

SUPPORTING INFORMATION

One-step Chemoselective Conversion of Tetrahydropyranyl Ethers to Silyl-protected Alcohols.

Julian Bergueiro, Javier Montenegro,* Carlos Saá and Susana Lopez.*

Departamento de Química Orgánica, Facultade de Química,
Universidade de Santiago de Compostela, 15782 Santiago de Compostela, SPAIN

javier.montenegro@usc.es

Table of Contents.

General Methods.....	S2
Experimental Procedures for Significant Intermediates.....	S2-S12
NMR Spectra of All Compounds.....	S13-S48

General Remarks. Solvents were dried according to published methods and distilled before use.¹ All other reagents were commercial compounds of the highest purity available. Reactions were carried out under atmosphere of argon in flame-dried glassware with magnetic stirring. Visualization of analytical thin-layer chromatography (TLC) was accomplished with phosphomolybdic acid ethanolic solution (10%) stain followed by heating. Proton (¹H) and carbon (¹³C) magnetic resonance spectra (NMR) were recorded using CDCl₃ or CD₂Cl₂ as solvent. Chemical shifts (δ) are expressed in parts per million (ppm) relative to tetramethylsilane as internal reference. ¹³C multiplicities were assigned with the aid of the DEPT pulse sequence. All the solutions employed were degassed by argon bubbling over 15 min.

Experimental procedures for significant experiments:

General procedure for the synthesis of tetrahydropyranyl protected alcohols **1x₁**:

To a suspension of alcohol (1 eq.) in dry THF at room temperature under argon was added DHP (1.5 eq.) dropwise, and the mixture was stirred for 5 min. *p*TSOH was added and the resulting solution was stirred for 4 h. Reaction was quenched with aqueous NaHCO₃ (20%), and extracted with diethyl ether. The organic phase was dried (Na₂SO₄) and filtered, and the solvent was removed. Chromatography column (SiO₂, 95:5 or 70:30 hexane/AcOEt) of the residue afforded the protected alcohol **1x₁**.

2-(Octyloxy)tetrahydro-2*H*-pyran (**1a₁**): Following the general procedure, reaction of octan-1-ol (1.00 g, 7.68 mmol) and DHP (1.01 mL, 11.52 mmol) with *p*TSOH (14.6 mg, 7.68 x 10⁻² mmol) in CH₂Cl₂ (20 mL) afforded compound **1a₁** (1.35 g, 82%) as a colourless oil.

¹H NMR (300 MHz, CDCl₃) δ 0.85 (t, *J* = 7.0 Hz, 3H, CH₃), 1.2-1.3 (m, 10H, 5xCH₂), 1.5-1.8 (m, 8H, 4xCH₂), 3.3-3.4 (m, 2H, CH₂), 3.7-3.9 (m, 2H, CH₂), 4.5-4.6 (m, 1H, CH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 13.9 (CH₃), 19.5 (CH₂), 22.5 (CH₂), 25.4 (CH₂), 26.1 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 30.6 (CH₂), 31.7 (CH₂), 62.1 (CH₂), 67.5 (CH₂), 98.6 (CH) ppm. MS (CI) *m/z* (%) 215 (M⁺+1, 9), 113 (M⁺-OTHP, 15), 85 (100). HMRS (CI) calc for C₁₃H₂₆O₂, 215.2011; found, 215.2007.

(*E*)-2-(Pent-2-en-4-yn-1-yloxy)tetrahydro-2*H*-pyran (**1b₁**):² Following the general procedure, reaction of (*E*)-pent-2-en-4-yn-1-ol (1.00 g, 12.18 mmol) and DHP (1.6 mL, 18.27 mmol) with *p*TSOH (13 mg, 0.122 mmol) in CH₂Cl₂ (20 mL) afforded compound **1b₁** (1.7 g, 84%) as a light yellow oil.

2-(Benzyloxy)tetrahydro-2*H*-pyran (**1c₁**): Following the general procedure, reaction of phenylmethanol (1.00 g, 9.25 mmol) and DHP (1.2 mL, 13.87 mmol) with *p*TSOH (18 mg, 9.25 x 10⁻² mmol) in CH₂Cl₂ (20 mL) afforded compound **1c₁** (1.40 g, 79%) as a colourless oil.

¹H NMR (300 MHz, CDCl₃) δ 1.5-1.9 (m, 6H, 3xCH₂), 3.5-3.6 (m, 1H, CH₂), 3.9-4.0 (m, 1H, CH₂), 4.52 (d, *J* = 12.0 Hz, 1H, CH₂), 4.72 (t, *J* = 3.1 Hz, 1H, CH), 4.81 (d, *J* = 12.0 Hz, 1H, CH₂), 7.3-7.4 (m,

¹Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th Ed; Butterworth-Heinemann: Oxford, 1996.

² J. Montenegro, J. Bergueiro, C. Saa, S. Lopez, *Org. Lett.* **2009**, *11*, 141-144.

5H, 5xCH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 18.8 (CH_2), 25.3 (CH_2), 30.4 (CH_2), 61.9 (CH_2), 68.6 (CH_2), 97.6 (CH), 127.3 (CH), 127.6 (2xCH), 128.2 (2xCH), 138.2 (C) ppm. MS (EI) m/z (%) 192 (M^+ , 1), 91 ($\text{M}^+ - \text{OTHP}$, 100). HMRS (EI) calc for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{Si}$, 192.1150; found, 192.1142.

2-(Prop-2-yn-1-yloxy)tetrahydro-2H-pyran (**1d₁**): Following the general procedure, reaction of prop-2-yn-1-ol (1.00 g, 17.84 mmol) and DHP (2.34 mL, 26.76 mmol) with *p*TSOH (34 mg, 0.178 mmol) in CH_2Cl_2 (20 mL) afforded compound **1d₁** (2.13 g, 85%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 1.5-1.8 (m, 6H, 3x CH_2), 2.38 (s, 1H, CH), 3.5-3.5 (m, 1H, CH_2), 3.8-3.8 (m, 1H, CH_2), 4.2-4.3 (m, 2H, CH_2), 4.77 (t, $J = 3.0$ Hz, 1H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 18.8 (CH_2), 25.2 (CH_2), 30.0 (CH_2), 53.8 (CH_2), 61.8 (CH_2), 73.8 (CH), 79.6 (C), 96.6 (CH) ppm. MS (ESI) m/z (%) 163 ($\text{M}^+ + \text{Na}$, 1). HMRS (ESI) calcd for $\text{C}_8\text{H}_{12}\text{O}_2$, 141.0837; found, 141.0835.

2-((6-Chlorohex-2-yn-1-yl)oxy)tetrahydro-2H-pyran (**1e₁**): Following the general procedure, reaction of 6-chlorohex-2-yn-1-ol (1.00 g, 7.54 mmol) and DHP (988 μL , 11.31 mmol) with *p*TSOH (14 mg, 7.54 $\times 10^{-2}$ mmol) in CH_2Cl_2 (20 mL) afforded compound **1e₁** (71.36 g, 83%) as a colourless oil.

^1H NMR (300 MHz, CDCl_3) δ 1.4-1.9 (m, 6H, 3x CH_2), 1.9-2.0 (m, 2H, CH_2), 2.4-2.4 (m, 2H, CH_2), 3.4-3.5 (m, 1H, CH_2), 3.61 (td, $J = 6.4, 1.2$ Hz, 2H, CH_2), 3.8-3.8 (m, 1H, CH_2), 4.1-4.3 (m, 2H, CH_2), 4.75 (t, $J = 3.0$ Hz, 1H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 16.1 (CH_2), 18.9 (CH_2), 25.2 (CH_2), 30.0 (CH_2), 31.1 (CH_2), 43.5 (CH_2), 54.3 (CH_2), 61.8 (CH_2), 73.8 (C), 84.3 (C), 96.6 (CH) ppm. MS (CI) m/z (%) 215 ($\text{M}^+ - 1$, 2), 115 ($\text{M}^+ - \text{OTHP}$, 55), 85 (OTHP^+ , 99). HMRS (EI) calc for $\text{C}_{11}\text{H}_{17}\text{ClO}_2$, 216.0917; found, 216.0919.

2-(Cyclohexyloxy)tetrahydro-2H-pyran (**1f₁**): Following the general procedure, reaction of cyclohexanol (1.00 g, 9.98 mmol) and DHP (1.31 mL, 14.98 mmol) with *p*TSOH (19 mg, 9.98 $\times 10^{-2}$ mmol) in CH_2Cl_2 (20 mL) afforded compound **1f₁** (1.47 g, 80%) as a colourless oil.

^1H NMR (300 MHz, CDCl_3) δ 0.7-0.9 (m, 2H, CH_2), 1.1-1.4 (m, 6H, 3x CH_2), 1.4-1.5 (m, 4H, 2x CH_2), 1.6-1.7 (m, 2H, CH_2), 1.8-2.0 (m, 2H, CH_2), 3.4-3.4 (m, 1H, CH), 3.5-3.6 (m, 1H, CH_2), 3.8-3.9 (m, 1H, CH_2), 4.6-4.7 (m, 1H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 20.5 (CH_2), 24.8 (CH_2), 25.0 (CH_2), 26.2 (CH_2), 26.3 (CH_2), 31.9 (CH_2), 32.4 (CH_2), 34.3 (CH_2), 63.2 (CH_2), 74.9 (CH), 97.1 (CH) ppm. MS (EI) m/z (%) 184 (M^+ , 6), 101 ($\text{M}^+ - \text{OTHP}$, 34), 83 (OTHP^+ , 20). HMRS (EI) calc for $\text{C}_{11}\text{H}_{20}\text{O}_2$, 184.1463; found, 184.1459.

2-(Hept-4-yn-2-yloxy)tetrahydro-2H-pyran (**1g₁**): Following the general procedure, reaction of hept-4-yn-2-ol (1.00 g, 8.92 mmol) and DHP (1.17 mL, 13.37 mmol) with *p*TSOH (17 mg, 8.91 $\times 10^{-2}$ mmol) in CH_2Cl_2 (20 mL) afforded compound **1g₁** (1.42 g, 81%) as a colourless oil.

^1H NMR (300 MHz, CDCl_3) δ 1.09 (t, $J = 7.5$ Hz, 3H, CH_3), 1.21 (d, $J = 6.2$ Hz, 1.5H, CH_3), 1.28 (d, $J = 6.2$ Hz, 1.5H, CH_3)^d, 1.4-1.9 (m, 6H, 3x CH_2), 2.1-2.6 (m, 4H, 2x CH_2), 3.4-3.5 (m, 1H, CH_2), 3.8-4.0 (m, 1H, CH_2), 3.8-4.0 (m, 1H, CH)^d, 4.7-4.8 (m, 1H, CH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 12.4 (CH_2), 14.2 (CH_3), 18.9 (CH_3), 19.5 (CH_2), 19.9 (CH_2)^d, 21.2 (CH_3)^d, 25.5 (CH_2), 25.5 (CH_2)^d, 26.2 (CH_2), 27.5 (CH_2)^d, 31.0 (CH_2), 31.0 (CH_2)^d, 62.2 (CH_2), 62.7 (CH_2)^d, 71.1 (CH), 71.7 (CH)^d, 76.1 (C), 76.5 (C)^d, 83.2

(C), 96.5 (CH), 97.9 (CH)^d ppm. MS (ESI) m/z (%) 219 ($M^{+}+23$, 100), 197 (M^{+} , 7). HMRS (ESI) calc for $C_{12}H_{20}NaO_2$, 219.1352; found, 219.1356.

2-((3*s*,5*s*,7*s*)-adamanatan-1-yloxy)tetrahydro-2*H*-pyran (**1h₁**): Following the general procedure, reaction of (3*s*,5*s*,7*s*)-adaman-1-ol (1.00 g, 6.57 mmol) and DHP (861 μ L, 9.85 mmol) with *p*TSOH (13 mg, 6.57×10^{-2} mmol) in CH_2Cl_2 (20 mL) afforded compound **1h₁** (1.37 g, 88%) as a light yellow oil.

¹H NMR (300 MHz, $CDCl_3$) δ 1.4-1.5 (m, 4H, 2xCH₂), 1.5-1.6 (m, 7H, CH₂), 1.7-1.8 (m, 7H, CH₂), 2.10 (s, 3H, 3xCH), 3.3-3.5 (m, 1H, CH₂), 3.9-4.0 (m, 1H, CH₂), 4.81 (m, 1H, CH) ppm. ¹³C NMR (75 MHz, $CDCl_3$) δ 20.9 (CH₂), 25.3 (CH₂), 30.5 (3xCH), 32.4 (CH₂), 36.2 (3xCH₂), 42.5 (3xCH₂), 63.3 (CH₂), 73.3 (C), 92.5 (CH) ppm. MS (EI) m/z (%) 236 (M^{+} , 1), 135 (M^{+} -OTHP, 100). HMRS (EI) calc for $C_{15}H_{24}O_2$, 236.1766; found, 236.1757.

2-Phenoxytetrahydro-2*H*-pyran (**1i₁**): Following the general procedure, reaction of phenol (1.00 g, 10.63 mmol) and DHP (1.39 mL, 15.94 mmol) with *p*TSOH (20 mg, 0.106 mmol) in CH_2Cl_2 (20 mL) afforded compound **1i₁** (1.80 g, 95%) as a colourless oil.

¹H NMR (300 MHz, $CDCl_3$) δ 1.5-1.8 (m, 4H, 2xCH₂), 1.8-2.0 (m, 2H, CH₂), 3.6-3.7 (m, 1H, CH₂), 3.9-4.0 (m, 1H, CH₂), 5.45 (t, $J = 3.3$ Hz, 1H, CH), 7.00 (t, $J = 7.9$ Hz, 1H, CH), 7.1-7.1 (m, 2H, 2xCH), 7.2-7.3 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, $CDCl_3$) δ 18.8 (CH₂), 25.2 (CH₂), 30.3 (CH₂), 62.0 (CH₂), 96.3 (CH), 116.4 (2xCH), 121.5 (CH), 129.3 (2xCH), 157.0 (C) ppm. MS (ESI-TOF) m/z (%) 201 ($M^{+}+23$, 3), 158 (100). HMRS (ESI-TOF) calc for $C_{11}H_{14}NaO_2$, 201.0886; found, 201.10885.

2-(4-bromophenoxy)tetrahydro-2*H*-pyran (**1j₁**): Following the general procedure, reaction of 4-bromophenol (1.00 g, 5.78 mmol) and DHP (757 μ L, 8.67 mmol) with *p*TSOH (11 mg, 5.78×10^{-2} mmol) in CH_2Cl_2 (20 mL) afforded compound **1j₁** (1.37 g, 92%) as a colourless oil.

¹H NMR (300 MHz, $CDCl_3$) δ 1.5-1.7 (m, 4H, 2xCH₂), 1.8-1.9 (m, 2H, CH₂), 3.5-3.6 (m, 1H, CH₂), 3.8-3.9 (m, 1H, CH₂), 5.35 (t, $J = 3.2$ Hz, 1H, CH), 6.9-6.9 (m, 2H, 2xCH), 7.3-7.4 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, $CDCl_3$) δ 18.6 (CH₂), 25.1 (CH₂), 30.2 (CH₂), 61.9 (CH₂), 96.4 (CH), 113.8 (C), 118.3 (2xCH), 132.2 (2xCH), 156.1 (C) ppm. MS (EI) m/z (%) 256 (M^{+} , 7), 76 (M^{+} -OTHP-Br, 3). HMRS (EI) calc for $C_{11}H_{13}BrO_2$, 256.0090; found, 256.0085.

7-((Tetrahydro-2*H*-pyran-2-yl)oxy)hepta-1-ol (**1k₁**): Following the general procedure, reaction of heptane-1,7-diol (1.00 g, 7.56 mmol) and DHP (991 μ L, 11.35 mmol) with *p*TSOH (14 mg, 7.56×10^{-2} mmol) in CH_2Cl_2 (20 mL) afforded compound **1k₁** (736 mg, 45%) as a colourless oil.

¹H NMR (300 MHz, $CDCl_3$) δ 1.2-1.4 (m, 6H, 3xCH₂), 1.4-1.8 (m, 10H, 5xCH₂), 1.96 (s, 1H, OH), 3.3-3.4 (m, 1H, CH₂), 3.4-3.5 (m, 1H, CH₂), 3.57 (t, $J = 6.6$ Hz, 2H, CH₂), 3.6-3.7 (m, 1H, CH₂), 3.8-3.9 (m, 1H, CH₂), 4.53 (t, $J = 4.2$ Hz, 1H, CH) ppm. ¹³C NMR (75 MHz, $CDCl_3$) δ 19.8 (CH₂), 25.7 (CH₂), 25.9 (CH₂), 26.4 (CH₂), 29.5 (CH₂), 29.8 (CH₂), 30.9 (CH₂), 32.9 (CH₂), 62.5 (CH₂), 63.0 (CH₂), 67.8 (CH₂), 99.0 (CH) ppm. MS (CI) m/z (%) 217 ($M^{+}+1$, 100), 133 ($M^{+}+1$ -OTHP, 68), 86 (THP⁺, 17). HMRS (CI) calcd for $C_{12}H_{24}O_3$, 217.1804; found, 217.1811.

4-((Tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-ol (**11₁**): Following the general procedure, reaction of but-2-yne-1,4-diol (1.00 g, 11.62 mmol) and DHP (1.52 mL, 17.42 mmol) with *p*TSOH (22 mg, 0.116 mmol) in CH₂Cl₂ (20 mL) afforded compound **11₁** (1.03 g, 52%) as a colourless oil.

¹H NMR (300 MHz, CDCl₃) δ 1.4-1.9 (m, 6H, 3xCH₂), 2.4-2.6 (m, 1H, OH), 3.5-3.6 (m, 1H, CH₂), 3.8-3.9 (m, 1H, CH₂), 4.2-4.4 (m, 4H, 2xCH₂), 4.79 (s, 1H, CH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 18.9 (CH₂), 25.2 (CH₂), 30.1 (CH₂), 50.9 (CH₂), 54.3 (CH₂), 61.9 (CH₂), 81.4 (C), 84.4 (C), 96.8 (CH) ppm. MS (CI) *m/z* (%) 171 (M⁺+1, 53), 85 (THP⁺, 100). HMRS (CI) calcd for C₉H₁₄O₃, 171.1021; found, 171.1022.

1-(Methoxymethoxy)octane (**1a₂**): To a cooled (0 °C) suspension of octan-1-ol (2.00 g, 15.38 mmol) in dry CH₂Cl₂ (35 mL) under argon was added diisopropylethylamine (13 mL, 76.9 mmol), and the mixture was stirred for 10 min. MOMCl (2.1 mL, 18.5 mmol) was added, then the resulting solution was stirred for 48 h at 65 °C. The reaction mixture was cooled (0 °C), quenched with aqueous NaHCO₃ (100 mL, 20%), and extracted with CH₂Cl₂ (3 x 50 mL). The organic phase was dried (Na₂SO₄) and filtered, and the solvent was removed. Chromatography column (SiO₂, 95:5 hexane/AcOEt) of the residue afforded **1a₂** (2.35 g, 75%).

¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, *J* = 6.6 Hz, 3H, CH₃), 1.2-1.4 (m, 10H, 5xCH₂), 1.5-1.6 (m, 2H, CH₂), 3.34 (s, 3H, CH₃), 3.50 (t, *J* = 6.6 Hz, 2H, CH₂), 4.60 (s, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.1 (CH₃), 22.7 (CH₂), 26.2 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 29.8 (CH₂), 31.8 (CH₂), 55.1 (CH₃), 67.9 (CH₂), 96.4 (CH₂) ppm. MS (ESI) *m/z* (%) 197 (M⁺+23, 3), 183 (M⁺-Me+23, 10), 167 (M⁺-OMe, 1). HMRS (ESI) calcd for C₁₀H₂₂NaO₂, 197.1517; found, 197.1518.

1-(1-Ethoxyethoxy)octane (**1a₃**): To a cooled (0 °C) suspension of octan-1-ol (2.00 g, 15.38 mmol) in dry CH₂Cl₂ (35 mL) under argon was added ethyl vinyl ether (8.9 g, 123.04 mmol) dropwise, and the mixture was stirred for 5 min. PPTS (590 mg, 3.1 mmol) was added, then the resulting solution was stirred for 30 min.. Reaction mixture was quenched with aqueous NaHCO₃ (40 mL, 20%), and extracted with diethyl ether (3 x 25 mL). The organic phase was dried (Na₂SO₄) and filtered, and the solvent was removed. Chromatography column (SiO₂, 95:5 hexane/AcOEt) of the residue afforded **1a₃** (2.34 g, 81%).

¹H NMR (300 MHz, CDCl₃) δ 0.7-0.9 (m, 6H, 2xCH₃), 1.18 (t, *J* = 7.0 Hz, 3H, CH₃), 1.2-1.3 (m, 10H, 5xCH₂), 1.54 (t, *J* = 7.0 Hz, 2H, CH₂), 3.3-3.7 (m, 4H, 2xCH₂), 4.65 (c, *J* = 5.4 Hz, 1H, CH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.0 (CH₃), 15.2 (CH₃), 19.8 (CH₃), 22.6 (CH₂), 26.2 (CH₂), 29.2 (CH₂), 29.4 (CH₂), 29.9 (CH₂), 31.8 (CH₂), 60.5 (CH₂), 65.2 (CH₂), 99.5 (CH) ppm. MS (CI) *m/z* (%) 202 (M⁺, 1), 113 (M⁺-OCHCH₃OCH₃, 5), 75 (OCHCH₃OCH₃⁺, 22).73 (100) HMRS (CI) calcd for C₁₂H₂₆O₂, 202.1933; found, 202.1931.

General procedure for the deprotection-protection reaction:

Silane was added to a suspension of Lewis acid (freshly sublimated in case of AlCl₃) in CH₂Cl₂, toluene or CH₃CN at 0 °C. The mixture was stirred for 5 min and then the protected alcohol was added dropwise. After 0.5-2 h reaction was quenched with activated alumina (IV), passed through a sintered glass filter and washed with CH₂Cl₂. Solvents were removed and the crude was purified by column chromatography (SiO₂, 95:5 or 70:30 hexane/AcOEt) to obtain the silylated alcohols **2x_x**.

Dimethyl(octyloxy)(phenyl)silane (**2a₁**):

From **1a₁**:

BF₃·OEt₂ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with BF₃·OEt₂ (3 μL, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 2 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (12 mg, 10%) as a light yellow oil.

InCl₃ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with InCl₃ (5.2 mg, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 2 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (23 mg, 19%) as a light yellow oil.

FeCl₃ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with FeCl₃ (3.8 mg, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 2 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (74 mg, 60%) as a light yellow oil.

Sn(OTf)₂ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with Sn(OTf)₂ (9.7 mg, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 2 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (99 mg, 81%) as a light yellow oil.

EtAlCl₂ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with EtAlCl₂ (2.9 mg, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 8 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (91 mg, 74%) as a light yellow oil.

AlCl₃ (0.025 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with AlCl₃ (1.6 mg, 1.17 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 1 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (101 mg, 82%) as a light yellow oil.

AlCl₃ (0.05 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with AlCl₃ (3.1 mg, 2.33 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 30 min afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (112 mg, 91%) as a light yellow oil.

AlCl₃ (0.1 eq): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with AlCl₃ (6.2 mg, 4.67 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 30 min afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (62 mg, 50%) as a light yellow oil.

AlCl₃ (Toluene): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and dimethylphenylsilane (89 μL, 0.583 mmol) with AlCl₃ (3.1 mg, 2.33 x 10⁻²

mmol) in toluene (2 mL) for 2 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (105 mg, 85%) as a light yellow oil.

From **1a₂**: Following the general procedure, reaction of 1-(methoxymethoxy)octane (**1a₂**) (100 mg, 0.574 mmol) and dimethylphenylsilane (110 μ L, 0.717 mmol) with AlCl₃ (3.8 mg, 2.87×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 1 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (118 mg, 78%) and 1-methoxyoctane (**4a₂**) (12 mg, 15%) and as light yellow oils.

From **1a₃**: Following the general procedure, reaction of 1-(1-ethoxymethoxy)octane (**1a₃**) (100 mg, 0.494 mmol) and dimethylphenylsilane (95 μ L, 0.618 mmol) with AlCl₃ (3.3 mg, 2.47×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 1 h afforded dimethyl(octyloxy)(phenyl)silane (**2a₁**) (89 mg, 68%) and 1-ethoxyoctane (**4a₃**) (20 mg, 25%) and as light yellow oils.

2a₁: ¹H NMR (300 MHz, CDCl₃) δ 0.44 (s, 6H, 2xCH₃), 0.94 (t, J = 7.0 Hz, 3H, CH₃), 1.2-1.4 (m, 10H, 5xCH₂), 1.60 (t, J = 7.0 Hz, 2H, CH₂), 3.65 (t, J = 7.0 Hz, 2H, CH₂), 7.4-7.5 (m, 3H, CH), 7.6-7.7 (m, 2H, CH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.8 (2xCH₃), 14.1 (CH₃), 22.6 (CH₂), 25.8 (CH₂), 29.3 (CH₂), 29.4 (CH₂), 31.8 (CH₂), 32.6 (CH₂), 63.1 (CH₂), 127.8 (2xCH), 129.5 (CH), 133.4 (2xCH), 138.1 (C) ppm. MS (EI) m/z (%) 264 (M⁺, 5), 249 (M⁺-CH₃, 18), 137 (100). HMRS (CI) calc for C₁₆H₂₈OSi, 264.1909; found, 264.1901.

4a₂: ¹H NMR (300 MHz, CDCl₃) δ 0.87 (t, J = 6.9 Hz, 3H, CH₃), 1.2-1.3 (m, 10H, 5xCH₂), 1.5-1.6 (m, 2H, CH₂), 3.18 (s, 3H, CH₃), 3.37 (t, J = 6.9 Hz, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.0 (CH₃), 22.6 (CH₂), 26.3 (CH₂), 29.2 (CH₂), 29.5 (CH₂), 30.0 (CH₂), 31.8 (CH₂), 48.3 (CH₃), 60.7 (CH₂) ppm. MS (CI) m/z (%) 167 (M⁺+23, 2). HMRS (ESI) calcd for C₉H₂₀NaO, 167.1412; found, 167.1412.

4a₃: ¹H NMR (300 MHz, CDCl₃) δ 0.8-1.0 (m, 3H, CH₃), 1.19 (t, J = 7.0 Hz, 3H, CH₃), 1.2-1.4 (m, 10H, 5xCH₂), 1.57 (t, J = 7.0 Hz, 2H, CH₂), 3.40 (t, J = 7.0 Hz, 2H, CH₂), 3.46 (c, J = 7.0 Hz, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 14.6 (CH₃), 15.8 (CH₃), 23.2 (CH₂), 26.9 (CH₂), 29.9 (CH₂), 30.5 (CH₂), 32.2 (CH₂), 32.5 (CH₂), 66.6 (CH₂), 71.4 (CH₂) ppm. MS (CI) m/z (%) 181 (M⁺+23, 2). HMRS (CI) calcd for C₁₀H₂₂O₂, 181.1671; found, 181.1669.

