Electronic Supplementary Material (ESI) for Chemical Communications.

Highly Diastereoselective Hydrosilylation of Allylic Alcohols: A Rapid Entry into Stereodefined 1,3-Diols

Mark G. McLaughlin and Matthew J. Cook*

School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, Northern Ireland
m.cook@qub.ac.uk

Contents

General Methods 3

General Procedures 4

General Procedure A: Synthesis of Allylic Alcohols via Addition of Organolithiums to Aldehydes 4

General Prodecure B: Synthesis of Allylic Alcohols 4

General Procedure C : Hydrosilyation-Fleming Tamao Oxidation to afford *syn* 1,3 diols. ... 4

Experimental procedures and characterisation data 6

Copies of ^{1}H / ^{13}C Spectra 27

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. ^{1}H NMR spectra were recorded on a Bruker AVX300 (300 MHz) spectrometer at ambient temperature. Data are reported as follows: chemical shift in parts per million (δ, ppm) from deuterated chloroform ($CDCl_3$) taken as 7.26 ppm, integration, multiplicity (s = singlet; d = doublet; t = triplet; dd = double doublets m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra were recorded on either a Bruker AVX300 (75 MHz) spectrometer. Chemical shifts are reported in ppm from $CDCl_3$ 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. When necessary, commonly used organic solvents were dried prior to use according to standard laboratory practices.[1] Optical rotations were recorded on a Perkin-Elmer 341 polarimeter, using $CHCl_3$ at 20 ^{o}C and 589 nm.

[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals; 3rd ed. Pergamon Press, Oxford, 1988*

General Procedures

General Procedure A: Synthesis of Allylic Alcohols via Addition of Organolithiums to Aldehydes

To a flame dried 25 mL round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added the corresponding organobromide (1.2 equiv.) followed by the addition of dry Et_2O or THF (0.3 M) and the mixture cooled to -78 ^oC. To this solution was added *t*-BuLi (1.7 M pentane) (2.1 equiv. to bromide) dropwise and the resulting yellow solution stirred at -78^oC for 1 hour followed by the addition of the corresponding aldehyde (1 equiv.) at -78^oC . The solution was then stirred for a further hour before being carefully quenched with sat. aq. NH_4Cl, extracted with Et_2O (3 x 15 mL), washed with brine (15 mL), dried with Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography to afford the requisite allylic alcohol.

General Prodecure B: Synthesis of Allylic Alcohols

Compounds.To a flame dried 25 mL round bottomed flask equipped with a magnetic stirrer bar was added the corresponding carbonyl compound and purged with argon followed by the addition of dry THF (0.3 M). The solution was subsequently cooled to 0 ^oC and isopropenyl magnesium bromide (0.5 M, 1.3 equiv) was added and stirred at 0 ^oC for 30 minutes before warming to room temperature overnight. The mixture was quenched by the addition of sat. aq. NH_4Cl, extracted with Et_2O (3 x 15 mL), washed with brine (15 mL), dried with Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography to afford the requisite allylic alcohol.

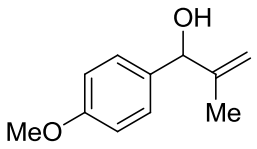
General Procedure C : Hydrosilyation-Fleming Tamao Oxidation to afford *syn* 1,3 diols.

To a flame dried 5 mL round bottomed flask equipped with a magnetic stirrer bar and reflux condenser was added the corresponding allylic alcohol (1 equiv.), $PtCl_2$ (1 mol %), 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (2 mol %) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 ^oC for 20 minutes until a yellow homogenous mixture was obtained after which dimethyltriethylaminosilane (1.5 equiv.) ($HSiMe_2NEt_2$) was added and the solution was stirred at 50 ^oC overnight. The mixture was filtered through a pad of Celite^{TM}, concentrated and a ^1H NMR taken of the crude mixture to ensure consumption of starting material. The

crude material was then redissolved in a 1:1 mixture of THF/MeOH, followed by the addition of $KHCO_3$ (3 equiv.), KF (5 equiv.) and H_2O_2 (10 equiv) (30% wt H_2O) and stirred at rt overnight. The mixture was diluted H_2O (5 ml), extracted with EtOAc (3 x 10 mL), dried with Na_2SO_4, filtered and concentrated. The mixture was subjected to ^1H NMR to determine diastereoselectivity and then applied to the top of a column and chromatographed to afford the requisite 1,3 diol

Experimental procedures and characterisation data

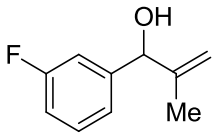
1-(4-methoxyphenyl)-2-methylprop-2-en-1-ol (1b)



The title compound was prepared according to general procedure A, from anisaldehyde (306 mg, 2.25 mmol), 2-bromopropene (300 mg, 2.48 mmol) and *t*-BuLi (3.1 mL, 5.21 mmol) in Et_2O (7.5 mL) which following conversion to the allylic alcohol and column chromatography (9:1 Hexane/EtOAc) afforded **1b** (319 mg, 79%) as a yellow oil.

R_f (4:1 hexane-ethyl acetate) = 0.45; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.32-7.25 (2H, m), 6.91-6.85 (2H, m), 5.20 (1H, s), 5.08 (1H, s), 4.95 (1H, s), 3.81 (3H, s), 2.17 (1H, s), 1.61 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 147.0, 134.2, 127.8, 113.8, 110.6, 77.4, 55.3, 18.5. All spectral data are in accordance to that previously reported[2]

1-(3-fluorophenyl)-2-methylprop-2-en-1-ol (1c)

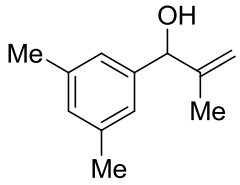


The title compound was prepared according to general procedure A, from 3-flurobenzaldehyde (280 mg, 2.25 mmol), 2-bromopropene (300 mg, 2.48 mmol) and *t*-BuLi (3.1 mL, 5.21 mmol) in THF (7.5 mL) which following conversion to the allylic alcohol and column chromatography (10 - 50% DCM/Hexane) afforded **1c** (110 mg, 27%) as a yellow oil.

R_f (4:1 hexane-ethyl acetate) = 0.39; IR: ν_{max} (thin film) / cm^{-1} 3366, 2900, 2799, 1550, 782, ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.35-7.25 (1H, m), 7.18-7.07 (2H, m), 7.01-6.94 (1H, m), 5.19 (1H, s), 5.15 (1H, s), 4.97 (1H, s), 1.85 (1H, br), 1.62 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 ($J_{C\text{-}F}$ = 244.0 Hz), 146.4, 144.5 ($J_{C\text{-}F}$ = 6.6 Hz), 129.8 ($J_{C\text{-}F}$ = 8.4 Hz), 122.0 ($J_{C\text{-}F}$ = 2.9 Hz), 114.5 ($J_{C\text{-}F}$ = 21.1 Hz), 113.3 ($J_{C\text{-}F}$ =21.4 Hz), 112.0, 77.3, 17.8.; HRMS (EI+) Calcd. For $C_{10}H_{12}OF$ $[M+H]^+$, 167.0872. Found 167.0870

[2] Miura, K.; Wang, D.; Hosomi, A. *J. Am. Chem. Soc.* **2005,** *127,* 9366

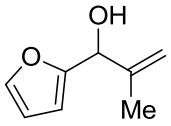
1-(3,5-dimethylphenyl)-2-methylprop-2-en-1-ol (1d)



The title compound was prepared according to general procedure A, from 1-bromo-3,5-dimethylbenzene (416 mg, 2.25 mmol), methacrolein (143 mg, 2.05 mmol) and *t*-BuLi (1.9 mL, 4.75 mmol) in Et_2O (7 mL) which following conversion to the allylic alcohol and column chromatography (9:1 Hexane/EtOAc) afforded **1d** (301 mg, 83%) as a colourless oil.

R_f (4:1 hexane-ethyl acetate) = 0.45; IR: ν_{max} (thin film) / cm^{-1} 3422, 2800, 1736, 1264, 1046; ^1H NMR: (400 MHz, $CDCl_3$) δ 6.97 (2H, s), 6.92 (1H, s), 5.21 (1H, s), 5.07 (1H, s), 4.95 (1H, s), 2.31 (6H, s), 1.83 (1H, br s), 1.62 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ; 146.9, 141.9, 138.0, 129.3, 124.2, 110.8, 77.9, 21.3, 18.4.; HRMS (EI+) Calcd. For $C_{12}H_{17}O$ $[M+H]^+$, 177.1279. Found 177.1285.

1-(furan-2-yl)-2-methylprop-2-en-1-ol (1e)

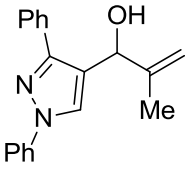


To a 50 mL round bottomed flask equipped with a magnetic stirrer and purged with argon was added furan (534 mg, 7.86 mmol) in dry THF (14 mL) and cooled to -78^{o}C followed the the dropwise addition of n-BuLi (2.5 M, 4 mL, 9.82 mmol) and the yellow solution turns green/blue and was stirred at -78^{o}C for 1 hour. Methacrolein (500 mg, 7.143 mmol) was then added and the subsequent orange solution was stirred at -78 ^{o}C for a further hour. The mixture was quenched by the careful addition of sat. aq. NH_4Cl at -78^{o}C and allowed to warm to room temperature, extracted with Et_2O (3 x 35 mL), washed with brine (35 mL), dried with $MgSO_4$, filtered and concentrated. Flash column chromatography afforded **1e** (149 mg, 15%) as a colourless oil.

R_f (20% EtOAc/Hexane) = 0.22; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.35 (1H, m), 6.34 (1H, dd, *J* = 3.1, 2.0 Hz), 6.27 (1H, d, *J* = 3.1 Hz), 5.19 (1H, s), 5.15 (1H, s), 5.04-5.01 (1H, m),

1.74 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 144.3, 142.2, 112.1, 110.3, 106.9, 71.4, 18.6. All spectral data are in accordance to that previously reported[3]

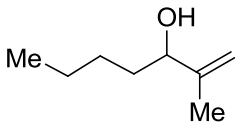
1-(1,3-diphenyl-1H-pyrazol-4-yl)-2-methylprop-2-en-1-ol (1f)



The title compound was prepared following general procedure B from 1,3-diphenylpyrazole-4-carboxaldehyde (300 mg, 1.21 mmol) and isopropenylmagnesium bromide (0.5 M, 2.7 mL, 1.33 mmol) in THF (4 mL) which following conversion to the allylic alcohol and column chromatography (10% EtOAc / hexane) afforded **1f** (326 mg, 93%) as a yellow oil.

R_f (20% EtOAc/Hexane) = 0.21; v_{max} cm^{-1} 3356, 158, 1502, 1059, 757, 691;^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.93 (1H, s), 7.86-7.81 (2H, m), 7.77-7.72 (2H, m), 7.49-7.41 (4H, m), 7.40-7.35 (1H, m), 7.31-7.25 (1H, m), 5.28-5.25 (2H, m), 5.02 (1H, br s), 2.04 (1H, d, *J* = 4.0 Hz), 1.74 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 146.6, 140.0, 133.0, 129.4, 128.5, 128.3, 128.1, 126.9, 126.4, 122.6, 119.0, 111.2, 69.4, 19.5; HRMS (EI+) Calcd. for $C_{19}H_{19}N_2O$ $[M+H]^+$ 291.1497. Found 291.1491.

2-methylhept-1-en-3-ol (1g)



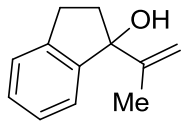
To a 25 mL round bottomed flask equipped with a magnetic stirrer bar ad purged with argon was added methacrolein (250 mg, 3.57 mmol) in dry THF (12 mL, 0.3 M) and cooled to -78^{o}C after which n-BuLi (1.7 mL, 4.28 mmol, 2.5 M in hexanes) was added dropwise. The reaction mixture was stirred for 1 hour at -78^{o}C, quenched with water, extracted with Et_2O (3 x 20 mL), washed with brine (20 mL), dried with $MgSO_4$, filtered and concentrated to afford a colouless oil which was chromatographed to afford **1g** (347 mg, 76%) as a colourless oil.

R_f (20% EtOAc/Hexane) = 0.41; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.94 (1H, t, *J* = 1.0 Hz), 4.84 (1H, t, *J* = 1.5 Hz), 4.06 (1H, t, *J* = 6.5 Hz), 1.73 (3H, s), 1.60-1.46 (3H, m), 1.40-1.24 (4H,

[3] Petrone, D.A.; Malik, H.A.; Clemenceau, A.; Lautens, M. *Org. Lett.* **2012,** *14,* 4806

m), 0.92 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 110.9, 76.0, 34.7, 27.8, 22.6, 17.5, 14.0. All spectral data are accordance with that previously reported.[4]

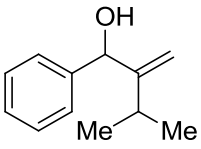
1-(prop-1-en-2-yl)-2,3-dihydro-1H-inden-1-ol (1j)



The title compound was prepared according to general procedure A from 1-indanone (250 mg, 1.89 mmol), 2-bromopropene (274 mg, 2.27 mmol) and t-BuLi (2.8 mL, 4.77 mmol) in THF (7.5 mL) which following conversion to the allylic alcohol and column chromatography (20% EtOAc/Hexane) afforded **1j** (171 mg, 43%) as a light yellow oil which solidified upon standing at -18 °C.

R_f (20% EtOAc/Hexane) = 0.44; ; IR v_{max} cm^{-1} 3349, 2955, 1458, 1099, 1073; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.29-7.17 (4H, m), 5.06-5.04 (1H, m), 4.97-4.93 (1H, m), 3.10 (1H, ddd, *J* = 15.9, 8.3, 5.5 Hz), 2.88 (1H, ddd, *J* = 15.9, 8.3, 5.5 Hz), 2.47 (1H, ddd, *J* = 13.6, 7.8, 5.6 Hz), 2.13 (1H, ddd, *J* = 13.6, 7.8, 5.6 Hz), 1.83 (1H, s), 1.74 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 146.3, 143.9, 128.4, 126.8, 124.9, 123.3, 110.8, 86.5, 39.9, 29.9, 19.4; HRMS (EI+) Calcd. for $C_{12}H_{12}$ $[M-H_2O]^+$156.0939. Found 156.0945.

3-methyl-2-methylene-1-phenylbutan-1-ol (1k)



The title compound was prepared following the procedure of Burton et al.[5] To a 25 mL round bottomed flask equipped with a magnetic stirrer bar and reflux condenser was added isovaleraldehyde (500 mg, 5.81 mmol), diethylammonium chloride (767 mg, 6.98 mmol) and aqueous formaldehyde solution (566 mg, 6.98 mmol, 37% *wt.*) and stirred at 70 ^{o}C for 24 hours. After cooling to room temperature, the layers were separated and the aqueous layer extracted with Et_2O (3 x 15 mL), dried (Na_2SO_4), filtered and concentrated to afford the α,β-unsaturated aldehyde as a colourless oil (399 mg, 70%) which was used without further purification.

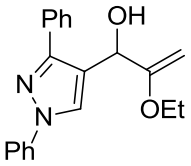
[4] Pace, V.; Castoldi, L.; Hoyos, P.; Sinisterra, J. V.; Pregnolato, M.; Sánchez-Montero, J. M. *Tetrahedron,* **2011,** *67,* 2670

[5] Logan, A. W. J. Parker, J. S.; Hallside, M. S.; Burton, J. W. *Org. Lett.* **2012,** *14,* 2940

To a THF (10 mL) solution on the α,β-unsaturated aldehyde (200 mg, 2.04 mmol) at 0 ^{o}C was added freshly prepared phenylmagnesium bromide (553 mg, 3.06 mmol) in THF and the mixture stirred at 0 ^{o}C for 1 hour before being quenched with sat. aq. NH_4Cl. The layers where separated and the aqueous layer extracted with Et_2O (3 x 20 mL), washed with brine, dried (Na_2SO_4), filtered and concentrated. Purification by flash chromatography (10% EtOAc/Hexane) afforded **1k** as a colourless oil (298 mg, 83%).

R_f (20% EtOAc/Hexane) = 0.39; v_{max} cm^{-1} 3403, 2966, 2561, 2460, 1000; ^{1}H NMR: (400 MHz, $CDCl_3$) 7.40-7.33 (5H, m), 5.27 (1H, dd, *J* = 1.0, 1.0 Hz), 5.22 (1H, s), 5.06 (1H, d, *J* = 1.0 Hz), 2.12 (1H, sept., *J* = 7.0 Hz), 1.89 (1H, d, *J* = 3.5 Hz), 0.99 (3H, d, *J* = 7.0 Hz), 0.97 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.3, 128.4, 127.0, 107.7, 76.2, 30.1, 23.1, 22.4. All spectral data are consistent with that previously reported.[6]

1-(1,3-diphenyl-1H-pyrazol-4-yl)-2-ethoxyprop-2-en-1-ol (1n)



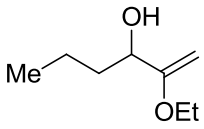
To a 25 mL round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added ethyl vinyl ether (269 mg, 3.73 mmol, 1.2 equiv.) and dry THF (10 mL, 0.4 M) and cooled to -78 ^{o}C followed by the dropwise addition of *t*-BuLi (1.82 mL, 3.10 mmol, 1.7 M in heptane) and the resulting yellow solution was stirred at -78 ^{o}C for 30 minutes before being warmed slowly to 0 ^{o}C. In a separate 50 mL round bottomed flask equipped with a magnetic stirrer bar was added 1,3-diphenylpyrazole-4-carboxaldehyde (640 mg, 2.58 mmol) in THF (5 mL, 0.5 M) and cooled to -78 ^{o}C followed by the addition of the lithiated ethyl vinyl ether via cannula. The mixture was allowed to stir at -78 ^{o}C for 1 hour followed by quenching with water, extraction with Et_2O and washing with brine. The organic layer was dried (Na_2SO_4), filtered and concentrated, which following purification by flash chromatography afforded **1n**, as a yellow oil (462 mg, 56%)

R_f (5% MeOH/DCM) = 0.26; v_{max} cm^{-1}3381, 1600, 1503, 1077, 697;^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.04 (1H, s), 7.83 (2H, dd, *J* = 8.5, 1.4 Hz), 7.73 (2H, dd, *J* = 8.5, 1.4 Hz), 7.46-7.40 (4H, m), 7.35-7.33 (1H, m), 7.29-7.23 (1H, m), 5.52 (1H, s), 4.26 (1H, d, *J* = 2.5 Hz), 4.07 (1H, d, *J* = 2.5 Hz), 3.82 (2H, q, *J* = 7.0 Hz), 2.65 (1H, br s), 1.32 (3H, t, *J* = 7.0 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 151.8, 140.0, 133.0, 129.3, 128.4, 128.3, 128.0, 127.0, 126.3,

[6] Breit, B.; Heckmann, G.; Zahn, S. K. *Chem. Eur. J.* **2003,** *9,* 425

122.0, 119.0, 82.6, 67.2, 63.3. 14.3; HRMS (EI+) Calcd. for $C_{20}H_{18}N_2O$ [M-H_2O] 302.1419. Found 302.1423.

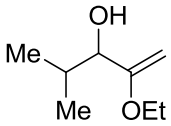
2-ethoxyhex-1-en-3-ol (1o)



To a 25 mL round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added ethyl vinyl ether (269 mg, 3.73 mmol, 1.2 equiv.) and dry THF (10 mL, 0.4 M) and cooled to -78 ^oC followed by the dropwise addition of *t*-BuLi (1.82 mL, 3.10 mmol, 1.7 M in heptane) and the resulting yellow solution was stirred at -78 ^oC for 30 minutes before being warmed slowly to 0 ^oC. In a separate 50 mL round bottomed flask equipped with a magnetic stirrer bar was added butryaldehyde (186 mg, 2.58 mmol) in THF (5 mL, 0.5 M) and cooled to -78 ^oC followed by the addition of the lithiated ethyl vinyl ether via cannula. The mixture was allowed to stir at -78 ^oC for 1 hour followed by quenching with water, extraction with Et_2O and washing with brine. The organic layer was dried (Na_2SO_4), filtered and concentrated, which following purification by flash chromatography afforded **1o**, as colourless oil (130 mg, 35%)

R_f (20% EtOAc/Hexane) = 0.30; ; IR v_{max} cm^{-1} 3420, 2961, 2866, 1460, 1073; ^1H NMR: (400 MHz, $CDCl_3$) δ 4.10 (1H, d, *J* = 2.0 Hz), 4.03-3.96 (1H, m), 3.94 (1H, d, *J* = 2.0 Hz), 3.76 (2H, q, *J* = 7.0 Hz), 2.18 (1H, d, *J* = 6.3 Hz), 1.68-1.52 (2H, m), 1.49-1.20 (2H, m), 1.30 (3H, t, *J* = 7.0 Hz), 0.93 (3H, t, *J* = 7.0 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 80.8, 72.9, 62.7, 37.8, 18.7, 14.2, 13.8; HRMS (EI+) Calcd. for $C_8H_{14}O$ [M-H_2O] 126.1045. Found 126.1051

2-ethoxy-4-methylpent-1-en-3-ol (1p)

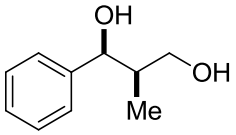


To a 25 mL round bottomed flask equipped with a magnetic stirrer bar and purged with argon was added ethyl vinyl ether (269 mg, 3.73 mmol, 1.2 equiv.) and dry THF (10 mL, 0.4 M) and cooled to -78 ^oC followed by the dropwise addition of *t*-BuLi (1.82 mL, 3.10 mmol, 1.7 M in heptane) and the resulting yellow solution was stirred at -78 ^oC for 30 minutes before being warmed slowly to 0 ^oC. In a separate 50 mL round bottomed flask equipped with a magnetic stirrer bar was added isobutryaldehyde (186 mg , 2.58 mmol) in THF (5 mL, 0.5 M)

and cooled to -78 ^{o}C followed by the addition of the lithiated ethyl vinyl ether via cannula. The mixture was allowed to stir at -78 ^{o}C for 1 hour followed by quenching with water, extraction with Et_2O and washing with brine. The organic layer was dried (Na_2SO_4), filtered and concentrated, which following purification by flash chromatography afforded **1p** as colourless oil (161 mg, 43%)

Rf (20% EtOAc/Hexane) = 0.34; IR Vmax cm^{-} 3356, 2920, 1456, 1114, 762; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.10 (1H, d, *J* = 2.1 Hz), 4.06 (1H, dt, *J* = 8.0, 6.0 Hz), 3.90 (1H, d, *J* = 2.1 Hz), 3.76 (2H, q, *J* = 7.0 Hz), 2.05 (1H, d, *J* = 6.5 Hz), 1.81-1.70 (1H, m), 1.55-1.43 (2H, m) 1.31 (3H, t, *J* = 7.0 Hz), 0.94 (3H, d, *J* - 2.1 Hz), 0.92 (3H, d, *J* = 2.1 Hz), ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 80.5, 71.2, 62.5, 44.1, 24.2, 22.8, 21.8, 13.9; HRMS (EI+) Calcd. for $C_8H_{14}O$ [M-H_2O] 126.1045. Found 126.1044

syn-2-methyl-1-phenylpropane-1,3-diol (2a)

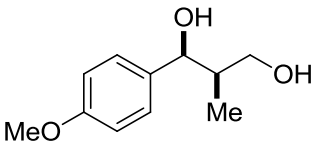


The title compound was prepared following general procedure **C** from 2-methyl-1-phenylprop-2-en-1-ol **1a** (150 mg, 1.01 mmol), $PtCl_2$ (2.7 mg, 10.1 µmol), XPhos (8 mg, 20.2 µmol) and $HSiMe_2NEt_2$ (216 mg, 1.65 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1246 mg, 11 mmol), KF (324mg, 5.5 mmol) and $KHCO_3$ (330mg, 3.3 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2a** as a colourless oil (139 mg, 83%, 96:4 dr)

Rf (50:50 EtOAc/Hexane) = 0.21; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.38-7.23 (5H, m), 4.91 (1H, d, *J* = 2.8 Hz), 3.64 (2H, d, *J* = 5.3 Hz), 3.13 (1H, br s), 2.66 (1H, br s), 2.09 (1H, m), 0.82 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.1, 127.2, 126.1, 76.6, 66.3, 41.3, 10.7. All spectral data are in accordance to that previously reported[7]

[7] O'Neil, G. W.; Miller, M. M.; Carter, K. P. *Org, Lett,* **2010,** *12,* 5350

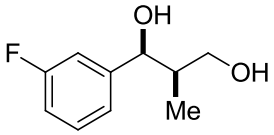
syn-1-(4-methoxyphenyl)-2-methylpropane-1,3-diol (2b)



The title compound was prepared following general procedure **C** from **1b** (80 mg, 0.45 mmol), $PtCl_2$ (1mg, $4.49x10^{-3}$ mmol), XPhos (4 mg, $8.98x10^{-3}$ mmol) and $HSiMe_2NEt_2$ (84 mg, 0.64 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 509 mg, 4.49 mmol), KF (130 mg, 2.25 mmol) and $KHCO_3$ (135mg, 1.35 mmol) in THF:MeOH (1:1, 4 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2b** as a yellow oil (72 mg, 82%, 94:6 dr)

Rf (50:50 EtOAc/Hexane) = 0.22; ; IR Vmax cm^{-1} 3456, 1831, 1430, 1058, 878; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.27-7.21 (2H, m), 6.92-6.84 (2H, m), 4.86 (1H, d, *J* = 4.0 Hz), 3.80 (3H, s), 3.63 (2H, d, *J* = 5.5 Hz), 2.10-1.96 (1H, m), 0.84 (3H, d, *J* = 7.0 Hz) ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 134.6, 127.3, 113.6, 76.6, 66.3, 55.2, 41.4, 11.1 All spectral data are in accordance to that previously reported[8]

syn-1-(3-fluorophenyl)-2-methylpropane-1,3-diol (2c)



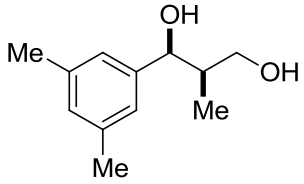
The title compound was prepared following general procedure **C** from **1c** (86 mg, 0.52 mmol), $PtCl_2$ (1.5 mg, $5.2x10^{-3}$ mmol), XPhos (5 mg, 0.01 mmol) and $HSiMe_2NEt_2$ (102 mg, 0.78 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 587 mg, 5.18 mmol), KF (152 mg, 2.60 mmol) and $KHCO_3$ (155mg, 1.55 mmol) in THF:MeOH (1:1, 5 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **5c** as a colourless oil (85 mg, 89%, 94:6 dr)

Rf (50:50 EtOAc/Hexane) = 0.19; IR Vmax cm^- 3345, 2900, 1503, 1030, 957, 614;^1H NMR: (400 MHz, $CDCl_3$) δ 7.33-7.25 (1H, m), 7.10-7.03 (2H, m), 7.00-6.90 (1H, m), 4.95 (1H, d, *J* = 3.5 Hz), 3.71 (1H, dd, *J* = 10.5, 4.2 Hz), 3.65 (1H, dd, *J* = 10.5, 6.5 Hz), 2.08-1.99 (1H, m), 0.81 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (J_{C-F} = 244 Hz), 145.6 (J_{C-F} =

[8] Akita, H.; Chen, C. Y.; Nagumo, S. *J. Chem. Soc. Perk. Trans. 1,* **1995,** 2159.

6.6 Hz), 129.6 ($J_{C\text{-}F}$ = 8.4), 121.6 ($J_{C\text{-}F}$ = 2.9), 113.9 ($J_{C\text{-}F}$ = 21.1 Hz), 113.1 ($J_{C\text{-}F}$ = 21.9 Hz), 75.8 ($J_{C\text{-}F}$ = 1.8 Hz), 66.4, 41.2, 10.3; HRMS (EI+) Calcd. for $C_{10}H_{13}FNaO_2$ $[M+Na]^+$ 207.0797. Found 207.0799.

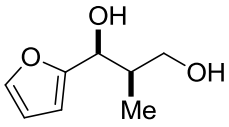
syn-1-(3,5-dimethylphenyl)-2-methylpropane-1,3-diol (2d)



The title compound was prepared following general procedure **C** from **1d** (80 mg, 0.45 mmol), $PtCl_2$ (1 mg, 4.5x10^{-3} mmol), XPhos (4 mg, 9.0x10^{-3} mmol) and $HSiMe_2NEt_2$ (84 mg, 0.64 mmol) in THF (0.9 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 509 mg, 4.50 mmol), KF (130 mg, 2.25 mmol) and $KHCO_3$ (135mg, 1.35 mmol) in THF:MeOH (1:1, 4 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2d** as a colourless oil (75 mg, 86%, 93:7 dr)

Rf (50:50 EtOAc/Hexane) = 0.33; IR Vmax cm^{-1} 3377, 1220, 1150, 723, 699; 503 ^{1}H NMR: (400 MHz, $CDCl_3$) δ 6.92 (2H, br s), 6.89 (1H, br s), 4.83 (1H, d, J = 4.0 Hz), 3.64 (4H, s), 3.63 (1H, s), 2.30 (6H, s), 2.09-1.98 (1H, m), 0.84 (3H, d, J = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.6, 128.8, 123.8, 76.6, 66.4, 41.4, 21.3, 10.8.; HRMS (EI+) Calcd. for $C_{12}H_{18}NaO_2$ $[M+Na]^+$ 217.1204. Found 217.1211.

syn-1-(furan-2-yl)-2-methylpropane-1,3-diol (2e)

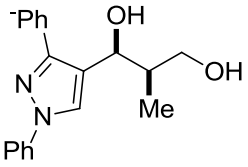


The title compound was prepared following general procedure **C** from **1e** (120 mg, 0.870 mmol), $PtCl_2$ (2 mg, 8.70x10^{-3} mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (171 mg, 1.30 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 985 mg, 8.70 mmol), KF (257 mg, 4.35 mmol) and $KHCO_3$ (261 mg, 2.61 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford the title compound as a dark yellow oil (112 mg, 85%, 85:15 dr)

Rf (50:50 EtOAc/Hexane) = 0.15; IR Vmax cm^{-1} 3390, 1216, 1148, 784, 740; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.39-7.35 (1H, m), 6.37-6.32 (1H, m), 6.28-6.24 (1H, m), 4.88 (1H, d, J = 4.0

Hz), 3.70-3.61 (2H, m), 2.27-2.17 (1H, m), 0.90 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 141.7, 110.1, 106.5, 71.0, 66.0, 39.6, 11.4; HRMS (EI+) Calcd. for $C_7H_9O_3$ $[M\text{-}CH_3]^+$ 141.0552. Found 141.0555.

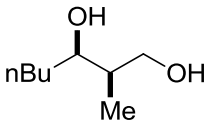
syn-1-(1,3-diphenyl-1H-pyrazol-5-yl)-2-methylpropane-1,3-diol (2f)



The title compound was prepared following general procedure **C** from **1f** (90 mg, 0.31 mmol), $PtCl_2$ (1 mg, $3.1x10^{-3}$ mmol), XPhos (3 mg, $6.2x10^{-3}$ mmol) and $HSiMe_2NEt_2$ (61 mg, 0.47 mmol) in THF (1 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 351 mg, 3.10 mmol), KF (92 mg, 1.55 mmol) and $KHCO_3$ (93 mg, 0.93 mmol) in THF:MeOH (1:1, 3 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **5f** as a colourless oil (82 mg, 85%, 89:11 dr)

Rf (70:30 EtOAc/Hexane) = 0.25; IR Vmax cm^{-1} 3400, 3111, 1222, 1110, 733, 729; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 8.08-8.07 (1H, s), 7.79-7.74 (2H, m), 7.71-7.67 (2H, m), 7.49-7.41 (4H, m), 7.39-7.34 (1H, m), 7.32-7.27 (2H, m), 5.31 (1H, d, *J* = 2.0 Hz), 3.83-.367 (2H, m), 2.06-1.98 (1H, m), 1.58 (1H, br s), 1.30-1.23 (1H, m), 0.92 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.4, 128.6, 128.2, 128.0, 126.5, 126.4, 123.7, 118.9, 69.4, 68.8, 39.9, 10.4.; HRMS (EI+) Calcd. for $C_{13}H_{15}N_2O_2$ $[M\text{-}C_6H_5]^+$ 231.1134. Found 231.1130.

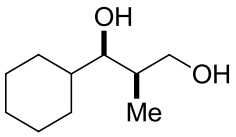
syn-2-methylheptane-1,3-diol (2g)



The title compound was prepared following general procedure **C** from **1g** (95 mg, 0.742 mmol), $PtCl_2$ (2 mg, 7.4 $x10^{-3}$ mmol), XPhos (7 mg, 0.01 mmol) and $HSiMe_2NEt_2$ (146 mg, 1.11 mmol) in THF (1 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 841 mg, 3.10 mmol), KF (219 mg, 3.71 mmol) and $KHCO_3$ (227 mg, 2.26 mmol) in THF:MeOH (1:1, 3 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **5g** as a colourless oil (88 mg, 81%, 87:13 dr)

Rf (50:50 EtOAc/Hexane) = 0.39; ; IR Vmax cm^{-1} 3404, 1933, 1700, 865, 677, ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.85-3.78 (1H, m), 3.66 (1H, d, *J* = 5.3 Hz), 3.45 (1H, s), 3.00 (1H, br s), 1.80-1.65 (1H, m), 1.60-1.21 (6H, m), 0.92 (3H, d, *J* = 7.0 Hz), 0.90 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 74.4 (major),77.3 (minor), 67.5 (minor) 67.0 (major), 50.61 (minor), 39.7 (minor), 39.0 (major), 35.0 (minor) 33.7 (major), 28.4 (major), 27.3 (minor), 22.7 (minor), 22.7 (major), 14.0 (major), 13.9 (minor), 10.0. All spectral data are in accordance to that previously published,[9]

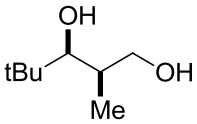
syn-1-cyclohexyl-2-methylpropane-1,3-diol (2h)



The title compound was prepared following general procedure **C** from **1h** (130 mg, 0.84 mmol), $PtCl_2$ (2 mg, $8.44x10^{-3}$ mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (166 mg, 1.27 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 952 mg, 8.4 mmol), KF (244 mg, 4.2 mmol) and $KHCO_3$ (252mg, 2.52 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2h** as a colourless oil (119 mg, 82%, 95:5 dr)

Rf (50:50 EtOAc/Hexane) = 0.33;^{1}H NMR: IR Vmax cm^{-} 3458, 2999, 1647, 1498, 1077, 989; ^{1}H NMR(400 MHz, $CDCl_3$) δ 3.75 (1H, dd, *J* = 10.8, 4.3 Hz), 3.70 (1H, dd, *J* = 10.5, 5.3 Hz), 3.49 (1H, dd, *J* = 8.8, 2.3 Hz), 2.08-2.00 (1H, m), 1.89-1.57 (6H, m), 1.46-1.32 (1H, m), 1.31-1.08 (4H, m), 0.93 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 78.7, 68.0, 40.8, 35.6, 29.6, 29.0, 26.3, 26.0, 25.8, 8.9. All spectral data are in accordance to that previously reported[10]

syn-2,4,4-trimethylpentane-1,3-diol (2i)



The title compound was prepared following general procedure **C** from **2i** (95 mg, 0.742 mmol), $PtCl_2$ (2 mg, $7.4 x10^{-3}$ mmol), XPhos (7 mg, 0.01 mmol) and $HSiMe_2NEt_2$ (146 mg,

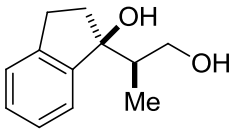
[9] O'Neil, G. W.; Miller, M. M.; Carter, K. P. *Org. Lett.* **2010,** *12,* 5350

[10] (a) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc,* **1990,** *112,* 6339 (b) Christlieb, M.; Davies, J. E.; Eames, J.; Hooley, R.; Warren, S. *J. Chem. Soc., Perkin. Trans. 1.* **2001,** 2983.

