SUPPORTING INFORMATION

$PtCl_2$/XPhos; A Highly Efficient and Readily Available Catalyst for the Regioselective Hydrometallation of Propargylic Alcohols

Mark G. McLaughlin and Matthew J. Cook*

School of Chemistry and Chemical Engineering
Queen's University Belfast
Belfast. BT9 5AG, Northern Ireland
Fax: (+)44 (0)28 9097 6524
E-mail: m.cook@qub.ac.uk
Homepage: http://www.ch.qub.ac.uk/staff/cook/index.html

Table of contents

Copies of ^{1}H & ^{13}C NMR Spectra– Pg 24

General Methods

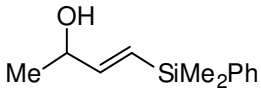
All reactions were carried out under an atmosphere of argon in oven-dried glassware with magnetic stirring. All reactions were monitored by thin layer chromatography (TLC) using Merck TLC silica gel 60 sheets, which were visualised with ultraviolet light and then developed with iodine and basic potassium 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]

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

General Procedure A: Hydrosilylation Secondary Propargyl Alcohols

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and magnetic stirrer was added $PtCl_2$ (1 mol%) and 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 °C for 20 minutes until a yellow homogenous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.5 eq.) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite *(E)* - vinyl silane.

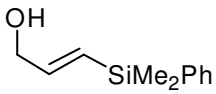
(E)-4-(dimethyl(phenyl)silyl)but-3-en-2-ol (2a)



The title compound was prepared according to general procedure A, from but-3-yn-2-ol (250 mg, 3.57 mmol) and dimethylphenylsilane (728 mg, 5.36 mmol) using $PtCl_2$ (10.0 mg, 0.0357 mmol) and XPhos (34.0 mg, 0.0714 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2a** (670 mg, 91%) as a colourless oil.

Rf (9:1 hexane-ethyl acetate) = 0.4; IR: ν_{max} (thin film) / cm^{-1} 3339, 2962, 2927, 1427, 1249, 1114, 990; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.5 (2H, m), 7.38 – 7.34 (3H, m), 6.17 (1H, dd, *J* = 18.8, 4.7 Hz), 5.96 (1H, dd, 18.8, 1.3 Hz), 4.31 (1H, m), 1.63 (1H, br), 1.27 (3H, d, *J* = 6.6), 0.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.4, 138.5, 133.8, 129, 127.8, 125.9, 70.4, 22.9, -2.7; HRMS (EI+) Calcd. For $C_{11}H_{15}OSi$ $[M\text{-}CH_3]^+$, 191.0892. Found 191.0899

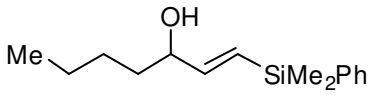
(E)-3-(dimethyl(phenyl)silyl)prop-2-en-1-ol (2b)



The title compound was prepared according to general procedure A, from propargyl alcohol (500 mg, 8.92 mmol) and dimethylphenylsilane (1.82 g, 13.4 mmol) using $PtCl_2$ (24.0 mg, 0.0892 mmol) and XPhos (85.0 mg, 0.178 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2b** (606 mg, 47%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.35; IR: ν_{max} (thin film) / cm^{-1} 3305, 1590, 1252, 1117, 829; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.54 – 7.50 (2H, m), 7.38 – 7.33 (3H, m), 6.25 (1H, ddd, *J* = 18.7, 8.1, 4.1 Hz), 6.07 (1H, ddd, *J* = 18.7, 3.4, 1.5 Hz), 4.21 (2H, d, *J*=2.8 Hz), 0.36 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.6, 138.4, 133.8, 129, 127.8, 127.1, 65.4, -2.69; HRMS (EI) Calcd. For $C_{10}H_{13}OSi$ $[M\text{-}CH_3]^+$, 177.0736. Found 177.0727

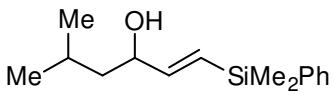
***(E)*-1-(dimethyl(phenyl)silyl)hept-1-en-3-ol (2c)**



The title compound was prepared according to general procedure A, from hept-1-yn-3-ol (320 mg, 2.86 mmol) and dimethylphenylsilane (583 mg, 4.29 mmol) using $PtCl_2$ (8.0 mg, 0.0286 mmol) and XPhos (28.0 mg, 0.0571 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2c** (603 mg, 85%) as a colourless oil.

Rf (9:1 hexane-ethyl acetate) = 0.45; IR: ν_{max} (thin film) / cm^{-1}; 3356, 2987, 2587, 1615, 1000, 960, 780; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.5 (2H, m), 7.37 – 7.35 (3H, m), 6.13 (1H, dd, *J* = 18.6, 5.5 Hz), 5.97 (1H, dd, *J* = 18.6, 1.1 Hz), 4.12 (1H, dt, *J* = 5.5, 5.5 Hz), 1.59 – 1.5 (2H, m), 1.4 – 1.25 (4H, m), 0.9 (3H, t, *J* = 7 Hz), 0.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.6, 138.5, 133.8, 129, 127.8, 126.8, 74.6, 36.6, 27.6, 14, -2.6; HRMS (EI) Calcd. For $C_{15}H_{24}OSi$ $[M]^+$,248.1565. Found 248.1583.

***(E)*-1-(dimethyl(phenyl)silyl)-5-methylhex-1-en-3-ol (2d)**

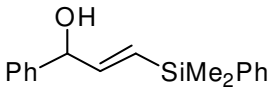


The title compound was prepared according to general procedure A, from 5-methylhex-1-yn-3-ol (250 mg, 2.23 mmol) and dimethylphenylsilane (455 mg, 3.35 mmol) using $PtCl_2$ (6.0 mg, 0.022 mmol) and XPhos (21 mg, 0.045 mmol) which following conversion to the vinyl

silane and column chromatography (9:1 Hexane/EtOAc) afforded **2d** (460 mg, 85%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.47; IR: ν_{max} (thin film) / cm^{-1}; 3368, 2956, 2870, 1618, 1428, 1249, 1117;^{1}H NMR: (400 MHz, $CDCl_3$) δ 7.64 – 7.43 (2H, m), 7.41 – 7.30 (3H, m), 6.13 (1H, dd, *J* = 18.7, 5.3 Hz), 5.98 (1H, dd, *J* = 18.7, 1.3 Hz), 4.25 – 4.15 (1H, m), 1.81 – 1.70 (1H, m) 1.50 – 1.25 (2H, m), 0.95 (3H, s), 0.92 (3H, s), 0.35 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 138.5, 133.8, 129.0, 127.8, 126.5, 72.8, 46.1, 24.6, 23.2, 22.2, -2.6, -2.6; HRMS (ES+) Calcd for $C_{15}H_{25}OSi$ [M+] 249.1675. Found 249.1670

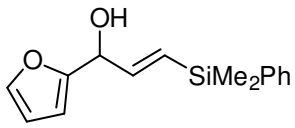
***(E)*-3-(dimethyl(phenyl)silyl)-1-phenylprop-2-en-1-ol (2e)**



The title compound was prepared according to general procedure A, from 1-phenyl-2-propyn-2-ol (250 mg, 1.89 mmol) and dimethylphenylsilane (386 mg, 2.84 mmol) using $PtCl_2$ (5.0 mg, 0.019 mmol) and XPhos (18 mg, 0.038 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2e** (460 mg, 87%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.44; IR: ν_{max} (thin film) / cm^{-1} ; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.62 – 7.59 (1H, m), 7.52 – 7.49 (2H, m), 7.40 – 7.29 (7H, m), 6.23 (1H, dd, *J* = 18.6, 4.8 Hz), 6.07 (1H, dd, *J* = 18.6, 1.1 Hz), 5.11 (1H, d, *J* = 4.8), 0.40 (3H,s), 0.30 (3H,s) ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 142.3, 138.3, 133.7, 132.9, 129.4, 128.4, 127.7, 127.3, 126.4, 76.5, -2.7; HRMS (EI+) Calcd. for $C_{16}H_{16}Si$ 236.1021. Found 236.1025.

(E)-3-(dimethyl(phenyl)silyl)-1-(furan-2-yl)prop-2-en-1-ol (2f)



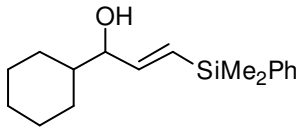
The title compound was prepared according to general procedure A, from freshly prepared 1-(furan-2-yl)prop-2-yn-1-oll[2] (250 mg, 1.89 mmol) and dimethylphenylsilane (386 mg, 2.84 mmol) using $PtCl_2$ (5.0 mg, 0.019 mmol) and XPhos (18 mg, 0.038 mmol) which following

[2] R. U. Braun, M. Ansorge, T. J. J. Mueller, *Chemistry – A European Journal,* **2006,** *12,* 9081

conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2f** (460 mg, 87%) as a yellow oil.

Rf (9:1 hexane – ethyl acetate) = 0.19; IR: ν_{max} (thin film) / cm^{-1} ; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.67 – 7.51 (2H, m), 7.45 – 7.34 (4H, m), 6.37 (2H, dd, *J* = 18.6, 4.8 Hz), 6.73 (1H, dd, *J* = 3.2, 1.9 Hz), 6.24 (1H, dd, *J* = 18.6, 1.3 Hz), 6.25 (1H, dt, *J* = 3.2, 0.8 Hz), 5.27 (1H, dd, *J* = 4.8, 4.8 Hz), 2.53 (1H, d, *J* = 5.5 Hz), 0.43 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 145.4, 142.4, 138.1, 133.8, 127.8, 110.2, 106.7, 69.8, -2.7; HRMS (EI) Calcd. for $C_{14}H_{15}O_2Si$ [M-CH_3] 243.0841. Found 243.0845

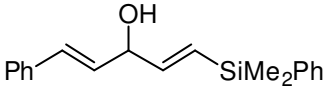
***(E)*-1-cyclohexyl-3-(dimethyl(phenyl)silyl)prop-2-en-1-ol (2g)**



The title compound was prepared according to general procedure A, from freshly prepared 1-cyclohexylprop-2-yn-1-ol[3] (471 mg, 3.41 mmol) and dimethylphenylsilane (695 mg, 5.115 mmol) using $PtCl_2$ (9.0 mg, 0.034 mmol) and XPhos (32 mg, 0.068 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2g** (664 mg, 72%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.34; IR: ν_{max} (thin film) / cm^{-1} 3380, 3068, 2998, 2925, 2852, 1958, 1618, 1247, 1113, 993; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.55 – 7.49 (2H, m), 7.39 – 7.32 (3H, m), 6.13 (1H, dd, *J* = 18.7, 5.5 Hz), 5.96 (1H, d, *J* = 18.6), 3.89 (1H, dt, *J* = 5.5, 5.5 Hz), 1.88 – 0.82 (11H, m), 0.35 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 133.8, 129, 128, 127.8, 79.1, 43.5, 29, 28.2, 26.5, 26.2, 26.1, -2.5; HRMS (EI) Calcd. for $C_{17}H_{24}Si$ [M-H_2O]$^+$ 256.1647. Found 256.1647.

***(1E,4E)*-1-(dimethyl(phenyl)silyl)-5-phenylpenta-1,4-dien-3-ol (2h)**



The title compound was prepared according to general procedure A, from freshly prepared *(E)*-1-phenylpent-1-en-4-yn-3-ol[2] (500 mg, 3.16 mmol) and dimethylphenylsilane (644 mg,

[3] Ye, L.; He, L.; Zhang, L. , *J. Am. Chem. Soc.* **2010**, *132,* 8550

4.74 mmol) using $PtCl_2$ (8.0 mg, 0.032 mmol) and XPhos (30 mg, 0.063 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **2h** (749 mg, 81%) as a colourless oil.

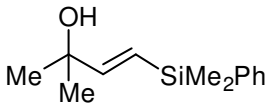
Rf (9:1 hexane – ethyl acetate) = 0.34; IR: ν_{max} (thin film) / cm^{-1} 3435, 2065, 1636, 1559, 1427, 1247, 1114, 965, 822; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.60 – 7.48 (2H, m), 7.43 – 7.19 (8H, m), 6.61 (1H, d, *J* = 15.9 Hz), 6.24 (1H, dd, *J* = 15.9, 6.4Hz), 6.18 (1H, dd, *J* = 18.7, 6.6 Hz), 6.10(1H, dd, *J* = 18.87 1.0 Hz), 4.86 – 4.8 (1H, m), 0.37 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.94, 136.6, 133.8, 130.9, 130.1, 129.1, 128.6, 128.2, 127.8, 126.6, 75.3, -2.7; HRMS (ES+) Cald for $C_{19}H_{21}OSi$ $[M-H]^+$ 293.1362. Found 293.1359

General Procedure B: Hydrosilylation of Disubstituted Propargyl Alcohols

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and magnetic stirrer was added $PtCl_2$ (0.5 mol%) and 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (1 mol%) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 °C for 20 minutes until a yellow homogenous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.1 eq.) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite *(E)* - vinyl silane.

.

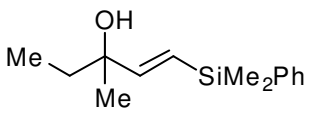
(E)-4-(dimethyl(phenyl)silyl)-2-methylbut-3-en-2-ol (4a)



The title compound was prepared according to general procedure B, from 2-methylbut-3-yn-2-ol (250 mg, 2.98 mmol) and dimethylphenylsilane (446 mg, 3.28 mmol) using $PtCl_2$ (4.0 mg, 0.015 mmol) and XPhos (14.0 mg, 0.0298 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4a** (597 mg, 91%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.33; IR: ν_{max} (thin film) / cm^{-1} 3460, 2957, 1490, 1427, 1248, 1117, 999; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.5 (2H, m), 7.41 – 7.34 (3H, m), 6.23 (1H, d, J = 19.4 Hz), 5.95 (1H, d, J = 19.1 Hz), 1.31 (6H, s), 0.35 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 138.7, 133.8, 129, 127.8, 122.5, 72.1, 29.4, -2.6; HRMS (EI) Calcd. for $C_{12}H_{17}OSi$ $[M\text{-}CH_3]^+$ 205.1049. Found 205.1051

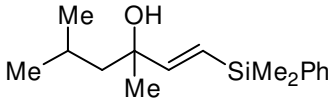
(E)-1-(dimethyl(phenyl)silyl)-3-methylpent-1-en-3-ol (4b)



The title compound was prepared according to general procedure B, from 3-Methyl-1-pentyn-3-ol (300 mg, 3.06 mmol) and dimethylphenylsilane (458 mg, 3.37 mmol) using $PtCl_2$ (4.0 mg, 0.015 mmol) and XPhos (14.5 mg, 0.0306 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4b** (666 mg, 93%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.42; IR: ν_{max} (thin film) / cm^{-1} 3486, 2963, 1635, 1478, 1456, 980, 885; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.54 – 7.49 (2H, m), 7.39 – 7.33 (3H, m), 6.14 (1H, d, *J* = 19 Hz), 5.95 (1H, d, 18.8 Hz), 1.56 (2H, qd, *J* = 7.5, 1.8 Hz), 1.26 (3H, s), 0.86 (3H, t, *J* = 7.4 Hz), 0.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1, 138.8, 133.8, 128.9, 127.7, 123.6, 74.4, 34.7, 27.2, 8.2, -2.5; HRMS (ES+) Calcd for $C_{14}H_{23}OSi$ $[M+H]^+$ 235.1518. Found 235.1518.

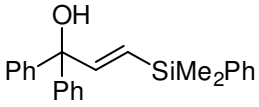
***(E)*-1-(dimethyl(phenyl)silyl)-3,5-dimethylhex-1-en-3-ol (4c)**



The title compound was prepared according to general procedure B, from 3,5-dimethyl-1-hexyn-3-ol (250 mg, 1.98 mmol) and dimethylphenylsilane (297 mg, 2.18 mmol) using $PtCl_2$ (3.0 mg, 0.010 mmol) and XPhos (10 mg, 0.021 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4c** (420 mg, 81%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.39 ; IR: ν_{max} (thin film) / cm^{-1} 3434, 2956, 1616, 1466, 1427, 1248, 1114; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.49 (2H, m), 7.37 – 7.34 (3H, m), 6.17 (1H, d, *J* = 18.8 Hz), 5.95 (1H, d, *J* = 19.4 Hz), 1.79 – 1.66 (1H, m), 1.49 – 1.44 (2H, m), 1.27 (3H, s), 0.93 (3H, d, *J* = 4.5 Hz), 0.91 (3H, d, *J* = 4.5 Hz), 0.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 133.8, 128.9, 127.7, 122.6, 99.8, 74.7, 50.8, 28.7, 24.6, 24.3, -2.5; HRMS (EI) Calcd for $C_{15}H_{23}OSi$ $[M-CH_3]^+$ 257.1518. Found 257.1523

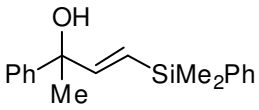
***(E)*-3-(dimethyl(phenyl)silyl)-1,1-diphenylprop-2-en-1-ol (4d)**



The title compound was prepared according to general procedure B, from 1,1-Diphenyl-2-propyn-1-ol (250 mg, 1.2 mmol) and dimethylphenylsilane (180mg, 1.32 mmol) using $PtCl_2$ (1.5 mg, 0.006 mmol) and XPhos (6.0 mg, 0.012 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4d** (305 mg, 79%) as a colourless solid.

Rf (9:1 hexane – ethyl acetate) = 0.49 ; IR: ν_{max} (thin film) / cm^{-1} 3436, 2067, 1734, 1363, 1559, 668 ; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.49 (2H, m), 7.36 – 7.28 (13H, m), 6.72 (1H, d, *J* = 18.8 Hz), 6.14 (1H, d, *J* = 18.6 Hz), 0.38 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 152, 145.7, 133.8, 129, 128.2, 127.8, 127.2, 126.9, 125.9, 802. -2.5; HRMS (EI) Calcd. for $C_{23}H_{24}OSi$ $[M]^+$, 344.1596. Found 344.1594

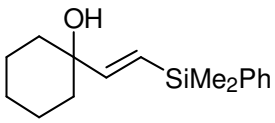
***(E)*-4-(dimethyl(phenyl)silyl)-2-phenylbut-3-en-2-ol (4e)**



The title compound was prepared according to general procedure B, from freshly prepared 2-Phenyl-3-butyn-2-ol[4] (330 mg, 2.26 mmol) and dimethylphenylsilane (338 mg, 2.49 mmol) using $PtCl_2$ (3.0 mg, 0.011 mmol) and XPhos (11 mg, 0.023 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4e** (535 mg, 84%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.55 ; IR: ν_{max} (thin film) / cm^{-1} 3475, 2945, 1687, 1456, 1001, 865, ; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.52 – 7.47 (2H, m), 7.44 – 7.40 (2H, m), 6.39 (1H, d, *J* = 18.8 Hz), 6.06 (1H, d, *J* = 18.8 Hz),1.93 (1H, s) 1.60 (3H, s), 0.35 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.5, 146.3, 138.5, 133.8, 129.0, 128.3, 127.8, 125.2, 124.1, 75.6, 29.3, -2.6 HRMS (EI+) Calcd. for $C_{18}H_{22}OSi$ $[M]^+$ 282.1445. Found 282.1440

***(E)*-1-(2-(dimethyl(phenyl)silyl)vinyl)cyclohexanol (4g)**

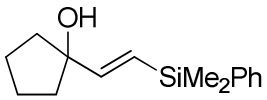


[4] Yeom, H. S. ; Lee, Y. ; Jeong, J. ; So, E.; Hwang, S.; Shin, S.; Lee, J.; Lee, S. S. *Angew. Chem. Int. Ed.* **2010,** *49*, 1611

The title compound was prepared according to general procedure B, from 1-Ethynyl-1-cyclohexanol (250 mg, 2.02 mmol) and dimethylphenylsilane (302 mg, 2.22 mmol) using $PtCl_2$ (3.0 mg, 0.010 mmol) and XPhos (10 mg, 0.020 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4g** (494 mg, 94%) as a colourless solid.

Rf (9:1 hexane – ethyl acetate) = 0.63; IR: ν_{max} (thin film) / cm^{-1} 3435, 2348, 2089, 1635, 1559, 1506, 1457, 895 , ^1H NMR: (300 MHz, $CDCl_3$) δ 7.53 – 7.49 (2H, m), 7.37 – 7.34 (3H, m), 6.22 (1H, d, *J* = 18.5 Hz), 6.00 (1H, d, *J* = 18.5 Hz), 1.7 – 1.25 (10H, m), 0.35 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 138.8, 133.8, 129, 127.7, 123.1, 72.7, 37.4, 25.5, 22, -2.5; HRMS (EI) Calcd. for $C_{16}H_{22}Si$ $[M-H_2O]^+$ 242.1491. Found 242.1489

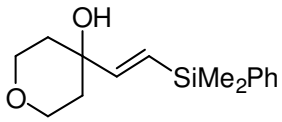
(E)-1-(2-(dimethyl(phenyl)silyl)vinyl)cyclopentanol (4g)



The title compound was prepared according to general procedure B, from 1-ethynylcyclopentanol (500 mg, 4.55 mmol) and dimethylphenylsilane (680 mg, 4.99 mmol) using $PtCl_2$ (10 mg, 0.0227 mmol) and XPhos (22.0 mg, 0.0455 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4g** (951 mg, 85%) as a colourless solid.

Rf (9:1 hexane – ethyl acetate) = 0.55 ; IR: ν_{max} (thin film) / cm^{-1} 3368, 1616, 1427,1314, 1247,1113, 993, 824, 698; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.60 – 7.57 (2H, m), 7.43 – 7.39 (3H, m), 6.32 (1H, d, *J* = 18.8 Hz), 6.09 (1H, d, *J* = 18.8 Hz), 1.98 – 1.04 (8H, m), 0.42 (6H, s) ;^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 138.7, 133.7, 128.8, 127.7,122.6, 83.1, 40.3, 23.9, -2.6; HRMS (EI) Calcd. for $C_{15}H_{22}OSi$ $[M]^+$, 246.1449. Found 246.1440

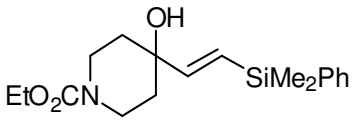
***(E)*-4-(2-(dimethyl(phenyl)silyl)vinyl)tetrahydro-pyran-4-ol (4h)**



The title compound was prepared according to general procedure B, from 4-ethynyltetrahydropyran-4-ol (81 mg, 0.31 mmol) and dimethylphenylsilane (96 mg, 0.70 mmol) using $PtCl_2$ (1.0 mg, 0.0032 mmol) and XPhos (3.0 mg, 0.0064 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4h** (107 mg, 87%) as a clear oil.

Rf (8:2 hexane – ethyl acetate) = 0.6; IR: ν_{max} (thin film) / cm^{-1} 3458, 2565, 1648, 1555, 890; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.52 – 7.47 (2H, m), 7.38 – 7.32 (3H, m), 6.17 (1H, d, *J* = 18.7 Hz), 6.02 (1H, d, *J* = 18.7 Hz), 3.82 (1H, dd, *J* = 11.3, 2.6 Hz), 3.76 (2H, dd, *J* = 5.8, 2.6 Hz), 3.74 – 3.69 (1H, m), 1.87 – 1.75 (3H, m), 1.49 – 1.45 (1H, m), 1.44 - 1.41 (1H, m), 0.35 (6H, s), ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 138.3, 133.7, 129.0, 127.8, 124.4, 70.2, 63.7, 37.36, -2.6 ; HRMS (EI) Calcd. for $C_{14}H_{19}O_2Si$ $[M\text{-}CH_3]^+$ 247.1154. Found 247.1156

***(E)*-ethyl 4-(2-(dimethyl(phenyl)silyl)vinyl)-4-hydroxypiperidine-1-carboxylate (4i)**



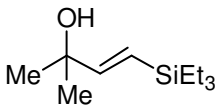
The title compound was prepared according to general procedure B, from ethyl 4-ethynyl-4-hydroxypiperidine-1-carboxylate (250 mg, 1.27 mmol) and dimethylphenylsilane (190 mg, 1.4 mmol) using $PtCl_2$ (2.0 mg, 0.0064 mmol) and XPhos (6.0 mg, 0.013 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **4i** (364 mg, 86%) as a clear oil.

Rf (9:1 hexane – ethyl acetate) = 0.33; IR: ν_{max} (thin film) / cm^{-1} 3456, 2900, 2245, 1458, 1400, 1250, 1100, 985, 852; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.51 – 7.49 (2H, m), 7.37 – 7.33 (3H, m), 6.14 (1H, d, *J* = 18.8 Hz), 6.02 (1H, d, *J* = 19 Hz), 4.11 (2H, q, *J* = 7.1 Hz), 3.89 (2H, br), 3.23 (2H, m), 1.77 – 1.48 (4H, m), 1.25 (3H, t, *J* = 7.2 Hz), 0.34 (6H, s) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.5, 153.7, 138.2, 133.7, 129, 12.8, 127.8, 124.4, 70.9, 61.2, 39.7, 36.4, 14.6, -2.7; HRMS (EI) Calcd. for $C_{18}H_{27}NO_3Si$ $[M]^+$ 333.1760. Found 333.1779

General Procedure C: $PtCl_2$ / Xphos Catalysed Hydrosilylation of Tertiary Propargyl Alcohols Using Alternative Silanes

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and magnetic stirrer was added $PtCl_2$ (0.5 mol%) and 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (1 mol%) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 °C for 20 minutes until a yellow homogenous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.1 eq.) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite *(E)* - vinyl silane.

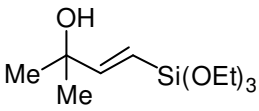
***(E)*-2-methyl-4-(triethylsilyl)but-3-en-2-ol (5a)**



The title compound was prepared according to general procedure C, from 2-Methyl-3-butyn-2-ol (300 mg, 3.57 mmol) and triethylsilane (456 mg, 3.93 mmol) using $PtCl_2$ (5.0 mg, 0.018 mmol) and XPhos (17 mg, 0.036 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **8a** (635 mg, 89%) as a colourless oil.