Benzyl dimethyl(octyloxy)silane (**2a₂**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2H-pyran (**1a₁**) (100 mg, 0.467 mmol) and benzyl dimethylsilane (92 μ L, 0.583 mmol) with AlCl₃ (3.1 mg, 2.33×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 30 min afforded benzyl dimethyl(octyloxy)silane (**2a₂**) (116 mg, 89%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.10 (s, 6H, 2xCH₃), 0.91 (t, J = 7.0 Hz, 3H, CH₃), 1.2-1.4 (m, 10H, 5xCH₂), 1.5-1.6 (m, 2H, CH₂), 2.20 (s, 2H, CH₂), 3.58 (t, J = 6.8 Hz, 2H, CH₂), 7.0-7.1 (m, 3H, 3xCH), 7.2-7.3 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -7.1 (2xCH₃), 9.4 (CH₃), 18.0 (CH₂), 21.1 (CH₂), 22.0 (CH₂), 24.6 (CH₂), 24.7 (CH₂), 27.2 (CH₂), 28.1 (CH₂), 58.4 (CH₂), 119.4 (CH), 123.5 (2xCH), 123.7 (2xCH), 134.5 (C) ppm. MS (EI) m/z (%) 278 (M⁺, 8), 263 (M⁺-CH₃, 3), 187 (M⁺-Bn, 100). HMRS (EI) calc for C₁₇H₃₀OSi, 278.2066; found, 278.2059.

Ethoxy dimethyl(octyloxy)silane (**2a₃**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2H-pyran (**1a₁**) (100 mg, 0.467 mmol) and ethoxy dimethylsilane (80 μ L, 0.583

mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 1 h afforded ethoxydimethyl(octyloxy)silane (**2a₃**) (87 mg, 80%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.98 (s, 6H, $2\times\text{CH}_3$), 0.85 (t, $J = 7.0$ Hz, 3H, CH_3), 1.19 (t, $J = 7.0$ Hz, 3H, CH_3), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.5-1.5 (m, 2H, CH_2), 3.64 (t, $J = 6.7$ Hz, 2H, CH_2), 3.73 (c, $J = 7.0$ Hz, 2H, CH_2) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -3.2 ($2\times\text{CH}_3$), 14.0 (CH_3), 18.3 (CH_3), 22.6 (CH_2), 25.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 32.6 (CH_2), 58.0 (CH_2), 62.6 (CH_2) ppm. MS (EI) m/z (%) 232 (M^+ , 1), 217 (M^+-CH_3 , 100). HMRS (EI) calc for $\text{C}_{12}\text{H}_{28}\text{O}_2\text{Si}$, 232.1859; found, 232.1855.

Tert-butyl(dimethyl)(octyloxy)silane (**2a₄**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and *tert*-butyl(dimethyl)silane (97 μL , 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 30 min afforded *tert*-butyl(dimethyl)(octyloxy)silane (**2a₄**) (95 mg, 83%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.06 (s, 6H, $2\times\text{CH}_3$), 0.87 (t, $J = 7.1$ Hz, 3H, CH_3), 0.87 (s, 9H, $3\times\text{CH}_3$), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.4-1.6 (m, 2H, CH_2), 3.57 (t, $J = 6.6$ Hz, 2H, CH_2) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -5.3 ($2\times\text{CH}_3$), 14.1 (CH_3), 18.4 (C), 22.6 (CH_2), 25.8 (CH_2), 26.0 ($3\times\text{CH}_3$), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 32.9 (CH_2), 63.3 (CH_2) ppm. MS (EI) m/z (%) 244 (M^+ , 1), 229 (M^+-CH_3 , 1), 187 (M^+-tBu , 100), 129 ($\text{M}^+-\text{SiMe}_2\text{tBu}$, 3), 115 ($\text{SiMe}_2\text{tBu}^+$, 4). HMRS (EI) calc for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{Si}$, 244.2222; found, 24.2215.

(Octyloxy)triphenylsilane (**2a₅**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and triphenylsilane (152 mg, 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 30 min afforded (octyloxy)triphenylsilane (**2a₅**) (143 mg, 79%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.95 (t, $J = 7.0$ Hz 3H, CH_3), 1.3-1.5 (m, 10H, $5\times\text{CH}_2$), 1.6-1.7 (m, 2H, CH_2), 3.88 (t, $J = 6.6$ Hz, 2H, CH_2), 7.3-7.6 (m, 9H, $9\times\text{CH}$), 7.6-7.7 (m, 6H, $6\times\text{CH}$) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 14.2 (CH_3), 22.8 (CH_2), 25.9 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 31.9 (CH_2), 32.6 (CH_2), 64.1 (CH_2), 128.1 ($6\times\text{CH}$), 130.0 ($3\times\text{CH}$), 133.4 ($3\times\text{C}$), 135.9 ($6\times\text{CH}$) ppm. MS (EI) m/z (%) 388 (M^+ , 1), 311 (M^+-Ph , 42), 259 (SiPh_3 , 90), 199 (100). HMRS (EI) calc for $\text{C}_{26}\text{H}_{32}\text{Osi}$, 388.2222; found, 388.2212.

Triethyl(octyloxy)silane (**2a₆**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and triethylsilane (93 μL , 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 30 min afforded triethyl(octyloxy)silane (**2a₆**) (98 mg, 86%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.57 (c, $J = 7.9$ Hz, 6H, $3\times\text{CH}_2$), 0.85 (t, $J = 7.0$ Hz, 3H, CH_3), 0.93 (t, $J = 7.9$ Hz, 9H, $3\times\text{CH}_3$), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.5-1.5 (m, 2H, CH_2), 3.56 (t, $J = 6.8$ Hz, 2H, CH_2), ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 4.4 ($3\times\text{CH}_2$), 6.8 ($3\times\text{CH}_3$), 14.1 (CH_3), 22.6 (CH_2), 25.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 32.9 (CH_2), 64.0 (CH_2) ppm. MS (EI) m/z (%) 245 (M^++1 , 10), 215 ($\text{M}^+-\text{CH}_2\text{CH}_3$, 36), 69 (100). HMRS (EI) calc for $\text{C}_{14}\text{H}_{32}\text{Osi}$, 244.2222; found, 244.2218.

Triisopropyl(octyloxy)silane (**2a₇**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2*H*-pyran (**1a₁**) (100 mg, 0.467 mmol) and triisopropylsilane (120 μL , 0.583 mmol)

with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 1 h afforded triisopropyl(octyloxy)silane (**2a₇**) (124 mg, 93%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 7.0$ Hz, 3H, CH_3), 1.0-1.1 (m, 21H, $3\times\text{CH}$, $6\times\text{CH}_3$), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.5-1.6 (m, 2H, CH_2), 3.65 (t, $J = 6.7$ Hz, 2H, CH_2) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 12.0 ($3\times\text{CH}$), 14.1 (CH_3), 18.0 ($6\times\text{CH}_3$), 22.7 (CH_2), 25.8 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 33.1 (CH_2), 63.5 (CH_2) ppm. MS (EI) m/z (%) 286 (M^+ , 1), 207 (100). HMRS (EI) calc for $\text{C}_{17}\text{H}_{38}\text{OSi}$, 286.2692; found, 286.2685.

Triethyl octyl orthosilicate (**2a₈**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2H-pyran (**1a₁**) (100 mg, 0.467 mmol) and triethylsilane (108 μL , 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 1 h afforded triethyl octyl orthosilicate (**2a₈**) (106 mg, 78%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.85 (t, $J = 7.0$ Hz, 3H, CH_3), 1.21 (t, $J = 7.0$ Hz, 9H, $3\times\text{CH}_3$), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.5-1.6 (m, 2H, CH_2), 3.74 (t, $J = 6.7$ Hz, 2H, CH_2), 3.82 (q, $J = 7.0$ Hz, 6H, $3\times\text{CH}_2$) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 14.0 (CH_3), 18.0 ($3\times\text{CH}_3$), 22.6 (CH_2), 25.6 (CH_2), 29.2 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 32.3 (CH_2), 59.1 ($3\times\text{CH}_2$), 63.5 (CH_2) ppm. MS (CI) m/z (%) 293 ($\text{M}^+ + 1$, 16), 209 (100). HMRS (CI) calc for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{Si}$, 292.2070; found, 292.2061.

Di-*tert*-butyl(methyl)(octyloxy)silane (**2a₉**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2H-pyran (**1a₁**) (100 mg, 0.467 mmol) and di-*tert*-butyl(methyl)silane (122 μL , 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 1 h afforded di-*tert*-butyl(methyl)(octyloxy)silane (**2a₉**) (107 mg, 80%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.02 (s, 3H, CH_3), 0.85 (t, $J = 7.0$ Hz, 3H, CH_3), 0.94 (s, 18H, $6\times\text{CH}_3$), 1.2-1.3 (m, 10H, $5\times\text{CH}_2$), 1.4-1.5 (m, 2H, CH_2), 3.63 (t, $J = 6.5$ Hz, 2H, CH_2) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -9.4 (CH_3), 14.1 (CH_3), 20.7 ($2\times\text{C}$), 22.7 (CH_2), 25.8 (CH_2), 27.7 ($6\times\text{CH}_3$), 29.3 (CH_2), 29.4 (CH_2), 31.8 (CH_2), 33.1 (CH_2), 64.3 (CH_2) ppm. MS (EI) m/z (%) 286 (M^+ , 1), 229 ($\text{M}^+ - ^i\text{Bu}$, 5), 85 (100). HMRS (EI) calc for $\text{C}_{14}\text{H}_{27}\text{O}_3\text{Si}$, 286.2692; found, 286.2687.

Tri-*tert*-butyl(octyloxy)silane (**2a₁₀**): Following the general procedure, reaction of 2-(octyloxy)tetrahydro-2H-pyran (**1a₁**) (100 mg, 0.467 mmol) and tri-*tert*-butylsilane (117 mg, 0.583 mmol) with AlCl_3 (3.1 mg, 2.33×10^{-2} mmol) in CH_2Cl_2 (2 mL) for 1 h afforded tri-*tert*-butyl(octyloxy)silane (**2a₁₀**) (121 mg, 79%) as a light yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 1.08 (s, 30H, $10\times\text{CH}_3$), 1.5-1.6 (m, 10H, $5\times\text{CH}_2$), 1.7-1.9 (m, 2H, CH_2), 3.88 (t, $J = 6.0$ Hz, 2H, CH_2) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 23.1 ($3\times\text{C}$), 23.5 (CH_2), 29.6 (CH_3), 30.0 ($9\times\text{CH}_3$), 32.2 (CH_2), 32.3 (CH_2), 32.7 (CH_2), 34.7 (CH_2), 44.9 (CH_2), 64.3 (CH_2) ppm. MS (EI) m/z (%) 328 (M^+ , 1), 207 (100). HMRS (EI) calc for $\text{C}_{20}\text{H}_{44}\text{OSi}$, 328.3161; found, 328.3158.

(*E*)-Dimethyl(pent-2-en-4-yn-1-yloxy)(phenyl)silane (**2b₁**): Following the general procedure, reaction of (*E*)-2-(pent-2-en-4-yn-1-yloxy)tetrahydro-2H-pyran (**1b₁**) (100 mg, 0.602 mmol) and dimethyl(phenyl)silane (115 μL , 0.752 mmol) with AlCl_3 (4.0 mg, 3.01×10^{-2} mmol) in CH_2Cl_2 (2 mL)

for 30 min afforded (*E*)-dimethyl(pent-2-en-4-yn-1-yloxy)(phenyl)silane (**2b₁**) (117 mg, 90%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.45 (s, 6H, 2xCH₃), 2.9-2.9 (m, 1H, CH), 4.2-4.3 (m, 2H, CH₂), 5.78 (dc, *J* = 2.1, 15.8 Hz, 1H, CH), 6.30 (dt, *J* = 4.4, 15.8 Hz, 1H, CH), 7.4-7.5 (m, 3H, CH), 7.6-7.7 (m, 2H, CH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.6 (2xCH₃), 62.8 (CH₂), 77.8 (C), 82.1 (CH), 108.5 (CH), 128.2 (2xCH), 130.0 (CH), 133.6 (2xCH), 137.4 (C), 143.9 (CH) ppm. MS (CI) *m/z* (%) 216 (M⁺+1, 3), 201 (M⁺-CH₃, 38), 135 (100). HMRS (CI) calcd for C₁₃H₁₆OSi, 216.0970; found, 216.0968.

(Benzyloxy)dimethyl(phenyl)silane (**2c₁**): Following the general procedure, reaction of 2-(benzyloxy)tetrahydro-2*H*-pyran (**1c₁**) (100 mg, 0.520 mmol) and dimethyl(phenyl)silane (100 μL, 0.650 mmol) with AlCl₃ (4.6 mg, 2.60 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 30 min afforded (benzyloxy)dimethyl(phenyl)silane (**2c₁**) (112 mg, 89%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.52 (s, 6H, 2xCH₃), 4.81 (s, 2H, CH₂), 7.3-7.5 (m, 8H, 8xCH), 7.7-7.8 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.2 (2xCH₃), 65.5 (CH₂), 127.0 (2xCH), 127.6 (CH), 128.4 (2xCH), 128.7 (2xCH), 130.1 (CH), 134.0 (2xCH), 138.0 (C), 141.2 (C) ppm. MS (EI) *m/z* (%) 242 (M⁺, 1), 227 (M⁺-Me, 52), 212 (M⁺-2xMe, 1), 165 (M⁺-Ph, 18), 107 (M⁺-SiMe₂Ph, 1). HMRS (EI) calc for C₁₅H₁₈OSi, 242.1127; found, 242.1121.

Dimethyl(phenyl)(prop-2-yn-1-yloxy)silane (**2d₁**): Following the general procedure, reaction of 2-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (**1d₁**) (100 mg, 0.713 mmol) and dimethyl(phenyl)silane (137 μL, 0.892 mmol) with AlCl₃ (4.7 mg, 3.57 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 30 min afforded dimethyl(phenyl)(prop-2-yn-1-yloxy)silane (**2d₁**) (120 mg, 88%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.45 (s, 6H, 2xCH₃), 2.39 (t, *J* = 2.4 Hz, 1H, CH), 4.26 (d, *J* = 2.4 Hz, 2H, CH₂), 7.5-7.5 (m, 3H, 3xCH), 7.6-7.6 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.5 (2xCH₃), 51.4 (CH₂), 73.4 (C), 82.1 (CH), 128.1 (2xCH), 130.0 (CH), 133.7 (2xCH), 137.0 (C) ppm. MS (ESI-TOF) *m/z* (%) 191 (M⁺+1, 14), 173 (6), 135 (5). HMRS (ESI-TOF) calcd for C₁₁H₁₅Osi, 191.0887; found, 191.0882.

((6-Chlorohex-2-yn-1-yl)oxy)dimethyl(phenyl)silane (**2e₁**): Following the general procedure, reaction of 2-((6-chlorohex-2-yn-1-yl)oxy)tetrahydro-2*H*-pyran (**1e₁**) (100 mg, 0.462 mmol) and dimethyl(phenyl)silane (88 μL, 0.577 mmol) with AlCl₃ (3.1 mg, 2.31 x 10⁻² mmol) in CH₂Cl₂ (2 mL) for 30 min afforded ((6-chlorohex-2-yn-1-yl)oxy)dimethyl(phenyl)silane (**2e₁**) (105 mg, 85%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.40 (s, 6H, 2xCH₃), 1.88 (q, *J* = 6.5 Hz, 2H, CH₂), 2.34 (tt, *J* = 6.8, 2.1 Hz, 2H, CH₂), 3.57 (t, *J* = 6.4 Hz, 2H, CH₂), 4.24 (t, *J* = 2.1 Hz, 2H, CH₂), 7.3-7.4 (m, 3H, 3xCH), 7.5-7.6 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.7 (2xCH₃), 16.2 (CH₂), 31.2 (CH₂), 43.6 (CH₂), 51.6 (CH₂), 79.2 (C), 83.7 (C), 127.8 (2xCH), 129.7 (CH), 133.5 (2xCH), 137.1 (C) ppm. MS (EI) *m/z* (%) 265 (M⁺-1, 6), 251 (M⁺-Me, 18), 237 (M⁺-2xMe, 15), 189 (M⁺-Ph, 100), 115 (M⁺-SiMe₂Ph, 14). HMRS (EI) calc for C₁₃H₁₇ClOSi, 266.0894; found, 266.0897.

(Cyclohexyloxy)dimethyl(phenyl)silane (**2f₁**): Following the general procedure, reaction of 2-(cyclohexyloxy)tetrahydro-2*H*-pyran (**1f₁**) (100 mg, 0.543 mmol) and dimethyl(phenyl)silane (166 μ L, 1.085 mmol) with AlCl₃ (3.6 mg, 2.71×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 30 min afforded (cyclohexyloxy)dimethyl(phenyl)silane (**2f₁**) (102 mg, 80%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.40 (s, 6H, 2xCH₃), 1.1-1.5 (m, 6H, 3xCH₂), 1.6-1.9 (m, 4H, 2xCH₂), 3.6-3.7 (m, 1H, CH), 7.3-7.5 (m, 3H, 3xCH), 7.6-7.7 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -0.7 (2xCH₃), 24.6 (2xCH₂), 25.8 (CH₂), 36.1 (2xCH₂), 71.6 (CH), 128.0 (2xCH), 129.6 (CH), 133.7 (2xCH), 139.1 (C) ppm. MS (CI) *m/z* (%) 235 (M⁺+1, 12), 219 (M⁺-Me, 48), 157 (M⁺-Ph, 23). HMRS (CI) calc for C₁₄H₂₂OSi, 235.1518; found, 235.1517.

(Hept-4-yn-2-yloxy)dimethyl(phenyl)silane (**2g₁**): Following the general procedure, reaction of 2-(hept-4-yn-2-yloxy)tetrahydro-2*H*-pyran (**1g₁**) (100 mg, 0.510 mmol) and dimethyl(phenyl)silane (98 μ L, 0.637 mmol) with AlCl₃ (3.4 mg, 2.55×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 30 min afforded (hept-4-yn-2-yloxy)dimethyl(phenyl)silane (**2g₁**) (102 mg, 81%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.40 (s, 6H, 2xCH₃), 1.10 (t, *J* = 7.4 Hz, 3H, CH₃), 1.20 (d, *J* = 6.1 Hz, 3H, CH₃), 2.1-2.4 (m, 4H, 2xCH₂), 3.8-4.0 (m, 1H, CH), 7.3-7.4 (m, 3H, 3xArCH), 7.6-7.7 (m, 2H, 2xArCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.1 (Si-CH₃), -1.0 (Si-CH₃), 12.5 (CH₂), 14.3 (CH₃), 23.2 (CH₃), 29.6 (CH₂), 68.4 (CH), 83.3 (2xC), 127.9 (2xCH), 129.6 (CH), 133.6 (2xCH), 138.3 (C) ppm. MS (ESI) *m/z* (%) 269 (M⁺+23, 25), 271 (M⁺-OSiMe₂Ph+23, 100). HMRS (ESI) calc for C₁₅H₂₂NaOSi, 269.1332; found, 269.1329.

((3*s*,5*s*,7*s*)-Adamantan-1-yloxy)dimethyl(phenyl)silane (**2h₁**): Following the general procedure, reaction of 2-((3*s*,5*s*,7*s*)-adamantan-1-yloxy)tetrahydro-2*H*-pyran (**1h₁**) (100 mg, 0.423 mmol) and dimethyl(phenyl)silane (130 μ L, 0.846 mmol) with AlCl₃ (2.8 mg, 2.12×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 30 min afforded ((3*s*,5*s*,7*s*)-adamantan-1-yloxy)dimethyl(phenyl)silane (**2h₁**) (97 mg, 80%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.39 (s, 6H, 2xCH₃), 1.5-1.6 (m, 6H, 3xCH₂), 1.7-1.8 (m, 6H, 3xCH₂), 2.06 (s, 3H, 3xCH), 7.3-7.4 (m, 3H, 3xCH), 7.5-7.7 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 1.8 (2xCH₃), 30.9 (3xCH), 36.2 (3xCH₂), 46.1 (3xCH₂), 72.0 (C), 127.6 (2xCH), 129.0 (CH), 133.3 (2xCH), 140.8 (C) ppm. MS (EI) *m/z* (%) 286 (M⁺, 10), 271 (M⁺-Me, 100), 151 (M⁺-SiMe₂Ph, 33), 135 (M⁺-OSiMe₂Ph, 44). HMRS (EI) calc for C₁₈H₂₆OSi, 286.1753; found, 286.1748.

Dimethyl(phenoxy)(phenyl)silane (**2i₁**): Following the general procedure, reaction of 2-phenoxytetrahydro-2*H*-pyran (**1i₁**) (100 mg, 0.561 mmol) and dimethyl(phenyl)silane (108 μ L, 0.701 mmol) with AlCl₃ (3.7 mg, 2.81×10^{-2} mmol) in CH₂Cl₂ (2 mL) for 30 min afforded dimethyl(phenoxy)(phenyl)silane (**2i₁**) (124 mg, 97%) as a light yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.60 (s, 6H, 2xCH₃), 6.9-6.9 (m, 2H, 2xCH), 7.0-7.0 (m, 1H, CH), 7.2-7.3 (m, 2H, 2xCH), 7.4-7.5 (m, 3H, 3xCH), 7.7-7.8 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -0.4 (2xCH₃), 120.7 (2xCH), 122.2 (CH), 128.7 (2xCH), 130.1 (2xCH), 130.6 (CH), 134.2 (2xCH),

137.9 (C), 155.8 (C) ppm. MS (EI) m/z (%) 228 (M^+ , 46), 213 (M^+ -Me, 100), 151 (M^+ -Ph, 3), 77 (M^+ -OSiMe₂Ph, 5). HMRS (EI) calc for C₁₄H₁₆OSi, 228.0970; found, 228.0962.

(4-Bromophenoxy)dimethyl(phenyl)silane (**2j₁**): Following the general procedure, reaction of 2-(4-bromophenoxy)tetrahydro-2*H*-pyran (**1j₁**) (100 mg, 0.389 mmol) and dimethyl(phenyl)silane (75 μ L, 0.486 mmol) with AlCl₃ (2.6 mg, 1.95 $\times 10^{-2}$ mmol) in CH₂Cl₂ (2 mL) for 30 min afforded (4-bromophenoxy)dimethyl(phenyl)silane (**2j₁**) (97 mg, 81%) as a light yellow oil.

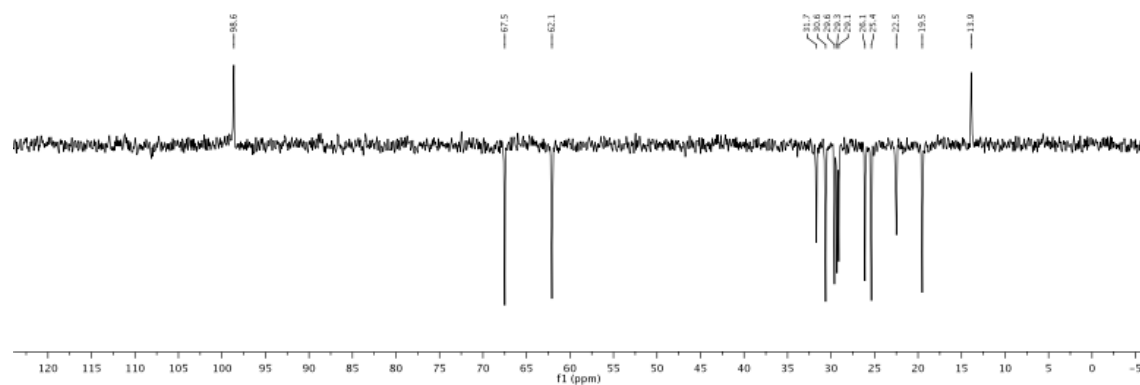
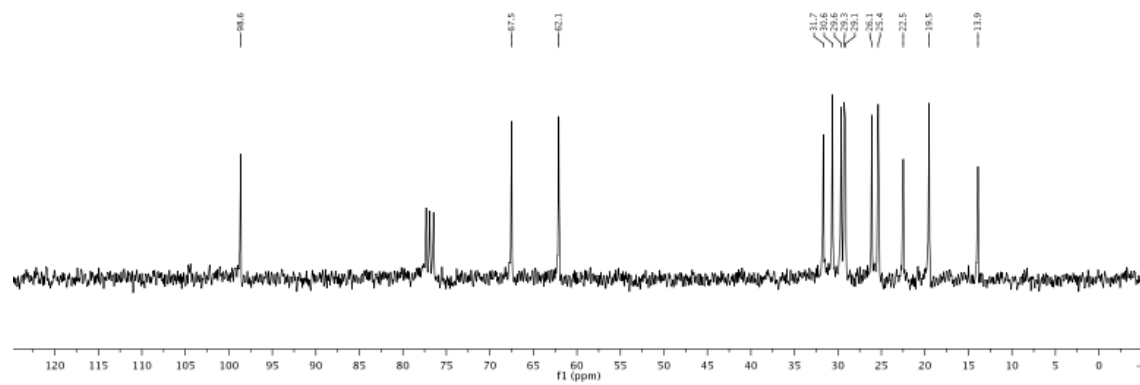
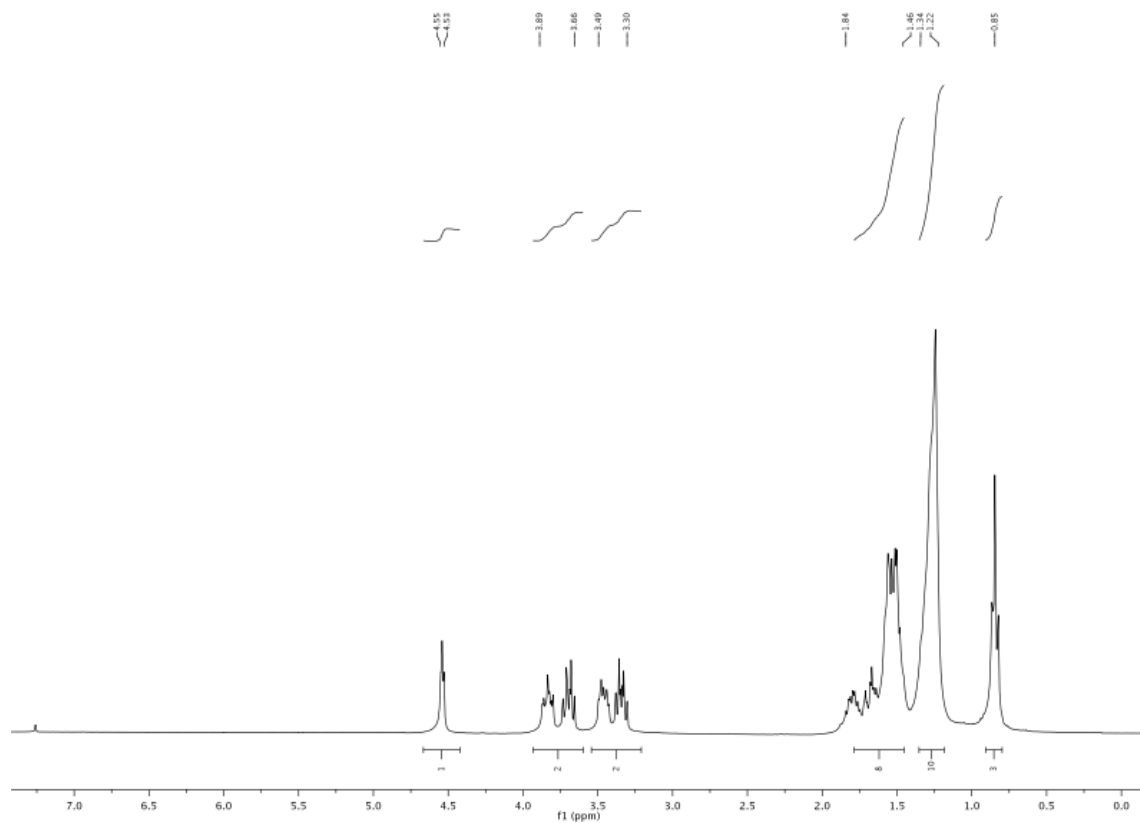
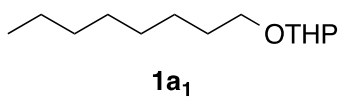
¹H NMR (300 MHz, CDCl₃) δ 0.50 (s, 6H, 2xCH₃), 6.6-6.7 (m, 2H, 2xCH), 7.2-7.3 (m, 2H, 2xCH), 7.3-7.4 (m, 3H, 3xCH), 7.6-7.6 (m, 2H, 2xCH) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.3 (2xCH₃), 113.9 (C), 121.8 (2xCH), 128.0 (2xCH), 130.1 (CH), 132.3 (2xCH), 133.4 (2xCH), 136.6 (C), 154.2 (C) ppm. MS (EI) m/z (%) 306 (M^+ , 73), 228 (M^+ -Br, 5), 213 (M^+ -Me-Ph, 14), 135 (M^+ -Me-Ph-Br, 58). HMRS (EI) calc for C₁₄H₁₅BrOSi, 306.0073; found, 306.0067.

