stir for 24 hr. After this point, the crude reaction was passed through a short plug of silica gel eluting with hexanes. The sample was concentrated in concentrated *in vacuo* and a mass of isolated product (combined mass of **2b-5b**) was recorded (0.0305 g, 98% yield). ^{1}H NMR analysis concluded that the sample consisted only of products **2b-5b** and a small amount (< 5%) of unreactive **Z-1b**. This material was subjected to flash column chromatography eluting with hexanes to separate product **3b** from alkene products **2b**, **4b**, and **5b**. **2b** was separated from **4b** and **5b** using commercially-available silver nitrate on silica gel (~10 wt. %, 230 mesh) eluting with 10% toluene in hexanes (v/v). Compounds **4b** and **5b** could not be separated from one another using any form of column chromatography surveyed; their structures were assigned based on comparison of NMR spectra to authentic samples of terpinolene and α-terpinene respectively as well as with data in the literature.[6]

(*S*)-4-(prop-1-en-2-yl)-2,3,4,5-tetrahydro-1,1'-biphenyl (2b)



isolated as a clear colorless oil; 87% ee

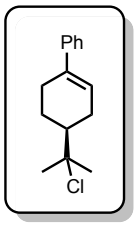
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.40 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 (m, 1H), 6.15 (m, 1H), 4.78 (s, 2H), 2.52 (tdd, *J* = 8.5, 4.2, 2.4 Hz, 2H), 2.30 (m, 2H), 2.15 (ddt, *J* = 17.2, 10.4, 3.2 Hz, 1H), 2.00 (dp, *J* = 12.6, 2.3 Hz, 1H), 1.80 (d, *J* = 1.2 Hz, 3H), 1.64 (tdd, *J* = 12.4, 10.7, 6.5 Hz, 1H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 149.8, 142.1, 136.2, 128.2, 126.6, 125.0, 124.1, 108.7, 40.7, 31.3, 27.9, 27.8, 20.8

HR-MS (EI): calcd. for $C_{15}H_{18}$ 198.1403 [$M^{+\bullet}$], found 198.1396

$[a]_D^{22} = -8.6$ (c =1.0, $CDCl_3$)

(*S*)-4-(2-chloropropan-2-yl)-2,3,4,5-tetrahydro-1,1'-biphenyl (3b)



isolated as a white solid; 86% ee

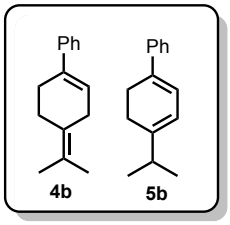
^{1}H NMR: (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.4 Hz, 2H), 7.32 (dd, *J* = 8.4, 6.8 Hz, 2H), 7.24 (m, 1H), 6.12 (dt, *J* = 5.0, 2.3 Hz, 1H), 2.59 (m, 1H), 2.48 (dddt, *J* = 30.6, 17.9, 5.5, 2.7 Hz, 2H), 2.19 (dddd, *J* = 24.6, 15.3, 4.7, 2.2 Hz, 2H), 1.89 (tdd, *J* = 11.5, 5.1, 2.5 Hz, 1H), 1.65 (s, 3H), 1.61 (s, 3H), 1.55 (m, 1H)

^{13}C NMR: (126 MHz, $CDCl_3$) δ 141.8, 136.5, 128.2, 126.7, 125.0, 123.5, 74.3, 46.2, 30.7, 29.9, 28.3, 28.1, 24.9

HR-MS (EI): calcd. for $C_{15}H_{19}Cl$ 234.1170 [$M^{+\bullet}$], found 234.1166

$[a]_D^{22} = -80.0$ (c =1.0, $CDCl_3$)

4-(propan-2-ylidene)-2,3,4,5-tetrahydro-1,1'-biphenyl and 4-isopropyl-2,3-dihydro-1,1'-biphenyl (4b and 5b)



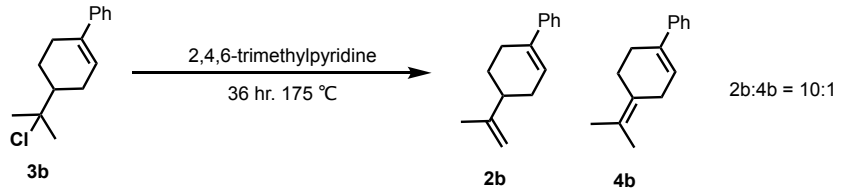
isolated as a clear oil

^{1}H NMR (4b): (600 MHz, $CDCl_3$) δ 7.39 (dt, *J* = 8.2, 1.4 Hz, 2H), 7.31 (td, *J* = 7.7, 1.4 Hz, 2H), 7.22 (m, 1H), 6.10 (tt, *J* = 4.1, 1.4 Hz, 1H), 2.99 (s, 2H), 2.50 (s, 4H), 1.75 (s, 3H), 1.71 (s, 3H) **^{1}H NMR (5b):** (600 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 8.1, 1.4 Hz, 2H), 6.34 (dd, *J* = 5.8, 1.4 Hz, 1H), 5.85 (dt, *J* = 6.0, 1.5 Hz, 1H), 2.40 (spt, *J* = 6.9 Hz, 1H), 2.29 (m, 4H), 1.10 (s, 3H), 1.09 (s, 3H)

^{13}C NMR (4b): (126 MHz, $CDCl_3$) δ 142.23, 136.98, 128.17, 126.89, 126.49, 124.97, 124.26, 122.24, 30.07, 28.82, 26.77, 20.21, 19.78. **^{13}C NMR (5b):** (126 MHz, $CDCl_3$) δ 142.23, 136.98, 128.30, 128.22, 124.73, 124.26, 29.70, 28.09, 25.63, 21.24, 21.12

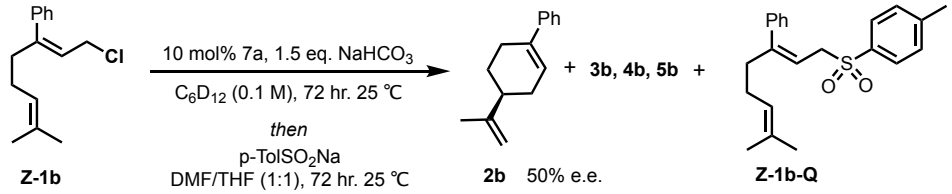
HR-MS (EI): calcd. for $C_{15}H_{18}$ 198.1403 [$M^{+\bullet}$], found 198.1398

6.4 Elimination of 3b



A flame-dried 1-dram vial containing a magnetic stir bar was charged with **3b** (0.043 mmol, 0.010 g) and subsequently evacuated and backfilled with nitrogen gas. Then, 430 μL of 2,4,6-trimethylpyridine (collidine) were added and the mixture was heated to 175 °C for 36 hours. After this point, TLC analysis indicated full consumption of **3b** and the reaction was passed through a short pad of silica gel eluting with 100% hexanes to provide products **2b** and **4b** in a 10:1 ratio (determined by ^{1}H NMR analysis) in 83% combined yield (0.0071g).

6.5 Cyclization reaction with Z-1b



Hydrogen bond donor catalyst **7a** (0.0075 mmol, 0.0047 g, 10 mol%) and sodium bicarbonate (0.113 mmol, 0.0095 g, 1.5 eq.) were weighed directly into a flame-dried 1 dram vial charged with a magnetic stir bar. Then, 250 μL of d12-cyclohexane were added, followed by 500 μL of a 0.15 M stock solution of substrate **Z-1b** in d12-cyclohexane and 5 μL of mesitylene internal standard. The reaction vial was capped and sealed with electrical tape. The reaction mixture was allowed to stir for 72 hours. After this time, 600 μL of the crude reaction were transferred to a flame-dried NMR tube for analysis by ^{1}H NMR. Conversion of **Z-1b** was determined using the mesitylene aromatic CH frequency (6.7 ppm) by ^{1}H NMR. Enantiomeric excess for product **2b** was determined using an Agilent 7890A series GC system outfitted with a commercially available cyclosil-β 30m column. **Z-1b** was found to undergo cyclization to form products **2-5b** using these GC conditions; hence, following ^{1}H NMR analysis of the crude reaction, the reaction was concentrated, taken in a mixture of THF (375 μL) and DMF (375 μL) and subjected to treatment with sodium p-toluenesulfinate (0.075 mmol, 0.113 g, 10 eq.) for 72 hr. to quench unreacted **Z-1b** (see section 8) prior to evaluation of e.e. of **2b**. After this time, NMR analysis revealed complete conversion of remaining **Z-1b** to the sulfone product, **Z-1b-Q**. No additional conversion to products **2-5b** or any other products were observed using these quench conditions and **Z-1b-Q** did not cyclize on the CG.

Note that **Z-1b** was synthesized (see section 3) as a 30:1 ratio of **Z-1b** to **1b** (3.2% 1b impurity). **Z-1b** and **1b** are inseparable by conventional column chromatography and both cyclize on silica to form products **2-5b**. Upon analysis of the reaction aliquot by ^{1}H NMR, no remaining **1b** was observed. The e.e. value for the cyclization of **Z-1b** was determined on the assumption that the small amount (3.2%) of **1b** present reacted to form **2b** in 87% e.e. (e.r. = 14.21:1) with the same product distribution as reported in section 6.2. The reaction of **Z-1b** proceeded to 9.6% conversion (with full conversion of **1b**, total conversion = 12.8%) and produced a total yield of **2b** of 7.24%. The measured e.e. value for product **2b** was 60% (e.r. = 4.0:1). Using the observed product distribution of pure **1b** (section 6.2), of the 7.24% yield of **2b** observed in this experiment, 2.03% comes from the reaction of **1b**. The remaining 5.21% comes from the cyclization of **Z-1b**.

Let R_{1b} and R_Z be the yields of the R enantiomers of substrates **1b** and **Z-1b** respectively. Let S_{1b} and S_Z be the yields of the S enantiomers of substrates **1b** and **Z-1b** respectively. Assuming R is the major enantiomer,

$$er_{obs} = \frac{R_{1b} + R_Z}{S_{1b} + S_Z} \; (eq. 1)$$

$$R_{1b} + S_{1b} = 2.03\% \; yield$$

$$\frac{R_{1b}}{S_{1b}} = er_{1b} = 14.21$$

hence,

$$R_{1b} = 1.90\% \; yield \; ; \; S_{1b} = 0.13\% \; yield$$

$$R_Z + S_Z = 5.21\%\ yield$$

$$\frac{R_Z}{S_Z} = er_Z$$

$$S_Z er_Z + S_Z = 5.21\%\ yield$$

$$S_Z = \frac{5.21\%\ yield}{er_Z + 1}$$

$$R_Z = \frac{(5.21\%\ yield) * er_Z}{er_Z + 1}$$

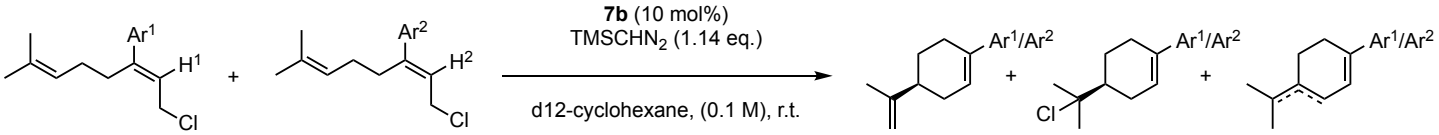
using eq. 1,

$$er_{obs} = \frac{R_{1b} + R_Z}{S_{1b} + S_Z} = \frac{1.90\%\ yield + \frac{(5.21\%\ yield) * er_Z}{er_Z + 1}}{0.13\%\ yield + \frac{(5.21\%\ yield)}{er_Z + 1}}$$

Solving for er_Z, we find that $er_Z = 2.97$. Hence, **Z-1b** reacts to form **2b** in 50% e.e. under these conditions.
Using the same conditions described above, the reaction of **Z-1b** proceeded to 5% conversion after 24 hr. (compared to 10% after 72 hr.). Hence, it is clear that the reaction does not stall after 24 hr.

7. Hammett Analysis

General procedure for Hammett experiments:

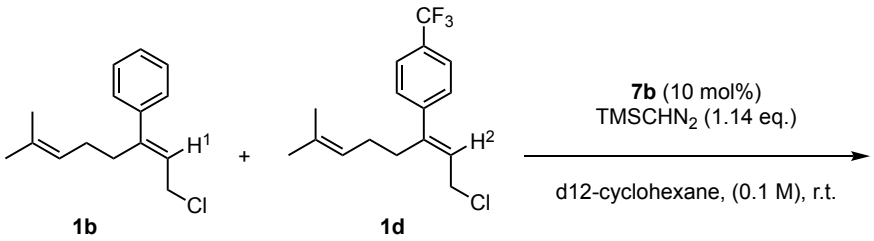


Two substrates were selected for each competition experiment. The primary criterion for substrate selection was that the NMR peaks of the styrenyl protons of the two substrates (H^1 and H^2) were sufficiently separated to allow for accurate quantitation of both substrates simultaneously (the more electron withdrawing the arene the further downfield the resonance). A stock-solution of the two substrates (0.076 mmol of each substrate in 1 mL, 0.076 M in each substrate) was prepared in d12-cyclohexane and 460 μL of this solution (0.035 mmol of each substrate, 0.5 equiv. of each substrate, 1 equiv. total substrate) was added to an NMR tube followed mesitylene as an internal standard (5 μL, 0.036 mmol, 0.51 equiv.) and a solution of $TMSCHN_2$ in hexanes (40 μL of a 2.0 M solution, 0.08 mmol, 1.14 equiv.). The NMR was locked and shimmed on this sample. Separately, a stock-solution of urea **7b** (20.5 mg in 1 mL, 0.035 mmol, 0.035 M) was prepared in d12-cyclohexane. This solution was immediately filtered through a syringe filter to remove any solids which could nucleate catalyst precipitation, and was used within 1 hour of preparation (while catalyst could be dissolved in cyclohexane to relatively high concentrations, it was found to gradually precipitate from solution. Filtering of the solution significantly delayed this precipitation, often allowing cyclohexane solutions of urea **7b** to remain stable for over 24 hours before forming visible precipitate. Because a series of one-pot competition experiments were used, any variation in catalyst precipitation between runs in the Hammett experiments shouldn't alter the relative rates within the competitions, but nevertheless every effort was made to avoid this variability). Then 200 μL of the catalyst stock solution (0.0071 mmol, 0.1 equiv.) was added to the NMR tube and the NMR was re-shimmed as quickly as possible. The reaction was then followed by NMR, spacing the acquisitions appropriately for the expected rates of reaction for the two substrates.

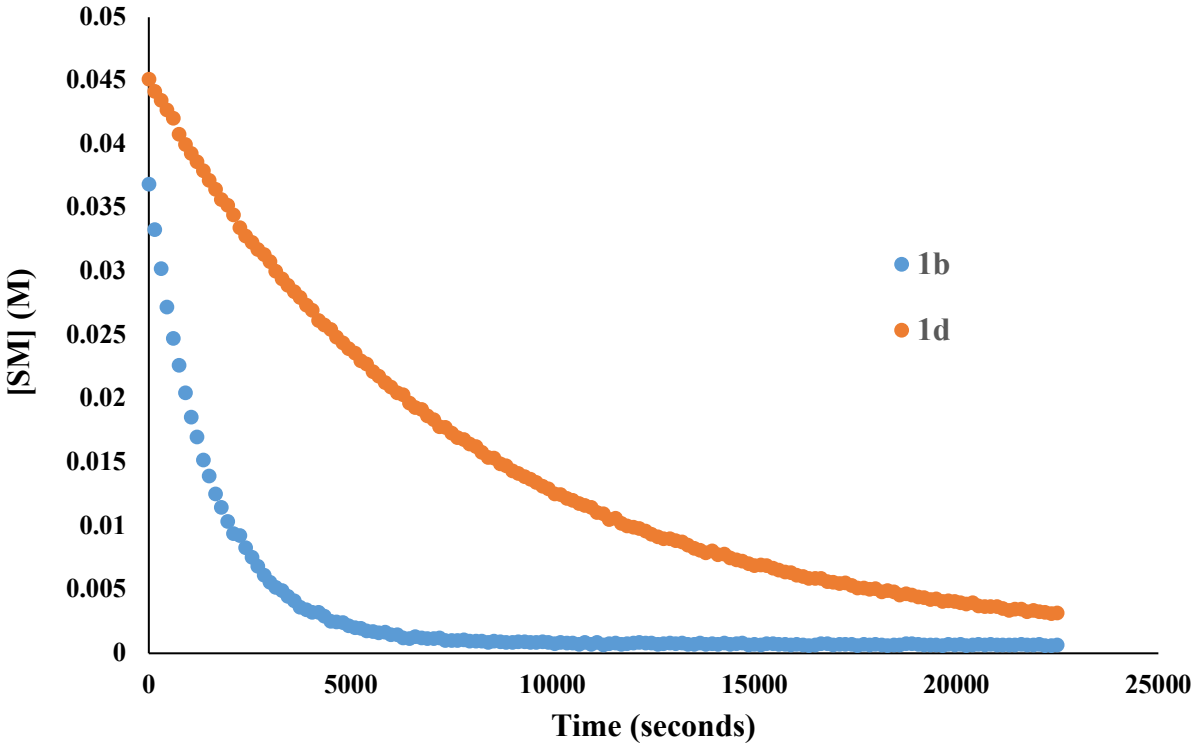
Sample measurement and analysis for Hammett experiments:

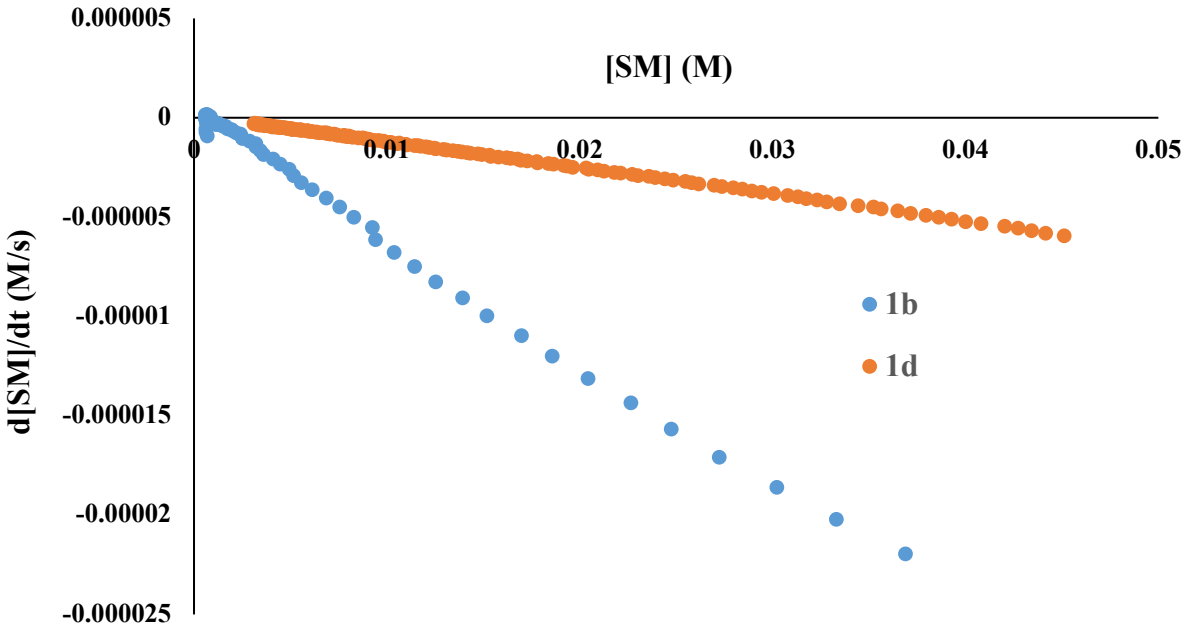
The spectra were recorded on a Varian NMR probe (600 MHz) at room temperature in d12-cyclohexane. In order to obtain quantitative results, an acquisition time of 2.5 seconds and a relaxation delay of >57.5 seconds were used. All spectra were processed using Mestrenova. The spectra were aligned by setting the mesitylene peak to 6.69 ppm and then phased using Mestrenova's automatic phase correction followed by a manual phase correction. Then a Bernstein polynomial baseline correction was applied. The

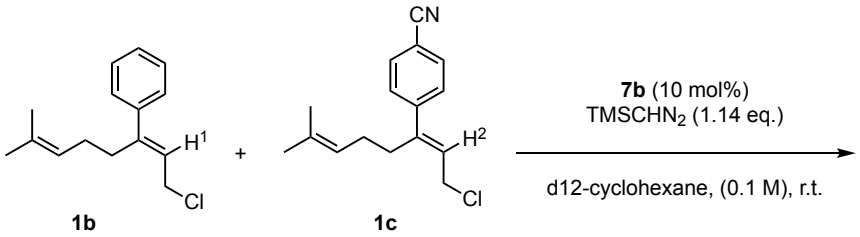
spectra were then normalized such that the integral of mesitylene peak at 6.69 ppm was set to 3000 units. The concentrations of the two starting materials were measured by their styrenyl protons which were integrated relative to the aryl proton of the mesitylene internal standard. The more upfield of the two vinyl protons from minor product **5** (the conjugated diene) overlaps with the styrenyl proton. This was accounted for by subtracting the value of the integral for the more downfield of the vinyl protons in **5** from the integral for the styreneyl proton in the corresponding starting material. Since so little **5** is formed, this correction did not qualitatively change the results of the Hammett analysis, but without it graphs of [SM] vs time do not go to zero. Using the dataset from the entire time course of the reaction, seventh order polynomial fittings of [SM] vs. time were generated using the LINEST feature of Microsoft Excel and the first derivative of the polynomial was taken to produce an expression for reaction rate vs. [SM].[9] The slope of the rate expression was determined using Microsoft Excel, and that value was used to determine relative reaction rates. In addition, the data were fit to a monoexponential function, which gave comparable results (for a comparison of polynomial and exponential fitting in determination of the rate law, see section 9) provided care was taken to exclude data points collected at very high conversions (>95%) in which errors could significantly skew the fit.



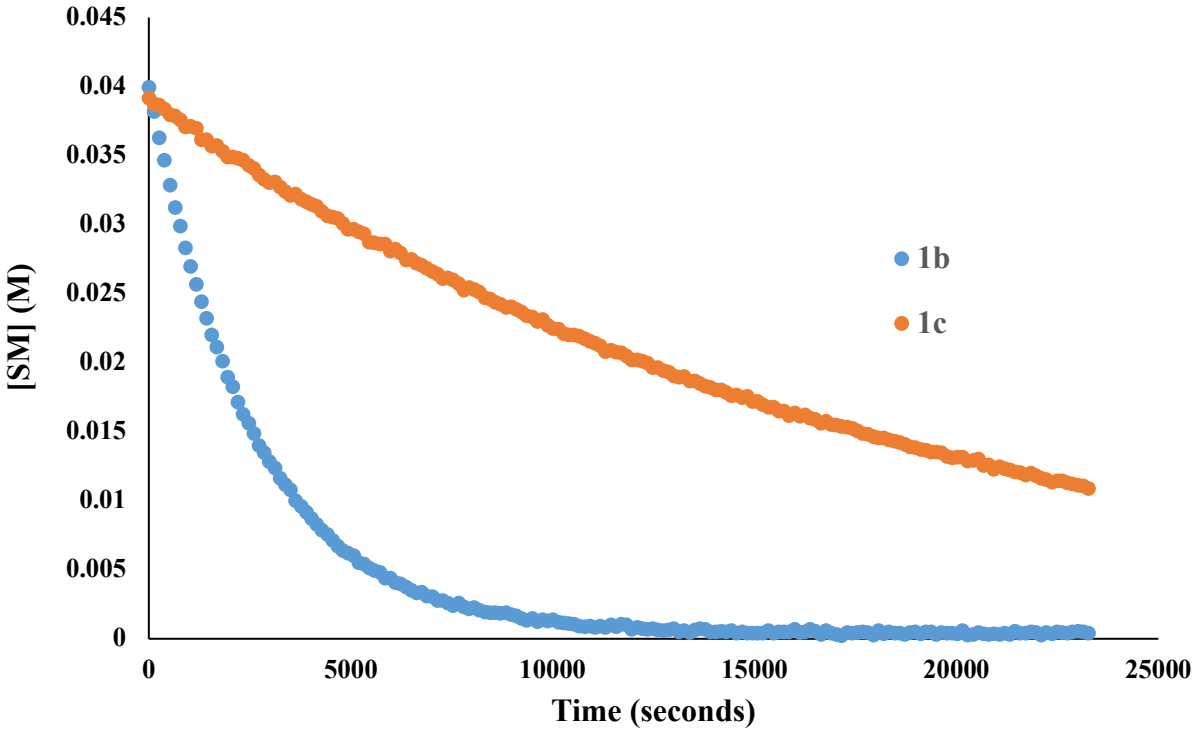
The competition between **1b** and **1d** was conducted according to the general procedure for Hammett experiments. Spectra were acquired every 150 seconds. The seventh order polynomial fits are as follows: [**1b**] = $-1.16*10^{-30}*t^7+1.05*10^{-25}*t^6-3.93*10^{-21}*t^5+7.82*10^{-17}*t^4-8.98*10^{-13}*t^3+5.99*10^{-9}*t^2-2.19*10^{-5}*t+0.0362$ and [**1d**] = $-2.37*10^{-33}*t^7+5.55*10^{-28}*t^6-3.58*10^{-23}*t^5+1.16*10^{-18}*t^4-2.47*10^{-14}*t^3+4.32*10^{-10}*t^2-5.94*10^{-6}*t+0.0452$. The rate constant for the conversion of **1b** was calculated to be -0.000640 and that for **1d** was -0.000132, giving a relative reaction rate d[**1d**]/d[**1b**] = 0.207. The exponential fits are as follows [**1b**] = $0.0369*e^{-0.000569*t}$ and [**1d**] = $0.0451*e^{-0.000120*t}$. The relative reaction rate from the exponential fitting is d[**1d**]/d[**1b**] = 0.211.

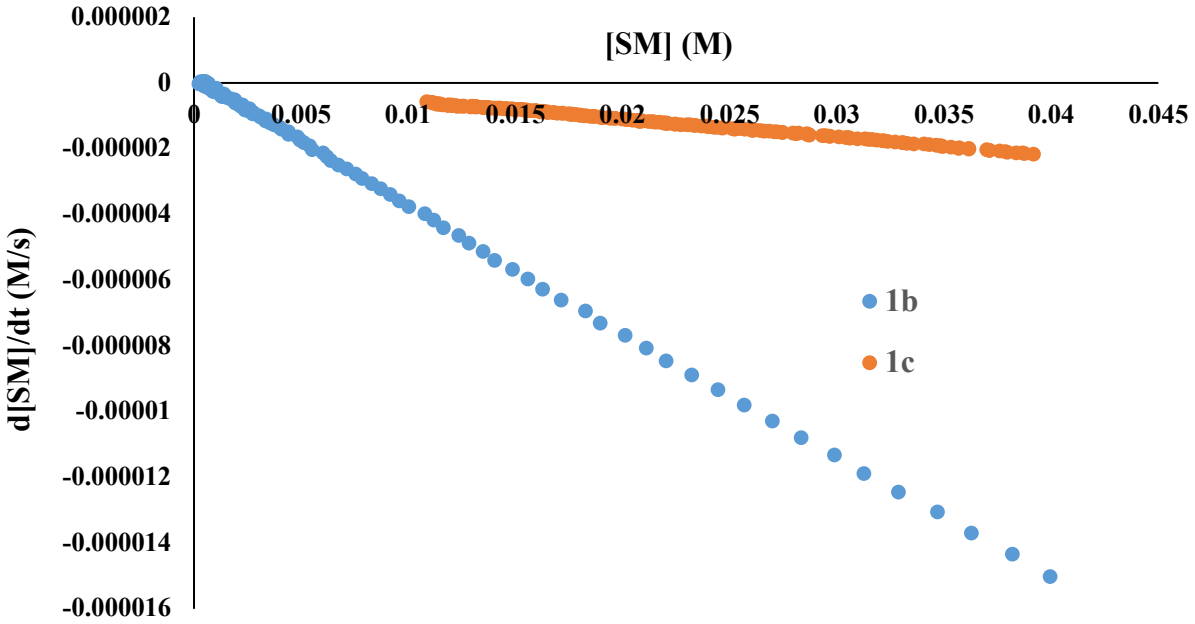


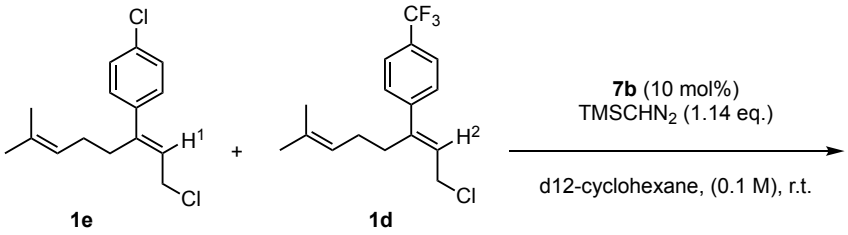




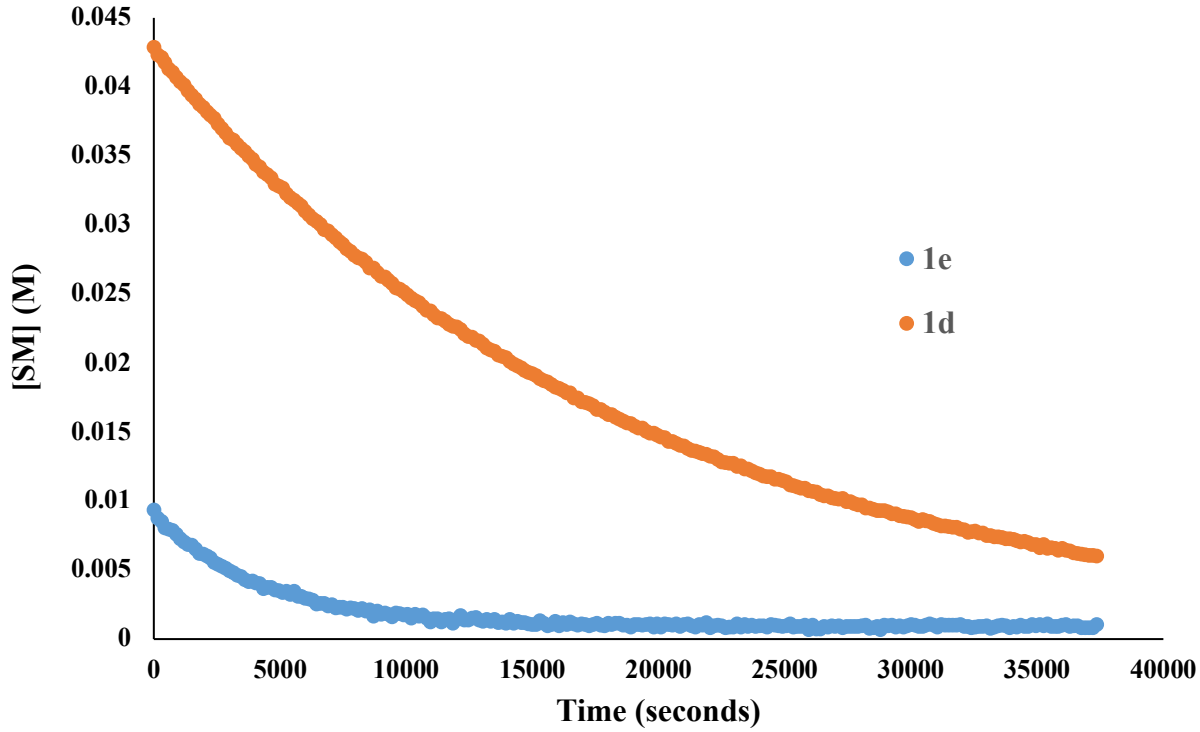
The competition between **1b** and **1c** was conducted according to the general procedure for Hammett experiments. Spectra were acquired every 130 seconds. The seventh order polynomial fits are as follows: [**1b**] = $-1.47*10^{-31}*t^7+1.59*10^{-26}*t^6-7.30*10^{-22}*t^5+1.85*10^{-17}*t^4-2.83*10^{-13}*t^3+2.68*10^{-9}*t^2-1.50*10^{-5}*t+0.0400$ and [**1c**] = $2.12*10^{-32}*t^7-1.56*10^{-27}*t^6+4.27*10^{-23}*t^5-5.09*10^{-19}*t^4+1.52*10^{-15}*t^3+5.76*10^{-11}*t^2-2.16*10^{-6}*t+0.0392$. The rate constant for the conversion of **1b** was calculated to be -0.000385 and that for **1c** was -0.0000552, giving a relative reaction rate of d[**1c**]/d[**1b**] = 0.143. The exponential fits are as follows [**1b**] = $0.0399*e^{-0.000366*t}$ and [**1c**] = $0.0392*e^{-0.0000546*t}$. The relative reaction rate from the exponential fitting is d[**1c**]/d[**1b**] = 0.149.

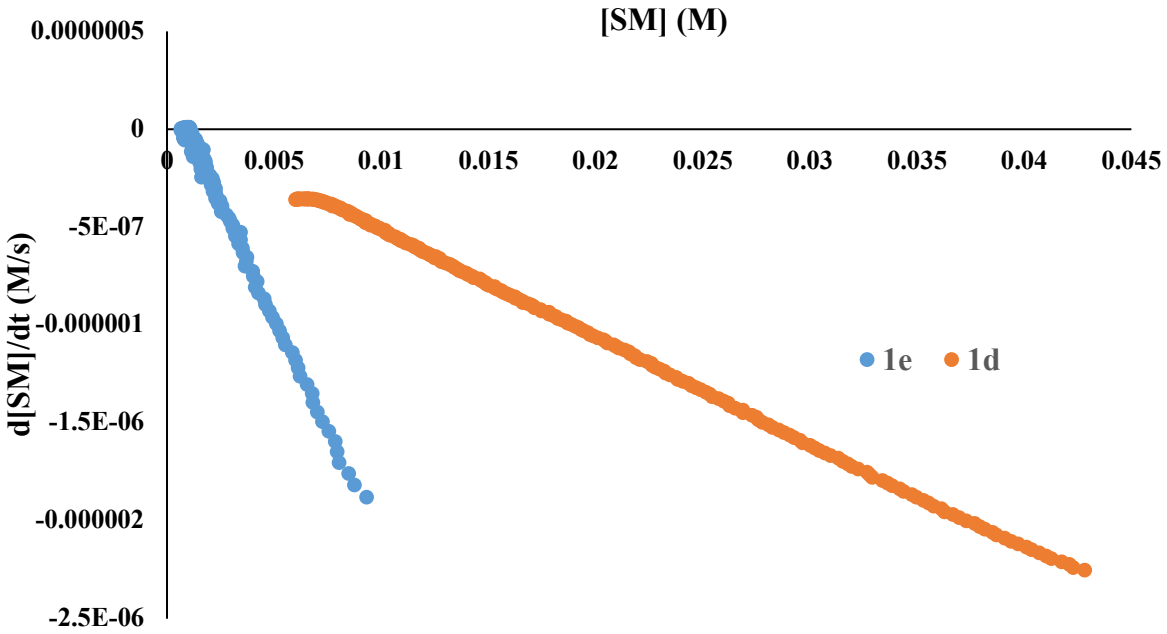

0.045
0.04
0.035
0.03
0.025
0.02
0.015
0.01
0.005
0
[SM] (M)
0
5000
10000
15000
20000
25000
Time (seconds)
1b
1c

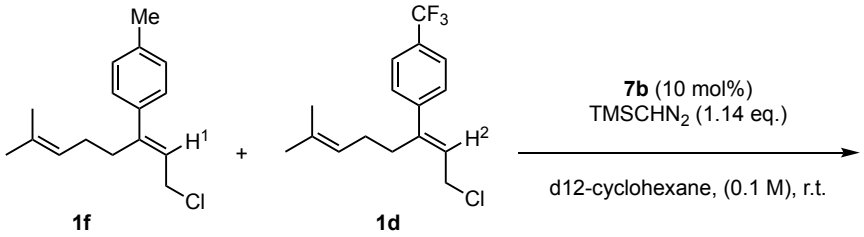

0.000002
0
-0.000002
-0.000004
-0.000006
-0.000008
-0.00001
-0.000012
-0.000014
-0.000016
d[SM]/dt (M/s)
[SM] (M)
0
0.005
0.01
0.015
0.02
0.025
0.03
0.035
0.04
0.045
1b
1c



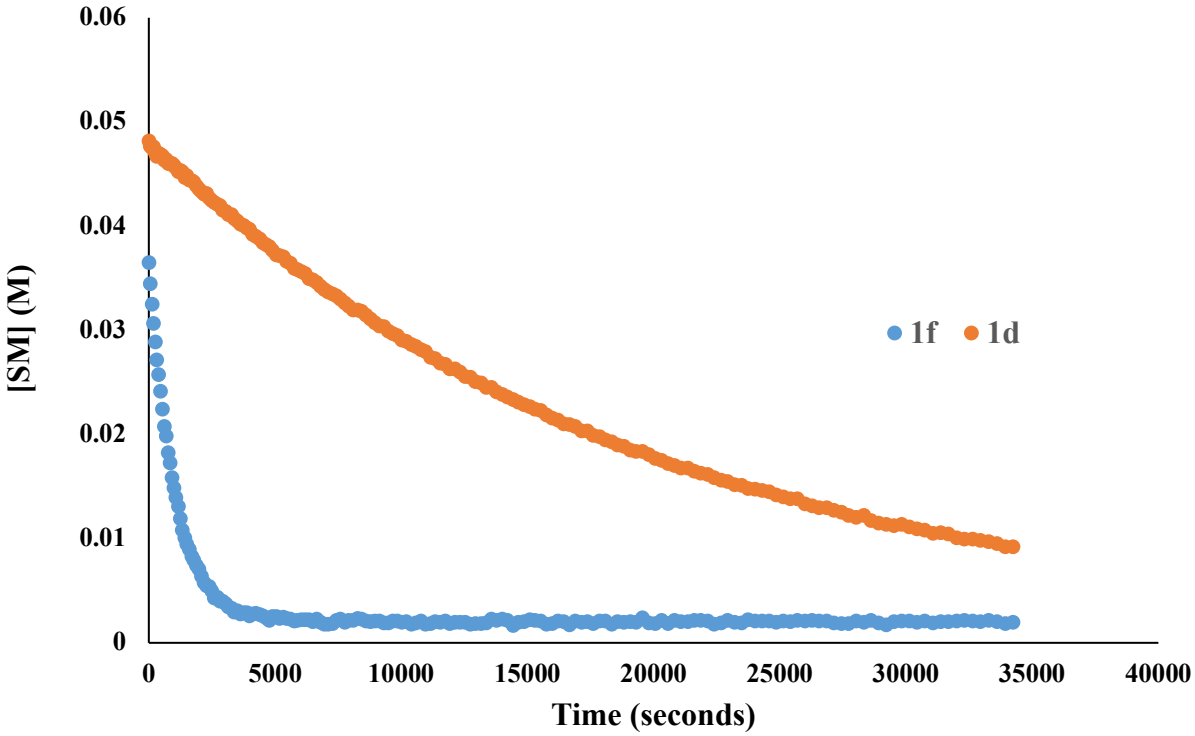
The competition between **1e** and **1d** was conducted according to the general procedure for Hammett experiments with the following modifications: the starting concentration of **1e** was ~0.01 M instead of 0.05 M and it was not possible to subtract trace product **5e** from **1e** due to a contaminant under the peak used to quantitate **5e**. The error introduced by this is negligible since **5e** is formed in less than 5% yield. Spectra were acquired every 150 seconds. The seventh order polynomial fits are as follows: [**1d**] = $1.74*10^{-34}*t^7$-$3.51*10^{-29}*t^6$+$2.45*10^{-24}*t^5$-$7.43*10^{-20}*t^4$+$4.39*10^{-16}*t^3$+$4.90*10^{-11}*t^2$-$2.25*10^{-6}*t$+0.0427 and [**1e**] = $1.27*10^{-33}*t^7$+$1.99*10^{-28}*t^6$-$1.36*10^{-23}*t^5$+$5.34*10^{-19}*t^4$-$1.31*10^{-14}*t^3$+$2.03*10^{-10}*t^2$-$1.88*10^{-6}*t$+0.00906. The rate constant for the conversion of **1e** was calculated to be -0.000233 and that for **1d** was -0.0000540, giving a relative reaction rate of d[**1e**]/d[**1d**] = 4.31. The relative reaction rate d[**1d**]/d[**1b**] = 0.207. Multiplying the relative rate d[**1e**]/d[**1d**] by the relative rate d[**1d**]/d[**1b**] gives d[**1e**]/d[**1b**] = 0.892. The exponential fits are as follows [**1d**] = $0.0428*e^{-0.0000525*t}$ and [**1e**] = $0.00932*e^{-0.000187*t}$ (data points with [**1e**] < 0.0025 M were excluded as they were highly inaccurate and skewed the fitting). The reaction rate from the exponential fitting is d[**1e**]/d[**1d**] = 3.56. The relative reaction rate from the exponential fitting for d[**1d**]/d[**1b**] = 0.211. Multiplying the relative rate d[**1e**]/d[**1d**] by the relative rate d[**1d**]/d[**1b**] gives d[**1e**]/d[**1b**] = 0.751. Although the 7th order polynomial and exponential fittings differ somewhat on the value of d[**1e**]/d[**1b**], both values lead to ρ = -1.3 and R^2 = 0.99, so the difference is not significant. The larger variability between the two fitting methods here is likely a consequence of the inability to correct for trace **5e** contamination under the peak used to quantitate **1e**.

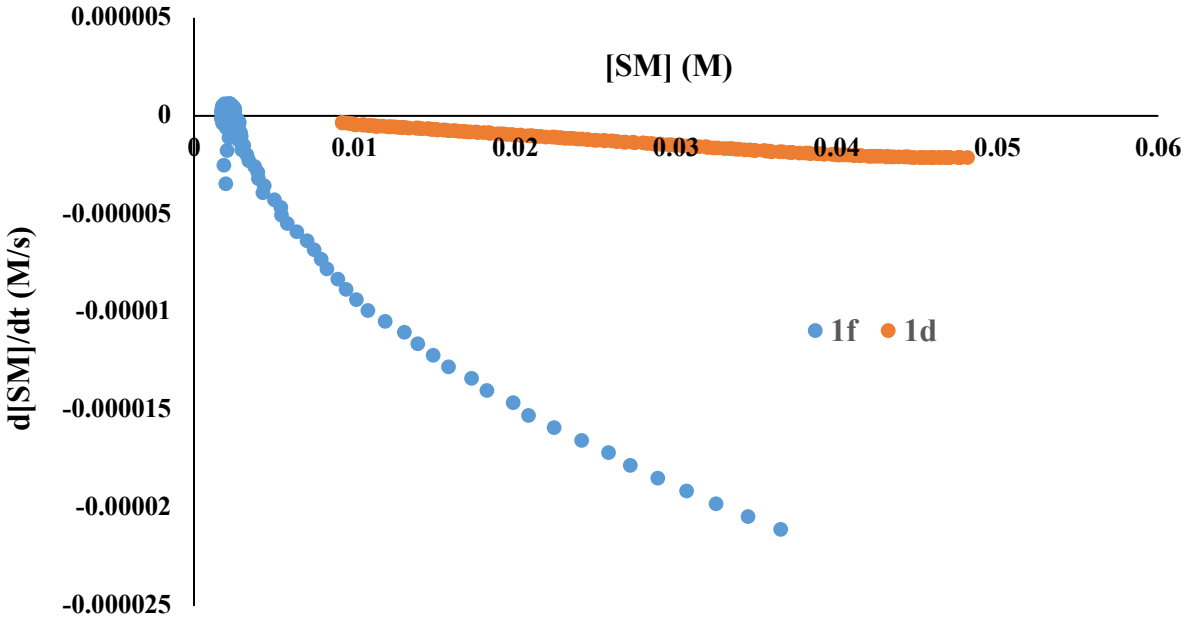




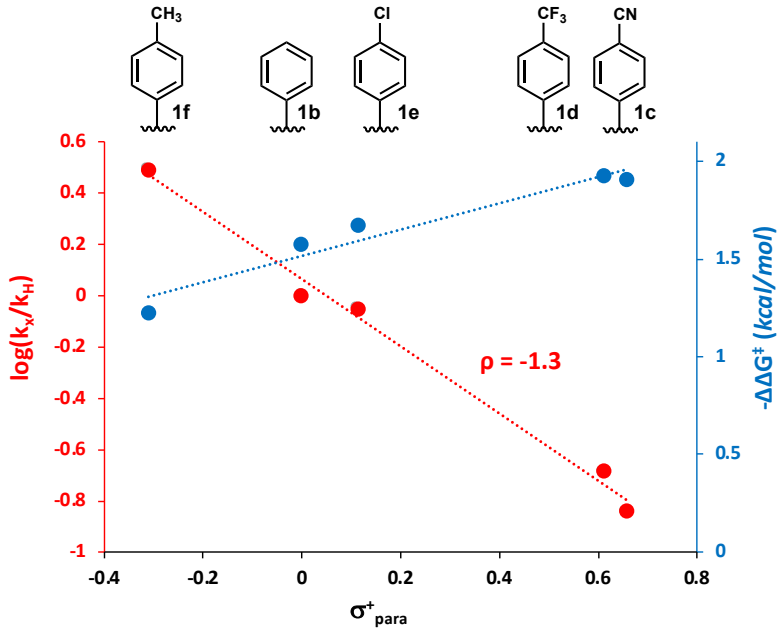


The competition between **1f** and **1d** was conducted according to the general procedure for Hammett experiments with the following modification: 0.005 M urea **7b** was used instead of the standard 0.01 M to try to slow down the reaction of **1f** sufficiently to allow for accurate measurement. The delay between acquisition of spectra started at 60 seconds and increased by 1.5 seconds after every acquisition to try to provide adequate coverage of both the slowly reacting **1d** and rapidly reacting **1f**. The seventh order polynomial fits are as follows: [**1d**] = $2.92*10^{-33}*t^7-3.70*10^{-28}*t^6+1.91*10^{-21}*t^5-5.14*10^{-19}*t^4+7.16*10^{-15}*t^3-8.87*10^{-12}*t^2-2.14*10^{-6}*t+0.0478$ and [**1f**] = $-2.45*10^{-31}*t^7+3.18*10^{-26}*t^6-1.66*10^{-21}*t^5+4.50*10^{-17}*t^4-6.69*10^{-13}*t^3+5.37*10^{-9}*t^2-2.11*10^{-5}*t+0.0329$. The rate constant for the conversion of **1f** was calculated to be -0.000730 and that for **1d** was -0.0000485, giving a relative reaction rate of d[**1f**]/d[**1d**] = 15.0. Multiplying this by the relative rate d[**1d**]/d[**1b**] gives d[**1f**]/d[**1b**] = 3.11. The graph of d[**1f**]/dt vs. [**1f**] exhibits curvature potentially consistent with sub-1st-order behavior in **1f**. Since **1f** is by far the most reactive substrate, it is possible the carbocyclization step is accelerated such that it becomes comparable in rate to some other step in the catalytic cycle (e.g. removal of HCl), which would account for the apparent sub-1st order. Another possible explanation is saturation behavior in **1f**, which could occur if the C-Cl bond of this substrate is sufficiently polarized to favor a catalyst-substrate complex as the resting state. The data from substrate **1d** could be fit to an exponential function as follows: [**1d**] = $0.0481*e^{-0.0000488*t}$. Since substrate **1f** did not undergo a clear first order decay, its data was not fit to an exponential function.





Enantioselectivity values are expressed in kcal/mol and were converted from e.r. values (see section 6.2) observed under optimal conditions using catalyst **7a**. This conversion was performed using the Eyring equation (see section 9.3) where R = 1.987E-03 kcal/(K*mol) and T = 298 K. We observed the best correlations for both rate and enantioselectivity Hammett studies using σ+ values. Hammett σ+ values for para substituents were drawn from the literature.[7]

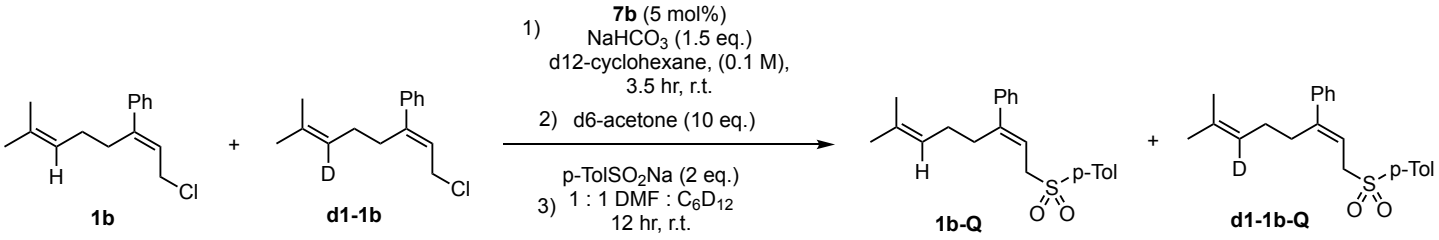


Substrate	sigma+	(-)DDG	log(kx/kH)
1f-4Me	-0.311	1.222985059	0.492622522
1b-Ph	0	1.571915111	0
1e-4Cl	0.114	1.672007875	-0.05032650
1d-4Cf3	0.612	1.926686338	-0.68490594
1c-4CN	0.659	1.90667417	-0.843703641

Figure S6. Hammett plots of reaction rate and enantioselectivity.

8. Kinetic Isotope Effect Studies

General procedure for KIE experiments:



A stock solution was prepared consisting of ~1 : 1 protio-**1b** and deutero-**1b** (~0.075 mmol protio-**1b** and ~0.075 mmol-deutero-**1b,** attempting to account for the partial enrichment of the deuterated material) and mesitylene (10 µL) in d12-cyclohexane (1.5 mL, 0.1 M total **1b**). 1 mL (0.1 mmol total **1b**, 1 eq.) of this stock solution was added to an oven-dried 0.5-dram vial which had been charged with $NaHCO_3$ (13 mg, 0.15 mmol, 1.5 eq.), urea **7b** (2.9 mg, 0.005 mmol, 0.05 eq.) and a magnetic stir-bar, and closed with a screw-cap containing a rubber septum. The reaction was allowed to stir at room temperature for 3.5 hours. The reminder of the stock-solution was set aside to use as the R_0 sample. After 3.5 hours (~80% conversion) the reaction as quenched by the addition of d6-acetone (67 µL, 1 mmol, 10 eq.) (a control experiment had shown that a reaction quenched in this manner exhibited <1% additional conversion in 17 hours following the quench). Immediately after quenching, 100 µL of the crude reaction mixture was diluted into 600 µL of pure d12-cyclohexane. Simultaneously, 100 µL of the residual starting material stock solution was diluted into 600 µL of pure d-12 cyclohexane, and these samples were analyzed by NMR to determine conversion of protio-**1b** relative to mesitylene. The remaining 900 µL of the crude, quenched reaction mixture were added to a pre-made suspension of sodium p-toluenesulfinate (36 mg, 0.2 mmol, 2 eq.) in DMF (1 mL), and the suspension was stirred vigorously overnight at room temperature to convert any unreacted allyl chloride into the sulfone **d1-1b-Q**. This derivatization was necessary because the starting allyl choride is not stable to silica, and therefore, the material recovered from a reaction run to partial conversion could not be purified without derivatization. While it is possible to measure the KIE based on the H/D ratios of the allyl chloride in the starting-material stock solution and the crude, quenched reaction mixture, and this gives numbers very similar to those measured using the sulfone (see below), we concluded that it was important to measure the H/D ratio in rigorously purified material as well because of the small magnitude of the kinetic isotope effect. The remainder of the R_0 sample was derivatized as the sulfone in an identical manner to the quenched reaction – it was added to

a suspension of p-toluenesulfinate (36 mg, 0.2 mmol) in DMF (1 mL) and stirred vigorously overnight. The following day both sulfone formations were worked up identically: the reactions were diluted with Et_2O and quenched with sat. aq. $NaHCO_3$. The aqueous layers were removed and the organic layers were washed 2x with sat. aq. $NaHCO_3$ and then 3x with brine. The organic layers were then dried over Na_2SO_4 for 15 minutes, filtered, concentrated, and analyzed by NMR to ensure complete conversion of the allyl chlorides to the sulfones, after which they was purified sequentially by preparatory TLC, preparatory-HPLC (Waters Prep-C18 SunFire® column, 5 μm, 19 × 250 mm, UV detection at 254 nm, gradient elution with 60→95% acetonitrile in water containing 0.1% formic acid over 30 minutes, flow rate: 15 mL/min., retention time = 21.82 min.), and then run through a silica plug eluting with 2:1 pentane : EtOAc. The sulfone R_0 and R_f samples were then analyzed by NMR.

Sample measurement for KIE experiments:

The conversion of protio-**1b** was determined through ^{1}H-NMR analysis of the diluted substrate stock solution and the diluted, crude, acetone-quenched reaction mixture. The spectra were recorded on a Varian NMR probe (600 MHz) at room temperature in d12-cyclohexane. In order to obtain reproducible and quantitative results spectra were recorded without sample spinning using a calibrated ninety-degree pulse with the transmitter offset frequency set to 269.9 Hz. An acquisition time of 2.5 seconds and relaxation delay of 57.5 seconds were used. Six spectra were recorded for each sample. These spectra could also be used to measure the H/D ratio in the R_0 and R_f samples, and these measurements gave isotope effects broadly in agreement with those measured using the purified sulfones (see below).

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The ratio of H to D in the purified sulfones was determined through ^{1}H-NMR analysis in $CDCl_3$. NMR measurements of the purified R_0 and R_f samples were conducted in 600 μL of $CDCl_3$ each at nearly-identical concentrations (as determined by integration of the tolyl methyl relative to the solvent residual peak). Spectra were obtained on a Varian NMR probe (600 MHz) at room temperature. In order to obtain reproducible and quantitative results spectra were recorded without sample spinning using a calibrated ninety-degree pulse with the transmitter offset frequency set to 160.5 Hz. An acquisition time of 2.5 seconds and relaxation delay of 57.5 seconds were used. Four spectra were recorded for each sample.

Data analysis for KIE experiments:

All spectra were processed using Mestrenova. Spectra of allyl chlorides in *d12*-cyclohexane were aligned by setting the mesitylene peak to 6.69 ppm and then phased using Mestrenova's automatic phase correction followed by a manual phase correction. Then a third-order polynomial baseline correction was applied. The spectra were then normalized such that the integral of mesitylene peak at 6.69 ppm was set to 3000 units. Spectra of sulfones in $CDCl_3$ were aligned by setting the solvent residual peak to 7.26 ppm, and then phased using Mestrenova's automatic phase correction followed by a manual phase correction. Then a third-order polynomial baseline correction was applied. The spectra were normalized such that the integral of the tolyl methyl peak at 2.44 ppm was set to 3000.

The kinetic isotope effect was computed using the following equation

$$\frac{k_H}{k_D} = \frac{\ln(1 - F_H)}{\ln((1 - F_H) * \frac{R_f}{R_0})}$$

where:

$$R_0 = \frac{[deutero - \mathbf{1b}]}{[protio - \mathbf{1b}]} \; in\ the\ stock\ solution\ of\ starting\ material\ added\ to\ the\ reaction$$

$$R_f = \frac{[deutero - \mathbf{1b}]}{[protio - \mathbf{1b}]} \; in\ the\ starting\ material\ recovered\ from\ a\ reaction\ run\ to\ partial\ conversion$$

and F_H is the fractional conversion of protio-**1b**

Error was determined using the following equation[8]

$$\Delta KIE = KIE * \sqrt{\left(\frac{\Delta KIE_F}{KIE}\right)^2 + \left(\frac{\Delta KIE_R}{KIE}\right)^2}$$

where:

$$\Delta KIE_F = \frac{-\ln\left(R_f/R_0\right)}{(1-F_H) * ln^2((1-F_H) * R_f/R_0)} * \Delta F_H$$

$$\Delta KIE_R = \frac{-\ln\left(1-F_H\right)}{\left(R_f/R_0\right) * ln^2((1-F_H) * R_f/R_0)} * \Delta\left(R_f/R_0\right)$$

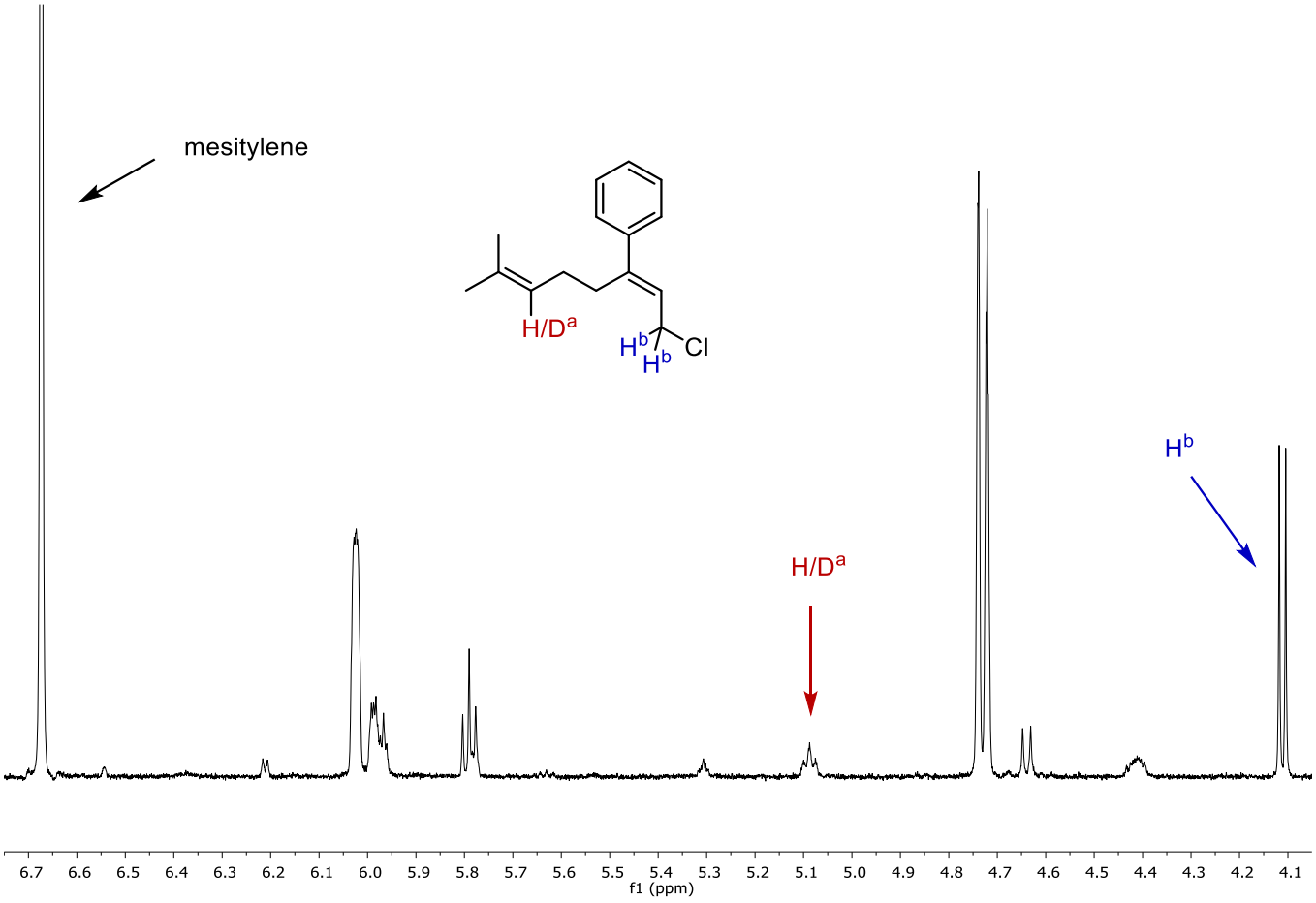


Figure S7. Representative ^{1}H NMR spectrum of the crude reaction mixture quenched at partial conversion showing the peaks of interest. Spectra were normalized using the mesitylene peak at 6.69 ppm. The vinyl peak at 5.09 ppm (H^a) allows for direct quantification of protio-**1b** relative to mesitylene in the stock solution and crude, quenched reaction mixture. The concentration of deutero-**1b** relative to mesitylene could be determined by subtracting the concentration of protio-**1b** from half the integral of H^b (4.11 ppm), which corresponds to two protons in the combined protio- and deutero-**1b**.

Run 1 – R_0 sample – chloride			
Measurement	**Normalized total 1b**	**Normalized protic-1b**	**Normalized deutero-1b**
1	1363.02	674.56	688.46
2	1363.25	674.35	688.90
3	1361.75	674.38	687.38
4	1360.58	674.97	685.61

5	1362.48	674.19	688.29
6	1361.96	674.31	687.65

Property	**Value**	**Standard Deviation**
Normalized protic-**1b**	674.46	0.28
Normalized deutero-**1b**	687.71	1.17

Figure S8. Tabulated data for R_0 sample for run 1 based on measurement of the allyl chloride. The R_0 sample for run 1 was prepared and measured according to the general procedure for KIE experiments.

Run 1 – R_f sample – chloride			
Measurement	**Normalized total 1b**	**Normalized protic-1b**	**Normalized deutero-1b**
1	197.96	101.73	96.23
2	199.42	103.96	95.46
3	197.79	104.97	92.83
4	198.92	105.14	93.78
5	196.44	101.33	95.11
6	196.84	103.37	93.46

Property	**Value**	**Standard Deviation**
Normalized protic-**1b**	103.42	1.61
Normalized deutero-**1b**	94.48	1.32

Figure S9. Tabulated data for R_f sample for run 1 based on measurement of the allyl chloride. The R_f sample for run 1 was prepared and measured according to the general procedure for KIE experiments.

Run 2 – R_0 sample – chloride			
Measurement	**Normalized total 1b**	**Normalized protic-1b**	**Normalized deutero-1b**
1	1483.47	730.26	753.20
2	1482.74	730.48	752.26
3	1483.07	730.82	752.25
4	1485.04	731.27	753.77
5	1484.36	731.60	752.76
6	1484.88	731.26	753.61

Property	**Value**	**Standard Deviation**
Normalized protic-**1b**	730.95	0.52
Normalized deutero-**1b**	752.98	0.66

Figure S10. Tabulated data for R_0 sample for run 2 based on measurement of the allyl chloride. The R_0 sample for run 2 was prepared and measured according to the general procedure for KIE experiments.

Run 2 – R_f sample – chloride			
Measurement	**Normalized total 1b**	**Normalized protic-1b**	**Normalized deutero-1b**
1	218.36	116.50	101.85
2	219.31	114.65	104.66
3	219.26	116.73	102.52
4	220.45	117.33	103.12
5	219.32	114.05	105.27
6	221.51	116.22	105.29

Property	**Value**	**Standard Deviation**
Normalized protic-**1b**	115.91	1.28
Normalized deutero-**1b**	103.79	1.48

Figure S11. Tabulated data for R_f sample for run 2 based on measurement of the allyl chloride. The R_f sample for run 2 was prepared and measured according to the general procedure for KIE experiments.

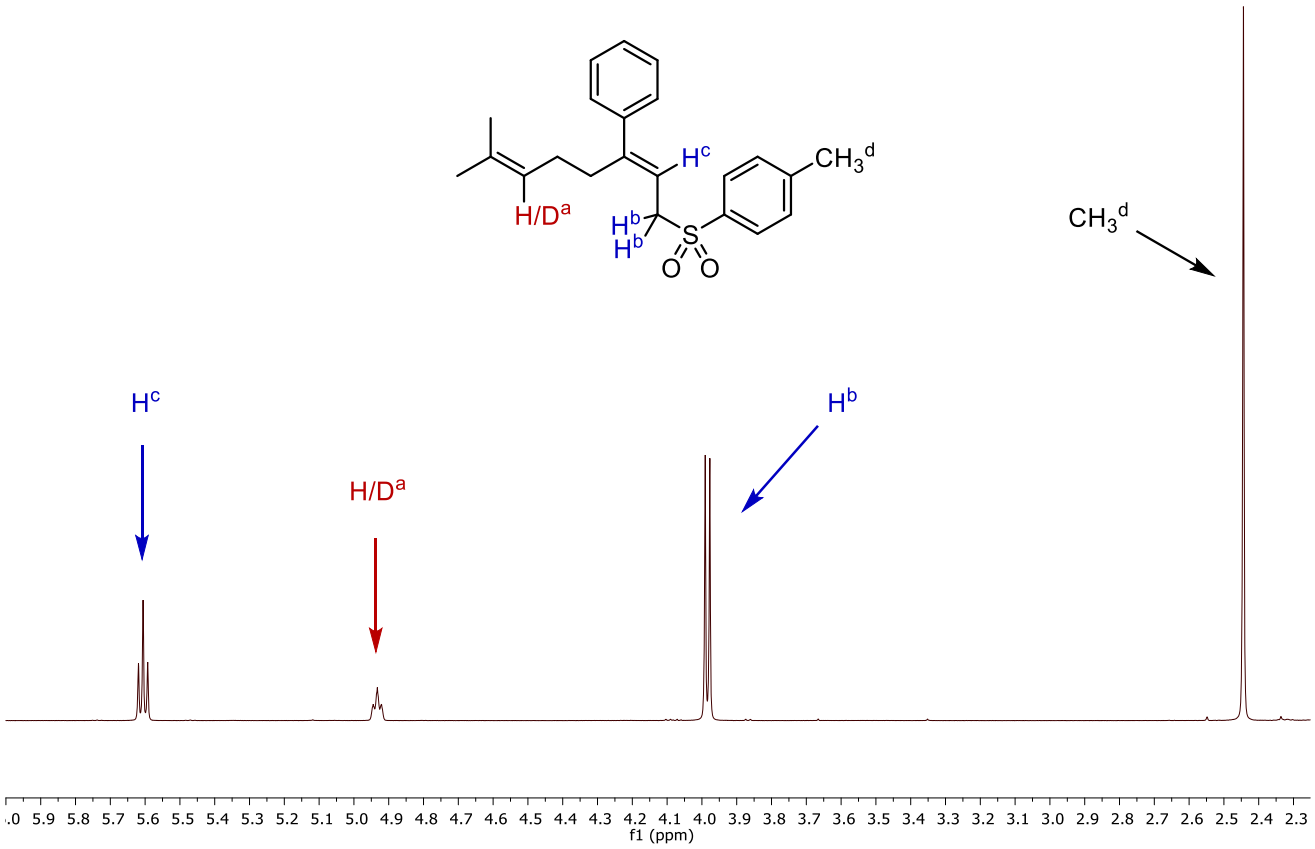


Figure S12. Representative ^{1}H NMR spectrum showing the peaks of interest for sulfone **1b-Q** and **d1-1b-Q**. Spectra were normalized using the tolyl methyl group CH_3^d (2.44 ppm). The vinyl peak at 4.93 ppm (H^a) allows for direct quantification of protio **1b-Q** normalized to total **1b-Q** + **d1-1b-Q.** The normalized concentration of **d1-1b-Q** could be determined by subtracting the concentration of **1b-Q** from the integral of H^c (5.61 ppm), which corresponds to the β-styrenyl proton present in both protio- and deutero-**1b-Q** or by subtracting the concentration of protio-**1b-Q** from half the integral of H^b (3.98 ppm), which corresponds to the methylene alpha to the sulfone in both protio- and **d1-1b-Q**. The average of these two values was used to determine the kinetic isotope effect

Run 1 – R_0 sample – sulfone					
Measurement	**Normalized total 1b-Q - vinyl**	**Normalized total 1b-Q - methylene**	**Normalized protic-1b-Q**	**Normalized deutero-1b-Q from vinyl**	**Normalized deutero-1b-Q from methylene**
1	993.32	997.12	484.99	508.33	512.12
2	993.29	996.34	484.79	508.50	511.55
3	994.42	996.65	485.03	509.39	511.62
4	993.06	996.64	484.07	508.99	512.56
Property		**Value**		**Standard Deviation**	
normalized protic-**1b-Q**		484.72		0.45	
normalized deutero-**1b-Q**		510.38		1.75	

Figure S13. Tabulated data for R_0 sample for run 1 based on measurement of the allyl sulfone. The R_0 sample for run 1 was prepared and measured according to the general procedure for KIE experiments.

Run 1 – R_f sample – sulfone					
Measurement	**Normalized total 1b-Q - vinyl**	**Normalized total 1b-Q - methylene**	**Normalized protic-1b-Q**	**Normalized deutero-1b-Q from vinyl**	**Normalized deutero-1b-Q from methylene**
1	981.87	989.52	510.20	471.67	479.32
2	981.67	989.68	509.67	472.00	480.01
3	982.57	989.76	510.34	472.24	479.42
4	982.31	990.01	508.49	473.83	481.52
Property		**Value**		**Standard Deviation**	
normalized protic-**1b-Q**		509.67		0.84	
normalized deutero-**1b-Q**		476.25		4.18	

Figure S14. Tabulated data for R_f sample for run 1 based on measurement of the allyl sulfone. The R_f sample for run 1 was prepared and measured according to the general procedure for KIE experiments.

Run 2 – R_0 sample – sulfone					
Measurement	**Normalized total 1b-Q - vinyl**	**Normalized total 1b-Q - methylene**	**Normalized protic-1b-Q**	**Normalized deutero-1b-Q from vinyl**	**Normalized deutero-1b-Q from methylene**
1	1000.42	998.98	488.10	512.32	510.88
2	999.77	998.65	487.96	511.81	510.69
3	999.77	999.20	487.61	512.17	511.60
4	999.41	999.34	488.17	511.24	511.18
Property		**Value**		**Standard Deviation**	
normalized protic-**1b-Q**		487.96		0.25	
normalized deutero-**1b-Q**		511.49		0.59	

Figure S15. Tabulated data for R_0 sample for run 2 based on measurement of the allyl sulfone. The R_0 sample for run 1 was prepared and measured according to the general procedure for KIE experiments.

Run 2 – R_f sample – sulfone					
Measurement	**Normalized total 1b-Q - vinyl**	**Normalized total 1b-Q - methylene**	**Normalized protic-1b-Q**	**Normalized deutero-1b-Q from vinyl**	**Normalized deutero-1b-Q from methylene**
1	995.75	997.44	512.35	483.40	485.09
2	997.08	997.62	512.55	484.53	485.07
3	996.39	997.93	512.93	483.46	485.00
4	995.64	997.47	512.57	483.07	484.90
Property		**Value**		**Standard Deviation**	
normalized protic-**1b-Q**		512.60		0.24	
normalized deutero-**1b-Q**		484.31		0.86	

Figure S16. Tabulated data for R_f sample for run 2 based on measurement of the allyl sulfone. The R_f sample for run 2 was prepared and measured according to the general procedure for KIE experiments.

KIE measurements				
Property	Run 1		Run 2	
	Value	Error	Value	Error
1-F_H	0.1533	0.0024	0.1586	0.0018
R_f/R_0 – chloride	0.8959	0.0188	0.8692	0.0157
R_f/R_0 - sulfone	0.8874	0.0085	0.9014	0.0020
KIE – chloride	**0.945**	0.010	**0.929**	0.008
KIE – sulfone	**0.940**	0.005	**0.947**	0.001

Figure S17. Tabulated data for KIE experiments**.** All values were calculated using the equations described above. The presence of a small, inverse secondary H/D KIE is consistent with the proposed mechanism and with literature precedent.

The reported KIE of 0.944(3) in the text is an average of the two sulfone numbers using standard propagation of error.

9. Kinetics Experiments

9.1 General considerations

All kinetics experiments were performed by collecting ^{1}H NMR spectra of reactions conducted in oven-dried 5 mm diameter NMR tubes using an INOVA-600 NMR spectrometer (600 MHz). Experiments were conducted at room temperature over a period of 4-10 hours, with spectra collection defined at fixed intervals (generally 100-200 sec.). Reactions were performed in a 6:1 (v/v) mixture of cyclohexane-d_{12} / dichloromethane-d_2 with 1.15 eq. of trimethylsilyldiazomethane (TMS-diazomethane) as the base, except when noted. This solvent blend was used to ensure that all reaction components remained soluble over the course of experiments. TMS-diazomethane was used as the base because sodium bicarbonate is not soluble in organic solvents and the spinning in the NMR probe was not found to be strong enough to promote phase-transfer to quench hydrochloric acid (a byproduct of the cyclization reaction). Hydrochloric acid inhibits catalysts **7a-7d**, and in the absence of base, the reaction stalls. Under these conditions, substrate **1b** was found to undergo reaction to produce products **2b-5b** quantitatively and with similar e.e. (under these conditions, 84% e.e. for **2b** using **7b**) to what was observed under optimal conditions reported in section 5.2. It was found that over all time scales surveyed, **1b** did not undergo a measurable background cyclization reaction (either in the presence or absence of added base). ^{1}H NMR spectra were analyzed in Mnova (Mestrelab Research) using phase and baseline corrections. Data extracted from these spectra were analyzed and plotted using Microsoft Excel. Curve-fitting was performed using Microsoft Excel's solver function to minimize the sum of the squared difference between fitted data and experimental data.

9.2 Derivation of the rate law

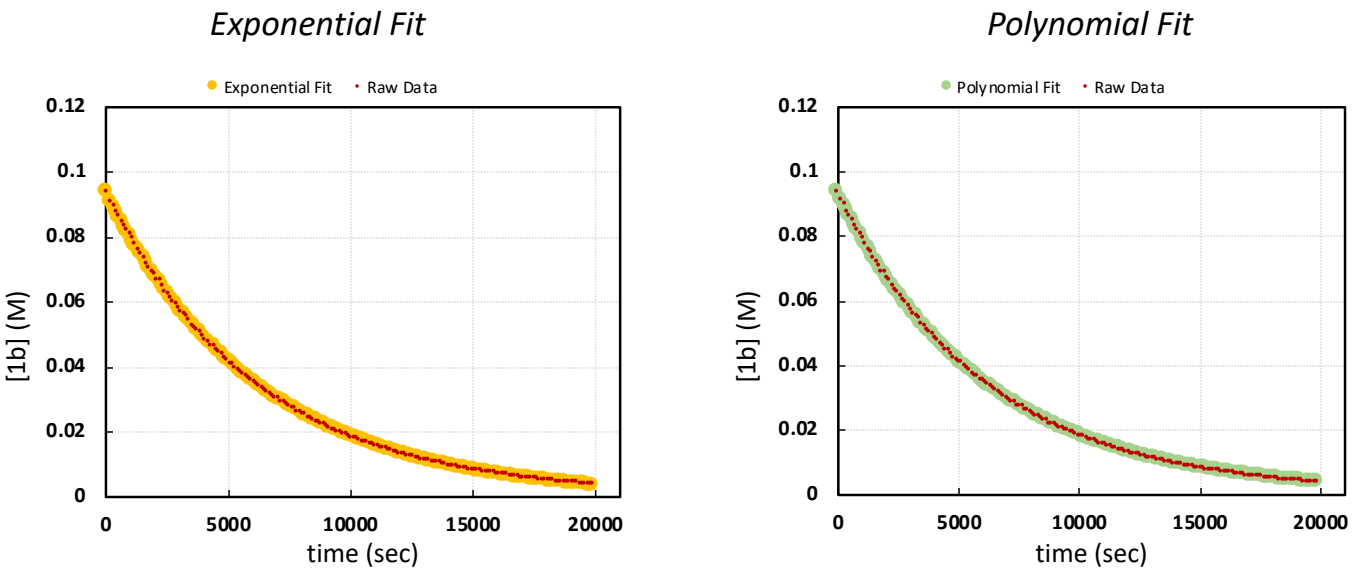
To determine the rate law for the cyclization reaction, model substrate **1b** was used with catalyst **7b** and TMS-diazomethane. A same excess experiment[9] was used to confirm that no catalyst deactivation or product inhibition were occurring under the reaction conditions. A different excess experiment[9] was used to determine the order in substrate **1b** and base by varying the concentration of base (TMS-diazomethane) present.

A representative procedure for kinetics experiments is provided:

An oven-dried 5mm NMR tube capped was charged with a 600 μL stock solution of substrate **1b** (0.07 mmol), TMS-diazomethane (2 M in Hexanes, 0.081 mmol), HPLC-grade hexanes (35 μL), and mesitylene (0.036 mmol) in C_6D_{12}. The tube was capped with a rubber septum and sealed with parafilm. Then, a single spectrum was obtained for the purposes of determining the appropriate acquisition parameters (shim, gain, etc.). The NMR tube was removed from the spectrometer and a 100 μL stock solution of catalyst **7b** (0.007 mmol) in CD_2Cl_2 was added to initiate reactions. The NMR tube was inverted several times and then returned to the NMR probe. The time delay between addition of catalyst stock solution and the beginning of data acquisition was recorded and factored into kinetic models. Spectra were collected at regular intervals (typically an acquisition time of 2.5 sec. with a 110 sec. relaxation delay).

Substrate concentration was determined by integration of the signals corresponding to the vinylogous proton on the electrophilic olefin of **1b** (δ = 5.8 ppm) against the mesitylene internal standard (using the aryl CH peak at δ = 6.7 ppm) (a resonance corresponding to product **5b** was found to overlap with this vinyl signal; the concentration of **5b** could be monitored using another vinyl peak at 6.27 ppm and was subtracted from the overall area of the peak corresponding to **1b**). For all reactions, it was found that no significant side

products were formed and that monitoring consumption of starting material or formation of product provided identical results (the mass balance is nearly unity). The [**1b**] versus time data were fit to a 7th order polynomial using a minimization of squares algorithm in Microsoft Excel. This fit was differentiated with respect to time to obtain rate verses [**1b**] data. This analysis established a first-order dependence of reaction rate on [**1b**] and a 0 order dependence on [TMS-diazomethane]. Hence, [**1b**] versus time data could also be fit to exponential functions of the form [**1b**]= $[\mathbf{1b}]_0$EXP(-*k*t) with identical results (where $[\mathbf{1b}]_0$ is the initial concentration of **1b**, *t* is time, and *k* is the first-order rate constant for the reaction).



Raw data: [**1b**]$_0$ = 0.1 M, [**7b**]$_T$ = 0.01 M, [TMS-diazomethane] = 0.115 M

Exponential fit of the following form: [**1b**] = [**1b**]$_0$ EXP(-*k**t)
[**1b**]$_{fit}$ = 0.0940 EXP(-*0.0001605**t)

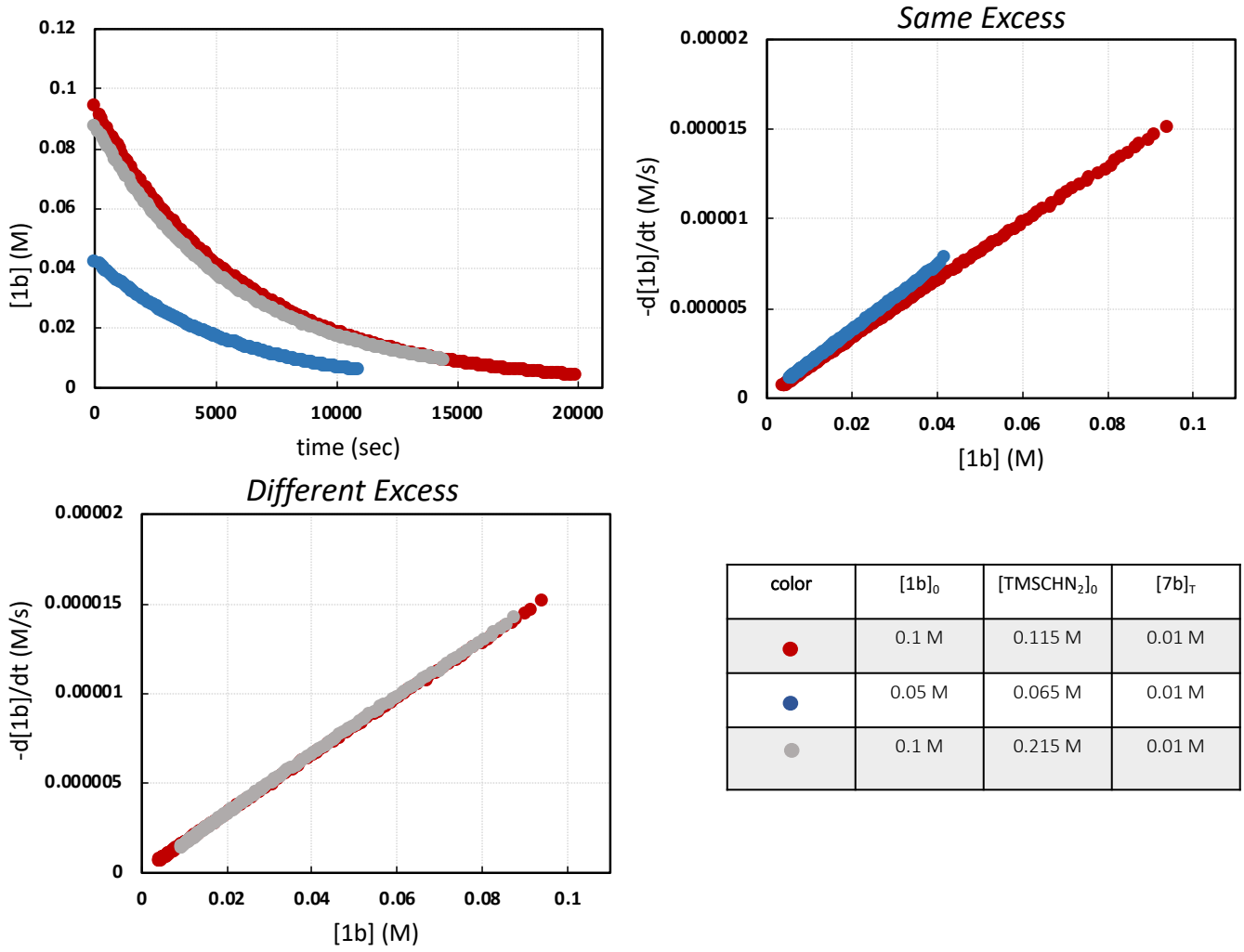
Polynomial fit of the following form:
[**1b**] = A*(t^7)+B*(t^6)+C*(t^5)+D*(t^4)+E*(t^3)+F*(t^2)+G*t+[**1b**]$_0$
[**1b**]$_{fit}$ = (2.46E-31)*(t^7)+(-1.65E-26)*(t^6)+(4.20E-22)*(t^5)+(-4.25E-18)*(t^4)+(-1.67E-14)*(t^3)+(1.06E-09)*(t^2)+(-1.51E-05)*t+9.44E-02

Figure S18. Concentration versus time profiles for the cyclization of substrate **1b** with catalyst **7b** and fits to exponential (left) and polynomial (right) functions.

The *same excess experiment* consisted of two runs: (Red: [**1b**]$_0$ = 0.1 M, [**7b**]$_T$ = 0.01 M, [TMS-diazomethane] = 0.115 M) and (Blue: [**1b**]$_0$ = 0.05 M, [**7b**]$_T$ = 0.01 M, [TMS-diazomethane] = 0.065 M).

The *different excess experiment* consisted of two runs: (Red: [**1b**]$_0$ = 0.1 M, [**7b**]$_T$ = 0.01 M, [TMS-diazomethane] = 0.115 M) and (Grey: [**1b**]$_0$ = 0.1 M, [**7b**]$_T$ = 0.01 M, [TMS-diazomethane] = 0.215 M).

From these data, it is concluded that the reaction is kinetically well-behaved, overall first-order, and that rate is proportional to [**1b**]^1



color	$[1b]_0$	$[TMSCHN_2]_0$	$[7b]_T$
●	0.1 M	0.115 M	0.01 M
●	0.05 M	0.065 M	0.01 M
●	0.1 M	0.215 M	0.01 M

Figure S19. Reaction profiles for the cyclization of substrate **1b** with catalyst **7b** using differentiated exponential fits for same and different excess experiments.

