Regioselective Iridium-catalyzed Asymmetric Monohydrogenation of 1,4-Dienes

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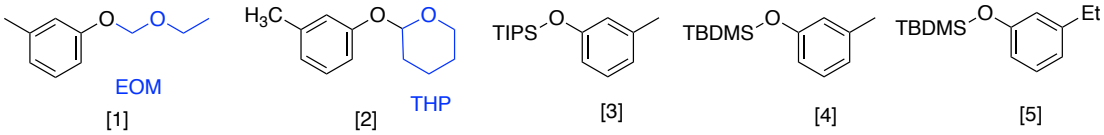
General methods

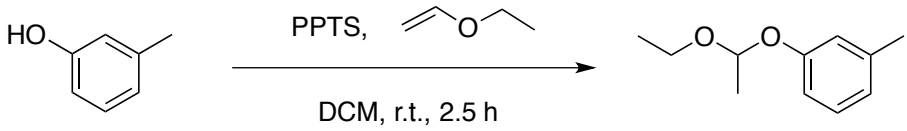
All reactions were conducted under nitrogen atmosphere using magnetic stirring.
CH_2Cl_2 was freshly distilled using CaH_2 under nitrogen atmosphere. THF was freshly distilled using sodium-benzophenone under nitrogen.
All reagents were used as supplied commercially without further purification. Chromatographic 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 aluminum 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 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 ESI direct inlet probe and methane as reagent gas.
Optical rotations were recorded on an Autopol IV polarimeter from Rudolp Research Analytical, equipped with a sodium lamp (589 nm) and a 10 mm cell.
IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer using samples that were prepared in $CHCl_3$.

General procedure for substrate synthesis

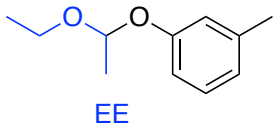
1. Synthesis of protected alkyl phenol

These compounds have been previously reported.



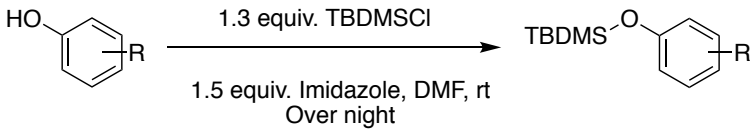


To a round-bottomed flask 5.17g (1 equiv., 5 mL, 47.8 mmol) of phenol and 1.2g (0.1 equiv., 4.78 mmol) PPTS (pyridinium p-toluenesulfonate) was added, and purged with N_2 three times. Then 100 mL of dry DCM was added and stirred at room temperature. Ethyl vinyl ether, 7 mL (1.53 equiv., 73.1 mmol) was added dropwise to the solution and continued stirring for 2.5 hours. The solution was diluted with Et_2O and washed with brine. The water-layer was extracted with Et_2O three times. The combined organic layers was washed with NaOH solution (1M) and dried over $MgSO_4$. After concentration under vacuum, the residue was purified by distillation. (4 mmbar, 119 ^{0}C).



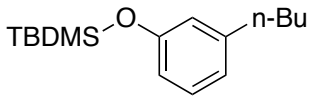
1-(1-ethoxyethoxy)-3-methylbenzene
Colourless oil. Yield = 65%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.13 (m, 1H), 6.84 – 6.78 (m, 3H), 5.37 (q, J = 5.3 Hz, 1H), 3.86 – 3.75 (m, 1H), 3.59 – 3.47 (m, 1H), 2.33 (s, 3H), 1.50 (d, J = 5.3 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 139.4, 129.1, 122.5, 118.0, 114.0, 99.4, 61.3, 21.4, 20.3, 15.1.
IR (Neat, cm^{-1}): ν = 2978, 2931, 1602, 1585, 1489, 1444, 1381, 1256, 1158, 1119, 954, 860, 779.
HRMS (ESI): *m*/*z* calcd for $C_{11}H_{16}NaO_2$ $[M + Na]^+$, 203.1043; found, 203.1034.

2. Synthesis of *tert*-butyl dimethylsilane



Aromatic phenol (1 equiv.) and imidazole (1.5 equiv.) were dissolved in dry DMF (4 mL/1mmol). To this mixture, TBDMSCl (1.3 equiv.) was added dropwise over 10 minutes. The mixture was stirred at room temperature, under nitrogen, overnight. The reaction was quenched with a saturated aqueous solution of NH_4Cl and the product was extracted 3 times with Et_2O. The combined organic layers was washed with water

and brine solution, dried over Na_2SO_4 and concentrated under vacuo. Flash chromatography on silica gel with 100% pentane as eluent yielded the desired product as colorless oil.



***tert*-Butyl (3-butylphenoxy) dimethylsilane**

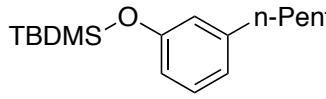
Colourless oil. Yield = 96%. R_f = 0.42, in pentane.

1H NMR (400 MHz, CDCl3): 7.13 (t, *J* = 7.6 Hz, 1H), 6.83 -6.76 (m, 1H), 6.67 (d, *J* = 8.1 Hz, 2H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.68- 1.51 (m, 2H), 1.36 (h, *J* = 7.8 Hz, 2H), 1.01 (d, *J* = 1.1 Hz, 9H), 0.21 (d, *J* = 1.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 155.6, 144.5, 129.0, 121.5, 120.2, 117.2, 35.6, 33.6, 25.7, 22.3, 18.2, 14.0, -4.4.

IR (Neat, cm-1): ν = 2930, 1603, 1484, 1276, 1157, 1003, 972, 838, 780, 694.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{28}NaOSi$ $[M + Na]^+$, 287.1802; found, 287.1785.



***tert*-Butyldimethyl (3-pentylphenoxy) silane**

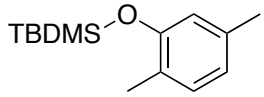
Colourless oil. Yield = 70%. R_f = 0.44, in pentane.

^1H NMR (400 MHz, $CDCl_3$): 7.16-7.12 (m, 1H), 6.80 - 6.78 (m, 1H), 6.69-6.65 (m, 2H), 2.50 - 2.54(m, 2H), 1.64- 1.57 (m, 3H), 1.39-1.34(m, 3H), 1.01 (s, 9H), 0.96-0.89(m, 3H), 0.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 155.5, 144.5, 129.0, 121.4, 120.2, 117.2, 35.8, 35.5, 33.5, 31.5, 31.1, 25.7, 22.6, 22.3, 18.2, 14.0, 14.0, -4.4.

IR (Neat, cm^{-1}): ν = 2956,1584, 1484, 1275, 1157, 1004, 825, 728.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{30}NaOSi$ $[M + Na]^+$, 301.1958; found, 301.1952.



***tert*-Butyl (2,5-dimethylphenoxy) dimethylsilane**

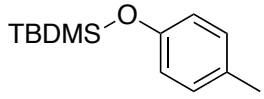
Colourless oil. Yield = 96%. R_f = 0.56, in pentane.

^1H NMR (400 MHz, $CDCl_3$) δ 7.03 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.6 Hz, 1H), 6.61 (s, 1H), 2.29 (s, 3H), 2.19 (s, 3H), 1.05 (s, 9H), 0.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 136.3, 130.6, 125.6, 121.7, 119.3, 25.8, 21.1, 18.3, 16.5, -4.2.

IR (Neat, cm^{-1}): ν = 2957, 2859, 1617, 1580, 1472, 1411, 1127, 1002, 954, 854, 779.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{25}OSi$ $[M + H]^+$, 237.1675; found, 237.1689.



***tert*-Butyldimethyl (*p*-tolyloxy) silane**

Colourless oil. Yield = 94%. R_f = 0.56, in pentane.

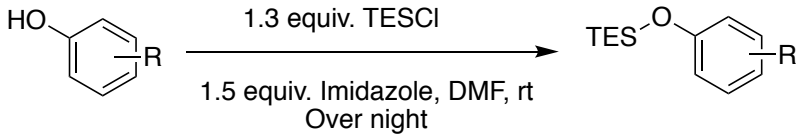
^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.1 Hz, 2H), 6.81 – 6.74 (m, 2H), 2.31 (s, 3H), 1.02 (s, 9H), 0.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 130.4, 129.8, 119.8, 25.7, 20.6, 18.2, -4.5.

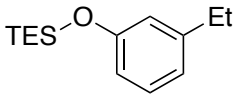
IR (Neat, cm^{-1}): ν = 2957, 2930, 2859, 1612, 1510, 1472, 1256, 915, 838, 779.

HRMS (ESI): *m*/*z* calcd for $C_{13}H_{23}OSi$ $[M + H]^+$, 223.1518; found, 223.1521.

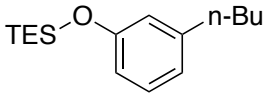
3. Synthesis of triethyl silane



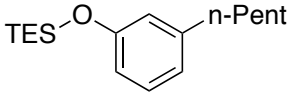
Aromatic phenol (1 equiv.) and imidazole (1.5 equiv.) were dissolved in dry DMF (4 mL/1mmol). To this mixture, TESCl (1.3 equiv.) was added dropwise over 10 minutes. The mixture was stirred at room temperature under nitrogen atmosphere over night. The reaction was quenched with saturated aqueous solution of NH_4Cl and the product was extracted 3 times with Et_2O. The combined organic layers was washed with water and brine solution, dried over Na_2SO_4 and concentrated under vacuo. Flash chromatography on silica gel with 100% pentane as eluent yielded the desired product as a colorless oil.



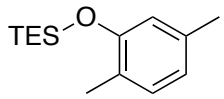
triethyl (3-ethylphenoxy) silane
Colourless oil. Yield = 58%. R_f = 0.77, in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.81 – 6.77 (m, 1H), 6.71 – 6.65 (m, 2H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.74 (q, *J* = 8.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 145.8, 129.1, 120.8, 119.5, 117.0, 28.7, 15.5, 6.7, 5.0.
IR (Neat, cm^{-1}): ν = 2960, 2877, 1603, 1584, 1484, 1274, 1157, 940, 809, 745
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{25}OSi$ $[M + H]^+$, 237.1669; found, 237.1624.



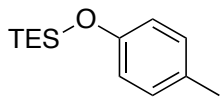
(3-Butylphenoxy) triethyl silane
Colourless oil. Yield = 87 %. R_f = 0.38, in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 1H), 6.79 – 6.75 (m, 1H), 6.69 – 6.64 (m, 2H), 2.59 – 2.50 (m, 2H), 1.62 – 1.51 (m, 2H), 1.39 – 1.26 (m, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.78 – 0.68 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 144.4, 129.0, 121.4, 120.0, 117.0, 35.5, 33.5, 22.3, 13.9, 6.6, 5.0.
IR (Neat, cm^{-1}): ν = 2957, 2877, 1603, 1585, 1484, 1277, 1157, 1003, 976, 826, 746.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{29}OSi$ $[M + H]^+$, 265.1988; found, 265.1991.



triethyl (3-pentylphenoxy) silane
Colourless oil. Yield = 82%. R_f = 0.41, in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 7.13-7.10 (m, 1H), 6.78 -6.76 (m, 1H), 6.69 -6.65 (m, 2H), 2.57-2.53 (m, 2H), 1.63-1.54 (m, 2H), 1.37-1.30 (m, 2H), 1.03-0.98 (m, 9H), 0.94-0.87 (m, 3H), 0.77-0.71 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): 155.5, 144.5, 129.0, 121.4, 120.1, 117.0, 35.8, 35.5, 33.5, 31.5, 31.0, 22.6, 22.3, 14.0, 14.0, 6.7, 5.0.
IR (Neat, cm^{-1}): ν = 2956, 1602, 1584, 1484, 1275, 1157, 1004, 978, 825, 728.
HRMS (ESI): *m*/*z* calcd for $C_{17}H_{30}NaOSi$ $[M + Na]^+$, 301.1958; found, 301.1952.

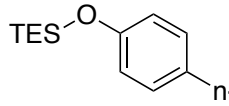


(2,5-Dimethylphenoxy) triethyl silane
Colourless oil. Yield = 97%. R_f = 0.40, in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 7.6 Hz, 1H), 6.58 (s, 1H), 2.26 (s, 3H), 2.16 (s, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.76 (q, *J* = 8.3 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 136.3, 130.5, 125.5, 121.6, 119.3, 21.1, 16.2, 6.7, 5.3.
IR (Neat, cm^{-1}): ν = 2956, 2877, 1617, 1580, 1507, 1411, 1280, 1127, 1002, 836, 743.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{25}OSi$ $[M + H]^+$, 237.1675; found, 237.1662.

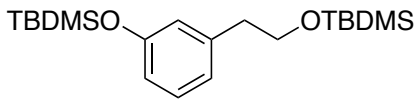


This compound has been previously reported. [6]

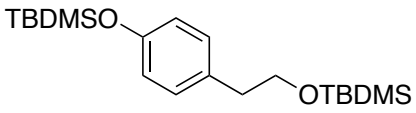
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.1 Hz, 2H), 6.80 – 6.75 (m, 2H), 2.30 (s, 3H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.75 (q, *J* = 8.5, 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 130.4, 129.8, 119.6, 20.5, 6.6, 5.0.



triethyl (4-propylphenoxy) silane
Colourless oil. Yield = 92%. R_f=0.36, in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 7.06 -7.02 (m, 2H), 6.81 -6.77 (m, 2H), 2.56-2.52 (m, 2H), 1.68- 1.56 (m, 2H), 1.05- 0.99 (m, 9H), 0.97-0.93 (m, 4H), 0.79-0.74 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 153.4, 135.3, 129.2, 119.6, 37.3, 24.7, 13.8, 6.8, 6.7, 6.5, 5.0.
IR (Neat, cm^{-1}): ν = 2958, 2877, 1609, 1510, 1458, 1260, 1168, 1016, 911, 806, 730.
HRMS (ESI): *m*/*z* calcd for $C_{15}H_{26}NaOSi$ $[M + Na]^+$, 273.1645; found, 273.1645.



This compound was prepared following the procedure described in literature. [7].

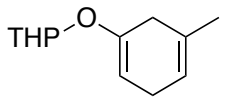


This compound was prepared following the procedure described in literature. [8].

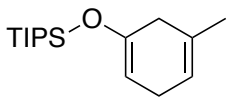
4. General procedure for the Birch reduction

General Procedure: The reactions were carried out in a 3-necked round-bottomed flask with a dry ice condenser, an NH_3 (g) inlet, and a stopper for Li or Na addition. To the round-bottomed flask, 1.5 mL of *tert*-BuOH and 3 mL THF was added. Ammonia was condensed from commercial NH_3 (15 mL) tube into the mixture while cooling the flask in a dry ice/acetone bath. Addition of the Li (10 equiv.) was done at reflux temperature of NH_3, with a speed so as to prevent vigorous reaction/foaming. The cooling bath was removed and the reaction mixture was stirred at reflux conditions for 20 minutes. The substrate was dissolved in 2 mL dried THF then added to the reaction mixture at -30°C and continuously stirred for 2 hours. The reaction was cooled to -78°C. Solid NH_4Cl was added and the dry-ice/acetone bath was removed. The NH_3 was allowed to evaporate. Then saturated aqueous solution of

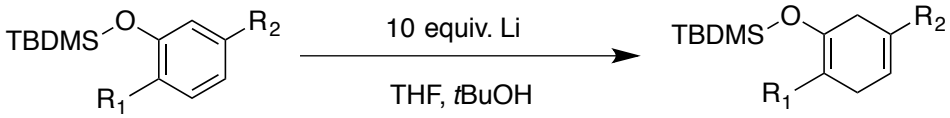
NH_4Cl was added. The mixture was extracted 3 times with pentane. The combined organic extracts were washed with brine and dried with Na_2SO_4. The solvent was removed and the product/s were purified either by distillation under reduced pressure or by chromatography on basic Al_2O_3 using pure pentane as eluent.
Procedure A: Li (10 equiv.) was used and reaction mixture was stirred at -30°C for 2 hours.
Procedure B: Li (60 equiv.) was used and reaction mixture was stirred at -30°C for 8 hours.

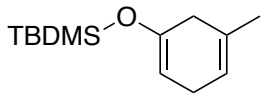


2-((5-Methylcyclohexa-1,4-dien-1-yl)oxy) tetrahydro-2*H*-pyran
Colourless oil. Yield = 79%. R_f = 0.8, in 20/1 pentane/Et_2O.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$): 5.38 (s, 1H), 5.23-5.16 (m, 1H), 4.97 (s, 1H), 3.88 (ddd, *J* = 11.6, 8.3, 3.3 Hz, 1H), 3.55 (dt, *J* = 11.0, 4.9 Hz, 1H), 2.75 (dd, *J* = 21.8, 6.0 Hz, 2H), 2.69- 2.59 (m, 2H), 1.98 -1.81 (m, 1H), 1.76 (ddd, *J* = 13.1, 9.6, 3.4 Hz, 1H), 1.68 (d, *J* = 1.9 Hz, 3H), 1.63 -1.49 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 130.5, 118.6, 95.8, 95.1, 62.4, 33.0, 30.5, 27.0, 25.3, 22.9, 19.3.
IR (Neat, cm^{-1}): ν = 2942, 1699, 1668, 1441, 1394, 1197, 1136, 1039, 975, 776.
HRMS (ESI): *m*/*z* calcd for $C_{12}H_{19}O_2$ $[M + H]^+$, 195.1385; found, 195.1391.

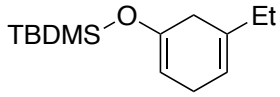


triisopropyl ((5-methylcyclohexa-1,4-dien-1-yl)oxy) silane
Colourless oil. Yield = 68%. R_f = 0.42, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$): 5.36 (qt, *J* = 3.6, 1.8 Hz, 1H), 4.85 (tq, *J* = 3.6, 1.3 Hz, 1H), 2.81- 2.71 (m, 2H), 2.64 -2.54 (m, 2H), 2.05 -1.93 (m, 2H), 1.06- 0.96 (m, 13H), 0.73 - 0.64 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 148.0, 136.4, 116.6, 100.5, 33.6, 29.6, 27.2, 12.0, 6.8, 6.8, 5.0.
IR (Neat, cm^{-1}): ν = 2918, 1721, 1459, 1365, 1212, 1018, 880, 775.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{31}OSi$ $[M + H]^+$, 267.2144; found, 267.2129.





***tert*-Butyldimethyl ((5-methylcyclohexa-1,4-dien-1-yl)oxy) silane**
Colorless oil. Yield = 92%. R_f = 0.40, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.33 (m, 1H), 4.87 – 4.82 (m, 0H), 2.78 – 2.68 (m, 2H), 2.59 – 2.51 (m, 2H), 1.72 – 1.66 (m, 3H), 0.93 (s, 9H), 0.15 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 130.9, 118.5, 100.8, 35.4, 27.2, 22.9, 18.0, -4.4.
IR (Neat, cm^{-1}): ν = 2957, 2857, 1699, 1667, 1472, 1385, 1253, 1220, 1136, 937, 832, 780.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{24}NaOSi$ $[M + Na]^+$, 247.1489; found, 247.1500.



***tert*-Butyl ((5-ethylcyclohexa-1,4-dien-1-yl)oxy) dimethylsilane**

Colorless oil. Yield = 95%. R_f = 0.41, in pentane.

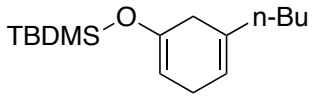
Followed **procedure A** for the birch reduction.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.34 (m, 1H), 4.87 – 4.82 (m, 1H), 2.80 – 2.70 (m, 2H), 2.57 (t, *J* = 7.9 Hz, 2H), 1.99 (q, *J* = 8.7, 8.1 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H), 0.93 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 136.3, 116.7, 100.8, 33.7, 29.6, 27.2, 25.7, 18.0, 12.0, -4.4.

IR (Neat, cm^{-1}): ν = 2959, 2858, 1698, 1666, 1462, 1381, 1214, 1142, 930.

HRMS (ESI): *m*/*z* calcd for $C_{14}H_{26}OSi$ $[M + Na]^+$, 238.1753; found, 238.1734.



***tert*-Butyl ((5-butylcyclohexa-1,4-dien-1-yl) oxy) dimethylsilane**

Colourless oil. Yield = 87%.

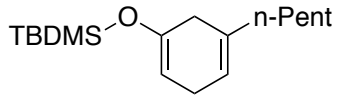
Followed **procedure A** for the birch reduction.

^{1}H NMR (400 MHz, $CDCl_3$): 5.38-5.36 (m, 1H), 4.85-4.83(m, 1H), 2.77-2.72 (m, 2H), 2.59 - 2.54 (m, 2H), 2.00 - 1.95 (m, 2H), 1.43 – 1.26 (m, 4H), 0.94 - 0.87 (m, 15H), 0.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 148.1, 134.9, 117.9, 100.8, 36.6, 33.6, 29.5, 27.2, 25.7, 22.4, 18.0, 14.0, -4.4.

IR (Neat, cm^{-1}): ν = 2928, 1697, 1665, 1471, 1384, 1254, 1217, 1141, 932, 836, 778.

HRMS (ESI): *m*/*z* calcd for $C_{16}H_{30}NaOSi$ $[M + Na]^+$, 289.1958; found, 289.1948.



***tert*-Butyldimethyl ((5-pentylcyclohexa-1,4-dien-1-yl) oxy) silane**

Colourless oil. Yield = 88%.

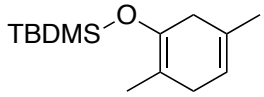
Followed **procedure A** for the birch reduction.

^{1}H NMR (400 MHz, $CDCl_3$): 5.38-5.35(m, 1H), 4.85-4.83(m, 1H), 2.77-2.72(m, 2H), 2.59-2.54(m, 2H), 2.00-1.95(m, 2H), 1.46- 1.26 (m, 6H), 0.94-0.87(m, 13H), 0.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 148.1, 134.9, 117.9, 100.8, 36.9, 36.6, 33.6, 31.6, 29.5, 27.2, 27.0, 25.7, 25.7, 22.6, 22.4, 18.0, 14.1, 14.0, -4.4.

IR (Neat, cm^{-1}): ν = 2928, 1697, 1463, 1254, 1217, 1141, 1006, 931, 836, 778, 684.

HRMS (ESI): *m*/*z* calcd for $C_{17}H_{32}NaOSi$ $[M + Na]^+$, 303.2115; found, 303.2108.



***tert*-Butyl ((2,5-dimethylcyclohexa-1,4-dien-1-yl)oxy) dimethylsilane**

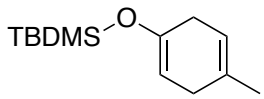
Colourless oil. Yield = 78%. R_f = 0.41, in pentane.

Followed **procedure A** for the birch reduction.

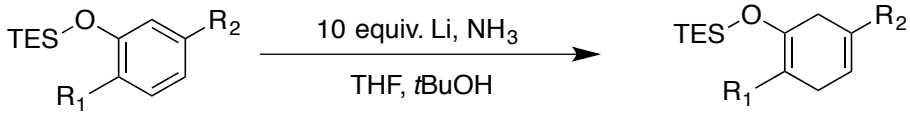
^{1}H NMR (400 MHz, CDCl3) δ 5.39 – 5.27 (m, 1H), 2.68 – 2.60 (m, 2H), 2.61 – 2.53 (m, 2H), 1.70 – 1.65 (m, 3H), 1.60 (s, 3H), 0.96 (s, 9H), 0.13 (s, 6H).

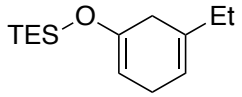
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 130.9, 118.9, 108.4, 36.1, 33.4, 25.9, 22.8, 18.2, 15.5, -3.7.

IR (Neat, cm^{-1}): ν = 2929, 2857, 1711, 1681, 1472, 1385, 1253, 1195, 1099, 931, 834, 777.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{26}OSi$ $[M]^+$, 238.1753; found, 238.1758.

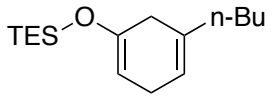


***tert*-Butyldimethyl ((4-methylcyclohexa-1,4-dien-1-yl)oxy) silane**
Colourless oil. Yield = 90%. R_f = 0.41, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.30 (m, 1H), 4.87 – 4.79 (m, 1H), 2.71 – 2.57 (m, 4H), 1.67 (s, 3H), 0.92 (s, 9H), 0.14 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 131.4, 118.1, 101.0, 77.3, 77.0, 76.7, 31.6, 31.3, 25.7, 22.7, 18.0, -4.4.
IR (Neat, cm^{-1}): ν = 2956, 2877, 1699, 1667, 1458, 1372, 1202, 1005, 869, 743.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{24}OSiNa$ $[M + Na]^+$, 224.1596; found, 224.1583.

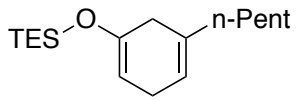




triethyl ((5-ethylcyclohexa-1,4-dien-1-yl) oxy) silane
Colourless oil. Yield = 80%. R_f = 0.41, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.33 (m, 1H), 4.89 – 4.80 (m, 1H), 2.77 – 2.67 (m, 2H), 2.62 – 2.54 (m, 2H), 1.68 (s, 2H), 1.21 – 1.01 (m, 12H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 130.1, 118.5, 100.0, 35.4, 27.3, 22.9, 18.0, 17.9,12.7.
IR (Neat, cm^{-1}): ν = 2962, 2867, 1697, 1667, 1465, 1385, 1219, 1138, 883.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{27}OSi$ $[M + H]^+$, 239.1831; found, 239.1809.

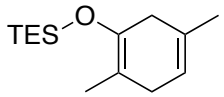


((5-Butylcyclohexa-1,4-dien-1-yl)oxy)triethylsilane
Colourless oil. Yield = 60%. R_f = 0.30, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, CDCl3) δ 5.39 – 5.33 (m, 1H), 4.87 – 4.82 (m, 1H), 2.79 – 2.69 (m, 2H), 2.58 (t, *J* = 7.9 Hz, 2H), 1.98 (t, *J* = 7.3 Hz, 2H), 1.45 – 1.35 (m, 2H), 1.34 – 1.26 (m, 2H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.68 (q, *J* = 8.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 134.9, 117.9, 100.4, 36.6, 33.6, 29.5, 27.2, 22.4, 14.0, 6.7, 5.1.
IR (Neat, cm^{-1}): ν = 2955, 2876, 1697, 1665, 1458, 1382, 1213, 1141, 1005, 928, 744.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{30}NaOSi$ $[M + Na]^+$, 289.1958; found, 289.1962.

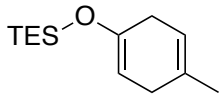


triethyl ((5-pentylcyclohexa-1,4-dien-1-yl) oxy) silane
Colourless oil. Mixture of starting material and birch product, Birch reaction conversion = 62%.
Followed **procedure B** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$): 7.12 (t, *J* = 7.7 Hz, 1H), 6.77 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.71 - 6.64 (m, 2H), 5.37 (dq, *J* = 3.4, 1.7 Hz, 2H), 4.85 (ddt, *J* = 3.5, 2.3, 1.3 Hz,

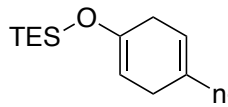
2H), 2.80 - 2.70 (m, 3H), 2.63 - 2.50 (m, 5H), 2.04 - 1.94 (m, 3H), 1.65 - 1.51 (m, 3H), 1.51 - 1.19 (m, 14H), 1.06 - 0.81 (m, 35H), 0.80 - 0.64 (m, 17H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 148.1, 144.5, 144.4, 134.9, 134.9, 129.0, 121.4, 120.1, 117.9, 117.0, 100.4, 36.9, 36.6, 35.8, 35.5, 33.6, 33.5, 31.6, 31.5, 31.0, 29.5, 27.2, 27.0, 22.6, 22.6, 22.4, 22.3, 14.1, 14.0, 14.0, 13.9, 7.7, 6.7, 6.6, 5.1, 5.0.
IR (Neat, cm^{-1}): ν = 2956, 1715, 1589, 1456, 1364, 1217, 1017, 849, 729.
HRMS (ESI): *m*/*z* calcd for $C_{17}H_{32}NaOSi$ $[M + Na]^+$, 303.2115; found, 303.2021.



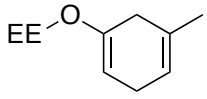
((2,5-Dimethylcyclohexa-1,4-dien-1-yl)oxy) triethyl silane
Colourless oil. Yield = 59%. R_f = 0.42, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 – 5.32 (m, 1H), 2.68 – 2.53 (m, 4H), 1.67 (s, 3H), 1.60 (s, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 8.2 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 130.9, 118.9, 108.4, 36.0, 33.2, 22.8, 15.3, 6.8, 6.4, 5.6.
IR (Neat, cm^{-1}): ν = 2955, 2877, 1710, 1445, 1365, 1237, 1196 1155, 1005, 927, 801.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{27}OSi$ $[M + H]^+$, 239.1831; found, 239.1802.



triethyl ((4-methylcyclohexa-1,4-dien-1-yl)oxy) silane
Colourless oil. Yield = 78%. R_f = 0.23, in pentane.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 – 5.31 (m, 1H), 4.85 – 4.82 (m, 1H), 2.65 (s, 3H), 1.67 (s, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 131.4, 118.2, 100.6, 31.6, 31.2, 22.7, 6.8, 6.7, 6.4, 5.1.
IR (Neat, cm^{-1}): ν = 2956, 2877, 1699, 1667, 1458, 1372, 1202, 1005, 869, 743.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{24}OSi$ $[M + H]^+$, 225.1675; found, 225.1672.

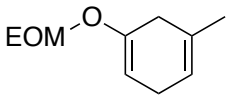


triethyl ((4-propylcyclohexa-1,4-dien-1-yl) oxy) silane
Colourless oil. Yield = 87%.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$): 5.34 (t, *J* = 1.6 Hz, 1H), 4.84 (d, *J* = 1.8 Hz, 1H), 2.66 (s, 4H), 1.94 (t, *J* = 7.6 Hz, 2H), 1.43 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.94 - 0.84 (m, 4H), 0.67 (q, *J* = 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 148.2, 135.1, 117.6, 100.7, 38.9, 31.2, 29.8, 20.8, 13.8, 6.8, 6.7, 6.4, 5.1.
IR (Neat, cm^{-1}): ν = 2957, 1697, 1664, 1508, 1458, 1377, 1203, 1071, 1016, 868, 743.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{31}OSi$ $[M + H]^+$, 267.2144; found, 267.2137.

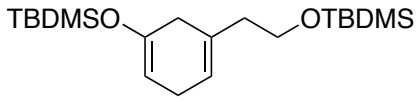


1-(1-Ethoxyethoxy)-5-methylcyclohexa-1,4-diene
Colourless oil. Yield = 97%.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.34 (m, 1H), 5.19 (q, *J* = 5.2 Hz, 1H), 4.80 – 4.73 (m, 1H), 3.76 – 3.66 (m, 1H), 3.51 – 3.41 (m, 1H), 2.79 – 2.70 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.70 – 1.65 (m, 3H), 1.39 (d, *J* = 5.2 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H).

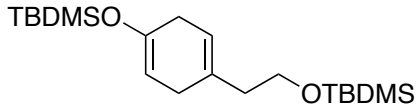
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 130.6, 118.5, 97.5, 95.1, 61.7, 33.3, 26.9, 22.8, 20.2, 15.2.
IR (Neat, cm^{-1}): ν = 2976, 2883, 1699, 1665, 1446, 1380, 1206, 1144, 1123, 953, 773.
HRMS (ESI): *m*/*z* calcd for $C_{11}H_{18}NaO_2$ $[M + Na]^+$, 205.1199; found, 205.1216.



1-(Ethoxymethoxy)-5-methylcyclohexa-1,4-diene
Colourless oil. Yield = 97%.
Followed **procedure A** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.35 (m, 1H), 5.02 (s, 2H), 4.90 (td, *J* = 3.5, 1.1 Hz, 1H), 3.65 (q, *J* = 7.1 Hz, 2H), 2.80 – 2.71 (m, 2H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.72 – 1.65 (m, 3H), 1.22 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 130.4, 118.6, 95.1, 91.9, 64.2, 32.9, 26.9, 22.9, 15.1.
IR (Neat, cm^{-1}): ν = 2974, 2886, 1700, 1668, 1388, 1200, 1131, 1065, 1005, 776.
HRMS (ESI): *m*/*z* calcd for $C_{10}H_{16}NaO_2$ $[M + Na]^+$, 191.1043; found, 191.1051.

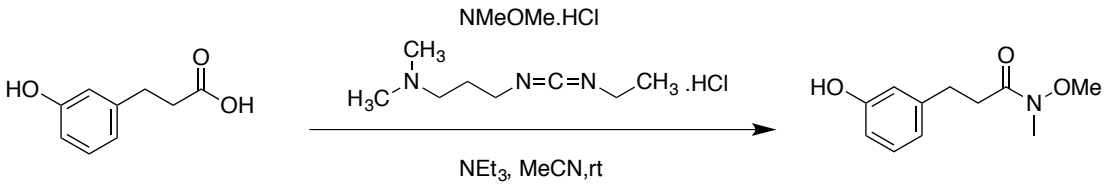


***tert*-Butyl(2-(5-((*tert*-butyl dimethylsilyl) oxy) cyclohexa-1,4-dien-1-yl)ethoxy) dimethylsilane**
Colourless oil. Yield = 70%. Followed **procedure B** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 – 5.39 (m, 1H), 4.83 – 4.81 (m, 1H), 3.70 (t, *J* = 6.9 Hz, 2H), 2.77-2.72 (m, 2H), 2.66 - 2.55 (m, 2H), 2.26 - 2.13 (m, 2H), 0.94 - 0.85 (m, 19H), 0.14 (s, 6H), 0.05 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 132.0, 120.0, 100.6, 62.1, 40.3, 34.1, 27.2, 25.9, 25.7, 18.3, 18.0, -4.4, -5.3.
IR (Neat, cm^{-1}): ν = 2857, 1698, 1665, 1604, 1585, 1472, 1387, 1255, 1220, 1099, 1005, 931, 836, 776, 662.
HRMS (ESI): *m*/*z* calcd for $C_{20}H_{40}NaO_2Si_2$ $[M + Na]^+$, 391.2459; found, 391.2452.

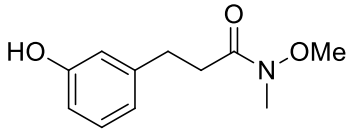


***tert*-Butyl(2-(4-((*tert*-butyl dimethylsilyl) oxy) cyclohexa-1,4-dien-1-yl)ethoxy) dimethylsilane**
Colourless oil. Yield = 76%. Followed **procedure B** for the birch reduction.
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 - 5.33 (m, 1H), 4.83-4.81 (m, 1H), 3.68 (t, *J* = 7.0 Hz, 2H), 2.75 - 2.60 (m, 4H), 2.24 - 2.16 (m, 2H), 0.94 - 0.87 (m, 20H), 0.13 (s, 6H), 0.04 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 132.4, 119.6, 101.0, 76.7, 62.3, 40.1, 31.2, 30.3, 26.0, 25.7, 18.4, 18.0, -4.4, -5.3.
IR (Neat, cm^{-1}): ν = 2929, 1697, 1665, 1472, 1377, 1254, 1204, 1100, 1050, 1005, 939, 882, 837, 776, 680.
HRMS (ESI): *m*/*z* calcd for $C_{20}H_{40}NaO_2Si_2$ $[M + Na]^+$, 391.2459; found, 391.2449.

5. Synthesis of functional substrates and acyclic substrates



In a schlenk flask, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide.HCl (24.4 mmol, 1.3 equiv.) and NMe(OMe).HCl (28.8 mmol, 1.5 equiv.) were dissolved in 60 mL of CH_3CN under N_2 atmosphere. Then Et_3N (24.4 mmol, 1.3 equiv.) was added at room temperature. A solution of phenol carboxylic acid (18.8 mmol, 1 equiv.) was added using an addition funnel. The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The crude residue was diluted with EtOAc and 2M HCl was added. The reaction mixture was extracted twice with EtOAc, washed with H_2O and brine, and dried over Na_2SO_4. The solvent was removed and the product was purified by column chromatography.



3-(3-Hydroxyphenyl)-*N*-methoxy-*N*-methyl propanamide

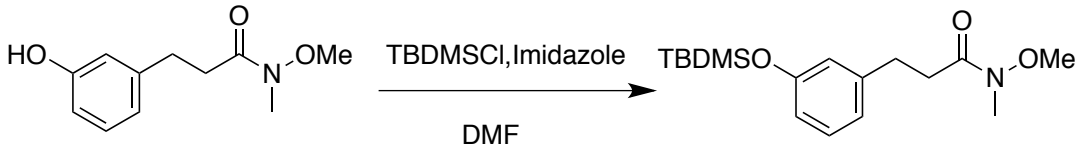
Colourless oil. Yield = 89%. R_f = 0.48, in 70/30 EtOAc/pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.9 Hz, 1H), 6.81 – 6.73 (m, 2H), 6.72 – 6.67 (m, 1H), 6.12 (s, 1H), 3.61 (s, 3H), 3.19 (s, 3H), 2.96 – 2.88 (m, 2H), 2.79 – 2.71 (m, 2H).

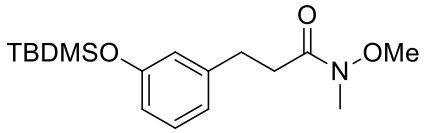
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 156.2, 142.9, 129.6, 120.3, 115.5, 113.2, 61.2, 33.5, 32.2, 30.6.

IR (Neat, cm^{-1}): ν = br_3284, 2938, 1668, 1603, 1585, 1485, 1442, 1278, 1158, 993, 839, 782.

HRMS (ESI): *m*/*z* calcd for $C_{11}H_{15}NNaO_3$ $[M + Na]^+$, 232.0944; found, 232.0942.

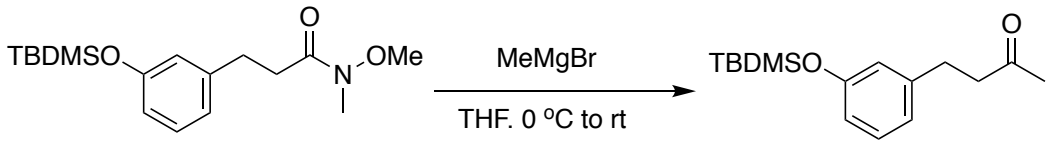


3-(3-hydroxyphenyl)-*N*-methoxy-*N*-methylpropanamide (8.1 mmol) and imidazole (12.15 mmol) were dissolved in 45 mL of dry DMF in a 100 mL round-bottomed flask. TBDMSCl (10.5 mmol) was added to the mixture. The reaction was stirred overnight at room temperature under N_2 atmosphere. Then a saturated aqueous solution of NH_4Cl was added. The mixture was extracted with ether, washed several times with H_2O, brine and dried over Na_2SO_4. The solvent was removed and the product was purified by column chromatography (40/60 of EtOAc/pentane) to yield the desired product.

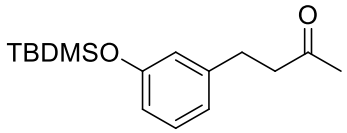


3-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)-*N*-methoxy-*N*-methyl propanamide

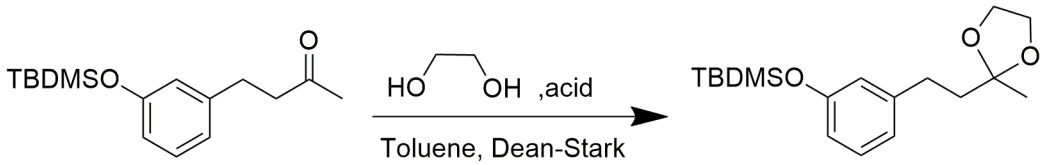
Colourless oil. Yield = 94%. R_f = 0.50, in 40/60 EtOAc/pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.73 – 6.65 (m, 2H), 3.61 (s, 3H), 3.18 (s, 3H), 2.94 – 2.86 (m, 2H), 2.75 – 2.67 (m, 2H), 0.98 (s, 9H), 0.19 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 155.6, 142.8, 129.2, 121.3, 120.1, 117.6, 61.1, 33.7, 32.1, 30.5, 25.6, 18.1, -4.5.
IR (Neat, cm^{-1}): ν = 2932, 2858, 1668, 1603, 1585, 1485, 1442, 1278, 1158, 993, 839, 782.
HRMS (ESI): *m*/*z* calcd for $C_{17}H_{29}NNaO_3S$ $[M + Na]^+$, 346.1809; found, 346.1805.



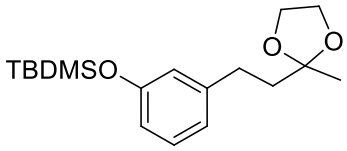
3-(3-((*tert*-butyldimethylsilyl)oxy)phenyl)-*N*-methoxy-*N*-methylpropanamide (5.7 mmol) was dissolved in 50 mL of dry THF and cooled to 0 °C. Then MeMgBr (2.5M, 2.3 mL, 5.7 mmol) was slowly added to the substrate solution. The reaction mixture was stirred at room temperature for 1 hour. Then a saturated aqueous solution of NH_4Cl was added. The mixture was extracted with ether (3 x 20mL), washed several times with H_2O, brine and dried over Na_2SO_4. The solvent was removed under vacuum and the product was purified by column chromatography (10/90 of EtOAc/pentane) to yield the desired product.



4-(3-((*tert*-Butyldimethylsilyl)oxy) phenyl) butan-2-one
Colourless oil. Yield = 89%. R_f = 0.40, in 10/90 EtOAc/pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 1H), 6.79 – 6.74 (m, 1H), 6.70 – 6.65 (m, 2H), 2.87 – 2.80 (m, 2H), 2.77 – 2.70 (m, 2H), 2.14 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.8, 155.7, 142.5, 129.3, 121.2, 120.0, 117.7, 45.1, 30.0, 29.6, 25.7, 18.2, -4.4.
IR (Neat, cm^{-1}): ν = 2930, 2858, 1719, 1602, 1585, 1486, 1272, 1158, 978, 839, 782.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{26}NaO_2Si$ $[M + Na]^+$, 301.1594; found, 301.1598.



4-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl)butan-2-one (4.3 mmol) was dissolved in 40 mL of toluene with 0.97 mL (17.2 mmol) ethylene glycol and 10 mol% of *p*-toluenesulphonic acid monohydrate, in a 100 mL round-bottomed flask connected to a Dean and Stark apparatus. The reaction mixture was heated overnight at 130 °C. The solvent was removed under vacuum and the product was purified by column chromatography (5/95 of Et_2O/pentane) to yield the desired product.



tert-Butyldimethyl(3-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)phenoxy) silane

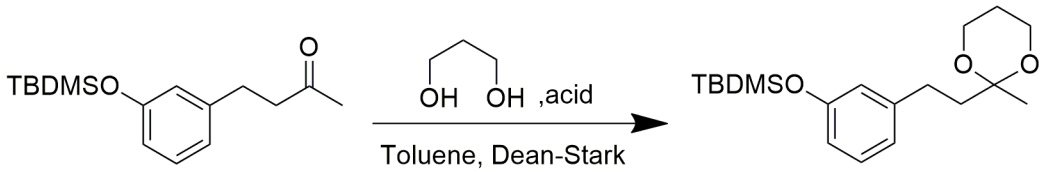
Colourless oil. Yield = 49%. R_f = 0.47, in 10/90 EtOAc/pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.70 – 6.63 (m, 2H), 4.02 – 3.94 (m, 4H), 2.70 – 2.61 (m, 2H), 1.98 – 1.90 (m, 2H), 1.37 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

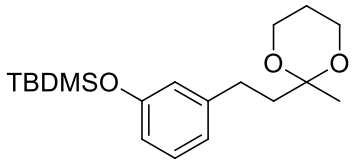
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 143.7, 129.1, 121.3, 120.1, 117.3, 109.6, 64.7, 40.9, 30.1, 25.7, 24.0, 18.1, -4.5.

IR (Neat, cm^{-1}): ν = 2955, 2859, 1604, 1585, 1487, 1259, 1158, 1056, 964, 841, 781.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{30}NaO_3Si$ $[M + Na]^+$, 345.1856; found, 345.1853.



4-(3-((*tert*-Butyldimethylsilyl)oxy)phenyl) butan-2-one (5.45 mmol) was dissolved in 50 mL of toluene with 1.8 mL (21.8 mmol) 1,3-propandiol and 10 mol% of *p*-toluenesulphonic acid monohydrate, in a 100 mL round-bottomed flask connected to a Dean and Stark apparatus. The reaction mixture was heated overnight at 130 °C. The solvent was removed under vacuum and the product was purified by column chromatography (5/95 of Et_2O/pentane) to yield the desired product.



tert-Butyldimethyl(3-(2-(2-methyl-1,3-dioxan-2-yl)ethyl)phenoxy)silane

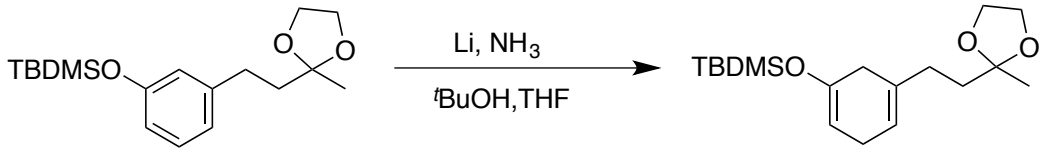
Colourless oil. Yield = 67%. R_f = 0.40, in 10/90 EtOAc/pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, *J* = 7.8 Hz, 1H), 6.82 – 6.79 (m, 1H), 6.70 (t, *J* = 1.9 Hz, 1H), 6.67 – 6.63 (m, 1H), 4.00 – 3.85 (m, 4H), 2.71 – 2.61 (m, 2H), 2.03 – 1.95 (m, 2H), 1.84 – 1.73 (m, 1H), 1.71 – 1.61 (m, 1H), 1.45 (s, 3H), 0.98 (s, 9H), 0.19 (s, 6H).

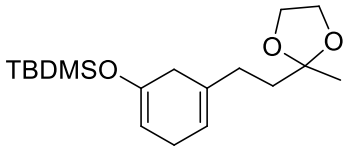
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 144.0, 129.1, 121.3, 120.2, 117.3, 98.8, 59.7, 39.7, 29.6, 25.7, 25.5, 21.3, 18.2, -4.4.

IR (Neat, cm^{-1}): ν = 2956, 2859, 1603, 1584, 1485, 1258, 1155, 1091, 967, 840, 781.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{32}NaO_3Si$ $[M + Na]^+$, 359.2013; found, 359.1998.



The Birch product was synthesized following the general Birch reduction **procedure A** . For this substrate, 30 equiv. of Li was used and the reaction time was 4 hours.



***tert*-Butyldimethyl ((5-(2-(2-methyl-1,3-dioxolan-2-yl) ethyl) cyclohexa-1,4-dien-1-yl) oxy) silane**

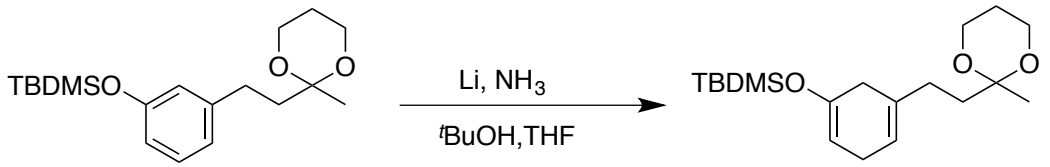
Colourless oil. Quantitative yield. R_f = 0.53, in 10% EtOAc/pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.42 – 5.36 (m, 1H), 4.86 – 4.81 (m, 1H), 3.99 – 3.91 (m, 4H), 2.78 – 2.70 (m, 2H), 2.57 (t, *J* = 7.9 Hz, 2H), 2.11 – 2.04 (m, 2H), 1.81 – 1.74 (m, 2H), 1.33 (s, 3H), 0.92 (s, 9H), 0.14 (s, 6H).

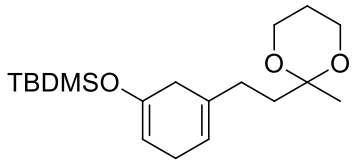
^{13}C NMR (100 MHz, $CDCl_3$) δ 147.9, 134.3, 117.9, 109.9, 100.8, 64.7, 37.0, 33.8, 31.2, 27.2, 25.7, 23.9, 18.0, -4.4.

IR (Neat, cm^{-1}): ν = 2953, 2858, 1697, 1665, 1472, 1376, 1215, 1126, 1057, 930, 836, 779.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{32}NaO_3Si$ $[M + Na]^+$, 347.2013; found, 347.2013.



The Birch product was synthesized following the general Birch reduction **procedure A** . For this substrate, 30 equiv. of Li was used and the reaction time was 4 hours.



***tert*-Butyldimethyl((5-(2-(2-methyl-1,3-dioxan-2-yl) ethyl) cyclohexa-1,4-dien-1-yl) oxy) silane**

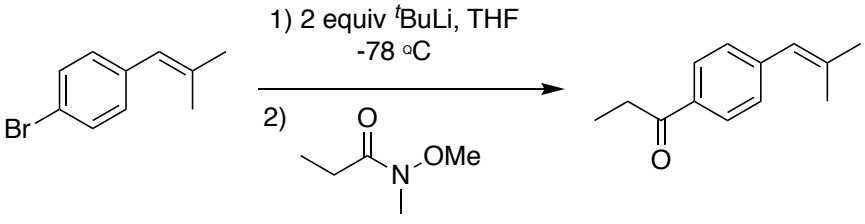
Colourless oil. Yield = 86%. R_f = 0.46, in 10/90 EtOAc/pentane.

^{1}H NMR (400 MHz, CDCl3) δ 5.43 – 5.37 (m, 1H), 4.86 – 4.81 (m, 1H), 3.97 – 3.84 (m, 4H), 2.79 – 2.69 (m, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 2.10 – 2.02 (m, 2H), 1.86 – 1.80 (m, 2H), 1.79 – 1.70 (m, 1H), 1.68 – 1.60 (m, 1H), 1.40 (s, 3H), 0.92 (s, 9H), 0.14 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 134.5, 117.9, 100.8, 99.0, 59.7, 35.7, 33.9, 30.5, 27.2, 25.7, 25.5, 21.2, 18.0, -4.4.

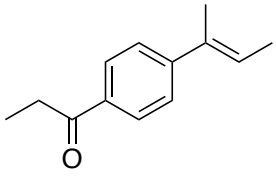
IR (Neat, cm^{-1}): ν = 2954, 2858, 1697, 1665, 1472, 1381, 1247, 1092, 929, 834, 778.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{34}NaO_3Si$ $[M + Na]^+$, 361.2169; found, 361.2158.



In the dried round bottom flask, 1-bromo-4-(2-methylprop-1-en-1-yl)benzene was dissolved in dried THF under nitrogen gas. The solution was cooled to -78 ˚C, then *t*-BuLi was slowly added. The reaction mixture was stirred for 1 hour. Then a solution of *N*-methoxy-*N*-methylpropionamide in THF was slowly added to the lithium aryl solution. The mixture stirred further at the same temperature for another 1 hour. the reaction was quenched by adding saturated NH_4Cl then extracted with Et_2O. The combined organic phase was dried over Na_2SO_4, and the solvent was removed under

vacuum. The crude product was purified by silica column chromatography with 5% EtOAc/Pentane to provide the pure product as a colorless oil.



1-(4-(2-methylprop-1-en-1-yl)phenyl)propan-1-one

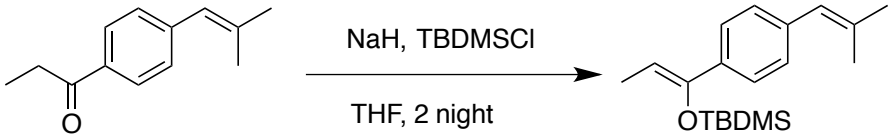
Colorless oil 268 mg 63% yield (R_f = 0.65 Pentane/EtOAc 9:1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.89 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 6.29 (s, 1H), 2.99 (q, *J* = 7.3 Hz, 2H), 1.93 (d, *J* = 1.3 Hz, 3H), 1.89 (d, *J* = 1.2 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H).

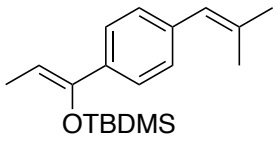
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.15, 143.33, 138.01, 134.19, 128.65, 127.81, 124.47, 31.57, 27.04, 19.55, 8.25.

IR (Neat, cm^{-1}): ν = 2976,1682, 1602, 1225, 1181, 952, 872, 786.

HRMS-ESI; *m/z* [M$^+$+Na] Calcd. for $C_{13}H_{16}NaO$ = 211.1099. Found: 211.1094.



The solution of 1-(4-(2-methylprop-1-en-1-yl)phenyl)propan-1-one and TBDMSCl in dry THF under N_2 was cooled to -78 ˚C. TBDMSCl was added to the reaction mixture which was slowly warmed up to room temperature and stirred for 48 hours. The reaction was quenched with saturated $NaHCO_3$ and extracted with Et_2O, dried over Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by column chromatography (Deactivated-silica) with Pentane as eluent.



(*Z*)-*tert*-butyldimethyl((1-(4-(2-methylprop-1-en-1-yl) phenyl)prop-1-en-1-yl)oxy) silane

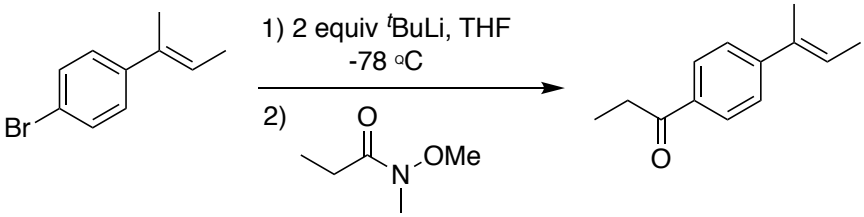
Colorless oil 67 mg 64% yield (R_f =0.60 Pentane/Et_2O 100:1)

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.53 – 7.47 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.27 (s, 1H), 5.21 (q, *J* = 6.8 Hz, 1H), 1.76 (d, *J* = 6.9 Hz, 3H), 1.72 (dd, *J* = 6.6, 1.2 Hz, 3H), 1.05 (s, 9H), 0.02 (s, 6H).

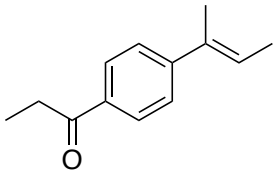
^{13}C NMR (101 MHz, C_6D6) δ 150.79, 138.35, 137.94, 135.17, 128.84, 125.91, 125.75, 105.58, 26.93, 26.17, 19.50, 18.64, 12.01, -3.72.

IR (Neat, cm^{-1}): ν = 2929,1652, 1602, 1471, 1319, 1255, 1060, 838, 779.

HRMS-ESI; *m/z* [M$^+$+Na] Calcd. for $C_{19}H_{31}NaOSi$ = 303.2144. Found: 303.2123.



Was prepared following the procedure described for 1-(4-(2-methylprop-1-en-1-yl)phenyl) propan-1-one.



(*E*)-1-(4-(but-2-en-2-yl)phenyl)propan-1-one

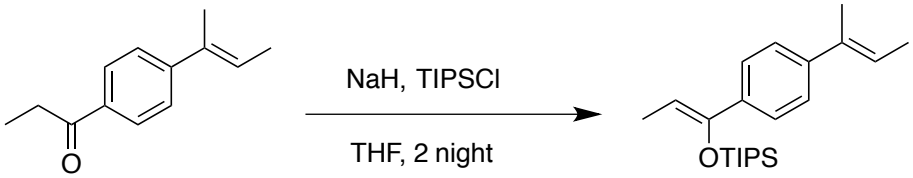
White solid (m.p. 44.5-45.7) 240 mg 47% yield (R_f = 0.65 Pentane/EtOAc 9:1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.44 (dd, *J* = 8.6, 1.9 Hz, 2H), 6.04 – 5.96 (m, 1H), 2.99 (q, *J* = 7.3 Hz, 2H), 2.08 – 2.01 (m, 3H), 1.83 (dd, *J* = 6.9, 1.1 Hz, 3H), 1.22 (t, *J* = 7.3 Hz, 3H).

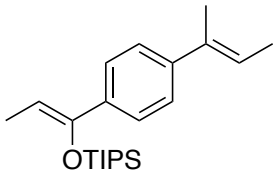
^{13}C NMR (101 MHz, $CDCl_3$) δ 200.33, 148.32, 134.85, 134.76, 128.00, 125.43, 124.82, 31.64, 15.19, 14.44, 8.30.

IR (Neat, cm^{-1}): ν = 2978, 1679, 1602, 1409, 1225, 952, 792.

HRMS-ESI; *m*/*z* [M$^+$+Na] Calcd. for $C_{13}H_{16}NaO$ = 211.1099. Found: 211.1092.



Was prepared following the procedure described for (*Z*)-*tert*-butyldimethyl((1-(4-(2-methylprop-1-en-1-yl)phenyl)prop-1-en-1-yl)oxy)silane.



(((*Z*)-1-(4-((*E*)-but-2-en-2-yl)phenyl)prop-1-en-1-yl)oxy) triisopropylsilane

Colorless oil 199 mg 69% yield (Rf = 0.68 Pentane/Et_2O 100:1)

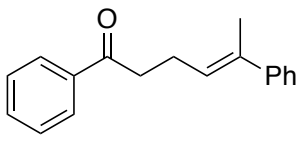
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.55 – 7.50 (m, 2H), 7.34 – 7.29 (m, 2H), 5.83 (m, 1H), 5.10 (q, *J* = 6.8 Hz, 1H), 1.87 – 1.84 (m, 3H), 1.81 (d, *J* = 6.9 Hz, 3H), 1.60 (dd, *J* = 6.9, 1.0 Hz, 3H), 1.13 (q, *J* = 4.2 Hz, 21H). Containing 8% *E* isomer silyl enolate.

^{13}C NMR (101 MHz, C_6D6) δ 151.81, 143.40, 139.11, 135.48, 126.19, 125.49, 122.33, 105.01, 67.84, 25.87, 18.26, 15.35, 14.30, 14.03, 12.00.

IR (Neat, cm^{-1}): ν = 2925, 2867, 1649, 1464, 1322, 1080, 1051, 883, 681.

HRMS-ESI; *m*/*z* [M$^+$+Na] Calcd. for $C_{22}H_{36}NaOSi$ = 367.2433. Found: 367.24396.

Alkyl bromide was added to a suspension of Mg turnings (activated by I_2) in THF (20 mL) at room temperature. The mixture was refluxed for 40 minutes. The mixture was cooled to room temperature and added dropwise to a solution of amide in 20 mL THF at 0 ˚C, then stirred at room temperature overnight. The reaction was quenched with saturated NH_4Cl, extracted with Et_2O, dried over Na_2SO_4 and purified by column chromatography 5%EtOAc/Pentane to yield desired product.

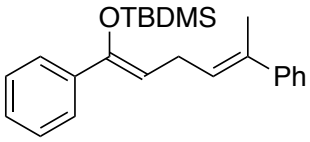


(*E*)-1,5-diphenylhex-4-en-1-one

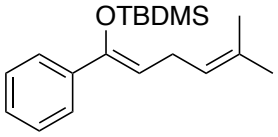
White solid (m.p.52.4-53.8) 2.224 g, 56.8% yield (R_f = Pentane/EtOAc 9:1)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dt, *J* = 8.5, 1.7 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.50 – 7.44 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 5.86 – 5.78 (m, 1H), 3.16 – 3.11 (m, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.08 (d, *J* = 1.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.59, 143.67, 137.00, 135.95, 132.96, 128.57, 128.13, 128.03, 126.65, 126.59, 125.64, 38.37, 23.57, 15.84.
IR (Neat, cm^{-1}): ν = 3056, 2984, 1685, 1597, 1447, 1362, 1202, 974, 757, 691.
HRMS-ESI; *m*/*z* [M^++Na] Calcd. for $C_{18}H_{18}NaO$ = 273.1250. Found: 273.1255.



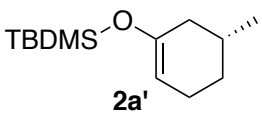
***tert*-butyl (((1*Z*,4*E*)-1,5-diphenylhexa-1,4-dien-1-yl)oxy) dimethylsilane.**
Colorless oil 140 mg, 48% yield (R_f = 0.43 Pentane/Et_2O 100:1)
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.88 – 5.78 (m, 1H), 5.23 (q, *J* = 6.8 Hz, 2H), 1.86 (s, 3H), 1.77 (d, *J* = 6.9 Hz, 3H), 1.65 – 1.59 (m, 3H), 1.07 (s, 9H), 0.03 (s, 6H).
^{13}C NMR (101 MHz, C_6D6) δ 150.20, 144.25, 140.19, 135.75, 128.51, 127.93, 126.94, 126.87, 126.37, 126.13, 110.26, 26.50, 26.11, 25.97, 18.60, 16.04, -3.78.
IR (Neat, cm^{-1}): ν = 2956, 2929, 1648, 1599, 1492, 1444, 1332, 1256, 1075, 1022, 839, 696.
HRMS-ESI; *m*/*z* [M^++Na] Calcd. For $C_{24}H_{32}OSiNa$ = 387.2115. Found: 387.2123.



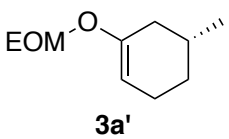
(*Z*)-*tert*-butyldimethyl((5-methyl-1-phenylhexa-1,4-dien-1-yl)oxy) silane
Colorless oil 250 mg, 47% yield (R_f = 0.23 Pentane 100%)
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.52 – 7.48 (m, 2H), 7.15 – 7.03 (m, 3H), 5.36 – 5.29 (m, 1H), 5.19 (t, *J* = 7.2 Hz, 0H), 3.10 (t, *J* = 7.1 Hz, 1H), 1.67 (d, 1H), 1.63 (s, 1H), 1.04 (s, 2H), 0.00 (s, 1H).
^{13}C NMR (101 MHz, C_6D6) δ 149.62, 140.31, 131.80, 128.29, 127.78, 126.30, 123.57, 111.16, 26.12, 25.87, 25.84, 18.59, 17.88, -3.80.
IR (Neat, cm^{-1}): ν = 2958, 2858, 1647, 1462, 1445, 1331, 1256, 1096, 838, 780, 697.
HRMS-ESI; *m*/*z* [M^++H] Calcd. For $C_{19}H_{31}OSi$ = 303.2139. Found: 303.2127.

6. Racemate preparation and *ee* determination of silyl enol ethers

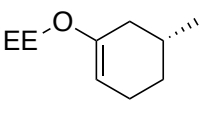
Procedure A: The freshly prepared silyl enol ether 1,4-cyclohexadiene was hydrogenated by the racemic Ir-N,P catalyst **A** and **E** and then the crude hydrogenated products were hydrolyzed to cyclohexanone using 1 mL of 2M HCl in 1mL of co-solvent (Et_2O:Pentane). The mixture was stirred overnight at room temperature. The reaction mixture was extracted with pentane and dried over Na_2SO_4. After removing the solvent, the hydrolyzed product was injected into a chiral GC. GC sample: 1 mg/mL, Et_2O. The *ee*'s of the following compounds (**2a′**, **3a′**, **4a′**, **5a′**, **6a′**, **7a′**, **19a′** and **20a′**) were determined using procedure **A**.



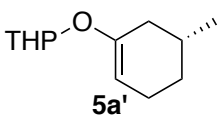
2a'



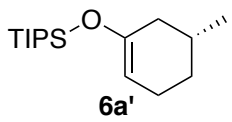
3a'



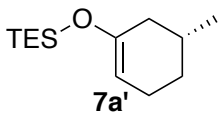
4a'



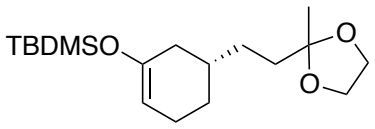
5a'



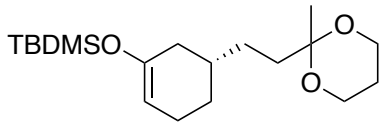
6a'



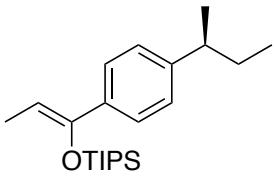
7a'



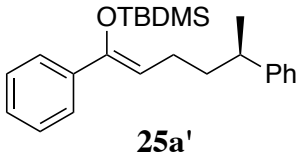
19a'



20a'

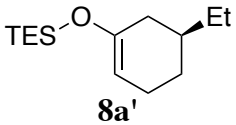


24a'

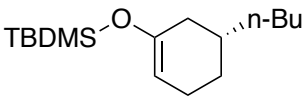


25a'

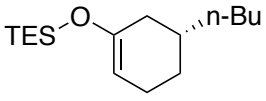
Procedure B: The freshly prepared silyl enol ether 1,4-cyclohexadiene was hydrogenated by the racemic Ir-N,P catalyst **A** and **E,** and then the crude hydrogenated products were passed through a short plug of silica, using Et_2O:Pentane(1/1) as an eluent. After removing the solvent, the hydrogenated products were injected into a chiral GC. GC sample: 1 mg/mL, Et_2O. The *ee*'s of the following compounds (**8a′**, **9a′**, **10a′**, **11a′**, **12a′**, **13a′**, **14a′**, **16a′** and **17a′**) were determined using this procedure **B**.



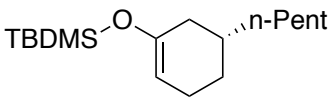
8a'



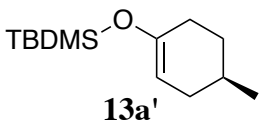
9a'



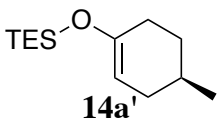
10a'



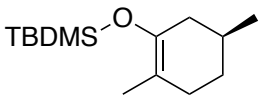
11a'



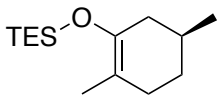
13a'



14a'

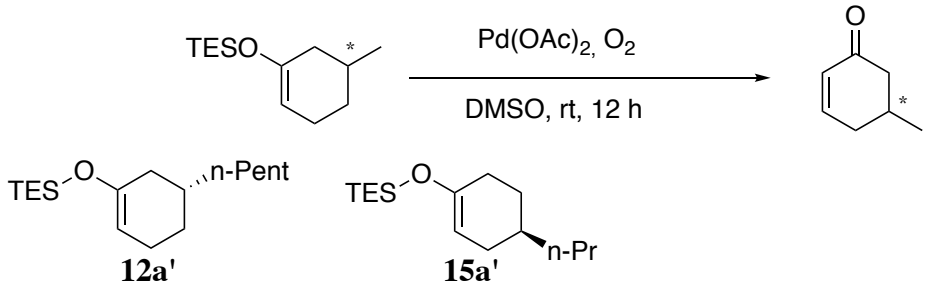


16a'

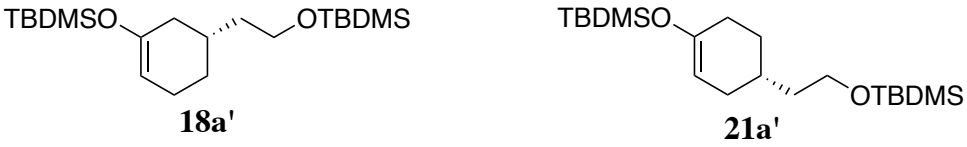


17a'

Procedure C: The freshly prepared silyl enol ether 1,4-cyclohexadiene was hydrogenated by the racemic Ir-N,P catalyst **A** and **E** and then the crude hydrogenated products were passed through a short plug of silica, using Et_2O:Pentane(1/1) as an eluent After removing the solvent, the hydrogenated products were oxidized by using the Saegusa oxidation reaction shown in the scheme below. Recently a modification was reported by Herzon [9] for the Saegusa oxidation. After working up the Saegusa oxidation and purification, the oxidized product was injected to a chiral GC. GC sample: 1 mg/mL, Et_2O. The *ee* of the following compound (**15a′**) was determined using procedure **C**.

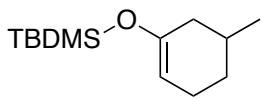


Procedure D: The freshly prepared silyl enol ether 1,4-cyclohexadiene was hydrogenated by the racemic Ir-N,P catalyst **A** and **E** and then the crude hydrogenated products were passed through a short plug of silica, using Et_2O:Pentane(1/1) as an eluent. After removing the solvent, the hydrogenated products were oxidized using the Saegusa oxidation in procedure **C.** After working up the Saegusa oxidation and purification, the oxidized product was hydrolyzed using 1 mL of 2M HCl in 1mL of co-solvent (Et_2O:Pentane). The mixture was stirred overnight at room temperature. The reaction mixture was extracted with pentane and dried over Na_2SO_4. After removing the solvent, the final hydrolyzed product was injected to chiral GC. GC sample: 1 mg/mL, Et_2O. The *ee*'s of the following compounds (**18a′** and **21a′**) were determined using procedure **D**.



