Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information for Platinum Catalysed Hydrosilylation of Propargylic Alcohols

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Compounds **2a-2g, 2o, 4a-4d, 4e, 4j-4k** and **4v** were fully characterised and reported previously.[1]

Contents

General Methods

All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualised with ultraviolet light and then developed with iodine and basic potassium permanganate solution. Flash chromatography was performed on Sigma-Aldrich silica gel 60 as the stationary phase and the solvents employed were of analytical grade. 1H NMR spectra were recorded on a Bruker AVX400 (400 MHz) spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from deuterated chloroform (CDCl3) taken as 7.26 ppm, integration, multiplicity (s = singlet; d = doublet; t = triplet; dd = double doublets m = multiplet), and coupling constant (Hz). 13C NMR spectra were recorded on either a Bruker AVX400 (100 MHz) spectrometer. Chemical shifts are reported in ppm from CDCl3 taken as 77.0 ppm. Infrared spectra were recorded on a Perkin Elmer RX I FT-IR spectrometer as liquid films or as dilute solutions between two KBr discs. Mass spectra were recorded on either a Micromass GCT Premier or a Waters Micromass LCT Premier spectrometer using electron ionisation (EI) at 70 eV or electrospray (ES) techniques, respectively. Unless stated otherwise, all commercially available reagents were used as received.

General Procedure A: Preparation of Propargyl Alcohols

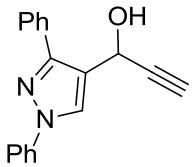
To an oven dried 10 mL round bottom flask equipped with a magnetic stirrer, and placed under argon, in an ice bath at 0 ^{o}C, was added Ethynyl Magnesium Bromide solution (0.5 M in THF) (1.1 equiv). In a separate flask, a solution of the aldehyde/ ketone in THF (3ml) was prepared. This was then added in a dropwise fashion to the stirring solution of the Grignard reagent. The reaction was left for one hour at 0 ^{o}C, or until it was complete by TLC. The reaction was quenched with NH_4Cl (3 mL), extracted with Et_2O (3 x 5mL) and the combined organic layers were washed with Brine (5 mL). The solvent was evaporated at reduced pressure, and the crude mixture was applied to the top of a column and chromatographed to afford the requisite propargyl alcohol.

General Procedure B: Preparation of Propargyl Alcohols

To an oven dried 10 mL round bottom flask equipped with a magnetic stirrer, and placed under argon, was added dry THF (2 mL) and TMS acetylene (1.5 equiv). The temperature was lowered to -78 ^{o}C. *n*-Butyl lithium (2.5 M solution in THF) (1.6 equiv.) was carefully added to the reaction flask. After 15 minutes at this temperature, a solution of the aldehyde / ketone (1 equiv.) in THF (2 mL) was added. The solution was stirred at to -78 ^{o}C for one hour, then allowed to warm to room temperature, where it was stirred for a further two hours. When the reaction was shown to be complete by TLC, the reaction was quenched with NH_4Cl (3 mL), extracted with Et_2O (3 x 5mL) and the combined organic layers were washed with Brine (5 mL). The solvent was evaporated at reduced pressure.

The crude mixture was transferred to an oven dried 10 mL round bottom flask, and dry THF (4mL) was added. The temperature was lowered to 0 ^{o}C, followed by addition of a 1 M solution of TBAF in THF (1.2 equiv.). When the reaction was shown to be complete by TLC, the reaction was quenched with NH_4Cl (3 mL), extracted with Et_2O (3 x 5mL) and the combined organic layers were washed with Brine (5 mL). The solvent was evaporated at reduced pressureand the crude mixture was applied to the top of a column and chromatographed to afford the requisite propargyl alcohol

1-(1,3-diphenyl-1H-pyrazol-4-yl)prop-2-yn-1-ol (1q)

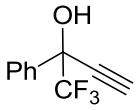


The title compound was prepared according to general procedure A, from 1 3-diphenyl-1H-pyrazole-4-carbaldehyde (300 mg, 1.21 mmol), using 0.5 M Ethynyl Magnesium Bromide solution in THF (2.54 ml, 0.5 M, 1.27 mmol) in THF (3 mL), which following the

conversion to the propargyl alcohol, extraction and column chromatography (3:1 Hexane/EtOAc) afforded **1q** (303 mg, 93 %) as a colourless oil.

Rf (3:1 hexane – ethyl acetate) = 0.29; IR: ν_{max} (thin film) / cm^{-1} 3290, 1639, 1517, 1503, 1486, 1247, 828, 756; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.21 (1H, s), 7.89 – 7.86 (2H, m), 7.77 - 7.74 (2H, m), 7.49- 7.43 (4H, m), 7.41- 7.36 (1H, m), 7.31- 7.28 (1H, m), 5.56 (1H, broad s), 2.63 (1H, d, J = 2.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 139.8, 132.4, 129.4, 128.7, 128.4, 127.8, 126.7, 121.4, 119.3, 83.6, 73.5, 56.3, 30.9; HRMS (ES) Calcd. for $C_{18}H_{14}N_2NaO$ $[M+Na^+]^+$ 297.1004. Found 297.1069

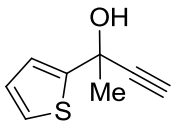
1,1,1-trifluoro-2-phenylbut-3-yn-2-ol (3g)



The title compound was prepared according to general procedure A, from 2,2,2-triflouroacetophenone (273 mg, 1.57 mmol), using 0.5 M Ethynyl Magnesium Bromide solution in THF (3.30 ml, 0.5 M, 1.65 mmol) in THF (3 mL), which following the conversion to the propargyl alcohol, extraction and column chromatography (9:1 Hexane/EtOAc) afforded **3g** (283 mg, 89 %) as a yellow oil.

Rf 9:1 hexane – ethyl acetate) = 0.39; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.75 (2H, m), 7.45-7.39 (3H, m), 2.82 (1H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 129.7, 128.3, 127.0 (t, $^{2}J_{C\text{-}F}$ = 223 Hz), 124.5, 79.5, 60.4, 21.0, 14.2

2-(thiophen-3-yl)but-3-yn-2-ol (3h)

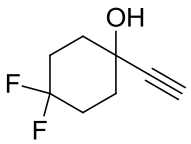


The title compound was prepared according to general procedure B, from 2-Acetylthiophene (252 mg, 2.00 mmol) and TMS acetylene (294 mg, 3.00 mmol), using 2.5 M *n*-butyl lithium solution in THF (1.28 ml, 3.20 mmol) in THF (3 mL), and TBAF (2.40 mL, 2.40mmol), which following the conversion to the propargyl alcohol, extraction

and column chromatography (19:1 Hexane/EtOAc) afforded **3h** (169 mg, 56%) as a yellow oil.

Rf (9:1 hexane – ethyl acetate) = 0.30; IR: ν_{max} (thin film) / cm^{-1} 3288, 2955, 2924, 2853, 1651, 1458, 1413, 1366, 1277, 1235, 1133, 1072, 925, 861, 834, 750, 688, 667; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.32 (2H, dd, J = 9.3, 3.7 Hz), 6.96 (1H, t J = 4.02 Hz), 2.69 (1H, s), 1.92 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6, 125.2, 124.1, 86.4, 72.5, 33.0, 29.7, 14.1; HRMS (ES) Calcd. for $C_8H_{10}O_2S$ $[M+H_2O]^+$ 170.0402. Found 170.0266

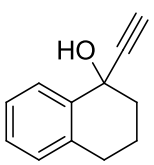
1-ethynyl-4,4-difluorocyclohexanol (3o)



The title compound was prepared according to general procedure B, from 4,4-difluorocyclohexanone (220 mg, 1.64 mmol) and TMS acetylene (241 mg, 2.46 mmol), using 2.5 M *n*-butyl lithium solution in THF (1.05 ml, 2.63 mmol) in THF (3 mL), and TBAF (2ml, 2mmol), which following the conversion to the propargyl alcohol, extraction and column chromatography (9:1 Hexane/EtOAc) afforded **3o** (130 mg, 50 %) as a pink solid.

Rf (3:1 hexane – ethyl acetate) = 0.47; IR: ν_{max} (thin film) / cm^{-1} 3290, 1639, 1607, 1517, 1503, 1486, 1443, 1247, 828, 756, 655, 648; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.53 (1H, s), 2.17 – 1.96 (8H, m) ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 178.6, 133.2, 121.3 (d, $^{1}J_{C\text{-}F}$ = 241.6 Hz), 72.8, 35.8 (t, $^{2}J_{C\text{-}F}$ = 5.1 Hz), 30.3 (t, $^{2}J_{C\text{-}F}$ = 25.6 Hz), 25.0; HRMS (ES) Calcd. for $C_9H_{14}F_2O$ $[M+CH_3]^+$ 176.1013. Found 176.1630

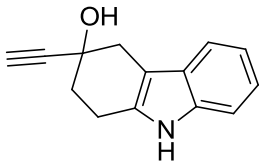
1-ethynyl-1,2,3,4-tetrahydronaphthalen-1-ol (3q)



The title compound was prepared according to general procedure B, from α–tetralone (244 mg, 1.67 mmol) and TMS acetylene (246 mg, 2.51 mmol), using 2.5 M *n*-butyl lithium solution in THF (1.07 mL, 2.67 mmol) in THF (3 mL). Following this potassium carbonate was used to remove the protecting group and following the conversion to the propargyl alcohol, extraction and column chromatography (19:1 Hexane/EtOAc) afforded **3q** (61 mg, 21 %) as an orange oil.

Rf (19:1 hexane – ethyl acetate) = 0.17; IR: ν_{max} (thin film) / cm^{-1} 3289, 2941, 2867, 1671, 1488, 1452, 1328, 1276, 1182, 1160, 1085, 1012, 964, 943; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.78 (1H, m), 7.27 – 7.19 (2H, m), 7.12 – 7.07 (1H, m), 2.84 – 2.78 (2H, dd, J = 11.8, 5.2 Hz), 2.59 (1H, s), 2.34 (1H, s, broad), 2.21 (2H, dd, J = 7.3, 4.1 Hz), 2.07 – 1.88 (2H, ddddd, J = 18.1, 12.3, 7.8, 6.0, 5.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 136.2, 129.1, 28.3, 127.7, 126.6, 88.2, 72.3, 67.8, 38.8, 39.2, 18.9 ; HRMS (ES) Calcd. for $C_{12}H_{11}O$ $[M\text{-}H^{+}]^{+}$ 171.0810 Found 171.1284

3-ethynyl-2,3,4,9-tetrahydro-1H-carbazol-3-ol (3r)

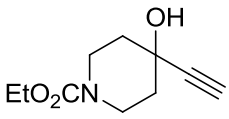


The title compound was prepared according to general procedure A, from4,9-dihydro -1H-carbazol-3 (2H)-one (100 mg, 0.474 mmol), using 0.5 M Ethynyl Magnesium Bromide solution in THF (0.995 mL, 0.5 M, 0.498 mmol) in THF (3 mL), which following the conversion to the propargyl alcohol, extraction and column chromatography (4:1 Hexane/EtOAc) afforded **3r** (60 mg, 53 %) as a brown solid.

Rf (1:1 hexane-ethyl acetate) = 0.31; IR: ν_{max} (thin film) / cm^{-1} 3402, 3284, 2340, 2275, 1704, 1667, 1604, 1468, 1329, m1052, 962, 748, 667; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.76 (1H, s), 7.47 – 7.42 (1H, d, J = 6.0,Hz), 7.15 – 7.14 (2H, ddd, J= 14.5, 7.0, 1.3 Hz), 2.95 (2H, d, J 15.6 Hz), 2.88 – 2.70 (2H, ddd, J = 14.4, 3.9, 1.9 Hz), 2.43 (1H, s), 2.04 – 1.87 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 127.5, 121.5, 119.4, 117.7,

110.6, 88.2, 71.3, 70.3, 67.4, 36.5, 36.0, 25.2, 20.9; HRMS (ES) Calcd. for $C_{14}H_{14}NO$ $[M+H^+]^+$ 212.1075. Found 212.1066

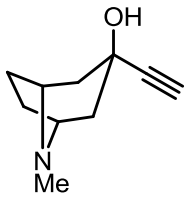
Ethyl 4-ethynyl-4-hydroxypiperidine-1-carboxylate (3t)



The title compound was prepared according to general procedure B, from Ethyl 4-oxo-1-piperidinecarboxylate (513 mg, 3.00 mmol) and TMS acetylene (441 mg, 4.50 mmol), using 2.5 M *n*-butyl lithium solution in THF (1.92 ml, 4.80 mmol) in THF (3 mL), and TBAF (3.60 mL, 3.60 mmol), which following the conversion to the propargyl alcohol, extraction and column chromatography (9:1 Hexane/EtOAc) afforded **3t** (165 mg, 84 %) as a yellow oil.

Rf (9:1 hexane – ethyl acetate) = 0.32; IR: ν_{max} (thin film) / cm^{-1}3396, 3296, 2959, 2932, 2874, 2104, 1676, 1483, 1439, 1387, 1338, 1276, 1245, 1153, 1076, 1030, 973, 956, 769; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.13 (2H, q, *J* = 7.1 Hz), 3.86 – 3.75 (2H, br), 3.34 (2H, ddd, J = 9.3, 4.0, 3.5 Hz), 2.54 (1H, s), 1.95 – 1.87 (2H, br), 1.73 (2H, ddd, J = 13.1, 4.2, 3.8 Hz), 1.27 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.27, 86.1, 73.2, 66.5, 61.5, 43.1, 41.1, 38.8, 14.6; HRMS (ES) Calcd. for $C_{10}H_{16}NO_3$ $[M+H^+]^+$ 198.1136 Found 198.1130

3-ethynyl-8-methyl-8-azabicyclo[3.2.1]octan-3-ol (3u)

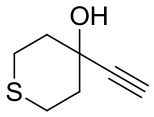


The title compound was prepared according to general procedure B, from Tropinone (201 mg, 1.45 mmol) and TMS acetylene (213 mg, 2.18 mmol), using 2.5 M *n*-butyl lithium solution in THF (0.928 ml, 2.32 mmol) in THF (3 mL), followed by deprotection

using Potassium Carbonate (43 mg, 2.16 mmol) in methanol (3mL), which, following conversion to the propargyl alcohol, extraction and concentration (used crude in next step), afforded **3u** (98 mg, 41 %) as an orange solid.

Rf (1:3 hexane – ethyl acetate) = 0.05; IR: ν_{max} (thin film) / cm^{-1} 3237, 3089, 2980, 2949, 2928, 2805, 1463, 1448, 1435, 1416, 1344, 1268, 1227, 1170, 1119, 1088, 1059, 953, 824, 785, 749; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 2.74 – 2.65 (1H, m), 2.59 – 2.50 (1H, m), 2.41 (1H, s), 2.20 (3H, d, J= 7.0 Hz), 2.24 – 2.18 (2H, ddd, J = 9.3, 3.7 Hz), 2.07 – 1.88 (6 H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 89.5, 74.7, 70.8, 70.0, 59.8, 26.5, 25.5; HRMS (ES) Calcd. for $C_{10}H_{16}NO$ $[M+H^+]^+$ 166.1218. Found 166.1232

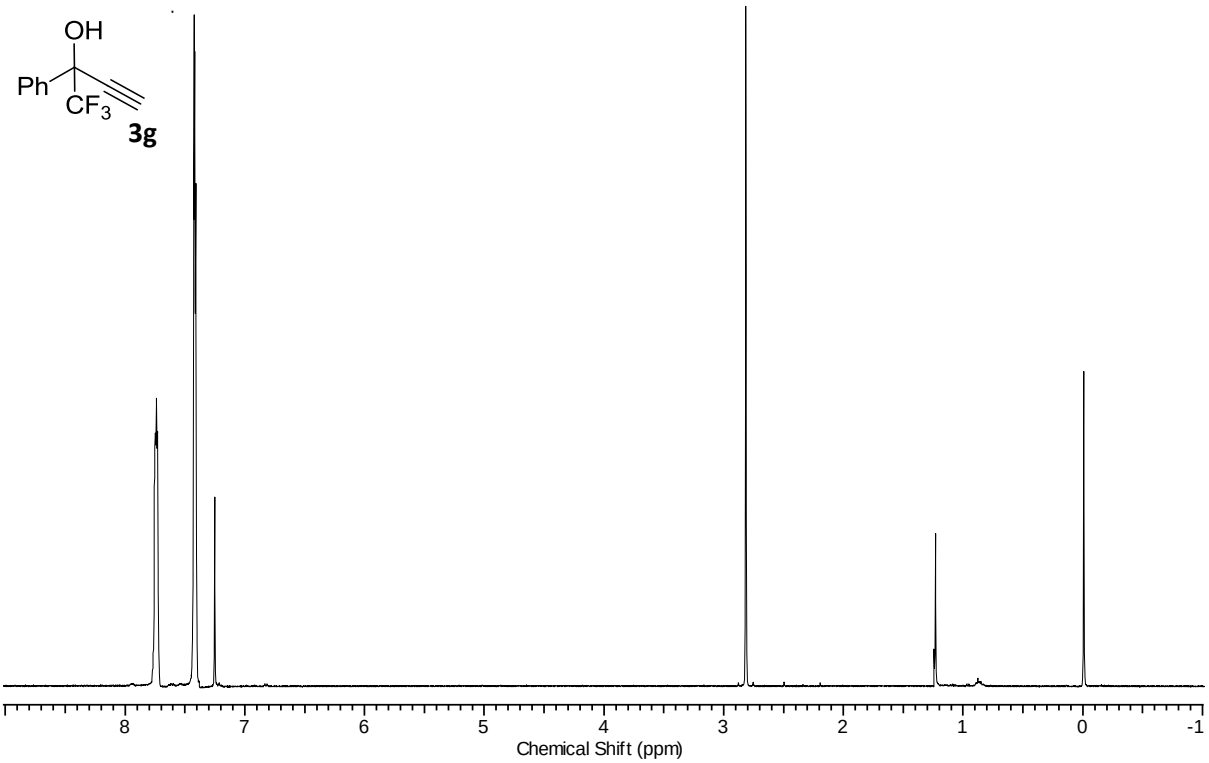
4-ethynyltetrahydro-2H-thiopyran-4-ol (3w)

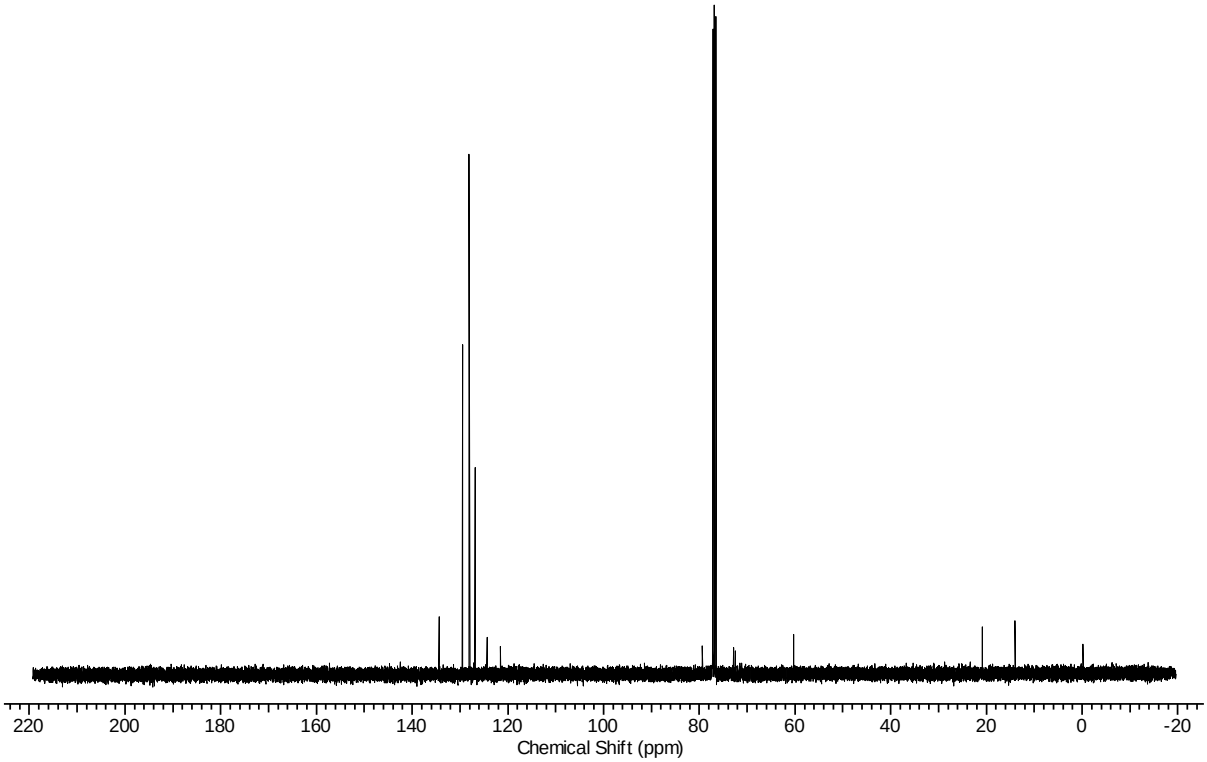


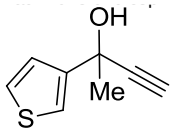
The title compound was prepared according to general procedure A, from Tetrahydro-4H-thiopyran-4-one (151 mg, 1.30 mmol), using 0.5 M Ethynyl Magnesium Bromide solution in THF (2.73 mL, 0.5 M, 1.37 mmol) in THF (3 mL), which following the conversion to the propargyl alcohol, extraction and column chromatography (9:1 Hexane/EtOAc) afforded **3w** (107 mg, 59 %) as a colourless solid.