Red			**Blue**			**Grey**		
Time (s)	[1b] (M)	rate (M/s)	Time (s)	[1b] (M)	rate (M/s)	Time (s)	[1b] (M)	rate (M/s)
0	0.09415391	1.5085E-05	0	0.04210802	7.7961E-06	0	0.08767717	1.4142E-05
195	0.09139376	1.462E-05	204	0.04131354	7.5125E-06	178	0.08583576	1.3739E-05
305	0.09012227	1.4364E-05	276	0.0408514	7.4149E-06	274	0.08458595	1.3527E-05
415	0.0879139	1.4113E-05	348	0.040412	7.3186E-06	370	0.08288591	1.3318E-05
525	0.08693511	1.3866E-05	420	0.03964442	7.2235E-06	466	0.08212147	1.3112E-05
635	0.08523127	1.3623E-05	492	0.03916763	7.1296E-06	562	0.08069982	1.2909E-05
745	0.08354983	1.3385E-05	564	0.03873277	7.037E-06	658	0.07930324	1.271E-05
855	0.08226607	1.315E-05	636	0.03815433	6.9456E-06	754	0.07810846	1.2513E-05
965	0.081254	1.292E-05	708	0.03775596	6.8553E-06	850	0.07647719	1.232E-05
1075	0.07999323	1.2694E-05	780	0.03720157	6.7663E-06	946	0.07547676	1.2129E-05
1185	0.07804206	1.2472E-05	852	0.0368093	6.6783E-06	1042	0.07411822	1.1942E-05
1295	0.07615363	1.2254E-05	924	0.03616138	6.5916E-06	1138	0.07319167	1.1757E-05
1405	0.07542339	1.2039E-05	996	0.03572475	6.5059E-06	1234	0.07165174	1.1575E-05

1515	0.07391039	1.1828E-05	1068	0.03529752	6.4214E-06	1330	0.07101331	1.1396E-05
1625	0.07225333	1.1621E-05	1140	0.03507455	6.338E-06	1426	0.06994665	1.122E-05
1735	0.07099064	1.1418E-05	1212	0.03441107	6.2556E-06	1522	0.06828565	1.1047E-05
1845	0.06954994	1.1218E-05	1284	0.03394573	6.1743E-06	1618	0.06691865	1.0876E-05
1955	0.06917613	1.1022E-05	1356	0.03348552	6.0941E-06	1714	0.06615265	1.0708E-05
2065	0.06727846	1.0829E-05	1428	0.03313524	6.0149E-06	1810	0.06515635	1.0542E-05
2175	0.06690348	1.0639E-05	1500	0.03272804	5.9368E-06	1906	0.06396705	1.0379E-05
2285	0.06506439	1.0453E-05	1572	0.03221794	5.8597E-06	2002	0.06331029	1.0219E-05
2395	0.06368217	1.027E-05	1644	0.03190201	5.7835E-06	2098	0.06186305	1.0061E-05
2505	0.06283945	1.009E-05	1716	0.03143342	5.7084E-06	2194	0.06143245	9.9054E-06
2615	0.0617299	9.9138E-06	1788	0.03104759	5.6342E-06	2290	0.06024119	9.7523E-06
2725	0.06051791	9.7402E-06	1860	0.03064501	5.561E-06	2386	0.05919035	9.6015E-06
2835	0.05982978	9.5697E-06	1932	0.03026277	5.4887E-06	2482	0.0583954	9.4531E-06
2945	0.05862272	9.4022E-06	2004	0.02989587	5.4174E-06	2578	0.0572176	9.307E-06
3055	0.05732525	9.2377E-06	2076	0.02938609	5.347E-06	2674	0.05635598	9.1631E-06
3165	0.0565858	9.076E-06	2148	0.02893727	5.2776E-06	2770	0.0555627	9.0214E-06
3275	0.05587157	8.9171E-06	2220	0.02875656	5.209E-06	2866	0.05462924	8.882E-06
3385	0.05483534	8.761E-06	2292	0.02842344	5.1413E-06	2962	0.0536337	8.7447E-06
3495	0.05318558	8.6077E-06	2364	0.02796885	5.0745E-06	3058	0.0528144	8.6095E-06
3605	0.05240671	8.457E-06	2436	0.02754673	5.0086E-06	3154	0.05201667	8.4764E-06
3715	0.05161076	8.309E-06	2508	0.02724228	4.9435E-06	3250	0.05126537	8.3454E-06
3825	0.05091351	8.1636E-06	2580	0.02690072	4.8793E-06	3346	0.05036093	8.2164E-06
3935	0.04999325	8.0207E-06	2652	0.02656475	4.8159E-06	3442	0.04976876	8.0893E-06
4045	0.04893656	7.8803E-06	2724	0.02618033	4.7533E-06	3538	0.04883526	7.9643E-06
4155	0.04819577	7.7423E-06	2796	0.02589687	4.6916E-06	3634	0.04836497	7.8412E-06
4265	0.04691722	7.6068E-06	2868	0.02558316	4.6306E-06	3730	0.04749146	7.72E-06
4375	0.04663768	7.4737E-06	2940	0.02513522	4.5704E-06	3826	0.04637521	7.6006E-06
4485	0.04534897	7.3429E-06	3012	0.0249031	4.511E-06	3922	0.04580807	7.4831E-06
4595	0.04507267	7.2143E-06	3084	0.02454881	4.4524E-06	4018	0.0451254	7.3674E-06
4705	0.04408244	7.0881E-06	3156	0.02418896	4.3946E-06	4114	0.04426474	7.2536E-06
4815	0.04298298	6.964E-06	3228	0.02383296	4.3375E-06	4210	0.04398219	7.1414E-06
4925	0.04239247	6.8421E-06	3300	0.02353194	4.2811E-06	4306	0.04332585	7.031E-06
5035	0.04146148	6.7223E-06	3372	0.02327645	4.2255E-06	4402	0.04253402	6.9223E-06
5145	0.04118008	6.6047E-06	3444	0.023021	4.1706E-06	4498	0.04180402	6.8153E-06
5255	0.04033515	6.4891E-06	3516	0.02271243	4.1164E-06	4594	0.04120496	6.71E-06
5365	0.03941679	6.3755E-06	3588	0.02238618	4.0629E-06	4690	0.04051869	6.6062E-06
5475	0.03895271	6.2639E-06	3660	0.02214822	4.0101E-06	4786	0.03993237	6.5041E-06
5585	0.03804034	6.1543E-06	3732	0.02180571	3.958E-06	4882	0.03912332	6.4036E-06
5695	0.03741533	6.0465E-06	3804	0.02144567	3.9066E-06	4978	0.03865928	6.3046E-06
5805	0.03691029	5.9407E-06	3876	0.02117702	3.8559E-06	5074	0.03803867	6.2071E-06
5915	0.03619176	5.8367E-06	3948	0.02090275	3.8058E-06	5170	0.03744461	6.1112E-06
6025	0.03562462	5.7346E-06	4020	0.02064454	3.7563E-06	5266	0.03676695	6.0167E-06

6135	0.03507563	5.6342E-06	4092	0.02038377	3.7075E-06	5362	0.036437	5.9237E-06
6245	0.03452231	5.5356E-06	4164	0.02015333	3.6593E-06	5458	0.03568023	5.8321E-06
6355	0.0337955	5.4387E-06	4236	0.01984666	3.6118E-06	5554	0.03509783	5.742E-06
6465	0.03312062	5.3435E-06	4308	0.01966963	3.5649E-06	5650	0.0345194	5.6532E-06
6575	0.03268689	5.25E-06	4380	0.0193841	3.5185E-06	5746	0.03409123	5.5658E-06
6685	0.03199762	5.1581E-06	4452	0.01912438	3.4728E-06	5842	0.03339965	5.4798E-06
6795	0.03147245	5.0678E-06	4524	0.01893331	3.4277E-06	5938	0.03298467	5.3951E-06
6905	0.03090707	4.9791E-06	4596	0.01861402	3.3832E-06	6034	0.03243389	5.3117E-06
7015	0.0306325	4.8919E-06	4668	0.01837794	3.3392E-06	6130	0.03215341	5.2295E-06
7125	0.02985554	4.8063E-06	4740	0.01814371	3.2958E-06	6226	0.03140474	5.1487E-06
7235	0.02932606	4.7222E-06	4812	0.01784768	3.253E-06	6322	0.03118669	5.0691E-06
7345	0.02890666	4.6395E-06	4884	0.01759718	3.2107E-06	6418	0.03072961	4.9907E-06
7455	0.02808159	4.5583E-06	4956	0.01738673	3.169E-06	6514	0.03023497	4.9136E-06
7565	0.02771917	4.4785E-06	5028	0.01724659	3.1278E-06	6610	0.02962242	4.8376E-06
7675	0.02760577	4.4001E-06	5100	0.01701162	3.0872E-06	6706	0.02916739	4.7629E-06
7785	0.02678102	4.3231E-06	5172	0.01681072	3.0471E-06	6802	0.02864467	4.6892E-06
7895	0.02640551	4.2474E-06	5244	0.01642709	3.0075E-06	6898	0.02843917	4.6167E-06
8005	0.02604493	4.1731E-06	5316	0.01629218	2.9684E-06	6994	0.02807104	4.5454E-06
8115	0.02556436	4.1001E-06	5388	0.01605669	2.9299E-06	7090	0.02700849	4.4751E-06
8225	0.02481401	4.0283E-06	5460	0.01592733	2.8918E-06	7186	0.02708294	4.4059E-06
8335	0.02457076	3.9578E-06	5532	0.01567249	2.8542E-06	7282	0.02674147	4.3378E-06
8445	0.02421052	3.8885E-06	5604	0.01548057	2.8171E-06	7378	0.02643192	4.2708E-06
8555	0.02366539	3.8204E-06	5676	0.0153162	2.7805E-06	7474	0.02595719	4.2047E-06
8665	0.02326236	3.7536E-06	5748	0.01514933	2.7444E-06	7570	0.02509292	4.1397E-06
8775	0.02259343	3.6879E-06	5820	0.01509681	2.7087E-06	7666	0.02526008	4.0757E-06
8885	0.02248905	3.6233E-06	5892	0.01473934	2.6735E-06	7762	0.02467605	4.0127E-06
8995	0.02210804	3.5599E-06	5964	0.01453088	2.6388E-06	7858	0.02422657	3.9507E-06
9105	0.02158571	3.4976E-06	6036	0.01432548	2.6045E-06	7954	0.02401669	3.8896E-06
9215	0.02109331	3.4364E-06	6108	0.01420723	2.5707E-06	8050	0.02365114	3.8295E-06
9325	0.02099461	3.3762E-06	6180	0.01394602	2.5373E-06	8146	0.02326022	3.7703E-06
9435	0.02041025	3.3171E-06	6252	0.01376869	2.5043E-06	8242	0.02284198	3.712E-06
9545	0.02021492	3.2591E-06	6324	0.01357771	2.4718E-06	8338	0.02267472	3.6546E-06
9655	0.01983015	3.202E-06	6396	0.01348688	2.4397E-06	8434	0.02238942	3.5981E-06
9765	0.01965542	3.146E-06	6468	0.0132963	2.408E-06	8530	0.02192986	3.5425E-06
9875	0.01930624	3.0909E-06	6540	0.01307979	2.3767E-06	8626	0.02118587	3.4878E-06
9985	0.0187689	3.0368E-06	6612	0.01289793	2.3458E-06	8722	0.02148776	3.4338E-06
10095	0.01872433	2.9837E-06	6684	0.01276855	2.3153E-06	8818	0.02113274	3.3808E-06
10205	0.01826945	2.9314E-06	6756	0.01262979	2.2852E-06	8914	0.02053143	3.3285E-06
10315	0.01802513	2.8801E-06	6828	0.01243491	2.2555E-06	9010	0.02029669	3.277E-06
10425	0.01748131	2.8297E-06	6900	0.01222184	2.2262E-06	9106	0.02025058	3.2264E-06
10535	0.01732422	2.7802E-06	6972	0.01209711	2.1973E-06	9202	0.01966527	3.1765E-06
10645	0.01711357	2.7315E-06	7044	0.01192834	2.1688E-06	9298	0.01954714	3.1274E-06

10755	0.01685301	2.6837E-06	7116	0.01174076	2.1406E-06	9394	0.01915771	3.0791E-06
10865	0.01640045	2.6367E-06	7188	0.01164536	2.1128E-06	9490	0.01895205	3.0315E-06
10975	0.0161784	2.5906E-06	7260	0.01143508	2.0853E-06	9586	0.01835687	2.9846E-06
11085	0.0160666	2.5452E-06	7332	0.01132742	2.0582E-06	9682	0.01822127	2.9385E-06
11195	0.01567501	2.5007E-06	7404	0.01125681	2.0315E-06	9778	0.01817005	2.893E-06
11305	0.01535039	2.4569E-06	7476	0.01106774	2.0051E-06	9874	0.01803626	2.8483E-06
11415	0.01510682	2.4139E-06	7548	0.01082666	1.979E-06	9970	0.01754317	2.8043E-06
11525	0.01472943	2.3717E-06	7620	0.0107573	1.9533E-06	10066	0.0173756	2.7609E-06
11635	0.0145286	2.3301E-06	7692	0.01068514	1.9279E-06	10162	0.01711258	2.7182E-06
11745	0.01417467	2.2894E-06	7764	0.01044584	1.9029E-06	10258	0.01687552	2.6762E-06
11855	0.01400347	2.2493E-06	7836	0.01030163	1.8782E-06	10354	0.01655318	2.6349E-06
11965	0.01384633	2.2099E-06	7908	0.01014946	1.8538E-06	10450	0.01640194	2.5941E-06
12075	0.01359842	2.1712E-06	7980	0.01006751	1.8297E-06	10546	0.01608281	2.554E-06
12185	0.0132967	2.1332E-06	8052	0.00997763	1.8059E-06	10642	0.01607105	2.5145E-06
12295	0.01324099	2.0959E-06	8124	0.00988202	1.7824E-06	10738	0.0157502	2.4757E-06
12405	0.01293551	2.0592E-06	8196	0.00966051	1.7593E-06	10834	0.01532313	2.4374E-06
12515	0.01269546	2.0232E-06	8268	0.00946291	1.7364E-06	10930	0.01527101	2.3997E-06
12625	0.01248756	1.9878E-06	8340	0.00942679	1.7139E-06	11026	0.01511301	2.3626E-06
12735	0.0124077	1.953E-06	8412	0.00928386	1.6916E-06	11122	0.01476242	2.3261E-06
12845	0.01192045	1.9188E-06	8484	0.00921287	1.6696E-06	11218	0.01455023	2.2901E-06
12955	0.01197824	1.8852E-06	8556	0.00910574	1.6479E-06	11314	0.01436593	2.2547E-06
13065	0.01163449	1.8522E-06	8628	0.00895359	1.6265E-06	11410	0.01412822	2.2199E-06
13175	0.01148838	1.8198E-06	8700	0.00874737	1.6054E-06	11506	0.0140362	2.1856E-06
13285	0.01125255	1.7879E-06	8772	0.00873709	1.5845E-06	11602	0.01382394	2.1518E-06
13395	0.01123735	1.7566E-06	8844	0.0085986	1.5639E-06	11698	0.01352234	2.1185E-06
13505	0.01107229	1.7259E-06	8916	0.00853619	1.5436E-06	11794	0.01341376	2.0858E-06
13615	0.01080857	1.6957E-06	8988	0.00838307	1.5236E-06	11890	0.01330207	2.0535E-06
13725	0.01051673	1.666E-06	9060	0.00823744	1.5038E-06	11986	0.01302328	2.0218E-06
13835	0.01031202	1.6368E-06	9132	0.00815492	1.4842E-06	12082	0.01283747	1.9905E-06
13945	0.01016257	1.6082E-06	9204	0.00807143	1.4649E-06	12178	0.01278151	1.9598E-06
14055	0.01005201	1.58E-06	9276	0.00799075	1.4459E-06	12274	0.01256611	1.9295E-06
14165	0.00979688	1.5524E-06	9348	0.00787488	1.4271E-06	12370	0.01237149	1.8996E-06
14275	0.00967317	1.5252E-06	9420	0.00780699	1.4086E-06	12466	0.0122478	1.8703E-06
14385	0.00943944	1.4985E-06	9492	0.00757452	1.3903E-06	12562	0.01203571	1.8414E-06
14495	0.0093159	1.4723E-06	9564	0.00753959	1.3722E-06	12658	0.01184698	1.8129E-06
14605	0.00929576	1.4465E-06	9636	0.00742971	1.3544E-06	12754	0.01173514	1.7849E-06
14715	0.00904769	1.4212E-06	9708	0.00734602	1.3368E-06	12850	0.0114668	1.7573E-06
14825	0.00892488	1.3963E-06	9780	0.00725522	1.3194E-06	12946	0.01138162	1.7301E-06
14935	0.00880381	1.3719E-06	9852	0.00714602	1.3023E-06	13042	0.01129391	1.7034E-06
15045	0.00866161	1.3479E-06	9924	0.00705136	1.2854E-06	13138	0.01121509	1.677E-06
15155	0.00858018	1.3243E-06	9996	0.00699156	1.2687E-06	13234	0.01094386	1.6511E-06
15265	0.00834106	1.3011E-06	10068	0.00689693	1.2522E-06	13330	0.01085443	1.6256E-06

15375	0.00819412	1.2783E-06	10140	0.00680307	1.2359E-06	13426	0.01069589	1.6004E-06
15485	0.00811173	1.2559E-06	10212	0.00677861	1.2198E-06	13522	0.01054991	1.5757E-06
15595	0.00781261	1.234E-06	10284	0.00669625	1.204E-06	13618	0.01041327	1.5514E-06
15705	0.00780446	1.2124E-06	10356	0.00655807	1.1884E-06	13714	0.01026298	1.5274E-06
15815	0.00774311	1.1911E-06	10428	0.00650409	1.1729E-06	13810	0.01015755	1.5038E-06
15925	0.00760936	1.1703E-06	10500	0.00633556	1.1577E-06	13906	0.01010122	1.4805E-06
16035	0.00753223	1.1498E-06	10572	0.00631243	1.1426E-06	14002	0.00991543	1.4576E-06
16145	0.00724486	1.1297E-06	10644	0.00628731	1.1278E-06	14098	0.00980836	1.4351E-06
16255	0.00719087	1.1099E-06	10716	0.00612758	1.1131E-06	14194	0.00964511	1.4129E-06
16365	0.00727972	1.0905E-06	10788	0.00603118	1.0987E-06	14290	0.00952332	1.3911E-06
16475	0.00691681	1.0714E-06	10860	0.00591613	1.0844E-06	14386	0.00945028	1.3696E-06
16585	0.00678051	1.0526E-06	10932	0.00593787	1.0703E-06	14482	0.00930143	1.3484E-06
16695	0.00672161	1.0342E-06						
16805	0.00656727	1.0161E-06						
16915	0.0064664	9.9833E-07						
17025	0.00633183	9.8085E-07						
17135	0.00625587	9.6368E-07						
17245	0.00624239	9.4682E-07						
17355	0.00607539	9.3024E-07						
17465	0.0060288	9.1396E-07						
17575	0.00593392	8.9796E-07						
17685	0.00579043	8.8225E-07						
17795	0.00577409	8.668E-07						
17905	0.00564857	8.5163E-07						
18015	0.00563546	8.3673E-07						
18125	0.00538907	8.2208E-07						
18235	0.00538119	8.0769E-07						
18345	0.00517893	7.9355E-07						
18455	0.00518702	7.7966E-07						
18565	0.00503583	7.6602E-07						
18675	0.0050546	7.5261E-07						
18785	0.0047302	7.3944E-07						
18895	0.00469701	7.2649E-07						
19005	0.00481653	7.1378E-07						
19115	0.00472644	7.0128E-07						
19225	0.00469	6.8901E-07						
19335	0.00455782	6.7695E-07						
19445	0.00440883	6.651E-07						
19555	0.0043486	6.5346E-07						
19665	0.00449484	6.4202E-07						
19775	0.0042381	6.3078E-07						
19885	0.00440942	6.1974E-07						

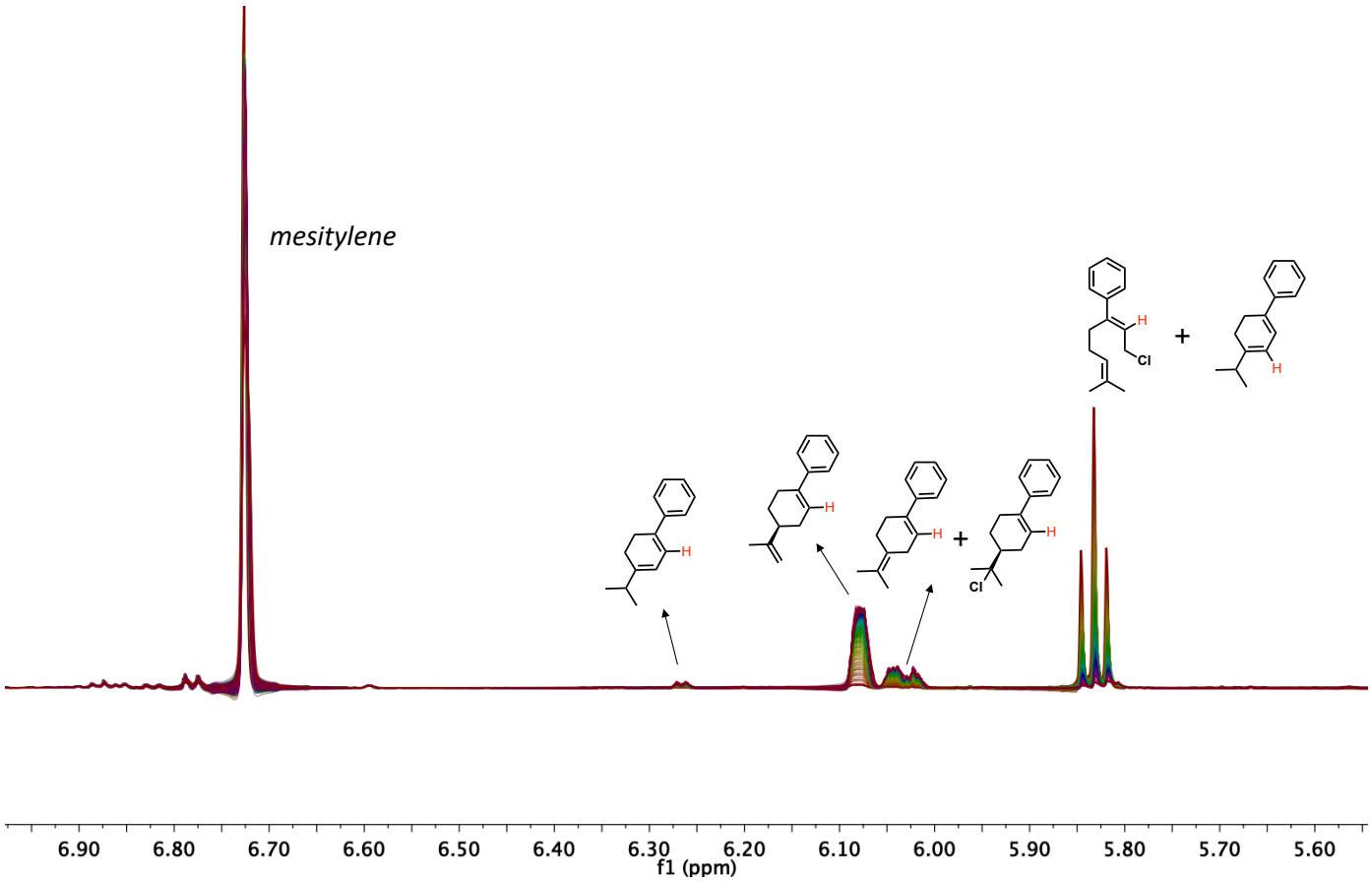
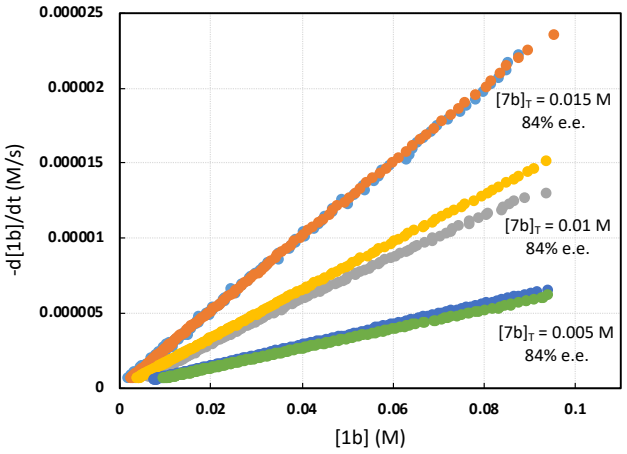
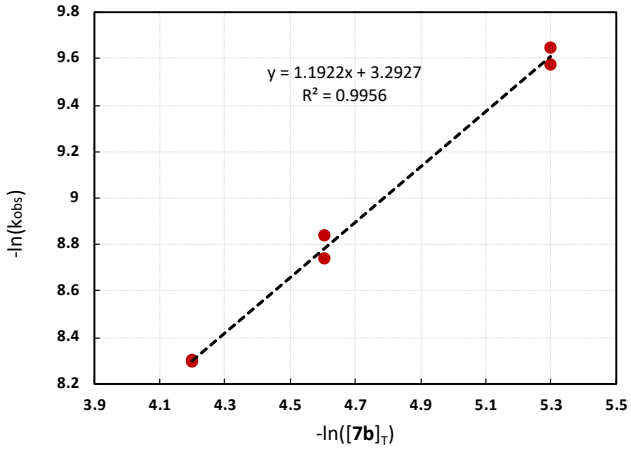


Figure S20. Representative ^{1}H NMR traces for cyclization of **1b** catalyzed by **7b.**

Determination of order in catalyst

The rate of cyclization of substrate **1b** catalyzed by **7b** was assessed at various concentrations of **7b** ([**7b**]$_T$ = 5 mM, 10 mM, and 15 mM respectively) with 1.15 eq. TMS-diazomethane as the base. Data acquisition and analysis was the same as described for same and different excess experiments (see above). All kinetics runs were conducted in duplicate. First order observed rate constants (k_{obs}) were extracted from the slopes of rate vs concentration plots following least-squares fitting. The negative natural logarithms of these values were plotted against the negative natural logarithms of total catalyst concentration, and from this, catalyst order was determined by linear least-squares fitting of the data. The slope of this linear fit was used to determine the apparent order in [**7b**] = 1.19 ± 0.04. For these experiments, [**1b**]$_0$ = 0.1 M, [TMS-diazomethane] = 0.115 M, and [**7b**]$_T$ = 0.005-0.015 M.





color	k_{obs} (1/s)	-ln([7b]$_T$)	-ln(k_{obs})
●	2.48E-04	4.200	8.302
●	2.50E-04	4.200	8.294
●	1.46E-04	4.605	8.834
●	1.61E-04	4.605	8.736
●	6.47E-05	5.298	9.646
●	6.98E-05	5.298	9.570

Linear Fit	Slope	Standard Error	Intercept	Standard Error
	1.1921670	0.0397365	3.2926932	0.187671

Figure S21. Reaction profiles for the cyclization of substrate **1b** with various loadings of catalyst **7b** (left). Determination of observed order (right).

9.3 Correlation of catalyst arene properties with reaction rate and enantioselectivity

Reaction rate and enantioselectivity of the cyclization reaction of **1b** were seen to be correlated for a series of four hydrogen bond donor catalysts bearing different aryl substituents (catalysts **7a-7d**). By plotting the negative natural logarithm of the rate constant corresponding to each of the enantiomeric pathways (k_{maj} and k_{min}) against the natural logarithm of the enantiomeric ratio (e.r.), good linear correlations were observed for both pathways indicating that both are stabilized by the presence of the catalyst. The slope of the least squares linear fit for the major pathway is larger than that of the minor pathway, indicating that it is stabilized to a greater extent.

The observed rate constants for each reaction were determined through reaction progress kinetic analysis as described previously in section 9.2. Reactions were conducted with the following concentrations: [**1b**]$_0$ = 0.1 M, [TMS-diazomethane] = 0.115 M, and [**7a-d**]$_T$ = 0.01 M using a 6:1 (v/v) blend of C_6D_{12} and CD_2Cl_2.

Substrate **1b** does not undergo a measurable background cyclization reaction; therefore, the observed rate constant (k_{obs}) in the presence of chiral hydrogen bond donor catalyst is a sum of the rate constants corresponding to the major and minor enantiomeric pathways:

$$k_{obs} = k_{maj} + k_{min}$$

Using the Eyring equation (in which the transmission coefficient is assumed to be unity, K_B is the Boltzmann constant, R is the gas constant, h is Planck's constant, and T is temperature), the expression becomes:

$$k = \left(\frac{K_B T}{h}\right)\left(e^{\frac{-\Delta G^{\ddagger}}{RT}}\right) \text{ (Eyring equation)}$$

$$k_{obs} = \left(\frac{K_B T}{h}\right)\left(e^{\frac{-\Delta G^{\ddagger}_{maj}}{RT}} + e^{\frac{-\Delta G^{\ddagger}_{min}}{RT}}\right)$$

$$\text{let } \left(\frac{K_B T}{h}\right) = a$$

$$k_{obs} = a\left(e^{\frac{-\Delta G^{\ddagger}_{maj}}{RT}} + e^{\frac{-\Delta G^{\ddagger}_{min}}{RT}}\right)$$

$\Delta\Delta G^{\ddagger}$ can be related to *e.r.* (expressed as a ratio of major to minor enantiomeric products) from the following expression where *R* is the gas constant and *T* is temperature:

$$\Delta\Delta G^{\ddagger} = -RTln(e.r.)$$

$$-\Delta G^{\ddagger}_{maj} = RTln(e.r.) - \Delta G^{\ddagger}_{min}$$

Hence, k_{obs} and $\Delta G^{\ddagger}_{min}$ can be related to the *e.r.* of the reaction:

$$k_{obs} = a\left(e^{\frac{RTln(e.r.) - \Delta G^{\ddagger}_{min}}{RT}} + e^{\frac{-\Delta G^{\ddagger}_{min}}{RT}}\right)$$

$$\left({}^{k_{obs}}/_{a}\right) - e^{\frac{-\Delta G^{\ddagger}_{min}}{RT}} = e^{\frac{RTln(e.r.) - \Delta G^{\ddagger}_{min}}{RT}} = \frac{e^{\ln(e.r.)}}{e^{\frac{\Delta G^{\ddagger}_{min}}{RT}}}$$

$$e^{\frac{\Delta G^{\ddagger}_{min}}{RT}}\left({}^{k_{obs}}/_{a}\right) - 1 = e.r.$$

$$\Delta G^{\ddagger}_{min} = RTln\left[(e.r.+1)\left({}^{a}/_{k_{obs}}\right)\right]$$

Using a similar mathematical approach, $\Delta G^{\ddagger}_{maj}$ can also be related to *e.r.* through the following expression:

$$\Delta G^{\ddagger}_{maj} = RTln\left[\left(\frac{1}{e.r.} + 1\right)\left({}^{a}/_{k_{obs}}\right)\right]$$

These expressions for $\Delta G^{\ddagger}_{maj}$ and $\Delta G^{\ddagger}_{min}$ were used to derive rate constants k_{maj} and k_{min} corresponding to each enantiomeric pathway using the Eyring equation (with R = 1.987E-03 kcal/(K*mol) and T = 298 K) and the observed rate constant k_{obs} measured using the same kinetics techniques described in section 9 . This was performed either in duplicate or triplicate for each of the four hydrogen bond donor catalysts surveyed. The results of this analysis for catalysts **7a-7d** are shown below. The plot in Figure 5 was generated using the average values for ln(k_{maj}) and ln(k_{min}). Note: under these conditions, e.e. values are slightly lower than those reported in section 5.2 due to the presence of CD_2Cl_2 in a 1:6 (v/v) ratio with C_6D_{12} (see section 9.2).

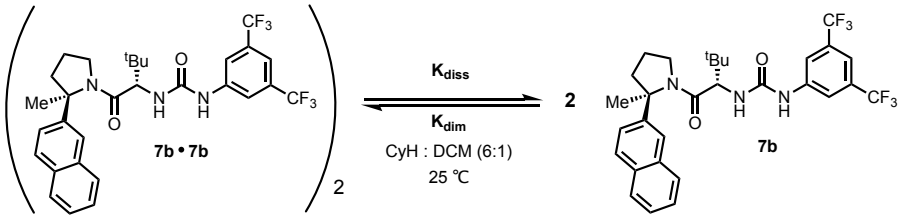
Catalyst	Run	k_{obs} (1/s)	k_{maj} (1/s)	k_{min} (1/s)	ln(k_{maj})	ln(k_{min})
2Phen (7a)	1	3.020E-04	2.794E-04	2.265E-05	-8.183045082	-10.69535071
	2	2.330E-04	2.155E-04	1.748E-05	-8.442433646	-10.95473927
	3	2.780E-04	2.572E-04	2.085E-05	-8.265850986	-10.77815661
2Nap (7b)	1	1.456E-04	1.340E-04	1.165E-05	-8.918029031	-11.36037607
	2	1.607E-04	1.478E-04	1.286E-05	-8.819352894	-11.26169993
3Phen (7c)	1	8.790E-05	7.428E-05	1.362E-05	-9.507729405	-11.20364092
	2	8.416E-05	7.112E-05	1.304E-05	-9.551209461	-11.24712097
	3	8.630E-05	7.292E-05	1.338E-05	-9.526099611	-11.22201112
Phenyl (7d)	1	4.976E-05	3.977E-05	9.942E-06	-10.13244799	-11.51874235
	2	4.971E-05	3.981E-05	9.952E-06	-10.13144266	-11.51773702

Catalyst	ln(e.r.)	Average ln(k_{maj})	Stdev.	Average ln(k_{min})	Stdev.
2Phen (7a)	2.512305624	-8.297109905	0.13248942	-10.80941553	0.132489421
2Nap (7b)	2.442347035	-8.868690963	0.06977457	-11.311038	0.069774566
3Phen (7c)	1.69591151	-9.528346159	0.02182691	-11.22425767	0.021826911
Phenyl (7d)	1.386294361	-10.13194533	0.00071087	-11.51823969	0.000710874

10. Isothermal Titration Calorimetry

A Nano ITC instrument (TA instruments) with a standard volume cell (1.0 mL) was used to collect all data at room temperature. Experiments were performed by charging both the sample and reference cells of the instrument with 1.0 mL of a 6:1 (v/v) mixture of cyclohexane and dichloromethane, the same solvent combination used for kinetics experiments (see section 9). Both solvents were distilled prior to use. A 250 µL titration burette was charged with a 10 mM stock solution of catalyst **7b** (the same concentration of catalyst under the catalytic reaction conditions). This concentrated stock solution was diluted in the sample cell over 25 injections of 10 µL each, with 200 second spacing between injections. Stirring was kept constant throughout the course of experiments (200 rpm). The volume for the first injection was kept as small as possible and was not considered in the subsequent data analysis due to errors associated with instrument calibration.

Data processing and analysis was performed using the program Nano Analyze (downloaded from the TA instruments website) and used according to the instructions provided. After integration of both the sample and the blank measurements, the heat release associated with solvent dilution was found to be negligible and was not considered in the analysis. The data was then fit to a dimer dissociation model and from this, thermodynamic parameters (K_{diss} and K_{dim}) could be extracted. This analysis was performed in duplicate for catalyst **7b**. The results are summarized below:



Run	K_{diss} (M)	K_{dim} (1/M)
1	0.002165	461.8
2	0.002472	404.5
Ave.	0.002319	433.1
Stdev.	0.000216	40.3

Figure S22. Measurement of K_{diss} and K_{dim} using ITC.

An average K_{dim} of 433 ± 40 M^{-1} indicates that under catalytic concentrations (total catalyst concentration = 10 mM), catalyst **7b** exists primarily as a resting state dimer (71.3% of catalyst molecules are dimerized).

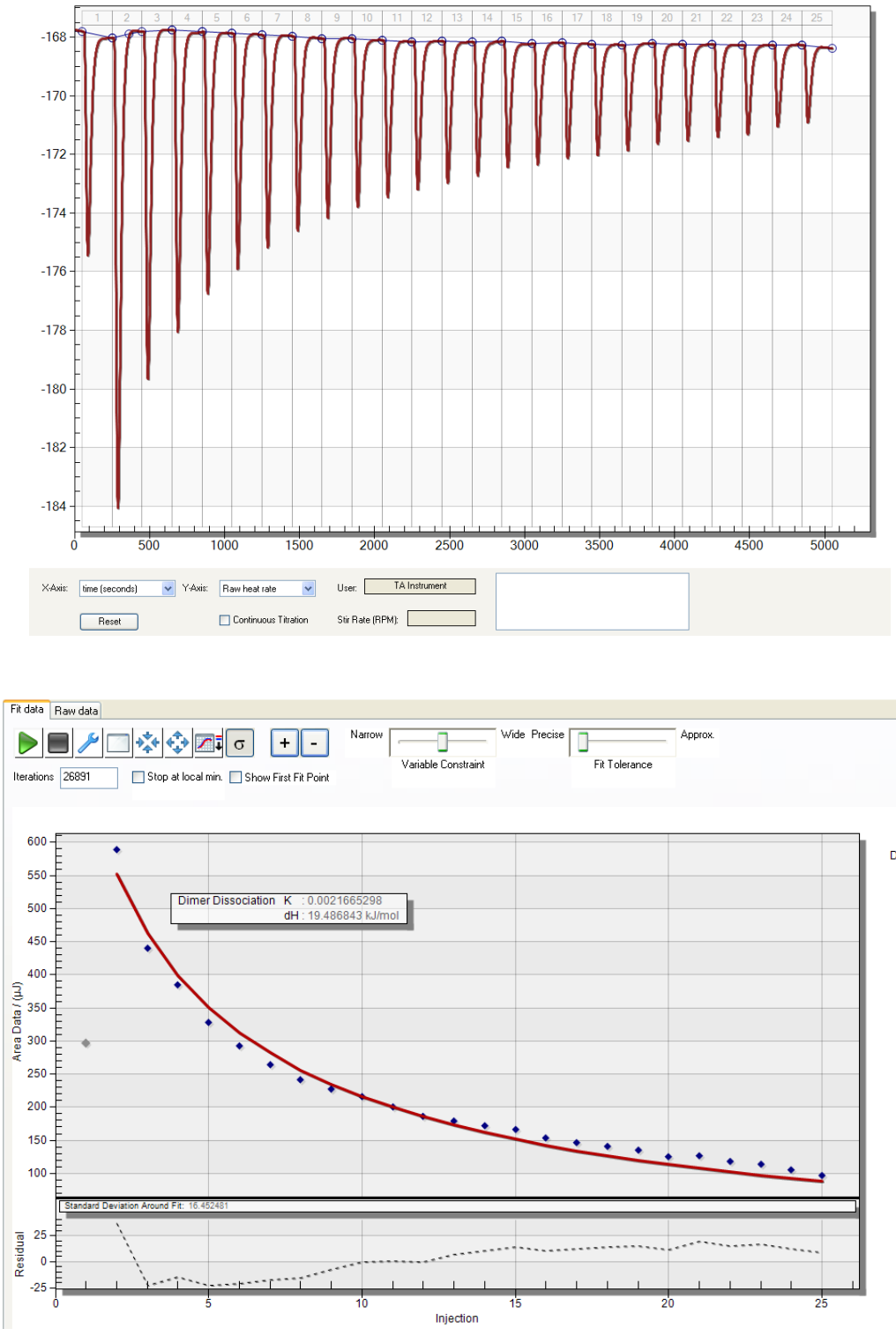


Figure S23. Trial 1: Above: raw heat trace from dilution of 10 mM solution of **7b**. Below: curve fitting of the heat data to determine K_{diss}

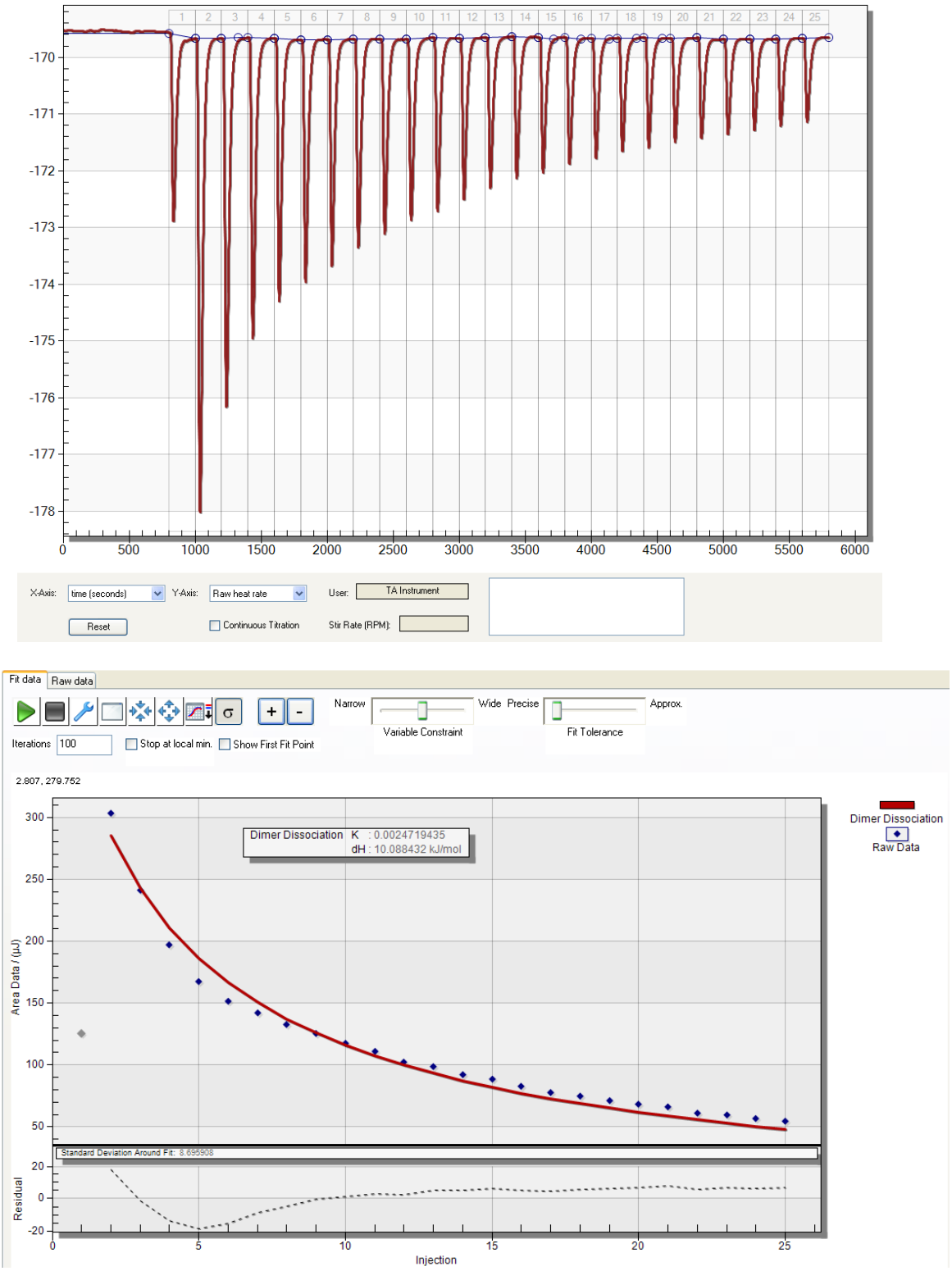
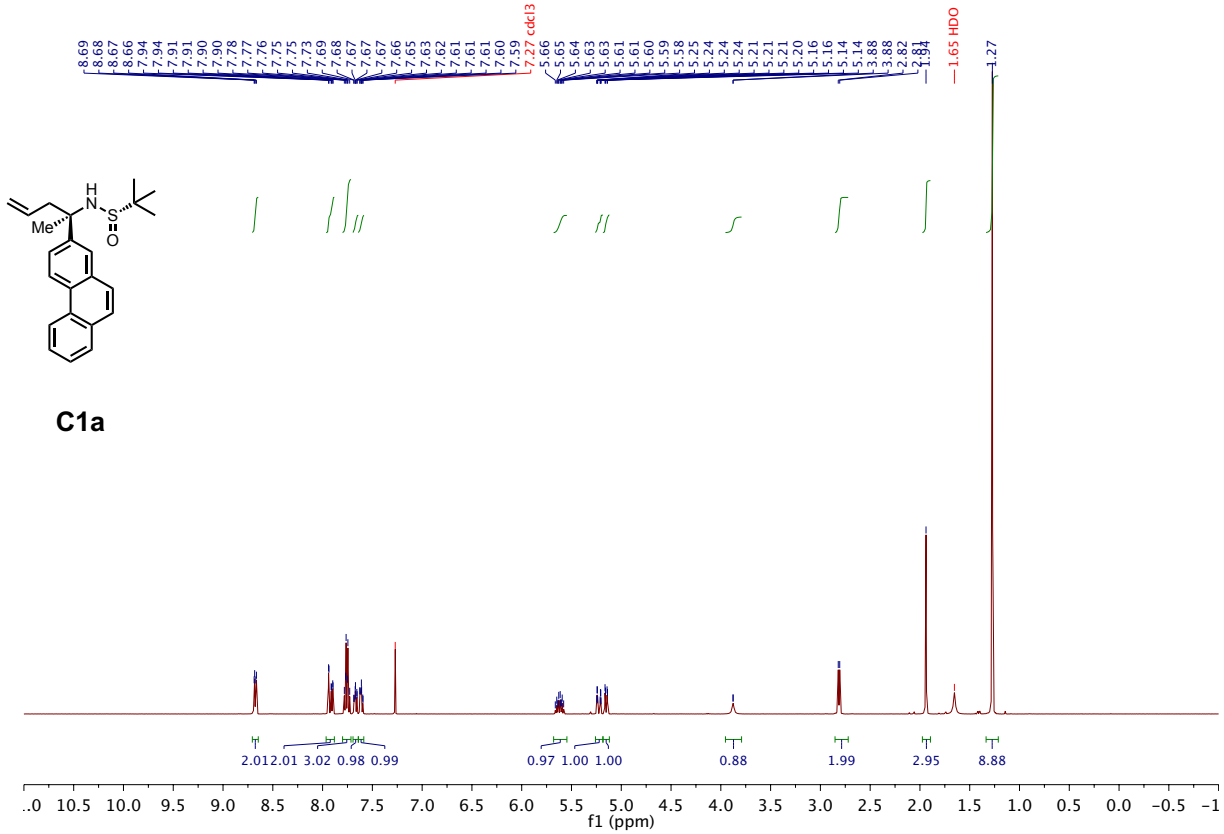


Figure S24. Trial 2: Above: raw heat trace from dilution of 10 mM solution of **7b**. Below: curve fitting of the heat data to determine K_{diss}

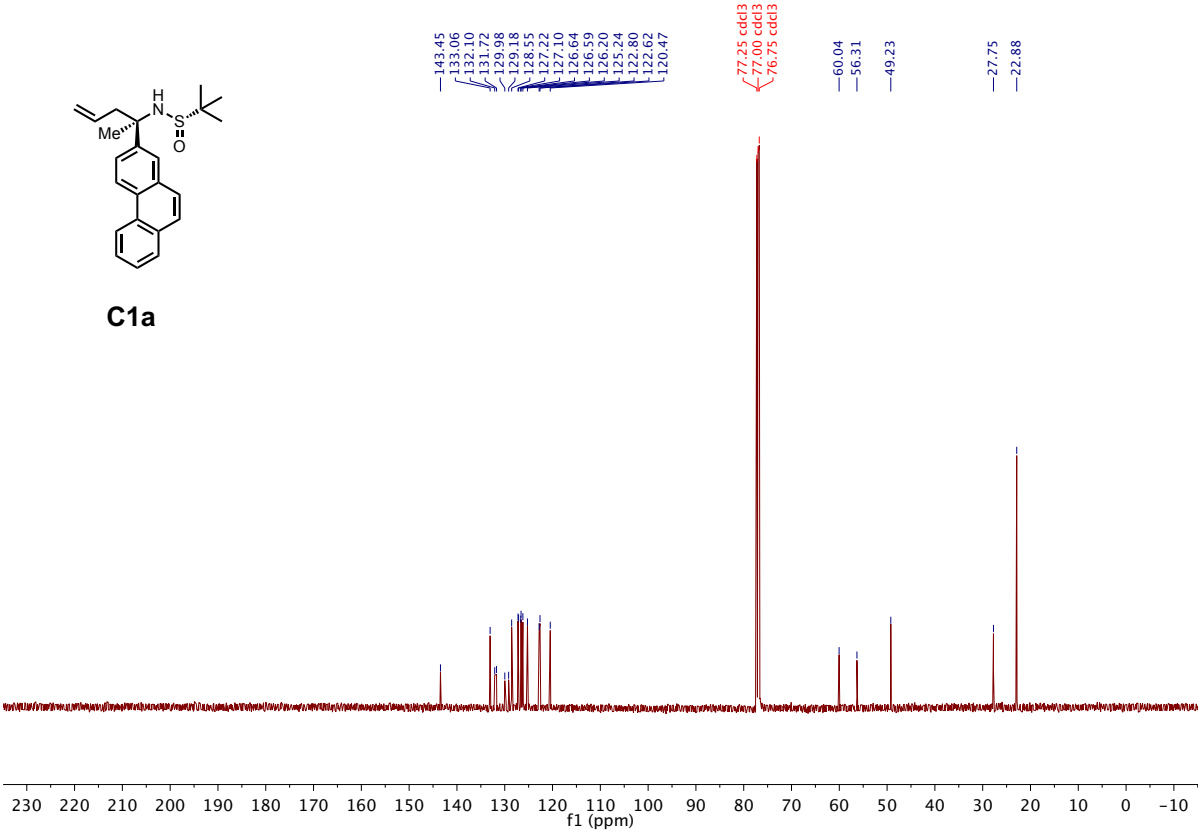
11. ^{1}H, ^{13}C, and ^{19}F NMR Spectra

^{1}H NMR, $CDCl_3$, 500 MHz



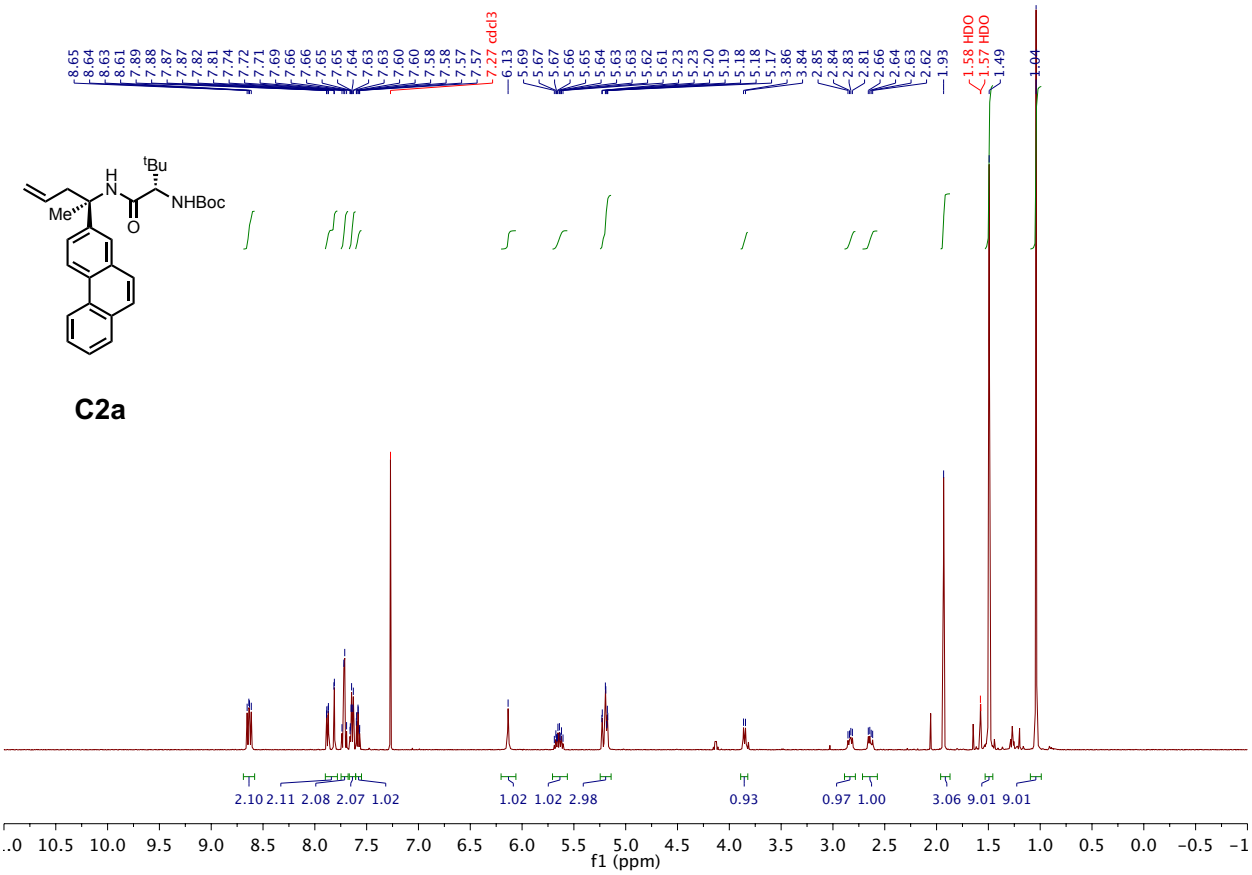
C1a

^{13}C NMR, $CDCl_3$, 126 MHz



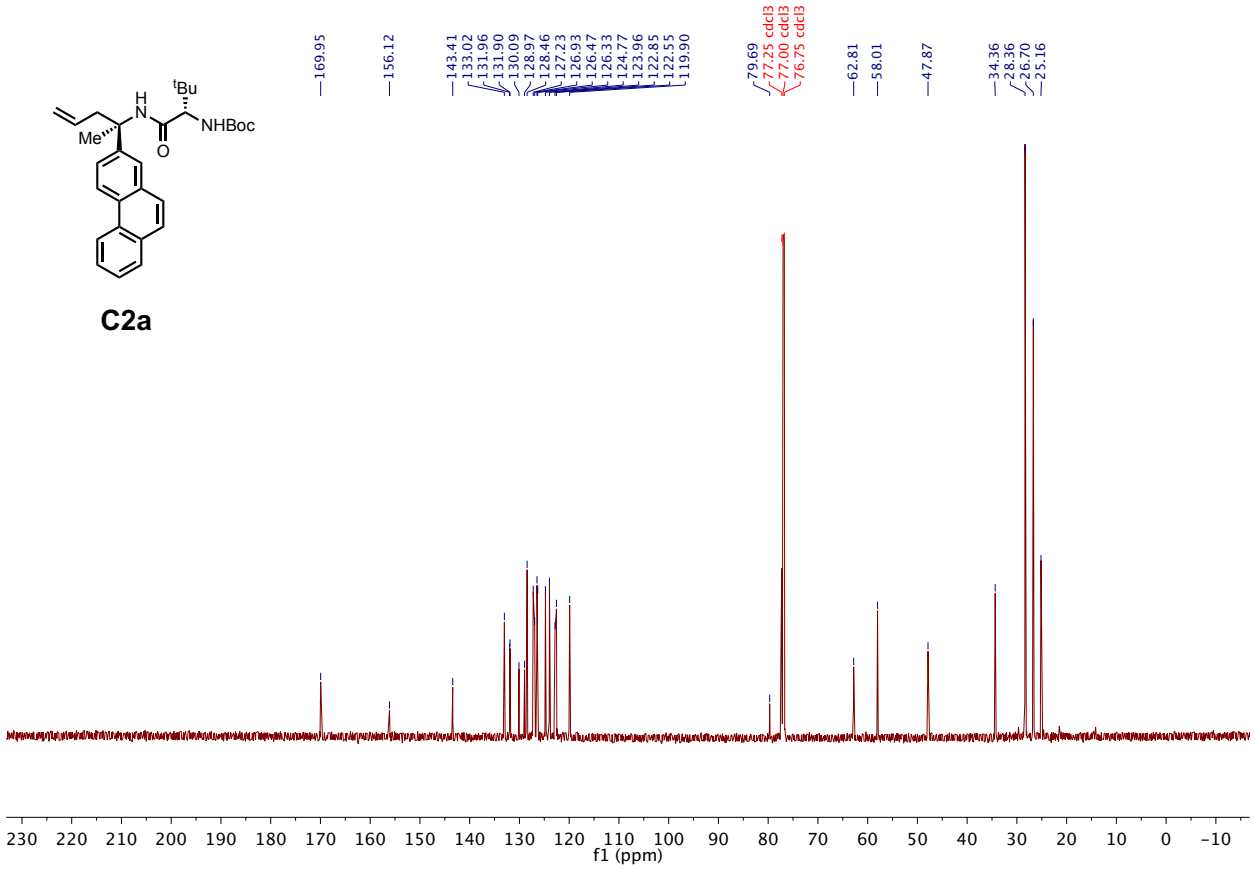
C1a

^{1}H NMR, $CDCl_3$, 500 MHz



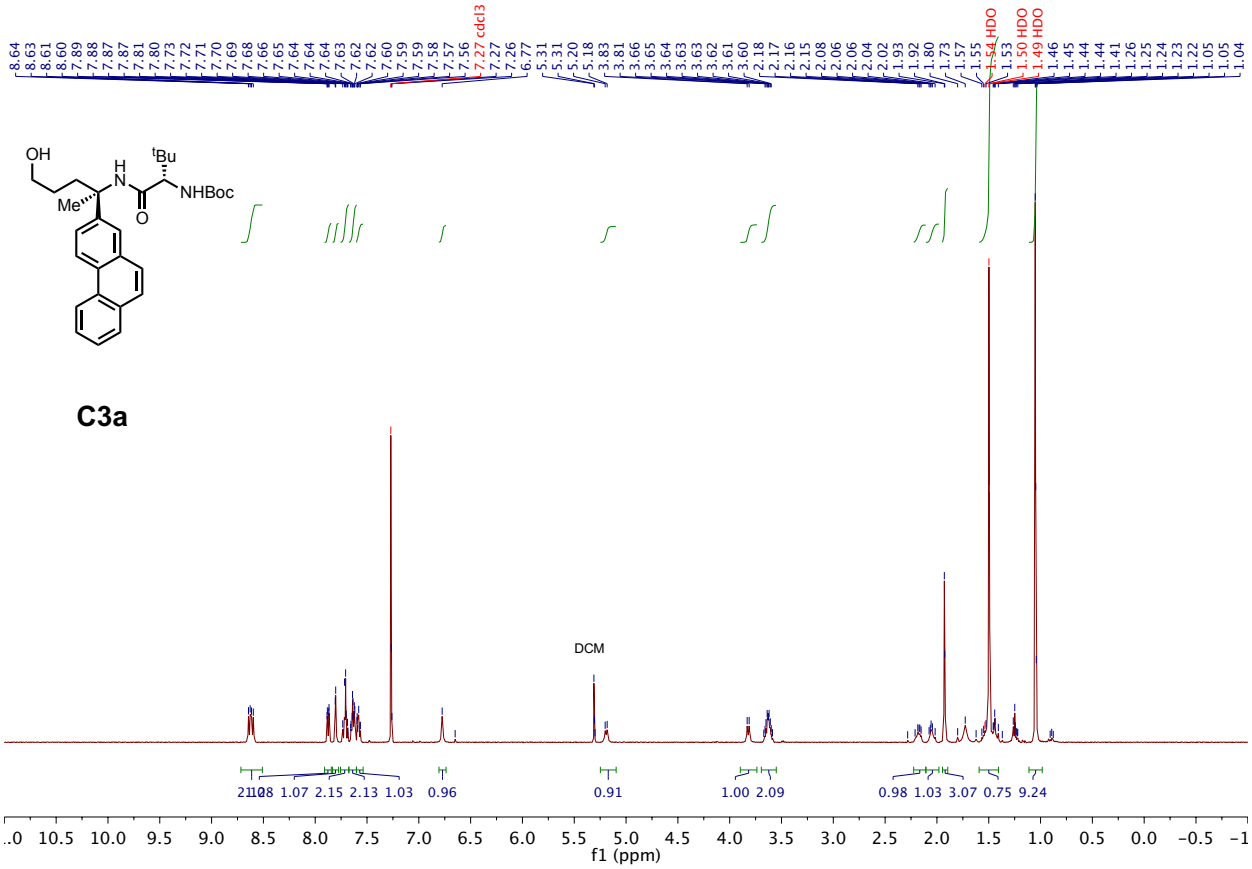
C2a

^{13}C NMR, $CDCl_3$, 126 MHz

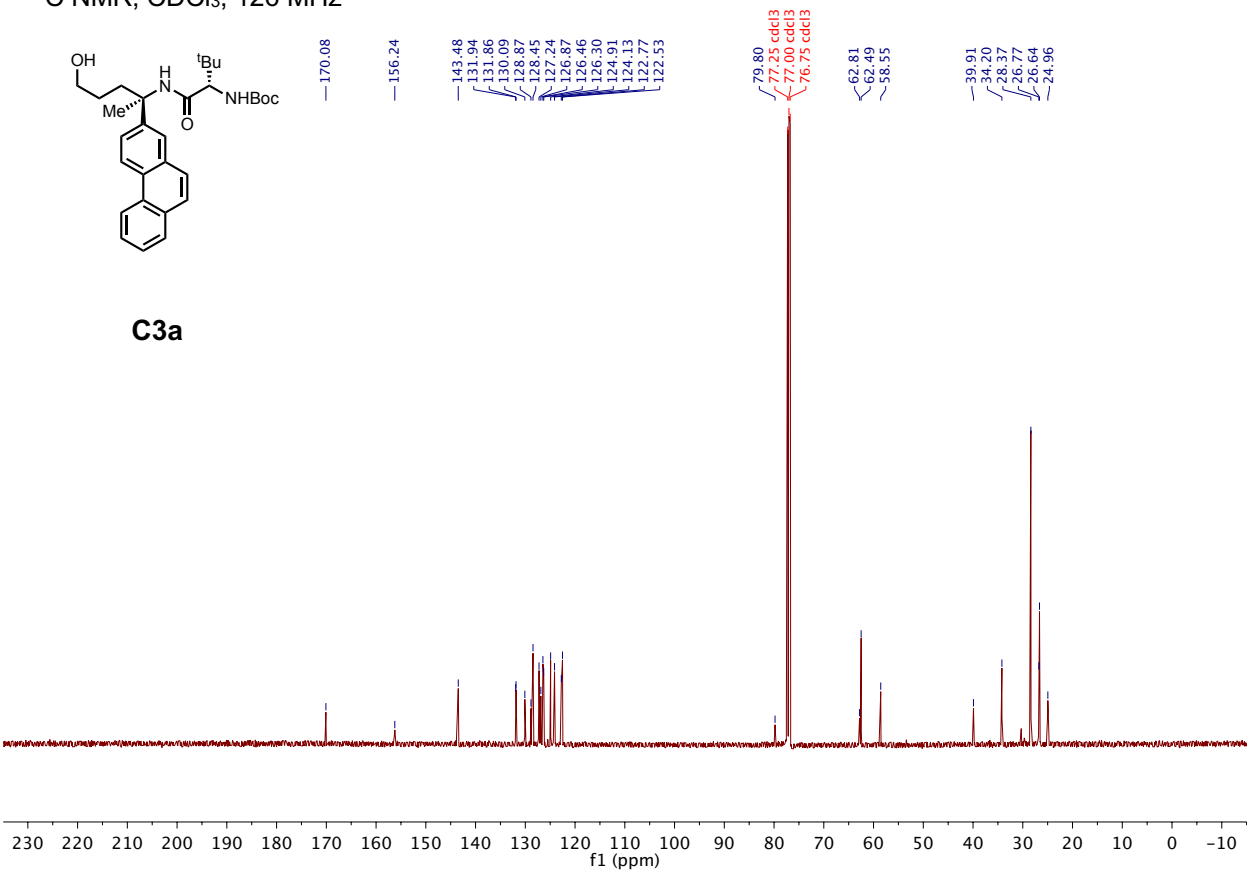


C2a

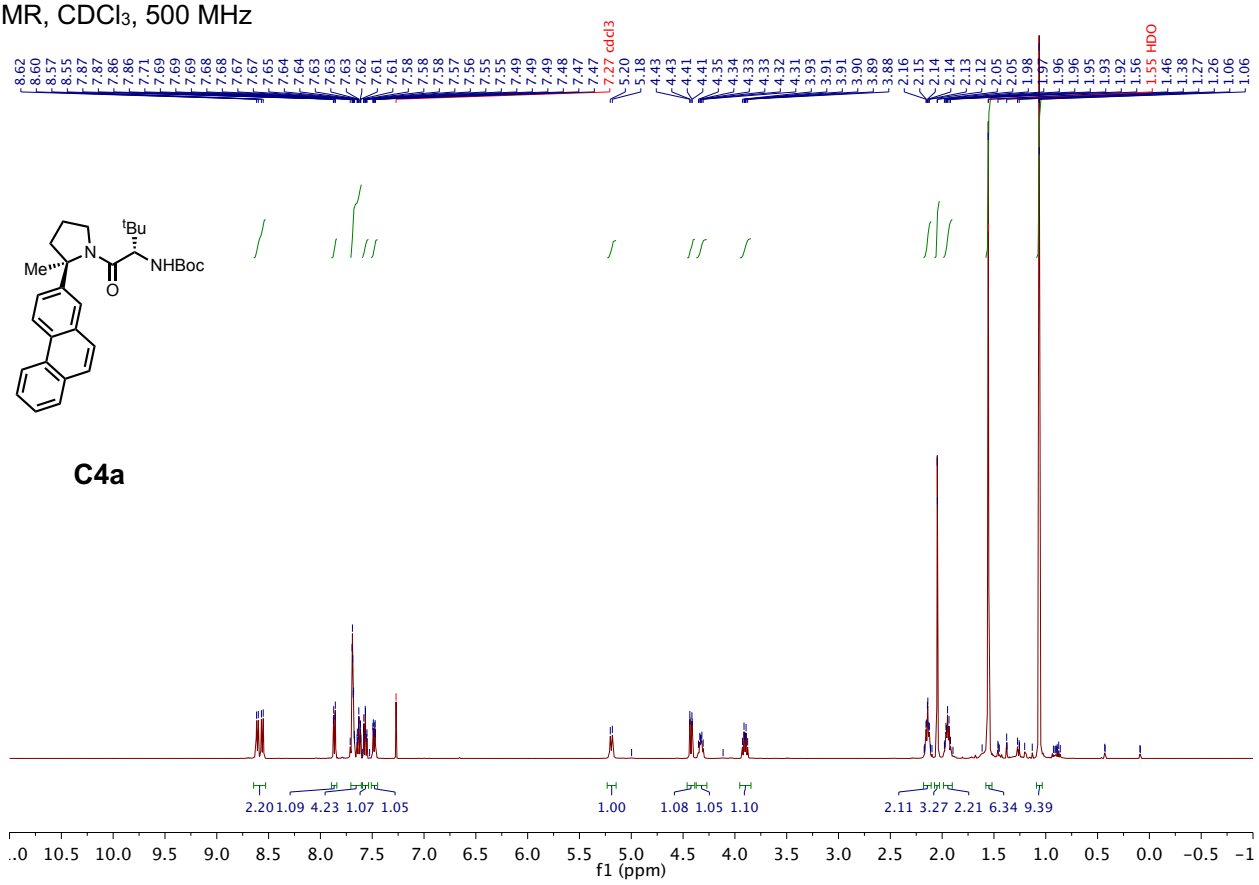
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