Rf (9:1 hexane – ethyl acetate) = 0.33 ; IR: ν_{max} (thin film) / cm^{-1} 3430, 2069, 1773, 1653, 1638, 1073, 830; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 6.17 (1H, d, *J* = 19.2 Hz), 5.74 (1H, d, *J* = 19.2 Hz), 1.50 (1H, s), 1.30 (6H, s), 0.93 (9H, t, *J* = 7.72 Hz), 0.57 (6H, q, *J* = 8.1 Hz)) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 120.4, 72.1, 29.4, 7.3, 3.4 HRMS (EI+) Calcd. for $C_{11}H_{24}OSi$ $[M]^+$, 200.1596. Found 200.1590

***(E)*-2-methyl-4-(triethoxysilyl)but-3-en-2-ol (5c)**

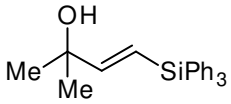


The title compound was prepared according to general procedure C, from 2-Methyl-3-butyn-2-ol (500 mg, 5.95 mmol) and triethoxysilane (1.07 g, 6.55 mmol) using $PtCl_2$ (8.0 mg, 0.030

mmol) and XPhos (28 mg, 0.060 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **8c** (1.120 g, 81%) as a clear oil.

Rf (9:1 hexane – ethyl acetate) = 0.40; IR: ν_{max} (thin film) / cm^{-1} 3421, 2977, 2066, 1653, 1638, 1073, 953; ^1H NMR: (300 MHz, $CDCl_3$) δ 6.54 (1H, d, *J* = 19.0 Hz), 5.63 (1H, d, *J* = 19.0 Hz), 3.84 (6H, q, *J* = 7.1 Hz), 1.32 (6H, s), 1.24 (9H, t, *J* = 7.1 Hz) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 114.1, 72.1, 58.5, 29.2, 15.2; HRMS (EI) Calcd. for $C_{11}H_{22}O_4Si$ $[M]^+$ 248.1444. Found 248.1450

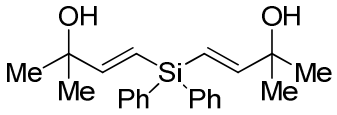
(E)-2-methyl-4-(triphenylsilyl)but-3-en-2-ol (5d)



The title compound was prepared according to general procedure C, from 2-Methyl-3-butyn-2-ol (300 mg, 4.29 mmol) and triphenylsilane (1.67 g, 6.44 mmol) using $PtCl_2$ (12 mg, 0.043 mmol) and XPhos (41 mg, 0.086 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **8d** (1.3 g, 88%) as a white powder.

Rf (9:1 hexane – ethyl acetate) = 0.40 ; IR: ν_{max} (thin film) / cm^{-1} 3689, 2458, 2311, 2000, 1569, 700, 565; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.66 – 7.48 (6H, m), 7.46 – 7.32 (9H, m), 6.41 (1H, dd, *J* =18.6, 1.3 Hz), 6.23 (1H, dd, *J* = 18.6, 4.3 Hz). 4.41 (1H, m), 1.31 (6H, d, *J* = 6.6 Hz); 13C NMR: (75 MHz, $CDCl_3$) δ 155.4, 135.9, 134.4, 129.6, 127.9, 121.7, 70.4, 23.0; HRMS (EI)+ Calcd for $C_{22}H_{20}Si$ $[M\text{-}CH_3OH]^+$ 312.1355. Found 312.1355

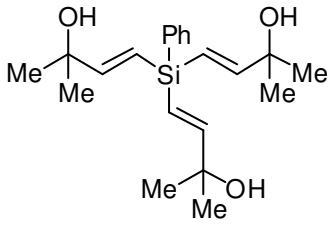
(3E,3'E)-4,4'-(diphenylsilanediyl)bis(2-methylbut-3-en-2-ol) (5e)



The title compound was prepared according to general procedure C, from 2-Methyl-3-butyn-2-ol (200 mg, 2.38 mmol) and diphenylsilane (0.5 eq, 219 mg, 1.19 mmol) using $PtCl_2$ (1 mol % 6.0 mg, 0.024 mmol) and XPhos (2 mol %, 23 mg, 0.048 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **8e** (618 mg, 72%) as a clear oil.

Rf (7:3 hexane – ethyl acetate) = 0.13; IR: ν_{max} (thin film) / cm^{-1} 3435, 3068, 2969, 2926, 2854, 2096, 1635, 1428, 1112, 813, 738; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.52 – 7.49 (4H, m), 7.41 – 7.34 (6H, m), 6.28 (2H, d, *J* = 18.5 Hz), 6.17 (2H, d, *J* = 18.5 Hz), 1.33 (12H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 135.8, 135.5, 129.5, 127.9, 118.8, 72.4, 29.4 HRMS (EI) Calcd. for $C_{22}H_{25}OSi$ $[M-H_3O]^+$ 334.1752. Found 334.1756

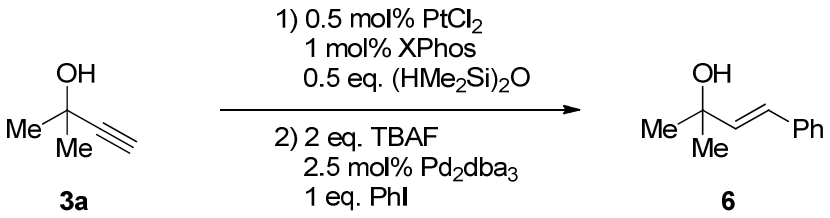
(E)-4,4'-((3-hydroxy-3-methylbut-1-en-1-yl)(phenyl)silanediyl)bis(2-methylbutan-2-ol) (5f)



The title compound was prepared according to general procedure C, from 2-Methyl-3-butyn-2-ol (300 mg, 3.57 mmol) and phenylsilane (0.3 eq, 129 mg, 1.19 mmol) using $PtCl_2$ (10 mg, 0.0357 mmol) and XPhos (34 mg, 0.0714 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc to 1:1 hexane/EtOAc) afforded **8f** (213 mg, 50%) as a colourless oil which solidified upon standing in the freezer.

Rf (7:3 hexane – ethyl acetate) = 0.11 ; IR: ν_{max} (thin film) / cm^{-1} 3420, 2973, 2286, 1734, 1635, 1540, 1217, 1115, 700; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.61 – 7.48 (2H, m), 7.41 – 7.27 (3H, m), 6.26 (3H, d, *J* = 18.8 Hz), 5.99 (3H, d, *J* = 18.8 Hz), 1.3 (18H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 135.0, 129.3, 127.8, 119.1, 72.3, 60.3, 29.2, 21.0, 14.1 HRMS (ES+) Calcd. For $C_{21}H_{32}O_3NaSi$ [M+Na] 383.2018. Found 383.2011

***(E)*-2-methyl-4-phenylbut-3-en-2-ol (6)**



3a **6**

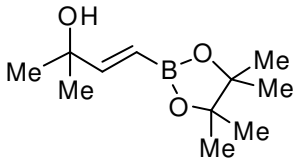
In a 50 mL oven dried round bottomed flask quipped with a reflux condenser and magnetic stirrer bar was added $PtCl_2$ (8.0 mg, 0.030 mmol) and Xphos (28 mg, 0.060 mmol). The flask was quickly flushed with argon before anhydrous THF (0.7 mL) was added. The mixture was stirred at 50 °C for 20 minutes until a yellow homogenous mixture was obtained. 2-Methyl-3-butyn-2-ol (500 mg, 5.95 mmol) and 1,1,3,3-Tetramethyldisiloxane (400 mg, 2.98 mmol) were then added via syringe and the mixture stirred at 50 °C overnight. Once the reaction was deemed complete by TLC analysis (hydrosilylation product Rf (9:1 hexane – ethyl acetate) – 0.15), TBAF (1M in THF, 11.9 mL, 11.9 mmol) was added at room temperature and the reaction stirred for 10 minutes after which Pd_2dba_3 (136 mg, 0.149 mmol) was added in one portion followed by the slow addition iodobenzene (1.22 ml, 5.95 mmol) in THF (10 ml) over 10 minutes. The reaction mixture was stirred for 30 minutes followed by addition of Et_2O (15 ml) and a further 5 minutes of stirring. The resulting suspension was passed through a pad of silica followed by flash chromatography (9:1 hexane –ethyl acetate/ 1% TEA) to yield the title compound (684 mg, 71%) as a dark yellow oil. All spectral data is consisted with previously published findings[5]

R_f (9:1 hexane-ethyl acetate) = 0.24; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (2H, m), 7.35 – 7.28 (2H, m), 7.24 – 7.2 (1H, m), 6.59 (1H, d, J = 16.1 Hz), 6.36 (1H, d, J = 16.1 Hz), 1.43 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.5, 136.9, 128.6, 127.4, 126.4, 71.0, 29.9

[5] Liu, Z-Q.; Sun, L.; Wang, J-G-; Han, J.; Zhao, Y-K.; Zhou, B. *Org. Lett.,* **2009,** *11*, 1437

Hydroboronation using $PtCl_2$ / XPhos Catalyst system

(E)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (8)



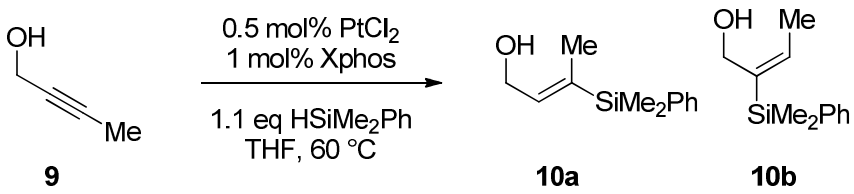
To an oven dried 5 mL round bottomed flask was equipped with a magnetic stirrer and reflux condenser was added $PtCl_2$ (0.5 mol%, 1 mg, 0.0039 mmol) and XPhos (1 mol%, 4.0 mg, 0.0078 mmol) in dry THF (0.4 mL) and stirred at 50 °C for 20 minutes until a yellow homogenous mixture is obtained. Trimethylsilyl protected 2-Methyl-3-butyn-2-ol[6] (122 mg, 0.779 mmol) was then added, followed by Pinacol Borane (100 mg, 0.779 mmol) and the mixture stirred at 50 °C overnight. After evaporation, the crude product was added directly to the top of a column and chromatographed (9:1 hexane – ethyl acetate, Rf – 0.25) to yield the title compound as a yellow oil (179 mg, 81%). Analysis was identical to that previously reported.[7]

^{1}H NMR: (300 MHz, $CDCl_3$) δ 6.72 (1H, d, J = 18.3 Hz), 5.61 (1H, d, J = 18.1 Hz), 1.65 (1H, br), 1.31 (6H, s), 1.28 (12H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 71.7, 29.1, 24.7, 19.0, 11.3.

[6] Berree, F.; Gernigon, N.; Hercourt, A.; Chia, H. L. ; Carboni, B. *Eur. J. Org. Chem.* **2009,** *3***,** 329
[7] Morrill, C.; Grubbs, R. H.; *J. Org. Chem.* **2003**, *68*, 6031

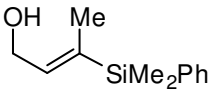
General procedure D: Hydrosilylation of Internal Alkynes

To an oven dried 5 mL round bottom flask equipped with a reflux condenser and magnetic stirrer was added $PtCl_2$ (0.5 mol%) and 2-Dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (1 mol%) (XPhos). The flask was then flushed quickly with argon and dry THF was added. The mixture was then stirred at 50 °C for 20 minutes until a yellow homogenous mixture was obtained. The corresponding propargyl alcohol (1 eq.) was added followed by the silane (1.1 eq.) *via* syringe (CAUTION: Rapid evolution of hydrogen gas) and the solution was stirred at 50 °C overnight. The solvent was evaporated and the crude mixture was applied to the top of a column and chromatographed to afford the requisite α or β *E*-vinyl silane. Regioselectivities were determined from ^{1}H NMR and isolated yields of the crude reaction mixture.



9 **10a** **10b**

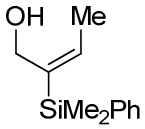
(*E*)-3-(dimethyl(phenyl)silyl)but-2-en-1-ol (10a)



The title compound was prepared according to general procedure D, from 2-butyn-1-ol (500 mg, 7.14 mmol) and dimethylphenylsilane (1.07 g, 7.85 mmol) using $PtCl_2$ (10 mg, 0.036 mmol) and XPhos (34 mg, 0.071 mmol) which following conversion to the vinyl silane and column chromatography (19:1 Hexane/EtOAc) afforded **10a** (573 mg, 39%) as a yellow oil.

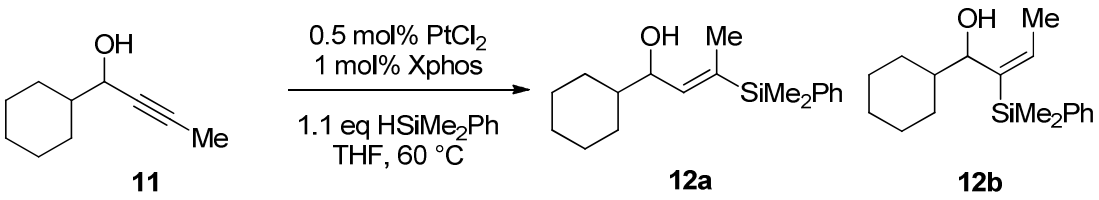
R_f (9:1 hexane-ethyl acetate) = 0.34 IR: υ_{max} (thin film) / cm^{-1} 3337, 2956, 1958, 1427, 1247, 1109, 1014, 943,731; ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.52 – 7.46 (2H, m), 7.38 – 7.31 (3H, m), 5.96 (1H, tq, *J*= 5.9, 1.7 Hz), 4.30 (2H, d, *J*= 5.9 Hz), 1.69 (3H, d, *J* = 0.9 Hz), 0.36 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.7, 137.4, 134.0, 129.0, 127.8, 59.7, 15.0, -3.7HRMS (EI) cald. For $C_{12}H_{18}OSi$ $[M]^+$ 206.1127. Found 206.1104

***(E)*-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (10b)**



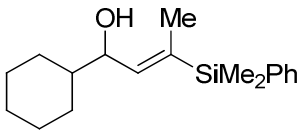
The title compound was prepared according to general procedure D, from 2-butyn-1-ol (500 mg, 7.14 mmol) and dimethylphenylsilane (1.07 g, 7.85 mmol) using $PtCl_2$ (10 mg, 0.036 mmol) and XPhos (34 mg, 0.071 mmol) which following conversion to the vinyl silane and column chromatography (19:1 Hexane/EtOAc) afforded **10b** (589 mg, 40%) as a colourless oil.

R_f (9:1 hexane-ethyl acetate) = 0.20 IR: υ_{max} (thin film) / cm^{-1} 3400, 2853, 1616, 1427, 1247, 1109, 815, 732 ; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.57 – 7.49 (2H, m), 7.37 – 7.30 (3H, m), 6.03 (1H, qt, *J*= 6.6, 1.1 Hz), 4.3 (2H, s), 1.77 (3H, d, *J*= 6.6 Hz), 0.40 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.1, 138.9, 133.9, 128.9, 127.8, 60.7, 31.5, 14.7, -2.6; HRMS (EI) Cald. For $C_{11}H_{15}OSi$ $[M\text{-}CH_3]^+$ 191.0892. Found 191.0872



11 **12a** **12b**

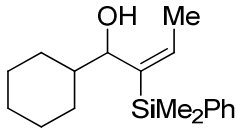
***(E)*-1-cyclohexyl-3-(dimethyl(phenyl)silyl)but-2-en-1-ol (12a)**



The title compound was prepared according to general procedure D, from 1-cyclohexylbut-2-yn-1-ol (502 mg, 3.30 mmol) and dimethylphenylsilane (494 mg, 3.63 mmol) using $PtCl_2$ (5.0 mg, 0.017 mmol) and XPhos (16 mg, 0.033 mmol) which following conversion to the vinyl silane and column chromatography (19:1 Hexane/EtOAc) afforded **12a** (555 mg, 69%) as a yellow oil.

R_f (9:1 hexane-ethyl acetate) = 0.6; IR: υ_{max} (thin film) / cm^{-1} 3367, 3049, 2852, 1878, 1449,1 247, 1004, 815, 774; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (2H, m), 7.36 – (3H, m), 5.77 (1H, dq, *J* = 8.6, 1.6 Hz), 5.2 (1H, s), 4.24 (3H, dd, *J* = 8.6, 7.0 Hz), 1.92 (1H, br d, *J* = 11.3 Hz), 1.76 – 1.72 (2H, m), 1.70 (3H, d, *J* = 1.6 Hz), 1.67 – 1.63 (2H, m), 1.45 – 1.41 (1H, m), 1.30 – 0.90 (5H, m), 0.35 (3H, s), 0.35 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.1, 137.9, 137.2, 133.8, 128.9, 127.7, 72.0, 44.0, 31.5, 28.7, 28.5, 26.5, 26.1, 26.0, 22.6, 15.4, 14.0, -3.5, -3.7; HRMS (EI) Cald. For $C_{18}H_{27}OSi$ $[M-H]^+$ 287.1831. Found 287.1842

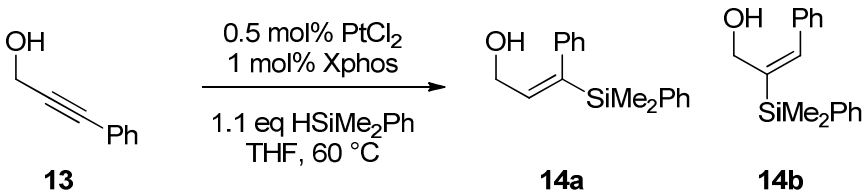
***(E)*-1-cyclohexyl-2-(dimethyl(phenyl)silyl)but-2-en-1-ol (12b)**



The title compound was prepared according to general procedure D, from 1-cyclohexylbut-2-yn-1-ol (502 mg, 3.30 mmol) and dimethylphenylsilane (494 mg, 3.63 mmol) using $PtCl_2$ (5.0 mg, 0.017 mmol) and XPhos (16 mg, 0.033 mmol) which following conversion to the vinyl silane and column chromatography (19:1 Hexane/EtOAc) afforded **12b** (250 mg, 26%) as a yellow oil.

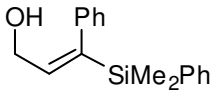
R_f (9:1 hexane-ethyl acetate) = 0.6; IR: υ_{max} (thin film) / cm^{-1} 3468, 1608, 1427, 1246, 1008, 891, 814, 734; ^1H NMR: (400 MHz, $CDCl_3$) δ 7.63 (2H, m), 7.39 – 7.33 (3H, m), 6.00 (1H, qd, *J* = 6.8, 1.2 Hz), 4.38 (1H, d, *J* = 8.8 Hz), 2.07 (1H, br d, *J*= 12.5 Hz) 1.75 (3H, d, *J*= 6.8 Hz), 1.71 – 1.64 (2H.m), 1.57 – 1.31 (3H, m), 1.18 – 0.79 (5H, m), 0.50 (3H, s), 0.46 (3H,s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 140.1, 137.9, 133.9, 128.6, 127.6, 76.6, 43.5, 29.7, 29.3, 26.4, 26.1, 26.1, 15.7, -0.8; HRMS (EI) Cald. For $C_{17}H_{25}OSi$ $[M-CH_3]^+$ 273.1675. Found 273.1702

;



13 **14a** **14b**

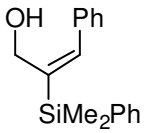
***(E)*-3-(dimethyl(phenyl)silyl)-3-phenylprop-2-en-1-ol (14a)**



The title compound was prepared according to general procedure D, from 3-phenyl-2-propyn-2-ol (300 mg, 2.27 mmol) and dimethylphenylsilane (289 mg, 2.49 mmol) using $PtCl_2$ (3.0 mg, 0.011 mmol) and XPhos (11 mg, 0.023 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **14a** (399 mg, 66%) as a colourless oil.

R_f (9:1 hexane-ethyl acetate) = 0.35; IR: ν_{max} (thin film) / cm^{-1} 3400, 2958,1489, 1112, 808, 734 ; ^1H NMR: (500 MHz, $CDCl_3$) δ 7.5 – 7.47 (2H, m), 7.37 – 7.33 (3H, m), 7.25 – 7.16 (3H, m), 6.84 – 6.81 (2H, m), 6.15 (1H, t, *J* = 6.0 Hz), 4.04 (2H, d, *J* = 6.0 Hz), 0.35 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.4, 141.1, 141.0, 137.4, 134.1, 129.1, 128.0, 127.7, 127.5, 125.9, 60.9, -3.2 HRMS (EI) Calcd. for $C_{17}H_{20}OSi$ $[M]^+$ 268.1283. Found 268.1285

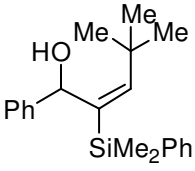
***(E)*-2-(dimethyl(phenyl)silyl)-3-phenylprop-2-en-1-ol (14b)**



The title compound was prepared according to general procedure D, from 3-phenyl-2-propyn-2-ol (300 mg, 2.27 mmol) and dimethylphenylsilane (289 mg, 2.49 mmol) using $PtCl_2$ (3.0 mg, 0.011 mmol) and XPhos (11 mg, 0.023 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **14b** (100 mg, 16%) as a clear oil.

R_f (9:1 hexane-ethyl acetate) = 0.8; IR: ν_{max} (thin film) / cm^{-1} 3401, 2960, 1636, 1427, 1186, 927, 700, 649; ^1H NMR: (300 MHz, $CDCl_3$) δ 7.55 – 7.51 (2H, m), 7.30 – 7.26 (3H, m), 7.24 – 7.16 (5H, m), 6.83 (1H, s), 4.39 (2H, d, *J* = 4.1 Hz), 0.44 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 141.3, 138.6, 137.2, 134.0, 139.1, 128.9, 128.1, 127.9, 127.3, 62.0, -2.3; HRMS (EI+) Calcd for $C_{17}H_{20}OSi$ $[M]^+$ 268.1283. Found 268.1294

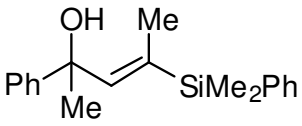
***(E)*-2-(dimethyl(phenyl)silyl)-4,4-dimethyl--phenylpent-2-en-1-ol (16b)**



The title compound was prepared according to general procedure D, from freshly prepared 4,4-dimethyl-1-phenylpent-2-yn-1-ol[8] (304 mg, 1.62 mmol) and dimethylphenylsilane (242 mg, 1.78 mmol) using $PtCl_2$ (4.0 mg, 0.016 mmol) and XPhos (15 mg, 0.032 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **15b** (398 mg, 76%) as a colourless oil.

R_f (9:1 hexane-ethyl acetate) = 0.76; IR: ν_{max} (thin film) / cm^{-1} 3436, 2956, 1653, 1440, 1247, 1030, 817, 734, 700 ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.45 – 7.31 (2H, m), 7.39 – 7.28 (7H, m), 7.25 – 7.19 (1H, m), 6.20 (1H, dd, *J* = 4.7, 1.1 Hz), 6.07 (1H, d, *J* = 1.1 Hz), 1.18 (9H, s), 0.19 (3H, s), 0.08 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 142.9, 140.5, 140.1, 133.9, 128.9, 127.9, 127.7, 126.8, 126.3, 71.5, 35.1, 31.7, -0.6; HRMS (EI) Calcd. For $C_{20}H_{25}OSi$ $[M\text{-}CH_3]^+$ 309.1675. Found 309.1676

(E)-4-(dimethyl(phenyl)silyl)-2-phenylpent-3-en-2-ol (18a)

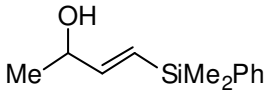


The title compound was prepared according to general procedure D, from freshly prepared 2-phenylpent-3-yn-2-ol[9] (500 mg, 3.157 mmol) and dimethylphenylsilane (468 mg, 3.43 mmol) using $PtCl_2$ (5.0 mg, 0.031 mmol) and XPhos (15 mg, 0.031 mmol) which following conversion to the vinyl silane and column chromatography (9:1 Hexane/EtOAc) afforded **17a** (656 mg, 71%) as a colourless oil.

