Supporting Information for:

Tandem Peterson Olefination and Asymmetric Hydrogenation of β-Hydroxy Silanes.

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(‡ S.K, H.W and J.L contributed equally.)

Contents

1. General methods

All reactions were conducted under nitrogen atmosphere using magnetic stirring.

CH_2Cl_2 was freshly distilled using CaH_2 under nitrogen atmosphere. THF was freshly distilled using sodium-benzophenone under nitrogen.

All reagents were used as supplied commercially without further purification. Chromatographic separations were performed on Kiesel gel 60 H silica gel (particle size: 0.063-0.100 mm) or Brockmann I, activated, basic Al_2O_3 (particle size: ~150 mesh). Thin layer chromatography (TLC) was performed on aluminium plates coated with Kieselgel 60 (0.20 mm, UV254) and visualized under ultraviolet light (ν = 254 nm), or by staining with ethanolic phosphomolybdic acid and heating.

^{1}H NMR spectra were recorded on a Bruker 400 MHz or 500 MHz at 400/500 MHz in $CDCl_3$ and referenced internally to the residual $CDCl_3$ peak (7.26 ppm). ^{13}C NMR spectra were recorded at 100/125 MHz in $CDCl_3$ and referenced to the central peak of $CDCl_3$ (77.0 ppm). Chemical shifts are reported in ppm (δ scale).

Enantiomeric excesses were determined by either using chiral HPLC with a diode array detector at 220 nm and 254 nm or using a chiral GC with an MS detector. (Refer to the individual compounds for specific chromatographic details.) Racemic compounds were used for comparison.

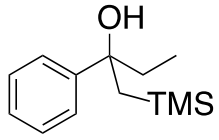
HRMS data were obtained using a Bruker MicroTOF-Q II instrument operation at ambient temperature.

Optical rotations were recorded on an Autopol IV polarimeter from Rudolp Research Analytical, equipped with a sodium lamp (589 nm) and a 10 cm cell.

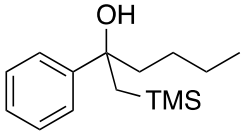
IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer using samples that were prepared in $CHCl_3$.

2. Procedure for synthesis of β-hydroxy silane

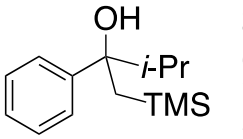
To a solution of ketones in dry Et_2O, the TMSCH2MgCl[1] solution (1.5 equiv.) was slowly added under N_2 atmosphere at 0°C. The reaction mixture was allowed to stir overnight at room temperature. After completion, checking by TLC, the reaction was quenched with 10% $NaHCO_3$ at 0°C. The aqueous phase was extracted with ether. The combined organic phase was dried over Na_2SO_4. The crude product was purified by deactivated silica gel (10% Et3N/pentane) with 10-15% of EtOAc/Pentane (1% Et_3N) as eluent.



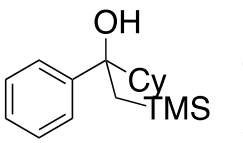
2-Phenyl-1-(trimethylsilyl)butan-2-ol
This compound has been reported.[2]
Colorless oil, 1.43g, 86%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.31 (tt, *J* = 8.4, 1.7 Hz, 2H), 7.24 – 7.18 (m, 1H), 1.98 – 1.78 (m, 2H), 1.65 (s, 1H), 1.34 (d, *J* = 4.6 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H), -0.17 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.62, 127.82, 126.12, 125.10, 77.37, 39.07, 33.08, 8.13, -0.02.



2-Phenyl-1-(trimethylsilyl)hexan-2-ol
Colorless oil, 1.29g, 84%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.36 (m, 2H), 7.34 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 1.93 – 1.75 (m, 2H), 1.67 (s, 1H), 1.57 (S, 1H), 1.34 (d, *J* = 3.5 Hz, 2H), 1.30 – 1.19 (m, 3H), 1.04 – 0.93 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H), -0.17 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.08, 127.88, 126.13, 125.02, 77.24, 46.50, 33.56, 26.01, 22.96, 14.01, 0.00.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3490, 2955, 1602, 1446, 1248, 1030, 961, 860, 839, 764.
HRMS-ESI; *m/z* [M+Na^+] = 273.1643, calcd. For $C_{15}H_{26}NaOSi$: 273.1645.

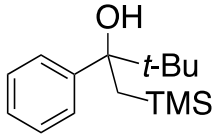


3-Methyl-2-phenyl-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.00 g, 85%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 1.98 (p, *J* = 6.8 Hz, 2H), 1.57 (d, *J* = 4.8 Hz, 2H), 1.35 (d, *J* = 8.6 Hz, 2H), 0.96 (d, *J* = 6.7 Hz, 3H), 0.69 (d, *J* = 6.8 Hz, 3H), -0.24 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.89, 127.59, 126.06, 125.61, 79.15, 40.74, 29.85, 17.56, 16.75, -0.02.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3620, 2958, 1446, 1386, 1247, 1175, 935, 857, 836, 702.
HRMS-ESI; *m/z* [M+Na^+] = 259.1501, calcd. For $C_{14}H2_4NaOSi$: 259.1489.

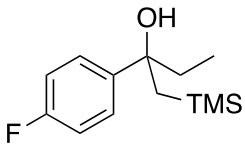


1-Cyclohexyl-1-phenyl-2-(trimethylsilyl)ethan-1-ol
Colorless oil, 1.39 g, 95%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.22 – 7.17 (m, 1H), 2.06 – 1.96 (m, 1H), 1.79 (dt, *J* = 12.9, 3.2 Hz, 1H), 1.72 – 1.50 (m, 5H), 1.46 – 0.81 (m, 8H), -0.23 (s, 9H).

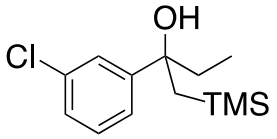
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.95, 127.53, 125.99, 125.67, 79.12, 51.13, 29.57, 27.50, 26.72, 26.70, 26.69, 26.38, 0.04.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3612, 2929, 1446, 1247, 838, 802.
HRMS-ESI; *m/z* [M+Na^+] = 299.1809, calcd. For $C_{17}H_{28}NaOSi$: 299.1802.



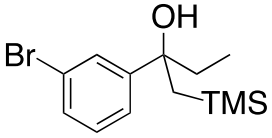
3,3-Dimethyl-2-phenyl-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.27 g, 82% yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.37 (m, 2H), 7.31 – 7.23 (m, 2H), 7.23 – 7.17 (m, 1H), 1.70 (s, 1H), 1.60 (d, *J* = 14.8 Hz, 1H), 1.33 (d, *J* = 14.8 Hz, 1H), 0.90 (s, 9H), -0.24 (d, *J* = 1.0 Hz, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 164.89, 146.75, 136.61, 121.50, 119.80, 38.91, 32.11, 7.97, -0.11.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3397, 2963, 1593, 1434, 1386, 1246, 1062, 969, 861, 841.
HRMS-ESI; *m/z* [M-MeOH]$^+$ = 206.1473, calcd. For $C_{13}H_{22}Si$: 206.1485.



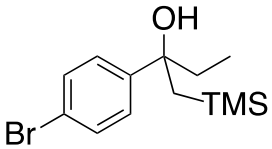
2-(4-Fluorophenyl)-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.37 g, 86%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.32 (m, 2H), 7.02 – 6.96 (m, 2H), 1.94 – 1.75 (m, 1H), 1.60 (s, 2H), 1.32 (d, *J* = 3.6 Hz, 2H), 0.72 (t, *J* = 7.4 Hz, 3H), -0.17 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, *J* = 243.0 Hz), 143.39, 143.36, 126.80 (d, *J* = 7.8 Hz), 114.51 (d, *J* = 21.0 Hz), 77.16, 39.35, 33.24, 8.09, -0.00.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3483, 2966, 1603, 1508, 1248, 1159, 912, 836.
HRMS-ESI; *m/z* [M+Na^+] = 263.1235, calcd. For $C_{13}H_{21}FNaOSi$: 263.1238.



2-(3-Chlorophenyl)-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.34 g, 88%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.38 (m, 1H), 7.28 – 7.23 (m, 2H), 7.23 – 7.16 (m, 2H), 1.93 – 1.75 (m, 2H), 1.63 (s, 1H), 1.31 (d, *J* = 1.0 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H), -0.15 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.99, 133.94, 129.13, 126.26, 125.59, 123.40, 77.17, 39.14, 33.09, 8.06, 0.01.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3606, 2965, 1596, 1419, 1248, 1095, 840, 776.
HRMS-ESI; *m/z* [M+Na^+] = 279.0951, calcd. For $C_{13}H_{21}ClNaOSi$: 279.0942.

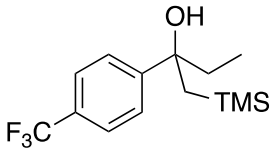


2-(3-Bromophenyl)-1-(trimethylsilyl)butan-2-ol
Colorless oil, 0.62 g, 88% yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (t, *J* = 1.8 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 1.94 – 1.75 (m, 2H), 1.63 (s, 1H), 1.31 (d, *J* = 0.9 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H), -0.15 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.28, 129.47, 129.24, 128.52, 123.87, 122.32, 77.18, 39.17, 33.15, 8.09, 0.04.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3481, 2965, 1564, 1416, 1248, 1095, 958, 859, 840, 780.
HRMS-ESI; *m/z* [M+Na^+] = 323.0439, calcd. For $C_{13}H_{21}BrNaOSi$: 323.0437.

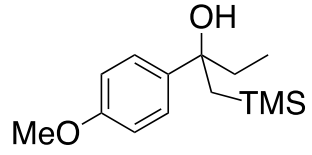


2-(4-Bromophenyl)-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.29 g, 89% yield.

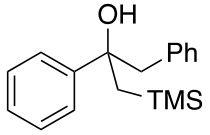
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 – 7.41 (m, 2H), 7.30 – 7.25 (m, 2H), 1.83 (dq, *J* = 9.8, 6.8 Hz, 2H), 1.60 (s, 1H), 1.31 (d, *J* = 2.7 Hz, 2H), 0.71 (t, *J* = 7.4 Hz, 3H), -0.15 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.79, 130.88, 127.12, 120.01, 77.21, 39.26, 33.04, 8.07, 0.07.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3601, 2965, 1487, 1394, 1248, 1009, 910, 860, 839, 691.
HRMS-ESI; *m/z* [M+Na^+] = 323.0440, calcd. For $C_{13}H_{21}BrNaOSi$: 323.0437.



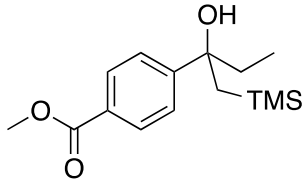
2-(4-(Trifluoromethyl)phenyl)-1-(trimethylsilyl)butan-2-ol
Colorless oil, 1.28 g, 89%yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.55 (m, 2H), 7.54 – 7.49 (m, 2H), 1.95 – 1.79 (m, 2H), 1.34 (d, *J* = 2.3 Hz, 2H), 0.72 (t, *J* = 7.4 Hz, 3H), -0.16 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.85, 128.52 (q, *J* = 32.3 Hz), 125.65, (d, *J* = 8.0 Hz), 124.84 (q, *J* = 3.8 Hz). 122.99, 77.39, 39.35, 33.17, 8.01, 0.00.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3490, 2966, 1618, 1410, 1326, 1127, 913, 839, 692.
HRMS-ESI; *m/z* [M^++Na] = 291.1399, calcd. For $C_{14}H_{22}FNaOSi$: 291.1387.



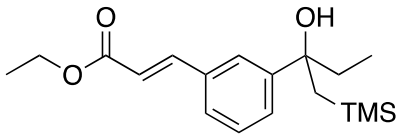
2-(4-Methoxyphenyl)-1-(trimethylsilyl)butan-2-ol
Color less oil, 1.17 g, 76% yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.27 (m, 2H), 6.88 – 6.82 (m, 2H), 3.80 (s, 3H), 1.94 – 1.74 (m, 2H), 1.61 (s, 1H), 1.31 (d, *J* = 4.1 Hz, 2H), 0.73 (t, *J* = 7.4 Hz, 3H), -0.16 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 157.93, 139.90, 126.24, 113.12, 77.13, 55.15, 33.05, 8.19, 0.04.
IR ($CHCl_3$, neat, cm^{-1}): ν = 3515, 2953, 1610, 1510, 1247, 1037, 912, 834, 691.
HRMS-ESI; *m/z* [M+Na^+] = 275.1450, calcd. For $C_{14}H_{24}NaO_2Si$: 275.1438.



1,2-Diphenyl-3-(trimethylsilyl)propan-2-ol
White solid, 0.72 g, 51% yiled.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 4H), 7.24 – 7.15 (m, 4H), 6.94 – 6.88 (m, 2H), 3.25 – 3.00 (m, 2H), 1.81 (s, 1H), 1.52 – 1.26 (m, 2H), -0.21 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.43, 136.61, 130.64, 128.00, 127.79, 126.59, 126.29, 125.29, 76.87, 53.39, 32.57, 0.01.
HRMS-ESI; *m/z* [M+Na^+] = 307.1482, calcd. For $C_{18}H_{24}NaOSi$: 307.1489.



Methyl 4-(2-hydroxy-1-(trimethylsilyl) butan-2-yl) benzoate
White solid, 524 mg, 71% yield.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.96 (m, 2H), 7.50 – 7.44 (m, 2H), 3.90 (s, 3H), 1.97 – 1.77 (m, 2H), 1.40 – 1.26 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 3H), -0.18 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.07, 153.07, 129.26, 128.05, 125.29, 51.96, 39.36, 33.08, 8.01, 0.02.
HRMS-ESI; *m/z* [M+Na^+] = 303.1391, calcd. For $C_{15}H_{24}NaO_3Si$: 303.1387.



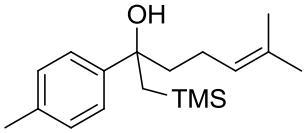
Ethyl (*E*)-3-(3-(2-hydroxy-1-(trimethylsilyl) butan-2-yl)phenyl)acrylate

Colorless oil, 0.774 g, 77%yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 16.0 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.40 (td, *J* = 8.5, 8.0, 3.0 Hz, 2H), 7.36 – 7.30 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 1.87 (tq, *J* = 14.0, 7.3 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 5H), 0.73 (t, *J* = 7.4 Hz, 3H), -0.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 148.48, 145.01, 134.03, 128.47, 127.29, 125.91, 125.07, 118.06, 77.27, 60.45, 39.23, 33.18, 14.33, 8.11, 0.03.

HRMS-ESI; *m/z* [M+Na$^+$] = 343.1697, calcd. For $C_{18}H_{28}NaO_3Si$: 343.1700.

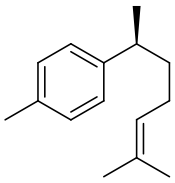


6-Methyl-2-(p-tolyl)-1-(trimethylsilyl)hept-5-en-2-ol

Colorless oil, 99% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 2H), 7.14 – 7.09 (m, 2H), 5.12 – 5.04 (m, 1H), 2.33 (s, 3H), 1.98 – 1.79 (m, 4H), 1.65 (s, 3H), 1.47 (s, 3H), 1.31 (s, 2H), -0.18 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 135.70, 132.27, 128.72, 125.13, 124.50, 46.41, 33.99, 25.88, 23.13, 21.11, 17.83, 0.22.

HRMS-ESI; *m/z* [M+Na$^+$] = 313.1944, calcd. For $C_{18}H_{28}NaO_3Si$: 313.1958.



(+) curmuene

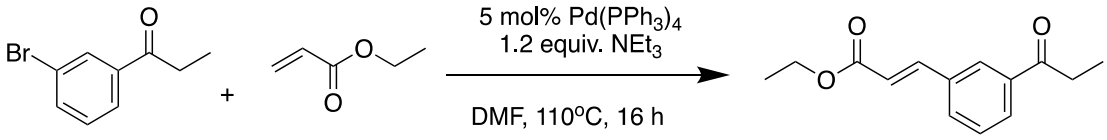
(S)-(+)-curcumene

Colorless oil, 76% yield.

$[\alpha]_D^{24.0}$ =+ 41 (*c* 0.83, $CHCl_3$) (Lit.[S6]: $[\alpha]_D^{20.0}$ =+48 (c. 1.19, $CHCl_3$))

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.05 (m, 4H), 5.17 – 5.06 (m, 1H), 2.76 – 2.59 (m, 1H), 2.35 (s, 3H), 1.97 – 1.82 (m, 2H), 1.70 (s, 3H), 1.67 – 1.57 (m, 2H), 1.56 (s, 3H), 1.25 (dd, *J* = 6.9, 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.06, 135.70, 132.27, 128.72, 125.13, 124.50, 46.41, 33.99, 25.88, 23.13, 21.11, 17.83.

Preparation of Ethyl (E)-3-(3-propionylphenyl)acrylate

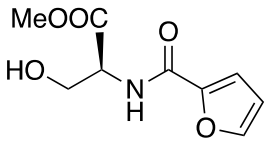


3-Bromo propiopheone (20 mmol) was placed in 100 mL round bottom flask, dissolved in DMF 40 mL. Following by addition of ethyl acrylate (24 mmol), 5 mol% of $Pd(PPh_3)_4$ and triethylamine 24 mmol. The reaction mixture was heated to 110 ^{o}C and was allowed to run for 16 h. The reaction mixture was allowed to cool down

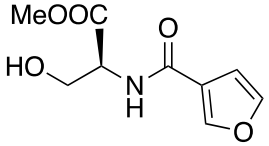
then was diluted with EtOAc. The mixture was added water. The aqoues phase was extracted with EtOAc. The combined organic phase was washed water several times, dried over Na_2SO_4. Removing the solvent under vecum. The crude mixture was purification by column chromatography to yield the desired product. NMR spectra are match with the literature. (Peacock, L. R.; Chapman, R. S. L.; Sedgwick, A. C.; Bull, S. D.; Mahon, M. F.; Amans, D. *Org. Lett*., 2015, 17, 994.)

3. Procedure for synthesis of Iridium complexes and intermediates

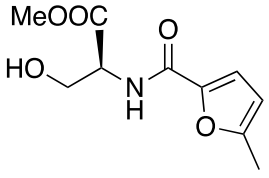
General procedure for the preparation of amides: To a solution of the corresponding acyl chloride (10 mmol) in CH_2Cl_2 (80 mL) was added in one portion the corresponding hydroxyl amino acid (10 mmol). A solution of triethylamine (3.5 mL, 25 mmol) in CH_2Cl_2 (20 mL) was added at 0°C over 30 min. The resulting mixture was stirred at room temperature for 3 h. The solvent was removed in vacuo and the residue purified by chromatography to afford the corresponding amides.



Methyl (furan-2-carbonyl)-*L*-serinate
Colorless oil, 2.04g, 96% yield.
$[\alpha]_D^{22.0}$ =+ 48.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.31 (d, *J* = 7.3 Hz, 1H), 7.12 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.48 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.80 (dt, *J* = 7.4, 3.6 Hz, 1H), 4.02 (ddd, *J* = 30.6, 11.3, 3.6 Hz, 2H), 3.79 (s, 3H), 2.91 (br, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.89, 158.60, 147.25, 144.63, 115.25, 112.33, 63.30, 54.54, 52.94.
HRMS-ESI; *m/z* [M+Na^+] = 236.0534, calcd. For $C_9H_{11}NNaO_5$: 236.0529.

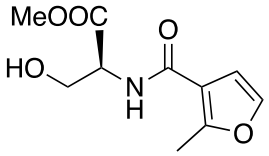


Methyl (furan-3-carbonyl)-*L*-serinate
Colorless oil, 1.98g, 93% yield.
$[\alpha]_D^{22.0}$ =+ 48.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 0.9 Hz, 1H), 7.43 (t, *J* = 1.7 Hz, 1H), 6.86 (d, *J* = 6.9 Hz, 1H), 6.68 (dd, *J* = 1.8, 0.6 Hz, 1H), 4.82 (dt, *J* = 7.3, 3.6 Hz, 1H), 4.06 – 3.94 (m, 2H), 3.80 (s, 3H), 2.95 (t, *J* = 6.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.18, 163.04, 145.52, 144.05, 121.94, 108.47, 63.50, 54.81, 53.02.
HRMS-ESI; *m/z* [M+Na^+] = 236.0534, calcd. For $C_9H_{11}NNaO_5$: 236.0529.

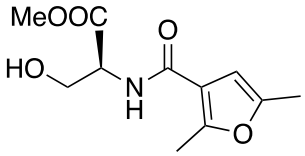


Methyl (5-methylfuran-2-carbonyl)-*L*-serinate
Colorless oil, 2.11g, 93% yield.
$[\alpha]_D^{22.0}$ =+ 56.00 (*c* 0.3, $CHCl_3$)

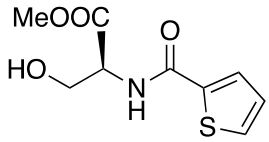
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (d, *J* = 2.0 Hz, 1H), 6.73 (d, *J* = 6.3 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.79 (dt, *J* = 7.3, 3.7 Hz, 1H), 4.07 – 3.94 (m, 2H), 3.80 (s, 3H), 3.02 (t, *J* = 6.0 Hz, 1H), 2.57 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.33, 164.28, 157.66, 140.63, 115.04, 108.66, 63.68, 54.80, 52.97, 13.71.
HRMS-ESI; *m/z* [M+Na$^+$] = 250.0695, calcd. For $C_{10}H_{13}NNaO_5$: 250.0686.



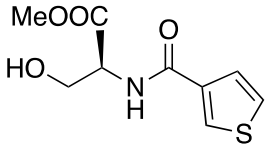
Methyl (2-methylfuran-3-carbonyl)-*L*-serinate
Colorless oil, 2.04g, 90% yield.
$[\alpha]_D^{22.0}$ =+ 42.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 3.4 Hz, 1H), 4.80 (dt, *J* = 7.5, 3.7 Hz, 1H), 4.05 (ddd, *J* = 11.1, 6.1, 3.9 Hz, 2H), 3.79 (s, 3H), 3.11 (t, *J* = 5.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 158.73, 155.37, 145.62, 116.58, 108.78, 63.48, 54.52, 52.91, 13.93.
HRMS-ESI; *m/z* [M+Na$^+$] = 250.0691, calcd. For $C_{10}H_{13}NNaO_5$: 250.0686.



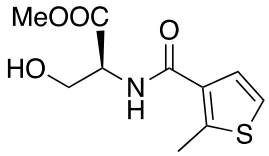
Methyl (2,5-dimethylfuran-3-carbonyl)-*L*-serinate
Colorless oil, 2.05g, 85% yield.
$[\alpha]_D^{22.0}$ =+ 40.67 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.64 (s, 1H), 6.09 (s, 1H), 4.80 – 4.74 (m, 1H), 4.06 – 3.90 (m, 2H), 3.79 (s, 3H), 2.51 (s, 3H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.34, 164.56, 155.95, 150.30, 115.51, 104.29, 63.74, 54.79, 52.92, 13.63, 13.34.
HRMS-ESI; *m/z* [M+Na$^+$] = 264.0843, calcd. For $C_{11}H_{15}NNaO_5$: 264.0842.



Methyl (thiophene-2-carbonyl)-*L*-serinate
Colorless oil, 2.10g, 92% yield.
$[\alpha]_D^{22.0}$ =+ 53.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.50 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.10 – 7.01 (m, 2H), 4.83 (dt, *J* = 7.2, 3.6 Hz, 1H), 4.11 – 3.97 (m, 2H), 3.80 (s, 3H), 2.96 (t, *J* = 5.3 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.12, 162.28, 138.00, 130.95, 129.02, 127.90, 63.46, 55.19, 53.03.
HRMS-ESI; *m/z* [M+Na$^+$] = 252.0302, calcd. For $C_9H_{11}NNaO_4S$: 252.0301.



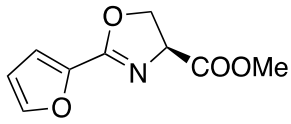
Methyl (thiophene-3-carbonyl)-*L*-serinate
Colorless oil, 2.01g, 87% yield.
$[\alpha]_D^{22.0}$ =+ 45.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.42 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.30 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 4.81 (dt, *J* = 7.3, 3.6 Hz, 1H), 4.09 – 3.93 (m, 2H), 3.78 (s, 3H), 3.30 (t, *J* = 6.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.24, 163.40, 136.50, 129.37, 126.74, 126.30, 63.35, 55.04, 52.95.
HRMS-ESI; *m/z* [M+Na$^+$] = 252.0308, calcd. For $C_9H_{11}NNaO_4S$: 252.0301.



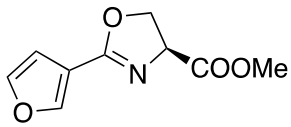
Methyl (2-methylfuran-3-carbonyl)-*L*-serinate

Colorless oil, 2.08 g, 86% yield.
$[\alpha]_D^{22.0}$ =+ 34.67 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 5.4 Hz, 1H), 7.03 (d, *J* = 5.4 Hz, 1H), 6.80 (d, *J* = 6.8 Hz, 1H), 4.82 (dt, *J* = 7.2, 3.6 Hz, 1H), 4.09 – 3.96 (m, 2H), 3.81 (s, 3H), 2.80 (t, *J* = 5.9 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.24, 164.74, 145.73, 131.05, 126.76, 122.15, 63.75, 55.02, 53.00, 15.09.
HRMS-ESI; *m/z* [M+Na^+] = 266.0468, calcd. For $C_{10}H_{13}NNaO_4S$: 266.0457.

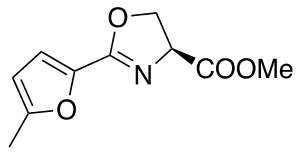
General procedure for the preparation of oxazoline esters:
To a solution of the corresponding amide (10 mmol) in CH_2Cl_2 (40 mL) was added dropwise diethylaminosulfur trifluoride (1.45 mL, 11 mmol) at -78°C. This solution was then stirred at this temperature for 1 h. Anhydrous K_2CO_3 (2.07 g, 15 mmol) was added in one portion and the reaction mixture allowed to warm to room temperature. After 2 h, saturated $NaHCO_3$ (aq) (50 mL) was added and the organic layer separated, dried over Na_2SO_4, filtered and the solvent removed in vacuum. The residue was purified by chromatography to give the desired oxazoline esters.



Methyl (*S*)-2-(furan-2-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 87% yield.
$[\alpha]_D^{22.0}$ =+ 144.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.04 – 6.99 (m, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.93 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.66 (dd, *J* = 8.6, 8.0 Hz, 1H), 4.56 (dd, *J* = 10.4, 8.7 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.39, 158.50, 145.84, 142.31, 115.69, 111.79, 69.80, 68.56, 52.87.
HRMS-ESI; *m/z* [M+Na^+] = 218.0428, calcd. For $C_9H_9NNaO_4$: 218.0424.

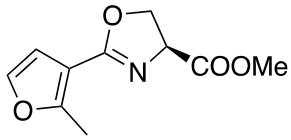


Methyl (*S*)-2-(furan-3-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 93% yield.
$[\alpha]_D^{22.0}$ =+ 146.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.42 (t, *J* = 1.7 Hz, 1H), 6.79 (d, *J* = 1.5 Hz, 1H), 4.87 (dd, *J* = 10.5, 7.9 Hz, 1H), 4.60 (t, *J* = 8.3 Hz, 1H), 4.50 (dd, *J* = 10.5, 8.7 Hz, 1H), 3.79 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 161.68, 145.62, 143.90, 115.00, 109.61, 69.30, 68.44, 52.82.
HRMS-ESI; *m/z* [M+Na^+] = 218.0426, calcd. For $C_9H_9NNaO_4$: 218.0424.

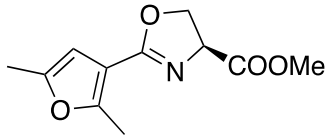


Methyl (*S*)-2-(5-methylfuran-2-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 85% yield.
$[\alpha]_D^{22.0}$ =+ 136.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.91 (d, *J* = 3.3 Hz, 1H), 6.11 – 6.07 (m, 1H), 4.90 (dd, *J* = 10.4, 7.9 Hz, 1H), 4.63 (t, *J* = 8.2 Hz, 1H), 4.53 (dd, *J* = 10.4, 8.6 Hz, 1H), 3.79 (s, 3H), 2.36 (s, 3H).

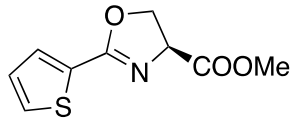
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.57, 158.62, 156.73, 140.62, 117.07, 108.22, 69.70, 68.54, 52.83, 13.99.
HRMS-ESI; *m/z* [M+Na^+] = 232.0585, calcd. For $C_{10}H_{11}NNaO_4$: 232.0580.



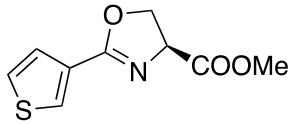
Methyl (*S*)-2-(2-methylfuran-3-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 92% yield.
$[\alpha]_D^{22.0}$ =+ 138.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 7.3 Hz, 1H), 7.02 (d, *J* = 3.4 Hz, 1H), 4.80 (dt, *J* = 7.5, 3.7 Hz, 1H), 4.05 (ddd, *J* = 11.1, 6.1, 3.9 Hz, 2H), 3.79 (s, 3H), 3.11 (t, *J* = 5.9 Hz, 1H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.04, 158.73, 155.37, 145.62, 116.58, 108.78, 63.48, 54.52, 52.91, 13.93.
HRMS-ESI; *m/z* [M+H^+] = 210.0765, calcd. For $C_{10}H_{12}NO_4$: 210.0761.



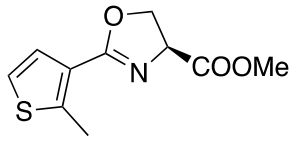
Methyl (*S*)-2-(2,5-dimethylfuran-3-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 94% yield.
$[\alpha]_D^{22.0}$ =+ 140.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.25 (s, 1H), 4.84 (dd, *J* = 10.4, 7.7 Hz, 1H), 4.61 – 4.53 (m, 1H), 4.48 (dd, *J* = 10.4, 8.6 Hz, 1H), 3.79 (s, 3H), 2.49 (s, 3H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.03, 163.00, 154.79, 150.42, 109.97, 106.27, 69.13, 68.26, 52.70, 13.81, 13.28.
HRMS-ESI; *m/z* [M+H^+] = 224.0920, calcd. For $C_{11}H_{14}NO_4$: 224.0917.



Methyl (*S*)-2-(thiophen-2-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 86% yield.
$[\alpha]_D^{22.0}$ =+ 134.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.48 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.08 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.92 (dd, *J* = 10.4, 7.8 Hz, 1H), 4.68 (t, *J* = 8.2 Hz, 1H), 4.58 (dd, *J* = 10.4, 8.6 Hz, 1H), 3.81 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.56, 162.11, 131.46, 130.80, 129.38, 127.79, 70.04, 68.77, 52.87.
HRMS-ESI; *m/z* [M+Na^+] = 234.0916, calcd. For $C_9H_9NNaO_3S$: 234.0195.



Methyl (*S*)-2-(thiophen-3-yl)-4,5-dihydrooxazole-4-carboxylate
Colorless oil, 91% yield.
$[\alpha]_D^{22.0}$ = + 128.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.57 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.34 (dd, *J* = 5.1, 3.0 Hz, 1H), 4.94 (dd, *J* = 10.5, 7.9 Hz, 1H), 4.67 (dd, *J* = 8.6, 7.9 Hz, 1H), 4.57 (dd, *J* = 10.5, 8.7 Hz, 1H), 3.83 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70, 162.67, 129.90, 129.20, 127.51, 126.37, 69.46, 68.66, 52.85.
HRMS-ESI; *m/z* [M+H^+] = 212.0372, calcd. For $C_9H_{10}NO_3S$: 212.0376.



Methyl (*S*)-2-(2-methylthiophen-3-yl)-4,5-dihydrooxazole-4-carboxylate

Colorless oil, 89% yield.

$[\alpha]_D^{22.0} =$ + 118.67 (*c* 0.3, $CHCl_3$)

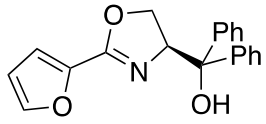
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.20 (d, *J* = 5.4 Hz, 1H), 7.03 (d, *J* = 5.4 Hz, 1H), 6.80 (d, *J* = 6.8 Hz, 1H), 4.82 (dt, *J* = 7.2, 3.6 Hz, 1H), 4.09 – 3.96 (m, 2H), 3.81 (s, 3H), 2.80 (t, *J* = 5.9 Hz, 1H), 2.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.24, 164.74, 145.73, 131.05, 126.76, 122.15, 63.75, 55.02, 53.00, 15.09.

HRMS-ESI; *m/z* [M+Na^+] = 248.0364, calcd. For $C_{10}H_{11}NNaO_3S$: 248.0352.

General procedure for the reduction of the oxazoline esters with Grignard reagents:

To a solution of the corresponding oxazoline ester (10 mmol) in THF/diethyl ether 1:1 (50 mL) was added dropwise a solution of the Grignard reagent in THF (22 mmol) at 0°C. The mixture was then stirred for 3 h, allowed to warm to room temperature and stirred overnight. The reaction was quenched with saturated NH_4Cl aq. (50 mL) and followed by the addition of additional diethyl ether (40 mL) and water (40 mL). The organic layer was separated, washed with water, dried over Na_2SO_4, filtered and the solvent removed in vacuo. The residue was purified by chromatography to give the desired tertiary oxazoline alcohols.



(*S*)-(2-(Furan-2-yl)-4,5-dihydrooxazol-4-yl) diphenylmethanol

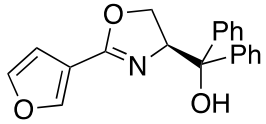
White solid, 87% yield.

$[\alpha]_D^{22.0} =$ - 74.00 (*c* 0.3, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.61 (m, 2H), 7.54 – 7.50 (m, 1H), 7.48 – 7.42 (m, 2H), 7.32 (dt, *J* = 11.7, 7.7 Hz, 4H), 7.25 – 7.17 (m, 2H), 6.97 (d, *J* = 3.4 Hz, 1H), 6.47 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.52 (t, *J* = 9.5 Hz, 1H), 4.29 – 4.14 (m, 2H), 2.63 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 145.79, 145.63, 144.22, 142.72, 128.48, 128.45, 127.26, 127.04, 125.75, 115.42, 111.73, 78.23, 73.22, 69.41.

HRMS-ESI; *m/z* [M+Na^+] = 342.1101, calcd. For $C_{20}H_{17}NNaO_3$: 342.1101.



(*S*)-(2-(Furan-3-yl)-4,5-dihydrooxazol-4-yl) diphenylmethanol

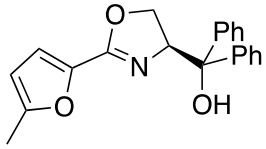
White solid, 90% yield.

$[\alpha]_D^{22.0} =$ - 47.00 (*c* 0.3, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 0.5 Hz, 1H), 7.69 – 7.62 (m, 2H), 7.49 – 7.44 (m, 2H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.37 – 7.28 (m, 4H), 7.28 – 7.18 (m, 2H), 6.74 (dd, *J* = 1.9, 0.7 Hz, 1H), 5.44 (t, *J* = 9.4 Hz, 1H), 4.22 – 4.11 (m, 2H), 2.66 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.07, 146.05, 145.49, 144.24, 143.70, 128.46, 128.35, 127.23, 127.06, 127.04, 125.82, 115.47, 109.80, 78.26, 73.07, 69.04.

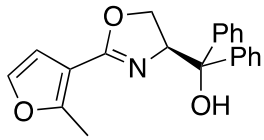
HRMS-ESI; *m/z* [M+H^+] = 320.1278, calcd. For $C_{20}H_{18}NO_3$: 320.1281.



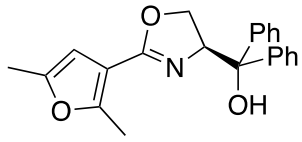
(*S*)-(2-(5-methylfuran-2-yl)-4,5-dihydrooxazol-4-yl)diphenylmethanol

White solid, 83% yield.

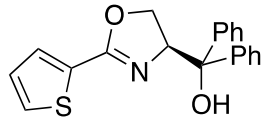
$[\alpha]_D^{22.0}$ = - 95.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.46 (dd, J = 5.2, 3.4 Hz,2H), 7.37 – 7.26 (m, 4H), 7.26 – 7.17 (m, 2H), 6.88 (d, J = 3.3 Hz, 1H), 6.08 (dd, J = 3.3, 0.9 Hz, 1H), 5.50 (t, J = 9.4 Hz, 1H), 4.19 (m, 2H), 2.64 (s, 1H), 2.35 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 156.36, 145.94, 144.29, 141.07, 128.45, 128.40, 127.22, 127.09, 127.00, 125.75, 116.82, 108.19, 78.25, 73.24, 69.20, 14.03.
HRMS-ESI; *m/z* [M+H$^+$] = 334.1440, calcd. For $C_{21}H_{20}NO_3$: 334.1438.



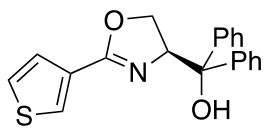
(*S*)-(2-(2-methylfuran-3-yl)-4,5-dihydrooxazol-4-yl)diphenylmethanol
White solid, 92% yield.
$[\alpha]_D^{22.0}$ = - 41.67 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.25 – 7.19 (m, 3H), 6.62 (d, *J* = 1.8 Hz, 1H), 5.40 (t, *J* = 9.4 Hz, 1H), 4.21 – 4.11 (m, 2H), 2.63 (s, 1H), 2.51 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.14, 156.39, 146.22, 144.36, 140.64, 128.41, 128.23, 127.21, 127.13, 127.01, 125.91, 110.80, 109.97, 78.29, 73.02, 68.87, 13.86.
HRMS-ESI; *m/z* [M+H$^+$] = 334.1447, calcd. For $C_{21}H_{20}NO_3$: 334.1438.



(*S*)-(2-(2,5-dimethylfuran-3-yl)-4,5-dihydrooxazol-4-yl)diphenylmethanol
White foam, 95% yield.
$[\alpha]_D^{22.0}$ = - 43.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.62 (m, 2H), 7.48 – 7.42 (m, 2H), 7.35 – 7.27 (m, 4H), 7.25 – 7.18 (m, 2H), 6.19 (d, *J* = 0.8 Hz, 1H), 5.38 (t, *J* = 9.3 Hz, 1H), 4.17 – 4.10 (m, 2H), 2.62 (s, 1H), 2.45 (s, 3H), 2.22 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 154.64, 150.27, 146.30, 144.39, 128.40, 128.22, 127.20, 127.09, 126.98, 125.92, 110.38, 106.38, 78.28, 72.96, 68.80, 13.81, 13.32.
HRMS-ESI; *m/z* [M+H$^+$] = 348.1600, calcd. For $C_{22}H_{22}NO_3$: 348.1594.

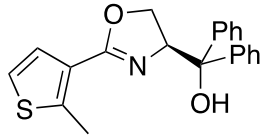


(*S*)-diphenyl(2-(thiophen-2-yl)-4,5-dihydrooxazol-4-yl)methanol
White solid, 86% yield.
$[\alpha]_D^{22.0}$ = - 71.33 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.4 Hz, 2H), 7.62 (dd, *J* = 3.6, 0.8 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.33 (dt, *J* = 14.0, 7.6 Hz, 4H), 7.28 – 7.19 (m, 2H), 7.06 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.47 (t, *J* = 9.4 Hz, 1H), 4.30 – 4.18 (m, 2H), 2.68 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.32, 145.95, 144.26, 131.11, 130.34, 130.06, 128.45, 128.31, 127.70, 127.22, 127.18, 127.05, 125.88, 78.33, 73.48, 69.73.
HRMS-ESI; *m/z* [M+H$^+$] = 336.1058, calcd. For $C_{20}H_{18}NO_2S$: 336.1053.



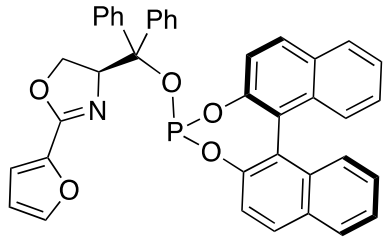
(*S*)-diphenyl(2-(thiophen-3-yl)-4,5-dihydrooxazol-4-yl)methanol
White solid, 90% yield.
$[\alpha]_D^{22.0}$ = - 62.67 (*c* 0.3, $CHCl_3$)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.52 – 7.44 (m, 3H), 7.38 – 7.19 (m, 7H), 5.47 (t, *J* = 9.4 Hz, 1H), 4.27 – 4.15 (m, 2H), 2.62 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.07, 146.13, 144.26, 129.83, 129.55, 128.46, 128.33, 127.69, 127.21, 127.10, 127.04, 126.13, 125.85, 78.32, 73.27, 69.20.
HRMS-ESI; *m/z* [M+H$^+$] = 336.1043, calcd. For $C_{20}H_{18}NO_2S$: 336.1053.



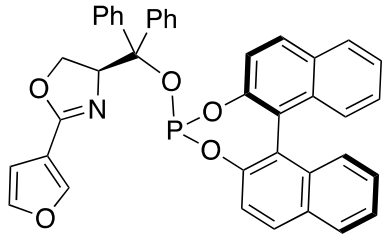
(*S*)-(2-(2-methylthiophen-3-yl)-4,5-dihydrooxazol-4-yl)diphenylmethanol
White solid, 87% yield.
$[\alpha]_D^{22.0}$ = - 56.00 (*c* 0.3, $CHCl_3$)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.47 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.26 – 7.19 (m, 2H), 6.98 (d, *J* = 5.4 Hz, 1H), 5.43 (t, *J* = 9.4 Hz, 1H), 4.24 – 4.11 (m, 2H), 2.66 (s, 3H), 2.60 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.85, 146.25, 145.65, 144.34, 129.00, 128.42, 128.20, 127.28, 127.13, 127.03, 125.98, 125.02, 121.51, 78.34, 73.30, 68.69, 15.57.
HRMS-ESI; *m/z* [M+H$^+$] = 350.1214, calcd. For $C_{21}H_{20}NO_2S$: 350.1209.

General procedure for the preparation of the phosphite–oxazoline ligands:
To a solution of PCl_3 (0.3 mL, 2.5 mmol) and pyridine (0.5 mL, 5.8 mmol) in toluene (5 mL) was added the solution of Binol (172 mg, 0.6 mmol) and pyridine (0.5 mL, 5.8 mmol) in toluene (5 mL) at 0 °C under argon, the resulting mixture was stirred at 0 °C for 30 min and then stirred overnight at 80 °C. The reaction was cooled to room temperature and the pyridine salt was removed by filtration under argon, evaporation of the solvent gave the phosphorochloridite as a white foam, which was used directly for next step without purification. The corresponding phosphorochloridite was dissolved in toluene (5 mL) and pyridine (0.5 mL, 5.8 mmol) was added. The corresponding hydroxyl-oxazoline compound (0.5 mmol) was azeotropically dried with toluene and then dissolved in toluene (5.0 mL) to which pyridine (0.5 mL, 5.8 mmol) was added. The oxazoline solution was transferred slowly at 0 °C to the solution of phosphorochloridite. The reaction mixture was stirred overnight at 80 °C, and the pyridine salts were removed by filtration. Evaporation of the solvent gave a white foam, which was purified by flash chromatography on neutral alumina eluting with 1 % triethylamine in toluene to produce the corresponding ligand.

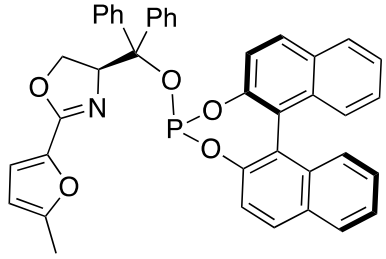


(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)diphenylmethyl)-2-(furan-2-yl)-4,5-dihydrooxazole
Pale yellow solid, 0.199 g, 63% yield.
$[\alpha]_D^{22.0}$ = + 79.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.79.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.74 (q, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.39 (m, 3H), 7.31 – 7.15 (m, 6H), 7.14 – 6.94 (m, 3H), 6.94 – 6.80 (m, 7H), 5.79 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.31 (t, *J* = 9.3 Hz, 1H), 4.37 (t, *J* = 8.6 Hz, 1H), 3.86 (t, *J* = 9.4 Hz, 1H).

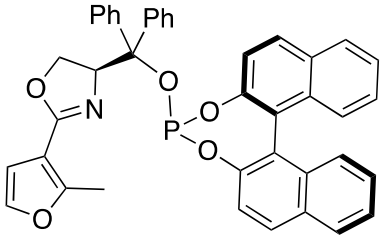
^{13}C NMR (100 MHz, Toluene-d_8): δ 159.37, 149.44, 149.39, 148.51, 148.49, 145.30, 144.47, 144.02, 143.60, 133.40-122.27 (other aromatic carbons), 115.31, 111.54, 86.03 (d, *J* = 7.9 Hz), 73.45, 69.26.
HRMS-ESI; *m/z* [M+Na$^+$] = 656.1590, calcd. For $C_{40}H_{28}NNaO_5P$: 656.1597.



(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(furan-3-yl)-4,5-dihydrooxazole
White solid, 0.208 g, 66% yield
$[\alpha]_D^{22.0}$ = +197.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.77.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.88 (d, *J* = 7.7 Hz, 2H), 7.77 (s, 1H), 7.70 (q, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.41 (m, 3H), 7.29 (d, *J* = 8.5 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 5H), 7.14 – 6.94 (m, 3H), 6.91 – 6.80 (m, 5H), 6.70 (dt, *J* = 3.4, 1.6 Hz, 2H), 5.28 (t, *J* = 9.3 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 3.83 (dd, *J* = 10.0, 8.8 Hz, 1H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 162.45, 149.41, 149.36, 148.52, 145.22, 144.52, 143.78, 133.40-122.27 (other aromatic carbons), 116.72, 110.19, 86.00 (d, *J* = 7.6 Hz), 73.15, 69.03.
HRMS-ESI; *m/z* [M+Na$^+$] = 656.1591, calcd. For $C_{40}H_{28}NNaO_5P$: 656.1597.

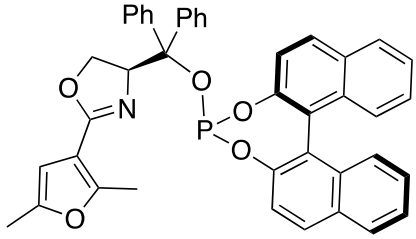


(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(5-methylfuran-2-yl)-4,5-dihydrooxazole
Pale yellow solid, 0.171 g, 53% yield.
$[\alpha]_D^{22.0}$ = + 35.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.76.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.76 (dd, *J* = 27.3, 8.8 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.40 (m, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.19 (dd, *J* = 12.4, 5.5 Hz, 2H), 7.13 – 6.92 (m, 7H), 6.90 – 6.78 (m, 5H), 5.54 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.34 (t, *J* = 9.3 Hz, 1H), 4.39 (t, *J* = 8.6 Hz, 1H), 3.89 (t, *J* = 9.3 Hz, 1H), 1.71 (s, 3H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 159.44, 155.99, 149.49, 149.44, 148.55, 148.53, 144.57, 142.46, 137.79, 133.39-122.30 (other aromatic carbons), 116.68, 108.17, 86.06(d, *J*=7.8 Hz), 73.53, 69.10, 13.27.
HRMS-ESI; *m/z* [M+H$^+$] = 648.1933, calcd. For $C_{41}H_{31}NO_5P$: 648.1934.

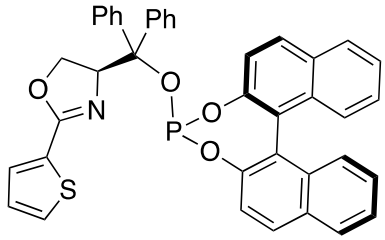


(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(2-methylfuran-3-yl)-4,5-dihydrooxazole
White solid, 0.213 g, 66% yield.
$[\alpha]_D^{22.0}$ = + 144.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.53.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.90 (d, *J* = 7.5 Hz, 2H), 7.71 (q, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.39 (m, 3H), 7.32 – 7.18 (m, 6H), 7.15 – 6.98 (m, 3H), 6.92

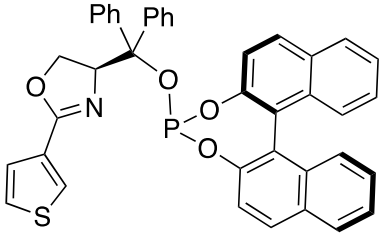
– 6.79 (m, 5H), 6.72 (dd, *J* = 4.5, 1.9 Hz, 2H), 5.29 (t, *J* = 9.3 Hz, 1H), 4.33 (t, *J* = 8.6 Hz, 1H), 3.83 (t, *J* = 9.4 Hz, 1H), 2.51 (s, 3H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 163.52, 156.94, 149.46, 149.41, 148.53, 144.63, 140.64, 133.41-122.29 (other aromatic carbons) 110.91, 86.04(d, *J*=7.7 Hz), 73.24, 68.62, 13.75.
HRMS-ESI; *m/z* [M+H$^+$] = 648.1926, calcd. For $C_{41}H_{31}NO_5P$: 648.1934.



(4*S*)-2-(2,5-dimethylfuran-3-yl)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)diphenylmethyl)-4,5-dihydrooxazole
Pale yellow solid, 0.237 g, 72% yield.
$[\alpha]_D^{22.0}$ = + 130.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.50.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.74 (s, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.40 (m, 3H), 7.29 – 7.17 (m, 6H), 7.13 – 6.99 (m, 3H), 6.91 – 6.77 (m, 5H), 6.38 (s, 1H), 5.30 (t, *J* = 9.4 Hz, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 3.84 (dd, *J* = 10.0, 8.7 Hz, 1H), 2.54 (s, 3H), 1.75 (s, 3H).
^{13}C NMR (100 MHz, Toluene-d_8) 163.84, 155.18, 150.18, 149.52, 149.47, 148.60, 144.72, 133.42-122.31 (other aromatic carbons), 111.37, 106.84, 86.07(d, *J*=7.5 Hz), 73.19, 68.57, 13.83, 12.85.
HRMS-ESI; *m/z* [M+H$^+$] = 662.2093, calcd. For $C_{42}H_{33}NO_5P$: 662.2091.

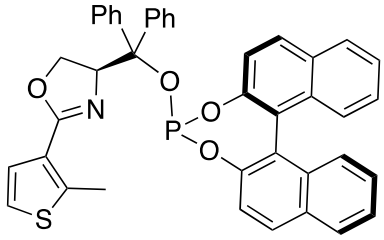


(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(thiophen-2-yl)-4,5-dihydrooxazole
Pale yellow solid, 0.201 g, 62% yield.
$[\alpha]_D^{22.0}$ = + 117.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.89.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.67 – 7.60 (m, 2H), 7.53 – 7.39 (m, 3H), 7.30 – 7.15 (m, 6H), 7.13 – 6.94 (m, 11H), 6.92 – 6.76 (m, 5H), 6.64 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.45 (dd, *J* = 4.9, 3.8 Hz, 1H), 5.32 (dd, *J* = 9.7, 8.8 Hz, 1H), 4.41 (t, *J* = 8.5 Hz, 1H), 3.89 (dd, *J* = 9.9, 8.8 Hz, 1H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 162.86, 149.41, 149.36, 148.50, 148.48, 144.44, 133.37-122.26 (other aromatic carbons), 86.06(d, *J*=7.6 Hz), 73.49, 69.70.
HRMS-ESI; *m/z* [M+H$^+$] = 650.1547, calcd. For $C_{40}H_{29}NO_4PS$: 650.1549.



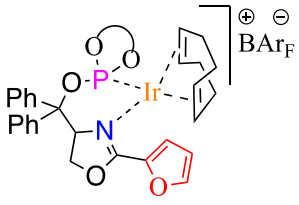
(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(thiophen-3-yl)-4,5-dihydrooxazole
Pale yellow solid, 0.223 g, 69% yield.
$[\alpha]_D^{22.0}$ = + 71.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.87.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.88 (d, *J* = 7.5 Hz, 2H), 7.76 – 7.62 (m, 4H), 7.55 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.22 (ddd, *J* = 15.6, 8.1, 3.5 Hz, 6H), 7.14

– 6.95 (m, 3H), 6.93 – 6.77 (m, 5H), 6.54 (dd, *J* = 5.1, 3.0 Hz, 1H), 5.31 (dd, *J* = 9.9, 8.8 Hz, 1H), 4.37 (t, *J* = 8.7 Hz, 1H), 3.87 (dd, *J* = 10.1, 8.7 Hz, 1H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 163.48, 149.40, 149.35, 148.52, 148.50, 144.54, 143.86, 137.79, 133.40-122.24 (other aromatic carbons), 86.03 (d, *J* = 7.6 Hz), 73.31, 69.19.
HRMS-ESI; *m/z* [M+H$^+$] = 650.1541, calcd. For $C_{40}H_{29}NO_4PS$: 650.1549.



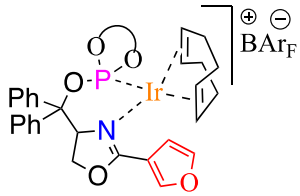
(4*S*)-4-((((11b*S*)-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy) diphenylmethyl)-2-(2-methylthiophen-3-yl)-4,5-dihydrooxazole
Pale yellow solid, 0.251 mg, 76% yield.
$[\alpha]_D^{22.0}$ = + 110.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR (162 MHz, Toluene-d_8) δ 150.43.
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.90 (d, *J* = 7.4 Hz, 2H), 7.74 – 7.60 (m, 3H), 7.54 – 7.39 (m, 4H), 7.22 (dt, *J* = 8.5, 7.4 Hz, 6H), 7.15 – 6.94 (m, 3H), 6.91 – 6.77 (m, 5H), 6.44 (d, *J* = 5.4 Hz, 1H), 5.29 (t, *J* = 9.5 Hz, 1H), 4.33 (t, *J* = 8.7 Hz, 1H), 3.82 (dd, *J* = 10.1, 8.7 Hz, 1H), 2.71 (s, 3H).
^{13}C NMR (100 MHz, Toluene-d_8) δ 164.13, 149.42, 149.37, 148.50, 146.28, 144.63, 137.79, 133.40-121.35 (other aromatic carbons), 86.02 (d, *J* = 7.6 Hz), 73.56, 68.34, 15.70, 15.67.
HRMS-ESI; *m/z* [M+H$^+$] = 664.1713, calcd. For $C_{41}H_{31}NO_4PS$: 664.1706.

Typical procedure for the preparation of [Ir(cod)(L)]-BArF.
The corresponding ligand (0.116 mmol) was dissolved in CH_2Cl_2 (2 mL) and $[Ir(COD)Cl]_2$ (38 mg, 0.058 mmol) was added. The reaction was refluxed at 50 °C for 1 h. After 5 min at room temperature, NaBArF (114 mg, 0.128 mmol) and water (2 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were filtered through a Celite plug, dried with Na_2SO_4 and the solvent was evaporated to give the product as an orange solid.

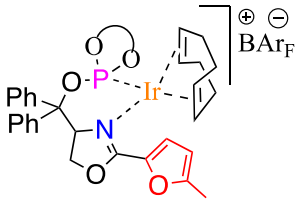


[Ir(cod)(L1a)]BArF.
Orange solid, 0.198 g, 95% yield.
$[\alpha]_D^{22.0}$ = + 60.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.12.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (t, *J* = 8.2 Hz, 2H), 7.97 (dd, *J* = 8.5, 3.5 Hz, 2H), 7.80 – 7.68 (m, 11H), 7.62 – 7.47 (m, 9H), 7.36(m, 5H), 7.17 (m, 4H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 6.1, 2.5 Hz, 2H), 6.21 – 6.18 (m, 1H), 5.93 (t, *J* = 10.7 Hz, 1H), 5.51 – 5.40 (m, 1H), 5.36 – 5.30 (m, 1H), 4.46 (t, *J* = 9.8 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.97 – 3.86 (m, 1H), 3.36 – 3.29 (m, 1H), 2.37 (s, 3H), 2.21 – 1.78 (m, 6H), 1.67 – 1.47 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.41, 161.84 (q, *J* = 49.8 Hz), 149.44, 146.49, 146.41, 146.27, 146.15, 144.00, 139.41, 139.33, 138.67, 134.95, 132.70-119.40 (other aromatic carbons), 117.61, 113.49, 103.72, 103.55, 102.12, 101.96, 88.32, 71.29,

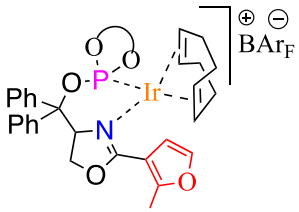
70.31, 63.36, 61.04, 33.05 (d, *J* = 3.8 Hz), 31.40 (d, *J* = 3.6 Hz), 28.29 (d, *J* = 2.6 Hz), 27.74 (d, *J* = 1.8 Hz).
HRMS-ESI; *m/z* $[C_{48}H_{40}IrNO_5P]^+$= 934.2269, calcd. For $[C_{48}H_{40}IrNO_5P]^+$: 934.2271.



[Ir(cod)(L1a)]BArF.
Orange solid, 0.179 g, 86% yield.
$[\alpha]_D^{22.0}$ = + 53.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.70.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 0.5 Hz, 1H), 8.10 – 8.02 (m, 2H), 7.97 (dd, *J* = 8.6, 3.3 Hz, 2H), 7.75 (dd, *J* = 12.2, 4.8 Hz, 10H), 7.64 – 7.50 (m, 9H), 7.47 – 7.33 (m, 5H), 7.21 – 7.13 (m, 5H), 7.05 (dd, *J* = 8.8, 0.8 Hz, 1H), 6.93 – 6.84 (m, 2H), 5.91 (dd, *J* = 11.9, 10.1 Hz, 1H), 5.36 – 5.24 (m, 1H), 5.02 – 4.88 (m, 1H), 5.01 – 4.91 (m, 1H), 4.43 (t, *J* = 10.0 Hz, 1H), 4.28 (dd, *J* = 12.0, 10.0 Hz, 1H), 3.91 (dt, *J* = 9.9, 3.4 Hz, 1H), 3.43 – 3.32 (m, 1H), 2.16 – 1.92 (m, 3H), 1.77 (dt, *J* = 22.9, 11.8 Hz, 4H), 1.54 – 1.41 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.62, 161.83 (q, *J* = 49.9 Hz), 149.46, 146.36, 144.99, 143.84, 143.80, 139.14, 139.06, 134.96, 132.02-119.23 (other aromatic carbons), 117.65, 117.61, 117.58, 111.92, 110.66, 102.88, 102.72, 101.07, 100.90, 88.27, 88.24, 71.38, 69.87, 64.68, 62.06, 33.49 (d, *J* = 3.9 Hz), 31.22 (d, *J* = 3.9 Hz), 28.14 (d, *J* = 2.9 Hz), 27.64 (d, *J* = 2.7 Hz).
HRMS-ESI; *m/z* $[C_{48}H_{40}IrNO_5P]^+$= 934.2291, calcd. For $[C_{48}H_{40}IrNO_5P]^+$: 934.2271.

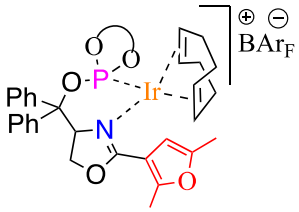


[Ir(cod)(L1a)]BArF.
Orange solid, 0.192 g, 92% yield.
$[\alpha]_D^{22.0}$ = + 48.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.12.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (t, *J* = 8.2 Hz, 2H), 7.97 (dd, *J* = 8.5, 3.5 Hz, 2H), 7.80 – 7.68 (m, 11H), 7.62 – 7.47 (m, 9H), 7.36 (m, 5H), 7.17 (m, 4H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 6.1, 2.5 Hz, 2H), 6.21 – 6.18 (m, 1H), 5.93 (t, *J* = 10.7 Hz, 1H), 5.51 – 5.40 (m, 1H), 5.36 – 5.30 (m, 1H), 4.46 (t, *J* = 9.8 Hz, 1H), 4.32 – 4.23 (m, 1H), 3.97 – 3.86 (m, 1H), 3.36 – 3.29 (m, 1H), 2.37 (s, 3H), 2.21 – 1.78 (m, 6H), 1.67 – 1.47 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.27, 161.85 (q, *J* = 49.8 Hz), 146.61, 146.53, 146.36, 146.24, 144.08, 144.05, 139.58, 139.50, 137.11, 134.97-117.60 (other aromatic carbons), 110.57, 103.38, 103.20, 102.46, 102.30, 88.31, 71.06, 70.30, 63.14, 61.05, 34.23 (d, *J* = 4.0 Hz), 30.61 (d, *J* = 3.5 Hz), 28.16 (d, *J* = 2.3 Hz), 27.49 (d, *J* = 2.8 Hz), 14.30.
HRMS-ESI; *m/z* $[C_{49}H_{42}IrNO_5P]^+$= 948.2444, calcd. For $[C_{49}H_{42}IrNO_5P]^+$: 948.2428.

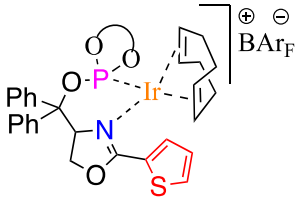


[Ir(cod)(L1a)]BArF.
Orange solid, 0.196 g, 94% yield.
$[\alpha]_D^{22.0}$ = + 58.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.56.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (t, *J* = 9.0 Hz, 2H), 7.97 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.83 (d, *J* = 2.0 Hz, 1H), 7.78 – 7.69 (m, 10H), 7.61 – 7.48 (m, 9H), 7.43 – 7.34 (m, 4H), 7.21 – 7.14 (m, 4H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.92 – 6.86 (m, 2H), 5.89 (dd, *J* = 12.2, 9.8 Hz, 1H), 5.34 – 5.25 (m, 1H),

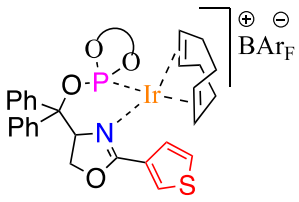
4.97 – 4.87 (m, 1H), 4.51 (t, *J* = 9.8 Hz, 1H), 4.30 (dd, *J* = 12.2, 9.9 Hz, 1H), 3.94 – 3.86 (m, 1H), 3.40 – 3.32 (m, 1H), 2.49 (s, 3H), 2.15 – 1.93 (m, 3H), 1.87 – 1.63 (m, 4H), 1.52 – 1.40 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.26, 161.85 (q, *J* = 49.8 Hz), 146.61, 146.53, 146.37, 146.25, 144.09, 144.05, 139.58, 139.50, 137.12, 134.96, 132.71-119.50 (other aromatic carbons), 117.61, 117.57, 110.57, 103.38, 103.21, 102.47, 102.31, 88.29, 71.07, 70.31, 63.15, 61.05, 34.24 (d, *J* = 4.1 Hz), 30.62 (d, *J* = 3.2 Hz), 28.16 (d, *J* = 2.3 Hz), 27.49 (d, *J* = 2.5 Hz), 14.30.
HRMS-ESI; *m/z* $[C_{49}H_{42}IrNO_5P]^+$= 948.2443, calcd. For $[C_{49}H_{42}IrNO_5P]^+$: 948.2428.



[Ir(cod)(L1a)]BArF.
Orange solid, 0.205 g, 97% yield.
$[\alpha]_D^{22.0}$ = + 57.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.42.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.96 (m, 4H), 7.73 (s, 10H), 7.62 – 7.47 (m, 10H), 7.44 – 7.35 (m, 4H), 7.22 – 7.10 (m, 5H), 6.94 – 6.85 (m, 2H), 5.87 (dd, *J* = 12.2, 9.8 Hz, 1H), 5.35 – 5.27 (m, 1H), 5.00 – 4.92 (m, 1H), 4.48 (t, *J* = 9.8 Hz, 1H), 4.27 (dd, *J* = 12.2, 9.9 Hz, 1H), 3.96 – 3.87 (m, 1H), 3.39 – 3.31 (m, 1H), 2.45 (s, 3H), 2.22 (s, 3H), 2.08 – 1.73 (m, 6H), 1.71 – 1.60 (m, 1H), 1.52 – 1.41 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.70, 161.70 (q, *J* = 49.9 Hz), 160.96, 159.57, 151.84, 146.57, 146.49, 146.36, 146.24, 143.84, 139.35, 139.27, 134.83, 132.65-119.42 (other aromatic carbons), 117.45, 108.24, 106.91, 103.00, 102.83, 101.50, 101.33, 87.75, 71.48, 69.21, 64.13, 61.11, 33.47 (d, *J* = 3.9 Hz), 30.97 (s), 27.85 (d, *J* = 2.3 Hz), 27.74 (d, *J* = 1.0 Hz), 14.29, 13.07.
HRMS-ESI; *m/z* $[C_{50}H_{44}IrNO_5P]^+$= 962.2569, calcd. For $[C_{50}H_{44}IrNO_5P]^+$: 962.2584.



[Ir(cod)(L1a)]BArF.
Orange solid, 0.191 g, 91% yield.
$[\alpha]_D^{22.0}$ = + 48.00 (*c* 0.1, $CHCl_3$)
^{31}P NMR ($CDCl_3$, 162 MHz): δ 112.67.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 3.9, 1.2 Hz, 1H), 8.06 – 7.94 (m, 4H), 7.81 – 7.67 (m, 11H), 7.62 – 7.47 (m, 9H), 7.42 – 7.30 (m, 4H), 7.22 – 7.15 (m, 4H), 7.12 (dd, *J* = 4.9, 3.9 Hz, 1H), 7.01 (dd, *J* = 8.8, 0.9 Hz, 1H), 6.89 (dd, *J* = 6.8, 2.9 Hz, 2H), 5.98 (dd, *J* = 11.6, 10.1 Hz, 1H), 5.45 – 5.36 (m, 1H), 4.93 – 4.84 (m, 1H), 4.56 – 4.48 (m, 1H), 4.31 (dd, *J* = 11.6, 10.0 Hz, 1H), 4.16 – 4.08 (m, 1H), 3.57 – 3.48 (m, 1H), 2.32 – 2.22 (m, 1H), 2.12 – 2.02 (m, 1H), 1.98 – 1.82 (m, 3H), 1.77 – 1.61 (m, 2H), 1.51 – 1.40 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.47, 161.84 (q, *J* = 49.9 Hz), 146.52, 146.43, 146.40, 146.28, 144.08, 144.05, 139.50, 139.42, 137.55, 136.82, 134.96, 132.73-119.32 (other aromatic carbons), 117.61, 117.58, 102.80, 102.64, 102.39, 102.21, 88.75, 71.82, 70.36, 65.89, 63.46, 34.33 (d, *J* = 4.7 Hz), 30.50 (d, *J* = 3.3 Hz), 28.31 (d, *J* = 1.9 Hz), 27.41 (d, *J* = 3.1 Hz).
HRMS-ESI; *m/z* $[C_{48}H_{40}IrNO_4PS]^+$= 950.2039, calcd. For $[C_{48}H_{40}IrNO_4PS]^+$: 950.2041.



[Ir(cod)(L1a)]BArF.
Orange solid, 0.198 g, 94% yield.

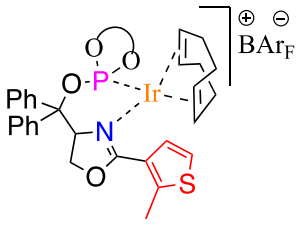
$[\alpha]_D^{22.0}$ = + 62.00 (*c* 0.1, $CHCl_3$)

^{31}P NMR ($CDCl_3$, 162 MHz): δ 113.08.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.86 (dd, *J* = 3.0, 1.1 Hz, 1H), 8.04 (dd, *J* = 8.5, 5.8 Hz, 2H), 7.98 (dd, *J* = 8.6, 3.9 Hz, 2H), 7.92 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.81 – 7.68 (m, 10H), 7.63 – 7.48 (m, 9H), 7.44 – 7.33 (m, 5H), 7.18 (dd, *J* = 7.5, 2.8 Hz, 4H), 7.07 (d, *J* = 8.8 Hz, 1H), 6.89 (dd, *J* = 6.7, 2.9 Hz, 2H), 5.94 (dd, *J* = 12.4, 9.9 Hz, 1H), 5.33 – 5.23 (m, 1H), 4.82 – 4.68 (m, 1H), 4.45 (t, *J* = 9.9 Hz, 1H), 4.31 (dd, *J* = 12.4, 10.0 Hz, 1H), 3.98 – 3.88 (m, 1H), 3.42 (td, *J* = 7.1, 3.3 Hz, 1H), 2.18 – 1.87 (m, 3H), 1.75 (dd, *J* = 21.2, 11.8 Hz, 4H), 1.52 – 1.39 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.58, 161.84 (q, *J* = 50.0 Hz), 146.53, 146.45, 146.37, 146.25, 143.92, 143.88, 139.25, 139.17, 135.79, 134.97, 132.74-119.34 (other aromatic carbons), 117.62, 103.18, 103.02, 101.75, 101.58, 88.12, 71.63, 69.93, 64.79, 61.63, 33.32 (d, *J* = 4.1 Hz), 31.40 (d, *J* = 3.8 Hz), 28.23 (d, *J* = 2.9 Hz), 27.62 (d, *J* = 2.2 Hz).

HRMS-ESI; *m/z* $[C_{48}H_{40}IrNO_4PS]^+$= 950.2027, calcd. For $[C_{48}H_{40}IrNO_4PS]^+$: 950.2041.



[Ir(cod)(L1a)]BArF.

Orange solid, 0.195 g, 92% yield.

$[\alpha]_D^{22.0}$ = + 61.00 (*c* 0.1, $CHCl_3$)

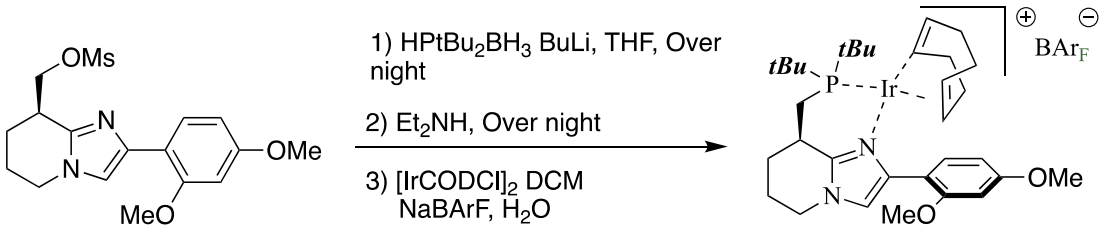
^{31}P NMR ($CDCl_3$, 162 MHz): δ 112.73.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 5.5 Hz, 1H), 8.06 (dd, *J* = 12.6, 8.6 Hz, 2H), 7.98 (d, *J* = 8.9 Hz, 2H), 7.73 (s, 10H), 7.64 – 7.47 (m, 9H), 7.45 – 7.34 (m, 4H), 7.22 – 7.14 (m, 5H), 7.07 (d, *J* = 5.4 Hz, 1H), 6.91 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.93 (dd, *J* = 12.9, 9.7 Hz, 1H), 5.28 – 5.20 (m, 1H), 4.64 – 4.47 (m, 2H), 4.37 (dd, *J* = 12.9, 10.0 Hz, 1H), 3.90 – 3.79 (m, 1H), 3.42 – 3.28 (m, 1H), 2.58 (s, 3H), 2.10 – 1.93 (m, 2H), 1.88 – 1.61 (m, 5H), 1.53 – 1.42 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.83, 161.84 (q, *J* = 99.7, 49.8 Hz), 150.18, 146.66, 146.58, 146.51, 146.39, 143.75, 139.29, 139.22, 134.96, 132.72-119.43 (other aromatic carbons), 117.60, 103.56, 103.40, 101.66, 101.49, 87.59, 87.56, 71.99, 69.48, 64.25, 61.14, 33.29 (d, *J* = 3.9 Hz), 31.37 (d, *J* = 3.6 Hz), 28.08 (d, *J* = 2.2 Hz), 27.80 (d, *J* = 2.3 Hz), 15.21.