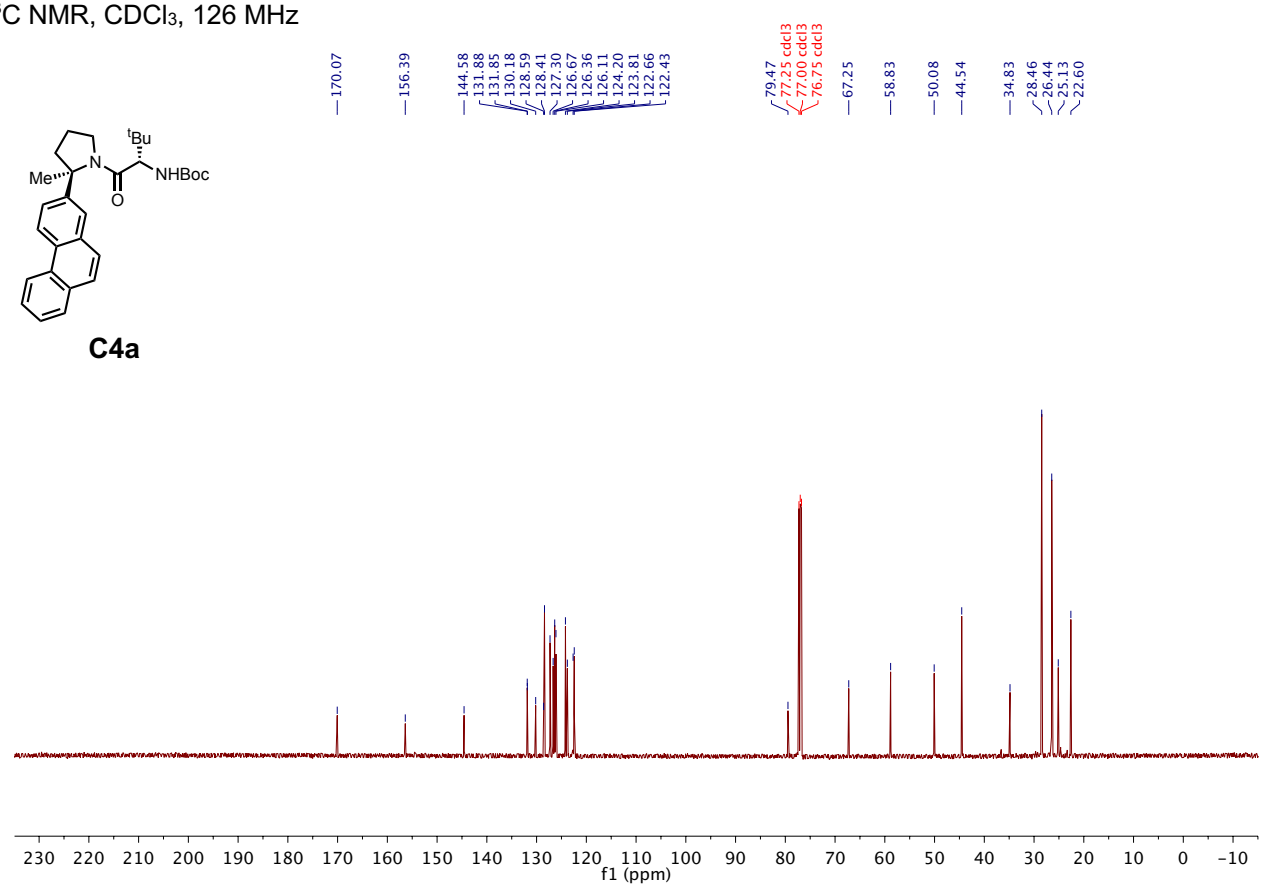


^{1}H NMR, $CDCl_3$, 500 MHz



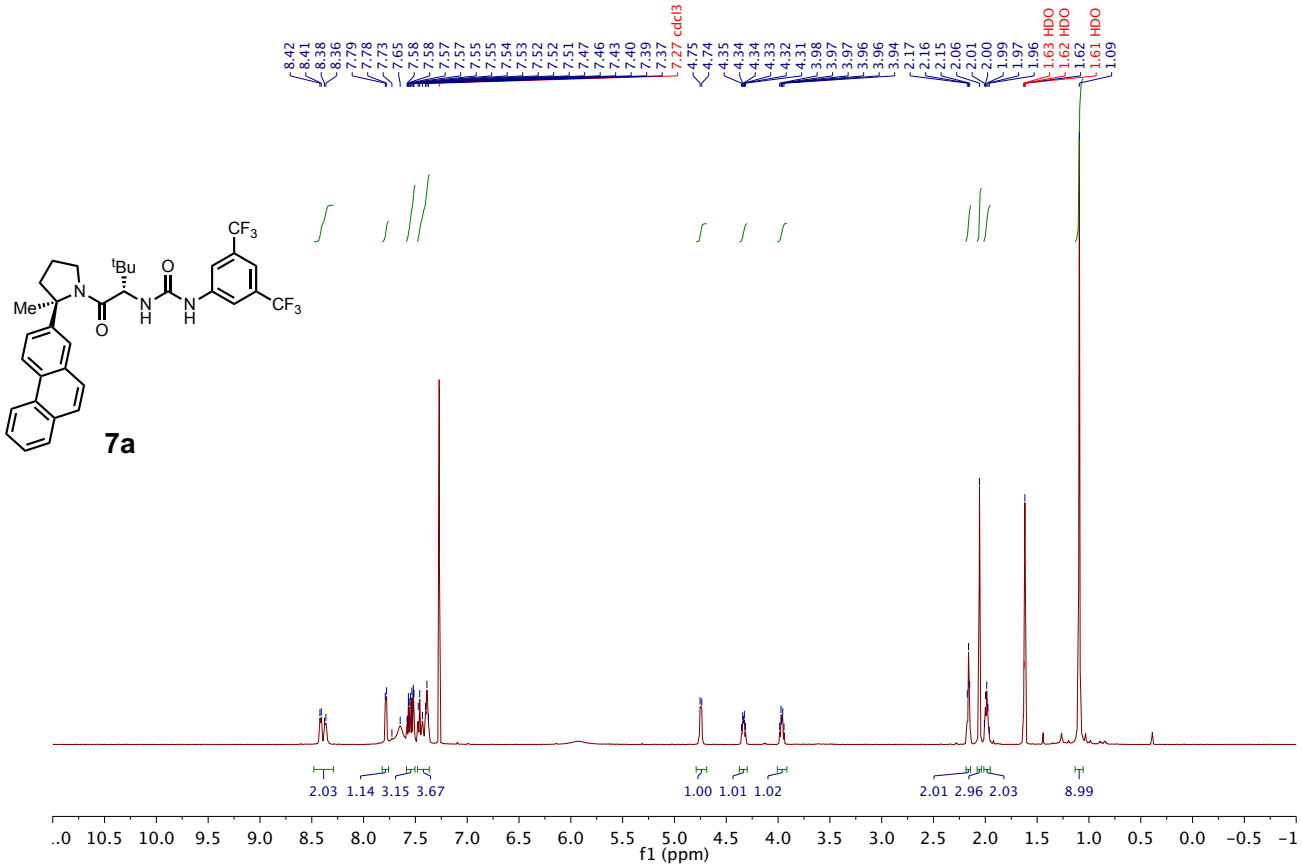
C4a

^{13}C NMR, $CDCl_3$, 126 MHz

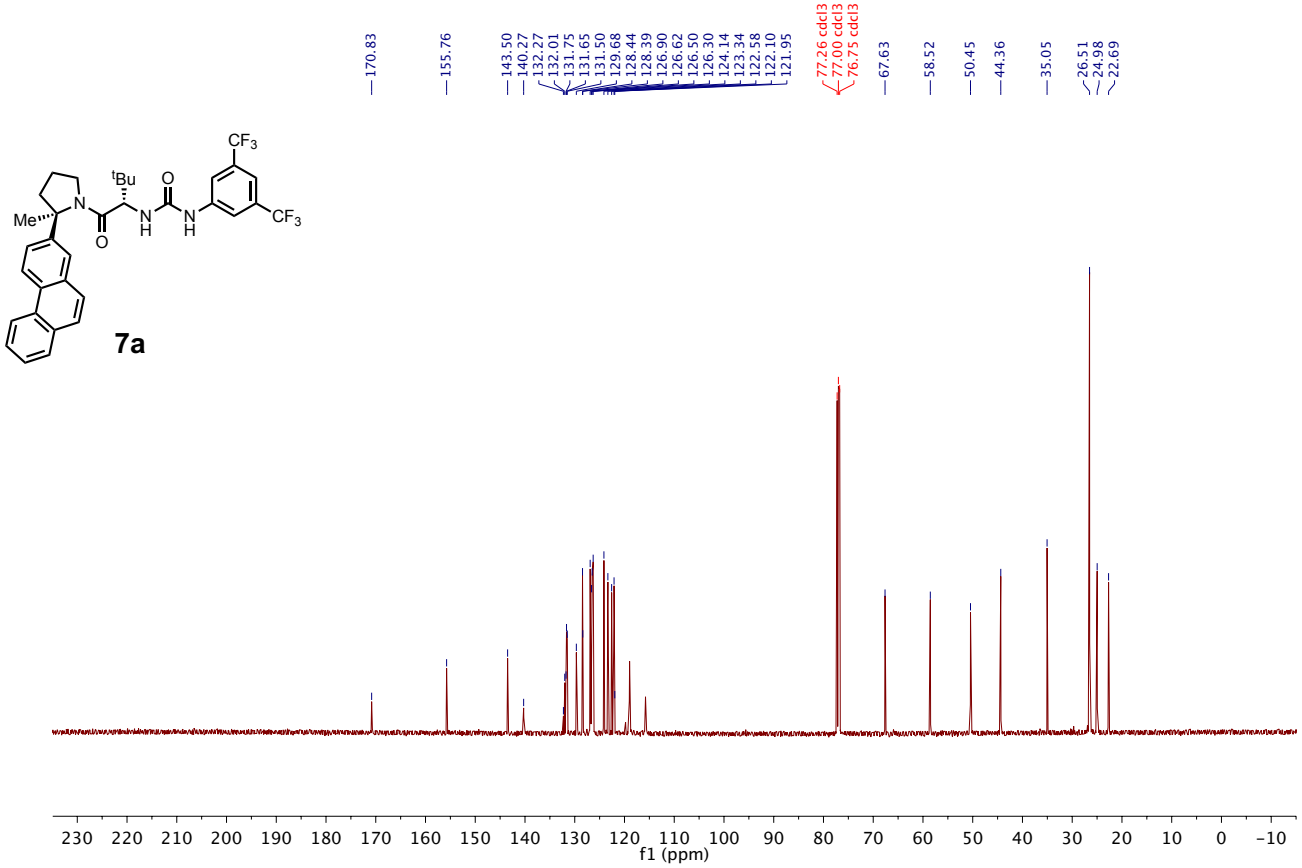


C4a

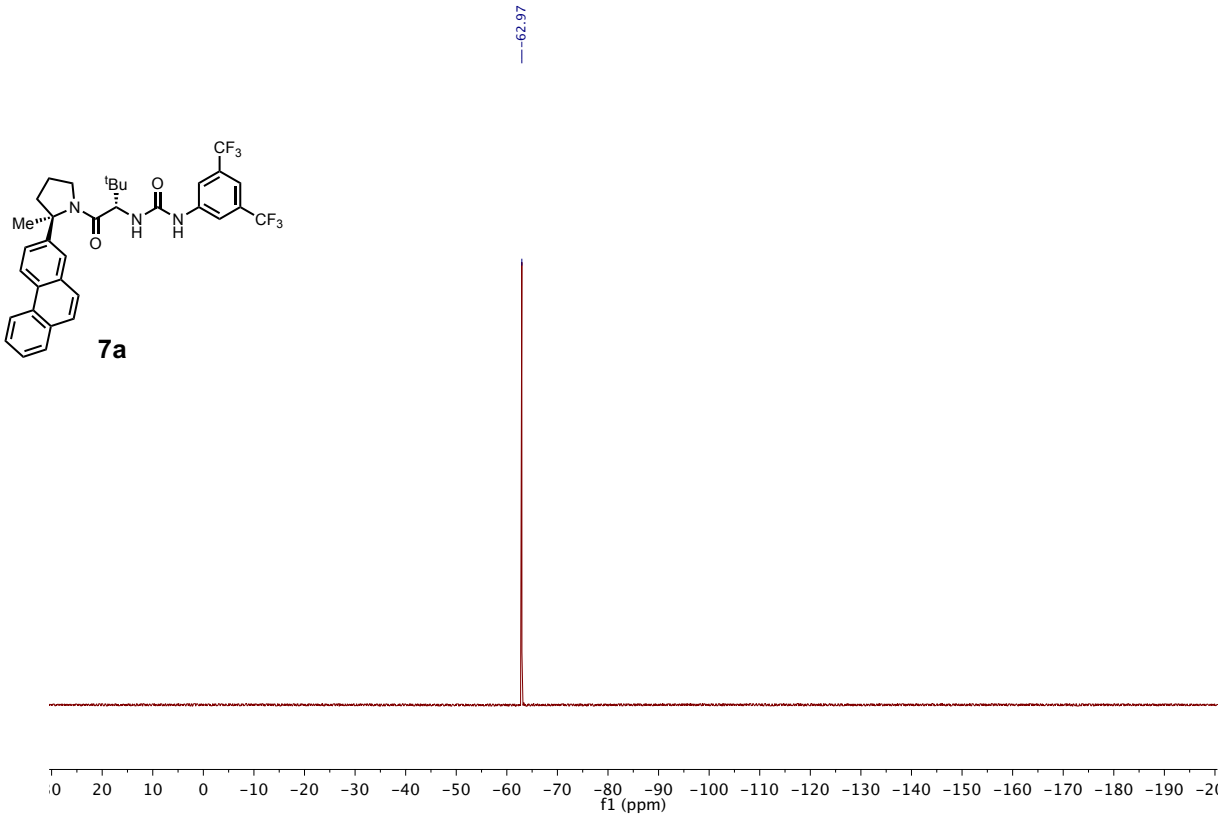
^{1}H NMR, $CDCl_3$, 600 MHz



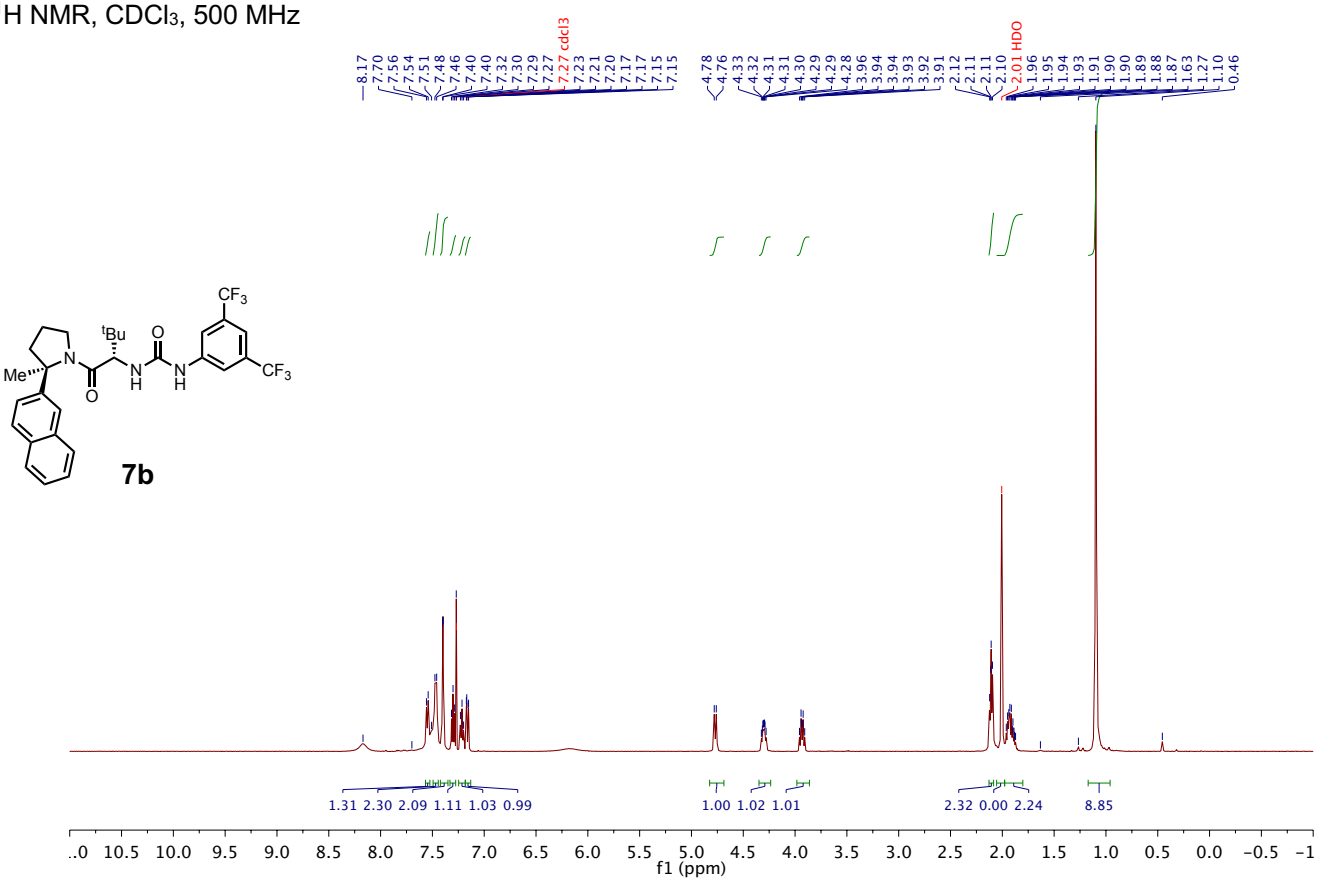
^{13}C NMR, $CDCl_3$, 126 MHz



^{19}F NMR, $CDCl_3$, 471 MHz

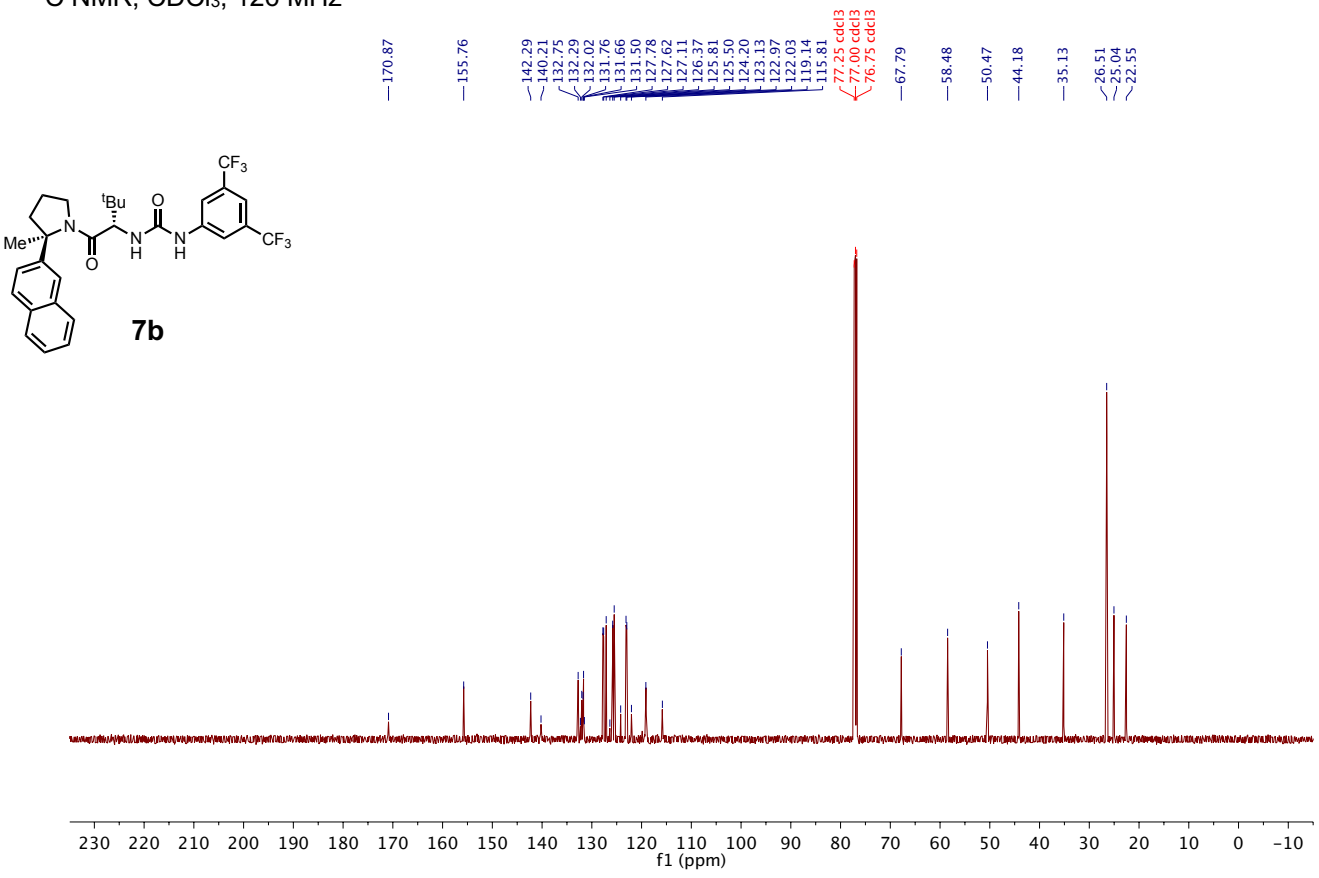


^{1}H NMR, $CDCl_3$, 500 MHz



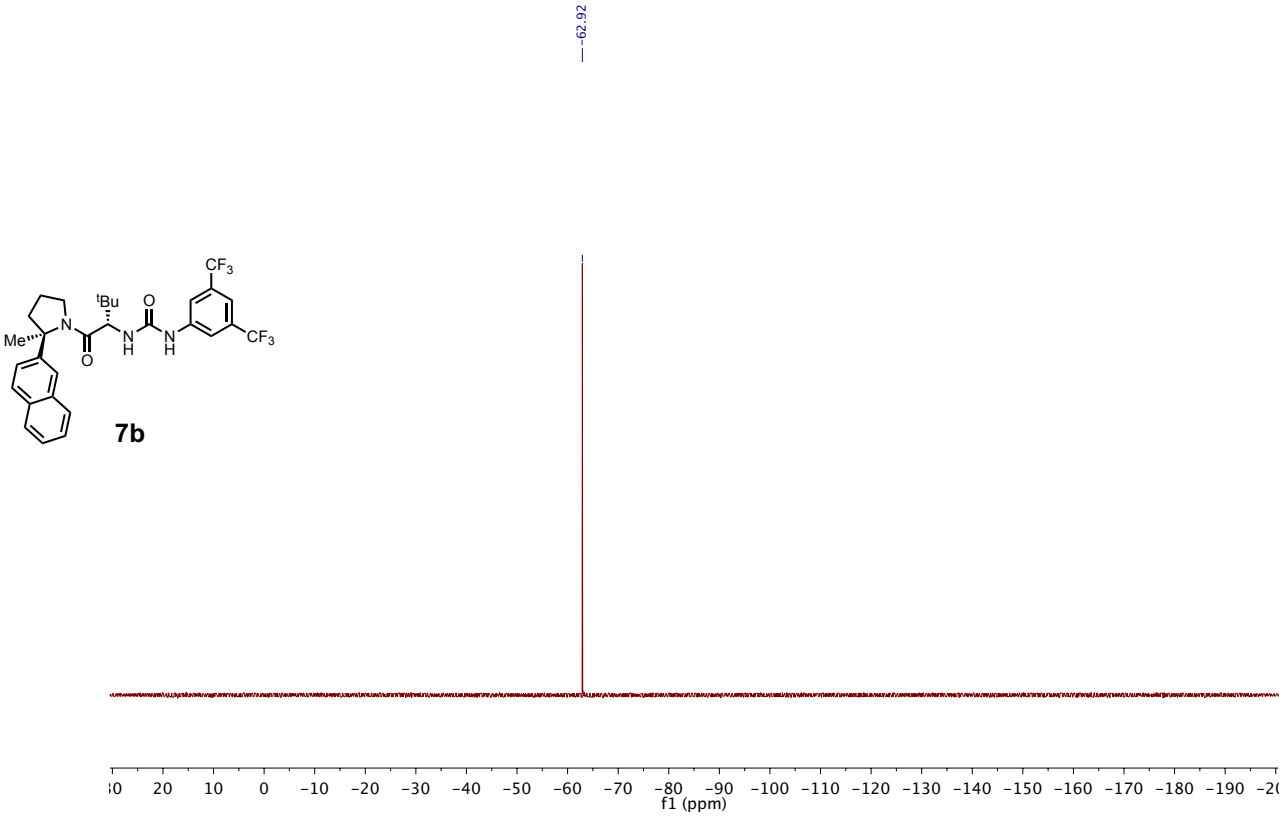
7b

^{13}C NMR, $CDCl_3$, 126 MHz

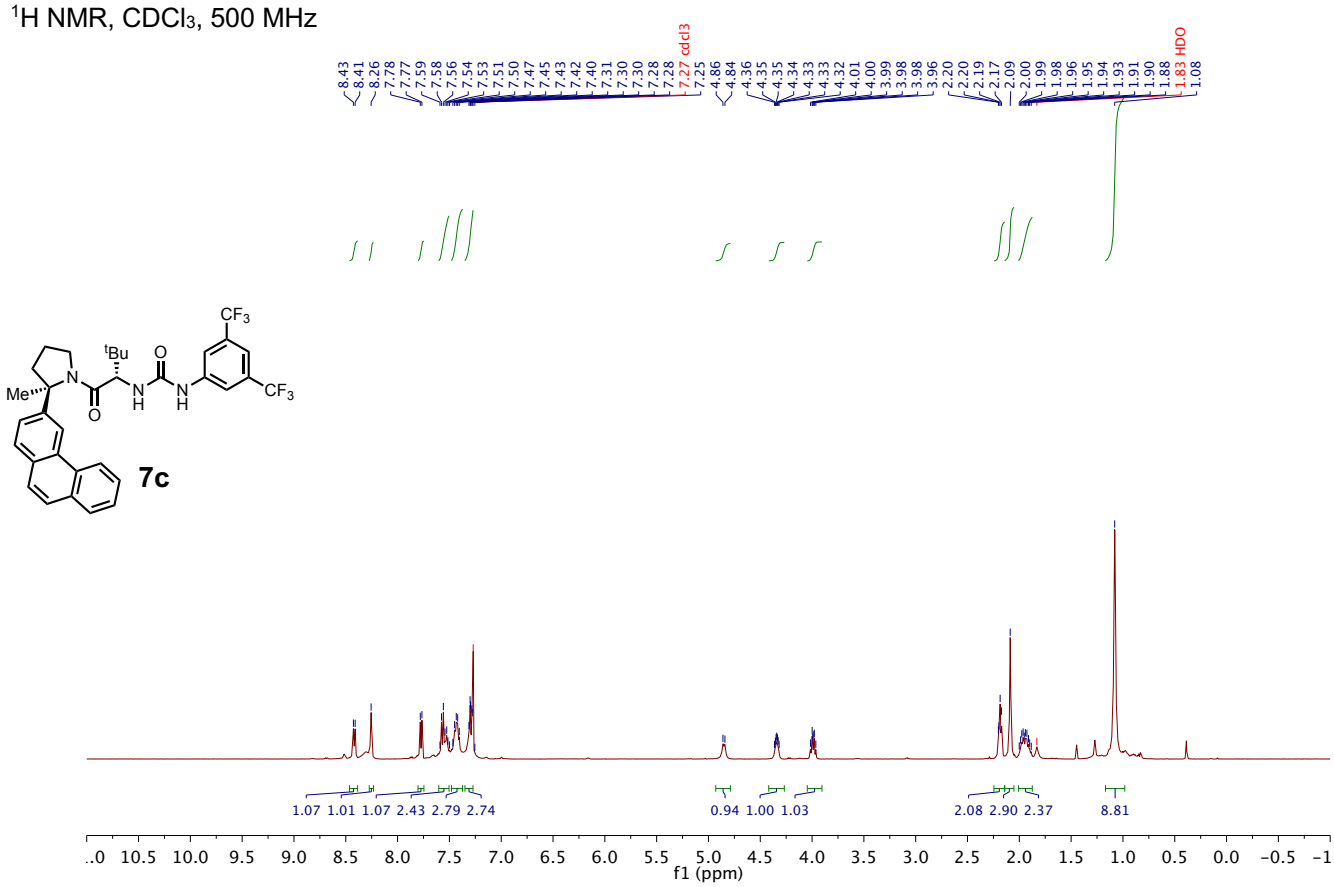


7b

^{19}F NMR, $CDCl_3$, 471 MHz

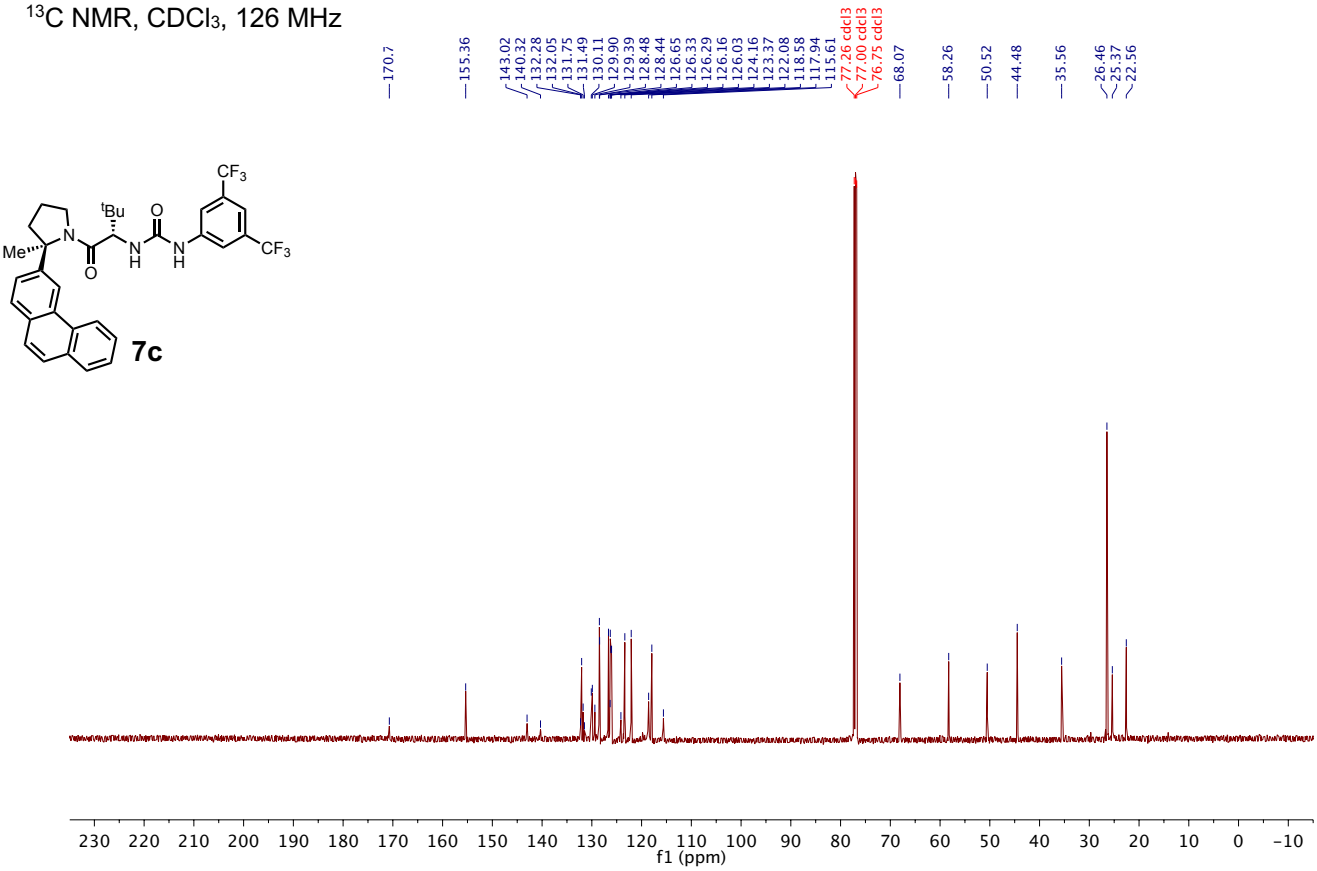


^{1}H NMR, $CDCl_3$, 500 MHz



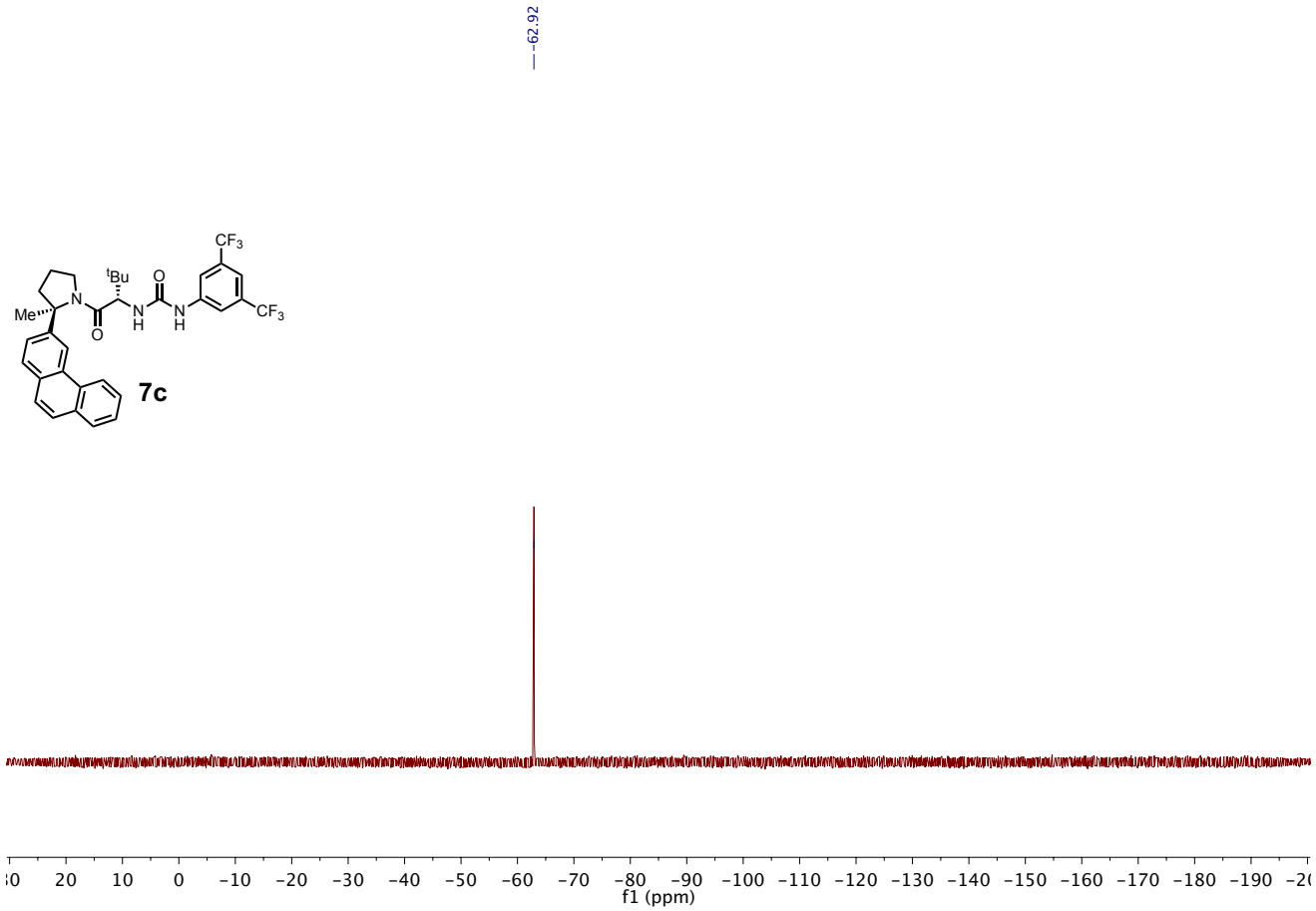
7c

^{13}C NMR, $CDCl_3$, 126 MHz

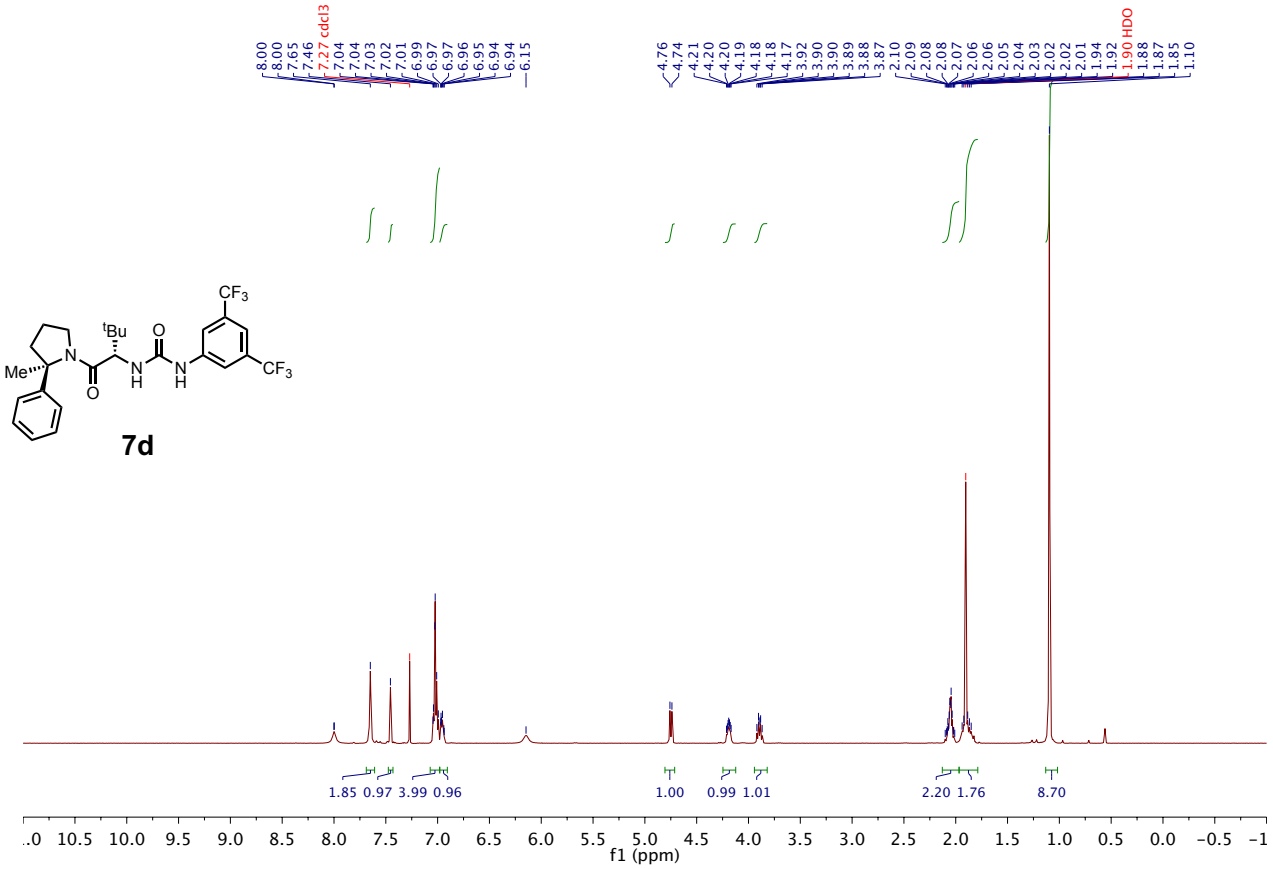


7c

^{19}F NMR, $CDCl_3$, 471 MHz

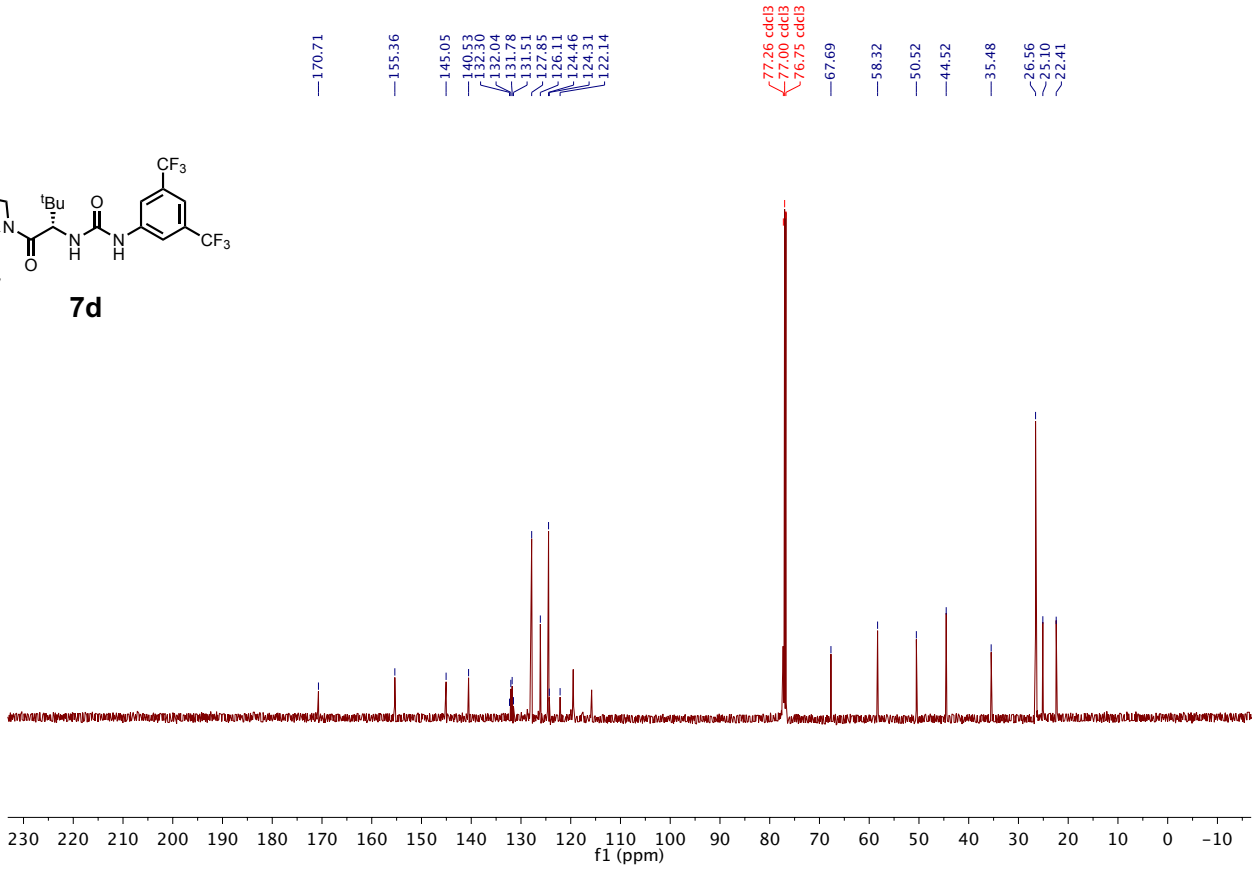


^{1}H NMR, $CDCl_3$, 500 MHz



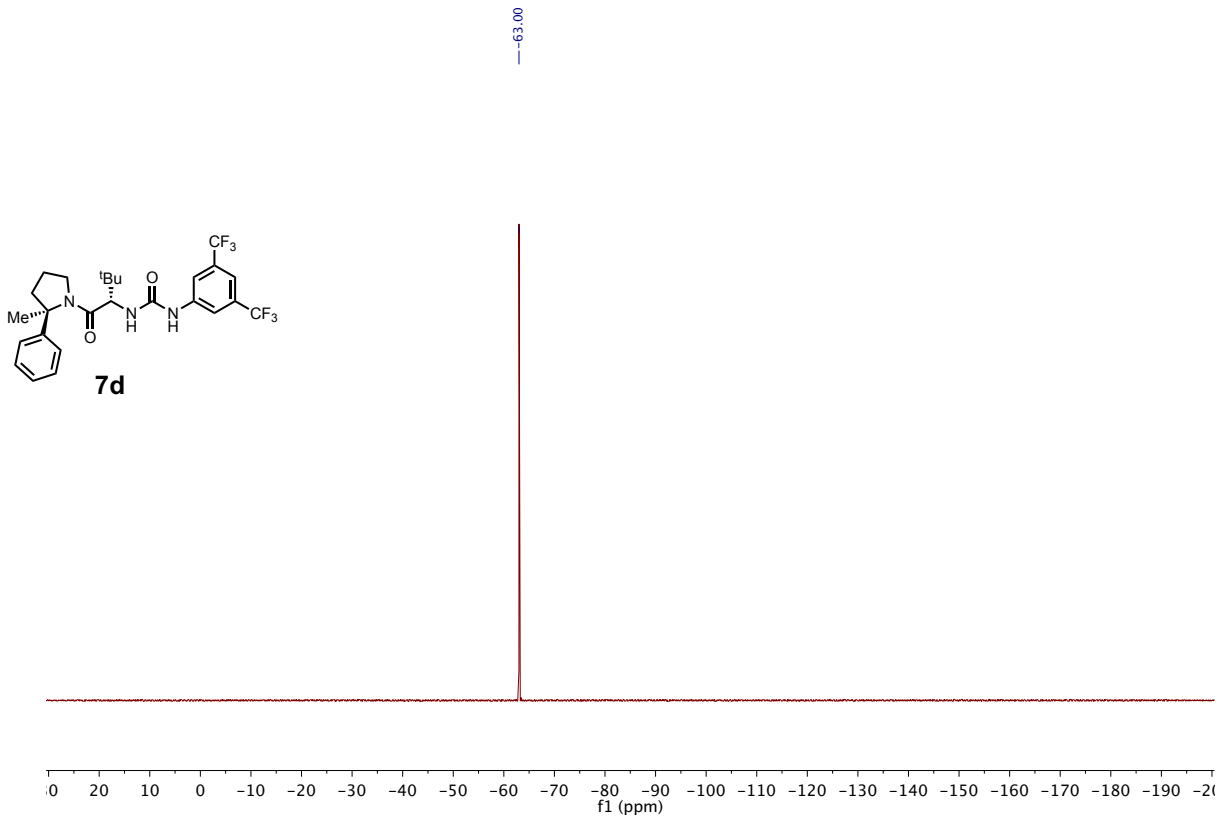
7d

^{13}C NMR, $CDCl_3$, 126 MHz

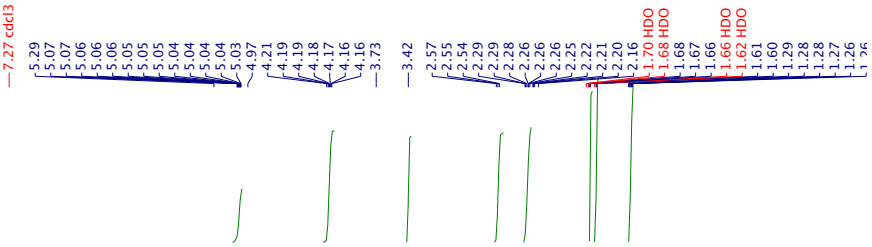


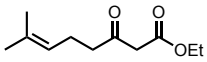
7d

^{19}F NMR, $CDCl_3$, 471 MHz

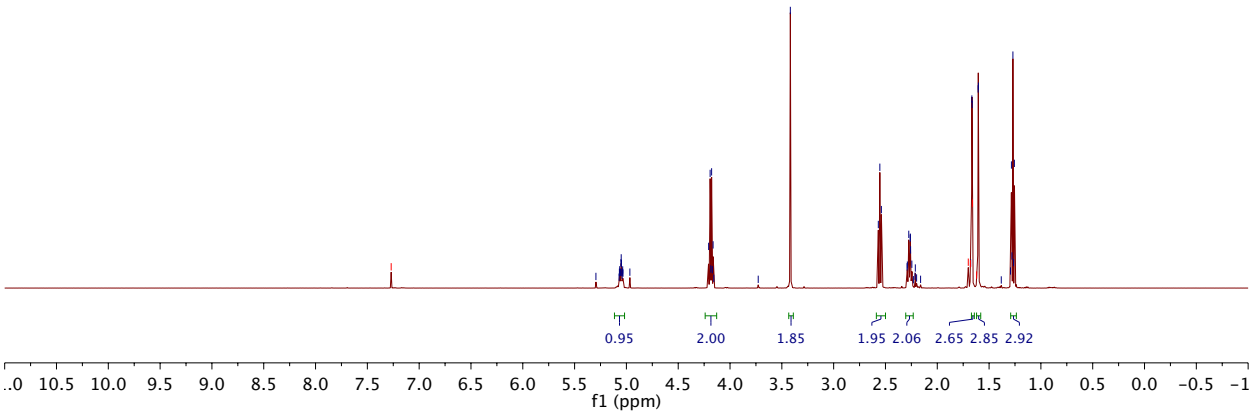


^{1}H NMR, $CDCl_3$, 500 MHz

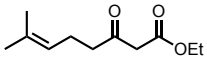




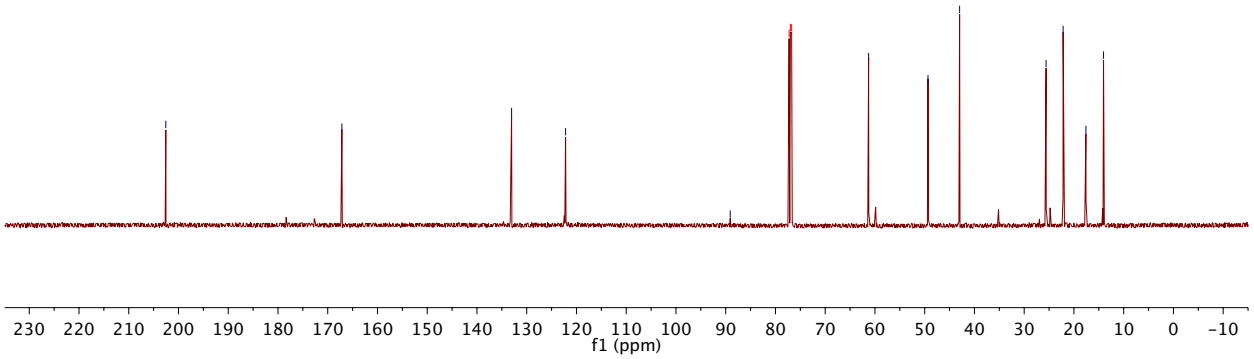
S1



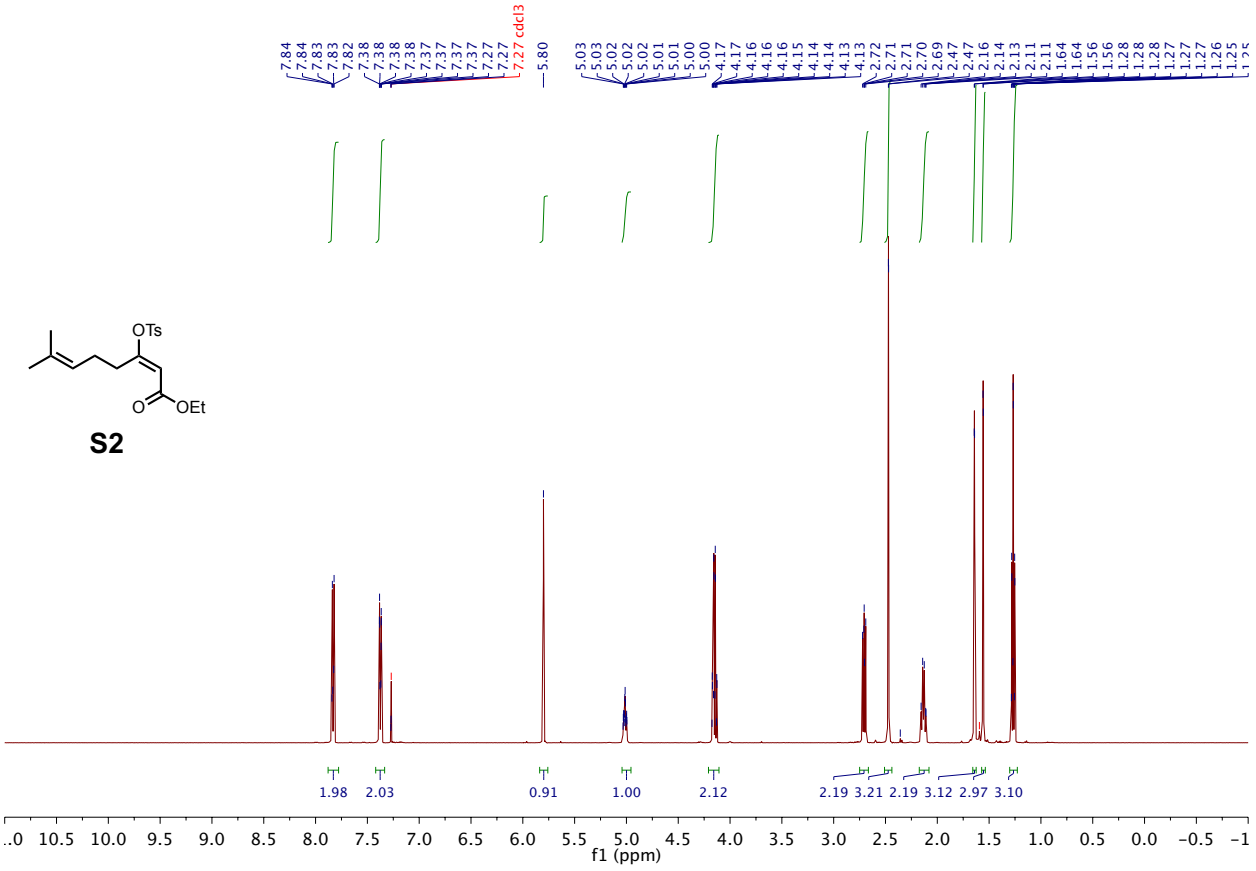
^{13}C NMR, $CDCl_3$, 126 MHz



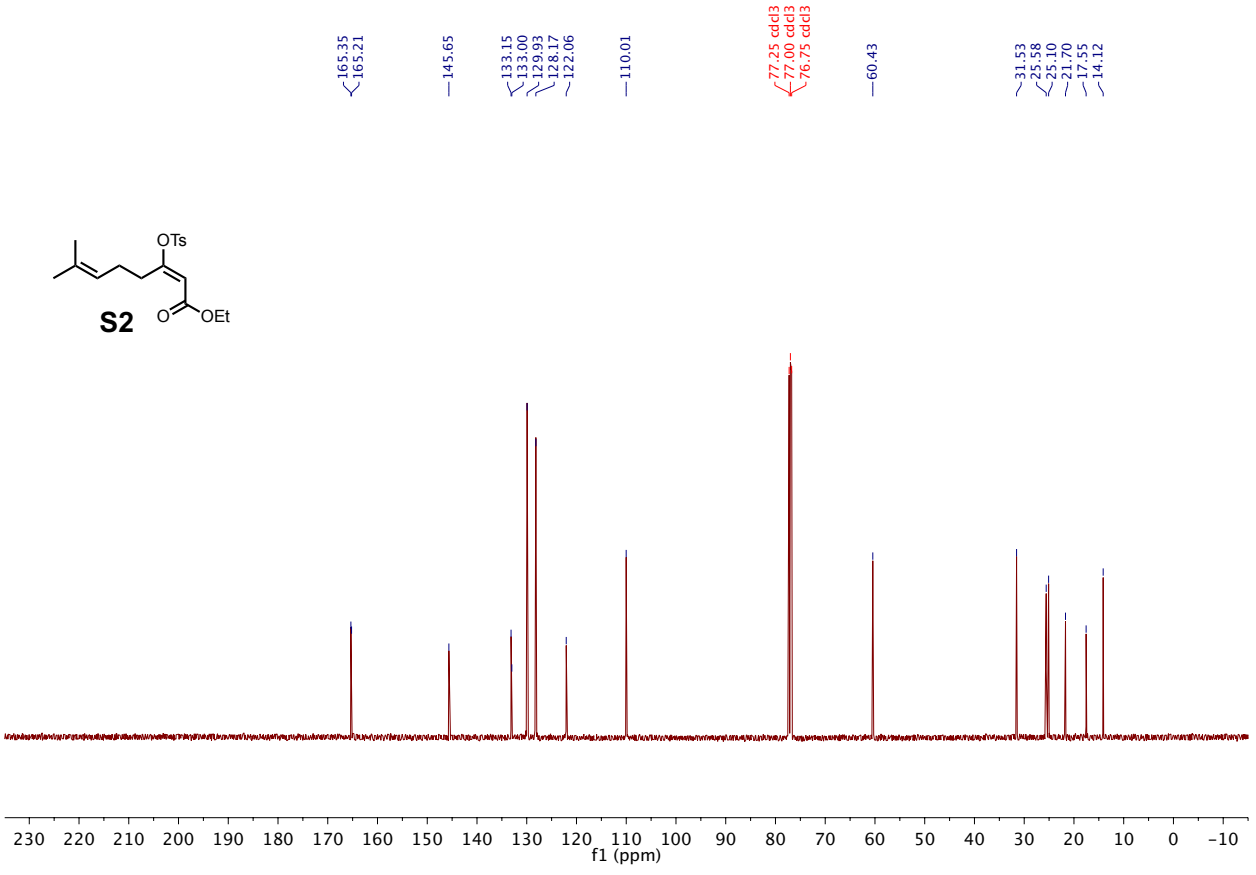
S1



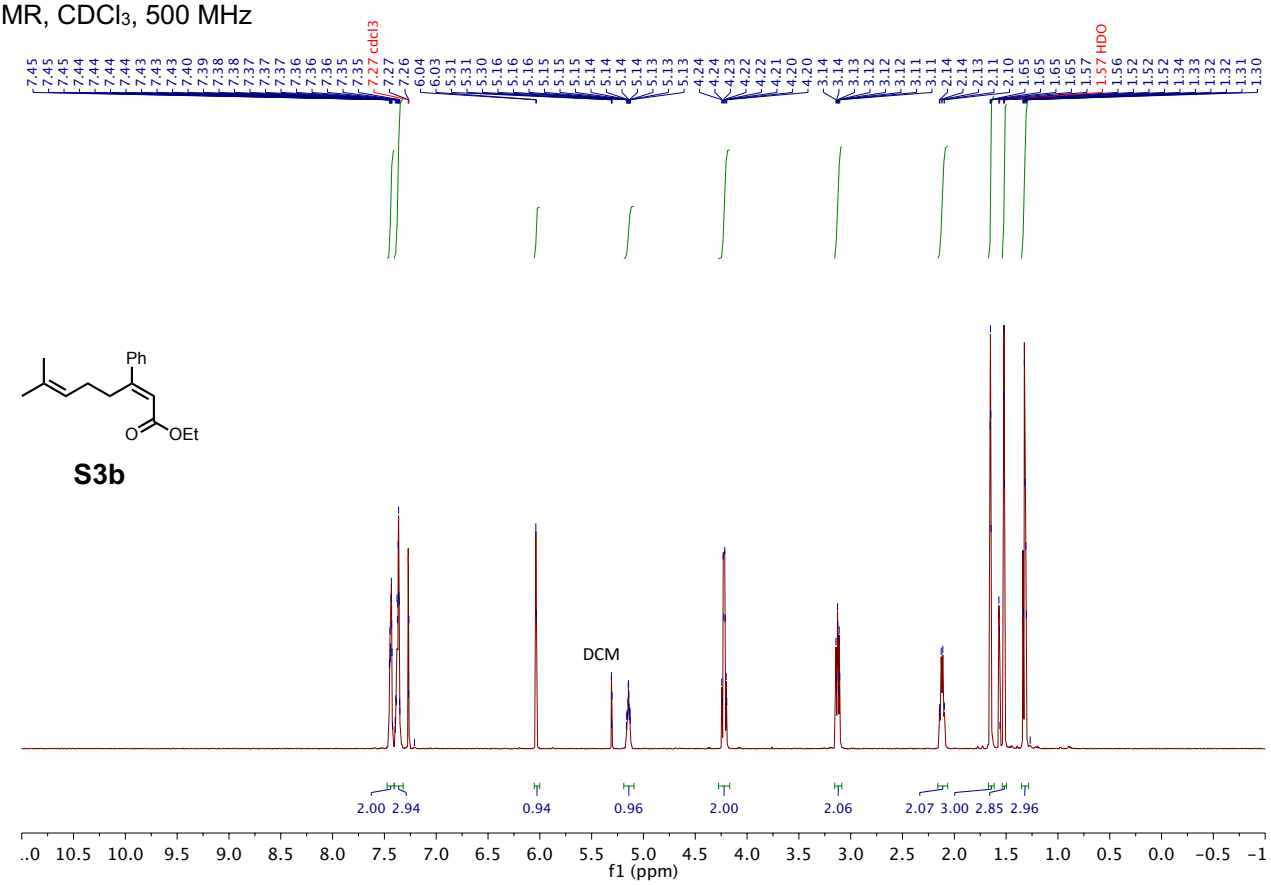
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

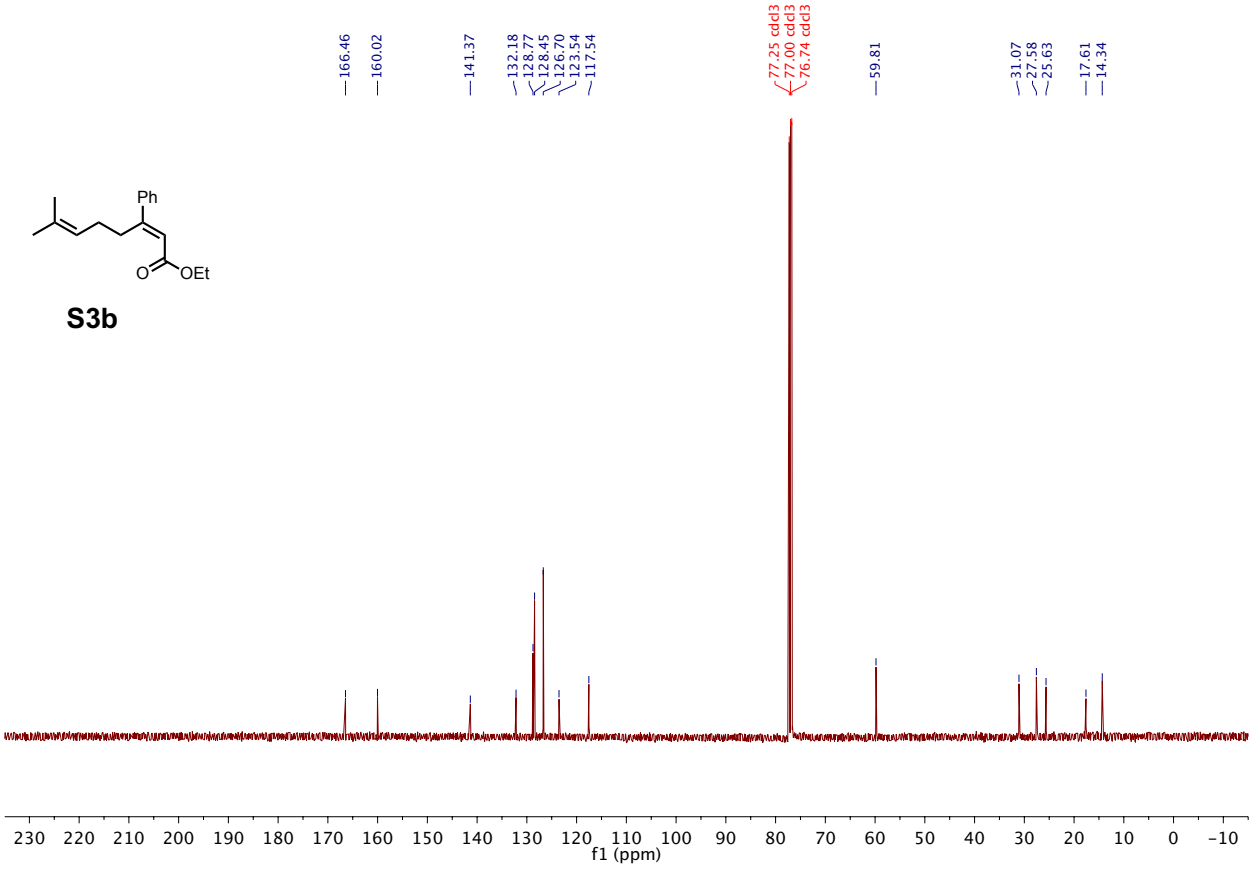


^{1}H NMR, $CDCl_3$, 500 MHz



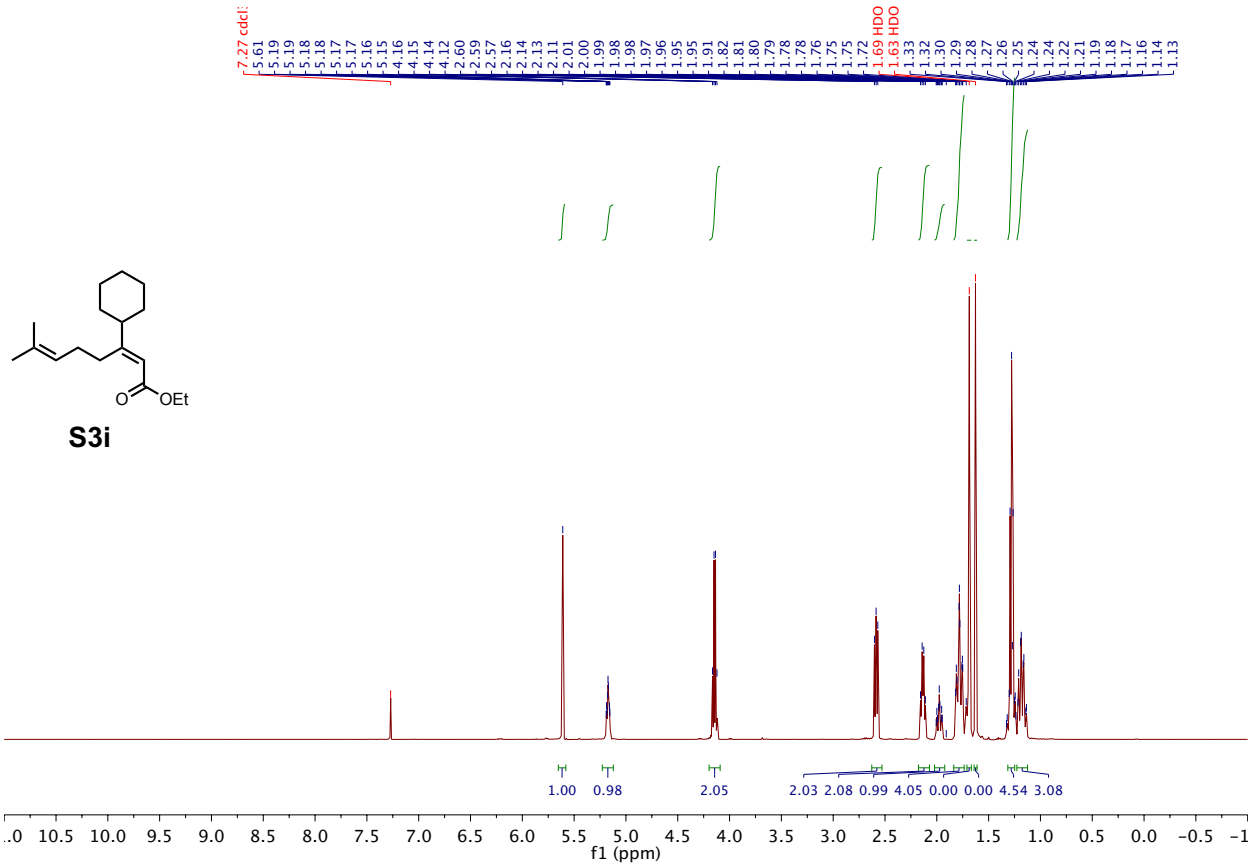
S3b

^{13}C NMR, $CDCl_3$, 126 MHz



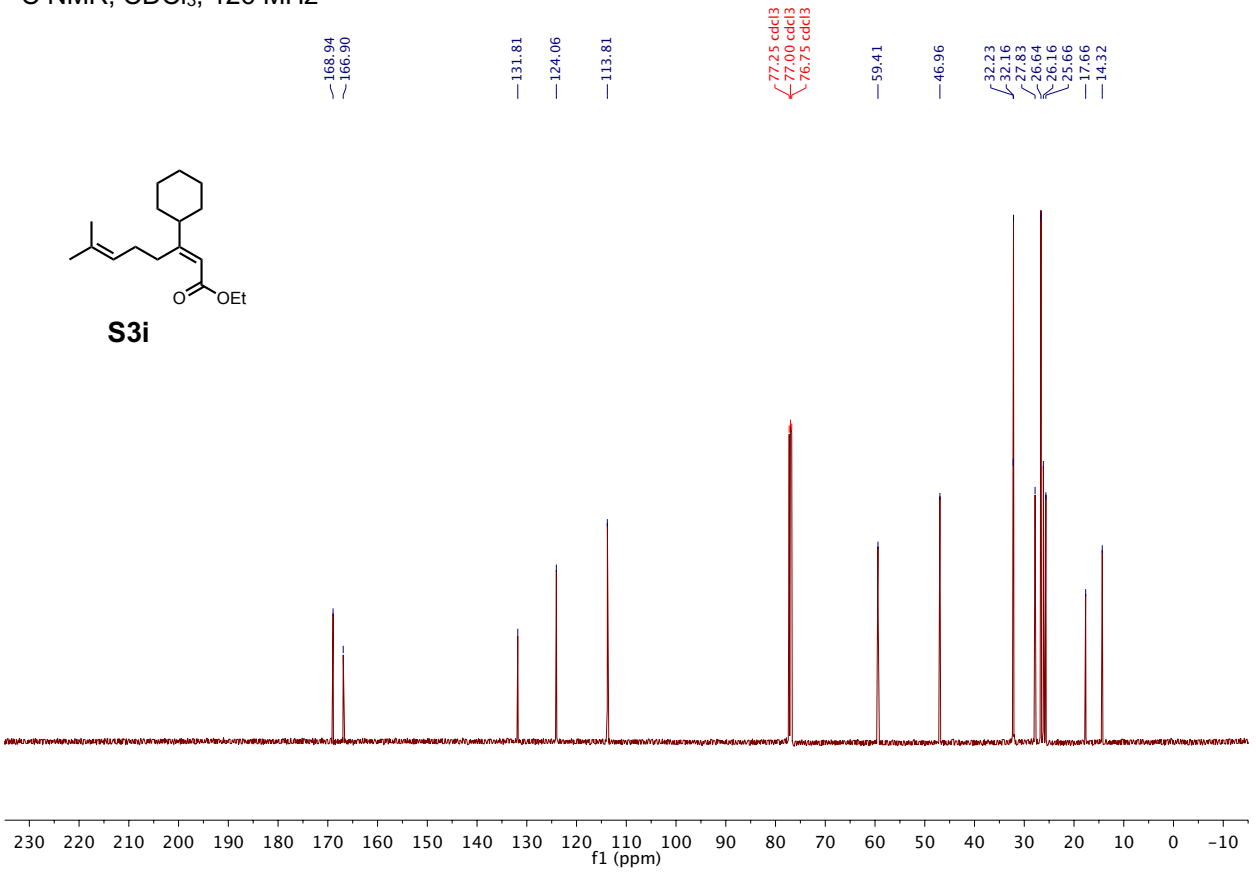
S3b

^{1}H NMR, $CDCl_3$, 500 MHz



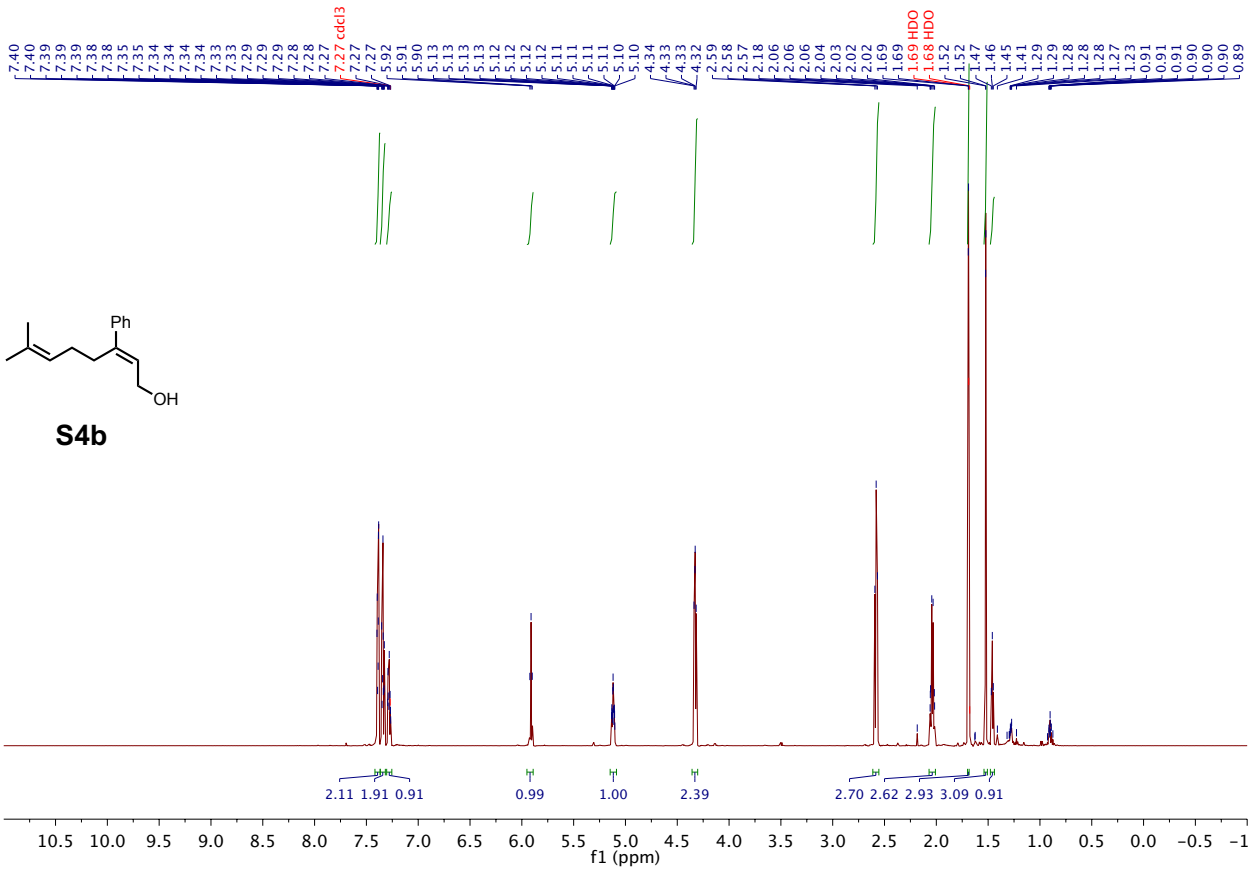
S3i

^{13}C NMR, $CDCl_3$, 126 MHz

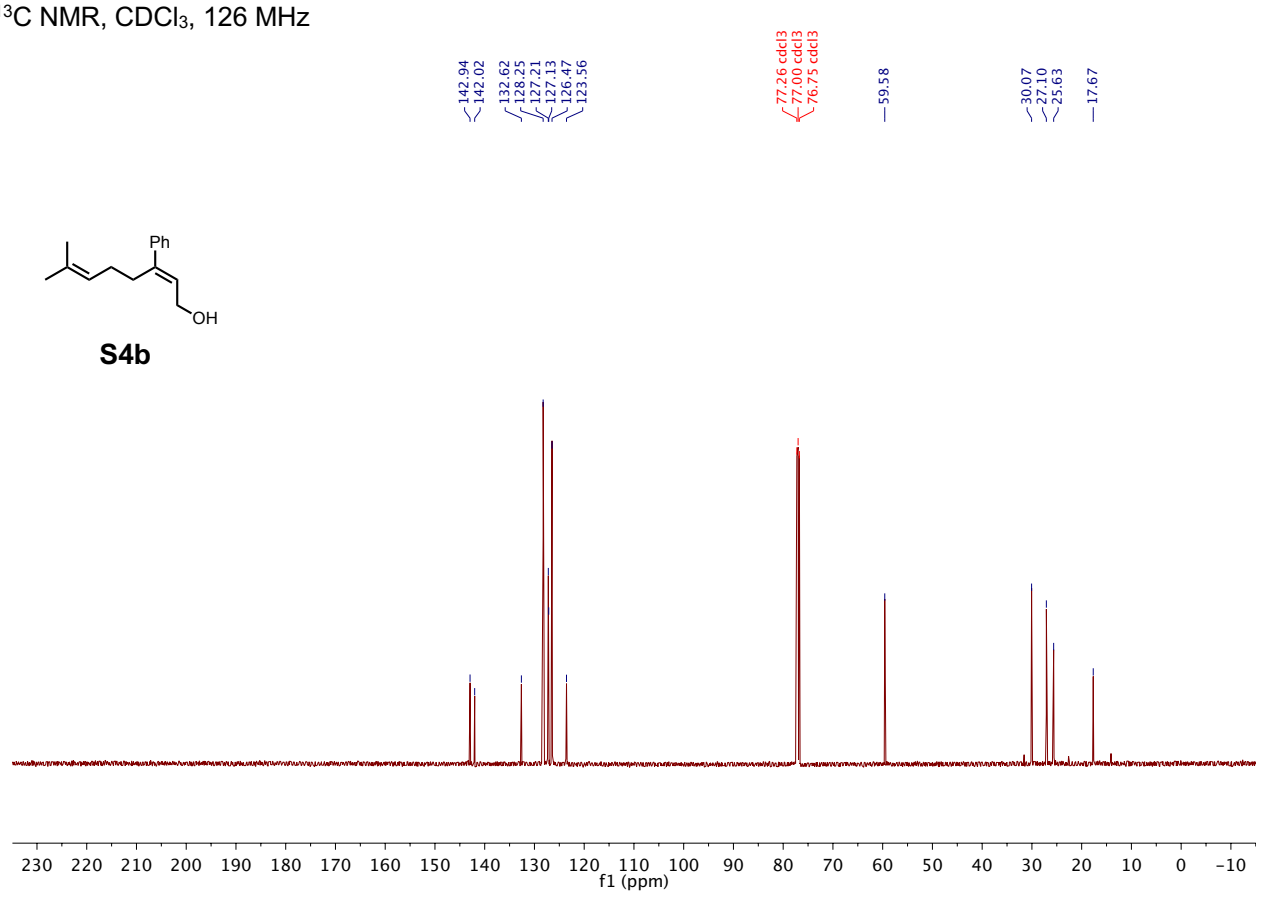


S3i

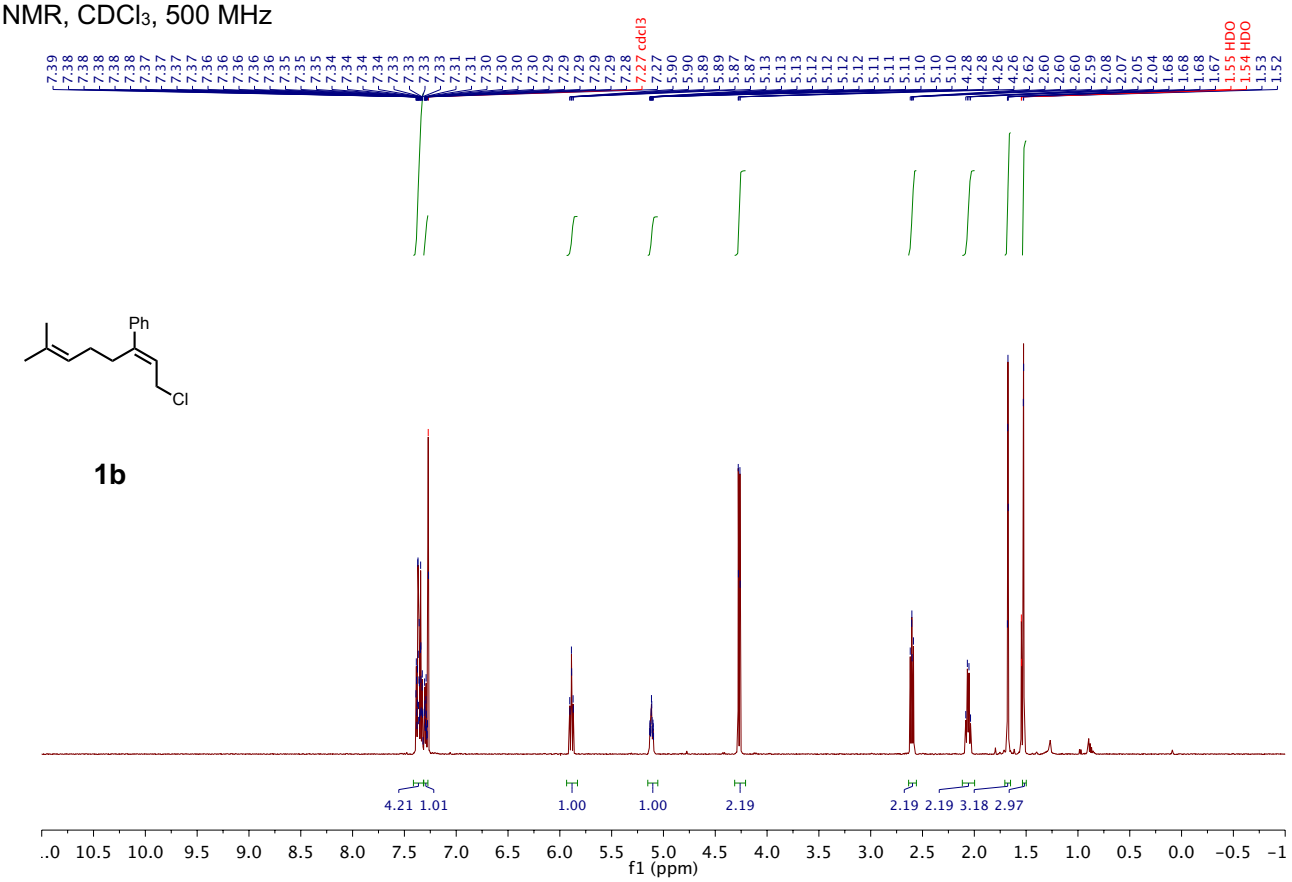
^{1}H NMR, $CDCl_3$, 600 MHz



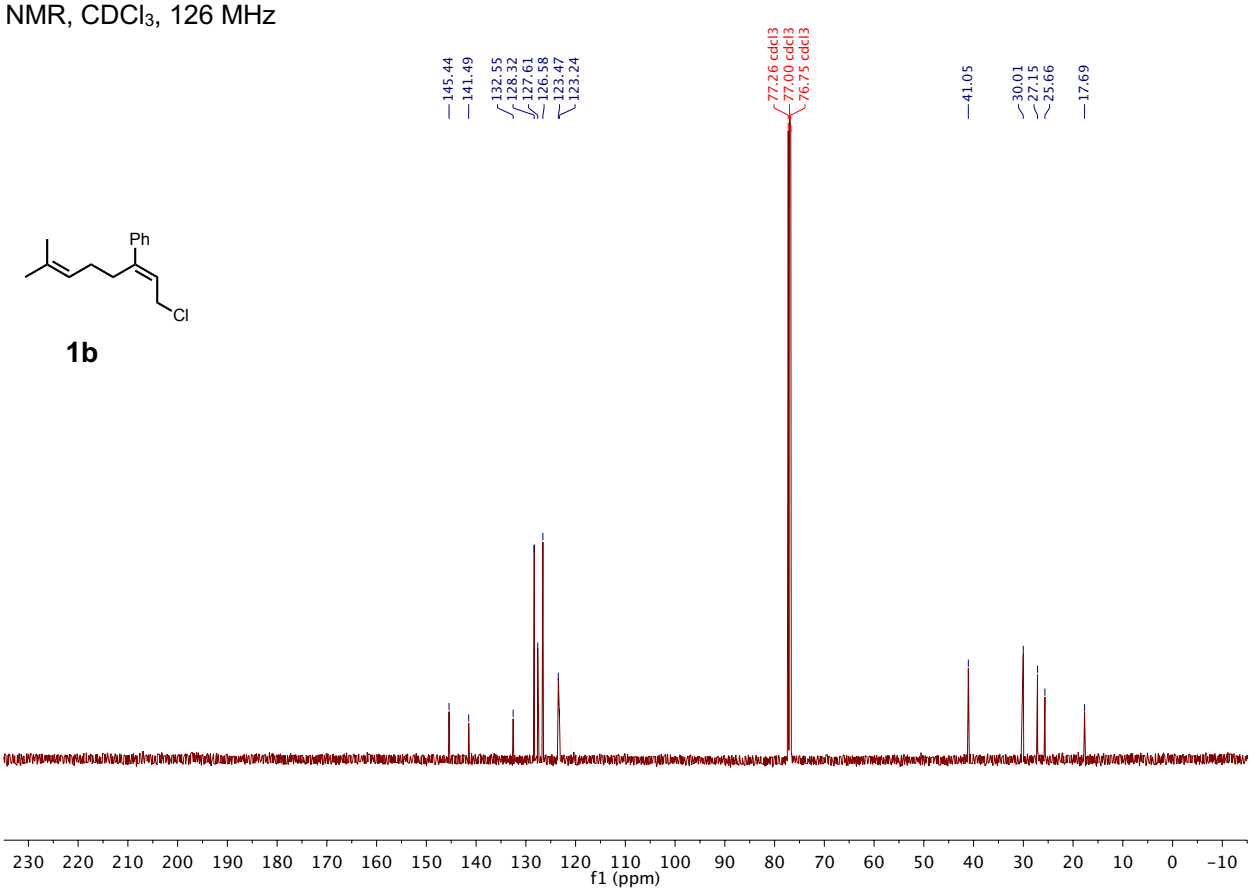
^{13}C NMR, $CDCl_3$, 126 MHz

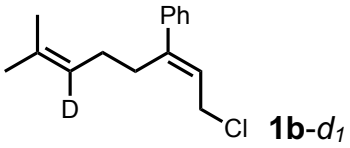


^{1}H NMR, $CDCl_3$, 500 MHz



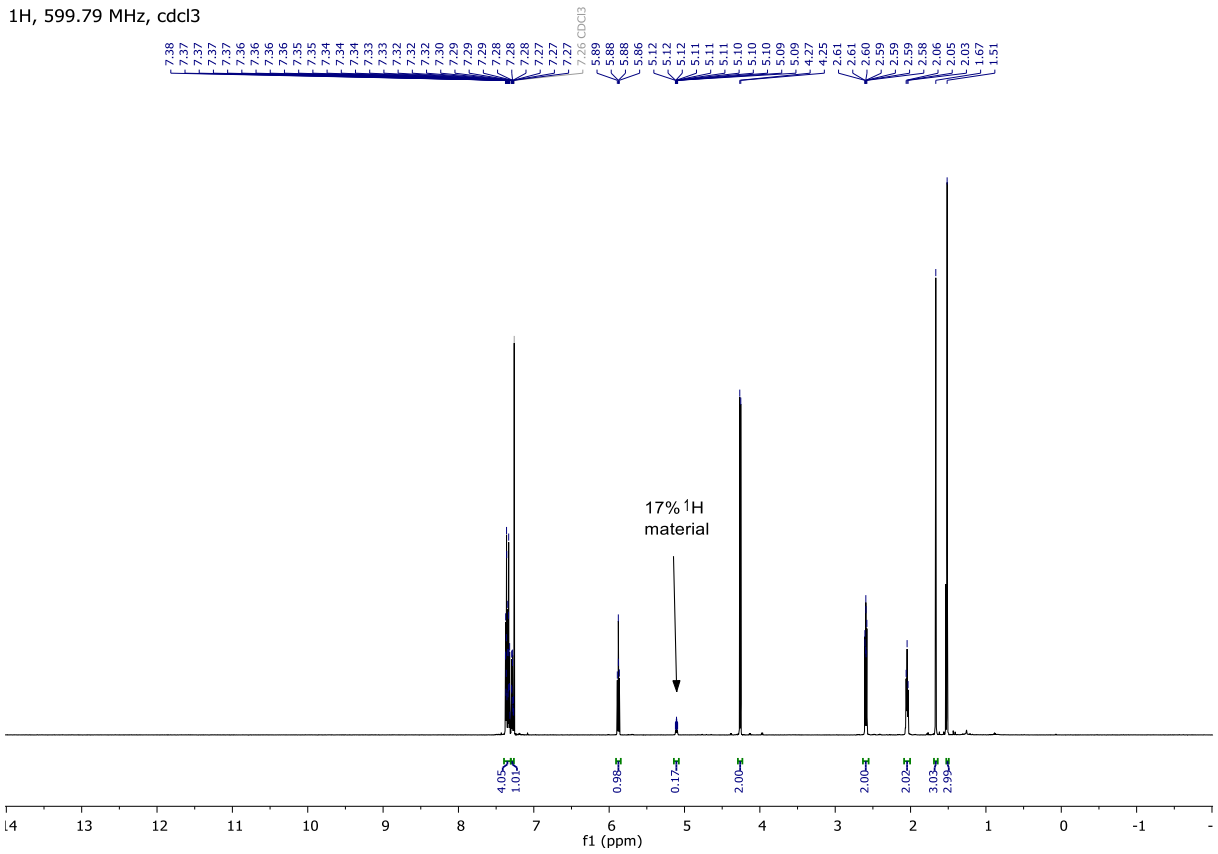
^{13}C NMR, $CDCl_3$, 126 MHz



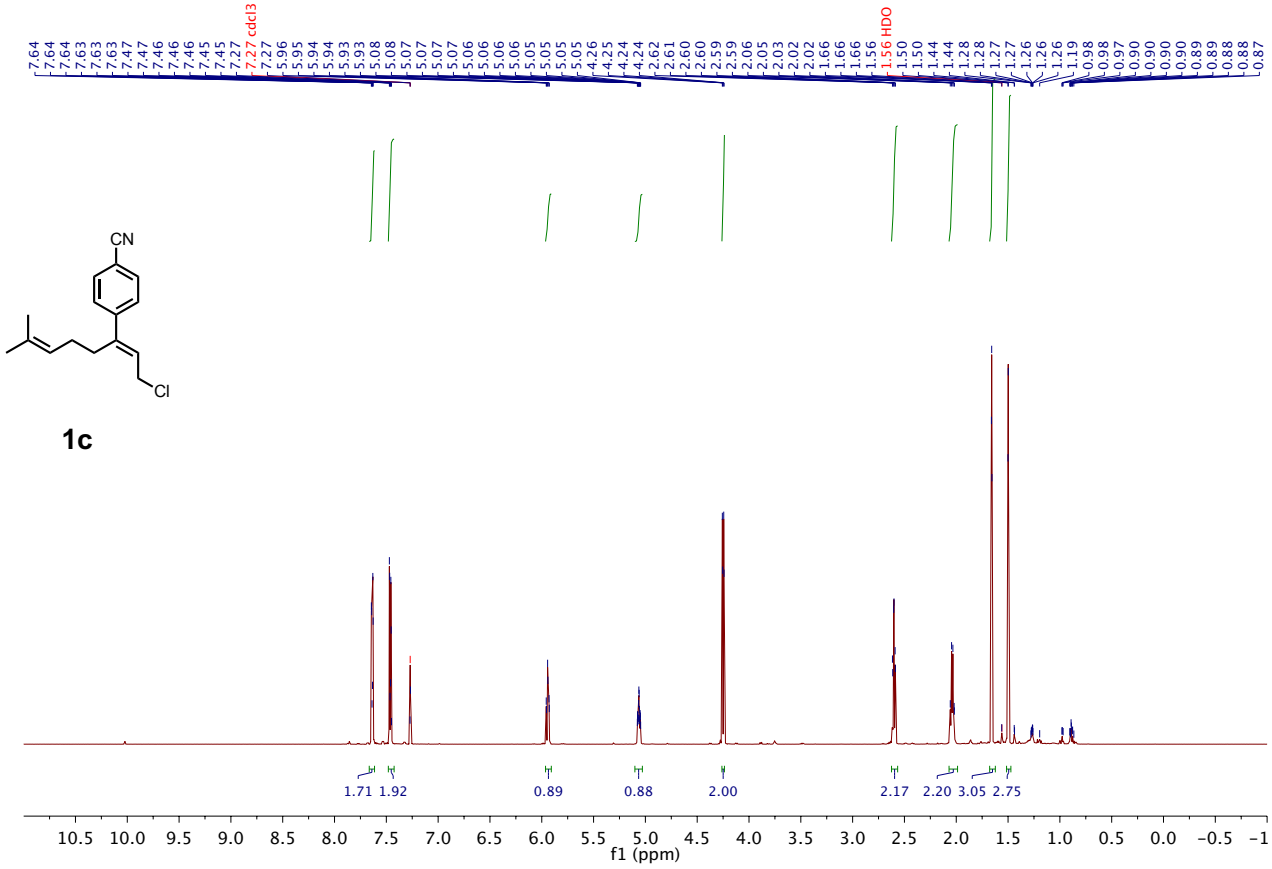


1b-d_1

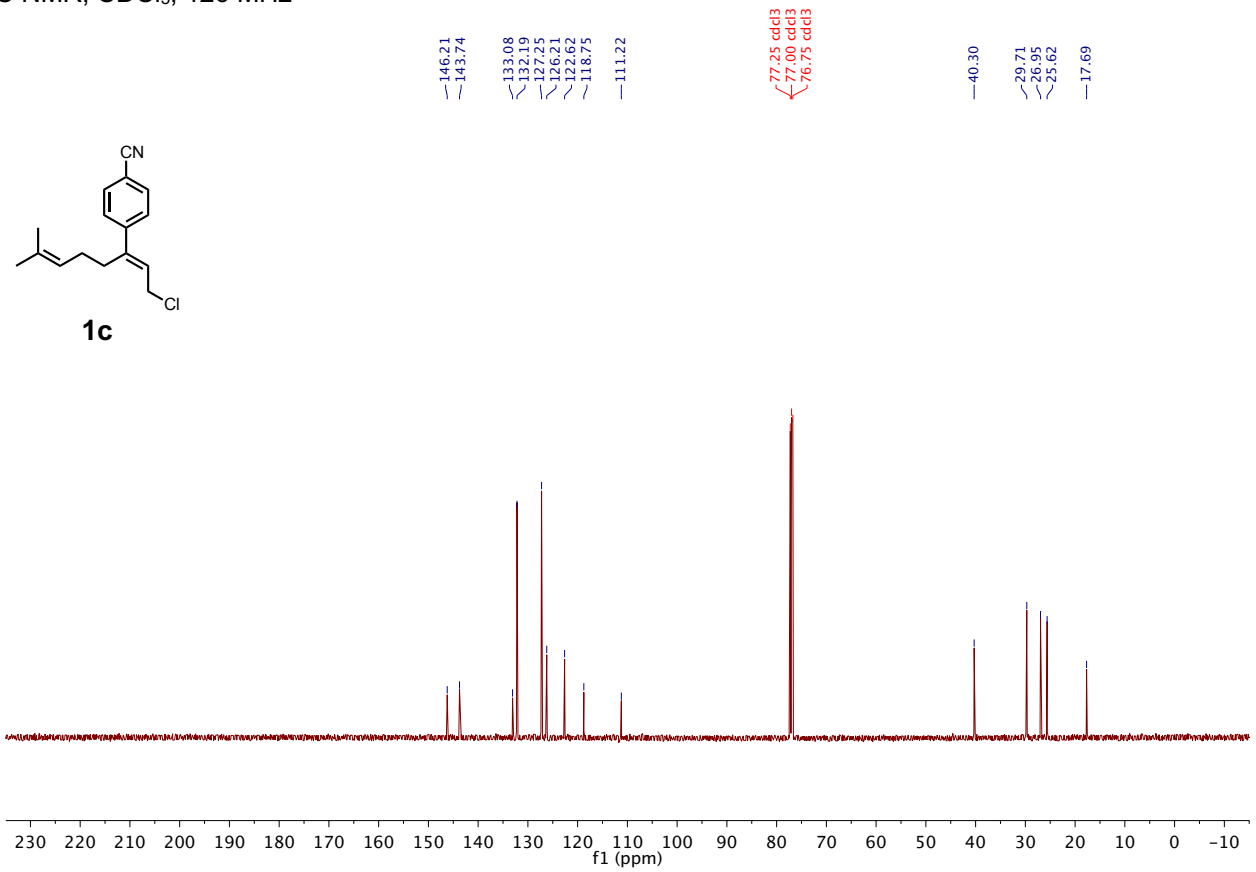
1H, 599.79 MHz, cdcl3



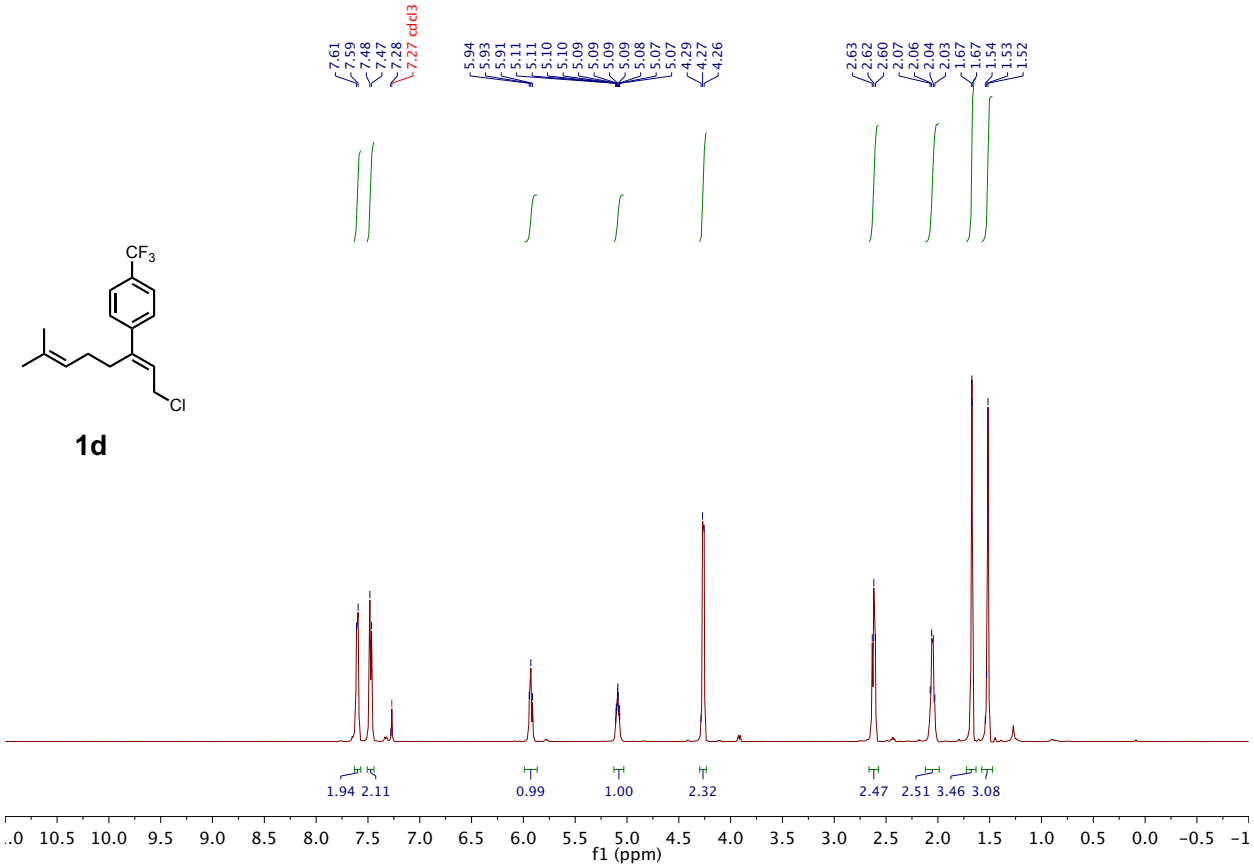
^{1}H NMR, $CDCl_3$, 600 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