R_f (9:1 hexane-ethyl acetate) = 0.41; IR: ν_{max} (thin film) / cm^{-1} 3436, 3067, 3023, 2959, 1957, 1427, 1248, 983, 832: ^{1}H NMR: (300 MHz, $CDCl_3$) δ 7.51 – 7.46 (4H, m), 7.36 – 7.2 (6H, m), 6.29 (1H, q, *J* = 1.7 Hz), 1.67 (3H, s), 1.54 (3H, d, *J* = 1.7 Hz), 0.35 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 147.0, 138.9, 138.0, 133.9, 129, 128.2, 127.8, 126.6, 125.1, 75.2, 32.4, 16, -3.5; HRMS (EI) Calcd. for $C_{18}H_{21}OSi$ $[M]^+$ 296.1596. Found 296.1591

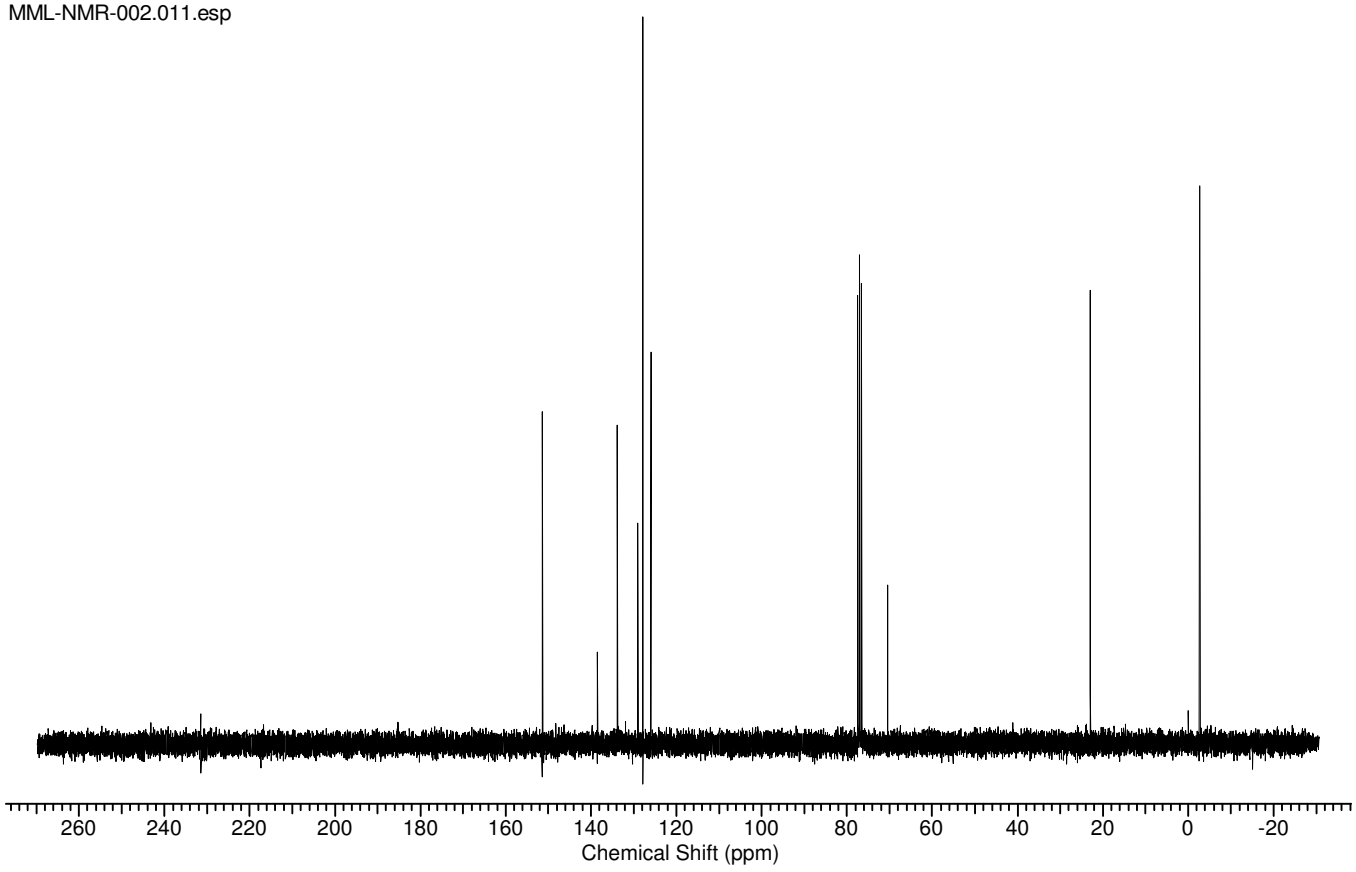
[8] Agosta, W. C.; Caldwell, R. A.; Jay, J.; Johnston, L. J.; Venepalli, B. R., *J. Am. Chem. Soc.* **1987***, 109*, 3050
[9] Suffert, J.; Toussaint, D. *J. Org. Chem.*, **1995,** *60*, 3550