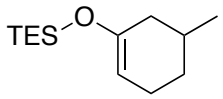
7. General procedure for asymmetric hydrogenations

A glass vial was charged with freshly prepared substrate (0.5 mmol), K_3PO_4 (10 mol%) and Ir-complex (0.5 mol %). $PhCF_3$ (4 mL) was added and the vial was placed in a high-pressure hydrogenation apparatus. The reactor was purged three times with Ar, then filled to the required pressure with H_2. The reaction was stirred at room temperature for 12 hours (unless otherwise stated). The crude product was purified through on a column of silica. The *ee* values were determined using chiral GC.

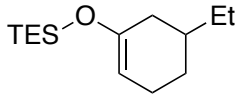


***tert*-Butyldimethyl ((5-methylcyclohex-1-en-1-yl)oxy) silane**
Colourless oil. Yield = 58% (NMR yield using internal standard 1,3,5-trimethoxybenzene.) R_f = 0.4 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 – 4.82 (m, 1H), 2.07 – 1.97 (m, 3H), 1.80 – 1.56 (m, 3H), 1.17 – 1.04 (m, 1H), 0.96 (d, *J* = 6.4 Hz, 3H), 0.92 (s, 9H), 0.12 (s, 3H), 0.12 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 103.8, 38.3, 30.6, 29.3, 25.7, 23.4, 21.6, 18.0, -4.3.
IR (Neat, cm^{-1}): ν = 2954, 2928, 2857, 1670, 1472, 1461, 1369, 1256, 1194, 890, 834, 778.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{27}OSi$ $[M + Na]^+$, 227.1831; found, 227.1813.

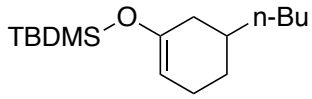
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 50.7 (*c* = 0.140 in $CHCl_3$)
GC-MS: column Chiraldex β-DM, 60 ˚C isothermal, t_R = 23.5 min (major)/24.9 min (minor), 96% *ee*.



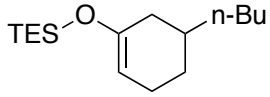
Triethyl ((5-methylcyclohex-1-en-1-yl)oxy)silane
Colourless oil. Yield = 79%. (Isolated yield, observed 12% over reduction product.) R_f = 0.3 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 – 4.83 (m, 1H), 2.07 – 1.99 (m, 3H), 1.78 – 1.56 (m, 3H), 1.16 – 1.03 (m, 1H), 1.01 – 0.94 (m, 9H), 0.65 (q, *J* = 8.4, 7.9 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 103.3, 38.3, 30.5, 29.4, 23.4, 21.6, 6.7, 5.1.
IR (Neat, cm^{-1}): ν = 2954, 2913, 2877, 1669, 1457, 1369, 1238, 1188, 1005, 886, 744.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{27}OSi$ $[M + Na]^+$, 227.1831; found, 227.1848.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 46.4 (*c* = 0.345 in $CHCl_3$)
GC-MS: column Chiraldex β-DM, 60 ˚C isothermal, t_R = 24.2 min (major)/26.5 min (minor), 94% *ee*.



Triethyl ((5-ethylcyclohex-1-en-1-yl) oxy) silane
Colourless oil. Yield = 56%. (Isolated yield, observed 11% hydrolysis product.) R_f = 0.32 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 4.88 -4.84 (m, 1H), 2.04-2.00 (m, 3H), 1.74-1.64 (m, 3H), 1.35-1.21(m, 4H), 0.99-0.89 (m, 12H), 0.68-0.62 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 150.1, 103.5, 36.3, 36.2, 28.9, 28.3, 23.4, 11.5, 6.7, 5.1.
IR (Neat, cm^{-1}): ν = 2917, 1669, 1461, 1371, 1188, 1016, 899, 870, 743.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{29}OSi$ $[M + H]^+$, 241.1982; found, 241.1990.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = -9.524, (*c* = 0.1050, $CHCl_3$).
GC-MS: column Chiraldex β-3p, 80 ˚C isothermal, t_R = 207.6 min (minor)/211.5 min (major), 99% *ee*.

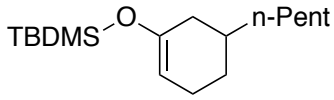


***tert*-Butyl ((5-butylcyclohex-1-en-1-yl) oxy) dimethylsilane**
Colourless oil. Yield = 54% (NMR yield using internal standard 1,3,5-trimethoxybenzene). R_f = 0.38 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 4.88 -4.83 (m, 1H), 2.06-2.00 (m, 3H), 1.74-1.54 (m, 3H), 1.35-1.26(m, 8H), 0.93-0.91 (m, 12H), 0.13-0.12 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 150.2, 103.9, 36.6, 36.0, 34.4, 29.2, 28.8, 25.7, 25.7, 23.4, 22.9, 18.0, 14.1, -4.3.
IR (Neat, cm^{-1}): ν = 2918, 1671, 1462, 1362, 1255, 1112, 1020, 928, 833, 776.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{32}NaOSi$ $[M + Na]^+$, 291.2115; found, 291.2109.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +36.413, (*c* = 0.1843, $CHCl_3$).
GC-MS: column Chiraldex β-DM, 70 ˚C isothermal, t_R = 67.9 min (minor)/69.7 min (major), 92% *ee*.

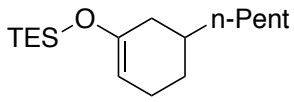


((5-Butylcyclohex-1-en-1-yl) oxy) triethyl silane
Colourless oil. Yield = 55% (Isolated yield). R_f = 0.30 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (q, *J* = 2.9, 2.1 Hz, 1H), 2.10 – 1.97 (m, 3H), 1.76 – 1.56 (m, 3H), 1.29 (t, *J* = 5.3 Hz, 6H), 1.16 – 1.04 (m, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.93 – 0.85 (m, 3H), 0.65 (q, *J* = 7.9 Hz, 6H).

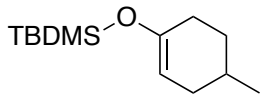
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 103.5, 36.6, 36.0, 34.5, 29.2, 28.8, 23.4, 22.9, 14.1, 6.7, 5.1.
IR (Neat, cm^{-1}): ν = 2956, 2917, 1669, 1458, 1371, 1184, 1005, 744.
HRMS-ESI; *m*/*z* [M^++Na] = 291.2106, calcd. For $C_{16}H_{32}NaOsi$: 291.2115.
HRMS (ESI): *m*/*z* calcd for $C_{16}H_{32}NaOSi$ $[M + Na]^+$, 291.2115; found, 291.2106.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 12.8 (*c* = 0.143 in $CHCl_3$)
GC-MS: column Chiraldex β-DM, 70 ˚C isothermal, t_R = 132.2 min (major)/126.8 min (minor), 95% *ee*.



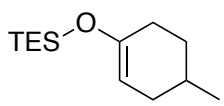
***tert*-Butyldimethyl ((5-pentylcyclohex-1-en-1-yl) oxy) silane**
Colourless oil. Yield = 78% (NMR yield using internal standard 1,3,5-trimethoxybenzene). R_f = 0.38 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 4.86-4.83(m, 1H), 2.06-1.99(m, 3H), 1.72-1.57(m, 3H), 1.34-1.26(m, 9H), 0.93-0.91(m, 12H), 0.13-0.11(m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): 150.2, 103.9, 36.6, 36.3, 36.0, 34.4, 32.1, 29.2, 28.8, 27.4, 26.6, 25.7, 23.4, 22.9, 22.7, 18.0, 14.1, -4.3, -4.5.
IR (Neat, cm^{-1}): ν = 2927, 1670, 1462, 1362, 1255, 1196, 1179, 1051, 939, 836, 777, 671.
HRMS (ESI): *m*/*z* calcd for $C_{17}H_{34}OSi$ $[M]^+$, 283.2379; found, 282.2358.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +32.022, (*c* = 0.1781, $CHCl_3$).
GC-MS: column Chiraldex β-DM, 80 ˚C isothermal, t_R = 68.1 min (minor)/70.2 min (major), 96% *ee*.



Triethyl ((5-pentylcyclohex-1-en-1-yl) oxy) silane
Colourless oil. Yield = 70% (NMR yield using internal standard 1,3,5-trimethoxybenzene). R_f = 0.36 in pentane.
GC-MS: column Chiraldex β-DM, 80 ˚C isothermal, t_R = 67.9 min (minor)/69.9 min (major), 95% *ee*.

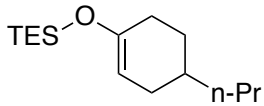


***tert*-butyldimethyl ((4-methylcyclohex-1-en-1-yl) oxy) silane**
Colourless oil. Yield = 45% (NMR yield using internal standard 1,3,5-Trimethoxybenzene). R_f = 0.40 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 – 4.79 (m, 1H), 2.16 – 1.91 (m, 3H), 1.74 – 1.56 (m, 3H), 1.39 – 1.22 (m, 1H), 0.94 (d, *J* = 6.3 Hz, 3H), 0.91 (s, 9H), 0.12 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 103.7, 32.3, 31.3, 29.6, 28.3, 25.7, 21.3, 18.0, -4.4.
IR (Neat, cm^{-1}): ν = 2954, 2928, 2857, 1670, 1461, 1370, 1256, 1194, 879, 777.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{27}OSi$ $[M + Na]^+$, 227.1831; found, 227.1830.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 46.1 (*c* = 0.193 in $CHCl_3$)
GC-MS: column Chiraldex β-DM, 80˚C isothermal, t_R = 48.2 min (major)/46.9 min (minor), 80% *ee*.

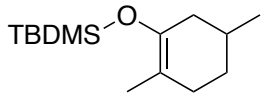


Triethyl ((4-methylcyclohex-1-en-1-yl)oxy) silane
Colourless oil. Yield = 75%. (Isolated yield, observed 20% over reduction product.) R_f = 0.36 in pentane.

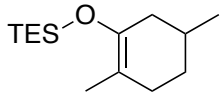
^{1}H NMR (400 MHz, $CDCl_3$): 4.88 -4.77 (m, 1H), 2.18 - 1.92 (m, 3H), 1.77 - 1.54 (m, 4H), 1.50 - 1.23 (m, 3H), 0.95 (dt, *J* = 16.4, 8.0 Hz, 21H), 0.72 - 0.46 (m, 11H).
^{13}C NMR (100 MHz, $CDCl_3$): 150.2, 103.3, 33.1, 32.3, 31.3, 29.6, 29.3, 28.4, 21.3, 6.9, 6.8, 6.7, 6.4, 5.1, 4.9.
IR (Neat, cm^{-1}): ν = 2914, 1670, 1457, 1414, 1370, 1237, 1190, 1073, 1017, 865, 742.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{26}NaOSi$ $[M + Na]^+$, 249.1645; found, 249.1652.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +23.348, (*c* = 0.2273, $CHCl_3$).
GC-MS: column Chiraldex β-DM, 80 ˚C isothermal, t_R = 77.5 min (minor)/79.4 min (major), 95% *ee*.



Triethyl ((4-propylcyclohex-1-en-1-yl) oxy) silane
Colourless oil. Yield = 56%. (Isolated yield, observed 24% over reduction product.) R_f = 0.36 in pentane.
^{1}H NMR (400 MHz, $CDCl_3$): 4.88 - 4.79 (m, 1H), 2.18 -1.93 (m, 3H), 1.80 - 1.55 (m, 3H), 1.52 -1.17 (m, 9H), 1.01 - 0.83 (m, 18H), 0.66 (t, *J* = 7.8 Hz, 6H), 0.55 (dq, *J* = 19.6, 7.9 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): 150.4, 103.3, 38.3, 33.1, 33.1, 30.4, 29.7, 29.4, 27.3, 20.3, 14.4, 6.9, 6.8, 6.7, 6.4, 5.1, 5.0.
IR (Neat, cm^{-1}): ν = 2876, 1670, 1458, 1415, 1374, 1188, 1017, 865, 770.
HRMS (ESI): *m*/*z* calcd for $C_{15}H_{30}OSiNa$ $[M + Na]^+$, 277.1958; found, 277.1961.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +31.364, (*c* = 0.2195, $CHCl_3$).
GC-MS: column Chiraldex β-DM, 70 ˚C isothermal, t_R = 104.2 min (major)/111.9 min (minor), 92% *ee*.

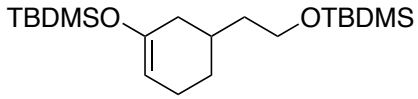


***tert*-Butyl ((2,5-dimethylcyclohex-1-en-1-yl)oxy) dimethyl silane**
Colourless oil. Yield = 81%. (Isolated yield, remaining 1% aromatized starting material) R_f = 0.40 in pentane.
^{1}H NMR (400 MHz, CDCl3) δ 2.12 – 2.00 (m, 2H), 1.98 – 1.88 (m, 1H), 1.81 – 1.61 (m, 3H), 1.60 (s, 3H), 1.23 – 1.10 (m, 1H), 0.97 (s, 9H), 0.14 (d, *J* = 1.1 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 111.0, 38.8, 31.2, 30.0, 25.9, 21.7, 18.2, 16.2, -3.7.
IR (Neat, cm^{-1}): ν = 2954, 2927, 1688, 1461, 1256, 1177, 835, 777.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{18}NaOSi$ $[M + H]^+$, 241.1982; found, 241.1979.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= -11.3 (*c* = 0.154 in $CHCl_3$)
GC-MS: column Chiraldex β-3P, 90 ˚C isothermal, t_R = 37.6 min (major)/35.7 min (minor), 95% *ee*.



((2,5-dimethylcyclohex-1-en-1-yl)oxy) triethyl silane
Colourless oil. Yield = 79%. (Isolated yield, remaining 0.05% aromatized starting material). R_f = 0.27 in pentene.
^{1}H NMR (400 MHz, CDCl3) δ 2.08 – 1.97 (m, 2H), 1.95 – 1.86 (m, 1H), 1.78 – 1.69 (m, 2H), 1.66 – 1.59 (m, 4H), 1.58 (s, 1H), 1.03 – 0.92 (m, 12H), 0.65 (q, *J* = 8.0 Hz, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 110.8, 38.7, 31.1, 30.0, 21.6, 16.0, 6.8, 5.7.
IR (Neat, cm^{-1}): ν = 2954, 2911, 1689, 1457, 1378, 1185, 1005, 803, 742.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{28}NaOSi$ $[M + Na]^+$, 263.1802; found, 263.1789.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= -45.4 (*c* = 0.275 in $CHCl_3$)

GC-MS: column Chiraldex β-DM, 100 ˚C isothermal, t_R = 32.6 min (major)/31.9 min (minor), 98% *ee*.



***tert*-Butyl(2-(3-((tert-butyldimethylsilyl)oxy) cyclohex-3-en-1-yl)ethoxy)dimethylsilane**

Colourless oil. Conversion = 89%. R_f = 0.40 in pentane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.88 – 4.80 (m, 1H), 3.72 – 3.59 (m, 4H), 2.47 – 2.11 (m, 3H), 2.11 – 1.86 (m, 6H), 1.87 – 1.04 (m, 12H), 0.95 – 0.83 (m, 31H), 0.12 (d, J = 1.5 Hz, 6H), 0.05 (s, 12H).

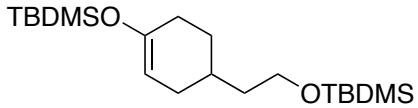
^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 149.9, 103.9, 61.1, 60.5, 48.1, 41.5, 39.3, 39.1, 36.5, 35.7, 31.3, 31.1, 28.6, 26.0, 25.9, 25.7, 25.3, 23.3, 18.3, 18.0, -4.3, -4.4, -5.3, -5.4.

IR (Neat, cm^{-1}): ν = 2928, 1670, 1463, 1361, 1255, 1199, 1103, 835, 775.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{42}O_2Si_2$ $[M + Na]^+$, 393.2616; found, 393.2624.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +22.286, (*c* = 0.1753, $CHCl_3$).

GC-MS: column Beta-dex 225, 125 ˚C isothermal, t_R = 20.4 min (minor)/22.5 min (major), 97% *ee*.



***tert*-Butyl(2-(4-((*tert*-butyldimethylsilyl)oxy) cyclohex-3-en-1-yl)ethoxy)dimethylsilane**

Colourless oil. Conversion = 94%. R_f = 0.38 in pentane.

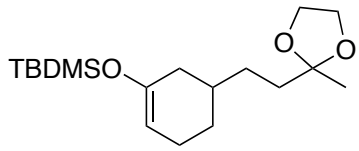
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83-4.81 (m, 1H), 3.67 (dt, J = 13.4, 6.7 Hz, 4H), 2.54 – 1.82 (m, 9H), 1.82 – 1.15 (m, 13H), 0.96 – 0.83 (m, 34H), 0.11 (d, J = 6.7 Hz, 8H), 0.06 (s, 11H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 150.4, 103.6, 61.4, 61.0, 40.8, 38.8, 38.3, 32.7, 30.4, 30.0, 29.5, 29.2, 26.0, 25.7, 18.4, 18.0, -3.6, -4.4, -4.5, -5.3.

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{42}O_2Si_2$ $[M + Na]^+$, 393.2616; found, 393.2612.

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$ = +20.225 (*c* = 0.178, $CHCl_3$)

GC-MS: column Beta-dex 225, 125 ˚C isothermal, t_R = 29.3 min (major)/38.4 min (minor), 94% *ee*.



***tert*-Butyldimethyl ((5-(2-(2-methyl-1,3-dioxolan-2-yl) ethyl) cyclohex-1-en-1-yl) oxy) silane**

Colourless oil. Yield = 89%. R_f = 0.46, in 10/90 EtOAc/pentane.

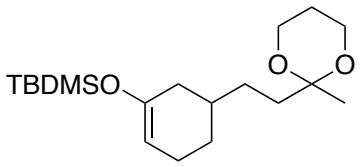
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 – 4.81 (m, 1H), 3.99 – 3.88 (m, 4H), 2.09 – 1.98 (m, 3H), 1.77 – 1.54 (m, 6H), 1.46 – 1.33 (m, 2H), 1.31 (s, 3H), 1.19 – 1.05 (m, 1H), 0.91 (s, 9H), 0.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 110.2, 103.9, 64.6, 36.7, 34.7, 30.4, 28.7, 25.7, 23.8, 23.4, 18.0, -4.5.

IR (Neat, cm^{-1}): ν = 2929, 2858, 1670, 1472, 1374, 1256, 1195, 1069, 836, 778.

HRMS (ESI): *m*/*z* calcd for $C_{18}H_{34}NaO_3Si$ $[M + Na]^+$, 349.2169; found, 349.2164.

GC-MS: column Chiraldex β-6TBDM, 80 ˚C isothermal, t_R = 170.6 min (major)/168.3 min (minor), 95% *ee*.



***tert*-Butyldimethyl ((5-(2-(2-methyl-1,3-dioxan-2-yl) ethyl) cyclohex-1-en-1-yl) oxy) silane**

Colourless oil. Yield = 82%. R_f = 0.46, in 10/90 EtOAc/pentane.

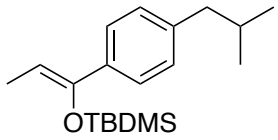
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 – 4.82 (m, 1H), 3.97 – 3.83 (m, 3H), 2.09 – 1.98 (m, 7H), 1.80 – 1.57 (m, 3H), 1.45 – 1.31 (m, 3H), 1.39 (s, 3H), 0.91 (s, 5H), 0.12 (s, 3H), 0.11 (s, 3H),

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 103.9, 99.3, 59.6, 36.5, 35.8, 34.8, 29.8, 28.7, 27.3, 25.7, 25.5, 23.4, 20.7, 18.0, -4.3, -4.5.

IR (Neat, cm^{-1}): ν = 2953, 2858, 1670, 1472, 1369, 1248, 1195, 1100, 836, 778.

HRMS (ESI): *m*/*z* calcd for $C_{19}H_{36}NaO_3Si$ $[M + Na]^+$, 363.2326; found, 363.2333.

GC-MS: column Chiraldex β-6TBDM, 80 ˚C isothermal, t_R = 171.6 min (major)/168.1 min (minor), 98% *ee*.



(*Z*)-*tert*-butyl((1-(4-isobutylphenyl)prop-1-en-1-yl)oxy)dimethylsilane

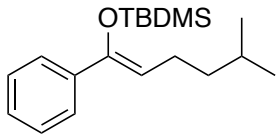
Colourless oil. Yield = 81%. (Isolated yield, observed 3% over reduction product.) R_f = 0.23 in pentane.

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.50 – 7.45 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 5.19 (q, *J* = 6.8 Hz, 1H), 2.34 (d, *J* = 7.2 Hz, 2H), 1.77 (d, *J* = 6.8 Hz, 2H), 1.05 (s, 9H), 0.84 (d, *J* = 6.6 Hz, 6H), 0.02 (s, 6H).

^{13}C NMR (101 MHz, C_6D6) δ 150.85, 141.06, 138.02, 129.06, 126.07, 105.25, 45.39, 26.14, 22.47, 18.62, 11.98, -3.77.

IR (Neat, cm^{-1}): ν = 2956, 2859, 1654, 1509, 1471, 1464, 1319, 1255, 1116, 1059, 871, 839, 779.

HRMS-ESI; *m*/*z* $[M^+ + Na]$ Calcd. for $C_{19}H_{32}NaOSi$ = 327.2115. Found: 327.2120.



(*Z*)-*tert*-butyldimethyl((5-methyl-1-phenylhex-1-en-1-yl)oxy) silane.

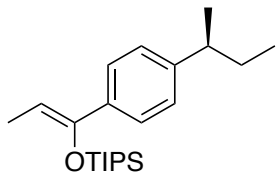
Colourless oil. Yield = 78%. (Isolated yield, observed 3% over reduction product.) R_f = 0.33 in pentane.

^{1}H NMR (400 MHz, Benzene-d_6) δ 7.55 – 7.51 (m, 2H), 7.17 – 7.11 (m, 3H), 7.10 – 7.04 (m, 1H), 5.15 (t, *J* = 7.2 Hz, 1H), 2.38 – 2.29 (m, 2H), 1.66 – 1.54 (m, 1H), 1.37 – 1.28 (m, 2H), 1.05 (s, 9H), 0.93 (d, *J* = 6.6 Hz, 6H), 0.01 (s, 6H).

^{13}C NMR (101 MHz, C_6D6) δ 149.74, 140.44, 127.73, 126.31, 112.47, 39.23, 28.25, 26.12, 24.68, 22.80, 18.59, -3.78.

IR (Neat, cm^{-1}): ν = 2955, 1650, 1471, 1335, 1256, 1080, 838, 779.

HRMS-ESI; *m*/*z* $[M^+ + Na]$ Calcd. for $C_{19}H_{32}NaOSi$ = 327.2115. Found: 327.2117.



(*S*,*Z*)-((1-(4-(*sec*-butyl)phenyl)prop-1-en-1-yl)oxy) triisopropylsilane.

Colourless oil. Yield = 82%. (Isolated yield, observed 2% over reduction product.) R_f = 0.30 in pentane.

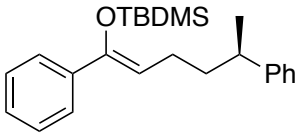
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 5.07 (q, *J* = 6.8 Hz, 1H), 2.48 – 2.36 (m, 2H), 1.81 (d, *J* = 6.8 Hz, 3H), 1.55 – 1.41 (m, 2H), 1.18 – 1.06 (m, 18H), 0.76 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, C_6D6) δ 151.91, 147.03, 138.74, 127.01, 126.47, 104.71, 41.73, 31.48, 22.08, 18.35, 18.20, 13.98, 12.39, 11.96.

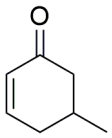
IR (Neat, cm^{-1}): ν = 2961, 2867, 1651, 1463, 1378, 1321, 1064, 883, 681.

HRMS-ESI; *m*/*z* $[M^+ + Na]$ Calcd. for $C_{22}H_{39}OSi$ = 347.2765. Found: 347.2775.

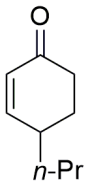
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 15.0 (*c* = 0.340 in $CHCl_3$)
GC-MS: column Chiraldex β-DM, 120 ˚C isothermal, t_R = 32.0 min (major)/33.5 min (minor), 99% *ee*.



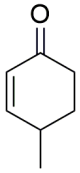
(*R*,*Z*)-*tert*-butyl((1,5-diphenylhex-1-en-1-yl)oxy) dimethylsilane.
Colourless oil. Yield = 93%. (Isolated yield, observed 5% over reduction product.) R_f = 0.74 in 4% Et_2O/pentane.
^{1}H NMR (400 MHz, Benzene-d_6) δ 7.54 – 7.47 (m, 2H), 7.24 – 7.02 (m, 8H), 5.10 (t, *J* = 7.1 Hz, 1H), 2.64 (h, *J* = 6.9 Hz, 1H), 2.20 (q, *J* = 7.7 Hz, 2H), 1.73 – 1.57 (m, 2H), 1.20 (d, *J* = 7.0 Hz, 3H), 0.98 (s, 9H), -0.08 (d, *J* = 4.9 Hz, 6H).
^{13}C NMR (101 MHz, C_6D6) δ 149.85, 147.62, 140.39, 128.72, 127.76, 127.45, 126.27, 112.05, 40.28, 38.81, 26.10, 25.07, 22.47, 18.53, -3.84.
IR (Neat, cm^{-1}): ν = 2957, 1648, 1493, 1331, 1256, 1068, 876, 838, 779.
HRMS-ESI; *m*/*z* [M^++Na] Calcd. for $C_{24}H_{34}NaOSi$ = 389.2271. Found: 389.2284.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$= 22.8 (*c* = 0.464 in $CHCl_3$)
SFC-HPLC: column OJ-H 10% MeOH, t_R = 6.2 min (major)/7.4 min (minor), 98% *ee*.



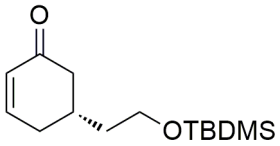
This compound has been previously reported. [10]



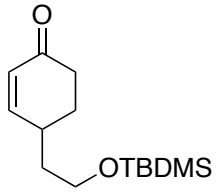
This compound has been previously reported. [11]



This compound has been previously reported. [12]

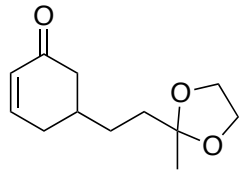


This compound has been previously reported. [13]

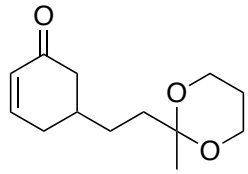


4-(2-((tert-Butyldimethylsilyl) oxy) ethyl)cyclohex-2-en-1-one
Colourless oil. Yield = 62%. R_f = 0.29, in 10/90 EtOAc/pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (ddd, *J* = 10.2, 2.8, 1.3 Hz, 1H), 5.97 (ddd, *J* = 10.2, 2.5, 0.8 Hz, 1H), 3.82 - 3.67 (m, 2H), 2.68 - 2.57 (m, 1H), 2.56 - 2.44 (m, 1H), 2.37 (ddd, *J* = 16.8, 12.1, 4.9 Hz, 1H), 2.19 - 2.07 (m, 1H), 1.82 -1.54 (m, 4H), 0.90 (s, 9H),

0.06 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.9, 155.3, 128.9, 60.4, 37.3, 36.9, 33.0, 28.6, 25.9, 18.3, -5.3, -5.4.
IR (Neat, cm^{-1}): ν = 2928, 1688, 1463, 1389, 1255, 1106, 836, 776.
HRMS (ESI): *m*/*z* calcd for $C_{14}H_{26}NaO_2Si$ $[M + Na]^+$, 277.1587; found, 277.1594.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$ = +29.078 (*c* = 0.1408, $CHCl_3$)

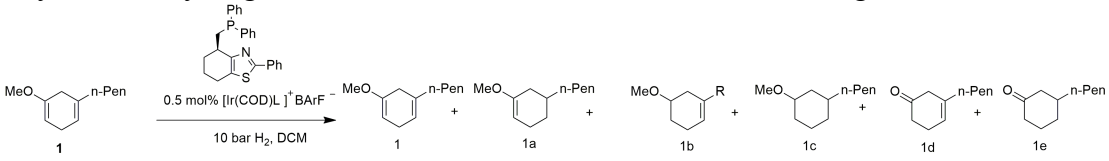


5-(2-(2-Methyl-1,3-dioxolan-2-yl) ethyl) cyclohex-2-en-1-one
Colourless oil. Yield = 56%. R_f = 0.30 in 30/70 EtOAc/pentane.
^{1}H NMR (400 MHz, CDCl3) δ 6.96 (ddd, *J* = 10.0, 5.7, 2.2 Hz, 1H), 6.01 (ddd, *J* = 10.1, 2.5, 1.1 Hz, 1H), 4.00 - 3.87 (m, 4H), 2.59 - 2.38 (m, 2H), 2.20 - 1.98 (m, 3H), 1.72 - 1.59 (m, 2H), 1.54 - 1.43 (m, 2H), 1.31 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 149.7, 129.8, 109.8, 64.7, 44.5, 36.2, 35.3, 32.2, 29.9, 23.8.
IR (Neat, cm^{-1}): ν = 2927, 1682, 1455, 1377, 1251, 1218, 1135, 1055, 947, 836, 756.
HRMS (ESI): *m*/*z* calcd for $C_{12}H_{18}NaO_3$ $[M + Na]^+$, 233.1148; found, 233.1156.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$ = -15.20 (*c* = 0.125, $CHCl_3$)



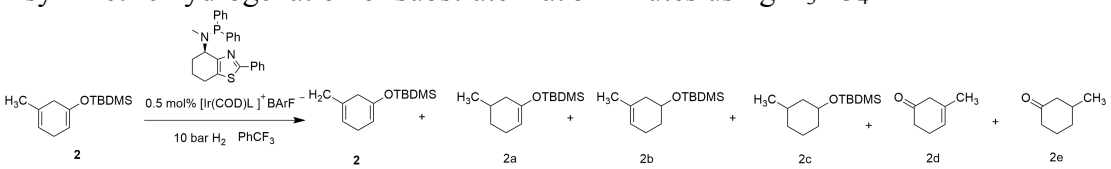
5-(2-(2-Methyl-1,3-dioxan-2-yl)ethyl) cyclohex-2-en-1-one
Colourless oil. Yield = 51%. R_f = 0.28 in 30/70 EtOAc/pentane.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (ddd, *J* = 10.1, 5.7, 2.2 Hz, 1H), 6.02 (ddt, *J* = 10.1, 2.6, 1.1 Hz, 1H), 4.03 - 3.75 (m, 4H), 2.62 - 2.37 (m, 2H), 2.21 - 1.98 (m, 3H), 1.92 -1.61 (m, 3H), 1.61 - 1.45 (m, 4H), 1.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 199.9, 149.8, 149.5, 129.8, 98.9, 59.7, 44.5, 44.1, 40.5, 36.1, 35.5, 34.7, 32.3, 32.2, 29.3, 25.5, 20.3.
IR (Neat, cm^{-1}): ν = 2924, 1668, 1455, 1386, 1248, 1095, 967, 879, 845, 753.
HRMS (ESI): *m*/*z* calcd for $C_{13}H_{20}NaO_3$ $[M + Na]^+$, 247.1305; found, 247.1313.
$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$ = -28.986 (*c* = 0.1375, $CHCl_3$)

Asymmetric hydrogenation of substrate **1** at 5 and 10 minutes using PVP



Entry	Time	Additive	1	1a	1b	1c	1d	1e
1	10 min	PVP	51.8	38.7	-	-	-	9.5
2	5 min	PVP	75.5	20	-	-	-	4.5
3	5 min	-	72	11	-	-	9	8

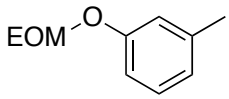
Asymmetric hydrogenation of substrate **2** at 5 minutes using K_3PO_4

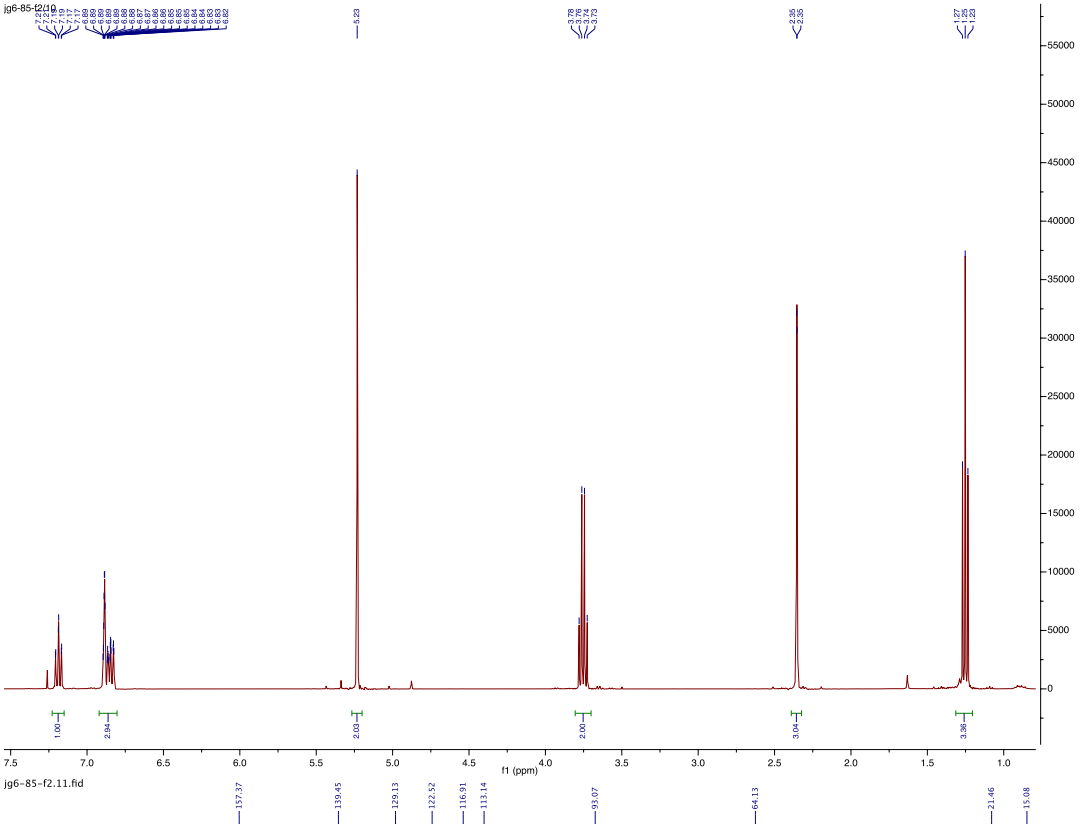


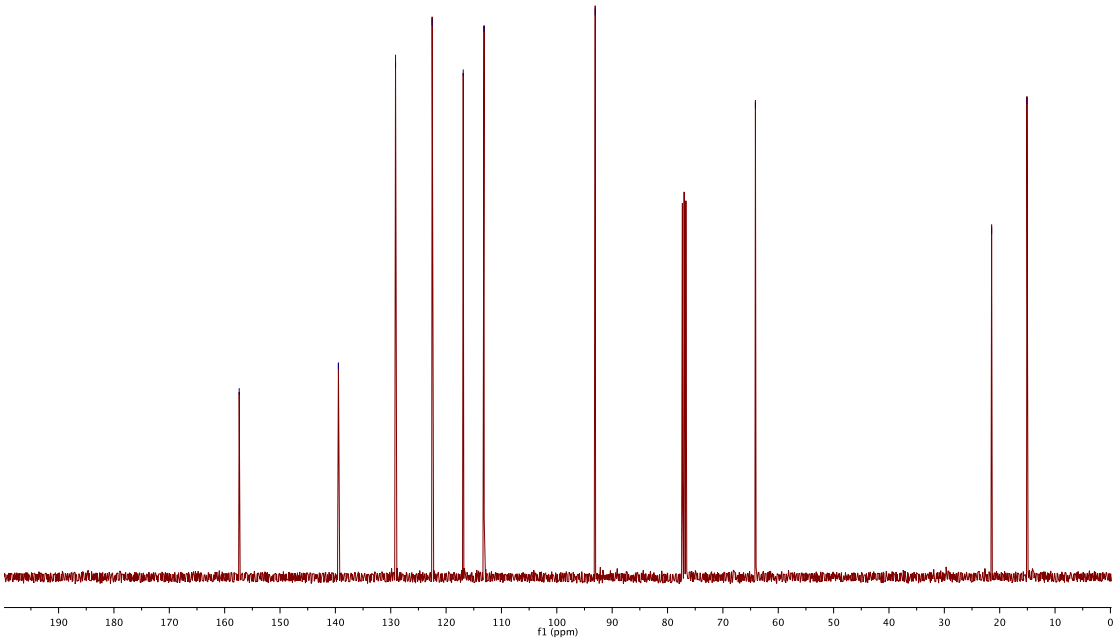
2 **2** 2a 2b 2c 2d 2e

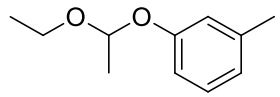
Entry	Time	Additive	**2**	2a	2b	2c	2d	2e
1	5 min	-	57.15	0.95	-	-	19.0	22.9
2	5 min	K_3PO_4	53.7	40.6	-	-	2.0	3.7

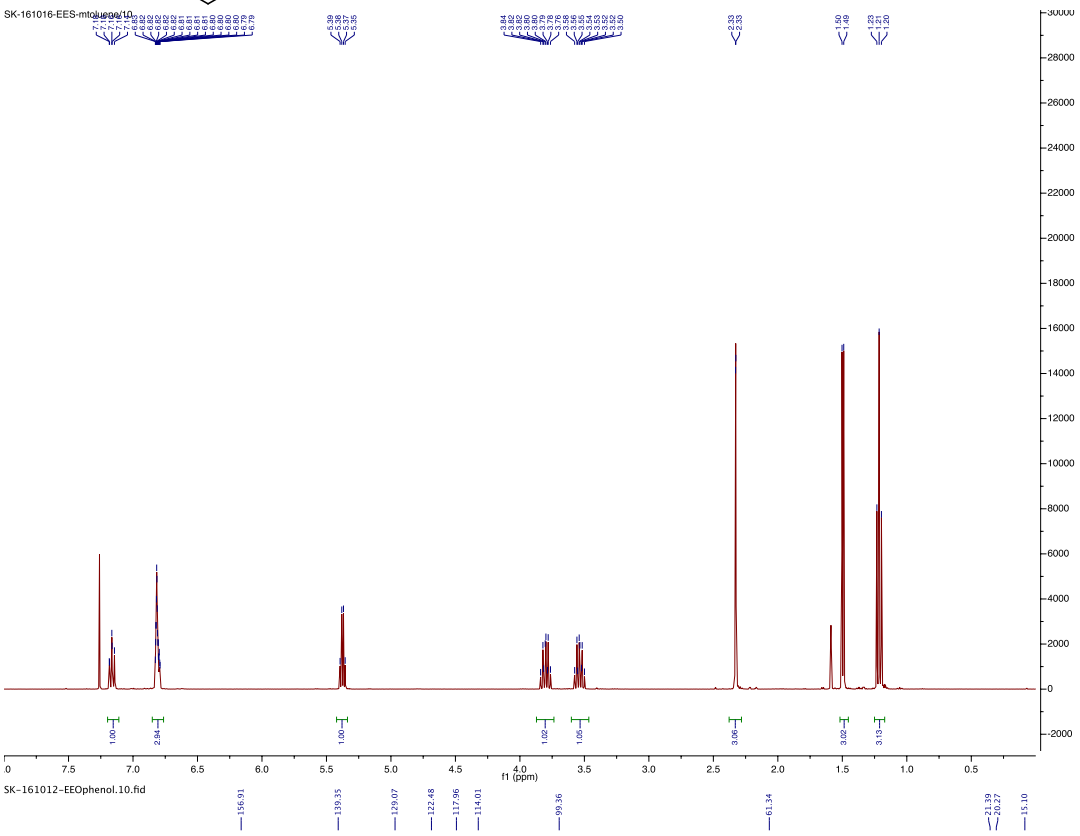
^{1}H and ^{13}C NMR Spectroscopic data of new compounds







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f1 (ppm)

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129.07
122.48
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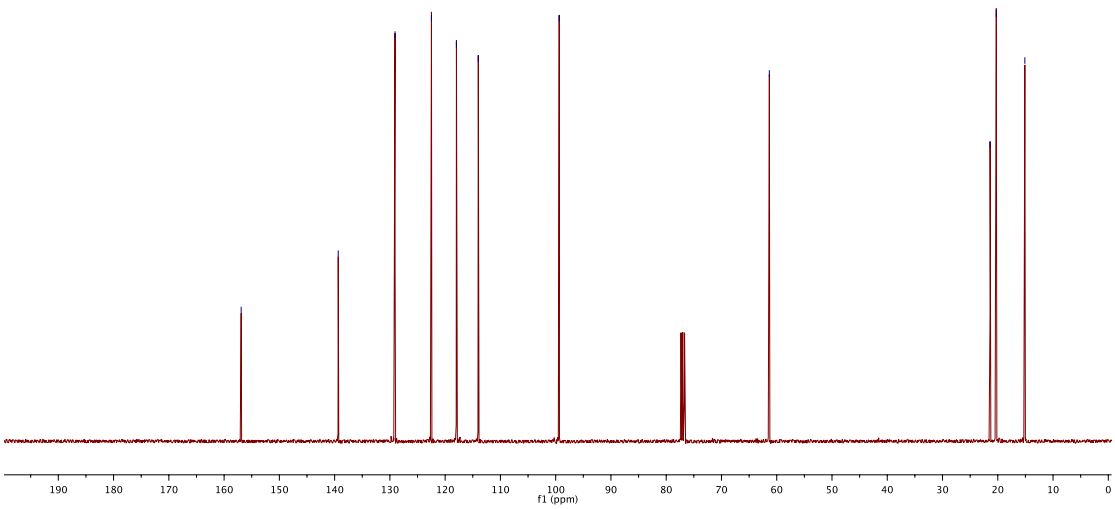
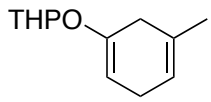
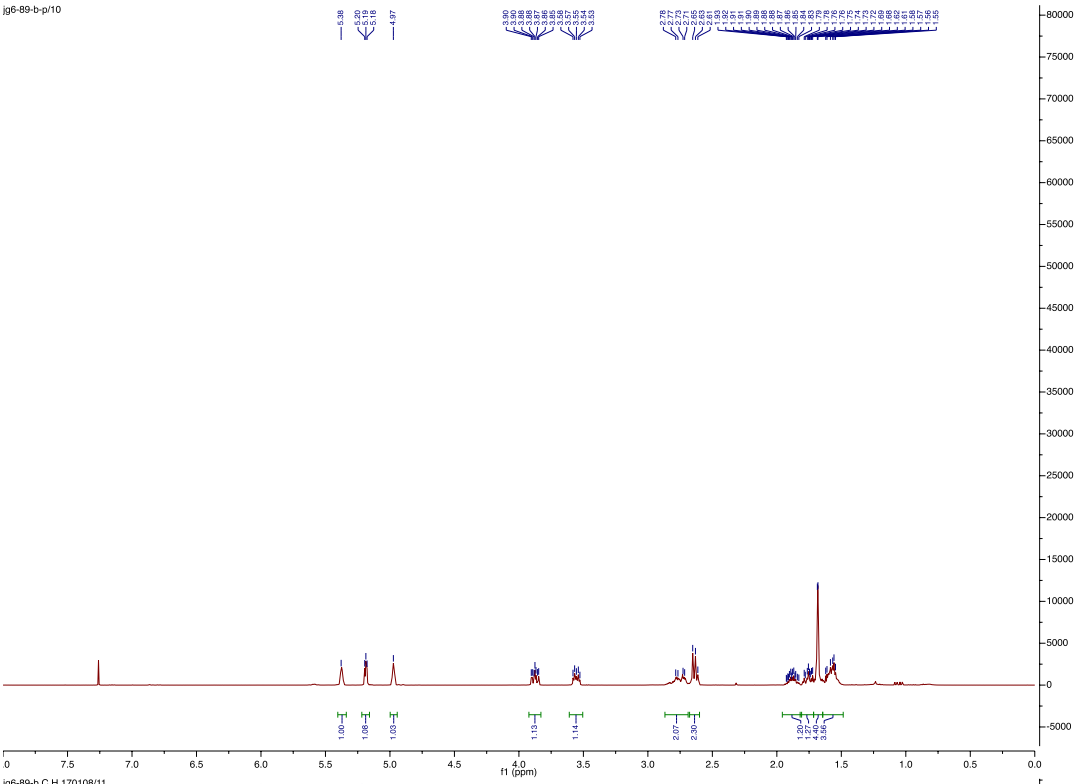
114.01
99.36
61.34
21.39
20.27
15.10

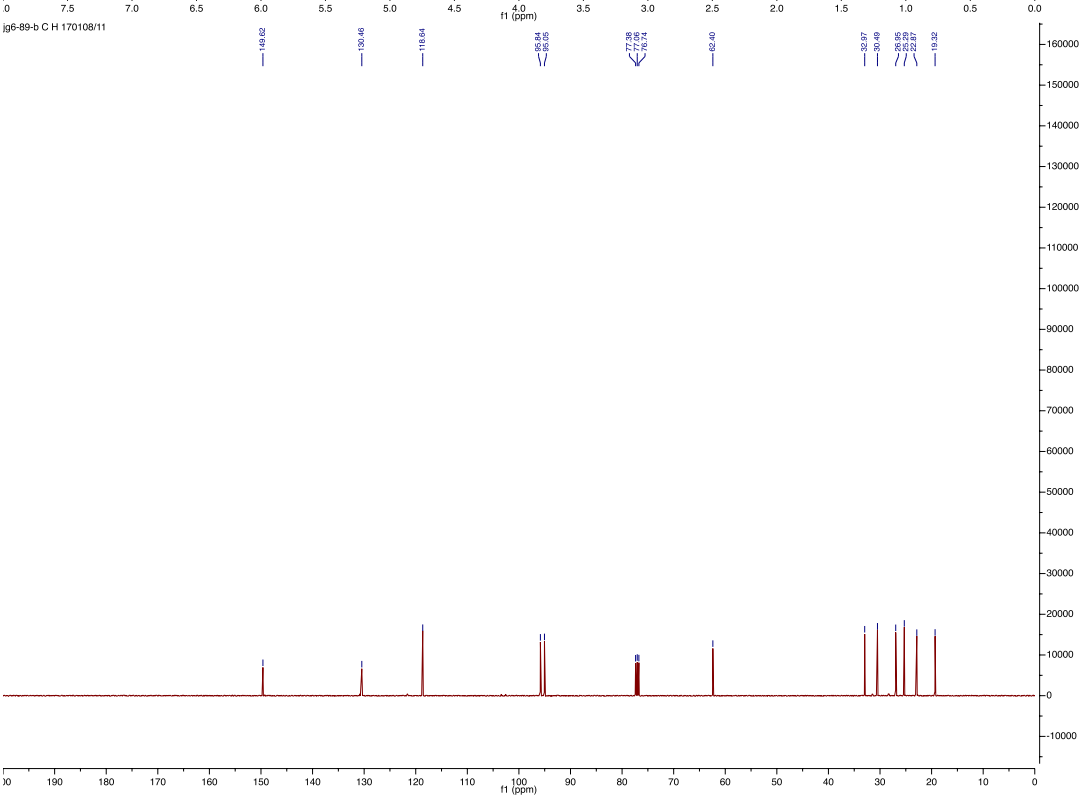

f1 (ppm)

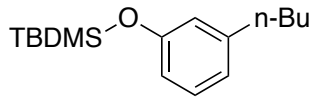


jg6-89-b-p/10



jg6-89-b C H 170108/11

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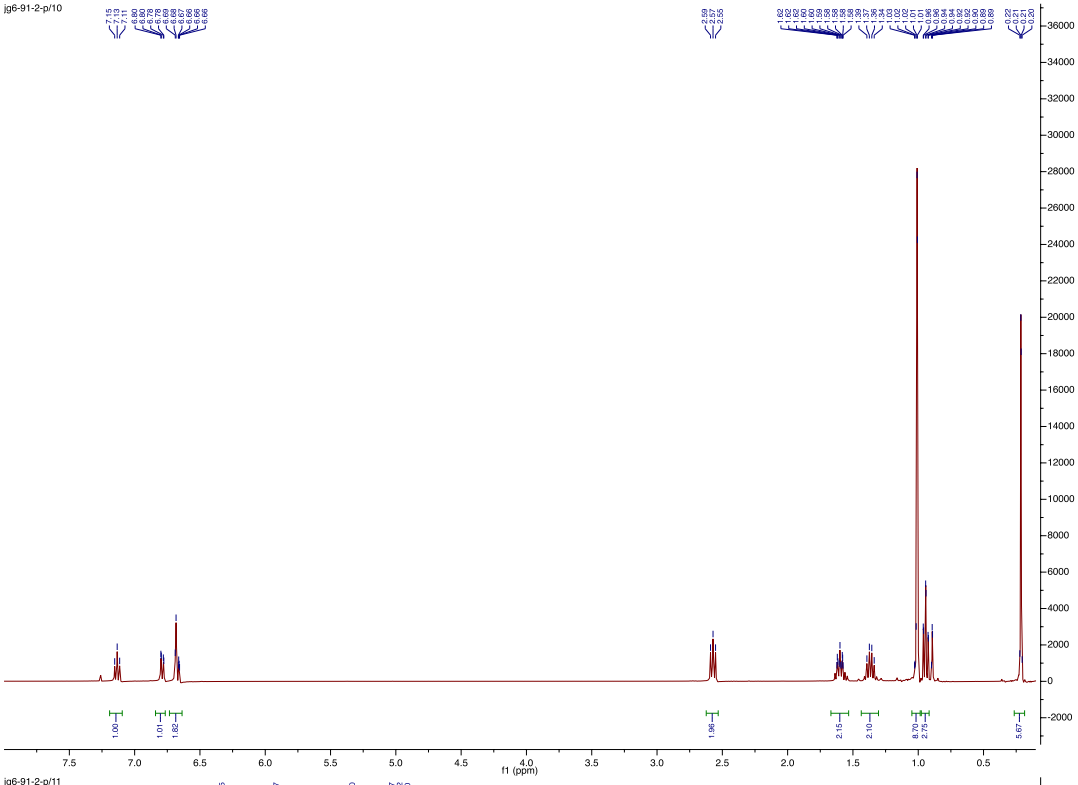
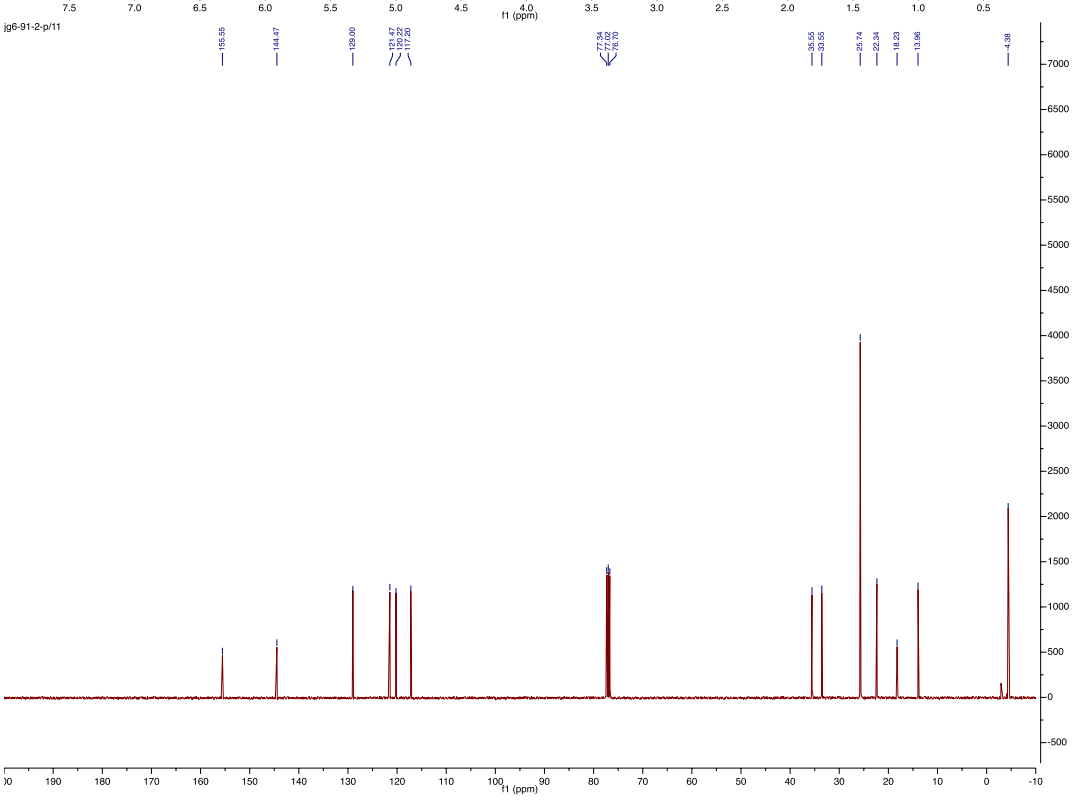
O
n-Bu


jg6-91-2-p/10
f1 (ppm)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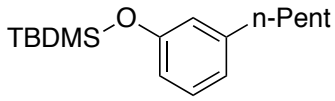
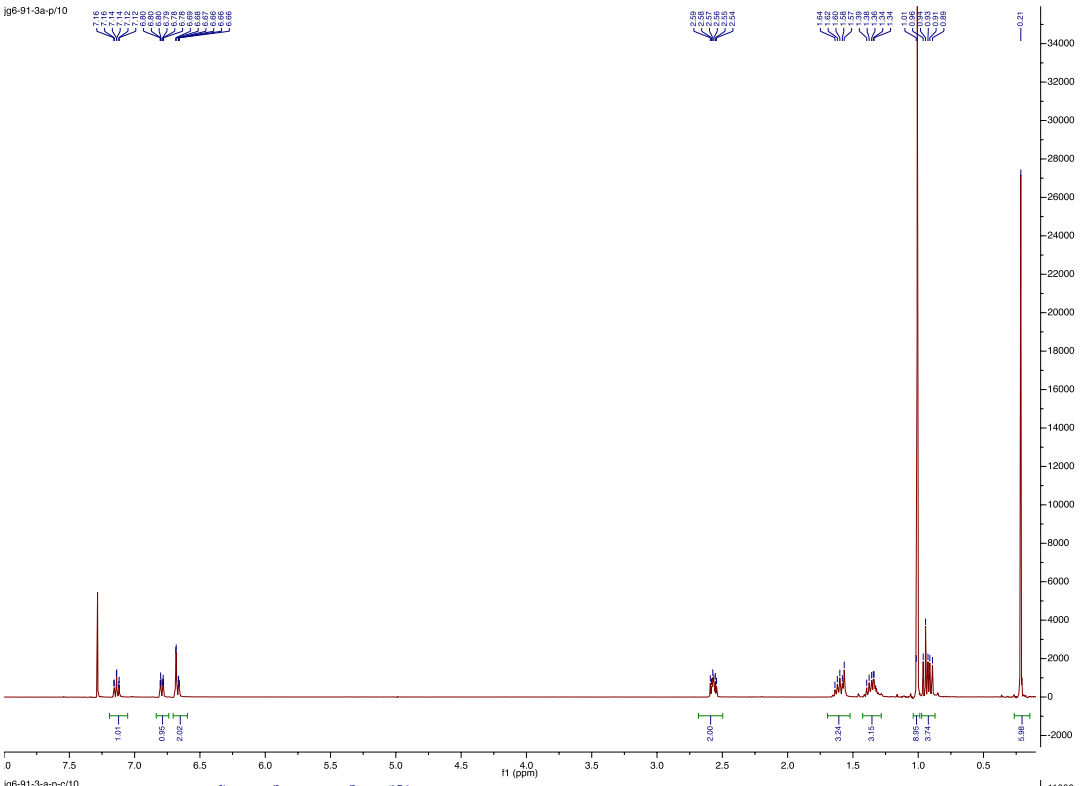
f1 (ppm)


TBDMS
O
n-Pent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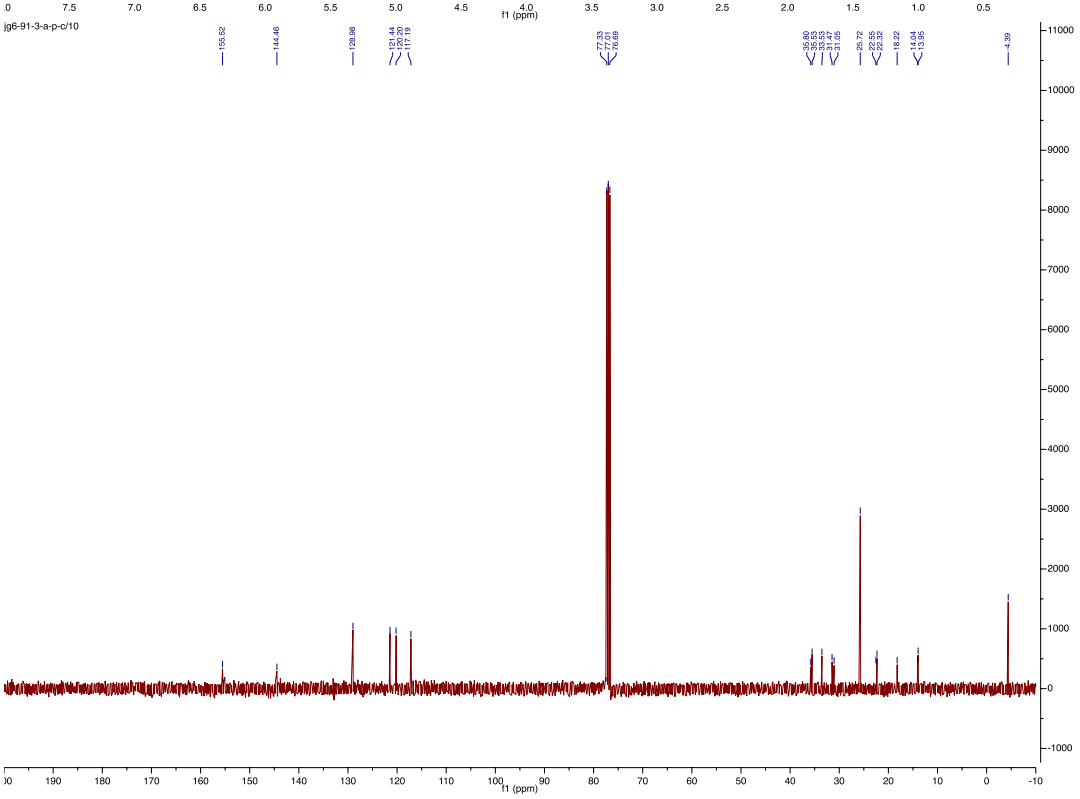
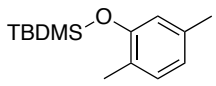
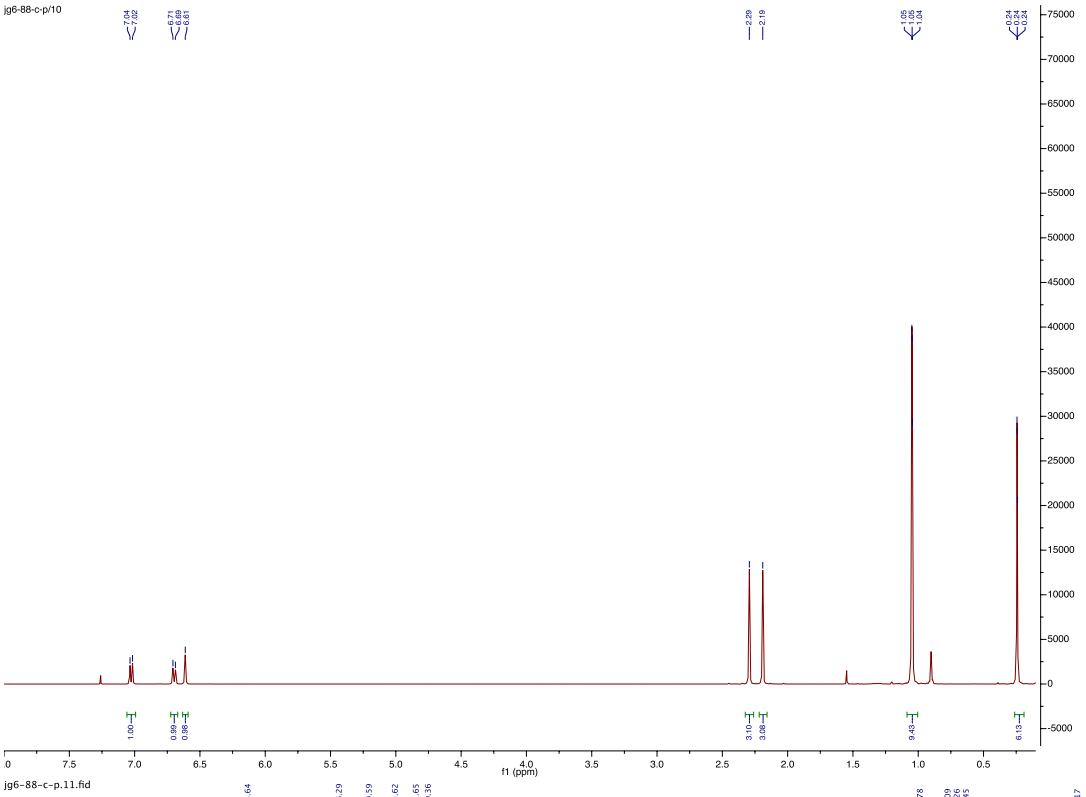
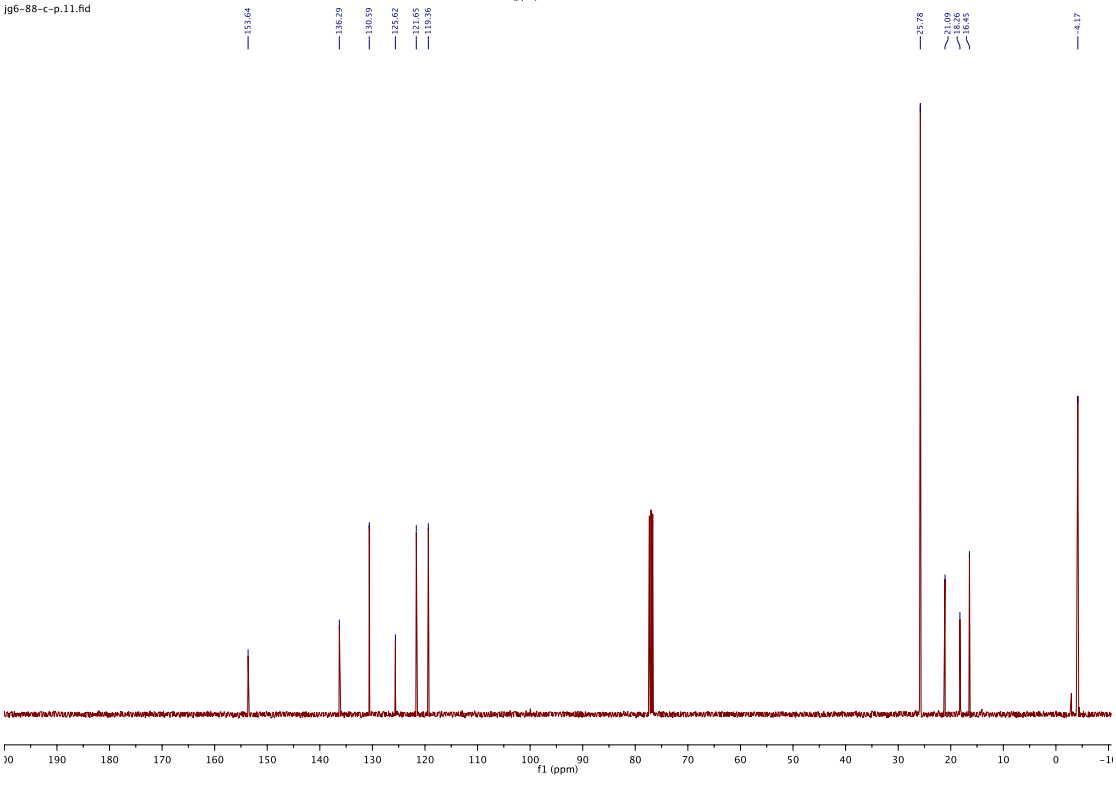
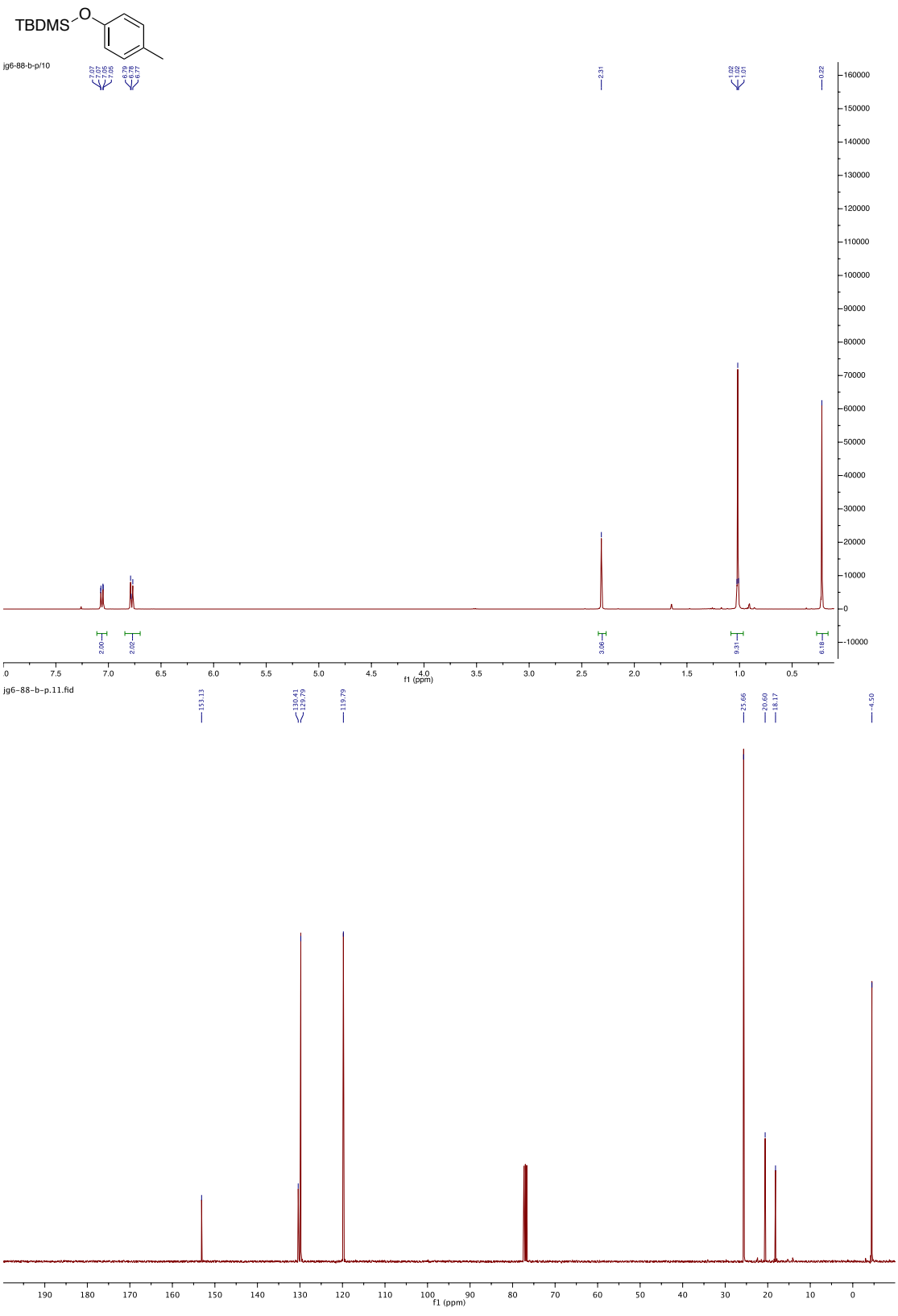
f1 (ppm)

