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Supporting Information

Base-catalyzed addition of silylacetylenes to ketones: a route to protected tertiary propargyl alcohols

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CONTENT

GENERAL INFORMATION

Air- and moisture-sensitive reactions were carried out under an argon atmosphere using standard Schlenk techniques. Bis(trimethylsilyl)acetylene was purchased from Sigma Aldrich (Merck, CAS: 14630-40-1, 99%) and used as received. Bis(trimethylsilyl)amide was purchased as the 1M solution in THF from Sigma Aldrich (CAS: 40949-94-8) and used as received. Solvents used for all experiments were purchased from Honeyweel or Sigma Aldrich (Merck), dried over calcium hydride (CaH_2) and purified by distillation. Most of the reagents (ketones and aldehydes) were commercially available and purchased from Sigma Aldrich (Merck), ABCR GmBH, Ambeed, or Apollo Scientific, and used as received. The progress of reactions (conversion of ketones) was monitored by GC chromatography using Bruker Scion 460-GC and Agilent 5977B GC/MSD with Agilent 8860 GC System). The structures of products were determined by NMR spectroscopy and MS spectrometry. The ^{1}H NMR (400 or 600 MHz), ^{13}C NMR (101 or 151 MHz) and ^{29}Si NMR (80 or 119 MHz) spectra were recorded on Bruker Avance III HD NanoBay spectrometer, using benzene-d_6 (C_6D_6), chloroform-d_1 ($CDCl_3$), or acetonitrile-d_3 (CD_3CN) as the solvents. Deuterated solvents were purchased from Merck and Deutero GmbH and used as received.

GENERAL SYNTHETIC PROCEDURES

KHMDS-CATALYZED ADDITION OF SILYLACETYLENES TO DIFFERENT KETONES

Compounds 3a-3d, 3f, 3k-3r, 3t-3x, 4a, 4c, and 4d

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), ketone (1 mmol), and bis(trimethylsilyl)acetylene (3 mmol, 0.51 g) were added under an argon atmosphere. Subsequently, 30 µL of 1M solution of KHMDS in THF was added (3 mol%). The reaction mixture was stirred at 80°C for a specified time (0.5-16 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **3a-3d**, **3f**, **3k-3r, 3t-3x, 4a**, **4c**, and **4d**. The pure products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

Compounds 3e, 3g-3j, 3s, and 4b

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), ketone (1 mmol), and bis(trimethylsilyl)acetylene (3 mmol, 0.51 g) were added under an argon atmosphere. Subsequently, 60 µL of 1M solution of KHMDS in THF was added (6 mol%). The reaction mixture was stirred at 80°C for a specified time (2-20 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **3e, 3g-3j, 3s, and 4b**. The pure products were identified by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopies and MS spectrometry.

Compounds 5a, 5c, 5d, 5f-5j

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), ketone (1 mmol), and silylacetylene (**2b**-**2e**; 3 mmol) were added under an argon atmosphere. Subsequently, 30 µL of 1M solution of KHMDS in THF was added (3 mol%). The reaction mixture was stirred at 80°C for a specified time (1-3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **5a, 5c, 5d, 5f-5j**. The pure products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

Compounds 5b and 5e

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), ketone (1 mmol), and 1-phenyl-2-trimethylsilylacetylene (**2b**; 3 mmol) were added under an argon atmosphere. Subsequently, 60 µL of 1M solution of KHMDS in THF was added (6 mol%). The reaction mixture was stirred at 80°C for a specified time (1-2 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **5b and 5e**. The pure products were identified by ^{1}H, ^{13}C, ^{19}F, and ^{29}Si NMR spectroscopies and MS spectrometry.

KHMDS-CATALYZED ADDITION OF BTMSA TO DIFFERENT ALDEHYDES

Compounds 7a and 7b

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), aldehyde (1 mmol), and bis(trimethylsilyl)acetylene (6 mmol, 1.02 g) were added under an argon atmosphere. Subsequently, 30 µL of 1M solution of KHMDS in THF was added (3 mol%). The reaction mixture was stirred at 80°C for 2 hours. After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **7a** and **7b**. The pure products were identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

KHMDS-CATALYZED SCALED UP ADDITION OF 2a TO 1a.

To a 50 mL vial, a magnetic stirring bar was added and stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (20 mL), acetophenone (10 mmol, 1.2 g), bis(trimethylsilyl)acetylene (30 mmol, 5.1 g), and solution of KHMDS in THF (1M; 3 mol%) were added under an argon atmosphere. The reaction mixture was stirred at 80°C for a specified time (2 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation (heat gun) under a high vacuum (0.47 mbar), to give a pure product **3a** (2.84 g, 98% yield).

KHMDS-CATALYZED ADDITION OF BTMSA TO ACETOPHENONE IN THE PRESENCE OF TEMPO

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), acetophenone (1 mmol, 0.12 g), bis(trimethylsilyl)acetylene (3 mmol, 0.51 g), and TEMPO (1 mmol, 0.156 g) were added under an argon atmosphere. Subsequently, 30 µL of 1M solution of KHMDS in THF was added (3 mol%). The reaction mixture was stirred at 80°C for a specified time (0.5-16 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude products were separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give a pure product **3a** (90%).

PROTODESILYLATION OF 3a USING KF/METHANOL SYSTEM

To a 10 mL vial equipped with a magnetic stirring bar, potassium fluoride (2.5 mmol, 0.145 g), methanol (2 mL), and **3a** (0.5 mmol, 0.145 g) were added. The reaction mixture was stirred at rt for a specified time (overnight). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* extraction with Et_2O/H_2O. Combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to give corresponding product **8a** (99%, 0.072 g).

SYNTHESIS OF 2f

In accordance with 10.1002/cctc.202200794. To a 25mL vial equipped with a magnetic stirring bar, potassium bis(trimethylsilyl)amide (0.03 mmol, 3 mol%) was added and stored under a high vacuum (10 min.). Subsequently, dry acetonitrile (1 mL), dry THF (0.5 mL), triisopropylsilylacetylene (10 mmol, 1,82 g), and bis(trimethylsilyl)acetylene (20 mmol, 3.4 g) were added under an argon atmosphere. The reaction mixture was stirred at rt for 3 hours. After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum, to give corresponding product **29**.

SYNTHESIS OF 5k

A 25 mL vial equipped with a magnetic stirring bar was stored under a high vacuum (10 min.). Subsequently, 1,2-dimethoxyethane (2 mL), ketone (1 mmol), and silylacetylene (**2f**; 3 mmol) were added under an argon atmosphere. Subsequently, 30 µL of 1M solution of KHMDS in THF was added (3 mol%). The reaction mixture was stirred at 80°C for a specified time (1-3 h). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* bulb-to-bulb distillation under a high vacuum (0.47 mbar), to give corresponding products **5k**. The pure product was identified by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies and MS spectrometry.

SELECTIVE PROTODESILYLATION OF 5i USING KF/METHANOL SYSTEM

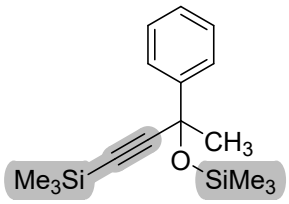
To a 10 mL vial equipped with a magnetic stirring bar, potassium fluoride (2.5 mmol, 0.145 g), methanol (2 mL), and **5i** (0.5 mmol, 0.194 g) were added. The reaction mixture was stirred at rt for a specified time (overnight). After this time, solvent and volatile residues were evaporated under reduced pressure. Next, the crude product was separated *via* extraction with Et_2O/H_2O. Combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to give corresponding product **8b** (99%, 0.156 g).

DERIVATIZATION OF 5e TO 9a UNDER ACIDIC CONDITIONS

To a 10 mL vial equipped with a magnetic stirring bar, 2M solution of HCl in Et_2O (2.5 mmol, 1.25 cm^3), Et_2O (2 mL), and **5e** (0.5 mmol, 0.163 g) were added. The reaction mixture was stirred at rt for a 1 hour. After this time, 2.5 mmol of K_2CO_3 were added to neutralize an acid. Next, the crude product was separated *via* extraction with Et_2O/H_2O. Combined organic layers were dried over anhydrous $MgSO_4$ and evaporated to give corresponding product **9a** (98%, 0.159 g).

CHARACTERIZATION DATA FOR ALL PRODUCTS

Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3a)



Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 95% yield.[1]

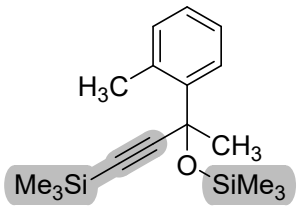
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.28 – 7.16 (m, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 1.38 (s, 3H), -0.07 (s, 9H), -0.13 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 145.7, 133.0, 128.2, 126.7, 108.9, 90.8, 77.5, 77.2, 76.8, 71.1, 36.2, 1.9, -0.1.

^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm) = 16.2, -17.8.

EI-MS m/z (rel. int.): 275 (100%, [M-CH_3]), 217 (5), 185 (15).

Trimethyl(3-(o-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3b)



Trimethyl(3-(o-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.78 – 7.69 (m, 1H), 7.22 – 7.09 (m, 3H), 2.59 (s, 3H), 1.80 (s, 3H), 0.21 (s, 9H), 0.20 (s, 9H).

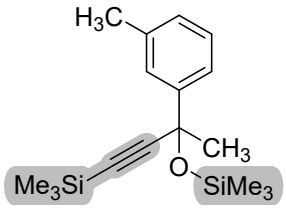
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.4, 135.6, 132.3, 127.4, 125.8, 125.6, 109.6, 90.4, 71.8, 32.9, 21.5, 2.0, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 14.9, -18.2.

EI-MS m/z (rel. int.): 289 (100%, [M-CH_3]), 231 (10), 183 (5).

EA: $C_{17}H_{28}OSi_2$ (304.168): calcd. C 67.04, H 9.27; found C 67.18, H 9.31.

Trimethyl(3-(m-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3c)



Trimethyl(3-(m-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 – 7.37 (m, 2H), 7.25 – 7.18 (m, 1H), 7.11 – 7.03 (m, 1H), 2.39 (s, 3H), 1.71 (s, 3H), 0.24 (s, 9H), 0.17 (s, 9H).

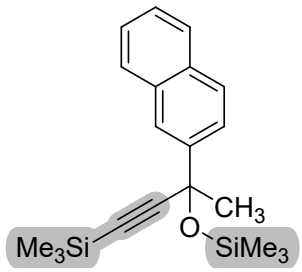
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 146.9, 137.6, 128.0, 125.9, 122.3, 109.7, 90.2, 71.6, 36.2, 21.8, 1.9, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.6, -18.0.

EI-MS m/z (rel. int.): 289 (100%, [M-CH_3]), 214 (15), 199 (45).

EA: $C_{17}H_{28}OSi_2$ (304.168): calcd. C 67.04, H 9.27; found C 66.88, H 9.22.

Trimethyl(3-(naphthalen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3d)



Trimethyl(3-(naphthalen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 91% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.09 (d, *J* = 2.0 Hz, 1H), 7.93 – 7.81 (m, 3H), 7.78 – 7.67 (m, 1H), 7.52 – 7.44 (m, 2H), 1.81 (s, 3H), 0.28 (s, 9H), 0.21 (s, 9H).

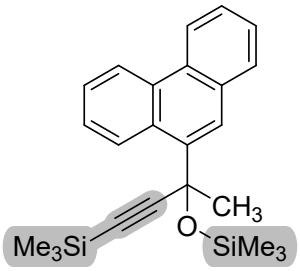
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 144.3, 133.1, 132.8, 128.5, 127.9, 127.7, 126.1, 125.9, 124.0, 123.6, 109.4, 90.7, 71.7, 36.0, 1.9, 0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.1, -17.9.

EI-MS m/z (rel. int.): 325 (100%, [M-CH_3]), 235 (10), 155 (35).

EA: $C_{20}H_{28}OSi_2$ (340.168): calcd. C 70.53, H 8.29; found C 70.62, H 8.31.

Trimethyl(3-(phenanthren-9-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3e)



Trimethyl(3-(phenanthren-9-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.98 – 8.91 (m, 1H), 8.81 – 8.75 (m, 1H), 8.71 – 8.65 (m, 1H), 8.29 (s, 1H), 7.92 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.78 – 7.56 (m, 4H), 2.11 (s, 3H), 0.29 (s, 9H), 0.20 (s, 9H).

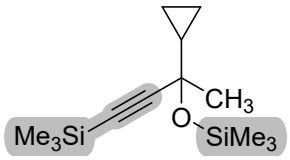
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 138.9, 131.7, 131.3, 130.6, 129.4, 129.3, 128.1, 126.9, 126.7, 126.1, 125.6, 125.0, 123.2, 122.5, 109.9, 91.6, 72.8, 33.8, 1.9, -0.1.

^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm) = 16.1, -19.2.

EI-MS m/z (rel. int.): 390 (10%, $[M]^+$), 375 (100, $[M\text{-}CH_3]$), 317 (20).

EA: $C_{24}H_{30}OSi_2$ (390.184): calcd. C 73.79, H 7.74; found C 74.09, H 7.77.

(3-Cyclopropyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3f)



(3-Cyclopropyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.53 (s, 3H), 1.12 – 1.00 (m, 1H), 0.67 – 0.51 (m, 1H), 0.49 – 0.34 (m, 3H), 0.20 (s, 9H), 0.17 (s, 9H).

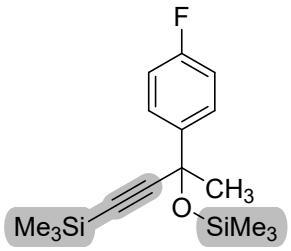
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 107.7, 88.8, 71.2, 32.3, 22.6, 2.6, 2.3, 2.1, -0.1.

^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm) = 13.1, -18.4.

EI-MS m/z (rel. int.): 239 (100%, $[M\text{-}CH_3]$), 213 (35), 147 (35).

EA: $C_{13}H_{26}OSi_2$ (254.152): calcd. C 61.35, H 10.30; found C 61.39, H 10.28.

(3-(4-Fluorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3g)



(3-(4-Fluorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 78% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 – 7.49 (m, 2H), 7.07 – 6.91 (m, 2H), 1.68 (s, 3H), 0.22 (s, 9H), 0.14 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.12 (d, *J* = 244.9 Hz), 142.89 (d, *J* = 3.1 Hz), 126.91 (d, *J* = 8.1 Hz), 114.77 (d, *J* = 21.3 Hz), 109.1, 90.7, 77.5, 77.2, 76.8, 71.1, 36.3, 1.8, -0.1.

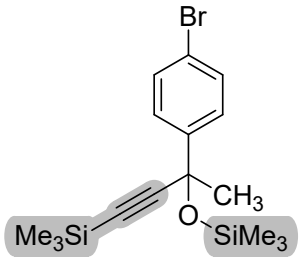
^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) = -116.3.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.0, -17.9.

EI-MS m/z (rel. int.): 293 (100%, [M-CH_3]), 123 (15), 73 (10).

EA: $C_{16}H_{25}FOSi_2$ (308.143): calcd. C 62.28, H 8.17; found C 62.14, H 8.18.

(3-(4-Bromophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3h)



(3-(4-Bromophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.39 (m, 4H), 1.68 (s, 3H), 0.23 (s, 9H), 0.17 (s, 9H).

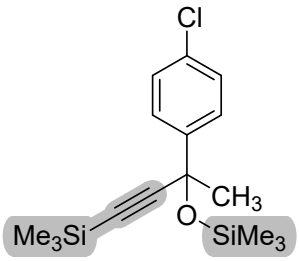
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 146.3, 131.2, 127.1, 121.2, 108.8, 90.8, 71.2, 36.1, 1.9, -0.1.

^{29}Si NMR (79 MHz, $CDCl_3$) δ (ppm) = 16.3, -17.8.

EI-MS m/z (rel. int.): 355 (100%, [M-CH_3]), 182 (50), 155 (40).

EA: $C_{16}H_{25}BrOSi_2$ (368.063): calcd. C 52.02, H 6.82; found C 51.87, H 6.84.

(3-(4-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3i)



(3-(4-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilanewas obtained as pale-yellow oil in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.30 (dd, *J* = 8.6, 1.4 Hz, 2H), 1.68 (s, 3H), 0.23 (s, 9H), 0.17 (s, 9H).

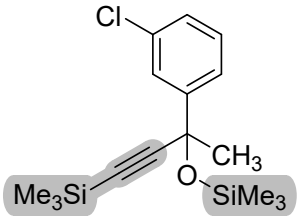
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 145.7, 133.0, 128.2, 126.7, 108.9, 90.8, 77.5, 77.2, 76.8, 71.1, 36.2, 1.9, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.2, -17.8.

EI-MS m/z (rel. int.): 309 (100%, [M-CH_3]), 162 (30), 139 (50).

EA: $C_{16}H_{25}ClOSi_2$ (324.113): calcd. C 59.13, H 7.75; found C 59.21, H 7.69.

(3-(3-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3j)



(3-(3-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilanewas obtained as pale-yellow oil in 76% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 (t, *J* = 1.9 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.25 – 7.18 (m, 2H), 1.66 (s, 3H), 0.20 (s, 9H), 0.15 (s, 9H).

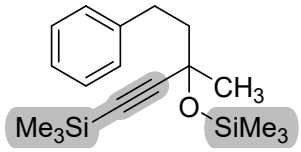
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.3, 134.0, 129.4, 127.4, 125.6, 123.4, 108.7, 91.0, 71.1, 36.1, 1.8, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.4, -17.7.

EI-MS m/z (rel. int.): 309 (100%, [M-CH_3]), 138 (35), 73 (30).

EA: $C_{16}H_{25}ClOSi_2$ (324.113): calcd. C 59.13, H 7.75; found C 59.32, H 7.79.

Trimethyl((3-methyl-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane (3k)



Trimethyl((3-methyl-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.34 – 7.25 (m, 2H), 7.24 – 7.13 (m, 3H), 2.95 – 2.55 (m, 2H), 2.05 – 1.78 (m, 2H), 1.49 (s, 3H), 0.23 (s, 9H), 0.20 (s, 9H).

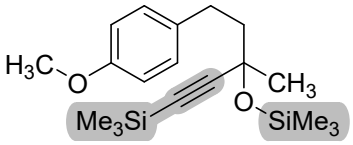
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.1, 128.9, 128.8, 126.1, 110.3, 89.3, 77.8, 77.5, 77.2, 69.9, 47.4, 31.7, 2.4, 0.3.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.8, -18.3.

EI-MS m/z (rel. int.): 303 (10%, [M-CH_3]), 213 (100), 155 (15).

EA: $C_{18}H_{30}OSi_2$ (318.184): calcd. C 67.86, H 9.49; found C 67.78, H 9.54.

((5-(4-Methoxyphenyl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (3l)



((5-(4-Methoxyphenyl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 79% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.14 (d, *J* = 8.6 Hz, 2H), 6.92 – 6.77 (m, 2H), 3.80 (s, 3H), 2.80 – 2.64 (m, 2H), 2.06 – 1.73 (m, 1H), 1.49 (s, 3H), 0.23 (s, 9H), 0.20 (s, 9H).

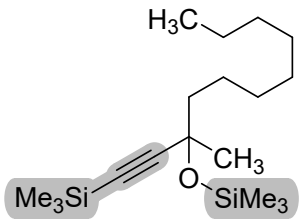
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 157.8, 134.8, 129.4, 113.9, 110.0, 89.0, 69.6, 55.4, 47.3, 31.4, 30.4, 2.1, -0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.7, -18.4.

EI-MS m/z (rel. int.): 317 (5%), 258 (30), 121 (100).

EA: $C_{19}H_{32}O_2Si_2$ (348.194): calcd. C 65.46, H 9.25; found C 65.53, H 9.24.

Trimethyl((3-methyl-1-(trimethylsilyl)undec-1-yn-3-yl)oxy)silane (3m)



Trimethyl((3-methyl-1-(trimethylsilyl)undec-1-yn-3-yl)oxy)silane was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.62 – 1.52 (m, 2H), 1.41 (s, 3H), 1.32 – 1.23 (m, 10H), 0.91 – 0.85 (m, 3H), 0.18 (s, 9H), 0.16 (s, 9H).

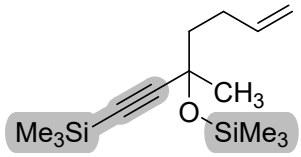
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 110.5, 88.4, 69.8, 45.1, 32.1, 31.3, 29.8, 29.7, 29.4, 24.7, 22.8, 14.3, 2.1, -0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.1, -18.6.

EI-MS m/z (rel. int.): 311 (5%, [M-CH_3]), 213 (100), 147 (5).

EA: $C_{18}H_{38}OSi_2$ (326.246): calcd. C 66.18, H 11.73; found C 66.01, H 11.75.

Trimethyl((3-methyl-1-(trimethylsilyl)hept-6-en-1-yn-3-yl)oxy)silane (3n)



Trimethyl((3-methyl-1-(trimethylsilyl)hept-6-en-1-yn-3-yl)oxy)silane was obtained as pale-yellow oil in 75% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.94 – 5.78 (m, 1H), 5.08 – 4.89 (m, 2H), 2.32 – 2.12 (m, 2H), 1.79 – 1.61 (m, 2H), 1.44 (s, 3H), 0.19 (s, 9H), 0.17 (s, 9H).

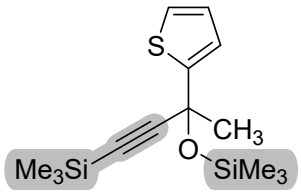
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.3, 114.6, 110.3, 89.2, 69.8, 44.6, 31.7, 29.6, 2.4, 0.3.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.6, -18.4.

EI-MS m/z (rel. int.): 253 (5%, [M-CH_3]), 213 (100), 147 (10).

EA: $C_{14}H_{28}OSi_2$ (268.168): calcd. C 62.62, H 10.51; found C 62.54, H 10.47.

Trimethyl(3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3o)



Trimethyl(3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane was obtained as pale-yellow oil in 70% yield.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.18 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.08 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.91 (dd, *J* = 5.0, 3.5 Hz, 1H), 1.82 (s, 3H), 0.21 (s, 9H), 0.15 (s, 9H).

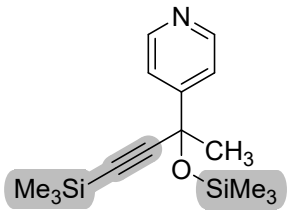
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 152.4, 126.4, 124.5, 123.5, 108.5, 89.9, 68.9, 36.3, 1.7, -0.2.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.5, -17.7.

EI-MS m/z (rel. int.): 281 (100%, [M-CH_3]), 207 (5), 110 (30).

EA: $C_{14}H_{24}OSSi_2$ (296.109): calcd. C 56.70, H 8.16; found C 56.84, H 8.11.

4-(4-(Trimethylsilyl)-2-((trimethylsilyl)oxy)but-3-yn-2-yl)pyridine (3p)



4-(4-(Trimethylsilyl)-2-((trimethylsilyl)oxy)but-3-yn-2-yl)pyridine was obtained as pale-yellow oil in 68% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.60 – 8.45 (m, 2H), 7.57 – 7.37 (m, 2H), 1.64 (s, 3H), 0.19 (s, 9H), 0.15 (s, 9H).

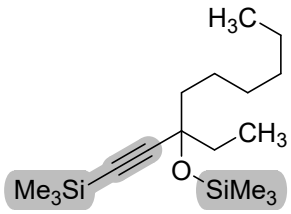
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 155.9, 151.1, 149.8, 121.3, 120.1, 107.8, 91.4, 70.6, 35.6, 1.8, -0.2.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 17.0, -17.6.

EI-MS m/z (rel. int.): 276 (100%, [M-CH_3]), 248 (5), 155 (10).

EA: $C_{15}H_{25}NOSi_2$ (291.147): calcd. C 61.80, H 8.64; found C 62.01, H 8.69.

((3-Ethyl-1-(trimethylsilyl)non-1-yn-3-yl)oxy)trimethylsilane (3q)



((3-Ethyl-1-(trimethylsilyl)non-1-yn-3-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =

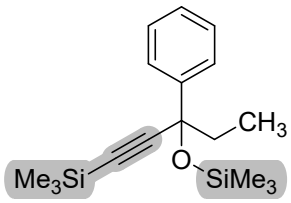
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 109.7, 89.6, 73.4, 42.6, 35.7, 32.0, 29.6, 24.3, 22.8, 14.3, 8.9, 2.2, -0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 12.9, -18.7.

EI-MS m/z (rel. int.): 297 (5%, [M-CH_3]), 283 (75), 227 (100).

EA: $C_{17}H_{36}OSi_2$ (312.230): calcd. C 65.31, H 11.61; found C 65.33, H 11.60.

Trimethyl((3-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane (3r)



Trimethyl((3-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56 – 7.43 (m, 2H), 7.32 – 7.24 (m, 2H), 7.22 – 7.15 (m, 1H), 1.90 – 1.59 (m, 2H), 0.83 (t, *J* = 7.3 Hz, 3H), 0.17 (s, 9H), 0.06 (s, 9H).

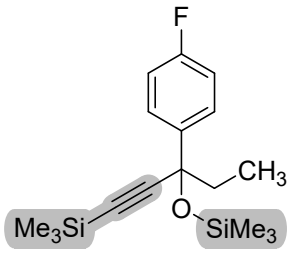
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 145.9, 127.9, 127.1, 125.8, 108.3, 91.6, 75.5, 40.9, 9.1, 1.8, -0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.9, -18.1.

EI-MS m/z (rel. int.): 275 (100%), 105 (40), 73 (30).

EA: $C_{17}H_{28}OSi_2$ (304.168): calcd. C 67.04, H 9.27; found C 66.94, H 9.28.

((3-(4-Fluorophenyl)-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (3s)



((3-(4-Fluorophenyl)-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.44 (m, 2H), 7.11 – 6.78 (m, 2H), 2.05 – 1.65 (m, 2H), 1.01 – 0.65 (m, 3H), 0.23 (s, 9H), 0.12 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.12 (d, *J* = 244.8 Hz), 141.70 (d, *J* = 3.1 Hz), 127.46 (d, *J* = 8.1 Hz), 114.61 (d, *J* = 21.4 Hz), 108.0, 92.0, 75.1, 41.0, 9.1, 1.8, -0.1.