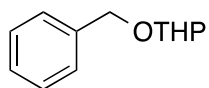
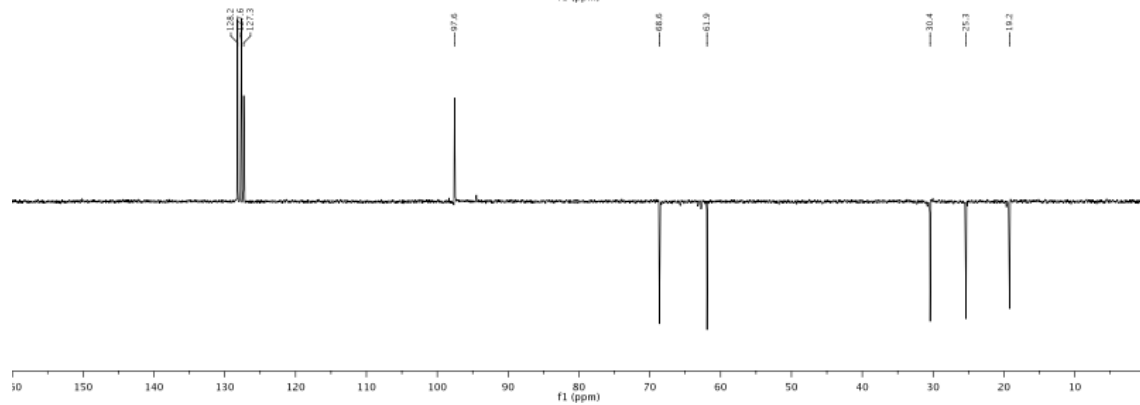
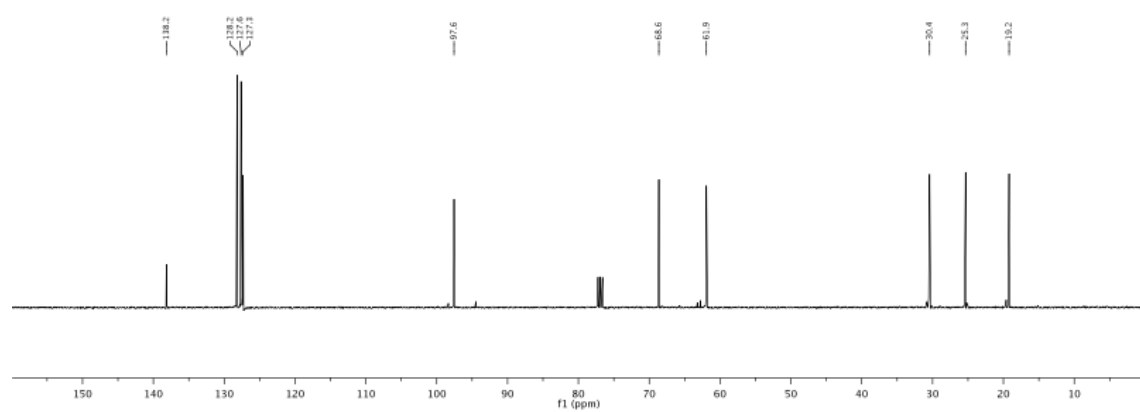
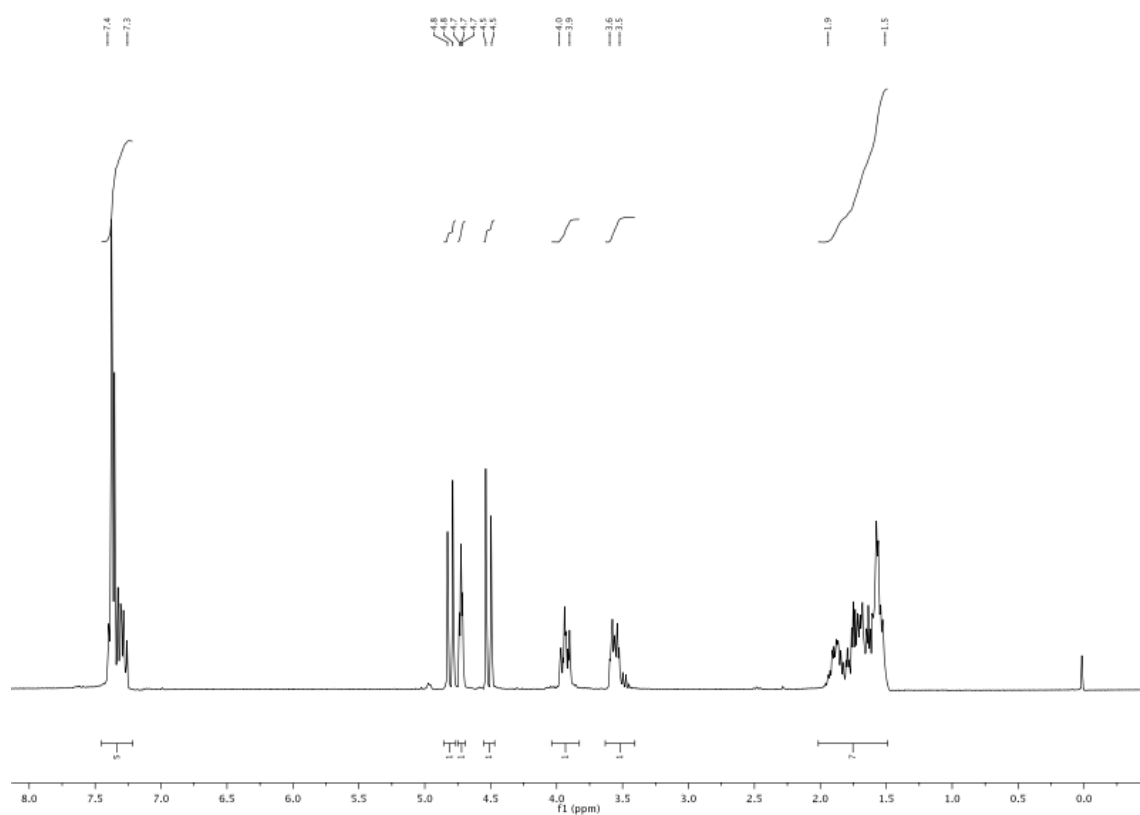
7-((Triisopropylsilyl)oxy)heptan-1-ol (**2k₆**): Following the general procedure, reaction of 7-((tetrahydro-2*H*-pyran-2-yl)oxy)heptan-1-ol (**1k₁**) (100 mg, 0.462 mmol) and triisopropylsilane (118 μ L, 0.578 mmol) with AlCl₃ (3.1 mg, 2.31 $\times 10^{-2}$ mmol) in toluene (2 mL) for 2 h afforded 7-((triisopropylsilyl)oxy)heptan-1-ol (**2k₆**) (77 mg, 58%) as a light yellow oil.

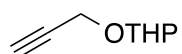
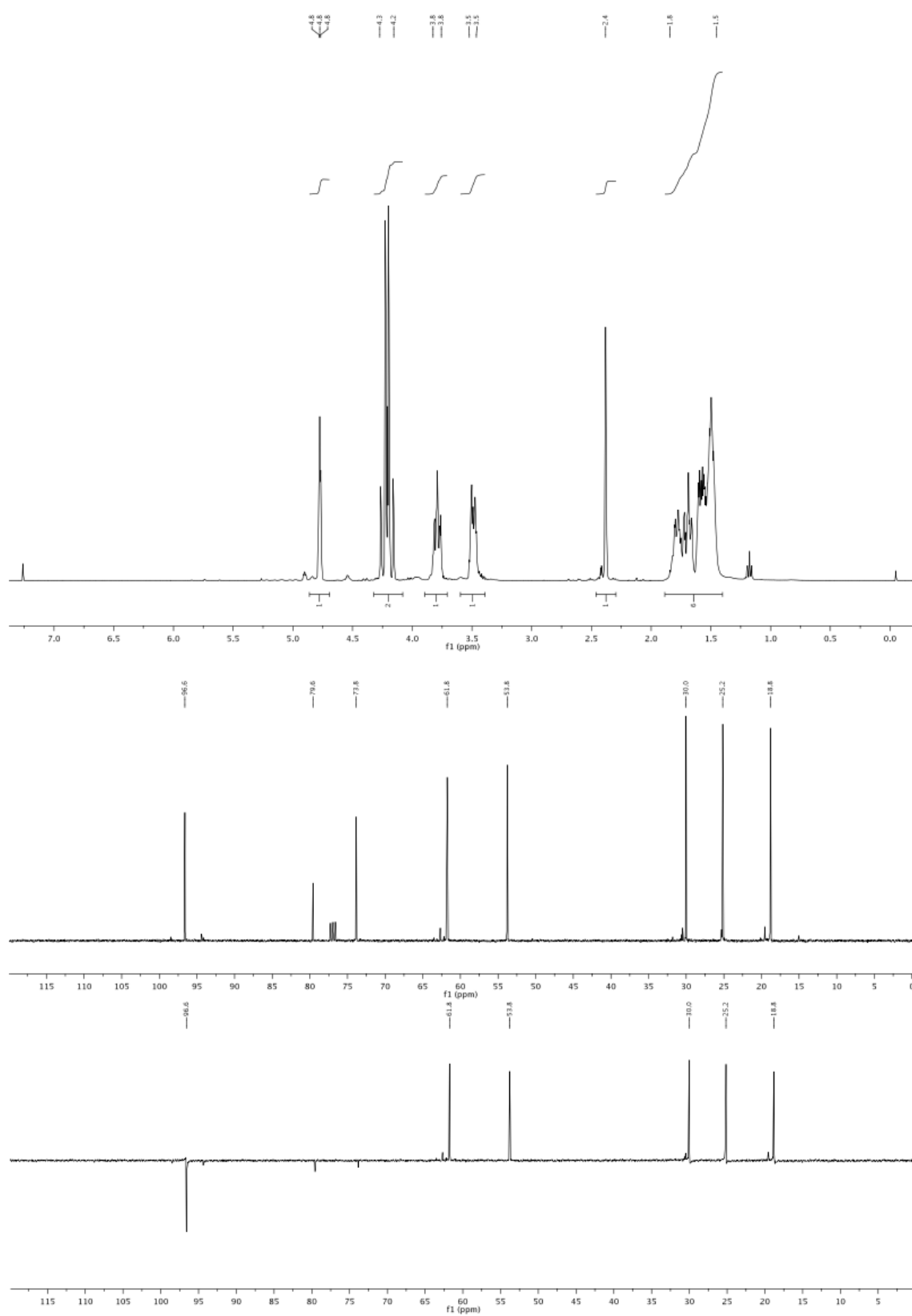
¹H NMR (300 MHz, CDCl₃) δ 1.0-1.1 (m, 21H, 3xCH + 6xCH₃), 1.3-1.4 (m, 6H, 3xCH₂), 1.5-1.6 (m, 4H, 2xCH₂), 3.61 (t, J = 6.7 Hz, 2H, CH₂), 3.64 (t, J = 6.5 Hz, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 12.0 (3xCH), 18.0 (6xCH₃), 25.7 (CH₂), 25.8 (CH₂), 29.2 (CH₂), 32.7 (CH₂), 32.9 (CH₂), 63.0 (CH₂), 63.4 (CH₂) ppm. MS (ESI) m/z (%) 311 (M^+ +23, 1), 230 (M^+ -3xCH₃, 100). HMRS (ESI) calcd for C₁₆H₃₆NaO₂Si, 311.2382; found, 311.2379.

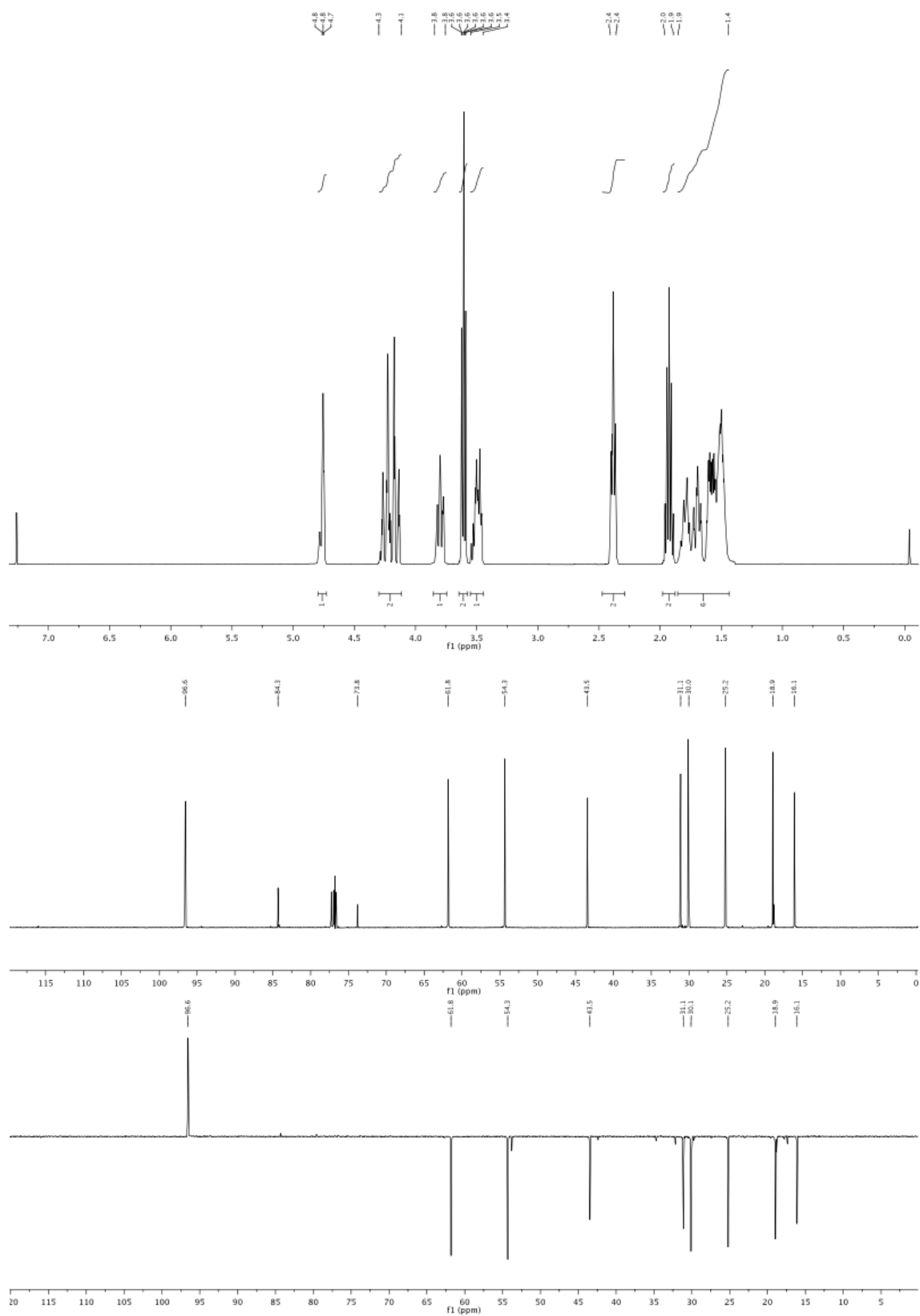
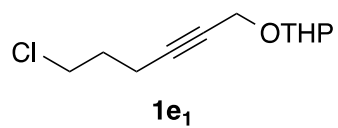
4-((Triisopropylsilyl)oxy)but-2-yn-1-ol (**2l₆**): Following the general procedure, reaction of 4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-2-yn-1-ol (**1l₁**) (100 mg, 0.588 mmol) and triisopropylsilane (151 μ L, 0.734 mmol) with AlCl₃ (3.9 mg, 2.94 $\times 10^{-2}$ mmol) in Toluene (2 mL) for 2 h afforded 4-((triisopropylsilyl)oxy)but-2-yn-ol (**2l₆**) (100 mg, 70%) as a light yellow oil.

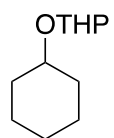
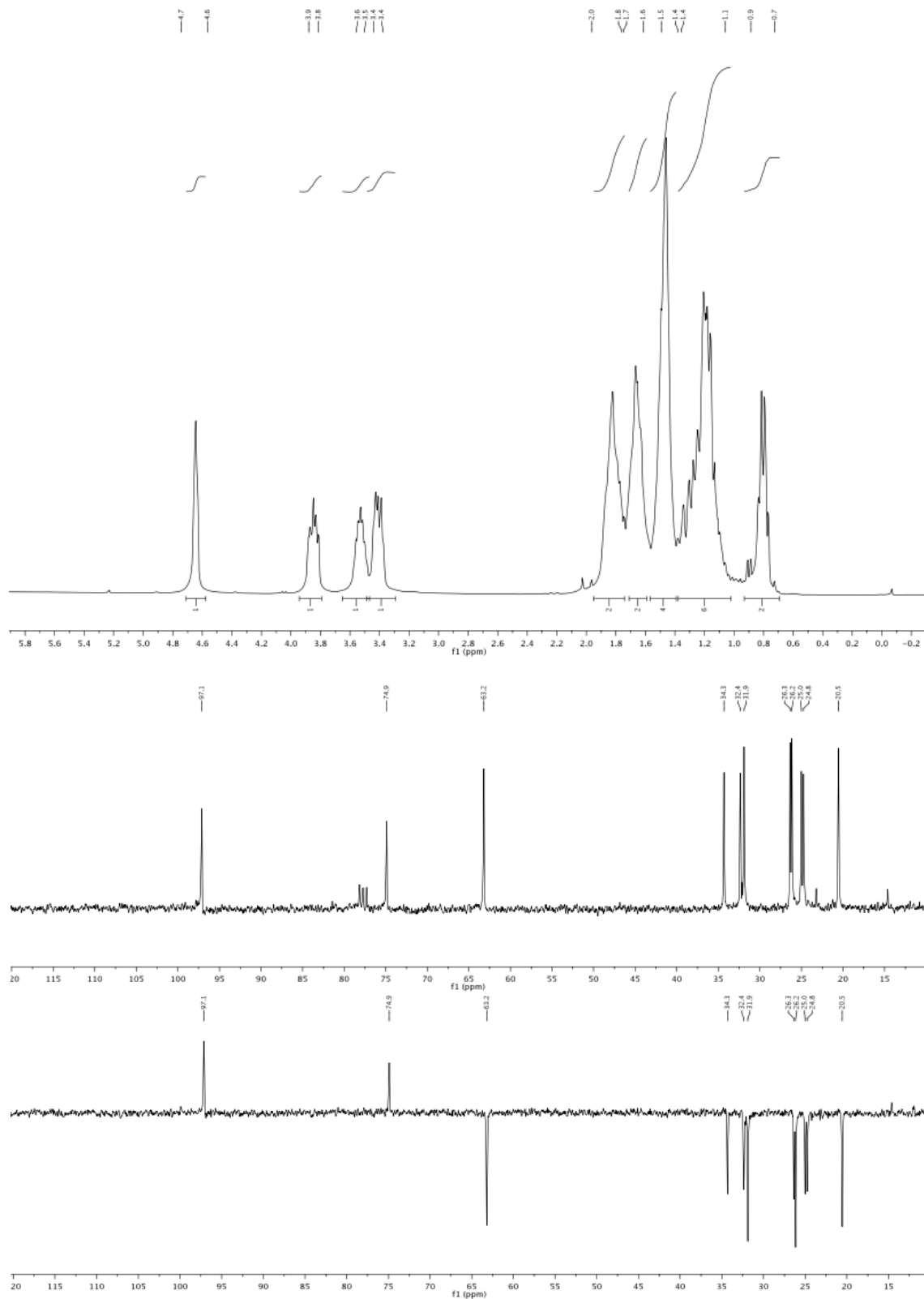
¹H NMR (300 MHz, CDCl₃) δ 1.0-1.2 (m, 21H, 3xCH + 6xCH₃), 4.30 (s, 2H, CH₂), 4.42 (t, J = 1.9 Hz, 2H, CH₂) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 12.2 (3xCH), 18.1 (6xCH₃), 51.5 (CH₂), 52.2 (CH₂), 82.9 (C), 84.9 (C) ppm. MS (ESI) m/z (%) 256 (M^+ +23, 81), 251 (M^+ -Me+23, 6), 237 (M^+ -Me₂+23, 4). HMRS (ESI) calcd for C₁₃H₂₆NaO₂Si, 256.1591; found, 256.1594.

