Supporting Information

Branch-Selective Addition of Unactivated Olefins into Imines and Aldehydes

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A. Materials and methods

All reactions were carried out under positive pressure of argon in a fume hood unless otherwise noted. Hexanes (ACS grade), ethyl acetate (ACS grade), diethyl ether (anhydrous ACS grade), dichloromethane (ACS grade), acetonitrile (ACS grade), chloroform (ACS grade), and isopropanol (ACS grade) were purchased from Fisher Chemical and used without further purification. Anhydrous tetrahydrofuran, dimethoxyethane, and acetonitrile were purchased from Sigma-Aldrich. Anhydrous ethanol was obtained from Pharmco-Aaper. $Fe(acac)_3$ was purchased from Sigma Aldrich at 99.9% purity. $CrCl_3$-anhydrous was purchased from Strem at 99% purity. Commercially available substrates were purchased from Sigma, Aldrich, Fluka, Oakwood, TCI Chemicals, Alfa Aesar, Fischer, Matrix Scientific, Combi-Blocks, ArK Pharm, Astatech and used without further purification unless otherwise noted. $PhSiH_2(O\textit{i}\text{-Pr})$[i] and $Co(Sal^{t\text{-Bu},t\text{-Bu}})$[ii] were prepared following previously reported procedures.

The reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates from EMD Chemicals (TLC Silica gel 60 F254); by GC/MS analysis performed on Agilent 7820A/5975 GC/MSD system with helium as the carrier gas; or by LC/MS on an Agilent 6120 Quadrupole system with an ESI probe. Flash column chromatography was performed over Silica gel 60 (particle size 0.04-0.063 mm) from Fischer Scientific. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker DPX-400, a Bruker DPX-500 or Bruker DPX-600 equipped with cryoprobe, and the residual solvent peaks were used as internal standard ($CDCl_3$ @ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; C_6D_6 @ 7.16 ppm ^{1}H NMR, 128.06 ppm ^{13}C NMR). NMR data is denoted with apparent multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, and combinations thereof.

B. Note on the toxicity of Cr^{+n} salts

Even though Cr^{+2} and Cr^{+3} are considered to be less toxic than Cr^{+6} (Oral-rat LD_{50} = 1870 mg/kg and > 2700 mg/kg respectively vs. 50−150 mg/kg for Cr^{+6}. See ref. 37 in the manuscript), trace oxidation of Cr^{+3} to Cr^{+6} can occur in the presence of air and elevated temperatures or in the presence of air and acidic conditions.[iii] We observe no oxidation of the alcohols to the ketone, and the benzaldehydes are almost always reduced by the end of the reaction (presence of Cr^{+6} would suggest that it should be oxidized). Nevertheless, all of the reaction procedure, including work up and purification, should be performed in a well-ventilated fume hood, and waste disposal should always be done in a separated labelled container.

C. Abbreviations

DMAP: 4-Dimethylaminopyridine
EDC: *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride
FCC: flash column chromatography
GC: gas chromatography
IY: isolated yield
LC: liquid chromatography
MS: mass spectrometry
Pyr-F(BF_4): 1-Fluoro-2,4,6-trimethylpyridinium tetrafluoroborate
Salen: 6,6'-(Cyclohexane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis(2,4-di-*tert*-butylphenol)

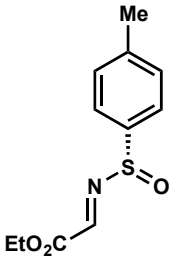
D. Synthesis of Starting Materials

The tolyl- and mesityl-derived imines were synthesized following a known procedure[iv] from commercially available starting materials.

Note: Commercial bottles of (*S*)–4-methylbenzenesulfinamide decompose over time into sulfinic acid (as determined by ^{1}H NMR in MeOD-d4 and LC/MS mass). The presence of the sulfinic acid is detrimental to the

synthesis of the imine and purification is necessary. We found that running a small SiO_2 plug of the starting material using $CHCl_3$ as the eluent was enough to remove the sulfinic acid, which is not soluble in chloroform. Although the same decomposition could be possible with the mesityl-derived sulfinamide, we did not encounter it. However, if synthesis of this imine is found to be problematic, sulfinic acid formation should be considered.

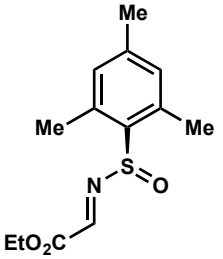
Similarly, in our experience it is best to depolymerize ethyl glyoxylate prior to condensation with the sulfinimine by heating it at 50 ºC for 5 minutes.



ethyl (*S*)-2-((*p*-tolylsulfinyl)imino)acetate
Synthesized according to the reported procedure.[iv] Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) delivered the desired imine as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (t, *J* = 1.1 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 1H), 2.39 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 2H).

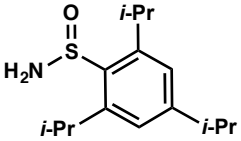
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.40, 153.23, 142.70, 139.33, 130.26, 124.87, 62.75, 21.61, 14.17.



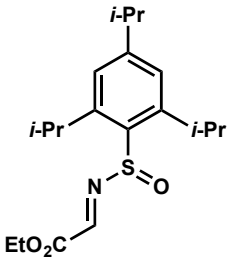
ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate
Synthesized according to the reported procedure.[iv] Purification by flash column chromatography (SiO_2, 100% dichloromethane) delivered the desired imine as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (s, 1H), 6.86 (s, 2H), 4.37 (qq, *J* = 7.0, 3.8 Hz, 2H), 2.45 (s, 6H), 2.28 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.54, 154.05, 142.64, 138.93, 133.16, 131.19, 62.76, 21.25, 19.00, 14.20.



2,4,6-triisopropylbenzenesulfinamide
The title compound was prepared according to a reported procedure[v] and the spectroscopy data matched those ones reported.

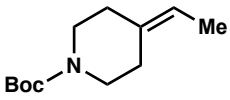


ethyl 2-(((2,4,6-triisopropylphenyl)sulfinyl)imino)acetate

The title compound was synthesized by stirring ethyl glyoxylate (2.24 mmol, 0.5 mL of a 50% solution in PhMe), the sulfinamide (600 mg, 2.24 mmol), and 4Å molecular sieves (3 g, 1.3g/mmol) in DCM (10 mL, 0.2 M) at room temperature until completion by TLC. The mixture was then filtered through Celite washing with DCM, and evaporated under reduced pressure. The crude was purified by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) which delivered 490 mg (62%) of the compound as a clear, viscous oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.07 (s, 2H), 4.38 (qd, J = 7.2, 1.2 Hz, 2H), 3.66 (hept, J = 6.8 Hz, 2H), 2.88 (hept, J = 6.9 Hz, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.26 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 7.0 Hz, 6H), 1.20 (d, J = 6.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.59, 154.09, 153.81, 150.19, 132.65, 123.42, 62.67, 34.59, 28.29, 24.36, 24.05, 23.87, 23.85, 14.22.



***tert*-butyl 4-ethylidenepiperidine-1-carboxylate**

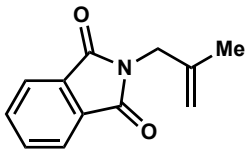
The title compound was synthesized following a modified procedure.[vi]

To a solution of ethyltriphenylphosphonium bromide (2.4 g, 6.5 mmol) in THF (20 mL) at -78 °C was added *n*-BuLi dropwise (3.1 mL, 6.5 mmol) over 5 minutes, then the mixture was warmed to room temperature and stirred for 30 minutes. The reaction mixture was cooled back to -78 °C and a 1 M solution of the ketone (1 gram, 5 mL in THF) was added dropwise over 5 minutes. After 20 minutes, the solution was warmed to room temperature and stirred for 18 hours. The reaction mixture was filtered through Celite and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/Et_2O) delivered 683 mg of the desired compound (65%) as a clear oil.

R_f: 0.66 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.27 (qt, J = 6.7, 1.3 Hz, 1H), 3.38 (t, J = 5.9 Hz, 4H), 2.16 (dt, J = 47.2, 6.0 Hz, 4H), 1.59 (dt, J = 6.7, 1.0 Hz, 3H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.01, 135.63, 118.02, 79.52, 35.94, 28.62, 28.00, 12.77.



2-(2-methylallyl)isoindoline-1,3-dione

The title compound was synthesized following a known procedure,[vii] and the data matched those ones reported.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.73 (dd, *J* = 5.5, 3.0 Hz, 2H), 4.89 (p, *J* = 1.4 Hz, 1H), 4.82 (p, *J* = 1.2 Hz, 1H), 4.22 (s, 2H), 1.78 (d, *J* = 0.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.23, 134.15, 132.19, 123.50, 123.50, 112.13, 43.41, 20.54.

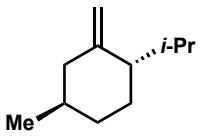
***tert*-butyl 3-methyleneazetidine-1-carboxylate**

To a suspension of methyltriphenylphosphonium bromide in diethyl ether (1.4 g, 3.9 mmol), potassium *tert*-butoxide (3.9 mL, 1 M in THF, 3.9 mmol) was added dropwise, and the mixture was left stirring for 30 minutes at room temperature. Then, 1-Boc-3-azetidinone (513 mg, 3 mmol) was added dropwise as a 1 M solution in Et_2O. The reaction was left stirring for 16 hours, then quenched by addition of H_2O and extracted with diethyl ether (3X), dried over Na_2SO_4 and rotoevaporated. Purification by FCC (hexanes then 9:1 hexanes:Et_2O) furnished the desired compound (411 mg, 80%) as a colorless oil.

R_f: 0.56 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.98 (p, *J* = 2.4 Hz, 2H), 4.47 (t, *J* = 2.5 Hz, 4H), 1.45 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.55, 137.92, 107.32, 79.76, 58.45 (broad singlet), 28.52.



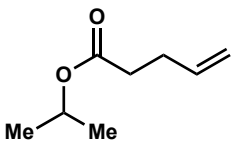
(1*S*,4*R*)-1-isopropyl-4-methyl-2-methylenecyclohexane

To a suspension of methyltriphenylphosphonium bromide in 20 mL of diethyl ether (3g, 8.45 mmol), potassium tert-butoxide (8.45 mL, 1 M in THF, 8.45 mmol) was added dropwise, and the mixture was left stirring for 30 minutes at room temperature. Then, (−)-menthone (1g, 6.5 mmol) was added dropwise as a 1 M solution in Et_2O. The reaction was left stirring until consumption of the starting material by TLC, then quenched by addition of H_2O and extracted with diethyl ether (3X), dried over Na_2SO_4 and rotoevaporated. Purification by FCC (hexanes) furnished the desired compound (550 mg, 56%) as a colorless oil.

R_f: 0.86 (hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.70 (d, *J* = 1.2 Hz, 1H), 4.58 (bs, 1H), 2.28 (dd, *J* = 12.4, 3.8 Hz, 1H), 2.02 – 1.92 (m, *J* = 6.7 Hz, 1H), 1.77 (qdd, *J* = 8.6, 3.6, 2.4 Hz, 1H), 1.69 – 1.63 (m, 1H), 1.63 – 1.49 (m, 1H), 1.34 – 1.22 (m, 2H), 1.21 – 1.12 (m, 1H), 1.12 – 1.01 (m, 1H), 0.94 – 0.86 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.34, 106.25, 49.53, 44.57, 34.16, 33.54, 27.53, 27.23, 22.26, 21.54, 19.15.



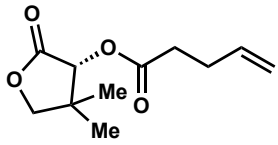
isopropyl pent-4-enoate

Synthesized from a modified procedure.[viii]

In a round-bottom flask , 4-pentenoic acid (401 μL, 4 mmol), isopropanol (337 μL, 4.4 mmol), EDC (843 mg, 4.4 mmol), and DMAP (525 mg, 4.3 mmol) were mixed together and stirred at room temperatures for 2 hours. To quench, the reaction was diluted with DCM, washed with H_2O (1X), sat. $NaHCO_3$ (2X), 1N HCl (2X), and brine (1X). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to afford the desired ester as a clear oil (357 mg, 63%). The product was used without further purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.87 – 5.78 (m, 1H), 5.08 – 4.97 (m, 3H), 2.49 – 2.28 (m, 4H), 1.23 (d, J = 6.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.76, 136.93, 115.52, 67.73, 34.05, 29.12, 22.00.

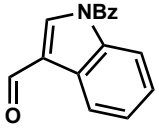


(*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl pent-4-enoate

In a flame-dried round-bottom flask equipped with a Teflon-coated stir bar, 4-pentenoic acid (0.362 mL, 3.5 mmol, 1 equiv.), (*R*)-(−)-pantolactone (500 mg, 3.8 mmol, 1.07 equiv.), DMAP (476 mg, 3.9 mmol, 1.1 equiv.), EDC (762 mg, 3.9 mmol, 1.1 equiv.) were mixed in DCM (5 mL, 0.7 M) at room temperature for two hours. The reaction was quenched by diluting with DCM (15 mL), washing with H_2O (10 mL), sat. aq. $NaHCO_3$ (2X 10 mL), 1 M HCl (2X 10 mL), and brine (10 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The crude was purified by flash column chromatography (SiO_2, 9:1 then 4:1 hexanes/EtOAc) delivered 650 mg (88%) of the title compound as a clear oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.84 (ddt, J = 16.7, 10.2, 6.4 Hz, 1H), 5.38 (s, 1H), 5.09 (dq, J = 17.1, 1.6 Hz, 1H), 5.04 (dq, J = 10.3, 1.4 Hz, 1H), 4.08 – 3.99 (m, 2H), 2.67 – 2.50 (m, 2H), 2.46 – 2.39 (m, 2H), 1.20 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.51, 172.00, 136.29, 116.08, 76.32, 75.09, 40.34, 33.30, 28.86, 23.18, 20.08.

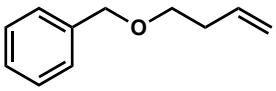


1-benzoyl-1*H*-indole-3-carbaldehyde

The title compound was synthesized following a known procedure[ix] and the data matched those ones reported.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.38 – 8.27 (m, 2H), 7.95 (s, 1H), 7.81 – 7.74 (m, 2H), 7.74 – 7.66 (m, 1H), 7.60 (dd, J = 8.5, 7.1 Hz, 2H), 7.53 – 7.39 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 185.79, 168.66, 137.67, 137.01, 133.21, 133.14, 129.60, 129.17, 126.75, 126.45, 125.74, 122.38, 122.21, 116.25.

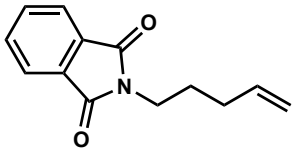


((but-3-en-1-yloxy)methyl)benzene

To a suspension of NaH (290 mg, 7.3 mmol) in THF (20 mL) at 0 °C was added 3-buten-1-ol (480 μL, 5.6 mmol) as a solution in THF (5 mL). After 1 hour, benzyl bromide was added (862 μL, 7.3 mmol) and the reaction was left stirring overnight. The reaction was quenched by addition sat. NH_4Cl, extracted with EtOAc, dried over $MgSO_4$, and evaporated. The product was purified by flash column chromatography (SiO_2, 9:1 hexanes/Et_2O) to yield 630 mg of the desired compound (69%) as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.5 Hz, 4H), 7.29 (ddd, *J* = 8.8, 5.1, 3.8 Hz, 1H), 5.86 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.12 (dq, *J* = 17.1, 1.7 Hz, 1H), 5.06 (ddt, *J* = 10.3, 2.3, 1.2 Hz, 1H), 4.53 (s, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.39 (qt, *J* = 6.8, 1.4 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.61, 135.41, 128.50, 127.79, 127.68, 116.50, 73.04, 69.75, 34.38.

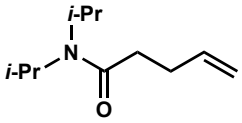


2-(pent-4-en-1-yl)isoindoline-1,3-dione

The title compound was synthesized according to a known procedure and the data matched those ones reported.[x]

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.72 – 7.67 (m, 2H), 5.81 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.04 (dq, *J* = 17.2, 1.7 Hz, 1H), 4.97 (dq, *J* = 10.2, 1.4 Hz, 1H), 3.71 – 3.67 (m, 2H), 2.16 – 2.06 (m, 2H), 1.78 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.53, 137.44, 133.99, 132.29, 123.30, 115.42, 37.69, 31.11, 27.76.



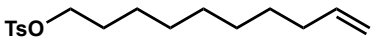
***N*,*N*-diisopropylpent-4-enamide**

In a flame-dried round-bottom flask equipped with a Teflon-coated stir bar, 4-pentenoic acid (0.350 mL, 3.5 mmol), diisopropylamine (0.525 mL, 3.75 mmol), DMAP (435 mg, 3.6 mmol), EDC (750 mg, 3.9 mmol) were mixed in DCM (5 mL, 0.7 M) at room temperature for two hours. The reaction was quenched by diluting with DCM (15 mL), washing with H_2O (10 mL), sat. aq. $NaHCO_3$ (2X 10 mL), 1 M HCl (2X 10 mL), and brine (10 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, 4:1 hexanes/EtOAc) delivered 455 mg of the title compound (71%) as a clear oil.

Spectra matched those ones reported previously.[xi]

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.92 – 5.83 (m, 1H), 5.08 – 5.02 (m, 1H), 5.00 – 4.96 (m, 1H), 3.97 (p, *J* = 7.1, 6.0 Hz, 1H), 3.66 – 3.32 (m, 1H), 2.37 (d, *J* = 2.6 Hz, 4H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.20 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.20, 138.08, 115.03, 48.38, 45.74, 34.64, 29.63, 21.19, 20.86.

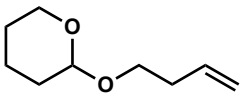


dec-9-en-1-yl 4-methylbenzenesulfonate

To a solution of 9-decen-1-ol (892 μL, 5 mmol) in DCM (18 mL, 0.3 M) at 0 °C was added triethylamine (1.2 mL, 8 mmol), 4-dimethylaminopyridine (61 mg, 0.5 mmol), and tosyl chloride (1.14 g, 6 mmol). The reaction was brought to room temperature and left stirring for 1 hour. Then it was quenched by the slow addition of aqueous NH_4Cl, extracted with EtOAc, dried over $MgSO_4$, and rotoevaporated. Purification by flash column chromatography (SiO_2, 9:1 hexanes/Et_2O) delivered 770 mg of the title compound (50%) as a white solid.

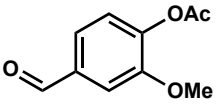
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 – 7.77 (m, 2H), 7.37 – 7.31 (m, 2H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.4, 1.2 Hz, 1H), 4.02 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 2.07 – 1.98 (m, 2H), 1.67 – 1.58 (m, 2H), 1.55 (s, 2H), 1.41 – 1.17 (m, 10H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.75, 139.25, 133.42, 129.94, 128.04, 114.35, 70.82, 33.89, 29.35, 29.08, 29.01, 28.98, 28.95, 25.45, 21.78.



2-(but-3-en-1-yloxy)tetrahydro-2*H*-pyran

The title compound was synthesized according to a known procedure[xii] and the data matched those ones reported.



4-formyl-2-methoxyphenyl acetate

The title compound was synthesized according to a known procedure[xiii] and the data matched those ones reported.

E. Optimization of the Imine Coupling

Initially we explored the use of Ellman's *tert*-butyl sulfinamide given its reported use in the synthesis of chiral amines by trapping of alkyl radicals generated from alkyl halides.[xiv] However, these sulfinimides led to poor yields and side products that were consistent with extrusion of a *tert*-butyl radical via formation of an iminosulfanone (radical migration has also been observed before[xv]). Although the yield of the desired coupled product could be improved by increasing the metal loading (Figure S1), we decided to explore aryl-sulfinyl derivatives similar to Davis' tolyl sulfinamide as we imagined that formation of an sp^2 radical should be unfavorable.

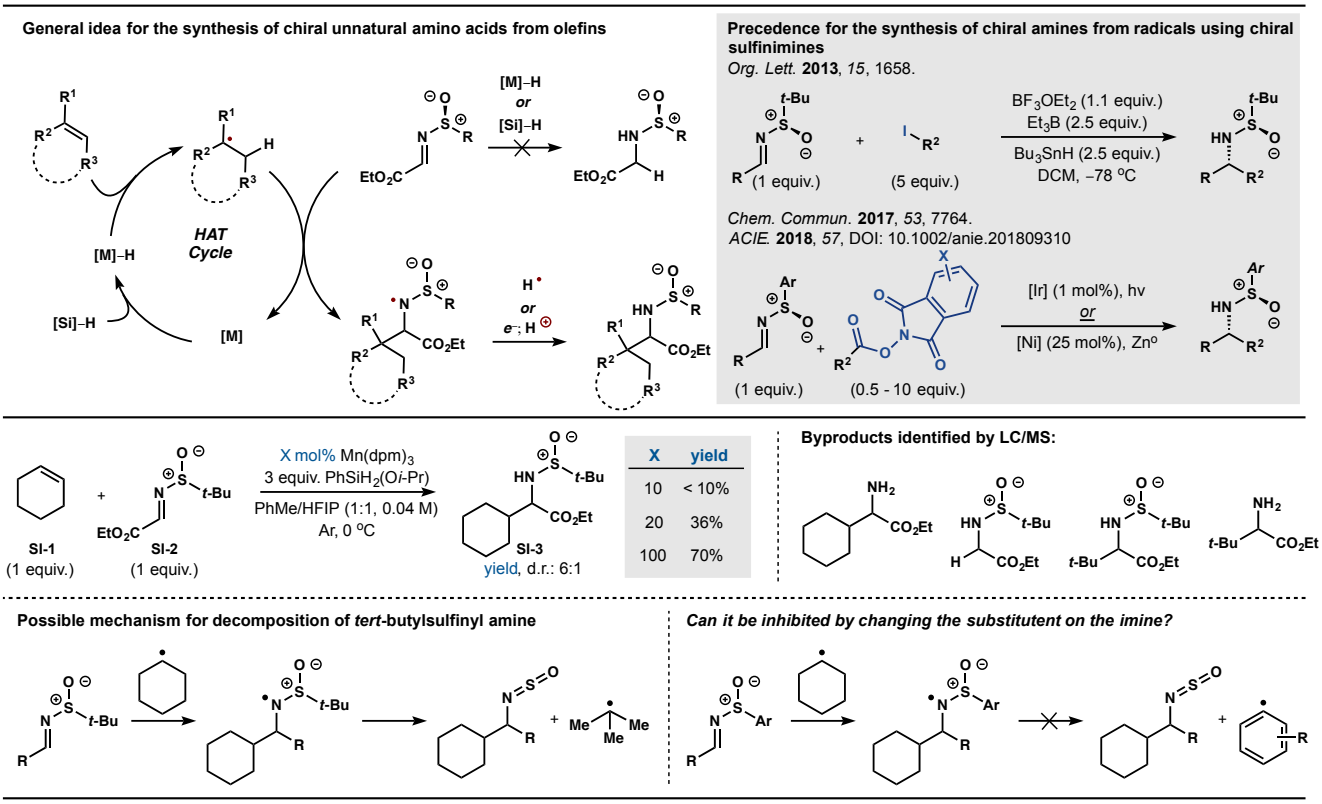
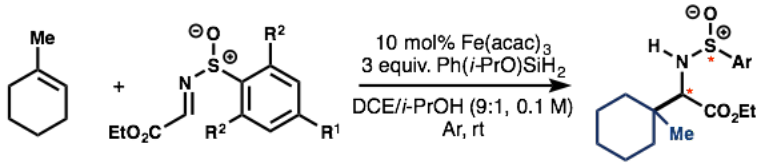


Figure S1: Combining MHAT with a chiral imine.

Exploration of different MHAT complexes suggested [Fe] and [Mn] β-diketonates pre-catalyst afforded the best yields, with $Fe(acac)_3$ behaving better than manganese because of decreased amount of imine reduction (note that the yield with [Mn] could be increased by using an excess of the olefin and TBHP as an additive (Table S1, Entry 17). The diastereoselectivity could be improved by use of more hindered imine with the more hindered triisopropyl phenyl and mesitylene imine affording d.r.'s higher than 20:1, but changing the ligand sphere of the metal, the temperature of the reaction, or the silane used did not have a major improvement (cryogenic temperatures were not compatible with this variation of HAT). Although the use of 10% of iron is not prohibitively expensive, only 5% could be used without a major decrease in yield. Informative variations are given below:



Entry	Conditions	R^1 (R^2)	Yield (amine)[a]	d.r.[a]
1	Same	Me (H)	**77%**[b]	**5:1**
2	Same	Me (Me)	**56%** [b]	**> 20:1**
3	no *i*-PrOH	Me (H)	**55%**	**5:1**
4	EtOH instead of *i*-PrOH	Me (H)	**74%**	**5:1**
5	MeOH instead of *i*-PrOH	Me (H)	**61%**	**5:1**
6	*t*-BuOH instead of *i*-PrOH	Me (H)	**42%**	**5:1**
7	DCM instead of DCE	Me (H)	**61%**	**7:1**
8	EtOAc instead of DCE	Me (H)	**62%**	**6:1**
9	Hexanes instead of DCE	Me (H)	**60%**	**5:1**
10	PhMe instead of DCE	Me (H)	**53%**	**6:1**
11	PhH instead of DCE	Me (H)	**56%**	**6:1**
12	$PhCF_3$ instead of DCE	Me (H)	**63%**	**6:1**
13	HFIP instead of DCE	Me (H)	**44%**	**4:1**
14	THF instead of DCE	Me (H)	**52%**	**6:1**
15	Only *i*-PrOH	Me (H)	**63%**	**5:1**
16	$Mn(dpm)_3$ instead of $Fe(acac)_3$	*i*-Pr (*i*-Pr)	**35%**	**> 20:1**
17	$Mn(dpm)_3$ (0.2 equiv.) instead of $Fe(acac)_3$ and 5 equiv. of olefin[c]	*i*-Pr (*i*-Pr)	**73%**	**> 20:1**
18	$Co(acac)_2$, $Co(dpm)_2$, Co(salen)Cl, or $Co(acac)_3$ instead of $Fe(acac)_3$	Me (H)	**traces**	**ND**
19	$Fe(dpm)_3$ instead of $Fe(acac)_3$	Me (H)	**72%**	**5:1**
20	$PhSiH_3$ instead of $Ph(i\text{-}PrO)SiH_2$	Me (H)	**27%**	**5:1**
21	0 °C instead of rt	Me (H)	**52%**	**5:1**
22	$Fe(acac)_3$ (5 mol%)	Me (H)	**69%**	**5:1**

a) Yield and diastereocontrol determined by ^{1}H-NMR of the crude mixture using trimethoxybenzene as the internal standard. b) Isolated yield. c) Using PhMe as the solvent and 1 equiv. of TBHP as an additive.

F. Determination of Stereochemistry

Imines containing chiral sulfinyl auxiliaries are known to be engaged by nucleophiles both in closed and in opened transition states; normally open transition states tend to transfer the absolute stereochemistry of the sulfinimine to the amine (i.e. (*R*)–sulfinimine to (*R*)–amine) whereas closed transition states tend to afford the opposite one ((*R*)–sulfinimine to (*S*)–amine).[xvi] To determine which stereochemistry was being productive in our case, we performed the reaction using isobutene as the olefin to build *tert*-butyl glycine derivatives **3** and **4**. These substrates could then be transformed into either the tosyl-derivative (**SI-9**) or the free amine (**SI-10**) and be compared to those same substrates derived from a commercially available enantiopure sample of *tert*-butyl glycine. It was determined that **SI-9** had an optical rotation of +38.37 (Figure S2, B). When we compared it **SI-9** derived from our reaction using the tolyl-derived sulfinimine **SI-4**, we found that the optical rotation of this sample also had a positive sign (+24.4), suggesting that it also had an (*S*)–configuration. Since we started with the (*S*)–sulfinimine, it appears as if the chirality is transferred to the amine. Using a similar approach, we

determined that the reaction with the (*R*)–enantiomer of the mesitylene imine-derivative gave the (*R*)–product. By analogy, we determined the stereochemistry of the rest of the substrates to be either (*R*) at the amine carbon for the substrates that reacted with the (*R*)–mesitylene imine **SI-5**, or (*S*) for those ones that reacted with the (*S*)–tolyl imine **SI-4**.

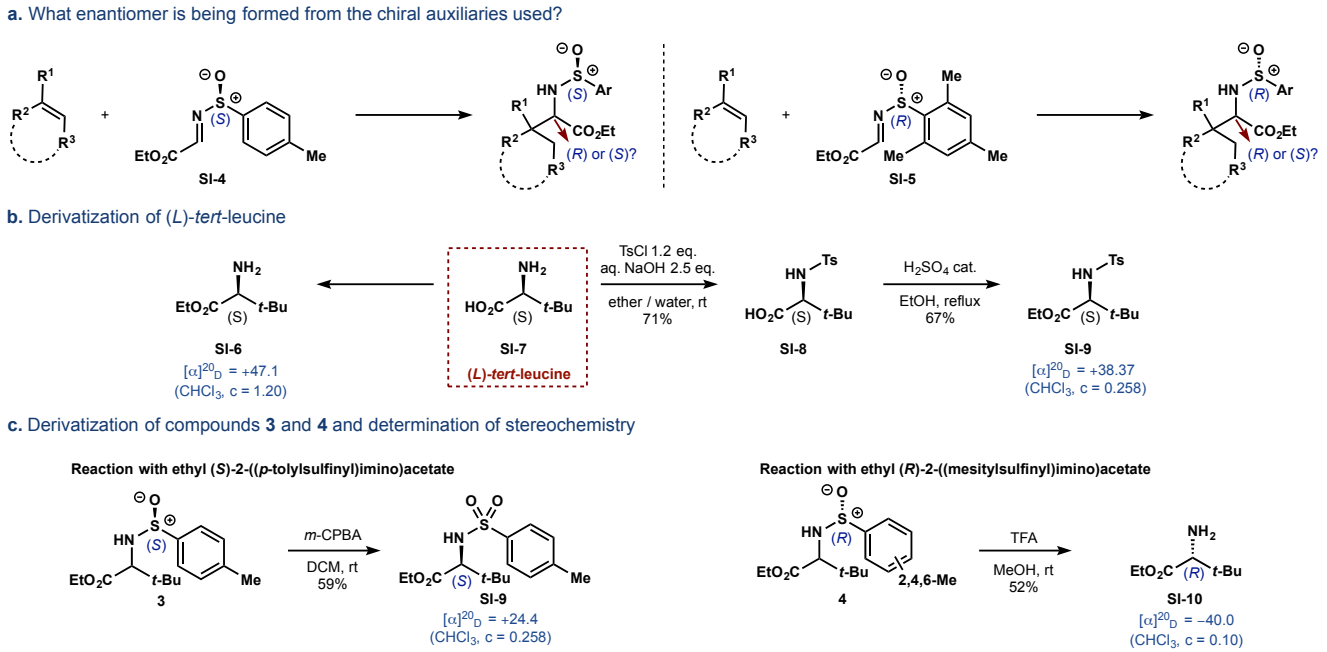


Figure S2: Determination of the stereochemistry imparted by the chiral auxiliary.

G. General procedures

I. **(Imine-Olefin coupling)** To a flame-dried reaction vial equipped with a Teflon-coated stir bar was added the imine (1 equiv.), $Fe(acac)_3$ (0.1 equiv.), and the olefin (1.2–2 equiv.) if this one was a solid. The solids were purged with argon for 15 minutes. Then, dichloroethane (0.1 M) and *i*-PrOH or EtOH (10 equiv.) were added, followed by the olefin if it was not added at the beginning. The reaction was stirred until dissolution of the solids, at which time $PhSiH_2(Oi\text{-}Pr)$ (3 equiv.) was added in one portion. The reaction was monitored by TLC or LCMS and upon consumption of the imine (1–16 hours), it was quenched by addition of 1 volume of isopropanol followed by aqueous saturated EDTA. The reaction was stirred until the orange color disappeared and a white slurry was formed. This slurry was extracted with EtOAc (3X), the organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The semi-crude mixture was analyzed by NMR to determine diastereoselectivity and purified by flash column chromatography.

Notes and Troubleshooting (Part 1):

1) To increase the yield the best approach seems to be increasing the equivalents of olefin used. Increasing the amount of the imine is detrimental (it appears to coordinate to the catalyst) and increasing the amount of catalyst increases reduction of the imine to the amine.
2) Although DCE was used as the solvent for exploration of the scope, other solvents are also competent (See **Table S1** for more information).
3) Purifying the imine before using it is good for consistent high yields.
4) We observed racemization of some substrates if they were sitting at room temperature for extended periods of time (Substrate **6**, for instance, racemized to an almost 1:1 mixture of diastereomers over the course of one week at room temperature). This process did not seem to occur if it was stored at –20 °C.

This racemization is something that should be kept in mind when storing the unnatural amino acids derivatives.

II. **(Aldehyde-Olefin coupling - $CrCl_3$ anhydrous, terminal olefins)** To a flame-dried vial equipped with a Teflon-coated stir bar Co(salen) (0.1 equiv.), 1-fluoro-2,4,6-trimethyl pyridinium tetrafluoroborate (0.1 equiv.), $CrCl_3$ (1 equiv.), were added (the olefin, 1 equiv., was also added at this point if it was a solid). The solids were vented with an argon balloon and an open needle for 15 minutes. Then, THF (0.2 M) and CH_3CN (1 M) were added, followed by the olefin if it was not added at the beginning (1 equiv.), $PhSiH_3$ (2 equiv.), and the aldehyde (1 – 2 equiv.) (Note: the reactions were placed in a water bath prior addition of the silane since this step is exothermic and doing so seemed to help in obtaining consistent yields). The reaction was stirred at a speed of at least 900 rpm for 24 h taking care of bringing the [Cr] back into the solvent if this one was accumulating at the sides of the vial. The reaction was quenched by addition of 1 volume 10% citric acid, followed by 1 volume 10% Na_2SO_4/ 5% $NaHCO_3$, extracted with EtOAc (3X), dried with Na_2SO_4 or $MgSO_4$, evaporated under reduced pressure, and purified by flash column chromatography.

III. **(Aldehyde-Olefin coupling - $CrCl_3$ anhydrous, internal olefins)** To a flame-dried vial equipped with a Teflon-coated stir bar was added Co(salen) (0.1 equiv.), 1-fluoro-2,4,6-trimethyl pyridinium tetrafluoroborate (0.1 equiv.), $CrCl_3$ (1 equiv.) and the olefin if it was a solid (1 equiv.). The solids were vented with an argon balloon and an open needle for 15 minutes. Then, DME (0.2 M) was added, followed by the olefin if that was not added at the beginning (1 equiv.). The reaction was placed in a water bath and $PhSiH_3$ (2 equiv.) was added, followed by the aldehyde (2 equiv.). The reaction was stirred at a speed of at least 900 rpm for 48 h taking care of bringing the Cr back into the solvent if this one was accumulating at the sides of the vial. The reaction was quenched by addition of 1 volume 10% citric acid, followed by 1 volume 10% Na_2SO_4/ 5% $NaHCO_3$, extracted with EtOAc (3X), dried with Na_2SO_4 or $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography.

IV. **(Aldehyde-Olefin coupling - $CrCl_3(THF)_3$, terminal olefins)** To a flame-dried reaction vial equipped with a Teflon-coated stir bar was added Co(salen) (0.2 equiv.) and 1-fluoro-2,4,6-trimethyl pyridinium tetrafluoroborate (0.2 equiv.). The solids were vented with an argon balloon and an open needle for 15 minutes. In the meantime, $CrCl_3(THF)_3$ was weighted out under in inert atmosphere using an oven-dried vial. It was dissolved in CH_3CN to obtain a 1 M solution by sonication (*only a little of sonication is required: too much sonication will turn the solution into a paste*). After degassing, THF (2 M) was added into the vial with Co(salen) and oxidant, followed by the olefin (2 equiv.), the silane (2 equiv.), and the aldehyde (2 equiv.) (Note: the reactions were placed in a water bath prior addition of the silane). 1 equiv. of the 1 M solution of [Cr] was added last. The reaction was stirred for 24 h, before being quenched by addition of 1 volume 10% citric acid, followed by 1 volume 10% Na_2SO_4/ 5% $NaHCO_3$, extracted with EtOAc (3X), dried with Na_2SO_4 or $MgSO_4$, concentrated under reduced pressure, and purified by flash column chromatography.

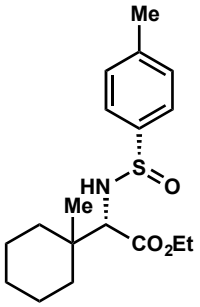
Notes and Troubleshooting (Part 2):

5) For the General Procedure **II** and **III**, the $CrCl_3$ does not dissolve in the reaction mixture at the beginning but dissolves over time. Consequently, although the reactions are heterogenous at the beginning, they are homogeneous towards the end (when using THF as the solvent the reactions have minimal viscosity, but with DME the reactions tend to form a more viscous liquid). Given the heterogeneous nature and the rapid stirring required, the [Cr] can start accumulating on the walls of the vials. It is important to make sure to bring this accumulated [Cr] back into solution in order to get good yields. We normally did it just by tilting the vial and washing the [Cr] down with the reaction mixture.
6) Rapid stirring is necessary for the heterogenous reactions in order to help the [Cr] dissolve. Sonication did not seem to help.
7) The use of CH_3CN as a cosolvent seems to be necessary for higher yields, and qualitatively it seemed to have an effect in the dissolution of the [Cr]. It is important to note, however, that the reaction does not

work in CH_3CN alone, and higher ratios of CH_3CN/THF seemed to be detrimental. We also noticed that in the case of the reactions that use $CrCl_3$ anhydrous (procedure **II**) the CH_3CN needed to be added last. HFIP can also be used as a co-solvent for the reactions with $CrCl_3$ anhydrous but not with those with $CrCl_3(THF)_3$. None of these co-solvents help with internal olefins.

8) For the General Procedure **IV**, it is important to add this [Cr] after the HAT cycle has started, otherwise only SM is recovered at the end of the reaction.
9) $CrCl_3(THF)_3$ is very hygroscopic and handling under an inert atmosphere is recommended.
10) The presence of acid is detrimental to the reaction. As a result, it is very important to purify the aldehydes since they may contain carboxylic acid impurities.
11) Presence of water is also detrimental (See Table 1 in the manuscript), and as a consequence we have noticed that the yield seemed to decrease if a) $CrCl_3$ that was not kept anhydrous was used, b) old batches of Co(salen) that were kept exposed to air were used, c) in general not having good technique to exclude moisture.
12) In terms of yield, both $CrCl_3$ and $CrCl_3(THF)_3$ work well with terminal olefins, with the advantage that $CrCl_3(THF)_3$ is soluble in the reaction system, so rapid stirring is not required. However, this form of [Cr] is also more expensive. $CrCl_3(THF)_3$ cannot be used for internal olefins.

H. Characterization of unnatural amino acids derivatives (only data for the major diastereomer is given)



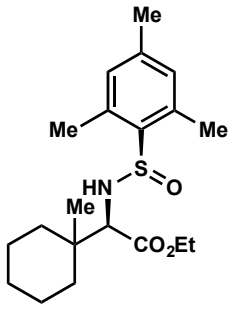
ethyl (S)-2-(1-methylcyclohexyl)-2-(((S)-p-tolylsulfinyl)amino)acetate (1)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of 1-methyl-1-cyclohexene as the olefin (18 μL, 0.15 mmol), ethyl (*S*)-2-((*p*-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent instead of *i*-PrOH. Purification by flash column chromatography (SiO_2, 7:3 hexanes/EtOAc) delivered 26 mg of the desired compound (77%) as a clear oil and a 8:1 mixture of diastereomers. Crude d.r. was determined to be 5:1 by integration of the α-methyl group by ^{1}H NMR.

R_f: 0.12 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 4.61 (d, *J* = 9.8 Hz, 1H), 4.18 – 4.01 (m, 2H), 3.82 (d, *J* = 9.8 Hz, 1H), 2.41 (s, 3H), 1.66 – 1.53 (m, 3H), 1.51 – 1.37 (m, 6H), 1.36 – 1.29 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.59, 142.26, 141.66, 129.68, 125.55, 61.18, 37.64, 34.96, 34.85, 26.11, 21.73, 21.69, 21.51, 14.24.

HRMS: m/z (ESI): Calcd. for $C_{18}H_{27}NO_3S$ [M+H]: 338.1790, found: 338.1791.



ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-(1-methylcyclohexyl)acetate (2)

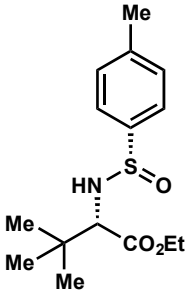
The General Procedure **I** was followed on a 0.2 mmol scale using 1.5 equiv. of 1-methyl-1-cyclohexene as the olefin (36 μL, 0.3 mmol), ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (53 mg, 0.2 mmol), and *i*-PrOH as the cosolvent. Purification by flash column chromatography (SiO_2, 4:1 hexanes/EtOAc) delivered 41 mg of the desired compound (56%) as a clear oil and a single diastereomer. Crude d.r. appears to be only one diastereomer.

R_f: 0.34 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.01 (d, J = 10.1 Hz, 1H), 4.32 – 4.12 (m, 2H), 3.83 (d, J = 10.1 Hz, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 1.61 (dt, J = 13.7, 4.2 Hz, 2H), 1.53 (ddd, J = 12.6, 8.9, 3.7 Hz, 1H), 1.45 (ttd, J = 12.0, 9.0, 4.8 Hz, 3H), 1.38 – 1.32 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H), 1.28 – 1.23 (m, 2H), 0.85 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.89, 140.97, 138.28, 136.87, 130.91, 61.37, 37.73, 34.95, 34.89, 26.07, 21.69, 21.66, 21.18, 19.44, 14.31.

HRMS: m/z (ESI): Calcd. for $C_{20}H_{31}NO_3S$ [M+H]: 366.2103, found: 366.2100.



ethyl (*S*)-3,3-dimethyl-2-(((*S*)-*p*-tolylsulfinyl)amino)butanoate (3)

The general procedure **I** was followed on a 0.4 mmol scale using ethyl (*S*)-2-((*p*-tolylsulfinyl)imino)acetate as the imine (95.6 mg, 0.4 mmol) with the following modifications:

- The atmosphere was replaced with an atmosphere of isobutene using a balloon using the following procedure: once the solvents were added (DCE and *i*-PrOH), isobutene was bubbled inside the solution for around 10 seconds. Then the silane was added, and the reaction was left to stir for 16 hours under an atmosphere of isobutene.

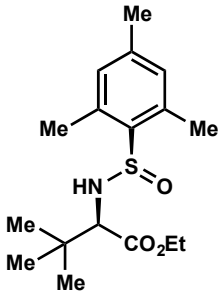
Purification of the crude mixture by flash column chromatography (SiO_2, 10:1 to 3:1 hexanes/EtOAc) delivered 64 mg of the title compound (54%) as a colorless oil and a 5:1 mixture of diastereomers.

R_f: 0.16 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.69 (d, J = 9.7 Hz, 1H), 4.18 – 4.05 (m, 2H), 3.64 (d, J = 9.7 Hz, 1H), 2.42 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.06 – 0.94 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.40, 142.00, 141.54, 129.54, 125.41, 65.00, 61.08, 34.85, 26.49, 21.36, 14.09.

HRMS: m/z (ESI): Calcd. for $C_{15}H_{23}NO_3S$ [M+ H]: 298.1477; found: 298.1472.



ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3,3-dimethylbutanoate (4)
The general procedure **I** was followed on a 0.2 mmol scale using ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (53 mg, 0.2 mmol), with the following modifications:

- The atmosphere was replaced with an atmosphere of isobutene using a balloon using the following procedure: once the solvents were added (DCE and EtOH instead of *i*-PrOH), isobutene was bubbled inside the solution for around 10 seconds. Then the silane was added as normal, and the reaction was left running for 16 hours under an atmosphere of isobutene.

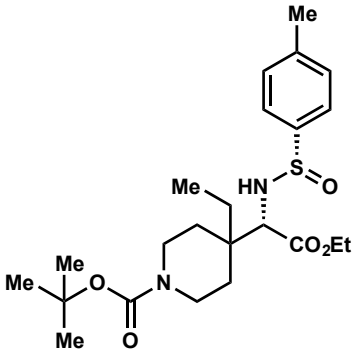
Purification of the crude mixture by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) delivered 57 mg of the title compound (88%) as a colorless oil and a single diastereomer.

R_f: 0.36 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 2H), 5.08 (d, J = 10.0 Hz, 1H), 4.35 – 4.16 (m, 2H), 3.63 (d, J = 10.0 Hz, 1H), 2.60 (s, 6H), 2.32 (s, 3H), 1.33 (t, J = 7.2 Hz, 3H), 0.99 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.70, 140.87, 138.06, 136.76, 130.80, 66.49, 61.30, 35.00, 26.47, 21.04, 19.31, 14.17.

HRMS: m/z (ESI): Calcd. for $C_{17}H_{27}NO_3S$ [M+H] 326.1790; found: 326.1788.



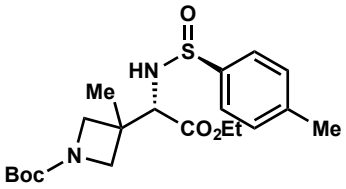
tert-butyl 4-((*S*)-2-ethoxy-2-oxo-1-(((*S*)-p-tolylsulfinyl)amino)ethyl)-4-ethylpiperidine-1-carboxylate (5)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of *tert*-butyl 4-ethylidenepiperidine-1-carboxylate as the olefin (32 mg, 0.15 mmol), ethyl (*S*)-2-((p-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent. Purification by PTLC (1:1 hexanes/EtOAc) delivered 19 mg of the desired compound (42%) as a clear oil and a 7:1 mixture of diastereomers. Crude d.r. was 6:1 by the tertbutyl group.

R_f: 0.17 (7:3 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 4.62 (d, J = 9.9 Hz, 1H), 4.19 – 4.05 (m, 2H), 3.96 (d, J = 9.9 Hz, 1H), 3.68 (dt, J = 13.6, 5.0 Hz, 2H), 3.27 – 3.08 (m, 2H), 2.41 (s, 3H), 1.72 – 1.54 (m, 4H), 1.55 – 1.47 (m, 2H), 1.45 (s, 9H), 1.24 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.32, 155.13, 141.92, 129.78, 125.39, 79.65, 61.59, 60.82, 39.70 (broad singlet), 38.91, 30.11 (broad singlet), 28.59, 24.23 (broad singlet), 21.53, 14.19, 7.57. Boc-carbonyl cannot be seen due to signal broadening.

HRMS: m/z (ESI): Calcd. For $C_{23}H_{36}N_2O_5S$ [M+H]: 453.2423, found: 453.2418.



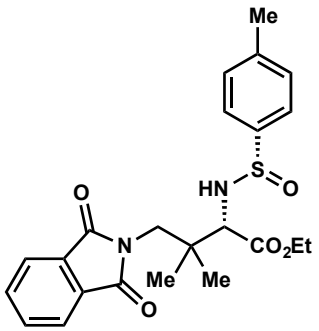
***tert*-butyl 3-((*S*)-2-ethoxy-2-oxo-1-(((*S*)-p-tolylsulfinyl)amino)ethyl)-3-methylazetidine-1-carboxylate (6)**
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of *tert*-butyl 3-methyleneazetidine-1-carboxylate as the olefin (25 mg, 0.15 mmol), ethyl (*S*)-2-((p-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent instead of *i*-PrOH. Purification by flash column chromatography (SiO_2, 4:1 then 3:2 hexanes/EtOAc) delivered 24 mg of the desired compound (58%) as a white solid and a 5:1 mixture of diastereomers. Note: This compound epimerizes at room temperature over a period of approximately 1 month as a pure compound, and 1 week as a crude.

R_f: 0.16 (7:3 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 4.81 (d, J = 8.6 Hz, 1H), 4.30 – 4.12 (m, 2H), 4.09 (t, J = 8.8 Hz, 2H), 4.03 (d, J = 8.9 Hz, 1H), 3.55 (dd, J = 8.8, 1.4 Hz, 2H), 2.41 (s, 3H), 1.45 (s, 9H), 1.20 (m, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.02, 156.54, 142.03, 129.81, 125.55, 79.85, 62.04, 37.18, 28.53, 28.44, 21.52, 20.90, 14.24. Boc-carbonyl cannot be seen due to signal broadening.

HRMS: m/z (ESI): Calcd. for $C_{20}H_{30}N_2O_5S$ [M+ Na]: 433.1773; found: 433.1768.



ethyl (*S*)-4-(1,3-dioxoisoindolin-2-yl)-3,3-dimethyl-2-(((*S*)-*p*-tolylsulfinyl)amino)butanoate (7)

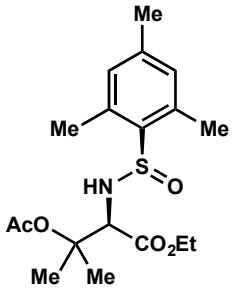
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of 2-(2-methylallyl)isoindoline-1,3-dione as the olefin (30 mg, 0.15 mmol), ethyl (*S*)-2-((p-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent. Purification by flash column chromatography (7:3 hexanes/EtOAc) delivered 22 mg of the desired compound (49%) as a clear oil and a 6:1 mixture of diastereomers. Crude d.r. was determine to be 5:1.

R_f: 0.27 (7:3 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 – 7.84 (m, 2H), 7.76 – 7.72 (m, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 4.90 (d, *J* = 10.3 Hz, 1H), 4.18 – 4.07 (m, 2H should be 2, integrates to 3 due to diastereomer overlapping), 3.82 (d, *J* = 10.4 Hz, 1H), 3.75 (s, 2H), 2.42 (s, 3H), 1.26 – 1.21 (m, 3H), 1.03 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.99, 169.15, 142.21, 141.75, 134.26, 132.09, 129.75, 125.58, 123.55, 63.39, 61.60, 45.29, 40.13, 23.93, 21.84, 21.53, 14.19.

HRMS: m/z (ESI): Calcd. for $C_{23}H_{26}N_2O_5S$ [M+Na]: 465.1460; found: 465.1464.



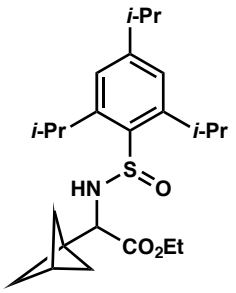
ethyl (*R*)-3-acetoxy-2-(((*R*)-mesitylsulfinyl)amino)-3-methylbutanoate (8)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of isopropenyl acetate as the olefin (16 μL, 0.15 mmol), ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (26 mg, 0.1 mmol)), and EtOH as the cosolvent. Purification by FCC (hexanes/EtOAc 4:1) delivered 25 mg of the desired compound (68%) as a clear oil and a single diastereomer.

R_f: 0.25 (7:3 hexanes:EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.26 (d, *J* = 9.8 Hz, 1H), 4.53 (d, *J* = 9.9 Hz, 1H), 4.24 (ddq, *J* = 37.8, 10.8, 7.2 Hz, 2H), 2.58 (s, 6H), 2.29 (s, 3H), 1.97 (s, 3H), 1.56 (s, 3H), 1.39 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.28, 170.26, 141.21, 137.92, 136.97, 130.99, 82.01, 62.90, 62.00, 24.02, 23.11, 22.36, 21.18, 19.41, 14.23.

HRMS: m/z (ESI): Calcd. for $C_{18}H_{27}NO_5S$ [M+ H]: 370.1688; found: 370.1682.



ethyl 2-(bicyclo[1.1.1]pentan-1-yl)-2-(((2,4,6-triisopropylphenyl)sulfinyl)amino)acetate (9)
The General Procedure **I** was followed on a 0.03 mmol scale using 2 equiv. of [1.1.1]propellane as the olefin (140 μL of a 0.43 M solution in diethyl ether, 0.06 mmol), ethyl 2-(((2,4,6-triisopropylphenyl)sulfinyl)imino)acetate (10 mg, 0.03 mmol) and with the following modifications:

- $Mn(dpm)_3$ (0.1 equiv, 20 μL of a 0.15 M solution in PhH, 3 μmol) instead of $Fe(acac)_3$ was used.
- PhH was used as the solvent (0.1 M, 300 μL) and no alcohol was used as co-solvent.
- 3.5 equiv of $PhSiH_2(O\textit{i}\text{-Pr})$ were used.

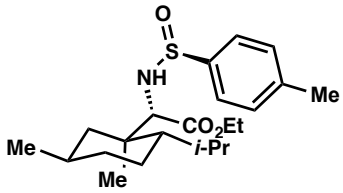
Purification by PTLC (4:1 hexanes/EtOAc) delivered 6 mg of the desired compound (48%) as a clear oil and a single diastereomer. Crude NMR showed d.r. of >20:1.

$\underline{R_f}$: 0.37 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (s, 2H), 5.19 (d, J = 8.5 Hz, 1H), 4.31 (dq, J = 10.7, 7.1 Hz, 1H), 4.24 – 4.17 (m, 1H), 4.02 (d, J = 8.5 Hz, 2H), 2.89 (hept, J = 7.0 Hz, 1H), 2.50 (s, 2H), 1.74 (d, J = 2.3 Hz, 6H), 1.34 (d, J = 6.9 Hz, 6H), 1.31 (t, J = 7.1 Hz, 3H), 1.26 (d, J = 2.3 Hz, 6H), 1.25 (d, J = 2.5 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.30, 152.09, 147.94, 137.90, 123.13, 61.66, 58.83, 49.21, 44.73, 34.46, 28.30, 27.45, 24.61, 24.26, 23.92, 14.52.

LRMS: m/z (ESI): Calcd. for $C_{24}H_{37}NO_3S$ [M+Na]: 442.2; found: 442.3.



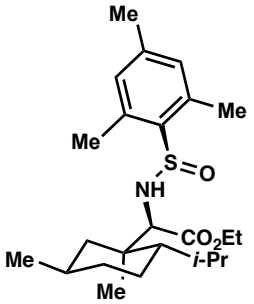
ethyl (*S*)-2-((1*R*,2*S*,5*R*)-2-isopropyl-1,5-dimethylcyclohexyl)-2-(((*S*)-*p*-tolylsulfinyl)amino)acetate (10)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv of (1*S*,4*R*)-1-isopropyl-4-methyl-2-methylenecyclohexane as the olefin (23 mg, 0.15 mmol), ethyl (*S*)-2-((p-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent. Purification by flash column chromatography (4:1 hexanes/EtOAc) delivered 22 mg of the desired compound (56%) as a clear oil white solid and a 7:1 mixture of major diastereomers. Crude d.r. was determined to be 5:1 of major diastereomers.

$\underline{R_f}$: 0.54 (7:3 hexanes/EtOAc)

^{1}H NMR (600 MHz, C_6D_6) δ 7.77 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.3 Hz, 2H), 4.79 (dd, J = 10.6, 3.9 Hz, 1H), 4.30 (d, J = 10.1 Hz, 1H), 3.97 (qq, J = 7.3, 3.7 Hz, 2H), 1.92 (s, 3H), 1.71 (dd, J = 12.9, 3.7 Hz, 1H), 1.58 (dq, J = 12.9, 3.3 Hz, 1H), 1.45 (dq, J = 13.5, 3.6 Hz, 1H), 1.40 – 1.27 (m, 2H), 1.22 – 1.10 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H), 0.96 (s, 3H), 0.94 – 0.89 (m, 1H), 0.89 – 0.84 (m, 1H), 0.75 (d, J = 4.1 Hz, 3H), 0.74 (d, J = 4.7 Hz, 3H).

^{13}C NMR (151 MHz, C_6D_6) δ 173.05, 143.92, 141.32, 129.81, 125.55, 62.97, 61.16, 44.38, 42.56, 42.33, 35.63, 27.94, 25.61, 24.57, 23.05, 21.87, 21.04, 19.14, 18.62, 14.15.

HRMS: m/z (ESI): Calcd. for $C_{22}H_{35}NO_3S$ [M+ H]: 394.2416; found: 394.2415.



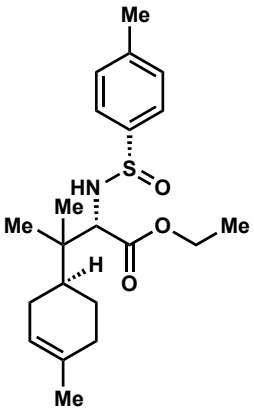
ethyl (*R*)-2-((1*R*,2*S*,5*R*)-2-isopropyl-1,5-dimethylcyclohexyl)-2-(((*R*)-mesitylsulfinyl)amino)acetate (11)
The General Procedure **I** was followed on a 0.2 mmol scale using 1.5 equiv of (1*S*,4*R*)-1-isopropyl-4-methyl-2-methylenecyclohexane as the olefin (45 mg, 0.3 mmol) and *i*-PrOH as the cosolvent. Purification by flash column chromatography (SiO_2, 3:1 hexanes/EtOAc) delivered 59 mg of the desired compound (70%) as a clear oil and a 5:1 mixture of diastereomers.

R_f: 0.45 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (s, 2H), 5.06 (d, J = 10.2 Hz, 1H), 4.36 – 4.18 (m, 2H), 4.09 (d, J = 10.2 Hz, 1H), 2.59 (s, 6H), 2.31 (s, 3H), 2.26-2.18 (m, 1H), 1.72-1.68 (br m, 1H), 1.55-1.48 (m, 1H), 1.46 – 1.38 (m, 1H), 1.37 – 1.31 (m, 3H), 1.25 (ddd, J = 12.7, 3.4, 2.1 Hz, 1H), 1.15 (dd, J = 12.5, 3.6 Hz, 1H), 1.06 (s, 3H), 0.95 (d, J = 6.8 Hz, 3H), 0.89 – 0.83 (m, 4H), 0.79 (d, J = 6.8, 3H), 0.73 (qd, J = 12.7, 3.8, 1.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.79, 140.85, 138.14, 136.80, 130.78, 65.37, 61.49, 46.25, 43.27, 41.94, 35.25, 27.64, 25.77, 23.86, 22.75, 21.79, 21.05, 19.32, 19.02, 18.39, 14.12.

HRMS: m/z (ESI): Calcd. for $C_{24}H_{39}NO_3S$ [M+H]: 422.2729; found: 422.2726.



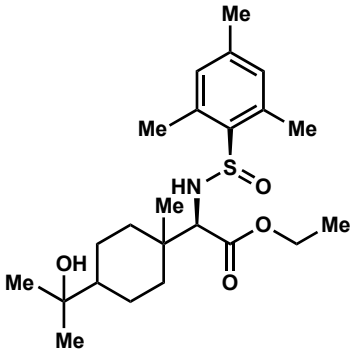
ethyl (*S*)-3-methyl-3-((*S*)-4-methylcyclohex-3-en-1-yl)-2-(((*S*)-*p*-tolylsulfinyl)amino)butanoate (12)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv of (−)-α-pinene as the olefin (24 μL, 0.15 mmol) and EtOH as the cosolvent. Purification by FCC (hexanes/EtOAc 4:1) delivered 16 mg of the desired compound (41%) as a white solid and a 4:1 mixture of diastereomers as well as 15% of a 4:1 mixture of diastereomers corresponding to the unrearranged pinene structure (not characterized).

R_f: 0.16 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, C_6D_6) δ 7.70 – 7.66 (m, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 5.39 (dd, *J* = 5.5, 2.5 Hz, 1H), 4.63 (d, *J* = 10.2 Hz, 1H), 4.13 (d, *J* = 10.3 Hz, 1H), 3.92 – 3.86 (m, 2H), 2.07 – 2.00 (m, 1H), 1.93 (s, 3H), 1.89 – 1.82 (m, 1H), 1.74 (dddd, *J* = 18.5, 9.5, 4.7, 2.7 Hz, 2H), 1.65 (t, *J* = 2.1 Hz, 3H), 1.38 – 1.24 (m, 1H), 0.90 (s, 3H), 0.78 (s, 3H).

^{13}C NMR (151 MHz, C_6D_6) δ 172.85, 143.81, 141.18, 133.63, 129.71, 125.67, 121.47, 62.89, 61.03, 40.22, 39.94, 31.56, 26.92, 24.19, 23.55, 21.05, 20.26, 20.10, 14.08.

HRMS: m/z (ESI): Calcd. for $C_{21}H_{31}NO_3S$ [M+ H]: 378.2103; found: 378.2101.



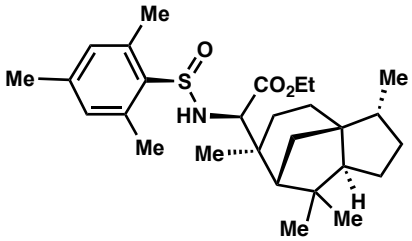
ethyl (*R*)-2-(4-(2-hydroxypropan-2-yl)-1-methylcyclohexyl)-2-(((*R*)-mesitylsulfinyl)amino)acetate (13)
The General Procedure **I** was followed on a 0.15 mmol scale using 1.5 equiv. of α-terpineol as the olefin (39 μL, 0.23 mmol), ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (38 mg, 0.15 mmol), and EtOH as the cosolvent. Purification by FCC (Hexanes/EtOAc 7:3) delivered 37 mg of the desired compound (59%) as a clear oil kind of fluffy and a 2:1 mixture of diastereomers.

R_f: 0.24 (3:2 hexanes/EtOAc)

Major diastereomer:
^{1}H NMR (600 MHz, C_6D_6) δ 6.55 (s, 2H), 5.24 (d, *J* = 10.3 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.66 (d, *J* = 10.4 Hz, 1H), 2.64 (s, 6H), 1.95 (d, *J* = 2.3 Hz, 3H), 1.72 – 1.60 (m, 2H), 1.57 – 1.46 (m, 4H), 1.17 – 1.07 (m, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 0.96 (s, 6H), 0.87 (s, 3H).

^{13}C NMR (151 MHz, C_6D_6) δ 172.92, 140.60, 139.27, 137.09, 131.13, 71.70, 68.42, 61.19, 48.93, 37.51, 34.65, 34.29, 27.31, 27.23, 22.64, 22.61, 20.85, 19.51, 18.25, 14.20.

HRMS: m/z (ESI): Calcd. for $C_{23}H_{37}NO_4S$ [M+ H]: 424.2522; found: 424.2523.



ethyl (*R*)-2-(((*R*)-mesitylsulfinyl)amino)-2-((3*R*,3a*S*,6*S*,7*R*,8a*S*)-3,6,8,8-tetramethyloctahydro-1*H*-3a,7-methanoazulen-6-yl)acetate (14)
The general procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv. of (−)-α-cedrene as the olefin (33 μL, 0.15 mmol), ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (26 mg, 0.1 mmol), and EtOH as the

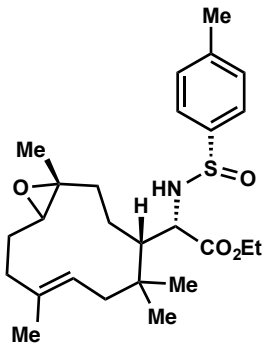
cosolvent. Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) delivered 13 mg of the desired compound (28%) as a clear oil and a single diastereomer.

R_f: 0.45 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 2H), 5.06 (d, J = 9.7 Hz, 1H), 4.35 (d, J = 9.7 Hz, 1H), 4.30 (dq, J = 10.8, 7.2 Hz, 1H), 4.17 (dq, J = 10.7, 7.1 Hz, 1H), 2.60 (s, 6H), 2.31 (s, 3H), 1.97 - 1.91 (m, 3H), 1.80 – 1.71 (m, 2H), 1.67 (ddd, J = 13.0, 4.8, 2.5 Hz, 1H), 1.58 – 1.50 (m, 2H), 1.46 – 1.38 (m, 3H), 1.36 – 1.27 (m, 5H), 1.23 (s, 3H), 1.03 (s, 3H), 0.91 (s, 3H), 0.90 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.14, 140.87, 138.21, 136.70, 130.81, 61.18, 61.11, 57.80, 56.85, 53.54, 44.99, 43.14, 41.75, 40.27, 36.97, 30.01, 29.97, 29.50, 29.32, 25.41, 21.05, 20.23, 19.33, 15.52, 14.13.

HRMS: m/z (ESI): Calcd. for $C_{28}H_{43}NO_3S$ [M + H]: 474.3042; found: 474.3043.



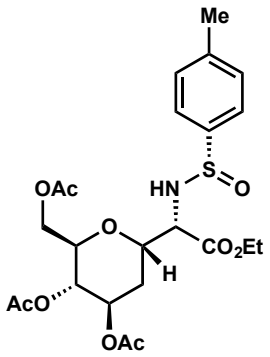
ethyl (2*S*)-2-((1*R*,4*S*,*E*)-1,5,5,8-tetramethyl-12-oxabicyclo[9.1.0]dodec-7-en-4-yl)-2-(((*S*)-*p*-tolylsulfinyl)amino)acetate (15)
The General Procedure **I** was followed on a 0.2 mmol scale using 1.5 equiv. of (−)-caryophyllene oxide the olefin (66 mg, 0.3 mmol) and EtOH as the cosolvent. Purification by flash column chromatography (SiO_2, 9:1 then 7:3 hexanes/EtOAc) delivered 23 mg of the desired compound (25% IY) as a clear oil and a 10:1 mixture of diastereomers.

R_f: 0.23 (7:3 hexanes/EtOAc)

^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 8.1 Hz, 2H), 5.14 (d, J = 10.0 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.41 (dd, J = 9.2, 2.0 Hz, 1H), 3.94 – 3.89 (m, 1H), 3.86 – 3.80 (m, 1H), 2.70 (dd, J = 10.9, 1.9 Hz, 1H), 2.13 (dd, J = 16.0, 10.0 Hz, 2H), 2.10 – 2.05 (m, 1H), 2.00 – 1.95 (m, 1H), 1.94 (s, 3H), 1.93 – 1.90 (m, 1H), 1.86 – 1.78 (m, 3H), 1.63 (ddd, J = 15.5, 4.1, 2.2 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.32 (t, J = 1.6 Hz, 3H), 1.30 – 1.23 (m, 1H), 1.19 (s, 3H), 0.99 (s, 3H), 0.98 (s, 3H), 0.96 - 0.94 (dd, J = 7.5, 2.2 Hz, 2H), 0.90 (t, J = 7.2 Hz, 5H), 0.81 – 0.79 (d, J = 1.8 Hz, 1H).

^{13}C NMR (126 MHz, C_6D_6) δ 174.03, 143.15, 141.03, 134.05, 129.46, 127.88, 127.69, 127.50, 125.49, 121.69, 63.05, 61.41, 61.27, 55.78, 49.12, 41.16, 37.55, 36.91, 36.76, 27.51, 24.69, 24.50, 20.72, 18.75, 17.05, 15.50, 13.64.

HRMS: m/z (ESI): Calcd. for $C_{26}H_{39}NO_4S$ [M+Na]: 462.2678; found: 462.2675.



(2*R*,3*S*,4*R*,6*S*)-2-(acetoxymethyl)-6-((*S*)-2-ethoxy-2-oxo-1-(((*S*)-*p*-tolylsulfinyl)amino)ethyl)tetrahydro-2*H*-pyran-3,4-diyl diacetate (16)

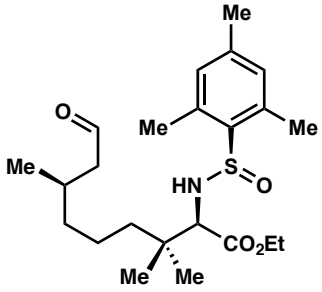
The General Procedure **I** was followed on a 0.1 mmol scale using 3 equiv. of tri-*O*-acetyl-D-glucal as the olefin (82 mg, 0.3 mmol) and EtOH as the cosolvent. Purification by PTLC (Hexanes/EtOAc 1:1) delivered 20 mg of the desired compound (39%) as a clear oil and a 4:1 mixture of diastereomers.

R_f: 0.16 (1:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 5.33 (ddd, *J* = 8.3, 6.9, 4.3 Hz, 1H), 5.18 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.62 (dd, *J* = 11.7, 5.4 Hz, 1H), 4.59 – 4.57 (br m, 1H), 4.21 (dd, *J* = 10.0, 8.7 Hz, 1H), 4.09 (dd, *J* = 14.3, 3.4 Hz, 1H), 4.10 – 4.06 (m, 1H), 4.04 – 4.00 (m, 1H), 3.99 (dt, *J* = 7.1, 1.0 Hz, 2H), 2.50 – 2.39 (m, 1H), 2.00 (s, 3H), 1.81 (s, 3H), 1.79 – 1.76 (m, 1H), 1.73 (s, 3H), 1.73 (s, 3H), 0.98 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, C_6D_6) δ 170.83, 169.89, 169.05, 169.01, 142.59, 141.10, 129.51, 125.72, 72.41, 72.02, 68.22, 68.22, 61.37, 61.11, 57.13, 28.79, 20.76, 20.23, 20.08, 20.07, 13.76.

HRMS: m/z (ESI): Calcd. for $C_{24}H_{39}NO_3S$ [M+H]: 514.1747; found: 514.1752.



ethyl (2*R*,7*R*)-2-(((*R*)-mesitylsulfinyl)amino)-3,3,7-trimethyl-9-oxononanoate (17)

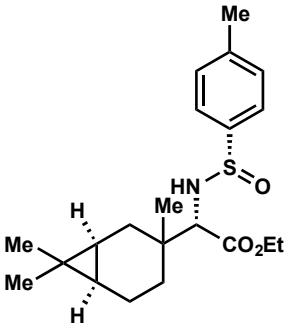
The General Procedure **I** was followed on a 0.2 mmol scale using 1.5 equiv of (*S*)-(−)-citronellal as the olefin (54 μL, 0.3 mmol), ethyl (*R*)-2-((mesitylsulfinyl)imino)acetate as the imine (53 mg, 0.2 mmol), and *i*-PrOH as the cosolvent. Purification by flash column chromatography (SiO_2, 9:1 then 4:1 hexanes/EtOAc) delivered 46 mg of the desired compound (54%) as a clear oil and a single diastereomer.

R_f: 0.27 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.3 Hz, 1H), 6.87 (s, 2H), 5.03 (d, *J* = 10.1 Hz, 1H), 4.31 – 4.16 (m, 2H), 3.71 (d, *J* = 10.1 Hz, 1H), 2.56 (s, 6H), 2.29 (s, 3H), 2.11 – 2.00 (m, *J* = 5.6 Hz, 1H), 1.34 – 1.29 (m, 10H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 4.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 202.94, 172.86, 141.09, 138.09, 136.89, 130.95, 64.87, 61.49, 51.25, 39.58, 37.72, 37.70, 28.28, 23.93, 23.80, 21.22, 21.17, 20.05, 19.42, 14.31.

HRMS: m/z (ESI): Calcd. for $C_{23}H_{37}NO_4S$ [M+H] 424.2522; found: 424.2518.



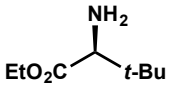
ethyl (2*S*)-2-(((*S*)-*p*-tolylsulfinyl)amino)-2-((1*S*,6*R*)-3,7,7-trimethylbicyclo[4.1.0]heptan-3-yl)acetate (18)
The General Procedure **I** was followed on a 0.1 mmol scale using 1.5 equiv of (+)-2-carene as the olefin (24 μL, 0.15 mmol), ethyl (*S*)-2-((p-tolylsulfinyl)imino)acetate as the imine (24 mg, 0.1 mmol), and EtOH as the cosolvent. Purification by flash column chromatography (SiO_2, 4:1 hexanes/EtOAc) delivered 16 mg of the desired compound (42%) as a white solid and a 1:1 mixture of major diastereomers.

R_f: 0.24 (4:1 hexanes/EtOAc)

Major two diastereomers:
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 4H), 7.29 (dtd, *J* = 8.6, 4.8, 4.3, 2.4 Hz, 4H), 4.60 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 4.32 – 4.04 (m, 6H), 3.54 (d, *J* = 9.8 Hz, 1H), 2.41 (d, *J* = 2.1 Hz, 6H), 2.03 – 1.96 (m, 2H), 1.88 – 1.75 (m, 3H), 1.72 (dddd, *J* = 13.3, 6.6, 3.4, 1.8 Hz, 1H), 1.67 – 1.60 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.15 – 1.08 (m, 2H), 1.03 (s, 3H), 0.99 (s, 3H), 0.95 (s, 6H), 0.90 (s, 3H), 0.72 – 0.68 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.02, 172.37, 142.35, 142.22, 141.67, 141.66, 129.68, 129.66, 125.53, 125.45, 66.17, 61.29, 61.21, 59.60, 36.24, 35.80, 31.93, 29.97, 29.19, 29.11, 28.15, 23.31, 21.51, 21.50, 19.14, 18.29, 17.80, 17.74, 17.34, 17.30, 16.01, 15.60, 15.40, 15.11, 14.31, 14.26.

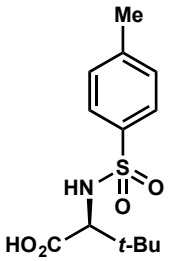
LRMS: m/z (ESI): Calcd. for $C_{21}H_{31}NO_3S$ [M+Na]: 400.2, found: 400.2.



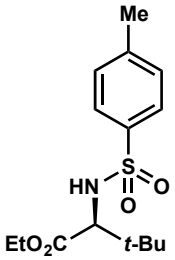
ethyl (*S*)-2-amino-3,3-dimethylbutanoate (SI-6)
Synthesized according to the known procedure[xvii] and worked up with $NaHCO_3$ (aq). Purified by FCC (5:1 to 0:1 hexanes/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.23 – 4.16 (m, 2H), 3.19 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.99 (s, 9H).

$[\alpha]^{20}_D$ = +47.1 ($CHCl_3$, c = 1.20).



(*S*)-3,3-dimethyl-2-((4-methylphenyl)sulfonamido)butanoic acid (SI-8)
Prepared according to a known procedure.[xviii] Data matched those ones reported.



ethyl (*S*)-3,3-dimethyl-2-((4-methylphenyl)sulfonamido)butanoate (SI-9)
Synthesis from (L)-*tert*-leucine:
To a stirred solution of (*S*)-3,3-dimethyl-2-((4-methylphenyl)sulfonamido)butanoic acid (**SI-8**) (300 mg, 1.05 mmol) in EtOH (5.0 mL) was added conc. H_2SO_4 (5 drops). After stirring for 15 hr at reflux, the reaction was cooled to room temperature and water was added. The aqueous layer was extracted with EtOAc. The organic layer was washed with aq. $NaHCO_3$, brine and dried over $MgSO_4$. To the solution of the crude product in ether was added hexanes to give precipitate, which was filtered an dried to give the title compounds (211 mg, 0.674 mmol, 64%) as a white solid. Characterization data (^1H, ^{13}C NMR and HRMS) were in accordance with those obtained below (*see synthesis of **SI-9** from 3*).

$[\alpha]^{20}_D$ = +38.37 ($CHCl_3$, c = 0.258)

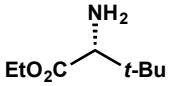
Synthesis from **3**:
To a stirred solution of **3** (18.5 mg, 0.062 mmol, dr = 5:1) in DCM (2 mL) was added *m*-CPBA (70 wt%, 24.0 mg, 0.10 mmol) at room temperature. After stirring for 1h at the same temperature, saturated aq. $Na_2S_2O_3$ was added. The aqueous layer was extracted with EtOAc. The organic layer was washed with aq. $NaHCO_3$, brine and dried over $MgSO_4$. The crude product was purified by silica-gel column chromatography (hexanes:EtOAc = 10:1 to 3:1) to give **SI-9** (er = 5:1, 10.9 mg, 59%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.28 (m, 2H), 5.13 (d, *J* = 10.7 Hz, 1H), 3.86 – 3.72 (m, 2H), 3.56 (d, *J* = 10.7 Hz, 1H), 2.43 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.98 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.89, 143.58, 136.54, 129.52, 127.49, 64.19, 61.05, 34.64, 26.33, 21.49, 13.86.

HRMS: m/z (ESI): Calcd. for $C_{15}H_{23}NO_4S$ [M+H]: 314.1426; found: 314.1425.

$[\alpha]^{20}_D$ = +24.4 ($CHCl_3$, c = 0.258)

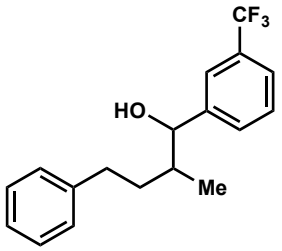


ethyl (*R*)-2-amino-3,3-dimethylbutanoate (SI-10)

To a stirred solution of **4** was added MeOH (1 mL) and TFA (1mL) at room temperature. After stirring for 30 minutes, solvents were evaporated and aq. $NaHCO_3$ was added. The aqueous layer was extracted EtOAc twice. Combined organic layers were washed with brine and dried over $MgSO_4$, concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (Hexanes/EtOAc = 5:1 - 0:1) to give **SI-10** (52%, 8.3 mg, 0.052 mmol).

$[\alpha]^{20}_D$ = –40.0 ($CHCl_3$, c = 0.10)

I. Characterization of alcohol derivatives



2-methyl-4-phenyl-1-(3-(trifluoromethyl)phenyl)butan-1-ol (21)
The General Procedure **IV** was followed in a 0.15 mmol scale, using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol), 3-(trifluoromethyl)benzaldehyde as the aldehyde (36 μl, 0.27 mmol), and with the following modifications:

- Co(salen)Cl was used instead of Co(salen) (19 mg, 0.03 mmol, 0.2 equiv.)
- No oxidant was added.

Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/EtOAc) delivered 33 mg of the desired compound (72%) as a pale yellow oil and a 1:1 mixture of diastereomers.

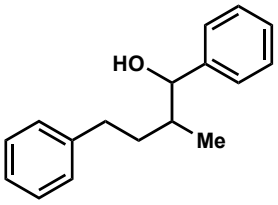
R_f: 0.64 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.50 – 7.41 (m, 4H), 7.28 (d, *J* = 7.5 Hz, 3H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.14 (td, *J* = 8.5, 7.8, 1.5 Hz, 4H), 4.69 (d, *J* = 5.2 Hz, 1H), 4.57 (d, *J* = 6.4 Hz, 1H), 2.74 (tdd, *J* = 13.5, 10.0, 5.3 Hz, 2H), 2.57 (dddd, *J* = 20.1, 13.7, 10.0, 6.6 Hz, 2H), 2.00 – 1.80 (m, 3H), 1.75 (dddd, *J* = 13.6, 9.9, 6.6, 4.9 Hz, 1H), 1.53 – 1.40 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.70, 144.44, 142.46, 142.26, 130.70 (q, *J* = 32.4 Hz), 130.13, 129.83, 128.77, 128.76, 128.52, 128.50, 128.47, 128.45, 125.98, 125.92, 124.41 (q, *J* = 3.9 Hz), 124.31 (q, *J* = 273.1 Hz), 124.24 (q, *J* = 3.9 Hz), 123.53 (q, *J* = 3.7 Hz), 123.23 (q, *J* = 3.9 Hz), 78.40, 77.27, 39.81, 39.76, 34.89, 33.74, 33.52, 33.37, 15.79, 14.07.
The diastereomer overlaps at 130.70 and 124.31 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76.

HRMS: *m/z* (APCI): Calcd. for $C_{18}H_{19}F_3O$ [M – H_2 + H] 307.1310; found: 307.1312.
Dehydrogenation appear to occur under the APCI conditions.



2-methyl-1,4-diphenylbutan-1-ol (22)

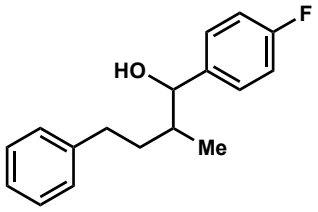
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol), and benzaldehyde as the aldehyde (30 μl, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/Et_2O) delivered 28 mg of the desired compound (78%) as a pale yellow oil and a 1:1.1 mixture of diastereomers.

R_f: 0.28 (9:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.0 Hz, 2H), 7.50 – 7.41 (m, 5H), 7.28 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 2.2 Hz, 2H), 7.22 – 7.17 (m, 2H), 7.14 (td, *J* = 8.5, 7.8, 1.5 Hz, 5H), 4.69 (d, *J* = 5.2 Hz, 1H), 4.57 (d, *J* = 6.4 Hz, 1H), 2.74 (tdd, *J* = 13.5, 10.0, 5.3 Hz, 2H), 2.57 (dddd, *J* = 20.1, 13.7, 10.0, 6.6 Hz, 2H), 2.00 – 1.80 (m, 3H), 1.75 (dddd, *J* = 13.6, 9.9, 6.6, 4.9 Hz, 1H), 1.53 – 1.40 (m, 2H), 0.95 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.69, 143.52, 142.81, 142.60, 128.52, 128.49, 128.44, 128.43, 128.38, 128.37, 127.64, 127.48, 126.81, 126.53, 125.83, 125.80, 79.09, 78.20, 39.89, 39.83, 34.93, 34.23, 33.59, 33.50, 15.83, 14.60.

HRMS: *m/z* (APCI): Calcd. for $C_{17}H_{20}O$ [M + Na]: 263.1412; found: 263.1414.



1-(4-fluorophenyl)-2-methyl-4-phenylbutan-1-ol (24)

Following General Procedure **IV**, a mixture of 4-fluorobenzaldehyde (33.0 μL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (24.0 μL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:1 to 7:3 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (35.0 mg, 90% yield) as an inseparable 1.1:1 mixture of diastereomers.

R_f: 0.25 (4:1 hexanes/EtOAc)

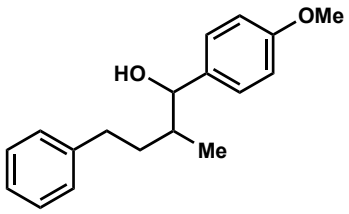
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 7H), 7.18 (ddt, *J* = 9.8, 7.5, 2.2 Hz, 4H), 7.14 – 7.09 (m, 2H), 7.06 – 6.98 (m, 4H), 4.56 (dd, *J* = 6.0, 2.2 Hz, 1H), 4.50 – 4.45 (m, 1H), 2.73 (dddd, *J* = 25.9, 13.7, 10.5, 5.2 Hz, 2H), 2.55 (ddt, *J* = 13.6, 10.0, 6.7 Hz, 2H), 1.97 (dddd, *J* = 13.9, 10.4, 6.5, 3.5 Hz, 1H), 1.89 – 1.76 (m, 4H), 1.70 (dddd, *J* = 13.5, 10.2, 6.5, 4.5 Hz, 1H), 1.50 – 1.34 (m, 2H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.85 (d, *J* = 6.8 Hz, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.27 (d, *J* = 245.1 Hz), 162.18 (d, *J* = 245.1 Hz), 142.66, 142.45, 139.27 (d, *J* = 18.96 Hz), 139.25 (d, *J* = 18.96 Hz), 128.49, 128.46, 128.35, 128.29, 128.10, 128.04, 125.89, 125.85, 115.24, 115.07, 78.38, 77.58, 39.93, 39.87, 34.82, 34.16, 33.54, 33.45, 15.72, 14.58.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.49, -115.69;

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): *tR* = 6.610 min;

MS: (EI, 70 eV): *m/z* (%) $C_{17}H_{19}FO$ calc. 258.14: 240.1 (5), 197.1 (7), 136.1 (37), 125.1 (100), 109.1 (7), 97.1 (23), 91.1 (33). Ion peak corresponds to M-OH



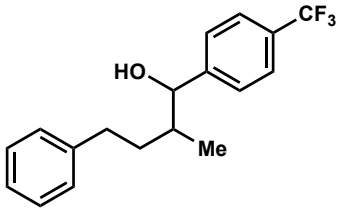
1-(4-methoxyphenyl)-2-methyl-4-phenylbutan-1-ol (25)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol), anisaldehyde as the aldehyde (36 μl, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/EtOAc) delivered 26 mg of the desired compound (63%) as a clear oil.

R_f: 0.34 (4:1 hexanes/EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dt, *J* = 8.2, 1.3 Hz, 2H), 7.25 – 7.13 (m, 10H), 7.13 – 7.09 (m, 2H), 6.91 – 6.84 (m, 4H), 4.50 (d, *J* = 6.2 Hz, 1H), 4.42 (d, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 3.81 (s, 3H), 2.73 (dddd, *J* = 27.0, 13.6, 10.5, 5.2 Hz, 2H), 2.54 (dddd, *J* = 19.9, 13.6, 10.3, 6.4 Hz, 2H), 2.01 (dddd, *J* = 17.0, 10.4, 6.3, 3.6 Hz, 1H), 1.91 – 1.79 (m, 2H), 1.74 – 1.65 (m, 1H), 1.52 – 1.41 (m, 1H), 1.41 – 1.32 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.13, 159.03, 142.89, 142.66, 135.83, 135.72, 128.54, 128.50, 128.44, 128.42, 127.95, 127.73, 125.81, 125.79, 113.77, 113.76, 78.69, 78.08, 55.41, 39.93, 39.85, 34.84, 34.48, 33.56, 33.52, 15.76, 14.93. The diastereomers overall at the OMe signal.

HRMS: *m/z* (APCI): Calcd. for $C_{18}H_{22}O_2$ [M – OH]: 253.1592; found: 253.1600.



2-methyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)butan-1-ol (26)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol), 4-(trifluoromethyl)benzaldehyde as the aldehyde (40 μl, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/Et_2O) delivered 37 mg of the desired compound (80%) as a pale yellow oil and a 1:1 mixture of diastereomers.

R_f: 0.23 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 8.3, 3.2 Hz, 4H), 7.43 (t, *J* = 9.0 Hz, 4H), 7.35 – 7.25 (m, 4H), 7.24 – 7.19 (m, 2H), 7.17 (t, *J* = 6.8 Hz, 4H), 4.72 (d, *J* = 5.1 Hz, 1H), 4.60 (d, *J* = 6.2 Hz, 1H), 2.77 (tdd, *J* = 13.5,

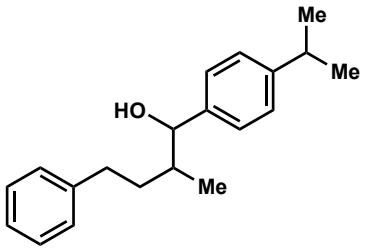
10.0, 5.3 Hz, 2H), 2.59 (dddd, *J* = 28.0, 13.8, 10.0, 6.6 Hz, 2H), 2.00 – 1.83 (m, 3H), 1.79 (dddd, *J* = 13.5, 10.0, 6.5, 4.8 Hz, 1H), 1.54 – 1.43 (m, 2H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.66, 147.38, 142.46, 142.28, 129.78 (q, *J* = 25.8 Hz), 129.56 (q, *J* = 25.8 Hz), 128.52, 128.49, 128.48, 128.47, 127.06, 126.74, 125.99, 125.92, 125.26 (q, *J* = 4.2, 3.7 Hz), 124.36 (q, *J* = 272.9 Hz), 78.38, 77.22, 39.83, 39.78, 34.89, 33.74, 33.58, 33.41, 15.76, 14.06.
The diastereomers overlap at 125.26 and at 124.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63, -62.65.

Diastereomer 1:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.508 min;
MS: (EI, 70 eV): *m/z* (%): 308.2 (0.4), 290.1 (6), 202.1 (10), 186.1 (11), 179.1 (10), 175.0 (48), 159.1 (3), 133.1 (7), 127.0 (30), 104.1 (50), 91.1 (100), 65.1 (10), 55.0 (1).

Diastereomer 2:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.536 min;
MS: (EI, 70 eV): *m/z* (%): 308.1 (0.2), 290.1 (6), 202.1 (6), 186.1 (24), 175.0 (49), 145.0 (8), 133.1 (5), 127.0 (34), 104.1 (71), 91.1 (100).



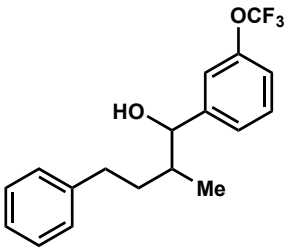
1-(4-isopropylphenyl)-2-methyl-4-phenylbutan-1-ol (27)
Following General Procedure **II**, a mixture of 4-isopropylbenzaldehyde (45.5 µL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (24.0 µL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:2 hexanes/EtOAc) furnished the title compound as clear oil (13.3 mg, 32% yield) as an inseparable 1:1 mixture of diastereomers.

R_f: 0.35 (9:1 hexanes/EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.08 (m, 18H), 4.55 (dd, J = 5.9, 2.6 Hz, 1H), 4.45 (d, J = 6.7 Hz, 1H), 3.01 – 2.84 (m, 2H), 2.74 (dddd, J = 24.2, 19.2, 10.5, 5.3 Hz, 2H), 2.55 (tdd, J = 13.8, 10.2, 6.4 Hz, 2H), 2.03 (dddd, J = 13.4, 10.3, 6.4, 3.6 Hz, 1H), 1.95 – 1.79 (m, 2H), 1.79 – 1.65 (m, 3H), 1.53 – 1.34 (m, 2H), 1.25 (dd, J = 6.9, 1.1 Hz, 12H), 1.01 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.8 Hz, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.31, 148.14, 142.89, 142.68, 141.08, 140.94, 128.53, 128.50, 128.42, 128.40, 126.79, 126.53, 126.42, 126.41, 125.79, 125.77, 78.99, 78.19, 39.85, 39.76, 34.89, 34.35, 33.95, 33.93, 33.59, 33.51, 24.16, 15.87, 14.76. 1 peak of the diastereomers is not observed due to overlap.

HRMS: m/z (APCI): Calcd. for $C_{20}H_{26}O$ [M-OH]: 265.1956; found: 265.1955.



2-methyl-4-phenyl-1-(3-(trifluoromethoxy)phenyl)butan-1-ol (28)

Following General Procedure **II**, a mixture of 3-trifluoromethoxybenzaldehyde (43.0 µL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (24.0 µL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (29.2 mg, 60% yield) as an inseparable 1.1:1 mixture of diastereomers.

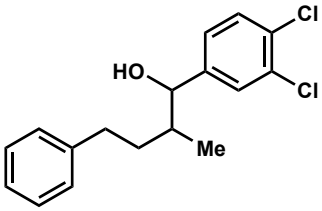
R_f: 0.25 (9:1 hexanes/EtOAc)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.37 (td, *J* = 7.9, 1.4 Hz, 2H), 7.30 – 7.08 (m, 15H), 4.66 (d, *J* = 5.0 Hz, 1H), 4.54 (d, *J* = 6.1 Hz, 1H), 2.73 (ddq, *J* = 14.7, 9.5, 5.1 Hz, 2H), 2.64 – 2.46 (m, 2H), 1.98 – 1.67 (m, 6H), 1.51 – 1.38 (m, 2H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.02, 148.97, 146.20, 145.90, 142.51, 142.31, 129.65, 128.51, 128.48, 128.47, 128.45, 125.97, 125.96, 125.90, 125.10, 124.81, 120.64 (q, *J* = 256 Hz), 119.95, 119.78, 119.38, 119.08, 118.08, 78.28, 39.79, 34.87, 33.79, 33.55, 33.41, 15.75, 14.14. 2 Carbons are missing due to overlapping.

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.00, -58.01;

HRMS: *m/z* (ESI): Calcd. for $C_{18}H_{19}F_3O_2$ [M+H]: 325.1407; found: 325.1415.



1-(3,4-dichlorophenyl)-2-methyl-4-phenylbutan-1-ol (29)

Following General Procedure **II**, a mixture of 3,4-dichlorobenzaldehyde (52.5 mg, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (24.0 µL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 8:2 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (29.2 mg, 63% yield) as an inseparable 1:1 mixture of diastereomers.

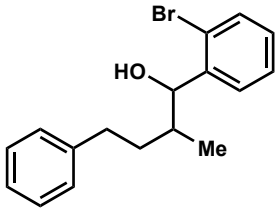
R_f: 0.30 (9:1 hexanes/EtOAc)

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.52 – 7.44 (m, 2H), 7.43 – 7.37 (m, 2H), 7.30 – 7.20 (m, 7H), 7.20 – 7.11 (m, 5H), 4.59 (d, J = 5.2 Hz, 1H), 4.47 (d, J = 6.4 Hz, 1H), 2.73 (ddt, J = 19.1, 11.1, 5.2 Hz, 2H), 2.62 – 2.46 (m, 2H), 1.99 – 1.66 (m, 6H), 1.51 – 1.37 (m, 2H), 0.93 (d, J = 6.7 Hz, 3H), 0.87 (d, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 146.13, 145.89, 142.56, 142.35, 130.67, 130.50, 129.93, 129.83, 129.56, 128.52, 128.51, 128.49, 128.48, 125.95, 125.89, 125.43, 125.11, 122.62, 122.61, 78.40, 77.29, 39.82, 39.78, 34.93, 33.87, 33.56, 33.42, 15.85, 14.23.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 70 °C/min to 250 °C, then 5 °C/min to 280 °C): *tR* = 8.090;

MS: (EI, 70 eV): *m/z* (%) $C_{17}H_{18}Cl_2O$ calc. 308.07: 292.1 (2), 188.1 (32), 186.1 (49), 176.9 (52), 174.9 (82), 148.9 (9), 113.1 (10), 112 (6), 111 (31), 104 (7), 92 (27), 91 (100), 77 (9). Ion peak corresponds to M-OH.



1-(2-bromophenyl)-2-methyl-4-phenylbutan-1-ol (30)

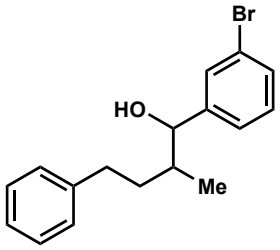
Following General Procedure **II**, a mixture of 2-bromobenzaldehyde (35.0 µL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (24.0 µL, 0.15 mmol, 1.0 equiv.) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (23.2 mg, 49% yield) as an inseparable 1.2:1 mixture of diastereomers.

R_f: 0.25 (9:1 hexanes/EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 4H), 7.36 – 7.23 (m, 4H), 7.21 – 7.09 (m, 8H), 5.05 (d, *J* = 4.2 Hz, 1H), 4.94 (d, *J* = 6.1 Hz, 1H), 2.84 – 2.61 (m, 3H), 2.48 (ddd, *J* = 13.6, 10.6, 6.2 Hz, 1H), 2.04 – 1.76 (m, 5H), 1.72 – 1.52 (m, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.86, 142.78, 142.57, 132.82, 128.88, 128.74, 128.53, 128.49, 128.46, 128.43, 128.40, 127.64, 127.39, 125.83, 125.76, 122.91, 122.37, 77.20, 75.90, 38.90, 37.71, 35.72, 33.66, 33.53, 32.85, 16.46, 13.28. 3 Peaks are missing due to overlapping.

HRMS: *m/z* (APCI): Calcd. for $C_{17}H_{19}BrO$ for [M + Na]: 341.0517; found: 341.0521.



1-(3-bromophenyl)-2-methyl-4-phenylbutan-1-ol (31)

Following General Procedure **II**, a mixture of 3-bromobenzaldehyde (35.0 µL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 µL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column

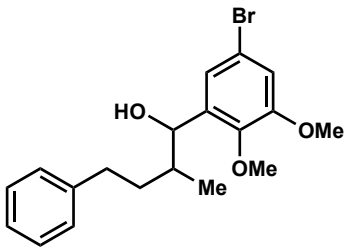
chromatography (SiO_2, 9:1 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (25.8 mg, 54% yield) as an inseparable 1.25:1 mixture of diastereomers.

R_f: 0.25 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (ddd, *J* = 8.2, 4.4, 2.6 Hz, 4H), 7.28 (td, *J* = 6.6, 5.8, 1.9 Hz, 4H), 7.21 – 7.07 (m, 8H), 4.58 (d, *J* = 5.1 Hz, 1H), 4.47 (d, *J* = 6.3 Hz, 1H), 2.74 (tdd, *J* = 14.4, 10.0, 5.3 Hz, 2H), 2.55 (dddd, *J* = 26.9, 13.7, 10.0, 6.6 Hz, 2H), 1.95 – 1.66 (m, 6H), 1.45 (dqt, *J* = 12.4, 9.1, 6.4 Hz, 2H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.00, 143.73, 142.39, 142.21, 132.47, 131.35, 131.17, 130.27, 128.73, 128.54, 128.50, 128.48, 128.46, 126.11, 126.01, 125.94, 125.82, 77.80, 76.67, 39.74, 39.72, 34.85, 33.69, 33.55, 33.38, 15.76, 14.07. 3 peaks are missing due to overlapping.