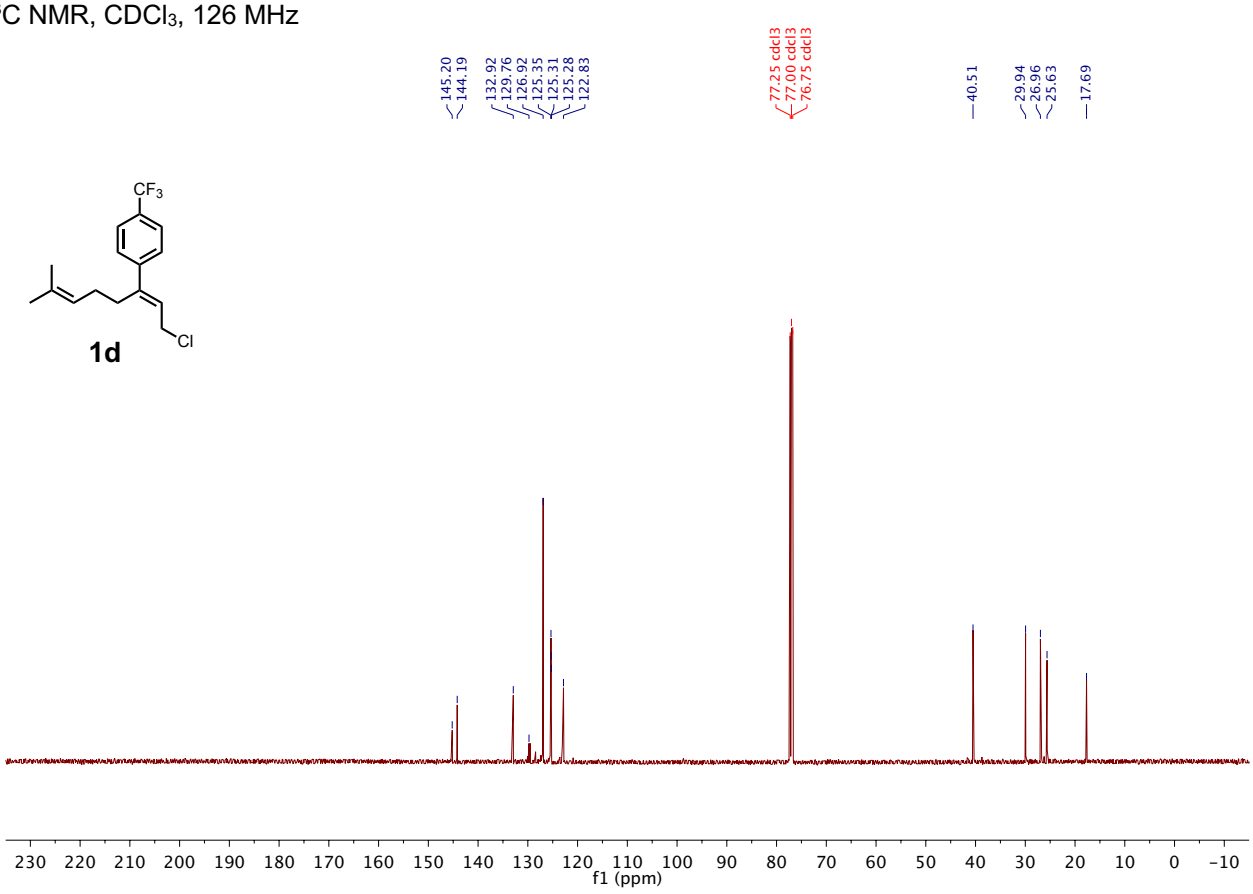


^{1}H NMR, $CDCl_3$, 500 MHz



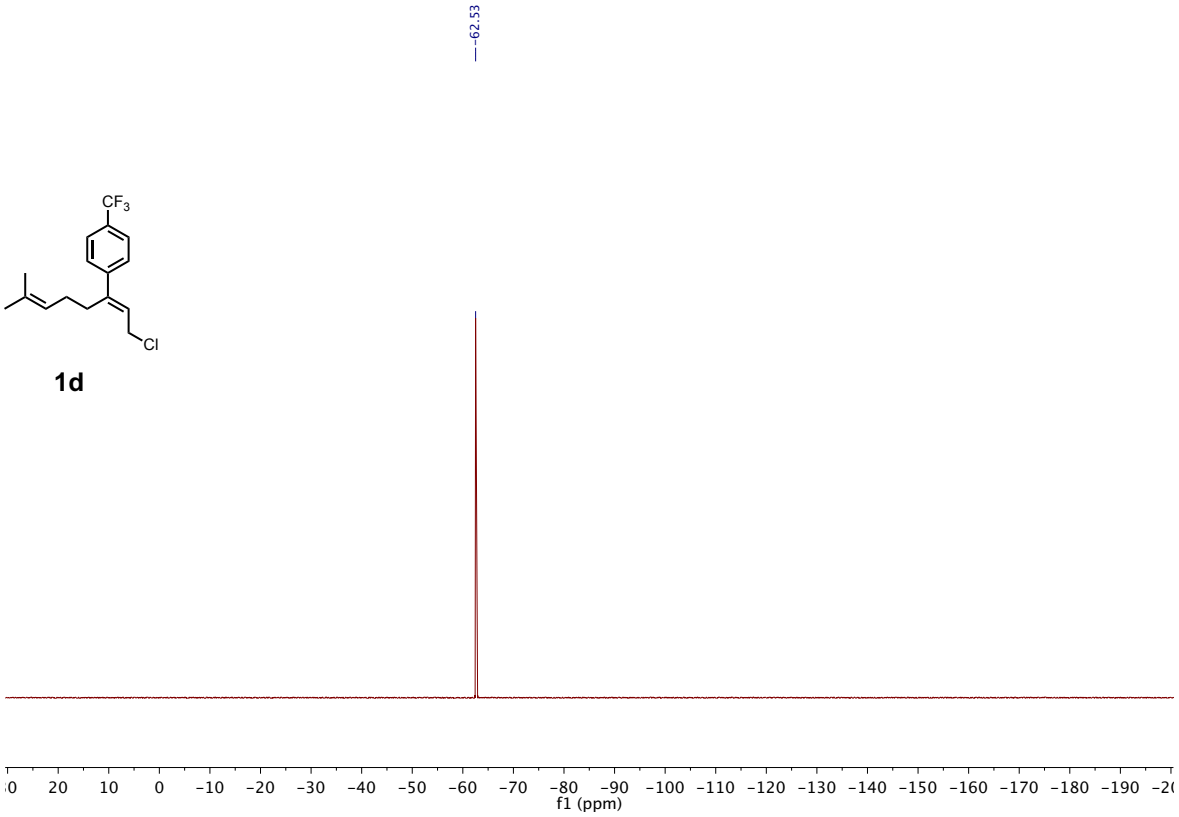
1d

^{13}C NMR, $CDCl_3$, 126 MHz

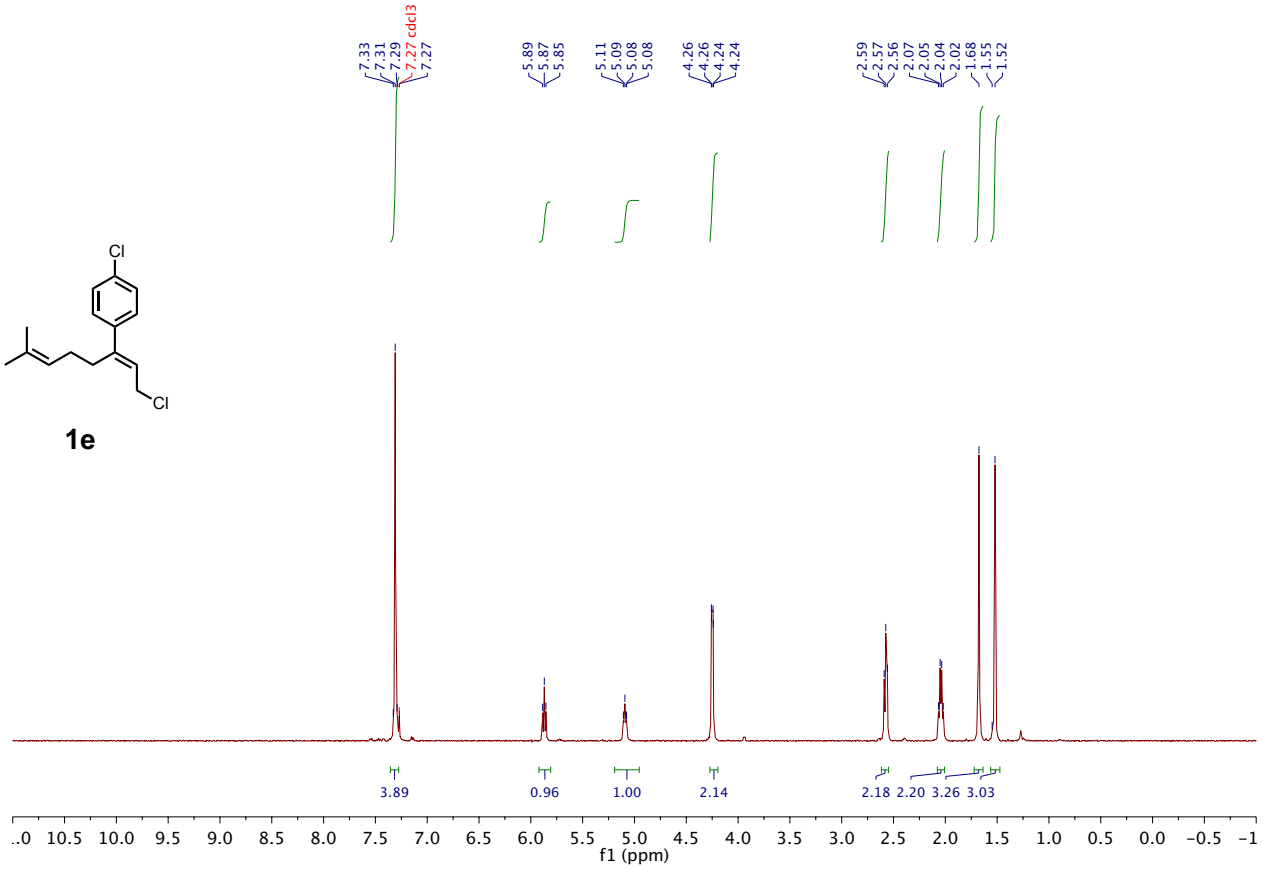


1d

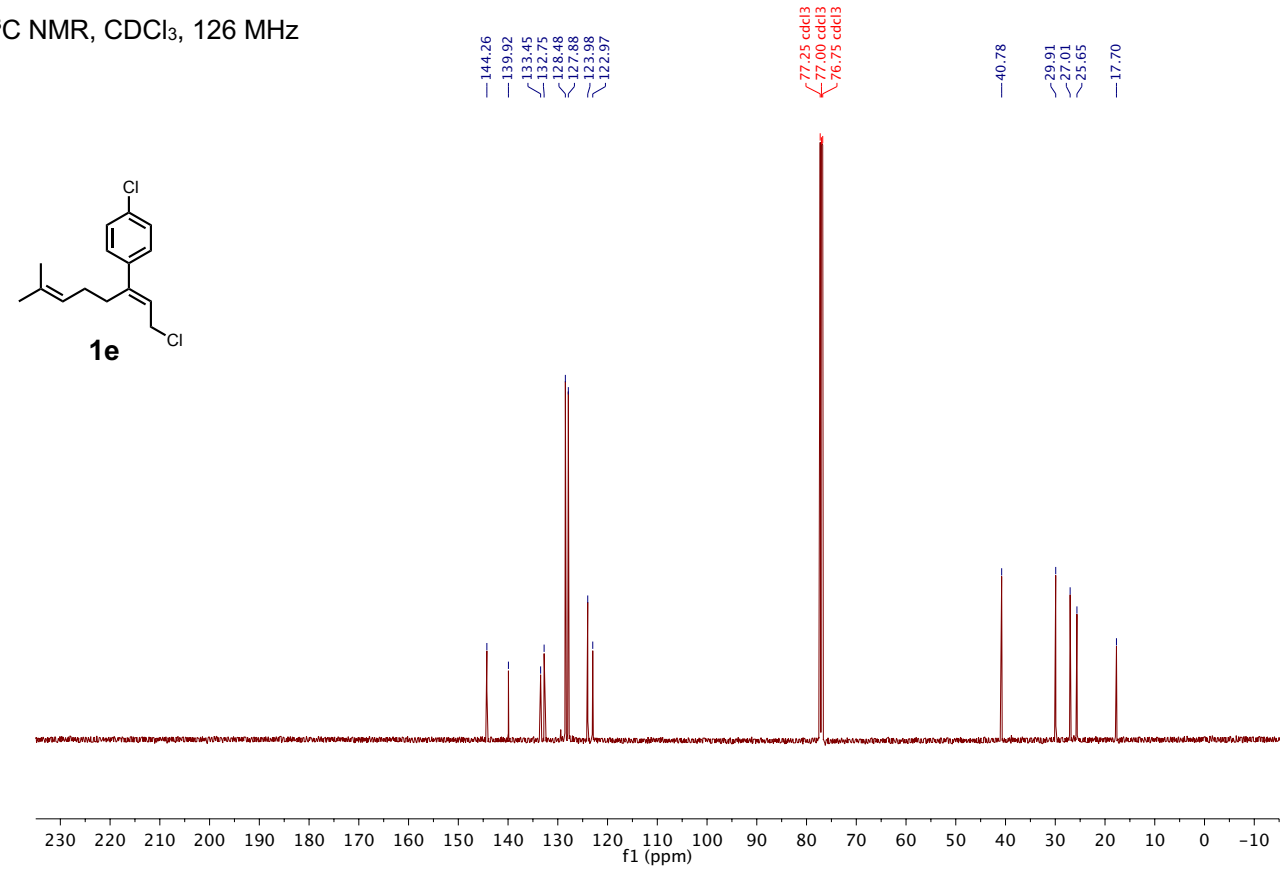
^{19}F NMR, $CDCl_3$, 471 MHz



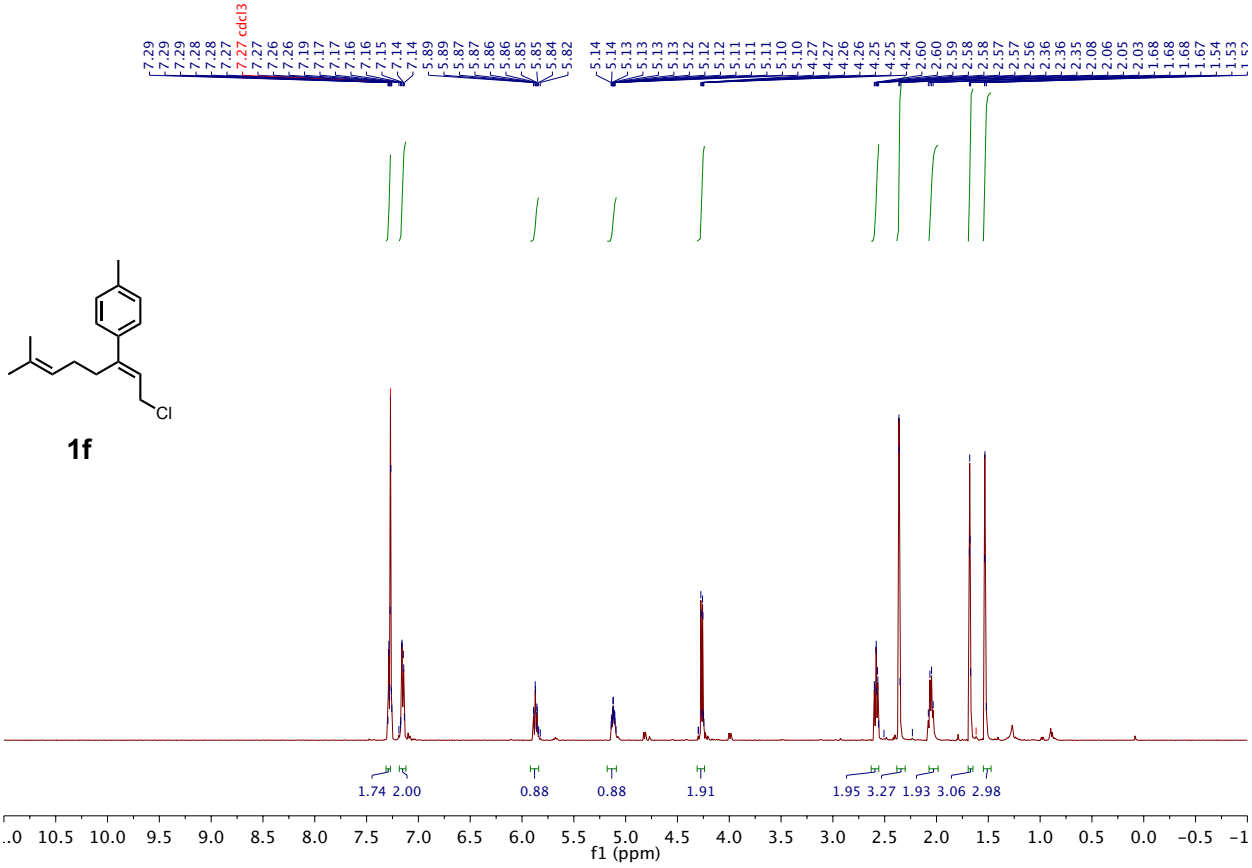
^{1}H NMR, $CDCl_3$, 600 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

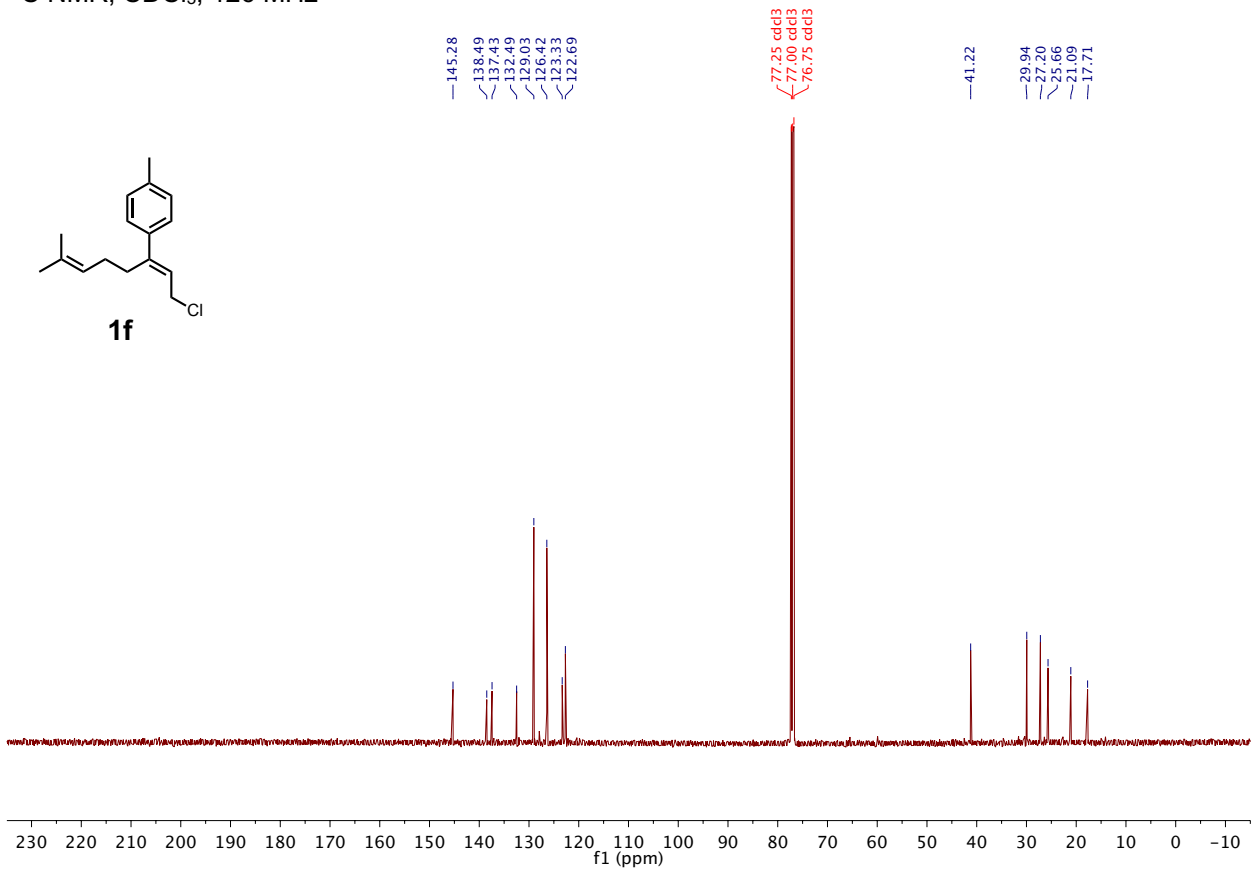


^{1}H NMR, $CDCl_3$, 500 MHz



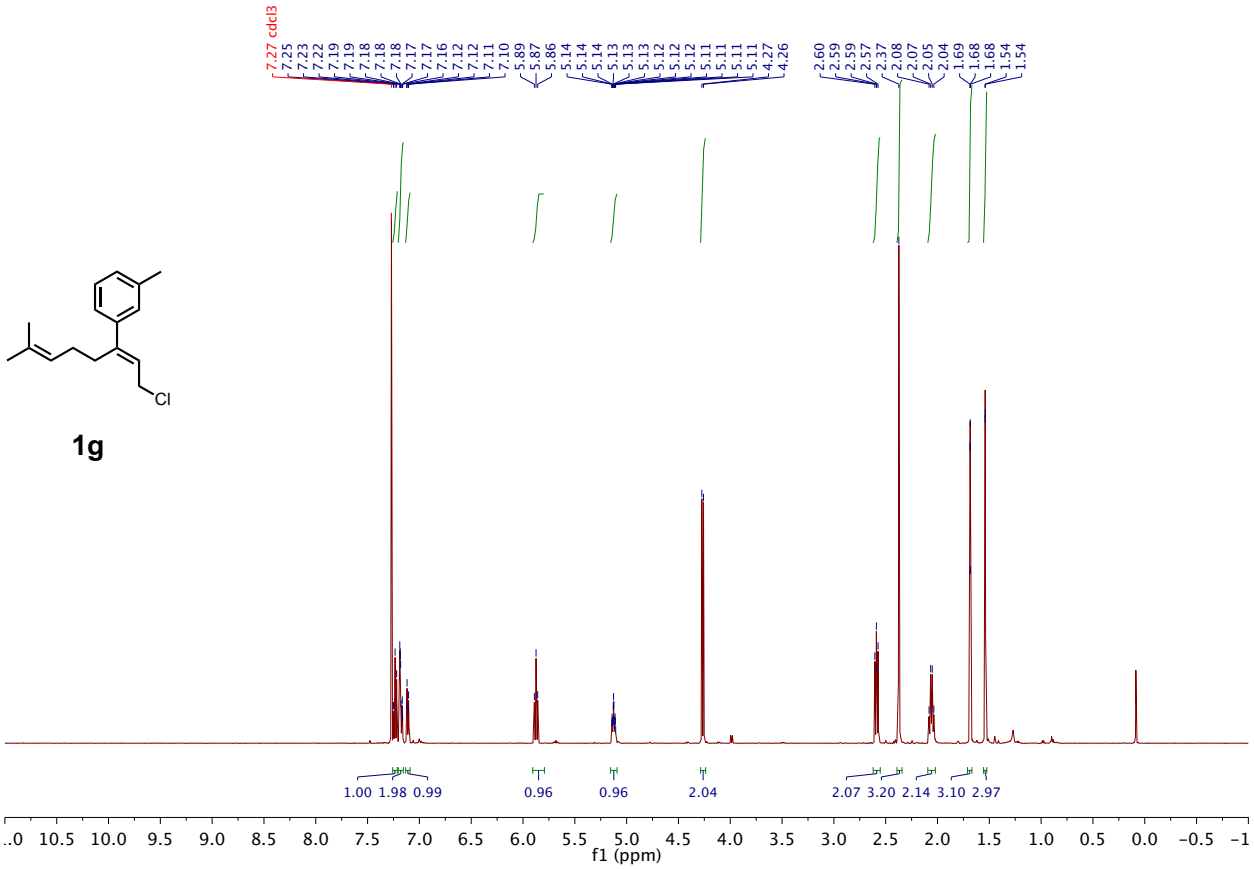
1f

^{13}C NMR, $CDCl_3$, 126 MHz

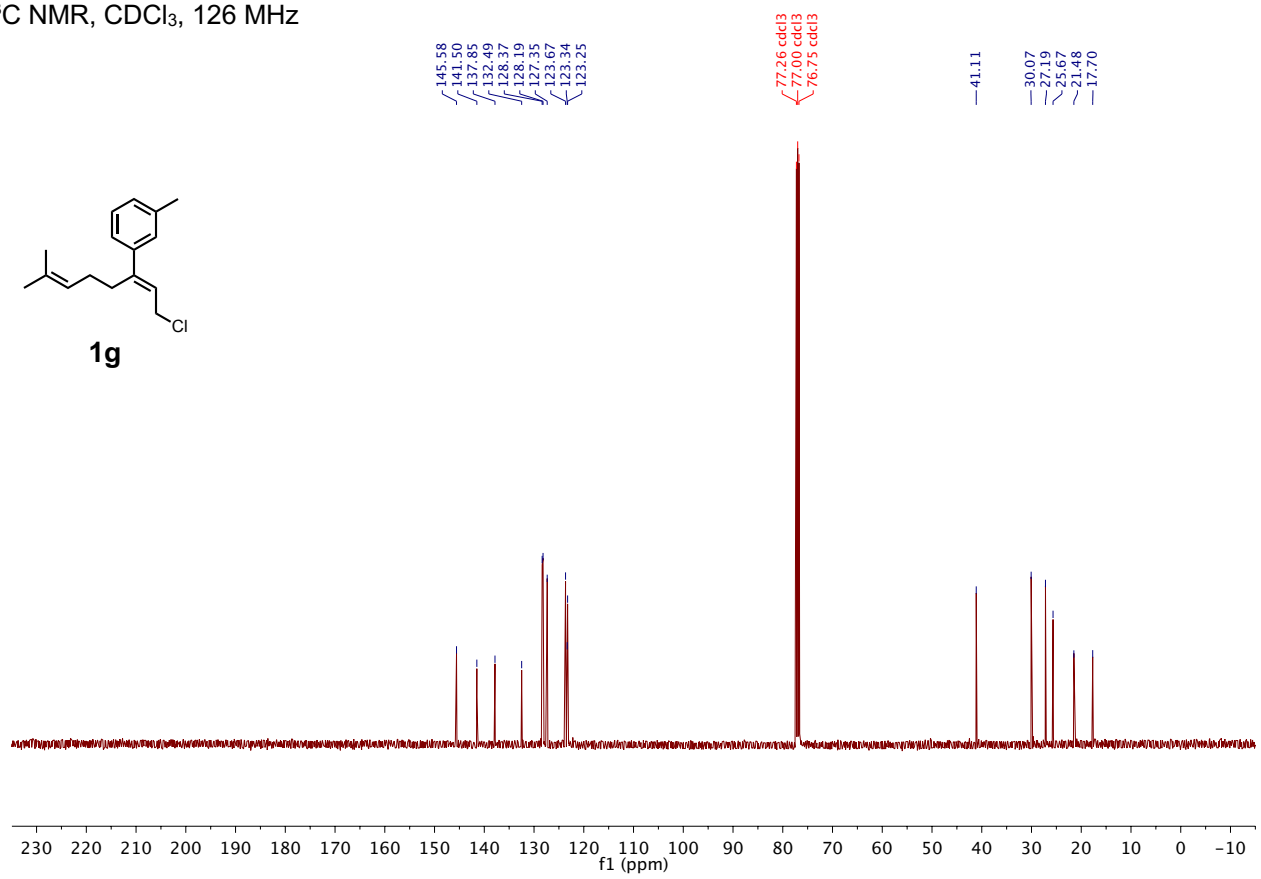


1f

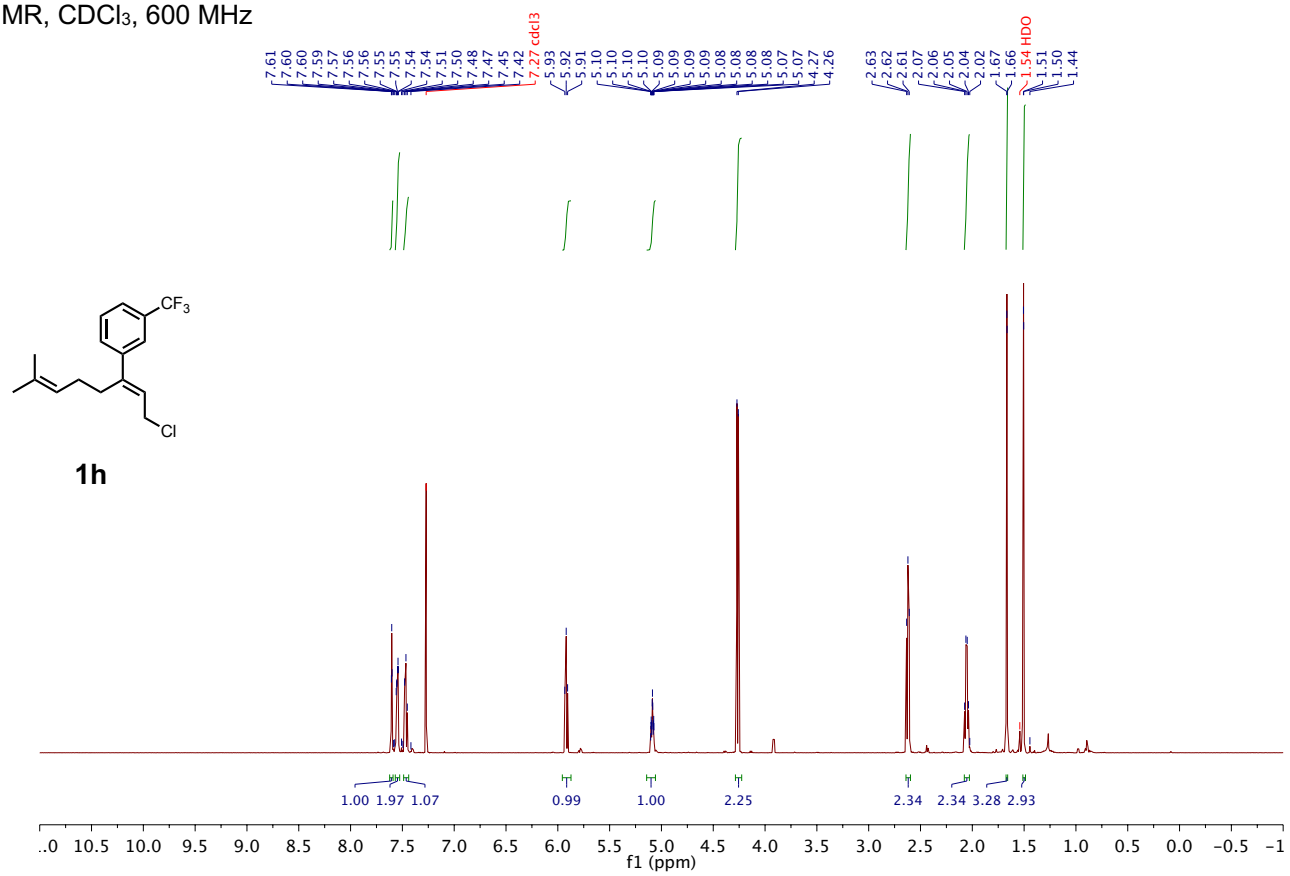
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

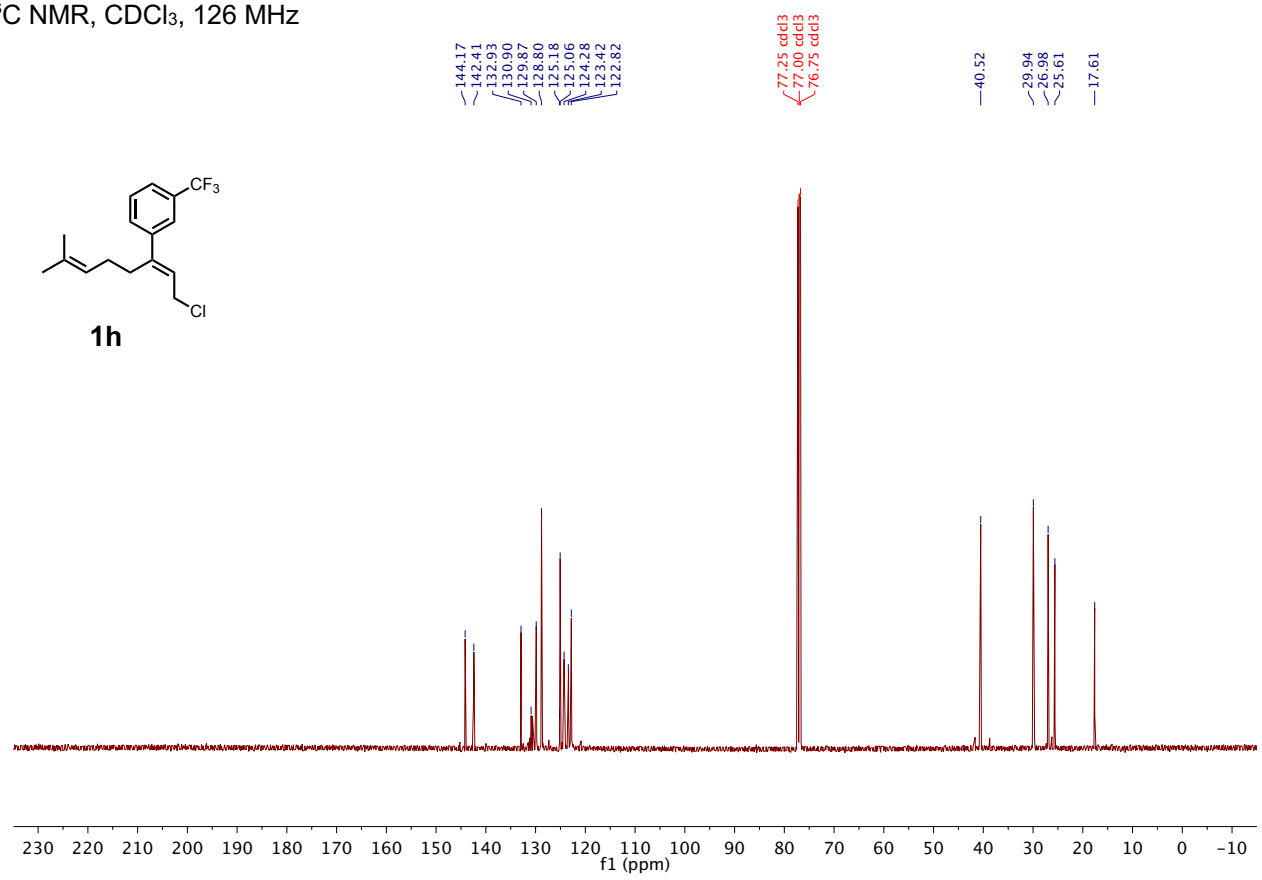


^{1}H NMR, $CDCl_3$, 600 MHz



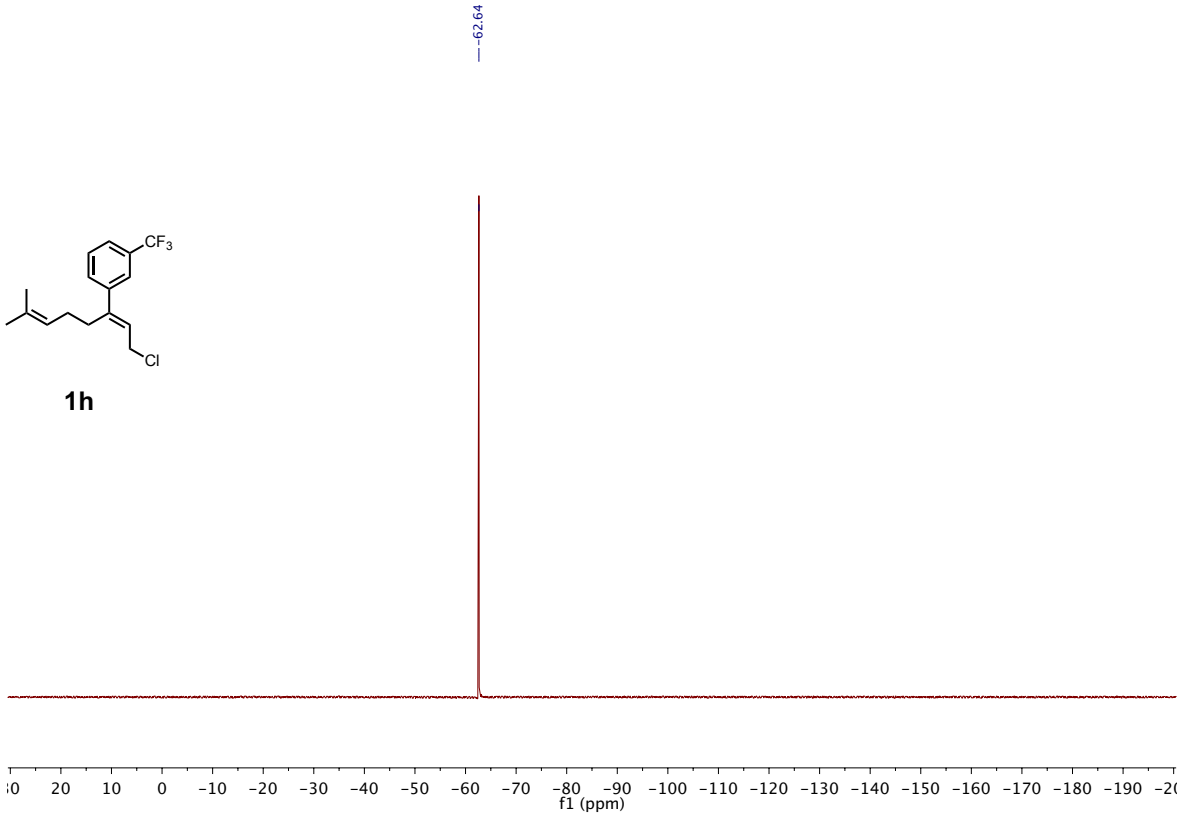
1h

^{13}C NMR, $CDCl_3$, 126 MHz

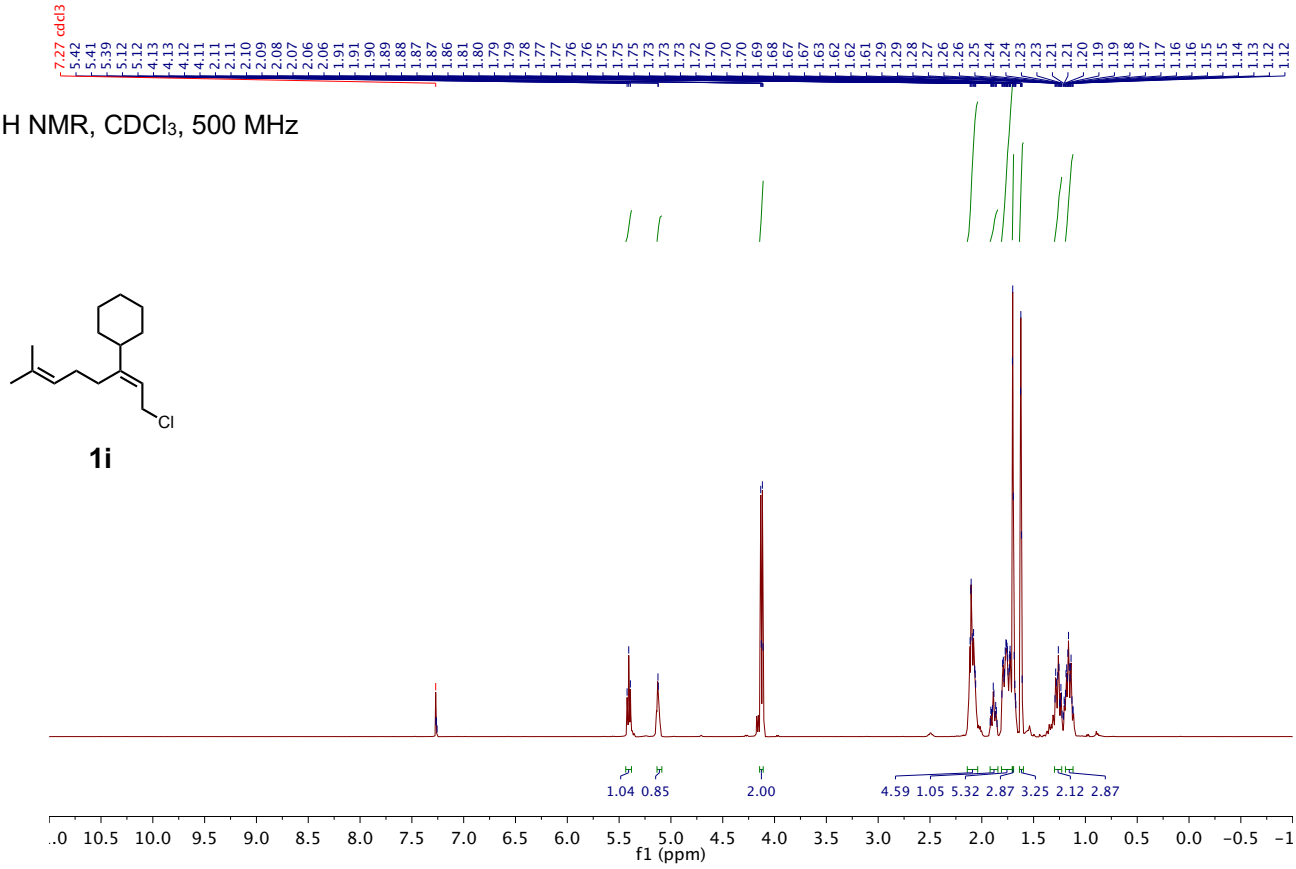


1h

^{19}F NMR, $CDCl_3$, 471 MHz

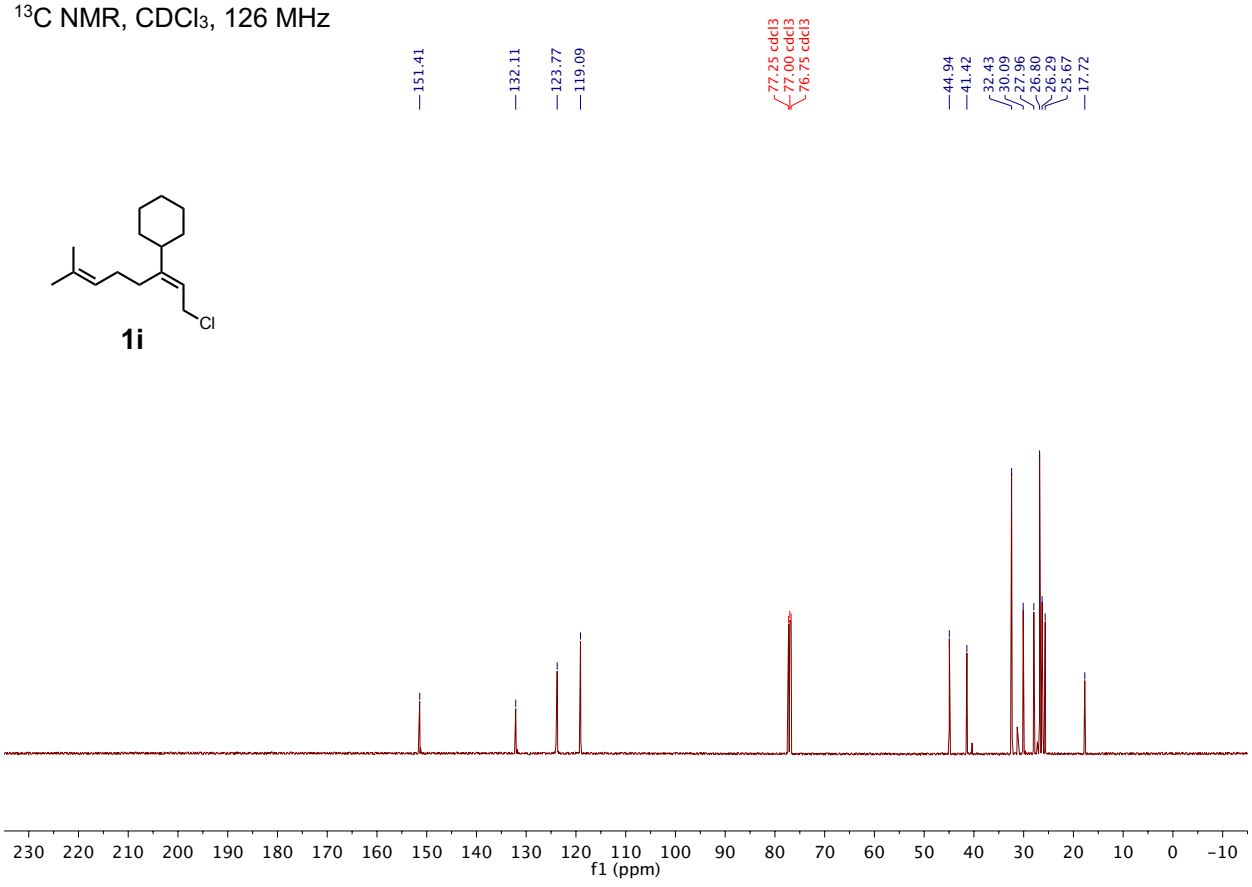


^{1}H NMR, $CDCl_3$, 500 MHz



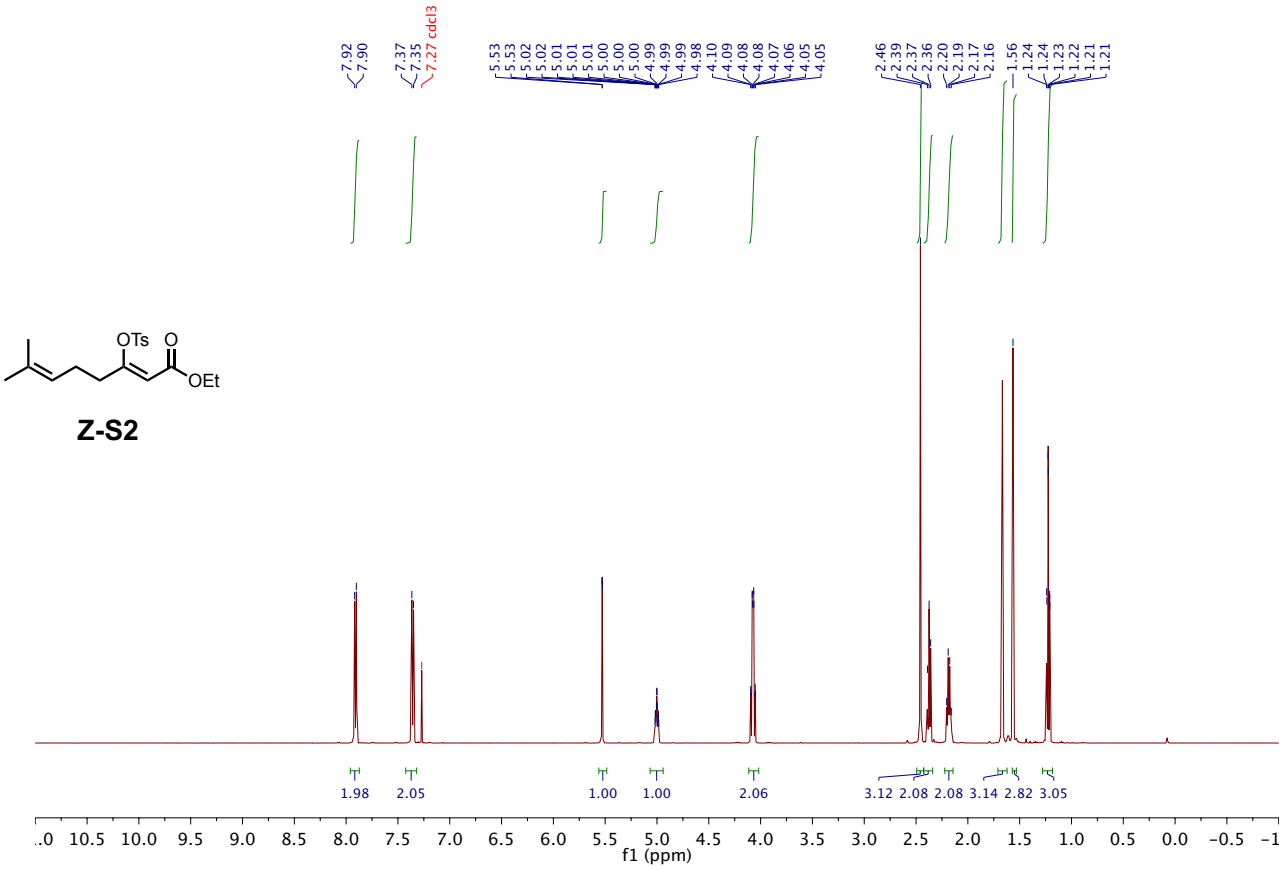
1i

^{13}C NMR, $CDCl_3$, 126 MHz



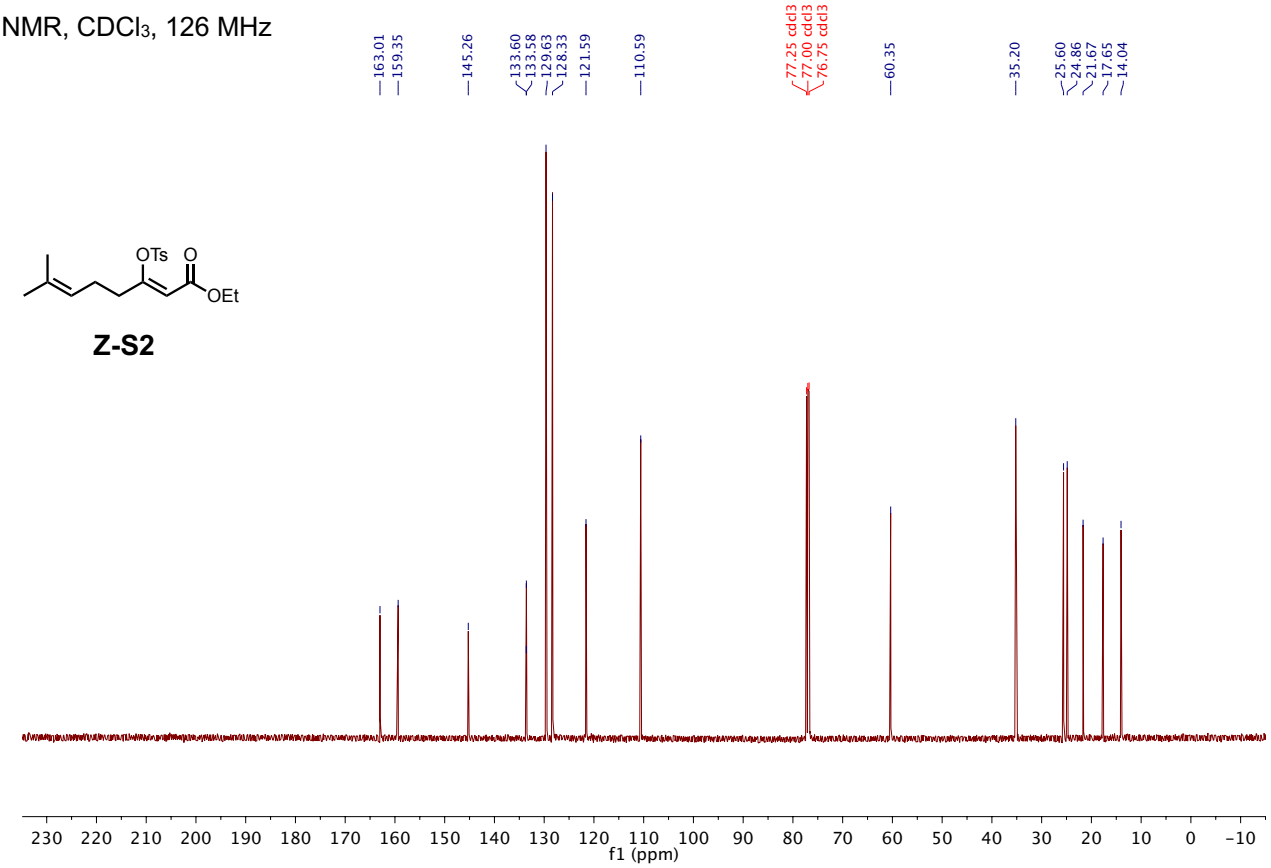
1i

^{1}H NMR, $CDCl_3$, 500 MHz



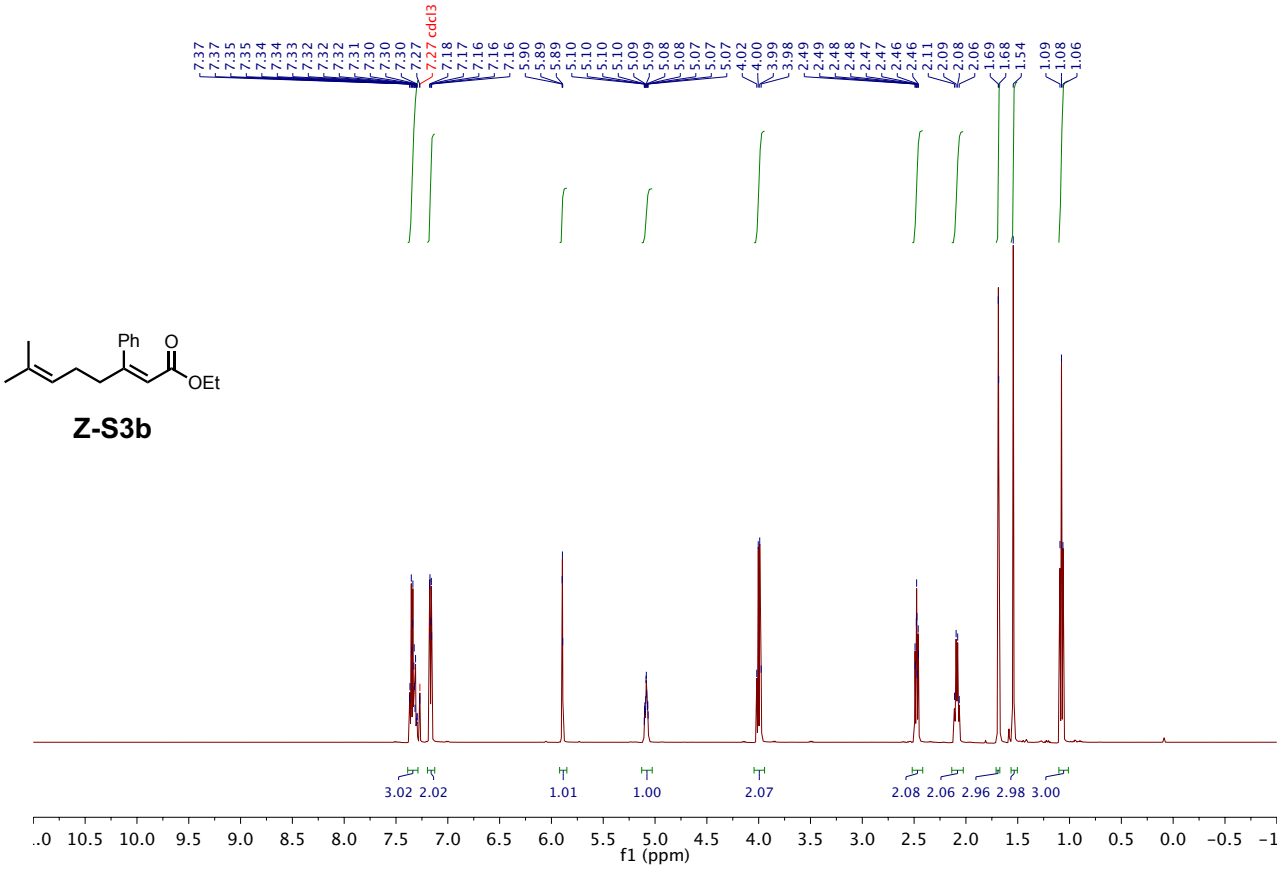
Z-S2

^{13}C NMR, $CDCl_3$, 126 MHz



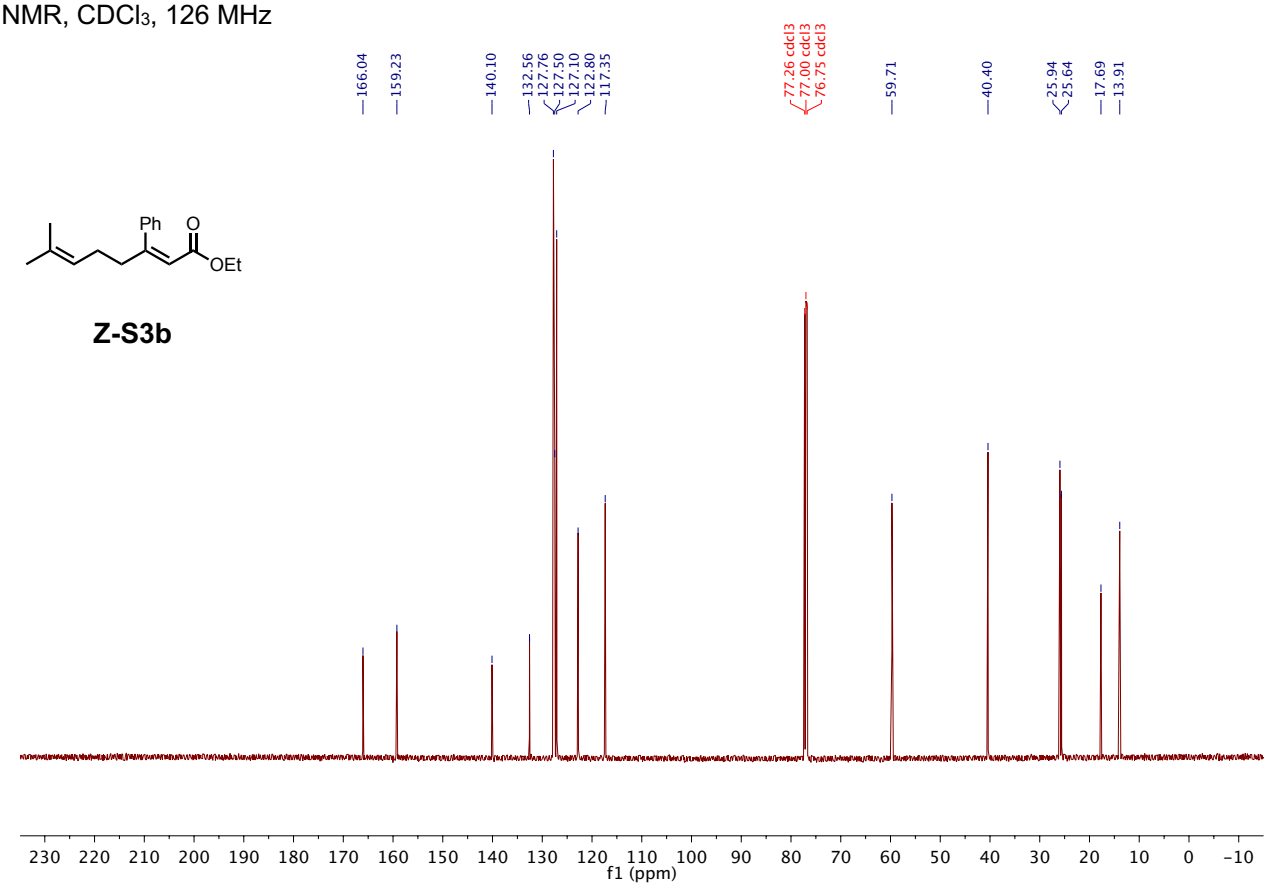
Z-S2

^{1}H NMR, $CDCl_3$, 500 MHz



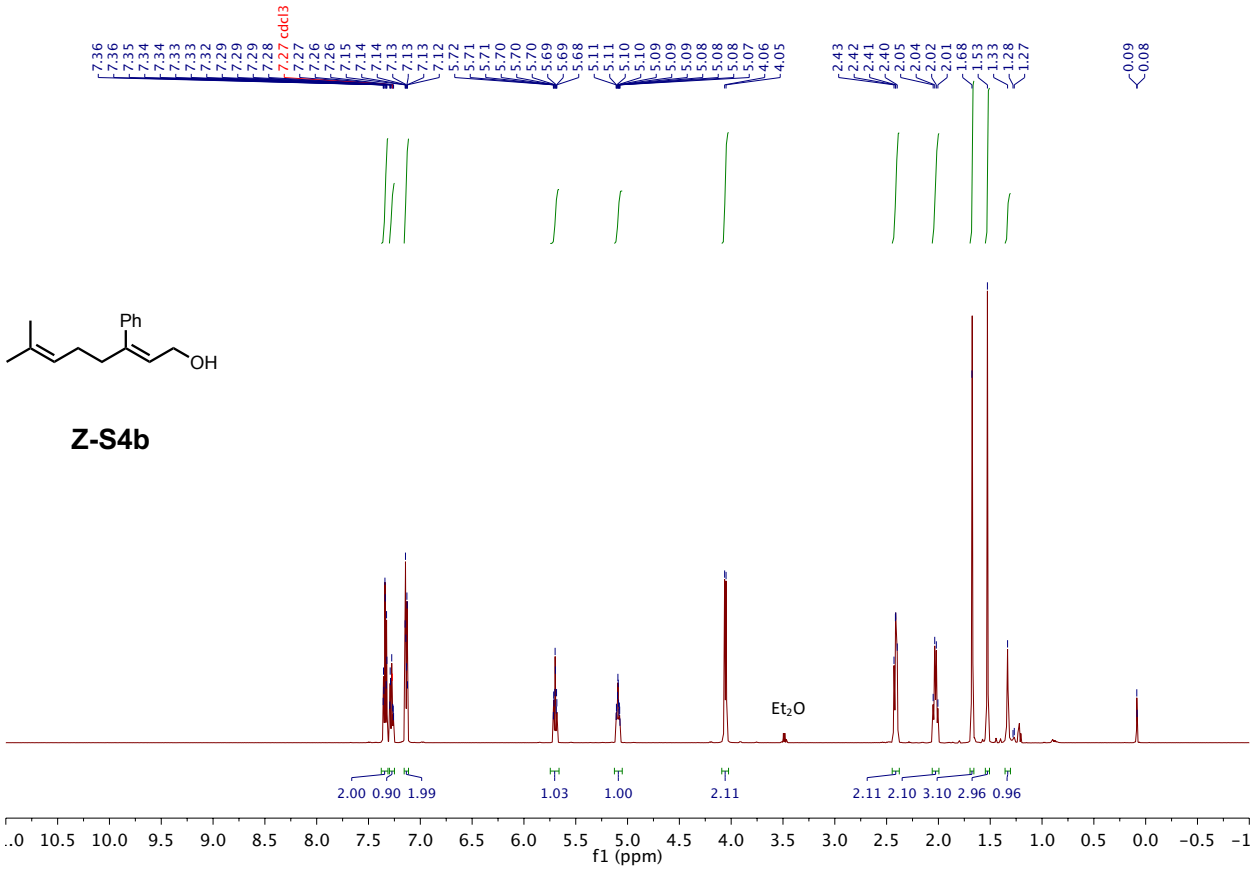
Z-S3b

^{13}C NMR, $CDCl_3$, 126 MHz



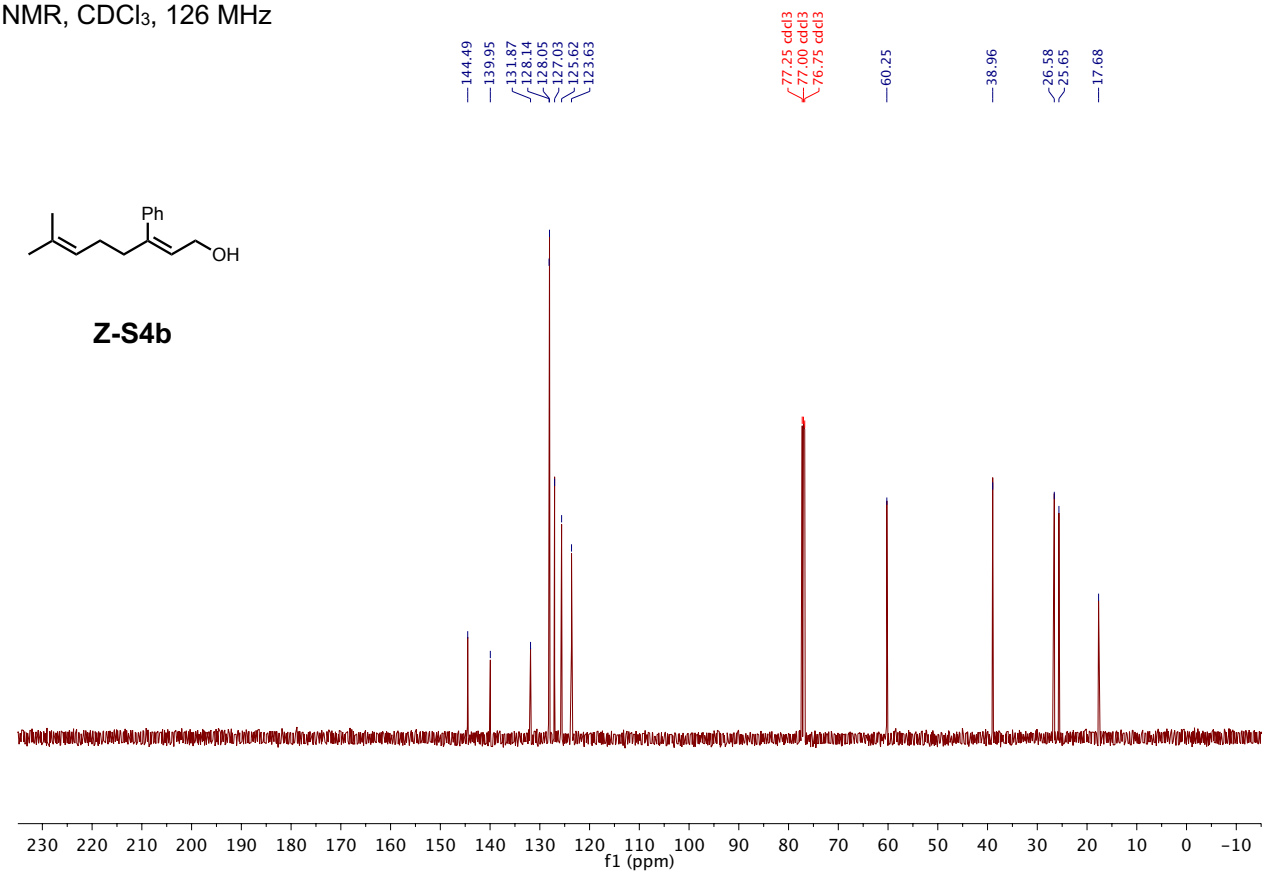
Z-S3b

^{1}H NMR, $CDCl_3$, 500 MHz



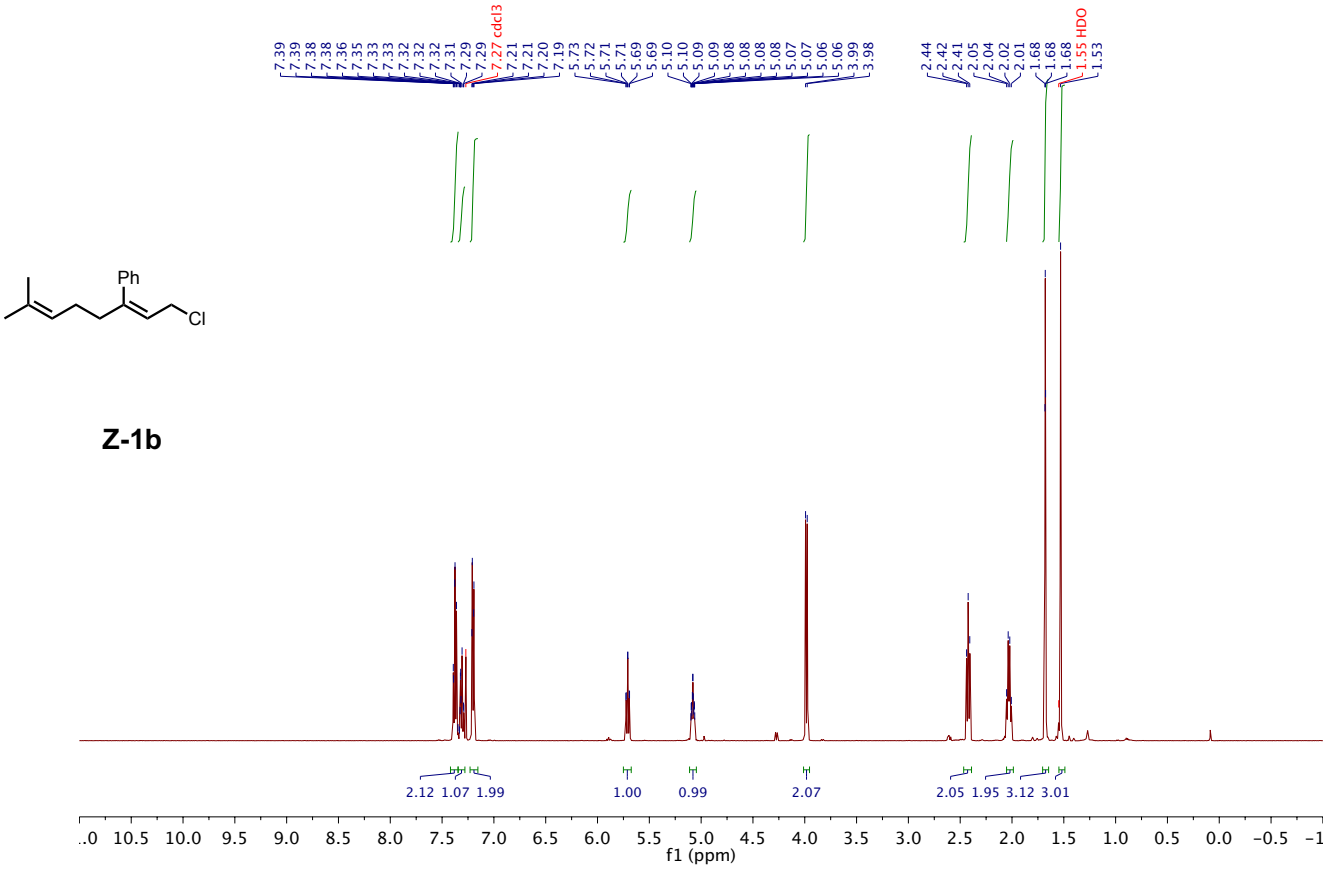
Z-S4b

^{13}C NMR, $CDCl_3$, 126 MHz



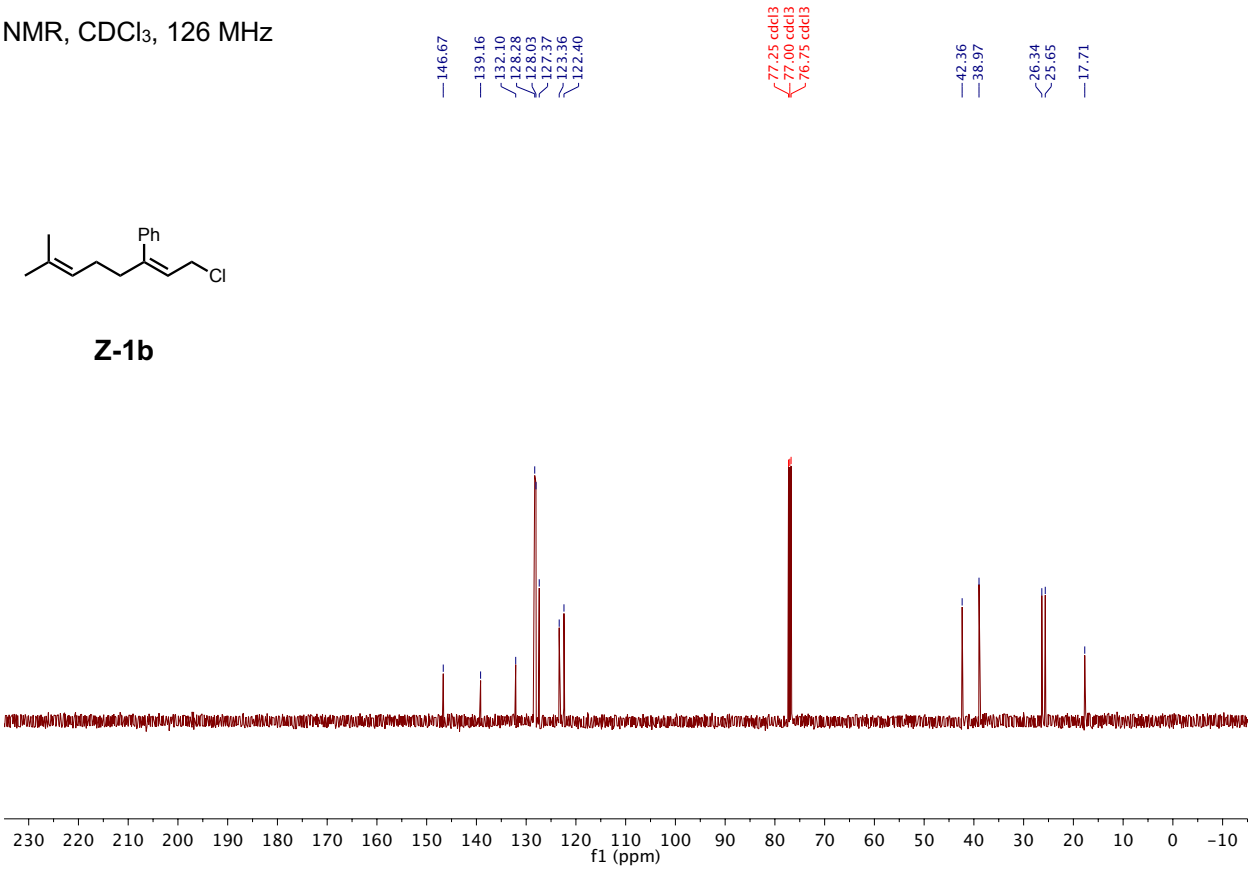
Z-S4b

^{1}H NMR, $CDCl_3$, 500 MHz



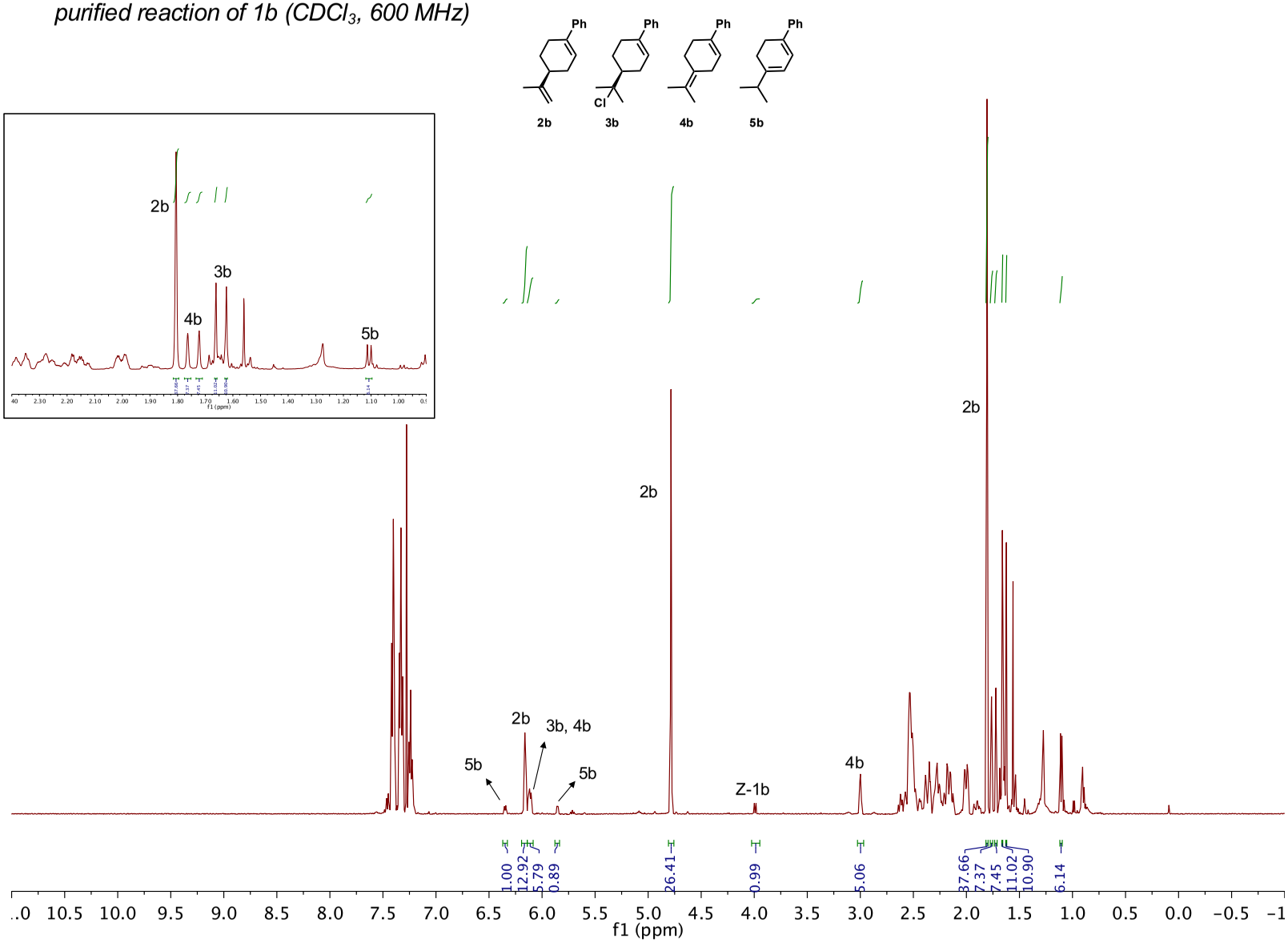
Z-1b

^{13}C NMR, $CDCl_3$, 126 MHz

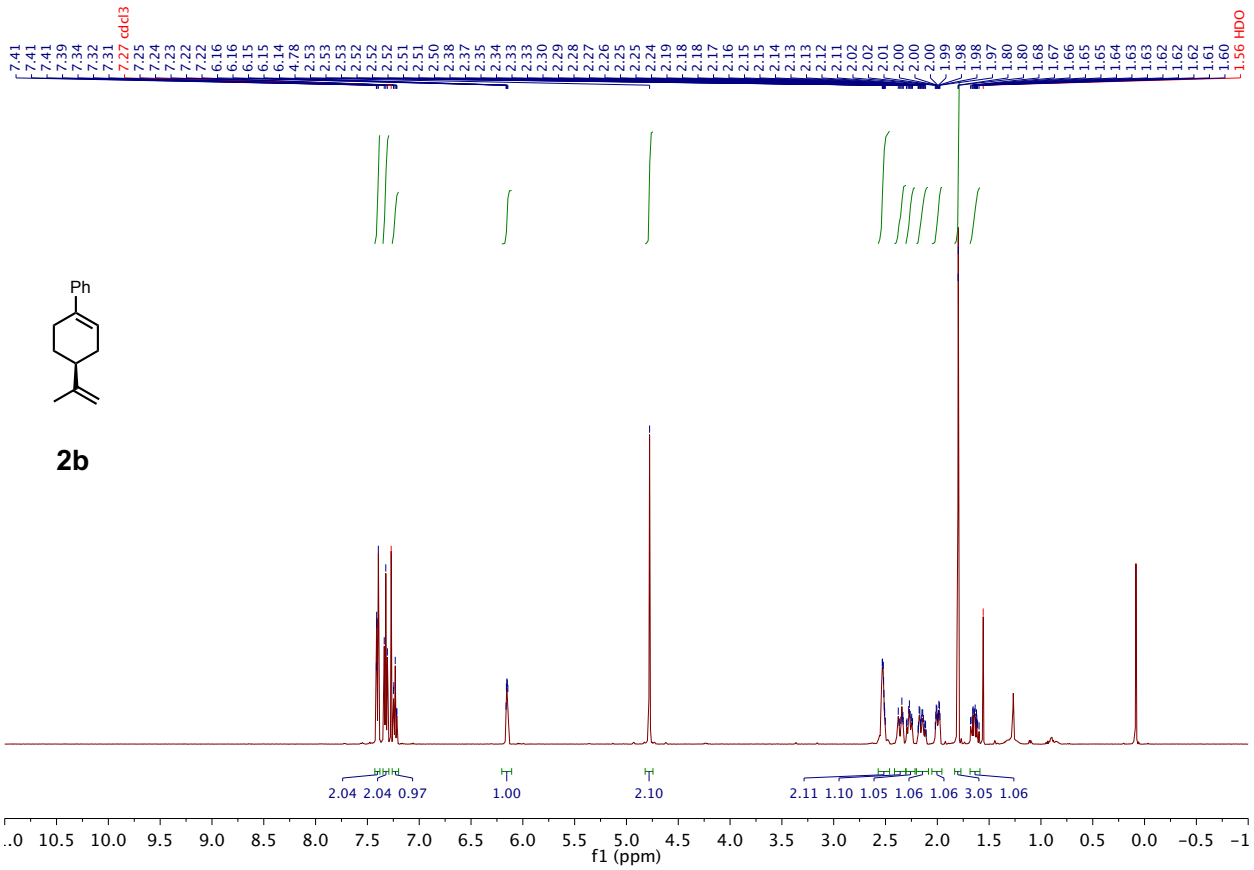


Z-1b

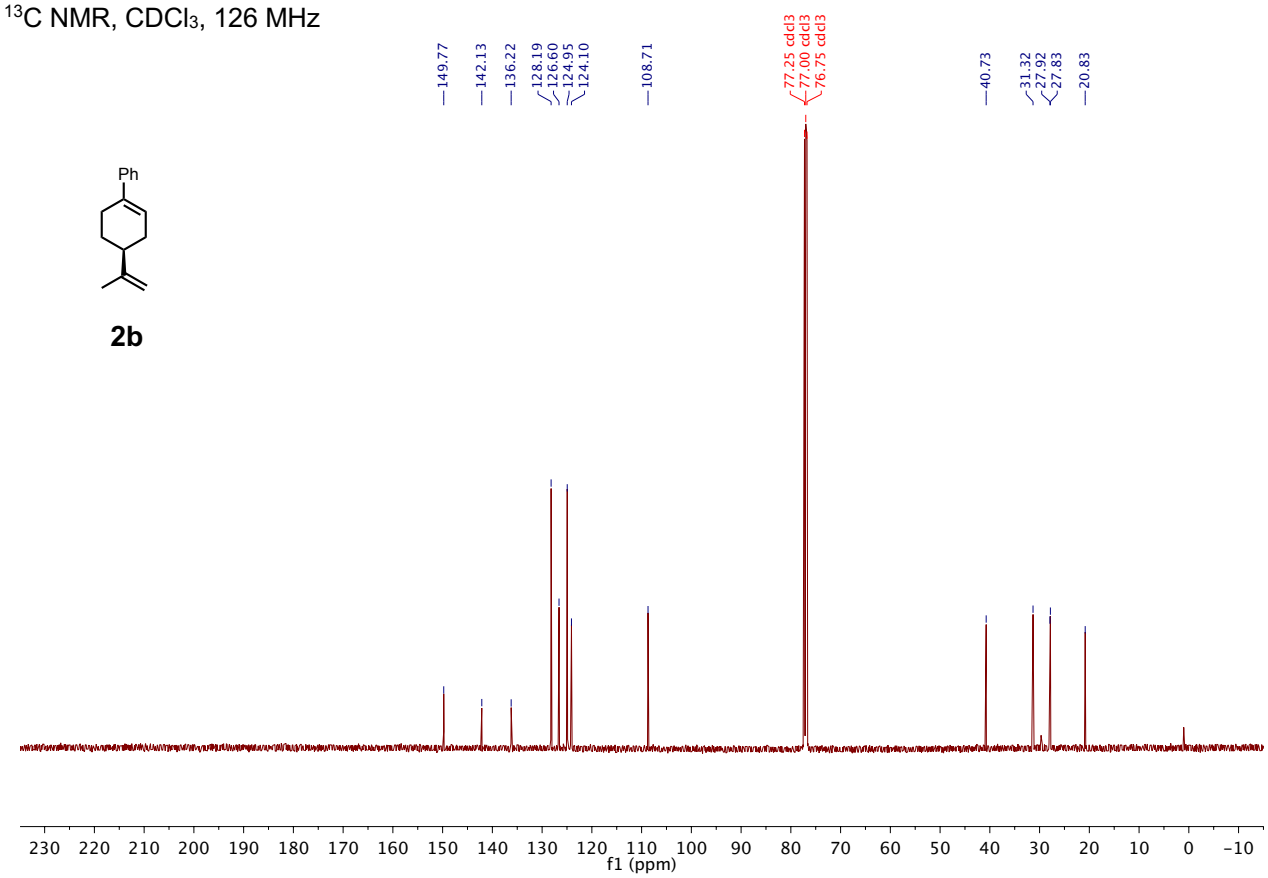
purified reaction of 1b ($CDCl_3$, 600 MHz)