1.11 mmol) in THF (1 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 841 mg, 3.10 mmol), KF (219 mg, 3.71 mmol) and $KHCO_3$ (227 mg, 2.26 mmol) in THF:MeOH (1:1, 3 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2i** as a colourless oil (96 mg, 89%, 98:2 dr)

Rf (50:50 EtOAc/Hexane) = 0.37;^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.66 (1H, dd, *J* = 10.3, 4.3 Hz), 3.61 (1H, dd, *J* = 10.3, 5.5 Hz), 3.50 (1H, d, *J* = 1.5 Hz), 1.98-1.89 (1H, m), 1.27 (1H, dd, *J* = 15.0, 7.0 Hz), 1.00 (3H, d, *J* = 7.0 Hz), 0.96 (9H, s).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 80.5, 69.6, 35.5, 35.5 26.8, 10.8. All spectral data are in accordance to that previously reported.[11]

syn-1-hydroxypropan-2-yl)-2,3-dihydro-1H-inden-1-ol (2j)

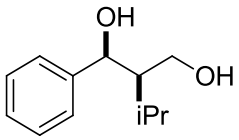


The title compound was prepared following general procedure **C** from **1j** (165 mg, 0.95 mmol), $PtCl_2$ (2.5 mg, 9.5 x^{-10} mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (186 mg, 1.45 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1076 mg, 9.5 mmol), KF (280 mg, 4.75 mmol) and $KHCO_3$ (285 mg, 2.85 mmol) in THF:MeOH (1:1, 5 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2j** as a colourless oil (130 mg, 71%, 62.38 dr)

Rf (50:50 EtOAc/Hexane) = 0.29; IR Vmax cm^{-1}3380, 2974, 1658, 1300, 959.; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.42-7.38 (0.7H, m), 7.36-7.32 (1H, m), 7.30-7.18 (4.9H, m), 3.84 (1H, dd, *J* = 11.0, 8.4 Hz), 3.74-3.68 (1.6 H, m), 3.60 (0.7 H, dd, *J* = 11.0, 4.5 Hz), 3.05 (1H, ddd, *J* = 16.0, 8.8, 5.3 Hz), 2.95-2.88 (0.7 H, m), 2.85-2.75 (1.7 H, m), 2.49-2.32 (2.8 H, m), 2.25-1.99 (2.5 H, m), 0.77 (1.9 H, d, *J* = 7.0 Hz), 0.66 (3H d, 7.0 Hz) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (major), 144.8 (minor), 143.5 (minor), 143.3 (major), 128.5 (major), 128.3 (minor), 126.8 (major), 126.5 (minor), 124.9 (major), 124.6 (minor), 123.0 (major), 83.3 (major), 87.5 (minor), 66.5 (major), 45.9 (minor), 43.1 (minor), 41.7 (major), 40.8 (minor), 34.7 (major), 30.0 (minor), 29.8 (major), 13.0 (major), 11.9 (minor) ; HRMS (EI+) Calcd. for $C_{12}H_{14}O$ [M-H_2O]$^+$ 174.1045. Found 174.1049.

[11] Nishiyama, H.; Kitajima, T.; Matsumoto, M.; Itoh, K. *J. Org. Chem.* **1984,** *49,* 2298

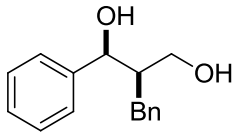
syn-2-isopropyl-1-phenylpropane-1,3-diol (2k)



The title compound was prepared following general procedure **C** from 1k (194 mg, 1.10 mmol), $PtCl_2$ (3 mg, 0.01 mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (216 mg, 1.65 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1246 mg, 11 mmol), KF (324mg, 5.5 mmol) and $KHCO_3$ (330mg, 3.3 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2k** as a colourless oil (171 mg, 80%, 98:2 dr)

Rf (50:50 EtOAc/Hexane) = 0.29; IR Vmax cm^{-1} 3444, 1337, 1150, 801, 722; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.41-7.32 (4H, m), 7.31-7.24 (1H, m), 4.96 (1H, br s), 3.71-3.59 (2H, m), 3.03 (1H, br s), 2.10 (1H, br s), 1.90-1.75 (2H, m), 1.00 (3H, d, *J* = 6.8 Hz), 0.86 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 128.4, 127.6, 126.6, 75.9, 61.5, 52.2, 26.0, 22.3, 19.2; HRMS (EI+) Calcd. for $C_{12}H_{16}O$ $[M-H_2O]^+$ 176.1201. Found 176.1209.

syn-2-benzyl-1-phenylpropane-1,3-diol (2l)

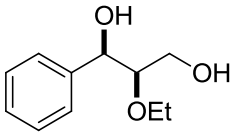


The title compound was prepared following general procedure **C** from **1l** (246 mg, 1.10 mmol), $PtCl_2$ (3 mg, 0.01 mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (216 mg, 1.65 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1246 mg, 11 mmol), KF (324mg, 5.5 mmol) and $KHCO_3$ (330mg, 3.3 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2l** as a colourless oil (205 mg, 77%, 94:6 dr)

Rf (50:50 EtOAc/Hexane) = 0.35; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.40-7.31 (4H, m), 7.30-7.25 (1H, m), 7.23-7.18 (2H, m), 7.14 (1H, d, *J* = 7.4 Hz), 7.05 (2H, d, *J* = 7.0 Hz), 5.03 (1H, d, *J* = 3.8 Hz), 3.57 (2H, d, *J* = 4.0 Hz), 2.61 (1H, dd, *J* = 14.0, 4.8 Hz), 2.55 (1H, dd, *J* = 14.0, 10.5 Hz), 2.20-2.13 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 140.4, 128.0, 128.3, 127.3,

126.1, 125.9, 63.1, 48.4, 30.9. All spectral data are in accordance to that previously reported[12]

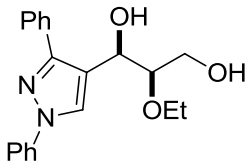
syn-2-ethoxy-1-phenylpropane-1,3-diol (2m)



The title compound was prepared following general procedure **C** from 2-ethoxy-1-phenylprop-2-en-1-ol (155 mg, 0.870 mmol), $PtCl_2$ (2 mg, $8.70x10^{-3}$ mmol), XPhos (8 mg, 0.02 mmol) and $HSiMe_2NEt_2$ (171 mg, 1.30 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 985 mg, 8.70 mmol), KF (257 mg, 4.35 mmol) and $KHCO_3$ (261 mg, 2.61 mmol) in THF:MeOH (1:1, 6 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2m** as a dark yellow oil (122 mg, 70%, 97:3 dr)

Rf (50:50 EtOAc/Hexane) = 0.33; IR Vmax cm^{-1} 3533, 1001, 801, 722, 601; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.41-7.23 (5H, m), 4.74 (1H, d, *J* = 6.3 Hz), 3.72-3.67 (2H, m), 3.56-3.47 (1H, m), 3.45-3.38 (2H, m), 3.12 (1H, br s), 2.17 (1H, br s), 1.21 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 128.4, 127.9, 126.7, 84.0, 73.6, 66.6, 60.8, 15.5; HRMS (EI+) Calcd. for $C_{11}H_{14}O2$ $[M-H_2O]^+$ 178.0994. Found 178.0991.

syn-1-(1,3-diphenyl-1H-pyrazol-5-yl)-2-ethoxypropane-1,3-diol (2n)

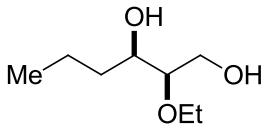


The title compound was prepared following general procedure **C** from **1n** (166 mg, 0.52 mmol), $PtCl_2$ (1.5 mg, $5.2x10^{-3}$ mmol), XPhos (5 mg, 0.01 mmol) and $HSiMe_2NEt_2$ (102 mg, 0.78 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 587 mg, 5.18 mmol), KF (152 mg, 2.60 mmol) and $KHCO_3$ (155mg, 1.55 mmol) in THF:MeOH (1:1, 5 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2n** as a colourless oil (124mg,71% , 98:2 dr)

[12] Faunce, J.; Friebe, T. L.; Grisso, B. A.; Losey, E. N.; Sabat, M.; Mackenzie, P. B. *J. Am. Chem. Soc.,* **1989,** *111,* 4508

Rf (50:50 EtOAc/Hexane) = 0.11; IR Vmax cm^{-1} 3422, 1933, 1800, 1011, 998, 752, 699; ^1H NMR: (400 MHz, $CDCl_3$) δ 8.08 (1H, s), 7.80-7.75 (2H, m), 7.75-7.71 (2H, m), 7.46-7.39 (4H, m) 7.38-7.32 (1H, m), 7.30-7.25 (1H, m), 4.98 (1H, d, *J* = 5.5 Hz), 3.77-3.67 (2H, m), 3.57-3.47 (3H, m), 3.18 (1H, br s), 2.20 (1H, br s), 1.20 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 139.9, 133.0, 129.4, 128.5, 128.5, 128.1, 127.0, 126.5, 120.9, 119.0, 82.1, 66.4, 66.2, 61.3, 15.5; HRMS (EI+) Calcd. $C_{20}H_{21}N_2O_3$ $[M]^+$ 338.1630. Found 321.1606

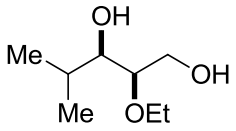
syn-2-ethoxyhexane-1,3-diol (2o)



The title compound was prepared following general procedure **C** from **1o** (228 mg, 1.58 mmol), $PtCl_2$ (4mg, 0.016 mmol), XPhos (15 mg, 0.032 mmol) and $HSiMe_2NEt_2$ (310 mg, 2.37 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1790 mg, 15.8 mmol), KF (466 mg, 7.90 mmol) and $KHCO_3$ (474 mg, 4.74mmol) in THF:MeOH (1:1, 7 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2o** as a colourless oil (204 mg, 80%, 98:2 dr)

Rf (50:50 EtOAc/Hexane) = 0.21; IR Vmax cm^{-1} 3425, 1857, 1756, 1477, 1058, 933; ^1H NMR: (400 MHz, $CDCl_3$) δ 3.91-3.51 (5H, m), 3.22 (1H, dd, *J* = 5.0, 4.5 Hz), 2.33 (1H, d, *J* = 4.5 Hz), 2.07 (1H, br s), 1.63-1.33 (5H, m), 1.24 (3H, t, *J* = 7.0 Hz), 0.95 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.9, 71.4, 66.4, 61.8, 35.6, 18.9, 15.6, 14.0; HRMS (EI+) Calcd. for $C_8H_{18}O_3$ $[M]^+$ 162.1256. Found 162.1257.

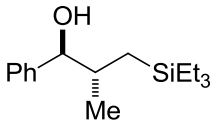
syn-2-ethoxy-4-methylpentane-1,3-diol (2p)



The title compound was prepared following general procedure **C** from **1p** (251 mg, 1.58 mmol), $PtCl_2$ (4mg, 0.016 mmol), XPhos (15 mg, 0.032 mmol) and $HSiMe_2NEt_2$ (310 mg, 2.37 mmol) in THF (1.5 mL) which following conversion to the cyclic ether, was subjected to the oxidation conditions using H_2O_2 (30%, 1790 mg, 15.8 mmol), KF (466 mg, 7.90 mmol) and $KHCO_3$ (474 mg, 4.74mmol) in THF:MeOH (1:1, 7 mL). Following conversion to the diol, the mixture was chromatographed (50:50 EtOAc/Hexane) to afford **2p** as a colourless oil (241 mg, 88%, >99:1 dr)

Rf (50:50 EtOAc/Hexane) = 0.23; IR Vmax cm^{-1} 3357, 1997, 1574, 1400, 1158, 1000, 843, 709; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.88-3.54 (5H, m), 3.19 (1H, q, *J* = 4.6 Hz), 2.31 (1H, br s), 2.12 (1H, br s), 1.93-1.80 (1H, m), 1.49 (1H, ddd, *J* = 13.8, 9.8, 4.8 Hz), 1.25 (3H, t, *J* = 7.0 Hz), 0.96 (3H, d, *J* = 6.5 Hz), 0.93 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 82.3, 69.8, 66.4, 61.8, 42.6, 24.5, 23.7, 21.7, 15.6. HRMS (EI+) Calcd. for $C_8H_{18}O_3$ $[M]^+$ 162.1256. Found 162.1257.

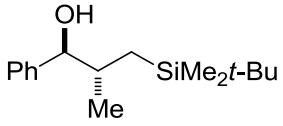
anti-2-methyl-1-phenyl-3-(triethylsilyl)propan-1-ol (3a)



To a 5 mL round bottomed flask was added $PtCl_2$ (3 mg, 0.01 mmol) and XPhos (10 mg, 0.02 mmol) and quickly purged with argon before adding anhydrous THF (1 mL) and stirring at 50 ^{o}C for 30 minutes until a yellow homogenous mixture was obtained. 2-methyl-1-phenylprop-2-en-1-ol (150 mg, 1.01 mmol) and triethylsilane (198 mg, 1.52 mmol) was then added dropwise and the solution was stirred at 50 ^{o}C overnight. The mixture was concentrated en vacuo and applied directly to the top of a silica column and chromatographed (20% EtOAc/Hexane) to afford **3a** as a light yellow oil (229 mg, 86%, 87:13 d.r.)

Rf (50:50 EtOAc/Hexane) = 0.49; IR Vmax cm^{-1} 3390, 2947, 1864, 1703, 1178, 1100, 987; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.33-7.19 (5H, m), 4.31 (1H, d, *J* = 6.0 Hz), 2.15 (1H, br s), 1.97-1.85 (2H, m), 0.89 (9H, t, *J* = 7.9 Hz), 0.82 (3H, d, *J* = 6.8 Hz), 0.50 (6H, q, *J* = 7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ143.6, 127.9, 127.1, 126.5, 80.7, 36.5, 18.9, 13.6, 7.3, 3.9; HRMS (EI+) Calcd. for $C_{16}H_{28}OSi$ $[M]^+$ 264.1909. Found 264.1905.

anti-3-(tert-butyldimethylsilyl)-2-methyl-1-phenylpropan-1-ol (3b)

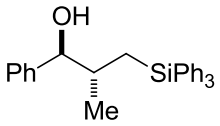


To a 5 mL round bottomed flask was added $PtCl_2$ (3 mg, 0.01 mmol) and XPhos (10 mg, 0.02 mmol) and quickly purged with argon before adding anhydrous THF (1 mL) and stirring at 50 ^{o}C for 30 minutes until a yellow homogenous mixture was obtained. 2-methyl-1-phenylprop-2-en-1-ol (150 mg, 1.01 mmol) and *tert*-butyldimethylsilane (176 mg, 1.52 mmol) was then added dropwise and the solution was stirred at 50 ^{o}C overnight. The mixture was

concentrated en vacuo and applied directly to the top of a silica column and chromatographed (10% EtOAc/Hexane) to afford **3b** as a colourless oil (218 mg, 82%, 90:10 d.r.)

Rf (50:50 EtOAc/Hexane) = 0.52; IR Vmax cm^{-1} 3357, 2899, 1680, 1230, 977; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.57-7.45 (5H, m), 4.60 (1H, d, *J* = 6.0 Hz), 2.25-2.09 (2H, m), 1.06 (9H, s), 1.03 (2H, d, *J* = 11.3 Hz), 0.18 (3H, s), 0.15 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.6, 128.1, 126.6, 80.8, 38.8, 26.5, 19..1, 16.6, 14.5, -4.5, -6.2; HRMS (EI+) Calcd. for $C_{16}H_{28}OSi$ $[M]^+$ 264.1909. Found 264.1910.

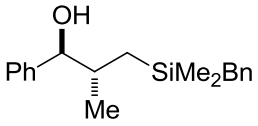
2-methyl-1-phenyl-3-(triphenylsilyl)propan-1-ol (3c)



To a 5 mL round bottomed flask was added $PtCl_2$ (3 mg, 0.01 mmol) and XPhos (10 mg, 0.02 mmol) and quickly purged with argon before adding anhydrous THF (1 mL) and stirring at 50 ^{o}C for 30 minutes until a yellow homogenous mixture was obtained. 2-methyl-1-phenylprop-2-en-1-ol (150 mg, 1.01 mmol) and triphenylsilane (397 mg, 1.52 mmol) was then added dropwise and the solution was stirred at 50 ^{o}C overnight. The mixture was concentrated en vacuo and applied directly to the top of a silica column and chromatographed (20% EtOAc/Hexane) to afford **3c** as a colourless oil which solidified upon standing (293 mg, 71%, 53:47 d.r.)

Rf (50:50 EtOAc/Hexane) = 0.42; IR Vmax cm^{-1} 3423, 2953, 2847, 1462, 1015, 762; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.91-3.51 (5H, m), 3.22 (1H, dd, *J* = 5.0, 4.5 Hz), 2.33 (1H, d, *J* = 4.5 Hz), 2.07 (1H, br s), 1.63-1.33 (5H, m), 1.24 (3H, t, *J* = 7.0 Hz), 0.95 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 81.9, 71.4, 66.4, 61.8, 35.6, 18.9, 15.6, 14.0; HRMS (ES+) Calcd. for $C_{28}H_{29}OSi$ $[M+H]^+$ 409.1988. Found 409.1989

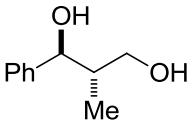
(1S,2R)-3-(benzyldimethylsilyl)-2-methyl-1-phenylpropan-1-ol (3d)



To a 5 mL round bottomed flask was added $PtCl_2$ (4.2 mg, 0.01 mmol) and XPhos (14.8 mg, 0.03 mmol) and quickly purged with argon before adding anhydrous THF (1.5 mL) and stirring at 50 ^oC for 30 minutes until a yellow homogenous mixture was obtained. 2-methyl-1-phenylprop-2-en-1-ol (231 mg, 1.56 mmol) and benzyldimethylsilane (351 mg, 2.34 mmol) was then added dropwise and the solution was stirred at 50 ^oC overnight. The mixture was concentrated en vacuo and applied directly to the top of a silica column and chromatographed (10% EtOAc/Hexane) to afford **3d** as a dark yellow oil (311 mg, 67%, 60:40 d.r.)

Rf (50:50 EtOAc/Hexane) = 0.39; IR Vmax cm^{-1} 3433, 2290, 2807, 1399, 762; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.40-6.92 (16.6 H, m), 4.43 (0.6H, dd, *J* = 5.1, 2.8 Hz, minor), 4.36 (1H, dd, *J* = .6.2, 3.2, minor), 2.07 (2H, s, major), 2.04 (1.2H, s, minor), 2.01 - 1.88 (1.6H, m, major+minor), 0.94 (1.8H, d, *J* = 6.6, minor), 0.84 (3H, d, *J* = 6.6, major), 0.71 (0.2 H, d, *J* = 3.4 Hz), 0.65 (0.3H, d, *J* = 3.4 Hz), 0.43-0.30 (2.6 H, m), 0.01- -0.03 (9.5 H, m, major+minor)^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 140.2 (minor), 140.1 (major), 128.2 (minor), 128.1 (major), 128.1 (major), 128.1 (minor), 128.1, 127.4 (minor), 127.3 (major), 126.6 (minor), 126.6 (major), 123.9 (major), 123.9 (minor) 80.7 (minor), 80.4 (major), 36.7 (minor), 36.5 (major), 26.3 (minor), 26.2 (major), 19.0 (minor), 18.9 (major), 17.7 (minor), 17.5 (major), -2.4 (minor), -2.4 (major), -2.8 (minor), -2.8 (major) ; HRMS (ES+) Calcd. for $C_{19}H_{26}OSi$ $[M]^+$ 298.1753 Found 298.1755

***anti*-2-methyl-1-phenylpropane-1,3-diol (4a)**

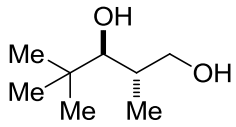


To a 5 mL round bottomed flask was added 2-methyl-1-phenylprop-2-en-1-ol (90 mg, 0.608 mmol), $PtCl_2$ (2 mg, $6.1x10^{-3}$ mmol) and 2-Dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (SPhos) (5 mg, 0.01 mmol) and purged with argon. Anhydrous THF (1 mL) was then added and the mixture was stirred at 50 ^oC for 30 minutes after which benzyldimethylsilane (137 mg, 0.912 mmol) and the mixture stirred at 50 ^oC overnight. The reaction was then filtered through a small pad of celite, washed with DCM (10 mL) and concentrated. The residue was redissolved in THF (10 mL, 0.06 M) followed the addition of TBAF (4.6 mL, 4.56 mmol, 7.5

equiv.) and stirred at room temperature for 20 minutes. Methanol (4.3 mL, 0.14) was then added to the solution and cooled to 0 ^{o}C, followed by the sequential addition of $KHCO_3$ (231 mg, 2.31 mmol, 3.8 equiv) and H_2O_2 (1.2 mL, 37%wt, 20 equiv) and the mixture stirred at room temperature for 3 hours. Solid sodium thiosulphate was then added to the mixture and stirred for a further 30 minutes before being diluted with water (5 mL), extracted with EtOAc (3 x 10 mL), and dried with Na_2SO_4. Purification by flash chromatography (50:50 EtOAc/Hexane) afforded **4a** as a colourless oil (83 mg, 82%, 62:38 d.r.)

Rf (50:50 EtOAc/Hexane) = 0.23; ^{1}H NMR: (400 MHz, $CDCl_3$) δ) 7.38-7.22 (8.3H, m, major + minor), 4.94 (0.6H, d, *J* = 3.8 Hz, minor), 4.53 (1H, d, *J* = 8.5 Hz), 3.81-3.62 (4.2 H, m, major + minor), 2.11-1.97 (1.6 H, m, major + minor), 0.84 (1.8 H, d, *J* = 7.0 Hz, minor), 0.68 (3H, d, *J* = 7.0 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3 (major), 142.6 (minor), 128.5 (major), 128.1 (minor), 127.2 (minor), 127.8 (major), 126.7 (major), 126.1 (minor), 80.9 (major), 76.6 (minor), 68.1 (major), 66.3, 41.6 (major), 41.3 (minor), 13.8 (major) 10.7 (minor); All spectral data are consistent with that previously reported[13]

anti-2,4,4-trimethylpentane-1,3-diol (4b)

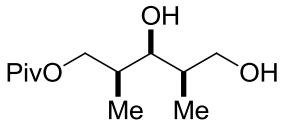


To a 5 mL round bottomed flask was added **1i** (131 mg, 1.02 mmol), $PtCl_2$ (5 mg, 0.02 mmol) and SPhos (16 mg, 0.04 mmol) and purged with argon. Anhydrous THF (1.5 mL) was then added and the mixture was stirred at 50 ^{o}C for 30 minutes after which benzyldimethylsilane (306 mg, 2.04 mmol) and the mixture stirred at 50 ^{o}C overnight. The reaction was then filtered through a small pad of celite, washed with DCM (10 mL) and concentrated. The residue was redissolved in THF (17 mL, 0.06 M) followed the addition of TBAF (7.65 mL, 7.65 mmol, 7.5 equiv.) and stirred at room temperature for 20 minutes. Methanol (7.3 mL, 0.14 M) was then added to the solution and cooled to 0 ^{o}C, followed by the sequential addition of $KHCO_3$ (388 mg, 3.88 mmol, 3.8 equiv) and H_2O_2 (1.9 mL, 30%wt, 20 equiv) and the mixture stirred at room temperature for 3 hours. Solid sodium thiosulphate was then added to the mixture and stirred for a further 30 minutes before being diluted with water (5 mL), extracted with EtOAc (3 x 10 mL), and dried with Na_2SO_4. Purification by flash chromatography (50:50 EtOAc/Hexane) afforded **4b** as a colourless solid (107 mg, 72%, 95:5 d.r.)

[13] Pietruszka, J.; Schöne, N.; *Eur. J. Org. Chem.* **2004,** 5011

Rf (50:50 EtOAc/Hexane) = 0.29; ^{1}H NMR: (400 MHz, $CDCl_3$) δ 3.84-3.78 (1H, m), 3.69-.3.61 (2H, m), 3.25 (1H, d, *J* = 4.8 Hz), 1.97-1.89 (1H, m), 1.05 (3H, d, *J* = 7.0 Hz), 0.96 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 85.0, 66.6, 35.9, 35.3, 26.0, 18.3. All spectral data are in accordance to that previously reported [14]

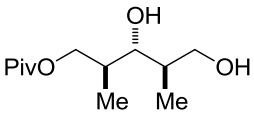
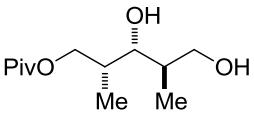
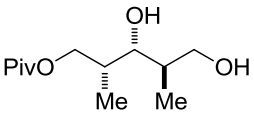
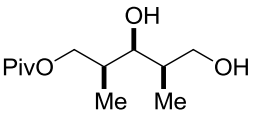
(2S,3S,4R)-3,5-dihydroxy-2,4-dimethylpentyl pivalate (6)



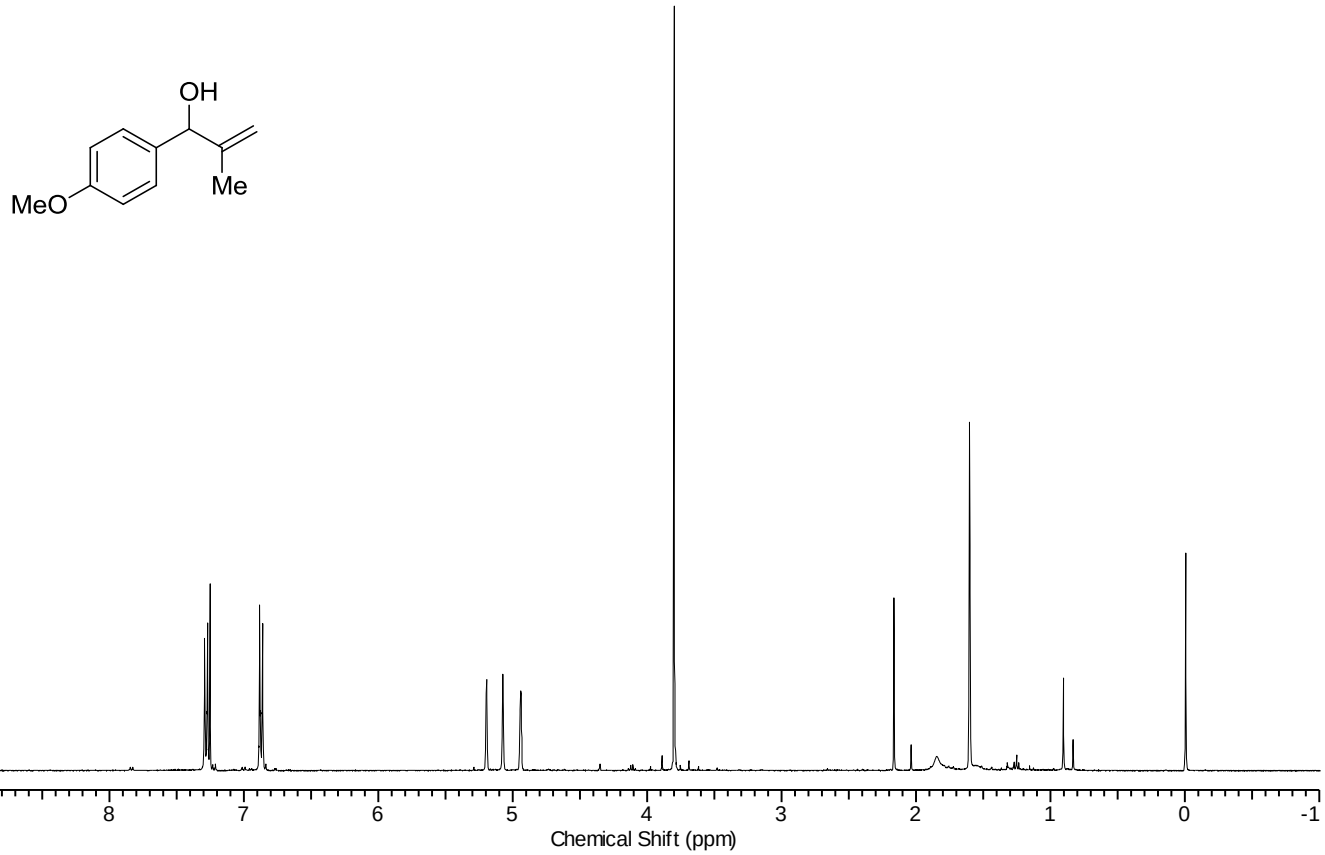
To a 5 mL round bottomed flask was added (2S,3R)-3-hydroxy-2,4-dimethylpent-4-en-1-yl pivalate (30 mg, 0.14 mmol), $PtCl_2$ (0.4 mg, 1.4 x10^{-3} mmol), and XPhos (1.3 mg, 2.8 x10^{-3} mmol) and flushed with argon. Anhydrous THF was then added and the mixture stirred at 50^{o}C for 30 minutes after which $HSiMe_2NEt_2$ (28 mg, 0.21 mmol) was added and the mixture stirred at 50^{o}C overnight. The reaction was then filtered through a small pad of celite, washed with DCM (10 mL) and concentrated. The residue was redissolved in THF (2.3 mL, 0.06 M) followed the addition of TBAF (1.1 mL, 1.05 mmol, 7.5 equiv.) and stirred at room temperature for 20 minutes. Methanol (1 mL, 0.14 M) was then added to the solution and cooled to 0 ^{o}C, followed by the sequential addition of $KHCO_3$ (53 mg, 0.53 mmol, 3.8 equiv) and H_2O_2 (0.32 mL, 30%wt, 20 equiv) and the mixture stirred at room temperature for 3 hours. Solid sodium thiosulphate was then added to the mixture and stirred for a further 30 minutes before being diluted with water (5 mL), extracted with EtOAc (3 x 10 mL), and dried with Na_2SO_4. Purification by flash chromatography (50:50 EtOAc/Hexane) afforded **6** as a colourless oil (24 mg, 74%, 93:7 d.r.)

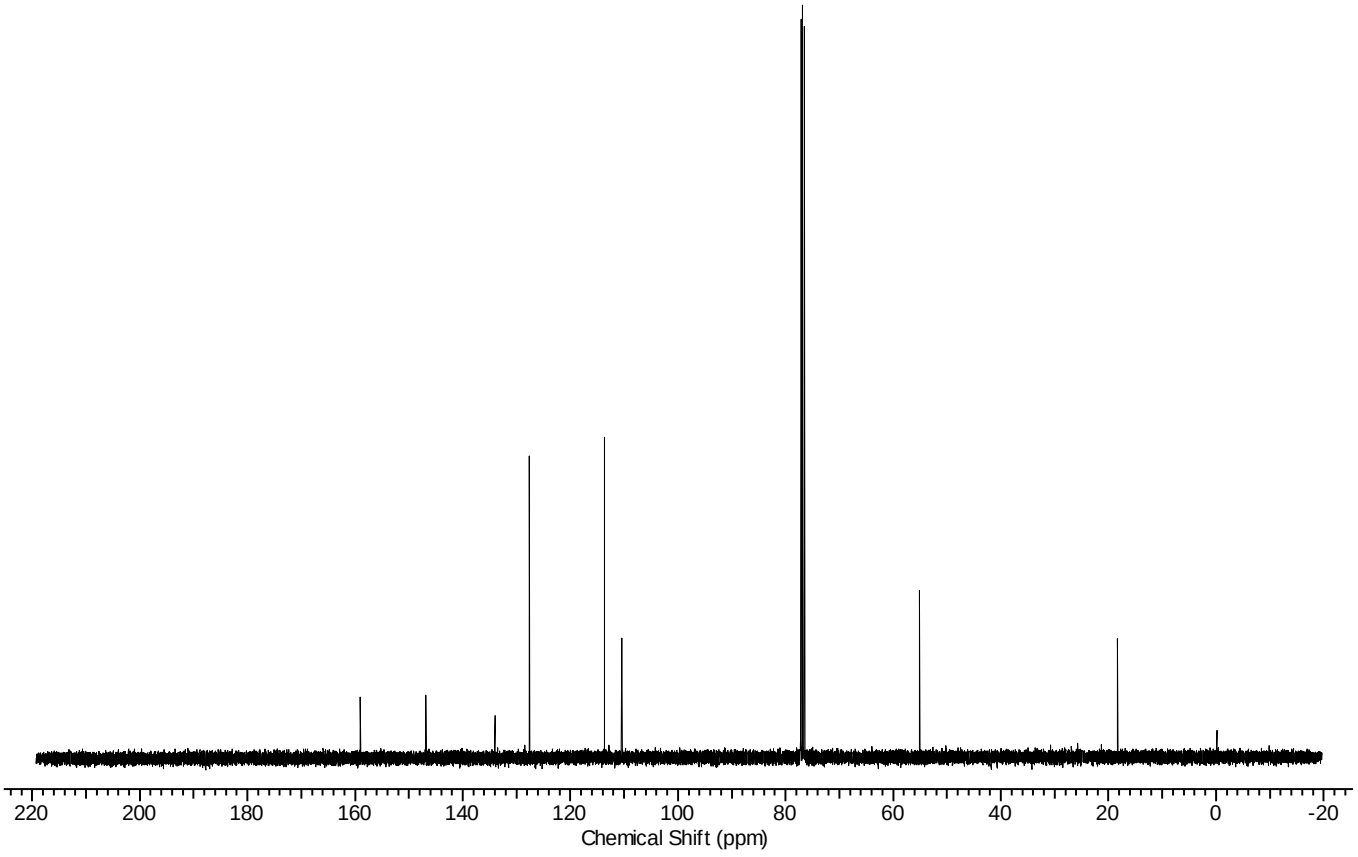
Rf (50:50 EtOAc/Hexane) = 0.33; $[\alpha]_D^{20}$ -15.8 (*c* = 0.26, $CHCl_3$) ; IR Vmax cm^{-1} 3401, 1866, 1499, 1200, 849 ^{1}H NMR: (400 MHz, $CDCl_3$) δ 4.10 (1H, dd, *J*= 10.8, 5.8 Hz), 3.94 (1H, dd, *J* = 11.0, 5.8 Hz), 3.70 (1H, d, *J* = 4.8 Hz), 3.67 (1H, dd, *J* = 6.5, 4.5 Hz), 2.02-1.96 (2H, m), 1.87-1.79 (1H, m), 1.23 (9H, s), 1.06 (3H, d, *J* = 6.9 Hz), 1.03 (3H, d, *J* = 6.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 77.2, 74.8, 67.1, 37.2, 36.5, 27.5, 13.0, 10.8; HRMS (EI+) Calcd. for $C_{12}H_{23}O_4$ $[M]^+$ 232.1675 Found 232.1677

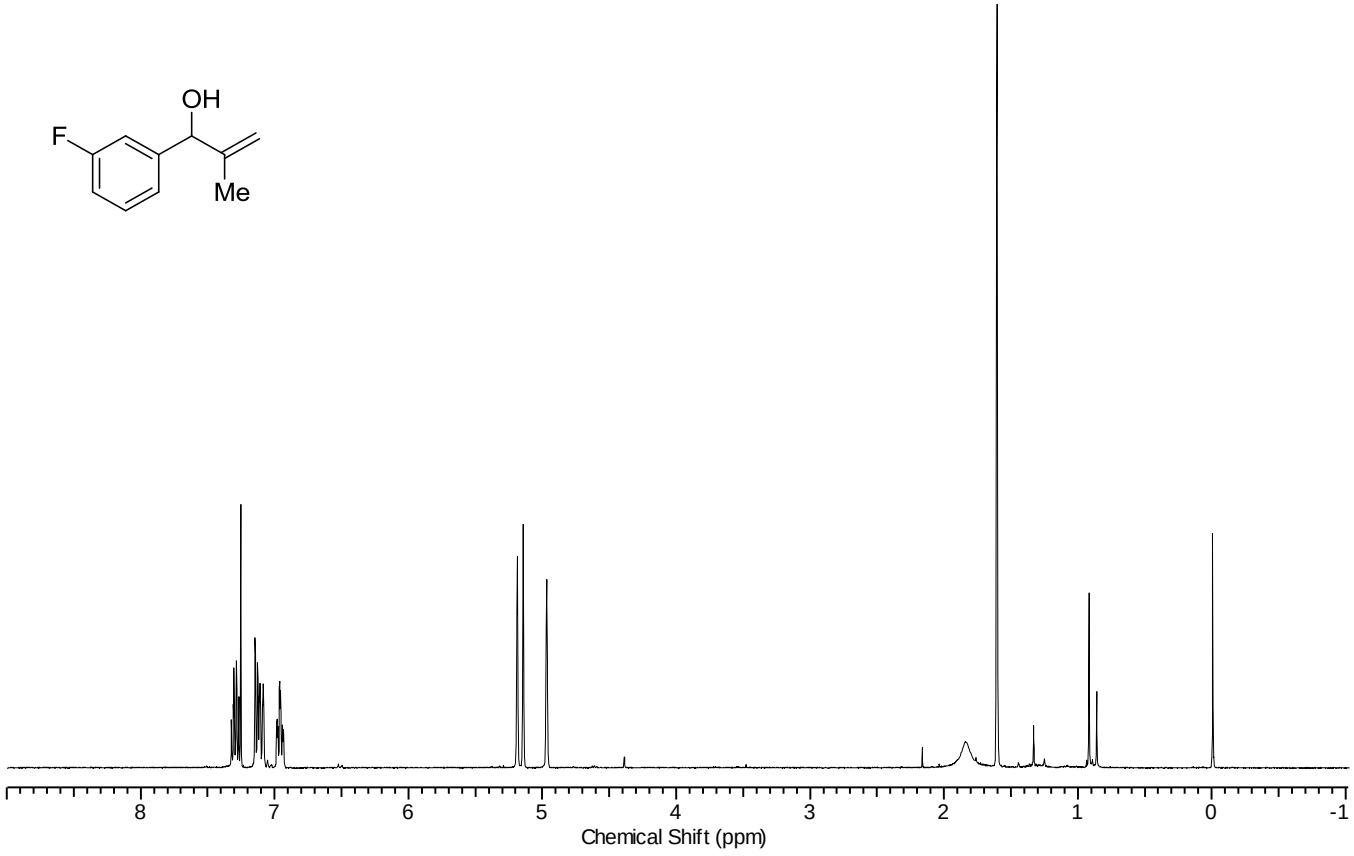
[14] Roush, W. R.; Ando, K.; Powers, D.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc,* **1990,** *112,* 6339.