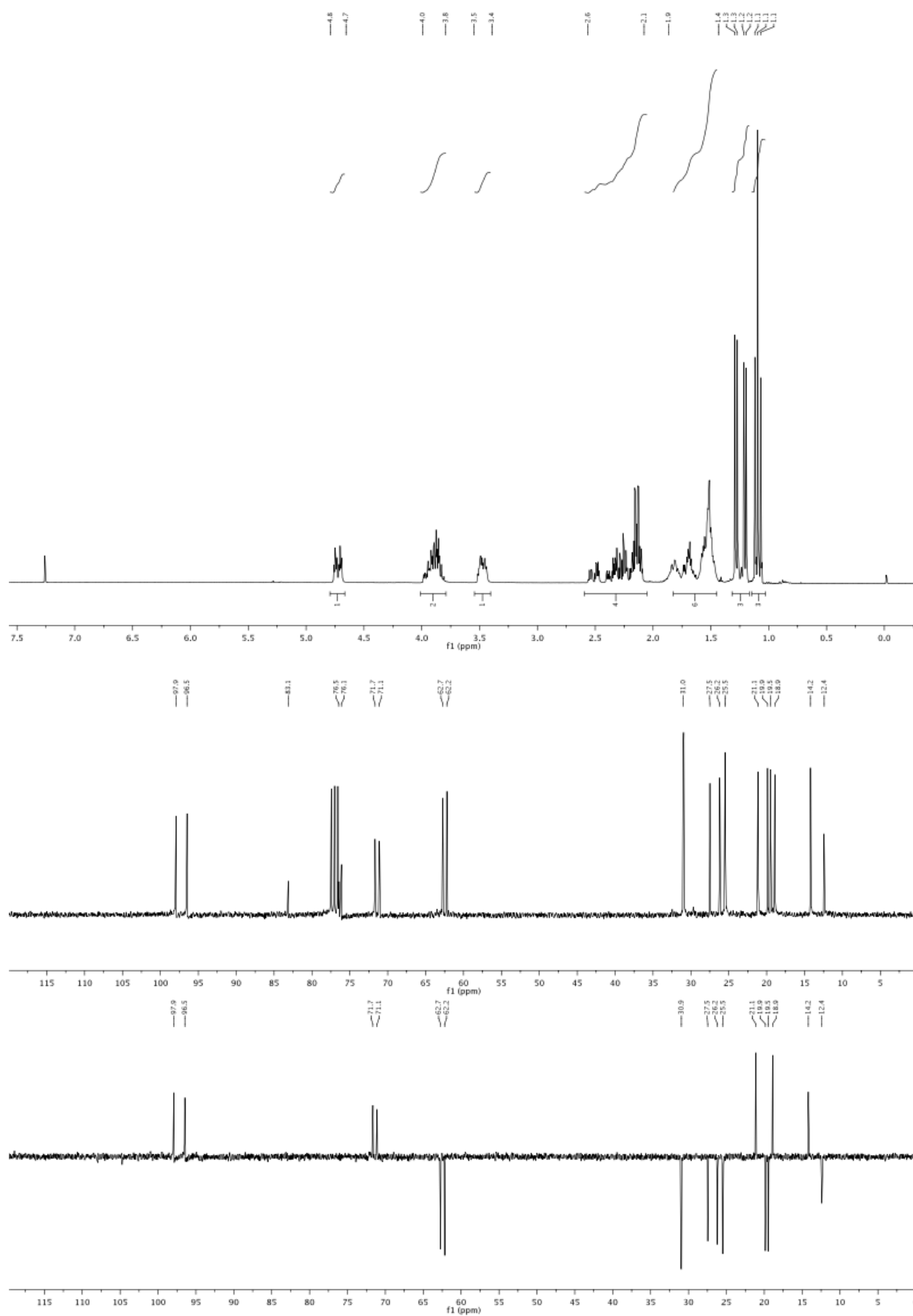
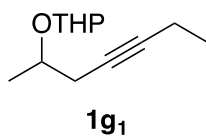


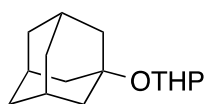
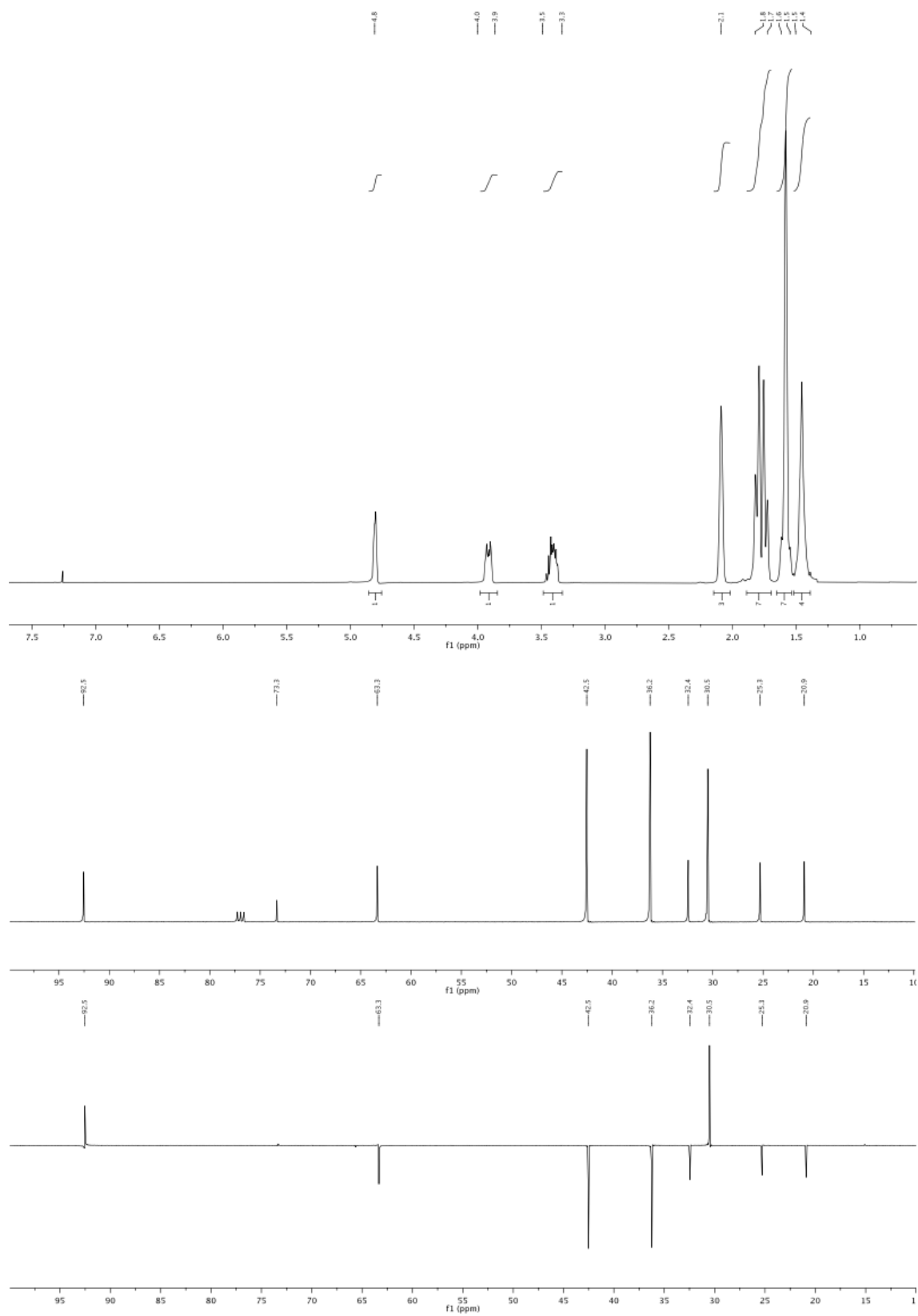
**1c₁**

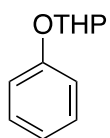
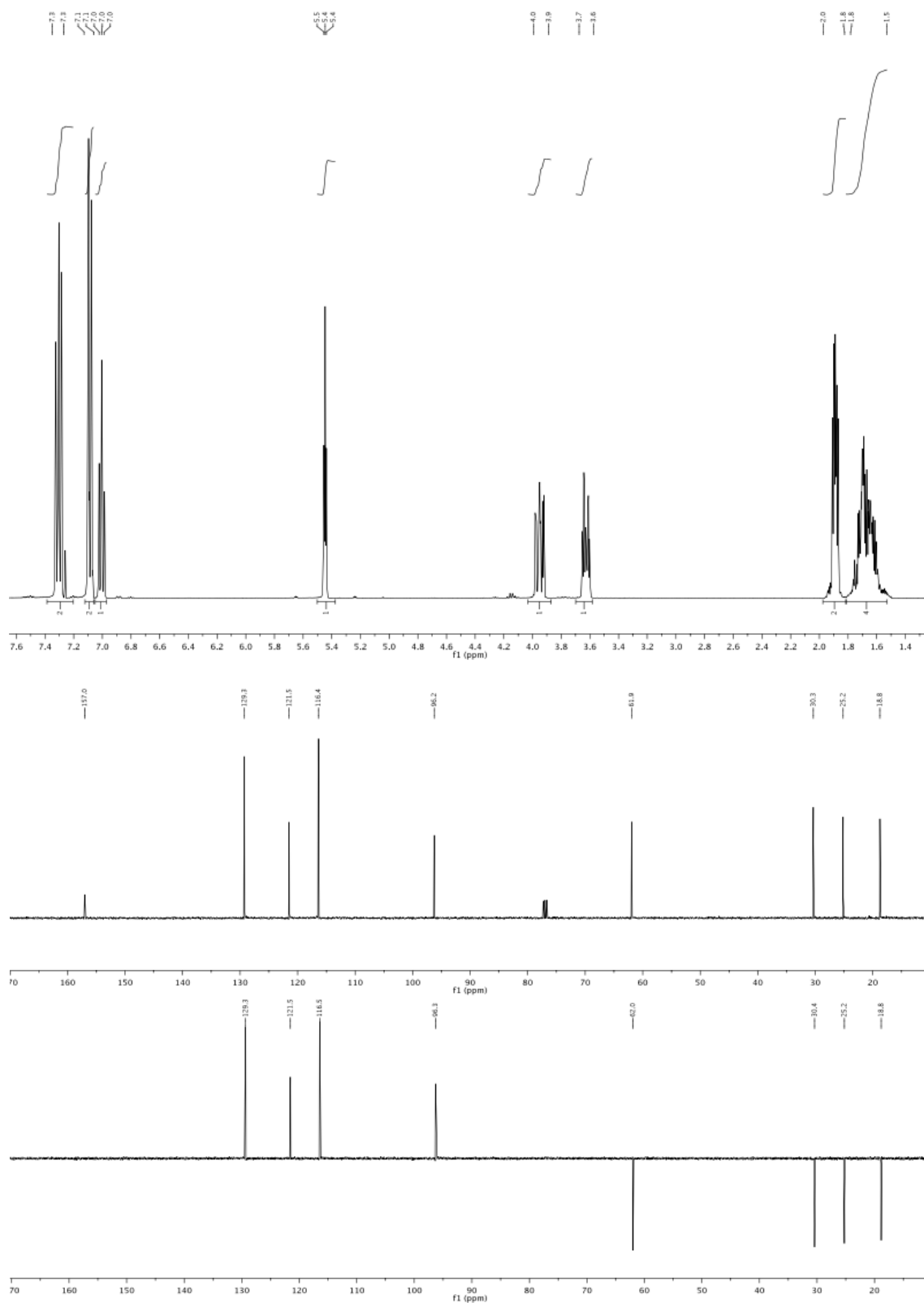
**1d₁**

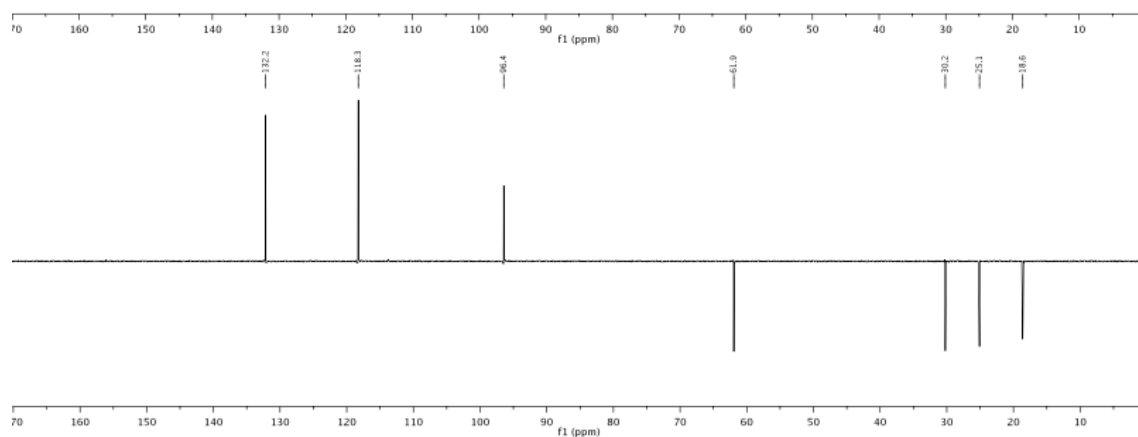
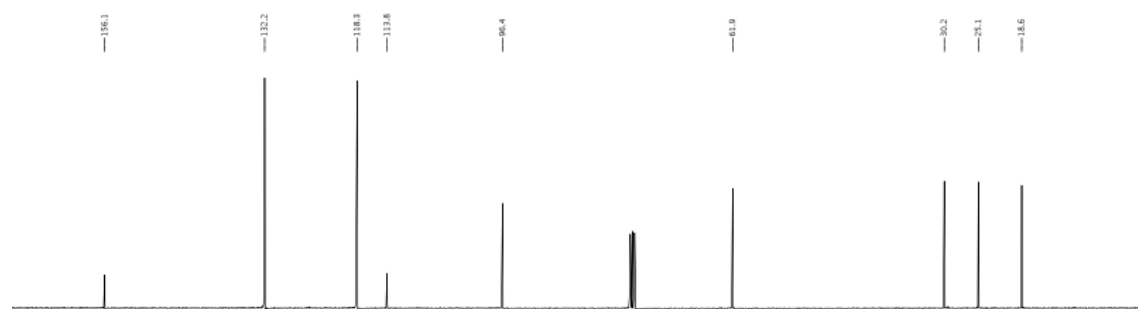
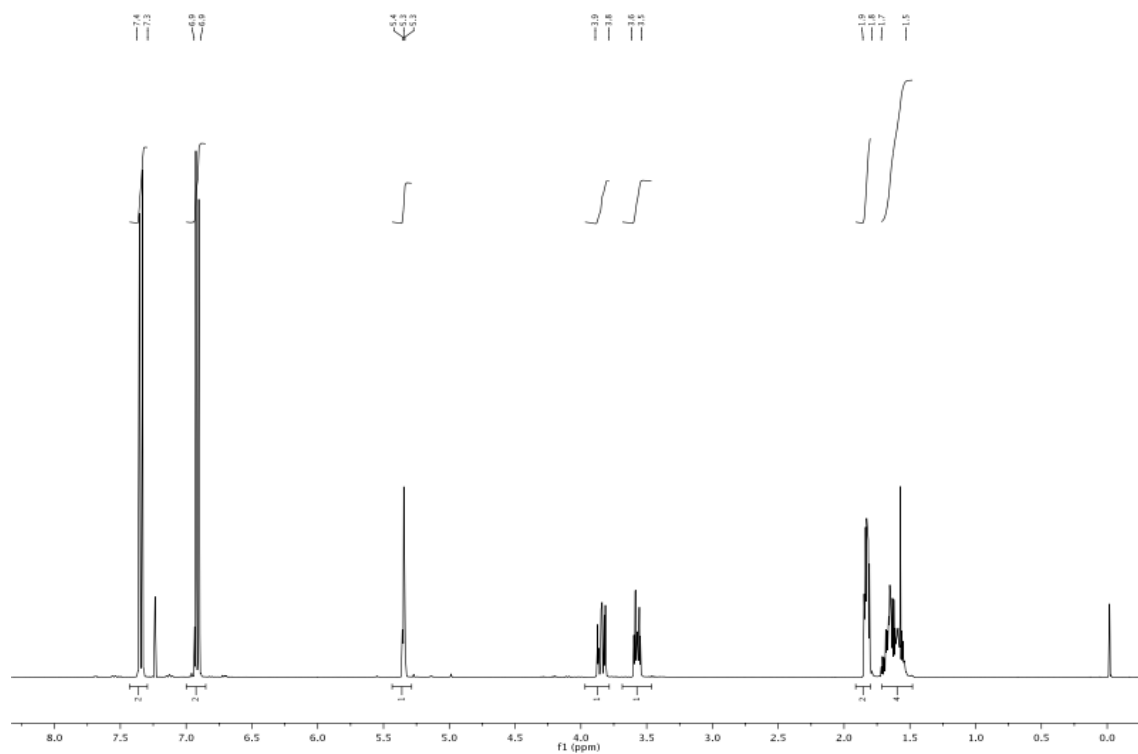
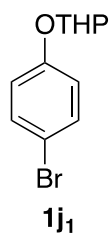


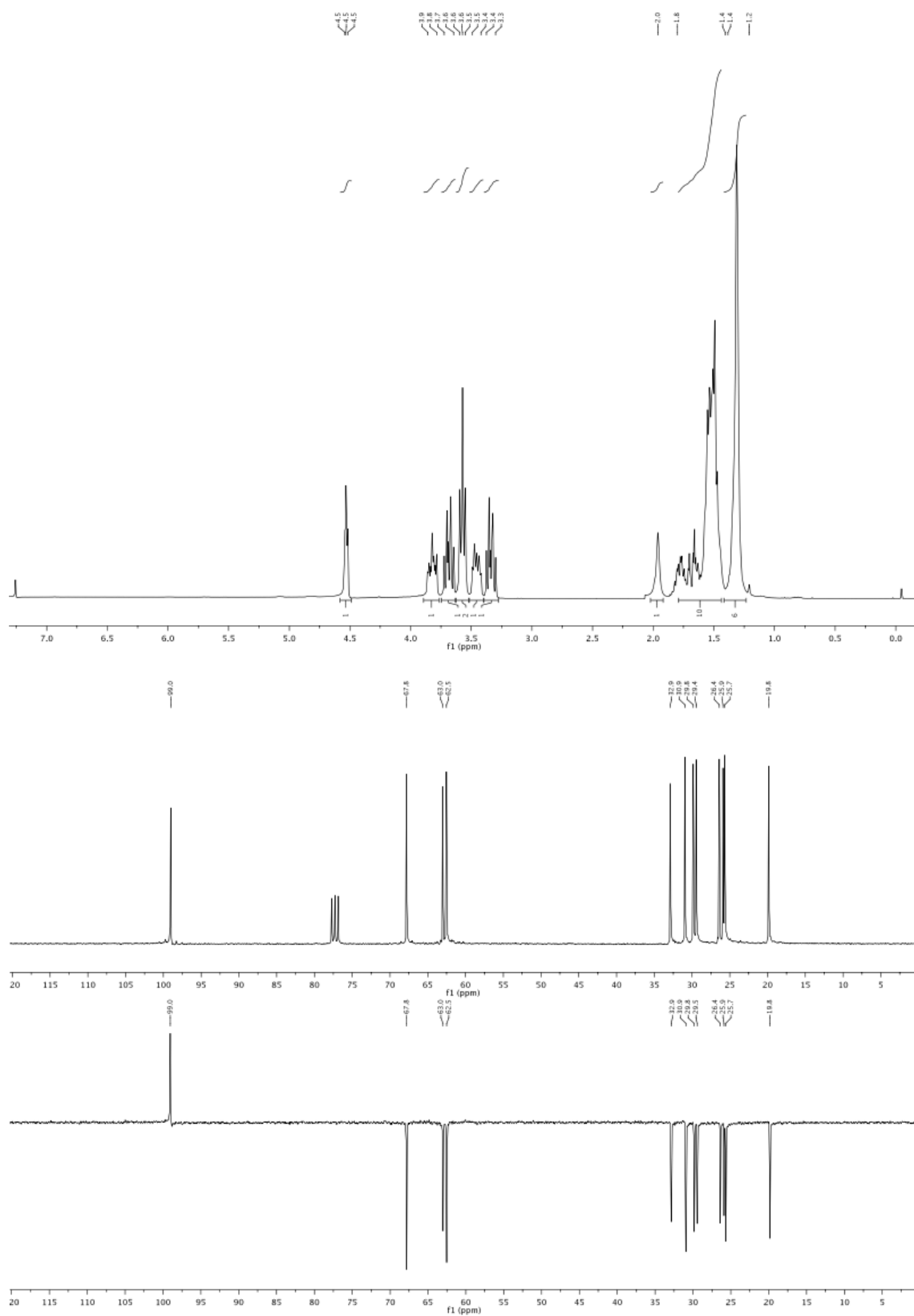
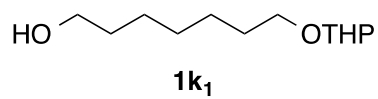
**1f₁**

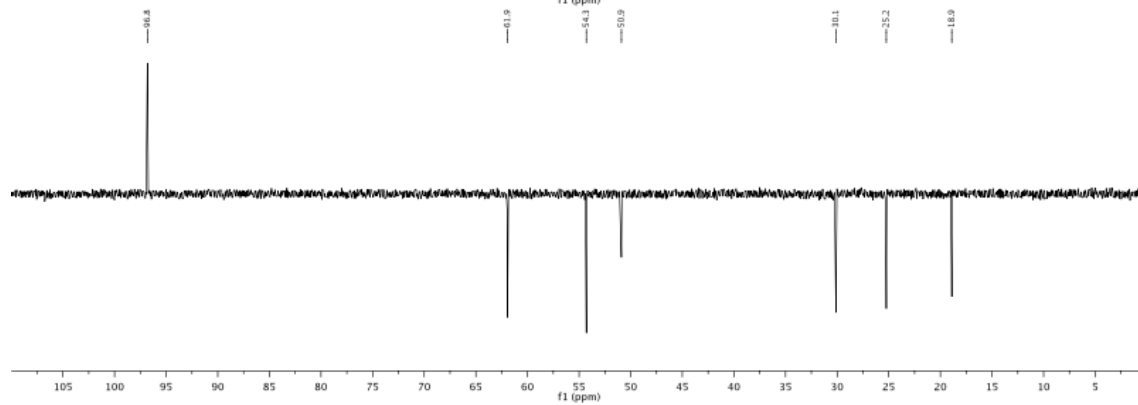
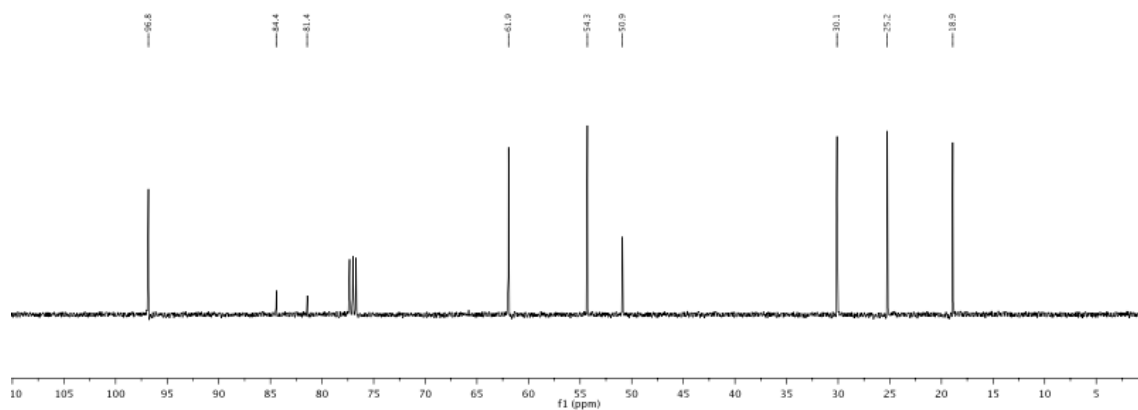
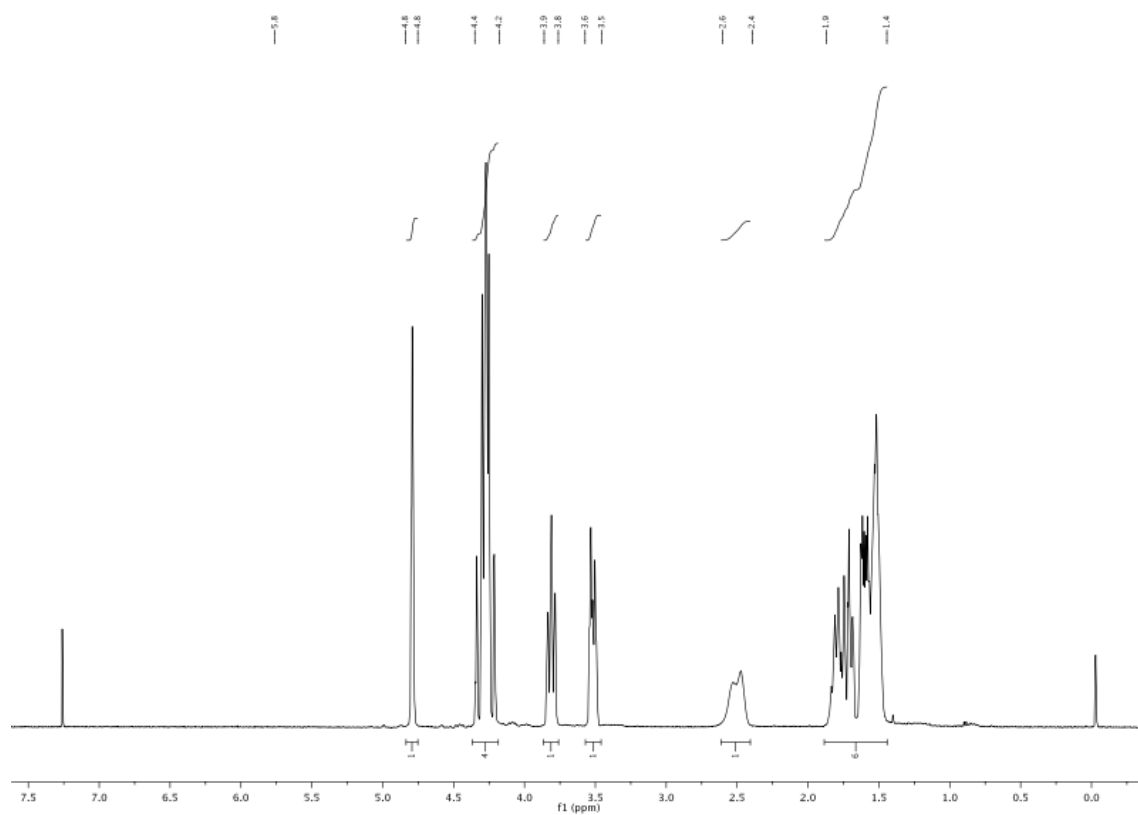
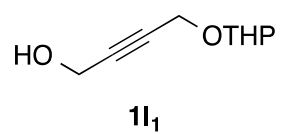


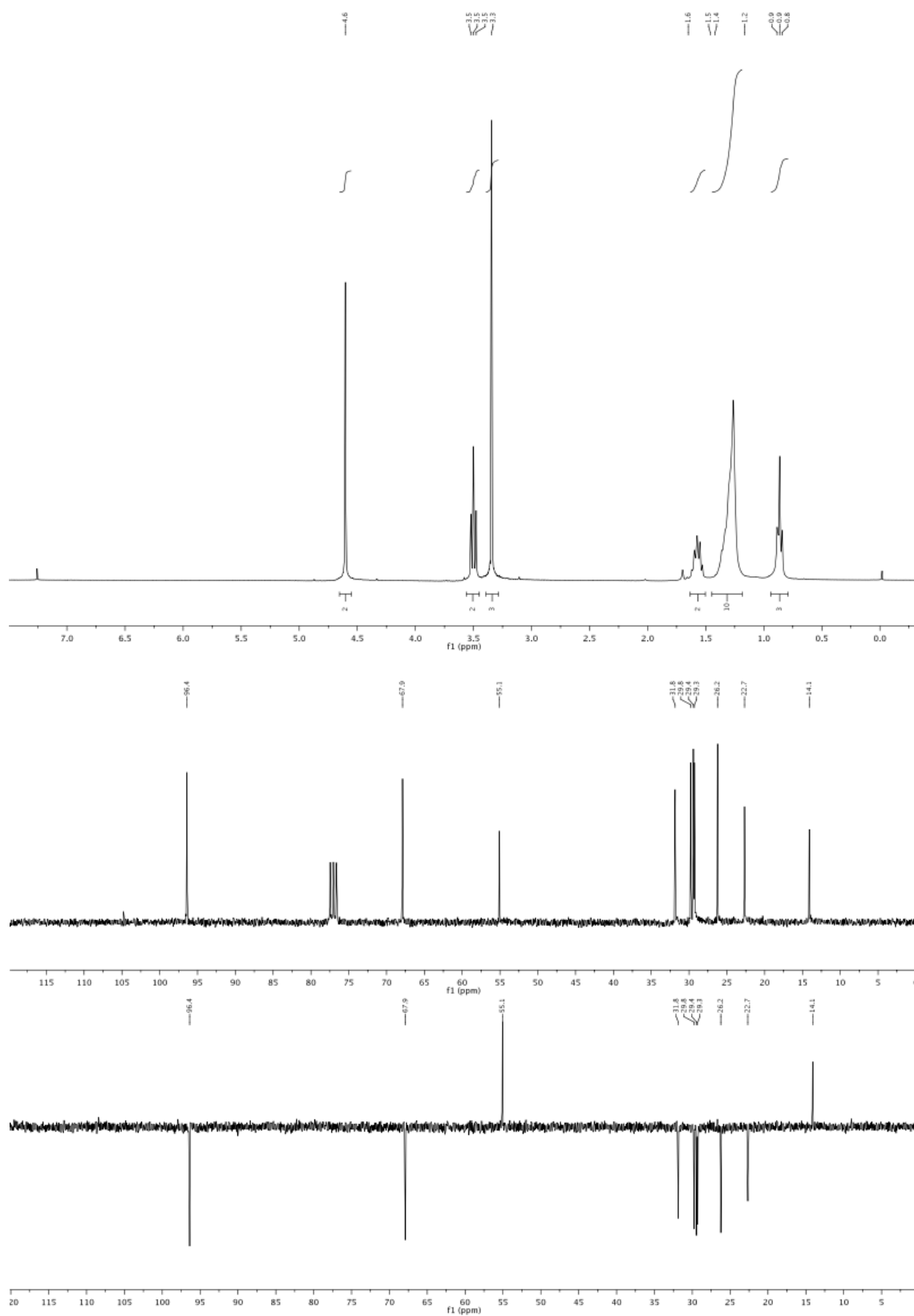
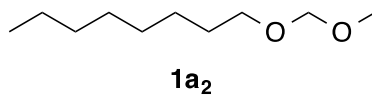
**1h₁**