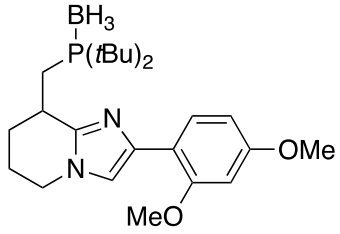
HRMS-ESI; *m/z* $[C_{49}H_{42}IrNO_4PS]^+$= 964.2163, calcd. For $[C_{49}H_{42}IrNO_4PS]^+$: 964.2198.

Synthesis of catalyst IC



The catalyst **IC** was prepared following the procedures that have been reported in the group.

Peters, B. K.; Liu, J.; Margarita, C.; Rabten, W.; Kerdphon, S.; Orebom, A.; Morsch, T.; Andersson, P. G. *Journal of the American Chemical Society* **2016**, *138*, 11930.



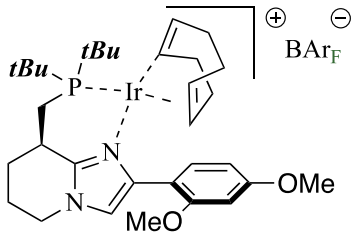
8-((di-*tert*-butylphosphaneyl)methyl)-2-(2,4-dimethoxyphenyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine

Yellow light oil, 115 mg, 65% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.6 Hz, 1H), 7.27 (s, 1H), 6.59 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.50 (d, *J* = 2.4 Hz, 1H), 4.06 – 3.98 (m, 1H), 3.96 – 3.86 (m, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.30 – 3.11 (m, 3H), 2.75 – 2.64 (m, 0H), 2.11 – 1.91 (m, 1H), 1.60 (s, 3H), 1.44 (d, *J* = 12.5 Hz, 9H), 1.26 (d, *J* = 12.5 Hz, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.95, 156.71, 147.07, 135.30, 127.57, 117.30, 116.38, 104.41, 98.14, 55.25, 44.75, 34.02, 33.55, 33.29, 32.57, 32.54, 31.70, 31.42, 30.04, 27.74, 27.73, 27.67, 27.66, 22.28, 22.20, 21.47, 21.17, 14.05.

HRMS-ESI; *m/z* $[C_{24}H_{30}BN_2O_2P\text{-}BH_3+H]^+$= 417.2659, calcd. For $[C_{24}H_{30}BN_2O_2P\text{-}BH_3+H]^+$: 417.2665.



[Ir(cod)]BArF.

Orange solid, 257 mg, 48% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.55 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.66 (m, 8H), 7.52 (s, 4H), 7.36 (s, 1H), 6.65 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 5.20 – 5.13 (m, 1H), 4.44 – 4.34 (m, 1H), 3.98 – 3.91 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.48 – 3.28 (m, 2H), 2.52 (dtd, *J* = 15.8, 10.4, 5.7 Hz, 1H), 2.32 – 1.79 (m, 8H), 1.75 – 1.63 (m, 1H), 1.42 (d, *J* = 12.9 Hz, 9H), 1.09 (d, *J* = 13.4 Hz, 9H).

^{31}P NMR (162 MHz, $CDCl_3$) δ 40.62.

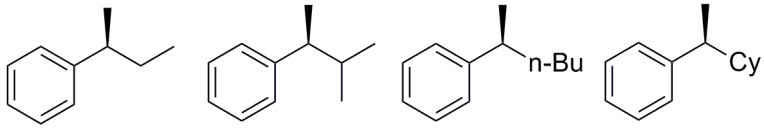
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.41, 161.92, 161.43, 161.20, 160.93, 157.48, 145.28, 145.25, 134.77, 131.44, 129.44 – 128.27 (m), 125.88, 123.17, 120.68, 120.46, 117.58 – 117.28 (m), 111.61, 104.35, 98.60, 90.27, 90.20, 80.54, 80.38, 67.71, 59.89, 55.57, 55.48, 45.70, 38.04, 37.74, 37.69, 35.68, 35.49, 35.03, 35.00, 34.10, 30.14, 29.85, 29.83, 28.29, 28.21, 28.10, 24.56, 24.53, 20.00, 19.76.

HRMS-ESI; *m/z* $[C_{32}H_{49}IrN_2O_2P]^+$= 717.3139, calcd. For $[C_{32}H_{49}IrN_2O_2P]^+$: 717.3157.

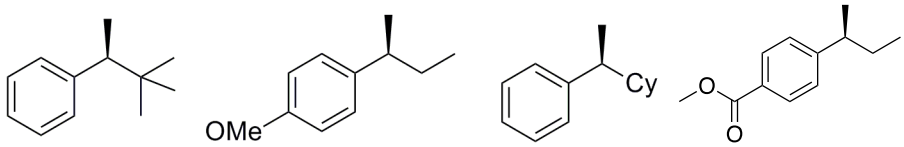
$[\alpha]_D^{22.0}$ = + 77.5 (*c* 0.04, $CHCl_3$)

4.General procedure for asymmetric hydrogenations

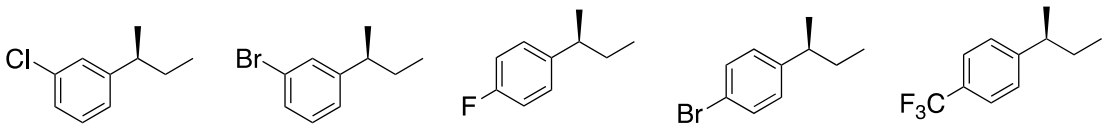
A vial was charged with the substrate and Ir-complex. Dry CH_2Cl_2 (4 ml) was added (to ensure the concentration of the substrate was 0.034 M) and the vial was placed in a high-pressure hydrogenation apparatus. The reactor was purged 3 times with N_2, then filled to pressure with H_2. The reaction was stirred at room temperature for 2 hours before the H_2 pressure was released and the solvent was removed *in vacuo*. The crude product was purified through silica column chromatography. Conversion was determined by ^1H NMR spectroscopy and *ee* values were determined using chiral GC or SFC.



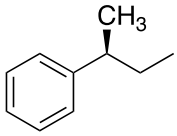
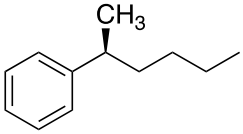
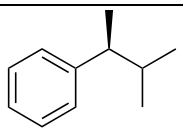
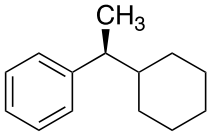
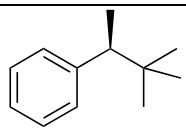
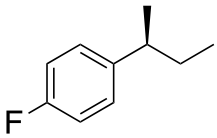
These compounds have been reported.[3]

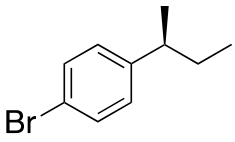
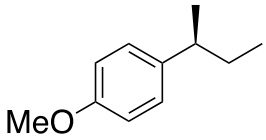
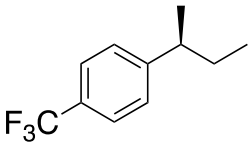
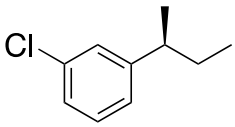
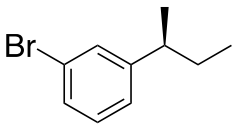
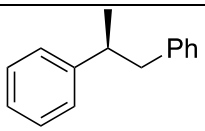


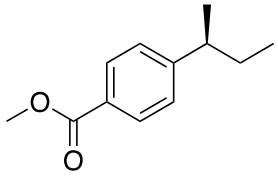
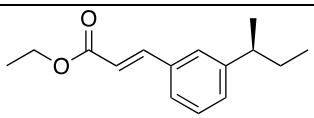
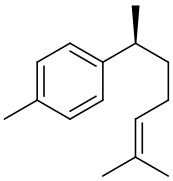
These compounds have been reported.[4]



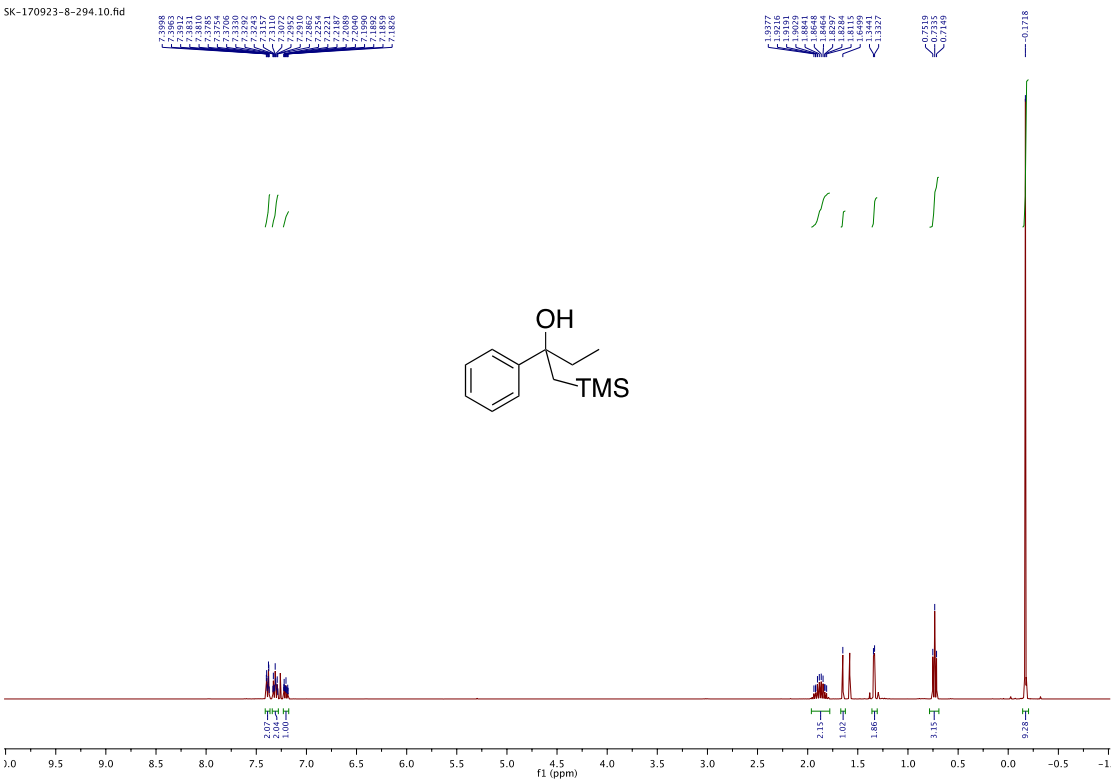
These compounds have been reported.[5]

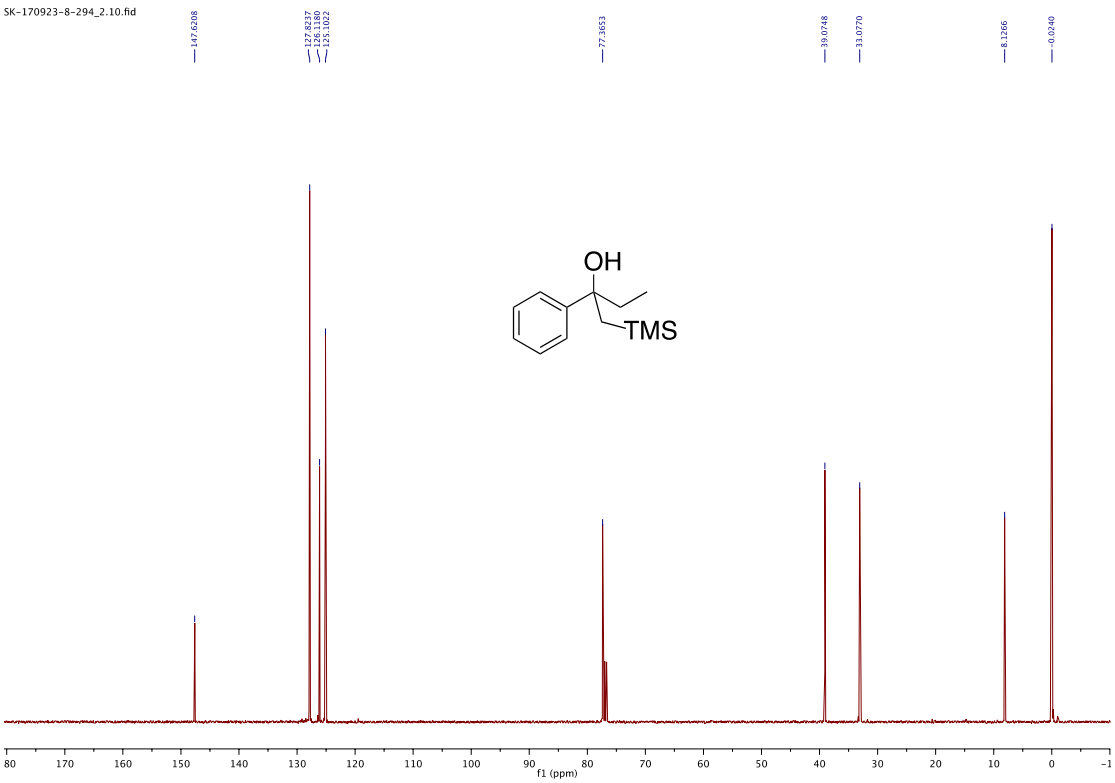
Entry	Product	Separation method	Optical rotation	*ee*
1		**GC-MS**: column Chiraldex β-3p, 50˚C isothermal, t_R = 35.2 min (minor)/36.8 (major)	$[\alpha]_D^{25.0} = 22.52$ (c = 0.37 in $CHCl_3$)	95%
2		**GC-MS**: column Chiraldex β-DM, 60˚C hold 30min to 175°C at 3°C/min. t_R = 39.4 min (major)/40.0 (minor)	$[\alpha]_D^{25.0} = 21.01$ (c = 0.49 in $CHCl_3$)	95%
3		**GC-MS**: column Chiraldex β-DM, 60˚C hold 30min to 175°C at 3°C/min. t_R = 25.9 min (major)/28.5 (minor)	$[\alpha]_D^{25.0} = 27.17$ (c = 0.38 in $CHCl_3$)	94%
4		**GC-MS**: column Chiraldex β-DM, 60˚C hold 30min to 175°C at 3°C/min. t_R = 55.1 min (major)/55.6 (minor)	$[\alpha]_D^{25.0} = 18.32$ (c = 0.19 in $CHCl_3$)	94%
5		**GC-MS**: column Chiraldex β-3p, 60˚C isothermal 60 min, t_R = 53.6 min (major)	$[\alpha]_D^{25.0} = 28.52$ (c = 0.24 in $CHCl_3$)	99%
6		**GC-MS**: column Chiraldex β-DM, 60˚C hold 30min to 175°C at 3°C/min. t_R = 21.8 min (major)/23.2 (minor)	$[\alpha]_D^{25.0} = 22.45$ (c = 0.44 in $CHCl_3$)	96%

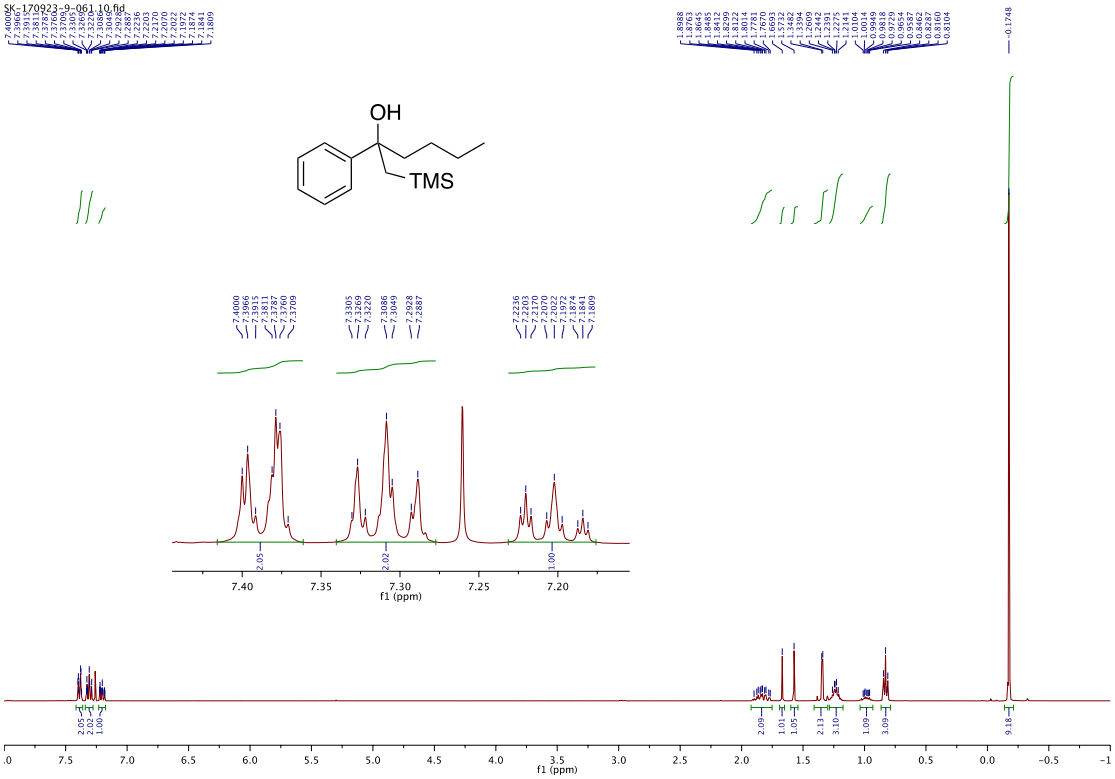
7		**GC-MS**: column Chiraldex β-6TBDM, 70˚C isothermal 90 min, t_R = 94.5 min (major)/94.7 (minor)	$[\alpha]_D^{25.0} = 22.05$ (c = 0.45 in $CHCl_3$)	94%
8		Chiraldex β-6TBDM, 60˚C hold 30 min to 175°C at 3°C/min. t_R = 47.0 min (major)/47.4 (minor)	$[\alpha]_D^{25.0} = 23.96$ (c = 0.41 in $CHCl_3$)	96%
9		**GC-MS**: column Chiraldex β-6TBDM, 80˚C isothermal 90 min, t_R = 16.8 min (major)/18.3 (minor)	$[\alpha]_D^{25.0} = 18.90$ (c = 0.36 in $CHCl_3$)	94%
10		**GC-MS**: column Chiraldex β-3p, 80˚C isothermal 60 min, t_R = 32.8 min (minor)/34.1 (major)	$[\alpha]_D^{25.0} = 25.14$ (c = 0.36 in $CHCl_3$)	94%
11		**GC-MS**: column Chiraldex β-3p, 70˚C isothermal 90 min, t_R = 82.2 min (minor)/82.4 (major)	$[\alpha]_D^{25.0} = 21.58$ (c = 0.45 in $CHCl_3$)	93%
12		**HPLC-SFC**, OJH column, 5% MeOH, 2 ml/min, 10min, t_R = 5.6 min (minor)/7.1 (major)	$[\alpha]_D^{25.0} = 75.06$ (c = 0.40 in $CHCl_3$)	97%

13		Chiraldex β-6TBDM, 60˚C hold 30 min to 175°C at 3°C/min. t_R = 53.7 min (major)/50.9 (minor)	$[\alpha]_D^{25.0}$ = 17.37(c = 0.305 in $CHCl_3$)	90%
14		**HPLC-SFC**, OJH column, 5% MeOH, 2 ml/min, 10min, t_R = 5.6 min (minor)/7.1 (major)	$[\alpha]_D^{25.0}$ = 16.76 (c = 0.32 in $CHCl_3$)	95%
15		**GC-MS**: column Chiraldex β-DM, 90˚C isothermal 150 min t_R = 71.2 min (major)/74.6 (minor)	$[\alpha]_D^{24.0}$ = +41.0 (c = 0.83 in $CHCl_3$)	95%

5.^{1}H and ^{13}C NMR spectroscopic data of the substrates



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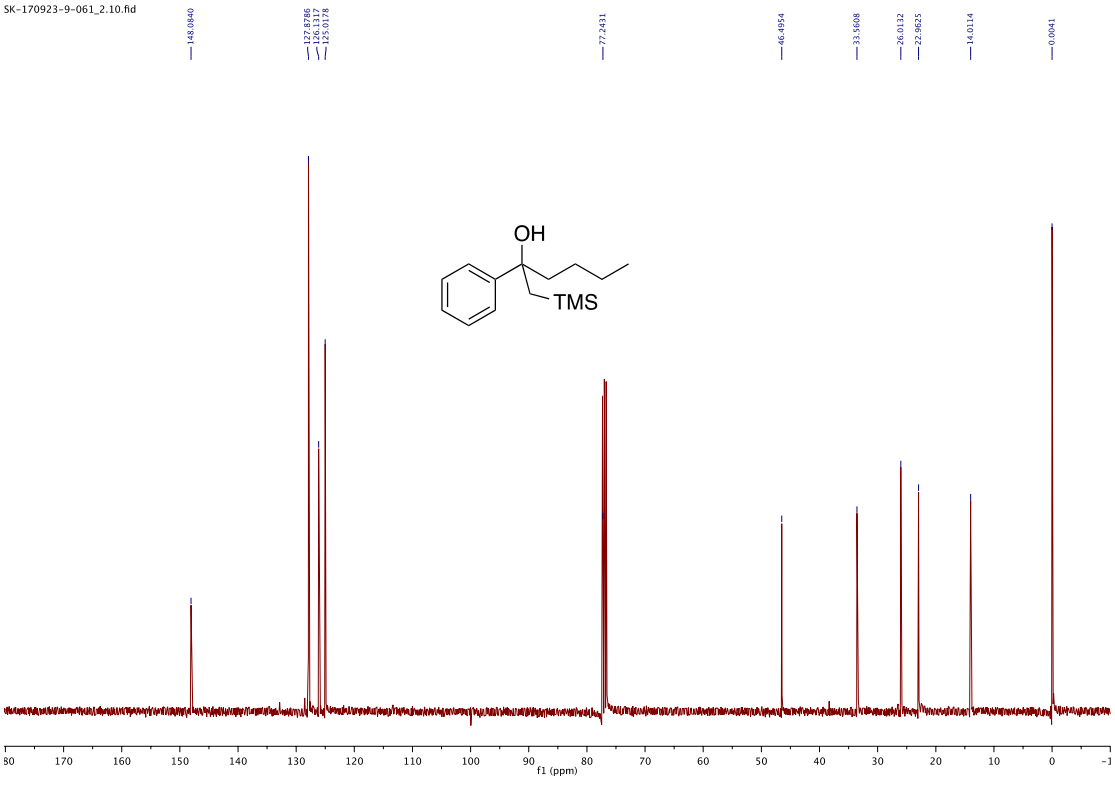
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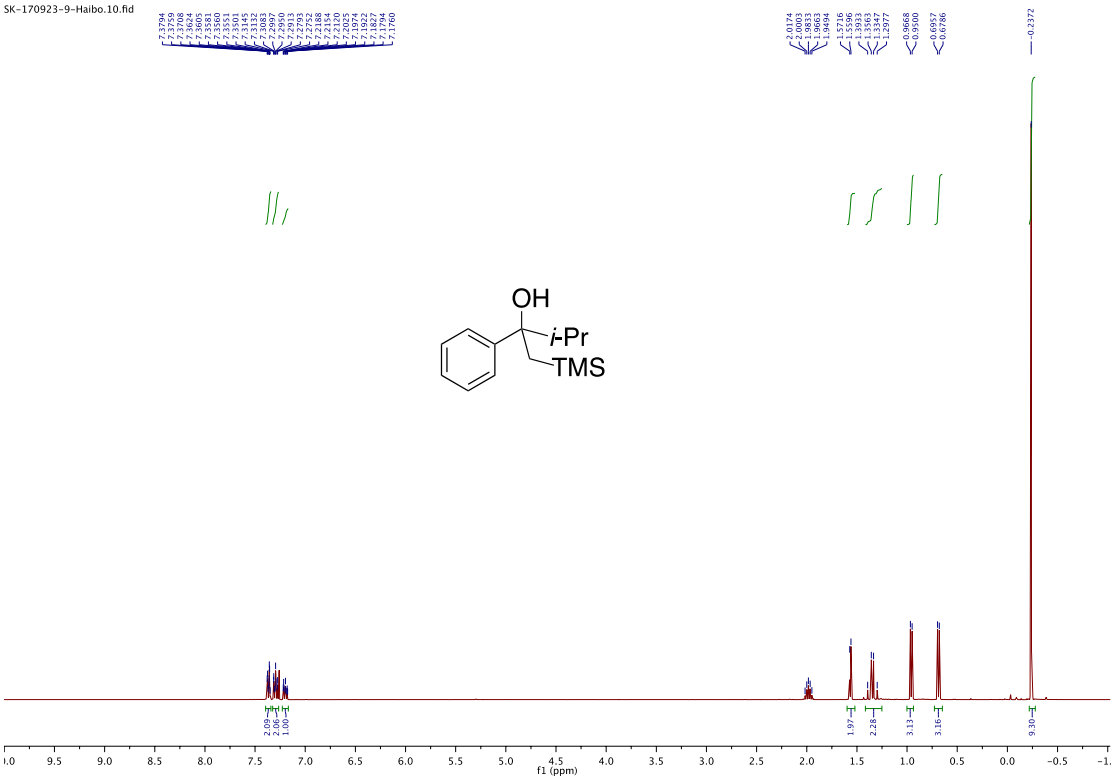
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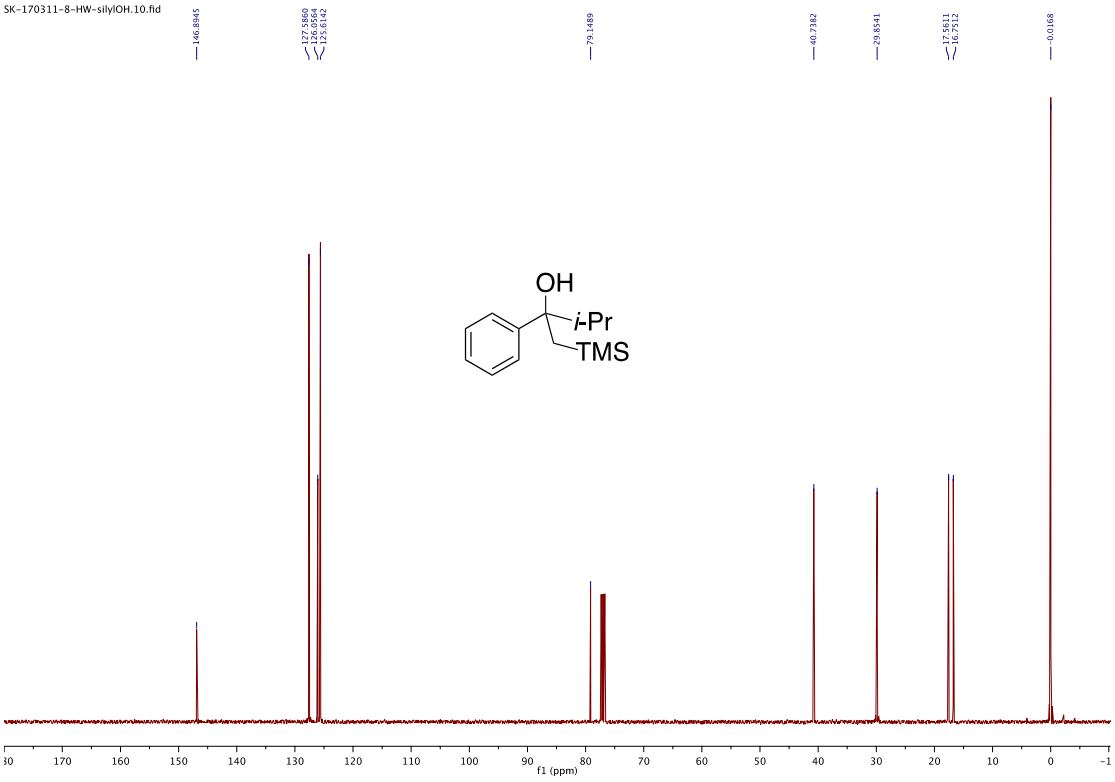
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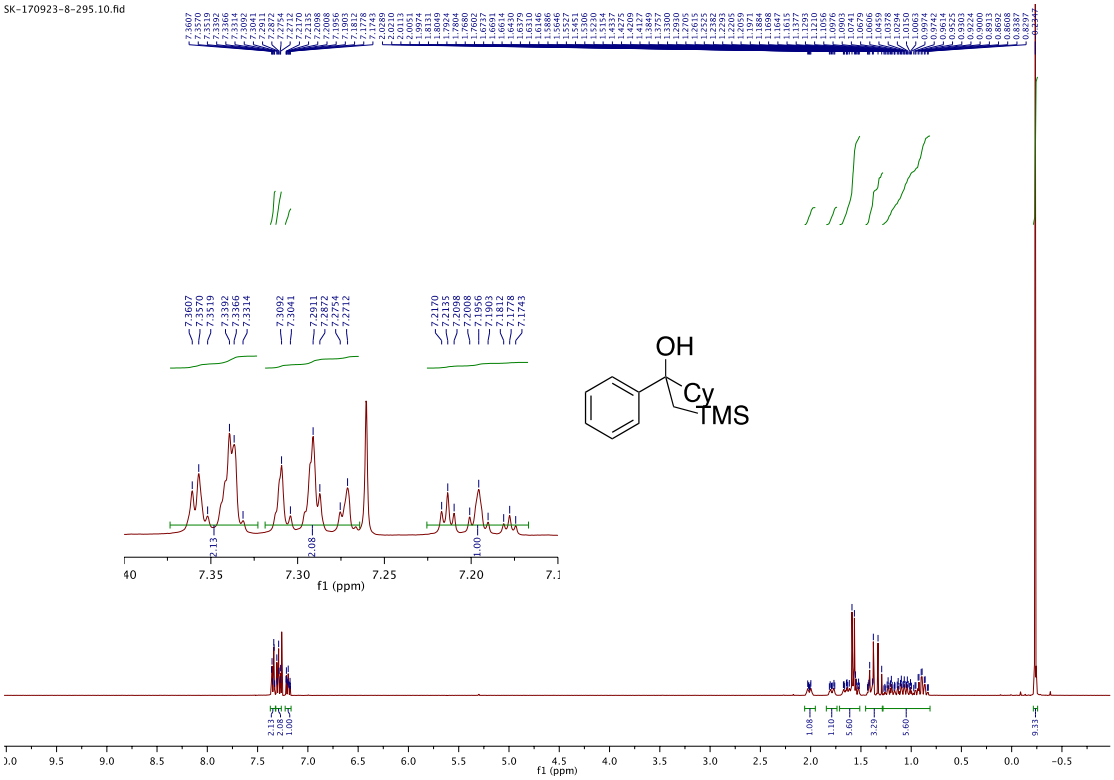
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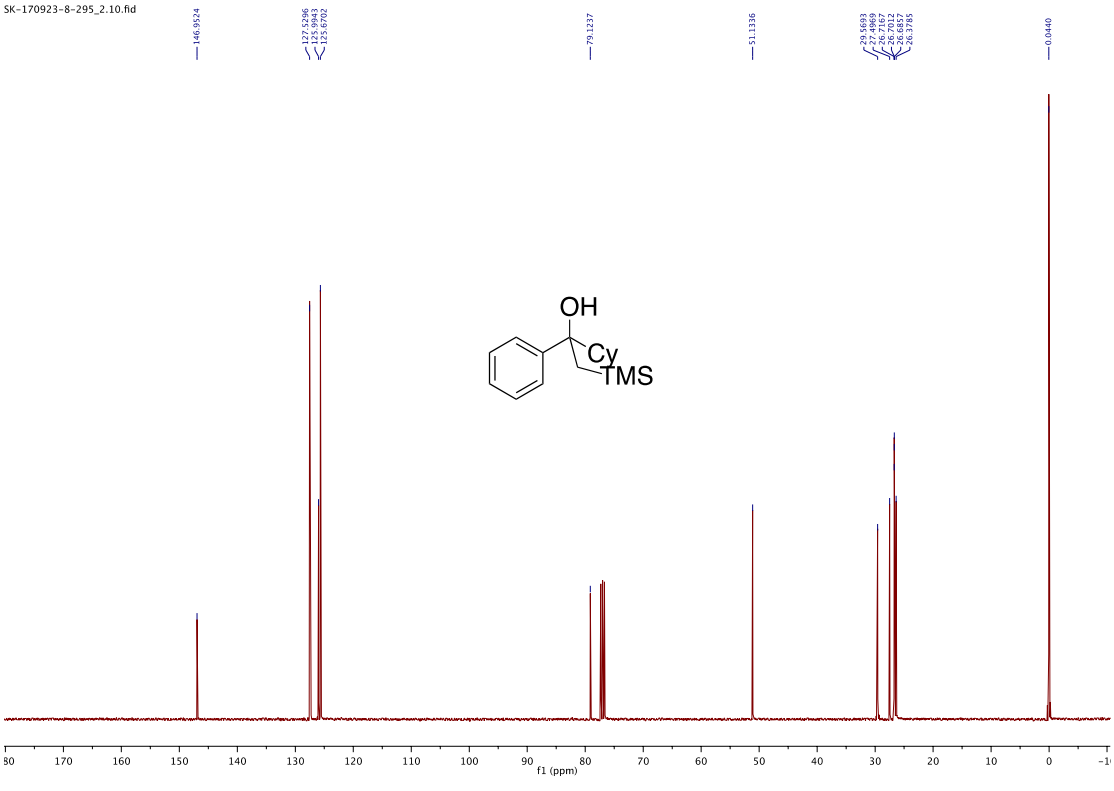
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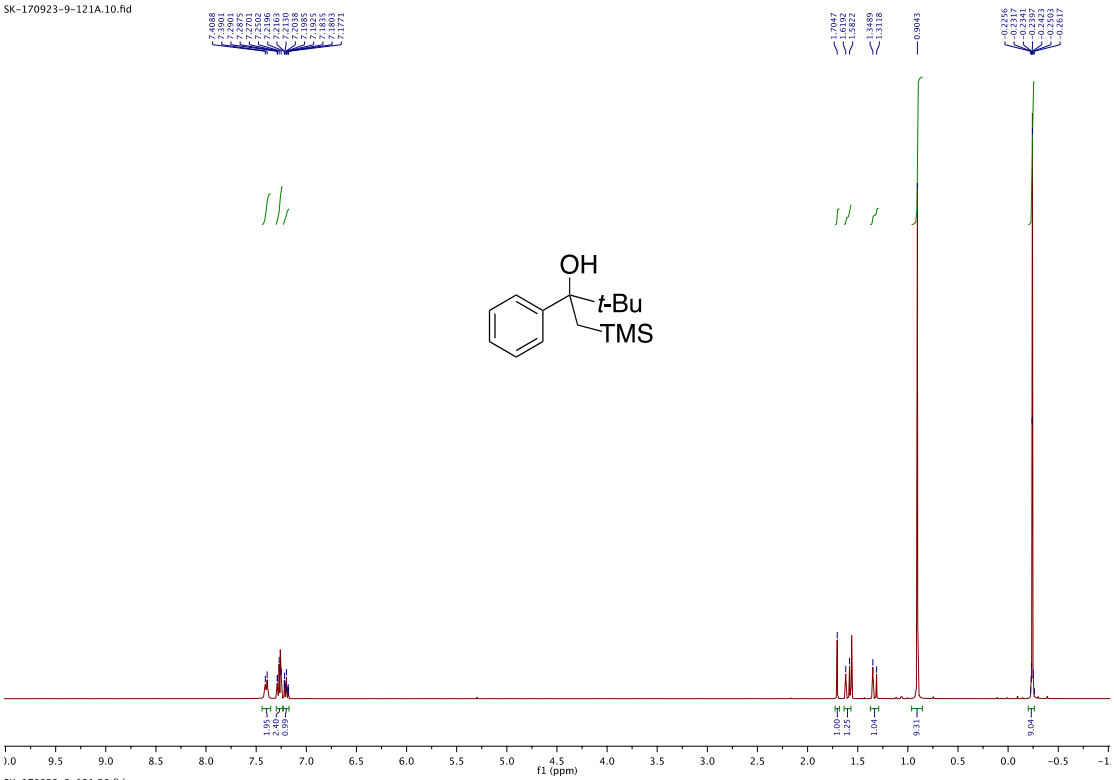
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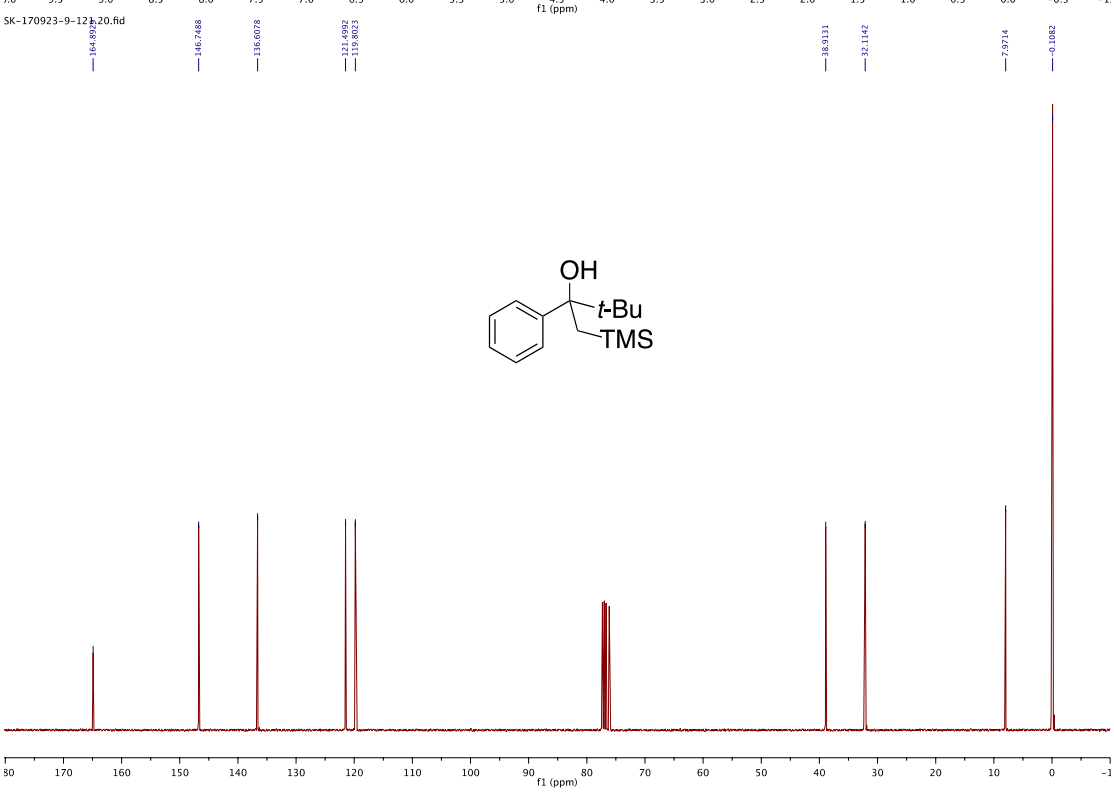
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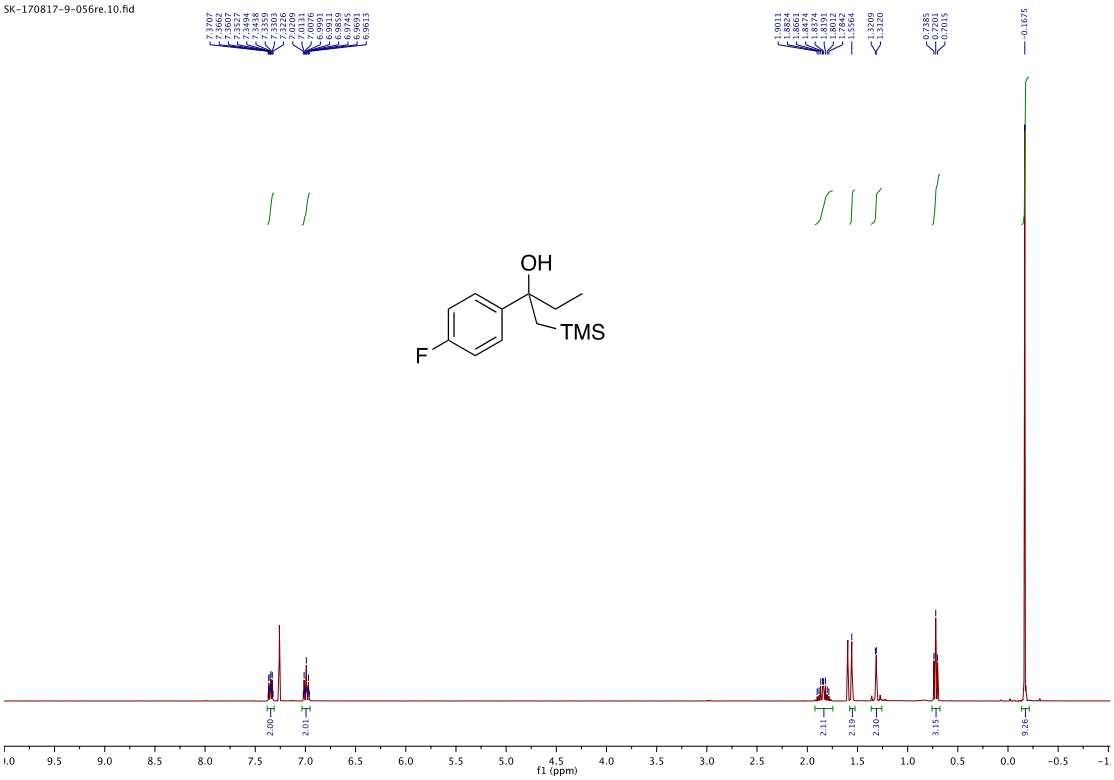
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F
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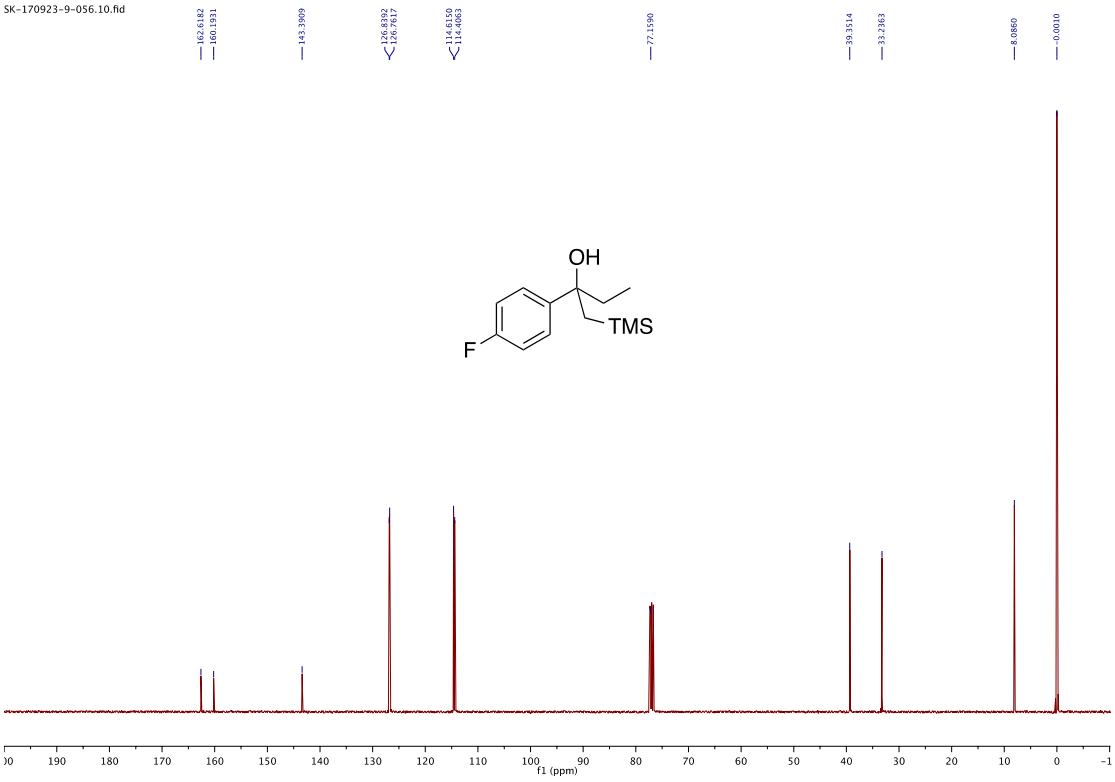
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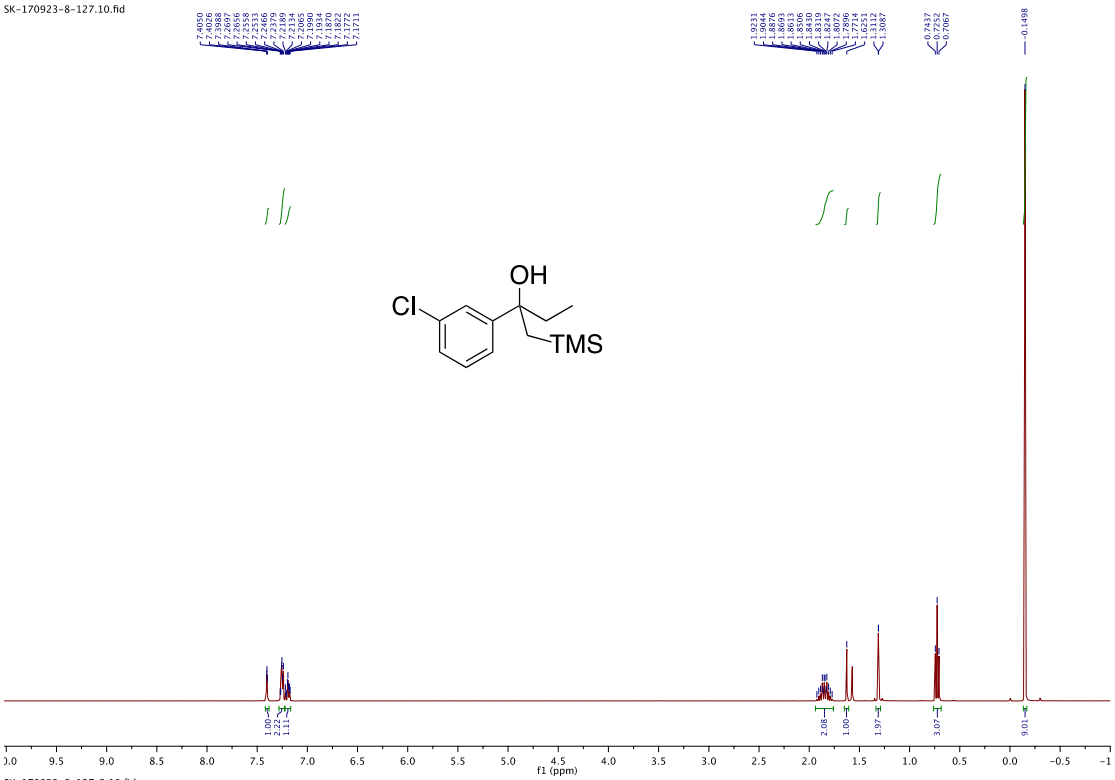
TMS
F
f1 (ppm)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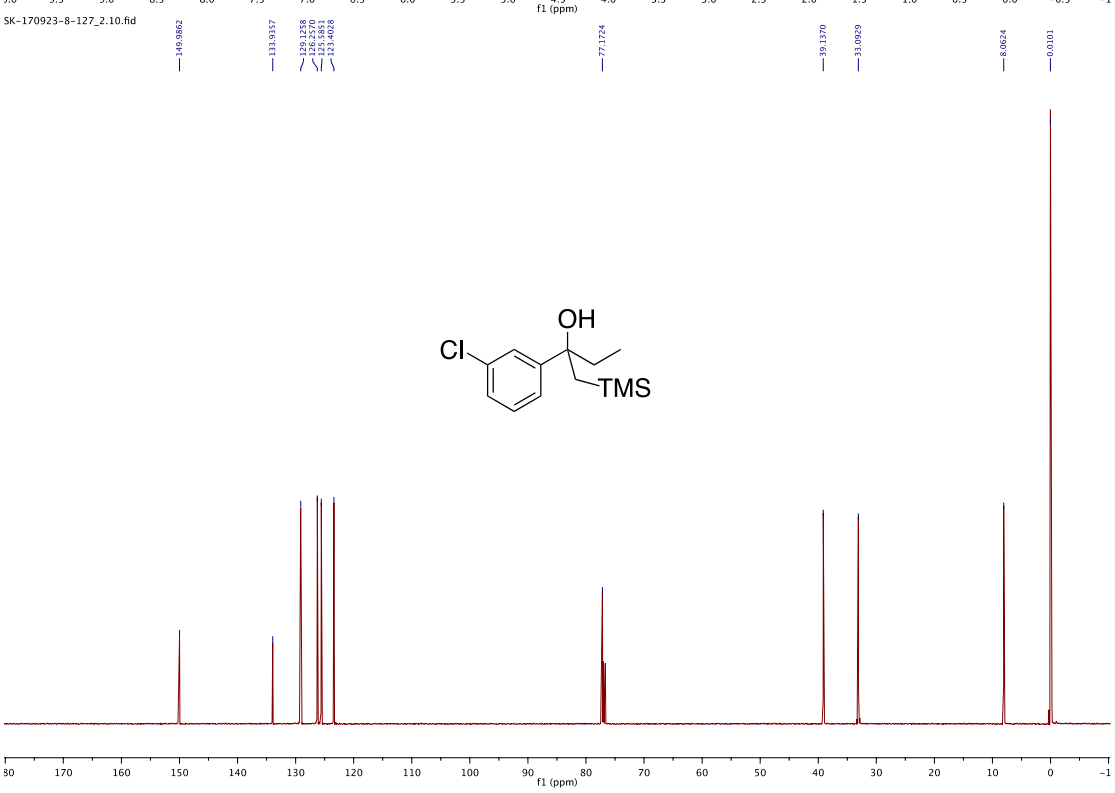
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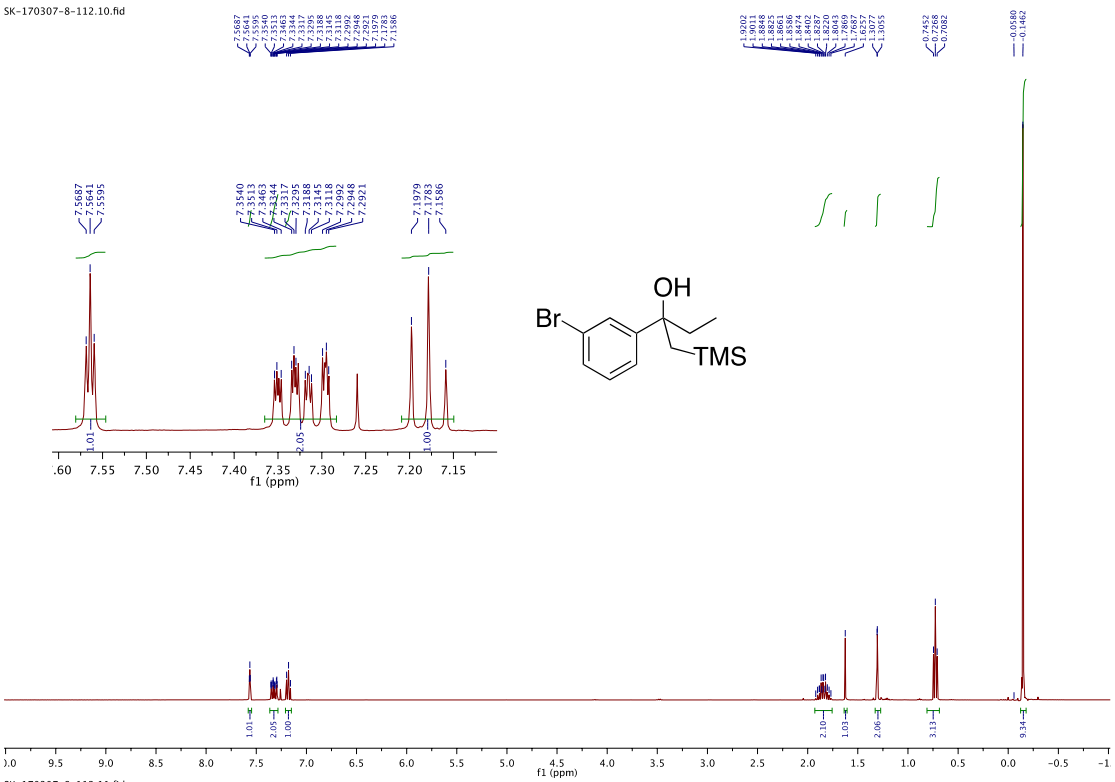
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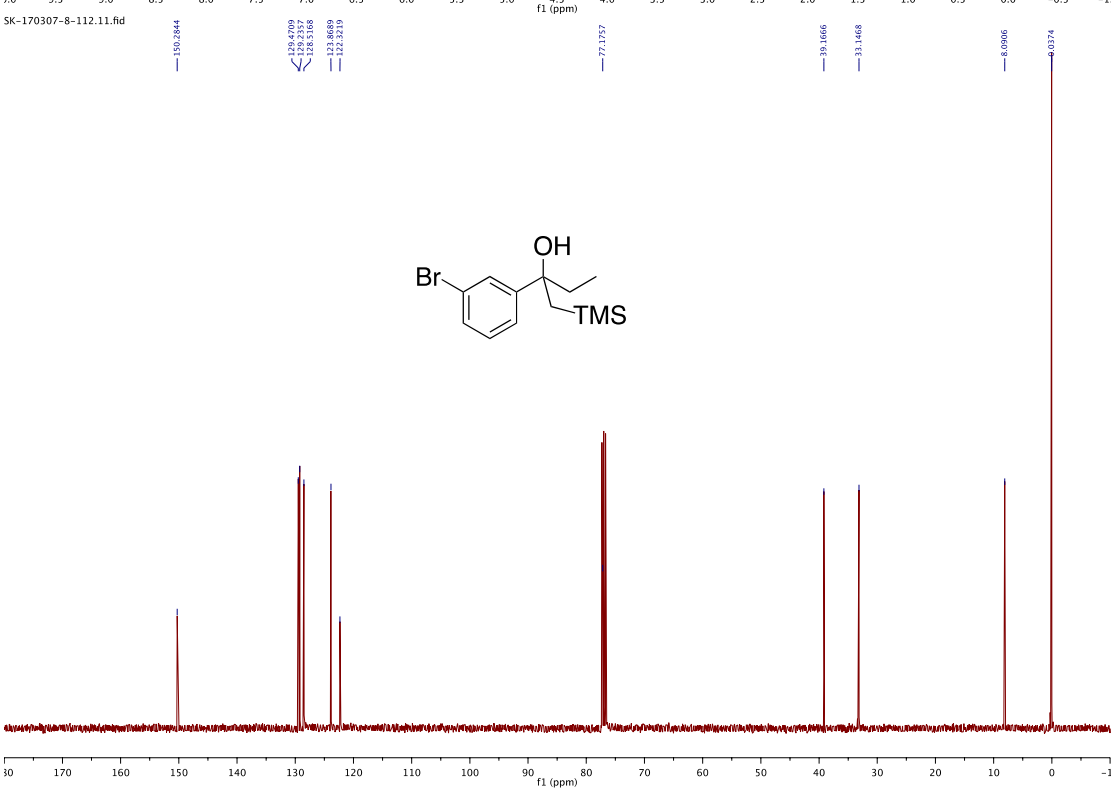
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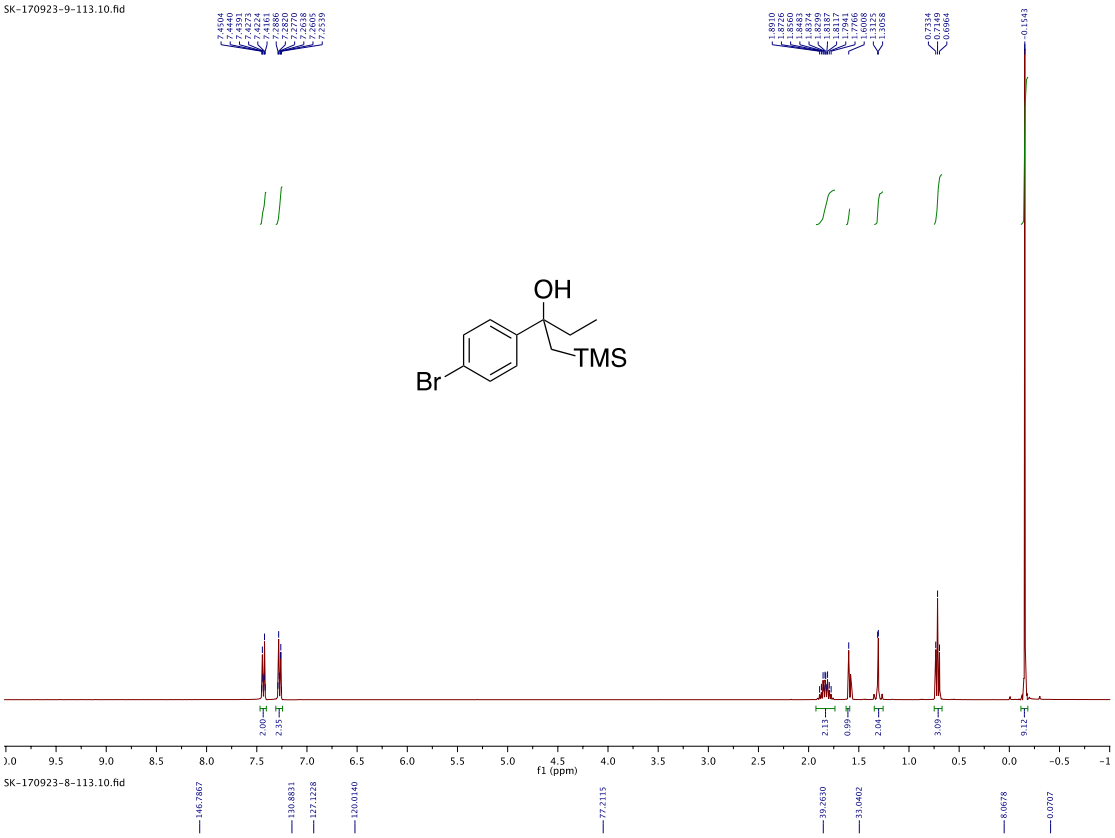
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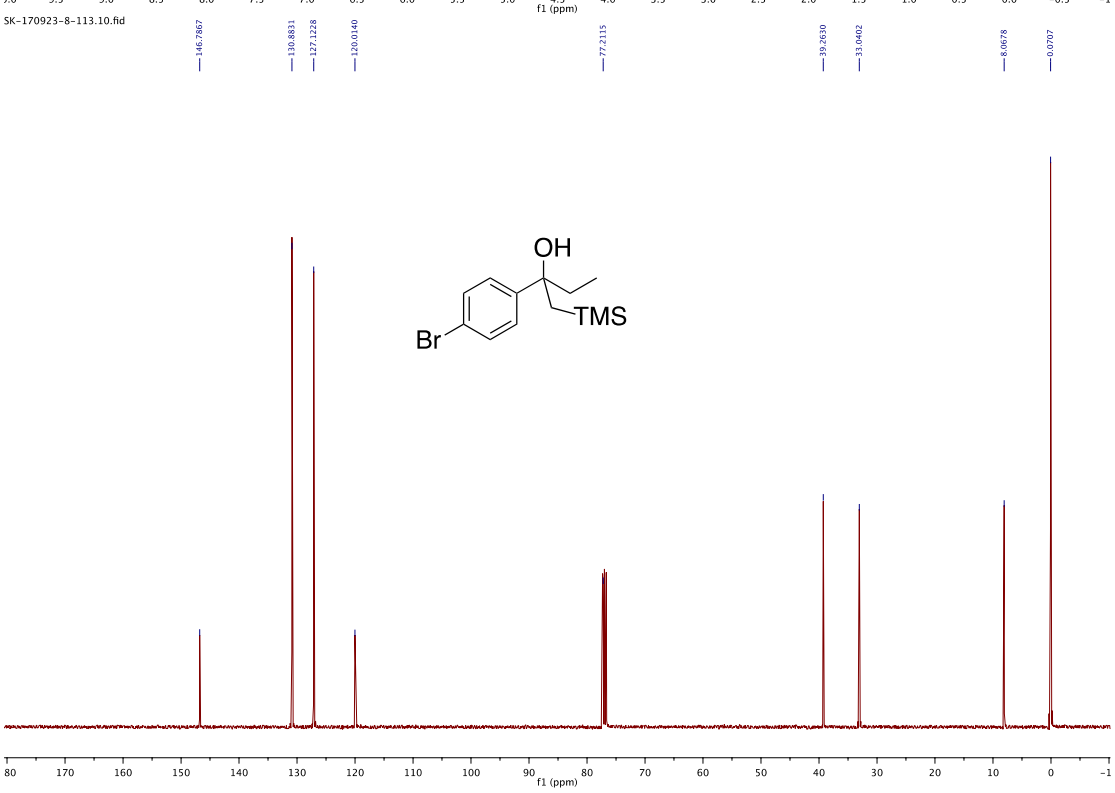
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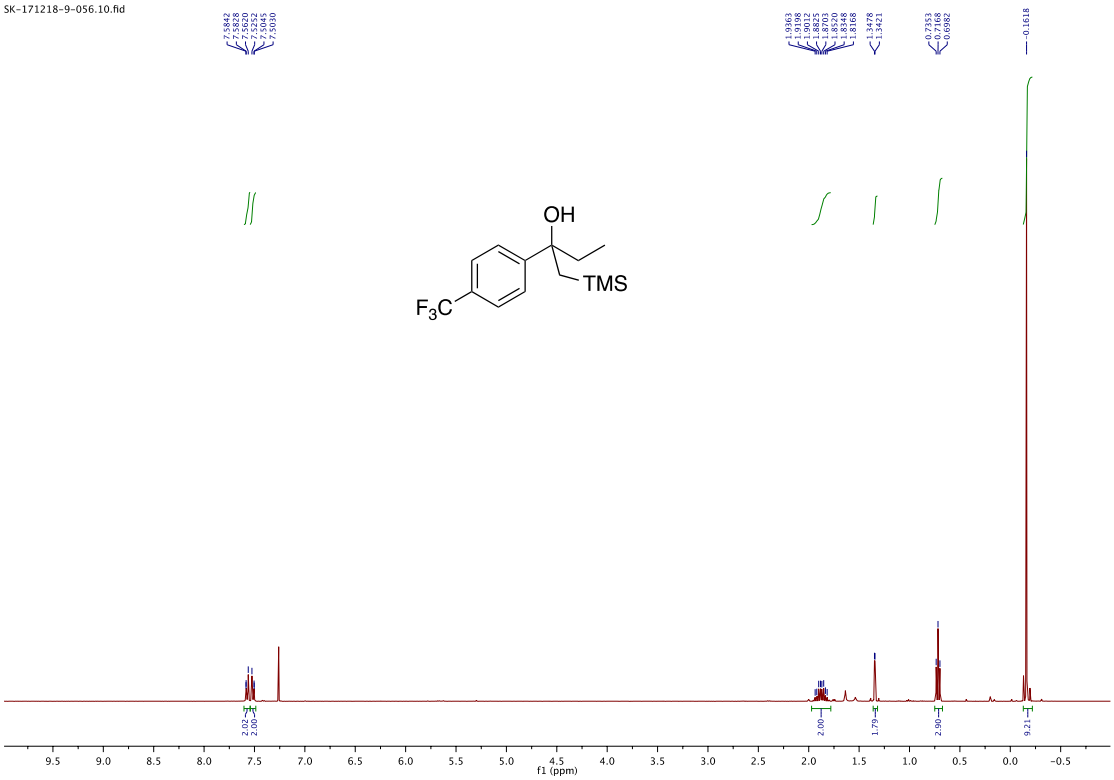
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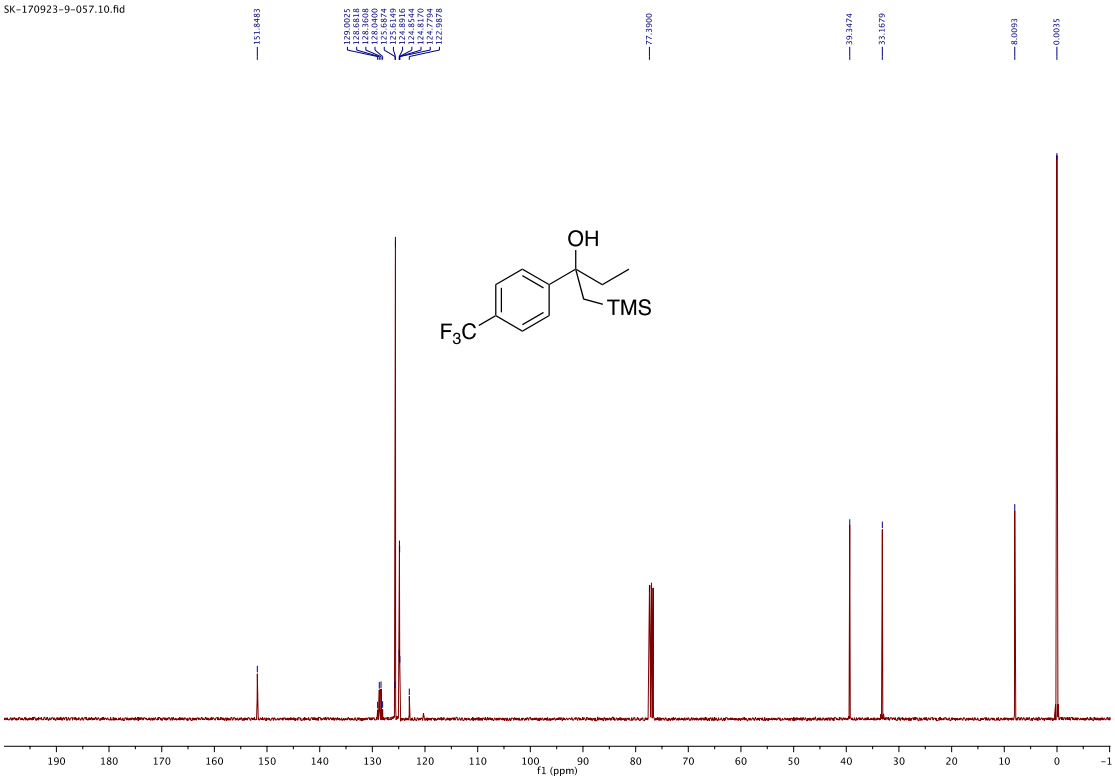
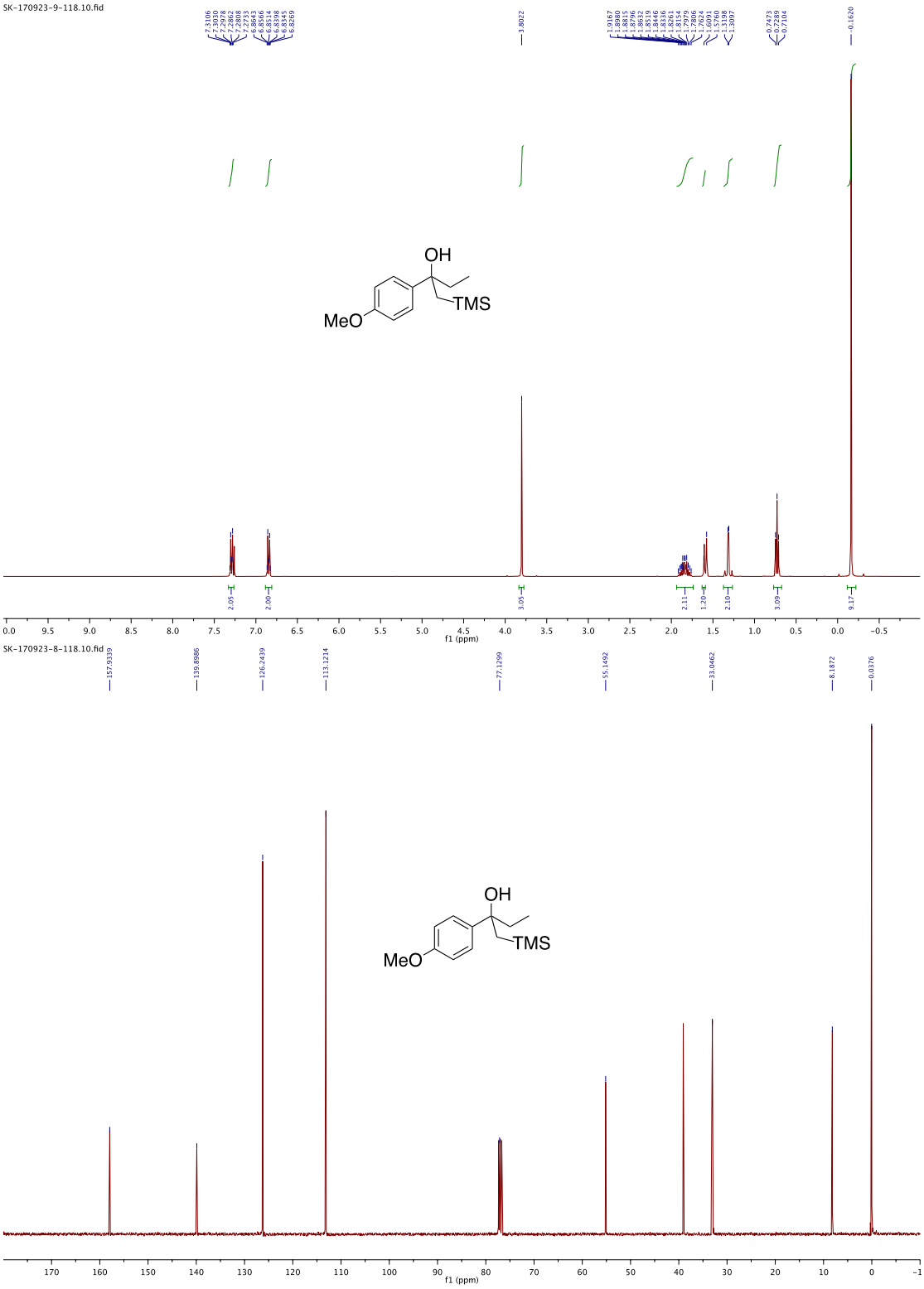
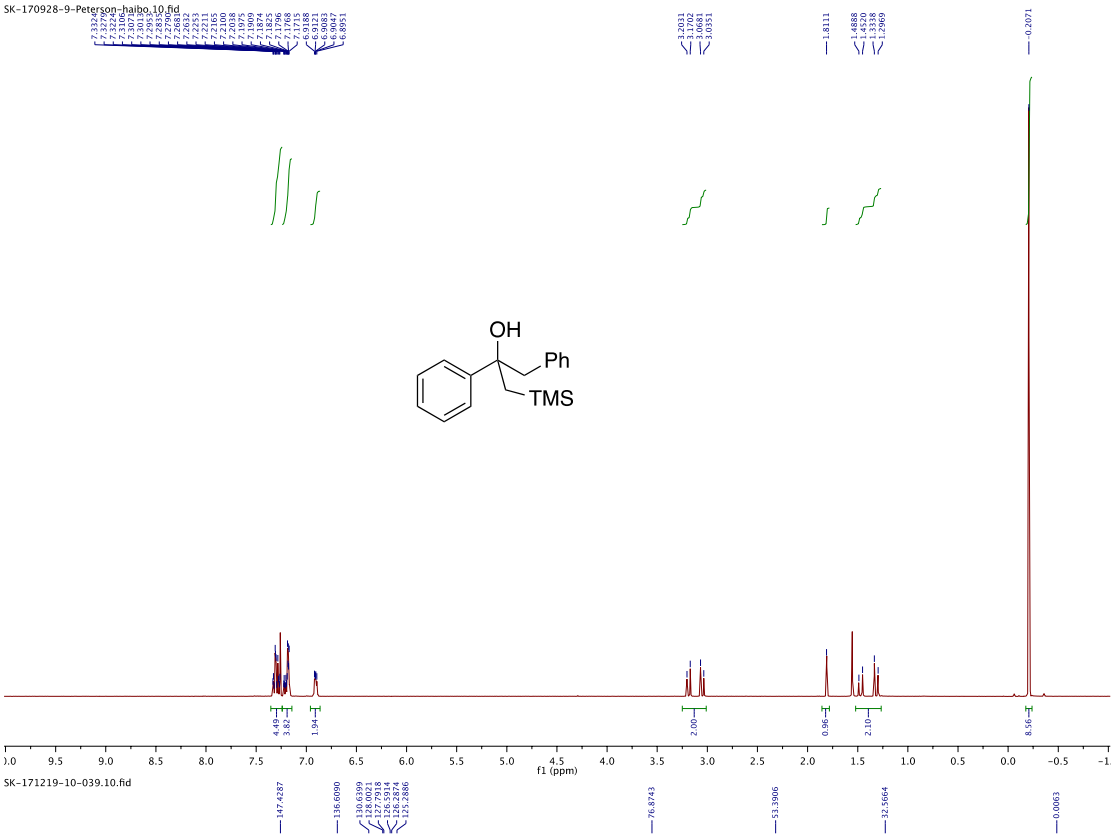
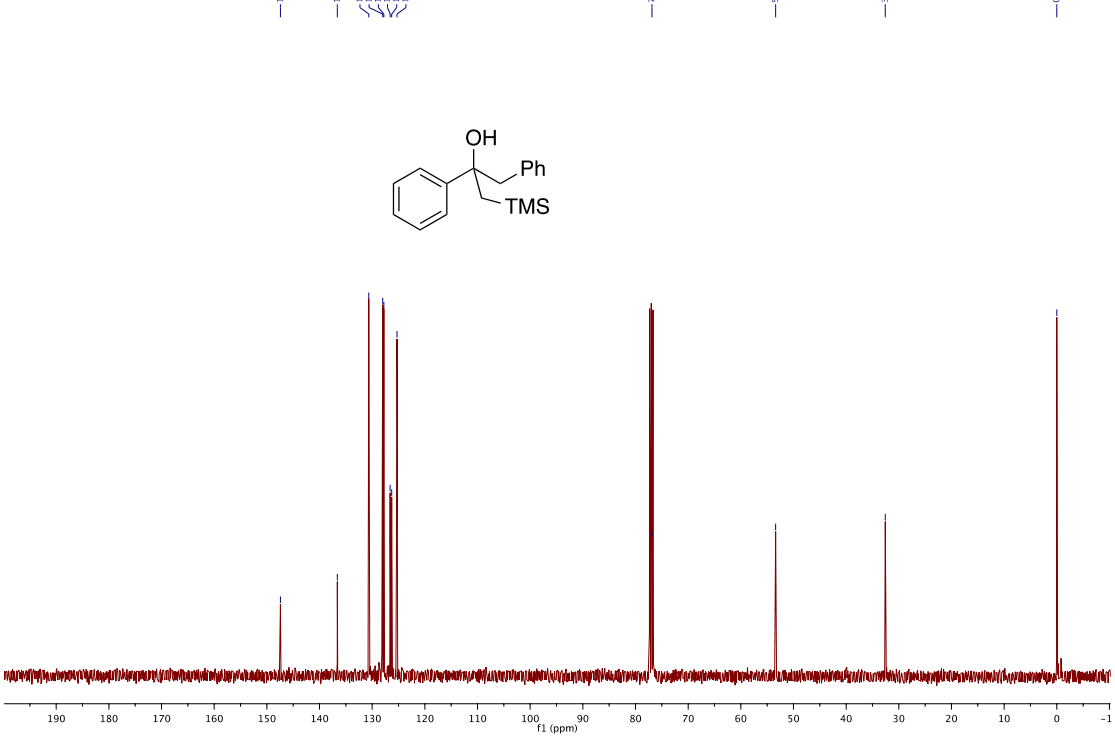
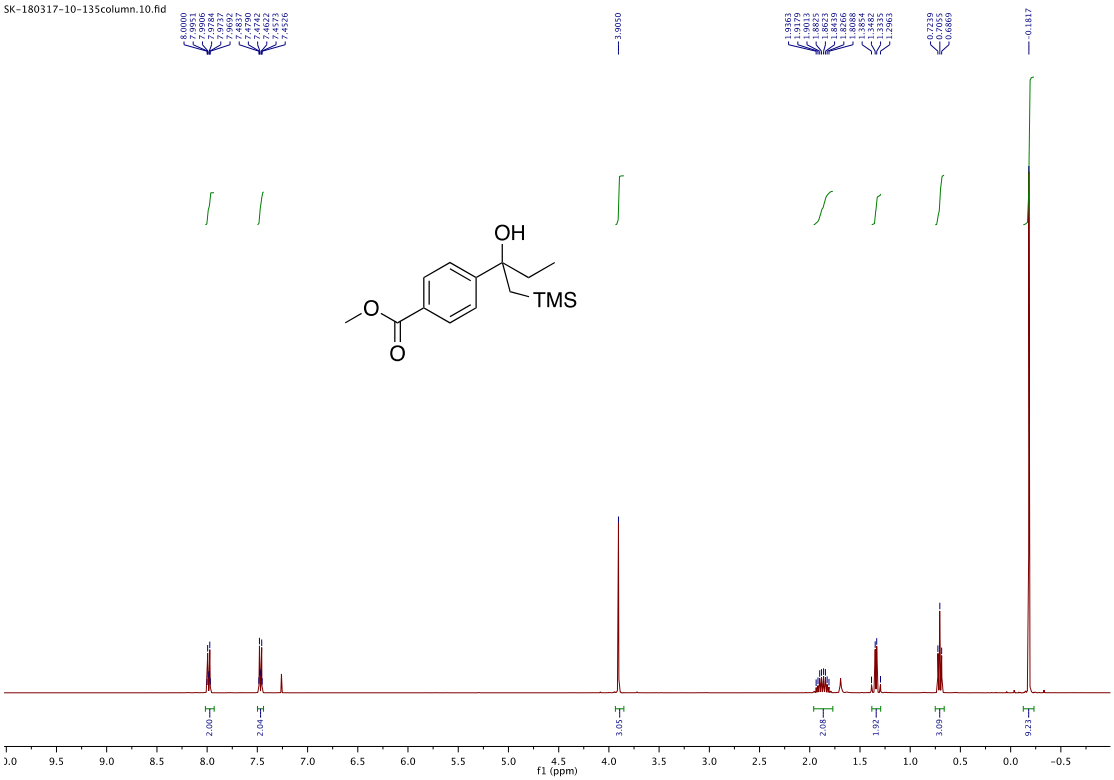
F3C
f1 (ppm)