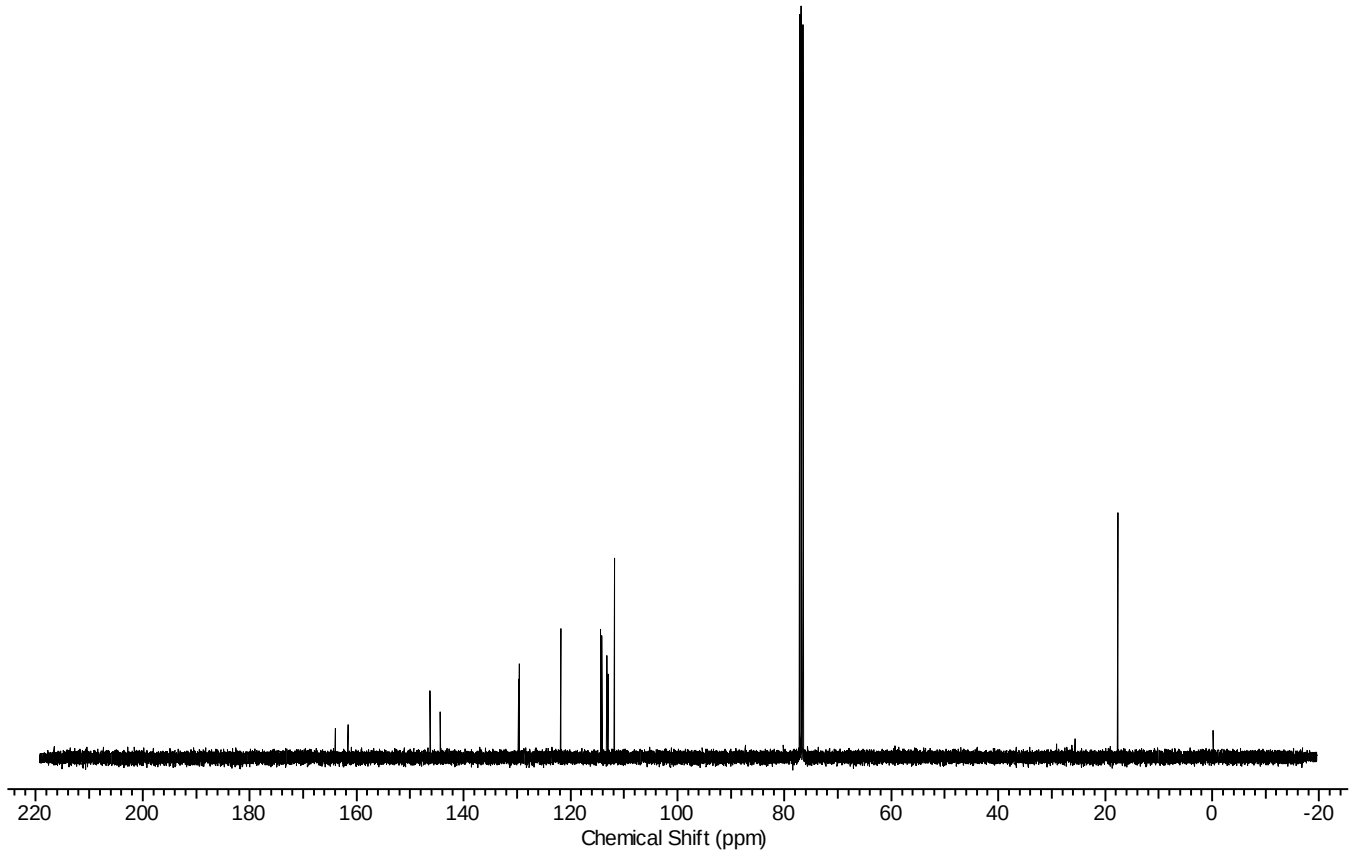
Reported Diastereomeric Forms (Cossy *Org. Lett.* 2001, 3, 2567)			Our Data
(2S*,3R*,4R*)-4'a	**(2R*,3S*,4R*)-4'b**	**(2S*,3R*,4S*)-4'c**	**(2S,3S,4R)-6**
			
^{1}H NMR (300 MHz, $CDCl_3$)	**^{1}H NMR (300 MHz, $CDCl_3$)**	**^{1}H NMR (300 MHz, $CDCl_3$)**	**^{1}H NMR (400 MHz, $CDCl_3$)**
4.22 (1H, dd, *J* = 11.0, 4.8 Hz)	4.25 (1H, dd, *J* = 11.0, 8.5 Hz)	4.35 (1H, dd, *J* = 11.0, 5.2 Hz)	4.10 (1H, dd, *J* = 10.8, 5.8 Hz)
4.13 (1H, dd, *J* = 11.0, 6.2 Hz)	3.91 (1H, dd, *J* = 11.0, 5.5 Hz)	4.09 (1H, dd, *J* = 11.0, 3.7 Hz)	3.94 (1H, dd, *J* = 11.0, 5.8 Hz)
3.84 (1H, dd, *J* = 10.8, 3.4 Hz)	3.78-3.60 (2H, m)	3.78-3.60 (2H+OH, m)	3.70 (1H, d, *J* = 4.8 Hz)
3.61 (1H, dd, *J* = 10.8, 6.3 Hz)	3.47 (1H, dd, *J* = 9.2, 2.2 Hz)	3.56 (1H, dd, *J* = 9.7, 2.0 Hz)	3.67 (1H, dd, *J* = 6.5, 4.5 Hz)
1.02 (3H, d, *J* = 7.0 Hz)	0.91 (3H, d, *J* = 7.0 Hz)	0.95 (3H, d, *J* = 7.0 Hz)	1.06 (3H, d, *J* = 6.9 Hz)
1.00 (3H, d, *J* = 7.0 Hz)	0.79 (3H, d, *J* = 7.0 Hz)	0.91 (3H, d, *J* = 7.0 Hz)	1.03 (3H, d, *J* = 6.9 Hz)
^{13}C NMR (75 MHz, $CDCl_3$)	**^{13}C NMR (75 MHz, $CDCl_3$)**	**^{13}C NMR (75 MHz, $CDCl_3$)**	**^{13}C NMR (100 MHz, $CDCl_3$)**
179.0	179.3	179.4	179.0
79.4	76.4	74.5	77.2
66.8	68.6	67.5	74.8
66.0	66.7	67.0	67.1
38.9	38.8	38.9	38.9
36.5	36.9	36.7	37.2
36.0	35.2	35.7	36.5
27.2	27.2	27.2	27.5
14.7	13.4	13.7	13.0
14.5	8.9	8.5	10.8

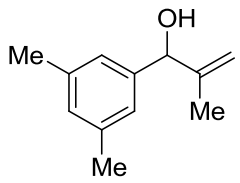
Copies of ^{1}H / ^{13}C Spectra


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

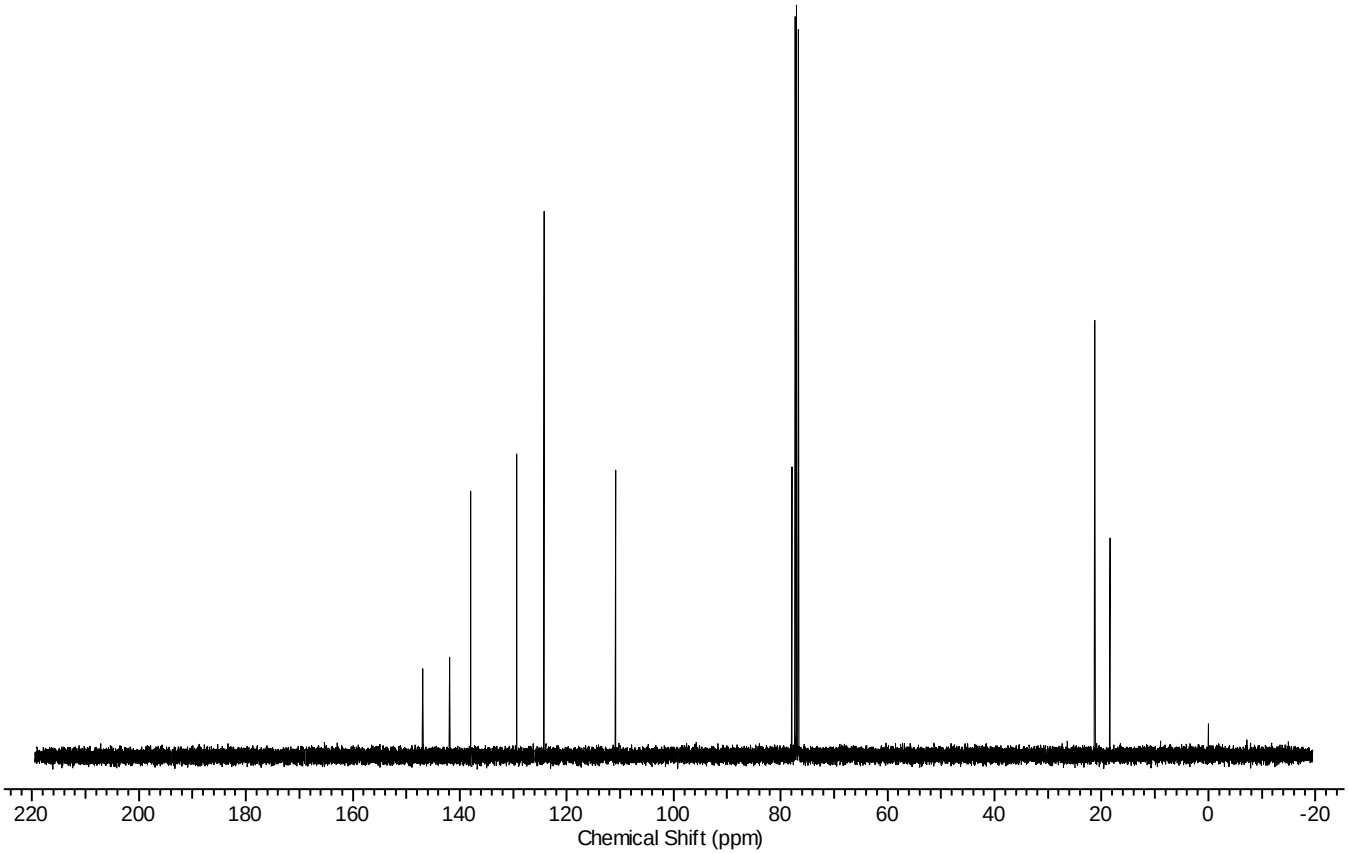

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

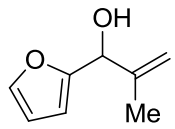

OH
F
Me
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

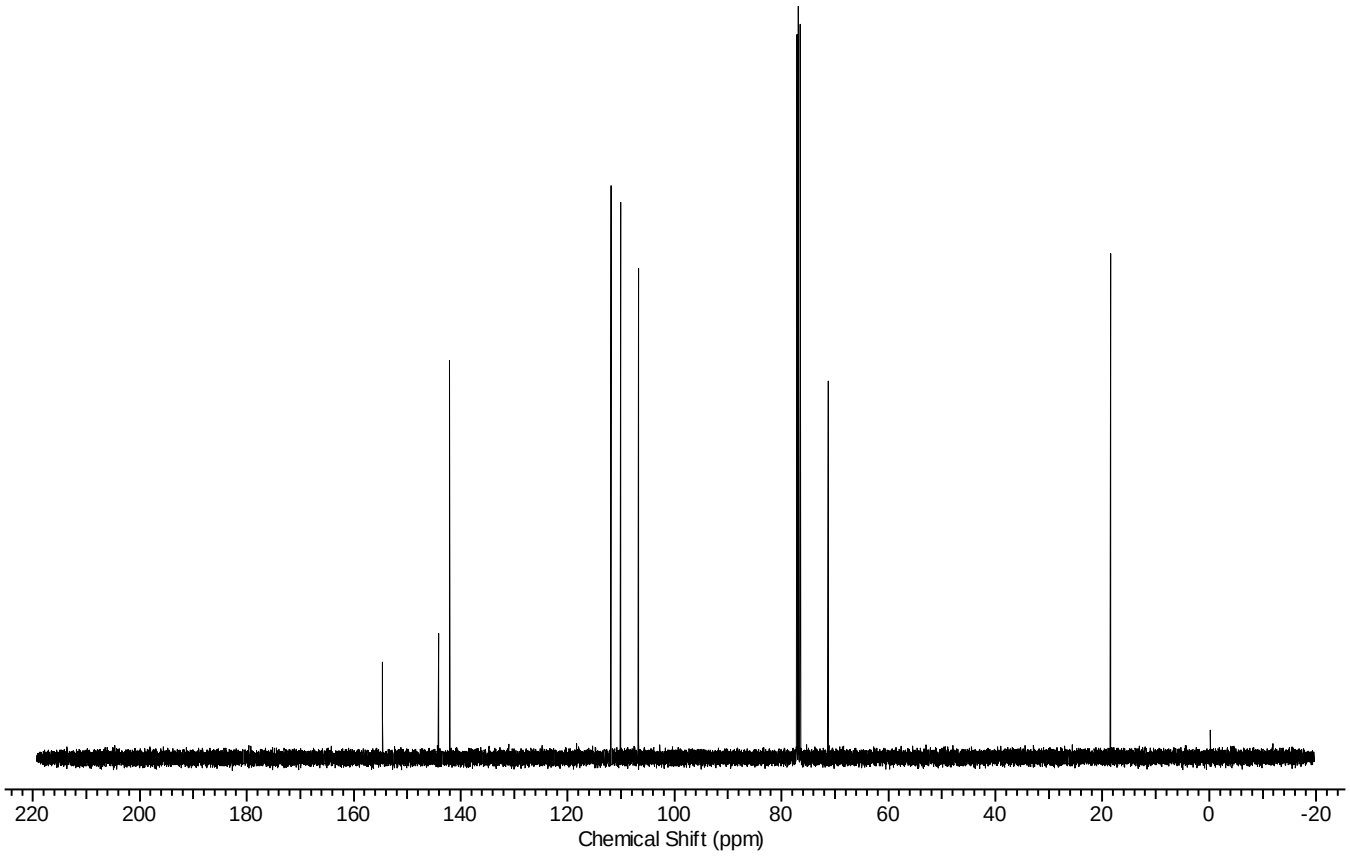

OH
Me
Me
Me

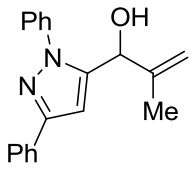
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

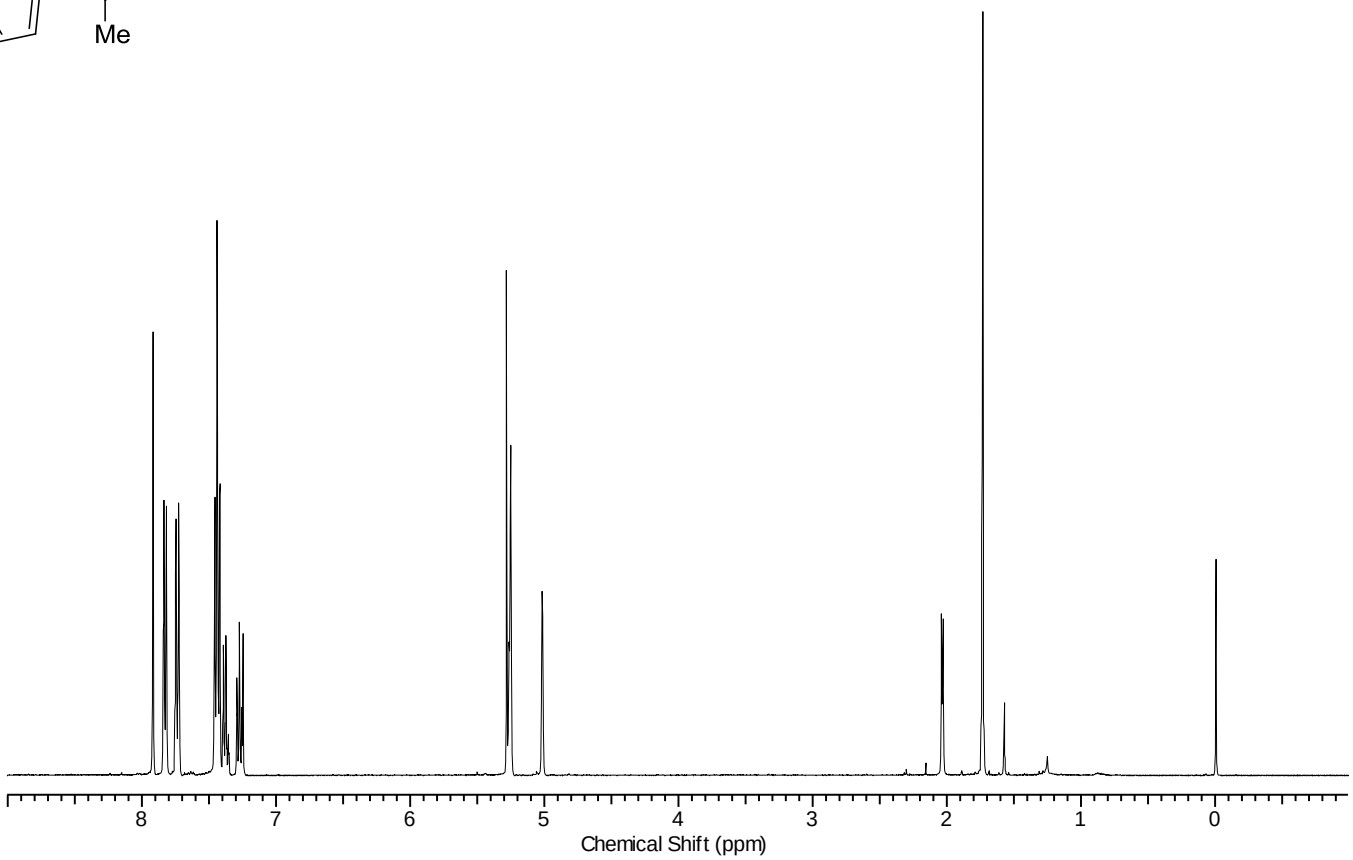

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

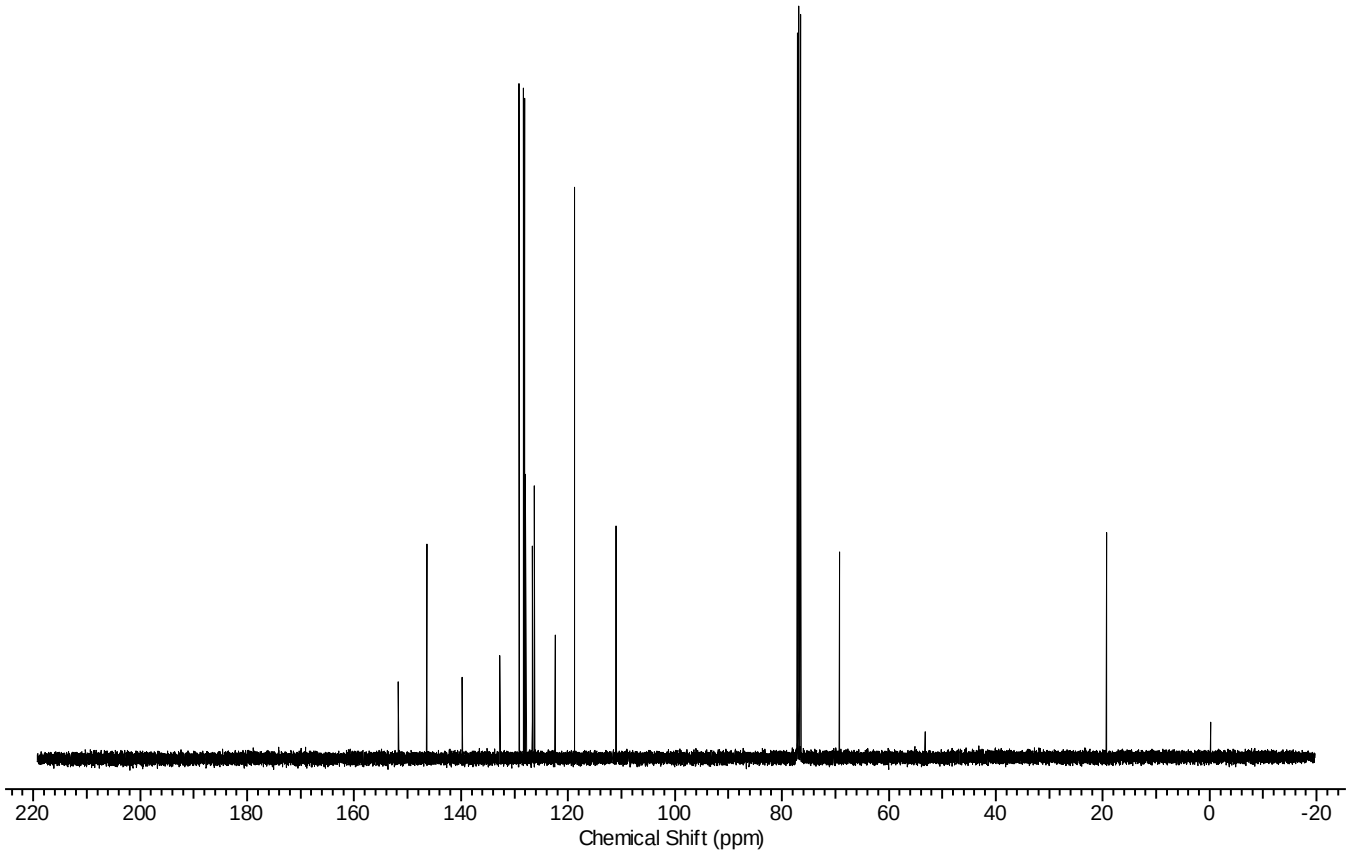

OH
O
Me

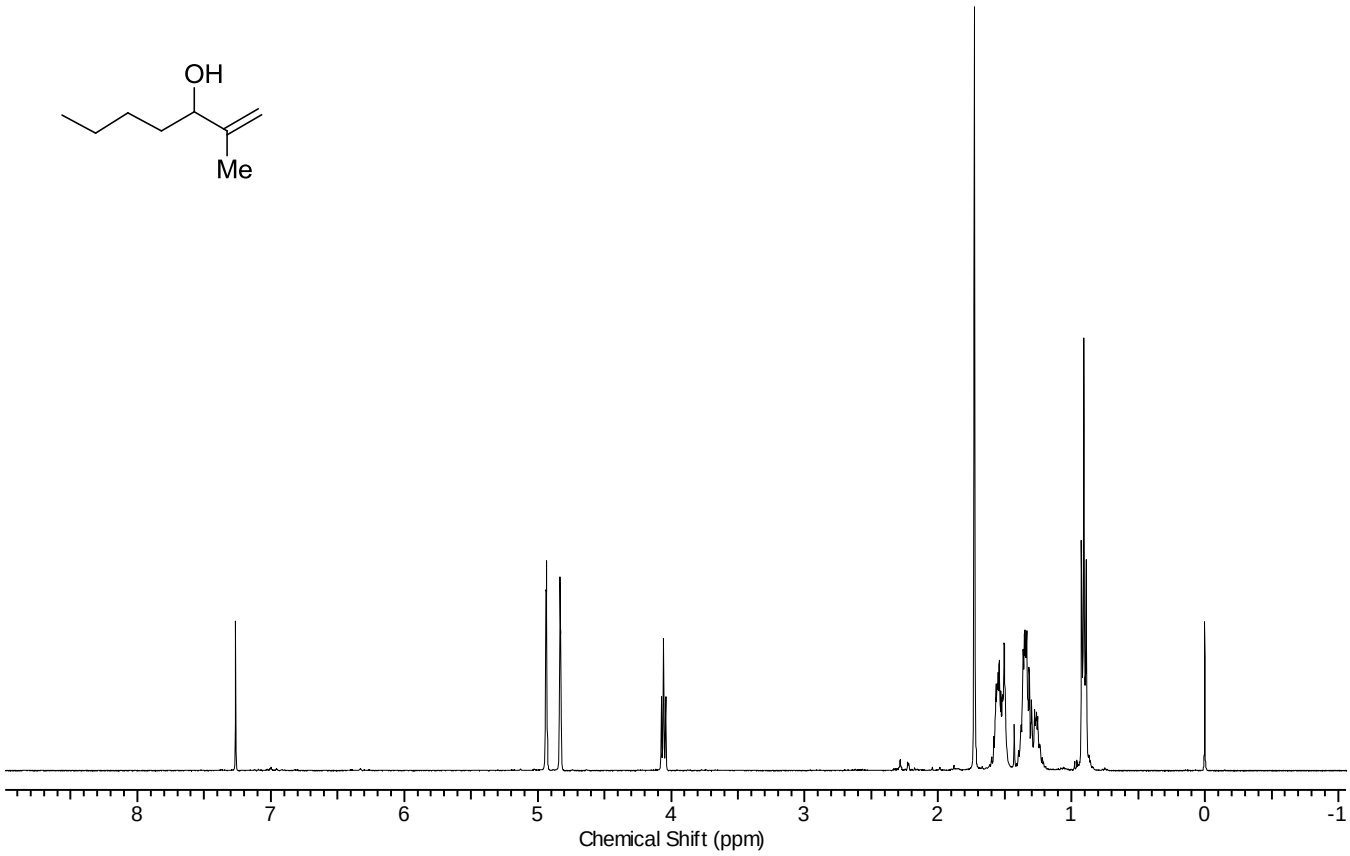
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