HRMS: *m/z* (APCI): Calcd. for $C_{17}H_{19}BrO$ [M + Na]: 341.0517; found: 341.0521.



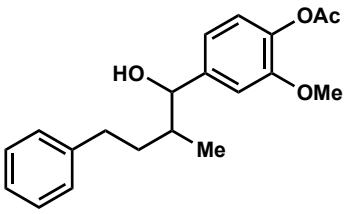
1-(5-bromo-2,3-dimethoxyphenyl)-2-methyl-4-phenylbutan-1-ol (32)
Following General Procedure **II**, a mixture of 5-bromo-2,3-dimethoxybenzaldehyde (39.9 mgL, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 μL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 7:3 to 6:4 hexanes/EtOAc) furnished the title compound as clear oil (25.7 mg, 46% yield) as an inseparable 1.1:1 mixture of diastereomers.

R_f: 0.2 (30% EtOAc in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 4H), 7.20 – 7.12 (m, 6H), 7.06 (dd, *J* = 2.3, 0.6 Hz, 2H), 6.94 (t, *J* = 2.4 Hz, 2H), 4.79 (d, *J* = 5.8 Hz, 1H), 4.62 (d, *J* = 7.6 Hz, 1H), 3.85 (d, *J* = 2.8 Hz, 6H), 3.76 (s, 3H), 3.73 (s, 3H), 2.82 – 2.69 (m, 2H), 2.56 (dddd, *J* = 20.1, 13.7, 9.8, 6.8 Hz, 2H), 2.09 (dtd, *J* = 13.7, 6.8, 3.4 Hz, 2H), 1.90 – 1.77 (m, 2H), 1.69 (dddd, *J* = 13.5, 9.7, 6.9, 5.0 Hz, 2H), 1.57 – 1.45 (m, 2H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.24, 153.21, 145.74, 145.40, 142.77, 142.48, 138.87, 138.68, 128.54, 128.51, 128.44, 128.43, 125.84, 125.78, 122.70, 122.46, 116.49, 116.44, 114.90, 114.81, 74.50, 73.31, 60.94, 60.84, 56.12, 39.38, 38.80, 35.37, 33.95, 33.46, 33.44, 16.42, 14.35; 1 carbon is missing due to overlap.

HRMS: *m/z* (ESI): Calcd. for $C_{19}H_{23}BrO_3$ [M+H]: 379.0909; found: 379.0912.



4-(1-hydroxy-2-methyl-4-phenylbutyl)-2-methoxyphenyl acetate (33)

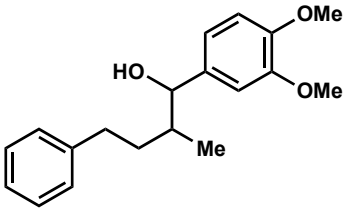
Following General Procedure **II**, a mixture of 4-formyl-2-methoxyphenyl acetate (58.2 mg, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 μL, 0.15 mmol, 1.0 equiv.) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 8:2 to 6:4 hexanes/EtOAc) furnished the title compound as clear oil (43.6 mg, 89% yield) as an inseparable 1.1:1 mixture of diastereomers.

R_f: 0.2 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 7.20 – 7.15 (m, 4H), 7.14 – 7.11 (m, 2H), 6.98 (dd, *J* = 8.1, 2.8 Hz, 2H), 6.92 (dd, *J* = 22.9, 1.9 Hz, 2H), 6.87 – 6.81 (m, 2H), 4.55 (d, *J* = 5.7 Hz, 1H), 4.45 (d, *J* = 6.9 Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 2.81 – 2.67 (m, 2H), 2.61 – 2.51 (m, 2H), 2.31 (d, *J* = 1.2 Hz, 6H), 2.01 (dddt, *J* = 13.9, 10.4, 6.5, 3.4 Hz, 1H), 1.94 – 1.67 (m, 5H), 1.54 – 1.39 (m, 2H), 1.00 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.21, 151.08, 142.82, 142.70, 142.62, 142.40, 139.04, 138.90, 128.49, 128.43, 125.84, 125.80, 122.43, 119.05, 118.78, 110.65, 110.41, 78.77, 77.80, 56.01, 39.82, 39.60, 34.87, 34.04, 33.46, 33.41, 20.81, 15.95, 14.50. 5 Peaks are missing due to overlap of the diastereomers.

HRMS: *m/z* (ESI): Calcd. for $C_{20}H_{24}O_4$ [M+H]: 329.1753; found: 329.1747.



1-(3,4-dimethoxyphenyl)-2-methyl-4-phenylbutan-1-ol (34)

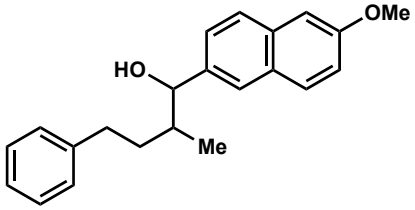
Following General Procedure **II**, a mixture of 3,4-dimethoxybenzaldehyde (49.9 mg, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 μL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 8:2 to 6:4 hexanes/EtOAc) furnished the title compound as clear oil (28.1 mg, 63% yield) as an inseparable 2.2:1 mixture of diastereomers.

R_f: 0.2 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4H), 7.20 – 7.13 (m, 2H), 7.12 – 7.08 (m, 2H), 6.85 – 6.79 (m, 4H), 4.47 (d, *J* = 6.4 Hz, 1H), 4.41 (d, *J* = 7.1 Hz, 0.45 H), 3.88 (d, *J* = 1.8 Hz, 6H), 3.85 (s, 3H), 2.73 (dddd, *J* = 32.9, 14.6, 9.2, 5.5 Hz, 2H), 2.55 (dddd, *J* = 20.5, 13.8, 10.1, 6.7 Hz, 2H), 2.07 – 1.97 (m, 0.55 H), 1.92 – 1.71 (m, 3H), 1.69 – 1.62 (m, 1H), 1.52 – 1.33 (m, 2H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 1.4 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.06, 148.42, 142.53, 136.41, 128.51, 128.44, 128.40, 125.82, 118.95, 110.86, 109.44, 78.95, 78.36, 56.06, 55.98, 39.93, 39.67, 34.84, 34.38, 33.49, 33.45, 15.94, 14.97. 9 of the expected 10 aromatic peaks of the minor diastereomer are not observed.

HRMS: *m/z* (APCI): Calcd. for $C_{19}H_{24}O_3$ [M+Na]: 323.1623; found: 323.1619.



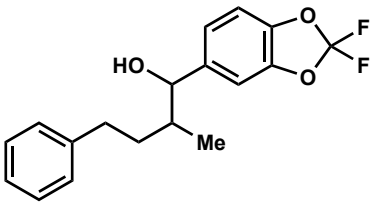
1-(6-methoxynaphthalen-2-yl)-2-methyl-4-phenylbutan-1-ol (35)
Following General Procedure **II**, a mixture of 6-methoxy-2-naphthaldehyde (55.9 mg, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 μL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) furnished the title compound as clear oil (33.4 mg, 70% yield) as an inseparable 2.5:1 mixture of diastereomers.

R_f: 0.3 (9:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.64 (m, 4H), 7.41 (dd, *J* = 8.5, 1.8 Hz, 0.4 H), 7.36 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.20 – 7.07 (m, 7H), 4.70 (d, *J* = 5.9 Hz, 1H), 4.60 (d, *J* = 6.9 Hz, 0.4 H), 3.93 (d, *J* = 1.0 Hz, 4H), 2.75 (dddd, *J* = 29.3, 13.8, 10.4, 5.2 Hz, 1.5H), 2.57 (tdd, *J* = 13.7, 10.2, 6.4 Hz, 1.5H), 2.11 – 1.84 (m, 3.7H), 1.79 – 1.70 (m, 1H), 1.56 – 1.37 (m, 2.7H), 1.04 (d, *J* = 6.7 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 1.2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.74, 142.82, 142.57, 138.85, 134.21, 134.11, 129.55, 128.75, 128.53, 128.49, 128.43, 128.41, 127.00, 126.98, 125.81, 125.79, 125.57, 125.35, 125.21, 119.04, 119.02, 105.79, 79.23, 78.39, 55.45, 39.81, 39.70, 35.02, 34.33, 33.59, 33.52, 15.96, 14.75. 3 Peaks from the aromatic section and the MeO- peak from the minor diastereomer are not observed due to overlap.

HRMS: *m/z* (ESI): Calcd. for $C_{20}H_{24}O$ [M+H]: 321.1855; found: 321.1853.



1-(2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)-2-methyl-4-phenylbutan-1-ol (36)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol) and 2,2-difluoro-1,3-benzodioxole-5-carbaldehyde as the aldehyde (55 mg, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes hexanes then 9:1 hexanes/EtOAc) delivered 34 mg of the desired compound (71%) as an oil and a 1:1.1 mixture of diastereomers.

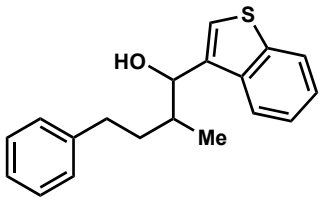
R_f: 0.19 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 4H), 7.21 – 7.14 (m, 4H), 7.14 – 7.10 (m, 2H), 7.06 – 7.04 (m, 1H), 7.02 (d, *J* = 1.6 Hz, 1H), 7.01 – 6.94 (m, 4H), 4.57 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.47 (dd, *J* = 6.8, 2.6 Hz, 1H), 2.74 (dddd, *J* = 21.9, 13.7, 10.2, 5.3 Hz, 2H), 2.55 (dddd, *J* = 14.0, 10.1, 6.6, 4.9 Hz, 2H), 1.94 (dddd, *J* = 13.7, 10.3, 6.7, 3.5 Hz, 1H), 1.88 – 1.74 (m, 2H), 1.70 (dddd, *J* = 13.5, 10.0, 6.7, 4.6 Hz, 1H), 1.49 – 1.38 (m, 2H), 0.97 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.98, 143.08, 142.96, 142.50, 142.28, 140.06, 139.86, 131.75 (t, *J* = 254.3 Hz), 128.51, 128.50, 128.47, 125.99, 125.93, 121.94, 121.65, 109.00, 108.99, 108.02, 107.84, 78.53, 77.56, 40.00, 39.95, 34.82, 33.98, 33.54, 33.41, 15.76, 14.38.
The diastereomers overlap at 143.98 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -50.18, -50.20.

HRMS: *m/z* (APCI): Calcd. for $C_{18}H_{18}F_2O_3$ [M – H_2 + H] 319.1146; found: 319.1147
Deydrogenation seem to occur under the APCI conditions.



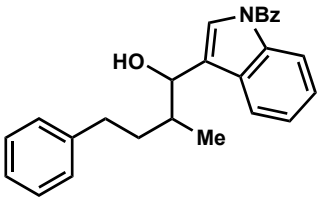
1-(benzo[*b*]thiophen-3-yl)-2-methyl-4-phenylbutan-1-ol (37)
Following General Procedure **II**, a mixture of benzo[*b*]thiophene-3-carbaldehyde (48.7 mg, 0.30 mmol, 1.5 equiv), and 4-phenyl-1-butene (**19**) (24.0 μL, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (29.8 mg, 68% yield) as an inseparable 1.3:1 mixture of diastereomers.

R_f: 0.3 (9:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.83 (m, 2H), 7.68 – 7.63 (m, 1H), 7.38 – 7.29 (m, 5H), 7.29 – 7.22 (m, 5H), 7.20 – 7.13 (m, 5H), 5.04 (d, *J* = 5.2 Hz, 1H), 4.90 (d, *J* = 6.7 Hz, 1H), 2.77 (dddd, *J* = 13.1, 10.5, 5.4, 2.9 Hz, 2H), 2.63 (ddd, *J* = 13.9, 9.7, 6.7 Hz, 1H), 2.53 (ddd, *J* = 13.7, 10.4, 6.4 Hz, 1H), 2.20 – 2.03 (m, 3H), 1.93 – 1.77 (m, 2H), 1.68 – 1.49 (m, 3H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.97 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.70, 142.35, 141.05, 139.10, 139.05, 137.39, 134.73, 128.52, 128.50, 128.41, 125.92, 125.79, 124.50, 124.45, 124.08, 124.06, 123.08, 123.05, 122.72, 122.60, 122.36, 74.93, 73.70, 38.59, 37.86, 35.39, 33.79, 33.60, 33.51, 16.70, 14.41. 3 Peaks in the aromatic part are not visible from the minor diastereomer due to overlap.

HRMS: m/z (APCI): Calcd. for $C_{19}H_{20}OS$ [M-OH]: 279.1207; found: 279.1211.



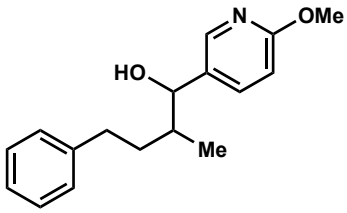
(3-(1-hydroxy-2-methyl-4-phenylbutyl)-1*H*-indol-1-yl)(phenyl)methanone (38)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol) and 1-benzoyl-1H-indole-3-carbaldehyde as the aldehyde (60 mg, 0.24 mmol). Purification by flash column chromatography (SiO_2, 4:1 hexanes/EtOAc) then further purification by PTLC (100% DCM) delivered 26 mg of the desired compound (46 %) as a clear oil and a 1:1.4 mixture of diastereomers. (Purification by PTLC was necessary to get rid of left over aldehyde).

R_f: 0.26 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.71 (td, *J* = 7.6, 7.1, 1.4 Hz, 5H), 7.66 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.55 – 7.45 (m, 6H), 7.39 (dddd, *J* = 8.5, 7.2, 5.8, 1.3 Hz, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 6H), 7.20 – 7.08 (m, 7H), 4.89 (d, *J* = 5.3 Hz, 1H), 4.76 (d, *J* = 6.7 Hz, 1H), 2.76 (ddt, *J* = 13.8, 10.0, 5.2 Hz, 2H), 2.62 (ddd, *J* = 13.9, 9.7, 6.7 Hz, 1H), 2.55 (ddd, *J* = 13.7, 10.4, 6.4 Hz, 1H), 2.12 (dtd, *J* = 13.1, 6.7, 6.0, 3.3 Hz, 1H), 2.09 – 2.00 (m, 2H), 1.82 (dddd, *J* = 13.5, 9.9, 6.7, 4.9 Hz, 2H), 1.54 – 1.45 (m, 1H), 1.02 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.72, 142.62, 142.30, 136.83, 134.71, 134.70, 132.09, 132.05, 129.31, 129.25, 129.13, 128.81, 128.79, 128.50, 128.48, 128.47, 128.45, 125.95, 125.86, 125.36, 125.33, 124.87, 124.71, 124.66, 124.43, 123.98, 123.95, 120.27, 119.95, 116.74, 116.73, 72.98, 71.93, 38.59, 38.00, 35.18, 33.94, 33.54, 33.49, 16.45, 14.52.
The diastereomers overlap at 168.72, 136.83, and 129.30.

HRMS: *m/z* (ESI): Calcd. for $C_{26}H_{25}NO_2$ [M+H]: 384.1964; found: 384.1963.



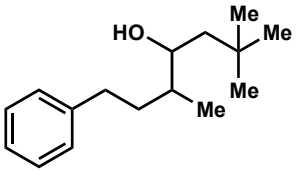
1-(6-methoxypyridin-3-yl)-2-methyl-4-phenylbutan-1-ol (39)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol) and 6-methoxy-3-pyridinecarboxaldehyde as the aldehyde (40 mg, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 4:1 hexanes/EtOAc) delivered 37 mg of the desired compound (90%) as a clear oil and a 1:1.3 mixture of diastereomers.

R_f: 0.29 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (t, *J* = 2.8 Hz, 2H), 7.55 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.50 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.32 – 7.22 (m, 4H), 7.22 – 7.14 (m, 4H), 7.14 – 7.06 (m, 2H), 6.72 (dd, *J* = 10.4, 8.5 Hz, 2H), 4.52 (d, *J* = 6.1 Hz, 1H), 4.45 (d, *J* = 7.0 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.73 (dddd, *J* = 33.9, 13.8, 10.3, 5.2 Hz, 2H), 2.55 (dddd, *J* = 20.4, 13.7, 10.1, 6.5 Hz, 2H), 2.03 – 1.77 (m, 5H), 1.68 (dtd, *J* = 14.1, 7.0, 4.1 Hz, 2H), 1.53 – 1.33 (m, 2H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.84 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.93, 163.83, 145.38, 145.20, 142.59, 142.34, 137.28, 137.13, 131.56, 131.44, 128.50, 128.48, 128.47, 128.46, 125.92, 125.88, 110.84, 110.77, 76.43, 75.87, 53.58, 39.70, 39.61, 34.59, 34.36, 33.47, 33.40, 15.54, 14.77.
The diastereomers from the Me-from the 2-Methoxy seem to be overlapping.

HRMS: *m/z* (ESI): Calcd. for $C_{17}H_{21}NO_2$ [M+H]: 272.1651; found: 272.1656.



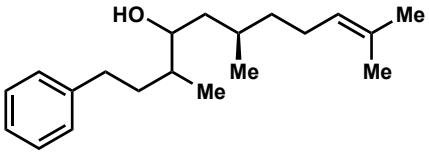
3,6,6-trimethyl-1-phenylheptan-4-ol (40)
The General Procedure **IV** was followed in a 0.3 mmol scale using 4-phenyl-1-butene as the olefin (46 μL, 0.15 mmol) and 3,3-dimethyl-butyraldehyde as the aldehyde (75 μL, 0.6 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/Et_2O) delivered 59 mg of the desired compound (84%) as a pale yellow oil and a 1:1.2 mixture of diastereomers.

R_f: 0.42 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 5H), 7.22 – 7.15 (m, 7H), 3.72 (dt, *J* = 8.3, 2.7 Hz, 1H), 3.66 (dd, *J* = 8.1, 3.8 Hz, 1H), 2.73 (tdd, *J* = 12.8, 10.4, 5.2 Hz, 2H), 2.57 (dddd, *J* = 30.1, 13.6, 9.9, 6.4 Hz, 2H), 1.86 – 1.77 (m, 1H), 1.50 – 1.38 (m, 4H), 1.38 – 1.20 (m, 7H), 0.99 – 0.90 (m, 27H). 57 total hydrogens probably due to the mixture of diastereomers (1 diastereomer = 26 H, 1.2* 26 = 31.2, 31+26 = 57H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.87, 142.84, 128.50, 128.47, 128.46, 125.86, 125.82, 73.20, 72.47, 48.48, 47.29, 40.09, 40.05, 34.86, 34.07, 33.92, 33.88, 30.36, 30.28, 30.27, 30.23, 14.94, 13.97.
The diastereomers overlap at 128.47

HRMS: *m/z* (APCI): Calcd. for $C_{16}H_{26}O$ [M + Na]: 257.1881; found: 257.1882.



(6*R*)-3,6,10-trimethyl-1-phenylundec-9-en-4-ol (41)
The General Procedure **II** was followed in a 0.15 mmol scale using 4-phenyl-1-butene as the olefin (23 μL, 0.15 mmol) and (–)-citronellal, as the aldehyde (54 μL, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/EtOAc) delivered 27 mg of the desired compound (62%) as a pale yellow oil and an inseparable 1:1:1:1 mixture of diastereomers.

R_f: 0.51 (4:1 Hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 10H), 7.24 – 7.16 (m, 10H), 5.12 (dddd, *J* = 8.5, 5.8, 2.8, 1.4 Hz, 4H), 3.69 (t, *J* = 13.0 Hz, 2H), 3.60 (d, *J* = 9.3 Hz, 2H), 2.81 – 2.69 (m, 4H), 2.66 – 2.52 (m, 4H), 2.06 – 1.90 (m, 8H),1.78 (dddd, *J* = 14.2, 10.5, 6.6, 3.3 Hz, 4H), 1.71 (dd, *J* = 2.9, 1.6 Hz, 12H), 1.63 (s, 12H), 1.49 – 1.27 (m, 18H), 1.24 – 1.07 (m, 10H), 1.05 – 0.84 (m, 24H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.25, 142.24, 142.23, 130.82, 130.76, 127.90, 127.87, 125.25, 125.23, 124.34, 124.32, 73.32, 72.84, 72.30, 72.13, 41.44, 41.19, 40.58, 40.08, 38.53, 38.14, 38.09, 37.76, 37.56, 37.41, 36.08, 35.74, 34.76, 34.60, 33.60, 33.29, 33.26, 33.20, 33.10, 29.02, 28.95, 28.64, 28.52, 25.27, 25.09, 25.05, 24.92, 20.20, 20.00, 18.66, 18.55, 17.21, 14.78, 14.56, 13.39, 12.93.

Diastereomer 1:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 8.040 min;

MS: (EI, 70 eV): *m/z* (%): 270.2 (2), 207.0 (10), 184.2 (6), 155.1 (5), 145.1 (13), 137.2 (6), 131.1 (16), 13.1 (14), 109.1 (50), 104.0 (23), 91.1 (100), 81.1 (31), 69.1 (47), 55.1 (20).

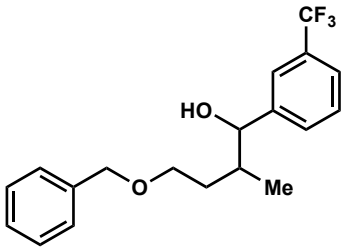
Diastereomer 2:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 8.069 min;

MS: (EI, 70 eV): *m/z* (%): 270.2 (2), 203.1 (2), 195.2 (3), 157.1 (5), 145.1 (12), 131.1 (16), 123.1 (17), 109.1 (50), 91.1 (100), 82.1 (43), 69.1 (47), 55.1 (21).

Diastereomer 3:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 8.097 min;

MS: (EI, 70 eV): *m/z* (%): 270.2 (2), 207.1 (5), 145.1 (12), 123.1 (17), 109.1 (50), 91.1 (100), 81.1 (26), 69.1 (45), 55.1 (20).

HRMS: m/z (ESI): Calcd. for $C_{20}H_{32}O$ [M + H]: 289.2531; found: 289.2525



4-(benzyloxy)-2-methyl-1-(3-(trifluoromethyl)phenyl)butan-1-ol (42)
The General Procedure **IV** was followed in a 0.15 mmol scale using 24 mg of ((but-3-en-1-yloxy)methyl)benzene as the olefin and 34 μL of 3-(trifluoromethyl)benzaldehyde as the aldehyde (0.3 mmol). Purification by flash column chromatography (SiO_2 hexanes then 9:1 hexanes/Et_2O) delivered 30 mg of the desired compound (59%) as a clear oil and a 1:1.3 mixture of diastereomers.

R_f: 0.38 (4:1 hexanes/EtOAc)

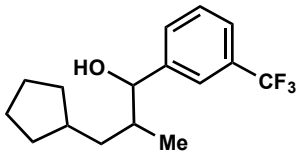
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.57 (m, 2H), 7.50 (ddd, *J* = 9.4, 7.6, 3.8 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38 – 7.32 (m, 8H), 7.30 (ddt, *J* = 8.5, 5.8, 2.2 Hz, 2H), 4.80 – 4.75 (m, 1H), 4.54 (s, 4H), 4.48 (dd, *J* = 7.2, 2.5 Hz, 1H), 3.67 – 3.57 (m, 4H), 3.54 (dddd, *J* = 9.5, 7.6, 6.5, 4.5 Hz, 2H), 2.08 – 1.99 (m, 2H), 1.85 – 1.75 (m, 2H), 1.69 – 1.59 (m, 2H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.01, 144.66, 137.94, 137.83, 130.62 (q, *J* = 32.4 Hz), 130.49 (q, *J* = 32.4 Hz), 130.25 (d, *J* = 1.2 Hz), 129. 76 (d, *J* = 1.2 Hz), 128.67, 128.65, 128.54, 128.00, 127.98, 127.96, 124.36 (q, *J* = 272.3 Hz), 124.18 (q, *J* = 3.8 Hz), 123.86 (q, *J* = 3.8 Hz), 123.62 (q, *J* = 3.8 Hz), 123.19 (q, *J* = 3.8 Hz), 78.37, 76.21, 73.43, 73.41, 68.18, 68.08, 38.99, 38.36, 33.60, 32.58, 17.02, 13.33.

The diastereomers overlap at 128.65, 127.98, and 124.36.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.71, -62.73.

HRMS: *m/z* (APCI): Calcd. for $C_{19}H_{21}F_3O_2$ [M + Na]: 361.1391; found: 361.1382



3-cyclopentyl-2-methyl-1-(3-(trifluoromethyl)phenyl)propan-1-ol (43)
The General Procedure **IV** was followed in a 0.15 mmol scale using allylcyclopentane as the olefin (21 μL, 0.15 mmol) and 3-(trifluoromethyl)benzaldehyde as the aldehyde (36 μl, 0.27 mmol). Purification by FCC (hexanes then 9:1 hexanes:Et_2O) delivered 20 mg of the desired compound (47% IY) as a pale yellow oil and as a 1:1.4 mixture of diastereomers.

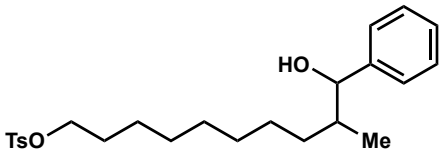
R_f: 0.43 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (bs, *J* = 2.6 Hz, 2H), 7.55 – 7.48 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.66 (dd, *J* = 5.0, 2.8 Hz, 1H), 4.54 (dd, *J* = 6.3, 2.5 Hz, 1H), 1.94 – 1.80 (m, 5H), 1.80 – 1.69 (m, 5H), 1.64 – 1.54 (m, 5H), 1.54 – 1.42 (m, 5H), 1.34 – 1.17 (m, 6H), 1.13 – 1.03 (m, 2H), 0.97 (dqd, *J* = 11.8, 8.3, 5.6 Hz, 2H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.81 (d, *J* = 6.8 Hz, 4H). 48 H total due to 1:1.4 mixture of diastereomers.

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.99, 144.50, 130.63 (q, *J* = 32.2 Hz), 130.17 (d, *J* = 1.1 Hz), 129.79 (d, *J* = 1.0 Hz), 128.69, 128.67, 124.35 (q, *J* = 272.4 Hz), 124.35 (q, *J* = 272.4 Hz), 124.29 (q, *J* = 3.9 Hz), 124.09 (q, *J* = 3.9 Hz), 123.57, (q, *J* = 3.9 Hz), 123.22 (q, *J* = 3.9 Hz), 78.80, 76.95, 39.80, 39.43, 39.40, 38.47, 37.65, 37.62, 33.88, 33.48, 32.45, 32.15, 25.22, 25.21, 25.19, 15.84, 14.02.
The diastereomers overlap at 28.21 and at 130.63.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.77, -62.78.

Both diastereomers overlap:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.650 min;
MS: (EI, 70 eV): *m/z* (%): 268.1 (2), 202.0 (10), 186.1 (11), 175.0 (100), 145.0 (11), 127.0 (38), 111.1 (52), 69.1 (68), 55.1 (20).



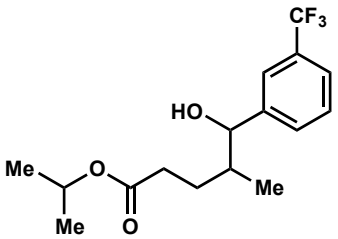
10-hydroxy-9-methyl-10-phenyldecyl 4-methylbenzenesulfonate (44)
The General Procedure **II** was followed in a 0.15 mmol scale using dec-9-en-1-yl 4-methylbenzenesulfonate (47 mg, 0.15 mmol) as the olefin and benzaldehyde as the aldehyde (30 μL, 0.3 mmol). Purification by FCC (hexanes then 9:1 hexanes:EtOAc then 4:1 hexanes:EtOAc) the preparative TLC (100% DCM) delivered 48 mg of the desired compound (76% IY) as a pale yellow oil and a 1:1.3 mixture of diastereomers. (preparative TLC was necessary to get rid of left over alcohol that overlapped with the compound).

R_f: 0.21 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.79 – 7.74 (m, 4H), 7.37 (ddd, *J* = 8.5, 2.8, 0.9 Hz, 5H), 7.35 – 7.28 (m, 9H), 7.25 (tdd, *J* = 8.5, 4.5, 2.7 Hz, 2H), 4.52 (d, *J* = 5.7 Hz, 1H), 4.42 (d, *J* = 6.9 Hz, 1H), 3.99 (td, *J* = 6.6, 4.3 Hz, 4H), 2.44 (s, 4H), 2.44 (s, 3H),1.86 – 1.69 (m, 2H), 1.65 – 1.54 (m, 6H), 1.41 – 1.03 (m, 22H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.74 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 145.45, 144.79, 144.47, 133.75, 130.39, 128.59, 128.34, 127.76, 127.59, 127.23, 126.90, 79.33, 78.41, 71.45, 71.43, 40.79, 40.72, 33.70, 32.58, 30.32, 30.16, 29.90, 29.84, 29.43, 29.39, 29.32, 27.63, 27.47, 25.84, 25.83, 21.92, 16.05, 14.59.

HRMS: *m/z* (APCI): Calcd. for $C_{24}H_{34}O_4S$ [M + Na] 441.2075; found: 441.2071.



isopropyl 5-hydroxy-4-methyl-5-(3-(trifluoromethyl)phenyl)pentanoate (45)
The general procedure **IV** was followed on a 0.1 mmol scale using isopropyl pent-4-enoate as the olefin (14 mg, 0.1 mmol) and 3-trifluoromethylbenzaldehyde as the aldehyde (27 μL, 0.2 mmol). Purification by PTLC (4:1 hexanes/EtOAc) delivered 21 mg of the desired compound as a clear oil and a 1:1 mixture of diastereomers.

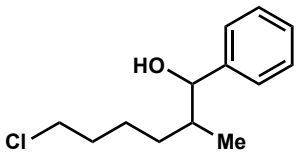
R_f: 0.31 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.5 Hz, 2H), 7.51 (dt, *J* = 12.7, 7.1 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.00 (hept, *J* = 6.3 Hz, 2H), 4.69 (d, *J* = 2.6 Hz, 1H), 4.49 (d, *J* = 7.1 Hz, 1H), 2.44 – 2.33 (m, 2H), 2.33 – 2.21 (m, 2H), 1.97 (dddd, *J* = 13.8, 8.6, 7.2, 3.7 Hz, 1H), 1.89 – 1.76 (m, 3H), 1.56 – 1.43 (m, 2H), 1.22 (d, *J* = 2.7 Hz, 6H), 1.21 (d, *J* = 2.7 Hz, 6H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.69, 173.62, 144.50, 144.44, 130.19, 129.72, 128.84, 128.75, 124.50 (q, *J* = 4.3 Hz), 124.17 (q, *J* = 4.2 Hz), 123.57 (q, *J* = 3.8 Hz), 123.12 (q, *J* = 3.8 Hz), 78.32, 76.30, 67.98, 67.89, 40.02, 39.96, 32.56, 32.19, 28.24, 27.31, 21.96, 21.94, 15.85, 13.67.

Diastereomer 1:
GC: GC/MSD (HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.501 min;
MS: (EI, 70 eV): *m/z* (%): 316.1 (0.02), 258.1 (21), 239.1 (19), 186.1 (15), 172.0 (27), 145.0 (27), 127.0 (12), 117.1 (26), 84.0 (40), 56.0 (100).

Diastereomer 2:
GC: GC/MSD (HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.541 min;
MS: (EI, 70 eV): *m/z* (%): 258.1 (26), 239.1 (23), 186.0 (6), 172.0 (25), 145.0 (30), 127.0 (14), 117.1 (12), 84.0 (40), 56.0 (100).



6-chloro-2-methyl-1-phenylhexan-1-ol (46)

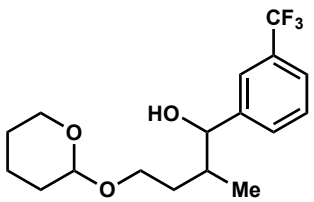
The General Procedure **II** was followed in a 0.15 mmol scale using 5-chloropent-1-ene as the olefin (16 mg, 0.15 mmol) and benzaldehyde as the aldehyde (30 μL, 0.3 mmol). Purification by FCC (hexanes then 9:1 hexanes/Et_2O) delivered 29 mg of the desired compound (86%) as a pale yellow oil and a 1:1.1 mixture of diastereomers.

R_f: 0.5 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 4H), 7.32 – 7.29 (m, 4H), 7.29 – 7.26 (m, 2H), 4.53 (d, *J* = 5.8 Hz, 1H), 4.43 (d, *J* = 7.0 Hz, 1H), 3.53 (td, *J* = 6.7, 1.0 Hz, 2H), 3.49 (td, *J* = 6.7, 1.3 Hz, 2H), 1.88 – 1.64 (m, 10H), 1.63 – 1.47 (m, 2H), 1.38 (tddd, *J* = 13.6, 10.3, 8.7, 5.4 Hz, 2H), 1.24 – 1.14 (m, 1H), 1.15 – 1.05 (m, 1H), 0.94 (d, *J* = 6.7 Hz, 3H), 0.77 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.77, 143.61, 128.39, 128.37, 127.66, 127.49, 126.77, 126.48, 79.09, 78.25, 45.24, 45.16, 40.19, 40.12, 32.99, 32.85, 32.41, 31.51, 24.61, 24.44, 15.84, 14.53.

HRMS: *m/z* (APCI): Calcd. for $C_{13}H_{19}ClO$ [M – H_2 + H]: 225.1046; found: 225.1051.
Dehydrogenation of the alcohol to the ketone seems to occur under the APCI conditions.



2-methyl-4-((tetrahydro-2*H*-pyran-2-yl)oxy)-1-(3-(trifluoromethyl)phenyl)butan-1-ol (47)

Following General Procedure **II**, a mixture of 3-trifluorobenzaldehyde (36.0 μL, 0.30 mmol, 1.5 equiv), and 2-(but-3-en-1-yloxy)tetrahydro-2H-pyran (23.4 mg, 0.15 mmol, 1.0 equiv) was stirred for 24 h. Purification by flash column chromatography (SiO_2, 8:2 hexanes/EtOAc) furnished the title compound as clear, pale yellow oil (36 mg, 72% yield) as an inseparable mixture of 4 diasteromers.

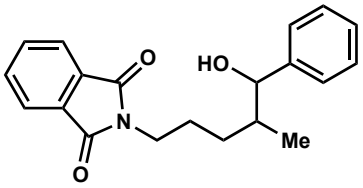
R_f: 0.30 (4:1 hexanes/EtOAc)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 3H), 7.55 – 7.48 (m, 6H), 7.44 (t, *J* = 7.7 Hz, 3H), 4.85 (d, *J* = 3.8 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.65 – 4.58 (m, 3H), 4.52 (dd, *J* = 7.3, 3.4 Hz, 1H), 3.95 (dddd, *J* = 10.0, 7.1, 4.7, 2.7 Hz, 2H), 3.86 (dddd, *J* = 17.4, 13.0, 7.0, 3.1 Hz, 4H), 3.60 – 3.46 (m, 5H), 3.43 (ddd, *J* = 9.9, 7.5, 4.6 Hz, 1H), 2.04 (dddd, *J* = 16.2, 13.1, 8.3, 4.5 Hz, 3H), 1.87 – 1.49 (m, 27H), 0.88 – 0.78 (m, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.97, 144.69, 144.67, 130.28, 129.78, 129.74, 128.69, 128.57, 128.53, 124.22, 124.20, 123.90, 123.88, 123.83, 123.80, 123.21, 123.20, 123.17, 99.63, 99.38, 99.08, 78.51, 78.35, 76.39, 75.90, 66.04, 65.64, 65.40, 65.33, 62.87, 62.63, 62.58, 62.56, 39.07, 39.01, 38.61, 38.40, 33.59, 32.78, 32.38, 30.81, 30.72, 30.71, 30.65, 25.48, 25.45, 19.89, 19.69, 19.62, 17.11, 16.87, 13.52, 13.32; Note: no C-F peaks coupling is reported as it is not clear to identify them in its entirety due to the mixture of 4 diastereomers.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73, -62.74, -62.76, -62.77.

HRMS: *m/z* (ESI): Calcd. for $C_{17}H_{23}F_3O_3$ [M+Na]: 355.1497; found: 355.1500.



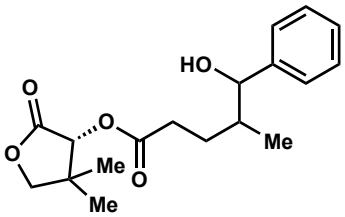
2-(5-hydroxy-4-methyl-5-phenylpentyl)isoindoline-1,3-dione (48)
The General Procedure **II** was followed in a 0.15 mmol scale using 2-(pent-4-en-1-yl)isoindoline-1,3-dione as the olefin (32 mg, 0.15 mmol) and benzaldehyde as the aldehyde (30 μL, 0.3 mmol) (. Purification by FCC (Hexanes:EtOAc 9:1 then 4:1) delivered 39 mg of the desired compound (80%) as a clear oil and a 1:1.2 mixture of diastereomers.

R_f: 0.16 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (td, *J* = 5.2, 3.0 Hz, 4H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 4H), 7.33 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 4.55 (d, *J* = 4.2 Hz, 1H), 4.40 (d, *J* = 6.6 Hz, 1H), 3.68 (t, *J* = 7.3 Hz, 2H), 3.62 (ddd, *J* = 7.7, 6.7, 1.9 Hz, 2H), 1.91 – 1.69 (m, 6H), 1.69 – 1.59 (m, 2H), 1.46 – 1.38 (m, 1H), 1.29 – 1.19 (m, 2H), 1.15 (dddd, *J* = 13.7, 10.5, 8.8, 5.0 Hz, 1H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.64, 168.57, 143.60, 143.56, 134.00, 132.32, 132.28, 128.40, 128.33, 127.66, 127.43, 126.78, 126.44, 123.32, 79.05, 78.06, 39.91, 39.83, 38.31, 38.15, 30.23, 29.45, 26.29, 26.19, 15.86, 14.40.

HRMS: *m/z* (ESI): Calcd. for $C_{20}H_{21}NO_3$ [M+H]: 324.1600; found: 324.1595.



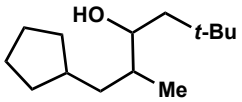
(*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl 5-hydroxy-4-methyl-5-phenylpentanoate (49)
The General Procedure **II** was followed in a 0.15 mmol scale using (*R*)-4,4-dimethyl-2-oxotetrahydrofuran-3-yl pent-4-enoate as the olefin (32 mg, 0.15 mmol) and benzaldehyde as the aldehyde (30 μL, 0.3 mmol). Purification by FCC (9:1 then 4:1 hexanes/EtOAc) delivered 33 mg of the desired compound (69%) as a viscous oil and a 1:1.6:2.2:2.4 mixture of diastereomers based on integration of the α-hydrogen in the lactone.

R_f: 0.19 (4:1 Hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 35H), 7.31 (dt, *J* = 6.0, 1.6 Hz, 3H), 7.27 (t, *J* = 1.6 Hz, 1H), 5.41 (s, 1H), 5.40 (s, 1H), 5.38 (s, 2H), 5.37 (s, 3H), 4.63 (t, *J* = 5.5 Hz, 6H), 4.44 (t, *J* = 7.8 Hz, 3H), 4.14 – 3.94 (m, 26H), 2.73 – 2.38 (m, 19H), 2.22 – 2.07 (m, 3H), 1.96 – 1.79 (m, 10H), 1.65 (d, *J* = 4.9 Hz, 4H), 1.61 – 1.57 (m, 2H), 1.53 (dtdd, *J* = 10.9, 8.7, 6.1, 3.6 Hz, 6H), 1.22 (dd, *J* = 9.5, 2.4 Hz, 28H), 1.15 – 1.06 (m, 32H), 0.95 (dd, *J* = 6.8, 4.7 Hz, 18H), 0.80 (dd, *J* = 6.9, 5.2 Hz, 9H).
The integration of the diastereomers was normalized to the closest integer.

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.77, 172.37, 172.27, 172.18, 172.15, 172.08, 172.07, 171.99, 142.87, 142.70, 142.64, 127.90, 127.89, 127.83, 127.79, 127.21, 127.17, 126.98, 126.93, 126.17, 126.17, 125.86, 125.83, 78.42, 78.40, 77.02, 76.91, 75.85, 75.80, 75.78, 75.77, 75.75, 75.30, 74.44, 74.42, 39.73, 39.70, 39.17, 39.14, 39.14, 39.08, 31.33, 31.28, 31.26, 31.17, 29.25, 27.67, 27.55, 27.21, 22.60, 22.58, 22.47, 19.47, 18.32, 15.42, 15.36, 13.62, 13.60.
The diastereomers overlap at 142.87 and 19.47.

HRMS: Calcd. for $C_{18}H_{24}O_5$ [M - OH]: 303.1596; found: 303.1599.



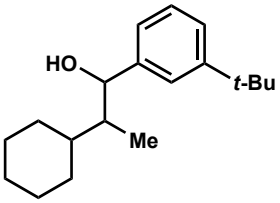
1-cyclopentyl-2,5,5-trimethylhexan-3-ol (50)
The General Procedure **IV** was followed in a 0.3 mmol scale and at 0 °C using allylcyclopentane as the olefin (42 μL, 0.3 mmol) and and 3,3-dimethyl-butyraldehyde as the aldehyde (75 μL, 0.6 mmol). Purification by FCC (hexanes then 9:1 hexanes/Et_2O) delivered 25 mg of the desired compound (39%) as a pale yellow oil and as a 1:1.5 mixture of diastereomers. Also, the reaction was ran at 0 °C.

R_f: 0.39 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.66 (dt, *J* = 6.2, 2.8 Hz, 1H), 3.64 – 3.60 (m, 2H), 1.92 – 1.80 (m, 3H), 1.79 – 1.69 (m, 4H), 1.61 (ttd, *J* = 9.6, 6.6, 4.0 Hz, 6H), 1.56 – 1.44 (m, 4H), 1.41 – 1.14 (m, 13H), 1.14 – 0.99 (m, 8H), 0.95 (s, 22H), 0.89 (d, *J* = 6.8 Hz, 4H), 0.85 (d, *J* = 6.8 Hz, 3H).
70 H because of 1:1.5 mixture of diastereomers.

^{13}C NMR (151 MHz, $CDCl_3$) δ 73.56, 72.67, 48.68, 47.23, 39.63, 39.47, 39.35, 38.49, 37.80, 37.76, 33.78, 33.56, 32.61, 32.39, 30.35, 30.28, 30.22, 25.31, 25.27, 25.24, 15.07, 13.98.
The diastereomers overlap at 25.27 and 30.27.

HRMS: *m/z* (APCI): Calcd. for $C_{14}H_{28}O$ [M – H_2 + H] 211.2062; found: 211.2062.
Dehydrogenation seem to occur under the APCI conditions.



1-(3-(*tert*-butyl)phenyl)-2-cyclohexylpropan-1-ol (52)
The General Procedure **IV** was followed on a 0.15 mmol scale using vinylcyclohexane (18 μL, 0.15 mmol) as the olefin and 3-(*tert*-butyl)benzaldehyde as the aldehyde (30 μL, 0.2 mmol). Purification by FCC (SiO_2, 9:1 hexanes/EtOAc) delivered 22 mg (53%) as a pale yellow oil and a 1:1.5 mixture of diastereomers.

R_f: 0.65 (4:1 hexanes/EtOAc)

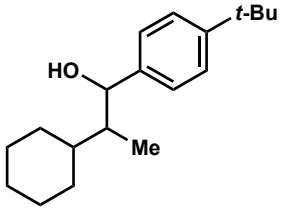
^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.32 (q, *J* = 2.0 Hz, 3H), 7.31 – 7.22 (m, 5H), 7.12 (dq, *J* = 7.5, 1.6 Hz, 3H), 4.72 (d, *J* = 5.8 Hz, 1H), 4.44 (d, *J* = 9.0 Hz, 1.5H), 1.89 – 1.51 (m, 20H), 1.31 (s, 18H), 1.30 – 0.97 (m, 16H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.53 (d, *J* = 7.1 Hz, 4H). (75 H total because of 1:1.5 mixture of diastereomers).

^{13}C NMR (151 MHz, CD_2Cl_2) δ 151.70, 151.54, 145.07, 144.72, 128.41, 128.36, 124.86, 124.58, 124.49, 124.37, 123.88, 123.69, 77.40, 76.51, 46.34, 45.73, 40.27, 38.38, 35.11, 32.73, 32.28, 31.69, 29.51, 27.73, 27.50, 27.40, 27.36, 27.26, 27.23, 27.18, 11.67, 10.73.
The diastereomers overlap at 31.69 and at a second peak.

Diastereomer 1 (minor):
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.714 min;
MS: (EI, 70 eV): *m/z* (%): 256.2 (23), 241.1 (10), 199.2 (10), 190.1 (24), 163.1 (100), 147.1 (13), 129.0 (11), 109.1 (29), 91.0 (25), 67.0 (11), 57.1 (56).

Diastereomer 2 (major):
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.760 min;
MS: (EI, 70 eV): *m/z* (%): 274.2 (0.3), 256.2 (19), 241.2 (8), 199.1 (8), 163.1 (100), 91.1 (16), 57.1 (43).

HRMS: *m/z* (APCI): Calcd. for $C_{19}H_{30}O$ [M + H]: 275.2375; found: 275.2777.



1-(4-(*tert*-butyl)phenyl)-2-cyclohexylpropan-1-ol (53)
The General Procedure **II** was followed on a 0.1 mmol scale using vinylcyclohexane (12 μL, 0.1 mmol) as the olefin and 4-(*tert*-butyl)benzaldehyde as the aldehyde (30 μL, 0.2 mmol), and the following modifications:

- 0.2 equiv. of Co(salen) and 0.2 equiv. of the oxidant were used. Purification by PTLC (4:1 hexanes:EtOAc) delivered 17 mg of the desired compound (63%) as a clear oil and a 1:1.3 mixture of diastereomers.

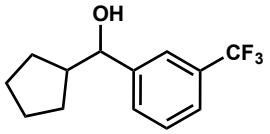
R_f: 0.58 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 5H), 7.24 (dt, *J* = 8.1, 3.5 Hz, 5H), 4.75 (d, *J* = 5.7 Hz, 1H), 4.43 (d, *J* = 9.4 Hz, 1H), 1.88 (tt, *J* = 11.9, 3.2 Hz, 1H), 1.82 – 1.65 (m, 13H), 1.65 – 1.52 (m, 5H), 1.42 – 1.35 (m, 1H), 1.32 (s, 9H), 1.32 (s, 13H), 1.28 – 1.09 (m, 5H), 1.07 – 0.95 (m, 2H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.54 (d, *J* = 7.1 Hz, 4H). (68H due to 1:1.3 mixture of diastereomers. It should be 69 H but the H adjacent to the alcohol in the product of the major diastereomer was normalized to 1H (integration is 1.3H)).

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.67, 150.08, 141.76, 141.49, 126.74, 125.91, 125.38, 125.26, 76.61, 75.65, 45.62, 45.22, 39.81, 37.81, 34.67, 34.62, 32.28, 31.85, 31.54, 31.52, 29.22, 27.22, 27.08, 26.87, 26.85, 26.82, 26.68, 26.66, 11.55, 10.41.

Diastereomer 1:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.891 min;
MS: (EI, 70 eV): *m/z* (%): 274 (0.3), 256.2 (2), 241.2 (2), 163.1 (100), 133.1 (5), 105.1 (3), 91.1 (6), 57.1 (13).

Diastereomer 2:
GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 7.937 min;
MS: (EI, 70 eV): *m/z* (%): 274.2 (0.4), 256.2 (2), 241.2 (3), 190.2 (3), 163.2 (100), 57.1 (14).



cyclopentyl(3-(trifluoromethyl)phenyl)methanol (54)
The General Procedure **III** was followed on a 0.15 mmol scale using cyclopentene (13 μL, 0.15 mmol) as the olefin and 3-(trifluoromethyl)benzaldehyde as the aldehyde (36 μl, 0.27 mmol). And the following modifications:

- 1 equiv. of $NaBF_4$ (16 mg, 0.15 mmol) was used as an additive

Purification by FCC (hexanes then 9:1 hexanes/Et_2O) delivered 27 mg of the desired compound (73%) as a pale yellow oil.

Note: $NaBF_4$ seemed to have a beneficial effect in the dissolution of the $CrCl_3$ anhydrous and in increasing the yield of product, but its benefit seems to be substrate-dependent. For instance, although it seemed to helped in increasing the yield of the reaction with cyclopentene (54% without it), it did not help in the case of cyclohexene below.

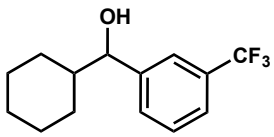
R_f: 0.27 (9:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.9 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 1H), 4.51 (d, *J* = 8.1 Hz, 1H), 2.27 – 2.16 (m, 1H), 1.86 (m, *J* = 11.9, 7.3, 4.7 Hz, 1H), 1.67 (m, *J* = 12.9, 9.1, 4.8, 3.1 Hz, 1H), 1.63 – 1.45 (m, 4H), 1.40 (m, *J* = 12.4, 11.5, 6.5, 3.1 Hz, 1H), 1.18 (m, *J* = 12.7, 8.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 145.50, 130.81 (q, *J* = 32.5 Hz), 129.97 (d, *J* = 1.2 Hz), 128.88, 124.44 (q, *J* = 3.8 Hz), 124.12 (q, *J* = 273.3 Hz), 123.38 (q, *J* = 3.8 Hz), 78.50, 47.91, 29.50, 29.29, 25.61, 25.55.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.79.

HRMS: *m/z* (APCI): Calcd. for $C_{13}H_{15}F_3O$ [M – OH] 227.1048; found: 227.1047.



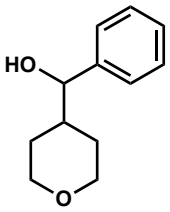
cyclohexyl(3-(trifluoromethyl)phenyl)methanol (55)
The General Procedure **III** was followed in a 0.15 mmol scale using cyclohexene as the olefin (15 μL, 0.15 mmol) and 3-(trifluoromethyl)benzaldehyde as the aldehyde (36 μL, 0.27 mmol). Purification by FCC (hexanes then 9:1 hexanes/Et_2O) delivered 20 mg of the desired compound (51%) as a pale yellow oil.

R_f: 0.52 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.1 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.50 – 7.47 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 4.46 (dd, *J* = 6.9, 2.6 Hz, 1H), 1.96 – 1.86 (m, 2H), 1.81 – 1.73 (m, 1H), 1.72 – 1.67 (m, 1H), 1.67 – 1.57 (m, 1H), 1.44 – 1.37 (m, 1H), 1.28 – 1.10 (m, 3H), 1.08 – 1.00 (m, 1H), 1.01 – 0.92 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.66, 130.66 (q, J = 32.5 Hz), 130.11 (q, J = 1.6, 1.1 Hz), 128.71, 124.34 (q, J = 273.5 Hz), 124.33 (q, J = 3.7 Hz), 123.51 (q, J = 3.7 Hz), 78.85, 45.18, 29.37, 28.51, 26.46, 26.17, 26.07.
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.77.

HRMS: *m/z* (APCI): Calcd. for $C_{14}H_{17}F_3O$ [M – OH] 241.1204; found: 241.1210.



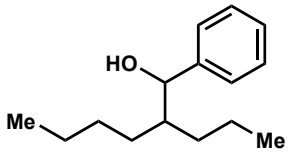
phenyl(tetrahydro-2*H*-pyran-4-yl)methanol (56)
The General Procedure **III** was followed in a 0.15 mmol scale using 3,6-dihydro-2*H*-pyran as the olefin (13 mg, 0.15 mmol) and benzaldehyde as the aldehyde (30 µl, 0.3 mmol). Purification by flash column chromatography (SiO_2, 9:1 hexanes/EtOAc then 4:1 hexanes/EtOAc) delivered 15 mg of the desired compound (52%) as a clear oil and a single regioisomer and diastereomer.

R_f: 0.25 (7:3 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 3H), 4.37 (d, J = 7.7 Hz, 1H), 4.02 (ddd, J = 11.5, 5.1, 1.7 Hz, 1H), 3.90 (ddd, J = 11.3, 5.5, 1.8 Hz, 1H), 3.37 (ddd, J = 12.3, 11.5, 2.3 Hz, 1H), 3.32 – 3.25 (m, 1H), 1.91 (ddq, J = 13.2, 4.2, 2.2 Hz, 1H), 1.85 (dtt, J = 11.7, 7.9, 3.8 Hz, 1H), 1.51 – 1.41 (m, 1H), 1.38 – 1.28 (m, 1H), 1.16 (ddq, J = 13.3, 4.2, 2.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.98, 128.57, 127.98, 126.76, 79.06, 68.03, 67.84, 42.58, 29.48, 29.36.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.518 min;
MS: (EI, 70 eV): *m/z* (%): 191.9 (3), 174.1 (8), 129.1 (19), 114.9 (10), 107.1 (100), 105.0 (22), 91.0 (12), 85.0 (22), 79.0 (42), 68.0 (11), 50.9 (10).



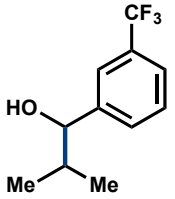
1-phenyl-2-propylhexan-1-ol (57)
The General Procedure **III** was followed in a 0.15 mmol scale using trans-4-octene as the olefin (24 µL, 0.15 mmol) and benzaldehyde as the aldehyde (30 µL, 0.3 mmol). Purification by flash column chromatography (SiO_2, hexanes then 9:1 hexanes/Et_2O) delivered 11 mg of the desired compound (33%) as a clear oil and a 1:1.1 mixture of diastereomers.

R_f: 0.71 (4:1 hexanes/EtOAc)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 8H), 7.27 (d, J = 2.1 Hz, 1H), 7.25 (t, J = 2.1 Hz, 1H), 4.67 (d, J = 2.5 Hz, 1H), 4.66 (d, J = 2.6 Hz, 1H), 1.74 – 1.50 (m, 4H), 1.47 – 1.05 (m, 16H), 0.85 (qt, J = 7.1, 5.3 Hz, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.16, 128.31, 127.33, 127.32, 126.55, 126.54, 76.43, 76.40, 44.88, 44.84, 32.38, 31.09, 29.79, 29.36, 29.22, 28.42, 23.26, 23.15, 20.27, 20.21, 14.64, 14.55, 14.22, 14.20.
The diastereomers overlap at 144.16 and 128.31.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 6.403 min (both diastereomers overlap);
MS: (EI, 70 eV): *m/z* (%): 219.0 (3), 202.1 (10), 129.0 (8), 117.0 (27), 107.0 (100), 91.0 (19), 79.1 (20), 55.0 (6).



2-methyl-1-(3-(trifluoromethyl)phenyl)propan-1-ol (58)

The title compound was prepared by treating 3-(trifluoromethyl)benzaldehyde (510 μL, 5 mmol) with isopropylmagnesium chloride (2.5 mL of a 2 M solution, 5 mmol) at room temperature in Et_2O (10 mL). After stirring overnight, the reaction was quenched by addition of NH_4Cl, extracted with Et_2O, dried with $MgSO_4$, and concentrated under vacuo. The desired compound was purified by flash column chromatography (SiO_2, pentanes/Et_2O 9:1) to afford 215 mg (20%) as a yellow oil (reduction of the aldehyde to the alcohol was a major by-product).

R_f: 0.57 in 9:1 hexanes/EtOAc

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.55 – 7.51 (m, 1H), 7.51 – 7.48 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 6.3 Hz, 1H), 1.95 (m, 1H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.83 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.68, 130.05, 128.72, 124.22 (q, *J* = 3.8 Hz), 123.44 (q, *J* = 3.8 Hz), 79.37, 35.46, 19.00, 17.87.

GC: (GC/MSD; HP-5MS UI; 139 Kpa; flow rate 2 mL/min; inlet temperature 250 °C; column temperature 50 °C for 0 min, then 20 °C/min to 100 °C, then 30°C/min to 280 °C): t_R = 4.366 min;
MS: (EI, 70 eV): *m/z* (%): 218.1 (1), 200.1 (8), 175.0 (100), 145.0 (10), 127.0 (48), 51.0 (2).

Stoichiometric experiments

Part 1: Formation of alkyl-cobalt and determination of its yield

Following a modified procedure,[xix] in a N_2-filled glove box, an oven-dried 1 dram vial containing Co(II) (30 mg, 0.05 mmol), pyridine-d5 (8 µL, 0.1 mmol), and ca. 20% Na/Hg (25 mg, 0.25 mmol) THF was added (0.6 mL, 0.08 M) to form a red suspension. The mixture was stirred for 30 minutes at room temperature at which point the suspension had turned into a homogeneous green solution. The stirring was stopped to allow residual Na/Hg to settle at the bottom of the vial and the solution was transferred to a 1-dram vial containing 2-bromopropane (5 µl, 0.06 mmol) in 0.6 mL of THF. The solution turned into a brown homogeneous solution right away. This reaction mixture was left stirring for 30 minutes, at which point trimethoxybenzene (150 µL of a 0.33 M solution in THF, 0.05 mmol) was added. An aliquot of approximately 50 µL of this solution was taken and diluted in 500 µL of d6-DMSO in an NMR tube. The NMR tubed was capped and covered with parafilm before being taken out of the glovebox. ^{1}H NMR analysis indicated that the alkyl cobalt was present in 21% yield. The reaction was repeated and a similar yield was obtained (19%). See reference **xx** for a discussion of possible reaction through the ligand under similar conditions in Co(salen) complexes.

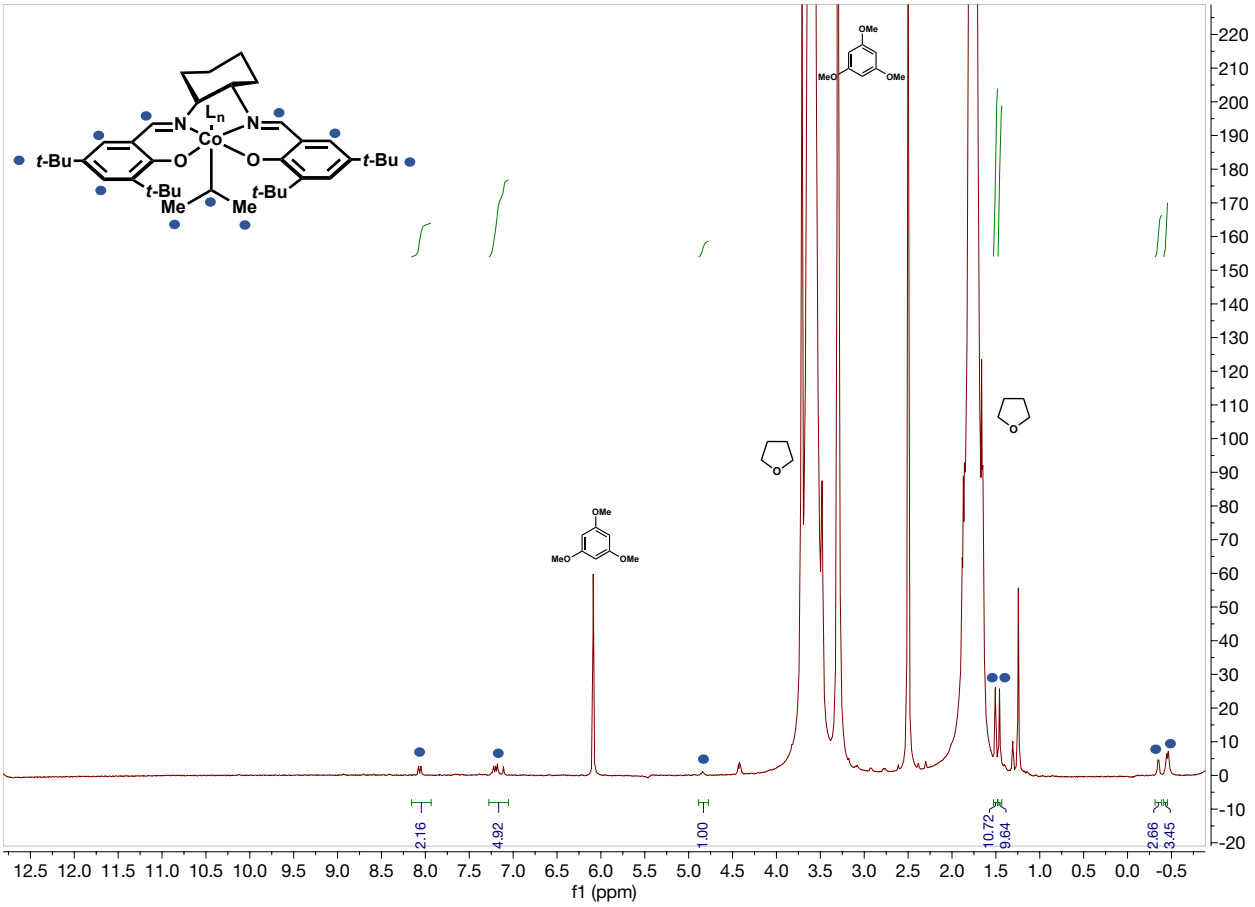


Figure S3a: Identification of the alkyl-cobalt by ^{1}H NMR using trimethoxybenzene as an internal standard. See reference **xix** for full characterization. Some peaks overlap with residual THF.

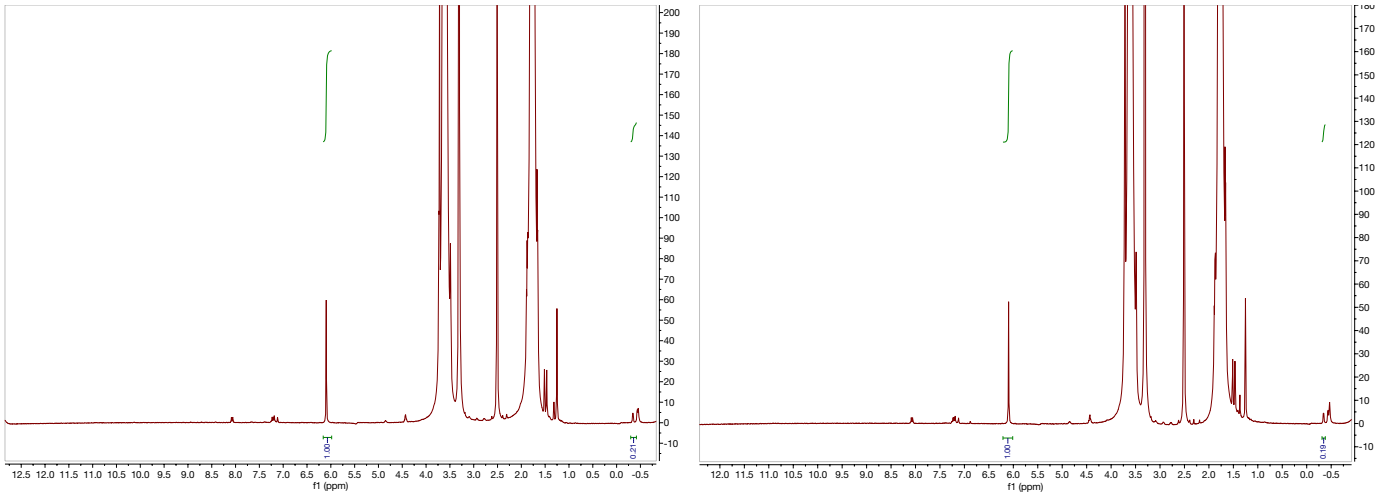


Figure S3b: Determination of the NMR yield of the alkyl-cobalt by S_N2 of $Co^{I}(Sal^{t\text{-}Bu,\ t\text{-}Bu})(py)_2$ with isopropyl bromide (two independent experiments).

Part 2: Reaction with Cr^{+2}

To the solution mentioned in Part 1, $CrCl_2$ (12 mg, 0.1 mmol), and 3-trifluoromethylbenzaldehyde (12 μL, 0.1 mmol) were added. The reaction was capped with a septum, covered with parafilm, and taken out of the glovebox. The mixture was stirred for 24 hours at room temperature at which point dodecane was added (11 μL, 0.05 mmol) and an aliquot was analyzed by GC-FID. The yield was determined to be 11% when compared to 0.05 mmol of dodecane. Given that the alkyl-cobalt was formed in 20% average, this correspond to a yield in the range of 52-57%.

Part 3: Reaction with Cr^{+3}

The procedure described in Part 1 was repeated. To the brown solution obtained at the end, $CrCl_3(THF)_3$ (37 mg, 0.1 mmol), and 3-trifluoromethylbenzaldehyde (12 μL, 0.1 mmol) were added. The reaction was capped with a septum, covered with parafilm, and taken out of the glovebox. The mixture was stirred for 24 hours at room temperature at which point dodecane was added (11 μL, 0.05 mmol) and an aliquot was analyzed by GC-FID. No product was observed on two repetitions of the reaction.

Part 4: Control experiment with bromopropane

To an oven-dried vial that contained $CrCl_2$ (15 mg, 0.12 mmol) in 600 μL of THF, 2 equiv. of aldehyde (12 μL, 0.1 mmol) and 1 equiv. of the isopropyl bromide (5 μL, 0.05 mmol) were added. The reaction was left stirring for 24 hours under Argon, then 11 μL of dodecane were added and the reaction was analyzed by GC/MS and GC/FID comparing to a sample of authentic material. No product was observed. Note: Due to the volatility of the alkyl-bromide, it was not possible to determine what happened to the starting material. Only recovered aldehyde was observed.

Observation of the alkyl–[Co] by ^{1}H NMR from the reaction system.

Like our group's previous identification of the alkyl–Co by ^{1}H NMR,[xix] we observe the characteristic doublets close to -0.4 and -0.5 ppm in our reaction mixture after addition of the silane (Figure S4a and Figure S4b), suggesting formation of an alkyl–Co organometallic after HAT. See reference **xix** for more details.

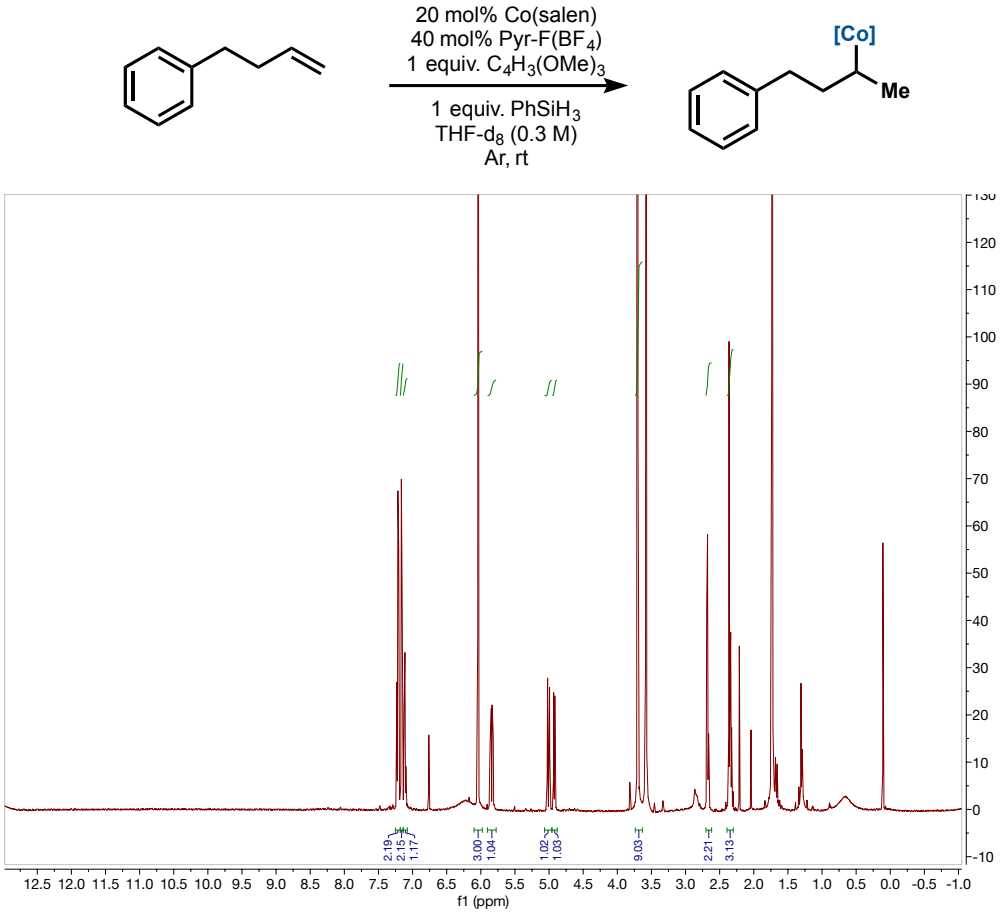


Figure S4a: Reaction mixture in THF-d8 prior addition of the $PhSiH_3$, aldehyde, and $CrCl_3$.

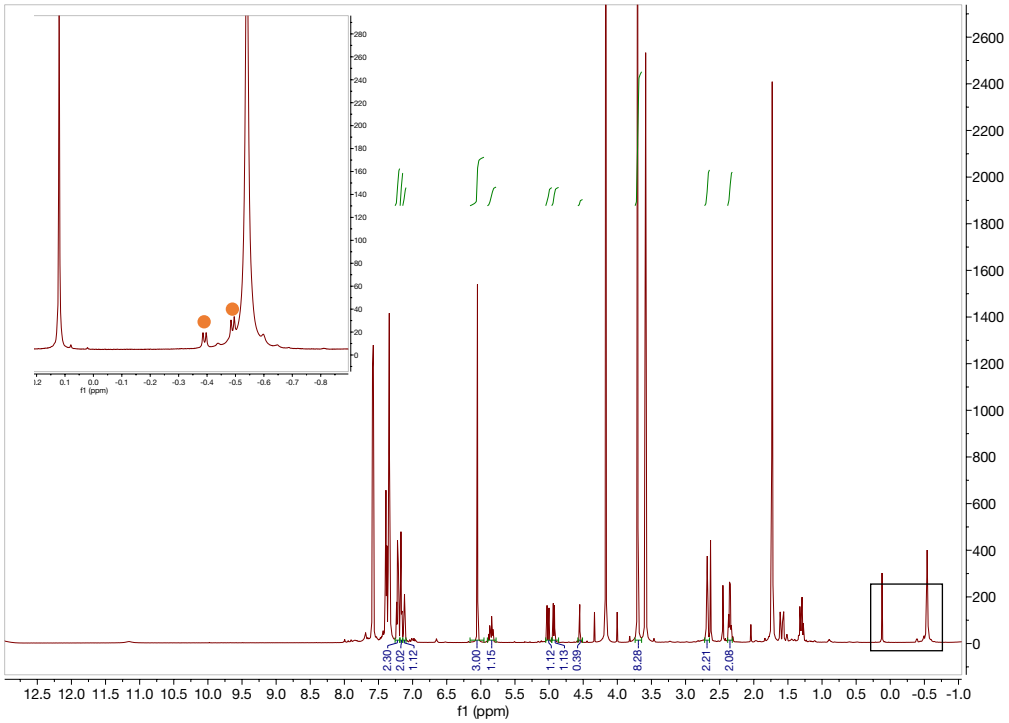
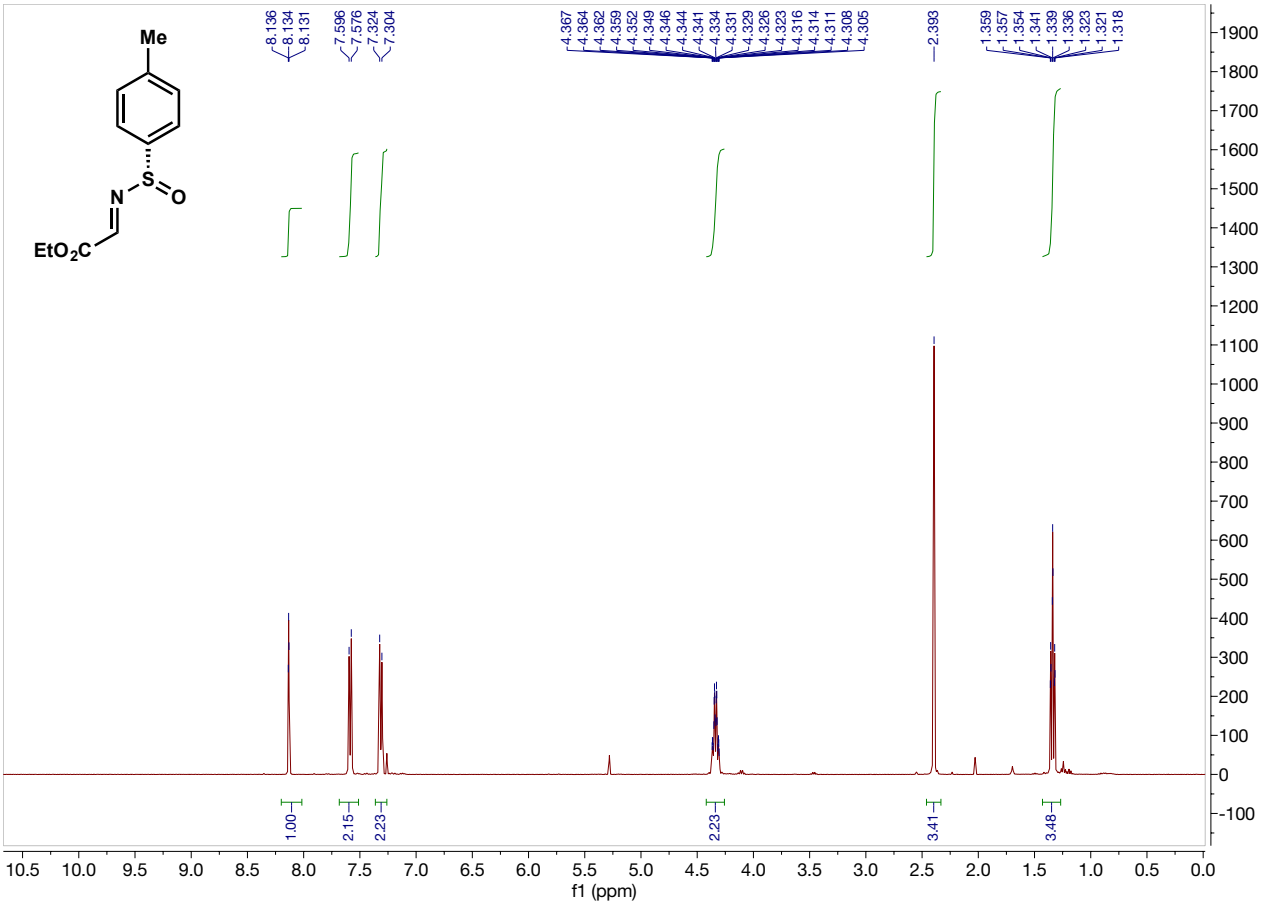