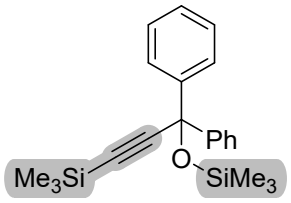
^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -116.4.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.1, -18.0.

EI-MS m/z (rel. int.): 293 (100%), 123 (30), 73 (15).

EA: $C_{17}H_{27}FOSi_2$ (322.158): calcd. C 63.30, H 8.44; found C 63.24, H 8.50.

(3,3-Diphenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (3t)



(3,3-Diphenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 97% yield.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.73 – 7.43 (m, 4H), 7.37 – 7.22 (m, 4H), 7.22 – 7.13 (m, 2H), 0.23 (s, 9H), 0.12 (s, 9H).

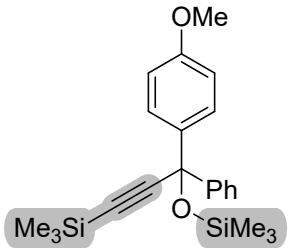
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 147.0, 128.4, 127.5, 126.4, 108.6, 93.4, 76.3, 2.1, 0.2.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 17.4, -17.6.

EI-MS m/z (rel. int.): 337 (10%, [M-CH_3]), 275 (45), 190 (100).

EA: $C_{21}H_{28}OSi_2$ (352.168): calcd. C 71.53, H 8.00; found C 71.54, H 8.02.

((1-(4-Methoxyphenyl)-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane (3u)



((1-(4-Methoxyphenyl)-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.55 (m, 2H), 7.55 – 7.46 (m, 2H), 7.36 – 7.26 (m, 2H), 7.27 – 7.17 (m, 1H), 6.90 – 6.71 (m, 2H), 3.79 (s, 3H), 0.27 (s, 9H), 0.15 (s, 9H).

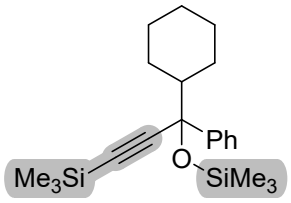
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.1, 159.1, 147.3, 139.3, 128.3, 127.7, 127.4, 126.4, 113.7, 108.8, 93.1, 75.9, 55.6, 2.1, 0.2.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 17.1, -17.7.

EI-MS m/z (rel. int.): 368 (100%, [M-CH_3]), 306 (5), 73 (45).

EA: $C_{22}H_{30}O_2Si_2$ (382.178): calcd. C 69.06, H 7.90; found C 68.97, H 7.88.

((1-Cyclohexyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane (3v)



((1-Cyclohexyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.52 – 7.41 (m, 2H), 7.29 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 1.90 – 1.73 (m, 1H), 1.71 – 1.42 (m, 4H), 1.39 – 1.25 (m, 1H), 1.15 – 0.81 (m, 5H), 0.17 (s, 9H), -0.00 (s, 9H).

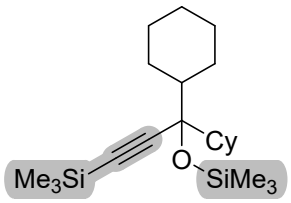
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 145.1, 127.5, 127.0, 126.6, 107.8, 92.4, 78.3, 51.8, 27.8, 27.5, 26.6, 26.5, 1.7, 0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.6, -18.2.

EI-MS m/z (rel. int.): 343 (5%, [M-CH_3]), 275 (100), 245 (10).

EA: $C_{21}H_{34}OSi_2$ (358.215): calcd. C 70.32, H 9.56; found C 70.36, H 9.56.

(3,3-Dicyclohexyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (3w)



(3,3-Dicyclohexyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.87 – 1.72 (m, 8H), 1.69 – 1.62 (m, 2H), 1.61 – 1.45 (m, 2H), 1.32 – 1.03 (m, 10H), 0.18 (s, 9H), 0.17 (s, 9H).

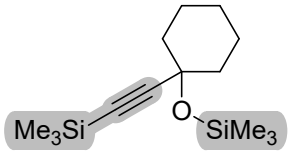
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 108.3, 91.0, 79.3, 44.8, 28.7, 26.9, 26.8, 26.8, 26.8, 2.9, 0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 11.9, -18.9.

EI-MS m/z (rel. int.): 349 (5%, [M-CH_3]), 281 (100), 73 (15).

EA: $C_{21}H_{40}OSi_2$ (364.262): calcd. C 69.16, H 11.06; found C 69.03, H 11.02.

Trimethyl((1-((trimethylsilyl)ethynyl)cyclohexyl)oxy)silane (3x)



Trimethyl((1-((trimethylsilyl)ethynyl)cyclohexyl)oxy)silane was obtained as pale-yellow oil in 91% yield.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 1.91 – 1.76 (m, 2H), 1.74 – 1.42 (m, 7H), 1.34 – 1.15 (m, 1H), 0.21 (s, 9H), 0.19 (s, 9H).

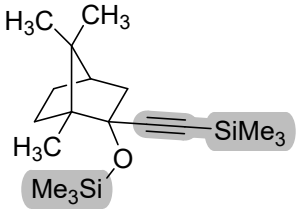
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 110.6, 90.0, 70.6, 41.7, 25.8, 23.6, 2.5, 0.4.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.0, -18.6.

EI-MS m/z (rel. int.): 253 (15%, [M-CH_3]), 225 (90), 73 (100).

EA: $C_{14}H_{28}OSi_2$ (268.168): calcd. C 62.62, H 10.51; found C 62.59, H 10.50.

Trimethyl(((1S,2S,4R)-1,7,7-trimethyl-2-((trimethylsilyl)ethynyl)bicyclo[2.2.1]heptan-2-yl)oxy)silane (4a)



Trimethyl(((1S,2S,4R)-1,7,7-trimethyl-2-((trimethylsilyl)ethynyl)bicyclo[2.2.1]heptan-2-yl)oxy)-silane was obtained as pale-yellow oil in 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 2.23 – 2.06 (m, 1H), 1.96 – 1.84 (m, 1H), 1.73 – 1.57 (m, 2H), 1.45 – 1.28 (m, 1H), 1.01 (s, 3H), 0.86 (s, 3H), 0.84 (s, 3H), 0.16 (s, 9H), 0.15 (s, 9H).

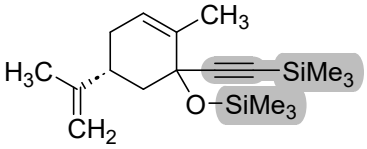
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 110.6, 88.4, 79.0, 54.2, 51.5, 48.2, 45.9, 31.9, 27.0, 21.8, 21.2, 10.9, 2.0, 0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 12.0, -18.9.

EI-MS m/z (rel. int.): 322 (5%, [M]), 307 (15, [M-CH_3]), 197 (100).

EA: $C_{18}H_{34}OSi_2$ (322.215): calcd. C 67.01, H 10.62; found C 66.93, H 10.65.

Trimethyl(((5R)-2-methyl-5-(prop-1-en-2-yl)-1-((trimethylsilyl)ethynyl)cyclohex-2-en-1-yl)oxy)silane (4b)



Trimethyl(((5R)-2-methyl-5-(prop-1-en-2-yl)-1-((trimethylsilyl)ethynyl)cyclohex-2-en-1-yl)oxy)silane was obtained as pale-yellow oil in 72% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 5.55 – 5.25 (m, 1H), 4.92 – 4.52 (m, 2H), 2.58 – 2.42 (m, 1H), 1.85 – 1.42 (m, 10H), 0.22 (s, 9H), 0.17 (s, 9H).

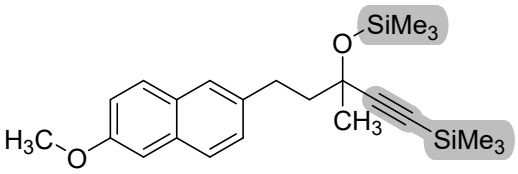
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.0, 137.4, 124.5, 123.7, 109.1, 90.0, 71.7, 45.2, 39.8, 31.1, 20.7, 17.9, 2.2, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.0, -18.2.

EI-MS m/z (rel. int.): 320 (5%, [M]), 305 (55, [M-CH_3]), 73 (100).

EA: $C_{18}H_{32}OSi_2$ (320.199): calcd. C 67.43, H 10.06; found C 67.69, H 10.11.

((5-(6-Methoxynaphthalen-2-yl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (4c)



((5-(6-methoxynaphthalen-2-yl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane was obtained as white solid in 96% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.74 – 7.64 (m, 2H), 7.61 – 7.51 (m, 1H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.19 – 7.07 (m, 2H), 3.92 (s, 3H), 3.00 – 2.85 (m, 2H), 2.11 – 1.87 (m, 2H), 1.51 (s, 3H), 0.24 (s, 9H), 0.21 (s, 9H).

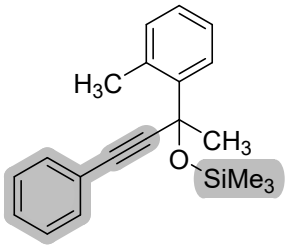
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 157.2, 137.9, 133.0, 129.3, 129.0, 128.1, 126.8, 126.3, 118.7, 110.0, 105.8, 89.1, 69.6, 55.4, 47.0, 31.4, 31.3, 2.1, 0.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.8, -18.3.

EI-MS m/z (rel. int.): 398 (10%, [M]), 308 (60), 171 (100).

EA: $C_{23}H_{34}O_2Si_2$ (398.210): calcd. C 69.29, H 8.60; found C 69.25, H 8.62.

Trimethyl((4-phenyl-2-(o-tolyl)but-3-yn-2-yl)oxy)silane (5a)



Trimethyl((4-phenyl-2-(o-tolyl)but-3-yn-2-yl)oxy)silane was obtained as pale-yellow oil in 93% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.81 (m, 1H), 7.60 – 7.47 (m, 2H), 7.44 – 7.35 (m, 3H), 7.30 – 7.19 (m, 3H), 2.73 (s, 3H), 2.00 (s, 3H), 0.31 (s, 9H).

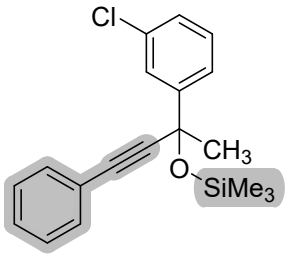
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.5, 135.7, 132.4, 131.5, 128.5, 128.4, 127.5, 125.8, 125.7, 123.2, 93.5, 85.8, 72.1, 32.9, 21.6, 2.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 14.7.

EI-MS m/z (rel. int.): 308 (10%, [M]), 293 (100, [M-CH_3]), 217 (70).

EA: $C_{20}H_{24}OSi$ (308.160): calcd. C 77.87, H 7.84; found C 77.74, H 7.79.

((2-(3-Chlorophenyl)-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane (5b)



((2-(3-Chlorophenyl)-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.69 (t, *J* = 1.8 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.55 – 7.48 (m, 2H), 7.40 – 7.35 (m, 3H), 7.33 (d, *J* = 2.3 Hz, 1H), 7.30 – 7.23 (m, 1H), 1.83 (s, 3H), 0.25 (s, 9H).

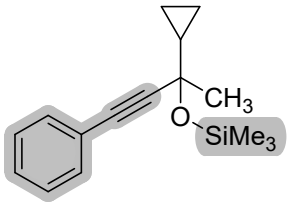
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.8, 134.4, 132.0, 129.8, 129.0, 128.9, 127.8, 125.9, 123.8, 123.0, 92.7, 86.5, 71.6, 36.4, 2.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.2.

EI-MS m/z (rel. int.): 328 (10%, [M]), 313 (100, [M-CH_3]), 202 (50).

EA: $C_{19}H_{21}ClOSi$ (328.105): calcd. C 69.38, H 6.44; found C 69.44, H 6.41.

((2-Cyclopropyl-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane (5c)



((2-Cyclopropyl-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 87% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 – 7.38 (m, 2H), 7.36 – 7.27 (m, 3H), 1.63 (s, 3H), 1.25 – 1.07 (m, 1H), 0.72 – 0.62 (m, 1H), 0.55 – 0.44 (m, 3H), 0.24 (s, 9H).

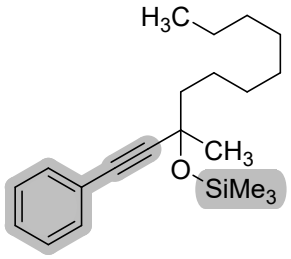
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 131.9, 128.7, 128.6, 123.4, 91.7, 84.8, 71.5, 32.6, 23.3, 3.0, 2.6, 2.4.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.0.

EI-MS m/z (rel. int.): 243 (100%, [M-CH_3]), 230 (30), 75 (40).

EA: $C_{16}H_{22}OSi$ (258.144): calcd. C 74.36, H 8.58; found C 74.38, H 8.57.

Trimethyl((3-methyl-1-phenylundec-1-yn-3-yl)oxy)silane (5d)



Trimethyl((3-methyl-1-phenylundec-1-yn-3-yl)oxy)silane was obtained as pale-yellow oil in 99% yield.[5]

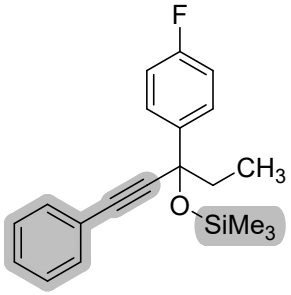
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 1.80 – 1.65 (m, 2H), 1.65 – 1.45 (m, 5H), 1.37 – 1.27 (m, 10H), 0.99 – 0.84 (m, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 131.6, 128.4, 128.2, 123.4, 93.9, 84.3, 70.1, 45.4, 32.1, 31.4, 29.9, 29.8, 29.5, 24.9, 22.8, 14.3, 2.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.0.

EI-MS m/z (rel. int.): 315 (5%, [M-CH_3]), 240 (10), 217 (100).

((3-(4-Fluorophenyl)-1-phenylpent-1-yn-3-yl)oxy)trimethylsilane (5e)



((3-(4-Fluorophenyl)-1-phenylpent-1-yn-3-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 – 7.54 (m, 2H), 7.56 – 7.46 (m, 2H), 7.44 – 7.29 (m, 3H), 7.10 – 6.90 (m, 2H), 2.17 – 1.74 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.17 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.16 (d, *J* = 244.9 Hz), 141.89 (d, *J* = 3.0 Hz), 131.7, 128.6, 128.6, 127.52 (d, *J* = 8.0 Hz), 122.9, 114.70 (d, *J* = 21.3 Hz), 91.7, 87.2, 77.5, 77.2, 76.8, 75.2, 41.1, 9.2, 1.7.

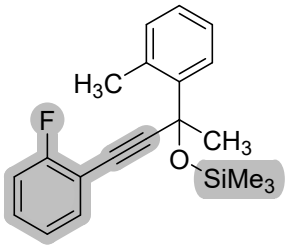
^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -116.2.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.9.

EI-MS m/z (rel. int.): 297 (100%), 236 (25), 123 (30).

EA: $C_{20}H_{23}FOSi$ (326.150): calcd. C 73.58, H 7.10; found C 73.47, H 7.11.

((4-(2-Fluorophenyl)-2-(o-tolyl)but-3-yn-2-yl)oxy)trimethylsilane (5f)



((4-(2-Fluorophenyl)-2-(o-tolyl)but-3-yn-2-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 92% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.86 – 7.76 (m, 1H), 7.57 – 7.40 (m, 1H), 7.37 – 7.27 (m, 1H), 7.25 – 7.16 (m, 3H), 7.17 – 7.04 (m, 2H), 2.67 (s, 3H), 1.95 (s, 3H), 0.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 163.02 (d, *J* = 251.8 Hz),143.2, 135.8, 133.4, 132.5, 130.14 (d, *J* = 7.9 Hz),, 127.5, 125.76 (d, *J* = 17.0 Hz), 124.08 (d, *J* = 3.8 Hz), 115.72 (d, *J* = 20.8 Hz), 111.69 (d, *J* = 15.7 Hz), 98.6, 79.5, 72.2, 32.8, 21.5, 1.9.

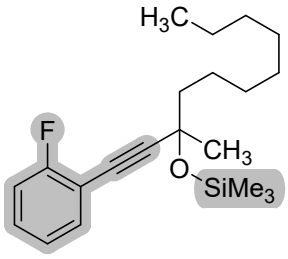
^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -109.6.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 15.1.

EI-MS m/z (rel. int.): 326 (5%, [M]), 311 (100, [M-CH_3]), 215 (30).

EA: $C_{20}H_{23}FOSi$ (326.150): calcd. C 73.58, H 7.10; found C 73.69, H 7.15.

((1-(2-Fluorophenyl)-3-methylundec-1-yn-3-yl)oxy)trimethylsilane (5g)



((1-(2-Fluorophenyl)-3-methylundec-1-yn-3-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 81% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.51 – 7.38 (m, 1H), 7.36 – 7.24 (m, 1H), 7.16 – 6.98 (m, 2H), 1.86 – 1.65 (m, 2H), 1.65 – 1.47 (m, 5H), 1.43 – 1.19 (m, 10H), 0.91 (t, *J* = 6.6 Hz, 3H), 0.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 162.95 (d, *J* = 251.7 Hz), 133.49 (d, *J* = 1.6 Hz), 129.88 (d, *J* = 7.8 Hz), 123.98 (d, *J* = 3.7 Hz), 115.65 (d, *J* = 21.0 Hz), 111.88 (d, *J* = 15.8 Hz), 99.1, 70.1, 45.3, 32.1, 31.3, 29.9, 29.7, 29.4, 24.8, 22.8, 14.3, 2.0.

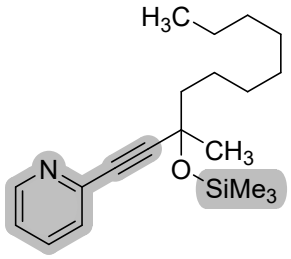
^{19}F NMR (377 MHz, $CDCl_3$) δ (ppm) = -109.9.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.4.

EI-MS m/z (rel. int.): 333 (10, [M-CH_3]), 235 (100), 158 (5).

EA: $C_{21}H_{33}FOSi$ (348.228): calcd. C 72.36, H 9.54; found C 72.54, H 9.60.

2-(3-Methyl-3-((trimethylsilyl)oxy)undec-1-yn-1-yl)pyridine (5h)



2-(3-methyl-3-((trimethylsilyl)oxy)undec-1-yn-1-yl)pyridine was obtained as pale-yellow oil in 85% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.60 – 8.53 (m, 1H), 7.72 – 7.56 (m, 1H), 7.42 – 7.33 (m, 1H), 7.24 – 7.05 (m, 1H), 1.81 – 1.64 (m, 2H), 1.60 – 1.45 (s, 5H), 1.39 – 1.15 (m, 10H), 0.94 – 0.76 (m, 3H), 0.23 (s, 9H).

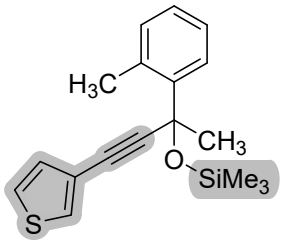
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 150.2, 143.5, 136.2, 127.0, 122.8, 93.8, 83.7, 70.0, 45.2, 32.0, 31.1, 29.9, 29.7, 29.4, 24.8, 22.8, 14.2, 2.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 13.4.

EI-MS m/z (rel. int.): 316 (15%, [M-CH_3]), 218 (100), 176 (40).

EA: $C_{20}H_{33}NOSi$ (331.233): calcd. C 72.45, H 10.03; found C 72.59, H 9.96.

Trimethyl((4-(thiophen-3-yl)-2-(o-tolyl)but-3-yn-2-yl)oxy)silane (5i)



Trimethyl((4-(thiophen-3-yl)-2-(o-tolyl)but-3-yn-2-yl)oxy)silane was obtained as pale-yellow oil in 69% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.81 – 7.72 (m, 1H), 7.48 – 7.42 (m, 1H), 7.32 – 7.26 (m, 1H), 7.23 – 7.15 (m, 3H), 7.17 – 7.11 (m, 1H), 2.64 (s, 3H), 1.90 (s, 3H), 0.21 (s, 9H).

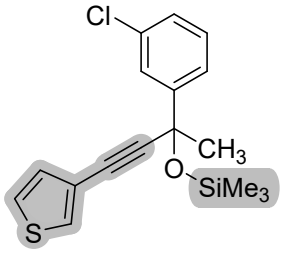
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 143.5, 135.7, 132.4, 129.7, 128.5, 127.5, 125.8, 125.7, 125.5, 122.2, 93.0, 81.2, 77.5, 77.2, 76.8, 72.1, 32.8, 21.5, 2.0.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 14.6.

EI-MS m/z (rel. int.): 299 (100%, [M-CH_3]), 283 (5), 119 (35).

EA: $C_{18}H_{22}OSSi$ (314.116): calcd. C 68.74, H 7.05; found C 68.60, H 7.09.

((2-(3-Chlorophenyl)-4-(thiophen-3-yl)but-3-yn-2-yl)oxy)trimethylsilane (5j)



((2-(3-Chlorophenyl)-4-(thiophen-3-yl)but-3-yn-2-yl)oxy)trimethylsilane was obtained as pale-yellow oil in 70% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.43 (s, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.13 – 7.07 (m, 1H), 7.07 – 7.02 (m, 1H), 6.98 – 6.92 (m, 3H), 1.58 (s, 1H), 0.00 (s, 9H).

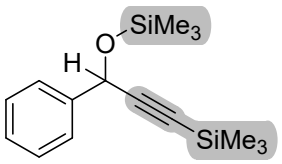
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 149.4, 134.1, 129.8, 129.5, 129.0, 127.5, 125.7, 125.6, 123.5, 121.8, 92.0, 81.5, 71.3, 36.0, 1.8.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 16.1.

EI-MS m/z (rel. int.): 334 (10%, [M]), 319 (100, [M-CH_3]), 208 (40).

EA: $C_{17}H_{19}ClOSSi$ (334.061): calcd. C 60.96, H 5.72; found C 61.11, H 5.79.

Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)silane (7a)



Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)silane was obtained as pale-yellow oil in 42% yield.[1]

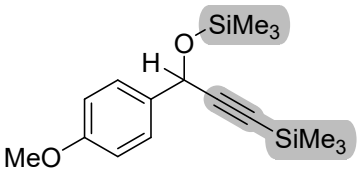
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54 – 7.36 (m, 2H), 7.31 – 7.23 (m, 2H), 7.22 – 7.14 (m, 1H), 5.39 (s, 1H), 0.12 (s, 9H), 0.09 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.3, 128.5, 127.9, 126.7, 106.1, 91.0, 65.2, 0.5, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 20.4, -17.8.

EI-MS m/z (rel. int.): 276 (50%, [M]), 261 (35, [M-CH_3]), 155 (100).

(3-(4-Methoxyphenyl)-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (7b)



(3-(4-Methoxyphenyl)-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane was obtained as pale-yellow oil in 45% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.42 (d, *J* = 8.7 Hz, 2H), 6.94 – 6.81 (m, 2H), 5.44 (s, 1H), 3.81 (s, 3H), 0.20 (s, 9H), 0.19 (s, 9H).

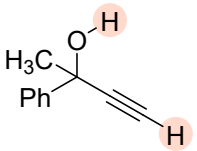
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.4, 133.6, 128.1, 127.9, 113.9, 113.8, 106.3, 90.7, 64.8, 55.4, 0.5, -0.1.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = 20.4, -13.2.

EI-MS m/z (rel. int.): 306 (70%, [M]), 291 (50, [M-CH_3]), 144 (100).

EA: $C_{16}H_{26}O_2Si_2$ (306.147): calcd. C 62.69, H 8.55; found C 62.66, H 8.53.

2-Phenylbut-3-yn-2-ol (8a)



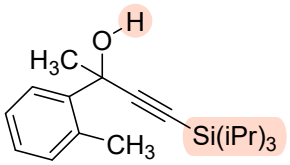
2-Phenylbut-3-yn-2-ol was obtained as pale-yellow oil in 99% yield.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.54 (m, 2H), 7.36 – 7.24 (m, 2H), 7.24 – 7.18 (m, 1H), 2.58 (s, 1H), 2.52 (s, 1H), 1.70 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 145.1, 128.4, 127.9, 125.0, 87.4, 73.2, 69.9, 33.2.

EI-MS m/z (rel. int.): 131 (100%, [M-CH_3]), 102 (30), 77 (35).

2-(o-Tolyl)-4-(triisopropylsilyl)but-3-yn-2-ol (8b)



2-(o-Tolyl)-4-(triisopropylsilyl)but-3-yn-2-ol was obtained as pale-yellow oil in 99% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 – 7.51 (m, 1H), 7.25 – 7.14 (m, 3H), 2.66 (s, 3H), 2.32 (s, 1H), 1.86 (s, 3H), 1.08 (s, 21H).

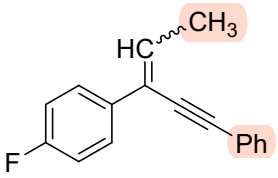
^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) = 142.2, 135.9, 132.3, 127.8, 125.8, 125.3, 111.5, 85.7, 70.3, 31.4, 21.4, 18.8, 11.4, 11.3.

^{29}Si NMR (80 MHz, $CDCl_3$) δ (ppm) = -2.1.

EI-MS m/z (rel. int.): 301 (10%, [M-CH_3]), 255 (30), 127 (100).

EA: $C_{20}H_{32}OSi$ (316.222): calcd. C 75.88, H 10.19; found C 76.15, H 10.25.

1-Fluoro-4-(1-phenylpent-3-en-1-yn-3-yl)benzene (8c)



1-Fluoro-4-(1-phenylpent-3-en-1-yn-3-yl)benzene was obtained as pale-yellow oil in 98% yield (isomer ratio ~ 8:1).

^{1}H NMR (400 MHz, C_6H_6) δ (ppm) = 7.29 – 7.14 (m, 3H), 6.91 – 6.90 (s, 2H), 6.80 – 6.70 (m, 2H), 6.59 (t, *J* = 8.7 Hz, 2H), 5.83 (q, *J* = 7.0 Hz, 3H), 1.73 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, C_6H_6) δ (ppm) = 162.85 (d, *J* = 246.3 Hz), 134.9, 133.07 (d, *J* = 1.8 Hz),131.9, 128.7, 128.6, 128.3, 128.1, 128.0, 127.8, 127.0, 124.01 (d, *J* = 16.1 Hz),115.48 (d, *J* = 21.5 Hz), 96.5, 87.2, 17.0.