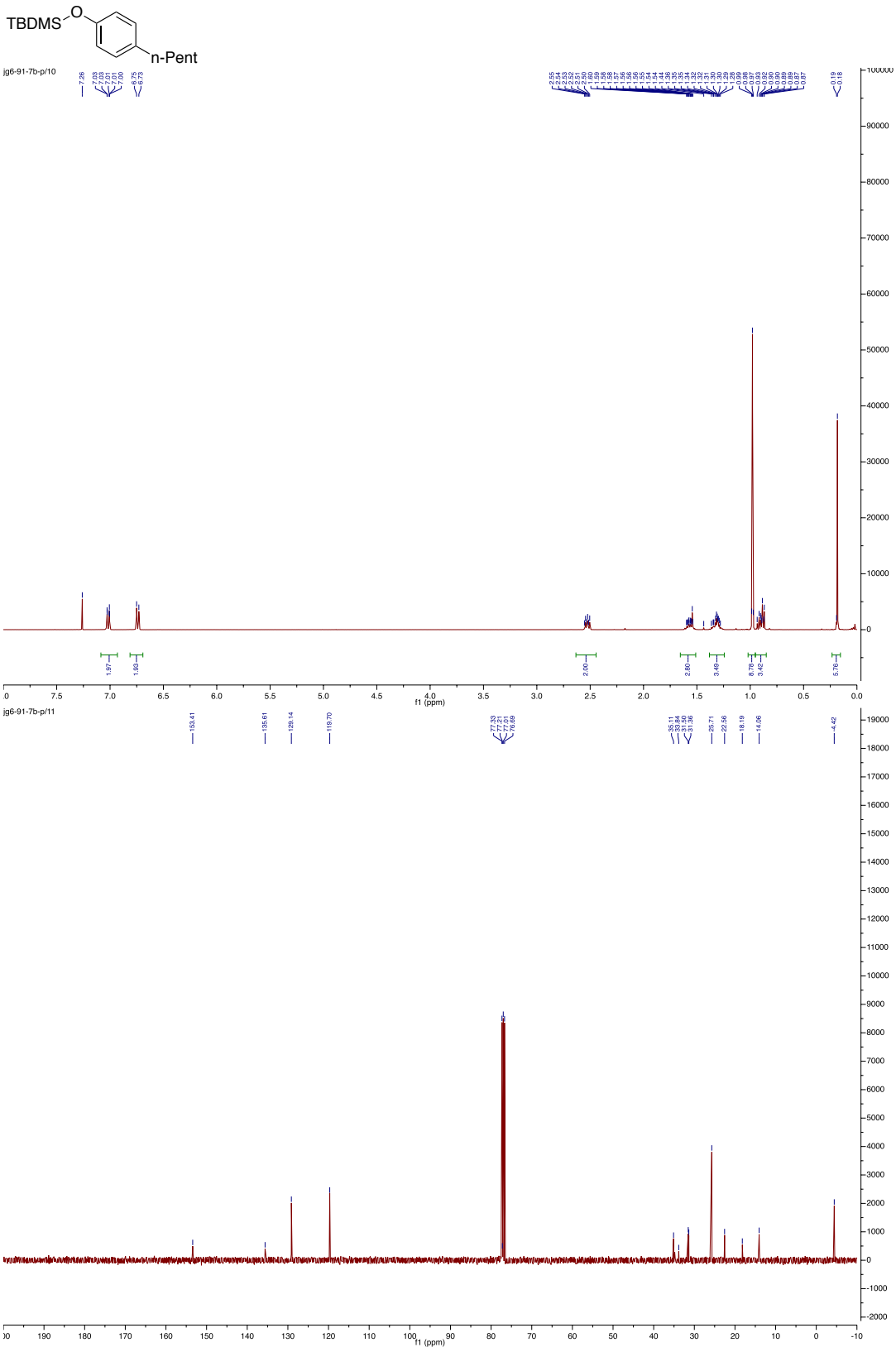

jg6-91-3-a-p-c/10
f1 (ppm)

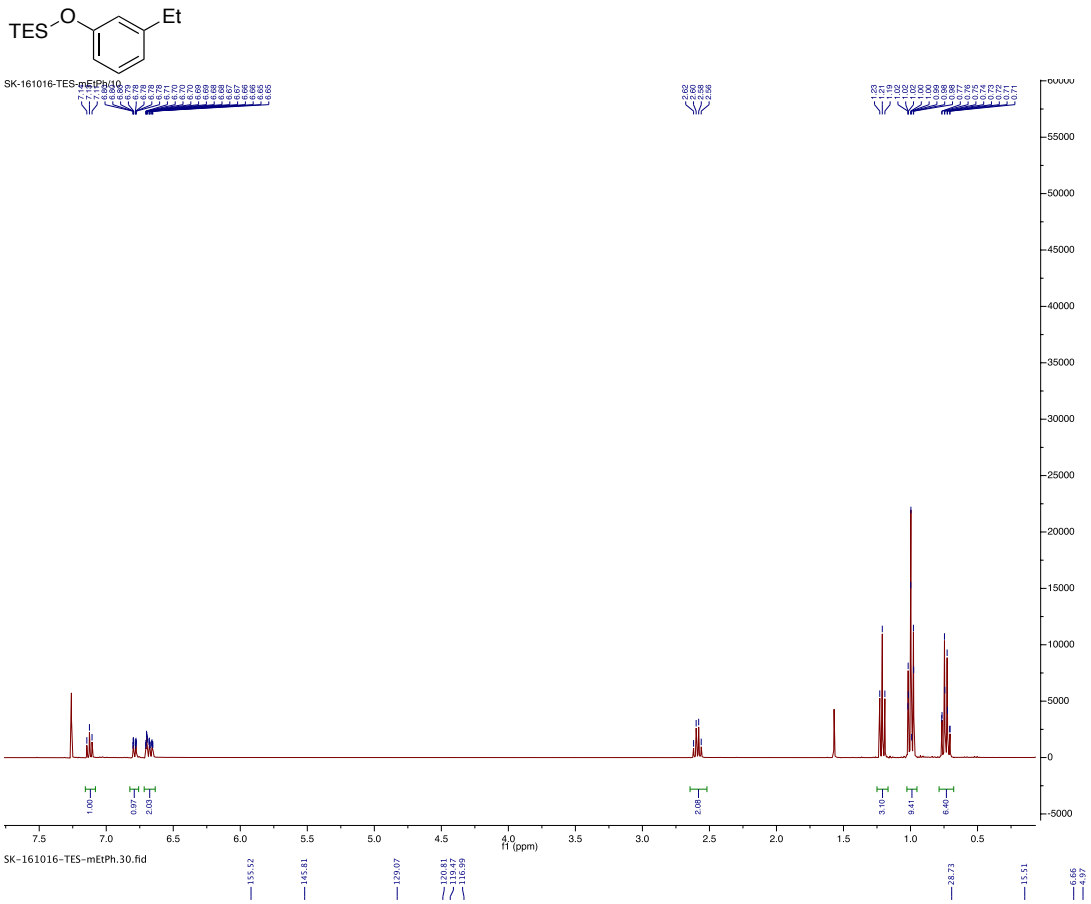

TBDMS
O


jg6-88-c-p/10
7.04
7.02
6.71
6.69
6.61
2.29
2.19
1.05
1.00
1.04
0.24
0.24
0.24
1.00
0.99
0.98
3.10
3.08
9.43
6.13
f1 (ppm)


jg6-88-c-p.11.fid
153.64
136.29
130.59
125.62
121.65
119.36
25.78
21.09
18.26
16.48
-4.17
f1 (ppm)


TBDMS
O
jg6-88-b-p/10
jg6-88-b-p.11.fid
f1 (ppm)


TBDMS
O
n-Pent
jg6-91-7b-p/10
jg6-91-7b-p/11
f1 (ppm)


TES
O
Et
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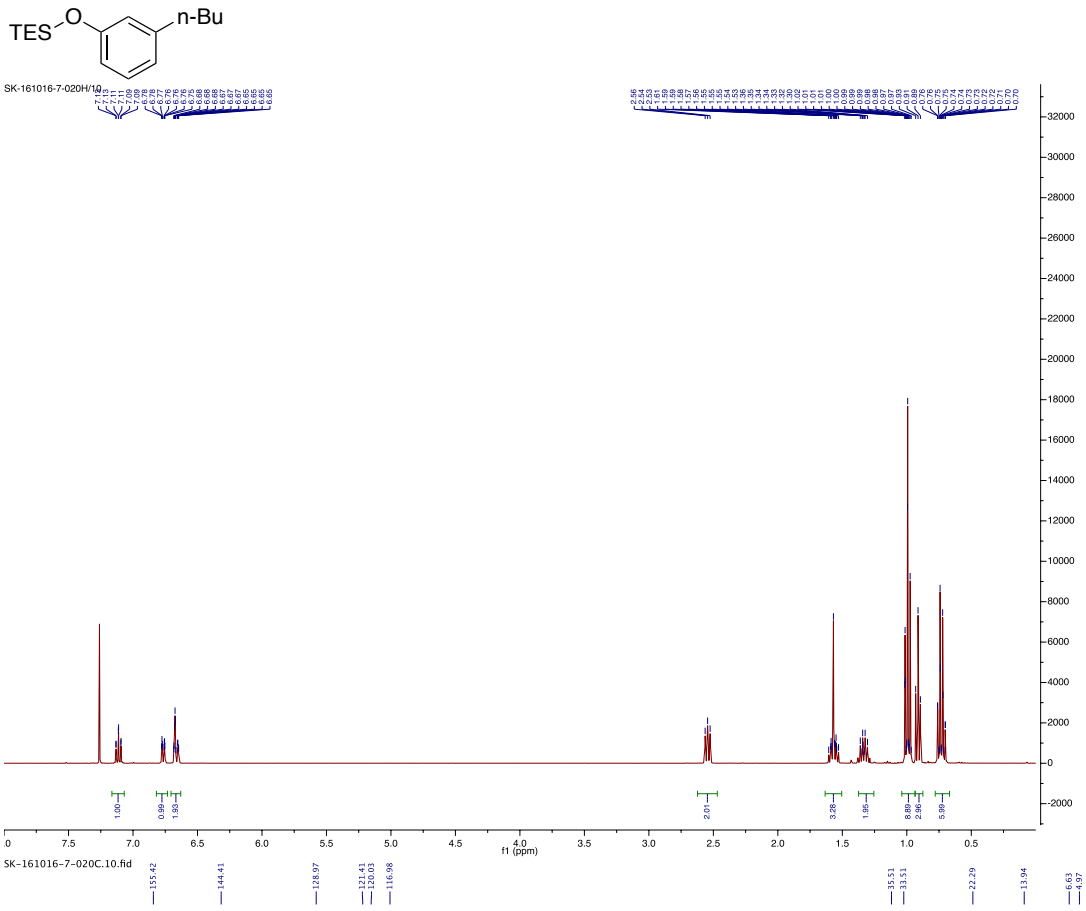
SK-161016-TES-mEtPh.30.fid
f1 (ppm)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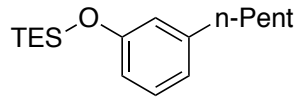
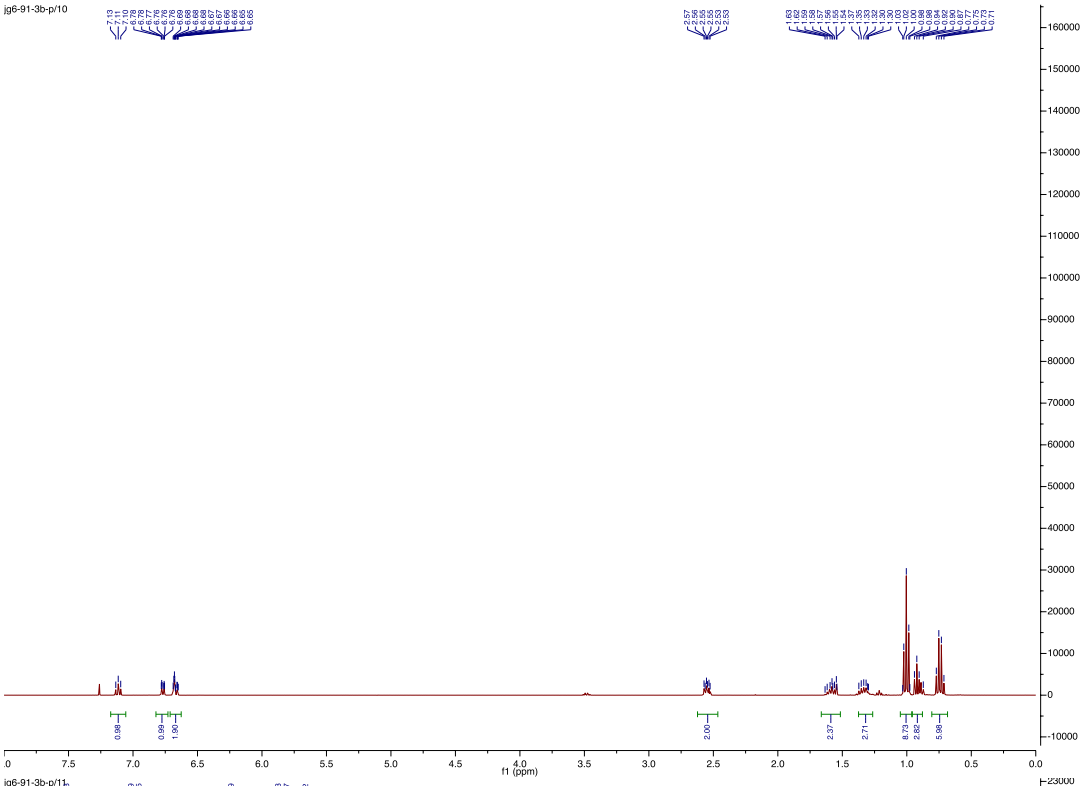
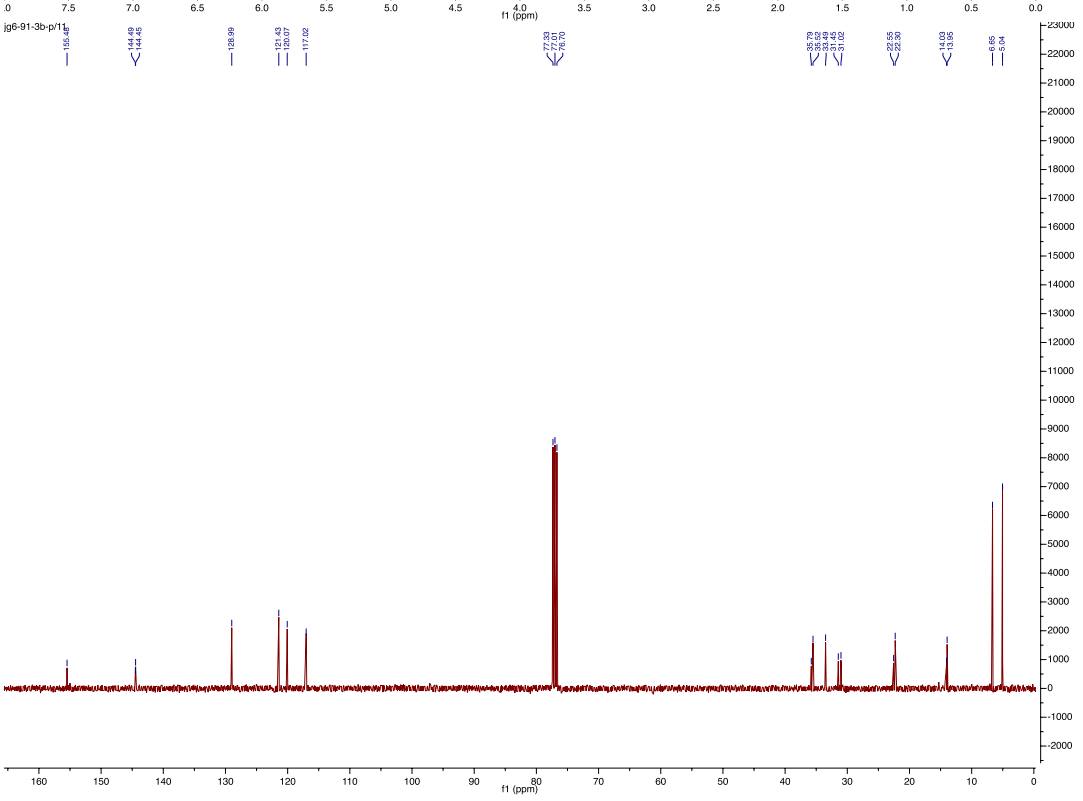
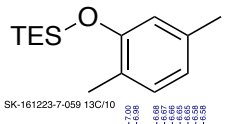
f1 (ppm)

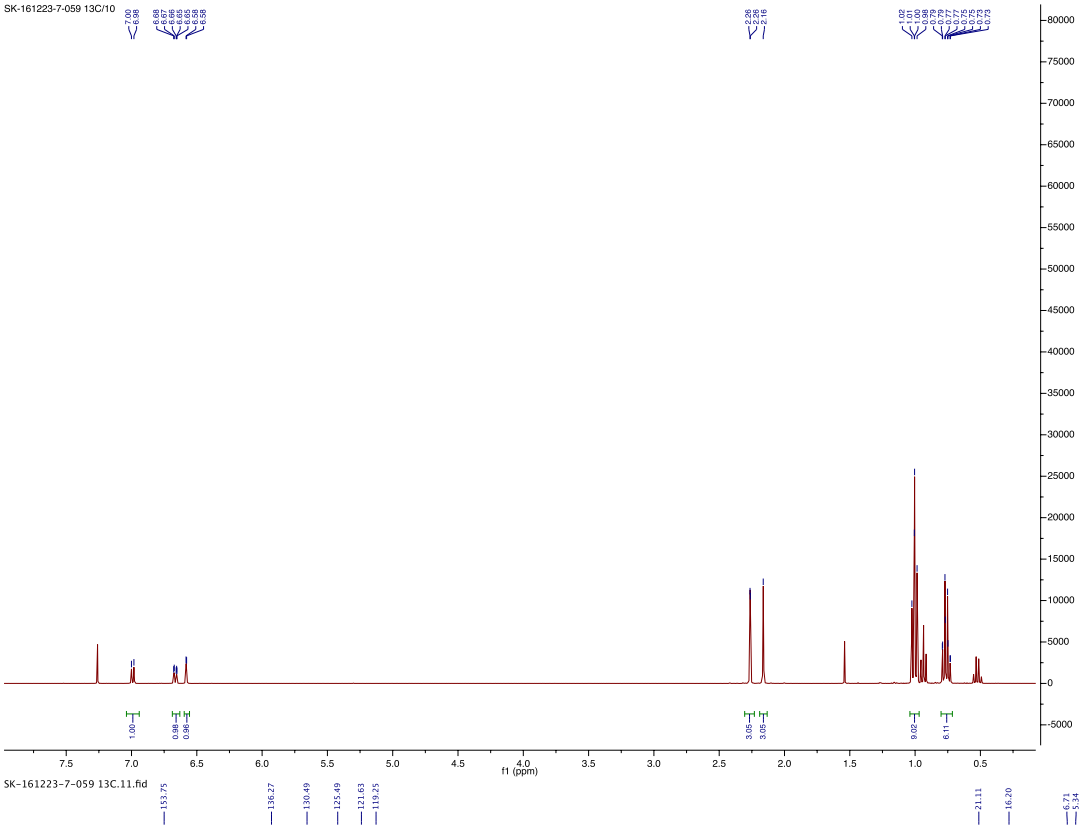

TES
O
n-Pent


jg6-91-3b-p/10
f1 (ppm)


jg6-91-3b-p/11
f1 (ppm)



SK-161223-7-059 13C/10



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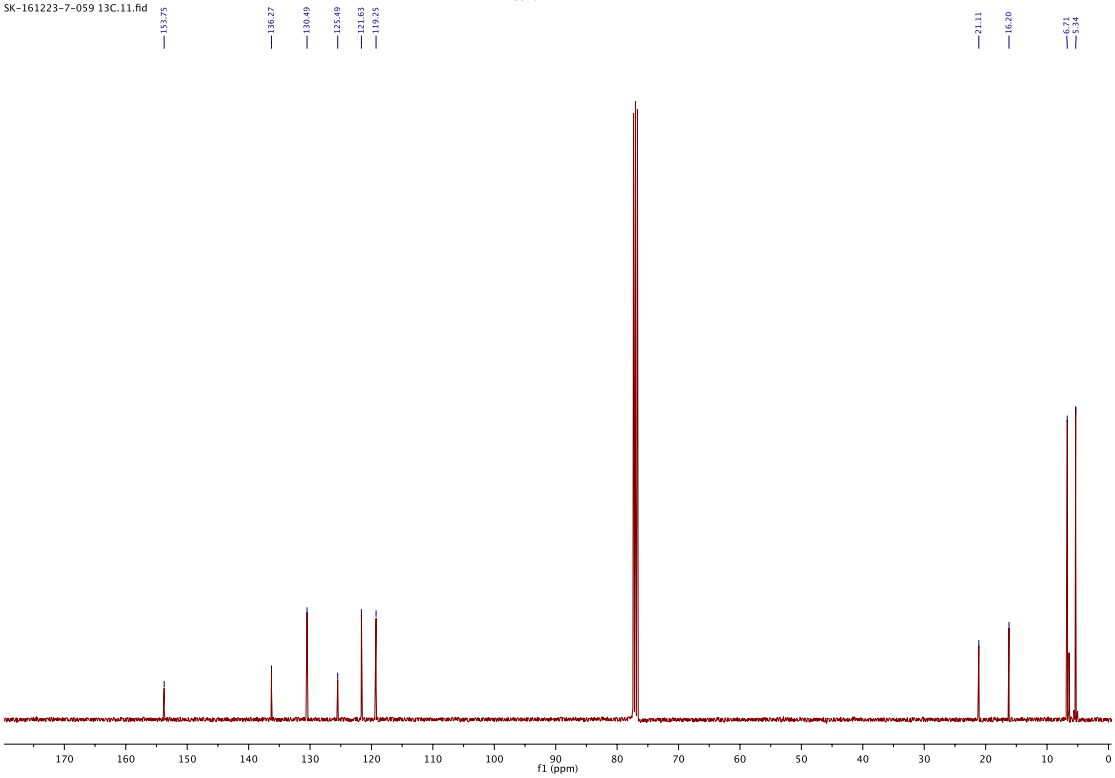
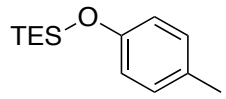
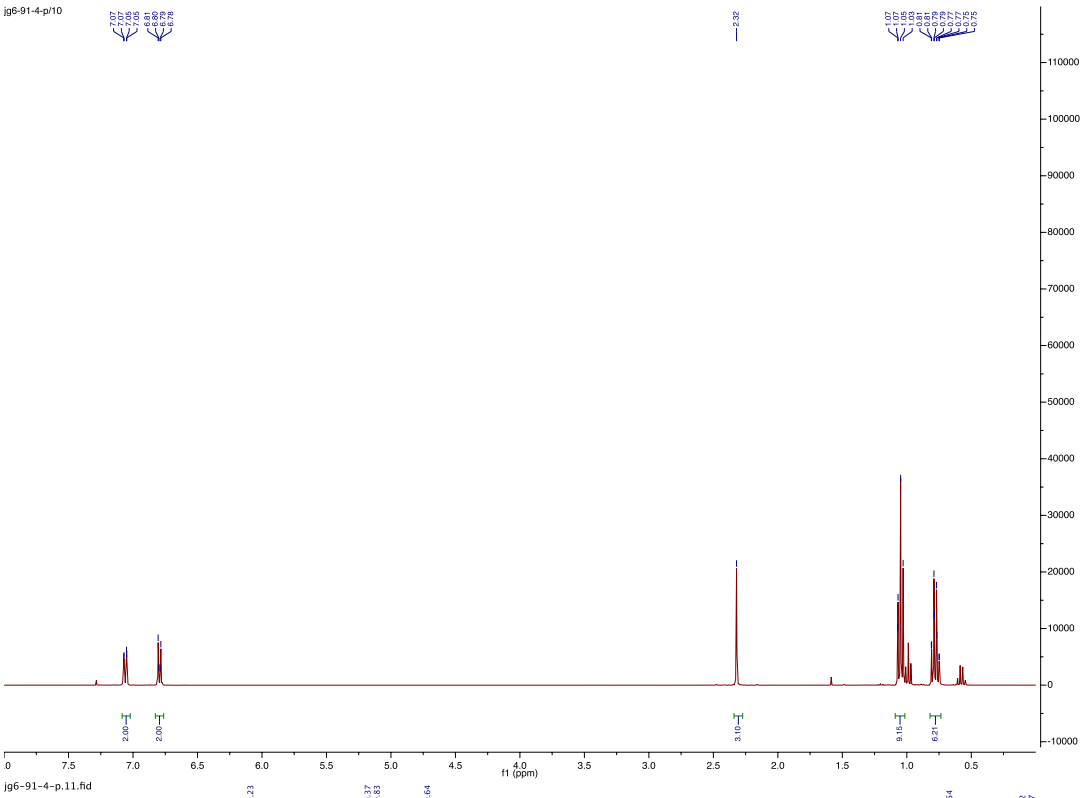
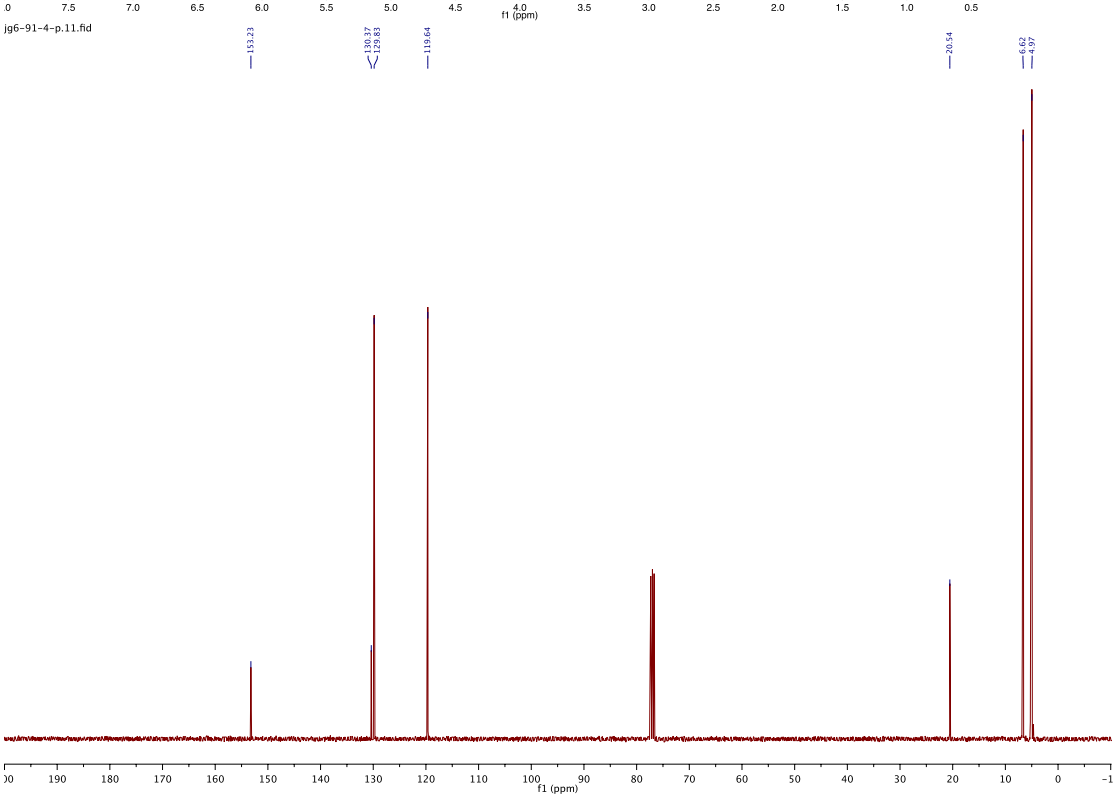
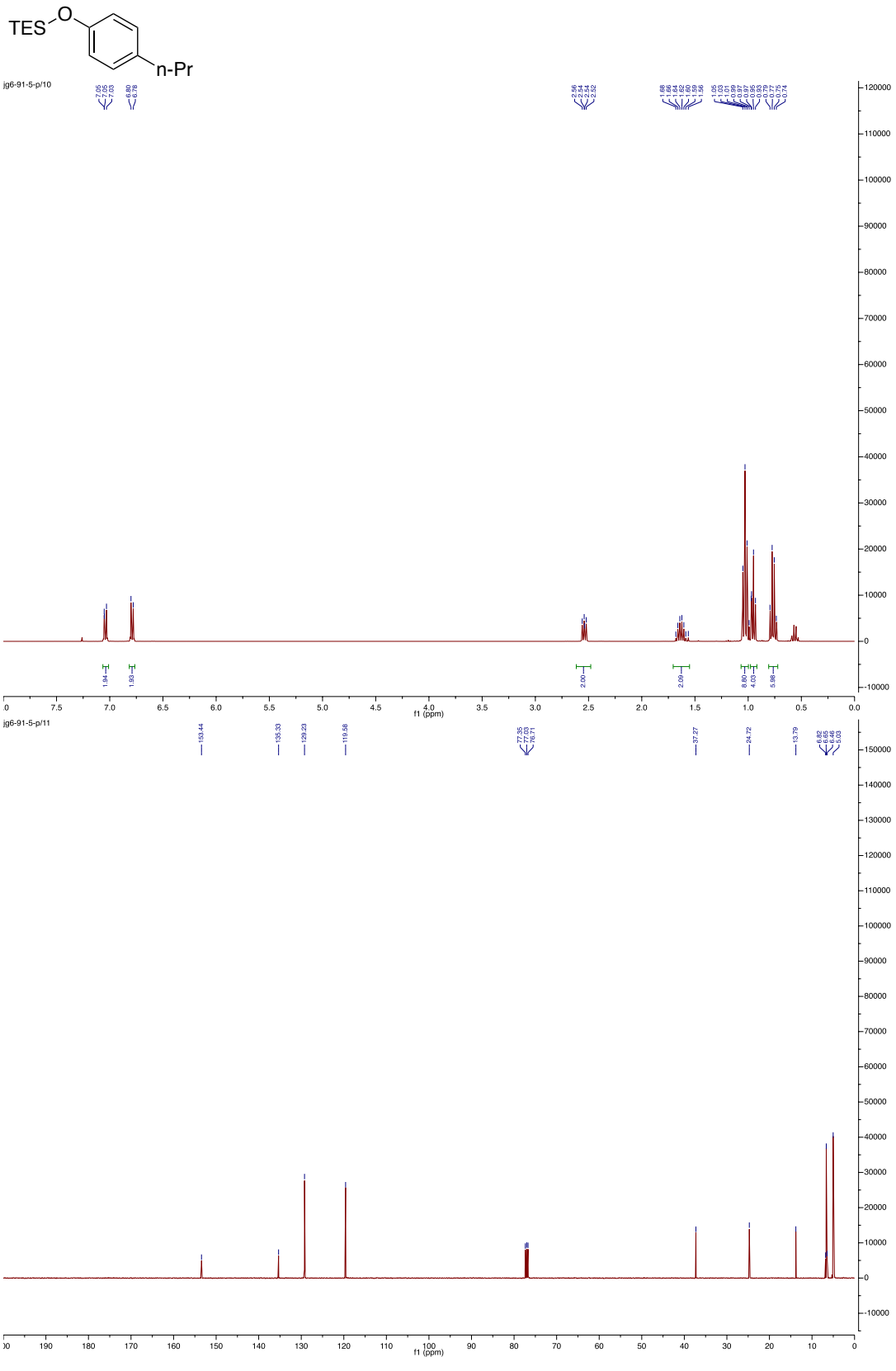
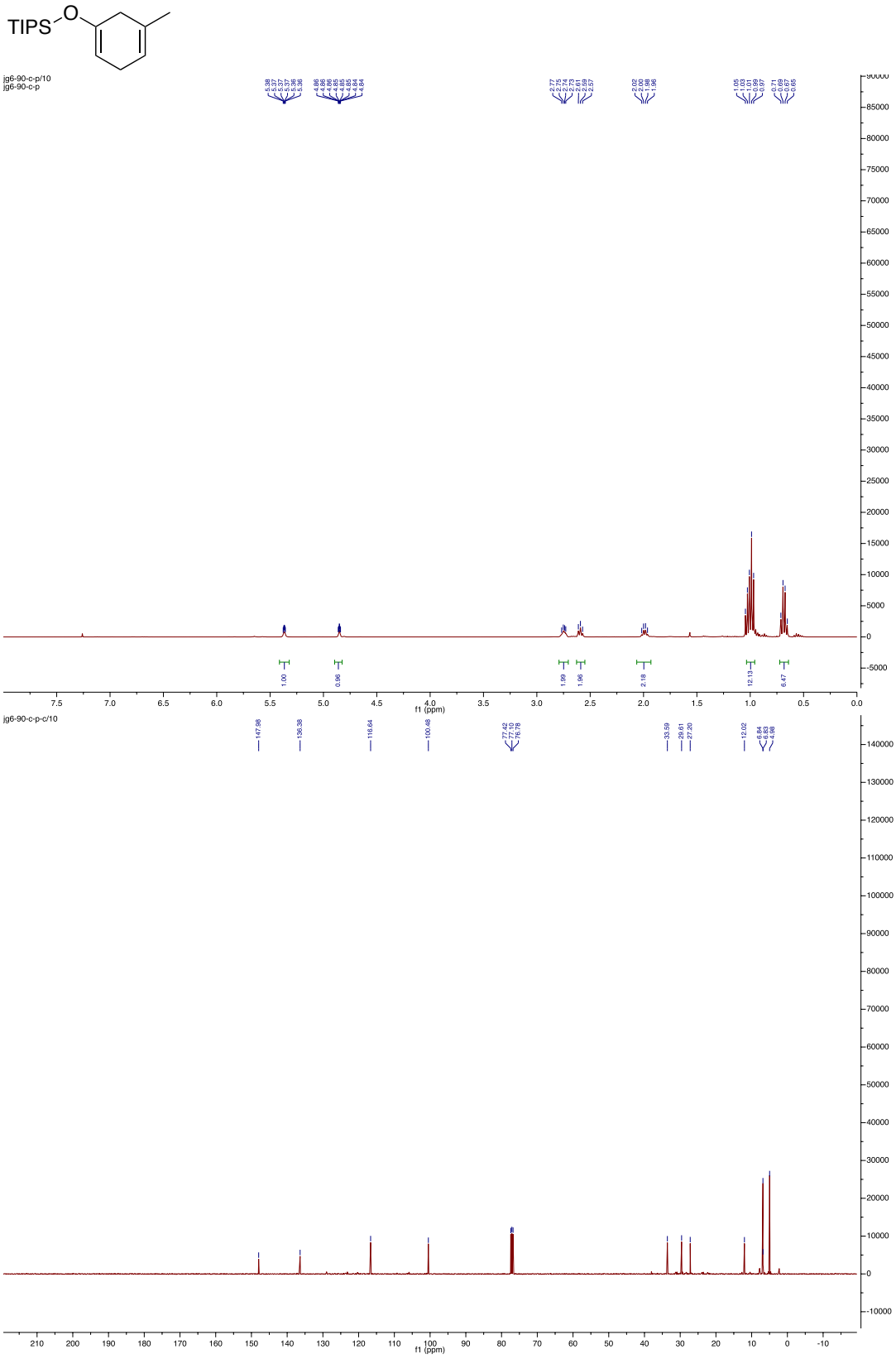


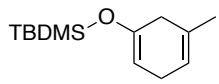

TES
O


jg6-91-4-p/10
7.07
7.07
7.05
7.05
6.81
6.80
6.79
6.78
2.32
1.07
1.05
1.03
0.81
0.79
0.79
0.77
0.77
0.75
0.75
2.00
2.00
3.10
9.15
6.21
f1 (ppm)

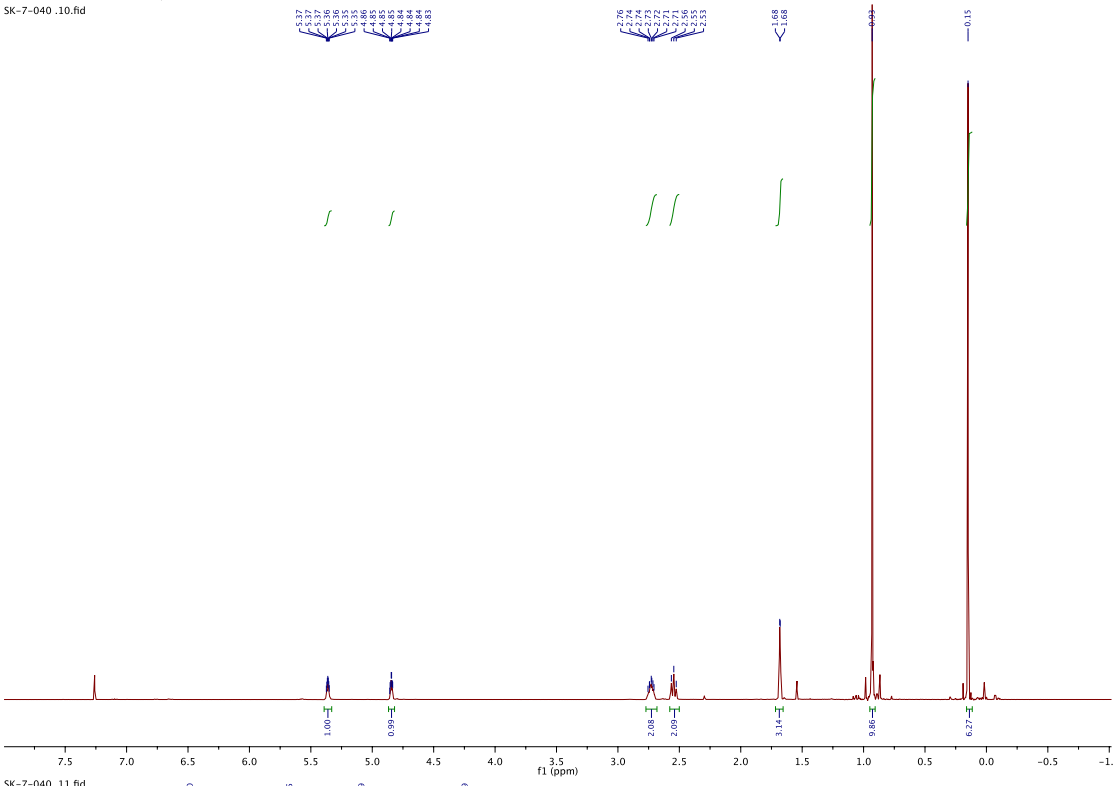

jg6-91-4-p.11.fid
153.23
130.17
129.83
119.64
20.54
6.62
4.97
f1 (ppm)


TES
O
n-Pr
jg6-91-5-p/10
jg6-91-5-p/11
f1 (ppm)

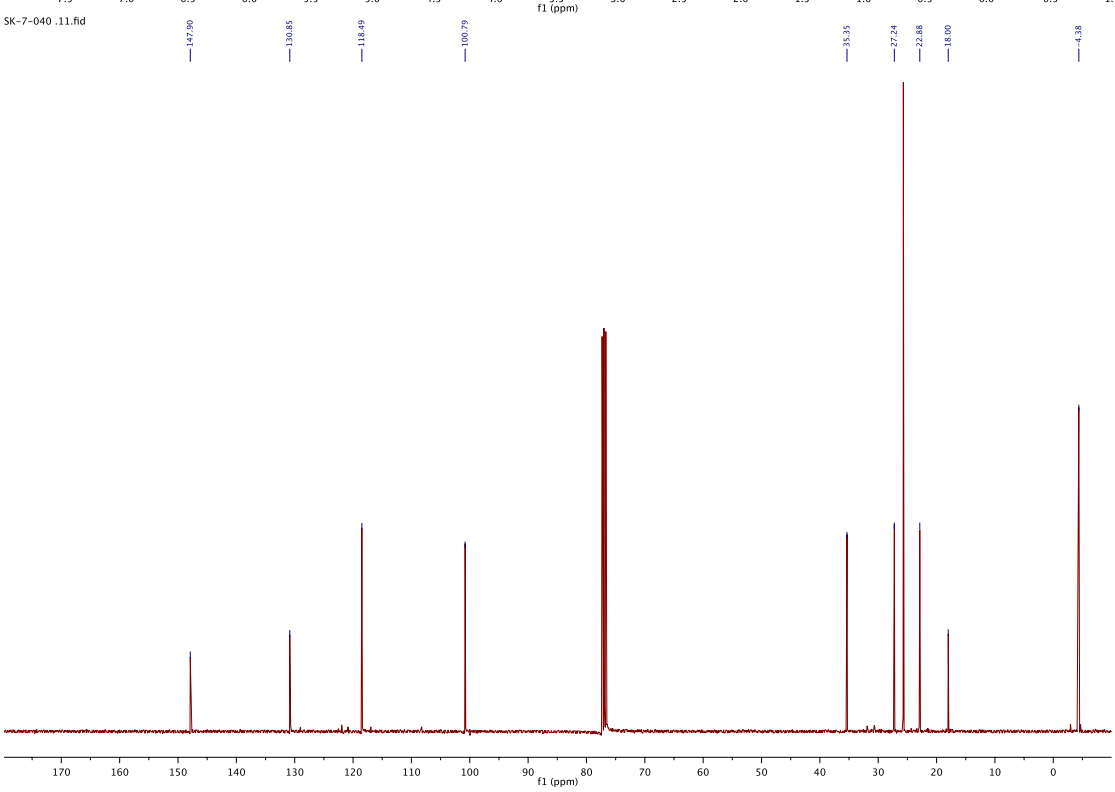

TIPS
O
jg6-90-c-p/10
jg6-90-c-p
5.38
5.37
5.37
5.37
5.36
5.36
4.86
4.86
4.85
4.85
4.85
4.84
4.84
4.84
2.77
2.75
2.74
2.73
2.71
2.69
2.69
2.67
2.02
2.00
1.98
1.96
1.05
1.03
1.01
0.98
0.97
0.71
0.69
0.67
0.65
1.00
0.96
1.99
1.98
2.18
12.13
6.47
f1 (ppm)
jg6-90-c-p-c/10
147.98
136.38
116.64
100.48
77.42
77.10
76.78
33.59
29.61
27.20
12.02
6.84
6.83
4.88
f1 (ppm)

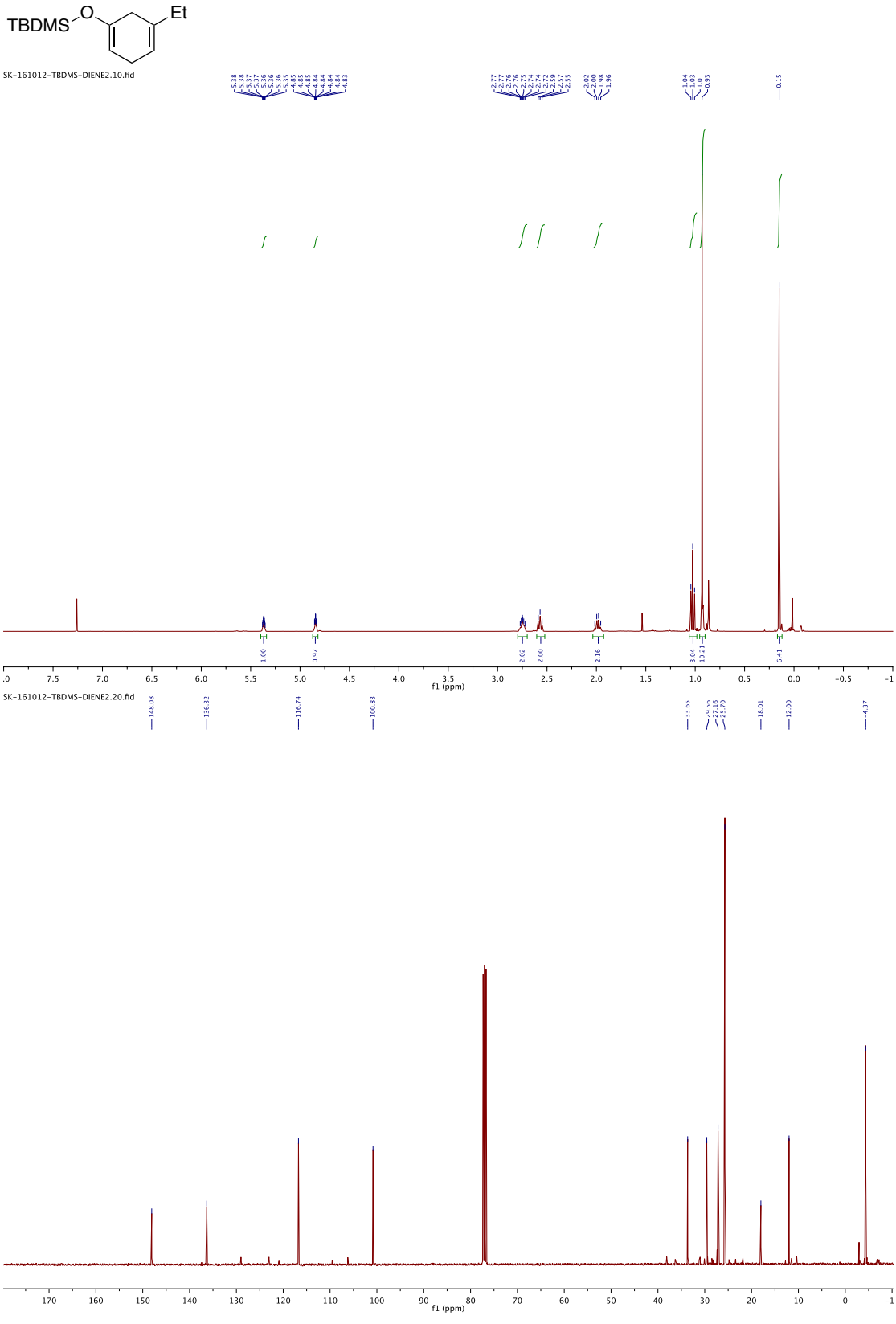


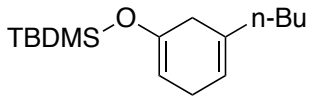
SK-7-040 .10.fid

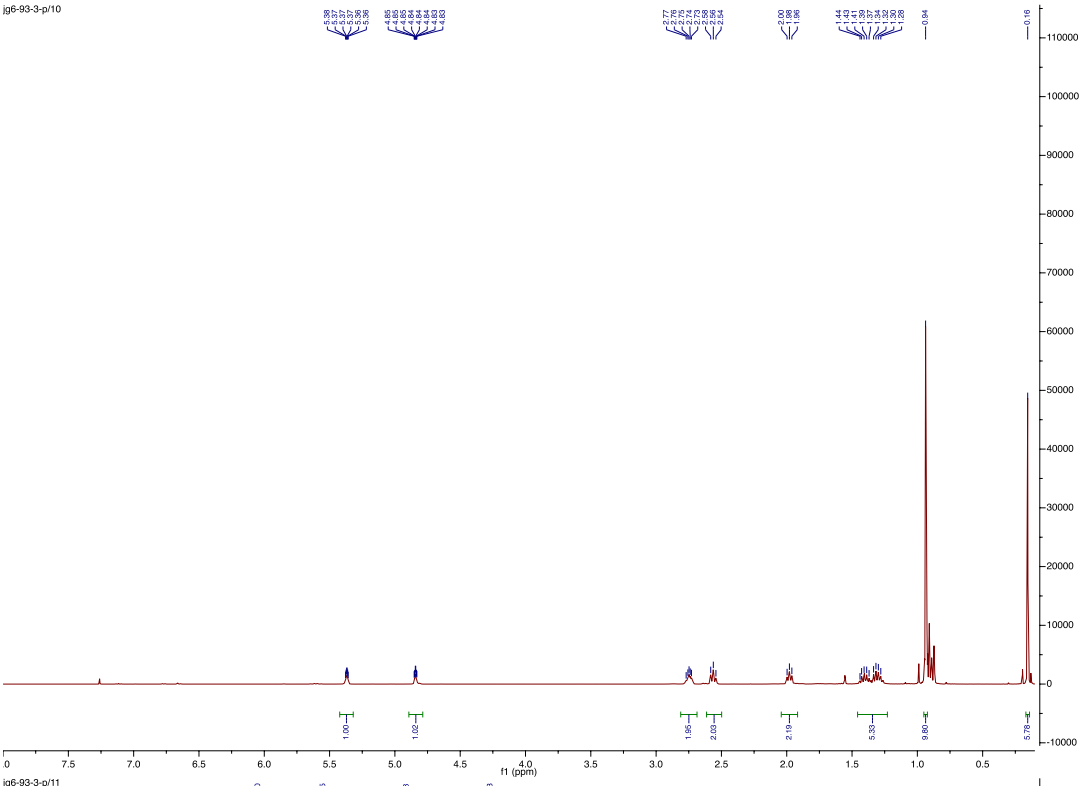


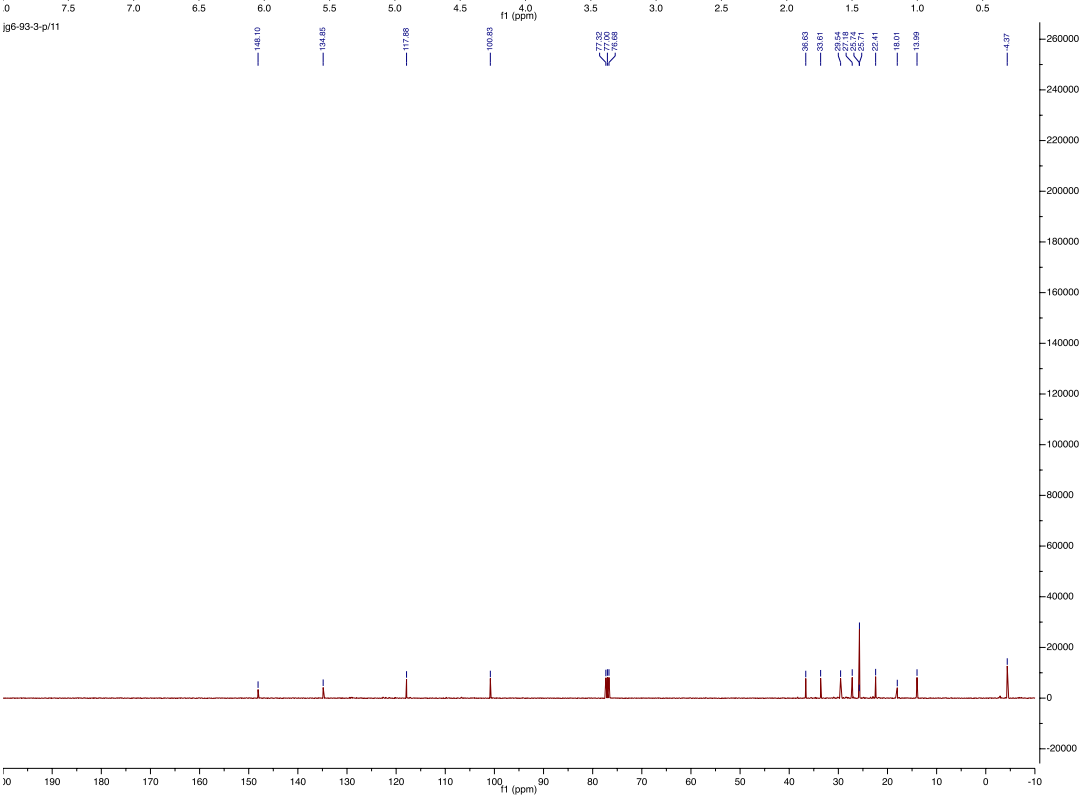
SK-7-040 .11.fid

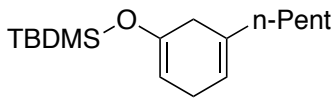


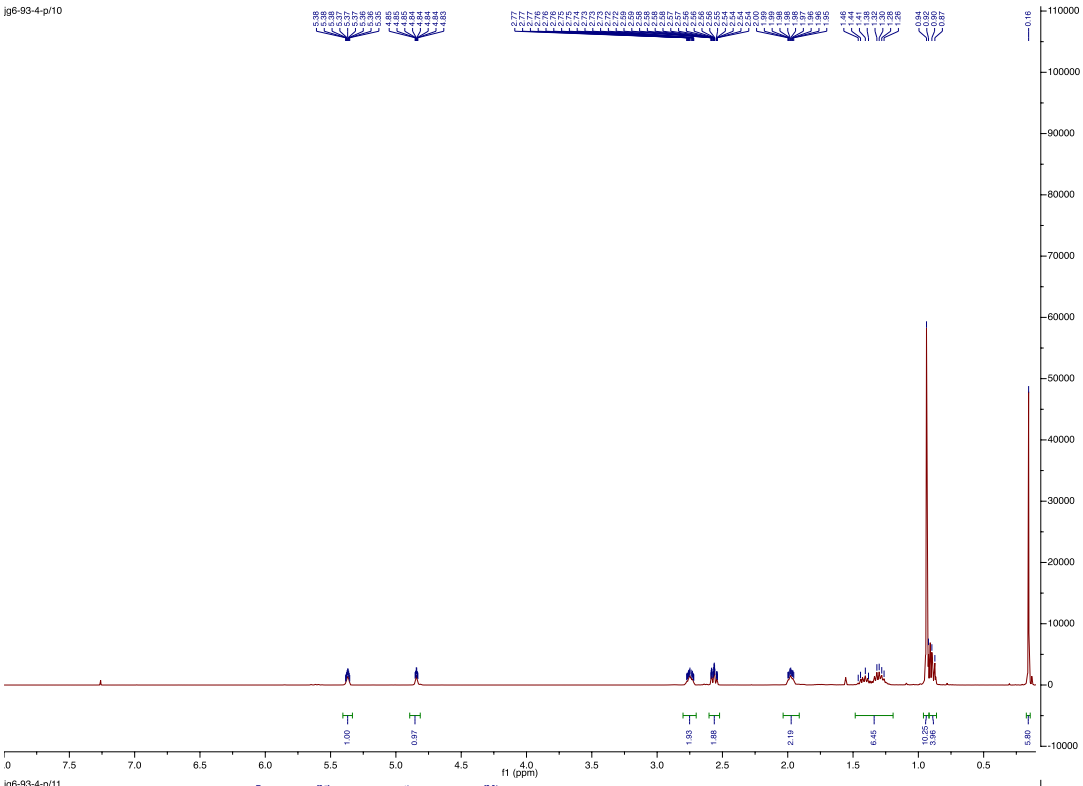

TBDMS
O
Et
SK-161012-TBDMS-DIENE2.10.fid
f1 (ppm)
SK-161012-TBDMS-DIENE2.20.fid
f1 (ppm)

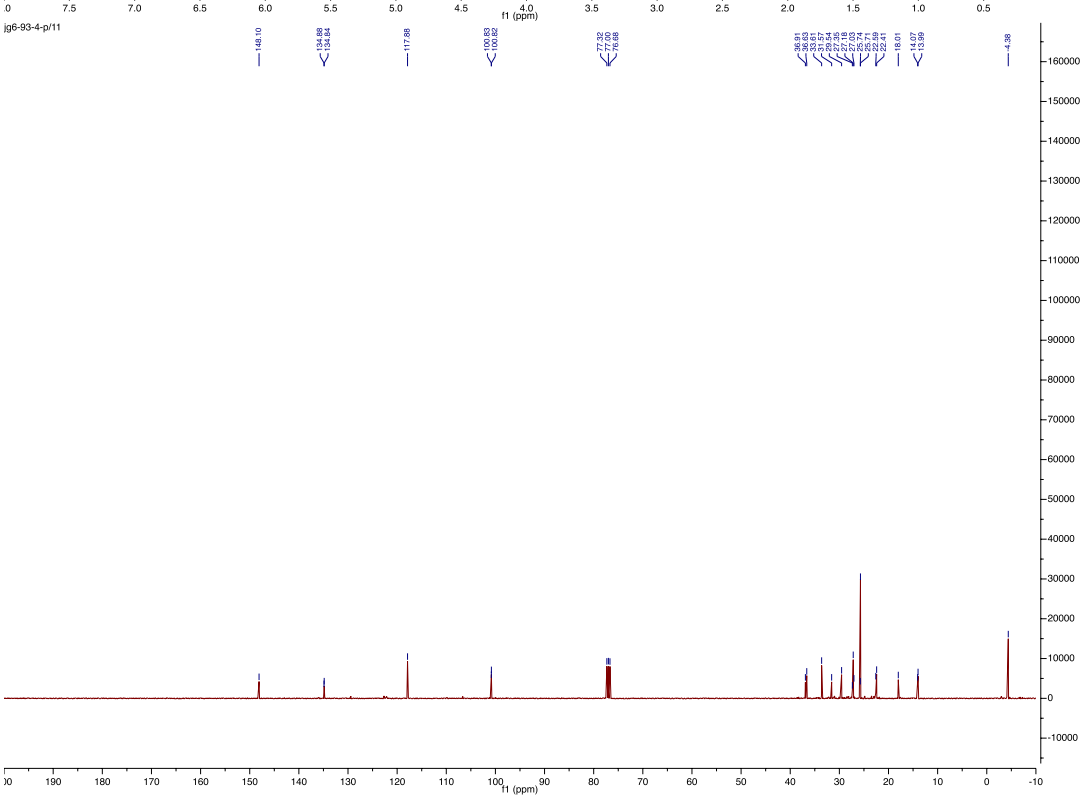

TBDMS
O
n-Bu

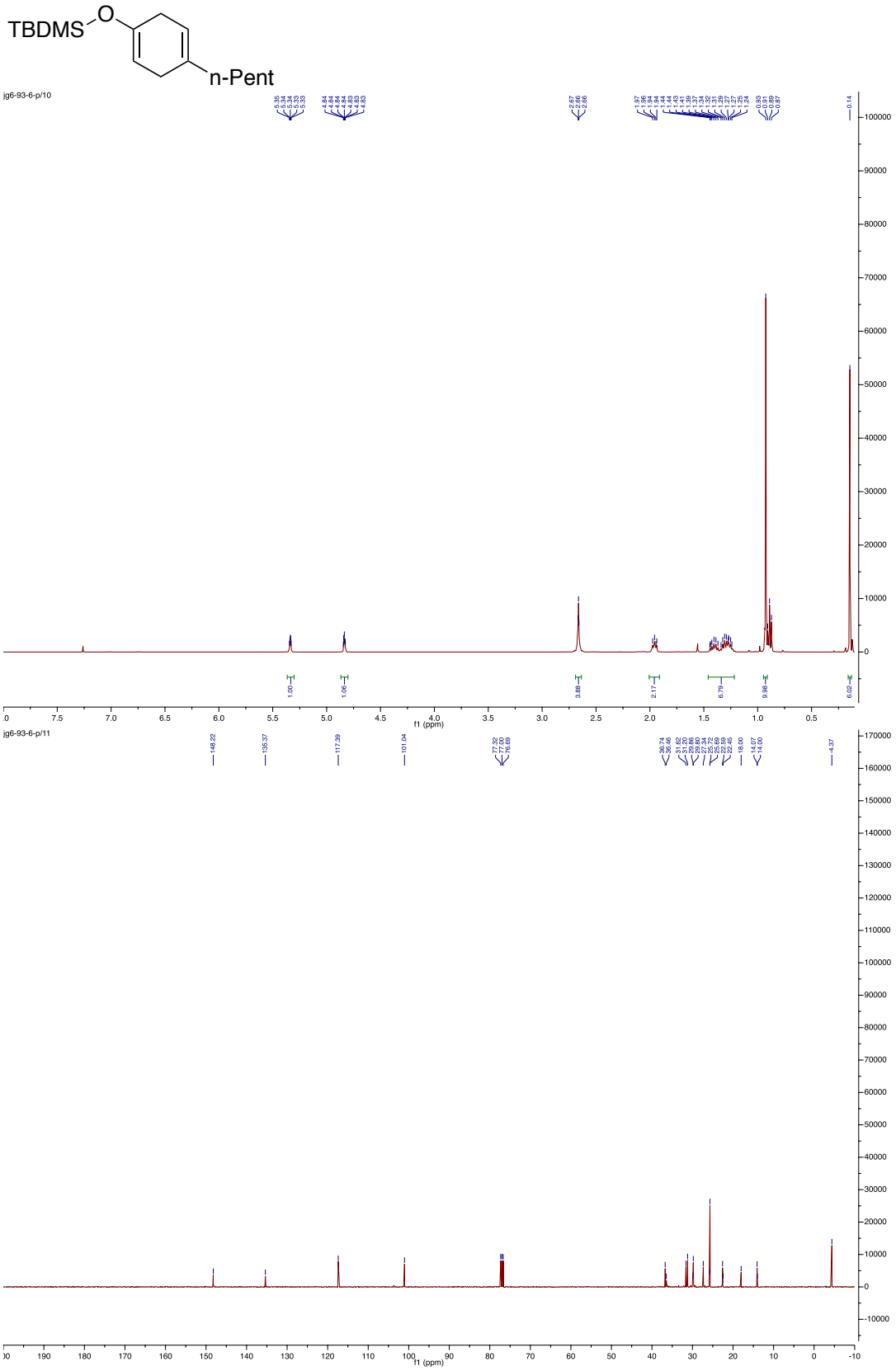

jg6-93-3-p/10
f1 (ppm)

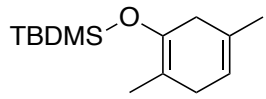

jg6-93-3-p/11
f1 (ppm)


TBDMS
O
n-Pent

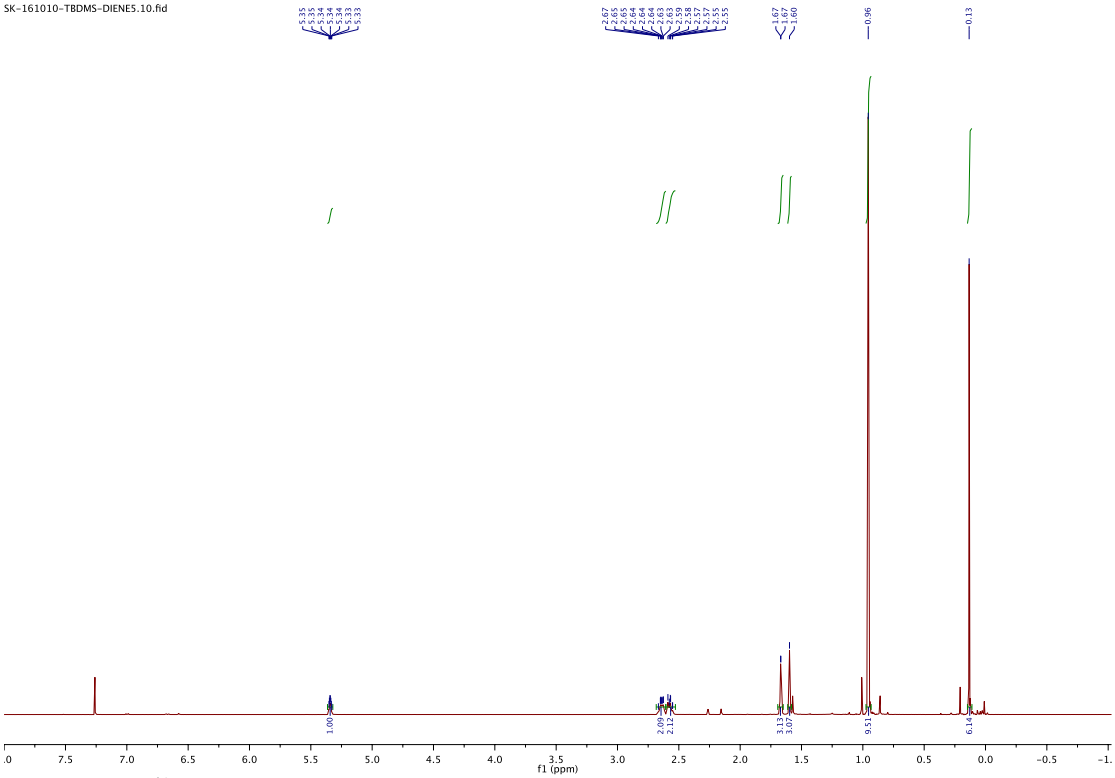

jg6-93-4-p/10
f1 (ppm)


jg6-93-4-p/11
f1 (ppm)

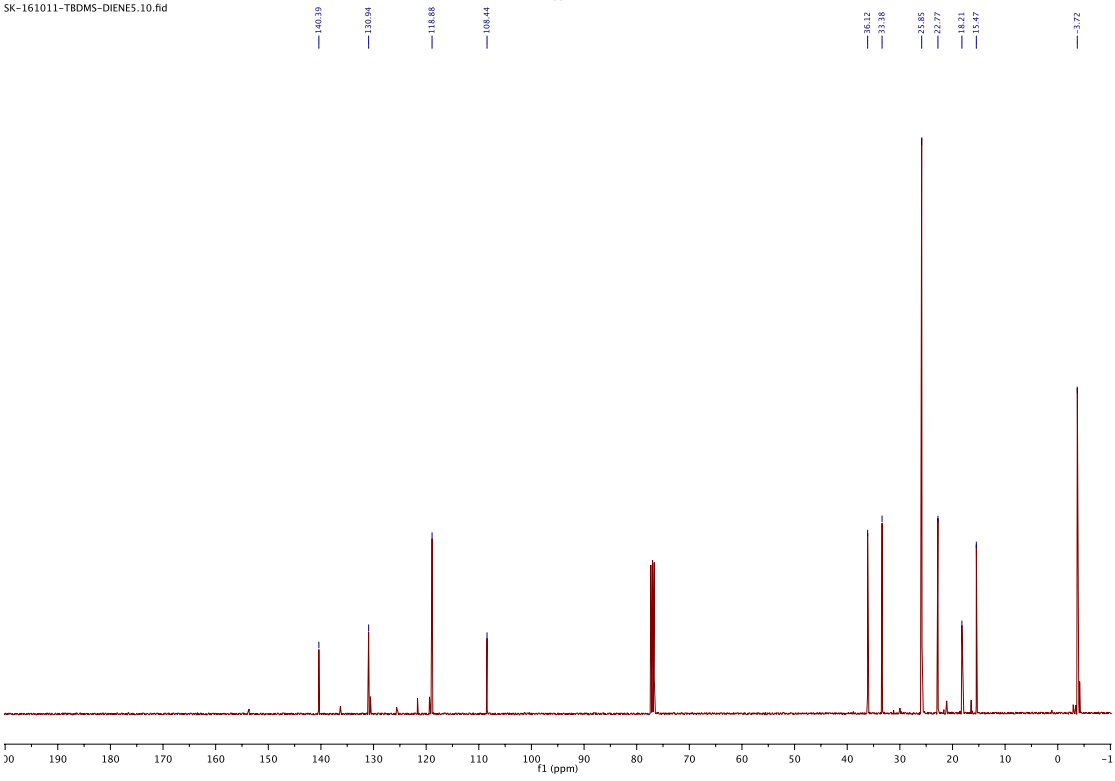

TBDMS
O
n-Pent
jg6-93-6-p/10
jg6-93-6-p/11
f1 (ppm)