Figure S4b: Reaction mixture in THF-d8 after addition of the $PhSiH_3$, and before addition of the aldehyde, and $CrCl_3$.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O
N
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8.134
8.131
7.596
7.576
7.324
7.304
4.367
4.364
4.362
4.359
4.352
4.349
4.346
4.344
4.341
4.334
4.331
4.329
4.326
4.323
4.316
4.314
4.311
4.308
4.305
2.393
1.359
1.357
1.354
1.341
1.339
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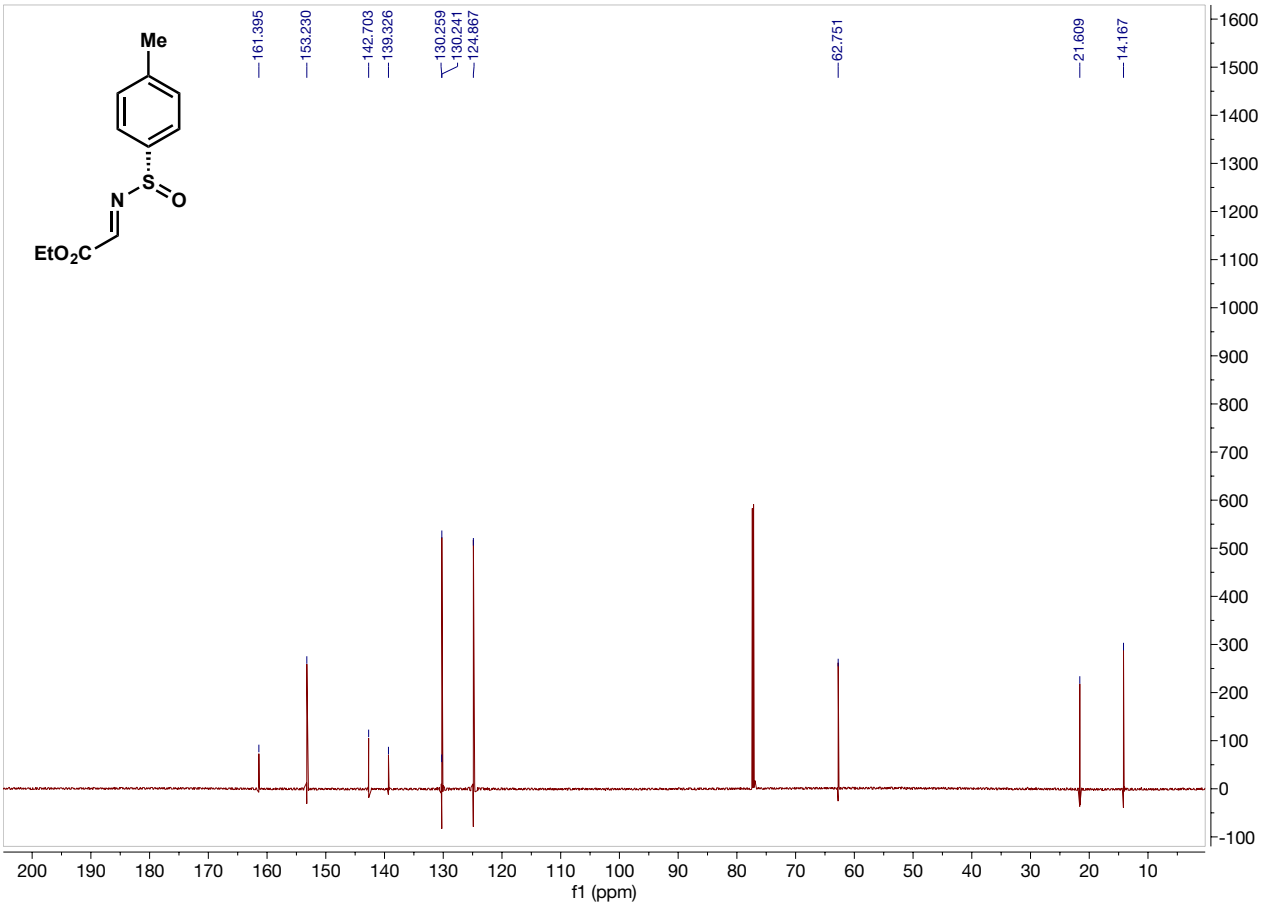
2.23
2.23
3.41
3.48
f1 (ppm)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S
O
N
EtO2C
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139.326
130.259
130.241
124.867
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21.609
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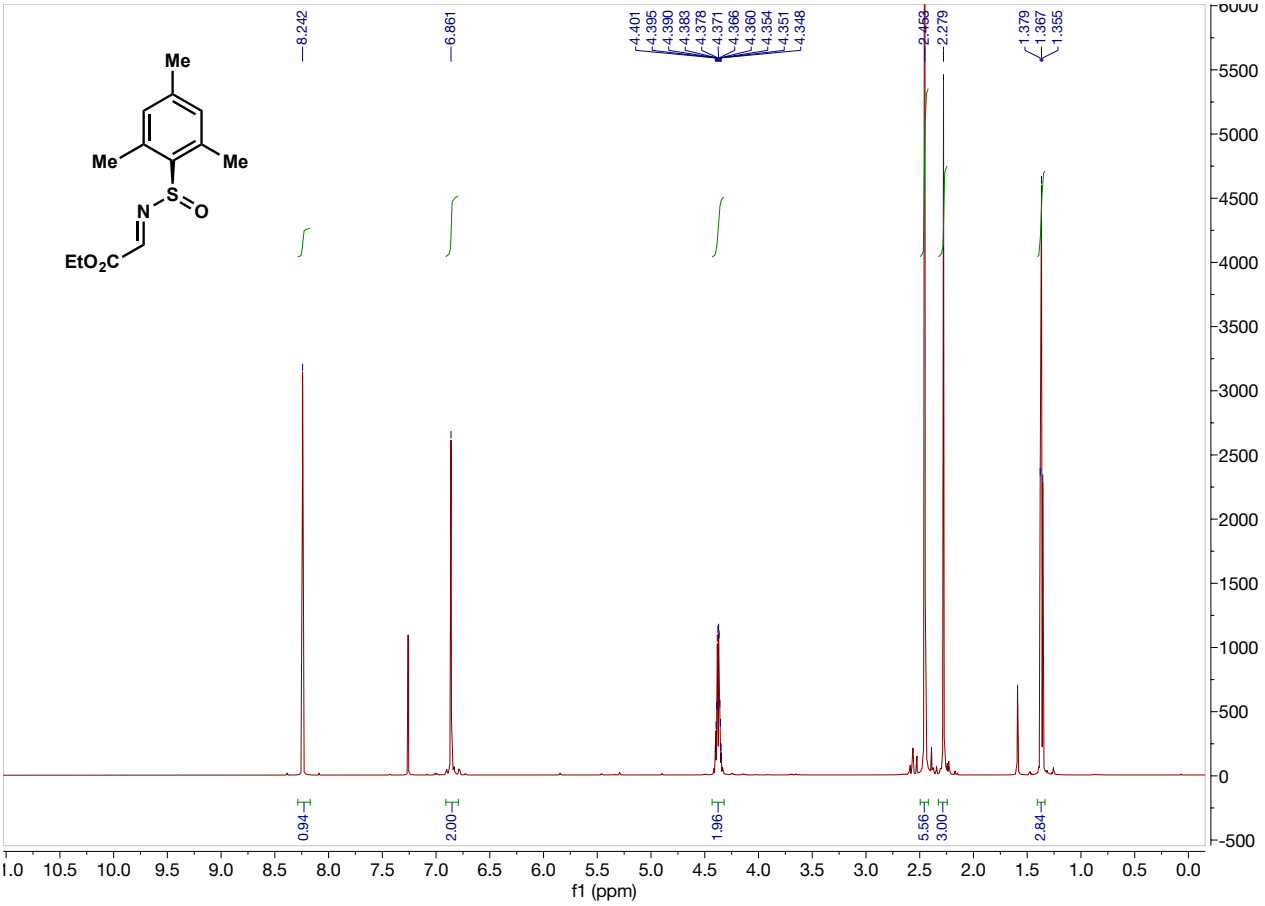
f1 (ppm)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Me
Me
S
O
N
EtO2C
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4.401
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4.390
4.383
4.378
4.371
4.366
4.360
4.354
4.351
4.348
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1.367
1.355
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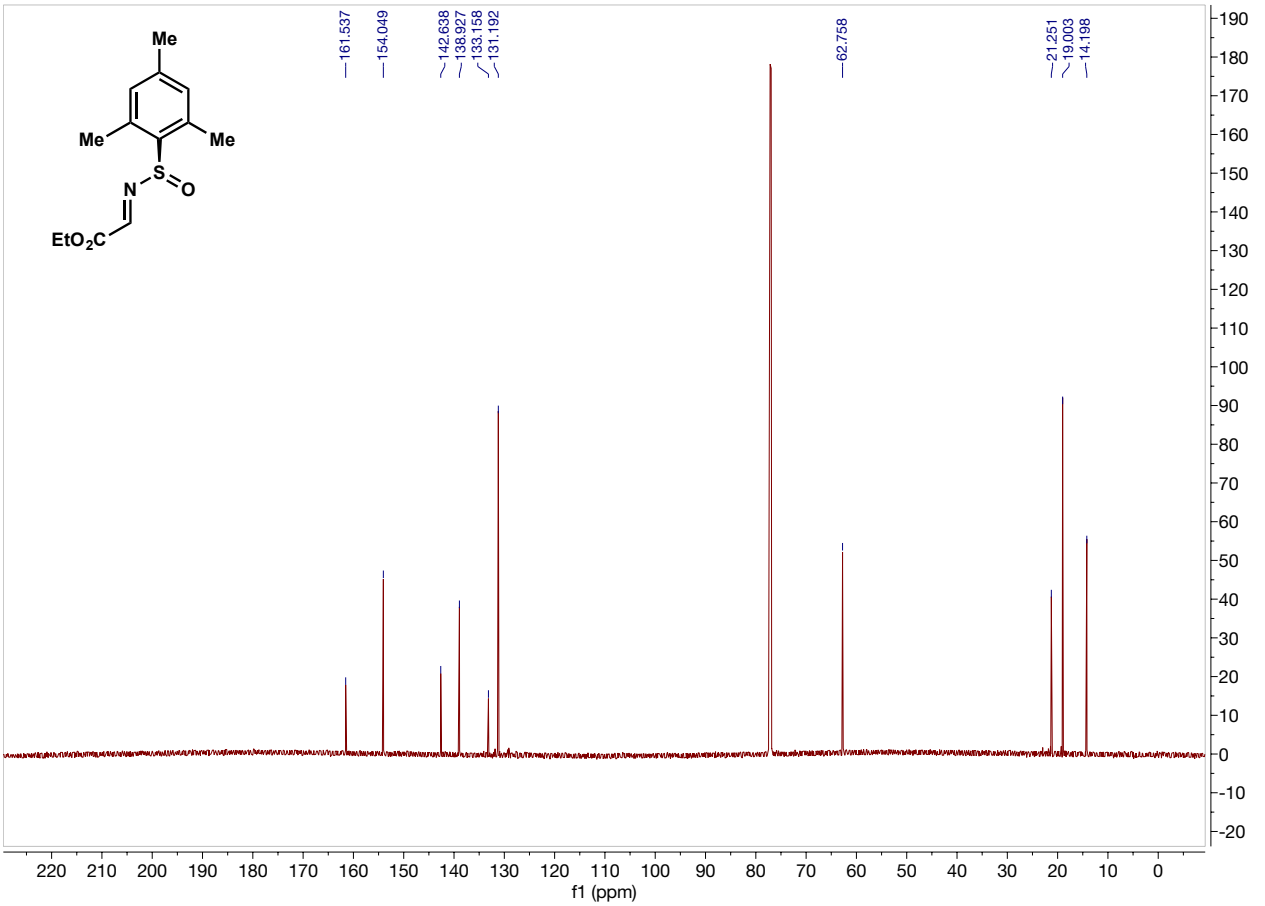
1.96
5.56
3.00
2.84
f1 (ppm)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Me
Me
S
O
N
EtO2C
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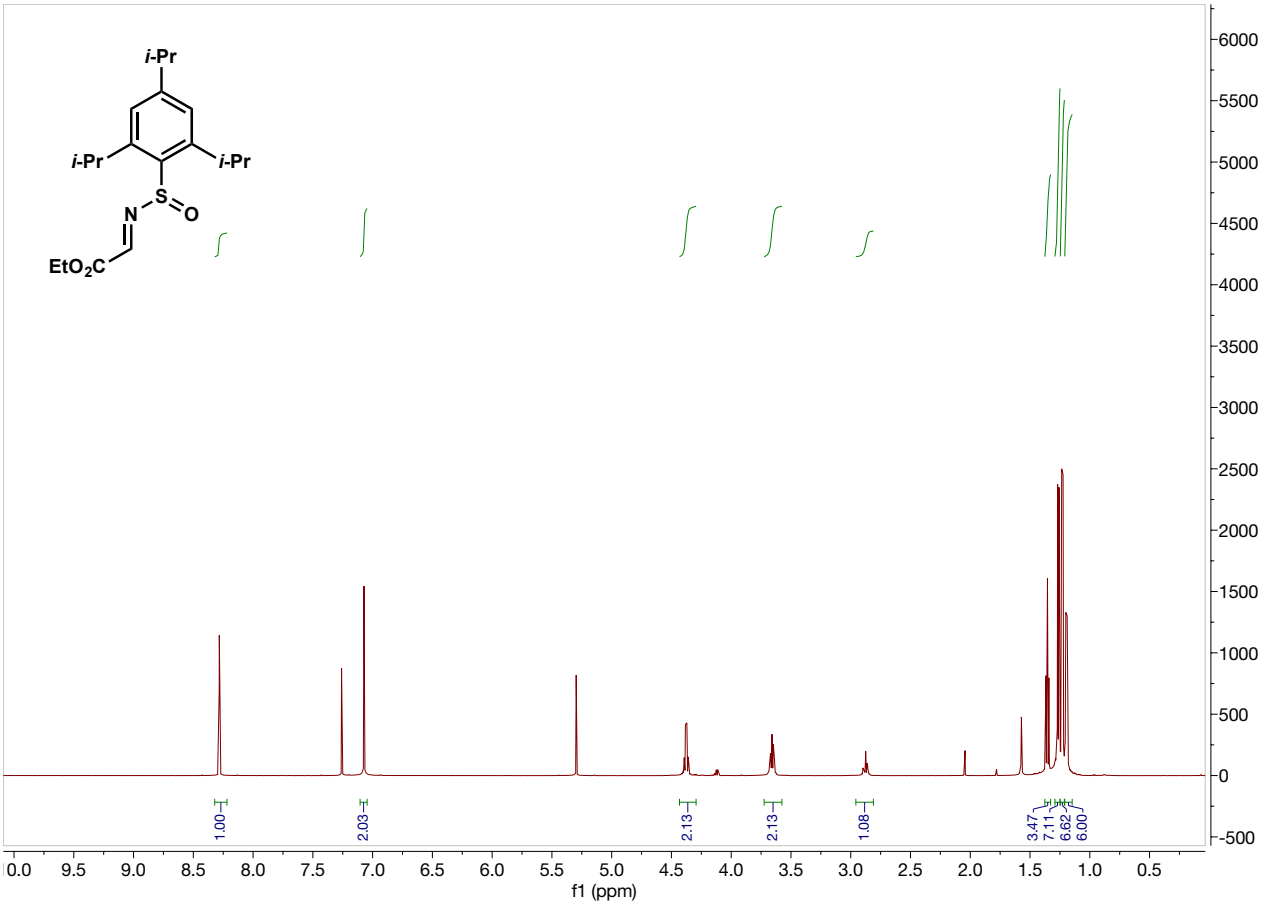
19.003
14.198
f1 (ppm)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i-Pr
i-Pr
N
S
O
EtO2C
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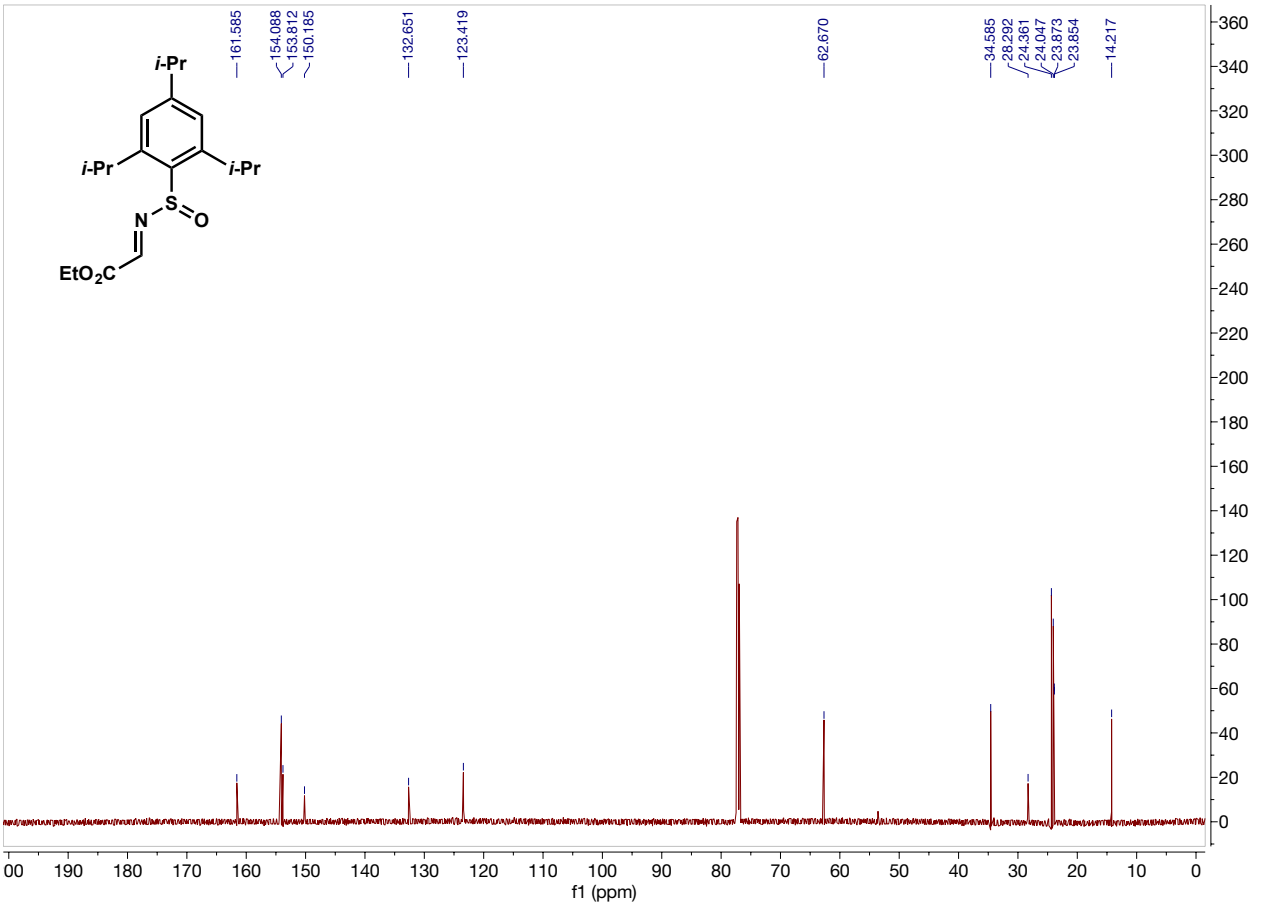
6.00
f1 (ppm)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153.812
150.185
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62.670
34.585
28.292
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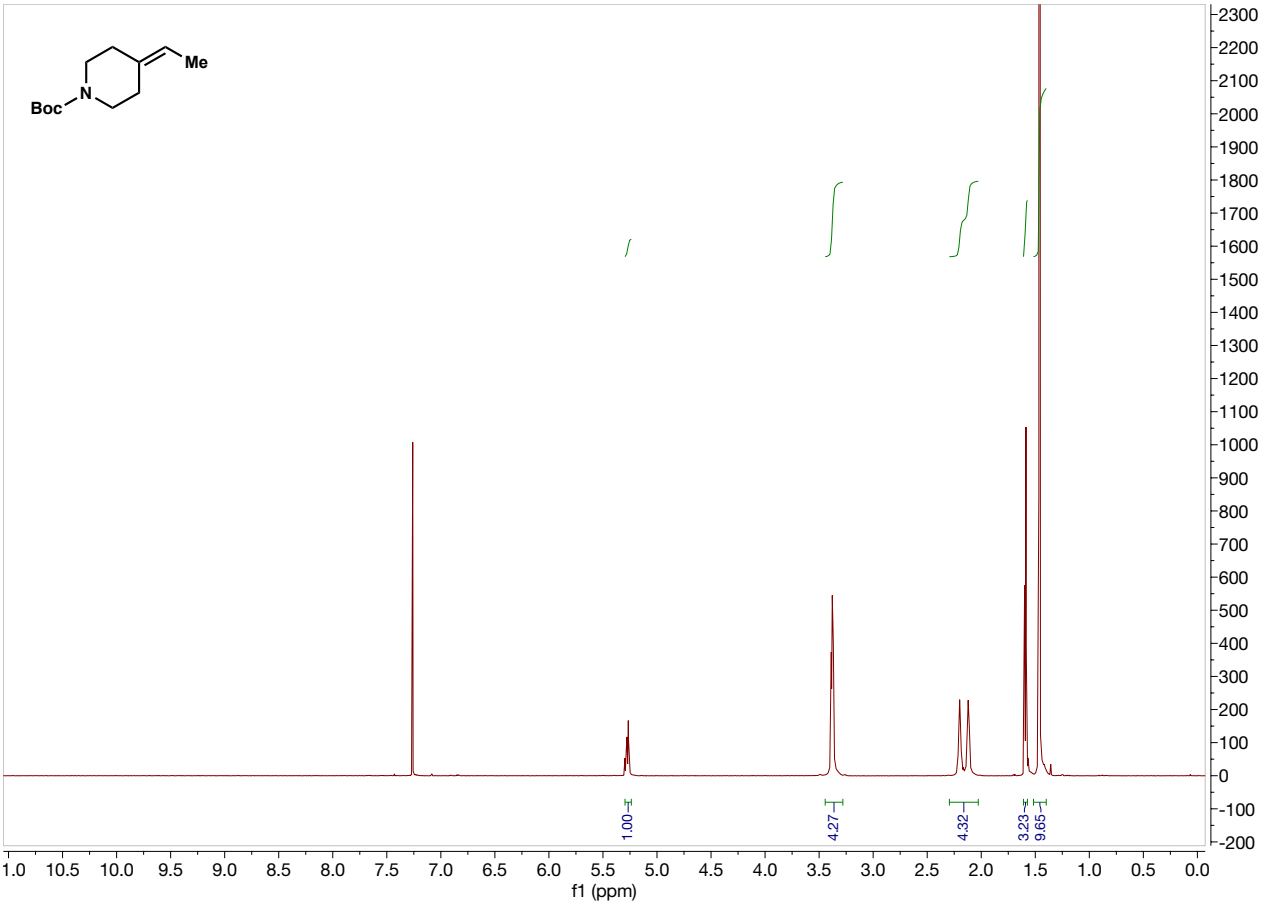
23.854
14.217
i-Pr
i-Pr
i-Pr
N
S
O
EtO2C
f1 (ppm)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Boc
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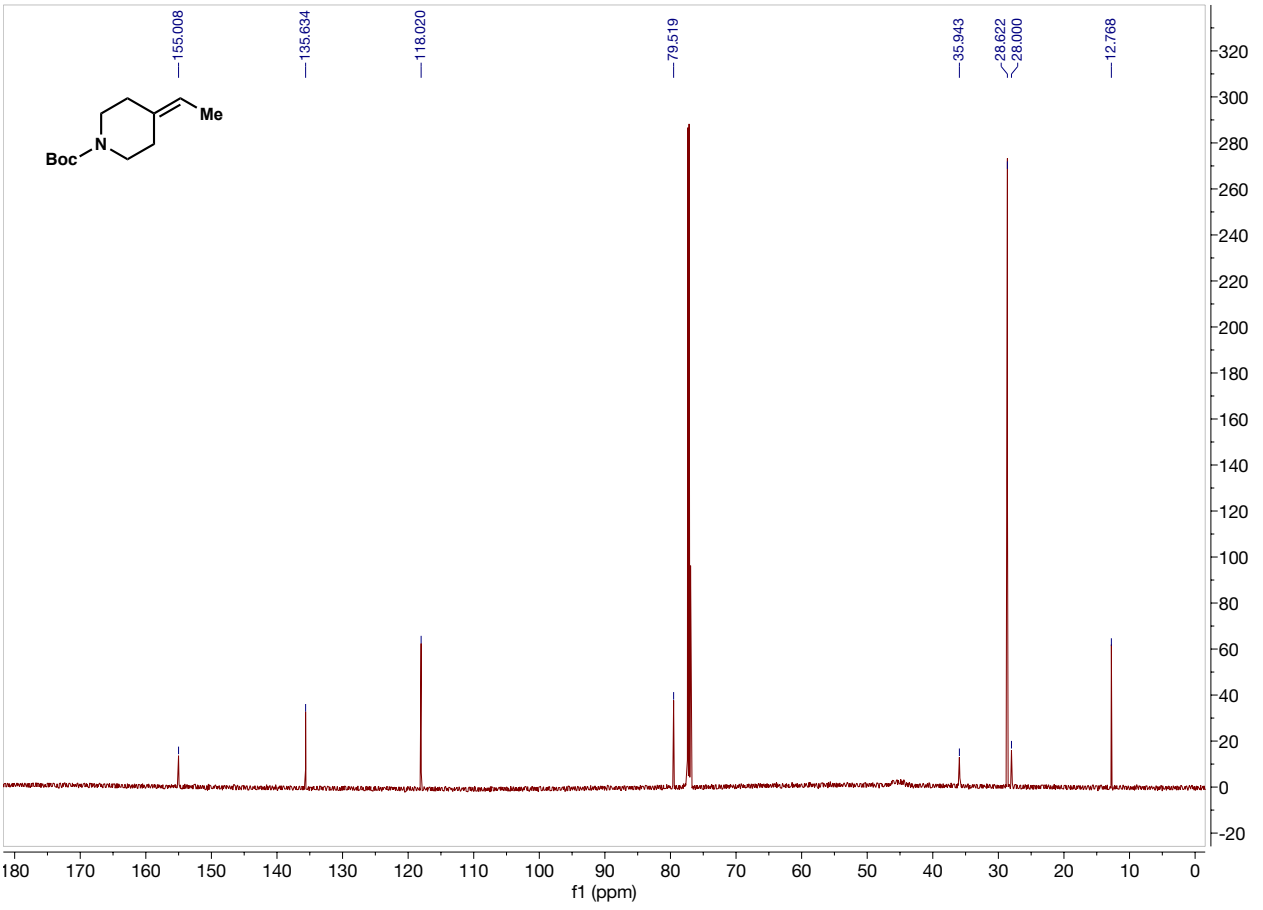
4.32
3.23
9.65
f1 (ppm)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28.000
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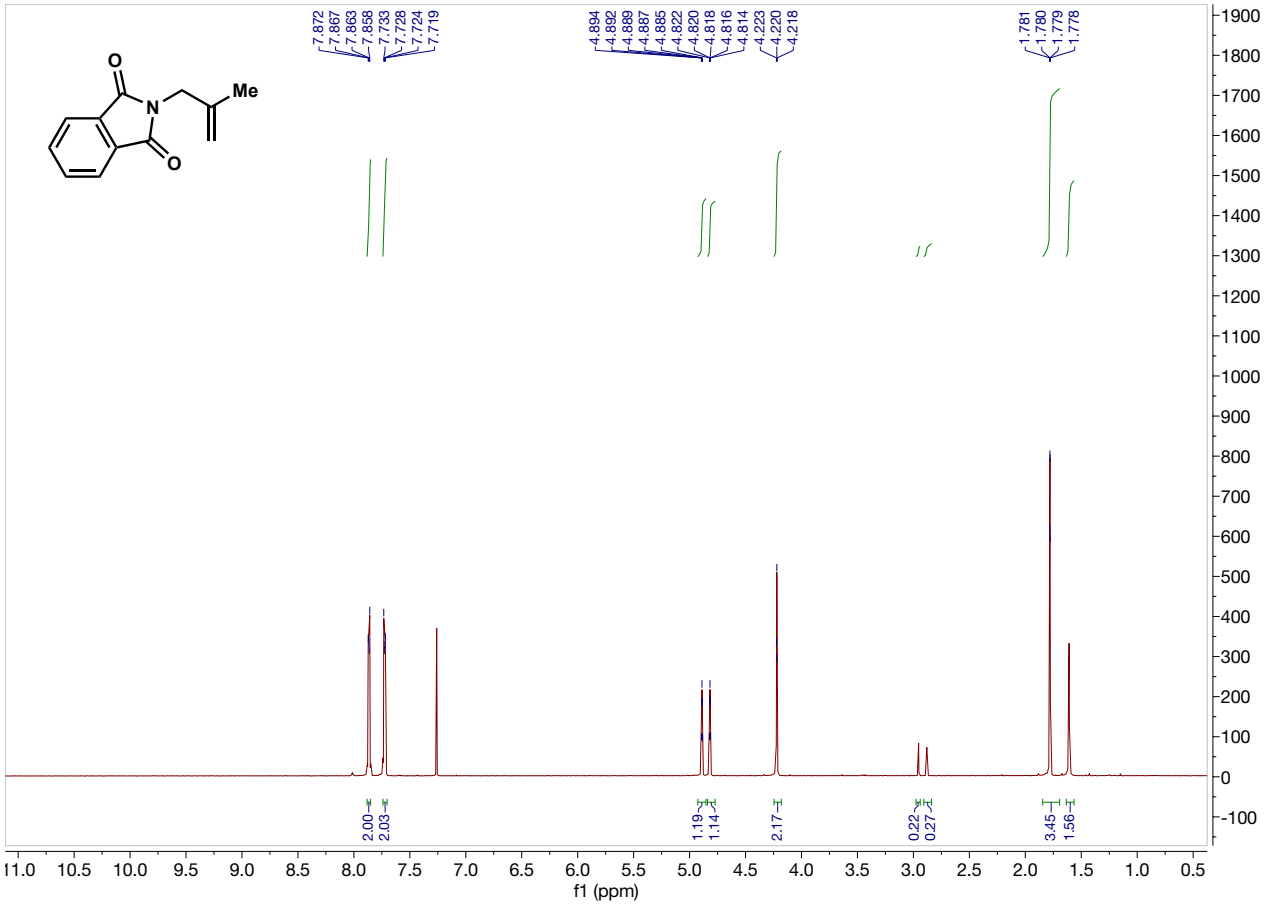
Me
Boc
N
f1 (ppm)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4.887
4.885
4.822
4.820
4.818
4.816
4.814
4.223
4.220
4.218
1.781
1.780
1.779
1.778
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Me
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0.27
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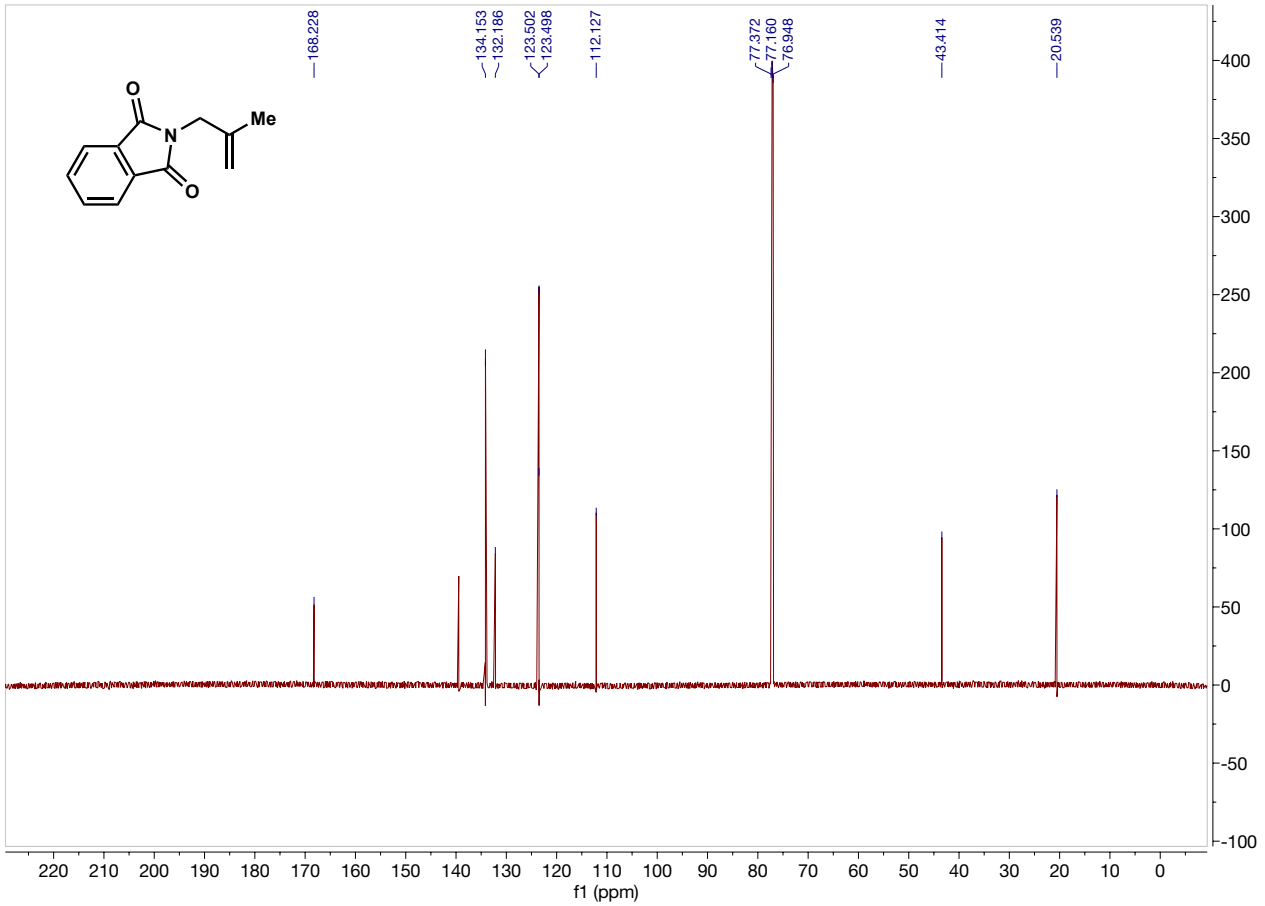
1.56
f1 (ppm)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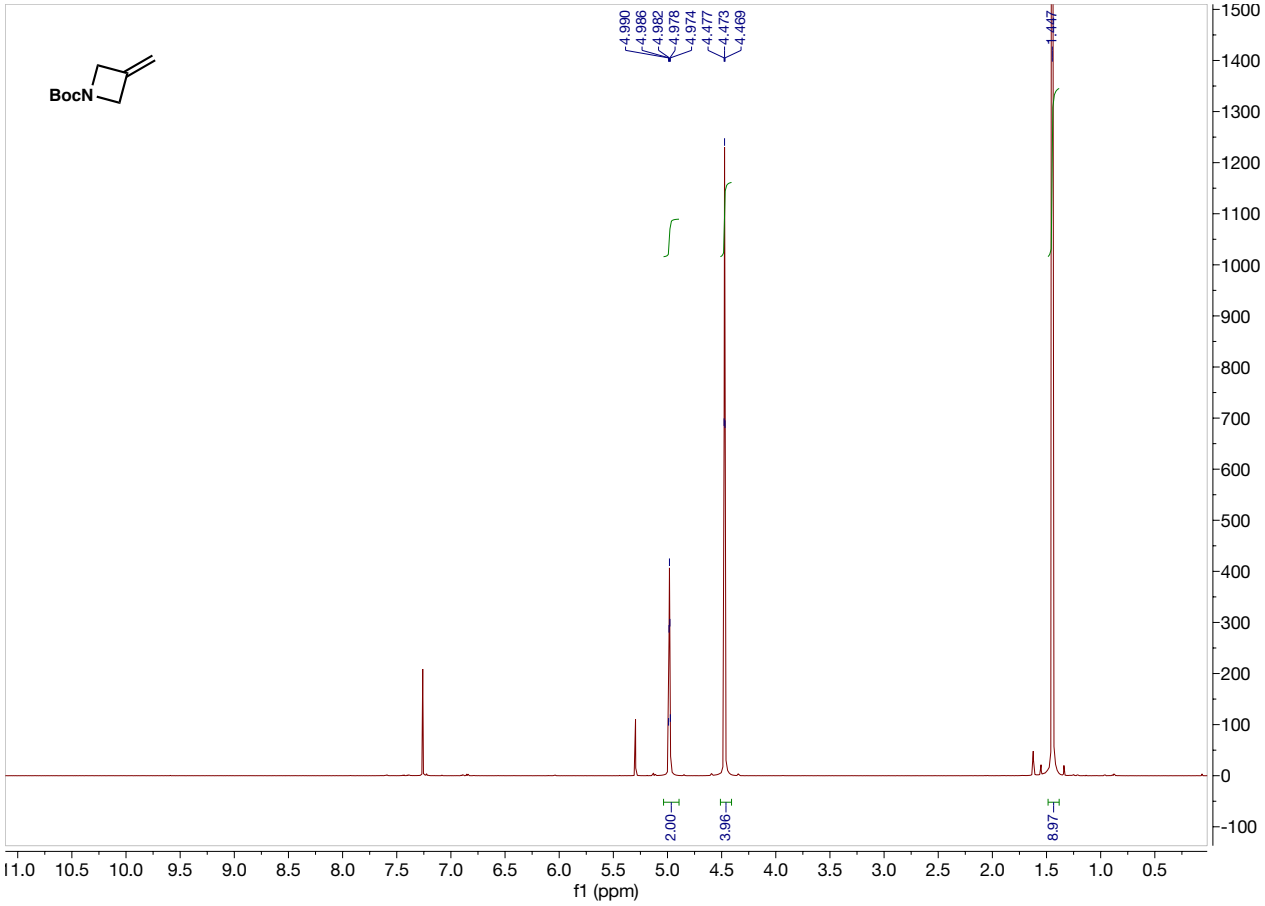
Me
O
f1 (ppm)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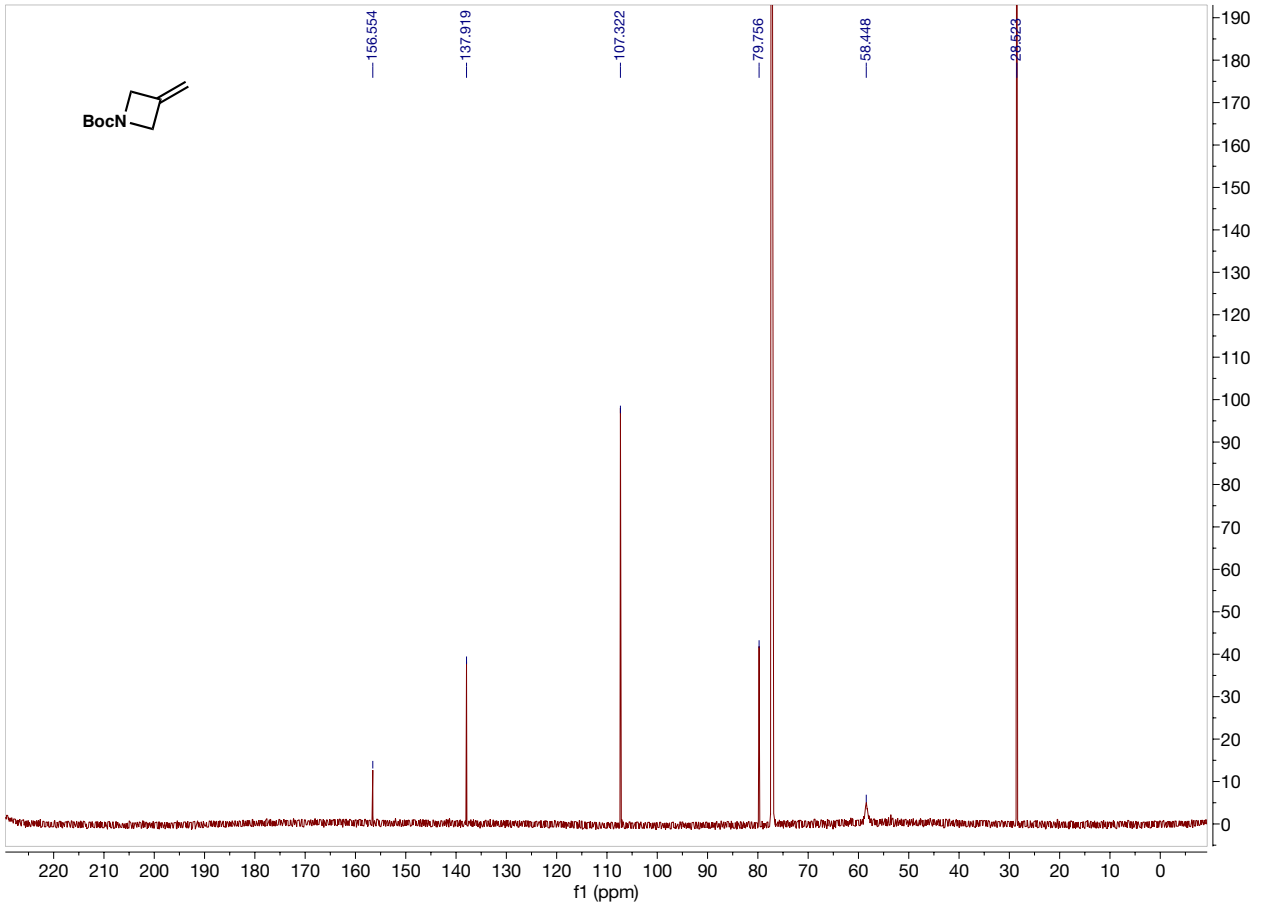
f1 (ppm)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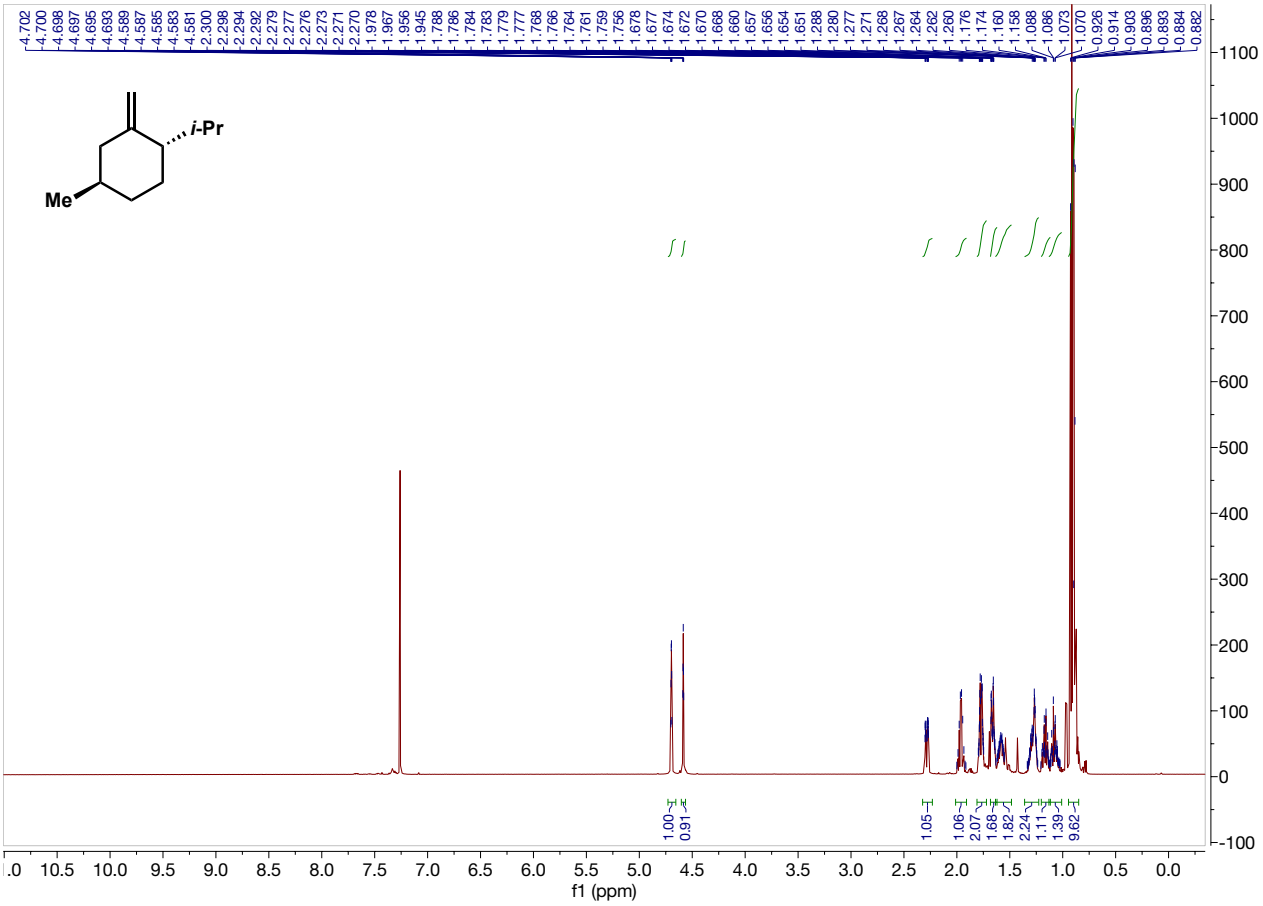
f1 (ppm)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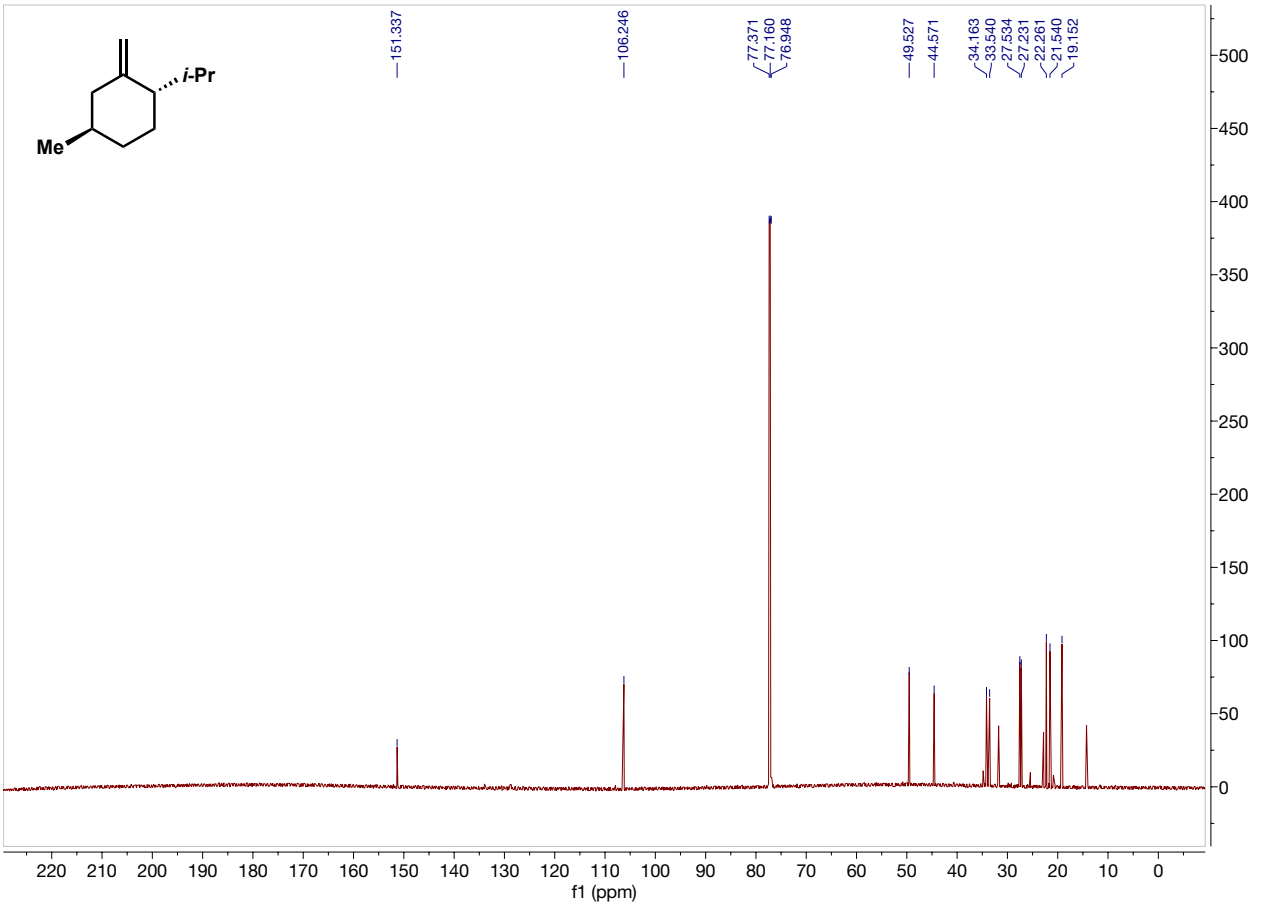
Me
f1 (ppm)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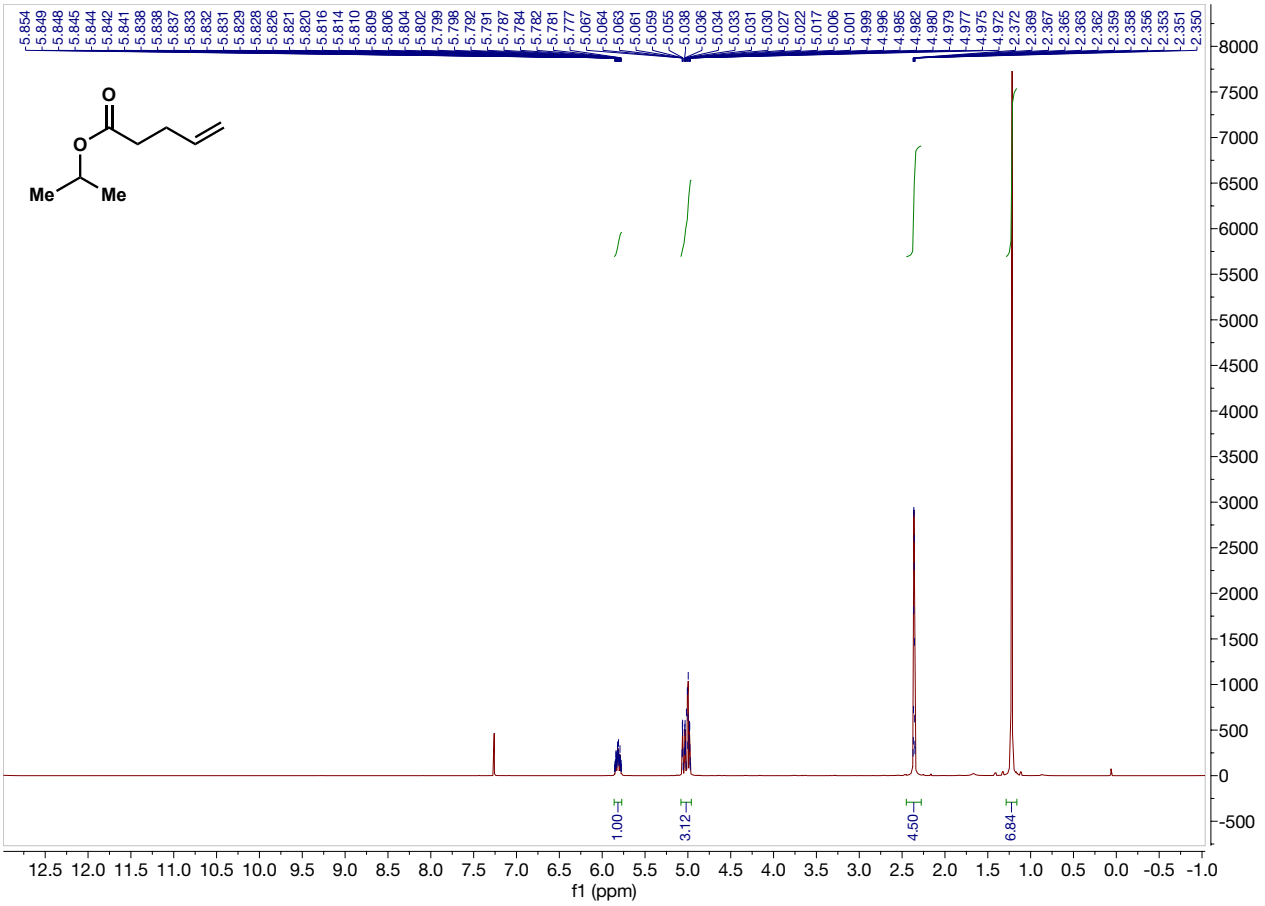
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O
Me
Me
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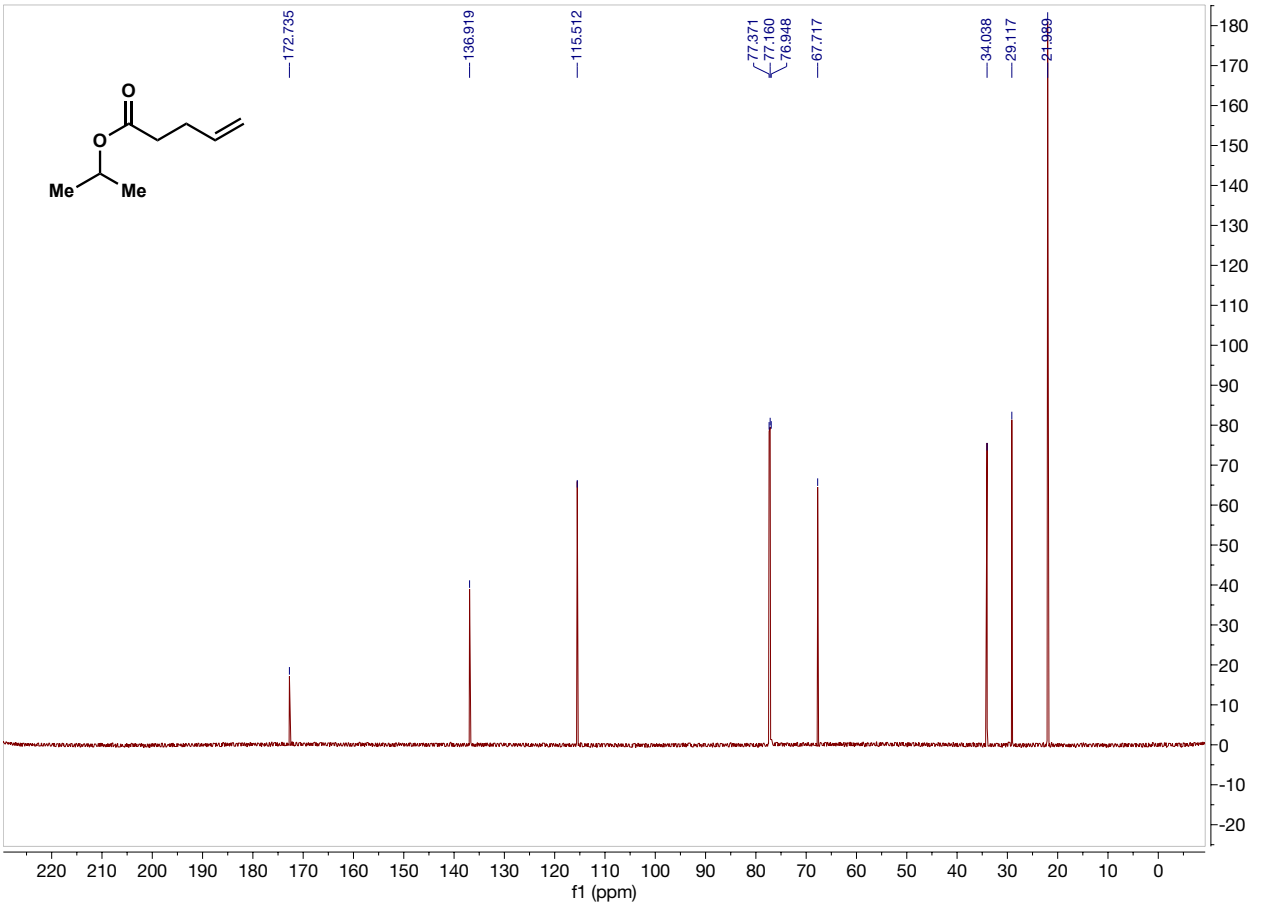
3.12
4.50
6.84
f1 (ppm)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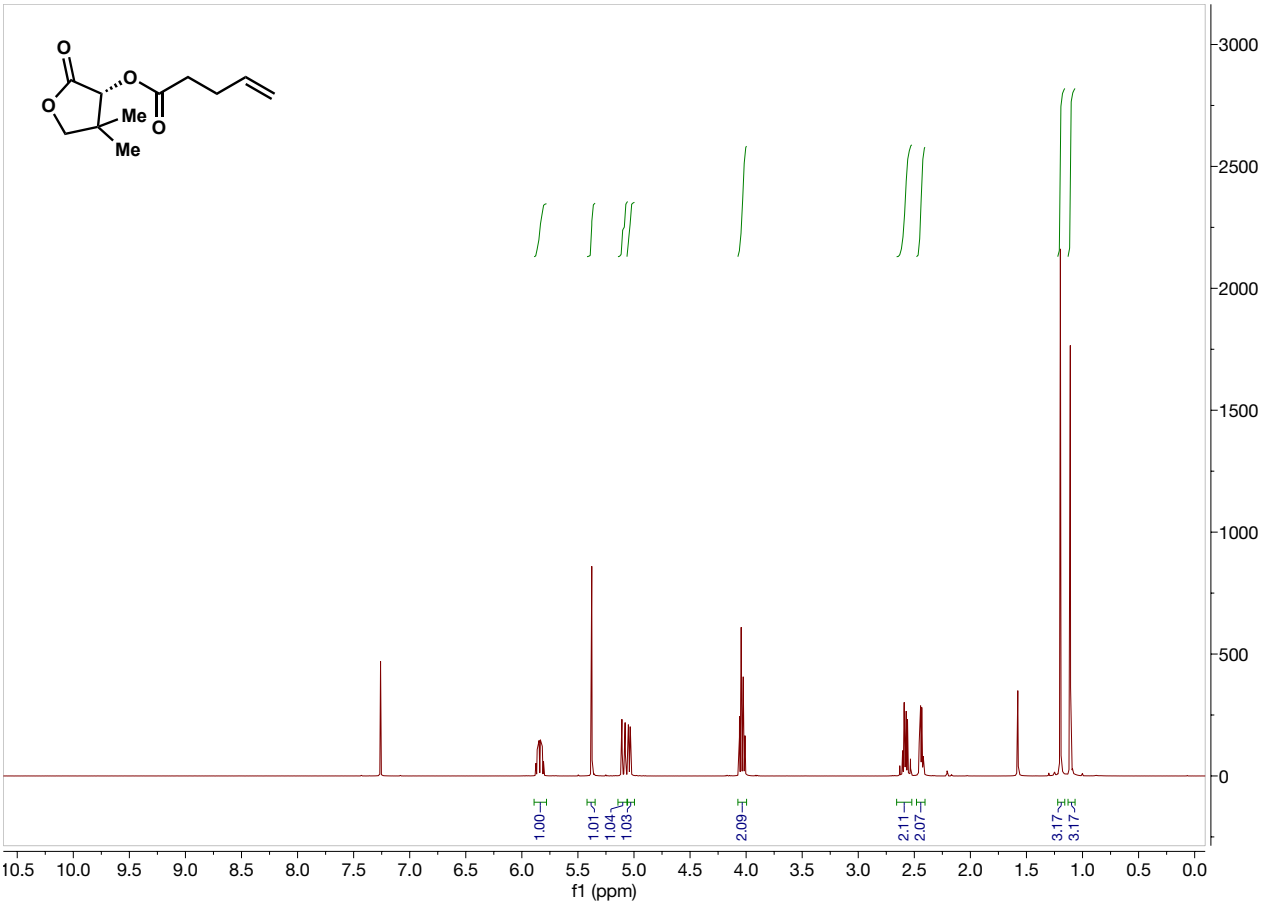
O
Me
Me
f1 (ppm)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2.11
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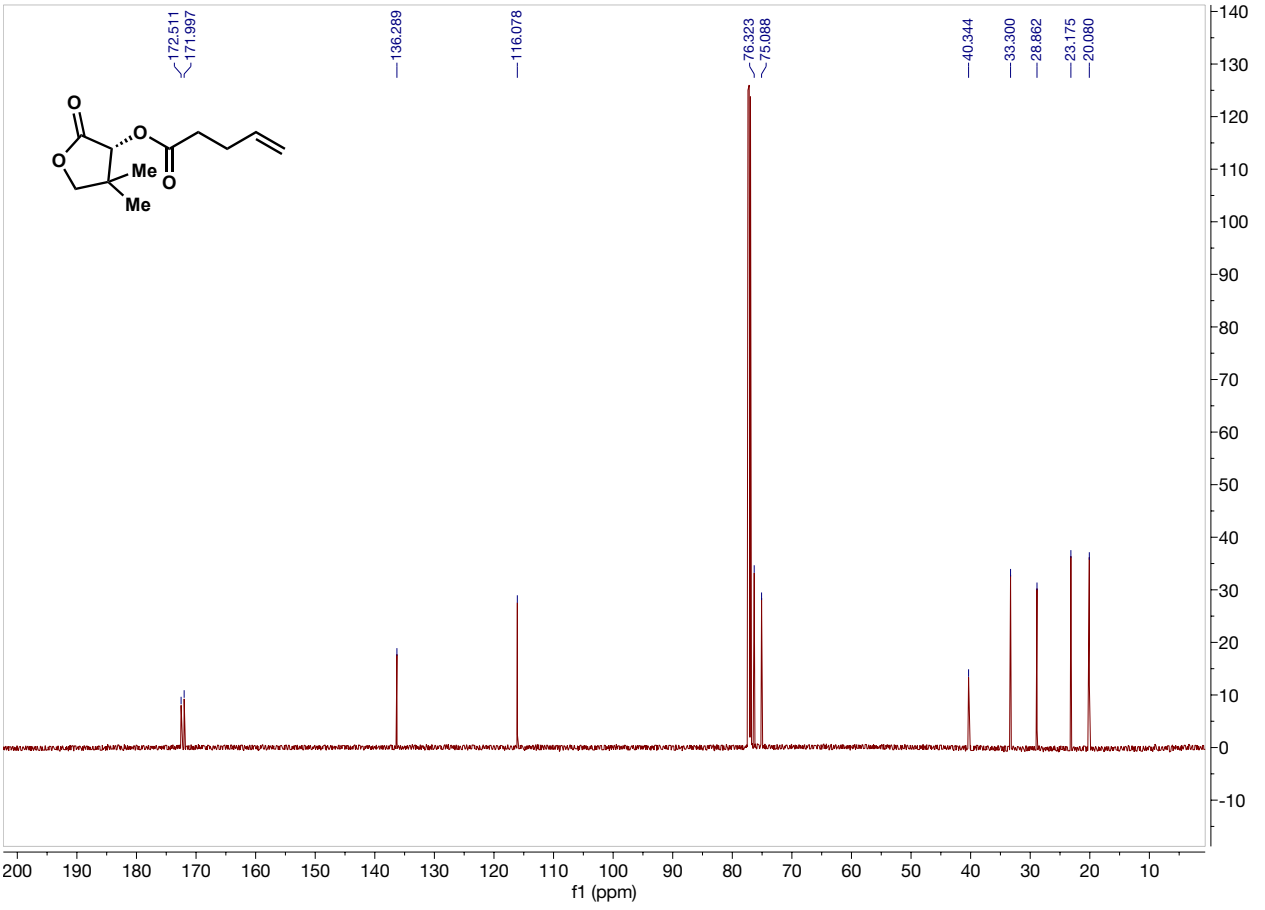
3.17
f1 (ppm)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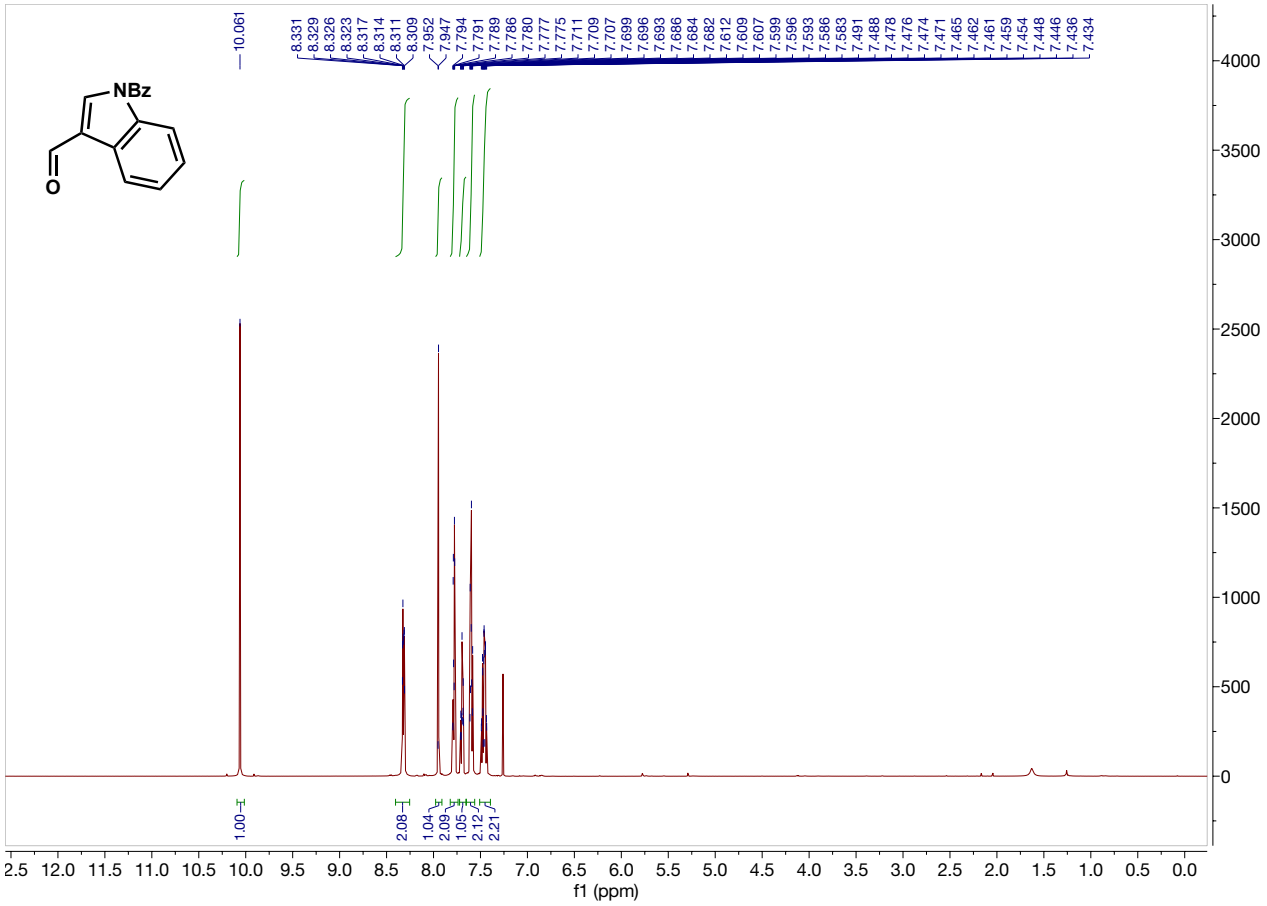
Me
Me
f1 (ppm)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7.789
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7.693
7.686
7.684
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7.612
7.609
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7.596
7.593
7.586
7.583
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7.478
7.476
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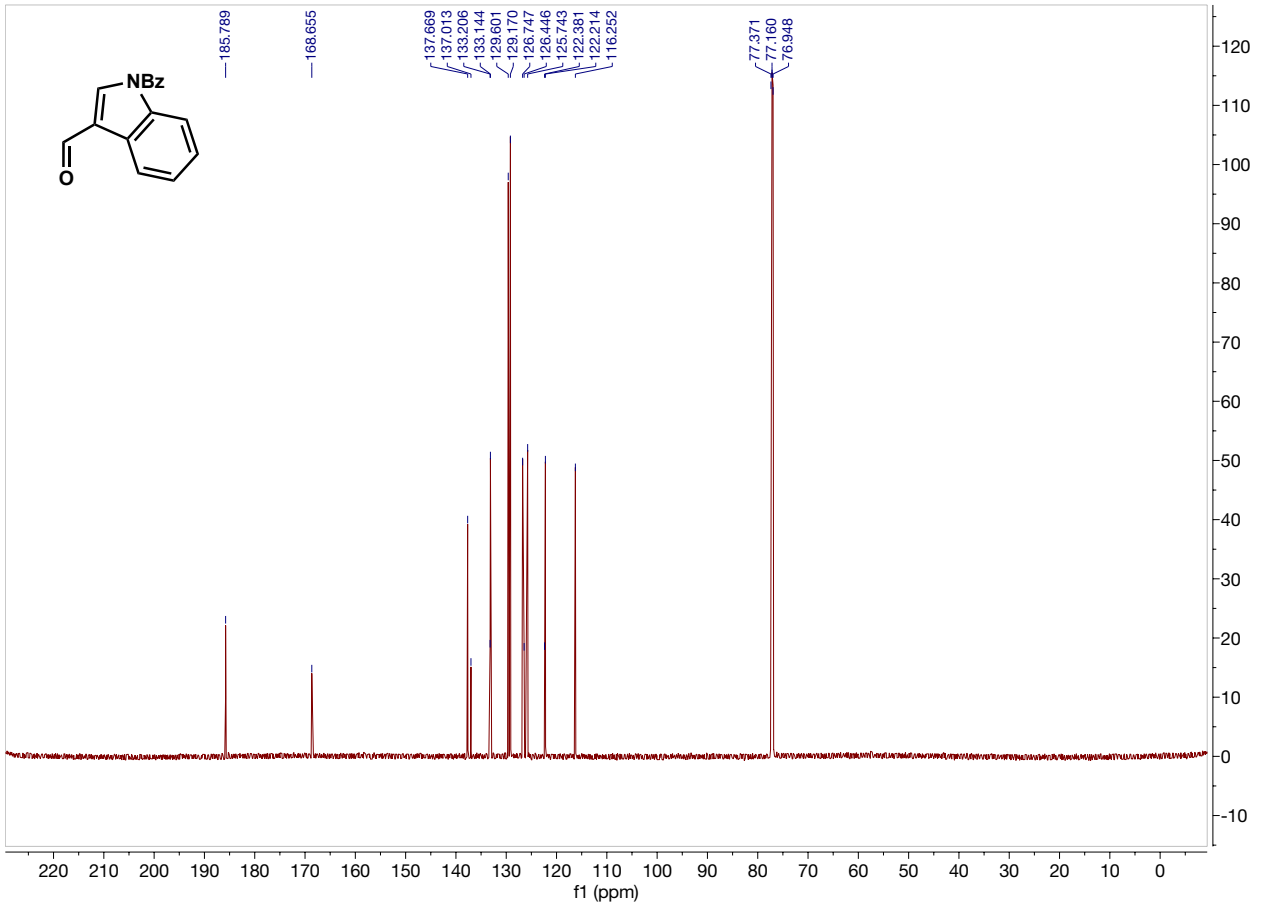
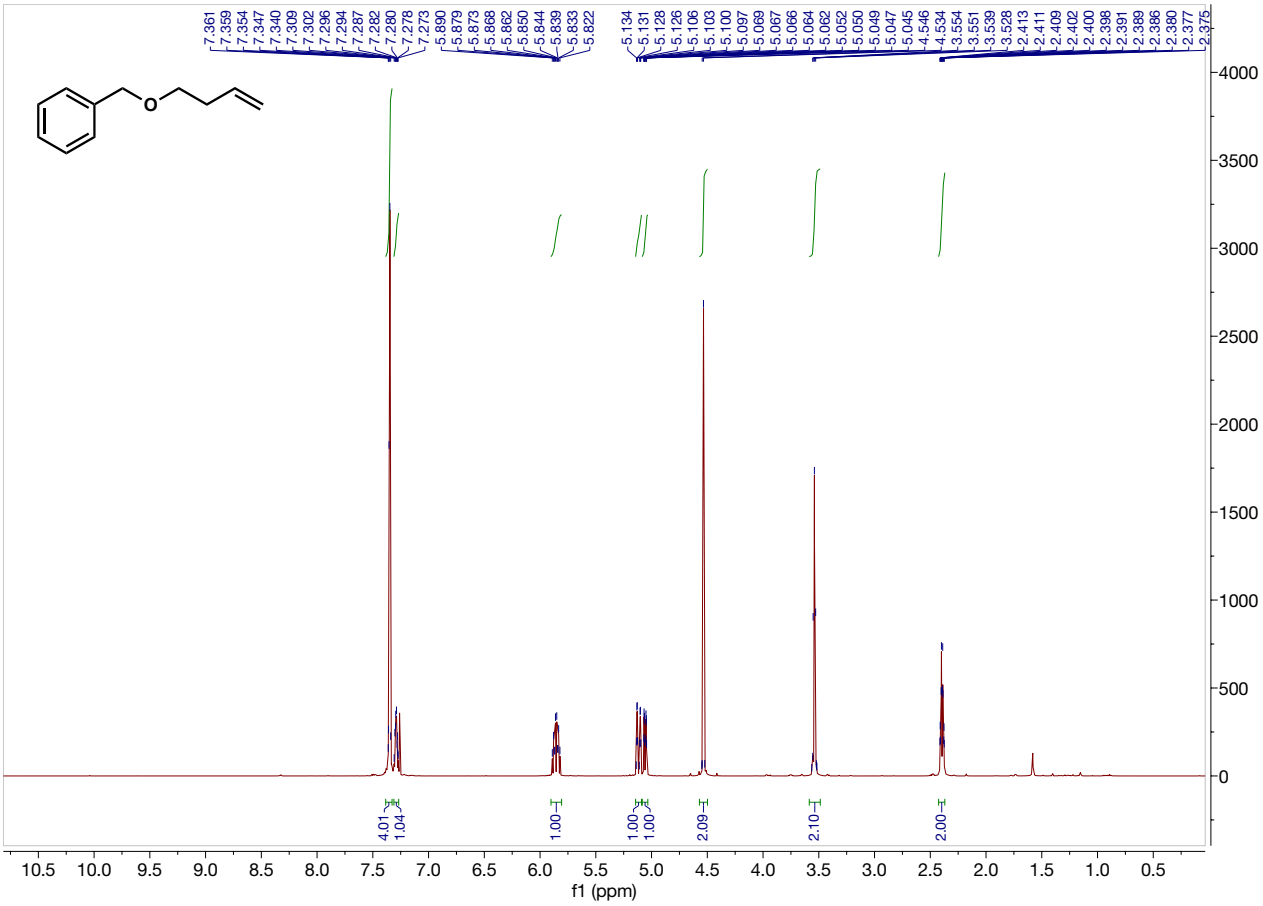
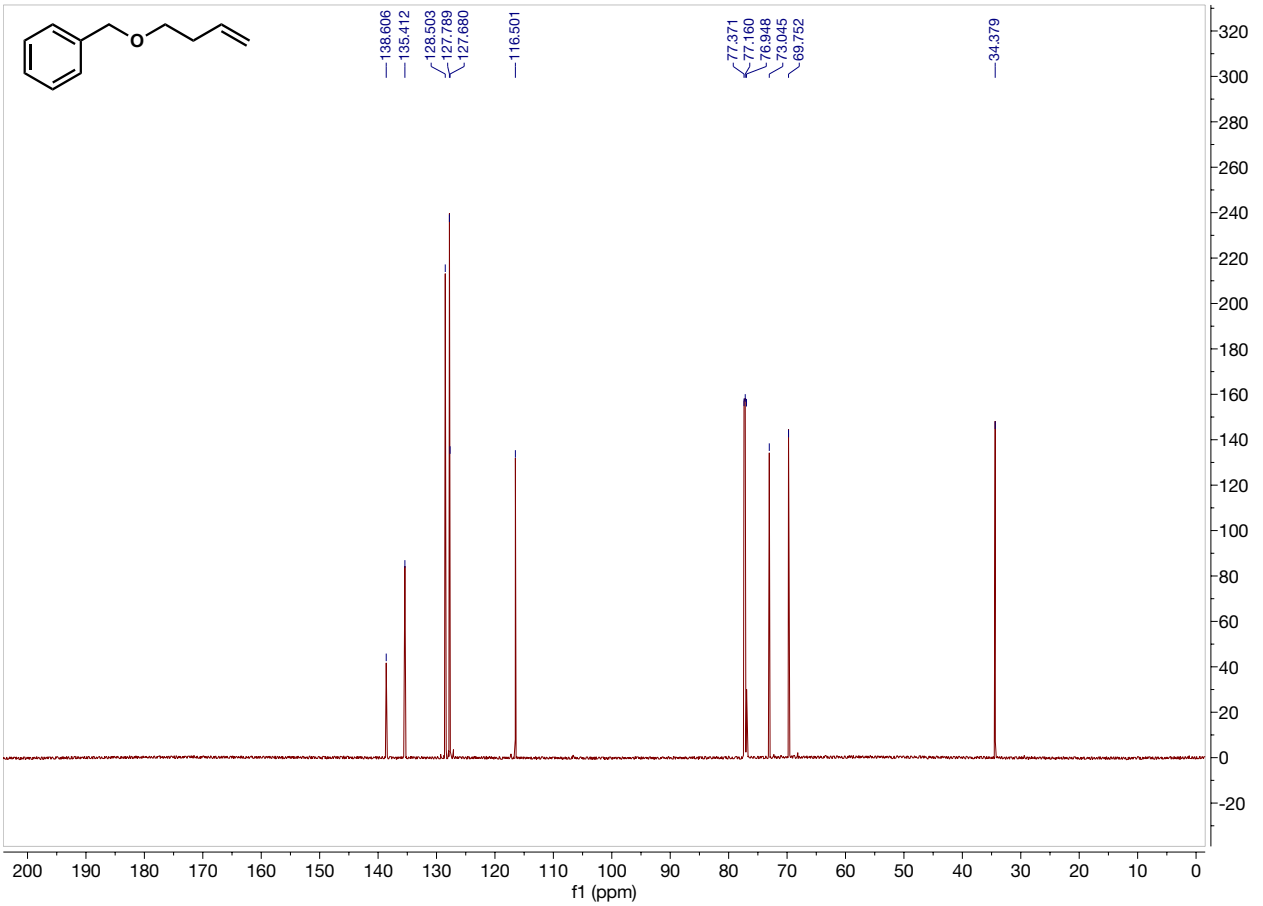
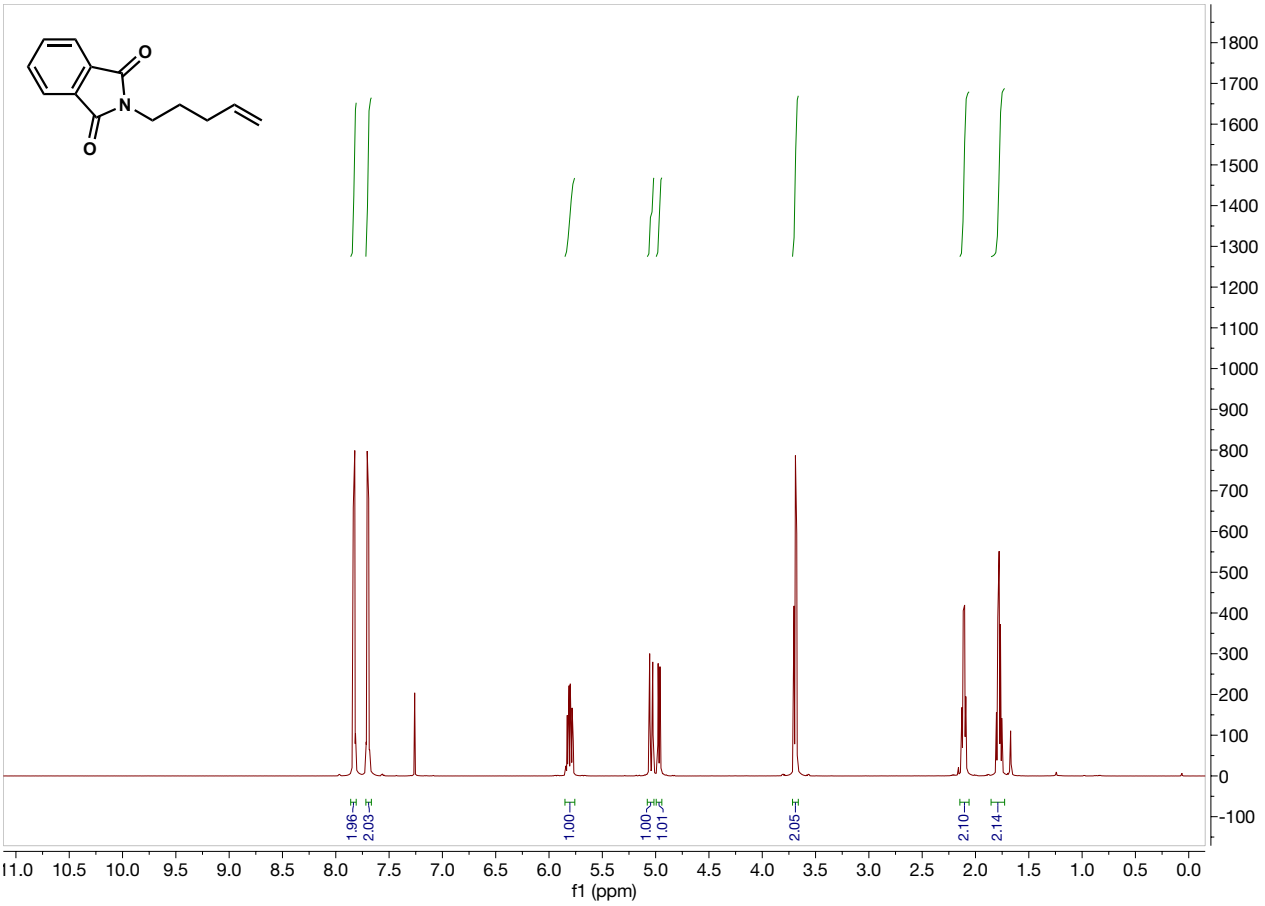
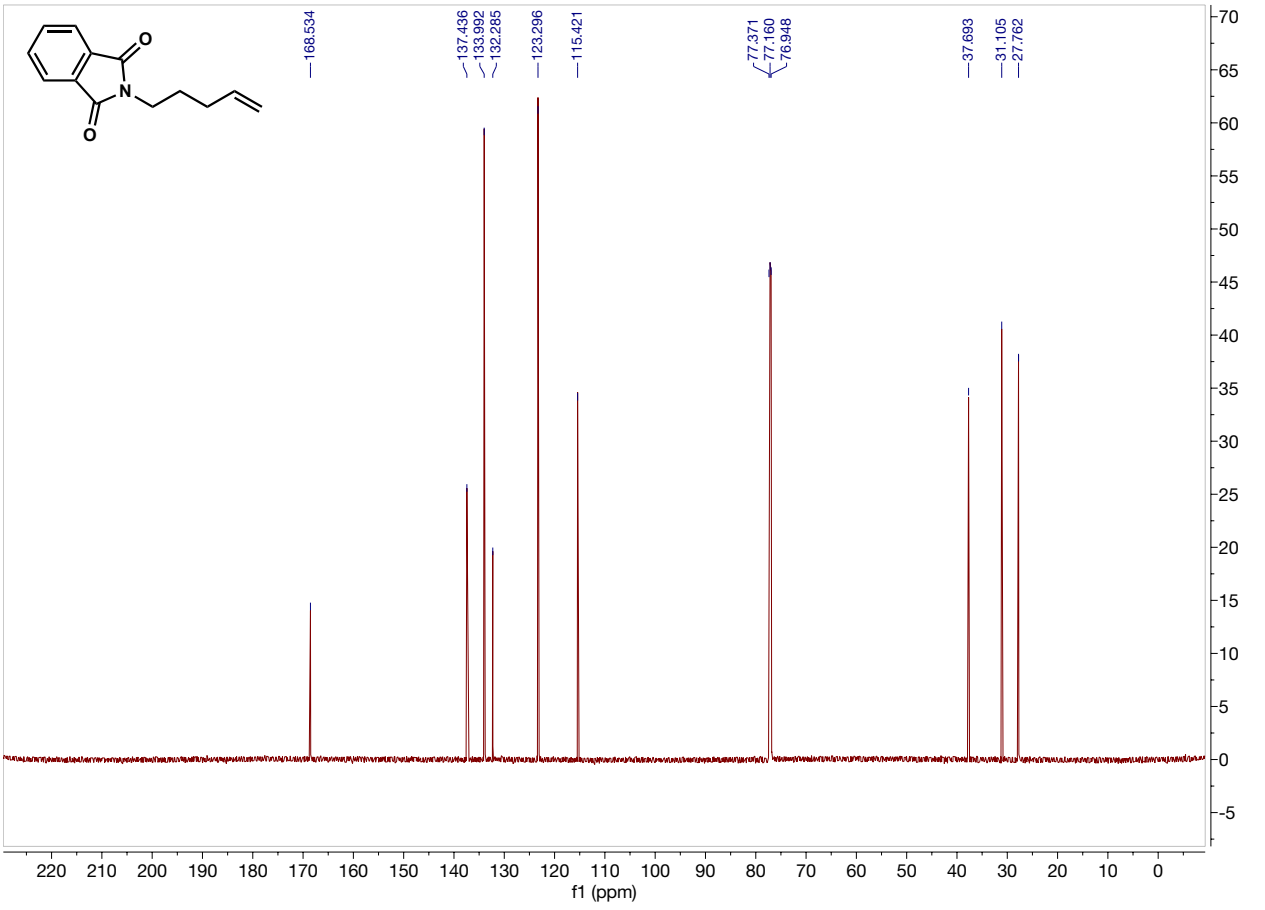
7.461
7.459
7.454
7.448
7.446
7.436
7.434
NBz
O
1.00
2.08
1.04
2.09
1.05
2.12
2.21
f1 (ppm)

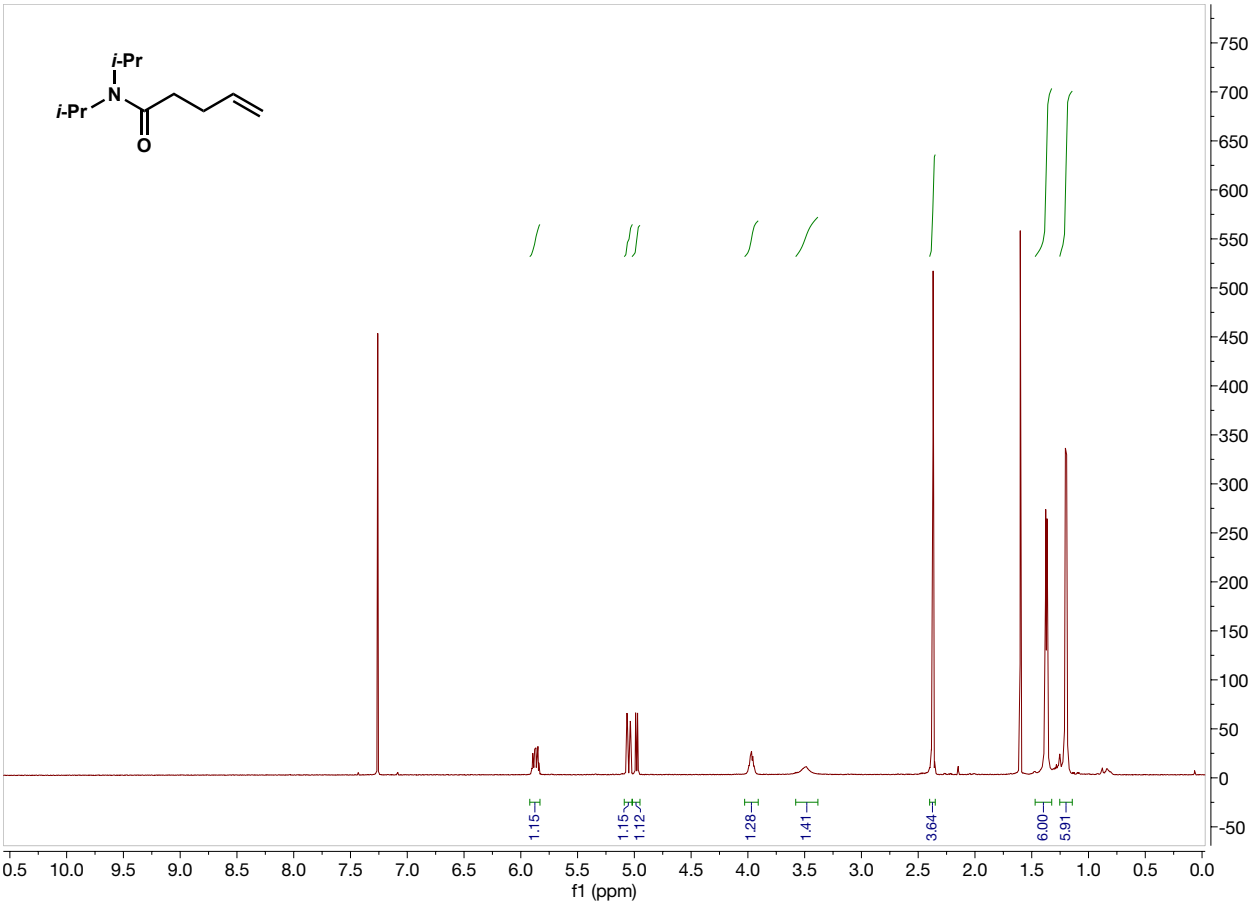

185.789
168.655
137.669
137.013
133.206
133.144
129.601
129.170
126.747
126.446
125.743
122.381
122.214
116.252
77.371
77.160
76.948
NBz
O
f1 (ppm)

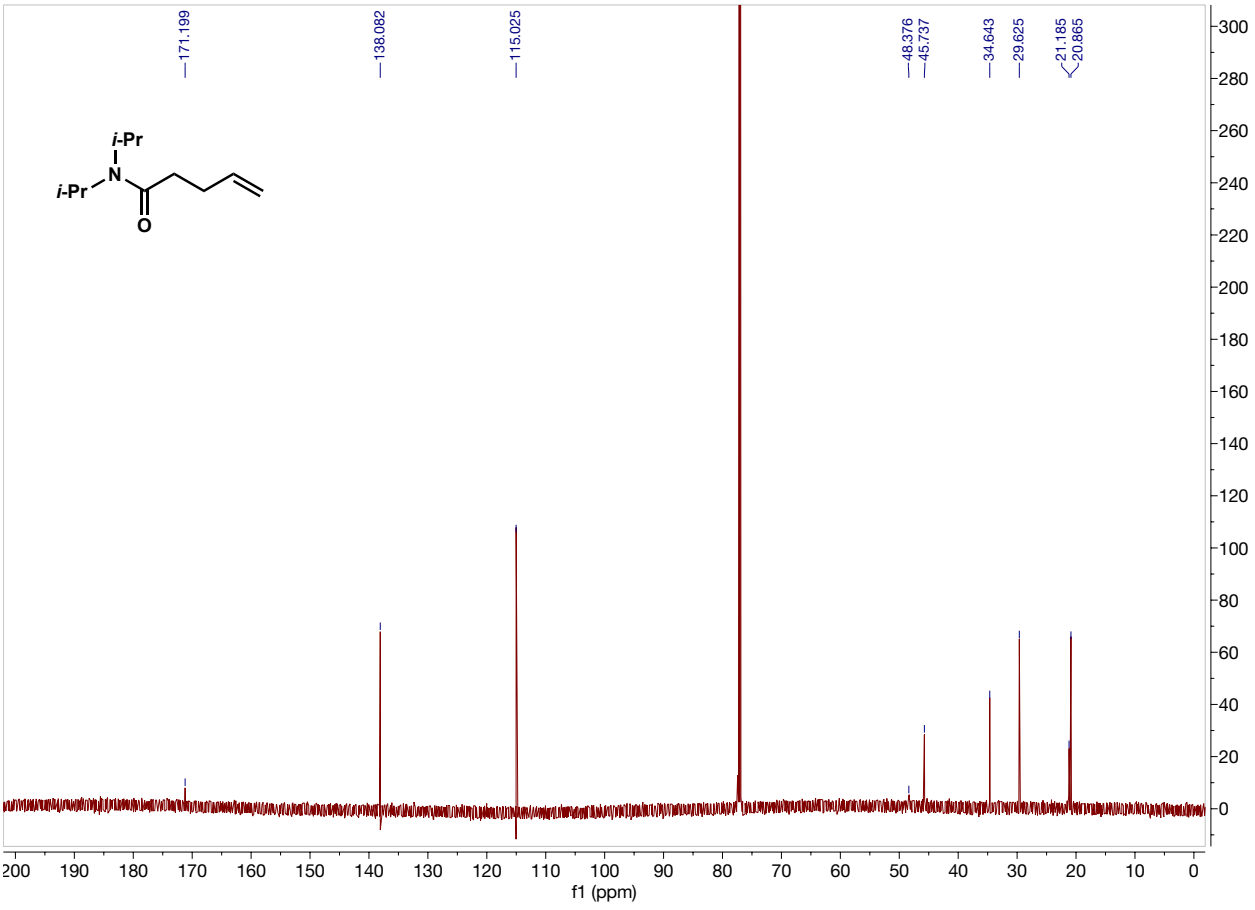

7.361
7.359
7.354
7.347
7.340
7.309
7.302
7.296
7.294
7.287
7.282
7.280
7.278
7.273
5.890
5.879
5.873
5.868
5.862
5.850
5.844
5.839
5.833
5.822
5.134
5.131
5.128
5.126
5.106
5.103
5.100
5.097
5.069
5.067
5.066
5.064
5.062
5.052
5.050
5.049
5.047
5.045
4.546
4.534
3.554
3.551
3.539
3.528
2.413
2.411
2.409
2.402
2.400
2.398
2.391
2.389
2.386
2.380
2.377
2.375
O
4.01
1.04
1.00
1.00
1.00
2.09
2.10
2.00
f1 (ppm)

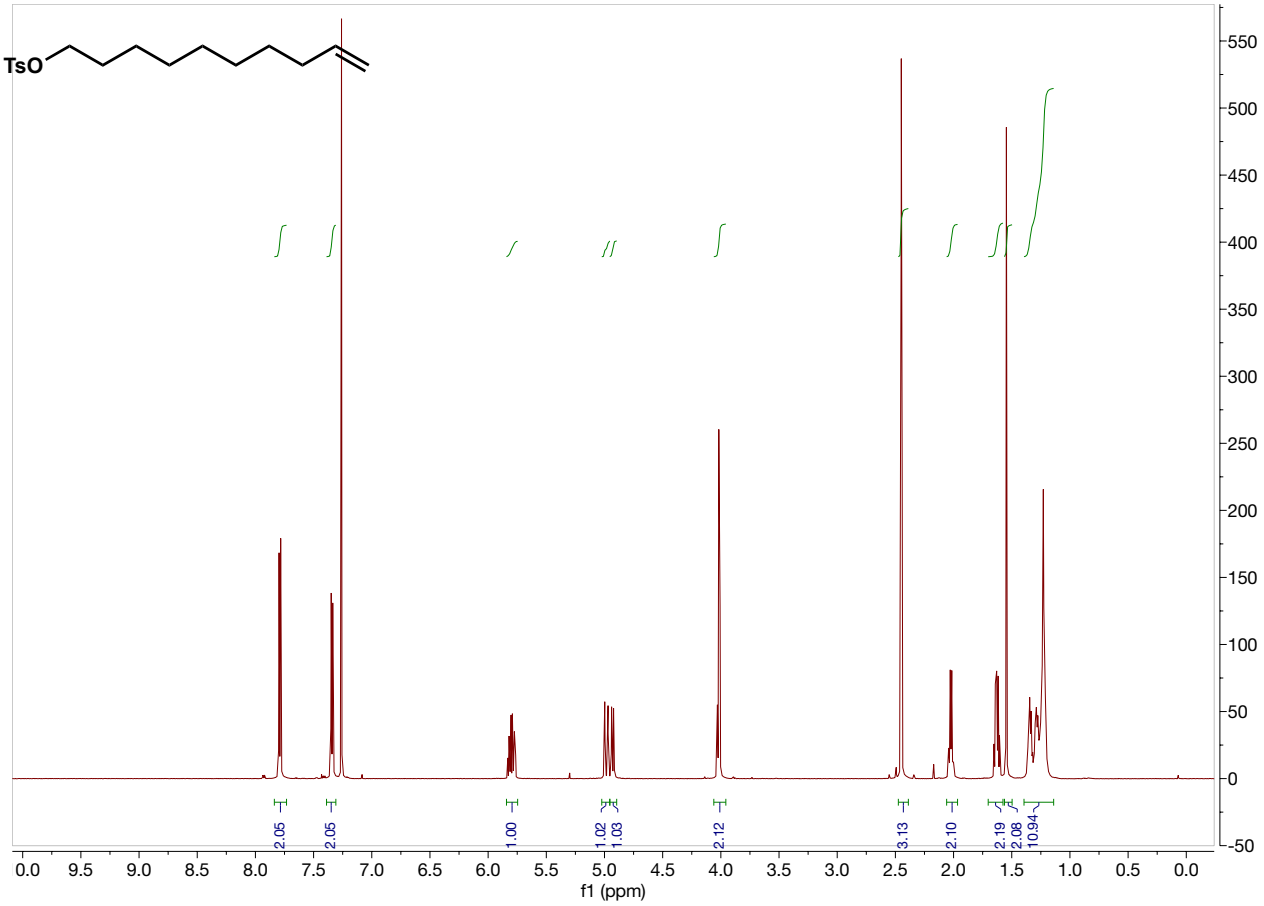

138.606
135.412
128.503
127.789
127.680
116.501
77.371
77.160
76.948
73.045
69.752
34.379
O
f1 (ppm)

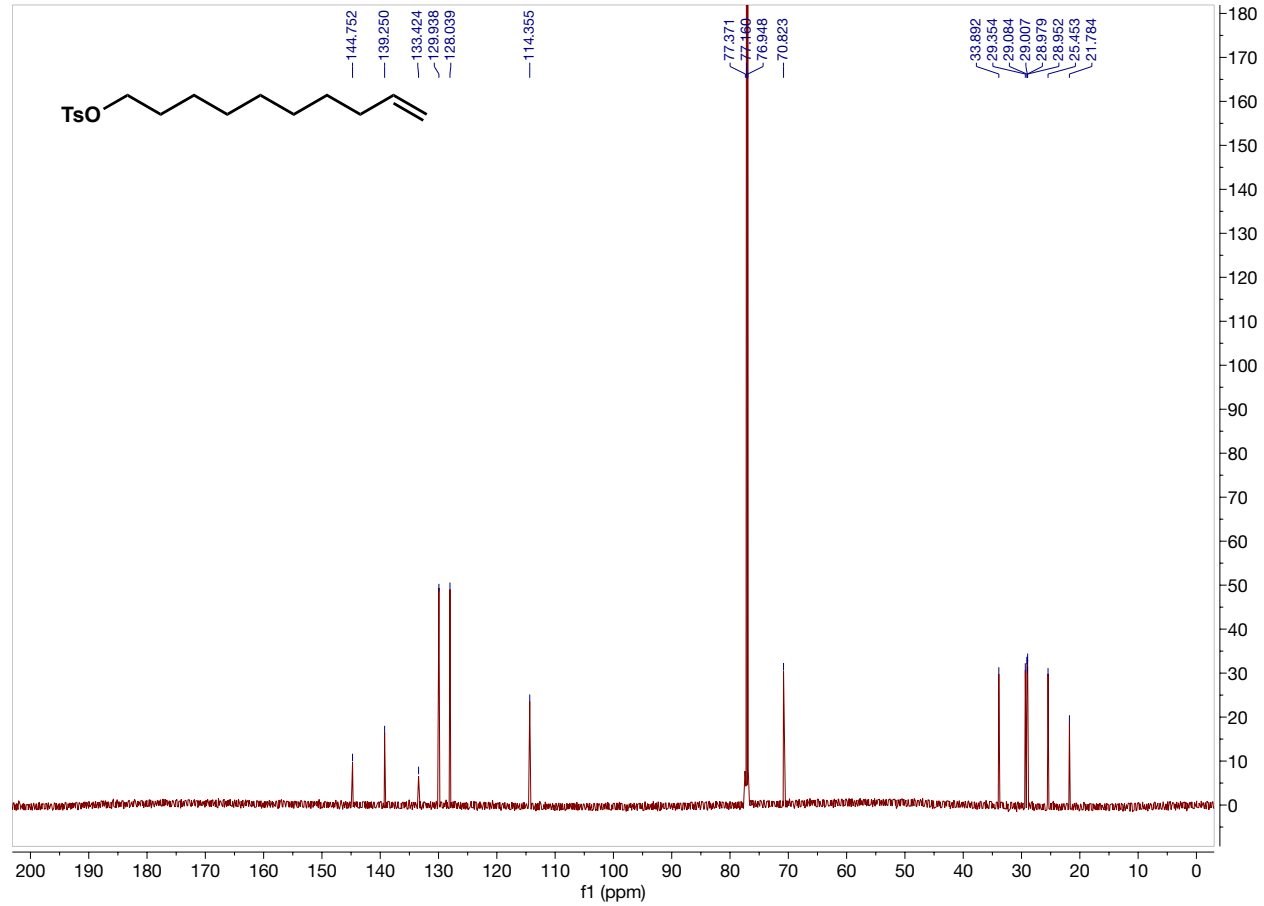

1.96
2.03
1.00
1.00
1.01
2.05
2.10
2.14
f1 (ppm)


168.534
137.436
133.992
132.285
123.296
115.421
77.371
77.160
76.948
37.693
31.105
27.762
f1 (ppm)


i-Pr
N
i-Pr
O
1.15
1.15
1.12
1.28
1.41
3.64
6.00
5.91
f1 (ppm)


171.199
138.082
115.025
48.376
45.737
34.643
29.625
21.185
20.865
i-Pr
N
i-Pr
O
f1 (ppm)


TsO
2.05
2.05
1.00
1.02
1.03
2.12
3.13
2.10
2.19
2.08
10.94
f1 (ppm)


TsO
144.752
139.250
133.424
129.938
128.039
114.355
77.371
77.160
76.948
70.823
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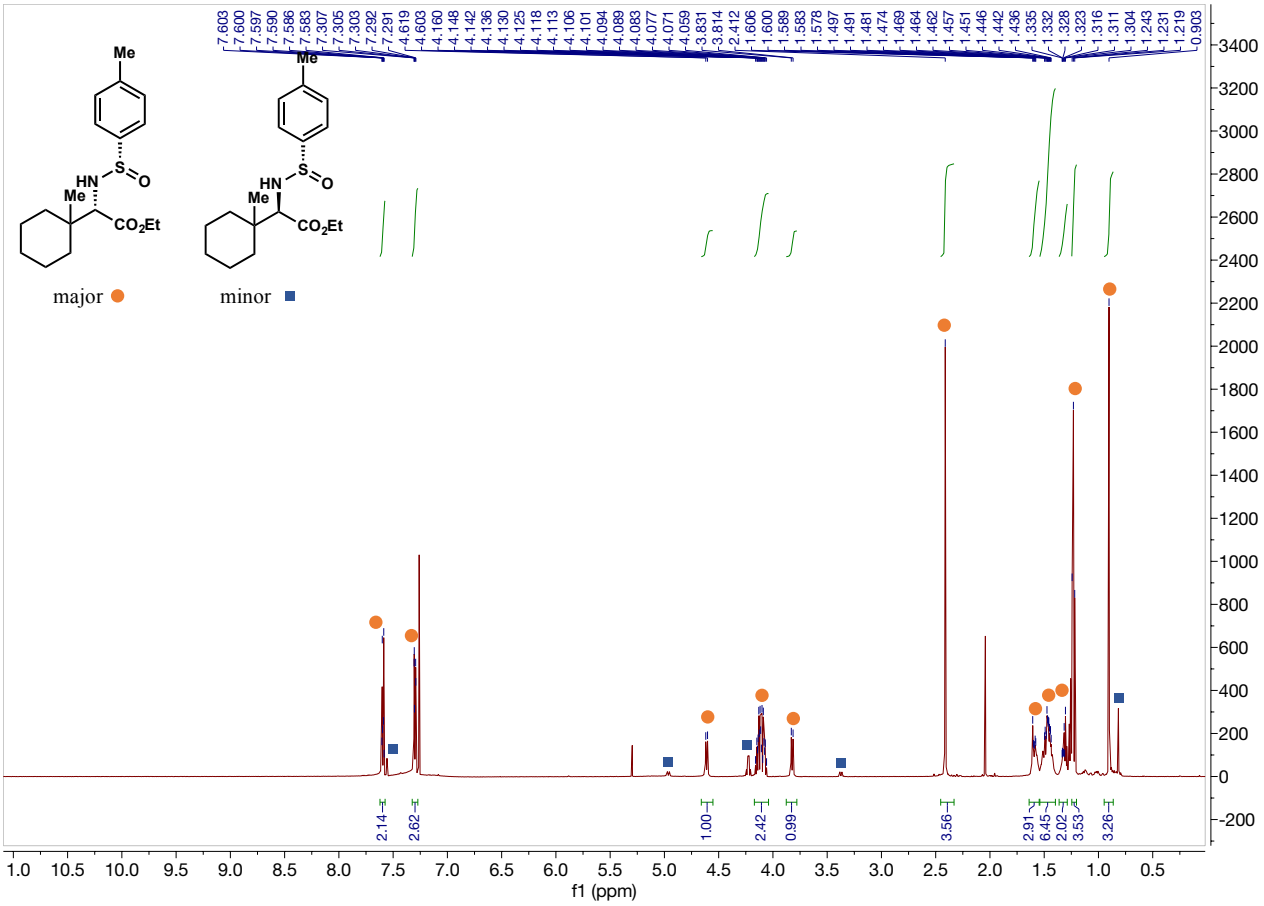
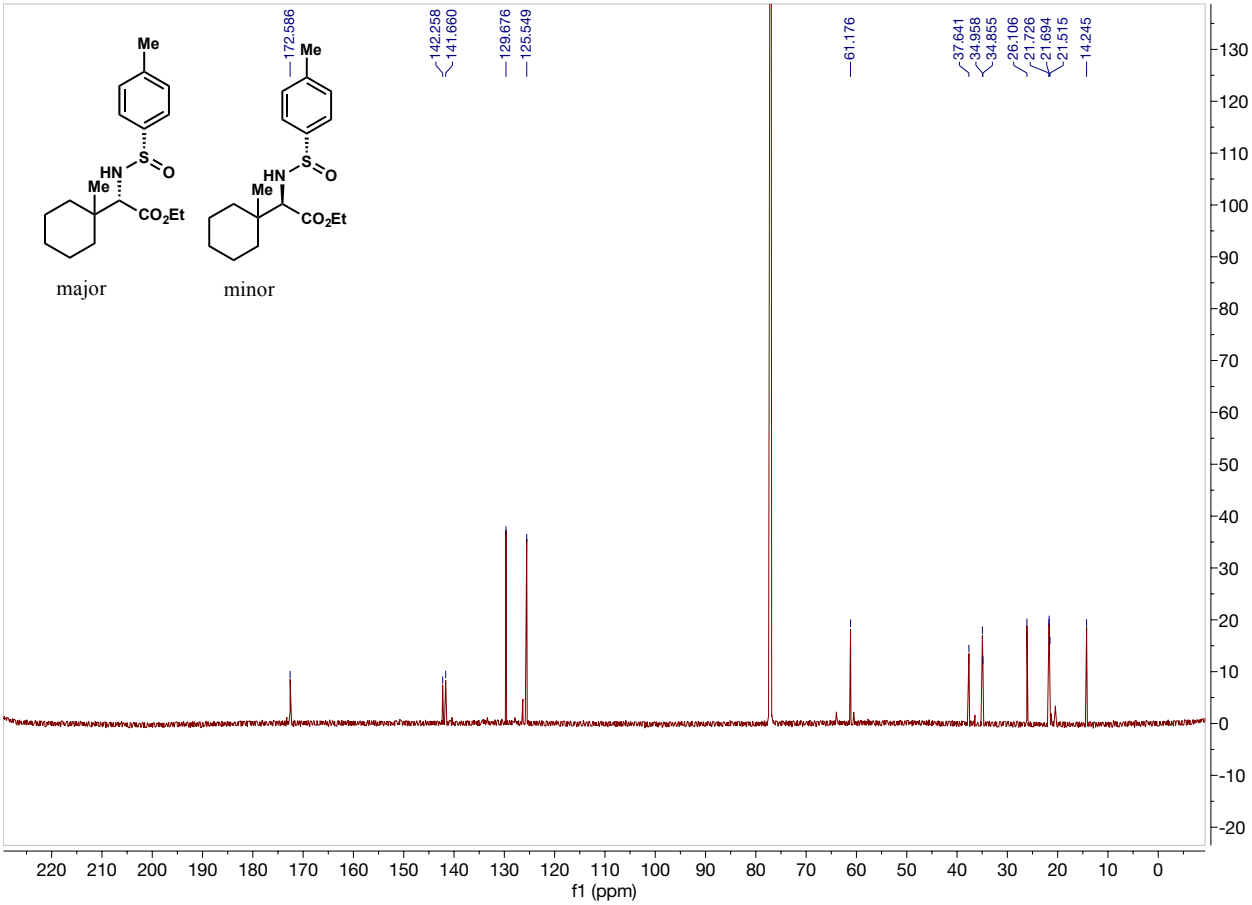
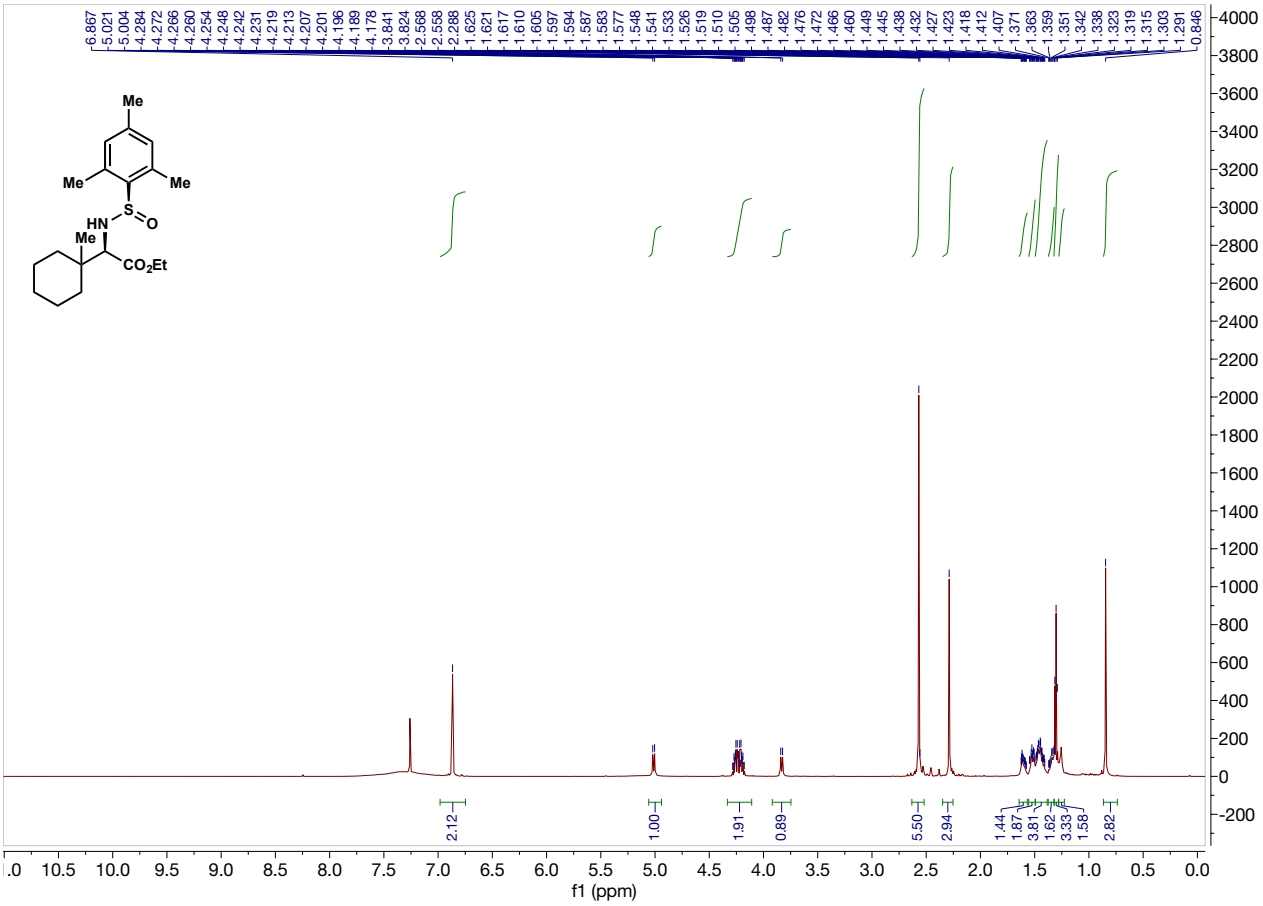
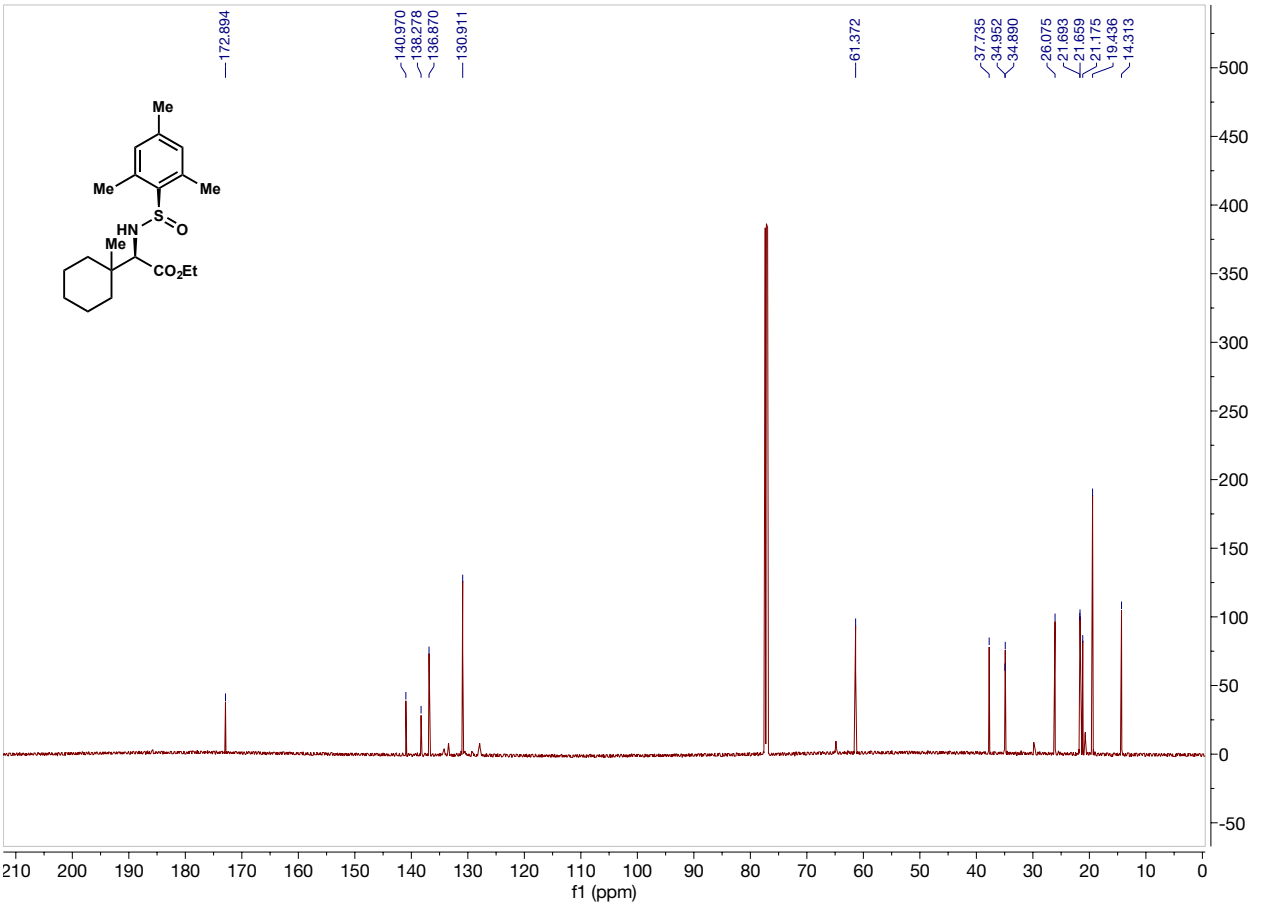
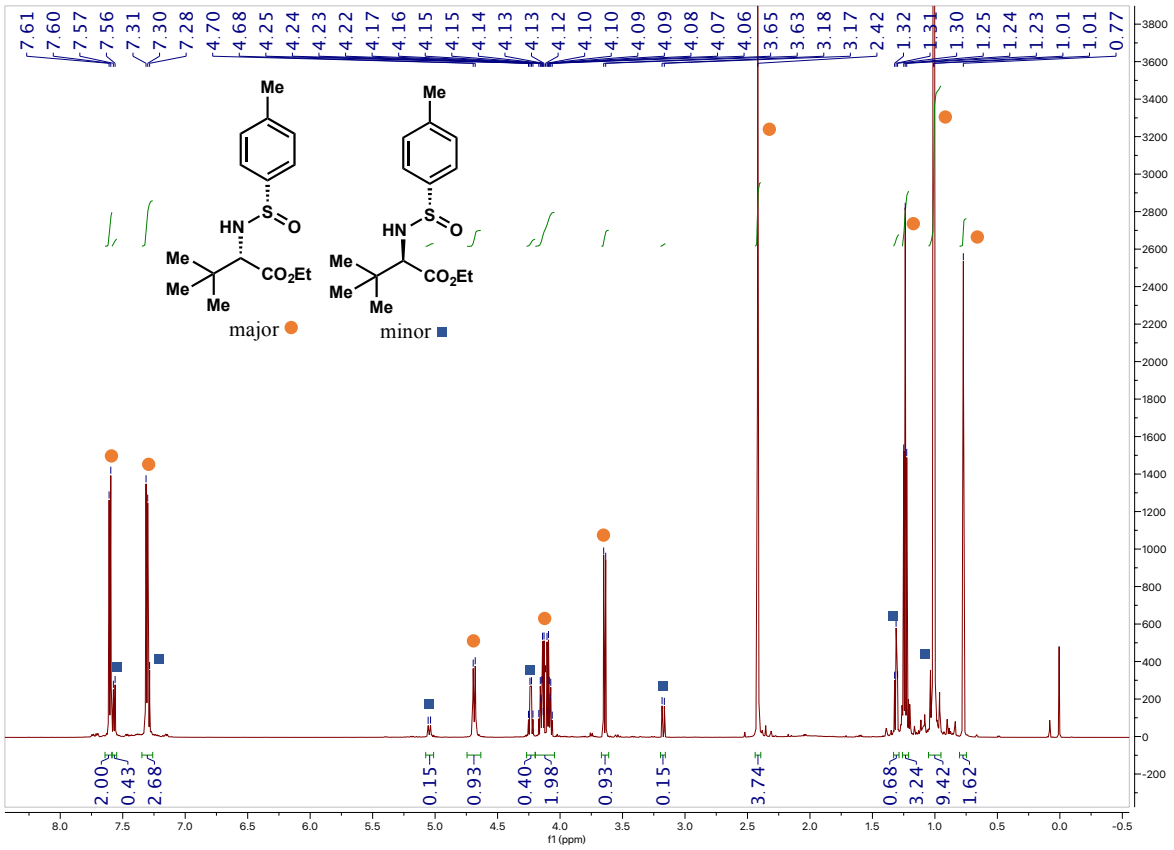
29.354
29.084
29.007
28.979
28.952
25.453
21.784
f1 (ppm)