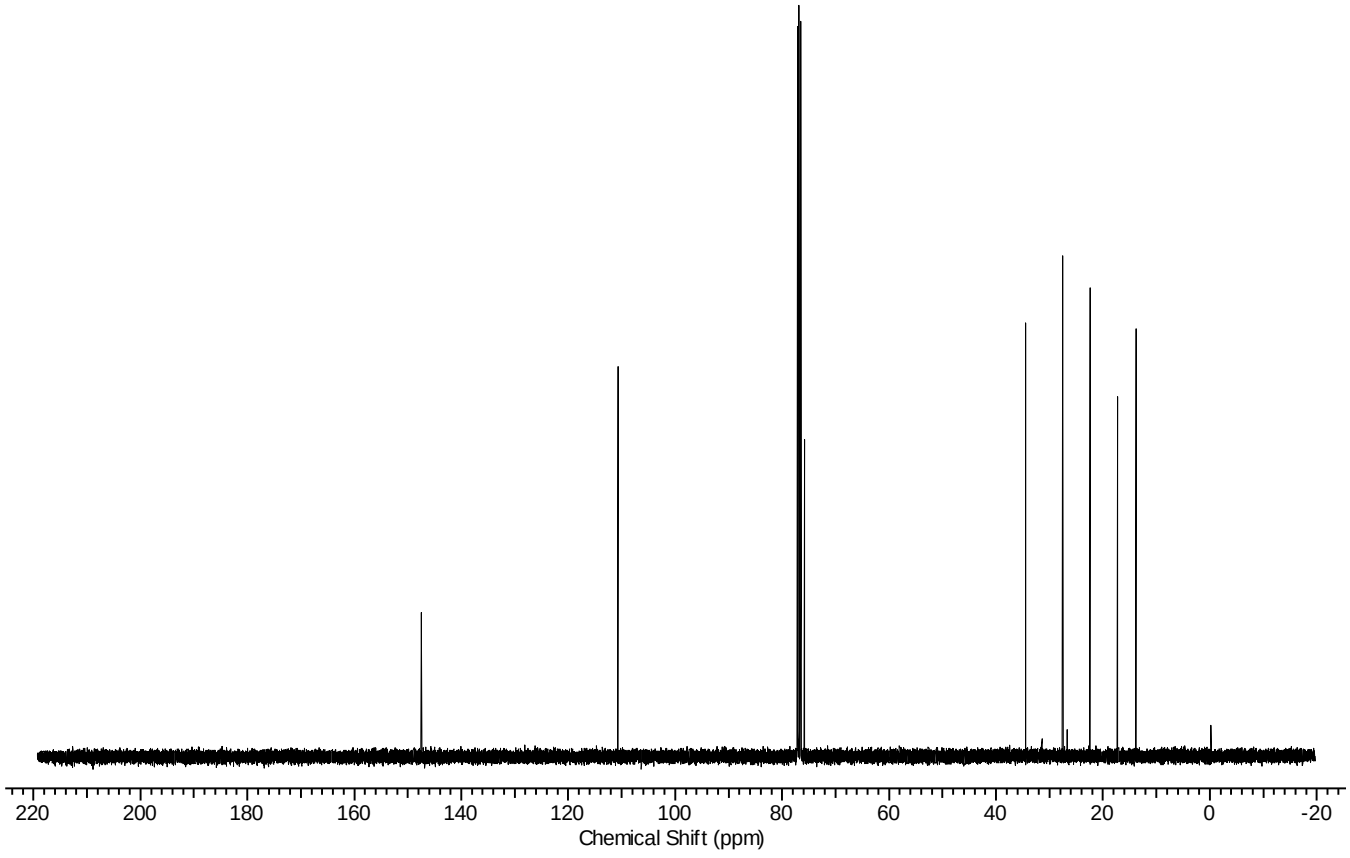

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

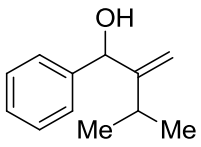

Ph
OH
N
N
Me
Ph


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

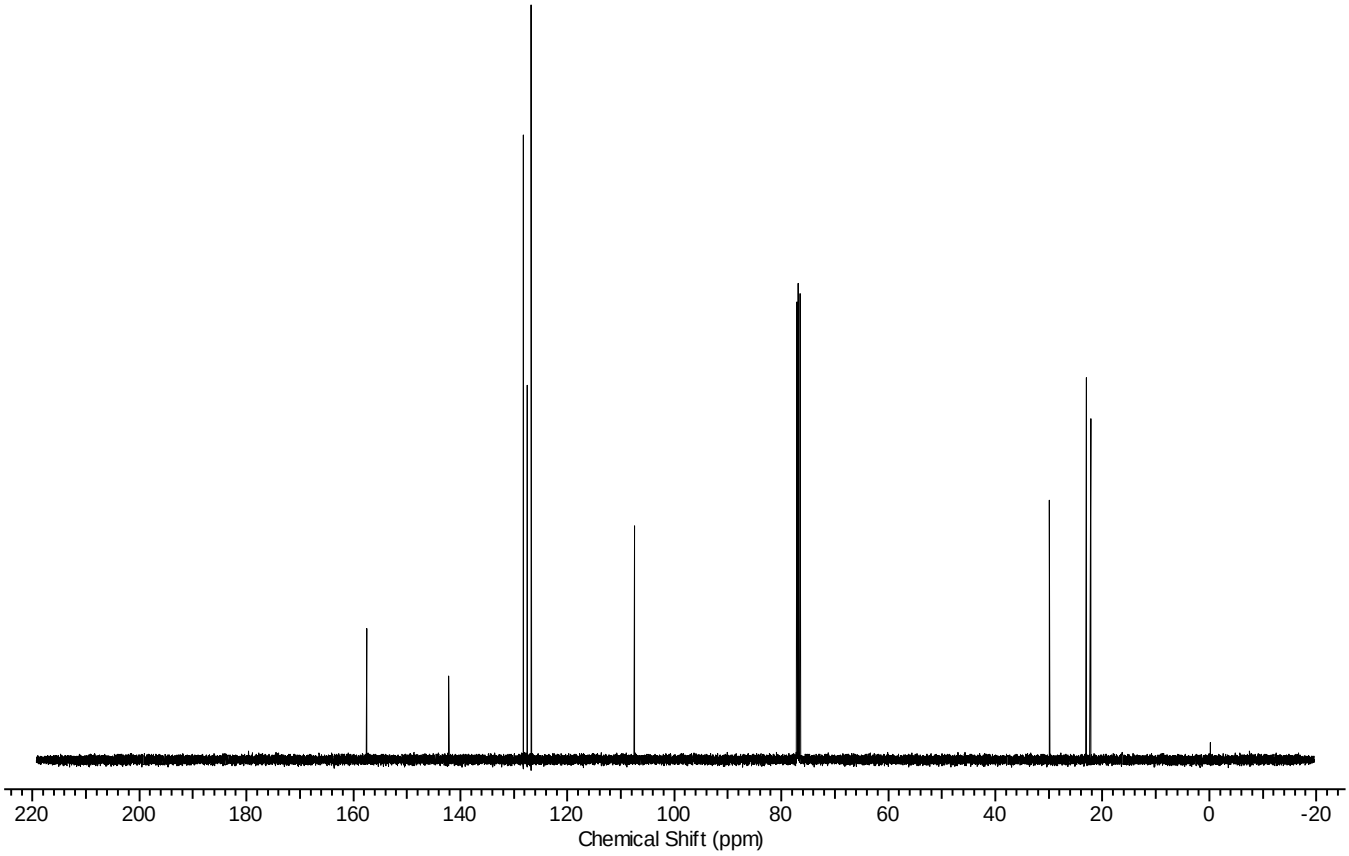

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

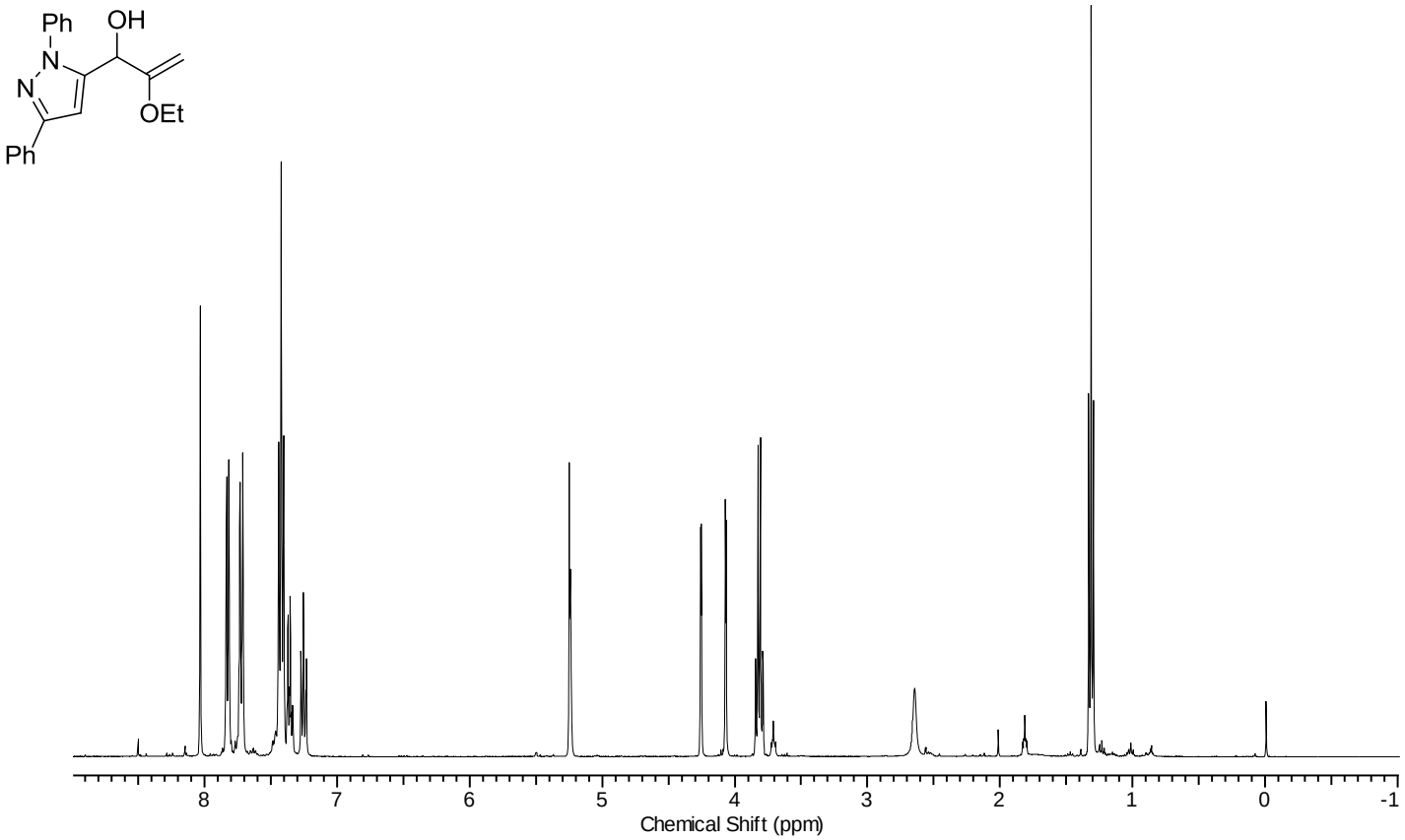

OH
Me
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

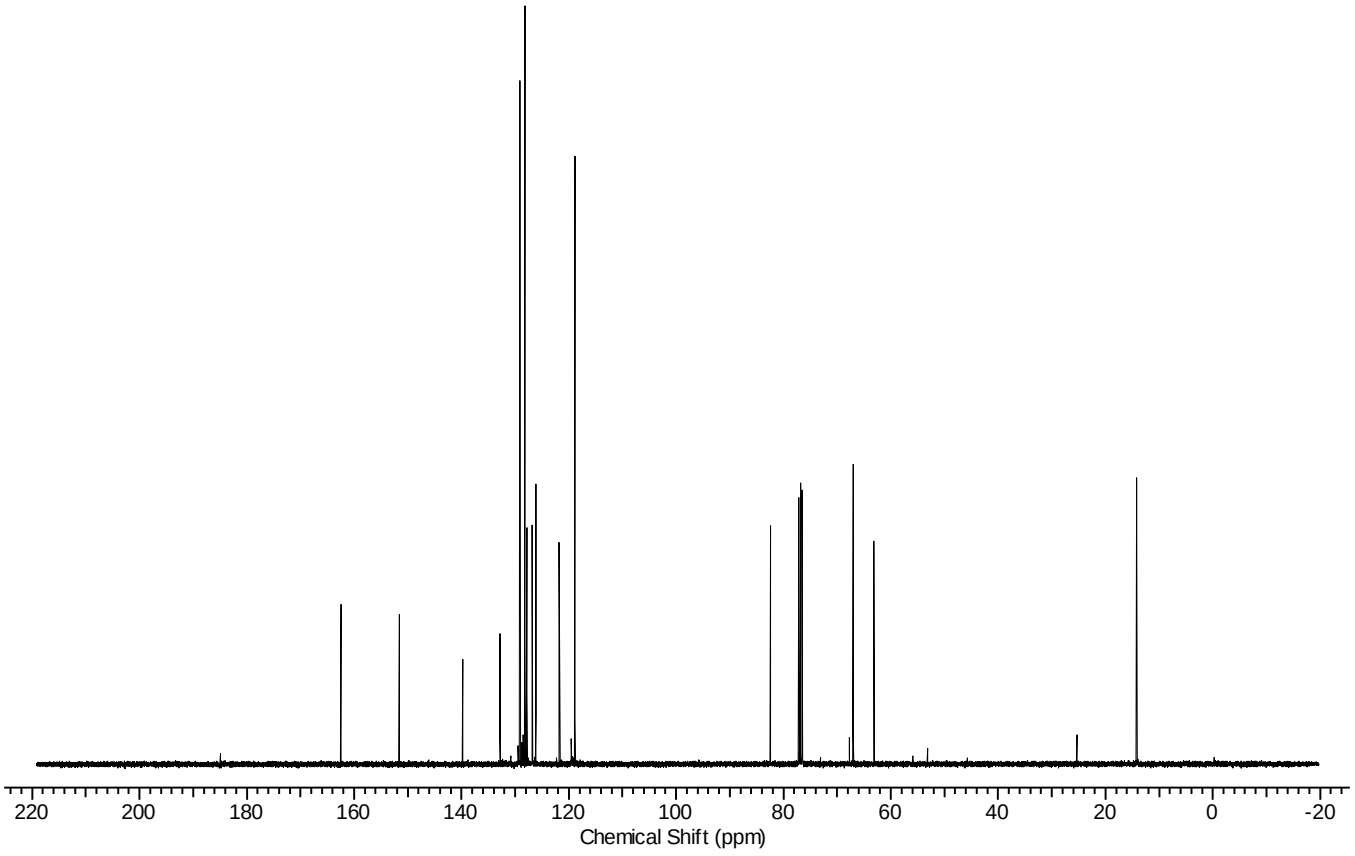

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

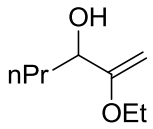

OH
Me
Me

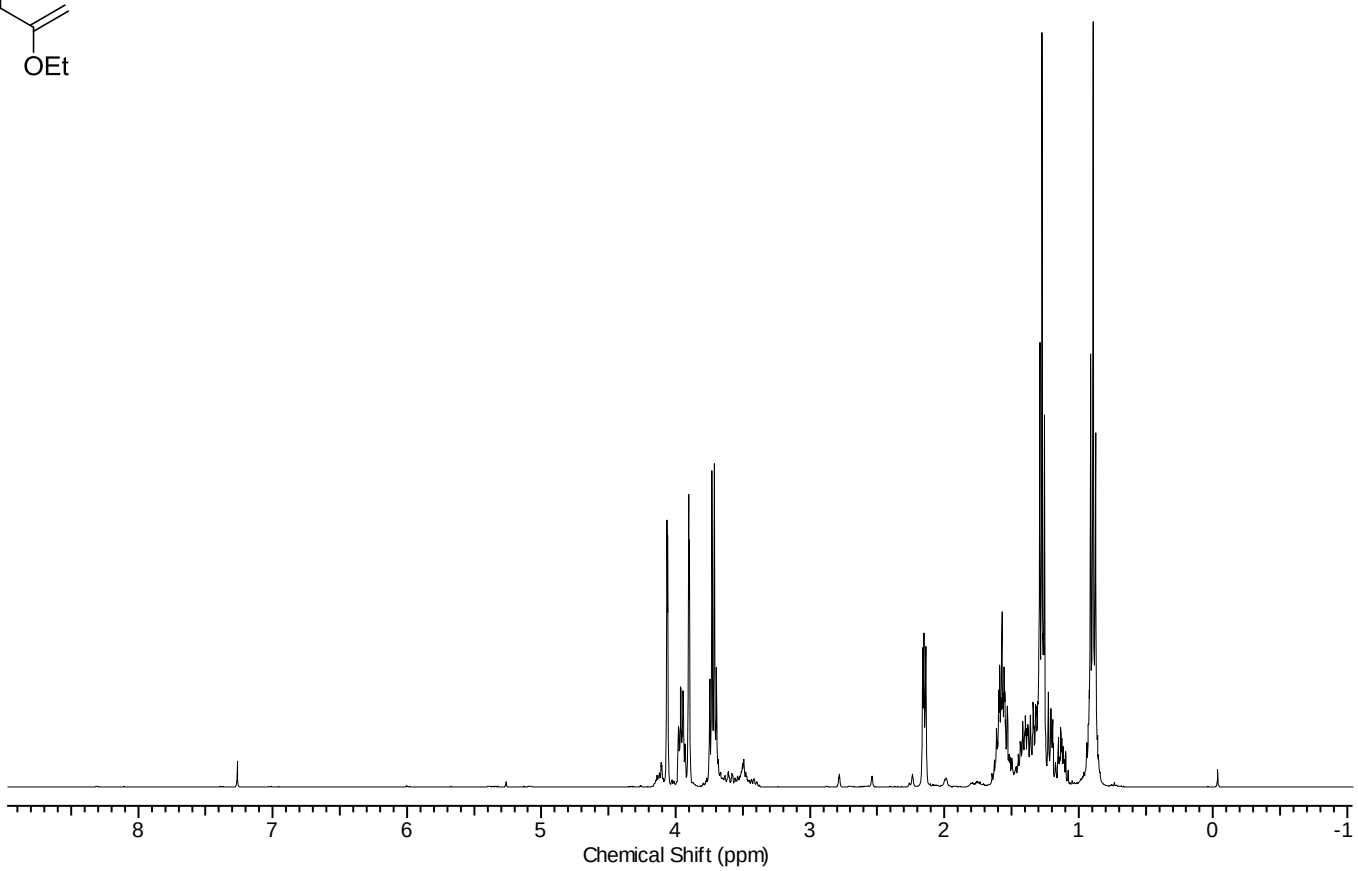
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

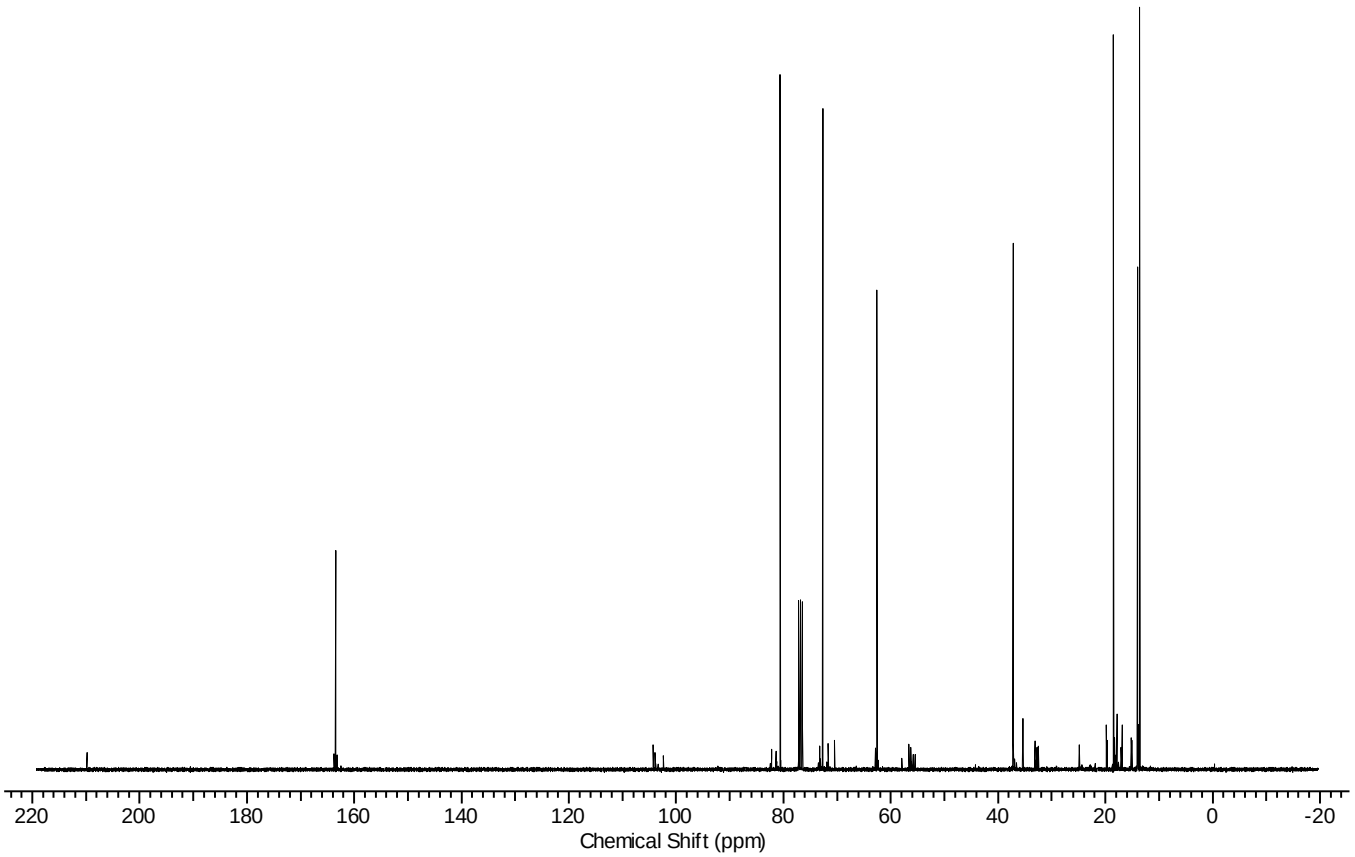

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

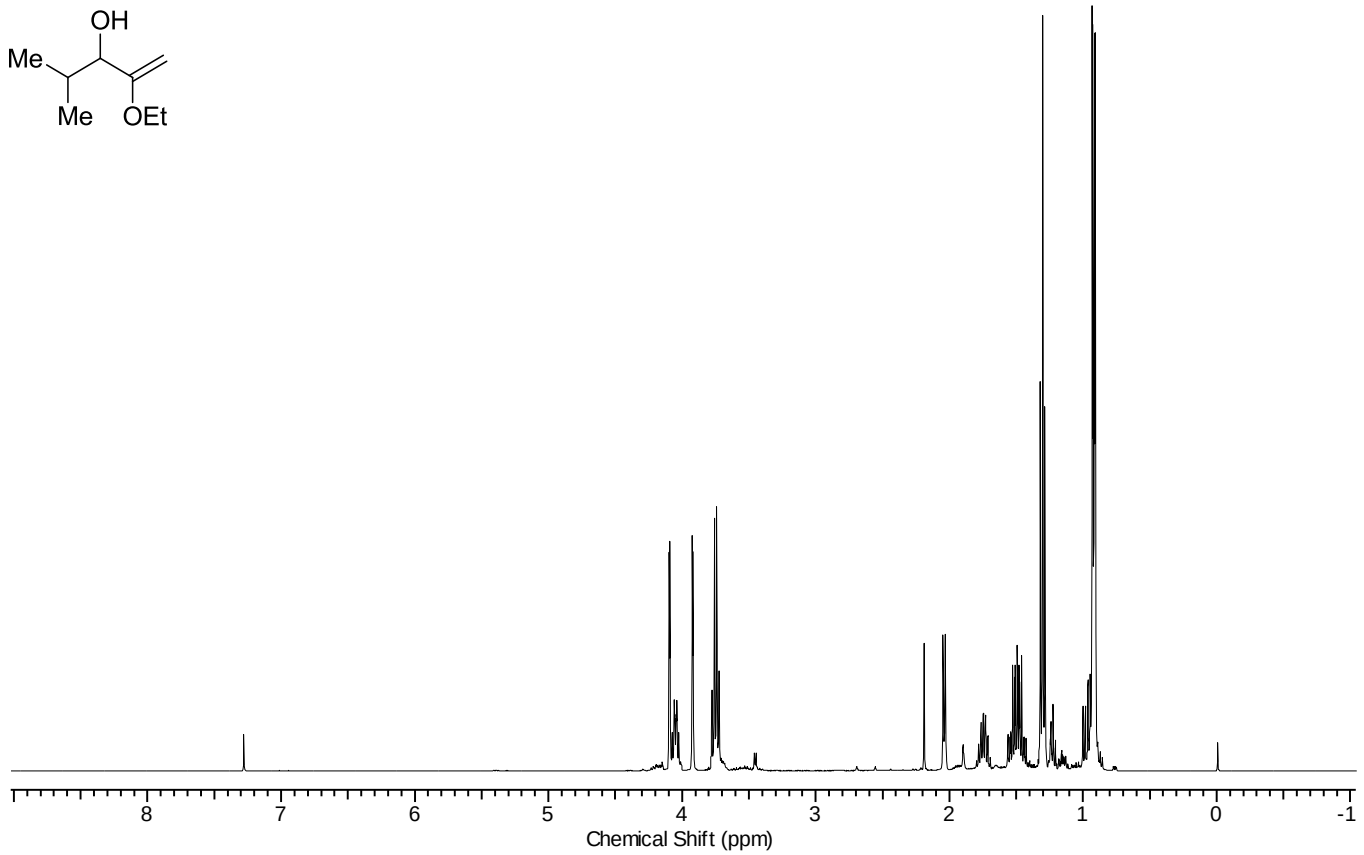

Ph
OH
N
N
OEt
Ph
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

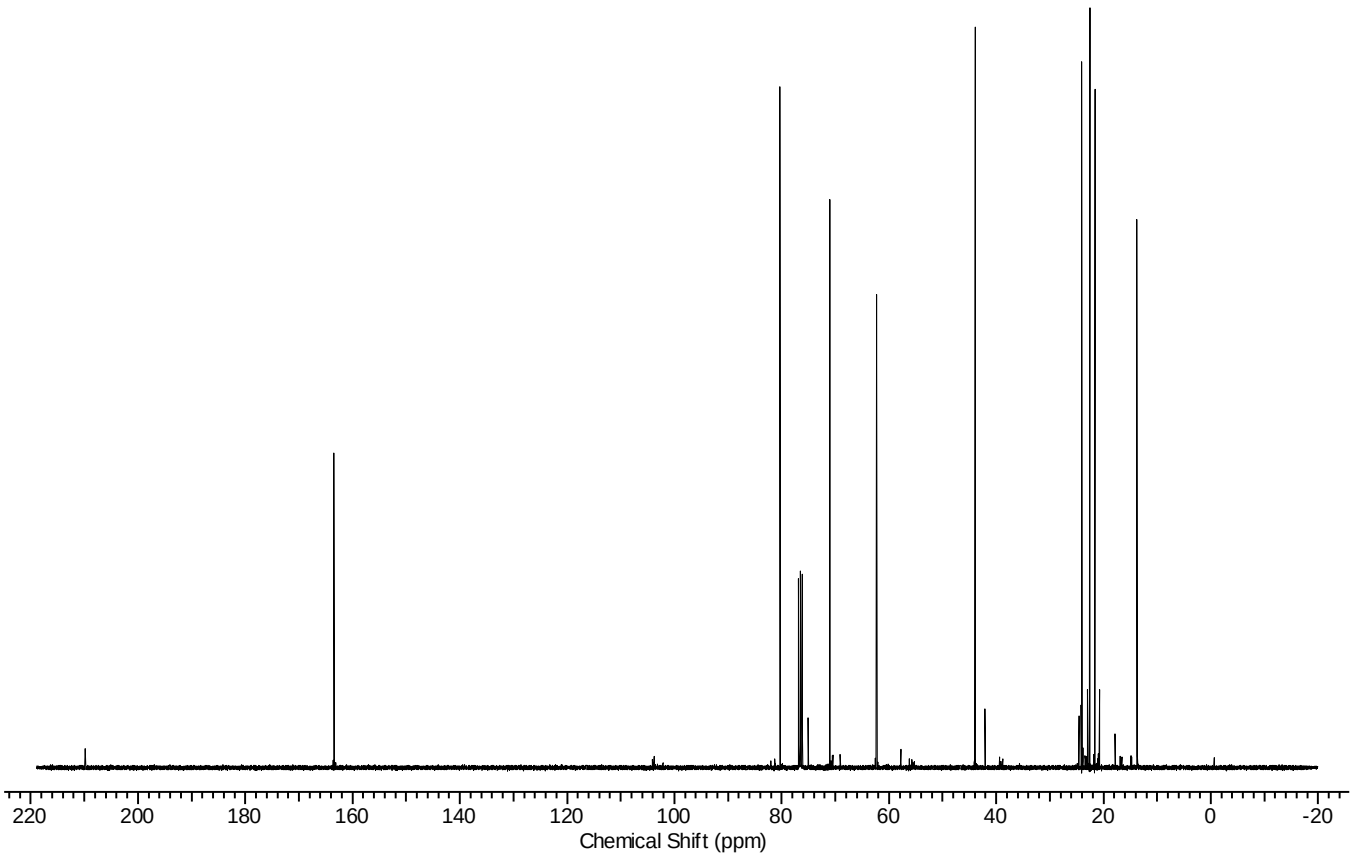

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

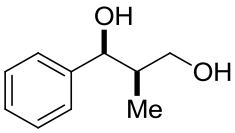

OH
nPr
OEt

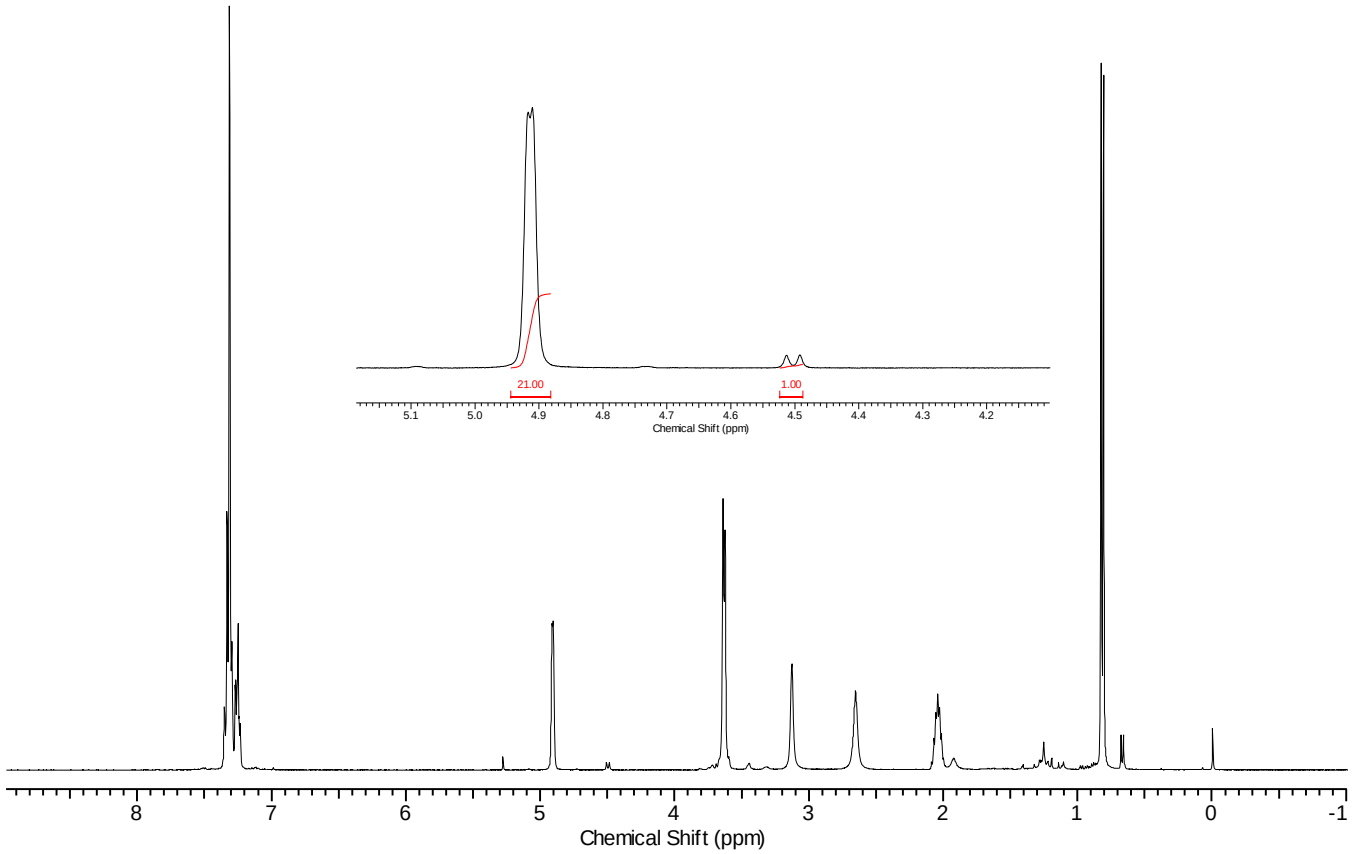

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

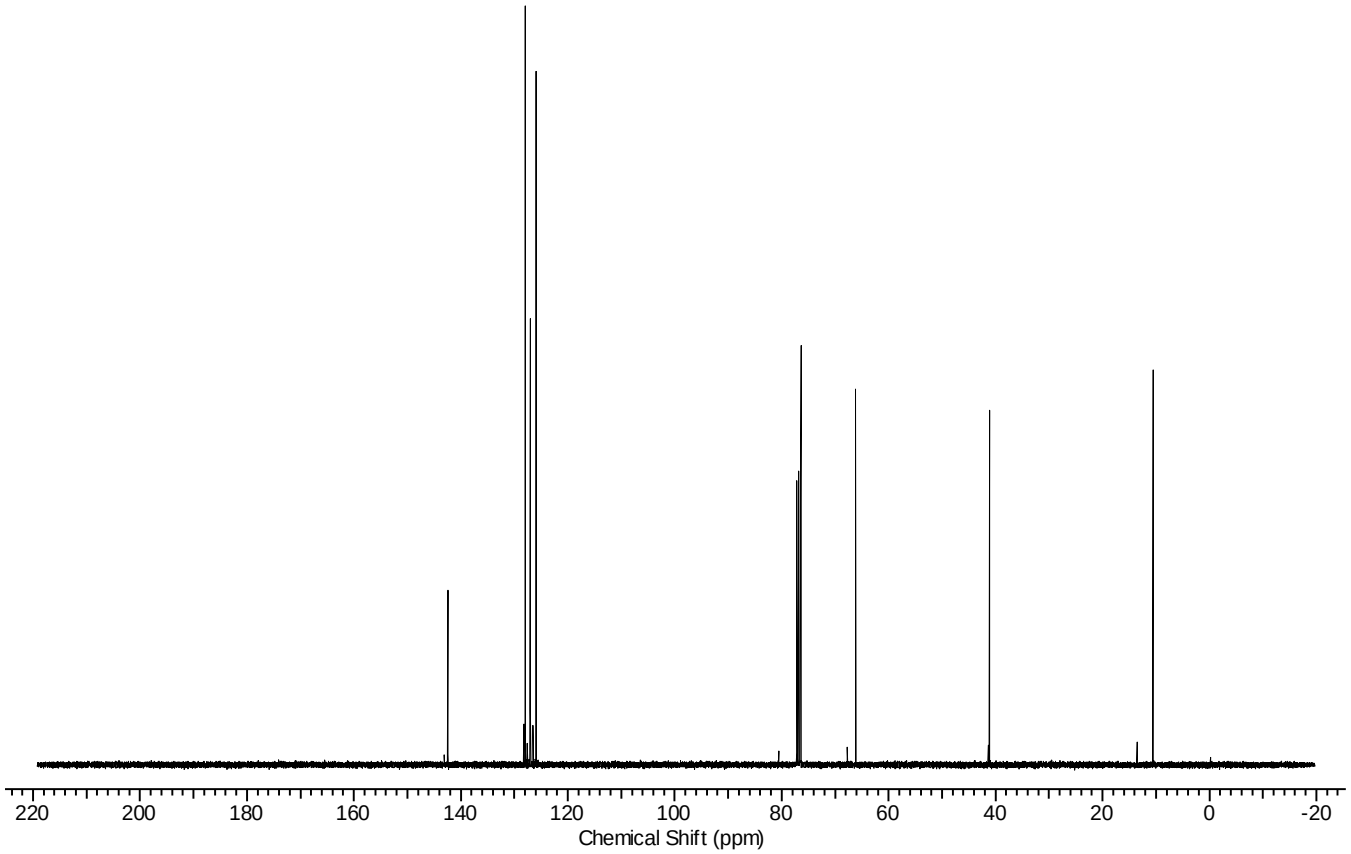

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

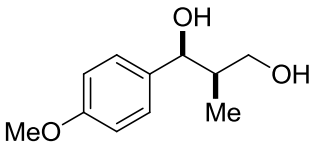

OH
Me
Me
OEt
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

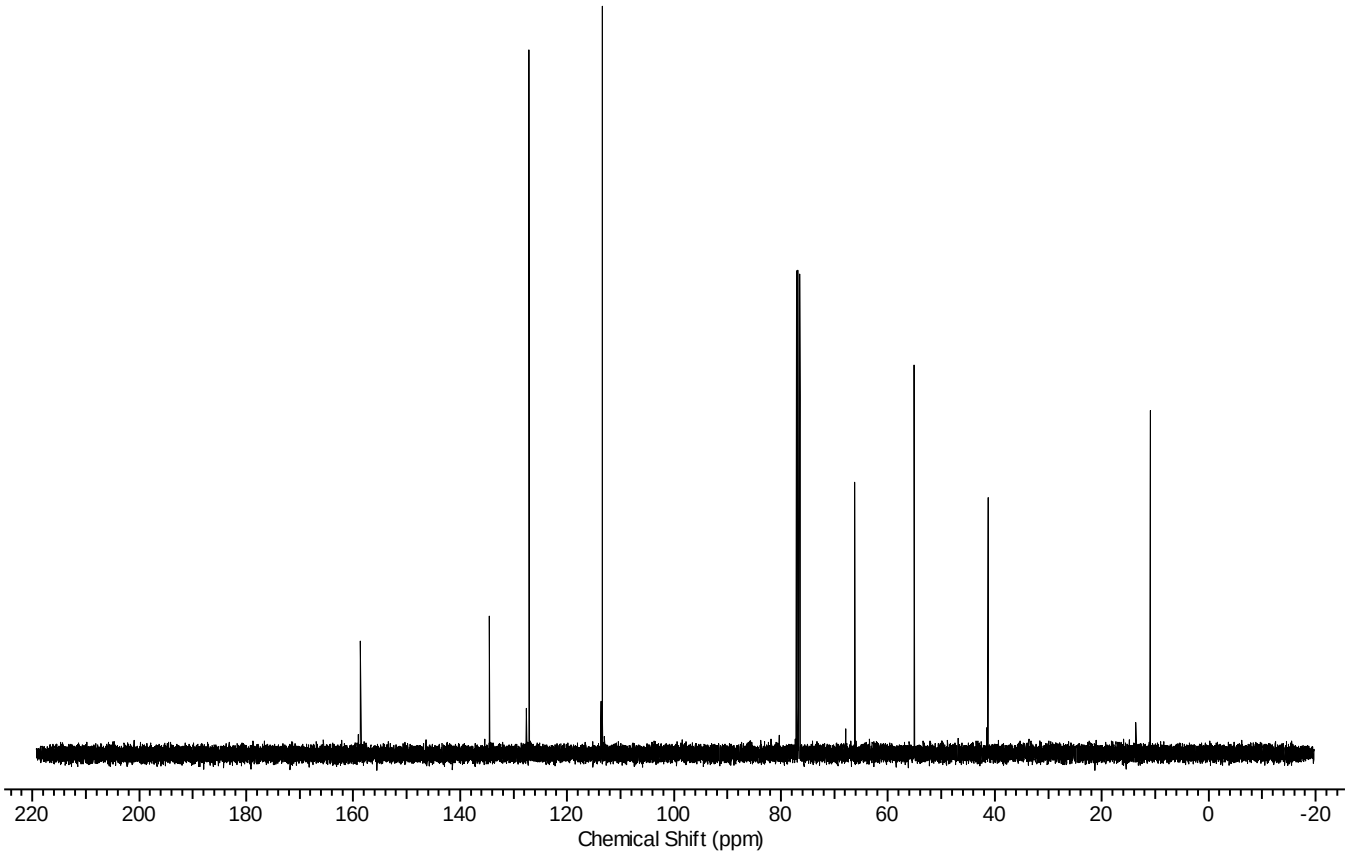

OH
OH
Me

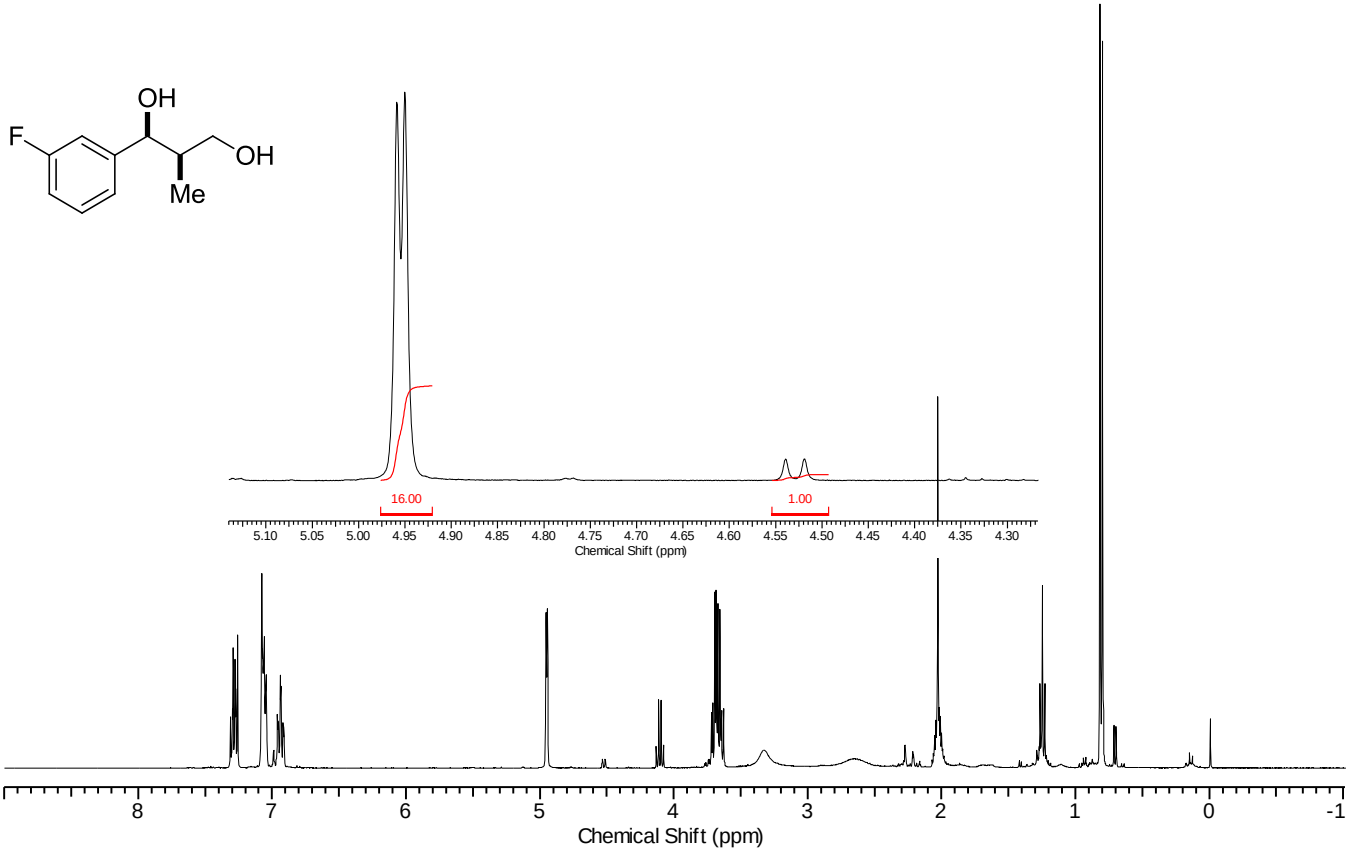

21.00
1.00
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

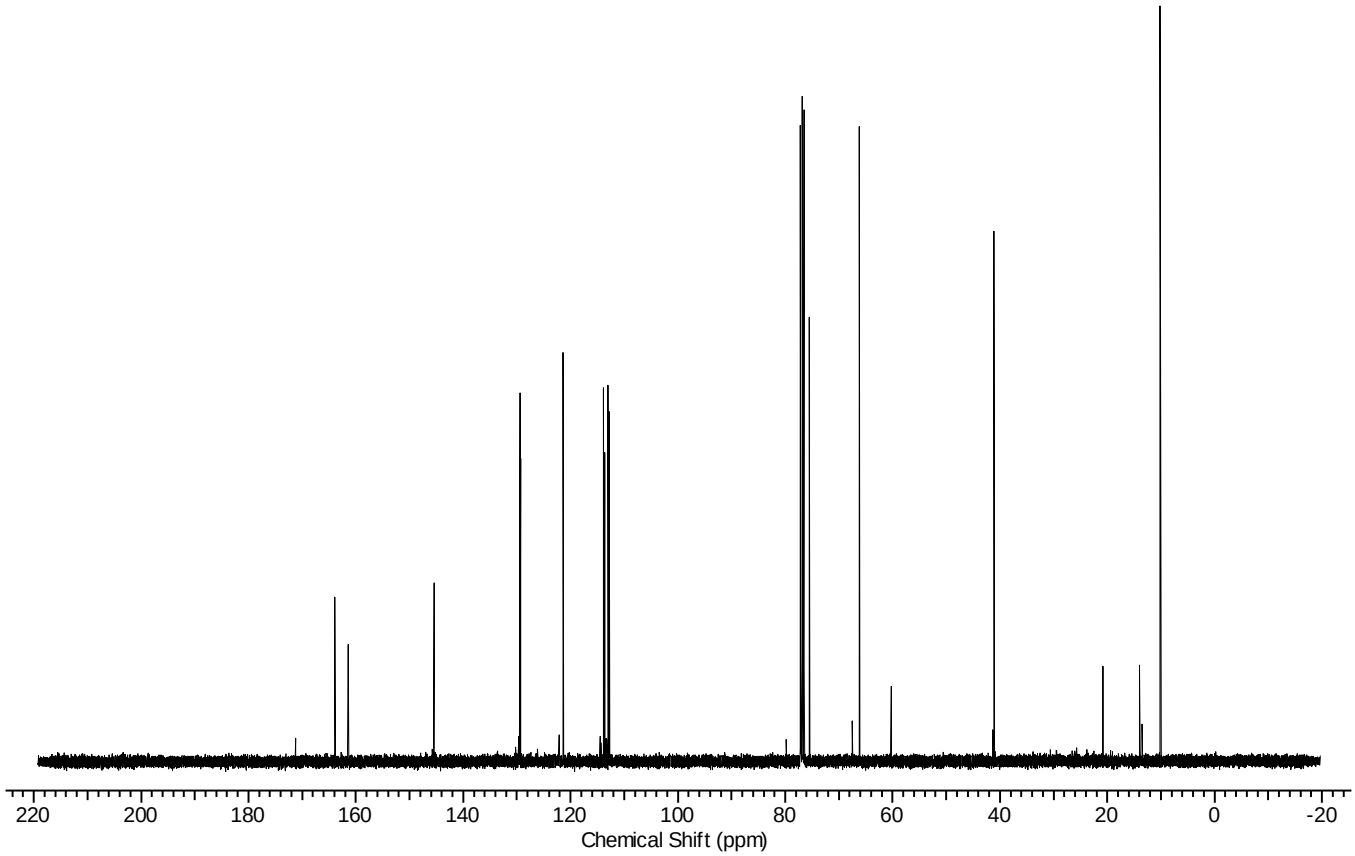

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

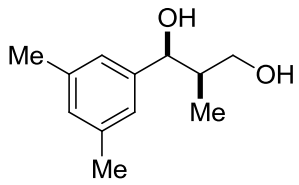

OH
OH
Me
MeO

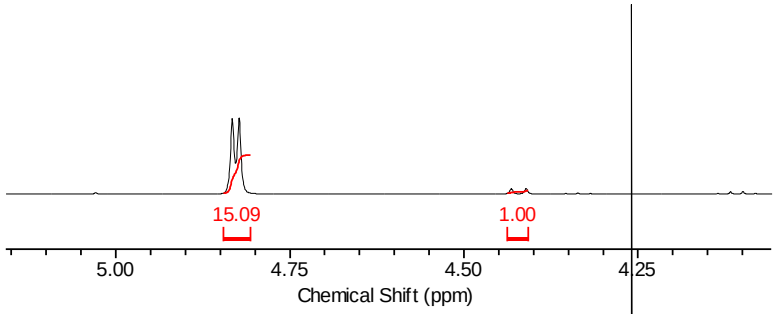
14.58
1.00
5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30
Chemical Shift (ppm)
8 7 6 5 4 3 2 1 0 -1
Chemical Shift (ppm)