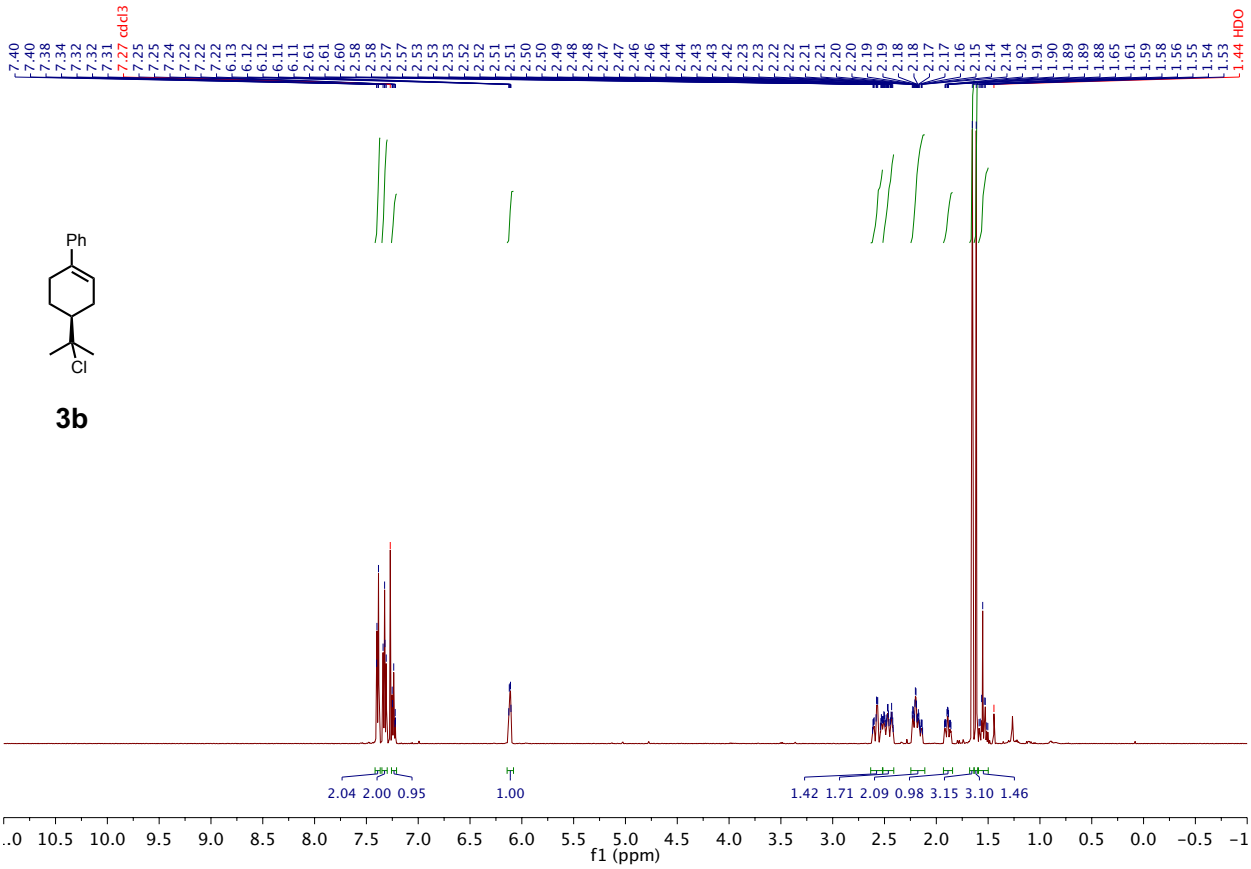
^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz

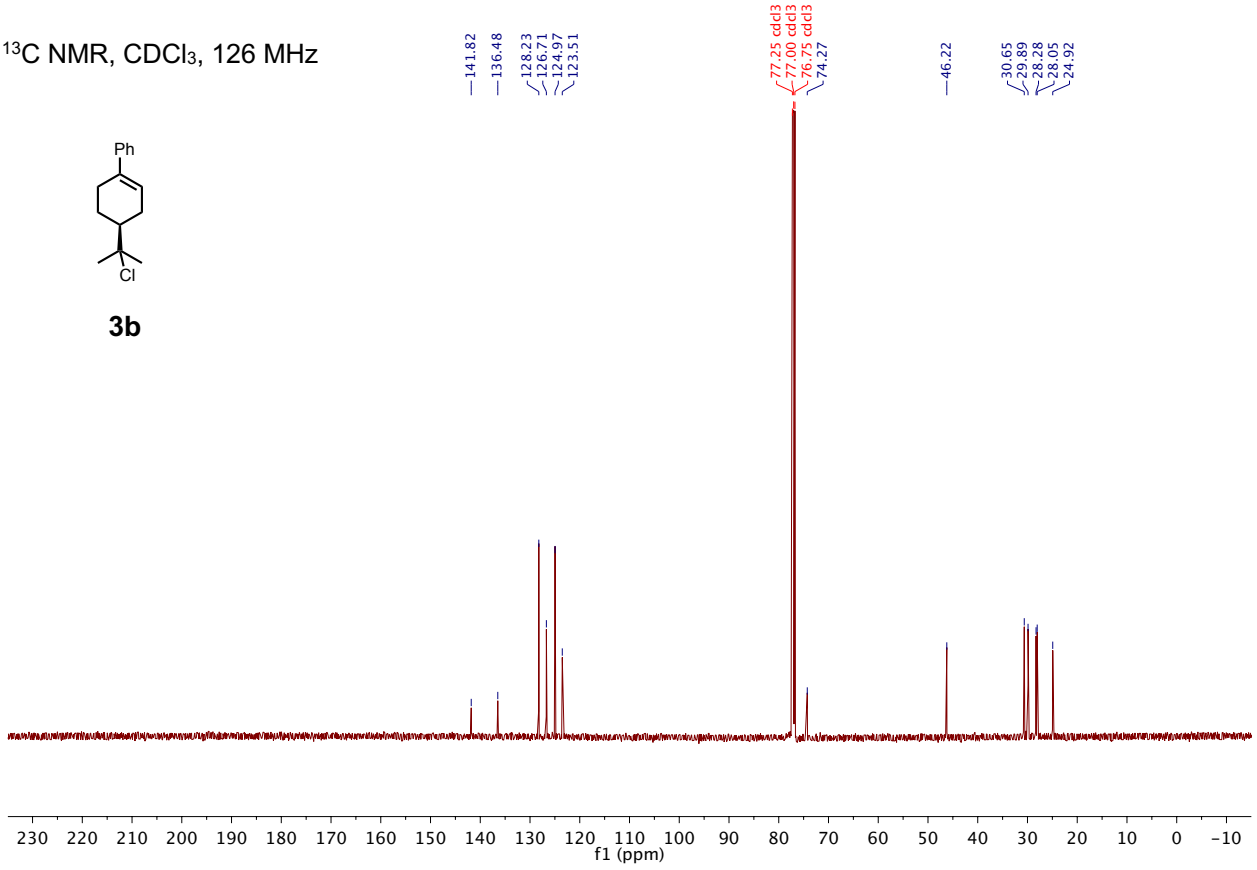


^{1}H NMR, $CDCl_3$, 500 MHz



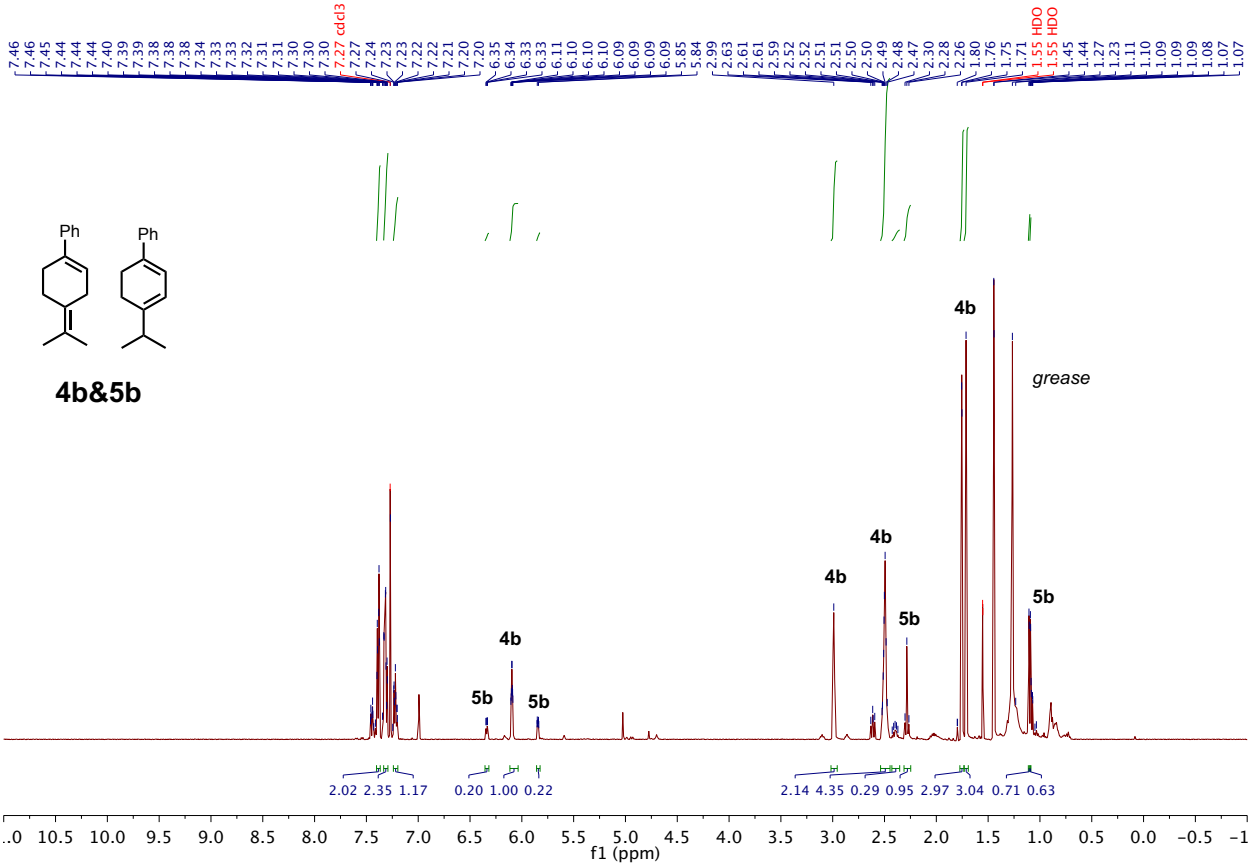
3b

^{13}C NMR, $CDCl_3$, 126 MHz

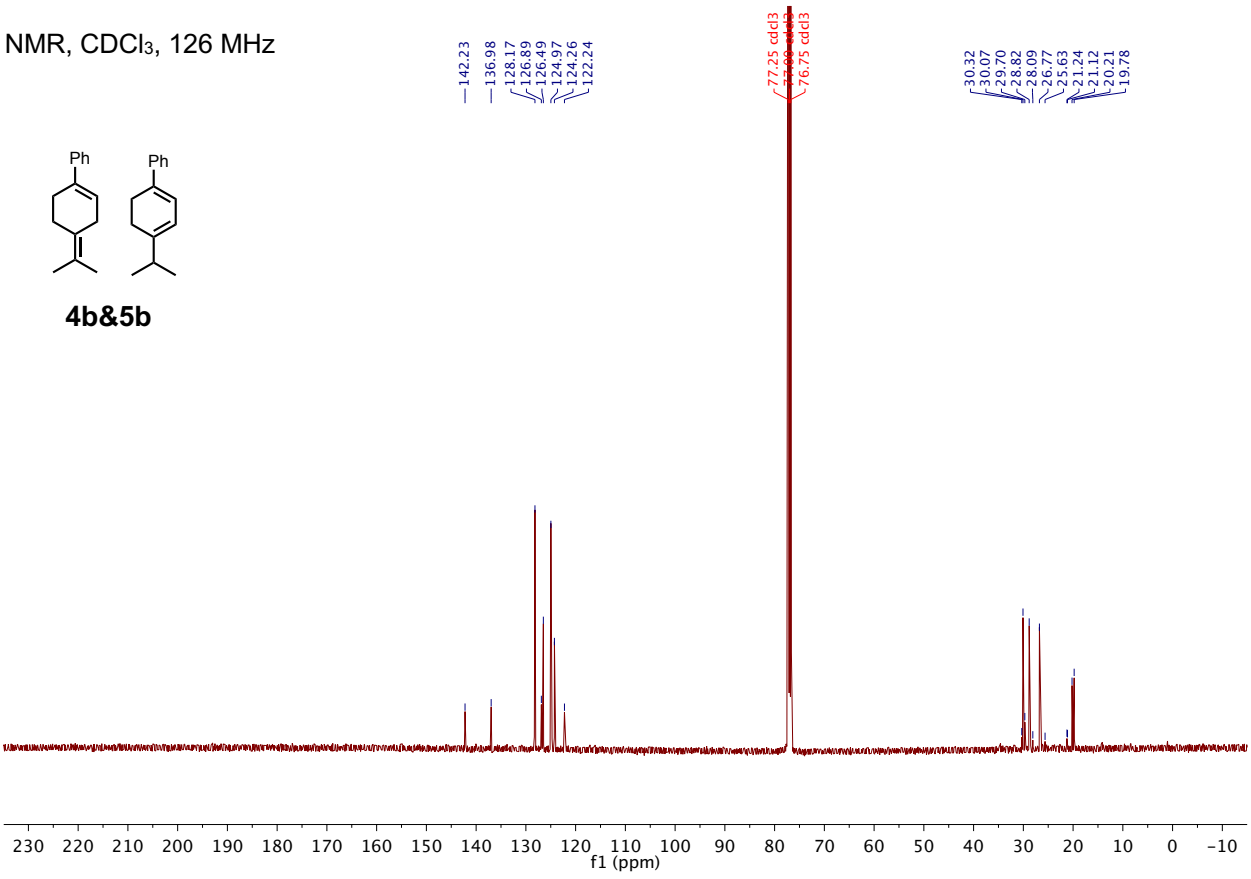


3b

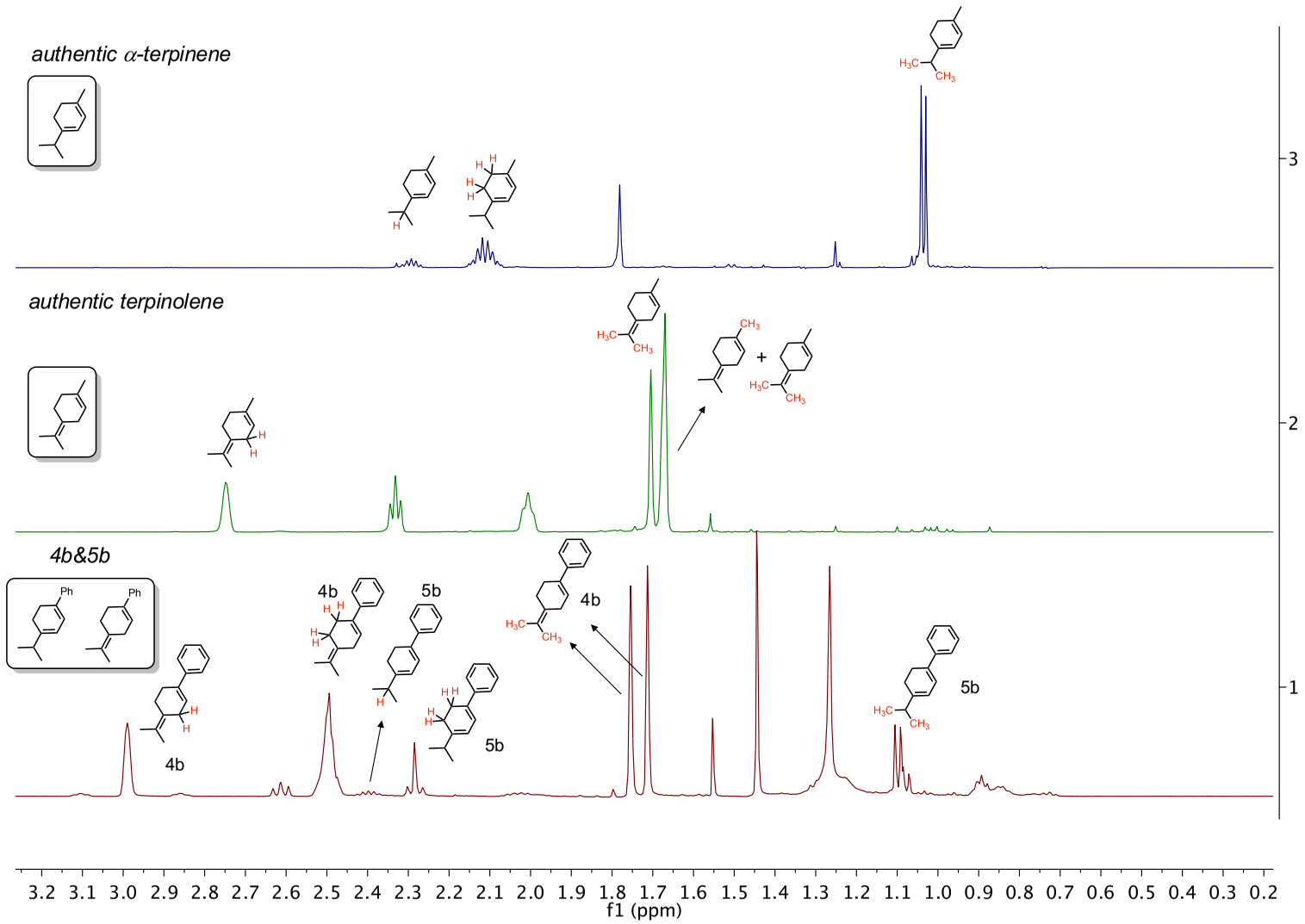
^{1}H NMR, $CDCl_3$, 500 MHz



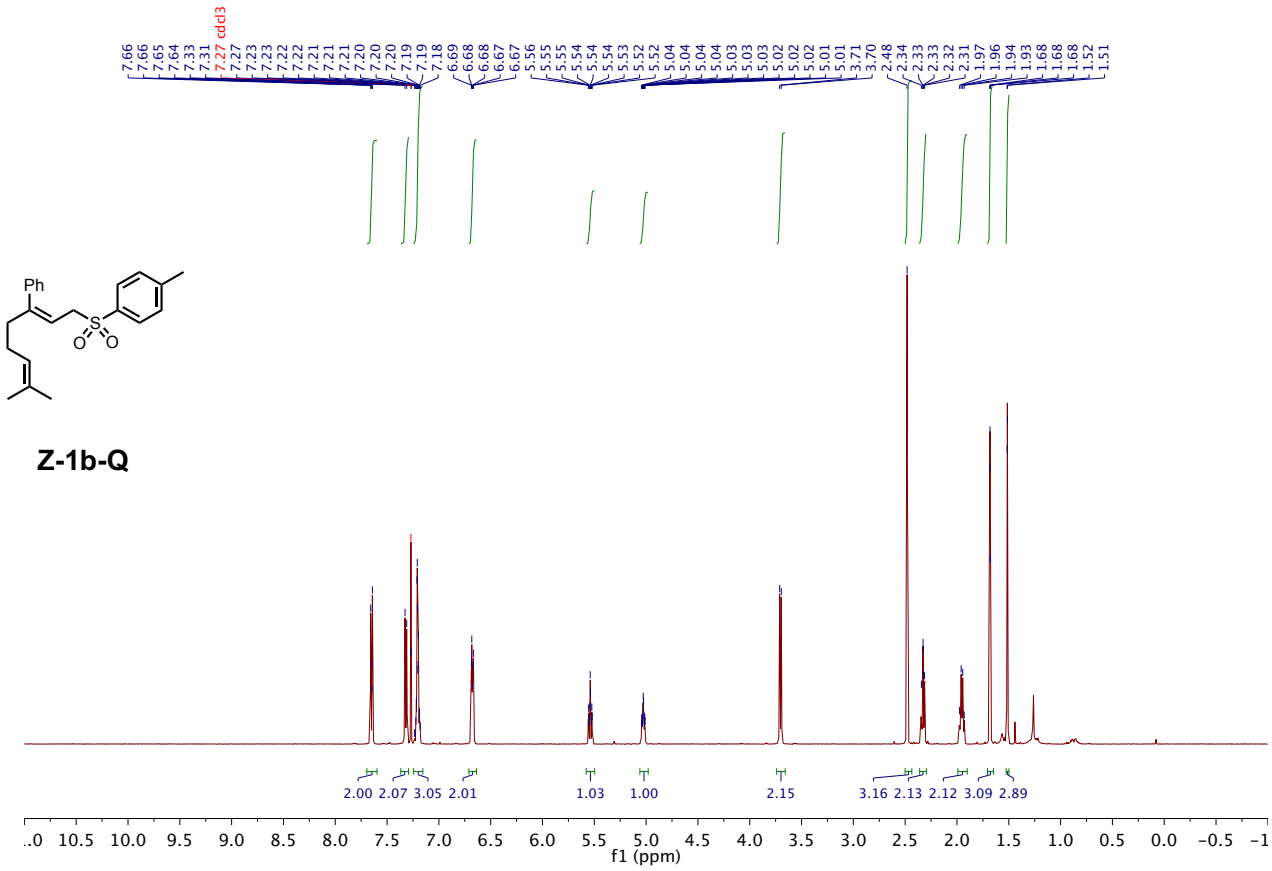
^{13}C NMR, $CDCl_3$, 126 MHz



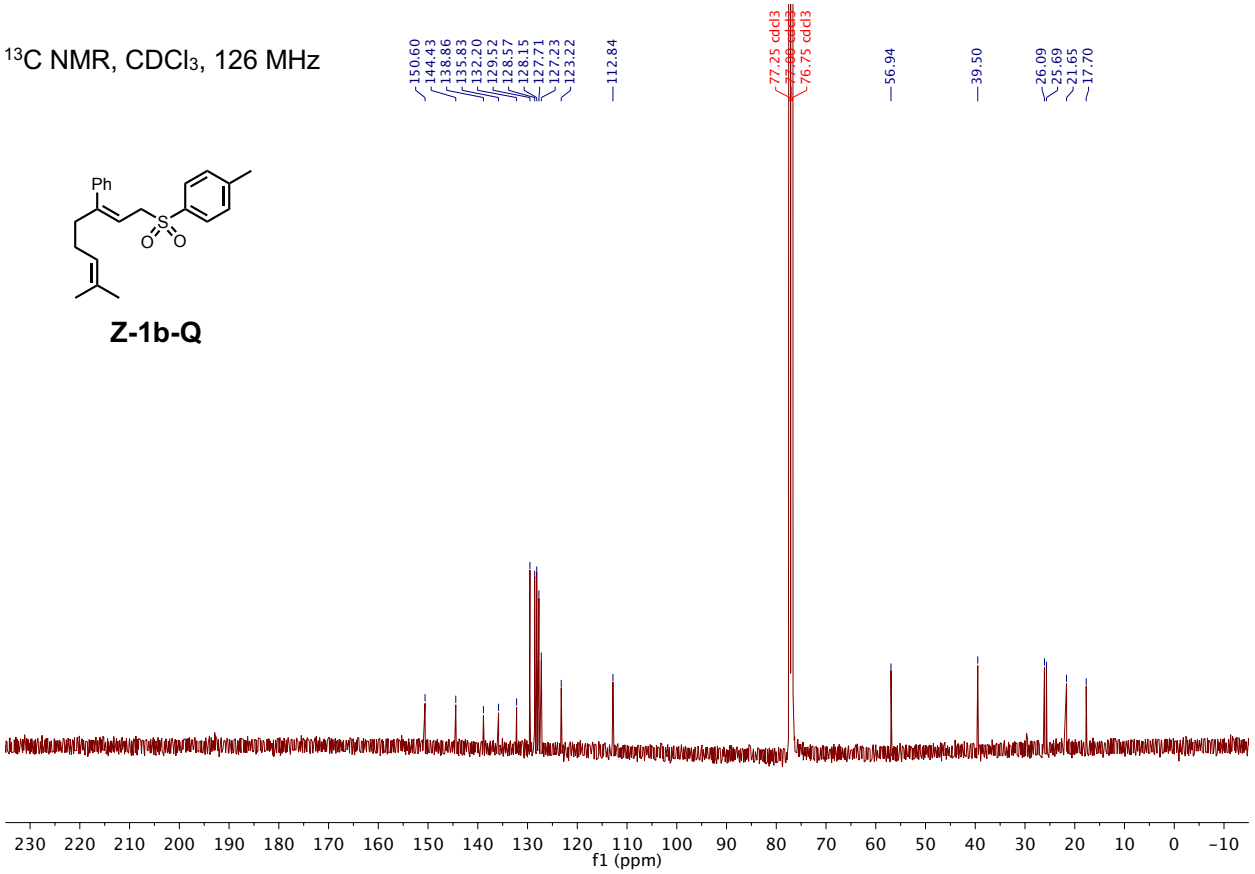
comparison of mixture of 4b&5b to monoterpene natural products ($CDCl_3$, 600 MHz)



^{1}H NMR, $CDCl_3$, 500 MHz



^{13}C NMR, $CDCl_3$, 126 MHz



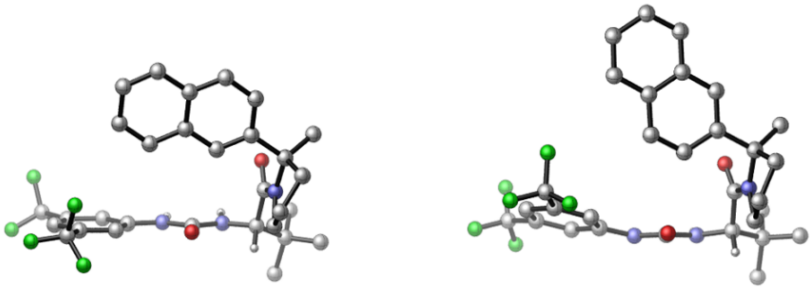
12. Computations

Density functional theory (DFT) calculations were performed with Gaussian 16.[10] The size of the system limited the number of structures that could be computed, but as thorough as possible searches were performed of catalyst conformations, substrate conformations, and relative binding orientations of the catalyst and substrate. Catalyst **7b** was used for the computational modeling since it was nearly as enantioselective as **7a** but contained fewer atoms, making it easier to compute. Substrate **1d** was used since the presence of the electron withdrawing group shortened the breaking C-Cl bond, which resulted in significantly easier optimization of transition states than for more electron rich substrates. Geometry optimizations and vibrational frequency calculations were performed at the B3LYP/6-31G(d) level of theory.[11] The choice of this model chemistry was based on the use of B3LYP in studies on cyclase chemistry by Tantillo and co-workers.[12] Free energy corrections were determined at the B3LYP/6-31G(d) level of theory at 298.15 K using Grimme's quasi-harmonic free energy correction.[13] In addition, the default Gaussian free energy correction and Truhlar's quasi-harmonic free energy correction[14] were calculated and are reported in Table S2. Quasi-harmonic corrections were computed using the GoodVibes Python package.[15] Single point energy refinements were determined at PCM-(Cyclohexane)-B3LYP-D3(BJ)/6-311+G(d,p).[11,16] Additional single-point energies were calculated for the lowest energy structure leading to each enantiomer of product and are reported in Table S2.[16d,17]

Transitions states with electronic energy differences of <0.1 kcal/mol were visually inspected for differences. If no differences could be identified, then only the lowest energy structure (based on single-point electronic energies) was retained (see Table S1 for a complete list of transition structures). All transition states were verified by the presence of one imaginary frequency. When possible, the imaginary frequency was inspected visually to ensure it corresponded to C-Cl bond breaking/C-C bond formation. However, the imaginary frequency for each of the three lowest energy transition structures leading to the minor enantiomer of product was very small, rendering their interpretation difficult. We suspect this is the consequence of a relatively flat potential energy surface for the key C-C bond forming event, which is a common feature in cyclase chemistry.[18] Non-covalent interaction analyses[19] were performed using Multiwfn software package NCIplot[20] with a box of grid data set visually using a GUI window. Structures were illustrated using CYLview v1.0.565 beta,[21] except in the case of the NCI analyses, where they were illustrated using VMD 1.9.3.[22]

Name	G[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)// B3LYP/6-31G(d)] (Hartree)	$\Delta\Delta G^{\ddagger}_{rel}$ (kcal/mol)		Name	G[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)// B3LYP/6-31G(d)] (Hartree)	$\Delta\Delta G^{\ddagger}_{rel}$ (kcal/mol)
TS-*S*-1	-5532.3442580	**0.00**		**TS-*R*-1**	-5532.3401350	**2.59**
TS-*S*-2	-5532.3430930	**0.73**		**TS-*R*-2**	-5532.3376340	**4.16**
TS-*S*-3	-5532.3428500	**0.88**		**TS-*R*-3**	-5532.3375850	**4.19**
TS-*S*-4	-5532.3406490	**2.26**		**TS-*R*-4**	-5532.3366120	**4.80**
TS-*S*-5	-5532.3403260	**2.47**		**TS-*R*-5**	-5532.3361110	**5.11**
TS-*S*-6	-5532.3398160	**2.79**		**TS-*R*-6**	-5532.3338120	**6.55**
TS-*S*-7	-5532.3394860	**2.99**		**TS-*R*-7**	-5532.3330730	**7.02**
TS-*S*-8	-5532.3284300	**9.93**		**TS-*R*-8**	-5532.3330180	**7.05**
TS-*S*-9	-5532.3246870	**12.28**		**TS-*R*-9**	-5532.3286510	**9.79**
TS-*S*-10	-5532.3238250	**12.82**		**TS-*R*-10**	-5532.3103610	**21.27**
TS-*S*-11	-5532.3229250	**13.39**				
TS-*S*-12	-5532.3215220	**14.27**				
TS-*S*-13	-5532.3207140	**14.77**				
TS-*S*-14	-5532.3150020	**18.36**				
TS-*S*-15	-5532.3133070	**19.42**				
TS-*S*-16	-5532.3129070	**19.67**				

Table S1. Computed transition structures. All geometry optimizations and vibrational frequency calculations were conducted at B3LYP/6-31G(d). Grimme's quasi-RRHO free energy correction was applied and single-point refinement of the electronic energy was performed at PCM-(CyH)-B3LYP-D3(BJ)/6-311+G(d,p). The relative free energies are defined relative to that of **TS-*S*-1**. The main structural feature that was considered for catalyst geometry was the rotamer about the naphthyl-pyrrolidine bond:



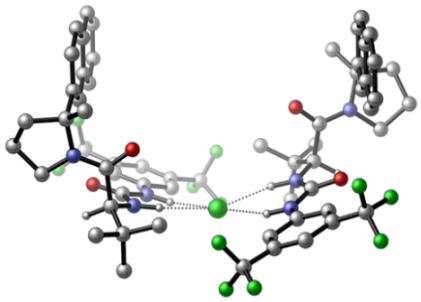
lower energy rotamer higher energy rotamer

In general, structures where one or both of the catalysts were in the rotamer depicted on the left were lower in energy (compare **TS-*S*-1**, **TS-*S*-2**, **TS-*S*-3**, **TS-*S*-4**, and **TS-*S*-5**). The urea conformations examined are consistent with those previously reported.[23] The main structural feature that was considered for the substrate was whether the nucleophilic olefin was positioned "endo" or "exo" to the forming ring:

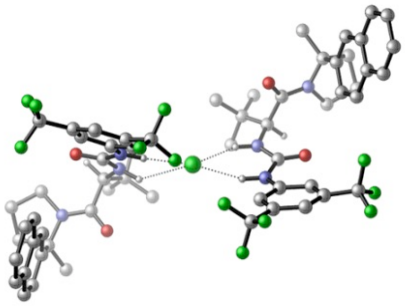
"endo" attack
(to *S*-enantiomer)

"exo" attack
(to *R*-enantiomer)

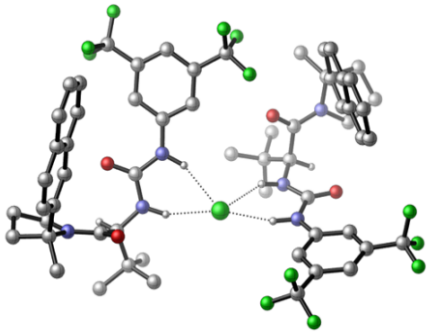
This was a critical factor as alternating between endo and exo attack for otherwise-identically positioned substrates inverts the forming stereocenter (see above). In our computational model endo attack was found to be strongly preferred (the lowest 8 major transition states and the lowest 4 minor transition states all have an endo orientation of the nucleophile), particularly for transition states leading to the major enantiomer of product where it positioned the methyls of the incoming nucleophile in proximity to a naphthyl on one of the catalysts (see below). Moreover, this orientation is consistent with the observed stereochemical outcome of stereospecific reactions of linalool derivatives[24] and a prior proposal for the displacement of neryl leaving groups.[25] On the basis of kinetic evidence indicating the presence of two molecules of catalyst in the transition state only dimeric structures were modeled. On the basis of prior studies from our it was assumed that the catalyst would bind chloride via a 4-H cooperative mechanism.[23] Four classes of 4-H structures were considered – "tail-to-head" distorted square planar dimers, "head-to-head" distorted square planar dimers, "tetrahedral" dimers, and "T-shaped" dimers:



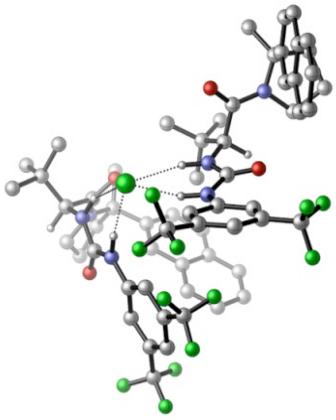
"tail-to-head" dimer



"head-to-head" dimer



"tetrahedral" dimer



"T-shaped" dimer

The "tail-to-head" distorted square planar dimers were found to be by far the lowest in energy (the 7 lowest major transition states and the 9 lowest minor transition states are all tail-to-head dimers), consistent with previous studies from our lab.[23] Consequently, the majority of the computational effort was focused on tail-to-head dimers. Efforts were made to vary the positioning of the substrate within the catalyst dimer, though due to the confined steric environment, not much variation was possible.

Entry	Model chemistry of single point calculation	TS-*S*-1 (Hartree)	TS-*R*-1 (Hartree)	$\Delta\Delta G^{\ddagger}_{rel}$ (kcal/mol)
1	PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)	-5532.3442580	-5532.3401350	2.59
2	PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p) (Truhlar-quasi-RRHO)	-5532.3367310	-5532.3324200	2.71
3	PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p) (Gaussian default RRHO)	-5532.3382100	-5532.3344170	2.38
4	PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p) (electronic energy)	-5533.6453190	-5533.6397050	3.52
5	SMD(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)	-5532.3872320	-5532.3843430	1.81
6	B3LYP-D3(BJ)/6-311+G(d,p)	-5532.3346990	-5532.3303950	2.70
7	PCM(CyH)-B3LYP/6-311+G(d,p)	-5531.8467870	-5531.8465940	0.12
8	B3LYP/6-31G(d)	-5530.3764570	-5530.3744940	1.23
9	PCM(CyH)-B3LYP-D3BJ/def2-TZVPP	-5532.9488020	-5532.9445510	2.67
10	PCM(CyH)-B97-D3/6-311+G(d,p)	-5528.9714570	-5528.9672730	2.63
11	PCM(CyH)-M062X/6-311+G(d,p)	-5529.9487430	-5529.9376390	6.97
12	PCM(CyH)-ωB97-xD/6-311+G(d,p)	-5530.3691160	-5530.3616590	4.68

Table S2. Comparison of TS-*S*-1 and TS-*R*-1 with different model chemistries and thermal corrections. Entry 1 shows the free energies of **TS-*S*-1** and **TS-*R*-1** computed using the standard model chemistry for the single point electronic energy and free energy correction (B3LYP-D3(BJ)/6-311+G(d,p) using Grimme's quasi-RRHO free energy correction). In entries 2-4 the free energy correction is varied and the standard model chemistry is used for the single-point electronic energy calculation. In entries 5-12 the model chemistry used to compute the electronic energy is varied and the standard free energy correction (Grimme's quasi-RRHO model) is applied. In entries 5-6 the solvent model is varied. In entry 7 the dispersion correction is removed. Entry 8 shows the energetic gap at the level of theory used for geometry optimization. Entry 9 shows an alternate basis set. Entries 10-12 show alternate

functionals. With the exception of entry 7 (no dispersion correction) which predicts a poorly-selective reaction, these were found to consistently predict the correct sense of enantioinduction, supporting the validity of the model.

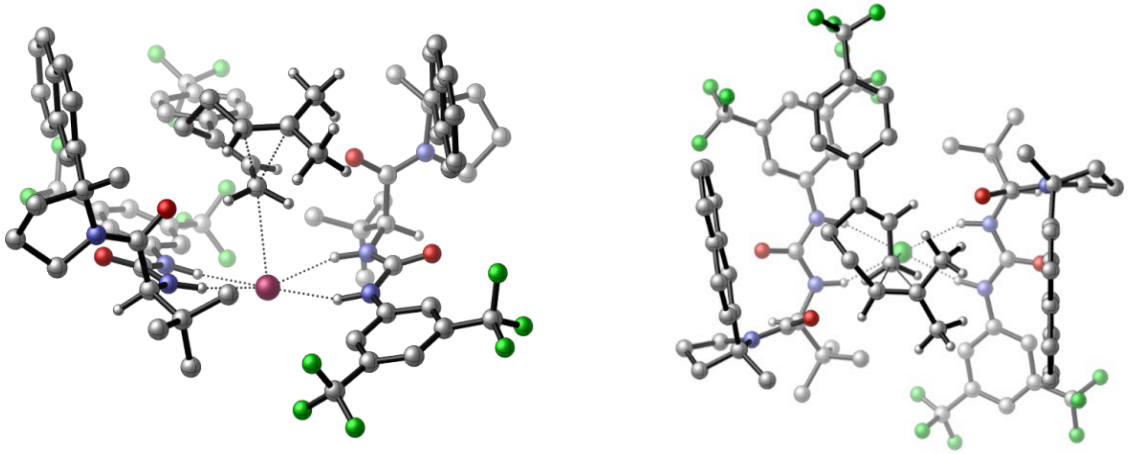


Figure S25. Two perspectives of TS-*S*-1. The lowest energy transition structure leading to the major enantiomer of **2d** with catalyst **7b** is depicted from the rear and from the top. The computed transition structure shows a highly asynchronous S_N2-type mechanism with extremely advanced bond-breaking. The two methyl substituents of the nucleophilic olefin are aligned over the rings of the naphthyl substituent of the catalyst on the right, suggesting a possible stabilizing interaction. Notably, this interaction is significantly attenuated in **TS-*R*-1** (see Figure S26 and S27), consistent with the experimental data in Figure 5 indicating preferential stabilization of the major pathway by the aryl substituent on catalyst pyrrolidine. The amides on both catalysts are also positioned in close proximity to the forming C-C bond, suggesting the possibility of stabilizing interactions with developing positive charge in the transition state or with acidified C-H bonds, but in the absence of a more detailed computational model or experimental support this remains speculative. The model also suggests a pi-stacking interaction between the aryl substituent on the substrate and the 3,5-bis(trifluoromethyl)aniline of the catalyst on the left, which also appears to be present in the minor pathway.

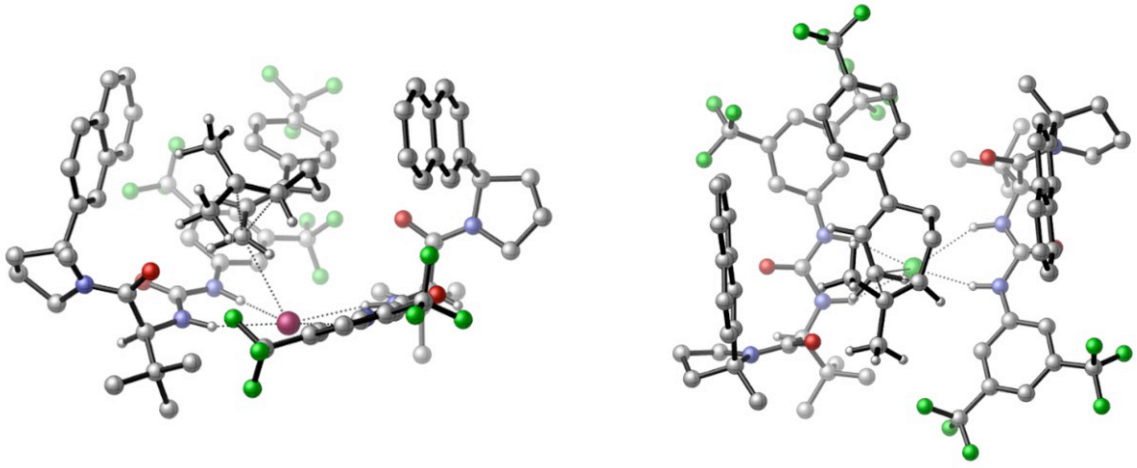


Figure S26. Two perspectives of TS-*R*-1. The lowest energy transition structure leading to the minor enantiomer of **2d** with catalyst **7b** is depicted from the rear and from the top. The computed transition structure shows a high degree of C-Cl bond breaking, including significant geometric reorganization away from the expect linear trajectory for an S_N2 reaction, but no earlier transition state was located along the reaction coordinate corresponding to C-Cl ionization. In comparison to the lowest energy major transition structure (see Figure S25 and S27) the alignment between the methyl substituents of the nucleophilic olefin and the naphthyl group of the catalyst on the left is relatively poor. This is consistent with the experimental data in Figure 5, which indicates stabilization of the minor transition state by the aryl substituent of the catalyst pyrrolidine, but to a lesser extent than in the major pathway. As with TS-S-1, the amide of the catalyst on the left is placed in close proximity to the forming C-C bond, and therefore, near developing positive charge and acidified C-H bonds, suggesting a potential role for the amide in transition state stabilization. Similarly, the model also suggests a pi-stacking interaction between the aryl substituent on the substrate and the 3,5-bis(trifluoromethyl)aniline of the catalyst on the left, which also appears to be present in the major pathway.

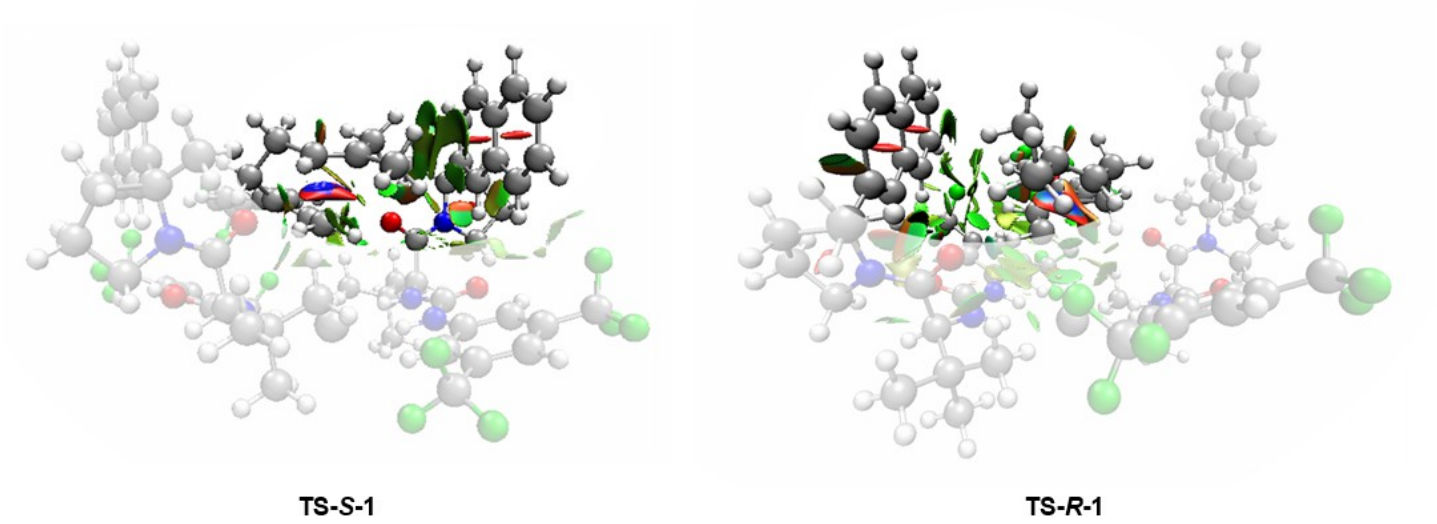


Figure S27. Comparison of NCI plots of the main aryl interaction for TS-*S*-1 and TS-*R*-1. Stabilizing noncovalent interactions are visualized in green. In **TS-*S*-1** a relatively large region of stabilizing interactions is visible between the methyl groups of the nucleophilic olefin and the 2-naphthyl group of the catalyst on the right. In comparison, **TS-*R*-1** shows sparser interactions between the nucleophile and the 2-naphthyl group of the catalyst on the left, suggesting weaker stabilization of the minor transition state through this interaction. This analysis is consistent both with the visual analysis of the computed transition structures (see Figures S25 and S26) as well as the experimental data presented in Figure 5.

Cartesian coordinates for transition structures

TS-*S*-1:

Imaginary frequency: -67.85 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.677518 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.645319 Hartree
Free energy correction: 1.307109 Hartree
Free energy correction – Grimme quasi-RRHO: 1.301061 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308588 Hartree

O	1.20073900	3.55519500	0.87749000
C	1.71252100	4.34134800	0.06606700
C	1.32858000	4.25642100	-1.43411200
H	2.04605400	4.82964500	-2.02526900
N	1.40747500	2.87705000	-1.87855100
C	2.61430400	2.24181300	-1.94353800
N	2.51455300	0.93501000	-2.40490400
H	1.56693200	0.60845300	-2.61055800
C	-0.08882200	4.86671200	-1.73180300
H	0.55724600	2.33869200	-2.03394700
C	-0.08421800	6.36340400	-1.36034000
H	-1.05873700	6.80470200	-1.59608700
H	0.10112200	6.52460200	-0.29270300
H	0.67314500	6.91710100	-1.92841200
C	-0.36870200	4.74542900	-3.24570500
H	-0.41002000	3.70341300	-3.57616900
H	-1.33558200	5.20396700	-3.48053300
H	0.40289800	5.25637200	-3.83479400
C	-1.21690400	4.16533500	-0.94845100
H	-1.05976600	4.23844800	0.13103800
H	-2.17449600	4.63805800	-1.18822200

H	-1.30030900	3.10449700	-1.20944400
N	2.58050300	5.31280100	0.45413700
C	3.42902500	6.10621600	-0.46772400
C	2.88729600	5.58663100	1.89199100
C	4.46038800	6.76917400	0.45352500
H	3.88950000	5.45120400	-1.21131600
C	3.70378000	6.90602200	1.77552800
H	5.33205700	6.11917000	0.57839400
H	4.35589600	7.05177600	2.64089900
H	3.00835000	7.75408100	1.72812100
H	4.80784600	7.72721500	0.05620100
H	2.82787200	6.86344300	-0.98497400
C	3.51503000	-0.03233700	-2.47055700
C	4.86206000	0.21020800	-2.14414700
C	3.14026400	-1.32301800	-2.88291400
C	5.78124700	-0.83551500	-2.19670100
H	5.16163200	1.20781700	-1.86061800
C	4.08153200	-2.34863600	-2.94156500
H	2.10789500	-1.51797100	-3.15676100
C	5.41192300	-2.12268400	-2.59244700
H	6.13653800	-2.92741600	-2.62651800
O	-1.84589700	-3.04140400	0.57827900
C	-2.71324000	-3.67780000	-0.03608000
C	-2.83114300	-3.52833600	-1.57584500
H	-3.77657300	-3.95509100	-1.90977200
N	-2.88547100	-2.11722900	-1.91936200
C	-4.03896700	-1.40978900	-1.72192700
N	-3.92326100	-0.07445200	-2.08207700
H	-2.99764500	0.22583500	-2.39940600
C	-1.70409100	-4.27000900	-2.37496100
H	-2.02063400	-1.60346300	-2.07442800
C	-1.74754300	-5.77202200	-2.02891300
H	-0.98012300	-6.30739800	-2.59893000
H	-1.55567100	-5.95538400	-0.96563300
H	-2.71690600	-6.21716900	-2.28440400
C	-1.99541200	-4.10344900	-3.88122700
H	-1.94578300	-3.05533500	-4.18991400
H	-1.25824500	-4.66338800	-4.46820400
H	-2.99123700	-4.48464100	-4.13942400
C	-0.29478200	-3.73006500	-2.06883400
H	-0.02835300	-3.87690500	-1.01963300
H	0.44413000	-4.25479900	-2.68310000
H	-0.20220900	-2.66138600	-2.29415000
N	-3.59005900	-4.51157000	0.59074300
C	-4.77260400	-5.13758300	-0.05395100
C	-3.55151700	-4.76388100	2.06313200
C	-5.59524400	-5.68704800	1.11807800
H	-5.32341000	-4.39589500	-0.63696700
C	-4.53691400	-5.95981300	2.18711200
H	-6.30607200	-4.93253700	1.46948400
H	-4.94554000	-6.04173000	3.19802800
H	-3.99915400	-6.88998100	1.96212600
H	-6.16236400	-6.57900400	0.83654400
H	-4.45448600	-5.94896600	-0.71938900
C	-4.89455900	0.92066300	-2.00871400
C	-6.20941200	0.70778400	-1.56486600
C	-4.51829300	2.21540300	-2.41670600
C	-7.10054500	1.78133300	-1.50445200
H	-6.51841000	-0.28997400	-1.28650300
C	-5.42875900	3.26480500	-2.36193300
H	-3.51134500	2.38663300	-2.78389100

C	-6.73167200	3.06506100	-1.89706000
H	-7.43918100	3.88345000	-1.85866600
C	1.60057800	5.83621400	2.70104500
H	1.05888800	4.91098600	2.89585300
H	1.83793600	6.31893900	3.65429200
H	0.94612500	6.51570200	2.14539200
C	-2.14829600	-5.18884600	2.53521000
H	-1.45892100	-4.34607700	2.56589000
H	-2.20546100	-5.64332200	3.52963500
H	-1.74791300	-5.94505900	1.85170300
O	-5.07736100	-1.92266200	-1.28565300
O	3.67695300	2.79329500	-1.62999700
C	3.77341000	4.49132300	2.51100300
C	4.49021700	3.60141200	1.73490300
C	3.94354400	4.44184700	3.92580500
C	5.38849000	2.66185200	2.31190800
H	4.36618600	3.58597000	0.65594900
C	4.79210500	3.53369900	4.51601700
H	3.39849500	5.13507200	4.55891000
C	6.14672300	1.76289600	1.51234900
C	5.54493800	2.61861000	3.73382600
H	4.90223700	3.51580100	5.59814100
C	7.01330400	0.86121900	2.09168000
H	6.04221300	1.80758700	0.43229400
C	6.44261700	1.67532000	4.30237600
C	7.15991800	0.81538300	3.50076500
H	7.58579500	0.18582400	1.46345800
H	6.55770200	1.64715600	5.38368500
H	7.84640300	0.10025400	3.94595000
C	-4.10214000	-3.56412500	2.85627500
C	-4.78819700	-2.53148300	2.24735700
C	-3.97939900	-3.54658800	4.27662600
C	-5.36119400	-1.46767000	2.99745300
H	-4.90267800	-2.50453300	1.16780300
C	-4.51368700	-2.52756000	5.03137300
H	-3.45726300	-4.35396100	4.78144500
C	-6.08331400	-0.41558100	2.36989000
C	-5.21817600	-1.45494800	4.42159000
H	-4.40680400	-2.53886900	6.11406000
C	-6.62924900	0.60638100	3.11487200
H	-6.20459500	-0.43495500	1.29048200
C	-5.78650000	-0.38367700	5.16221400
C	-6.47502200	0.62480400	4.52359500
H	-7.18783800	1.39383300	2.61836800
H	-5.67666800	-0.37745500	6.24455400
H	-6.91193000	1.43538400	5.10091000
Cl	-0.73365800	0.42113000	-2.52491100
C	-8.47790500	1.51945000	-0.95676600
C	-4.99054700	4.65038300	-2.75334200
C	7.20527000	-0.60434500	-1.77137100
C	3.63278500	-3.73445600	-3.32546400
F	8.09012200	-1.04776200	-2.68721300
F	7.47840800	0.69645800	-1.53499100
F	7.48841300	-1.27506700	-0.61419700
F	4.64654900	-4.48332000	-3.80384200
F	2.66455700	-3.70622100	-4.27071300
F	3.11211700	-4.40482400	-2.26600000
F	-8.43768500	1.27827600	0.38198900
F	-9.04831700	0.43432200	-1.52131200
F	-9.31435500	2.56210300	-1.14134300
F	-3.98961200	4.63408300	-3.66263000

F	-6.00326200	5.37314700	-3.27589300
F	-4.52860100	5.35029200	-1.68263200
C	-0.26973500	0.53546300	0.70179200
H	-1.30538900	0.46230200	0.39093200
H	0.18212800	1.51351500	0.55805100
C	0.51775900	-0.64144900	0.71437000
H	0.05811500	-1.54366600	0.32337900
C	1.77687100	-0.65469800	1.26129000
C	2.23836400	0.55214400	2.02254100
H	3.24091500	0.41349800	2.42822700
H	2.25247900	1.45449800	1.40251400
C	1.26890200	0.83361400	3.23355300
H	1.73957700	1.62782800	3.82398700
H	1.21963100	-0.05860100	3.86351000
C	-0.09194400	1.31255300	2.82743700
H	-0.13122000	2.36049400	2.54008600
C	-1.29348500	0.64578400	2.93532100
C	-2.58510100	1.37544000	2.68119500
H	-2.42607200	2.35681300	2.22565400
H	-3.11423700	1.51758000	3.63323200
H	-3.26060000	0.78776700	2.05003300
C	-1.42958600	-0.78191100	3.37411500
H	-0.48583100	-1.22994500	3.68834800
H	-1.84567600	-1.39657800	2.56538500
H	-2.14225400	-0.84553100	4.20511500
C	2.61460500	-1.86533700	1.19804600
C	4.01676300	-1.74549100	1.13192600
C	2.04832000	-3.15320800	1.11440300
C	4.81845400	-2.86183000	0.92550700
H	4.48696300	-0.76952600	1.18448300
C	2.85197200	-4.27179300	0.92447000
H	0.97391300	-3.27957700	1.20286900
C	4.23644100	-4.12626700	0.80993900
H	5.89147200	-2.74231200	0.82337000
H	2.40480100	-5.25692000	0.85262600
C	5.11336000	-5.30409500	0.48256400
F	4.49176800	-6.48242400	0.69706500
F	6.24711900	-5.30106600	1.22008300
F	5.49633500	-5.28346000	-0.81701100

TS-*S*-2:

Imaginary frequency: -105.50 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.676193 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.642879 Hartree
Free energy correction: 1.304258 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299786 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308639 Hartree

O	1.31623800	3.40228800	1.22177000
C	1.83357100	4.29969700	0.53897000
C	1.41944500	4.46907100	-0.94609900
H	2.13098400	5.12619200	-1.44935300
N	1.48349400	3.18113100	-1.61328300
C	2.69083500	2.56755300	-1.79263100
N	2.58316300	1.31016800	-2.36882400
H	1.63112900	0.96746200	-2.52267000
C	0.00478200	5.12830400	-1.11553200
H	0.63254200	2.64499300	-1.77070900
C	0.02672700	6.53645600	-0.48750400

H	-0.94353000	7.02291700	-0.63609000
H	0.21845100	6.50499100	0.59083200
H	0.78867300	7.17324500	-0.95323700
C	-0.28807600	5.27202900	-2.62458900
H	-0.32424100	4.30218100	-3.12932500
H	-1.25856900	5.75822600	-2.77098600
H	0.47729400	5.88125100	-3.12102400
C	-1.12158600	4.30815700	-0.45451600
H	-0.95619500	4.19771500	0.62062600
H	-2.07877400	4.81721100	-0.60510600
H	-1.21199800	3.30623900	-0.88911800
N	2.74255600	5.16622000	1.05797100
C	3.59197600	6.08165200	0.25754700
C	3.10463900	5.17328400	2.50898000
C	4.68394100	6.52604700	1.23787400
H	3.99634900	5.55476400	-0.60963400
C	3.97890200	6.45739700	2.59318300
H	5.52589400	5.82714900	1.20978700
H	4.66535100	6.42006800	3.44333400
H	3.32418000	7.32879300	2.72410700
H	5.06512400	7.52372100	1.00165600
H	3.00603400	6.94208600	-0.08799000
C	3.60625600	0.38680300	-2.57670600
C	4.97153200	0.71883800	-2.56947900
C	3.23473600	-0.94526700	-2.82812800
C	5.92493200	-0.27791400	-2.78050100
H	5.26624500	1.74506500	-2.40081900
C	4.20395800	-1.92133900	-3.04292100
H	2.18150100	-1.20969500	-2.84977000
C	5.56216700	-1.60365100	-3.01576600
H	6.31270500	-2.36464400	-3.18363700
O	-1.91392100	-3.04788100	0.25378900
C	-2.77927200	-3.58466900	-0.45262800
C	-2.84034100	-3.26640700	-1.96964200
H	-3.78057400	-3.63567100	-2.37828200
N	-2.85956500	-1.82507200	-2.15917500
C	-4.00735800	-1.12071600	-1.92166100
N	-3.86164600	0.24328200	-2.13196300
H	-2.92271300	0.56044500	-2.38843100
C	-1.70038500	-3.94225000	-2.80804100
H	-1.98286000	-1.31480600	-2.24216800
C	-1.77605600	-5.47035500	-2.61622400
H	-1.00374800	-5.95983100	-3.21983900
H	-1.61227200	-5.76265000	-1.57280900
H	-2.74608400	-5.87000800	-2.93644900
C	-1.94733300	-3.61957600	-4.29685000
H	-1.87508100	-2.54650000	-4.49598100
H	-1.20153000	-4.12879100	-4.91803200
H	-2.94046200	-3.95669000	-4.61888100
C	-0.29177300	-3.46068300	-2.41252600
H	-0.05116700	-3.72419500	-1.38010200
H	0.45510300	-3.92681900	-3.06358400
H	-0.17992400	-2.37557500	-2.52094300
N	-3.70063100	-4.44936100	0.05538900
C	-4.87787000	-4.96874300	-0.68633800
C	-3.71663000	-4.85341900	1.49443700
C	-5.76105100	-5.59507500	0.39965900
H	-5.38148900	-4.15576700	-1.21392900
C	-4.75165700	-6.01324200	1.46892900
H	-6.45477100	-4.84953400	0.80090000
H	-5.19760800	-6.17563900	2.45401600

H	-4.24274900	-6.93894700	1.17039400
H	-6.35118700	-6.43164600	0.01452500
H	-4.56157700	-5.72530200	-1.41457300
C	-4.82031600	1.24110200	-1.97226800
C	-6.15097400	1.00137100	-1.59311700
C	-4.41414800	2.56748700	-2.21724000
C	-7.02845800	2.07578500	-1.43352800
H	-6.48210700	-0.01617300	-1.44072900
C	-5.31163700	3.61912300	-2.06684400
H	-3.39447500	2.76268400	-2.53407200
C	-6.63021000	3.38962500	-1.66469000
H	-7.32713600	4.21025200	-1.55196600
C	1.85384400	5.33093300	3.39423800
H	1.27243200	4.41035300	3.43952100
H	2.13913600	5.62355100	4.40961700
H	1.21970000	6.12711000	2.99064300
C	-2.34667200	-5.38639000	1.95545400
H	-1.62889100	-4.58171200	2.10993000
H	-2.45524600	-5.95316900	2.88590800
H	-1.94983400	-6.07174800	1.19910000
O	-5.06615400	-1.65873100	-1.57323800
O	3.76294000	3.09709800	-1.47289700
C	3.95234300	3.94848400	2.89650600
C	4.58329300	3.16198600	1.95249000
C	4.17226000	3.65595700	4.27470200
C	5.43633900	2.08644300	2.32481000
H	4.42591400	3.33735800	0.89225200
C	4.98323700	2.61628300	4.66792300
H	3.69767800	4.26544700	5.03763100
C	6.09678300	1.28571900	1.35287300
C	5.64328600	1.79974500	3.71182200
H	5.13438500	2.41447100	5.72618100
C	6.92347900	0.25158000	1.73652400
H	5.94693400	1.50753200	0.30028000
C	6.49546200	0.72270500	4.07582700
C	7.12225000	-0.03426500	3.11078000
H	7.43270000	-0.33636700	0.97909800
H	6.64994500	0.50952600	5.13126100
H	7.77822700	-0.85091800	3.40041500
C	-4.24010500	-3.71823200	2.39374900
C	-4.88549700	-2.61033000	1.87975800
C	-4.13421100	-3.83970200	3.81032600
C	-5.43284500	-1.60407900	2.72263700
H	-4.98438100	-2.47629700	0.80661000
C	-4.64438300	-2.87962500	4.65388500
H	-3.64408200	-4.70778700	4.24079300
C	-6.11298900	-0.47354700	2.19198600
C	-5.30633300	-1.73107200	4.14280900
H	-4.55059200	-2.99711100	5.73144400
C	-6.63376200	0.49108800	3.02608400
H	-6.22353500	-0.38686400	1.11479300
C	-5.84749700	-0.71597000	4.97707600
C	-6.49501100	0.37115600	4.43144700
H	-7.16166900	1.33959800	2.60185100
H	-5.75012000	-0.81606300	6.05598500
H	-6.91187200	1.13765900	5.07945200
Cl	-0.65352100	0.73374900	-2.43458400
C	-8.42344300	1.77894600	-0.95225200
C	-4.84390200	5.03329200	-2.28240300
C	7.37801000	0.10669500	-2.70835500
C	3.75262900	-3.34103100	-3.26034500

F	7.63469900	1.24406000	-3.38775900
F	7.76792600	0.33384500	-1.42294100
F	8.19085300	-0.85294400	-3.19671000
F	4.76687800	-4.15589200	-3.61563800
F	2.80871700	-3.42364900	-4.22877300
F	3.19442800	-3.86154100	-2.13927300
F	-8.42558600	1.42733600	0.36257600
F	-8.98162900	0.74914800	-1.62235400
F	-9.24828000	2.83991500	-1.07405100
F	-3.82160500	5.10641500	-3.16431100
F	-5.83296100	5.82977700	-2.73871400
F	-4.39842700	5.59469700	-1.12626700
C	-0.19319300	0.45316800	0.73490300
H	-1.21615300	0.49078900	0.37999100
H	0.33590600	1.39972500	0.65083900
C	0.50010300	-0.78952800	0.65443700
H	-0.02146100	-1.61154700	0.17493600
C	1.71916100	-0.96123900	1.25125100
C	2.25144900	0.15405600	2.10505500
H	3.21850000	-0.09527000	2.54294000
H	2.37375200	1.08502000	1.54222900
C	1.25173800	0.44458800	3.28449300
H	1.73705600	1.18187300	3.93356000
H	1.11925800	-0.47047200	3.86839700
C	-0.06331000	1.02206100	2.84359600
H	-0.04208100	2.09187200	2.65262000
C	-1.30506100	0.41569100	2.87722000
C	-2.54786300	1.23099000	2.64751400
H	-2.32667700	2.22944400	2.26069400
H	-3.08466100	1.33968800	3.59984400
H	-3.24228700	0.72234800	1.96999300
C	-1.52647100	-1.03096900	3.19783800
H	-0.62078600	-1.54783300	3.51737400
H	-1.93181400	-1.56151600	2.32599600
H	-2.28179500	-1.12020600	3.98765900
C	2.41911800	-2.26005900	1.20405500
C	3.82499000	-2.31679800	1.25538000
C	1.70497900	-3.46971800	1.08526300
C	4.49320100	-3.53435500	1.17576200
H	4.40758200	-1.40328100	1.31969600
C	2.37326500	-4.68666400	1.01924100
H	0.61985200	-3.45846100	1.06115600
C	3.76969600	-4.72310900	1.06197800
H	5.57758600	-3.55939100	1.19402100
H	1.81107400	-5.61032000	0.93100900
C	4.48885800	-6.04510100	1.05173000
F	3.80700200	-6.98457600	0.36163000
F	4.65684700	-6.52596600	2.30769700
F	5.71870100	-5.94549500	0.50311000

TS-*S*-3:

Imaginary frequency: -90.79 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.675994 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.643523 Hartree
Free energy correction: 1.306083 Hartree
Free energy correction – Grimme quasi-RRHO: 1.300673 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308846 Hartree

O	1.35809400	3.48109400	0.77991200

C	1.76752300	4.37433500	0.02221000
C	1.20253000	4.47451900	-1.42077800
H	1.83851600	5.13362300	-2.01472900
N	1.24630700	3.16091400	-2.04095000
C	2.45383900	2.55195700	-2.23270600
N	2.34787500	1.25426400	-2.71699900
H	1.39611200	0.91803800	-2.88638300
C	-0.24316000	5.08196700	-1.47468700
H	0.40063300	2.59662800	-2.09961900
C	-0.20803100	6.51568600	-0.90804000
H	-1.20477600	6.96503000	-0.97649700
H	0.09189300	6.53625100	0.14569900
H	0.48060000	7.15507800	-1.47367400
C	-0.68777100	5.15171100	-2.95160300
H	-0.74370100	4.16014100	-3.41032800
H	-1.68233300	5.60527400	-3.02028700
H	0.00588400	5.75884200	-3.54626700
C	-1.26985300	4.25706000	-0.67237100
H	-0.99653100	4.19963100	0.38490200
H	-2.25451800	4.72911300	-0.74809000
H	-1.36697800	3.23488500	-1.05517300
N	2.68686500	5.28986200	0.42538400
C	3.41182200	6.21547300	-0.47796000
C	3.21131400	5.32765800	1.82820100
C	4.60046000	6.70199800	0.36009400
H	3.72843300	5.68775200	-1.38042800
C	4.06921700	6.62614700	1.79222600
H	5.45561800	6.03100000	0.23201900
H	4.85485900	6.60468300	2.55170800
H	3.42065200	7.48726000	1.99901200
H	4.91778600	7.70884100	0.07343200
H	2.76587900	7.05457000	-0.76360600
C	3.34846100	0.28500400	-2.75678300
C	4.66225100	0.49833200	-2.30452000
C	2.99917700	-0.98734600	-3.24552000
C	5.57580100	-0.55539200	-2.31651800
H	4.94537900	1.47951800	-1.95372400
C	3.93501700	-2.01735000	-3.26580500
H	1.99020100	-1.16344200	-3.60469600
C	5.23534400	-1.81840100	-2.79970200
H	5.95848900	-2.62476700	-2.81410900
O	-1.78072200	-3.05407800	0.34674600
C	-2.68066100	-3.64497600	-0.26671600
C	-2.87617100	-3.38539200	-1.78365100
H	-3.83385400	-3.79792800	-2.10035000
N	-2.95785400	-1.95343800	-2.02058000
C	-4.10302700	-1.27494700	-1.70868500
N	-4.02243700	0.08346900	-1.98156600
H	-3.12211100	0.41778000	-2.33634600
C	-1.78608800	-4.05748600	-2.68841200
H	-2.11014700	-1.42189600	-2.20721000
C	-1.80695100	-5.58067800	-2.44900600
H	-1.06854100	-6.06898100	-3.09455100
H	-1.55906900	-5.83777500	-1.41293800
H	-2.78707800	-6.01302400	-2.68482700
C	-2.15358800	-3.78593500	-4.16253900
H	-2.12127300	-2.71841300	-4.39865700
H	-1.44603700	-4.29904500	-4.82402900
H	-3.16047500	-4.15315200	-4.39699100
C	-0.36470200	-3.53098300	-2.41544800
H	-0.04122500	-3.75626400	-1.39658600

H	0.34218100	-4.00198200	-3.10625900
H	-0.28719200	-2.44773300	-2.56374500
N	-3.52549200	-4.52149700	0.34420800
C	-4.74124600	-5.10344800	-0.27916600
C	-3.40786200	-4.87613200	1.79143100
C	-5.50860800	-5.72070200	0.89636700
H	-5.31507200	-4.32549300	-0.78757500
C	-4.39969200	-6.06948800	1.88921900
H	-6.19219900	-4.98473900	1.33128500
H	-4.75619700	-6.21298200	2.91291400
H	-3.88502000	-6.98766400	1.57756500
H	-6.09909300	-6.58850300	0.58860100
H	-4.46048500	-5.87371900	-1.00757300
C	-4.99638900	1.05713700	-1.77334000
C	-6.28124100	0.79161700	-1.27262000
C	-4.65693000	2.38526700	-2.09744000
C	-7.17693300	1.84422600	-1.07409400
H	-6.56419400	-0.22920600	-1.05783800
C	-5.57240500	3.41437300	-1.90488000
H	-3.67525900	2.59899900	-2.50847500
C	-6.84335900	3.16028100	-1.38238500
H	-7.55459700	3.96320800	-1.23687300
C	2.06760300	5.49047200	2.84506500
H	1.50173600	4.56708300	2.96639900
H	2.46443300	5.79763300	3.81803800
H	1.38763300	6.27861100	2.50556500
C	-1.98603000	-5.34690100	2.15169000
H	-1.28699600	-4.51387000	2.21520700
H	-1.99521300	-5.88103900	3.10737800
H	-1.63046500	-6.04724600	1.38857500
O	-5.10836000	-1.83013500	-1.24693900
O	3.52768300	3.11996300	-2.00152300
C	4.11251200	4.11487900	2.13222600
C	4.39295700	3.74491600	3.43569800
C	4.75710600	3.40666300	1.07846100
C	5.29430700	2.68901500	3.74239900
H	3.93138700	4.26563000	4.27037400
C	5.64532000	2.38855800	1.34099300
H	4.52342700	3.64431000	0.04714100
C	5.58164500	2.30038800	5.07974400
C	5.94071000	1.99275400	2.67113600
H	6.13480500	1.87145900	0.51996500
C	6.46032500	1.27312900	5.34205500
H	5.09611900	2.83101600	5.89602400
C	6.83937700	0.93351200	2.97283500
C	7.09362600	0.58099700	4.27931900
H	6.67207000	0.98779900	6.36909700
H	7.31588200	0.40583900	2.14990900
H	7.78252000	-0.22938900	4.50157900
C	-3.89571400	-3.72901900	2.69565500
C	-4.62054700	-2.66125600	2.20304600
C	-3.66976000	-3.79908600	4.10159300
C	-5.13343200	-1.64632700	3.05713300
H	-4.81111300	-2.56666500	1.13808800
C	-4.14344400	-2.82873900	4.95458500
H	-3.11497100	-4.63525600	4.51647800
C	-5.89568300	-0.55805200	2.55035800
C	-4.88644100	-1.72111700	4.46511100
H	-3.95725400	-2.90643900	6.02370800
C	-6.38133100	0.41583000	3.39481700
H	-6.09678900	-0.51123700	1.48386000

C	-5.39423100	-0.69754000	5.30988700
C	-6.12370200	0.34796500	4.78683400
H	-6.97252000	1.23145500	2.99000800
H	-5.20501100	-0.75786800	6.37951200
H	-6.51376800	1.12127400	5.44338500
Cl	-0.87854400	0.65055000	-2.62161400
C	-8.51617800	1.52235300	-0.46703700
C	-5.17034100	4.83276300	-2.20714800
C	6.92694400	-0.35326300	-1.68908000
C	3.51775200	-3.39187000	-3.71704400
F	7.32756100	0.93528200	-1.71237700
F	6.91123000	-0.71926600	-0.36659300
F	7.88734400	-1.09454300	-2.27367800
F	4.53981300	-4.06986200	-4.28130100
F	2.50987600	-3.35030500	-4.61763700
F	3.07748300	-4.14225000	-2.67570000
F	-8.39544700	1.20445800	0.85077600
F	-9.09945300	0.46092600	-1.06236100
F	-9.37911600	2.55705300	-0.54180700
F	-4.24412700	4.90441400	-3.18970200
F	-6.22265800	5.58860600	-2.58400000
F	-4.62723300	5.44195400	-1.11883300
C	-0.14921500	0.49079000	0.54499400
H	-1.19702700	0.46451500	0.27012000
H	0.32671000	1.45683300	0.39500700
C	0.59893500	-0.71582500	0.46476400
H	0.08848300	-1.58474800	0.06187600
C	1.87104800	-0.79664300	0.96588100
C	2.40651600	0.37356200	1.73852800
H	3.41638600	0.18849900	2.10630800
H	2.43414000	1.29027800	1.14093500
C	1.48822600	0.65361400	2.98652100
H	1.99166300	1.42936000	3.57368800
H	1.44448600	-0.24826400	3.60302400
C	0.11978800	1.16139100	2.63707700
H	0.08103900	2.22180200	2.40063700
C	-1.08775900	0.50715300	2.78370000
C	-2.37866400	1.26147700	2.61778200
H	-2.22959700	2.25315600	2.18190300
H	-2.85201600	1.38316500	3.60158600
H	-3.09576200	0.69999500	2.00913700
C	-1.22255100	-0.93300200	3.17587400
H	-0.27310900	-1.40159800	3.43786200
H	-1.67609600	-1.51365500	2.36180300
H	-1.90524300	-1.01844800	4.02973900
C	2.64496200	-2.04990300	0.88596400
C	4.04884900	-2.00934700	0.79344000
C	2.00888400	-3.30715100	0.85311500
C	4.78987000	-3.17648400	0.64592200
H	4.56907600	-1.05859100	0.78017400
C	2.75113200	-4.47575100	0.72445500
H	0.92882800	-3.37047600	0.94146800
C	4.14303800	-4.41382700	0.61467000
H	5.86714200	-3.11697000	0.53512300
H	2.24988200	-5.43731100	0.70071100
C	4.95572200	-5.67644900	0.51305500
F	4.23793400	-6.70265100	0.00904700
F	5.41113900	-6.07161500	1.72629400
F	6.04048600	-5.50926200	-0.27517200

TS-*S*-4:

Imaginary frequency: -99.52 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.674214 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.640237 Hartree
Free energy correction: 1.303830 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299588 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308711 Hartree

O	1.32646900	3.36822500	1.15328500
C	1.90227500	4.25592800	0.50532100
C	1.57271200	4.44362000	-0.99872300
H	2.32306300	5.08990200	-1.45785700
N	1.64609400	3.15894400	-1.67140900
C	2.84677900	2.51594600	-1.77869900
N	2.74393100	1.26216700	-2.36349400
H	1.79466000	0.94206900	-2.57361200
C	0.18247900	5.13304400	-1.23634200
H	0.79368100	2.64354700	-1.88191900
C	0.20106200	6.53650600	-0.59775000
H	-0.74895900	7.04514400	-0.79493100
H	0.33315200	6.49397800	0.48910300
H	1.00102500	7.15906700	-1.01664400
C	-0.03103900	5.29205000	-2.75717800
H	-0.05712700	4.32643100	-3.27060900
H	-0.98539400	5.79511700	-2.94781100
H	0.76761200	5.89243800	-3.20999300
C	-0.99310200	4.33273600	-0.64008800
H	-0.88005300	4.20349300	0.43961400
H	-1.92846600	4.86942200	-0.82541400
H	-1.08896100	3.34006700	-1.09428400
N	2.80214200	5.09706200	1.07869100
C	3.71792800	5.99327000	0.33172100
C	3.08074500	5.09098600	2.54805400
C	4.76512400	6.40397900	1.37361000
H	4.15536500	5.45946200	-0.51489600
C	3.98349600	6.35043400	2.68702000
H	5.58760400	5.68188500	1.38928600
H	4.61979600	6.29160700	3.57415700
H	3.34649200	7.23911400	2.78509000
H	5.18637400	7.39142300	1.16395700
H	3.17481700	6.87066200	-0.04035900
C	3.75429600	0.31215300	-2.50249500
C	5.12457300	0.61230700	-2.42147600
C	3.36546600	-1.01376300	-2.75996000
C	6.06415500	-0.40887400	-2.56766900
H	5.43398200	1.63320200	-2.24696500
C	4.32151200	-2.01498700	-2.90798900
H	2.30904700	-1.25350600	-2.83863400
C	5.68326200	-1.72866200	-2.80798400
H	6.42358800	-2.50900200	-2.92489900
O	-2.12858100	-2.90251400	-0.03033100
C	-2.93410000	-3.43453500	-0.80807300
C	-2.82774000	-3.15862900	-2.33263000
H	-3.73186400	-3.51239800	-2.82718900
N	-2.78532700	-1.72016500	-2.55091700
C	-3.92050100	-0.98381900	-2.34952400
N	-3.72351800	0.38292200	-2.48462500
H	-2.77258100	0.68057300	-2.71887300
C	-1.63167900	-3.88677700	-3.03488700
H	-1.88913500	-1.23721600	-2.53330300

C	-1.78068000	-5.40678600	-2.82240000
H	-0.96986400	-5.93615400	-3.33501300
H	-1.73352900	-5.68012600	-1.76207400
H	-2.72780500	-5.78017500	-3.23089700
C	-1.71283900	-3.58875500	-4.54689000
H	-1.58525300	-2.52282600	-4.75634200
H	-0.92449300	-4.13435200	-5.07815900
H	-2.67833600	-3.90133000	-4.96369900
C	-0.25580700	-3.44231300	-2.50457300
H	-0.13187200	-3.69376900	-1.44878400
H	0.53815700	-3.94381000	-3.06764600
H	-0.09821400	-2.36343800	-2.61777200
N	-3.93504000	-4.24775400	-0.37149500
C	-5.05038600	-4.74941000	-1.21371400
C	-4.12058500	-4.58470200	1.07475500
C	-6.08201700	-5.26482700	-0.20348900
H	-5.44693300	-3.94324300	-1.83410200
C	-5.22012800	-5.68157300	0.98806300
H	-6.76754100	-4.46043700	0.08221600
H	-5.77529000	-5.76492500	1.92587800
H	-4.74214100	-6.64941800	0.78842900
H	-6.67878600	-6.08595200	-0.61115400
H	-4.69906700	-5.56179000	-1.86168300
C	-4.63263500	1.40073000	-2.20101500
C	-5.89708300	1.18517100	-1.63078400
C	-4.23403400	2.72177100	-2.48528900
C	-6.71318000	2.27548500	-1.32355100
H	-6.22874000	0.17356000	-1.44565700
C	-5.07418600	3.78989600	-2.19051400
H	-3.26641700	2.90040100	-2.94265600
C	-6.32320400	3.58333500	-1.59713900
H	-6.97488000	4.41771000	-1.36965700
C	1.78544400	5.28106800	3.36000000
H	1.17690500	4.37702900	3.36640600
H	2.01884500	5.56177900	4.39182700
H	1.19855700	6.09636100	2.92434300
C	-2.84053600	-5.18031100	1.68891900
H	-2.08468700	-4.41641000	1.86716200
H	-3.07269000	-5.68257900	2.63372800
H	-2.42794900	-5.93400100	1.00996700
O	-5.01494400	-1.49933100	-2.09041900
O	3.91006500	3.01830300	-1.39256400
C	3.87042200	3.84241400	2.97976700
C	4.53352100	3.04037000	2.07155800
C	4.00079700	3.54120800	4.36746900
C	5.33273600	1.94049800	2.48961500
H	4.44349500	3.22202800	1.00451500
C	4.75743400	2.47815200	4.80394900
H	3.49973500	4.16249100	5.10345500
C	6.02739900	1.12389700	1.55548500
C	5.44931400	1.64512900	3.88536100
H	4.84024000	2.27007400	5.86852500
C	6.80091000	0.06624500	1.98340400
H	5.94714800	1.35252200	0.49678600
C	6.24801100	0.54378100	4.29499900
C	6.90965600	-0.22828600	3.36584800
H	7.33804800	-0.53360700	1.25517600
H	6.33368800	0.32408700	5.35690300
H	7.52447700	-1.06352500	3.69065800
C	-4.65464000	-3.37740000	1.87357500
C	-4.65296500	-3.39350700	3.25712600

C	-5.24233300	-2.26012300	1.21471500
C	-5.21273700	-2.33642900	4.02442200
H	-4.22202200	-4.23150200	3.79888500
C	-5.80346500	-1.22360100	1.92749300
H	-5.24385800	-2.21067600	0.13140200
C	-5.20448000	-2.34385100	5.44696000
C	-5.80834100	-1.22444700	3.34643800
H	-6.26255200	-0.38875900	1.40287900
C	-5.75811700	-1.30471700	6.16102800
H	-4.75494200	-3.18875700	5.96415700
C	-6.37520500	-0.16885400	4.11127000
C	-6.35036800	-0.20668300	5.48756000
H	-5.74677800	-1.32479400	7.24752900
H	-6.83528500	0.66521300	3.58609400
H	-6.78942700	0.60322300	6.06384300
Cl	-0.49115700	0.76560600	-2.62888300
C	-8.01678000	1.99879000	-0.62397500
C	-4.62490200	5.20052300	-2.46166200
C	7.52001200	-0.05899900	-2.41709900
C	3.84984700	-3.42746500	-3.12894900
F	7.83936100	1.07386500	-3.07704900
F	7.84667300	0.15442700	-1.11187500
F	8.33446000	-1.03651300	-2.86590000
F	4.86026200	-4.26628100	-3.43627400
F	2.94248600	-3.50166700	-4.13225700
F	3.23848100	-3.92475700	-2.02500700
F	-7.80689400	1.62188800	0.66959100
F	-8.70316400	0.99418500	-1.20614300
F	-8.82408500	3.07864100	-0.58702600
F	-3.62619200	5.25995600	-3.36999600
F	-5.63570500	5.97118800	-2.91603700
F	-4.16160600	5.80222100	-1.33300700
C	-0.25931700	0.46074600	0.56168900
H	-1.25409000	0.51918700	0.13666200
H	0.29978800	1.39166700	0.50338900
C	0.40570200	-0.79971100	0.54409100
H	-0.10388300	-1.61475400	0.04052300
C	1.57762000	-0.99255500	1.22285500
C	2.08071600	0.12090300	2.09649400
H	3.00949800	-0.14718500	2.60126800
H	2.26449400	1.04079100	1.53211400
C	1.01246700	0.45371100	3.20301000
H	1.47287900	1.18864400	3.87244400
H	0.81828300	-0.44861100	3.78933500
C	-0.25530700	1.05683500	2.66820100
H	-0.19450500	2.12310700	2.46669500
C	-1.51000500	0.47912300	2.62139800
C	-2.71548500	1.31798700	2.29568300
H	-2.44617700	2.30762400	1.91701500
H	-3.31589900	1.44647600	3.20671000
H	-3.36617200	0.81410600	1.57204700
C	-1.78832200	-0.95675100	2.94477600
H	-0.90979200	-1.50089300	3.29336700
H	-2.18879200	-1.47792100	2.06552500
H	-2.56587500	-1.01192900	3.71634200
C	2.24675700	-2.30832700	1.23680500
C	3.64546200	-2.39689000	1.37015100
C	1.51173200	-3.50265700	1.09492400
C	4.28742900	-3.63080700	1.34624000
H	4.24506800	-1.49614500	1.45519200
C	2.15266600	-4.73592800	1.08458300