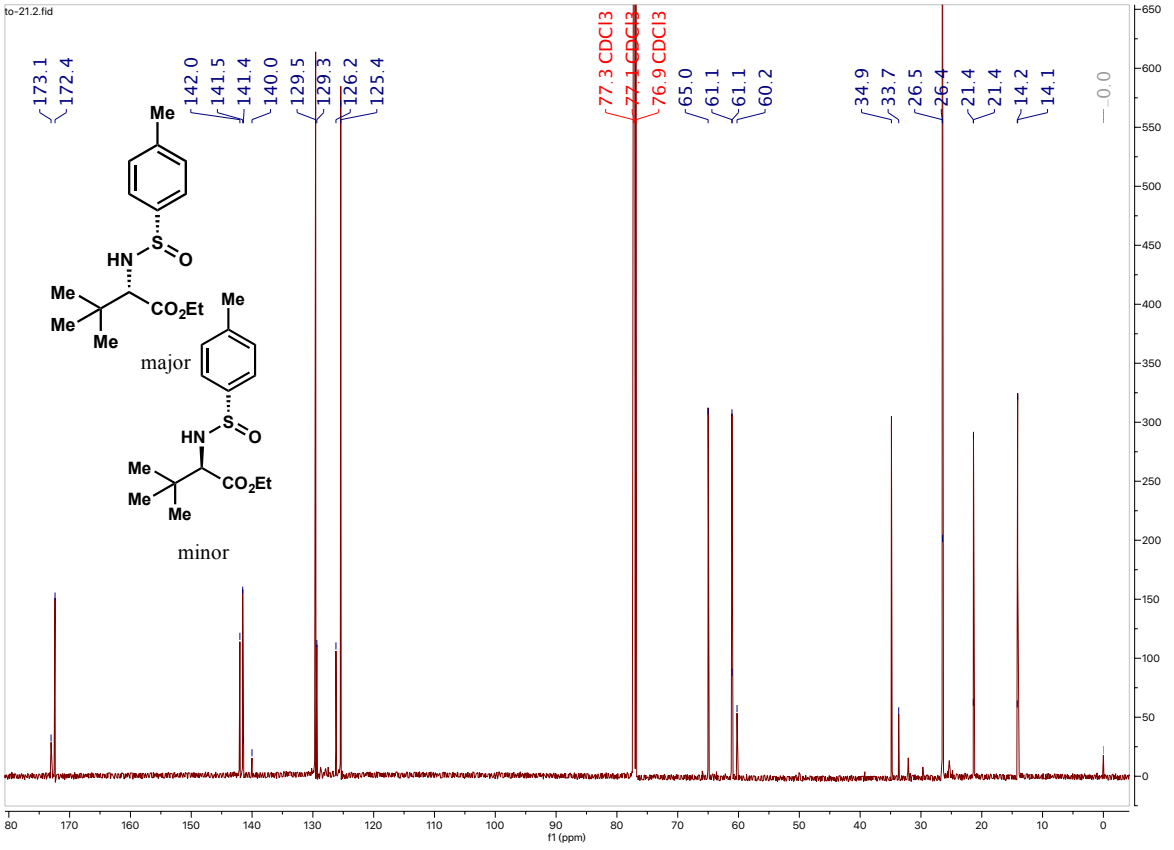

major
minor
f1 (ppm)

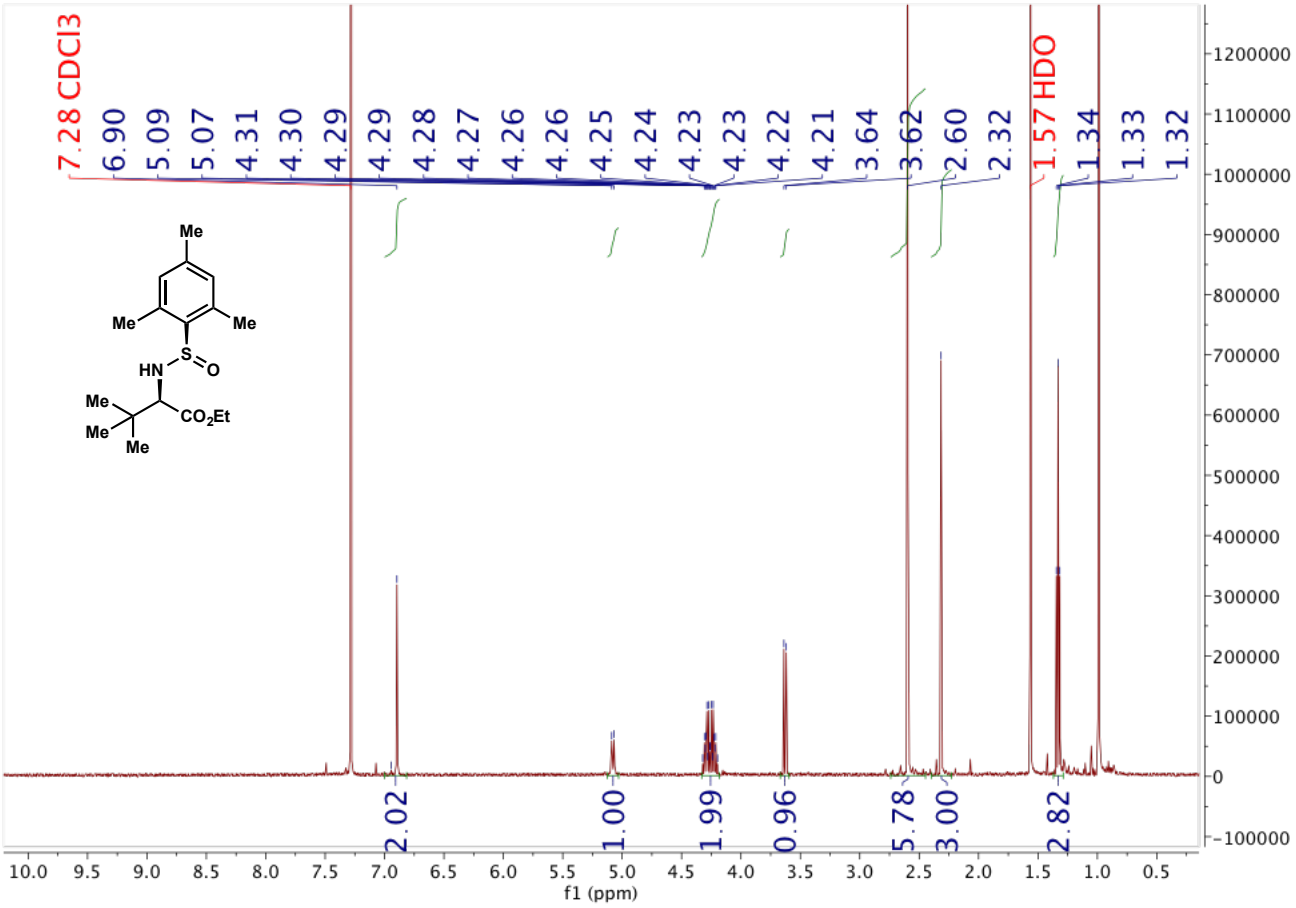

major
minor
f1 (ppm)

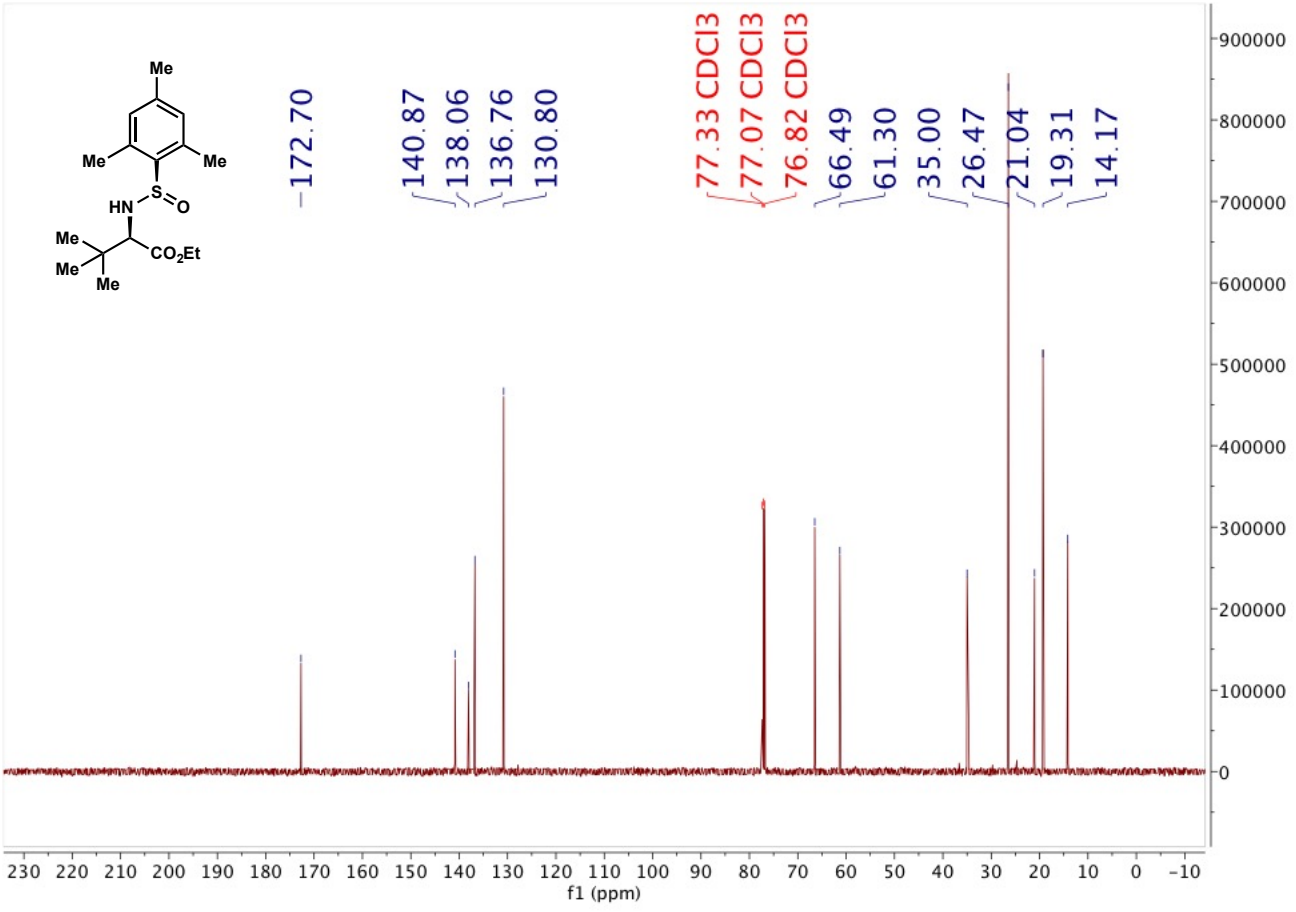

Me
Me
Me
S
O
HN
Me
CO2Et
f1 (ppm)

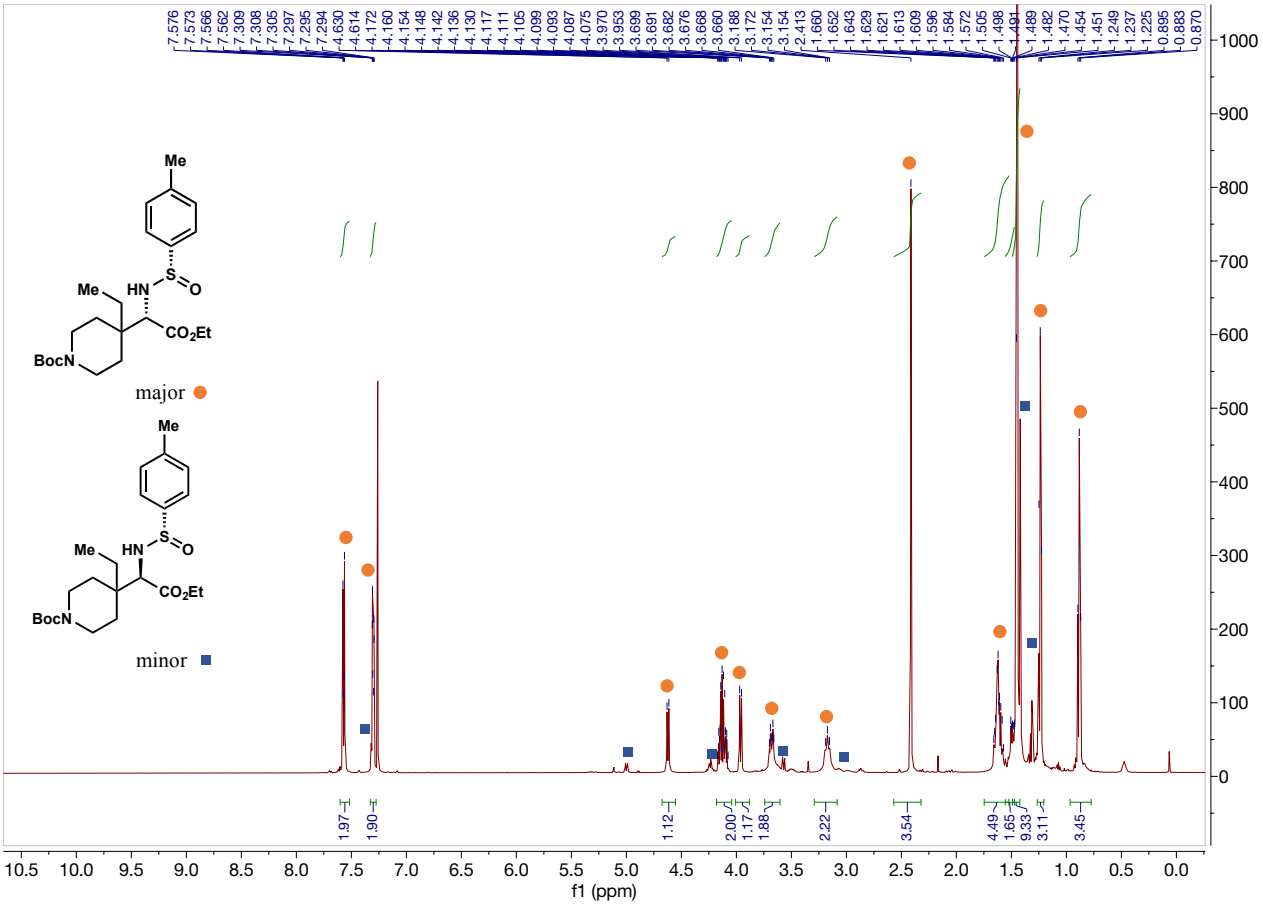

Me
Me
Me
S
O
HN
Me
CO2Et
f1 (ppm)

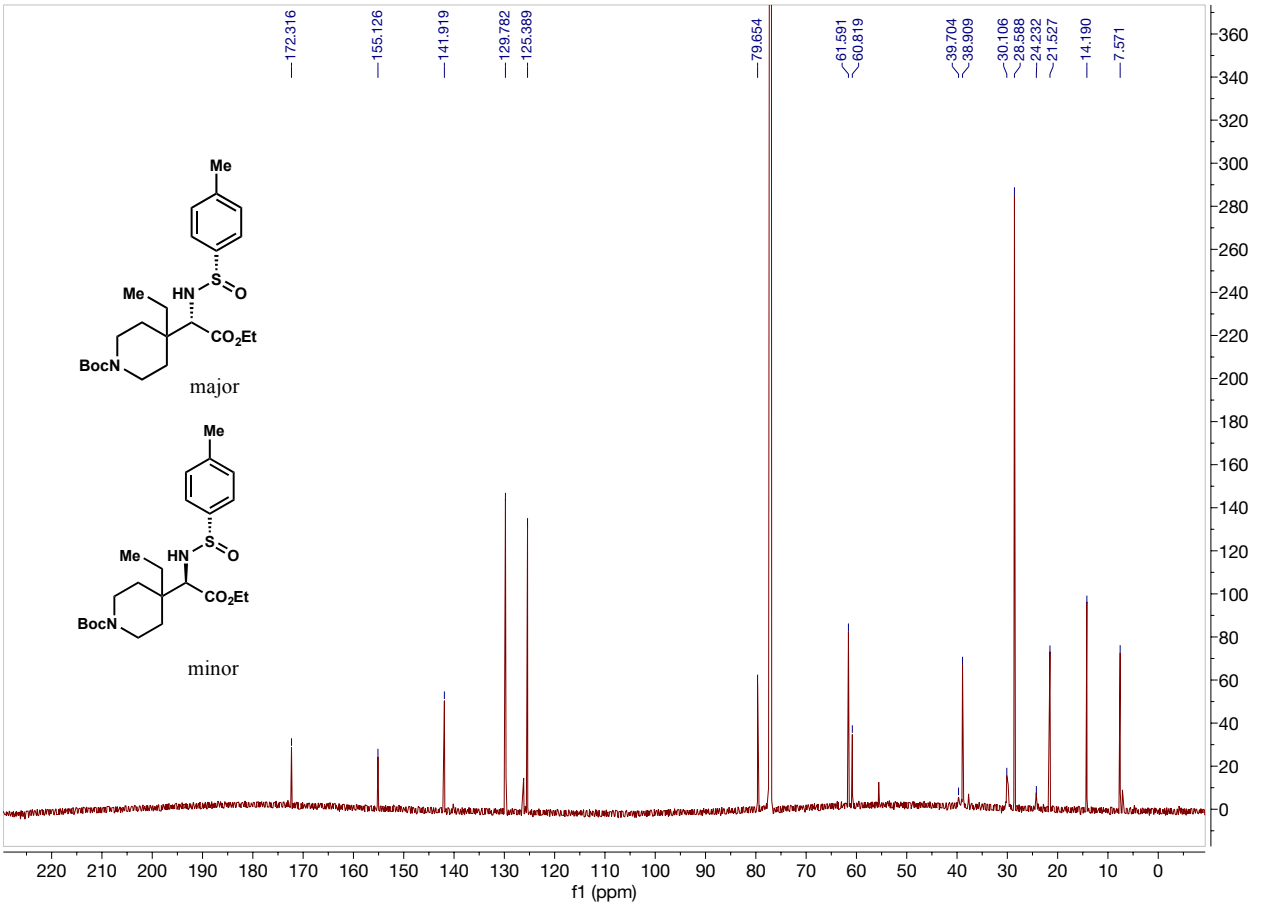

major
minor
f1 (ppm)

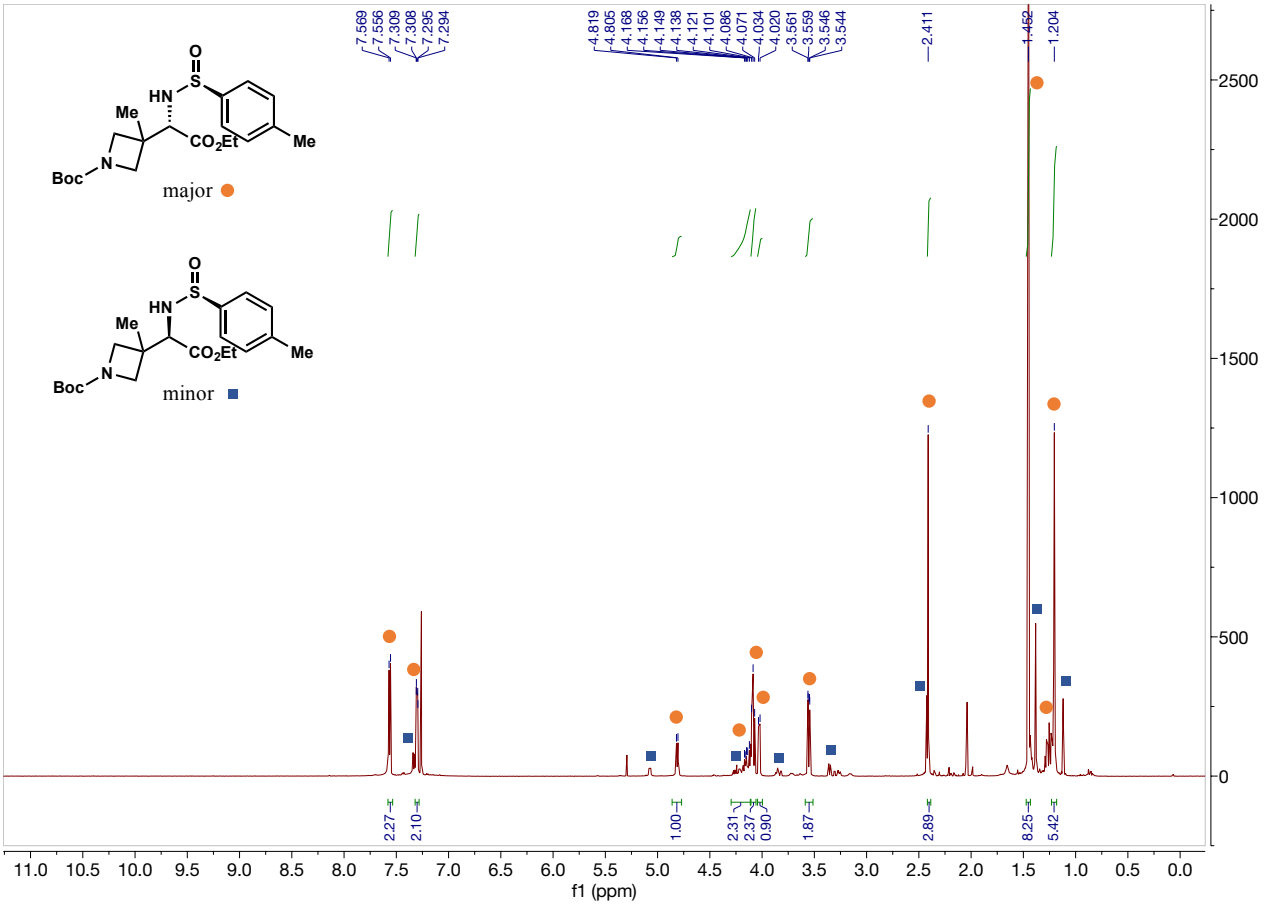

major
minor
f1 (ppm)

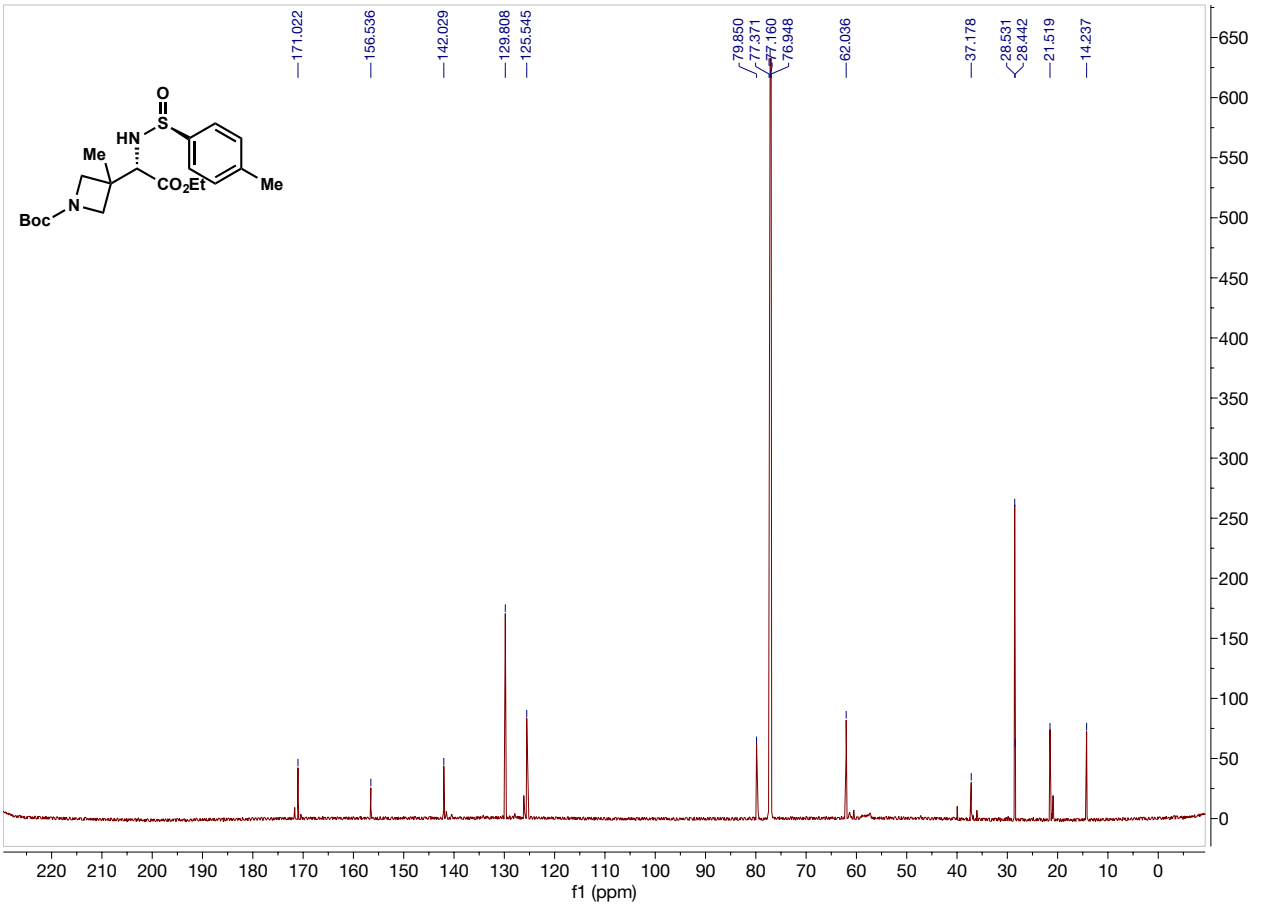

7.28 CDCl3
6.90
5.09
5.07
4.31
4.30
4.29
4.29
4.28
4.27
4.26
4.26
4.25
4.24
4.23
4.23
4.22
4.21
3.64
3.62
2.60
2.32
1.57 HDO
1.34
1.33
1.32
Me
Me
Me
HN
S
O
Me
Me
Me
CO2Et
2.02
1.00
1.99
0.96
5.78
3.00
2.82
f1 (ppm)

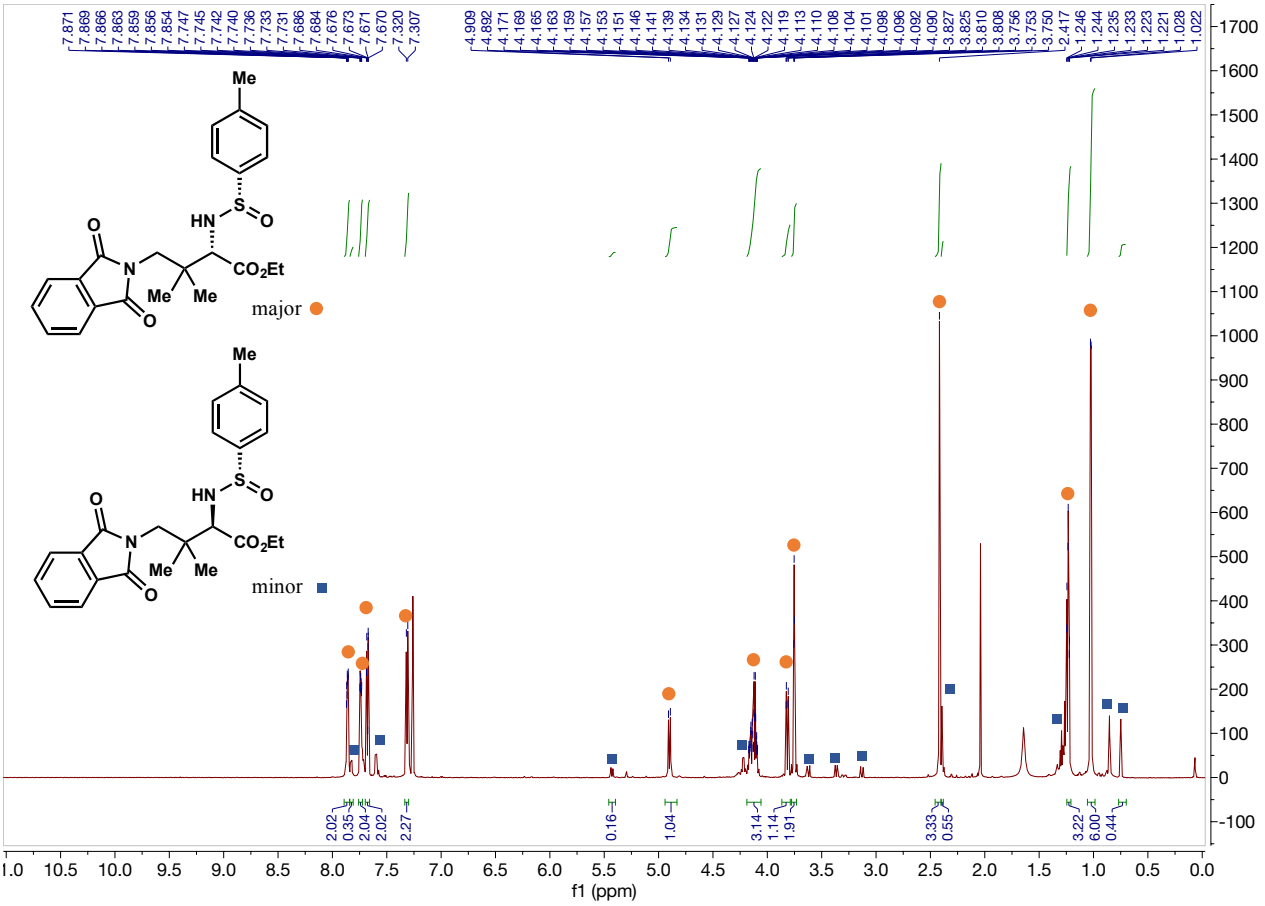

Me
Me
Me
HN
S
O
Me
Me
Me
CO2Et
172.70
140.87
138.06
136.76
130.80
77.33 CDCl3
77.07 CDCl3
76.82 CDCl3
66.49
61.30
35.00
26.47
21.04
19.31
14.17
f1 (ppm)

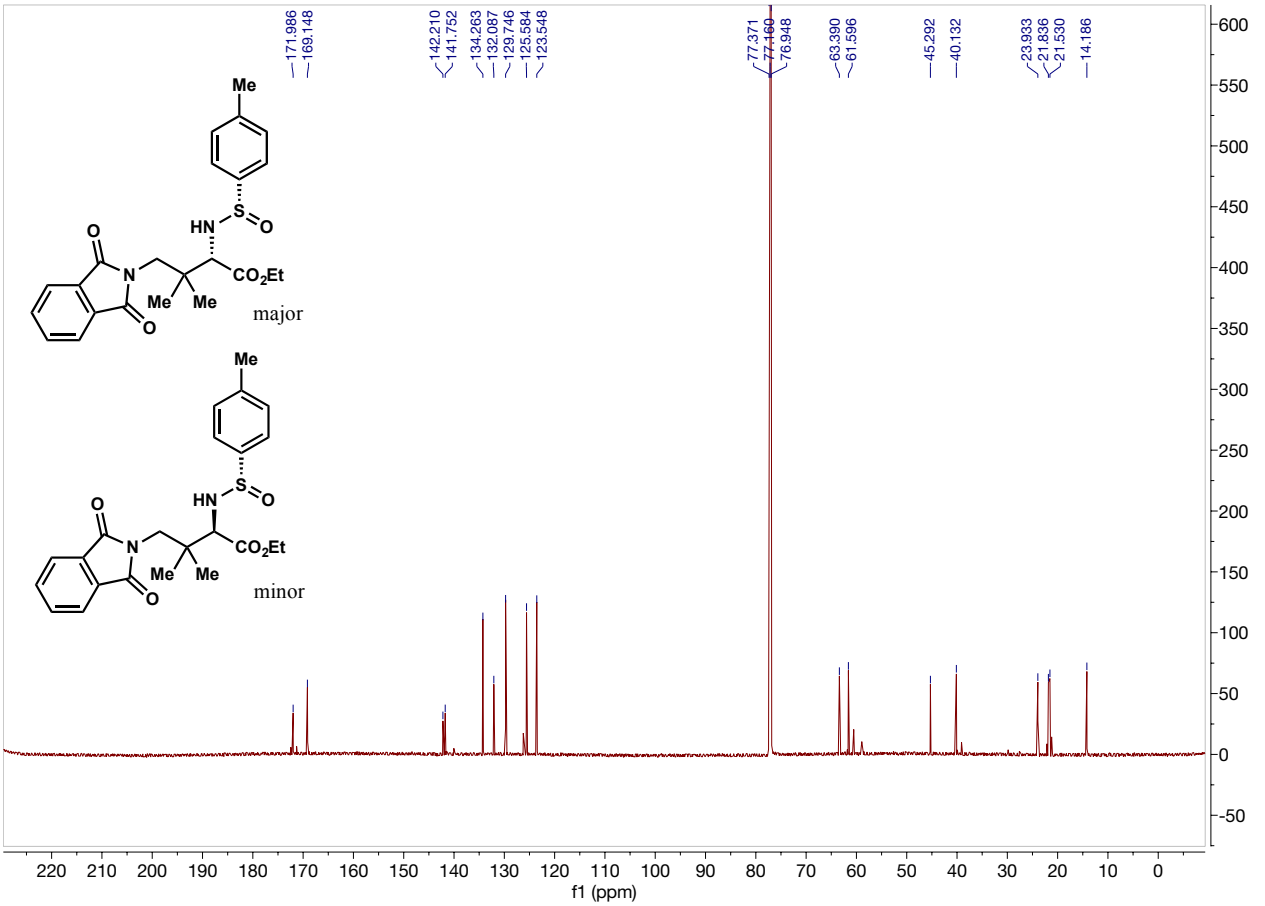

major
minor
f1 (ppm)

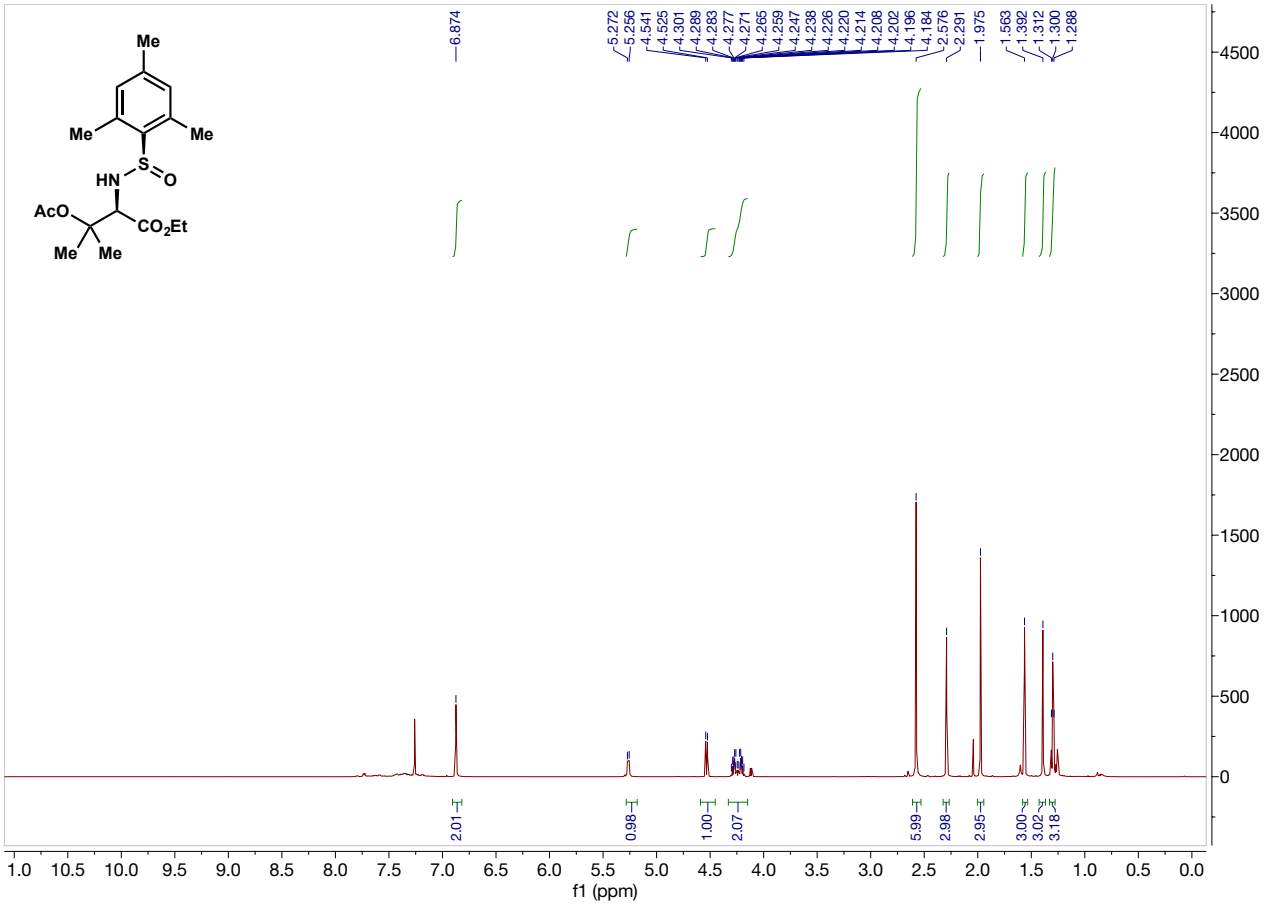

major
minor
f1 (ppm)

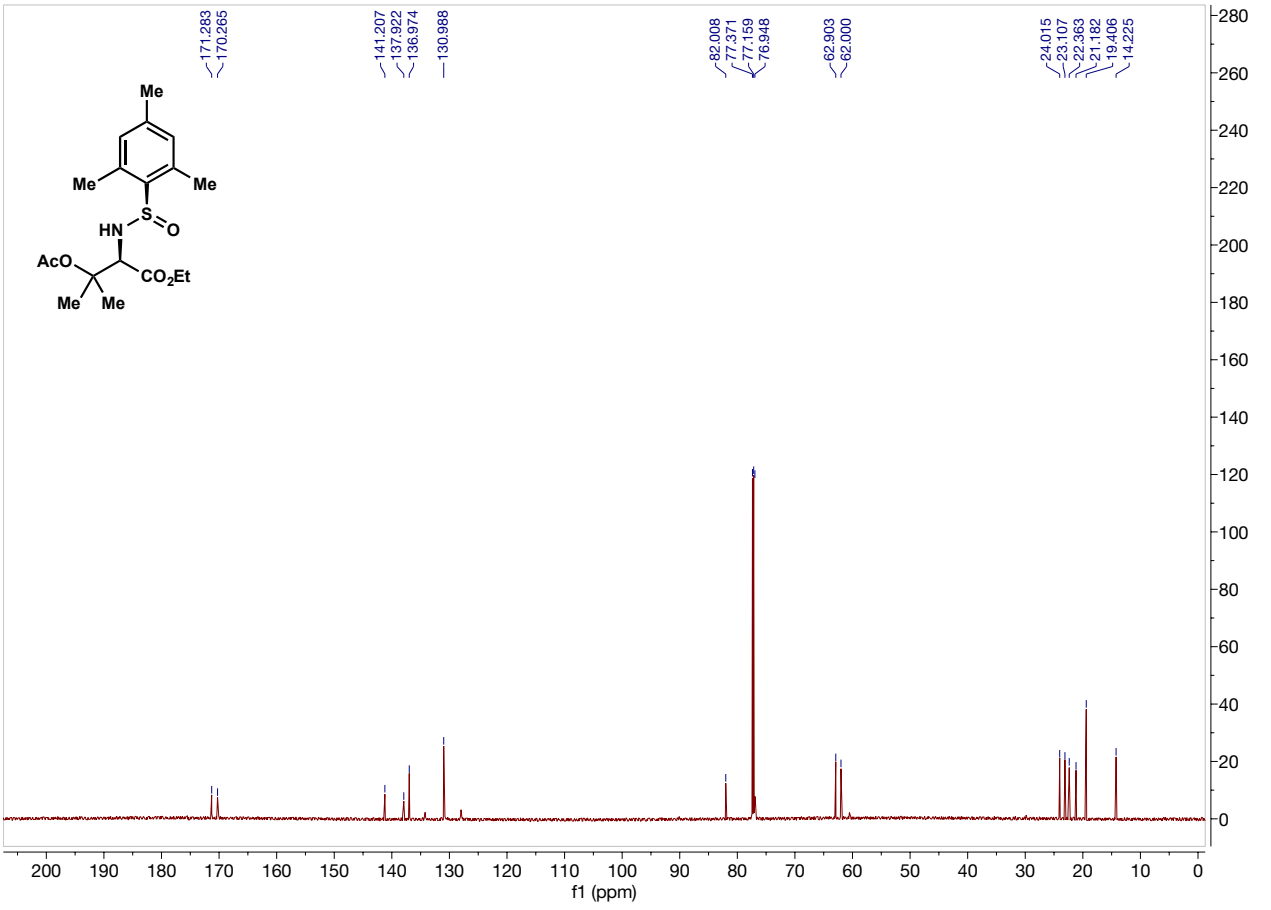

major
minor
f1 (ppm)

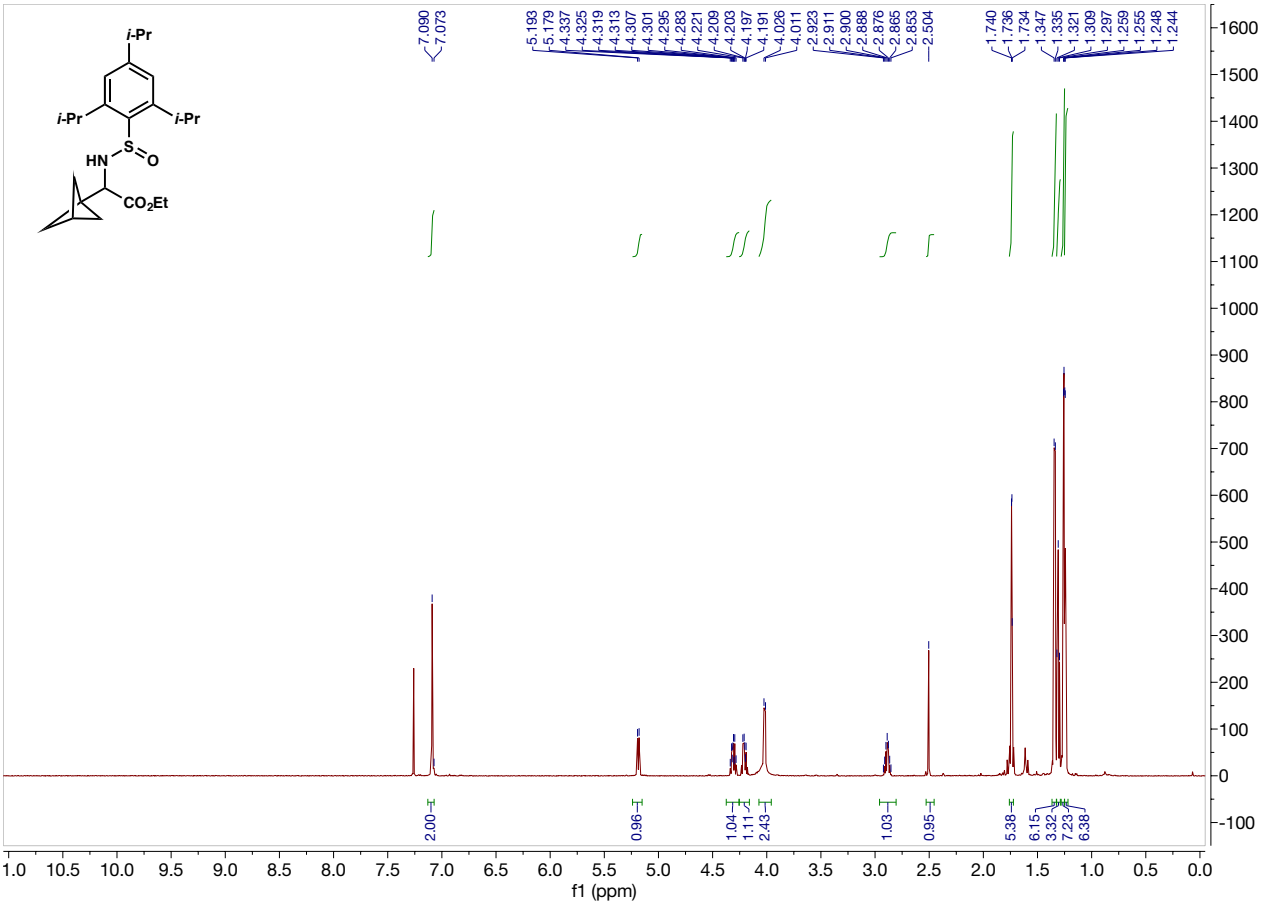

f1 (ppm)

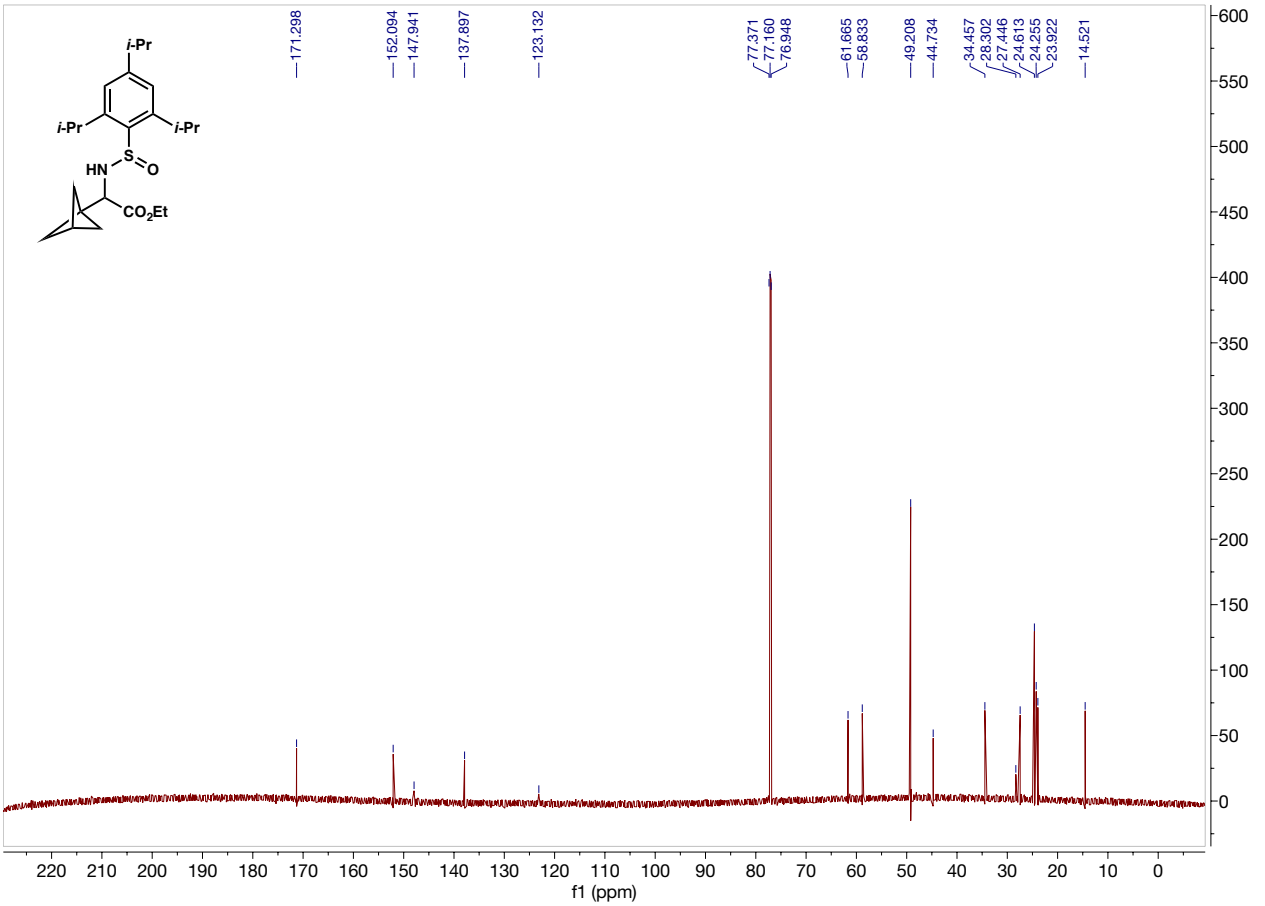

major
minor
f1 (ppm)

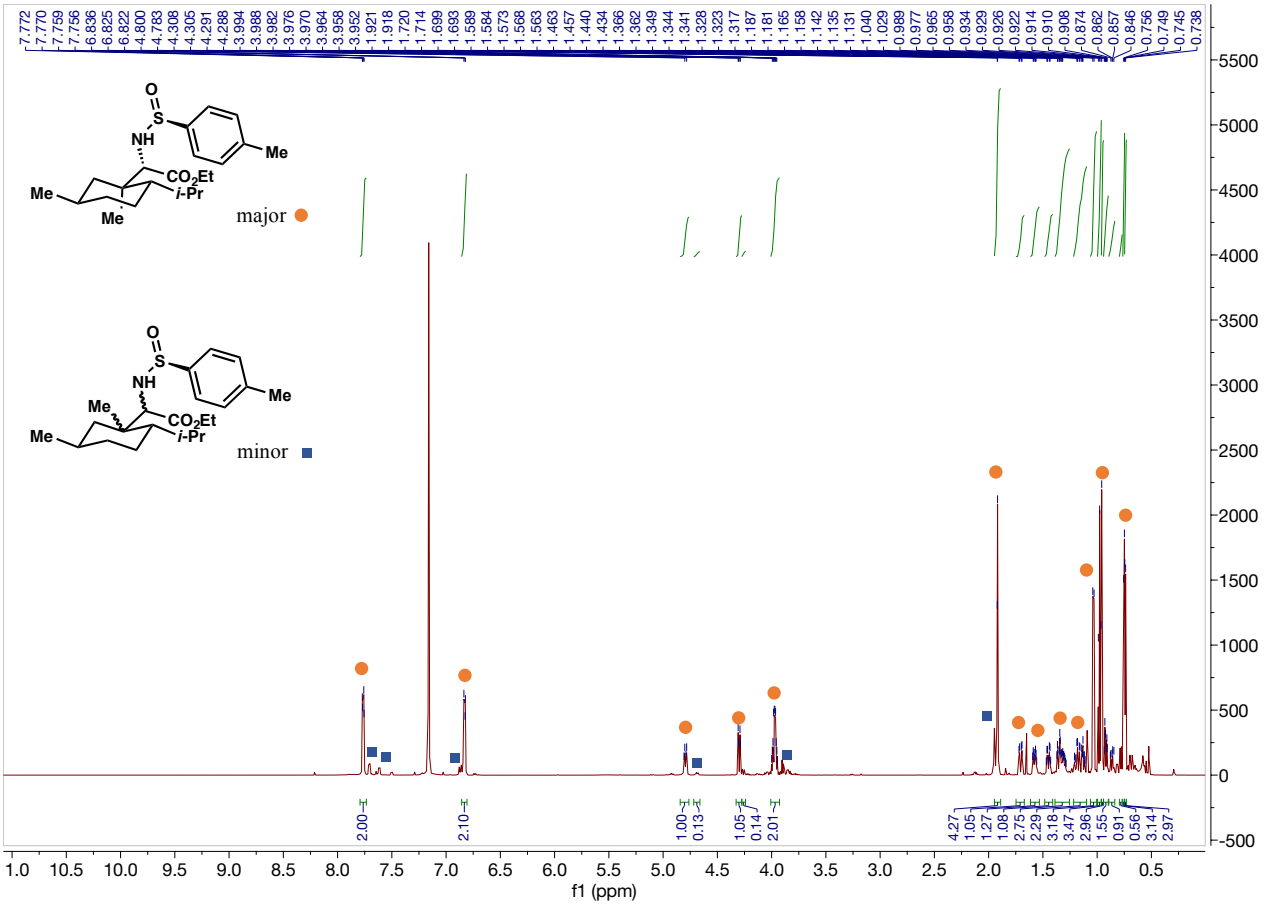

major
minor
f1 (ppm)

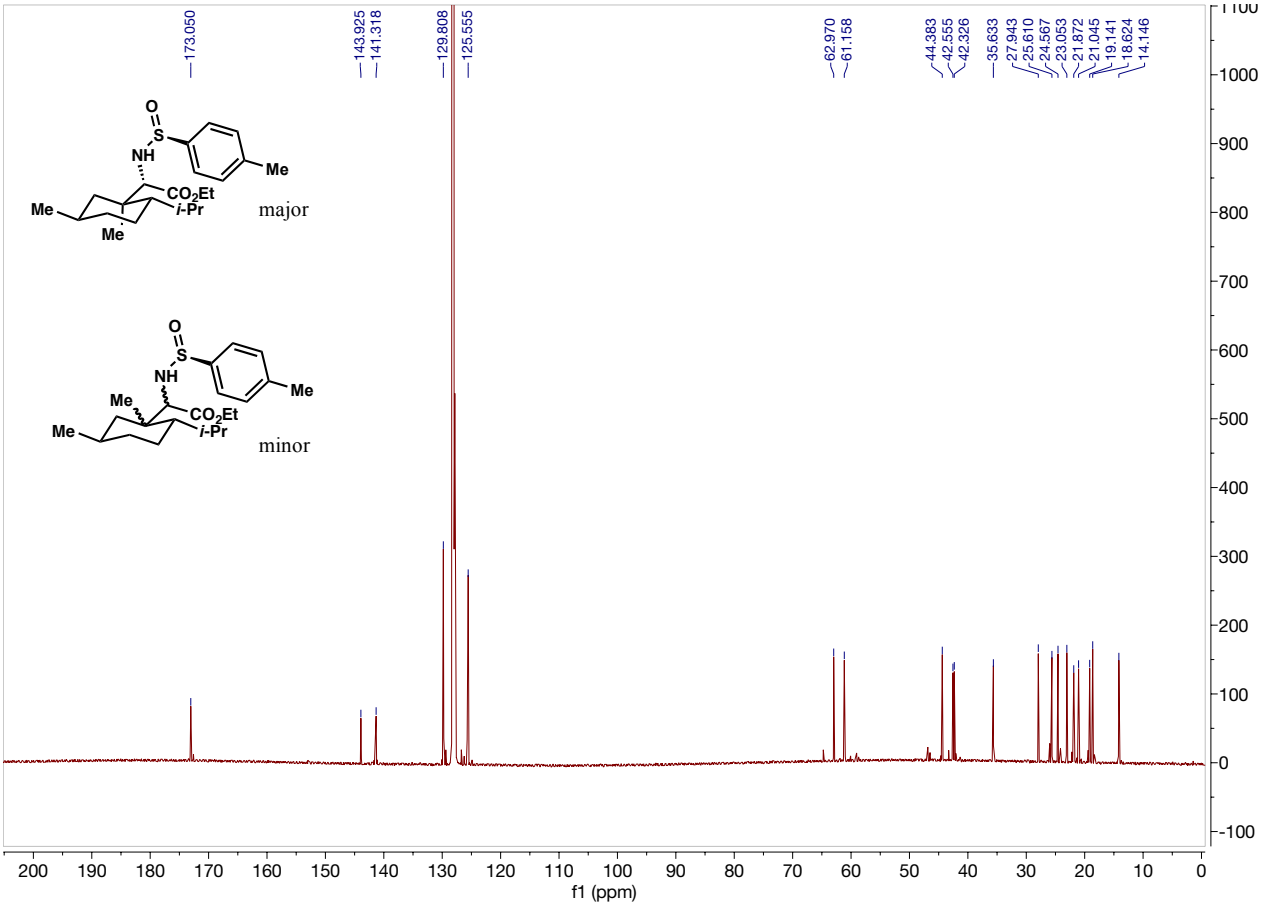

Me
Me
Me
S
O
HN
AcO
CO2Et
Me
Me
6.874
5.272
5.256
4.541
4.525
4.301
4.289
4.283
4.277
4.271
4.265
4.259
4.247
4.238
4.226
4.220
4.214
4.208
4.202
4.196
4.184
2.576
2.291
1.975
1.563
1.392
1.312
1.300
1.288
2.01
0.98
1.00
2.07
5.99
2.98
2.95
3.00
3.02
3.18
f1 (ppm)

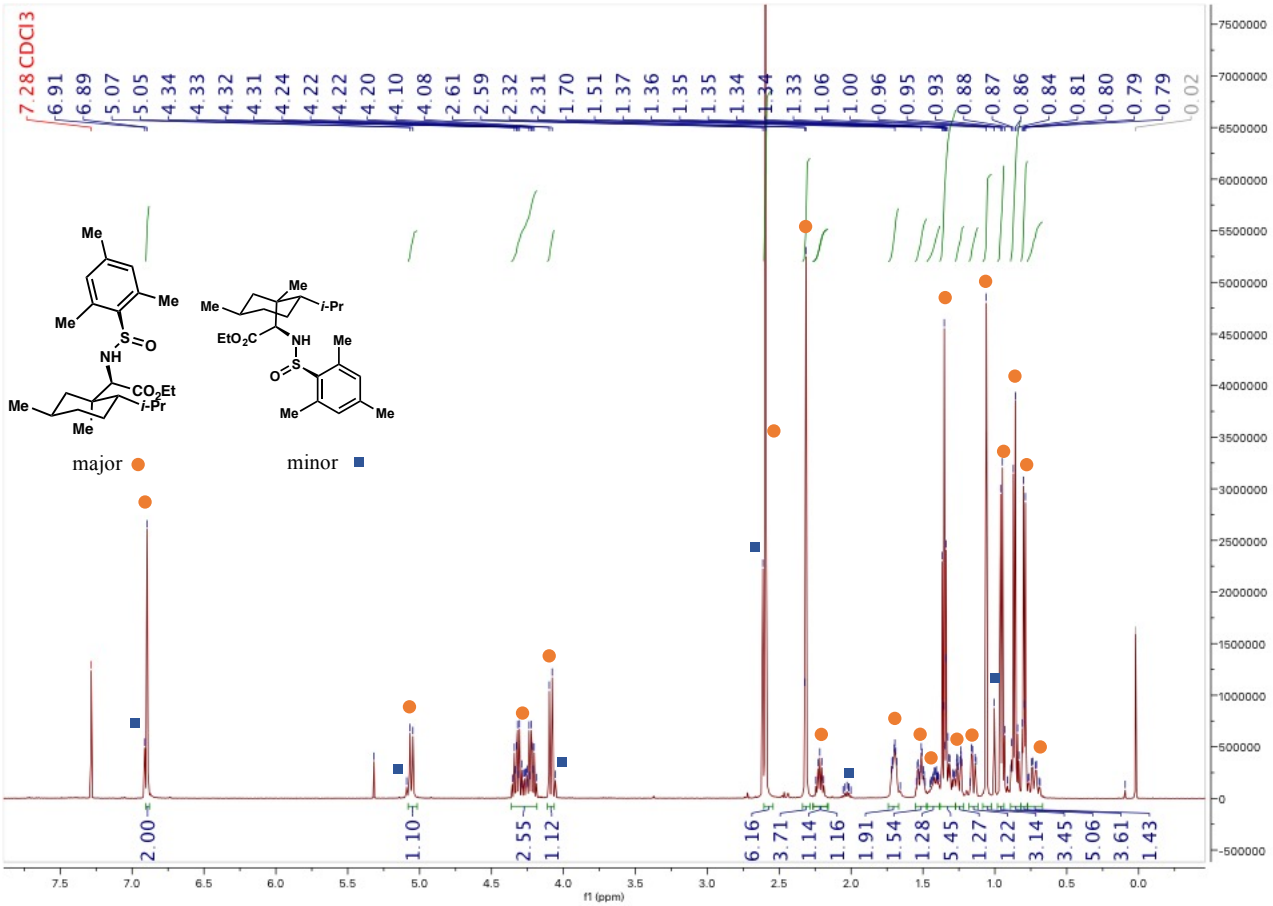

Me
Me
Me
S
O
HN
AcO
CO2Et
Me
Me
171.283
170.265
141.207
137.922
136.974
130.988
82.008
77.371
77.159
76.948
62.903
62.000
24.015
23.107
22.363
21.182
19.406
14.225
f1 (ppm)

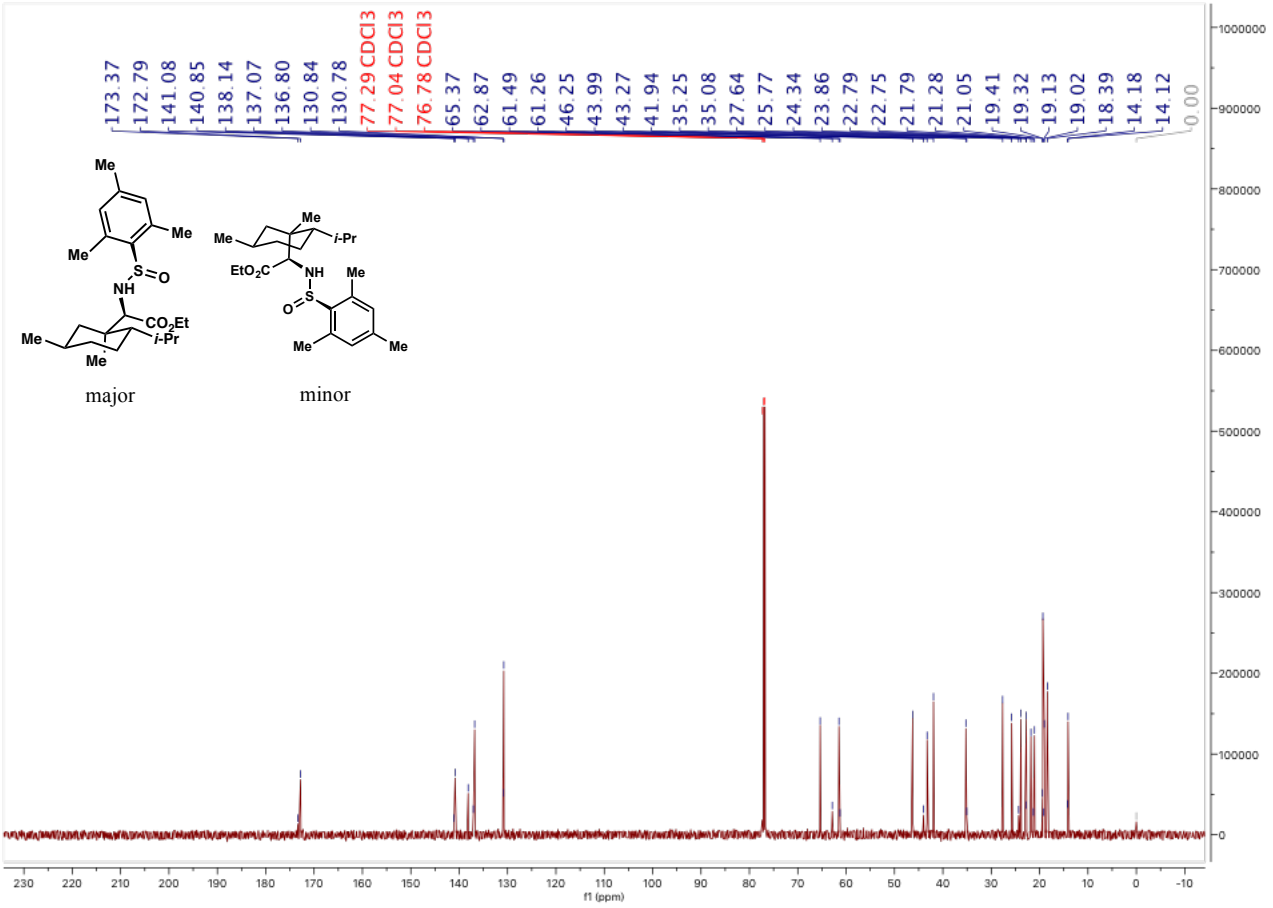

i-Pr
i-Pr
i-Pr
HN
S
O
CO2Et
7.090
7.073
5.193
5.179
4.337
4.325
4.319
4.313
4.307
4.301
4.295
4.283
4.221
4.209
4.203
4.197
4.191
4.026
4.011
2.923
2.911
2.900
2.888
2.876
2.865
2.853
2.504
1.740
1.736
1.734
1.347
1.335
1.321
1.309
1.297
1.259
1.255
1.248
1.244
2.00
0.96
1.04
1.11
2.43
1.03
0.95
5.38
6.15
3.32
7.23
6.38
f1 (ppm)

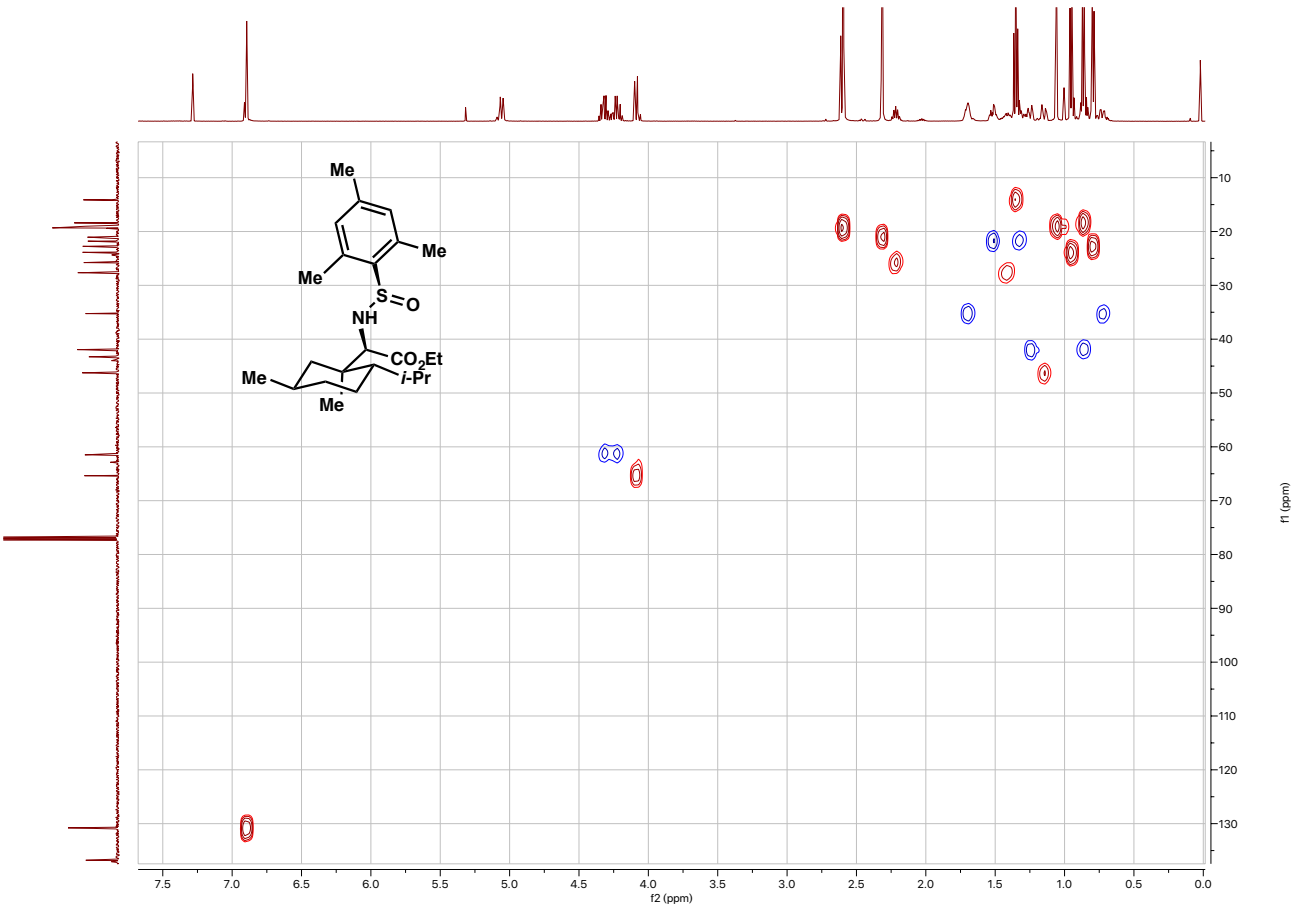

i-Pr
i-Pr
i-Pr
HN
S
O
CO2Et
171.298
152.094
147.941
137.897
123.132
77.371
77.160
76.948
61.665
58.833
49.208
44.734
34.457
28.302
27.446
24.613
24.255
23.922
14.521
f1 (ppm)

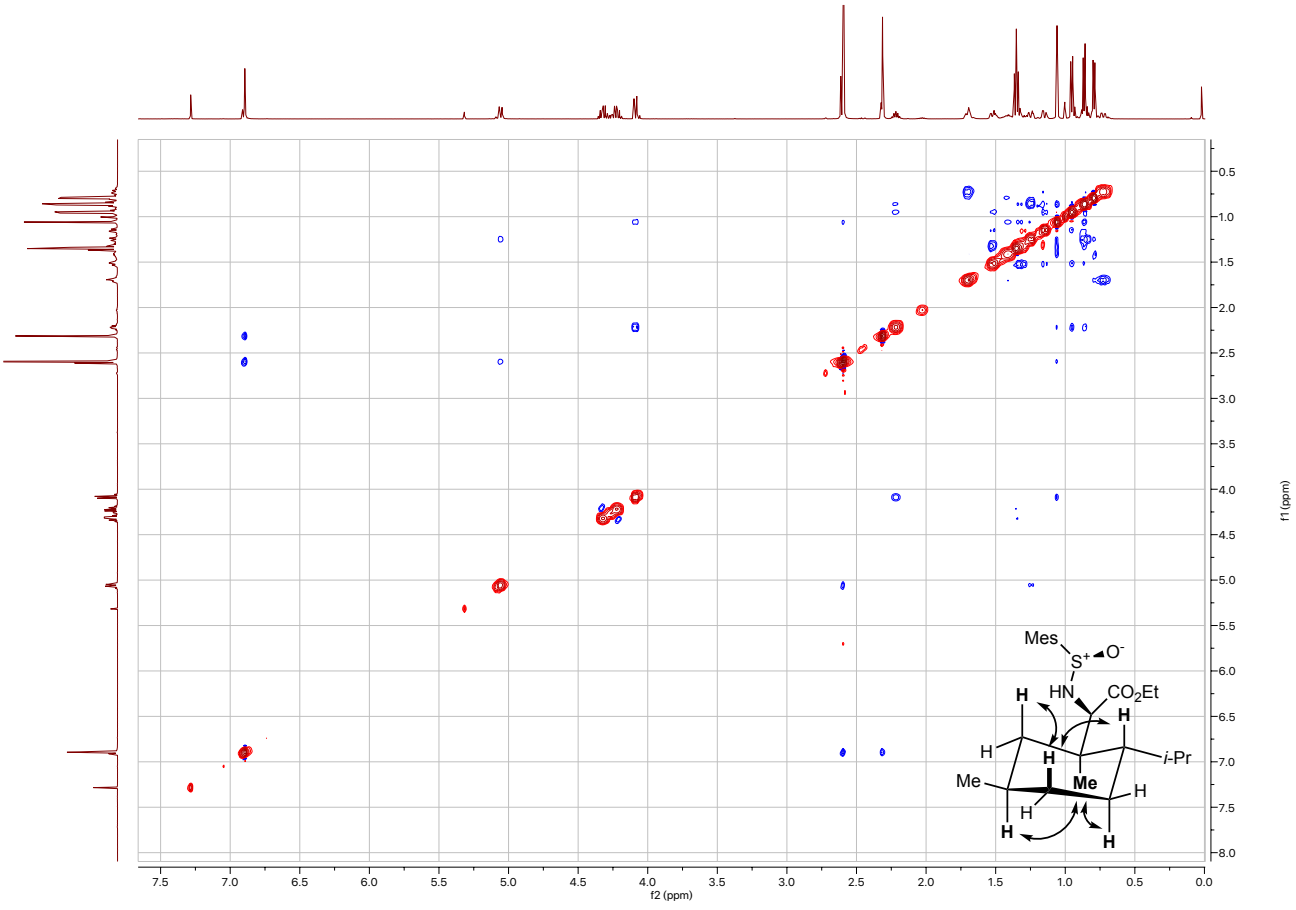

major
minor
f1 (ppm)

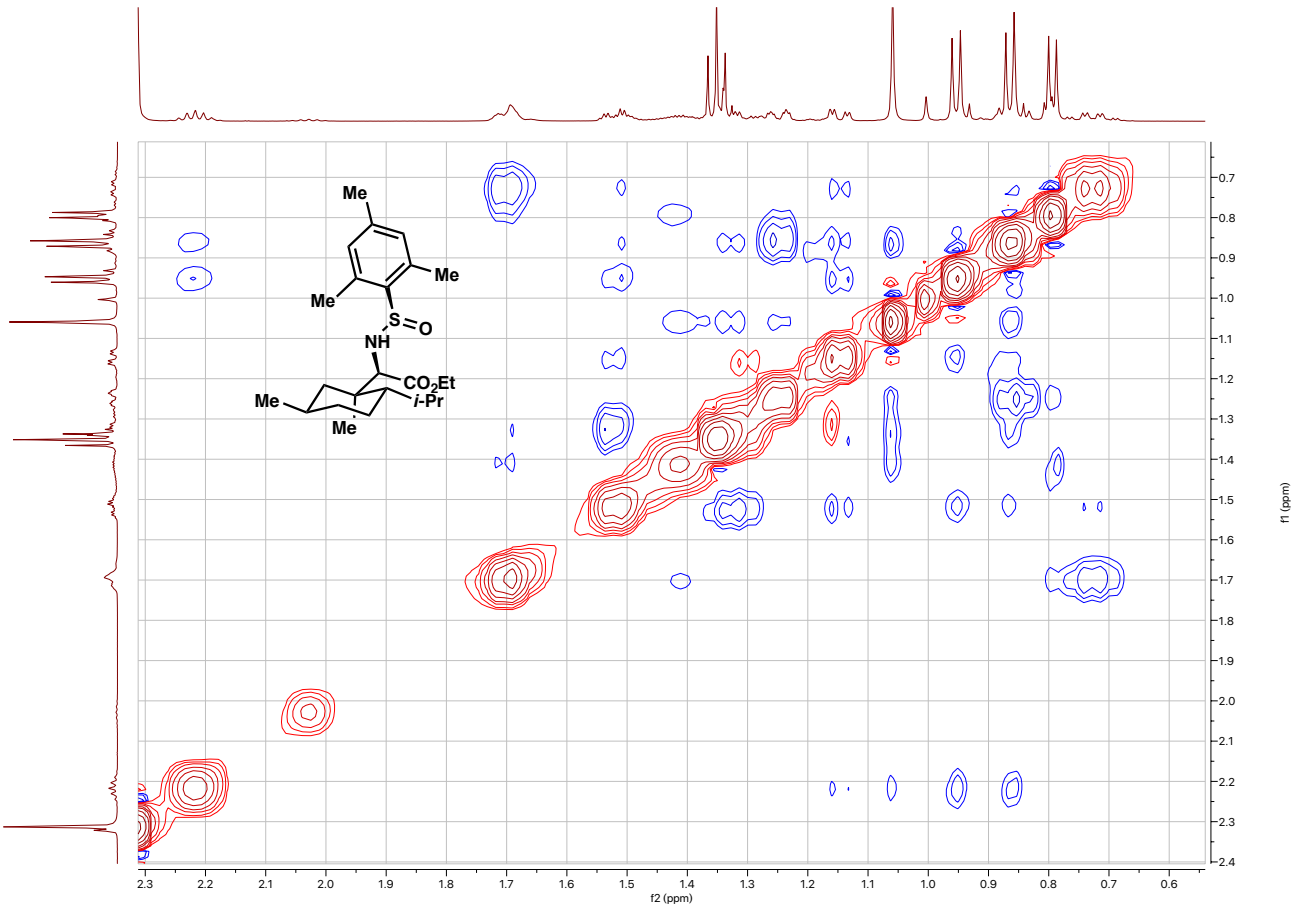

major
minor
f1 (ppm)

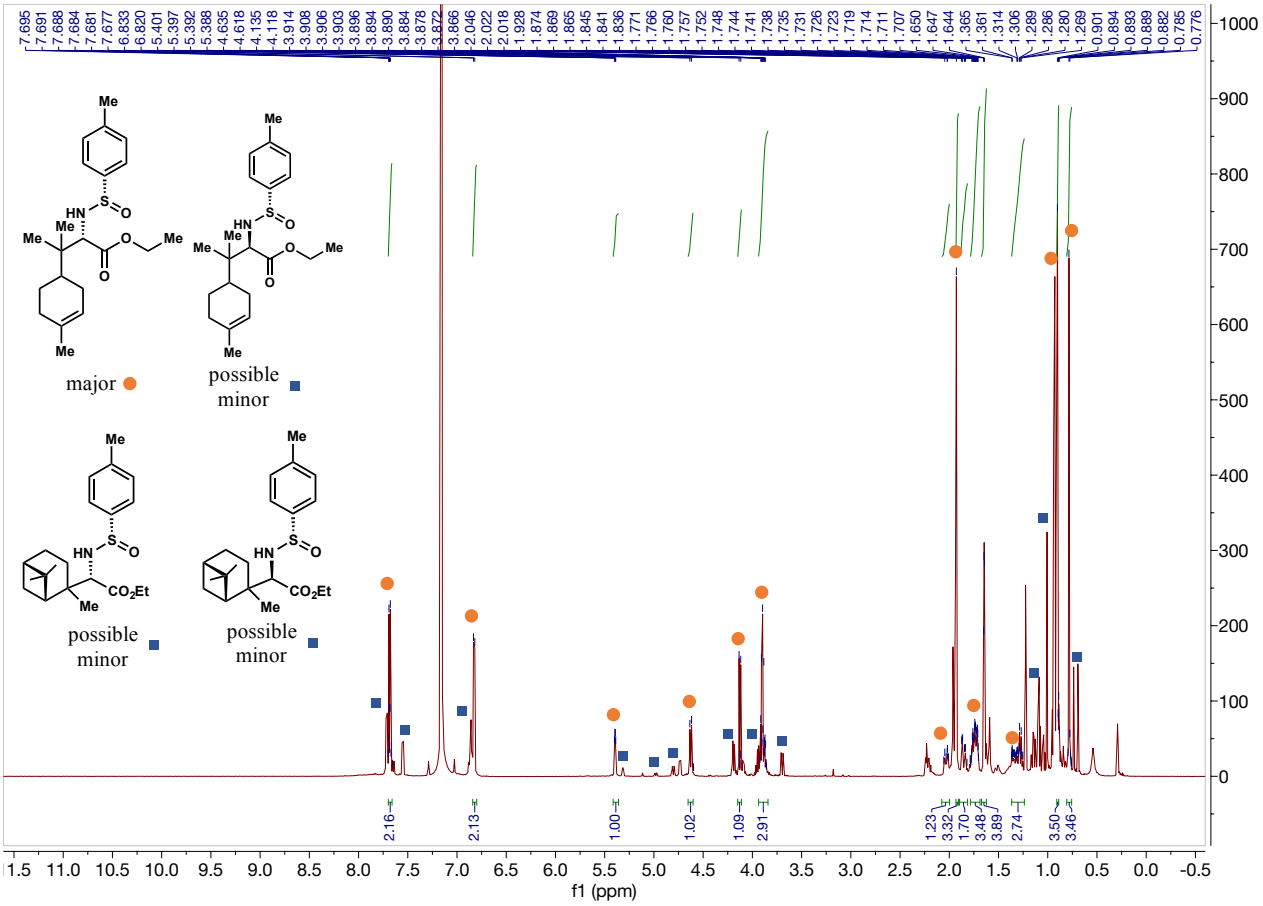

major
minor

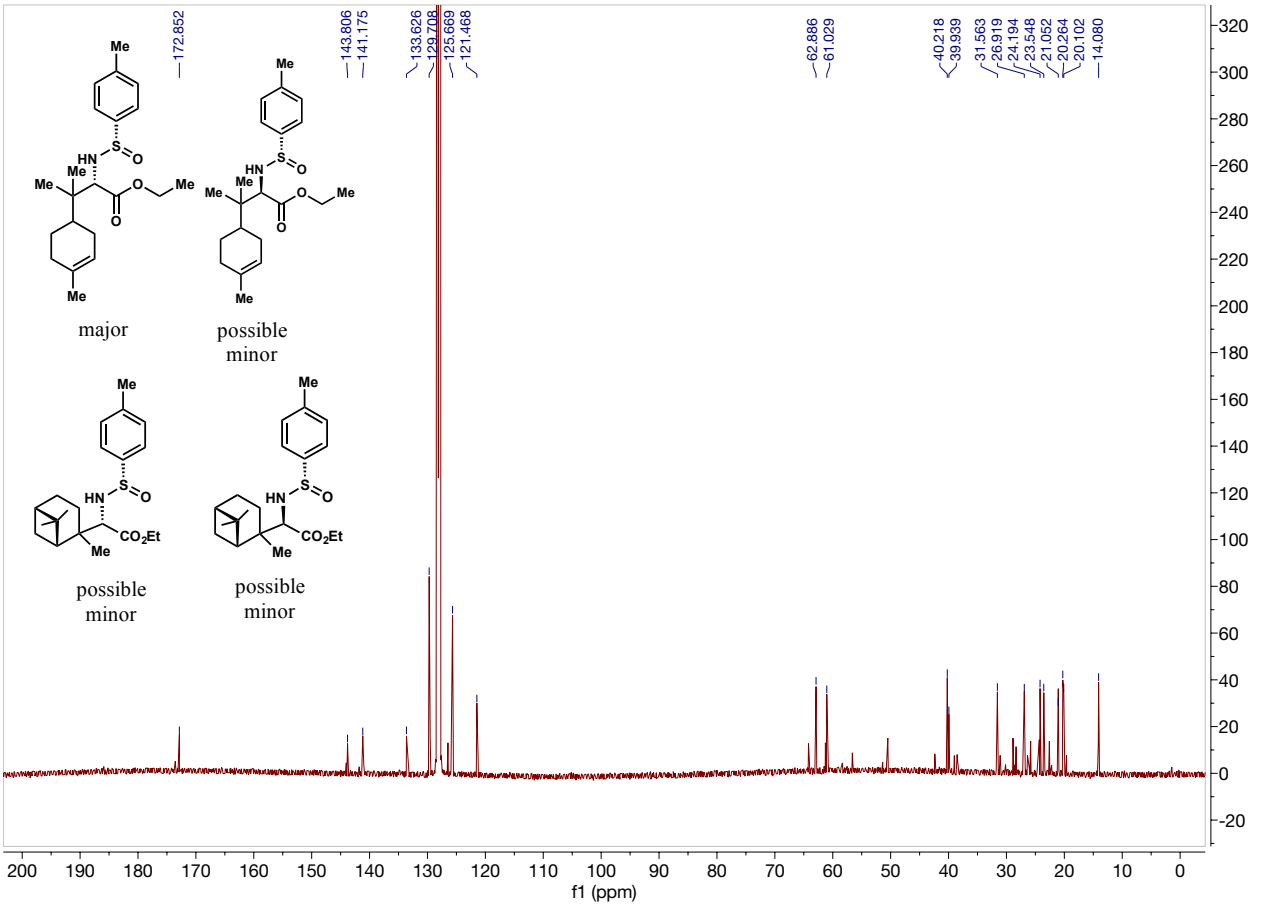

major
minor

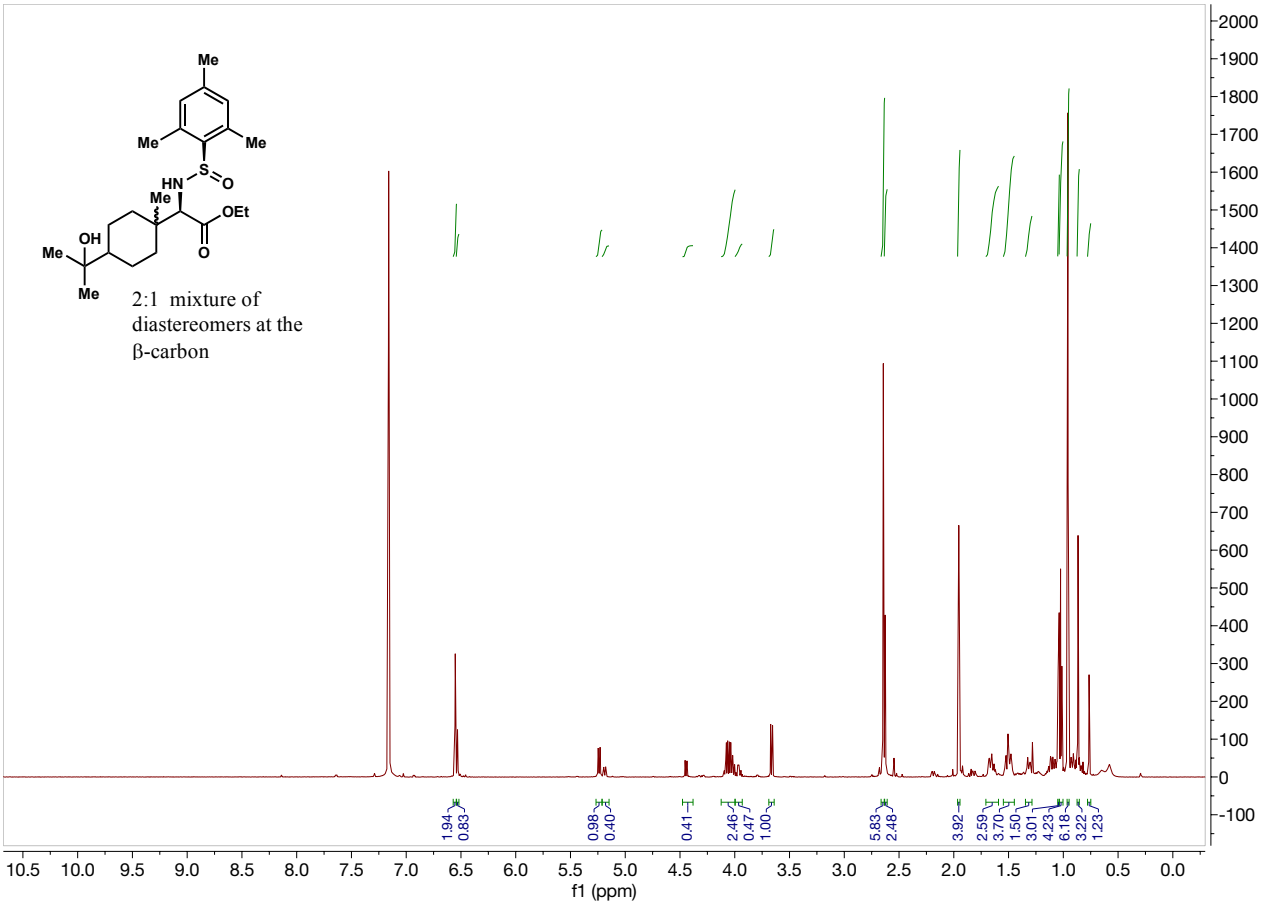

Me
Me
Me
S
O
NH
CO2Et
i-Pr
Me
Me
f2 (ppm)
f1 (ppm)

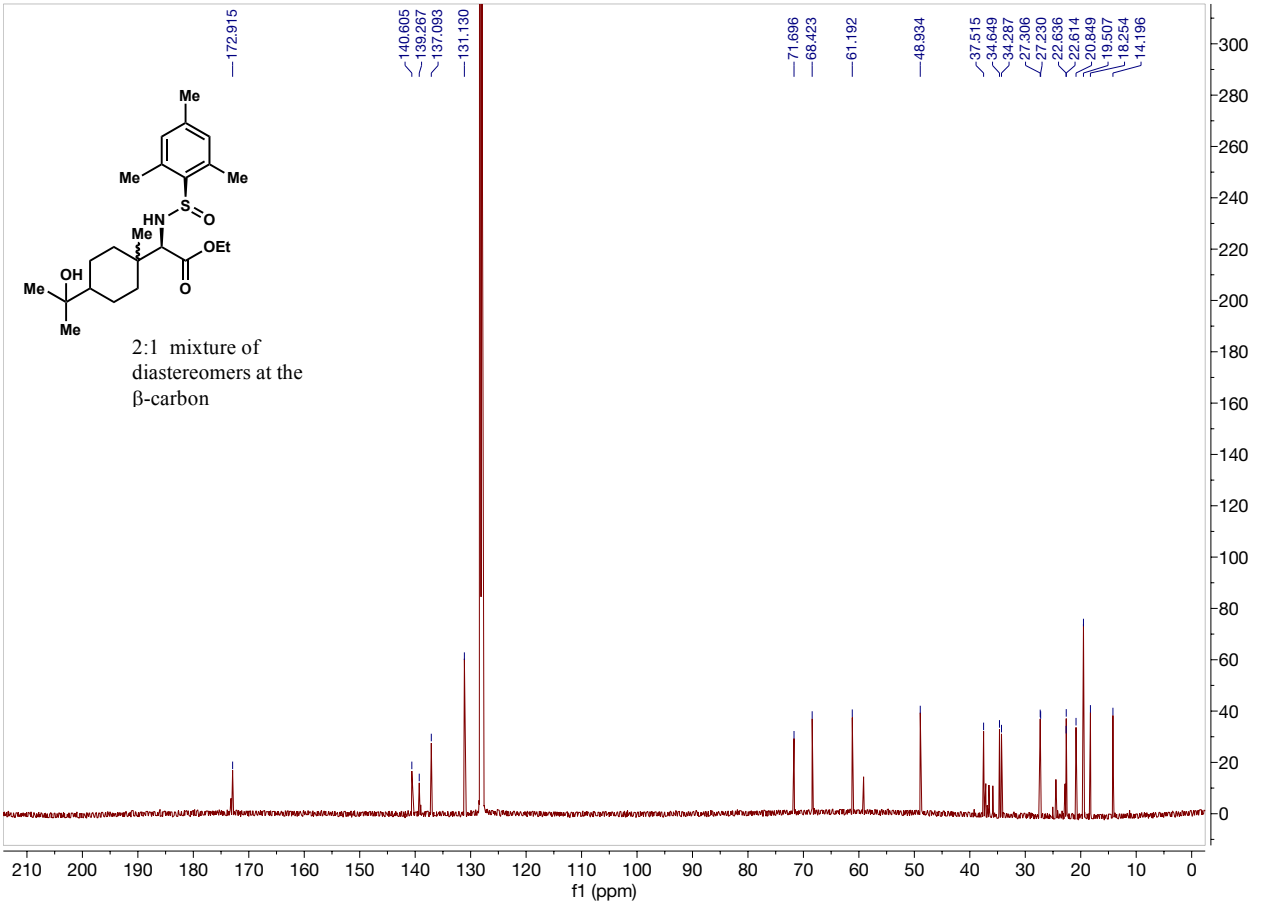

Mes
S+
O-
HN
CO2Et
H
H
H
H
H
H
H
i-Pr
Me
Me
H
H
H
f2 (ppm)
f1 (ppm)