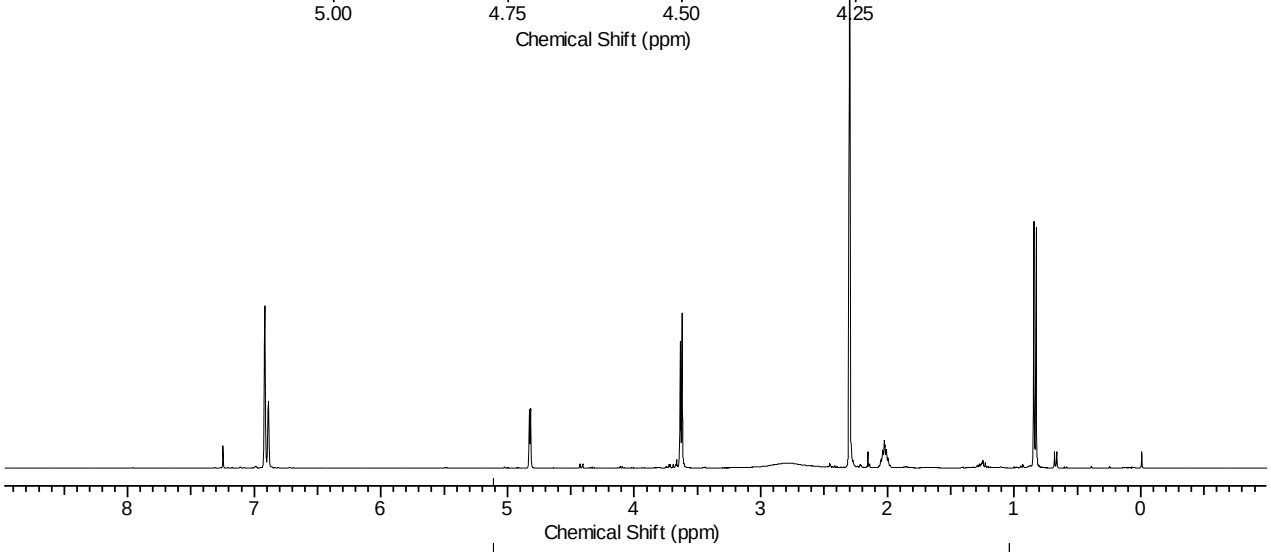

220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

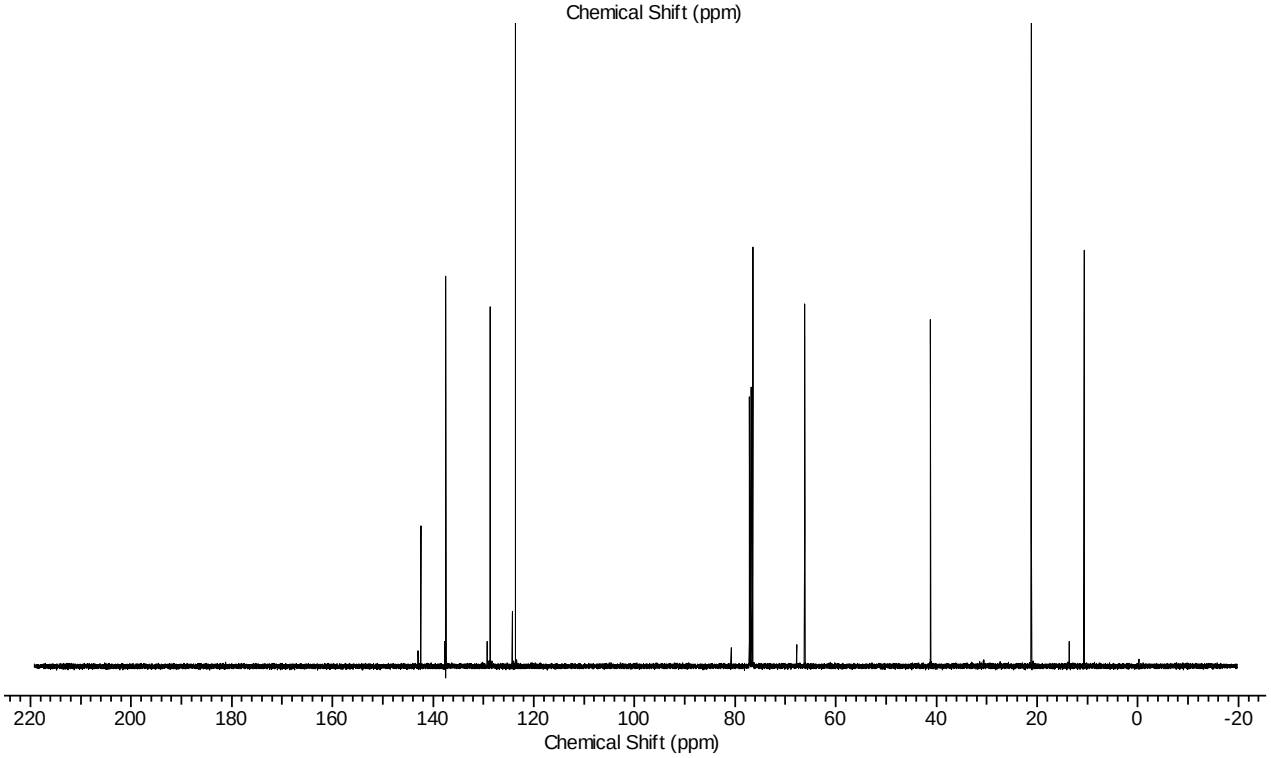

OH
F
OH
Me
16.00
1.00
5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30
Chemical Shift (ppm)
8 7 6 5 4 3 2 1 0 -1
Chemical Shift (ppm)

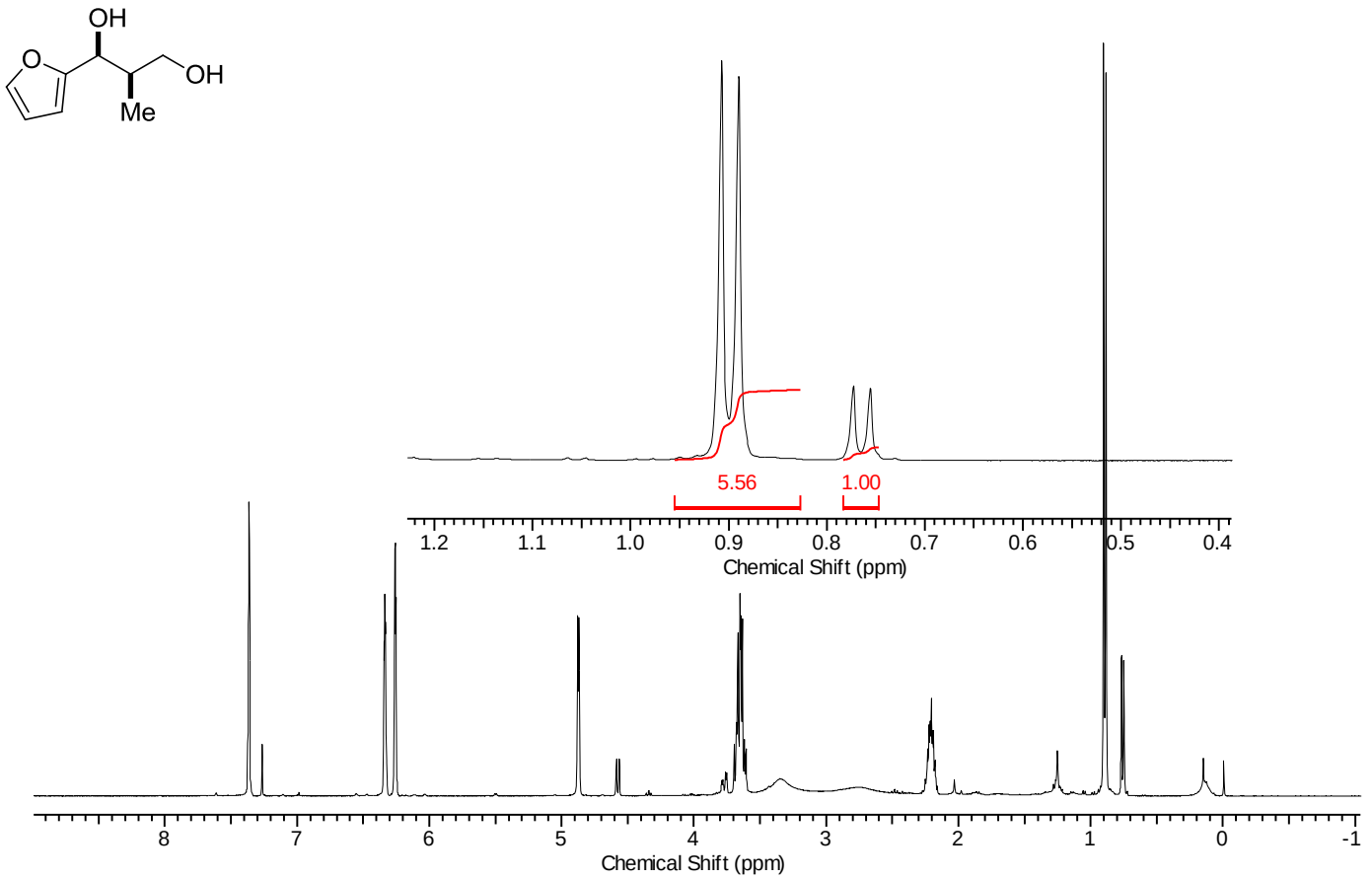

220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

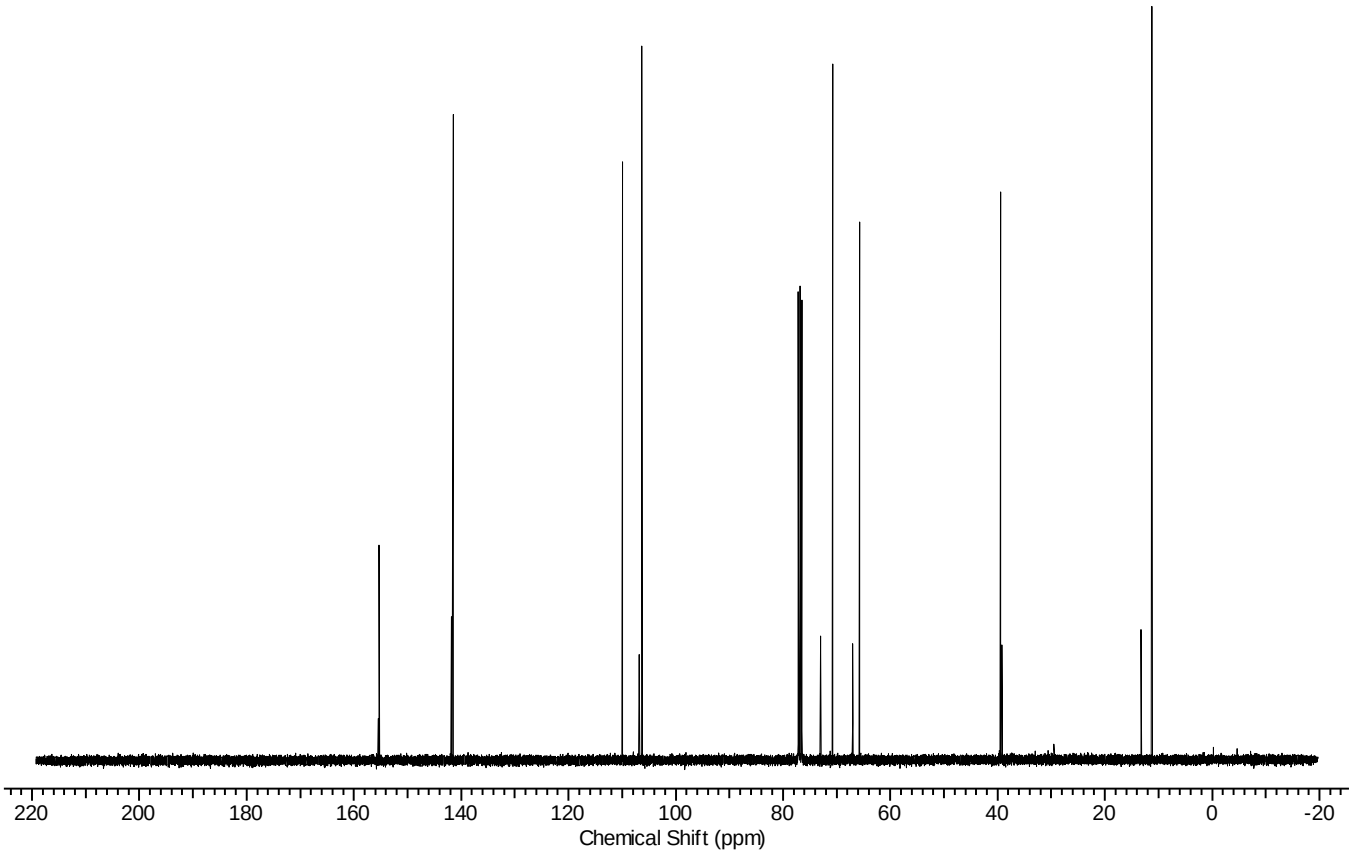

OH
Me
OH
Me
Me

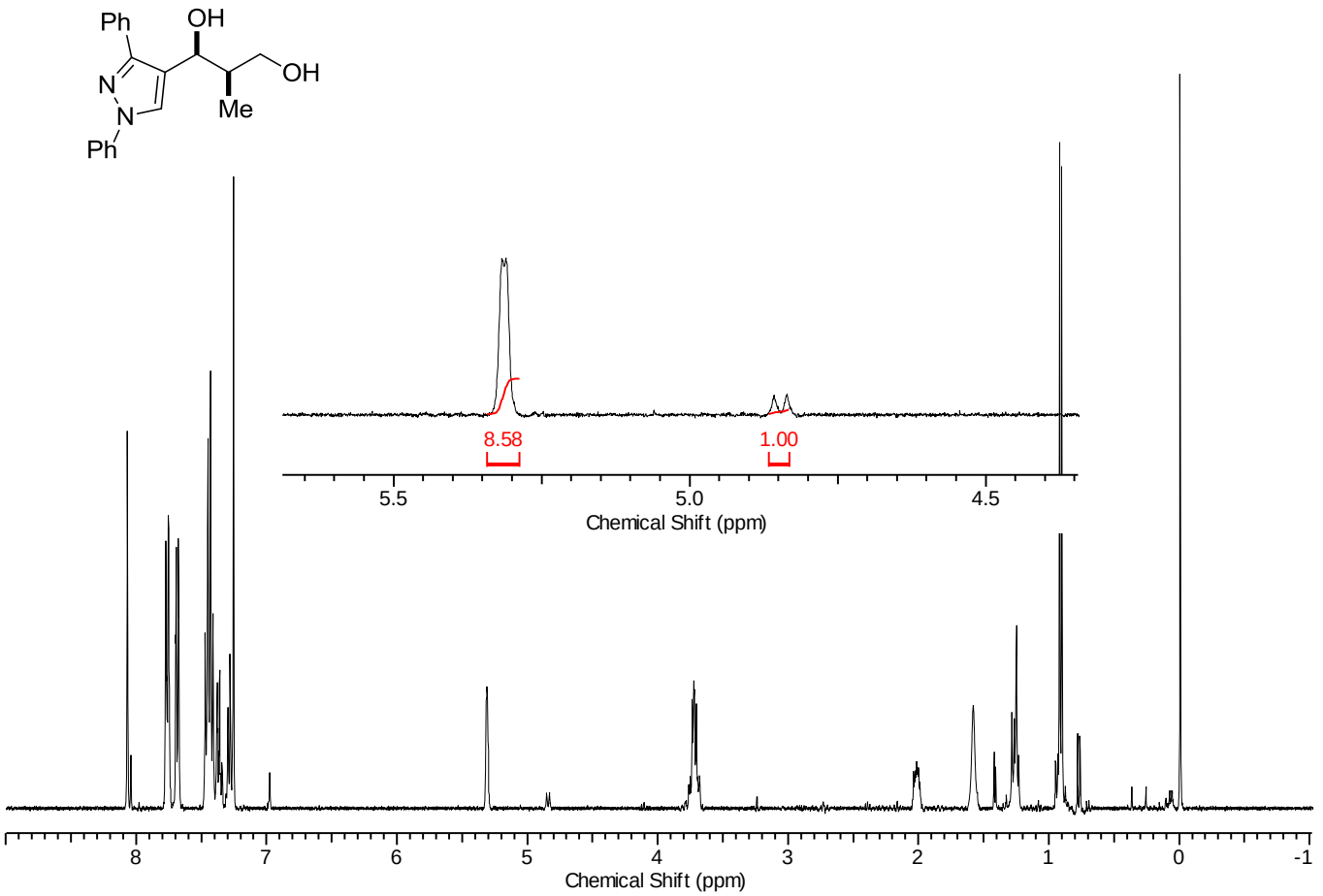

15.09
1.00
5.00
4.75
4.50
4.25
Chemical Shift (ppm)

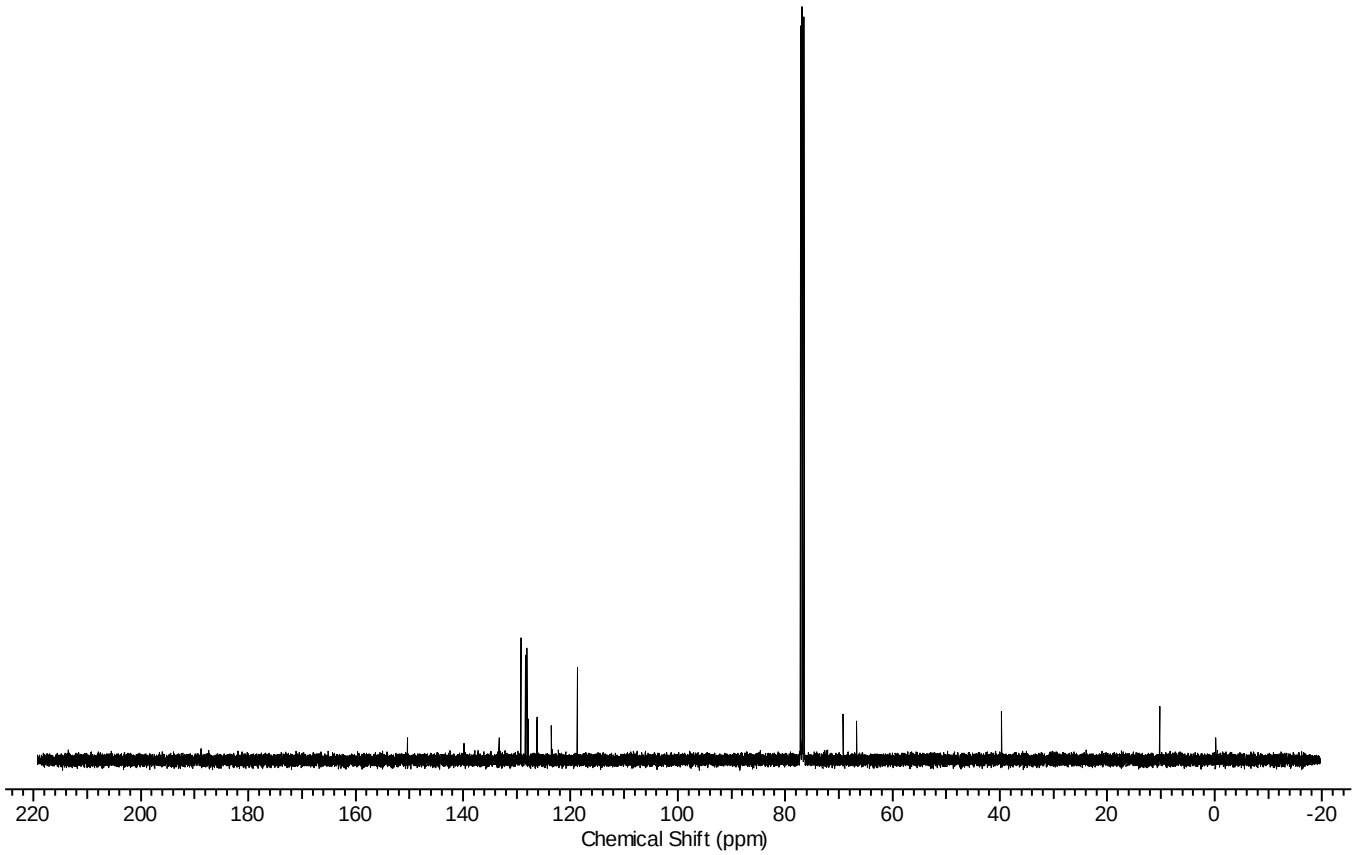

8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

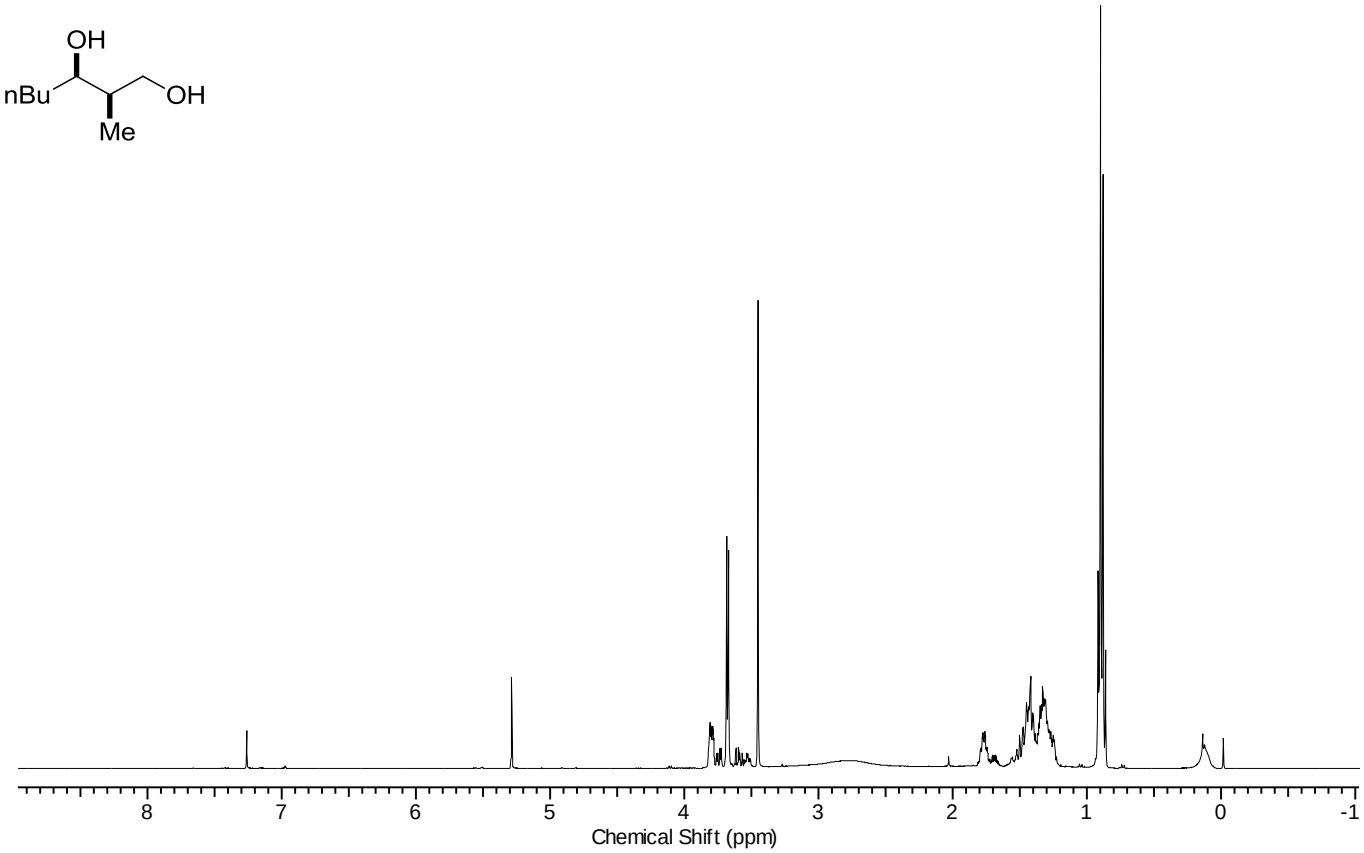

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

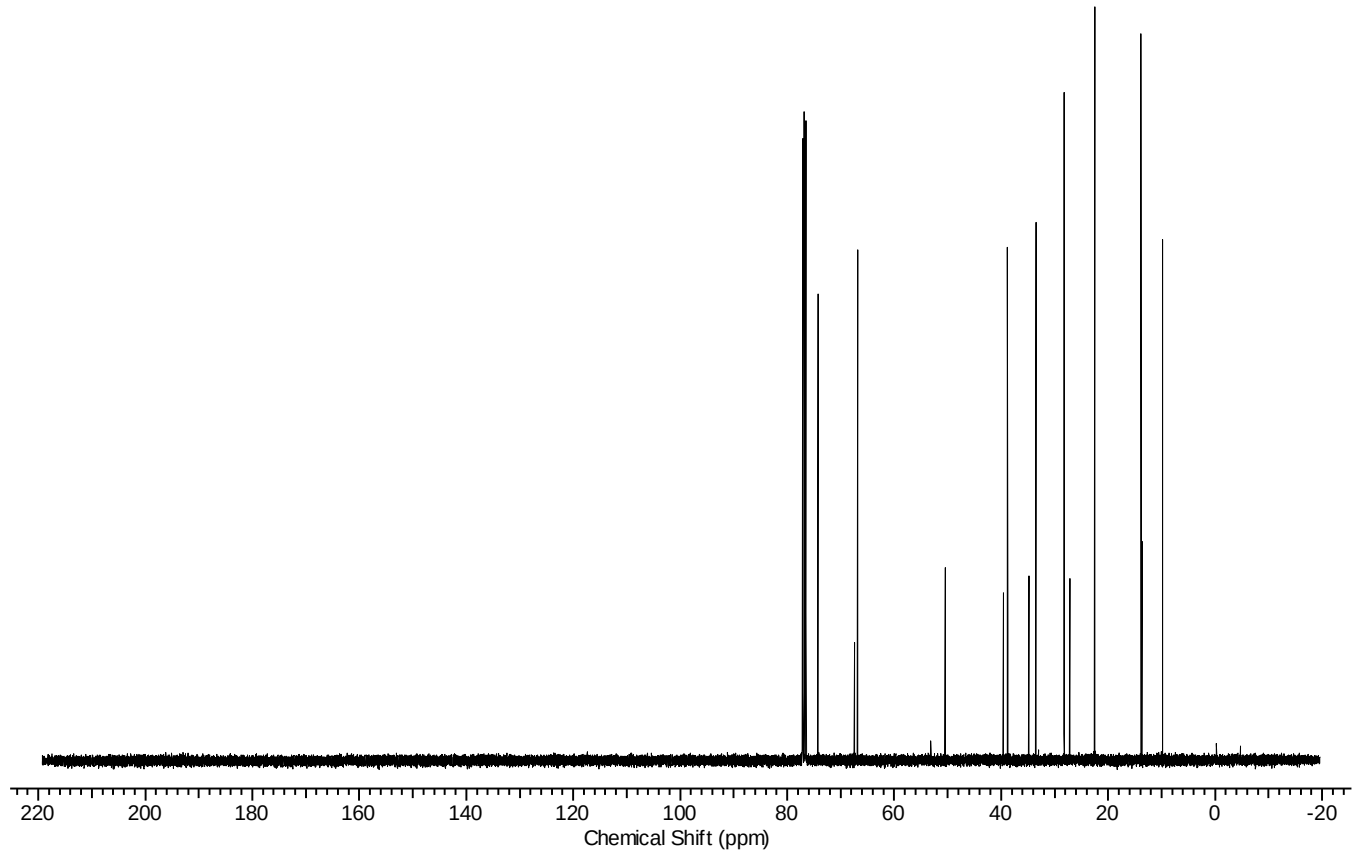

OH
O
OH
Me
5.56
1.00
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

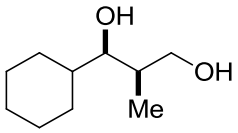

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

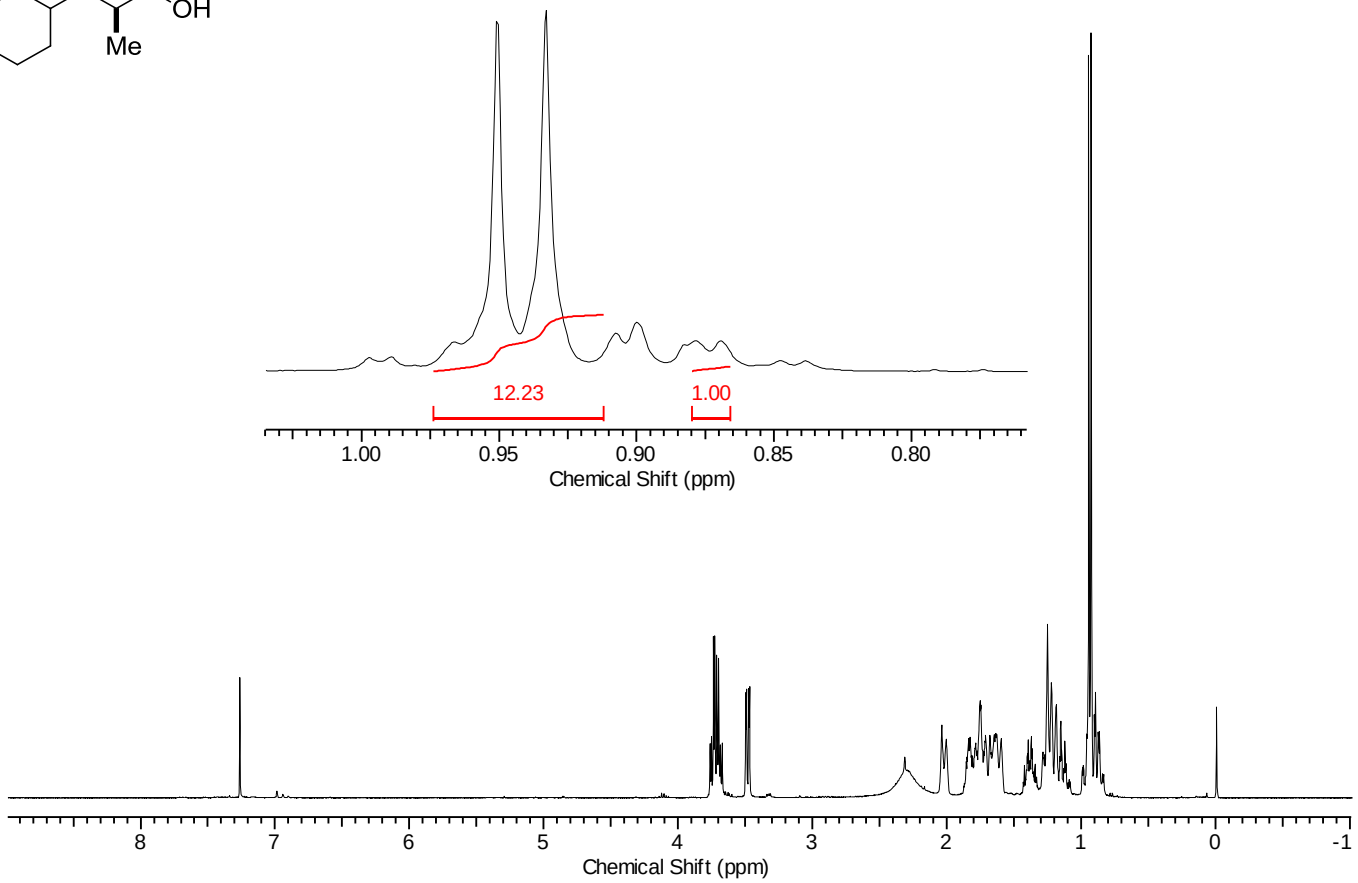

Ph
OH
N
N
Ph
Me
OH
8.58
1.00
5.5
5.0
4.5
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