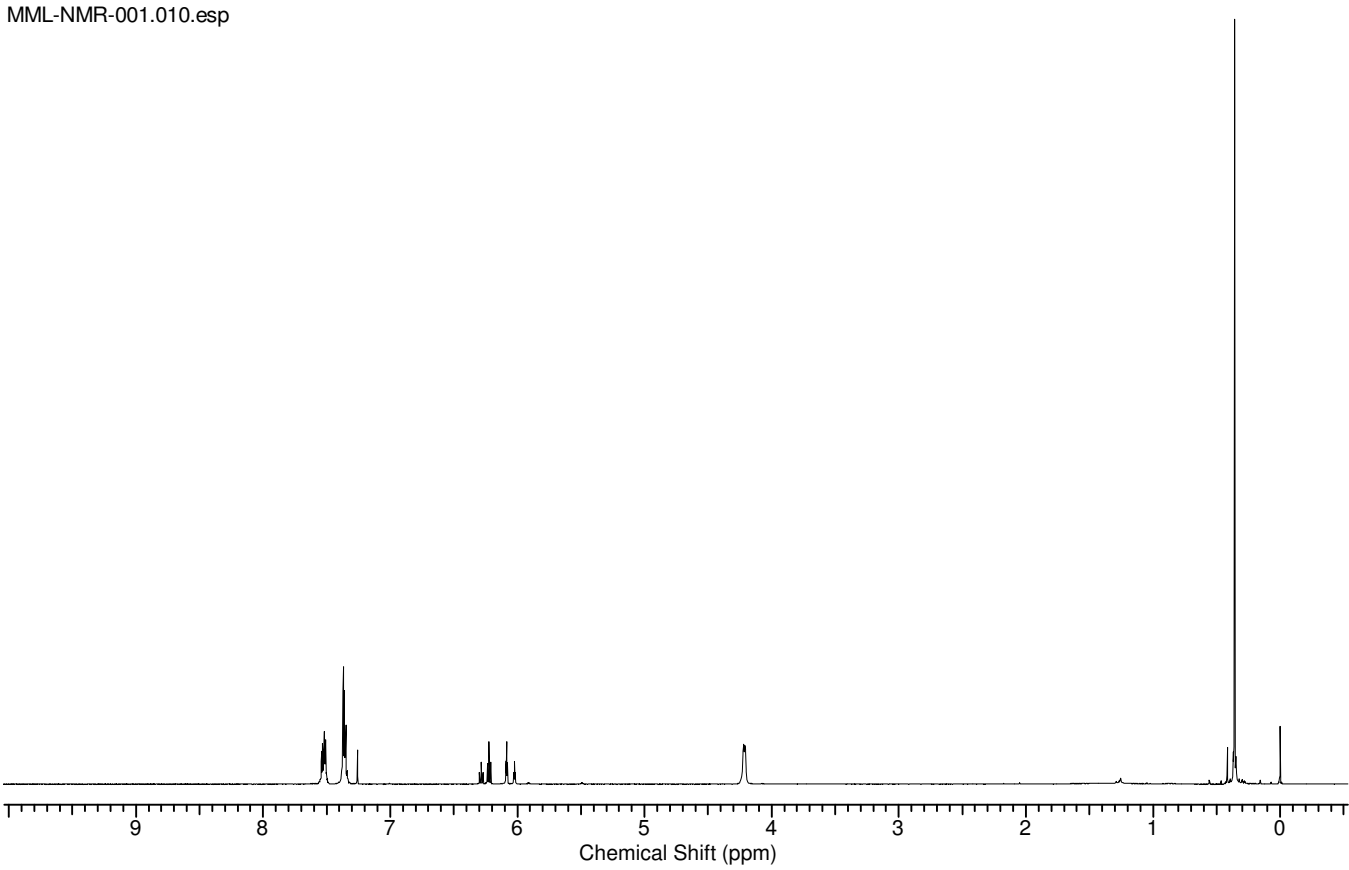
MML-NMR-002.010.esp

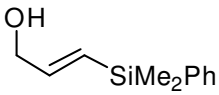


2a

MML-NMR-002.011.esp

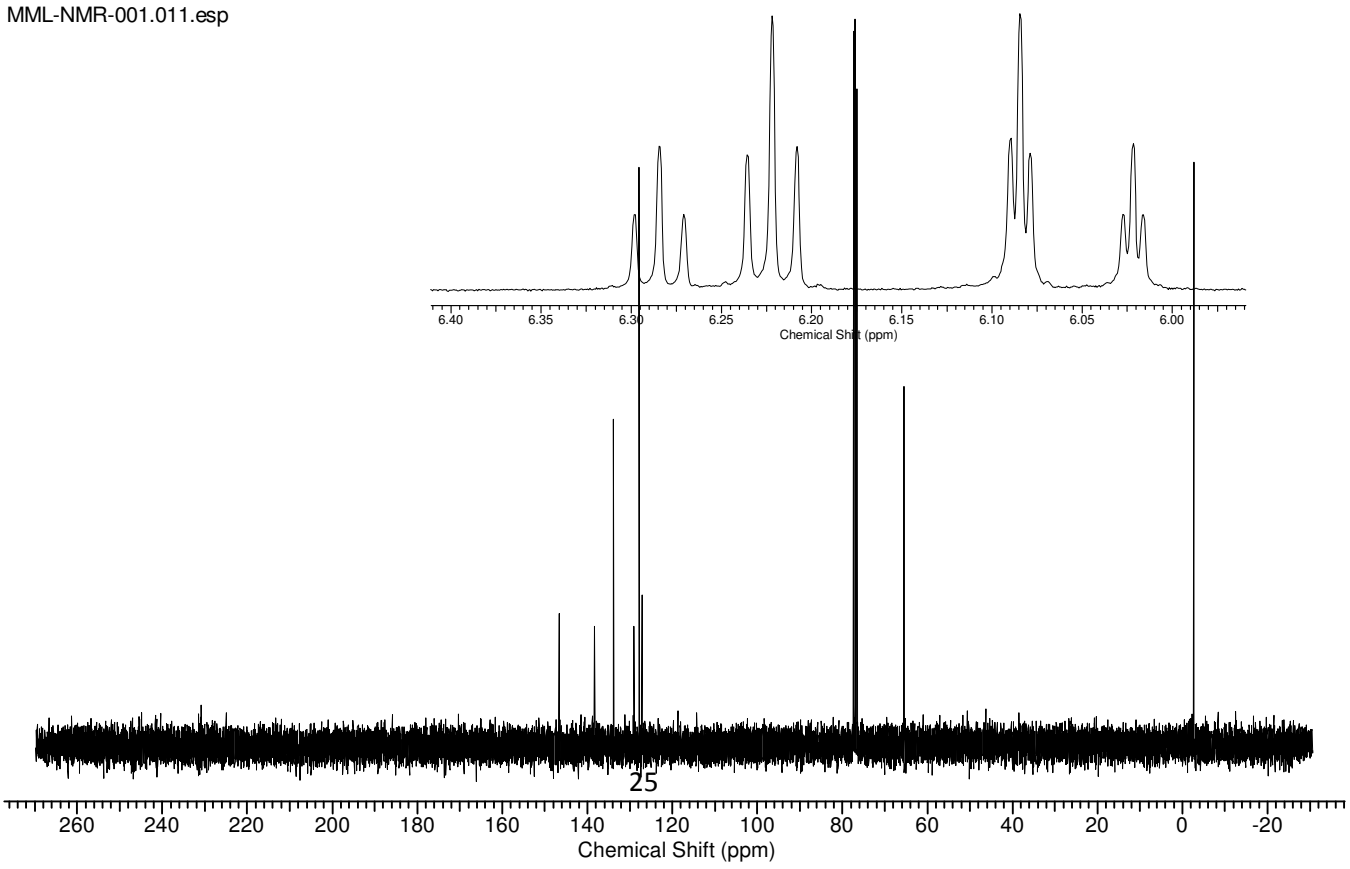


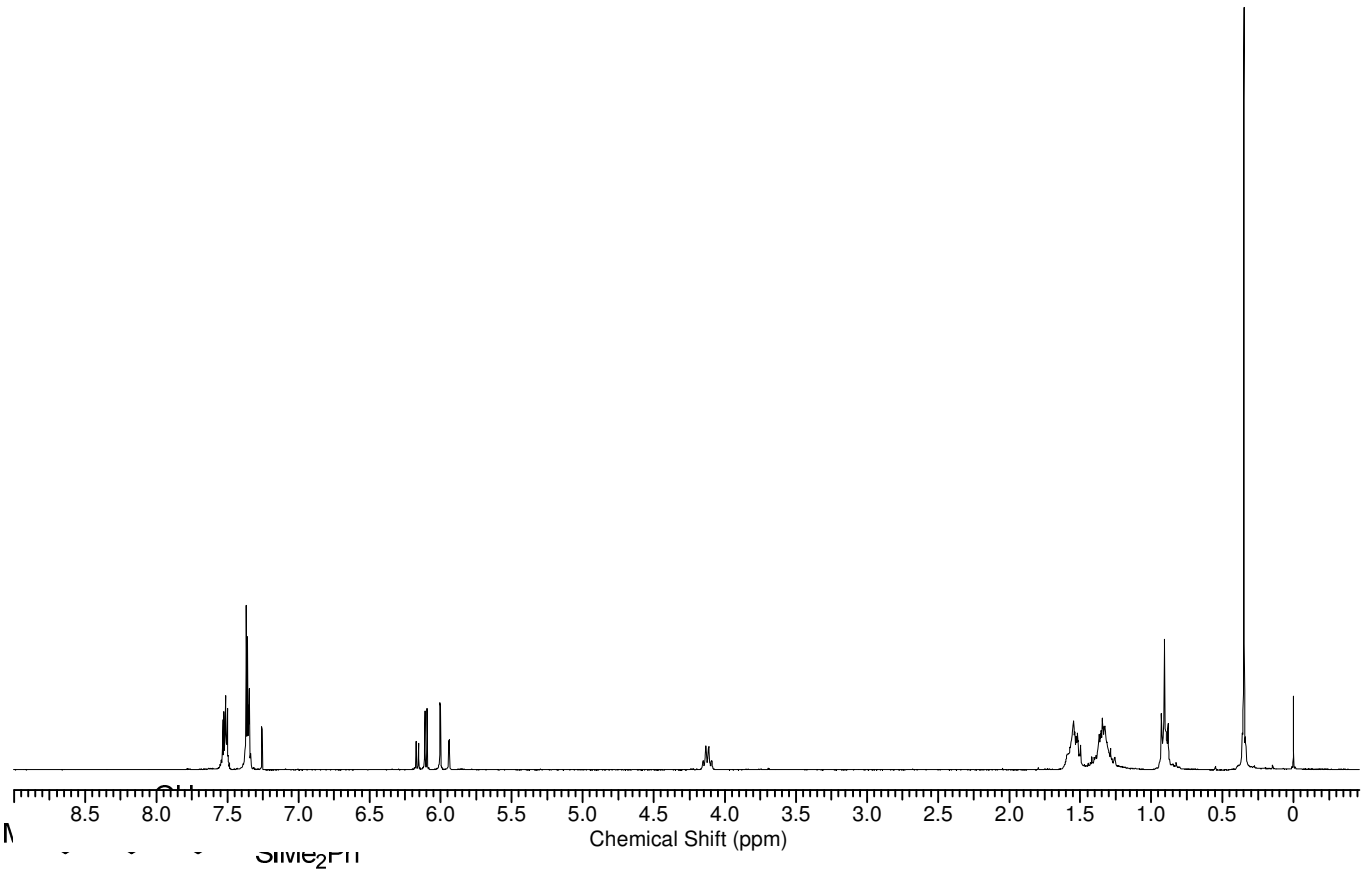




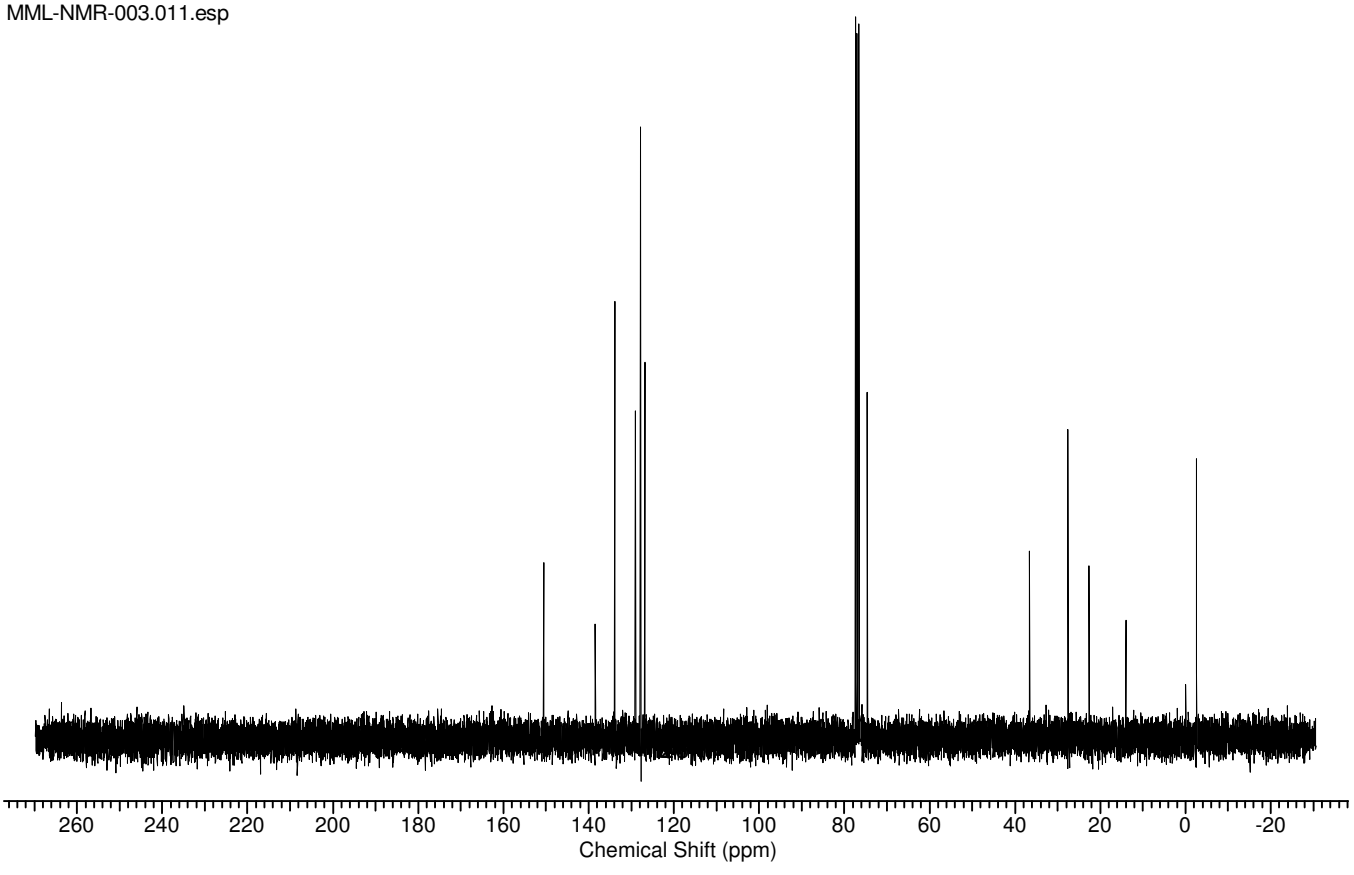
MML-NMR-001.010.esp

2b

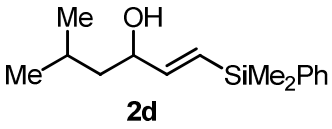



8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

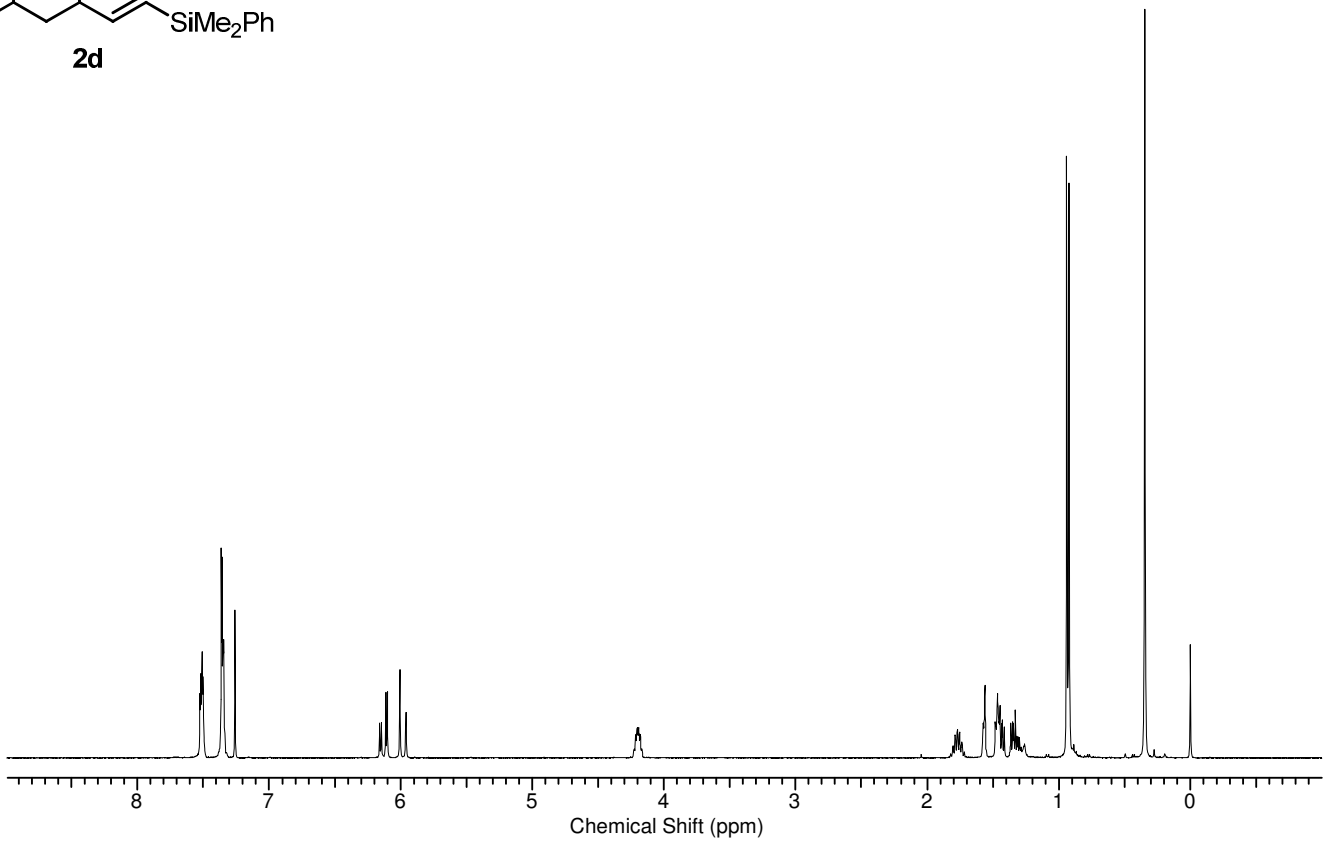
2c

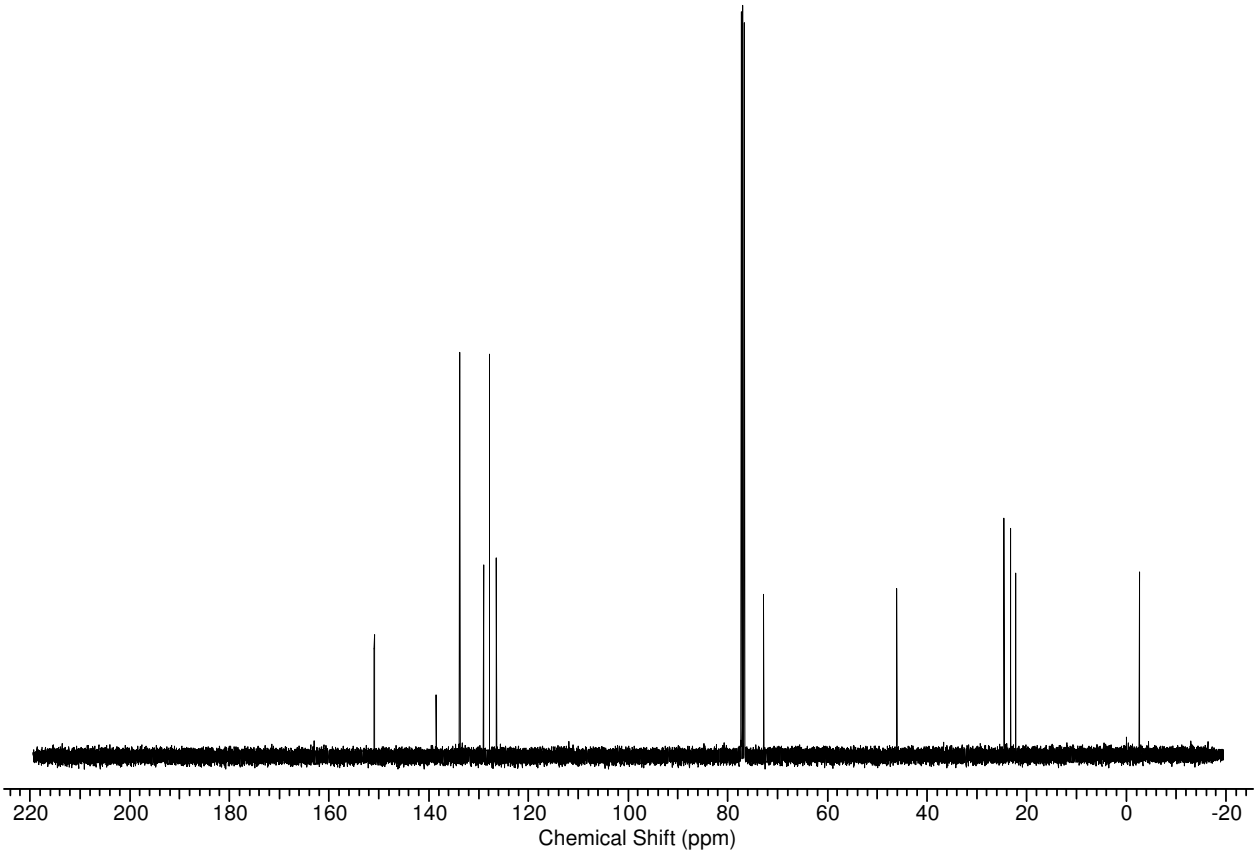

MML-NMR-003.011.esp
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

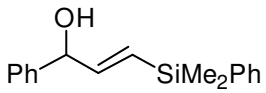
2d



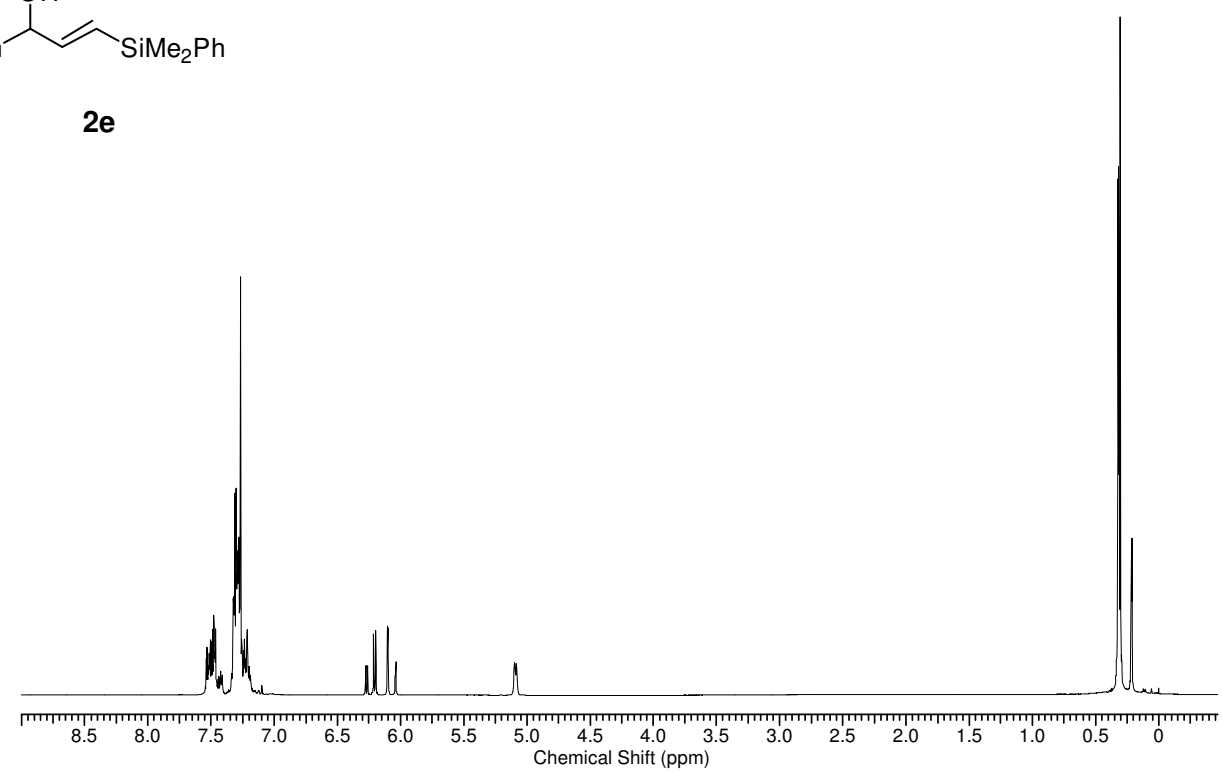
2d

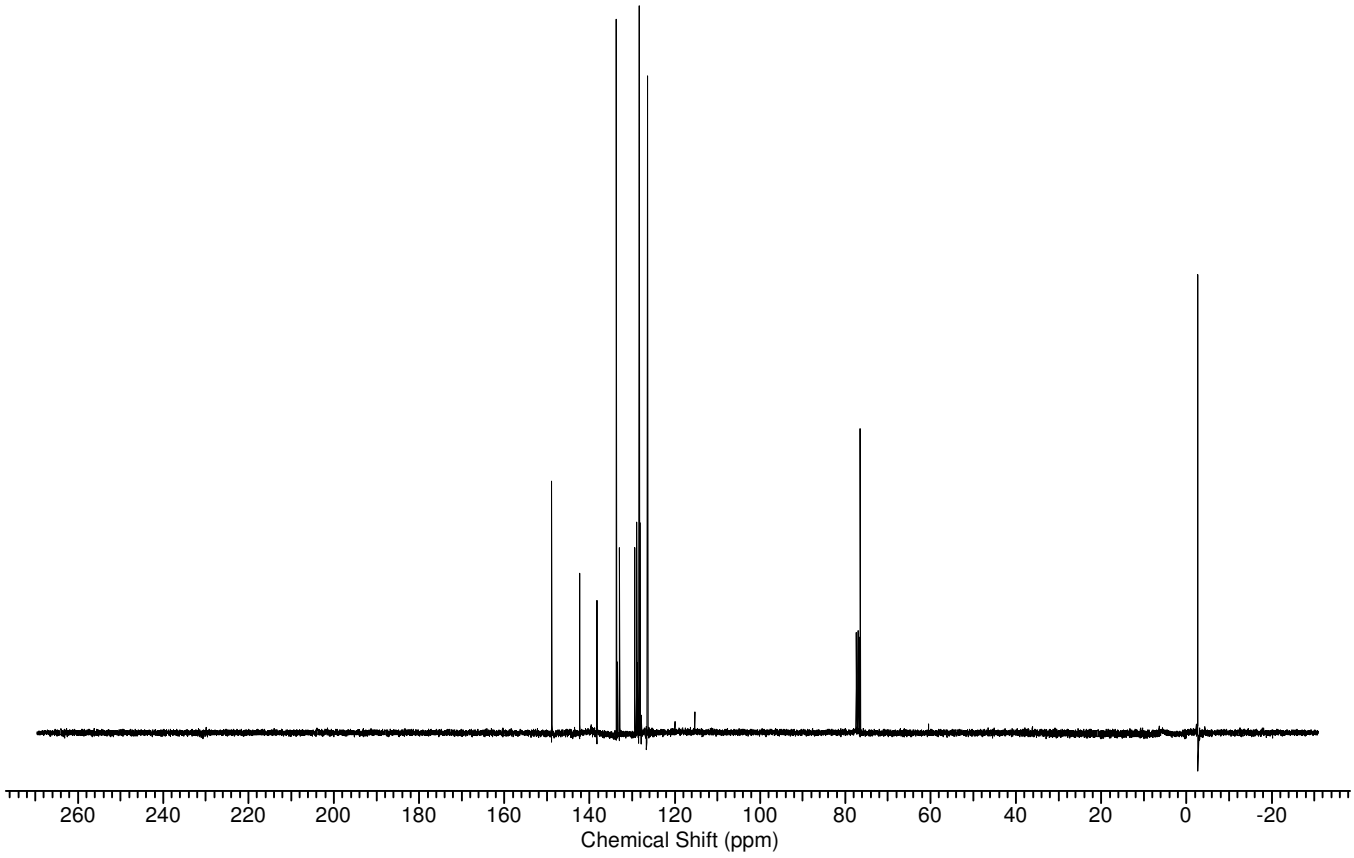


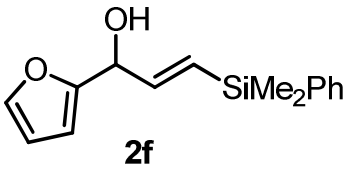



OH
Ph
SiMe2Ph

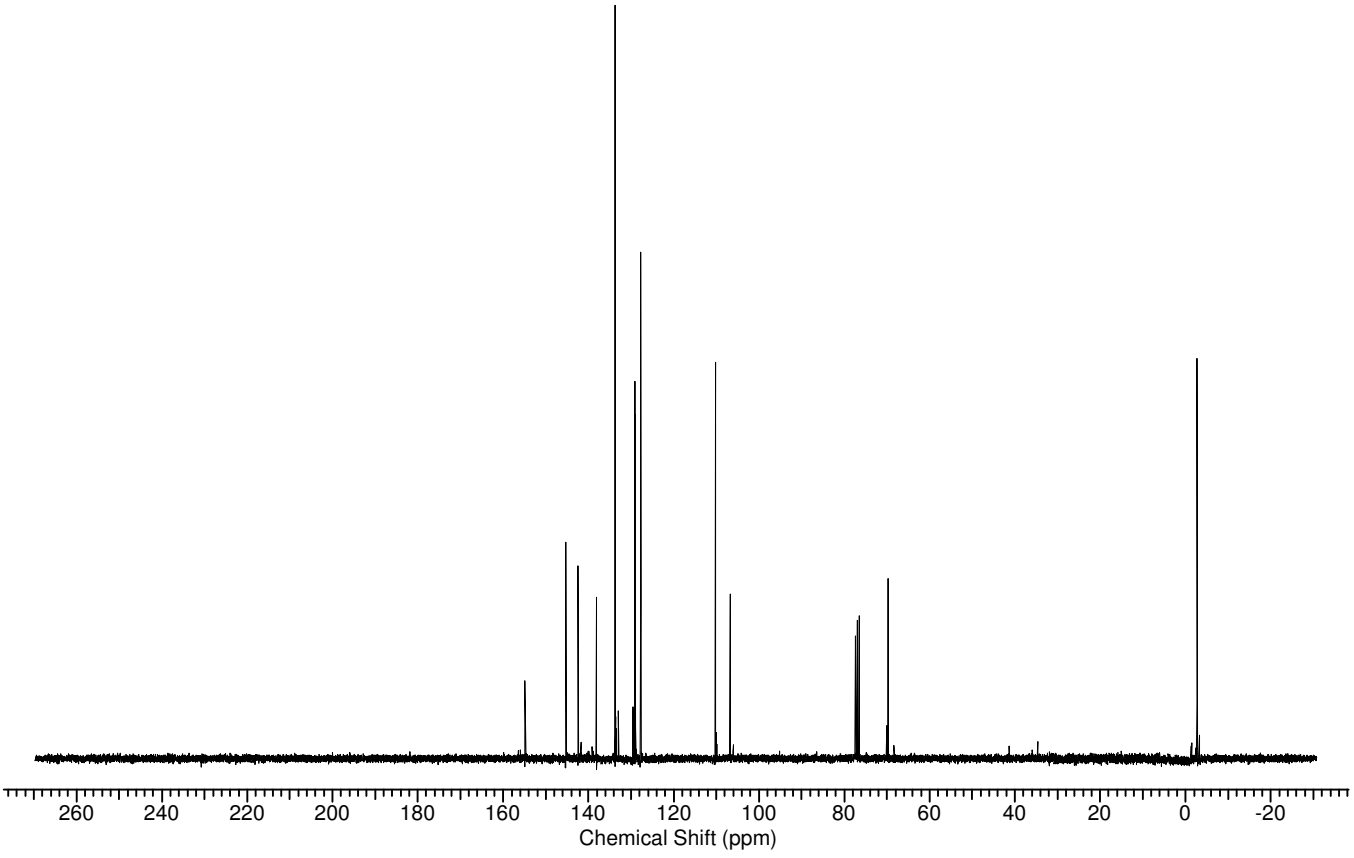
2e

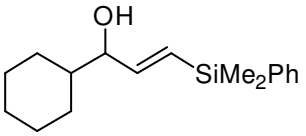

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)