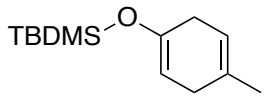


SK-161010-TBDMS-DIENE5.10.fid

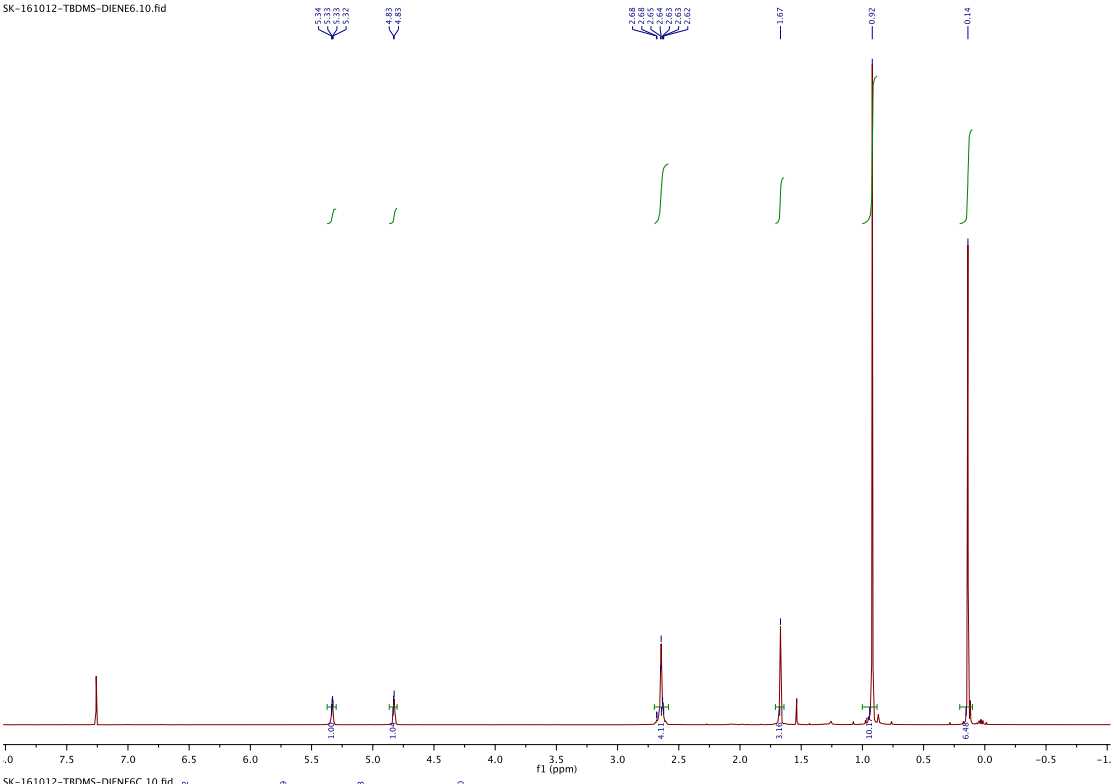


SK-161011-TBDMS-DIENE5.10.fid

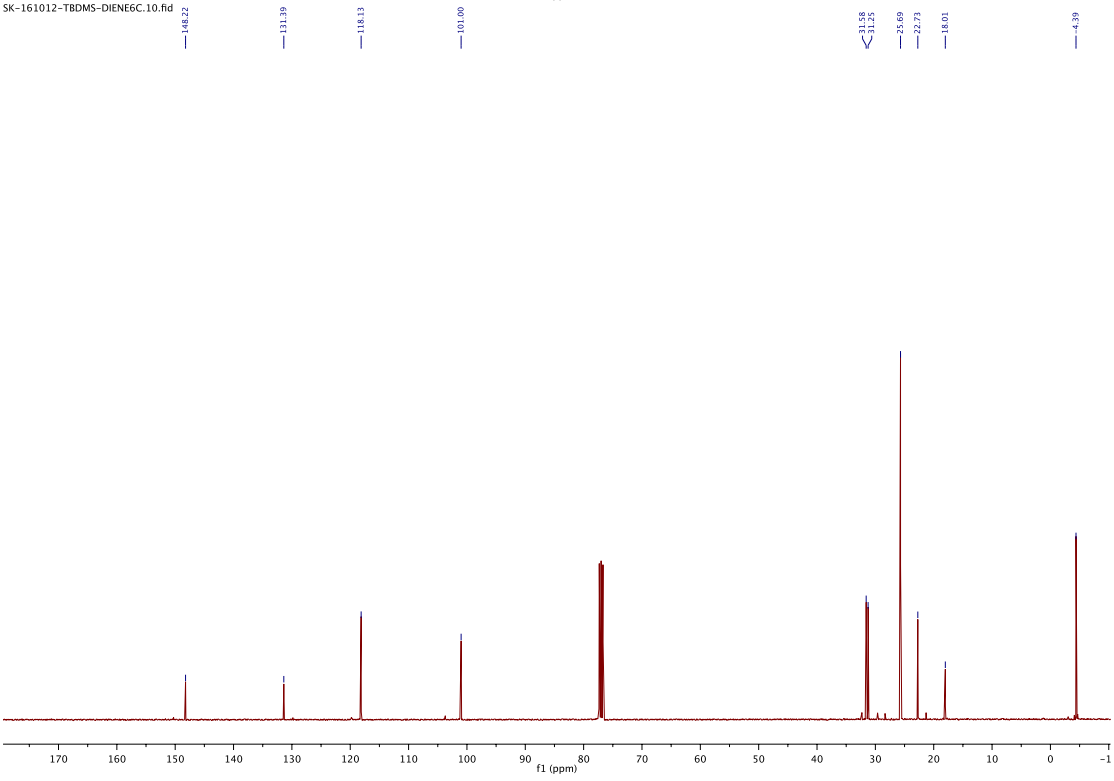


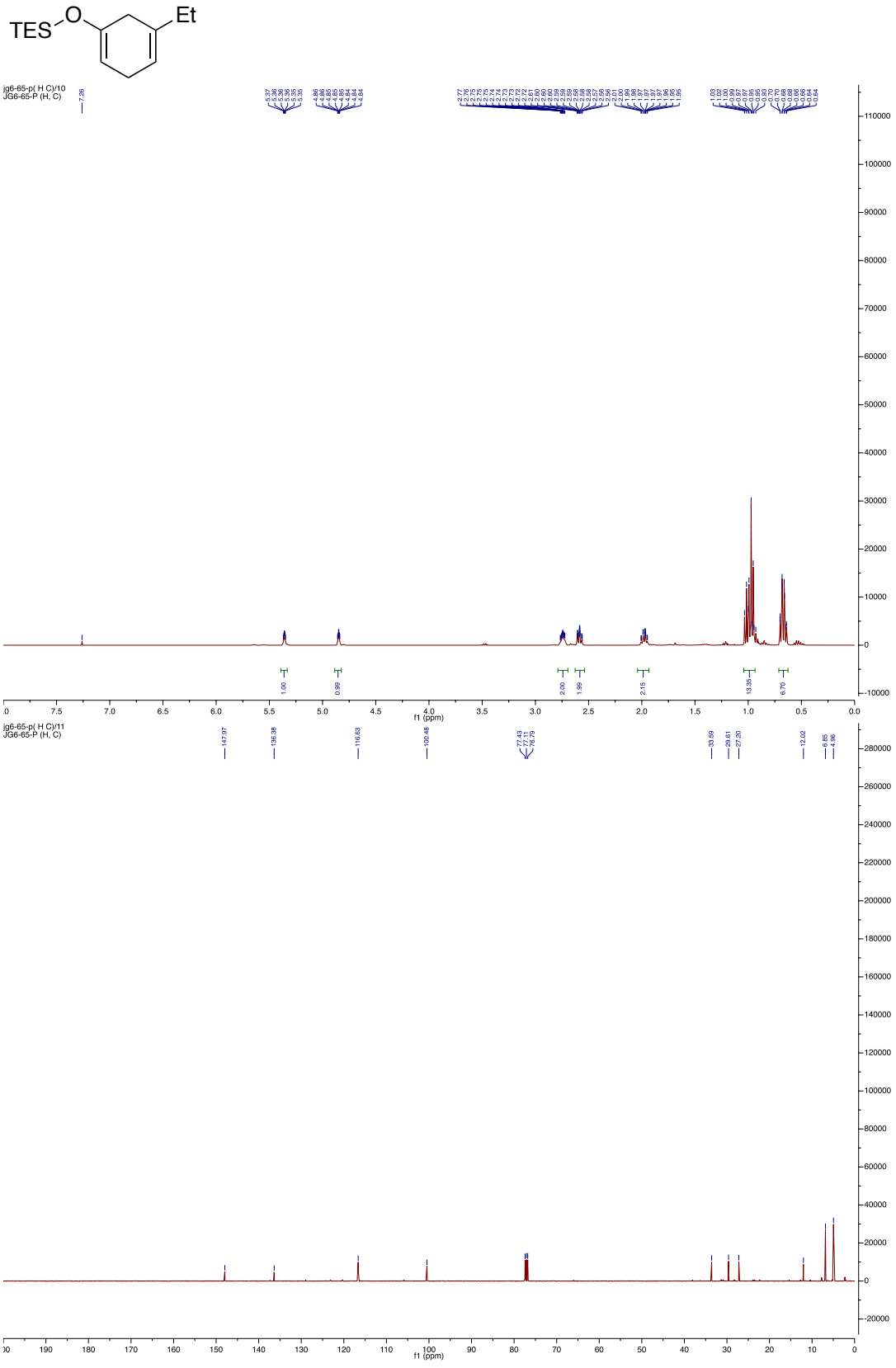


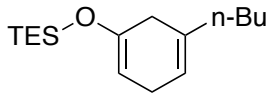
SK-161012-TBDMS-DIENE6.10.fid



SK-161012-TBDMS-DIENE6C.10.fid




TES
O
Et
jg6-65-p(H C)/10
JG6-65-P (H, C)
f1 (ppm)
jg6-65-p(H C)/11
JG6-65-P (H, C)
f1 (ppm)



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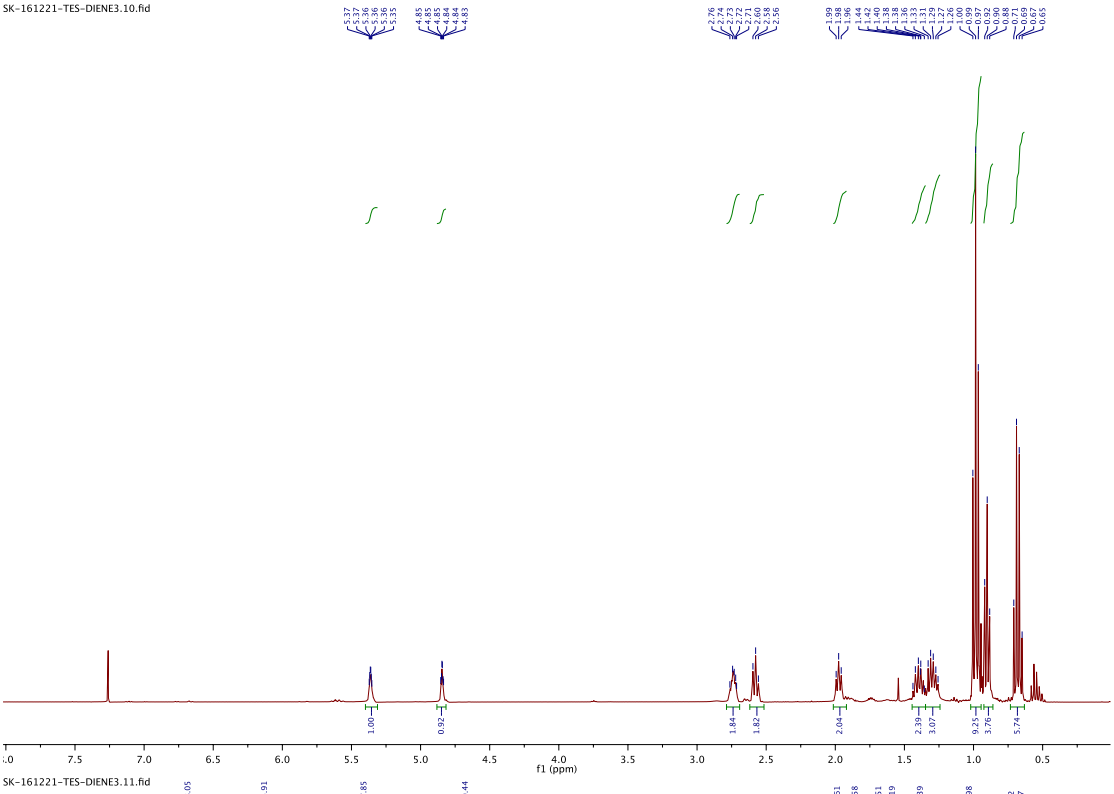

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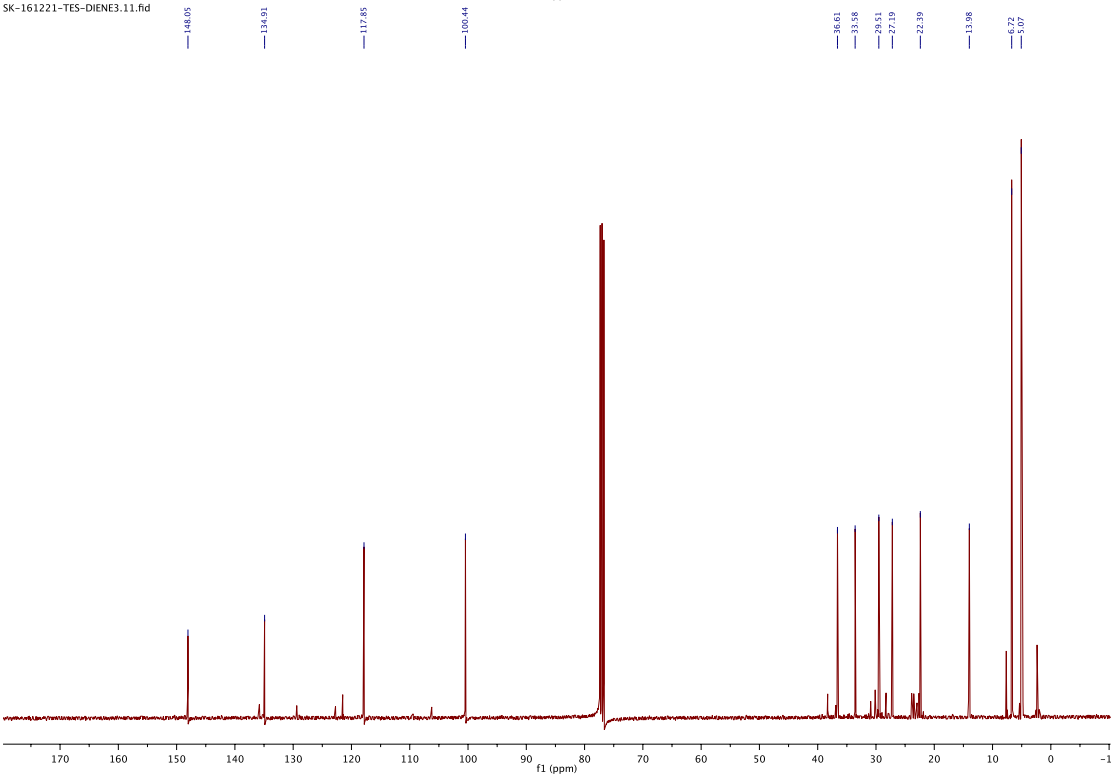
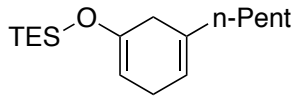
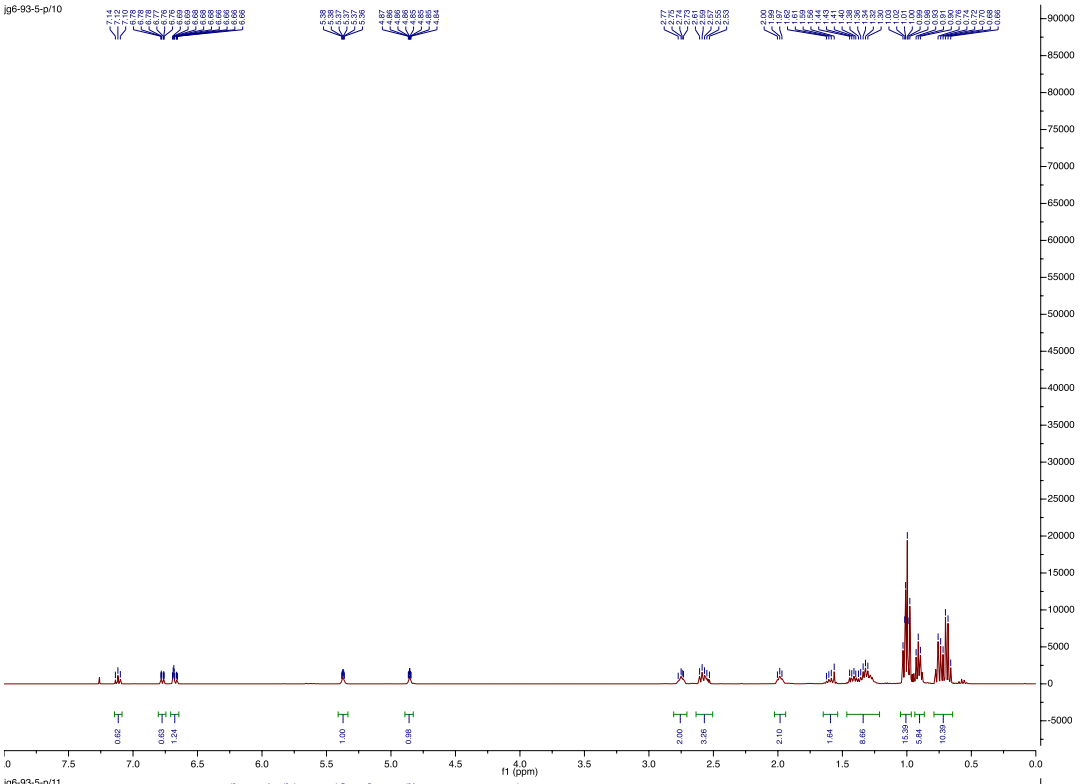
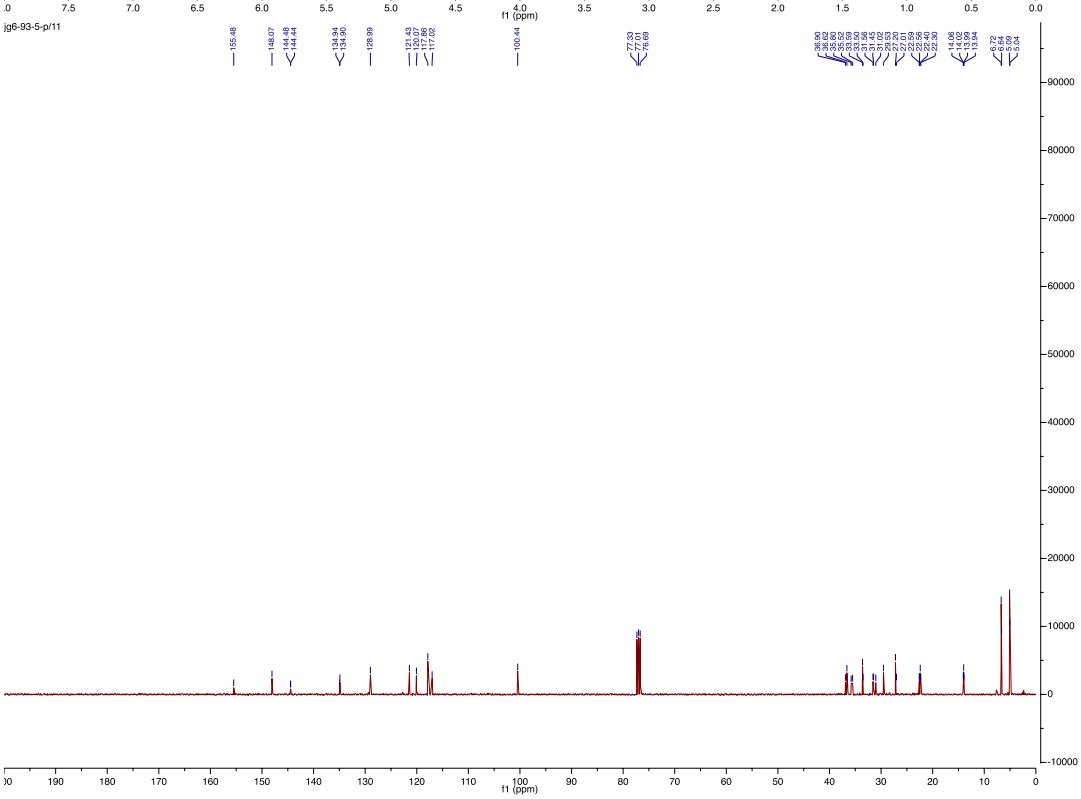
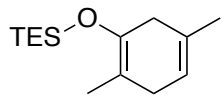


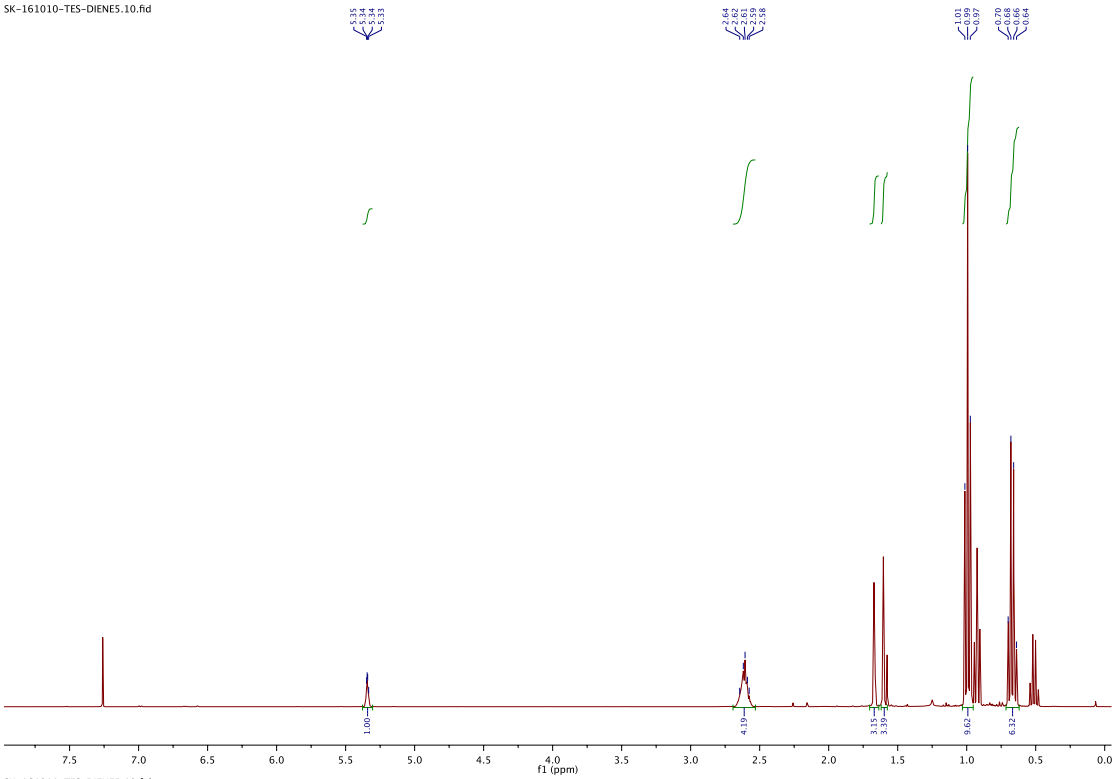

TES
O
n-Pent


jg6-93-5-p/10
f1 (ppm)

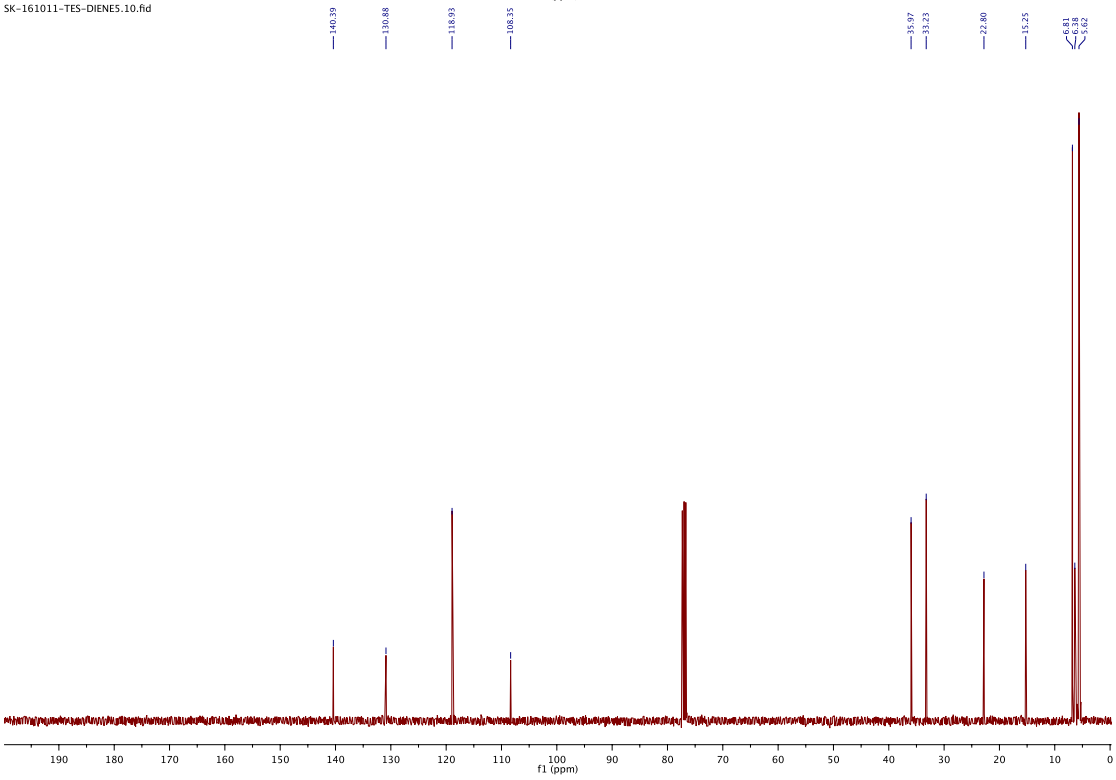

jg6-93-5-p/11
f1 (ppm)

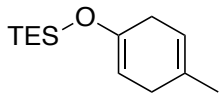


SK-161010-TES-DIENE5.10.fid

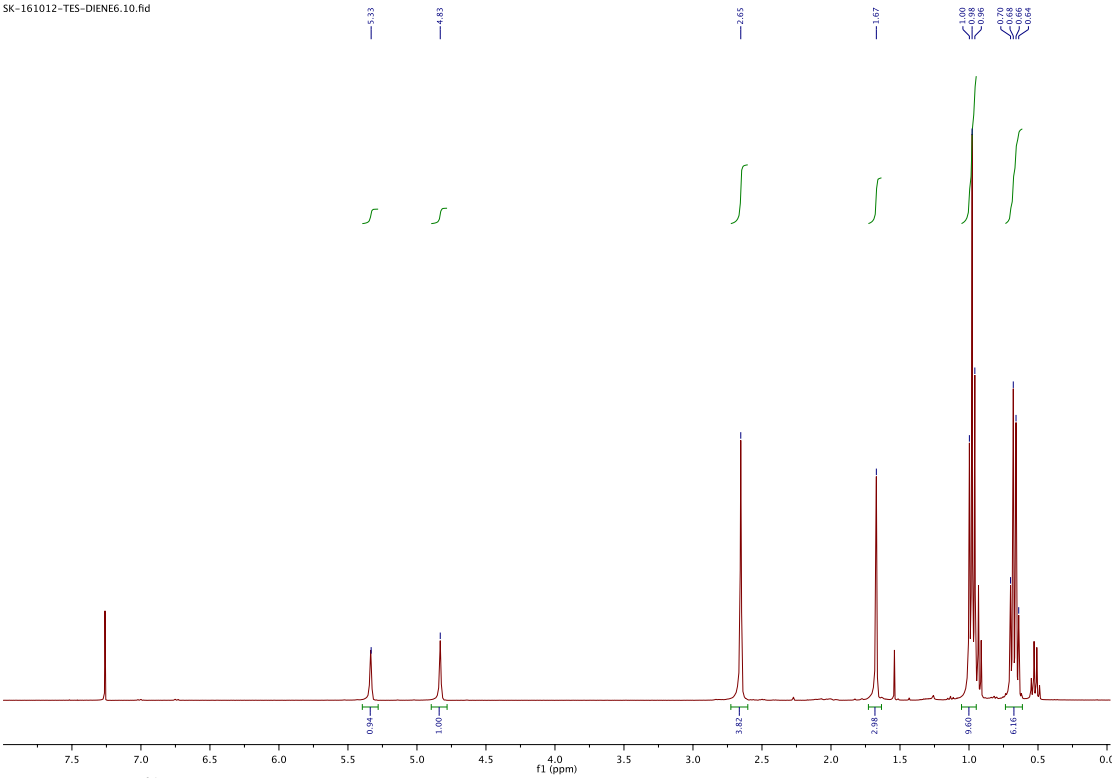


SK-161011-TES-DIENE5.10.fid

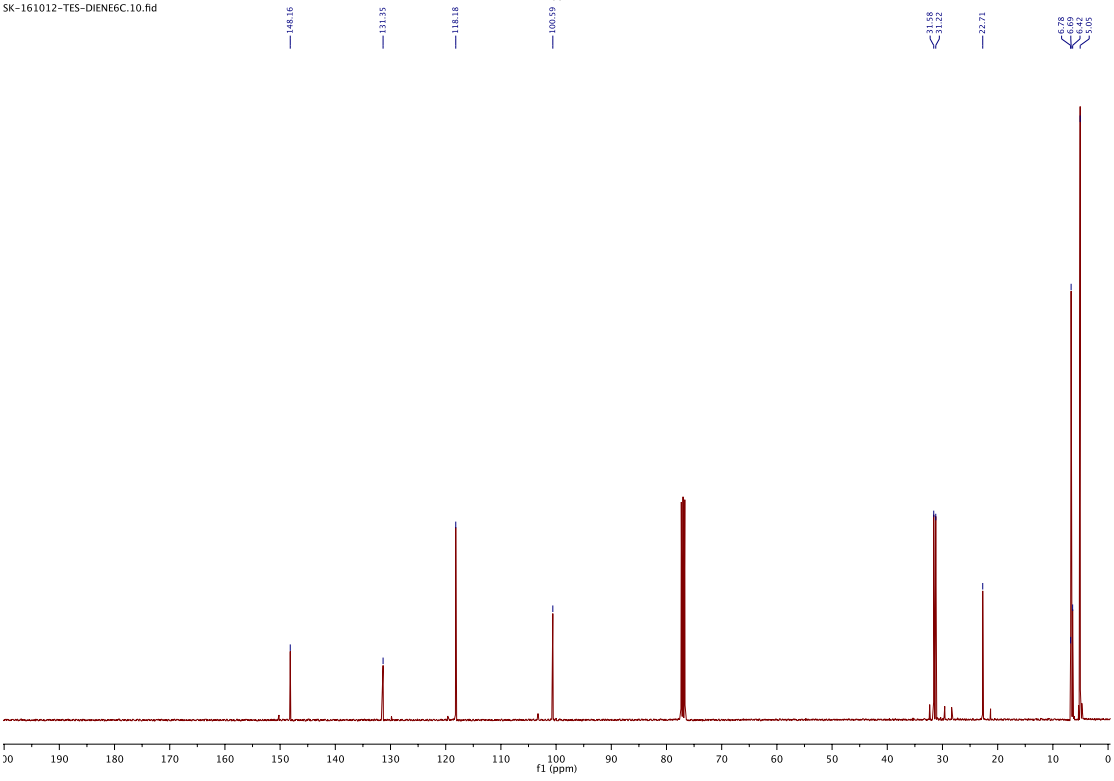


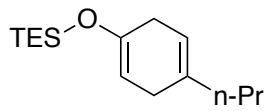


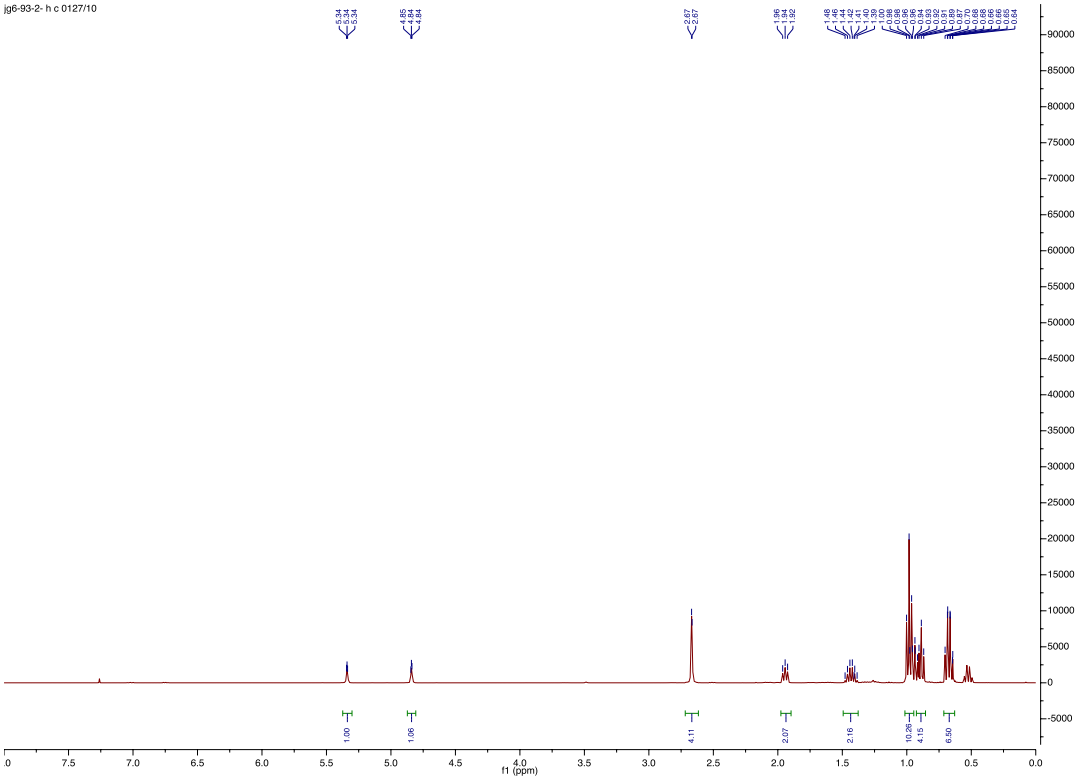
SK-161012-TES-DIENE6.10.fid

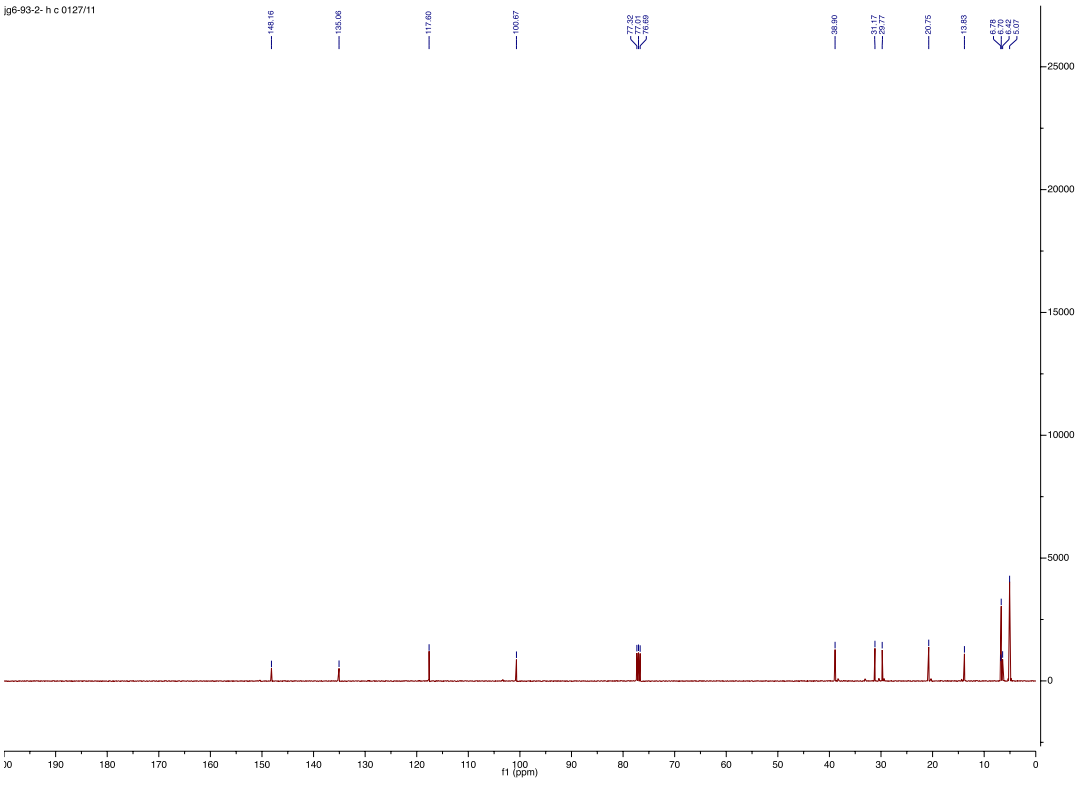


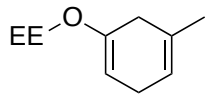
SK-161012-TES-DIENE6C.10.fid



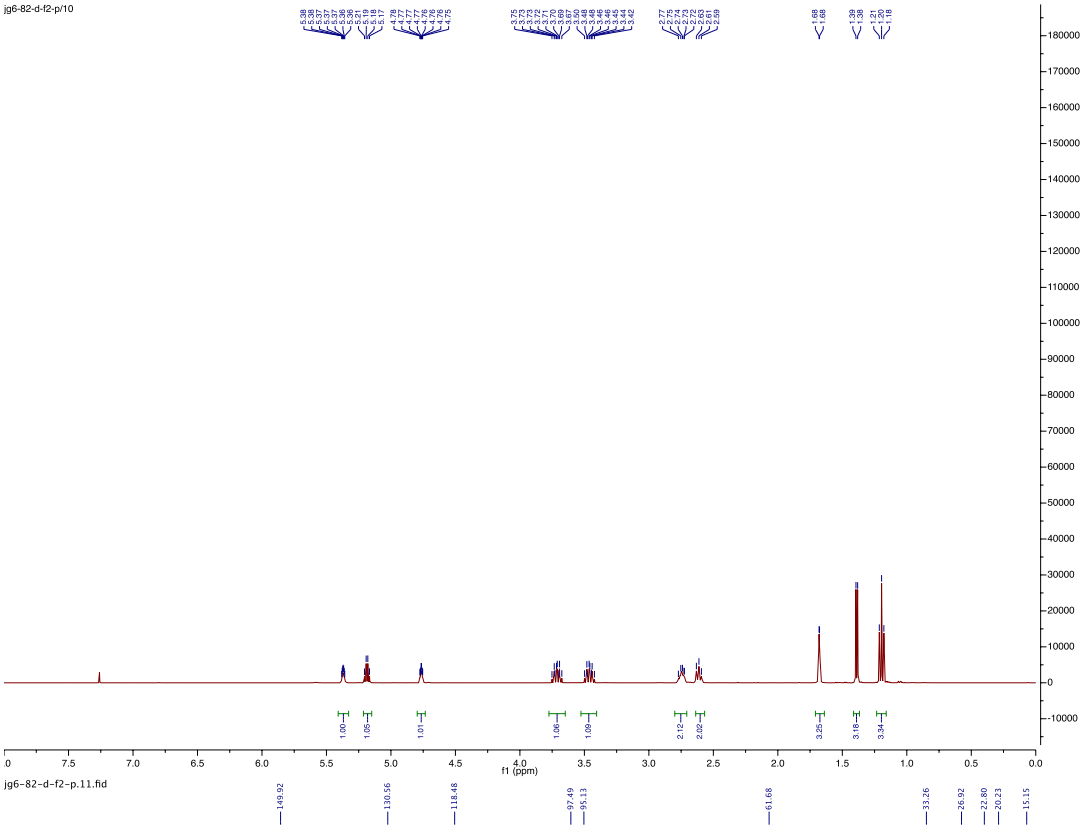

TES
O
n-Pr


jg6-93-2- h c 0127/10
f1 (ppm)

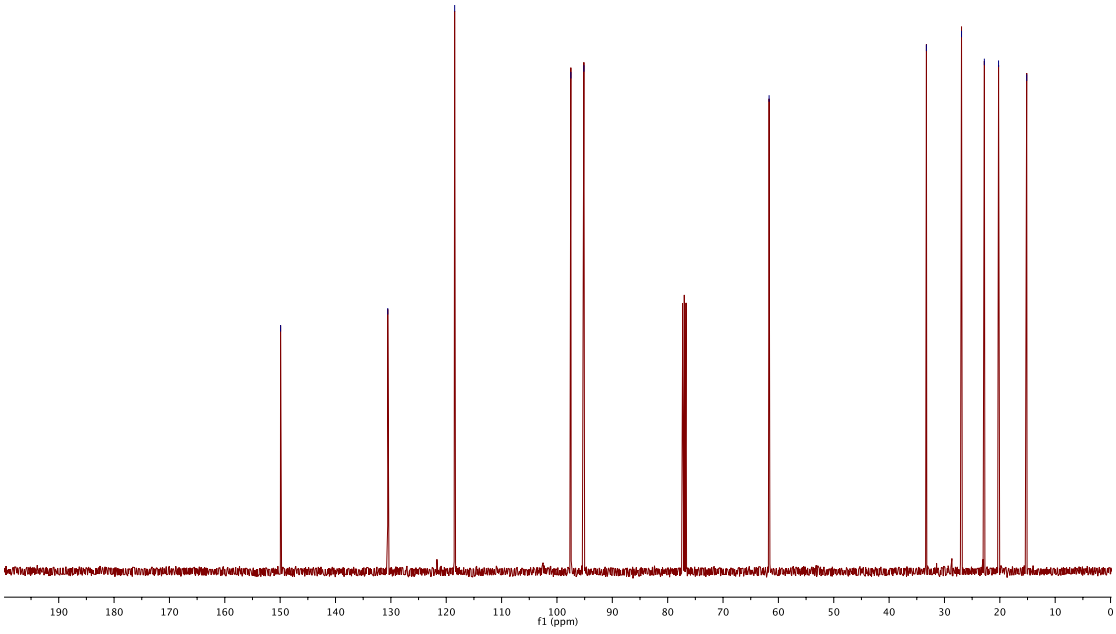

jg6-93-2- h c 0127/11
f1 (ppm)

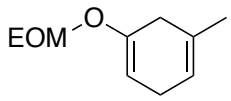


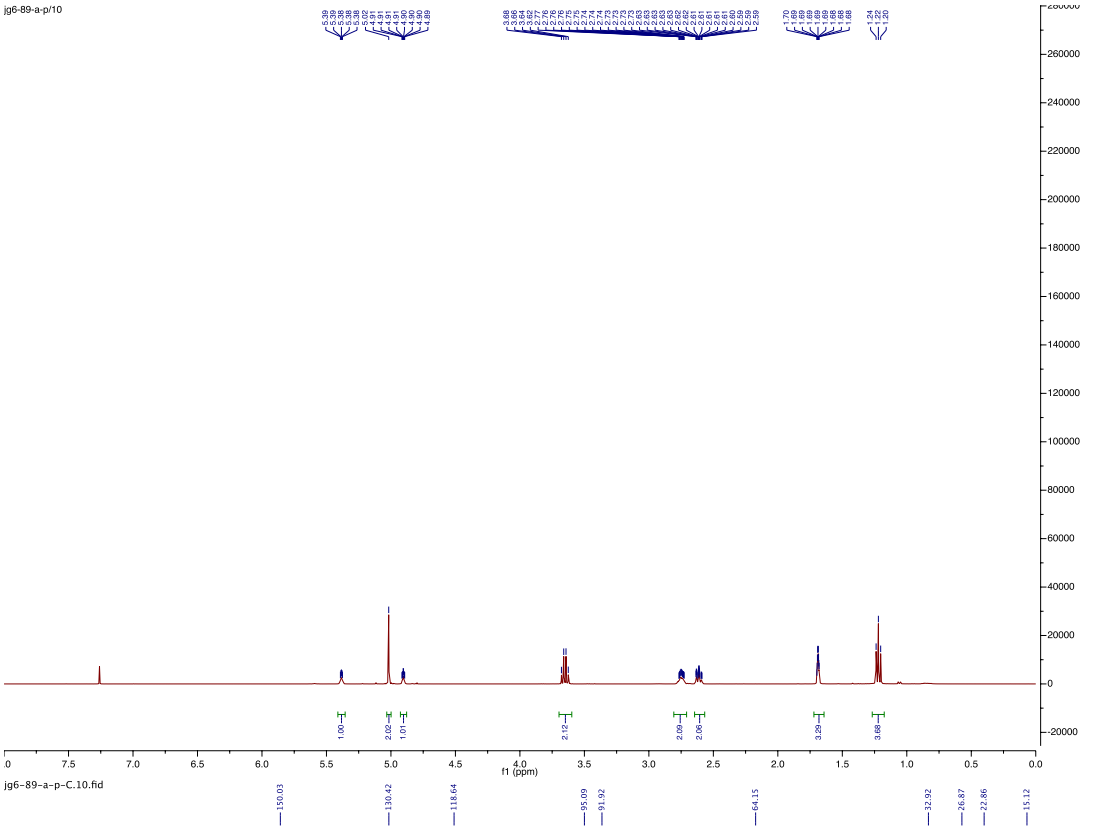
jg6-82-d-f2-p/10

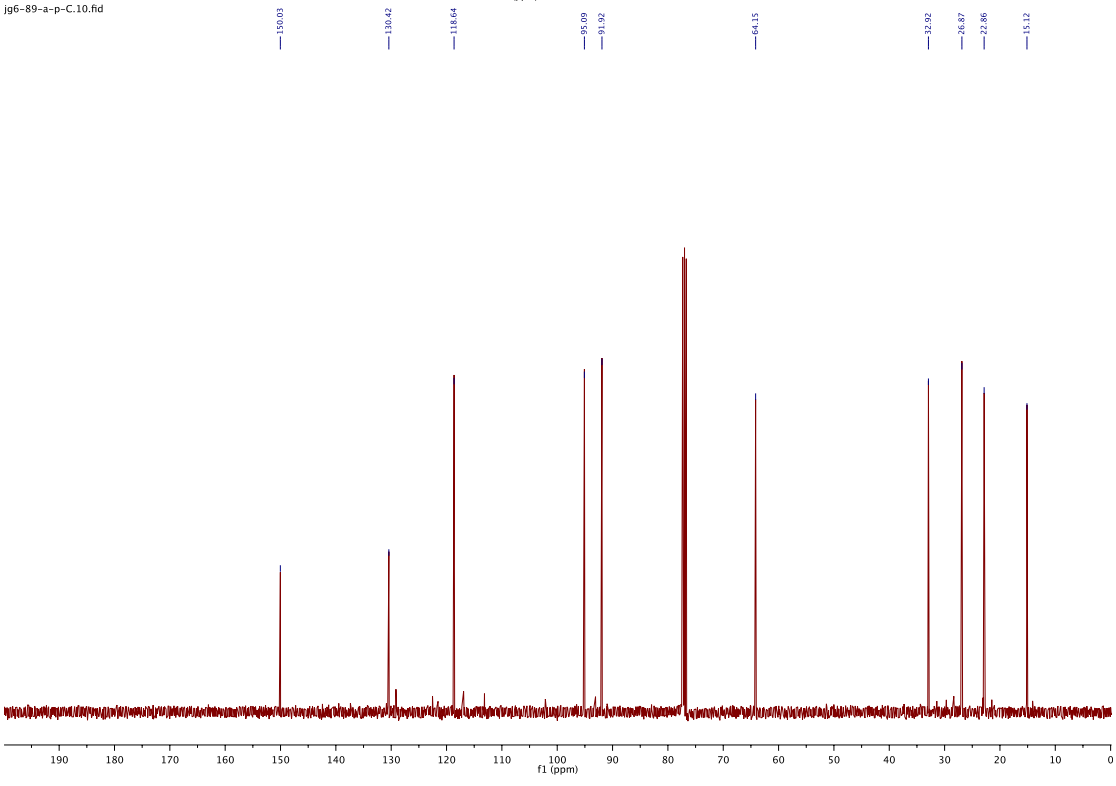


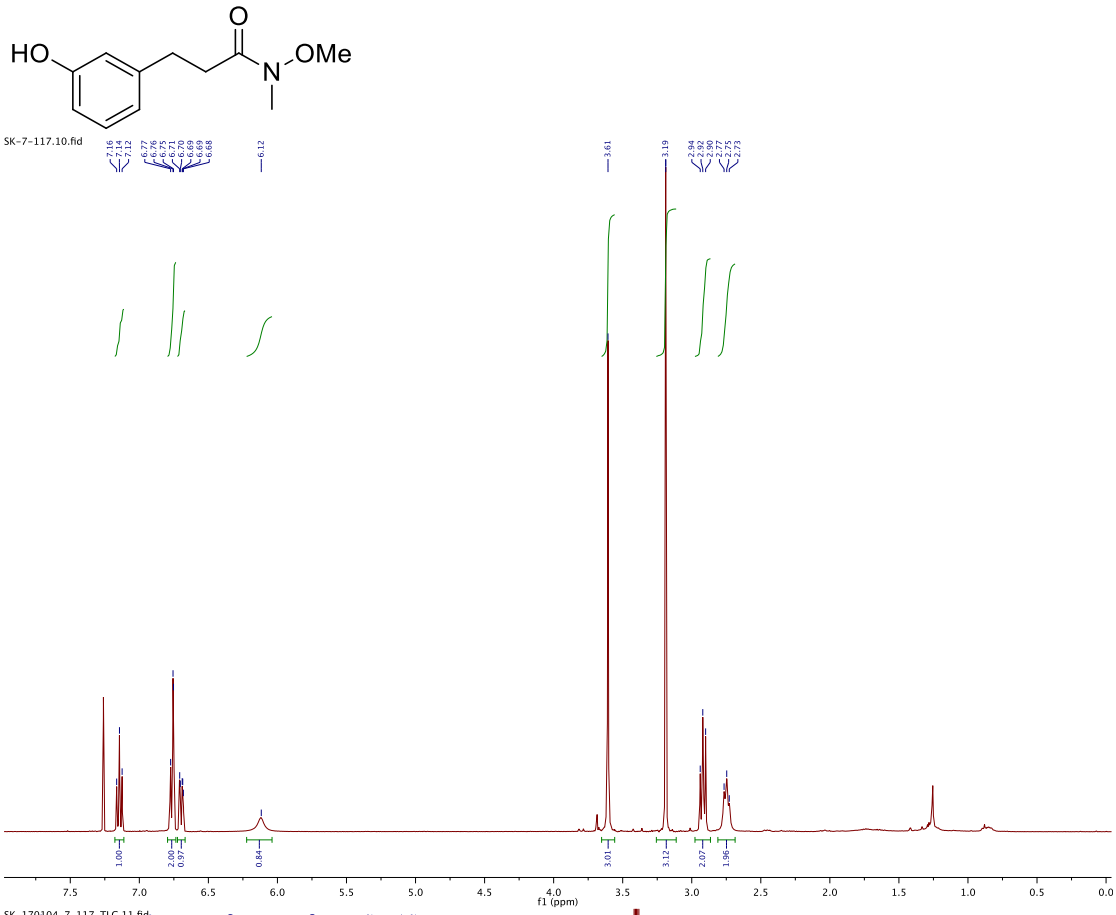
jg6-82-d-f2-p.11.fid

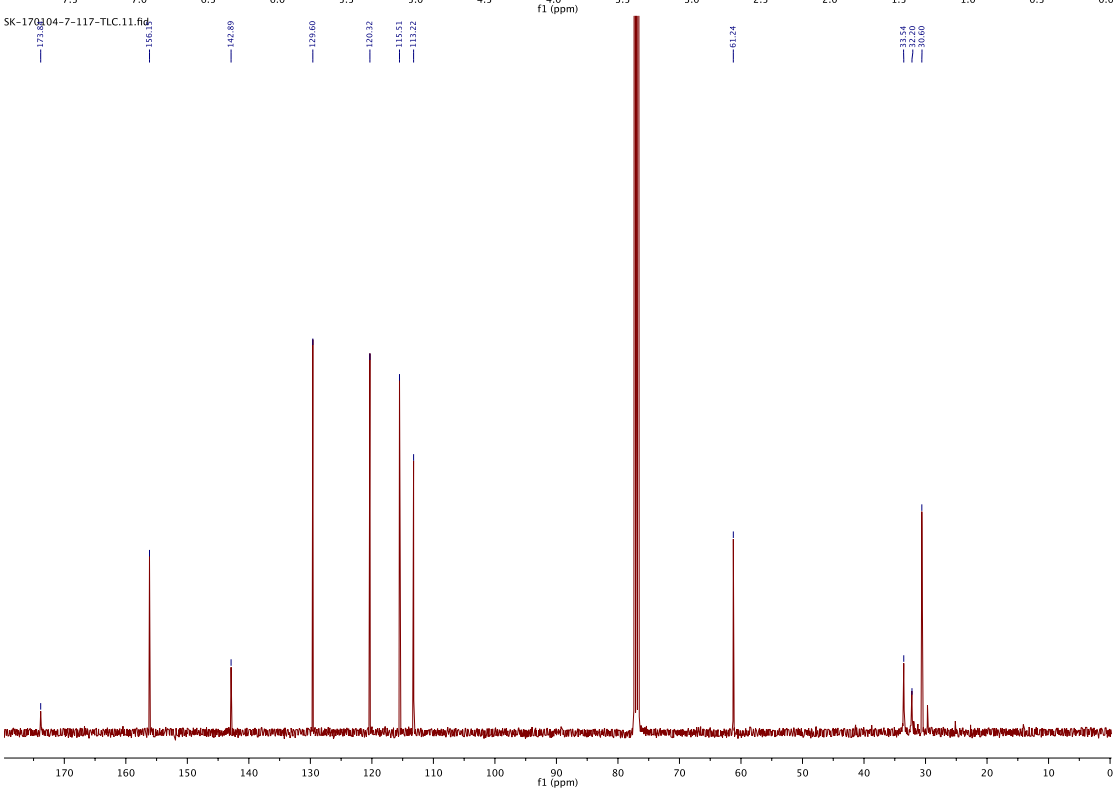


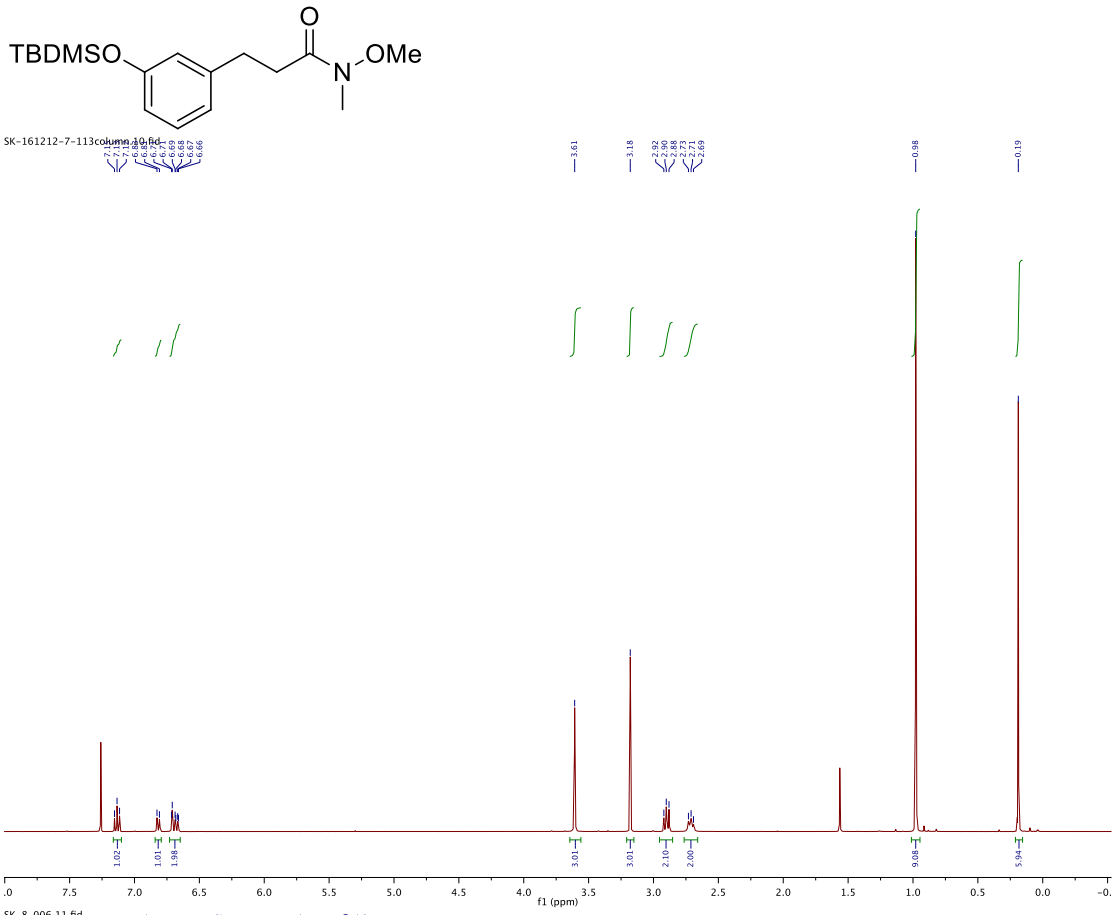

EOM
O

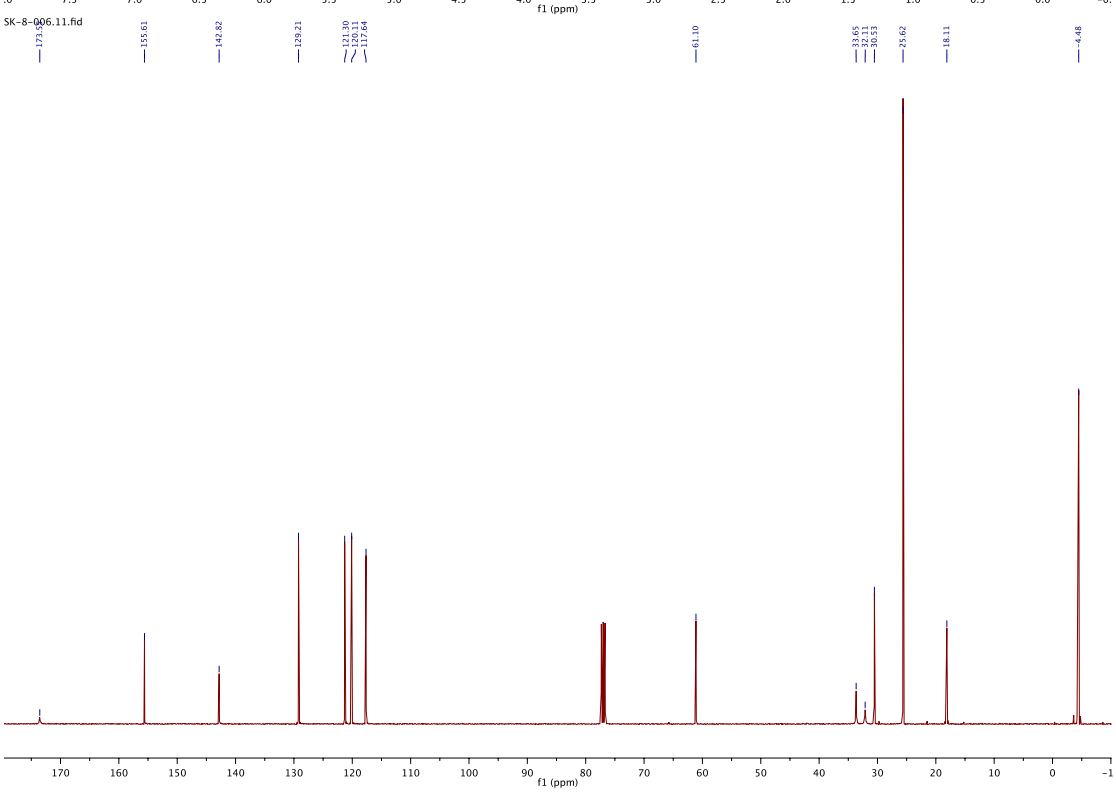

jg6-89-a-p/10
f1 (ppm)

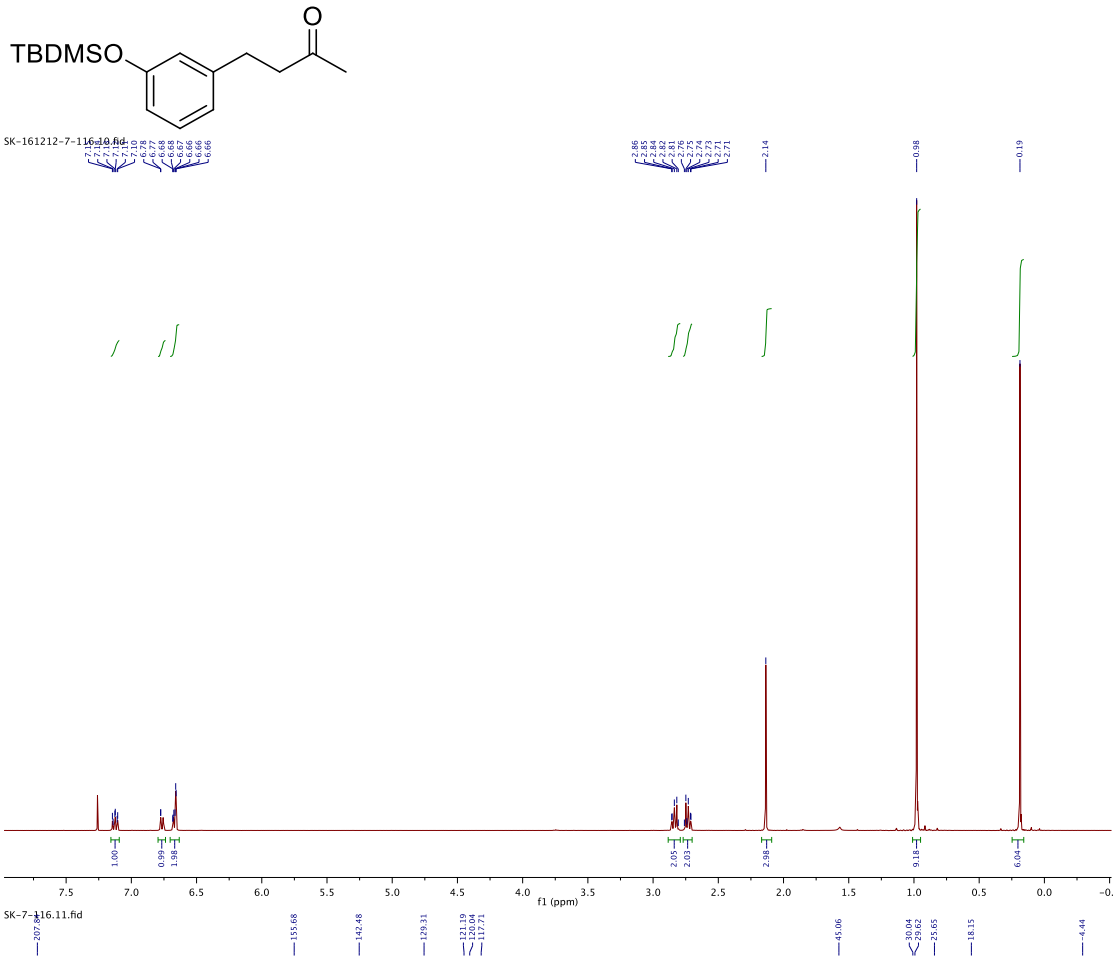

jg6-89-a-p-C.10.fid
f1 (ppm)

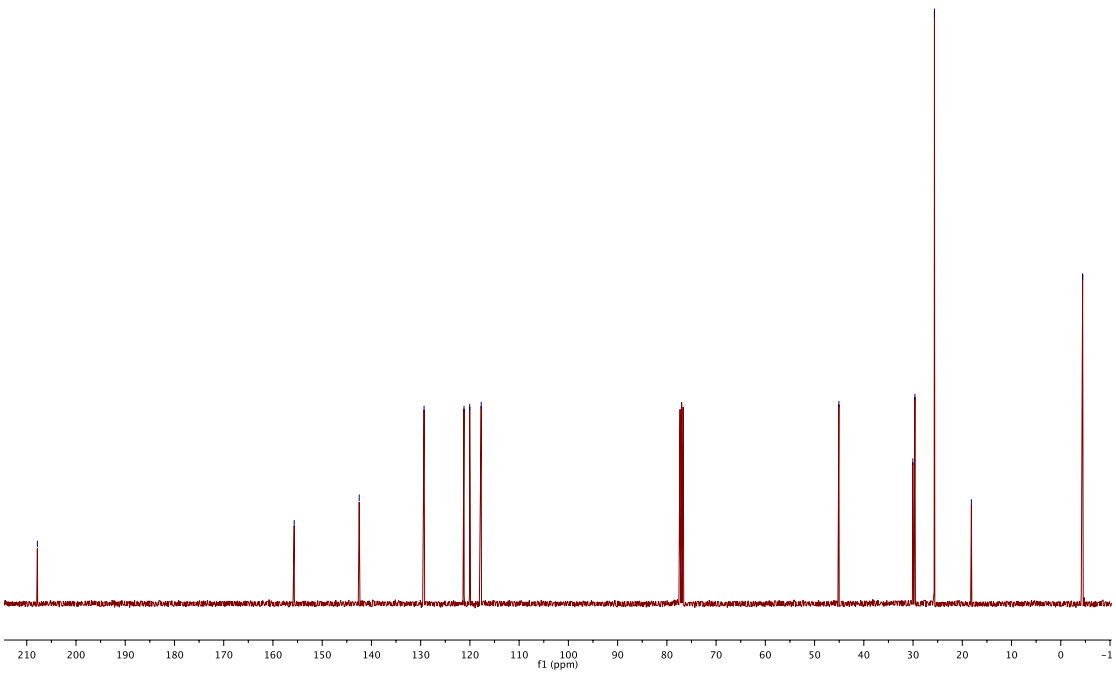

HO
O
N
OMe
SK-7-117.10.fid
7.16
7.14
7.12
6.77
6.76
6.75
6.71
6.70
6.69
6.69
6.68
6.68
6.12
3.61
3.19
2.94
2.92
2.90
2.77
2.75
2.73
1.00
2.00
0.97
0.84
3.01
3.12
2.07
1.96
f1 (ppm)


SK-170104-7-117-TLC.11.fid
173.82
156.15
142.89
129.60
120.32
115.51
113.22
61.24
33.54
32.30
30.60
f1 (ppm)


TBDMSO
O
N
OMe
SK-161212-7-113column10.fid
f1 (ppm)


SK-8-006.11.fid
f1 (ppm)