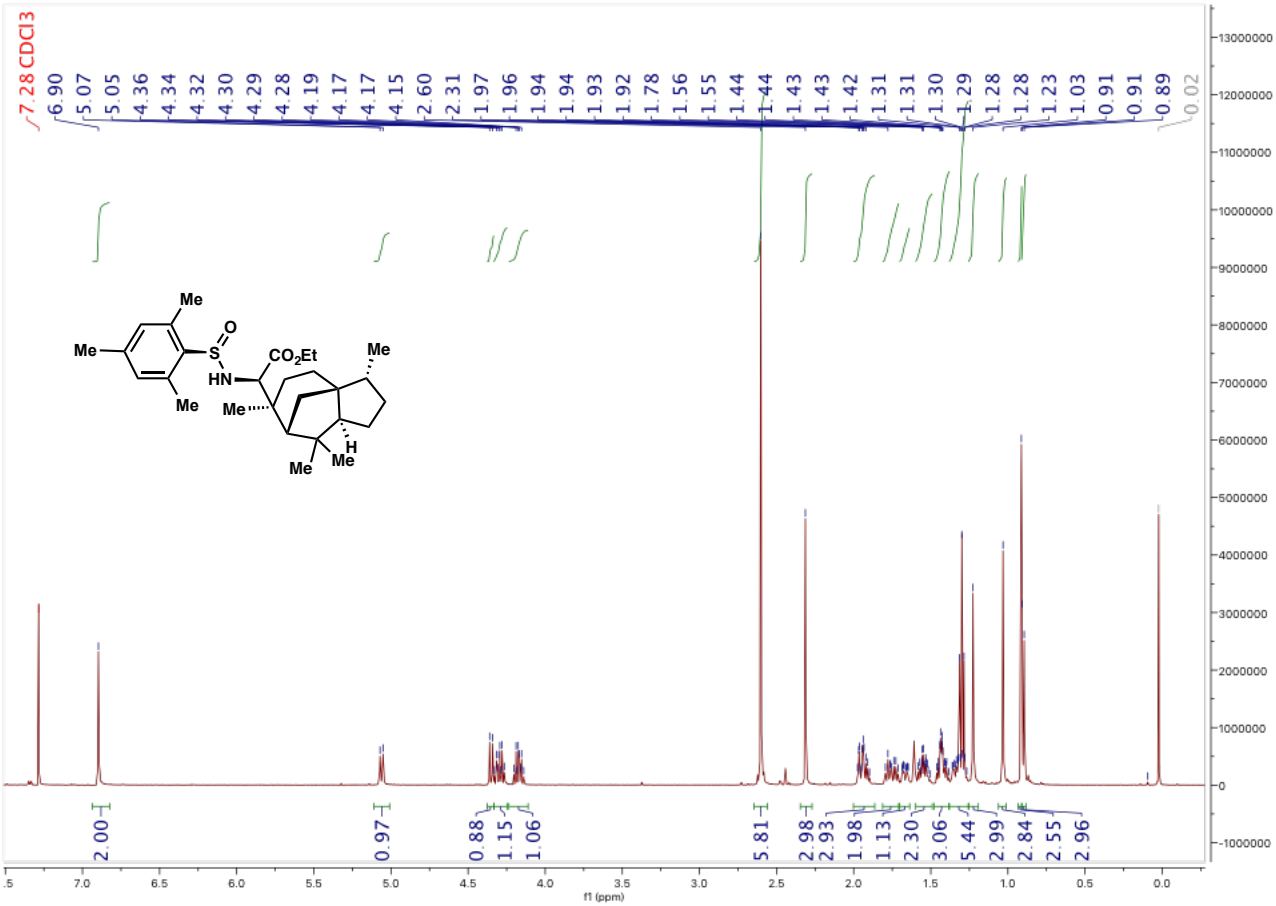

Me
Me
Me
S
O
NH
CO2Et
i-Pr
Me
Me
f2 (ppm)
f1 (ppm)

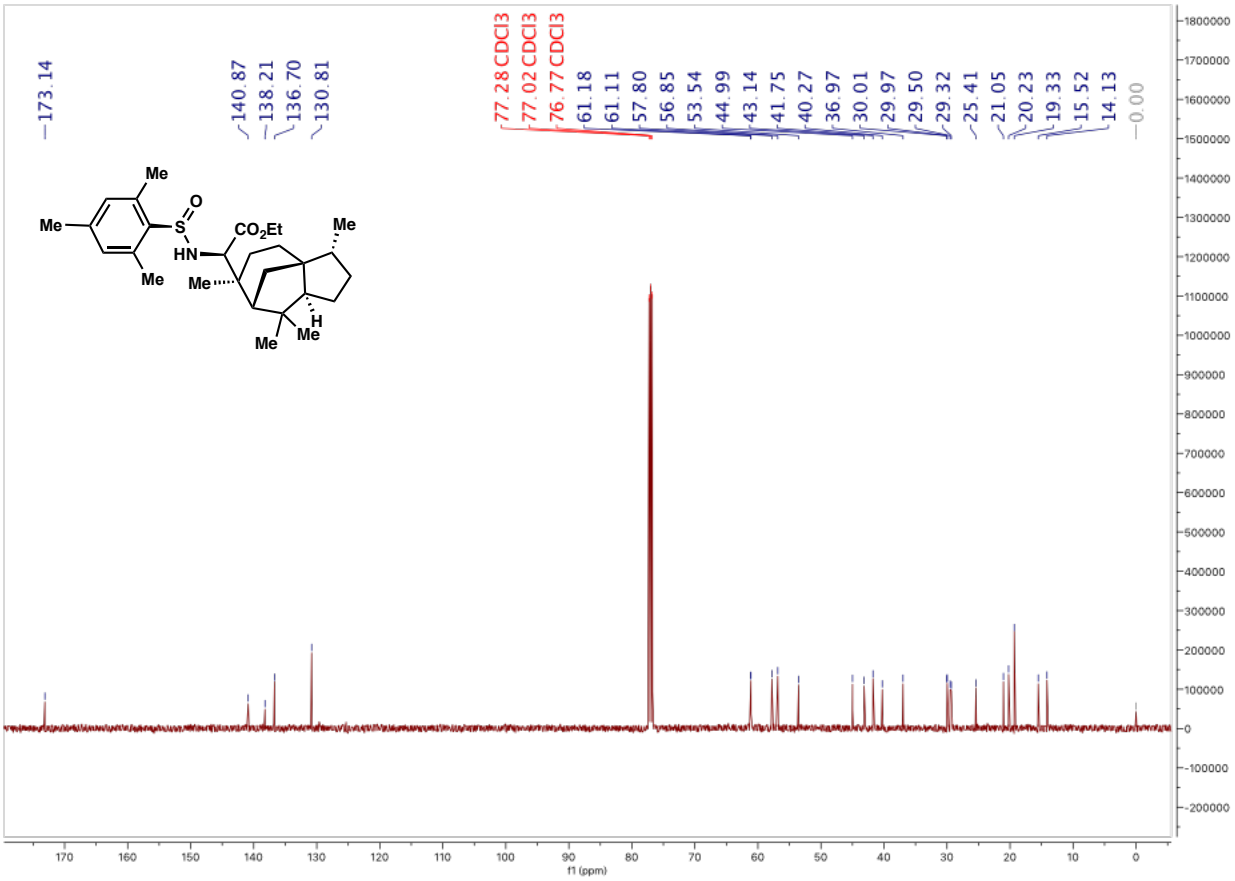

major
possible minor
possible minor
possible minor
possible minor
f1 (ppm)

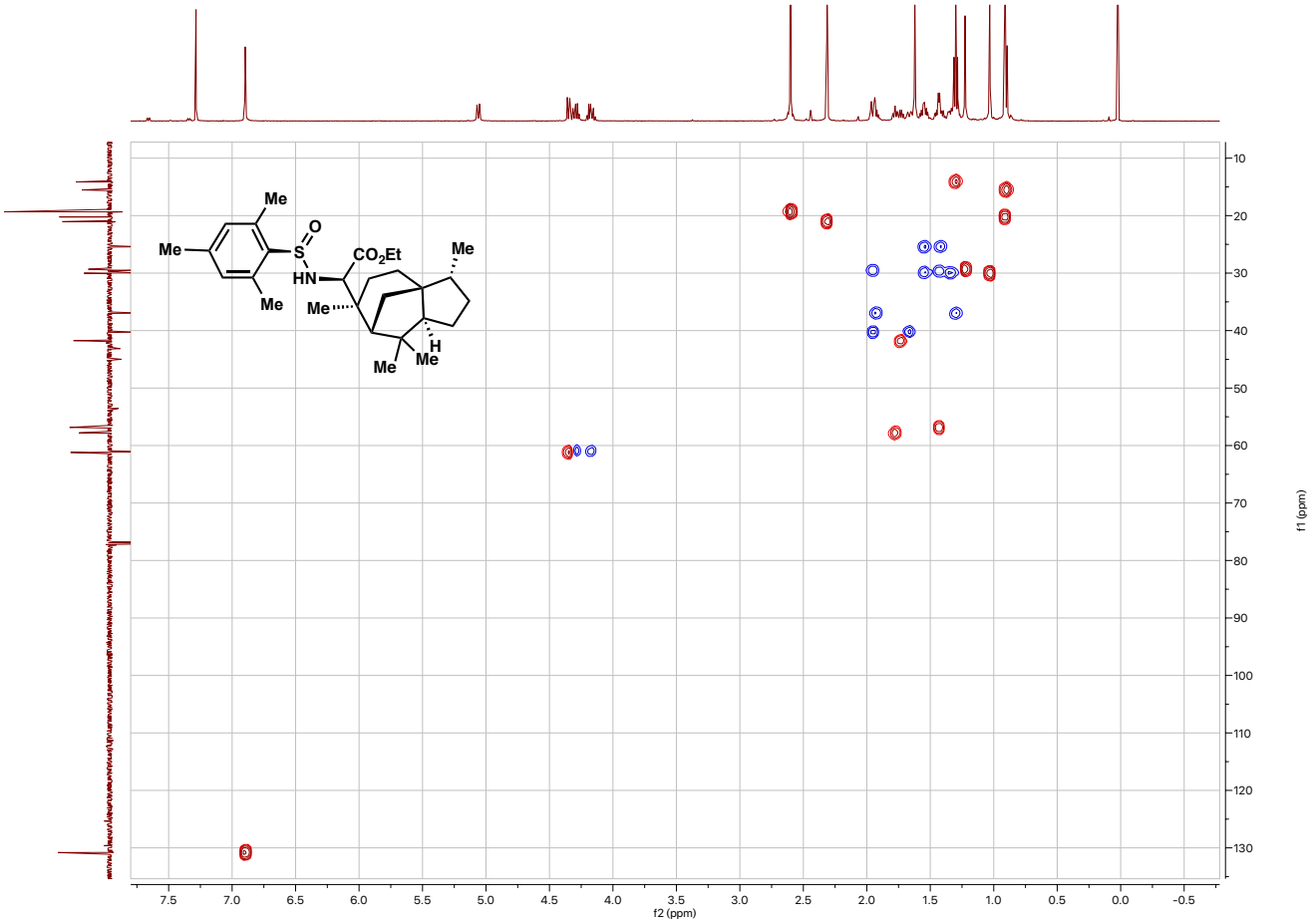

major
possible minor
possible minor
possible minor
f1 (ppm)

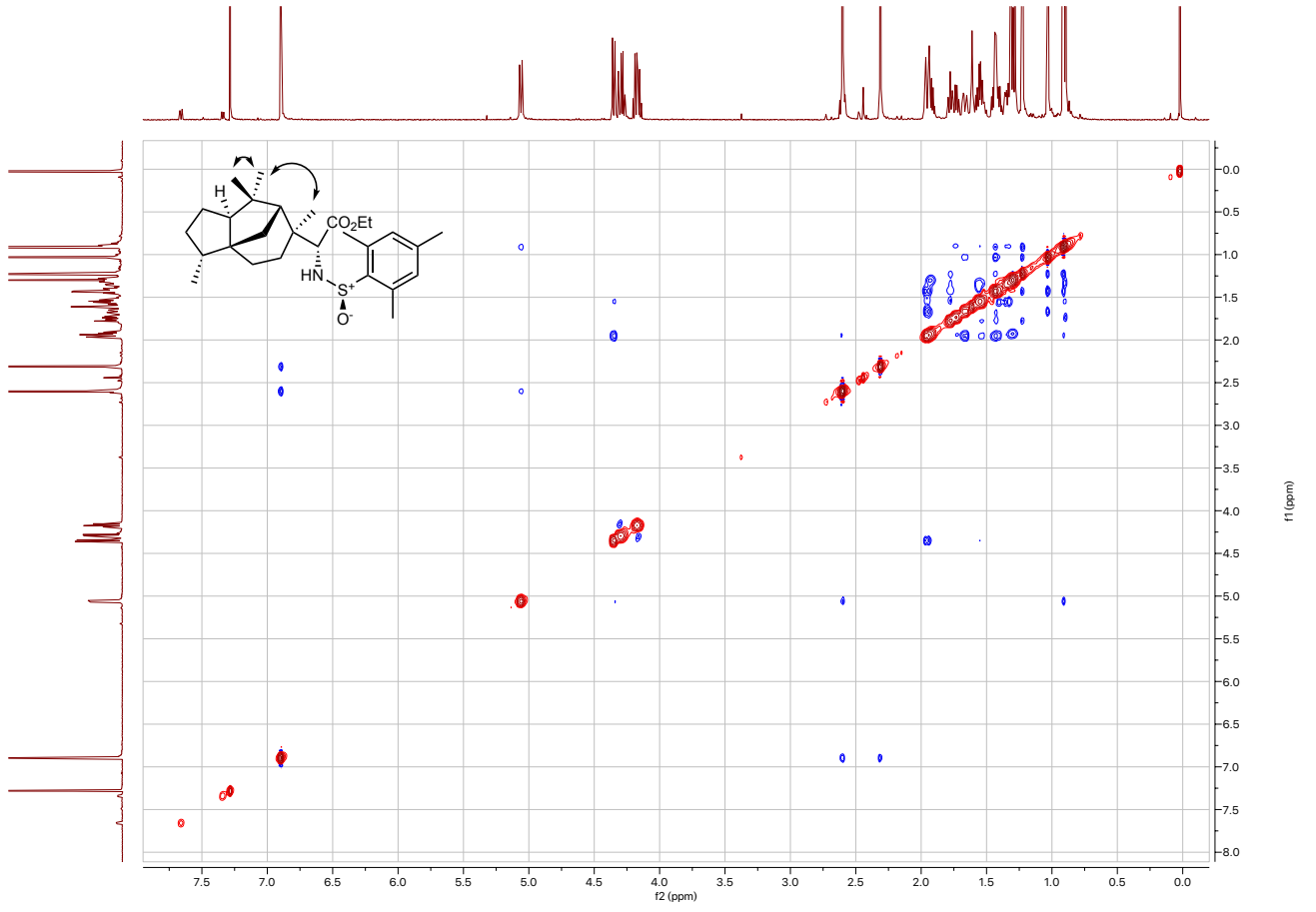

Me
Me
Me
S
O
HN
Me
OEt
OH
Me
O
Me
2:1 mixture of diastereomers at the β-carbon
1.94
0.83
0.98
0.40
0.41
2.46
0.47
1.00
5.83
2.48
3.92
2.59
3.70
1.50
3.01
4.23
6.18
3.22
1.23
f1 (ppm)

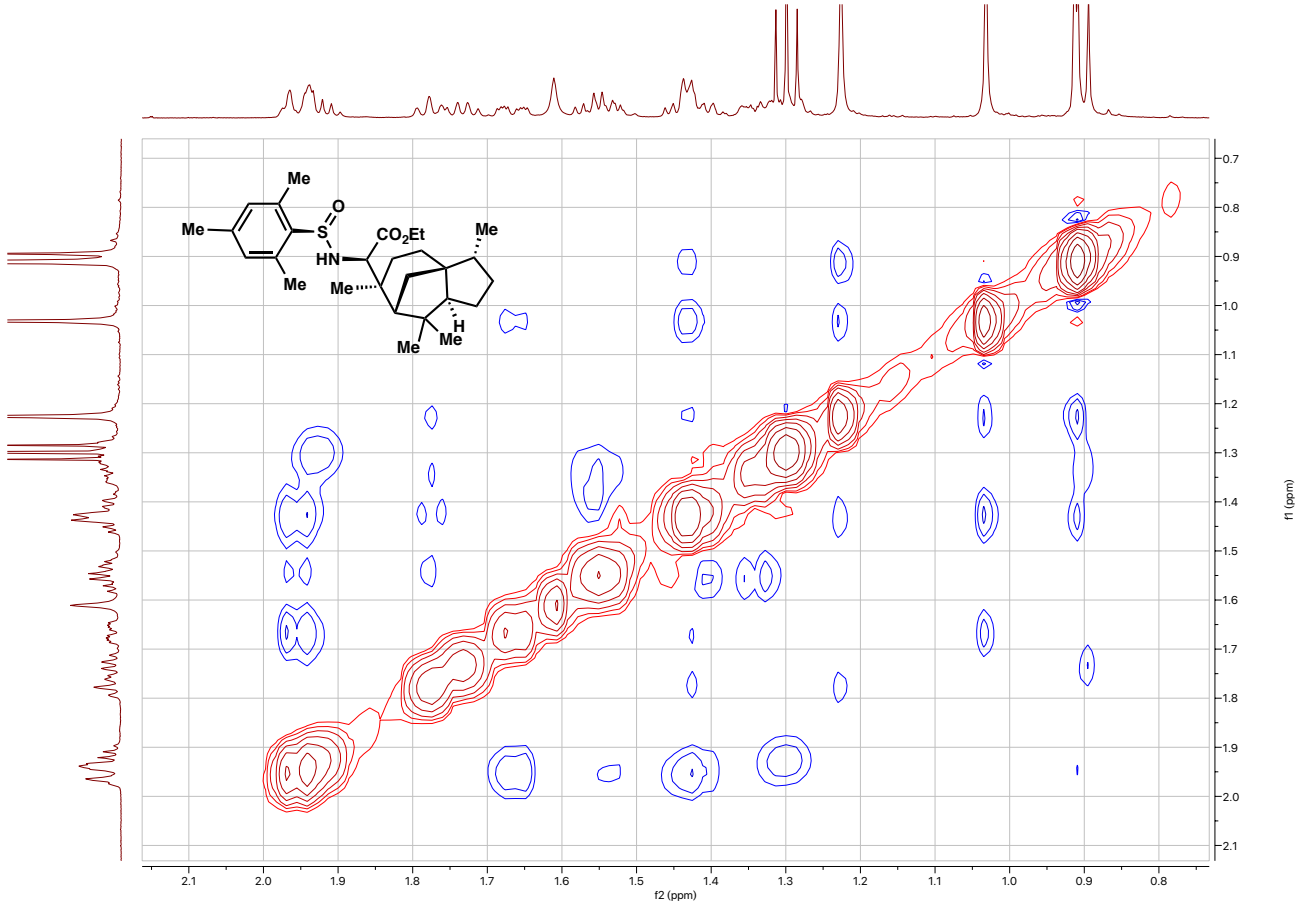

172.915
140.605
139.267
137.093
131.130
71.696
68.423
61.192
48.934
37.515
34.649
34.287
27.306
27.230
22.636
22.614
20.849
19.507
18.254
14.196
Me
Me
Me
S
O
HN
Me
OEt
OH
Me
O
Me
2:1 mixture of diastereomers at the β-carbon
f1 (ppm)

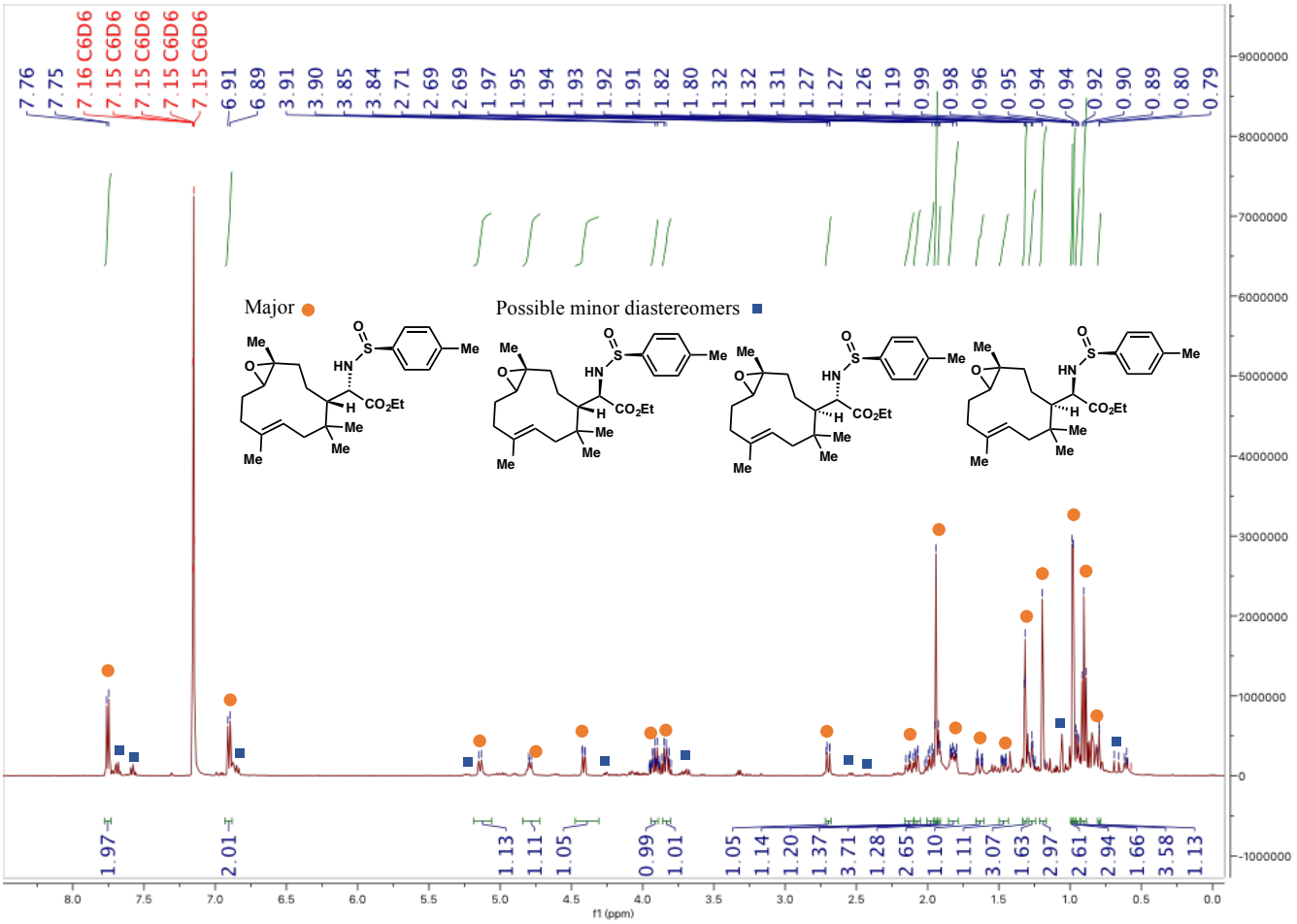

7.28 CDCl3
6.90
5.07
5.05
4.36
4.34
4.32
4.30
4.29
4.28
4.19
4.17
4.17
4.15
2.60
2.31
1.97
1.96
1.94
1.94
1.93
1.92
1.78
1.56
1.55
1.44
1.44
1.43
1.43
1.42
1.31
1.31
1.30
1.29
1.28
1.28
1.23
1.03
0.91
0.91
0.89
0.02
Me
Me
S
O
HN
CO2Et
Me
Me
Me
H
Me
Me
2.00
0.97
0.88
1.15
1.06
5.81
2.98
2.93
1.98
1.13
2.30
3.06
5.44
2.99
2.84
2.55
2.96
f1 (ppm)

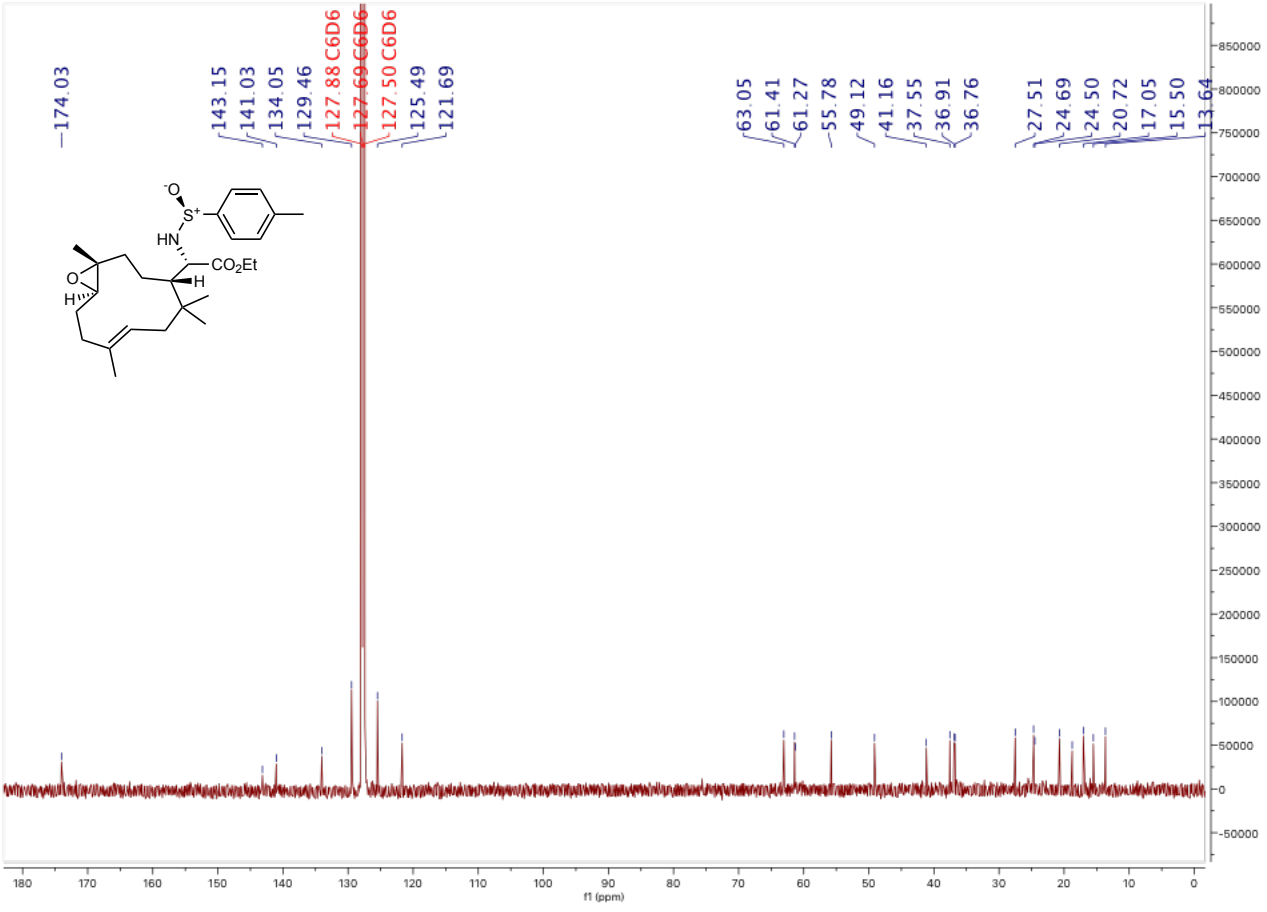

173.14
140.87
138.21
136.70
130.81
77.28 CDCl3
77.02 CDCl3
76.77 CDCl3
61.18
61.11
57.80
56.85
53.54
44.99
43.14
41.75
40.27
36.97
30.01
29.97
29.50
29.32
25.41
21.05
20.23
19.33
15.52
14.13
0.00
Me
Me
S
O
HN
CO2Et
Me
Me
Me
H
Me
Me
f1 (ppm)

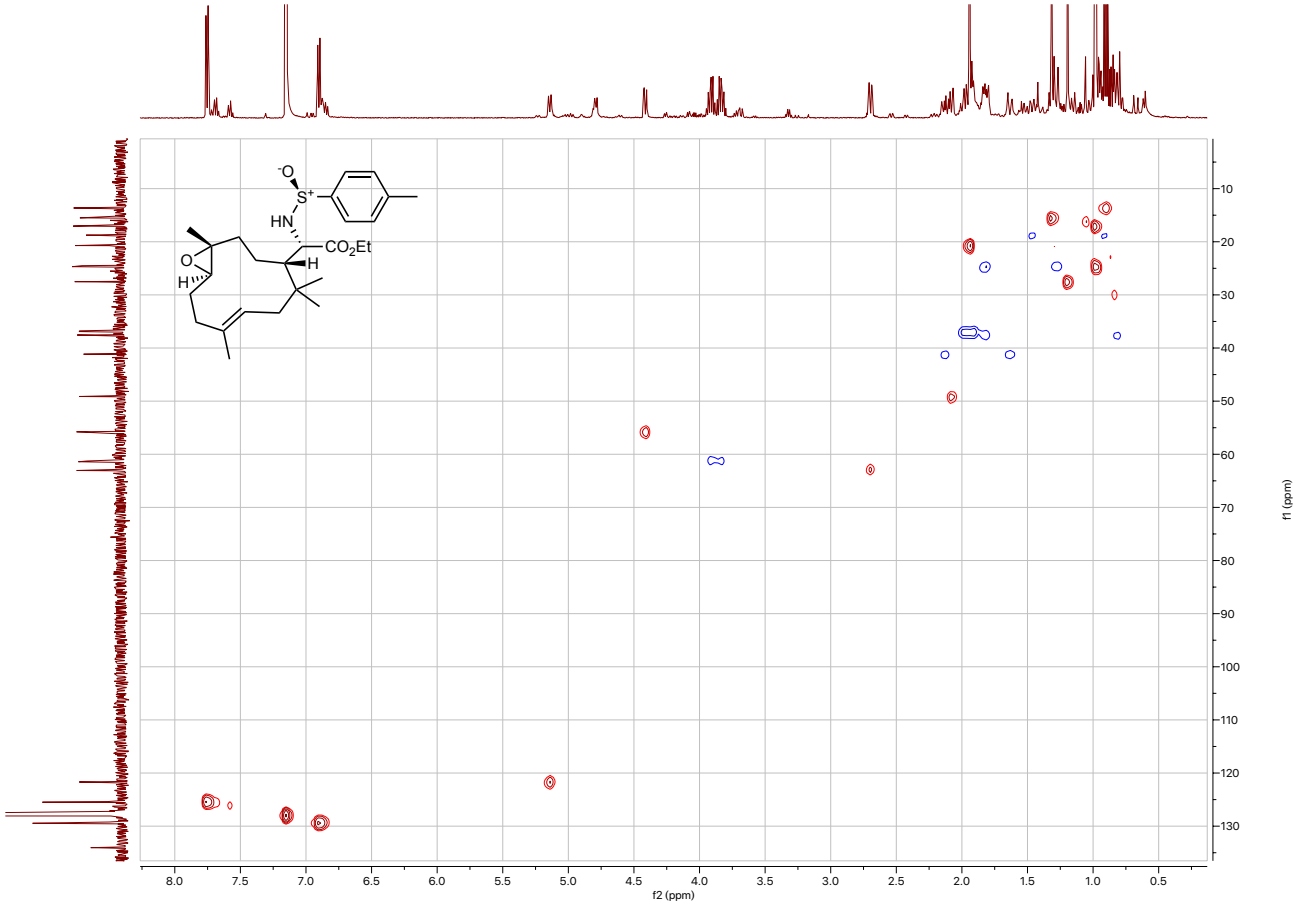

Me
Me
Me
S
O
HN
CO2Et
Me
Me
Me
H
Me
Me
f2 (ppm)
f1 (ppm)

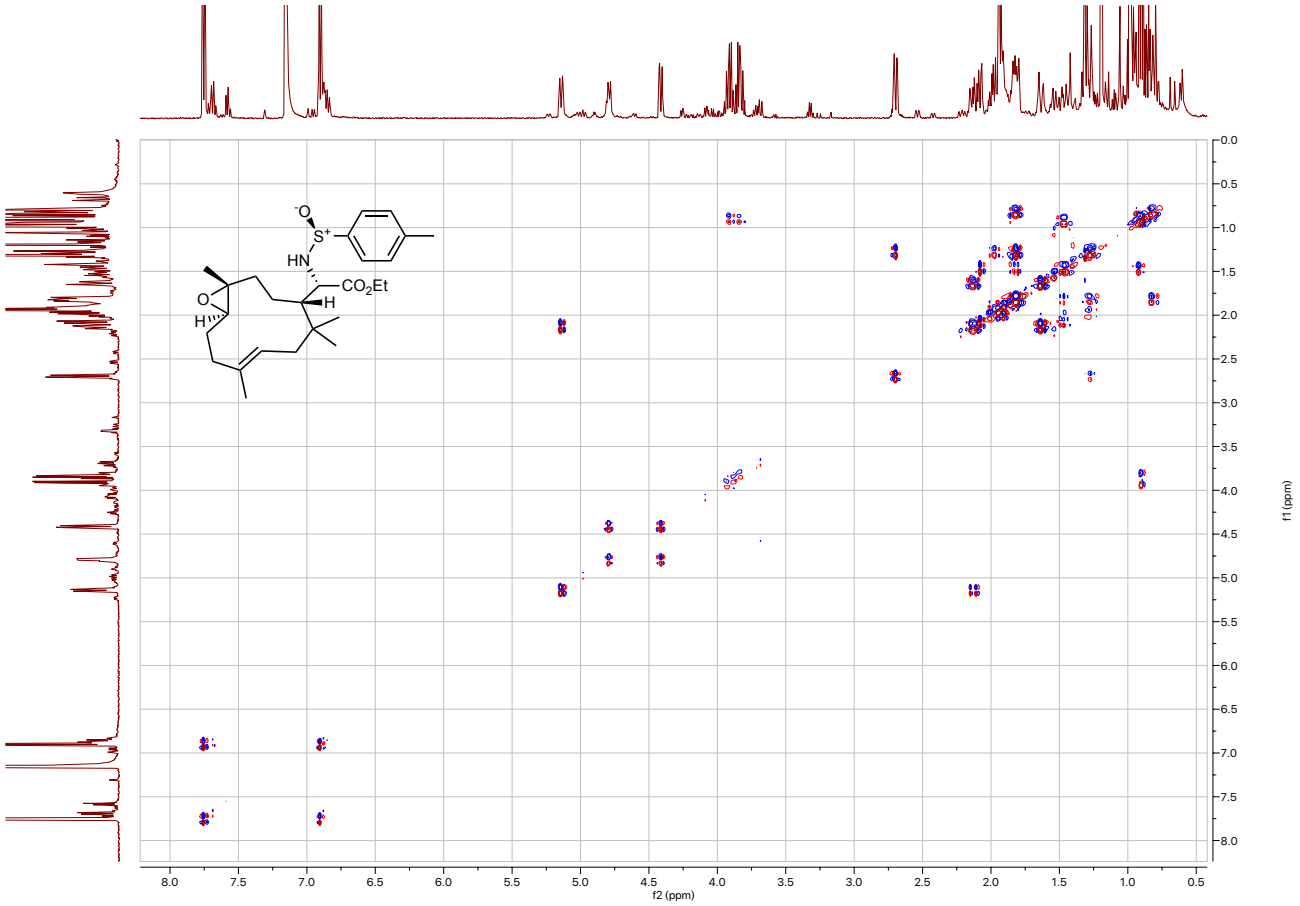

H
CO2Et
HN
S+
O-
f2 (ppm)
f1 (ppm)

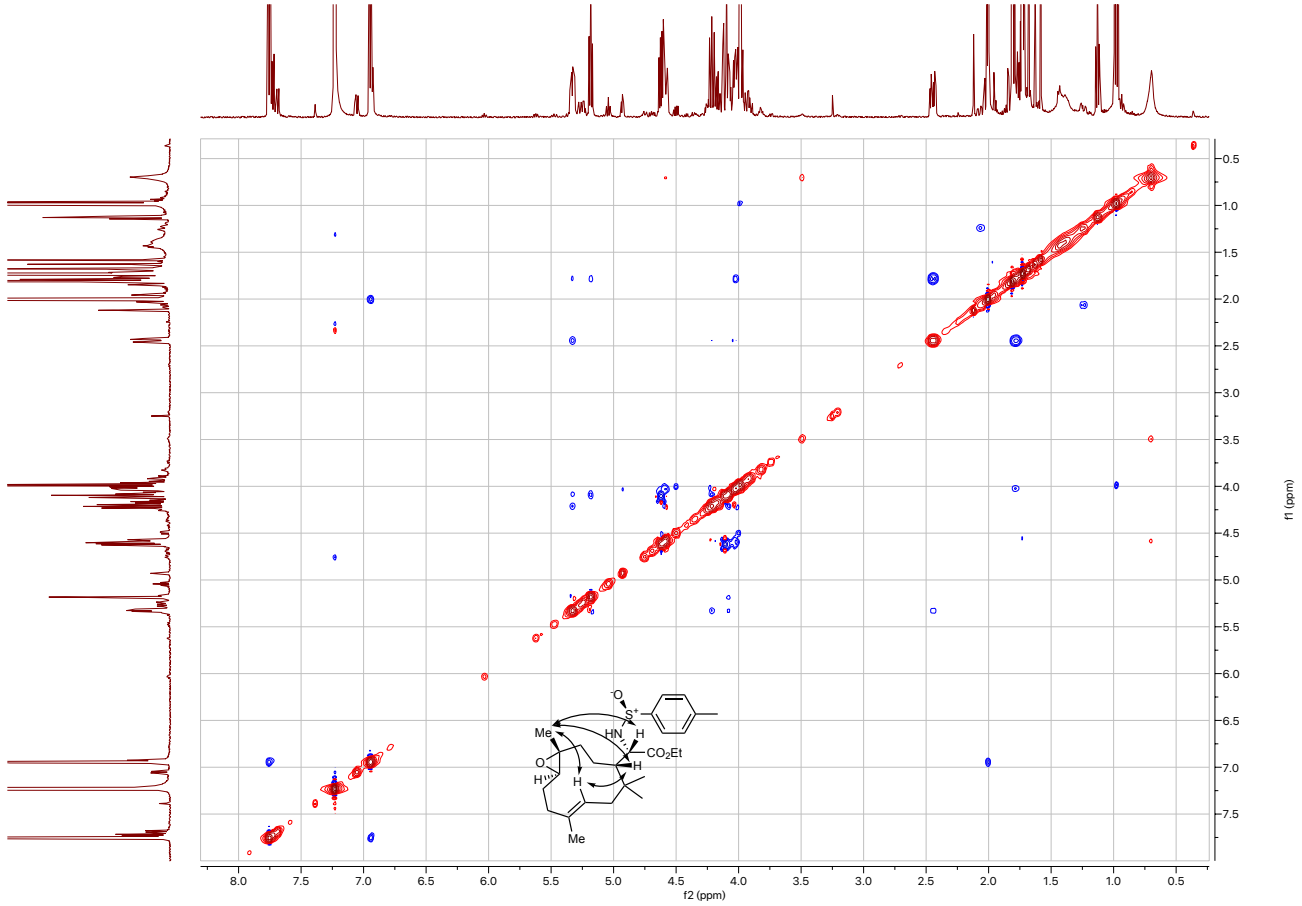

Me
Me
Me
O
S
HN
CO2Et
Me
Me
Me
H
Me
f2 (ppm)
f1 (ppm)

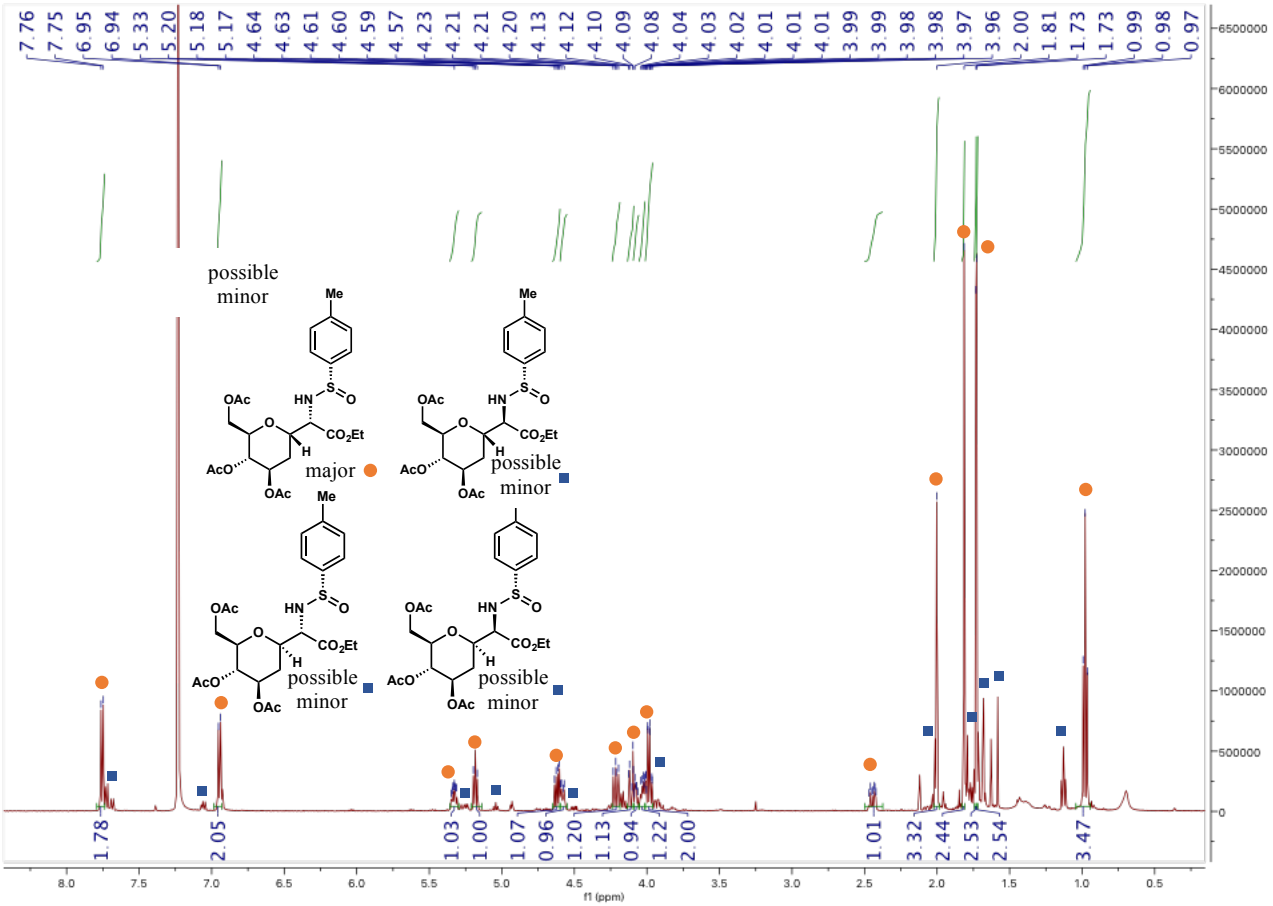

Major
Possible minor diastereomers

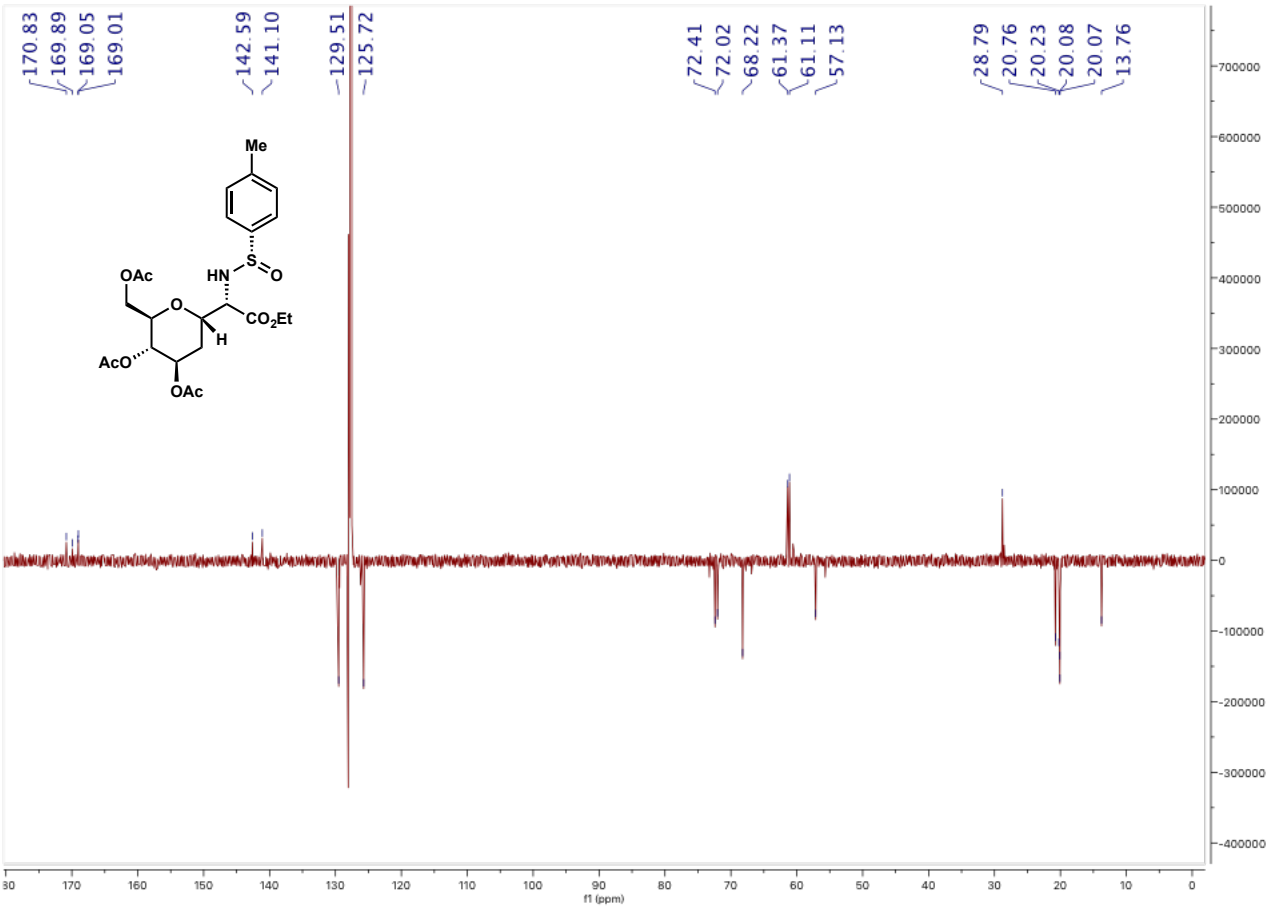


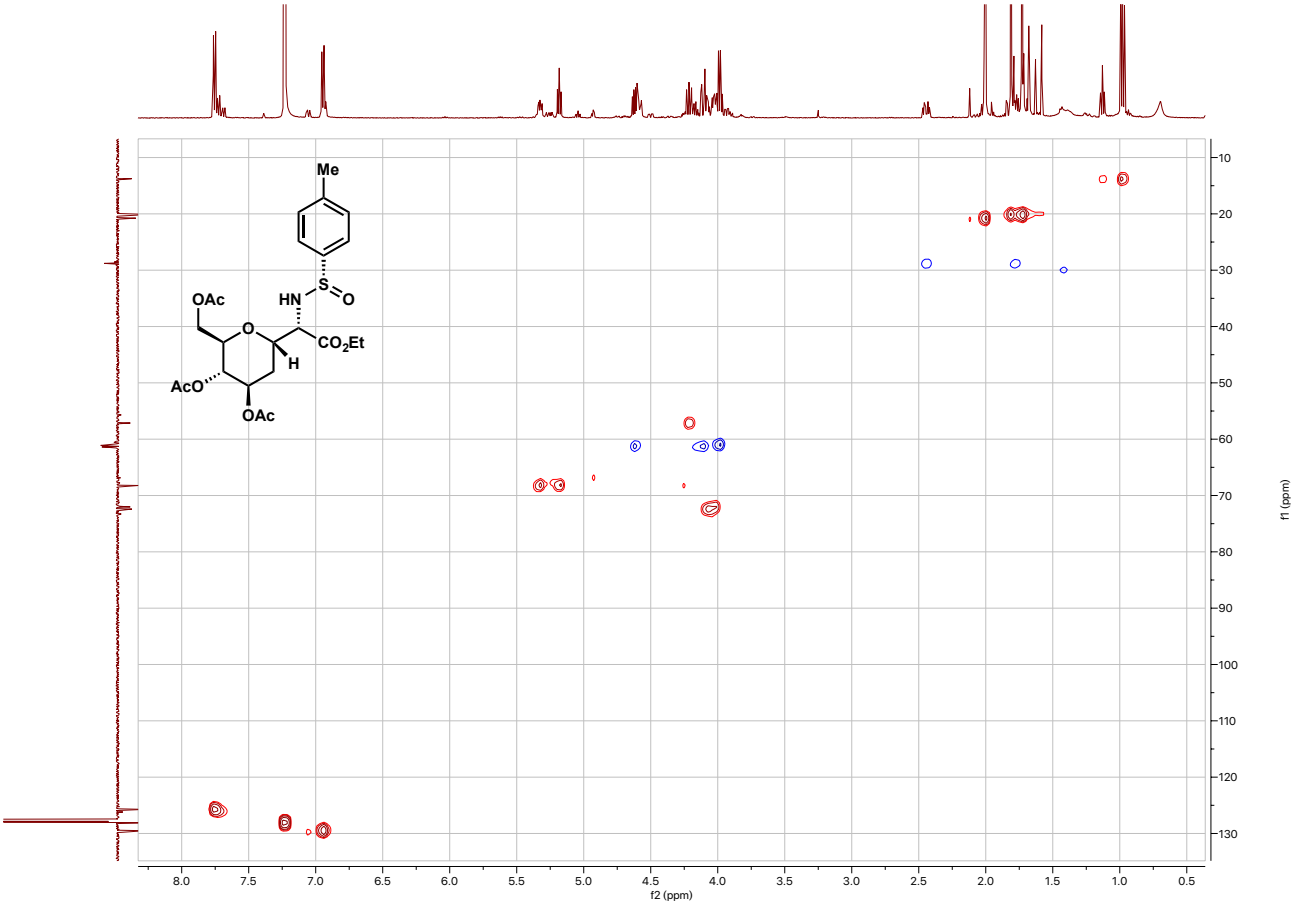

f2 (ppm)
f1 (ppm)

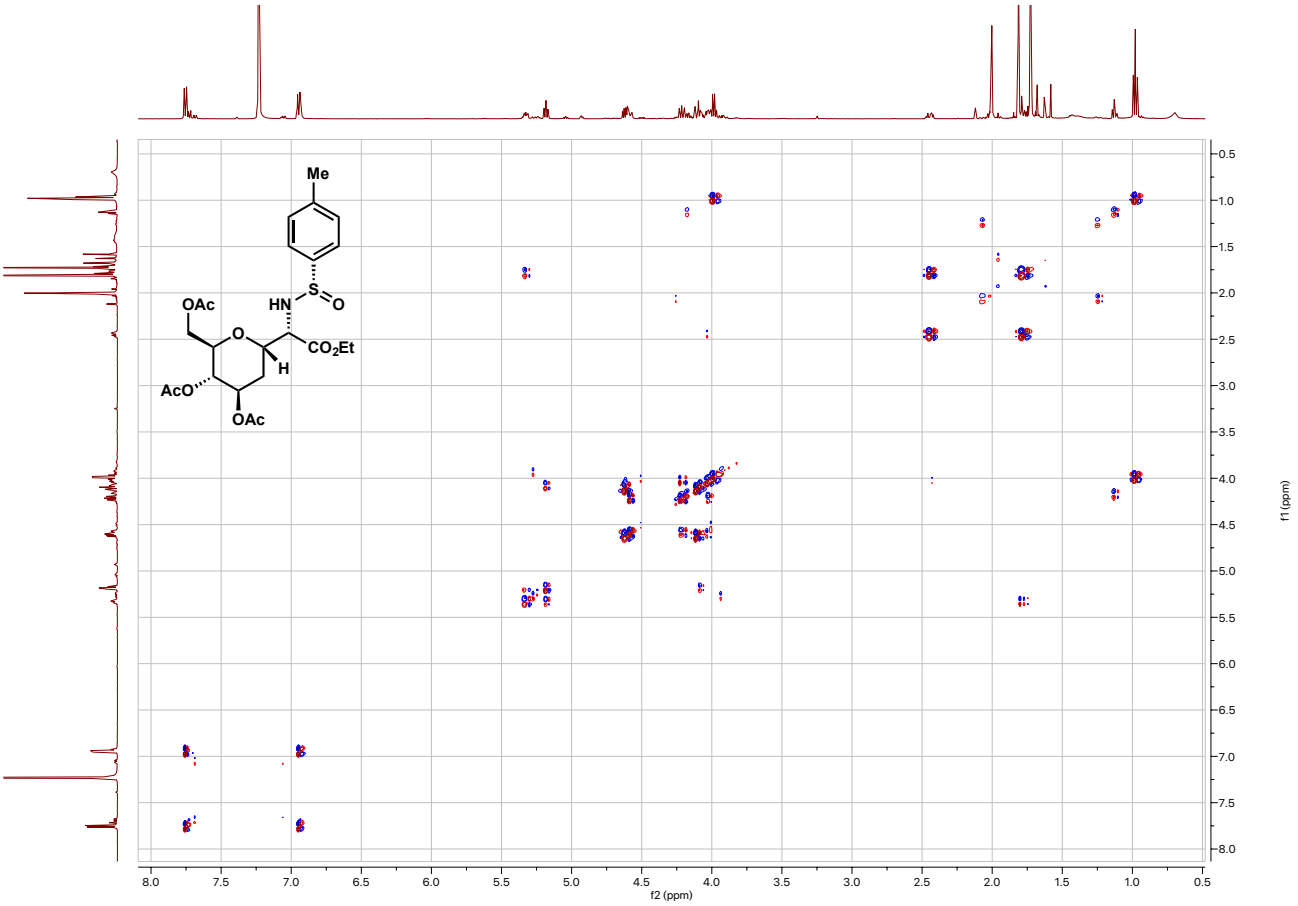

f2 (ppm)
f1 (ppm)

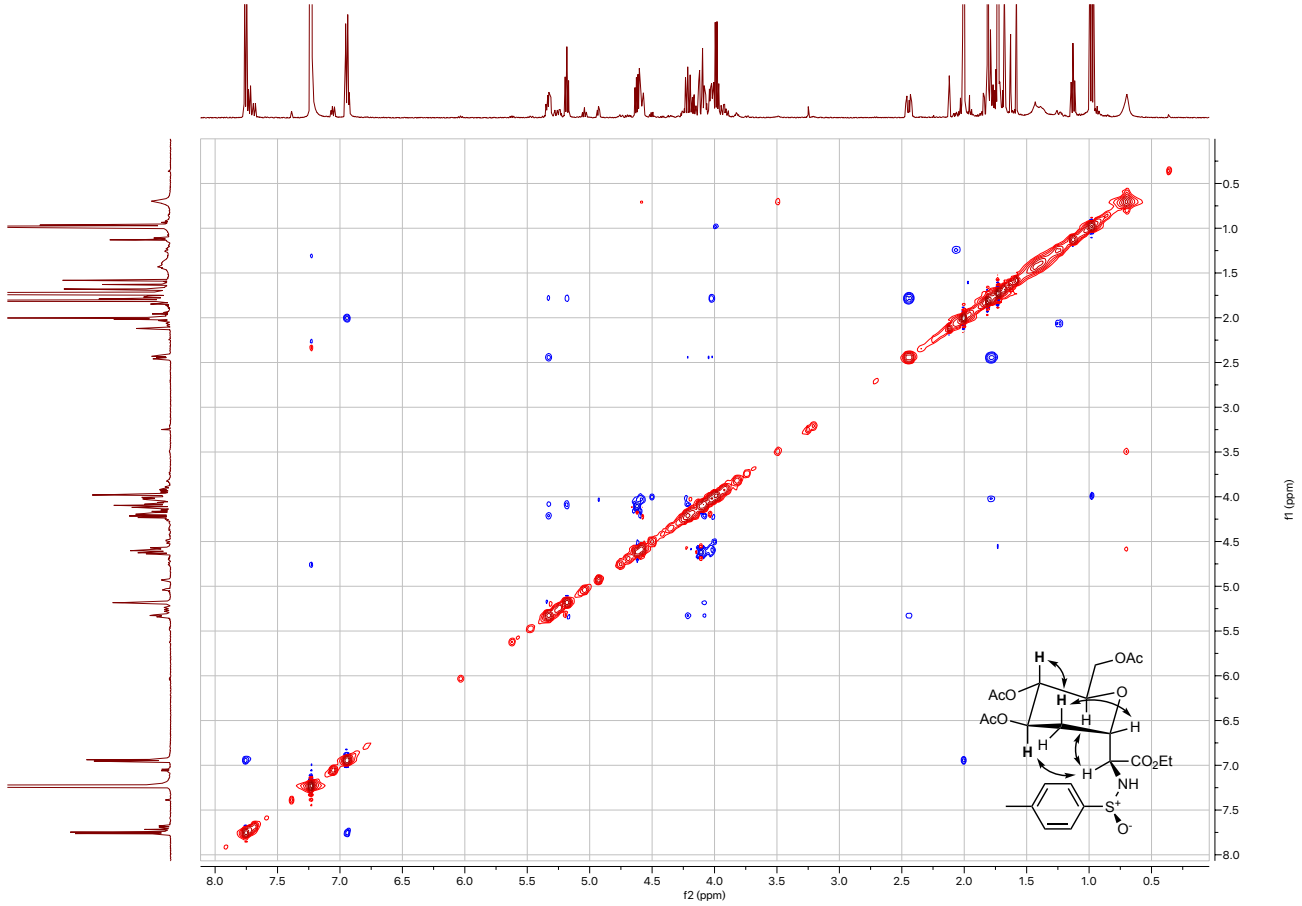

f2 (ppm)
f1 (ppm)
Me
HN
H
CO2Et
O
H
H
Me

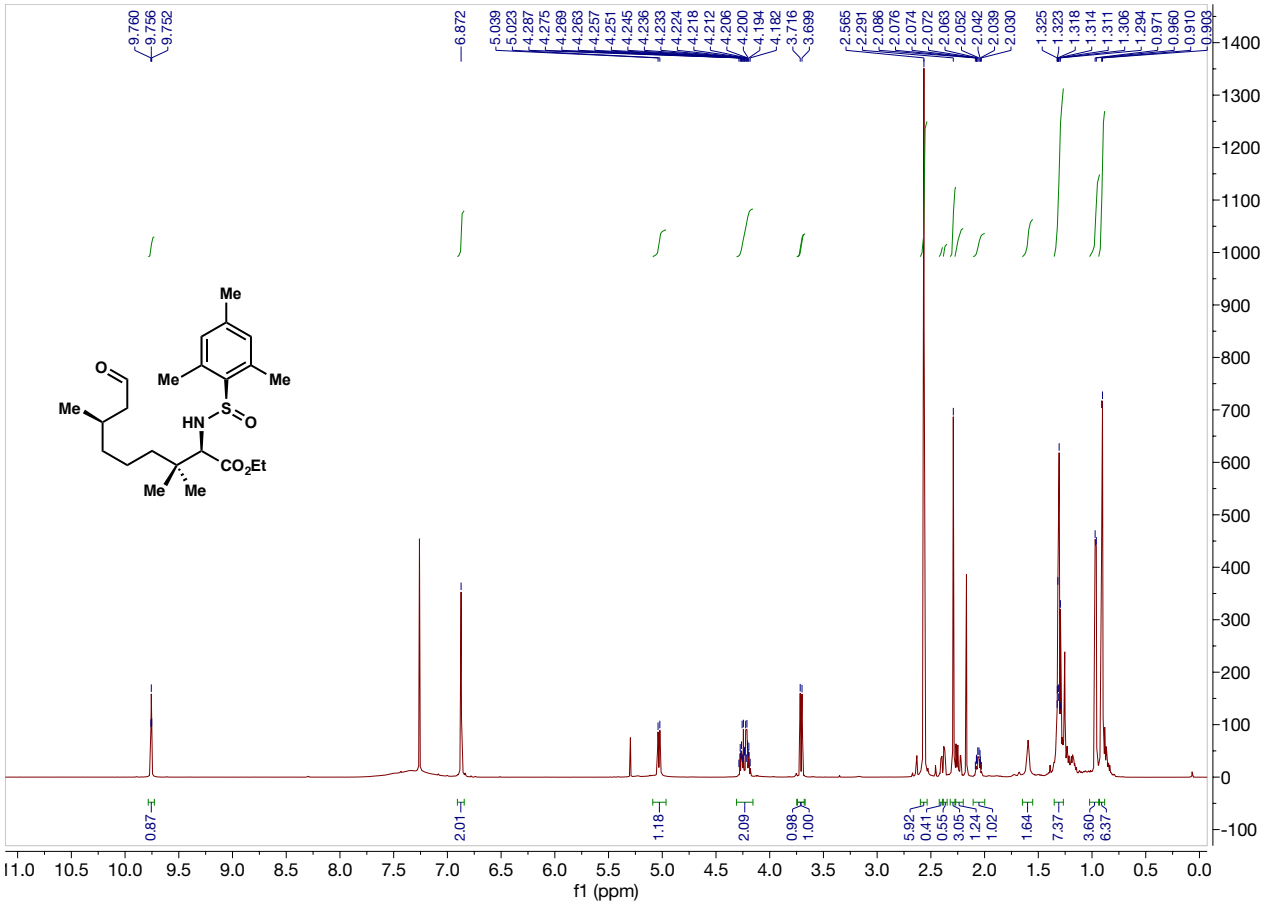

possible minor
major
possible minor
possible minor
possible minor
possible minor
f1 (ppm)

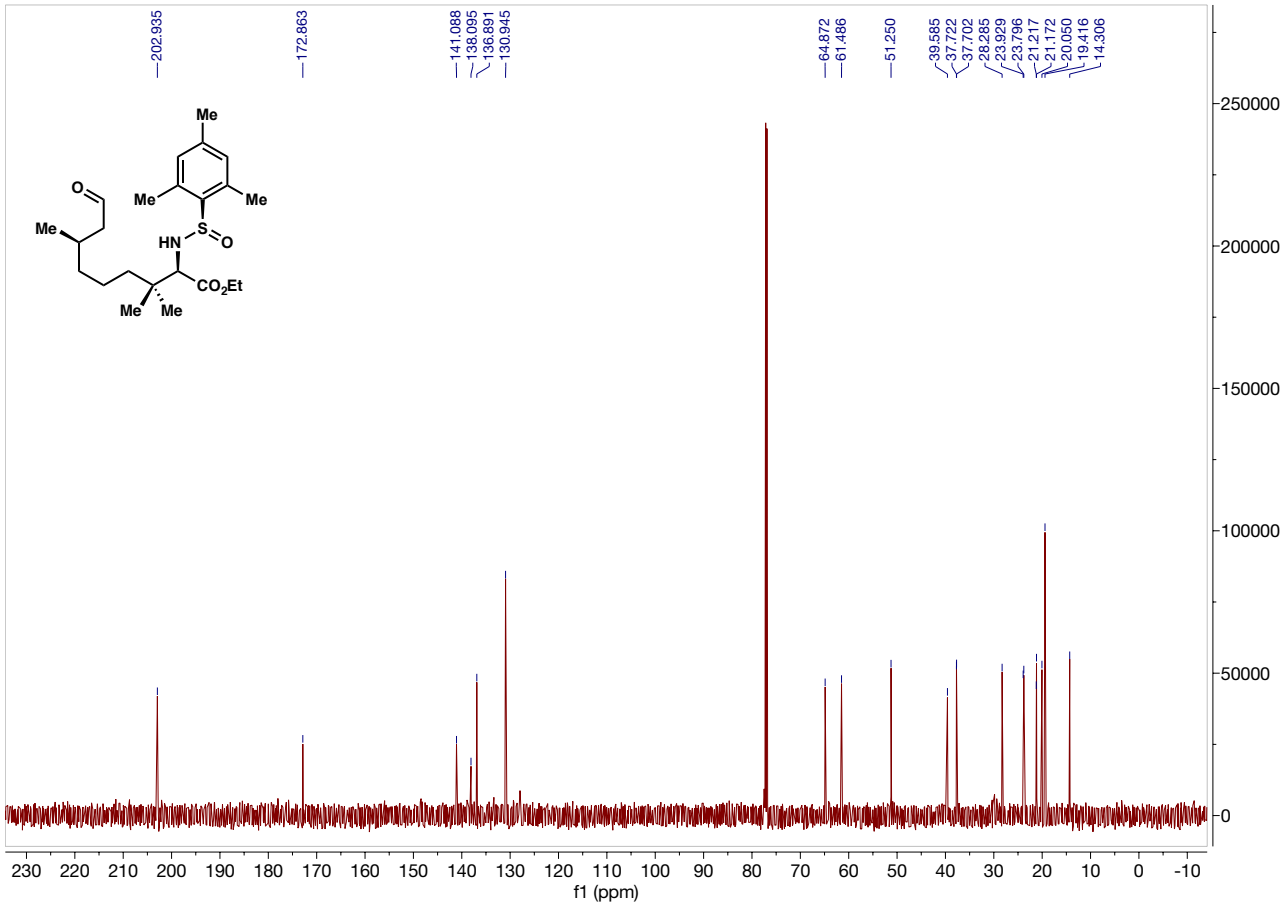

f1 (ppm)

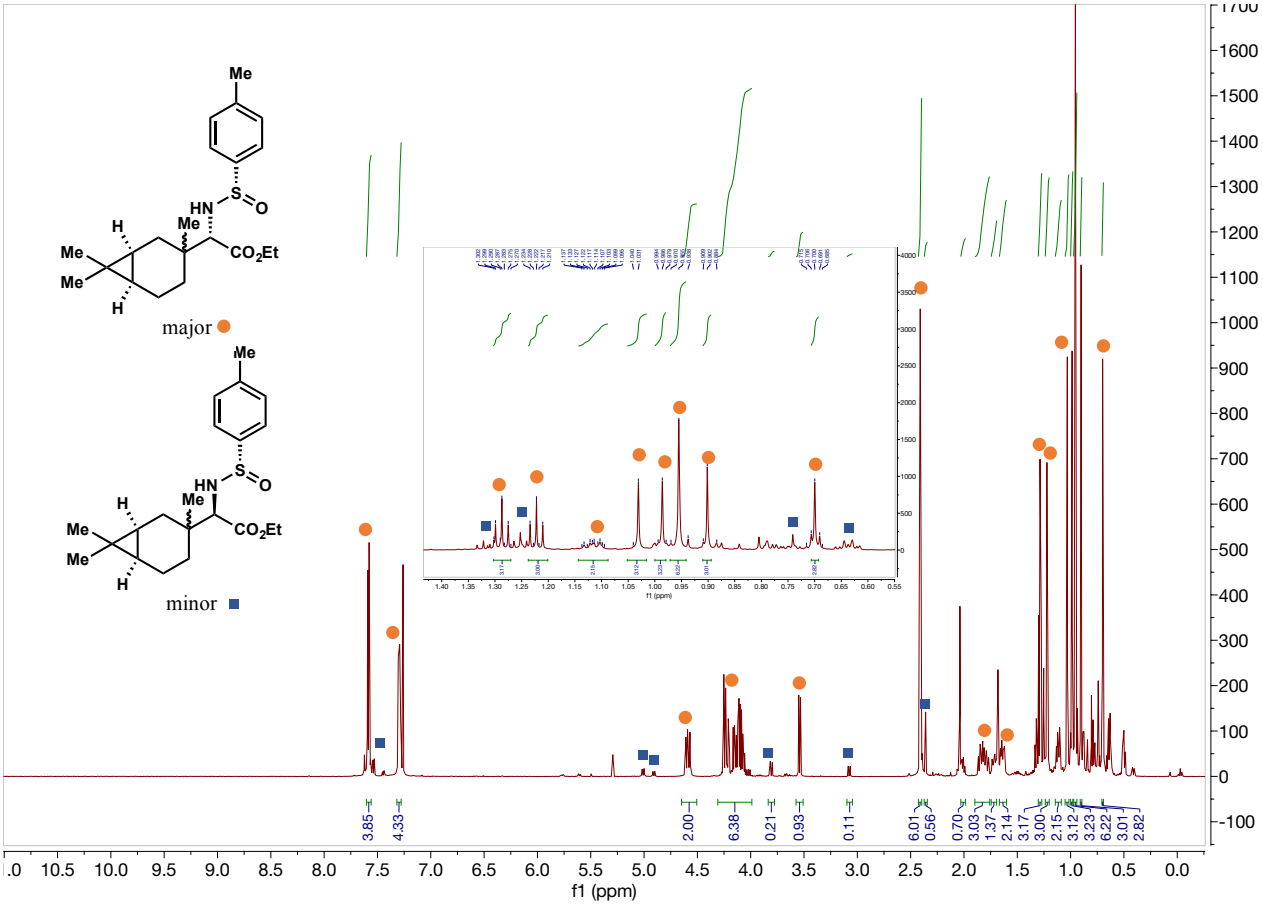

Me
OAc
HN
S
O
O
CO2Et
H
AcO
OAc
f2 (ppm)
f1 (ppm)

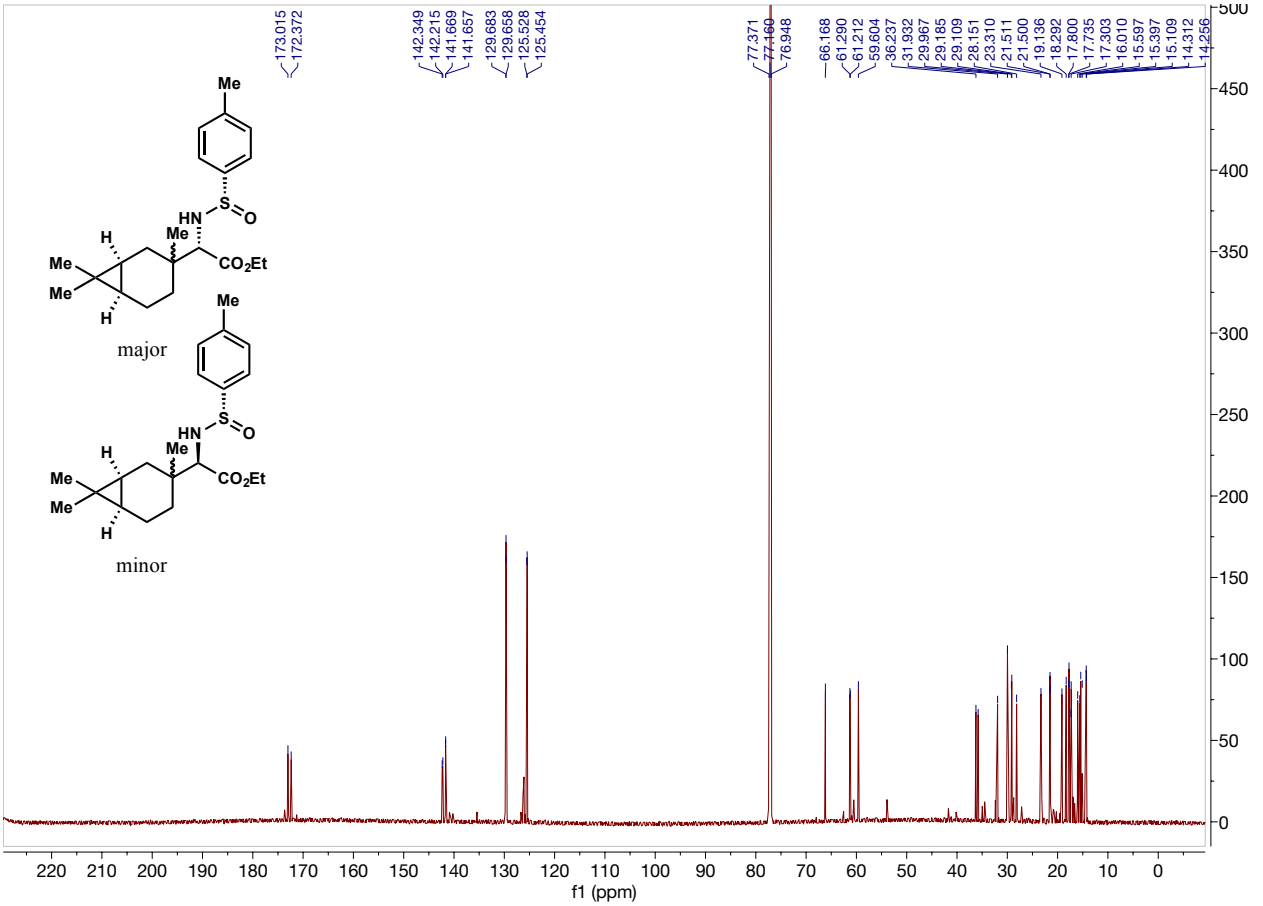

Me
OAc
HN
S
O
O
CO2Et
H
AcO
OAc
f2 (ppm)
f1 (ppm)

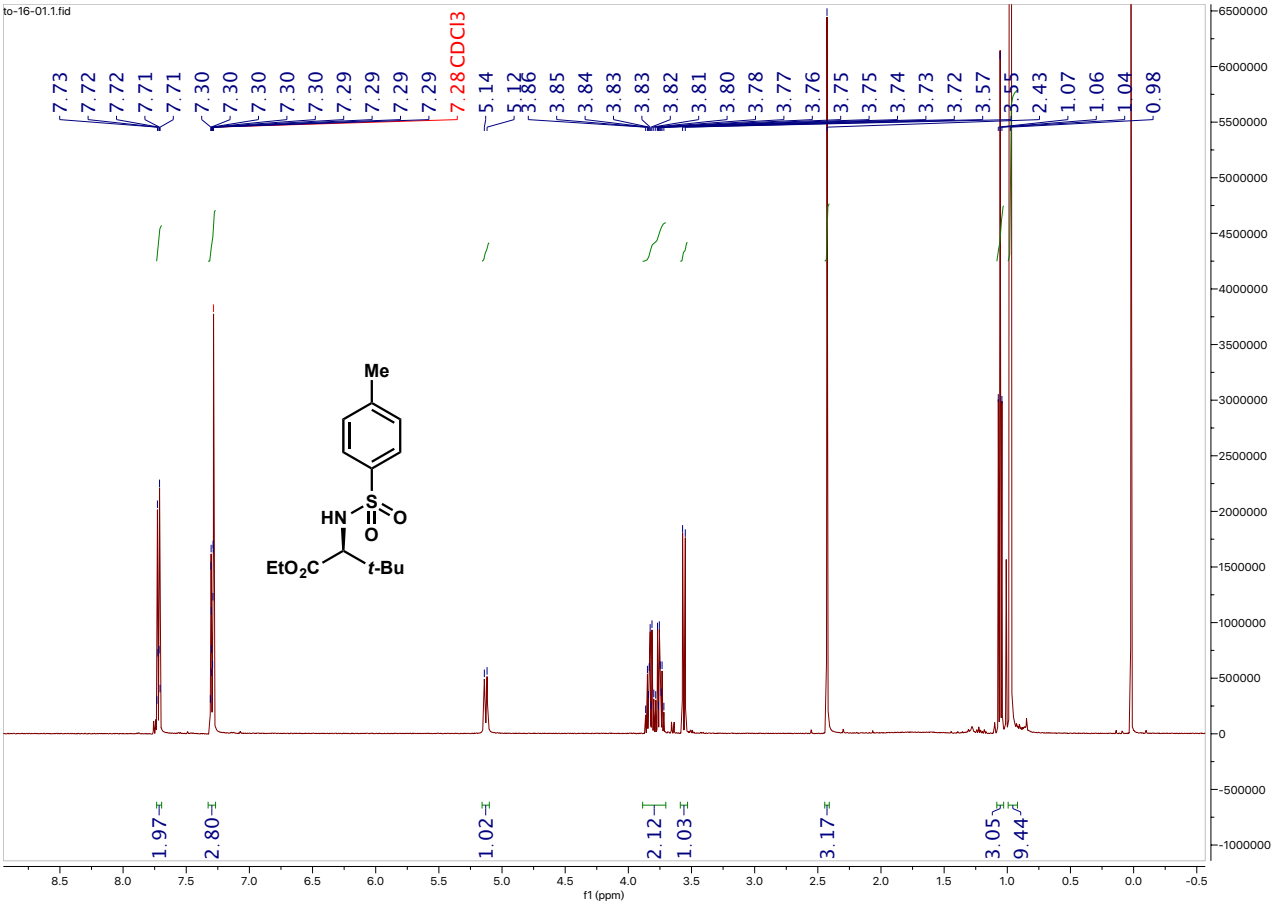

f2 (ppm)
f1 (ppm)
H
OAc
AcO
O
H
AcO
H
H
H
H
H
CO2Et
NH
S+
O-

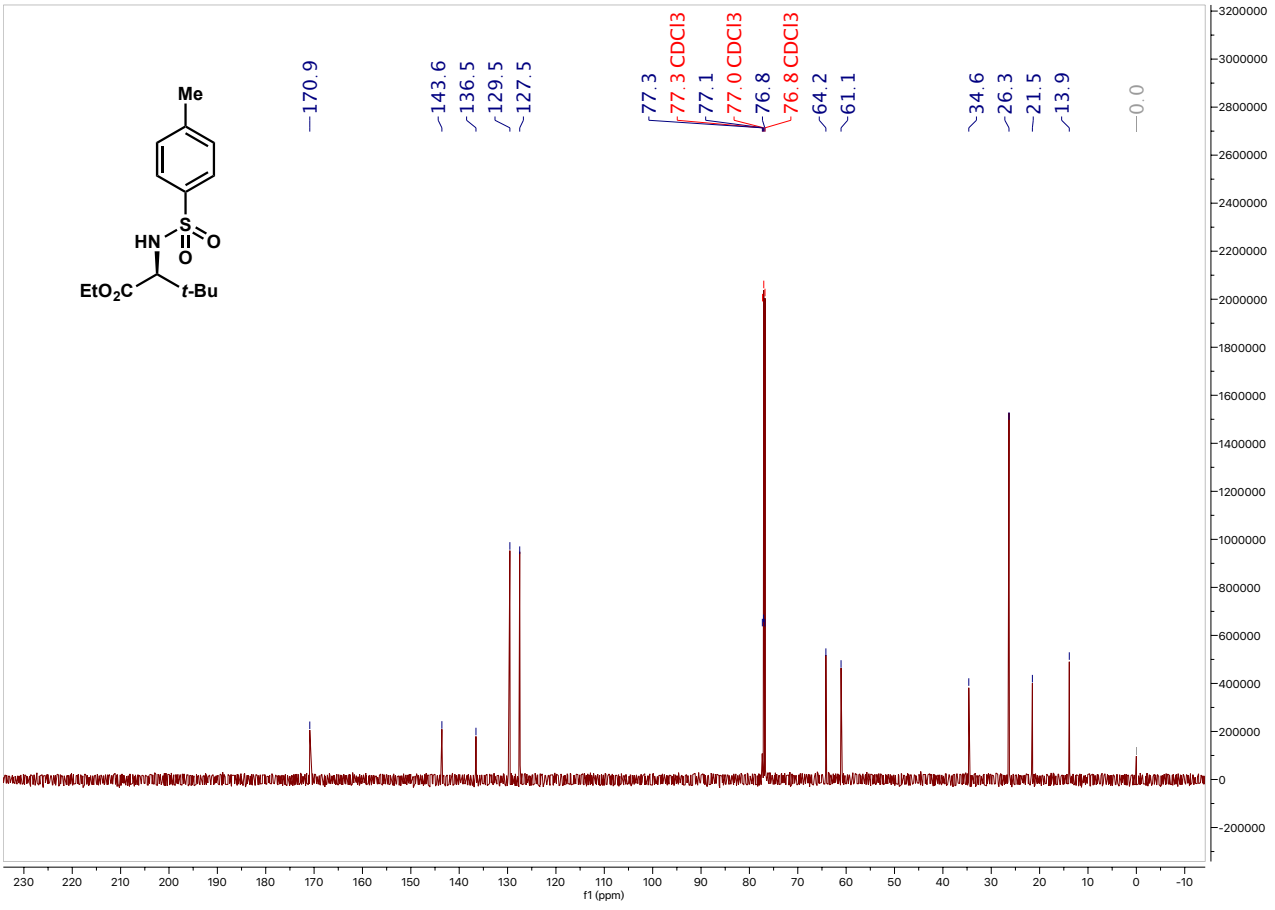

9.760
9.756
9.752
6.872
5.039
5.023
4.287
4.275
4.269
4.263
4.257
4.251
4.245
4.236
4.233
4.224
4.218
4.212
4.206
4.200
4.194
4.182
3.716
3.699
2.565
2.291
2.086
2.076
2.074
2.072
2.063
2.052
2.042
2.039
2.030
1.325
1.323
1.318
1.314
1.311
1.306
1.294
0.971
0.960
0.910
0.903
0.87
2.01
1.18
2.09
0.98
1.00
5.92
0.41
0.55
3.05
1.24
1.02
1.64
7.37
3.60
6.37
f1 (ppm)

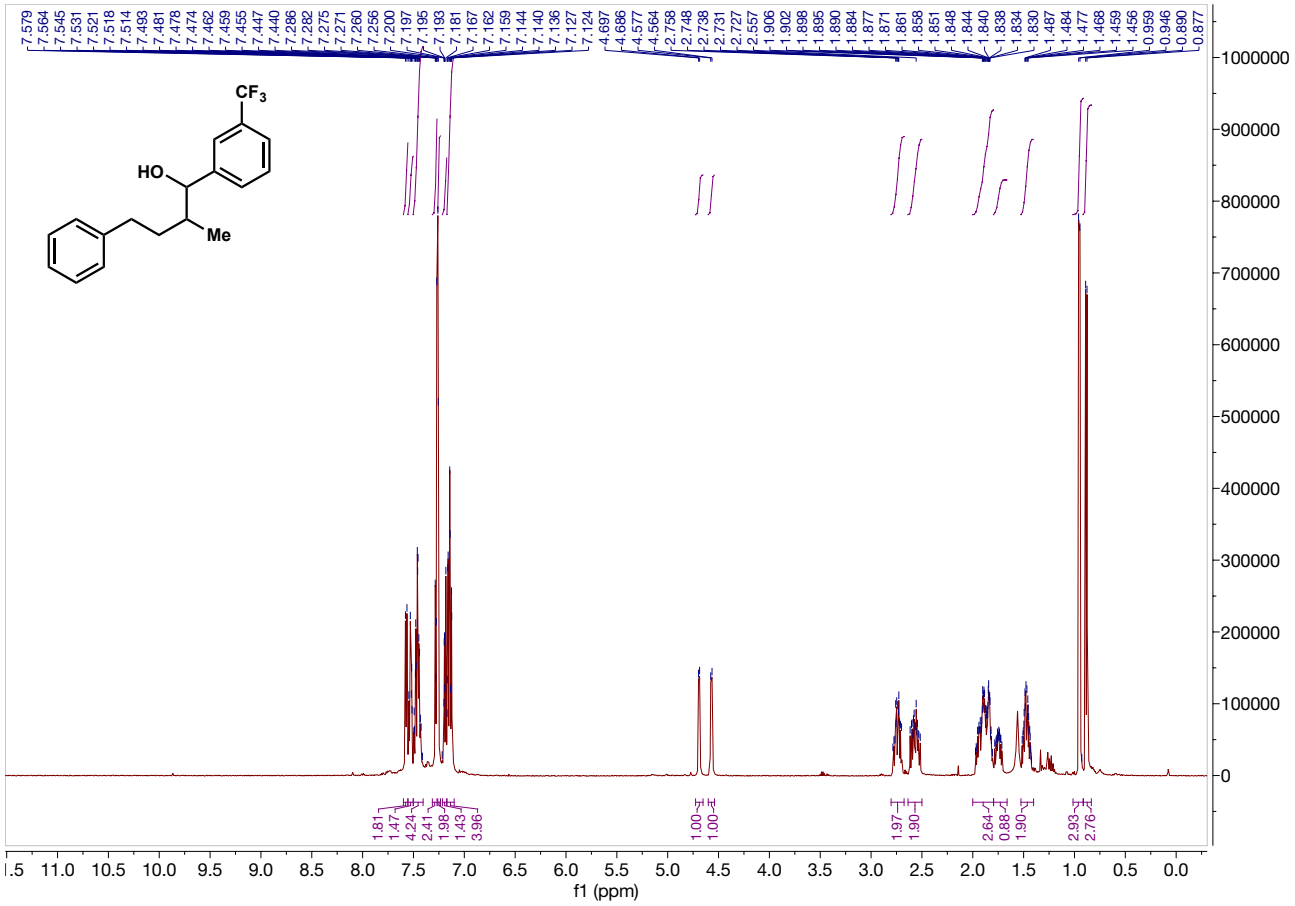

202.935
172.863
141.088
138.095
136.891
130.945
64.872
61.486
51.250
39.585
37.722
37.702
28.285
23.929
23.796
21.217
21.172
20.050
19.416
14.306
f1 (ppm)

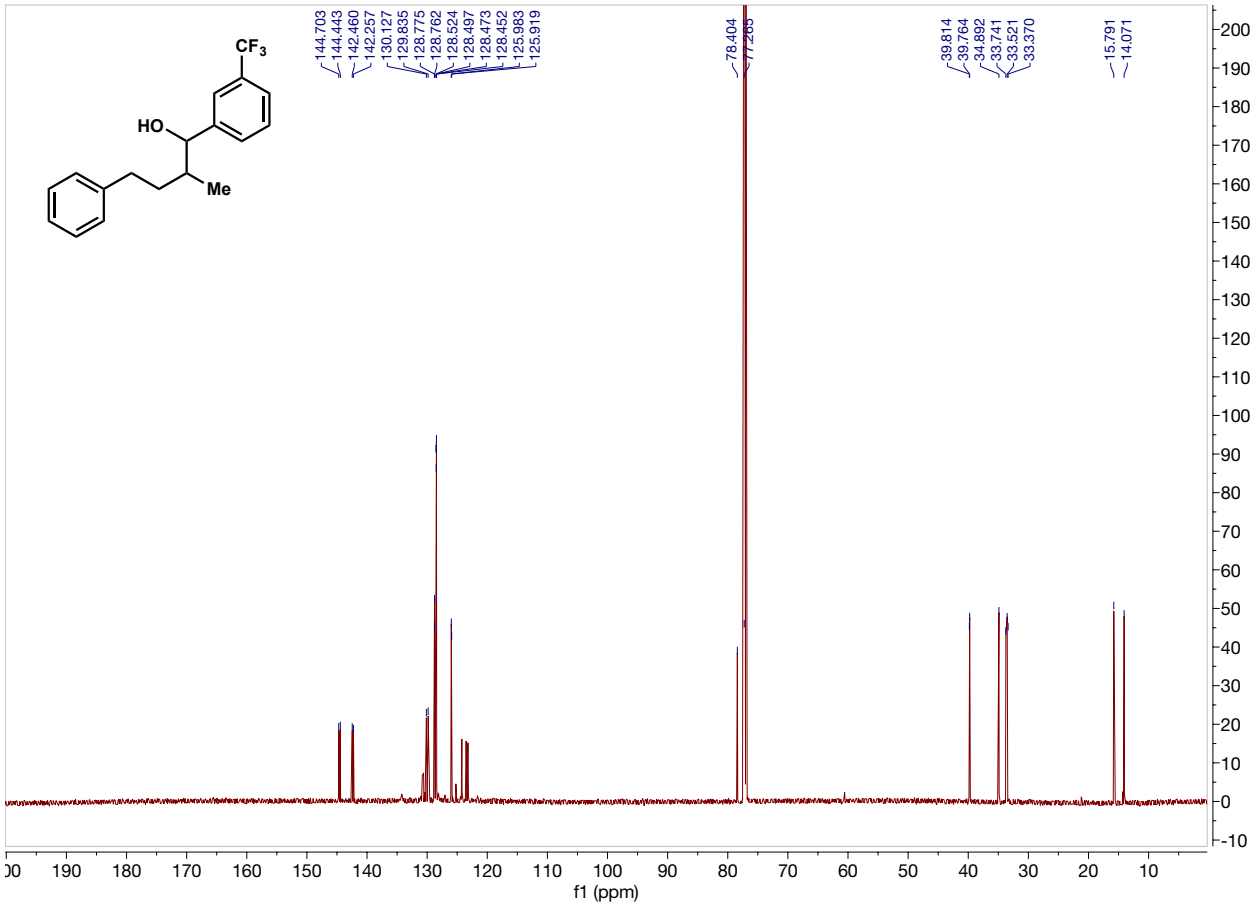

major
minor
3.85
4.33
2.00
6.38
0.21
0.93
0.11
6.01
0.56
0.70
3.03
1.37
2.14
3.17
3.00
2.15
3.12
3.23
6.22
3.01
2.82
f1 (ppm)

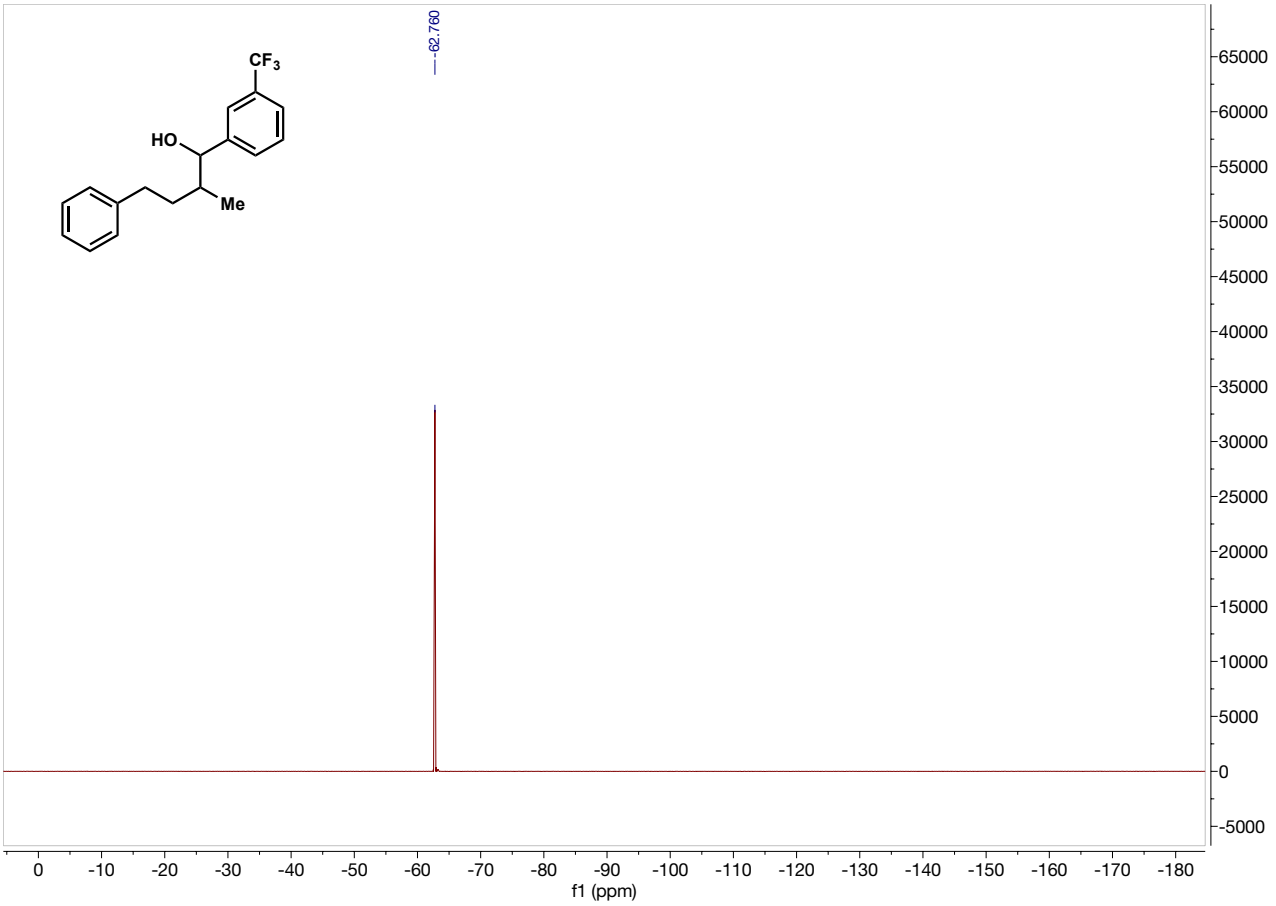

major
minor
173.015
172.372
142.349
142.215
141.669
141.657
129.683
129.658
125.528
125.454
77.371
77.160
76.948
66.168
61.290
61.212
59.604
36.237
31.932
29.967
29.185
29.109
28.151
23.310
21.511
21.500
19.136
18.292
17.800
17.735
17.303
16.010
15.597
15.397
15.109
14.312
14.256
f1 (ppm)

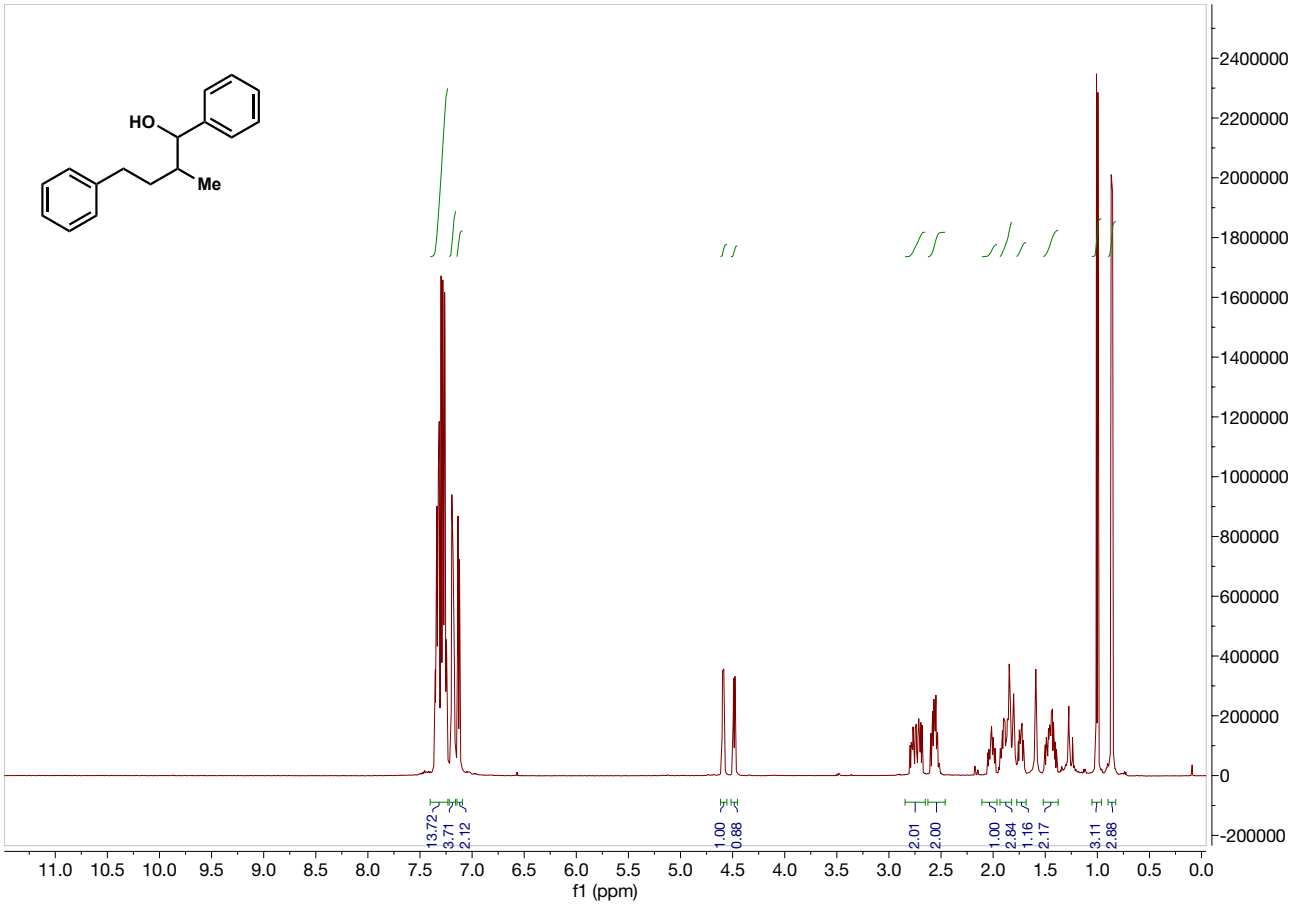

to-16-01.1.fid
7.73 7.72 7.72 7.71 7.71 7.30 7.30 7.30 7.30 7.30 7.29 7.29 7.29 7.29 7.28 CDCl3 5.14 5.12 3.86 3.85 3.84 3.83 3.83 3.82 3.81 3.80 3.78 3.77 3.76 3.75 3.75 3.74 3.73 3.72 3.57 3.55 2.43 1.07 1.06 1.04 0.98
Me
HN
S
O
O
EtO2C
t-Bu
1.97 2.80 1.02 2.12 1.03 3.17 3.05 9.44
f1 (ppm)