2f

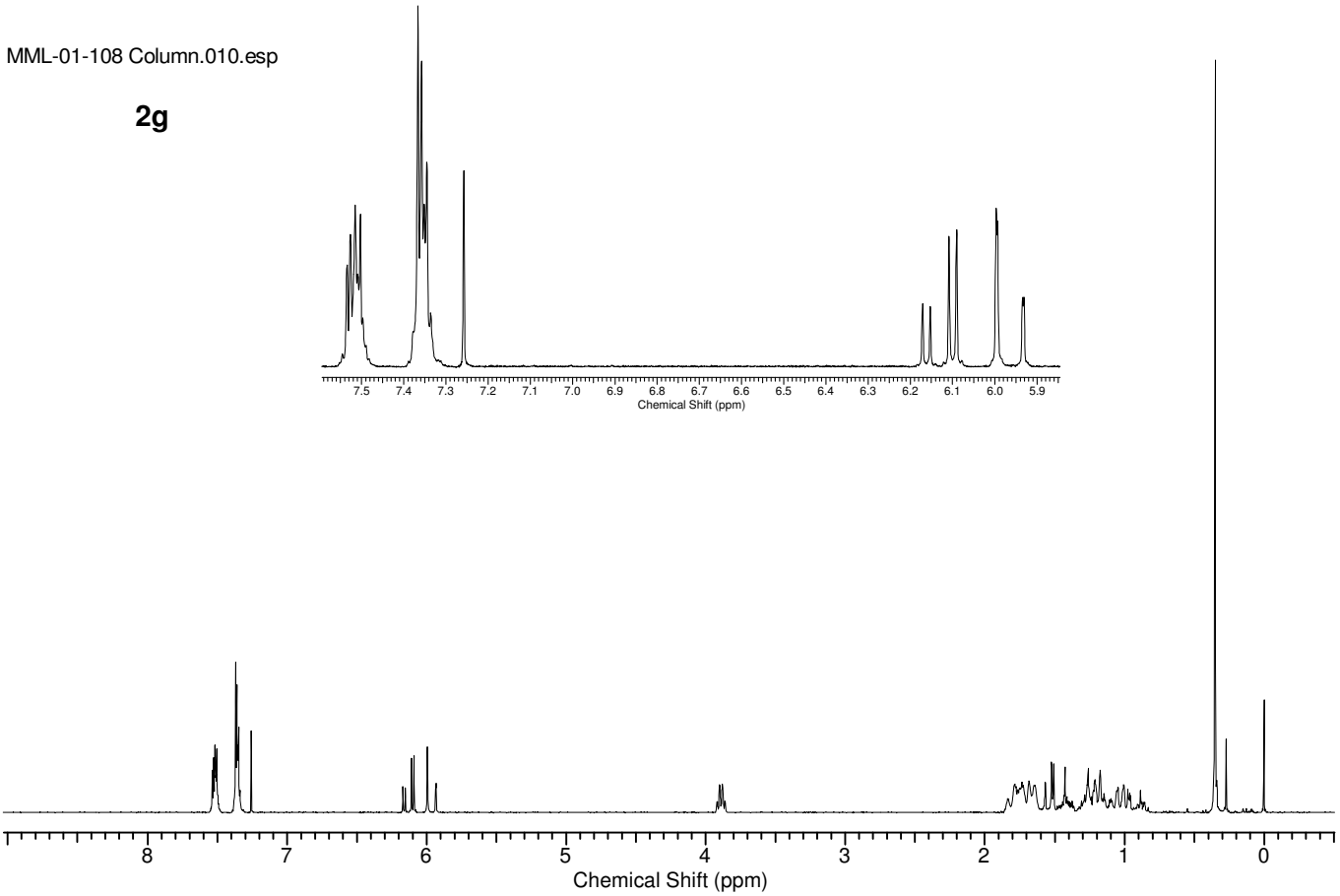




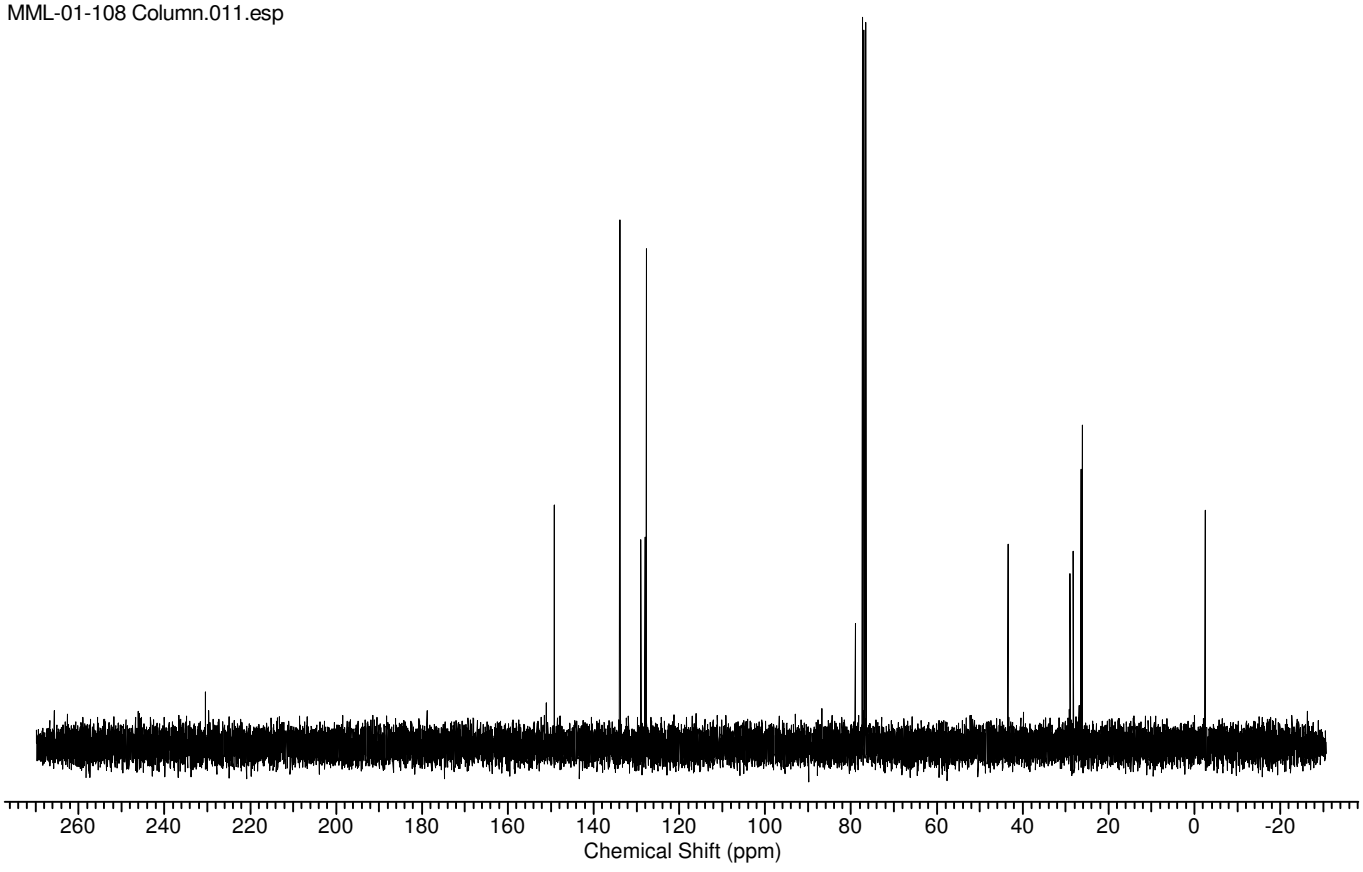
MML-01-108 Column.010.esp

MML-01-108 Column.010.esp

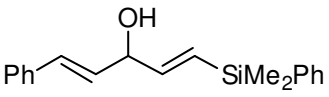
2g



MML-01-108 Column.011.esp

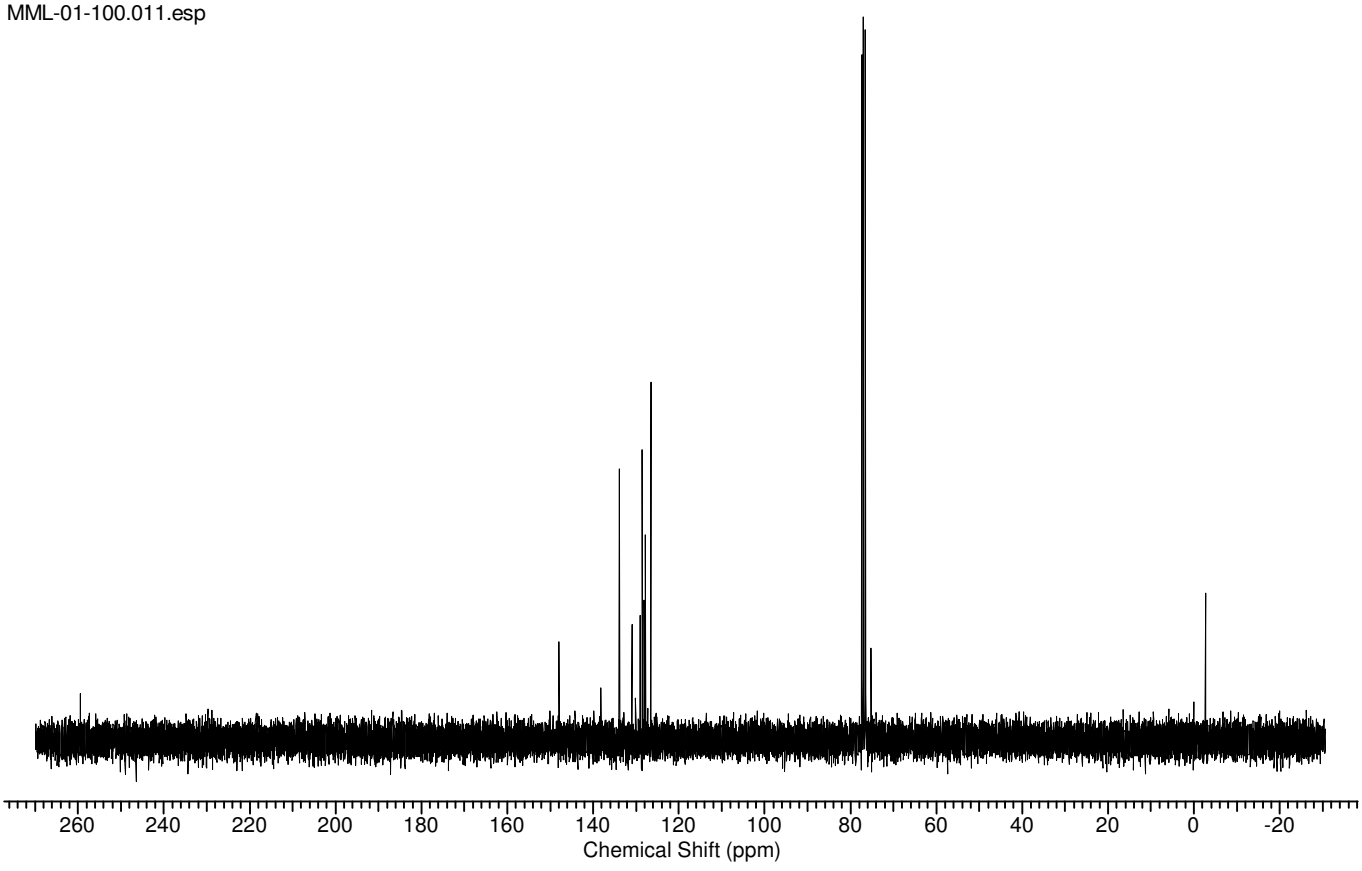


MML-01-100.010.esp

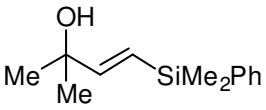


2h

MML-01-100.011.esp

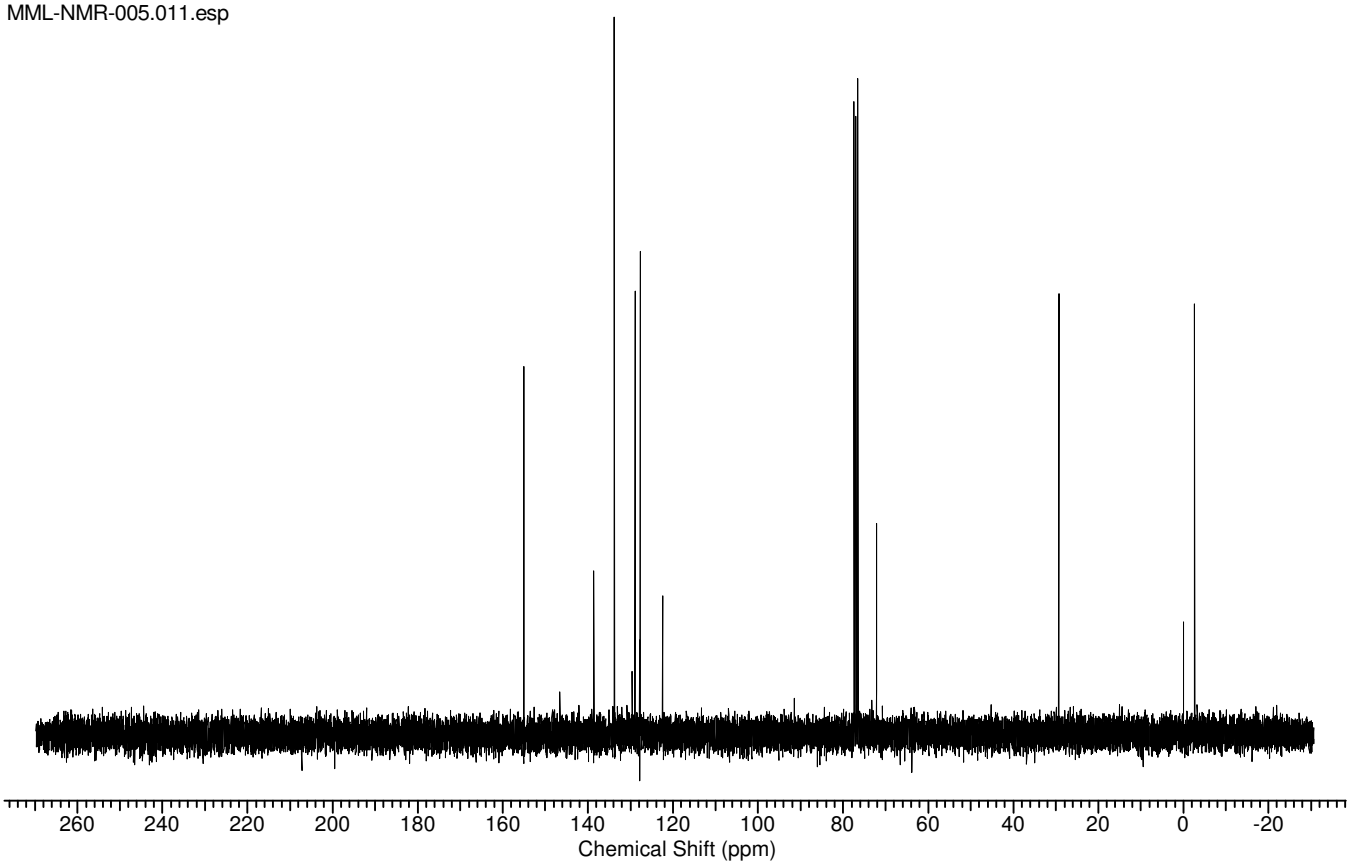


MML-NMR-005.010.esp

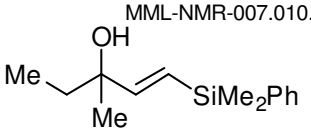


4a

MML-NMR-005.011.esp

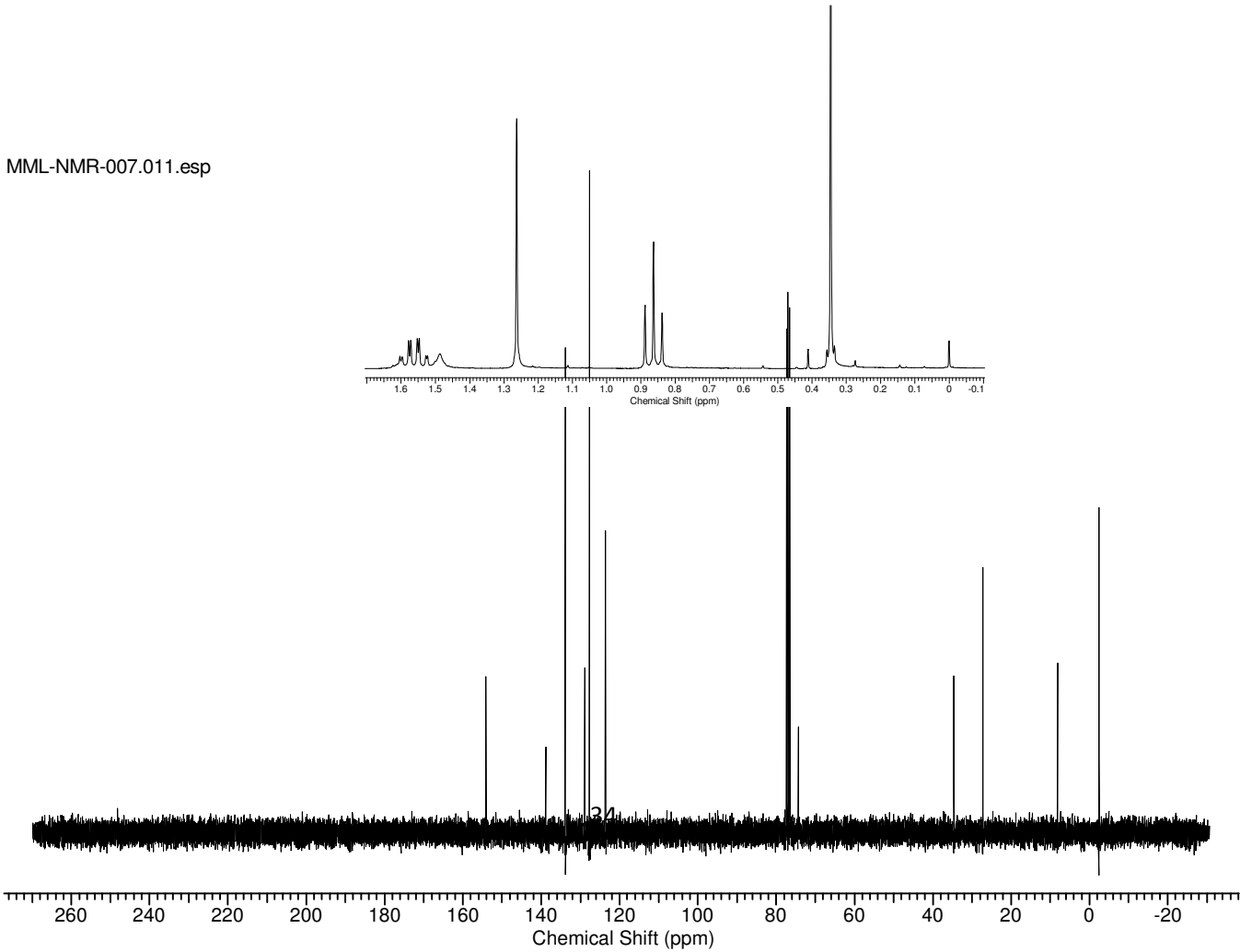


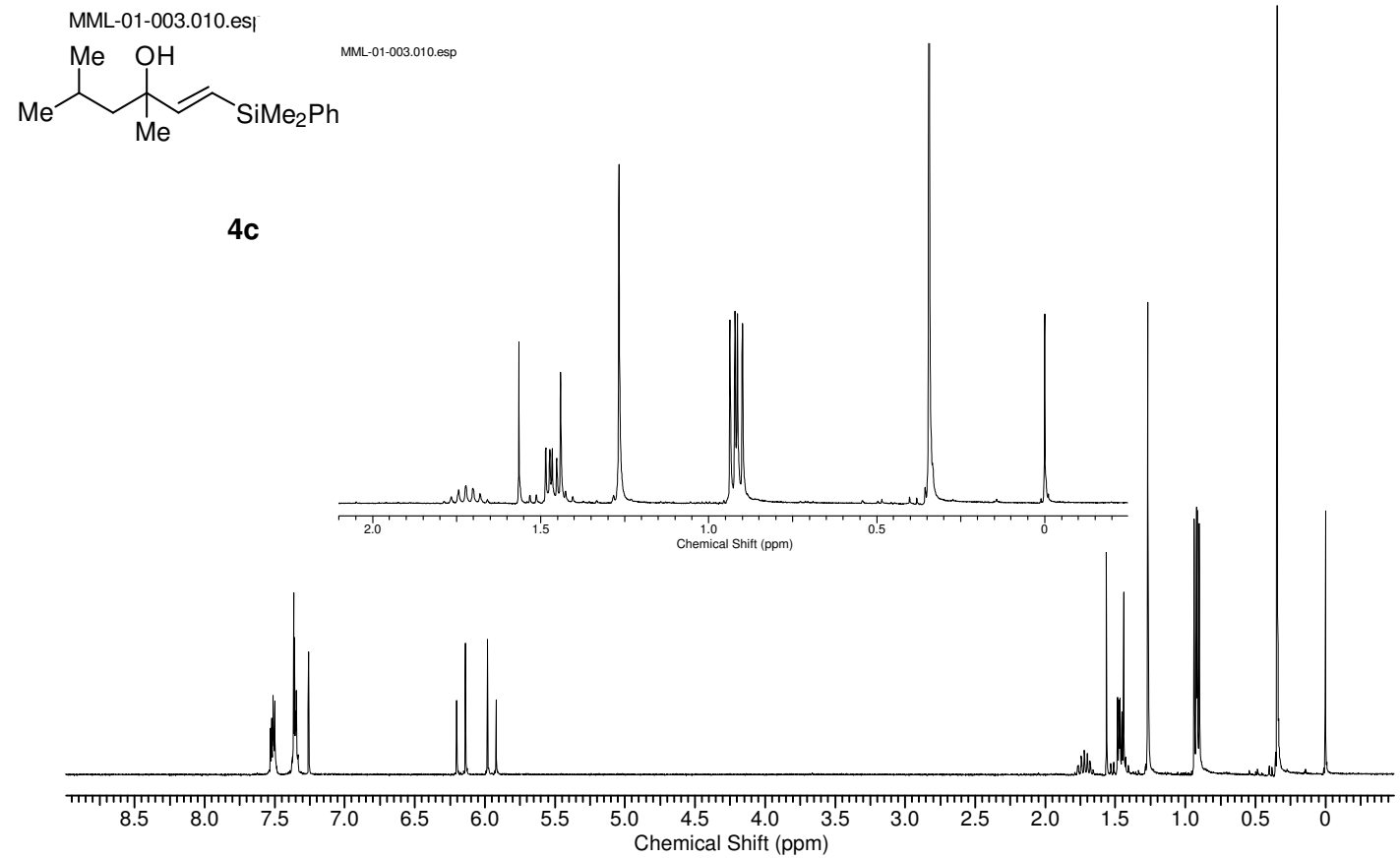
MML-NMR-007.010.esp



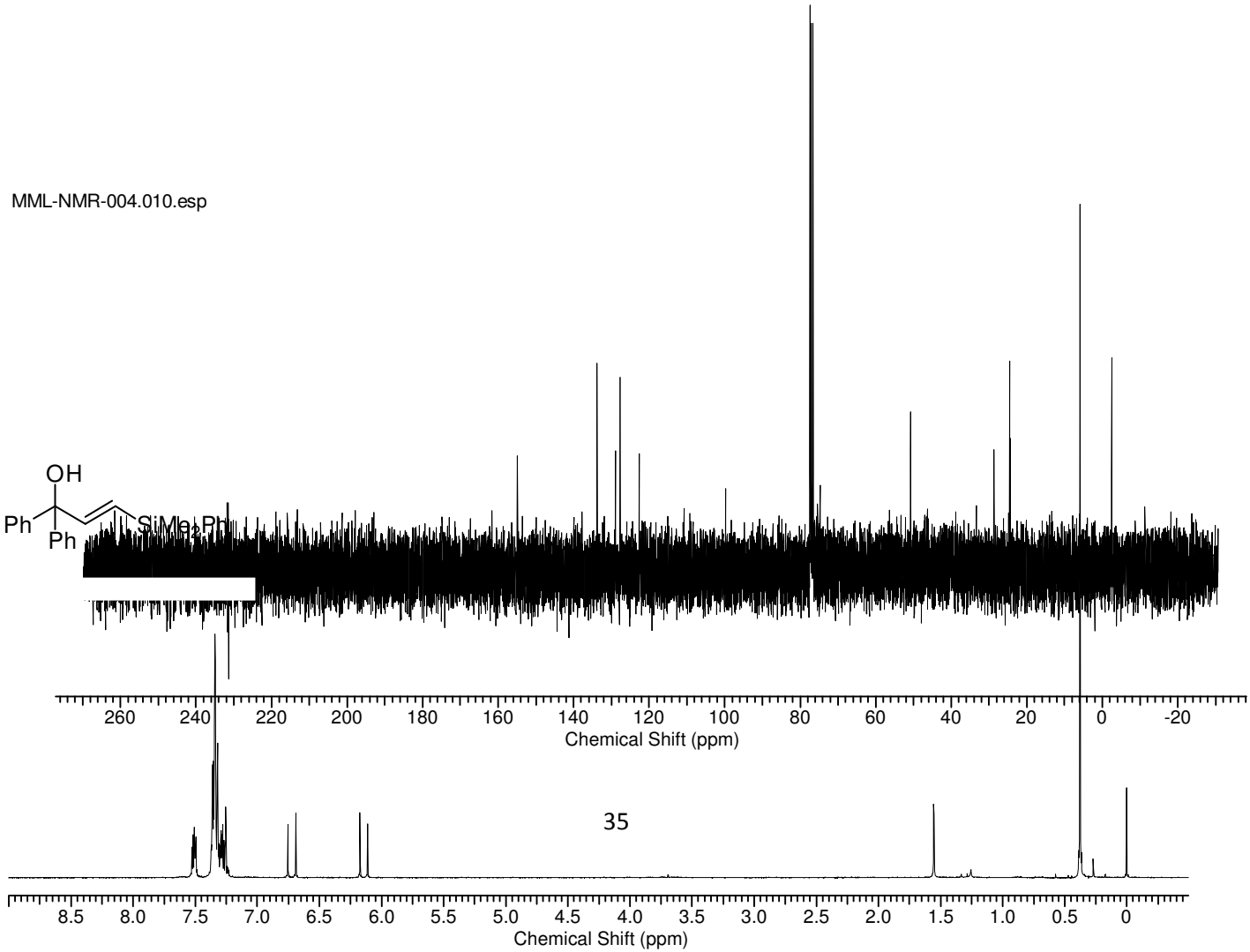
4b

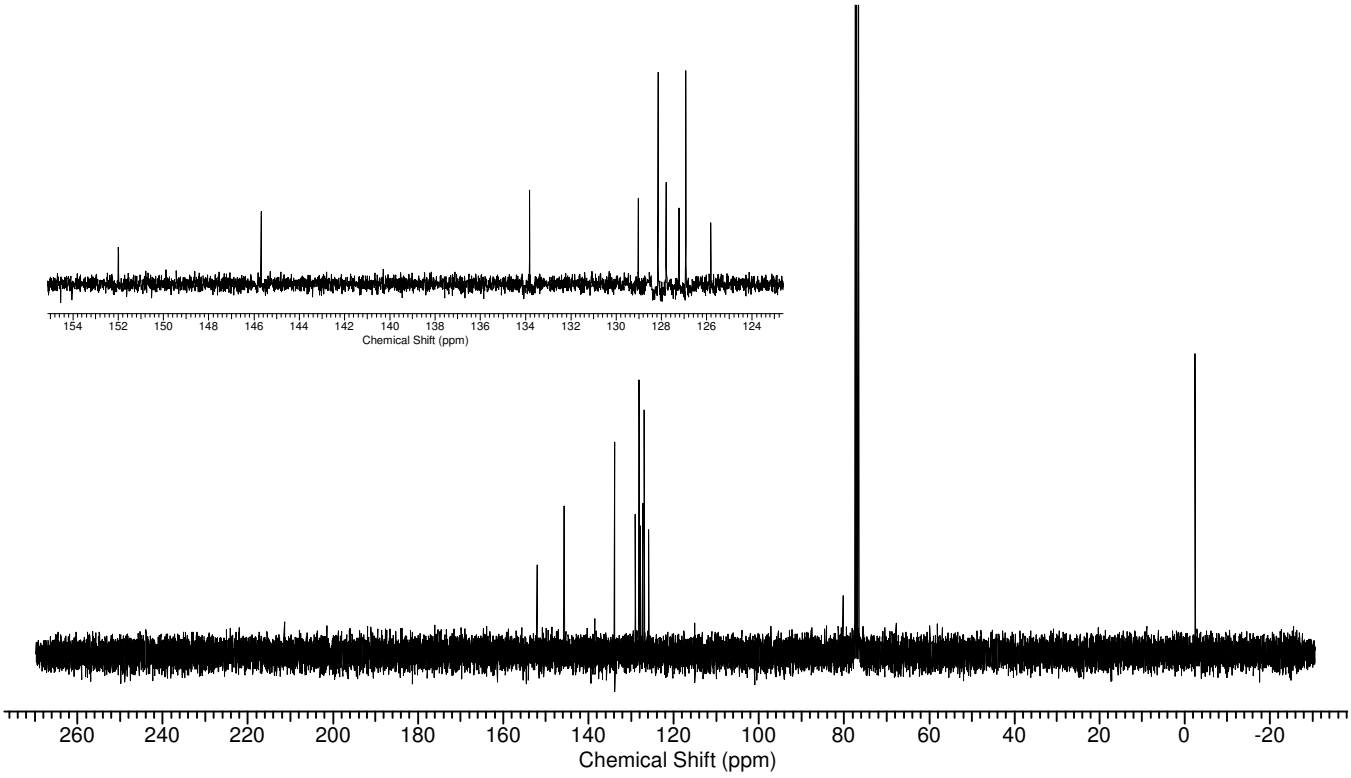
MML-NMR-007.011.esp

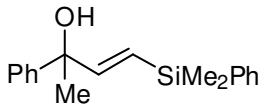



MML-01-003.010.esp
Me
OH
Me
Me
SiMe2Ph
MML-01-003.010.esp
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

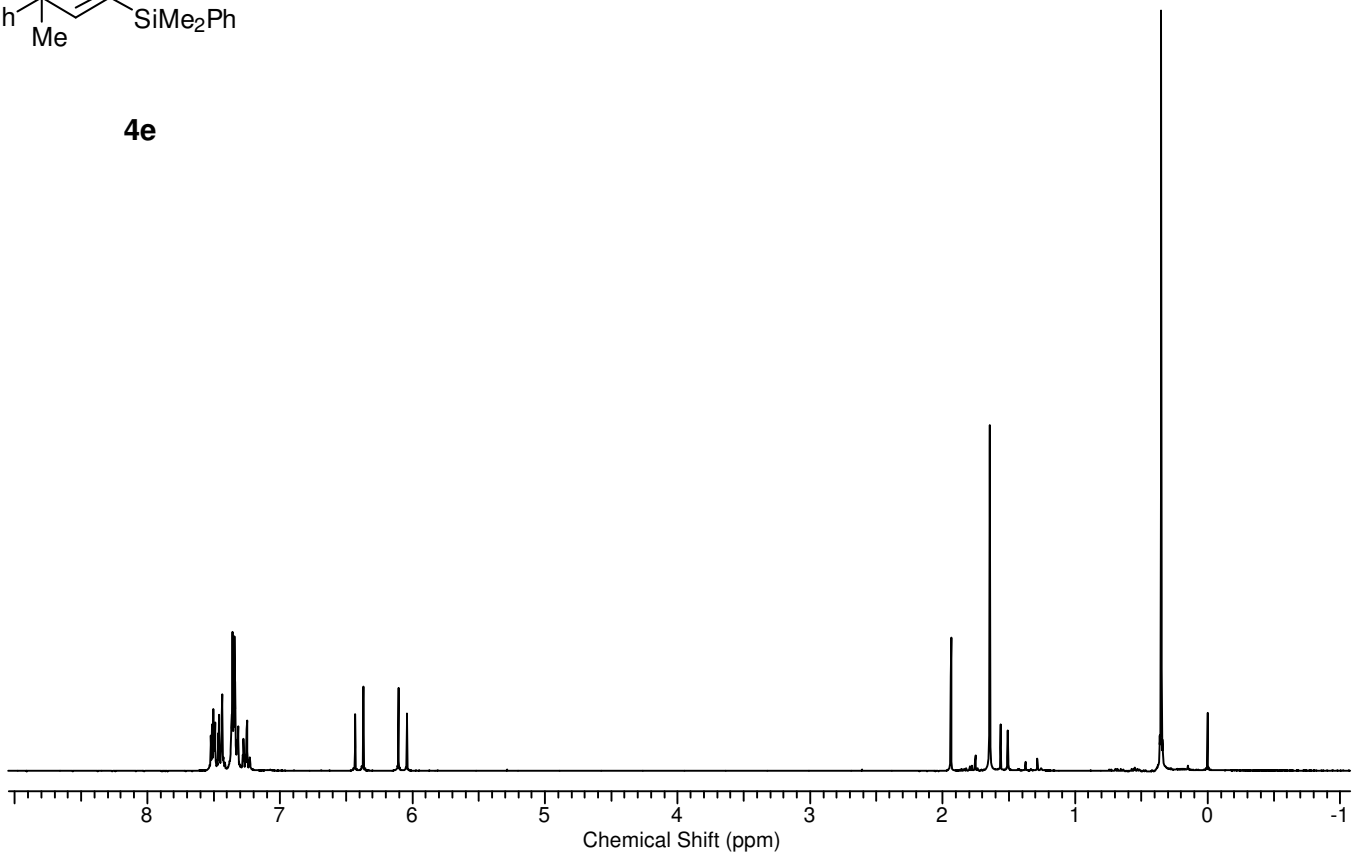
4c

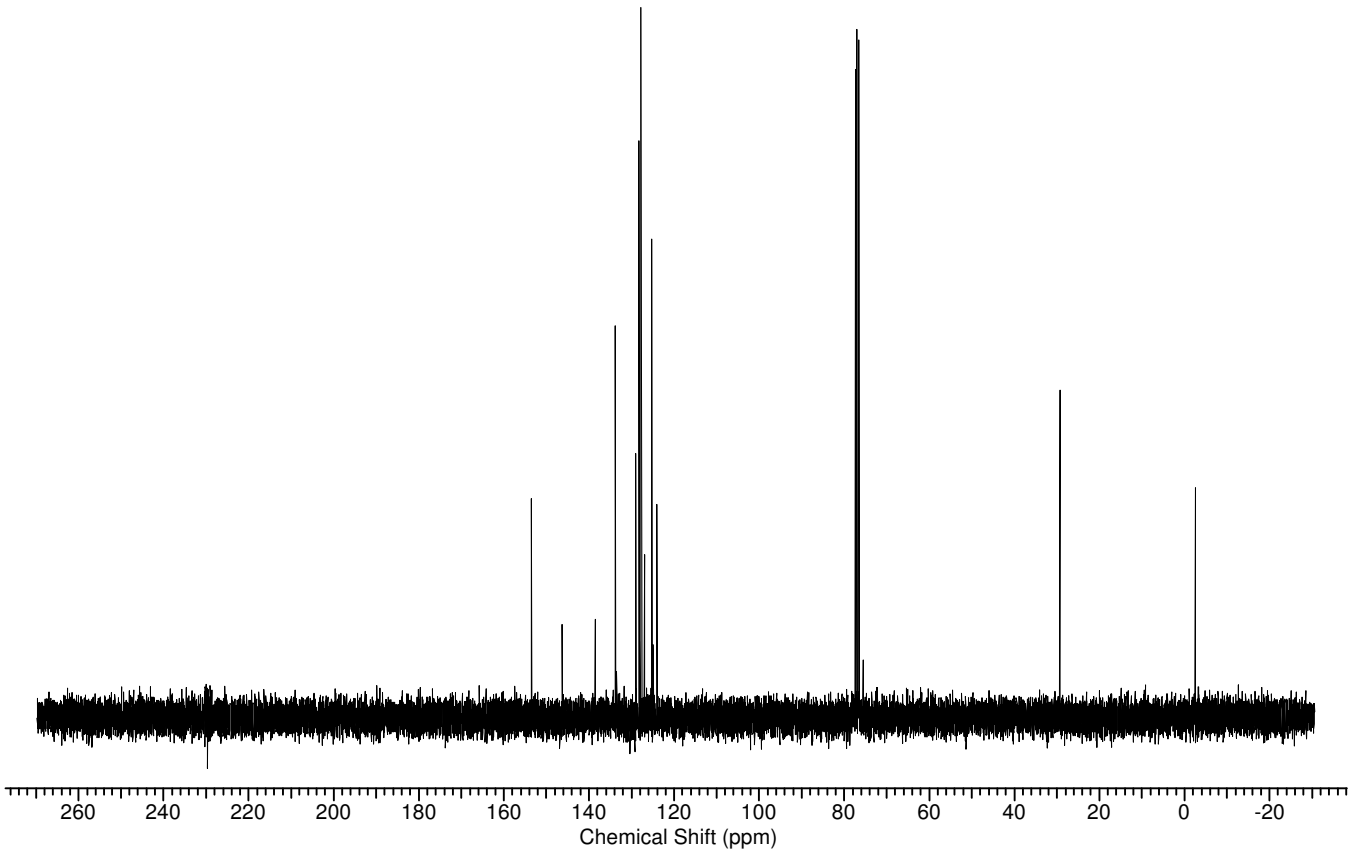

MML-NMR-004.010.esp
OH
Ph
Ph
SiMe2Ph
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

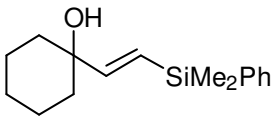

154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124
Chemical Shift (ppm)
260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)