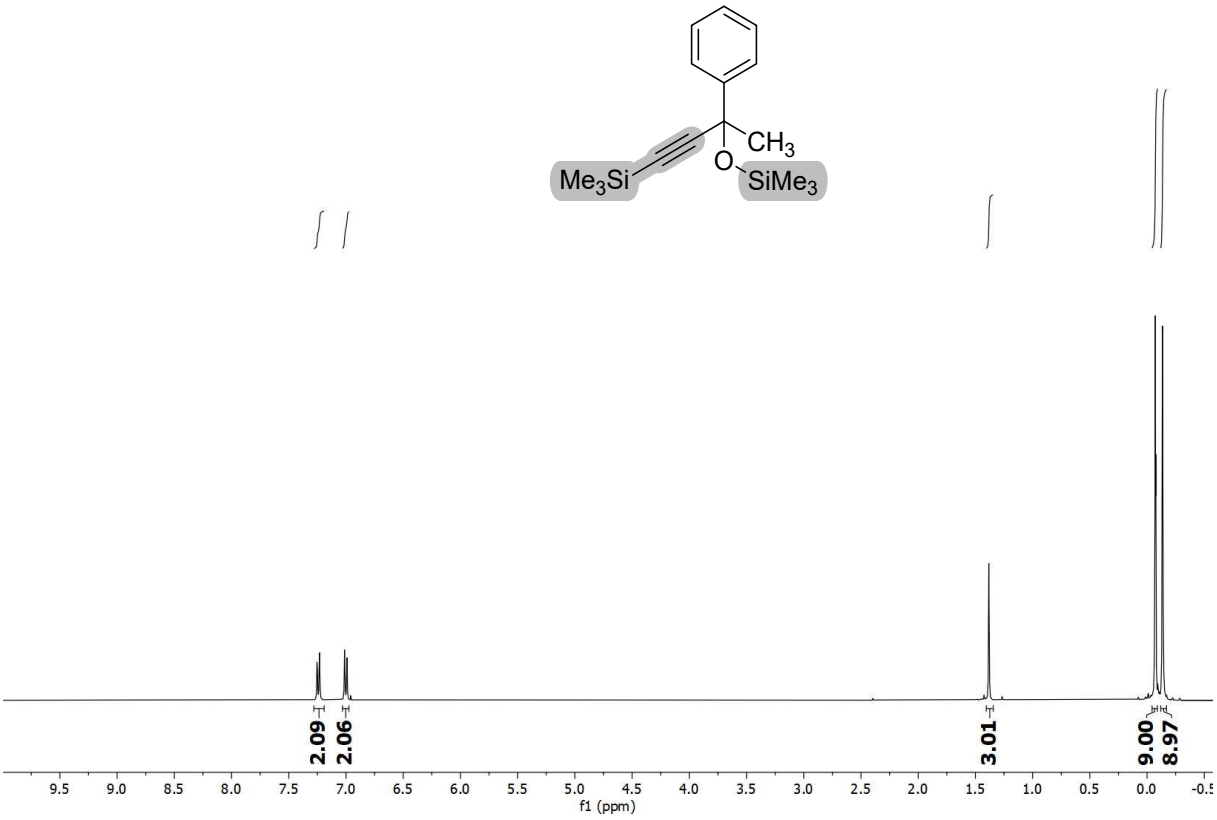
^{19}F NMR (377 MHz, C_6H_6) δ (ppm) = -115.0 (major), -115.5 (minor).

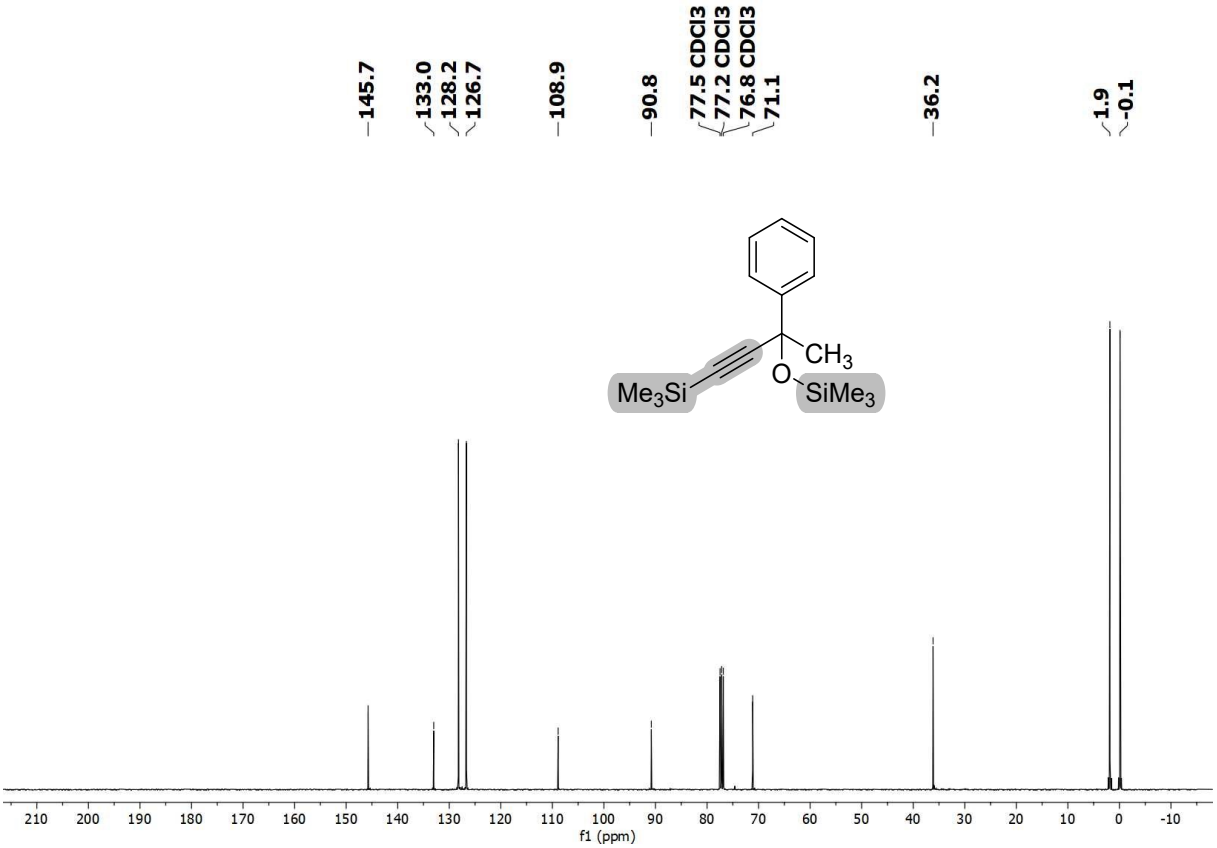
EI-MS m/z (rel. int.): 236 (100%, [M]), 221 (50, [M-CH_3]), 133 (20).

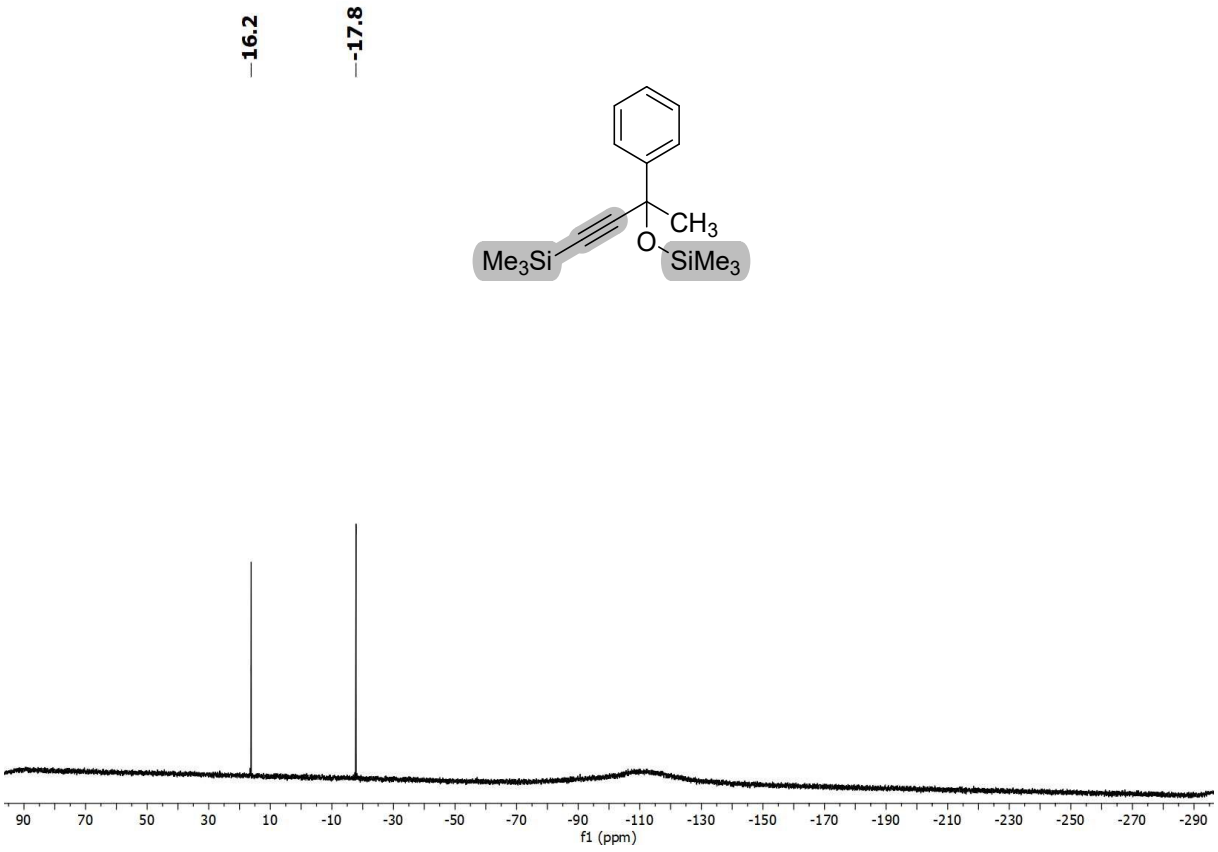
EA: $C_{17}H_{13}F$ (236.100): calcd. C 86.41, H 5.55; found C 86.33, H 5.49.

SPECTRA FOR ALL PRODUCTS

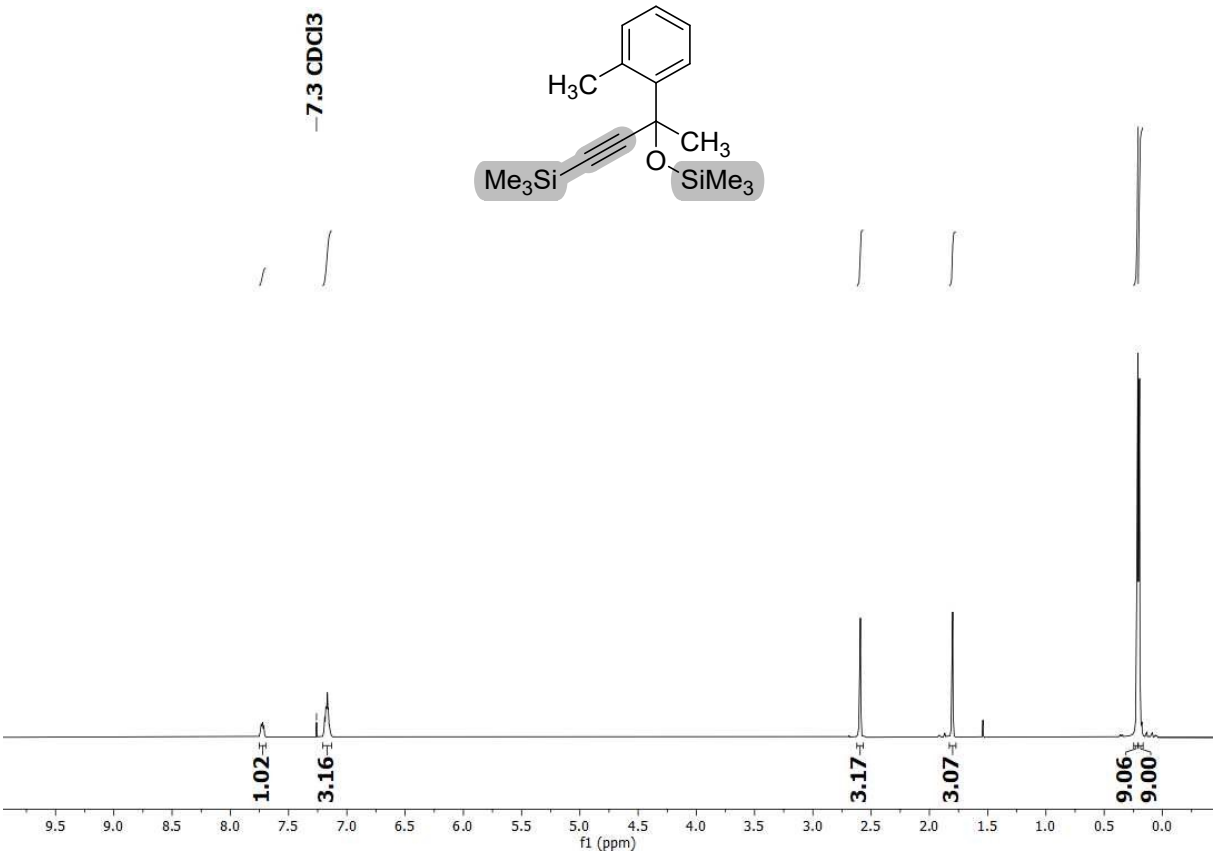
Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3a)

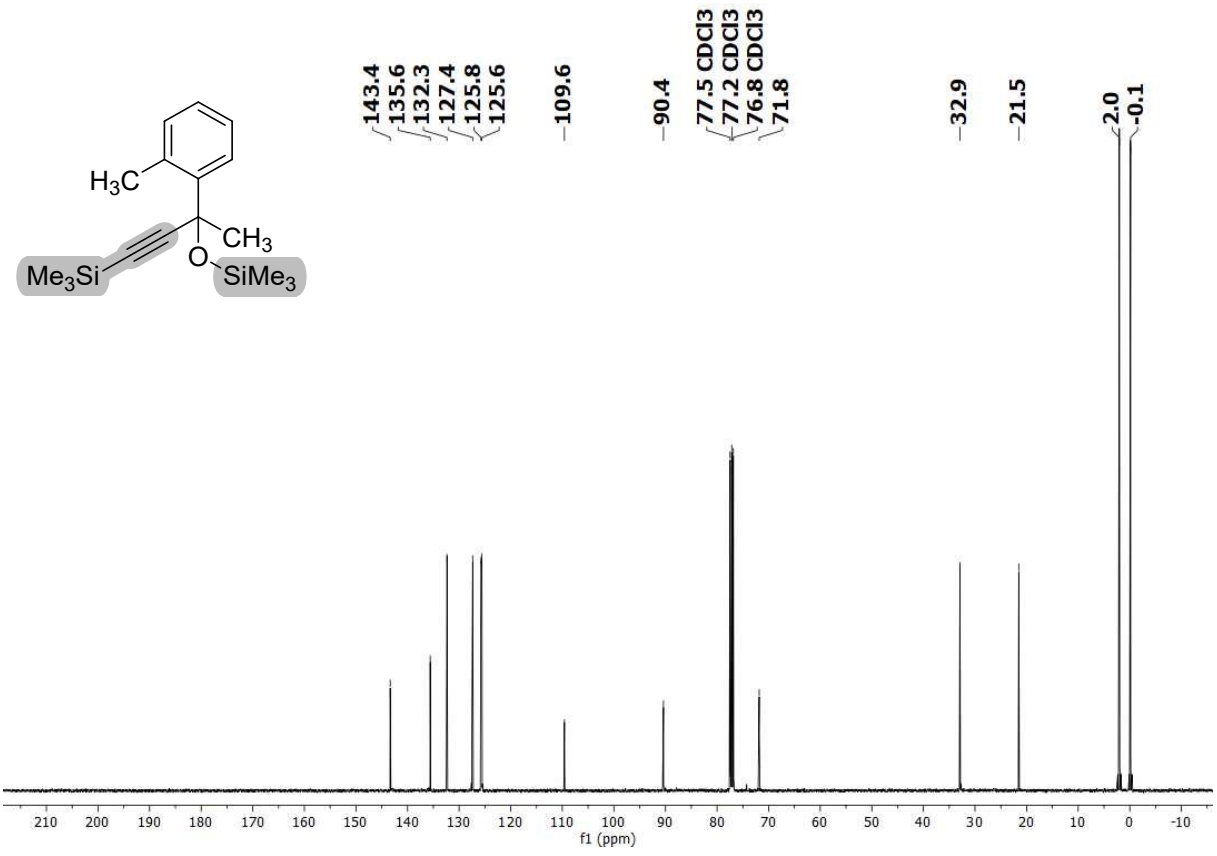


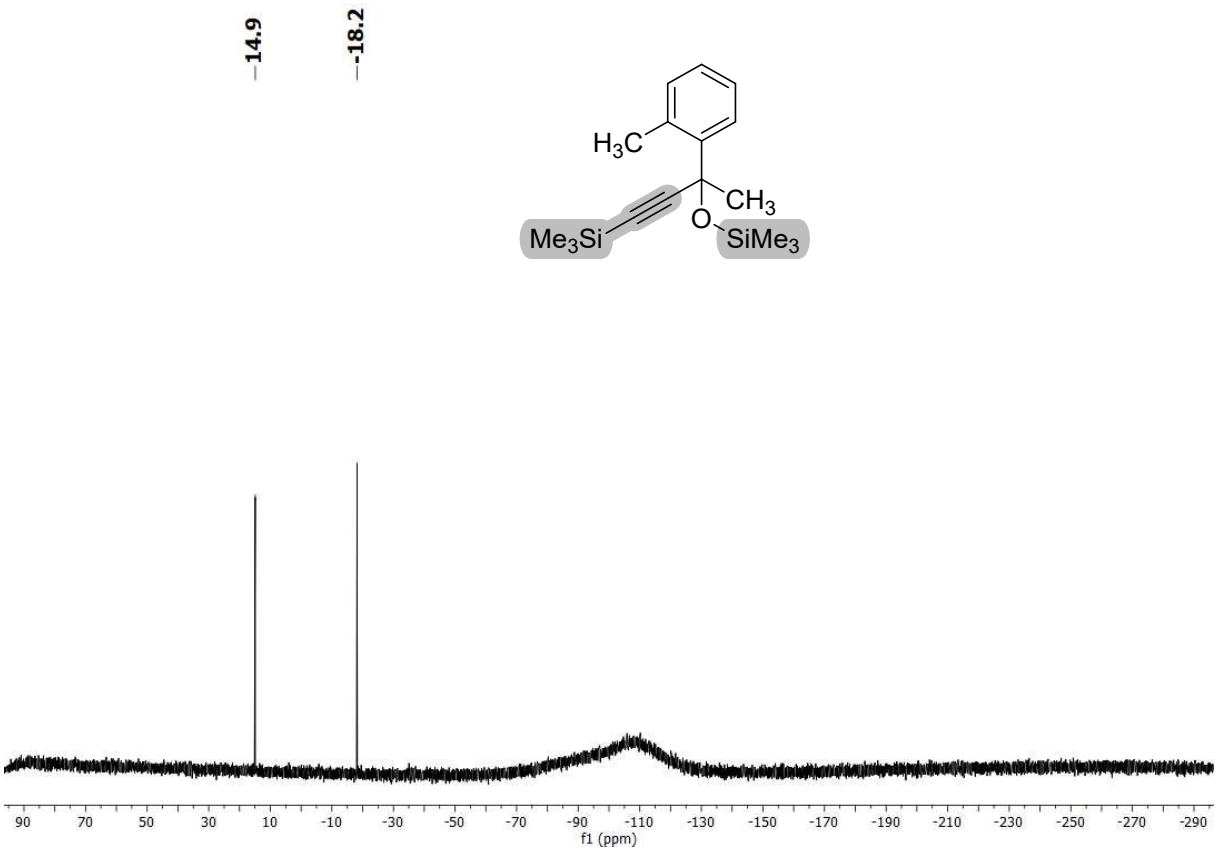



-16.2
-17.8
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

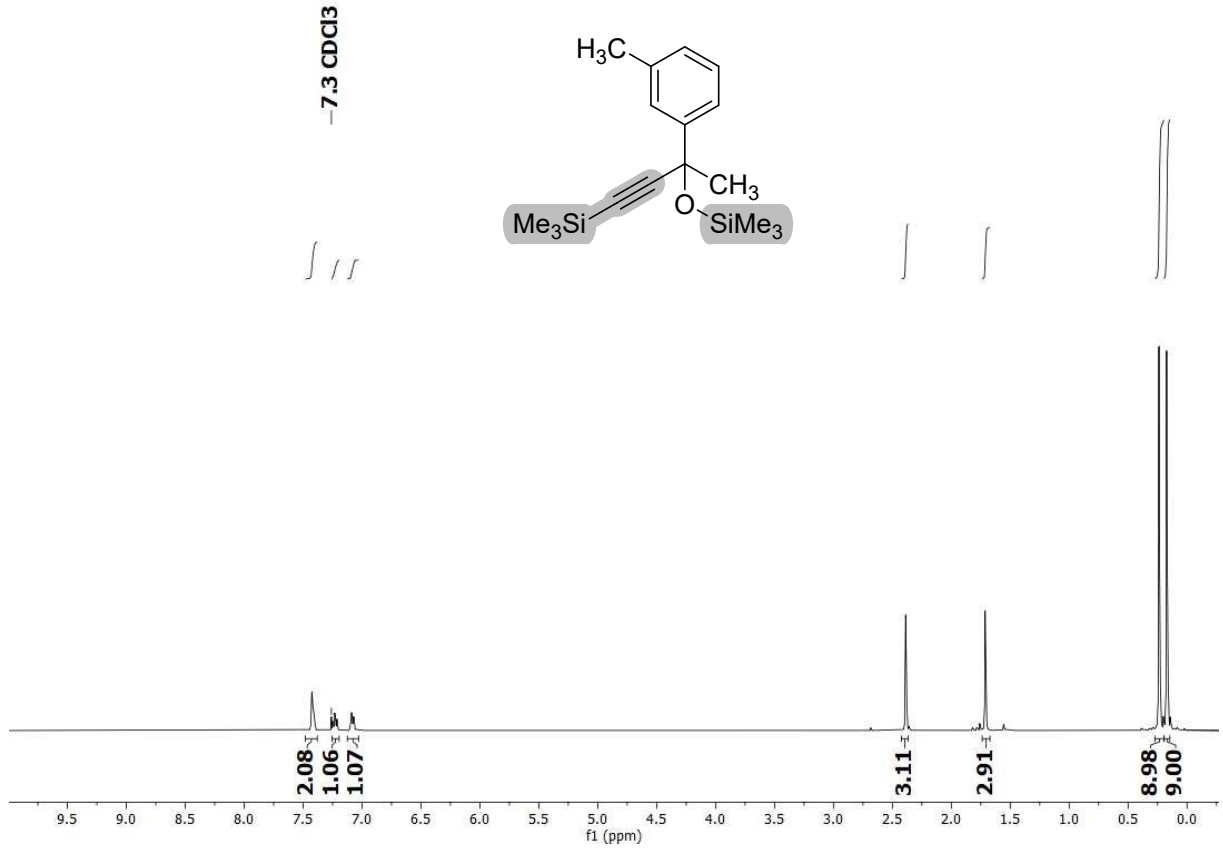
Trimethyl(3-(o-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3b)