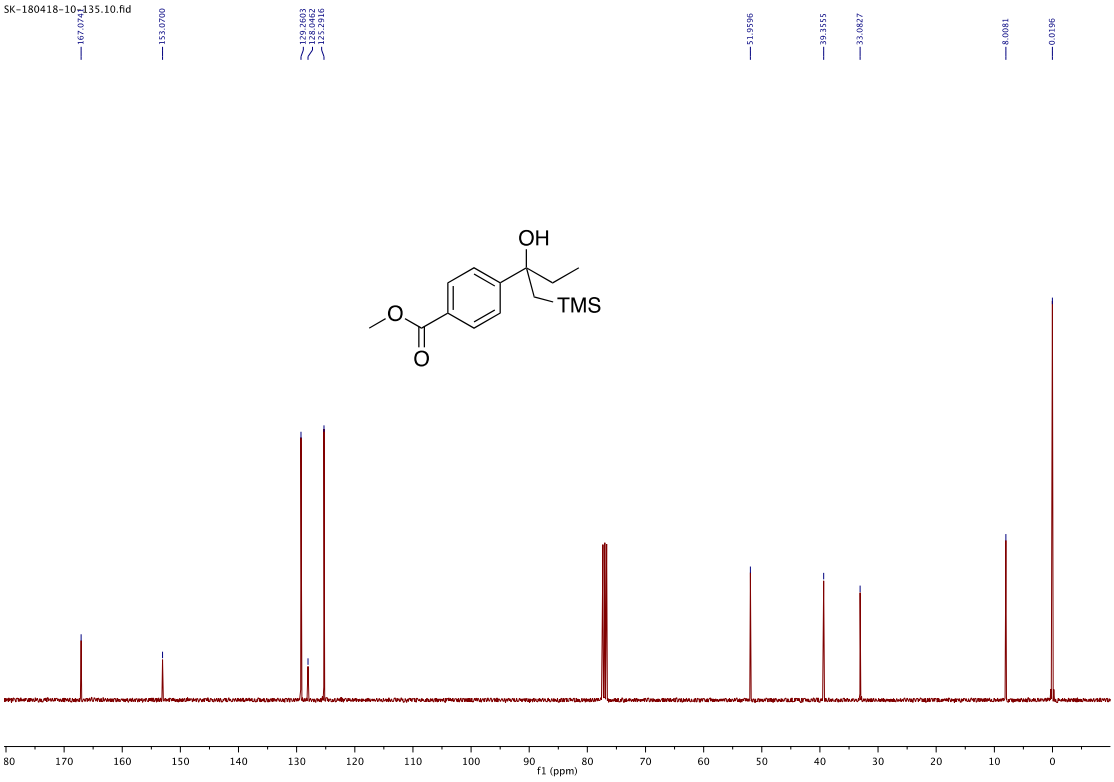

SK-170923-9-057.10.fid
OH
TMS
F3C
f1 (ppm)

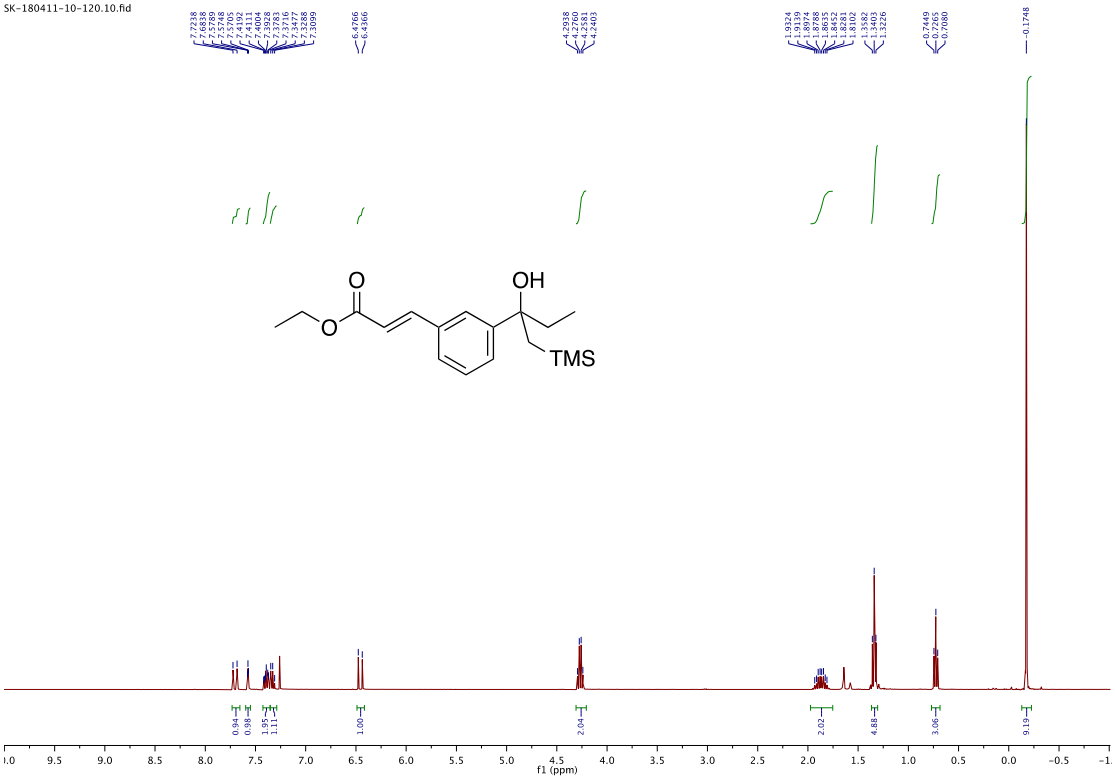

SK-170923-9-118.10.fid
OH
TMS
MeO
f1 (ppm)
SK-170923-8-118.10.fid
OH
TMS
MeO
f1 (ppm)

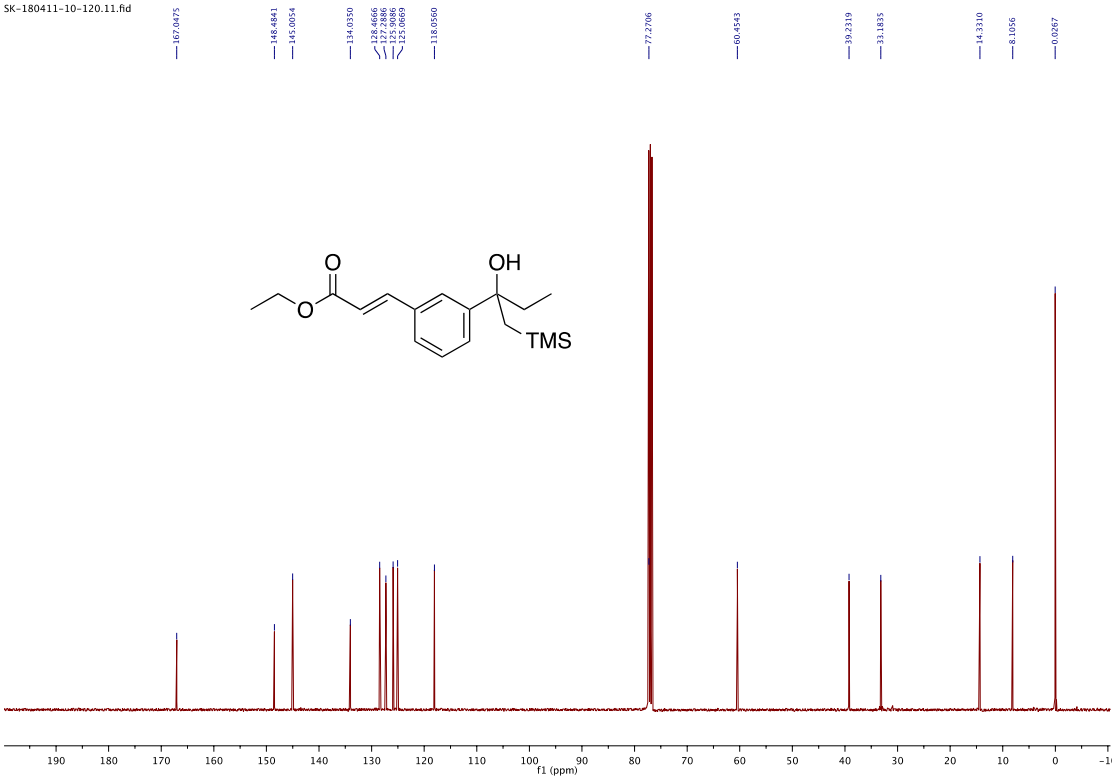

SK-170928-9-Peterson-haibo_10.fid
OH
Ph
TMS
f1 (ppm)

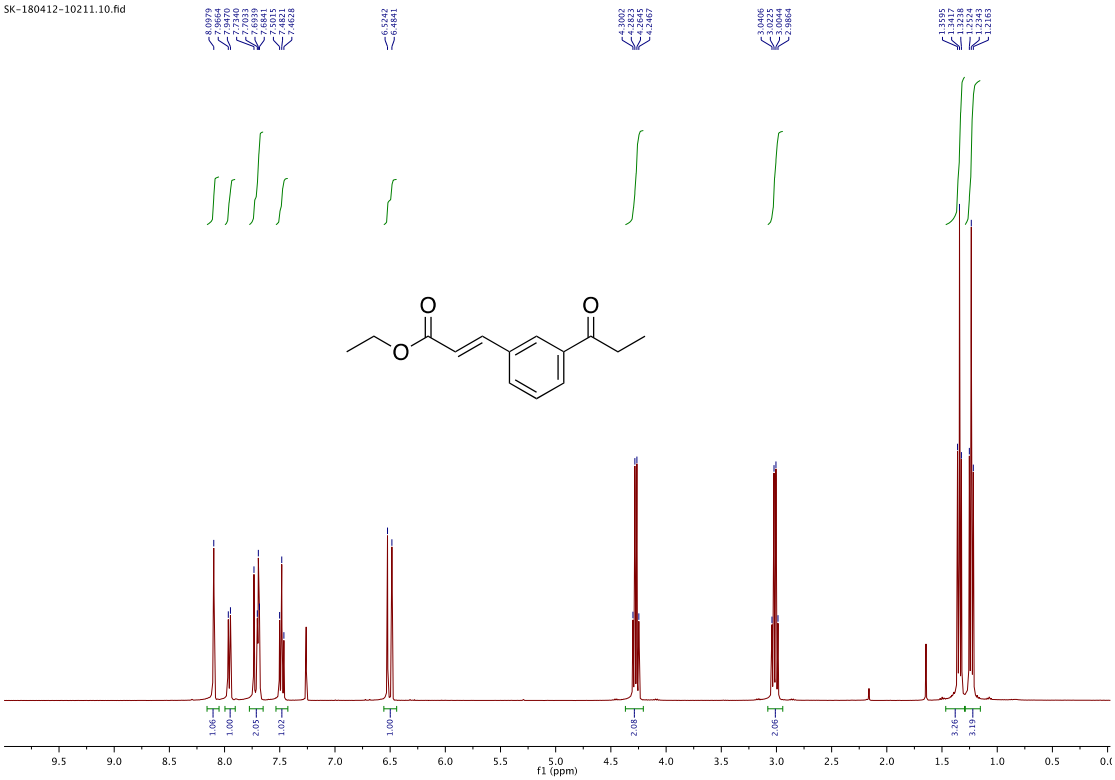

SK-171219-10-039.10.fid
OH
Ph
TMS
f1 (ppm)


SK-180317-10-135column.10.fid
OH
TMS
O
O
f1 (ppm)


SK-180418-10-135.10.fid
OH
TMS
O
O
f1 (ppm)


SK-180411-10-120.10.fid
O
OH
O
TMS
f1 (ppm)


SK-180411-10-120.11.fid
O
OH
O
TMS
f1 (ppm)


SK-180412-10211.10.fid
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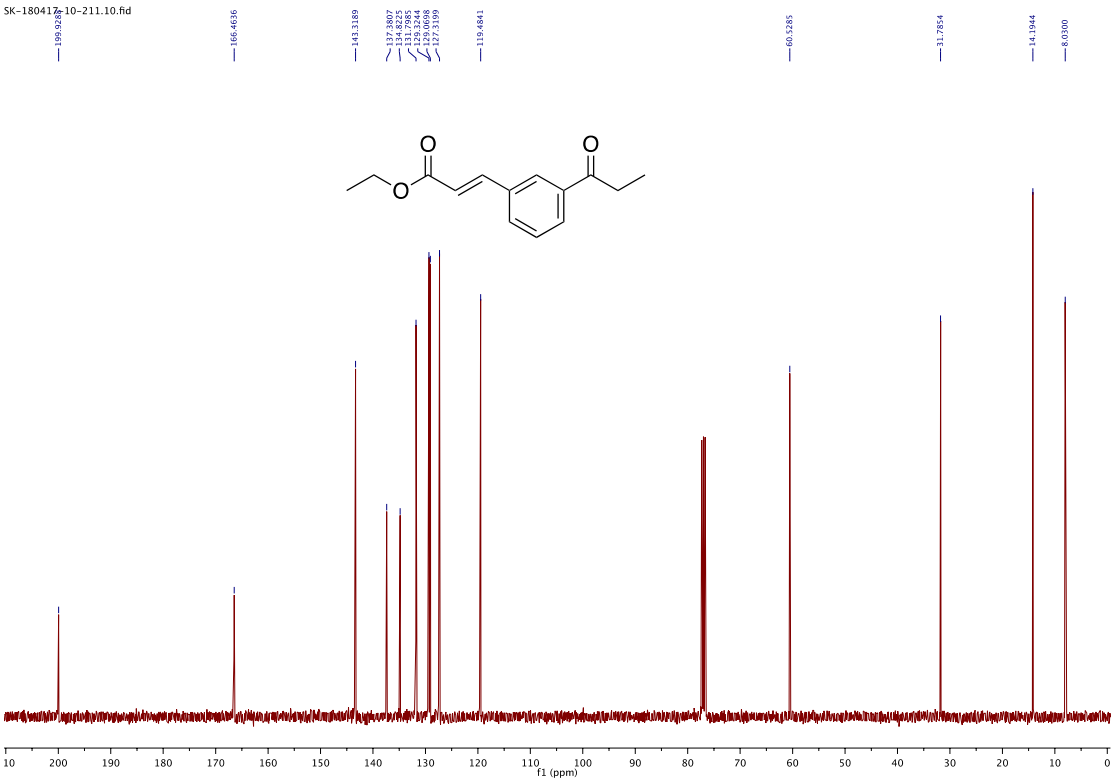
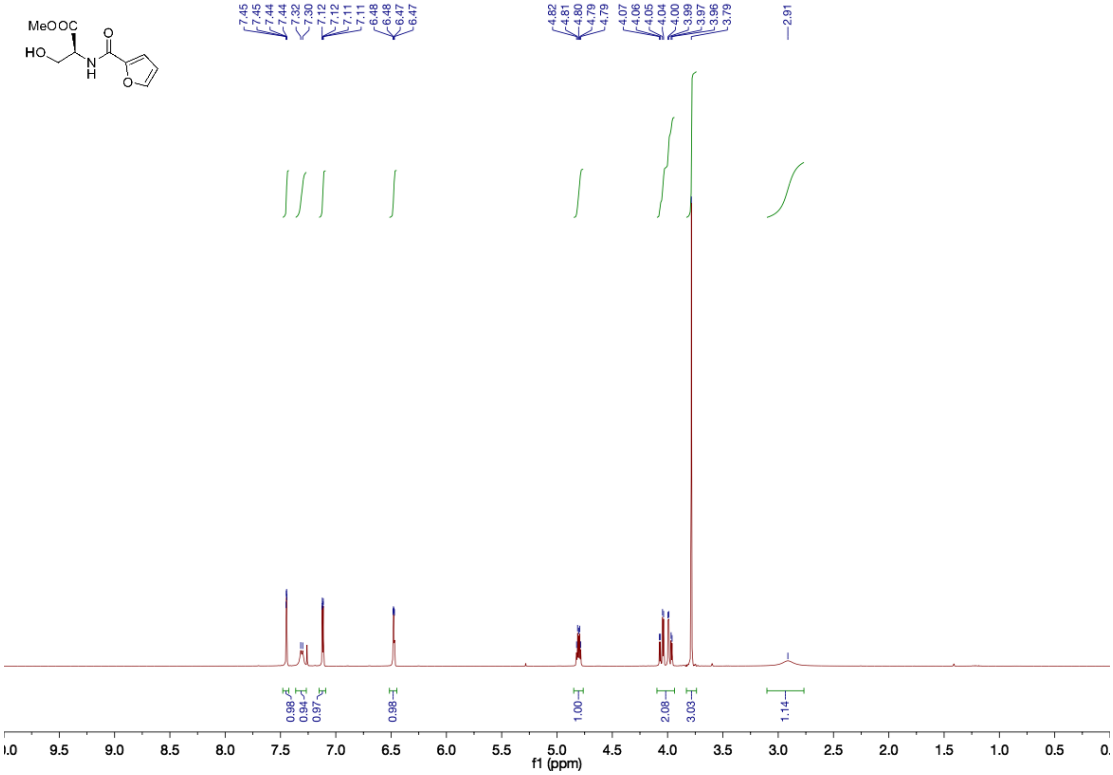
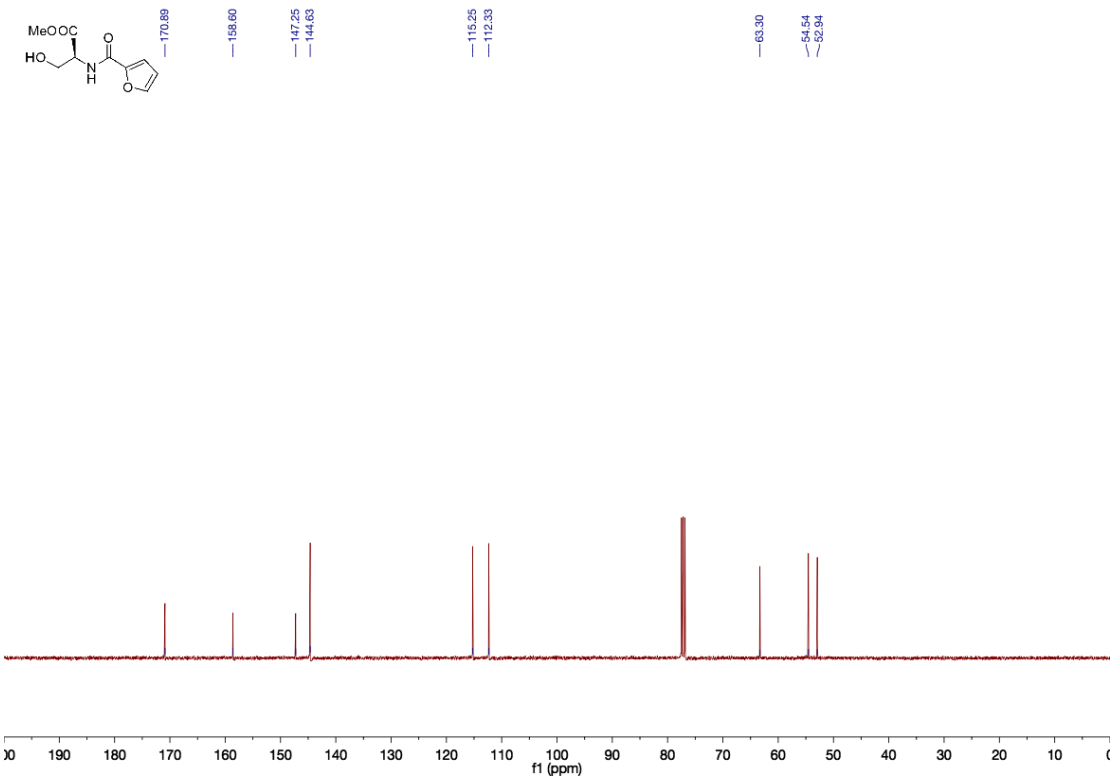
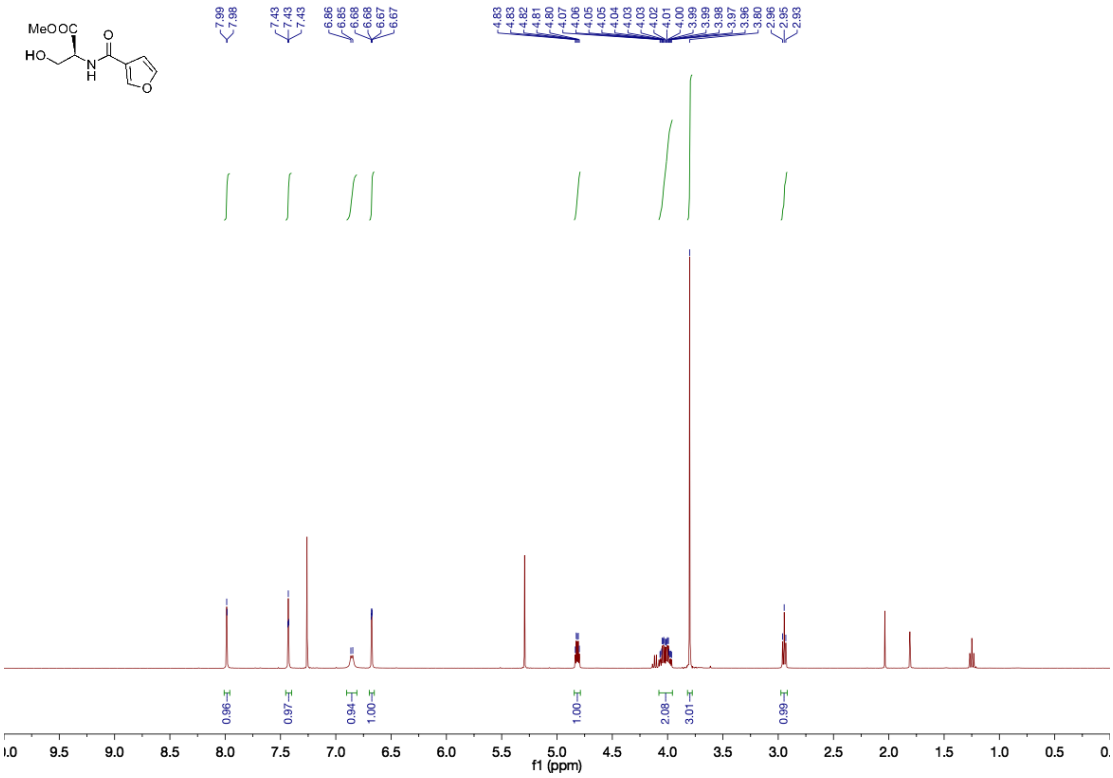
7.9664
7.9470
7.7340
7.7033
7.6839
7.6841
7.5015
7.4821
7.4628
6.5242
6.4841
4.3002
4.2833
4.2645
4.2467
3.0046
3.0052
3.0044
2.9864
1.3258
1.3157
1.3052
1.3238
1.2534
1.2343
1.2163
1.06
1.00
2.05
1.02
1.00
2.08
2.06
3.26
3.19
f1 (ppm)

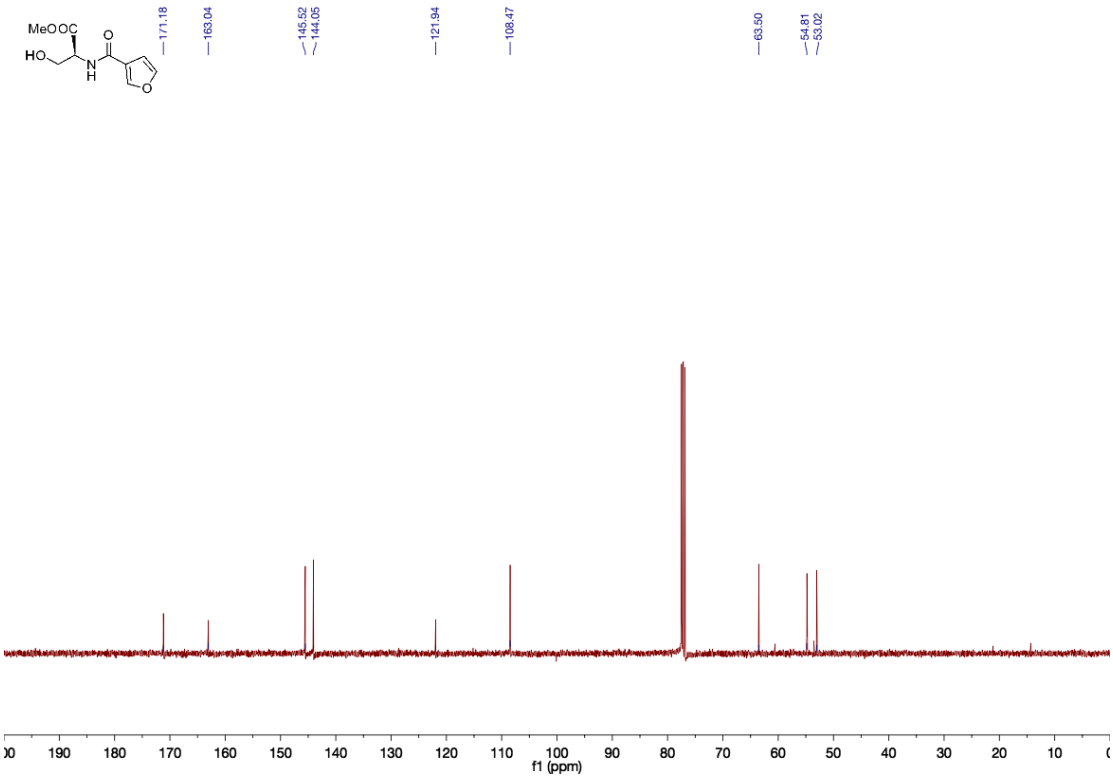

SK-180417-10-211.10.fid
199.9285
166.4636
143.3189
137.3807
134.8225
131.7895
129.3244
129.0698
127.7199
119.4841
60.5285
31.7854
14.1944
8.0300
f1 (ppm)

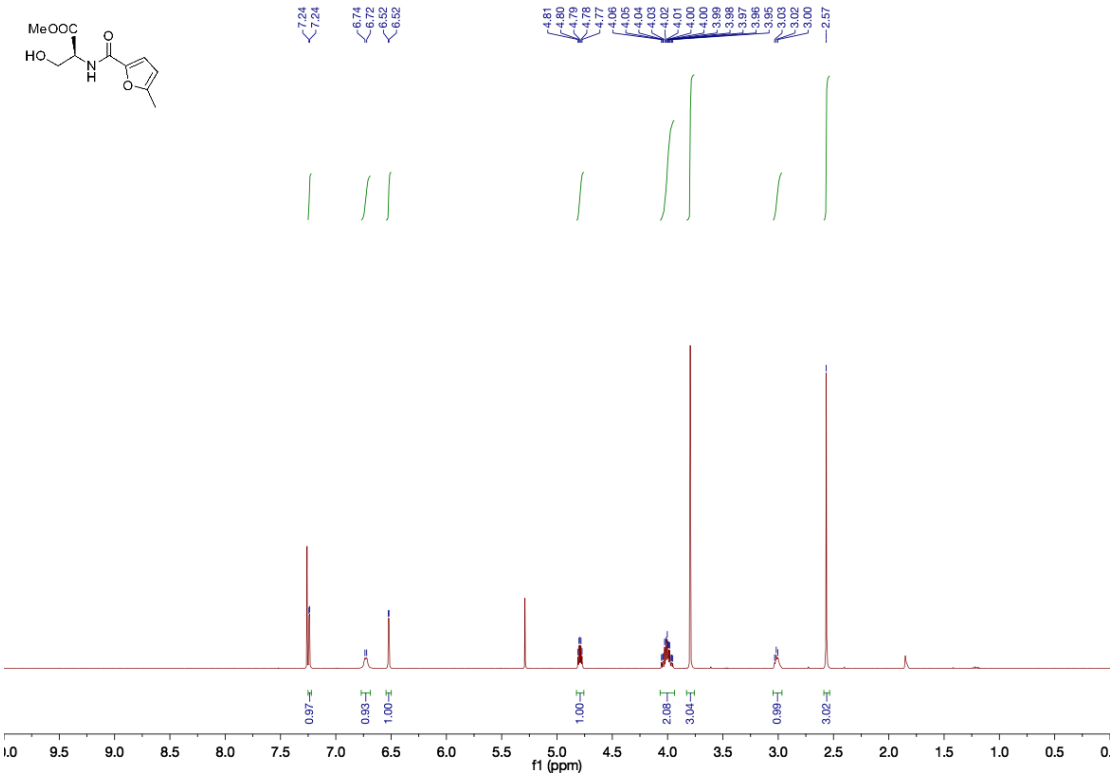
NMR spectroscopic data for intermediates of Iridium complexes.

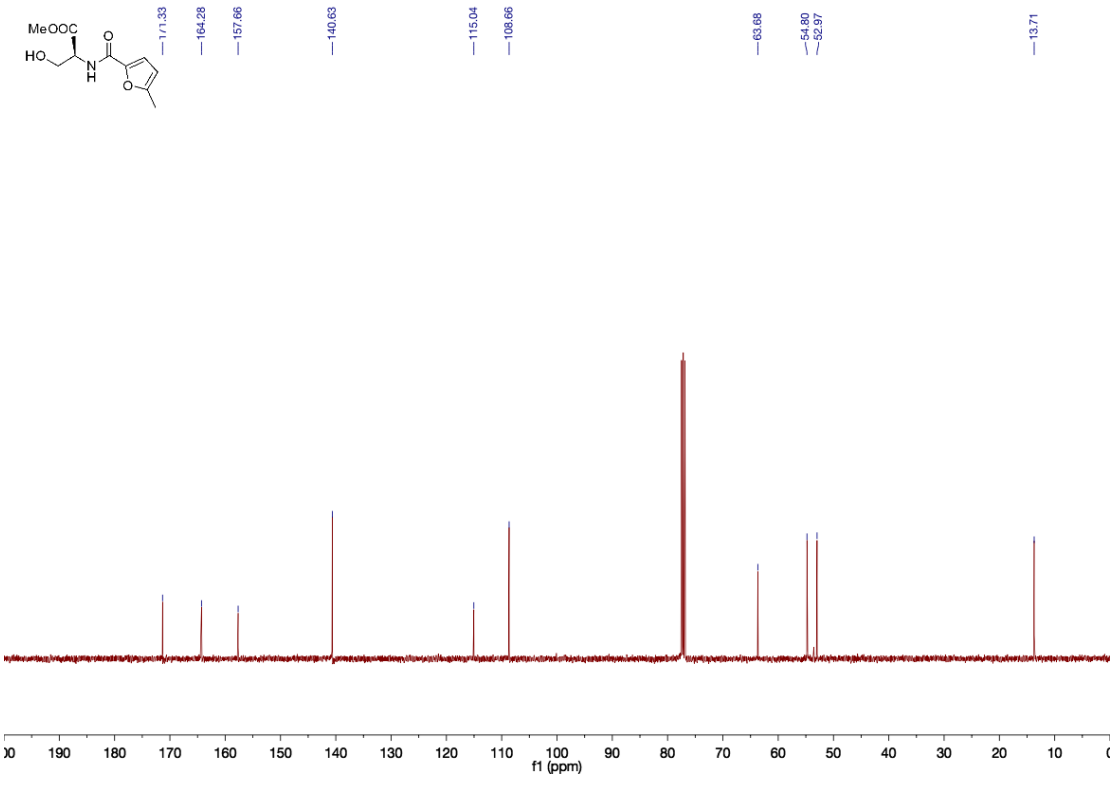


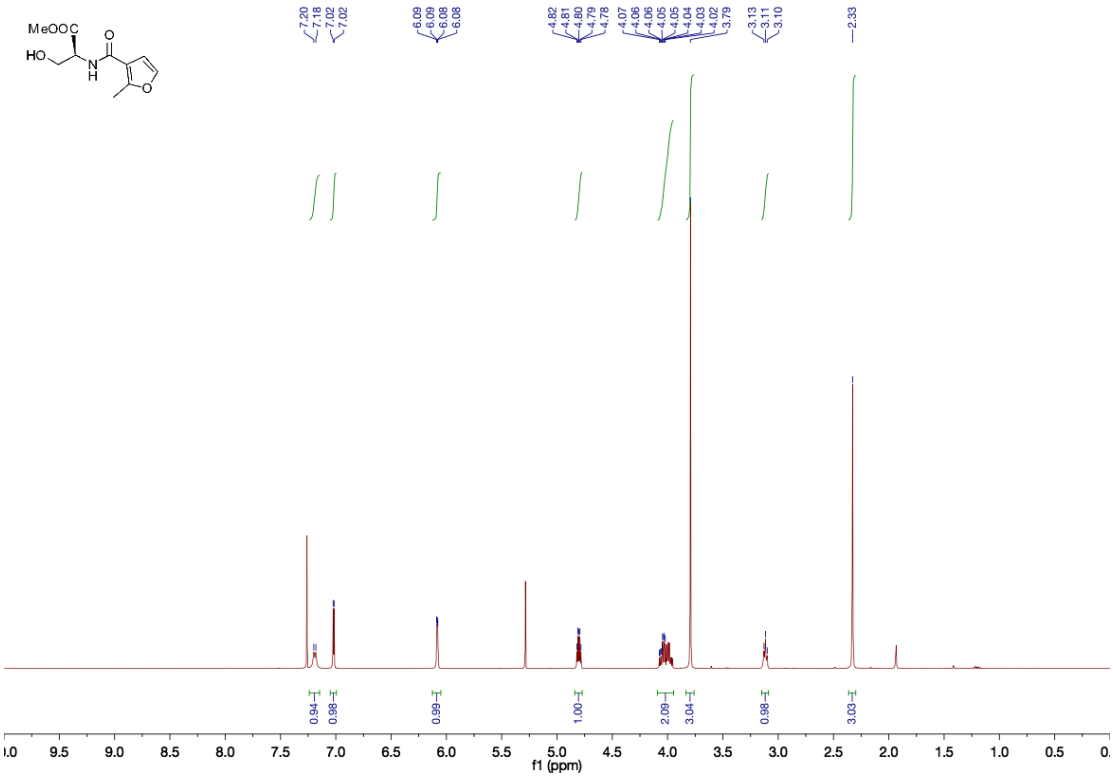


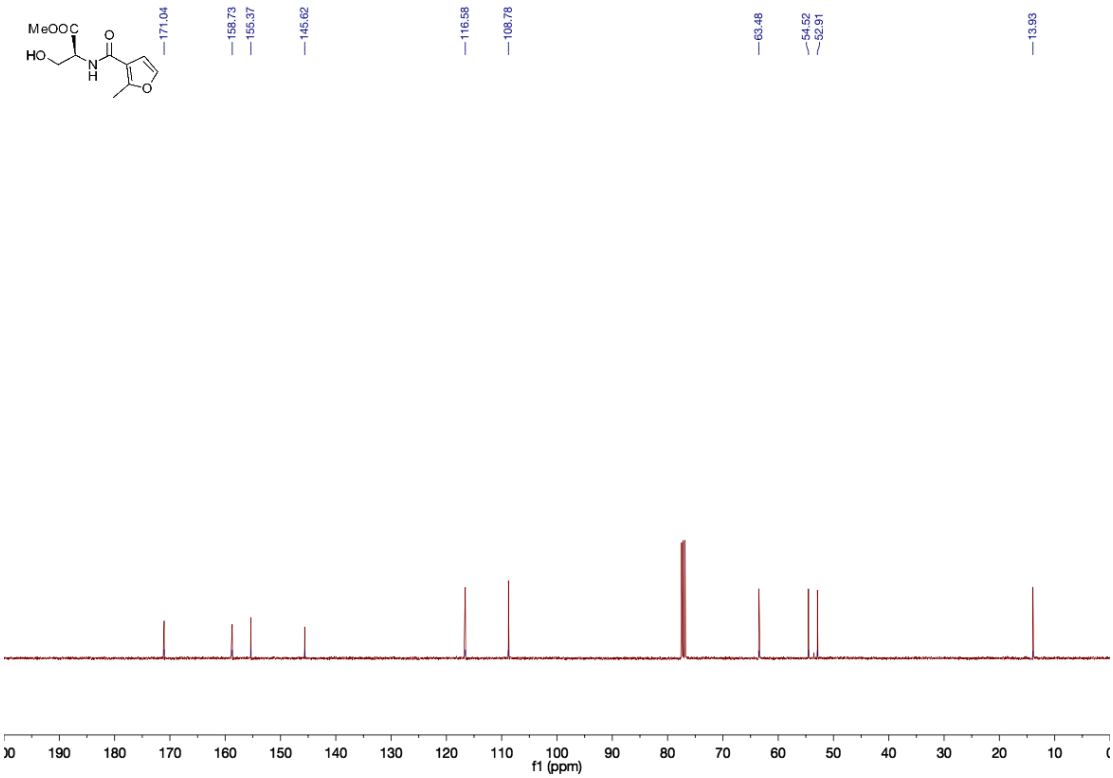

MeOOC
HO
O
N
H
O
7.99
7.98
7.43
7.43
7.43
6.86
6.85
6.68
6.68
6.67
6.67
4.83
4.83
4.82
4.81
4.80
4.07
4.06
4.05
4.05
4.04
4.03
4.03
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.93
2.96
2.95
2.93
0.96
0.97
0.94
1.00
1.00
2.08
3.01
0.99
f1 (ppm)

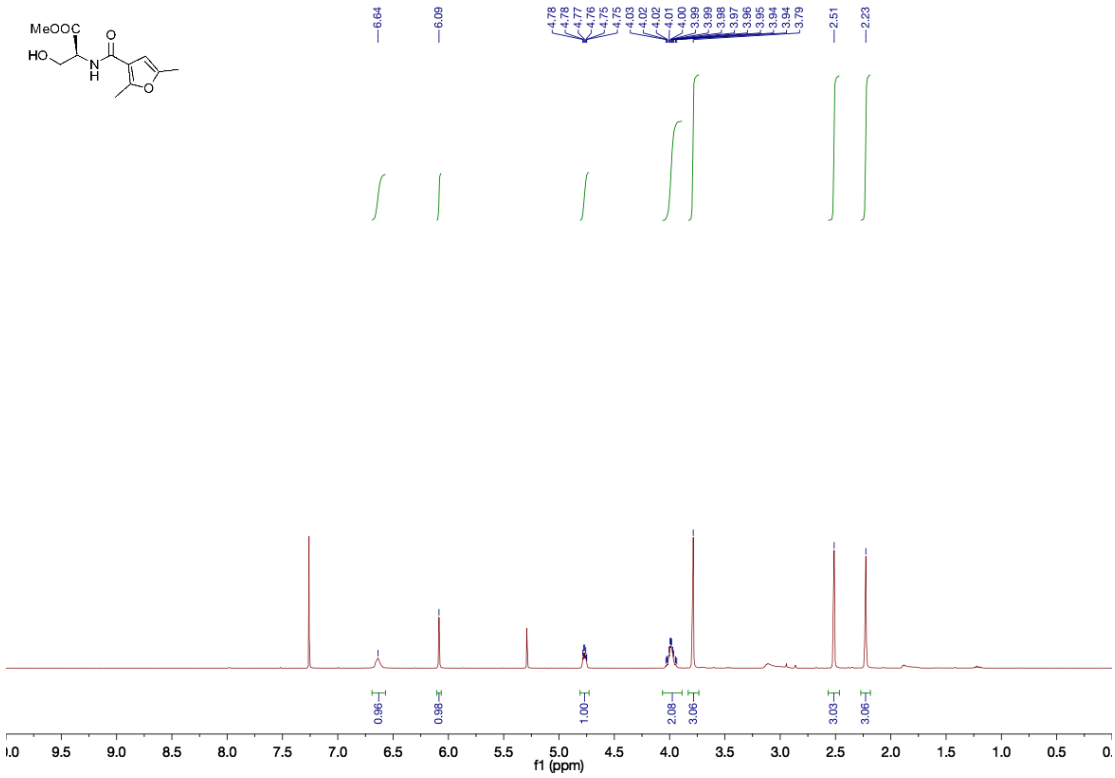

MeOOC
HO
O
N
H
O
171.18
163.04
145.52
144.05
121.94
108.47
63.50
54.81
53.02
f1 (ppm)

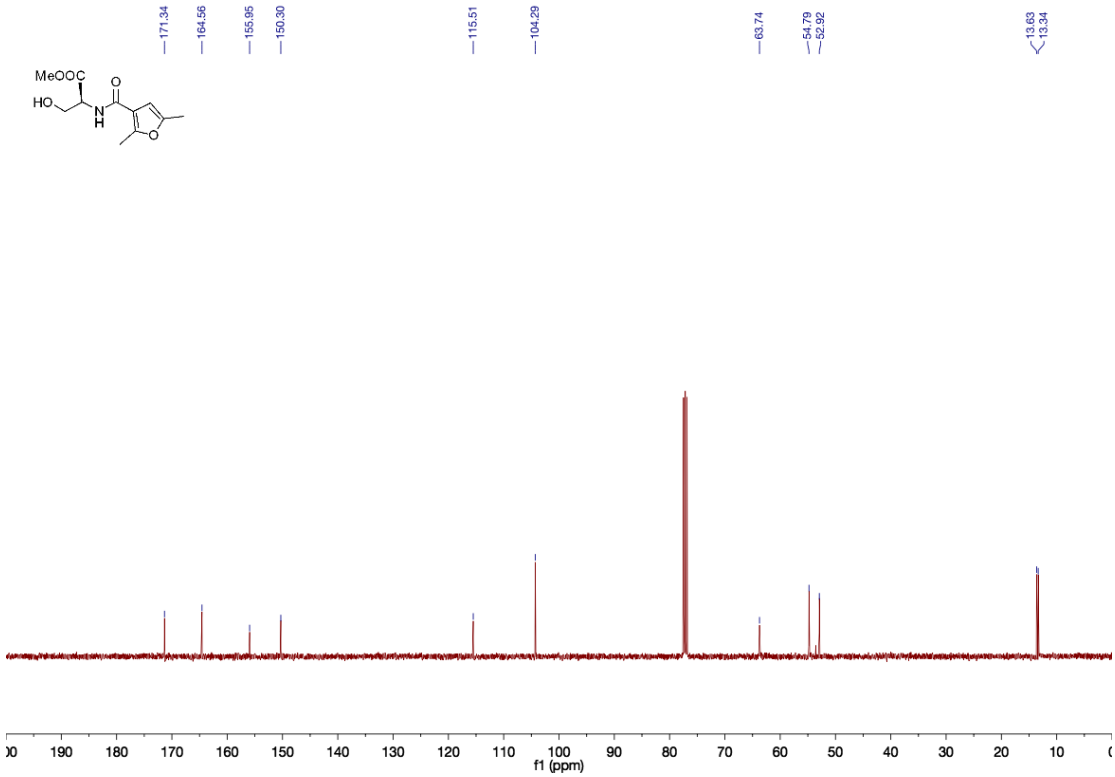

MeOOC
HO
N
H
O
7.24
7.24
6.74
6.72
6.52
6.52
4.81
4.80
4.79
4.78
4.77
4.06
4.05
4.04
4.03
4.02
4.01
4.00
4.00
3.99
3.98
3.97
3.96
3.95
3.03
3.02
3.00
2.57
0.97
0.93
1.00
1.00
2.08
3.04
0.99
3.02
f1 (ppm)

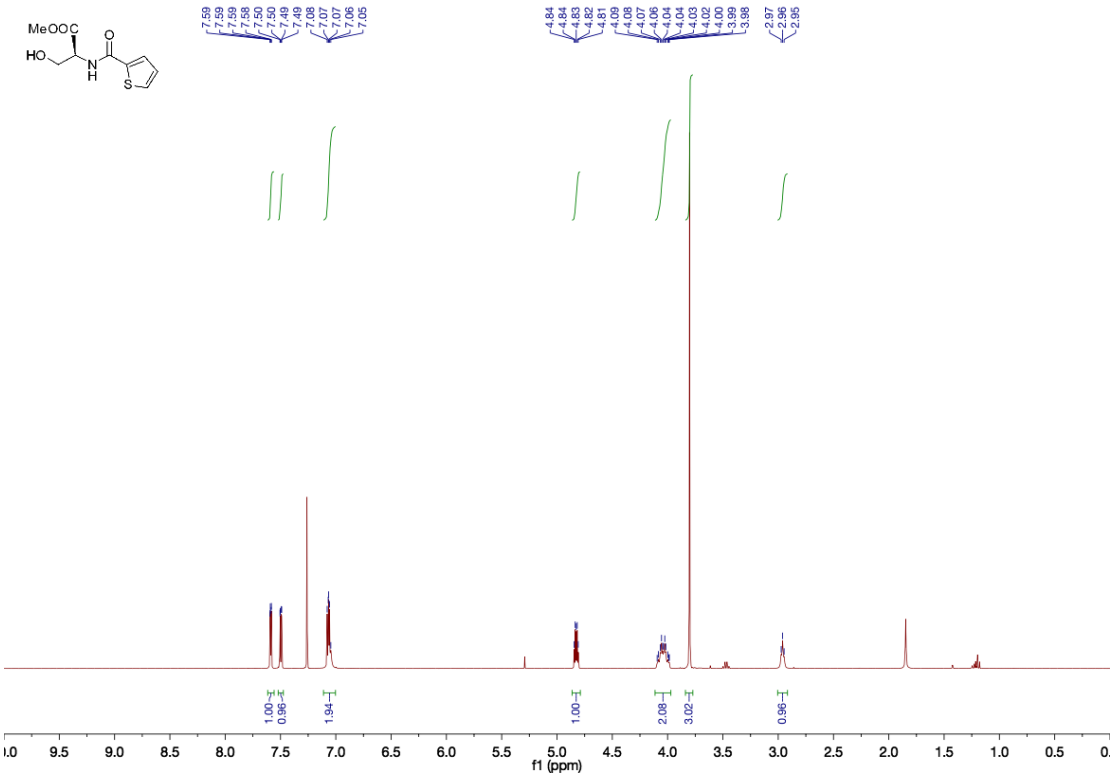

MeOOC
HO
N
H
O
171.33
164.28
157.66
140.63
115.04
108.66
63.68
54.80
52.97
13.71
f1 (ppm)

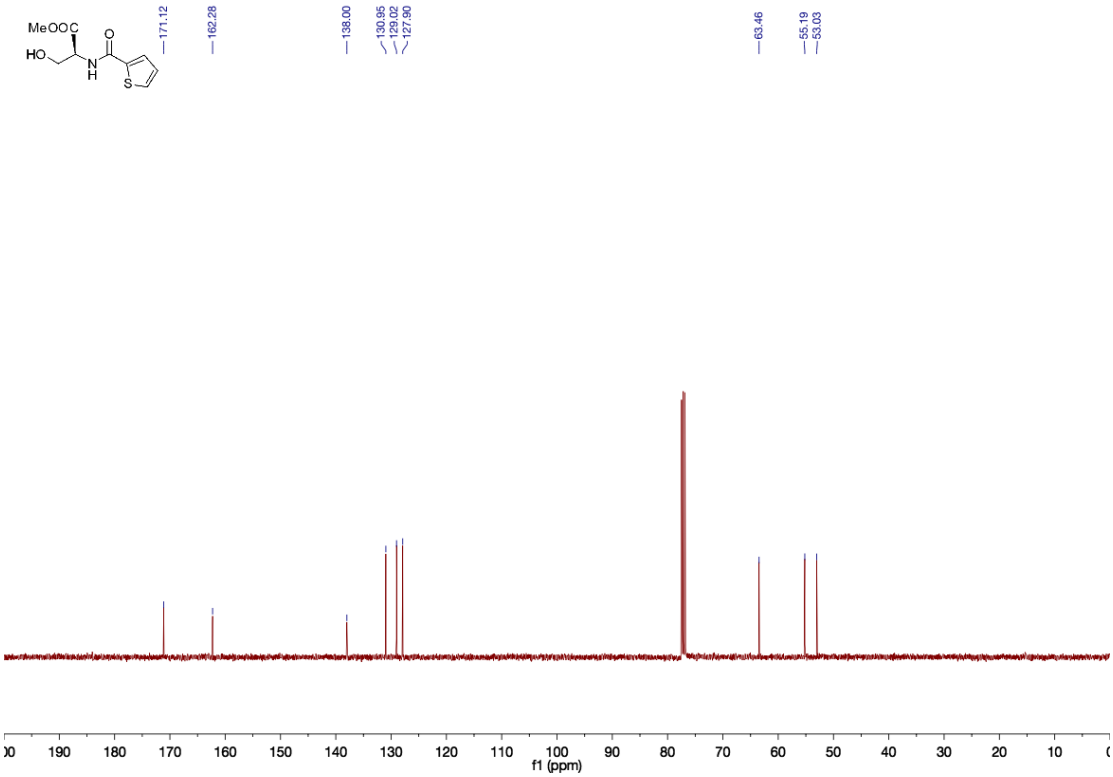

MeOOC
HO
N
H
O
7.20
7.18
7.02
7.02
6.09
6.09
6.08
6.08
4.82
4.81
4.80
4.79
4.78
4.07
4.06
4.06
4.05
4.05
4.04
4.03
4.02
3.79
3.13
3.11
3.10
2.33
0.94
0.98
0.99
1.00
2.09
3.04
0.98
3.03
f1 (ppm)

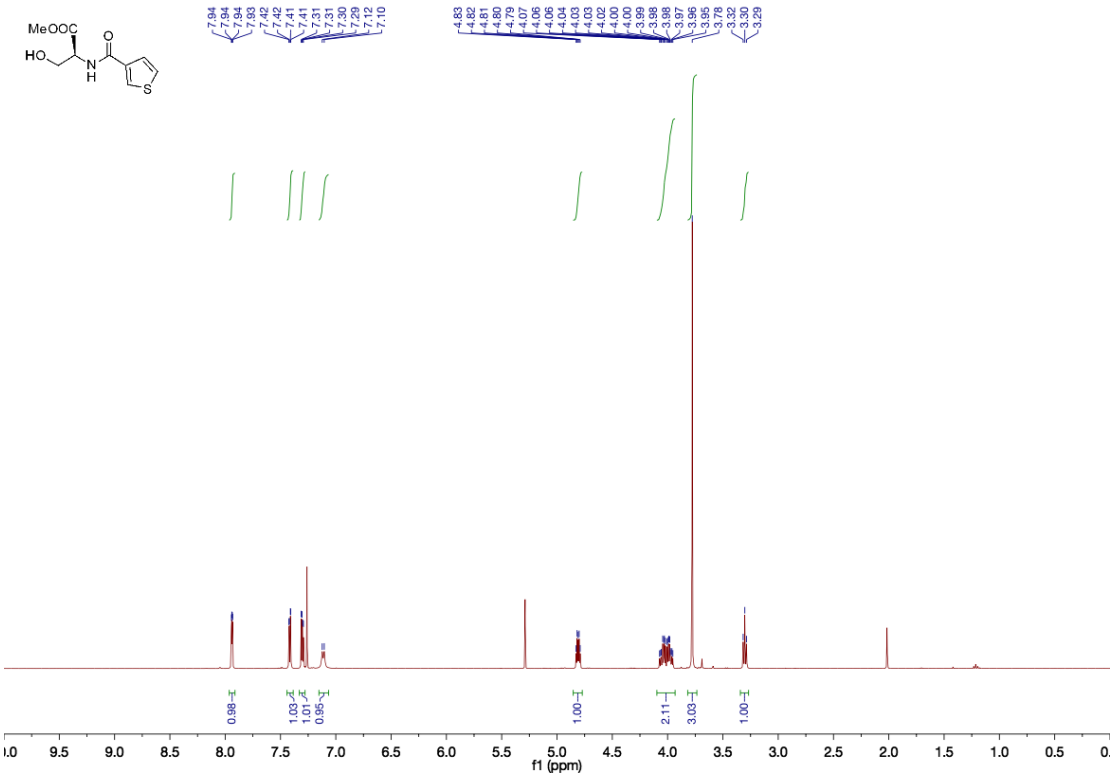

MeOOC
HO
N
H
O
171.04
158.73
155.37
145.62
116.58
108.78
63.48
54.52
52.91
13.93
f1 (ppm)

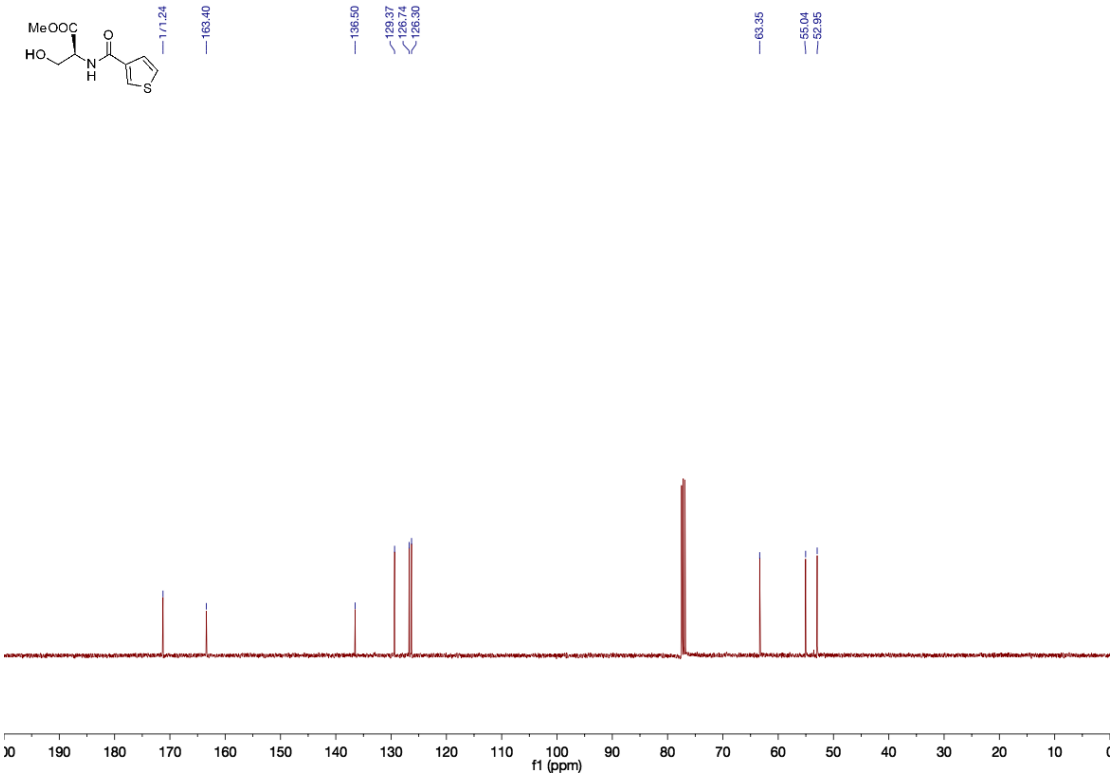

MeOOC
HO
N
H
O
6.64
6.09
4.78
4.78
4.77
4.76
4.75
4.75
4.03
4.02
4.02
4.01
4.00
3.99
3.99
3.98
3.97
3.96
3.95
3.94
3.79
2.51
2.23
0.96
0.98
1.00
2.08
3.06
3.03
3.06
f1 (ppm)

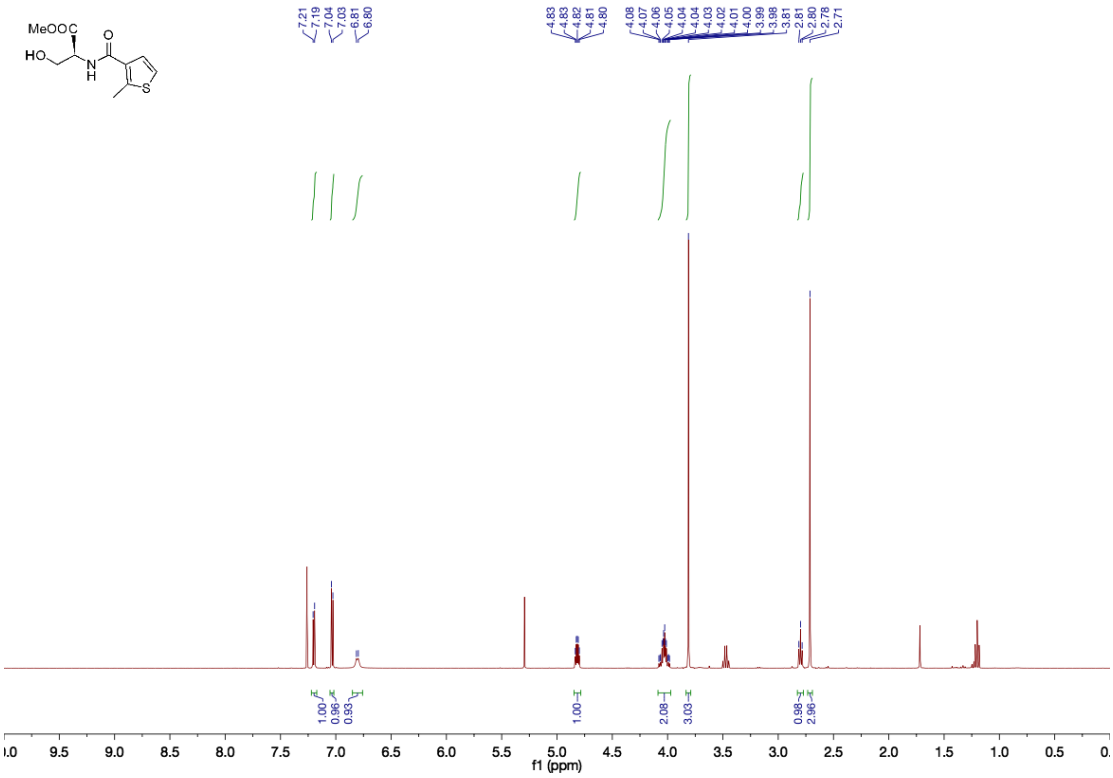

MeOOC
HO
N
H
O
171.34
164.56
155.95
150.30
115.51
104.29
63.74
54.79
52.92
13.63
13.34
f1 (ppm)

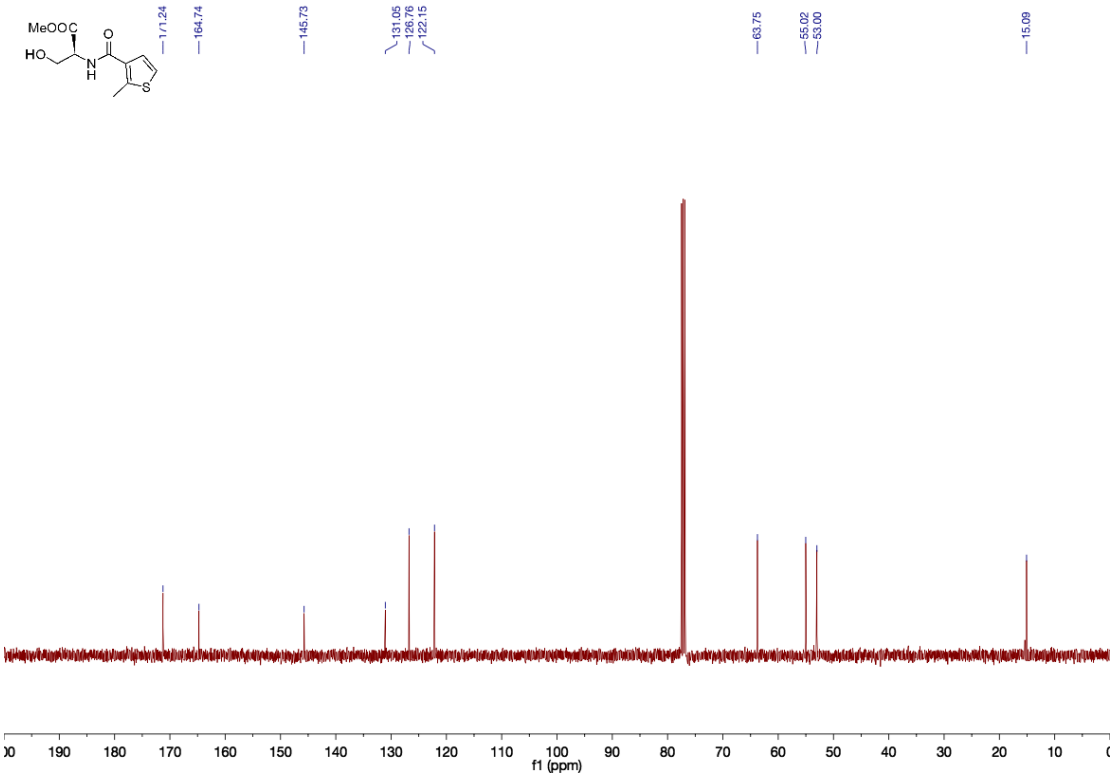

MeOOC
HO
N
H
O
S
7.59
7.59
7.59
7.58
7.50
7.50
7.49
7.49
7.08
7.07
7.07
7.06
7.05
4.84
4.84
4.83
4.82
4.81
4.09
4.08
4.07
4.06
4.04
4.04
4.03
4.02
4.00
3.99
3.98
2.97
2.96
2.95
1.00
0.98
1.94
1.00
2.08
3.02
0.96
f1 (ppm)

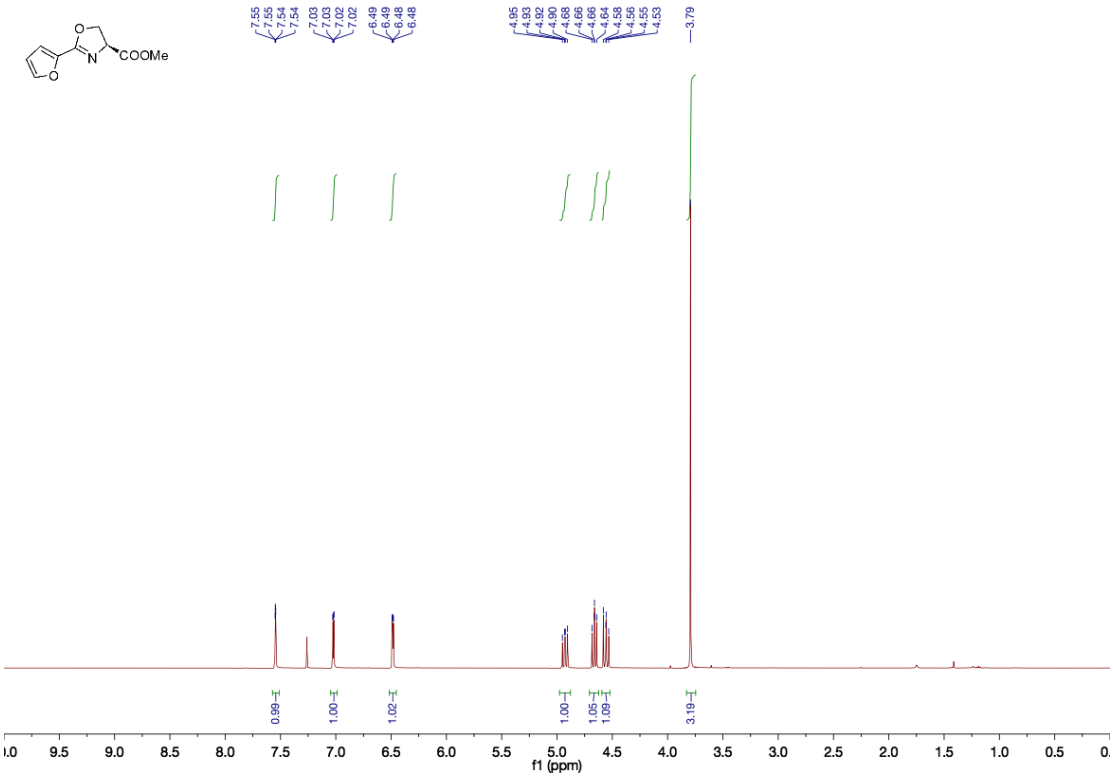

MeOOC
HO
N
H
O
S
171.12
162.28
138.00
130.95
129.02
127.90
63.46
55.19
53.03
f1 (ppm)