OH
Ph
Me
SiMe2Ph

4e

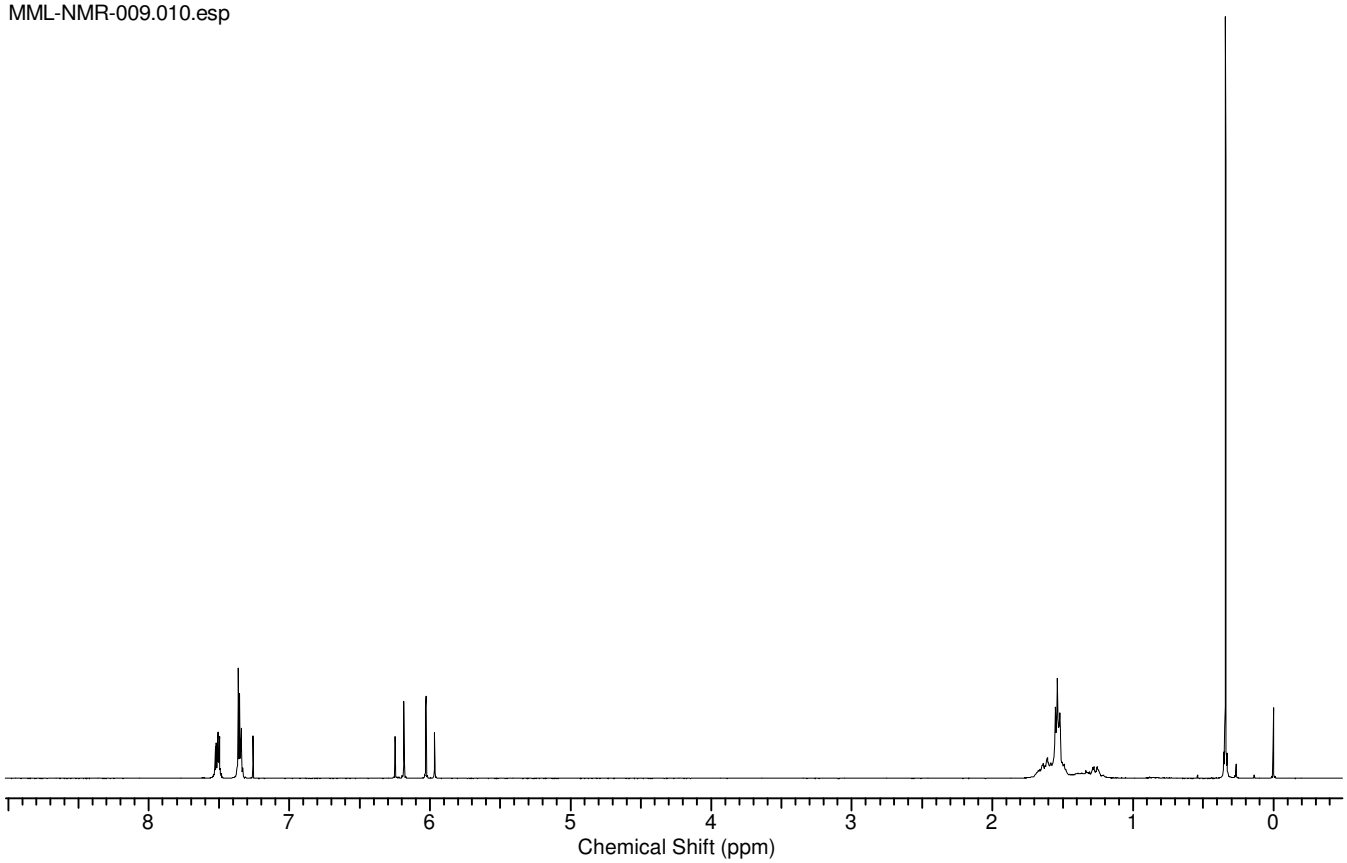

8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

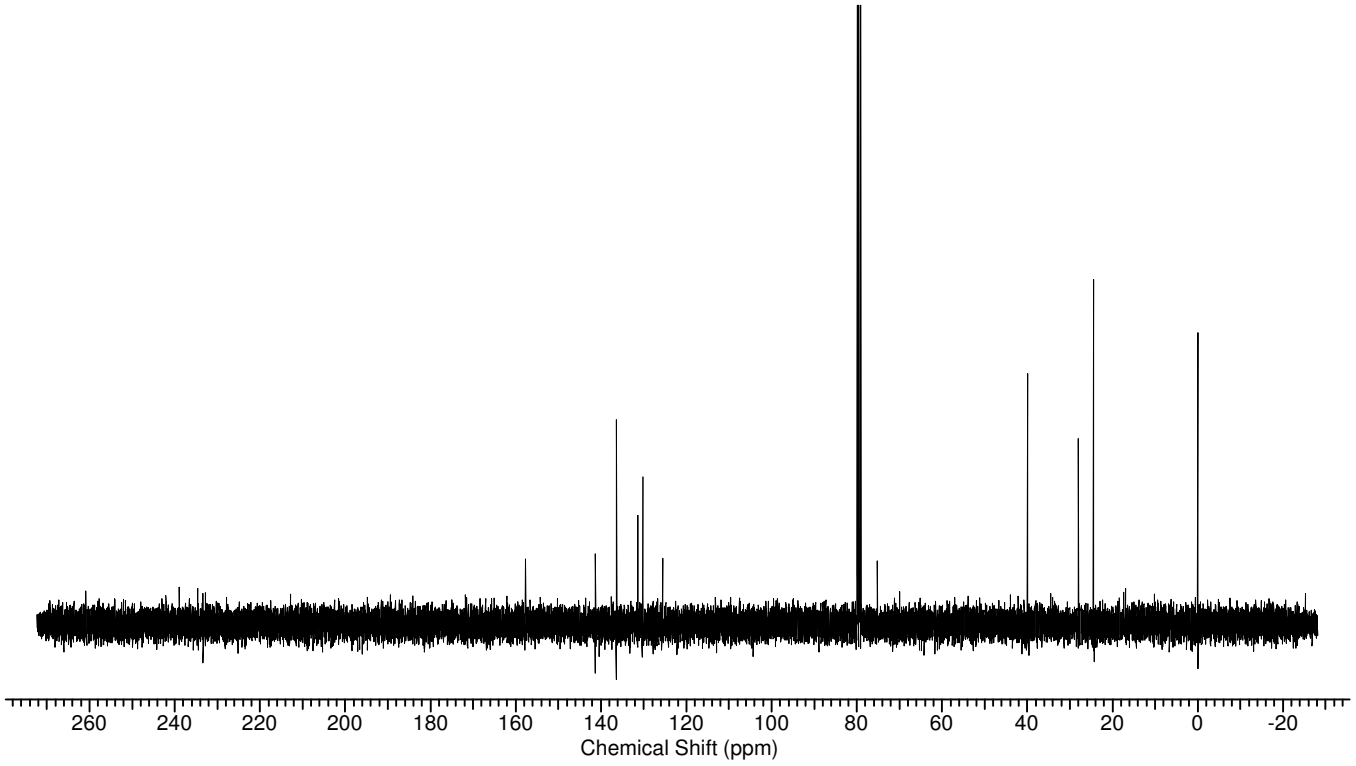


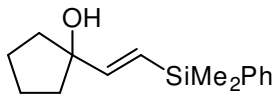
4f

MML-NMR-009.010.esp



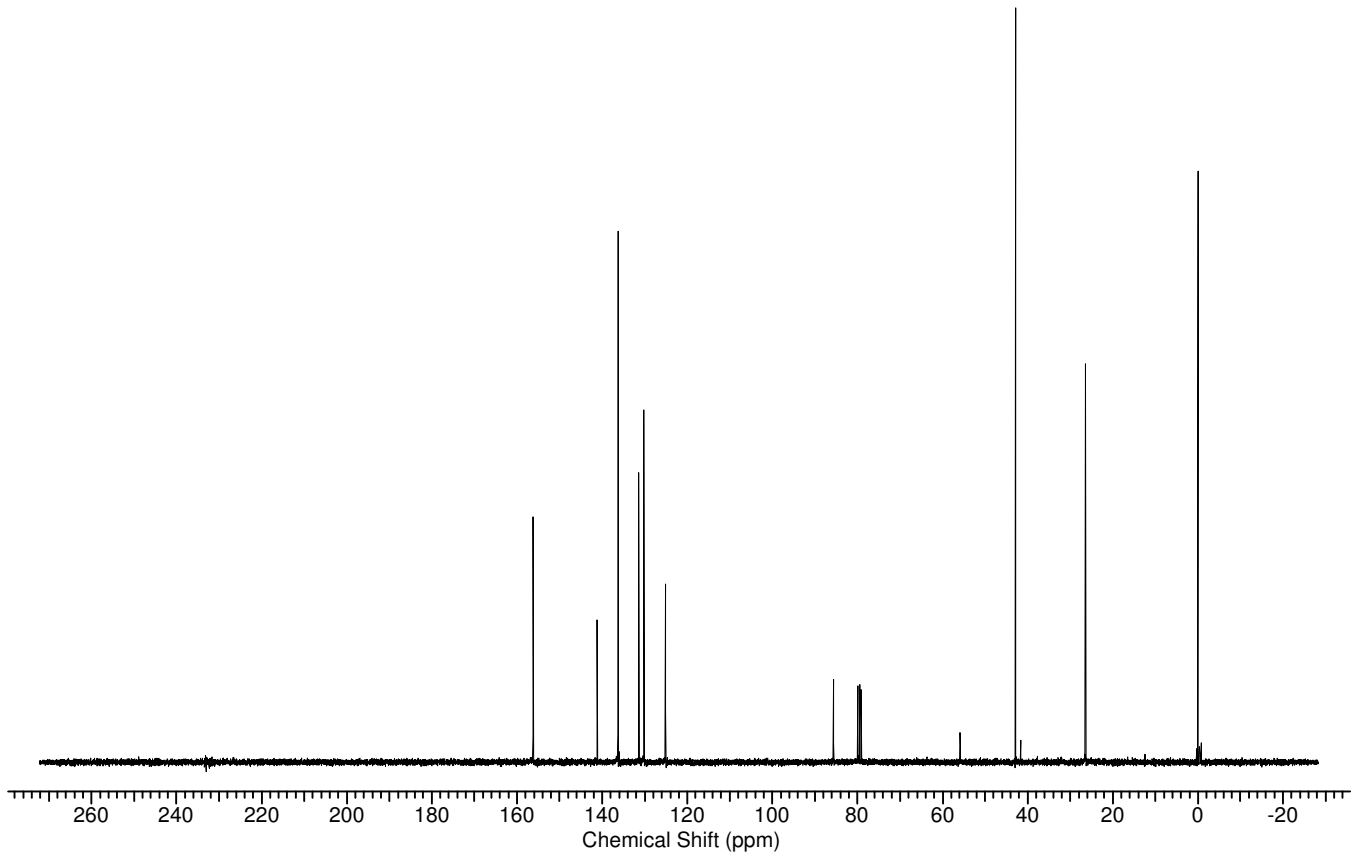
MML-NMR-009.011.esp

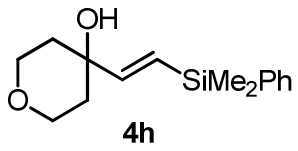



OH
SiMe2Ph

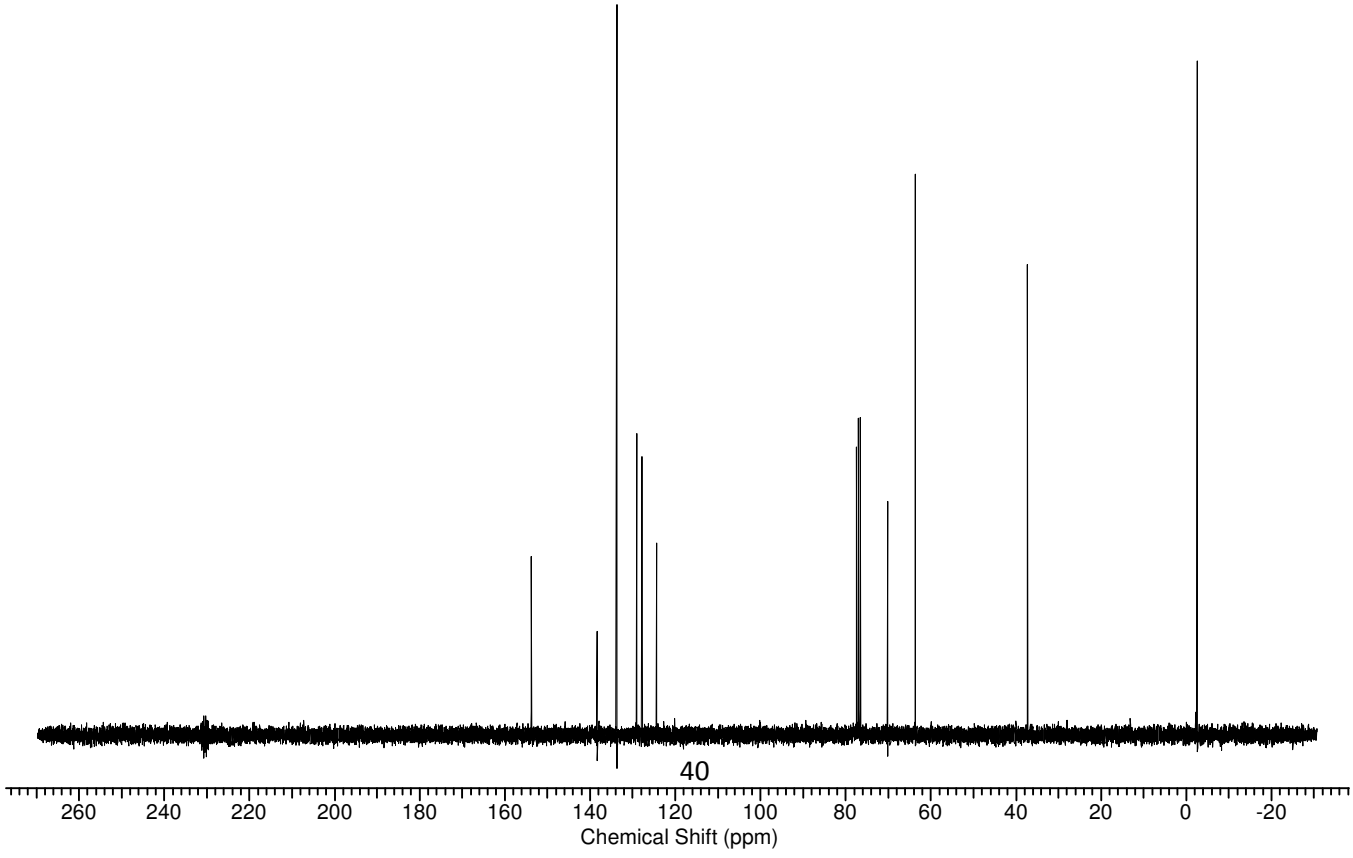
4g

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)

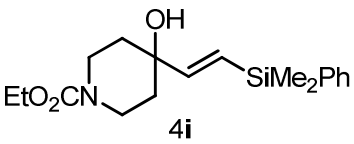

260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)



4h

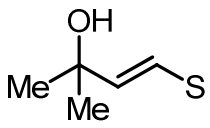


MML-NMR-010.010.esp

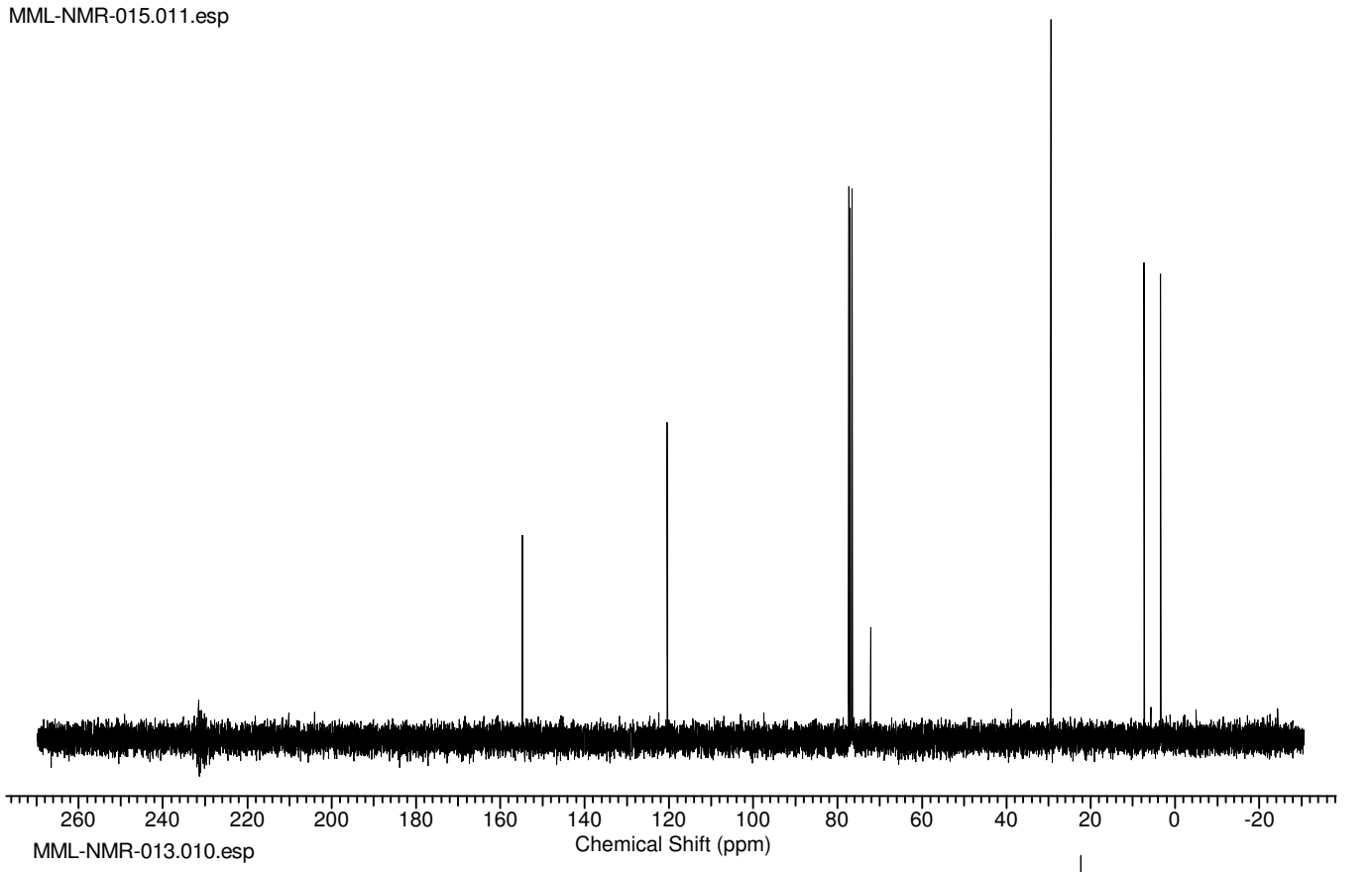


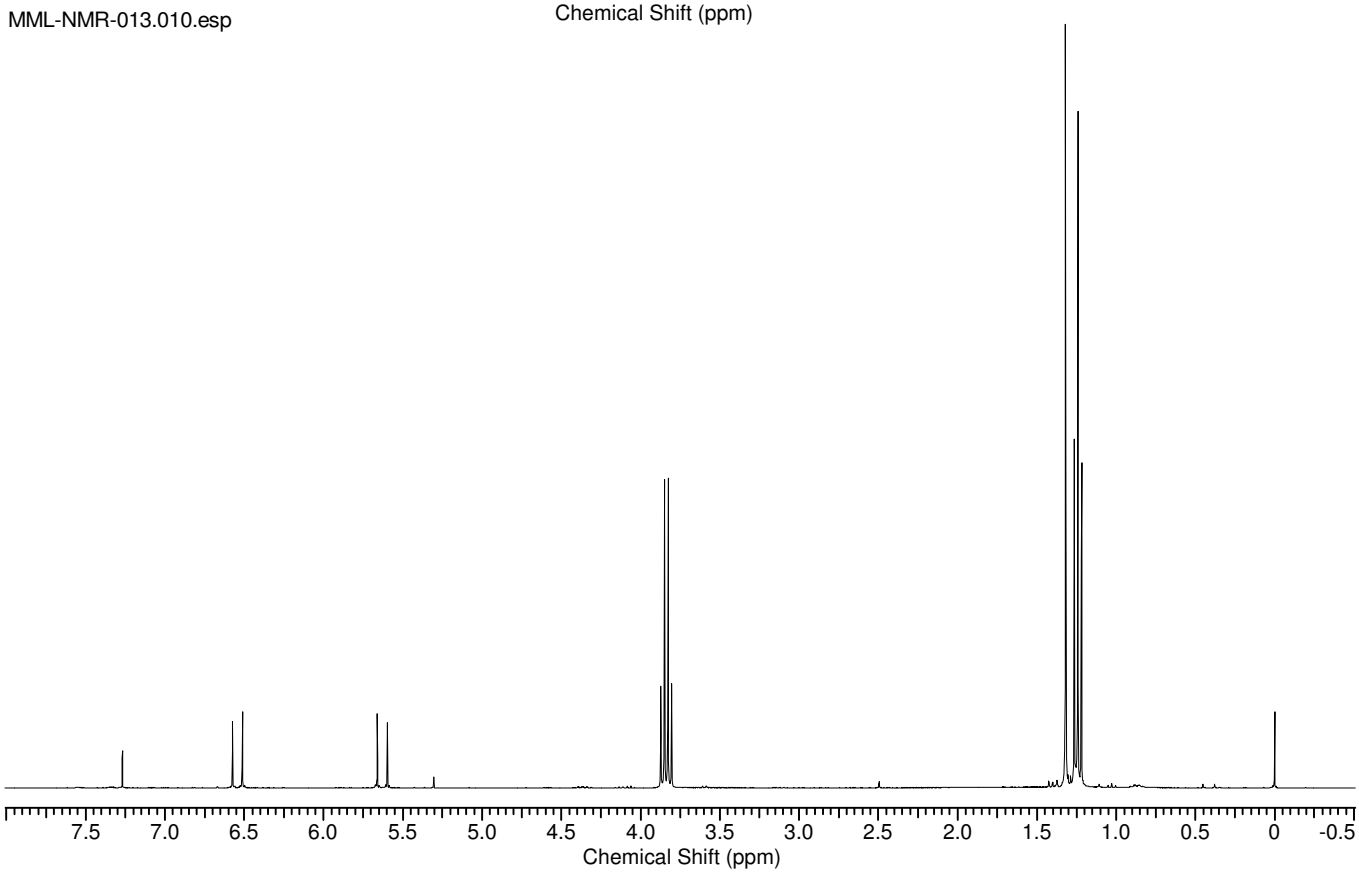
4i

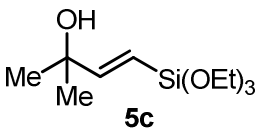
L-NMR-015.010.esp



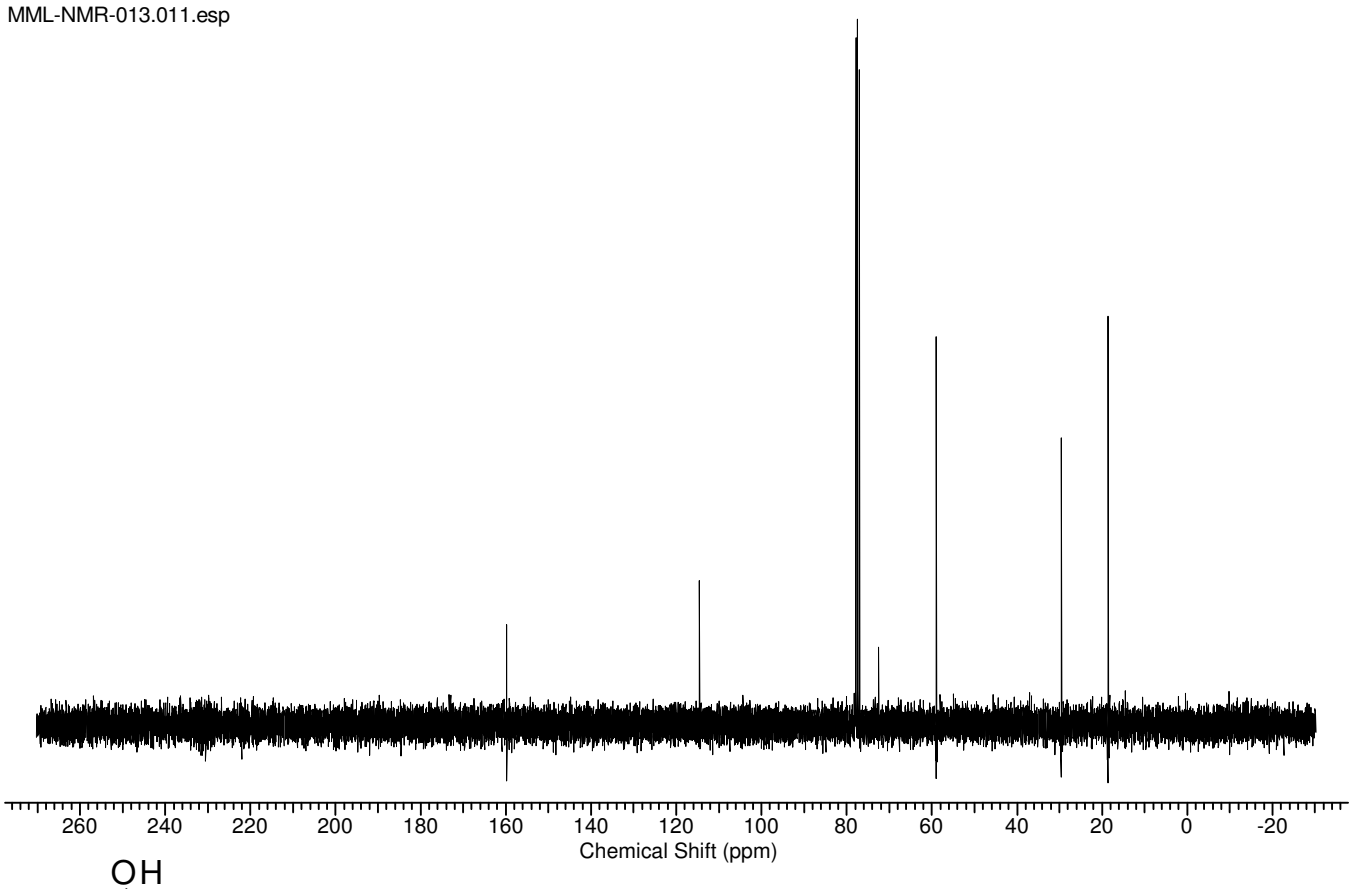
MML-NMR-010.015.esp **5a**

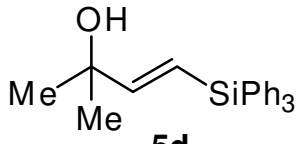

MML-NMR-015.011.esp
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


MML-NMR-013.010.esp
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)