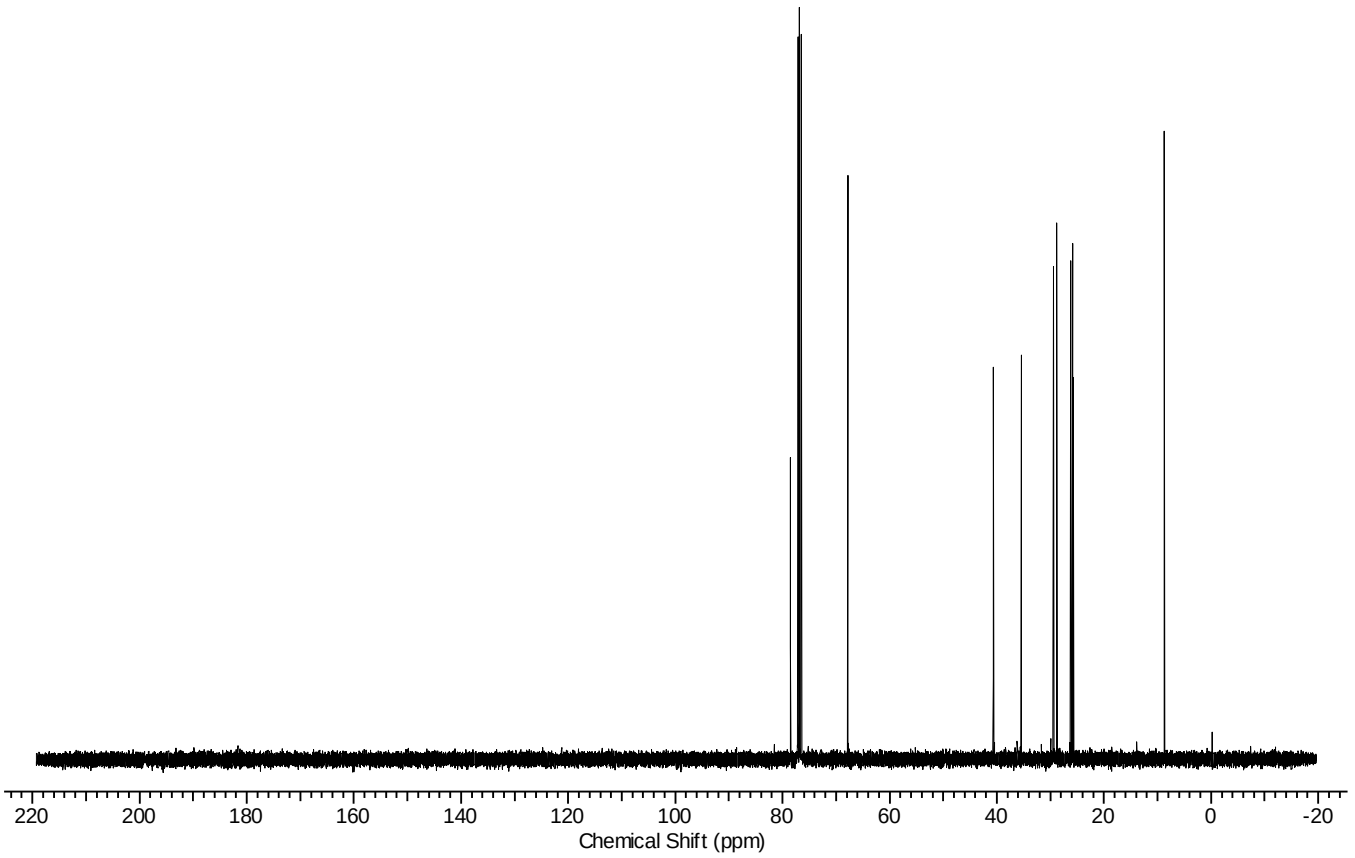

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

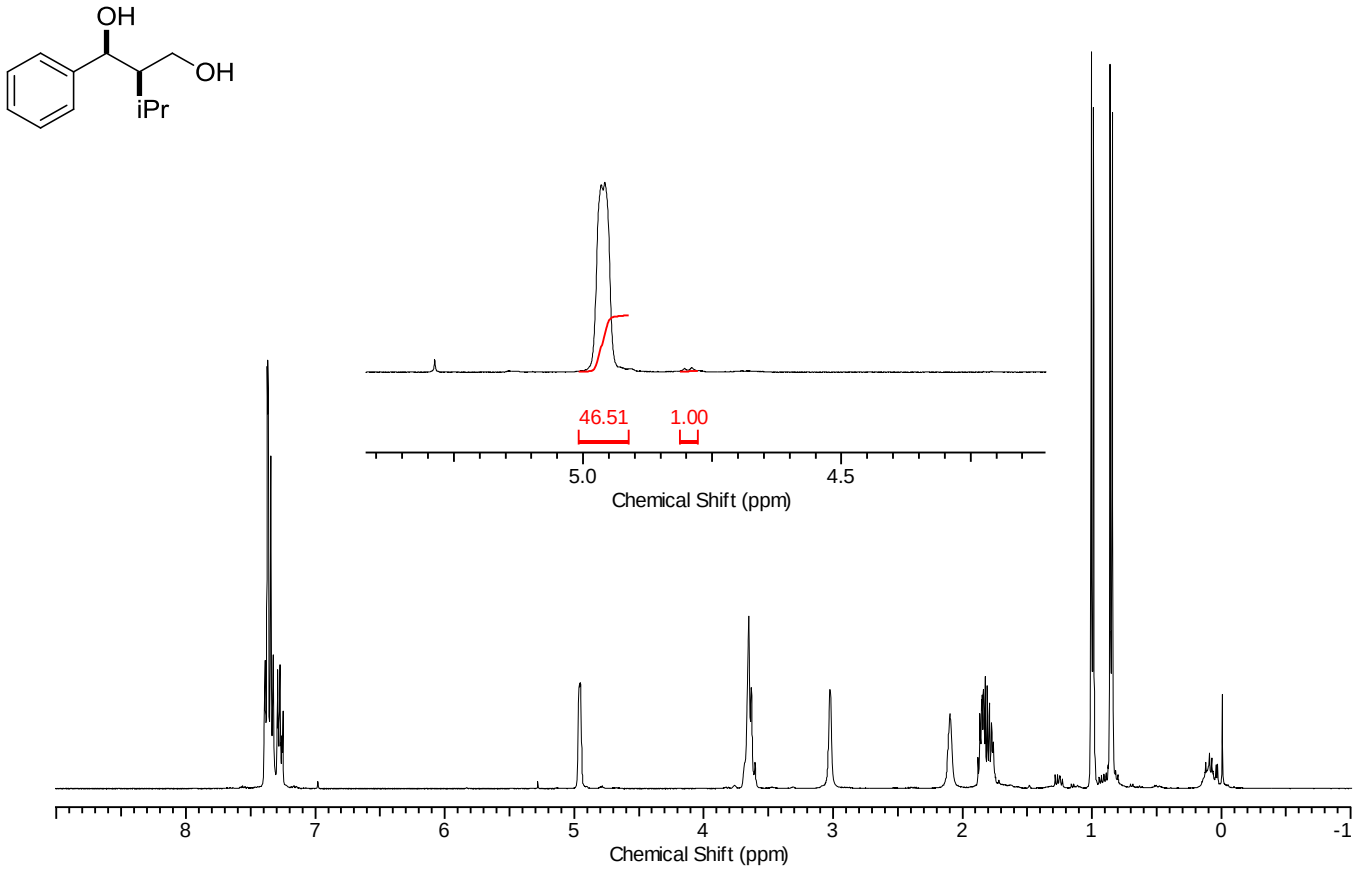

OH
nBu
OH
Me
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

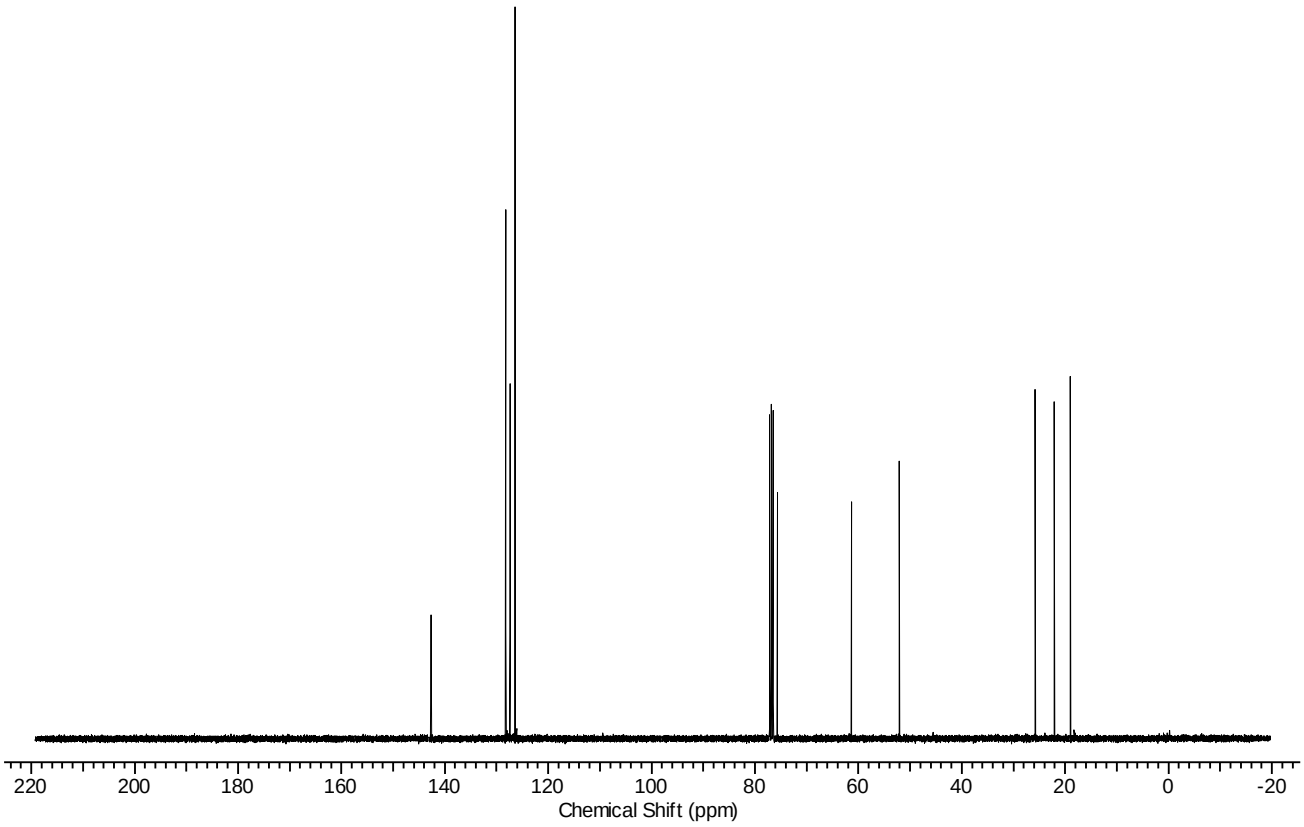

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

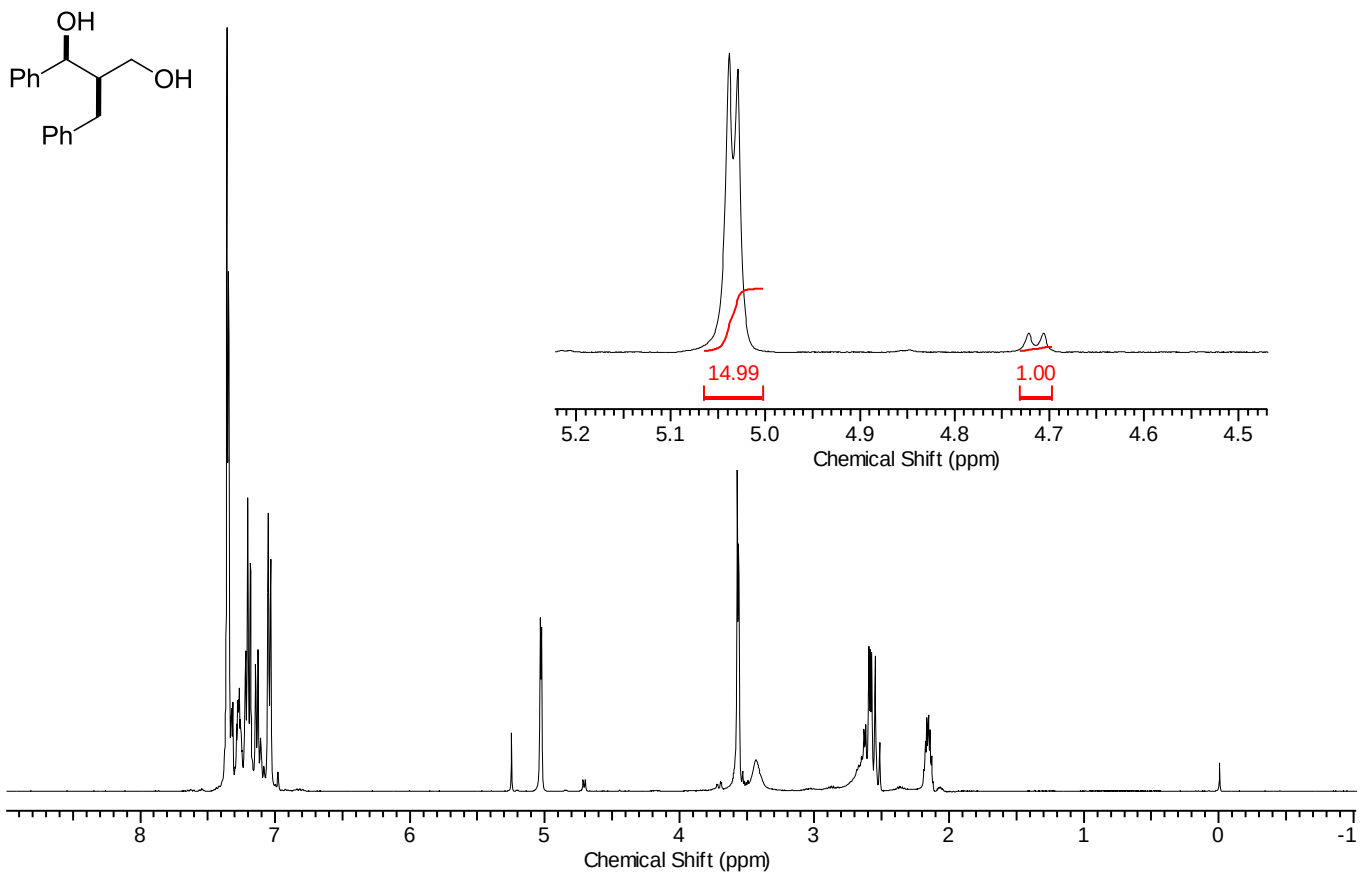

OH
OH
Me

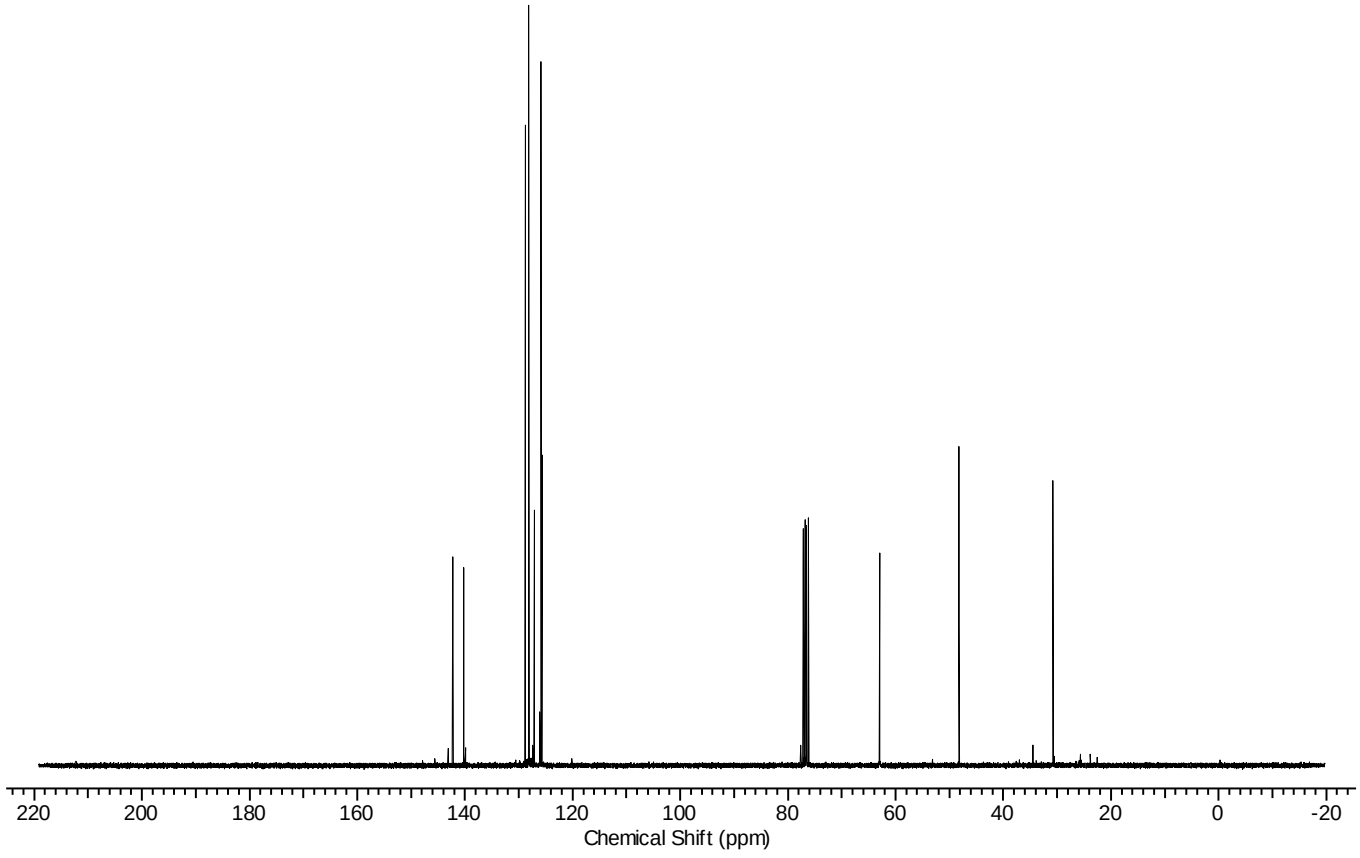

12.23
1.00
1.00
0.95
0.90
0.85
0.80
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

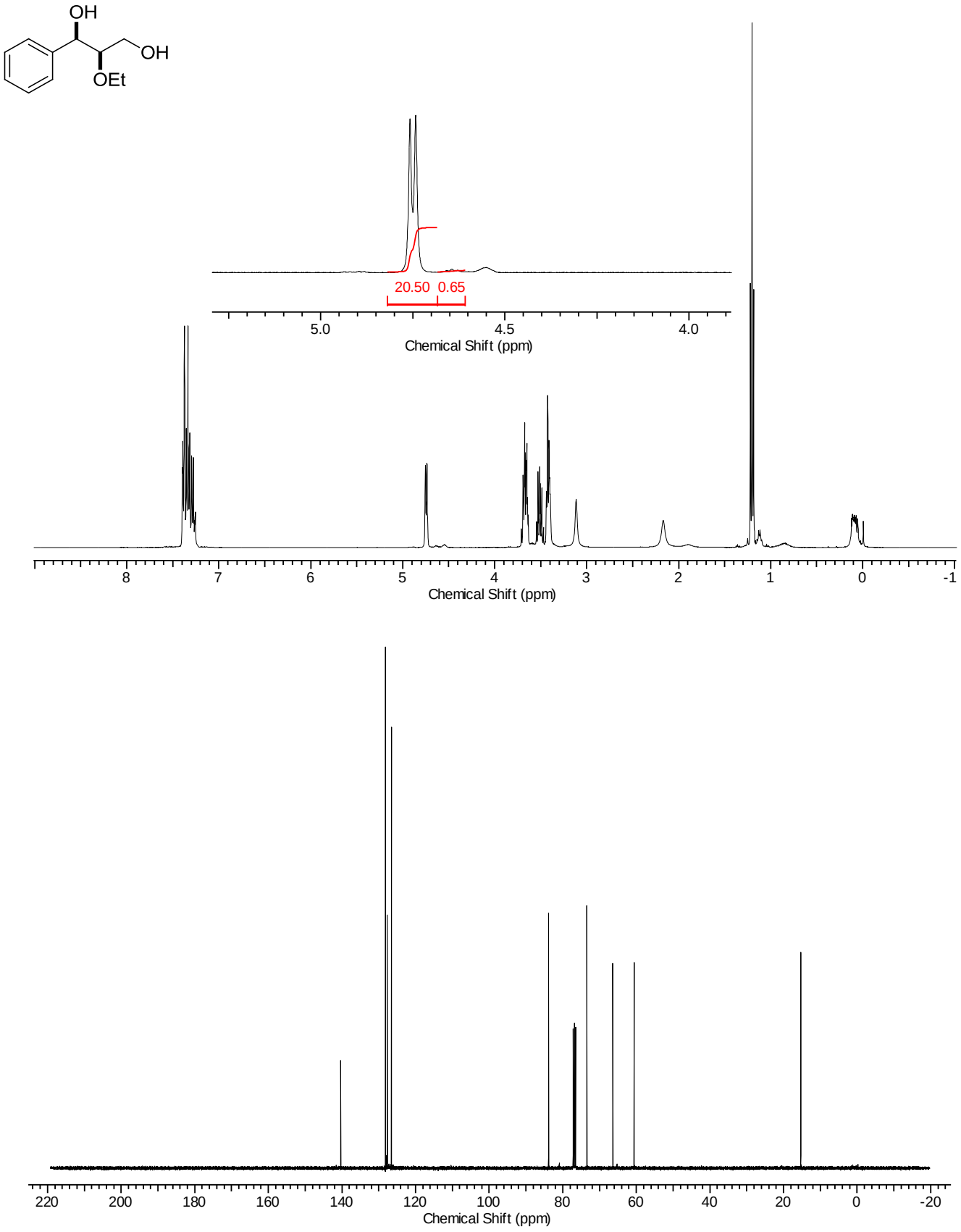

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

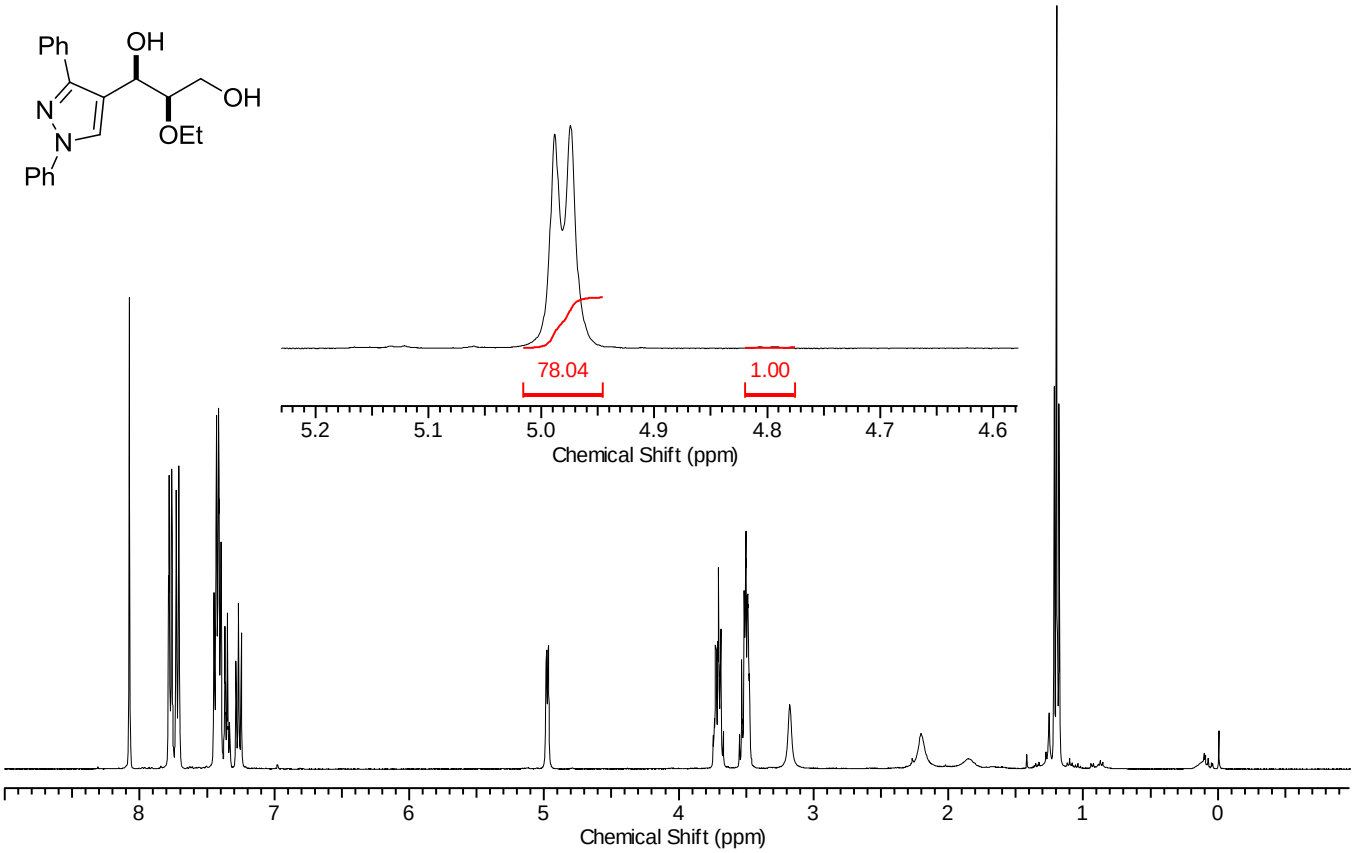

OH
OH
iPr
46.51
1.00
5.0
4.5
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

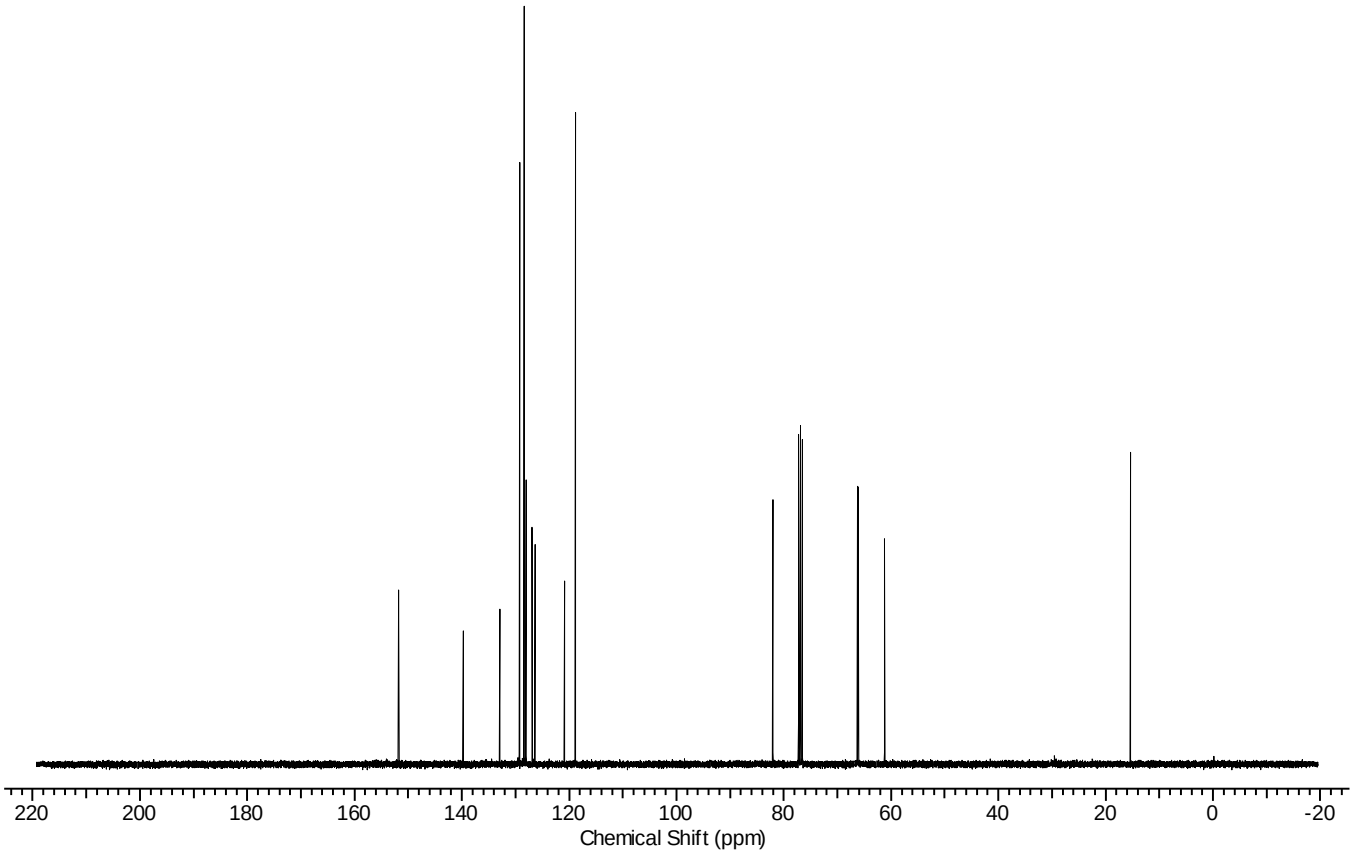

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

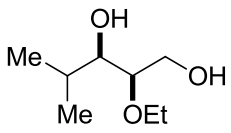

OH
Ph
OH
Ph
14.99
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

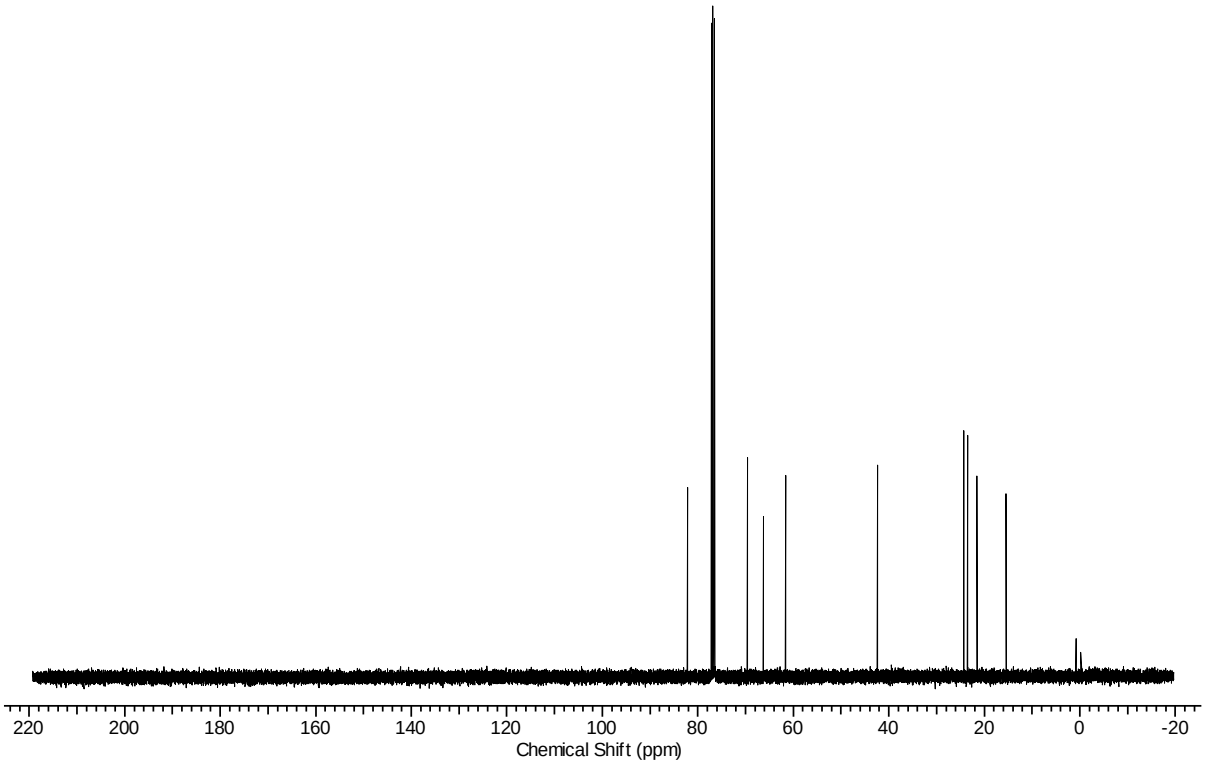

OH
OH
OEt
20.50
0.65
5.0
4.5
4.0
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

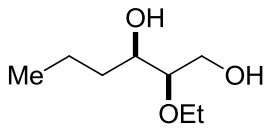

Ph
OH
N
OH
N
OEt
Ph
78.04
1.00
5.2
5.1
5.0
4.9
4.8
4.7
4.6
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