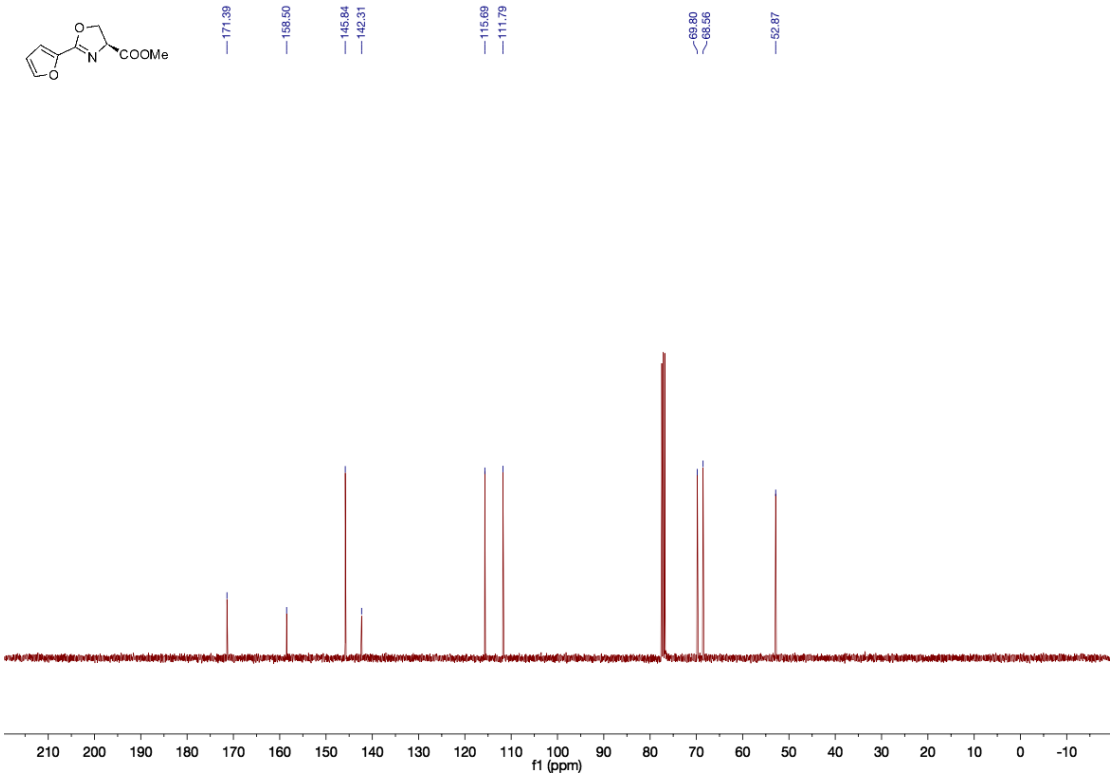

MeOOC
HO
N
H
O
S
7.94
7.94
7.94
7.93
7.42
7.42
7.41
7.41
7.31
7.31
7.30
7.29
7.12
7.10
4.83
4.82
4.81
4.80
4.79
4.07
4.06
4.06
4.04
4.03
4.03
4.02
4.00
4.00
3.99
3.98
3.98
3.97
3.96
3.95
3.78
3.32
3.30
3.29
0.98
1.03
1.01
0.95
1.00
2.11
3.03
1.00
f1 (ppm)

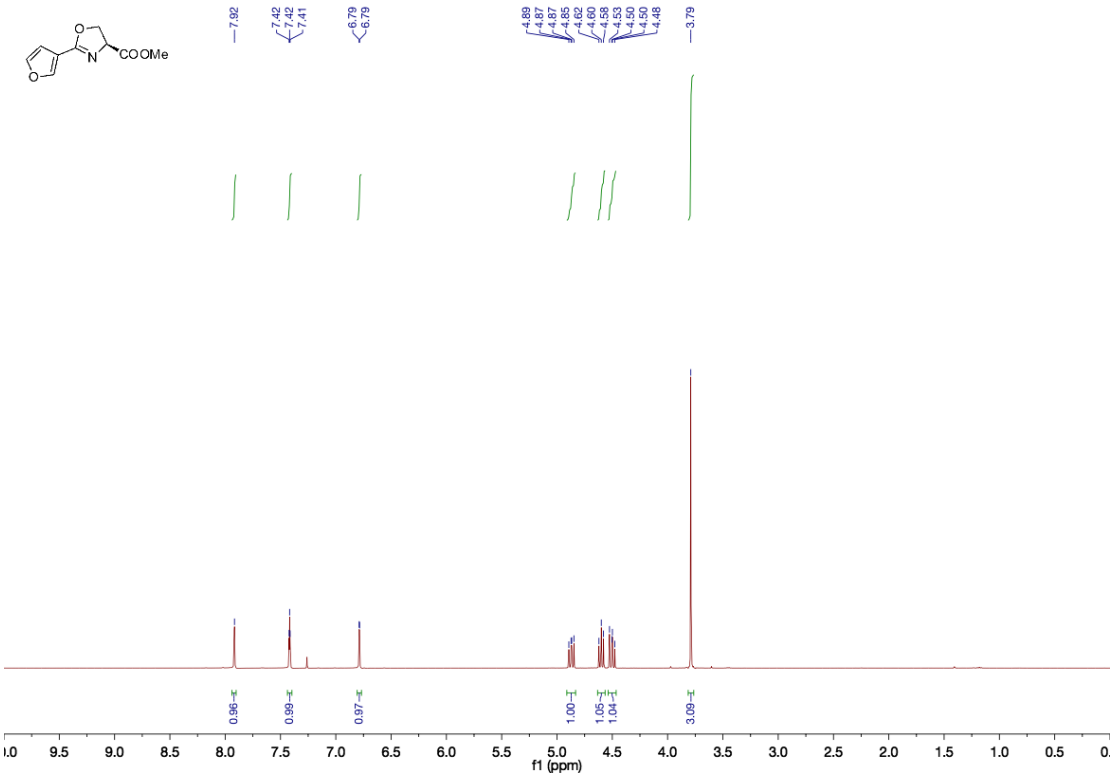

MeOOC
HO
N
H
O
S
171.24
163.40
136.50
129.37
126.74
126.30
63.35
55.04
52.95
f1 (ppm)

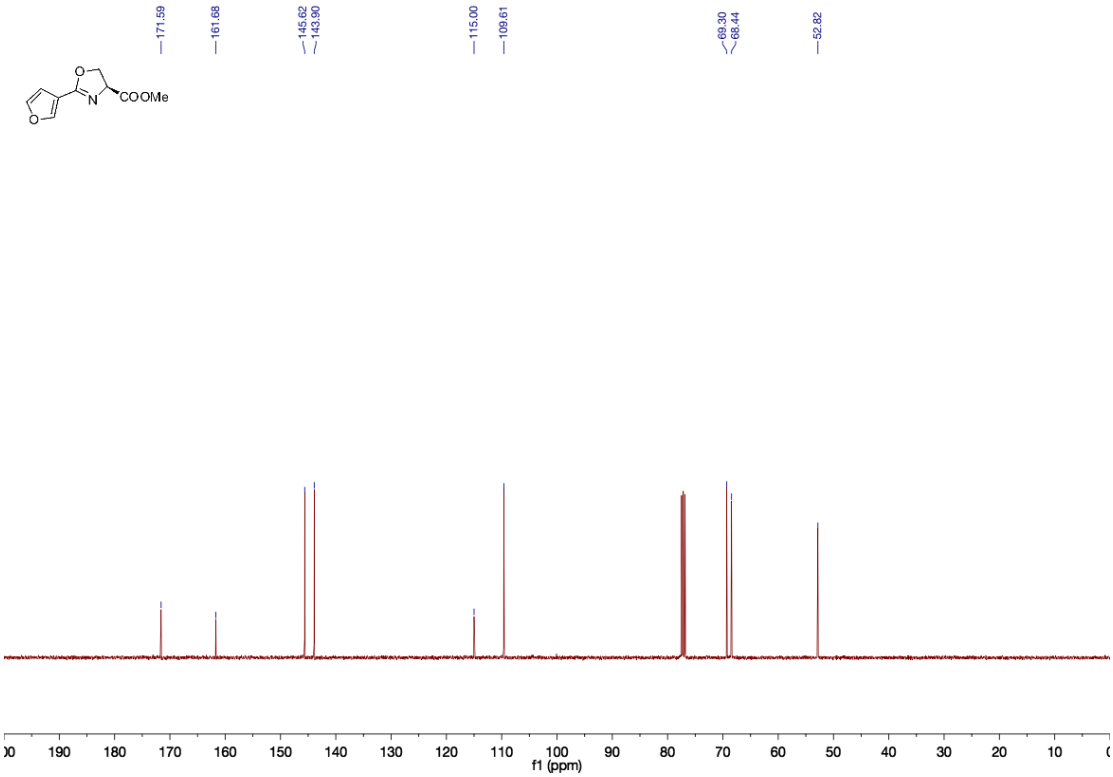

MeOOC
HO
N
H
O
S
7.21
7.19
7.04
7.03
6.81
6.80
4.83
4.82
4.81
4.80
4.08
4.07
4.06
4.05
4.04
4.03
4.02
4.01
4.00
3.99
3.98
3.81
2.80
2.78
2.71
1.00
0.96
0.93
1.00
2.08
3.03
0.98
2.96
f1 (ppm)

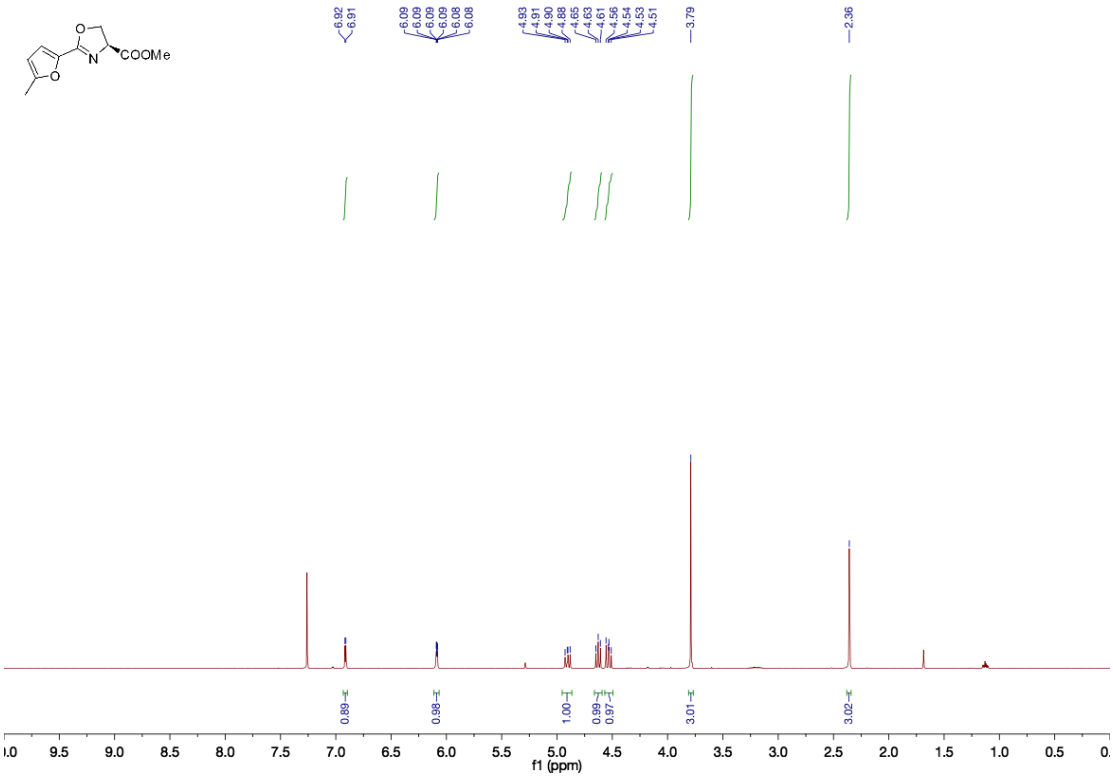

MeOOC
HO
N
H
O
S
171.24
164.74
145.73
131.05
126.76
122.15
63.75
55.02
53.00
15.09
f1 (ppm)

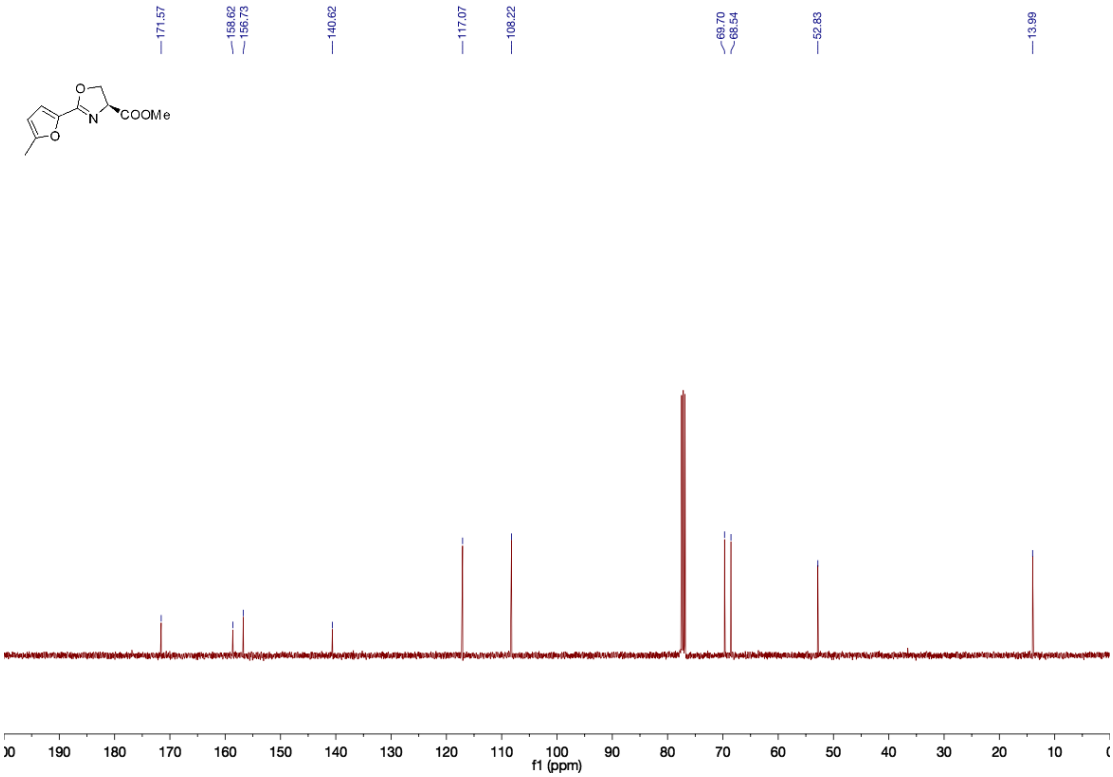

COOMe
7.55
7.55
7.54
7.54
7.03
7.03
7.02
7.02
6.49
6.49
6.48
6.48
4.95
4.93
4.92
4.90
4.68
4.66
4.66
4.64
4.58
4.56
4.55
4.53
3.79
0.99
1.00
1.02
1.00
1.05
1.09
3.19
f1 (ppm)

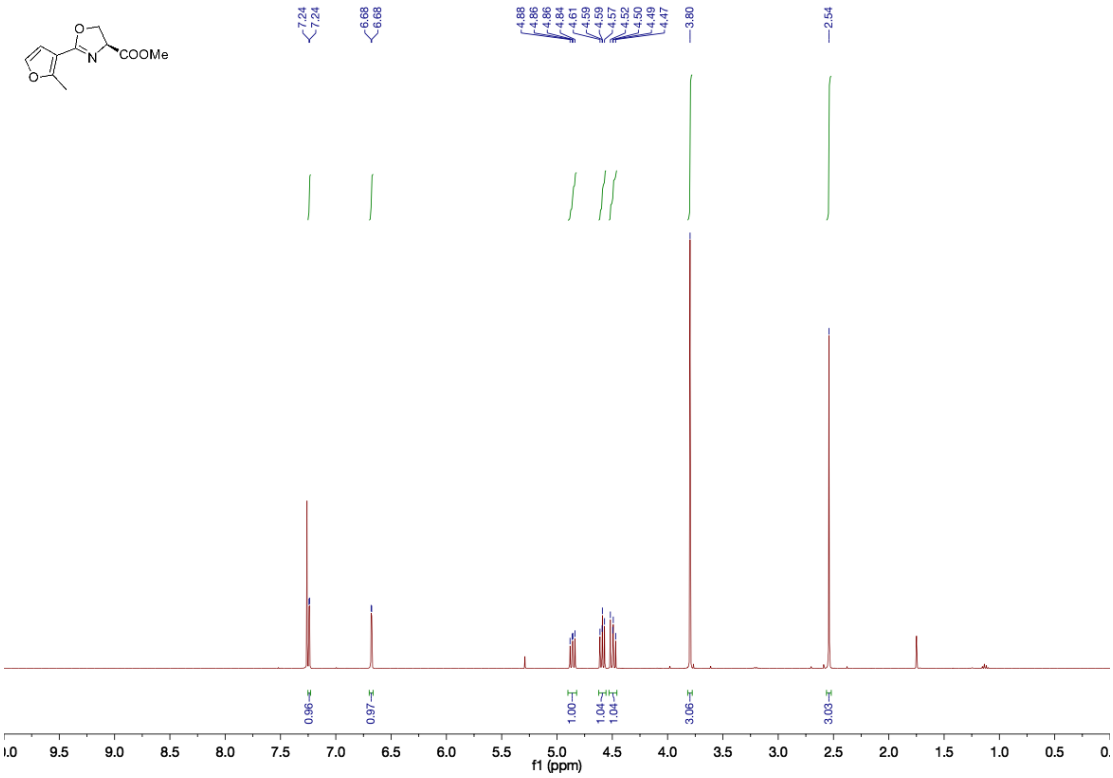

COOMe
171.39
158.50
145.84
142.31
115.69
111.79
69.80
68.56
52.87
f1 (ppm)

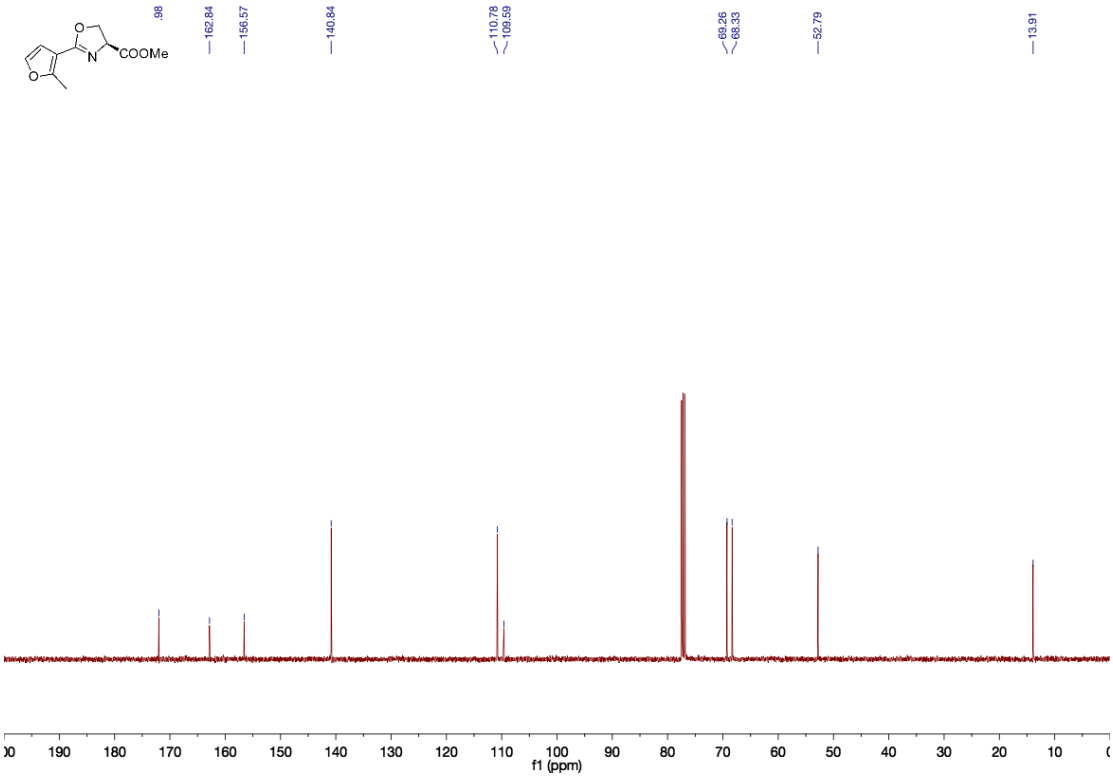

COOMe
7.92
7.42
7.42
7.41
6.79
6.79
4.89
4.87
4.87
4.85
4.62
4.60
4.58
4.55
4.50
4.50
4.48
3.79
0.96
0.99
0.97
1.00
1.05
1.04
3.09
f1 (ppm)

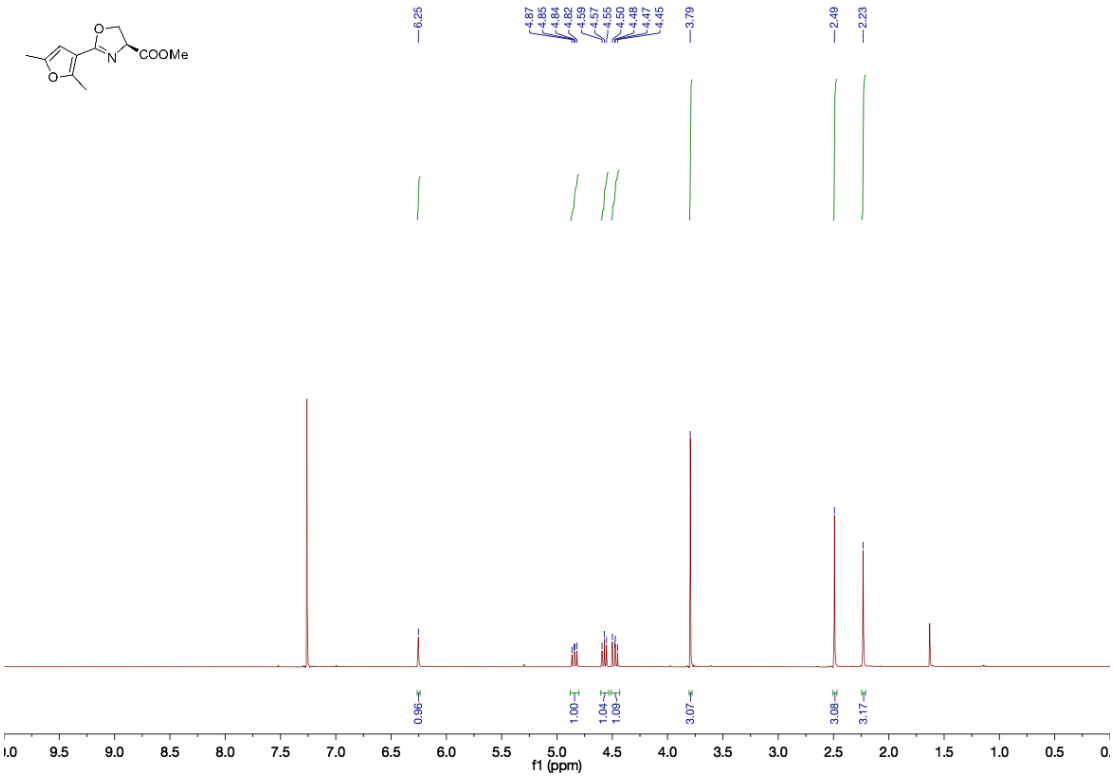

COOMe
171.59
161.68
145.62
143.90
115.00
109.61
69.30
68.44
52.82
f1 (ppm)


COOMe
6.92
6.91
6.09
6.09
6.09
6.09
6.08
6.08
4.93
4.91
4.90
4.88
4.65
4.63
4.61
4.56
4.54
4.53
4.51
3.79
2.36
0.89
0.98
1.00
0.99
0.97
3.01
3.02
f1 (ppm)


COOMe
171.57
158.62
156.73
140.62
117.07
108.22
69.70
68.54
52.83
13.99
f1 (ppm)


COOMe
7.24
7.24
6.68
6.68
4.88
4.86
4.86
4.84
4.61
4.59
4.59
4.57
4.52
4.50
4.49
4.47
3.80
2.54
0.96
0.97
1.00
1.04
1.04
3.06
3.03
f1 (ppm)


COOMe
98
162.84
156.57
140.84
110.78
109.59
69.26
68.33
52.79
13.91
f1 (ppm)


COOMe
6.25
4.87
4.85
4.84
4.82
4.59
4.57
4.55
4.50
4.48
4.47
4.45
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2.23
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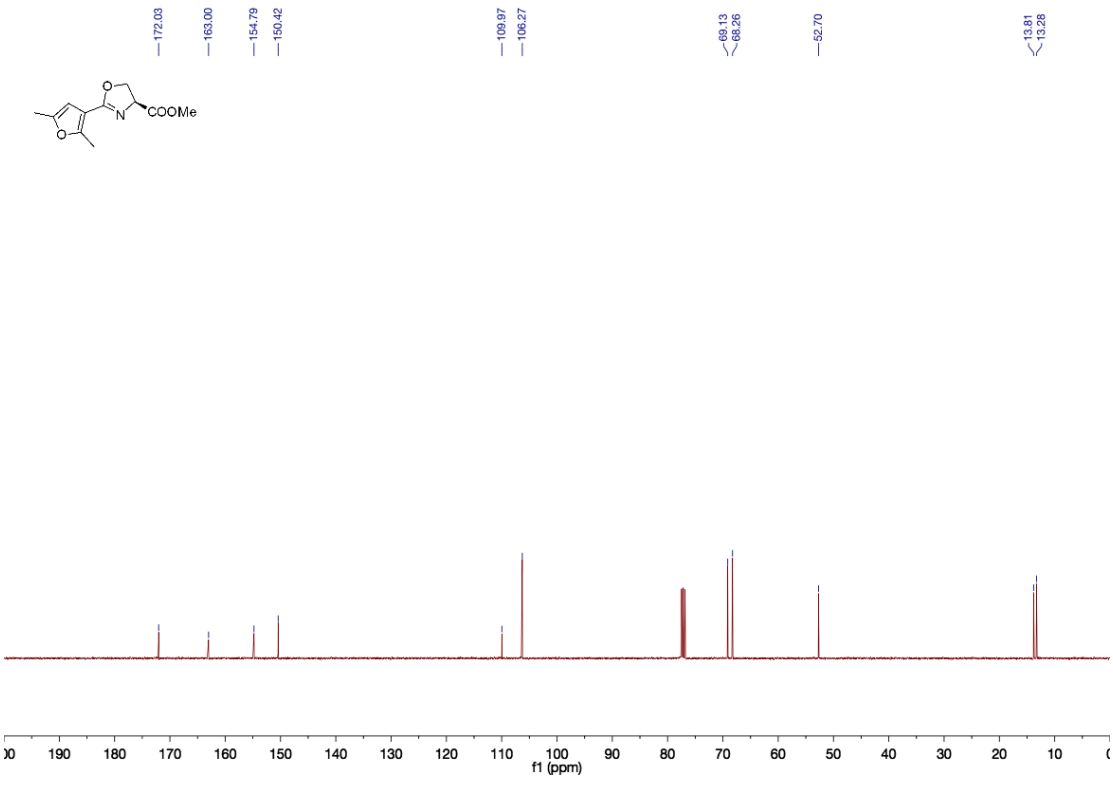
1.04
1.09
3.07
3.08
3.17
f1 (ppm)


COOMe
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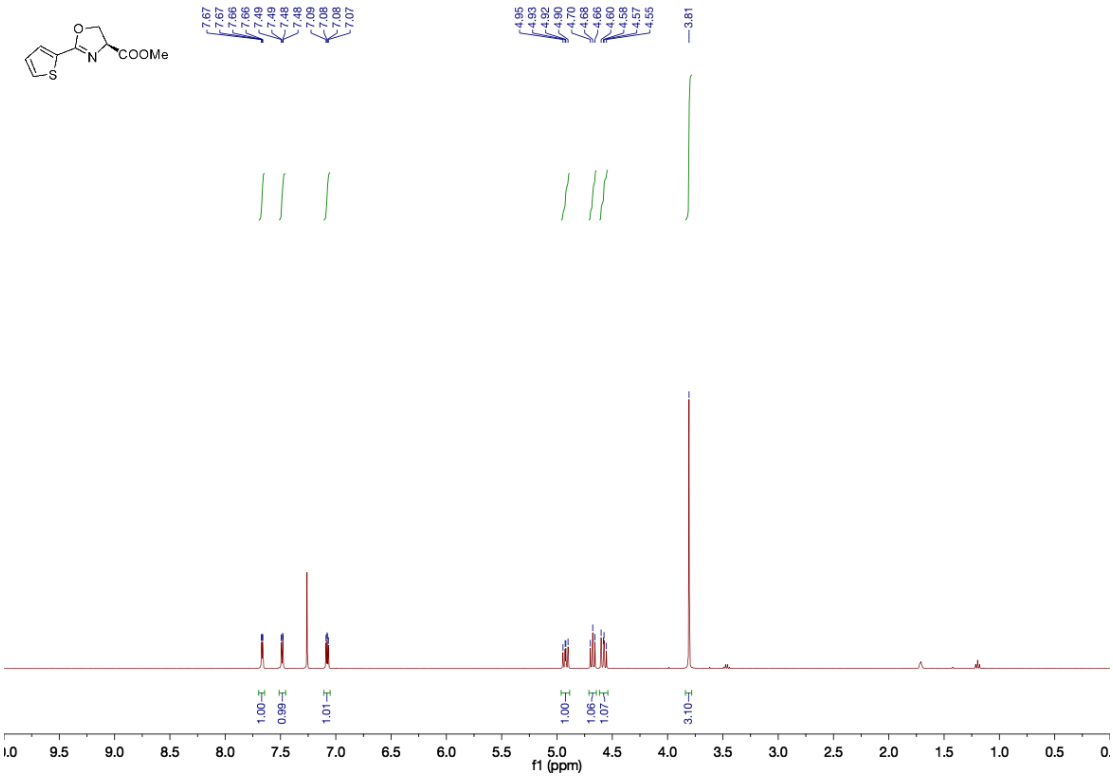
150.42
109.97
106.27
69.13
68.26
52.70
13.81
13.28
f1 (ppm)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7.48
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7.08
7.08
7.07
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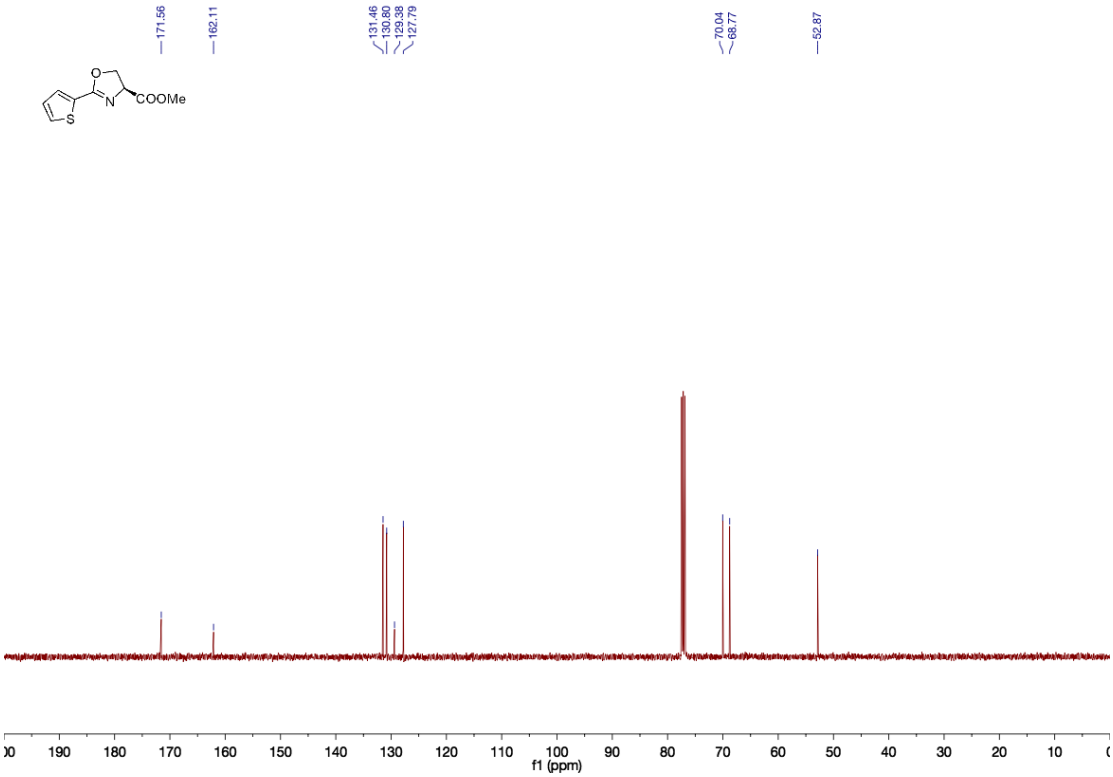
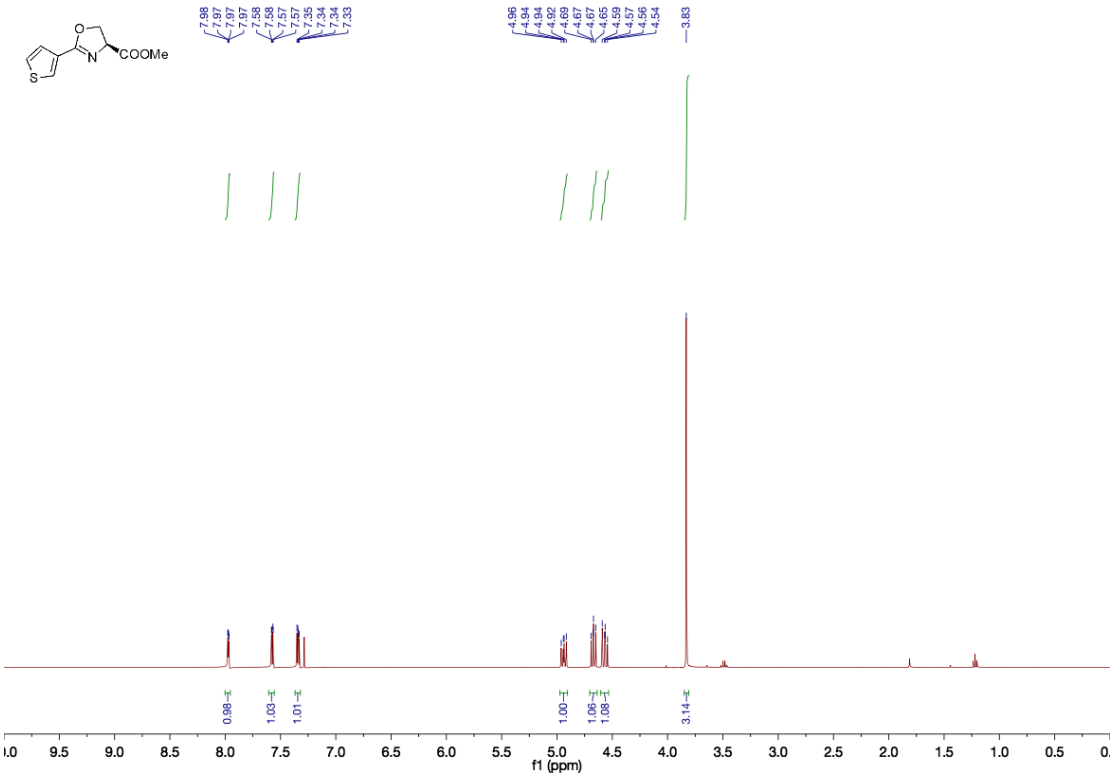
4.93
4.92
4.90
4.70
4.68
4.66
4.60
4.58
4.57
4.55
3.81
COOMe
1.00
0.99
1.01
1.00
1.06
1.07
3.10
f1 (ppm)


171.56
162.11
131.46
130.80
129.38
127.79
70.04
68.77
52.87
COOMe
f1 (ppm)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7.58
7.57
7.57
7.35
7.34
7.34
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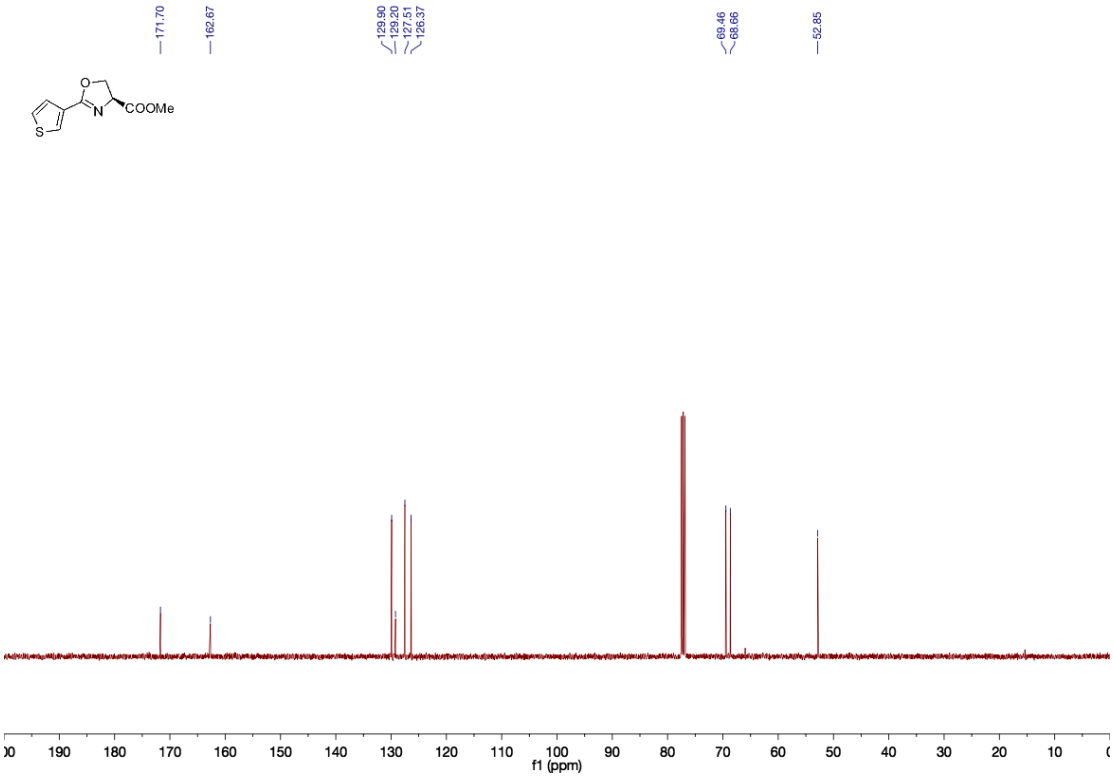
4.96
4.94
4.94
4.92
4.69
4.67
4.67
4.65
4.59
4.57
4.56
4.54
3.83
0.98
1.03
1.01
1.00
1.06
1.08
3.14
f1 (ppm)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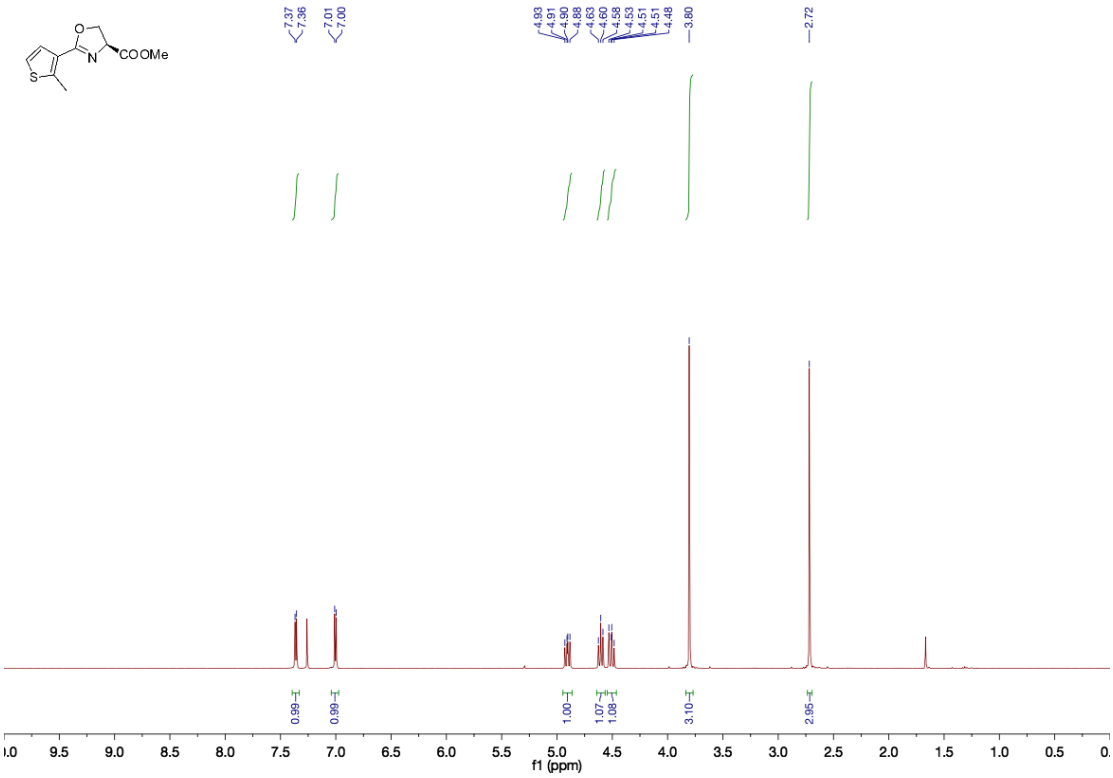
68.66
52.85
f1 (ppm)


COOMe
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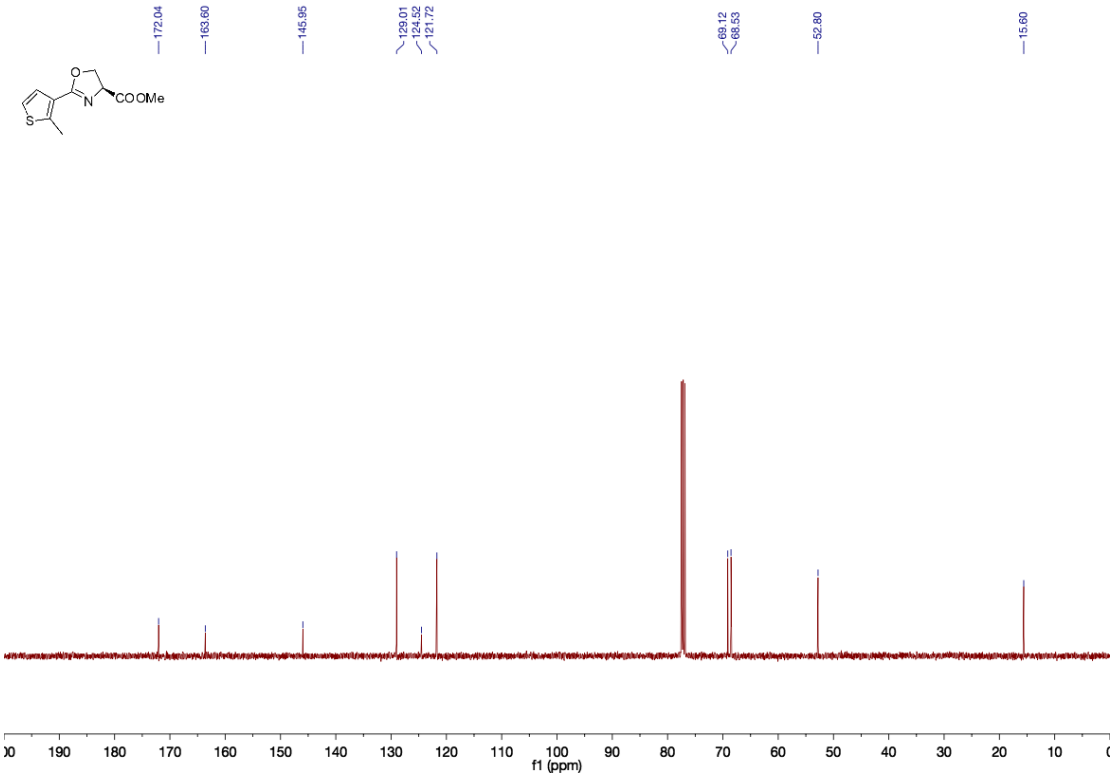
7.00
4.93
4.91
4.90
4.88
4.63
4.60
4.58
4.53
4.51
4.51
4.48
3.80
2.72
0.99
0.99
1.00
1.07
1.08
3.10
2.95
f1 (ppm)


COOMe
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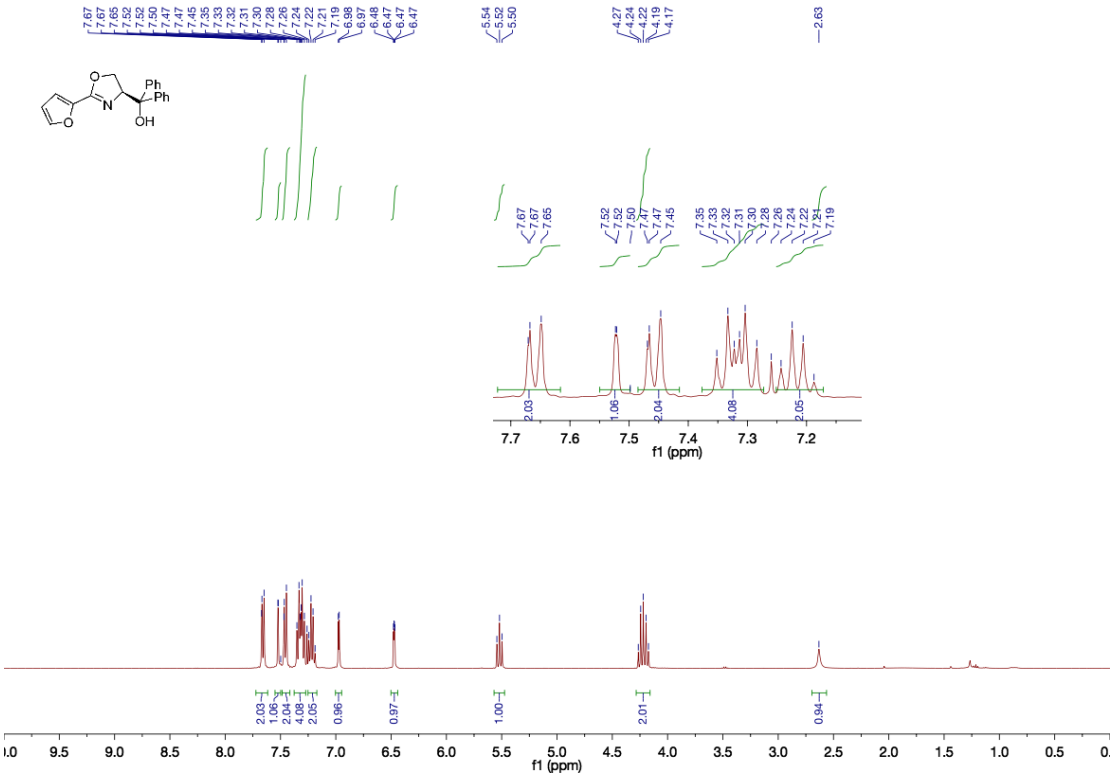
124.52
121.72
69.12
68.53
52.80
15.60
f1 (ppm)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7.67
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7.32
7.31
7.30
7.28
7.26
7.24
7.22
7.21
7.19
6.98
6.97
6.48
6.47
6.47
6.47
5.54
5.52
5.50
4.27
4.24
4.22
4.19
4.17
2.63
Ph
Ph
OH
2.03
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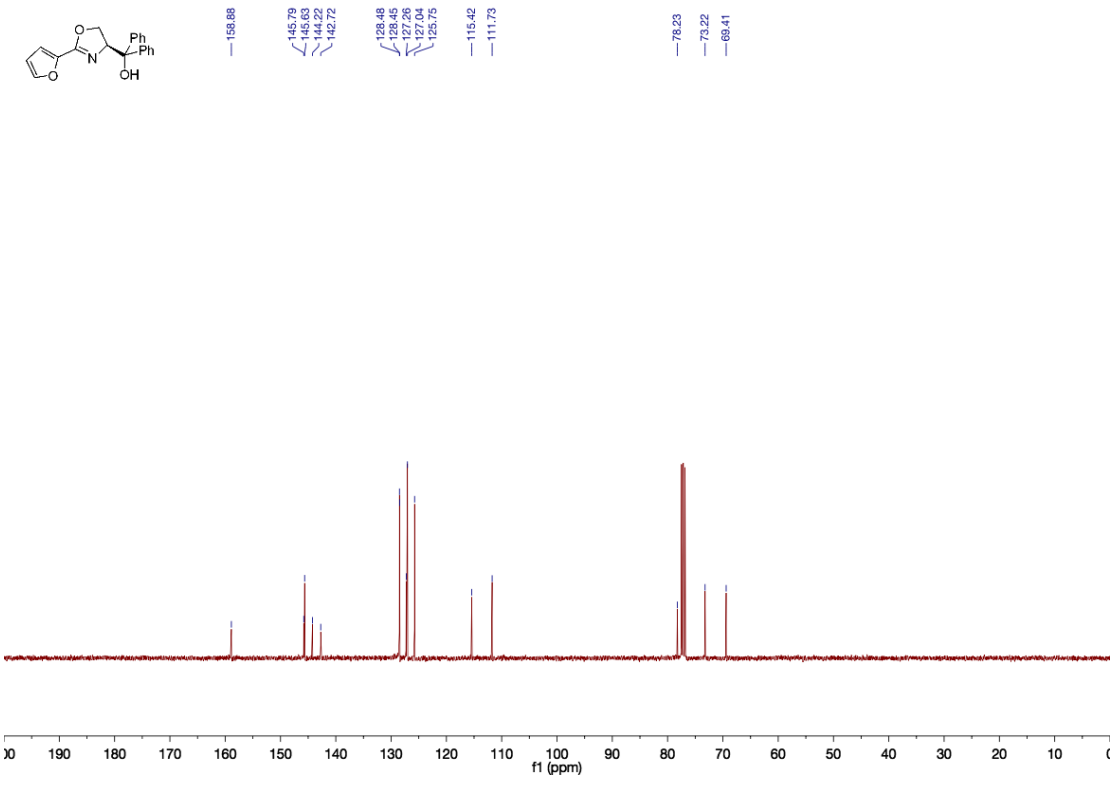
2.04
4.08
2.05
0.96
0.97
1.00
2.01
0.94
f1 (ppm)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144.22
142.72
128.48
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127.26
127.04
125.75
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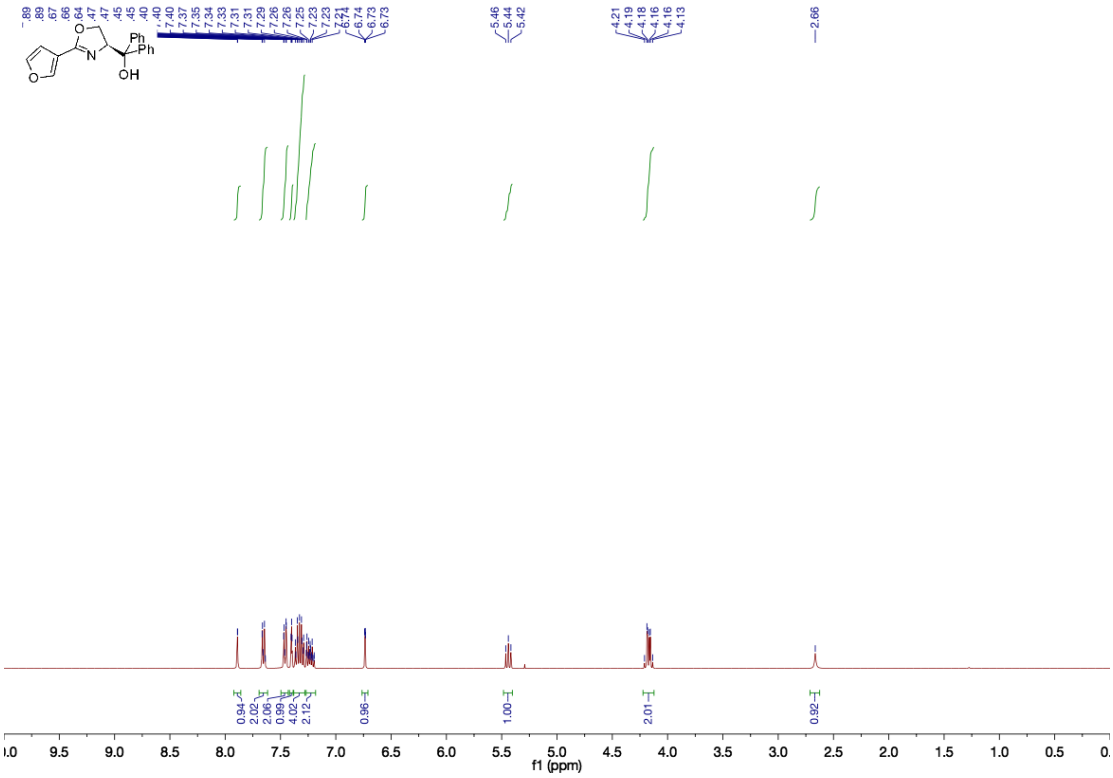
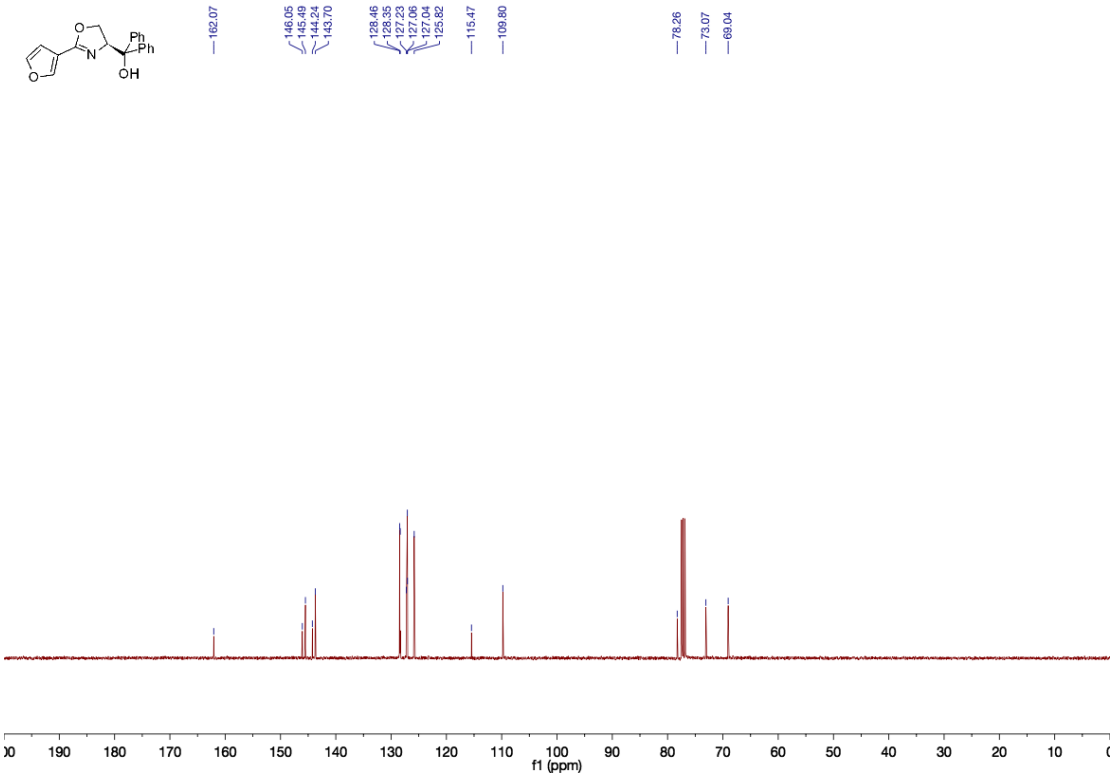
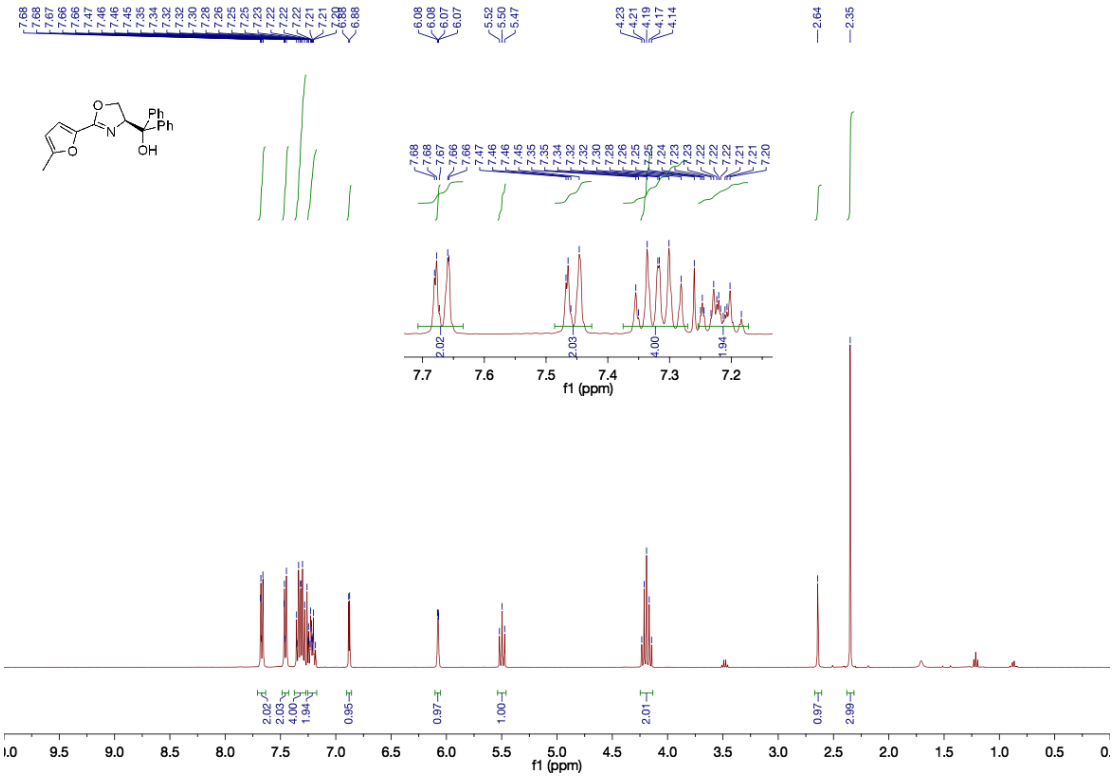
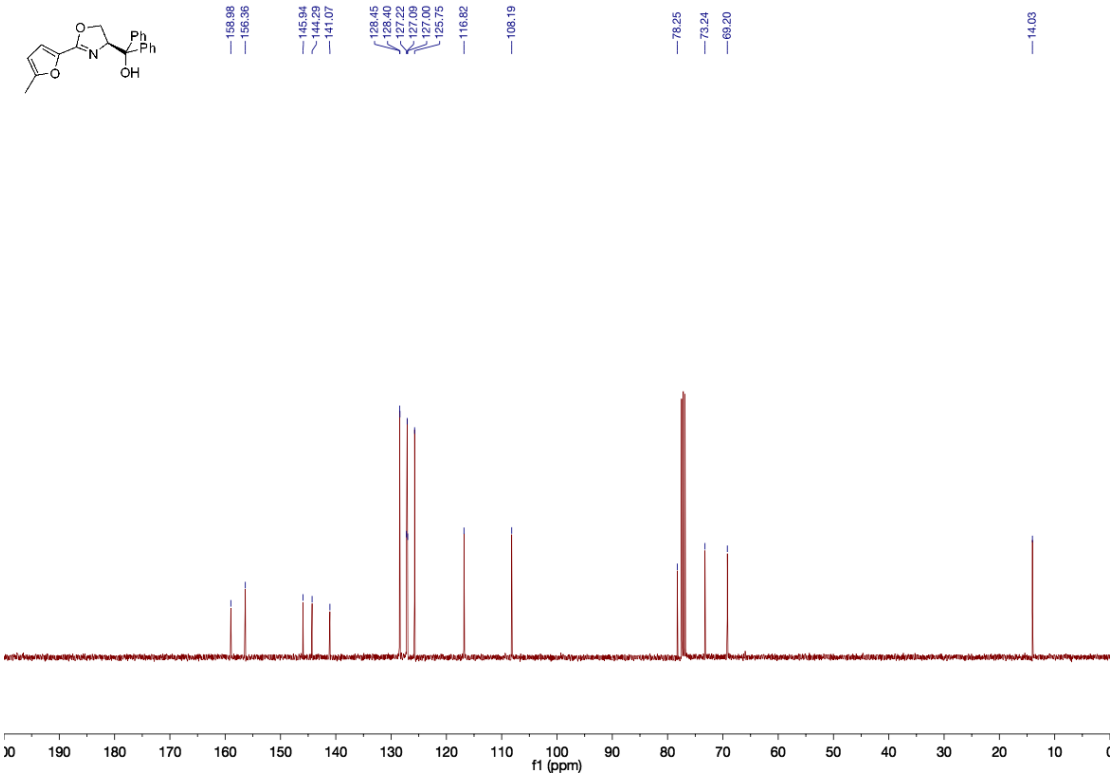
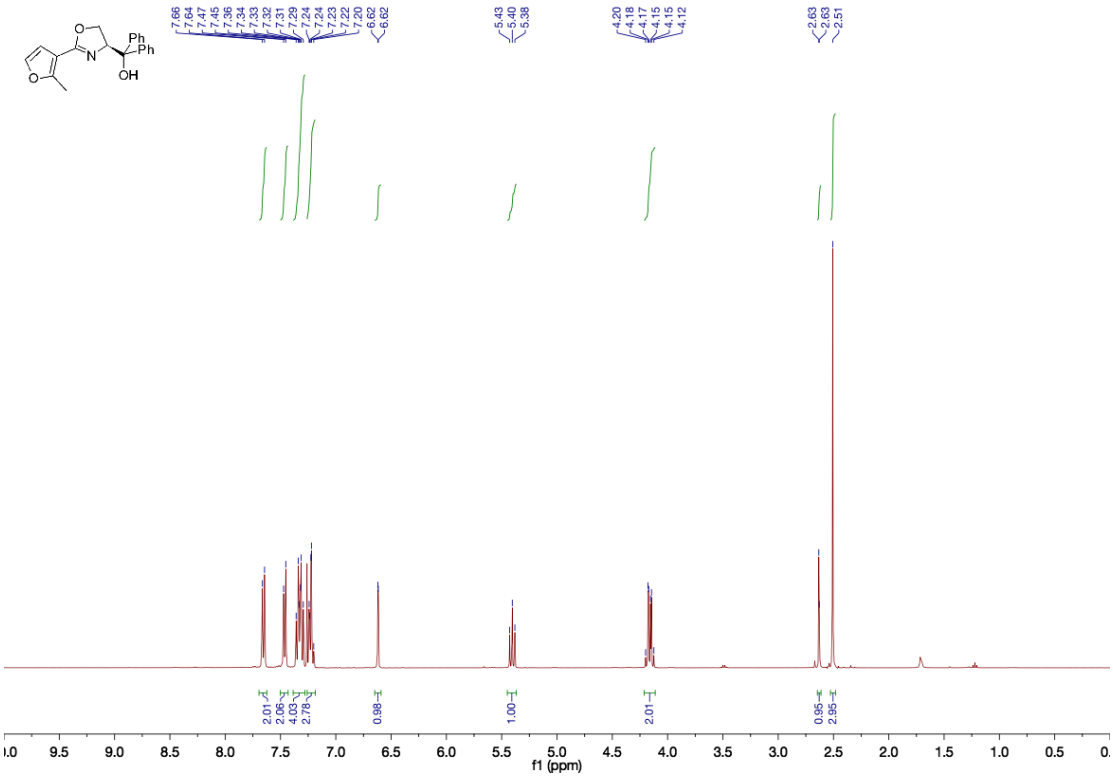
111.73
78.23
73.22
69.41
Ph
Ph
OH
f1 (ppm)


f1 (ppm)


f1 (ppm)


f1 (ppm)