TBDMSO
O
SK-161212-7-116-10.fid
f1 (ppm)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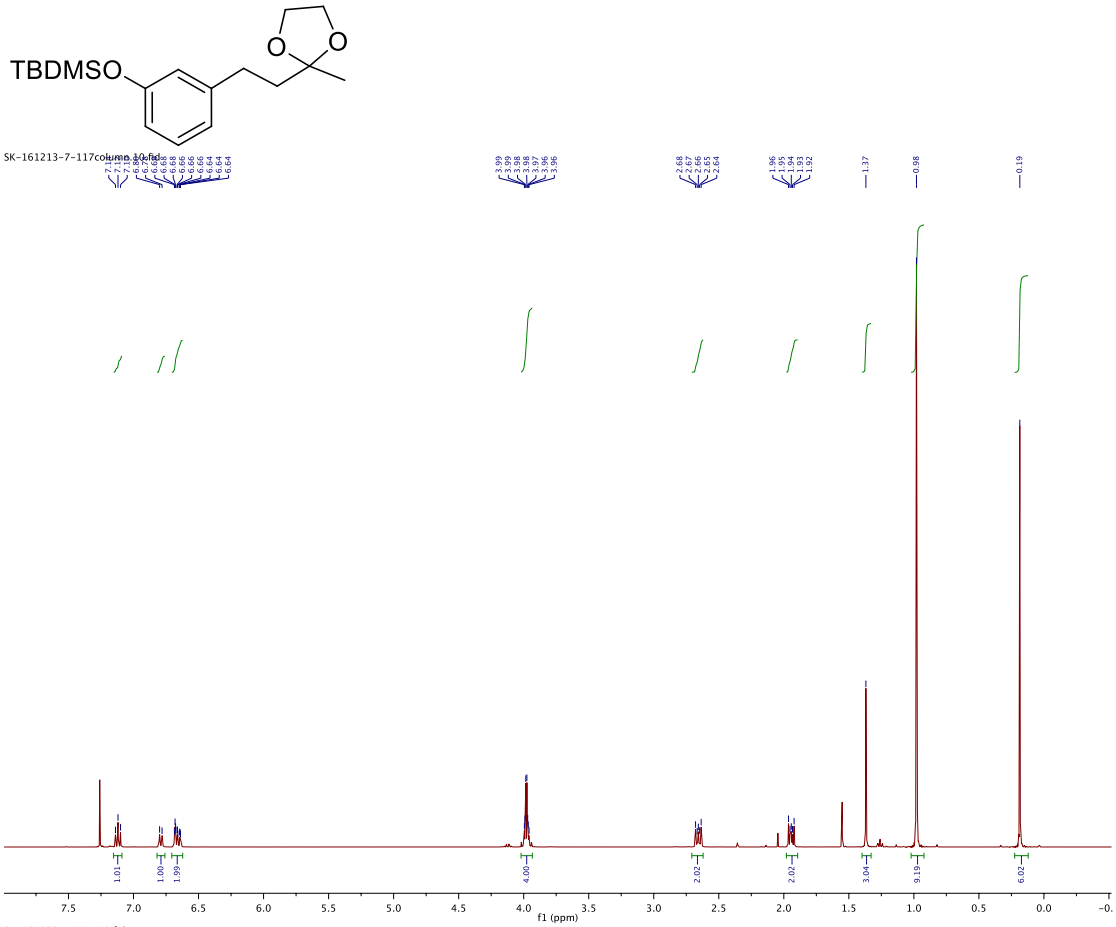
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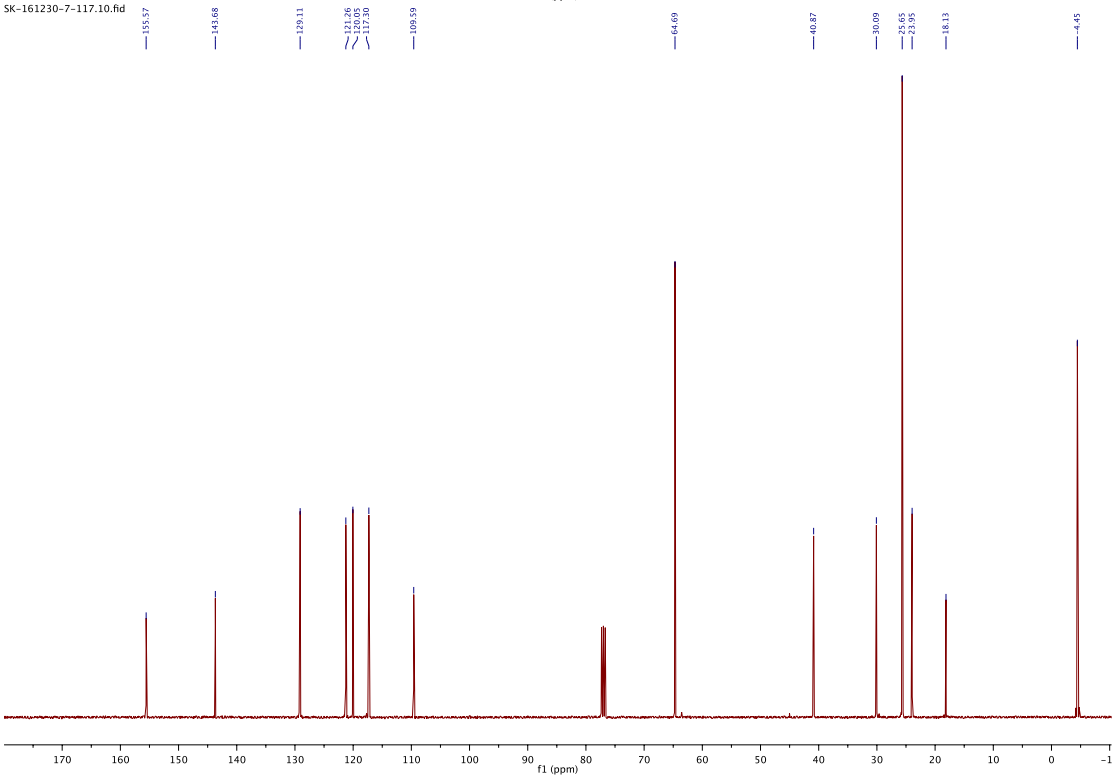
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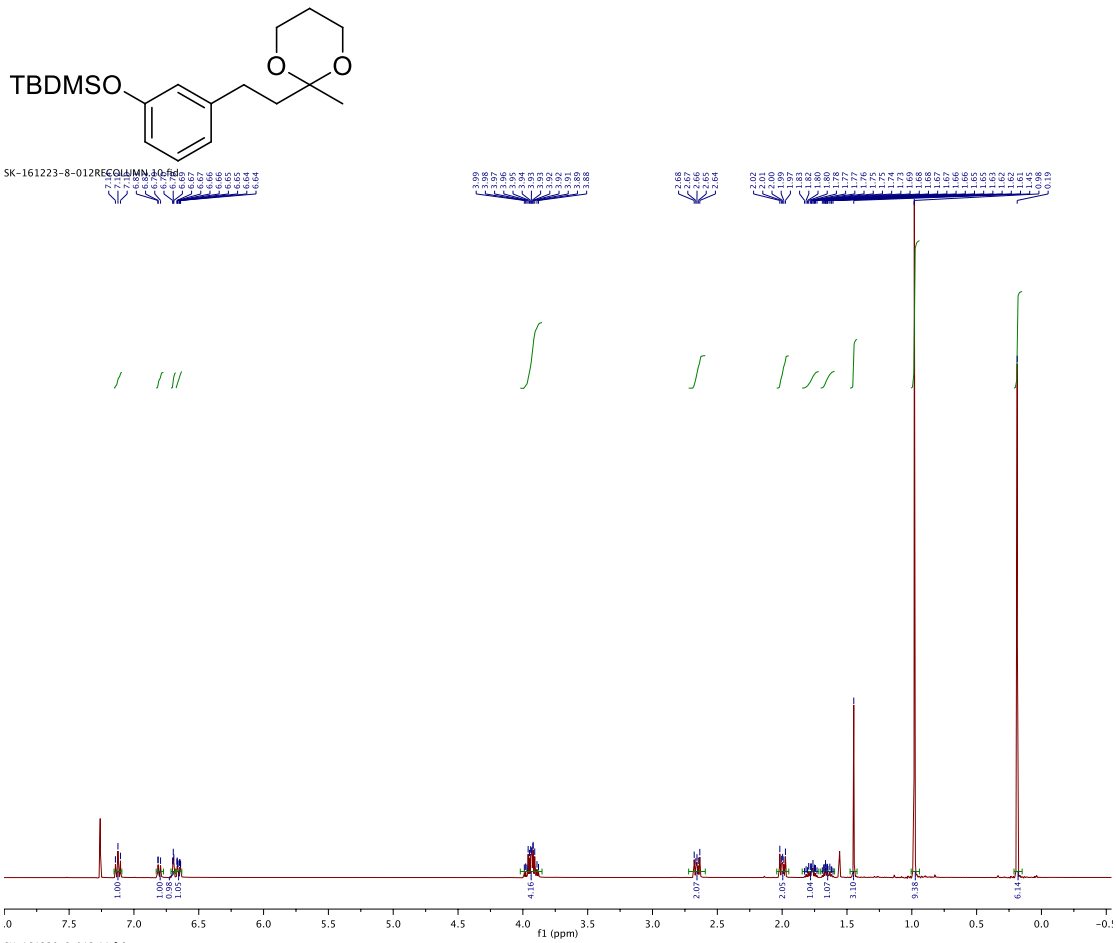
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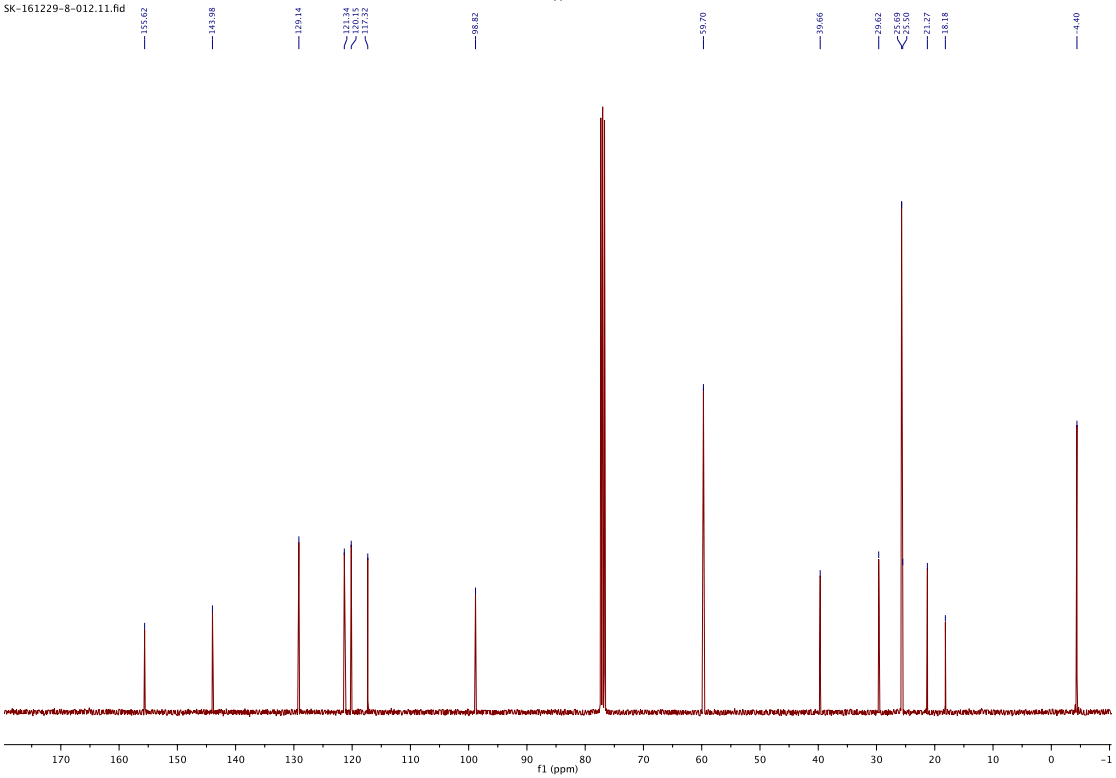
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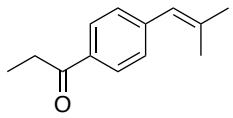

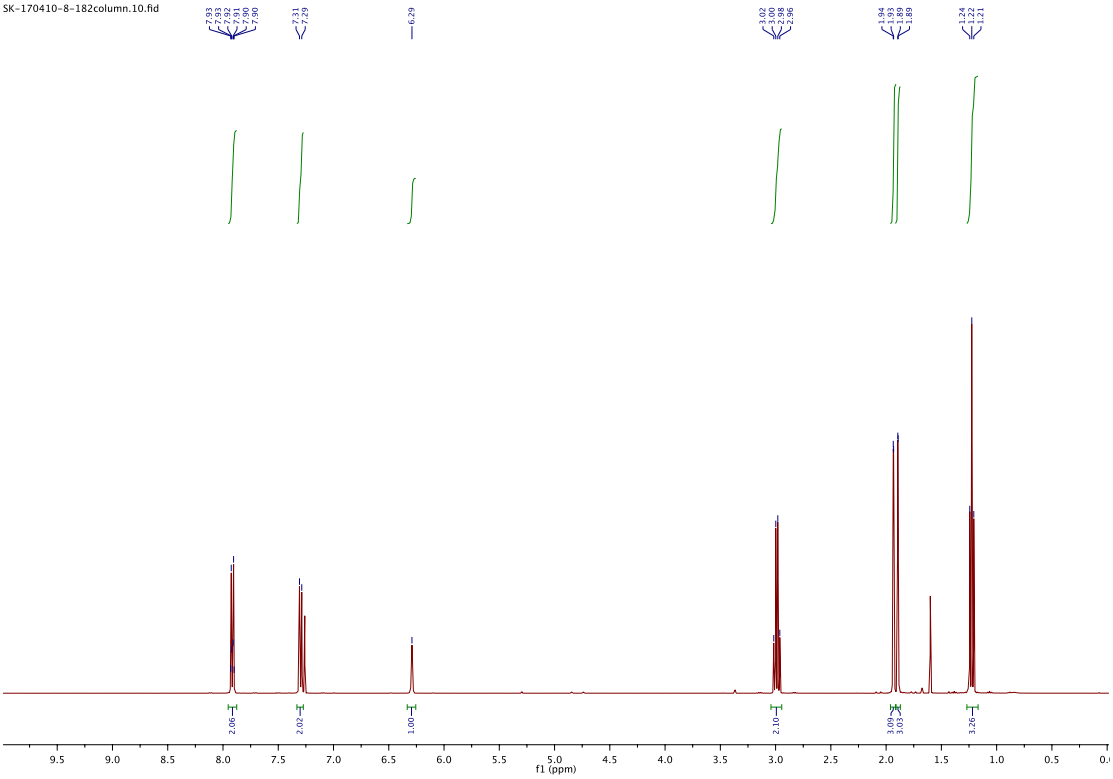
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2.98
2.96
1.94
1.93
1.89
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2.02
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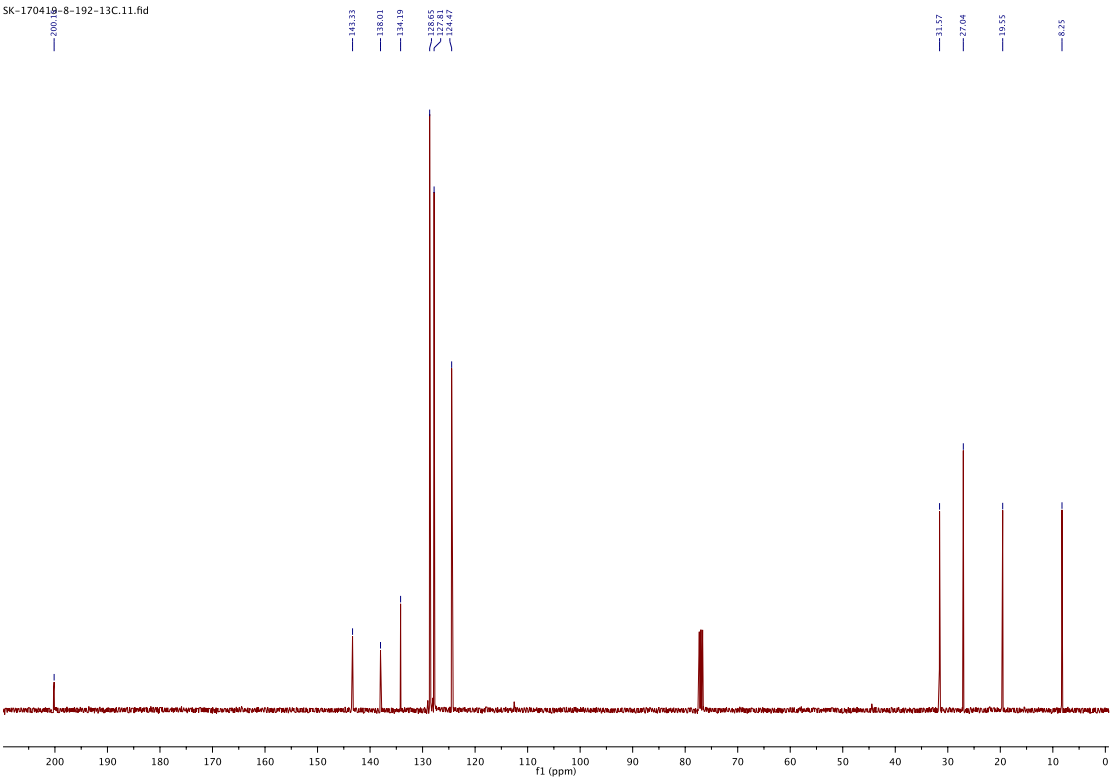
f1 (ppm)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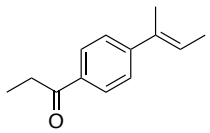

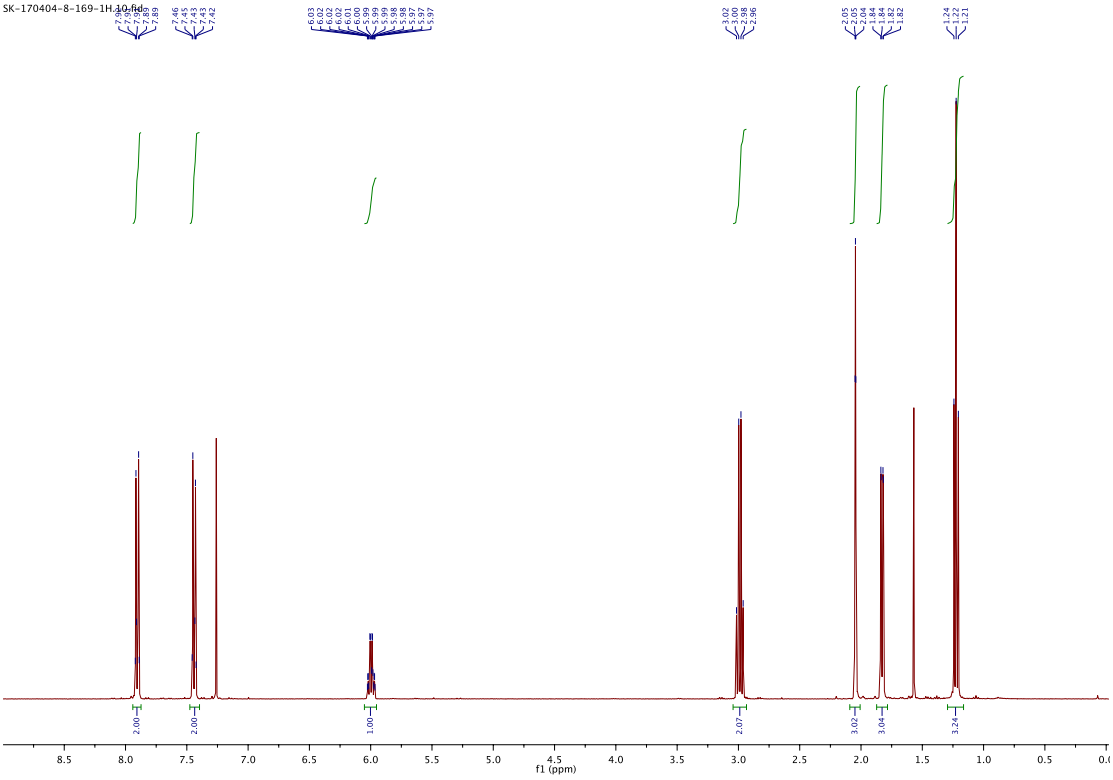
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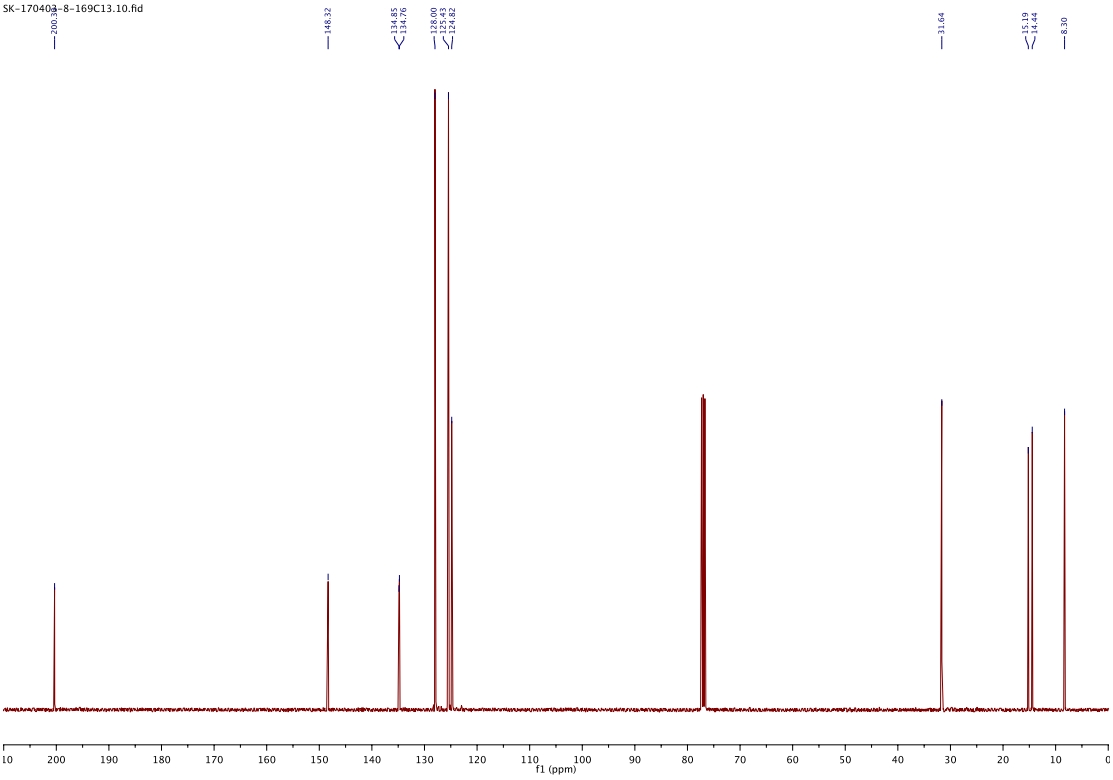
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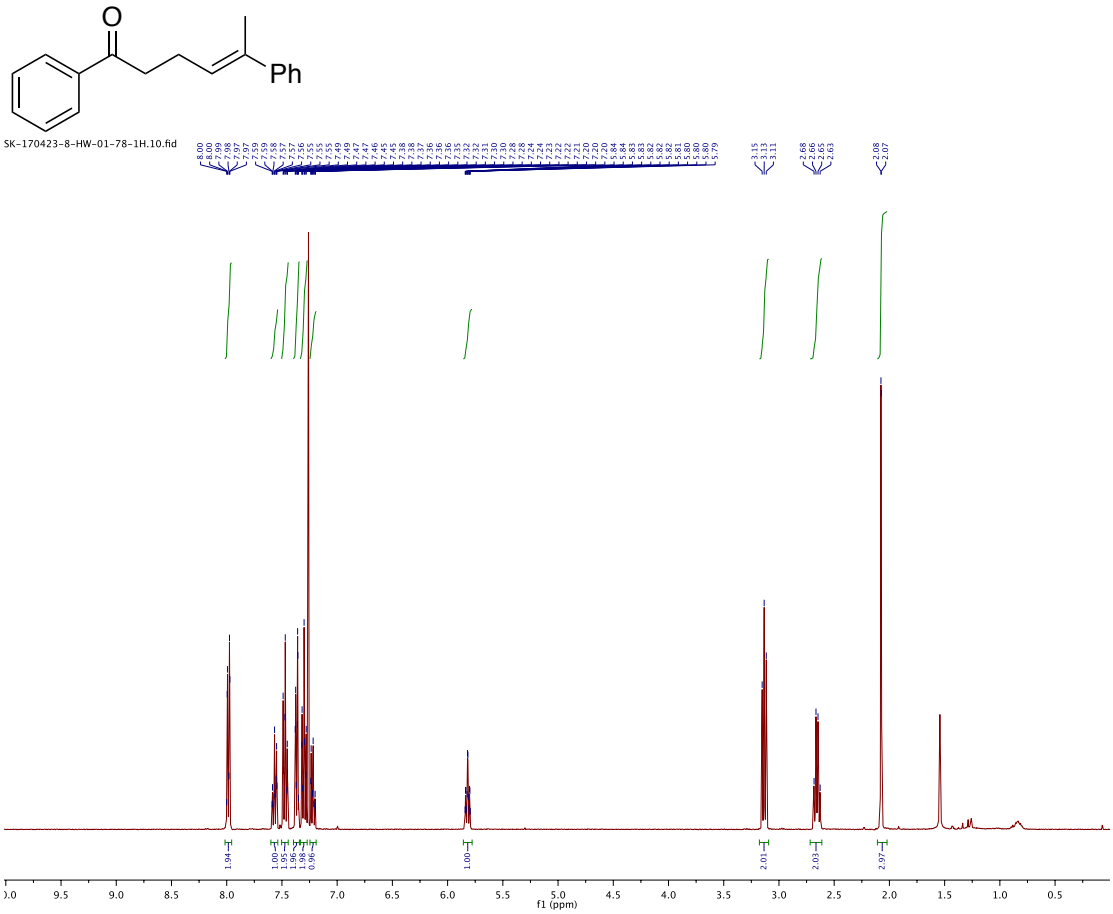
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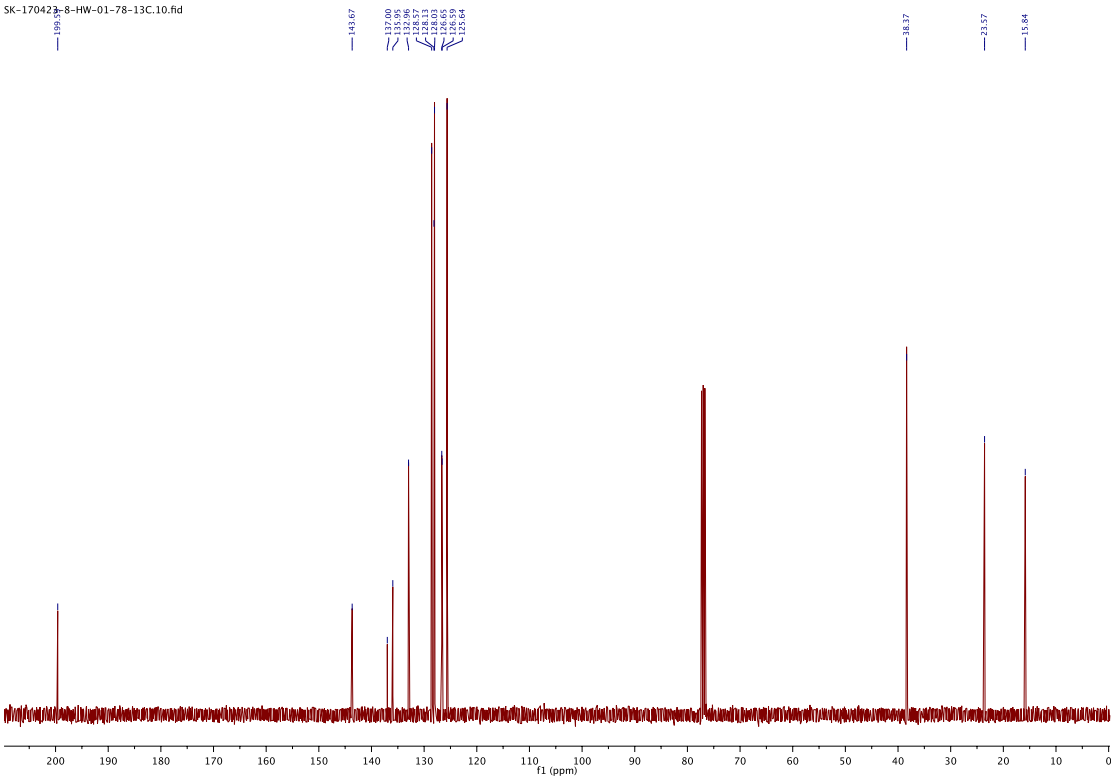
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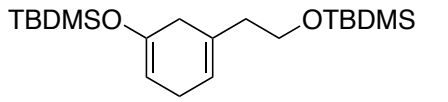
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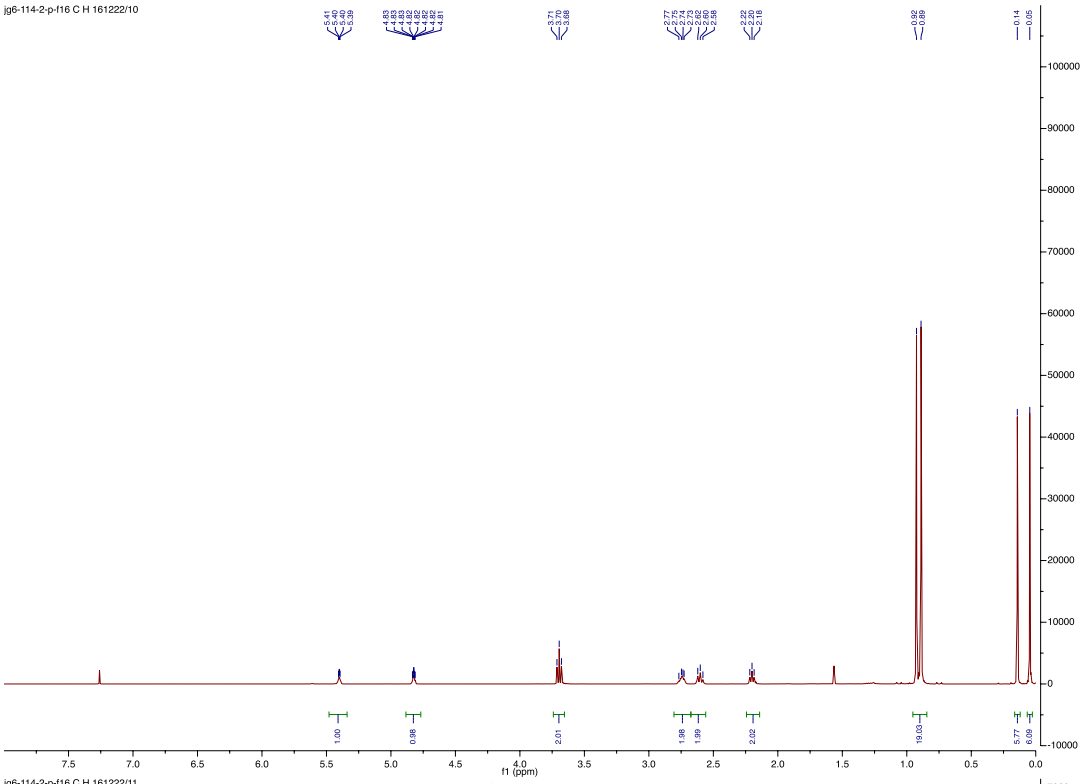
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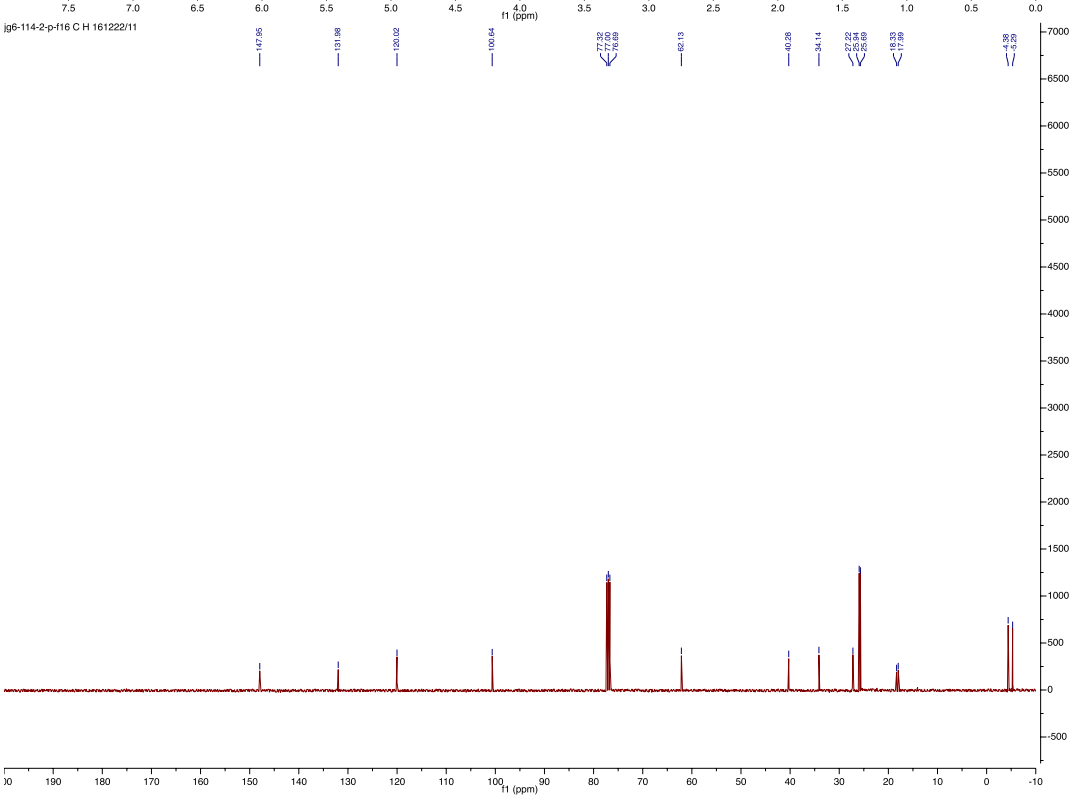
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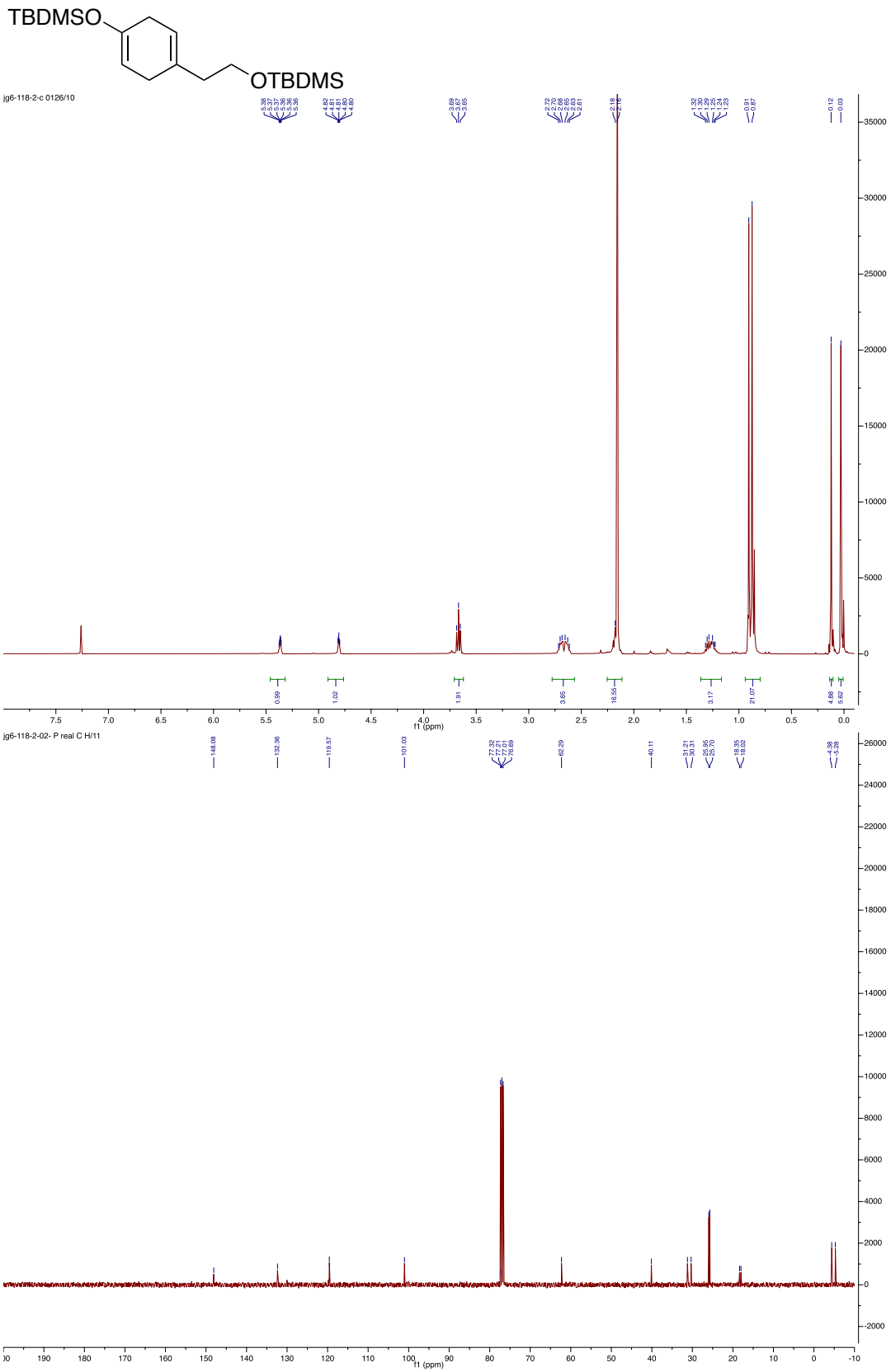
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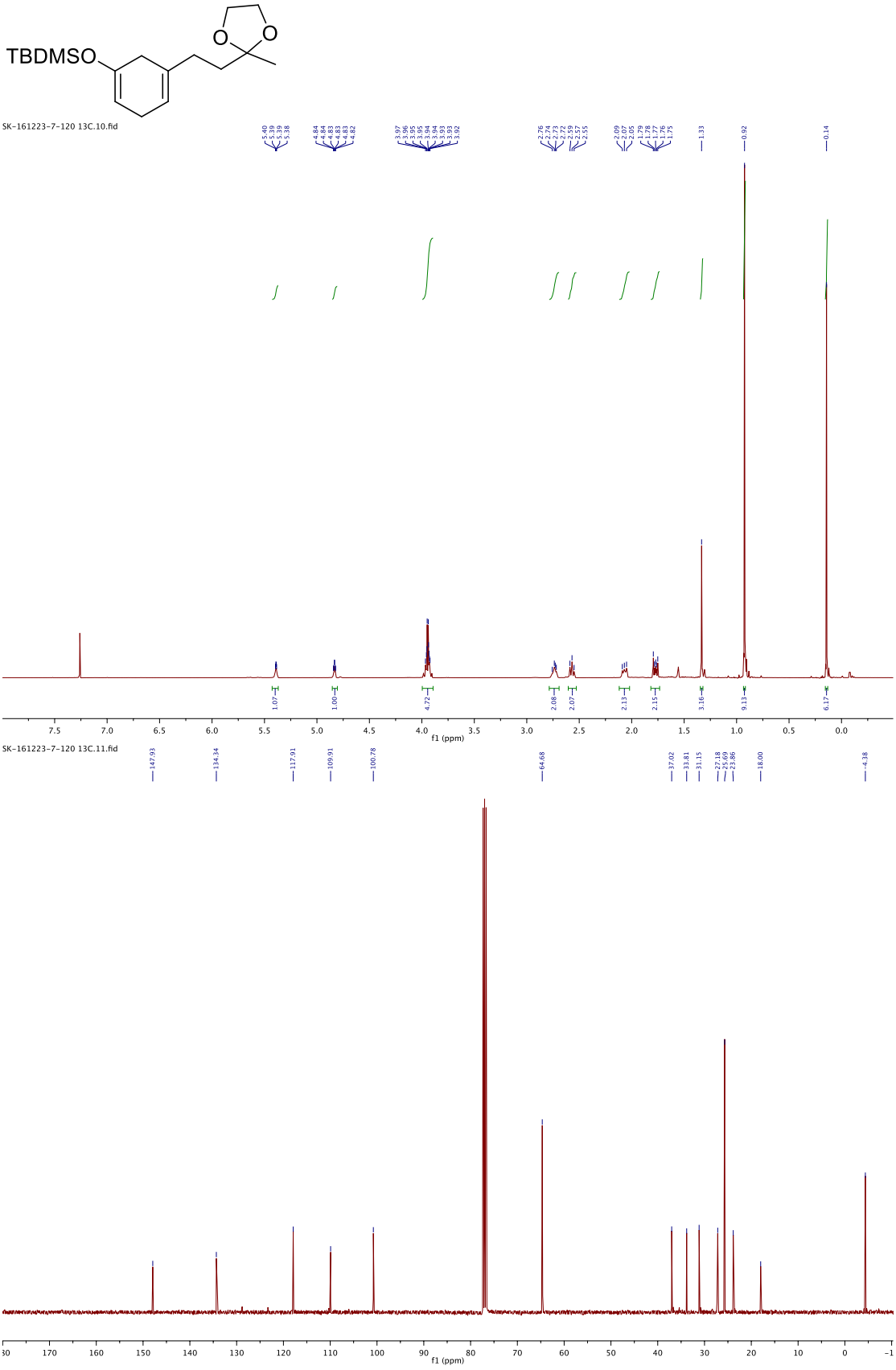
f1 (ppm)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2.59
2.57
2.55
2.09
2.07
2.05
1.79
1.78
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1.76
1.75
1.33
0.92
0.14
1.07
1.00
4.72
2.08
2.07
2.13
2.15
3.16
9.13
6.17
f1 (ppm)
SK-161223-7-120 13C.11.fid
147.93
134.34
117.91
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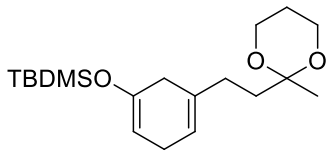

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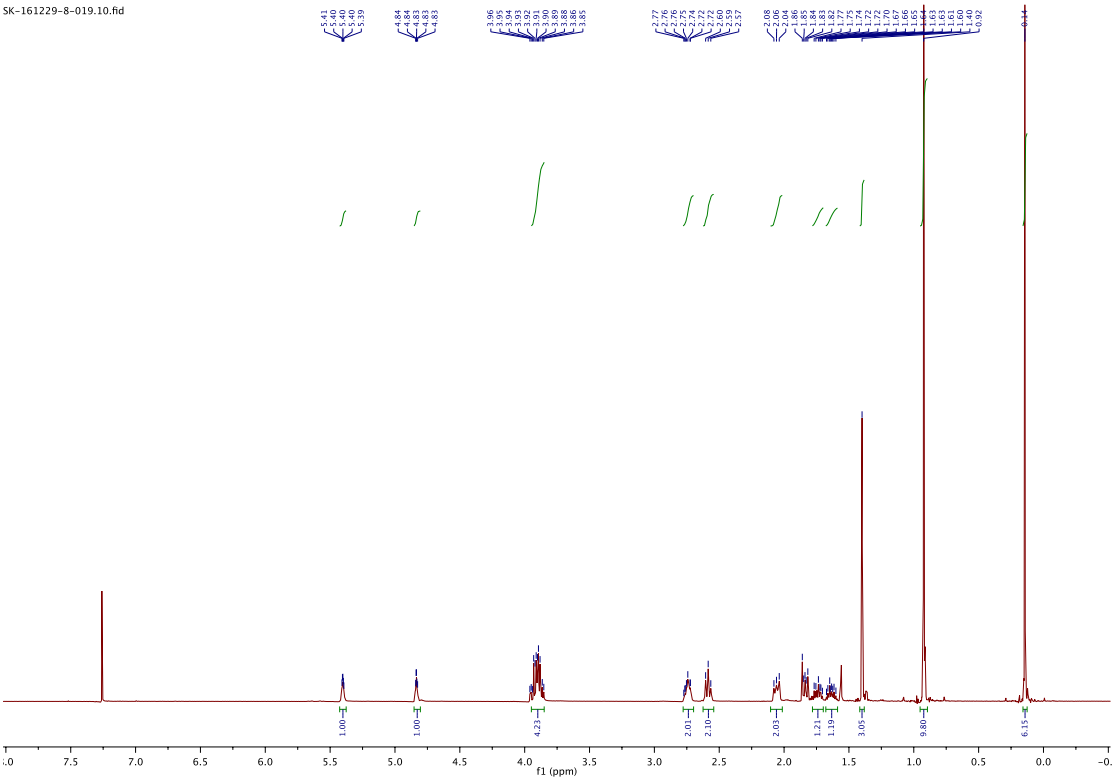

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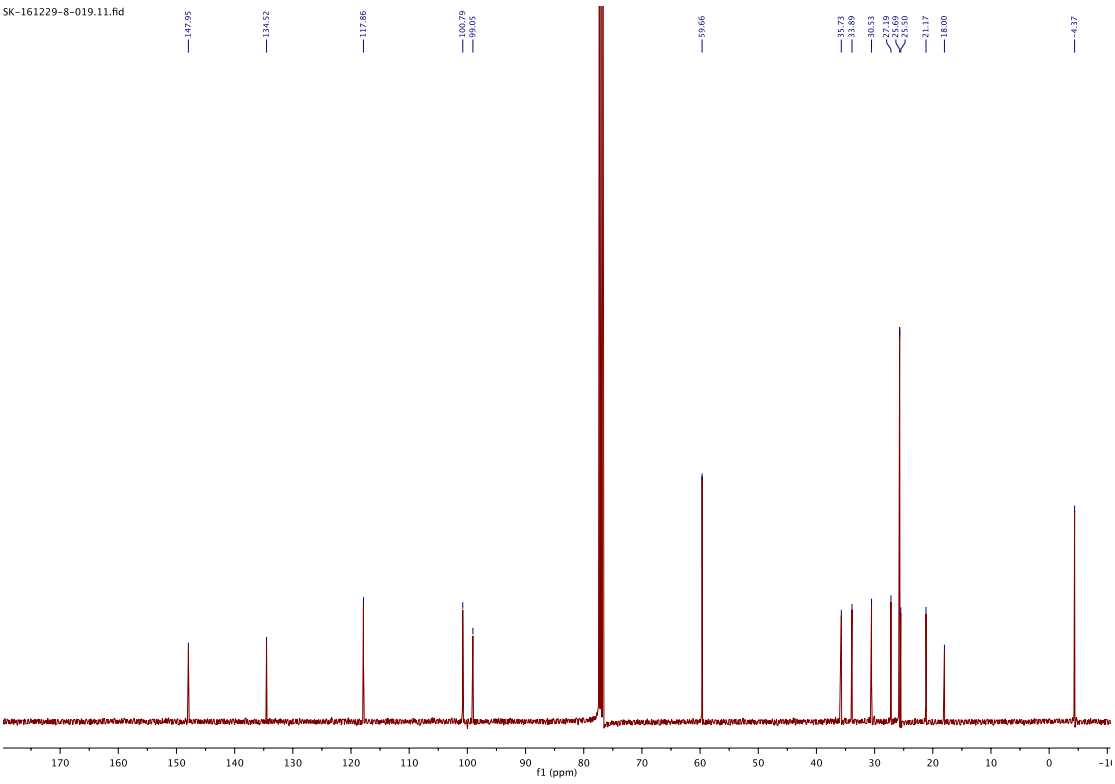

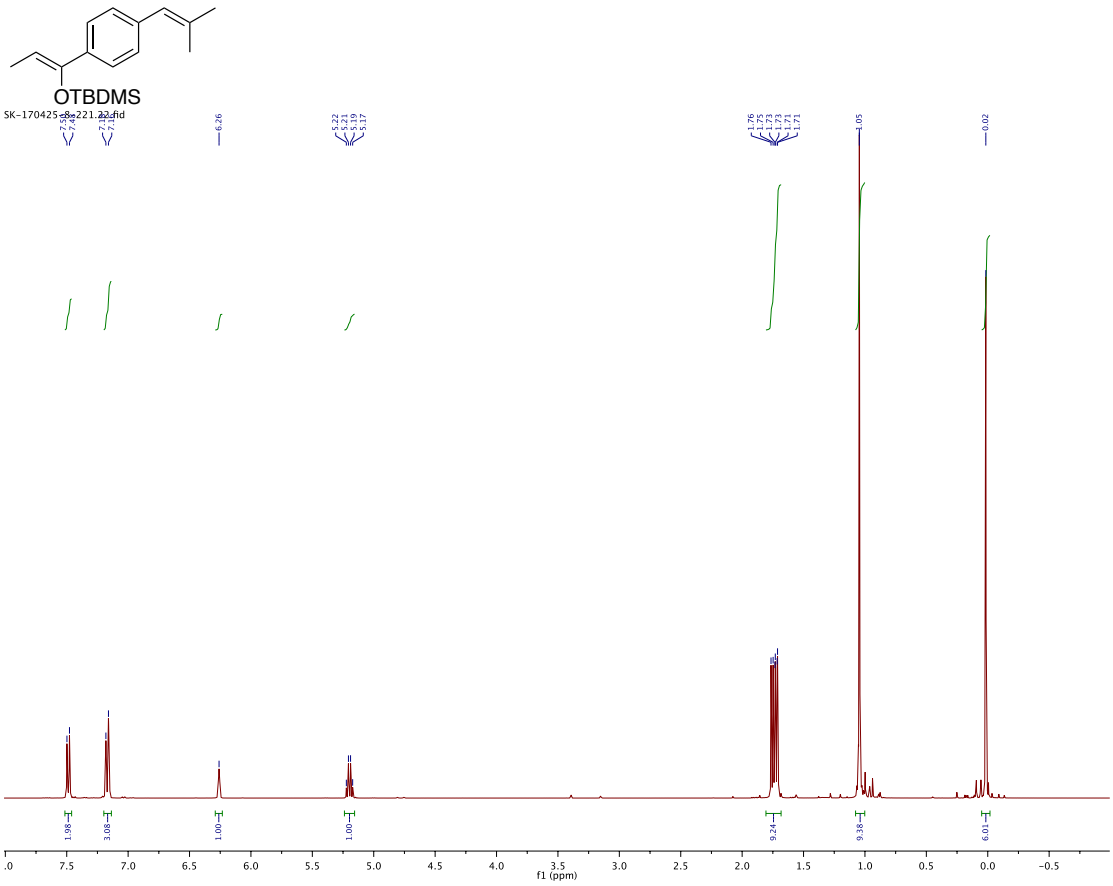
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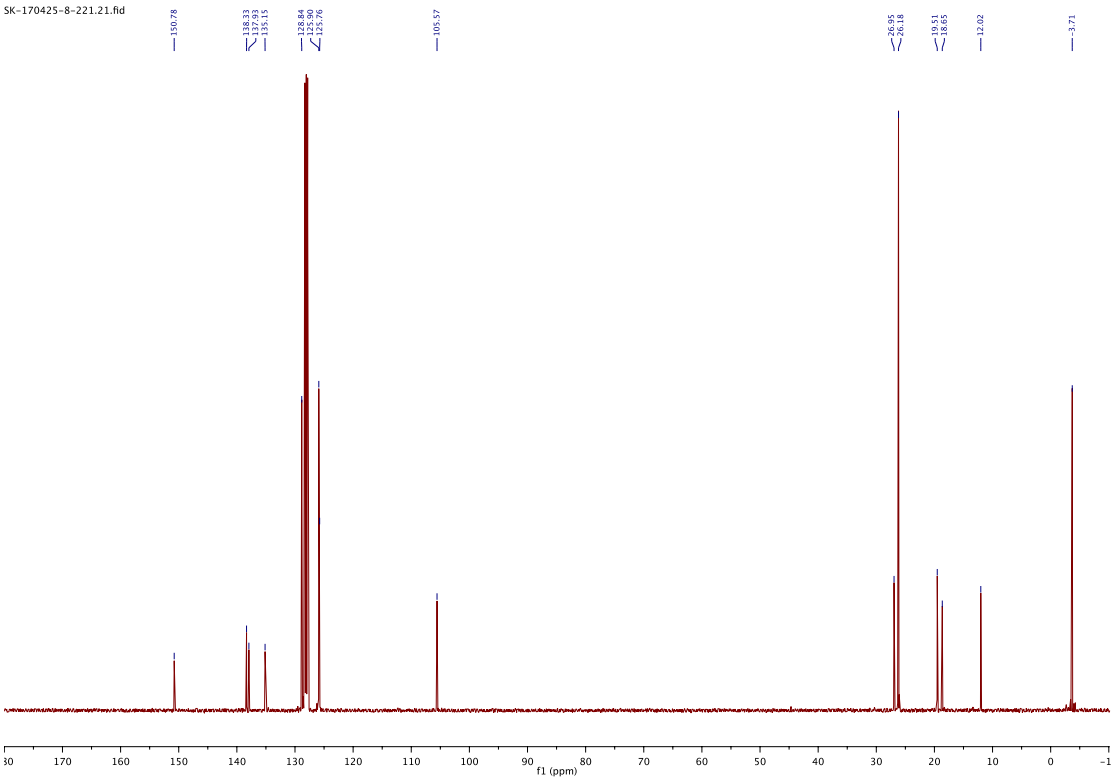
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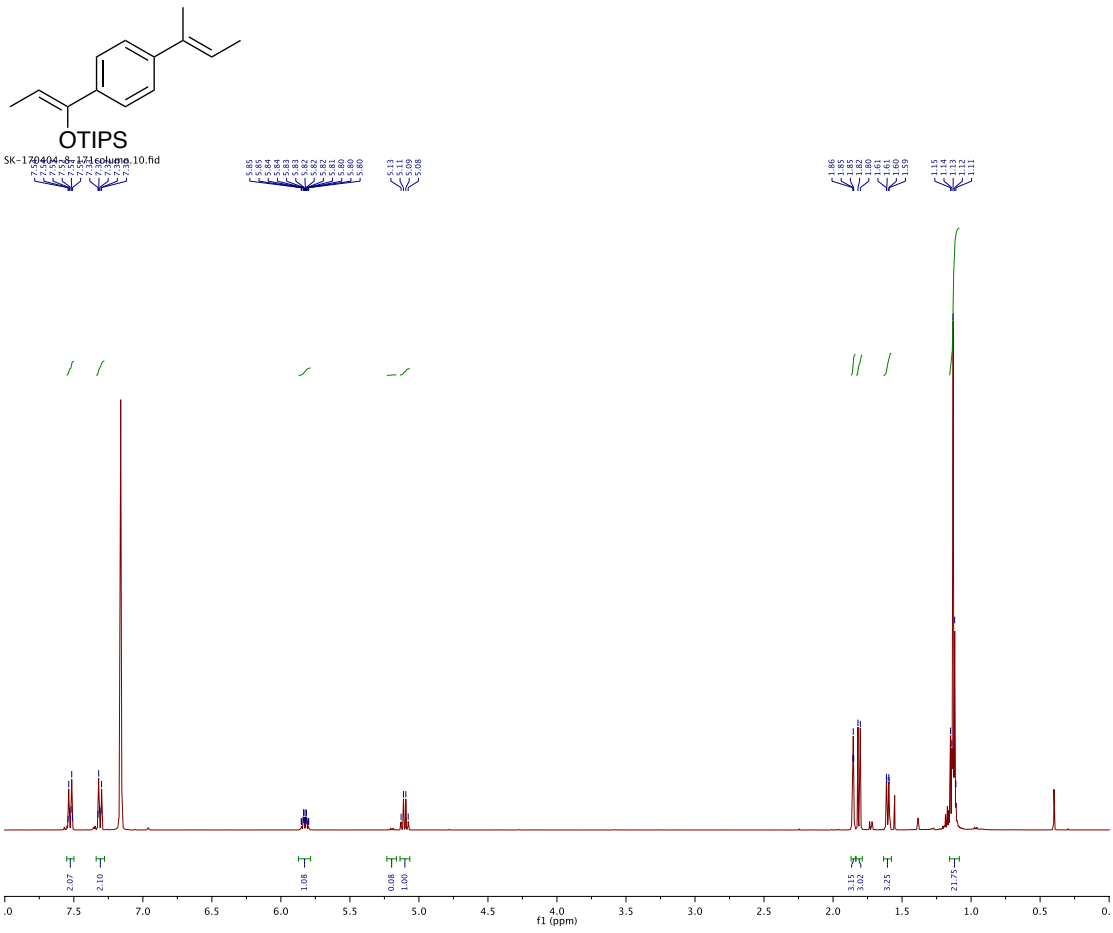
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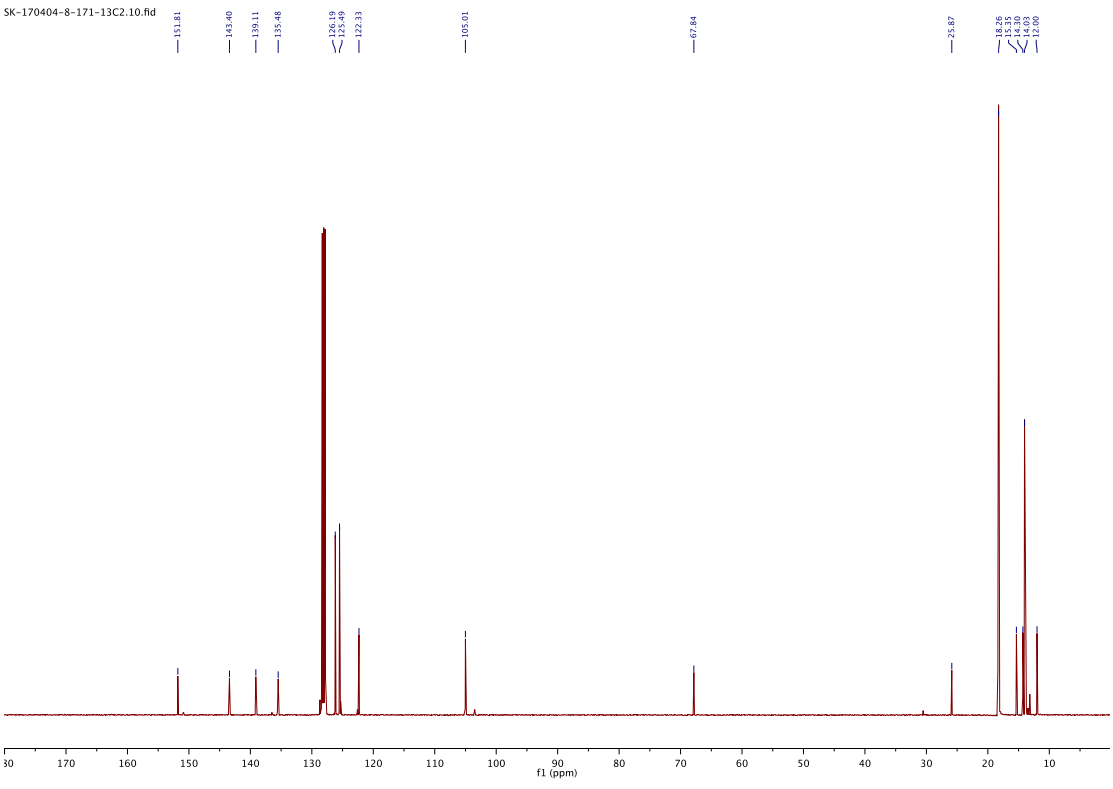
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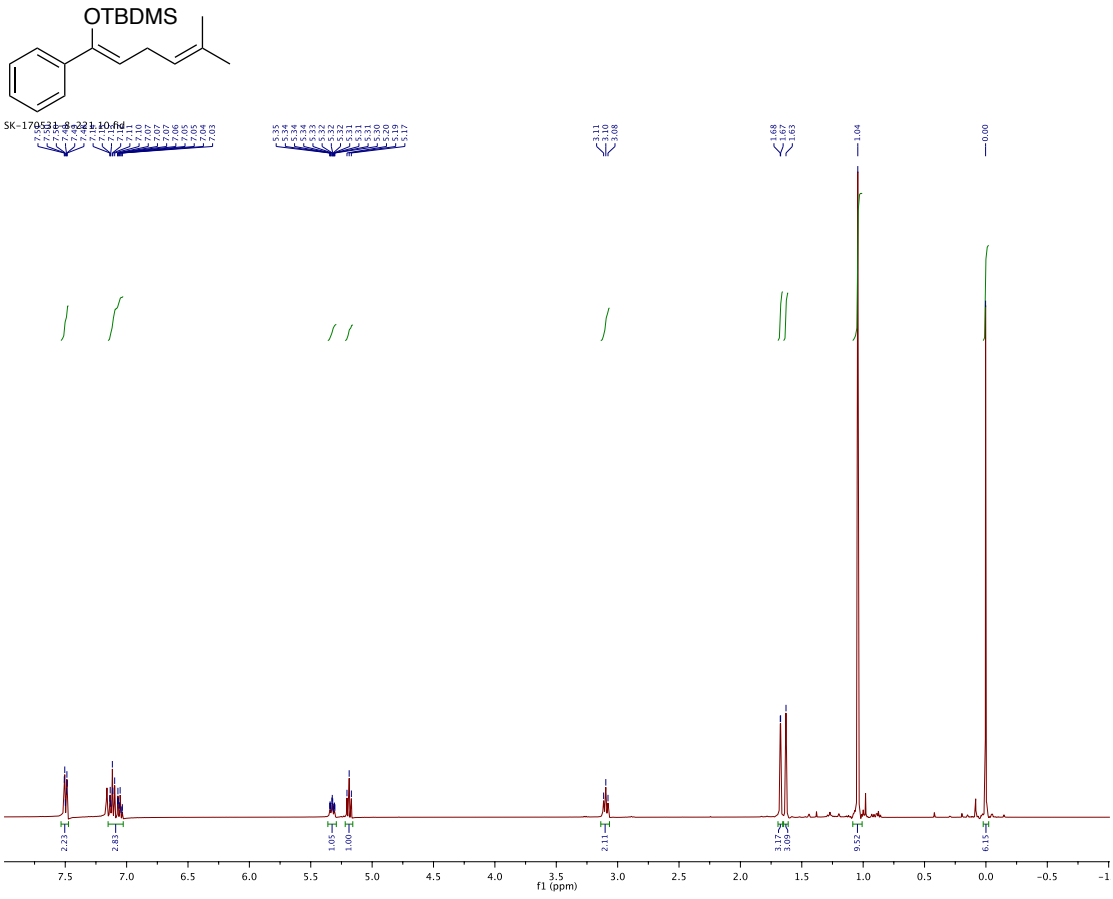
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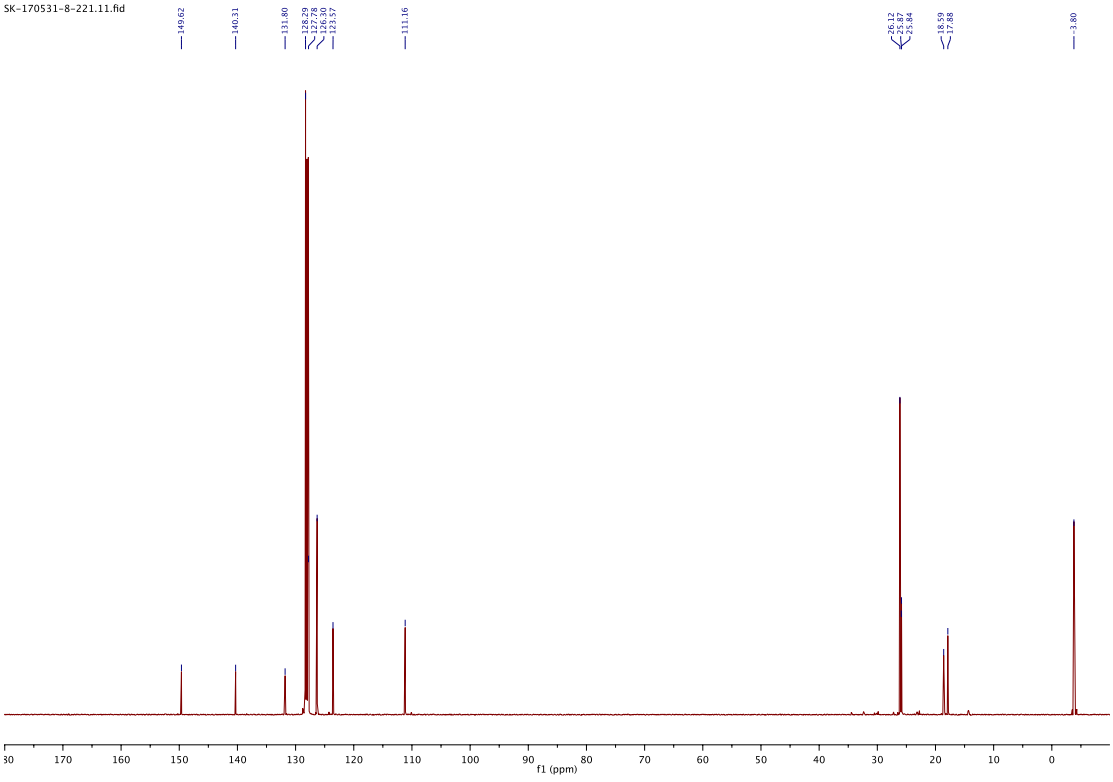
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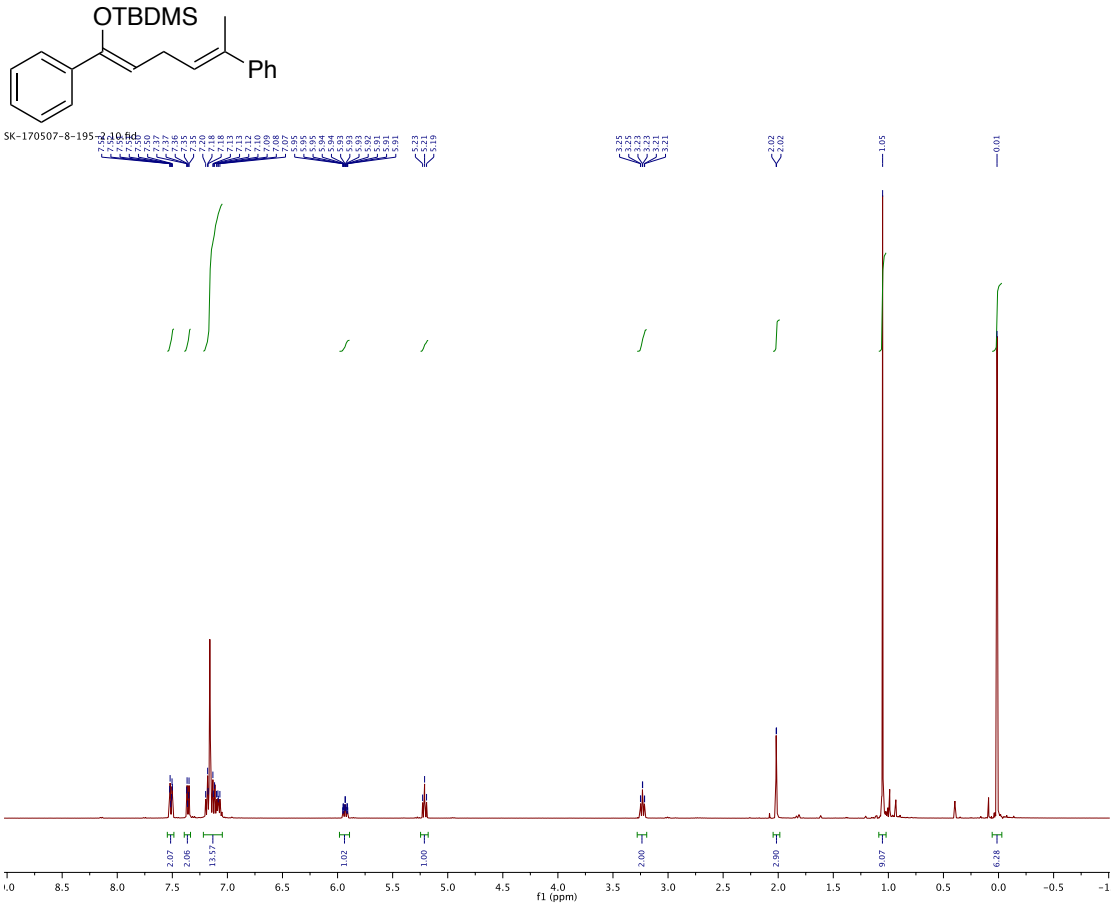
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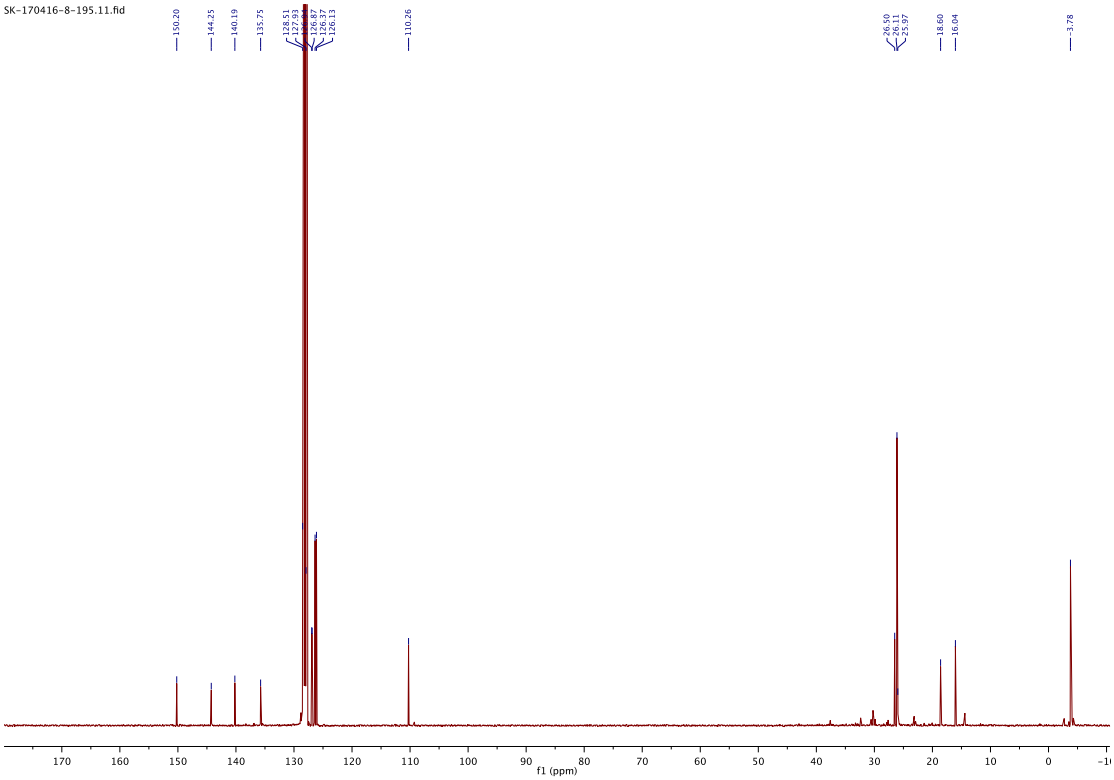
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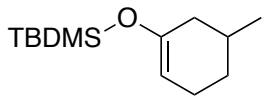

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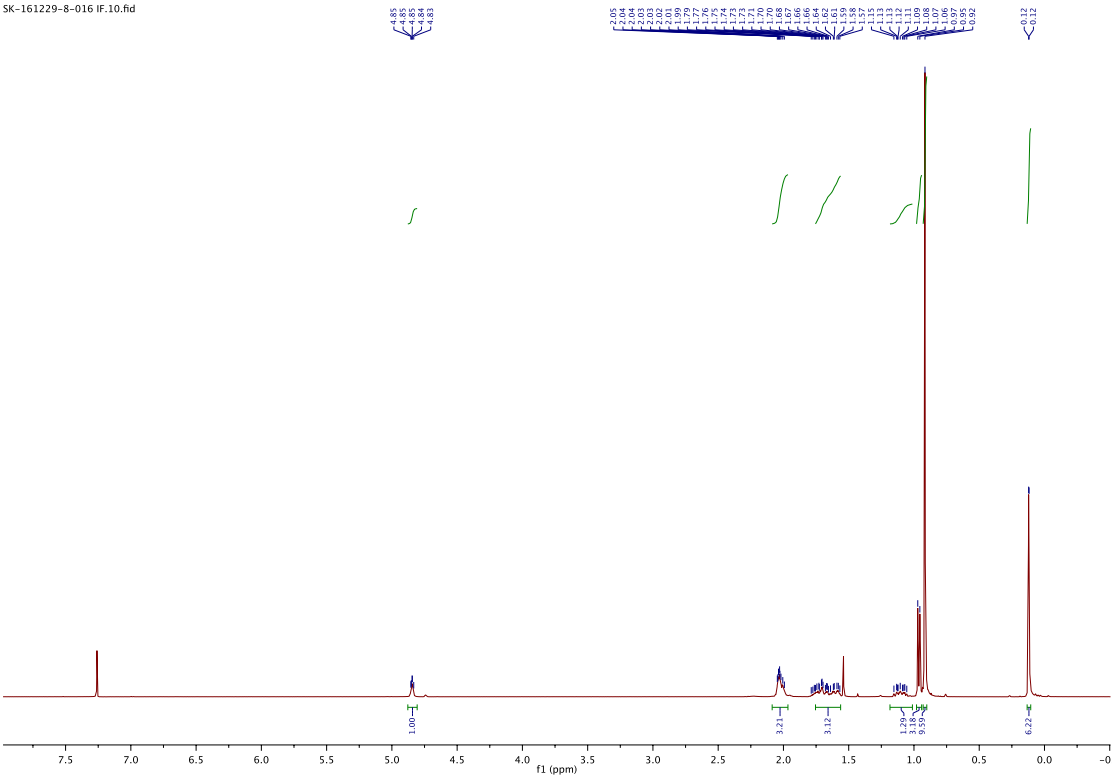