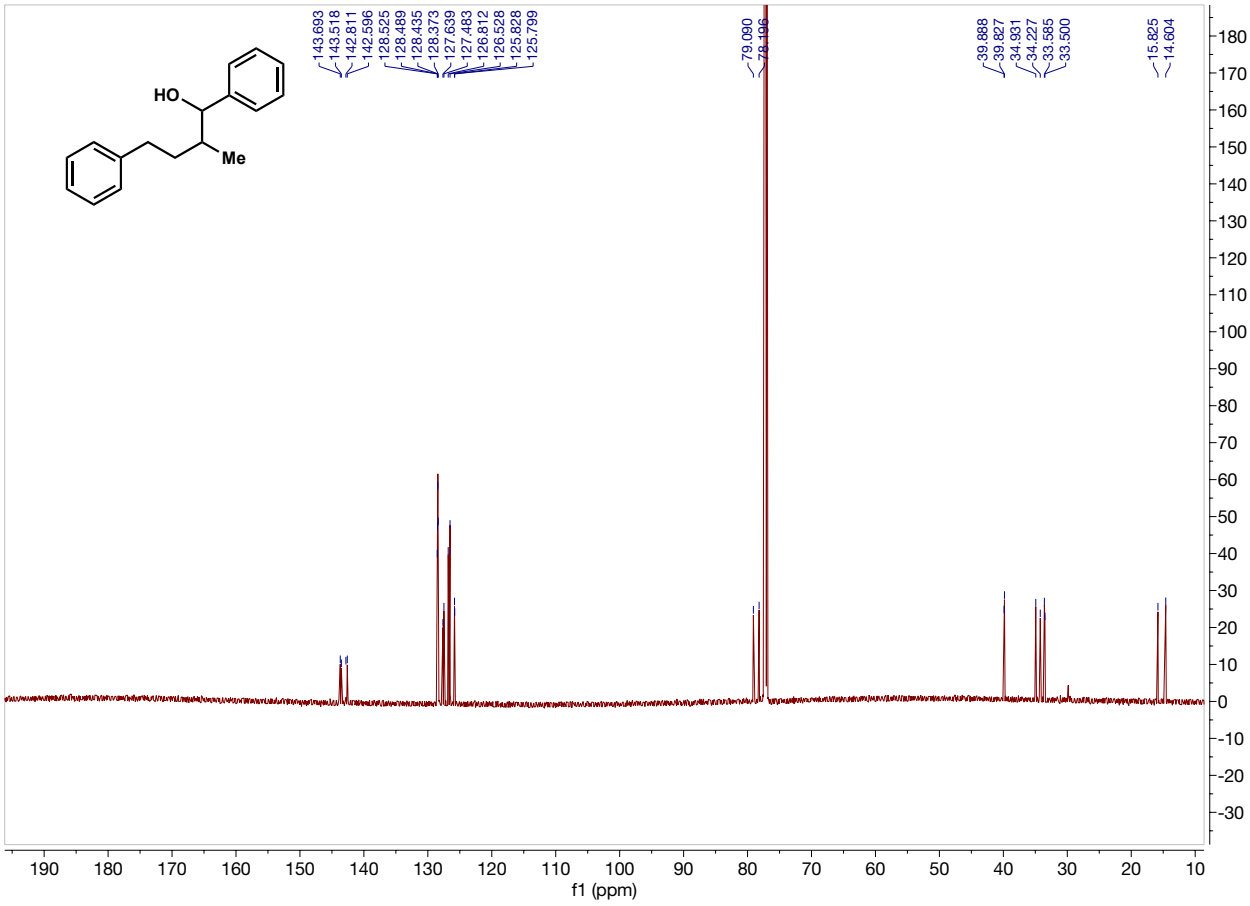

Me
HN
S
O
O
EtO2C
t-Bu
170.9 143.6 136.5 129.5 127.5 77.3 77.3 CDCl3 77.1 77.0 CDCl3 76.8 76.8 CDCl3 64.2 61.1 34.6 26.3 21.5 13.9 0.0
f1 (ppm)

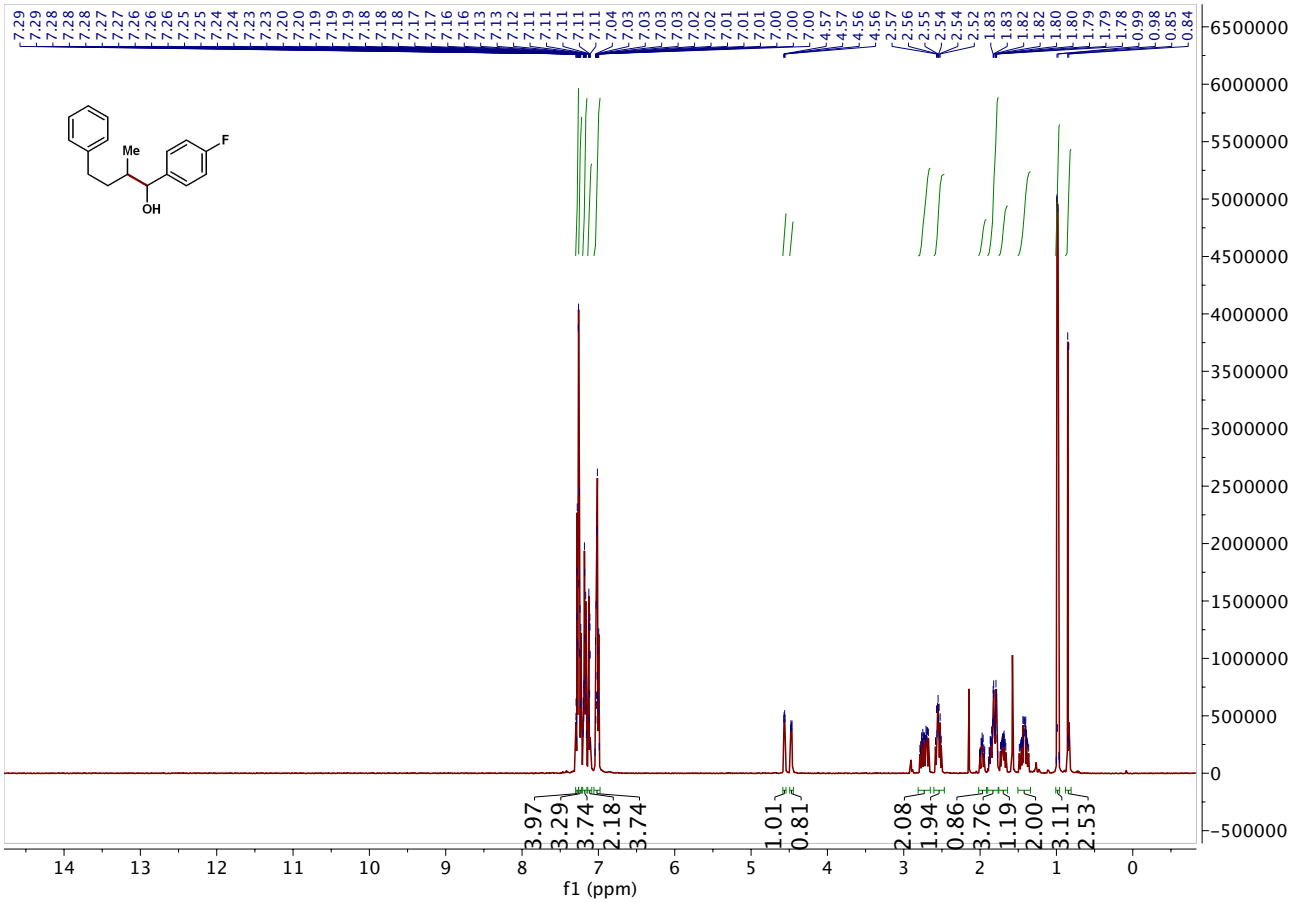

CF3
HO
Me
f1 (ppm)

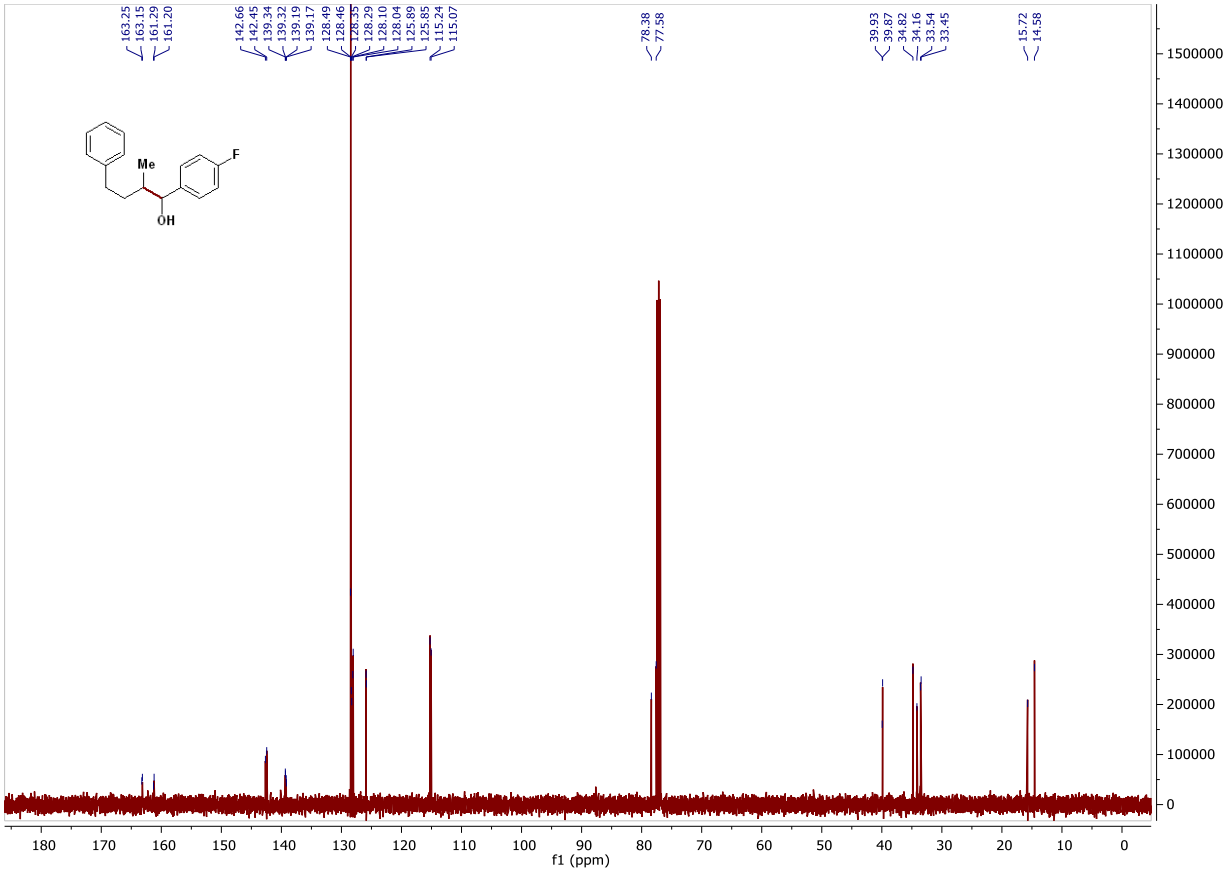

CF3
HO
Me
f1 (ppm)

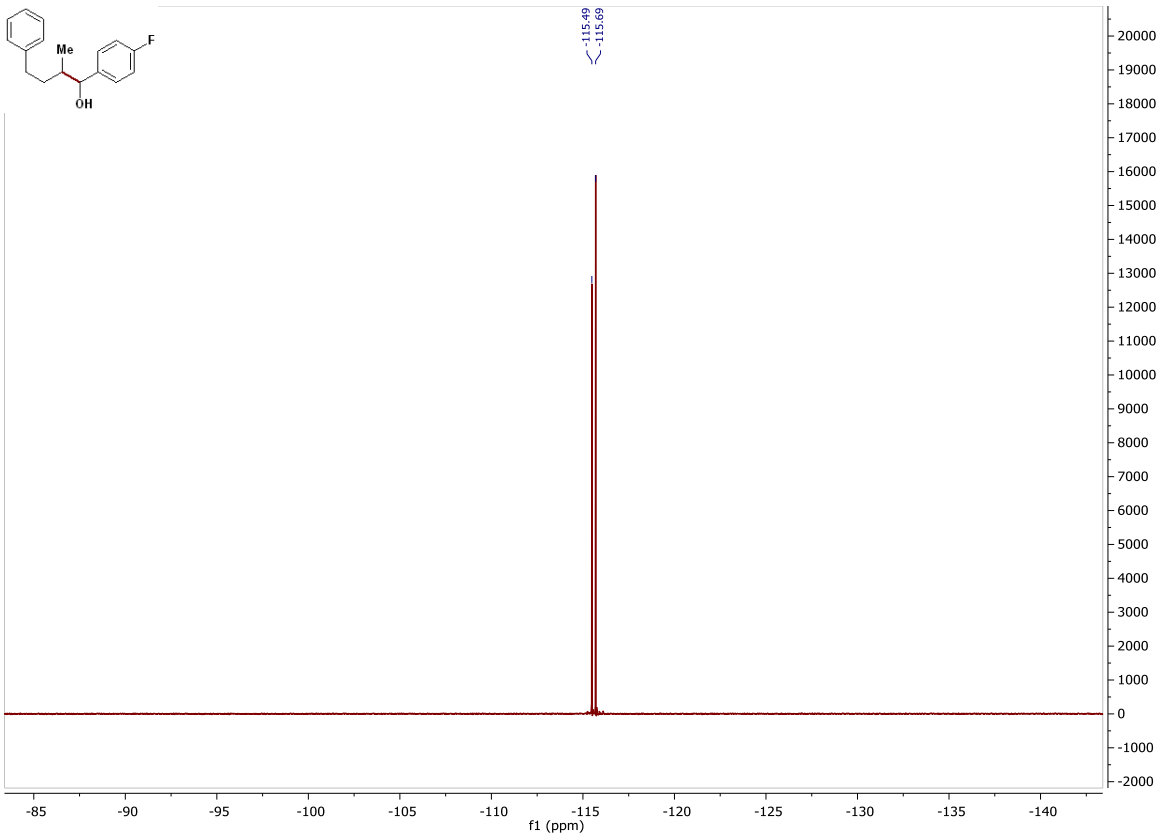

-62.760
CF3
HO
Me
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)

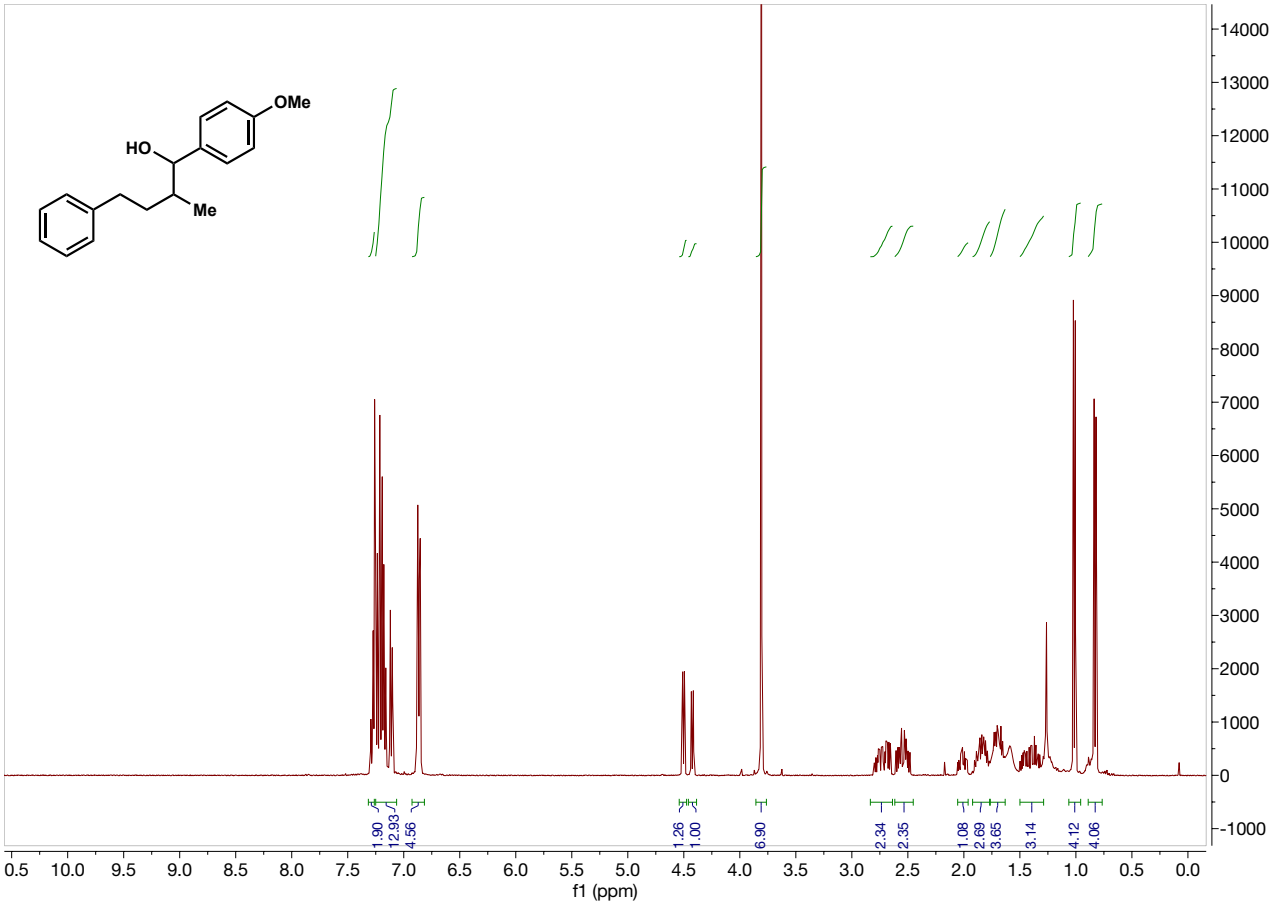

HO
Me
13.72
3.71
2.12
1.00
0.88
2.01
2.00
1.00
2.84
1.16
2.17
3.11
2.88
f1 (ppm)

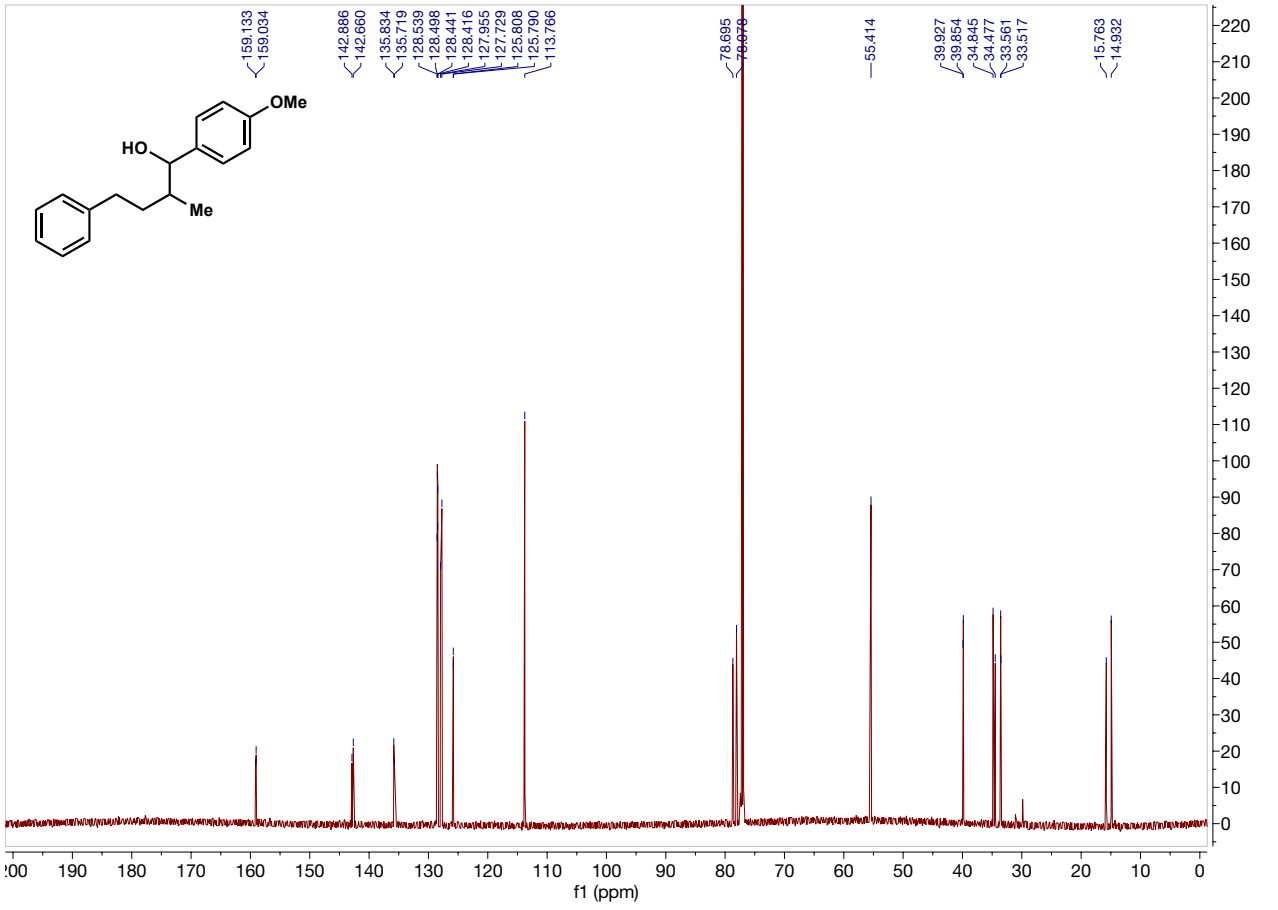

HO
Me
143.693
143.518
142.811
142.596
128.525
128.489
128.435
128.373
127.639
127.483
126.812
126.528
125.828
125.799
79.090
78.196
39.888
39.827
34.931
34.227
33.585
33.500
15.825
14.804
f1 (ppm)

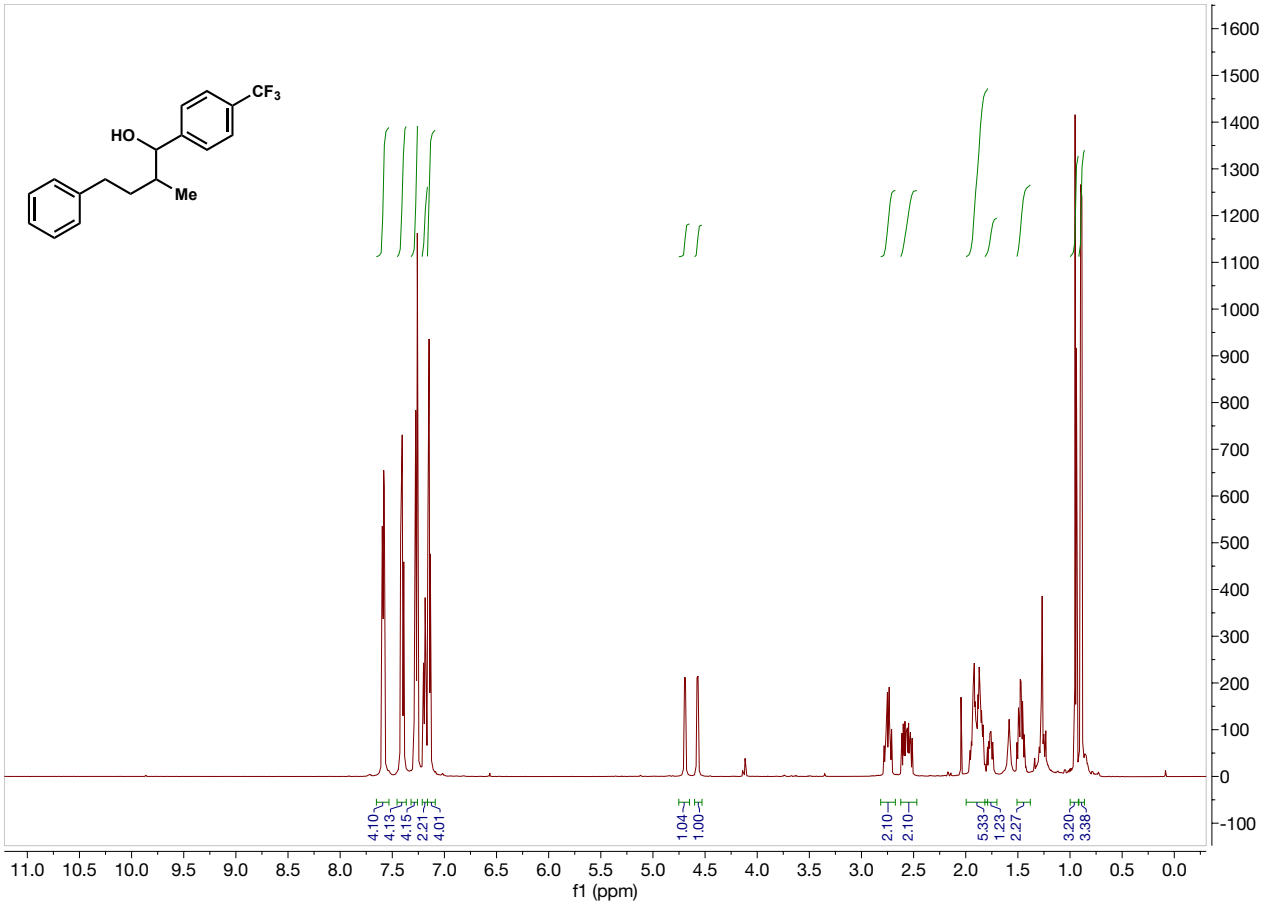

Me
F
OH
f1 (ppm)

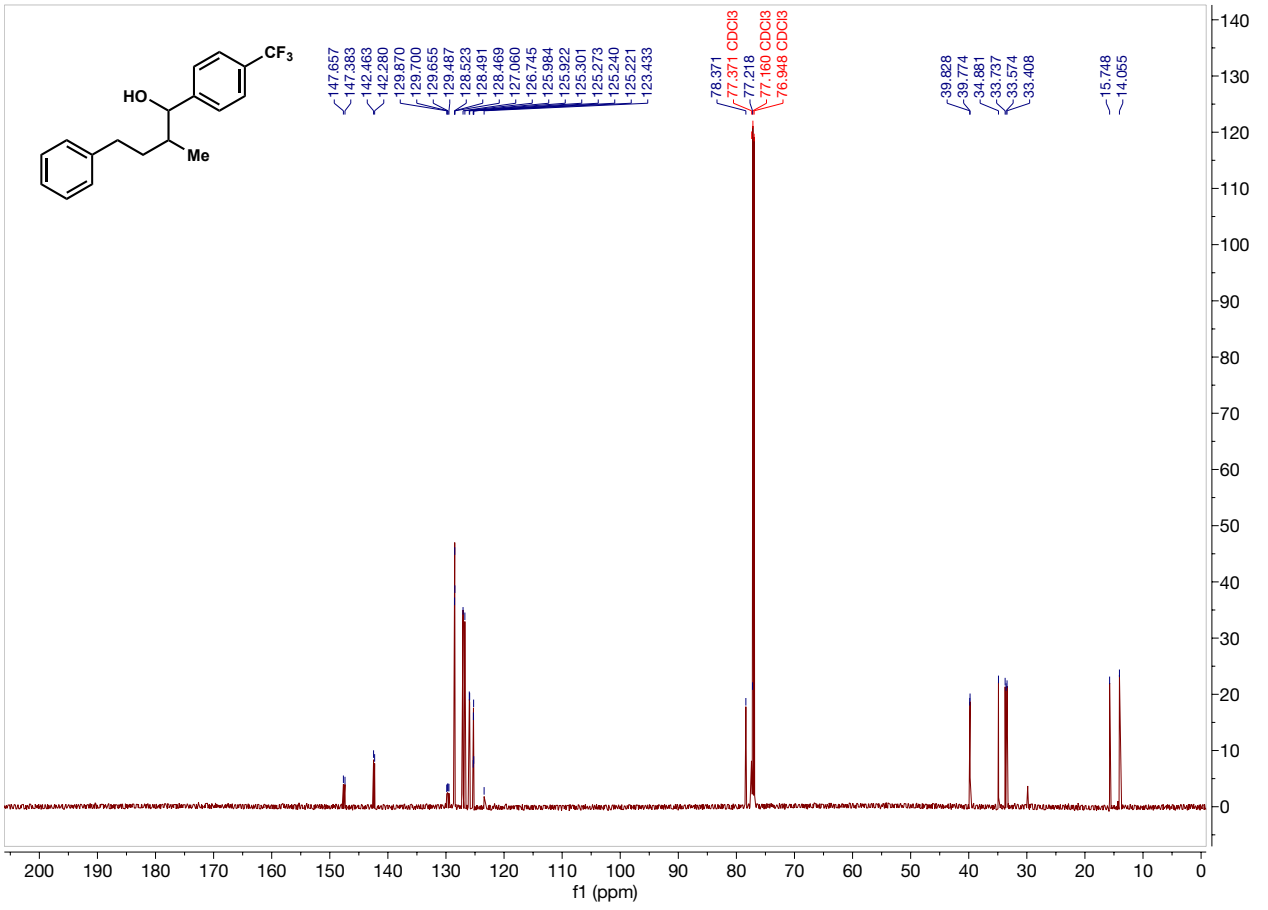

Me
F
OH
f1 (ppm)

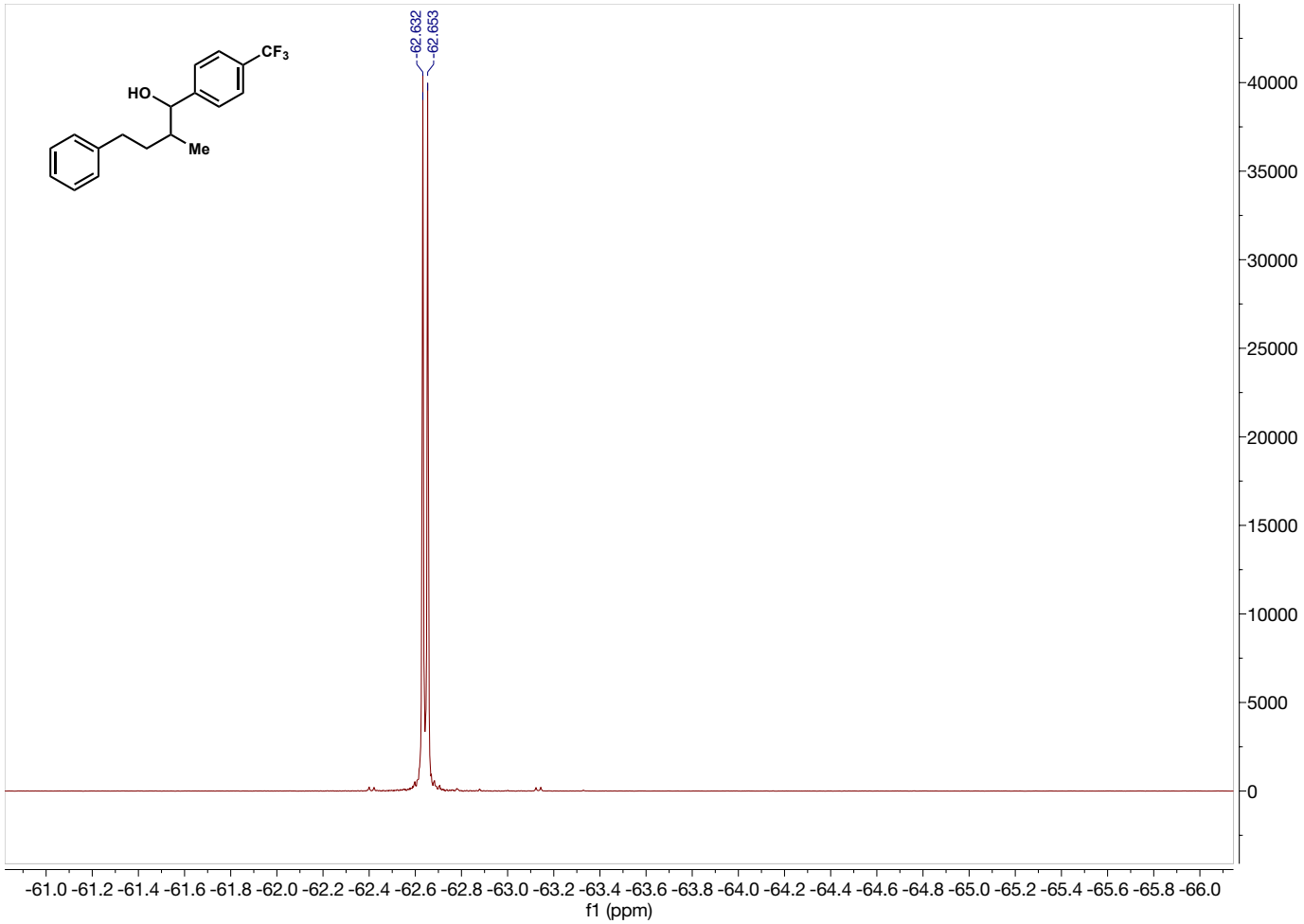

Me
F
OH
-115.49
-115.69
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)

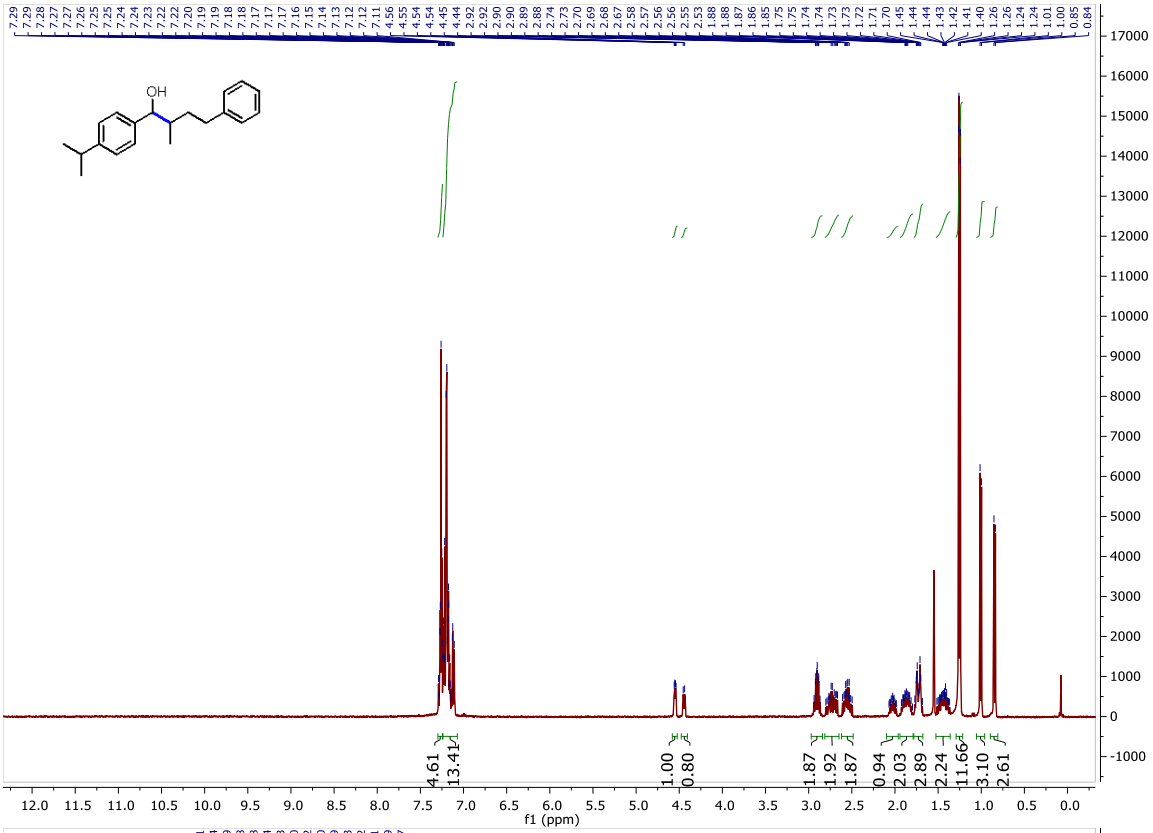

OMe
HO
Me
1.90
12.93
4.56
1.26
1.00
6.90
2.34
2.35
1.08
2.69
3.65
3.14
4.12
4.06
f1 (ppm)

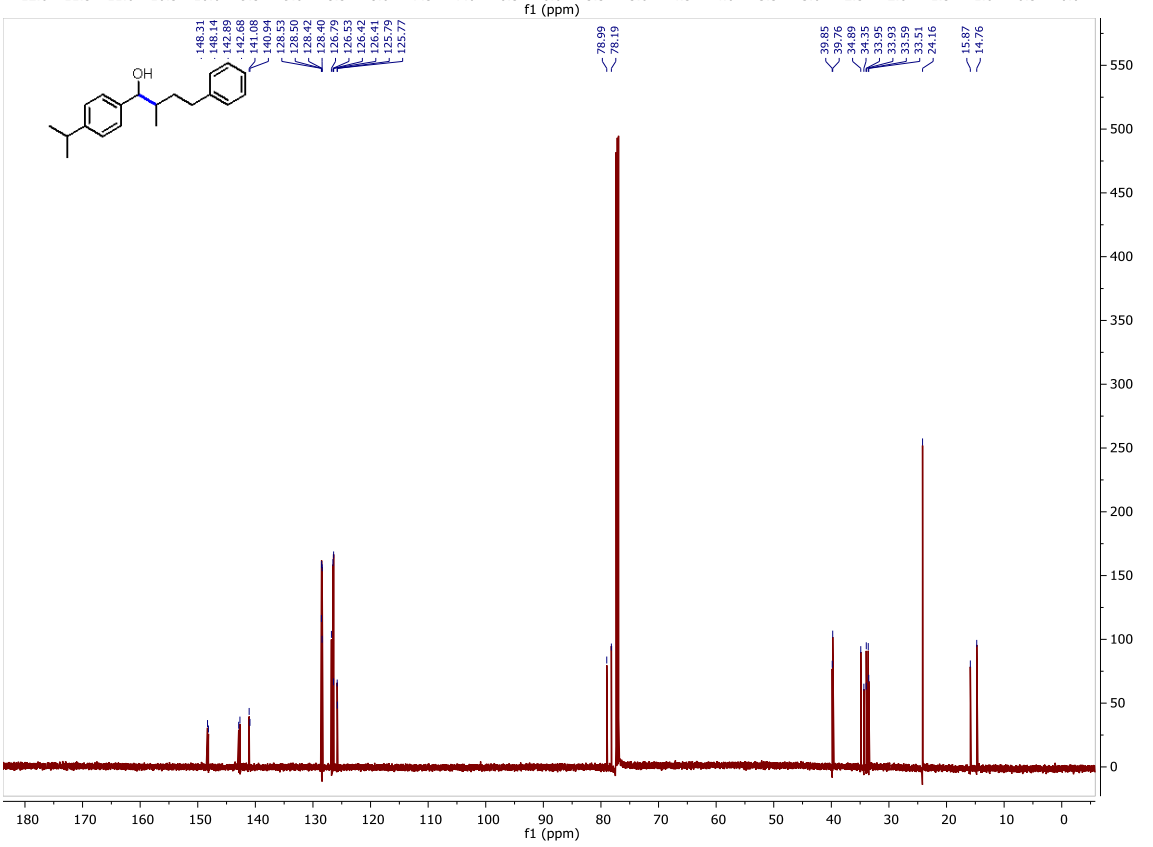

159.133
159.034
142.886
142.660
135.834
135.719
128.539
128.498
128.441
128.416
127.955
127.729
125.808
125.790
113.766
78.695
78.076
55.414
39.927
39.854
34.845
34.477
33.561
33.517
15.763
14.932
OMe
HO
Me
f1 (ppm)


HO
CF3
Me
4.10
4.13
4.15
2.21
4.01
1.04
1.00
2.10
2.10
5.33
1.23
2.27
3.20
3.38
f1 (ppm)


HO
CF3
Me
147.657
147.383
142.463
142.280
129.870
129.700
129.655
129.487
128.523
128.491
128.469
127.060
126.745
125.984
125.922
125.301
125.273
125.240
125.221
123.433
78.371
77.371 CDCl3
77.218
77.160 CDCl3
76.948 CDCl3
39.828
39.774
34.881
33.737
33.574
33.408
15.748
14.055
f1 (ppm)


-62.632
-62.653
CF3
HO
Me
40000
35000
30000
25000
20000
15000
10000
5000
0
-61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0 -63.2 -63.4 -63.6 -63.8 -64.0 -64.2 -64.4 -64.6 -64.8 -65.0 -65.2 -65.4 -65.6 -65.8 -66.0
f1 (ppm)


OH
4.61
13.41
1.00
0.80
1.87
1.92
1.87
0.94
2.03
2.89
2.24
11.66
3.10
2.61
f1 (ppm)


OH
148.31
148.14
142.89
142.68
141.08
140.94
128.53
128.50
128.42
128.40
126.79
126.53
126.42
126.41
125.79
125.77
78.99
78.19
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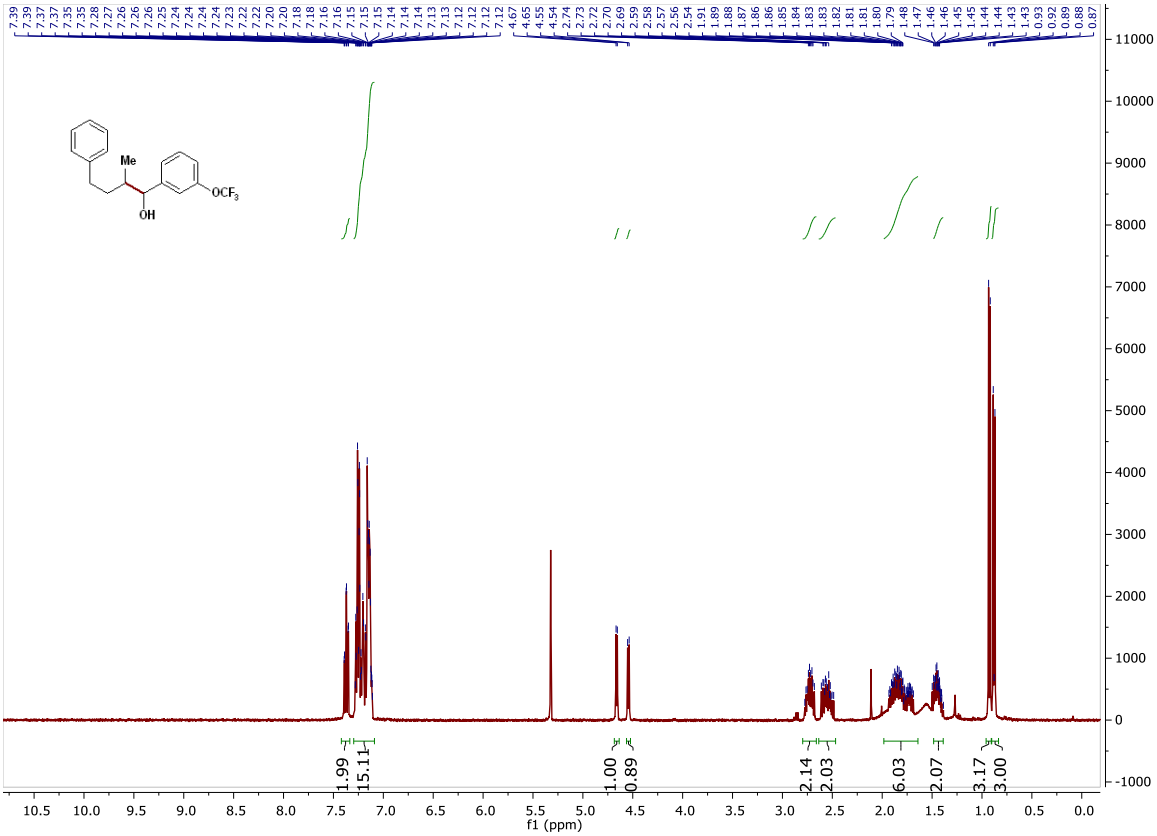
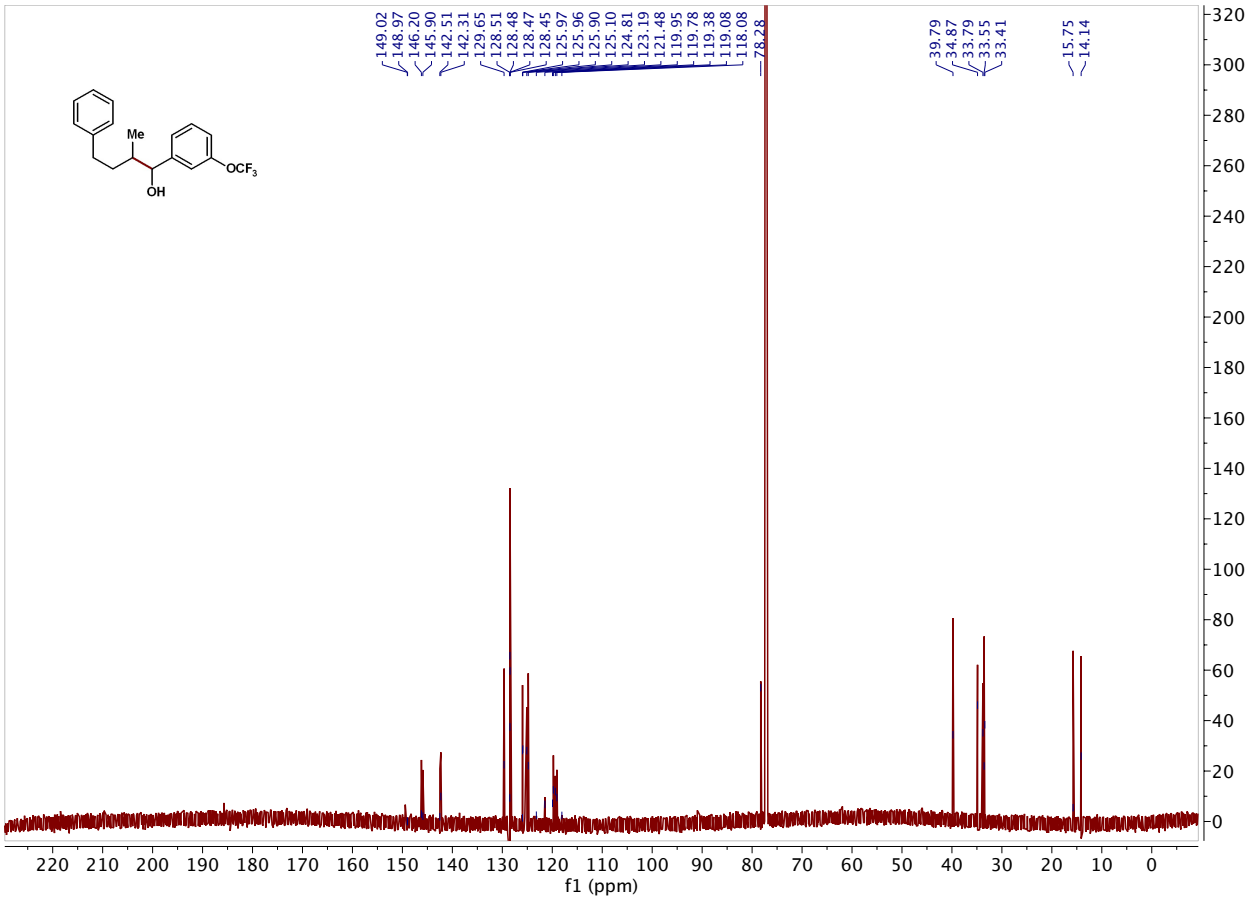
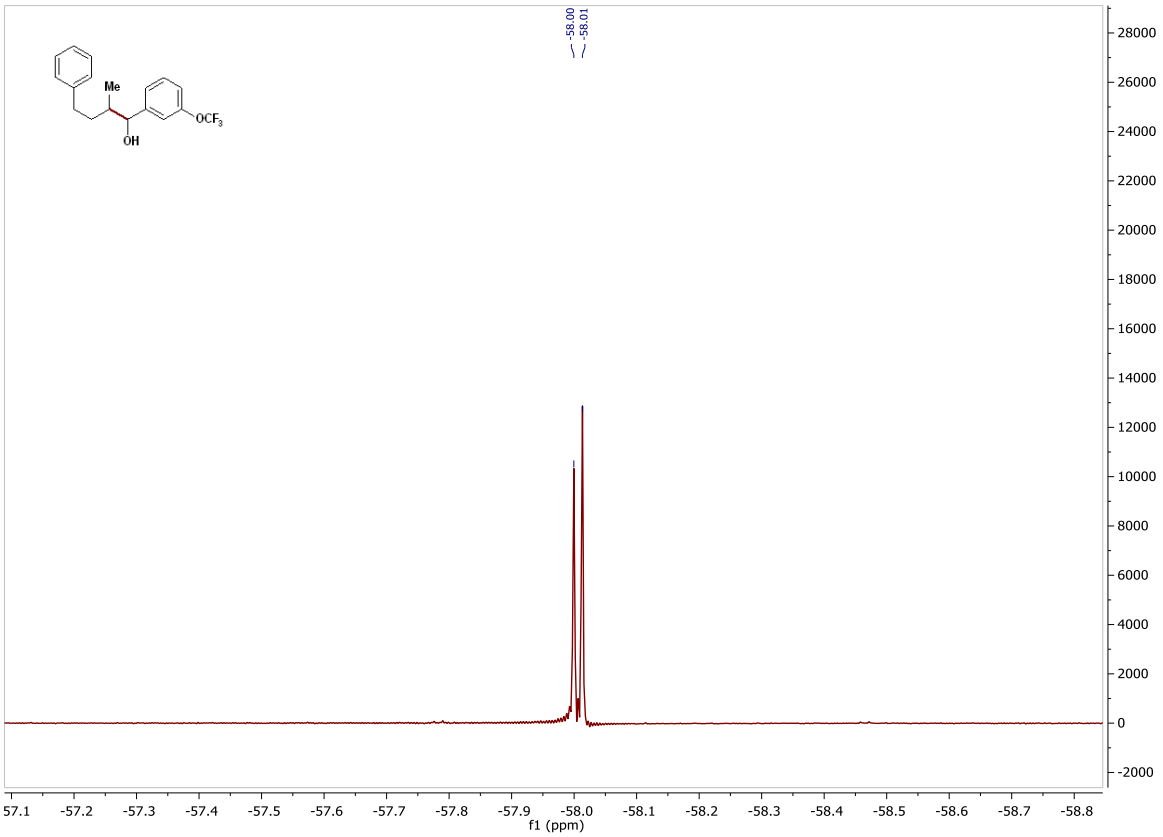
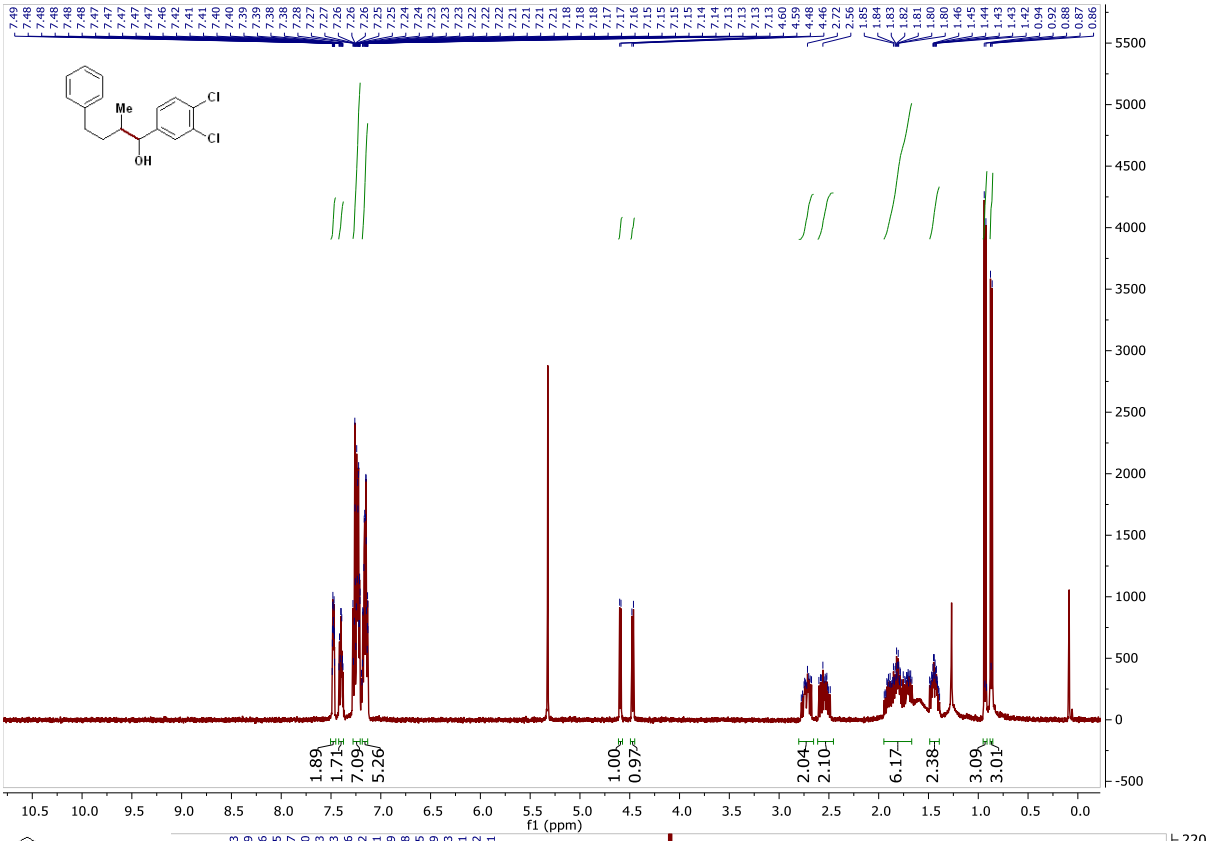
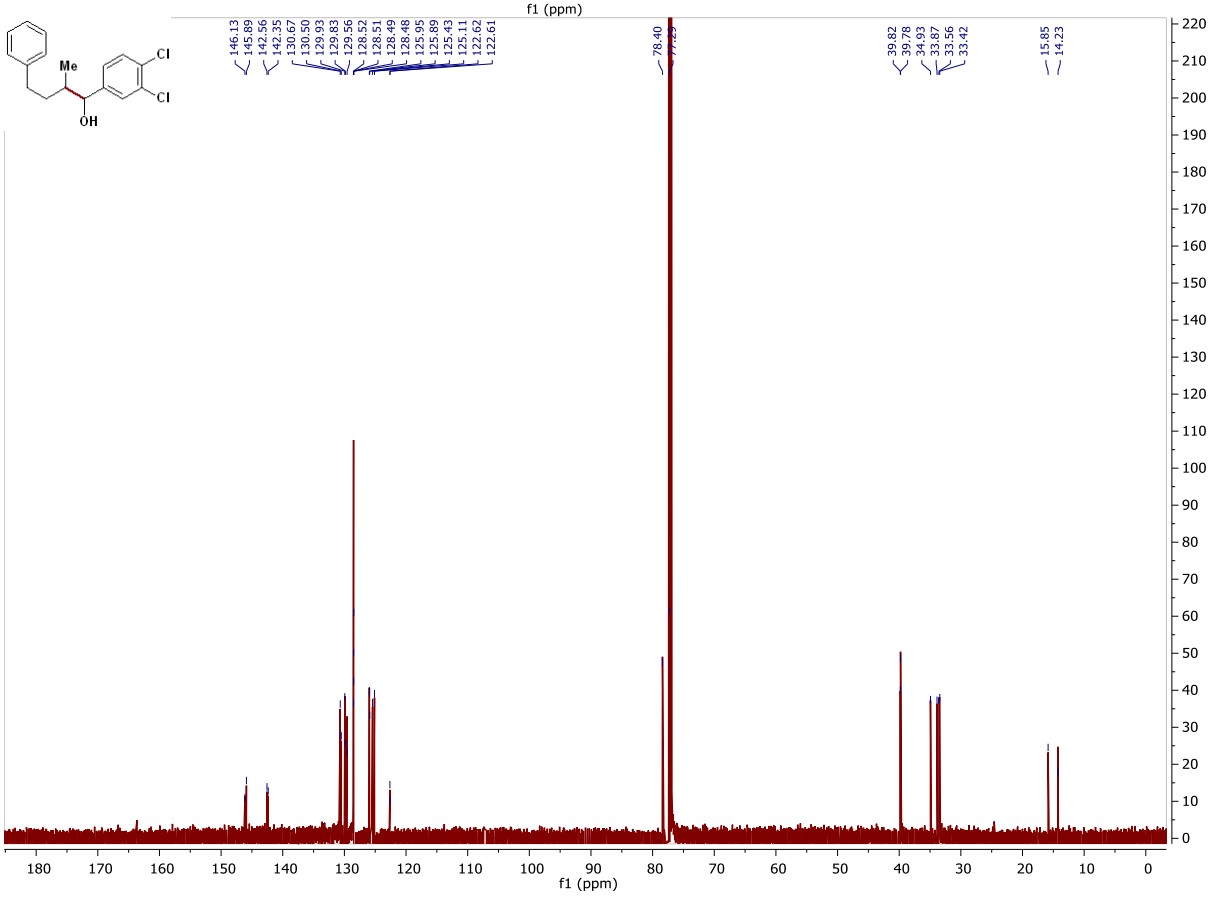
33.59
33.51
24.16
15.87
14.76
f1 (ppm)

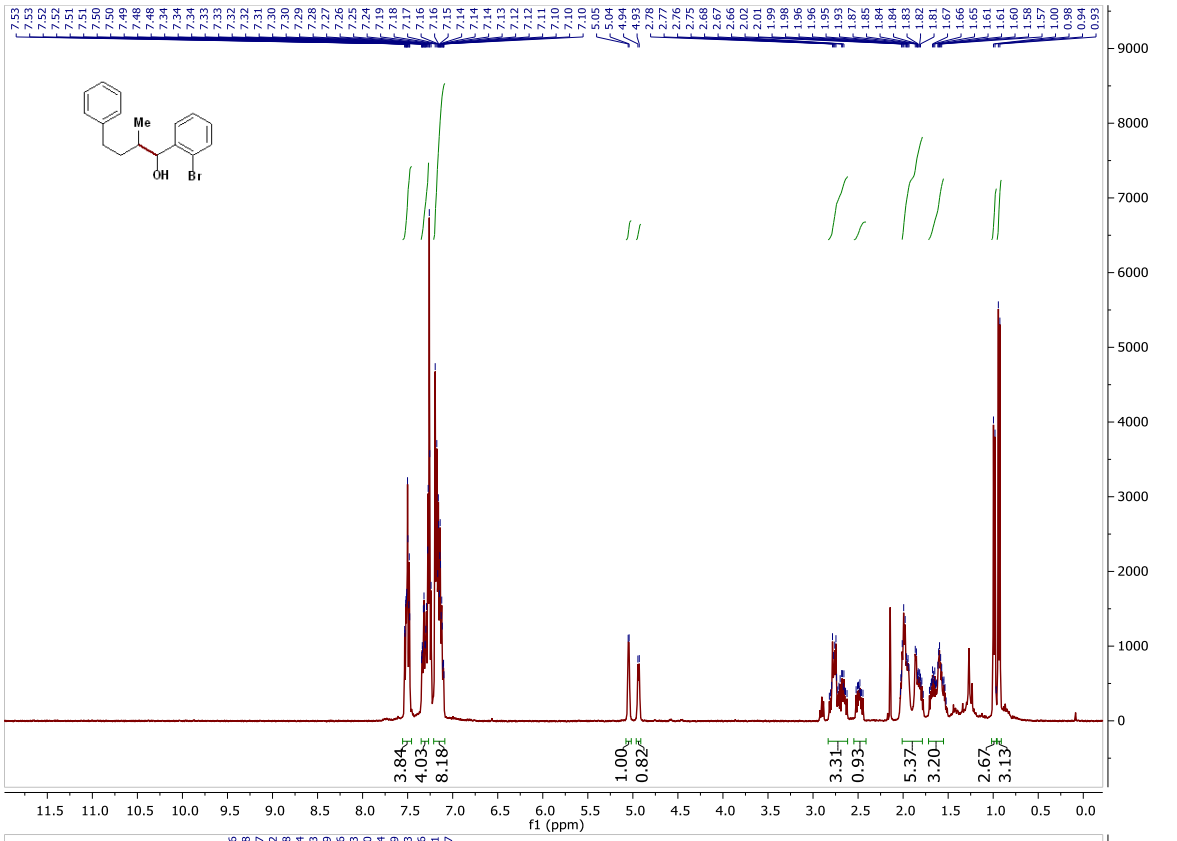

Me
OCF3
OH
1.99
15.11
1.00
0.89
2.14
2.03
6.03
2.07
3.17
3.00
f1 (ppm)

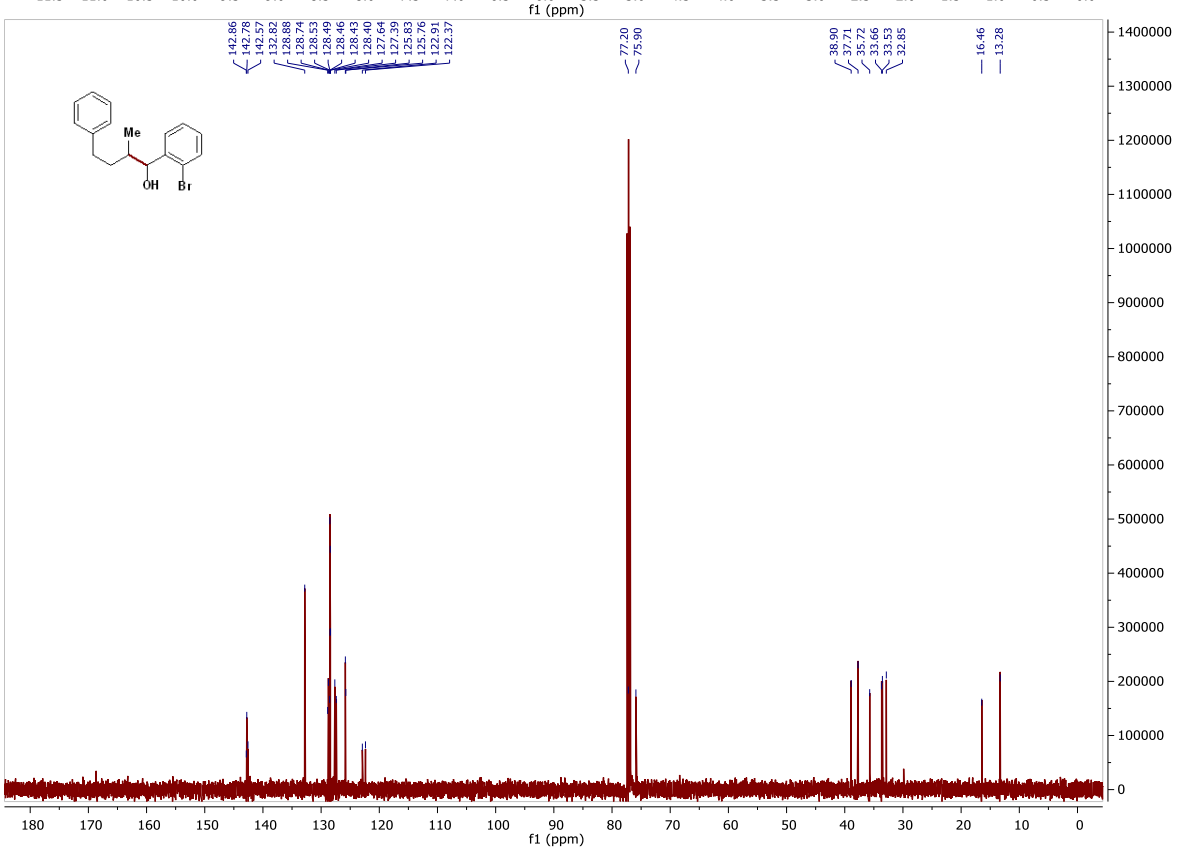

Me
OCF3
OH
149.02
148.97
146.20
145.90
142.51
142.31
129.65
128.51
128.48
128.47
128.45
125.97
125.96
125.90
125.10
124.81
123.19
121.48
119.95
119.78
119.38
119.08
118.08
78.28
39.79
34.87
33.79
33.55
33.41
15.75
14.14
f1 (ppm)

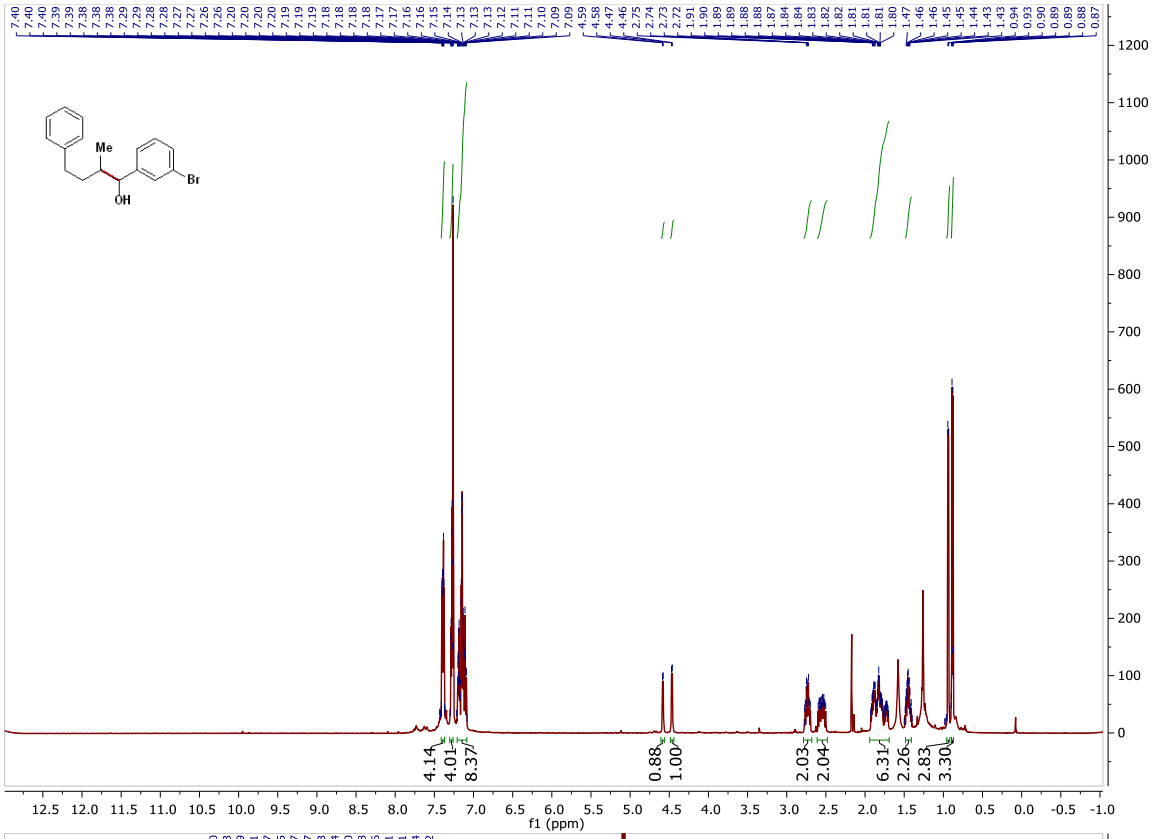

-58.00
-58.01
Me
OCF3
OH
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
57.1
-57.2
-57.3
-57.4
-57.5
-57.6
-57.7
-57.8
-57.9
-58.0
-58.1
-58.2
-58.3
-58.4
-58.5
-58.6
-58.7
-58.8
f1 (ppm)

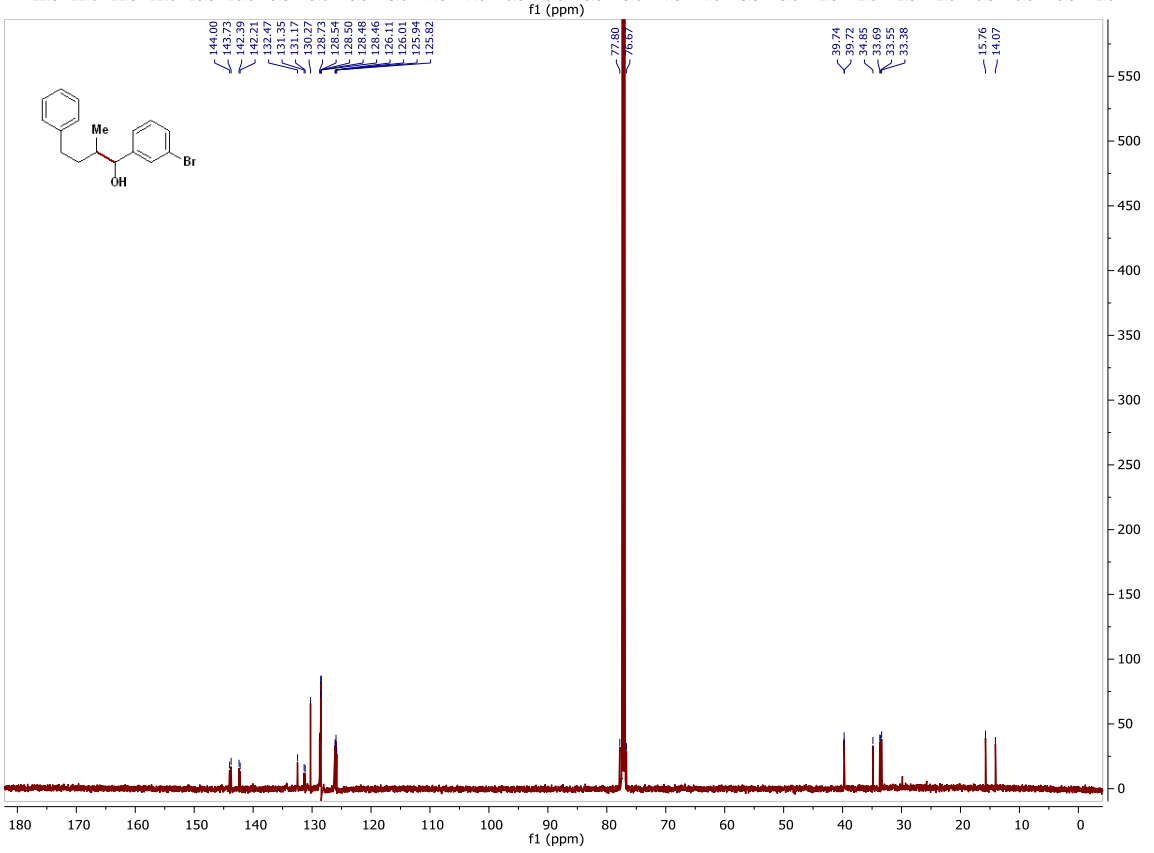

Me
Cl
Cl
OH
1.89
1.71
7.09
5.26
1.00
0.97
2.04
2.10
6.17
2.38
3.09
3.01
f1 (ppm)

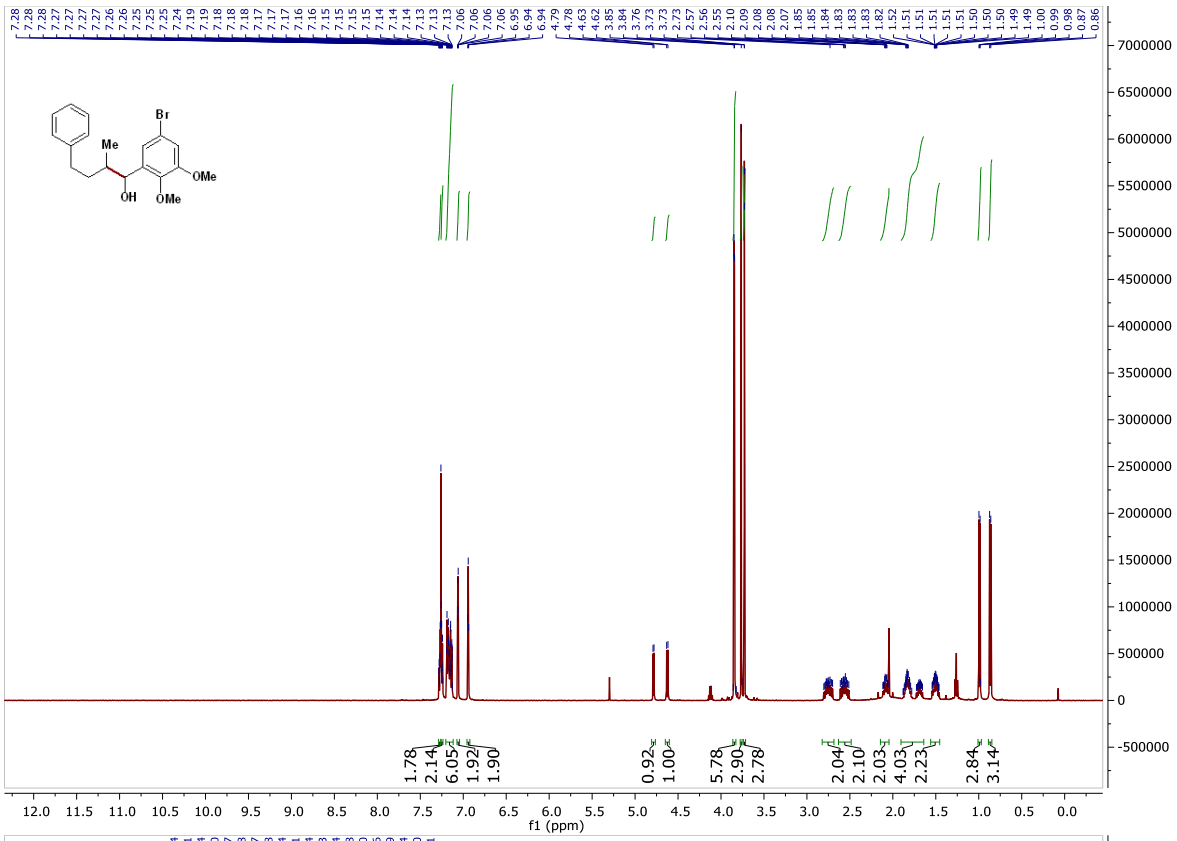

Me
Cl
Cl
OH
146.13
145.89
142.56
142.35
130.67
130.50
129.93
129.83
129.56
128.52
128.51
128.49
128.48
125.95
125.89
125.43
125.11
122.62
122.61
78.40
77.29
39.82
39.78
34.93
33.87
33.56
33.42
15.85
14.23
f1 (ppm)

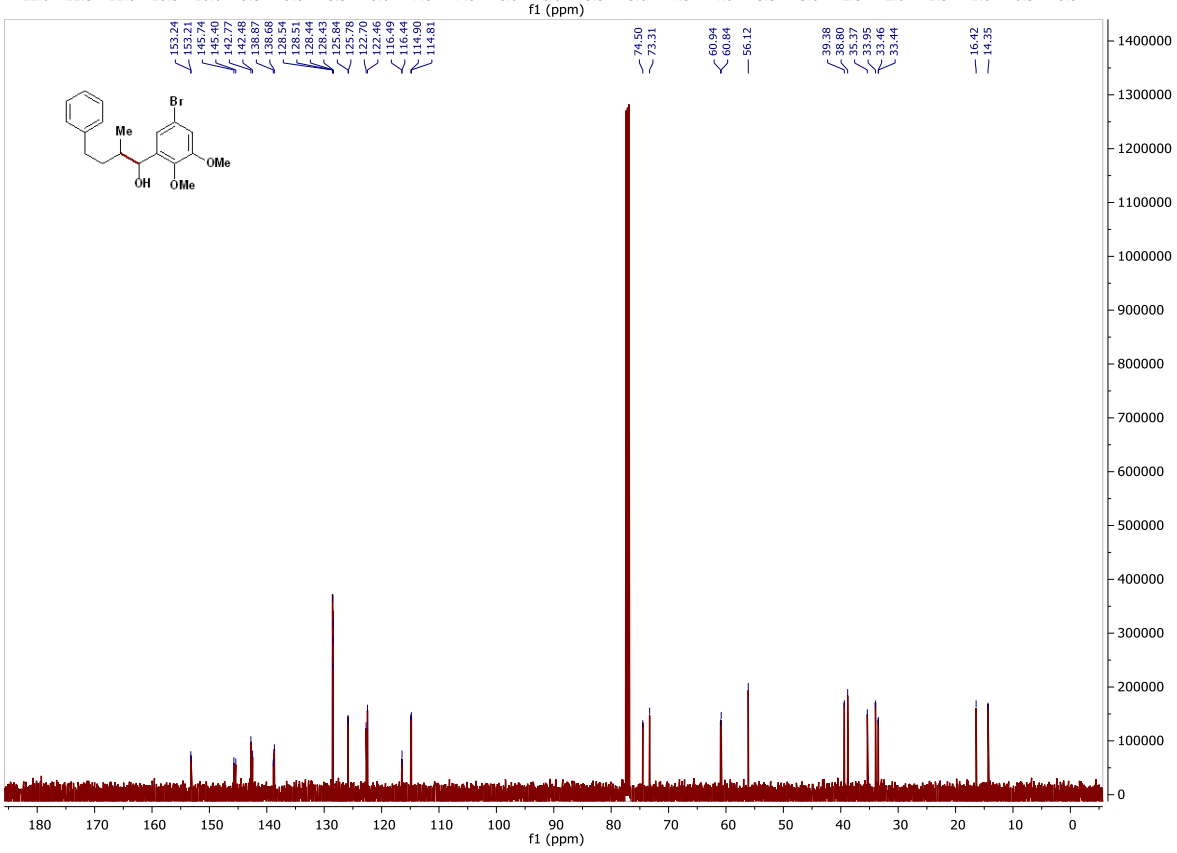

Me
OH
Br
f1 (ppm)

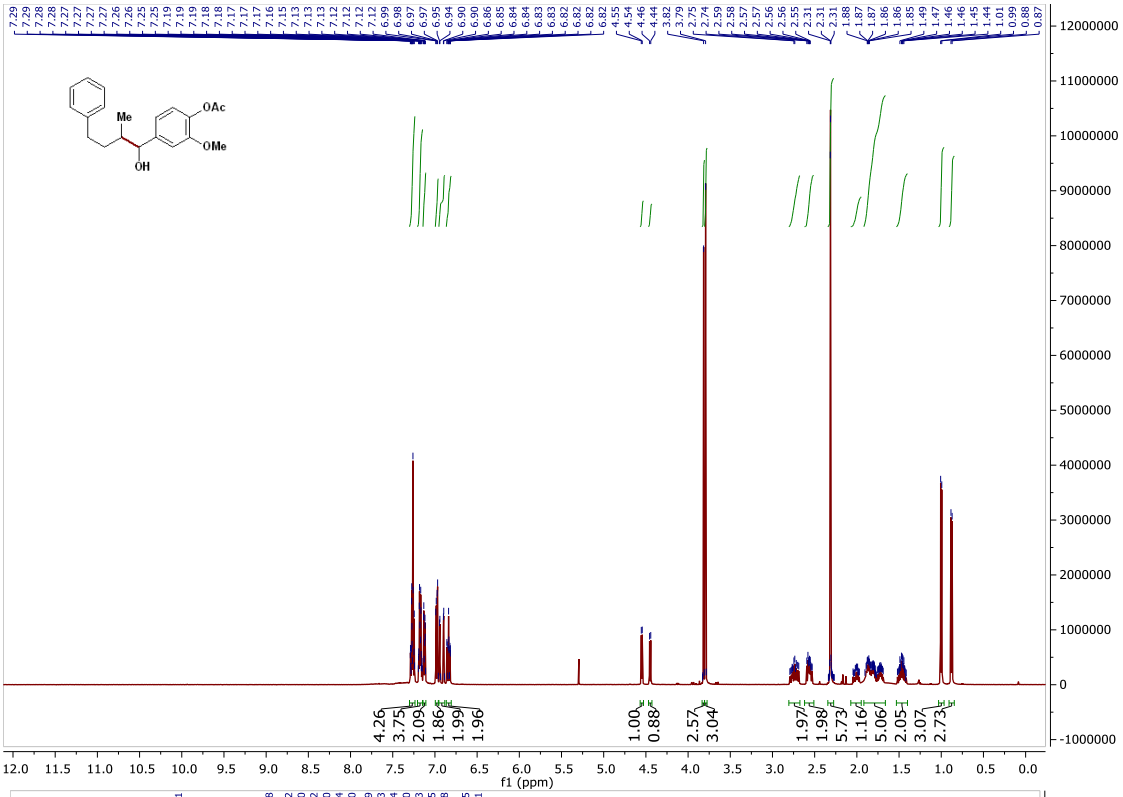

Me
OH
Br
f1 (ppm)

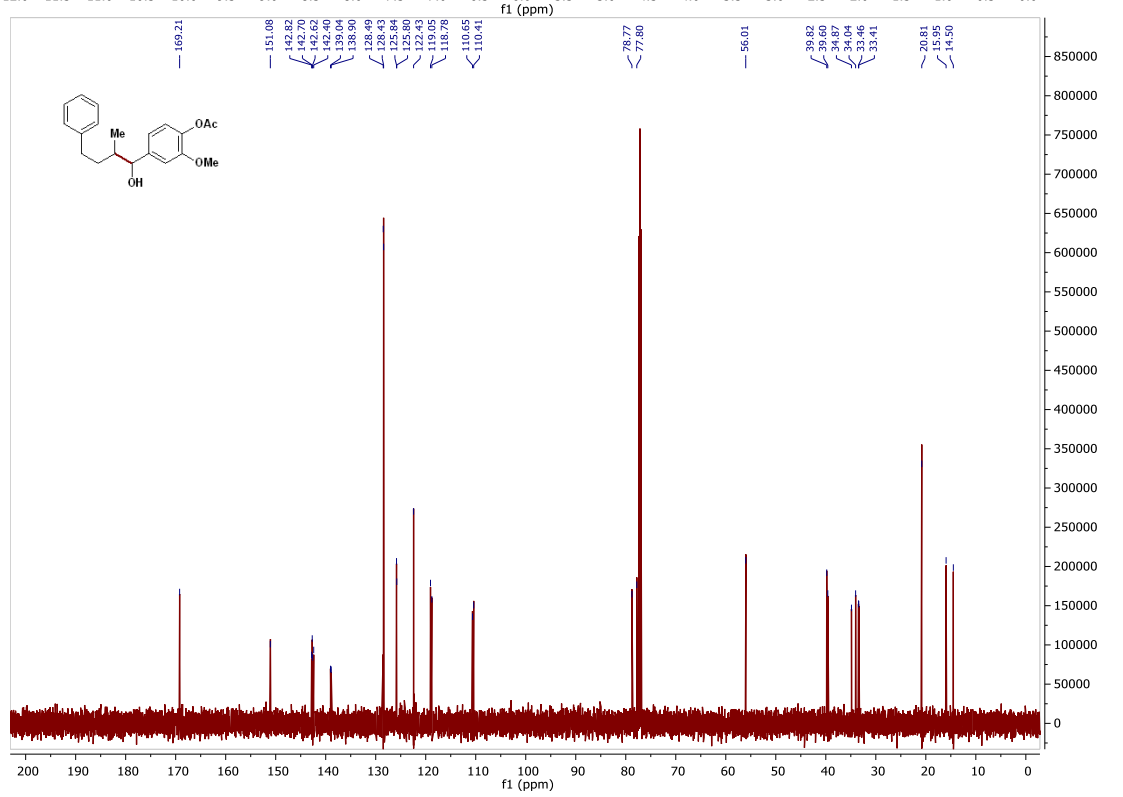

Me
Br
OH
4.14
4.01
8.37
0.88
1.00
2.03
2.04
6.31
2.26
2.83
3.30
f1 (ppm)


Me
Br
OH
144.00
143.73
142.39
142.21
132.47
131.35
131.17
130.27
128.73
128.54
128.50
128.48
128.46
126.11
126.01
125.94
125.82
77.80
76.67
39.74
39.72
34.85
33.69
33.55
33.38
15.76
14.07
f1 (ppm)


Br
Me
OMe
OH
OMe
f1 (ppm)


Br
Me
OMe
OH
OMe
f1 (ppm)


OAc
OMe
Me
OH
4.26
3.75
2.09
1.86
1.99
1.96
1.00
0.88
2.57
3.04
1.97
1.98
5.73
1.16
5.06
2.05
3.07
2.73
f1 (ppm)


OAc
OMe
Me
OH
169.21
151.08
142.82
142.70
142.62
142.40
139.04
138.90
128.49
128.43
125.84
125.80
122.43
120.95
118.78
110.65
110.41
78.77
77.80
56.01
39.82
39.60
34.87
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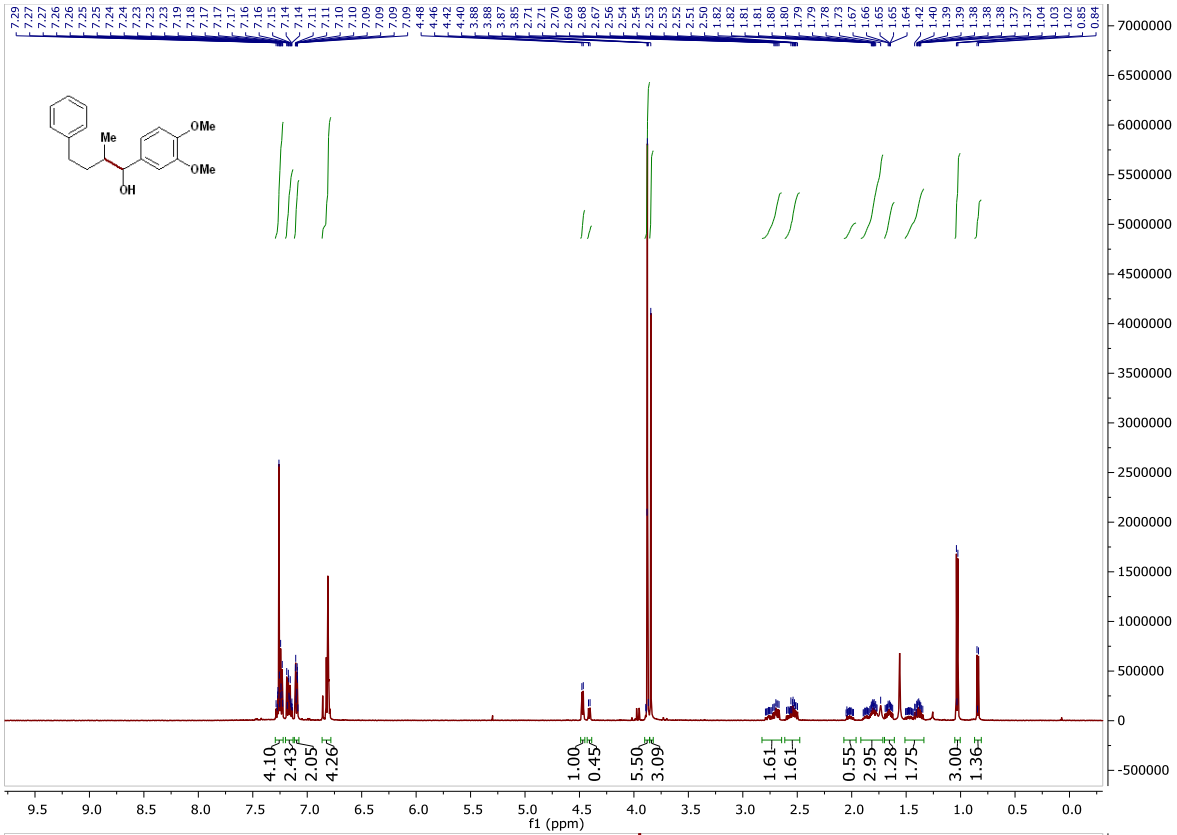
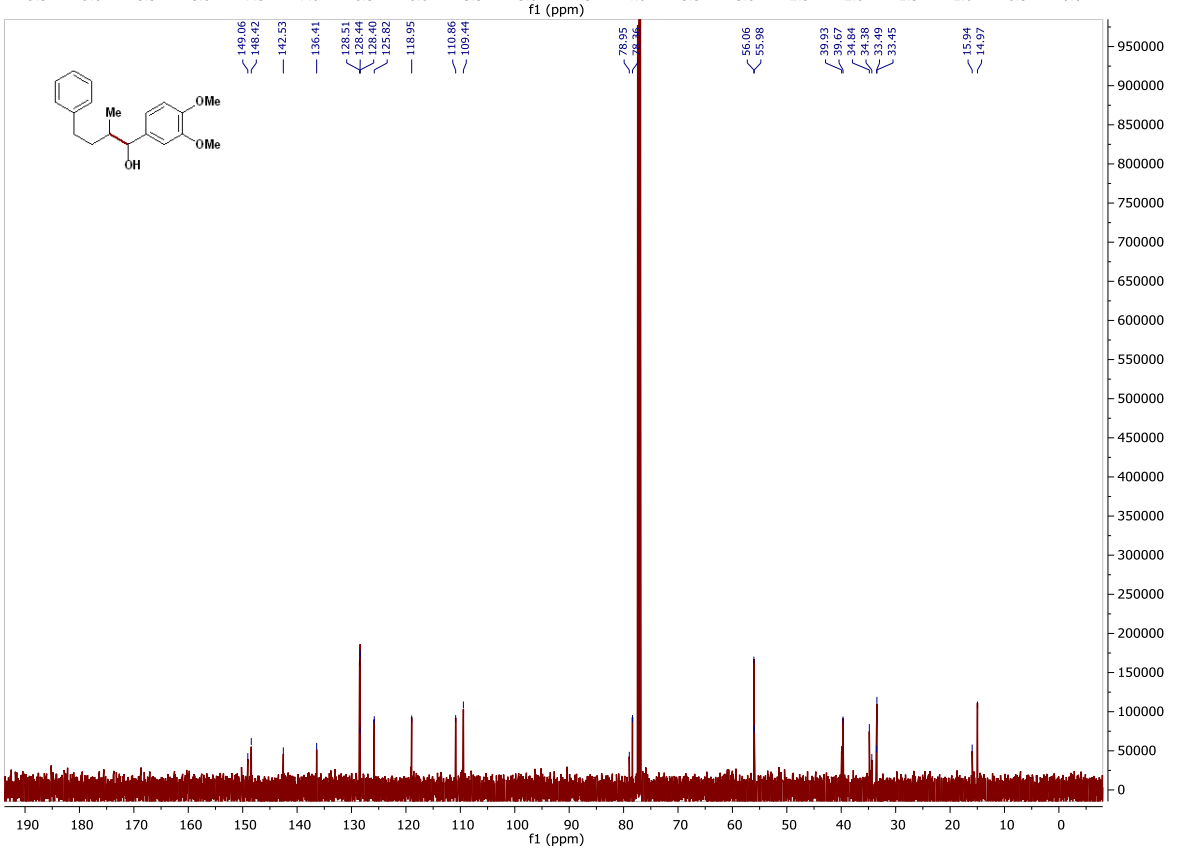
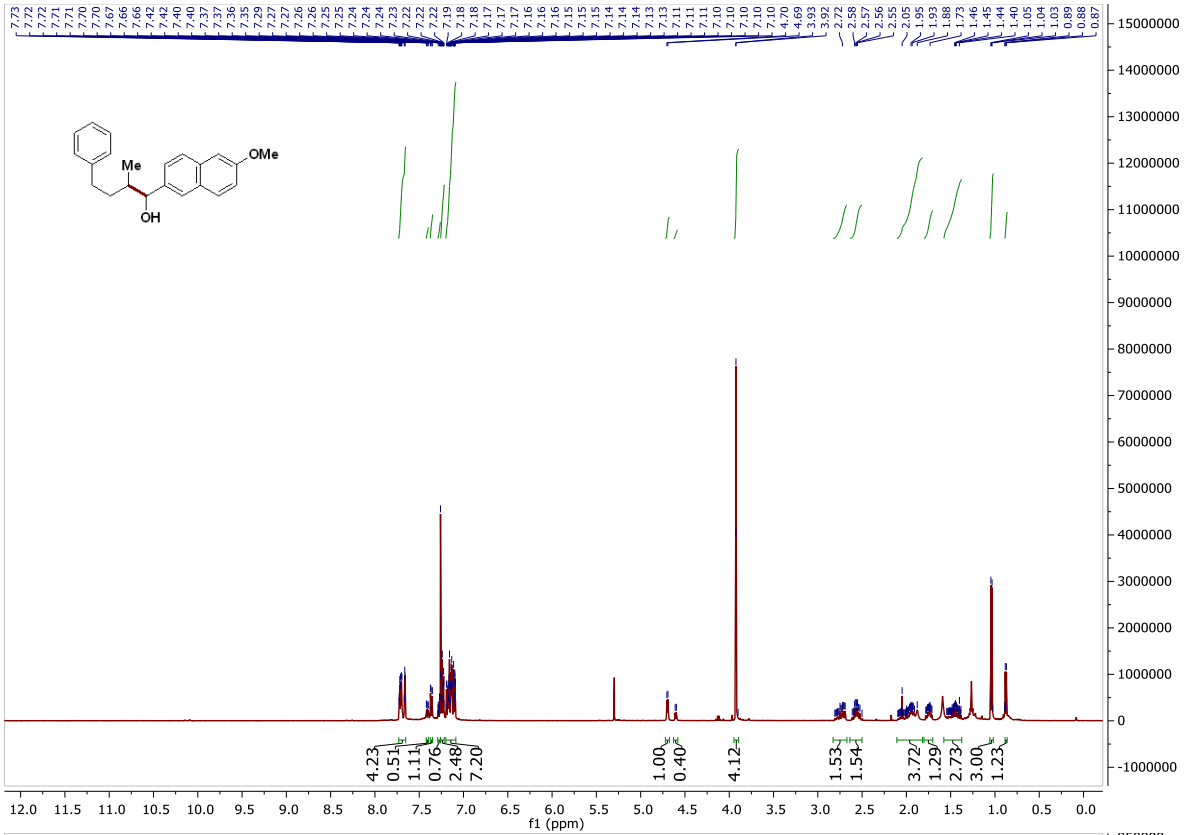
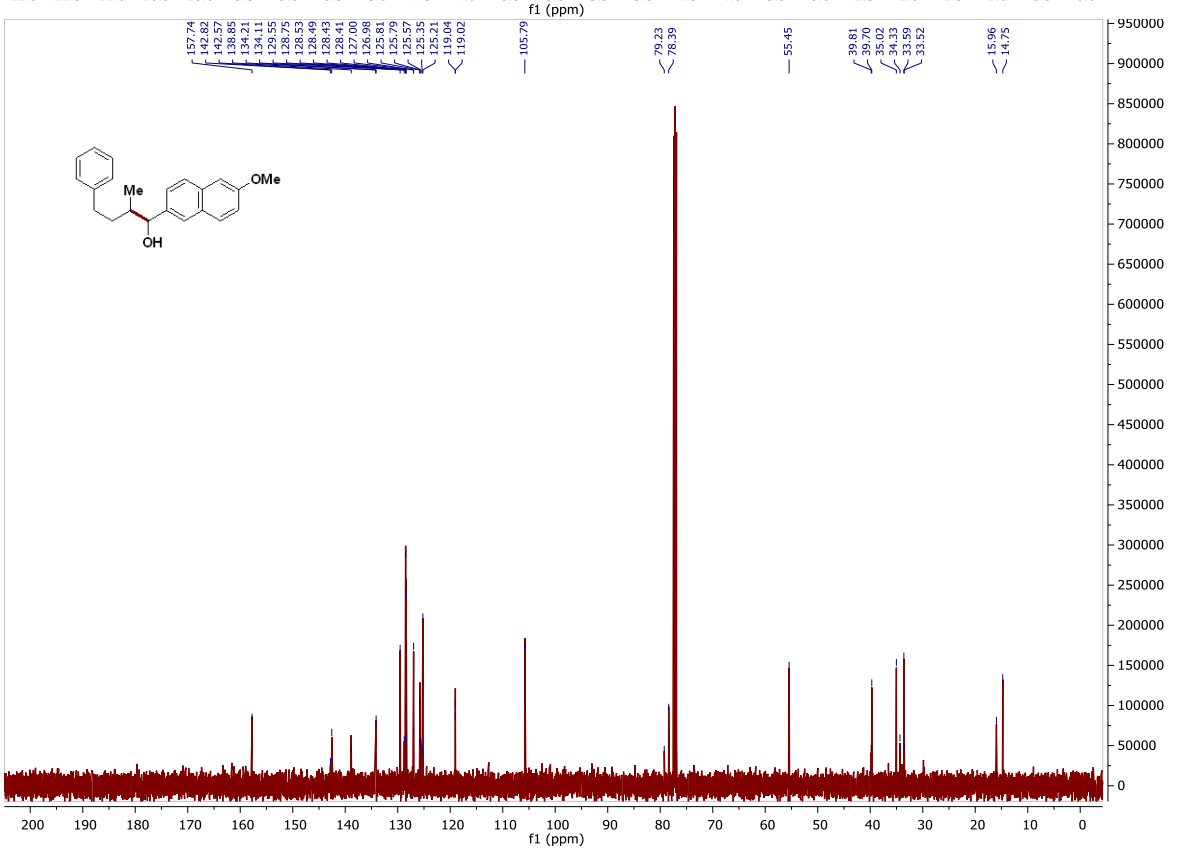
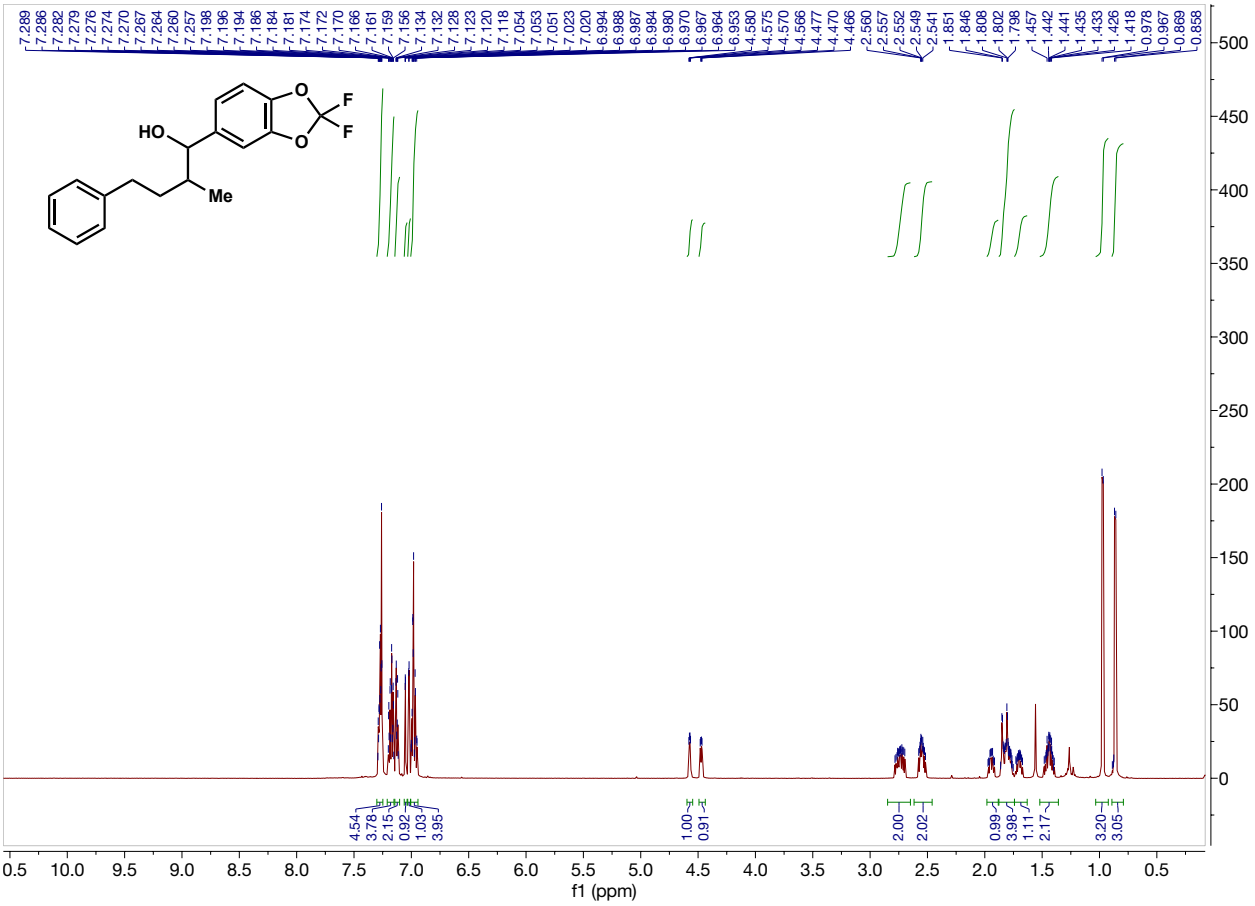
33.41
20.81
15.95
14.50
f1 (ppm)