H	0.43017100	-3.46578800	1.01069800
C	3.54315800	-4.80399000	1.20770400
H	5.36803800	-3.68075700	1.42739700
H	1.57433100	-5.64757600	0.97777500
C	4.22932200	-6.14258900	1.25728300
F	3.56728200	-7.07502100	0.53887100
F	4.30960600	-6.60988300	2.52690100
F	5.49187500	-6.07961000	0.78273100

TS-*S*-5:

Imaginary frequency: -86.92 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.674061 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.640952 Hartree
Free energy correction: 1.305857 Hartree
Free energy correction – Grimme quasi-RRHO: 1.300626 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.309042 Hartree

O	1.36211800	3.45249000	0.71201900
C	1.82772400	4.33835500	-0.02162700
C	1.34134600	4.45001500	-1.49220600
H	2.01749000	5.10048300	-2.05038500
N	1.39610700	3.13685800	-2.11256000
C	2.60095800	2.50540400	-2.23659000
N	2.49832600	1.21040900	-2.72920900
H	1.55160500	0.89384800	-2.95558800
C	-0.09030200	5.08026600	-1.61753400
H	0.54472400	2.58852800	-2.22068000
C	-0.06071600	6.51264400	-1.04714500
H	-1.04524800	6.97826800	-1.16540500
H	0.18525800	6.52689400	0.02055500
H	0.66645600	7.14126400	-1.57541400
C	-0.46141400	5.15819000	-3.11421300
H	-0.50466200	4.16830000	-3.57792100
H	-1.44727700	5.62188800	-3.22914600
H	0.26582400	5.76017000	-3.67288700
C	-1.16828700	4.27092000	-0.86857600
H	-0.94247900	4.19874200	0.19880600
H	-2.13754200	4.76608700	-0.98152300
H	-1.27105500	3.25478500	-1.26563900
N	2.73994200	5.23705200	0.43191400
C	3.53043900	6.14865100	-0.42950700
C	3.18582100	5.26630000	1.86189800
C	4.68162800	6.61045300	0.47228700
H	3.88439200	5.61531900	-1.31459700
C	4.07163700	6.54648300	1.87330700
H	5.52823400	5.92160400	0.39045700
H	4.81415200	6.50903400	2.67441100
H	3.43112200	7.42124300	2.04485500
H	5.03519200	7.61029400	0.20408600
H	2.91763700	7.00083400	-0.74783800
C	3.47794500	0.21953200	-2.70499500
C	4.76752400	0.40738700	-2.17795000
C	3.12974000	-1.04838400	-3.20631200
C	5.65706100	-0.66581800	-2.13154900
H	5.05107500	1.38447400	-1.81618800
C	4.04229700	-2.09842300	-3.16627800
H	2.13963400	-1.20523800	-3.62232000
C	5.31760000	-1.92435000	-2.62673800
H	6.02276200	-2.74605300	-2.59516400

O	-2.00130800	-2.92811300	0.08649000
C	-2.84786400	-3.52344200	-0.59551400
C	-2.88671200	-3.30714600	-2.13302300
H	-3.81666900	-3.71202300	-2.53131900
N	-2.91734700	-1.87849300	-2.40886000
C	-4.05451700	-1.17221800	-2.12844000
N	-3.92154400	0.19340400	-2.33519400
H	-3.00927400	0.51146200	-2.67361900
C	-1.72943300	-4.02198900	-2.90963500
H	-2.04184800	-1.36635000	-2.49796100
C	-1.80964400	-5.53768600	-2.63742200
H	-1.02506500	-6.05903100	-3.19695600
H	-1.66887600	-5.77282300	-1.57624800
H	-2.77325900	-5.95398700	-2.95587200
C	-1.94433900	-3.77940800	-4.41849200
H	-1.86790300	-2.71832800	-4.67265900
H	-1.18566100	-4.32069700	-4.99548100
H	-2.93059600	-4.13371700	-4.74308500
C	-0.33025900	-3.51794800	-2.51005100
H	-0.11436300	-3.72587100	-1.45947500
H	0.43048300	-4.01949000	-3.11694600
H	-0.21471800	-2.44023900	-2.67322400
N	-3.77016900	-4.35835300	-0.04171200
C	-4.93404300	-4.93473100	-0.76126800
C	-3.81192800	-4.64601700	1.42615900
C	-5.84727600	-5.45404100	0.35547400
H	-5.41936400	-4.16839400	-1.36901600
C	-4.86444300	-5.79004100	1.47702700
H	-6.53954000	-4.66852100	0.67541800
H	-5.32937900	-5.86105700	2.46364700
H	-4.36361500	-6.74410700	1.26728700
H	-6.44108000	-6.31374400	0.03160300
H	-4.60791100	-5.75545900	-1.41181800
C	-4.83564700	1.19209100	-2.00440200
C	-6.03262900	0.95952200	-1.30883200
C	-4.51284500	2.51258700	-2.37437200
C	-6.85467100	2.03475100	-0.96644000
H	-6.30917500	-0.05392100	-1.05564000
C	-5.35878700	3.56451600	-2.04038200
H	-3.59943000	2.70324100	-2.92822700
C	-6.53866700	3.34237400	-1.32397100
H	-7.19540500	4.16401500	-1.06672100
C	1.99018700	5.45505500	2.81239700
H	1.39814600	4.54437300	2.90093100
H	2.33774200	5.75406100	3.80650600
H	1.34811700	6.25776000	2.43533500
C	-2.45672000	-5.16313900	1.94236400
H	-1.72121800	-4.36306100	2.01700800
H	-2.57948500	-5.63089200	2.92465100
H	-2.07614200	-5.93000900	1.25944900
O	-5.09986700	-1.71205400	-1.74566100
O	3.67039100	3.05253200	-1.94306800
C	4.04237400	4.03534000	2.21735000
C	4.23961300	3.66125200	3.53482800
C	4.73139800	3.31243100	1.20246900
C	5.09954100	2.58715500	3.89296100
H	3.74189900	4.19252200	4.34159200
C	5.58163400	2.27642100	1.51574200
H	4.56235600	3.55373400	0.15944800
C	5.30121500	2.19435400	5.24466800
C	5.79189500	1.87629400	2.86073900

H	6.10665400	1.74836200	0.72425200
C	6.14176700	1.14941600	5.55724100
H	4.78054700	2.73591100	6.03157700
C	6.64981000	0.79926700	3.21383500
C	6.82088700	0.44313400	4.53280500
H	6.28791700	0.86096500	6.59478500
H	7.16218700	0.26099900	2.41986200
H	7.47898500	-0.38097400	4.79445500
C	-4.32713300	-3.43213800	2.22746500
C	-4.21057100	-3.39941900	3.60582200
C	-5.01169000	-2.36163300	1.58483200
C	-4.74650500	-2.33734800	4.38312300
H	-3.70335600	-4.20133000	4.13608800
C	-5.55217800	-1.32176700	2.30860100
H	-5.10573500	-2.35091100	0.50455800
C	-4.62077600	-2.29441900	5.79946600
C	-5.43934900	-1.27247600	3.72216100
H	-6.08510900	-0.52298200	1.79784700
C	-5.15416100	-1.25176700	6.52372700
H	-4.09709700	-3.10353400	6.30399100
C	-5.98211900	-0.21190500	4.49751200
C	-5.84245100	-0.20036800	5.86738000
H	-5.05246500	-1.23315300	7.60554800
H	-6.51617300	0.58589500	3.98617900
H	-6.26378700	0.61287300	6.45214100
Cl	-0.73671900	0.67201100	-2.82491900
C	-8.07738200	1.74503300	-0.13790300
C	-4.98543600	4.97639900	-2.40395400
C	6.97438500	-0.48894200	-1.42918500
C	3.62290300	-3.46730200	-3.63229700
F	7.40279000	0.79077300	-1.43402800
F	6.87577800	-0.84863900	-0.10858300
F	7.95054200	-1.25279400	-1.95573900
F	4.65841000	-4.16459600	-4.14636400
F	2.65841100	-3.41287900	-4.57821200
F	3.12303200	-4.20621000	-2.60948200
F	-7.73575000	1.42610100	1.14307400
F	-8.77930100	0.69729100	-0.61630600
F	-8.91503000	2.79965700	-0.06460100
F	-4.08738000	5.03055200	-3.41233500
F	-6.06147300	5.70091500	-2.77703100
F	-4.42810100	5.63238500	-1.35045900
C	-0.21449700	0.48777500	0.37654600
H	-1.24300400	0.47379200	0.03621700
H	0.28582400	1.44475900	0.25210000
C	0.51797600	-0.73007300	0.35934000
H	0.01996400	-1.59536500	-0.06615300
C	1.75502200	-0.82418800	0.94029900
C	2.26037500	0.34506700	1.73388200
H	3.24250700	0.14745600	2.16491300
H	2.33917100	1.25581800	1.13183100
C	1.27147700	0.65201500	2.92113100
H	1.75275600	1.42377100	3.53162500
H	1.17288800	-0.24314100	3.54105300
C	-0.06223000	1.18205600	2.48379200
H	-0.06500000	2.24005500	2.23395000
C	-1.28743700	0.54946500	2.55282600
C	-2.55214500	1.32321400	2.29555400
H	-2.35818400	2.30945800	1.86516700
H	-3.08774700	1.45816400	3.24518100
H	-3.23191200	0.76659300	1.64059800

C	-1.47427600	-0.88329800	2.94977600
H	-0.54492200	-1.37852200	3.23389500
H	-1.93065500	-1.45291500	2.13012700
H	-2.17408000	-0.93960700	3.79251700
C	2.51291400	-2.08960800	0.91975400
C	3.92019200	-2.07014600	0.90300900
C	1.86118000	-3.33797900	0.86824100
C	4.65050300	-3.24954700	0.80929700
H	4.45431400	-1.12701000	0.90780700
C	2.59135900	-4.51877900	0.79375300
H	0.77719900	-3.38429200	0.90178700
C	3.98789800	-4.47784500	0.75784700
H	5.73291700	-3.20681800	0.75612000
H	2.07790300	-5.47339500	0.75527300
C	4.78553200	-5.75351800	0.71618900
F	4.08221600	-6.77394000	0.18097900
F	5.16281300	-6.14253700	1.95780200
F	5.91683500	-5.61101000	-0.00872400

TS-*S*-6:

Imaginary frequency: -65.66 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.676391 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.639594 Hartree
Free energy correction: 1.304150 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299778 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308628 Hartree

O	1.59032500	-3.18692400	-1.61771100
C	2.20660100	-4.09846200	-1.04273000
C	1.79422800	-4.51733600	0.39191100
H	2.55393600	-5.17976400	0.80919000
N	1.74913400	-3.34324300	1.24436200
C	2.90595300	-2.71758300	1.62133000
N	2.68143500	-1.60782700	2.41954100
H	1.70018300	-1.36068300	2.57285300
C	0.44106200	-5.31177300	0.43683200
H	0.86218200	-2.87727400	1.42186100
C	0.58784800	-6.59429000	-0.40654200
H	-0.33324700	-7.18465000	-0.34887500
H	0.77232000	-6.37349800	-1.46400900
H	1.40672100	-7.22535600	-0.04003300
C	0.16227700	-5.71473200	1.90064700
H	0.04993900	-4.84142600	2.54960900
H	-0.76687000	-6.29242900	1.95799900
H	0.97388600	-6.33231900	2.30464100
C	-0.75459600	-4.49880100	-0.09938800
H	-0.61043300	-4.22522200	-1.14801300
H	-1.66868800	-5.09633900	-0.02015700
H	-0.91763600	-3.57866000	0.47338500
N	3.23421100	-4.75954400	-1.63644300
C	4.15630600	-5.69281800	-0.94213600
C	3.64955700	-4.49369000	-3.04835000
C	5.32616100	-5.85540600	-1.91955200
H	4.46692700	-5.26926300	0.01525500
C	4.66836000	-5.64550400	-3.28384000
H	6.08185100	-5.08483900	-1.73723800
H	5.37658000	-5.39798100	-4.07916400
H	4.12313900	-6.54955600	-3.58477000
H	5.80922100	-6.83180900	-1.82105800

H	3.65998000	-6.65506400	-0.76537600
C	3.61323900	-0.69509000	2.90667900
C	5.00351300	-0.86427100	2.82075500
C	3.10626200	0.45752700	3.53695600
C	5.85035900	0.12332600	3.32986300
H	5.40111800	-1.76133100	2.36665600
C	3.96913600	1.42038700	4.04682900
H	2.03213100	0.58691100	3.62555200
C	5.35503200	1.27057300	3.94449300
H	6.02525100	2.02011900	4.34539500
O	-2.02022800	2.92288800	-0.10077800
C	-2.80084100	3.37472000	0.74950100
C	-2.68647200	2.90715900	2.22514400
H	-3.56366400	3.24014700	2.78071600
N	-2.69945300	1.45445900	2.27109900
C	-3.86032500	0.76639100	2.05420400
N	-3.69484400	-0.60927000	2.12905800
H	-2.74114100	-0.93675100	2.30786400
C	-1.43999100	3.49486200	2.97570100
H	-1.82137700	0.94114200	2.28659300
C	-1.54446700	5.03330100	2.98100700
H	-0.69918200	5.46202400	3.53051400
H	-1.52400100	5.45030000	1.96764200
H	-2.46398400	5.37320500	3.47320600
C	-1.47193200	2.99371000	4.43537100
H	-1.39454500	1.90411300	4.49325100
H	-0.62844300	3.41677600	4.99256000
H	-2.39868100	3.29315600	4.94036300
C	-0.09871400	3.09081400	2.33365600
H	-0.00506200	3.48429700	1.31891500
H	0.72908500	3.48839200	2.92993000
H	0.03006400	2.00331600	2.28811500
N	-3.77136200	4.27645400	0.43747000
C	-4.86427800	4.69819100	1.34944800
C	-3.93681400	4.83194800	-0.94075400
C	-5.86563200	5.40829100	0.43072500
H	-5.29920900	3.82738600	1.84449900
C	-4.97988700	5.95723100	-0.68786500
H	-6.58632500	4.68930900	0.02848300
H	-5.52864100	6.20773800	-1.59984300
H	-4.45585400	6.86032700	-0.34873700
H	-6.42437800	6.18673800	0.95827600
H	-4.47760800	5.38717400	2.11047500
C	-4.64086400	-1.60392700	1.89689700
C	-6.00694900	-1.36087700	1.68242800
C	-4.17874700	-2.93457700	1.89008500
C	-6.86748200	-2.43297100	1.43553600
H	-6.37628300	-0.34550500	1.72065600
C	-5.05733800	-3.98554600	1.65258600
H	-3.12842900	-3.13380400	2.07895800
C	-6.41410700	-3.74966400	1.41470100
H	-7.09701000	-4.56999500	1.23448700
C	2.46252400	-4.63943500	-4.01931300
H	1.78147200	-3.79131200	-3.95487300
H	2.82187400	-4.73398400	-5.04891300
H	1.90759500	-5.55293500	-3.78139700
C	-2.62593900	5.44562900	-1.46916300
H	-1.92246900	4.67991200	-1.79436900
H	-2.83392500	6.11826700	-2.30761100
H	-2.15918500	6.04271800	-0.67862700
O	-4.94169100	1.32386900	1.82683500

O	4.02679900	-3.12316800	1.28714200
C	4.36653600	-3.13825500	-3.18730700
C	4.85981700	-2.45070900	-2.09529400
C	4.61458600	-2.60711100	-4.48731200
C	5.60443500	-1.24749200	-2.24264800
H	4.67989400	-2.81134300	-1.08663700
C	5.32239100	-1.44052400	-4.66393700
H	4.24714900	-3.13285100	-5.36338500
C	6.13014500	-0.55187700	-1.11955700
C	5.84430000	-0.72459800	-3.55370700
H	5.49995800	-1.05858700	-5.66700300
C	6.86194900	0.60336700	-1.28547300
H	5.95166600	-0.95031400	-0.12517100
C	6.59581200	0.47346400	-3.69304600
C	7.09643700	1.12133200	-2.58418200
H	7.26589900	1.11203600	-0.41583100
H	6.77934000	0.86492600	-4.69125500
H	7.68302400	2.02881500	-2.70275900
C	-4.52789500	3.78891900	-1.90688100
C	-5.12405000	2.62570100	-1.46002400
C	-4.53771500	4.05706900	-3.30715100
C	-5.73296300	1.70471400	-2.35663000
H	-5.13061200	2.37841200	-0.40250500
C	-5.11139600	3.18350500	-4.20188000
H	-4.08662900	4.97009300	-3.68371500
C	-6.35734100	0.51376400	-1.89469000
C	-5.72495600	1.98044400	-3.76132700
H	-5.10456200	3.41196700	-5.26555200
C	-6.93826500	-0.36679400	-2.78063400
H	-6.37634300	0.31278600	-0.82736400
C	-6.32710700	1.05031400	-4.65095200
C	-6.91897900	-0.09803800	-4.17202300
H	-7.42211200	-1.26374600	-2.40664600
H	-6.31964400	1.26408100	-5.71761600
H	-7.38276200	-0.79920300	-4.86089000
Cl	-0.52071500	-1.12632500	2.31562100
C	-8.31150900	-2.12455800	1.14297600
C	-4.52484800	-5.39163600	1.58190900
C	7.33349600	-0.06941500	3.16320600
C	3.39925600	2.67289100	4.65777800
F	7.72813600	-1.30385600	3.54146200
F	7.70647300	0.06789300	1.86096500
F	8.05463600	0.82368300	3.87197400
F	4.20811900	3.18552900	5.60936800
F	2.18858600	2.46060000	5.22271300
F	3.22496400	3.64761500	3.72820700
F	-8.45799300	-1.58186700	-0.09645000
F	-8.82381700	-1.22944700	2.01321400
F	-9.09218800	-3.22452500	1.18204800
F	-3.43906300	-5.56833700	2.36815700
F	-5.44820400	-6.30376700	1.95061600
F	-4.14190700	-5.71611500	0.31769600
C	-0.19747400	-0.48646200	-0.88314900
H	-1.14340600	-0.60650100	-0.36917700
H	0.39888800	-1.39389900	-0.94427600
C	0.40706700	0.79564600	-0.90103200
H	-0.08832700	1.58237200	-0.34091400
C	1.49361600	1.05742500	-1.69775000
C	1.94783100	-0.00954600	-2.64853600
H	2.81874500	0.30334200	-3.22546100
H	2.20480100	-0.94198400	-2.13656000

C	0.79271800	-0.33875100	-3.67136900
H	1.22089300	-1.02680700	-4.40878900
H	0.51849500	0.57729200	-4.20160300
C	-0.40159900	-1.00870100	-3.05809600
H	-0.28933100	-2.07854700	-2.89939200
C	-1.65915600	-0.47423000	-2.86567900
C	-2.80307000	-1.36042500	-2.45378800
H	-2.47234500	-2.36012000	-2.15940700
H	-3.50302000	-1.45914600	-3.29448200
H	-3.37912700	-0.91409600	-1.63540600
C	-2.00567700	0.96424700	-3.10553900
H	-1.18699800	1.54182600	-3.53651400
H	-2.30840400	1.45205500	-2.16965300
H	-2.87072300	1.02706900	-3.77672600
C	2.08752400	2.40646600	-1.75974400
C	3.45046900	2.57300800	-2.07203000
C	1.31679100	3.55712000	-1.49182700
C	4.02519100	3.83924100	-2.10797600
H	4.08280100	1.70952400	-2.24741900
C	1.88913800	4.82279300	-1.54229800
H	0.26044700	3.46235000	-1.26117600
C	3.24506800	4.96848000	-1.85081500
H	5.08211400	3.94506700	-2.32734400
H	1.28322000	5.69987300	-1.34048000
C	3.84604000	6.34399500	-1.96591500
F	3.24897400	7.22453200	-1.13374100
F	3.71349500	6.83737900	-3.22045600
F	5.16607300	6.34246200	-1.68185600

TS-*S*-7:

Imaginary frequency: -71.43 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.675733 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.638942 Hartree
Free energy correction: 1.303681 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299456 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308500 Hartree

O	-1.77714500	3.32780000	-1.35252500
C	-2.52831100	4.11271500	-0.75202500
C	-2.24292800	4.46554400	0.73017500
H	-3.10494800	4.98441700	1.15041700
N	-2.08447600	3.24344900	1.49823400
C	-3.17879500	2.47934500	1.79764800
N	-2.86708100	1.34773400	2.53396200
H	-1.87178800	1.18713100	2.70875400
C	-1.01623200	5.42489800	0.91378000
H	-1.15691500	2.85802600	1.66242500
C	-1.29021200	6.73905600	0.15488100
H	-0.45577200	7.43377600	0.30131000
H	-1.39853900	6.57748000	-0.92354400
H	-2.19814100	7.23376800	0.52086400
C	-0.87527300	5.74577700	2.41688800
H	-0.64234600	4.85315100	3.00443900
H	-0.06533300	6.46846100	2.56897800
H	-1.79748800	6.18327700	2.81871000
C	0.30409400	4.82007800	0.39876700
H	0.25782400	4.61771300	-0.67469800
H	1.12472200	5.52022100	0.58221100
H	0.55505400	3.88429900	0.91166900

N	-3.60090900	4.69048400	-1.35415900
C	-4.65522200	5.46207200	-0.64816000
C	-3.92416900	4.47935700	-2.79885300
C	-5.78536900	5.57989000	-1.67752400
H	-4.96579700	4.93321400	0.25545500
C	-5.04235200	5.53919900	-3.01306100
H	-6.46563000	4.72664400	-1.59318600
H	-5.68074400	5.28290400	-3.86286100
H	-4.57777300	6.51227600	-3.21902500
H	-6.37096000	6.49328100	-1.53901500
H	-4.27686600	6.45353400	-0.37124100
C	-3.73054600	0.34415200	2.96776100
C	-5.12336400	0.37698300	2.79864000
C	-3.15302400	-0.75833400	3.62684400
C	-5.89983000	-0.69096600	3.25391500
H	-5.57875000	1.23510200	2.32468100
C	-3.94888500	-1.80221000	4.08473200
H	-2.07902400	-0.78442500	3.78153500
C	-5.33408900	-1.78752200	3.89815800
H	-5.95126800	-2.60069100	4.25826000
O	2.10694600	-2.77090600	-0.08598000
C	2.84068500	-3.24780000	0.79134300
C	2.64543200	-2.82795000	2.27321000
H	3.49641200	-3.17107400	2.86281700
N	2.63654500	-1.37685500	2.36671300
C	3.79075900	-0.67461600	2.17097800
N	3.61429400	0.70121400	2.25035300
H	2.65452600	1.02460400	2.40454700
C	1.36784800	-3.45189000	2.93594600
H	1.75194700	-0.87460100	2.37555000
C	1.48559400	-4.98887100	2.89539700
H	0.62006000	-5.44090100	3.39206500
H	1.51412500	-5.37263600	1.86933100
H	2.38482200	-5.33820800	3.41754800
C	1.31914100	-3.00202800	4.41187900
H	1.23590500	-1.91509800	4.50405400
H	0.44896200	-3.44486400	4.90838100
H	2.21916300	-3.31751000	4.95415900
C	0.05946000	-3.03656000	2.23540300
H	0.03187500	-3.38085900	1.19904400
H	-0.79280400	-3.47695900	2.76257600
H	-0.08622600	-1.95012700	2.23394700
N	3.82197700	-4.14636600	0.50487400
C	4.87801400	-4.58173300	1.45215700
C	4.03838000	-4.68307500	-0.87383100
C	5.92086100	-5.26474100	0.55960900
H	5.28510800	-3.71908800	1.98376000
C	5.08242100	-5.80289400	-0.59988800
H	6.64758600	-4.53104300	0.19661500
H	5.66655500	-6.03358200	-1.49494000
H	4.55519700	-6.71616500	-0.29453100
H	6.46845100	-6.04655800	1.09389800
H	4.46616300	-5.29055200	2.18126800
C	4.54570000	1.68472000	1.92341000
C	5.93183100	1.45818800	1.85586900
C	4.05748900	2.97629400	1.65938000
C	6.78473700	2.50208100	1.49697400
H	6.31887900	0.47463200	2.08148100
C	4.92906400	4.00137800	1.30003100
H	2.99062300	3.16752300	1.73230900
C	6.30287500	3.77902900	1.20905800

H	6.97727400	4.57871900	0.93199300
C	-2.71875700	4.80184200	-3.70191100
H	-1.95877900	4.02255000	-3.65602500
H	-3.04437500	4.92608000	-4.73959100
H	-2.26824100	5.74815600	-3.38470400
C	2.75030800	-5.30238000	-1.45010000
H	2.05693100	-4.53918800	-1.80208000
H	2.99135800	-5.97327000	-2.28103100
H	2.25742200	-5.90213400	-0.67770800
O	4.88056500	-1.21829800	1.95303300
O	-4.32582800	2.79325800	1.45326400
C	-4.49873200	3.07375200	-3.05391400
C	-4.94906000	2.26465800	-2.02868900
C	-4.66356300	2.61803900	-4.39514500
C	-5.57469600	1.01253400	-2.28308300
H	-4.83096700	2.56690500	-0.99210600
C	-5.25483300	1.40768200	-4.67518000
H	-4.32608600	3.23828900	-5.22007300
C	-6.06237000	0.19299600	-1.22849600
C	-5.73556400	0.56849800	-3.63466600
H	-5.37235300	1.08556500	-5.70763800
C	-6.68446500	-1.00590300	-1.49776200
H	-5.94368300	0.53131700	-0.20335000
C	-6.37470300	-0.67682900	-3.88116200
C	-6.84214300	-1.44504800	-2.83636300
H	-7.06114000	-1.61093500	-0.67902400
H	-6.50030800	-1.00793000	-4.90974100
H	-7.34381700	-2.38841200	-3.03641700
C	4.64883000	-3.62568300	-1.81107900
C	5.23677400	-2.47046300	-1.33427200
C	4.68543800	-3.87205200	-3.21487800
C	5.86431000	-1.53698300	-2.20473300
H	5.21840800	-2.23817400	-0.27348600
C	5.27606700	-2.98524100	-4.08463200
H	4.23979800	-4.77779800	-3.61450600
C	6.48005700	-0.35381900	-1.71291800
C	5.88246300	-1.79059500	-3.61348000
H	5.28745600	-3.19586600	-5.15190300
C	7.07740100	0.54021900	-2.57423600
H	6.48063800	-0.17055200	-0.64231100
C	6.50069200	-0.84676000	-4.47726800
C	7.08354200	0.29388300	-3.96975700
H	7.55624900	1.42985500	-2.17715700
H	6.51268600	-1.04395900	-5.54708600
H	7.55979200	1.00575600	-4.63890400
Cl	0.40564400	1.19375200	2.45887400
C	8.25553600	2.21029000	1.36274400
C	4.34565200	5.33871500	0.93508600
C	-7.38151300	-0.63970500	2.99538400
C	-3.30718400	-2.99603600	4.73948900
F	-7.91987900	0.53854600	3.37603500
F	-7.65605000	-0.77383000	1.66889900
F	-8.05303400	-1.61954200	3.63487500
F	-4.10649000	-3.54851000	5.67665600
F	-2.13460100	-2.68377800	5.33696100
F	-3.03383100	-3.97518500	3.83801000
F	8.53196700	1.60493700	0.17580800
F	8.69878300	1.37994600	2.32861100
F	9.00604300	3.33130900	1.41066000
F	3.43766300	5.76179200	1.84461100
F	5.28306700	6.30025000	0.81990100

F	3.69059700	5.27863200	-0.25669800
C	0.25620600	0.76488500	-0.76737000
H	1.14767600	0.90909000	-0.16990500
H	-0.40782600	1.62601600	-0.79351100
C	-0.24424900	-0.55152700	-0.93667700
H	0.26437100	-1.34789000	-0.40152400
C	-1.24769600	-0.81760100	-1.83472600
C	-1.70505100	0.29557700	-2.73102700
H	-2.49837500	-0.02631000	-3.40659500
H	-2.07830000	1.15516600	-2.16547900
C	-0.50248100	0.79974100	-3.61695000
H	-0.92073000	1.52059700	-4.32852200
H	-0.11544600	-0.04131600	-4.19854100
C	0.58652900	1.49420500	-2.85041400
H	0.38304100	2.53632000	-2.61462200
C	1.86674100	1.03772800	-2.61108100
C	2.91104900	1.95942200	-2.04254300
H	2.49877200	2.90633300	-1.68385200
H	3.65303400	2.18045800	-2.82202700
H	3.46570200	1.47848600	-1.22890300
C	2.33702200	-0.34721800	-2.94230900
H	1.59760800	-0.94107100	-3.48035900
H	2.60873300	-0.89473800	-2.03030300
H	3.24961700	-0.29136100	-3.54785400
C	-1.74376700	-2.19105500	-2.04391300
C	-3.05869500	-2.41470800	-2.49548800
C	-0.92821600	-3.31100400	-1.77756100
C	-3.54458800	-3.70641200	-2.66961100
H	-3.72766300	-1.58030100	-2.67428400
C	-1.41067200	-4.60083500	-1.96598300
H	0.09269100	-3.17286500	-1.43645000
C	-2.71987400	-4.80350900	-2.41330900
H	-4.56834200	-3.85649900	-2.99459700
H	-0.77011700	-5.45279600	-1.76336600
C	-3.21718300	-6.19992700	-2.67524300
F	-2.64374300	-7.10128500	-1.84855100
F	-2.93814200	-6.59479400	-3.94063400
F	-4.55527400	-6.29589600	-2.52015400

TS-*S*-8:

Imaginary frequency: -129.92 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.667936 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.628361 Hartree
Free energy correction: 1.305201 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299931 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308040 Hartree

O	-4.46972100	2.64223300	0.39716300
C	-5.03249800	2.34496500	1.46229500
C	-4.19812100	2.23246000	2.76450100
H	-4.79281800	1.73235800	3.53047800
N	-3.03512200	1.39742500	2.52334700
C	-3.20663100	0.06033600	2.30019500
N	-2.02615700	-0.61350300	2.01887100
H	-1.18850800	-0.03431700	1.93000600
C	-3.79283600	3.62692800	3.35993000
H	-2.13040000	1.82219500	2.31996800
C	-5.07369400	4.41244000	3.70775100
H	-4.80829200	5.37424600	4.16057600

H	-5.68239800	4.62280100	2.82126400
H	-5.69568600	3.87024100	4.43032400
C	-3.00043200	3.38246800	4.66201800
H	-2.05135900	2.87317800	4.47302600
H	-2.77607900	4.34028200	5.14591200
H	-3.57648100	2.77485100	5.37073200
C	-2.93574400	4.47129800	2.39530900
H	-3.47155800	4.68280500	1.46577300
H	-2.68957700	5.42656000	2.87452900
H	-1.98928300	3.98166900	2.14267400
N	-6.37290700	2.13268400	1.53218700
C	-7.07775500	1.52960500	2.68985800
C	-7.27283400	2.33049600	0.35425100
C	-8.44211000	1.12162500	2.12160700
H	-6.51108200	0.67688500	3.06989800
C	-8.67275400	2.14407000	1.00809100
H	-8.39322900	0.10960500	1.70756800
H	-9.41950900	1.83149100	0.27320400
H	-8.99844800	3.10138500	1.43525700
H	-9.22480800	1.13563700	2.88555200
H	-7.19508000	2.26823200	3.49219500
C	-1.88678200	-1.96304600	1.68251900
C	-2.91305100	-2.90690700	1.84239200
C	-0.64483800	-2.38595400	1.16658600
C	-2.70382400	-4.23121000	1.45047000
H	-3.85693100	-2.59697100	2.26680100
C	-0.46370800	-3.71036500	0.78272000
H	0.17608700	-1.68135700	1.07424000
C	-1.49189700	-4.64876700	0.91103400
H	-1.34433300	-5.67630900	0.60209200
O	2.90924300	-1.71670000	2.40172400
C	3.88081300	-1.26210600	3.01027200
C	3.70347700	-0.00458900	3.89528500
H	4.67227800	0.35939500	4.23455500
N	3.13695500	1.06670400	3.08443500
C	3.95216800	1.78463500	2.24644800
N	3.24100600	2.66997000	1.44469200
H	2.22236900	2.63814300	1.53705700
C	2.84519700	-0.26958800	5.17856600
H	2.16070900	0.97593500	2.81375100
C	3.46426000	-1.45036400	5.95303900
H	2.93322900	-1.59675000	6.90074400
H	3.39756100	-2.38670300	5.38871400
H	4.51967500	-1.26748600	6.19162200
C	2.90264300	0.99320300	6.06158900
H	2.50869500	1.86605800	5.53206300
H	2.30668200	0.84781700	6.97059200
H	3.93165400	1.21973300	6.36821400
C	1.37350000	-0.59687400	4.85437000
H	1.29390300	-1.45862600	4.18786100
H	0.83537000	-0.82023800	5.78377200
H	0.86117800	0.24942900	4.38178200
N	5.12390800	-1.82020100	2.92804100
C	6.37004900	-1.24733200	3.48388300
C	5.36351500	-3.05449200	2.12079900
C	7.48264700	-1.99388200	2.73800600
H	6.40755700	-0.17000400	3.31009800
C	6.85462200	-3.35920300	2.45291600
H	7.72112000	-1.47823800	1.80240300
H	7.34156600	-3.90484900	1.63994100
H	6.89742500	-3.98695000	3.35239100

H	8.40146000	-2.05927000	3.32879400
H	6.43201200	-1.43663300	4.56479700
C	3.72544500	3.45820000	0.41002800
C	5.07701600	3.52775200	0.03149700
C	2.78475600	4.23148300	-0.29853300
C	5.45154900	4.32723700	-1.04973900
H	5.80975400	2.96040700	0.58810800
C	3.18707400	5.03536700	-1.35879900
H	1.74238900	4.19731000	0.00123200
C	4.52580500	5.09112900	-1.75638400
H	4.83715300	5.71920200	-2.58169000
C	-7.14774100	3.75939600	-0.20739100
H	-6.21928100	3.90011800	-0.76049800
H	-7.99295600	3.98755700	-0.86443500
H	-7.17434800	4.47700600	0.61914100
C	4.47952900	-4.21535000	2.61110100
H	3.44242500	-4.09397700	2.30566300
H	4.85693300	-5.17055100	2.23013100
H	4.52611200	-4.26025900	3.70457200
O	5.18216600	1.68294600	2.23419800
O	-4.31952000	-0.48101000	2.35573400
C	-7.05674800	1.24562600	-0.71639900
C	-6.43883600	0.04424200	-0.42541500
C	-7.58437500	1.43135200	-2.02743100
C	-6.32739300	-0.99381000	-1.39091100
H	-6.00029700	-0.12920800	0.55303400
C	-7.48041900	0.45220900	-2.98956200
H	-8.08452600	2.36086300	-2.28095400
C	-5.70743500	-2.23636000	-1.08389900
C	-6.85251900	-0.78994700	-2.70694700
H	-7.89268500	0.61969600	-3.98236400
C	-5.60916800	-3.22802300	-2.03560100
H	-5.31799400	-2.39658300	-0.08294400
C	-6.72899200	-1.82858700	-3.66906300
C	-6.12085900	-3.02041300	-3.34168900
H	-5.14949300	-4.17647800	-1.77508400
H	-7.13010100	-1.66956500	-4.66762700
H	-6.03872500	-3.81106700	-4.08274300
C	5.21032200	-2.77059500	0.61464700
C	5.43743700	-1.51220300	0.08999400
C	4.90867300	-3.82876100	-0.28890300
C	5.39991500	-1.26350900	-1.30789000
H	5.62922500	-0.66867800	0.74684800
C	4.84459500	-3.61947700	-1.64715400
H	4.70327100	-4.82197100	0.09553400
C	5.66640700	0.02387400	-1.84947700
C	5.09670900	-2.33828600	-2.20267700
H	4.58502900	-4.43937700	-2.31163500
C	5.63213900	0.24123600	-3.20852800
H	5.91022400	0.83850000	-1.17334700
C	5.06110100	-2.08260500	-3.60112200
C	5.32225300	-0.82181700	-4.09369600
H	5.85271800	1.23038300	-3.59977300
H	4.82992300	-2.90350800	-4.27613900
H	5.30284100	-0.64109300	-5.16564100
Cl	0.06809300	1.97501100	1.63185100
C	6.89072500	4.29374600	-1.49117800
C	2.16359500	5.80990600	-2.13609800
C	-3.85147600	-5.19559700	1.57239200
C	0.85847200	-4.17517800	0.22998300
F	-4.49334800	-5.07424800	2.75318000

F	-4.78831400	-4.97796400	0.60556100
F	-3.46157000	-6.48124000	1.44954700
F	1.53422800	-4.92882300	1.13252300
F	1.65518600	-3.16128600	-0.13746000
F	0.67861400	-4.97083400	-0.85838800
F	7.16104400	3.15931500	-2.18995700
F	7.74354900	4.31565300	-0.44673100
F	7.20467600	5.33214100	-2.29620000
F	1.02592600	6.02385700	-1.42528300
F	2.61917300	7.01206000	-2.53662100
F	1.78250800	5.14916000	-3.26808400
C	-1.56842000	2.22064100	-1.05098900
H	-0.97074900	3.08019400	-0.76998800
H	-2.44341500	2.10096800	-0.41502800
C	-0.88787600	1.09208900	-1.61027000
H	0.19630700	1.11476600	-1.57413400
C	-1.55077500	0.03955800	-2.17588000
C	-3.04211800	0.15628000	-2.33944100
H	-3.46566100	-0.71229700	-2.84358500
H	-3.54779400	0.24817900	-1.37181000
C	-3.38611800	1.42523900	-3.18923000
H	-4.46090100	1.39299700	-3.40357200
H	-2.85890900	1.37105700	-4.14576400
C	-3.11790100	2.71210800	-2.46410700
H	-3.85900000	2.96491100	-1.70969000
C	-2.21547600	3.69883500	-2.81291900
C	-2.28553400	5.04920000	-2.15589900
H	-2.94661700	5.05008300	-1.28542700
H	-2.67521100	5.77567400	-2.88352400
H	-1.29263400	5.40643600	-1.86435100
C	-1.20866900	3.54266200	-3.91517100
H	-0.97761600	2.49766400	-4.13199400
H	-0.28145000	4.07343400	-3.68317300
H	-1.61378600	3.99230100	-4.83316800
C	-0.82927800	-1.12587900	-2.72358900
C	-1.45785700	-2.38504800	-2.79618300
C	0.51109500	-1.03096100	-3.14714100
C	-0.76904200	-3.50143000	-3.25648900
H	-2.47849800	-2.50755400	-2.44902800
C	1.20050600	-2.14403600	-3.61298400
H	1.02197700	-0.07419300	-3.12992500
C	0.56085500	-3.38465200	-3.66696900
H	-1.25748500	-4.46961000	-3.27557800
H	2.23610900	-2.04533200	-3.91992000
C	1.27697700	-4.58914200	-4.21756800
F	2.61863700	-4.49673500	-4.07046100
F	1.03995300	-4.73641700	-5.54392500
F	0.87824100	-5.72979800	-3.61949400

TS-*S*-9:

Imaginary frequency: -201.47 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.664891 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.622564 Hartree
Free energy correction: 1.301407 Hartree
Free energy correction – Grimme quasi-RRHO: 1.297877 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.306965 Hartree

O	-2.28933900	-3.14521200	0.18514200
C	-3.06791500	-3.47936000	-0.71530700

C	-2.79605600	-3.02999200	-2.17333300
H	-3.64229000	-3.30155500	-2.80528000
N	-2.69189900	-1.57836600	-2.22648300
C	-3.81026000	-0.79924400	-2.13780500
N	-3.53004700	0.56049600	-2.19675900
H	-2.54046600	0.81578700	-2.28357300
C	-1.53287300	-3.71446300	-2.79919900
H	-1.78104000	-1.13996100	-2.12118600
C	-1.69729100	-5.24402000	-2.69400000
H	-0.86744400	-5.74357700	-3.20593200
H	-1.69495400	-5.58465200	-1.65259800
H	-2.62856400	-5.58372100	-3.16480900
C	-1.46325200	-3.32359600	-4.29026300
H	-1.39336500	-2.23899200	-4.41869900
H	-0.57930900	-3.77232100	-4.75557300
H	-2.34971900	-3.67109100	-4.83573400
C	-0.22023600	-3.30320000	-2.10275600
H	-0.24111100	-3.53742200	-1.03687200
H	0.61846100	-3.83639700	-2.56084200
H	-0.01343400	-2.23110900	-2.20504000
N	-4.16967500	-4.24069700	-0.46493100
C	-5.25486100	-4.53779300	-1.42837900
C	-4.47072600	-4.73357900	0.91363900
C	-6.42338200	-4.98047900	-0.54018900
H	-5.49492900	-3.64835300	-2.01335000
C	-5.72470800	-5.62178800	0.65967400
H	-7.00781000	-4.11025800	-0.22481300
H	-6.35457400	-5.68826400	1.55107300
H	-5.39552100	-6.63719000	0.40392900
H	-7.09783600	-5.66741900	-1.05987900
H	-4.95207700	-5.34573900	-2.10806700
C	-4.40458400	1.61335300	-1.94970200
C	-5.80185600	1.47453000	-1.86382800
C	-3.84063000	2.89056000	-1.77598600
C	-6.58952200	2.58731800	-1.56928500
H	-6.24619900	0.50266000	-2.02580300
C	-4.65020300	3.98616100	-1.48549100
H	-2.76424600	3.01103600	-1.86335600
C	-6.03416900	3.85126800	-1.37124400
H	-6.65946200	4.70496100	-1.14492000
O	1.92949200	3.53347100	1.13698400
C	2.78727200	4.14503800	0.48433700
C	2.59966600	4.34216500	-1.04290400
H	3.53259400	4.69599700	-1.47980000
N	2.33513300	3.05498800	-1.66467900
C	3.37177200	2.19562100	-1.91430900
N	2.96397700	0.99885900	-2.48322800
H	1.95444500	0.86837200	-2.58429700
C	1.50604000	5.40094900	-1.41541300
H	1.38487200	2.69065600	-1.69037000
C	1.87985300	6.75426300	-0.77783700
H	1.13983200	7.51387500	-1.05385600
H	1.90494200	6.70080500	0.31658800
H	2.85812800	7.10721800	-1.12614600
C	1.49701500	5.56307200	-2.94955200
H	1.21656600	4.63283900	-3.45169900
H	0.77610600	6.33593500	-3.24065000
H	2.48305200	5.86462100	-3.32408300
C	0.09804400	4.99855600	-0.93934200
H	0.06330300	4.90696700	0.14889500
H	-0.62967800	5.75640000	-1.24713200

H	-0.22699700	4.04554500	-1.37264900
N	3.91262500	4.64812300	1.06127100
C	5.05437400	5.24348000	0.32089000
C	4.19838700	4.50719900	2.52163100
C	6.16810800	5.35661200	1.36967300
H	5.33731400	4.60451900	-0.51875400
C	5.39753400	5.48325200	2.68403000
H	6.77966600	4.44907100	1.37284000
H	5.99477600	5.24222800	3.56760200
H	5.01198300	6.50439100	2.80271000
H	6.82796000	6.20687200	1.17440500
H	4.77856800	6.23339100	-0.06198100
C	3.76452900	-0.07083700	-2.88202800
C	5.16057200	-0.10273700	-2.73794800
C	3.11958100	-1.17453500	-3.47304800
C	5.87328900	-1.23095200	-3.14868900
H	5.66893700	0.75483900	-2.32086000
C	3.85399300	-2.27843300	-3.89279900
H	2.04313300	-1.15390000	-3.60996000
C	5.24106300	-2.32664100	-3.72868300
H	5.80950600	-3.18690400	-4.05838100
C	-3.32650900	-5.60938500	1.45906400
H	-2.47496500	-5.01126800	1.78249900
H	-3.67677000	-6.21614200	2.30083400
H	-2.99513300	-6.29819200	0.67530300
C	3.01989500	4.98070500	3.39314200
H	2.21990500	4.24219400	3.42348000
H	3.36367700	5.18071200	4.41339100
H	2.61951700	5.91751100	2.99161900
O	4.55102600	2.48253000	-1.67255600
O	-4.95133100	-1.26416200	-2.02927900
C	-4.83294000	-3.56947800	1.85508100
C	-5.34548000	-2.38031000	1.37198300
C	-4.72214200	-3.72837900	3.26675600
C	-5.77109200	-1.33926900	2.24068200
H	-5.41829800	-2.20529500	0.30262000
C	-5.10312600	-2.73092600	4.13551400
H	-4.32655300	-4.65248200	3.67551200
C	-6.34267400	-0.13592700	1.74279500
C	-5.64298300	-1.50828100	3.65680600
H	-5.00272300	-2.87774600	5.20879500
C	-6.76403900	0.85431700	2.60287500
H	-6.45998600	-0.01591900	0.66985100
C	-6.07065900	-0.46161000	4.51822300
C	-6.61997800	0.69308000	4.00417800
H	-7.22112200	1.75394100	2.20154700
H	-5.97221200	-0.59455500	5.59350000
H	-6.95961100	1.47910800	4.67387000
C	4.65284400	3.07801500	2.87203900
C	5.02789800	2.16611500	1.90497600
C	4.79182400	2.70471700	4.24098900
C	5.56410500	0.89288100	2.24402000
H	4.93142900	2.40593600	0.85023800
C	5.29276300	1.47590200	4.60294500
H	4.50600600	3.40404700	5.02115000
C	5.99352300	-0.02622700	1.24775800
C	5.70510400	0.53451500	3.62268700
H	5.39208300	1.21721400	5.65496300
C	6.54248500	-1.23952600	1.59760500
H	5.89250300	0.24966100	0.20208500
C	6.26554300	-0.72902000	3.95310400

C	6.67963100	-1.59465400	2.96323400
H	6.87807400	-1.92121900	0.82227900
H	6.37622500	-0.99607900	5.00186800
H	7.11801900	-2.55379500	3.22669700
C	7.35878100	-1.24774900	-2.90716200
C	3.14700600	-3.46491000	-4.49097000
C	-8.07068500	2.38643800	-1.39060500
C	-3.98957800	5.30938500	-1.21786200
F	-8.57872100	1.51560700	-2.28553700
F	-8.35110400	1.88210500	-0.15725100
F	-8.76183000	3.54040300	-1.50365200
F	-4.86884000	6.32672700	-1.14561600
F	-3.07490900	5.62483100	-2.15993500
F	-3.31651000	5.28890500	-0.02708800
F	7.64111400	-1.35630200	-1.58082700
F	7.95208700	-0.11092400	-3.33003100
F	7.97112100	-2.27997200	-3.52396800
F	1.97398300	-3.12225100	-5.07137400
F	3.89915500	-4.07887000	-5.42943700
F	2.85767300	-4.40369200	-3.55328800
C	-0.21616600	1.22711400	1.08617200
H	0.23425600	2.18807500	0.85605700
H	-1.15424600	1.00692300	0.59448600
C	0.66647700	0.14791600	1.40170100
H	1.73196300	0.32906800	1.28670900
C	0.18249400	-1.03357500	1.89292400
C	-1.27520000	-1.06410600	2.25297500
H	-1.58238600	-2.03105800	2.65025500
H	-1.89179900	-0.89487000	1.36364300
C	-1.59053200	0.03395900	3.32593500
H	-2.67395300	0.04574400	3.47779600
H	-1.14518200	-0.27916600	4.27711600
C	-1.07326600	1.42910800	3.02483100
H	-0.13239700	1.70268300	3.49617600
C	-1.86114800	2.48774800	2.61186000
C	-1.35501800	3.89539600	2.68158300
H	-0.28540900	3.94730700	2.89623300
H	-1.56213800	4.43433200	1.75092100
H	-1.90209100	4.42852000	3.47380400
C	-3.25130900	2.30111800	2.08801800
H	-3.44838000	1.28982800	1.72547500
H	-3.97016000	2.48726900	2.90001700
H	-3.47434100	3.02163900	1.29595400
Cl	-0.32168600	1.00432500	-2.11800700
C	1.05336800	-2.18121200	2.19336400
C	0.55980200	-3.49237400	2.04038800
C	2.38566800	-2.00679200	2.61319200
C	1.37584100	-4.58934700	2.29504900
H	-0.44694600	-3.64293300	1.66360800
C	3.19510800	-3.10434300	2.88431900
H	2.78778900	-1.00912200	2.75720900
C	2.69157200	-4.39816500	2.72620600
H	0.99512600	-5.59486500	2.14958000
H	4.21734500	-2.94975100	3.21073900
C	3.54827800	-5.58461200	3.07856300
F	3.22813800	-6.67300000	2.34533600
F	4.86159400	-5.33397300	2.88575600
F	3.40199900	-5.93156700	4.38018900

TS-*S*-10:

Imaginary frequency: -62.31 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.661842 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.621505 Hartree
Free energy correction: 1.301136 Hartree
Free energy correction – Grimme quasi-RRHO: 1.297680 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307324 Hartree

O	3.09632500	3.21883500	1.22159900
C	3.27577400	4.06227400	0.32738500
C	2.13654600	4.37310400	-0.68343900
H	2.54992000	4.93121700	-1.52536900
N	1.60714400	3.12817600	-1.21194700
C	2.42947000	2.30778200	-1.93245600
N	1.84469000	1.09578700	-2.27378800
H	0.88076600	0.96512200	-1.95424000
C	0.99662900	5.26532800	-0.07850400
H	0.72901500	2.75204200	-0.85682000
C	1.59982600	6.60277700	0.39622300
H	0.80576200	7.25093500	0.78330500
H	2.33301400	6.46433400	1.19848000
H	2.08797400	7.13925700	-0.42621600
C	-0.02710200	5.56048700	-1.19552400
H	-0.52082700	4.65154400	-1.55047300
H	-0.80312900	6.23764300	-0.82007900
H	0.45234400	6.04302600	-2.05600700
C	0.27558500	4.59508300	1.10901900
H	0.97178000	4.37513600	1.92362700
H	-0.49772000	5.27249300	1.49069500
H	-0.22489400	3.66419800	0.82045600
N	4.44165400	4.74951300	0.21476900
C	4.82593400	5.57190700	-0.95956600
C	5.56292300	4.59956900	1.19652900
C	6.33153200	5.80244300	-0.78121400
H	4.59215600	5.03769300	-1.88329000
C	6.51259200	5.74270300	0.73583600
H	6.89917800	5.00226600	-1.26650700
H	7.54273500	5.55510800	1.04877800
H	6.18388800	6.68512100	1.19290600
H	6.65301700	6.75361900	-1.21514400
H	4.28300100	6.52436200	-0.95114000
C	2.51120800	-0.06827800	-2.66232600
C	3.85837900	-0.10120000	-3.06284900
C	1.78980500	-1.27364300	-2.61262200
C	4.46043000	-1.32509100	-3.35341800
H	4.41352100	0.82307500	-3.12611400
C	2.41064800	-2.48223700	-2.92079900
H	0.74875200	-1.26048100	-2.30254900
C	3.75509700	-2.52732000	-3.28938800
H	4.24195100	-3.47258200	-3.49299600
O	-6.03605300	1.93233900	-2.27652400
C	-6.53180700	2.45298100	-1.27746000
C	-5.59831100	3.15050900	-0.25467900
H	-6.13015500	3.34817400	0.67568200
N	-4.51057700	2.24095500	0.08850600
C	-4.75606400	1.18724000	0.93501400
N	-3.67981200	0.31377700	1.02065800
H	-2.85461400	0.54564200	0.45801600
C	-5.03820500	4.52089300	-0.77044400
H	-3.80444100	2.09643700	-0.62603700
C	-6.21698900	5.43196700	-1.16664000

H	-5.84311600	6.41928800	-1.46161300
H	-6.78091100	5.02583400	-2.01291700
H	-6.91175600	5.57988200	-0.33066500
C	-4.26147800	5.18810500	0.38277000
H	-3.43069700	4.55935400	0.71732000
H	-3.85227500	6.15181700	0.05545600
H	-4.91258900	5.37697600	1.24578000
C	-4.10373600	4.35403100	-1.98655900
H	-4.59634400	3.81734700	-2.80057500
H	-3.79720100	5.34229100	-2.35073500
H	-3.18723000	3.80995800	-1.72908000
N	-7.87489900	2.44772500	-1.02795700
C	-8.50838000	2.87094200	0.24128200
C	-8.85381500	1.85402200	-1.98746200
C	-9.94826900	2.35217300	0.13034400
H	-7.97718300	2.44553600	1.09672900
C	-10.19797800	2.34473100	-1.37899300
H	-10.01539300	1.33557800	0.53054100
H	-11.03330200	1.70705900	-1.68100400
H	-10.40174500	3.36314700	-1.73523200
H	-10.65454100	2.98011800	0.68182600
H	-8.49743800	3.96552100	0.32927900
C	-3.62693600	-0.90559800	1.68438100
C	-4.60092700	-1.35625500	2.59184400
C	-2.50932000	-1.72424100	1.42684300
C	-4.45595800	-2.60714100	3.19518100
H	-5.45504600	-0.72839900	2.80444200
C	-2.37876800	-2.95669000	2.05832600
H	-1.76804500	-1.38956300	0.70767300
C	-3.35286600	-3.42103500	2.94643500
H	-3.25683500	-4.38845300	3.42300700
C	5.08941200	4.86463600	2.63674400
H	4.50156900	4.03456000	3.02722400
H	5.94935500	5.03430800	3.29246700
H	4.47651800	5.77171100	2.65954900
C	-8.67088600	2.42562400	-3.40624900
H	-7.78116800	2.02153600	-3.88773300
H	-9.54928800	2.20438200	-4.02122000
H	-8.57697800	3.51566800	-3.34953200
O	-5.80299300	1.05808000	1.57515900
O	3.58131800	2.63532500	-2.24254100
C	6.27964900	3.24301700	1.04500200
C	7.14796800	2.79090200	2.02337200
C	6.14685400	2.47401000	-0.14563200
C	7.91097800	1.60273400	1.86342600
H	7.28248400	3.35095300	2.94514500
C	6.88004600	1.32437600	-0.33743600
H	5.44021600	2.77636200	-0.91013000
C	8.80707900	1.13488000	2.86378500
C	7.78537300	0.85430600	0.64895300
H	6.76625100	0.75582200	-1.25628000
C	9.54296800	-0.01276300	2.67066700
H	8.90648300	1.70314500	3.78613100
C	8.56160300	-0.32485100	0.47704800
C	9.42056000	-0.74977200	1.46582700
H	10.22600000	-0.35706300	3.44255400
H	8.46661100	-0.87812900	-0.45454700
H	10.01233100	-1.65009600	1.32490400
C	-8.81322800	0.31462600	-1.96593200
C	-8.18137000	-0.39277100	-0.96302200
C	-9.52188500	-0.41813400	-2.96225700

C	-8.22927200	-1.81223700	-0.90176600
H	-7.61981000	0.12658700	-0.19235100
C	-9.57719800	-1.79183900	-2.93996700
H	-10.03092400	0.11312300	-3.76069200
C	-7.60298800	-2.53856600	0.14674300
C	-8.93909100	-2.53461600	-1.91225400
H	-10.11985700	-2.32718700	-3.71618900
C	-7.67070500	-3.91307700	0.19148100
H	-7.07284200	-1.98927800	0.91983400
C	-8.98457600	-3.95249500	-1.84425000
C	-8.36471700	-4.62742700	-0.81609500
H	-7.19358100	-4.44894500	1.00660700
H	-9.52157500	-4.49723000	-2.61783600
H	-8.40854200	-5.71264000	-0.77235200
Cl	-1.02130600	1.15862800	-0.64758800
C	-5.56220100	-3.09499800	4.09326400
C	-1.14408500	-3.77887000	1.82338400
C	5.93579200	-1.35391700	-3.64322500
C	1.59882600	-3.74944600	-2.85251300
F	6.37338800	-0.21954900	-4.22498400
F	6.66142500	-1.49061100	-2.48675000
F	6.28848000	-2.38666300	-4.43270600
F	2.38055100	-4.85098900	-2.78781100
F	0.79551100	-3.89345800	-3.92808300
F	0.79647300	-3.76409600	-1.75997500
F	-6.63012300	-3.52448300	3.37545100
F	-6.01320400	-2.11980900	4.91126800
F	-5.17050500	-4.12788800	4.87164200
F	-0.56460500	-3.51703300	0.62785400
F	-0.18237500	-3.51883900	2.76355200
F	-1.38288900	-5.10158600	1.88272200
C	1.35717000	0.50300700	1.54618500
H	0.27952000	0.62771300	1.55375400
H	1.90284800	1.42155800	1.33619000
C	1.89563300	-0.75839200	1.18848000
H	1.20405400	-1.52313500	0.84787500
C	3.23761300	-1.03388700	1.29771900
C	4.11164500	-0.03212700	1.99534700
H	5.14529400	-0.37420100	2.05458700
H	4.11082800	0.93785100	1.48577000
C	3.59144700	0.19609300	3.46444600
H	4.36124500	0.78012800	3.98238600
H	3.51770700	-0.76725400	3.97579400
C	2.31311900	0.97490900	3.53146000
H	2.42309200	2.03756100	3.32636400
C	1.07931700	0.55003200	3.97217500
C	-0.03435400	1.54276600	4.17522800
H	0.21084700	2.53038700	3.77625200
H	-0.23618400	1.64567600	5.25042000
H	-0.96704200	1.19616200	3.71553100
C	0.77715200	-0.86283100	4.38028000
H	1.54470200	-1.57668400	4.07936400
H	-0.17915400	-1.19502500	3.96447300
H	0.67917400	-0.90688500	5.47392800
C	3.78582600	-2.32382200	0.84510600
C	5.10278700	-2.39049100	0.35004600
C	2.99663500	-3.49200100	0.80938100
C	5.59472400	-3.56483400	-0.20864200
H	5.73014400	-1.50638500	0.34416100
C	3.49374100	-4.66921900	0.26421900
H	1.99620700	-3.48870800	1.22558200

C	4.78874500	-4.70384400	-0.26010200
H	6.59652400	-3.58774500	-0.62263000
H	2.87301300	-5.55764300	0.23548700
C	5.28809900	-5.93732100	-0.96442400
F	4.68437300	-7.05684800	-0.51596500
F	6.62039600	-6.09864400	-0.80748500
F	5.05539100	-5.86579200	-2.29747300

TS-*S*-11:

Imaginary frequency: -161.53 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.659898 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.620507 Hartree
Free energy correction: 1.300526 Hartree
Free energy correction – Grimme quasi-RRHO: 1.297582 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307711 Hartree

O	3.38339000	-1.39909400	2.15371400
C	4.21009800	-0.92107600	2.93340100
C	3.76030800	0.19641100	3.91027600
H	4.62521900	0.71988500	4.31684500
N	3.00051800	1.18881300	3.16108900
C	3.66964400	2.06443700	2.33838400
N	2.79964600	2.78368200	1.52687000
H	1.81843300	2.49652200	1.56652800
C	2.92503800	-0.34178000	5.12462600
H	2.08438100	0.88917800	2.83731200
C	3.74383000	-1.40722900	5.87989700
H	3.18660400	-1.75080700	6.75907000
H	3.95200800	-2.28380400	5.25719800
H	4.69963300	-1.00388500	6.23561600
C	2.64919100	0.83802400	6.07870800
H	2.08893600	1.63263200	5.57742700
H	2.06428500	0.49820900	6.94195100
H	3.58385700	1.27096800	6.45682500
C	1.58471900	-0.96443800	4.68223700
H	1.73175900	-1.76588700	3.95412900
H	1.06684800	-1.37641100	5.55699600
H	0.91619100	-0.22033500	4.23371500
N	5.51065800	-1.33306700	2.98100800
C	6.58912800	-0.64698100	3.73014700
C	6.02443100	-2.45939200	2.14568900
C	7.87763400	-1.30909600	3.22344700
H	6.56772000	0.42888800	3.53567700
C	7.40913600	-2.70501000	2.80816900
H	8.26669500	-0.76672200	2.35606400
H	8.09791900	-3.21273800	2.12750800
H	7.27474100	-3.34065900	3.69327000
H	8.65817700	-1.32573000	3.98996000
H	6.46967600	-0.81011000	4.80847400
C	3.12885400	3.59219600	0.44620500
C	4.40644300	4.13288600	0.21959800
C	2.09869200	3.88955900	-0.46205100
C	4.63022400	4.92009400	-0.91083500
H	5.20076400	3.92423400	0.92322800
C	2.34686500	4.67594800	-1.58229200
H	1.10839500	3.48337600	-0.27837700
C	3.61645600	5.20057400	-1.82751000
H	3.80943600	5.80999100	-2.70042700
O	-4.46304600	-0.52503800	0.79788100

C	-4.48186600	-1.45542600	1.61747500
C	-3.46838900	-1.47153900	2.79344100
H	-3.47033500	-2.45933400	3.25463800
N	-2.12344200	-1.26215400	2.28436100
C	-1.52476600	-2.24701900	1.54426300
N	-0.28094700	-1.88223400	1.05117000
H	0.01495300	-0.92085400	1.23594900
C	-3.81408000	-0.45030100	3.93359500
H	-1.76264600	-0.31360400	2.20348800
C	-5.22540100	-0.75609200	4.47469100
H	-5.46147300	-0.07672000	5.30136900
H	-5.99834800	-0.62383900	3.70947900
H	-5.29711400	-1.77983000	4.86155400
C	-2.79815700	-0.64997400	5.07801500
H	-1.77672600	-0.42628200	4.75794300
H	-3.04309500	0.01378900	5.91545700
H	-2.81614400	-1.68167100	5.45066700
C	-3.76924100	1.01770800	3.46494100
H	-4.49664000	1.20887700	2.67202200
H	-4.00824600	1.67398500	4.31041400
H	-2.78036900	1.31469500	3.09857800
N	-5.37734500	-2.47685100	1.53389000
C	-5.31112900	-3.72826000	2.33003800
C	-6.46069800	-2.51698600	0.50476300
C	-6.30497100	-4.66772400	1.63642700
H	-4.29194000	-4.12123300	2.32815900
C	-7.32135400	-3.70356100	1.02446800
H	-5.80187000	-5.24075800	0.85129600
H	-7.92004200	-4.14600700	0.22362600
H	-8.00819200	-3.33457300	1.79733500
H	-6.75367600	-5.37775100	2.33711900
H	-5.61804600	-3.53630600	3.36515300
C	0.45643400	-2.56729100	0.08203900
C	0.35534700	-3.94997200	-0.13404000
C	1.34385500	-1.81685700	-0.70791100
C	1.10945400	-4.54549600	-1.14781400
H	-0.30537100	-4.53867800	0.48644900
C	2.07040700	-2.42794800	-1.72429200
H	1.46022700	-0.75448500	-0.51807400
C	1.96230800	-3.79979500	-1.95944600
H	2.53882600	-4.27306900	-2.74402600
C	5.13828900	-3.71242200	2.27648600
H	4.19580800	-3.59293300	1.74368400
H	5.66497600	-4.59072600	1.88954200
H	4.92314000	-3.89867400	3.33439900
C	-7.29877400	-1.22409800	0.50809900
H	-6.78127500	-0.40419600	0.01104400
H	-8.25823800	-1.39403800	0.00900300
H	-7.51494900	-0.93243200	1.54122800
O	-2.04673900	-3.35205700	1.35151400
O	4.89296000	2.21662600	2.34658300
C	6.23065200	-2.03927700	0.67893000
C	6.19019000	-0.72069300	0.27282900
C	6.56463800	-3.03227000	-0.28805900
C	6.48076600	-0.33978400	-1.06593000
H	5.92681700	0.06453400	0.97526400
C	6.83725400	-2.69931400	-1.59367300
H	6.60694500	-4.07667400	0.00630300
C	6.46290500	1.01959000	-1.47897100
C	6.81015600	-1.34758300	-2.02602700
H	7.08335000	-3.47671400	-2.31384800

C	6.75265600	1.36472700	-2.78017700
H	6.22097000	1.78637400	-0.74817600
C	7.09634400	-0.96202700	-3.36222700
C	7.06917800	0.36425100	-3.73183500
H	6.74130000	2.40966800	-3.07430100
H	7.34045200	-1.73359400	-4.08925300
H	7.29345200	0.64897500	-4.75669700
C	-5.91221900	-2.85801600	-0.89226900
C	-4.65028100	-3.38818900	-1.07919600
C	-6.75831200	-2.71032900	-2.03044900
C	-4.19037200	-3.78767600	-2.36487600
H	-3.96836800	-3.50184500	-0.24122000
C	-6.33945700	-3.07460400	-3.28893800
H	-7.75823600	-2.30522000	-1.90899900
C	-2.90031400	-4.35440400	-2.55439800
C	-5.04675400	-3.62400500	-3.50060100
H	-7.00459200	-2.95040600	-4.14086500
C	-2.47414600	-4.73084900	-3.80958000
H	-2.25739200	-4.49616400	-1.69042900
C	-4.57610000	-4.01501100	-4.78309600
C	-3.31735900	-4.55458400	-4.93472600
H	-1.49133500	-5.17477700	-3.93085900
H	-5.23053500	-3.88940600	-5.64301000
H	-2.96992800	-4.85749500	-5.91897500
Cl	-0.15686500	1.38284600	1.50236300
C	0.94231600	-6.02067600	-1.39038300
C	2.89116600	-1.56980100	-2.64805000
C	6.02526000	5.43358500	-1.15222700
C	1.20704100	4.94216300	-2.51963000
F	6.57896400	5.93268100	-0.02735800
F	6.85130800	4.44530400	-1.58317900
F	6.05791700	6.40708700	-2.08832000
F	1.57713200	5.58350000	-3.64082700
F	0.22462800	5.67806000	-1.93869700
F	0.59781600	3.77715300	-2.91222200
F	-0.19725500	-6.28342700	-2.09012500
F	0.84927800	-6.71813800	-0.23933600
F	1.96187500	-6.54333300	-2.10372400
F	3.43272400	-0.51132700	-2.02142900
F	3.88056100	-2.26078200	-3.24659900
F	2.11073700	-1.06508600	-3.65313500
C	-1.64688400	1.54072300	-1.14968800
H	-1.30730900	0.54575500	-0.89345600
H	-0.84119700	2.22174700	-1.39715500
C	-2.85931800	2.02437000	-0.56845300
H	-3.31921000	1.39391800	0.18610100
C	-3.45450700	3.17057600	-1.01217300
C	-2.86298900	3.85338300	-2.21669700
H	-3.44298200	4.73213500	-2.50469300
H	-1.83866600	4.19173100	-2.03069600
C	-2.85099300	2.87670800	-3.44571900
H	-2.48112600	3.44130500	-4.30913200
H	-3.88269200	2.59158800	-3.66810000
C	-1.97181200	1.66257700	-3.28794800
H	-0.92923500	1.81488800	-3.55961800
C	-2.38196200	0.34674900	-3.15872900
C	-1.39678500	-0.77331800	-3.32384100
H	-0.35940700	-0.43562700	-3.38097300
H	-1.63345900	-1.31268500	-4.25157100
H	-1.49423900	-1.51280900	-2.52111800
C	-3.79591600	-0.06075000	-2.88284200

H	-4.50770500	0.76313900	-2.93867000
H	-3.87710300	-0.51150500	-1.88415000
H	-4.09839700	-0.84116500	-3.59062700
C	-4.72970800	3.64595600	-0.43831100
C	-5.06989900	5.01173500	-0.47014600
C	-5.63145700	2.75075000	0.17410400
C	-6.25833800	5.47038000	0.08967800
H	-4.38492200	5.73367600	-0.90282300
C	-6.82330200	3.20738000	0.72442100
H	-5.40559200	1.68987100	0.20995300
C	-7.14255700	4.56792600	0.68360800
H	-6.49400100	6.52912200	0.07390600
H	-7.50819700	2.50521000	1.18828300
C	-8.46325500	5.04652400	1.22507700
F	-8.87315200	4.30236000	2.27524700
F	-9.43751100	4.97340300	0.28763700
F	-8.40420700	6.33246700	1.63251200

TS-*S*-12:

Imaginary frequency: -142.72 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.663278 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.617876 Hartree
Free energy correction: 1.297916 Hartree
Free energy correction – Grimme quasi-RRHO: 1.296354 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307306 Hartree

O	-2.93223200	-2.56579100	-0.67535700
C	-3.69141300	-2.50534700	-1.65139900
C	-3.16424700	-1.93455900	-2.99219500
H	-3.98266200	-1.85841600	-3.70744800
N	-2.68845100	-0.57268500	-2.77627100
C	-3.59070800	0.44660800	-2.62496500
N	-2.99589100	1.66894700	-2.34442000
H	-1.97283300	1.67524700	-2.29326000
C	-2.06966700	-2.83014000	-3.66290100
H	-1.74603500	-0.43441500	-2.42119100
C	-2.63532300	-4.25530200	-3.82621100
H	-1.92016600	-4.88136800	-4.37123700
H	-2.82183900	-4.73359100	-2.85798100
H	-3.57388700	-4.25410000	-4.39497900
C	-1.76768000	-2.24937200	-5.05979300
H	-1.41082400	-1.21692100	-4.99388400
H	-0.99179100	-2.84173200	-5.55581500
H	-2.66160800	-2.25657000	-5.69608500
C	-0.76315700	-2.89951300	-2.84775000
H	-0.93644500	-3.30015100	-1.84717400
H	-0.04353000	-3.54409900	-3.36153000
H	-0.29150800	-1.91562500	-2.73752700
N	-4.98884300	-2.90527200	-1.57287800
C	-6.00920800	-2.75745500	-2.63707100
C	-5.56238900	-3.41987600	-0.28868200
C	-7.34213800	-2.89014000	-1.89216000
H	-5.90836200	-1.78772300	-3.12595300
C	-7.00155800	-3.82386400	-0.72965300
H	-7.66597100	-1.91251700	-1.52140800
H	-7.70428400	-3.76131400	0.10526000
H	-6.98570300	-4.86430400	-1.07874600
H	-8.13453300	-3.28227600	-2.53662600
H	-5.89608900	-3.55463500	-3.38421600

C	-3.62913400	2.83275200	-1.91351400
C	-5.00734300	2.92721600	-1.65390800
C	-2.82310900	3.96630700	-1.69869700
C	-5.53623900	4.11400700	-1.14733800
H	-5.64325200	2.07723600	-1.85561900
C	-3.37763400	5.14490900	-1.20569700
H	-1.76128300	3.91334100	-1.91887000
C	-4.74000600	5.23416600	-0.91482500
H	-5.16796600	6.15147900	-0.53175500
O	2.90548100	3.22734700	1.49575700
C	3.89727300	3.57740900	0.83873100
C	3.74500200	3.90190500	-0.66588600
H	4.72764800	4.06926700	-1.10328800
N	3.20394900	2.73673800	-1.35130300
C	4.04657900	1.72464300	-1.73591400
N	3.39023800	0.65614500	-2.32534100
H	2.37008400	0.71612400	-2.36499700
C	2.91360900	5.19765800	-0.95208600
H	2.20655300	2.54174500	-1.29222200
C	3.53402700	6.36585200	-0.15962800
H	3.02023200	7.30153200	-0.40726500
H	3.44461800	6.21769900	0.92259400
H	4.59613900	6.49887700	-0.40137200
C	3.01957900	5.50370400	-2.46014500
H	2.61326600	4.68563000	-3.06243700
H	2.45838400	6.41398900	-2.70090900
H	4.06202600	5.66120900	-2.76375100
C	1.42862500	5.06086400	-0.56890900
H	1.30944300	4.85553700	0.49719900
H	0.89556700	5.98790500	-0.80417600
H	0.93645500	4.25689400	-1.12826900
N	5.13538700	3.65574400	1.39636400
C	6.40112300	3.91683400	0.66742200
C	5.35955200	3.33768200	2.84089500
C	7.48607500	3.41882600	1.62752100
H	6.41063500	3.37789400	-0.28100100
C	6.87268600	3.67206600	3.00521000
H	7.66454500	2.34963300	1.47346400
H	7.32608300	3.08111400	3.80523200
H	6.97423200	4.73209200	3.27079800
H	8.43586700	3.94095700	1.47936900
H	6.51208500	4.99247800	0.47533300
C	3.96840200	-0.46424700	-2.92620800
C	5.33434300	-0.78262700	-2.83770600
C	3.12025700	-1.31498100	-3.65791300
C	5.82041500	-1.92472600	-3.47418100
H	5.99502600	-0.13265900	-2.28329800
C	3.62922000	-2.44871800	-4.28560700
H	2.06510100	-1.07500900	-3.74279100
C	4.98516500	-2.76916200	-4.20272000
H	5.37818000	-3.64909500	-4.69630500
C	-4.81198700	-4.67179700	0.20162000
H	-3.84685300	-4.41854000	0.63941500
H	-5.41225800	-5.20843300	0.94409300
H	-4.65169900	-5.35037400	-0.64261900
C	4.52784800	4.25933200	3.75193600
H	3.47381900	3.98308500	3.75006300
H	4.90740600	4.22593700	4.77860300
H	4.62227400	5.29246700	3.40207000
O	5.27300300	1.78292100	-1.58709800
O	-4.81013000	0.28975400	-2.75152800

C	-5.62355500	-2.30494100	0.77374200
C	-5.63001000	-2.60151700	2.12386000
C	-5.76634100	-0.94111200	0.38512200
C	-5.77883000	-1.59492300	3.11611900
H	-5.52220000	-3.62691700	2.46537600
C	-5.92750200	0.05738100	1.31858900
H	-5.72507200	-0.67391000	-0.66522200
C	-5.77835800	-1.89676600	4.50554700
C	-5.94161700	-0.23241400	2.70836600
H	-6.05912100	1.08760600	0.99477900
C	-5.93546000	-0.90159600	5.44439200
H	-5.65547200	-2.93200700	4.81642900
C	-6.10501200	0.77158800	3.70049400
C	-6.10228200	0.44607600	5.03850600
H	-5.93666800	-1.14756100	6.50304800
H	-6.23825500	1.80291000	3.38144700
H	-6.23220600	1.22116100	5.78914300
C	5.11491900	1.84282400	3.12235100
C	4.83870700	1.39656300	4.40169500
C	5.25140100	0.87270100	2.08735800
C	4.69470600	0.01625000	4.70539200
H	4.72861700	2.10204600	5.22021500
C	5.12264100	-0.47262300	2.34748600
H	5.44465400	1.19338900	1.06882100
C	4.41021400	-0.44311600	6.02072800
C	4.84447700	-0.94692400	3.65656800
H	5.23350900	-1.19123700	1.53874500
C	4.28236300	-1.78779600	6.28765300
H	4.29920000	0.28840800	6.81808000
C	4.70803900	-2.32872700	3.96306300
C	4.43418100	-2.74101900	5.24926300
H	4.06992100	-2.12468400	7.29865600
H	4.83427700	-3.05671700	3.16489500
H	4.34578500	-3.80043200	5.47545000
C	7.29903900	-2.20798900	-3.41749900
C	2.69919600	-3.37012700	-5.02760900
C	-6.99434400	4.13303700	-0.77400700
C	-2.47269500	6.31345000	-0.92504000
F	-7.76472900	3.52056400	-1.69613000
F	-7.20391900	3.47942600	0.40192700
F	-7.46843600	5.38621300	-0.61161400
F	-3.14458100	7.48096100	-0.86638900
F	-1.50634700	6.44484900	-1.86102900
F	-1.83018500	6.17474000	0.26918800
F	7.83519300	-1.85332800	-2.22805000
F	7.97586500	-1.52571200	-4.37009700
F	7.56987500	-3.51940800	-3.60678500
F	1.63893400	-2.71027900	-5.54938900
F	3.32022800	-4.00556400	-6.04390700
F	2.19434300	-4.33612300	-4.21737600
C	1.11622900	0.60297400	1.80582700
H	1.90559400	1.27002400	2.14234700
H	0.61044700	0.91781100	0.89776700
C	1.16116000	-0.76984900	2.12946600
H	2.03913200	-1.14162300	2.65076300
C	0.08228700	-1.59144000	1.86816100
C	-1.17540600	-0.92123200	1.41502000
H	-1.97450000	-1.62050100	1.17901000
H	-0.98709000	-0.33278700	0.50867300
C	-1.70418000	0.05754100	2.53426500
H	-2.59141500	0.54619400	2.12153700

H	-2.04785100	-0.54777400	3.37942900
C	-0.71920300	1.07476100	3.05055500
H	-0.22343100	0.82669300	3.98615700
C	-0.62337700	2.39331800	2.65487400
C	0.22894400	3.35768800	3.42205200
H	0.68403500	2.90042500	4.30532900
H	1.02777900	3.74819100	2.77882300
H	-0.38096900	4.21358700	3.73992900
C	-1.30304900	2.92826600	1.43290500
H	-2.24898900	2.42484200	1.21870900
H	-1.48073600	4.00370300	1.51005100
H	-0.65963600	2.77378500	0.55310100
Cl	0.16776800	1.18478800	-1.69709300
C	0.11027600	-3.03131200	2.16542900
C	-0.73644900	-3.91443900	1.46331000
C	0.98867400	-3.57047900	3.12972000
C	-0.68817100	-5.28425700	1.70462200
H	-1.41381500	-3.53576400	0.70468000
C	1.02171800	-4.93591700	3.38002300
H	1.63057400	-2.91922700	3.71316500
C	0.18532800	-5.79894300	2.66475000
H	-1.33761900	-5.95297600	1.14982500
H	1.68633100	-5.33271700	4.14021000
C	0.26695500	-7.28496800	2.89765400
F	-0.90021400	-7.90283300	2.61699100
F	1.21528800	-7.85536200	2.12077600
F	0.58317700	-7.57230800	4.18008300

TS-*S*-13:

Imaginary frequency: -206.05 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.655169 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.617944 Hartree
Free energy correction: 1.299822 Hartree
Free energy correction – Grimme quasi-RRHO: 1.297230 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307645 Hartree

O	3.95702200	2.54680500	-0.05574900
C	4.94765000	2.27691600	-0.73995700
C	4.75184700	1.79787700	-2.20038300
H	5.69529100	1.43236000	-2.60381300
N	3.84472000	0.65827300	-2.22111000
C	4.31276200	-0.59145600	-1.88892600
N	3.31377100	-1.55106100	-1.88631800
H	2.37045100	-1.22394000	-2.10687500
C	4.25810900	2.93455200	-3.16048000
H	2.85717500	0.84227600	-2.07312800
C	5.22314500	4.13253400	-3.05732800
H	4.94163500	4.90374900	-3.78375900
H	5.19960100	4.59112800	-2.06292000
H	6.25725100	3.83792100	-3.27515200
C	4.29137200	2.39029900	-4.60301700
H	3.64608400	1.51342800	-4.71179400
H	3.94666400	3.15830900	-5.30608800
H	5.30789300	2.09998200	-4.89677400
C	2.82955800	3.41241400	-2.82987000
H	2.75301500	3.75731400	-1.79634900
H	2.55812500	4.23988400	-3.49733200
H	2.08590400	2.62094700	-2.98023300
N	6.22208300	2.38278500	-0.26362500

C	7.43946100	1.90886500	-0.96369200
C	6.51053300	2.87174100	1.11830500
C	8.52164000	1.92009600	0.12305200
H	7.27755200	0.91197600	-1.37992300
C	8.05666500	3.03323900	1.06319000
H	8.53884900	0.96022100	0.64886100
H	8.50170300	2.97929900	2.06055600
H	8.29882600	4.01545500	0.63635400
H	9.51854900	2.09522800	-0.29238900
H	7.70218900	2.59601000	-1.77924200
C	3.40924300	-2.89131900	-1.51818400
C	4.59388000	-3.51284200	-1.09091200
C	2.23043100	-3.65536900	-1.58563100
C	4.56699000	-4.85523900	-0.70877200
H	5.51344200	-2.94474500	-1.07197500
C	2.23095500	-4.99531300	-1.21358600
H	1.31658700	-3.18804200	-1.93826100
C	3.39819800	-5.61302800	-0.76107300
H	3.39805500	-6.65580900	-0.47176700
O	-2.47864500	2.14199700	1.14784700
C	-2.03328100	1.69526300	2.21613600
C	-0.66680200	0.95955500	2.23852700
H	-0.57366700	0.39911700	3.16970000
N	-0.63669700	-0.01546100	1.16169200
C	-1.42865200	-1.12386900	1.22078900
N	-1.32076300	-1.92816700	0.09034800
H	-0.71747000	-1.56889400	-0.65602400
C	0.57756500	1.91361000	2.16519800
H	-0.18521100	0.22174400	0.28209600
C	0.55906200	2.86246900	3.38024500
H	1.43675500	3.51701200	3.34843900
H	-0.33095200	3.50260300	3.39402300
H	0.59964700	2.30772900	4.32551900
C	1.85213600	1.04646900	2.24314400
H	1.93520700	0.36390000	1.39311700
H	2.74195700	1.68195000	2.22832700
H	1.86820300	0.44612600	3.16115900
C	0.60998600	2.75958700	0.87741100
H	-0.24304000	3.44223900	0.82266900
H	1.53375200	3.34539200	0.85480600
H	0.61521200	2.14569500	-0.02978400
N	-2.70759400	1.83172000	3.39006000
C	-2.36199400	1.13064000	4.65182700
C	-3.99041800	2.59141800	3.49591600
C	-3.58952100	1.34020700	5.54750500
H	-2.16576700	0.07386100	4.45518900
C	-4.16837500	2.66095100	5.03927400
H	-4.30879900	0.52798900	5.40308300
H	-5.21454800	2.81713200	5.31641400
H	-3.58488700	3.50594200	5.42727900
H	-3.32172300	1.36834900	6.60762000
H	-1.46922400	1.57880900	5.10257400
C	-2.15157700	-2.99128000	-0.26113400
C	-2.94379400	-3.69737100	0.66192700
C	-2.19906800	-3.35611600	-1.61530700
C	-3.79047000	-4.70725100	0.21014300
H	-2.89759200	-3.43302400	1.70787900
C	-3.04754300	-4.37536200	-2.04184100
H	-1.57817700	-2.82854000	-2.33404900
C	-3.86112100	-5.05779800	-1.14025400
H	-4.53332900	-5.83631500	-1.47954000