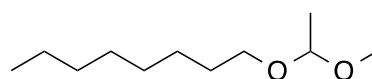
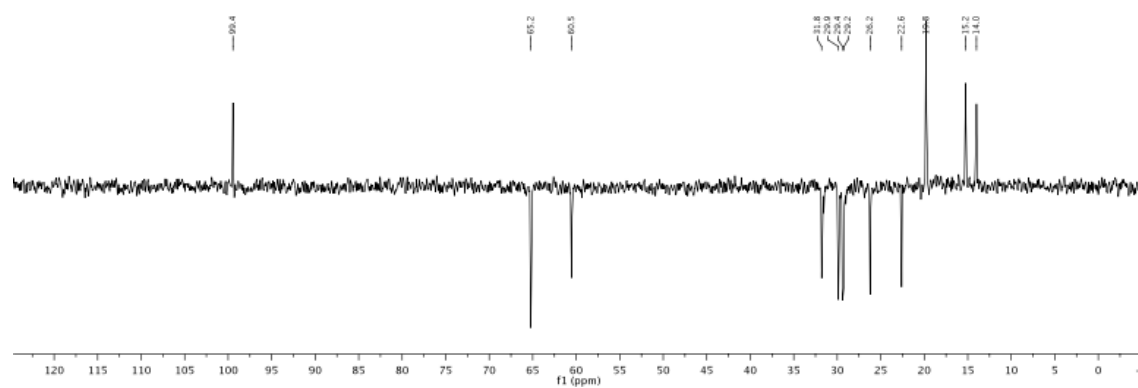
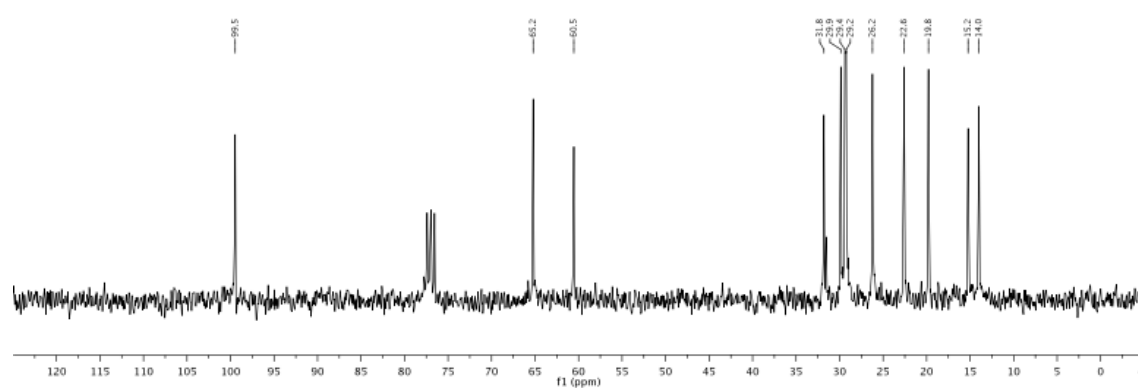
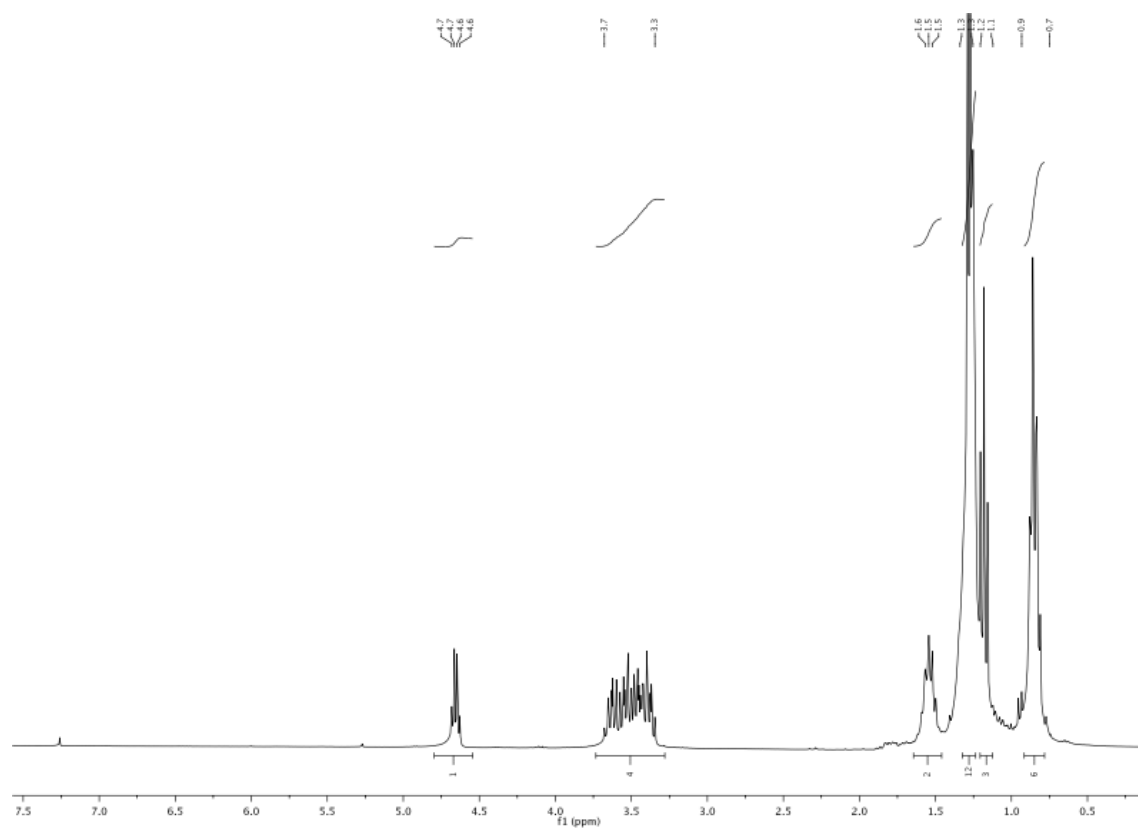
**1i₁**

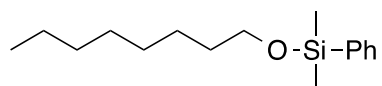
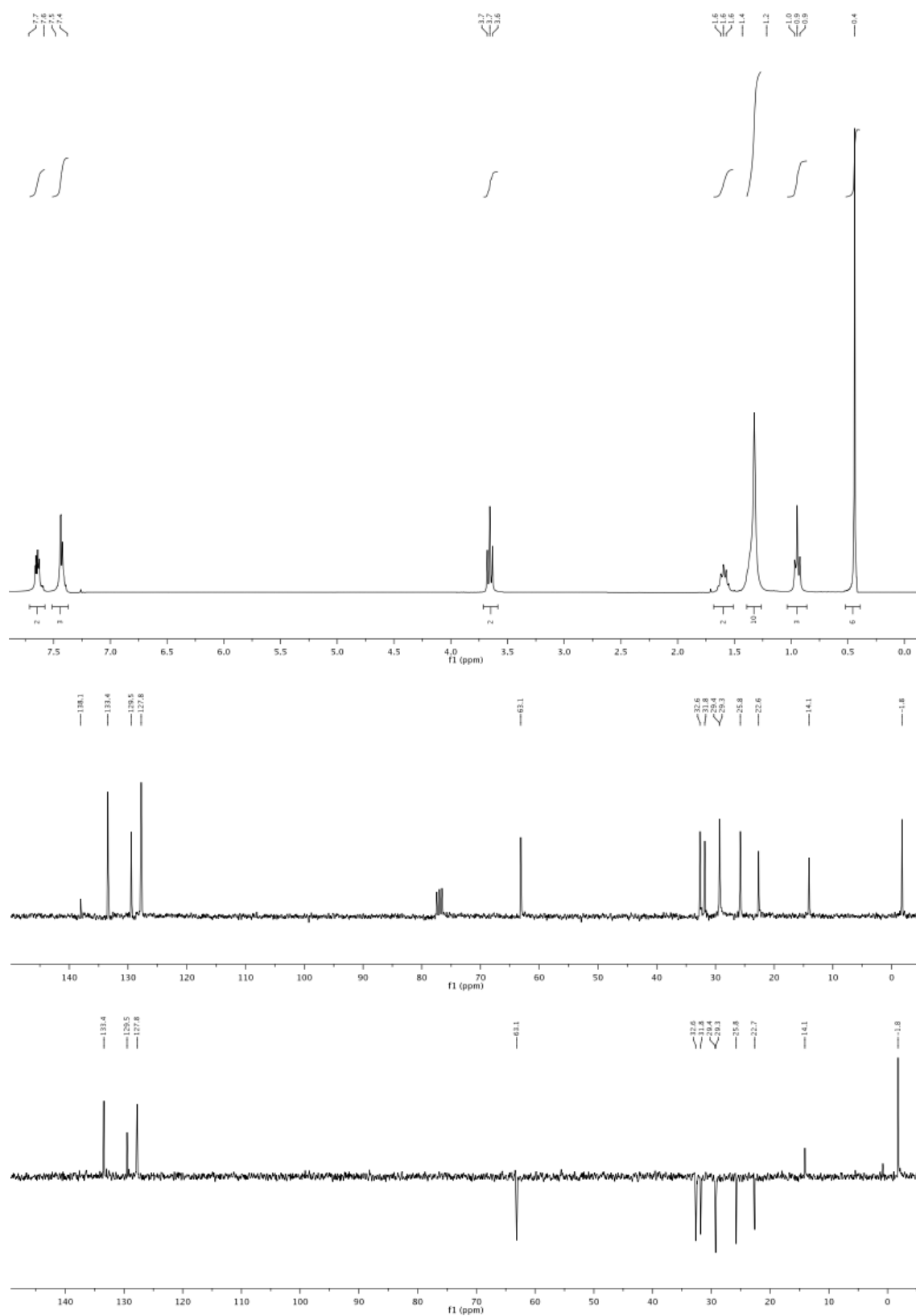


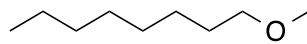
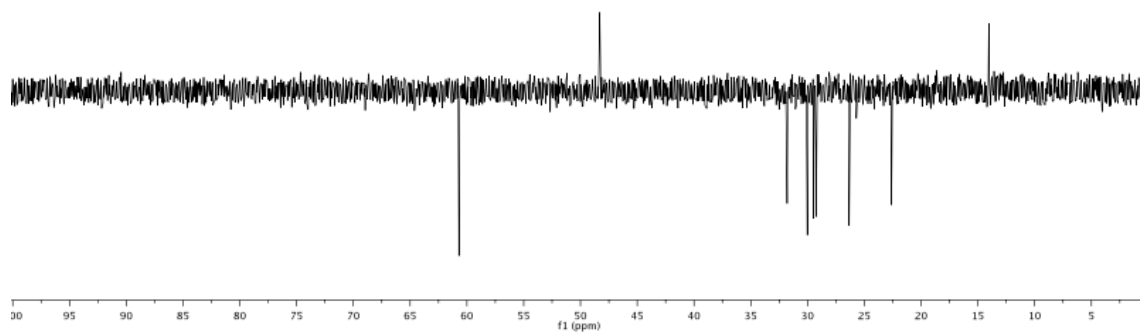
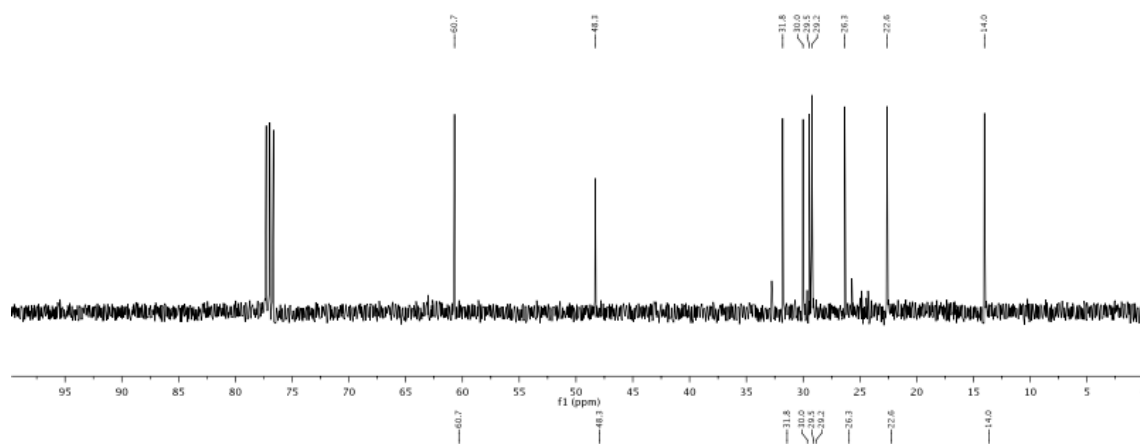
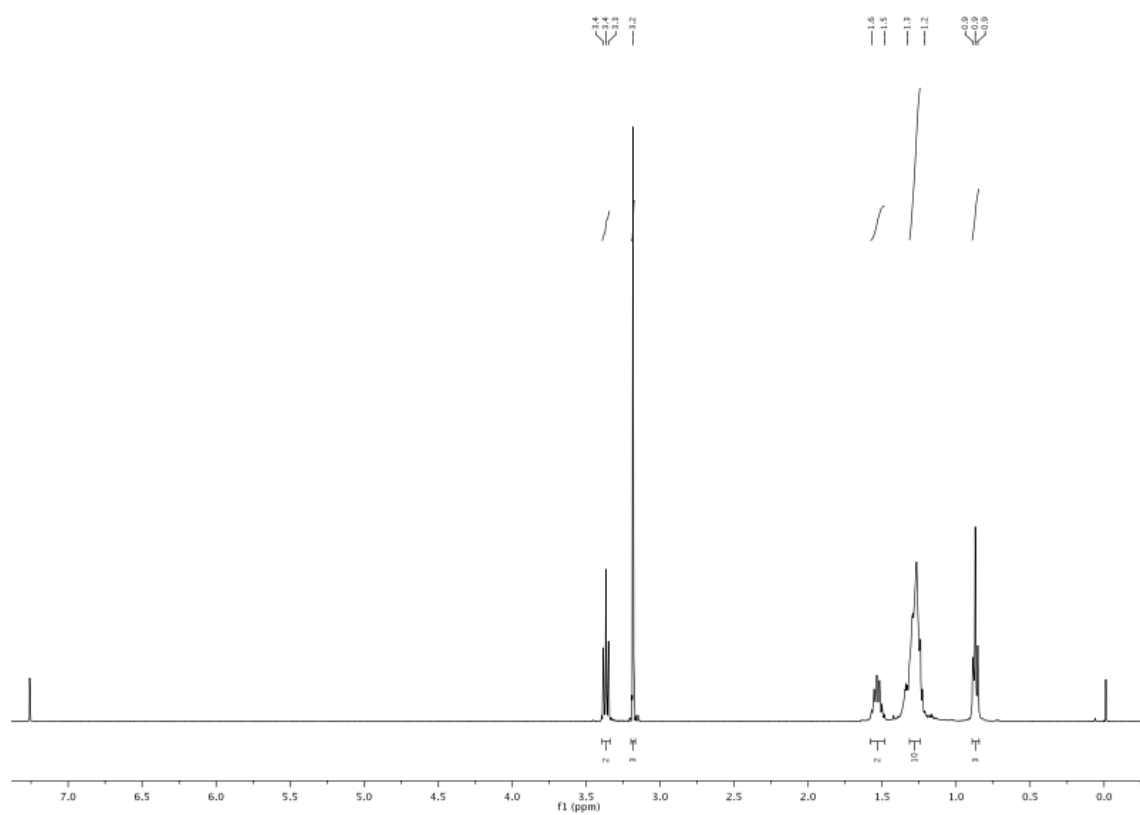


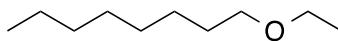
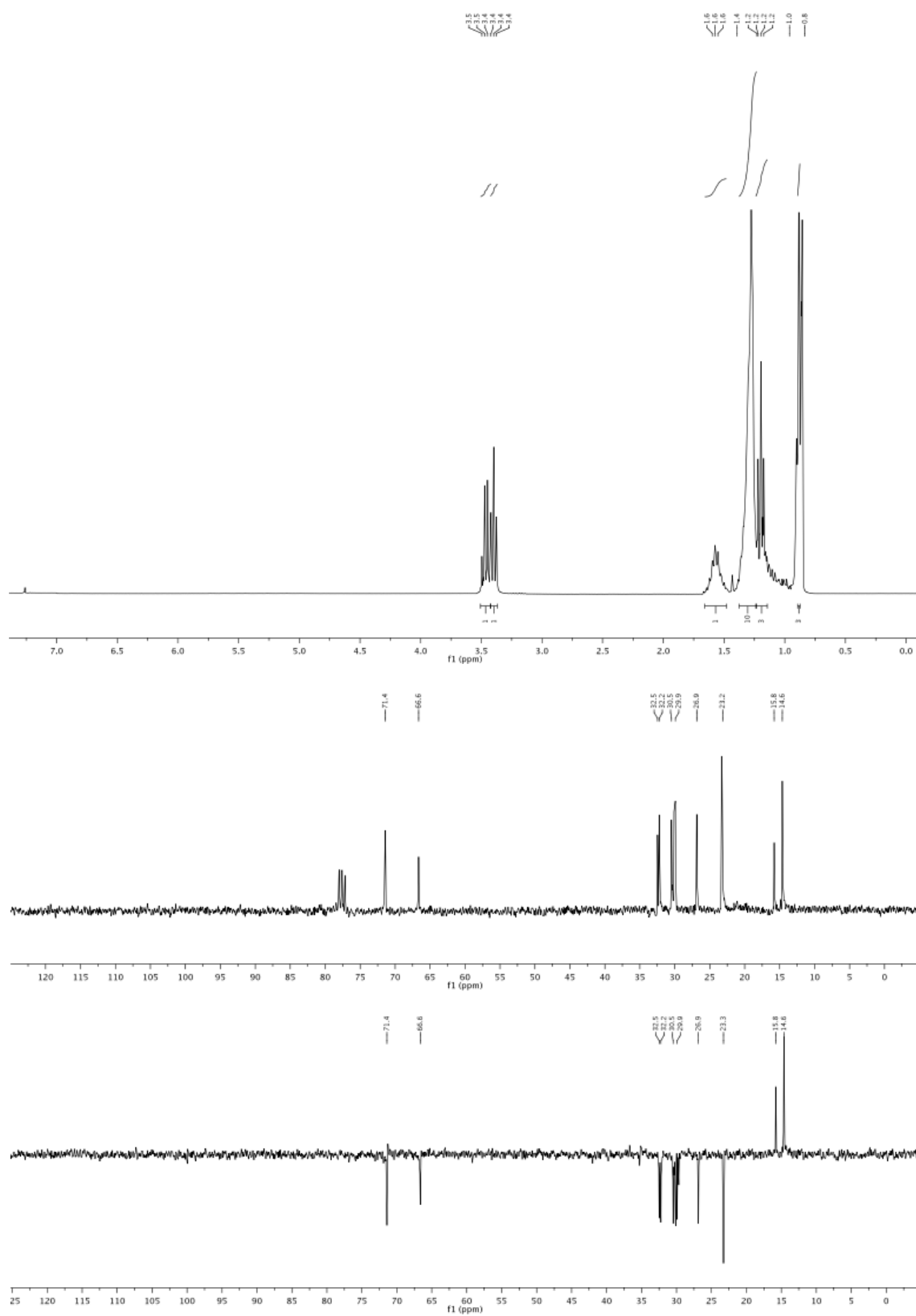


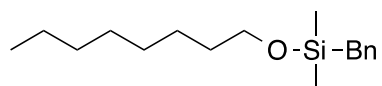
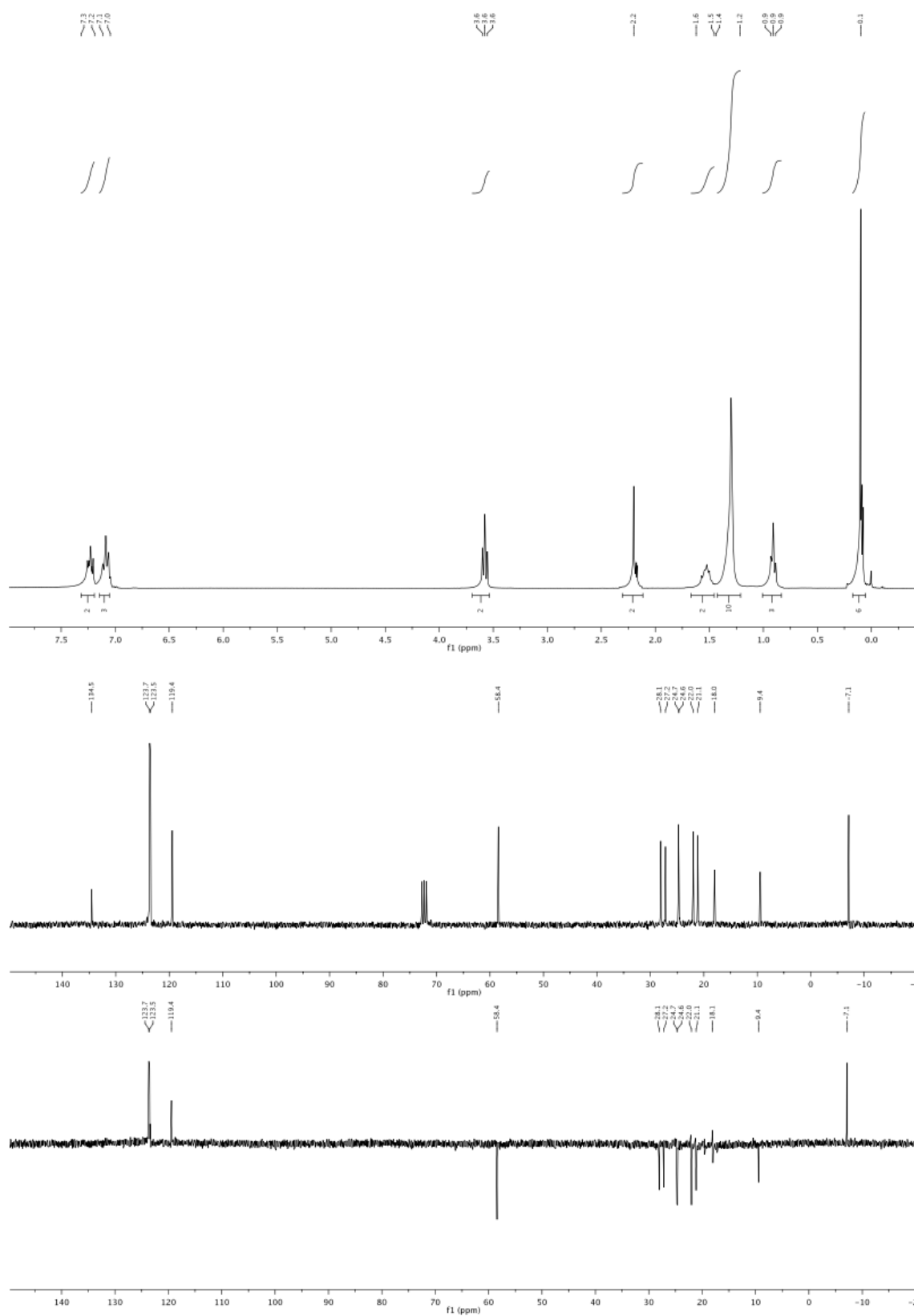


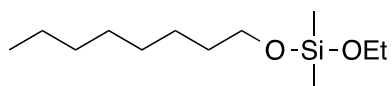
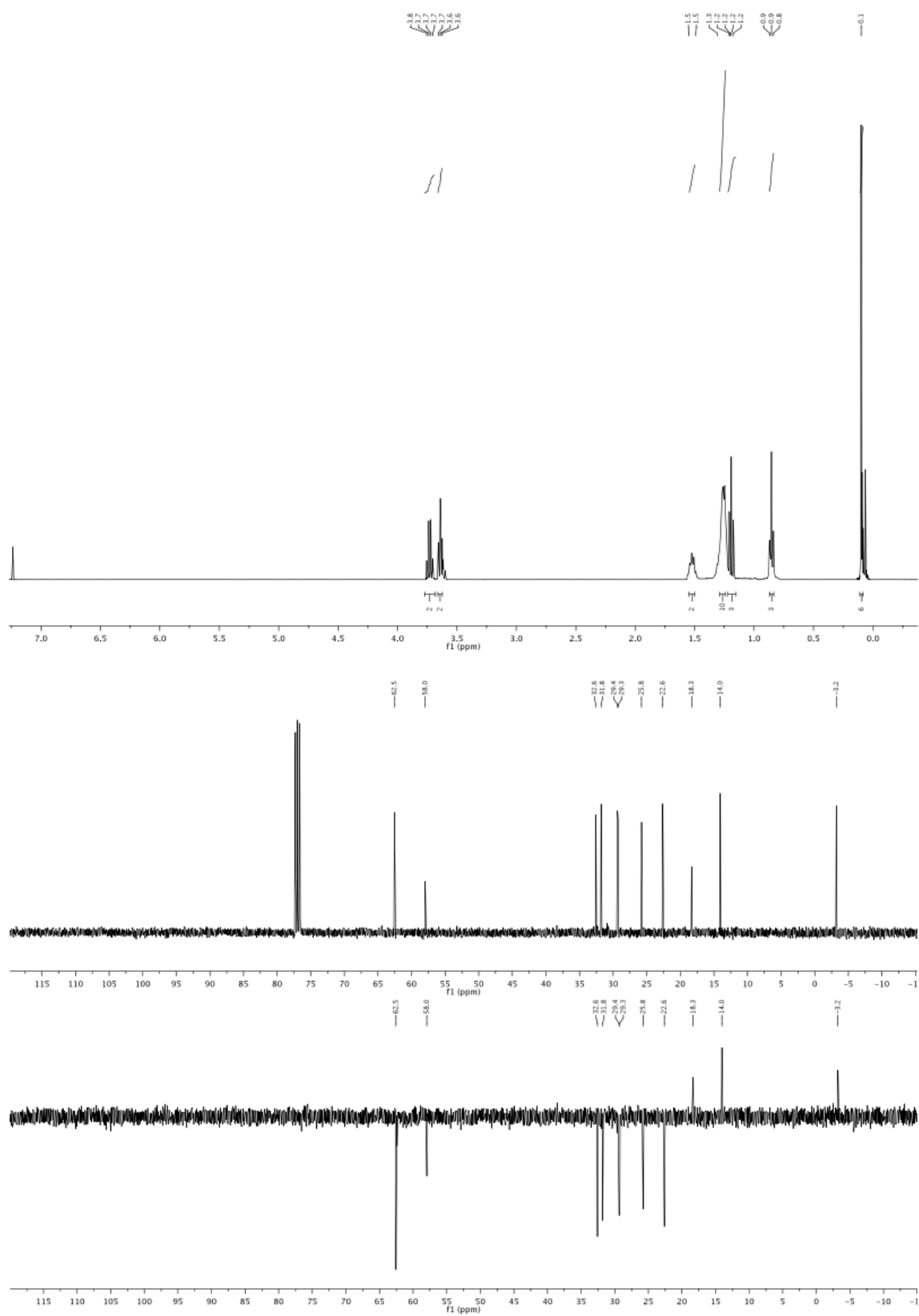
**1a₃**