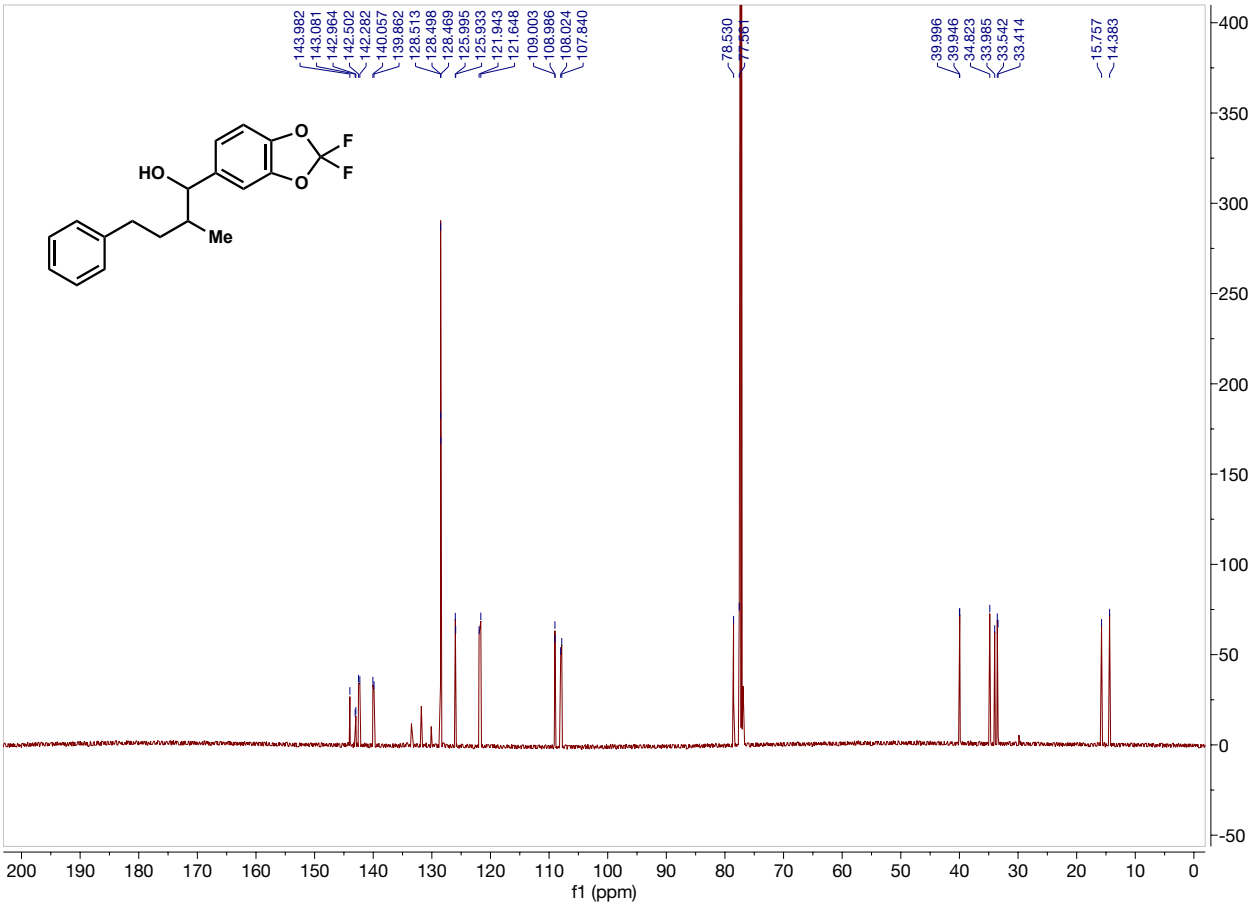

Me
OMe
OMe
OH
4.10
2.43
2.05
4.26
1.00
0.45
5.50
3.09
1.61
1.61
0.55
2.95
1.28
1.75
3.00
1.36
f1 (ppm)

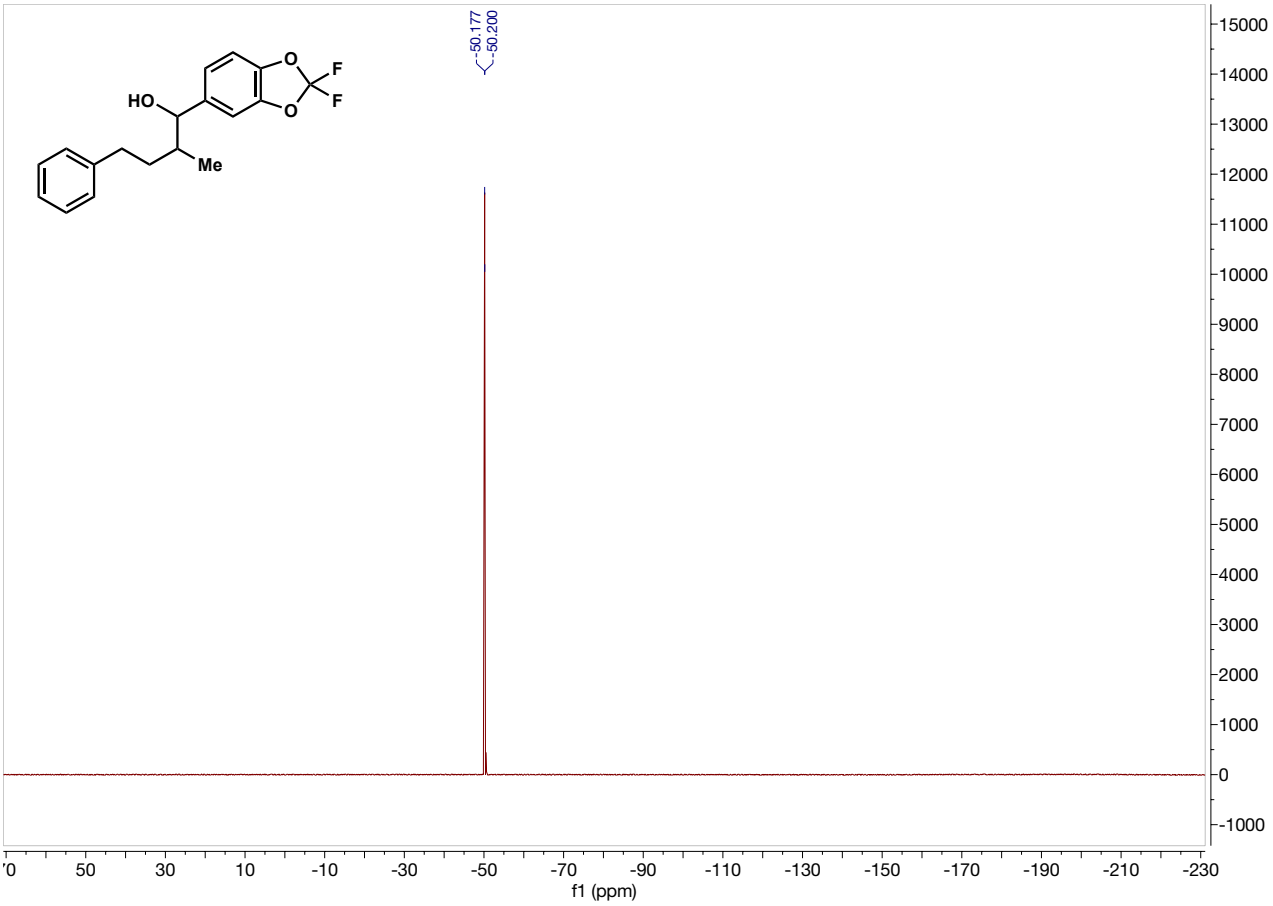

Me
OMe
OMe
OH
149.06
148.42
142.53
136.41
128.51
128.44
128.40
125.82
118.95
110.86
109.44
78.95
78.26
56.06
55.98
39.93
39.67
34.84
34.38
33.49
33.45
15.94
14.97
f1 (ppm)

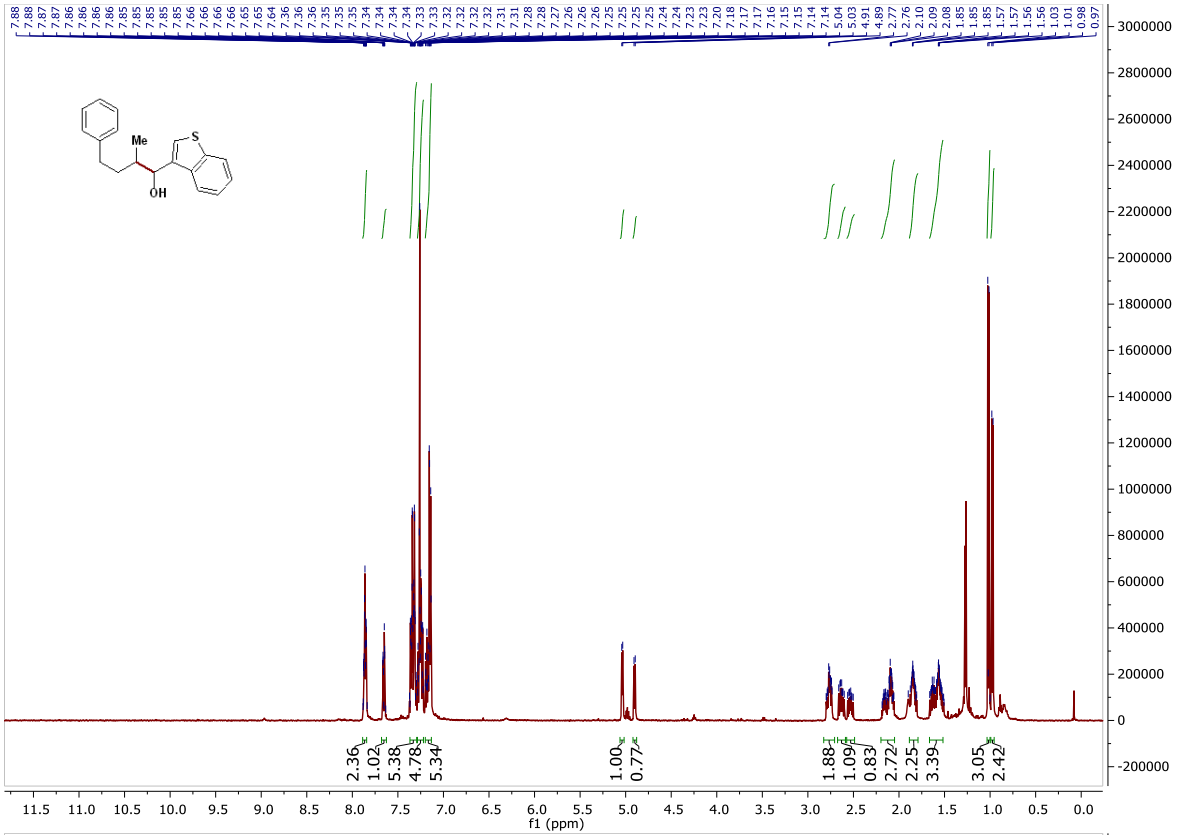

Me
OMe
OH
4.23
0.51
1.11
0.76
2.48
7.20
1.00
0.40
4.12
1.53
1.54
3.72
1.29
2.73
3.00
1.23
f1 (ppm)

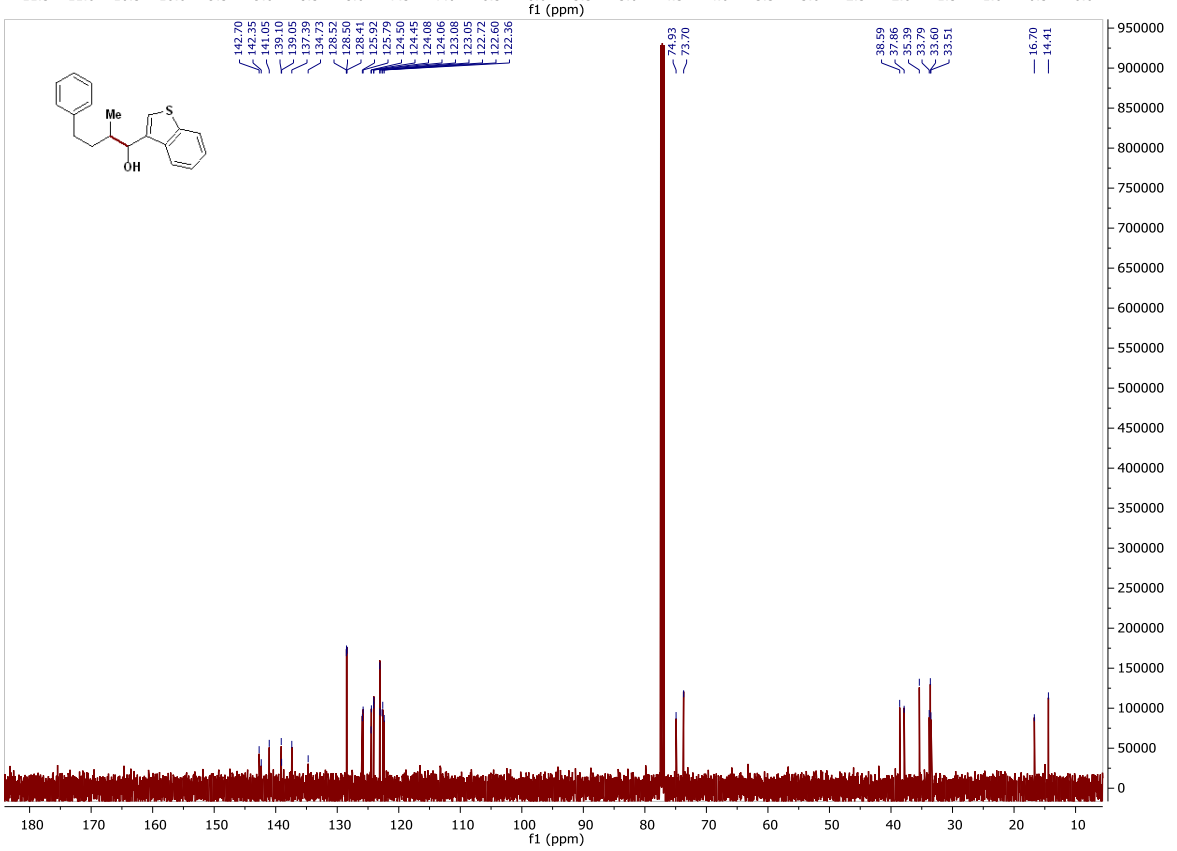

Me
OMe
OH
157.74
142.82
142.57
138.85
134.21
134.11
129.55
128.75
128.53
128.49
128.43
128.41
127.00
126.98
125.81
125.79
125.57
125.35
125.21
119.04
119.02
105.79
79.23
78.39
55.45
39.81
39.70
35.02
34.33
33.59
33.52
15.96
14.75
f1 (ppm)

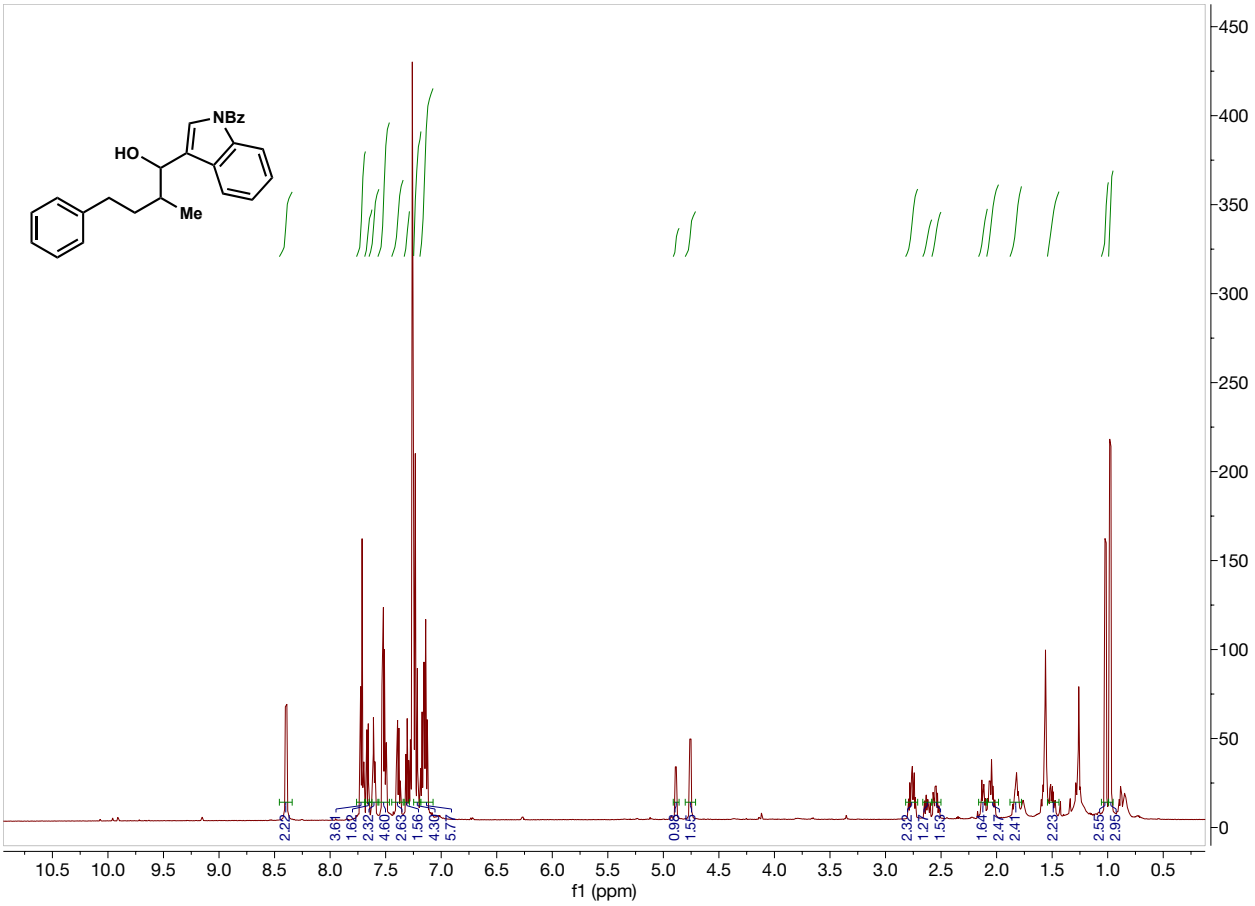

HO
F
F
O
O
O
Me
f1 (ppm)

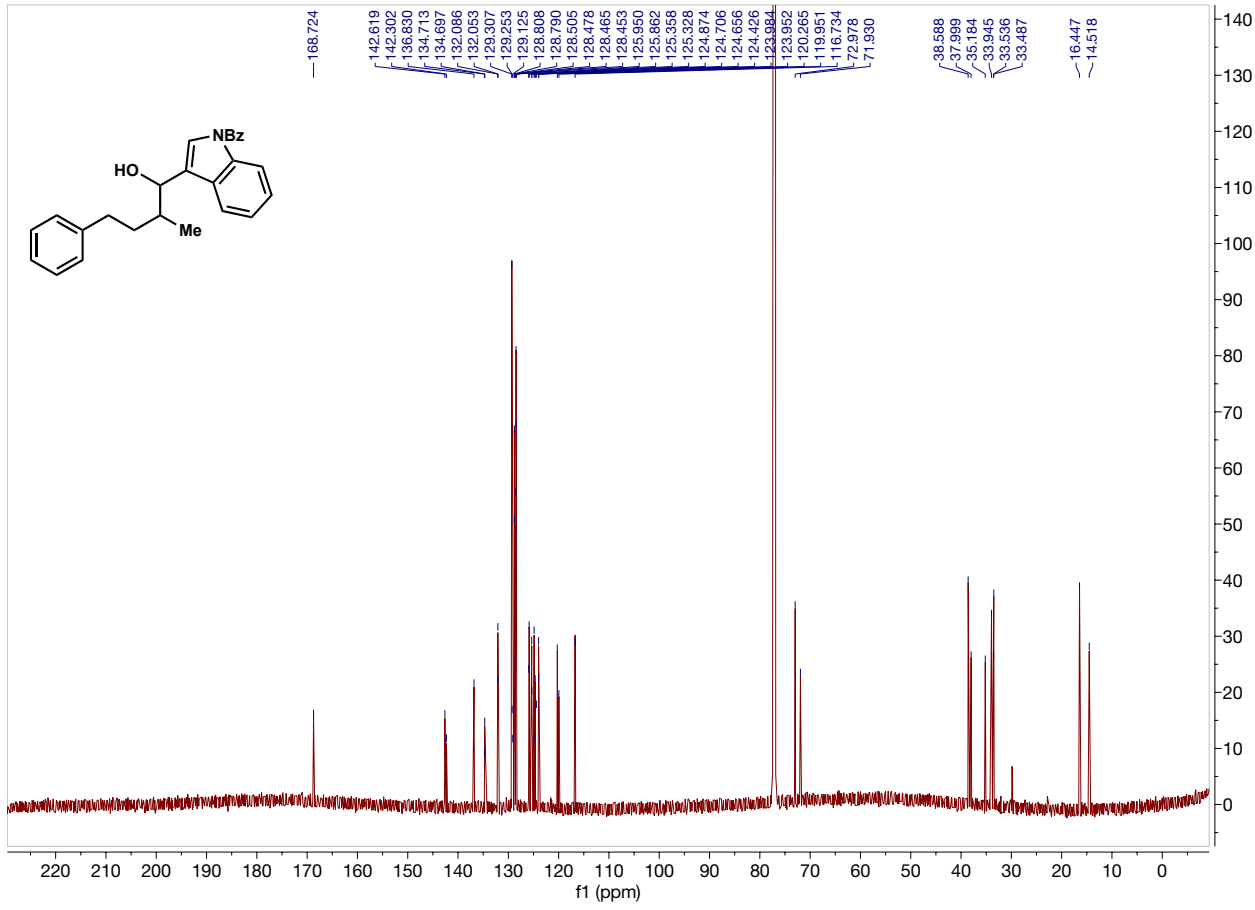

HO
F
F
O
O
O
Me
f1 (ppm)

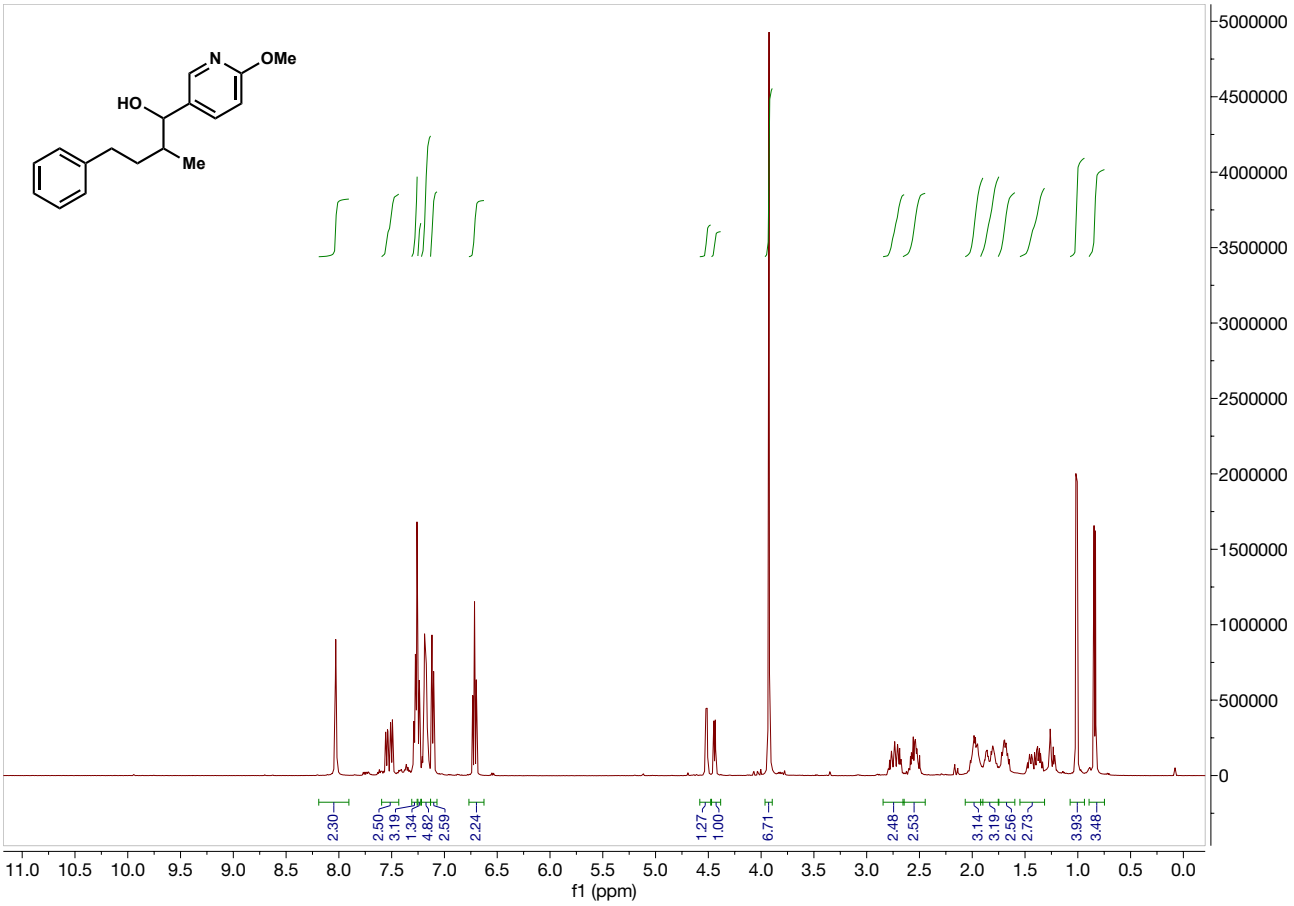

-50.177
-50.200
HO
O
F
F
O
Me
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
'0
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

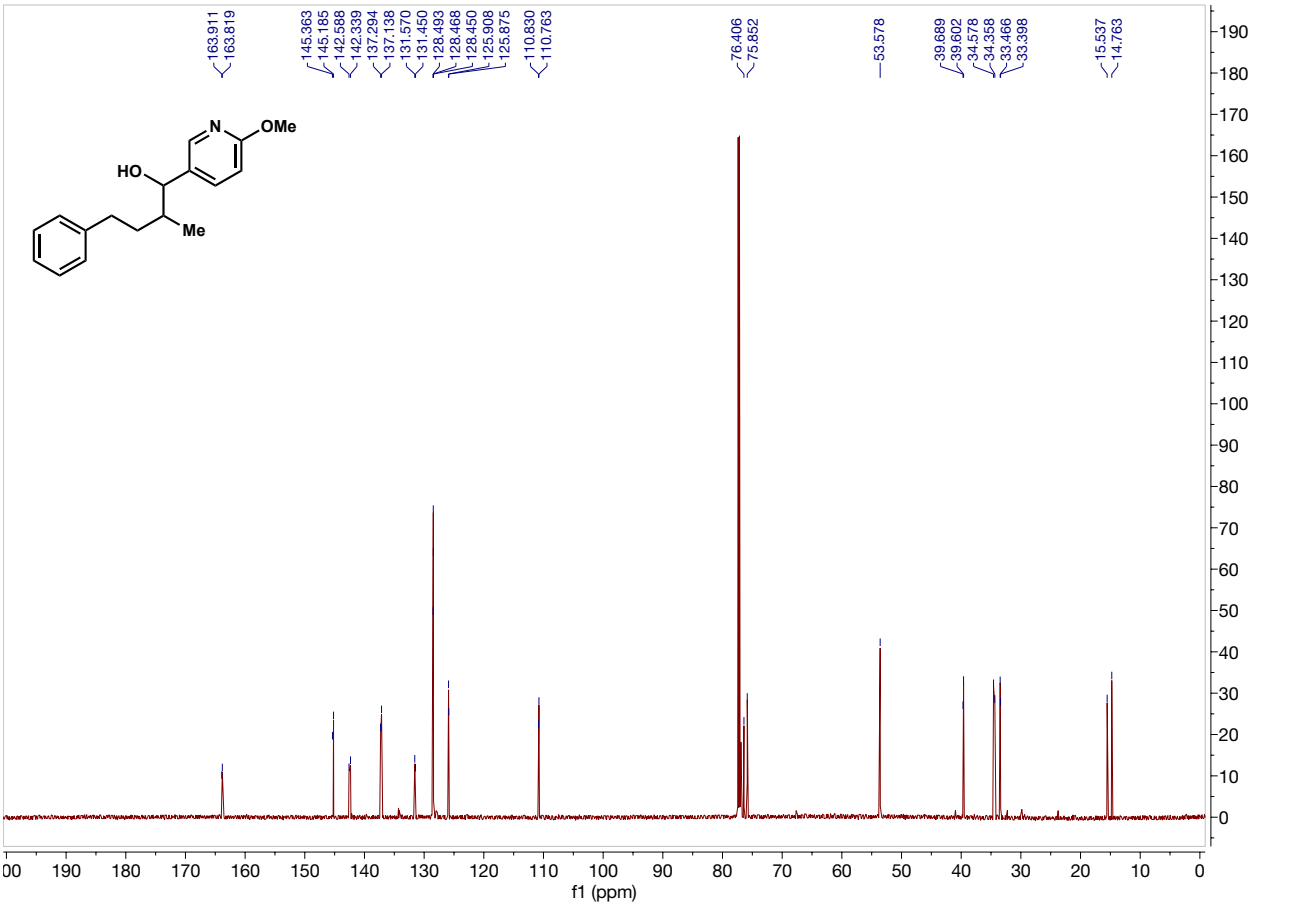

Me
S
OH
2.36
1.02
5.38
4.78
5.34
1.00
0.77
1.88
1.09
0.83
2.72
2.25
3.39
3.05
2.42
f1 (ppm)

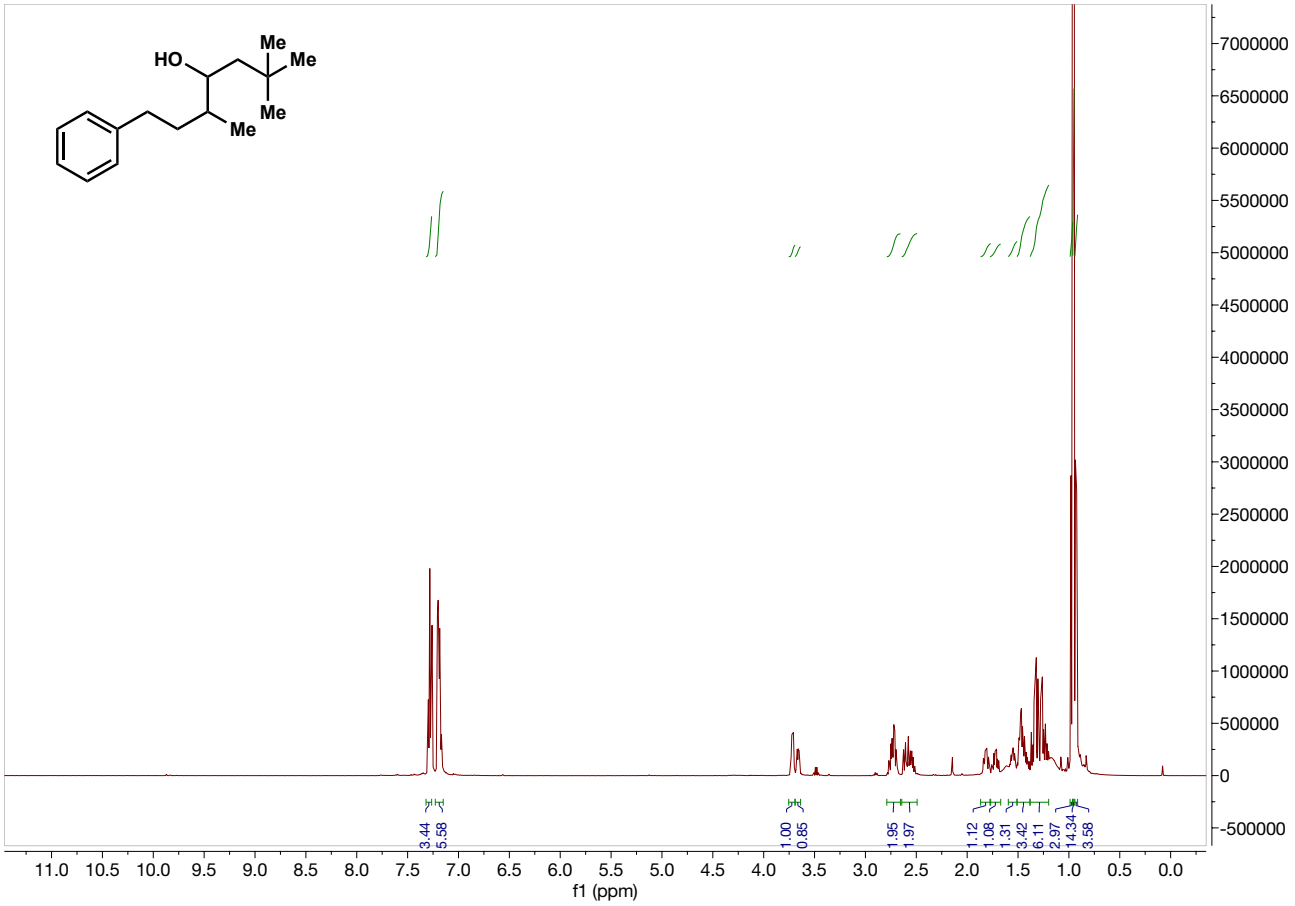

Me
S
OH
142.70
142.35
141.05
139.10
139.05
137.39
134.73
128.52
128.50
128.41
125.92
125.79
124.50
124.45
124.08
124.06
123.08
123.05
122.72
122.60
122.36
74.93
73.70
38.59
37.86
35.39
33.79
33.60
33.51
16.70
14.41
f1 (ppm)

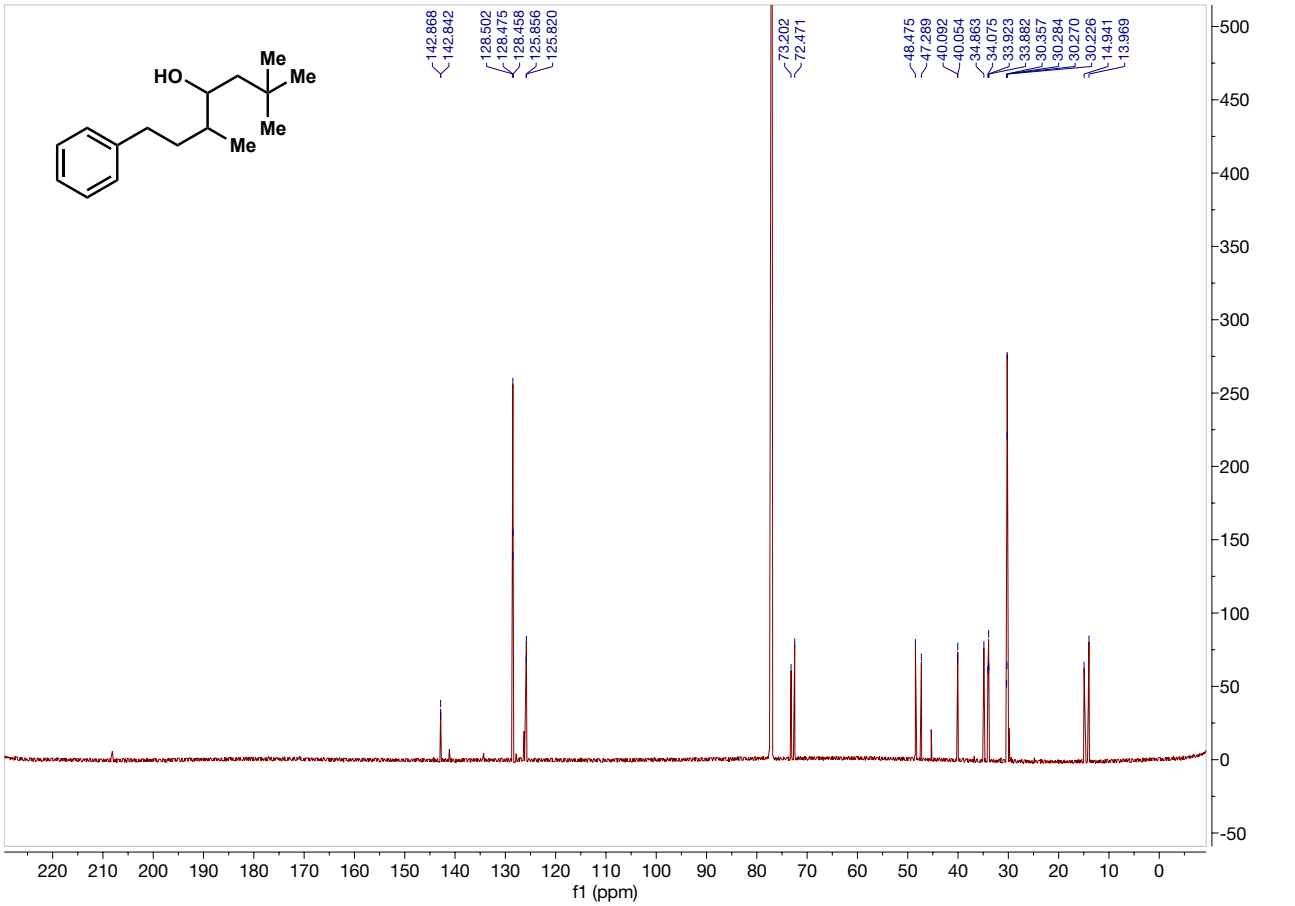

NBz
HO
Me
f1 (ppm)

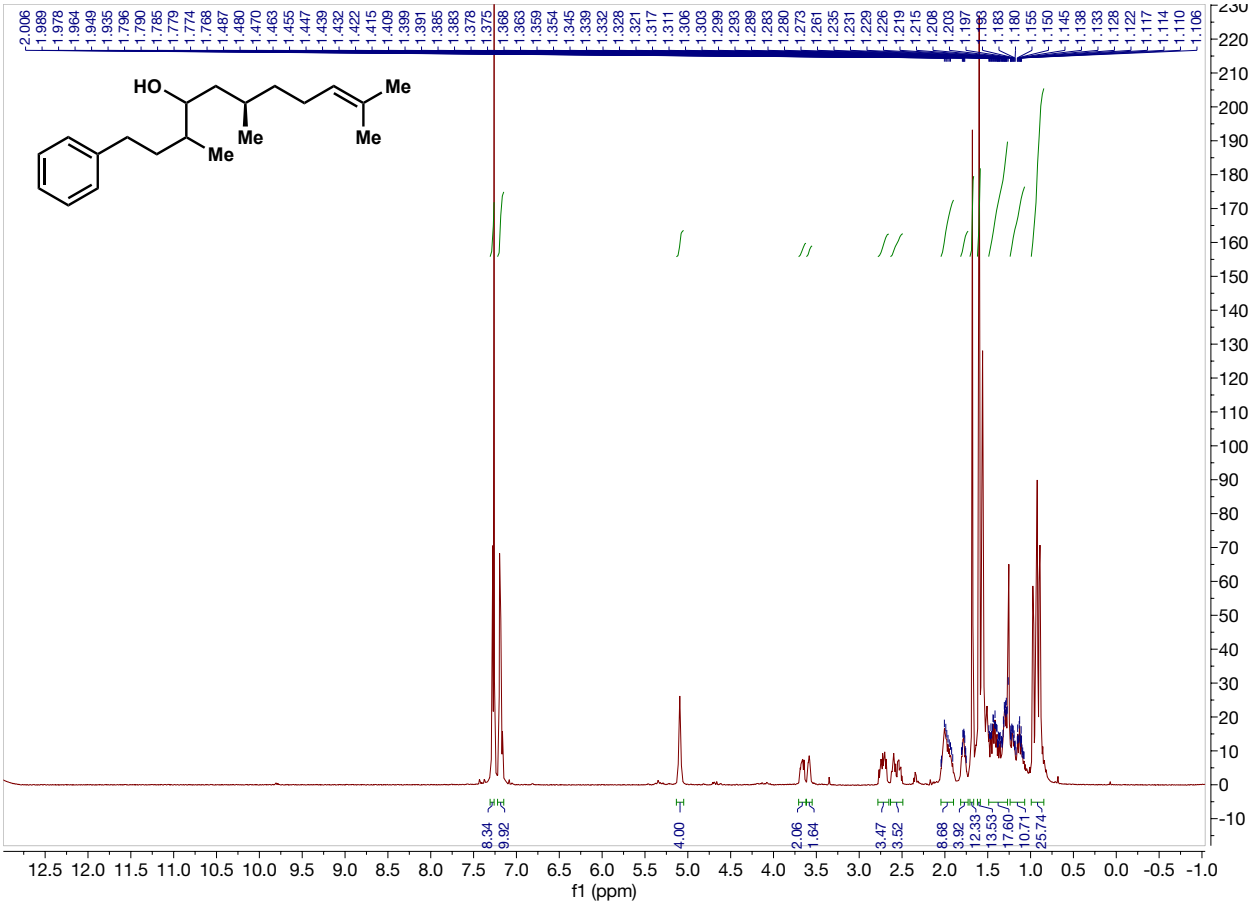

NBz
HO
Me
f1 (ppm)

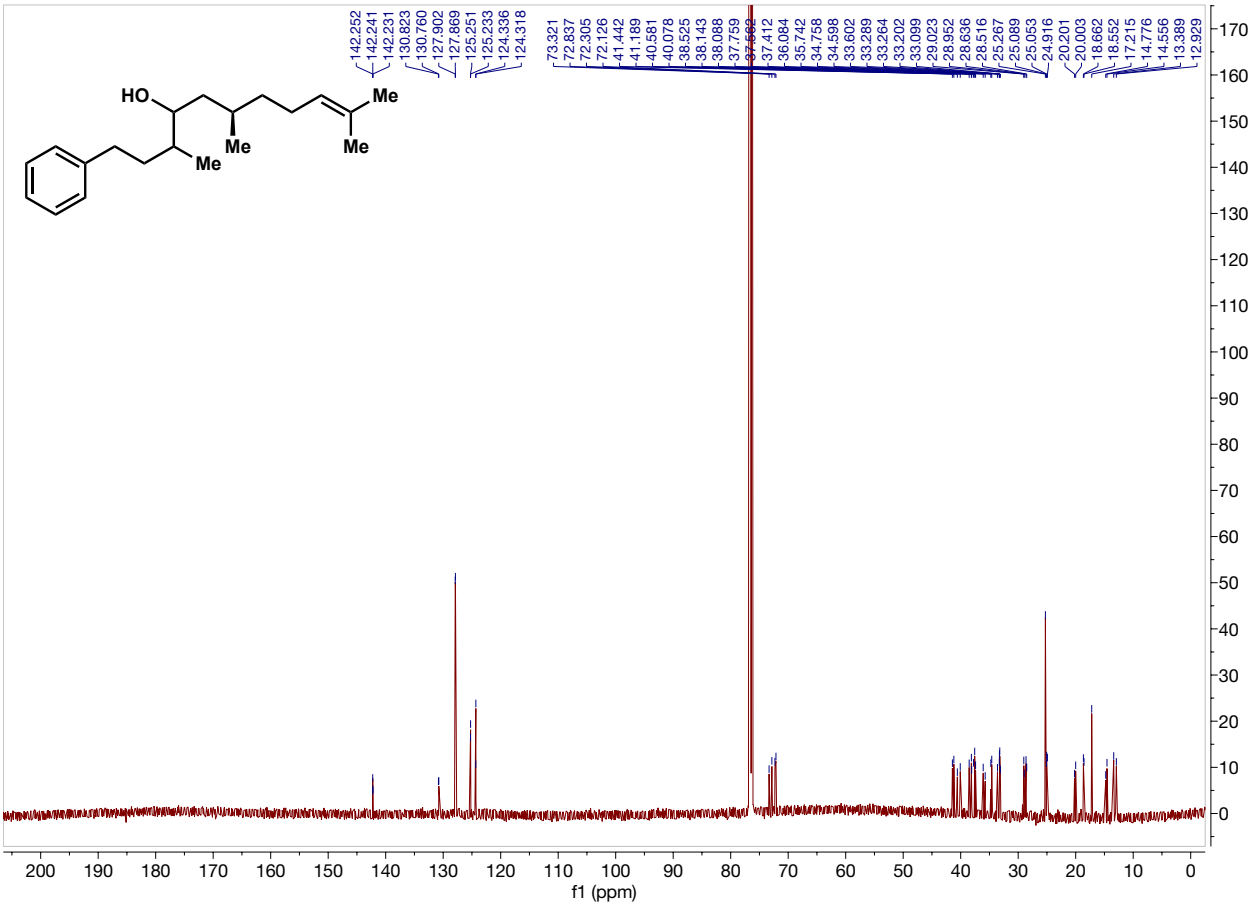

N
OMe
HO
Me
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
2.30
2.50
3.19
1.34
4.82
2.59
2.24
1.27
1.00
6.71
2.48
2.53
3.14
3.19
2.56
2.73
3.93
3.48
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

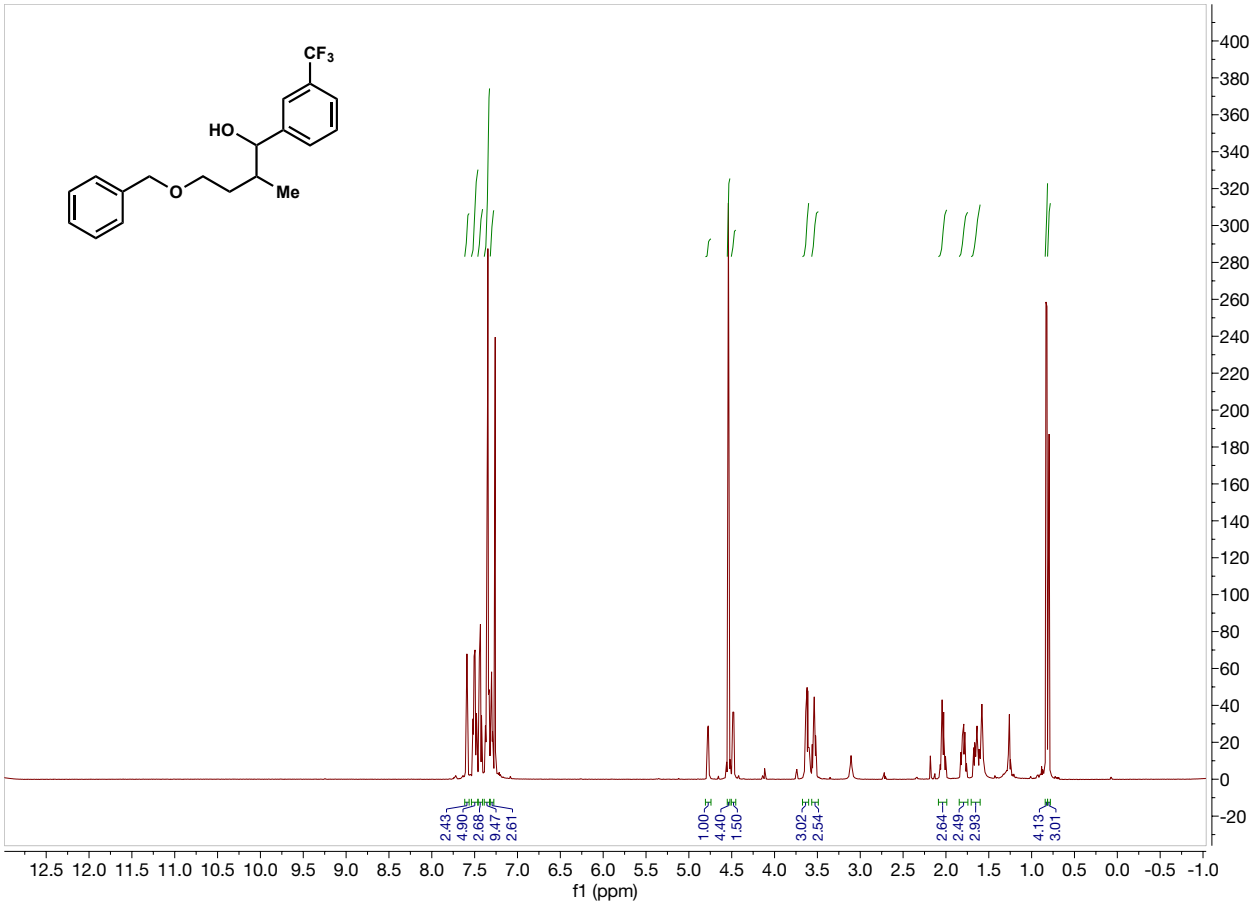

163.911
163.819
145.363
145.185
142.588
142.339
137.294
137.138
131.570
131.450
128.493
128.468
128.450
125.908
125.875
110.830
110.763
76.406
75.852
53.578
39.689
39.602
34.578
34.358
33.466
33.398
15.537
14.763
N
OMe
HO
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

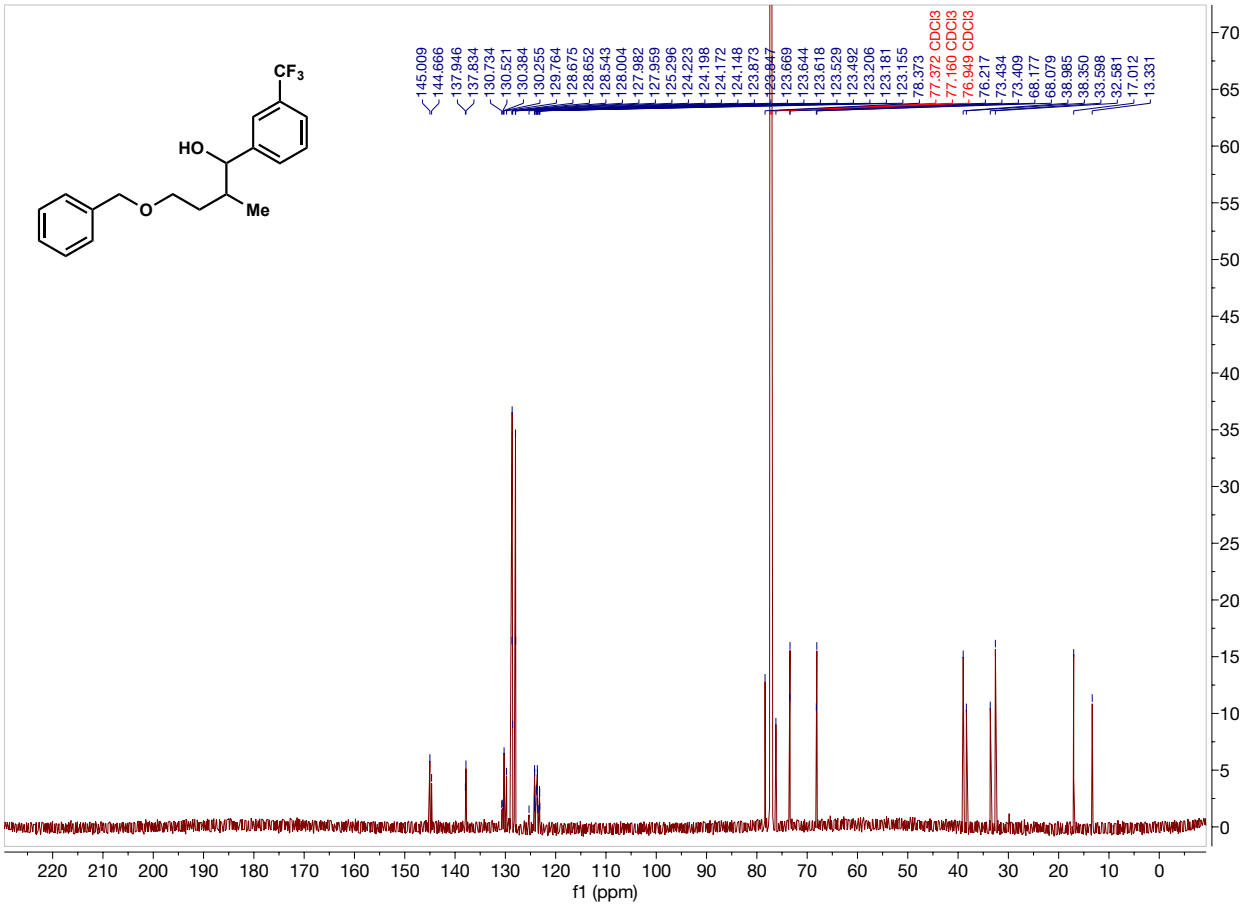

HO
Me
Me
Me
Me
3.44
5.58
1.00
0.85
1.95
1.97
1.12
1.08
1.31
3.42
6.11
2.97
14.34
3.58
f1 (ppm)

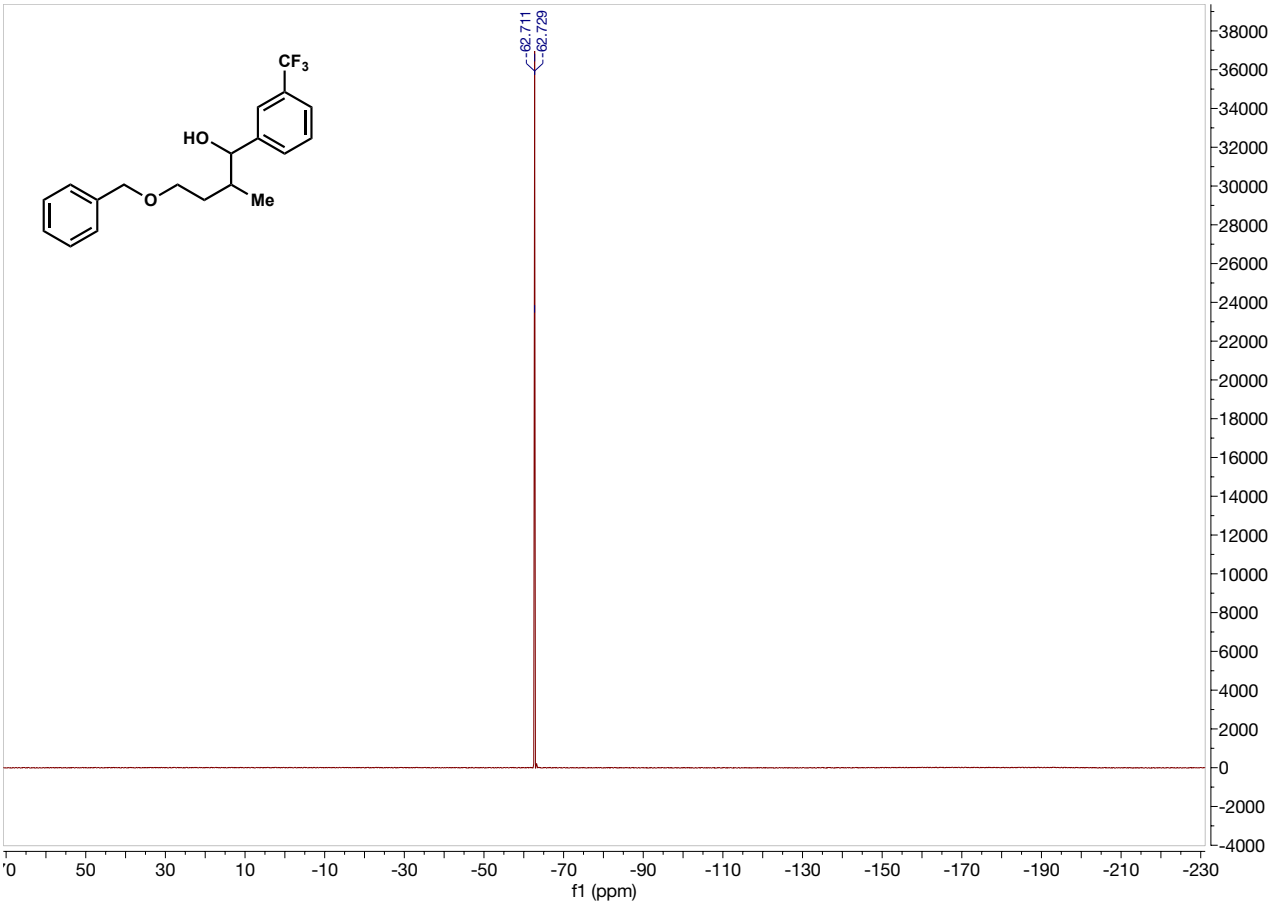

HO
Me
Me
Me
Me
142.868
142.842
128.502
128.475
128.458
125.856
125.820
73.202
72.471
48.475
47.289
40.092
40.054
34.863
34.075
33.923
33.882
30.357
30.284
30.270
30.226
14.941
13.969
f1 (ppm)

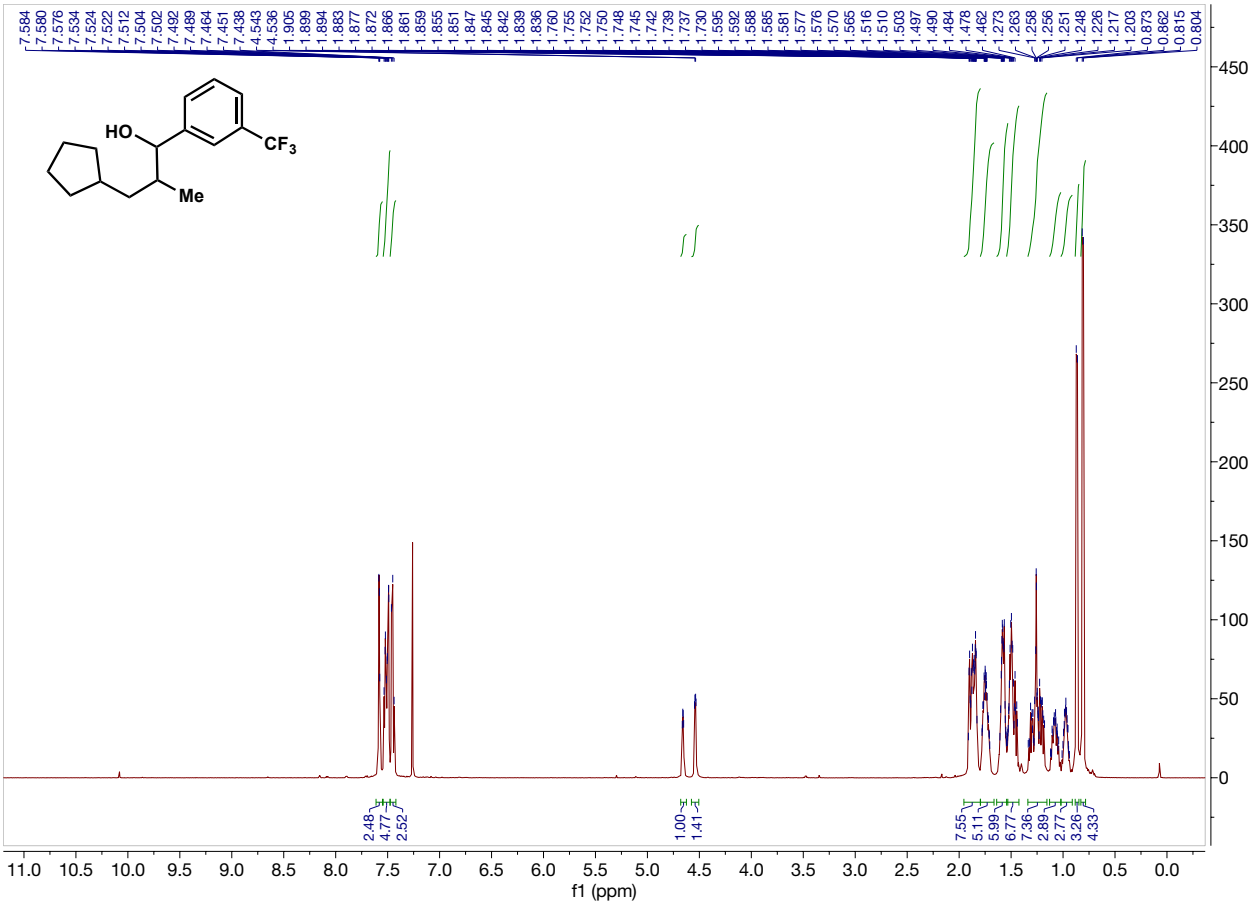

HO
Me
Me
Me
f1 (ppm)

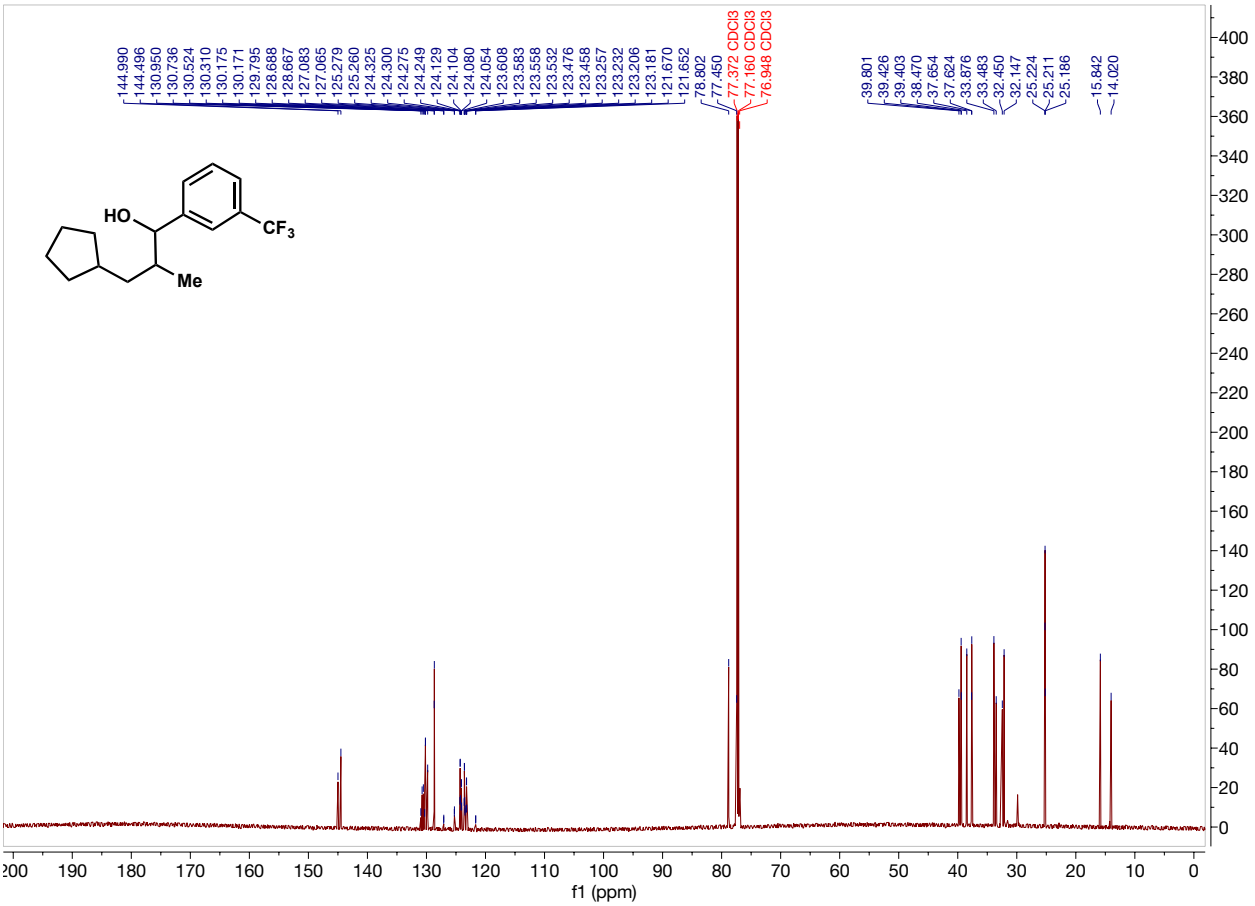

HO
Me
Me
Me
f1 (ppm)

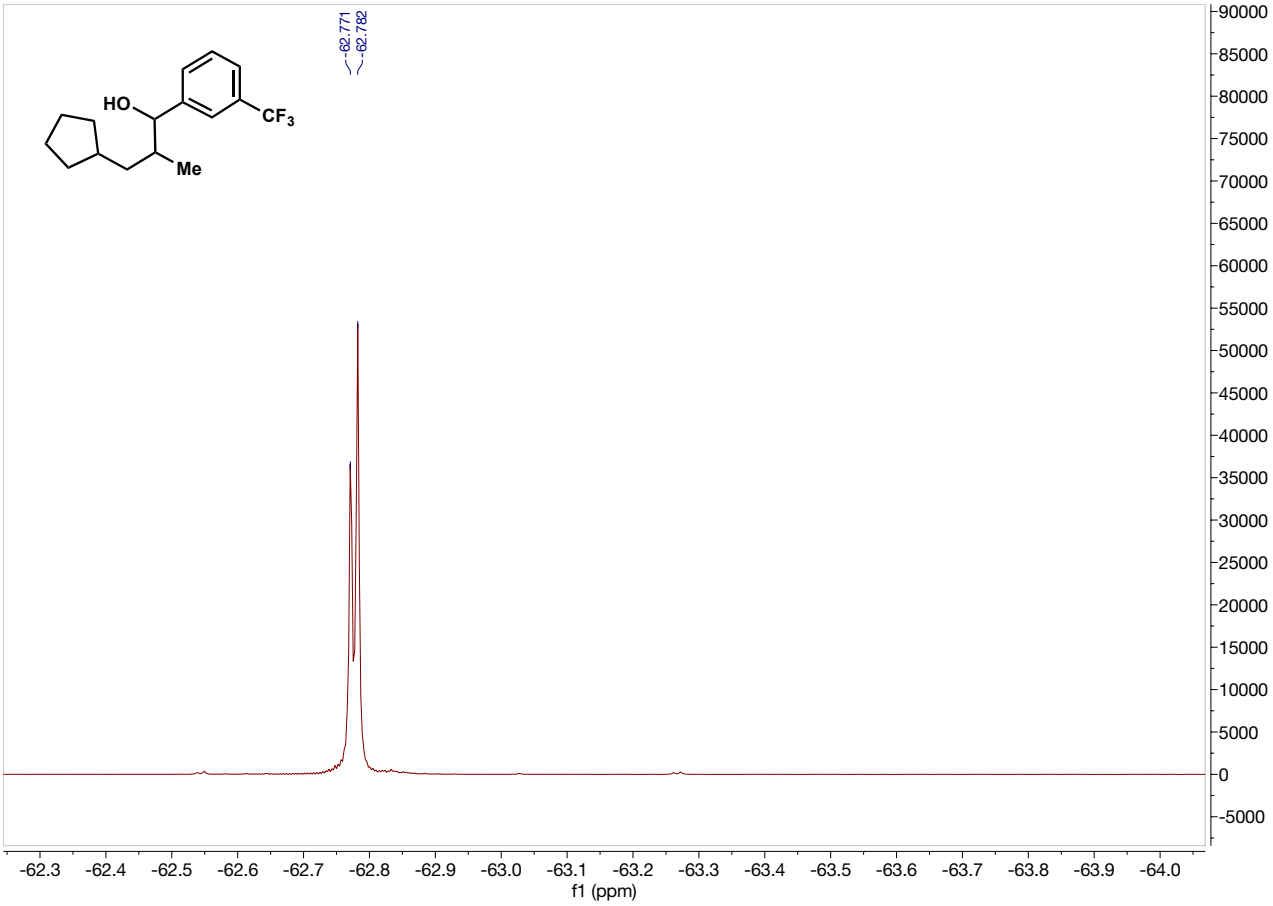

CF3
HO
O
Me
2.43
4.90
2.68
9.47
2.61
1.00
4.40
1.50
3.02
2.54
2.64
2.49
2.93
4.13
3.01
f1 (ppm)

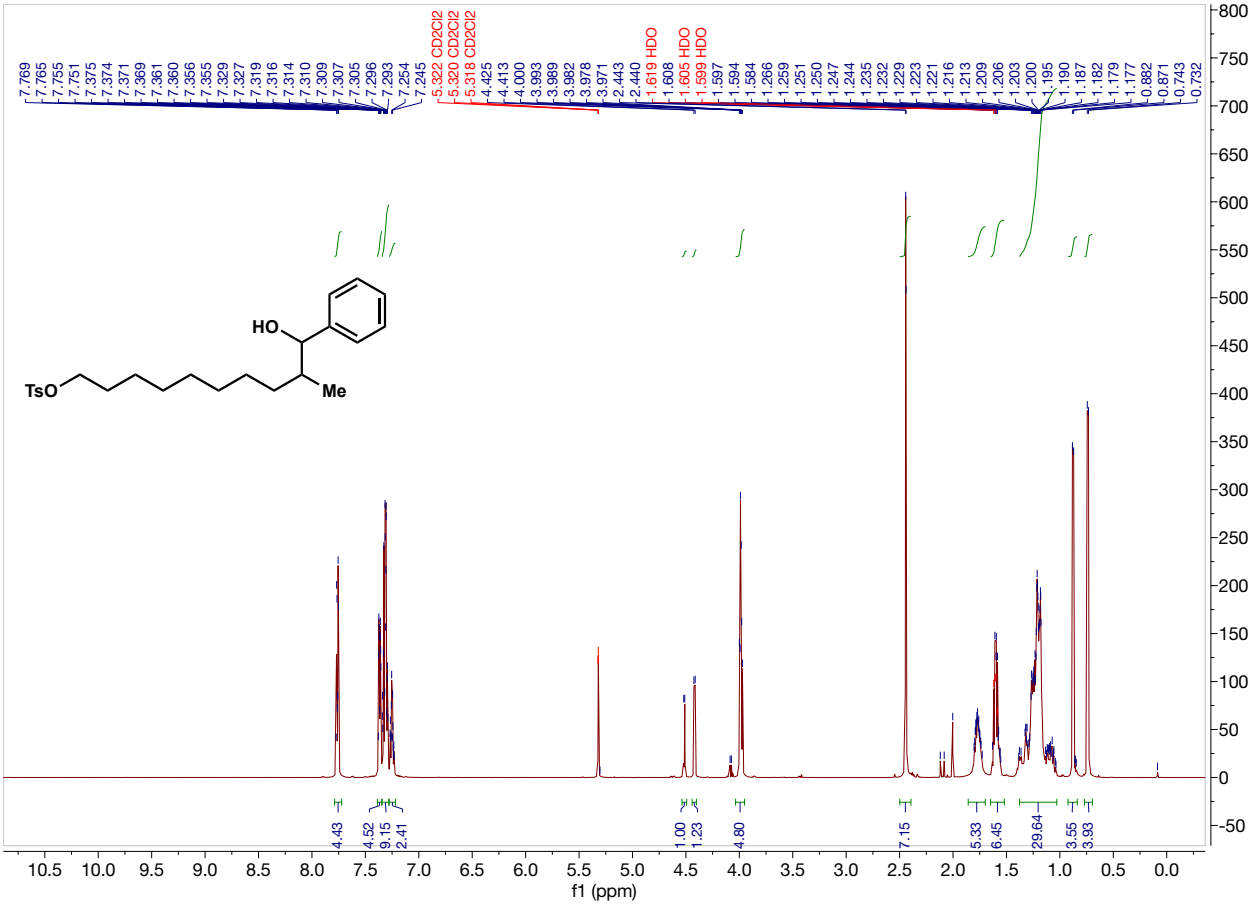

CF3
HO
O
Me
145.009
144.666
137.946
137.834
130.734
130.521
130.384
130.255
129.764
128.675
128.652
128.543
128.004
127.982
127.959
125.296
124.223
124.198
124.172
124.148
123.873
123.847
123.669
123.644
123.618
123.529
123.492
123.206
123.181
123.155
78.373
77.372 CDCl3
77.160 CDCl3
76.949 CDCl3
76.217
73.434
73.409
68.177
68.079
38.985
38.350
33.598
32.581
17.012
13.331
f1 (ppm)

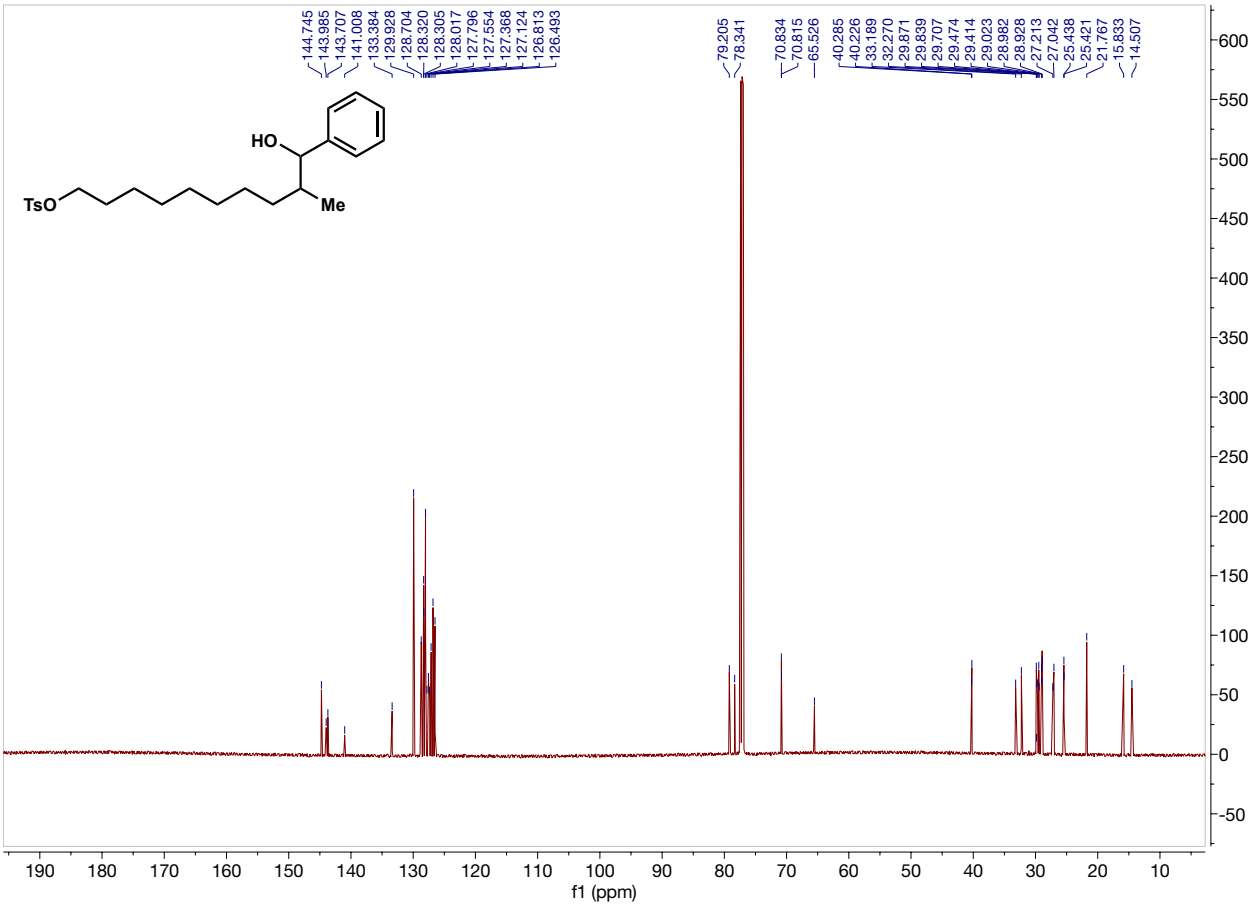

62.711
62.729
CF3
HO
O
Me
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
'0
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

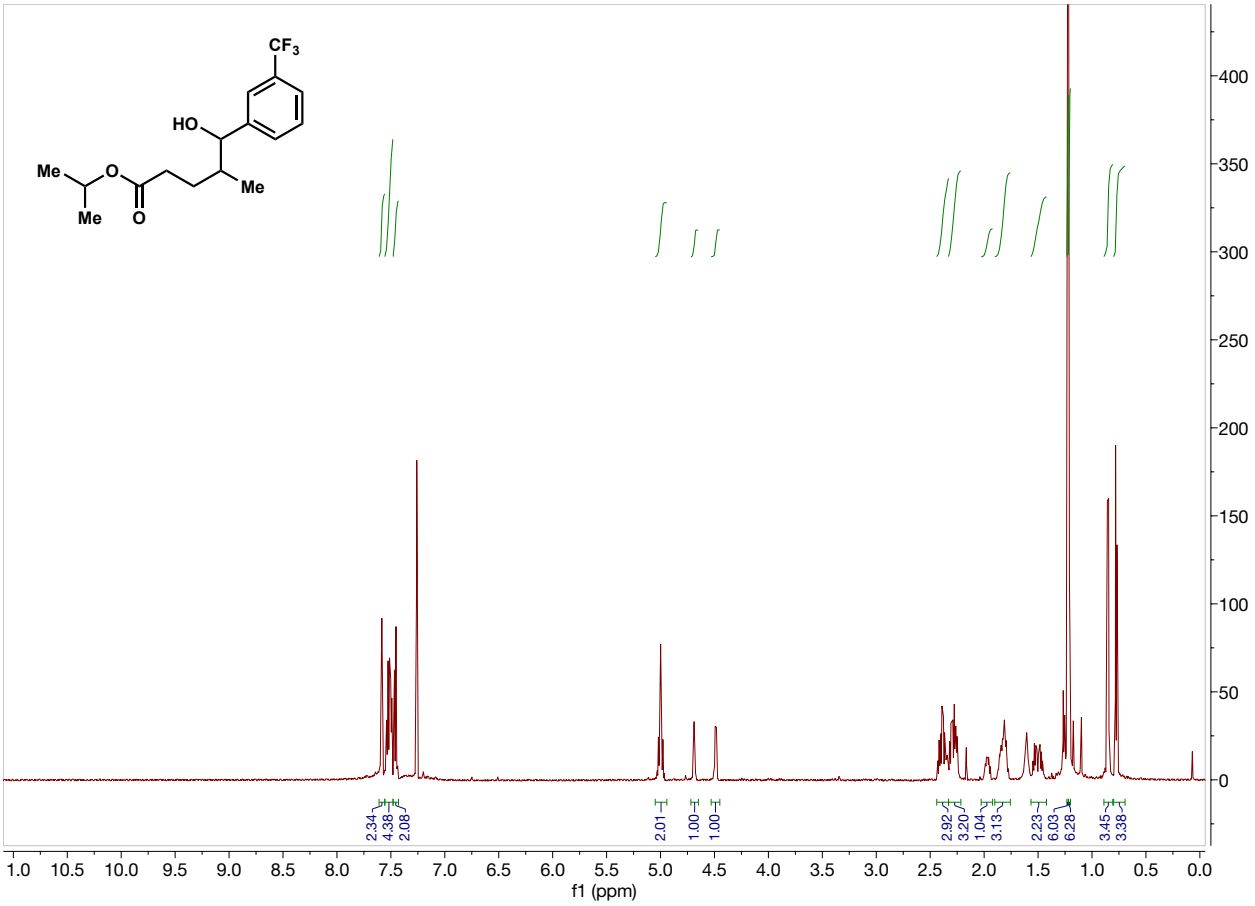

HO
CF3
Me
f1 (ppm)

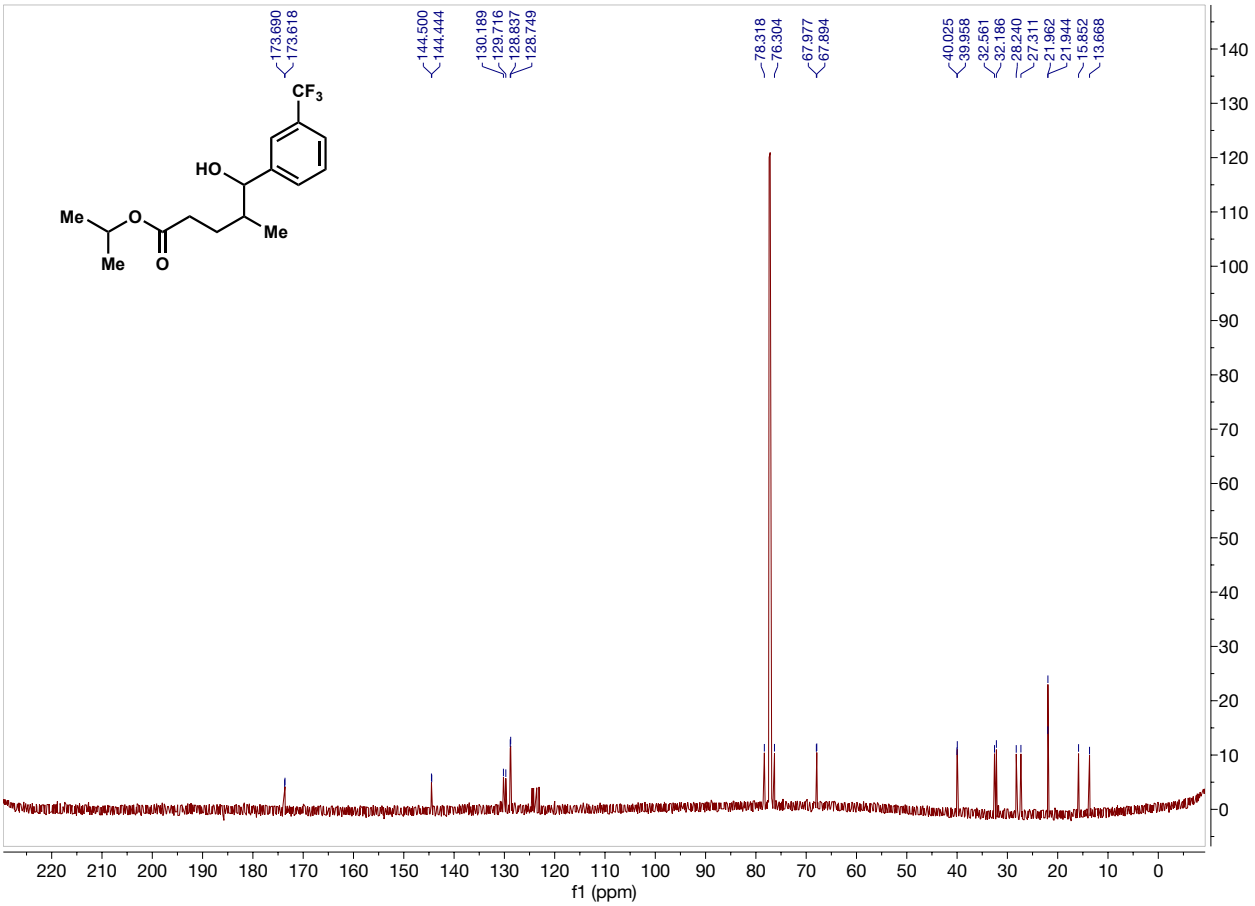

HO
CF3
Me
77.372 CDCl3
77.160 CDCl3
76.948 CDCl3
f1 (ppm)

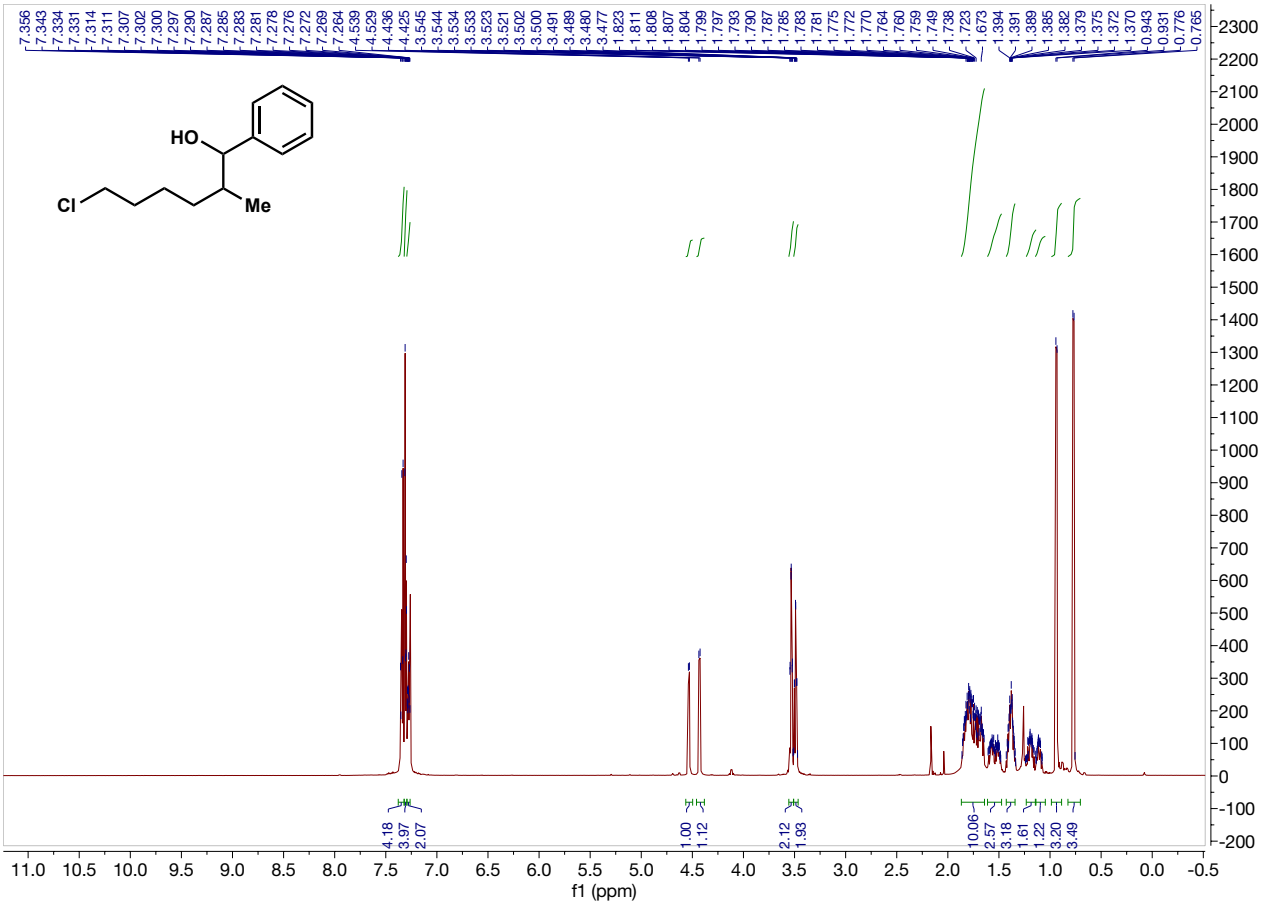

-62.771
-62.782
HO
CF3
Me
90000
85000
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
-62.3
-62.4
-62.5
-62.6
-62.7
-62.8
-62.9
-63.0
-63.1
-63.2
-63.3
-63.4
-63.5
-63.6
-63.7
-63.8
-63.9
-64.0
f1 (ppm)

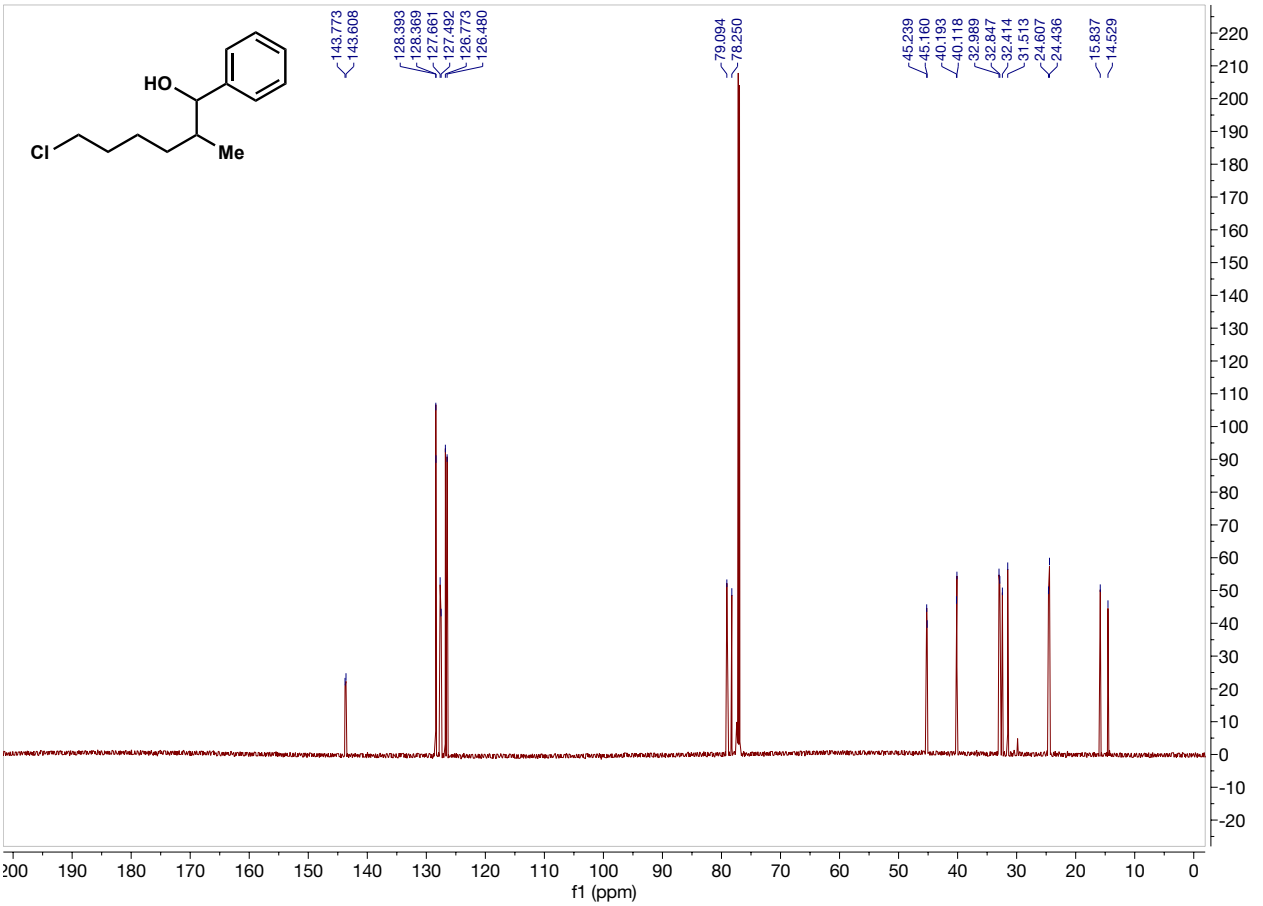

HO
TsO
Me
f1 (ppm)