Rf (9:1 hexane – ethyl acetate) = 0.2; IR: ν_{max} (thin film) / cm^{-1} 3284, 2961, 2867, 1469, 1338, 1301, 1233, 1159, 1133, 1094, 1010, 988, 838; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.91 (2H, ddd, J = 11.5, 4.5, 4.2 Hz), 3.67 (2H, ddd J= 11.8, 9.0, 2.8 Hz), 2.55 (1H, s), 2.29 (1H, s), 1.95 (2H, ddd, J = 13.3, 3.0, 2.0 Hz), 1.81 (2H, ddd, J = 12.8, 9.3, 3.8 Hz) ^{13}C NMR (75 MHz, $CDCl_3$) δ 87.7, 73.1, 65.6, 64.8, 39.3

Spectral Index







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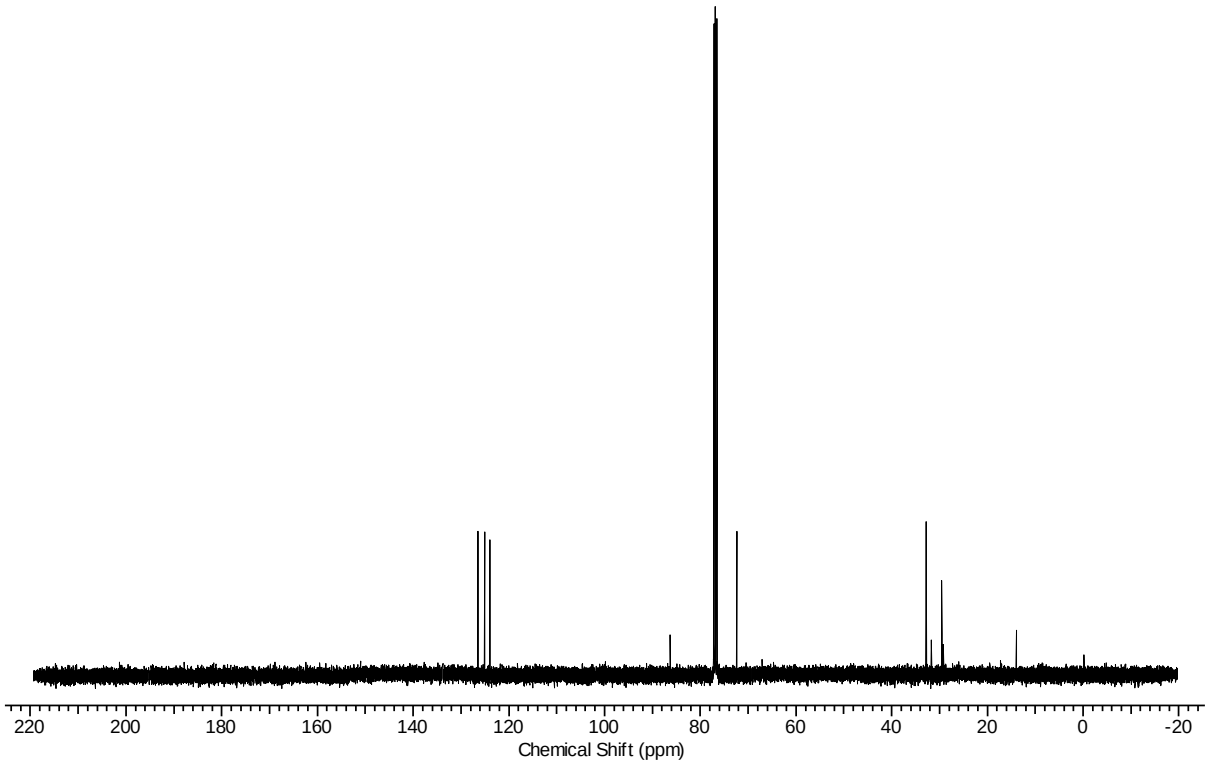

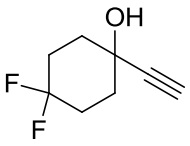

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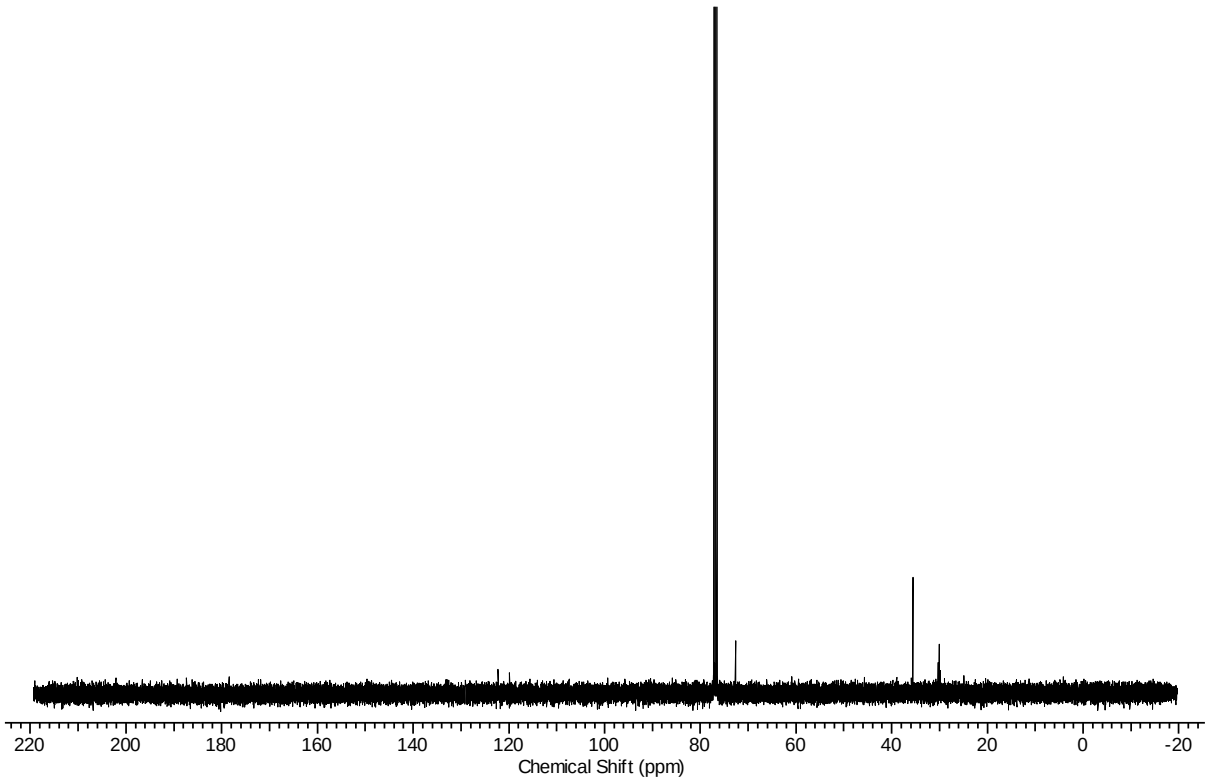
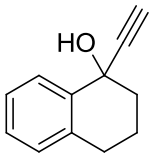
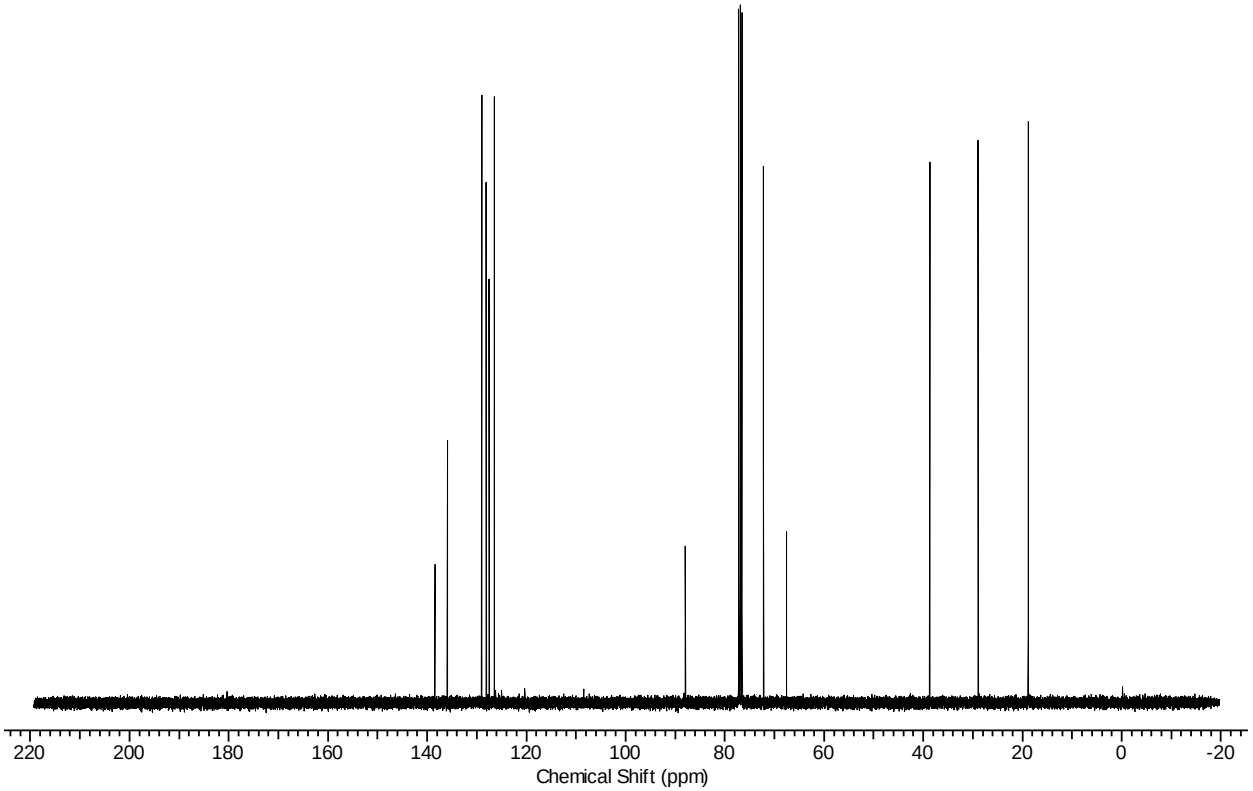
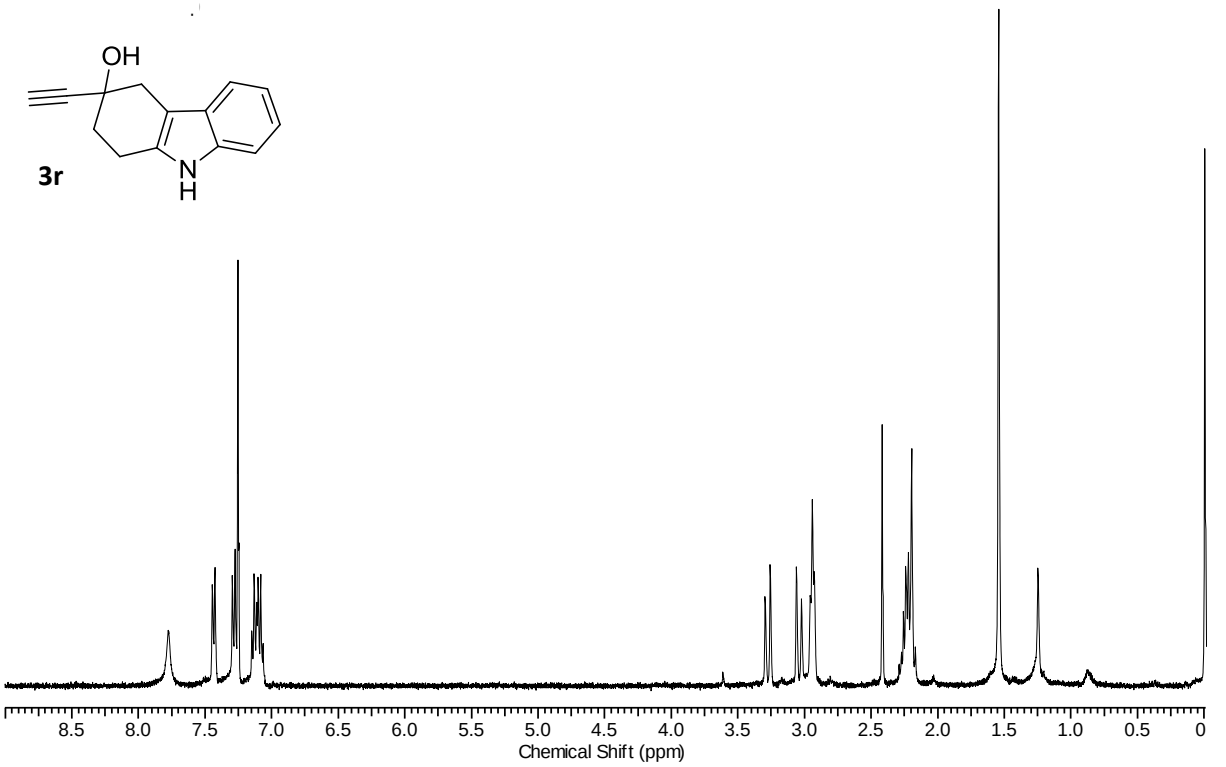
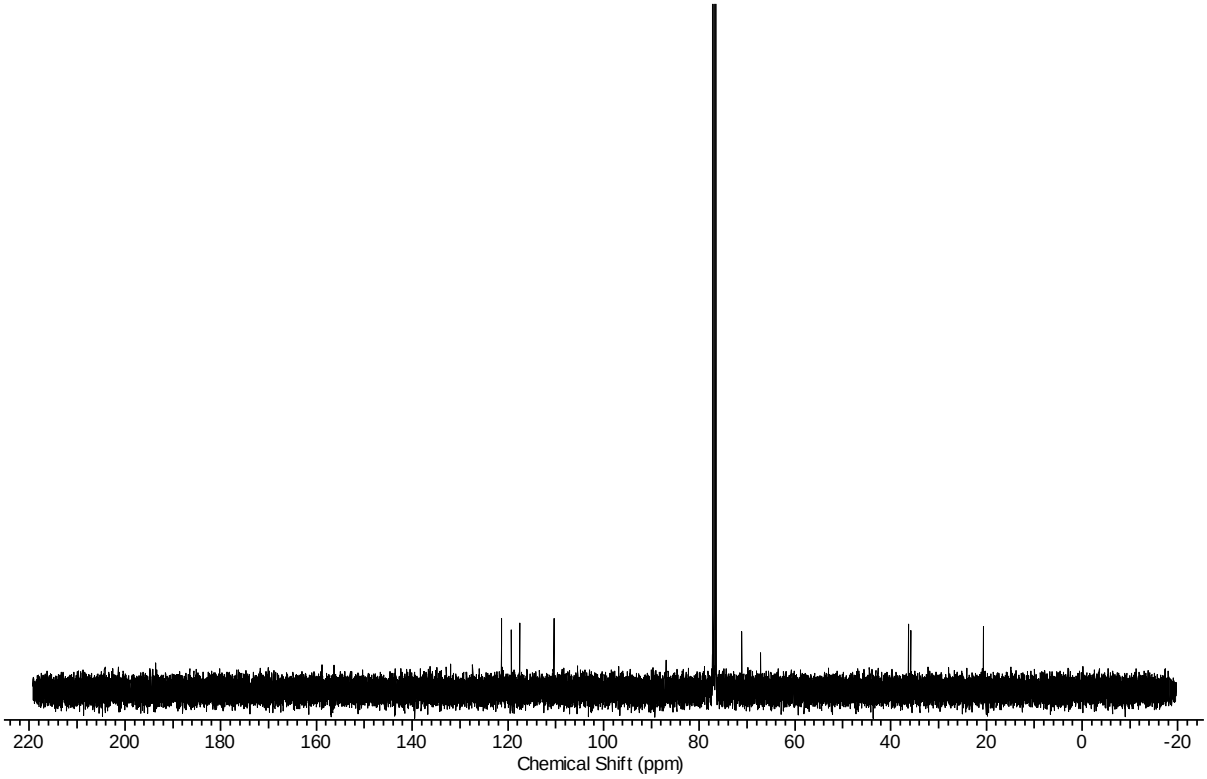