f1 (ppm)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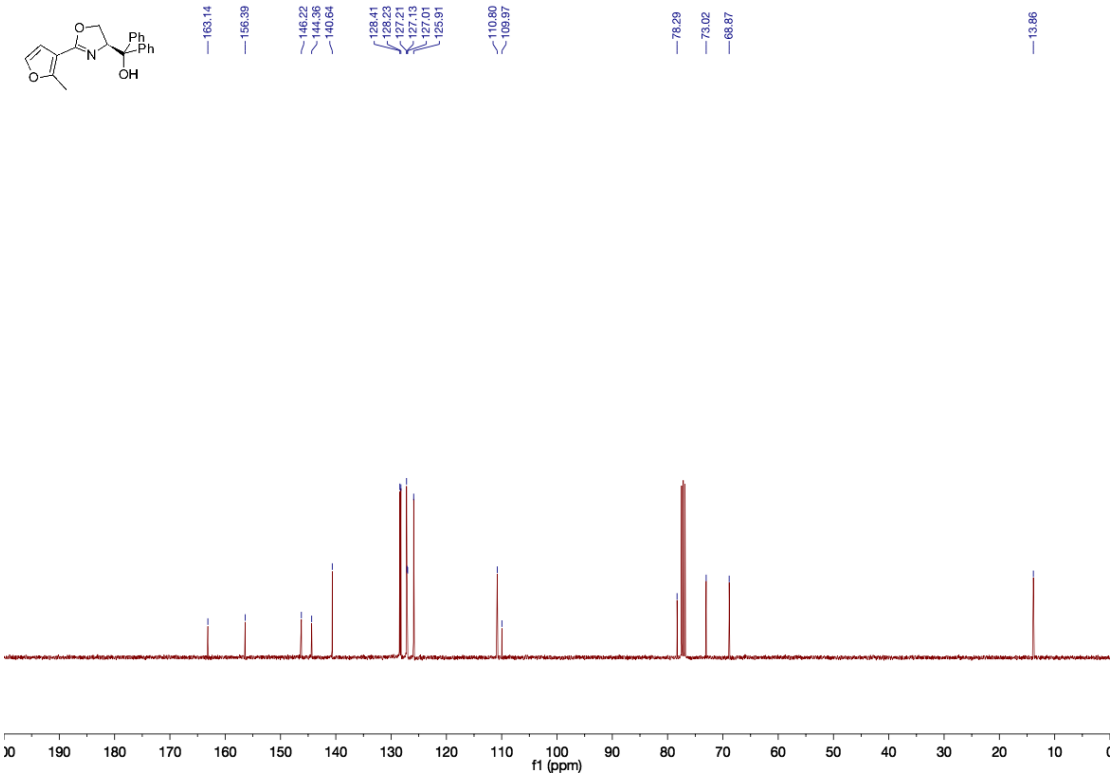
7.24
7.23
7.22
7.20
6.62
6.62
5.43
5.40
5.38
4.20
4.18
4.17
4.15
4.15
4.12
2.63
2.63
2.51
2.01
2.06
4.03
2.78
0.98
1.00
2.01
0.95
2.99
f1 (ppm)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73.02
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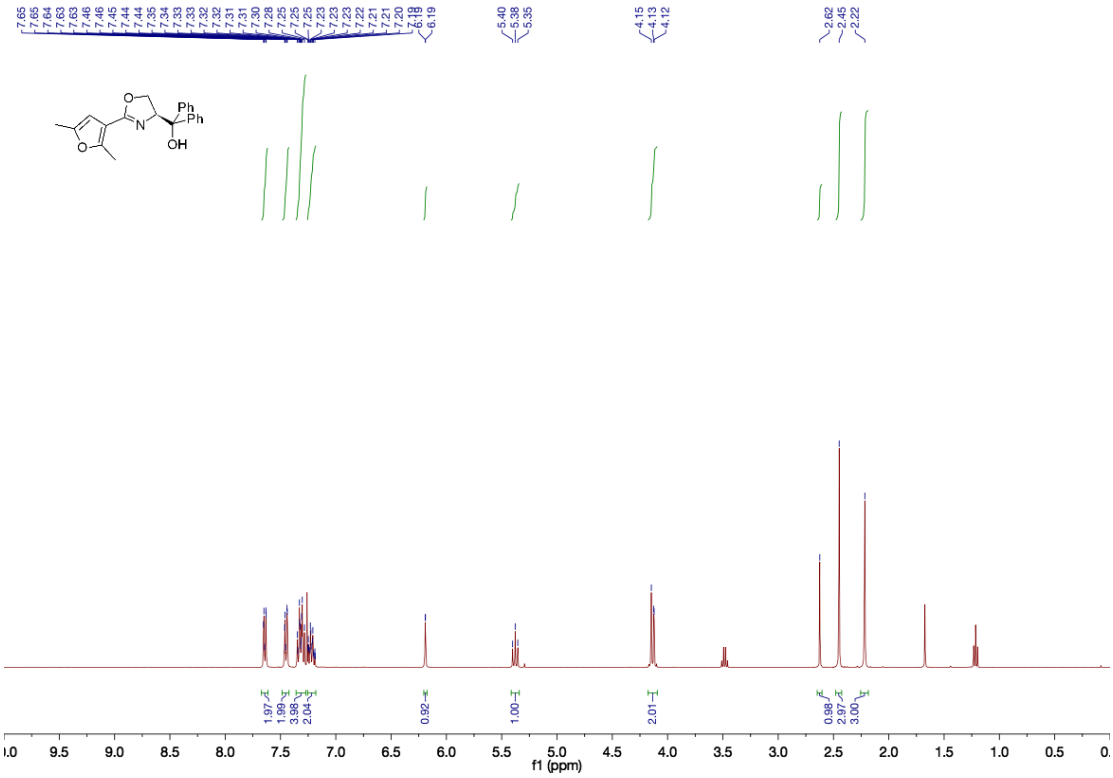
13.86
f1 (ppm)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7.25
7.23
7.22
7.21
7.20
6.19
5.40
5.38
5.35
4.15
4.13
4.12
2.62
2.45
2.22
Ph
Ph
OH
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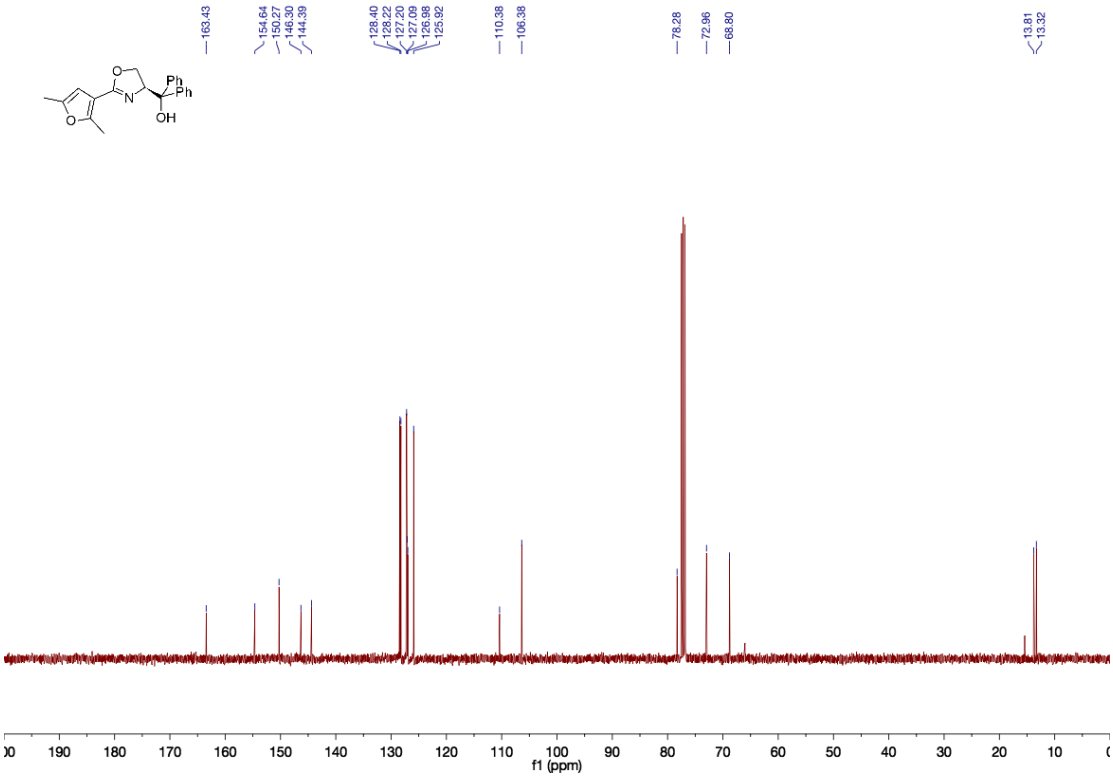
1.99
3.98
2.04
0.92
1.00
2.01
0.98
2.97
3.00
f1 (ppm)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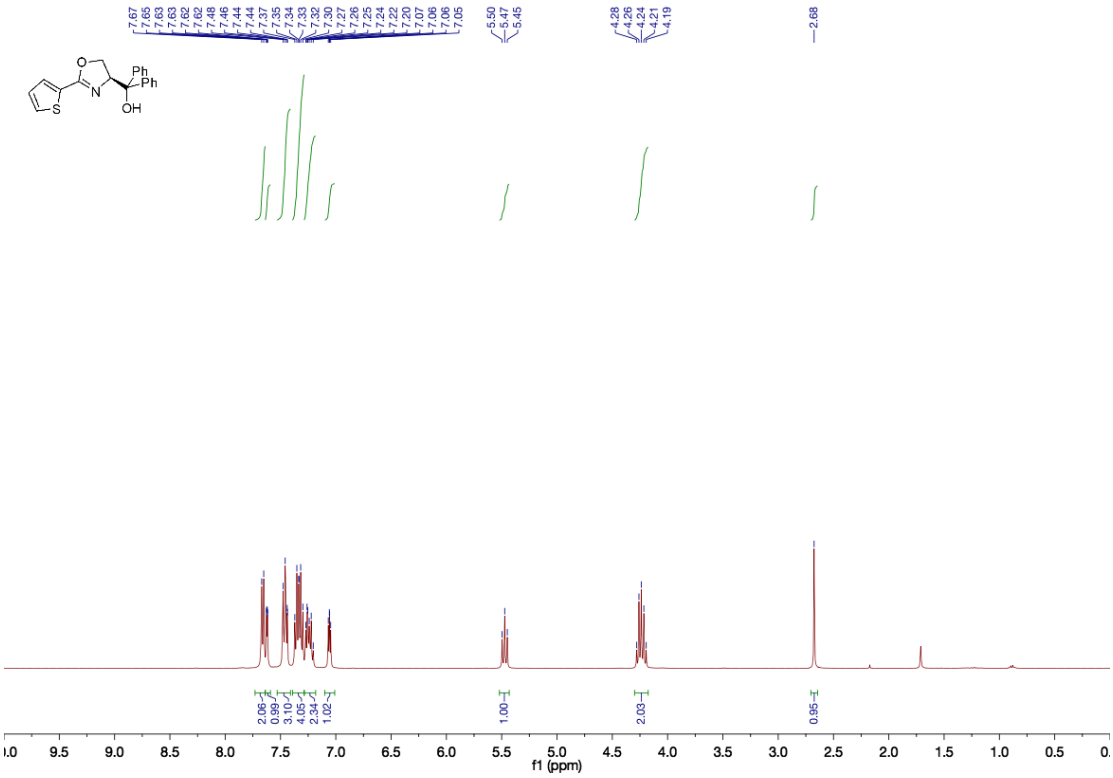
13.81
13.32
Ph
Ph
OH
f1 (ppm)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7.32
7.30
7.27
7.26
7.25
7.24
7.22
7.20
7.07
7.06
7.06
7.05
5.50
5.47
5.45
4.28
4.26
4.24
4.21
4.19
2.68
Ph
Ph
OH
O
N
S
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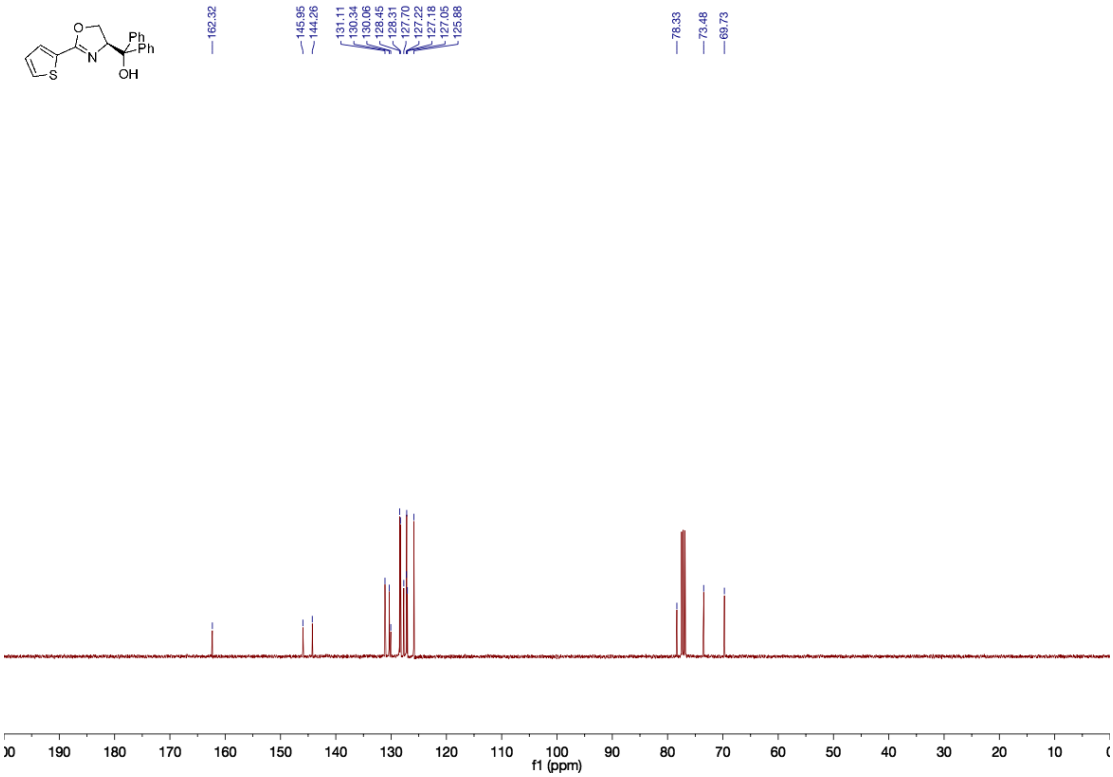
0.99
3.10
4.05
2.34
1.02
1.00
2.03
0.95
f1 (ppm)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125.88
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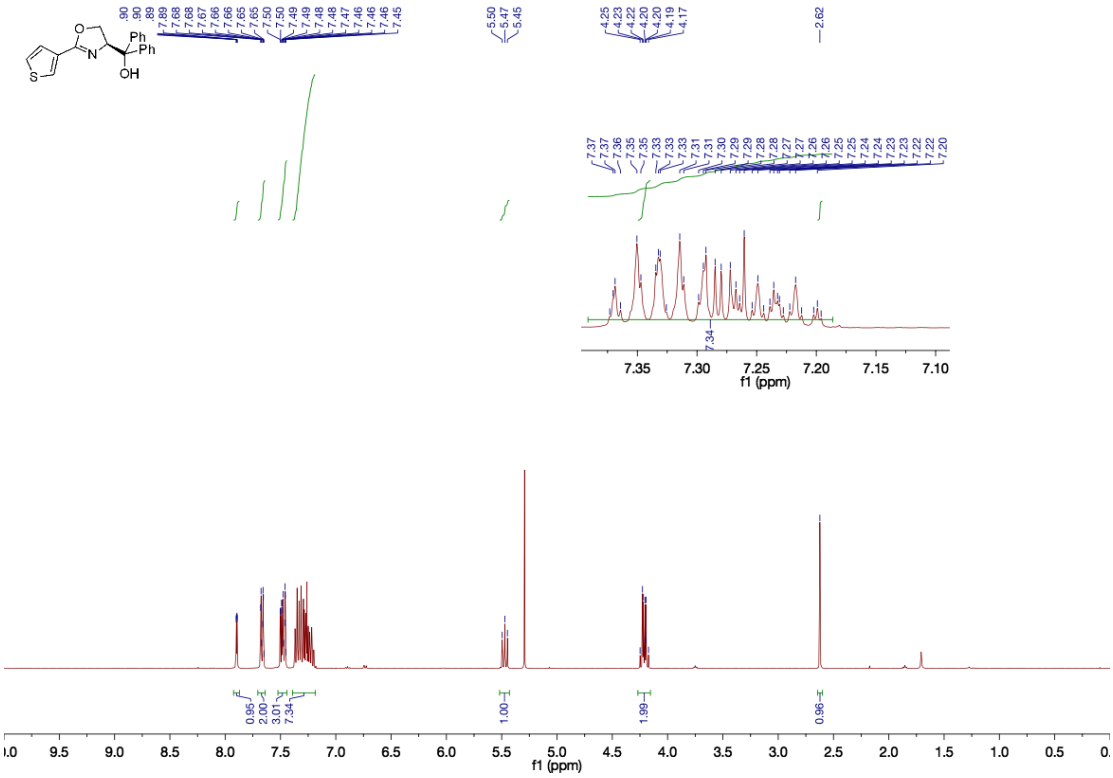
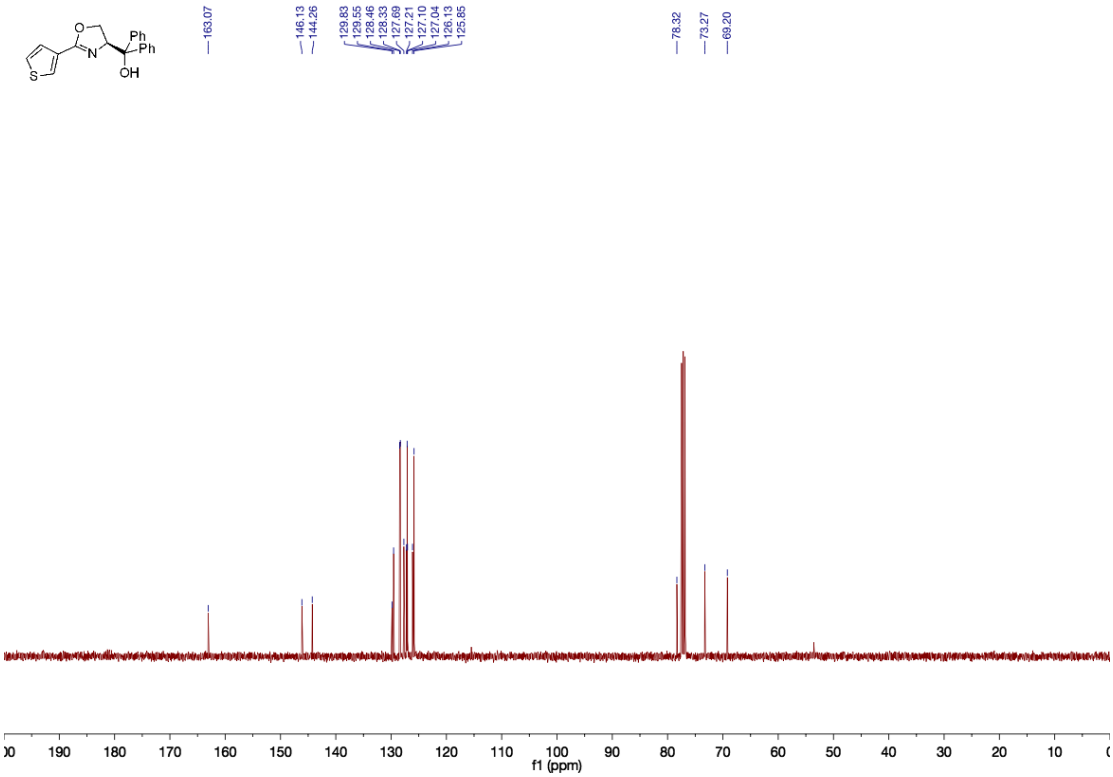
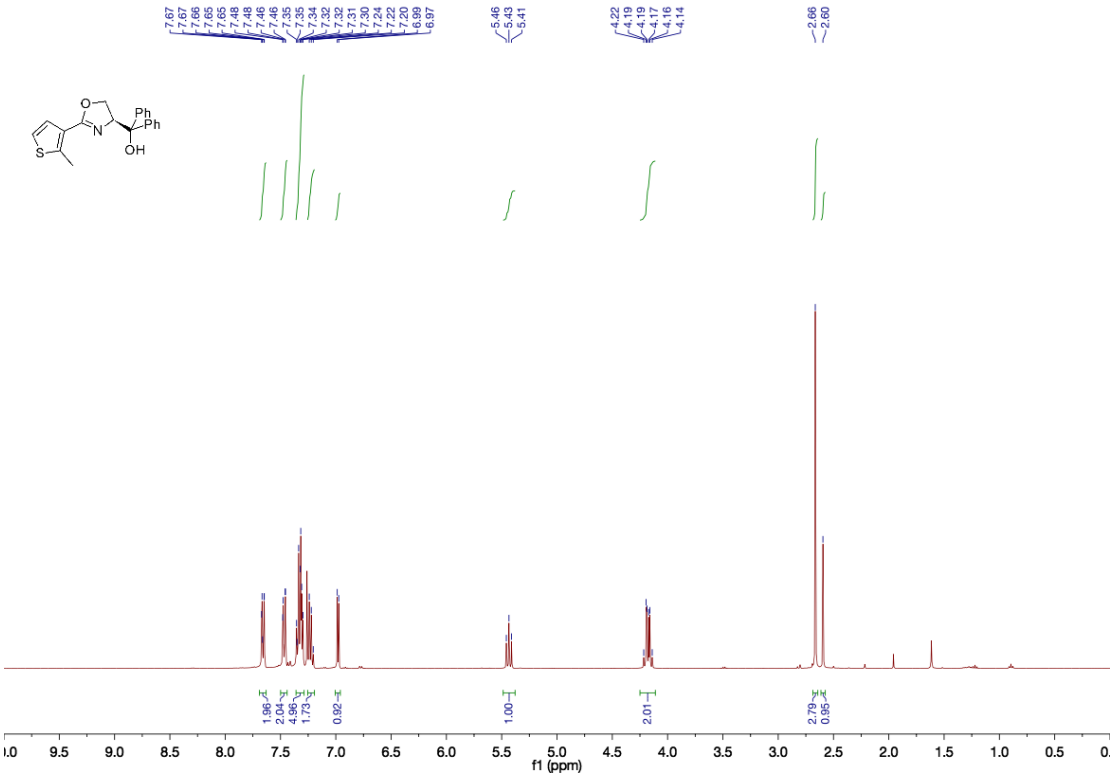
73.48
69.73
Ph
Ph
OH
O
N
S
f1 (ppm)


Ph
Ph
OH
S
N
O
f1 (ppm)


Ph
Ph
OH
S
N
O
f1 (ppm)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7.46
7.46
7.35
7.35
7.34
7.32
7.32
7.31
7.30
7.24
7.22
7.20
6.99
6.97
5.46
5.43
5.41
4.22
4.19
4.19
4.17
4.16
4.14
2.66
2.60
Ph
Ph
OH
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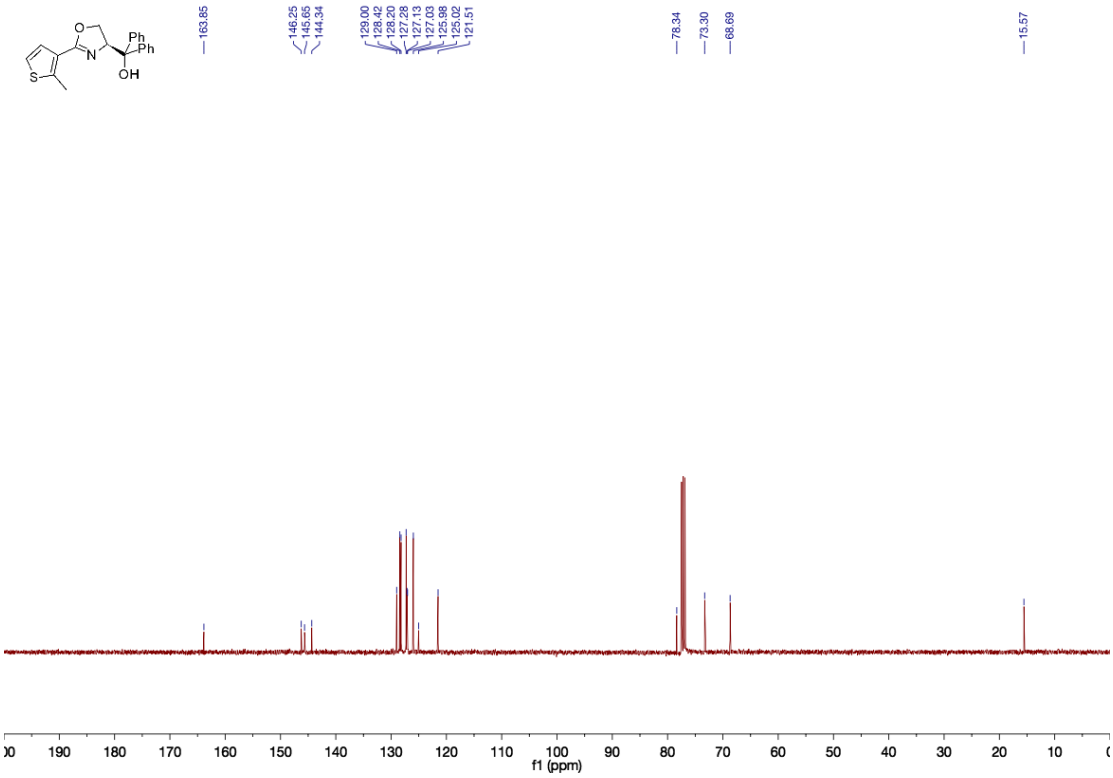
2.04
4.96
1.73
0.92
1.00
2.01
2.79
0.95
f1 (ppm)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125.02
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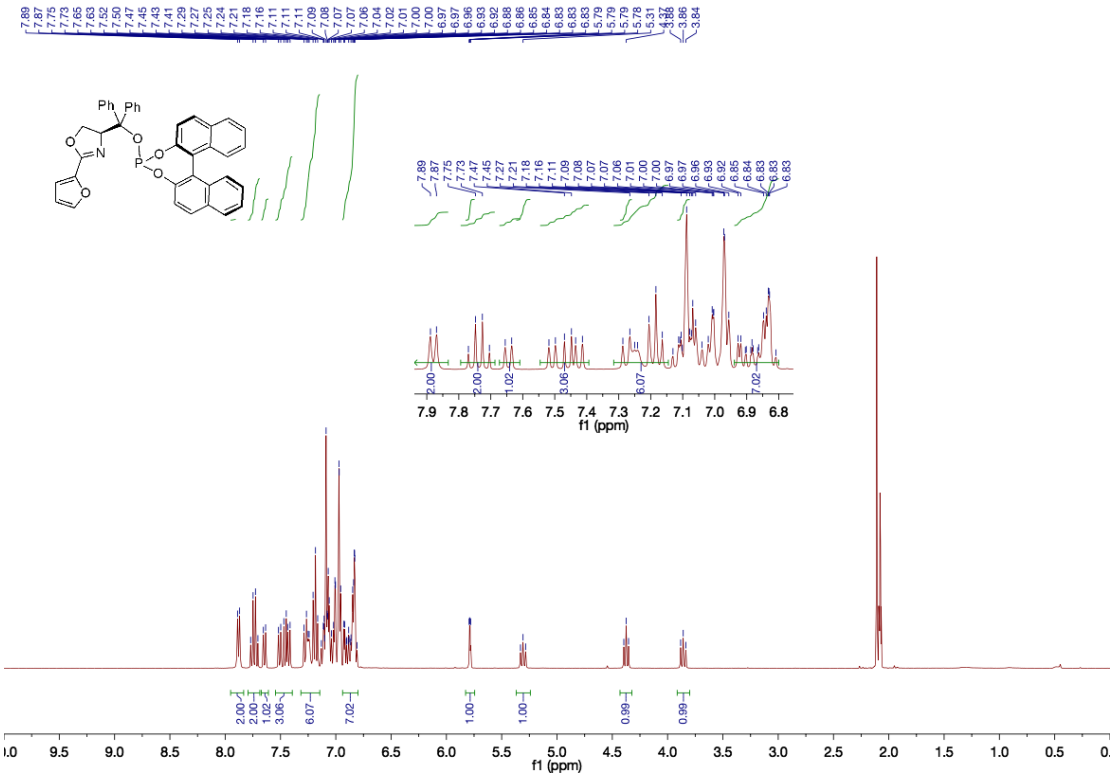
78.34
73.30
68.69
15.57
Ph
Ph
OH
f1 (ppm)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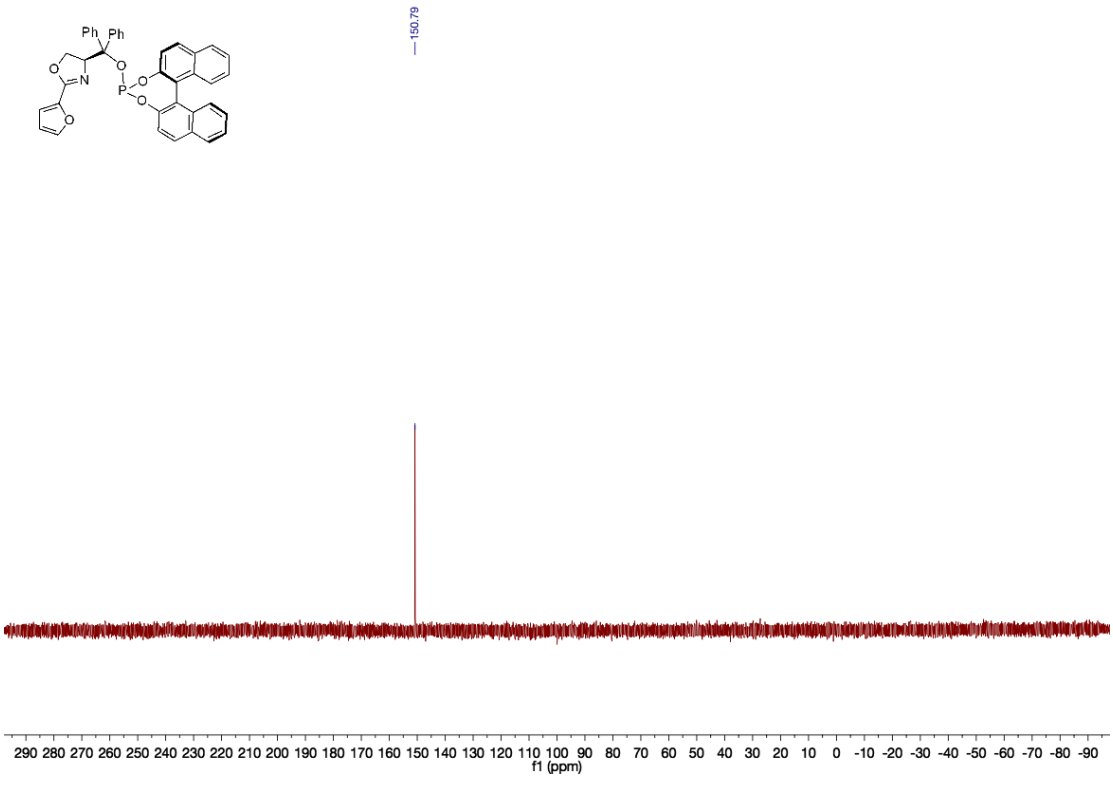
Ph
O
N
O
P
O
O
f1 (ppm)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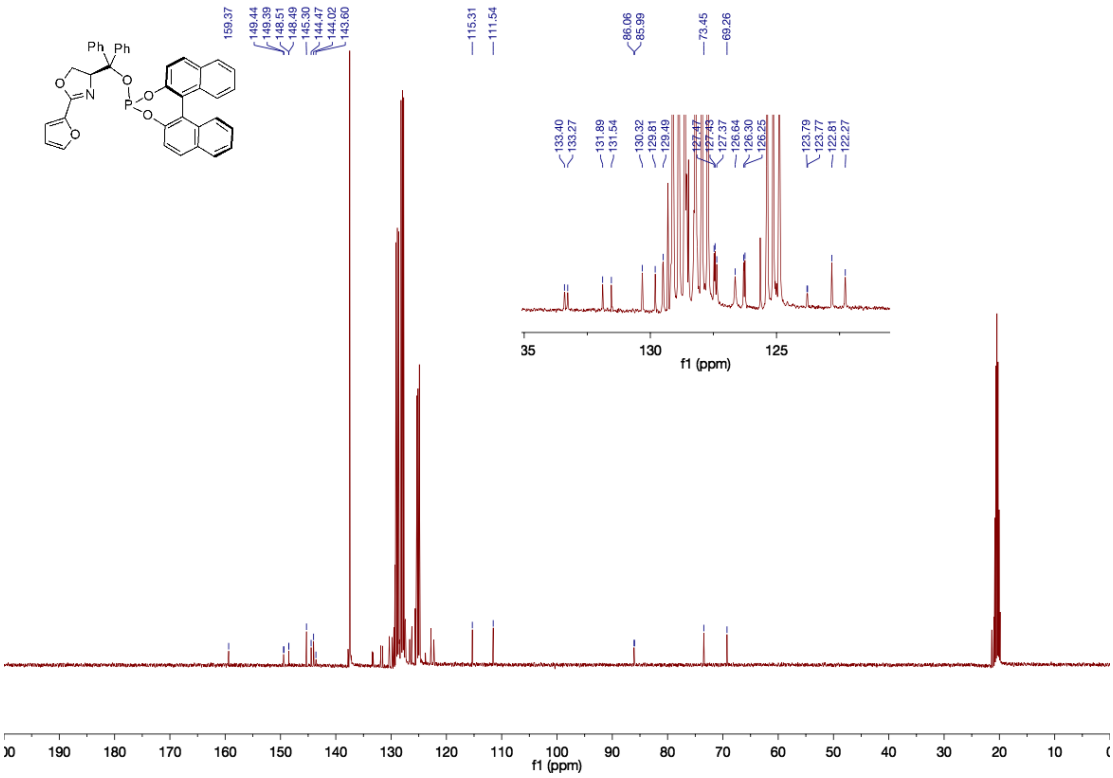
Ph
Ph
O
N
O
P
O
O
f1 (ppm)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144.02
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111.54
86.06
85.99
73.45
69.26
133.40
133.27
131.89
131.54
130.32
129.81
129.49
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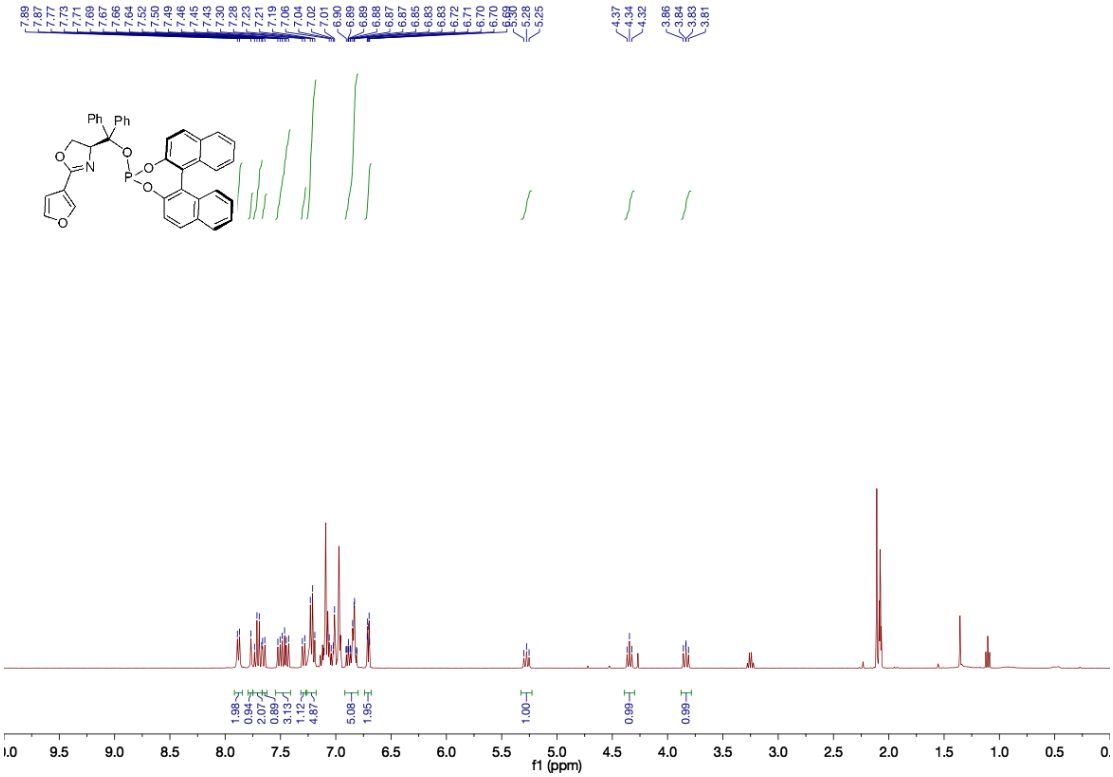
126.64
126.30
126.25
123.79
123.77
122.81
122.27
f1 (ppm)
f1 (ppm)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7.43
7.30
7.28
7.23
7.21
7.19
7.06
7.04
7.02
7.01
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6.88
6.87
6.87
6.85
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5.28
5.25
4.37
4.34
4.32
3.86
3.84
3.83
3.81
1.98
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2.07
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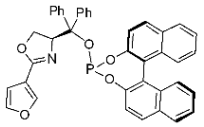
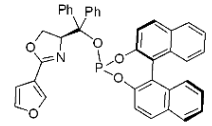
3.13
1.12
4.87
5.08
1.95
1.00
0.99
0.99
f1 (ppm)


Ph
Ph
O
N
O
P
O
O

150.77
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Ph
Ph
O
N
O
P
O
O

162.45
149.41
149.36
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145.22
144.52
143.78
116.72
110.19
86.04
85.97
73.15
69.03
133.40
133.29
131.89
131.54
130.33
129.77
126.58
126.34
126.30
125.64
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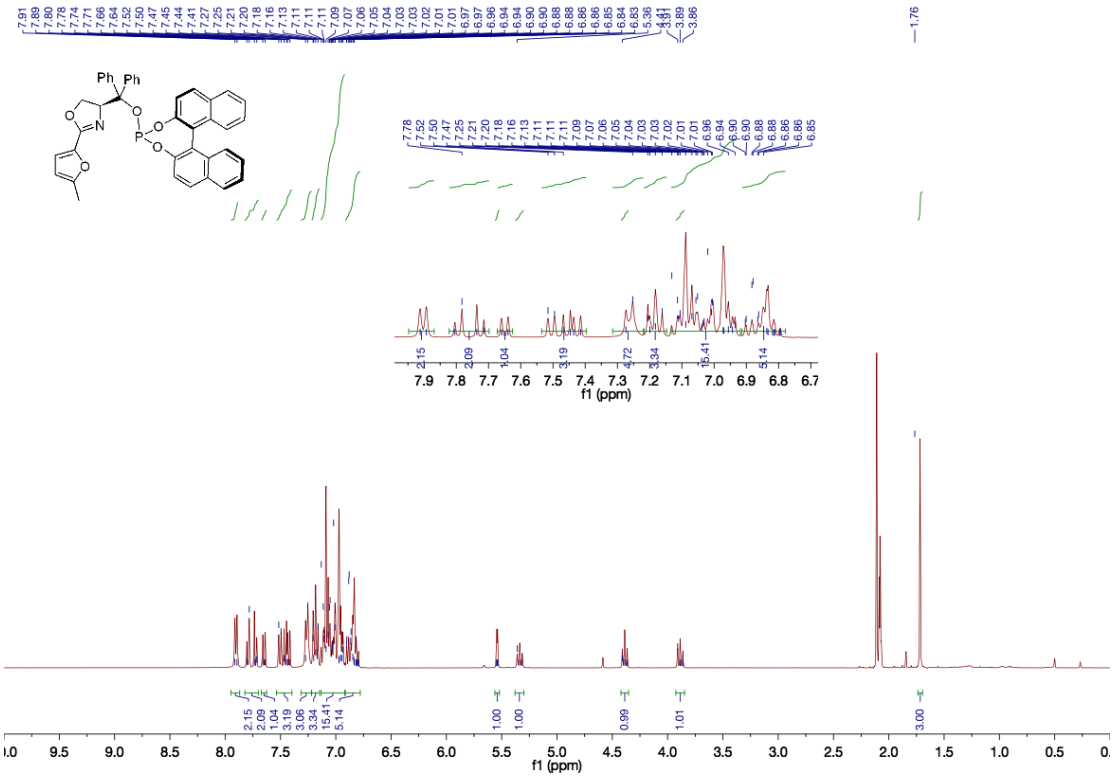
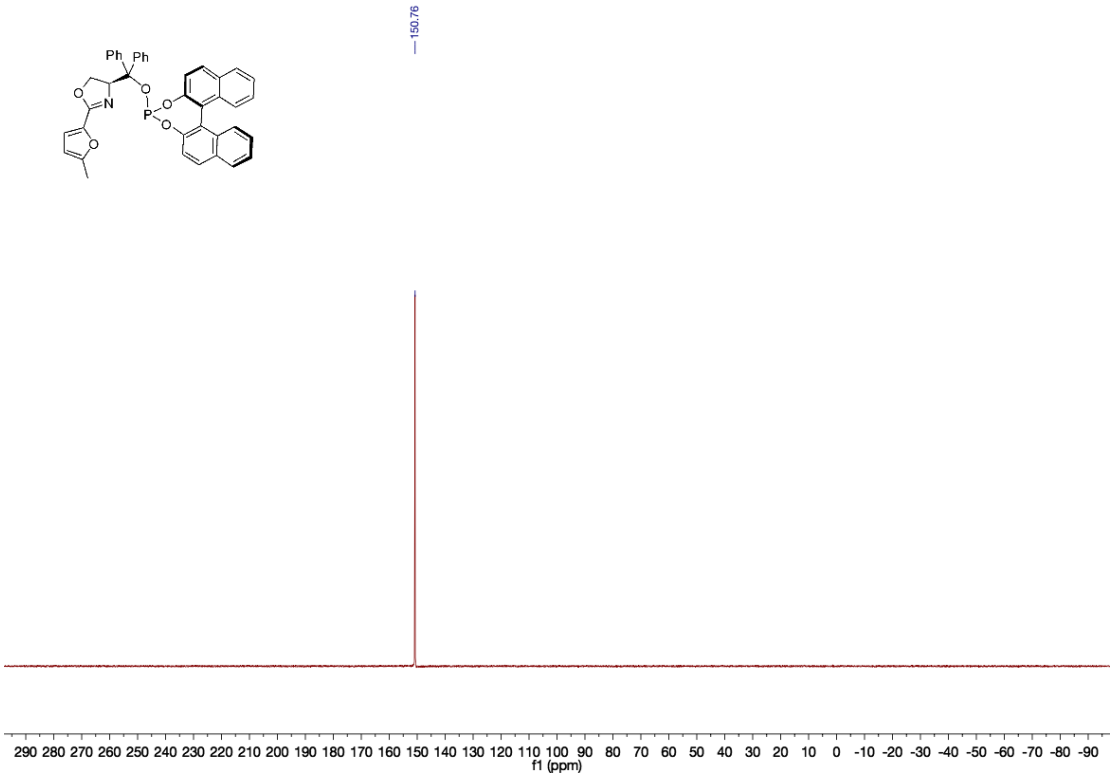
122.27
134 132 130 128 126 124 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
Ph
O
N
O
P
O
O
f1 (ppm)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Ph
O
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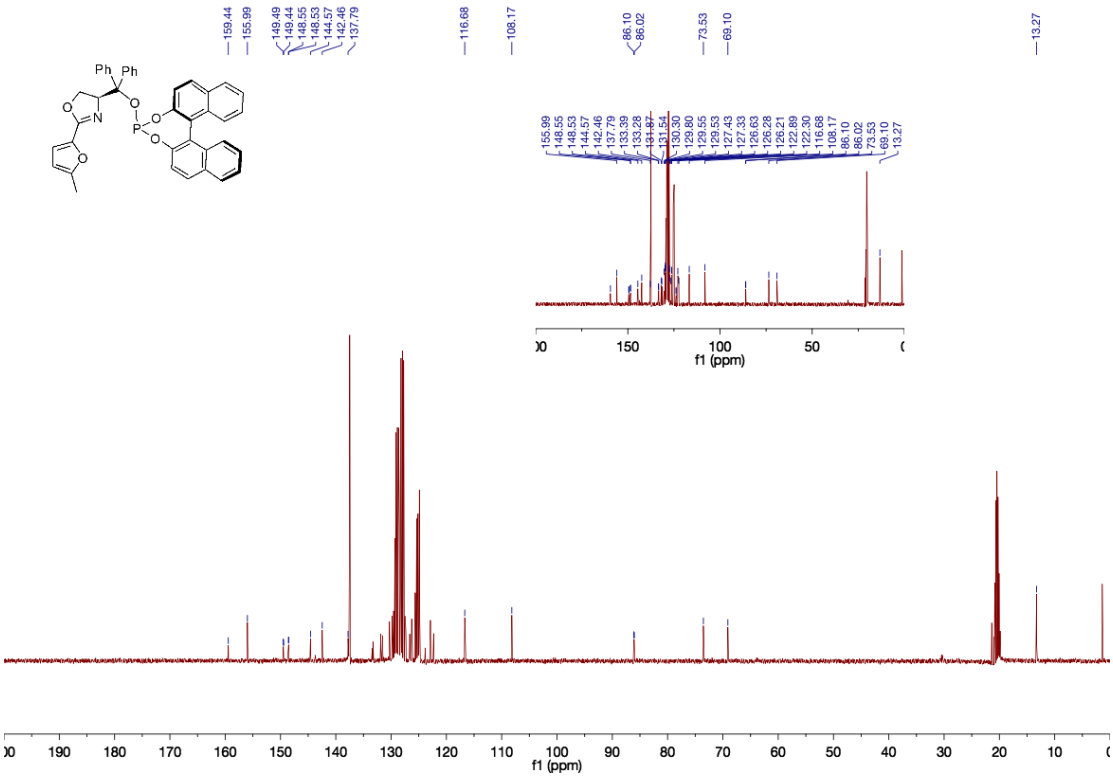
P
O
O
f1 (ppm)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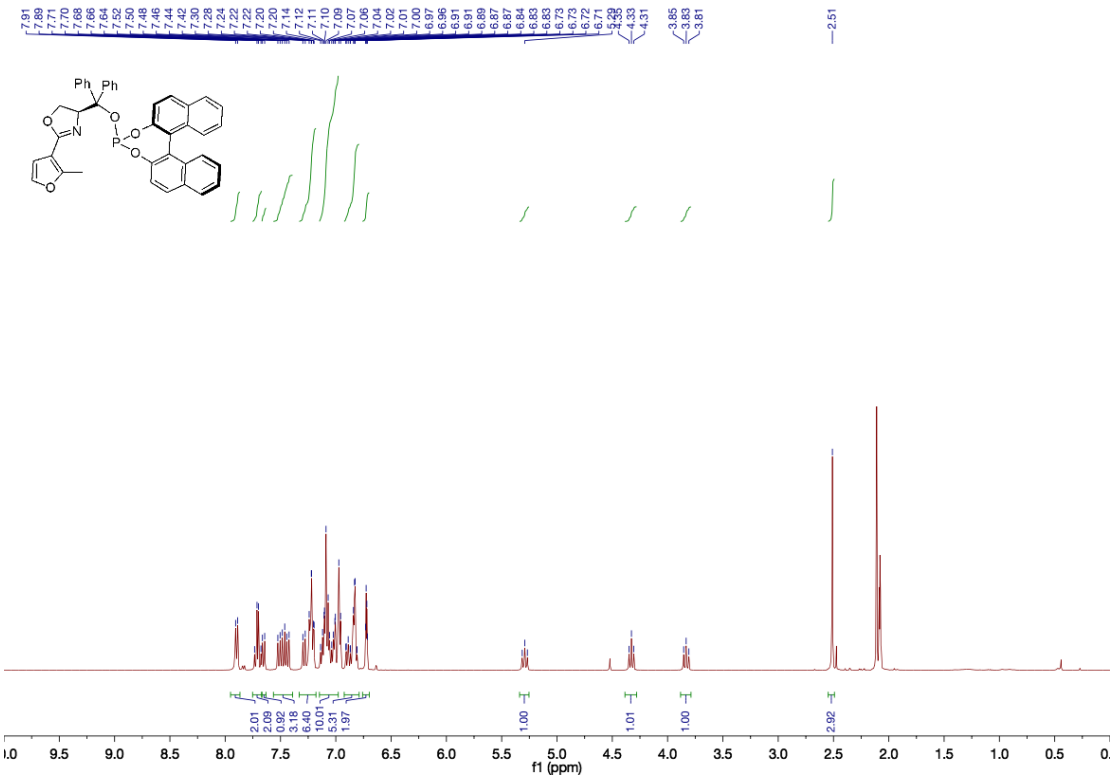
137.79
116.68
108.17
86.10
86.02
73.53
69.10
13.27
f1 (ppm)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7.44
7.42
7.30
7.28
7.24
7.22
7.22
7.20
7.20
7.14
7.12
7.11
7.10
7.09
7.07
7.06
7.04
7.02
7.01
7.00
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6.96
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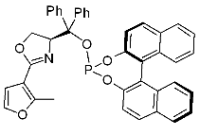
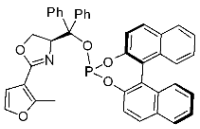
6.73
6.73
6.72
6.71
4.33
4.31
3.85
3.83
3.81
2.51
2.01
2.09
0.92
3.18
6.40
10.01
5.31
1.97
1.00
1.01
1.00
2.92
f1 (ppm)



150.53
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)



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156.94
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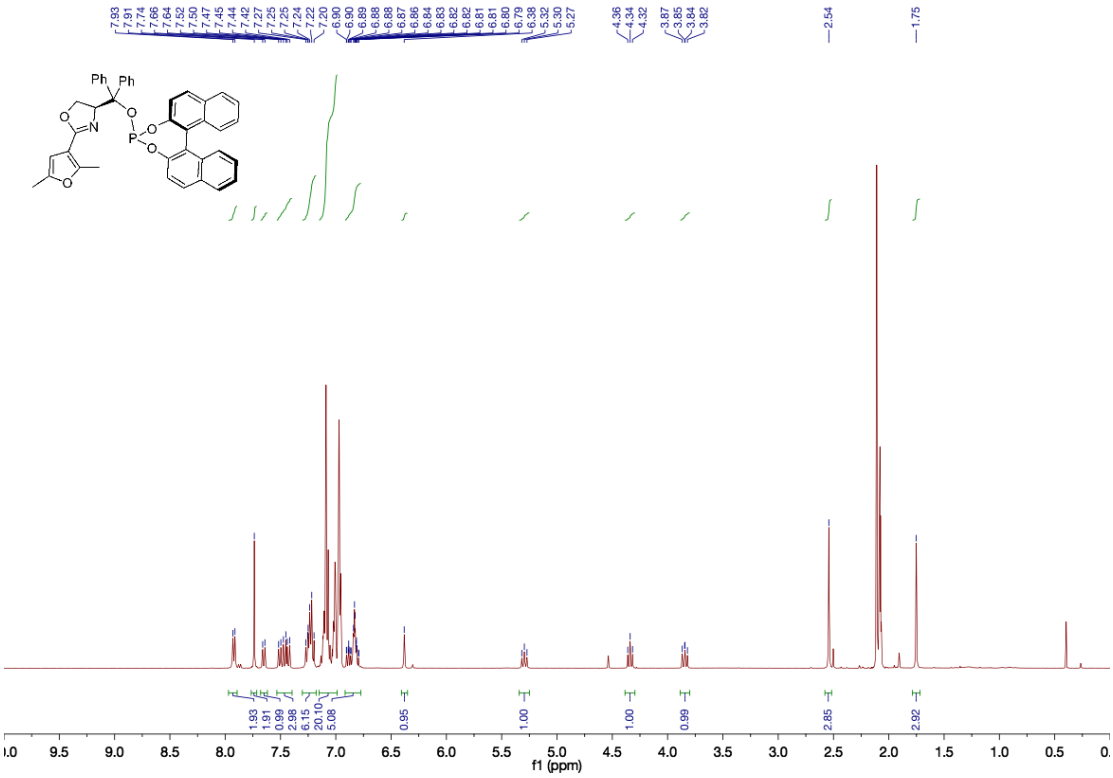
144.63
140.64
110.91
86.08
86.01
73.24
68.62
13.75
133.41
133.30
131.88
131.54
130.31
129.76
129.56
127.45
127.28
126.48
126.32
126.30
125.64
123.87
122.70
122.29
133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.52
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7.47
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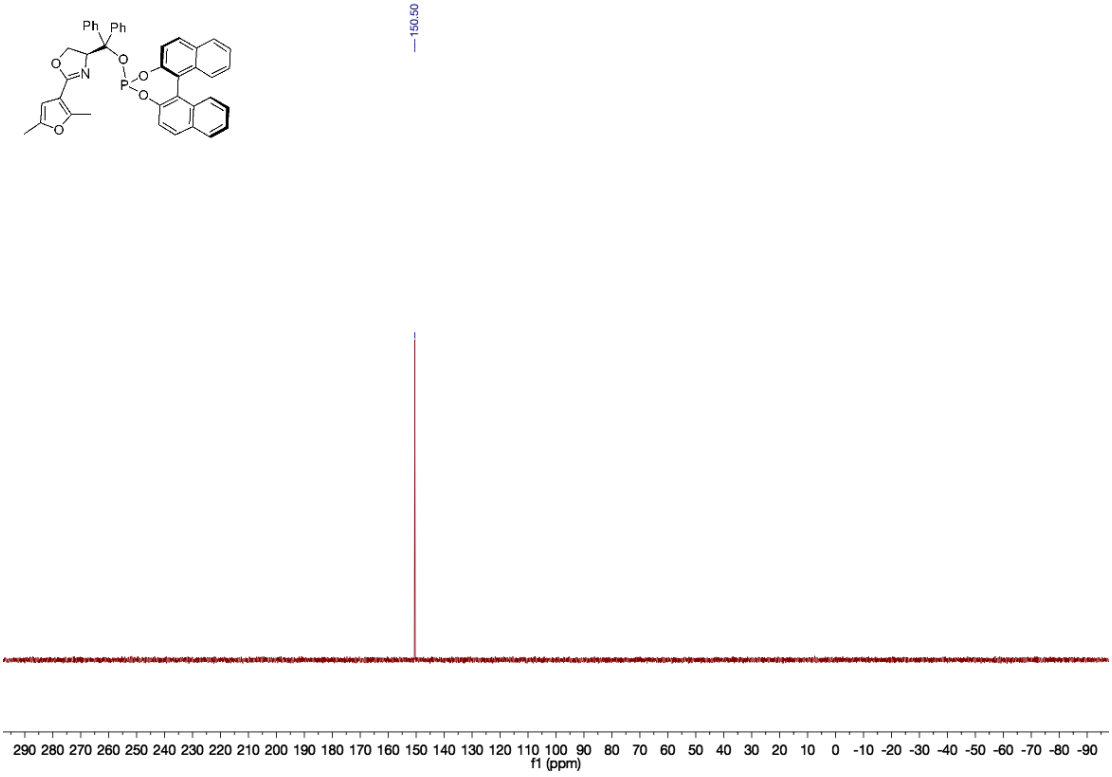
7.44
7.42
7.27
7.25
7.25
7.24
7.22
7.20
6.90
6.90
6.89
6.88
6.88
6.87
6.86
6.84
6.83
6.82
6.82
6.81
6.81
6.80
6.79
6.38
5.32
5.30
5.27
4.36
4.34
4.32
3.87
3.85
3.84
3.82
2.54
1.75
Ph
Ph
O
N
O
P
O
O
O
1.93
1.91
0.99
2.98
6.15
20.10
5.08
0.95
1.00
1.00
0.99
2.85
2.92
f1 (ppm)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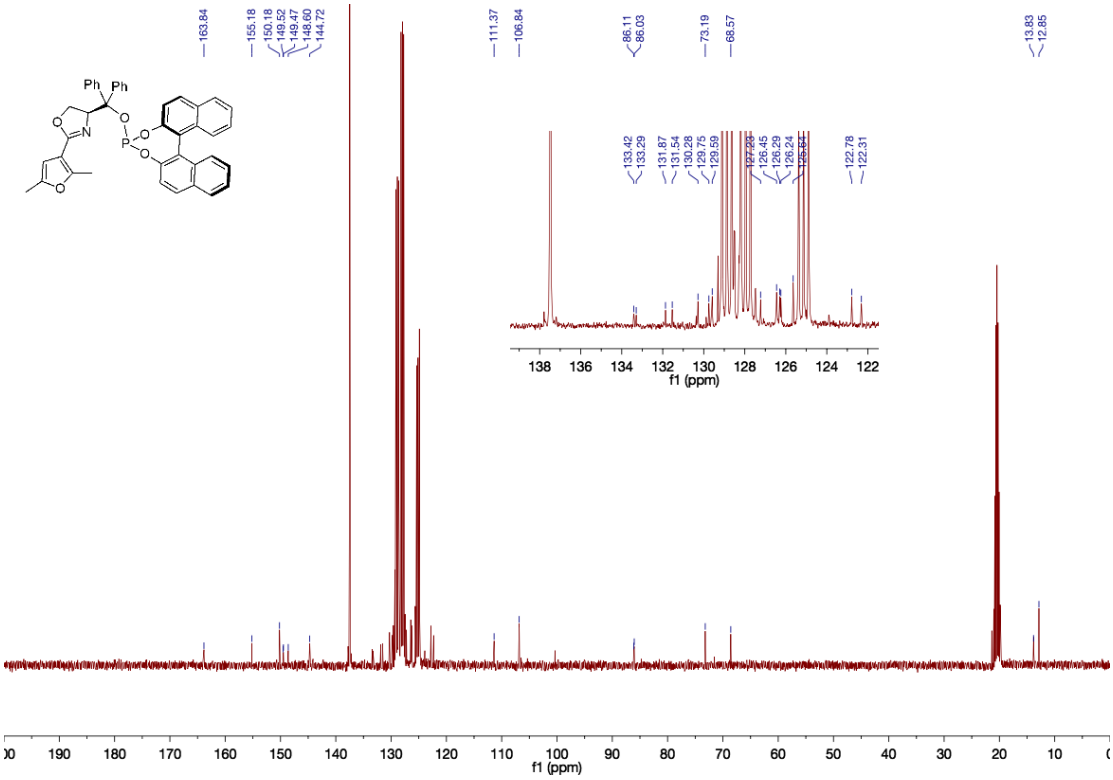
Ph
Ph
O
N
O
P
O
O
O
f1 (ppm)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111.37
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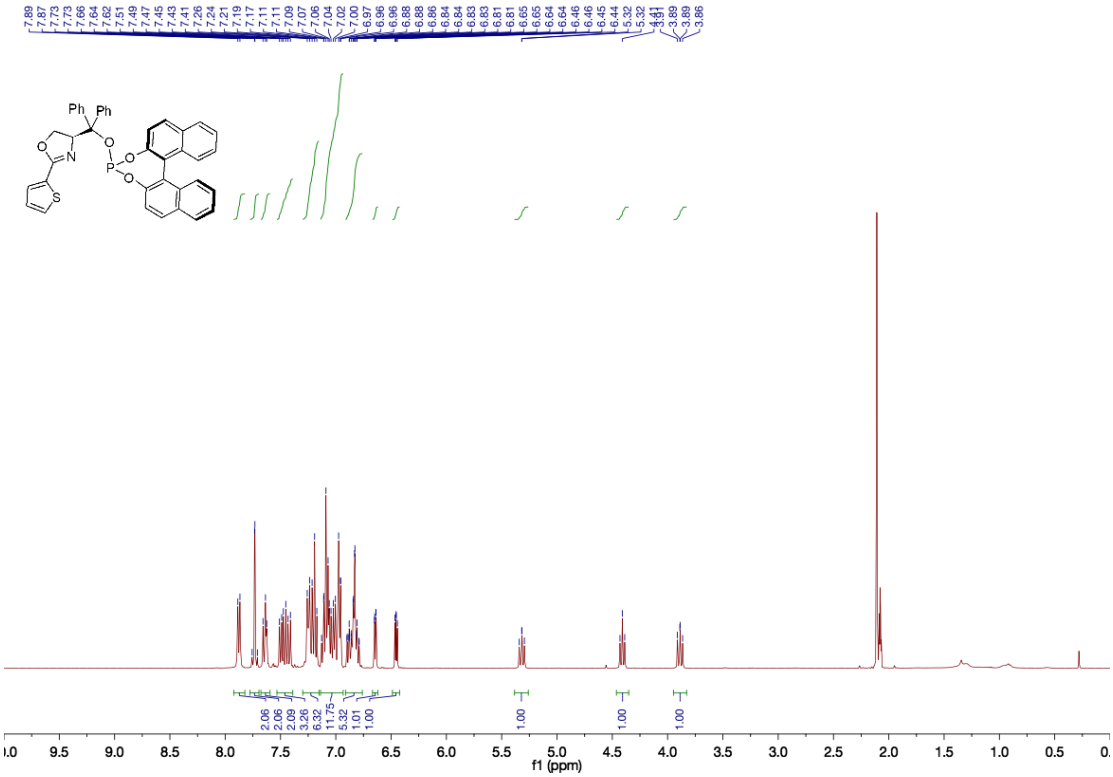
86.03
73.19
68.57
13.83
12.85
133.42
133.29
131.87
131.54
130.28
129.75
129.59
127.23
126.45
126.29
126.24
125.82
122.78
122.31
Ph
Ph
O
N
O
P
O
O
138 136 134 132 130 128 126 124 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.26
7.24
7.21
7.19
7.17
7.11
7.11
7.09
7.07
7.06
7.04
7.02
7.00
6.97
6.96
6.96
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6.86
6.86
6.84
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6.65
6.65
6.64
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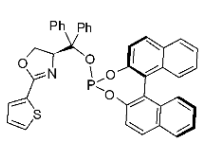
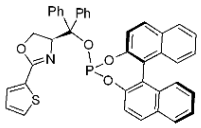
6.46
6.45
6.44
5.32
5.32
4.41
4.41
3.89
3.89
3.86
Ph
Ph
O
N
O
P
O
O
S
2.06
2.06
2.09
3.26
6.32
11.75
5.32
1.01
1.00
1.00
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Ph
Ph
O
N
S
O
P
O

150.89
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Ph
Ph
O
N
S
O
P
O

162.86
149.41
149.36
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148.48
144.44
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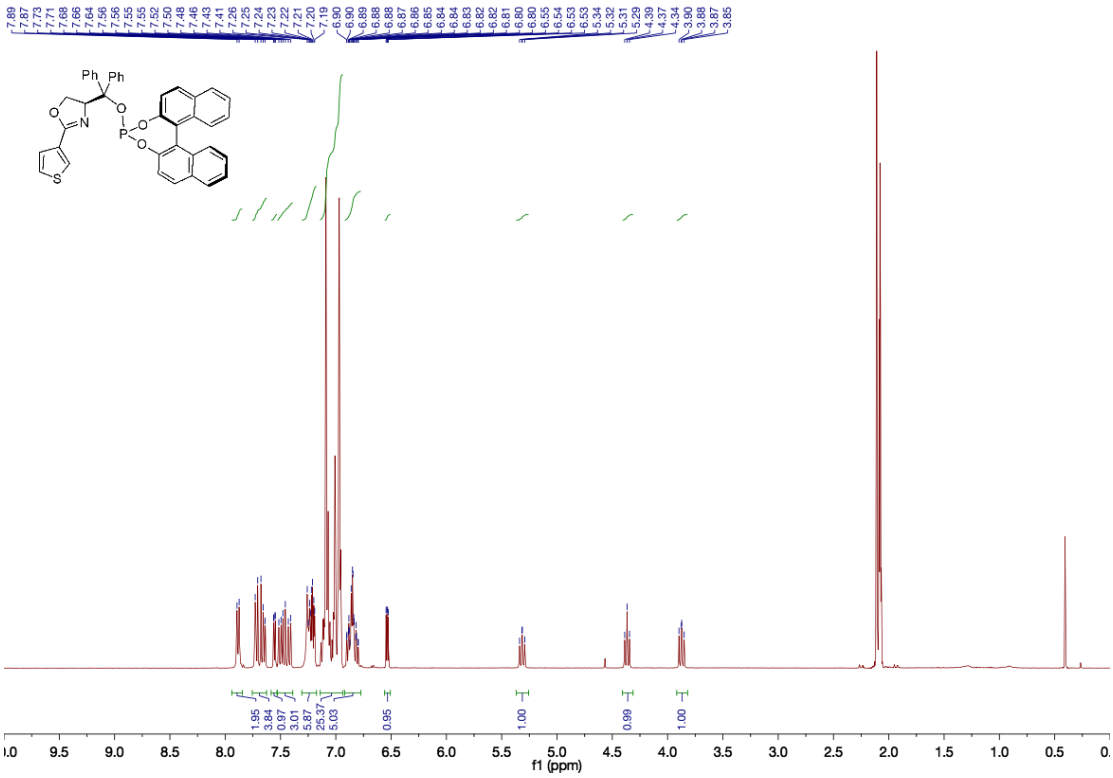
86.02
73.49
69.70
137.78
137.48
133.37
133.26
131.86
131.52
131.04
130.99
130.37
130.32
129.77
129.43
127.46
127.41
127.37
126.59
126.31
126.25
125.64
125.01
124.96
123.83
123.80
122.80
122.26
136 134 132 130 128 126 124 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.64
7.56
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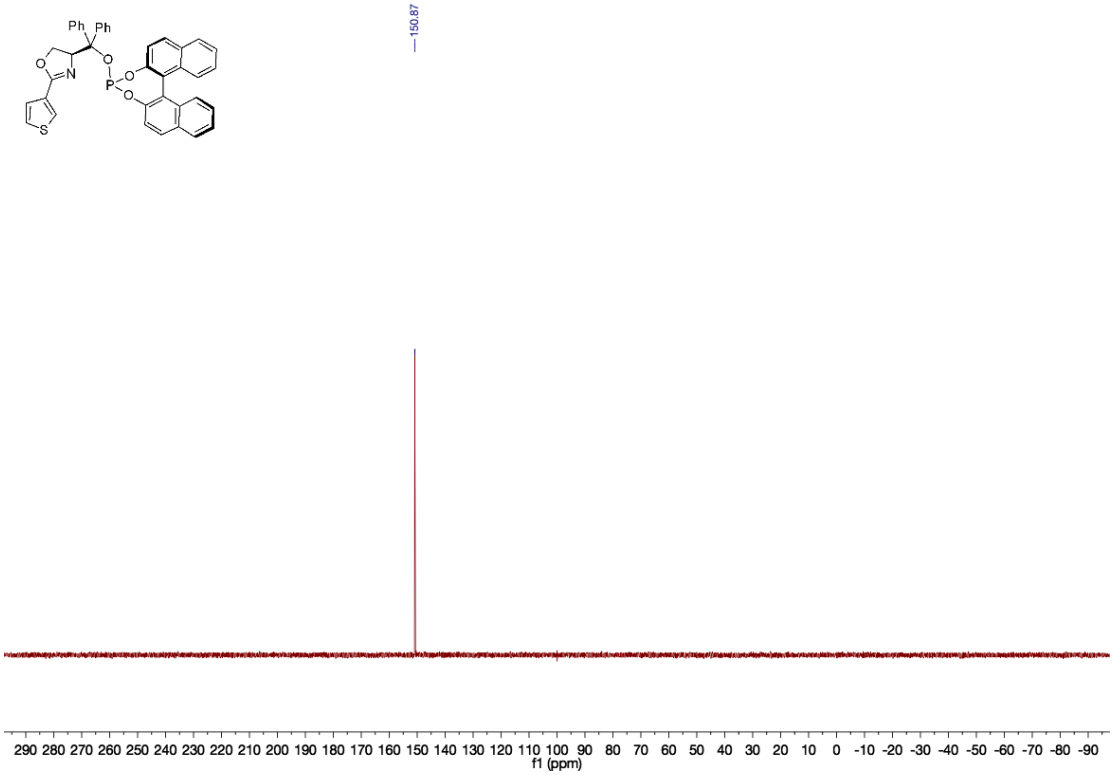
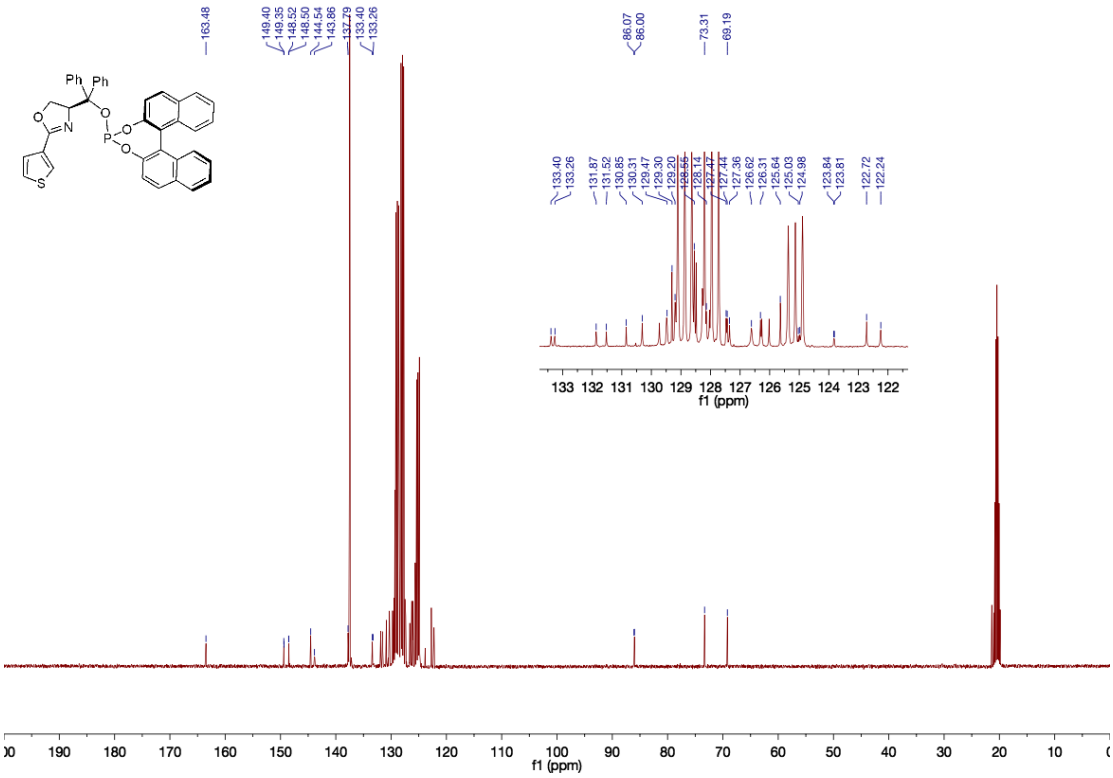
7.55
7.55
7.52
7.50
7.48
7.46
7.43
7.41
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
6.90
6.90
6.89
6.88
6.88
6.87
6.86
6.85
6.84
6.84
6.83
6.82
6.82
6.81
6.80
6.80
6.55
6.54
6.53
6.53
5.34
5.32
5.31
5.29
4.39
4.37
4.34
4.34
3.90
3.88
3.87
3.85
Ph
Ph
O
N
O
P
O
O
S
1.95
3.84
3.07
3.01
5.87
25.37
5.03
0.95
1.00
0.99
1.00
f1 (ppm)


150.87
Ph
Ph
O
N
O
P
O
O
S
f1 (ppm)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144.54
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137.79
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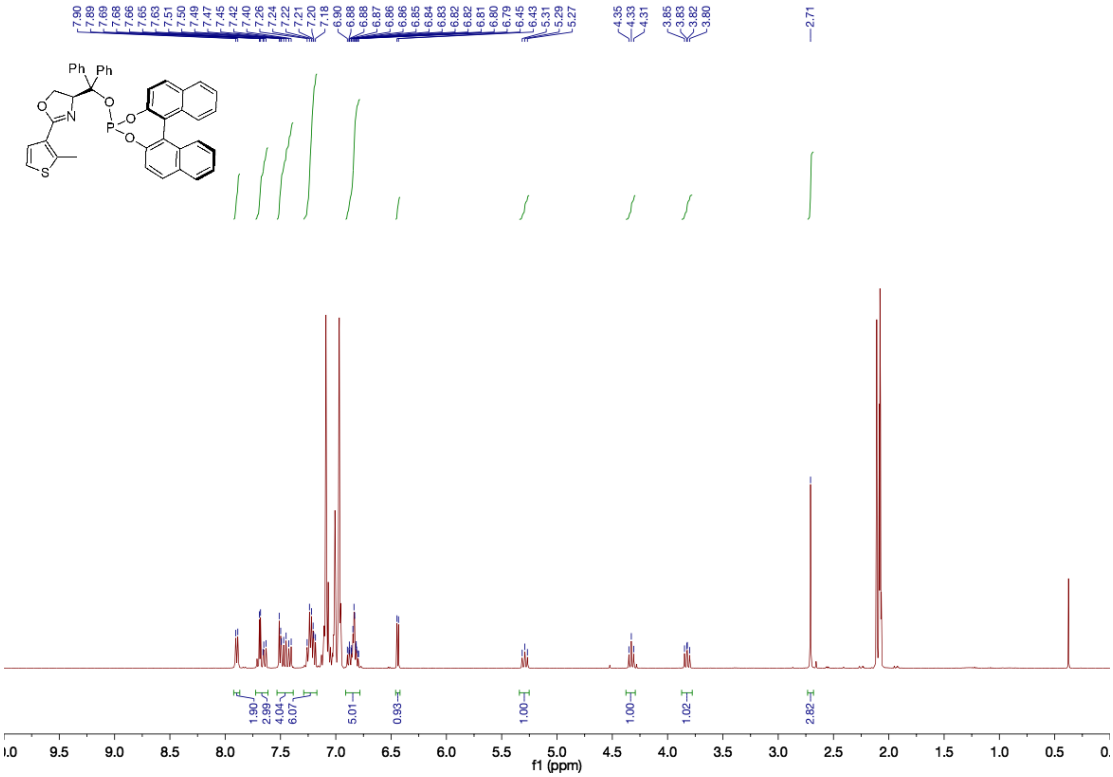
133.26
86.07
86.00
73.31
69.19
133.40
133.26
131.87
131.52
130.85
130.31
129.47
129.30
129.20
128.55
128.14
127.47
127.44
127.36
126.62
126.31
125.64
125.03
124.98
123.84
123.81
122.72
122.24
133 132 131 130 129 128 127 126 125 124 123 122
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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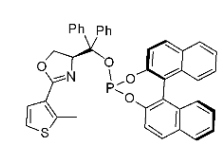
7.63
7.51
7.50
7.49
7.47
7.45
7.42
7.40
7.26
7.24
7.22
7.21
7.20
7.18
6.90
6.88
6.88
6.87
6.86
6.86
6.85
6.84
6.83
6.82
6.82
6.81
6.80
6.79
5.45
5.43
5.31
5.29
5.27
4.35
4.33
4.31
3.85
3.83
3.82
3.80
2.71
1.90
2.99
4.04
6.07
5.01
0.93
1.00
1.00
1.02
2.82
f1 (ppm)