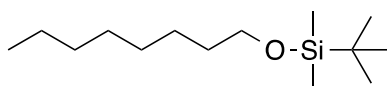
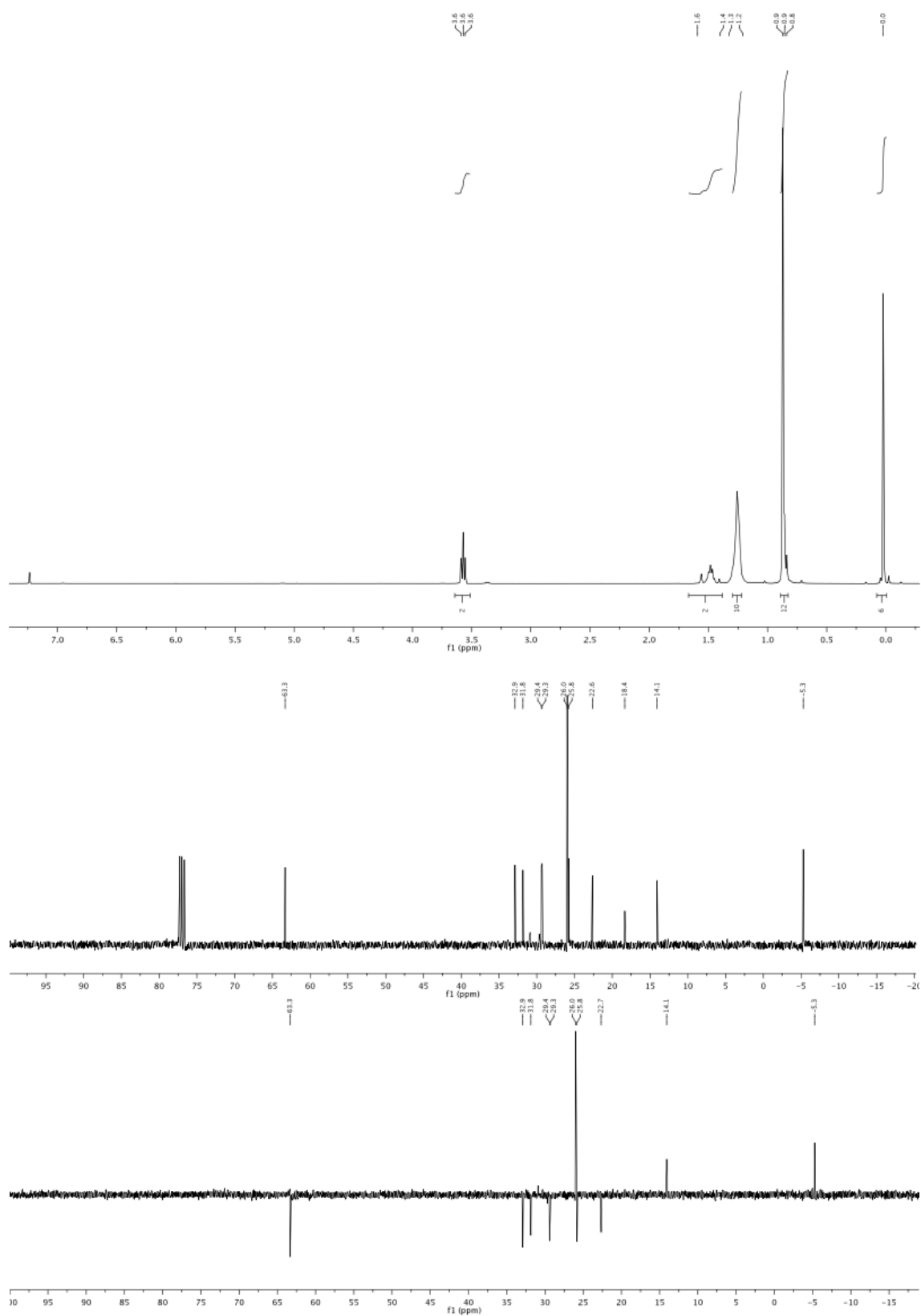
**2a₁**

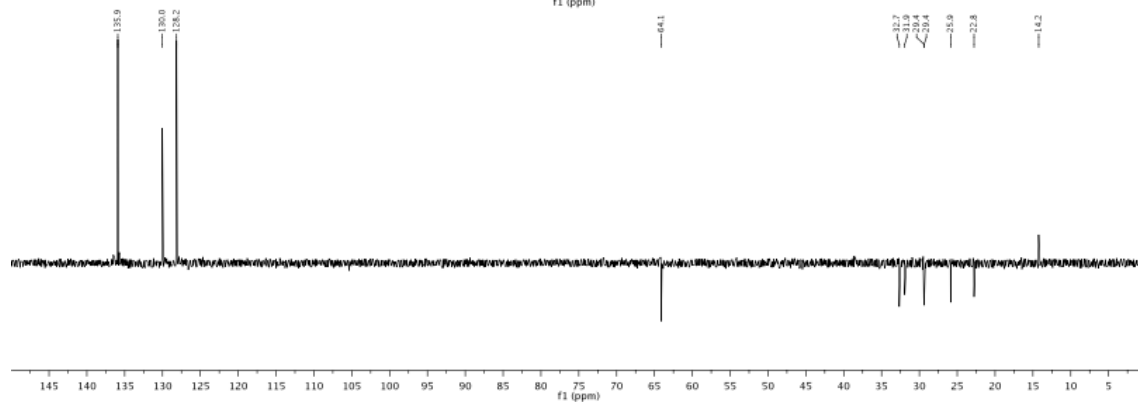
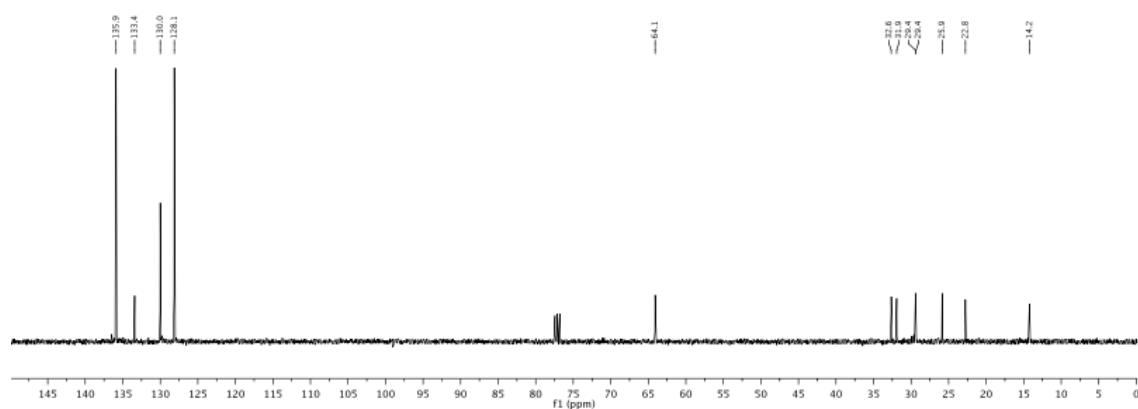
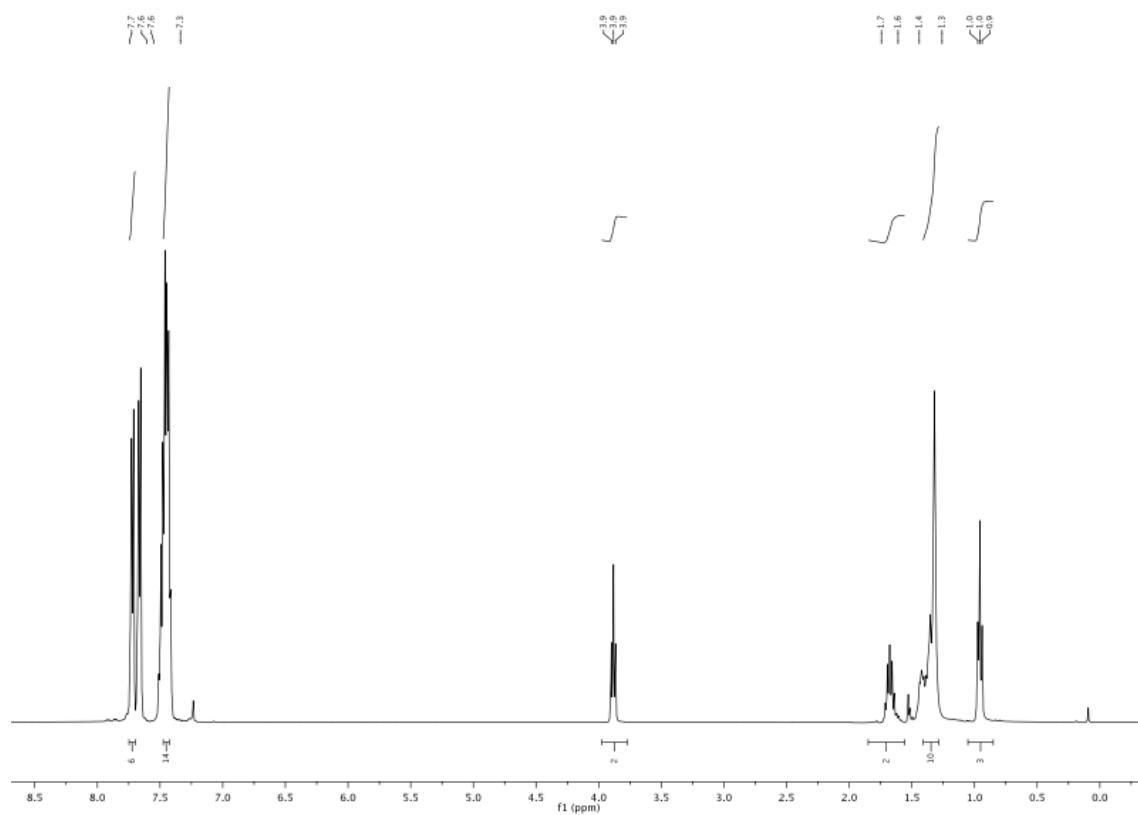
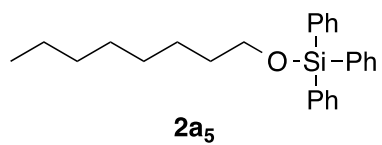
**4a₂**

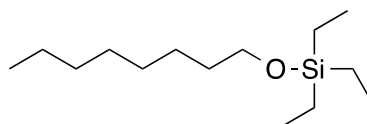
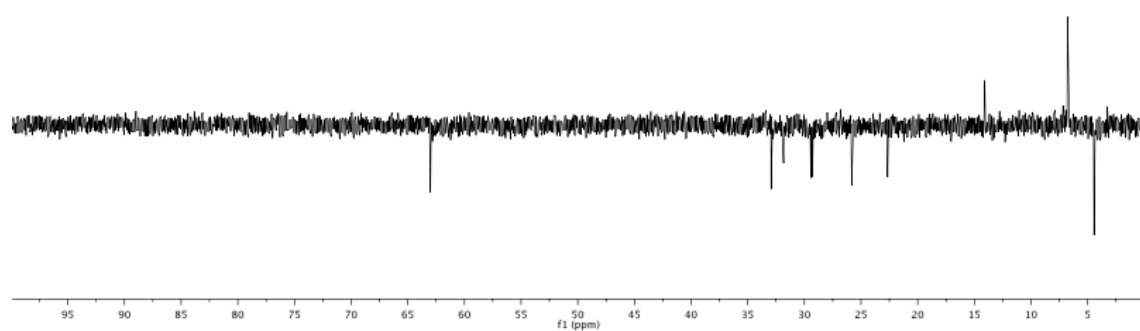
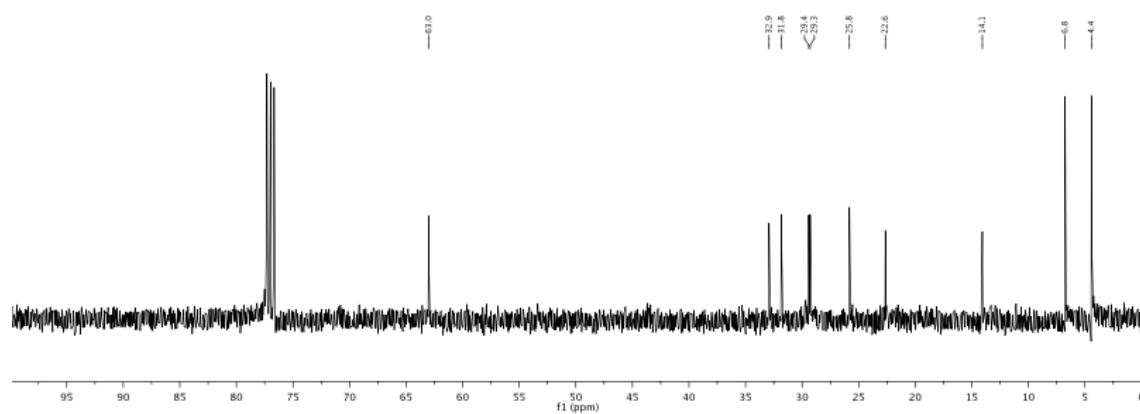
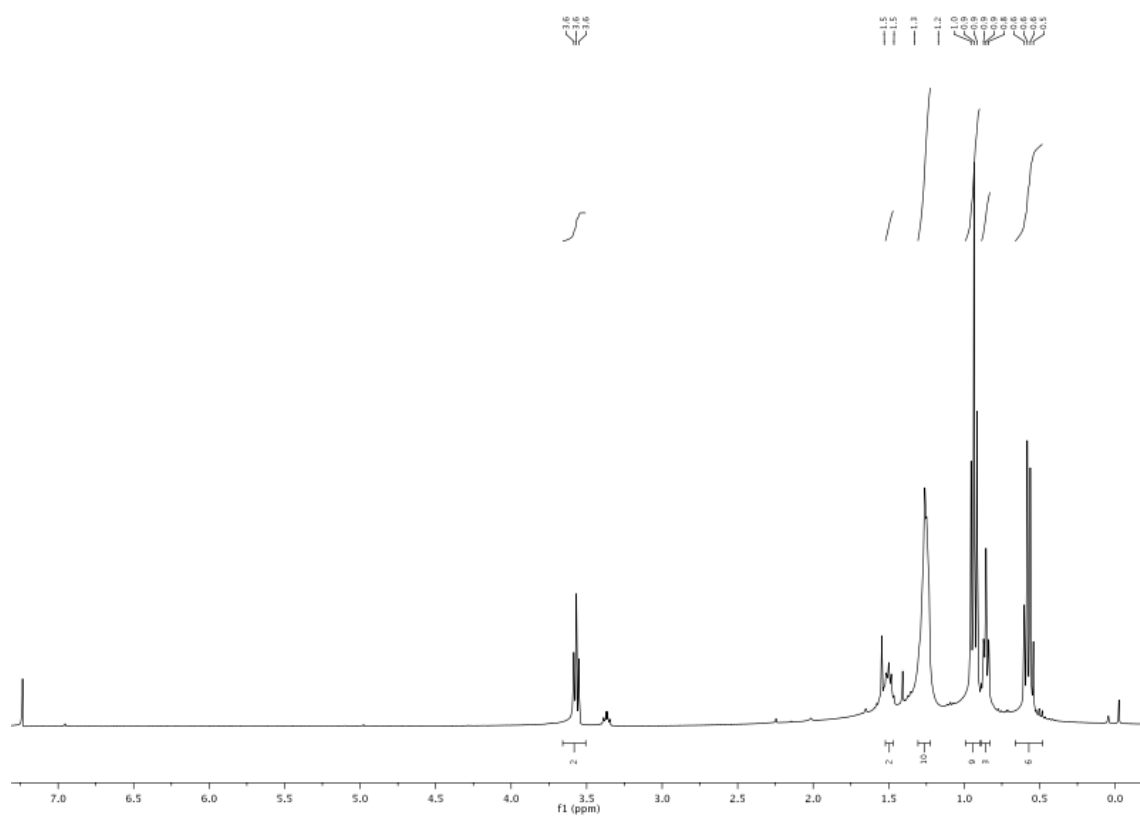
**4a₃**

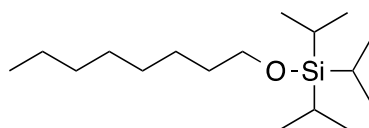
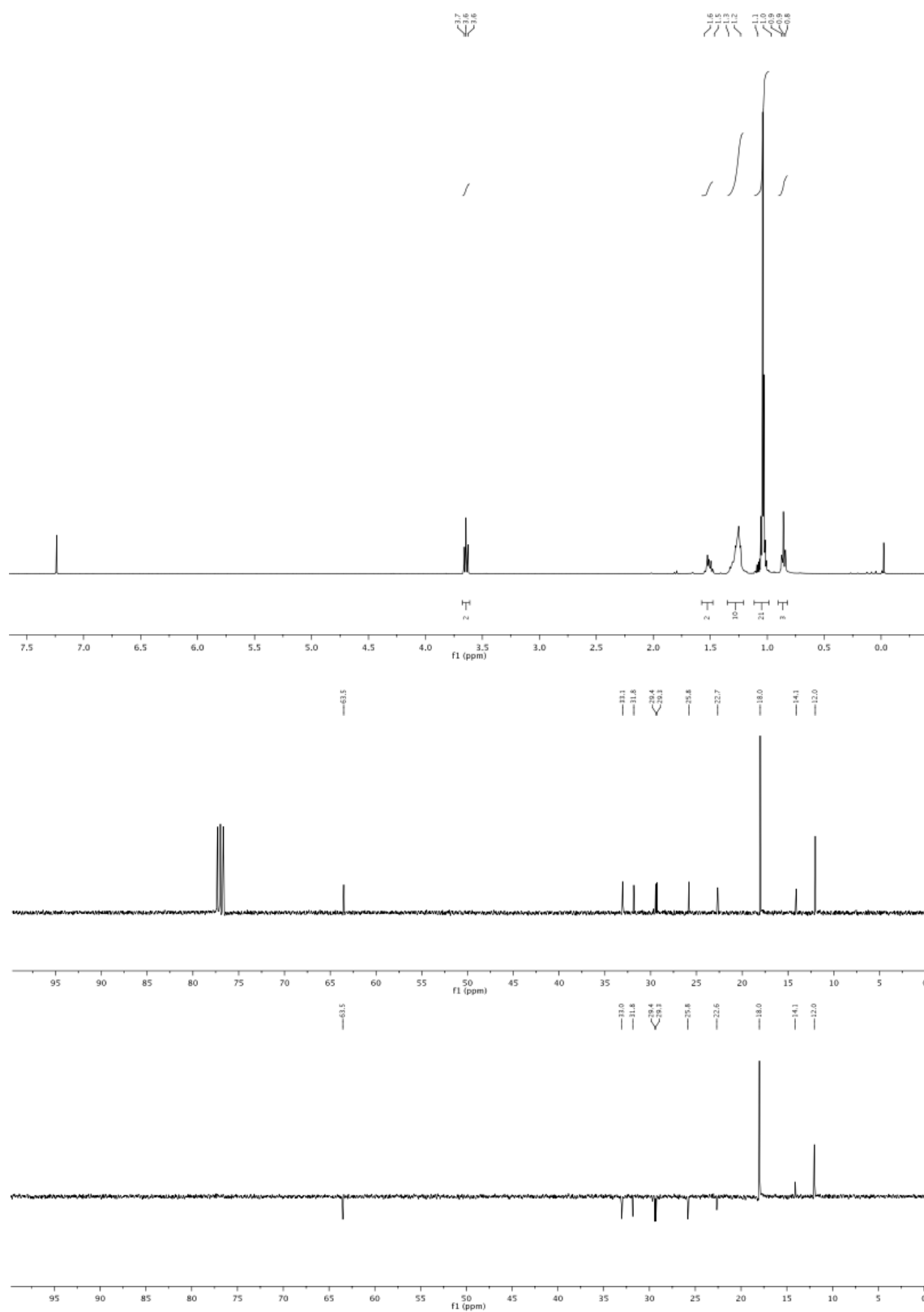
**2a₂**

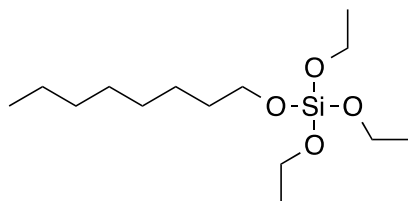
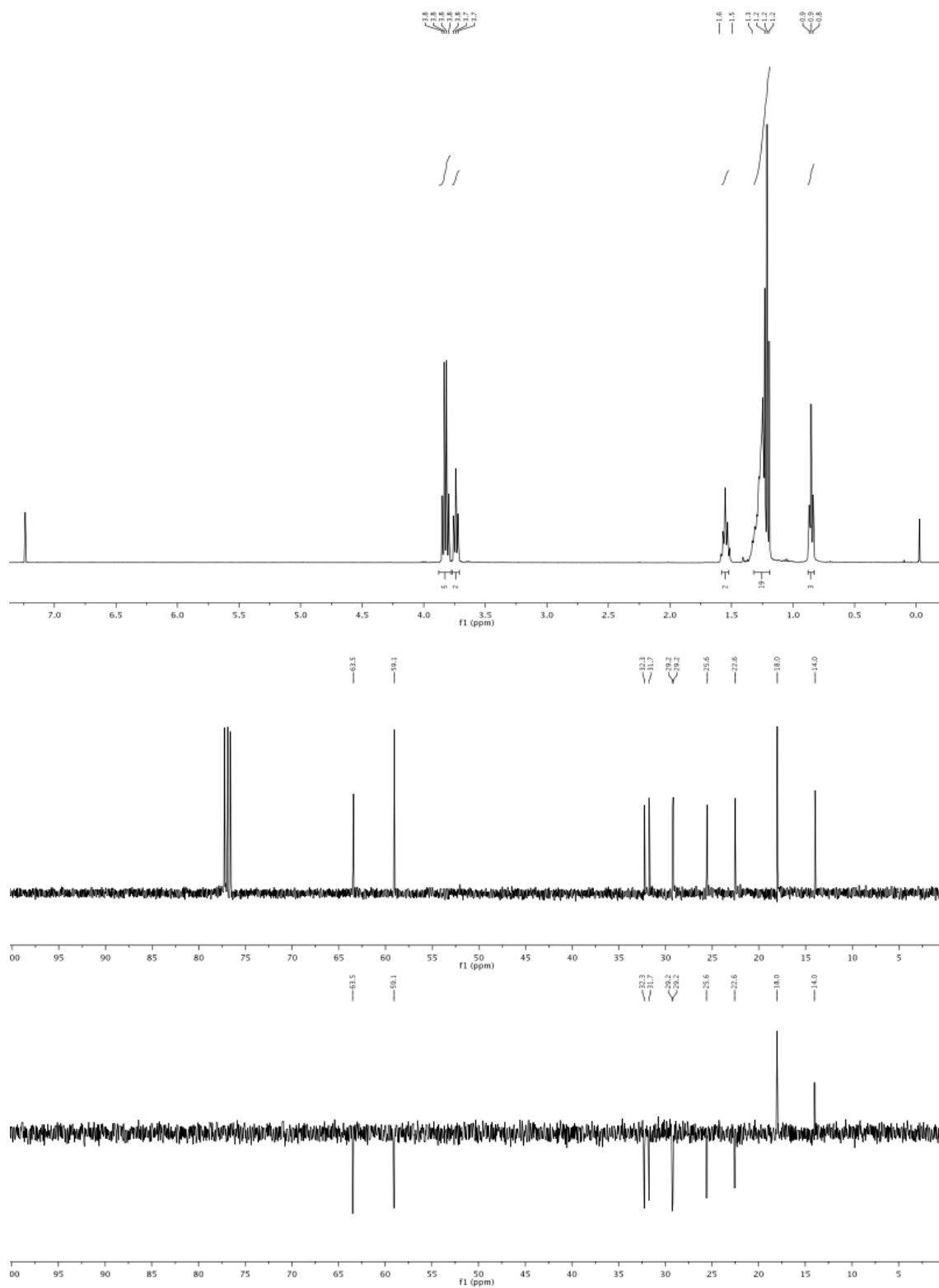
**2a₃**