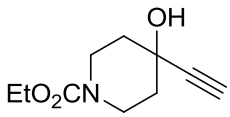


3q









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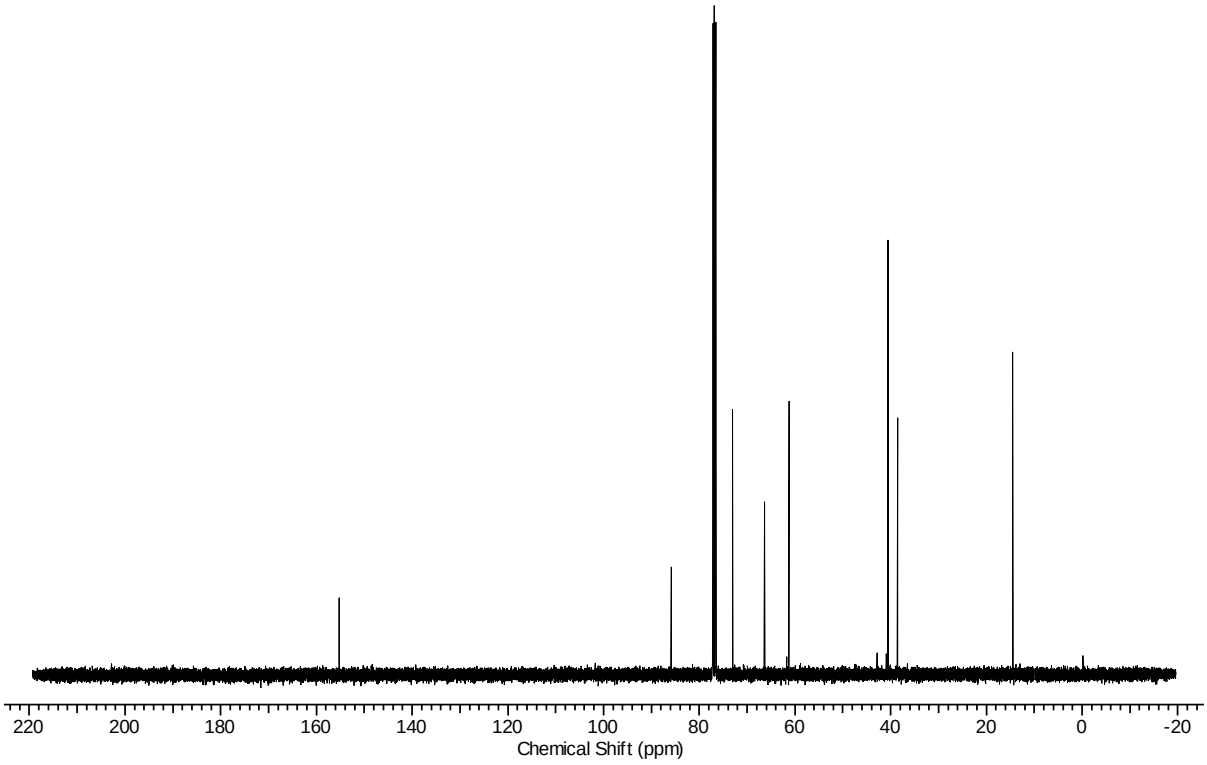
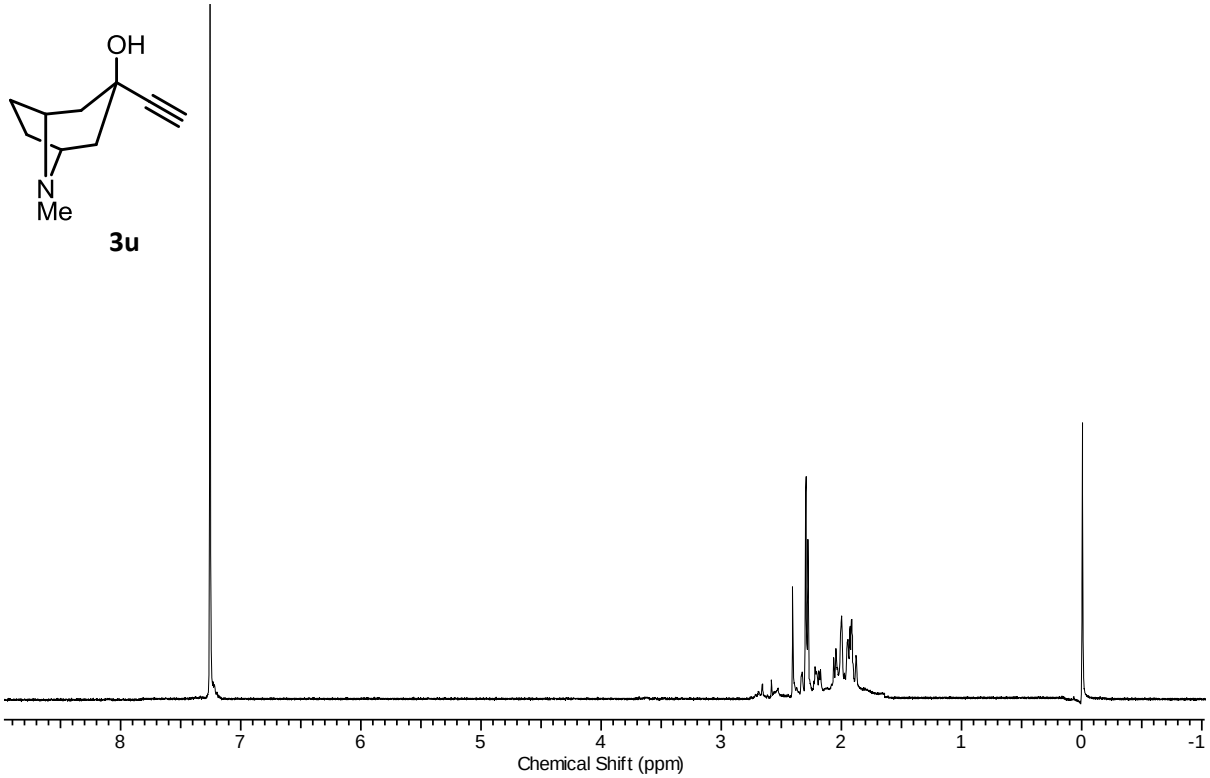
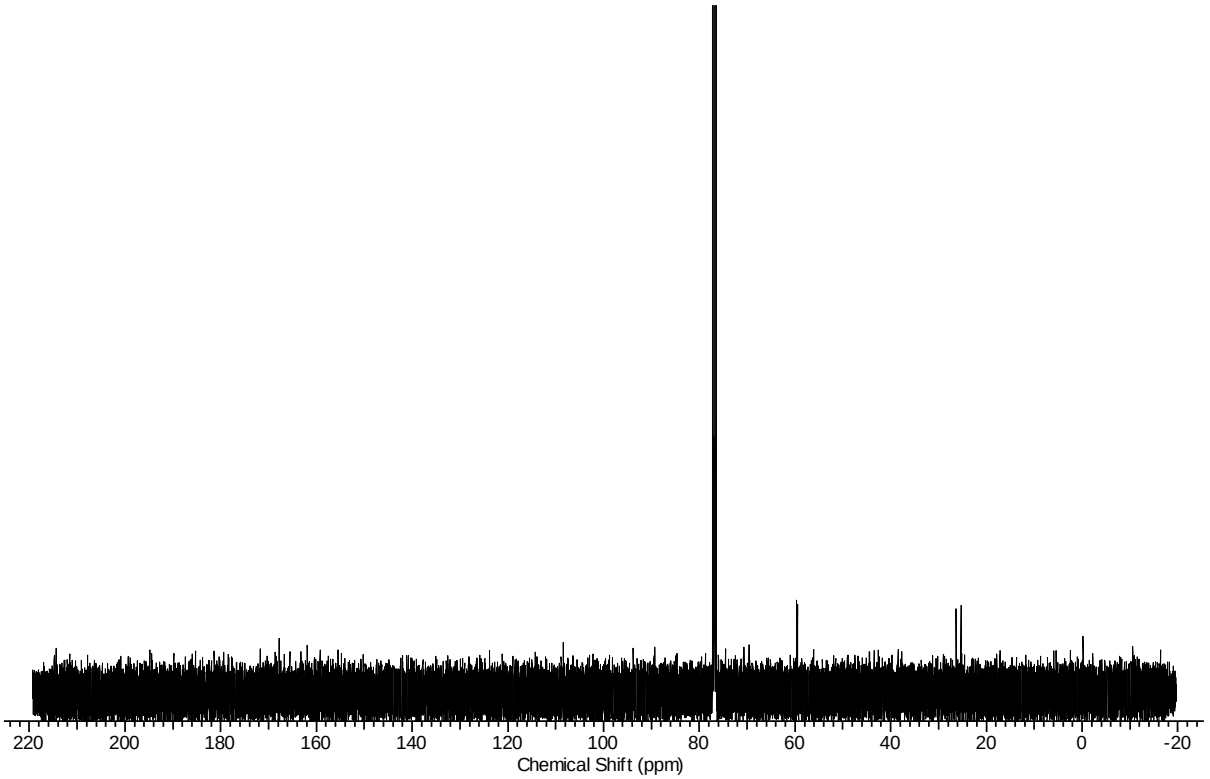
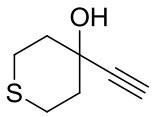
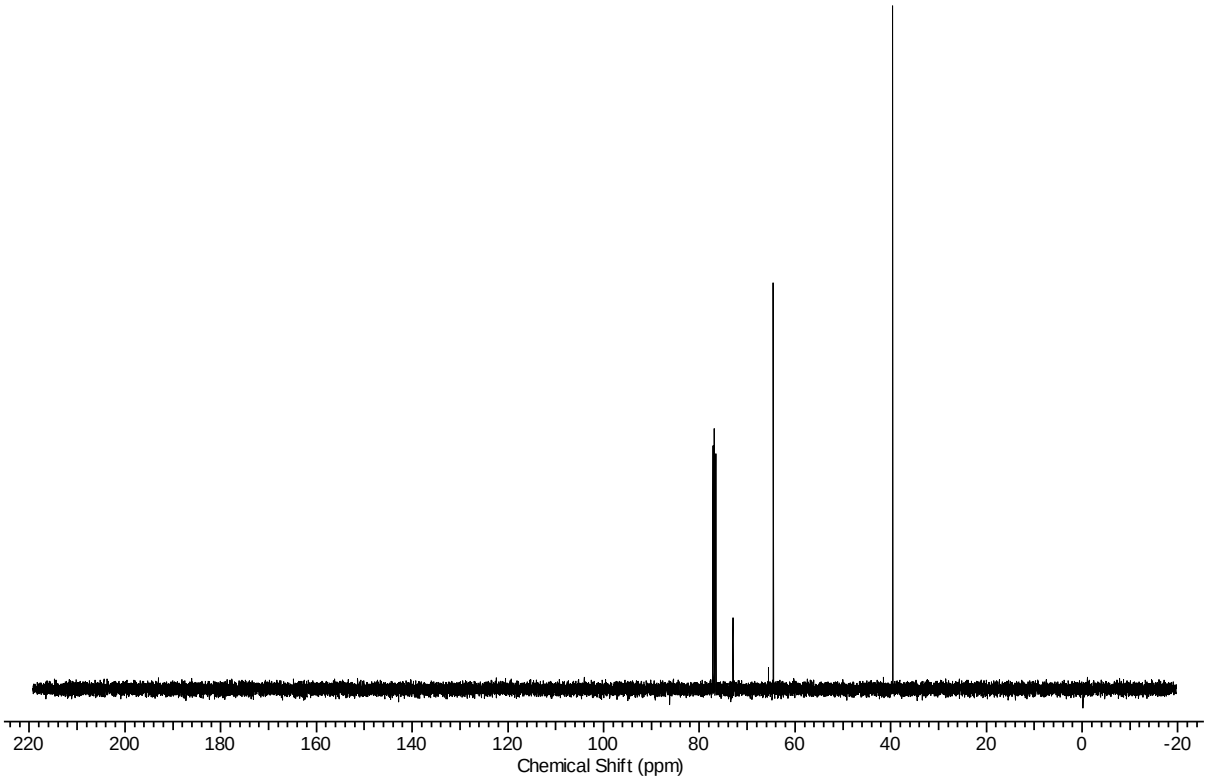


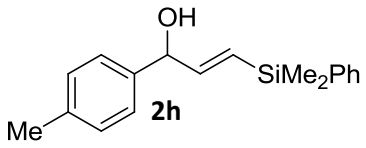






3w





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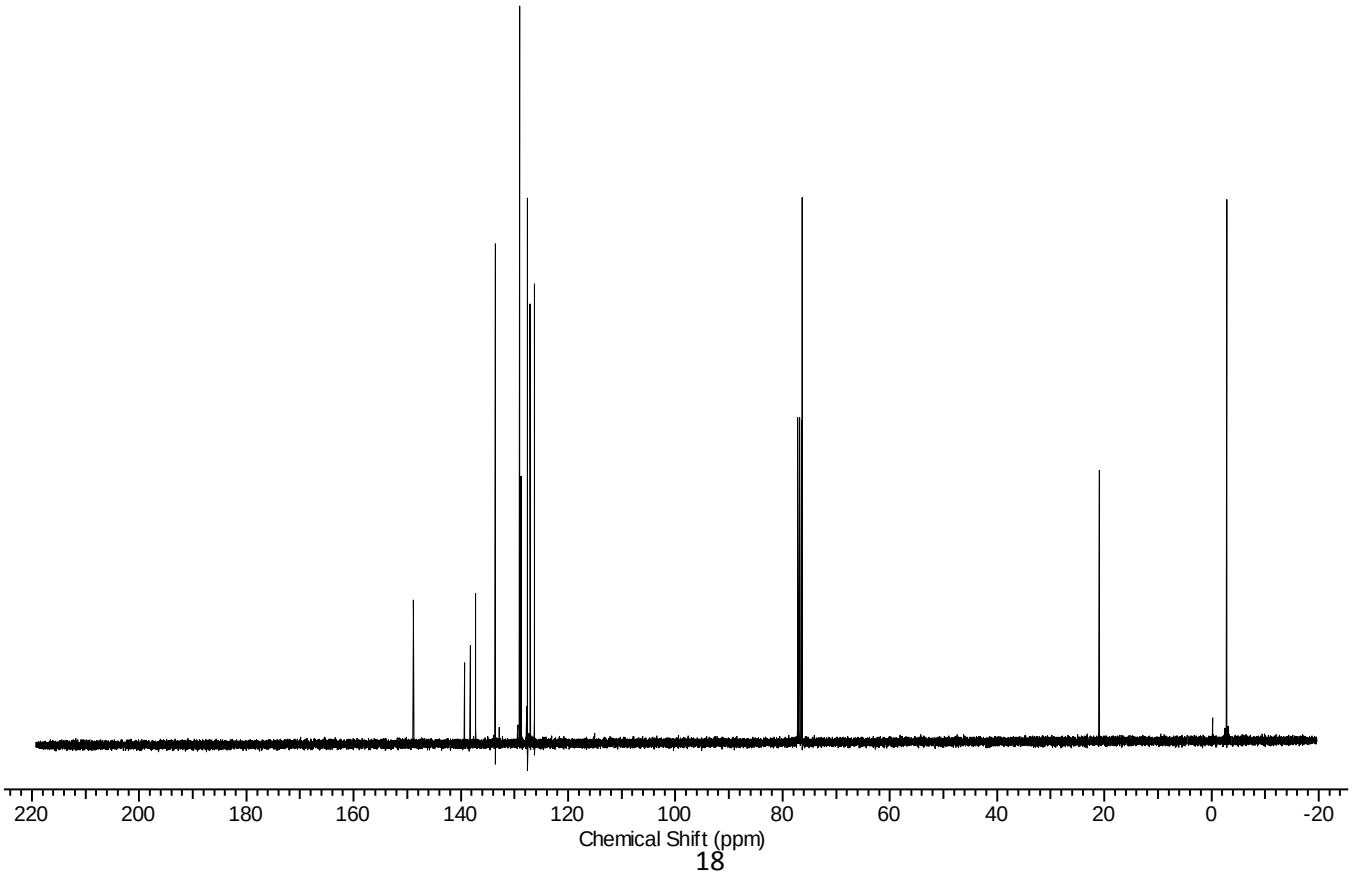

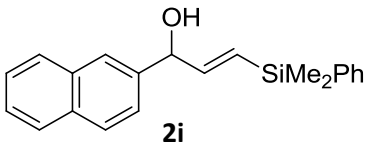

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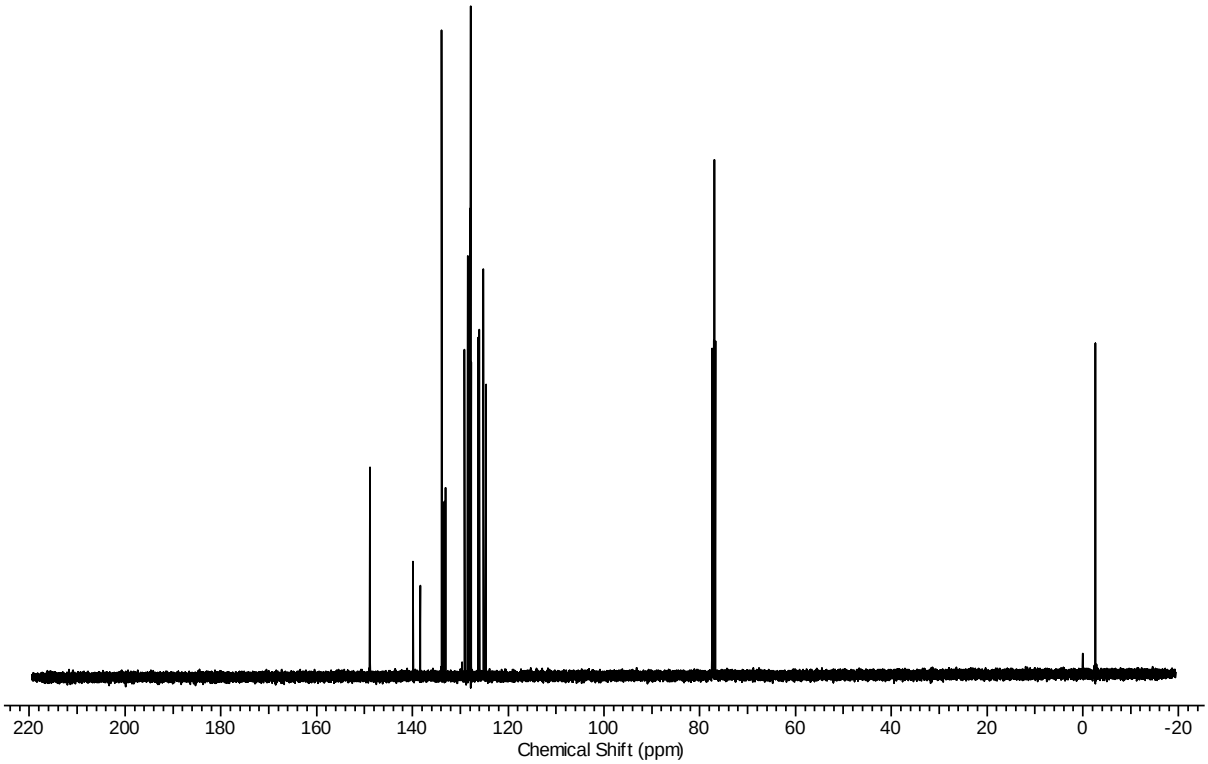