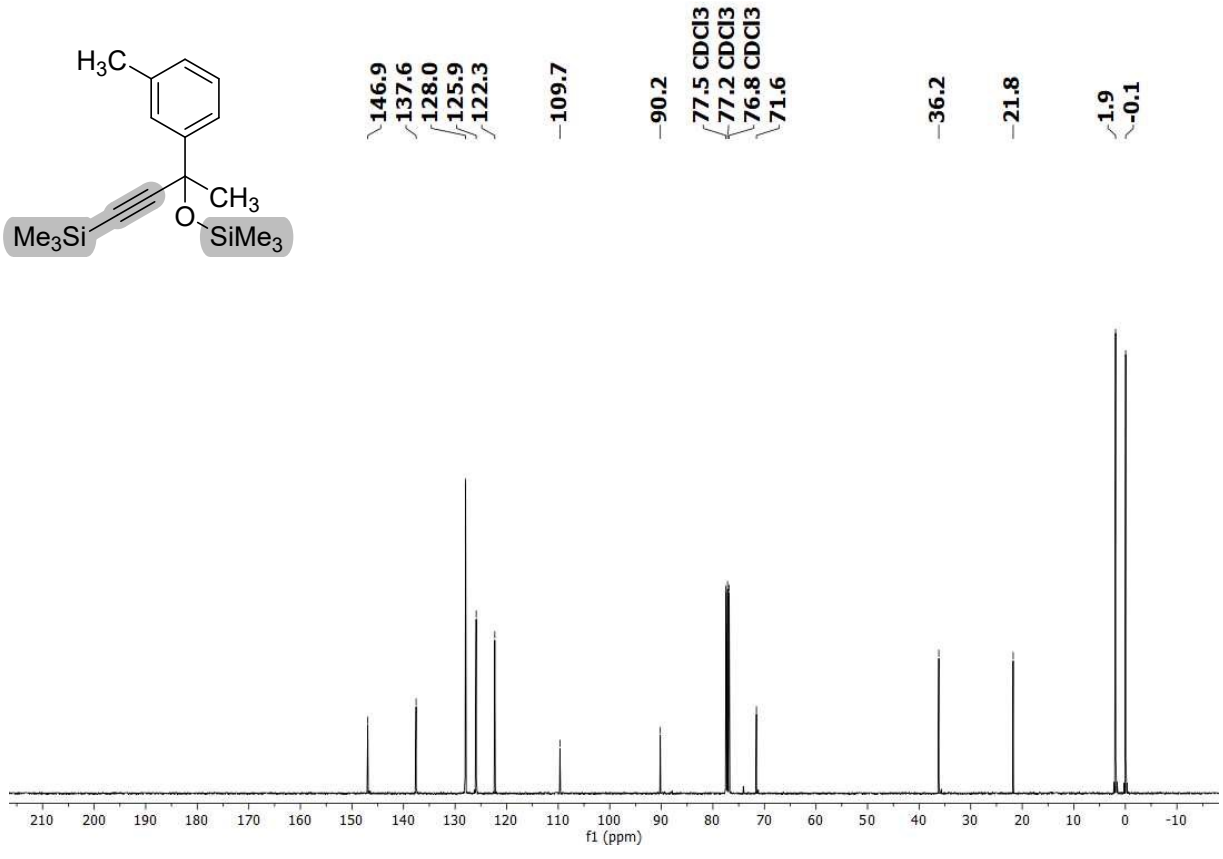


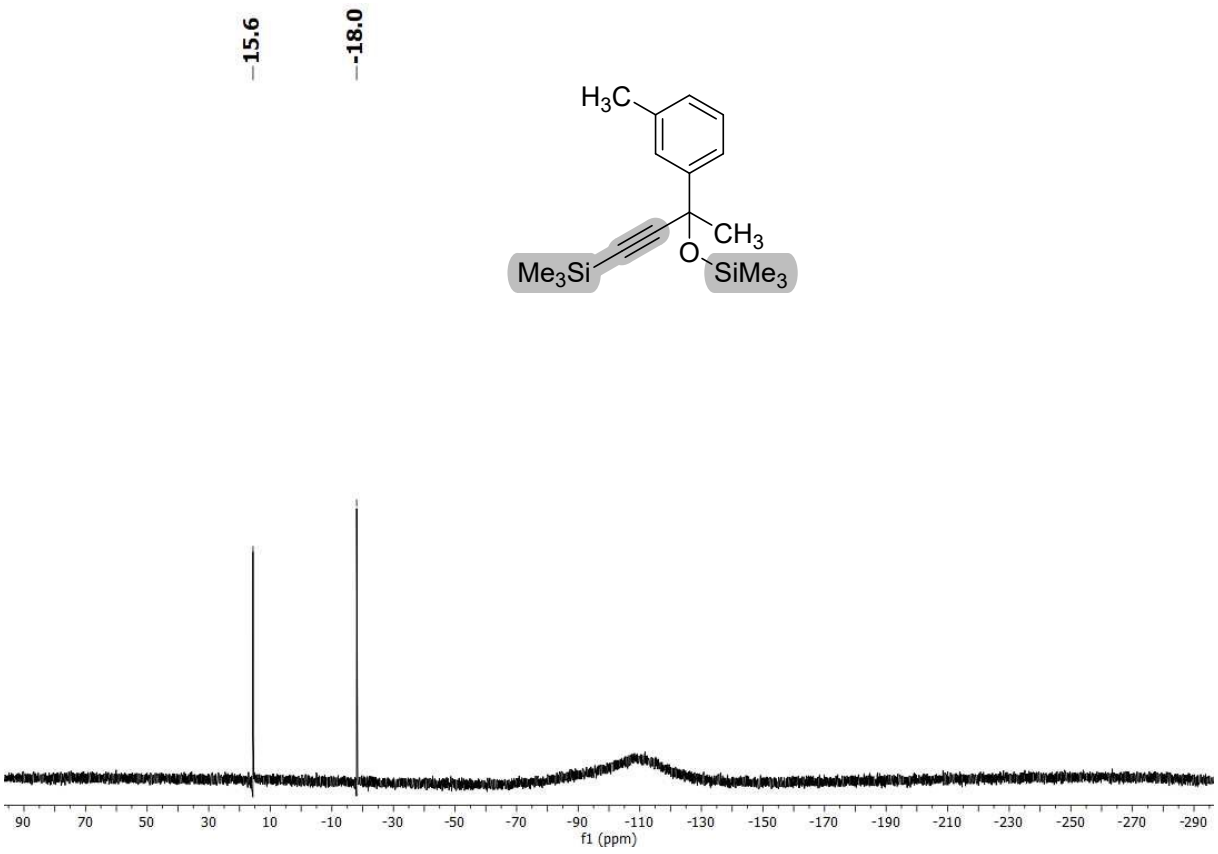



-14.9
-18.2
H3C
CH3
Me3Si
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

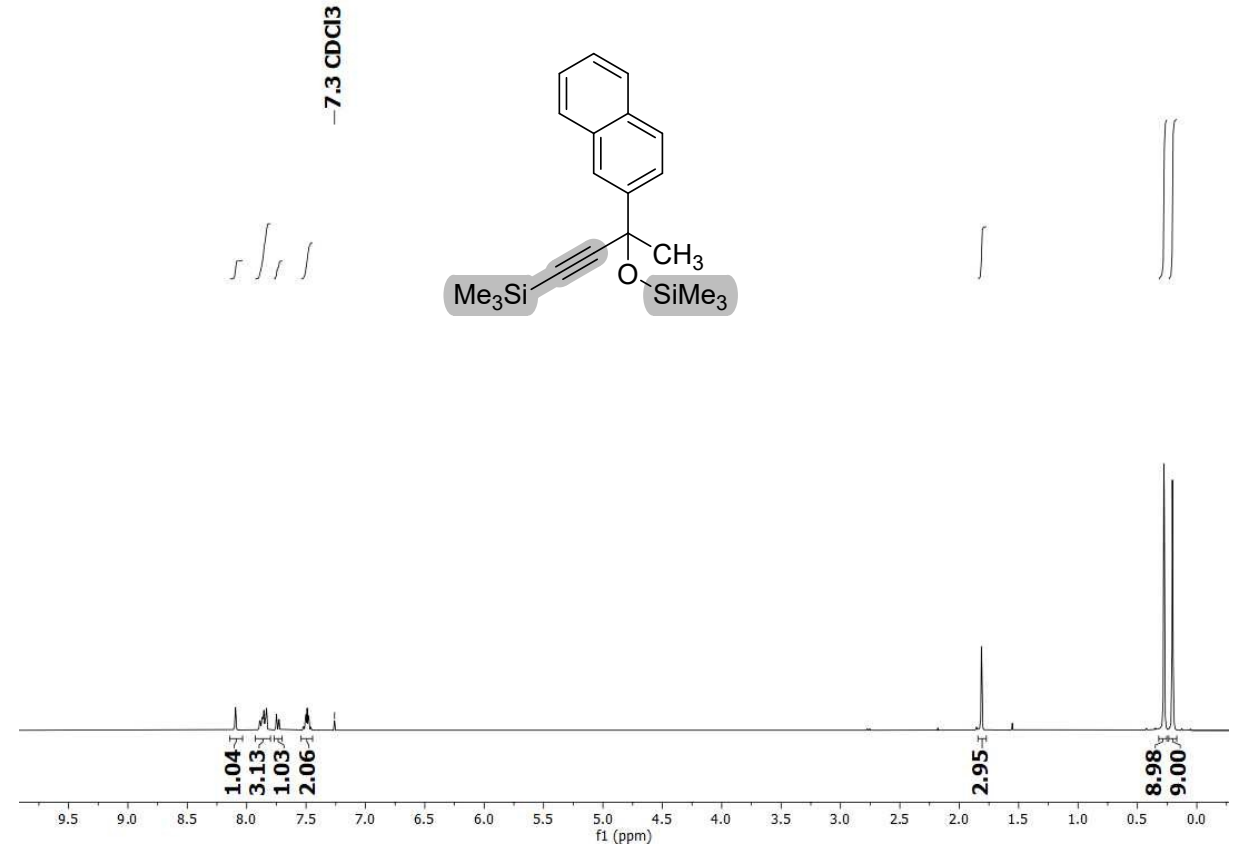
Trimethyl(3-(m-tolyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3c)

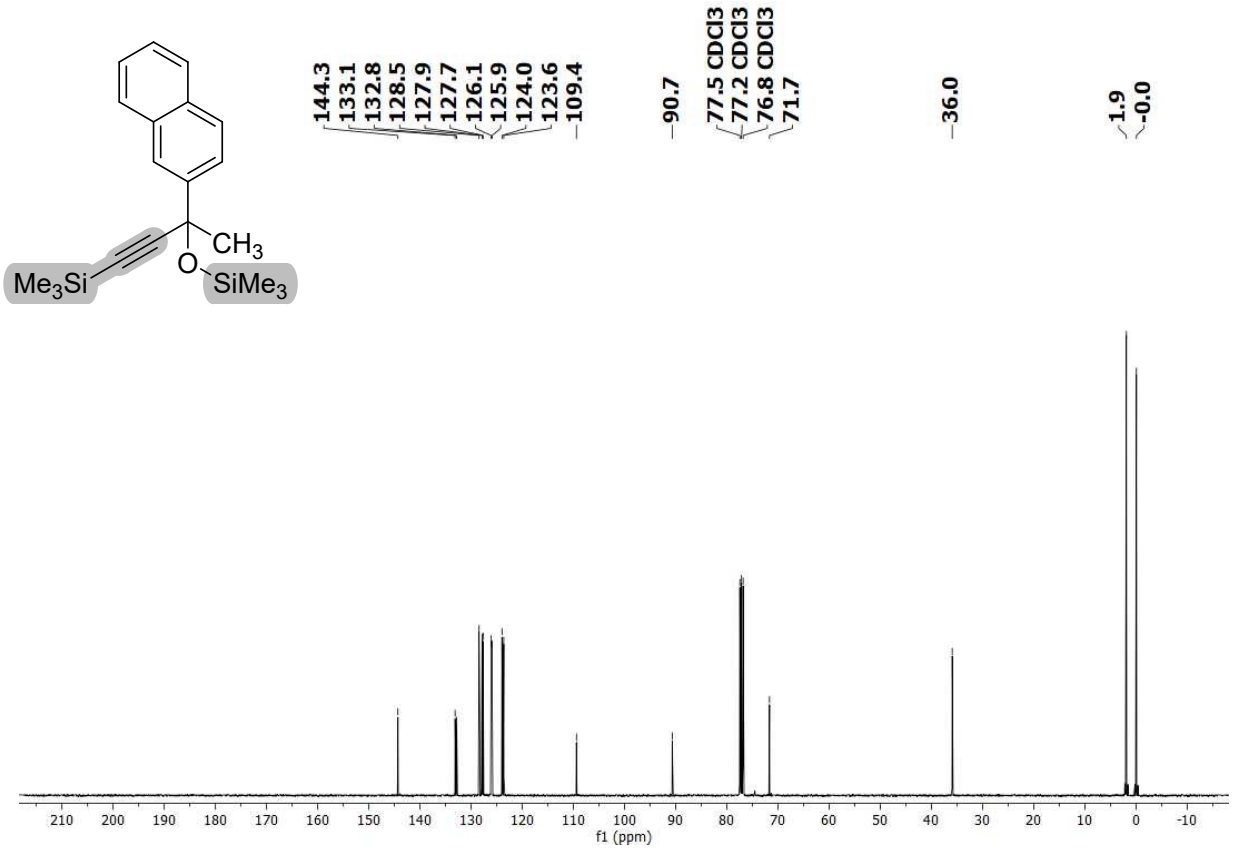


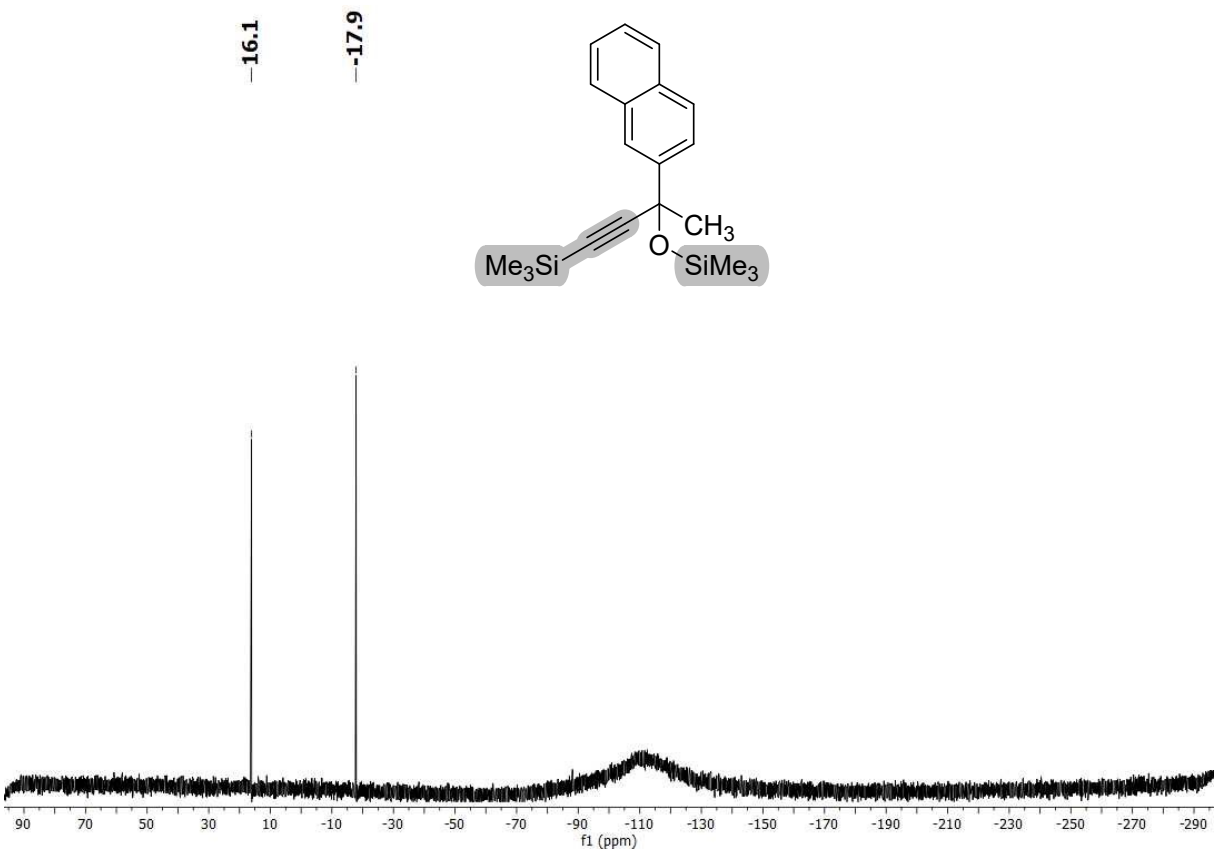



-15.6
-18.0
H3C
CH3
Me3Si
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

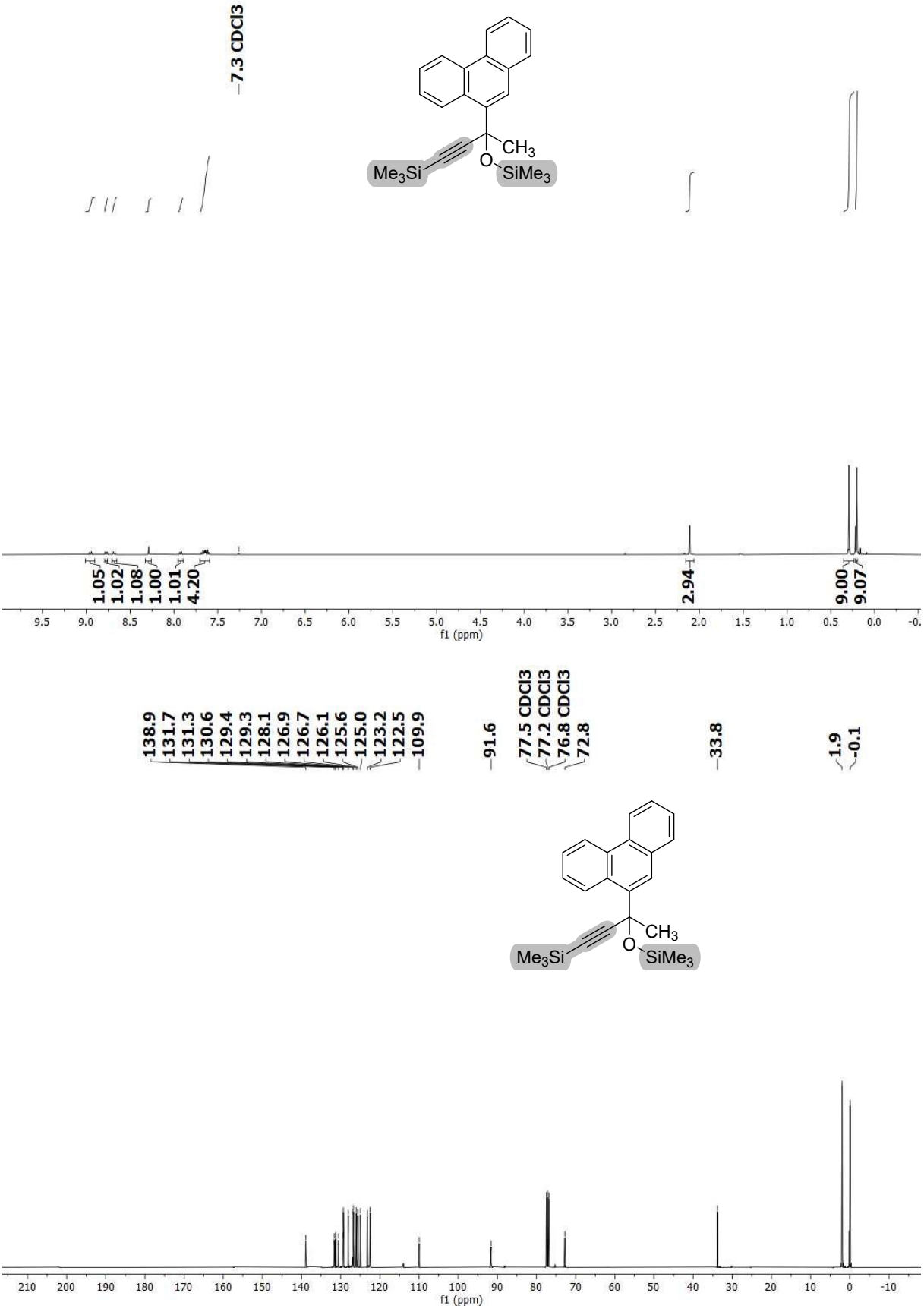
Trimethyl(3-(naphthalen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3d)

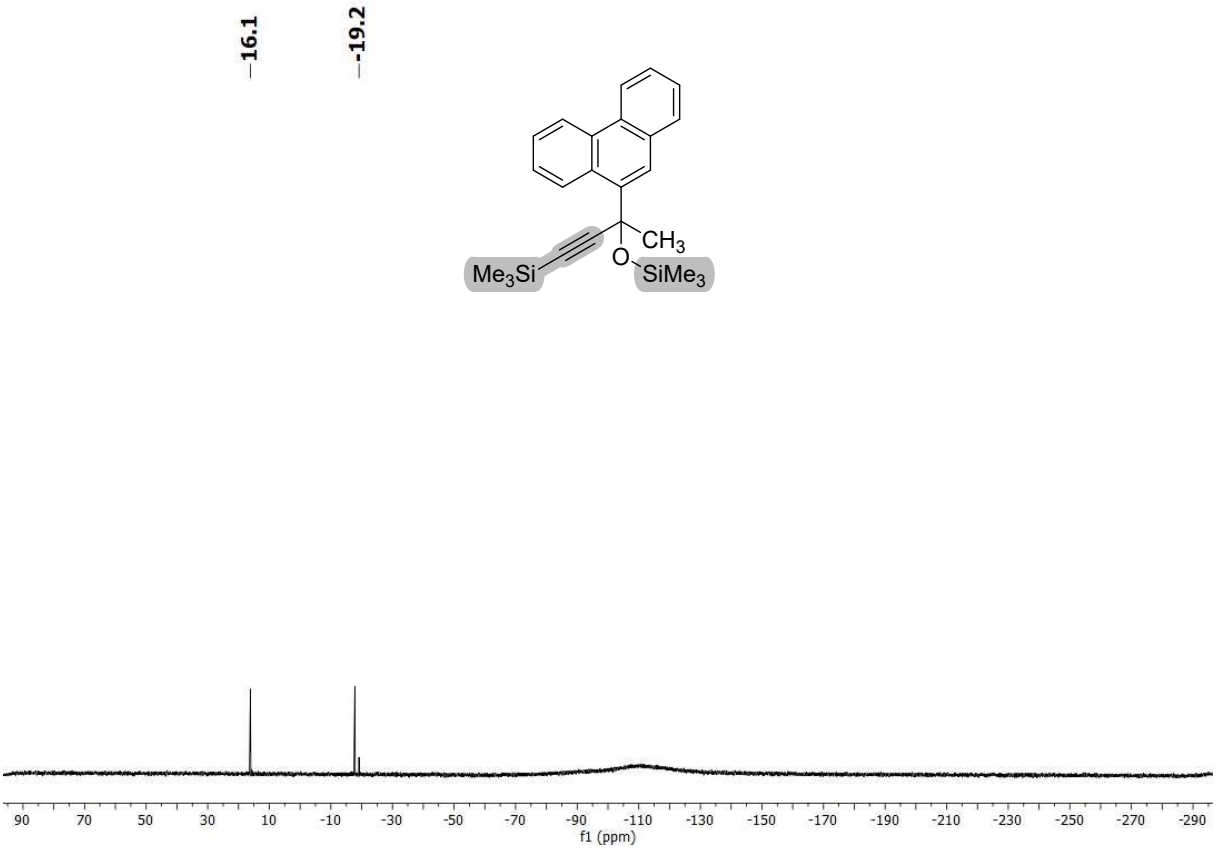




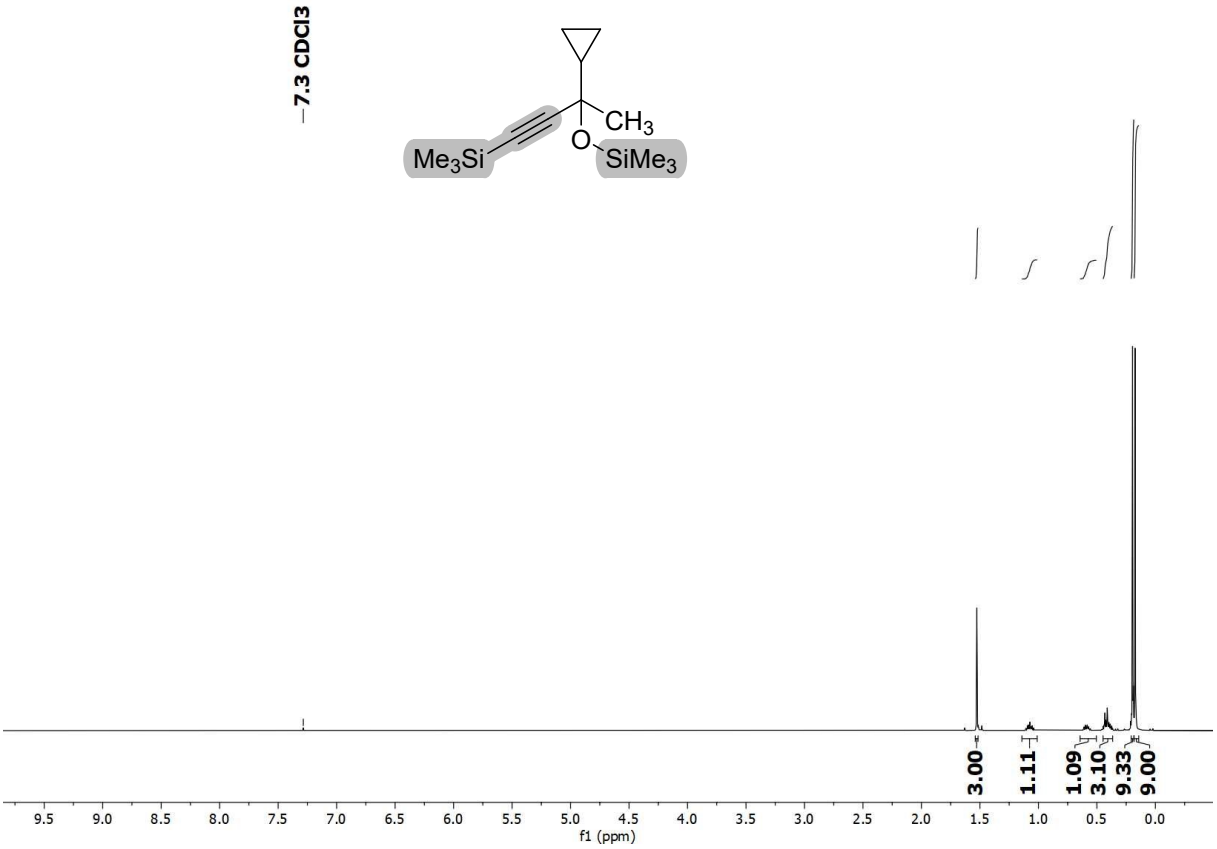

16.1
-17.9
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

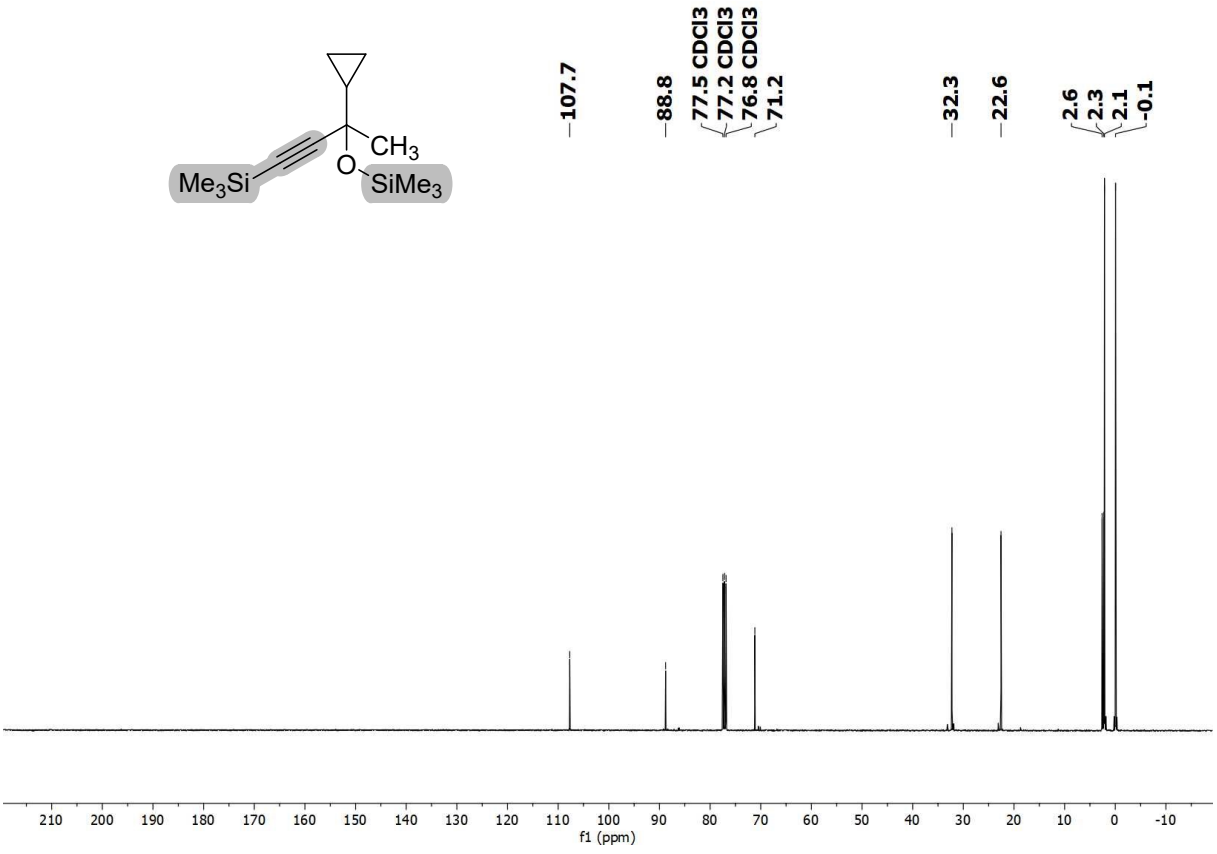
Trimethyl(3-(phenanthren-9-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3e)