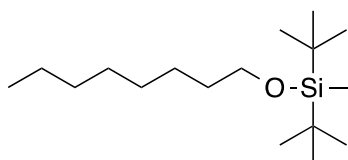
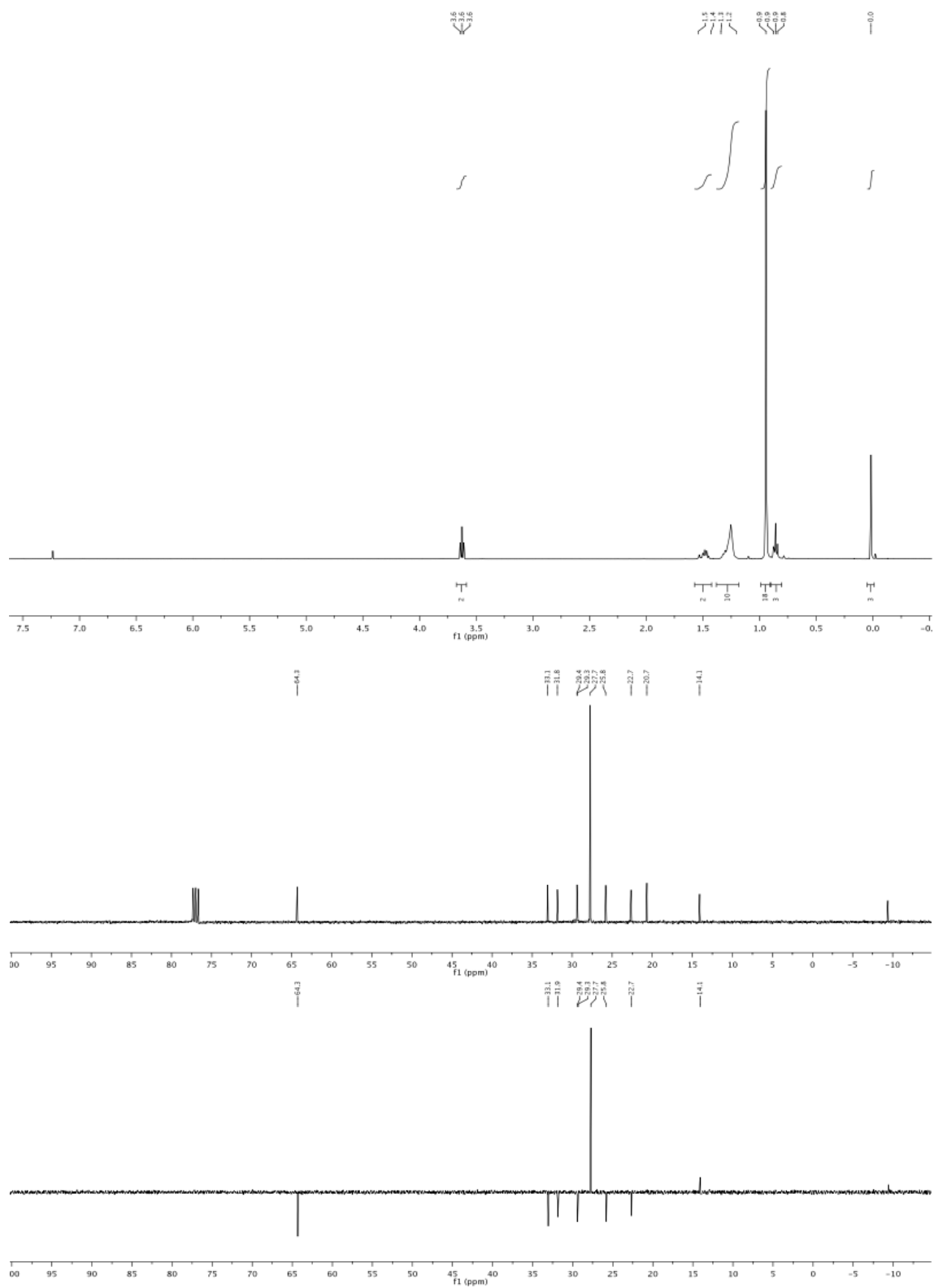
**2a₄**

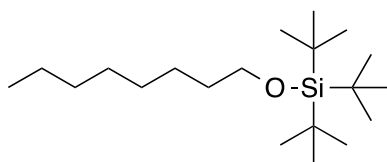
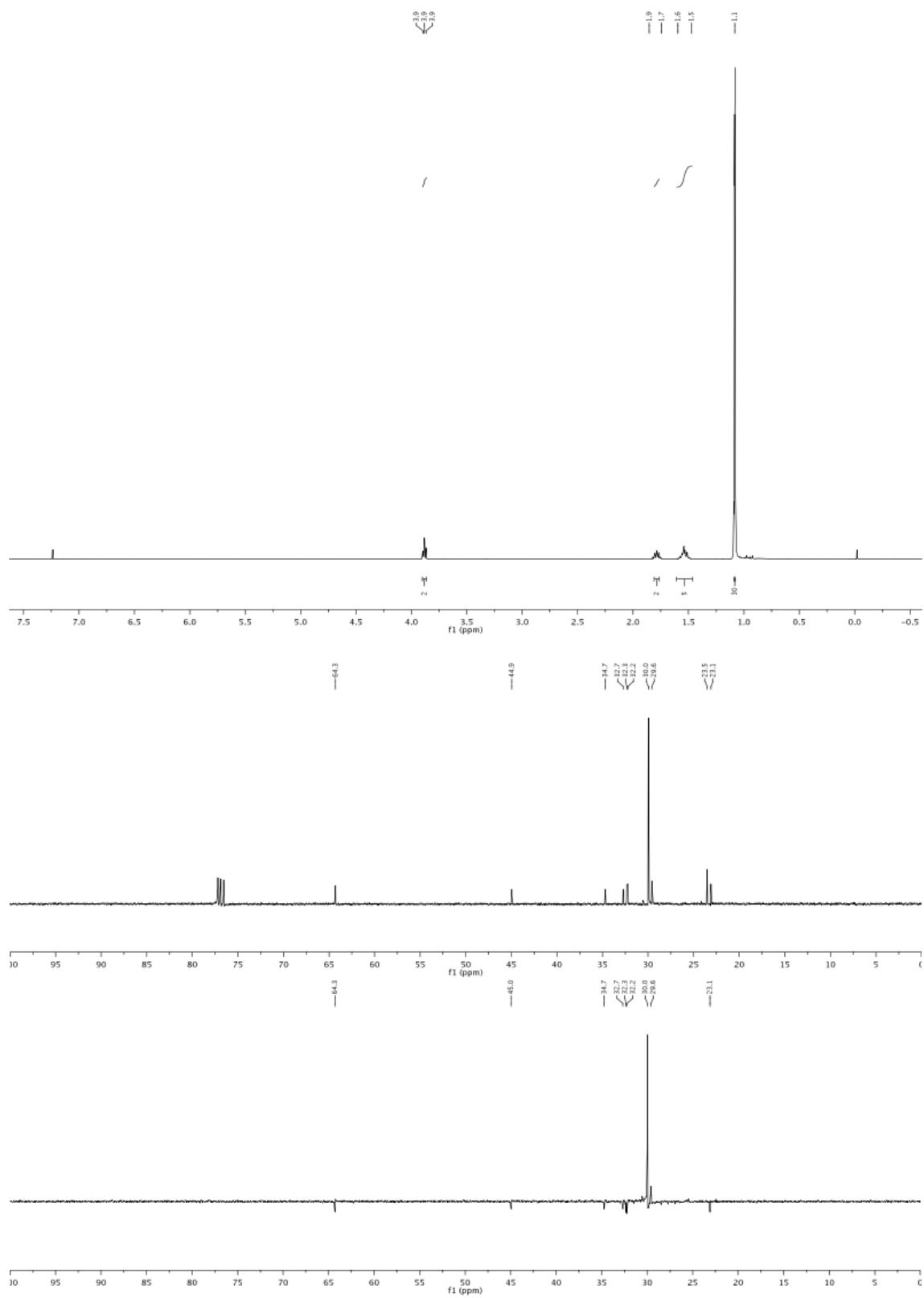


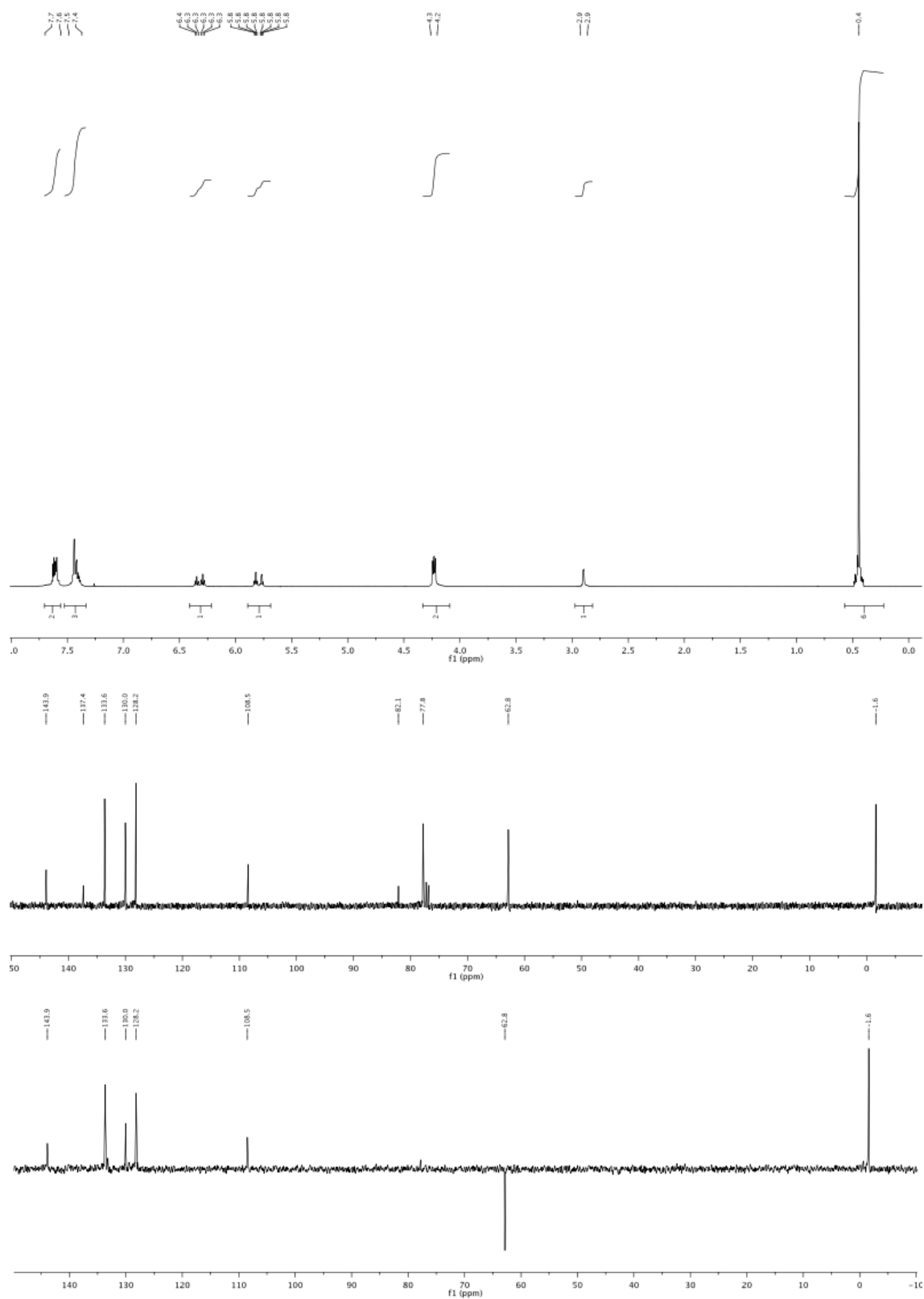
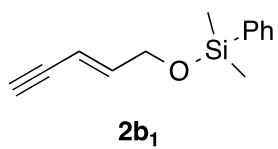
**2a₆**

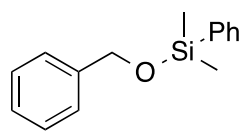
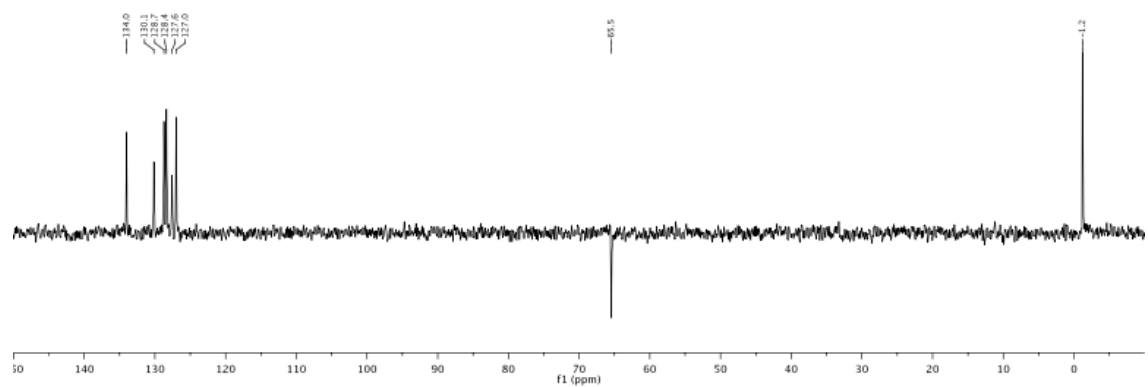
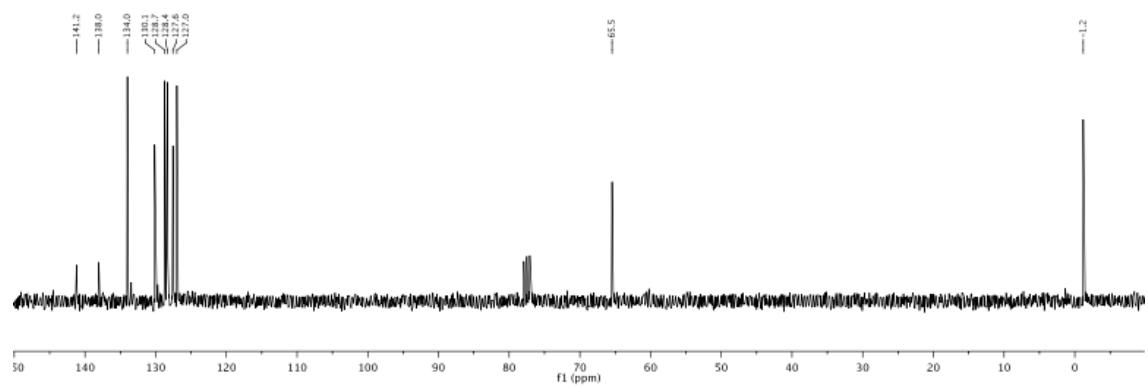
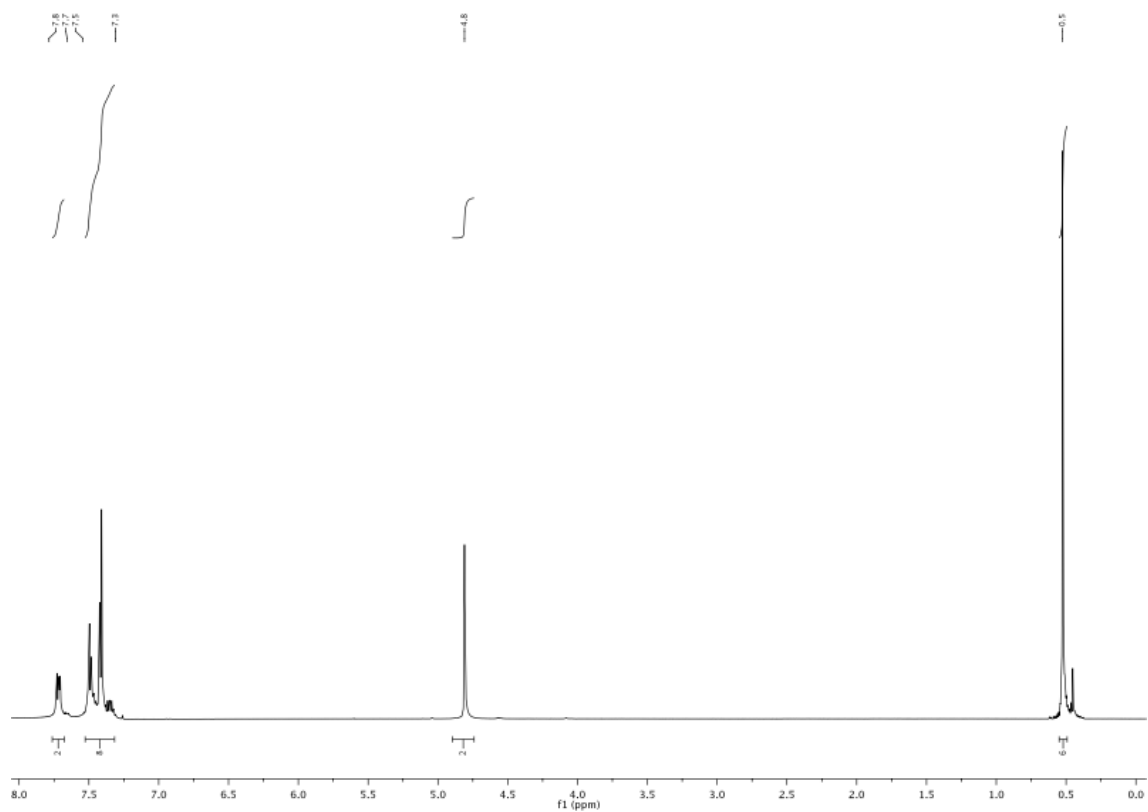
**2a₇**

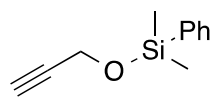
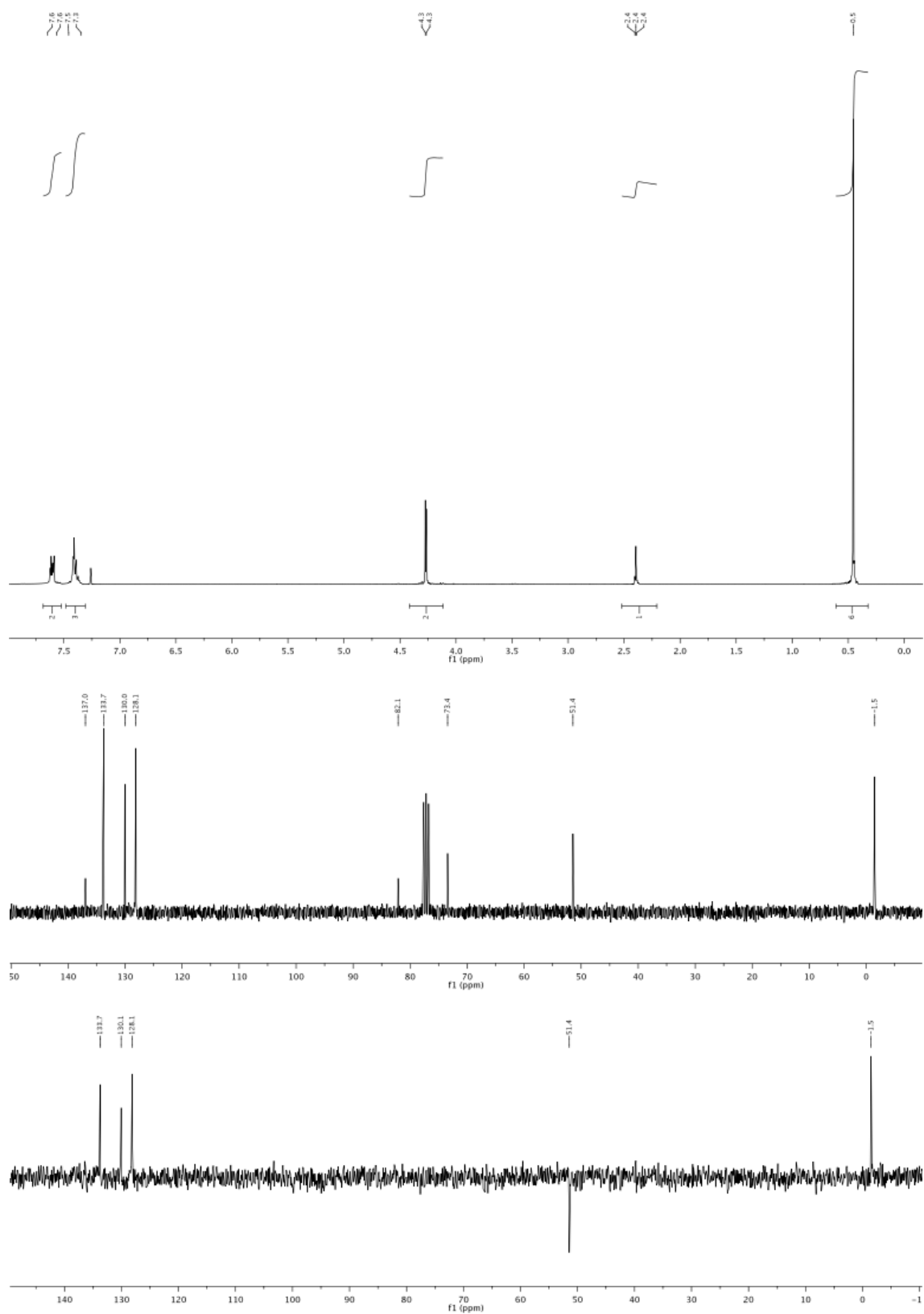
**2a₈**

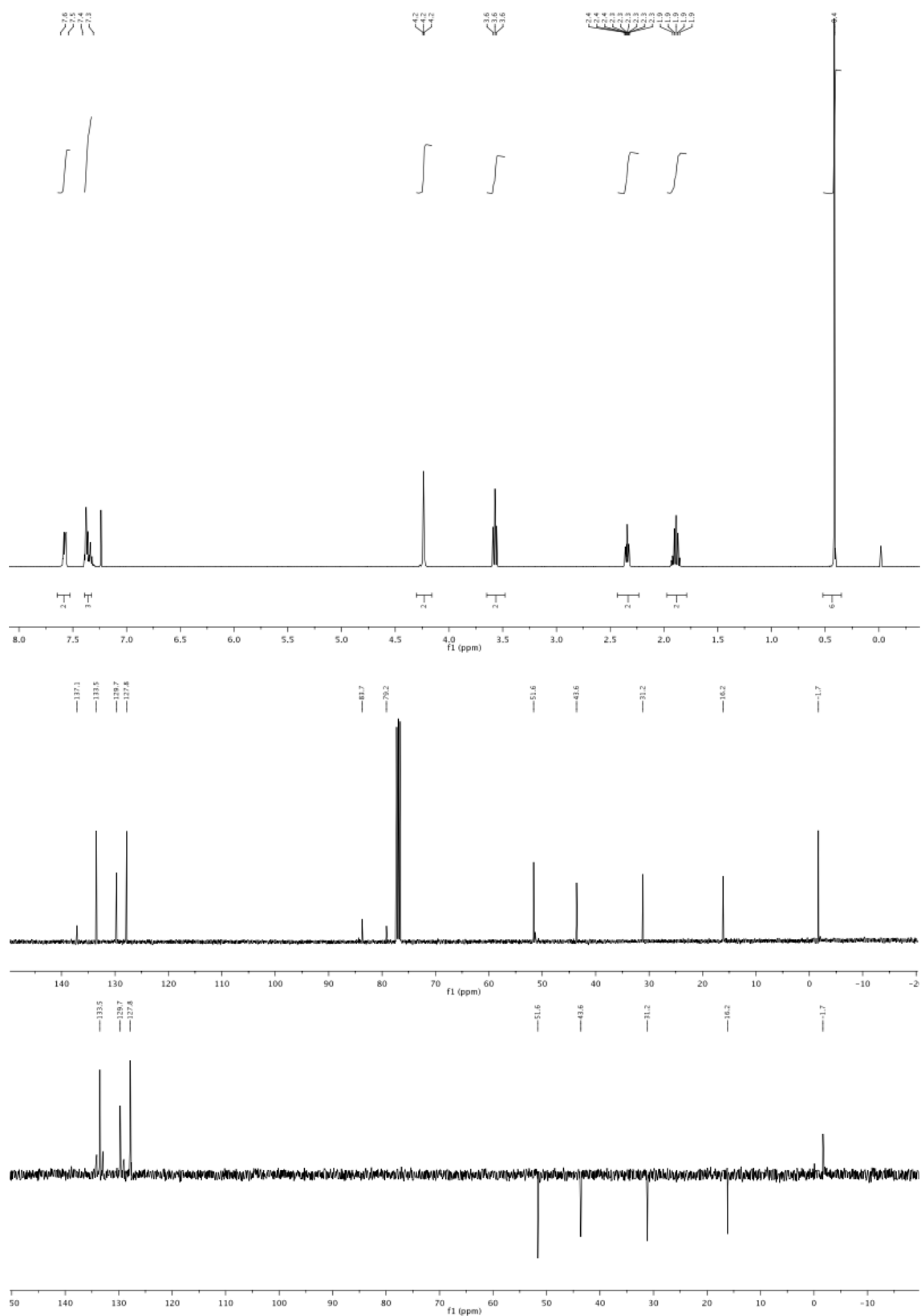
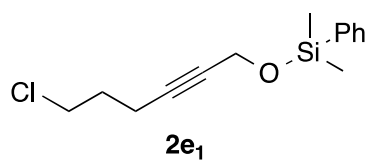
**2a₉**

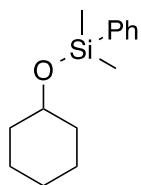
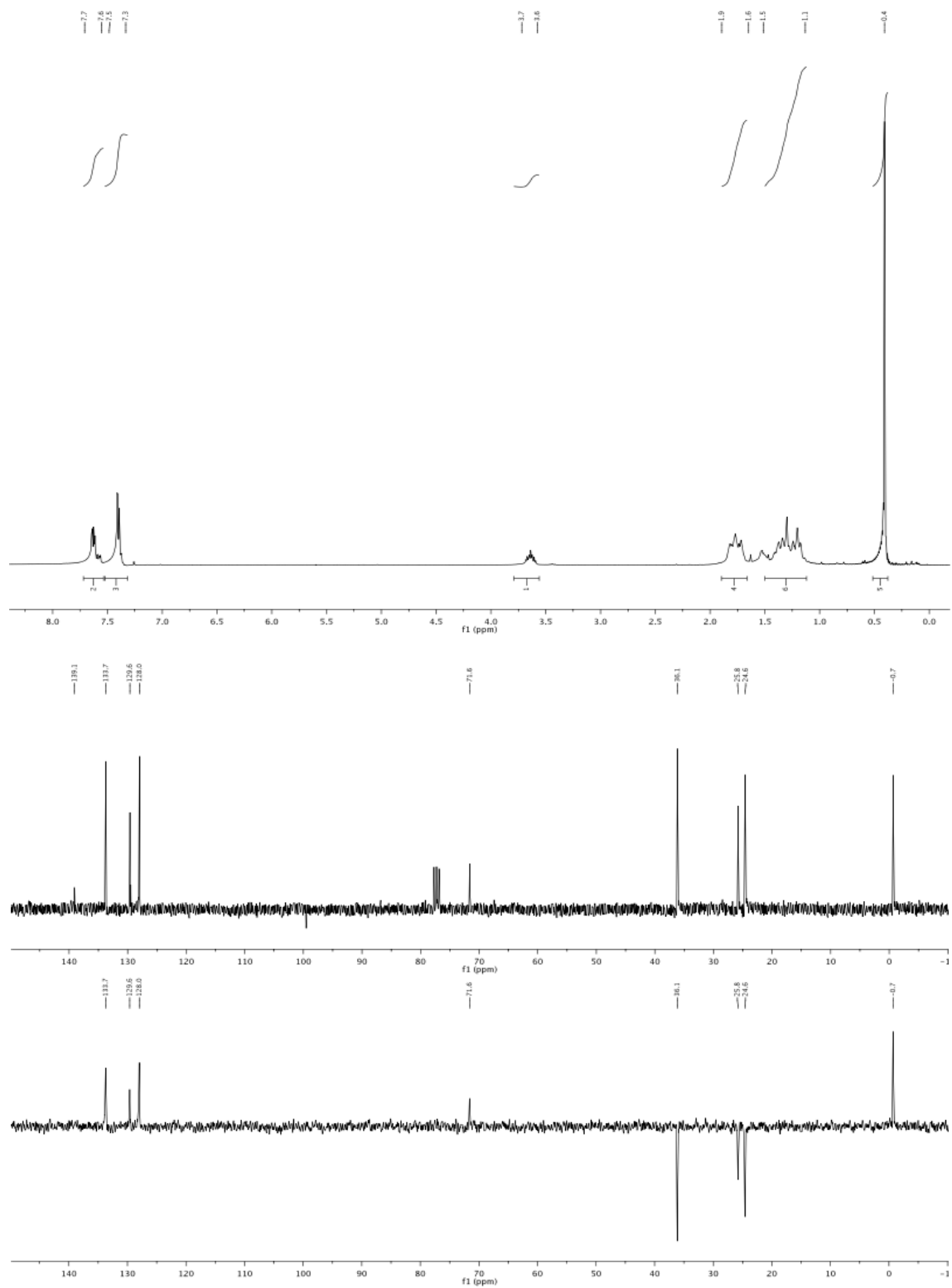
**2a₁₀**