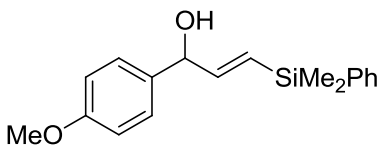

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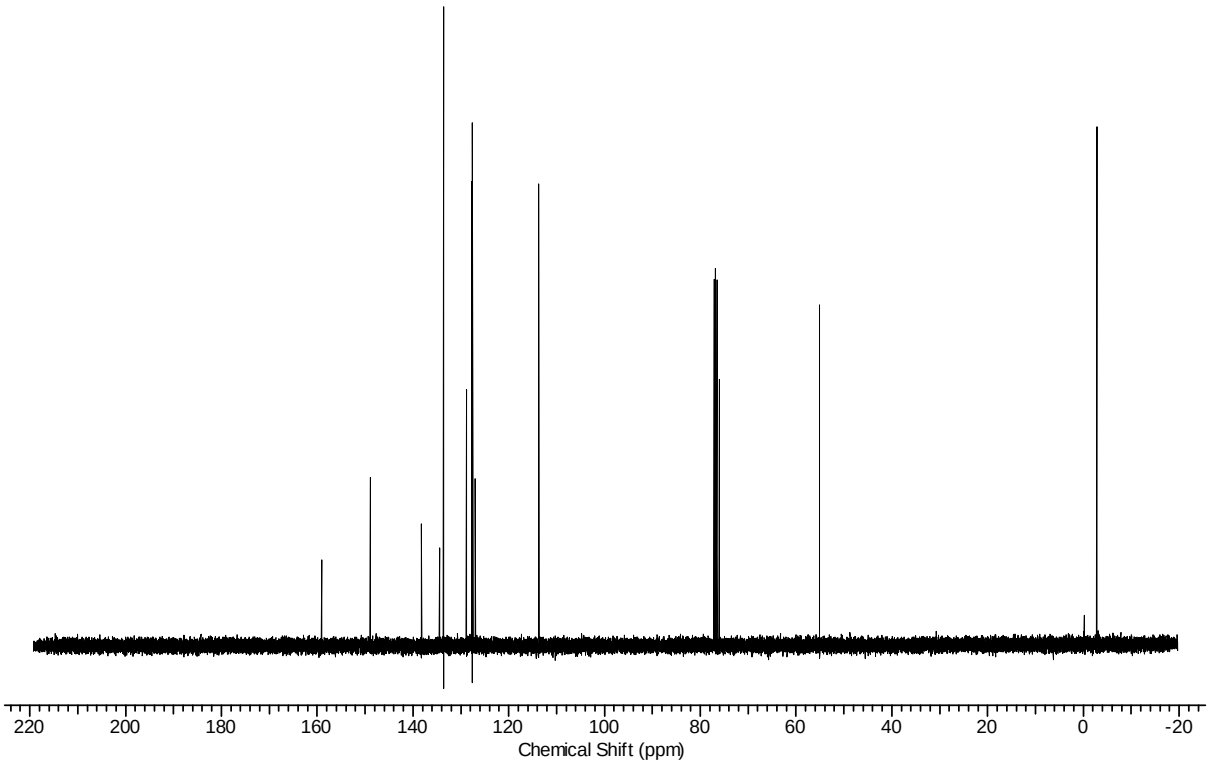

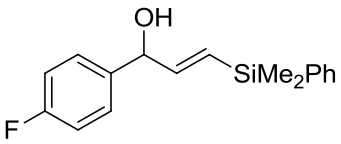

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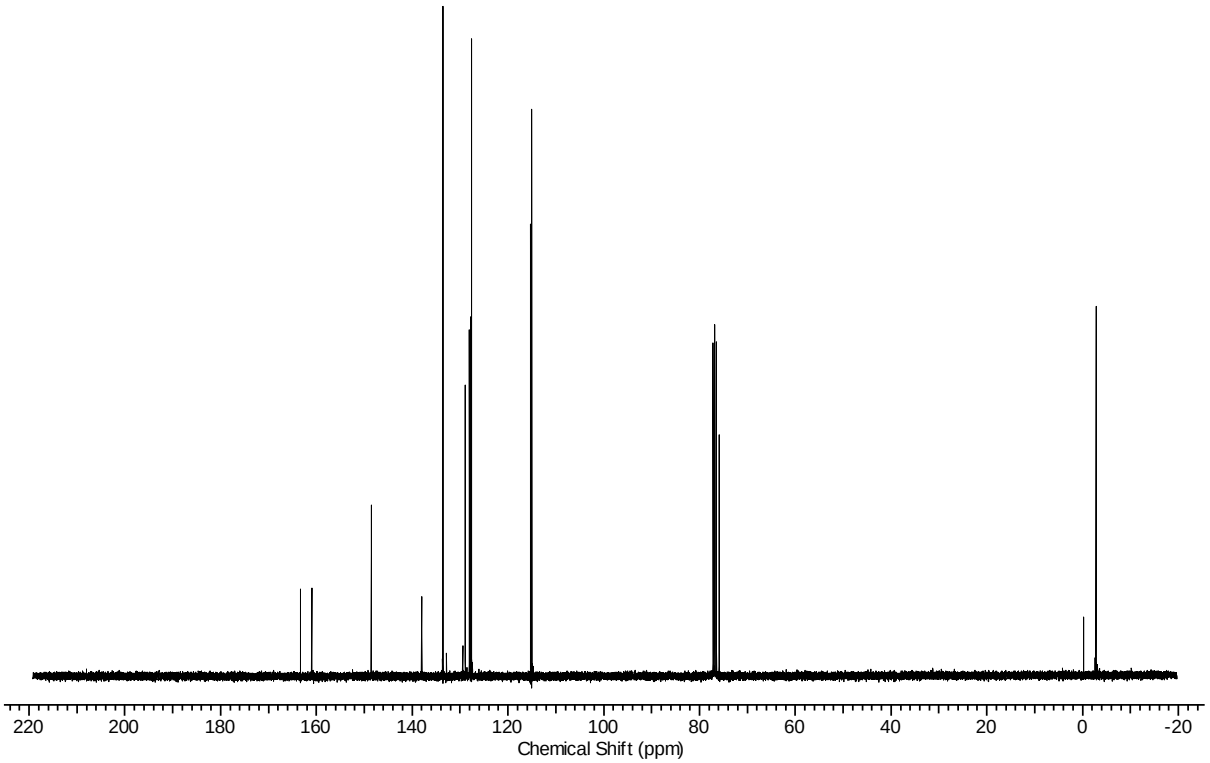

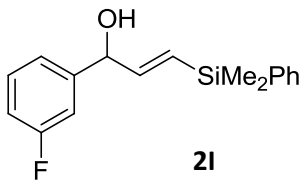

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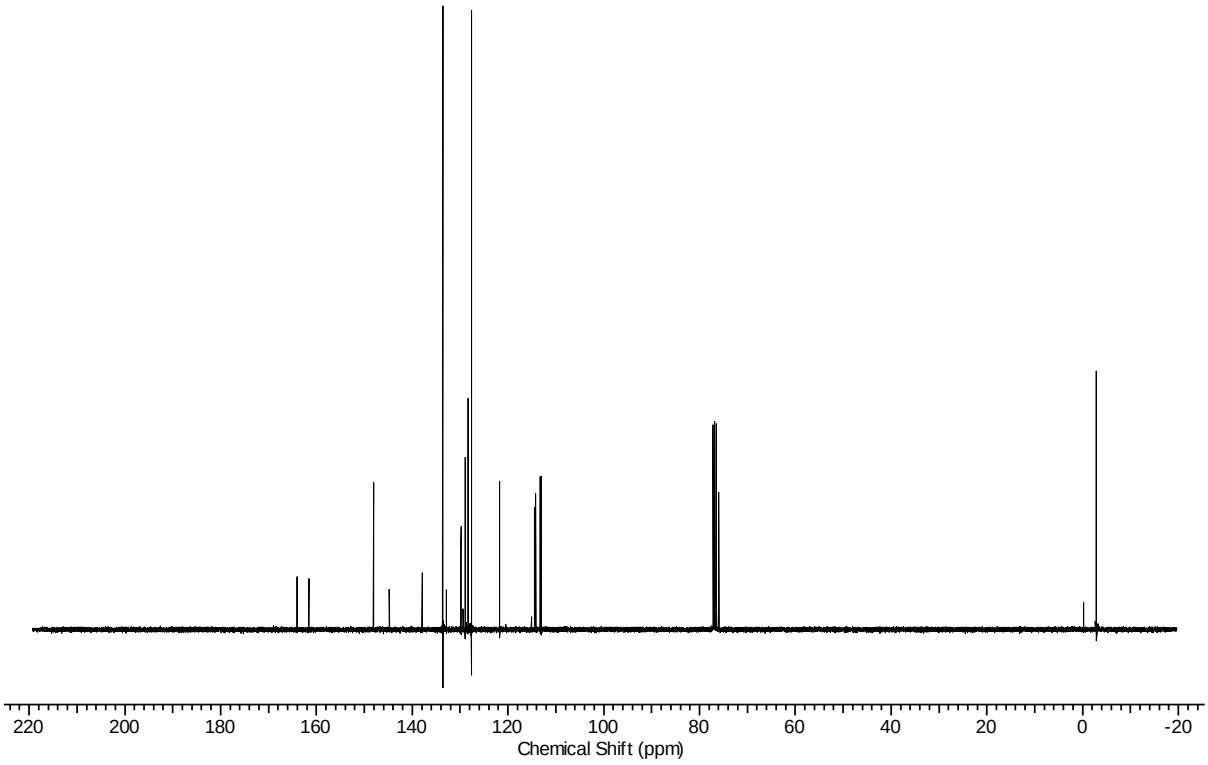

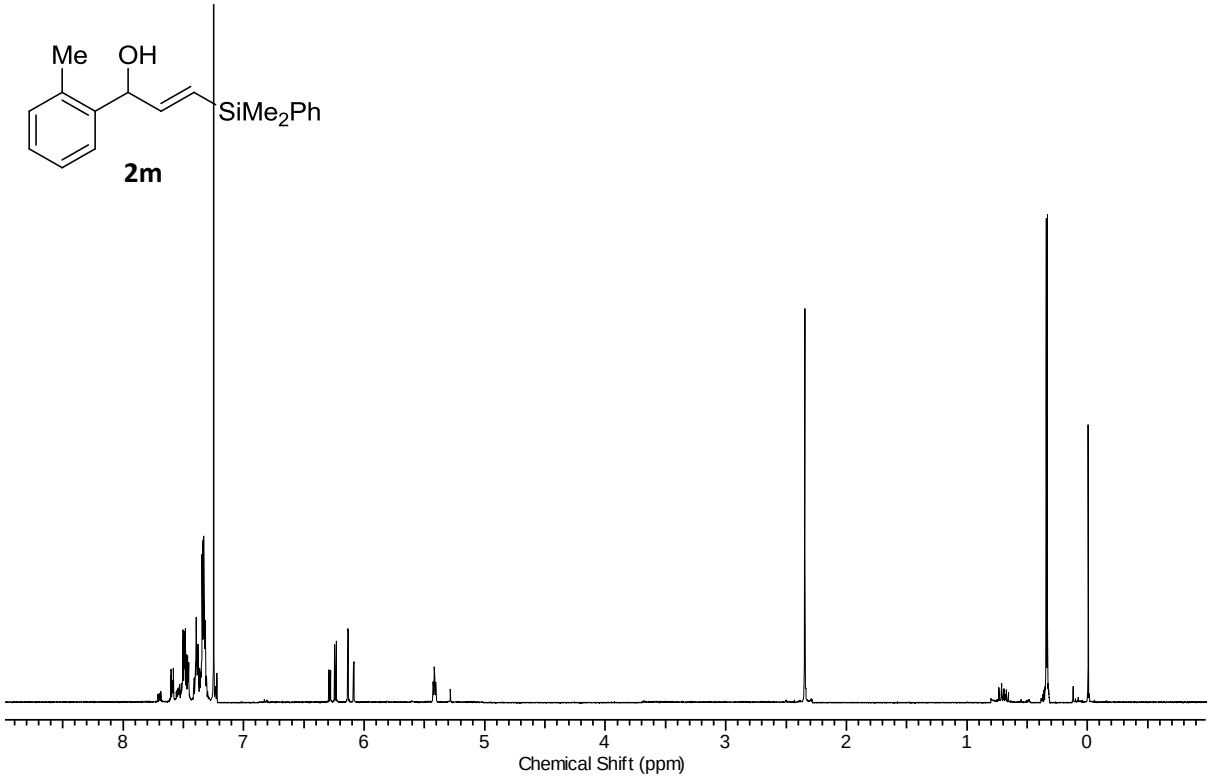

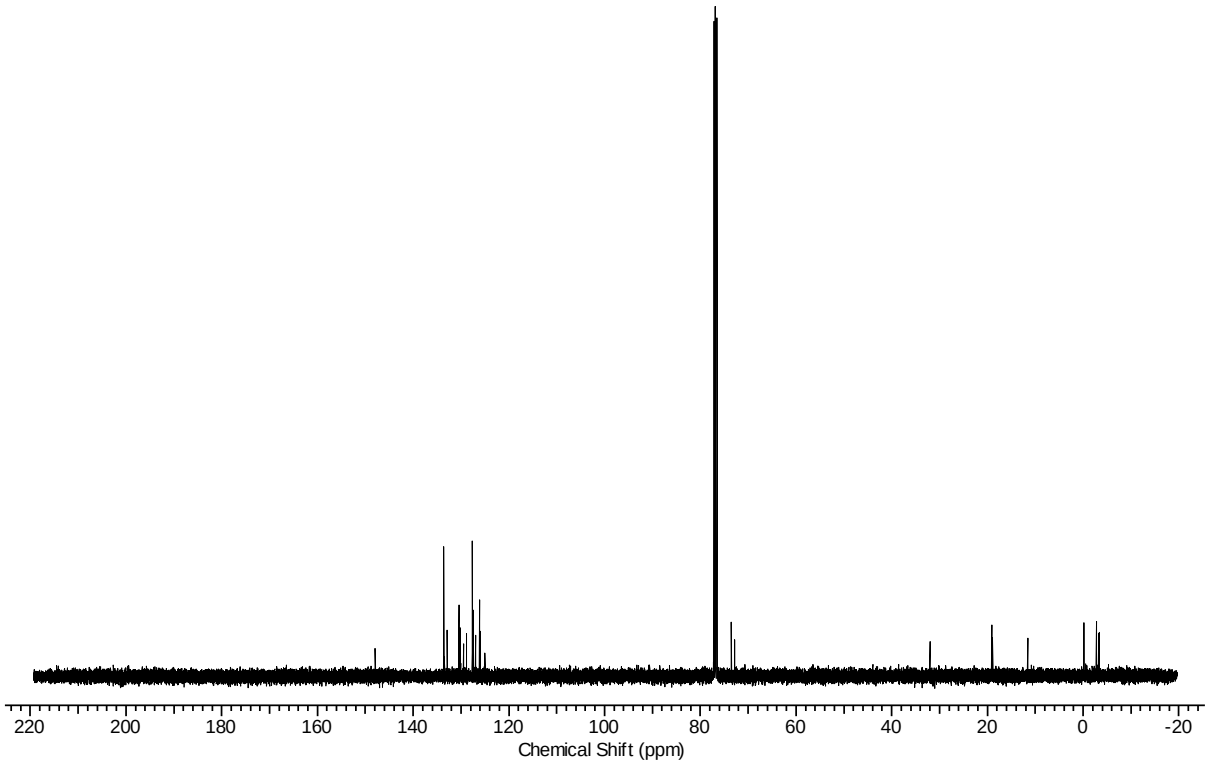

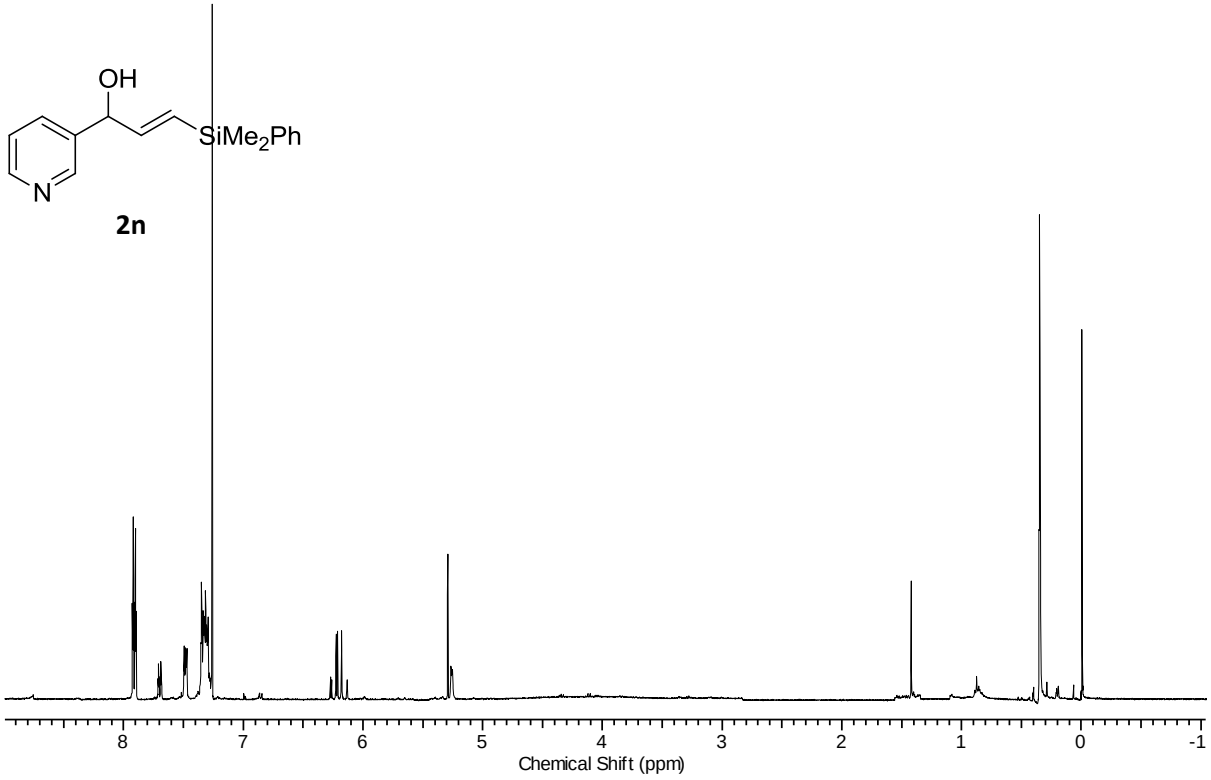

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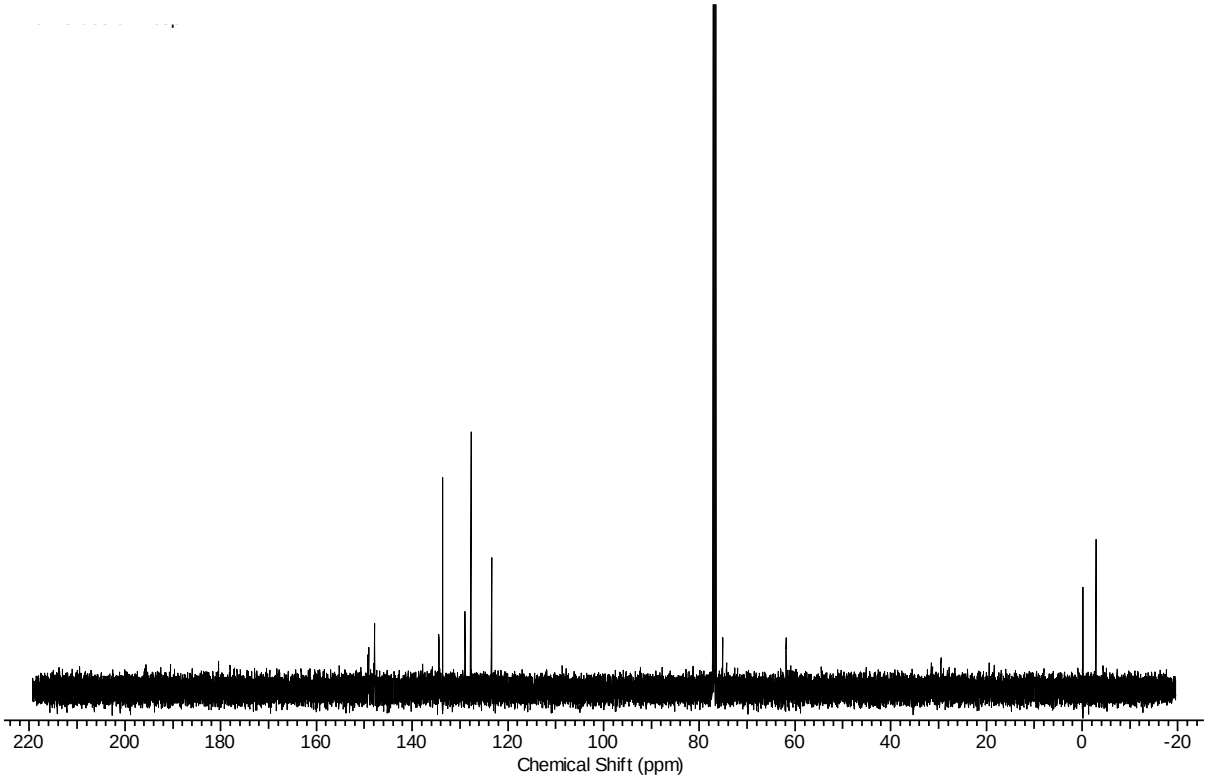