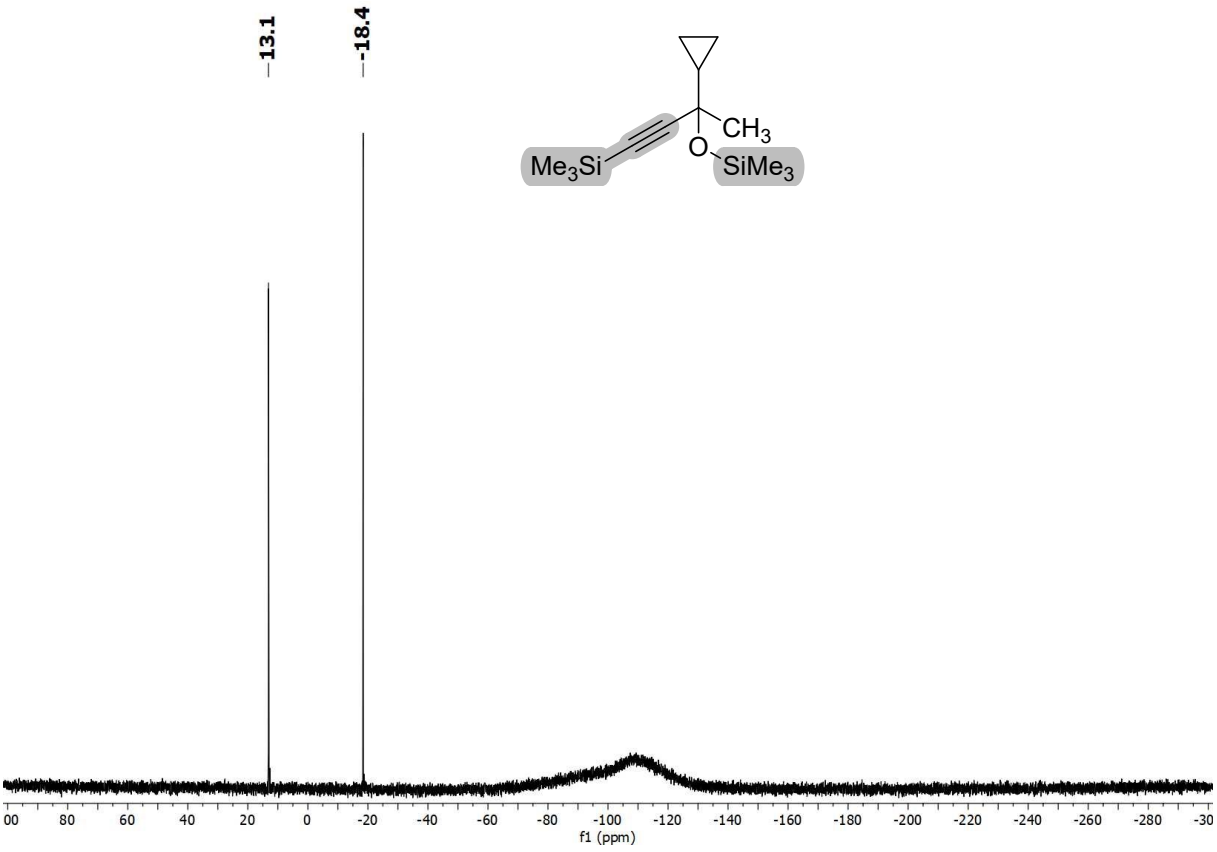



16.1
-19.2
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

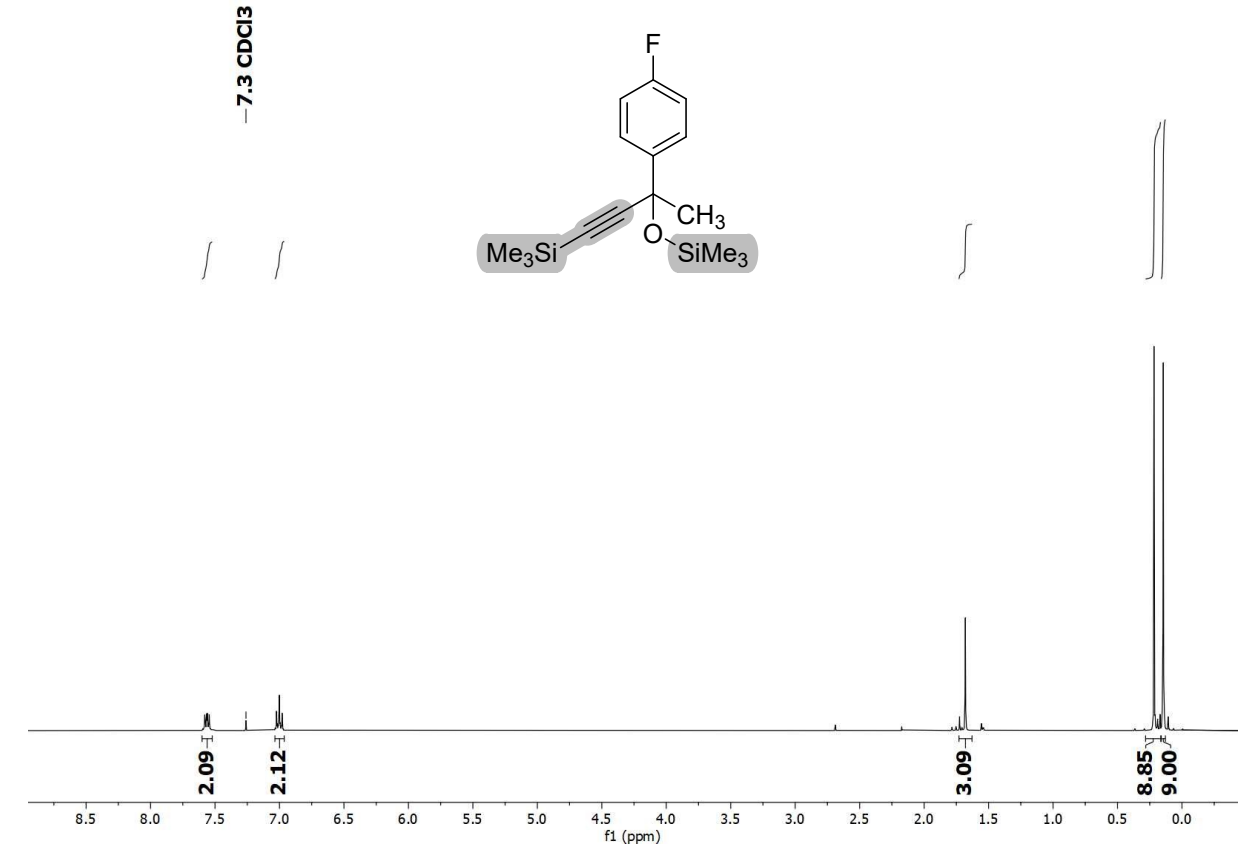
(3-Cyclopropyl-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3f)

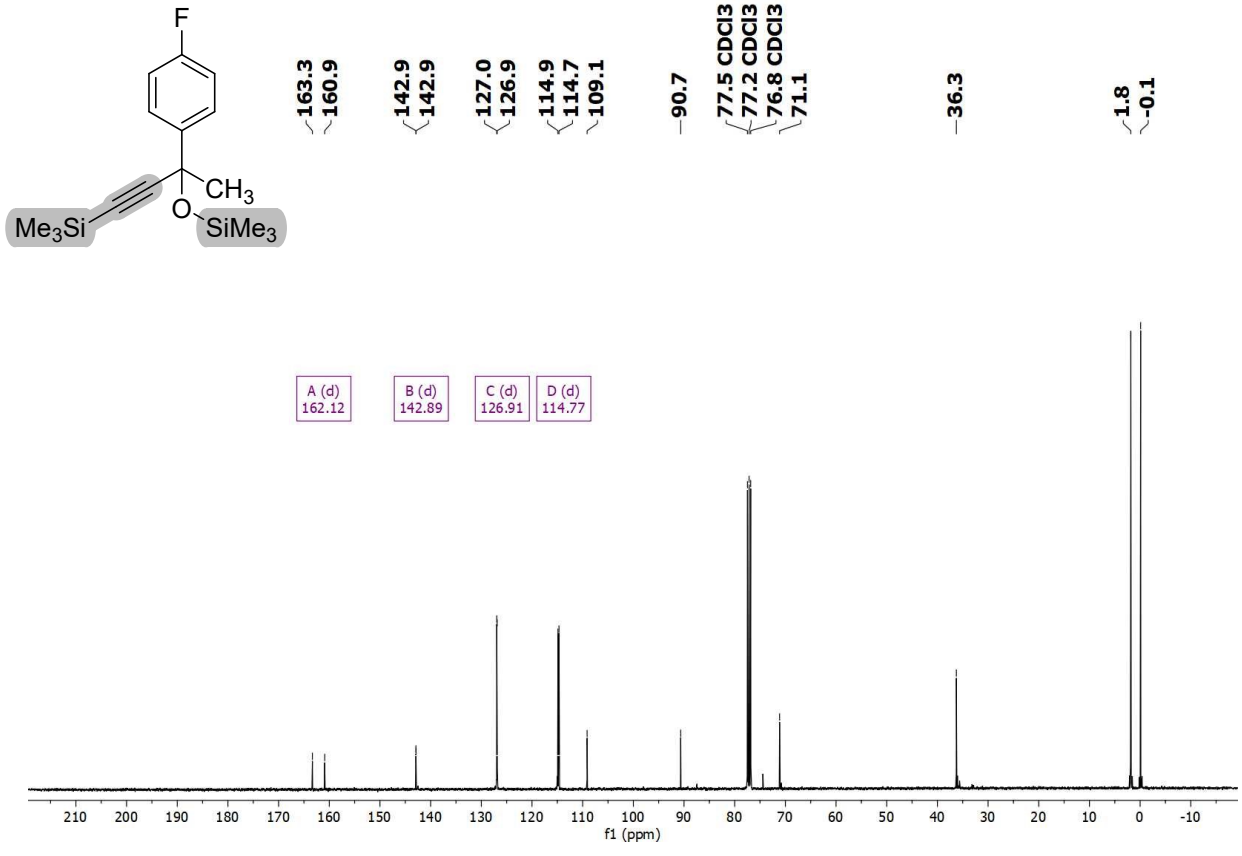


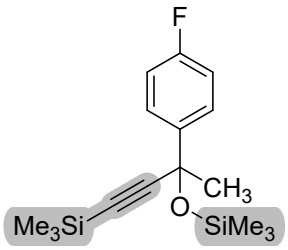



-13.1
-18.4
CH3
O
Me3Si
SiMe3
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

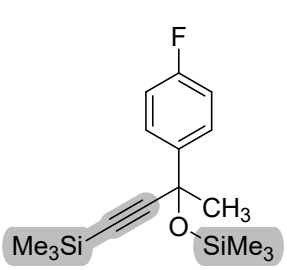
(3-(4-Fluorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3g)





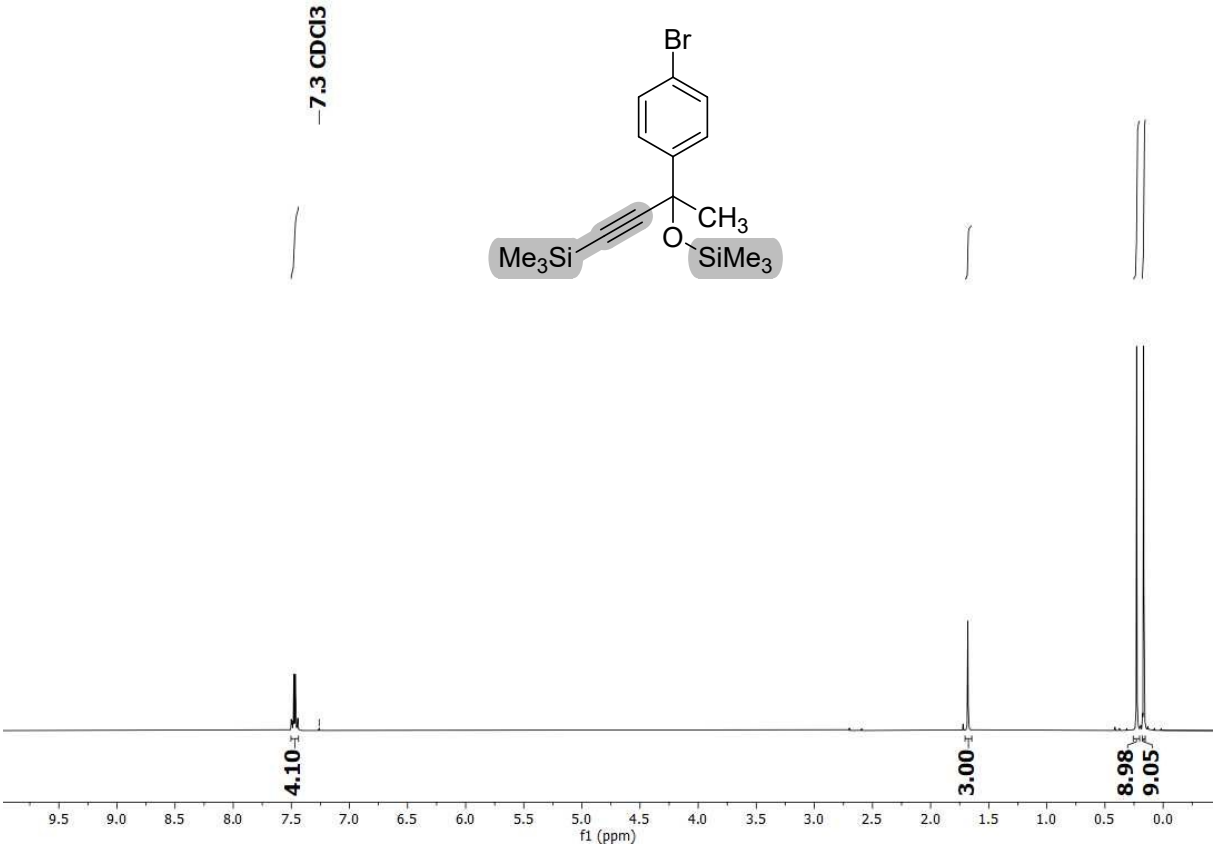

F
CH3
O
Me3Si
SiMe3

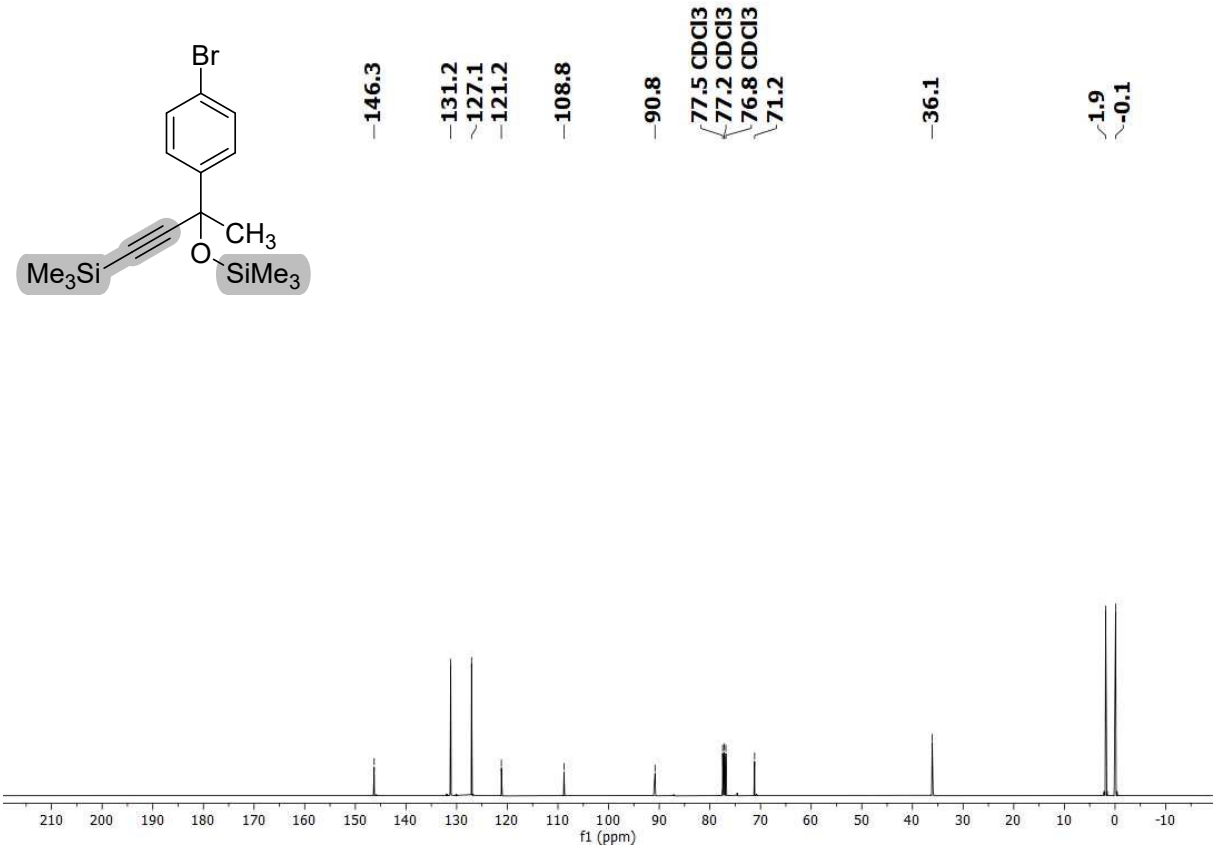
-116.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)

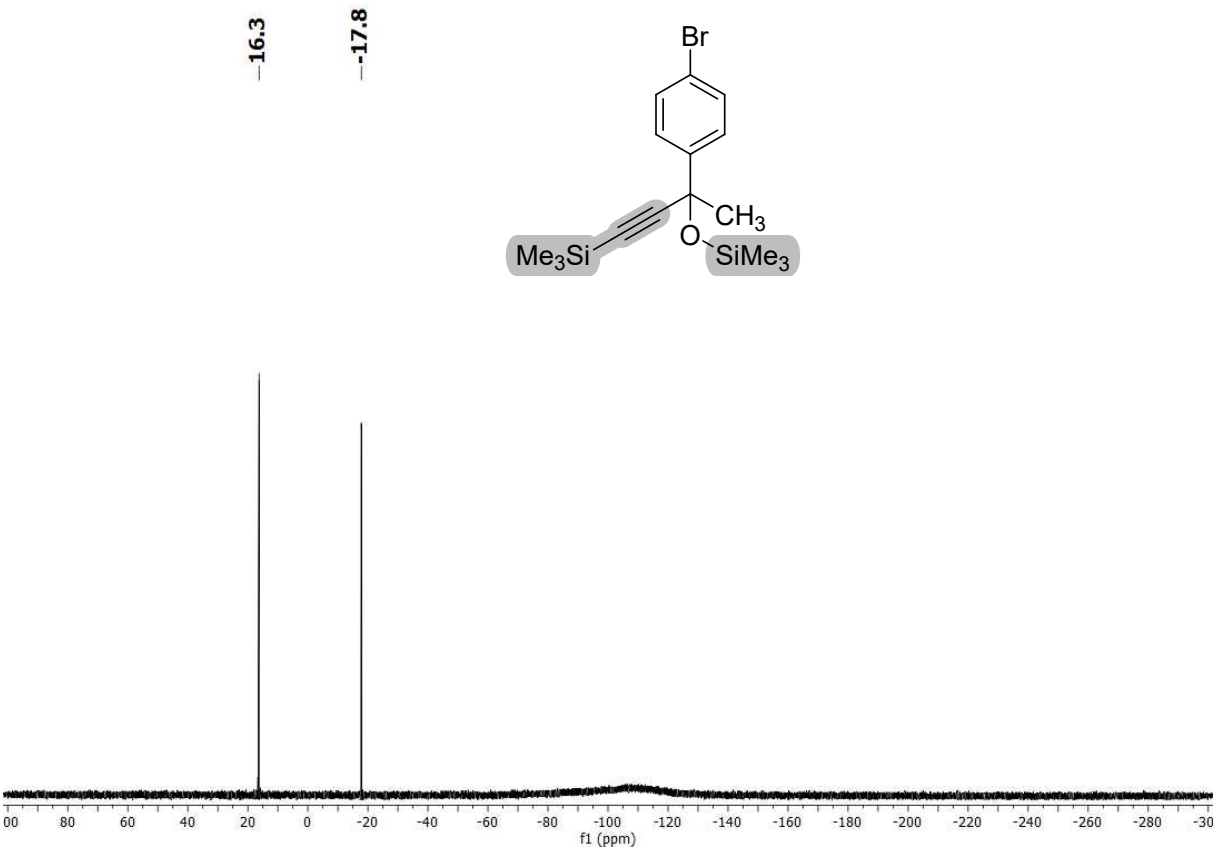

F
CH3
O
Me3Si
SiMe3

-16.0
-17.9
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

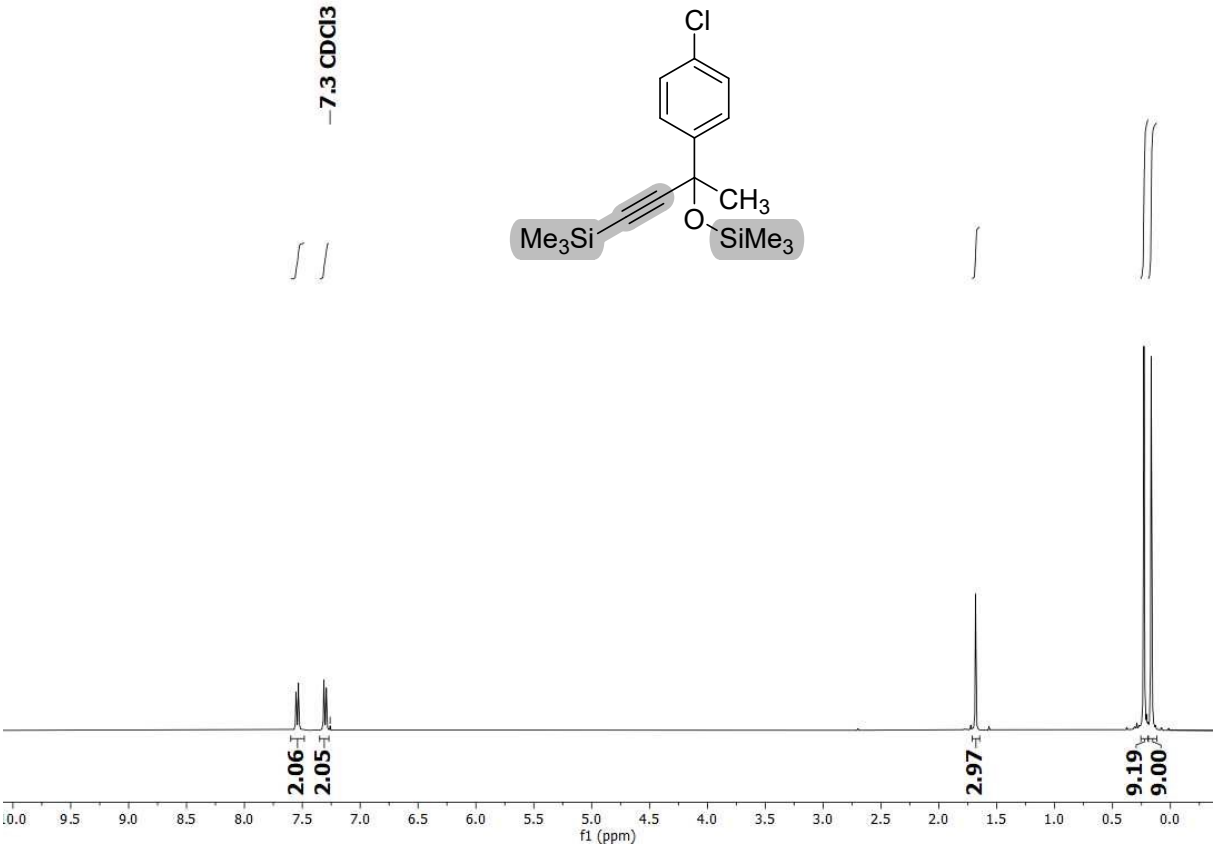
(3-(4-Bromophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3h)