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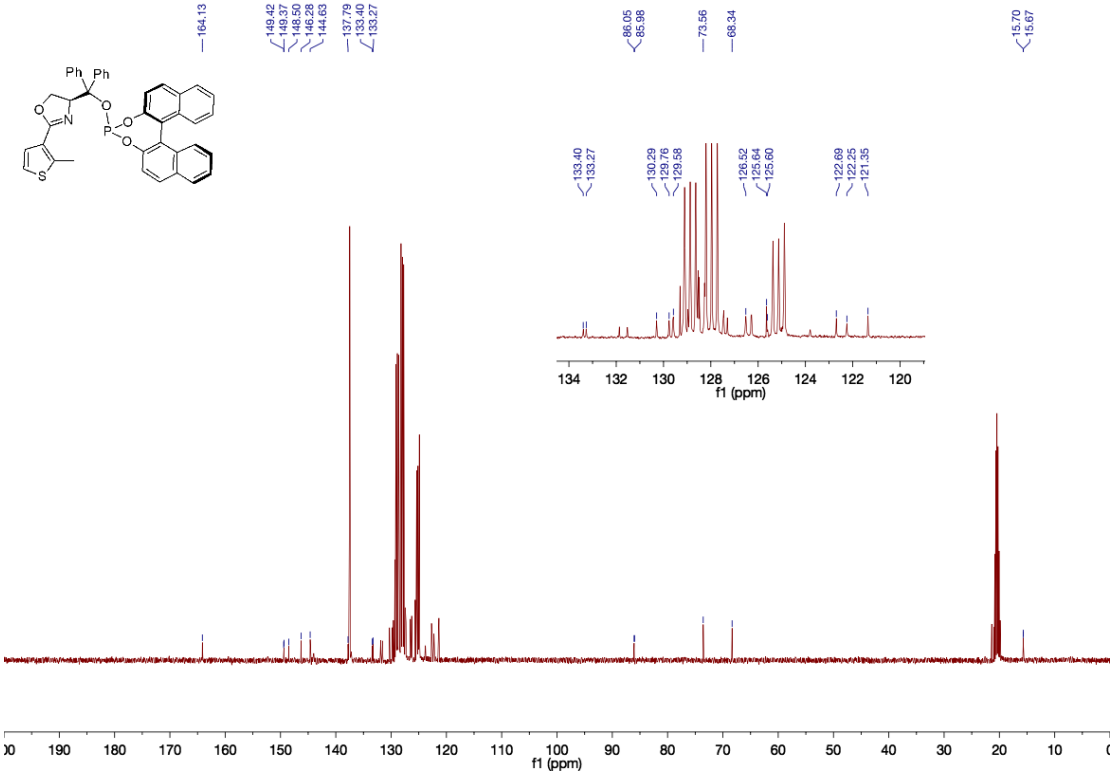
f1 (ppm)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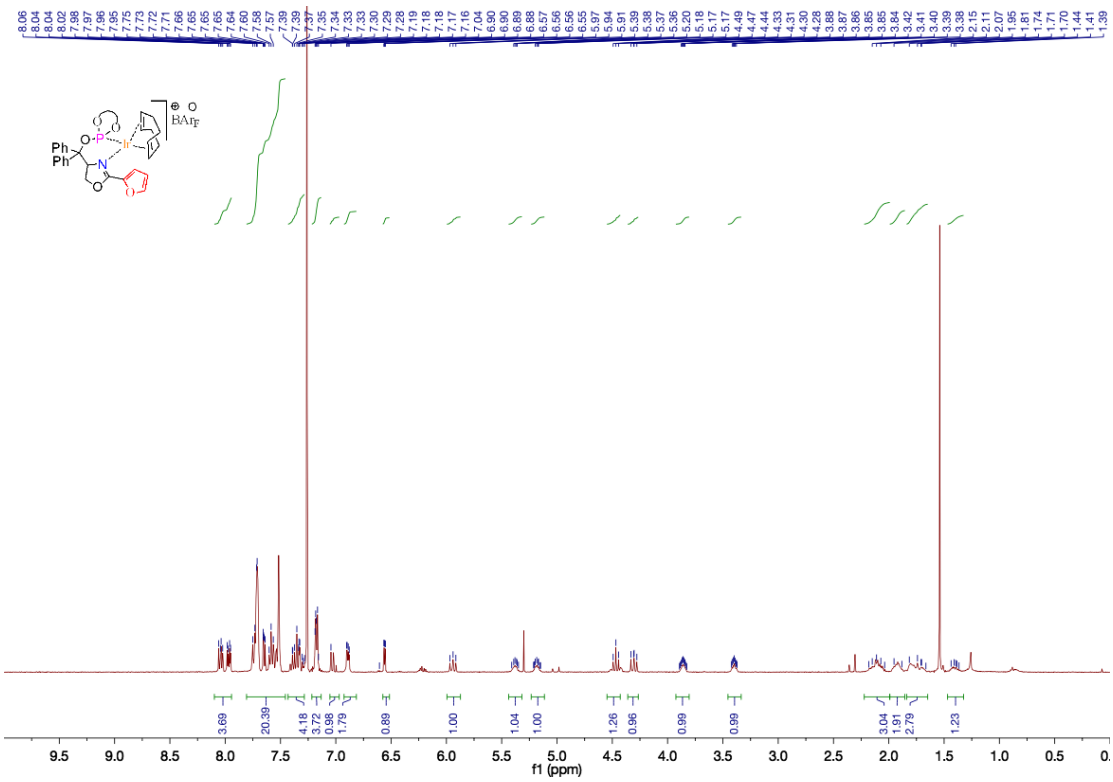
149.30
146.28
144.63
137.79
133.40
133.27
86.05
85.98
73.56
68.34
15.70
15.67
133.40
133.27
130.29
129.76
129.58
126.52
125.64
125.60
122.69
122.25
121.35
134 132 130 128 126 124 122 120
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
Ph
BArF
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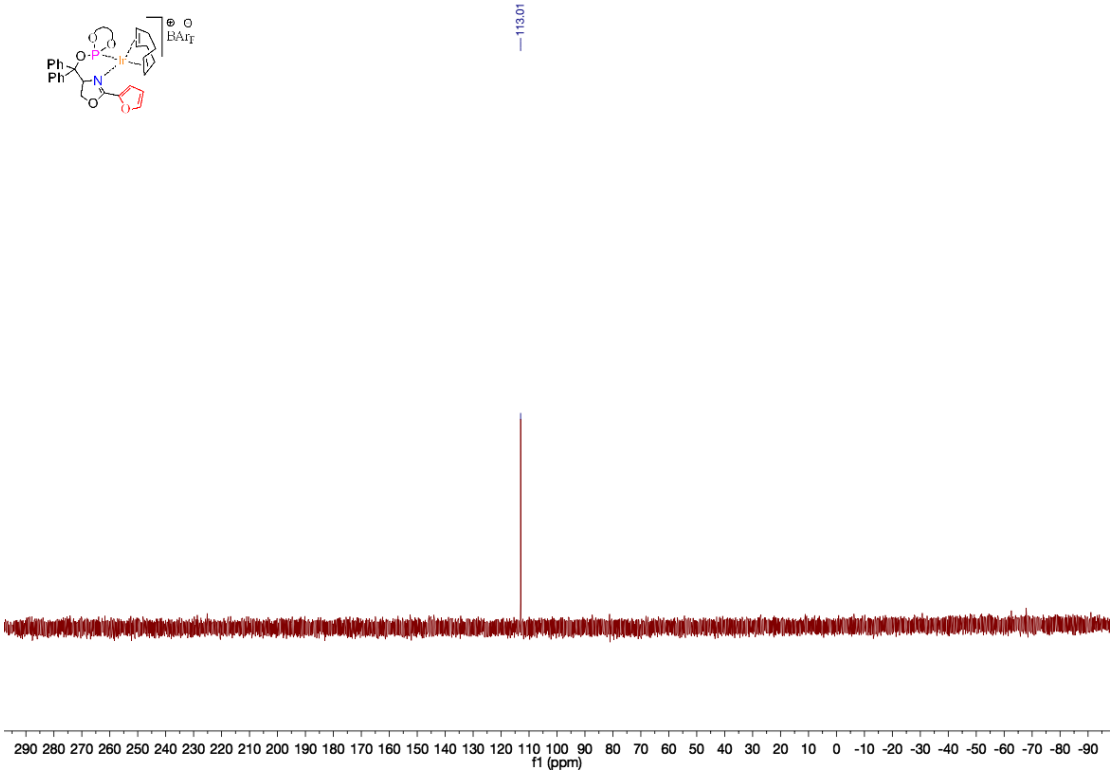
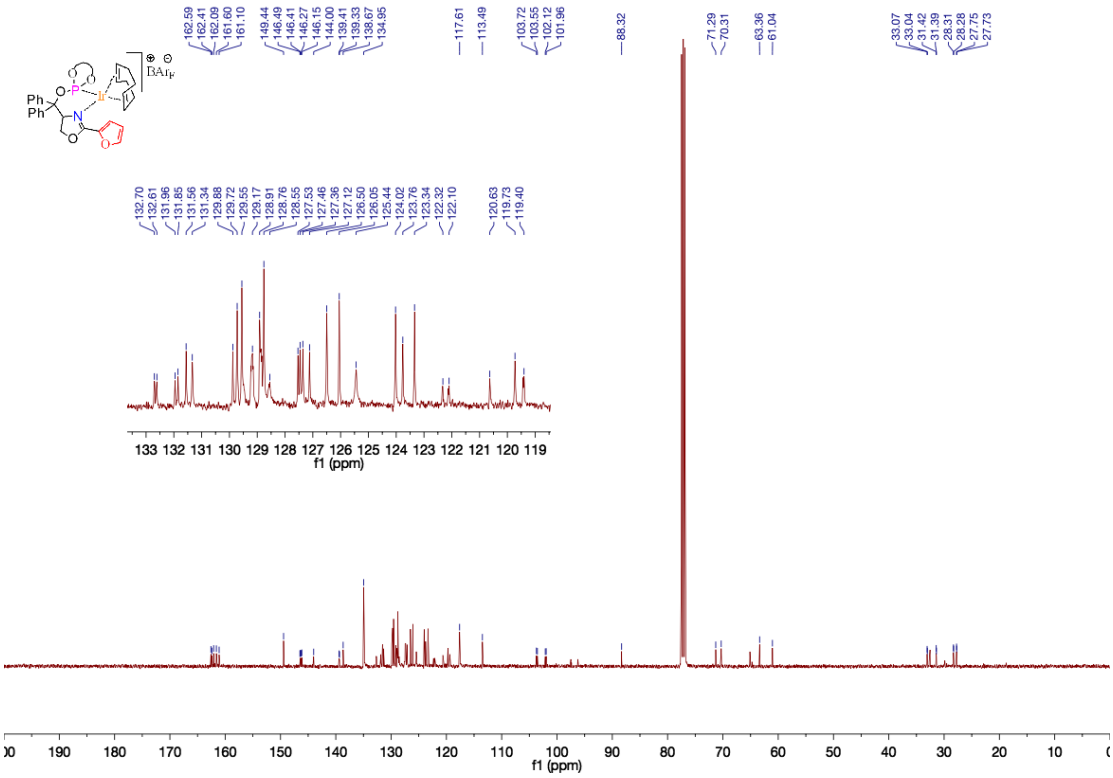
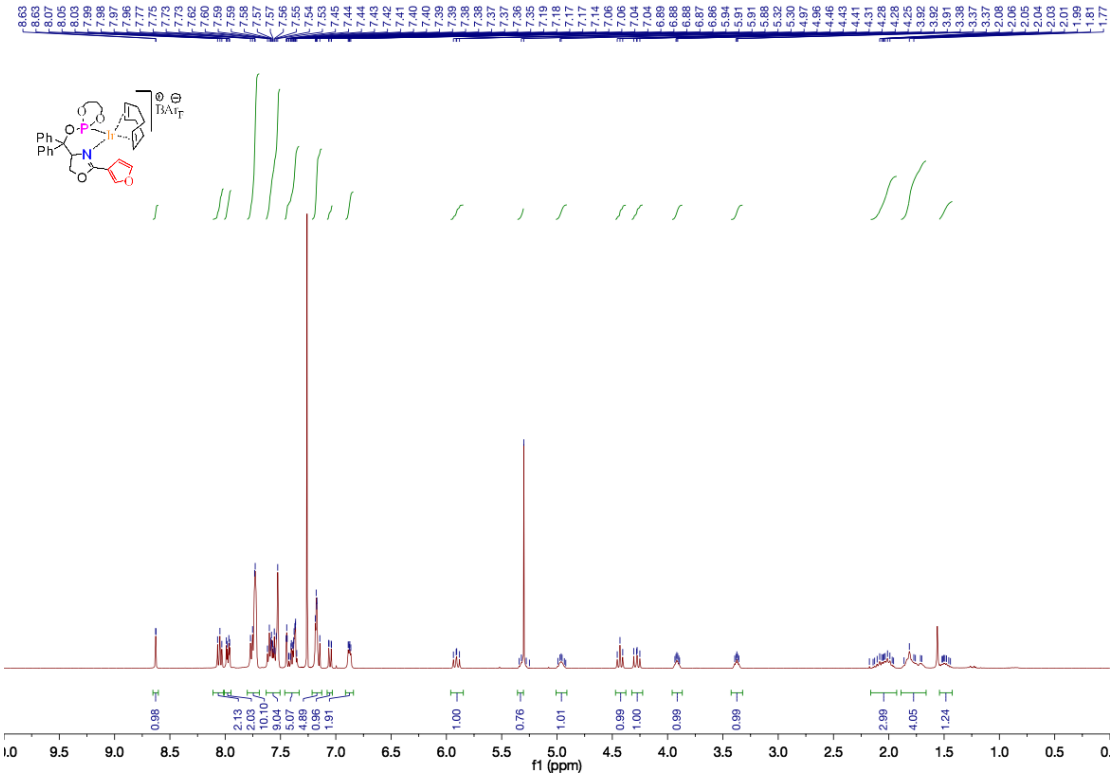
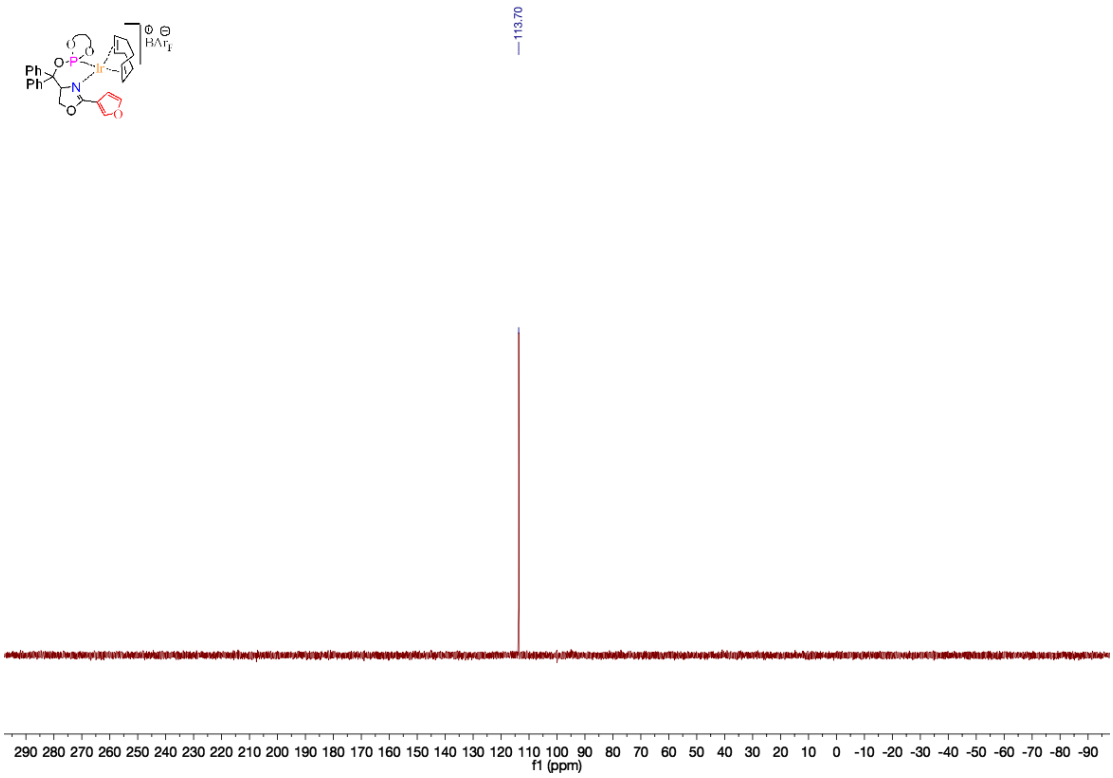
20.39
4.18
3.72
0.98
1.79
0.89
1.00
1.04
1.00
1.26
0.96
0.99
0.99
3.04
1.91
2.79
1.23
f1 (ppm)


Ph
Ph
BArF
113.01
f1 (ppm)


f1 (ppm)


f1 (ppm)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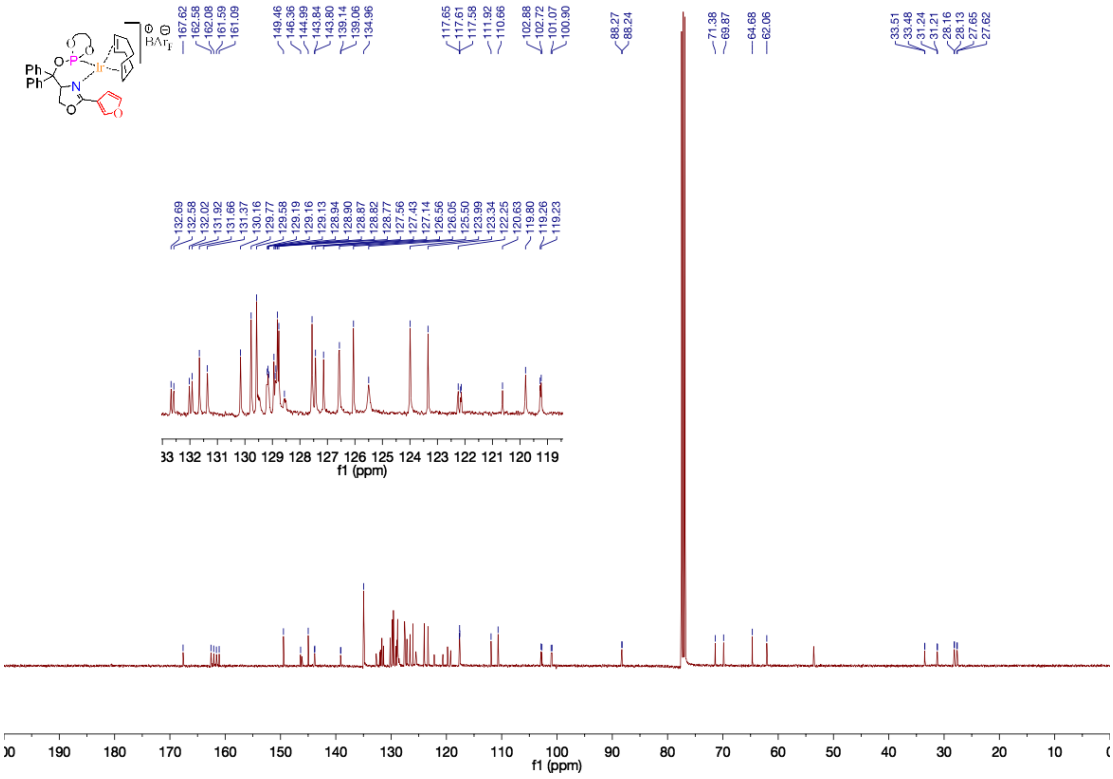
f1 (ppm)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117.61
117.58
111.92
110.66
102.88
102.72
101.07
100.90
88.27
88.24
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64.68
62.06
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33.48
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27.65
27.62
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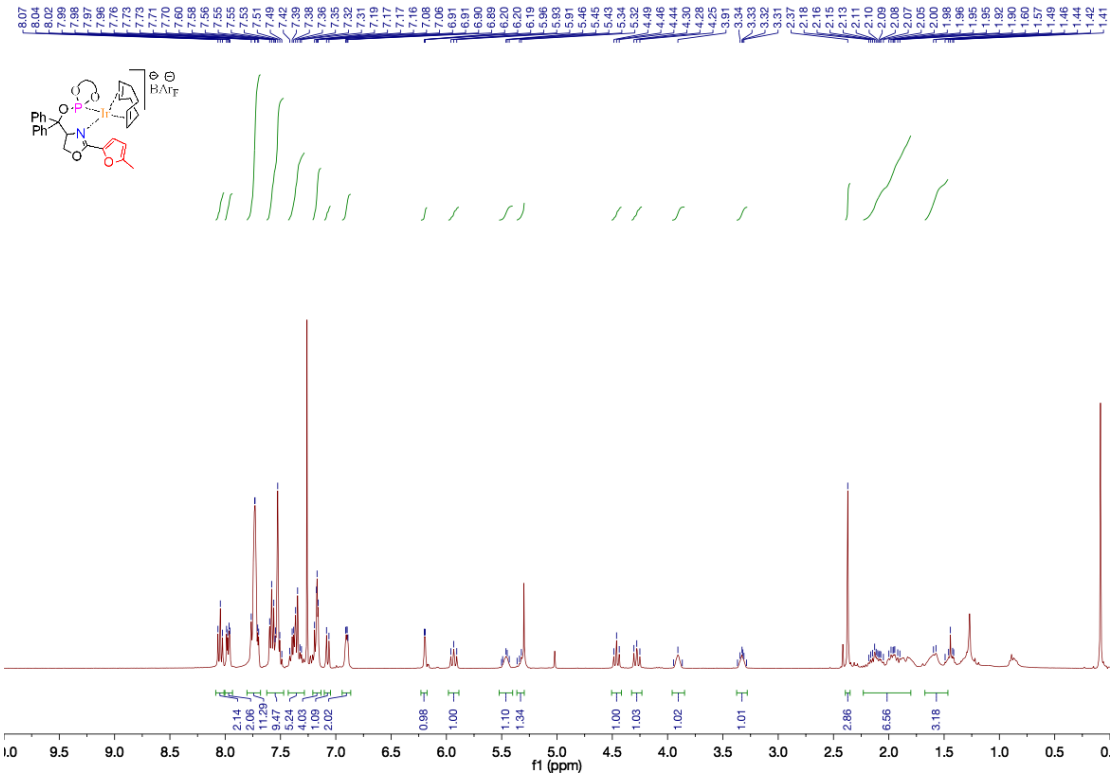
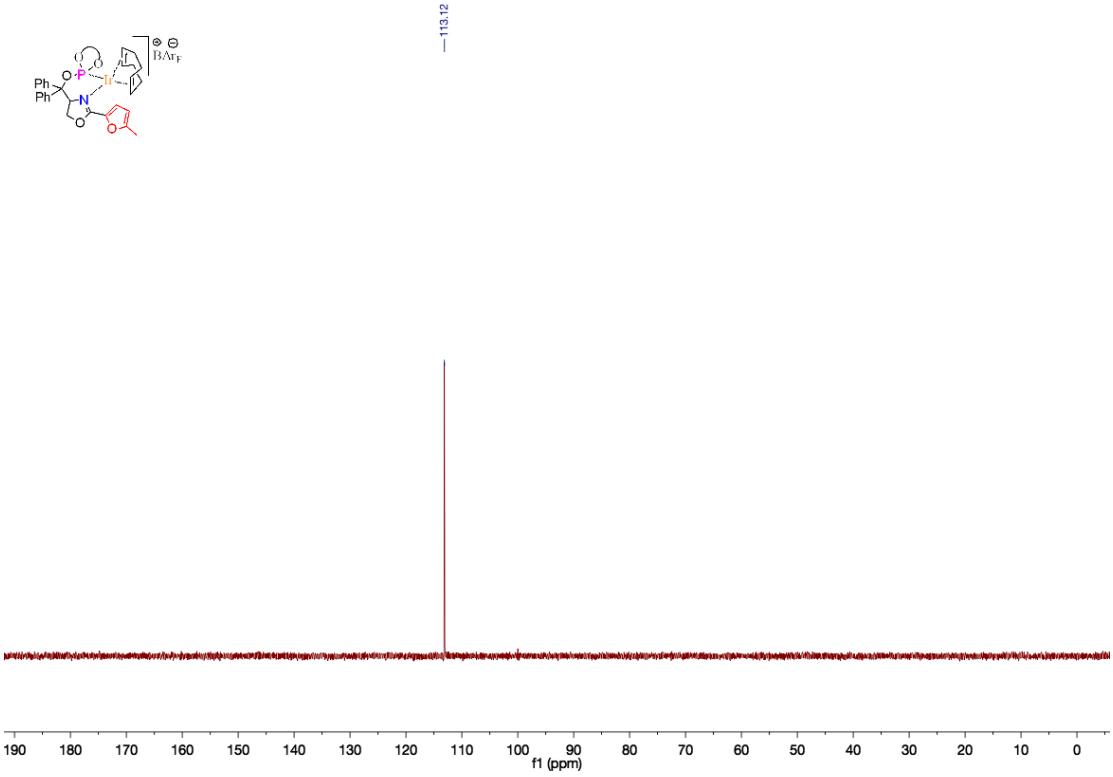
126.56
126.05
125.50
123.99
123.34
122.25
120.63
119.80
119.26
119.23
33 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Ph
Ph
P
Ir
N
O
BArF
f1 (ppm)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P
Ir
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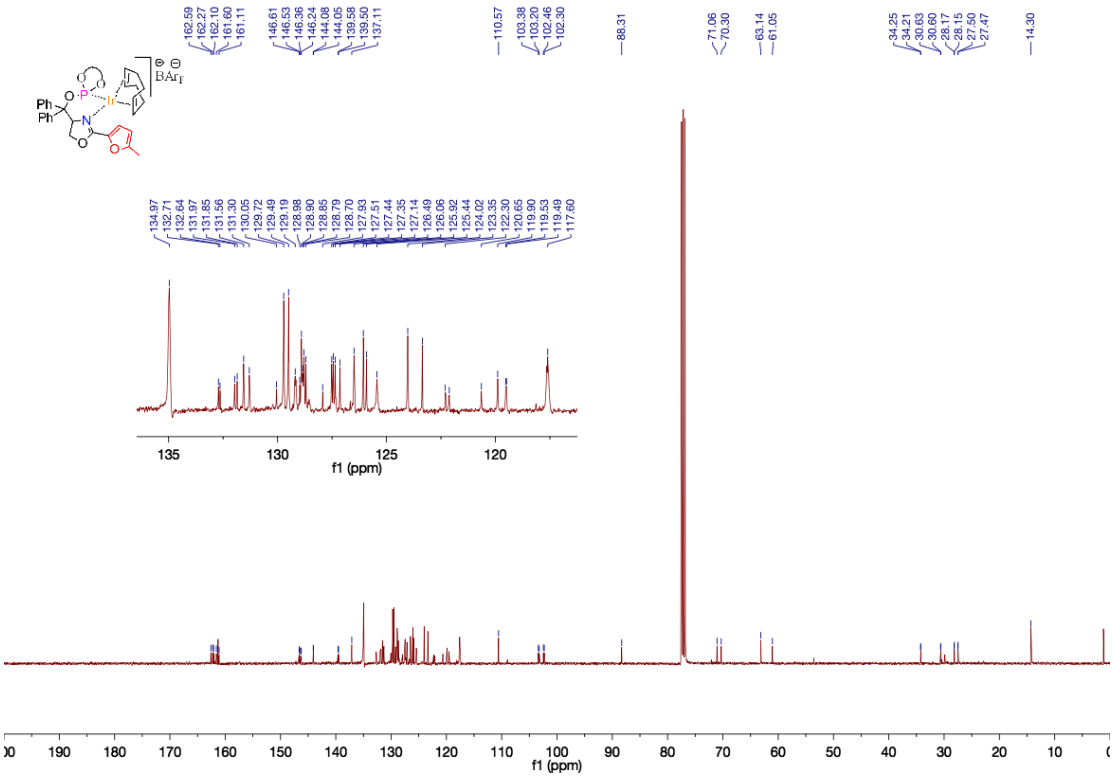
BArF
f1 (ppm)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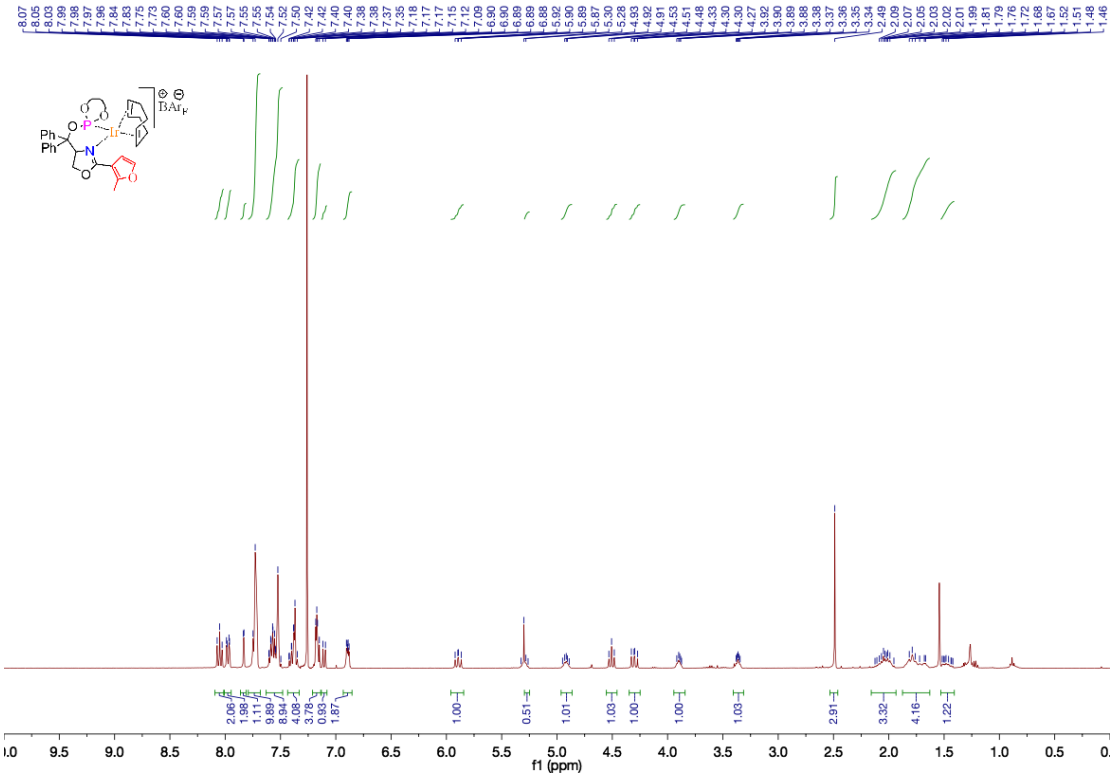
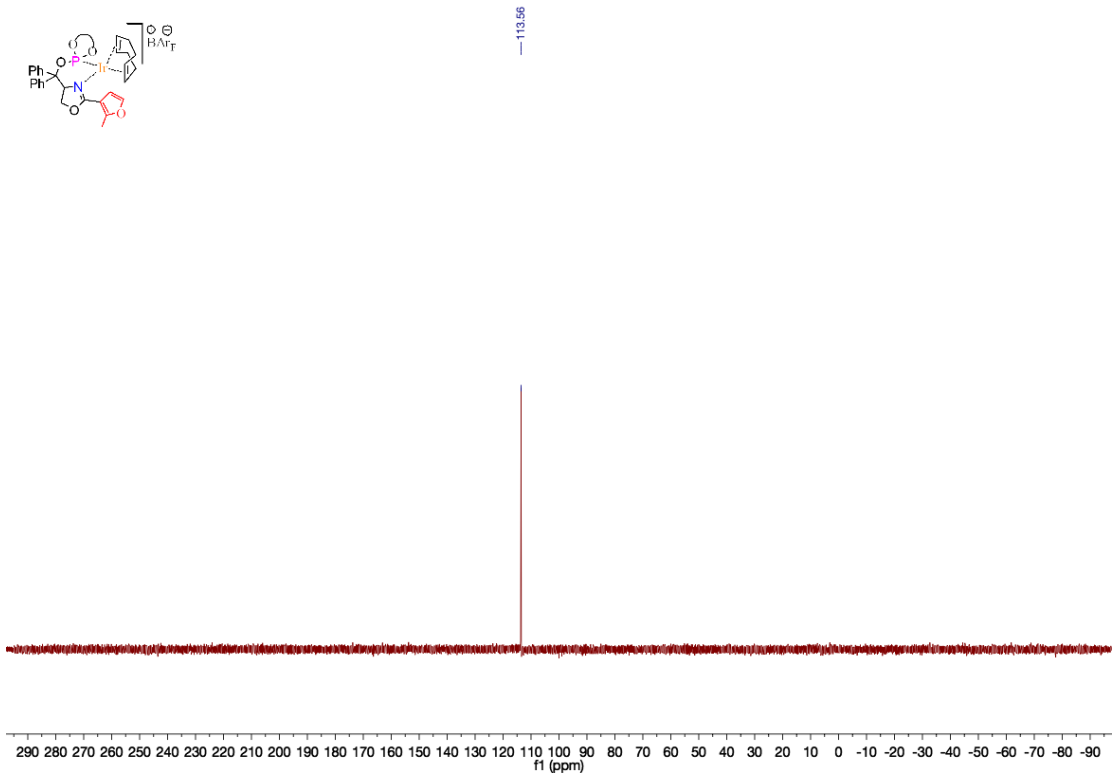
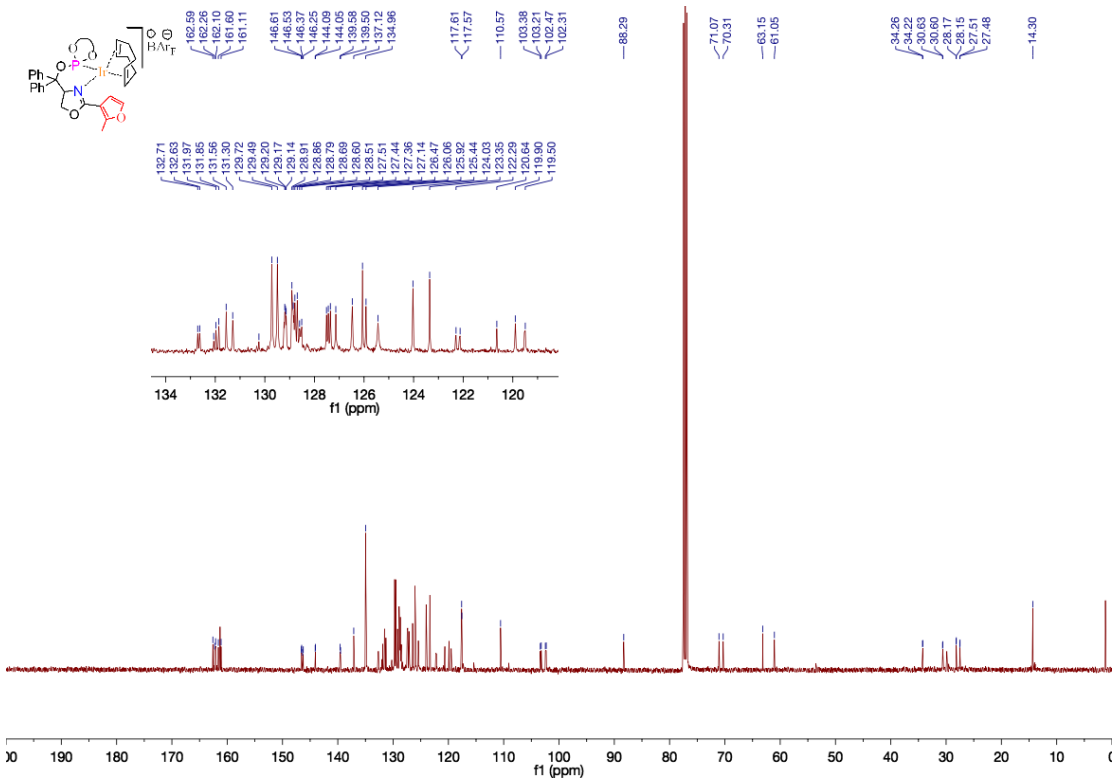

f1 (ppm)


113.56
f1 (ppm)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144.09
144.05
139.58
139.50
137.12
134.96
117.61
117.57
110.57
103.38
103.21
102.47
102.31
88.29
71.07
70.31
63.15
61.05
34.26
34.22
30.63
30.60
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27.51
27.48
14.30
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132.63
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131.55
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127.44
127.36
127.14
126.47
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125.44
124.03
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122.29
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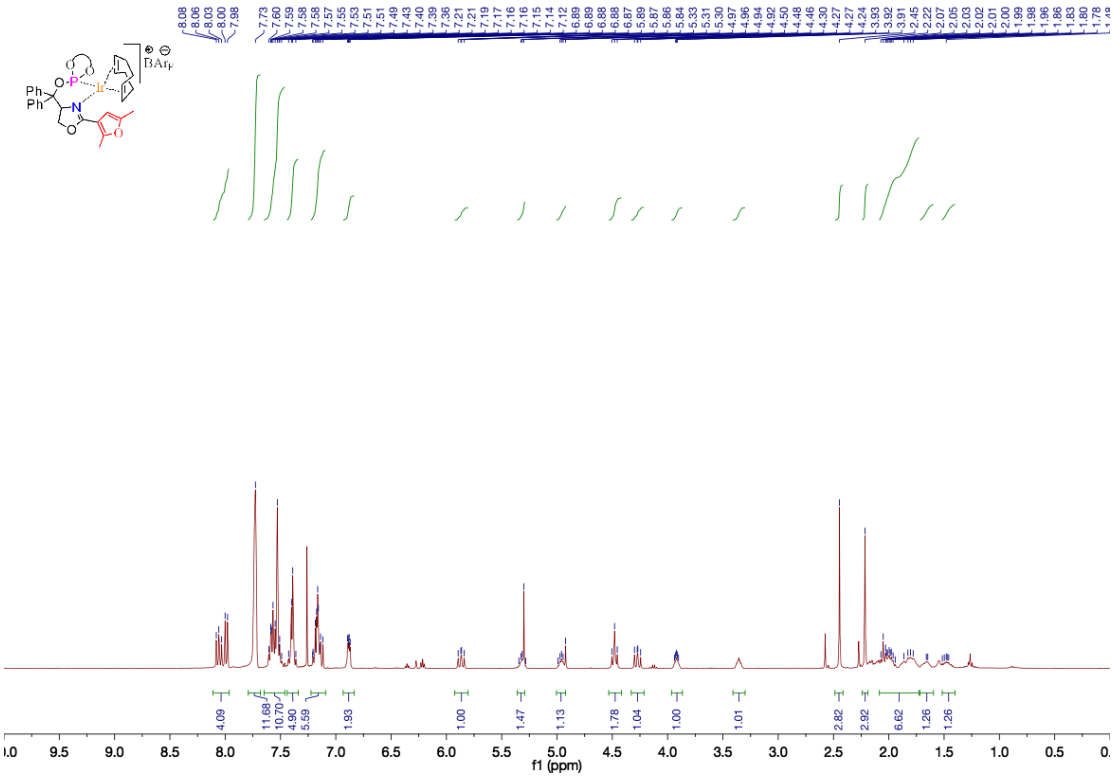
119.50
f1 (ppm)
f1 (ppm)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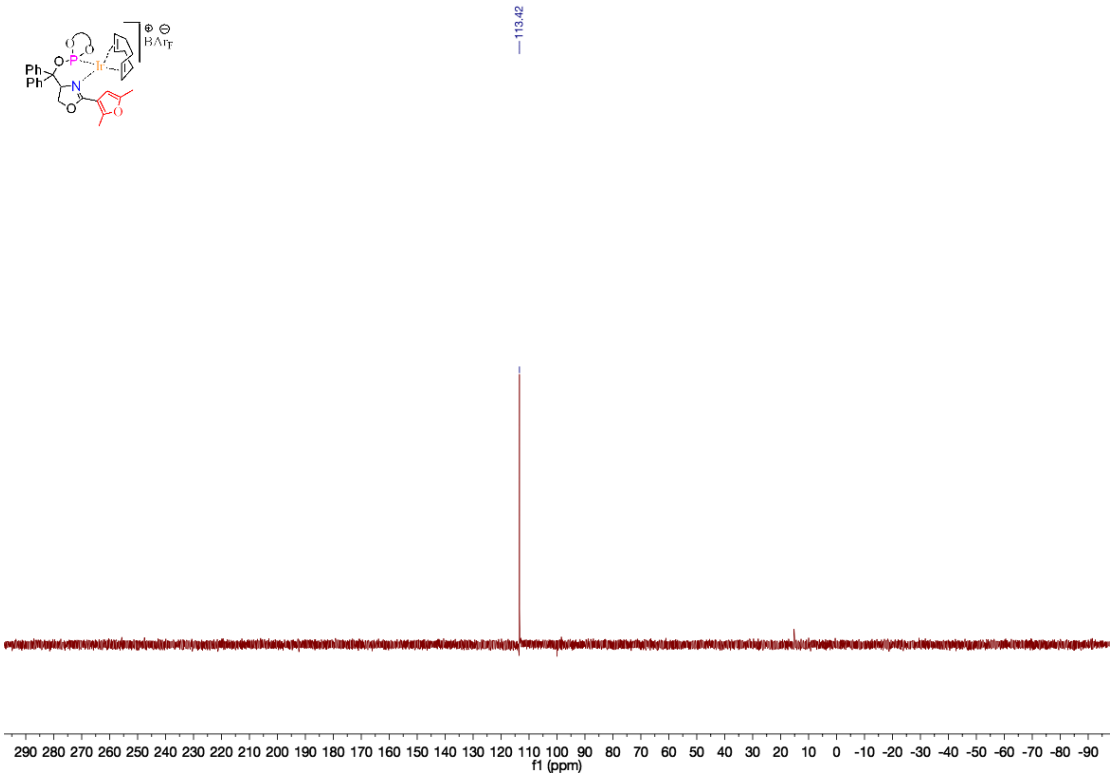
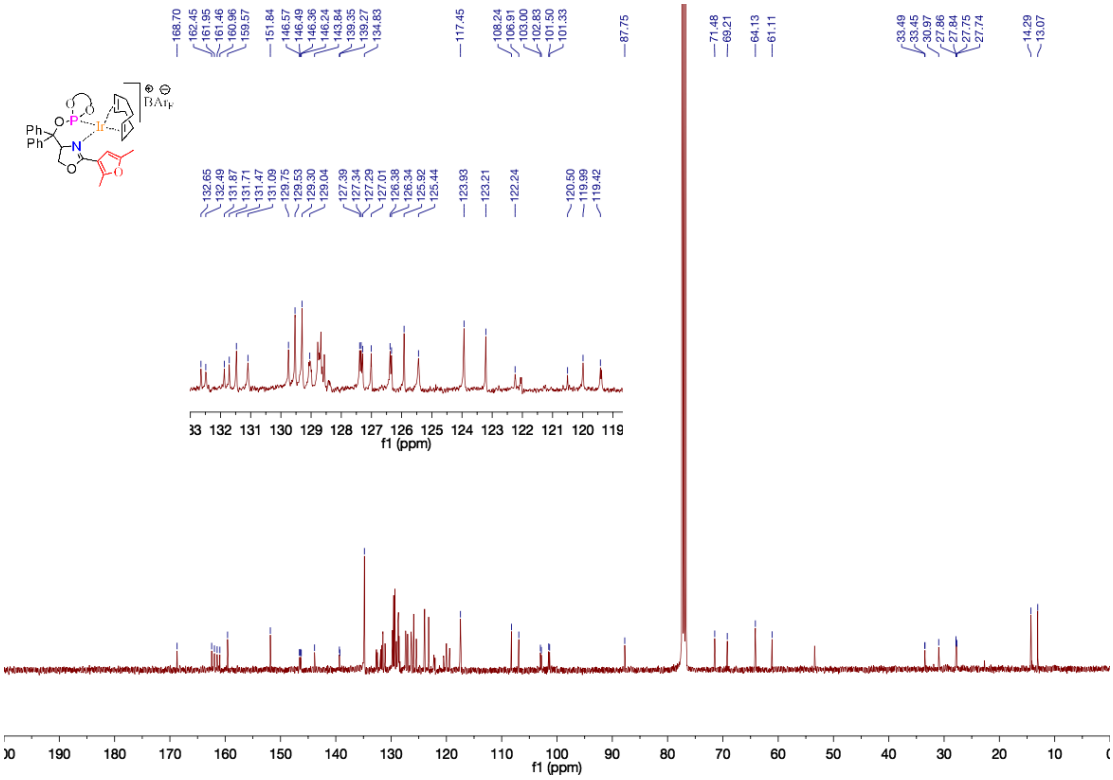
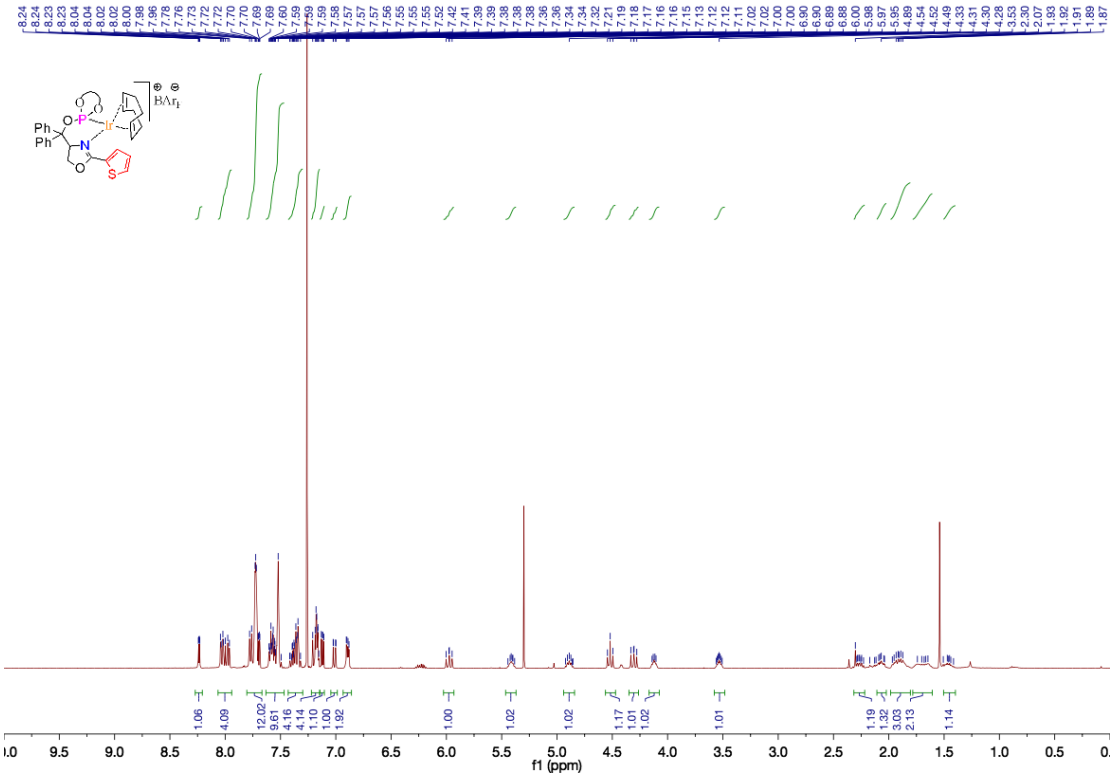
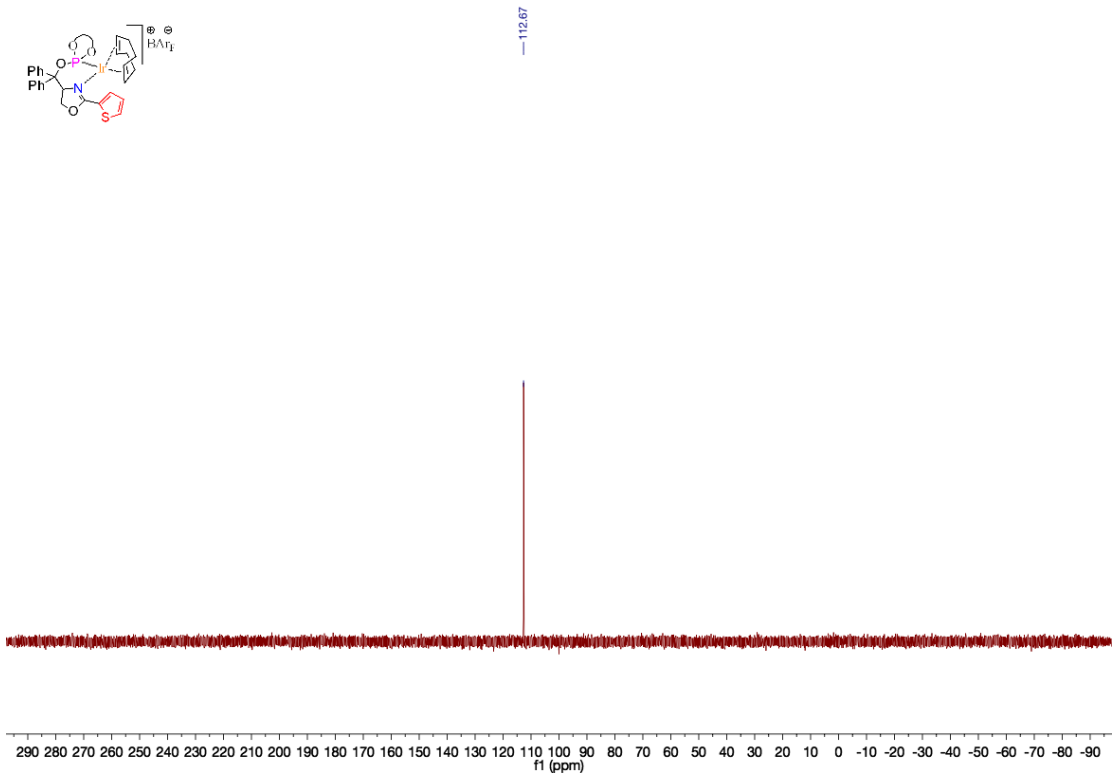
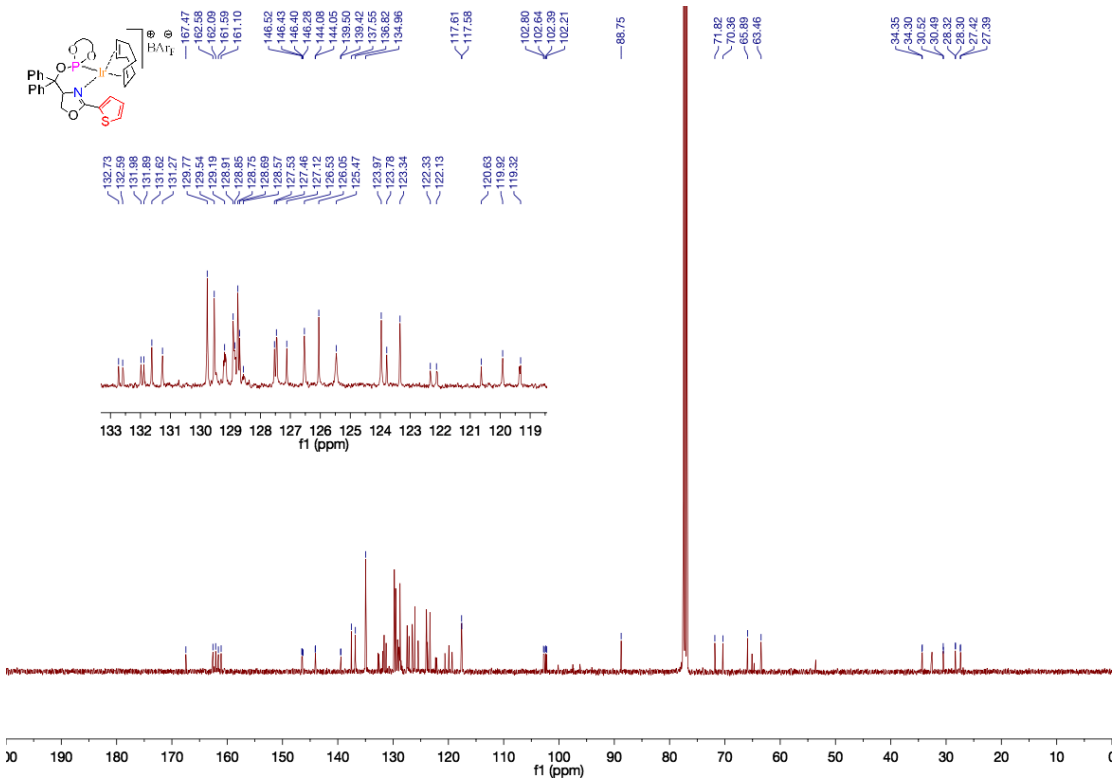

113.42
f1 (ppm)


f1 (ppm)


f1 (ppm)


112.67
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)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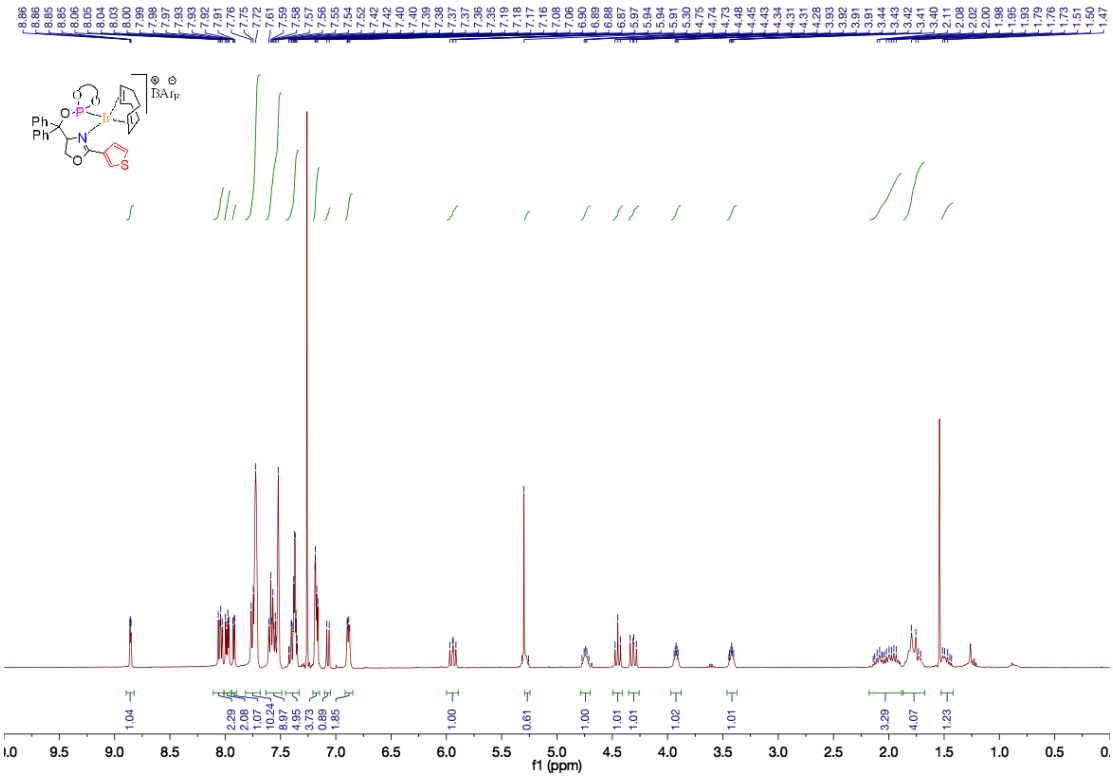
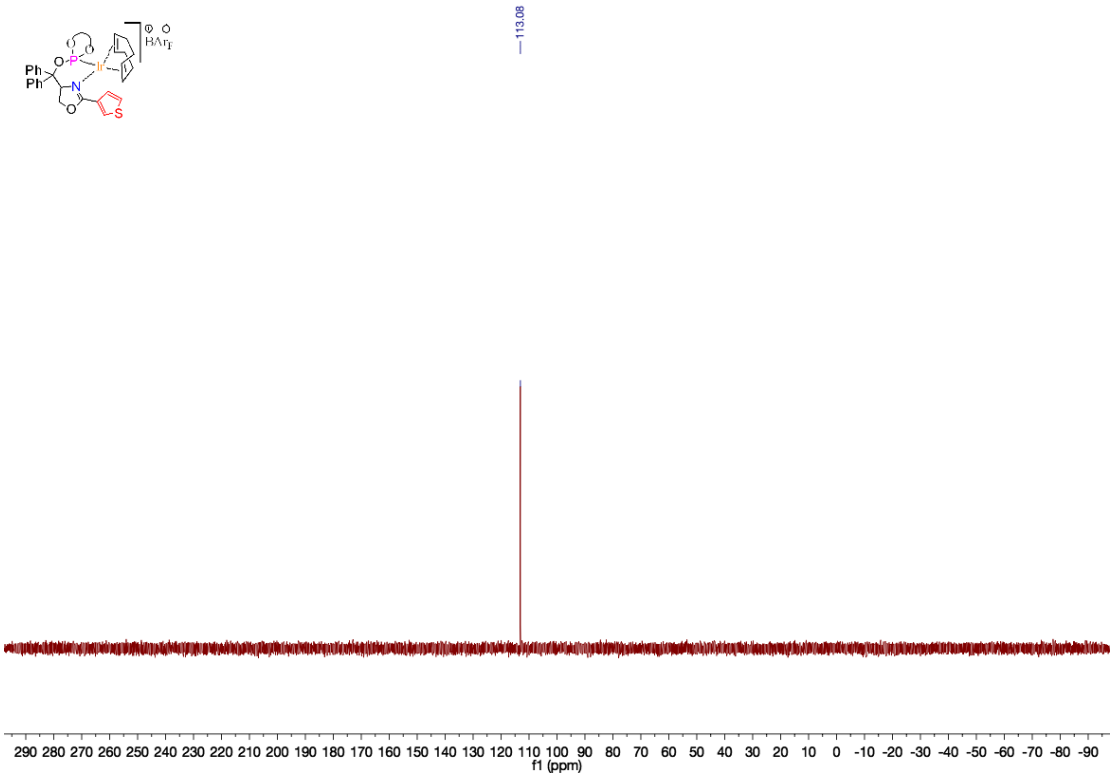
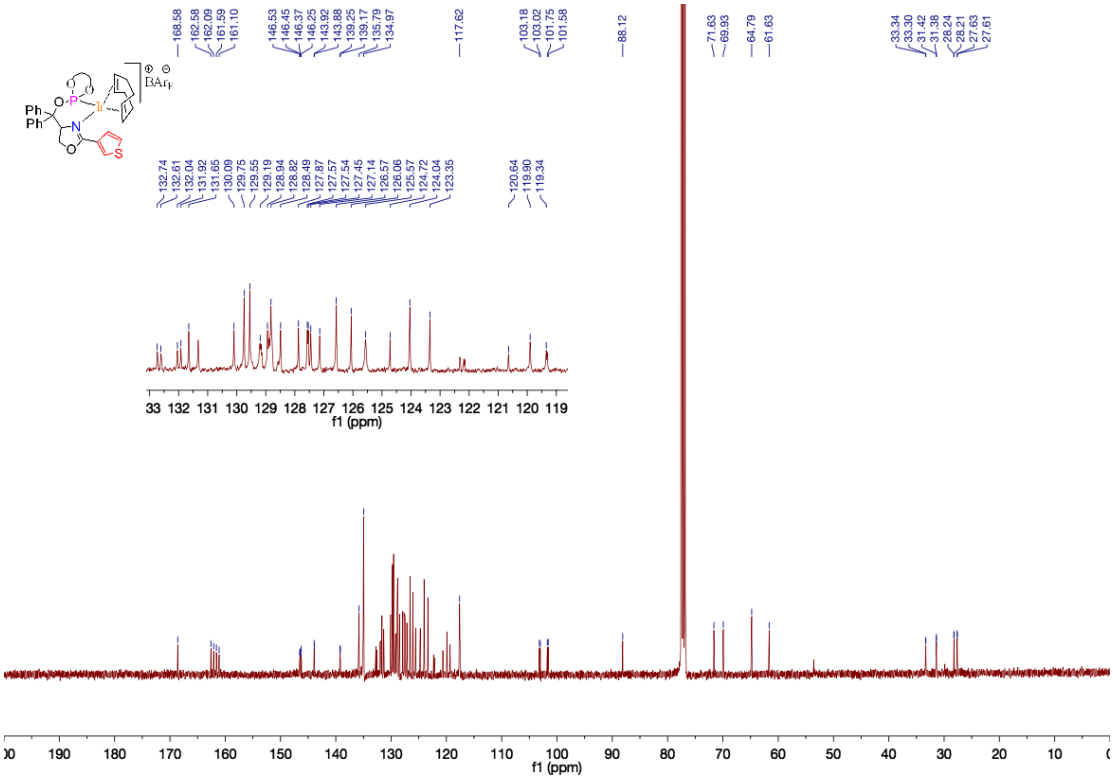
144.05
139.50
139.42
137.55
136.82
134.96
117.61
117.58
102.80
102.64
102.39
102.21
88.75
71.82
70.96
65.89
63.46
34.35
34.30
30.52
30.49
28.32
28.30
27.42
27.39
132.73
132.59
131.98
131.89
131.62
131.27
129.77
129.54
129.19
128.91
128.85
128.75
128.69
128.57
127.53
127.46
127.12
126.53
126.05
125.47
123.97
123.78
123.34
122.33
122.13
120.63
119.92
119.32
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


f1 (ppm)


113.08
f1 (ppm)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162.58
162.09
161.59
161.10
146.53
146.45
146.37
146.25
143.92
143.88
139.25
139.17
135.79
134.97
117.62
103.18
103.02
101.75
101.58
88.12
71.63
69.93
64.79
61.63
33.34
33.30
31.42
31.38
28.24
28.21
27.63
27.61
132.74
132.61
132.04
131.92
131.65
130.09
129.75
129.55
129.19
128.94
128.82
128.49
127.87
127.57
127.54
127.45
127.14
126.57
126.06
125.57
124.72
124.04
123.35
120.64
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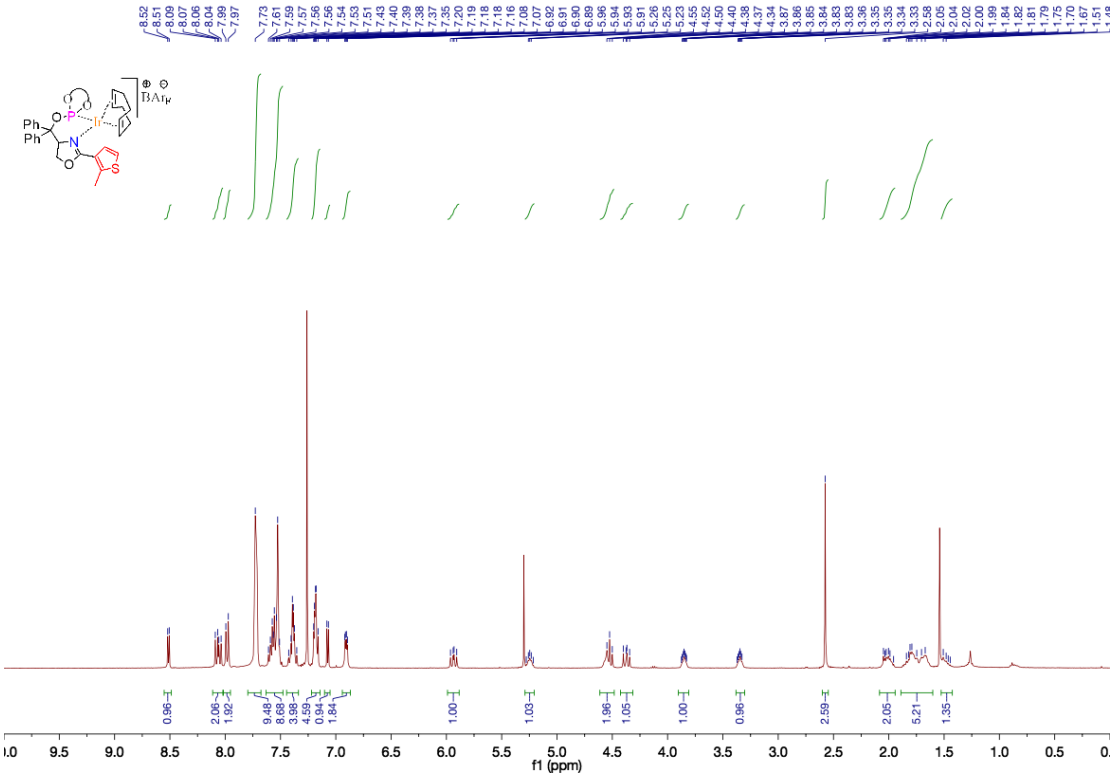
119.34
33 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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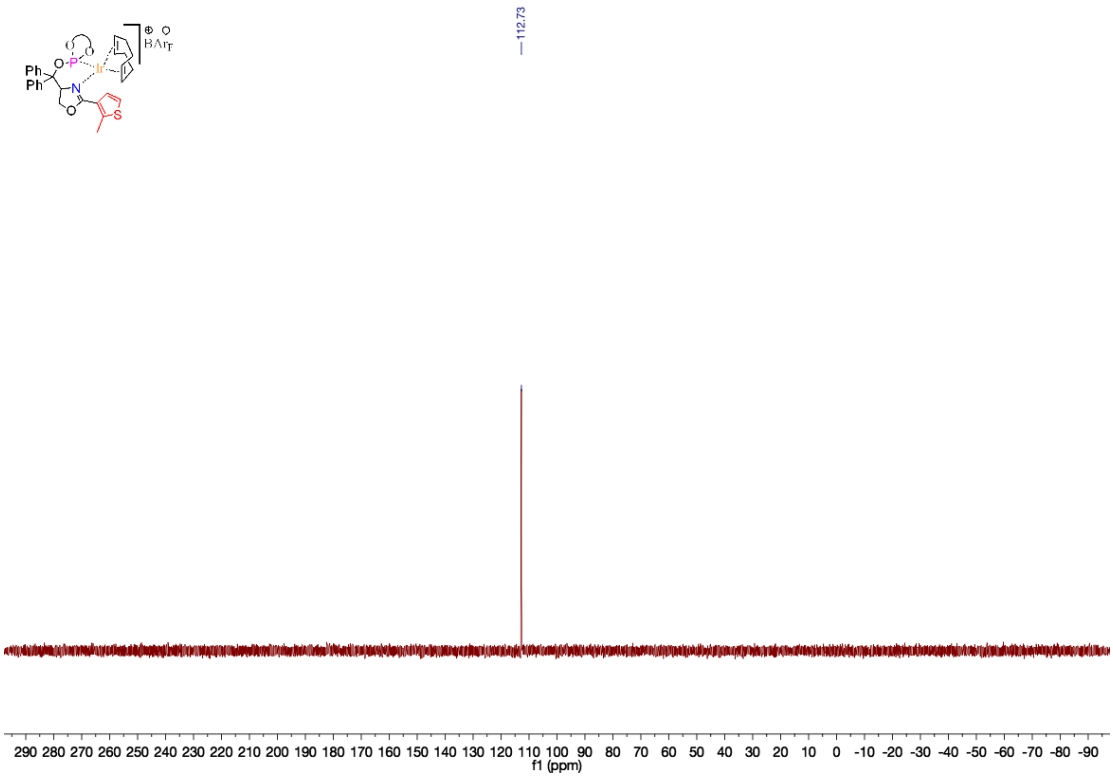
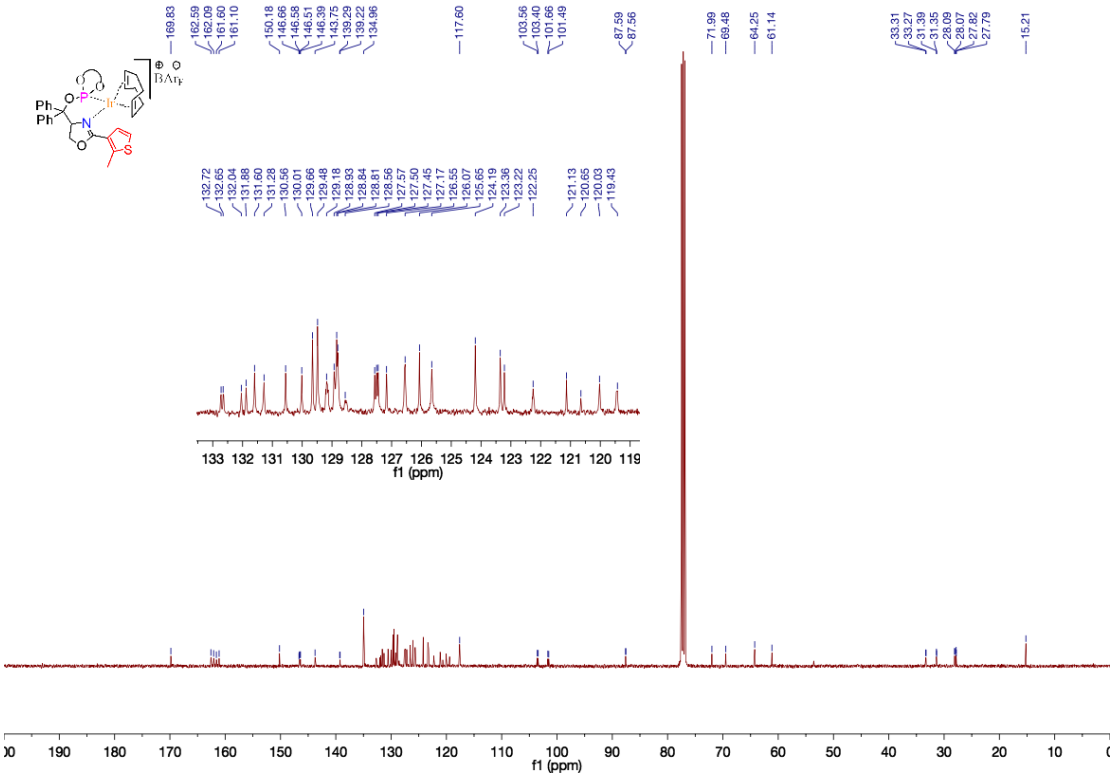
8.51
8.09
8.07
8.06
8.04
7.99
7.97
7.73
7.61
7.59
7.57
7.56
7.54
7.53
7.51
7.43
7.40
7.39
7.38
7.37
7.35
7.20
7.19
7.18
7.16
7.08
7.07
6.92
6.91
6.90
6.88
5.96
5.94
5.93
5.91
5.26
5.25
5.23
4.55
4.52
4.50
4.40
4.38
4.37
4.34
3.87
3.86
3.85
3.84
3.83
3.83
3.36
3.35
3.34
3.33
2.58
2.05
2.04
2.02
2.00
1.99
1.84
1.82
1.81
1.79
1.75
1.70
1.67
1.51
0.96
2.08
1.92
9.48
8.68
3.98
4.59
0.94
1.84
1.00
1.03
1.96
1.05
1.00
0.96
2.59
2.05
5.21
1.35
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
f1 (ppm)