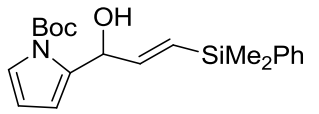

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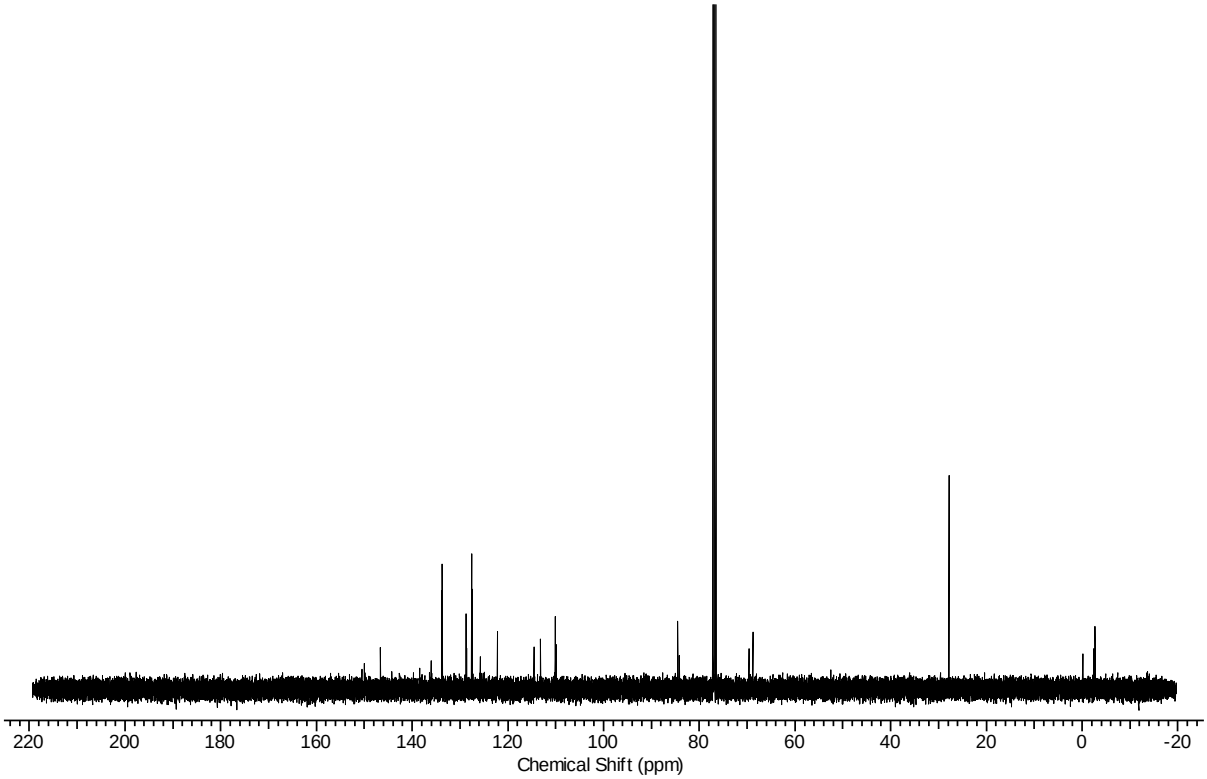

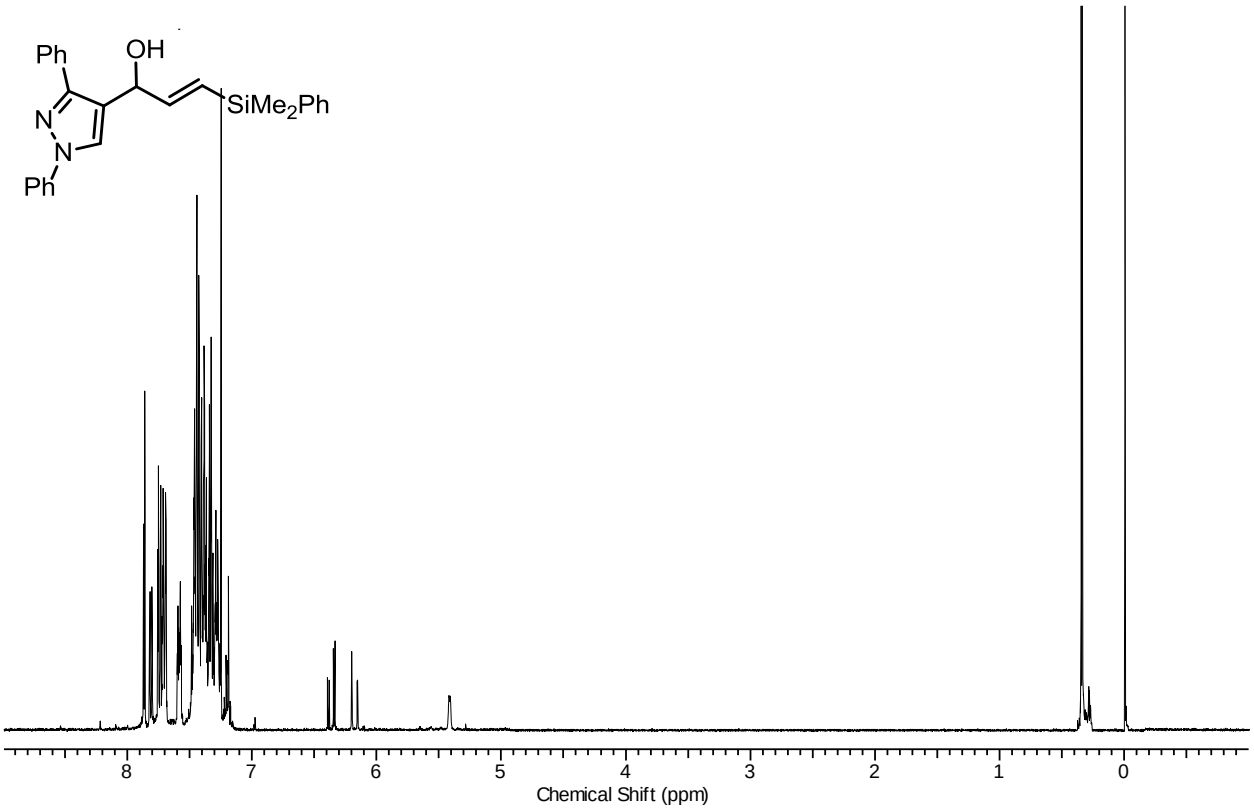

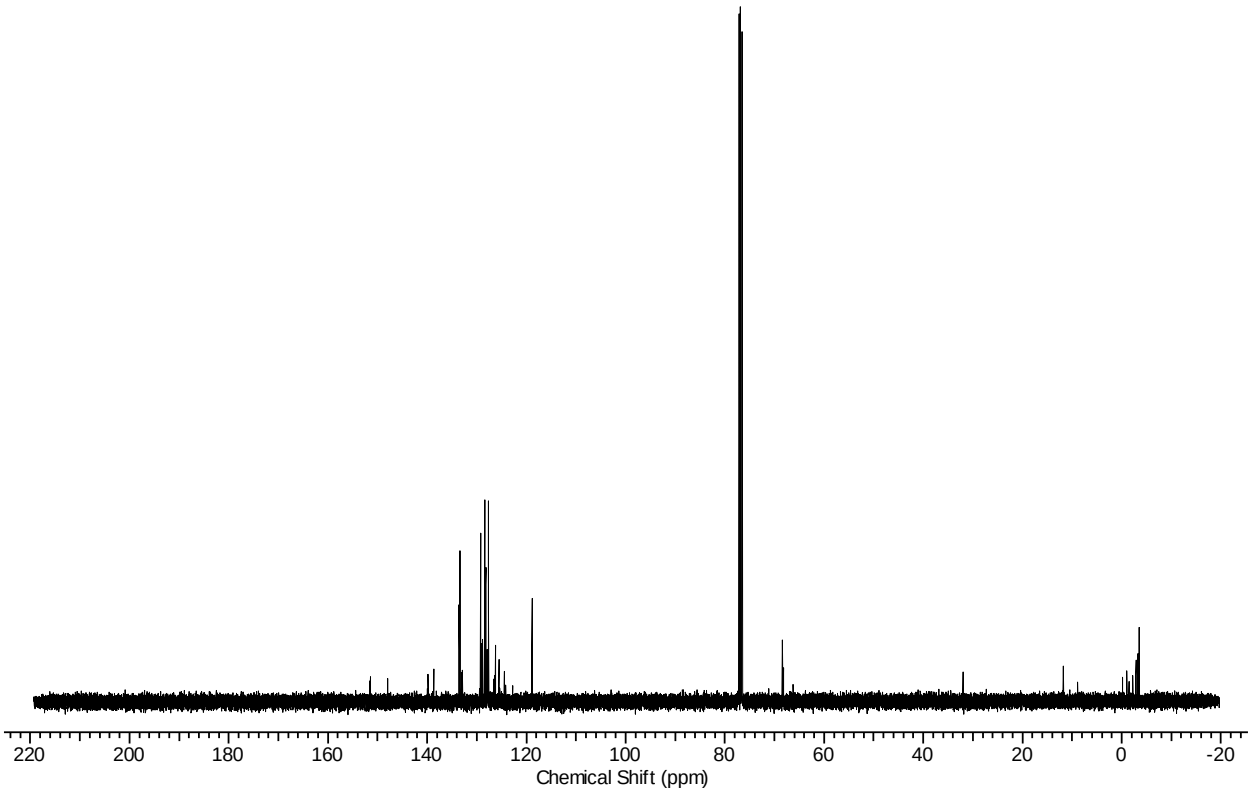

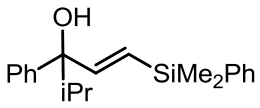

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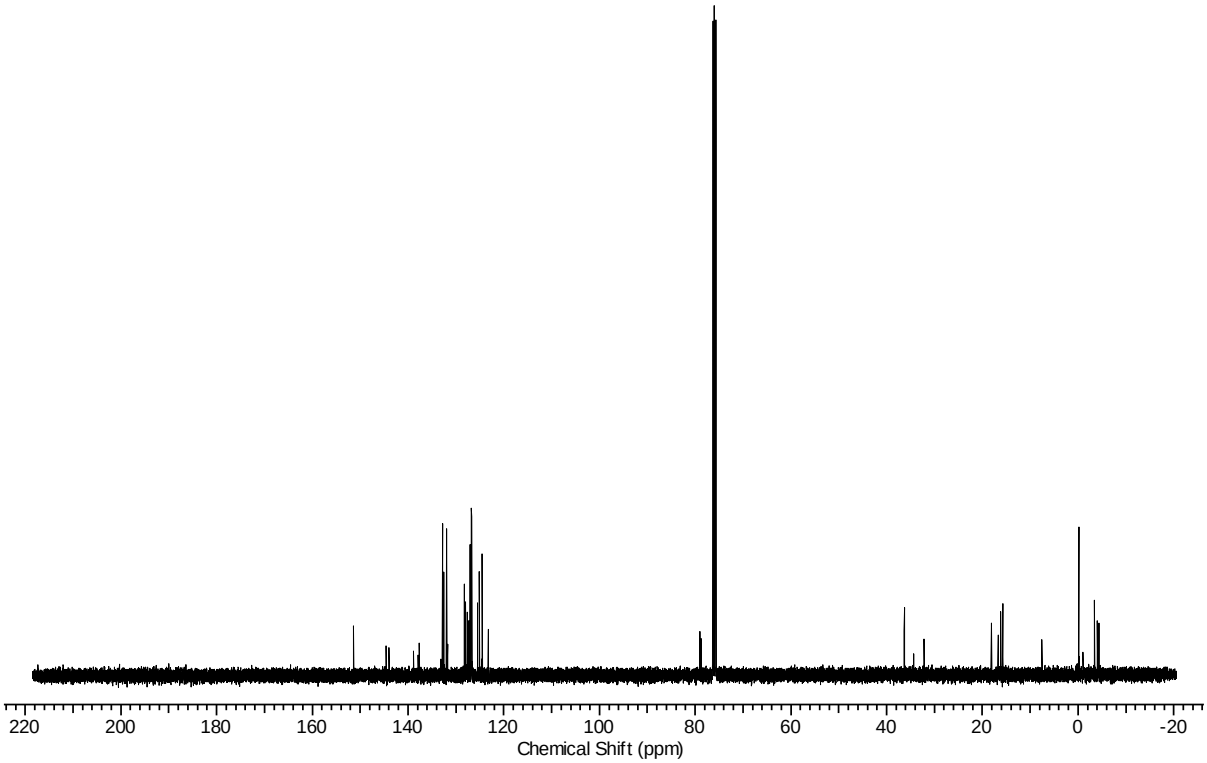
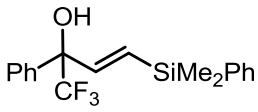
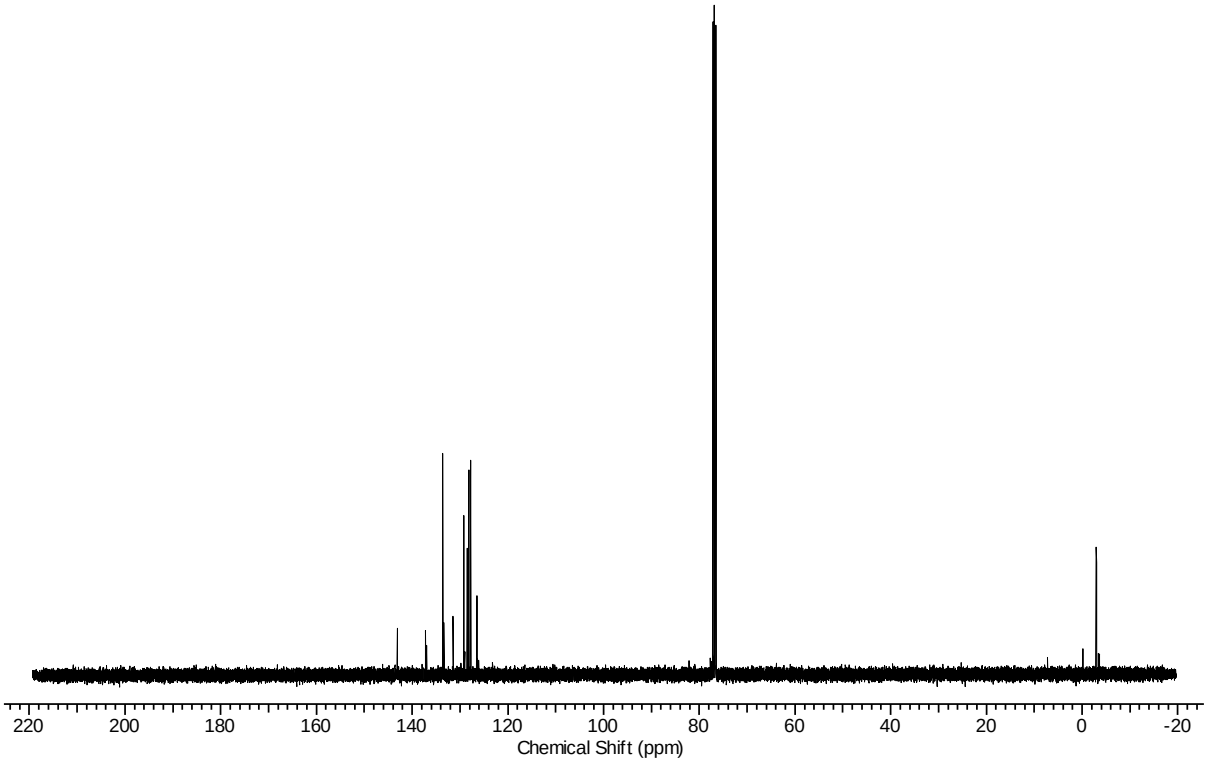