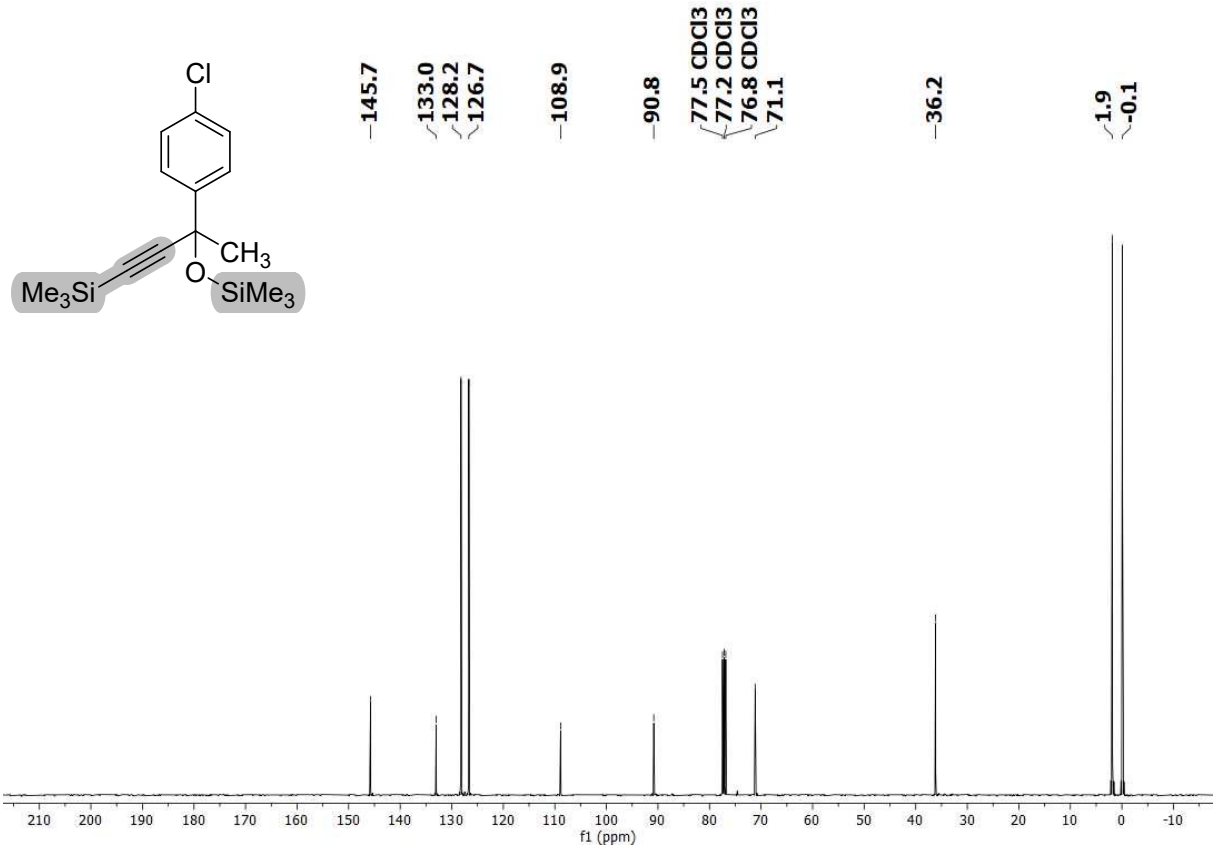


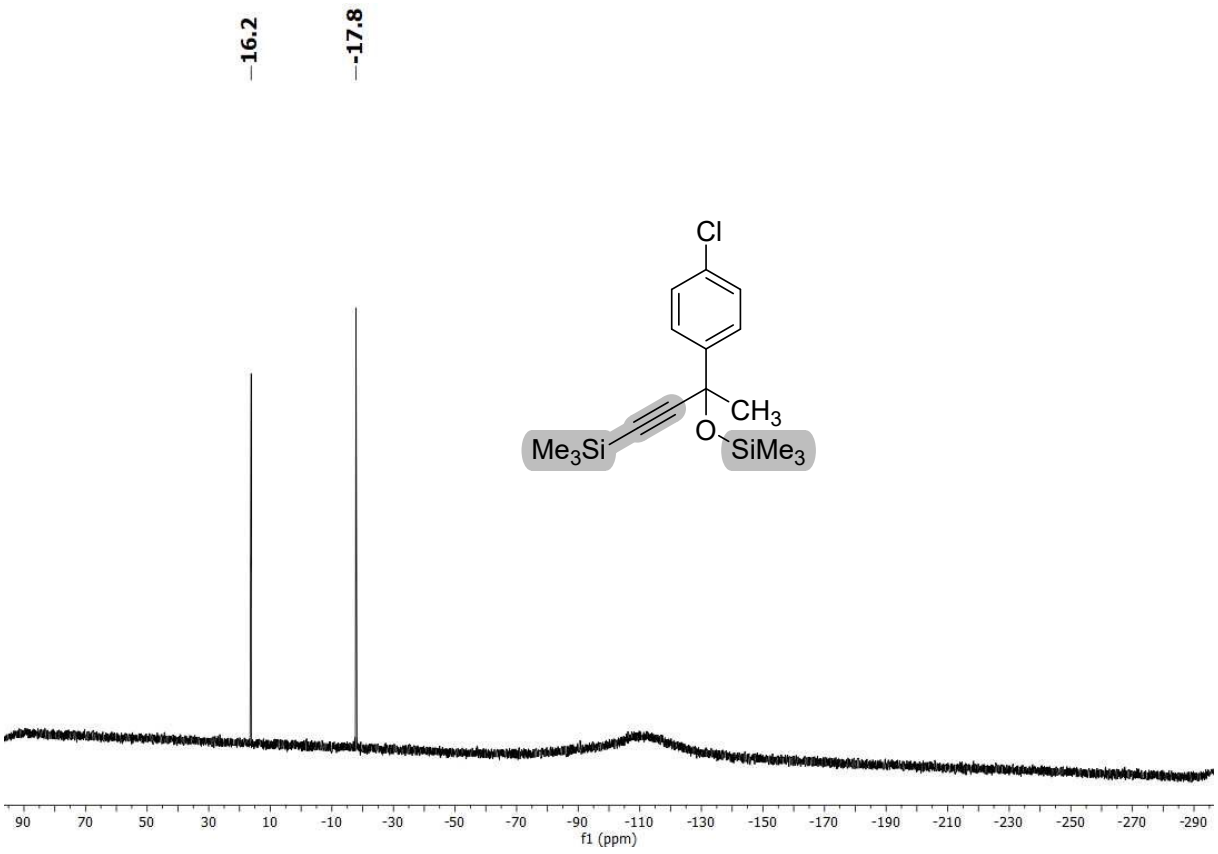



16.3
-17.8
Br
CH3
O
Me3Si
SiMe3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

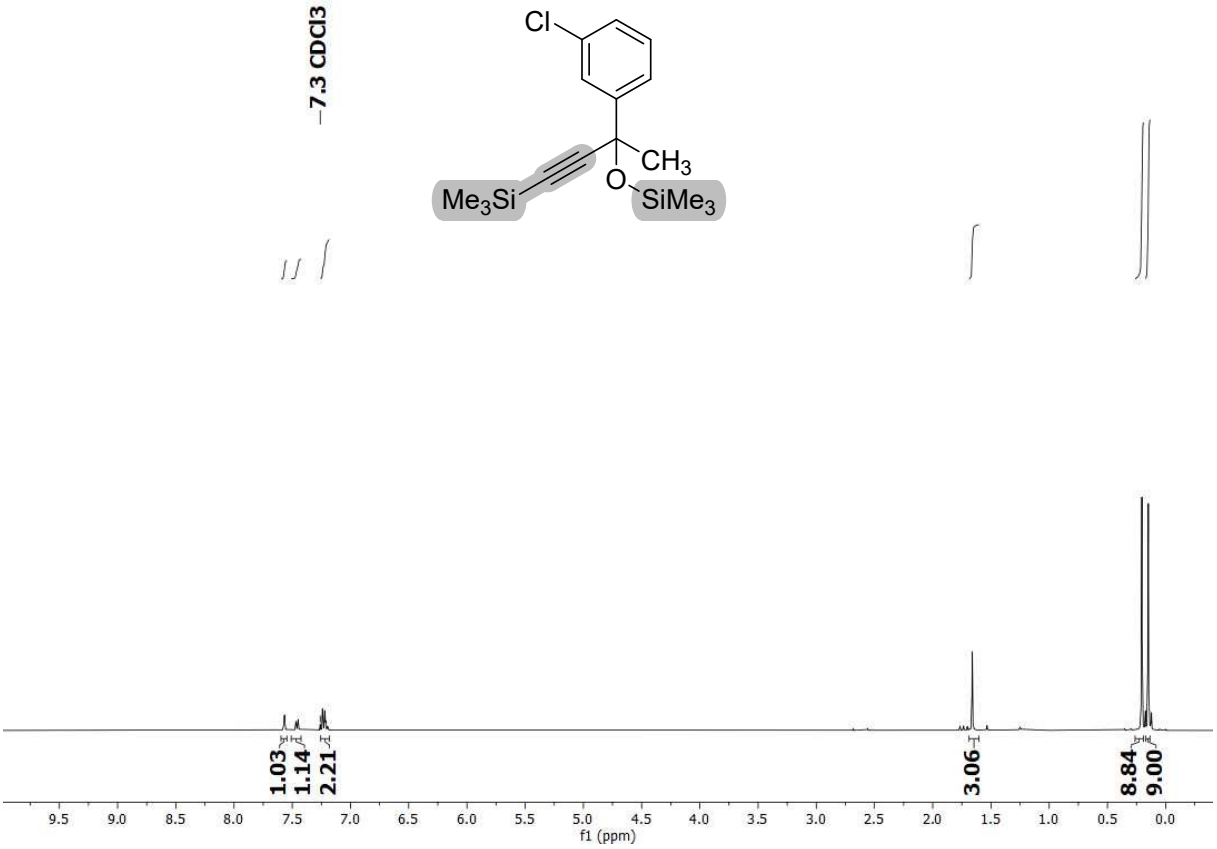
(3-(4-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3i)

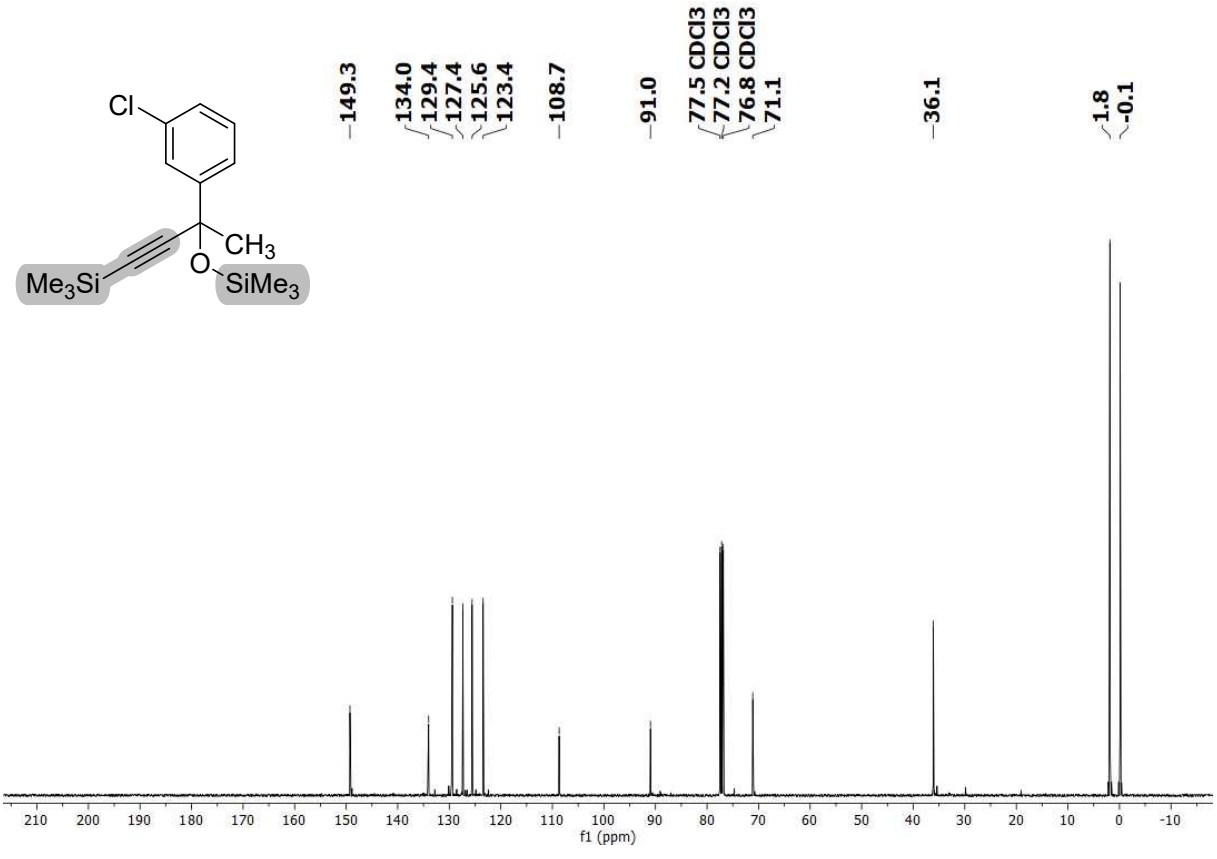


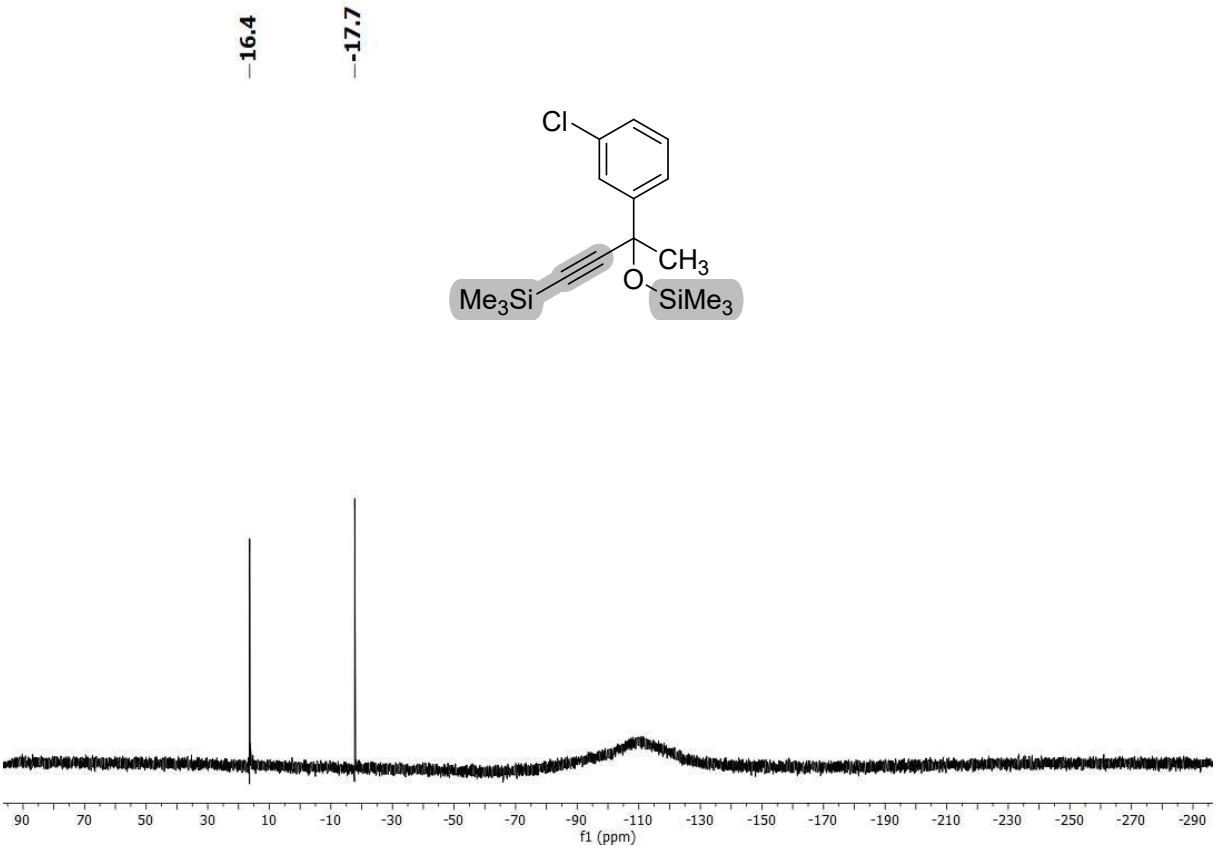



-16.2
-17.8
Cl
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

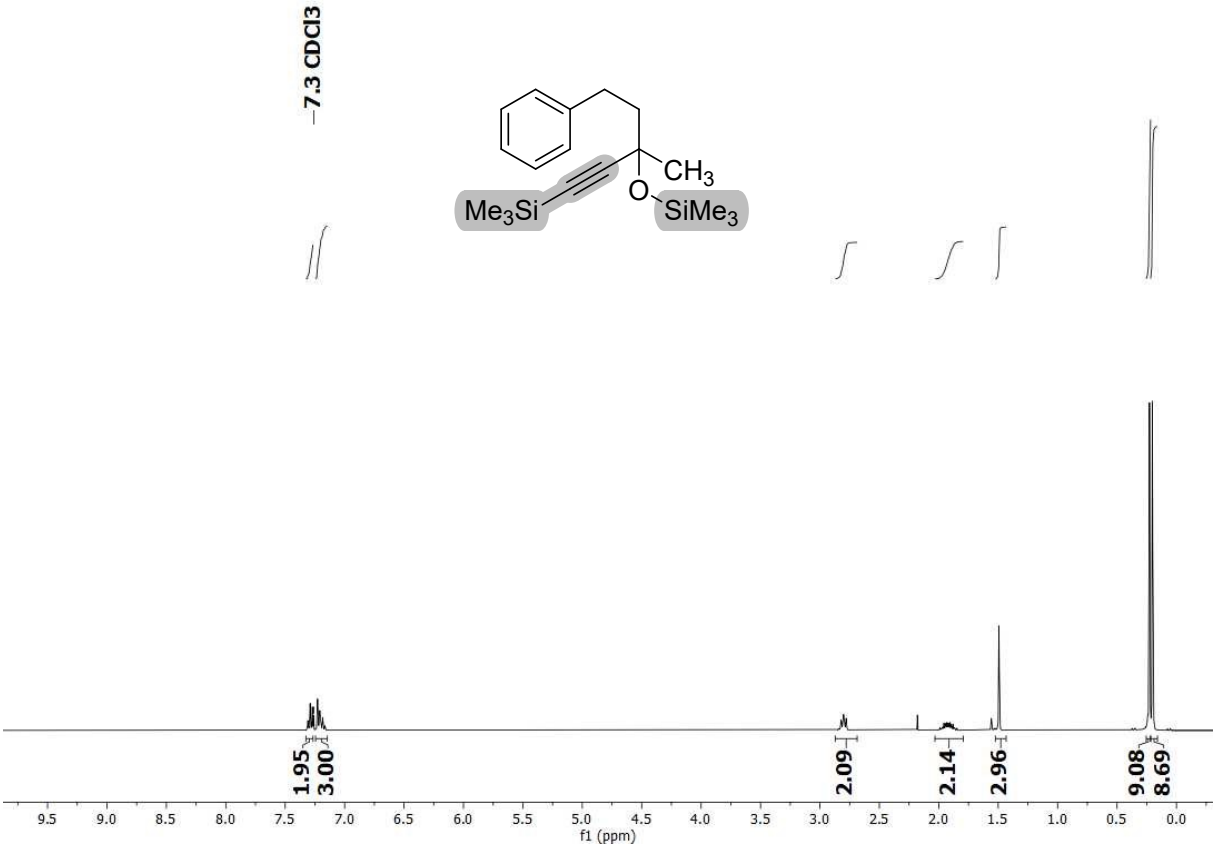
(3-(3-Chlorophenyl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)trimethylsilane (3j)