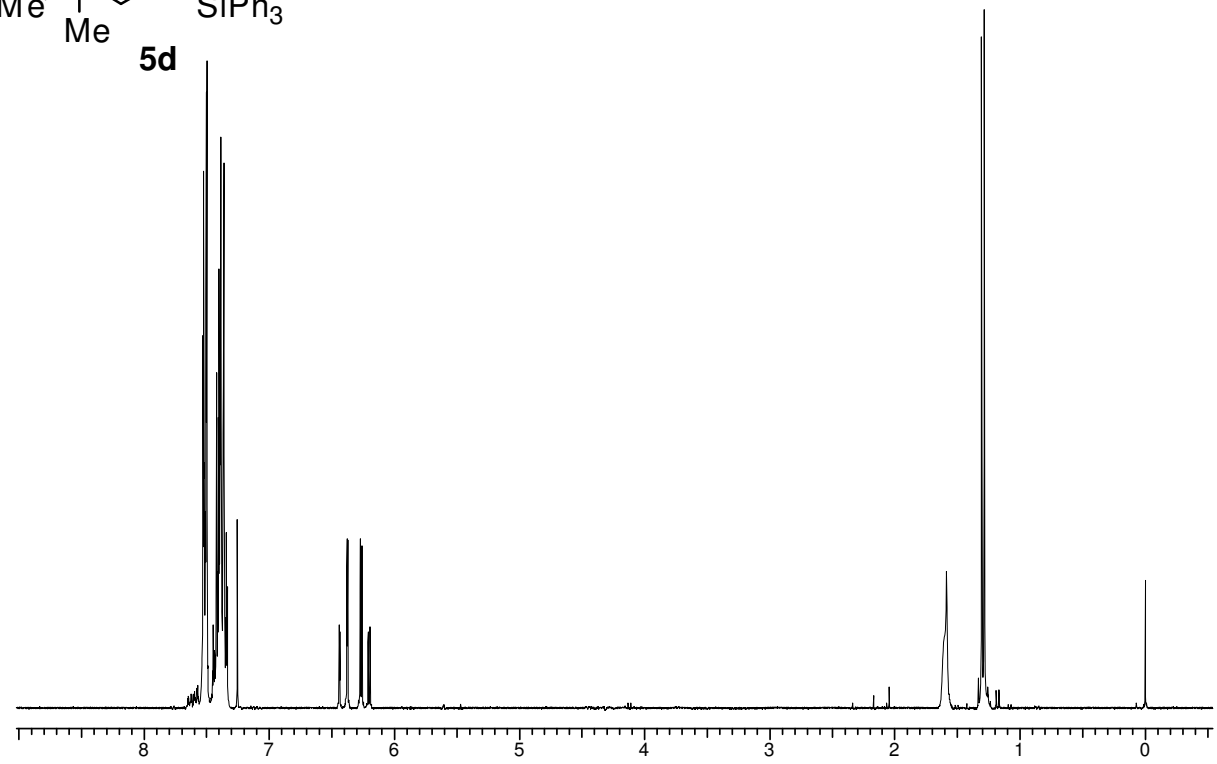

OH
Me
Me
Si(OEt)3

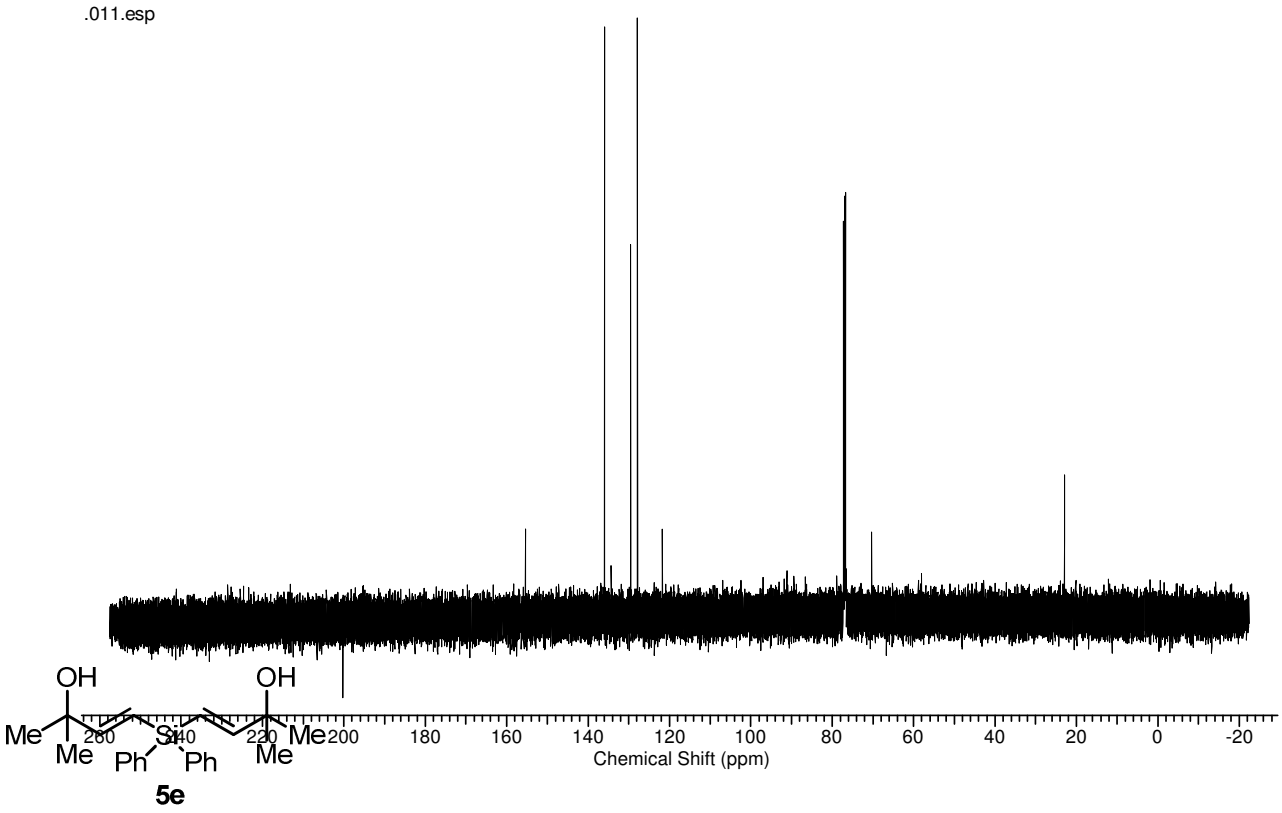
5c


MML-NMR-013.011.esp
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

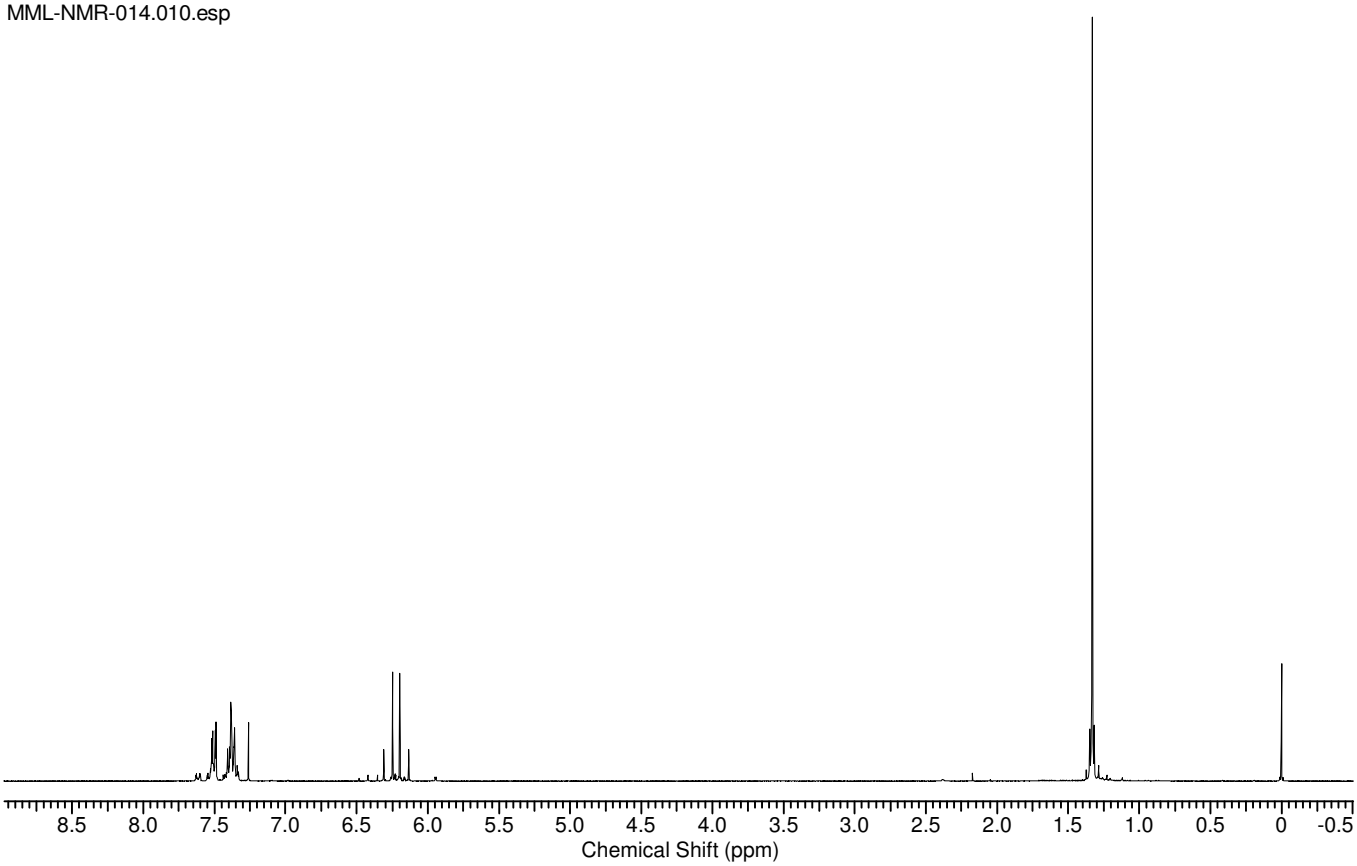

OH
Me
Me
SiPh3

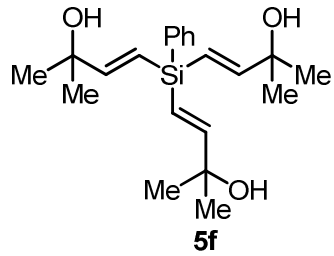
5d


8
7
6
5
4
3
2
1
0


.011.esp
OH
OH
Me
Me
Ph
Si
Ph
Me
Me
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

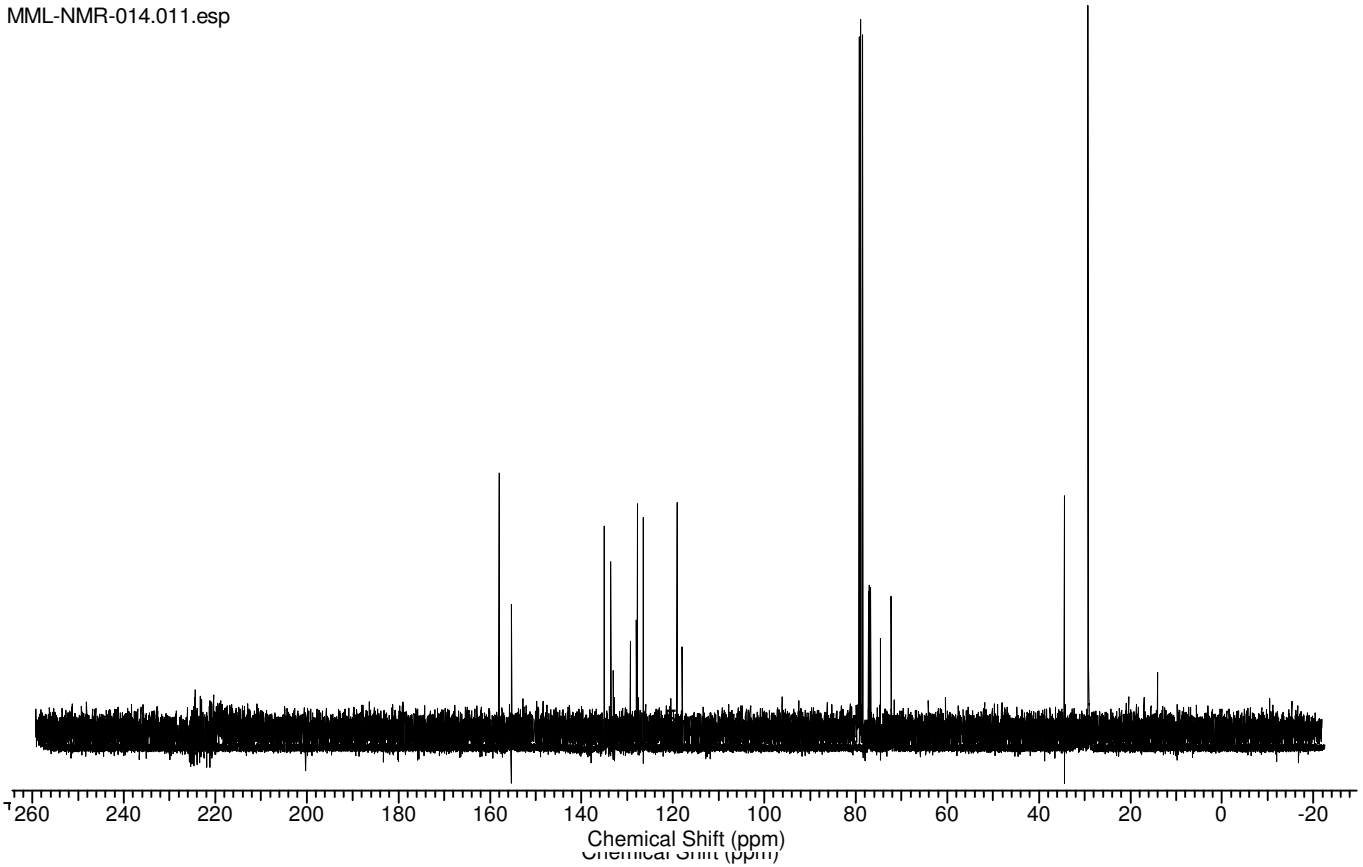
5e

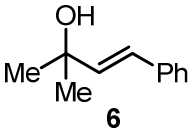

MML-NMR-014.010.esp
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


OH
Ph
OH
Me
Me
Si
Me
Me
Me
OH
Me

5f

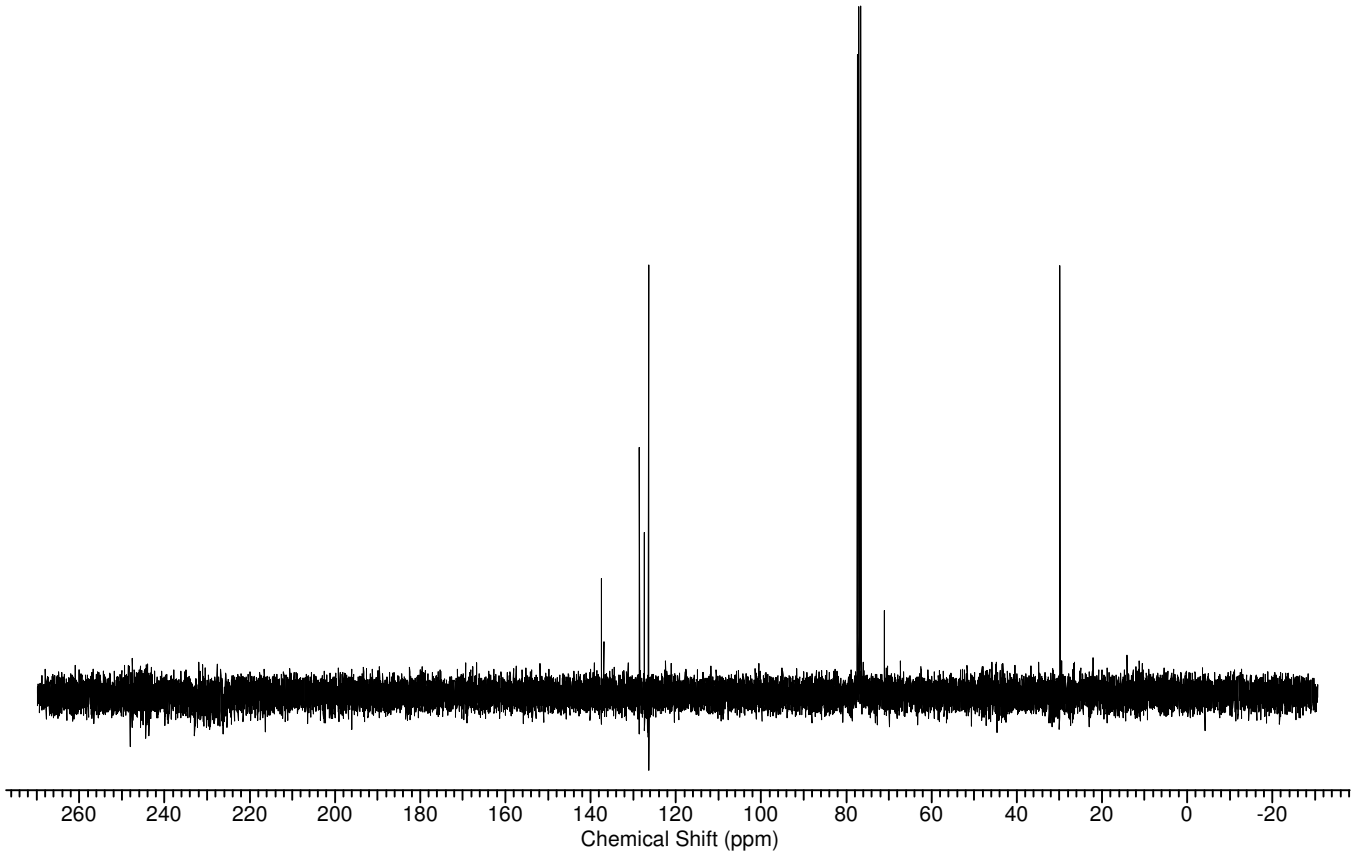
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

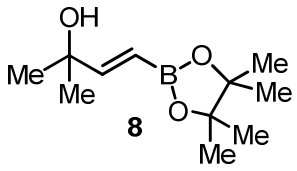

MML-NMR-014.011.esp
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


OH
Me
Me
Ph

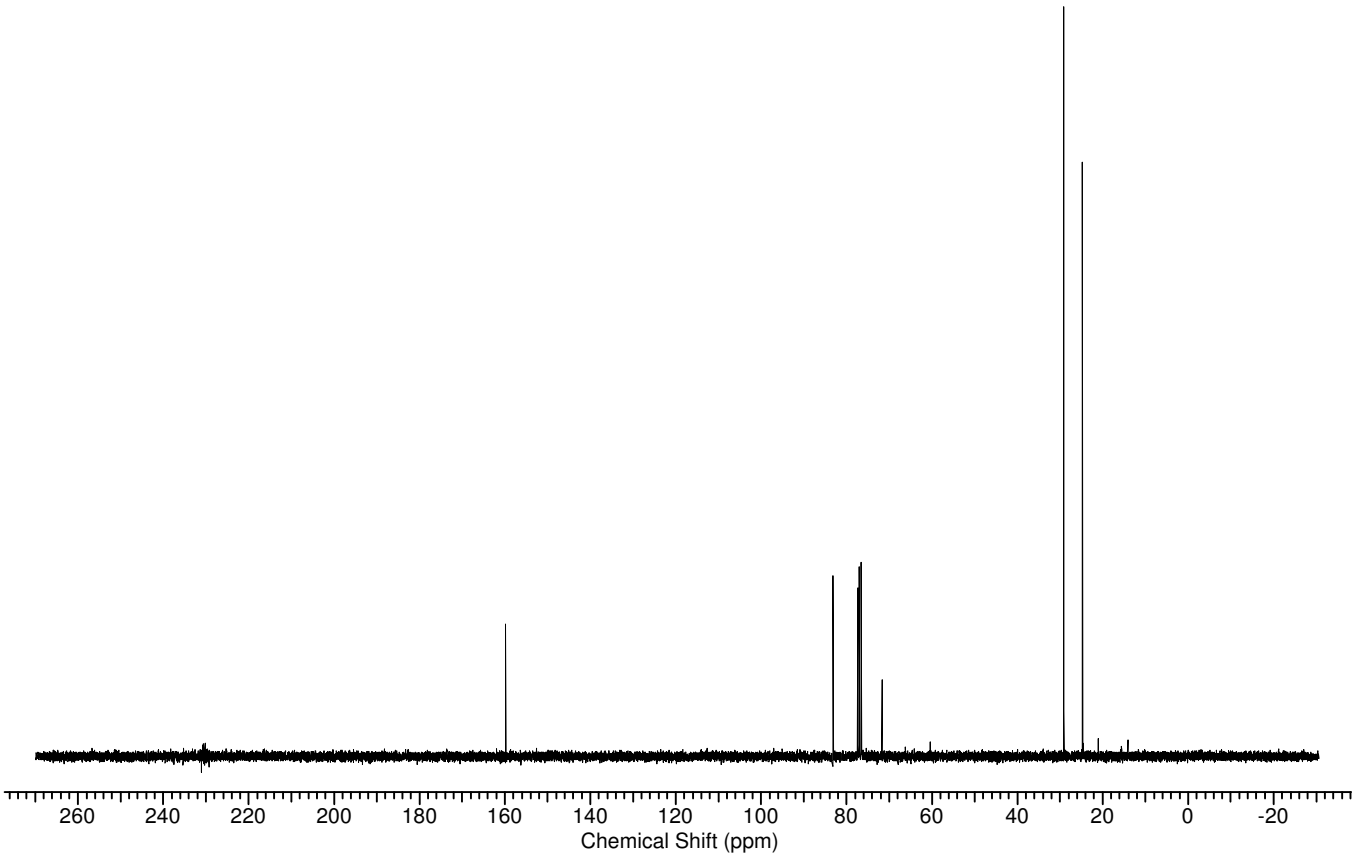
6

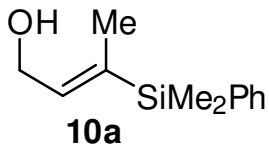
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5
Chemical Shift (ppm)


260 240 220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)



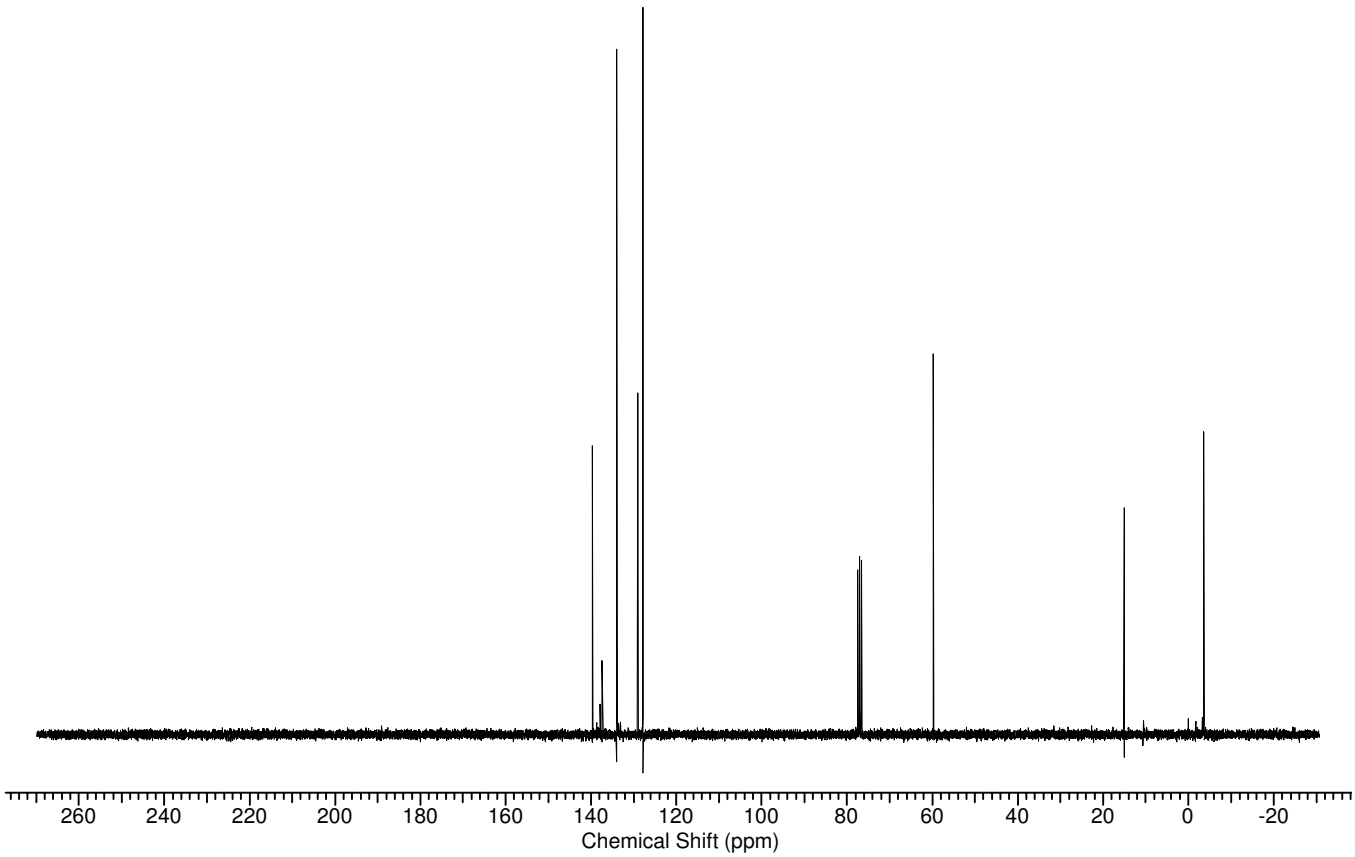
8

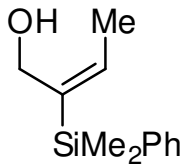



OH
Me
SiMe2Ph

10a

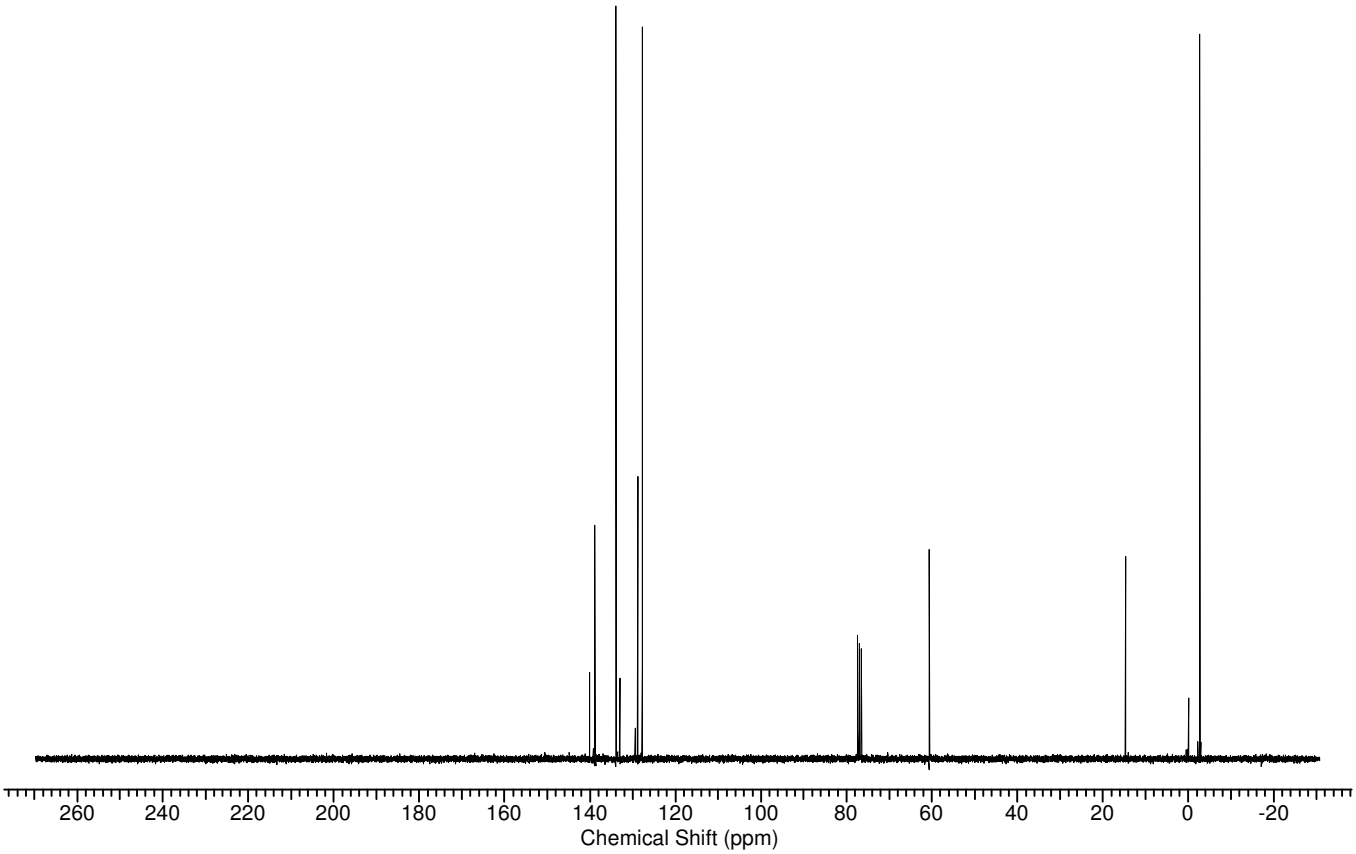
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