112.73
290 280 270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)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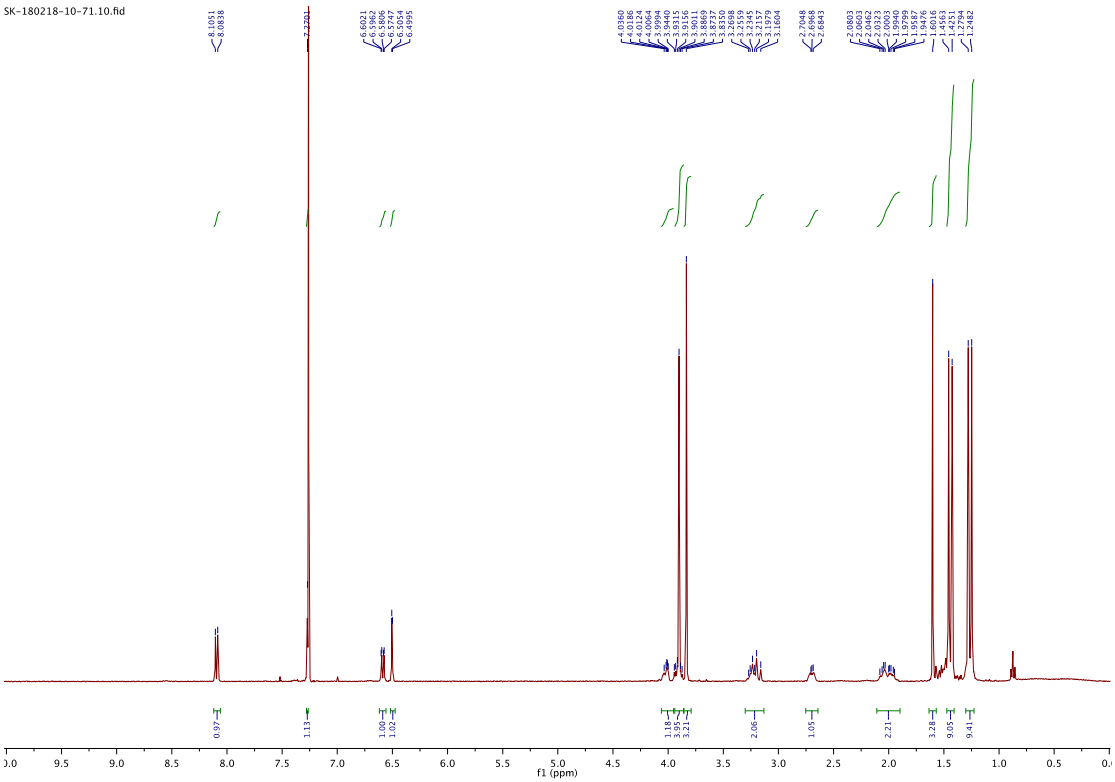
146.39
143.75
139.29
139.22
134.96
117.60
103.56
103.40
101.66
101.49
87.59
87.56
71.99
69.48
64.25
61.14
33.31
33.27
31.39
31.35
28.09
28.07
27.82
27.79
15.21
132.72
132.65
132.04
131.88
131.60
131.28
130.96
130.01
129.66
129.48
129.18
128.93
128.84
128.81
128.56
127.57
127.50
127.45
127.17
126.55
126.07
125.65
124.19
123.95
123.22
122.25
121.13
120.65
120.03
119.43
133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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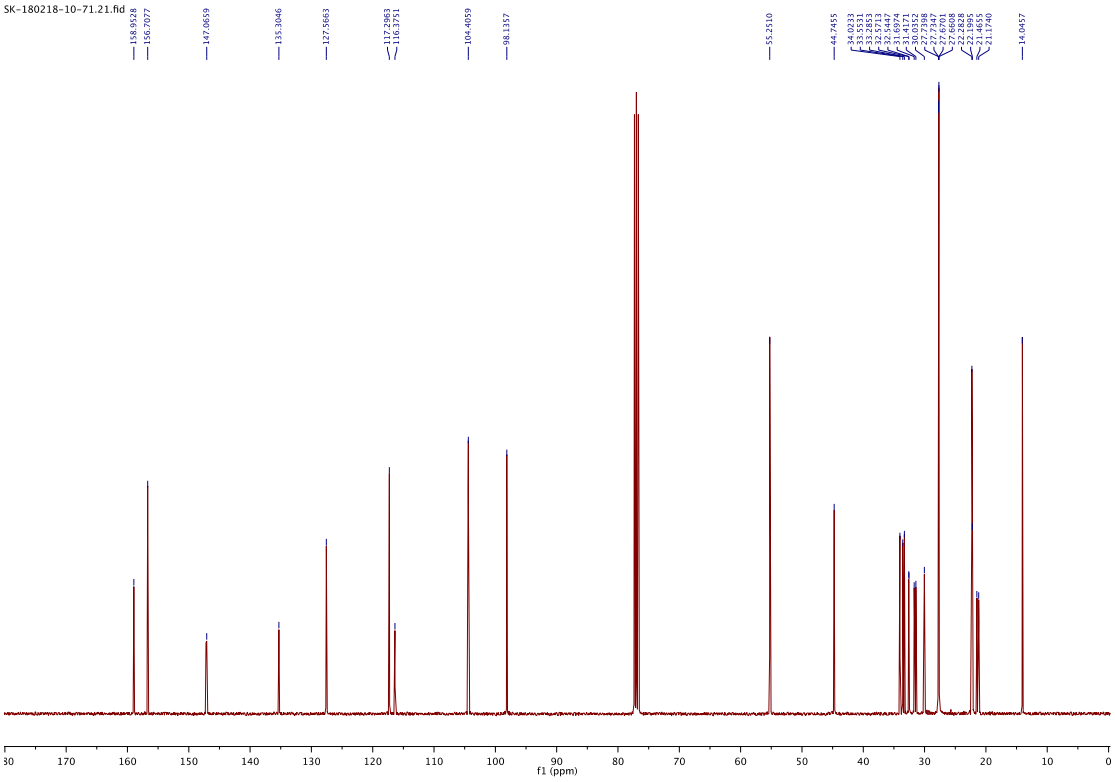
f1 (ppm)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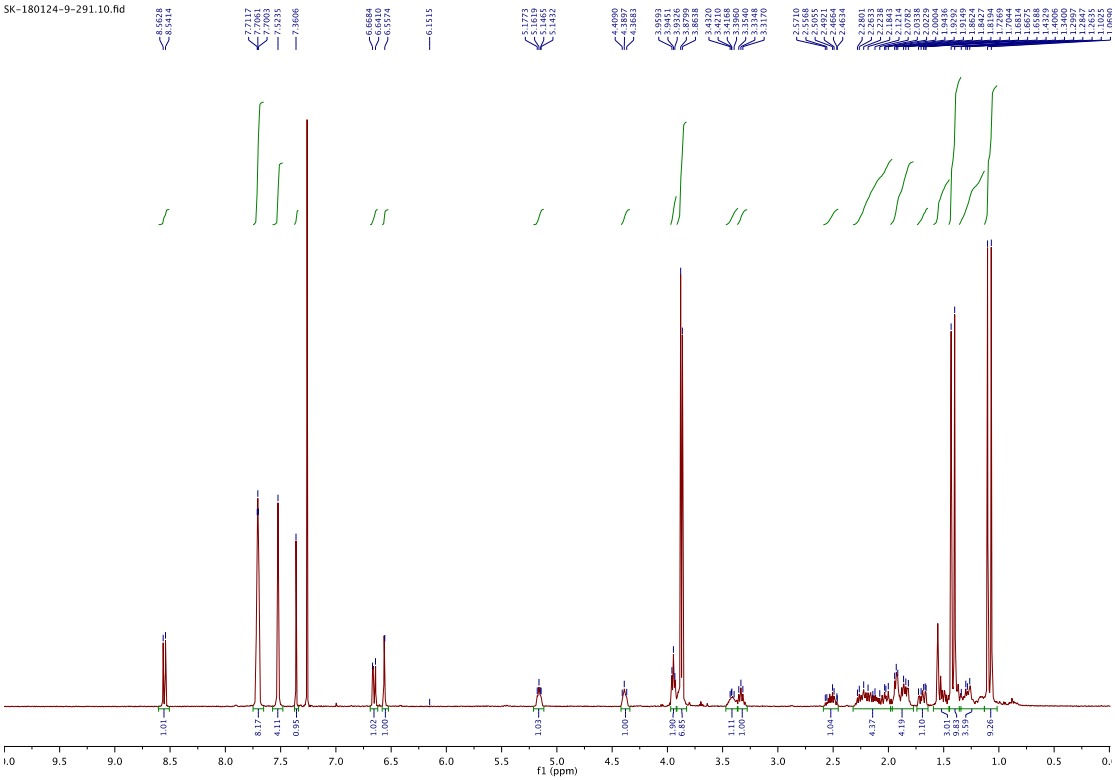
f1 (ppm)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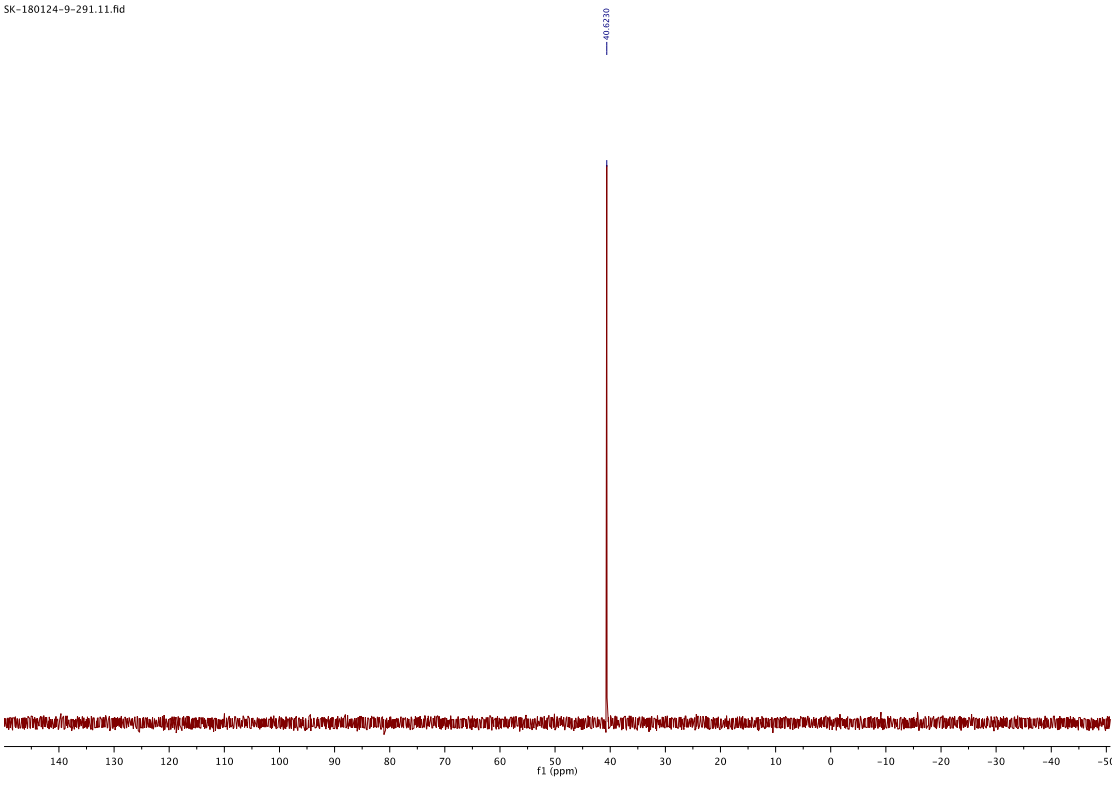
f1 (ppm)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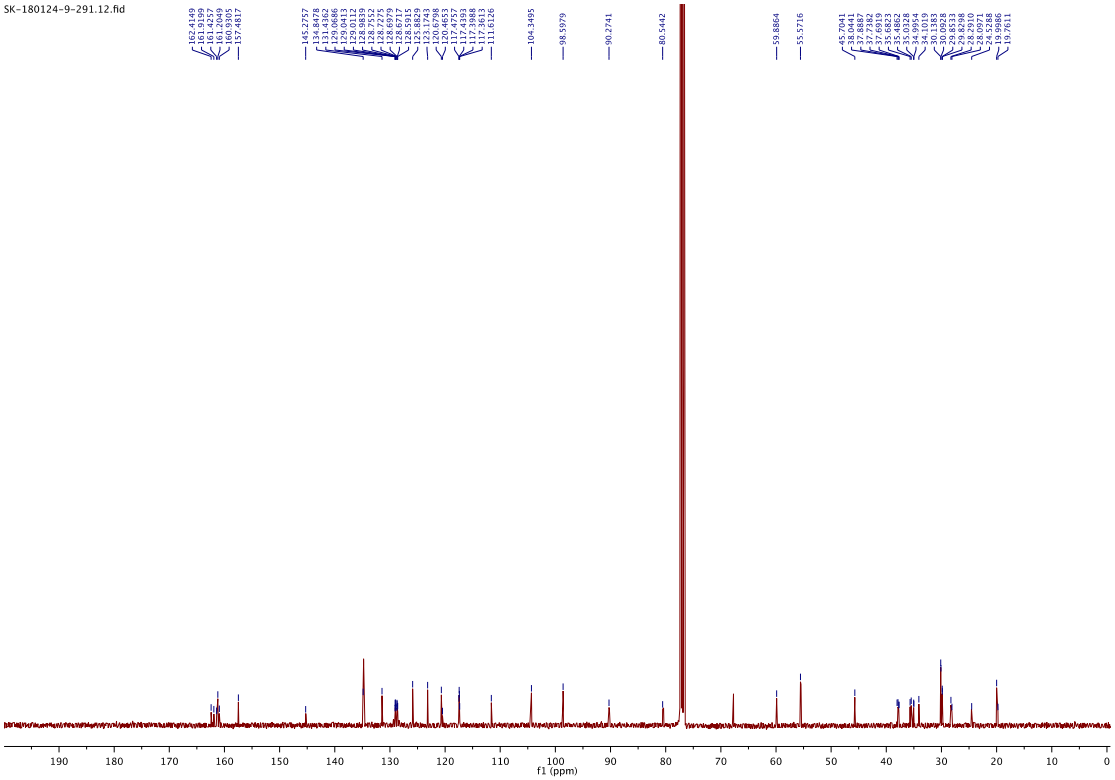
40.6230
f1 (ppm)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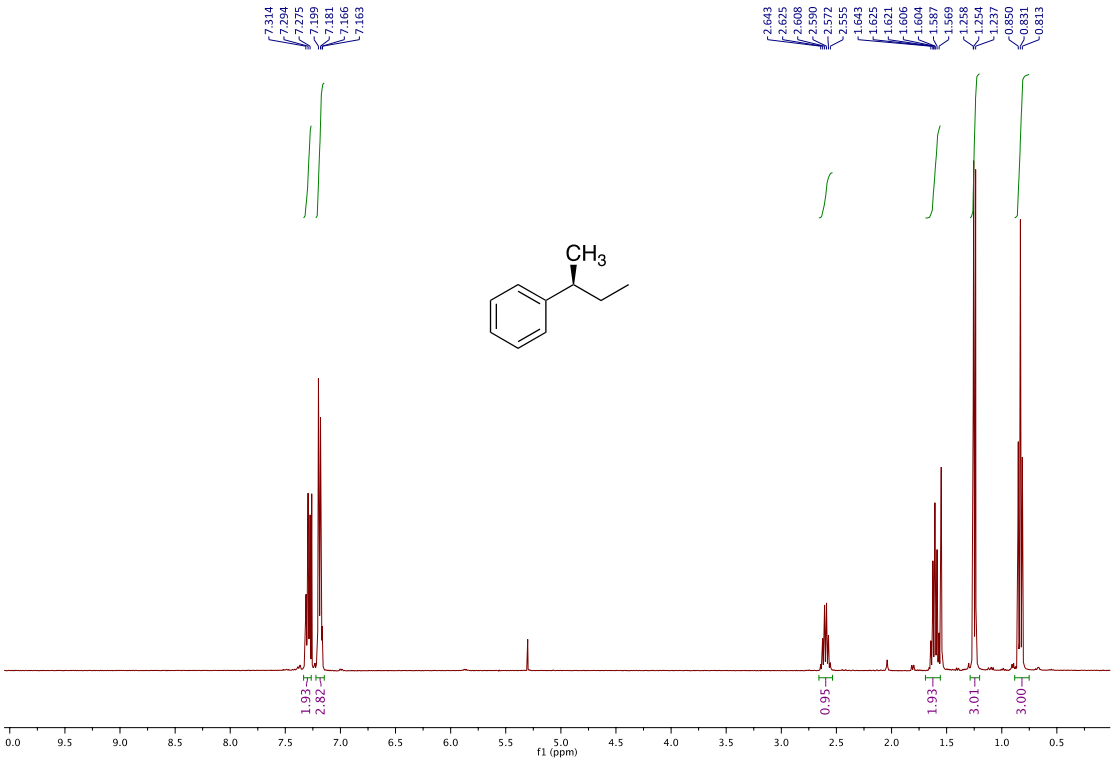
161.2049
160.9305
157.4817
145.2757
134.8478
134.5482
129.0686
129.0413
128.8839
128.7552
128.7375
128.6979
128.6717
125.9585
125.8829
123.1743
120.7698
120.4653
117.4757
117.3988
117.3613
117.1038
111.6126
104.3495
98.5979
90.2741
80.5442
59.8864
55.5716
45.7041
38.0441
37.8887
37.7734
37.6919
35.6823
35.4662
35.0328
34.9954
34.7619
30.1383
30.0928
29.8633
29.8298
28.2910
26.0671
24.5288
19.5986
19.3761
f1 (ppm)

6. ^{1}H and ^{13}C NMR spectroscopic data for the hydrogenated products

All the hydrogenated products in this study have been reported.

SK-170925-9-147column.10.fid



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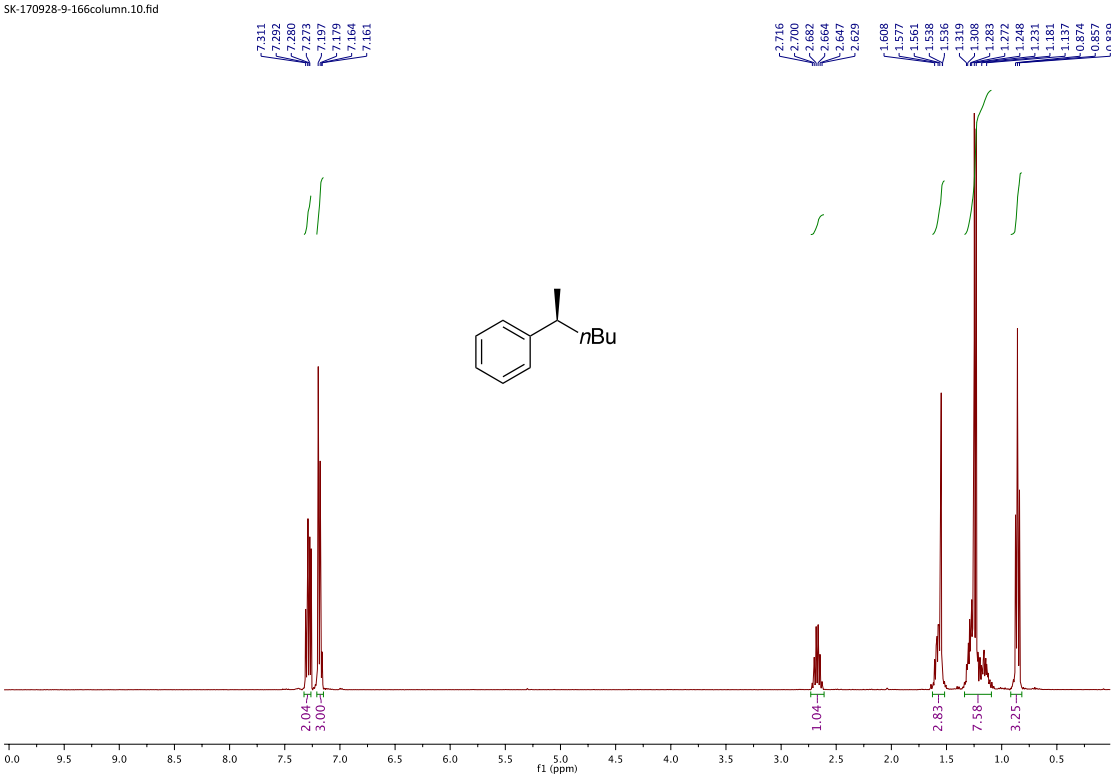
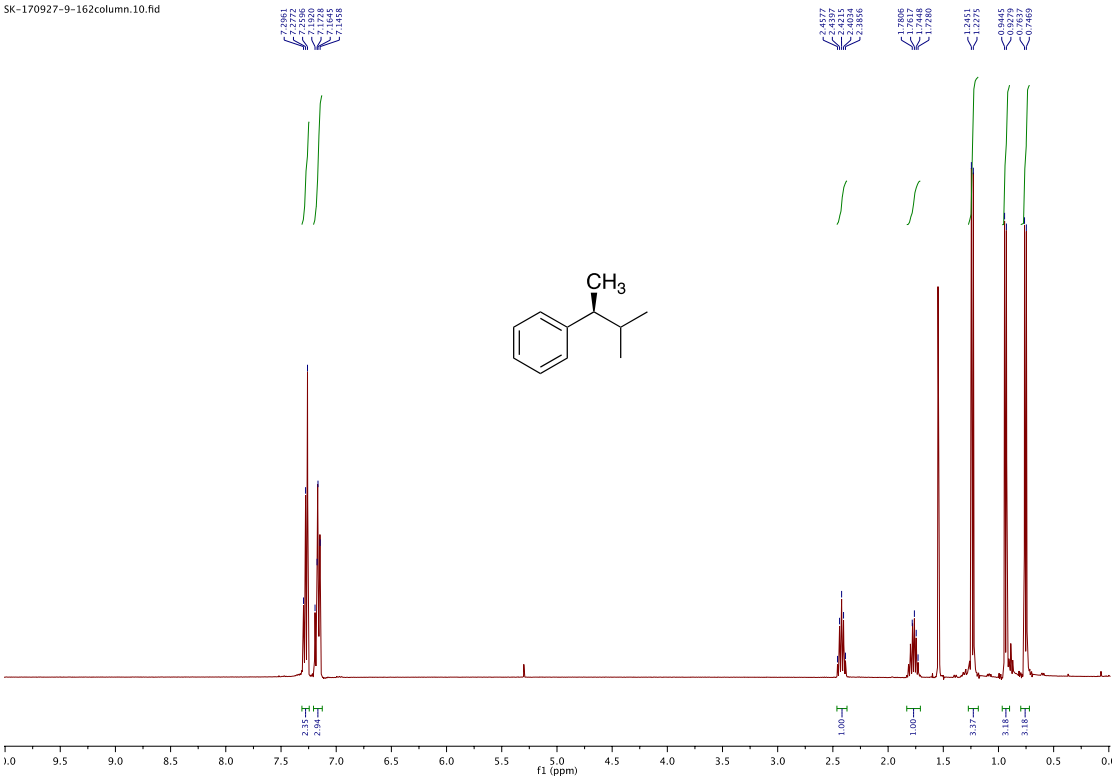
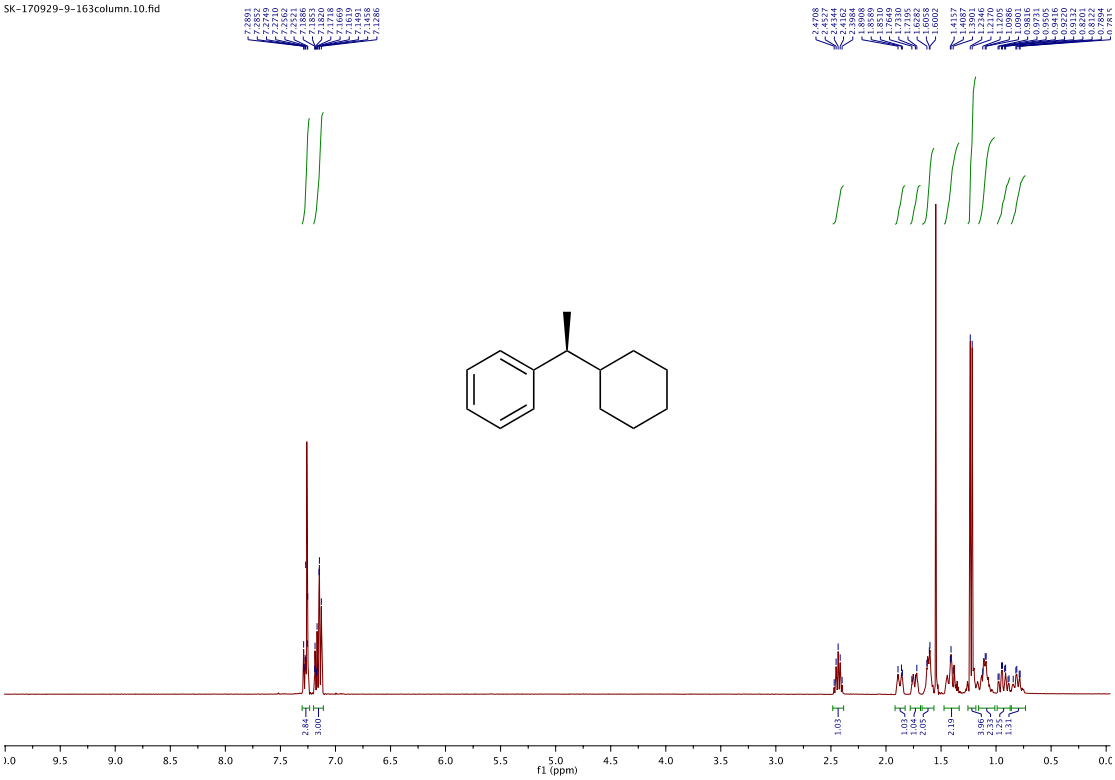
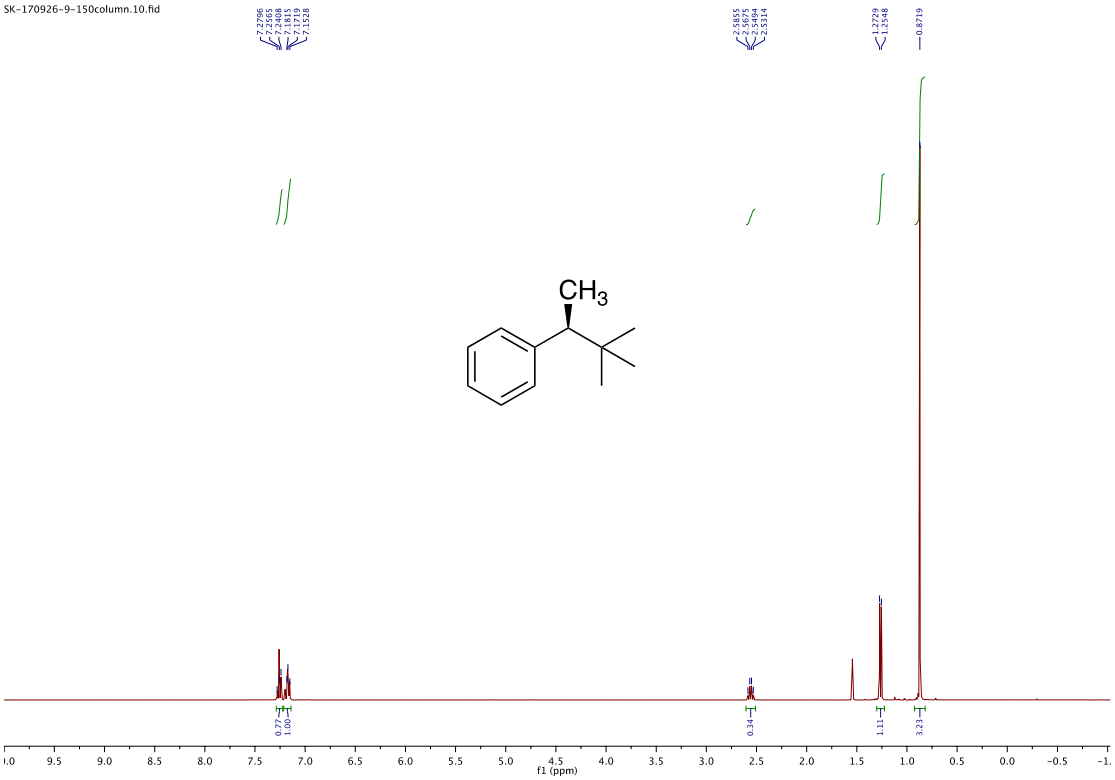



SK-170927-9-162column.10.fid
CH3
f1 (ppm)


SK-170929-9-163column.10.fid
f1 (ppm)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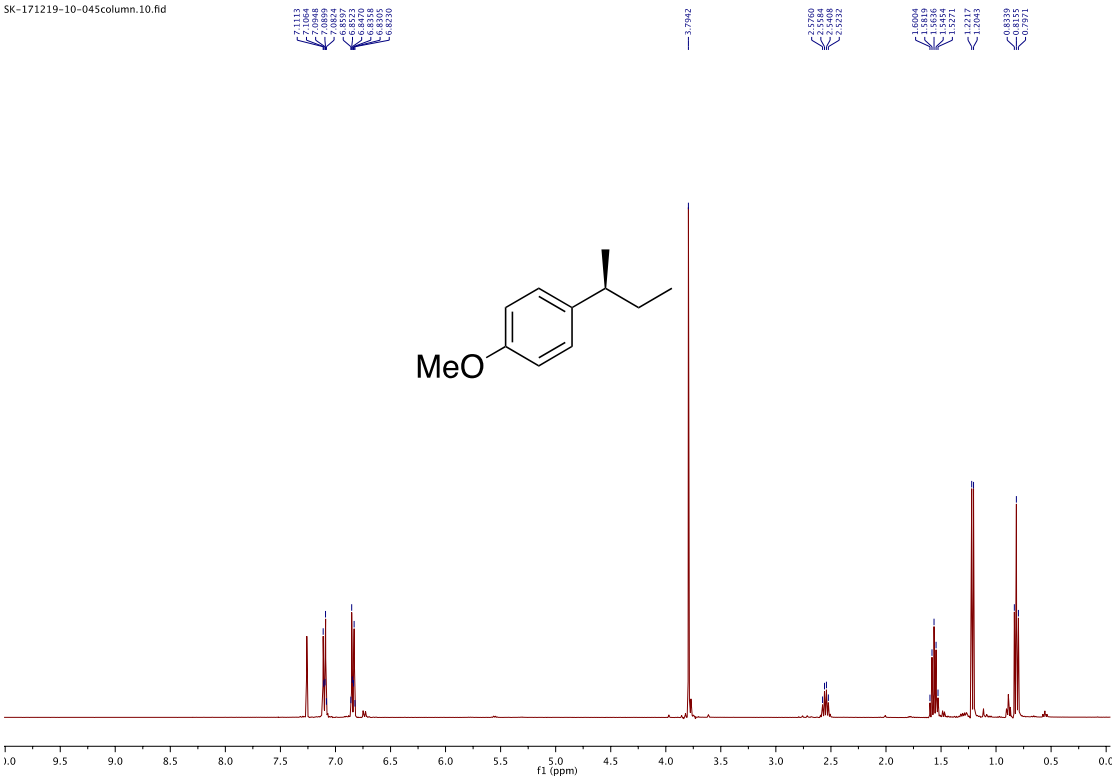
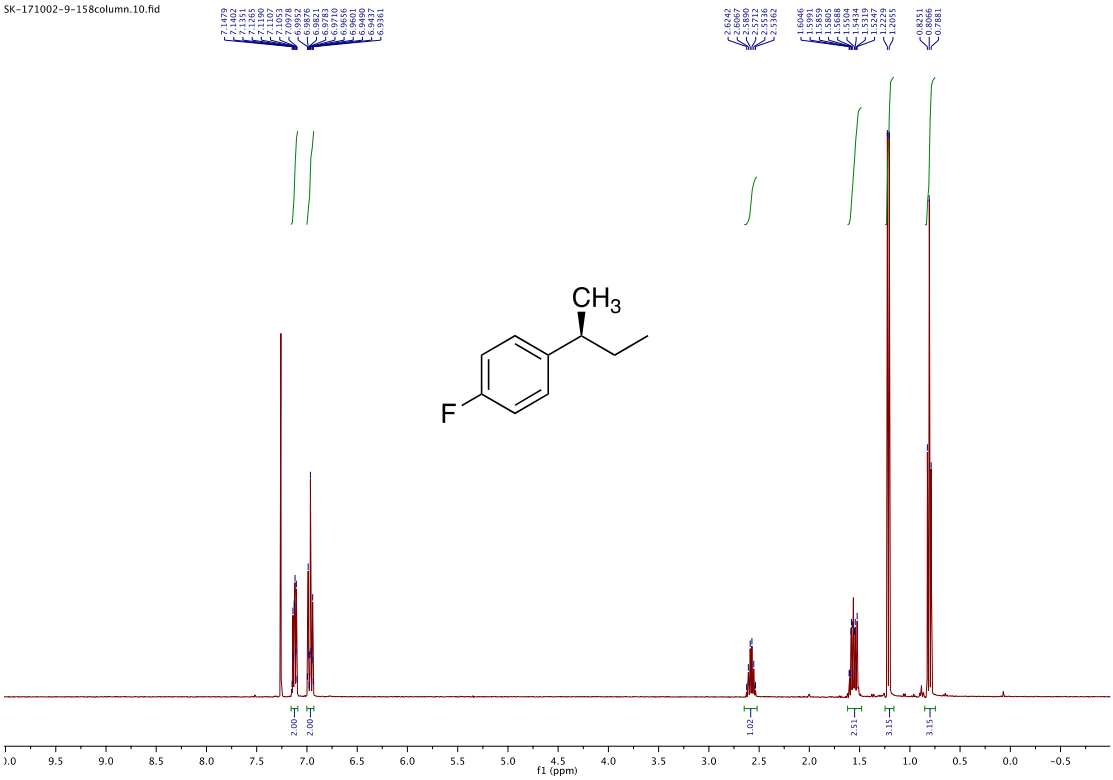
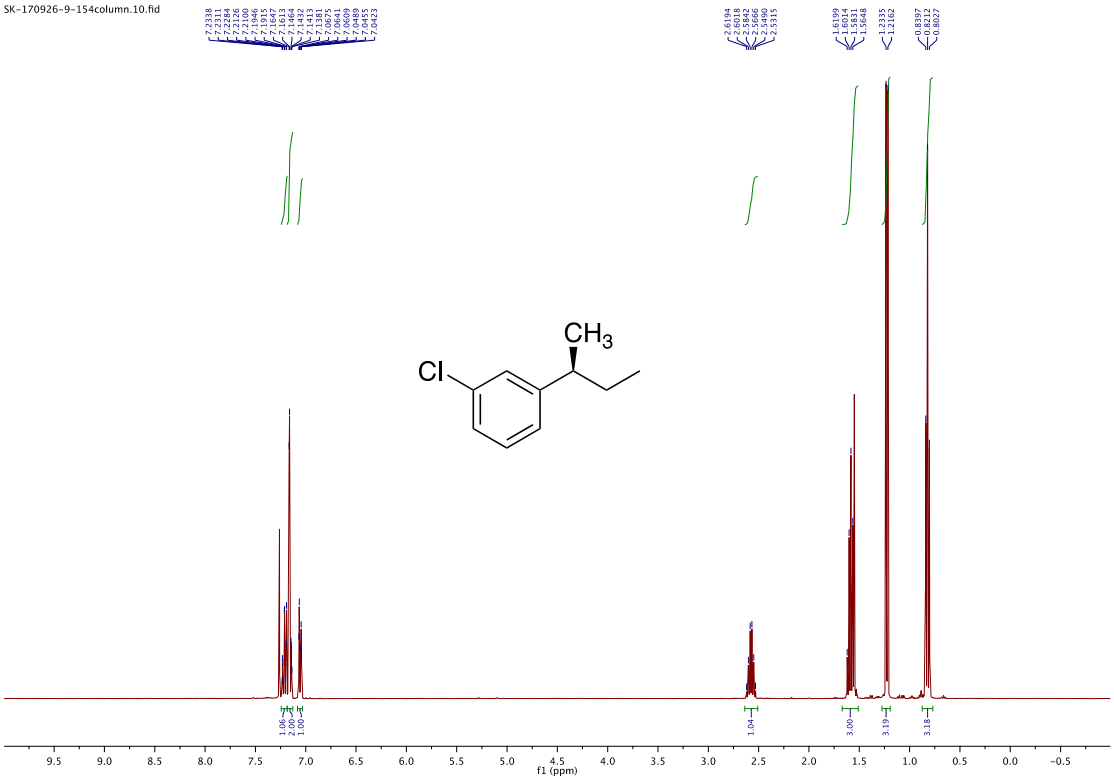
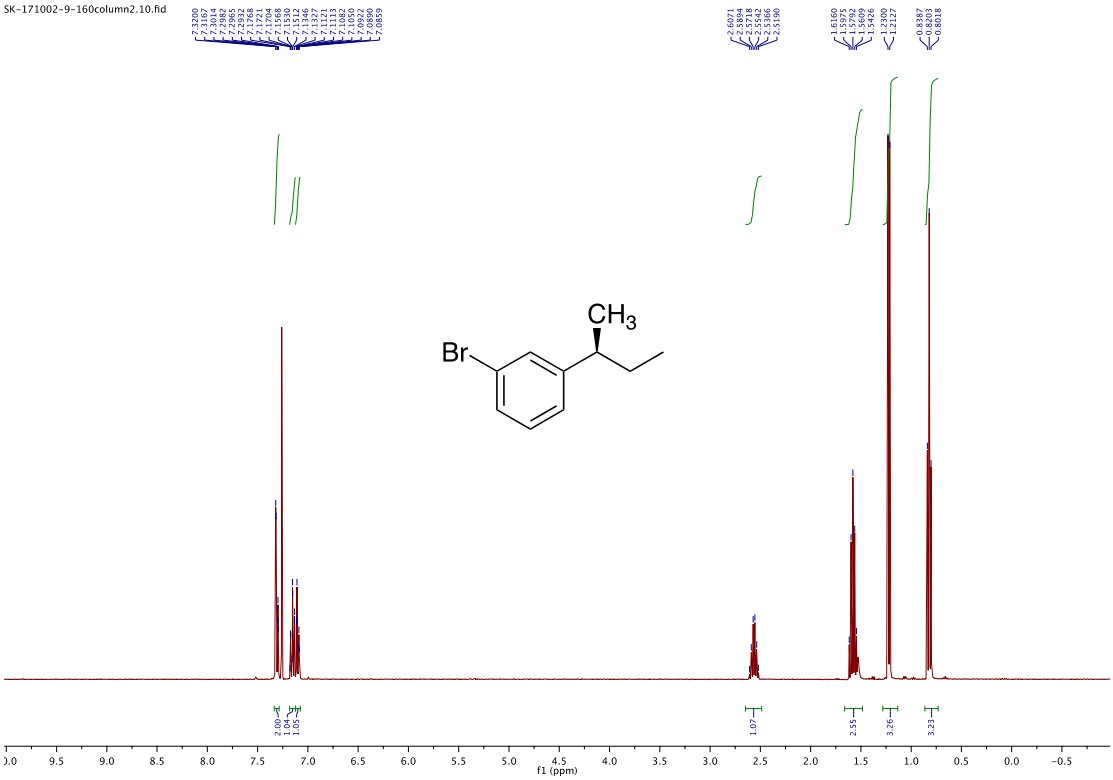
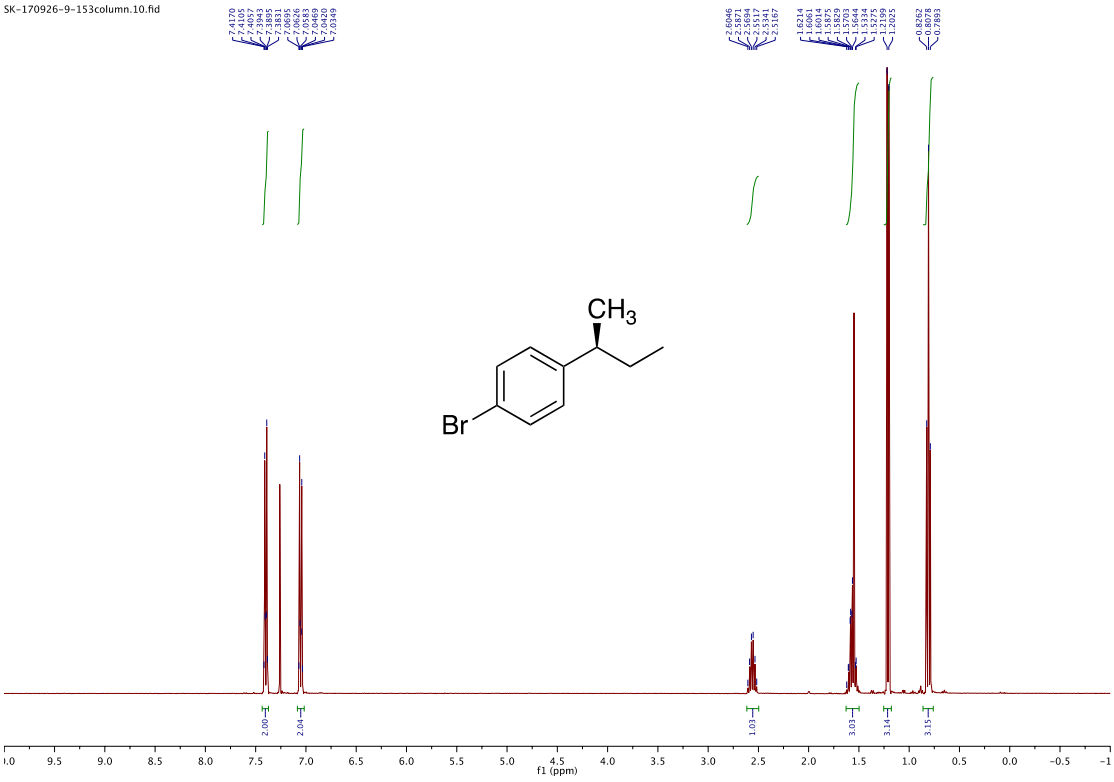
CH3
f1 (ppm)

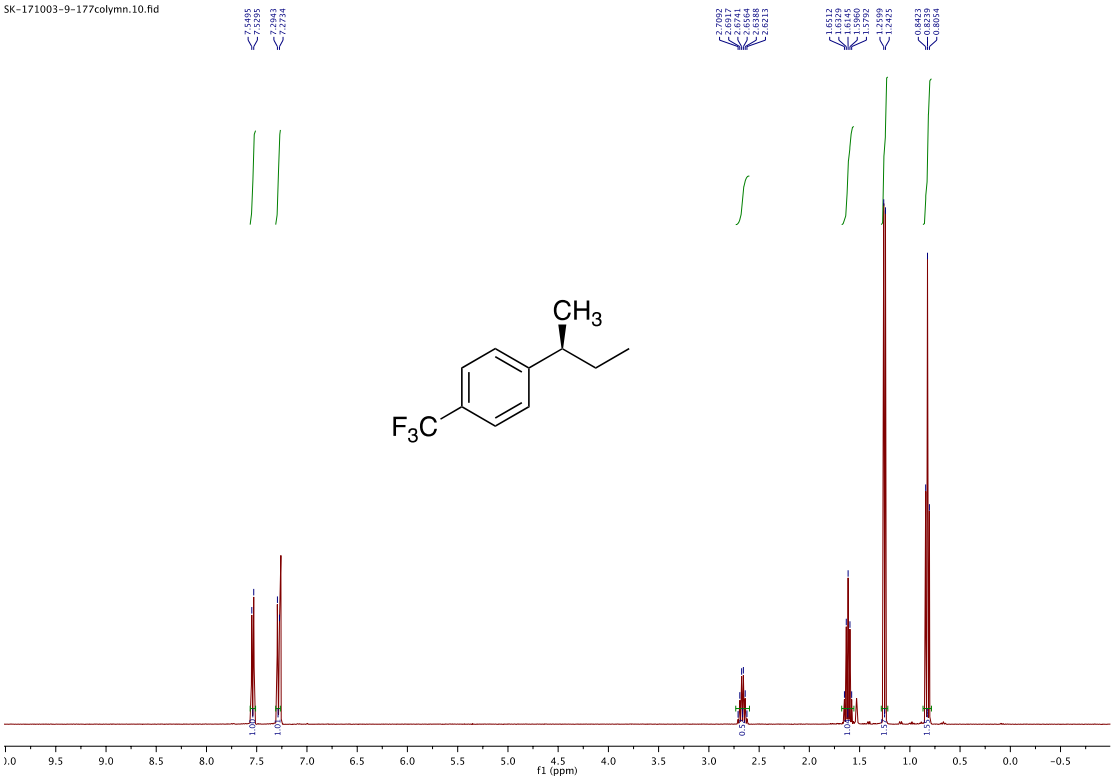

SK-171219-10-045column.10.fid
MeO
f1 (ppm)

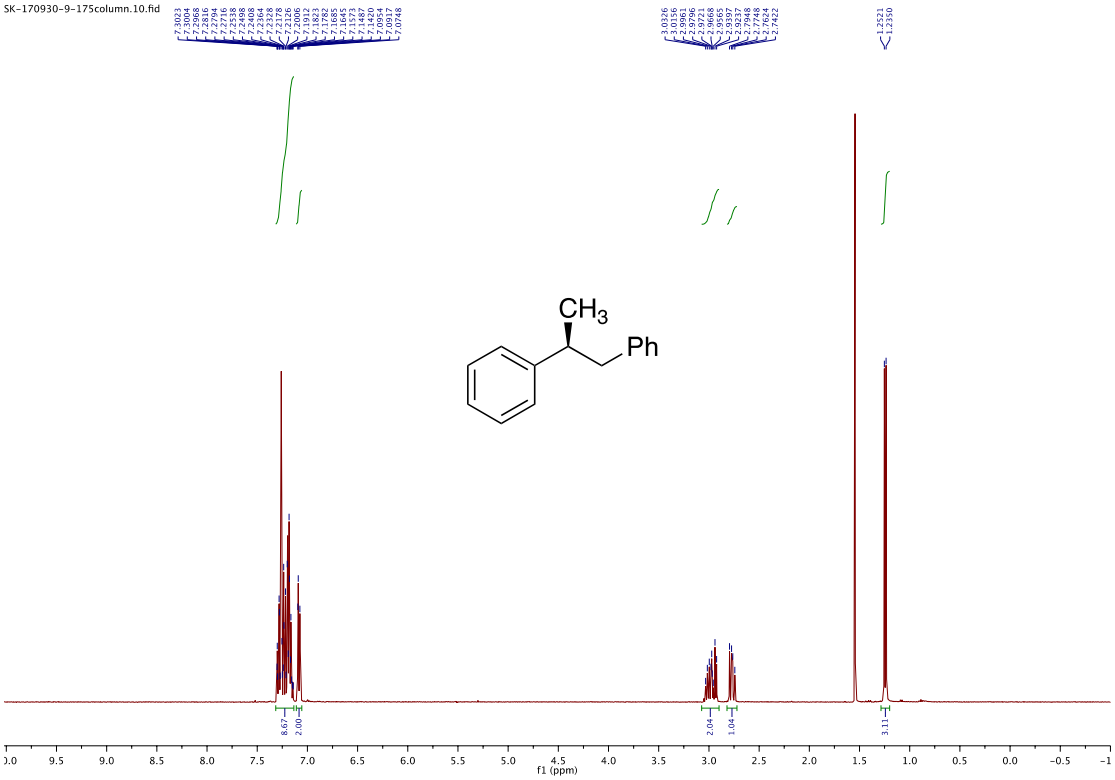

SK-171002-9-158column.10.fid
CH3
F
f1 (ppm)

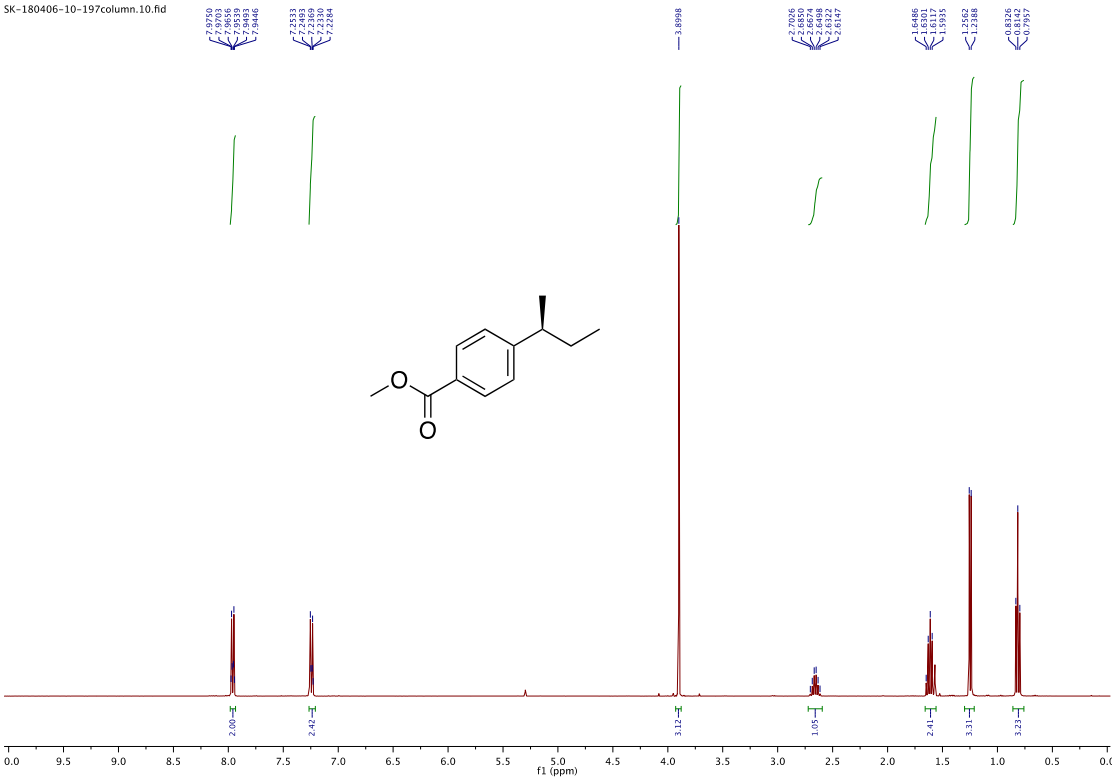

SK-170926-9-154column.10.fid
CH3
Cl
f1 (ppm)


SK-171002-9-160column2.10.fid
Br
CH3
f1 (ppm)


SK-170926-9-153column.10.fid
Br
CH3
f1 (ppm)


SK-171003-9-177colymn.10.fid
CH3
F3C
f1 (ppm)


SK-170930-9-175column.10.fid
CH3
Ph
f1 (ppm)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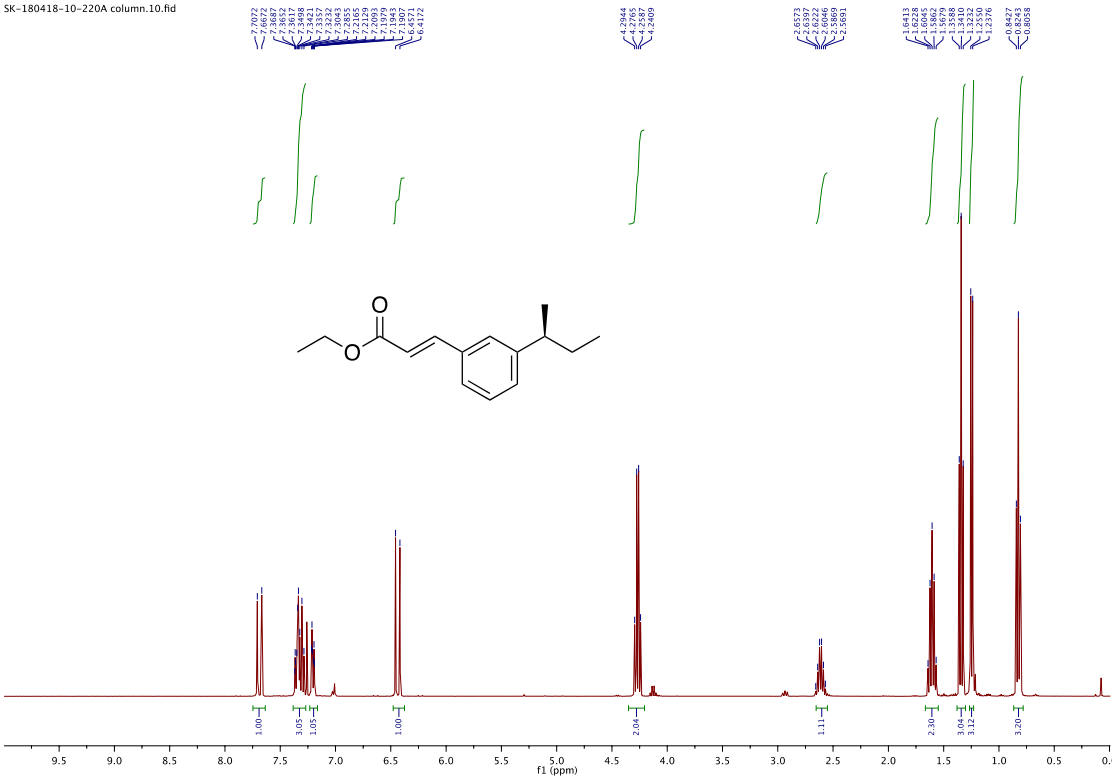
f1 (ppm)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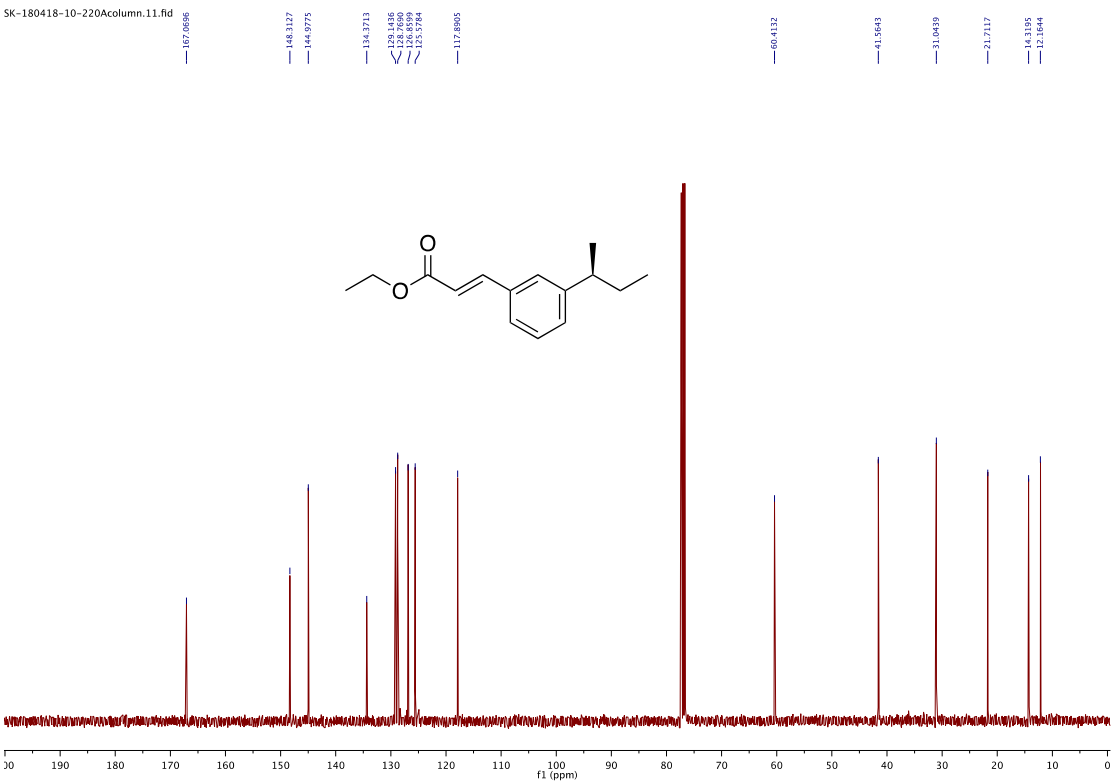
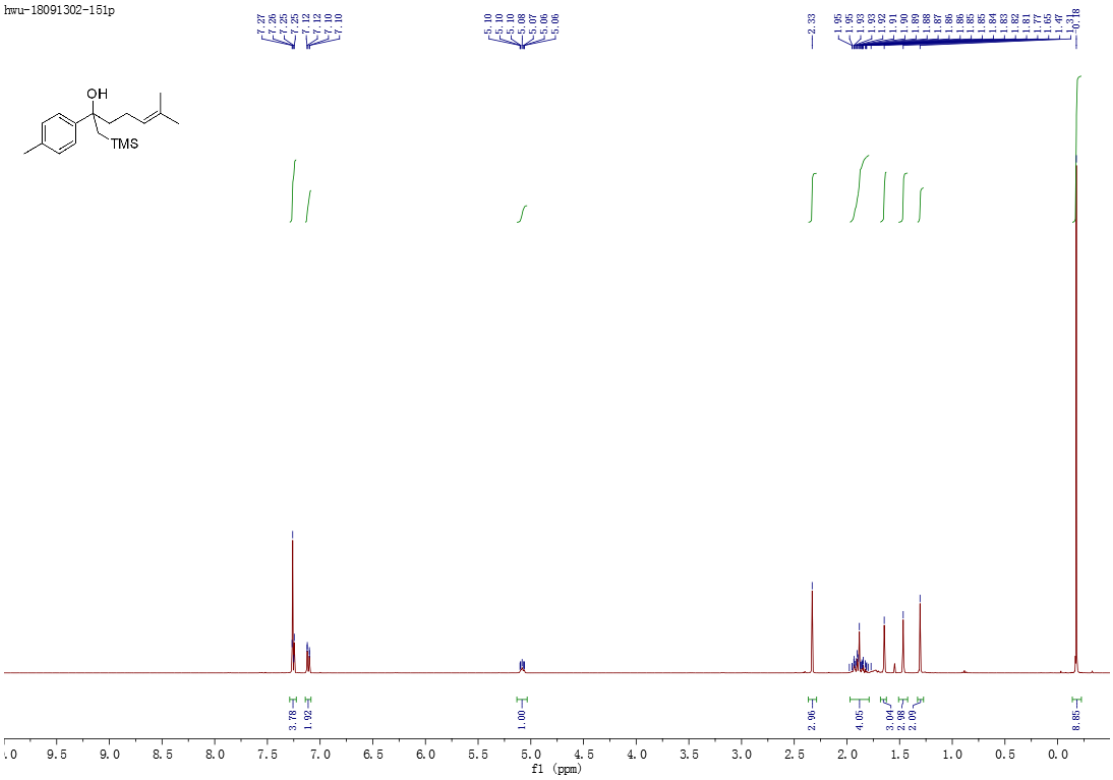
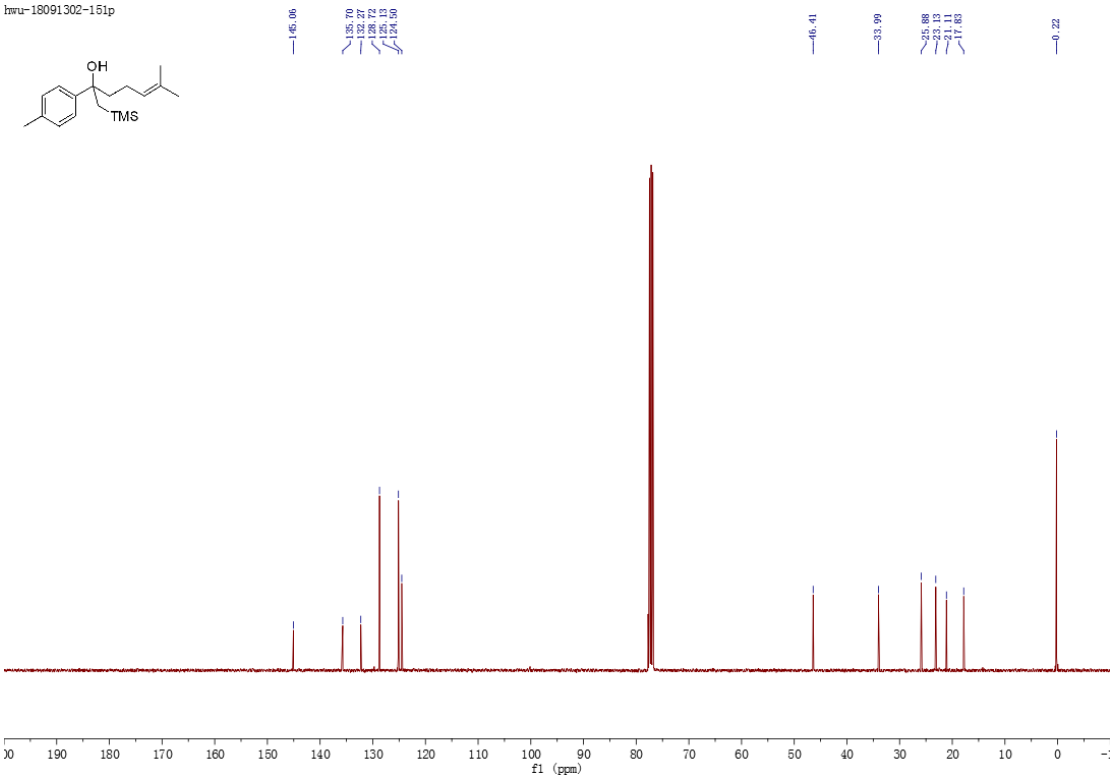
f1 (ppm)


SK-180418-10-220Acolumn.11.fid
167.0696
148.3127
144.9775
134.3713
129.1436
128.7690
126.8799
125.5794
117.8905
60.4132
41.5643
31.0439
21.7117
14.3195
12.1644
O
O
f1 (ppm)