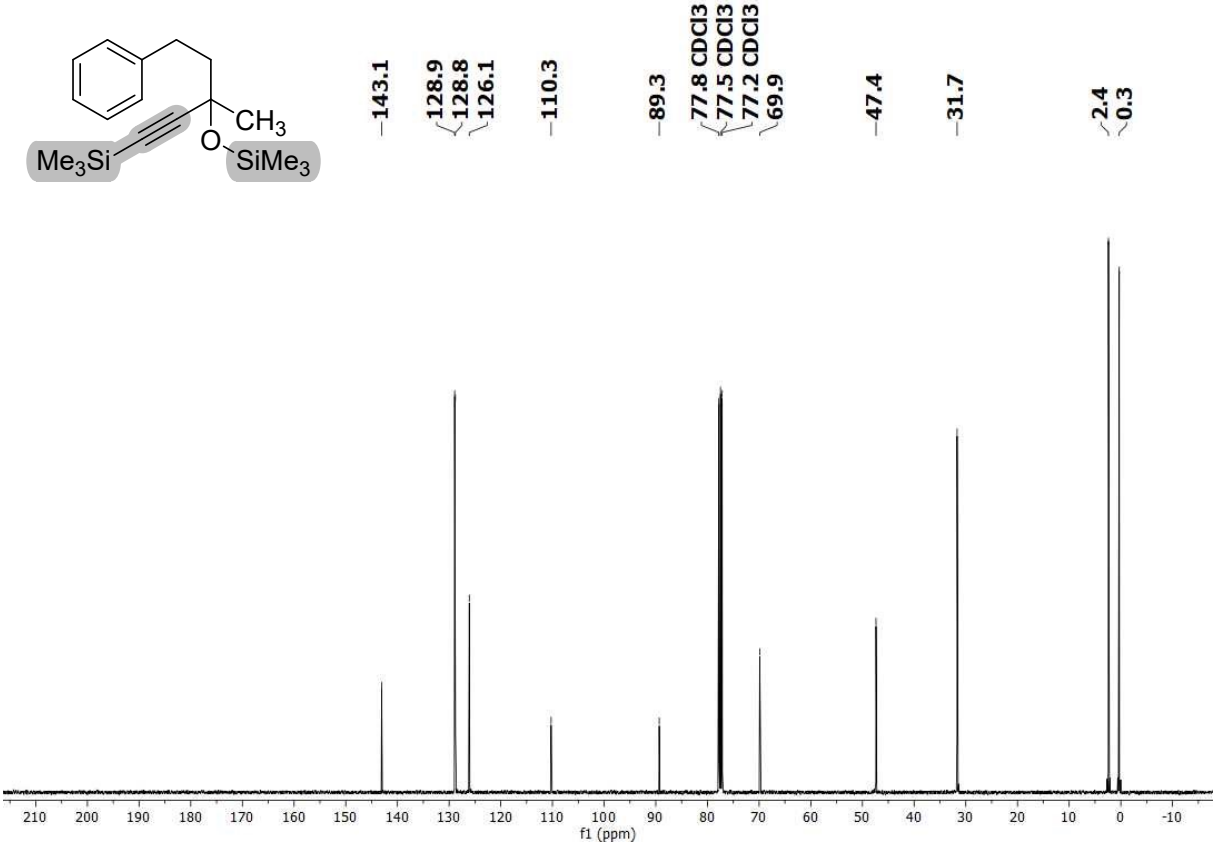


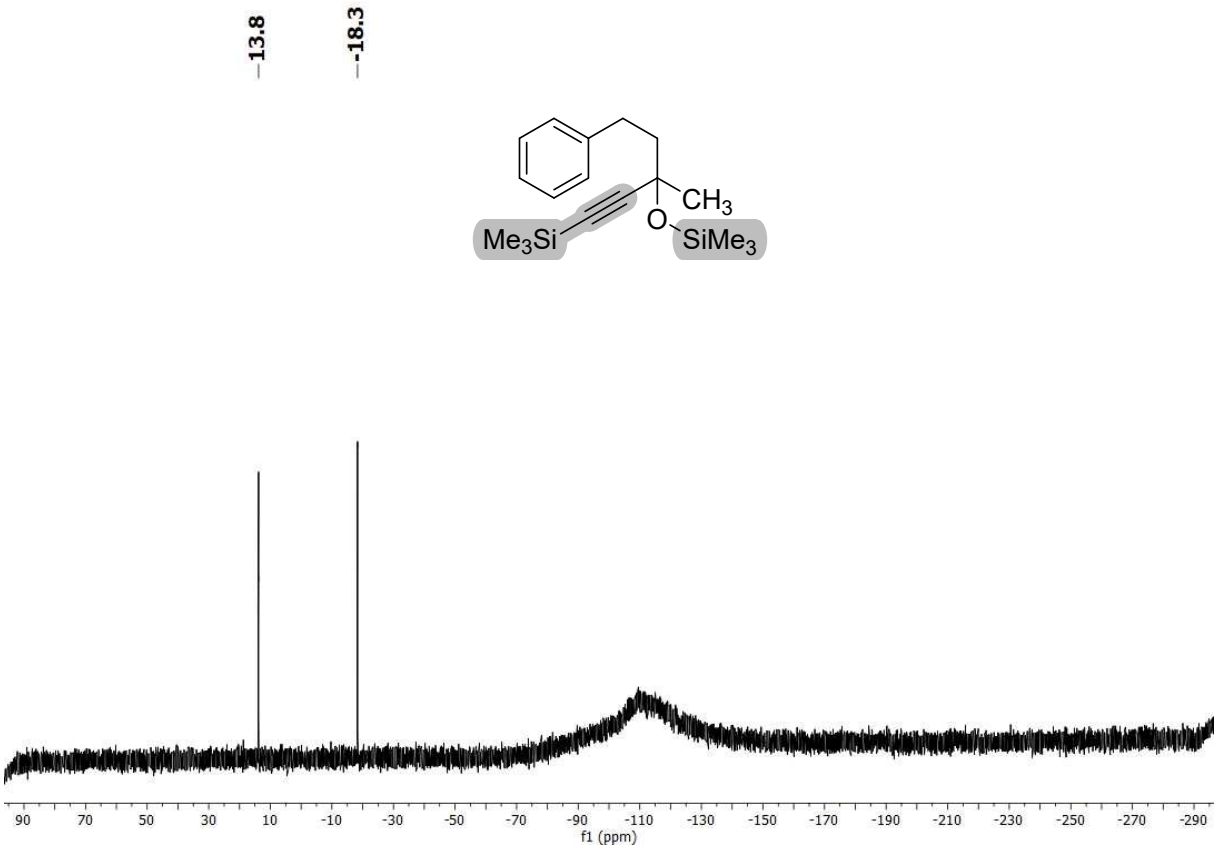



-16.4
-17.7
Cl
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

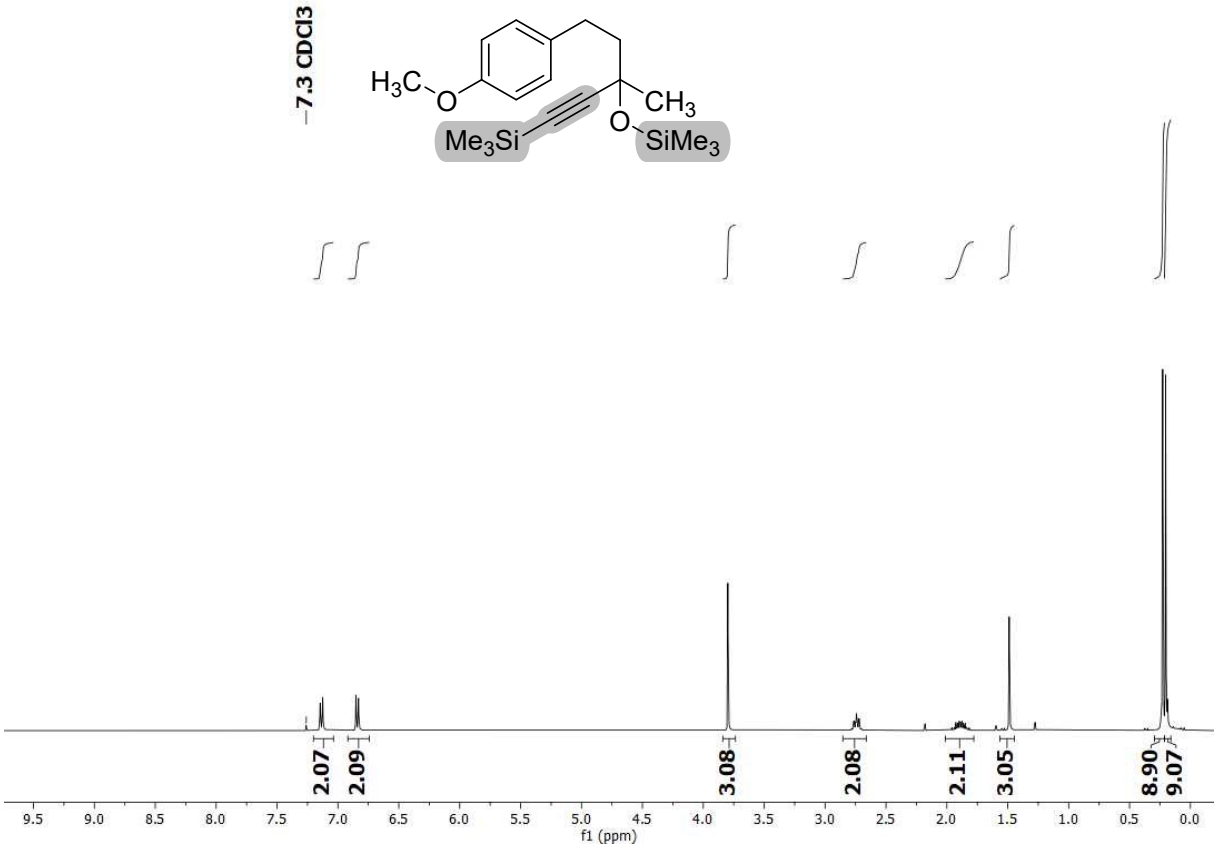
Trimethyl((3-methyl-5-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane (3k)

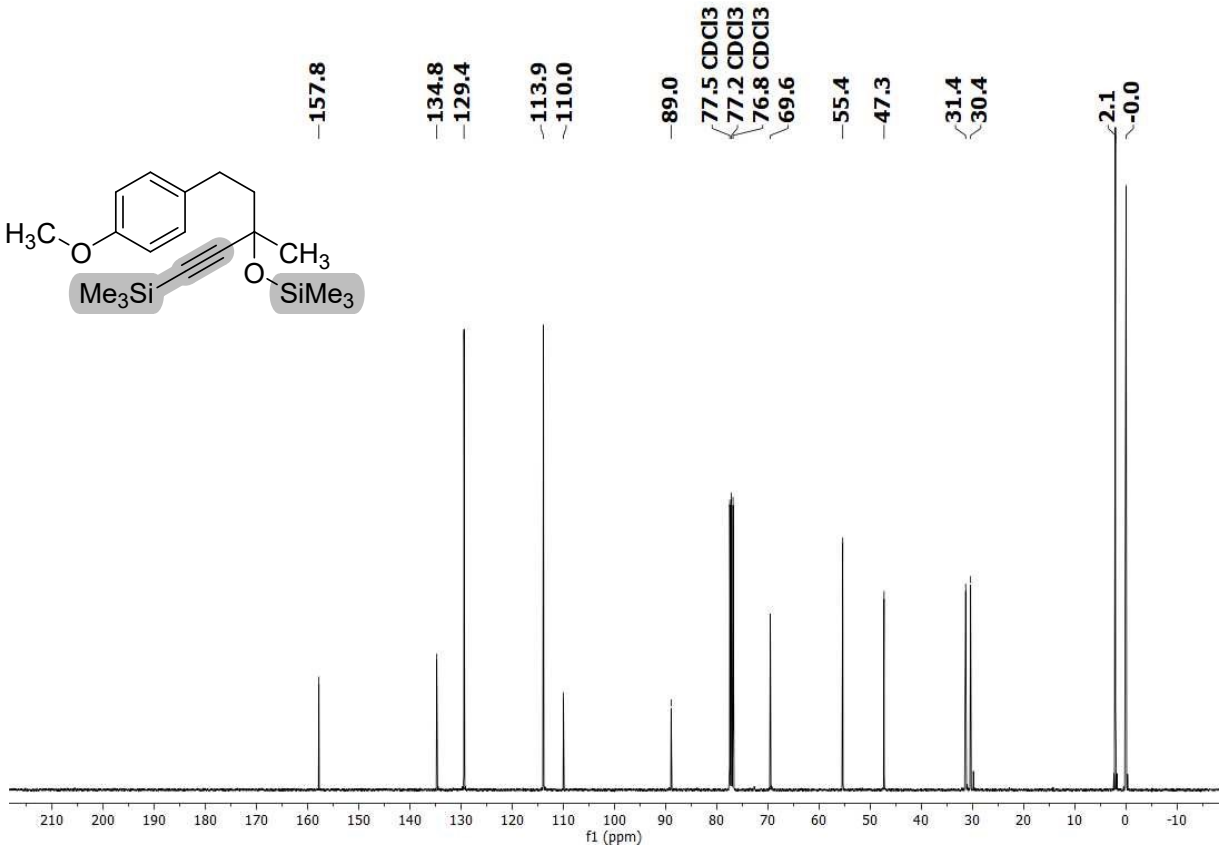


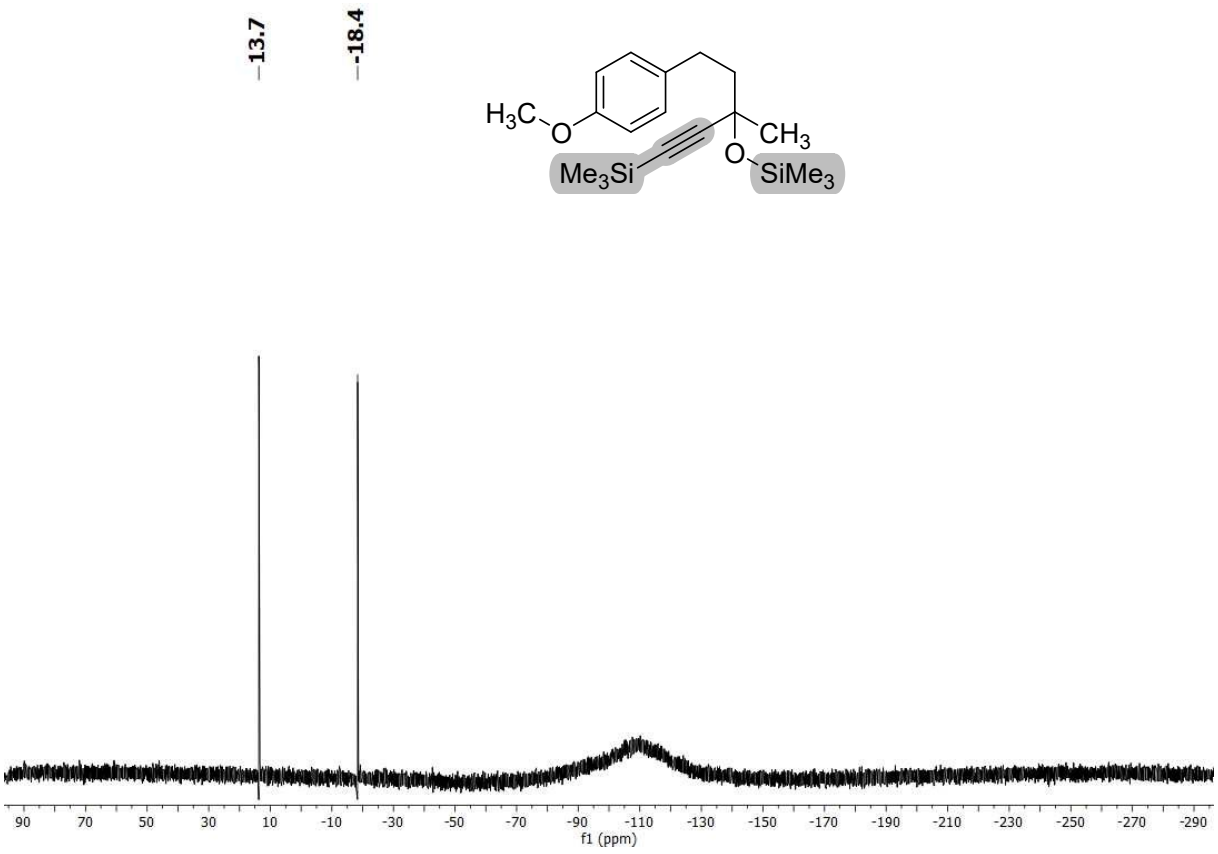



-13.8
-18.3
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

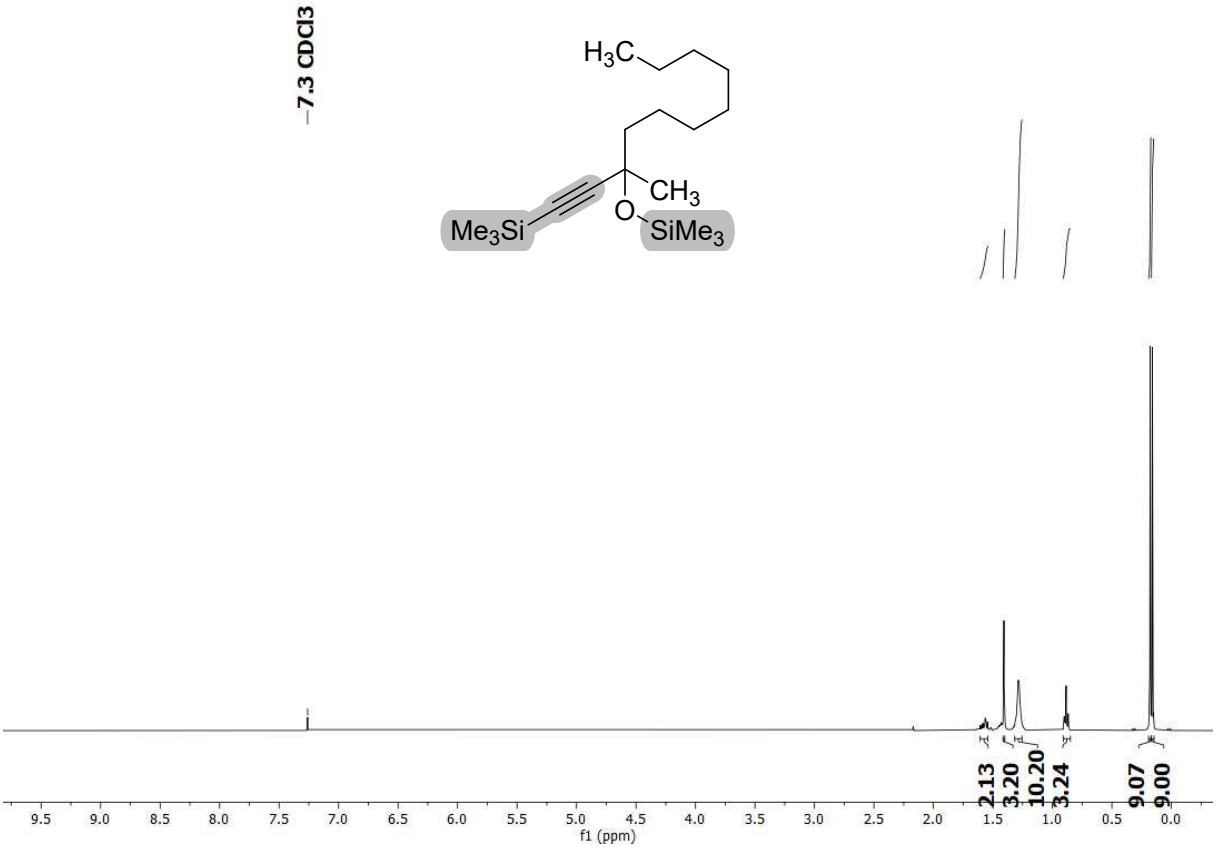
((5-(4-Methoxyphenyl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (3l)

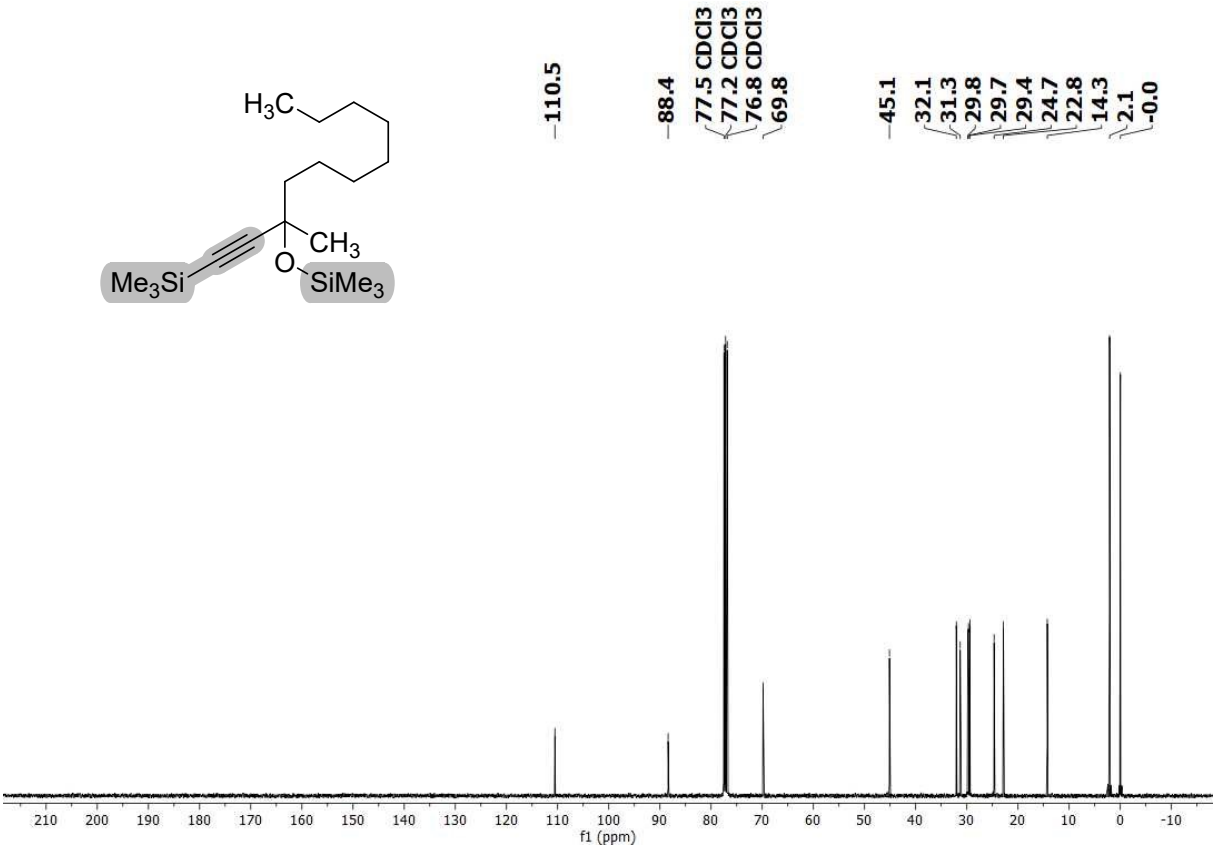


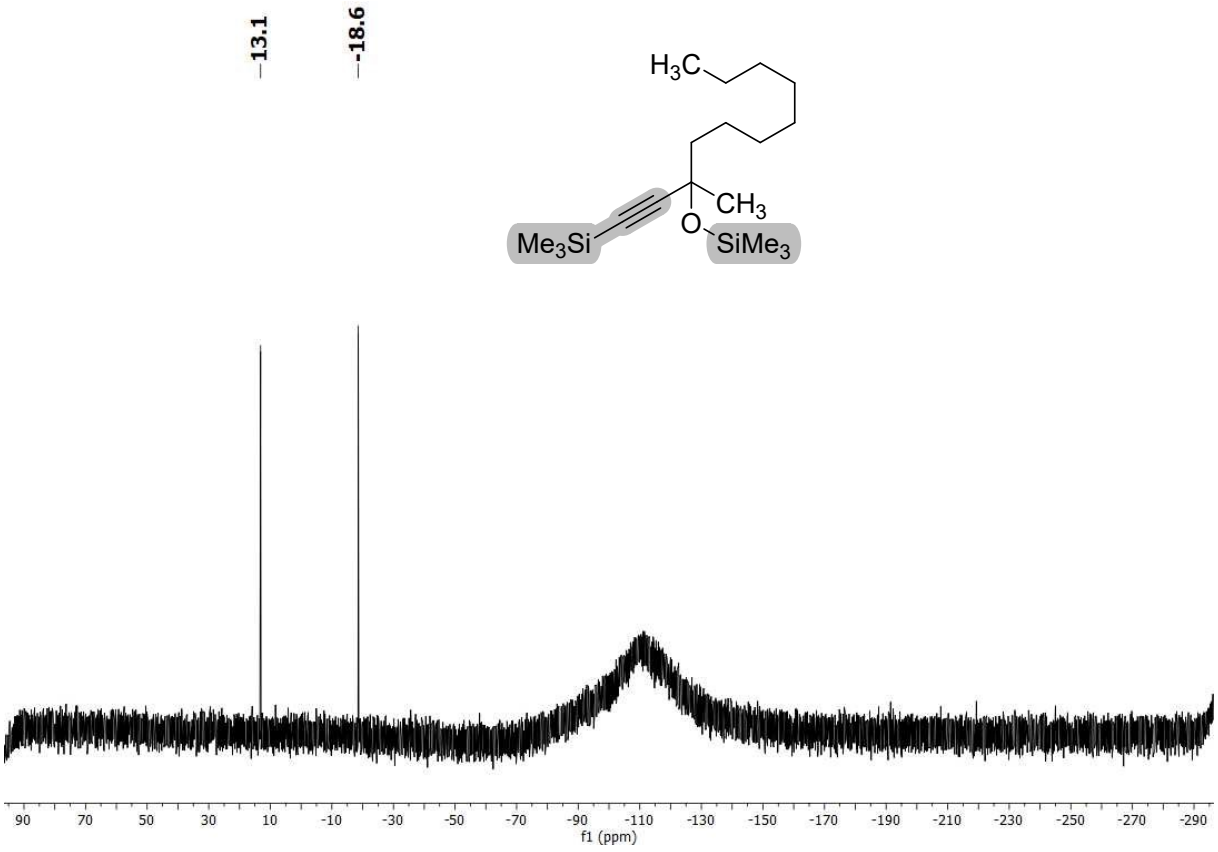



-13.7
-18.4
H3C
O
CH3
Me3Si
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

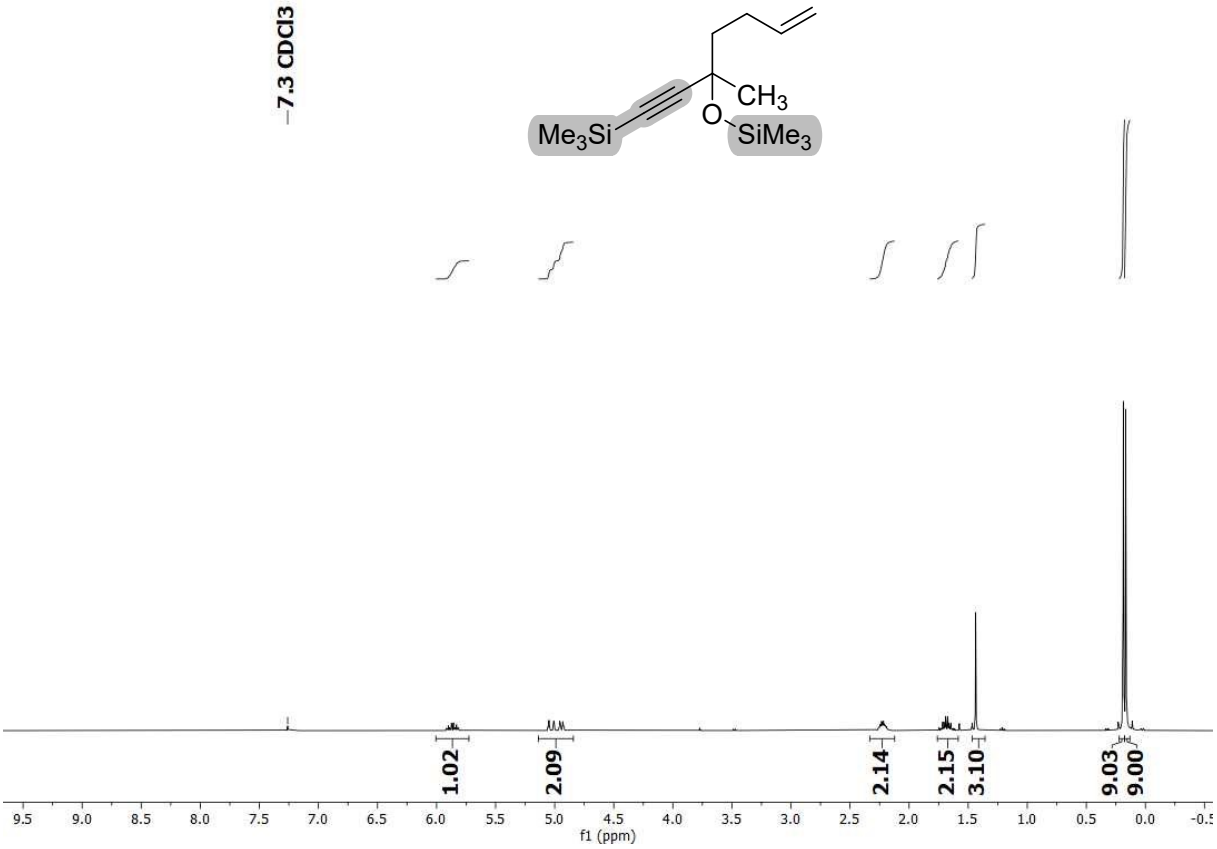
Trimethyl((3-methyl-1-(trimethylsilyl)undec-1-yn-3-yl)oxy)silane (3m)