OH
Ph
CF3
SiMe2Ph

4g

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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200
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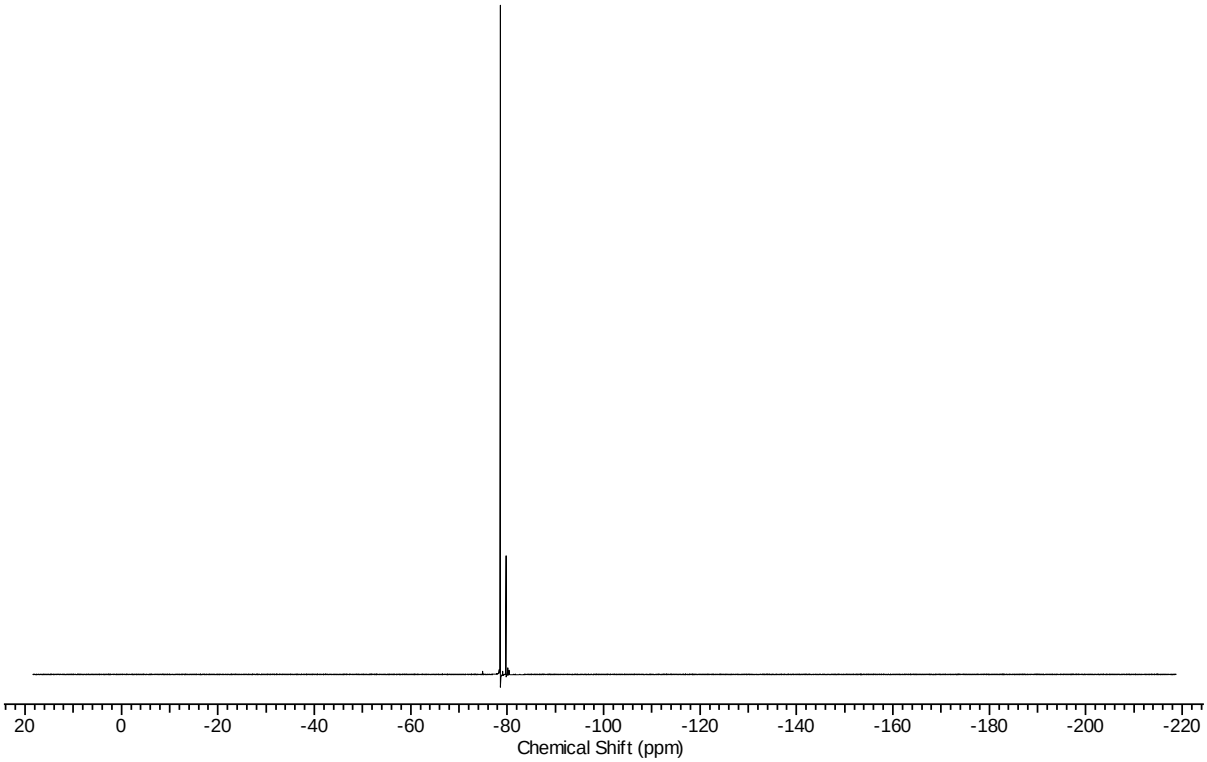
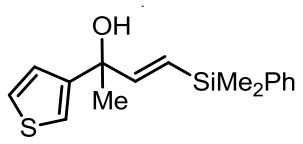
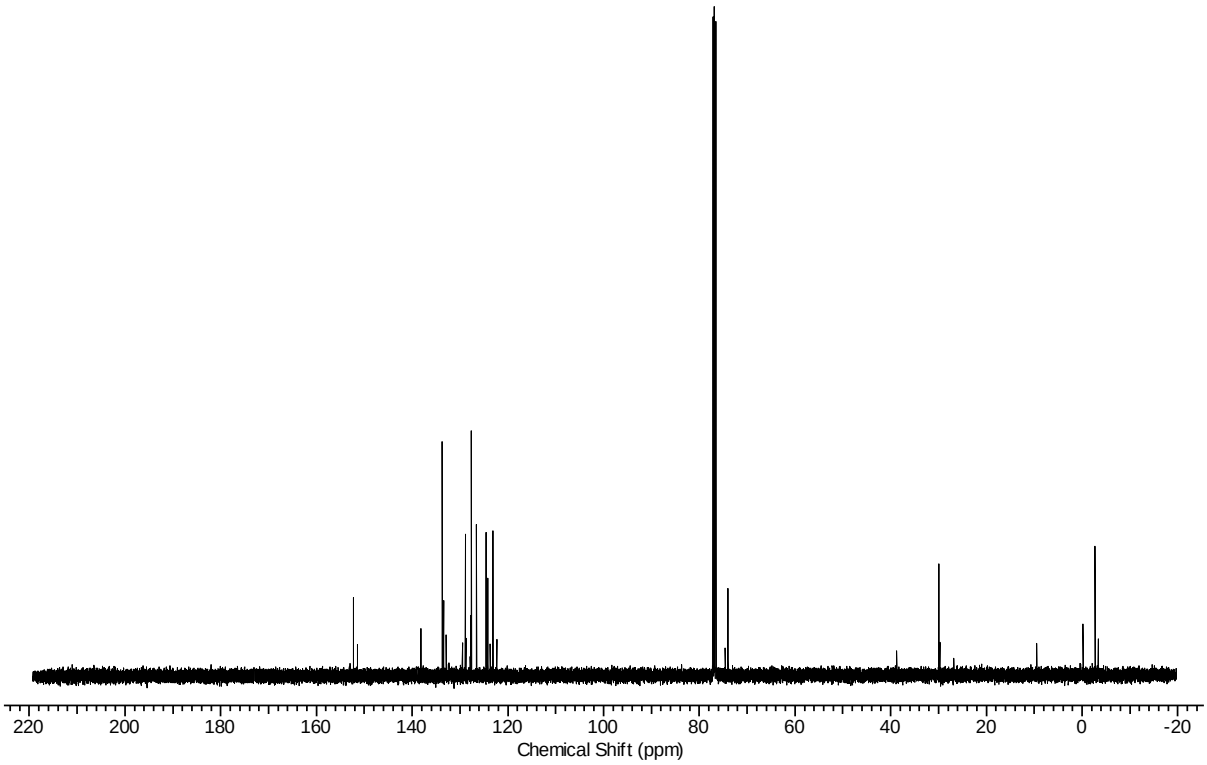
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)




OH
Me
SiMe2Ph
S

4h

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
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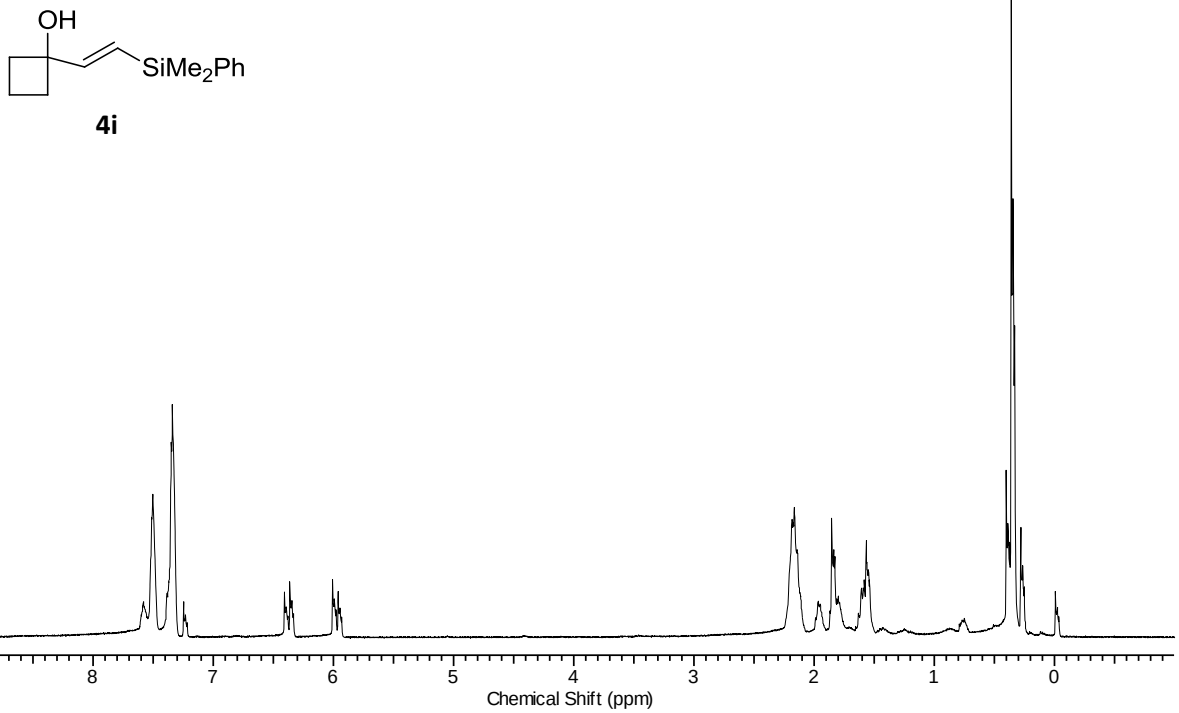
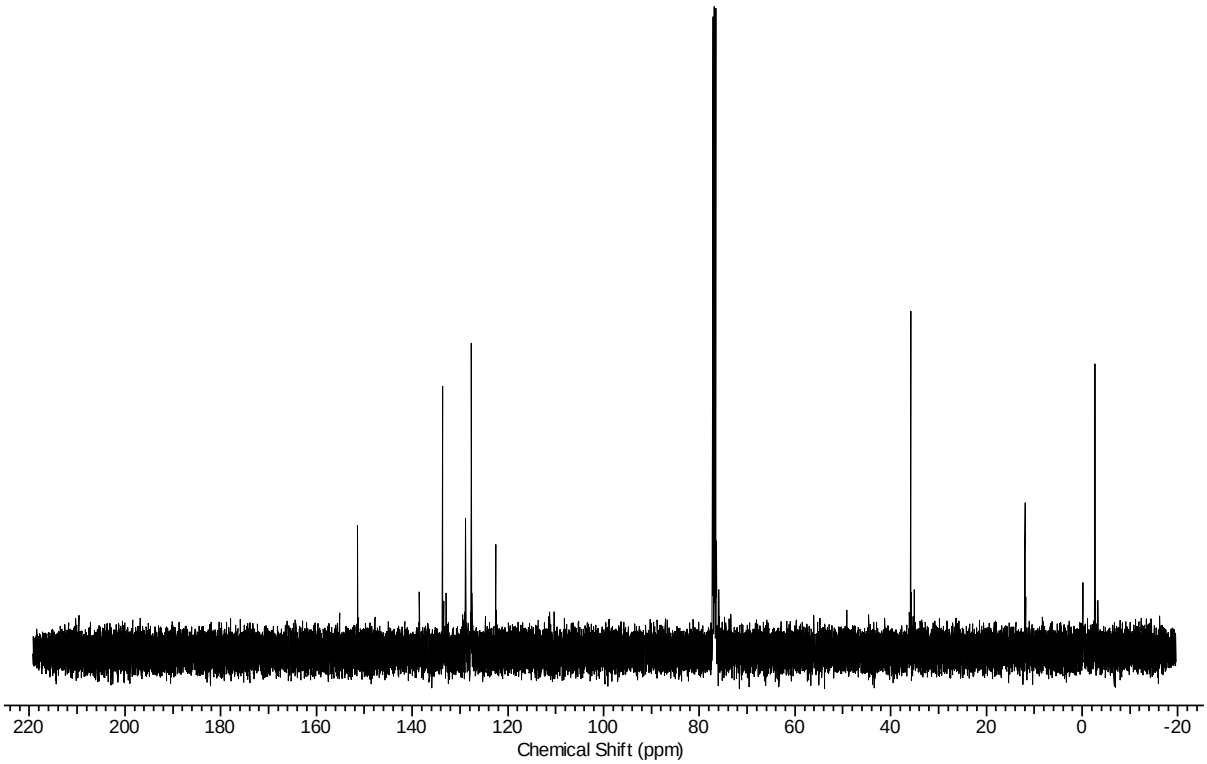
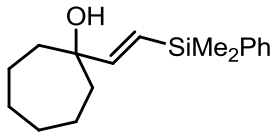
20
0
-20
Chemical Shift (ppm)