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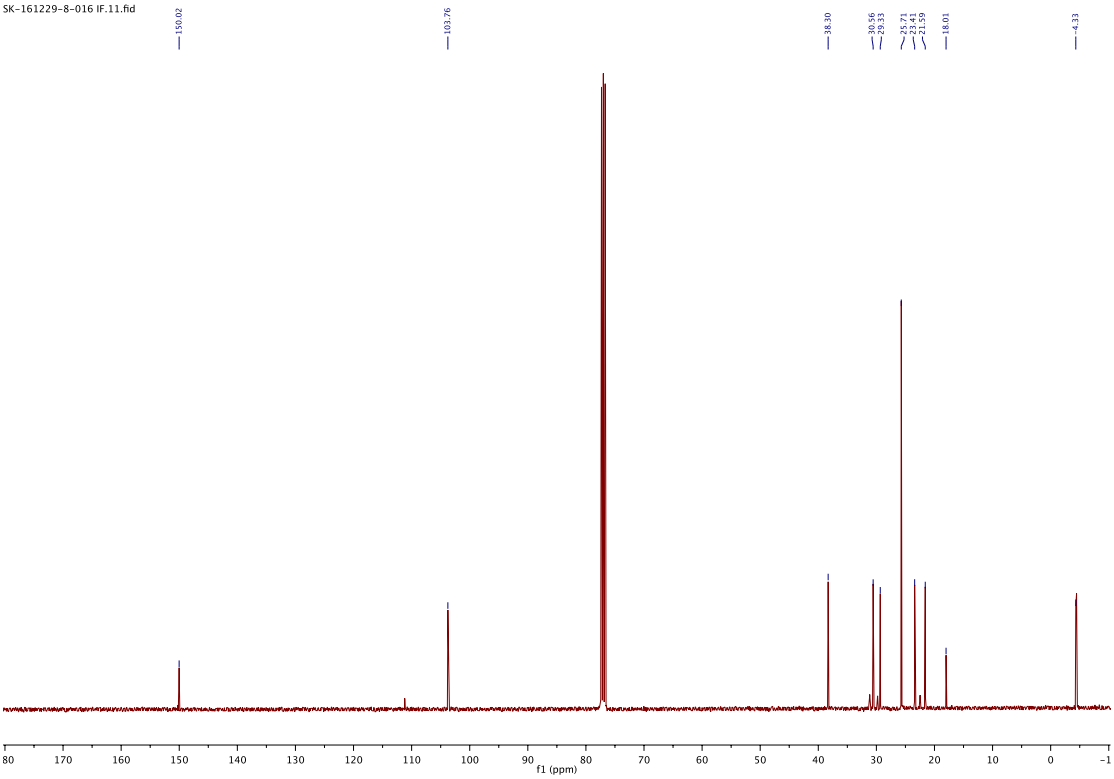

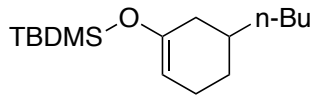
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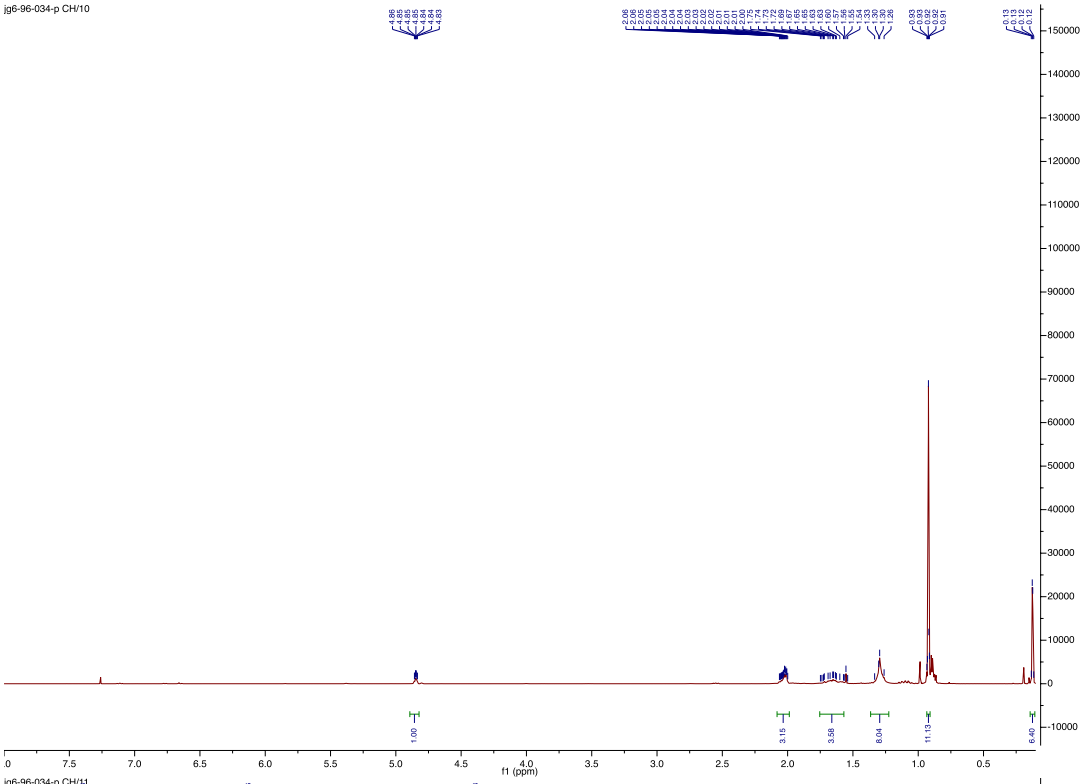
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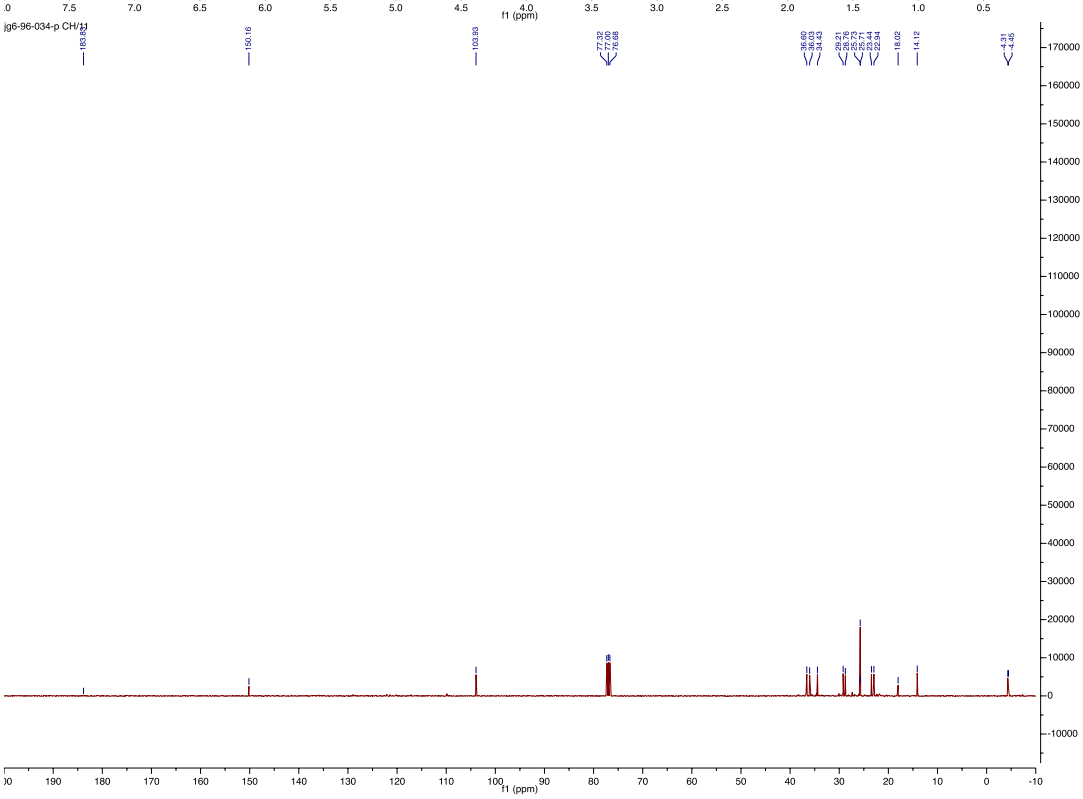
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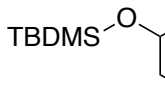
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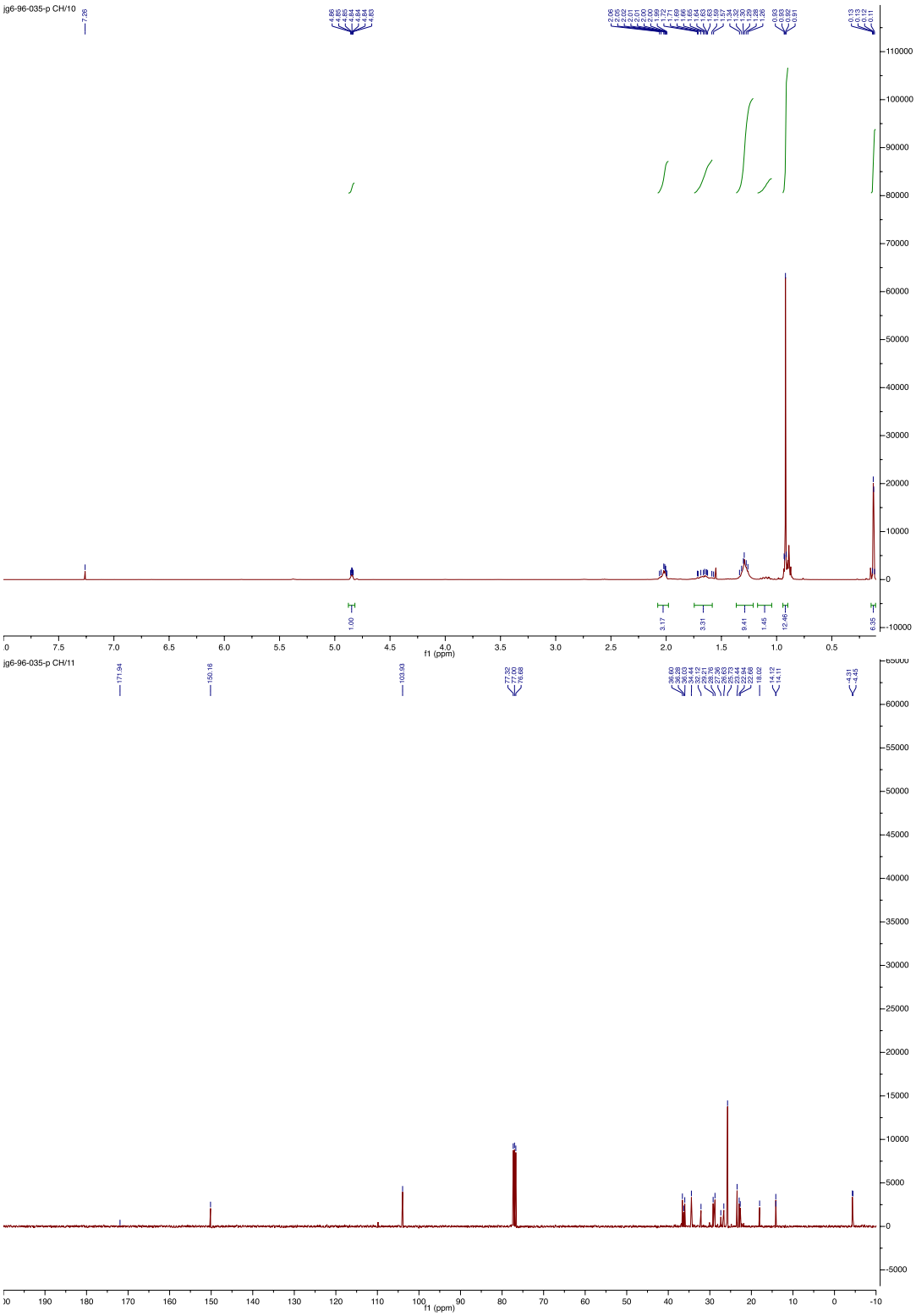
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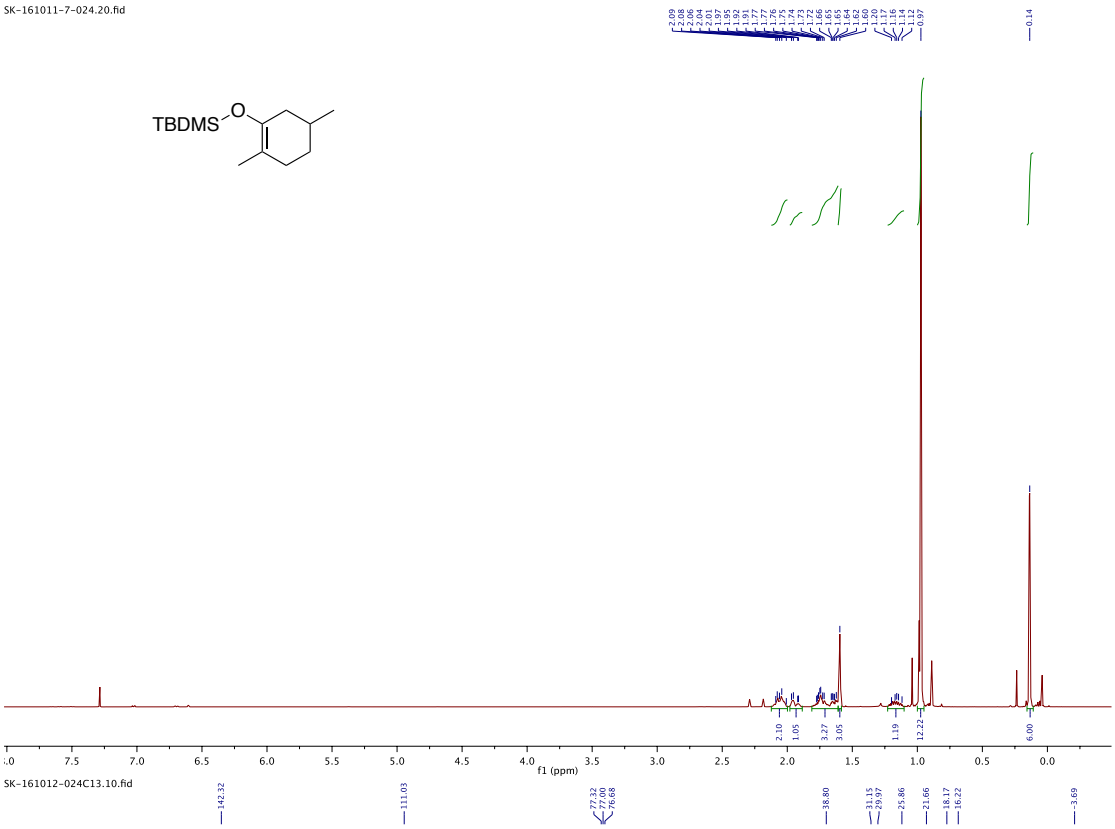
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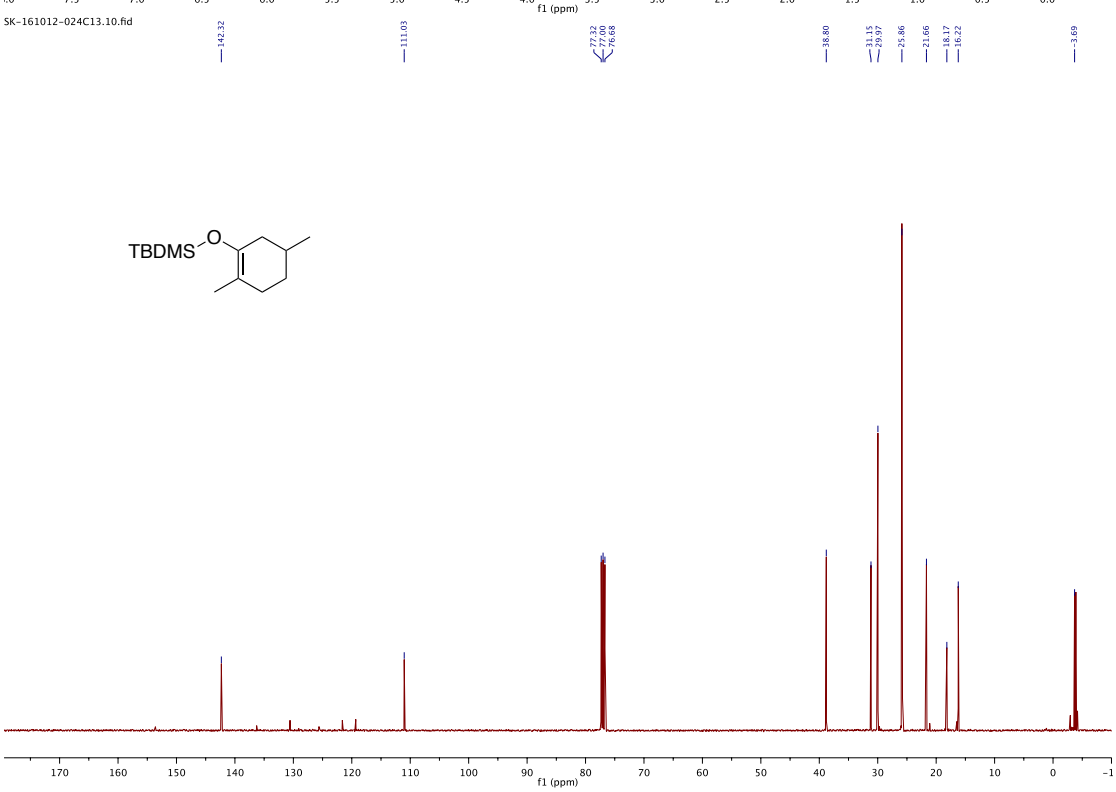
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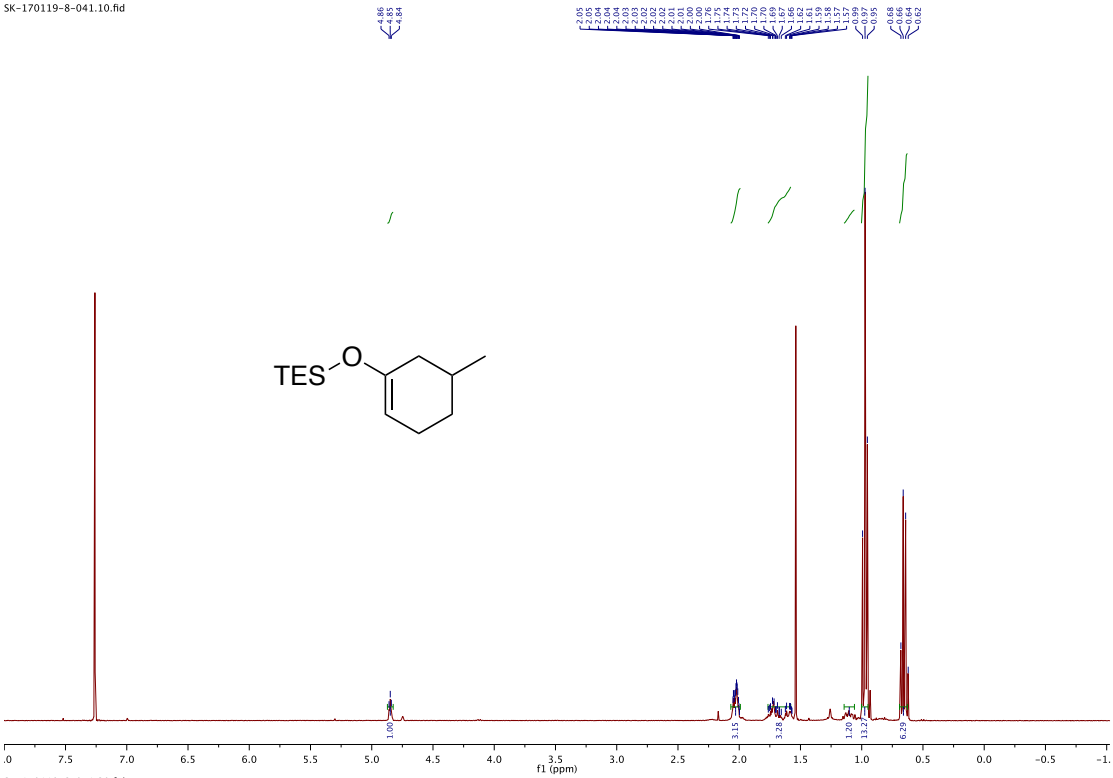
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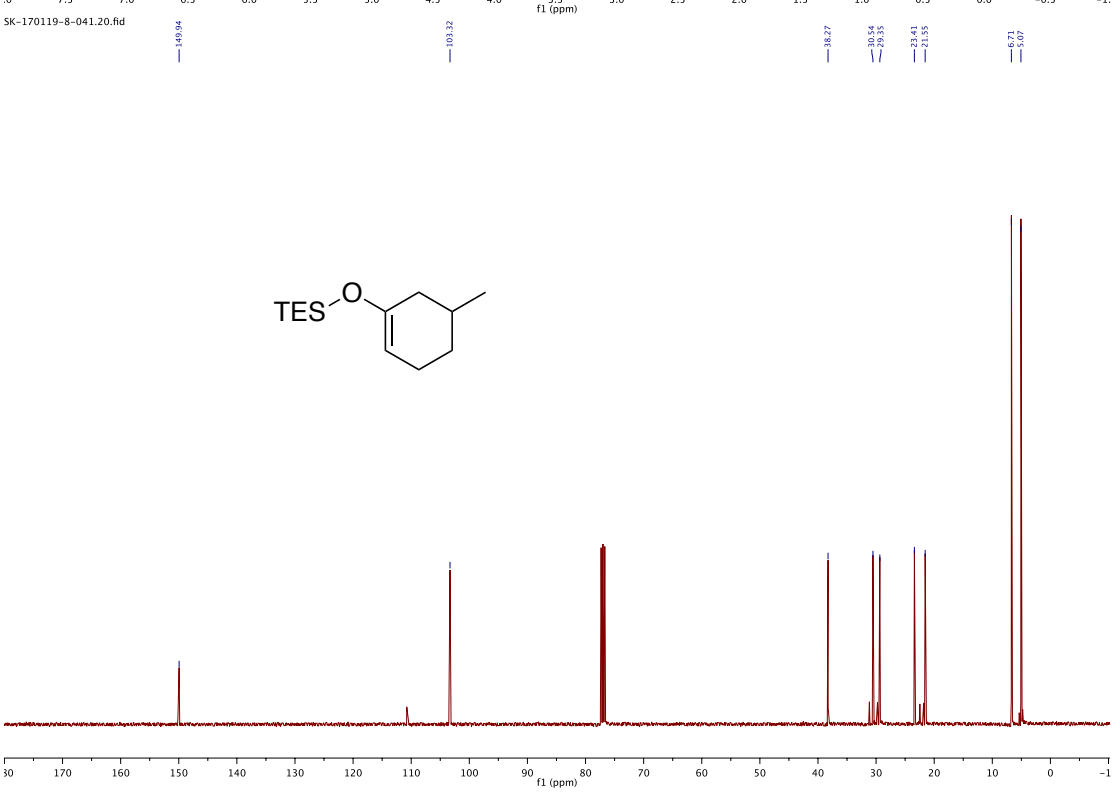
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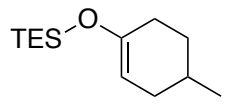
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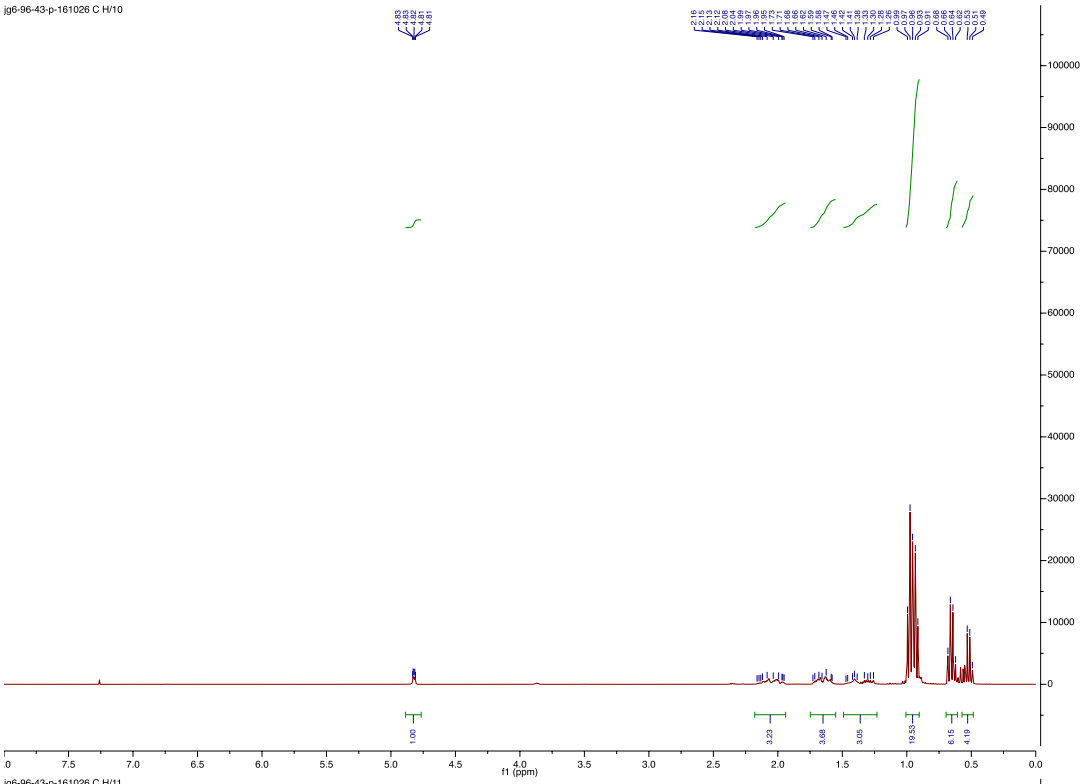
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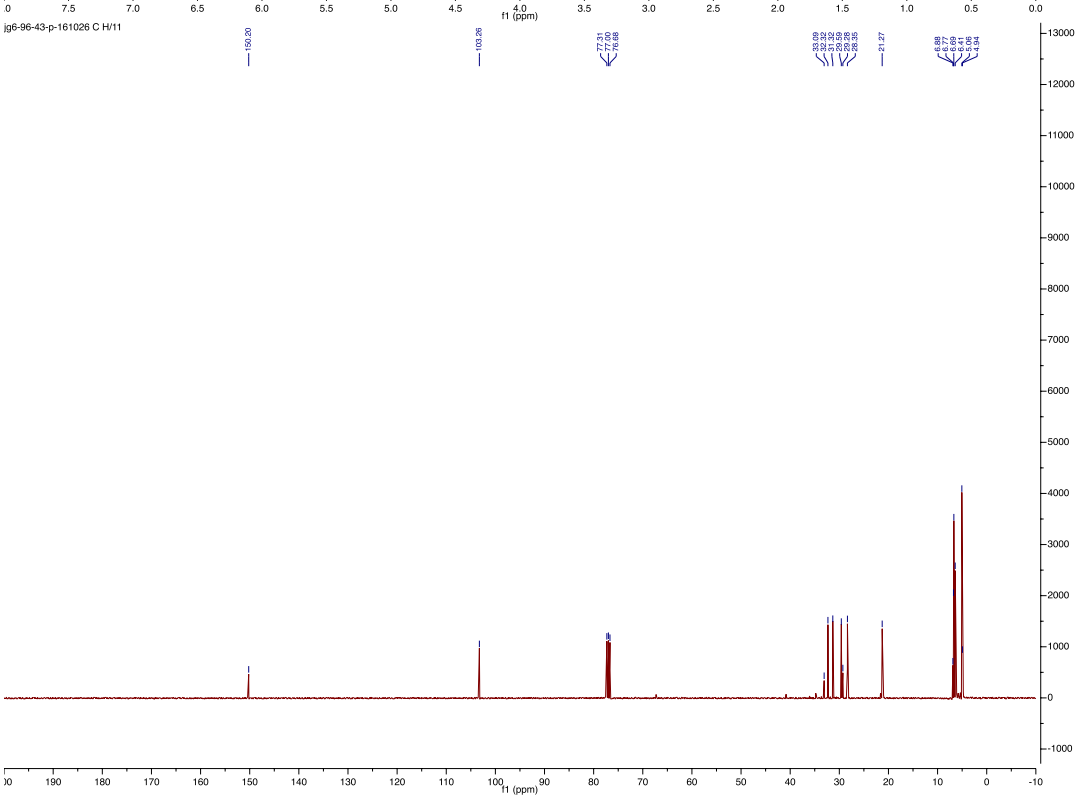
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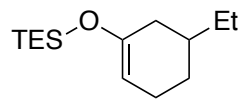
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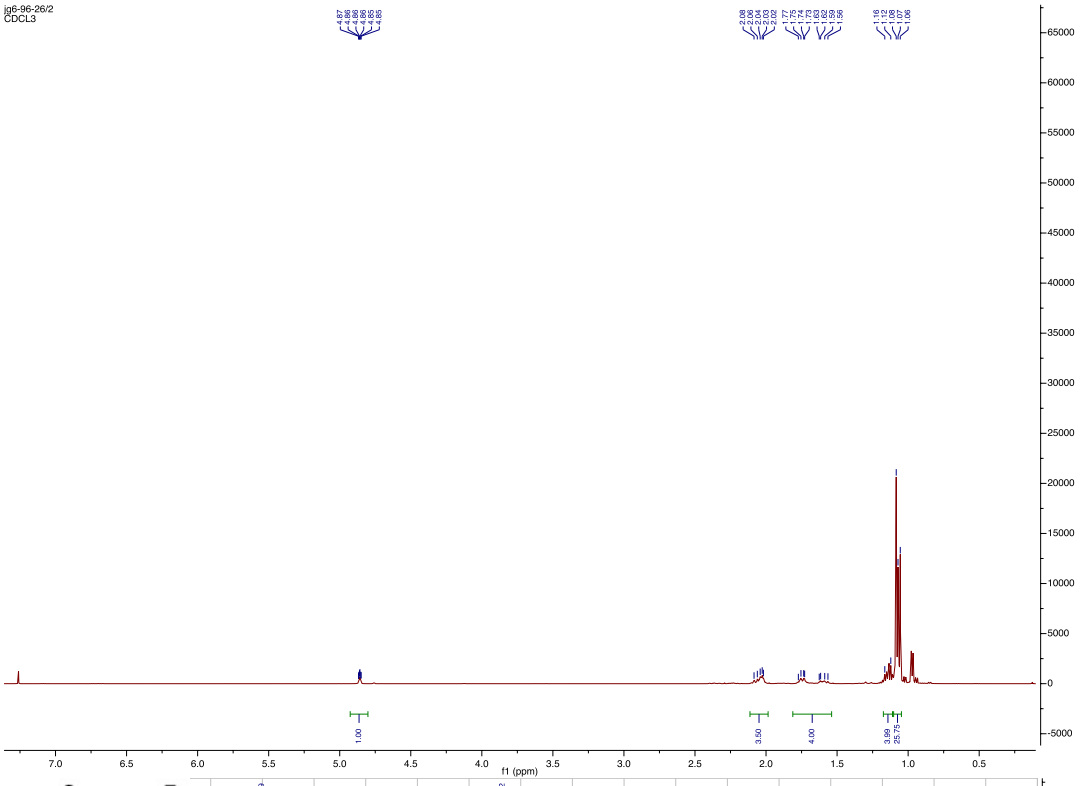
Et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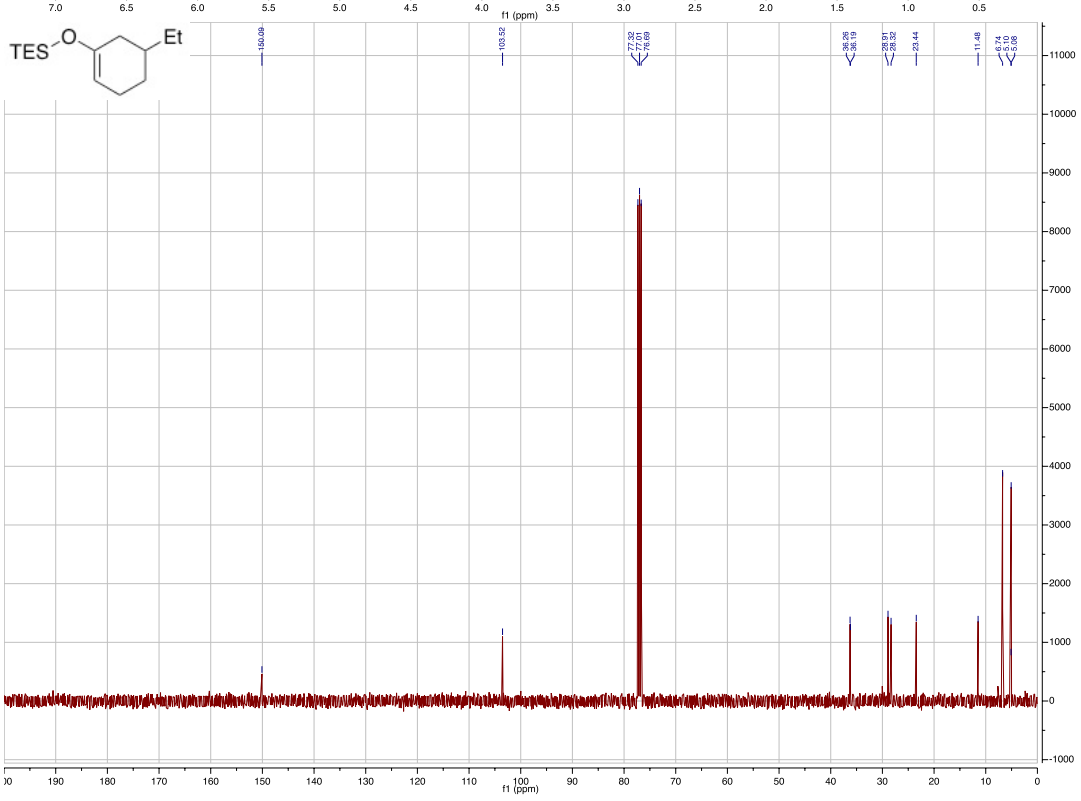
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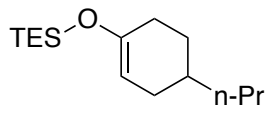
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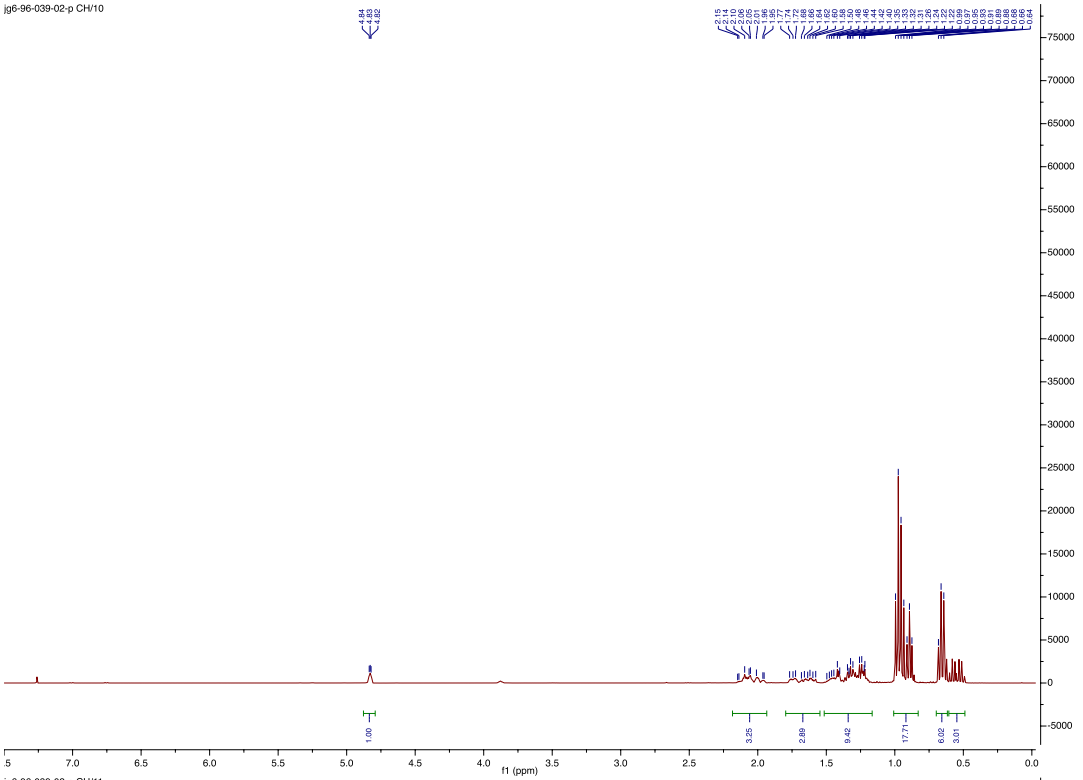
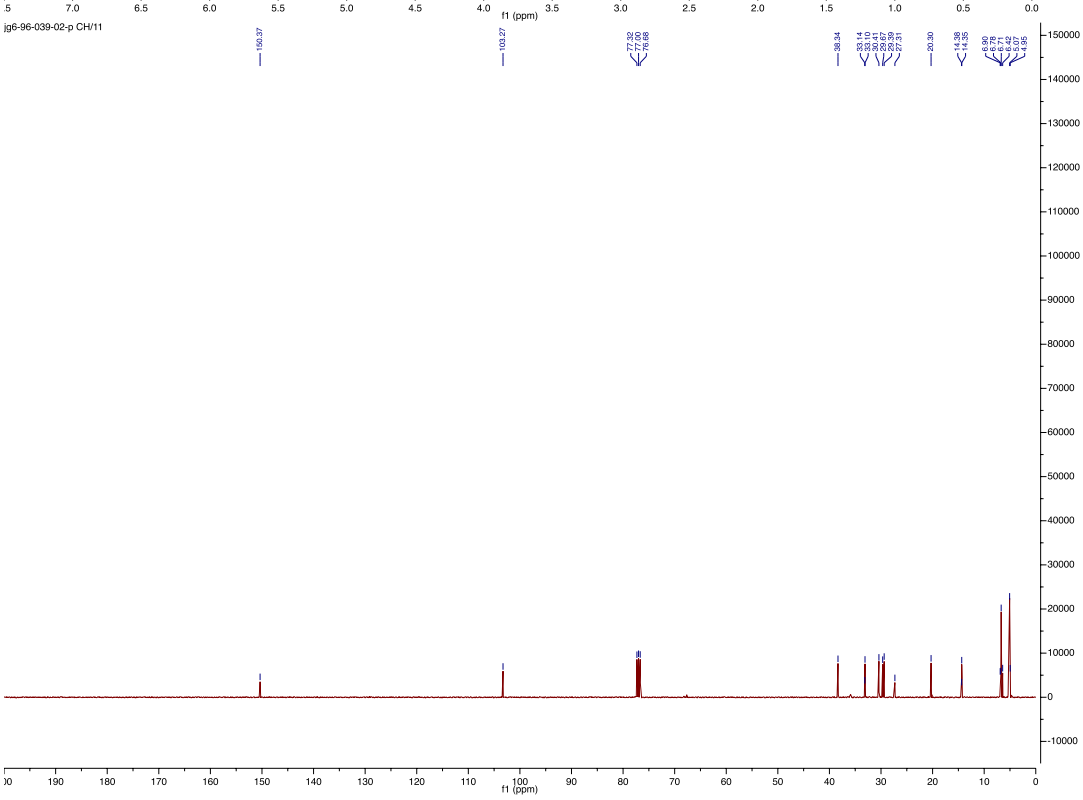
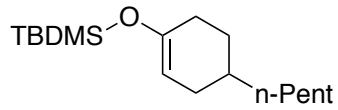
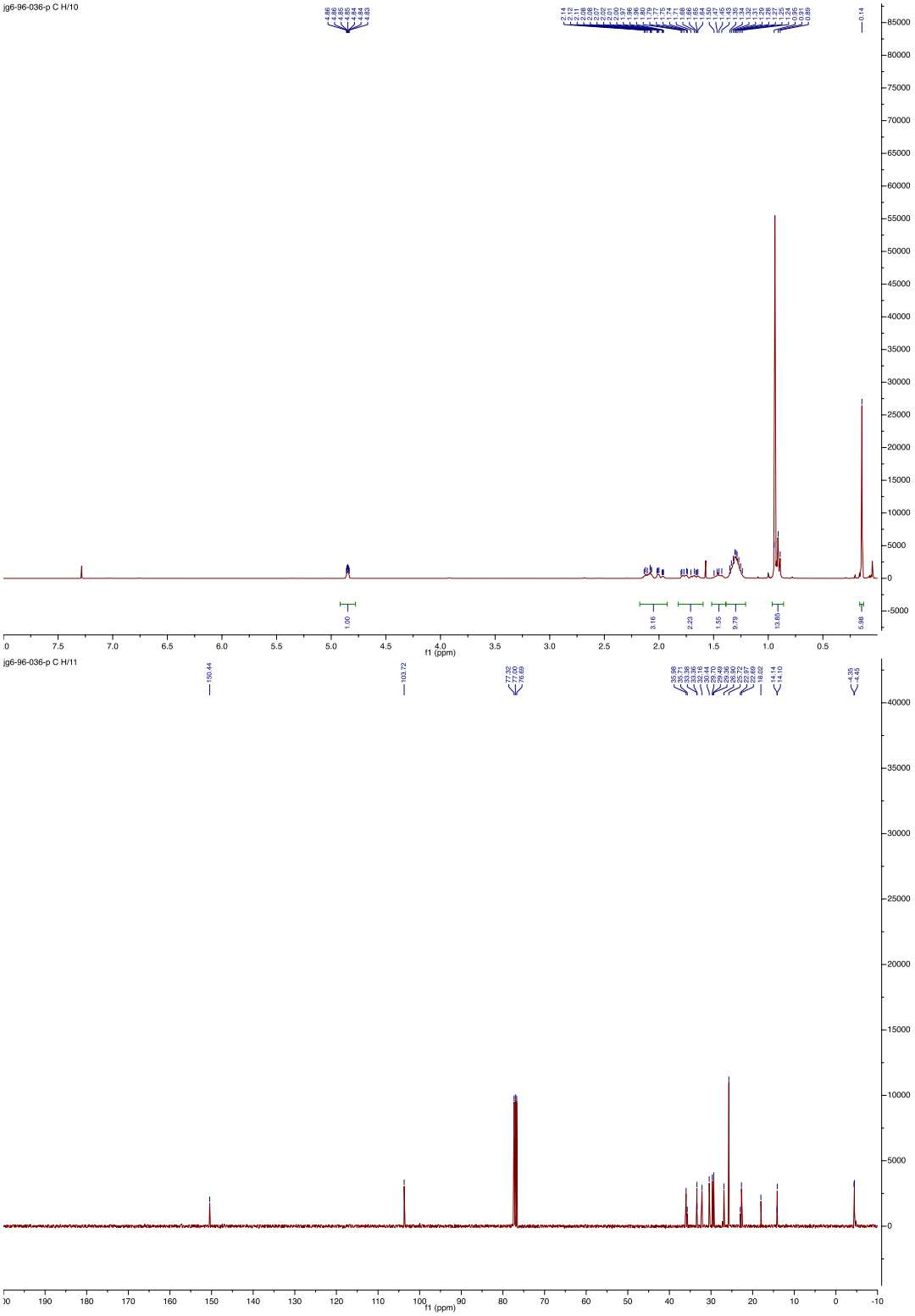
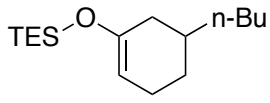

jg6-96-039-02-p CH/10
f1 (ppm)

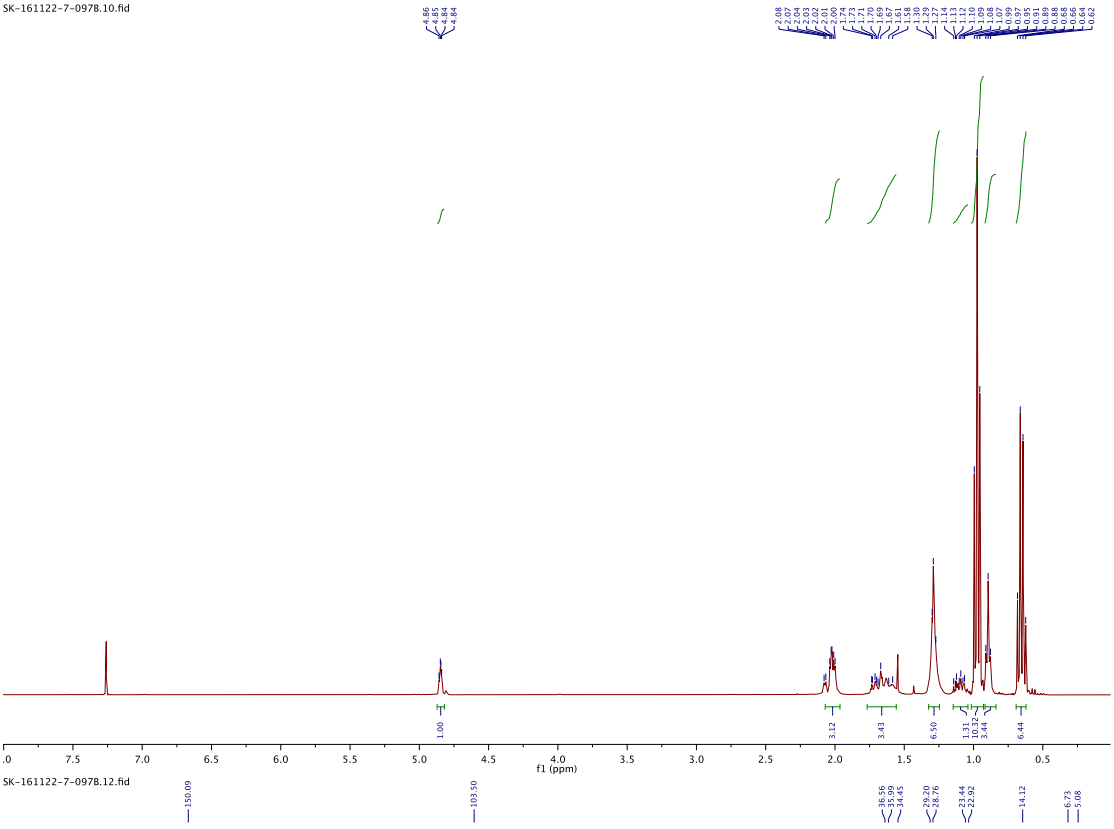

jg6-96-039-02-p CH/11
f1 (ppm)


TBDMS
O
n-Pent

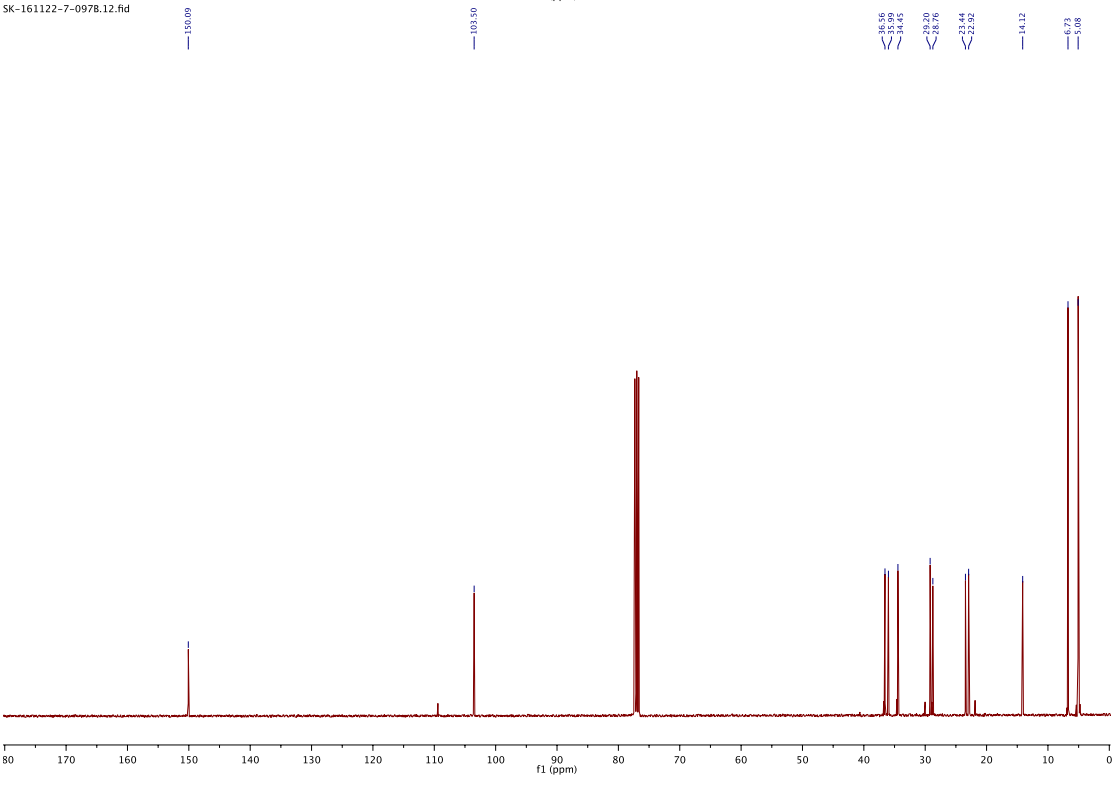

jg6-96-036-p C H/10
jg6-96-036-p C H/11
f1 (ppm)

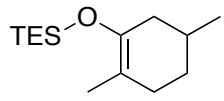


SK-161122-7-097B.10.fid

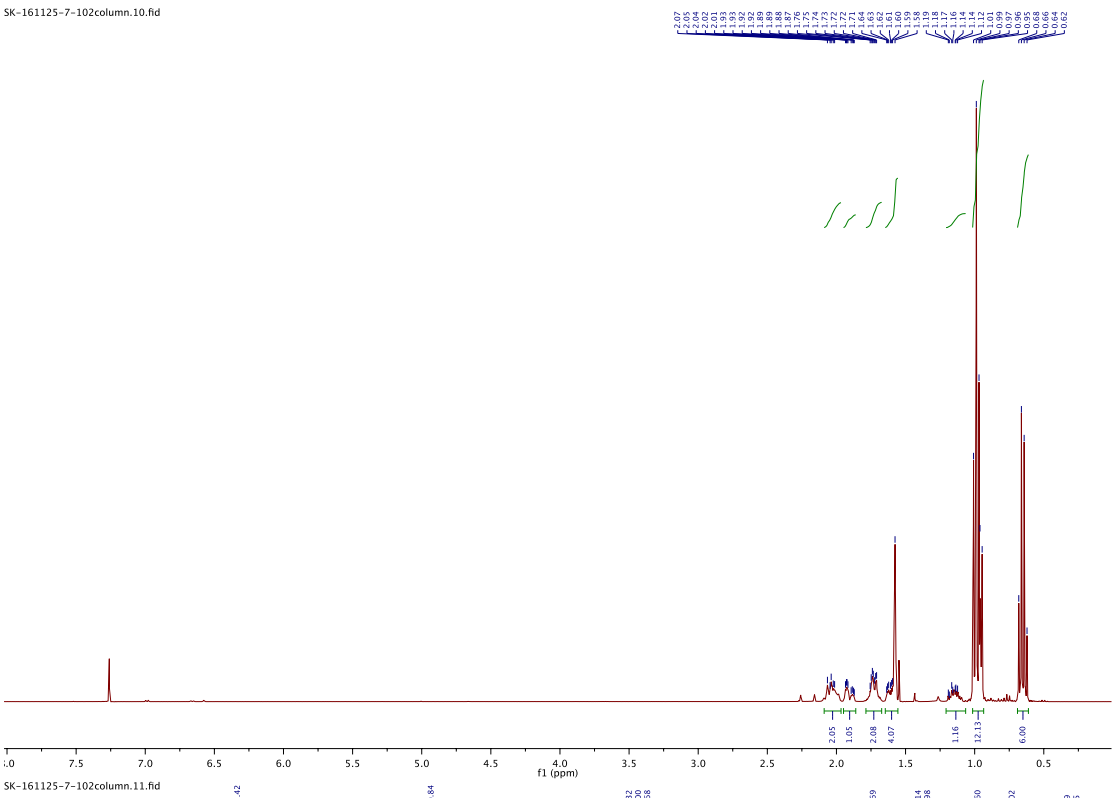


SK-161122-7-097B.12.fid





SK-161125-7-102column.10.fid



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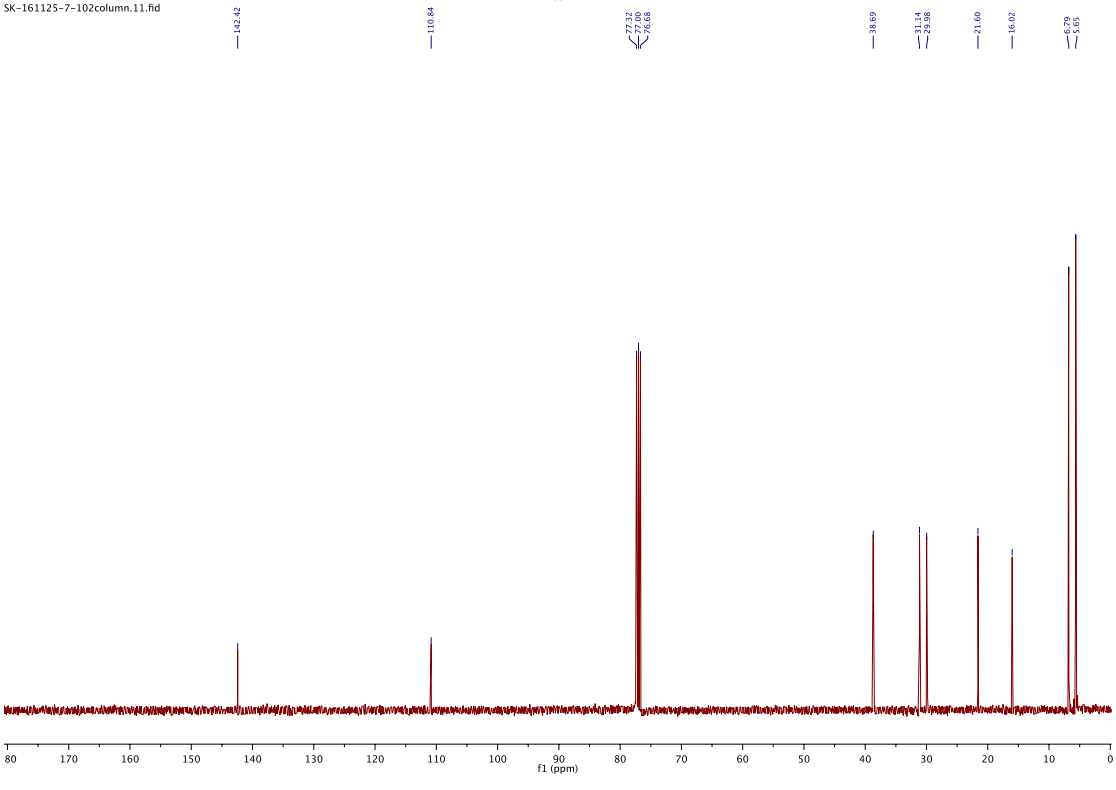
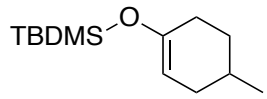
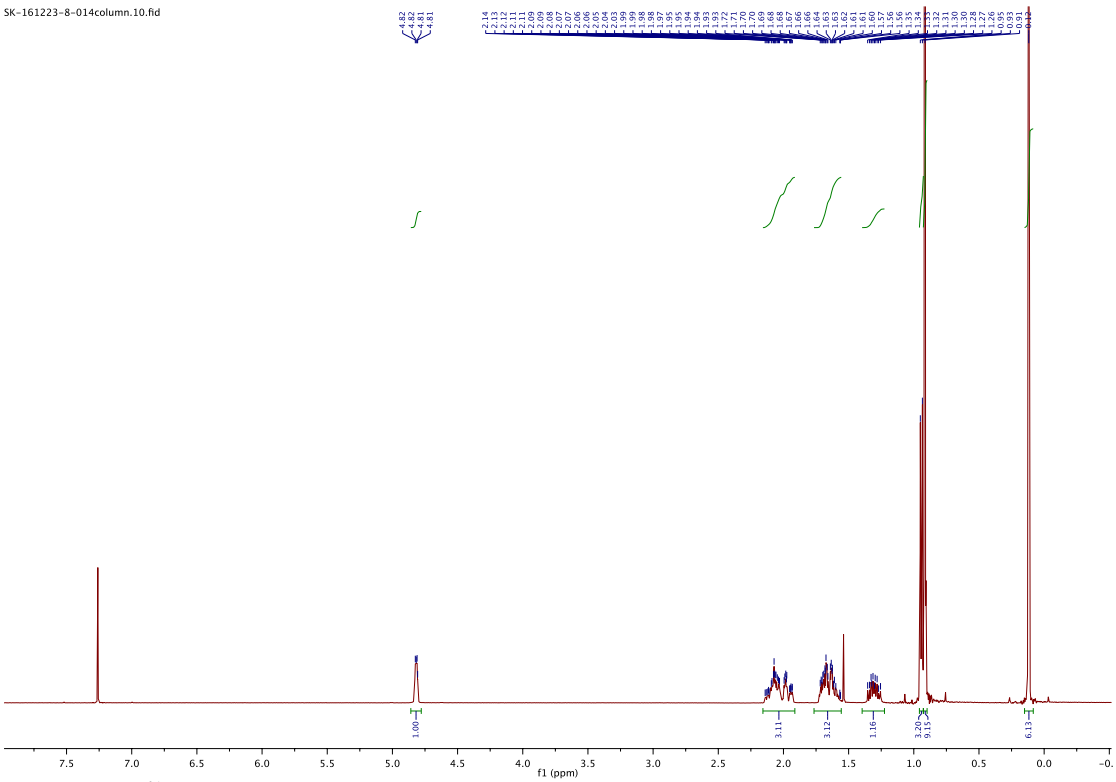
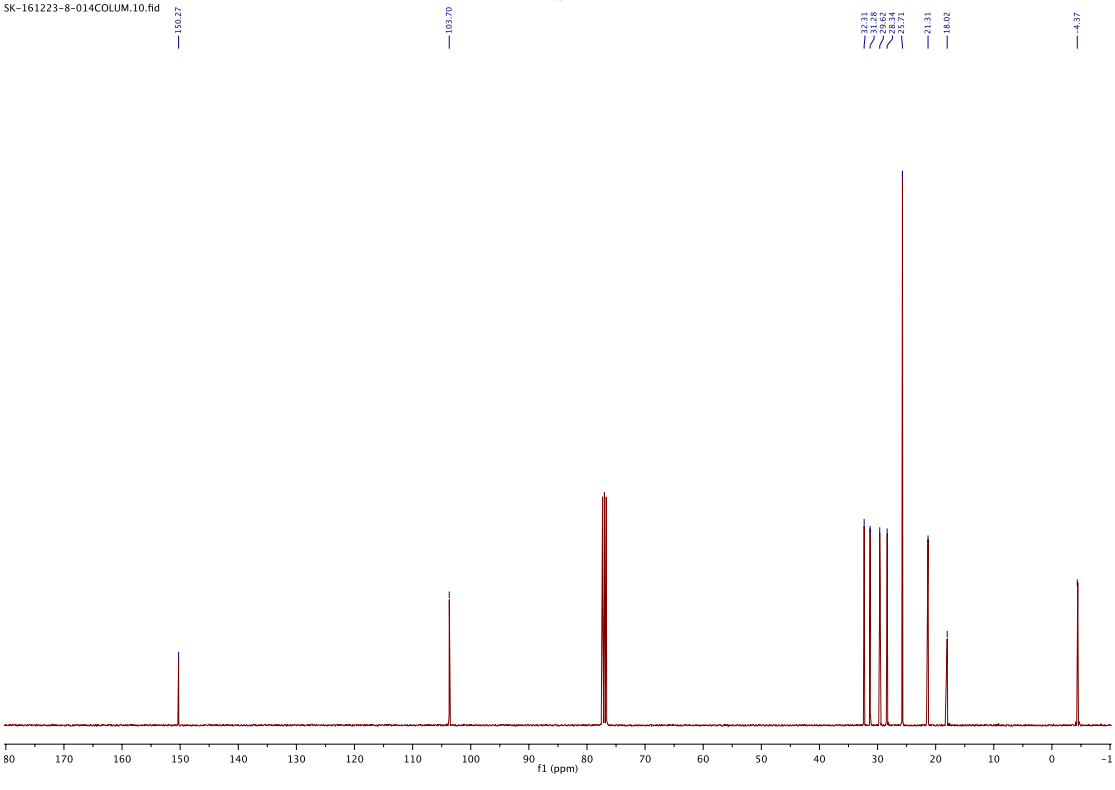


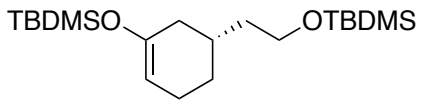


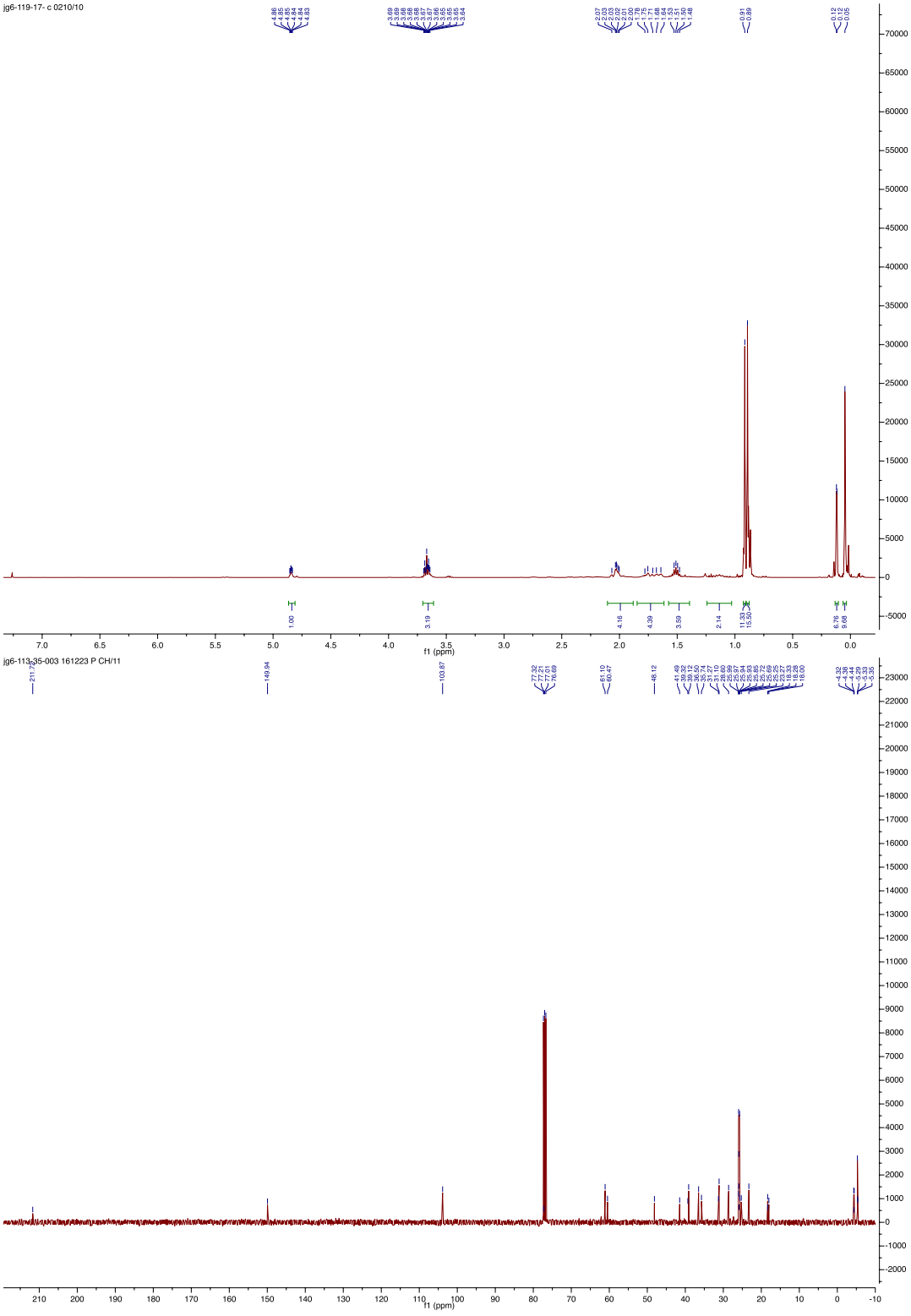
SK-161223-8-014column.10.fid

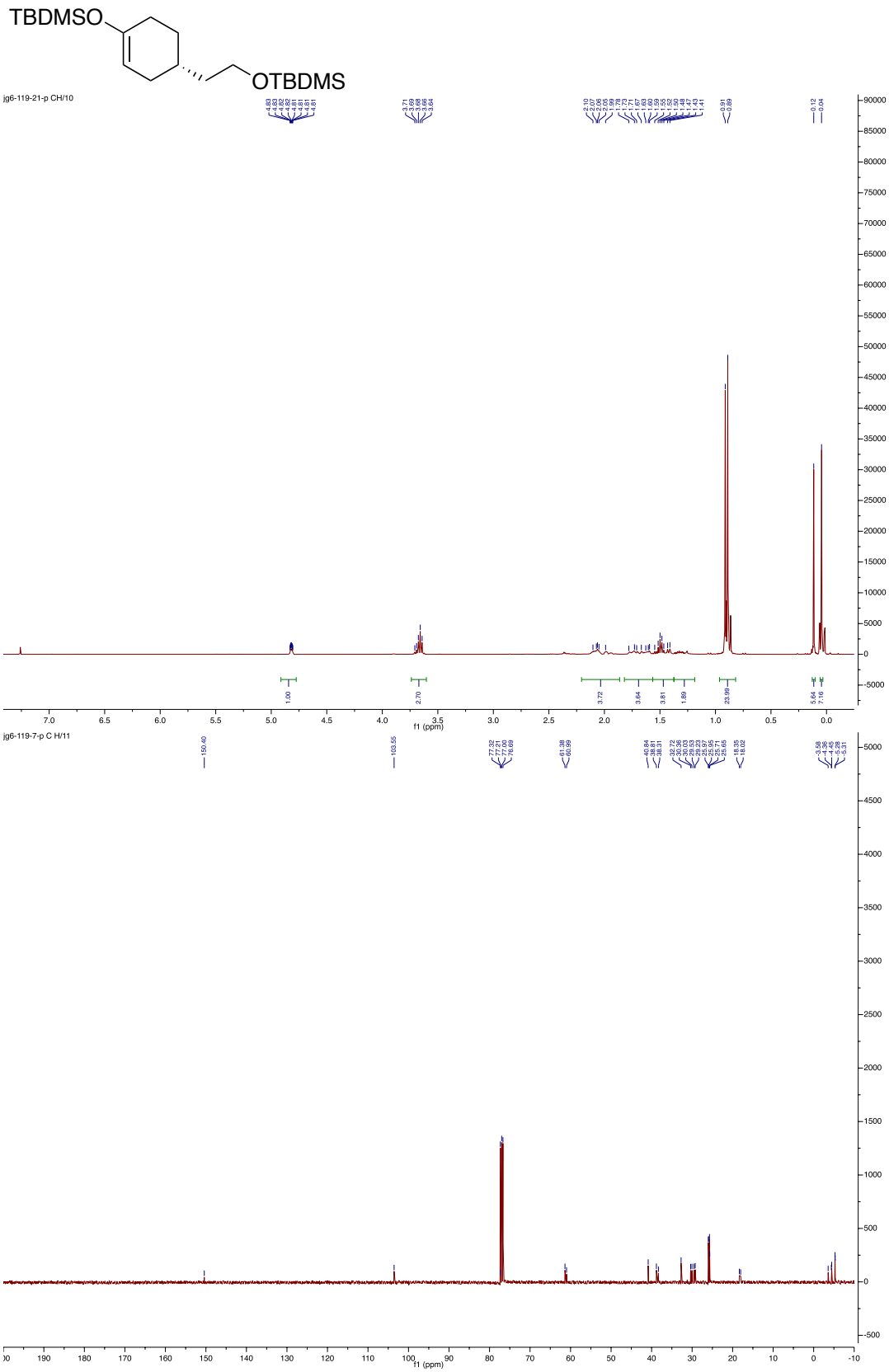


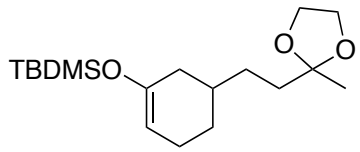
SK-161223-8-014COLUM.10.fid



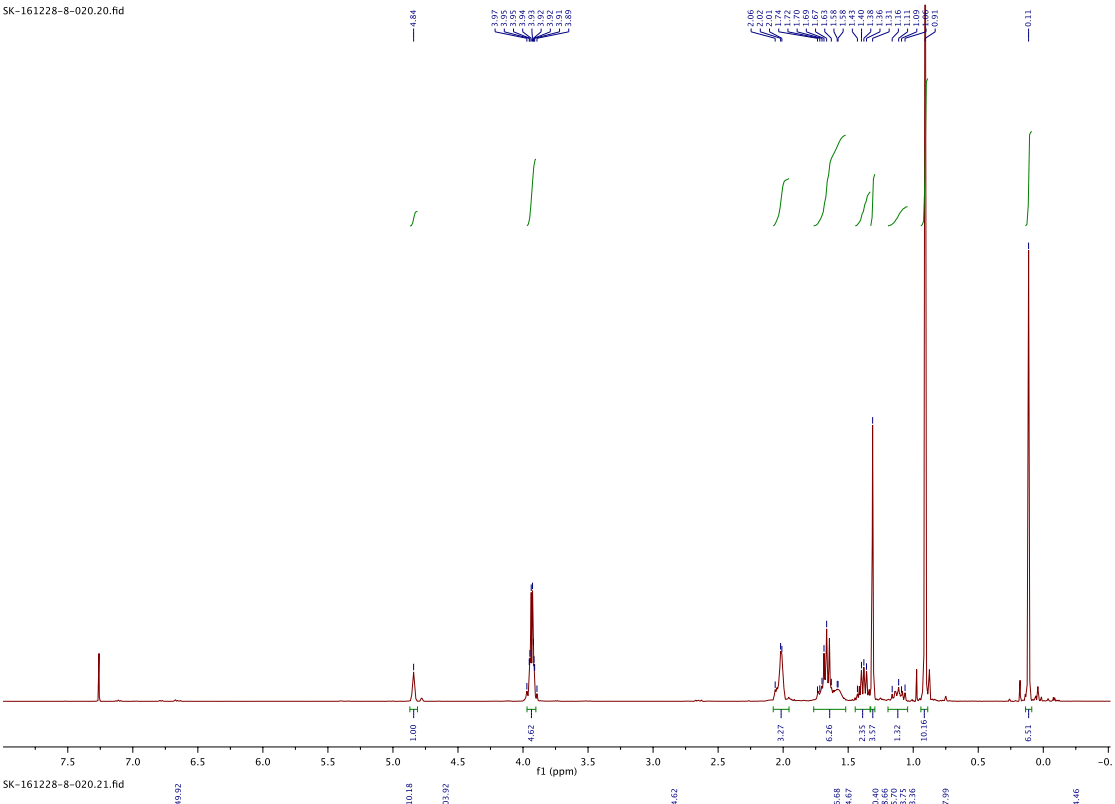

TBDMSO
OTBDMS


jg6-119-17- c 0210/10
f1 (ppm)
jg6-113-35-003 161223 P CH/11
f1 (ppm)