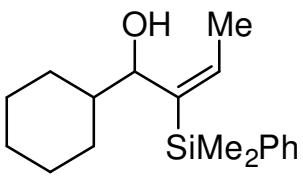

260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


OH
Me
SiMe2Ph

10b

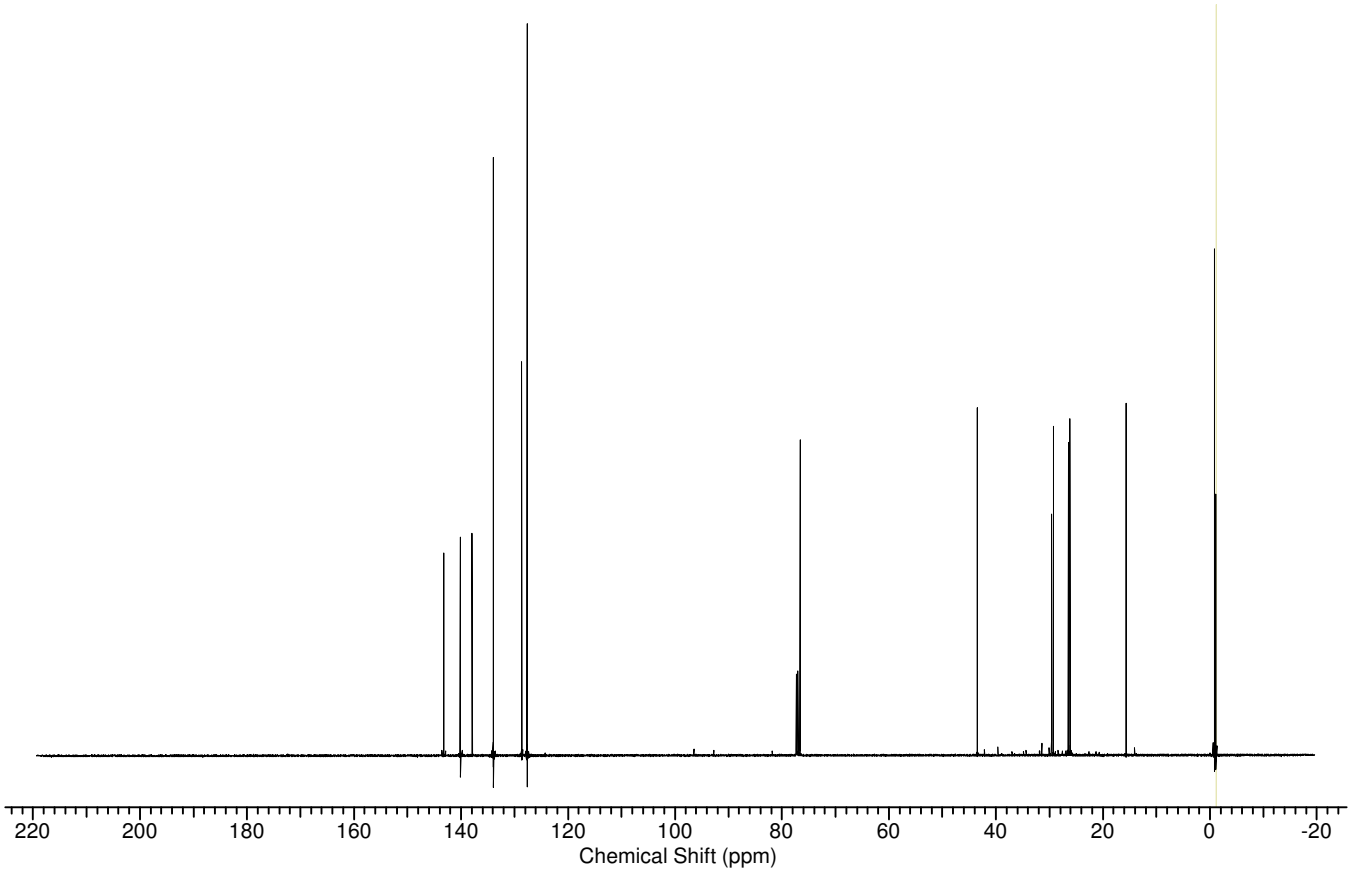
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

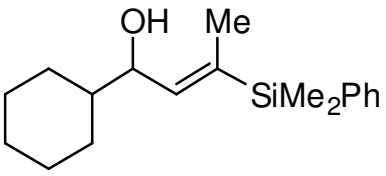

260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


OH
Me
SiMe2Ph

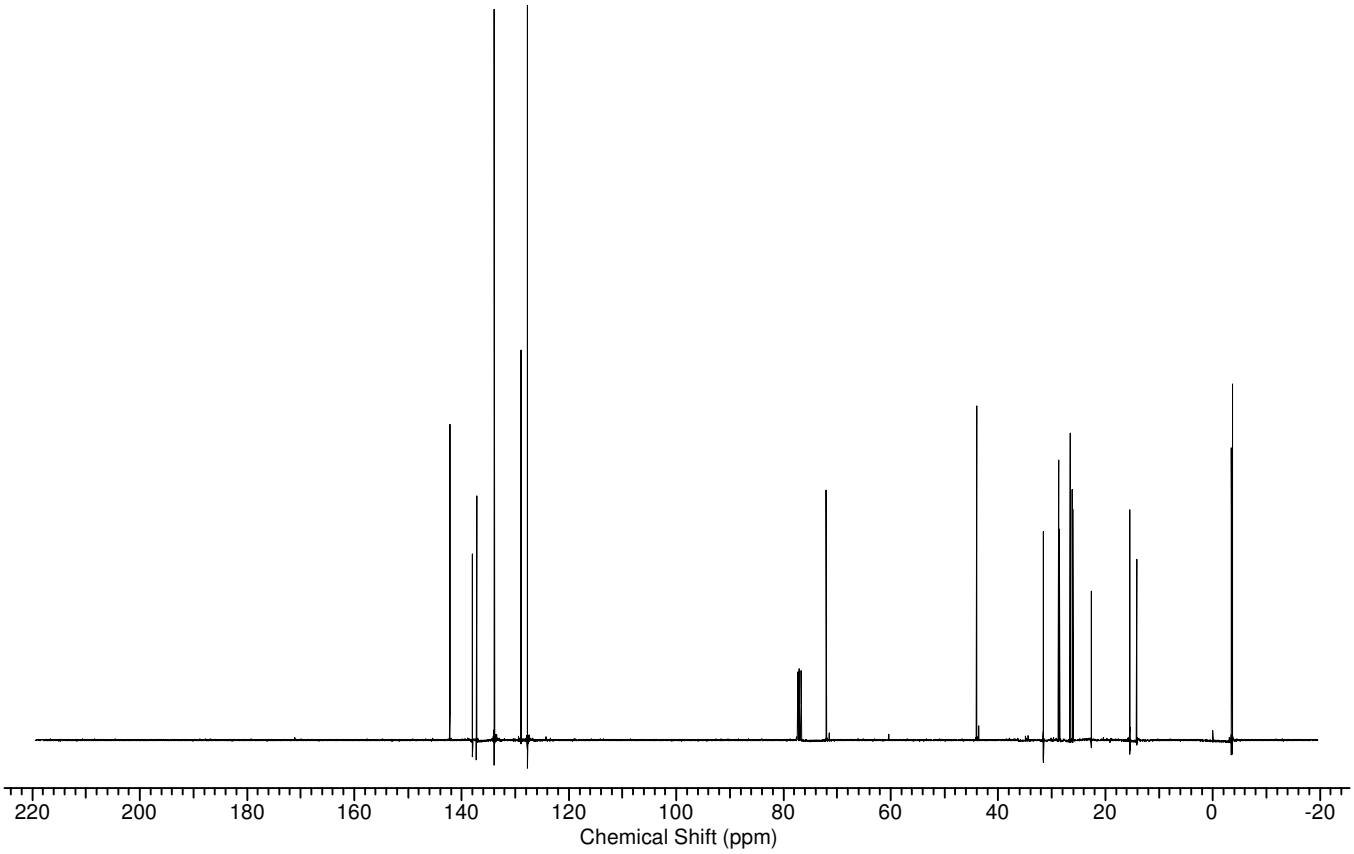
12a

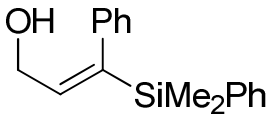
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
-0.5
Chemical Shift (ppm)


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



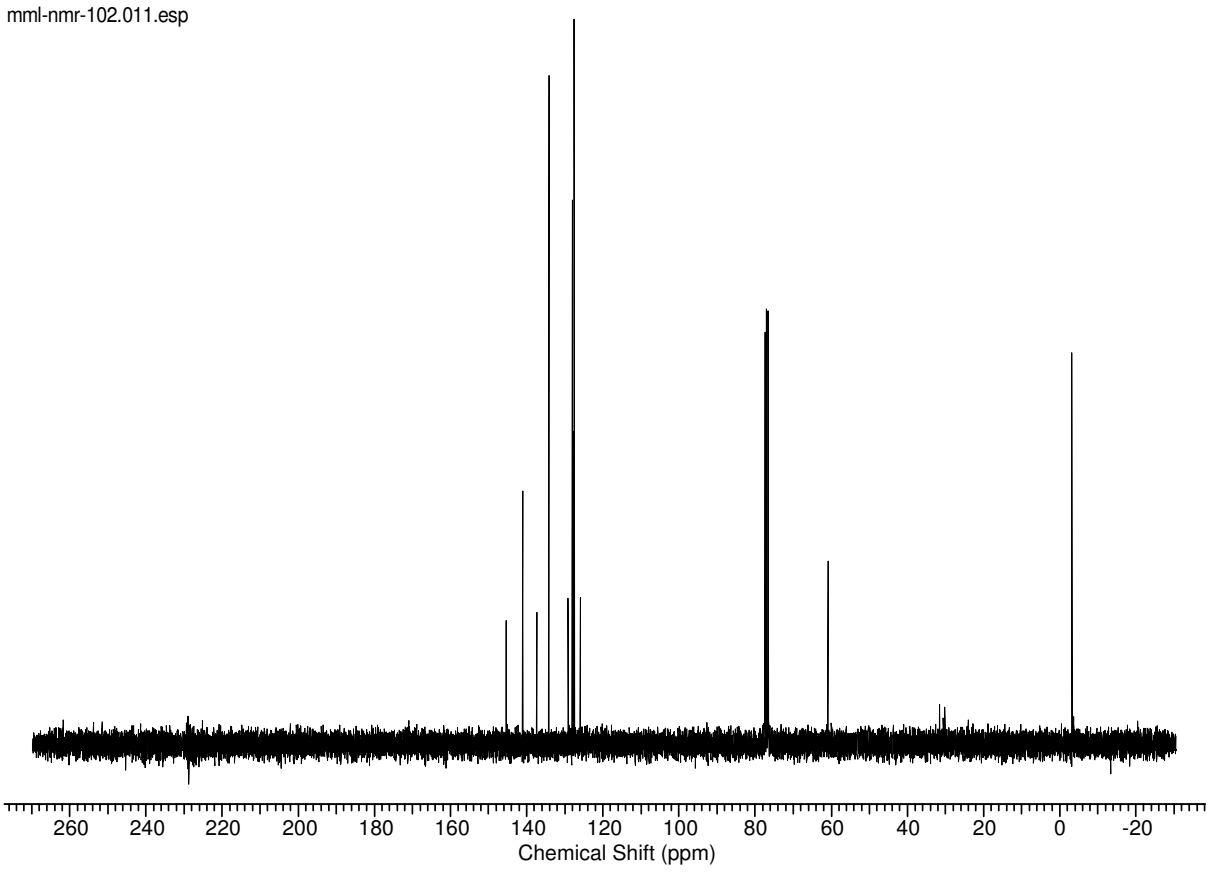
12b

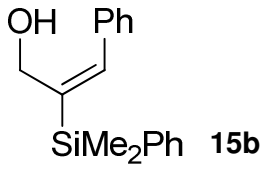



OH
Ph
SiMe2Ph

14a

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

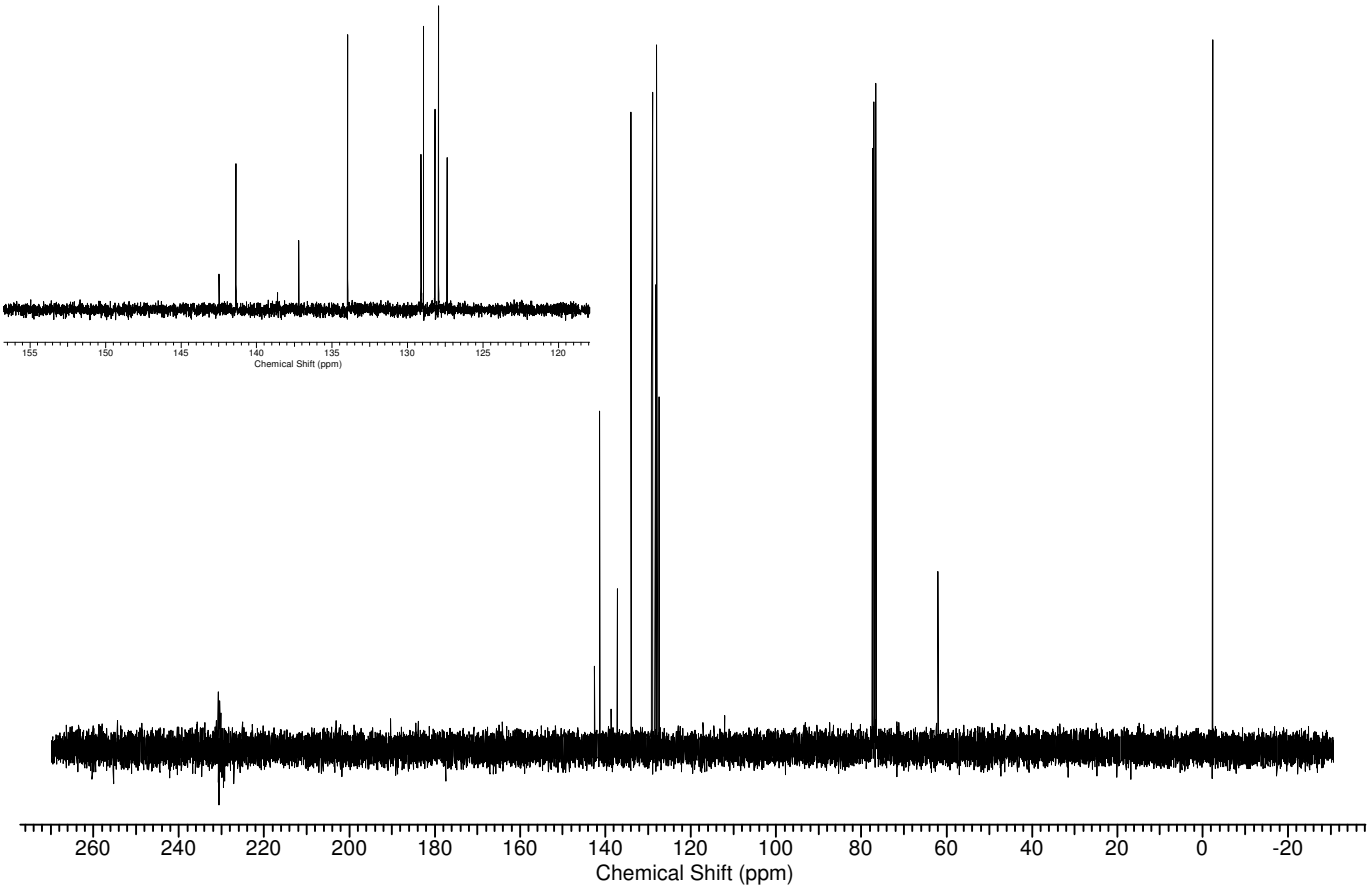

mml-nmr-102.011.esp
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)


OH
Ph
SiMe2Ph

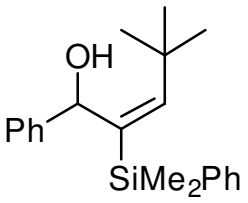
15b

14b

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

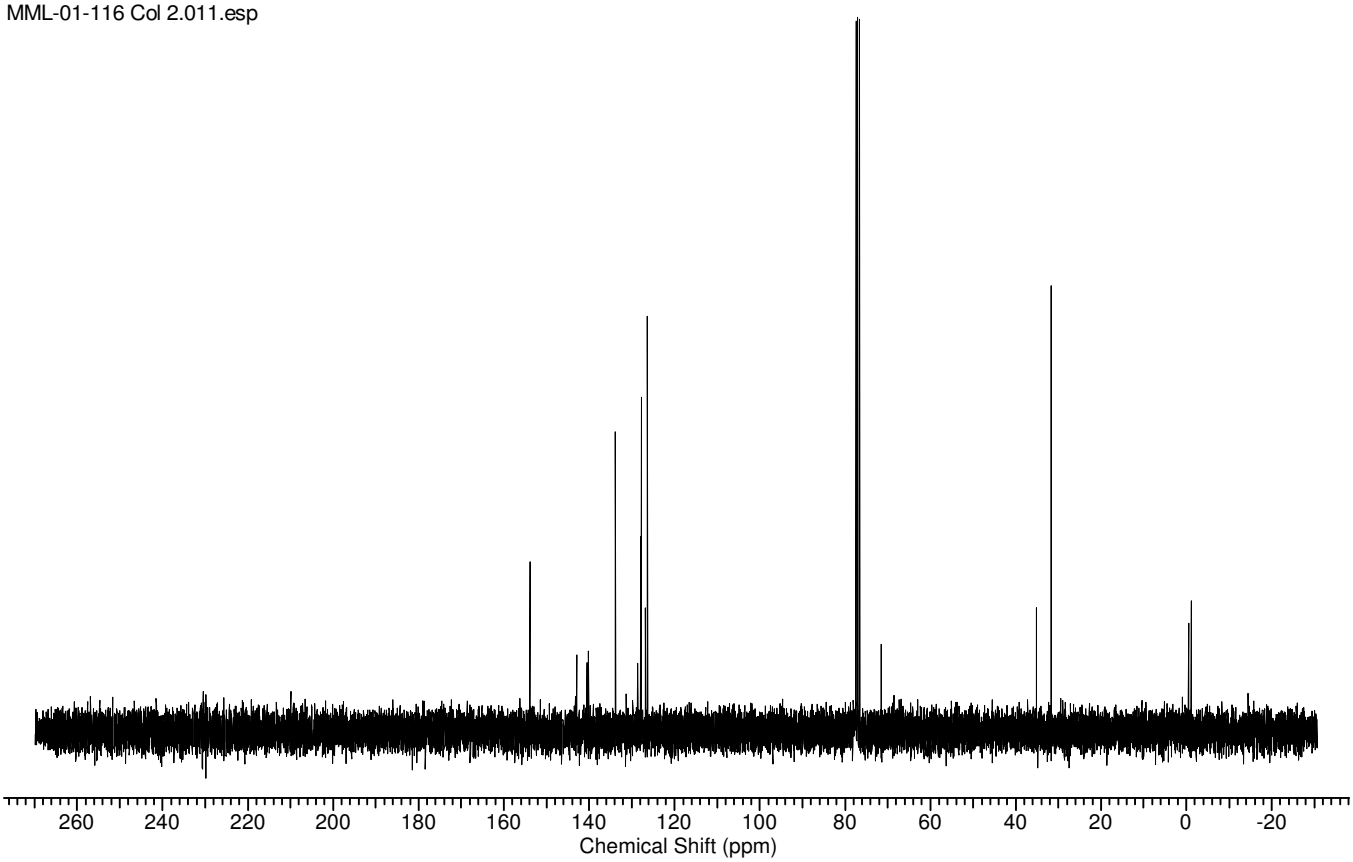

155
150
145
140
135
130
125
120
Chemical Shift (ppm)
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

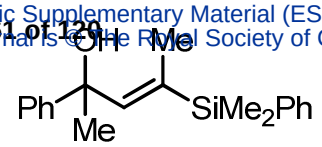
MML-01-116 Col 2.010.esp



17a

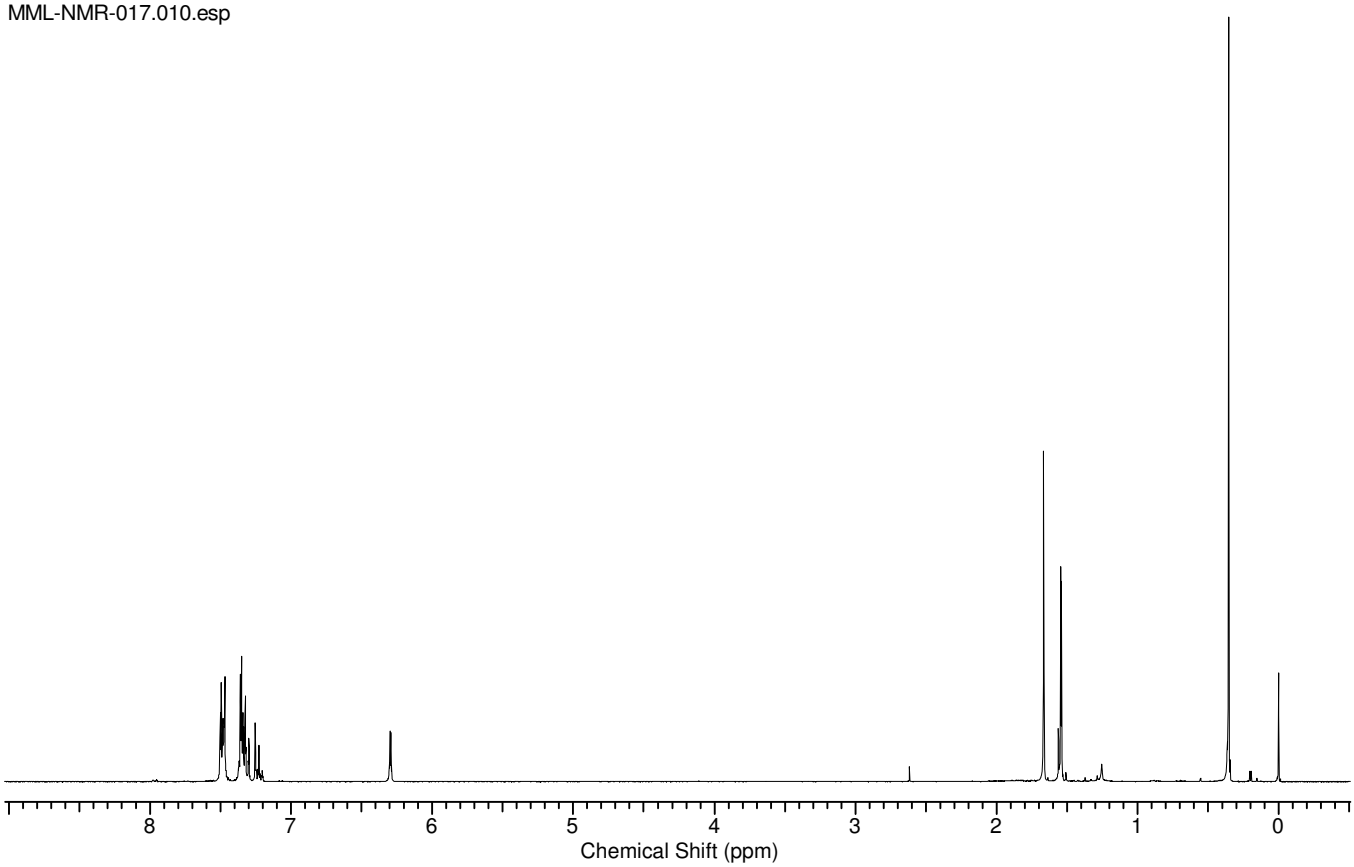
MML-01-116 Col 2.011.esp





18a

MML-NMR-017.010.esp



MML-NMR-017.011.esp