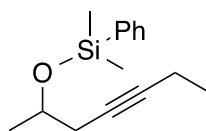
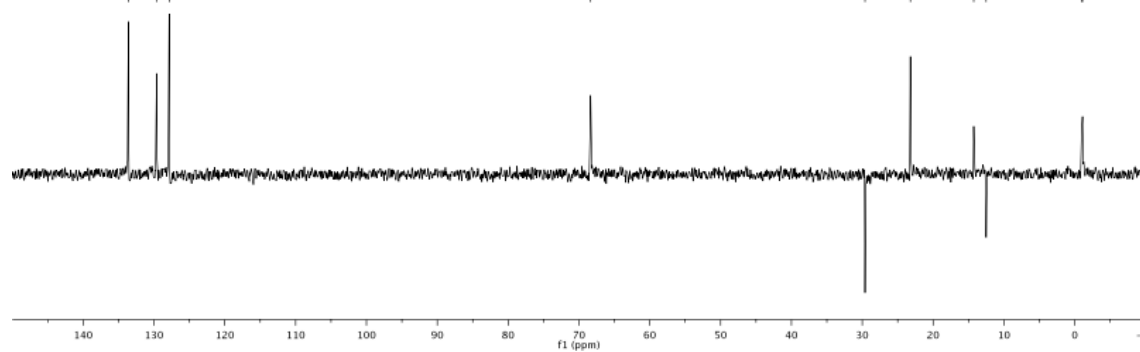
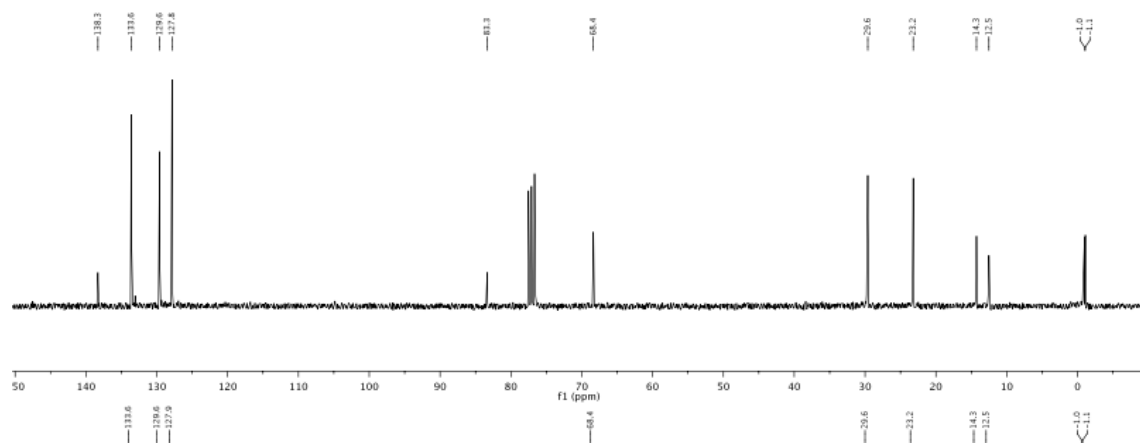
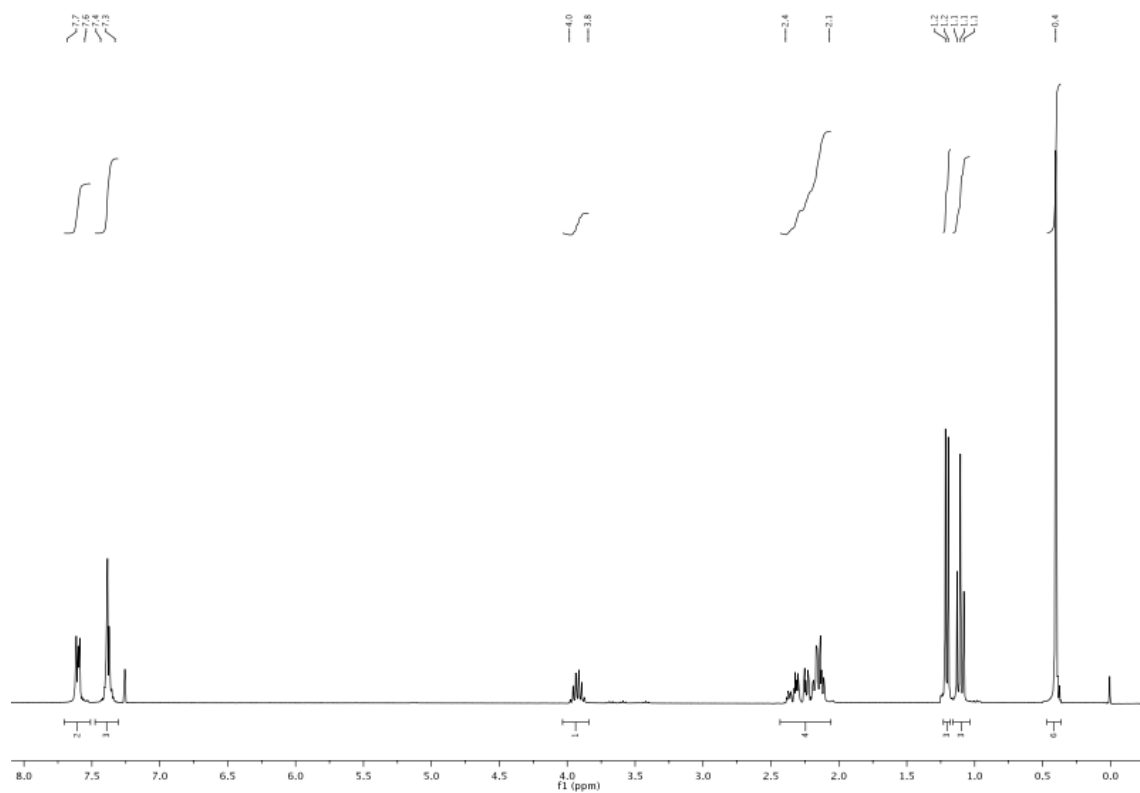


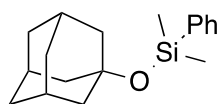
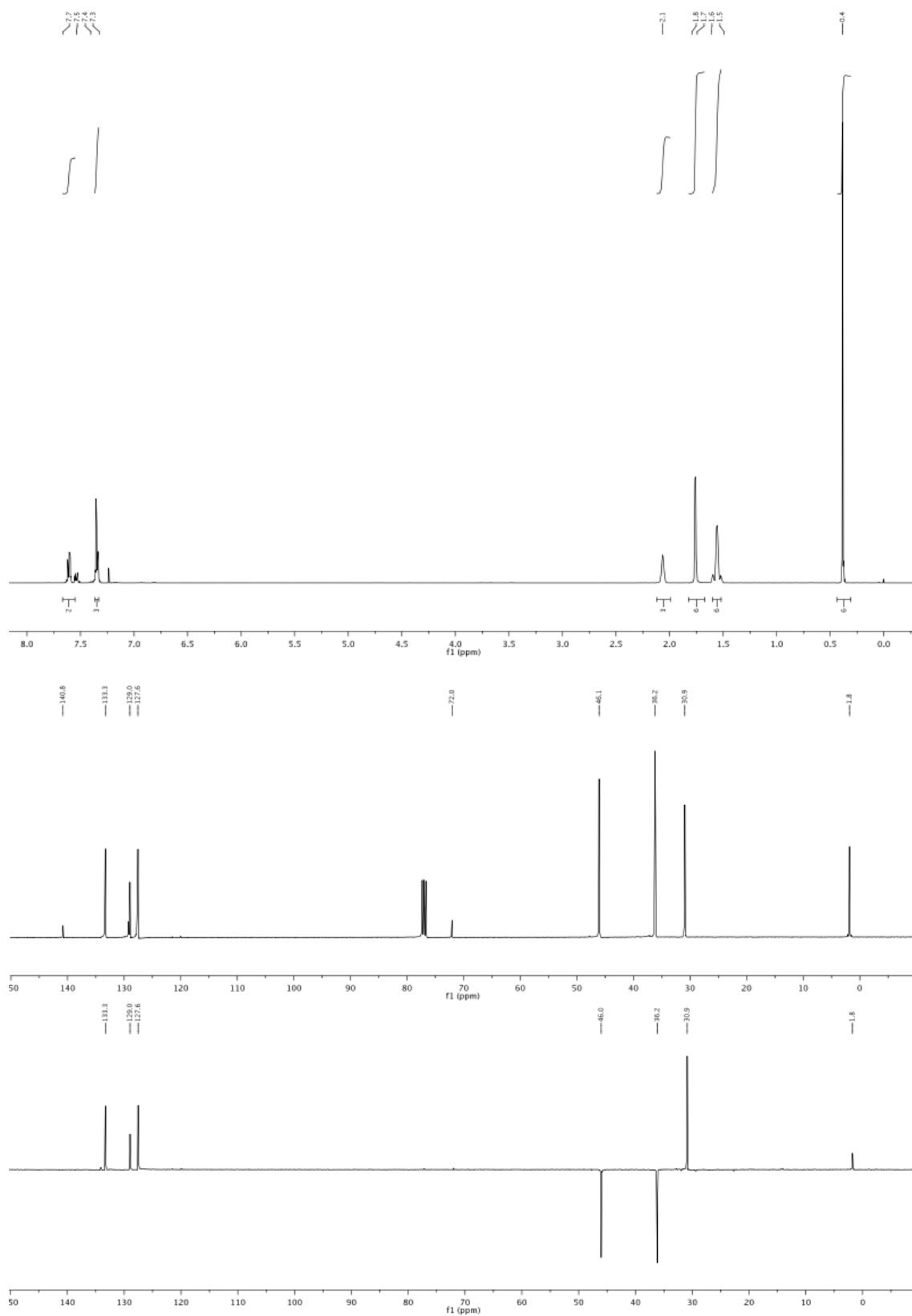
**2c₁**

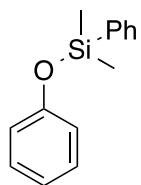
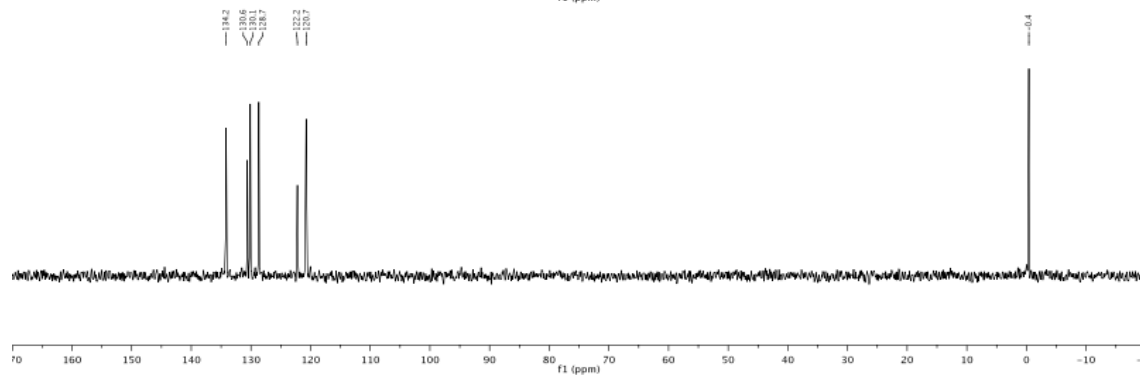
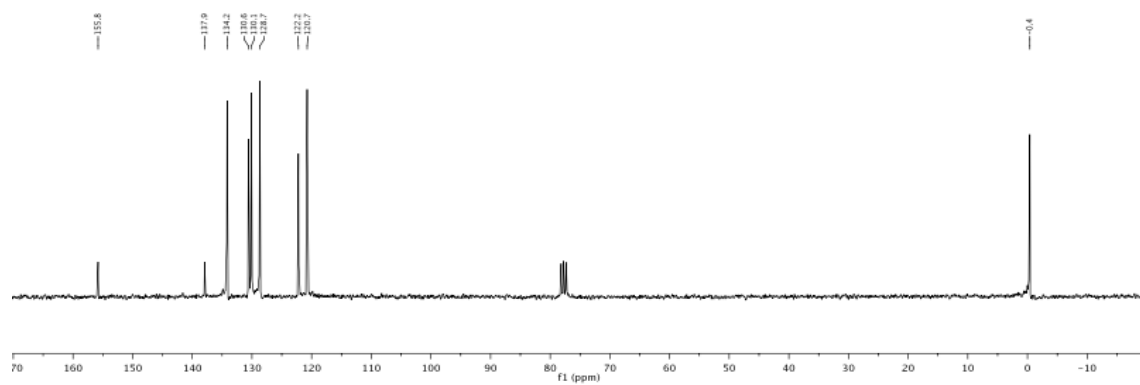
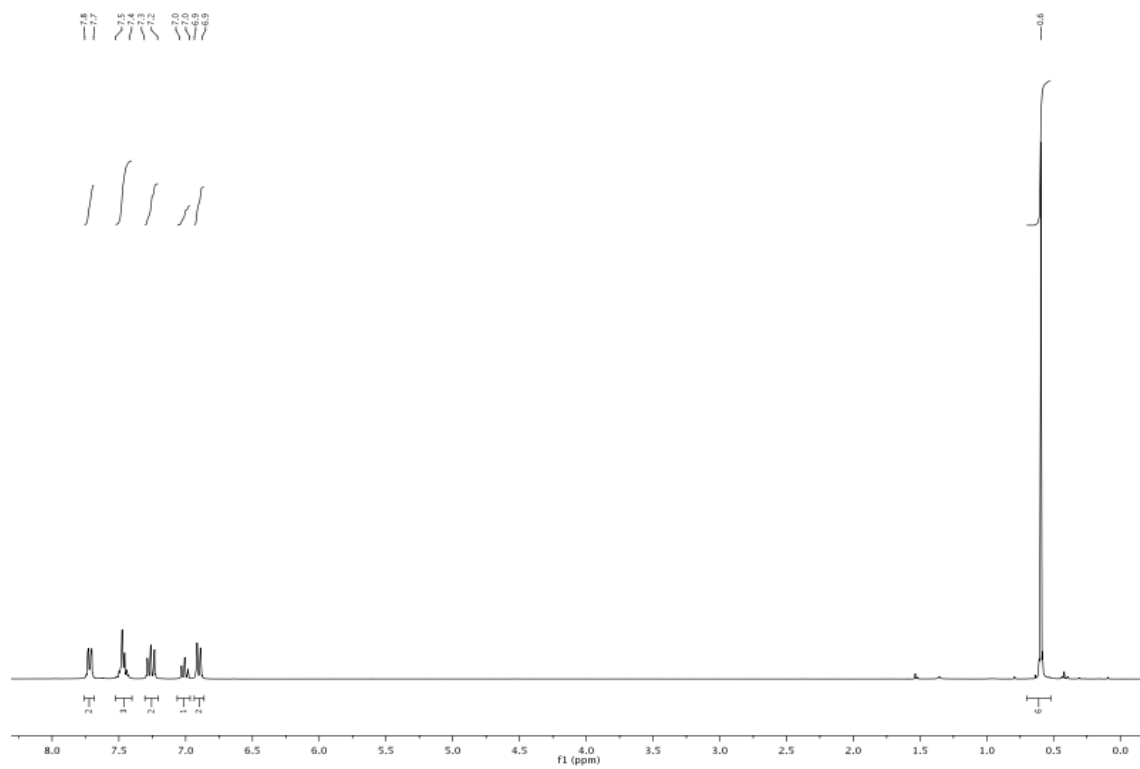
**2d₁**

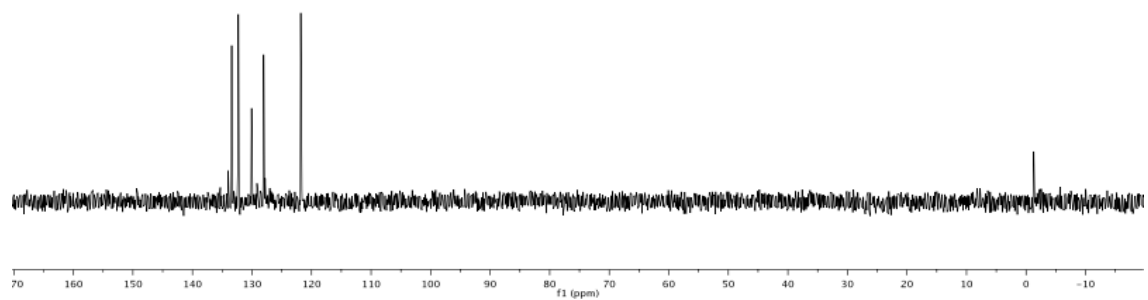
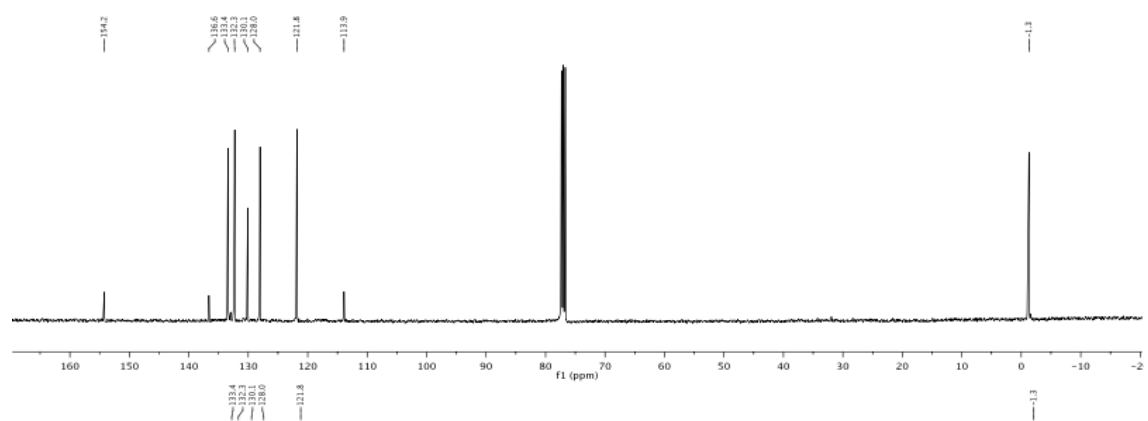
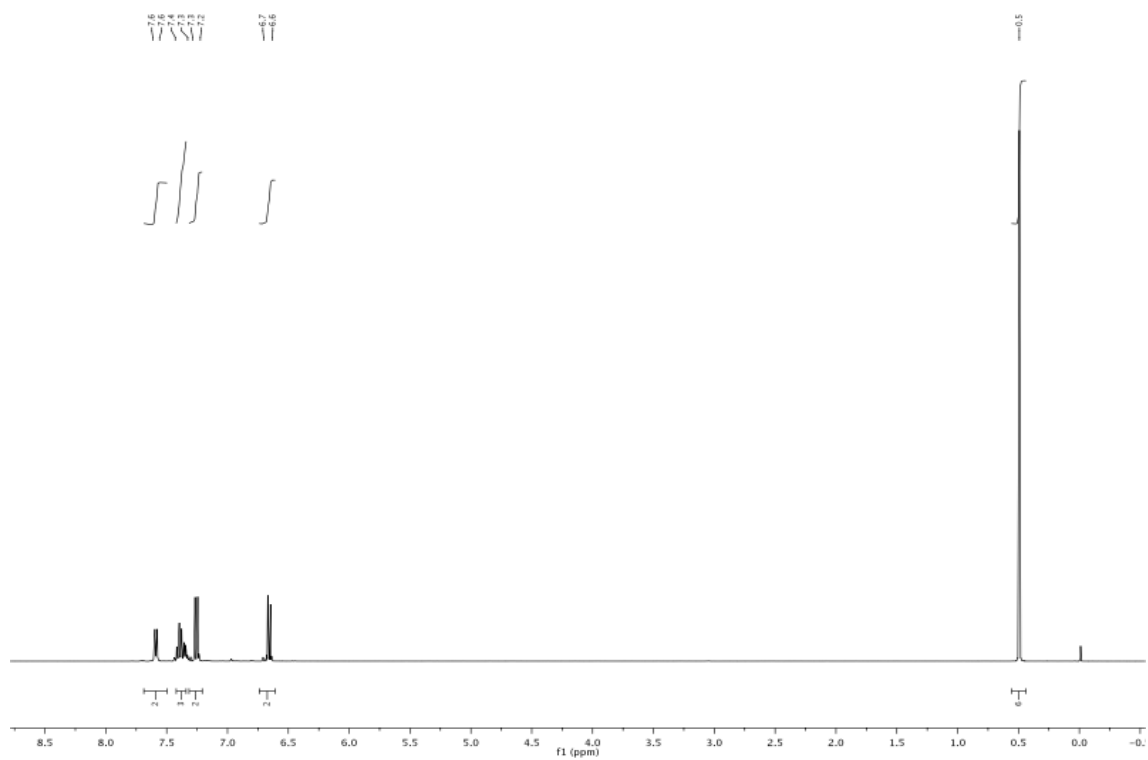
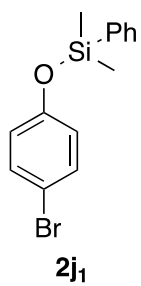


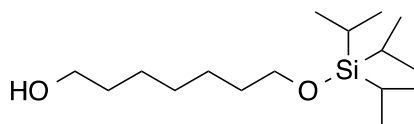
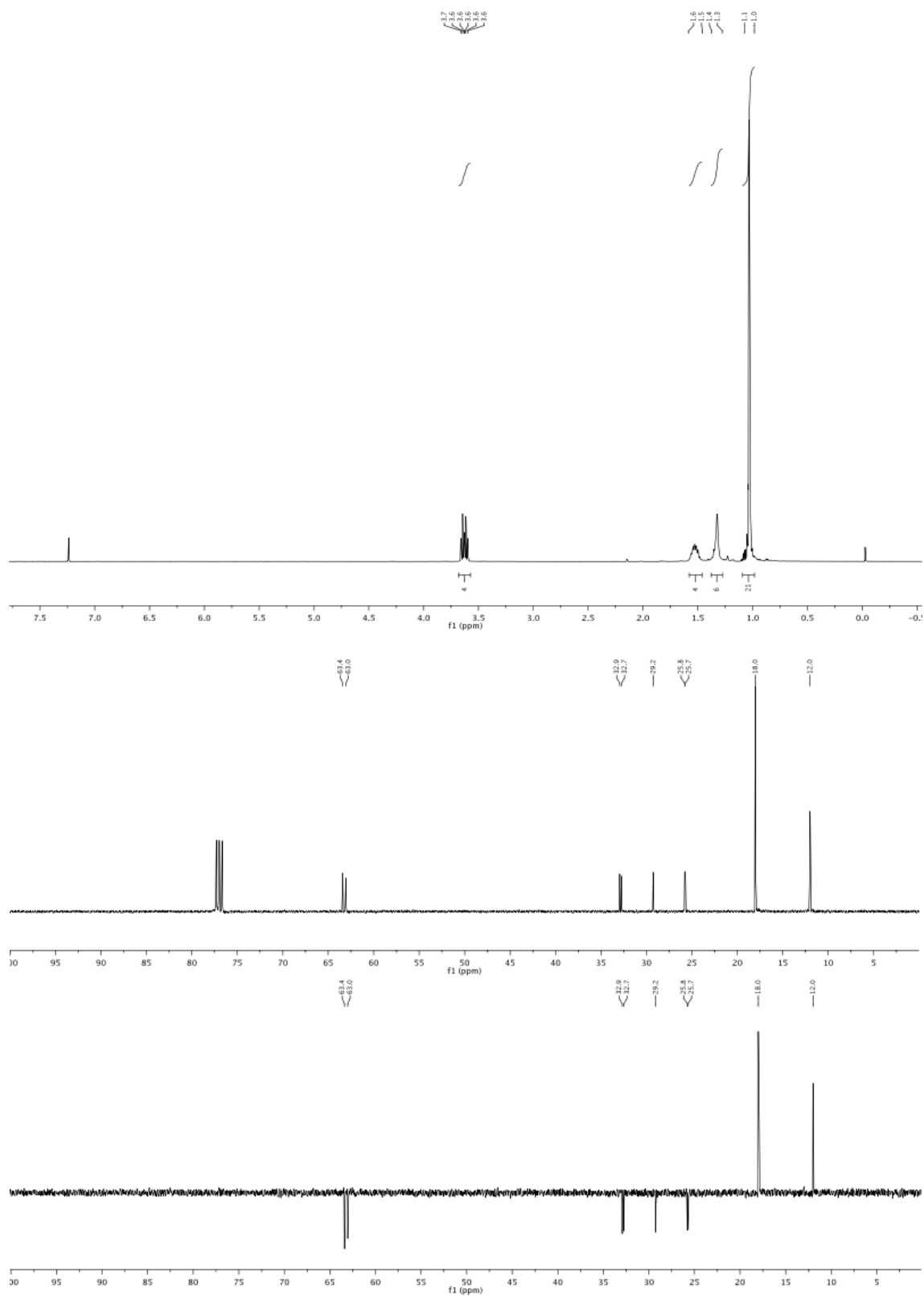
**2f₁**

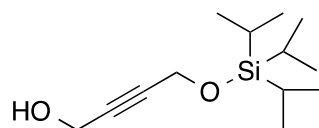
**2g₁**

**2h₁**

**2i₁**



 $2k_6$ 

**2l₆**