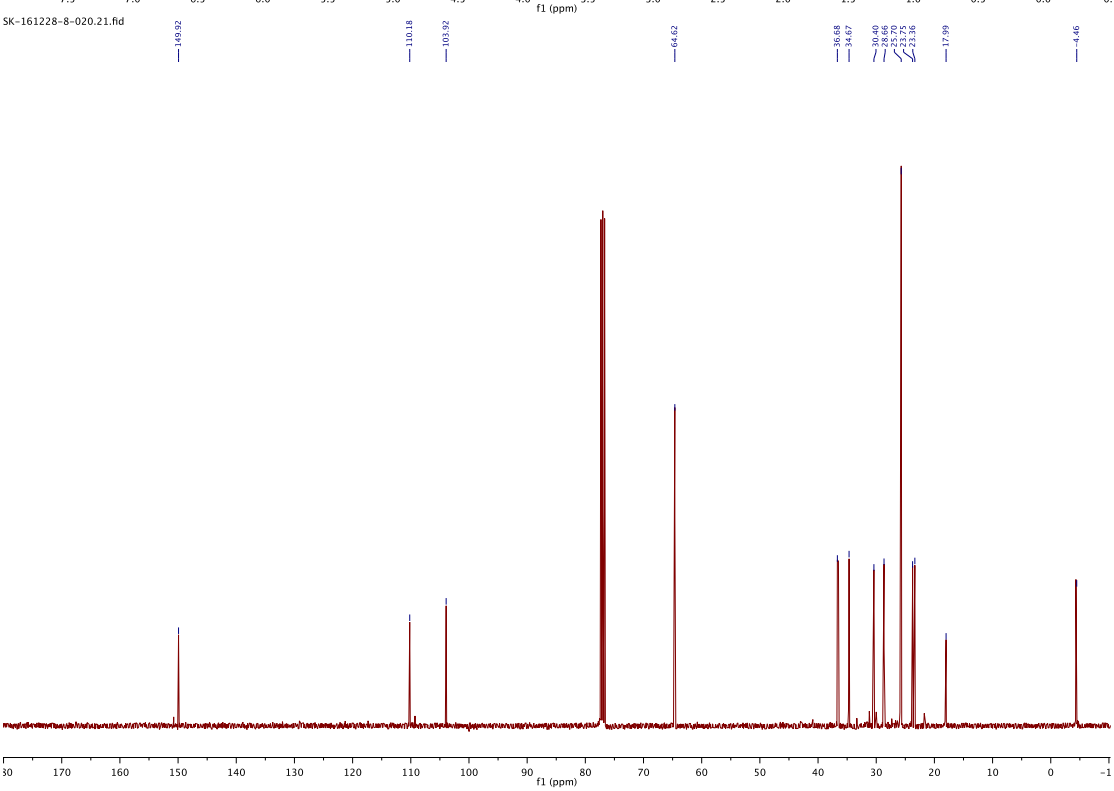

TBDMSO
OTBDMS
jg6-119-21-p CH/10
jg6-119-7-p C H/11
f1 (ppm)
f1 (ppm)

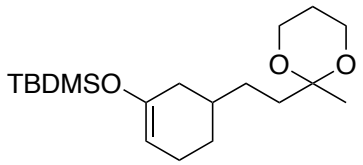


SK-161228-8-020.20.fid

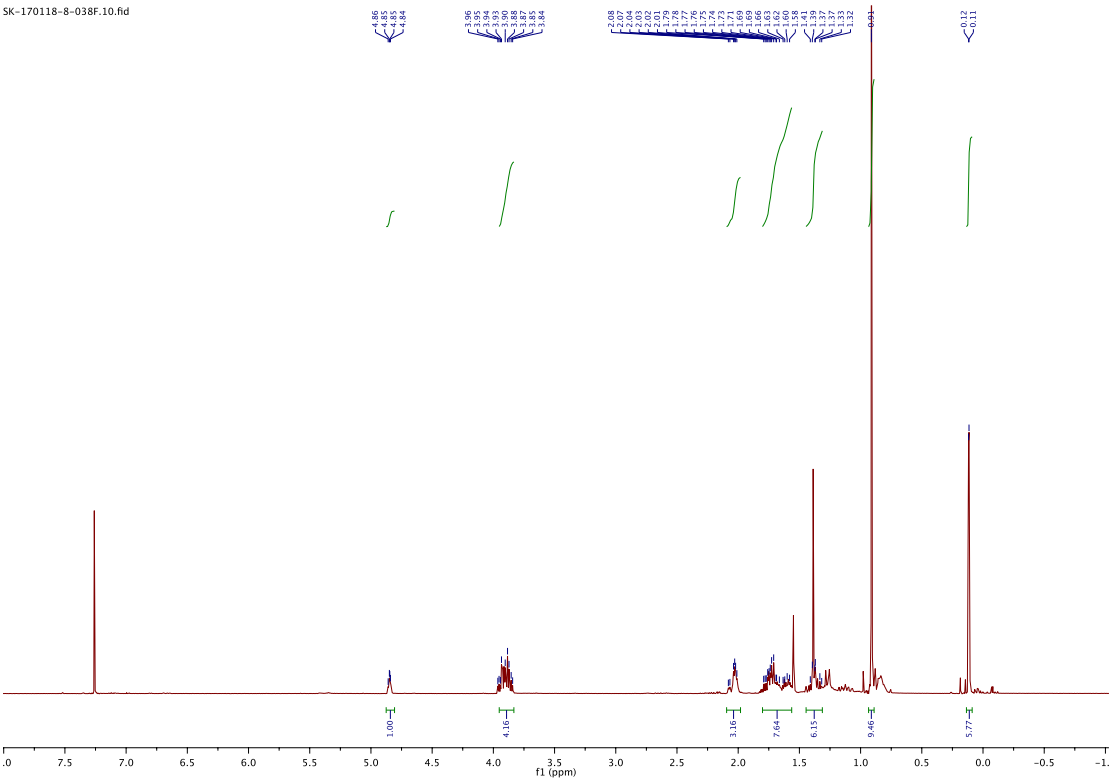


SK-161228-8-020.21.fid

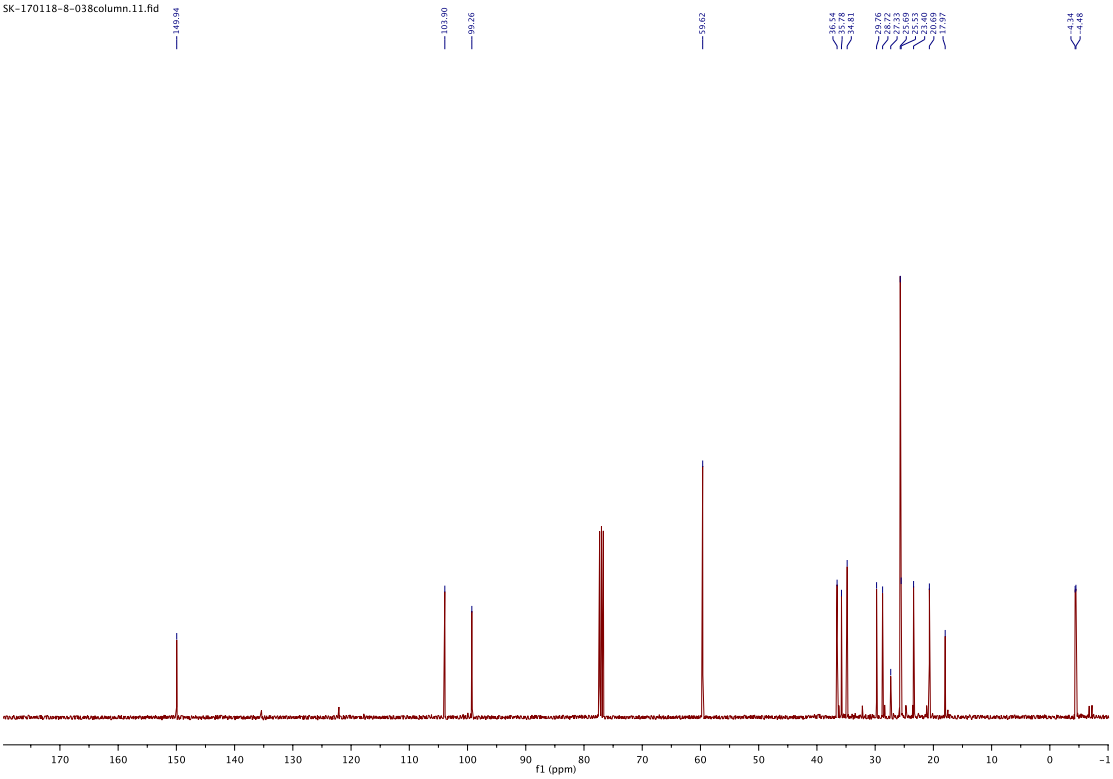


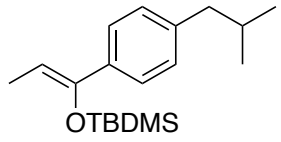


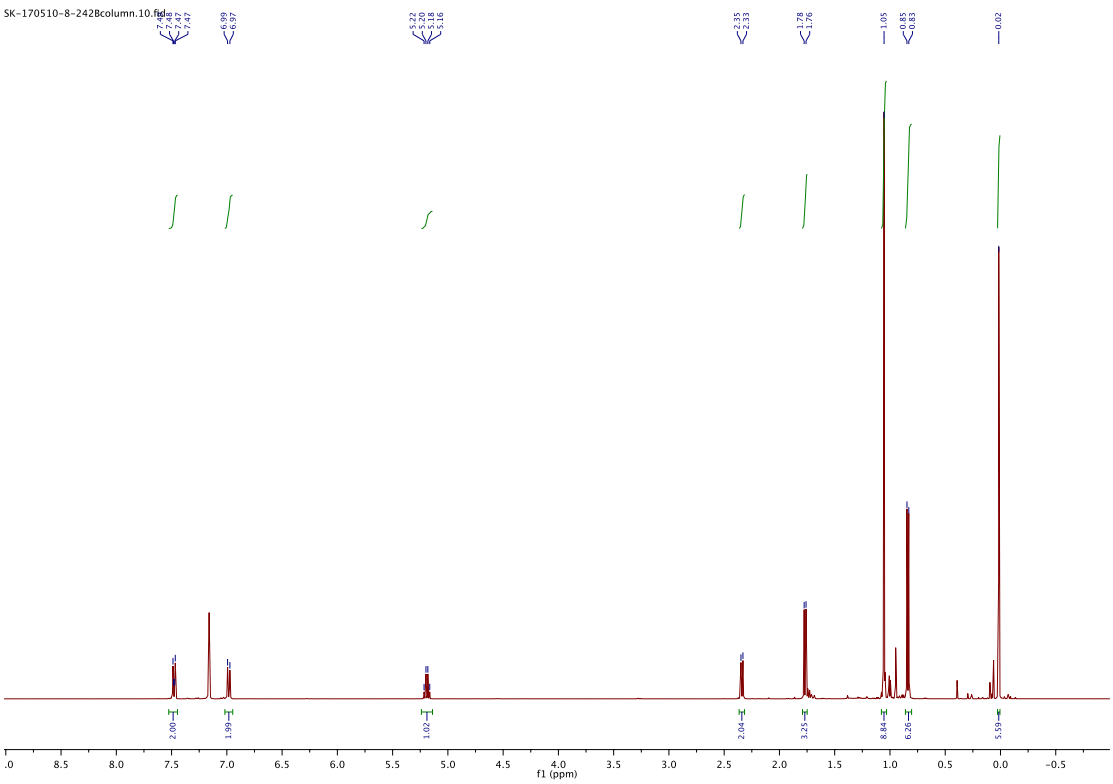
SK-170118-8-038F.10.fid

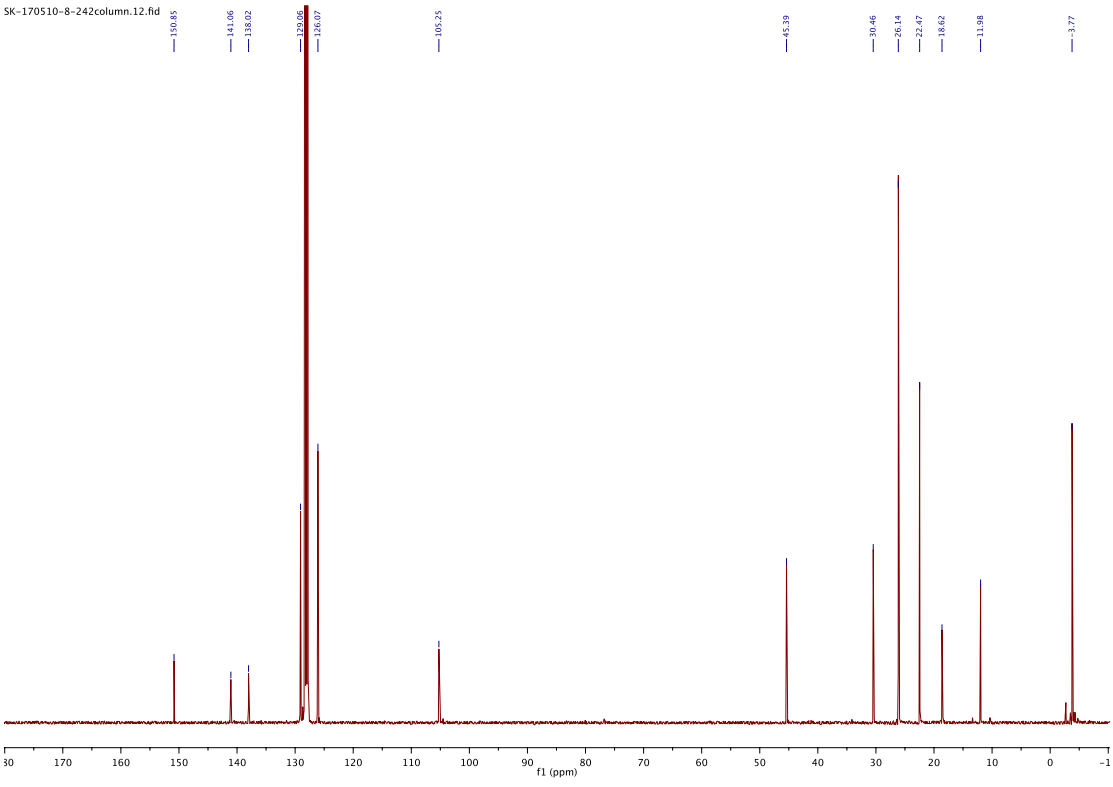


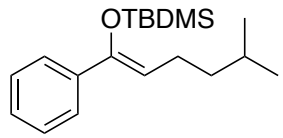
SK-170118-8-038column.11.fid

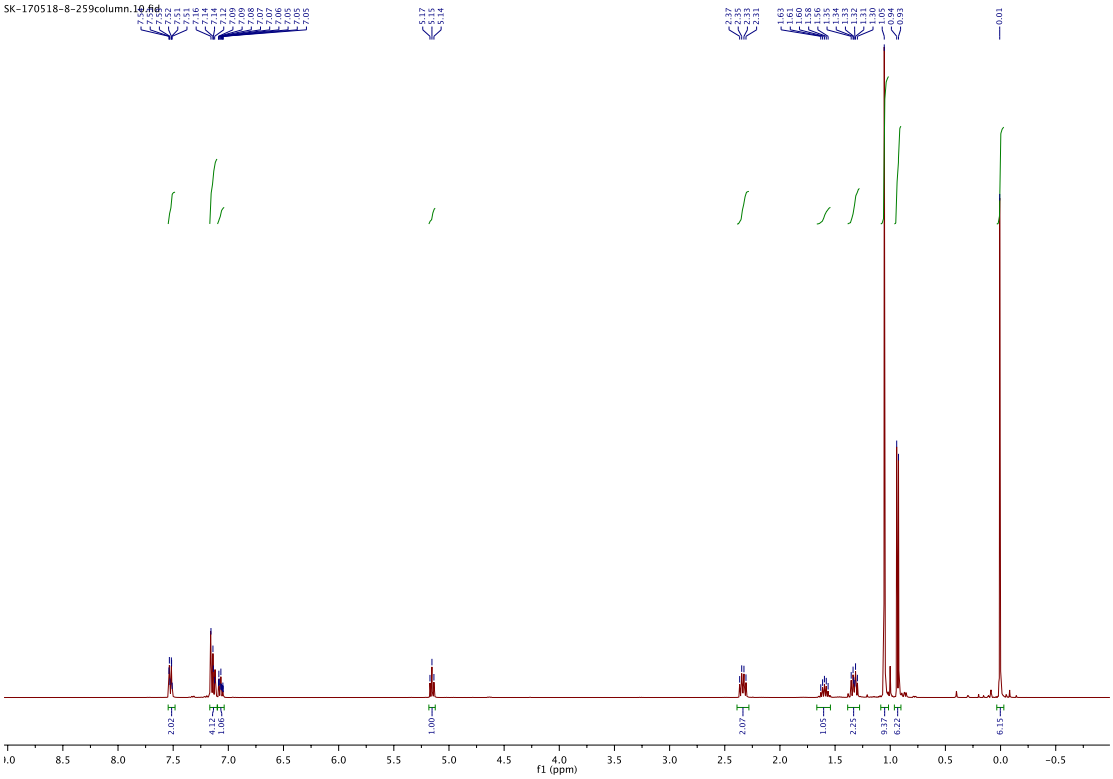


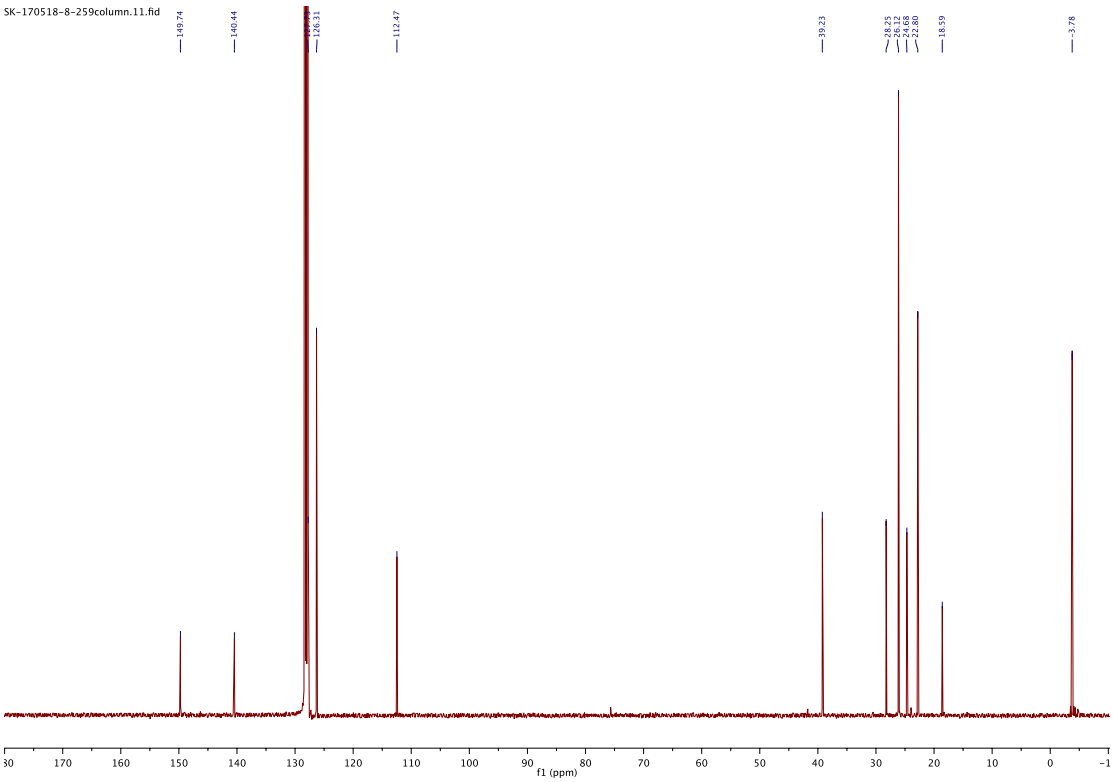

OTBDMS

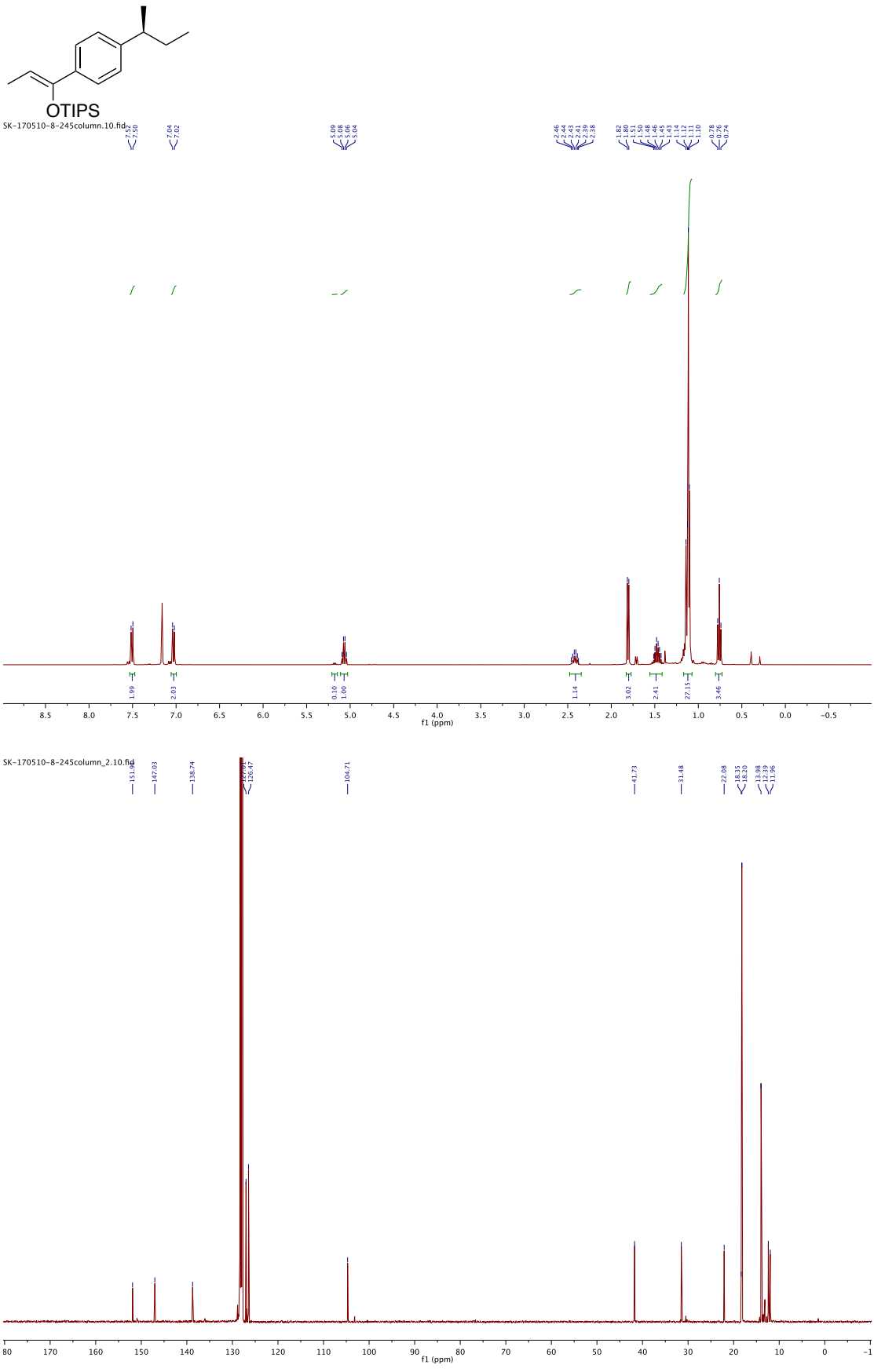

SK-170510-8-242Bcolumn.10.fid
7.48
7.47
7.47
6.99
6.97
5.22
5.20
5.18
5.16
2.35
2.33
1.78
1.76
1.05
0.85
0.83
0.02
2.00
1.99
1.02
2.04
3.25
8.84
6.26
5.59
f1 (ppm)

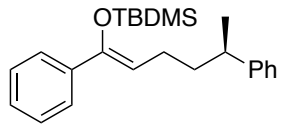

SK-170510-8-242column.12.fid
150.85
141.06
138.02
129.06
126.07
105.25
45.39
30.46
26.14
22.47
18.62
13.98
-3.77
f1 (ppm)

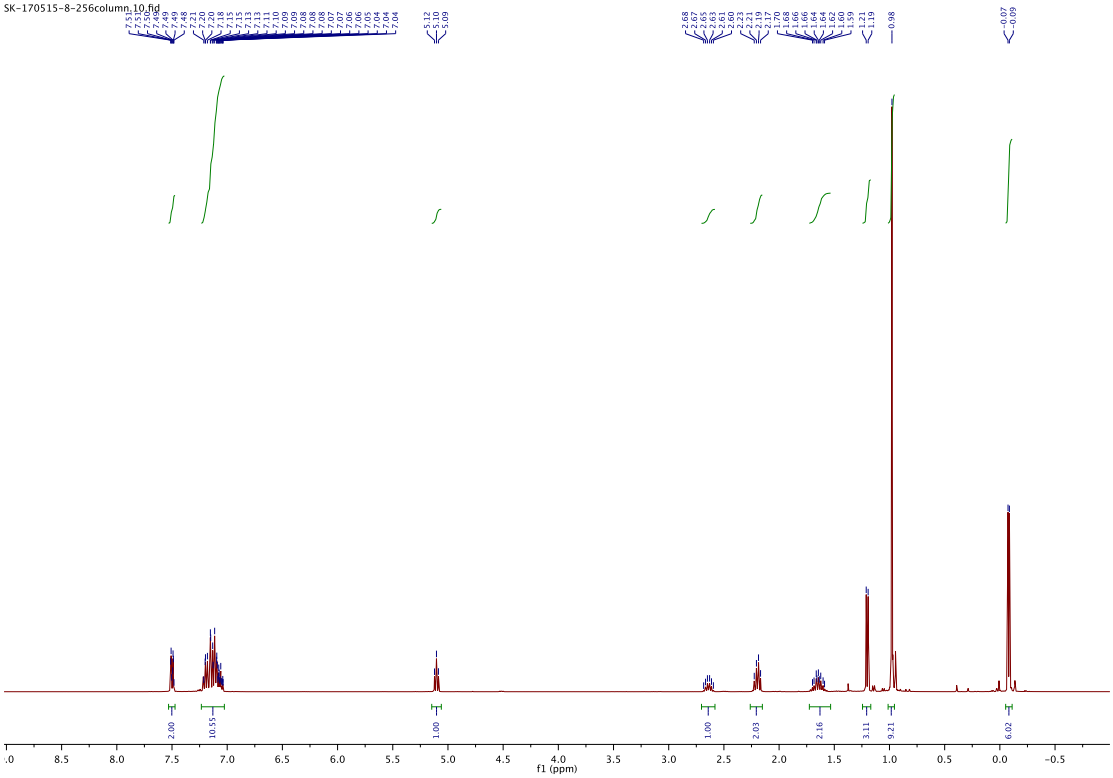

OTBDMS

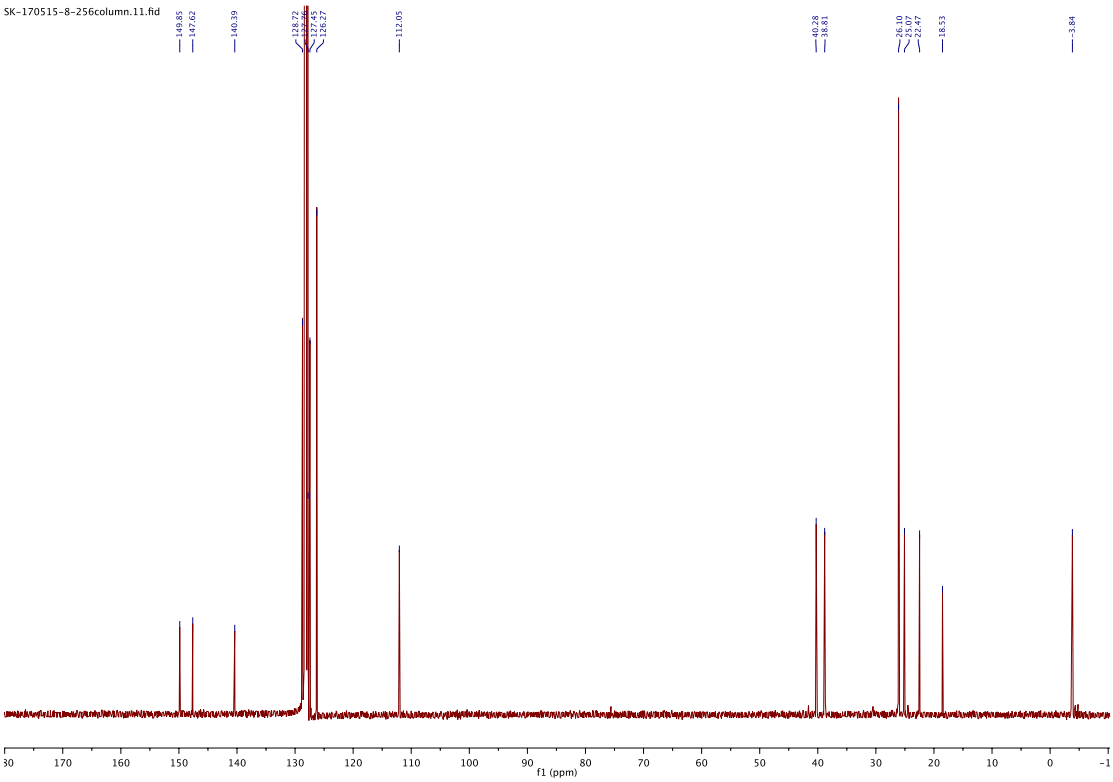

SK-170518-8-259column.10.fid
f1 (ppm)

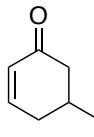

SK-170518-8-259column.11.fid
149.74
140.44
126.31
112.47
39.23
28.25
25.72
24.68
22.80
18.59
-3.78
f1 (ppm)

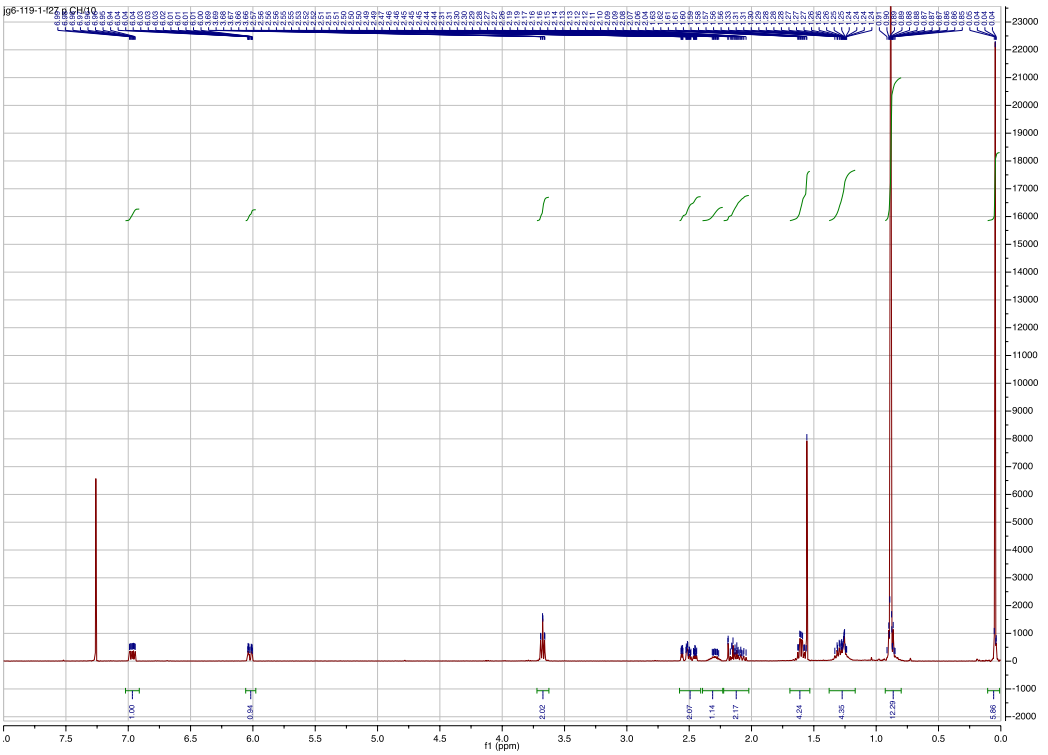

OTIPS
SK-170510-8-245column.10.fid
7.52
7.50
7.04
7.02
6.09
6.08
5.06
5.04
2.46
2.44
2.43
2.41
2.39
2.38
1.82
1.80
1.51
1.50
1.48
1.46
1.45
1.43
1.14
1.12
1.11
1.10
0.78
0.76
0.74
1.99
2.03
0.10
1.00
1.14
3.02
2.41
27.15
3.46
f1 (ppm)
SK-170510-8-245column_2.10.fid
151.96
147.03
138.74
127.07
126.47
104.71
41.73
31.48
22.08
18.35
18.20
13.98
12.39
11.96
f1 (ppm)

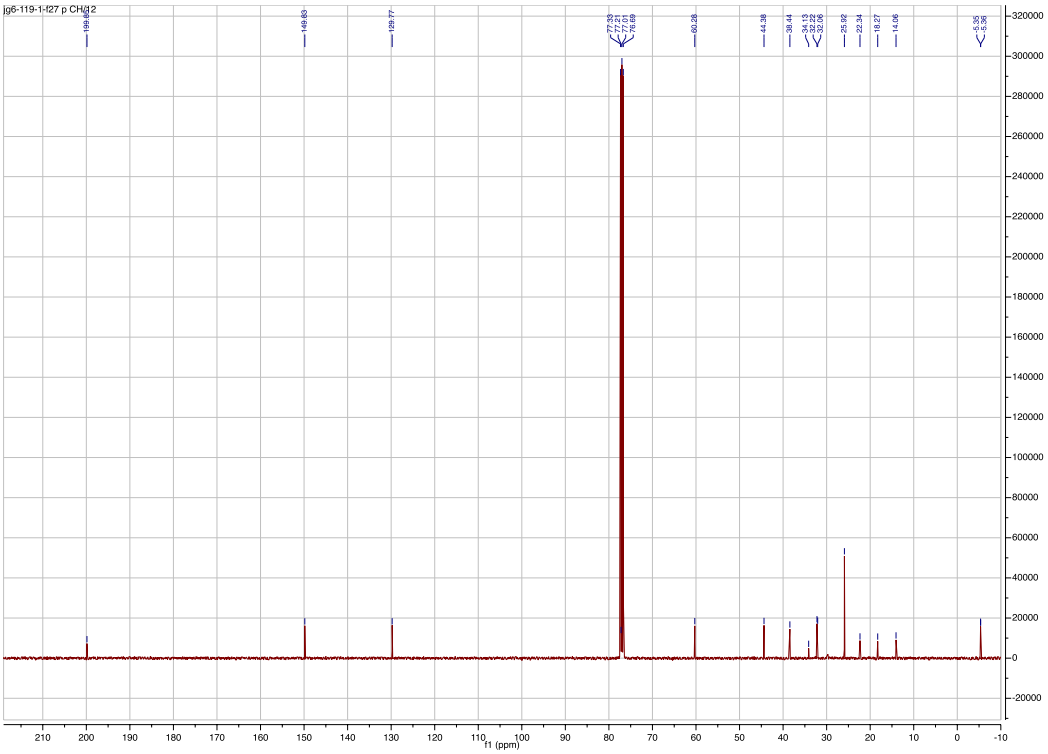

OTBDMS
Ph

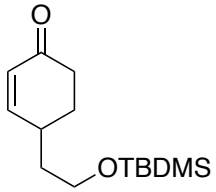

SK-170515-8-256column.10.fid
f1 (ppm)

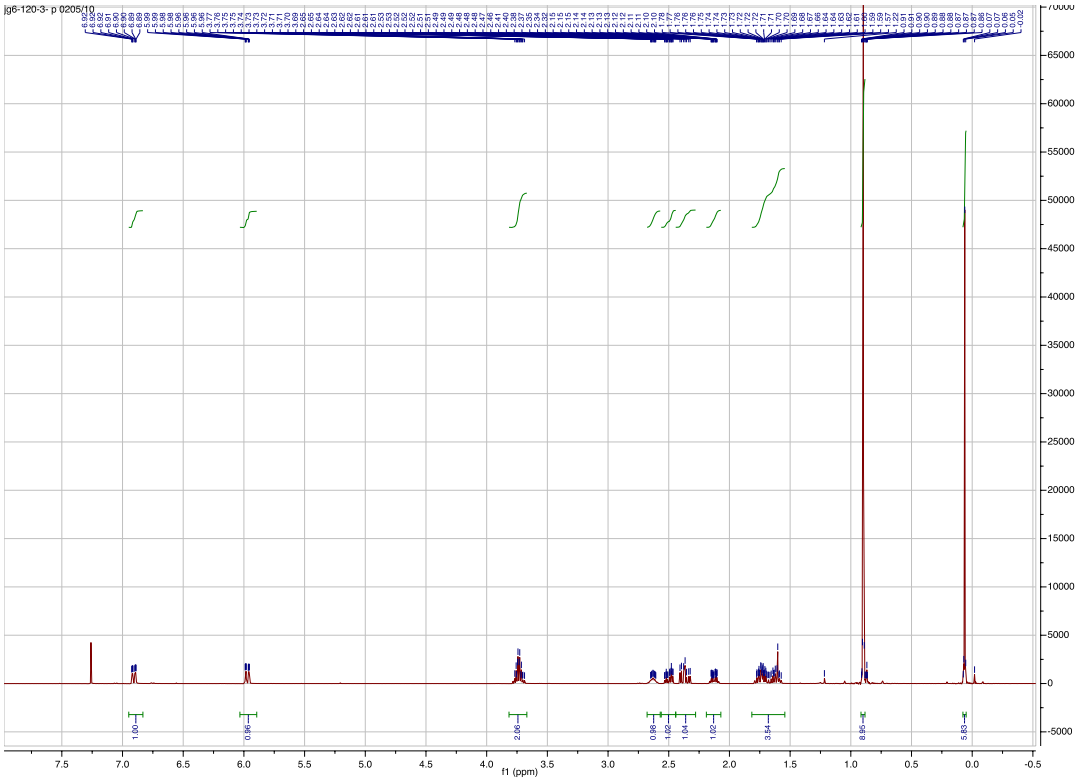

SK-170515-8-256column.11.fid
f1 (ppm)

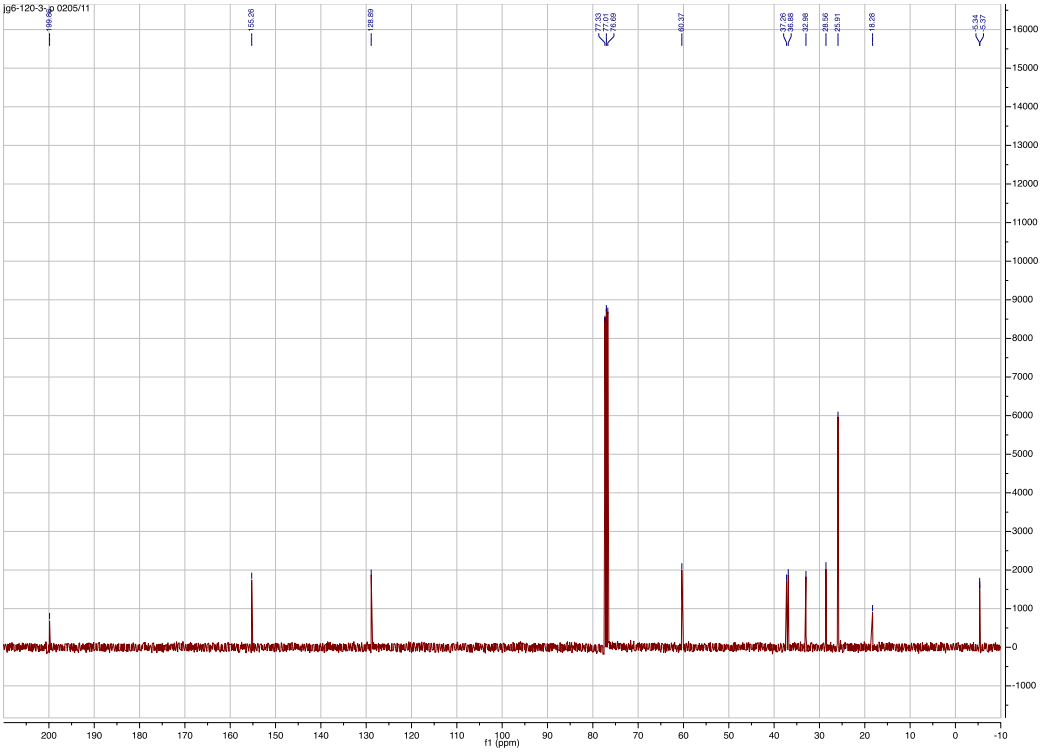

O
OTBDMS

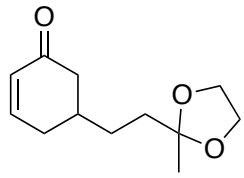

jg6-119-1-f27 p CHJ10
f1 (ppm)

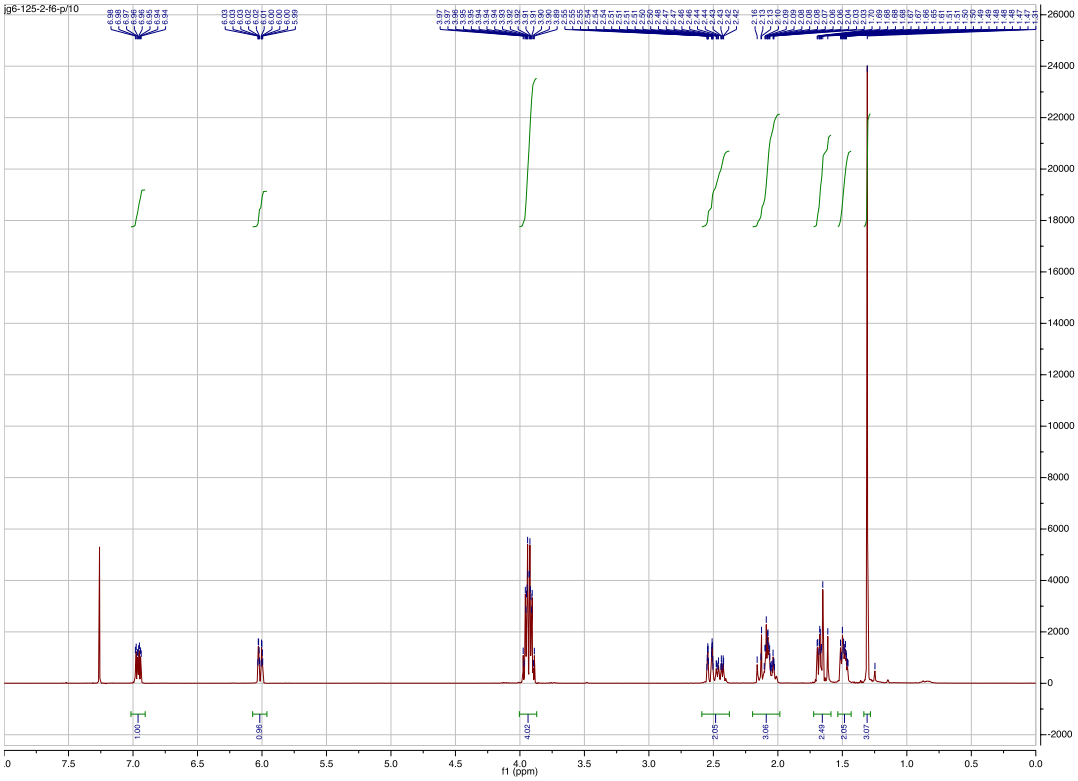

jg6-119-1-f27 p CHJ12
199.85
149.69
129.77
77.33
77.21
77.10
76.69
60.28
44.38
38.44
34.13
32.72
32.56
25.92
22.34
18.27
14.06
-5.35
-5.96
f1 (ppm)

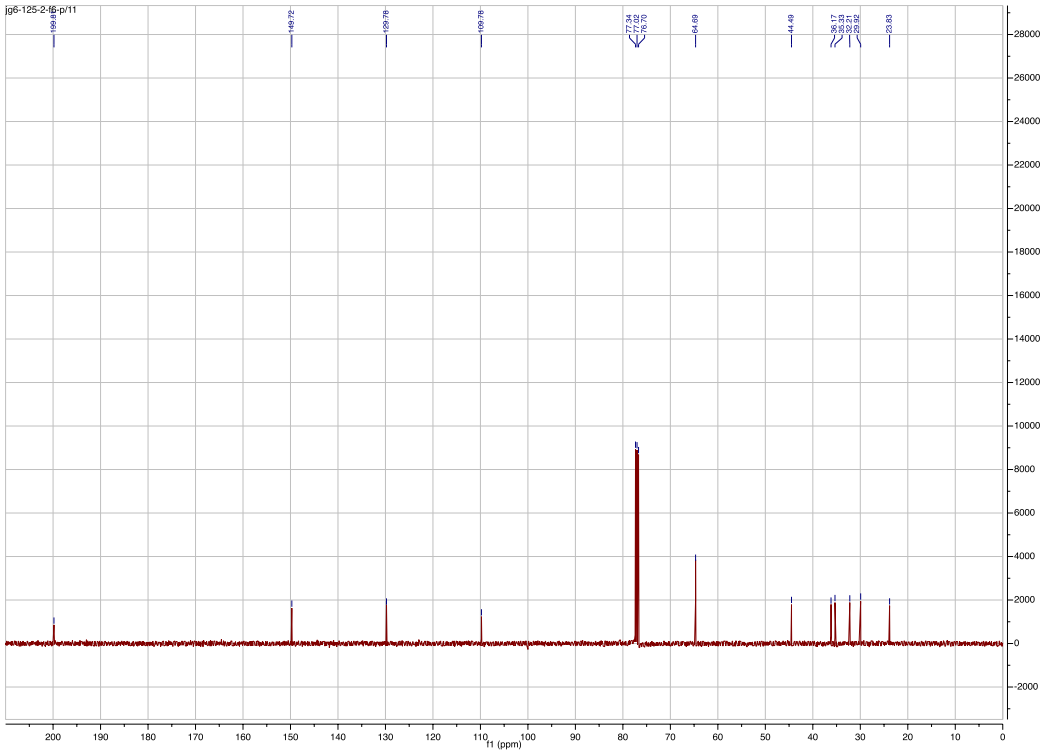

O
OTBDMS

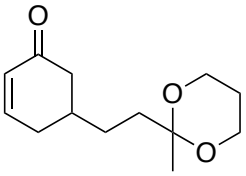

jg6-120-3- p 0205/10
f1 (ppm)

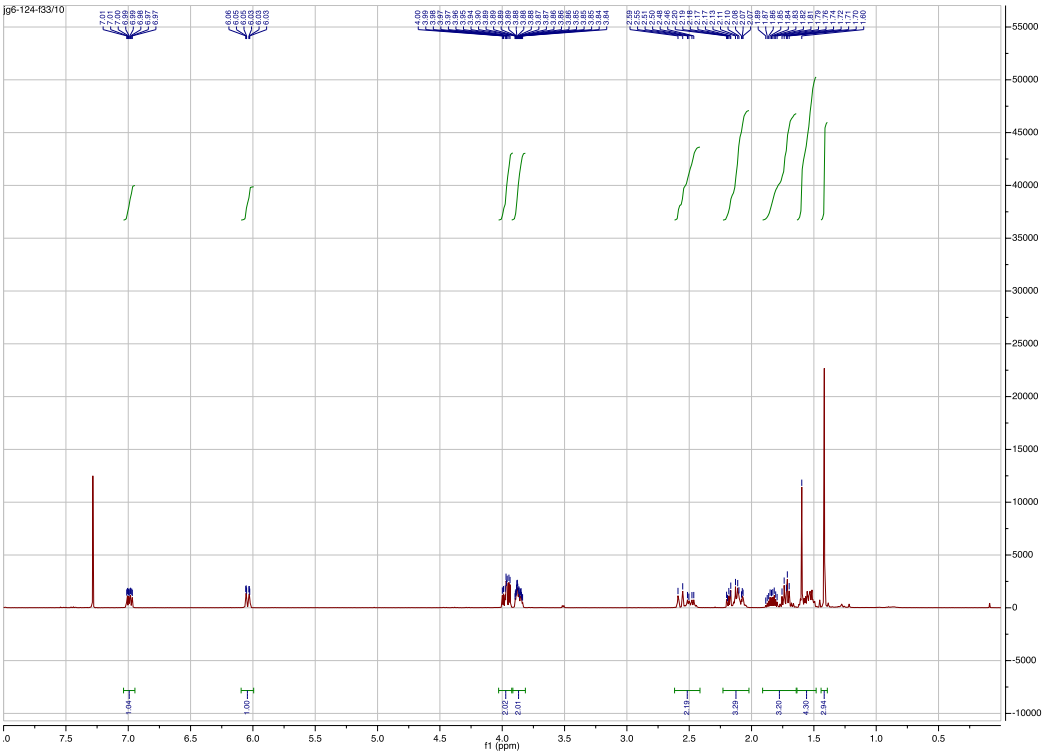

jg6-120-3- p 0205/11
199.86
155.26
128.69
77.33
77.01
76.69
60.37
37.26
32.68
32.06
25.96
25.91
18.26
-5.34
-5.37
f1 (ppm)

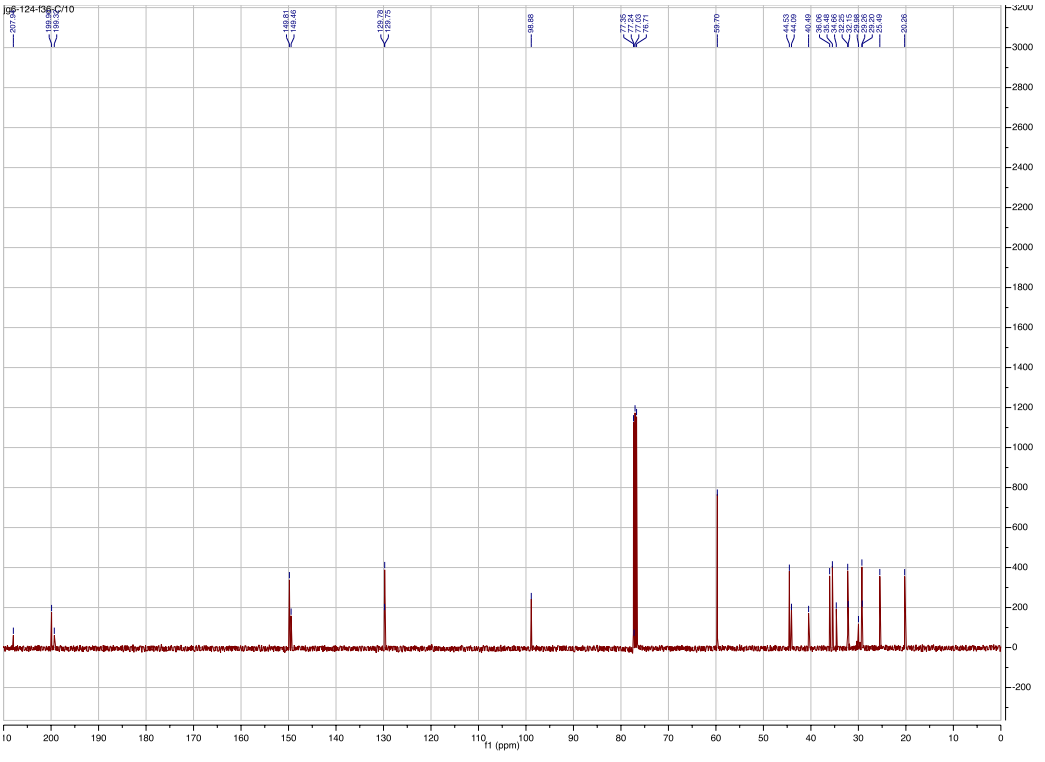

O
O
O


jg6-125-2-f6-p/10
f1 (ppm)

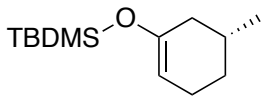

jg6-125-2-f6-p/11
198.49
148.72
129.78
109.78
77.34
77.02
76.70
64.69
44.49
36.17
35.31
30.21
29.92
23.83
f1 (ppm)



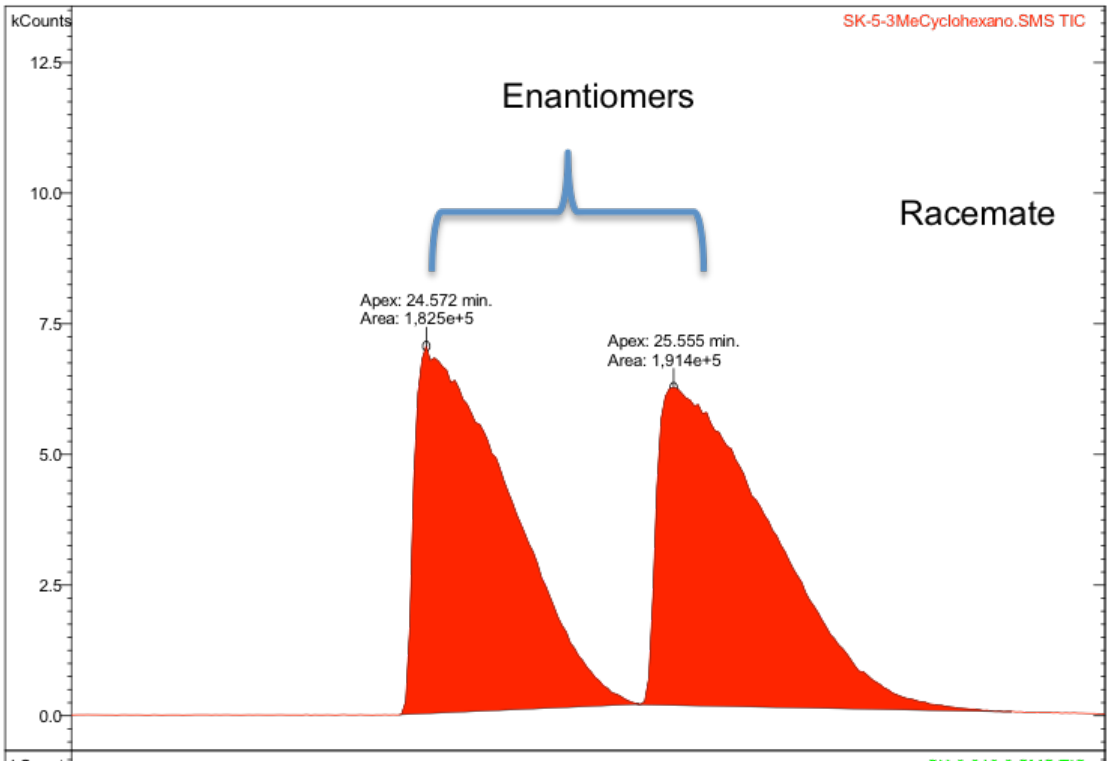

jg6-124-f33/10
f1 (ppm)


jg6-124-f36-C/10
f1 (ppm)

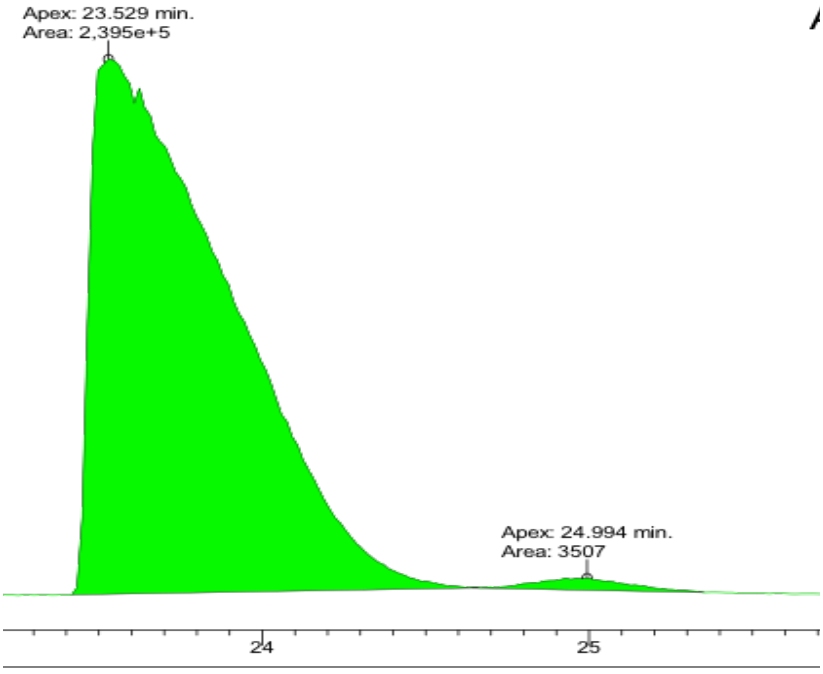
GC Chromatograms

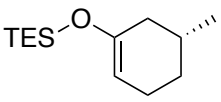


2a'

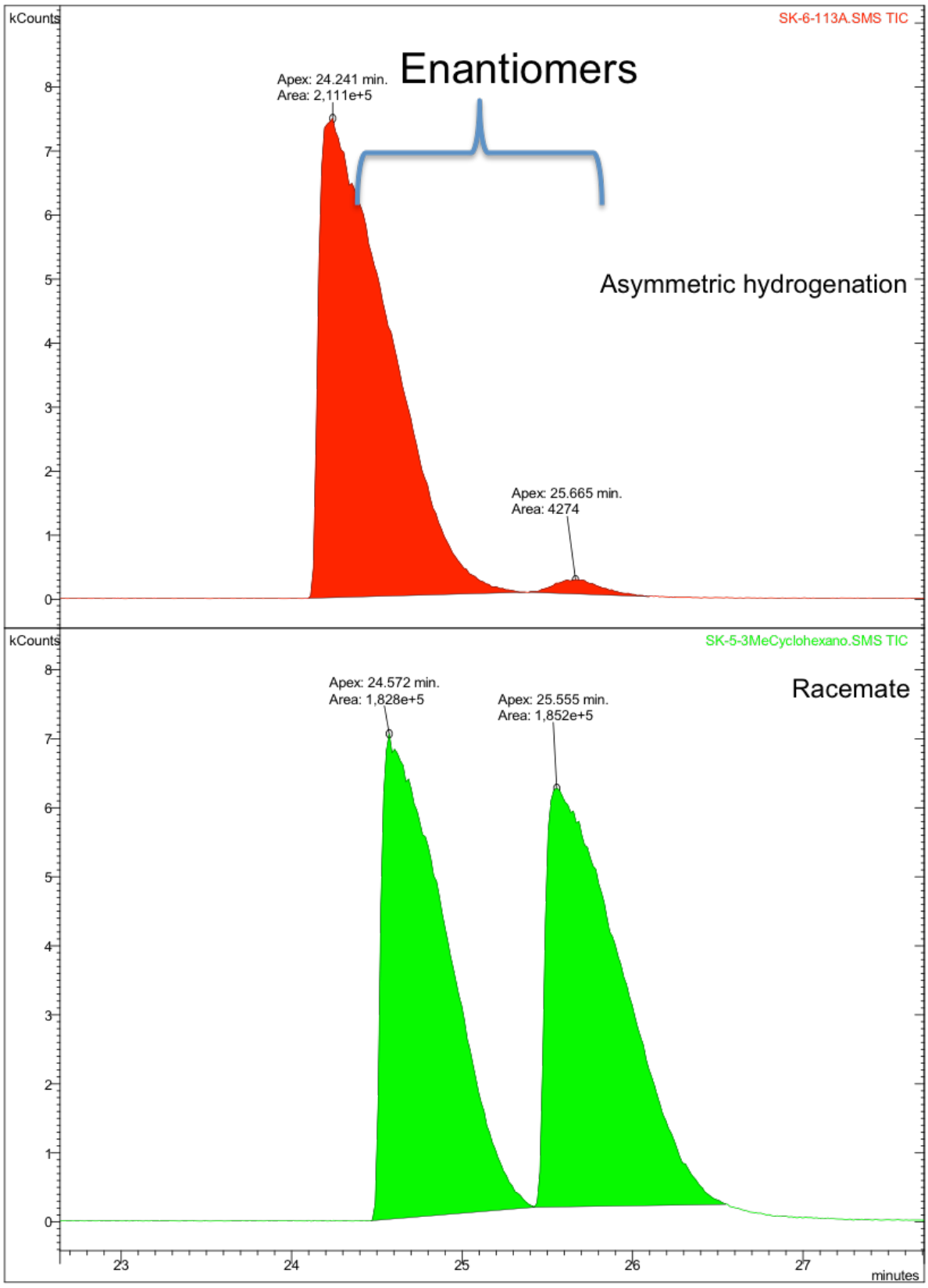


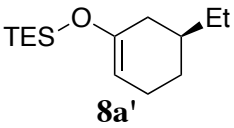
Asymmetric hydrogenation




TES
O

7a'

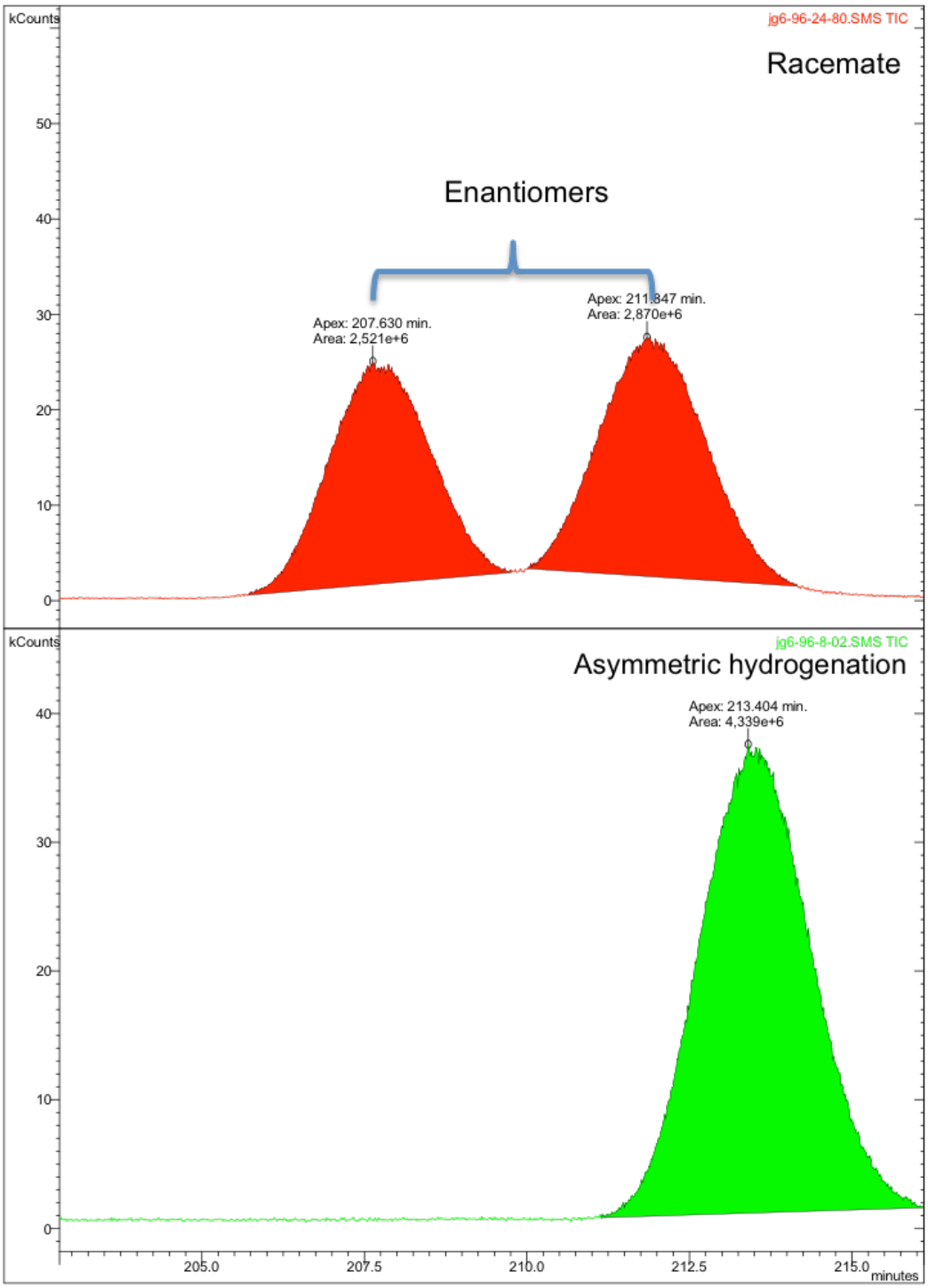

kCounts
SK-6-113A.SMS TIC
Enantiomers
Apex: 24.241 min.
Area: 2,111e+5
Asymmetric hydrogenation
Apex: 25.665 min.
Area: 4274
kCounts
SK-5-3MeCyclohexano.SMS TIC
Racemate
Apex: 24.572 min.
Area: 1,828e+5
Apex: 25.555 min.
Area: 1,852e+5
0
1
2
3
4
5
6
7
8
23
24
25
26
27
minutes