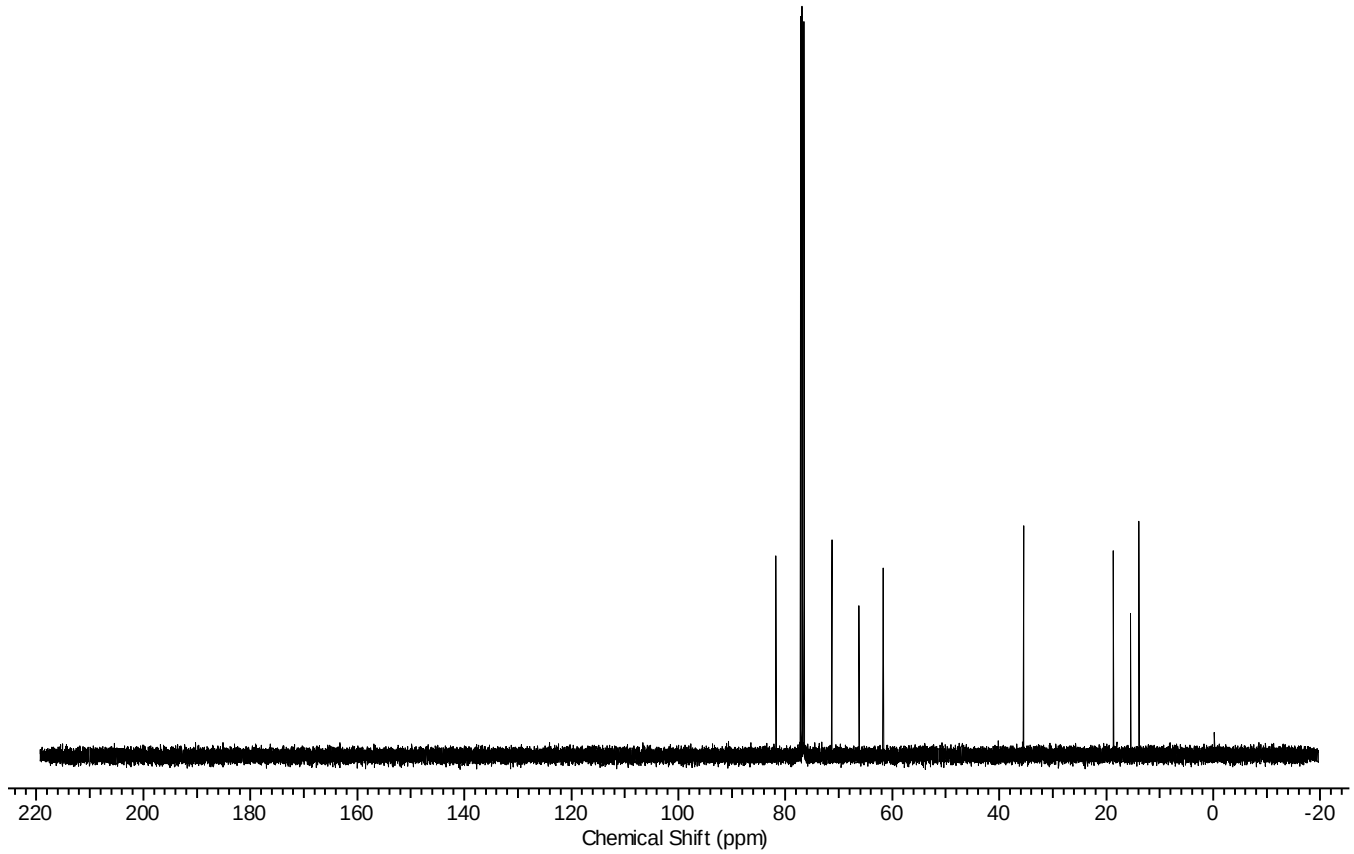

OH
Me
OH
Me
OEt

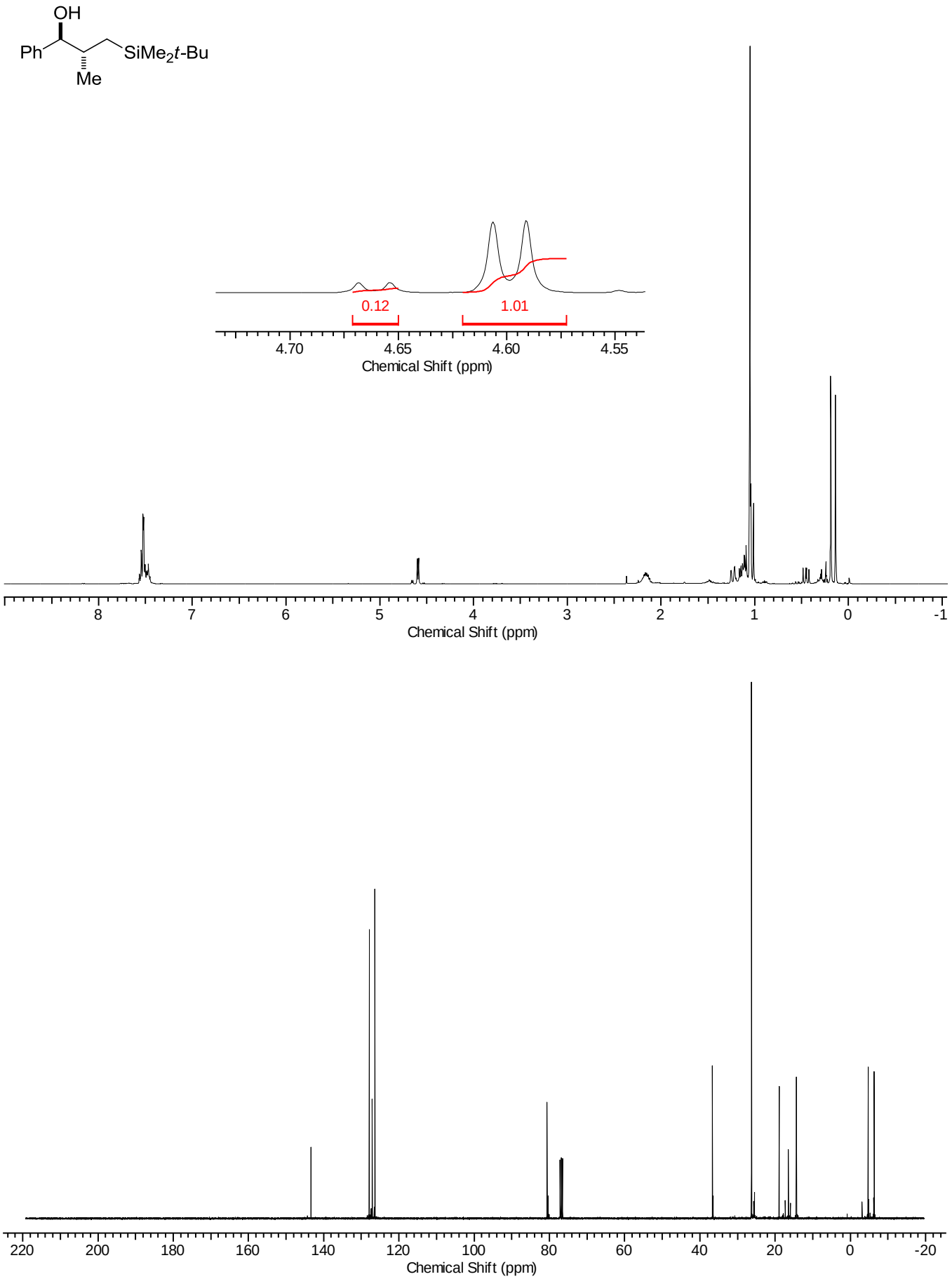
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

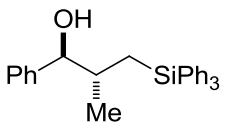

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

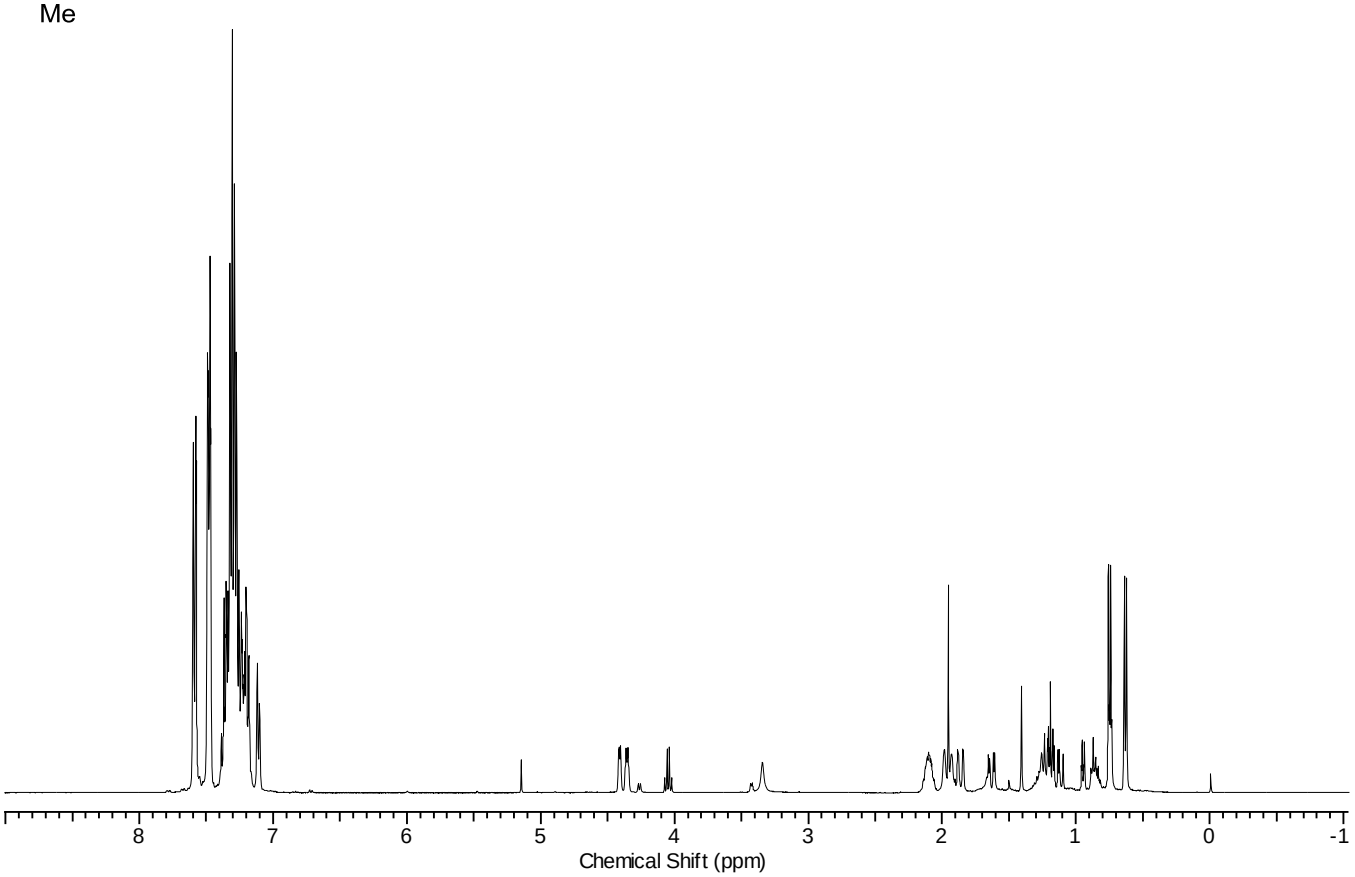

OH
Me
OH
OEt

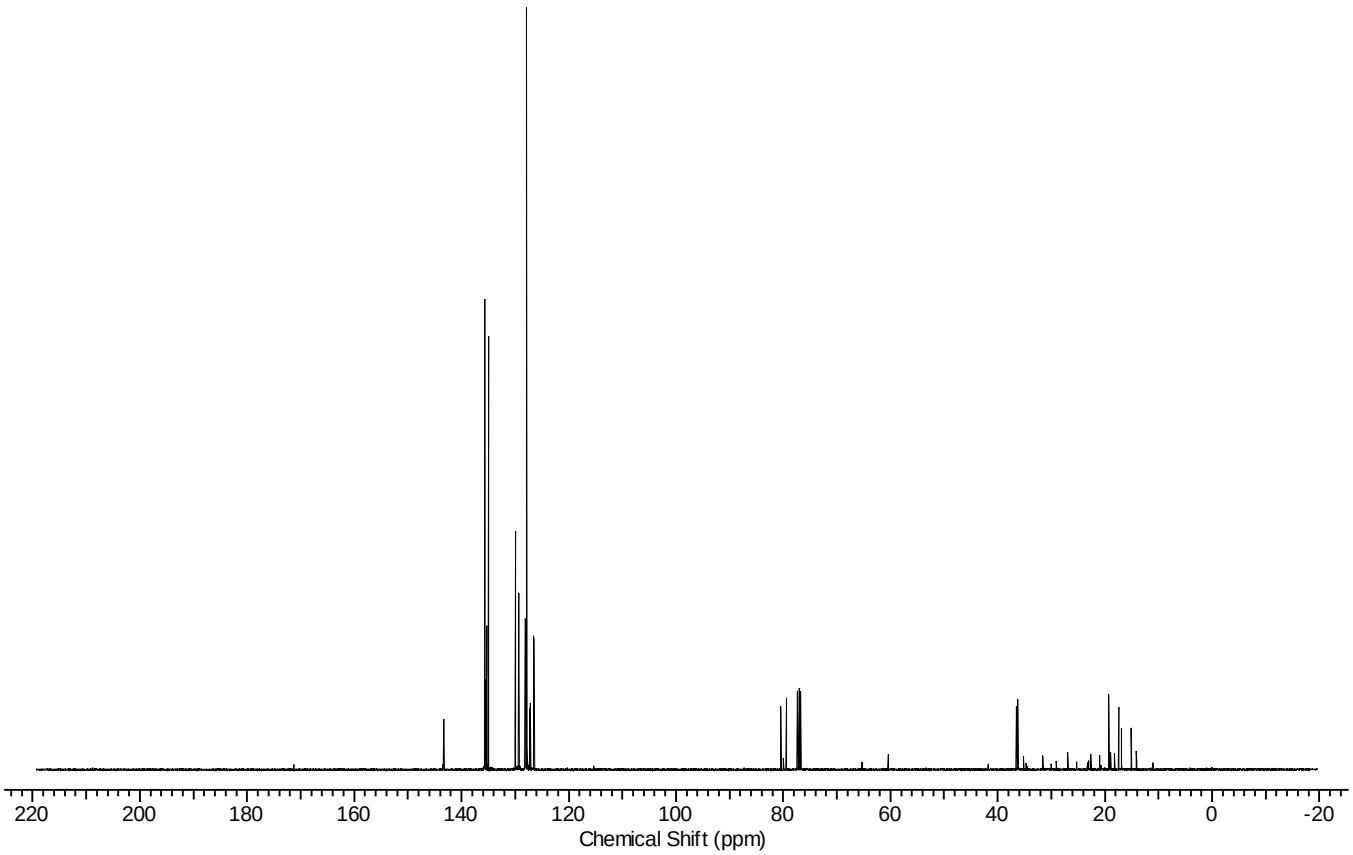
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

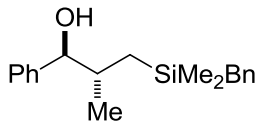

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

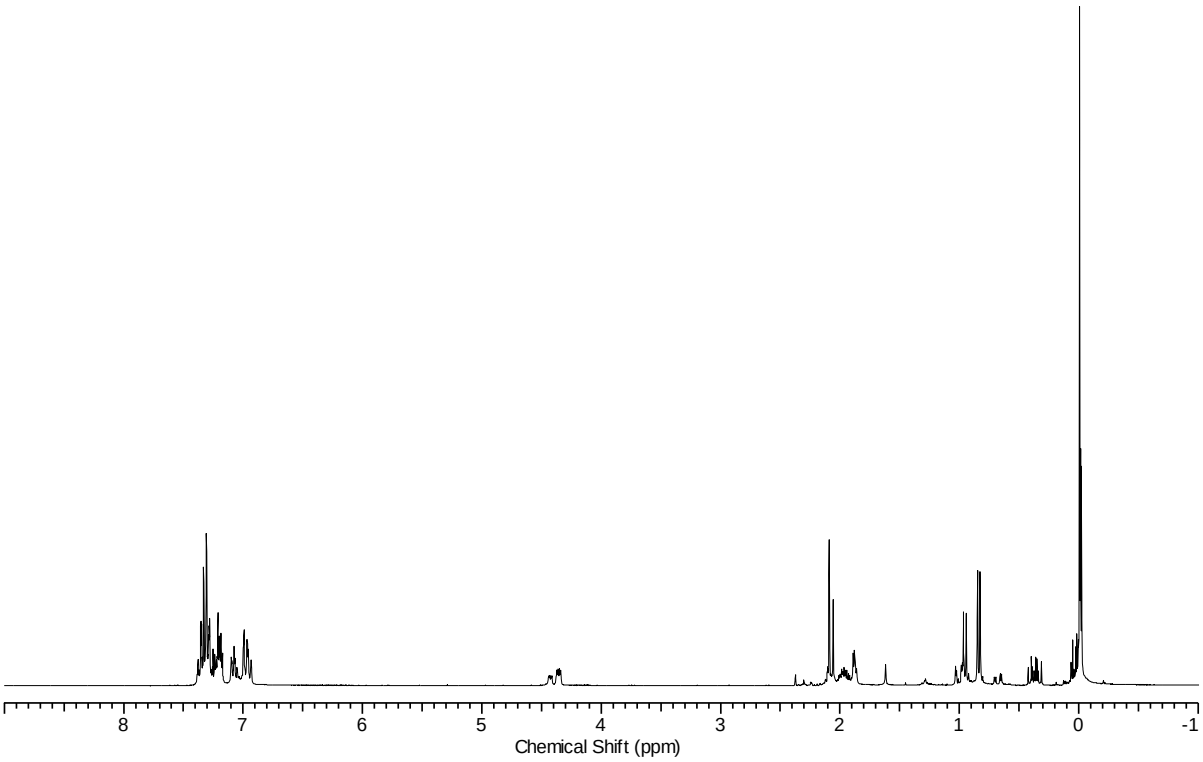

OH
Ph
SiMe2t-Bu
Me
0.12
1.01
4.70
4.65
4.60
4.55
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

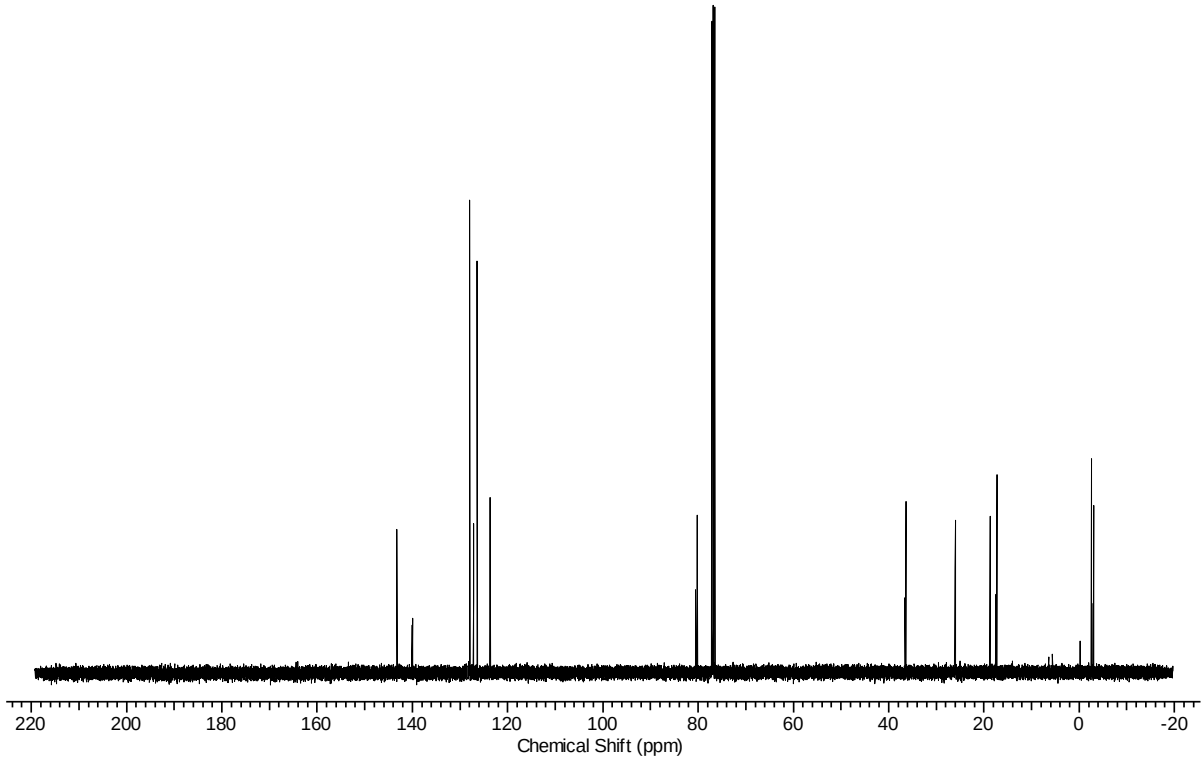

OH
Ph
SiPh3
Me

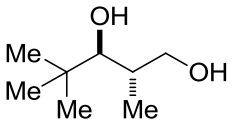

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

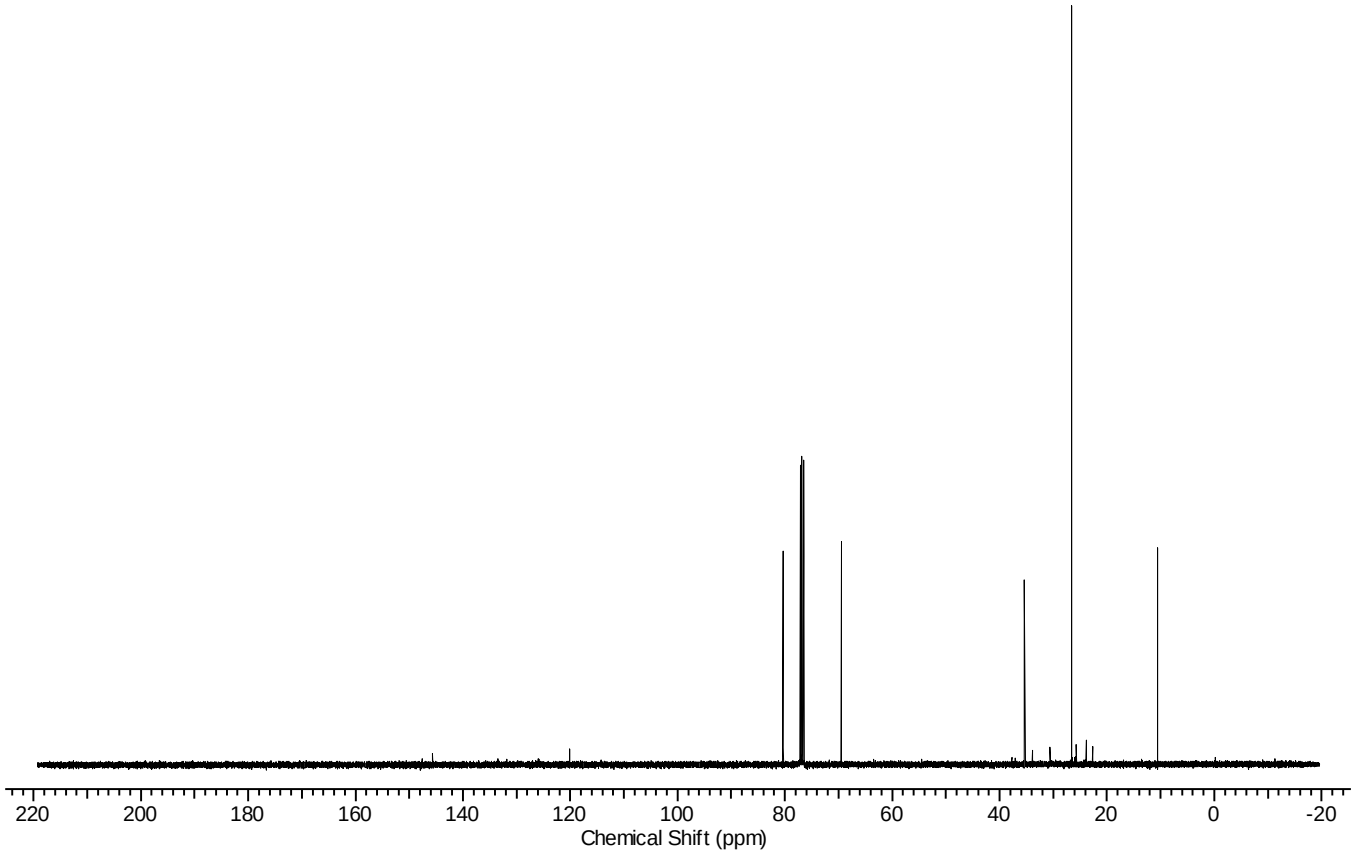

OH
Ph
SiMe2Bn
Me

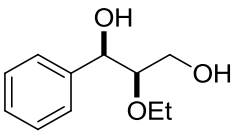

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

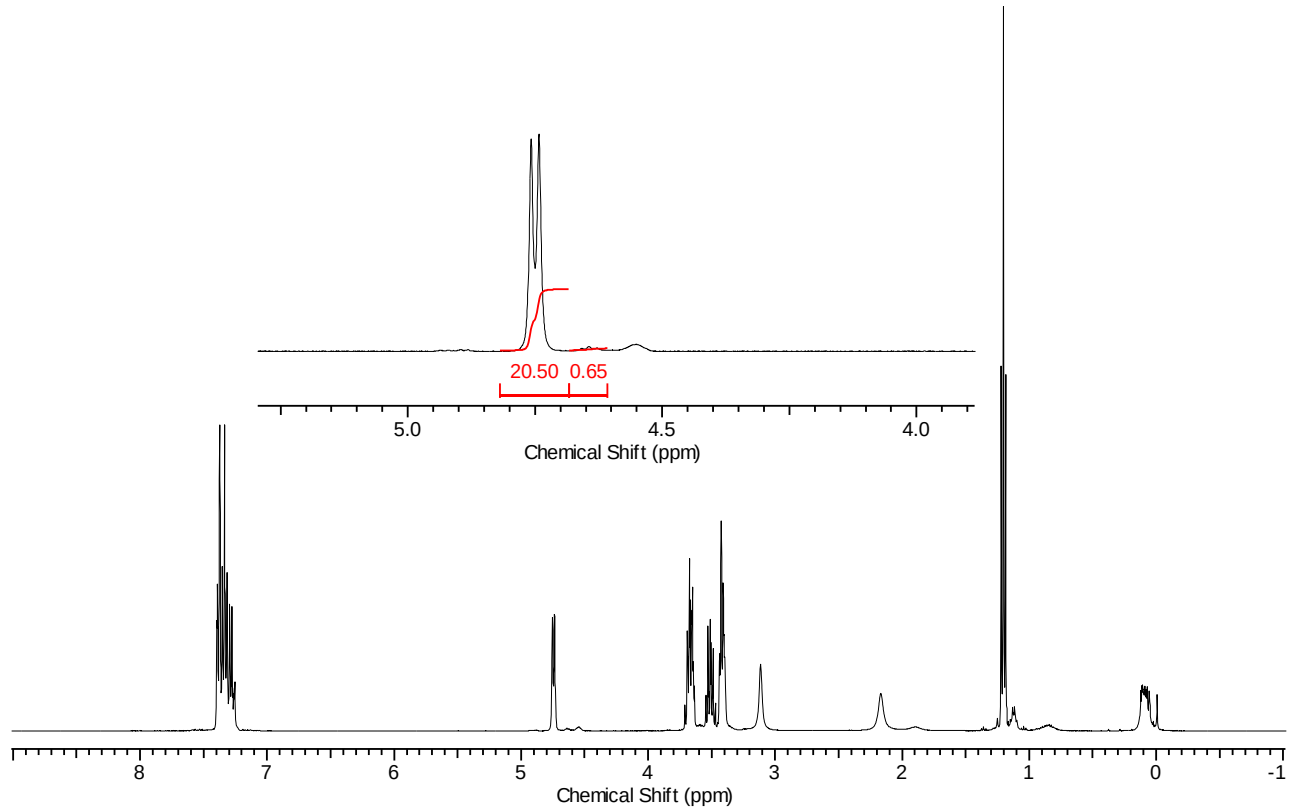

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

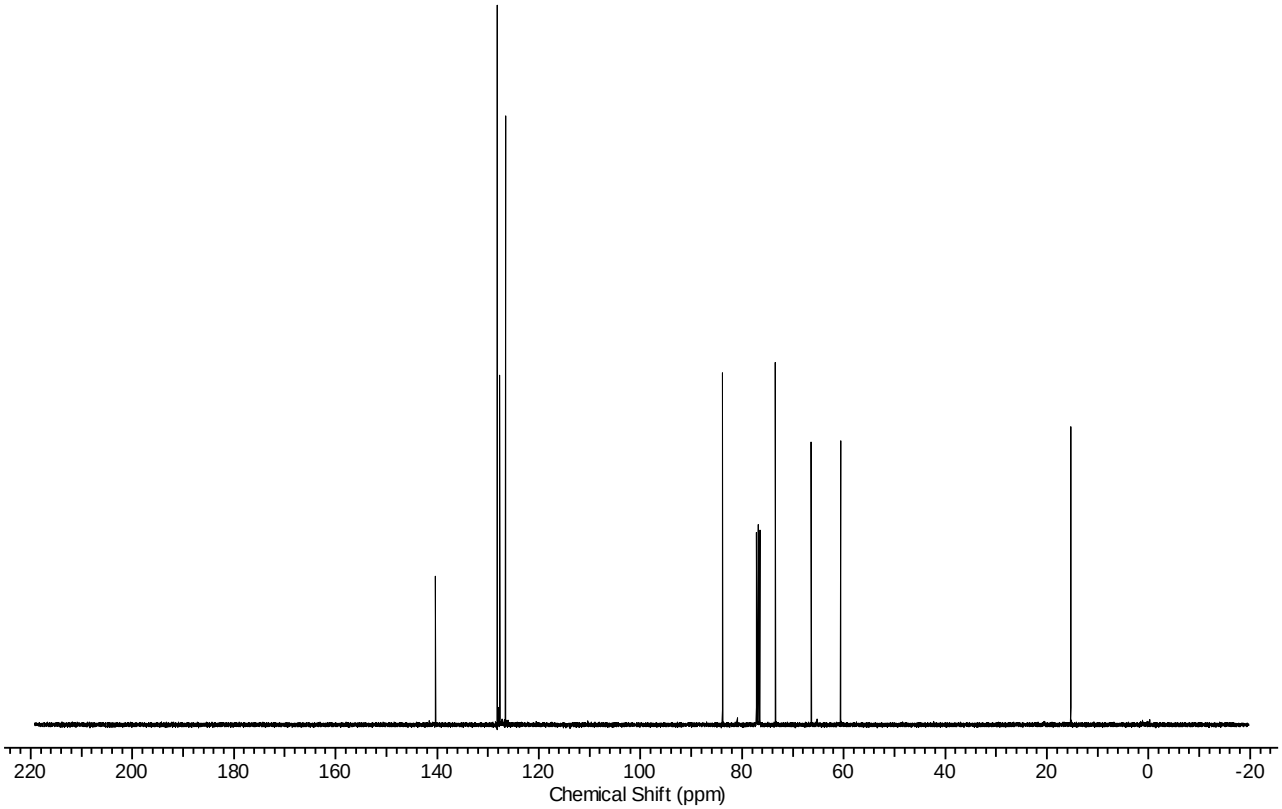

OH
Me
Me
Me
Me
OH

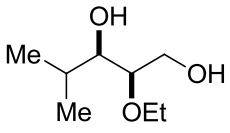
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