7.^{1}H and ^{13}C NMR spectroscopic data of (S)-(+)-curmurene





hwu-181004-202-166np

(+) curmuene

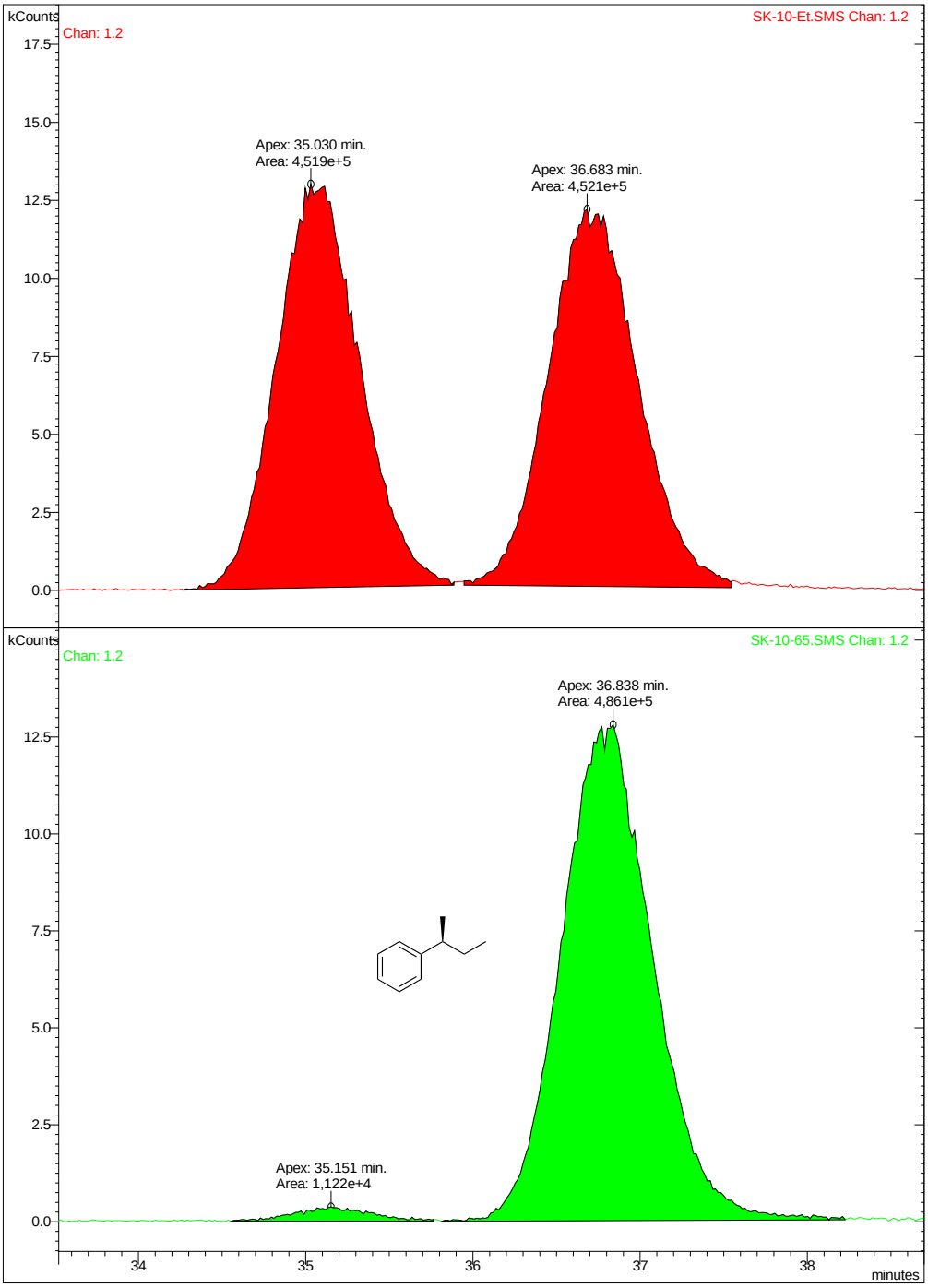
hwu-18091302-151p

(+) curmuene

8. GC and SFC Chromatograms

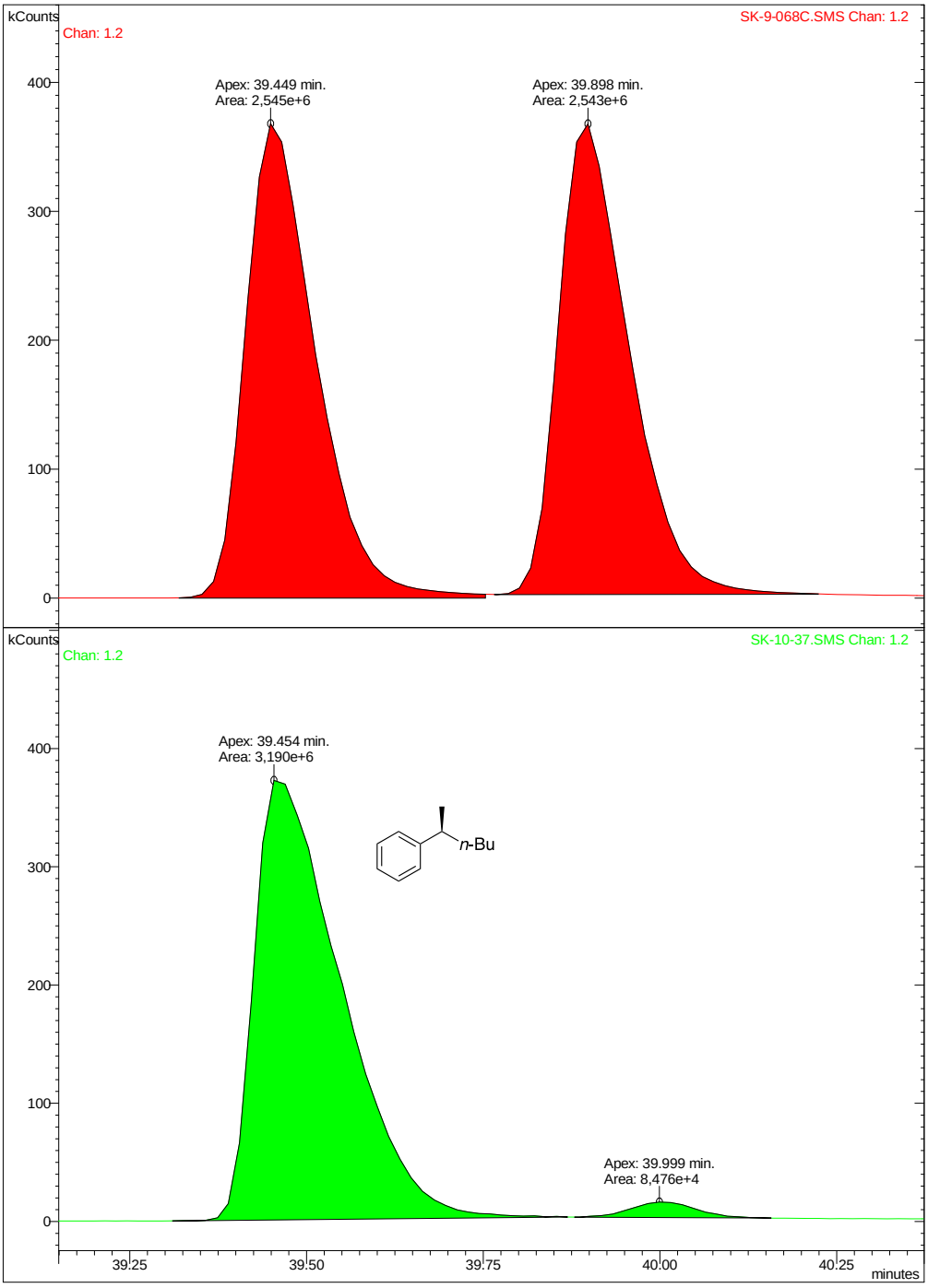
Print Date: 28 Dec 2017 18:43:10

Chromatogram Plots

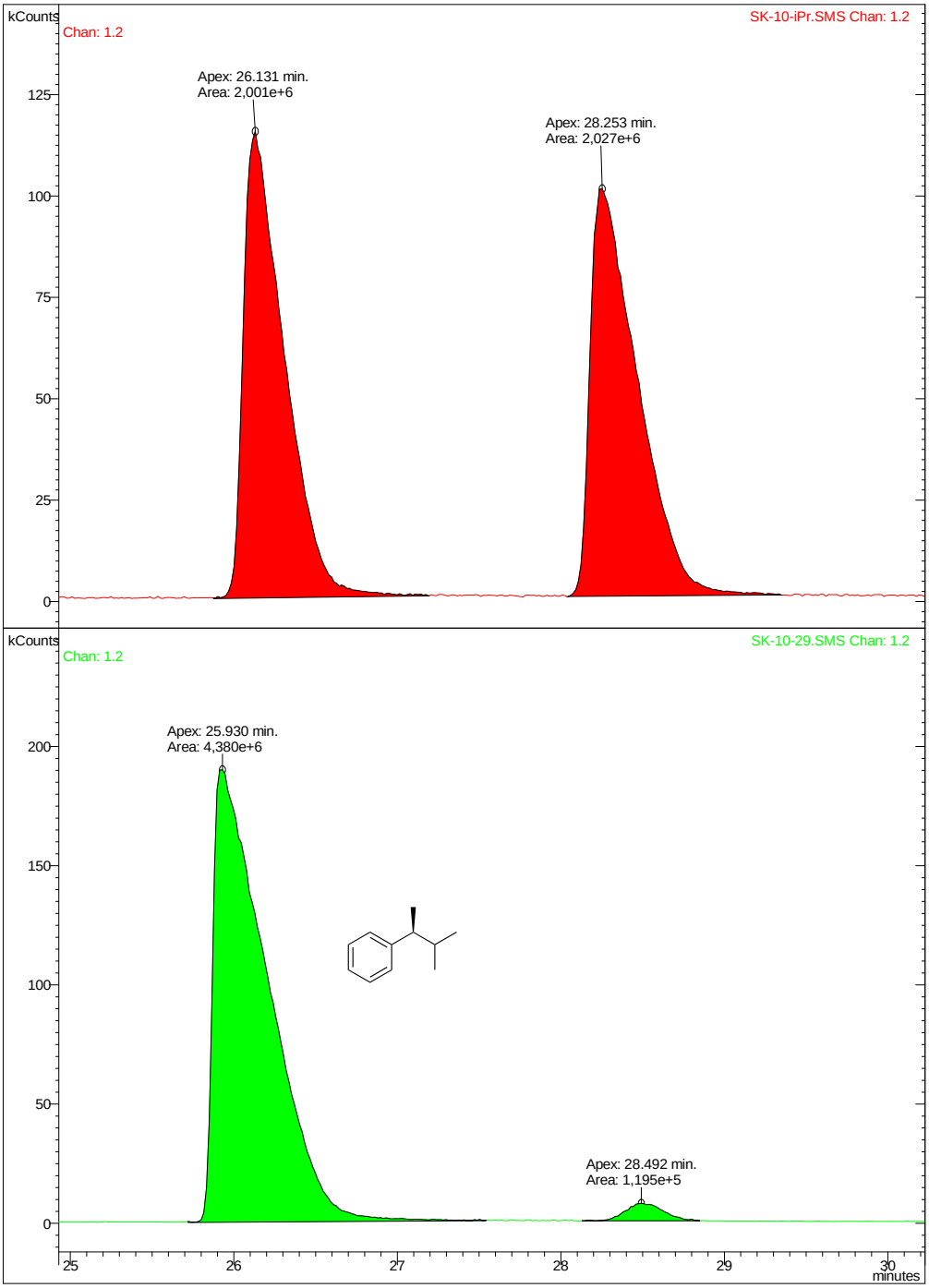


Print Date: 28 Dec 2017 18:25:48

Chromatogram Plots

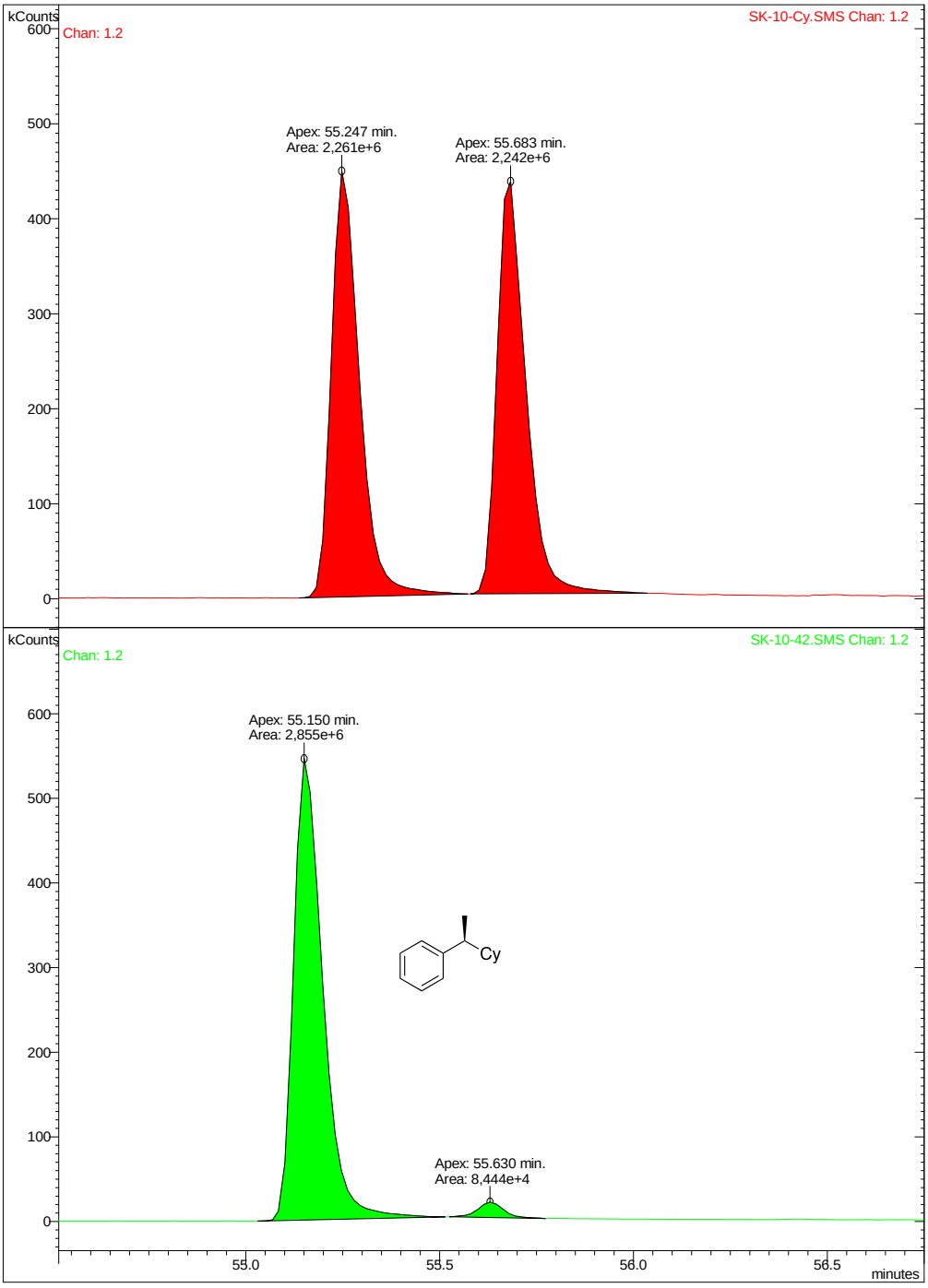


Chromatogram Plots



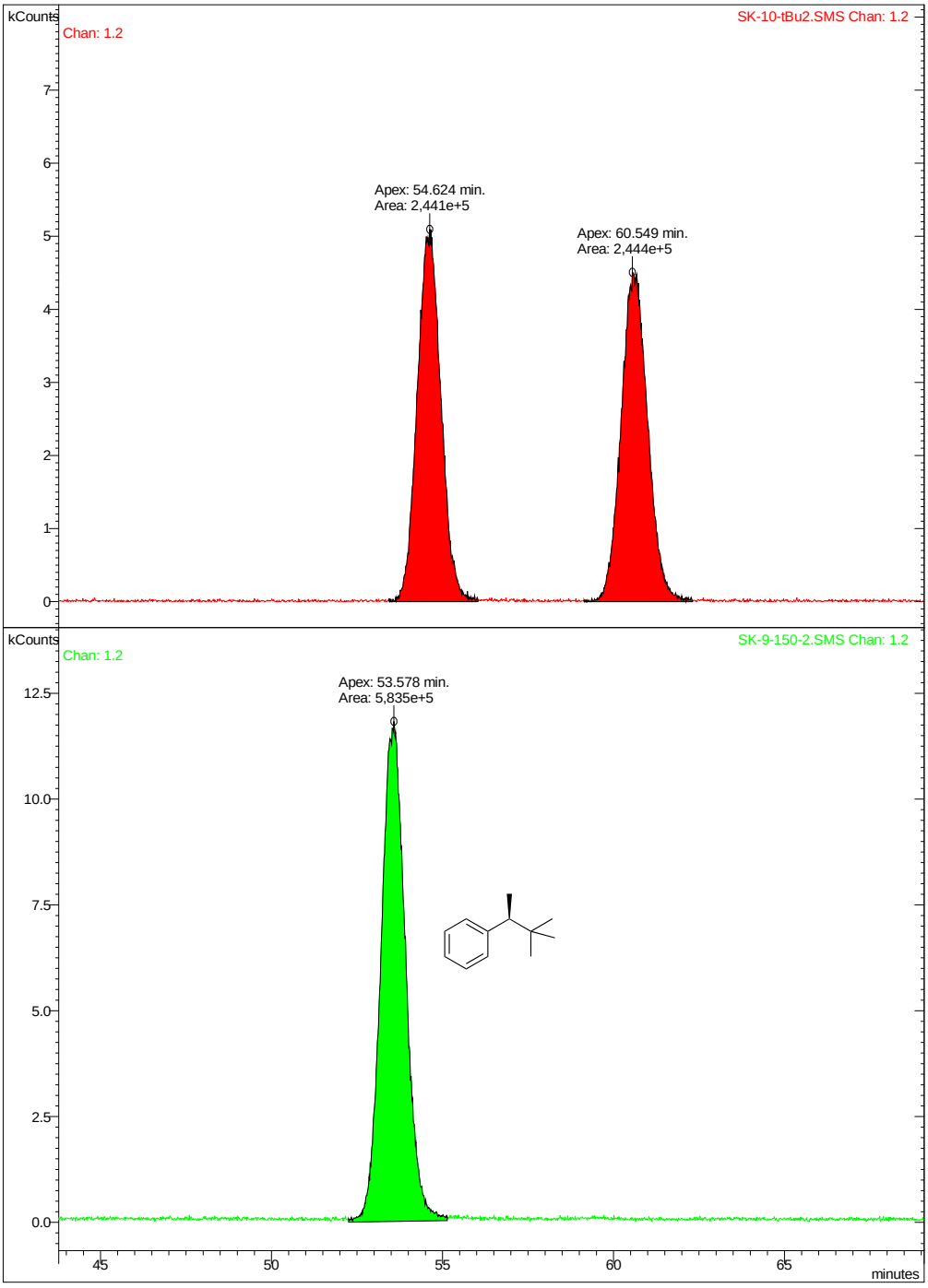
Print Date: 29 Dec 2017 14:48:24

Chromatogram Plots



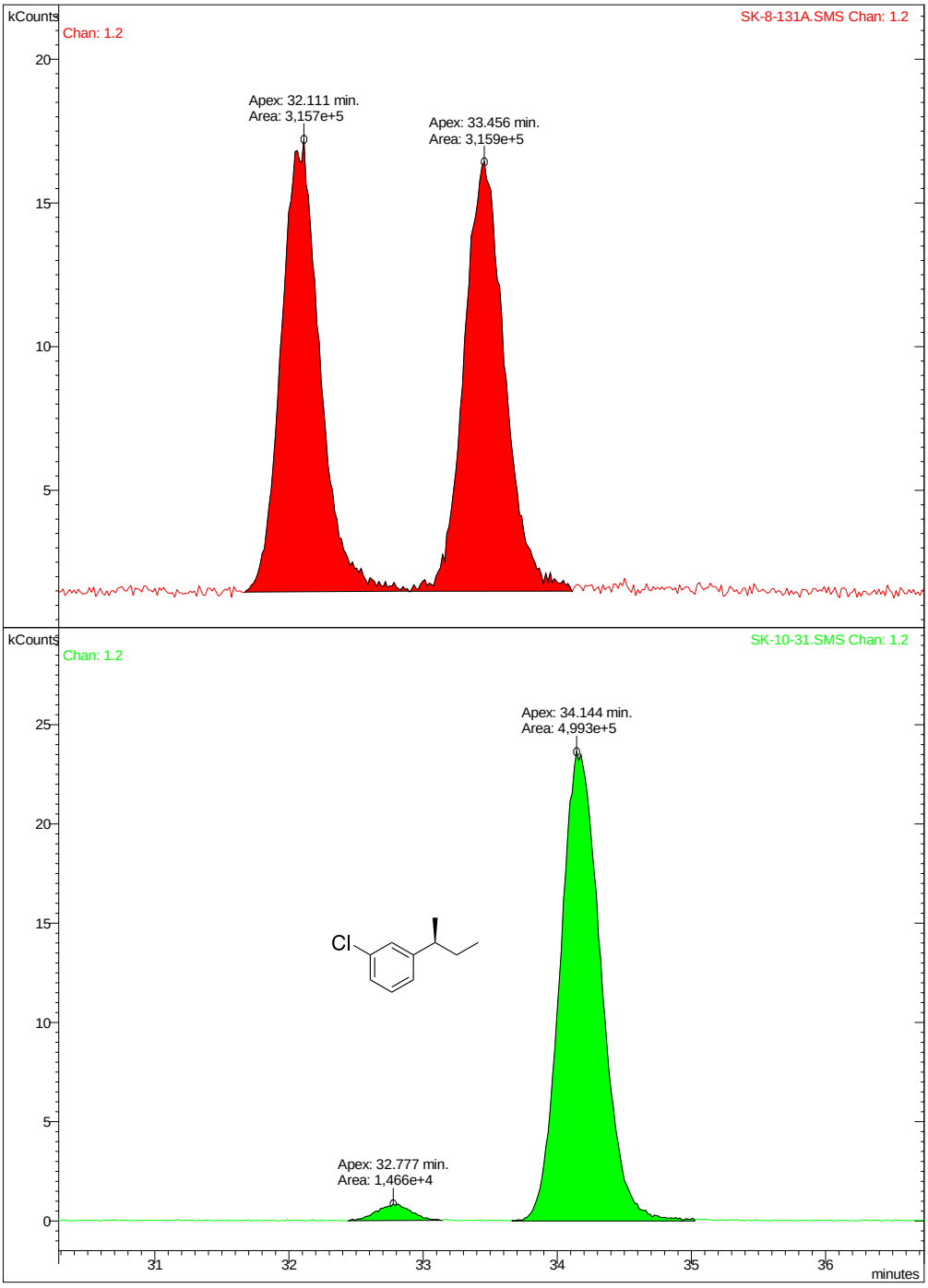
Print Date: 29 Dec 2017 14:51:11

Chromatogram Plots



Print Date: 28 Dec 2017 18:46:13

Chromatogram Plots



Print Date: 28 Dec 2017 18:52:26

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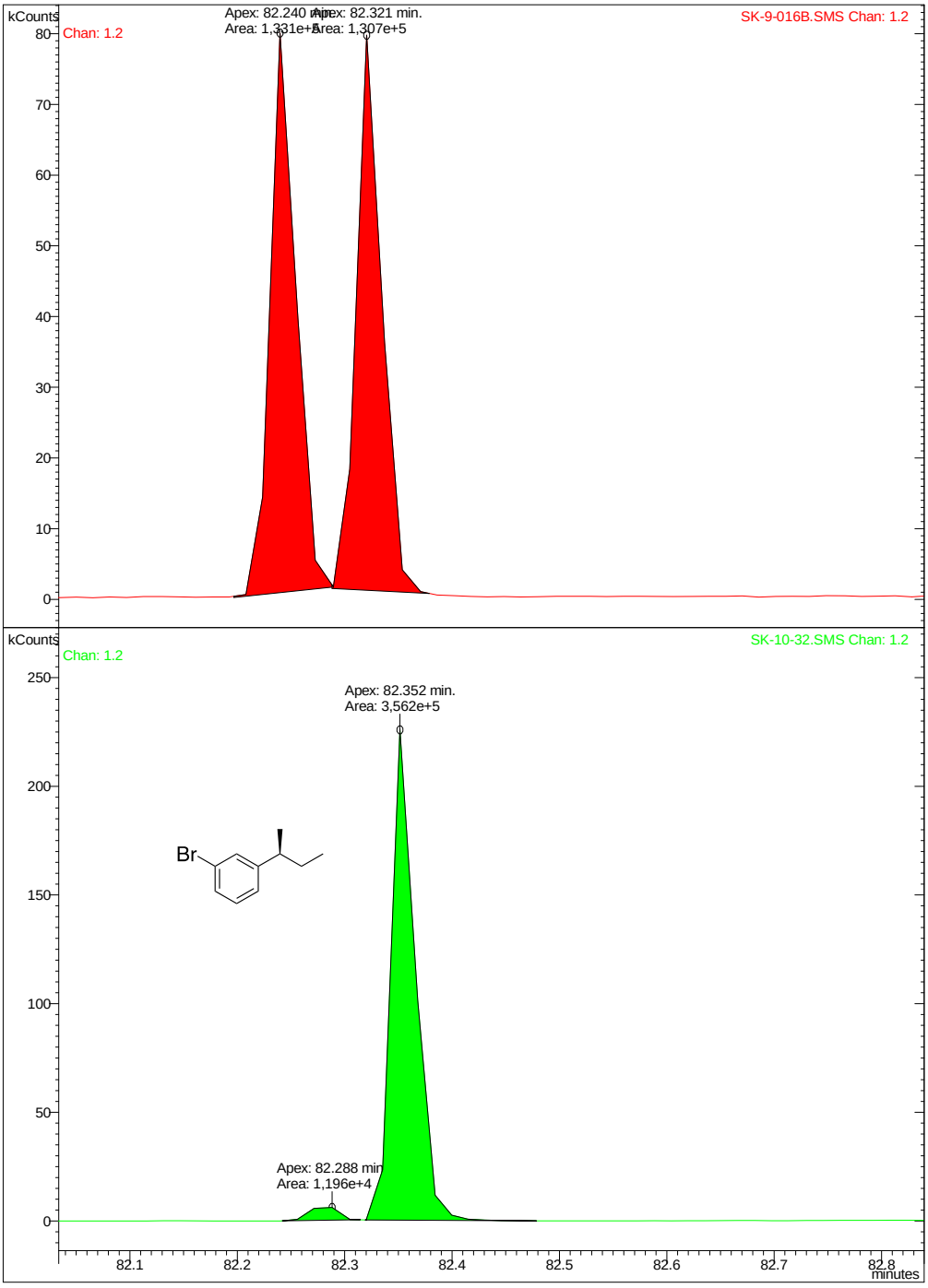
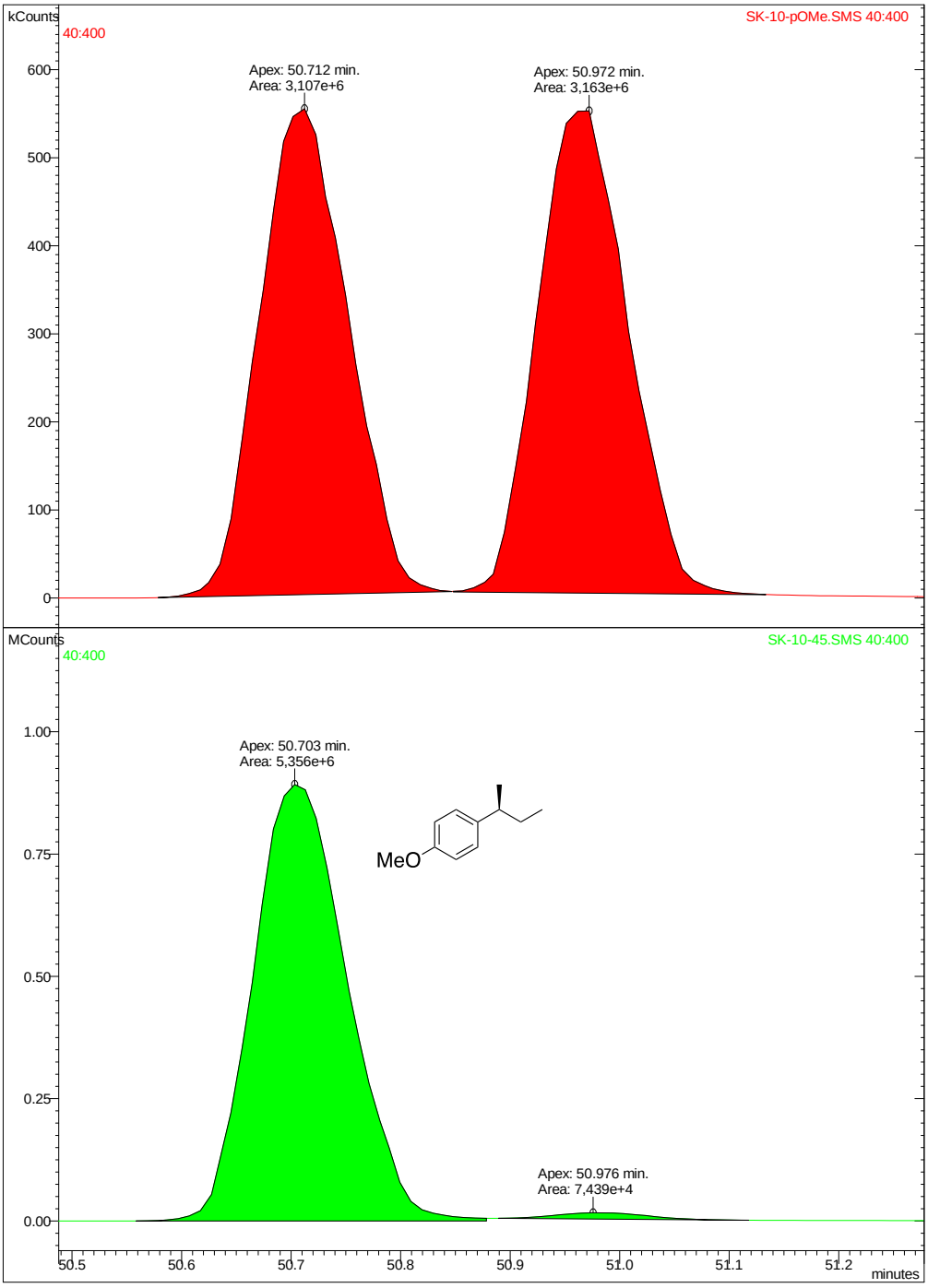


Print Date: 29 Dec 2017 09:58:25

Chromatogram Plots



Print Date: 29 Dec 2017 14:44:53

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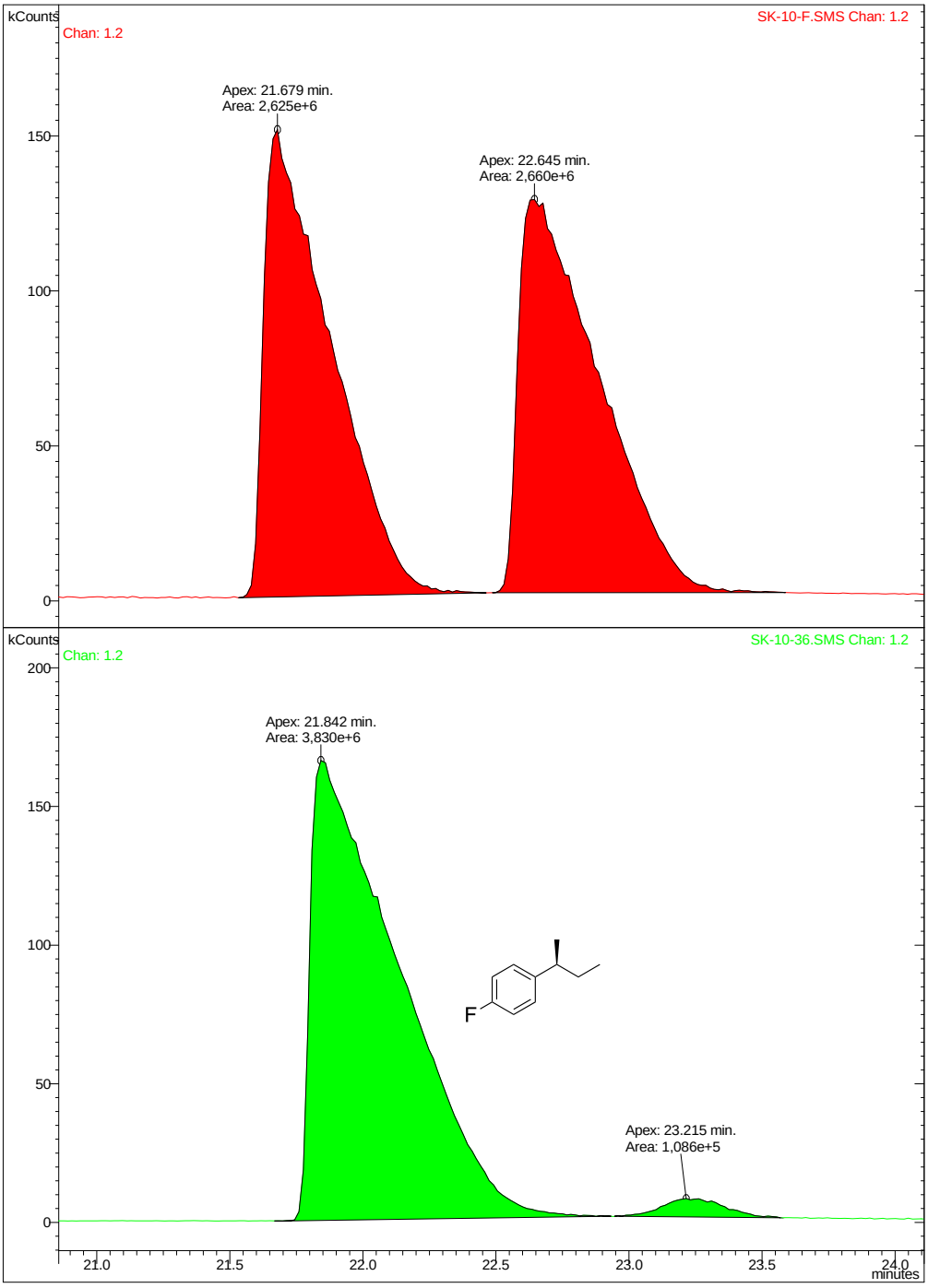
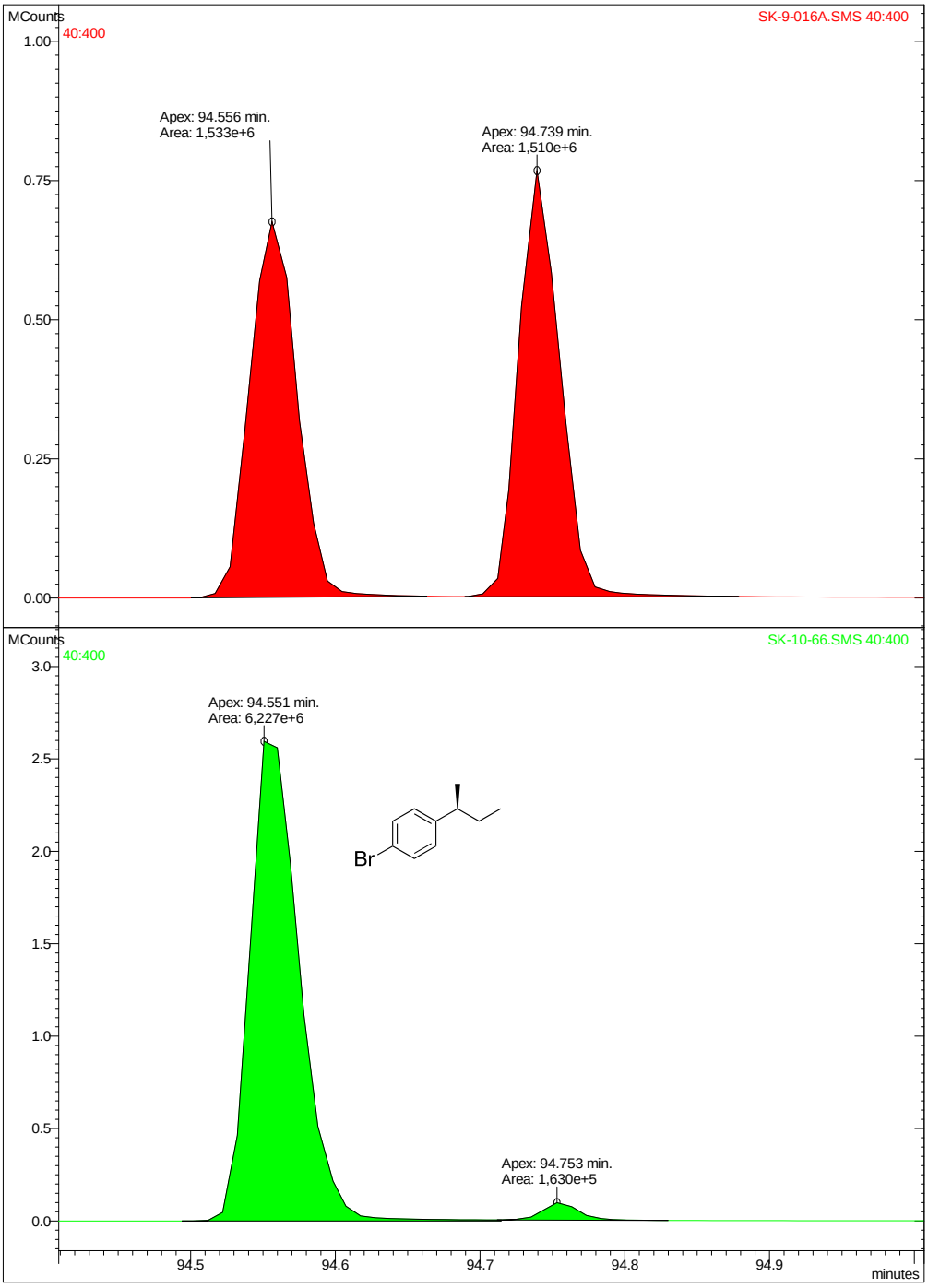


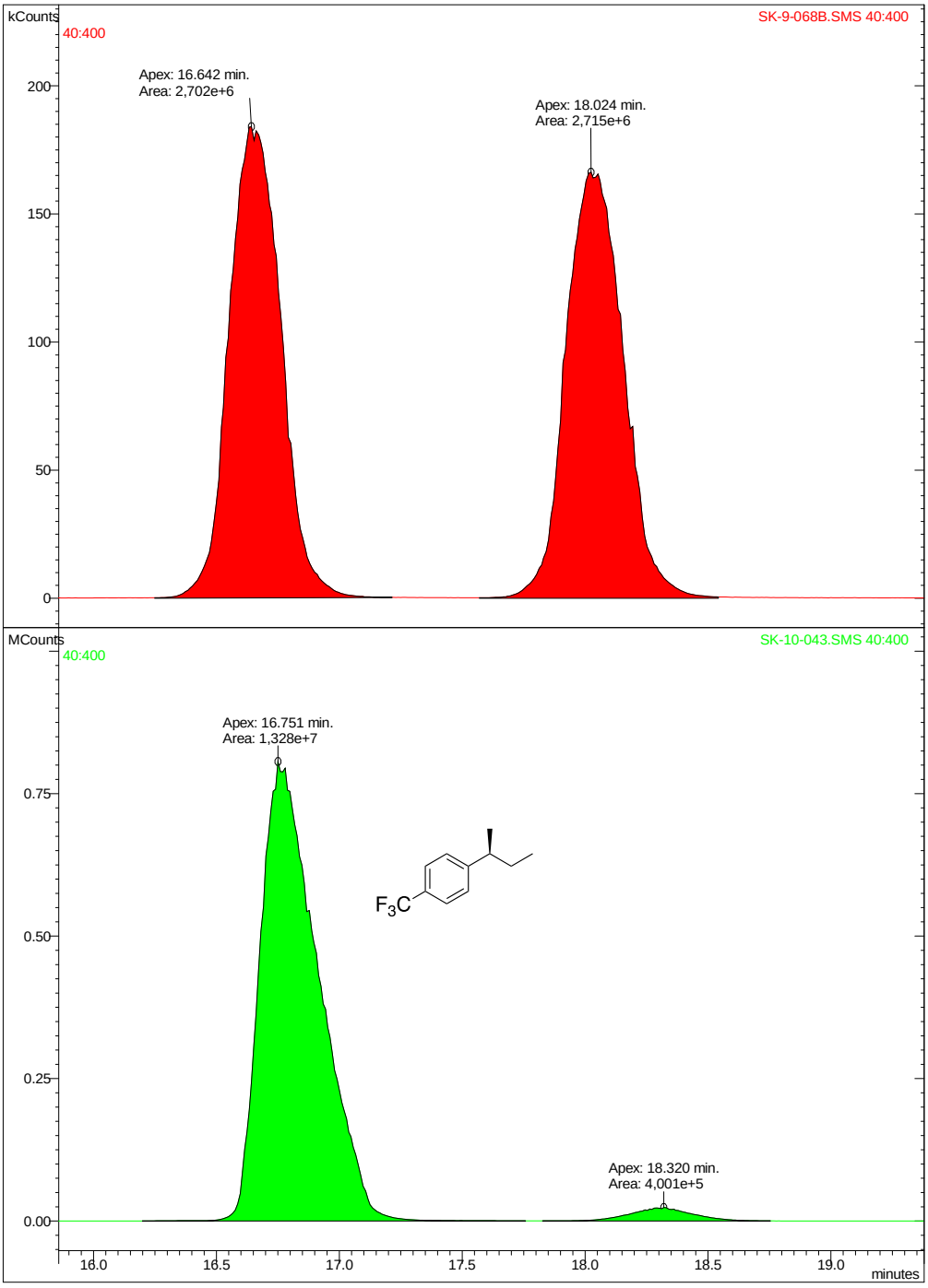
Print Date: 28 Dec 2017 18:19:49

Chromatogram Plots

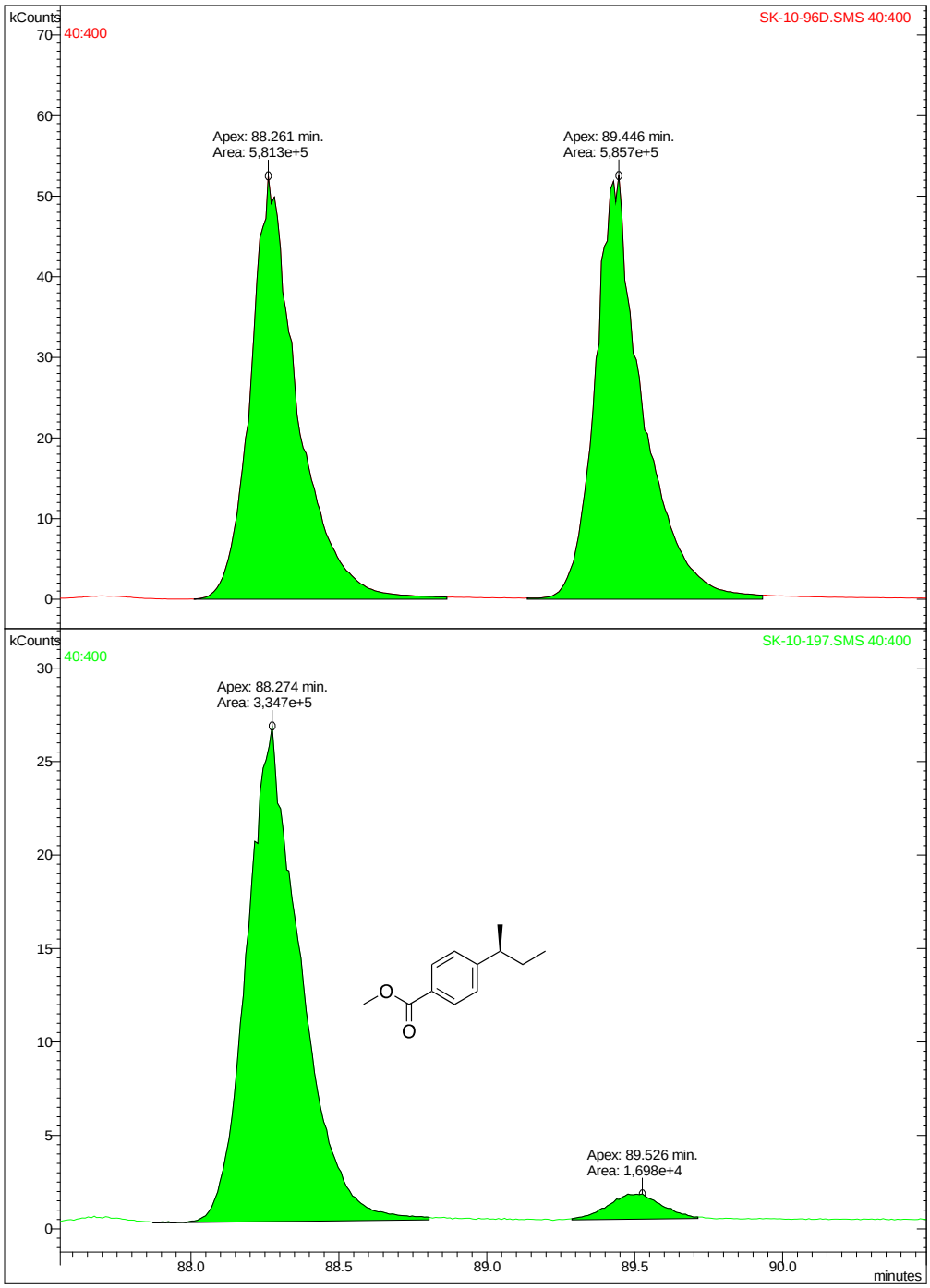


Print Date: 28 Dec 2017 18:23:03

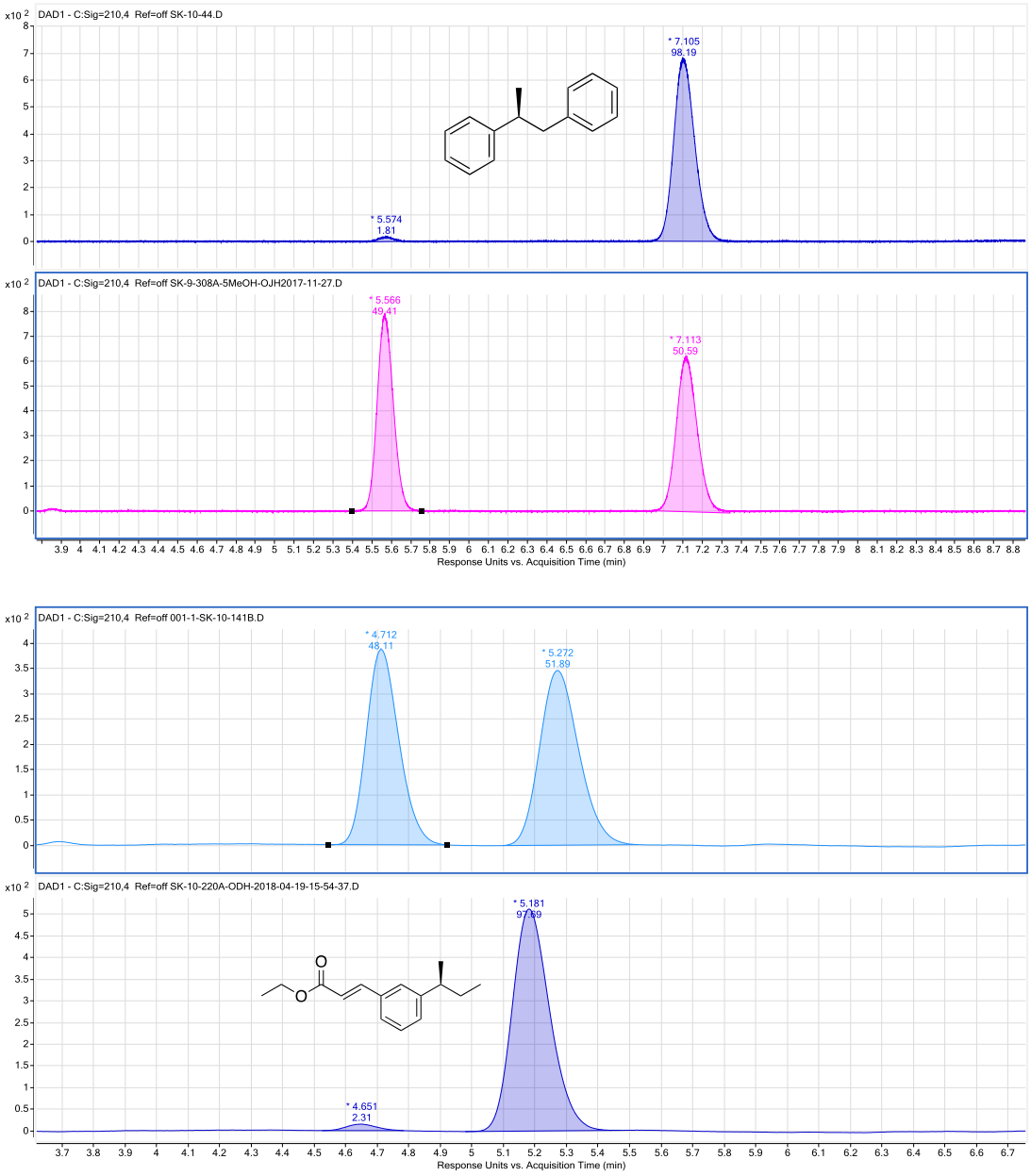
Chromatogram Plots

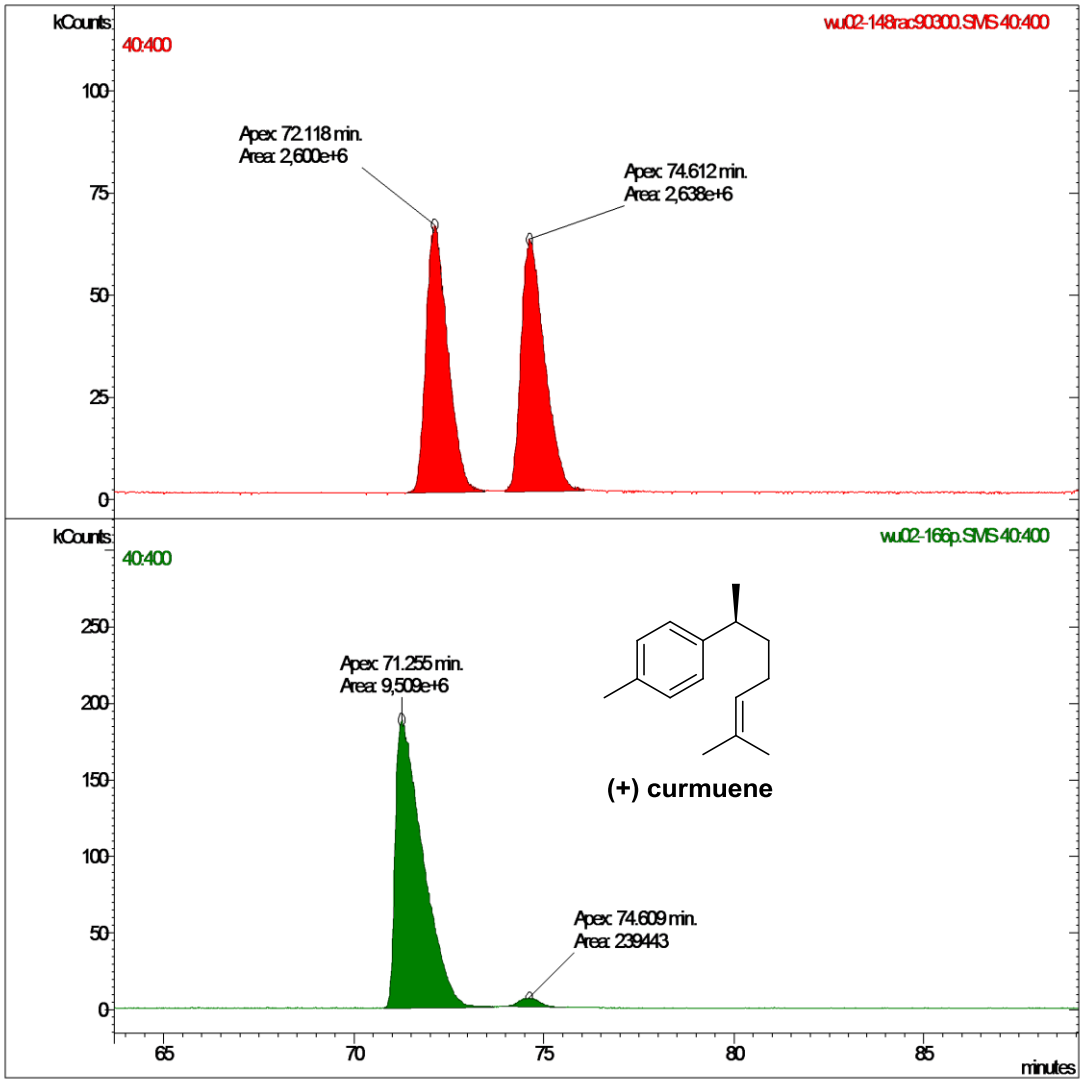


Chromatogram Plots

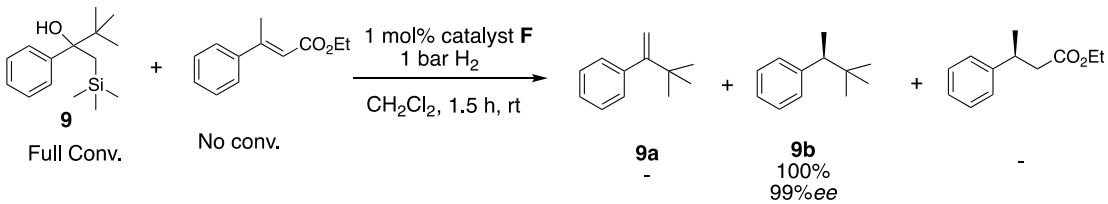


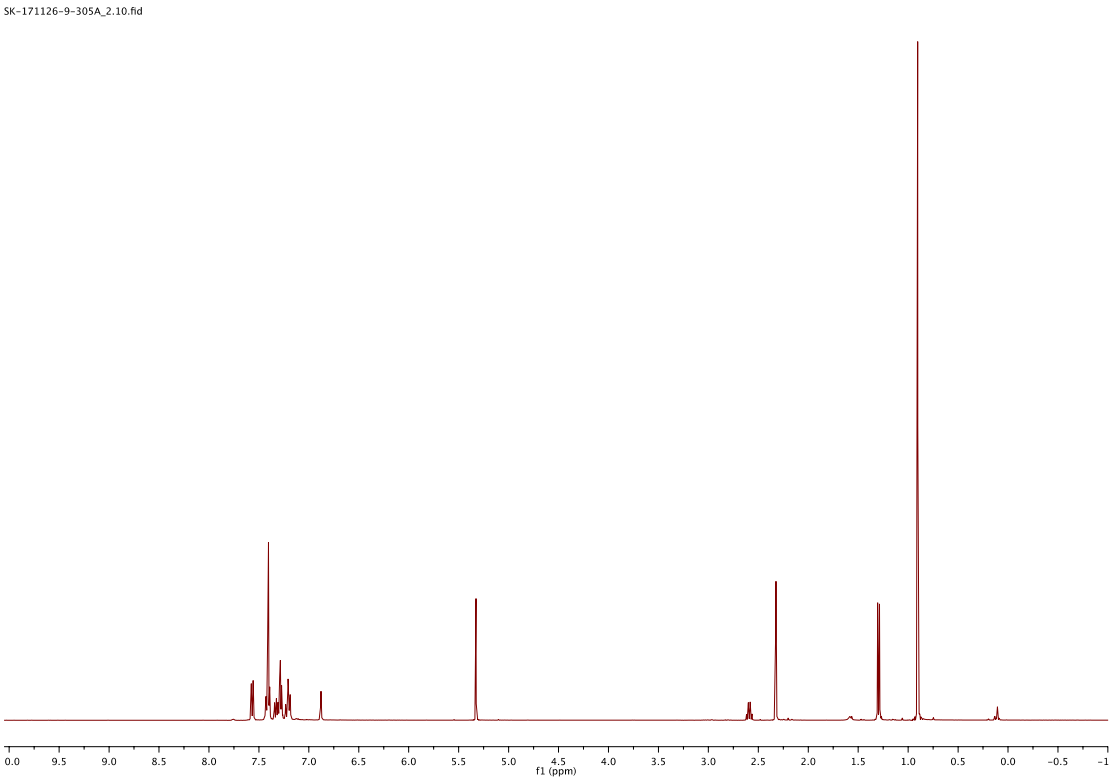
SFC chromatograp





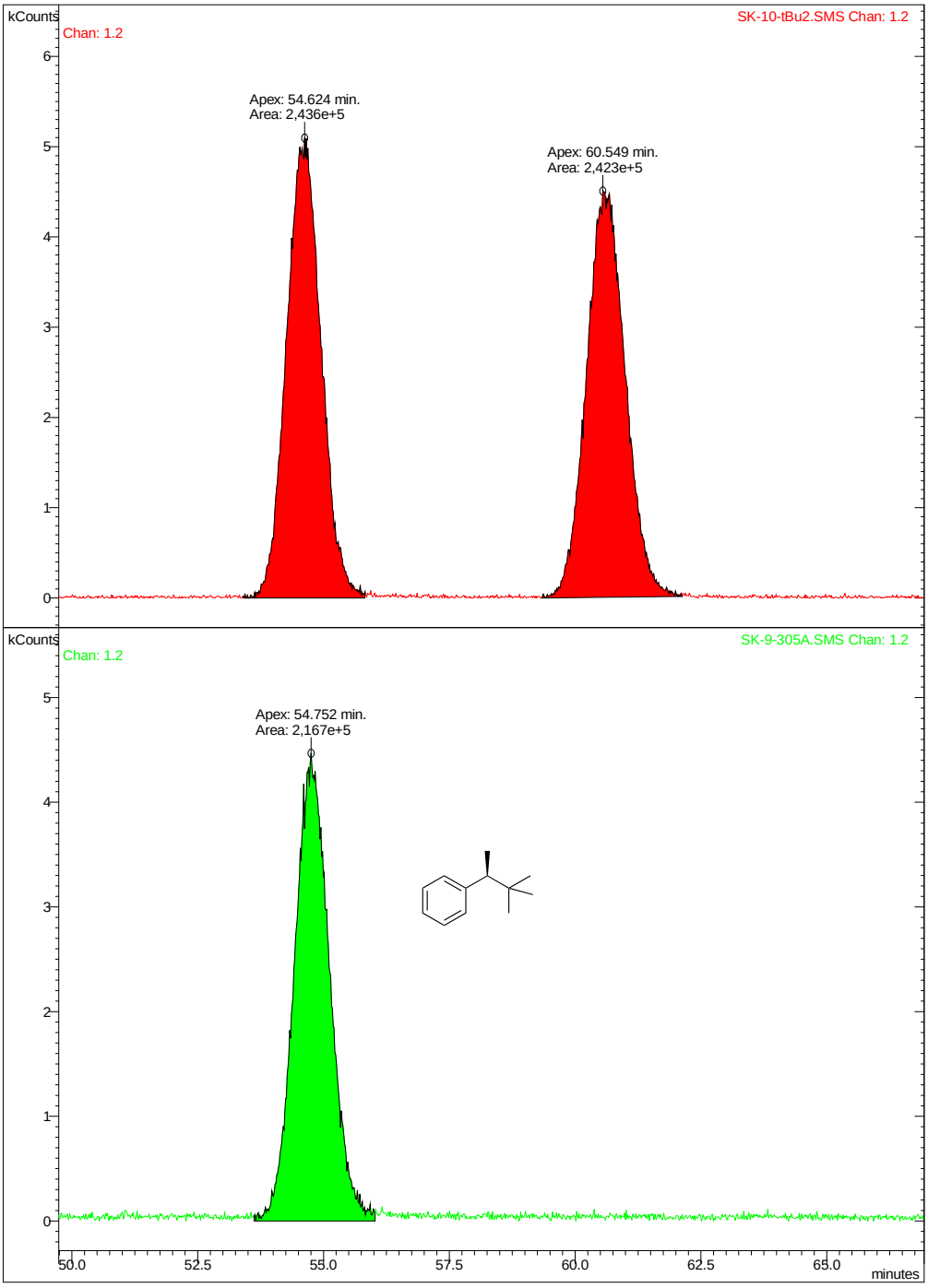
9. NMR spectra and chromatograms for the competition study

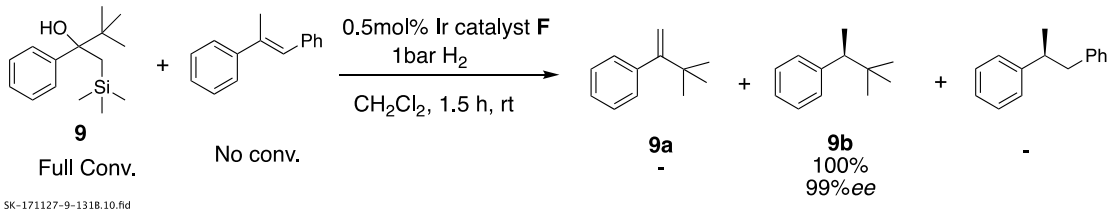



SK-171126-9-305A_2.10.fid
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

Print Date: 30 Dec 2017 14:55:22

Chromatogram Plots





9
Full Conv.

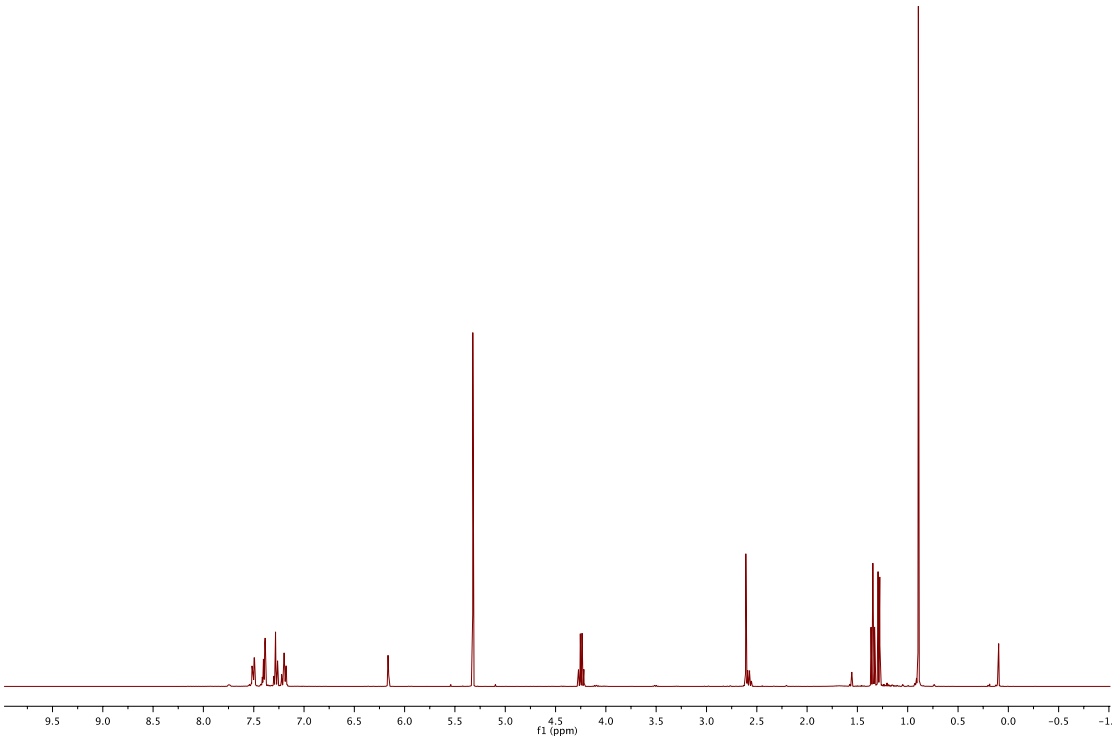
No conv.

9a
-

9b
100%
99%*ee*

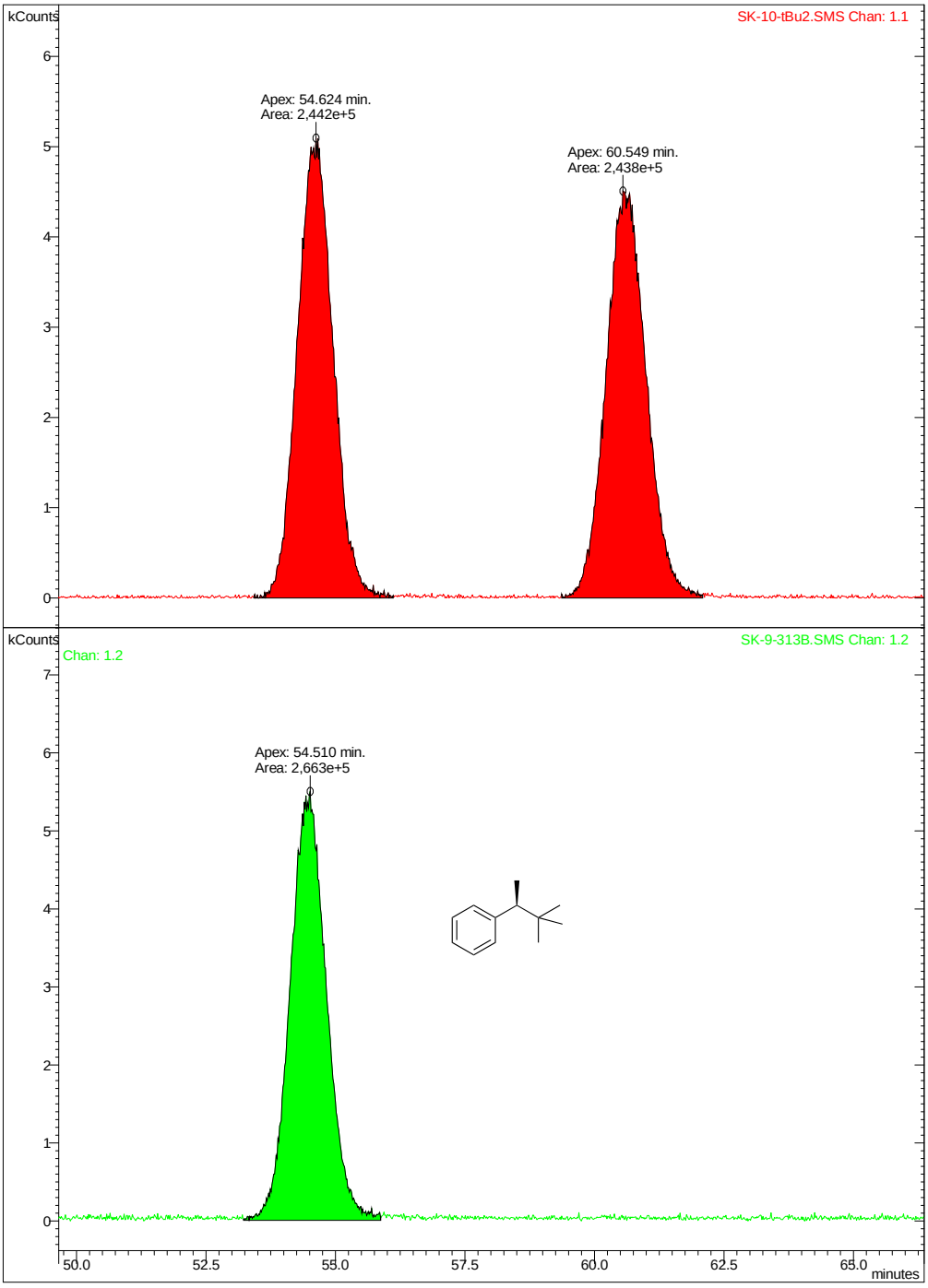
-

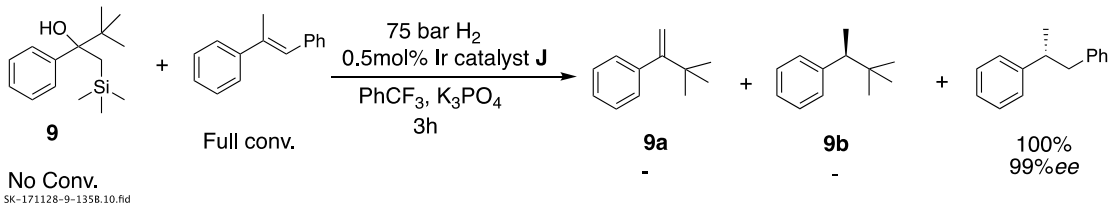
SK-171127-9-131B.10.fid



Print Date: 30 Dec 2017 14:57:04

Chromatogram Plots





9

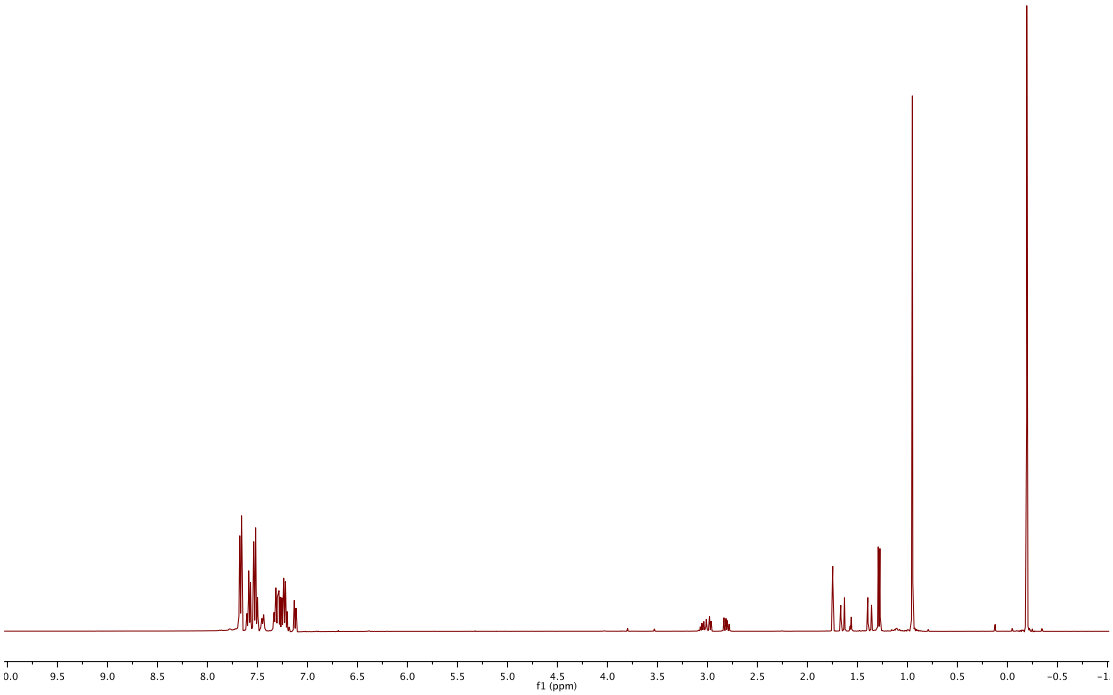
Full conv.

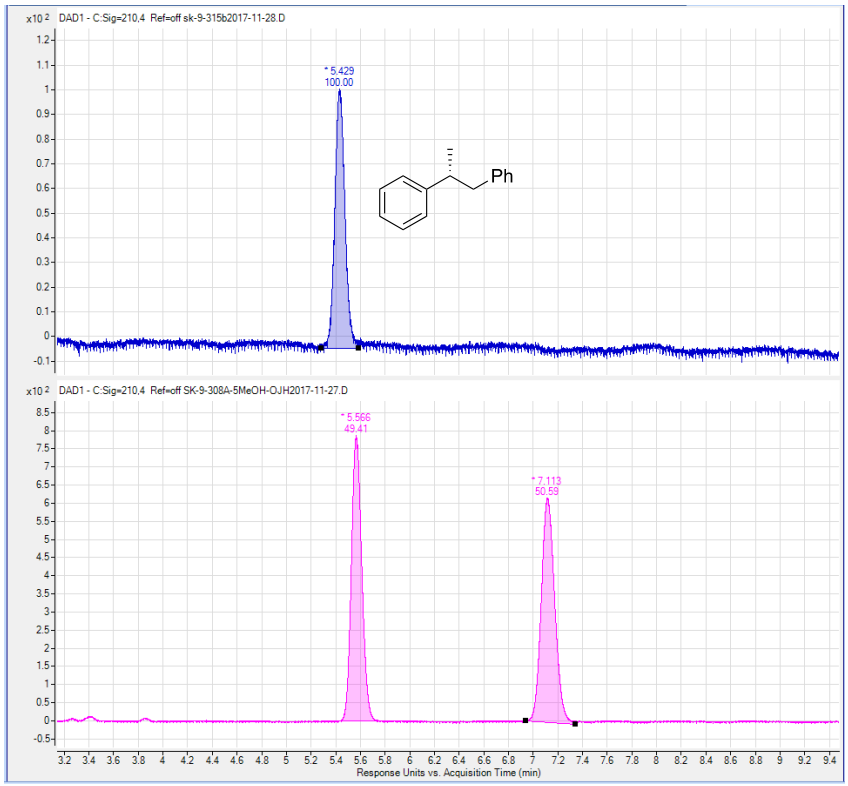
9a
-

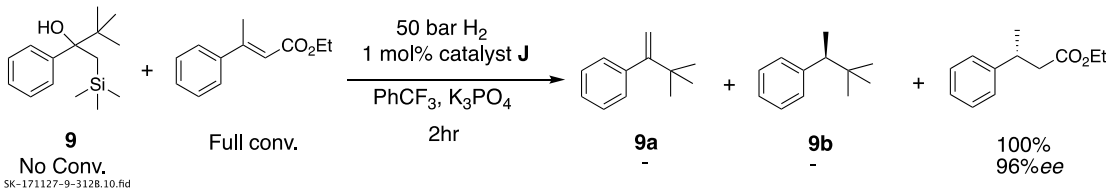
9b
-

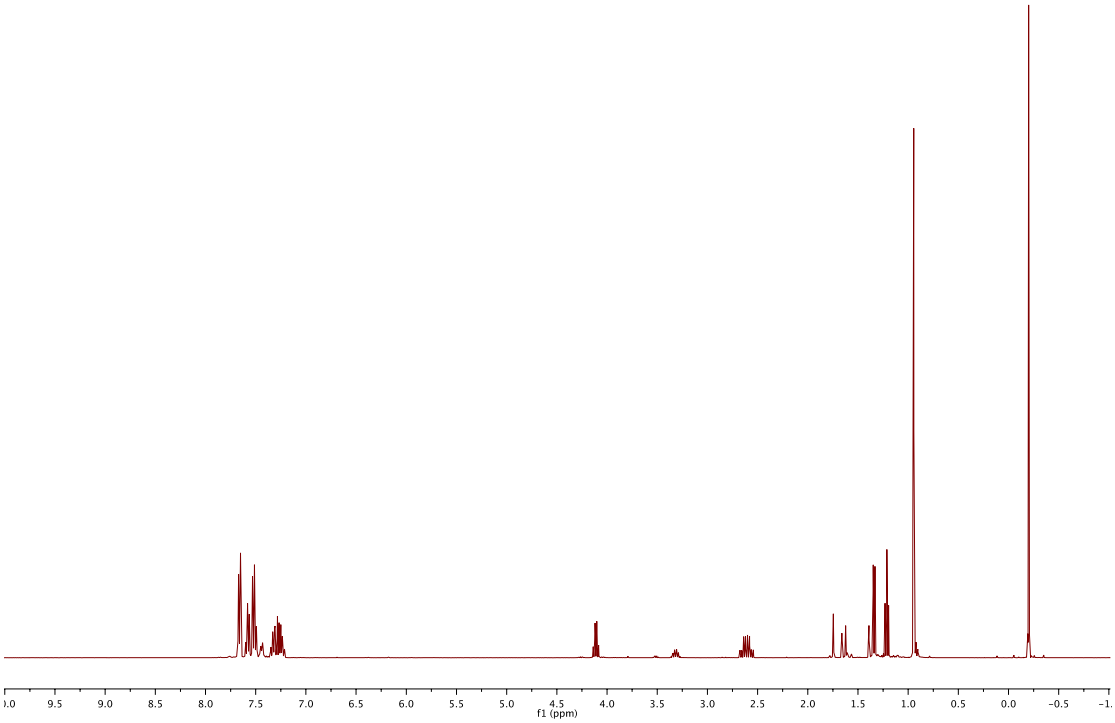
100%
99%*ee*

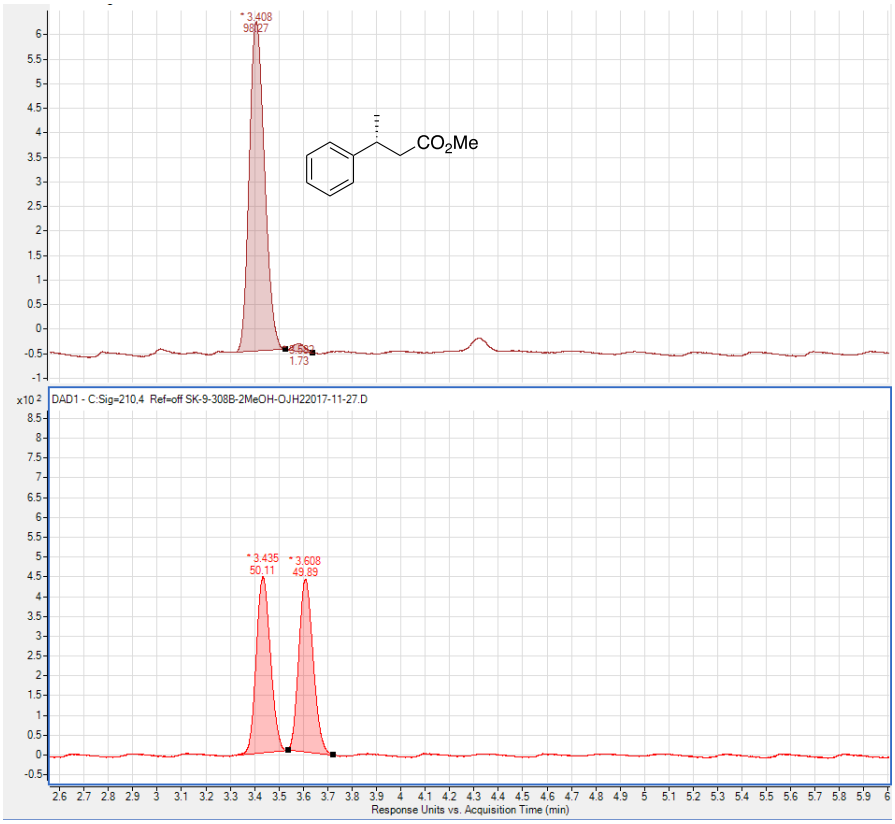
No Conv.
SK-171128-9-135B.10.fid





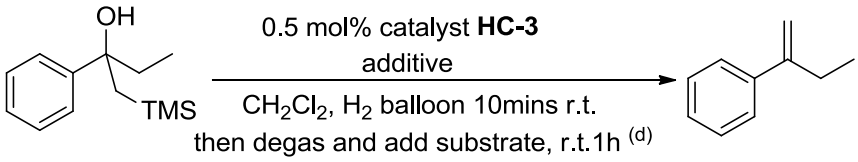

HO
Si
CO2Et
50 bar H2
1 mol% catalyst J
PhCF3, K3PO4
2hr
CO2Et
9
No Conv.
SK-171127-9-312B.10.fid
Full conv.
9a
-
9b
-
100%
96%ee


f1 (ppm)


CO2Me
DAD1 - C:Sig=210,4 Ref=off SK-9-308B-2MeOH-OJH22017-11-27.D
Response Units vs. Acquisition Time (min)

10. Additional experiments for mechanistic study.

Separeted experiments for Peterson elimination (Step 1)



1a

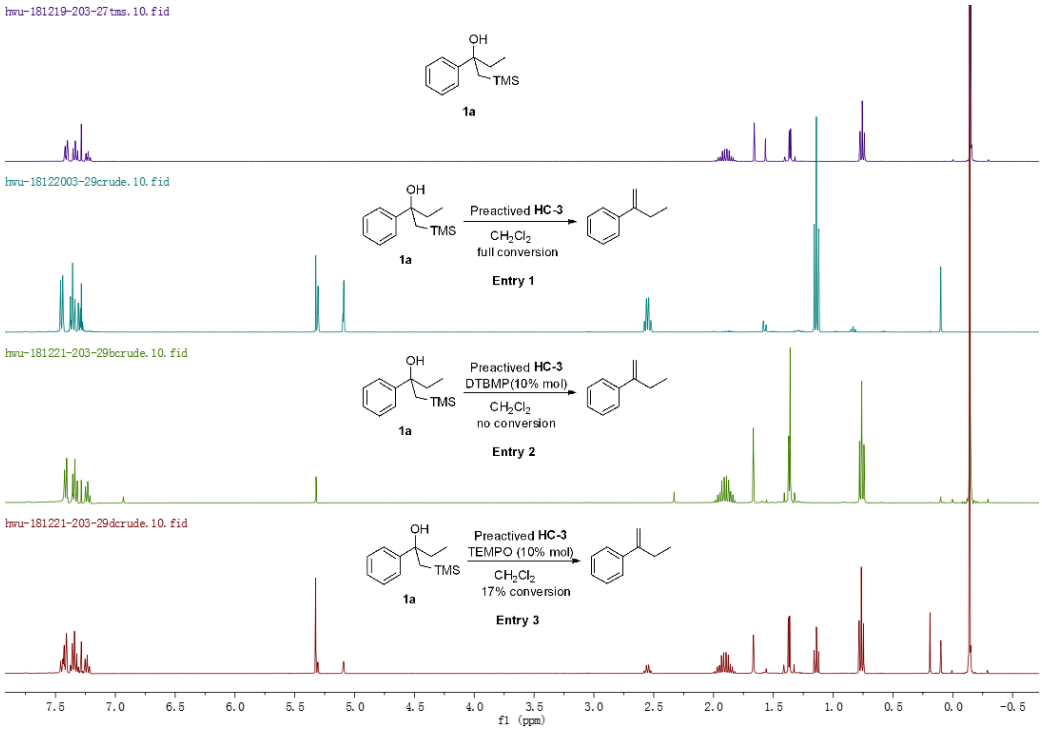
Entry	additive	conversion
1	none	>99%
2	DTBMP (10 mol%)	no conv.
3	TEMPO (10 mol%)	17%

Note: a)reaction carried out in 0.05 mmol scale, conversion determined by ^{1}NMR.
b)DTBMP = 2,6-di-tert-butyl-4-methylpridine.
c)TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

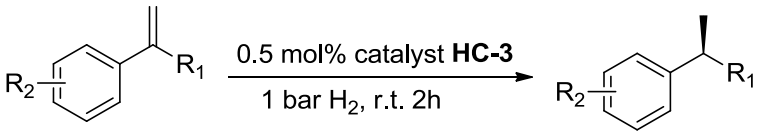
d) Experimental procedure: A 5 ml vial was charged with Ir complex and sealed with rubber septum. It was then purged by three successive vacuum/nitrogen sequences and then filled with H_2 (connected with a hydrogen balloon). CH_2Cl_2 (0.5ml) was added, then stirred for 10 mins, during which time the orange solution became yellow. Then the hydrogen balloon was removed and the solution was degassed through three freeze-pump-thaw cycles, a solution of the substrate in 0.5 ml CH_2Cl_2 was added, the reaction was stirred under nitrogen for 1h.

Results discussion:
1. When the β-hydroxy silane was added to the catalyst, activated by hydrogen gas, in CH_2Cl_2, full conversion to the terminal olefin was obtained, with no hydrogenated product being observed.
2. When the experiment was carried out with a bulky non-coordinating base DTBMP (10 mol%) as an additive, no trace of the terminal olefin was detected. This result further supports the assumption that the free proton is responsible for Peterson elimination.
3. When the experiment was carried out with an Ir-H trap TEMPO (10 mol%) as an additive, 17% conversion to the terminal olefin is still obtained. Although not conclusive, this result further supports the assumption that Ir-H is not directly responsible for the Peterson elimination.

NMR results:



Separated experiments for asymmetric hydrogenation of terminal olefins (Step 2)



Entry	substrate	conversion	*ee*[a]	*ee*[b]
1	R_1=Et, R_2=H	>99%	94%	94%
2	R_1=Et, R_2=4-OMe	>99%	98%	97%
3	R_1=*t*-Bu, R_2=H	>99%	99%	99%

Note: a)terminal olefin was used as the substrate.
b)β-hydro silane was used as the substrate.

11. References

1 $TMSCH_2MgCl$ was prepared by following the procedure reported in: Yoshida, S.; Nakamura, Y.; Uchida, K.; Hazama, Y.; Hosoya, T. *Org. Lett*. 2016, ***18***, 6212.

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3 Mazuela, J.; Pàmies, O.; Diéguez, M. *Chem. Cat. Chem* 2013, ***5***, 2410.

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5 Forman, G. S.; Ohkuma, T.; Hems, W. P.; Noyori, R. *Tetrahedron Lett.* 2000, ***41***, 9471.

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