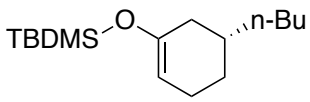


8a'

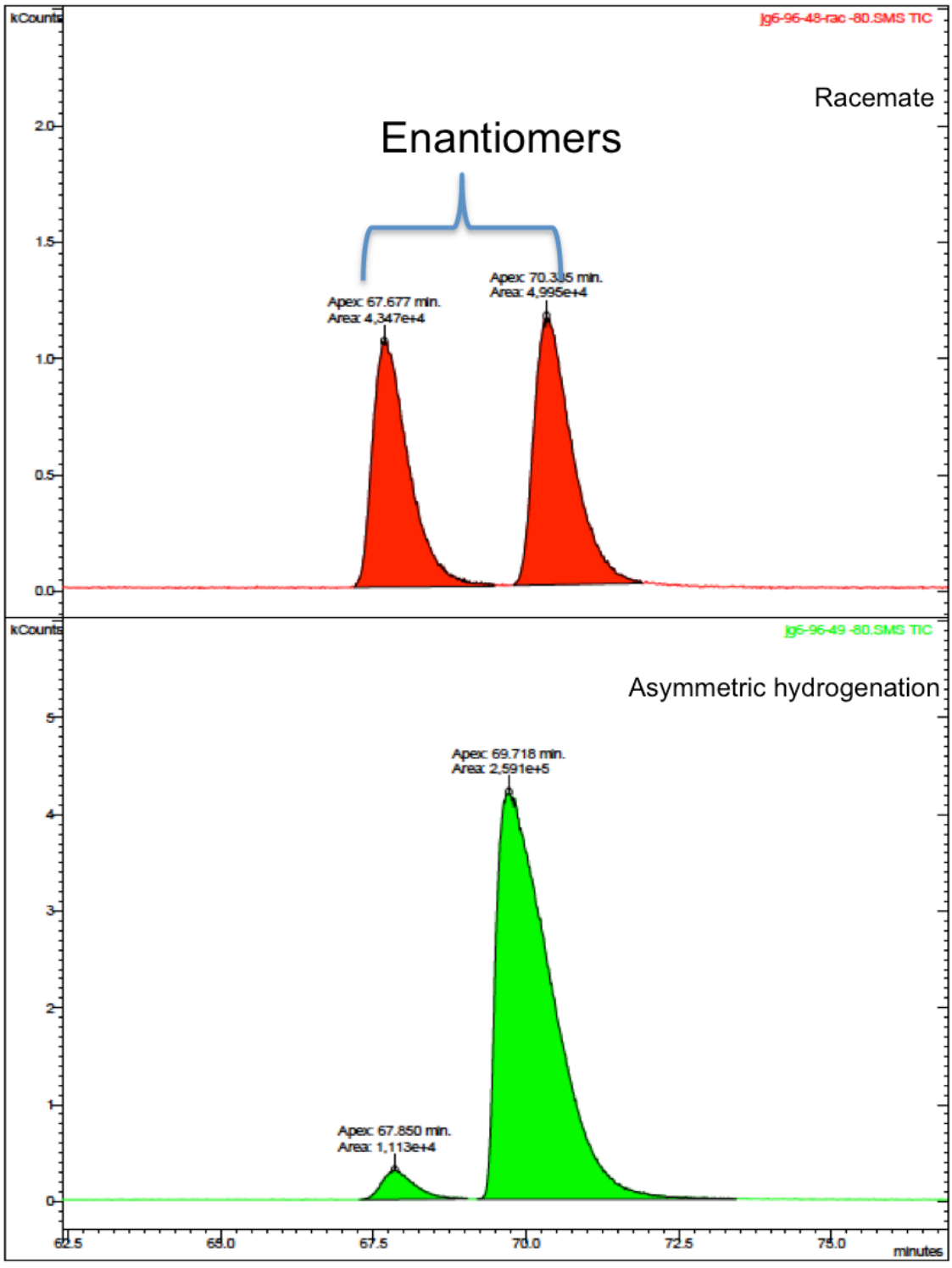
Print Date: 30 Sep 2016 12:06:17

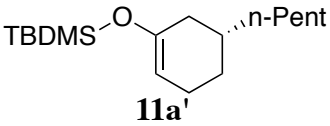
Chromatogram Plots



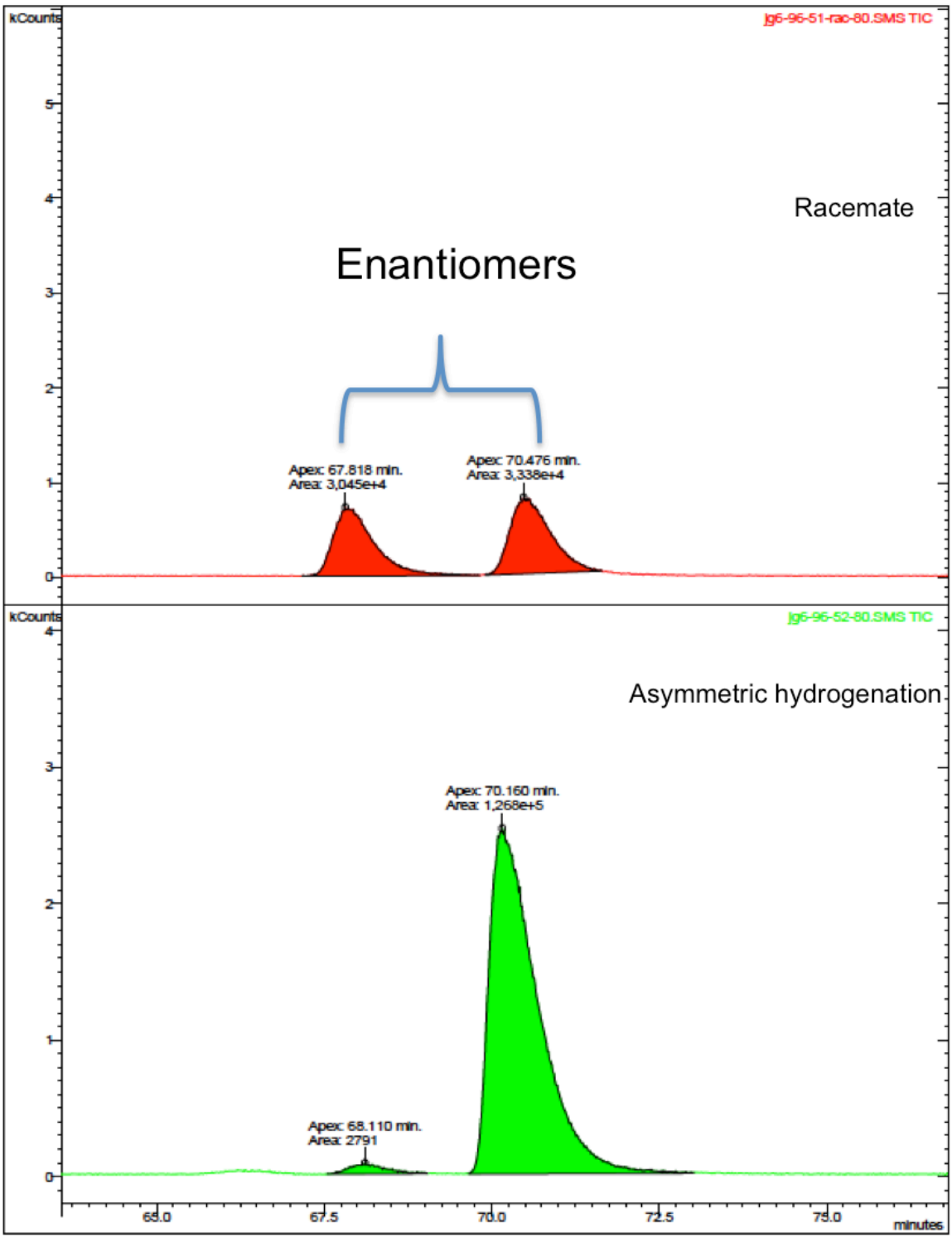

TBDMS
O
n-Bu

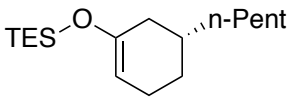
9a'


kCounts
lg6-96-48-rac -80.SMS TIC
Racemate
Enantiomers
Apex: 67.677 min.
Area: 4,347e+4
Apex: 70.305 min.
Area: 4,995e+4
kCounts
lg6-96-49 -80.SMS TIC
Asymmetric hydrogenation
Apex: 69.718 min.
Area: 2,591e+5
Apex: 67.850 min.
Area: 1,113e+4
minutes


TBDMS
O
n-Pent

11a'

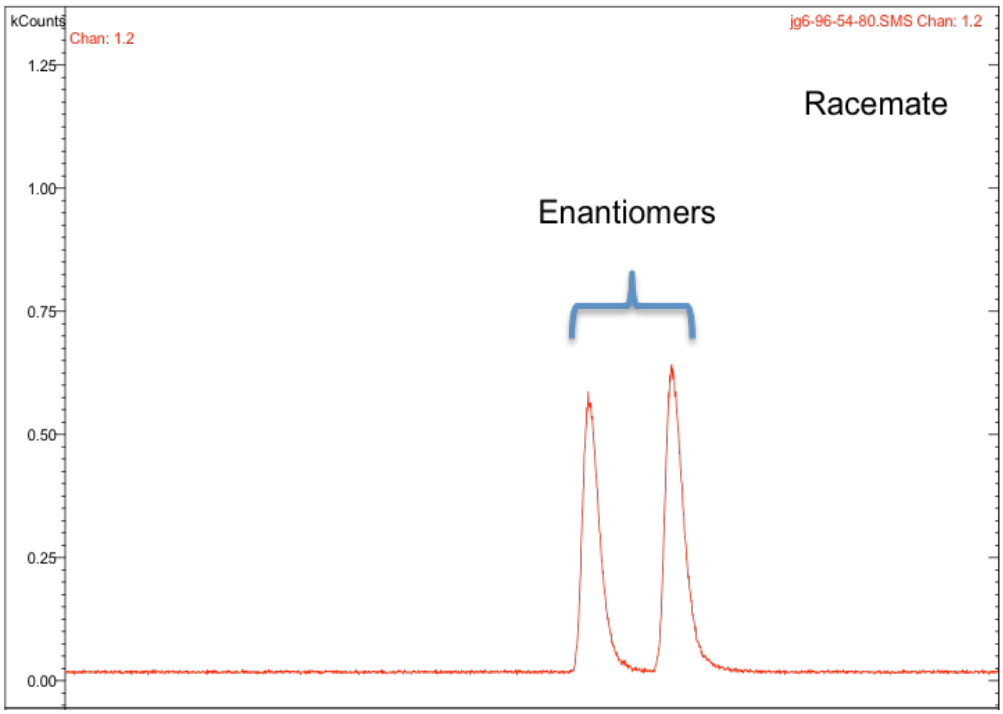

kCounts
jg6-96-51-rac-80.SMS TIC
Racemate
Enantiomers
Apex: 67.818 min.
Area: 3,045e+4
Apex: 70.476 min.
Area: 3,338e+4
kCounts
jg6-96-52-80.SMS TIC
Asymmetric hydrogenation
Apex: 70.160 min.
Area: 1,268e+5
Apex: 68.110 min.
Area: 2791
65.0
67.5
70.0
72.5
75.0
minutes

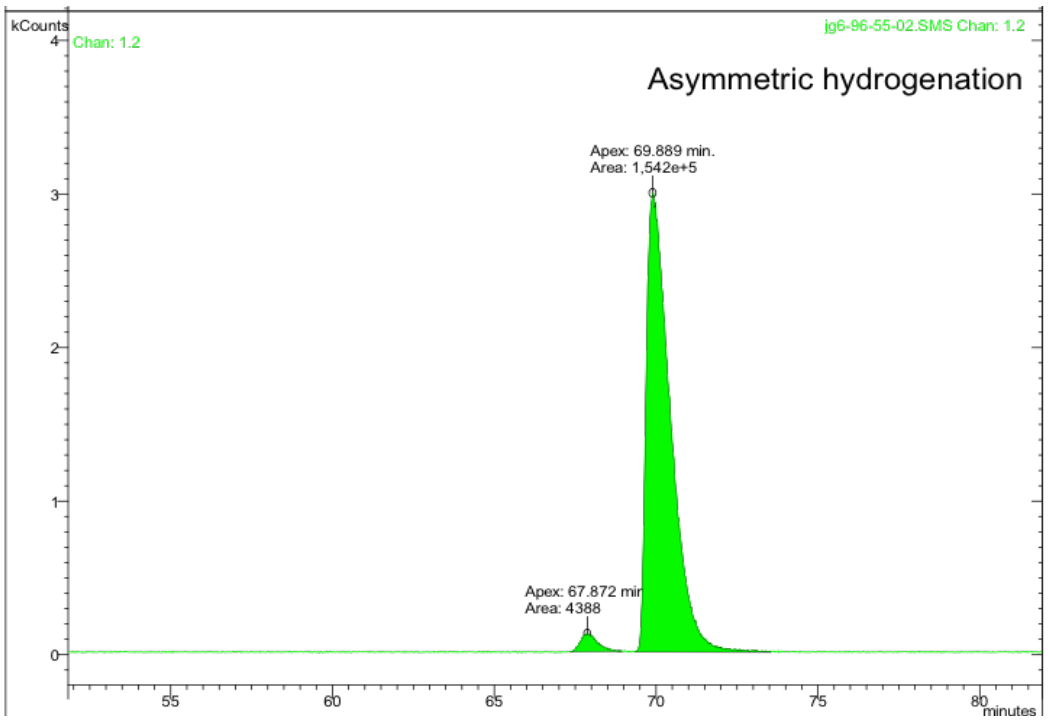


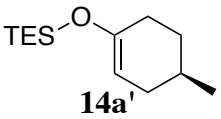
12a'

Print Date: 19 Jan 2017 14:46:45

Chromatogram Plots



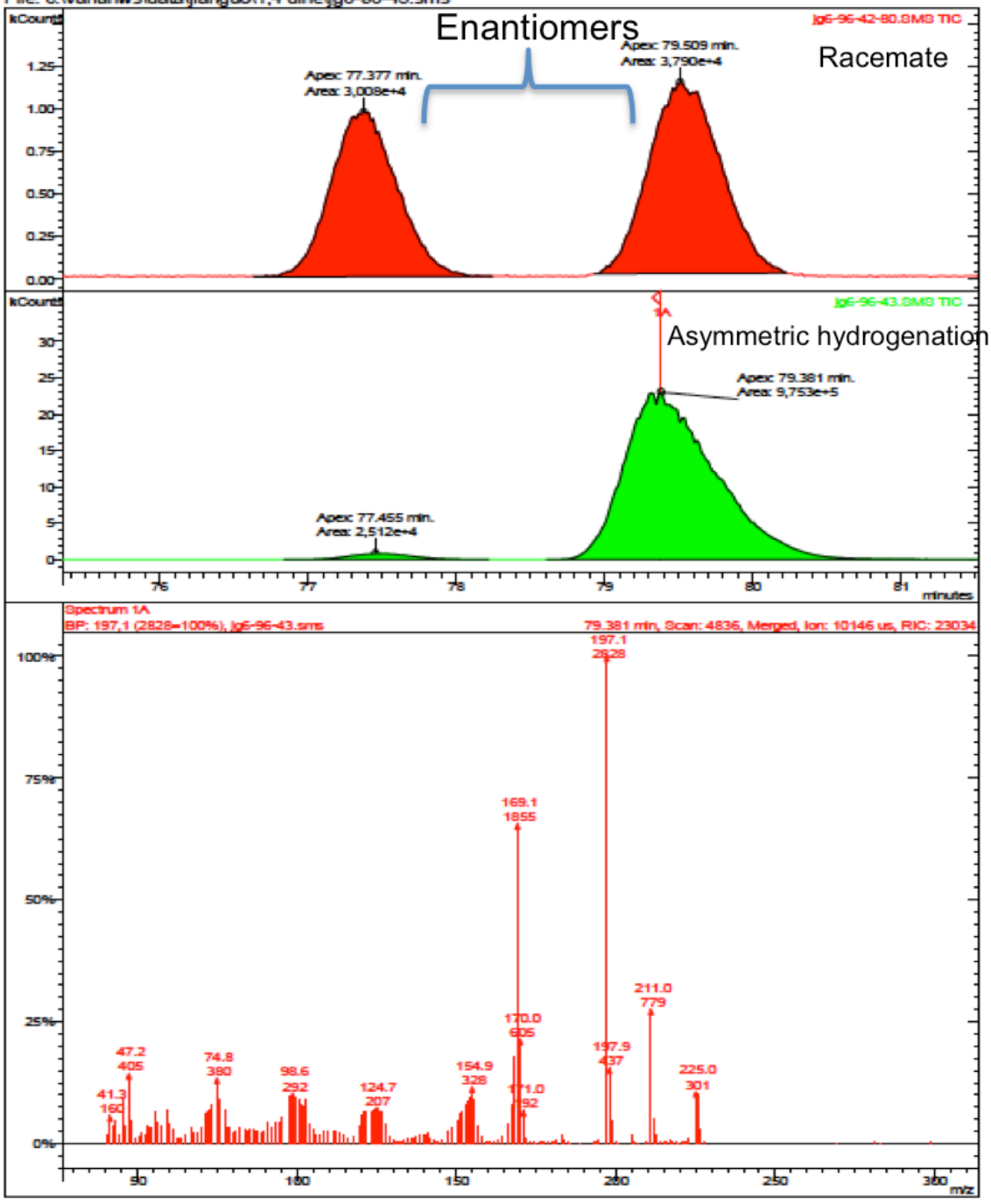


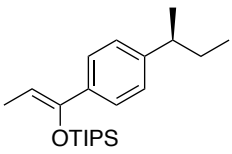


14a'

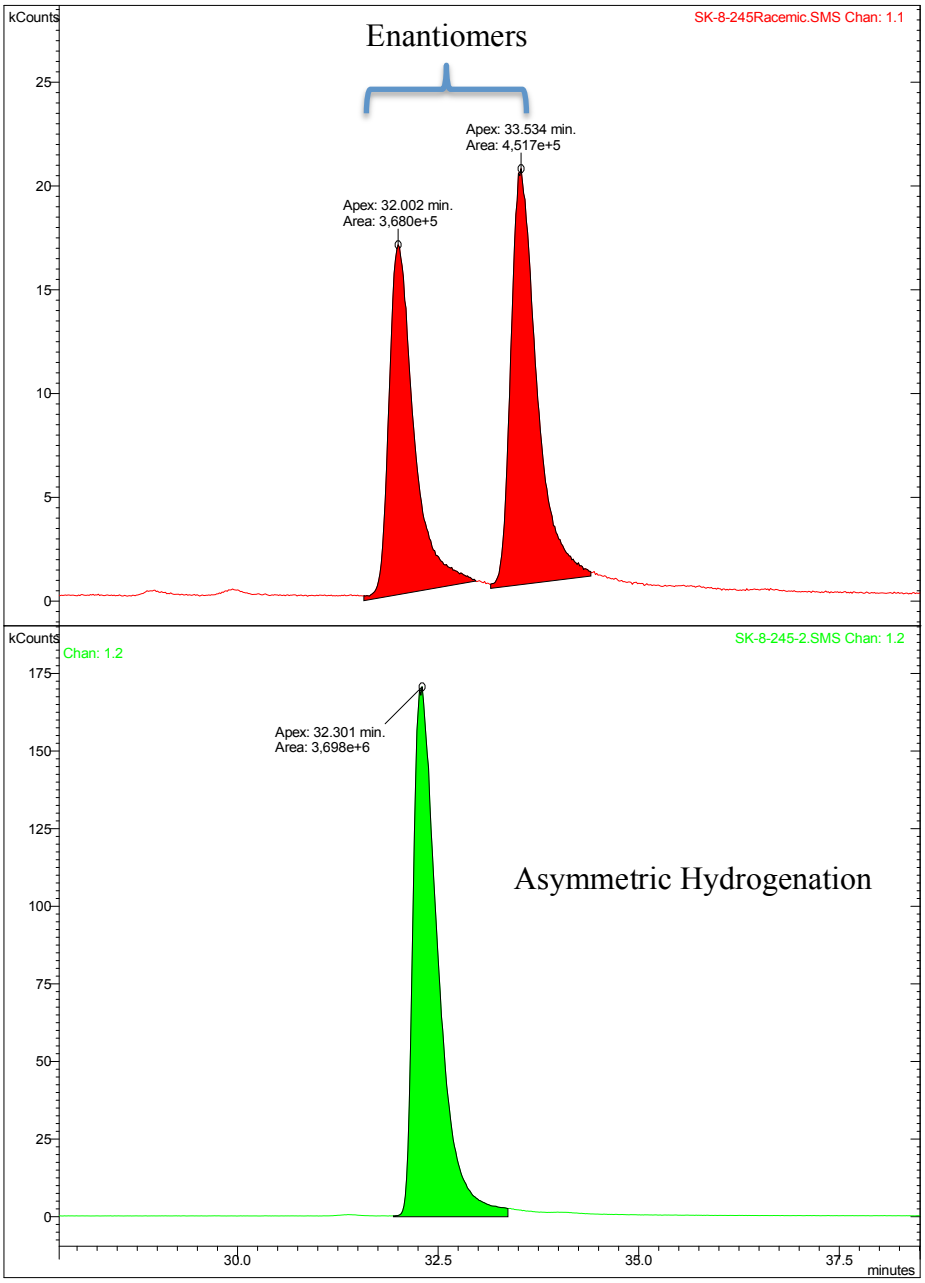
MS Data Review All Plots - 12/12/2016 2:45 PM

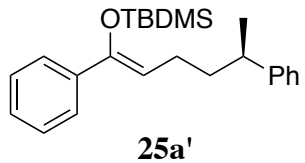
File: c:\varianws\data\jianguo\1,4 dine\jg6-96-42-80.sms
File: c:\varianws\data\jianguo\1,4 dine\jg6-96-43.sms



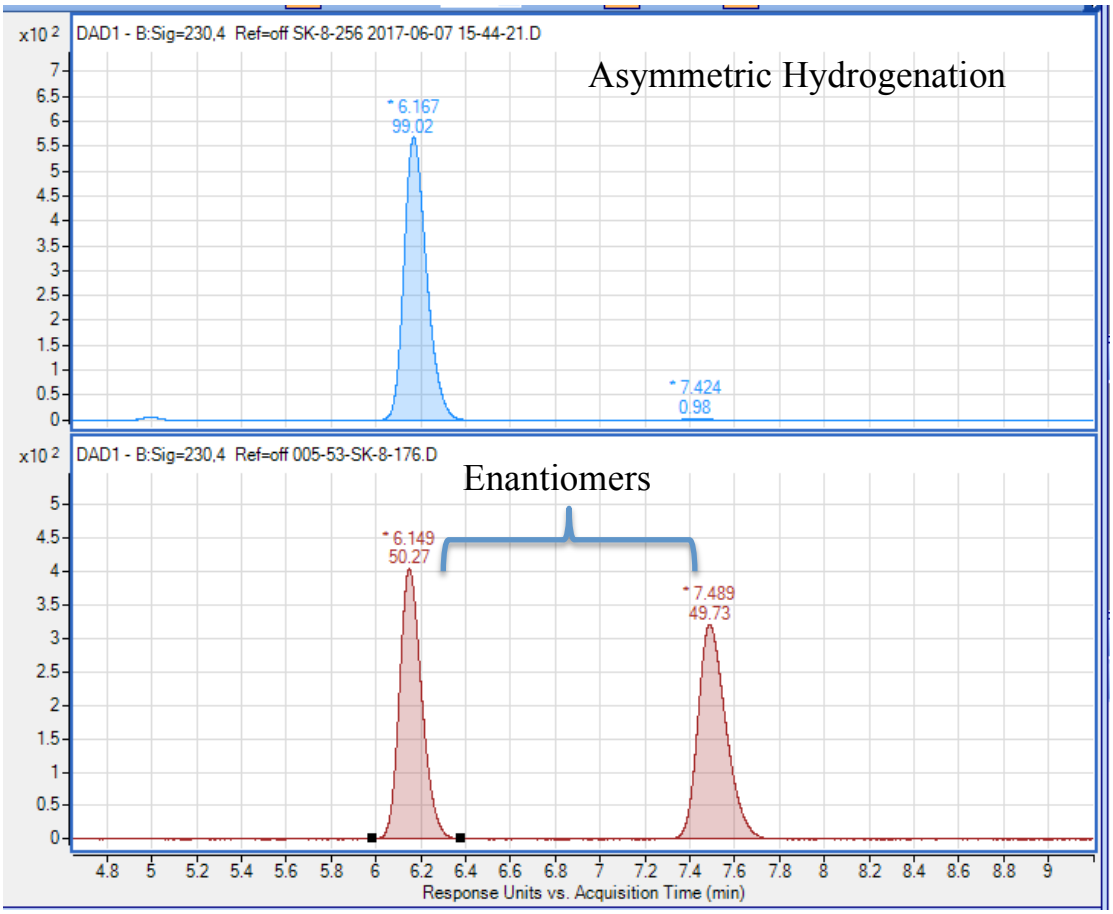

OTIPS

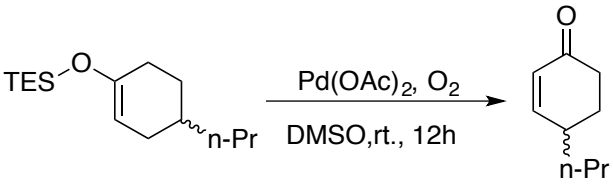
24a'


kCounts
SK-8-245Racemic.SMS Chan: 1.1
Enantiomers
Apex: 33.534 min.
Area: 4,517e+5
Apex: 32.002 min.
Area: 3,680e+5
25
20
15
10
5
0
kCounts
Chan: 1.2
SK-8-245-2.SMS Chan: 1.2
Apex: 32.301 min.
Area: 3,698e+6
Asymmetric Hydrogenation
175
150
125
100
75
50
25
0
30.0
32.5
35.0
37.5
minutes

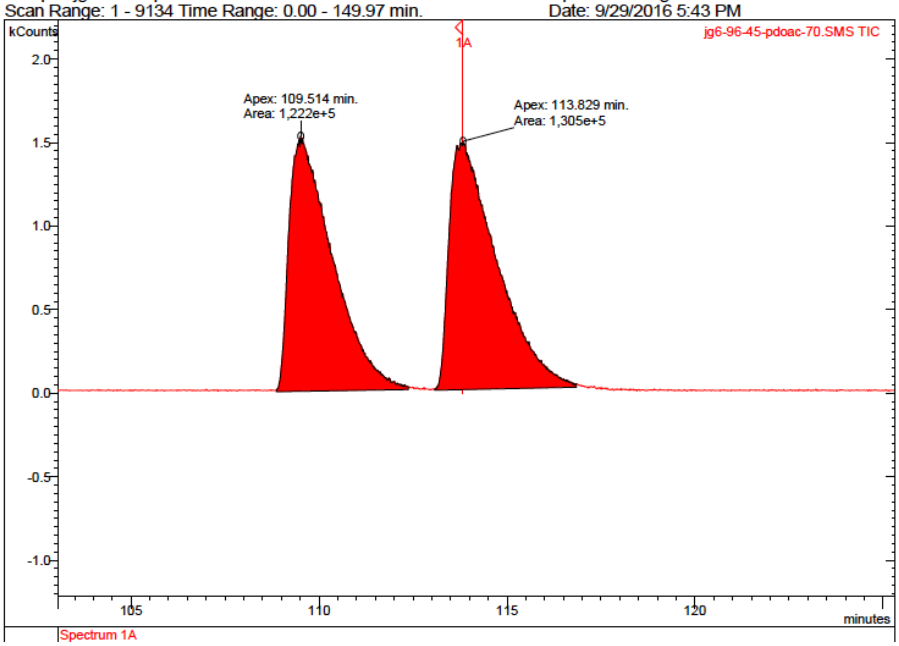

OTBDMS
Ph

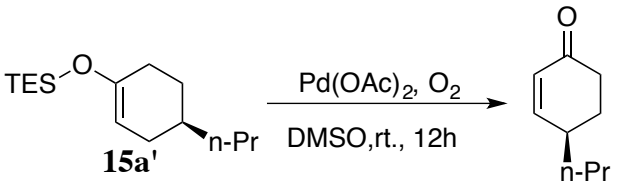
25a'


x10 2
DAD1 - B:Sig=230,4 Ref=off SK-8-256 2017-06-07 15-44-21.D
Asymmetric Hydrogenation
6.167
99.02
7.424
0.98
x10 2
DAD1 - B:Sig=230,4 Ref=off 005-53-SK-8-176.D
Enantiomers
6.149
50.27
7.489
49.73
Response Units vs. Acquisition Time (min)



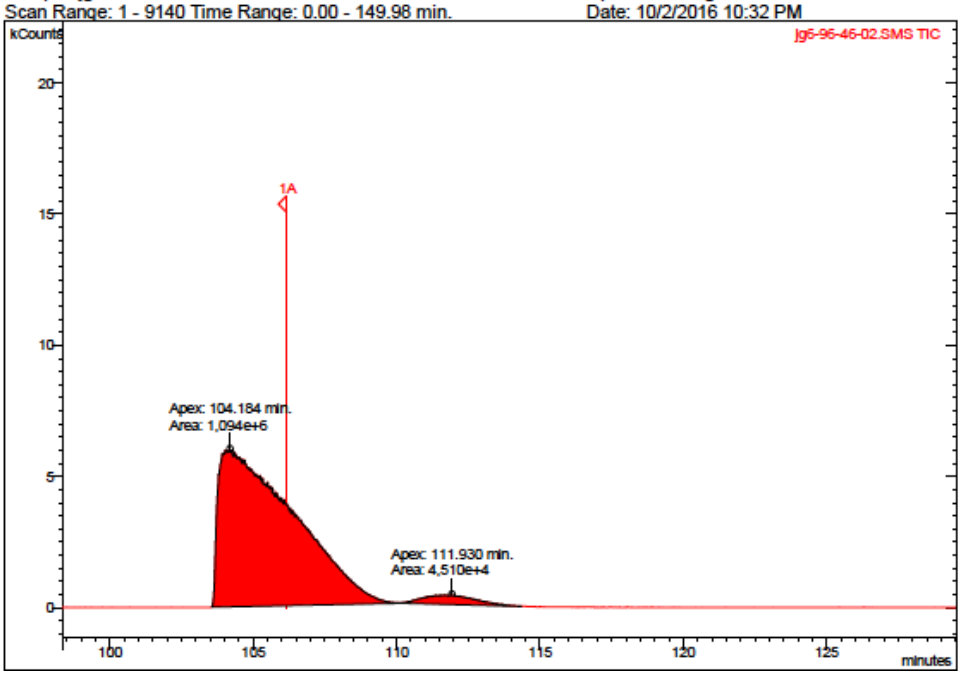
File: c:\varianws\data\jianguo\1,4 dine\jg6-96-45-pdoac-70.sms
Sample: jg6-96-45-pdoac-70
Scan Range: 1 - 9134 Time Range: 0.00 - 149.97 min.
Operator: wangchuk
Date: 9/29/2016 5:43 PM

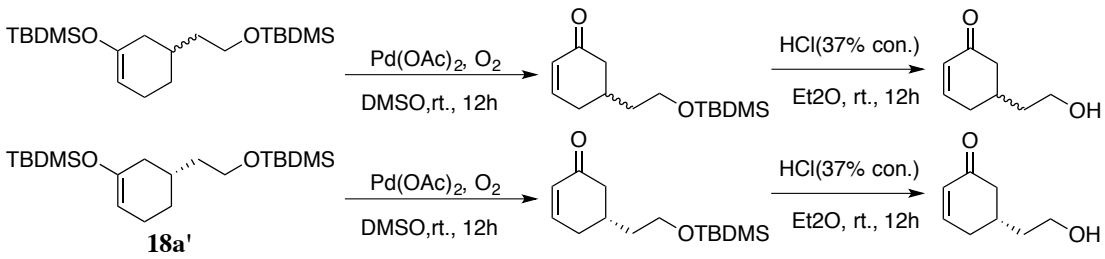




15a'

File: c:\varianws\data\jianguo\1,4 dine\jg6-96-46-02.sms
Sample: jg6-96-46
Scan Range: 1 - 9140 Time Range: 0.00 - 149.98 min.
Operator: wangchuk
Date: 10/2/2016 10:32 PM





Print Date: 19 Jan 2017 14:57:20

MS Data Review All Plots - 1/19/2017 2:56 PM

File: c:\varianws\data\jianguo\1,4 dine\jg6-119-1-pd-hcl125001.sms
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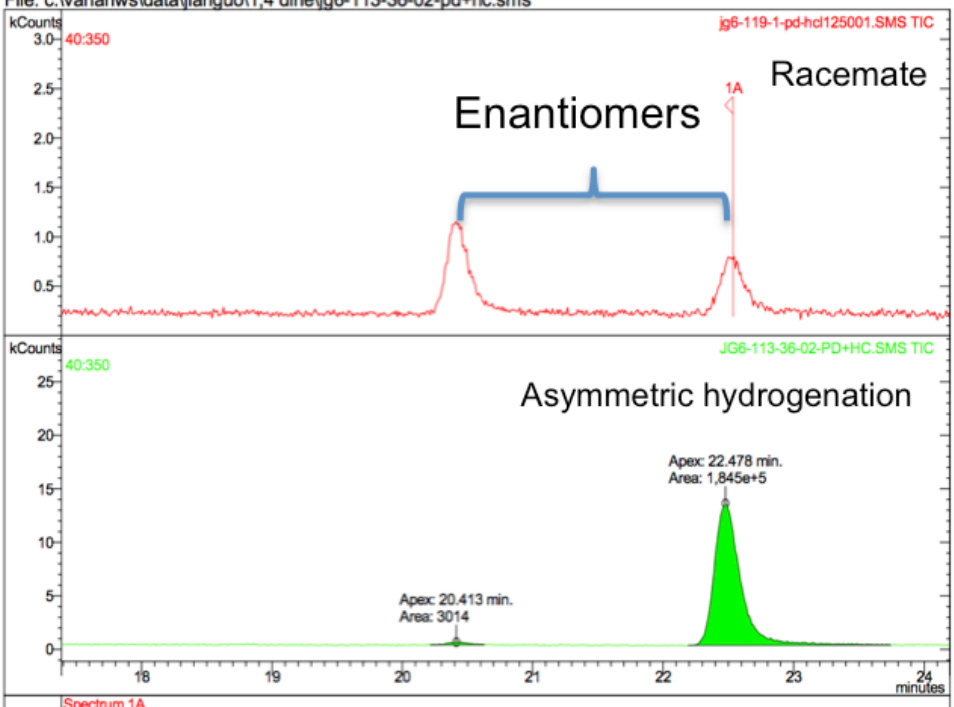
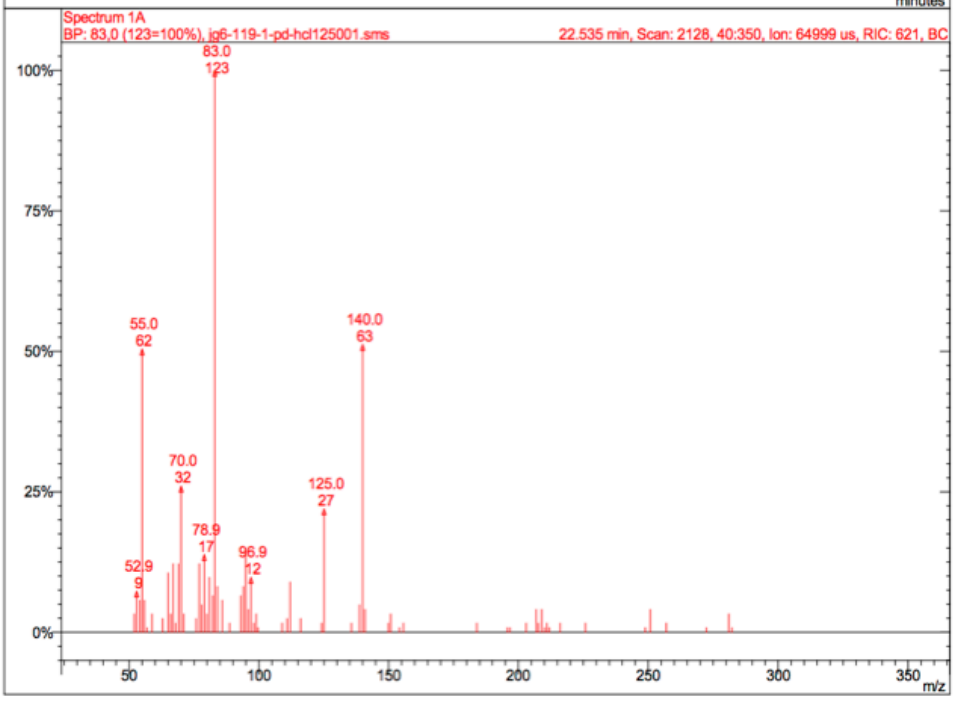
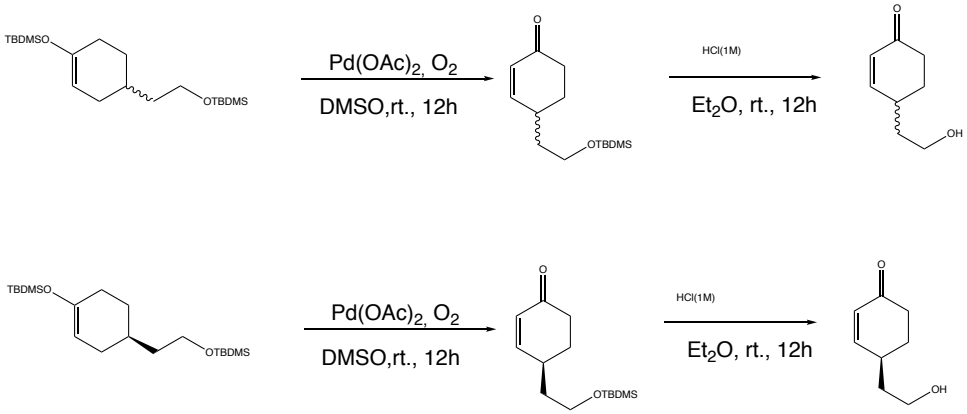


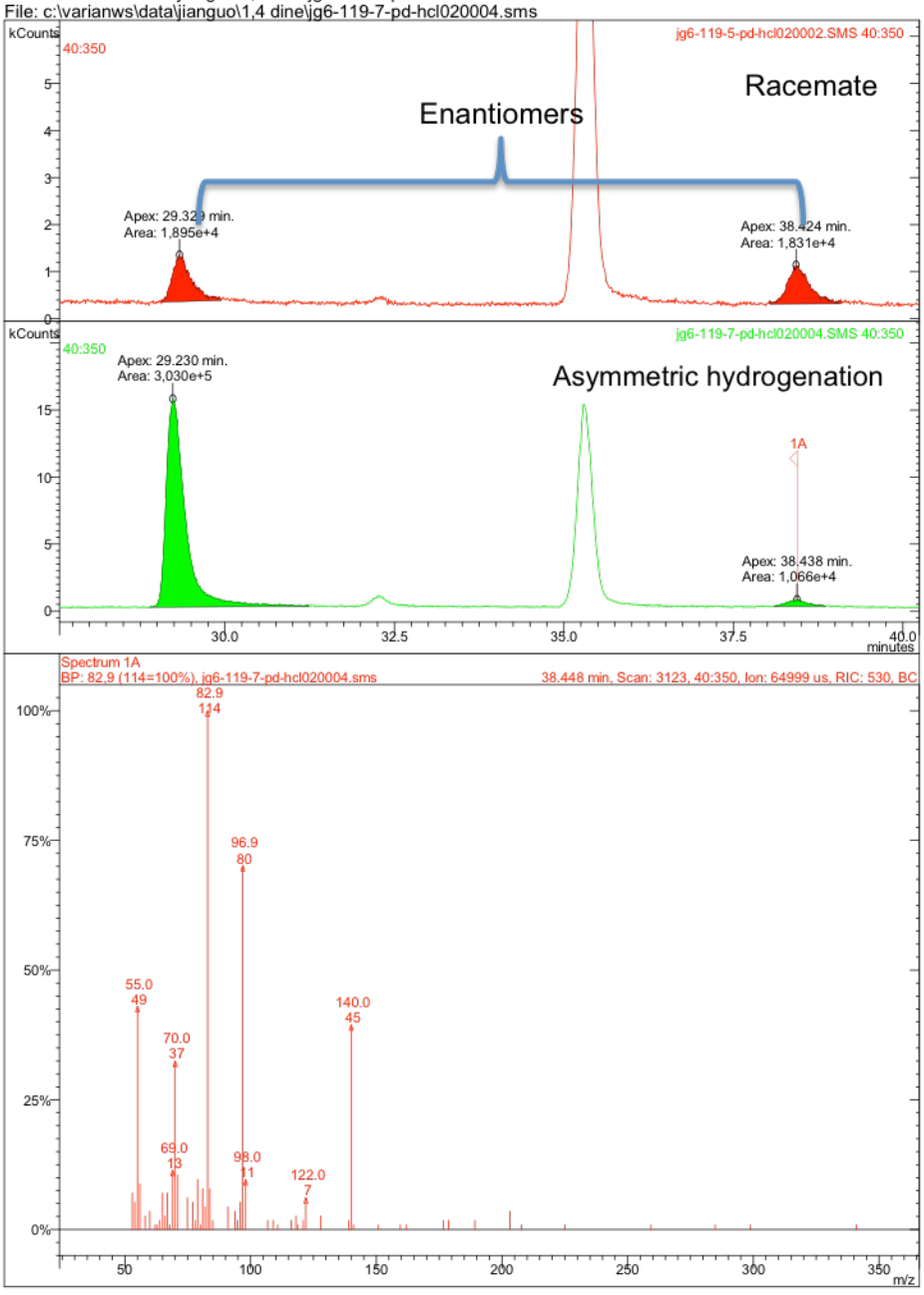


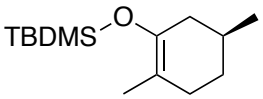


Print Date: 05 Feb 2017 12:35:01

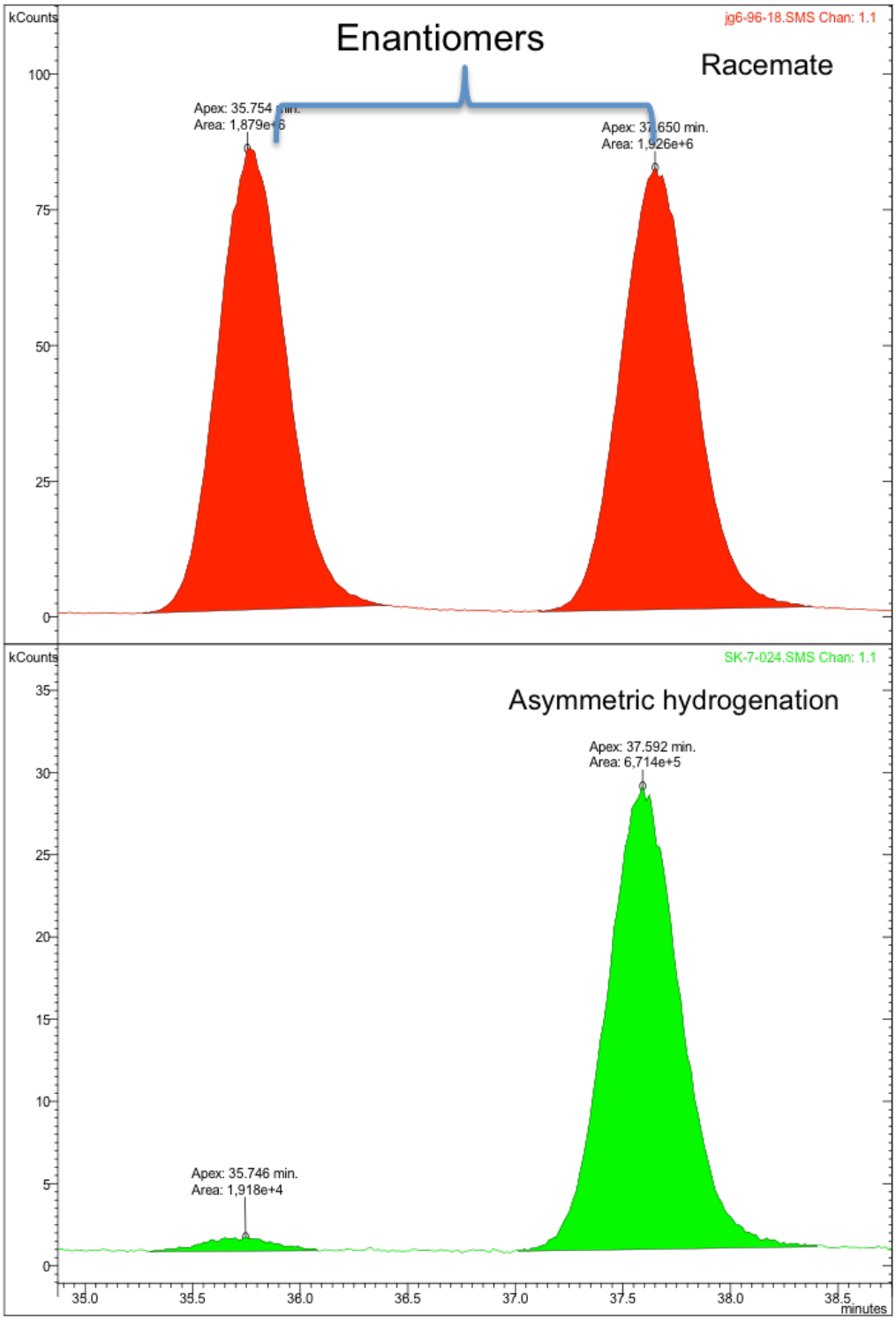
MS Data Review All Plots - 2/5/2017 12:34 PM

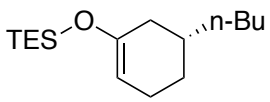
File: c:\varianws\data\jianguo\1,4 dine\jg6-119-5-pd-hcl020002.sms
File: c:\varianws\data\jianguo\1,4 dine\jg6-119-7-pd-hcl020004.sms



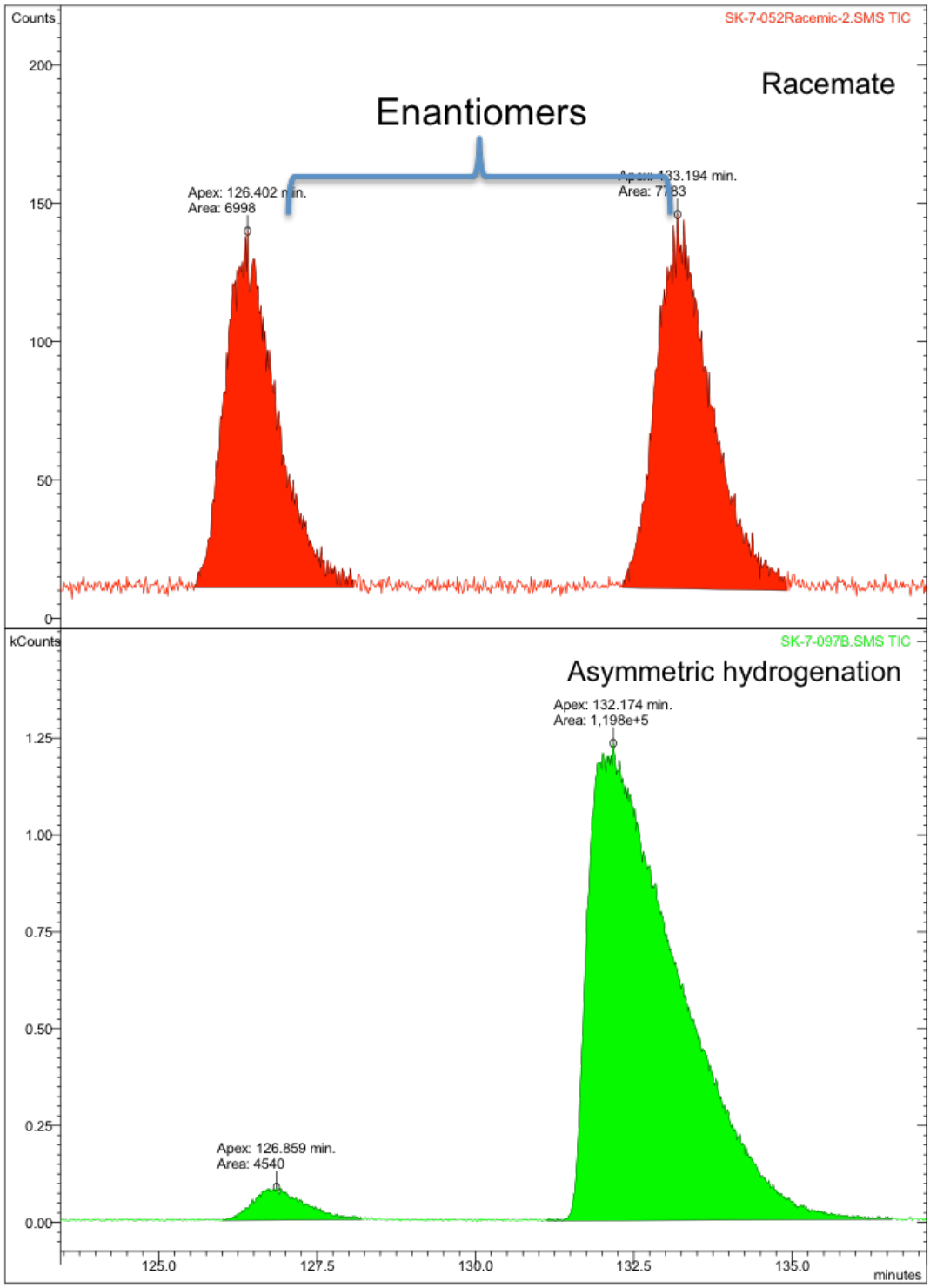

TBDMS
O

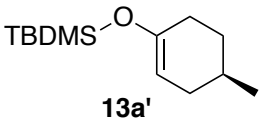
16a'


kCounts
jg6-96-18.SMS Chan: 1.1
Enantiomers
Racemate
Apex: 35.754 min.
Area: 1,879e+6
Apex: 37.650 min.
Area: 1,926e+6
100
75
50
25
0
kCounts
SK-7-024.SMS Chan: 1.1
Asymmetric hydrogenation
Apex: 37.592 min.
Area: 6,714e+5
Apex: 35.746 min.
Area: 1,918e+4
35
30
25
20
15
10
5
0
35.0
35.5
36.0
36.5
37.0
37.5
38.0
38.5
minutes

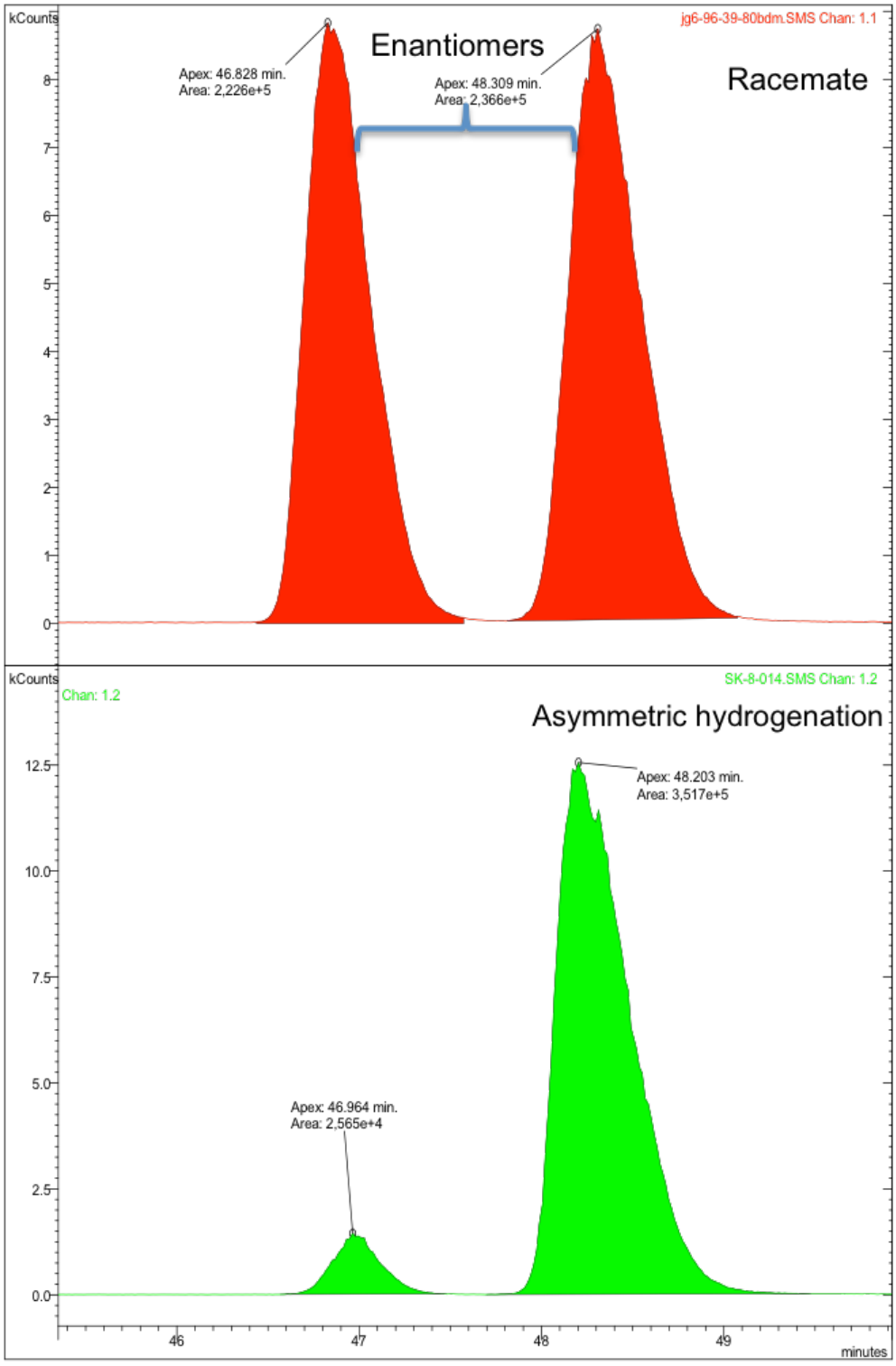

TES
O
n-Bu

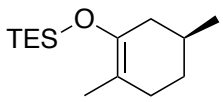
10a'


Counts
SK-7-052Racemic-2.SMS TIC
Racemate
Enantiomers
Apex: 126.402 min.
Area: 6998
Apex: 133.194 min.
Area: 7183
200
150
100
50
0
kCounts
SK-7-097B.SMS TIC
Asymmetric hydrogenation
Apex: 132.174 min.
Area: 1,198e+5
Apex: 126.859 min.
Area: 4540
1.25
1.00
0.75
0.50
0.25
0.00
125.0
127.5
130.0
132.5
135.0
minutes

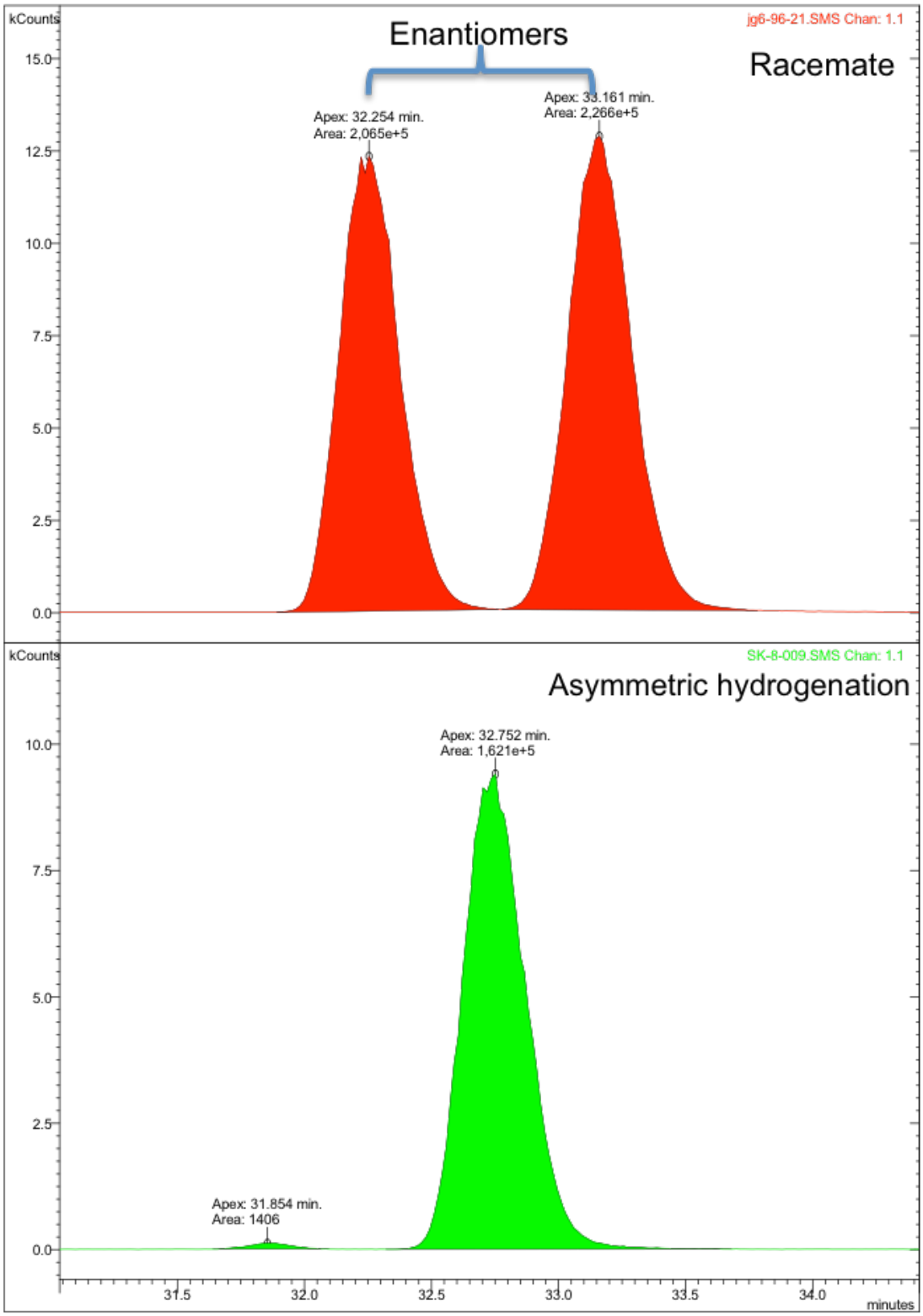

TBDMS
O

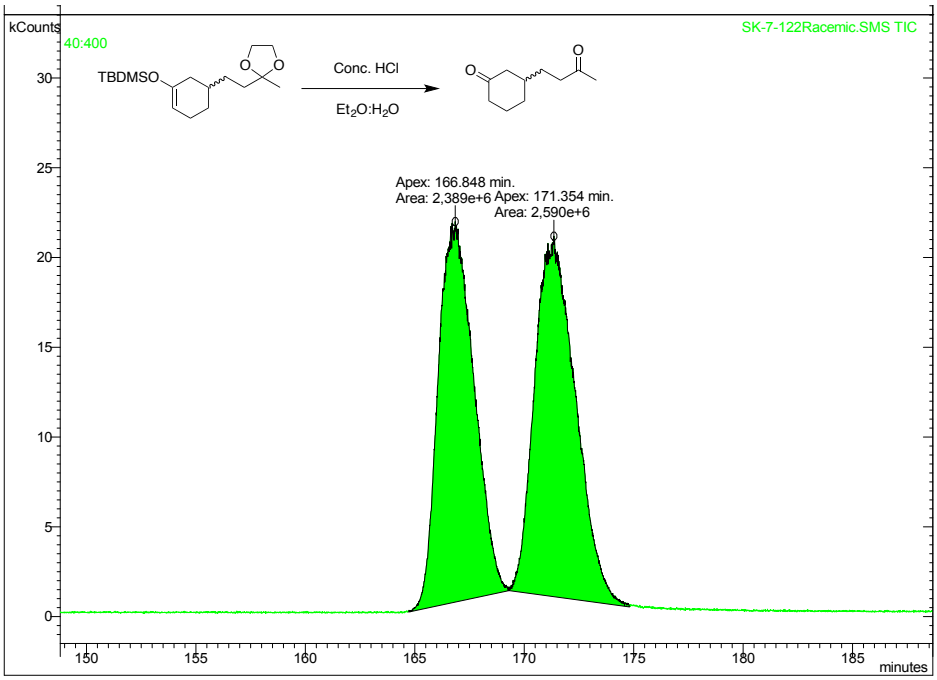
13a'

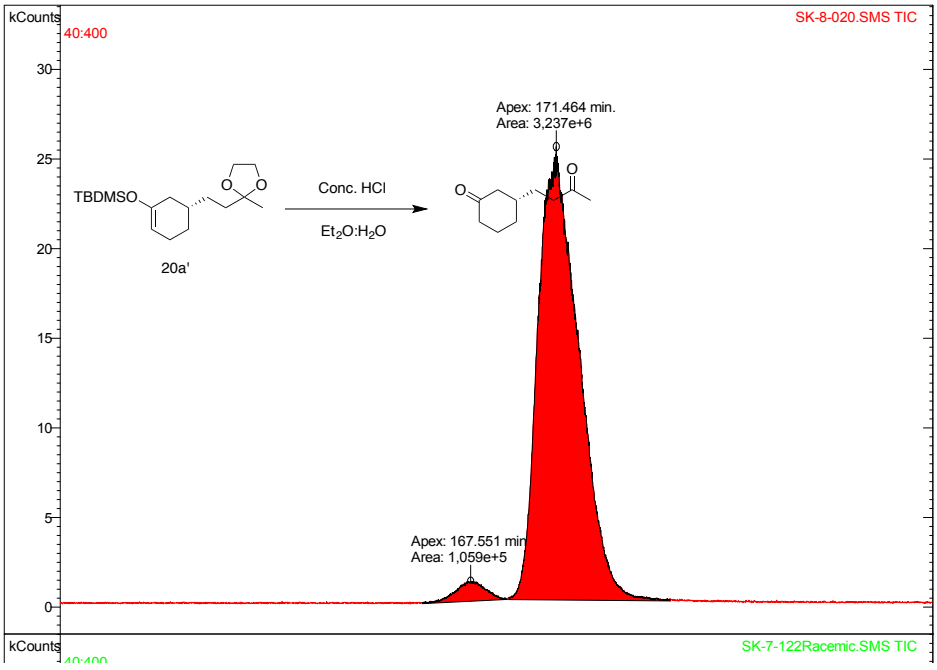

kCounts
jg6-96-39-80bdm.SMS Chan: 1.1
Enantiomers
Racemate
Apex: 46.828 min.
Area: 2,226e+5
Apex: 48.309 min.
Area: 2,366e+5
kCounts
Chan: 1.2
SK-8-014.SMS Chan: 1.2
Asymmetric hydrogenation
Apex: 48.203 min.
Area: 3,517e+5
Apex: 46.964 min.
Area: 2,565e+4
minutes

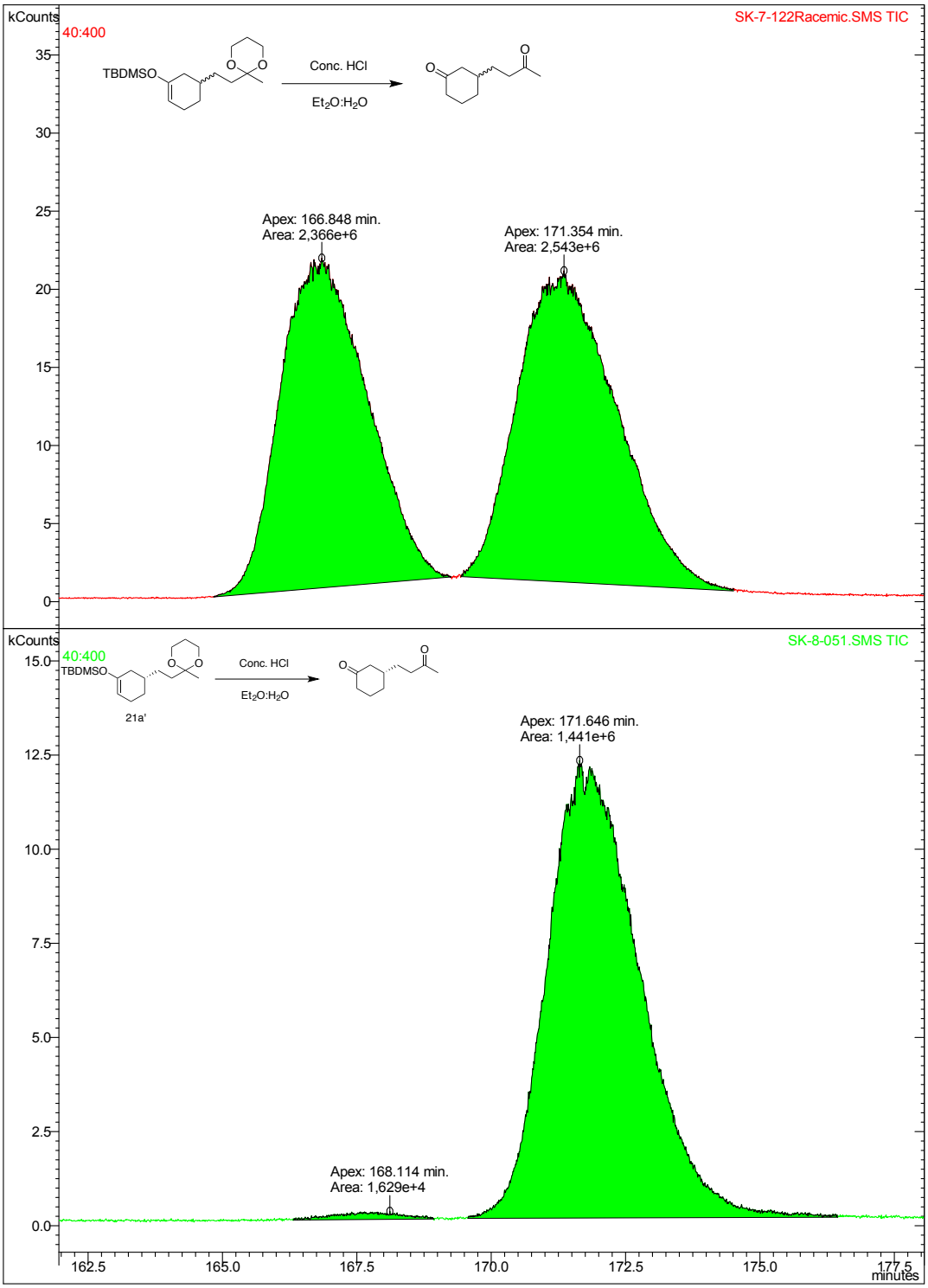

TES
O

17a'


kCounts
Enantiomers
jg6-96-21.SMS Chan: 1.1
Racemate
Apex: 32.254 min.
Area: 2,065e+5
Apex: 33.161 min.
Area: 2,266e+5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
kCounts
SK-8-009.SMS Chan: 1.1
Asymmetric hydrogenation
Apex: 32.752 min.
Area: 1,621e+5
Apex: 31.854 min.
Area: 1406
10.0
7.5
5.0
2.5
0.0
31.5
32.0
32.5
33.0
33.5
34.0
minutes


kCounts
40:400
SK-7-122Racemic.SMS TIC
TBDMSO
Conc. HCl
Et2O:H2O
Apex: 166.848 min.
Area: 2,389e+6
Apex: 171.354 min.
Area: 2,590e+6
30
25
20
15
10
5
0
150
155
160
165
170
175
180
185
minutes


kCounts
40:400
SK-8-020.SMS TIC
Apex: 171.464 min.
Area: 3,237e+6
TBDMSO
Conc. HCl
Et2O:H2O
20a'
Apex: 167.551 min
Area: 1,059e+5
30
25
20
15
10
5
0
kCounts
SK-7-122Racemic.SMS TIC


kCounts
40:400
SK-7-122Racemic.SMS TIC
TBDMSO
Conc. HCl
Et2O:H2O
Apex: 166.848 min.
Area: 2,366e+6
Apex: 171.354 min.
Area: 2,543e+6
kCounts
40:400
SK-8-051.SMS TIC
TBDMSO
21a'
Conc. HCl
Et2O:H2O
Apex: 171.646 min.
Area: 1,441e+6
Apex: 168.114 min.
Area: 1,629e+4
minutes

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