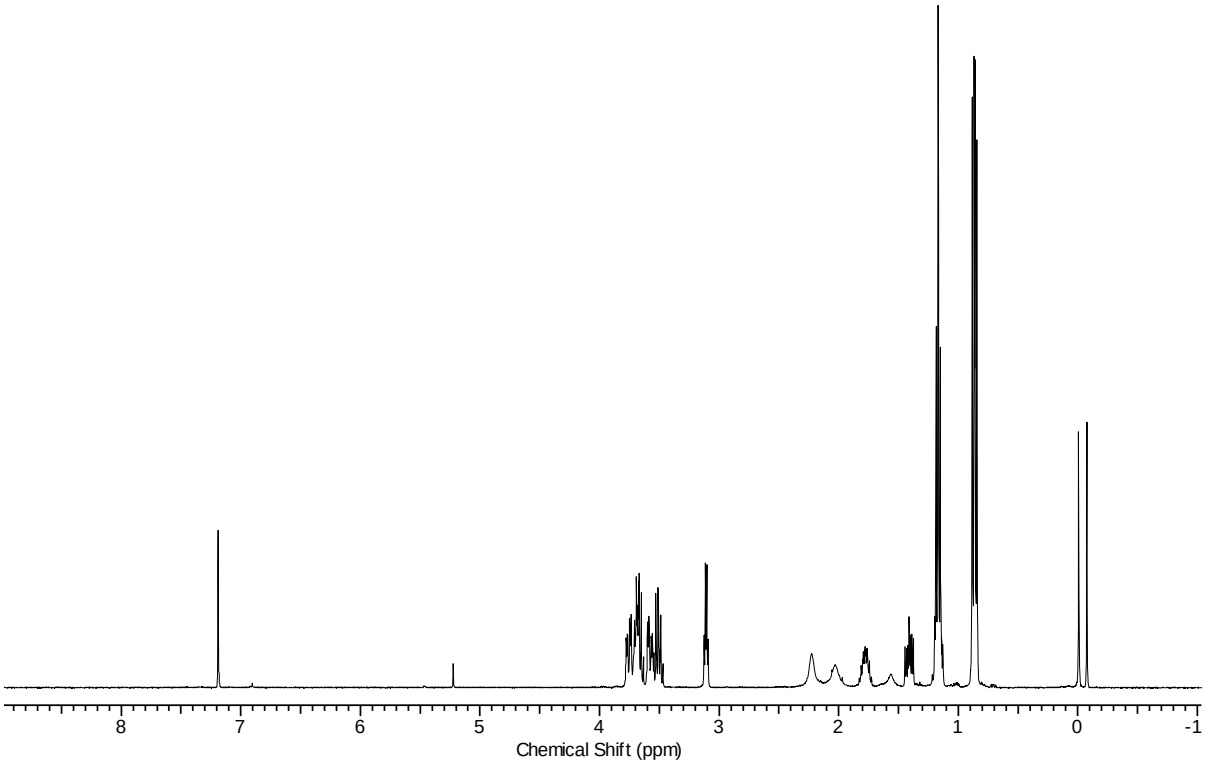

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

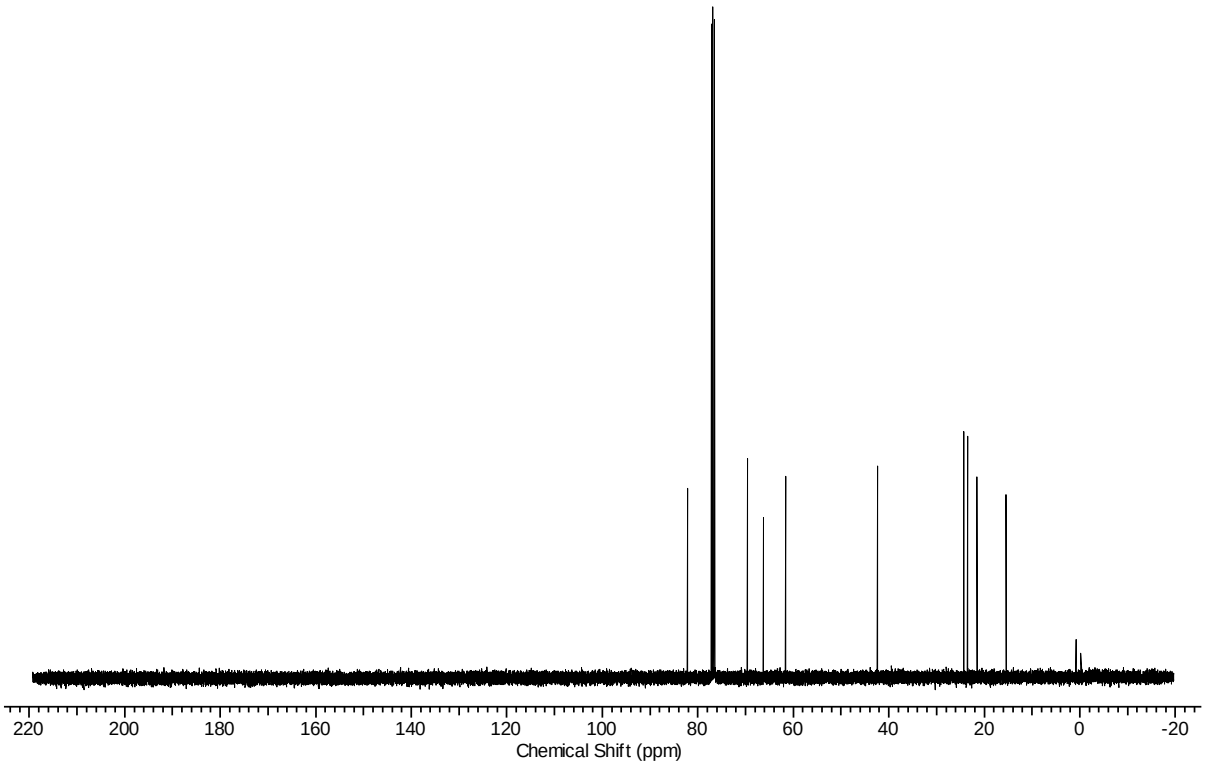

OH
OH
OEt

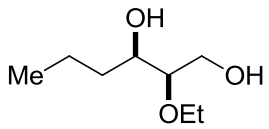

20.50
0.65
5.0
4.5
4.0
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

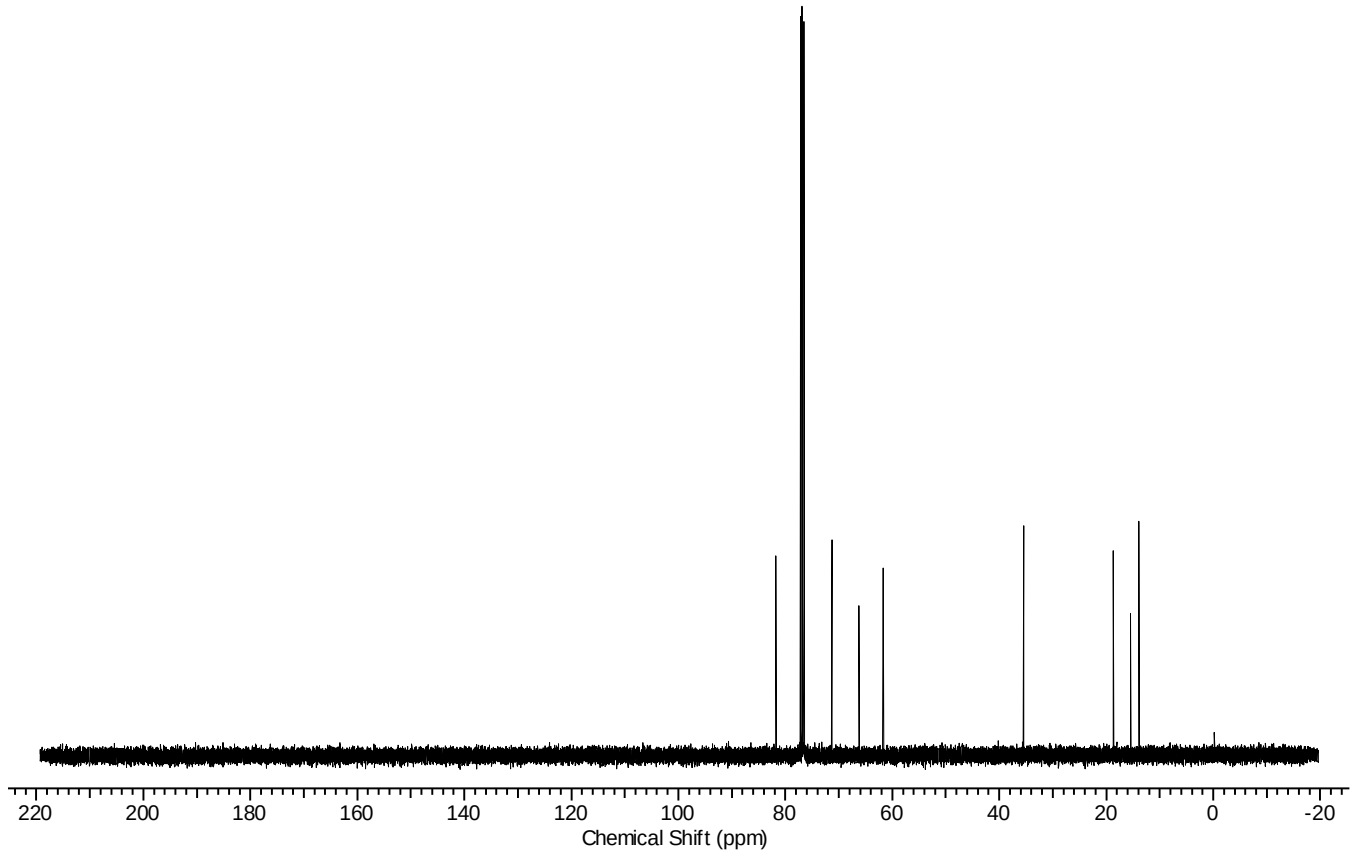

OH
Me
OH
Me
OEt

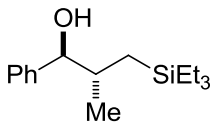

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

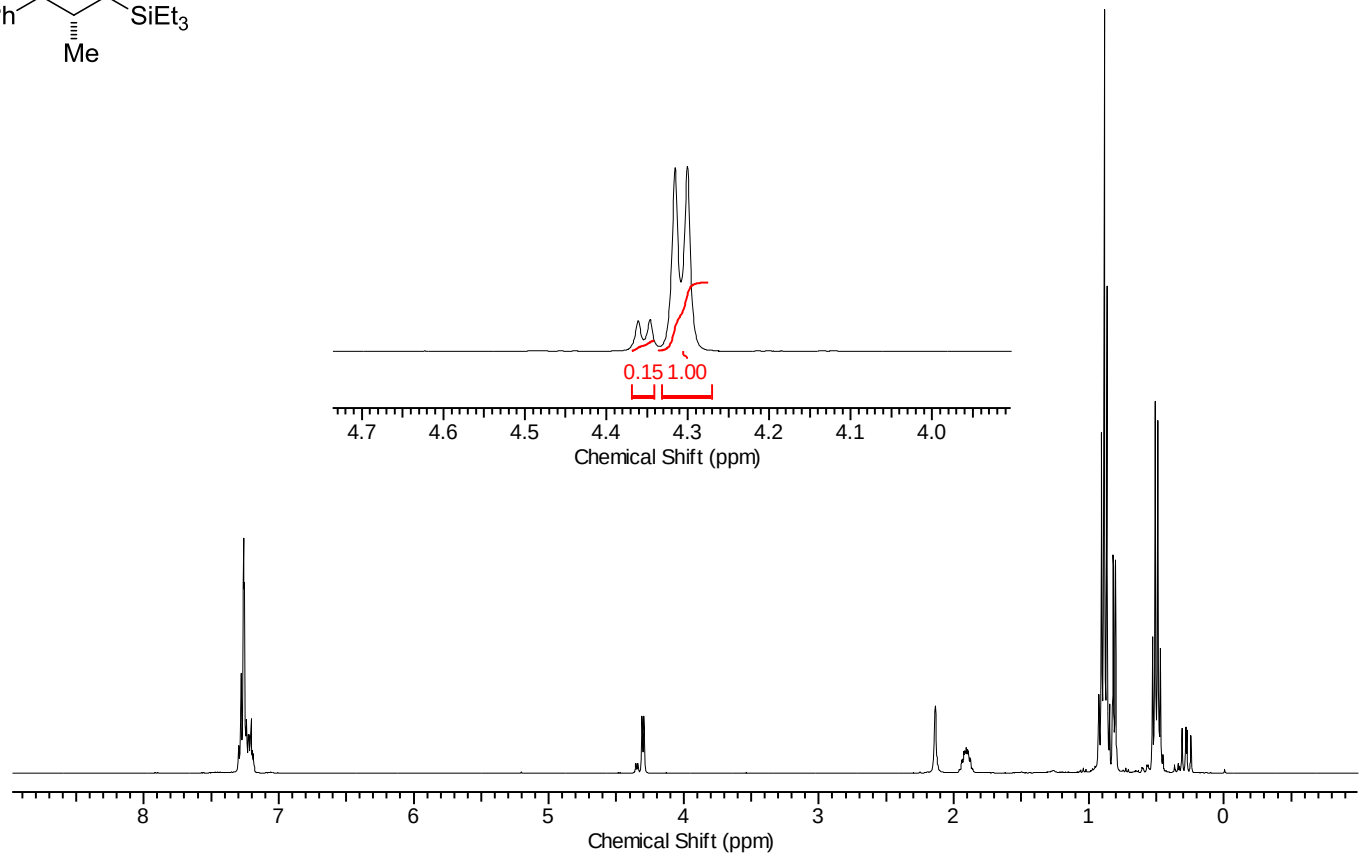

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

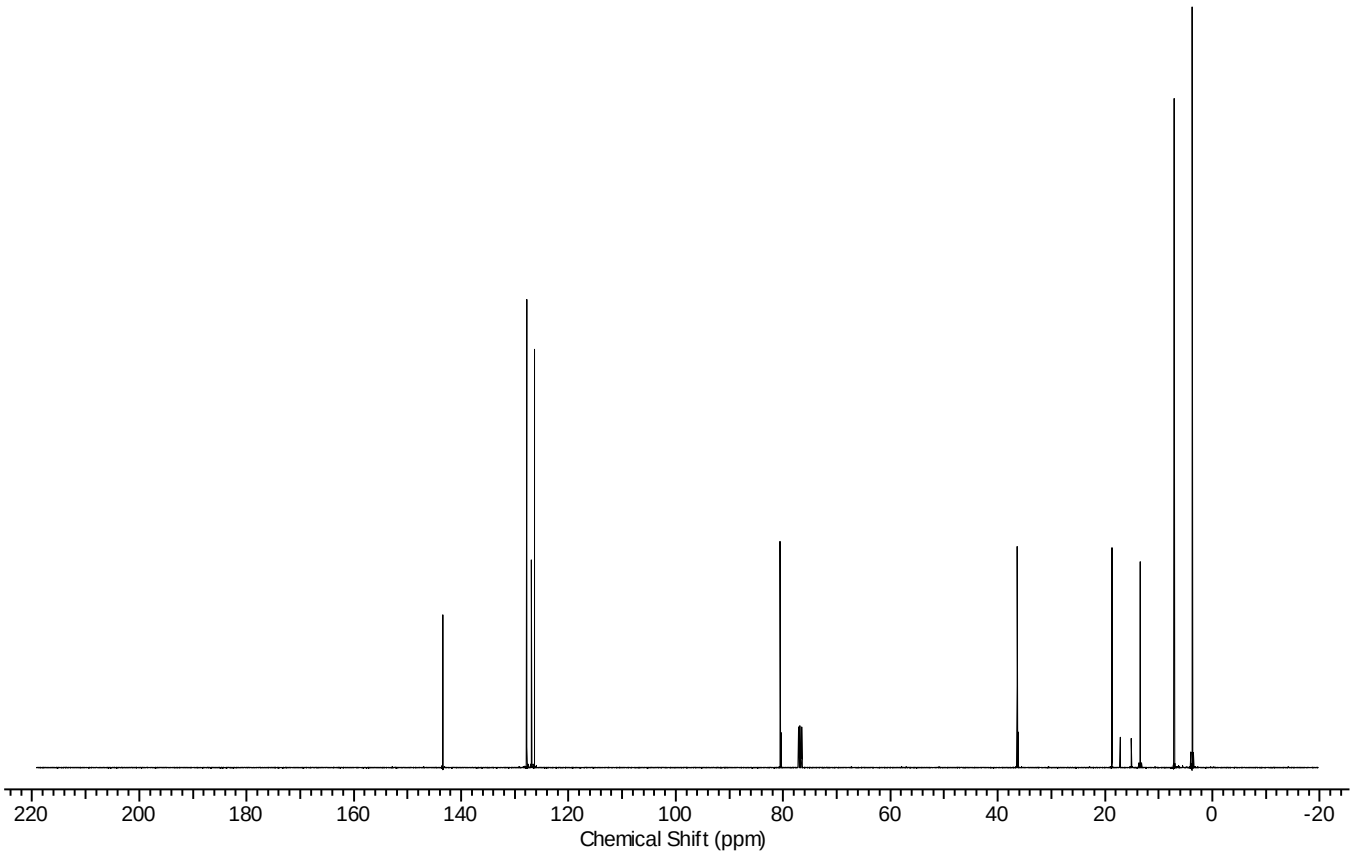

OH
Me
OH
OEt

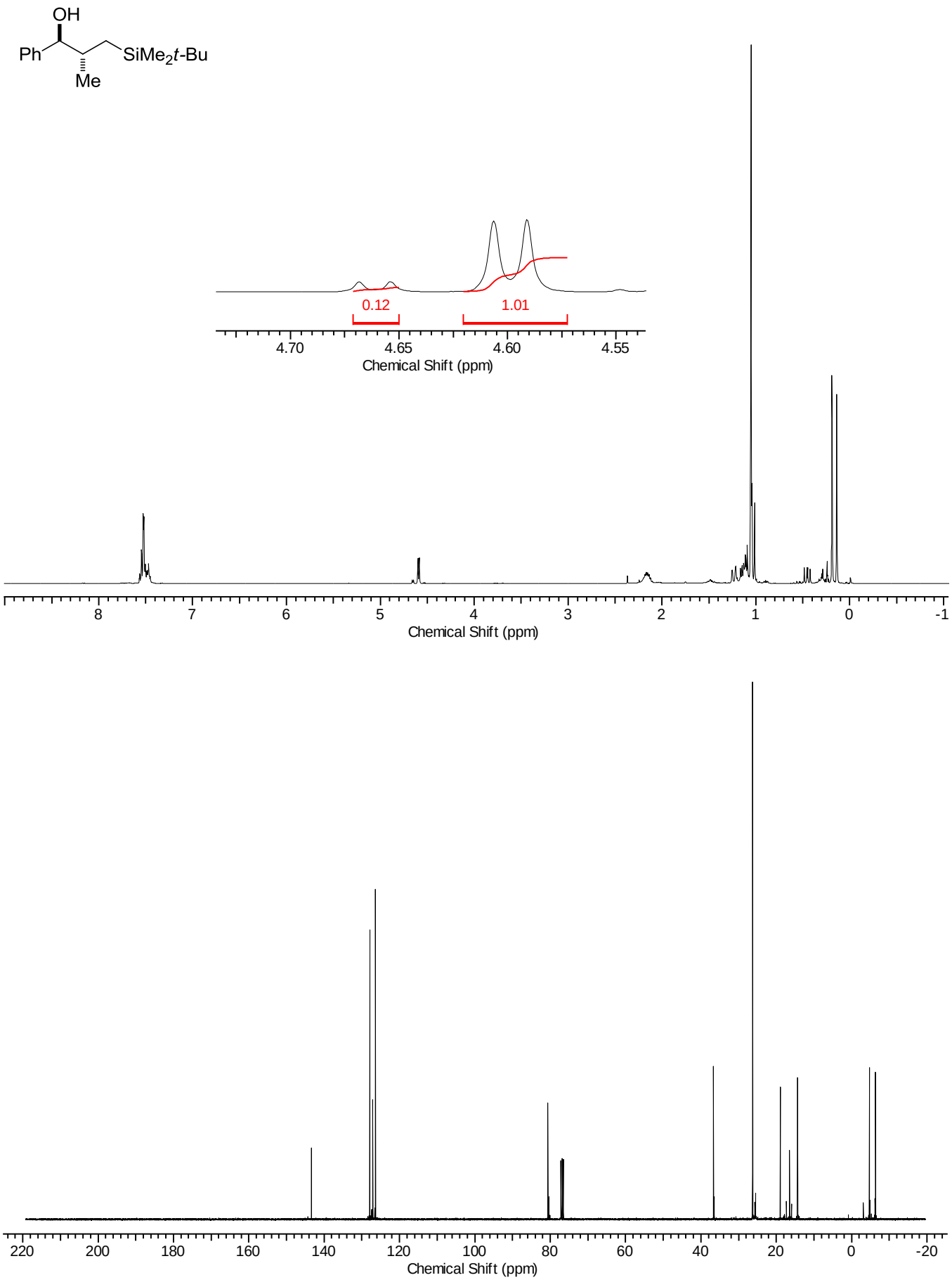
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

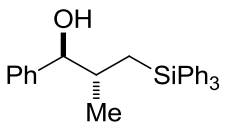

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

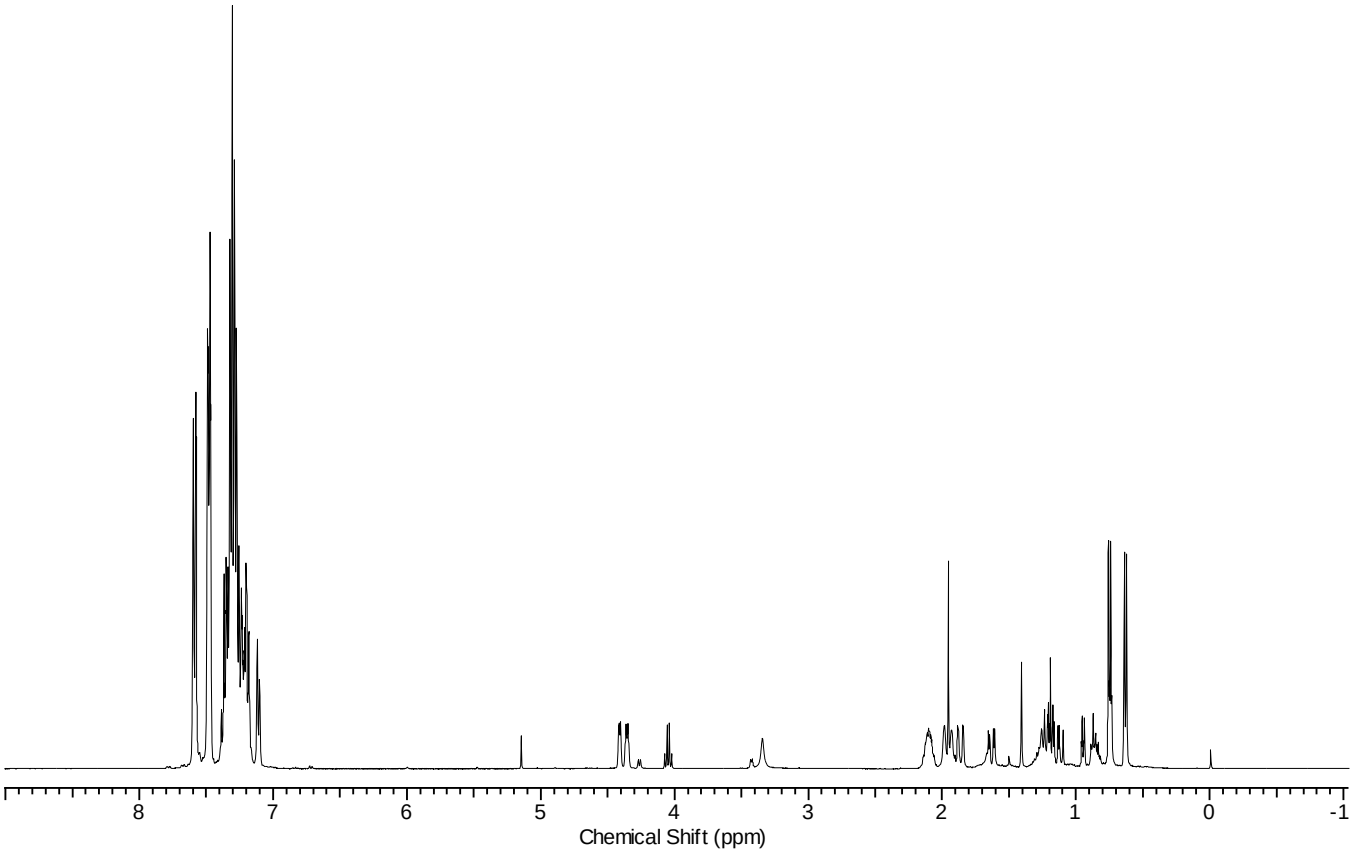

OH
Ph
SiEt3
Me

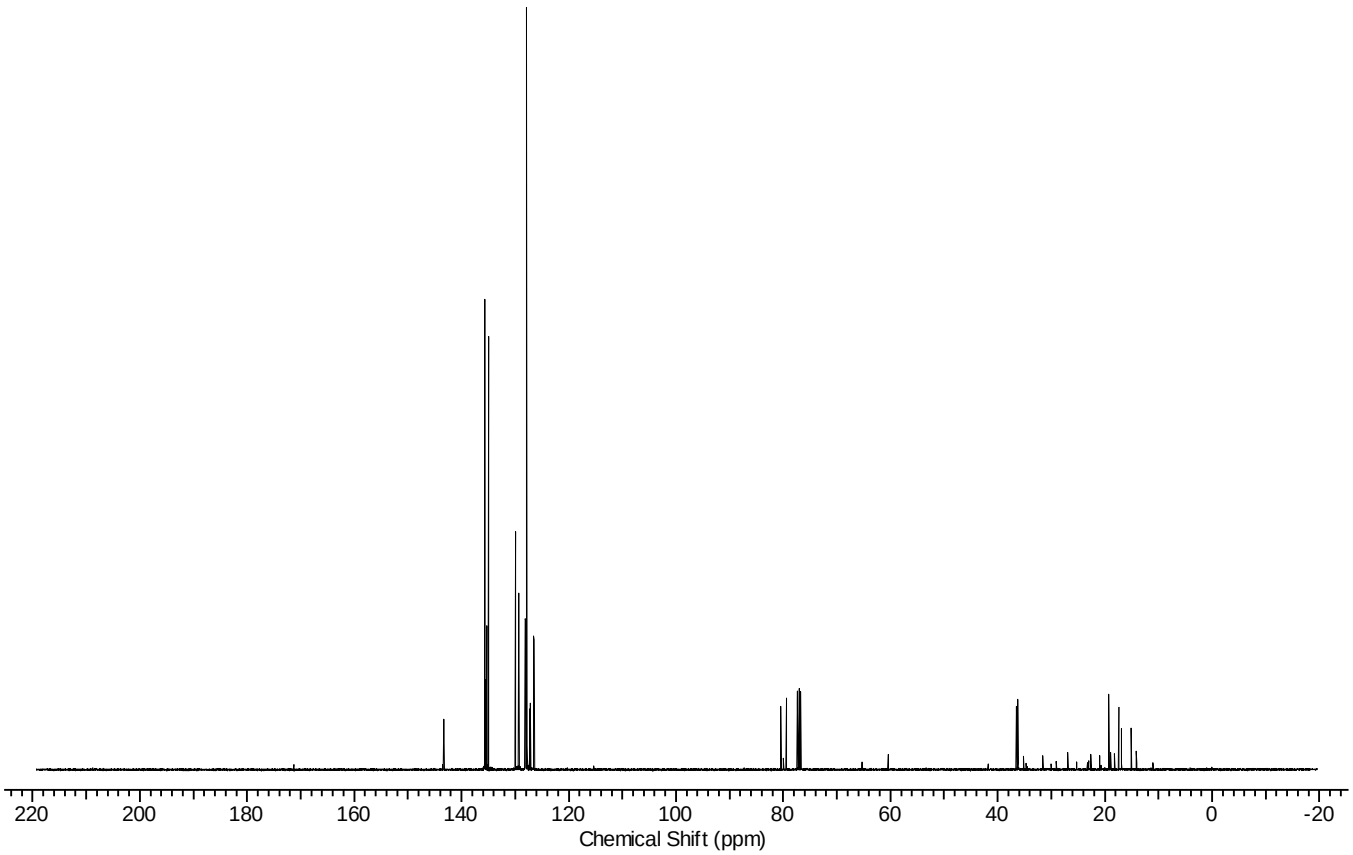

0.15 1.00
4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0
Chemical Shift (ppm)
8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

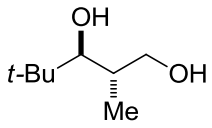

220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

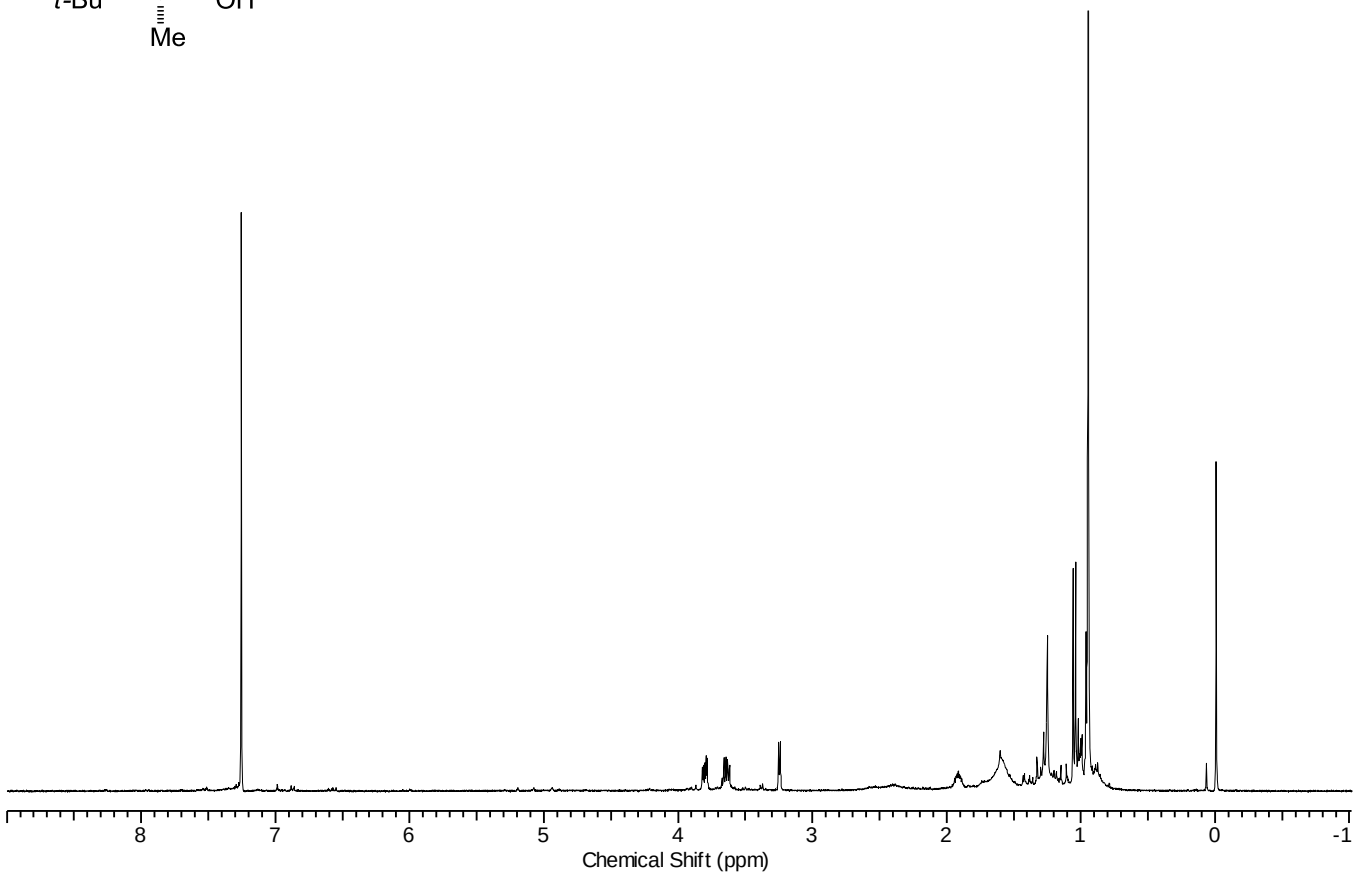

OH
Ph
SiMe2t-Bu
Me
0.12
1.01
4.70
4.65
4.60
4.55
Chemical Shift (ppm)
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

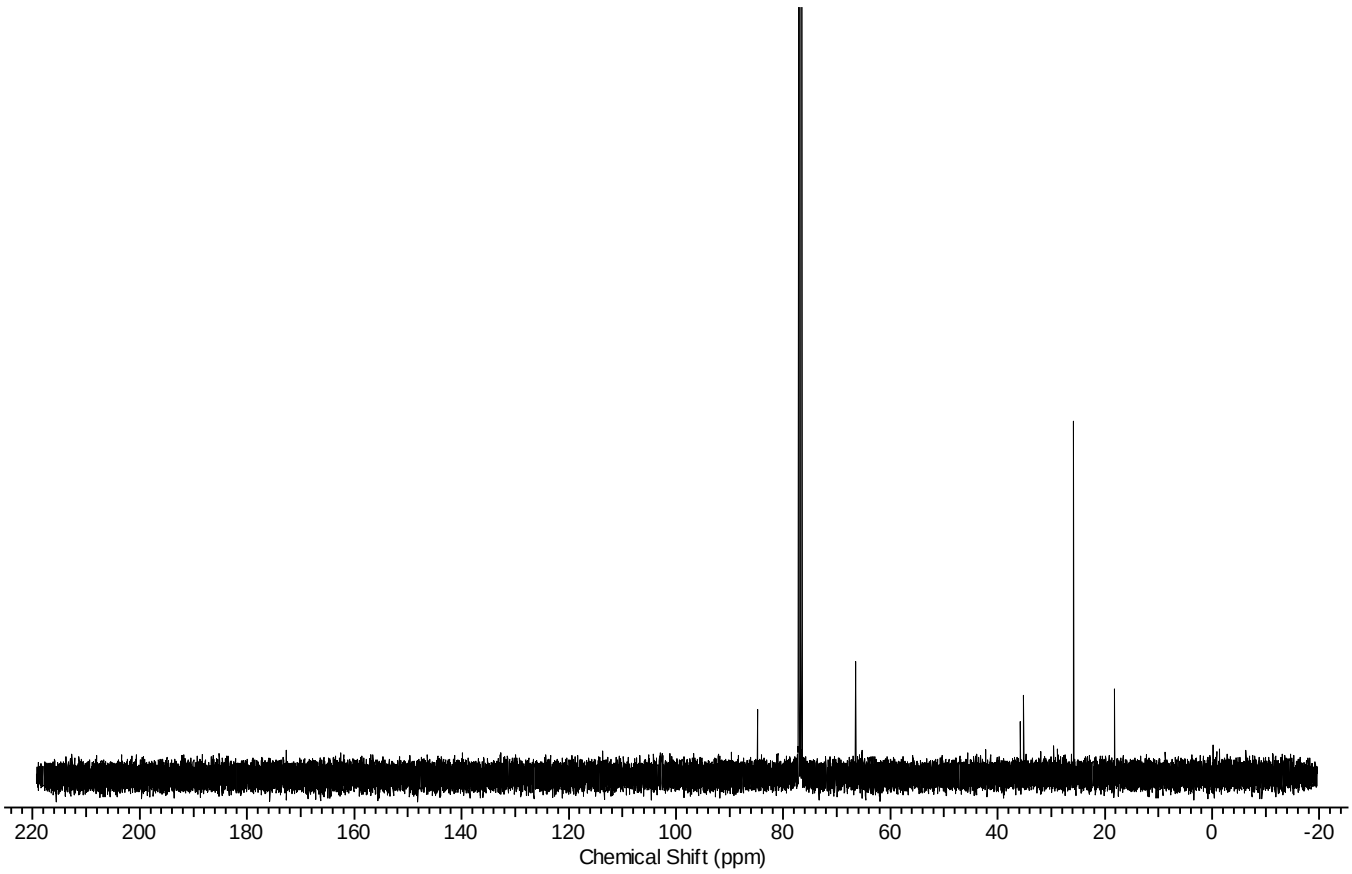

OH
Ph
SiPh3
Me

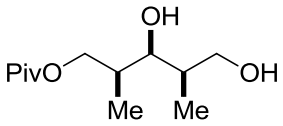

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

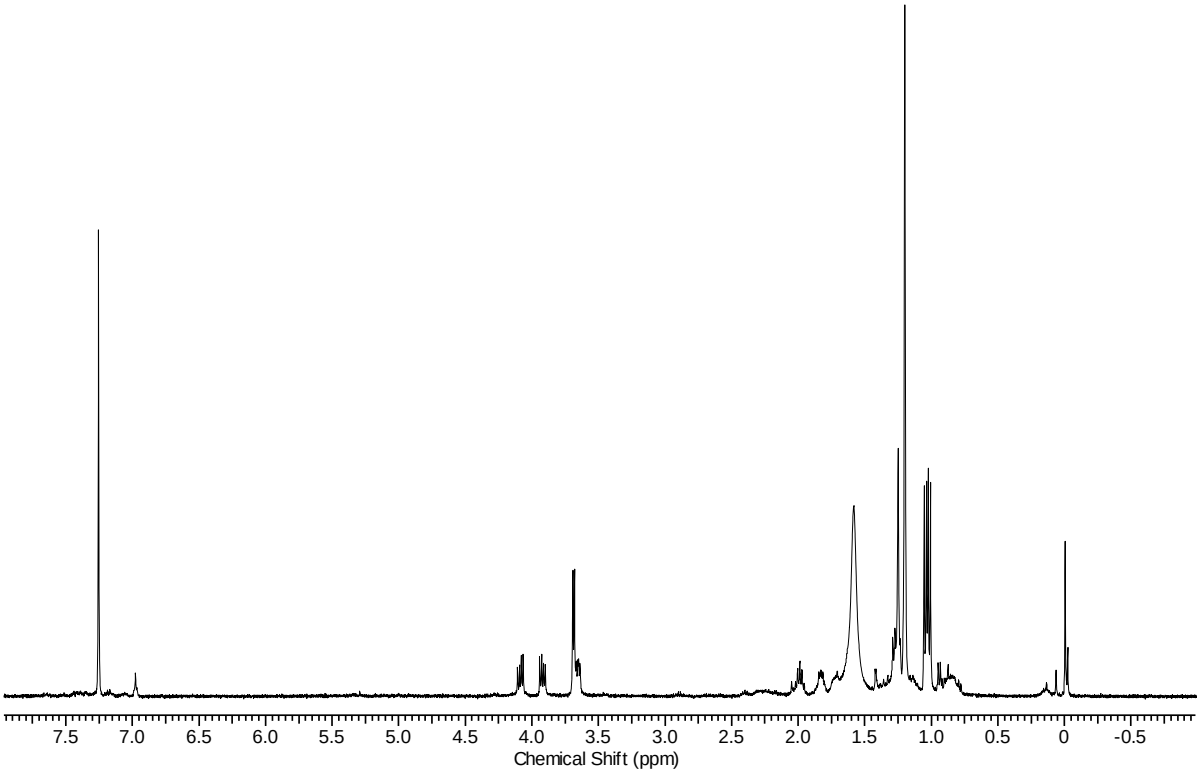

220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

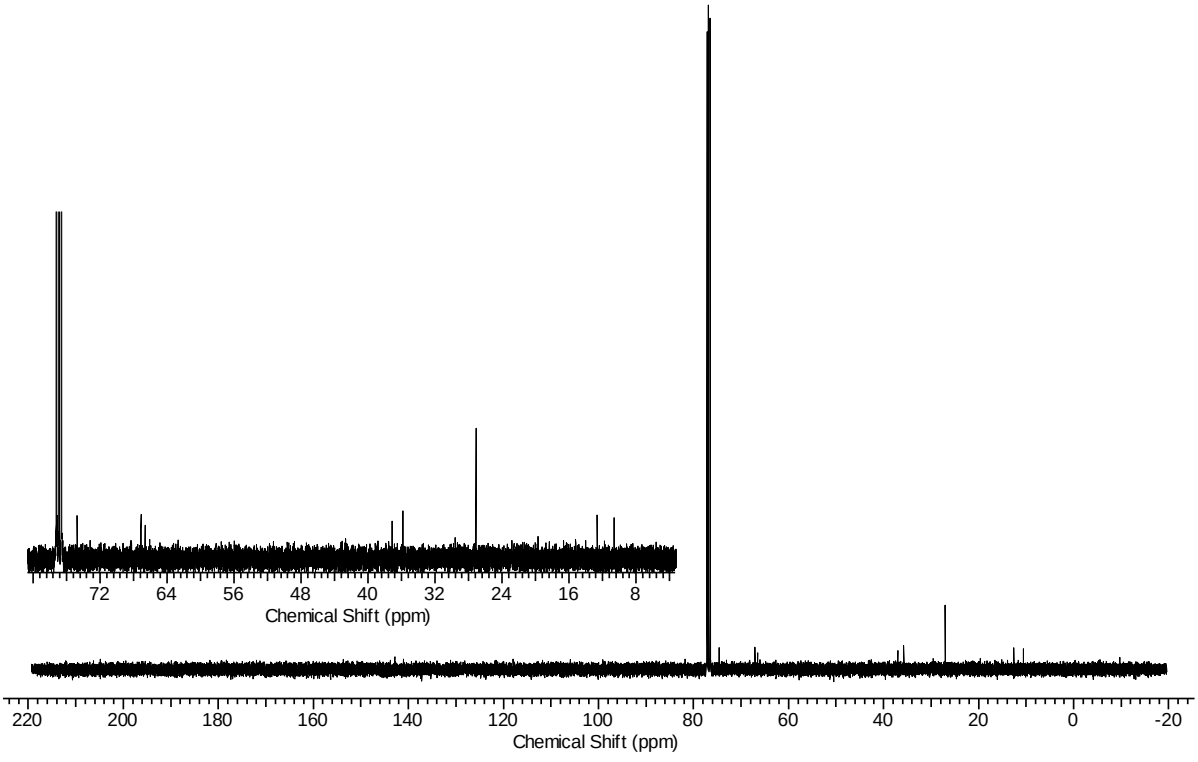

OH
t-Bu
OH
Me


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


220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


OH
PivO
OH
Me
Me


7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)


72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)