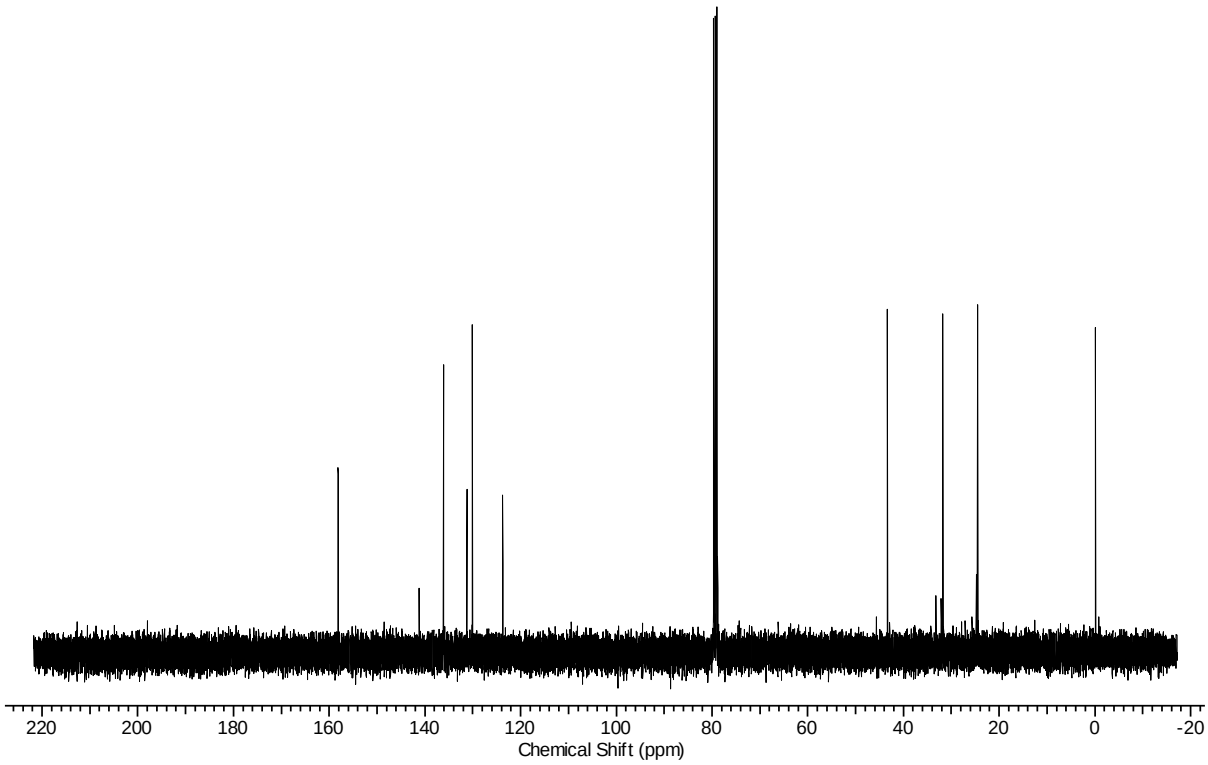


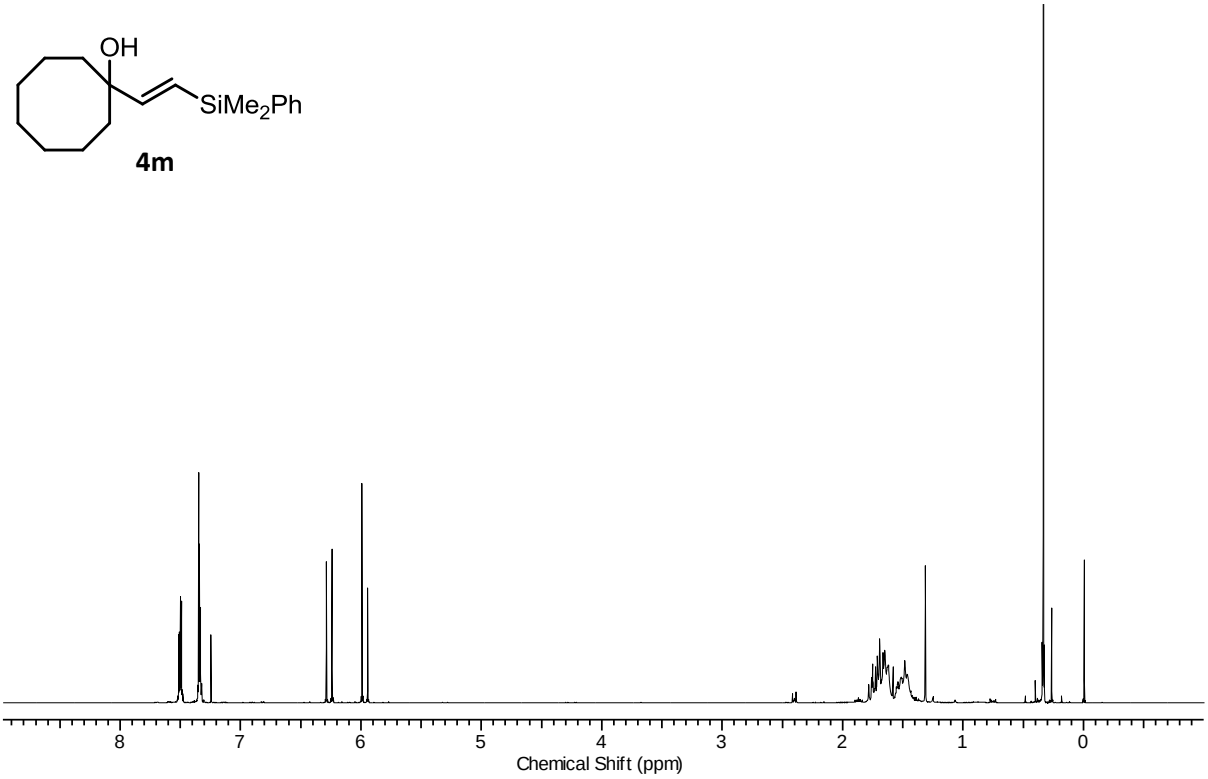
4i



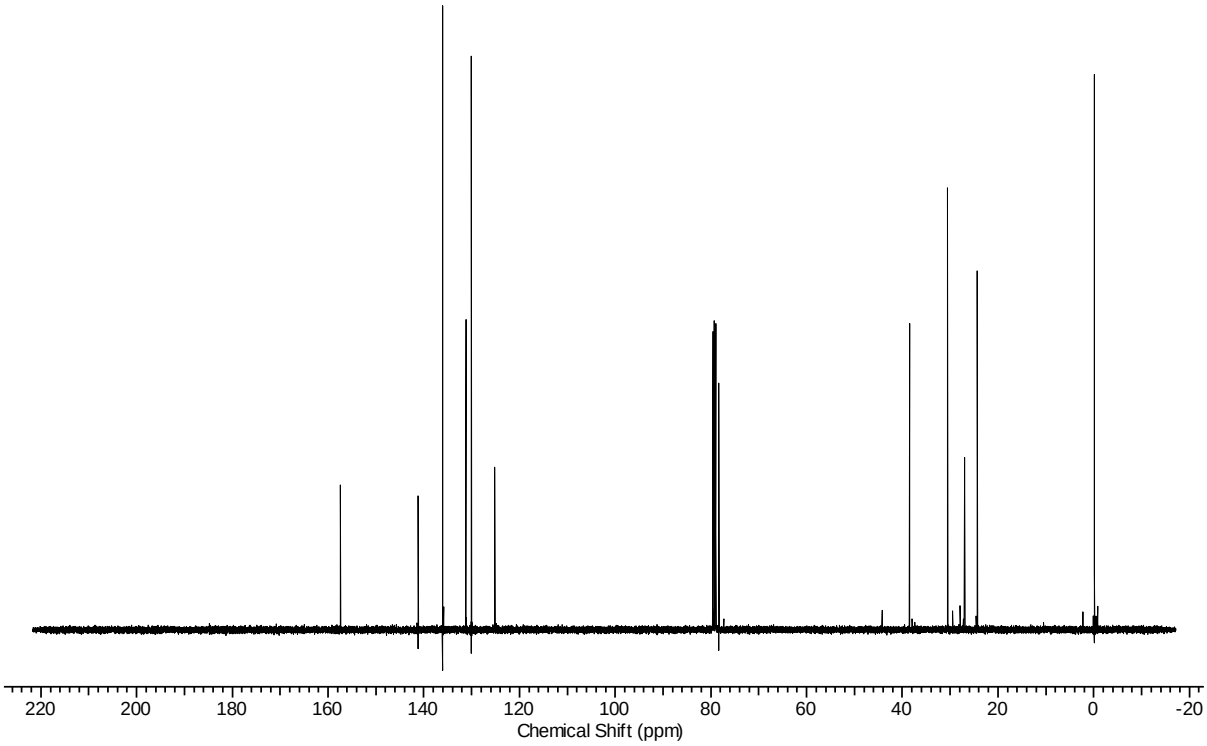


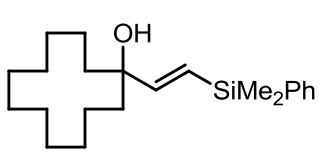
4l





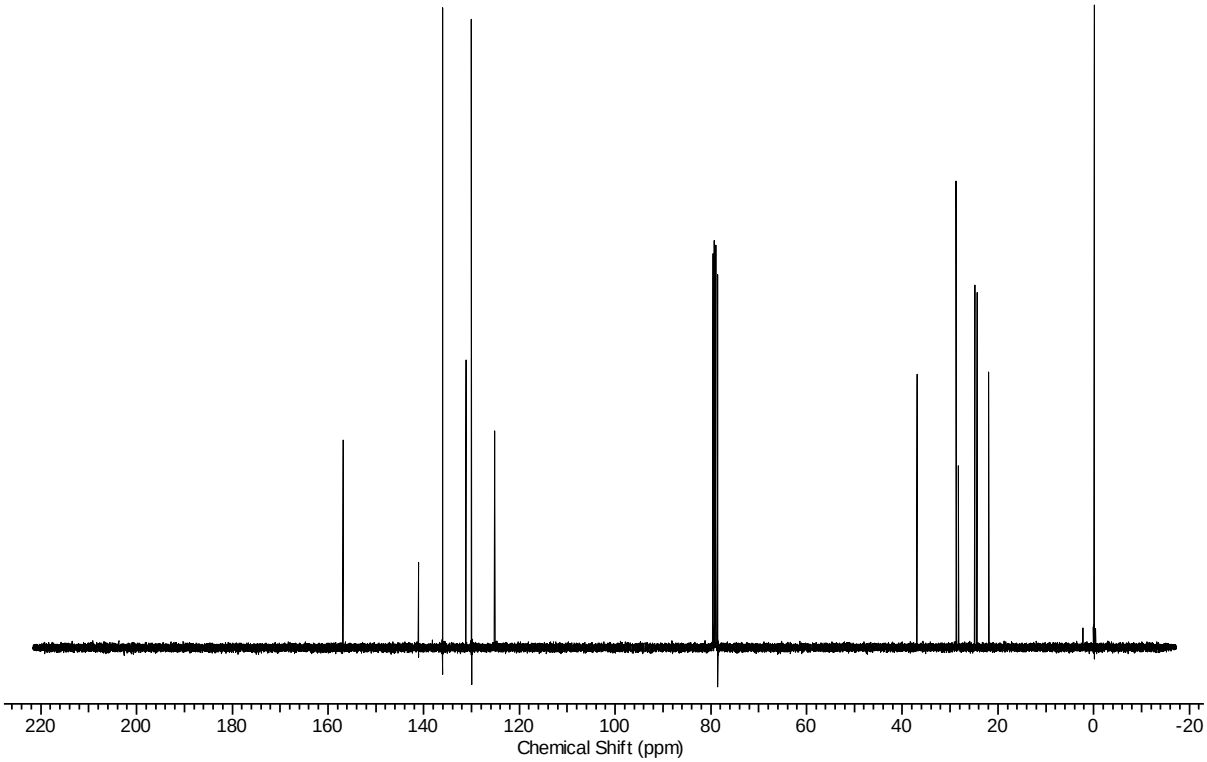
4m




OH
SiMe2Ph

4n

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)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200
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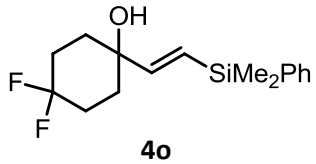
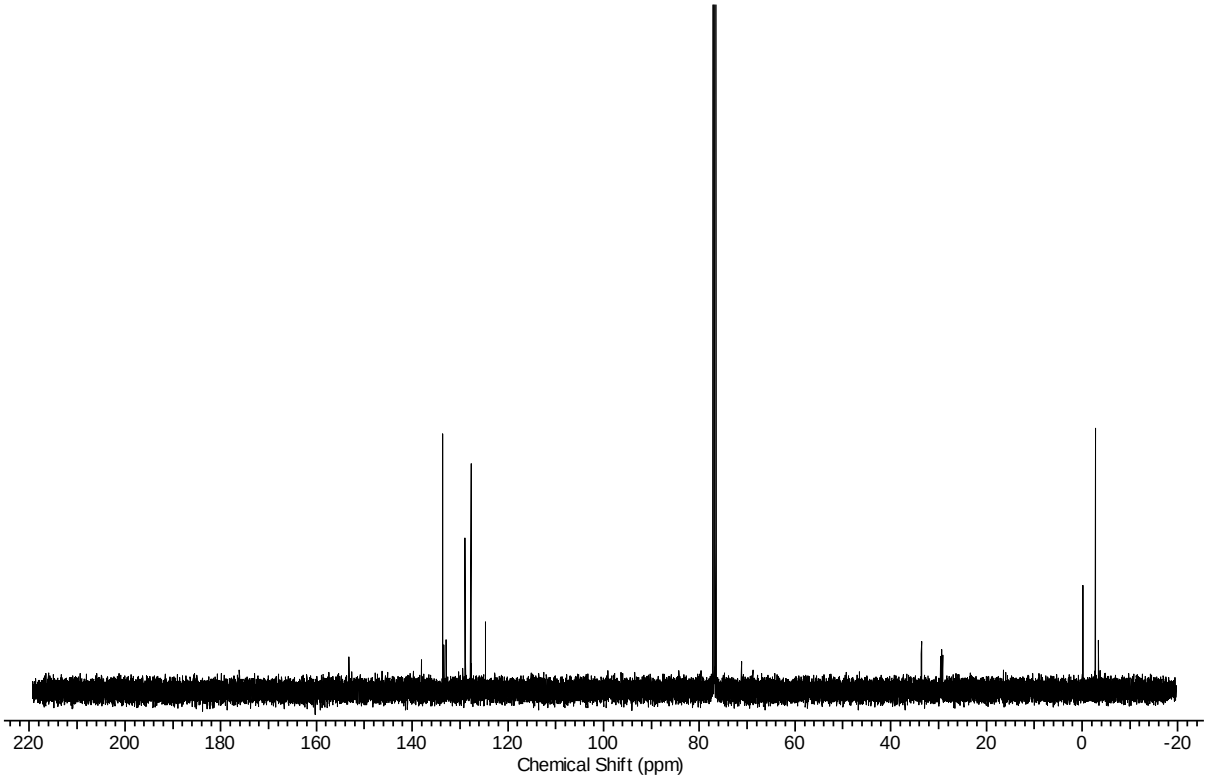
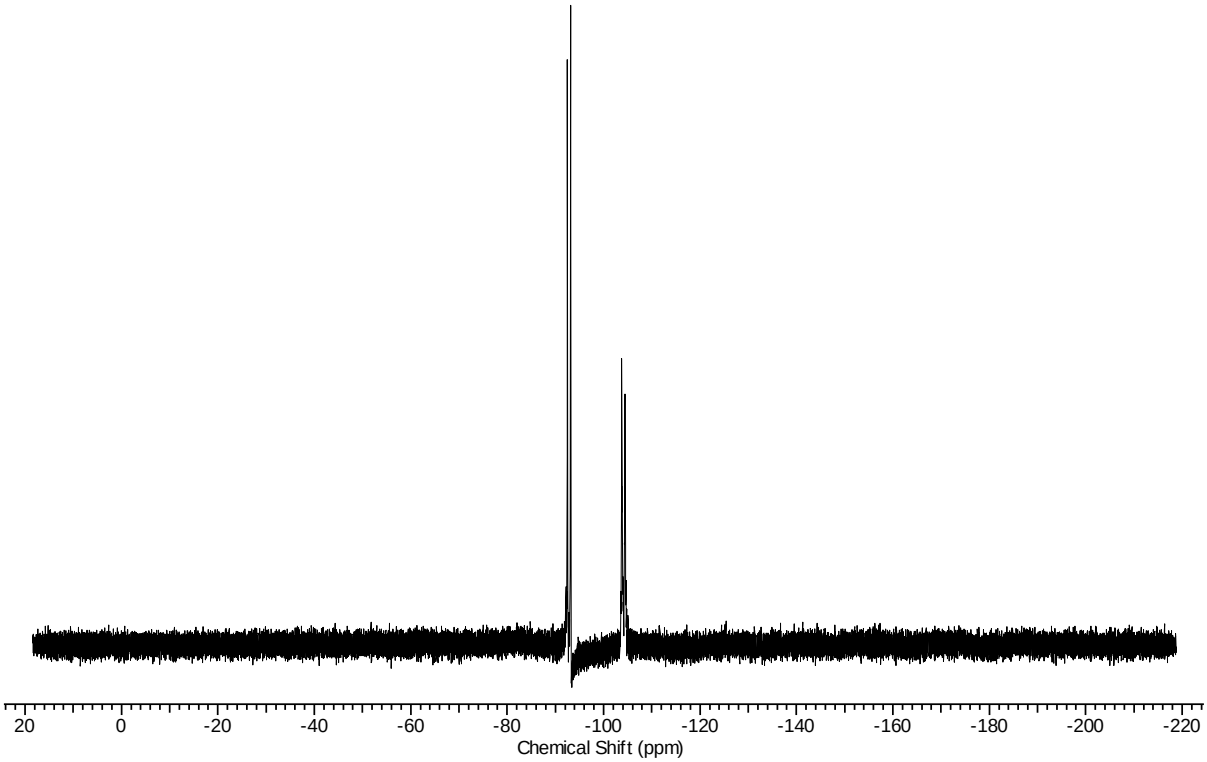
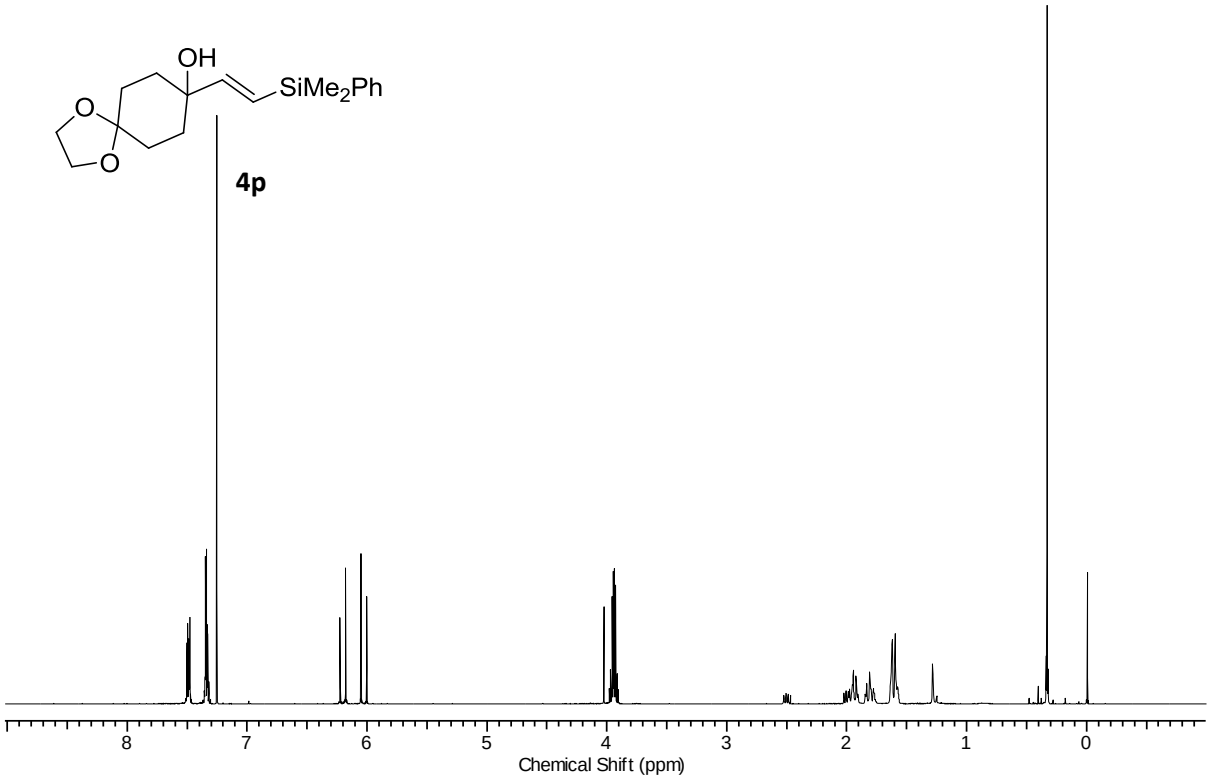
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

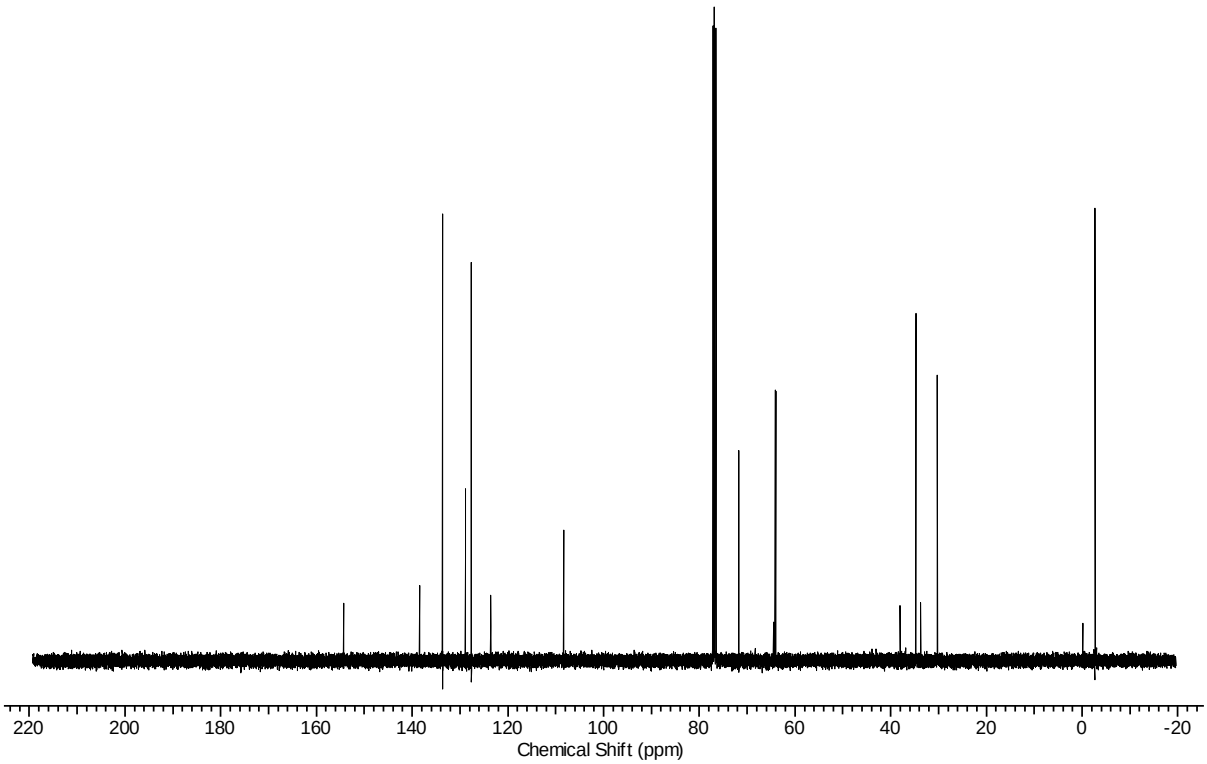


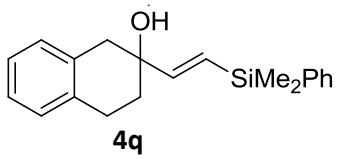
4o





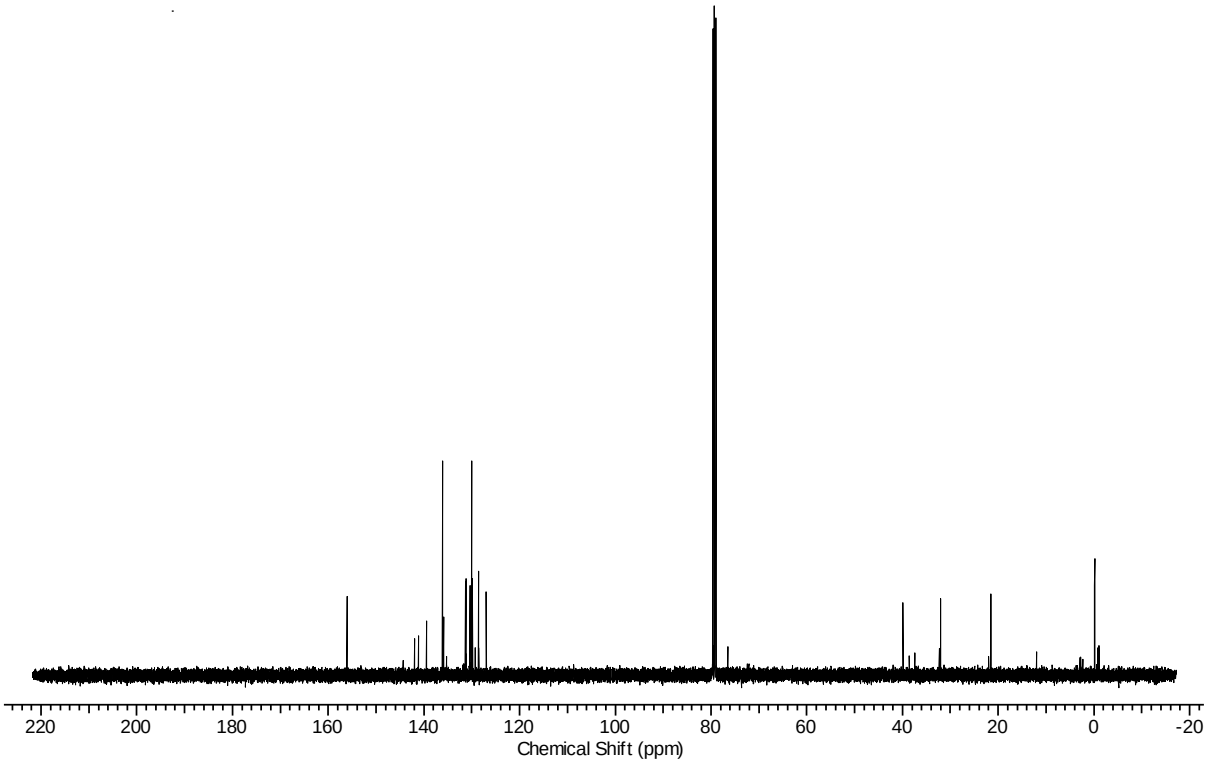





OH
SiMe2Ph

4q

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
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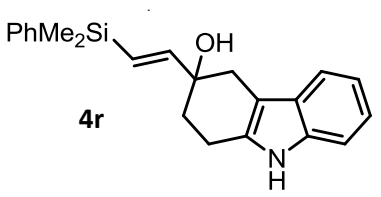
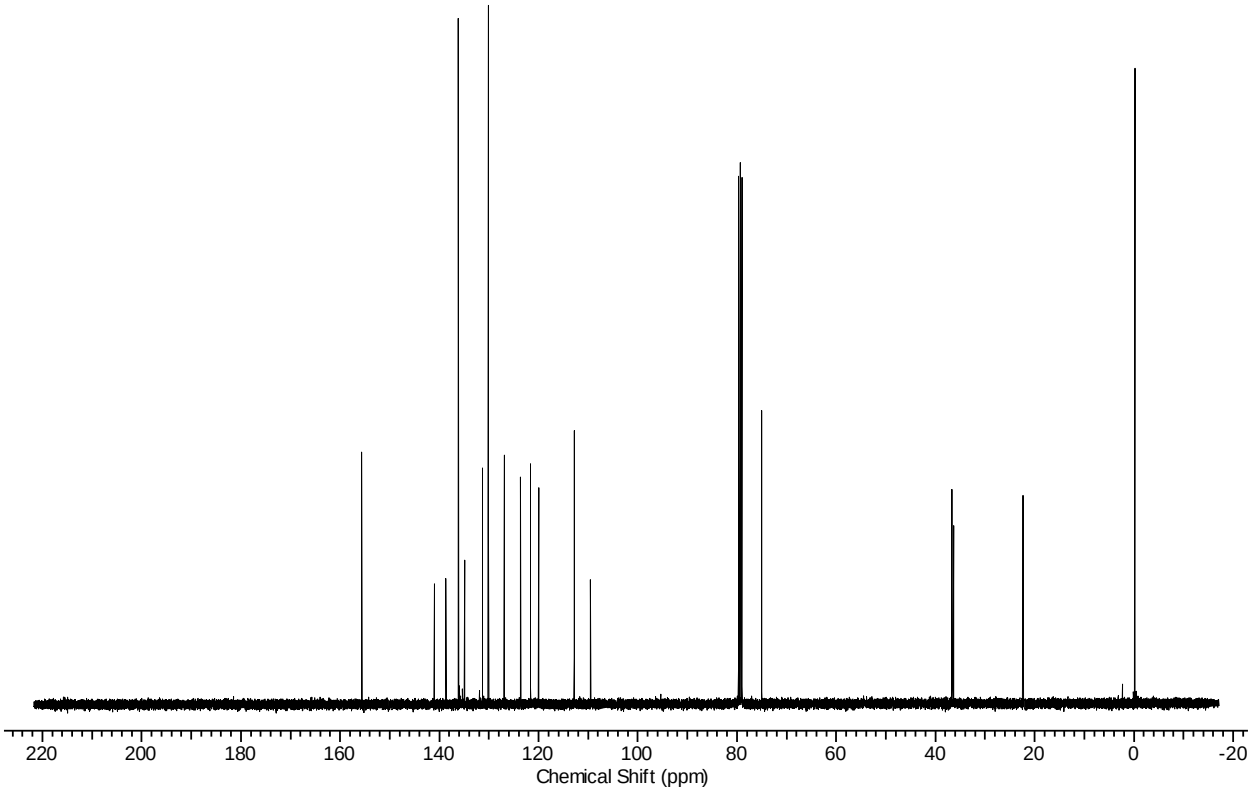
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