C	5.84887000	4.23744600	1.38371600
H	4.77299400	4.14182100	1.52471000
H	6.29070900	4.70911100	2.26758400
H	6.03362200	4.90092800	0.53195500
C	-3.86043100	4.01508000	2.92161700
H	-3.88278900	4.01639700	1.83230500
H	-4.67040300	4.64933700	3.29641400
H	-2.91629400	4.45756200	3.25576600
O	-2.16126700	-1.37956700	2.18366400
O	5.50233600	-0.82851900	-1.65775300
C	6.14206500	1.81827900	2.17973300
C	5.92836600	0.49279400	1.85580700
C	6.10611000	2.18808600	3.55596300
C	5.68518100	-0.49338300	2.85043800
H	5.93543600	0.17118300	0.81861800
C	5.86183700	1.26107200	4.54238700
H	6.27597200	3.22213600	3.84008900
C	5.49408500	-1.86175200	2.51749600
C	5.64729800	-0.10646100	4.22754400
H	5.83675100	1.57055000	5.58519100
C	5.27262600	-2.80222500	3.49828700
H	5.53263100	-2.15810500	1.47306100
C	5.40798200	-1.09771700	5.21636400
C	5.22507200	-2.41572900	4.86063700
H	5.14058200	-3.84434000	3.22323900
H	5.37755900	-0.79849900	6.26196100
H	5.04741300	-3.16677800	5.62603900
C	-5.16703900	1.81234200	2.88005200
C	-5.08729800	0.46125600	2.60285000
C	-6.41285500	2.47213900	2.66630300
C	-6.20873800	-0.27183600	2.12523900
H	-4.15142700	-0.07487600	2.72904100
C	-7.51214300	1.79554700	2.18976900
H	-6.50515300	3.53172400	2.88437300
C	-6.13180800	-1.66775800	1.86599900
C	-7.45046600	0.40520100	1.90432900
H	-8.45044200	2.32378700	2.03419100
C	-7.22764600	-2.36002300	1.39822700
H	-5.19381700	-2.18165800	2.05249400
C	-8.56177300	-0.33427300	1.41637600
C	-8.45253900	-1.68515100	1.16696200
H	-7.15213300	-3.42688600	1.20965500
H	-9.50449400	0.18290400	1.25100800
H	-9.31098700	-2.24181100	0.80038900
Cl	0.32536800	-0.21805000	-2.15740700
C	-4.64023300	-5.46164300	1.19828600
C	-3.15433700	-4.63622800	-3.51814000
C	5.83659600	-5.46250900	-0.17510600
C	0.93246200	-5.75624300	-1.25446000
F	6.91095700	-5.12821100	-0.92155100
F	6.09681300	-5.03199000	1.08797100
F	5.78107200	-6.81087100	-0.12431100
F	1.12371600	-7.09258300	-1.26132600
F	0.20237500	-5.44567500	-2.35281300
F	0.15294300	-5.47303700	-0.18274100
F	-5.88837900	-5.68193200	0.70612100
F	-4.79035100	-4.78966000	2.36214200
F	-4.12507600	-6.67141500	1.49852300
F	-1.95128200	-4.64833800	-4.12380200
F	-3.77084000	-5.80089700	-3.79663900
F	-3.88135200	-3.65129200	-4.12776800

C	-2.47497800	0.77840100	-2.46602300
H	-2.50258800	0.01148200	-1.70209300
H	-2.13525700	0.41140900	-3.42702700
C	-2.20223200	2.12592700	-2.06565900
H	-1.92867900	2.27436500	-1.02562700
C	-2.37308600	3.16886300	-2.92762100
C	-2.98048900	2.86641500	-4.27285000
H	-3.10553800	3.76790900	-4.87521400
H	-2.35077800	2.17622900	-4.84860200
C	-4.39395600	2.21914100	-4.07838800
H	-4.85233700	2.10189400	-5.06744800
H	-5.01849300	2.92211000	-3.52073900
C	-4.37939100	0.86098500	-3.41956200
H	-4.21925000	0.02672400	-4.10126800
C	-4.90999600	0.52420700	-2.18378000
C	-5.13285100	-0.91645900	-1.83286200
H	-4.70869800	-1.60741300	-2.56564600
H	-6.21564400	-1.09582100	-1.77418300
H	-4.74239400	-1.15197700	-0.83656900
C	-5.29025900	1.52409400	-1.13828600
H	-5.32678000	2.54988900	-1.50653800
H	-4.57374700	1.48990100	-0.30435900
H	-6.26362100	1.26144000	-0.70889000
C	-2.13577000	4.56469500	-2.50920900
C	-1.80230200	5.55582800	-3.45153000
C	-2.22571900	4.94136100	-1.15280300
C	-1.55792900	6.86832100	-3.05941700
H	-1.69998400	5.29825800	-4.50078100
C	-1.99080400	6.25411800	-0.76190100
H	-2.49792300	4.20681000	-0.40173000
C	-1.65667200	7.22307100	-1.71288100
H	-1.29562900	7.61715700	-3.79910900
H	-2.08059800	6.53118500	0.28322700
C	-1.35335000	8.63199700	-1.27644200
F	-0.05374900	8.77681400	-0.93335700
F	-2.08738700	8.98954600	-0.19957100
F	-1.60553200	9.52648700	-2.25728400

TS-*S*-14:

Imaginary frequency: -168.95 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.659354 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.611580 Hartree
Free energy correction: 1.298530 Hartree
Free energy correction – Grimme quasi-RRHO: 1.296578 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307786 Hartree

O	-4.63226500	1.00769400	-3.22242300
C	-5.29674900	1.98721300	-2.88138400
C	-4.56286300	3.22075700	-2.29812100
H	-5.26956800	3.89877400	-1.82131300
N	-3.66443200	2.77032200	-1.24041300
C	-4.18157300	2.47047900	0.00013800
N	-3.23863000	1.89372600	0.83701300
H	-2.30273400	1.74846200	0.44781000
C	-3.78361200	4.04480200	-3.38060100
H	-2.87929900	2.20534600	-1.54759000
C	-4.75122300	4.43331500	-4.51599500
H	-4.23716100	5.07333200	-5.24244700
H	-5.12404100	3.55531100	-5.05423300

H	-5.61379300	4.99499600	-4.13667100
C	-3.25315100	5.33057100	-2.71523300
H	-2.59283400	5.09771900	-1.87443800
H	-2.68677400	5.92764800	-3.44016500
H	-4.07472600	5.95271100	-2.33831700
C	-2.60074300	3.25524000	-3.97862500
H	-2.92556500	2.29730400	-4.39180600
H	-2.13386600	3.84386100	-4.77777000
H	-1.82334300	3.05848700	-3.23068200
N	-6.65710100	2.03442400	-2.98938000
C	-7.52087800	3.09530600	-2.42241300
C	-7.44323400	0.90822200	-3.57655600
C	-8.93751700	2.51307600	-2.51644600
H	-7.23067700	3.31893300	-1.39255100
C	-8.84482800	1.56695900	-3.71506600
H	-9.17631900	1.95160100	-1.60770300
H	-9.64074900	0.81772100	-3.74356700
H	-8.88107000	2.13714300	-4.65269200
H	-9.69435900	3.29351300	-2.64009100
H	-7.43925400	4.01422400	-3.01788100
C	-3.43362800	1.36704800	2.10821900
C	-4.61924900	1.49069000	2.85267900
C	-2.35144600	0.66923800	2.67259900
C	-4.70396500	0.89919300	4.11469000
H	-5.45110600	2.04153500	2.43586400
C	-2.45447900	0.10570200	3.93901400
H	-1.44132700	0.56885900	2.09017800
C	-3.63394700	0.20566100	4.67943400
H	-3.71808500	-0.24315800	5.66065200
O	4.47102100	0.76529900	-1.14688900
C	4.48211700	0.44218900	-2.34382200
C	3.20934100	0.64474600	-3.21060300
H	3.30833800	0.07325300	-4.13425300
N	2.05748300	0.10346500	-2.51083200
C	1.94344000	-1.24729100	-2.33805600
N	0.84635100	-1.60635400	-1.56481800
H	0.29817600	-0.83349000	-1.17289600
C	2.96696400	2.13610500	-3.63446300
H	1.48501400	0.71610800	-1.93284800
C	4.17366800	2.62869400	-4.45861300
H	4.00591900	3.66225200	-4.78138100
H	5.10394200	2.61130900	-3.87986000
H	4.31956100	2.02356000	-5.36151400
C	1.71152000	2.18235800	-4.53140700
H	0.80999300	1.88409600	-3.98886600
H	1.55769700	3.20174800	-4.90420600
H	1.81710800	1.51972400	-5.39916500
C	2.76755600	3.08039300	-2.43210200
H	3.65134100	3.10526800	-1.78924700
H	2.58577100	4.09775800	-2.79876600
H	1.90552400	2.80277700	-1.81563100
N	5.58520800	-0.08364000	-2.94299900
C	5.60046000	-0.70793300	-4.28979700
C	6.89171100	-0.23661700	-2.23313800
C	6.95385200	-1.42664900	-4.35670200
H	4.75697400	-1.39424700	-4.39662200
C	7.83201400	-0.59930000	-3.41749100
H	6.85883700	-2.45173700	-3.98527800
H	8.72572900	-1.12725500	-3.07389700
H	8.15394800	0.32550200	-3.91371700
H	7.34177000	-1.47294500	-5.37833600

H	5.53205500	0.06293800	-5.06618100
C	0.56412900	-2.87836200	-1.06508100
C	1.01199100	-4.06429200	-1.66823000
C	-0.22017200	-2.96175300	0.09918000
C	0.69775100	-5.29469200	-1.08809400
H	1.59759700	-4.01053000	-2.57525700
C	-0.51343700	-4.19907000	0.66445600
H	-0.58909500	-2.05192700	0.56313800
C	-0.05716600	-5.38218700	0.08020300
H	-0.29307500	-6.34309500	0.51919600
C	-6.90536300	0.50498400	-4.96256700
H	-5.96692700	-0.04235800	-4.88294100
H	-7.64136500	-0.10944300	-5.49137800
H	-6.73818900	1.40570800	-5.56334500
C	7.34805000	1.08576300	-1.58819700
H	6.79522100	1.30240900	-0.67469000
H	8.41755900	1.04521800	-1.35804100
H	7.19665800	1.90782600	-2.29558200
O	2.73963300	-2.05856800	-2.82625100
O	-5.34090600	2.72401500	0.33571000
C	-7.53172500	-0.28782600	-2.61027500
C	-7.19772500	-0.18294100	-1.27496300
C	-8.05693400	-1.52816300	-3.07656000
C	-7.37086400	-1.26595000	-0.37063900
H	-6.78381000	0.74064100	-0.88164000
C	-8.22549400	-2.59965400	-2.23138100
H	-8.33154100	-1.63732000	-4.12133900
C	-7.05306400	-1.14798900	1.00931500
C	-7.89347500	-2.50680600	-0.85427700
H	-8.62316200	-3.53718000	-2.61420000
C	-7.23820800	-2.20722800	1.86926600
H	-6.66565900	-0.20230200	1.37833000
C	-8.06593000	-3.58422700	0.05487100
C	-7.74583600	-3.43870500	1.38653400
H	-6.99809500	-2.09348500	2.92214100
H	-8.45953300	-4.52716900	-0.31865400
H	-7.88474300	-4.26912800	2.07400600
C	6.86395300	-1.40364500	-1.22963800
C	5.87350500	-2.36665900	-1.24866000
C	7.93807000	-1.55788200	-0.30477400
C	5.91028100	-3.49458500	-0.38249300
H	5.02767200	-2.27702000	-1.92407200
C	7.99549100	-2.62859700	0.55706500
H	8.73416700	-0.82018300	-0.27616200
C	4.90471500	-4.49925900	-0.42044400
C	6.98916000	-3.63121600	0.54874200
H	8.82572100	-2.72202700	1.25390100
C	4.95893400	-5.58187400	0.43023900
H	4.09456800	-4.40360800	-1.13781600
C	7.01347100	-4.75527900	1.41770600
C	6.02015000	-5.70847800	1.36089300
H	4.18760900	-6.34358700	0.37830300
H	7.83537000	-4.85554600	2.12331400
H	6.05229200	-6.56820400	2.02497100
Cl	-0.23740200	1.19321100	-0.31630500
C	1.23647900	-6.54247500	-1.73516300
C	-1.23386600	-4.24317300	1.98503000
C	-6.01856600	0.97121200	4.84579800
C	-1.24758800	-0.57207300	4.51458400
F	-6.58758100	2.19060100	4.74314300
F	-6.91290400	0.08203700	4.34314900

F	-5.88759700	0.69333100	6.16183700
F	-0.32461600	0.33162200	4.97221700
F	-0.58036200	-1.31056100	3.58262500
F	-1.53340800	-1.38429700	5.54393600
F	2.57049200	-6.68528400	-1.49872100
F	1.08939600	-6.52068700	-3.07559100
F	0.63833800	-7.66041000	-1.27515600
F	-2.14537300	-3.25846500	2.10606900
F	-1.86404500	-5.41811400	2.18577500
F	-0.35592100	-4.09041000	3.01741100
C	1.92378400	0.38519600	1.72535600
H	1.89160200	-0.37705800	0.95665200
H	1.02594000	0.42617700	2.32805800
C	2.69715400	1.56205100	1.48232600
H	3.12529100	1.65978600	0.48999200
C	2.95270200	2.46227400	2.47535000
C	2.50755100	2.11342100	3.87046800
H	2.78544600	2.88615500	4.58952500
H	1.42076600	1.98420000	3.93323500
C	3.18875000	0.77244100	4.31928800
H	2.93166400	0.60642800	5.37179900
H	4.27331100	0.89992400	4.26792500
C	2.73518300	-0.43963500	3.54966700
H	1.80694700	-0.87928800	3.90427200
C	3.48511800	-1.22259200	2.68813600
C	2.97046800	-2.56676900	2.26232500
H	1.93761000	-2.74812600	2.56971000
H	3.60544600	-3.34215900	2.71298500
H	3.06167800	-2.70612200	1.17956500
C	4.82875000	-0.83181200	2.15615900
H	5.24191800	0.06010700	2.62849100
H	4.77214800	-0.64917600	1.07401800
H	5.53201000	-1.66252300	2.28591800
C	3.78665800	3.65648900	2.23296500
C	3.62359700	4.82028900	3.00771400
C	4.75482800	3.67173500	1.20751500
C	4.38850800	5.95748200	2.76701900
H	2.86609600	4.85521200	3.78408000
C	5.52598000	4.80376800	0.97268000
H	4.91532000	2.78675100	0.60011100
C	5.34666100	5.95088700	1.75165200
H	4.23453400	6.85228300	3.36060000
H	6.26927100	4.79824100	0.18229900
C	6.22766600	7.15223600	1.53402900
F	6.58840300	7.28026500	0.23865300
F	7.37109900	7.06334300	2.25358000
F	5.61682700	8.29787000	1.90454300

TS-*S*-15:

Imaginary frequency: -172.16 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.658303 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.610369 Hartree
Free energy correction: 1.299282 Hartree
Free energy correction – Grimme quasi-RRHO: 1.297062 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308004 Hartree

O	-5.00129400	0.60548100	-3.19567800
C	-5.61392000	1.60215900	-2.81104900
C	-4.81171800	2.79678100	-2.23559800

H	-5.47408600	3.49100200	-1.71971600
N	-3.88862700	2.29504800	-1.22357800
C	-4.36740800	1.96859900	0.02409000
N	-3.40952900	1.34220300	0.80783500
H	-2.49051600	1.19400300	0.38099000
C	-4.04580600	3.61242700	-3.33382800
H	-3.11720700	1.73476800	-1.57124600
C	-5.04355200	4.06156700	-4.41967900
H	-4.53473500	4.69488000	-5.15563200
H	-5.47381800	3.20996900	-4.95738100
H	-5.86588800	4.64949900	-3.99364700
C	-3.43814200	4.86302300	-2.66723500
H	-2.75155000	4.58816600	-1.86087600
H	-2.88120900	5.45360300	-3.40473200
H	-4.21833900	5.50738800	-2.24268600
C	-2.92084000	2.79036000	-3.99651400
H	-3.29967400	1.85386100	-4.41267900
H	-2.46597300	3.37678100	-4.80418500
H	-2.12027600	2.54860900	-3.28704700
N	-6.97484500	1.70264300	-2.86480400
C	-7.77475000	2.78266100	-2.24313000
C	-7.82575000	0.61858900	-3.44077700
C	-9.21565200	2.25724300	-2.29459700
H	-7.43757800	2.97192000	-1.22065600
C	-9.20467000	1.33317800	-3.51377900
H	-9.44213800	1.68644700	-1.38851700
H	-10.02989800	0.61589200	-3.52630600
H	-9.25329500	1.92337400	-4.43837600
H	-9.94554900	3.06847000	-2.37429400
H	-7.67985700	3.71088400	-2.82194600
C	-3.57010000	0.78993100	2.07224400
C	-4.71270300	0.95052700	2.87439100
C	-2.49747200	0.02685000	2.56868500
C	-4.76666200	0.33521800	4.12676000
H	-5.53665000	1.54719800	2.50811100
C	-2.56609200	-0.55558400	3.82897800
H	-1.62562900	-0.11196200	1.93795600
C	-3.70454400	-0.41693100	4.62638500
H	-3.76361700	-0.88264500	5.60177700
O	4.25732200	1.18207000	-1.16048300
C	4.37877700	1.03463500	-2.38583300
C	3.13898000	1.19906400	-3.30982400
H	3.36732300	0.79074000	-4.29452500
N	2.04100400	0.40551700	-2.77898400
C	2.15544800	-0.95822800	-2.77106400
N	1.13024000	-1.59243000	-2.07984300
H	0.43340000	-0.97217600	-1.65399200
C	2.71049100	2.68933000	-3.53786000
H	1.39622800	0.83293000	-2.11672000
C	3.88892300	3.45795300	-4.16915400
H	3.59373800	4.49423900	-4.36802400
H	4.76371900	3.48529600	-3.50974600
H	4.19357400	3.01475500	-5.12499000
C	1.52841300	2.70109900	-4.53008900
H	0.65016800	2.19226500	-4.12275000
H	1.24367700	3.73461200	-4.75938700
H	1.79512600	2.20902700	-5.47350500
C	2.28984400	3.40352300	-2.23808200
H	3.11191700	3.44688100	-1.51910300
H	1.98905200	4.43174500	-2.47199900
H	1.43493500	2.92303000	-1.74935000

N	5.57230100	0.72450100	-2.96087400
C	5.74771300	0.30451500	-4.37383700
C	6.83384200	0.58762800	-2.16656500
C	7.15814800	-0.29588900	-4.41608500
H	4.97988600	-0.42182300	-4.64901800
C	7.88773600	0.45661200	-3.30312000
H	7.12173200	-1.36718400	-4.19398900
H	8.79263500	-0.04581000	-2.95200500
H	8.16750700	1.46104800	-3.64648100
H	7.62583000	-0.17193000	-5.39708700
H	5.67351600	1.17271900	-5.03960400
C	1.15775000	-2.89317100	-1.57551500
C	2.01927700	-3.89827400	-2.04646500
C	0.27753600	-3.19110000	-0.51782900
C	2.01096800	-5.15402500	-1.43538600
H	2.68211200	-3.68398700	-2.87249600
C	0.28876200	-4.44999900	0.07349400
H	-0.40084700	-2.42419200	-0.15626100
C	1.15643100	-5.44856500	-0.37456600
H	1.15809000	-6.42872000	0.08608400
C	-7.35691100	0.22077700	-4.85319700
H	-6.43798200	-0.36316600	-4.81925600
H	-8.13571100	-0.35554300	-5.36328900
H	-7.17803500	1.12532500	-5.44480400
C	7.12006500	1.85077800	-1.33452800
H	6.47002300	1.91456600	-0.46254700
H	8.16386900	1.85736000	-1.00420800
H	6.96752000	2.73933200	-1.95611700
O	3.08198100	-1.55524100	-3.33061800
O	-5.50773100	2.23799900	0.40950700
C	-7.92467100	-0.59133200	-2.49287500
C	-7.53154200	-0.52639200	-1.17122600
C	-8.52056900	-1.79951600	-2.95866100
C	-7.71269700	-1.61888600	-0.27995900
H	-7.06324000	0.37132100	-0.77913300
C	-8.69932900	-2.87938500	-2.12632600
H	-8.84248800	-1.87671500	-3.99275700
C	-7.33308100	-1.54101600	1.08717300
C	-8.30704300	-2.82723700	-0.76297200
H	-9.15189000	-3.79190400	-2.50861600
C	-7.52755500	-2.60800400	1.93543900
H	-6.89041700	-0.61961700	1.45548100
C	-8.48747700	-3.91387700	0.13357200
C	-8.10681300	-3.80758000	1.45296700
H	-7.23965900	-2.52480600	2.97918200
H	-8.93594800	-4.83217400	-0.23951600
H	-8.25269200	-4.64455300	2.13101000
C	6.83163400	-0.69642000	-1.31209600
C	7.76906300	-0.87888100	-0.31052300
C	5.92969800	-1.76204700	-1.59192700
C	7.85263200	-2.08733200	0.43304200
H	8.48042600	-0.09312000	-0.06988800
C	5.99171900	-2.95064900	-0.89922400
H	5.16511100	-1.64087000	-2.35101300
C	8.80680700	-2.27686500	1.47093900
C	6.94732800	-3.15454000	0.12947700
H	5.30329800	-3.75581700	-1.14165900
C	8.86112600	-3.46142700	2.17123100
H	9.49794100	-1.46917100	1.70200100
C	7.02989600	-4.36692500	0.86739500
C	7.96509100	-4.51733200	1.86697300

H	9.59673100	-3.59312500	2.96021500
H	6.34318300	-5.17345100	0.62025300
H	8.02382800	-5.44848700	2.42397100
Cl	-0.46245300	0.75691000	-0.51949100
C	3.00921800	-6.18381300	-1.89254200
C	-0.55498500	-4.69973200	1.29423800
C	-6.04175500	0.44942500	4.92000500
C	-1.36809100	-1.29191700	4.35062200
F	-6.55974600	1.69448500	4.86679000
F	-6.99674800	-0.38931300	4.44359200
F	-5.86255900	0.13931200	6.22313200
F	-0.46665300	-0.44205500	4.93784300
F	-0.67473300	-1.91626700	3.36049900
F	-1.67727000	-2.21570000	5.27492500
F	4.21790500	-5.99883600	-1.28418700
F	3.23622600	-6.12514000	-3.21901000
F	2.62169200	-7.44099600	-1.59579500
F	-1.64892000	-3.91721900	1.33679700
F	-0.95763900	-5.98375000	1.38142100
F	0.15712700	-4.44034200	2.42972000
C	1.73455800	0.12437700	1.54078100
H	1.87597400	-0.55773400	0.71134700
H	0.81010700	-0.04312300	2.07803900
C	2.30243300	1.43351900	1.44769900
H	2.75868600	1.69263800	0.49780500
C	2.34483600	2.26880900	2.52533100
C	1.88421200	1.72835000	3.85222400
H	1.99071000	2.46717300	4.64872800
H	0.83129800	1.42642200	3.82784000
C	2.74427900	0.47613100	4.24610000
H	2.43517000	0.16826700	5.25123500
H	3.79244200	0.78074400	4.30810100
C	2.56966700	-0.71509100	3.34051500
H	1.72270200	-1.35113300	3.58513400
C	3.50530600	-1.25687200	2.47483800
C	3.28893500	-2.62651000	1.90038100
H	2.29869700	-3.03071100	2.12183000
H	4.04239200	-3.30338500	2.32712300
H	3.45772800	-2.63569200	0.81751300
C	4.77703100	-0.57297200	2.08132000
H	4.95220400	0.36255400	2.61328000
H	4.77561300	-0.36137600	1.00361800
H	5.62432300	-1.24629500	2.25745700
C	2.97418000	3.60207700	2.43918600
C	2.56608500	4.64897500	3.28692000
C	3.98752000	3.86895700	1.49547300
C	3.13840600	5.91393700	3.19424900
H	1.76692800	4.48836200	4.00339000
C	4.56684000	5.12926800	1.40869200
H	4.33455900	3.08035100	0.83551900
C	4.14529900	6.15666100	2.25805100
H	2.79650100	6.71428700	3.84177300
H	5.34819000	5.31737100	0.67978800
C	4.81954300	7.50169700	2.20273800
F	5.23846000	7.80056400	0.95378000
F	5.91069500	7.54080100	3.00327200
F	3.99781400	8.49341500	2.60766000

TS-*S*-16:

Imaginary frequency: -133.31 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.657864 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.608926 Hartree
Free energy correction: 1.298170 Hartree
Free energy correction – Grimme quasi-RRHO: 1.296019 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.306714 Hartree

O	-2.94019800	4.05047300	-1.11400000
C	-2.96236200	4.57224900	0.00996800
C	-1.71326300	4.47528800	0.92244200
H	-1.97887500	4.77668000	1.93622000
N	-1.28446100	3.08809300	1.00565200
C	-2.02029200	2.19955400	1.73830900
N	-1.52607200	0.90159800	1.69402800
H	-0.70608100	0.75314400	1.10128100
C	-0.54178800	5.41516500	0.47279700
H	-0.58601000	2.73143100	0.35540000
C	-1.03818900	6.87519400	0.49750600
H	-0.22006600	7.55119300	0.22478400
H	-1.85598800	7.04477900	-0.21193200
H	-1.38466000	7.16614000	1.49666900
C	0.60889700	5.27011500	1.49080700
H	1.02576900	4.25913100	1.49479900
H	1.41865800	5.96568800	1.24186900
H	0.27069000	5.49902500	2.50892000
C	-0.01751300	5.09147400	-0.94044600
H	-0.79850300	5.21466000	-1.69515100
H	0.80771500	5.77129400	-1.18376800
H	0.37130700	4.07011500	-1.01705000
N	-4.05477500	5.23598800	0.47319700
C	-4.24780600	5.69451200	1.87050000
C	-5.27409400	5.43549600	-0.36853300
C	-5.74748500	6.00285300	1.95595700
H	-3.94175400	4.91271100	2.56899700
C	-6.10043000	6.40603700	0.52355300
H	-6.30249600	5.10581700	2.24815500
H	-7.16912500	6.34398200	0.30098900
H	-5.77329100	7.43556700	0.32835400
H	-5.96366600	6.78616300	2.68817400
H	-3.65306800	6.59665500	2.06011800
C	-2.05303700	-0.22985700	2.31957600
C	-3.15501300	-0.19469600	3.18995300
C	-1.43218000	-1.46784900	2.06376000
C	-3.62985300	-1.37900600	3.75456400
H	-3.61671400	0.75487500	3.41928500
C	-1.91294400	-2.63346900	2.65500900
H	-0.56880000	-1.51135300	1.40713000
C	-3.02351300	-2.60634100	3.50130900
H	-3.39175600	-3.51431600	3.96089100
O	5.59288800	2.66780100	1.05101900
C	6.33966400	2.62383800	0.07163900
C	5.72353200	2.79535900	-1.33891200
H	6.42765400	2.48338300	-2.10873000
N	4.58146800	1.89158700	-1.45380100
C	4.81978000	0.55868900	-1.72832200
N	3.67856900	-0.21804200	-1.62175900
H	2.80972400	0.25793200	-1.36501000
C	5.30757100	4.27285100	-1.65642300
H	3.82865500	2.07854100	-0.79902300
C	6.52306700	5.19903200	-1.45437700
H	6.26289900	6.22531800	-1.73862700

H	6.85368100	5.21869400	-0.41039800
H	7.37211300	4.89168000	-2.07710700
C	4.86942300	4.34093600	-3.13303700
H	4.03267200	3.66328400	-3.32778000
H	4.55385300	5.35952700	-3.38976800
H	5.69131700	4.06557000	-3.80584300
C	4.15158000	4.75896800	-0.75924300
H	4.39676700	4.66071300	0.30104900
H	3.93726800	5.81304800	-0.97537000
H	3.22940800	4.19762300	-0.94881500
N	7.68544900	2.42258200	0.17283900
C	8.59839900	2.17490300	-0.96669800
C	8.36669500	2.27928300	1.49492300
C	9.89345600	1.68238400	-0.30723400
H	8.17164200	1.43524200	-1.64915100
C	9.85987300	2.35321900	1.06730300
H	9.87170800	0.59351500	-0.19844300
H	10.51298000	1.87588300	1.80294200
H	10.15620700	3.40710400	0.98296200
H	10.77833900	1.94568800	-0.89439200
H	8.77604100	3.10454800	-1.52307100
C	3.58205900	-1.60466900	-1.72255700
C	4.63341300	-2.45124700	-2.10555700
C	2.33033300	-2.17087900	-1.41654000
C	4.42562200	-3.83355900	-2.14134300
H	5.59220000	-2.02484300	-2.36522500
C	2.14501600	-3.54496100	-1.47869700
H	1.51992000	-1.51623300	-1.11546600
C	3.19238400	-4.40096800	-1.83284000
H	3.05055300	-5.47439500	-1.86440800
C	-4.92981100	6.11806800	-1.70601300
H	-4.45298200	5.42724400	-2.40054900
H	-5.83379700	6.52735300	-2.16839100
H	-4.24959200	6.95609500	-1.52140300
C	8.02502800	3.44906300	2.43700300
H	7.01163800	3.36511200	2.82765800
H	8.73443500	3.48479000	3.27023700
H	8.11475200	4.39401200	1.88999300
O	5.92169200	0.12450200	-2.07064900
O	-3.02311700	2.53692100	2.38076100
C	-6.05431000	4.12151300	-0.55789500
C	-5.85645200	3.02587300	0.26014600
C	-7.08250000	4.04996700	-1.54277600
C	-6.65784000	1.85582700	0.15049000
H	-5.07275400	3.03132100	1.01223800
C	-7.86424600	2.92724200	-1.68592000
H	-7.26223200	4.89820900	-2.19589600
C	-6.48091500	0.74378500	1.02001800
C	-7.68584800	1.79797900	-0.84417200
H	-8.64240700	2.89958600	-2.44562200
C	-7.28456700	-0.37045200	0.91266600
H	-5.71079400	0.79132800	1.78442900
C	-8.49058500	0.63082200	-0.93853900
C	-8.29799000	-0.42793800	-0.07725600
H	-7.14464100	-1.20025300	1.59843100
H	-9.27353900	0.59328000	-1.69282100
H	-8.93413300	-1.30695800	-0.14488000
C	8.08339900	0.90658900	2.13319600
C	7.55814000	-0.14684500	1.41181300
C	8.45464000	0.67366200	3.48945800
C	7.39182700	-1.43849600	1.98162700

H	7.25061800	-0.00848600	0.37957200
C	8.29420000	-0.55977800	4.07575900
H	8.87293100	1.48323300	4.07966200
C	6.88075300	-2.53000100	1.22896600
C	7.76362700	-1.65566800	3.34593500
H	8.57999200	-0.70932100	5.11477400
C	6.73895100	-3.77526100	1.79897100
H	6.60887700	-2.36892400	0.18946900
C	7.59753000	-2.94886000	3.90913600
C	7.09660700	-3.98573000	3.15358000
H	6.35625000	-4.59857100	1.20329800
H	7.87707400	-3.10764800	4.94843700
H	6.97670400	-4.97219900	3.59394400
Cl	0.71766600	1.06214500	-0.76430100
C	5.60102400	-4.71794600	-2.46215700
C	0.79062900	-4.12281600	-1.18675800
C	-4.85652300	-1.30143300	4.62299500
C	-1.25960100	-3.95477500	2.33974900
F	-4.77723900	-0.29936000	5.52333100
F	-5.97172500	-1.05909700	3.87886000
F	-5.08232600	-2.44432800	5.30246900
F	-1.44344400	-4.85448800	3.33020700
F	0.06859000	-3.83132400	2.14415800
F	-1.77614100	-4.51060000	1.21220300
F	6.44133900	-4.82688200	-1.40087000
F	6.33484100	-4.23133500	-3.48558100
F	5.22359000	-5.97214400	-2.79339000
F	-0.04032500	-3.21815600	-0.60745800
F	0.15290200	-4.52635300	-2.32640000
F	0.84984500	-5.19991300	-0.38420000
C	-2.75956400	0.94375500	-1.74501700
H	-3.17447500	1.93898300	-1.59862000
H	-1.67591300	0.88830400	-1.68184000
C	-3.54759900	-0.19568900	-1.48009000
H	-4.53074900	-0.04546600	-1.04144100
C	-3.12638200	-1.45554000	-1.85775100
C	-1.88028400	-1.52231600	-2.68538800
H	-1.57073000	-2.54570200	-2.89608300
H	-1.05034100	-1.02401800	-2.17143300
C	-2.09816900	-0.78914800	-4.06884400
H	-1.13197500	-0.80297200	-4.58112300
H	-2.78522300	-1.39789100	-4.66656300
C	-2.64834500	0.61269400	-4.00015300
H	-3.72717100	0.70298100	-4.09837000
C	-1.93640600	1.78517400	-4.14795300
C	-2.65762000	3.09434700	-4.26689200
H	-3.74418300	2.97305600	-4.28179800
H	-2.39825300	3.74565200	-3.42242300
H	-2.34320200	3.60801900	-5.18481000
C	-0.44072000	1.85176900	-4.14558500
H	0.02932900	0.94392900	-4.53178300
H	-0.09099100	2.70906400	-4.72910500
H	-0.06881300	1.98049600	-3.11582900
C	-3.94974700	-2.65053800	-1.62557200
C	-3.35071200	-3.92070700	-1.50232400
C	-5.35256600	-2.55863200	-1.49649700
C	-4.12062900	-5.05003300	-1.24594500
H	-2.27492900	-4.02544300	-1.55867000
C	-6.12177100	-3.68981300	-1.25973600
H	-5.85294300	-1.60350600	-1.60845400
C	-5.50786500	-4.93963900	-1.13192200

H	-3.64051100	-6.01460100	-1.12298500
H	-7.19925600	-3.60255500	-1.17031600
C	-6.35270000	-6.17149400	-0.93197800
F	-5.68056800	-7.14204500	-0.28058300
F	-7.47104300	-5.89941200	-0.22505000
F	-6.75131700	-6.68903800	-2.11718100

TS-*R*-1:

Imaginary frequency: -23.56 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.674064 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.639705 Hartree
Free energy correction: 1.305288 Hartree
Free energy correction – Grimme quasi-RRHO: 1.29957 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307285 Hartree

O	2.88118900	3.58953300	-0.04652700
C	3.79238900	3.61328300	-0.88516000
C	3.49421000	3.26190300	-2.36570000
H	4.43690100	3.15198600	-2.90453600
N	2.81103800	1.98038700	-2.44561000
C	3.50070600	0.82356000	-2.22001700
N	2.74021600	-0.32113000	-2.42091700
H	1.76670000	-0.17196900	-2.69935300
C	2.68840000	4.38553500	-3.10765400
H	1.80806100	1.93831000	-2.61470000
C	3.47020800	5.71090800	-3.00608200
H	2.95745300	6.48794200	-3.58371200
H	3.54486000	6.06549200	-1.97256000
H	4.48494900	5.61492000	-3.41188500
C	2.57768000	3.99446200	-4.59683800
H	2.01225400	3.06819000	-4.73594300
H	2.06120600	4.78598900	-5.15206300
H	3.56821700	3.85877600	-5.04874800
C	1.27577900	4.59291000	-2.52774900
H	1.30611200	4.84461700	-1.46572300
H	0.77726700	5.41185600	-3.05815900
H	0.64772300	3.70274500	-2.65102200
N	5.06105300	3.97282700	-0.55137500
C	6.25520900	3.80400000	-1.41248000
C	5.40614600	4.44403000	0.82519000
C	7.43157500	3.92190600	-0.43660700
H	6.22362100	2.83397800	-1.91267000
C	6.89359700	4.86550400	0.64006300
H	7.66524600	2.94291600	-0.00623000
H	7.44430300	4.81460400	1.58324500
H	6.92918500	5.90318700	0.28395600
H	8.33445900	4.29924600	-0.92558000
H	6.29708700	4.59715000	-2.17020200
C	3.10989400	-1.64299100	-2.16871900
C	4.32179100	-2.00866100	-1.55306900
C	2.20666600	-2.65466400	-2.53440600
C	4.57969500	-3.34917700	-1.28018200
H	5.04018400	-1.24045700	-1.31110200
C	2.49921200	-3.99330900	-2.27266100
H	1.27673300	-2.38883100	-3.02819700
C	3.68174400	-4.35860800	-1.63333300
H	3.89468800	-5.39704900	-1.41369400
O	-3.07322600	-2.68652200	-0.47949100
C	-4.11805400	-2.60438100	-1.13465900

C	-4.08805100	-1.96232000	-2.54544800
H	-5.10837900	-1.79477900	-2.89136000
N	-3.46060000	-0.65127500	-2.47169000
C	-4.13760700	0.39814000	-1.91889800
N	-3.39302100	1.57145700	-1.88861400
H	-2.44406500	1.51374700	-2.27154400
C	-3.39396200	-2.86552500	-3.62245700
H	-2.45673300	-0.56664700	-2.61215400
C	-4.08946600	-4.24149100	-3.64373800
H	-3.66646700	-4.85905900	-4.44385800
H	-3.95225600	-4.78438300	-2.70227500
H	-5.16594600	-4.14811200	-3.83404400
C	-3.57849900	-2.19594600	-5.00023900
H	-3.10684900	-1.20938100	-5.03601800
H	-3.12346700	-2.81541800	-5.78185000
H	-4.64085600	-2.07259900	-5.24550700
C	-1.89073700	-3.06954500	-3.35221900
H	-1.71193500	-3.50817100	-2.36892000
H	-1.46899500	-3.74235800	-4.10718000
H	-1.33061500	-2.12858400	-3.41297700
N	-5.30942300	-3.06687900	-0.66289400
C	-6.63182300	-2.81496200	-1.28412900
C	-5.41970700	-3.76363700	0.65467100
C	-7.63404400	-3.17640900	-0.18143800
H	-6.71179600	-1.77068800	-1.59311100
C	-6.89636700	-4.25208900	0.61661600
H	-7.83425700	-2.30359900	0.44825100
H	-7.29498600	-4.40278000	1.62359300
H	-6.94101900	-5.21299400	0.08770000
H	-8.58751100	-3.52274800	-0.59089700
H	-6.77000300	-3.45945500	-2.16192800
C	-3.76312900	2.80110500	-1.35130900
C	-5.02767400	3.06982000	-0.79624600
C	-2.80337500	3.83009900	-1.37164200
C	-5.29146900	4.32691900	-0.25363000
H	-5.78301600	2.29684000	-0.80713300
C	-3.09775800	5.08279200	-0.83694200
H	-1.83117500	3.64266300	-1.81934600
C	-4.34108500	5.34737900	-0.26289500
H	-4.56495700	6.32048400	0.15338000
C	4.56419600	5.67266400	1.21854100
H	3.53475300	5.40323600	1.45350700
H	5.00754300	6.18036200	2.08118500
H	4.55821800	6.38679000	0.38869100
C	-4.47189800	-4.97600600	0.73277800
H	-3.43713200	-4.67155200	0.88669800
H	-4.77315300	-5.64330600	1.54674600
H	-4.53551500	-5.54707000	-0.19923000
O	-5.29886300	0.30601100	-1.50302000
O	4.69054500	0.81476300	-1.87912300
C	5.31820300	3.30286200	1.85479400
C	5.37757300	1.97450400	1.47894500
C	5.26973500	3.60629000	3.24644800
C	5.41013300	0.92609800	2.43823500
H	5.38765300	1.69894100	0.42830400
C	5.27897000	2.61387800	4.20013400
H	5.22608000	4.64097300	3.57108000
C	5.52087100	-0.43826100	2.05277600
C	5.35563600	1.24480100	3.83258300
H	5.23943600	2.87407900	5.25570500
C	5.56974100	-1.43885800	2.99919100

H	5.59685700	-0.67901100	0.99660400
C	5.39399500	0.19072000	4.78482900
C	5.49842500	-1.12122700	4.37907500
H	5.68250900	-2.47144000	2.68204700
H	5.35075000	0.43881600	5.84308100
H	5.53798300	-1.91837300	5.11662200
C	-5.22823800	-2.78757700	1.83001700
C	-5.32793400	-1.41914500	1.67024200
C	-5.02450900	-3.29909900	3.14483300
C	-5.23592200	-0.52795800	2.77443300
H	-5.47000500	-0.98765300	0.68381400
C	-4.91956700	-2.46384500	4.23271800
H	-4.94928000	-4.37090100	3.29979300
C	-5.36103300	0.87979700	2.61278300
C	-5.02231900	-1.05526000	4.08799300
H	-4.76030300	-2.88060700	5.22485100
C	-5.27263200	1.72508100	3.69716300
H	-5.54000100	1.27920200	1.61850600
C	-4.92863100	-0.15759300	5.18524800
C	-5.05022700	1.20136600	4.99526700
H	-5.38681900	2.79541400	3.55433000
H	-4.76568200	-0.56309900	6.18145100
H	-4.98372000	1.87786700	5.84331000
C	-6.62687100	4.54666700	0.40623500
C	-2.03683100	6.14865200	-0.88917800
C	5.82600400	-3.73301700	-0.53026800
C	1.49642300	-5.04558300	-2.66799200
F	6.70230600	-2.71336000	-0.41478200
F	5.52901500	-4.13511900	0.74151100
F	6.47203800	-4.76541100	-1.10919500
F	2.01394000	-6.28898300	-2.62337600
F	1.03188500	-4.84267800	-3.92338500
F	0.41029900	-5.03983500	-1.85369700
F	-6.67844100	3.94251300	1.62432900
F	-7.64114100	4.03227100	-0.31902100
F	-6.89121300	5.85468000	0.60849500
F	-1.62978000	6.39125700	-2.15535100
F	-2.45279500	7.31948700	-0.36673200
F	-0.92478700	5.77782200	-0.19708500
Cl	-0.34844900	0.82200100	-2.79408600
C	0.71637600	1.33287500	0.35555100
H	1.45263500	2.12394000	0.21608200
H	-0.24786100	1.50239700	-0.10035800
C	1.10834400	0.04693900	0.72442200
H	2.17240100	-0.16139000	0.78881700
C	0.18557400	-0.94169400	1.03923200
C	-1.24552200	-0.55052100	1.20923600
H	-1.88798700	-1.40937400	1.39232200
H	-1.63129200	-0.05071400	0.31430900
C	-1.38265300	0.43979400	2.44316100
H	-2.45347600	0.48128500	2.67156900
H	-0.88634400	-0.00582100	3.30912800
C	-0.91155200	1.83031100	2.17220100
H	-1.57782600	2.42306200	1.54530900
C	0.18622100	2.47489000	2.67544500
C	0.41866100	3.93356500	2.38558600
H	-0.34277100	4.35648400	1.72636800
H	0.42109100	4.50344600	3.32504500
H	1.39899400	4.07899100	1.91682000
C	1.17639200	1.83881200	3.61247500
H	1.10443900	0.75013100	3.64770400

H	2.20069400	2.11263700	3.33656100
H	1.01183000	2.21981600	4.63017200
C	0.62270100	-2.31529500	1.31735400
C	-0.24335400	-3.39225500	1.03143900
C	1.92575800	-2.60126900	1.78035400
C	0.19724600	-4.70425300	1.16565900
H	-1.23472200	-3.20670300	0.63185900
C	2.35722200	-3.91301800	1.92294000
H	2.60515800	-1.79935400	2.04944300
C	1.49657700	-4.96759200	1.60256900
H	-0.46409400	-5.52419700	0.90808100
H	3.36491100	-4.11898000	2.26372900
C	1.99757700	-6.38709500	1.63604500
F	2.46989100	-6.76526700	0.42217800
F	3.00360100	-6.54962700	2.52038500
F	1.01940600	-7.25819700	1.96345000

TS-*R*-2:

Imaginary frequency: -22.57 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.673850 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.638945 Hartree
Free energy correction: 1.307840 Hartree
Free energy correction – Grimme quasi-RRHO: 1.301311 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308567 Hartree

O	0.72538600	3.04659000	0.93688000
C	1.07885400	4.01714700	0.25453500
C	0.69146300	4.08088600	-1.24718500
H	1.33172200	4.80011300	-1.76033400
N	0.93576700	2.79018300	-1.86509100
C	2.21514900	2.33244500	-2.00959200
N	2.26655200	1.04823500	-2.54290900
H	1.36172300	0.59574400	-2.69116300
C	-0.79144000	4.53817000	-1.48603800
H	0.17566800	2.11589200	-1.91738800
C	-0.98368000	5.97581200	-0.96274800
H	-2.01765700	6.29315700	-1.13669800
H	-0.78872700	6.05474400	0.11253000
H	-0.33046000	6.68525200	-1.48488100
C	-1.05734300	4.54159900	-3.00690100
H	-0.98211900	3.53947000	-3.43901500
H	-2.06374000	4.92040400	-3.21004600
H	-0.34040600	5.18512200	-3.53176600
C	-1.81290200	3.62099100	-0.78368900
H	-1.67707400	3.62689800	0.30115700
H	-2.82489200	3.97413500	-1.00356900
H	-1.74670700	2.58163900	-1.12381800
N	1.78199600	5.06278300	0.77275500
C	2.45885900	6.10385000	-0.04052600
C	2.09513600	5.19012200	2.22751400
C	3.34819600	6.84970800	0.96269000
H	3.03458000	5.63999100	-0.84588100
C	2.61025400	6.65667800	2.28787100
H	4.34005000	6.38962600	1.00891300
H	3.23696600	6.82801600	3.16716700
H	1.74916100	7.33502200	2.34652100
H	3.47621700	7.90154700	0.69114400
H	1.72033600	6.78247900	-0.48124100
C	3.37356200	0.20470200	-2.62196900

C	4.70107600	0.64308900	-2.46503200
C	3.13030400	-1.15852700	-2.85628700
C	5.73820200	-0.28546200	-2.50237500
H	4.89271800	1.69256700	-2.29897900
C	4.18706000	-2.06595200	-2.90511100
H	2.10758800	-1.50591500	-2.96940000
C	5.50304900	-1.64499600	-2.72361300
H	6.31765000	-2.35826300	-2.71726100
O	-2.15317900	-3.24573700	0.61835200
C	-3.06545700	-3.85217100	0.03779200
C	-3.17261600	-3.78141300	-1.50531300
H	-4.13131300	-4.19120100	-1.82149300
N	-3.17551600	-2.38862500	-1.92342400
C	-4.31359600	-1.64576700	-1.75995400
N	-4.16716500	-0.32146700	-2.14954100
H	-3.23045400	-0.04125400	-2.44360400
C	-2.07337800	-4.61122200	-2.25531800
H	-2.28825900	-1.89763000	-2.02374000
C	-2.18358700	-6.08662600	-1.82048800
H	-1.45480500	-6.69357500	-2.36944700
H	-1.98079500	-6.21572700	-0.75119500
H	-3.17902100	-6.49636100	-2.03185800
C	-2.35934700	-4.51927700	-3.76881500
H	-2.27012300	-3.49227600	-4.13404300
H	-1.64542700	-5.13958300	-4.32308600
H	-3.36948800	-4.87526300	-4.00633500
C	-0.64026000	-4.11472800	-1.98132800
H	-0.37140900	-4.23480400	-0.92901400
H	0.07157500	-4.69312400	-2.58163300
H	-0.50437600	-3.06082300	-2.24699000
N	-3.99143900	-4.58018100	0.71745000
C	-5.23426900	-5.14344900	0.13489400
C	-3.92246400	-4.76126800	2.20046000
C	-6.10571400	-5.45081500	1.35741600
H	-5.69819800	-4.41762200	-0.53542400
C	-5.07698700	-5.77709700	2.44057200
H	-6.68873800	-4.56743100	1.63690200
H	-5.47075200	-5.70151300	3.45772000
H	-4.69316400	-6.79615700	2.30138500
H	-6.80477100	-6.27051600	1.16765700
H	-5.01049400	-6.06067200	-0.42513000
C	-5.12709300	0.68913000	-2.09384900
C	-6.40131700	0.52668700	-1.52516400
C	-4.78715600	1.94055900	-2.64090100
C	-7.28233400	1.60771300	-1.47814700
H	-6.68878200	-0.44120000	-1.14055900
C	-5.69030700	2.99898500	-2.59844200
H	-3.81632700	2.07529800	-3.10695200
C	-6.94761900	2.85051300	-2.00914800
H	-7.64835200	3.67509300	-1.98052500
C	0.83348700	5.04283000	3.09744200
H	0.49553300	4.00915700	3.15375200
H	1.02785500	5.41091600	4.10993000
H	0.02628300	5.65165700	2.67675100
C	-2.58035300	-5.39210800	2.61769300
H	-1.76198700	-4.67553900	2.55091000
H	-2.63833900	-5.77712000	3.64069300
H	-2.35868400	-6.24013400	1.96125000
O	-5.37164500	-2.12525900	-1.33503800
O	3.20969300	3.00375900	-1.71301000
C	3.23198200	4.24506500	2.65610500

C	4.02336700	3.58364300	1.73791700
C	3.56410600	4.13372800	4.03850100
C	5.16945000	2.84189800	2.13753200
H	3.79075400	3.62282600	0.67782600
C	4.65190300	3.40505300	4.45939500
H	2.95589100	4.64285100	4.78037700
C	6.02324400	2.21803400	1.18717200
C	5.49945200	2.74993300	3.52718200
H	4.88611400	3.33947300	5.51971200
C	7.15604500	1.54473300	1.59243100
H	5.77873900	2.29813900	0.13194300
C	6.66243500	2.03268000	3.91519600
C	7.47558900	1.44694100	2.97011400
H	7.80604300	1.08969100	0.85079600
H	6.90804500	1.96447300	4.97269100
H	8.36985200	0.91103700	3.27675000
C	-4.22131400	-3.44942300	2.94876900
C	-4.85833800	-2.38570900	2.33932400
C	-3.91494400	-3.34439600	4.33711100
C	-5.21038100	-1.21074400	3.05845100
H	-5.10003700	-2.42082500	1.28104000
C	-4.23161800	-2.21677900	5.05927300
H	-3.42550300	-4.16949000	4.84541600
C	-5.88945000	-0.12752700	2.43645900
C	-4.88916900	-1.11598800	4.45014800
H	-3.98540700	-2.16233500	6.11756400
C	-6.23126800	0.99620400	3.15492700
H	-6.14710700	-0.20340800	1.38411200
C	-5.24621000	0.06024400	5.16255800
C	-5.90253100	1.09297800	4.53001500
H	-6.76437000	1.80524800	2.66448600
H	-5.00020300	0.12773900	6.22010900
H	-6.17774900	1.98508700	5.08641000
C	-8.59745500	1.41585100	-0.77123700
C	-5.29017200	4.34113300	-3.14889000
C	7.15709700	0.16308200	-2.27449700
C	3.88201600	-3.51674000	-3.16698400
F	7.93882900	-0.05430400	-3.35272800
F	7.24514100	1.47724500	-1.96948000
F	7.72888500	-0.51634700	-1.24235400
F	4.88791000	-4.32917500	-2.77231300
F	3.66560500	-3.76117700	-4.47785000
F	2.76407100	-3.91995600	-2.50875500
F	-8.42955400	1.39990400	0.57856400
F	-9.18315700	0.24483900	-1.09800800
F	-9.47732000	2.40234300	-1.04400200
F	-4.40708800	4.23413600	-4.16647900
F	-6.35106500	5.04064300	-3.60169500
F	-4.69405500	5.11554200	-2.20044800
Cl	-0.82720400	-0.04658800	-2.31832000
C	0.01485500	-0.38235900	0.57336000
H	-0.24386400	0.66218100	0.44496800
H	-0.78386700	-1.10610900	0.47389000
C	1.36915700	-0.75908600	0.56114000
H	2.09290300	-0.01057900	0.25196000
C	1.80535400	-1.99545500	0.99116500
C	0.84753100	-2.91221200	1.67915600
H	1.32069700	-3.86712600	1.91630600
H	-0.05149400	-3.10615900	1.08780100
C	0.37601000	-2.25988300	3.04571400
H	-0.12848800	-3.06019500	3.59973600

H	1.25545400	-1.96825800	3.62602100
C	-0.59612300	-1.14017900	2.87022700
H	-1.59628300	-1.45593800	2.57835100
C	-0.40117500	0.19287300	3.11363200
C	-1.55380700	1.15756900	3.01425900
H	-2.45706900	0.68967900	2.61365400
H	-1.79349200	1.55102200	4.01178200
H	-1.28076500	2.01685500	2.39088900
C	0.90052900	0.79604800	3.56354700
H	1.72085200	0.07797300	3.61879500
H	1.18866700	1.60835200	2.88574200
H	0.77445000	1.24238000	4.55941300
C	3.23337500	-2.35592600	0.93400000
C	3.60644500	-3.68541200	0.64972400
C	4.25113100	-1.40071300	1.11796800
C	4.94413300	-4.04034500	0.52480900
H	2.84343300	-4.43520600	0.47011500
C	5.59071600	-1.76042000	1.01783600
H	4.00122500	-0.37522900	1.37047500
C	5.93956100	-3.07810200	0.71416600
H	5.21505900	-5.06112800	0.27771600
H	6.35910800	-1.01390400	1.17660700
C	7.38545300	-3.45426600	0.52261600
F	8.21469300	-2.64204800	1.20896500
F	7.62697400	-4.72167900	0.92677900
F	7.74937800	-3.38543900	-0.78058700

TS-*R*-3:

Imaginary frequency: -23.66 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.672534 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.637052 Hartree
Free energy correction: 1.305094 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299467 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307261 Hartree

O	3.13225700	3.41252500	-0.04561300
C	4.07144900	3.35157400	-0.85071700
C	3.79861100	3.00025500	-2.33586900
H	4.74855300	2.81521100	-2.84040200
N	3.02708500	1.77032100	-2.42343600
C	3.62402900	0.56954100	-2.16594800
N	2.79297800	-0.52040200	-2.39066800
H	1.84531000	-0.30570300	-2.71249800
C	3.10222600	4.16827100	-3.11858800
H	2.03224600	1.79717000	-2.63830100
C	3.97498700	5.43462700	-3.00542400
H	3.54136900	6.23811300	-3.61104100
H	4.03859400	5.79839600	-1.97435300
H	4.99379200	5.25889100	-3.37257400
C	3.01379700	3.76462700	-4.60599400
H	2.38493600	2.88164000	-4.75420200
H	2.57823900	4.58449600	-5.18878300
H	4.00626200	3.54829900	-5.02073400
C	1.68936400	4.48664200	-2.59159900
H	1.70139600	4.75856700	-1.53410800
H	1.26923400	5.32728100	-3.15496400
H	1.00406900	3.64046200	-2.71912600
N	5.35163900	3.61719700	-0.47572700
C	6.55925600	3.34532900	-1.29022300

C	5.68227300	4.08131500	0.90688900
C	7.70447700	3.38133000	-0.27184700
H	6.46960700	2.37517600	-1.78295700
C	7.20491500	4.37892700	0.77428300
H	7.84248000	2.39236900	0.17669600
H	7.71423300	4.29602800	1.73821900
H	7.33776300	5.40563200	0.40951500
H	8.65228100	3.67874300	-0.73000600
H	6.69142800	4.12429800	-2.05238800
C	3.05940900	-1.86289600	-2.11852400
C	4.21168400	-2.30617400	-1.44260300
C	2.10922500	-2.81348800	-2.52716300
C	4.36536200	-3.65979700	-1.15568100
H	4.96773700	-1.58692300	-1.16715800
C	2.29800300	-4.16747200	-2.24976100
H	1.22538300	-2.48817000	-3.06771600
C	3.42046300	-4.60830500	-1.55210000
H	3.55301500	-5.65795100	-1.32276900
O	-3.31887500	-2.28507000	-0.64049200
C	-4.31454500	-2.17107300	-1.36523300
C	-4.14832400	-1.64521600	-2.81556000
H	-5.12899200	-1.42867200	-3.23948200
N	-3.42535500	-0.38075700	-2.78567300
C	-4.04232800	0.72912500	-2.27951400
N	-3.20377000	1.83362400	-2.19370200
H	-2.24913700	1.70545500	-2.54426500
C	-3.46481000	-2.67332100	-3.77904800
H	-2.40882900	-0.39015400	-2.82622400
C	-4.26722400	-3.98969500	-3.75004300
H	-3.84900200	-4.69678400	-4.47504500
H	-4.23203100	-4.46893700	-2.76548000
H	-5.31925500	-3.82796600	-4.01645600
C	-3.51217500	-2.09389700	-5.20824300
H	-2.96310500	-1.15016900	-5.27857800
H	-3.06139200	-2.80063000	-5.91467800
H	-4.54474700	-1.90955500	-5.53033400
C	-2.00160900	-2.97016300	-3.39873500
H	-1.91799900	-3.35869900	-2.38213900
H	-1.58697900	-3.71754600	-4.08400300
H	-1.36801700	-2.07824400	-3.47531300
N	-5.56442600	-2.48573800	-0.92727200
C	-6.82539800	-2.19079800	-1.64845800
C	-5.80090200	-3.01988400	0.45053200
C	-7.90830100	-2.31759300	-0.57055200
H	-6.78825400	-1.18888900	-2.08014600
C	-7.32081200	-3.35214300	0.38996100
H	-8.05029200	-1.35830900	-0.06250300
H	-7.77191400	-3.33517000	1.38539900
H	-7.44724600	-4.36164000	-0.02221000
H	-8.87175100	-2.62063400	-0.99100100
H	-6.98553500	-2.92245900	-2.45111700
C	-3.46661800	3.04506700	-1.55952200
C	-4.64738500	3.31703300	-0.84499300
C	-2.47217000	4.03891400	-1.62133200
C	-4.79251800	4.53724200	-0.18657900
H	-5.43411100	2.57658900	-0.82460600
C	-2.65007900	5.25855900	-0.97095800
H	-1.56615300	3.85129500	-2.19033400
C	-3.80675900	5.52237000	-0.23643600
H	-3.94084900	6.47040100	0.26754500
C	4.92807600	5.37982700	1.25055100

H	3.87135000	5.19799500	1.44515700
H	5.37573100	5.86316900	2.12487100
H	5.01415200	6.07938400	0.41275400
C	-5.00076300	-4.31187500	0.69870800
H	-3.94369600	-4.10650900	0.86457800
H	-5.40178000	-4.84670000	1.56595900
H	-5.10064800	-4.97275200	-0.16851400
O	-5.23329200	0.74223300	-1.94795000
O	4.79624000	0.47939600	-1.77882600
C	5.46250600	2.96734900	1.94660700
C	5.43333600	1.63255900	1.59030400
C	5.37769600	3.29560500	3.33078000
C	5.33919800	0.60018000	2.56272800
H	5.46718100	1.34050200	0.54461800
C	5.26589800	2.32072800	4.29603600
H	5.40208200	4.33545200	3.64053900
C	5.35589800	-0.77466800	2.19941100
C	5.24837900	0.94424700	3.94915200
H	5.20086300	2.59994700	5.34546900
C	5.28005700	-1.76081500	3.15907300
H	5.46005200	-1.03741600	1.15086100
C	5.15823100	-0.09434400	4.91490900
C	5.17304600	-1.41665500	4.53029100
H	5.32227900	-2.80403800	2.86003600
H	5.08799200	0.17314900	5.96697100
H	5.11408500	-2.20263200	5.27844500
C	-5.54282500	-1.94453100	1.52525500
C	-5.34998500	-2.29727900	2.84878400
C	-5.59351000	-0.55875600	1.19994000
C	-5.21410700	-1.32564200	3.87660900
H	-5.30522600	-3.34283500	3.14083900
C	-5.47658000	0.40927100	2.17230700
H	-5.70883700	-0.25171900	0.16626700
C	-5.01544000	-1.68510400	5.23785800
C	-5.28860800	0.06295800	3.53619500
H	-5.53621000	1.46130900	1.90277900
C	-4.90014500	-0.71980900	6.21295900
H	-4.95870000	-2.73975800	5.49827200
C	-5.16877900	1.03617400	4.56517600
C	-4.97894900	0.65445200	5.87439400
H	-4.75120600	-1.00924700	7.24986200
H	-5.23663400	2.08828900	4.29722800
H	-4.89251100	1.40569100	6.65489900
C	-6.02788900	4.74530900	0.64843400
C	-1.54876300	6.28130900	-1.04662000
C	5.54304100	-4.12098600	-0.34129800
C	1.24751100	-5.15287900	-2.69108000
F	6.49000500	-3.16954300	-0.20543000
F	5.15885500	-4.46868900	0.92345100
F	6.13150100	-5.21365100	-0.86852100
F	1.68552100	-6.42611800	-2.63881600
F	0.84321700	-4.91335300	-3.96106400
F	0.13429500	-5.08536500	-1.91753600
F	-5.95087600	4.04827300	1.81732200
F	-7.14338900	4.31943700	0.02232500
F	-6.21320600	6.03950900	0.98138600
F	-1.08951800	6.43479200	-2.30816400
F	-1.94041500	7.49367200	-0.60585900
F	-0.47552300	5.91639600	-0.29191100
Cl	-0.18365300	0.83682700	-2.90674600
C	0.79960600	1.32788100	0.29552600

H	1.60402800	2.05611600	0.19694500
H	-0.12277600	1.57520600	-0.20961400
C	1.06545400	0.01456900	0.68009100
H	2.10450900	-0.28033900	0.79492800
C	0.05006300	-0.89354000	0.94902400
C	-1.34946100	-0.38406700	1.05496400
H	-2.06948400	-1.18462500	1.20890800
H	-1.65224600	0.14151700	0.14312700
C	-1.46037200	0.61843200	2.28041700
H	-2.53423700	0.74279900	2.45969200
H	-1.04353400	0.13753700	3.16904700
C	-0.86419100	1.96446100	2.03154900
H	-1.44596100	2.60709200	1.37062800
C	0.25631900	2.51835700	2.58980100
C	0.62438800	3.95089500	2.31089100
H	-0.06523200	4.43310800	1.61452000
H	0.62867400	4.52281500	3.24910000
H	1.63538600	4.01160100	1.89110400
C	1.14137600	1.80621100	3.57596200
H	0.97825900	0.72732400	3.60722400
H	2.19759800	1.99367600	3.35342000
H	0.95672100	2.20324200	4.58404000
C	0.35685600	-2.29930600	1.24030300
C	-0.58720400	-3.29816000	0.91919700
C	1.61191100	-2.69659600	1.75122200
C	-0.26692200	-4.64326000	1.06604800
H	-1.54347900	-3.02727200	0.48422400
C	1.92317900	-4.04063800	1.90578000
H	2.34715000	-1.95630900	2.04856700
C	0.98763600	-5.01734900	1.55043700
H	-0.98630400	-5.40343600	0.78221400
H	2.89638200	-4.33255100	2.28238200
C	1.36463400	-6.47429900	1.59913600
F	1.86667900	-6.88732400	0.40887900
F	2.30628300	-6.72312900	2.53312600
F	0.30124600	-7.26077700	1.86947300

TS-*R*-4:

Imaginary frequency: -84.43 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.671254 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.636209 Hartree
Free energy correction: 1.304959 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299597 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307774 Hartree

O	-3.08588900	-2.53184900	-0.58667400
C	-4.10913500	-2.51426000	-1.28041400
C	-4.04085400	-1.97126100	-2.73232900
H	-5.05051100	-1.85495100	-3.12637200
N	-3.45065200	-0.63917400	-2.71768800
C	-4.16683400	0.40403400	-2.20220300
N	-3.44725300	1.59190700	-2.14744100
H	-2.49918600	1.56659600	-2.53693700
C	-3.28517400	-2.92233700	-3.72019800
H	-2.44101000	-0.54098500	-2.79489600
C	-3.94372400	-4.31557700	-3.66826900
H	-3.47939800	-4.97476300	-4.41013000
H	-3.82372200	-4.78851200	-2.68738000
H	-5.01565100	-4.26495600	-3.89708400

C	-3.43914800	-2.35217400	-5.14557500
H	-2.99706400	-1.35489800	-5.23012500
H	-2.93698700	-3.00650500	-5.86764500
H	-4.49499600	-2.28007900	-5.43532000
C	-1.78754000	-3.06314900	-3.38781600
H	-1.63054600	-3.43281100	-2.37287100
H	-1.32089200	-3.76866800	-4.08369500
H	-1.25327600	-2.11074300	-3.48948400
N	-5.30901800	-2.95050300	-0.80591600
C	-6.61438000	-2.78450500	-1.48755200
C	-5.44811800	-3.49900400	0.57933800
C	-7.64538000	-2.99981500	-0.37355700
H	-6.68700800	-1.78862400	-1.92841000
C	-6.93404700	-3.96541300	0.57512700
H	-7.85976600	-2.05242300	0.13136800
H	-7.35040300	-3.97665000	1.58570800
H	-6.98385100	-4.98727100	0.17741000
H	-8.58957600	-3.39539900	-0.75942100
H	-6.73025300	-3.53716700	-2.27845100
C	-3.82399800	2.77627300	-1.52038500
C	-4.99479800	2.91943400	-0.75395100
C	-2.95962500	3.88056600	-1.64290700
C	-5.25568800	4.12604200	-0.10600300
H	-5.68623500	2.09173900	-0.68741000
C	-3.25331500	5.08219900	-1.00142900
H	-2.06540400	3.79208200	-2.25295300
C	-4.39898300	5.22045500	-0.21627100
H	-4.62342900	6.15567400	0.27963700
O	2.84889800	3.42403800	-0.05491000
C	3.75174100	3.54808500	-0.89643700
C	3.43309300	3.37994900	-2.40630500
H	4.36802000	3.34894900	-2.96730300
N	2.77187500	2.10162200	-2.62292200
C	3.48604600	0.94808800	-2.46959500
N	2.74256000	-0.20702000	-2.66580400
H	1.76049300	-0.07649000	-2.92233300
C	2.60646800	4.56981100	-3.00239200
H	1.75977500	2.05022800	-2.72731000
C	3.39074800	5.87800500	-2.77441100
H	2.86117600	6.71540200	-3.24208700
H	3.49884800	6.11118400	-1.70932600
H	4.39247000	5.83140500	-3.21946000
C	2.46212100	4.33873300	-4.52176200
H	1.88873500	3.43386000	-4.74379800
H	1.93966900	5.18669700	-4.97956100
H	3.44206900	4.24657800	-5.00633000
C	1.20652800	4.71070500	-2.37497100
H	1.26162900	4.89683600	-1.30025000
H	0.67943900	5.55202600	-2.83775900
H	0.59176700	3.81754800	-2.53680900
N	5.02782300	3.83717500	-0.52987700
C	6.21003600	3.78298900	-1.42298800
C	5.39933400	4.06698200	0.90265700
C	7.39685900	3.68936000	-0.45805600
H	6.14316500	2.91497500	-2.08060000
C	6.90280800	4.45249600	0.77126800
H	7.59753300	2.64281000	-0.20705300
H	7.45407900	4.21906300	1.68567600
H	6.97905700	5.53355800	0.59710500
H	8.30937600	4.11285500	-0.88784100
H	6.27088700	4.69499200	-2.03097500

C	3.14336600	-1.51601300	-2.38663000
C	4.33682000	-1.83738300	-1.71752100
C	2.28342700	-2.56094600	-2.76847800
C	4.61932600	-3.16623700	-1.40427900
H	5.02848000	-1.04880900	-1.45993800
C	2.59928600	-3.88383000	-2.46518400
H	1.36884900	-2.33100200	-3.30661700
C	3.76464300	-4.20510300	-1.76809700
H	3.99324500	-5.23120400	-1.51399800
C	-4.52905400	-4.71466100	0.79856000
H	-3.48859100	-4.41733900	0.92550600
H	-4.84966400	-5.28034100	1.67968600
H	-4.60195700	-5.38410300	-0.06469000
C	4.61490800	5.25123300	1.49662600
H	3.57728100	4.98835500	1.70054500
H	5.08522700	5.59372700	2.42415000
H	4.63411500	6.08890600	0.79189500
O	4.69139700	0.94958300	-2.18723600
O	-5.34286400	0.29563700	-1.83652500
C	-5.24747400	-2.40000100	1.64213900
C	-4.94642500	-2.72420800	2.95260600
C	-5.46275900	-1.02856300	1.32197600
C	-4.85953900	-1.73855800	3.97281500
H	-4.77417000	-3.75750200	3.24055300
C	-5.39759100	-0.04920700	2.28731100
H	-5.66269400	-0.74026200	0.29585900
C	-4.54979600	-2.06832000	5.32071400
C	-5.10056200	-0.36732100	3.63870900
H	-5.58166500	0.98952300	2.02233900
C	-4.48505400	-1.09179300	6.28941300
H	-4.36675800	-3.10967100	5.57640300
C	-5.02935000	0.61784200	4.66105200
C	-4.72839100	0.26459500	5.95755500
H	-4.24973700	-1.35909100	7.31618000
H	-5.22508900	1.65535500	4.39891500
H	-4.68067500	1.02427300	6.73320100
C	5.25997900	2.77911800	1.73847300
C	5.18845300	2.83524800	3.11887300
C	5.30151800	1.49693500	1.11897900
C	5.16423900	1.66255300	3.92196800
H	5.15991500	3.79248700	3.63223300
C	5.29127100	0.34131000	1.86755400
H	5.32519300	1.42242600	0.03723400
C	5.08933500	1.71686900	5.34080300
C	5.22645900	0.38212700	3.28509400
H	5.34398500	-0.62689300	1.37472800
C	5.08052000	0.56246200	6.09156100
H	5.04411300	2.68929700	5.82650600
C	5.22150400	-0.79082800	4.08720600
C	5.14912900	-0.70425200	5.45954100
H	5.02588600	0.61884700	7.17547400
H	5.28616400	-1.75886900	3.59523300
H	5.14908100	-1.60709000	6.06417800
C	5.83925200	-3.45067000	-0.57227500
C	1.63958500	-4.97353100	-2.86575900
C	-6.46833500	4.19989100	0.78329800
C	-2.28483000	6.22646700	-1.13076900
F	-7.55458200	3.64393300	0.21028700
F	-6.25969900	3.52632800	1.95009900
F	-6.78509100	5.46735400	1.11949200
F	-2.82818100	7.40426100	-0.76353300

F	-1.82956800	6.36376400	-2.39562400
F	-1.18593300	6.04133800	-0.34705200
F	5.61235800	-3.14940200	0.74600500
F	6.90190800	-2.71049600	-0.94583100
F	6.20478800	-4.74619600	-0.60975100
F	1.15381900	-4.77610800	-4.11467500
F	2.21288200	-6.19302100	-2.84302800
F	0.56319800	-5.02762500	-2.04124900
Cl	-0.36681300	0.93637300	-2.98386200
C	0.45079900	1.37780300	0.21840100
H	1.15816300	2.18508300	0.03403300
H	-0.50151600	1.47482700	-0.28574500
C	0.94500500	0.09303200	0.53931700
H	2.02081000	-0.05370900	0.50129000
C	0.11020600	-0.93025400	0.92263900
C	-1.32195100	-0.60093700	1.21681000
H	-1.88679000	-1.47826600	1.52646400
H	-1.83172800	-0.20035300	0.33399800
C	-1.38062200	0.46492100	2.37730500
H	-2.42412800	0.51139500	2.70872900
H	-0.79168300	0.10189600	3.22365400
C	-0.97031100	1.84117200	1.95773700
H	-1.71638400	2.37831300	1.37260600
C	0.12854900	2.57135500	2.35174600
C	0.24155200	4.02679100	1.99164300
H	-0.57104800	4.36787900	1.34665600
H	0.22736700	4.62826300	2.91121200
H	1.19565900	4.22297500	1.49035300
C	1.22593700	2.03385600	3.22461800
H	1.19103300	0.95105800	3.35228200
H	2.20421800	2.30927200	2.81527900
H	1.15561300	2.49540400	4.21907200
C	0.62444700	-2.28868600	1.16064900
C	-0.20317600	-3.39884800	0.89737300
C	1.95205600	-2.51859300	1.57351700
C	0.29562500	-4.69191600	1.01221700
H	-1.21497400	-3.24618700	0.53523600
C	2.44549800	-3.81188500	1.69564700
H	2.59919800	-1.68306200	1.82016100
C	1.61864800	-4.90135300	1.40688400
H	-0.33918200	-5.53938700	0.77723400
H	3.47438000	-3.97408700	1.99520800
C	2.17513200	-6.29929600	1.43104400
F	2.61402900	-6.67458900	0.20266600
F	3.22200900	-6.41509900	2.27514700
F	1.24581900	-7.20507900	1.80473400

TS-*R*-5:

Imaginary frequency: -177.75 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.670823 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.636199 Hartree
Free energy correction: 1.305809 Hartree
Free energy correction – Grimme quasi-RRHO: 1.300088 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307738 Hartree

O	-1.94918400	-3.07550300	0.09117300
C	-2.87249900	-3.60675700	-0.53744800
C	-3.04090800	-3.31441200	-2.05146500
H	-4.02645100	-3.64469600	-2.37950100

N	-3.00348000	-1.87633100	-2.26915800
C	-4.07841400	-1.11381100	-1.91098200
N	-3.86432100	0.24976100	-2.09200500
H	-2.93121900	0.52018900	-2.41688300
C	-1.99522800	-4.05456300	-2.95444400
H	-2.10487800	-1.41590600	-2.39995800
C	-2.11628300	-5.57450000	-2.72547800
H	-1.41398500	-6.10512500	-3.37779800
H	-1.88163300	-5.85559000	-1.69285800
H	-3.12360100	-5.93922700	-2.96098200
C	-2.33432200	-3.75071300	-4.42884100
H	-2.24391000	-2.68399300	-4.65325100
H	-1.64892400	-4.29425100	-5.08944300
H	-3.35698800	-4.06241200	-4.67545300
C	-0.54531600	-3.62181500	-2.66687200
H	-0.25447700	-3.83443600	-1.63563500
H	0.13634600	-4.16423100	-3.32986800
H	-0.39162400	-2.55136800	-2.84741800
N	-3.76054500	-4.45098800	0.05704600
C	-5.00588800	-4.95679900	-0.57005500
C	-3.65055700	-4.83440100	1.49739000
C	-5.80399400	-5.54394600	0.60093400
H	-5.53750500	-4.14297500	-1.06889500
C	-4.71373000	-5.96644600	1.58611400
H	-6.44407400	-4.77611600	1.04668700
H	-5.07441200	-6.09857800	2.60985500
H	-4.25592000	-6.91062400	1.26347700
H	-6.44300200	-6.37377100	0.28521800
H	-4.77143700	-5.73290200	-1.30874000
C	-4.72158200	1.28906800	-1.74029500
C	-6.06959600	1.10435100	-1.38244200
C	-4.20160200	2.59621000	-1.75600300
C	-6.84644100	2.20395300	-1.02000800
H	-6.48538100	0.10684400	-1.39277800
C	-5.00102400	3.67977800	-1.39515200
H	-3.16954800	2.75615200	-2.05603300
C	-6.33111500	3.49980000	-1.01543400
H	-6.94787100	4.34330100	-0.73537400
O	1.50783500	3.75717300	0.25684800
C	2.27122800	4.29740200	-0.55691400
C	2.08770800	4.03630300	-2.07516300
H	2.98924900	4.34689000	-2.60543600
N	1.94057400	2.61045100	-2.30569000
C	3.02022600	1.79258600	-2.14045500
N	2.74197600	0.45293200	-2.38608600
H	1.77606500	0.23519200	-2.63661000
C	0.89975500	4.84412600	-2.70674300
H	1.01486900	2.19853300	-2.41437500
C	1.18348700	6.35342400	-2.56662700
H	0.36547300	6.92716000	-3.01616800
H	1.26559500	6.66307800	-1.51888200
H	2.10761900	6.63927400	-3.08344300
C	0.82544300	4.50101300	-4.21022100
H	0.55540200	3.45491100	-4.37962100
H	0.06563900	5.12517900	-4.69498500
H	1.78384600	4.68950500	-4.70956200
C	-0.45554000	4.53034000	-2.04556000
H	-0.46064800	4.80115000	-0.98691800
H	-1.24731600	5.09881000	-2.54461000
H	-0.71298300	3.46846800	-2.12769800
N	3.26544200	5.14053600	-0.16729800

C	4.36598400	5.61248500	-1.04359800
C	3.44710600	5.56486600	1.25472100
C	5.39037200	6.20817400	-0.07019100
H	4.77151600	4.77749100	-1.61988200
C	4.52324300	6.67806700	1.09801800
H	6.09305700	5.43759300	0.26171200
H	5.08106000	6.82923500	2.02614800
H	4.02494400	7.62273100	0.84398500
H	5.96792100	7.01625600	-0.52841400
H	3.99966100	6.37842100	-1.73718300
C	3.60923700	-0.63288500	-2.25734000
C	4.93392300	-0.51793100	-1.79479600
C	3.12330700	-1.90515900	-2.60029800
C	5.71532400	-1.66053300	-1.64889700
H	5.32548600	0.46104400	-1.56576200
C	3.93163800	-3.03347000	-2.46097800
H	2.11119500	-2.00864700	-2.97970200
C	5.23330900	-2.92931600	-1.97645800
H	5.85022800	-3.81081900	-1.85500600
C	-2.25872200	-5.40216900	1.83551100
H	-1.51313900	-4.61530100	1.94308500
H	-2.30245600	-5.98075200	2.76412900
H	-1.94051300	-6.08442300	1.04037500
C	2.15493100	6.17165100	1.83280500
H	1.42496800	5.40542200	2.09088900
H	2.38053200	6.76318700	2.72598400
H	1.70807700	6.84831300	1.09724400
O	4.13593800	2.22231600	-1.82027600
O	-5.13531900	-1.59389000	-1.48568600
C	-4.05797200	-3.67572400	2.42593100
C	-4.78077500	-2.59006300	1.97169500
C	-3.77106600	-3.75889000	3.81975800
C	-5.25642400	-1.58404900	2.85733200
H	-5.00100400	-2.47589900	0.91441700
C	-4.19747900	-2.79203700	4.70010400
H	-3.20491900	-4.60214800	4.20303100
C	-6.04359500	-0.49252000	2.39721300
C	-4.95858000	-1.67941400	4.25433900
H	-3.96261200	-2.87869000	5.75879200
C	-6.51113100	0.45979200	3.27655100
H	-6.28195700	-0.42691600	1.33939100
C	-5.44405800	-0.67505900	5.13404800
C	-6.20438500	0.37018000	4.65732900
H	-7.12433800	1.27609200	2.90718800
H	-5.21460600	-0.75198400	6.19468000
H	-6.58047400	1.12633500	5.34165500
C	4.01318300	4.42971800	2.12599200
C	4.64511600	3.33058800	1.57733900
C	3.98496900	4.55220100	3.54613400
C	5.27880100	2.35023800	2.38957900
H	4.66022000	3.18273100	0.50131400
C	4.56837900	3.60916300	4.36034700
H	3.49805400	5.40791900	4.00344900
C	5.97155100	1.24403100	1.82502200
C	5.24023400	2.48413400	3.81406000
H	4.53032400	3.72534000	5.44131500
C	6.59093700	0.31253700	2.63016300
H	6.02276300	1.15415300	0.74398900
C	5.87956900	1.50256900	4.61824900
C	6.53977800	0.44077600	4.04079500
H	7.12328000	-0.51874200	2.17788900

H	5.84563600	1.60856900	5.70032100
H	7.03057000	-0.30073400	4.66539800
C	7.09964300	-1.55163100	-1.07066300
C	3.36023800	-4.38542600	-2.79966200
C	-8.26460900	1.95313500	-0.58010600
C	-4.38579800	5.05249800	-1.39505000
F	-8.90413200	1.09650900	-1.40226500
F	-8.30513800	1.39749300	0.66151000
F	-8.99339800	3.08749600	-0.52375200
F	-5.27198900	6.01870200	-1.08511500
F	-3.84746000	5.36536600	-2.59538900
F	-3.37129800	5.14096100	-0.48923900
F	7.15810200	-2.10746800	0.17603200
F	7.51432200	-0.27336600	-0.93932200
F	8.01598400	-2.20366100	-1.81527500
F	2.64679400	-4.34999500	-3.95214000
F	4.31627800	-5.32323600	-2.94772900
F	2.51191400	-4.82969100	-1.83947600
C	-0.68899300	0.84420600	0.42262600
H	-1.69560300	0.83475000	0.02269400
H	-0.12581800	1.75509000	0.24352100
C	-0.01349100	-0.40054200	0.57150600
H	-0.51748200	-1.28435800	0.19051300
C	1.18120600	-0.47014000	1.24322300
C	1.64740200	0.78661400	1.92372300
H	2.58600900	0.64472300	2.46010800
H	1.81932400	1.57628200	1.18273600
C	0.59282800	1.34951200	2.94817100
H	0.86455900	2.38995800	3.14377800
H	0.70381800	0.80545900	3.89364200
C	-0.85971300	1.22884800	2.54446700
H	-1.32667500	0.27531300	2.77849600
C	-1.73713400	2.26618900	2.29778500
C	-3.21223600	2.01049700	2.24263700
H	-3.47164400	0.95941200	2.38449800
H	-3.63426700	2.36141700	1.29215300
H	-3.71233800	2.59355600	3.02893400
C	-1.29834100	3.68188700	2.07385500
H	-0.27455000	3.76157500	1.70170200
H	-1.36180500	4.22801400	3.02753400
H	-1.96985200	4.18969800	1.37432400
Cl	-0.64587100	0.55523000	-2.71658900
C	1.92913700	-1.73311400	1.35116800
C	3.32375900	-1.72414000	1.55225100
C	1.28612300	-2.97940000	1.18963200
C	4.05491000	-2.90690200	1.54911200
H	3.85860800	-0.78765300	1.66448100
C	2.01624100	-4.16125000	1.20168600
H	0.21102500	-3.02758700	1.05356500
C	3.40342500	-4.12881100	1.36894800
H	5.13313900	-2.87440600	1.65810800
H	1.50944400	-5.11127800	1.07325200
C	4.21212500	-5.39364000	1.27440300
F	4.70716900	-5.57428900	0.02441500
F	3.48022900	-6.48926900	1.56907400
F	5.27296400	-5.37461900	2.11191300

TS-*R*-6:

Imaginary frequency: -184.25 cm^{-1}

E[B3LYP/6-31G(d)]: -5531.668694 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.632704 Hartree
Free energy correction: 1.302974 Hartree
Free energy correction – Grimme quasi-RRHO: 1.298892 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307978 Hartree

O	1.59539700	3.67177100	0.58684800
C	2.35027500	4.28918700	-0.18021400
C	2.11064000	4.22119200	-1.71195900
H	2.99401300	4.59302500	-2.23185300
N	1.95617800	2.83173700	-2.10755600
C	3.04671100	2.01041200	-2.08272800
N	2.75630500	0.68841500	-2.39077700
H	1.76860600	0.46241300	-2.52399800
C	0.90781400	5.09897500	-2.20107600
H	1.02735900	2.41907500	-2.17793300
C	1.19561900	6.57602000	-1.86382500
H	0.37070700	7.20522800	-2.21610500
H	1.29761000	6.74045200	-0.78513400
H	2.11108600	6.93005000	-2.35317800
C	0.80028200	4.95819300	-3.73444300
H	0.54199700	3.93835400	-4.03326900
H	0.02047000	5.62801700	-4.11533000
H	1.74352200	5.22624000	-4.22617200
C	-0.43240400	4.69518500	-1.55874900
H	-0.41226200	4.82392400	-0.47389100
H	-1.23529400	5.32116700	-1.96130800
H	-0.69189000	3.65235400	-1.77375800
N	3.39170200	5.03527000	0.27523100
C	4.46047900	5.60912100	-0.58062700
C	3.67204000	5.21783300	1.73286700
C	5.55641300	6.01906700	0.41058900
H	4.80665900	4.86357200	-1.29988900
C	4.77333300	6.31572100	1.68947700
H	6.25142900	5.18937000	0.57261000
H	5.38768200	6.30219700	2.59384400
H	4.29283400	7.30045600	1.62044600
H	6.13277600	6.87645800	0.05117700
H	4.08183200	6.48221000	-1.12517000
C	3.65320100	-0.38101500	-2.41594900
C	5.04997400	-0.22059300	-2.41722900
C	3.12376500	-1.68203200	-2.46106300
C	5.87584100	-1.34378800	-2.43314300
H	5.46822800	0.77531300	-2.40136400
C	3.96985200	-2.78901000	-2.49570400
H	2.04674200	-1.82145800	-2.46039700
C	5.35585500	-2.63635900	-2.47454000
H	6.00868400	-3.49890300	-2.49191600
O	-1.96526400	-3.03935500	-0.10947300
C	-2.88201000	-3.53620300	-0.77520300
C	-3.01626500	-3.18858500	-2.28043700
H	-3.99199300	-3.50937300	-2.64360400
N	-2.98459700	-1.74225800	-2.44183300
C	-4.08727500	-1.00628900	-2.10738000
N	-3.87712000	0.36555400	-2.20651700
H	-2.92484100	0.65911100	-2.44318600
C	-1.94712900	-3.88886300	-3.18695500
H	-2.08260300	-1.27071400	-2.46729900
C	-2.02544200	-5.41388500	-2.97442400
H	-1.32006500	-5.91879700	-3.64365800
H	-1.76671200	-5.69983400	-1.94892800