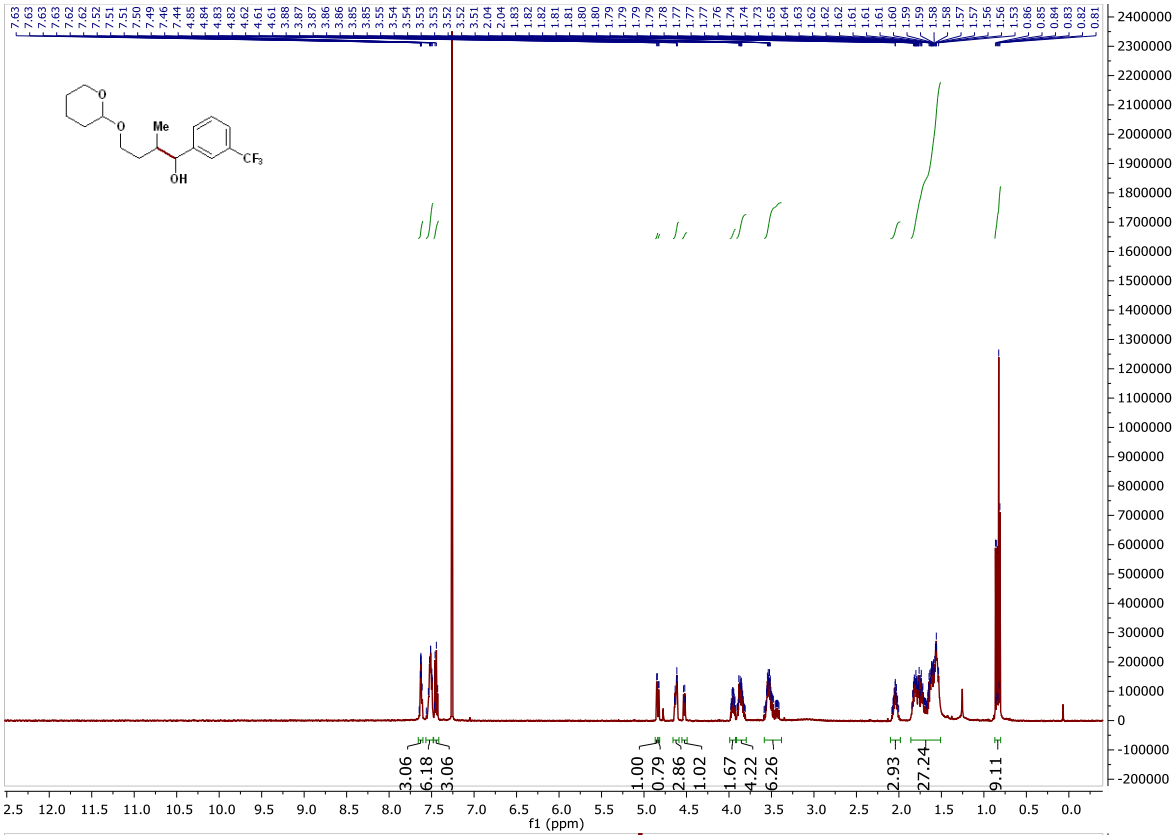

HO
TsO
Me
f1 (ppm)

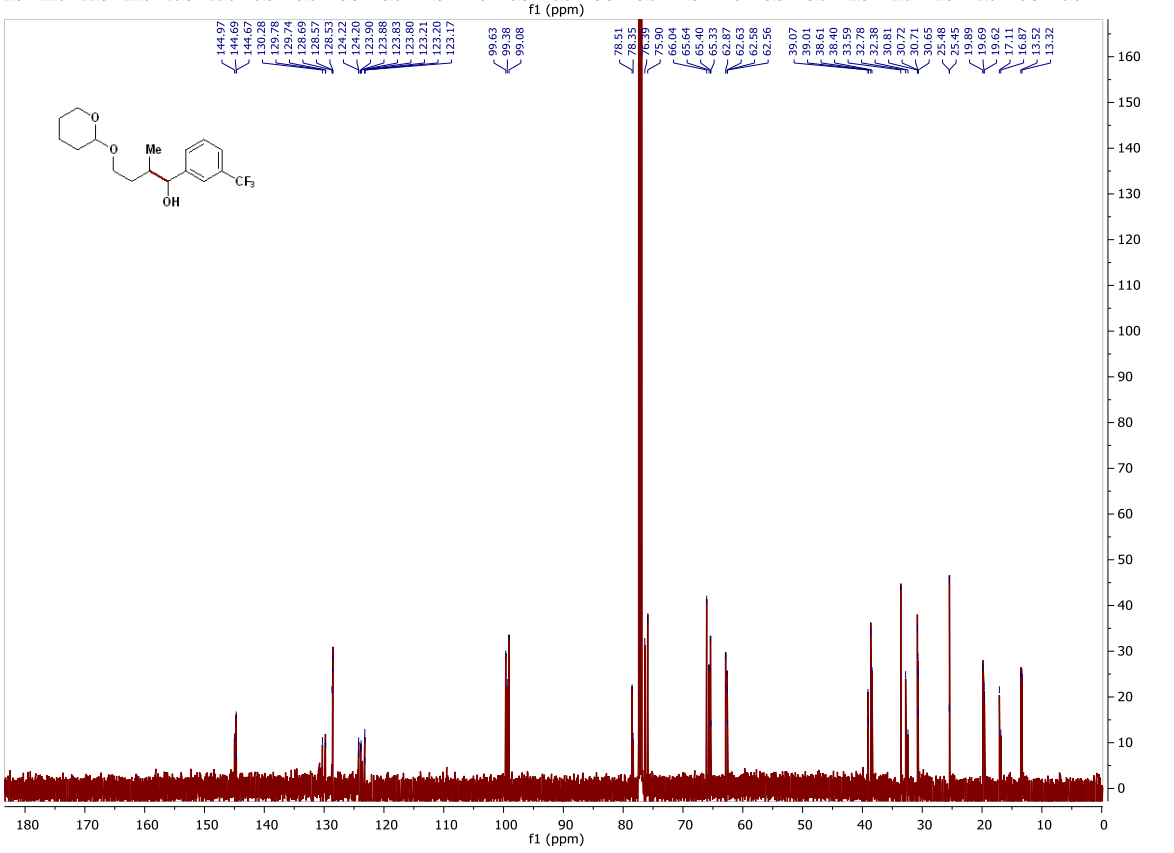

CF3
HO
Me
O
Me
Me
O
2.34
4.38
2.08
2.01
1.00
1.00
2.92
3.20
1.04
3.13
2.23
6.03
6.28
3.45
3.38
f1 (ppm)

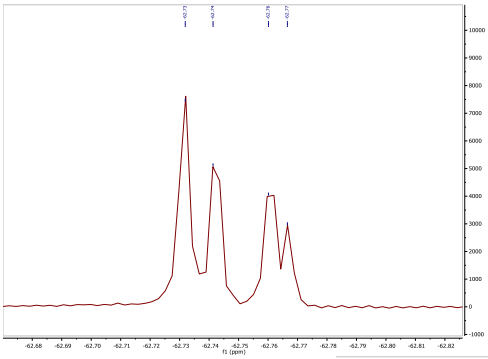

173.690
173.618
144.500
144.444
130.189
129.716
128.837
128.749
78.318
76.304
67.977
67.894
40.025
39.958
32.561
32.186
28.240
27.311
21.962
21.944
15.852
13.668
CF3
HO
Me
O
Me
Me
O
f1 (ppm)

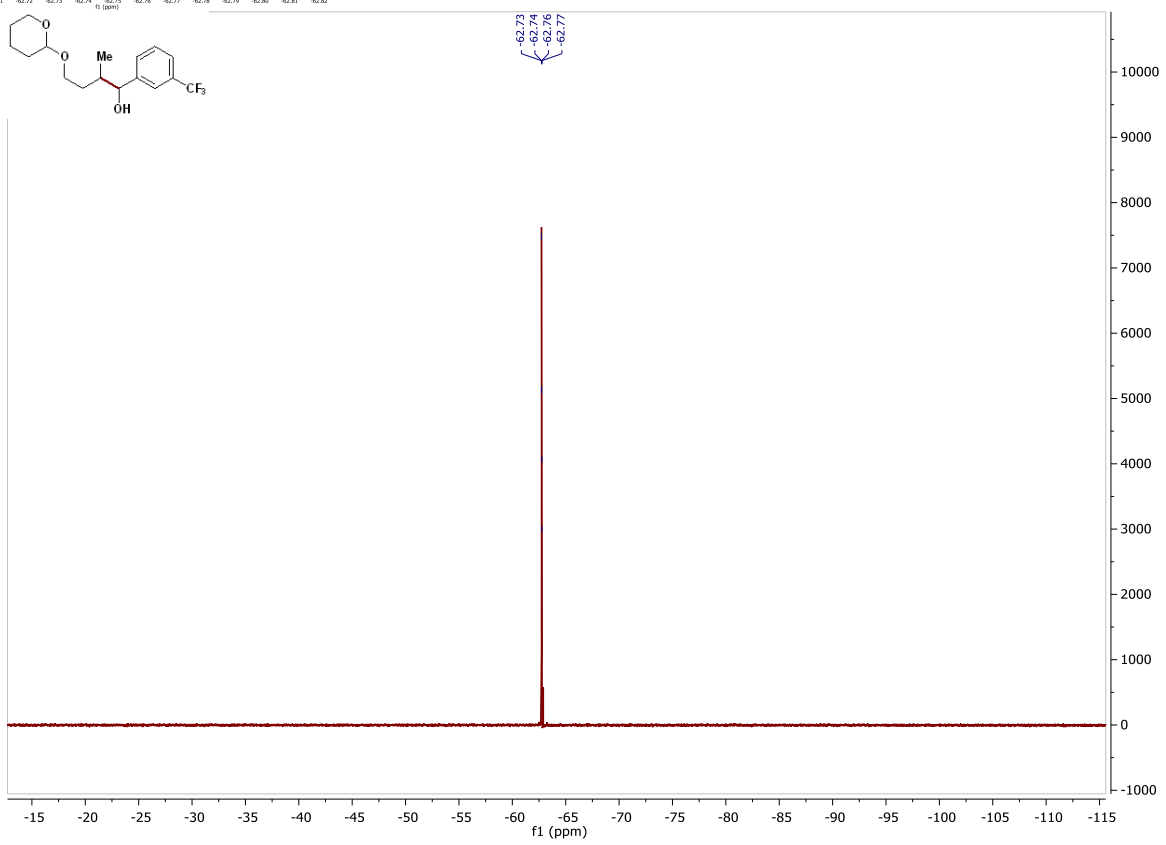

HO
Cl
Me
f1 (ppm)

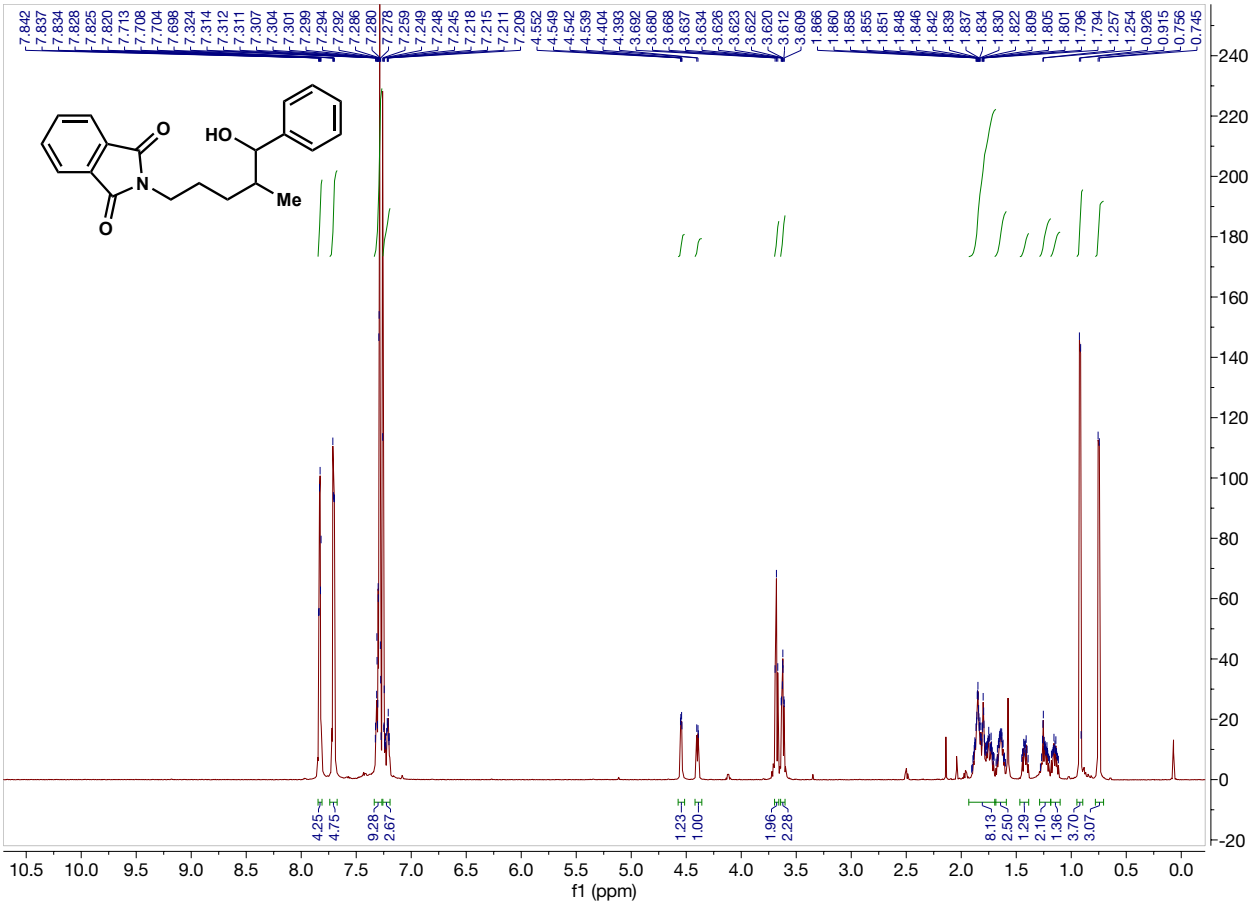

HO
Cl
Me
f1 (ppm)

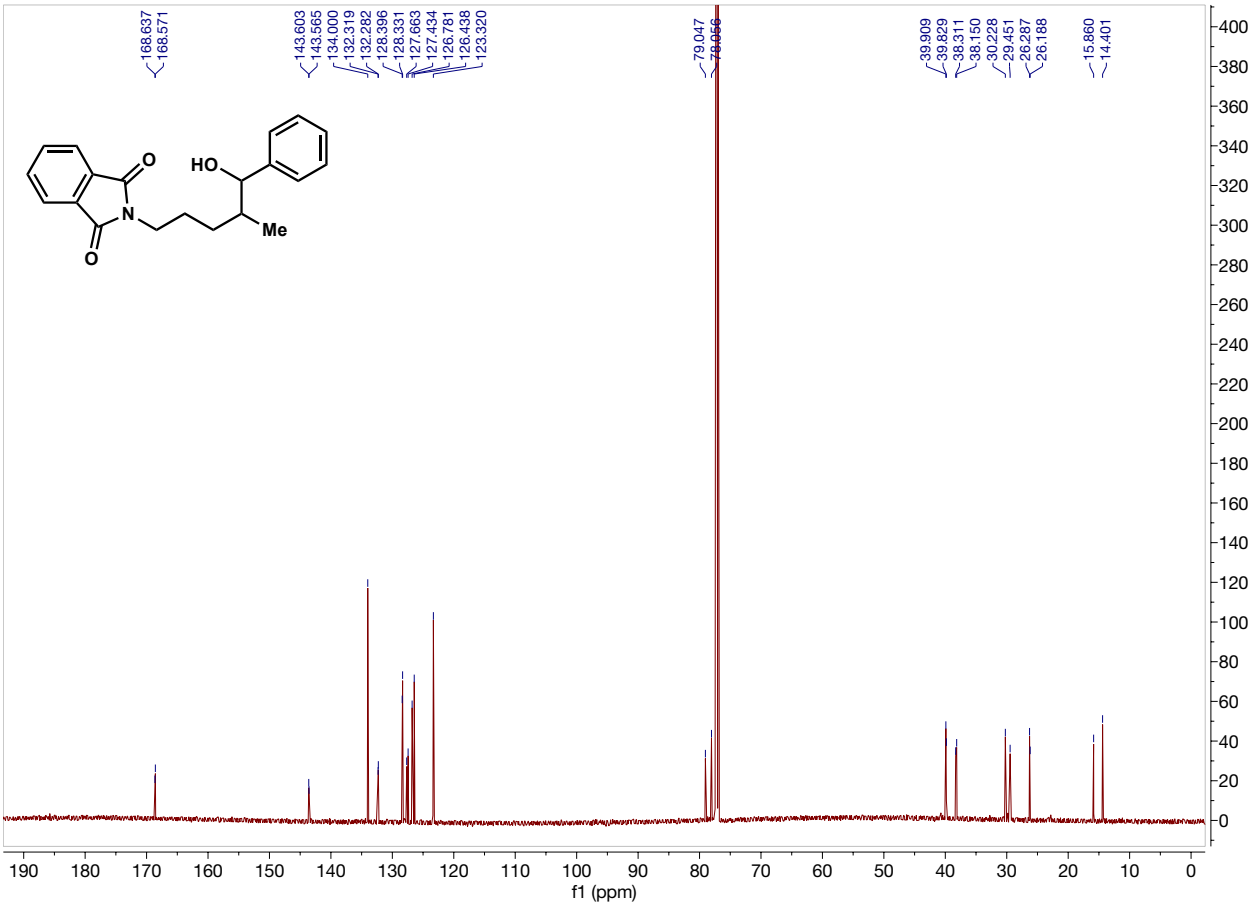

Me
CF3
OH
3.06
6.18
3.06
1.00
0.79
2.86
1.02
1.67
4.22
6.26
2.93
27.24
9.11
f1 (ppm)

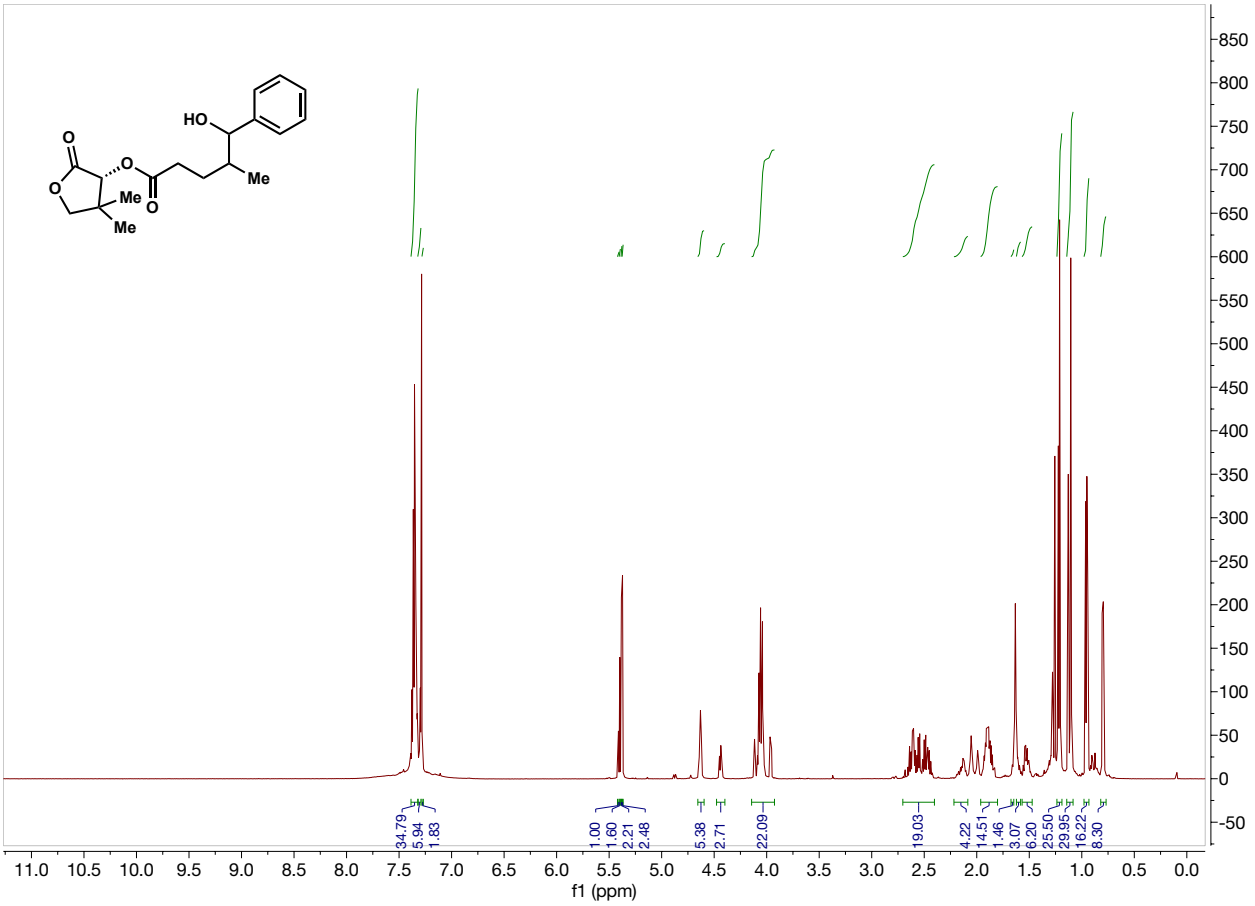

Me
CF3
OH
f1 (ppm)

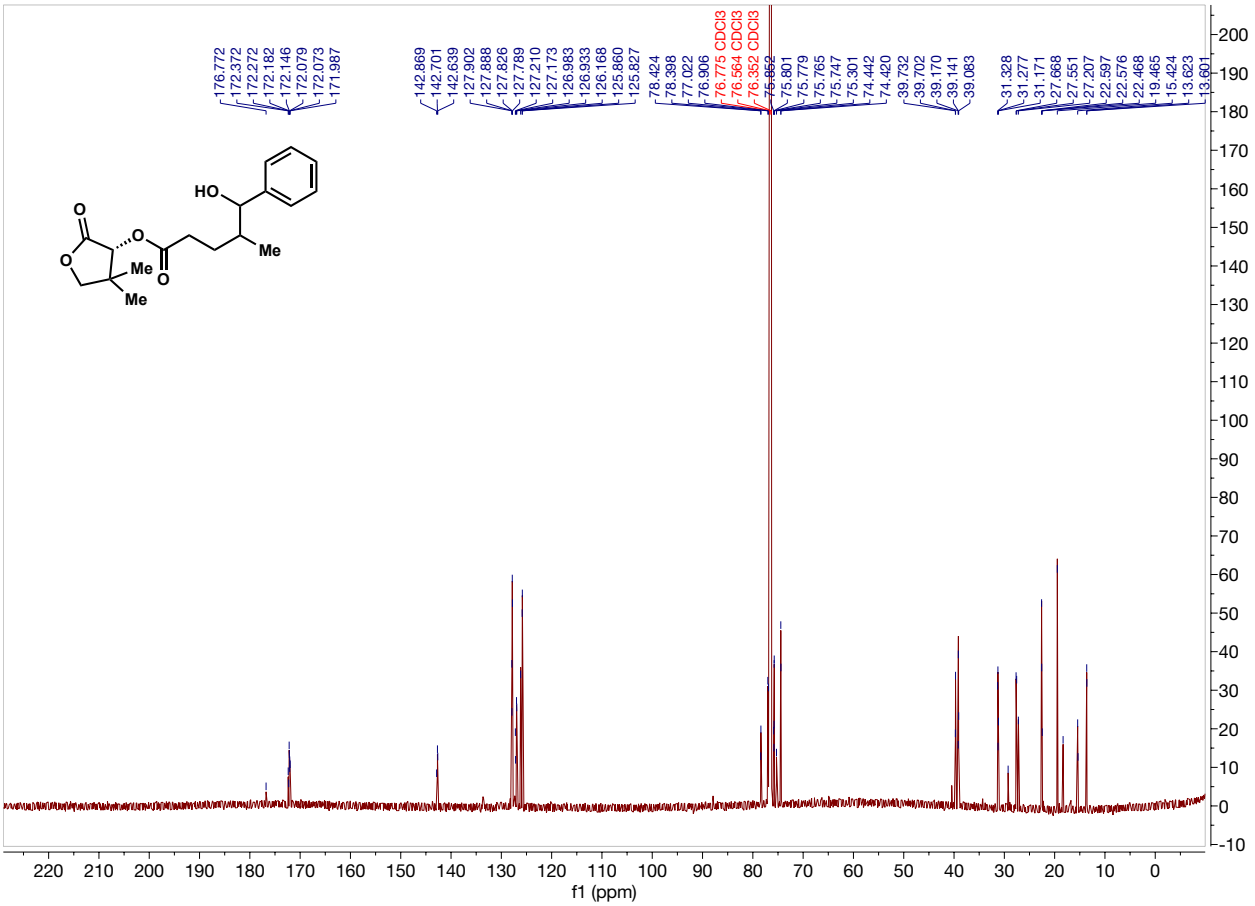


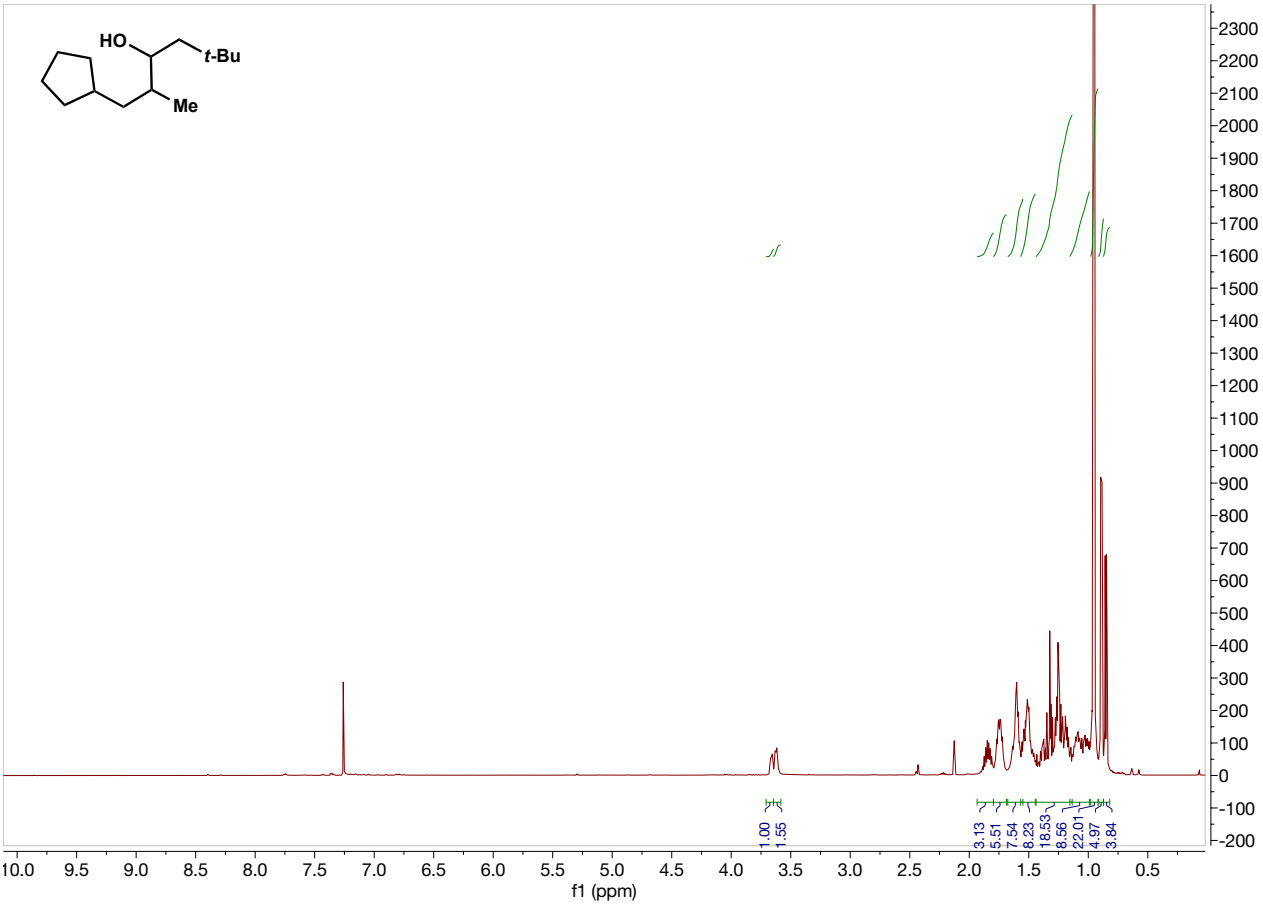

-62.73
-62.74
-62.76
-62.77
O
O
Me
OH
CF3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)

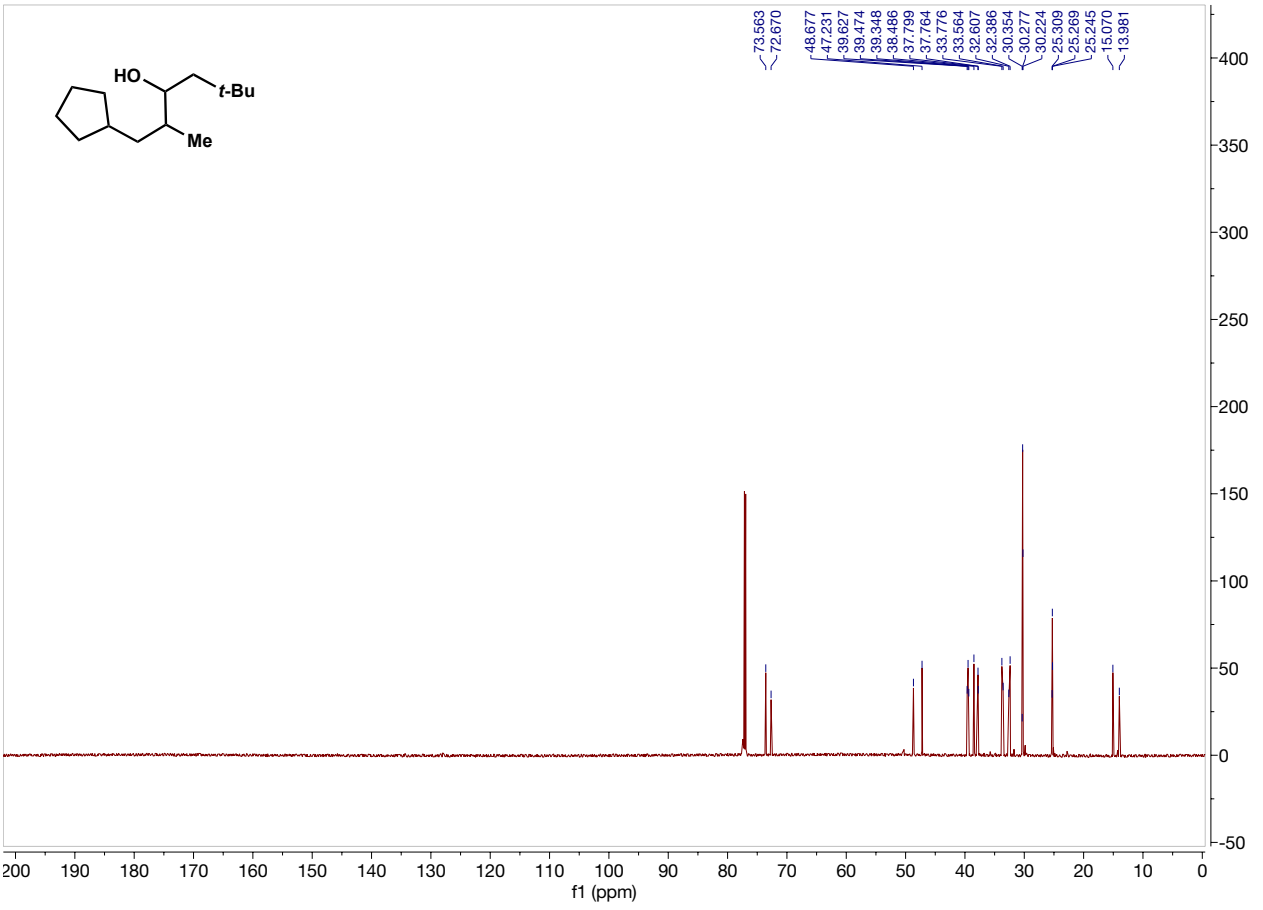

HO
Me
O
N
O
f1 (ppm)

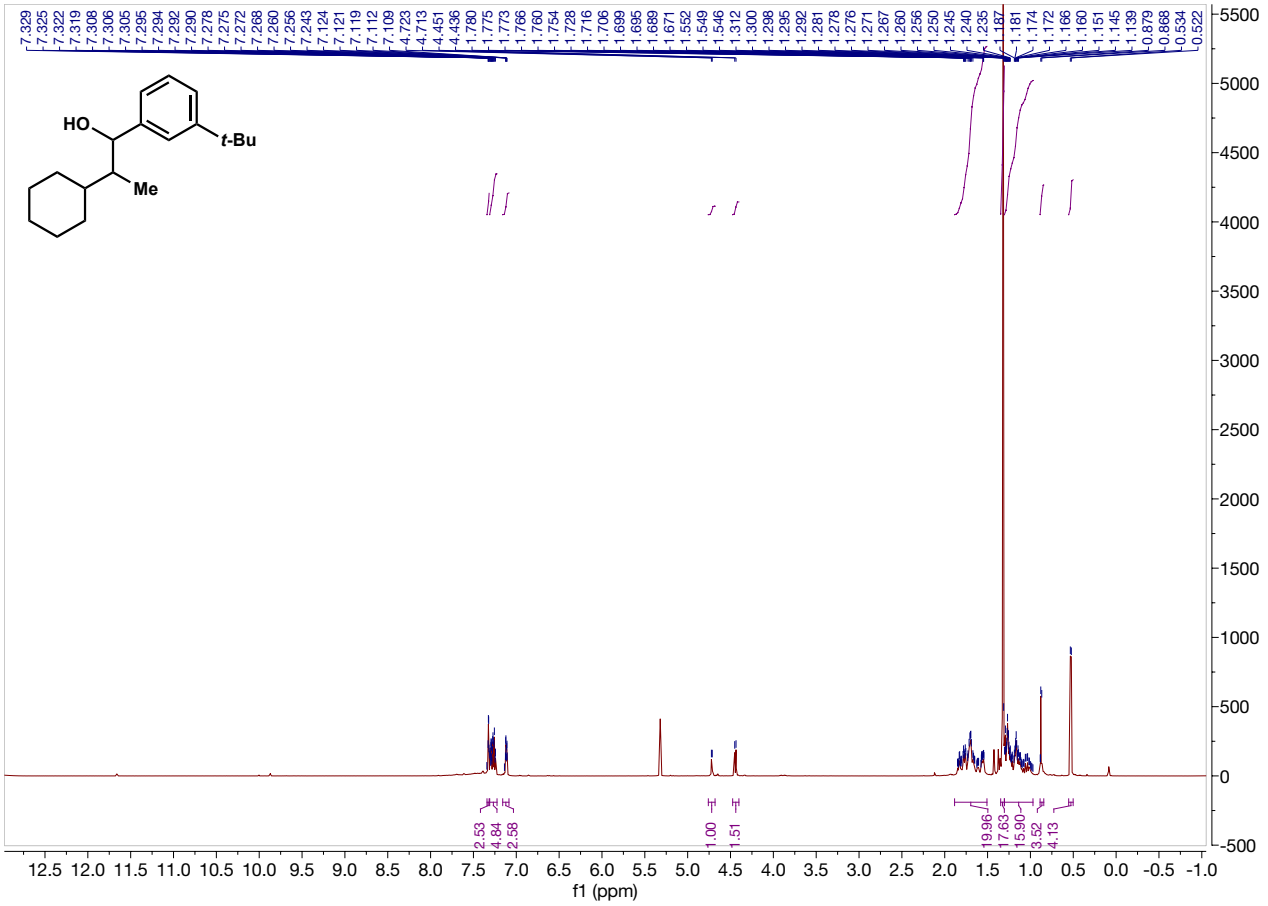

HO
Me
O
N
O
f1 (ppm)

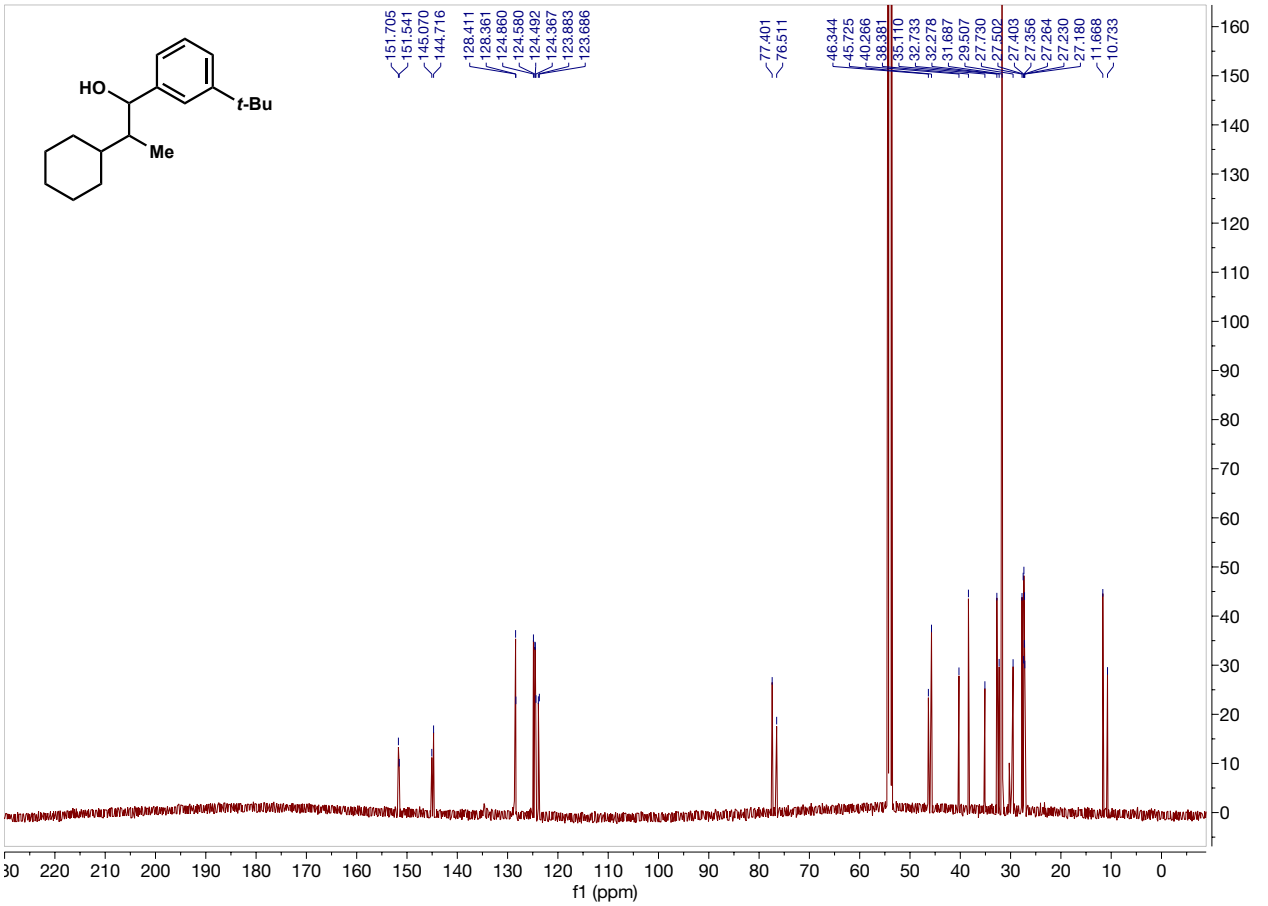

HO
O
O
O
O
Me
Me
Me
34.79
5.94
1.83
1.00
1.60
2.21
2.48
5.38
2.71
22.09
19.03
4.22
14.51
1.46
3.07
6.20
25.50
29.95
16.22
8.30
f1 (ppm)

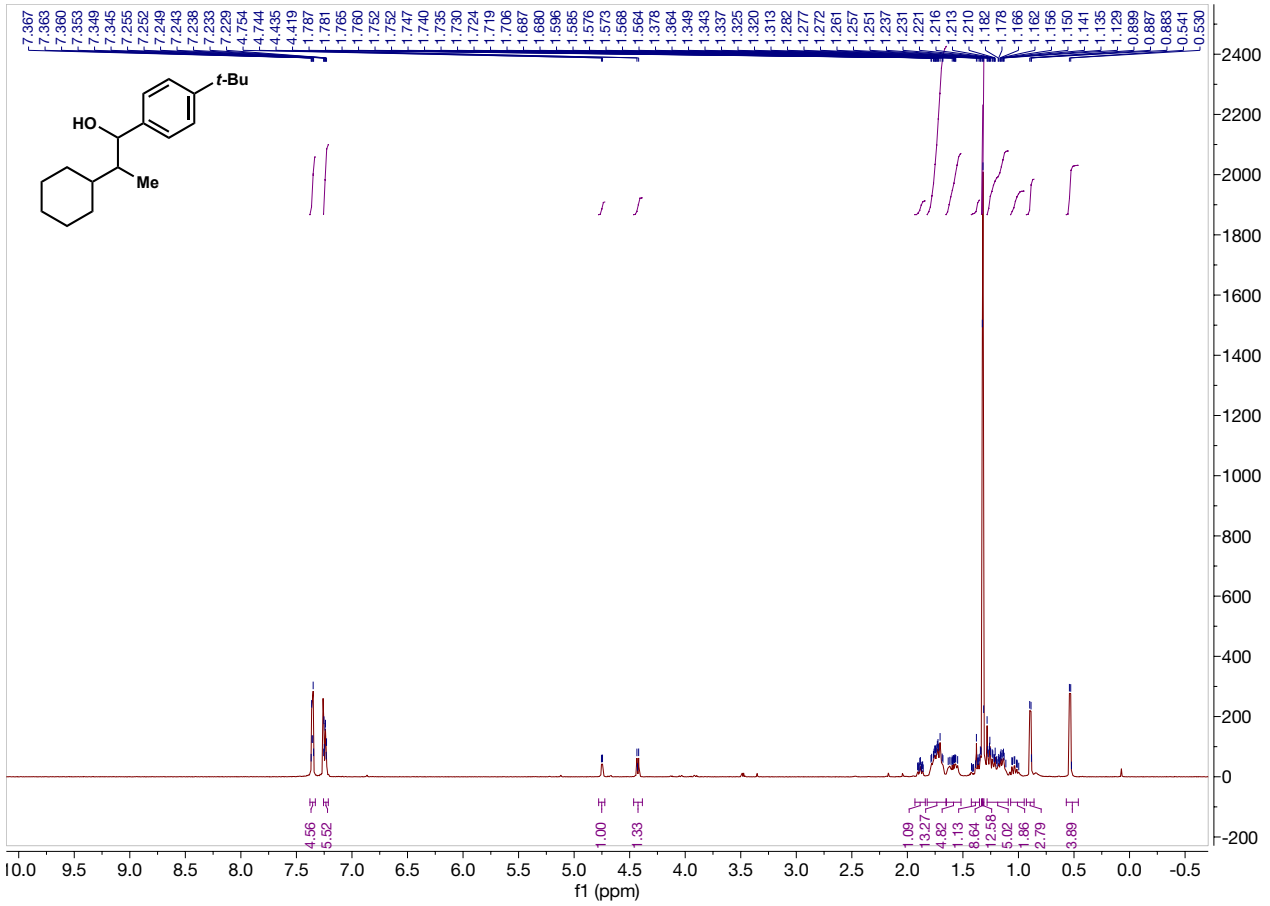

176.772
172.372
172.272
172.182
172.146
172.079
172.073
171.987
142.869
142.701
142.639
127.902
127.888
127.826
127.789
127.210
127.173
126.983
126.933
126.168
125.860
125.827
78.424
78.398
77.022
76.906
76.775 CDCl3
76.564 CDCl3
76.352 CDCl3
75.862
75.801
75.779
75.765
75.747
75.301
74.442
74.420
39.732
39.702
39.170
39.141
39.083
31.328
31.277
31.171
27.668
27.551
27.207
22.597
22.576
22.468
19.465
15.424
13.623
13.601
HO
O
O
O
O
Me
Me
Me
f1 (ppm)

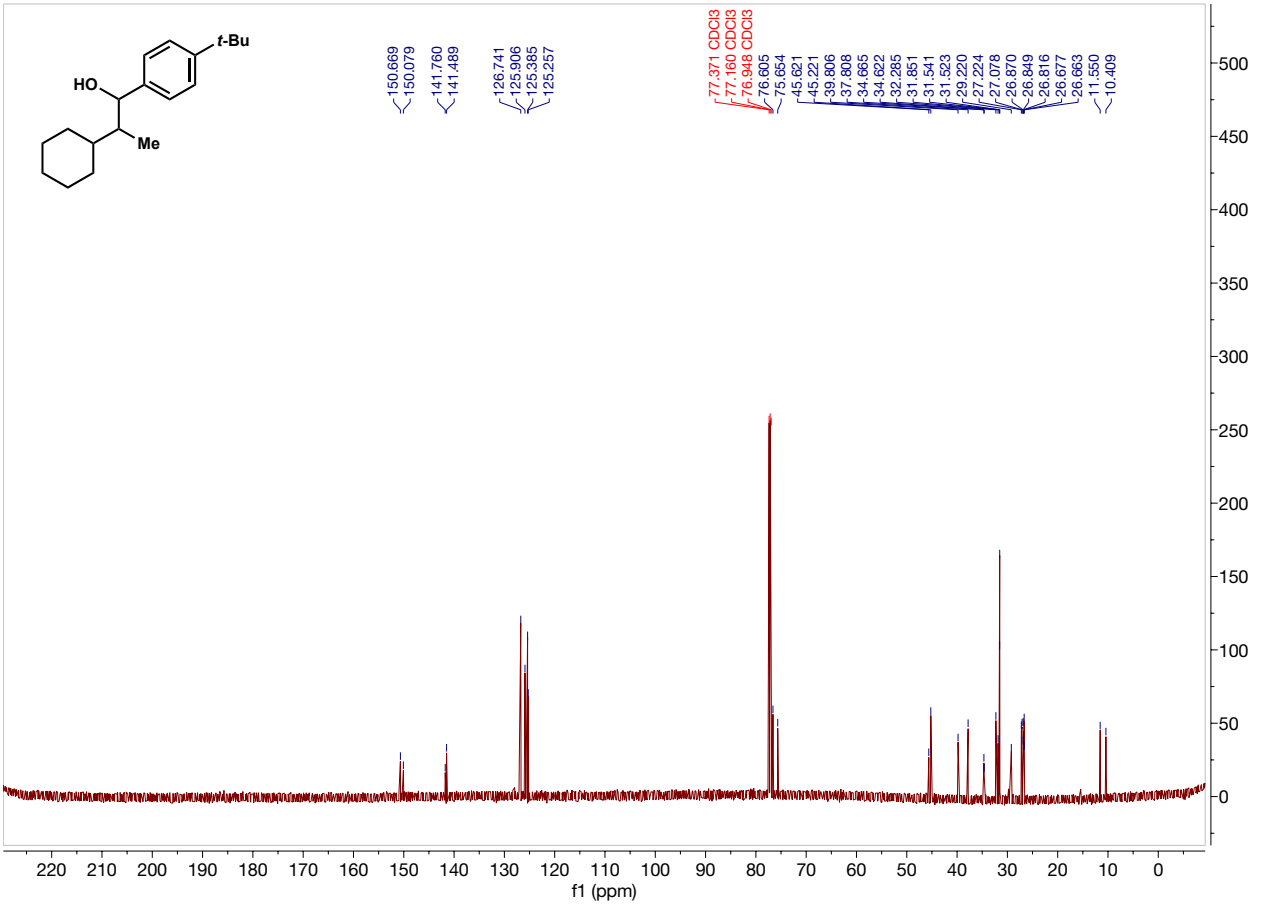

HO
t-Bu
Me
1.00
1.55
3.13
5.51
7.54
8.23
18.53
8.56
22.01
4.97
3.84
f1 (ppm)

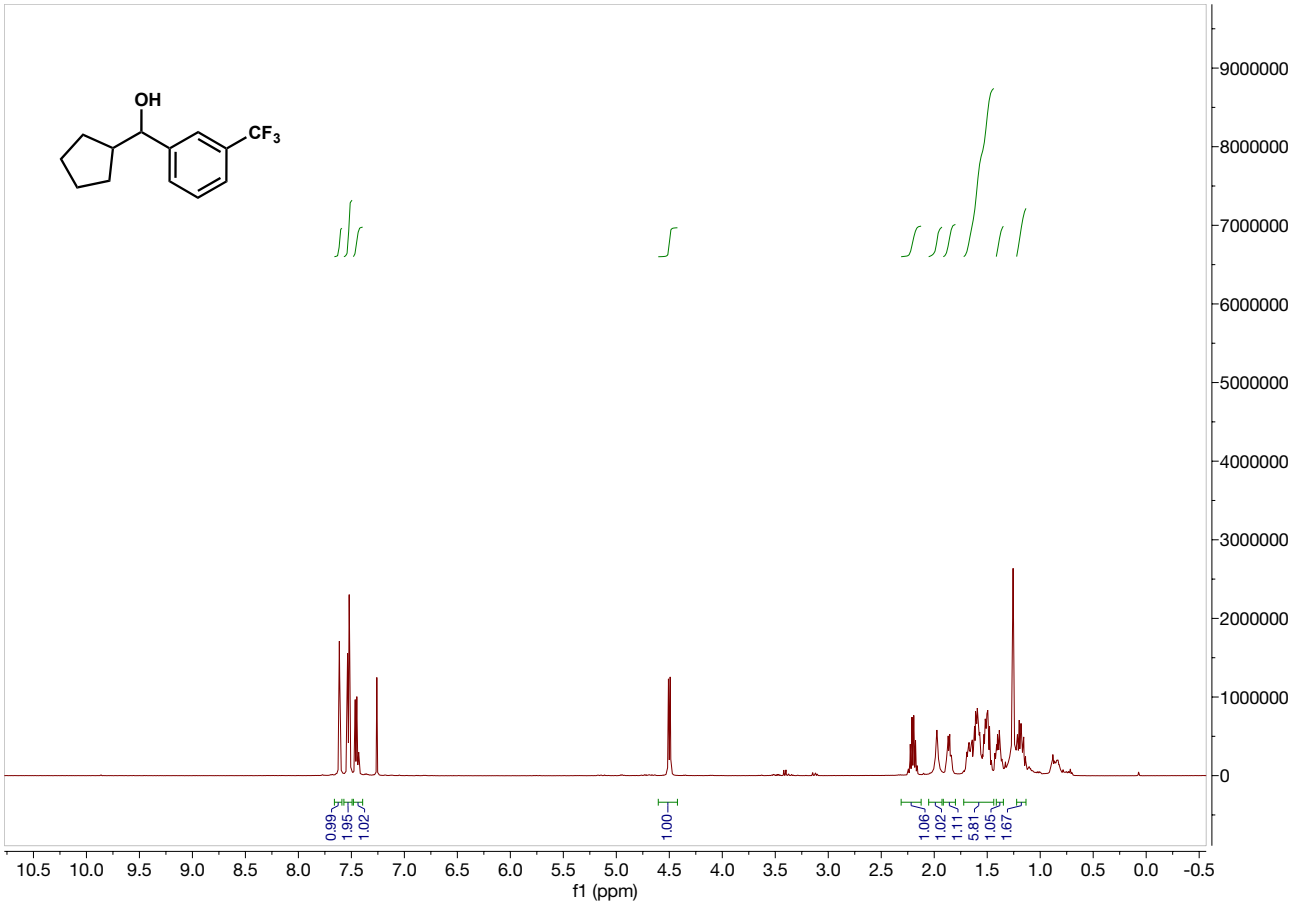

HO
t-Bu
Me
73.563
72.670
48.677
47.231
39.627
39.474
39.348
38.486
37.799
37.764
33.776
33.564
32.607
32.386
30.354
30.277
30.224
25.309
25.269
25.245
15.070
13.981
f1 (ppm)

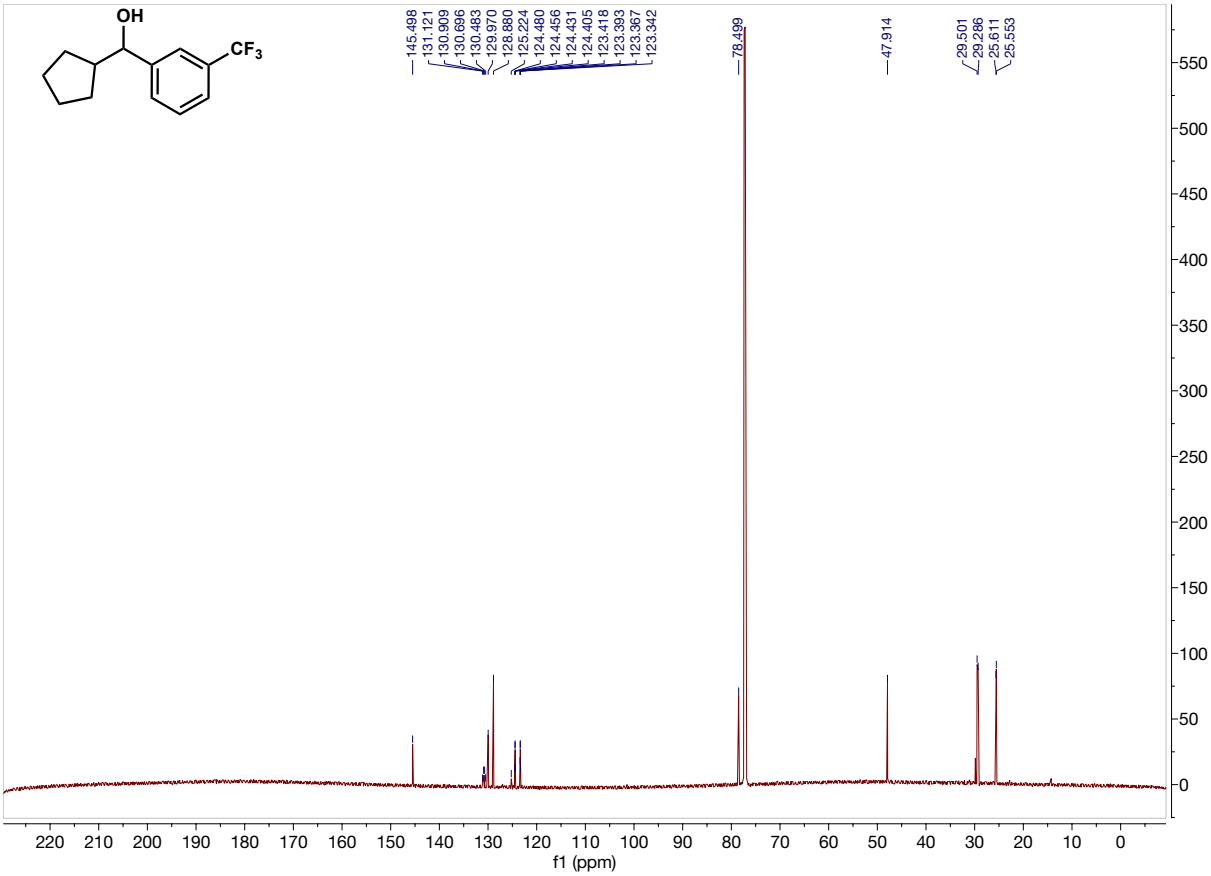

HO
t-Bu
Me
f1 (ppm)

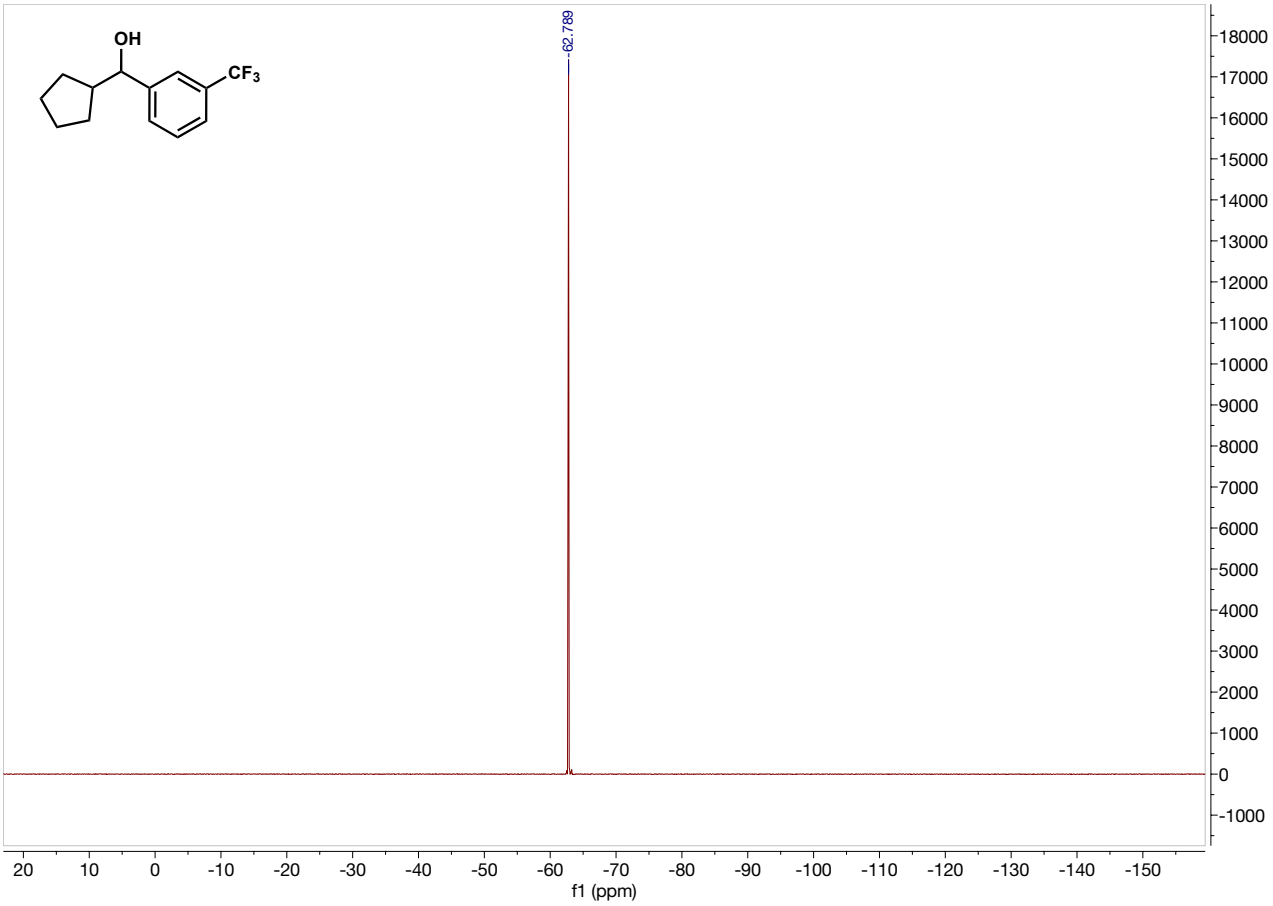

HO
t-Bu
Me
f1 (ppm)

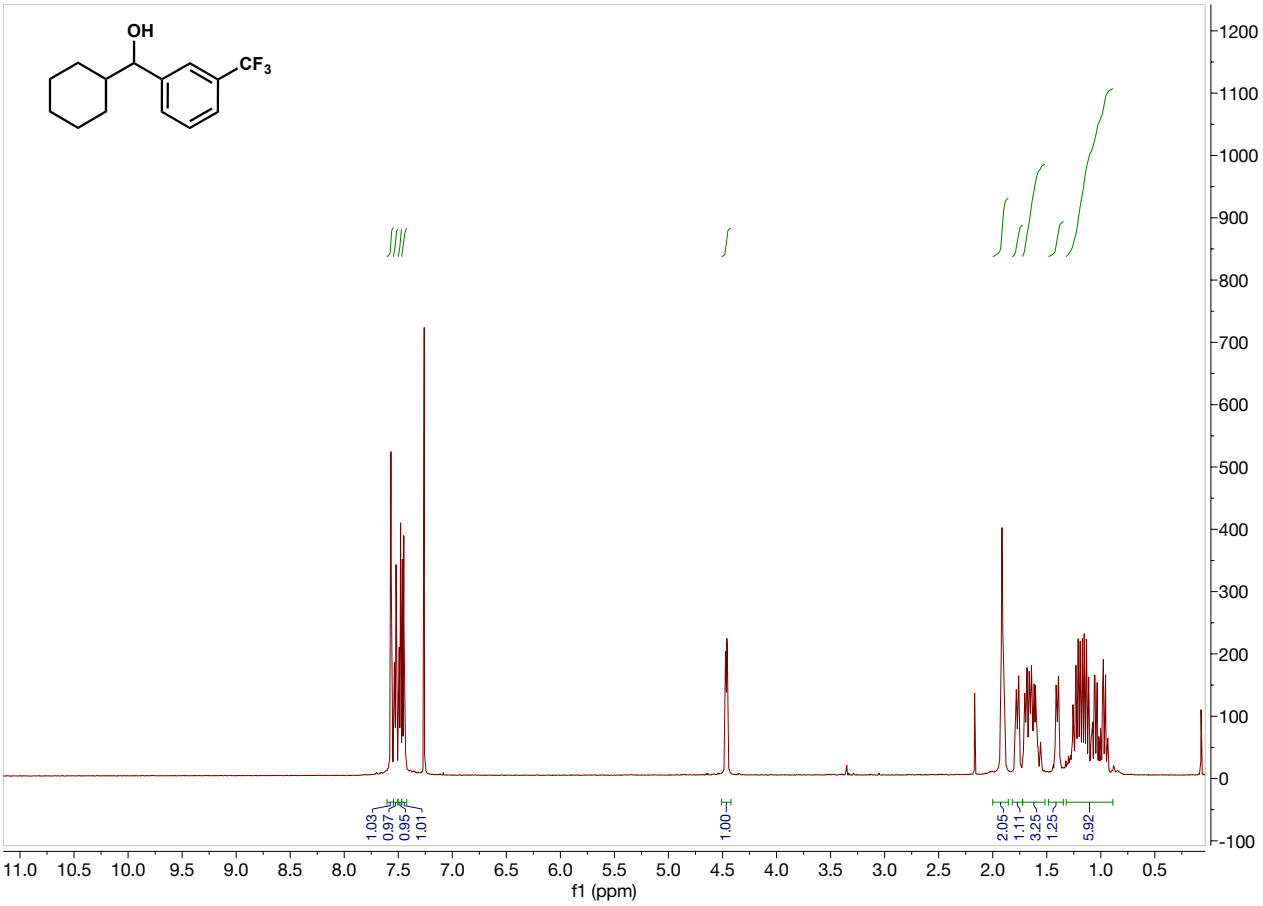

t-Bu
HO
Me
f1 (ppm)

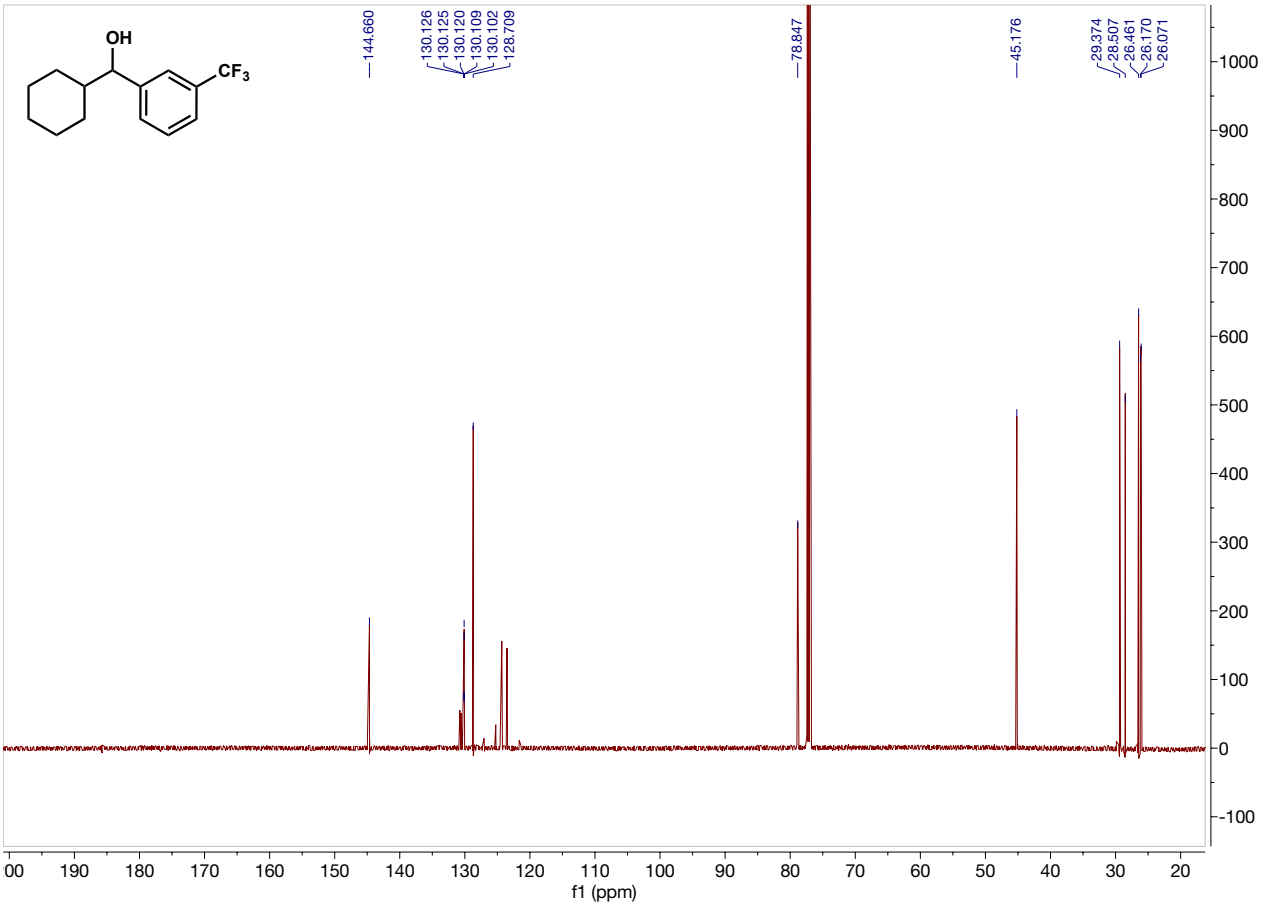

t-Bu
HO
Me
f1 (ppm)

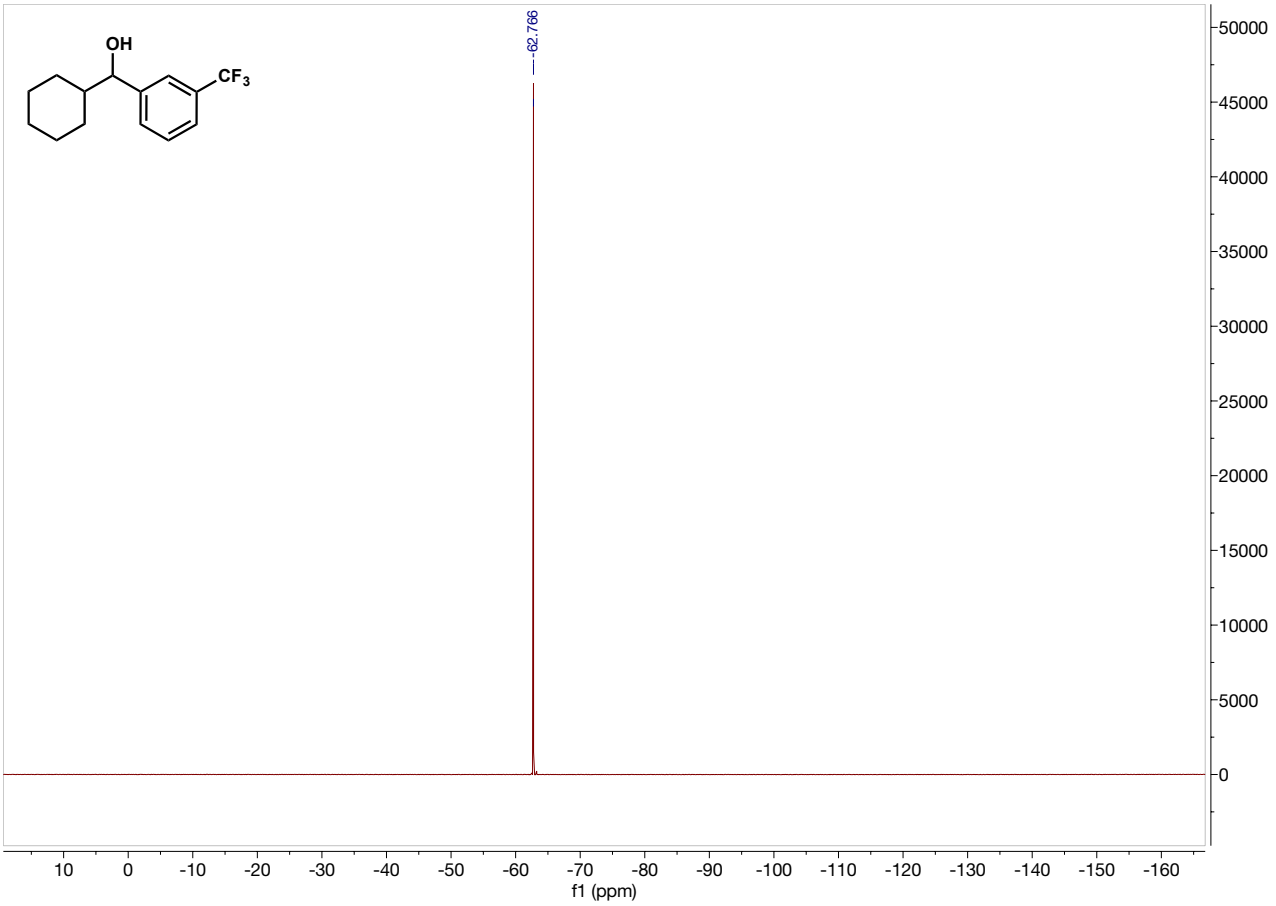

OH
CF3
0.99
1.95
1.02
1.00
1.06
1.02
1.11
5.81
1.05
1.67
f1 (ppm)

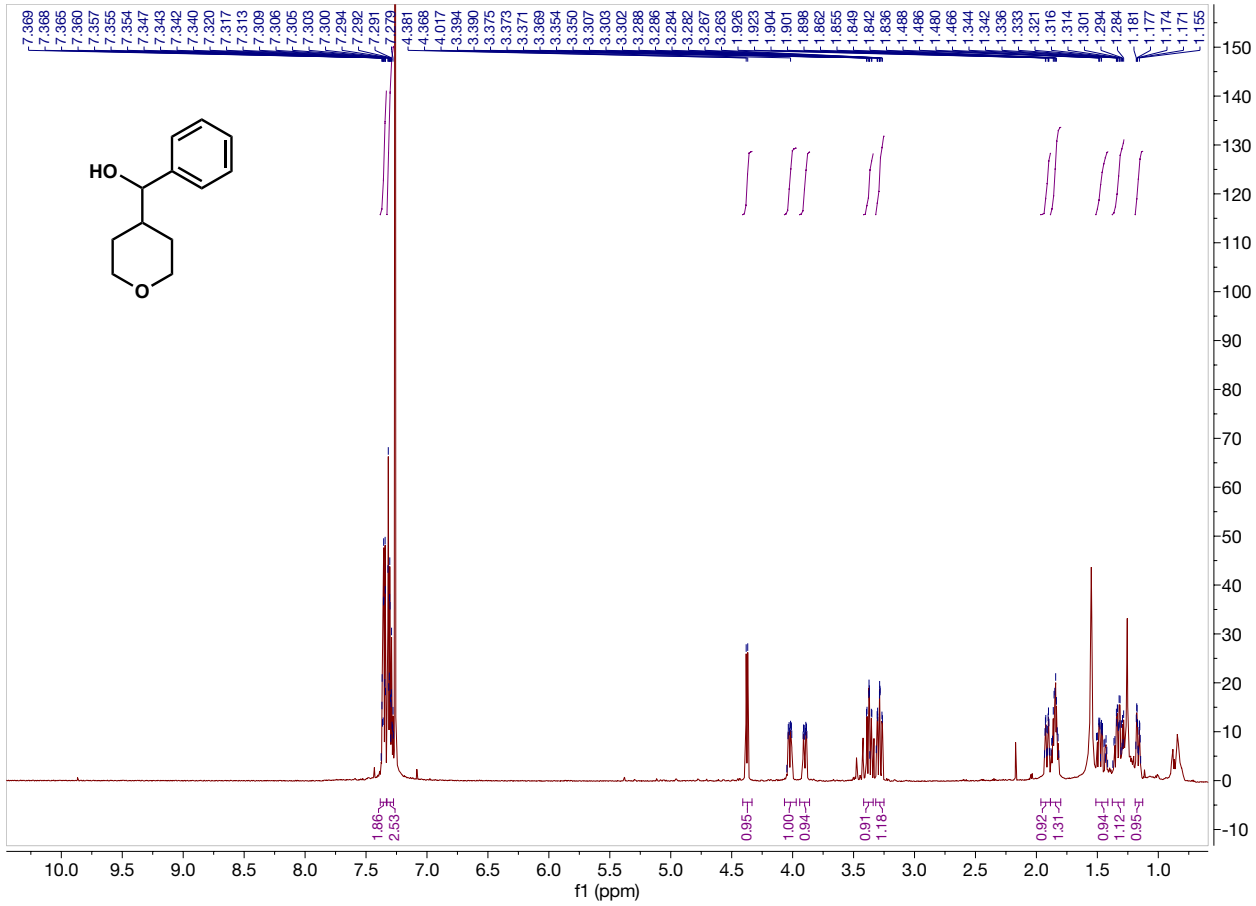

OH
CF3
145.498
131.121
130.909
130.696
130.483
129.970
128.880
125.224
124.460
124.456
124.431
124.405
123.418
123.393
123.367
123.342
78.499
47.914
29.501
29.286
25.611
25.553
f1 (ppm)

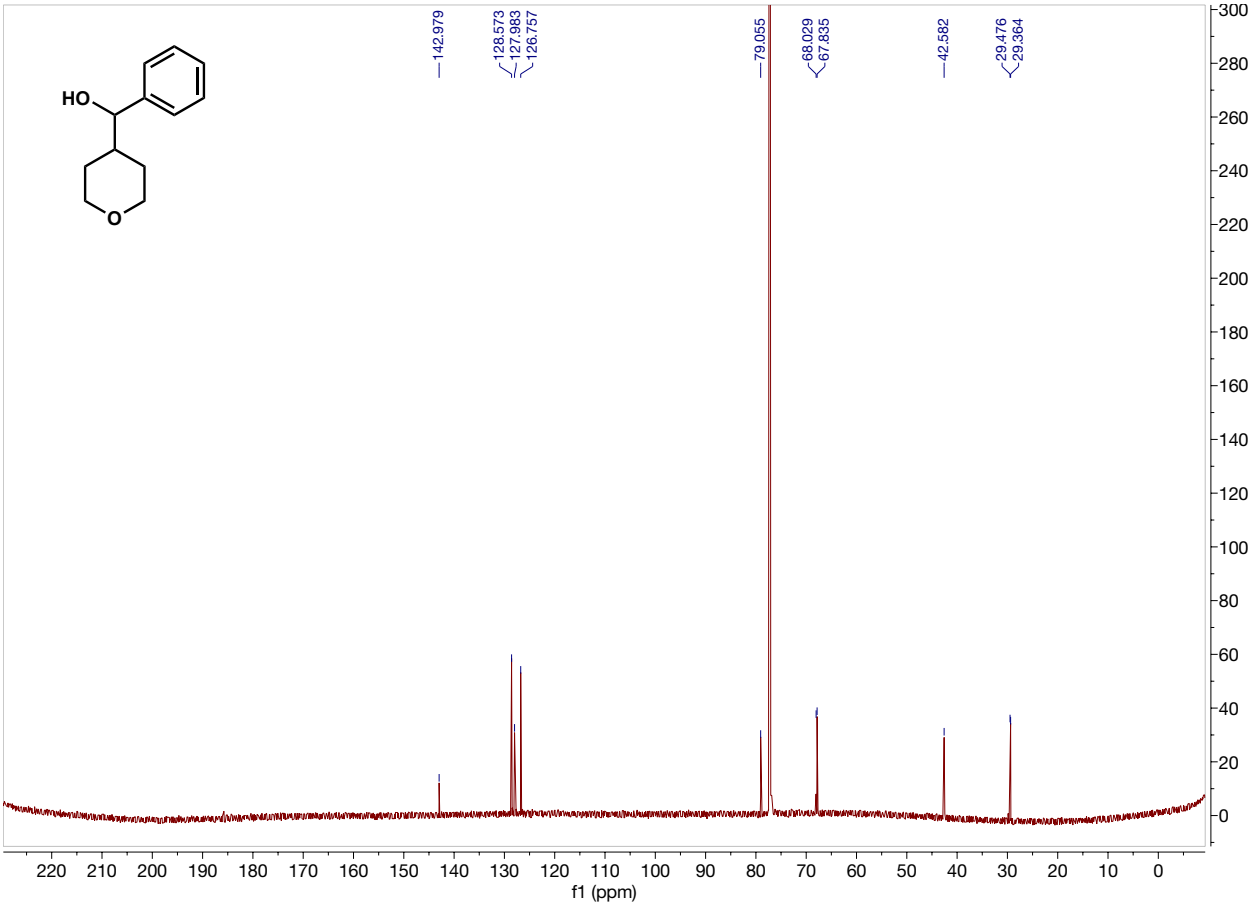

OH
CF3
-62.789
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

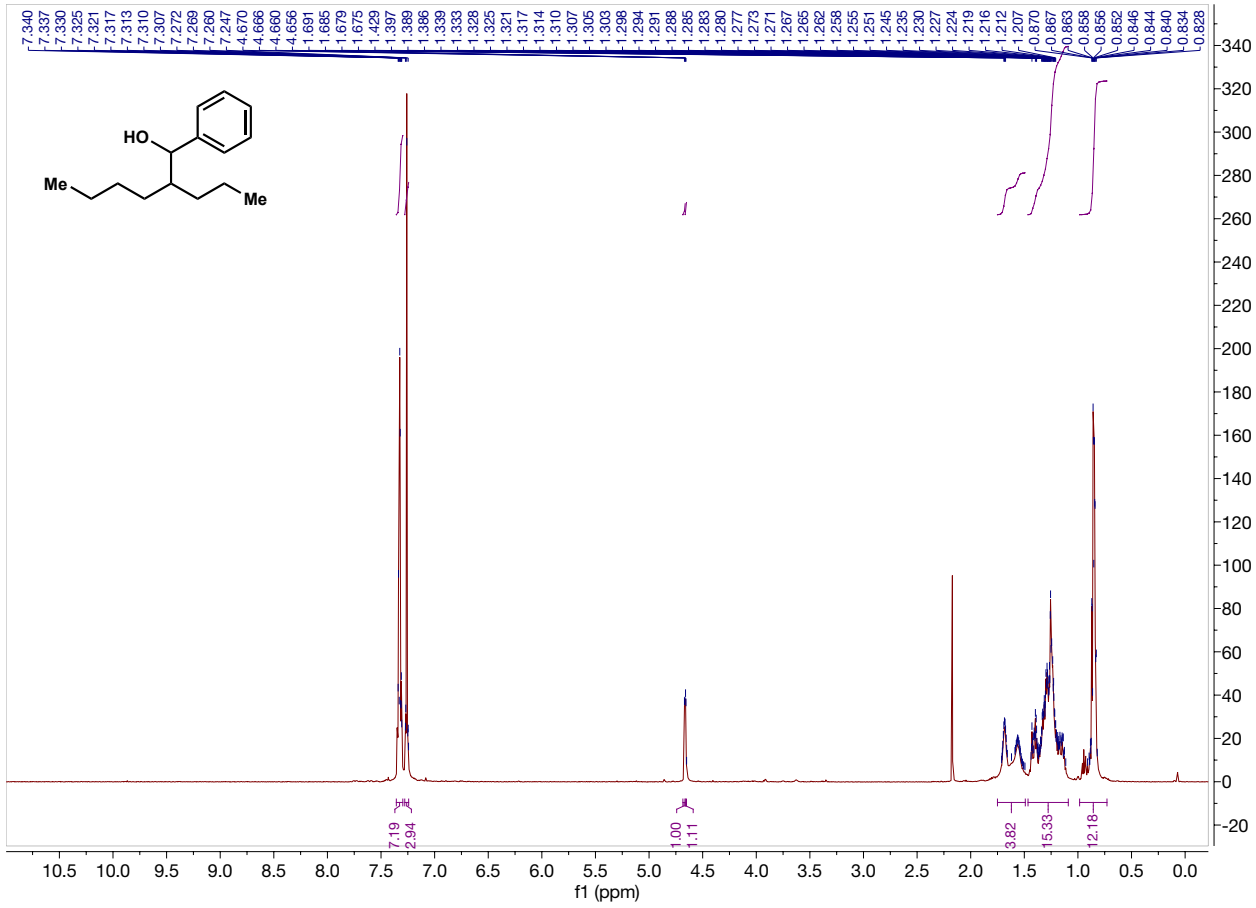

OH
CF3
1.03
0.97
0.95
1.01
1.00
2.05
1.11
3.25
1.25
5.92
f1 (ppm)

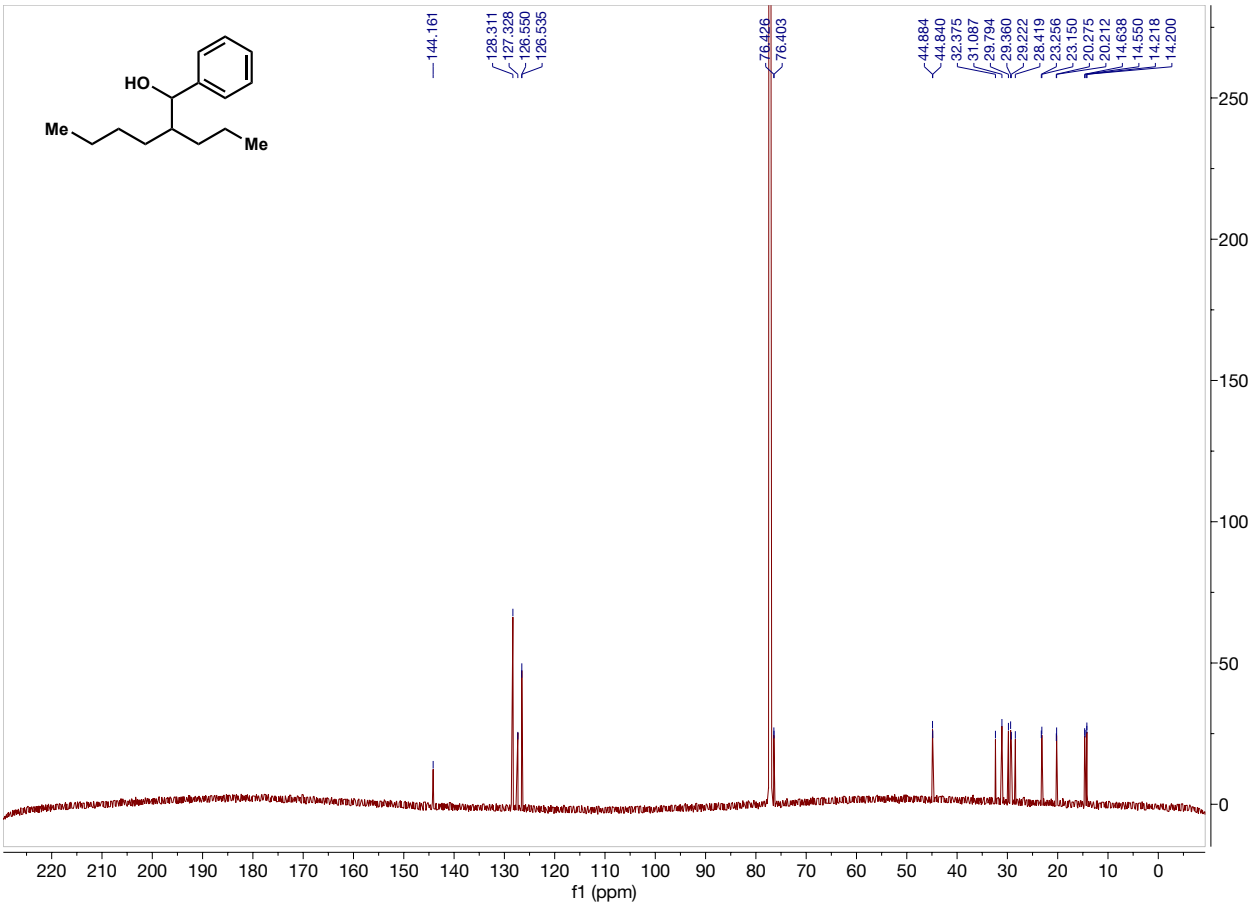

OH
CF3
144.660
130.126
130.125
130.120
130.109
130.102
128.709
78.847
45.176
29.374
28.507
26.461
26.170
26.071
f1 (ppm)

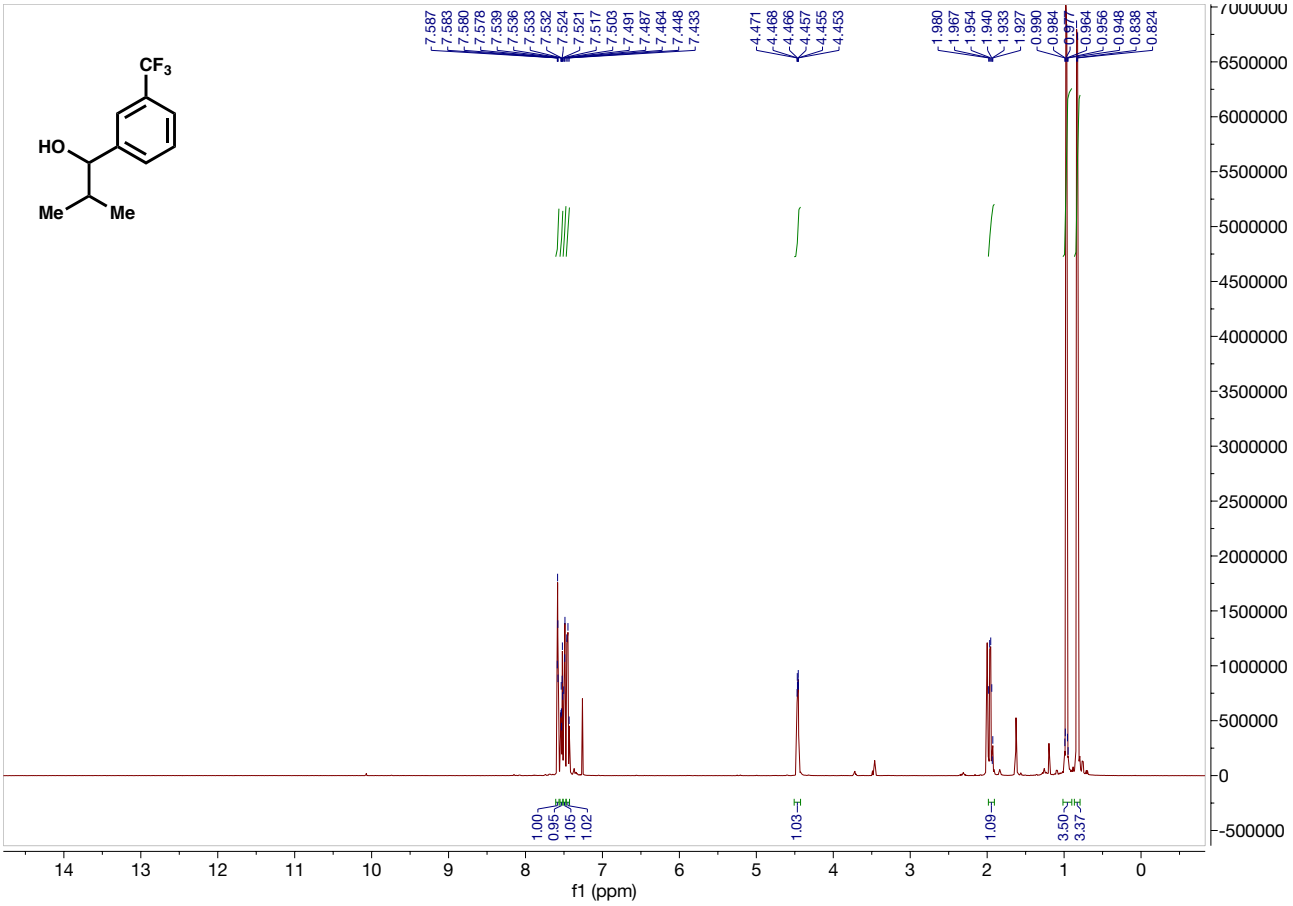

OH
CF3
-62.766
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

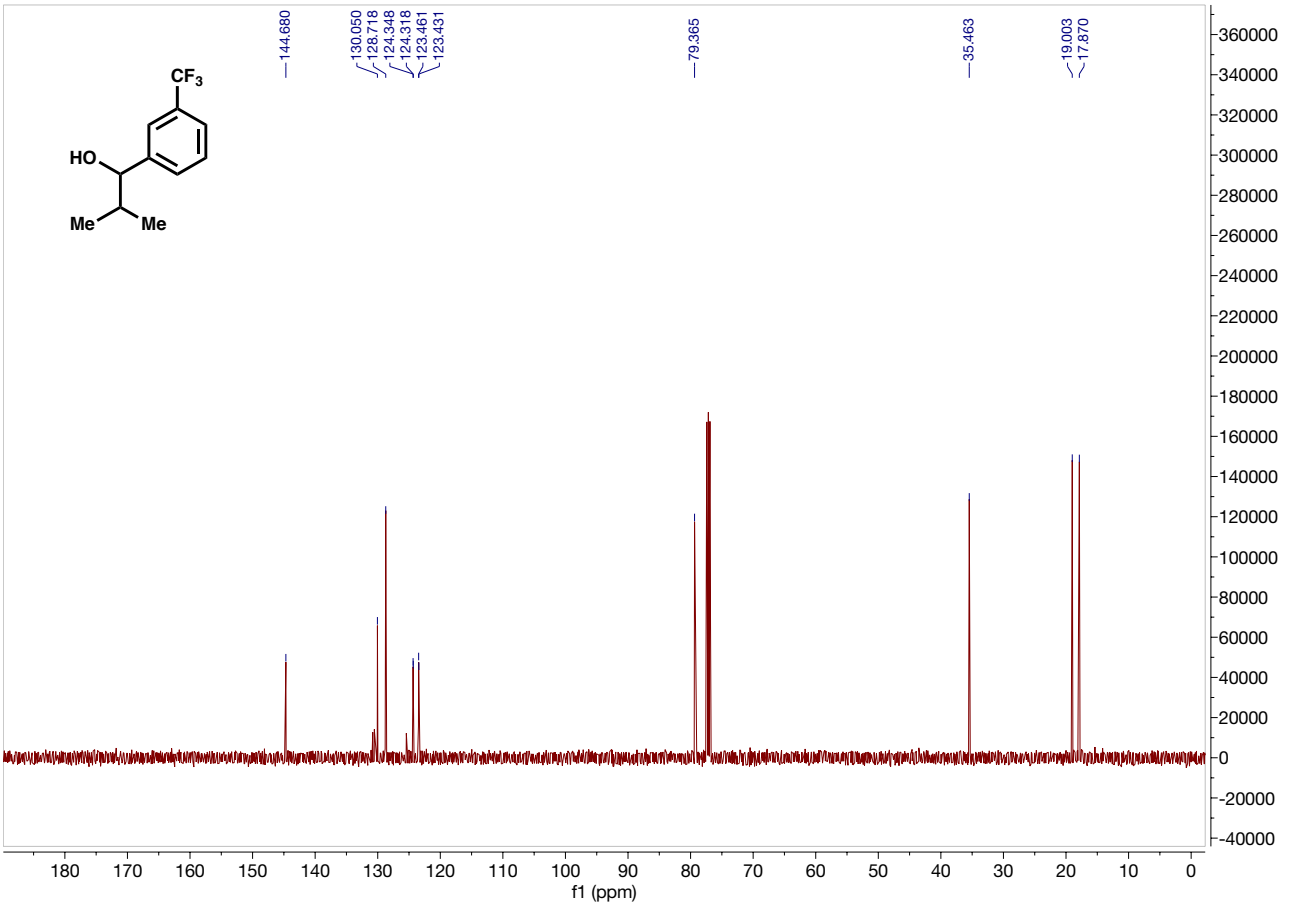

HO
O
f1 (ppm)


HO
O
142.979
128.573
127.983
126.757
79.055
68.029
67.835
42.582
29.476
29.364
f1 (ppm)


HO
Me
Me
7.340
7.337
7.330
7.325
7.321
7.317
7.313
7.310
7.307
7.272
7.269
7.260
7.247
4.670
4.666
4.660
4.656
1.691
1.685
1.679
1.675
1.429
1.397
1.389
1.386
1.339
1.333
1.328
1.325
1.321
1.317
1.314
1.310
1.307
1.305
1.303
1.298
1.294
1.291
1.288
1.285
1.283
1.280
1.277
1.273
1.271
1.267
1.265
1.262
1.258
1.255
1.251
1.245
1.235
1.230
1.227
1.224
1.219
1.216
1.212
1.207
0.870
0.867
0.863
0.858
0.856
0.852
0.846
0.844
0.840
0.834
0.828
7.19
2.94
1.00
1.11
3.82
15.33
12.18
f1 (ppm)


HO
Me
Me
144.161
128.311
127.328
126.550
126.535
76.426
76.403
44.884
44.840
32.375
31.087
29.794
29.360
29.222
28.419
23.256
23.150
20.275
20.212
14.638
14.550
14.218
14.200
f1 (ppm)


7.587
7.583
7.580
7.578
7.539
7.536
7.533
7.532
7.524
7.521
7.517
7.503
7.491
7.487
7.464
7.448
7.433
4.471
4.468
4.466
4.457
4.455
4.453
1.980
1.967
1.954
1.940
1.933
1.927
0.990
0.984
0.977
0.964
0.956
0.948
0.838
0.824
1.00
0.95
1.05
1.02
1.03
1.09
3.50
3.37
f1 (ppm)


144.680
130.050
128.718
124.348
124.318
123.461
123.431
79.365
35.463
19.003
17.870
f1 (ppm)

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