PhMe2Si
OH
N
H

4r

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
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140
120
100
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60
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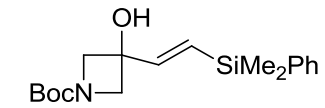
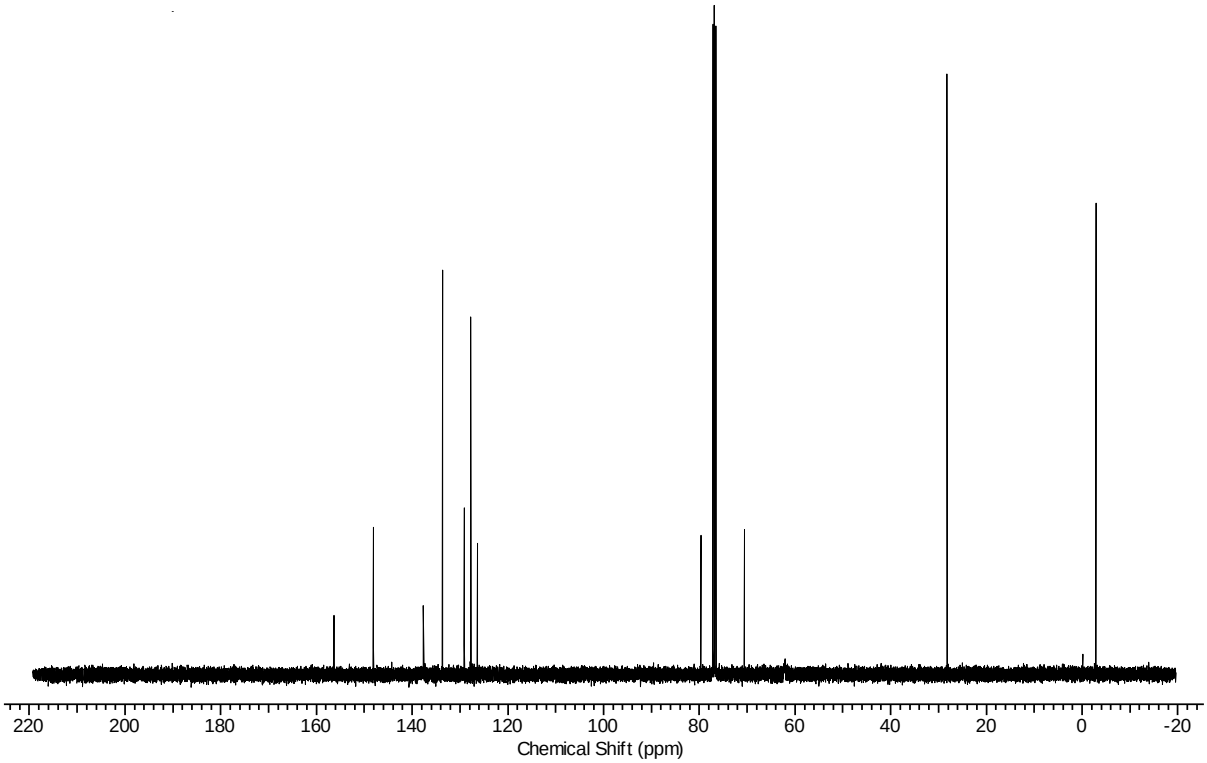
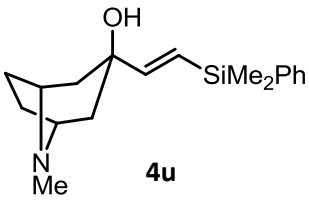
20
0
-20
Chemical Shift (ppm)

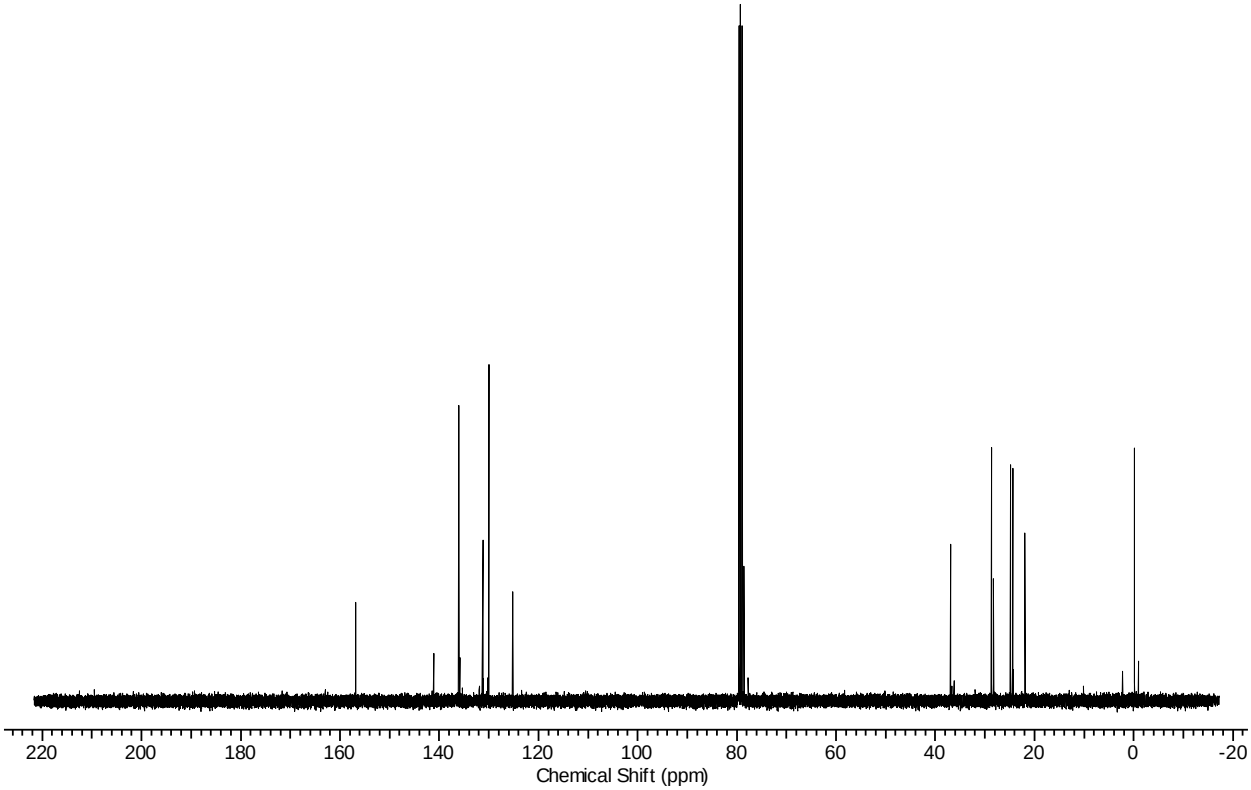


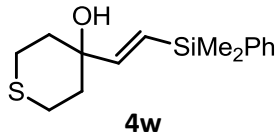
4s



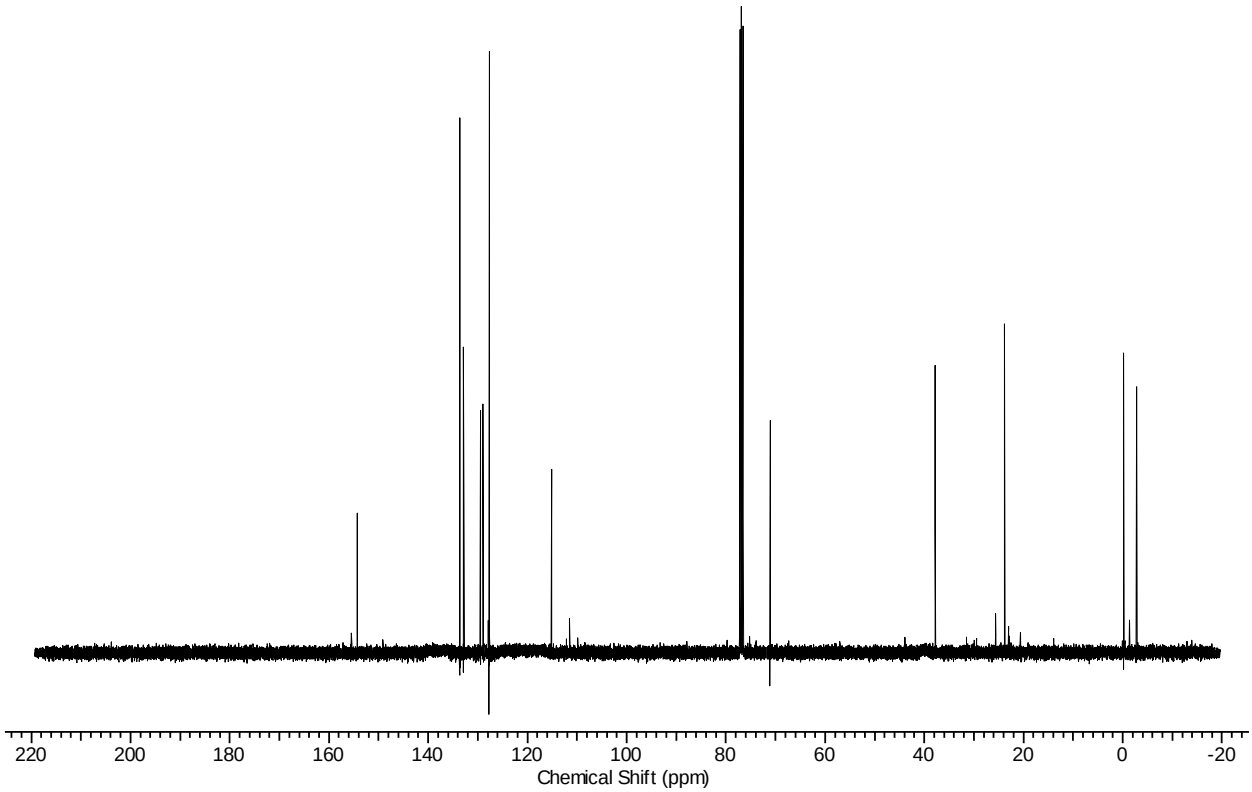


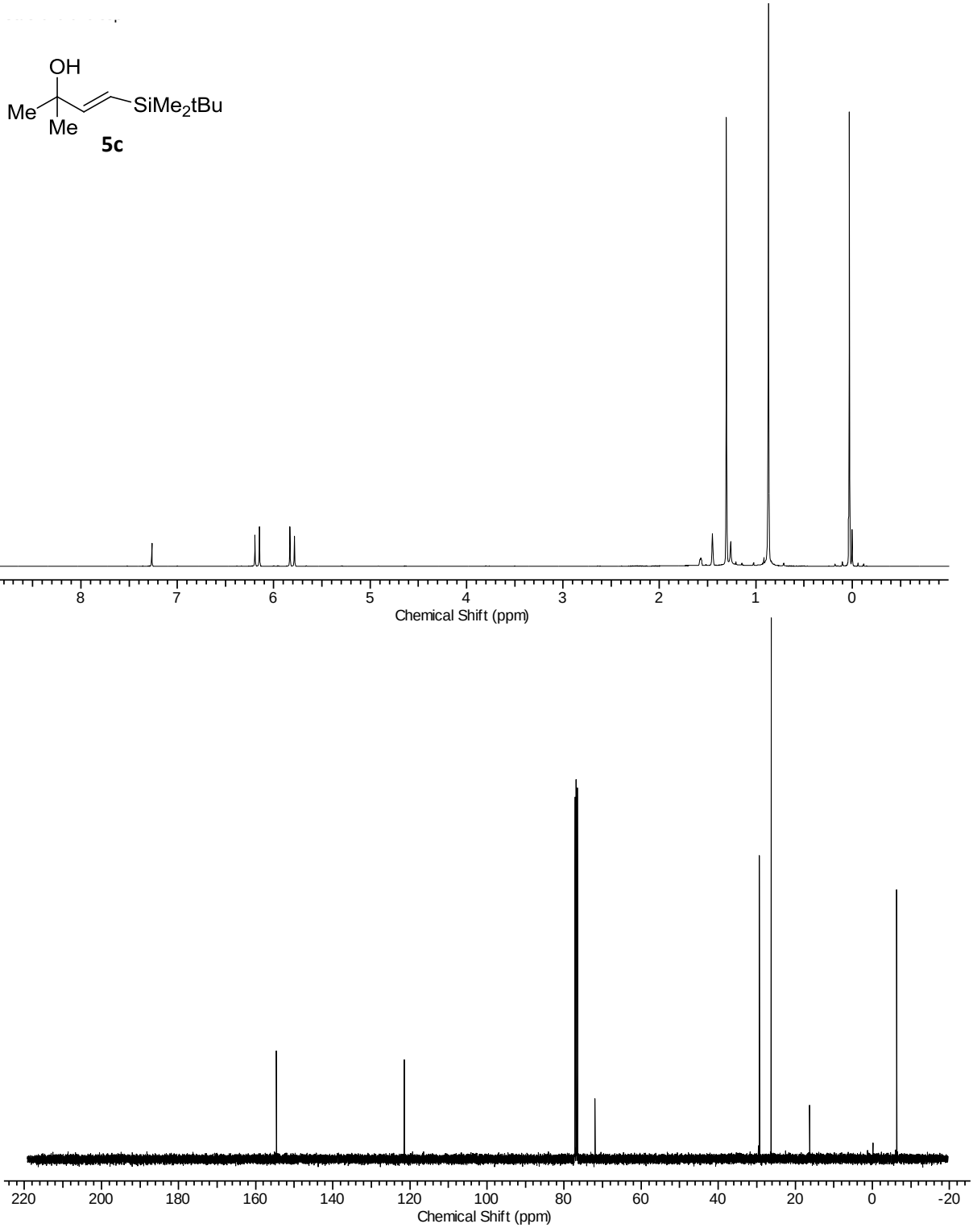
4u

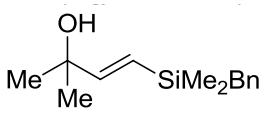




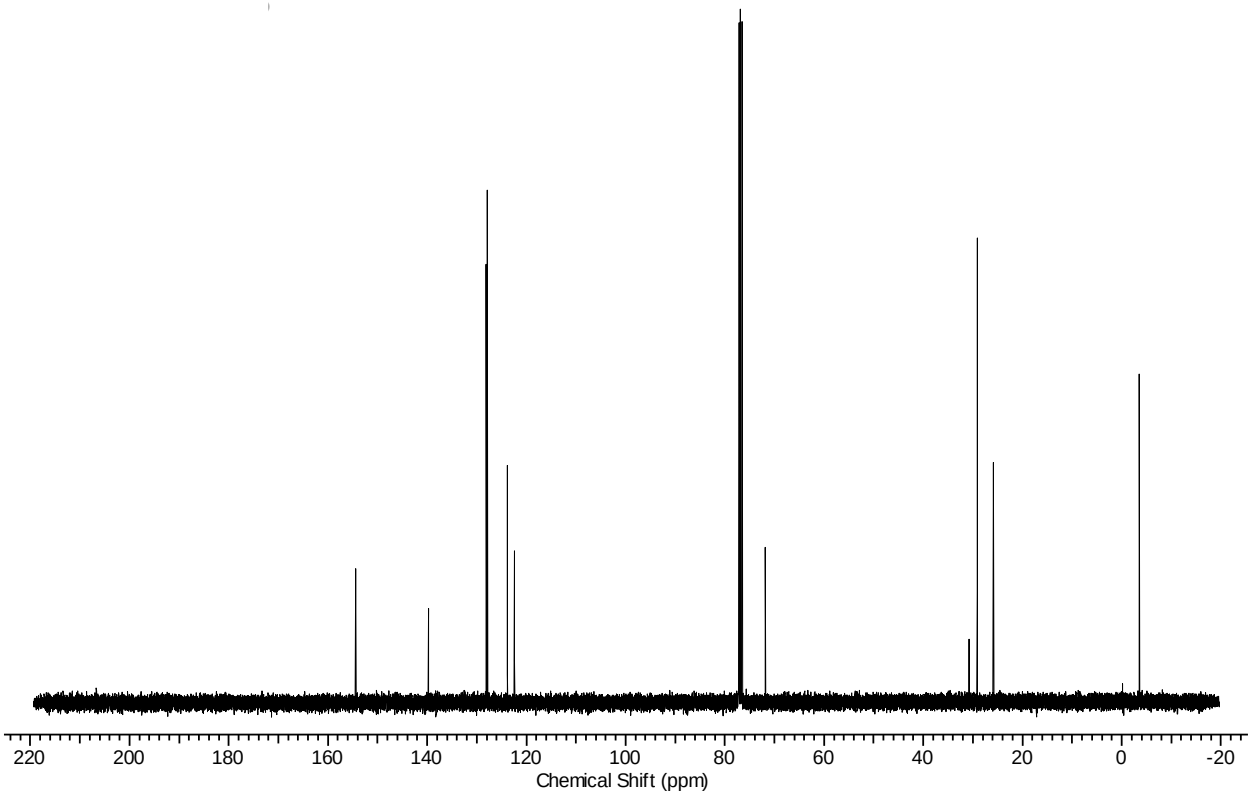
4w







5f



1. McLaughlin, M. G.; Cook, M. J., *Chem. Commun.* **2011,** *47,* 11104-11106.