H	-3.02658100	-5.80251600	-3.19814400
C	-2.28938900	-3.57593300	-4.65828500
H	-2.25418700	-2.50116000	-4.85908400
H	-1.57094400	-4.06878700	-5.32352800
H	-3.29208800	-3.93633500	-4.92033900
C	-0.51255400	-3.41631300	-2.88699200
H	-0.23439500	-3.60470900	-1.84775200
H	0.19371200	-3.95218800	-3.52961000
H	-0.38370300	-2.34587000	-3.08696300
N	-3.79594400	-4.38472000	-0.22763800
C	-5.02736500	-4.86419900	-0.90143500
C	-3.72966200	-4.80213100	1.20598000
C	-5.87156400	-5.45318600	0.23550700
H	-5.53117800	-4.03675200	-1.40618800
C	-4.82039700	-5.91105200	1.24672700
H	-6.51105000	-4.67994400	0.67269800
H	-5.21384800	-6.04882400	2.25760700
H	-4.37365100	-6.86078500	0.92497300
H	-6.51587300	-6.26607700	-0.11194900
H	-4.77977100	-5.63477100	-1.64205400
C	-4.75325600	1.37530500	-1.81752500
C	-6.11985200	1.16682900	-1.55510300
C	-4.23319600	2.67557800	-1.68993200
C	-6.91529800	2.23387500	-1.14017000
H	-6.53450800	0.17607800	-1.67416700
C	-5.05076400	3.72640000	-1.27660200
H	-3.18479800	2.85463800	-1.91282500
C	-6.39993600	3.52122600	-0.98975000
H	-7.03026400	4.33932300	-0.66725000
C	2.44026300	5.75155500	2.48796300
H	1.70861300	4.96763100	2.67875500
H	2.74450300	6.19405700	3.44216300
H	1.96328700	6.54113000	1.89820900
C	-2.36122900	-5.41284900	1.56393300
H	-1.60016700	-4.64844900	1.71529300
H	-2.44382200	-6.01742400	2.47327300
H	-2.03816500	-6.07880400	0.75713700
O	-5.16278600	-1.51418900	-1.77076700
O	4.18362200	2.42464500	-1.82012200
C	4.24983300	3.93948000	2.36685700
C	4.78832600	2.92144500	1.60416900
C	4.32929700	3.83343000	3.78660700
C	5.43080500	1.80057200	2.19931000
H	4.72688800	2.94903500	0.52027700
C	4.92640500	2.75302600	4.39386400
H	3.91705200	4.62136300	4.40958500
C	6.02505000	0.77593200	1.41271000
C	5.50419800	1.70712700	3.62604500
H	4.97399500	2.69670100	5.47924800
C	6.66607100	-0.28801700	2.00980600
H	5.97629200	0.85001900	0.33034900
C	6.15835700	0.59056100	4.21235800
C	6.72981200	-0.38348500	3.42283300
H	7.12999000	-1.04963600	1.39051000
H	6.21119300	0.52316200	5.29674600
H	7.24009500	-1.22603200	3.88225400
C	-4.13122000	-3.65181000	2.14750600
C	-4.85265400	-2.56081900	1.70328500
C	-3.84311200	-3.74659000	3.54019500
C	-5.32737000	-1.56225800	2.59734300
H	-5.07214300	-2.43635500	0.64699700

C	-4.26757800	-2.78621200	4.42887400
H	-3.27699500	-4.59302900	3.91608400
C	-6.11650700	-0.46806400	2.14698500
C	-5.02881600	-1.66960000	3.99336500
H	-4.03169000	-2.88199900	5.48656200
C	-6.58644500	0.47505400	3.03479200
H	-6.35690100	-0.39440900	1.09020200
C	-5.51534400	-0.67335000	4.88187600
C	-6.27852100	0.37421300	4.41464400
H	-7.20344700	1.29175800	2.67263800
H	-5.28594000	-0.75937900	5.94184000
H	-6.65690600	1.12289500	5.10592000
Cl	-0.62386600	0.75248300	-2.54427800
C	-8.35239900	1.95480400	-0.78813500
C	-4.42906500	5.08321300	-1.09480100
C	7.36297800	-1.13096700	-2.34760300
C	3.36122600	-4.16374300	-2.57519400
F	7.77728400	-0.11992600	-3.13985900
F	7.74395400	-0.80542200	-1.08107200
F	8.06199700	-2.23236800	-2.69233400
F	4.27512700	-5.14121900	-2.40693100
F	2.76578000	-4.37781900	-3.77486800
F	2.40302700	-4.34249200	-1.63448000
F	-8.45425000	1.37359800	0.43849400
F	-8.93369400	1.10853200	-1.66201200
F	-9.09809000	3.07916200	-0.74866100
F	-3.79648400	5.50729200	-2.21180800
F	-5.32747200	6.02732900	-0.75525600
F	-3.48587500	5.06185000	-0.10869500
C	-0.66628700	0.87753400	0.57354500
H	-1.64636500	0.91198700	0.11488300
H	-0.06984800	1.77813200	0.46076600
C	-0.02876600	-0.39316200	0.70047800
H	-0.52917700	-1.24225600	0.24314000
C	1.10927700	-0.53022200	1.45374200
C	1.55147900	0.68233600	2.22608100
H	2.44998900	0.49673800	2.81510900
H	1.78204800	1.50818700	1.54303000
C	0.43522700	1.19186800	3.20898200
H	0.72162700	2.19869300	3.52483300
H	0.44670400	0.56040100	4.10526000
C	-0.98132800	1.17215000	2.67475300
H	-1.51917000	0.23760500	2.81409000
C	-1.77693300	2.27879100	2.44496800
C	-3.25275500	2.12543600	2.24944000
H	-3.58295000	1.08464400	2.25476300
H	-3.57392600	2.60815300	1.31809800
H	-3.77942600	2.65232800	3.05836300
C	-1.23576800	3.67555700	2.37925400
H	-0.20920000	3.71687000	2.00599400
H	-1.24705000	4.11043400	3.39040700
H	-1.86715900	4.30955100	1.75014200
C	1.79578500	-1.82504400	1.60067500
C	3.15412300	-1.88100700	1.97086700
C	1.12360300	-3.04090400	1.34936600
C	3.81584600	-3.09863600	2.08593800
H	3.72034200	-0.97052700	2.13012000
C	1.78403700	-4.25658900	1.47419800
H	0.07713500	-3.04031400	1.06387900
C	3.13147900	-4.29151400	1.84514500
H	4.86722200	-3.11612800	2.35195600

H	1.25385200	-5.18175300	1.27523700
C	3.82717200	-5.61159400	2.04003400
F	3.31058400	-6.57679200	1.25022100
F	3.71210400	-6.04677000	3.31861200
F	5.14902400	-5.52821800	1.77349900

TS-*R*-7:

Imaginary frequency: -179.01 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.668250 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.633607 Hartree
Free energy correction: 1.306538 Hartree
Free energy correction – Grimme quasi-RRHO: 1.300534 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308087 Hartree

O	1.66383500	3.62705400	0.07492300
C	2.44926400	4.17394900	-0.71466500
C	2.21861900	4.04085000	-2.24461400
H	3.12064700	4.35084200	-2.77296500
N	2.01048200	2.63954100	-2.57157800
C	3.06040100	1.77628400	-2.44141200
N	2.72847900	0.44753700	-2.67155700
H	1.75409600	0.26288800	-2.91683900
C	1.05889500	4.94249000	-2.78822400
H	1.06541600	2.26156400	-2.62590000
C	1.41192200	6.42074500	-2.52614900
H	0.61955900	7.06765500	-2.91877500
H	1.51342300	6.63670900	-1.45653600
H	2.34656400	6.70608500	-3.02422200
C	0.95324600	4.72572600	-4.31280000
H	0.64949800	3.70434500	-4.55903800
H	0.20729800	5.40964200	-4.73441800
H	1.91044900	4.92368100	-4.81076800
C	-0.30114100	4.63321500	-2.13576500
H	-0.28146400	4.81809700	-1.05900600
H	-1.07190000	5.27370800	-2.57648100
H	-0.60683200	3.59341800	-2.29805000
N	3.51810600	4.89533700	-0.28321100
C	4.62190300	5.37562600	-1.15123000
C	3.79405900	5.12350700	1.17056800
C	5.74060700	5.74219700	-0.16883900
H	4.92214400	4.58876000	-1.84633500
C	4.97594600	6.13383500	1.09559100
H	6.37862000	4.87354000	0.02206400
H	5.58254300	6.10419100	2.00427900
H	4.56986500	7.14838300	0.99101200
H	6.37467900	6.54645500	-0.55325100
H	4.30060400	6.25487600	-1.72252500
C	3.53853700	-0.66841300	-2.45037600
C	4.81293400	-0.59857300	-1.86138900
C	3.03445200	-1.92947500	-2.81478100
C	5.52458900	-1.77034500	-1.60869500
H	5.22844600	0.36734300	-1.61579200
C	3.77339900	-3.08522900	-2.57016400
H	2.06214200	-1.99990500	-3.29265700
C	5.02366700	-3.02430300	-1.95392500
H	5.58370500	-3.92696500	-1.74862800
O	-2.14237600	-2.93137000	-0.22623100
C	-3.07390800	-3.41775700	-0.87954900
C	-3.18024000	-3.12890600	-2.40044700

H	-4.16402700	-3.42882900	-2.76077500
N	-3.08953000	-1.69094900	-2.61637600
C	-4.13496200	-0.90080100	-2.23006600
N	-3.87267300	0.46098200	-2.35271400
H	-2.94592000	0.70866700	-2.71236100
C	-2.13324100	-3.90787900	-3.26526100
H	-2.17061000	-1.26056000	-2.70560300
C	-2.30932100	-5.41998300	-3.01996500
H	-1.61670800	-5.98308500	-3.65519800
H	-2.09873800	-5.69485300	-1.98041800
H	-3.32565400	-5.75294600	-3.26440900
C	-2.42417700	-3.61083400	-4.75121800
H	-2.30226000	-2.54845200	-4.98167500
H	-1.73414800	-4.17657600	-5.38790800
H	-3.44686300	-3.90043300	-5.02341200
C	-0.67894900	-3.51588700	-2.94433200
H	-0.42203200	-3.72400100	-1.90332400
H	0.00248800	-4.08774600	-3.58231300
H	-0.48780600	-2.45299000	-3.13360900
N	-4.02613700	-4.19889700	-0.29983900
C	-5.27952700	-4.64614200	-0.95337900
C	-3.98471600	-4.53834000	1.15719200
C	-6.17074000	-5.09086400	0.21246700
H	-5.72336600	-3.82649200	-1.52212400
C	-5.16094300	-5.55281100	1.26341800
H	-6.75513900	-4.24440500	0.58712800
H	-5.56590500	-5.58756900	2.27804300
H	-4.78882800	-6.55456100	1.01243500
H	-6.87118100	-5.87699600	-0.08448000
H	-5.07712100	-5.48415000	-1.63227800
C	-4.63396900	1.50967400	-1.84302700
C	-5.85532400	1.33442300	-1.16633500
C	-4.12933800	2.81521900	-1.99585700
C	-6.51389700	2.43908500	-0.62841300
H	-6.26800500	0.34029000	-1.07369400
C	-4.81596700	3.90458400	-1.46232500
H	-3.19876200	2.96866800	-2.53447300
C	-6.01241600	3.73299700	-0.76428300
H	-6.54198100	4.58212400	-0.35210600
C	2.59681400	5.78550900	1.87575800
H	1.79270400	5.07471100	2.06199100
H	2.91356200	6.22347600	2.82799800
H	2.21073700	6.59924200	1.25325100
C	-2.66736500	-5.23748000	1.53992100
H	-1.84061400	-4.53184200	1.61339600
H	-2.77877700	-5.75669100	2.49761900
H	-2.42400400	-5.99246500	0.78515800
O	-5.21057600	-1.35844700	-1.82865000
O	4.20224700	2.16130100	-2.15923500
C	4.26042000	3.83212900	1.87139400
C	4.24084900	3.72955600	3.25113300
C	4.82042500	2.75674700	1.12461600
C	4.77103000	2.60017200	3.93147700
H	3.82626000	4.52944400	3.85881500
C	5.35506500	1.65423100	1.75278000
H	4.80847800	2.78773900	0.04070000
C	4.75478300	2.49135800	5.34917100
C	5.35330200	1.53858400	3.16738300
H	5.78979600	0.85023600	1.16396400
C	5.28949800	1.38932300	5.97793000
H	4.31474900	3.29777600	5.93190900

C	5.89956700	0.41483300	3.84518500
C	5.86836400	0.34081100	5.21955500
H	5.27229900	1.32023800	7.06235100
H	6.34680100	-0.38200300	3.25515100
H	6.29007900	-0.52115700	5.72927900
C	-4.27903000	-3.30419400	2.03316700
C	-3.94461300	-3.29269800	3.37510900
C	-4.99152100	-2.18834300	1.50896700
C	-4.30180500	-2.21768300	4.23255500
H	-3.39921400	-4.12284800	3.81533200
C	-5.36737000	-1.13702000	2.31468300
H	-5.23153600	-2.14907500	0.45214700
C	-3.95856100	-2.20244000	5.61241900
C	-5.04299200	-1.11653500	3.69649500
H	-5.92996400	-0.30560100	1.89618400
C	-4.33456700	-1.15395700	6.42184300
H	-3.39486200	-3.03821400	6.02114100
C	-5.42107300	-0.05110700	4.55800800
C	-5.07529300	-0.06821900	5.89069900
H	-4.06795400	-1.15727800	7.47541300
H	-5.99629300	0.77410700	4.14359900
H	-5.37311100	0.74867000	6.54272200
C	-0.72040400	0.90846300	0.20158900
H	-1.70761400	0.95195300	-0.24176300
H	-0.10526700	1.79081700	0.05202900
C	-0.10991300	-0.36946000	0.35860100
H	-0.63766000	-1.22364800	-0.05628000
C	1.05074000	-0.50354900	1.07795500
C	1.54509700	0.71895000	1.79908600
H	2.44976300	0.52348700	2.37527600
H	1.78895500	1.50998400	1.08012400
C	0.47256000	1.31264100	2.78507900
H	0.78578500	2.33350600	3.01859600
H	0.50991000	0.74455500	3.72201200
C	-0.96401600	1.27688800	2.31236900
H	-1.49588000	0.35115600	2.51790700
C	-1.76681000	2.36809900	2.04391200
C	-3.25233200	2.20636500	1.93438400
H	-3.57745800	1.17141300	2.06271200
H	-3.61754000	2.58626900	0.97246200
H	-3.73806300	2.81991100	2.70677800
C	-1.23322100	3.75557200	1.84877700
H	-0.19524700	3.77289600	1.50820700
H	-1.28960100	4.29648600	2.80579800
H	-1.84946500	4.31141000	1.13499600
Cl	-0.64954000	0.66782000	-2.95806500
C	1.73518200	-1.80101300	1.19940800
C	3.11992900	-1.85801900	1.45282500
C	1.04167000	-3.01488300	1.00535900
C	3.79427900	-3.07371700	1.47466500
H	3.69027800	-0.94528800	1.58297300
C	1.71493000	-4.22976400	1.03895300
H	-0.02834500	-3.01079100	0.82709100
C	3.09389200	-4.26309100	1.26364600
H	4.86677800	-3.09161000	1.63162500
H	1.17019700	-5.15451200	0.88373100
C	-7.75614900	2.19729800	0.18732200
C	-4.21082600	5.27665700	-1.58222400
C	6.82060300	-1.66266200	-0.85412300
C	3.18352200	-4.42322000	-2.93154800
F	6.59302900	-1.53630800	0.49338500

F	7.53918000	-0.57976300	-1.21139500
F	7.60405600	-2.74738400	-1.00658400
F	4.12328600	-5.38333600	-3.03759900
F	2.28718100	-4.84627000	-2.00582100
F	2.51955900	-4.37485300	-4.11242800
F	-7.43745500	1.77461500	1.44415600
F	-8.54366200	1.24528200	-0.34975300
F	-8.50045300	3.31304300	0.33330600
F	-5.11549000	6.25634300	-1.38642700
F	-3.22513800	5.46644000	-0.65946000
F	-3.64427300	5.47970000	-2.79163800
C	3.84673400	-5.56305200	1.19017900
F	4.37506100	-5.75990500	-0.04408900
F	3.05673400	-6.62551000	1.45324400
F	4.87884000	-5.59572200	2.06257900

TS-*R*-8:

Imaginary frequency: -169.33 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.667112 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.631072 Hartree
Free energy correction: 1.301321 Hartree
Free energy correction – Grimme quasi-RRHO: 1.298054 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.307775 Hartree

O	1.40575200	3.49346700	1.09962100
C	2.02463800	4.28559000	0.37100600
C	1.65252200	4.39827400	-1.13153800
H	2.42710000	4.96059200	-1.65447400
N	1.63331300	3.07056800	-1.72008000
C	2.80721100	2.39259800	-1.88905300
N	2.63668600	1.11028400	-2.38949900
H	1.66971700	0.79856400	-2.50768800
C	0.30591700	5.16193800	-1.38346700
H	0.75452900	2.56522900	-1.81661100
C	0.43964100	6.59960200	-0.84172000
H	-0.48052900	7.15959100	-1.04178900
H	0.60812300	6.61834600	0.24109800
H	1.26392800	7.13717600	-1.32605100
C	0.06152500	5.23130800	-2.90594000
H	-0.05481400	4.23665700	-3.34575700
H	-0.85621700	5.79522100	-3.10859000
H	0.89013700	5.73327200	-3.42050500
C	-0.90405200	4.48780200	-0.70869200
H	-0.78212100	4.44733300	0.37596300
H	-1.81147100	5.05763700	-0.93107900
H	-1.06115000	3.46596100	-1.07247800
N	3.02253400	5.07433900	0.84844600
C	3.95273400	5.86720200	0.00606400
C	3.40233100	5.09942800	2.29515600
C	5.09310400	6.24134000	0.95999200
H	4.29548000	5.26721200	-0.83948200
C	4.40117000	6.29217500	2.32209500
H	5.86402200	5.46451900	0.95209500
H	5.08980000	6.21779100	3.16808600
H	3.83691500	7.22828400	2.42552400
H	5.56513900	7.18817900	0.68222700
H	3.45006300	6.76605100	-0.37146900
C	3.62596400	0.14575300	-2.58071500
C	5.00025200	0.43873300	-2.62343400

C	3.21337200	-1.18540200	-2.75890200
C	5.92101800	-0.59211000	-2.80879100
H	5.32721600	1.46223500	-2.50882000
C	4.15141500	-2.19669600	-2.95462300
H	2.15386300	-1.42351400	-2.73579500
C	5.51712400	-1.91638400	-2.97564900
H	6.24263200	-2.70528800	-3.12325400
O	-1.84267300	-3.08422200	0.11946500
C	-2.72958600	-3.62873600	-0.55040900
C	-2.85929600	-3.30746200	-2.06176200
H	-3.81783000	-3.67067700	-2.43078700
N	-2.88366100	-1.86453100	-2.24293400
C	-4.02635300	-1.16265000	-1.97035800
N	-3.86856100	0.20804200	-2.12954800
H	-2.92735000	0.52737800	-2.37557500
C	-1.75533200	-3.97810600	-2.94992500
H	-2.00363800	-1.35530300	-2.28547400
C	-1.80247600	-5.50560800	-2.74551400
H	-1.05685200	-5.98972500	-3.38590700
H	-1.58078000	-5.78945800	-1.71054600
H	-2.78283900	-5.91872000	-3.01266800
C	-2.07669000	-3.66774300	-4.42678200
H	-2.04208700	-2.59346500	-4.62964100
H	-1.34681000	-4.15935200	-5.08031200
H	-3.07427000	-4.03150300	-4.70296000
C	-0.33605600	-3.47650900	-2.62447500
H	-0.05092100	-3.70567800	-1.59511400
H	0.38654600	-3.95760200	-3.29123400
H	-0.23804800	-2.39424800	-2.77085600
N	-3.61899200	-4.50235900	-0.00161200
C	-4.81019000	-5.05364400	-0.69448300
C	-3.57657200	-4.88116300	1.44335700
C	-5.63876100	-5.69186900	0.42784400
H	-5.35347500	-4.25795100	-1.20978400
C	-4.58447300	-6.06533500	1.47018100
H	-6.34249000	-4.96289700	0.84155000
H	-4.99392500	-6.22147900	2.47201600
H	-4.06192700	-6.98310500	1.17060400
H	-6.21465900	-6.55125700	0.07242900
H	-4.50424000	-5.80767500	-1.42958600
C	-4.81838500	1.20646800	-1.93132400
C	-6.15882900	0.96183500	-1.59170200
C	-4.39334100	2.53985100	-2.09490600
C	-7.02892900	2.03585100	-1.39416600
H	-6.50166000	-0.05902300	-1.49783100
C	-5.28360700	3.59185000	-1.90721200
H	-3.36560300	2.73992500	-2.38192100
C	-6.61304800	3.35587900	-1.54622700
H	-7.30401600	4.17688700	-1.40428100
C	2.19224700	5.41898800	3.19323300
H	1.54593100	4.55249700	3.32772700
H	2.53059900	5.76527500	4.17523700
H	1.60746400	6.22866700	2.74465400
C	-2.18250500	-5.37668000	1.87255500
H	-1.48657400	-4.55295400	2.02572500
H	-2.25812200	-5.95843200	2.79729300
H	-1.77862800	-6.04073900	1.10122800
O	-5.08788300	-1.70345900	-1.63840900
O	3.90883500	2.89283900	-1.62599000
C	4.12995400	3.81056400	2.71808600
C	4.69809200	2.95254500	1.79662200

C	4.31417400	3.53075200	4.10405600
C	5.46782300	1.82620600	2.19942600
H	4.56162300	3.11428200	0.73135200
C	5.03691200	2.43917600	4.52670800
H	3.88224900	4.19160500	4.84933800
C	6.08854200	0.96831200	1.25071100
C	5.64378200	1.55625100	3.59441500
H	5.16252600	2.24857100	5.59038800
C	6.85092500	-0.10315100	1.66270600
H	5.96193400	1.17728600	0.19264000
C	6.42292100	0.43537100	3.98829100
C	7.01654400	-0.37430500	3.04434200
H	7.33215500	-0.73436000	0.92209400
H	6.55395100	0.23391800	5.04919500
H	7.62337700	-1.22005400	3.35730600
C	-4.10184600	-3.74327500	2.33838500
C	-4.84597000	-2.69534400	1.83190500
C	-3.90608200	-3.81033200	3.74883400
C	-5.42790100	-1.71170300	2.67855700
H	-5.00244000	-2.59405600	0.76204300
C	-4.43771200	-2.86396600	4.59391500
H	-3.32728000	-4.62491300	4.17319300
C	-6.22799600	-0.65627100	2.15980600
C	-5.21879100	-1.78926000	4.09267900
H	-4.27109000	-2.93767800	5.66647300
C	-6.78997000	0.28040100	2.99919700
H	-6.39624800	-0.60374400	1.08794100
C	-5.80359500	-0.80300000	4.93169600
C	-6.57236300	0.20847700	4.39817100
H	-7.40808900	1.07060400	2.58413200
H	-5.64325900	-0.86649400	6.00585600
H	-7.02433300	0.95082600	5.05098600
C	-8.44144500	1.72411700	-0.97736200
C	-4.79359600	5.00929100	-2.03424200
C	7.38626700	-0.25198500	-2.76967200
C	3.65705300	-3.60824900	-3.12518500
F	7.66049500	0.88990900	-3.43455400
F	7.81676100	-0.06367000	-1.49123300
F	8.15536300	-1.22680900	-3.29801600
F	4.66211200	-4.49053100	-3.29786300
F	2.83300500	-3.72362100	-4.19555200
F	2.94292000	-4.01792300	-2.04807700
F	-8.47979300	1.19500500	0.27628500
F	-9.01823400	0.81461600	-1.79042100
F	-9.23057100	2.81837600	-0.96484200
F	-3.76283900	5.11969500	-2.90234100
F	-5.76653800	5.84758300	-2.44823900
F	-4.34759200	5.49061600	-0.84291600
C	-0.52139100	0.59597600	0.78021600
H	-1.49823500	0.60737100	0.31281000
H	-0.00027000	1.54956800	0.79748100
C	0.21673400	-0.62303400	0.75347000
H	-0.22060400	-1.44797100	0.19967700
C	1.35244900	-0.77030700	1.50756800
C	1.68664600	0.35307800	2.44849900
H	2.59776700	0.16231300	3.01719700
H	1.83957500	1.28773300	1.89655900
C	0.52067600	0.60155600	3.47630100
H	0.72127000	1.55973700	3.96373700
H	0.57344700	-0.17020700	4.25314100
C	-0.88070800	0.56607300	2.90538800

H	-1.35324700	-0.41238800	2.87593600
C	-1.74334900	1.64122400	2.81451300
C	-3.19143400	1.42835000	2.50475000
H	-3.44724000	0.37795200	2.35432000
H	-3.48589500	2.00161400	1.61542700
H	-3.80646500	1.81378800	3.32993400
C	-1.29584900	3.05863600	3.01823600
H	-0.30301100	3.24769600	2.59930100
H	-1.25110200	3.27171300	4.09665200
H	-2.00442400	3.76501900	2.57668200
Cl	-0.66179600	0.73907400	-2.39968600
C	2.12482200	-2.02375200	1.50737200
C	3.49765800	-2.01924800	1.82265100
C	1.51998900	-3.25316000	1.16870600
C	4.24135200	-3.19374700	1.79134100
H	4.00605500	-1.08907300	2.05090500
C	2.26258500	-4.42761000	1.15001700
H	0.46005000	-3.29417700	0.93876800
C	3.62539900	-4.40265300	1.46034800
H	5.30249900	-3.16488600	2.01420600
H	1.78497600	-5.36613800	0.88985800
C	4.41520100	-5.68321800	1.50058900
F	5.70980600	-5.48588100	1.16881700
F	3.91424200	-6.61327000	0.66029900
F	4.40769100	-6.22903800	2.74117700

TS-*R*-9:

Imaginary frequency: -185.77 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.669106 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.627804 Hartree
Free energy correction: 1.303346 Hartree
Free energy correction – Grimme quasi-RRHO: 1.299153 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.308021 Hartree

O	-2.13540500	-2.91892100	0.15940600
C	-2.88349600	-3.39730300	-0.70225700
C	-2.67771900	-3.02435100	-2.19362100
H	-3.53272800	-3.36608600	-2.77822100
N	-2.63690200	-1.57645400	-2.33031200
C	-3.77908200	-0.84500300	-2.17430500
N	-3.56782100	0.52542600	-2.28364000
H	-2.59667400	0.82100500	-2.42492600
C	-1.40802300	-3.69361900	-2.82577000
H	-1.74140400	-1.09442100	-2.30648600
C	-1.55137400	-5.22570400	-2.72511900
H	-0.69758300	-5.71127700	-3.21034800
H	-1.57772700	-5.56885100	-1.68485500
H	-2.46092300	-5.57944400	-3.22626900
C	-1.34566500	-3.30265100	-4.31761100
H	-1.25555100	-2.22039900	-4.45037700
H	-0.47458200	-3.76986000	-4.78964100
H	-2.24353400	-3.63354400	-4.85439500
C	-0.09704300	-3.27097300	-2.13400700
H	-0.08925700	-3.55318600	-1.07910900
H	0.74875400	-3.76170700	-2.62527800
H	0.07559400	-2.18984200	-2.19204400
N	-3.88730500	-4.26030600	-0.38547200
C	-4.96403200	-4.69248300	-1.30848200
C	-4.10253000	-4.74417500	1.01267000

C	-6.03090700	-5.28404900	-0.37985900
H	-5.33576200	-3.83928000	-1.87960000
C	-5.20855800	-5.81652200	0.79406600
H	-6.71492500	-4.49900700	-0.04193900
H	-5.79398700	-5.97879100	1.70317200
H	-4.73446500	-6.76867500	0.52227100
H	-6.62365500	-6.05808100	-0.87606800
H	-4.58796600	-5.45347400	-2.00432600
C	-4.47744900	1.53918700	-1.99798300
C	-5.86698400	1.34203600	-1.90079600
C	-3.96370600	2.83407500	-1.80478800
C	-6.69628400	2.41682600	-1.58159900
H	-6.27338000	0.35535900	-2.07237500
C	-4.81371400	3.89114900	-1.48548100
H	-2.89453300	3.00199900	-1.90236500
C	-6.18970200	3.69830300	-1.36405300
H	-6.84671100	4.52188800	-1.11715600
O	1.74401100	3.50019700	1.06627200
C	2.58586600	4.15202600	0.42793800
C	2.41656600	4.33799500	-1.10216900
H	3.34146100	4.73311000	-1.52045400
N	2.21942900	3.04181000	-1.72654600
C	3.29180700	2.21742900	-1.93592100
N	2.94514800	1.01591600	-2.53352100
H	1.94562400	0.86256100	-2.68580100
C	1.28610700	5.34895500	-1.49928800
H	1.28251200	2.64887800	-1.79365800
C	1.58263800	6.71622200	-0.85106600
H	0.81746500	7.44253000	-1.14714000
H	1.57926400	6.66264600	0.24365300
H	2.55337300	7.11320900	-1.17212400
C	1.31035700	5.51397300	-3.03318800
H	1.08325900	4.57369800	-3.54350600
H	0.56422600	6.25545000	-3.34171100
H	2.29161200	5.85917500	-3.38178500
C	-0.11533800	4.88416600	-1.06233500
H	-0.18133900	4.79054000	0.02369300
H	-0.86532500	5.61087200	-1.39113200
H	-0.38529300	3.91826700	-1.50451700
N	3.67422700	4.71158400	1.02126100
C	4.80392400	5.34576700	0.29267400
C	3.93543800	4.61390900	2.49013600
C	5.89300800	5.51836400	1.35832400
H	5.12643100	4.70772900	-0.53306400
C	5.09359900	5.63857400	2.65544300
H	6.53846800	4.63511700	1.38836900
H	5.68214900	5.43675200	3.55453600
H	4.66734000	6.64611200	2.74769800
H	6.52357200	6.38978900	1.15986200
H	4.49393800	6.31846000	-0.10730200
C	3.78734100	-0.03725200	-2.88533000
C	5.17564000	-0.03543900	-2.67931900
C	3.19438300	-1.16040400	-3.49392100
C	5.93103600	-1.15074300	-3.04747200
H	5.64492200	0.83730900	-2.24786000
C	3.97059400	-2.25132300	-3.86891100
H	2.12488000	-1.16541400	-3.67828200
C	5.34999100	-2.26612600	-3.64337300
H	5.95156300	-3.11645500	-3.93815300
C	-2.83504900	-5.41361500	1.57874100
H	-2.09238100	-4.67826600	1.88712300

H	-3.08879500	-6.04302700	2.43788400
H	-2.39580100	-6.06429200	0.81534400
C	2.72300600	5.06622900	3.32530400
H	1.94677500	4.30311800	3.36157200
H	3.03787900	5.30450100	4.34656400
H	2.29867700	5.97780700	2.89184700
O	4.45030400	2.53765100	-1.63971800
O	-4.88592900	-1.35679600	-1.96919000
C	-4.63601000	-3.62801200	1.92886200
C	-5.20049100	-2.47225800	1.42654800
C	-4.62940400	-3.81612200	3.34173500
C	-5.77359100	-1.48874000	2.27848500
H	-5.20988200	-2.28168900	0.35745100
C	-5.16143700	-2.87716900	4.19446100
H	-4.19651500	-4.71817300	3.76286000
C	-6.38770200	-0.31581000	1.75938100
C	-5.75322300	-1.68699400	3.69595800
H	-5.14052700	-3.04461100	5.26919500
C	-6.95013300	0.61808600	2.60213800
H	-6.42072700	-0.17494100	0.68279800
C	-6.33128000	-0.70085900	4.53956700
C	-6.91686700	0.42616900	4.00600500
H	-7.43310900	1.49614400	2.18412200
H	-6.31313700	-0.85639200	5.61616600
H	-7.36618600	1.16839500	4.66082100
C	4.43711200	3.21213500	2.88268300
C	4.88677800	2.30240800	1.94557100
C	4.54076300	2.86689100	4.26238300
C	5.46327500	1.05878900	2.32582700
H	4.81349100	2.51853200	0.88376600
C	5.07966400	1.66634300	4.66358700
H	4.19757600	3.56567500	5.01947500
C	5.96243900	0.14078300	1.36166000
C	5.56780200	0.72823800	3.71490300
H	5.15168400	1.42912400	5.72285900
C	6.54454500	-1.04446500	1.75251700
H	5.88608400	0.39328600	0.30812000
C	6.16458100	-0.50663100	4.08751400
C	6.64688800	-1.37110000	3.12817300
H	6.93177400	-1.72581100	1.00140200
H	6.24736800	-0.75213200	5.14401200
H	7.11763200	-2.30500800	3.42459300
C	7.40575500	-1.12575700	-2.74818800
C	3.31523900	-3.46011200	-4.48135800
C	-8.16905700	2.15656200	-1.40670200
C	-4.20303000	5.23539000	-1.20246000
F	-8.64301500	1.28564300	-2.32021900
F	-8.43174200	1.61826900	-0.18508400
F	-8.90223300	3.28643300	-1.49891500
F	-5.12402000	6.20797500	-1.06351500
F	-3.34530400	5.62085100	-2.17292000
F	-3.47950200	5.21030000	-0.04401200
F	7.63768700	-1.16195900	-1.40764000
F	7.99408100	0.00104500	-3.20385300
F	8.06166800	-2.17385800	-3.28792300
F	2.16015000	-3.15104900	-5.11416200
F	4.11936200	-4.06859500	-5.37922400
F	3.00674000	-4.39313300	-3.54392100
C	-0.66470900	0.89290300	0.82622900
H	-1.57419200	0.98120600	0.24491200
H	-0.00735600	1.75672200	0.78460600

C	-0.12164100	-0.41220700	1.02591700
H	-0.61936400	-1.23876900	0.52530900
C	0.90434400	-0.60858400	1.91522700
C	1.32365400	0.58319600	2.72980300
H	2.13085600	0.34870800	3.42492700
H	1.68399600	1.38673800	2.07714900
C	0.12403800	1.16396400	3.56550400
H	0.41823800	2.16059200	3.90582900
H	-0.00667500	0.54675500	4.46229200
C	-1.21702500	1.20498700	2.86251700
H	-1.80757700	0.29523300	2.93656300
C	-1.93591700	2.34528700	2.55301900
C	-3.38774700	2.25549800	2.19951500
H	-3.76005700	1.22942400	2.15925900
H	-3.59000800	2.75857000	1.24604700
H	-3.97354300	2.79945400	2.95509000
C	-1.33253400	3.71767700	2.55524700
H	-0.26353700	3.71390900	2.32684000
H	-1.46512800	4.16308100	3.55314000
H	-1.84643600	4.37048200	1.84362500
Cl	-0.35405800	0.97580100	-2.35218300
C	1.47432400	-1.94288900	2.16752700
C	2.78644800	-2.08366300	2.66011500
C	0.72870000	-3.11341400	1.90932200
C	3.33593000	-3.34169100	2.88372500
H	3.40501100	-1.21060700	2.83503100
C	1.27535200	-4.36897900	2.14510500
H	-0.28772200	-3.04286400	1.53708000
C	2.57994400	-4.48859900	2.63422900
H	4.35631600	-3.42537600	3.24078300
H	0.68800200	-5.25941700	1.94651800
C	3.14426600	-5.84794900	2.94806600
F	4.48997600	-5.87447000	2.83410400
F	2.64607600	-6.80110500	2.13068100
F	2.84982800	-6.22554100	4.21561300

TS-*R*-10:

Imaginary frequency: -230.57 cm^{-1}
E[B3LYP/6-31G(d)]: -5531.650620 Hartree
E[PCM(CyH)-B3LYP-D3(BJ)/6-311+G(d,p)]: -5533.605454 Hartree
Free energy correction: 1.296333 Hartree
Free energy correction – Grimme quasi-RRHO: 1.295093 Hartree
Free energy correction – Truhlar quasi-RRHO: 1.306175 Hartree

O	3.10194600	3.22182900	0.11439400
C	4.07478700	3.29361000	-0.64041200
C	3.93974000	2.78629100	-2.09800300
H	4.91987600	2.73330200	-2.56970700
N	3.43463500	1.41936200	-2.08324600
C	4.30277700	0.38248700	-1.83092800
N	3.66112800	-0.84261600	-1.73894800
H	2.64304600	-0.82763600	-1.83105700
C	3.05299800	3.71359900	-2.99810900
H	2.46254400	1.28570100	-1.81851300
C	3.60677100	5.15111300	-2.93588900
H	3.04645300	5.79902400	-3.62009100
H	3.52005100	5.57843900	-1.93106400
H	4.66140800	5.19082200	-3.23547700
C	3.15031200	3.20408900	-4.45033300

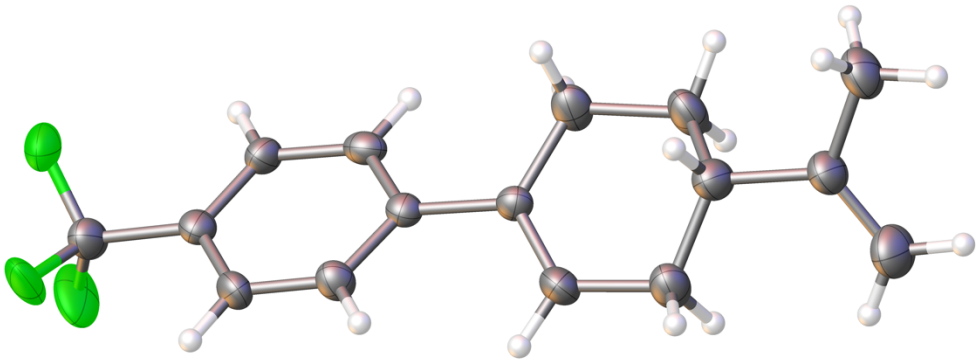
H	2.79879900	2.17113200	-4.53203100
H	2.53895800	3.82859500	-5.11332400
H	4.18367300	3.23878300	-4.81753600
C	1.57426500	3.72663800	-2.56204900
H	1.46719000	4.04299500	-1.52223000
H	1.01065900	4.42043100	-3.19867200
H	1.10729400	2.74019800	-2.66513100
N	5.27910600	3.79768100	-0.24206800
C	6.53103800	3.75420900	-1.03342100
C	5.49323400	4.32000900	1.14119700
C	7.62823600	4.08119300	-0.01268100
H	6.66523300	2.76875600	-1.48541500
C	6.90344200	4.96285200	1.00546300
H	7.98519900	3.16324400	0.46475500
H	7.41084000	5.02414900	1.97216200
H	6.79529400	5.98299300	0.61399100
H	8.48663200	4.57579800	-0.47707400
H	6.50487700	4.50943200	-1.83050100
C	4.22026800	-2.08113900	-1.43116900
C	5.58818600	-2.29035400	-1.18929400
C	3.34472100	-3.17980000	-1.35907200
C	6.04059100	-3.56668300	-0.85191100
H	6.27320300	-1.45814400	-1.26912000
C	3.82301300	-4.44762100	-1.04404500
H	2.28622800	-3.02799000	-1.54552300
C	5.17695800	-4.65791600	-0.77710000
H	5.54503600	-5.64216700	-0.51825700
O	-3.09093500	1.91440400	1.18291400
C	-2.70439300	1.56310800	2.30570400
C	-1.24737500	1.07282600	2.50357900
H	-1.14954900	0.60595500	3.48451900
N	-0.95115200	0.04183200	1.52170800
C	-1.49618300	-1.20217000	1.64347700
N	-1.10847600	-2.06420100	0.62406700
H	-0.49042600	-1.66742000	-0.09206700
C	-0.18582100	2.22671000	2.45100400
H	-0.45265200	0.28530600	0.67042200
C	-0.50836500	3.24696700	3.56123900
H	0.25252800	4.03499300	3.57059100
H	-1.48102900	3.72898000	3.40948900
H	-0.50813000	2.77810200	4.55315300
C	1.20400100	1.61666100	2.73187300
H	1.49444200	0.89071200	1.96764700
H	1.96738400	2.40074100	2.73162000
H	1.22690300	1.11181800	3.70588300
C	-0.15913400	2.95728600	1.09453800
H	-1.11507000	3.44117200	0.87839900
H	0.62978700	3.71517200	1.10907000
H	0.08144000	2.28719000	0.26229600
N	-3.52569200	1.60039200	3.38992800
C	-3.22932800	0.98387200	4.70573900
C	-4.92128600	2.12955200	3.30749100
C	-4.59314100	0.92892400	5.40405800
H	-2.79298100	-0.00763500	4.56814000
C	-5.33502100	2.12529300	4.80715600
H	-5.10871500	-0.00368100	5.15334600
H	-6.42091500	2.07133900	4.92323200
H	-4.99026000	3.05634600	5.27557200
H	-4.49903300	0.98064400	6.49265400
H	-2.52605000	1.60908500	5.27002600
C	-1.56034100	-3.35763700	0.38263900

C	-2.34005500	-4.10486300	1.28168200
C	-1.20158900	-3.93829800	-0.84801100
C	-2.76410700	-5.38624400	0.92566700
H	-2.59784700	-3.67691900	2.24041800
C	-1.62759100	-5.22187200	-1.17446500
H	-0.58202000	-3.37546100	-1.54009000
C	-2.42191300	-5.96242300	-0.29684900
H	-2.75038600	-6.96144100	-0.55287000
C	4.45805000	5.40170200	1.50337300
H	3.47944400	4.96907000	1.70755800
H	4.79265500	5.97191500	2.37630800
H	4.36360200	6.10560100	0.66944700
C	-4.94646300	3.57163000	2.76463900
H	-4.79682100	3.59939300	1.68560700
H	-5.90087800	4.05171900	3.00391200
H	-4.15579500	4.15554800	3.24713800
O	-2.25274900	-1.52178100	2.56815900
O	5.52498700	0.53216500	-1.73786500
C	5.54599800	3.17718900	2.17250200
C	5.76933500	1.86584100	1.80078600
C	5.45805500	3.47519700	3.56351400
C	5.92272800	0.82862500	2.76016100
H	5.82709900	1.59280300	0.75135200
C	5.58772500	2.49267400	4.51774300
H	5.28611200	4.49769900	3.88541500
C	6.18580400	-0.51404700	2.37579500
C	5.82852600	1.14211700	4.15297200
H	5.51242800	2.74659700	5.57304700
C	6.34513600	-1.50054000	3.32273600
H	6.26758700	-0.75098400	1.31872600
C	5.98753900	0.10134000	5.10649500
C	6.24061800	-1.19053100	4.70144800
H	6.55795500	-2.51785500	3.00794000
H	5.91152100	0.34349700	6.16443900
H	6.36531500	-1.97821000	5.44001300
C	-5.84277800	1.18634700	2.51271300
C	-5.49607800	-0.12221600	2.24027300
C	-7.13251500	1.63986100	2.10973200
C	-6.39028300	-1.01097500	1.58356300
H	-4.51806900	-0.50424200	2.51720700
C	-8.01641600	0.80928000	1.46092300
H	-7.43276900	2.66235200	2.31730300
C	-6.04543700	-2.36792800	1.33286000
C	-7.68019000	-0.54089800	1.17916300
H	-8.99431900	1.18151100	1.16320200
C	-6.93388200	-3.21812800	0.71020600
H	-5.07373800	-2.72961000	1.65768600
C	-8.56974800	-1.43824000	0.52939200
C	-8.20649300	-2.74707300	0.30015100
H	-6.66021500	-4.25676100	0.54995100
H	-9.54948300	-1.07625900	0.22501000
H	-8.90024400	-3.42761400	-0.18673400
C	-2.54692000	-0.12546500	-2.33063500
H	-2.51013300	-0.85031900	-1.52594300
H	-1.96411700	-0.39748300	-3.20108800
C	-2.69959000	1.25810800	-1.98237300
H	-2.66068500	1.50624100	-0.92336400
C	-2.95281500	2.19297000	-2.94769600
C	-3.20717600	1.66199900	-4.33446600
H	-3.43106200	2.45496600	-5.04969800
H	-2.31562900	1.13938500	-4.70503300

C	-4.41016900	0.65949100	-4.34193900
H	-4.44997400	0.18654800	-5.32800000
H	-5.33582200	1.23601000	-4.23636200
C	-4.41390400	-0.39015200	-3.24165700
H	-5.00372900	-0.14056500	-2.36292000
C	-4.19307900	-1.74447400	-3.43597200
C	-4.60848500	-2.74466600	-2.40504500
H	-5.03457200	-2.28850000	-1.50869400
H	-3.77064700	-3.39467800	-2.12634500
H	-5.36876100	-3.40785700	-2.84365900
C	-3.51337200	-2.29436100	-4.65238800
H	-3.02328000	-1.53186900	-5.26152500
H	-4.26156300	-2.79720200	-5.28283700
H	-2.78466500	-3.06367500	-4.37501000
Cl	0.39478000	-0.38612400	-1.69490900
C	-3.09662100	3.62682200	-2.64197400
C	-2.90069000	4.60293800	-3.63907400
C	-3.41050400	4.06383000	-1.33719200
C	-3.01239300	5.95902400	-3.35087500
H	-2.62186700	4.30882400	-4.64542900
C	-3.53084100	5.41852300	-1.05249100
H	-3.56767600	3.34375000	-0.54162500
C	-3.33524000	6.37146800	-2.05664000
H	-2.83955500	6.69643400	-4.12743700
H	-3.77407300	5.73727700	-0.04433200
C	-3.66363900	-6.12402100	1.88186700
C	-1.30184100	-5.76140000	-2.53920100
C	7.49289100	-3.73061800	-0.49274900
C	2.86603400	-5.60960600	-1.04908500
F	8.30260700	-3.04238600	-1.32549600
F	7.74585500	-3.26843900	0.76054600
F	7.88671100	-5.02240600	-0.51893400
F	3.32577600	-6.65125800	-0.32257700
F	2.64390600	-6.07024200	-2.30266900
F	1.65627000	-5.26841100	-0.54329700
F	-4.92655200	-5.61580300	1.85609400
F	-3.23792600	-6.02486600	3.15699800
F	-3.76546600	-7.43587200	1.58383500
F	-0.08054100	-5.39162100	-2.96400300
F	-1.37710000	-7.10334900	-2.59683700
F	-2.19229900	-5.28453100	-3.46903800
C	-3.53000400	7.83392300	-1.75594300
F	-2.78781500	8.61730900	-2.56814700
F	-3.19741000	8.13270300	-0.48214600
F	-4.82168400	8.20392100	-1.92328200

13. X-Ray Crystallographic Information

Absolute configuration was assigned for compounds **2&3** by analogy to the reported crystal structure of **2d** (shown below).



X-ray Crystallography: A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in ω at -30°, -55°, -80°, 30°, 55°, 80° and 115° in 2θ. Data integration down to 0.84 Å resolution was carried out using SAINT V8.37 A (Bruker diffractometer, 2015) with reflection spot size optimization. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2015). The structure was solved by the Intrinsic Phasing methods and refined by least-squares methods again F^2 using SHELXT-2014 (Sheldrick, 2015) and SHELXL-2014 (Sheldrick, 2015) with OLEX 2 interface (Dolomanov, et al., 2009). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, and geometric parameters are shown in Table2. The Ortep plots produced with SHELXL-2014 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Table 1. Experimental details

	DAS-I
Crystal data	
Chemical formula	$C_{16}H_{17}F_3$
M_r	266.25
Crystal system, space group	Triclinic, *P*1
Temperature (K)	100
a, *b*, *c* (Å)	7.9199 (2), 11.2795 (3), 14.9844 (4)
α, β, γ (°)	91.4157 (17), 90.3788 (19), 90.853 (2)
V (Å^3)	1338.00 (6)
Z	4
Radiation type	Cu *K*α
μ (mm^{-1})	0.88
Crystal size (mm)	0.10 × 0.08 × 0.02

Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector
Absorption correction	Multi-scan *SADABS*
T_{min}, T_{max}	0.757, 0.840
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	27812, 8000, 6944
R_{int}	0.043
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.136, 1.03
No. of reflections	8000
No. of parameters	807
No. of restraints	1378
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, -0.27
Absolute structure	Flack x determined using 2599 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.20 (11)

Computer programs: *APEX3* v2016.9-0 (Bruker-AXS, 2016), *SAINT* 8.37A (Bruker-AXS, 2015), *SHELXT2014* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2015), Bruker *SHELXTL* (Sheldrick, 2015).

Table 2. Selected geometric parameters (Å, º)

C1—F2	1.299 (12)	C34A—C36A	1.50 (2)
C1—F3	1.332 (15)	C35A—H35D	0.9500
C1—F1	1.395 (12)	C35A—H35E	0.9500
C1—C2	1.497 (6)	C36A—H36C	0.9800
C1A—F3A	1.30 (2)	C36A—H36D	0.9800
C1A—F2A	1.33 (2)	C36A—H36E	0.9800
C1A—F1A	1.35 (2)	C41—F9	1.32 (2)
C1A—C2	1.497 (6)	C41—F8	1.34 (2)
C1B—F1B	1.309 (10)	C41—F7	1.35 (2)
C1B—F3B	1.331 (13)	C41—C42	1.487 (6)
C1B—F2B	1.409 (11)	C41A—F7A	1.286 (8)
C1B—C2	1.497 (6)	C41A—F9A	1.313 (12)
C2—C3	1.385 (7)	C41A—F8A	1.434 (9)
C2—C7	1.393 (6)	C41A—C42	1.487 (6)

C3—C4	1.370 (6)	C41B—F8B	1.276 (12)
C4—C5	1.405 (6)	C41B—F9B	1.305 (18)
C4—H4	0.9500	C41B—F7B	1.477 (13)
C5—C6	1.402 (6)	C41B—C42	1.487 (6)
C5—C10	1.486 (6)	C42—C43	1.382 (7)
C6—C7	1.384 (6)	C42—C47	1.387 (7)
C6—H6	0.9500	C43—C44	1.386 (6)
C7—H7	0.9500	C43—H43	0.9500
C8—C13	1.518 (7)	C44—C45	1.391 (6)
C8—C9	1.525 (6)	C44—H44	0.9500
C8—H8A	0.9900	C45—C46	1.409 (6)
C8—H8B	0.9900	C45—C50	1.487 (6)
C9—C10	1.464 (6)	C46—C47	1.389 (6)
C9—H9A	0.9900	C46—H46	0.9500
C9—H9B	0.9900	C47—H47	0.9500
C10—C11	1.364 (6)	C48—C49	1.503 (6)
C11—C12	1.485 (6)	C48—C53	1.535 (6)
C11—H11	0.9500	C48—H48A	0.9900
C12—C13	1.504 (6)	C48—H48B	0.9900
C12—H12A	0.9900	C49—C50	1.332 (6)
C12—H12B	0.9900	C49—H49	0.9500
C13—C14	1.518 (6)	C50—C51	1.513 (6)
C13—H13	1.0000	C51—C52	1.528 (6)
C14—C15	1.327 (7)	C51—H51A	0.9900
C14—C16	1.484 (7)	C51—H51B	0.9900
C15—H15A	0.9500	C52—C53	1.523 (6)
C15—H15B	0.9500	C52—H52A	0.9900
C16—H16A	0.9800	C52—H52B	0.9900
C16—H16B	0.9800	C53—C54	1.511 (6)
C16—H16C	0.9800	C53—H53	1.0000
C21—F5	1.325 (10)	C54—C55	1.317 (7)
C21—F6	1.389 (13)	C54—C56	1.503 (6)
C21—F4	1.396 (11)	C55—H55A	0.9500
C21—C22	1.489 (6)	C55—H55B	0.9500
C21A—F4A	1.283 (9)	C56—H56A	0.9800
C21A—F6A	1.312 (13)	C56—H56B	0.9800
C21A—F5A	1.385 (10)	C56—H56C	0.9800
C21A—C22	1.489 (6)	C61—F12	1.294 (8)
C21B—F6B	1.281 (12)	C61—F10	1.363 (8)
C21B—F4B	1.360 (15)	C61—F11	1.412 (8)

C21B—F5B	1.378 (11)	C61—C62	1.474 (6)
C21B—C22	1.489 (6)	C61A—F10A	1.263 (10)
C22—C23	1.389 (6)	C61A—F12A	1.324 (11)
C22—C27	1.389 (6)	C61A—F11A	1.388 (11)
C23—C24	1.373 (6)	C61A—C62	1.474 (6)
C23—H23	0.9500	C61B—F10B	1.293 (11)
C24—C25	1.394 (6)	C61B—F11B	1.351 (11)
C24—H24	0.9500	C61B—F12B	1.413 (12)
C25—C26	1.400 (6)	C61B—C62	1.474 (6)
C25—C30A	1.494 (6)	C62—C63	1.387 (6)
C25—C30	1.494 (6)	C62—C67	1.393 (6)
C26—C27	1.384 (6)	C63—C64	1.384 (6)
C26—H26	0.9500	C63—H63	0.9500
C27—H27	0.9500	C64—C65	1.402 (6)
C28—C33	1.50 (2)	C64—H64	0.9500
C28—C29	1.55 (2)	C65—C66	1.401 (6)
C28—H28A	0.9900	C65—C70	1.495 (6)
C28—H28B	0.9900	C66—C67	1.384 (6)
C29—C30	1.48 (2)	C66—H66	0.9500
C29—H29A	0.9900	C67—H67	0.9500
C29—H29B	0.9900	C68—C73	1.513 (6)
C30—C31	1.35 (2)	C68—C69	1.514 (6)
C31—C32	1.48 (2)	C68—H68A	0.9900
C31—H31	0.9500	C68—H68B	0.9900
C32—C33	1.553 (13)	C69—C70	1.325 (7)
C32—H32A	0.9900	C69—H69	0.9500
C32—H32B	0.9900	C70—C71	1.507 (6)
C33—C34	1.517 (13)	C71—C72	1.532 (6)
C33—H33	1.0000	C71—H71A	0.9900
C34—C36	1.340 (18)	C71—H71B	0.9900
C34—C35	1.473 (18)	C72—C73	1.515 (6)
C35—H35A	0.9800	C72—H72A	0.9900
C35—H35B	0.9800	C72—H72B	0.9900
C35—H35C	0.9800	C73—C74A	1.526 (6)
C36—H36A	0.9500	C73—C74	1.526 (6)
C36—H36B	0.9500	C73—H73	1.0000
C28A—C29A	1.48 (4)	C73—H73A	1.0000
C28A—C33A	1.54 (3)	C74—C76	1.32 (2)
C28A—H28C	0.9900	C74—C75	1.50 (2)
C28A—H28D	0.9900	C75—H75A	0.9800

C29A—C30A	1.37 (4)	C75—H75B	0.9800
C29A—H29C	0.9500	C75—H75C	0.9800
C30A—C31A	1.48 (3)	C76—H76A	0.9500
C31A—C32A	1.58 (4)	C76—H76B	0.9500
C31A—H31A	0.9900	C74A—C75A	1.33 (2)
C31A—H31B	0.9900	C74A—C76A	1.48 (2)
C32A—C33A	1.50 (2)	C75A—H75D	0.9500
C32A—H32C	0.9900	C75A—H75E	0.9500
C32A—H32D	0.9900	C76A—H76C	0.9800
C33A—C34A	1.52 (2)	C76A—H76D	0.9800
C33A—H33A	1.0000	C76A—H76E	0.9800
C34A—C35A	1.32 (2)		
F2—C1—F3	108.7 (16)	C28A—C33A—H33A	106.6
F2—C1—F1	106.7 (7)	C35A—C34A—C36A	121 (3)
F3—C1—F1	101.7 (14)	C35A—C34A—C33A	127 (6)
F2—C1—C2	115.5 (7)	C36A—C34A—C33A	111 (5)
F3—C1—C2	112.6 (17)	C34A—C35A—H35D	120.0
F1—C1—C2	110.5 (6)	C34A—C35A—H35E	120.0
F3A—C1A—F2A	108 (2)	H35D—C35A—H35E	120.0
F3A—C1A—F1A	109 (2)	C34A—C36A—H36C	109.5
F2A—C1A—F1A	105 (2)	C34A—C36A—H36D	109.5
F3A—C1A—C2	116.0 (13)	H36C—C36A—H36D	109.5
F2A—C1A—C2	109.8 (16)	C34A—C36A—H36E	109.5
F1A—C1A—C2	108.4 (14)	H36C—C36A—H36E	109.5
F1B—C1B—F3B	110.8 (13)	H36D—C36A—H36E	109.5
F1B—C1B—F2B	105.5 (7)	F9—C41—F8	108 (2)
F3B—C1B—F2B	101.1 (12)	F9—C41—F7	108 (3)
F1B—C1B—C2	115.8 (6)	F8—C41—F7	105 (3)
F3B—C1B—C2	112.0 (15)	F9—C41—C42	115.4 (17)
F2B—C1B—C2	110.5 (6)	F8—C41—C42	112.4 (19)
C3—C2—C7	119.4 (4)	F7—C41—C42	107 (2)
C3—C2—C1A	120.3 (4)	F7A—C41A—F9A	112.9 (15)
C7—C2—C1A	120.2 (4)	F7A—C41A—F8A	103.2 (6)
C3—C2—C1B	120.3 (4)	F9A—C41A—F8A	101.1 (12)
C7—C2—C1B	120.2 (4)	F7A—C41A—C42	115.0 (5)
C3—C2—C1	120.3 (4)	F9A—C41A—C42	112.8 (16)
C7—C2—C1	120.2 (4)	F8A—C41A—C42	110.4 (5)
C4—C3—C2	120.6 (4)	F8B—C41B—F9B	114 (2)
C4—C3—H3	119.7	F8B—C41B—F7B	102.9 (8)

C2—C3—H3	119.7	F9B—C41B—F7B	98 (2)
C3—C4—C5	121.7 (4)	F8B—C41B—C42	115.9 (7)
C3—C4—H4	119.1	F9B—C41B—C42	116 (2)
C5—C4—H4	119.1	F7B—C41B—C42	107.7 (6)
C6—C5—C4	116.7 (4)	C43—C42—C47	118.9 (4)
C6—C5—C10	122.2 (4)	C43—C42—C41A	120.3 (5)
C4—C5—C10	121.1 (4)	C47—C42—C41A	120.8 (4)
C7—C6—C5	121.9 (4)	C43—C42—C41B	120.3 (5)
C7—C6—H6	119.0	C47—C42—C41B	120.8 (4)
C5—C6—H6	119.0	C43—C42—C41	120.3 (5)
C6—C7—C2	119.6 (4)	C47—C42—C41	120.8 (4)
C6—C7—H7	120.2	C42—C43—C44	120.8 (4)
C2—C7—H7	120.2	C42—C43—H43	119.6
C13—C8—C9	113.0 (4)	C44—C43—H43	119.6
C13—C8—H8A	109.0	C43—C44—C45	121.4 (4)
C9—C8—H8A	109.0	C43—C44—H44	119.3
C13—C8—H8B	109.0	C45—C44—H44	119.3
C9—C8—H8B	109.0	C44—C45—C46	117.5 (4)
H8A—C8—H8B	107.8	C44—C45—C50	120.3 (4)
C10—C9—C8	115.6 (4)	C46—C45—C50	122.1 (4)
C10—C9—H9A	108.4	C47—C46—C45	120.7 (4)
C8—C9—H9A	108.4	C47—C46—H46	119.7
C10—C9—H9B	108.4	C45—C46—H46	119.7
C8—C9—H9B	108.4	C42—C47—C46	120.8 (4)
H9A—C9—H9B	107.4	C42—C47—H47	119.6
C11—C10—C9	120.7 (4)	C46—C47—H47	119.6
C11—C10—C5	120.2 (4)	C49—C48—C53	113.1 (4)
C9—C10—C5	119.1 (4)	C49—C48—H48A	109.0
C10—C11—C12	123.6 (4)	C53—C48—H48A	109.0
C10—C11—H11	118.2	C49—C48—H48B	109.0
C12—C11—H11	118.2	C53—C48—H48B	109.0
C11—C12—C13	113.2 (4)	H48A—C48—H48B	107.8
C11—C12—H12A	108.9	C50—C49—C48	125.0 (4)
C13—C12—H12A	108.9	C50—C49—H49	117.5
C11—C12—H12B	108.9	C48—C49—H49	117.5
C13—C12—H12B	108.9	C49—C50—C45	122.9 (4)
H12A—C12—H12B	107.8	C49—C50—C51	120.4 (4)
C12—C13—C8	109.7 (4)	C45—C50—C51	116.7 (4)
C12—C13—C14	116.3 (4)	C50—C51—C52	112.6 (4)
C8—C13—C14	111.8 (4)	C50—C51—H51A	109.1

C12—C13—H13	106.1	C52—C51—H51A	109.1
C8—C13—H13	106.1	C50—C51—H51B	109.1
C14—C13—H13	106.1	C52—C51—H51B	109.1
C15—C14—C16	121.5 (4)	H51A—C51—H51B	107.8
C15—C14—C13	122.9 (5)	C53—C52—C51	111.3 (3)
C16—C14—C13	115.6 (4)	C53—C52—H52A	109.4
C14—C15—H15A	120.0	C51—C52—H52A	109.4
C14—C15—H15B	120.0	C53—C52—H52B	109.4
H15A—C15—H15B	120.0	C51—C52—H52B	109.4
C14—C16—H16A	109.5	H52A—C52—H52B	108.0
C14—C16—H16B	109.5	C54—C53—C52	115.8 (3)
H16A—C16—H16B	109.5	C54—C53—C48	111.1 (3)
C14—C16—H16C	109.5	C52—C53—C48	108.2 (3)
H16A—C16—H16C	109.5	C54—C53—H53	107.1
H16B—C16—H16C	109.5	C52—C53—H53	107.1
F5—C21—F6	103.5 (10)	C48—C53—H53	107.1
F5—C21—F4	112.3 (7)	C55—C54—C56	121.5 (4)
F6—C21—F4	101.3 (8)	C55—C54—C53	123.1 (4)
F5—C21—C22	115.9 (6)	C56—C54—C53	115.4 (4)
F6—C21—C22	109.6 (9)	C54—C55—H55A	120.0
F4—C21—C22	112.8 (6)	C54—C55—H55B	120.0
F4A—C21A—F6A	114.3 (9)	H55A—C55—H55B	120.0
F4A—C21A—F5A	107.6 (7)	C54—C56—H56A	109.5
F6A—C21A—F5A	100.2 (9)	C54—C56—H56B	109.5
F4A—C21A—C22	112.6 (6)	H56A—C56—H56B	109.5
F6A—C21A—C22	112.8 (9)	C54—C56—H56C	109.5
F5A—C21A—C22	108.3 (5)	H56A—C56—H56C	109.5
F6B—C21B—F4B	104.2 (10)	H56B—C56—H56C	109.5
F6B—C21B—F5B	105.7 (9)	F12—C61—F10	107.3 (6)
F4B—C21B—F5B	100.2 (9)	F12—C61—F11	104.0 (6)
F6B—C21B—C22	118.8 (7)	F10—C61—F11	102.1 (6)
F4B—C21B—C22	112.2 (8)	F12—C61—C62	116.0 (5)
F5B—C21B—C22	113.6 (6)	F10—C61—C62	113.8 (4)
C23—C22—C27	119.5 (4)	F11—C61—C62	112.3 (4)
C23—C22—C21A	121.5 (4)	F10A—C61A—F12A	115.8 (8)
C27—C22—C21A	119.0 (4)	F10A—C61A—F11A	105.0 (8)
C23—C22—C21B	121.5 (4)	F12A—C61A—F11A	98.7 (7)
C27—C22—C21B	119.0 (4)	F10A—C61A—C62	114.6 (6)
C23—C22—C21	121.5 (4)	F12A—C61A—C62	112.6 (6)
C27—C22—C21	119.0 (4)	F11A—C61A—C62	108.3 (5)

C24—C23—C22	120.1 (4)	F10B—C61B—F11B	114.2 (9)
C24—C23—H23	120.0	F10B—C61B—F12B	106.4 (8)
C22—C23—H23	120.0	F11B—C61B—F12B	98.1 (9)
C23—C24—C25	122.0 (4)	F10B—C61B—C62	112.7 (6)
C23—C24—H24	119.0	F11B—C61B—C62	113.7 (6)
C25—C24—H24	119.0	F12B—C61B—C62	110.6 (7)
C24—C25—C26	117.0 (4)	C63—C62—C67	119.0 (4)
C24—C25—C30A	122.1 (4)	C63—C62—C61A	121.7 (4)
C26—C25—C30A	120.9 (4)	C67—C62—C61A	119.2 (4)
C24—C25—C30	122.1 (4)	C63—C62—C61B	121.7 (4)
C26—C25—C30	120.9 (4)	C67—C62—C61B	119.2 (4)
C27—C26—C25	121.6 (4)	C63—C62—C61	121.7 (4)
C27—C26—H26	119.2	C67—C62—C61	119.2 (4)
C25—C26—H26	119.2	C64—C63—C62	120.5 (4)
C26—C27—C22	119.8 (4)	C64—C63—H63	119.7
C26—C27—H27	120.1	C62—C63—H63	119.7
C22—C27—H27	120.1	C63—C64—C65	121.5 (4)
C33—C28—C29	111 (2)	C63—C64—H64	119.2
C33—C28—H28A	109.5	C65—C64—H64	119.2
C29—C28—H28A	109.5	C66—C65—C64	116.9 (4)
C33—C28—H28B	109.5	C66—C65—C70	121.1 (4)
C29—C28—H28B	109.5	C64—C65—C70	122.0 (4)
H28A—C28—H28B	108.1	C67—C66—C65	121.9 (4)
C30—C29—C28	114 (2)	C67—C66—H66	119.1
C30—C29—H29A	108.9	C65—C66—H66	119.1
C28—C29—H29A	108.9	C66—C67—C62	120.1 (4)
C30—C29—H29B	108.9	C66—C67—H67	119.9
C28—C29—H29B	108.9	C62—C67—H67	119.9
H29A—C29—H29B	107.7	C73—C68—C69	111.2 (4)
C31—C30—C29	121.3 (13)	C73—C68—H68A	109.4
C31—C30—C25	122.9 (9)	C69—C68—H68A	109.4
C29—C30—C25	115.7 (13)	C73—C68—H68B	109.4
C30—C31—C32	124.2 (16)	C69—C68—H68B	109.4
C30—C31—H31	117.9	H68A—C68—H68B	108.0
C32—C31—H31	117.9	C70—C69—C68	124.4 (4)
C31—C32—C33	111.8 (11)	C70—C69—H69	117.8
C31—C32—H32A	109.3	C68—C69—H69	117.8
C33—C32—H32A	109.3	C69—C70—C65	121.3 (4)
C31—C32—H32B	109.3	C69—C70—C71	120.8 (4)
C33—C32—H32B	109.3	C65—C70—C71	117.9 (4)

H32A—C32—H32B	107.9	C70—C71—C72	113.7 (4)
C28—C33—C34	113.9 (19)	C70—C71—H71A	108.8
C28—C33—C32	108.3 (14)	C72—C71—H71A	108.8
C34—C33—C32	111.5 (12)	C70—C71—H71B	108.8
C28—C33—H33	107.6	C72—C71—H71B	108.8
C34—C33—H33	107.6	H71A—C71—H71B	107.7
C32—C33—H33	107.6	C73—C72—C71	111.7 (4)
C36—C34—C35	122 (2)	C73—C72—H72A	109.3
C36—C34—C33	124 (3)	C71—C72—H72A	109.3
C35—C34—C33	115 (3)	C73—C72—H72B	109.3
C34—C35—H35A	109.5	C71—C72—H72B	109.3
C34—C35—H35B	109.5	H72A—C72—H72B	107.9
H35A—C35—H35B	109.5	C68—C73—C72	108.1 (4)
C34—C35—H35C	109.5	C68—C73—C74A	113.3 (4)
H35A—C35—H35C	109.5	C72—C73—C74A	112.8 (4)
H35B—C35—H35C	109.5	C68—C73—C74	113.3 (4)
C34—C36—H36A	120.0	C72—C73—C74	112.8 (4)
C34—C36—H36B	120.0	C68—C73—H73	107.5
H36A—C36—H36B	120.0	C72—C73—H73	107.5
C29A—C28A—C33A	115 (5)	C74—C73—H73	107.5
C29A—C28A—H28C	108.6	C68—C73—H73A	107.5
C33A—C28A—H28C	108.6	C72—C73—H73A	107.5
C29A—C28A—H28D	108.6	C74A—C73—H73A	107.5
C33A—C28A—H28D	108.6	C76—C74—C75	122 (2)
H28C—C28A—H28D	107.6	C76—C74—C73	123 (3)
C30A—C29A—C28A	126 (5)	C75—C74—C73	115 (2)
C30A—C29A—H29C	117.0	C74—C75—H75A	109.5
C28A—C29A—H29C	117.0	C74—C75—H75B	109.5
C29A—C30A—C31A	120 (3)	H75A—C75—H75B	109.5
C29A—C30A—C25	123 (3)	C74—C75—H75C	109.5
C31A—C30A—C25	116.1 (15)	H75A—C75—H75C	109.5
C30A—C31A—C32A	112 (2)	H75B—C75—H75C	109.5
C30A—C31A—H31A	109.2	C74—C76—H76A	120.0
C32A—C31A—H31A	109.2	C74—C76—H76B	120.0
C30A—C31A—H31B	109.2	H76A—C76—H76B	120.0
C32A—C31A—H31B	109.2	C75A—C74A—C76A	122 (3)
H31A—C31A—H31B	107.9	C75A—C74A—C73	119 (3)
C33A—C32A—C31A	115 (2)	C76A—C74A—C73	119 (2)
C33A—C32A—H32C	108.6	C74A—C75A—H75D	120.0
C31A—C32A—H32C	108.6	C74A—C75A—H75E	120.0

C33A—C32A—H32D	108.6	H75D—C75A—H75E	120.0
C31A—C32A—H32D	108.6	C74A—C76A—H76C	109.5
H32C—C32A—H32D	107.6	C74A—C76A—H76D	109.5
C32A—C33A—C34A	115 (3)	H76C—C76A—H76D	109.5
C32A—C33A—C28A	109 (3)	C74A—C76A—H76E	109.5
C34A—C33A—C28A	113 (3)	H76C—C76A—H76E	109.5
C32A—C33A—H33A	106.6	H76D—C76A—H76E	109.5
C34A—C33A—H33A	106.6		
F3A—C1A—C2—C3	179.7 (19)	C31A—C32A—C33A—C28A	56 (3)
F2A—C1A—C2—C3	-57 (2)	C29A—C28A—C33A—C32A	-37 (5)
F1A—C1A—C2—C3	56.9 (18)	C29A—C28A—C33A—C34A	-166 (5)
F3A—C1A—C2—C7	-1.9 (19)	C32A—C33A—C34A—C35A	-16 (7)
F2A—C1A—C2—C7	121 (2)	C28A—C33A—C34A—C35A	110 (7)
F1A—C1A—C2—C7	-124.7 (18)	C32A—C33A—C34A—C36A	173 (5)
F1B—C1B—C2—C3	-8.0 (10)	C28A—C33A—C34A—C36A	-62 (6)
F3B—C1B—C2—C3	120.3 (11)	F7A—C41A—C42—C43	91.5 (8)
F2B—C1B—C2—C3	-127.9 (7)	F9A—C41A—C42—C43	-137.1 (13)
F1B—C1B—C2—C7	170.3 (8)	F8A—C41A—C42—C43	-24.8 (7)
F3B—C1B—C2—C7	-61.4 (12)	F7A—C41A—C42—C47	-87.4 (8)
F2B—C1B—C2—C7	50.5 (8)	F9A—C41A—C42—C47	44.1 (14)
F2—C1—C2—C3	-95.5 (11)	F8A—C41A—C42—C47	156.3 (6)
F3—C1—C2—C3	138.7 (15)	F8B—C41B—C42—C43	14.5 (11)
F1—C1—C2—C3	25.7 (9)	F9B—C41B—C42—C43	-122 (2)
F2—C1—C2—C7	82.8 (11)	F7B—C41B—C42—C43	129.1 (7)
F3—C1—C2—C7	-43.0 (15)	F8B—C41B—C42—C47	-164.4 (9)
F1—C1—C2—C7	-156.0 (8)	F9B—C41B—C42—C47	59 (2)
C7—C2—C3—C4	0.9 (7)	F7B—C41B—C42—C47	-49.8 (7)
C1A—C2—C3—C4	179.3 (4)	F9—C41—C42—C43	177 (2)
C1B—C2—C3—C4	179.3 (4)	F8—C41—C42—C43	-58 (2)
C1—C2—C3—C4	179.3 (4)	F7—C41—C42—C43	56 (3)
C2—C3—C4—C5	-1.5 (7)	F9—C41—C42—C47	-2 (2)
C3—C4—C5—C6	1.3 (7)	F8—C41—C42—C47	123 (2)
C3—C4—C5—C10	-178.3 (4)	F7—C41—C42—C47	-122 (3)
C4—C5—C6—C7	-0.5 (6)	C47—C42—C43—C44	-1.0 (7)
C10—C5—C6—C7	179.0 (4)	C41A—C42—C43—C44	-179.9 (4)
C5—C6—C7—C2	0.0 (6)	C41B—C42—C43—C44	-179.9 (4)
C3—C2—C7—C6	-0.2 (6)	C41—C42—C43—C44	-179.9 (4)
C1A—C2—C7—C6	-178.5 (4)	C42—C43—C44—C45	0.7 (7)
C1B—C2—C7—C6	-178.5 (4)	C43—C44—C45—C46	0.0 (6)

C1—C2—C7—C6	-178.5 (4)	C43—C44—C45—C50	179.2 (4)
C13—C8—C9—C10	-36.5 (6)	C44—C45—C46—C47	-0.4 (6)
C8—C9—C10—C11	8.2 (7)	C50—C45—C46—C47	-179.5 (4)
C8—C9—C10—C5	-171.0 (4)	C43—C42—C47—C46	0.6 (7)
C6—C5—C10—C11	-156.2 (4)	C41A—C42—C47—C46	179.5 (4)
C4—C5—C10—C11	23.3 (7)	C41B—C42—C47—C46	179.5 (4)
C6—C5—C10—C9	23.0 (6)	C41—C42—C47—C46	179.5 (4)
C4—C5—C10—C9	-157.5 (4)	C45—C46—C47—C42	0.1 (6)
C9—C10—C11—C12	-0.4 (8)	C53—C48—C49—C50	13.8 (6)
C5—C10—C11—C12	178.8 (4)	C48—C49—C50—C45	-177.2 (4)
C10—C11—C12—C13	21.2 (7)	C48—C49—C50—C51	0.9 (7)
C11—C12—C13—C8	-47.7 (6)	C44—C45—C50—C49	162.5 (4)
C11—C12—C13—C14	-175.7 (4)	C46—C45—C50—C49	-18.4 (6)
C9—C8—C13—C12	56.0 (6)	C44—C45—C50—C51	-15.7 (6)
C9—C8—C13—C14	-173.5 (4)	C46—C45—C50—C51	163.4 (4)
C12—C13—C14—C15	16.5 (8)	C49—C50—C51—C52	16.3 (6)
C8—C13—C14—C15	-110.5 (6)	C45—C50—C51—C52	-165.4 (4)
C12—C13—C14—C16	-161.9 (5)	C50—C51—C52—C53	-48.5 (5)
C8—C13—C14—C16	71.1 (6)	C51—C52—C53—C54	-172.3 (4)
F4A—C21A—C22—C23	84.8 (8)	C51—C52—C53—C48	62.3 (5)
F6A—C21A—C22—C23	-144.1 (8)	C49—C48—C53—C54	-172.2 (4)
F5A—C21A—C22—C23	-34.1 (7)	C49—C48—C53—C52	-44.0 (5)
F4A—C21A—C22—C27	-95.3 (8)	C52—C53—C54—C55	-7.8 (7)
F6A—C21A—C22—C27	35.8 (10)	C48—C53—C54—C55	116.2 (5)
F5A—C21A—C22—C27	145.8 (7)	C52—C53—C54—C56	171.1 (4)
F6B—C21B—C22—C23	-89.8 (9)	C48—C53—C54—C56	-64.9 (5)
F4B—C21B—C22—C23	148.4 (8)	F10A—C61A—C62—C63	-116.3 (9)
F5B—C21B—C22—C23	35.5 (10)	F12A—C61A—C62—C63	18.9 (9)
F6B—C21B—C22—C27	90.1 (9)	F11A—C61A—C62—C63	126.9 (7)
F4B—C21B—C22—C27	-31.7 (9)	F10A—C61A—C62—C67	63.9 (9)
F5B—C21B—C22—C27	-144.6 (9)	F12A—C61A—C62—C67	-160.9 (7)
F5—C21—C22—C23	-7.3 (10)	F11A—C61A—C62—C67	-52.9 (8)
F6—C21—C22—C23	-123.8 (8)	F10B—C61B—C62—C63	-73.9 (9)
F4—C21—C22—C23	124.2 (8)	F11B—C61B—C62—C63	154.1 (9)
F5—C21—C22—C27	172.6 (9)	F12B—C61B—C62—C63	45.0 (9)
F6—C21—C22—C27	56.1 (9)	F10B—C61B—C62—C67	106.3 (8)
F4—C21—C22—C27	-55.9 (9)	F11B—C61B—C62—C67	-25.7 (10)
C27—C22—C23—C24	0.3 (7)	F12B—C61B—C62—C67	-134.8 (8)
C21A—C22—C23—C24	-179.8 (4)	F12—C61—C62—C63	93.0 (7)
C21B—C22—C23—C24	-179.8 (4)	F10—C61—C62—C63	-32.2 (8)

C21—C22—C23—C24	-179.8 (4)	F11—C61—C62—C63	-147.5 (6)
C22—C23—C24—C25	-0.2 (7)	F12—C61—C62—C67	-86.8 (7)
C23—C24—C25—C26	-0.4 (7)	F10—C61—C62—C67	148.1 (6)
C23—C24—C25—C30A	178.7 (4)	F11—C61—C62—C67	32.7 (7)
C23—C24—C25—C30	178.7 (4)	C67—C62—C63—C64	0.5 (7)
C24—C25—C26—C27	0.8 (7)	C61A—C62—C63—C64	-179.3 (4)
C30A—C25—C26—C27	-178.3 (4)	C61B—C62—C63—C64	-179.3 (4)
C30—C25—C26—C27	-178.3 (4)	C61—C62—C63—C64	-179.3 (4)
C25—C26—C27—C22	-0.7 (7)	C62—C63—C64—C65	0.3 (7)
C23—C22—C27—C26	0.1 (7)	C63—C64—C65—C66	-1.4 (6)
C21A—C22—C27—C26	-179.8 (4)	C63—C64—C65—C70	179.3 (4)
C21B—C22—C27—C26	-179.8 (4)	C64—C65—C66—C67	1.9 (7)
C21—C22—C27—C26	-179.8 (4)	C70—C65—C66—C67	-178.8 (4)
C33—C28—C29—C30	-42 (3)	C65—C66—C67—C62	-1.2 (7)
C28—C29—C30—C31	4 (3)	C63—C62—C67—C66	0.0 (7)
C28—C29—C30—C25	-170.7 (16)	C61A—C62—C67—C66	179.8 (4)
C24—C25—C30—C31	-13.1 (12)	C61B—C62—C67—C66	179.8 (4)
C26—C25—C30—C31	165.9 (11)	C61—C62—C67—C66	179.8 (4)
C24—C25—C30—C29	161.7 (15)	C73—C68—C69—C70	18.8 (7)
C26—C25—C30—C29	-19.3 (16)	C68—C69—C70—C65	-175.5 (4)
C29—C30—C31—C32	10 (3)	C68—C69—C70—C71	5.6 (8)
C25—C30—C31—C32	-175.1 (10)	C66—C65—C70—C69	17.2 (7)
C30—C31—C32—C33	12 (2)	C64—C65—C70—C69	-163.6 (5)
C29—C28—C33—C34	-172.4 (19)	C66—C65—C70—C71	-163.9 (5)
C29—C28—C33—C32	63 (2)	C64—C65—C70—C71	15.3 (6)
C31—C32—C33—C28	-48.4 (17)	C69—C70—C71—C72	4.7 (7)
C31—C32—C33—C34	-174.4 (18)	C65—C70—C71—C72	-174.2 (4)
C28—C33—C34—C36	-22 (4)	C70—C71—C72—C73	-39.2 (6)
C32—C33—C34—C36	101 (3)	C69—C68—C73—C72	-51.3 (6)
C28—C33—C34—C35	162 (3)	C69—C68—C73—C74A	-177.1 (4)
C32—C33—C34—C35	-75 (3)	C69—C68—C73—C74	-177.1 (4)
C33A—C28A—C29A—C30A	7 (8)	C71—C72—C73—C68	62.8 (6)
C28A—C29A—C30A—C31A	6 (7)	C71—C72—C73—C74A	-171.2 (4)
C28A—C29A—C30A—C25	177 (4)	C71—C72—C73—C74	-171.2 (4)
C24—C25—C30A—C29A	161 (3)	C68—C73—C74—C76	33 (3)
C26—C25—C30A—C29A	-20 (3)	C72—C73—C74—C76	-91 (3)
C24—C25—C30A—C31A	-27 (2)	C68—C73—C74—C75	-143 (3)
C26—C25—C30A—C31A	152 (2)	C72—C73—C74—C75	93 (3)
C29A—C30A—C31A—C32A	12 (5)	C68—C73—C74A—C75A	-146 (3)
C25—C30A—C31A—C32A	-159.8 (18)	C72—C73—C74A—C75A	91 (3)

C30A—C31A—C32A—C33A	-45 (3)	C68—C73—C74A—C76A	44 (2)
C31A—C32A—C33A—C34A	-176 (3)	C72—C73—C74A—C76A	-80 (2)

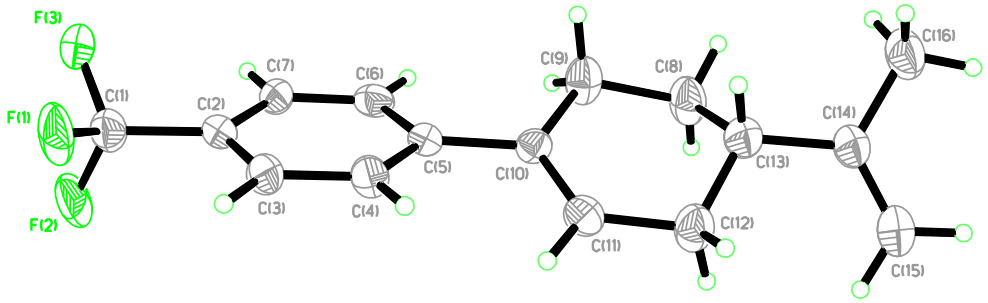


Figure S28. Perspective views showing 50% probability displacement

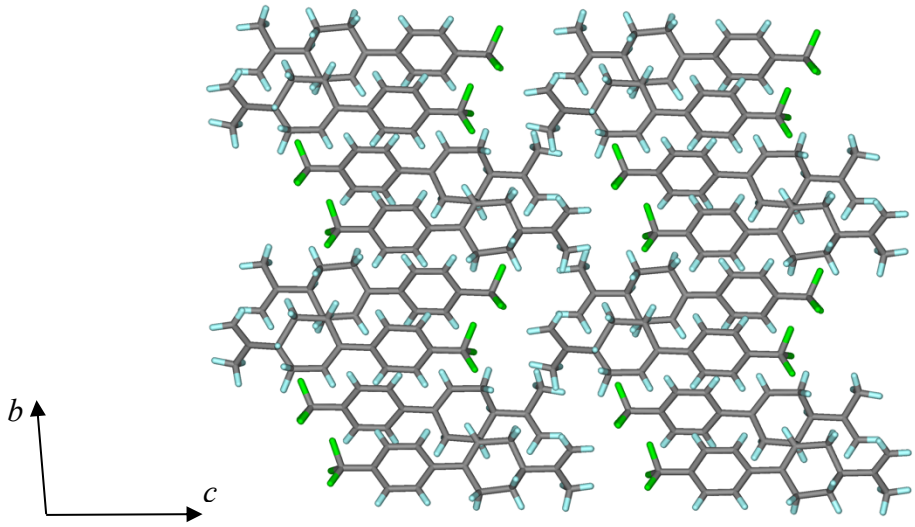


Figure S29. Three-dimensional supramolecular architecture viewed along the *a*-axis direction.

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