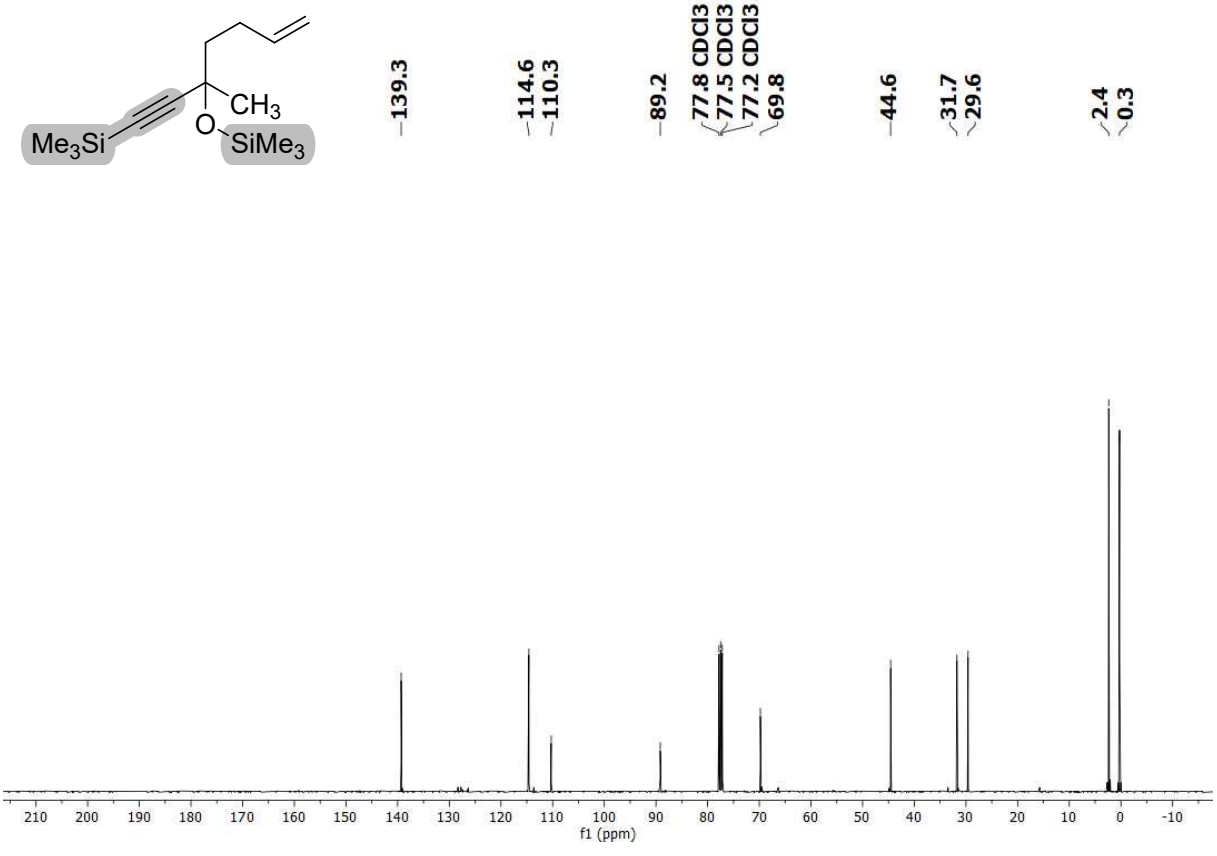


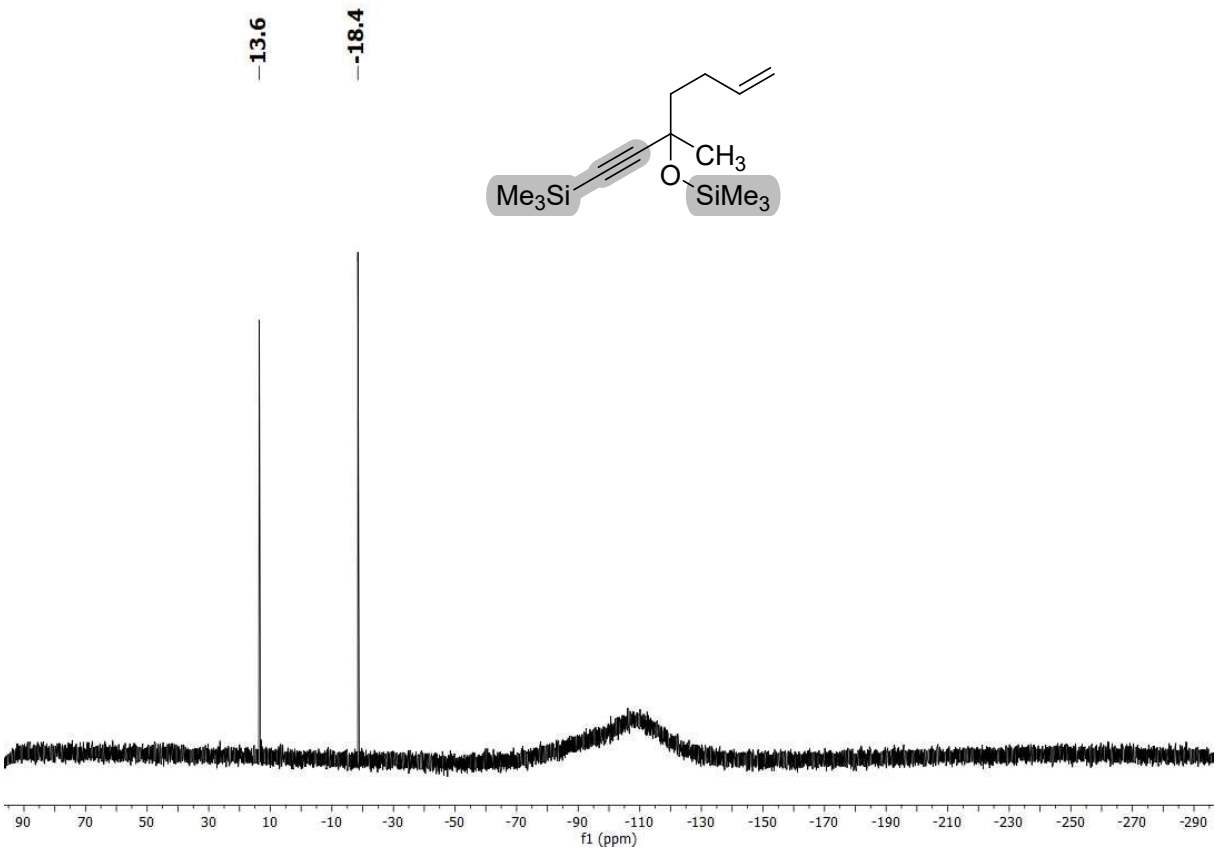



-13.1
-18.6
H3C
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

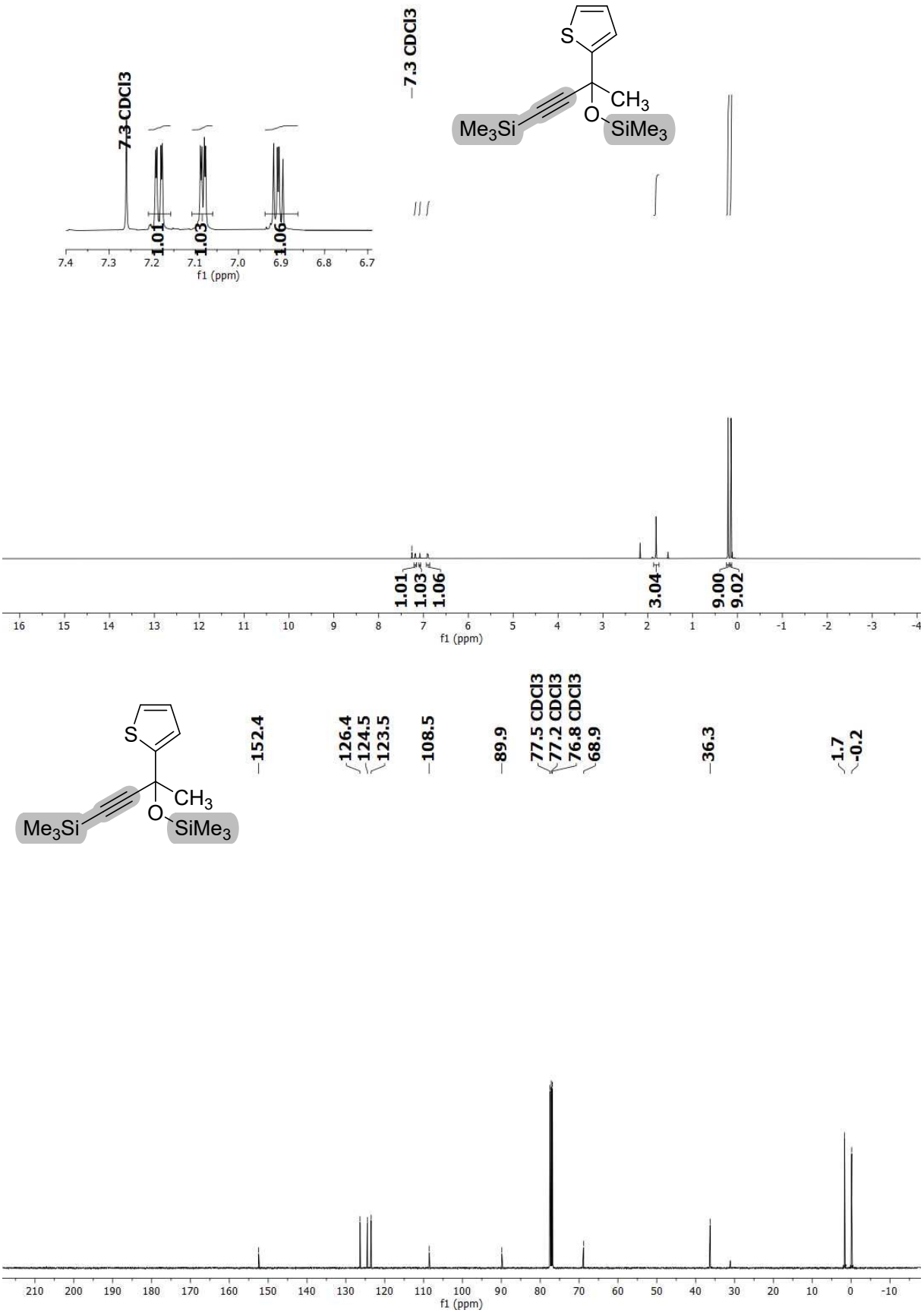
Trimethyl((3-methyl-1-(trimethylsilyl)hept-6-en-1-yn-3-yl)oxy)silane (3n)

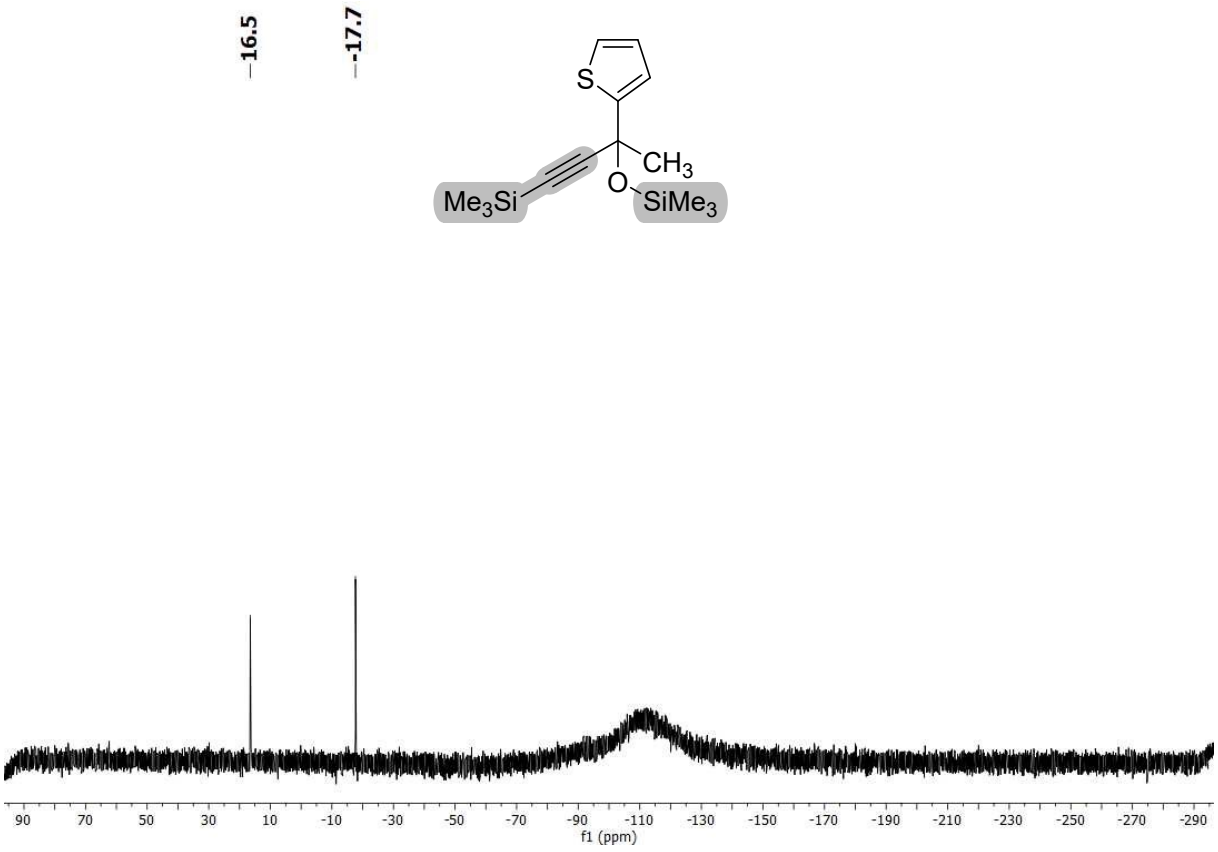




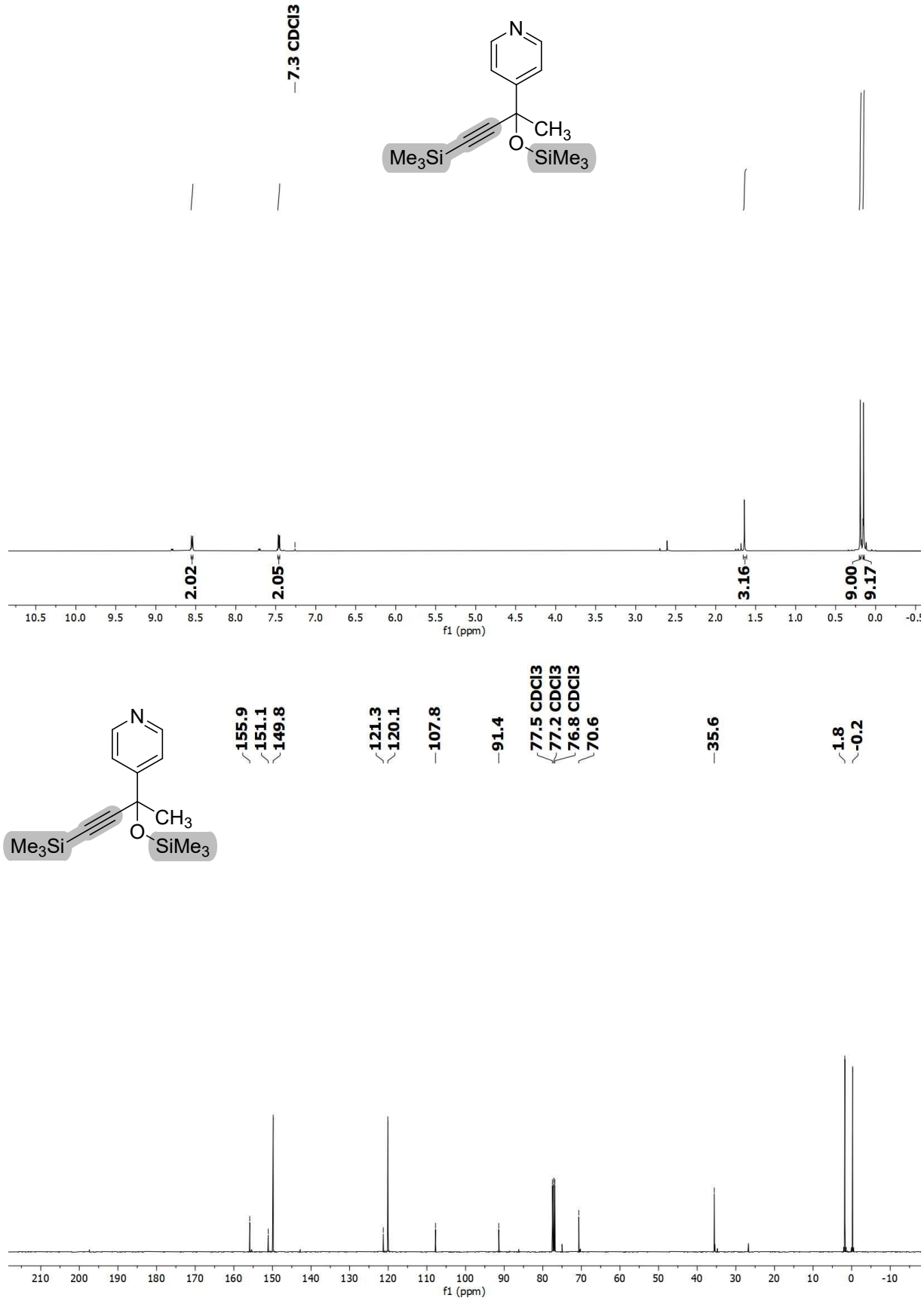

-13.6
-18.4
Me3Si
CH3
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

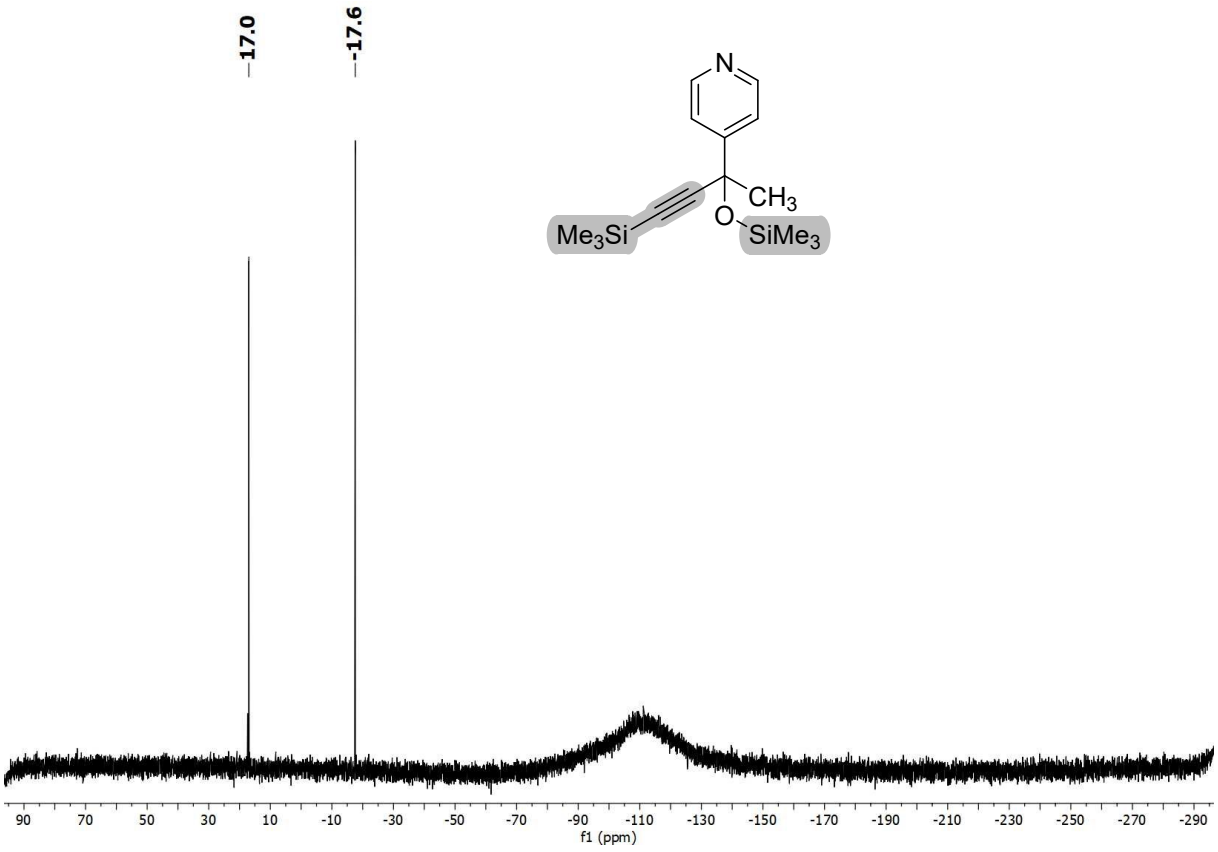
Trimethyl(3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)but-1-yn-1-yl)silane (3o)



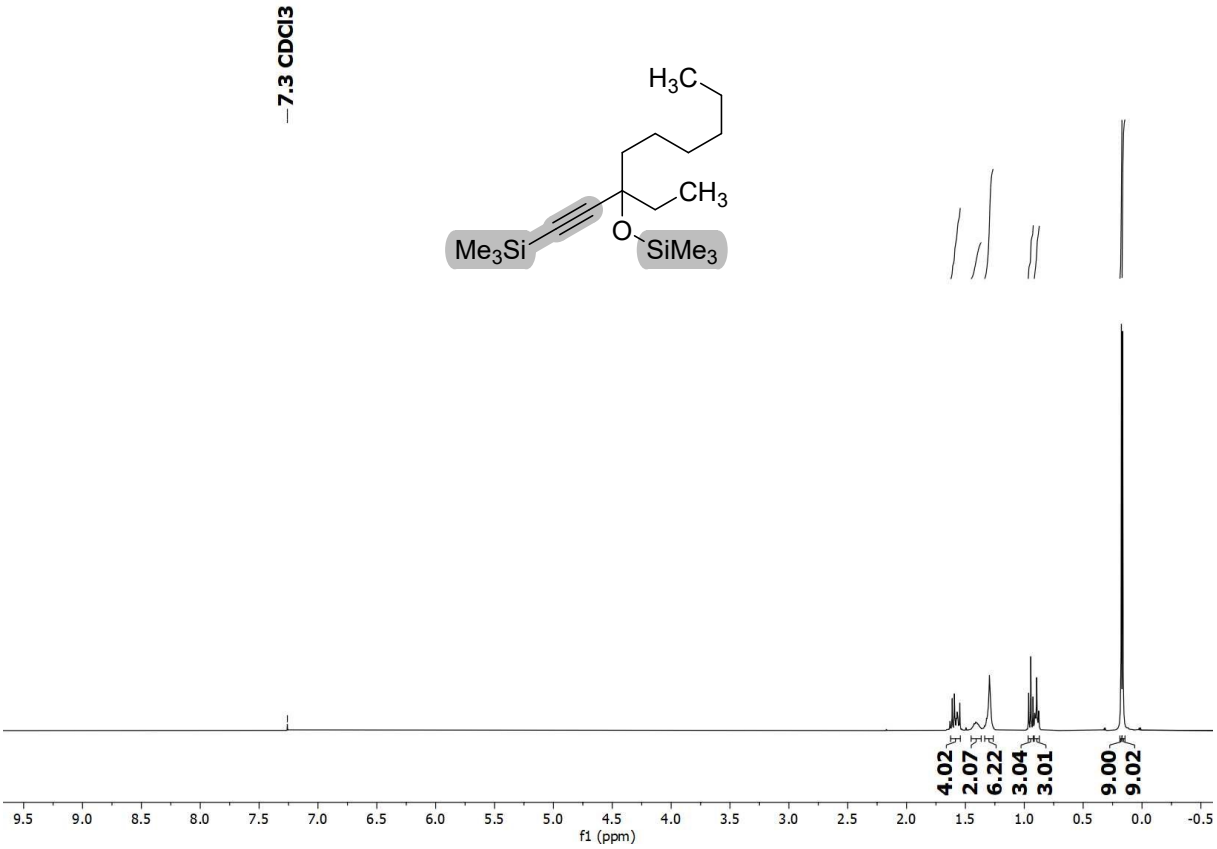

-16.5
-17.7
S
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

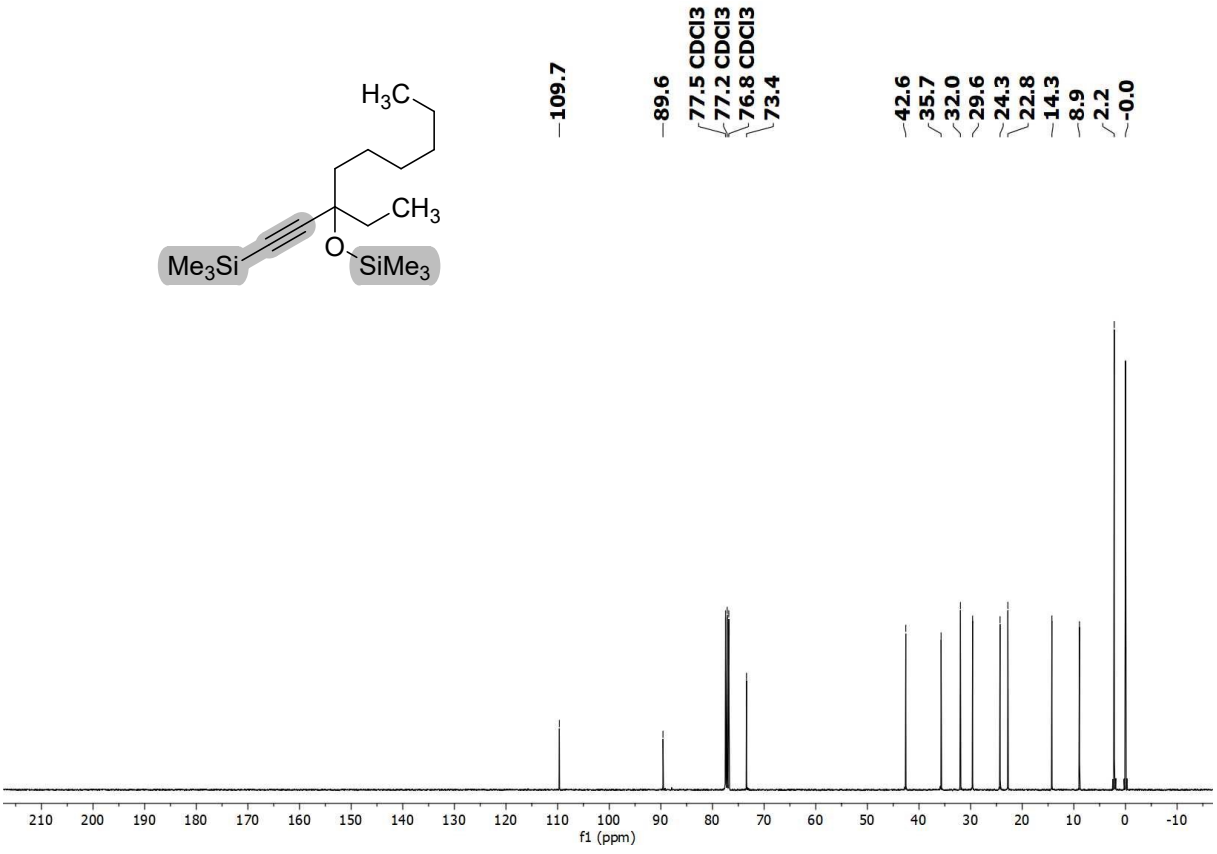
4-(4-(Trimethylsilyl)-2-((trimethylsilyl)oxy)but-3-yn-2-yl)pyridine (3p)

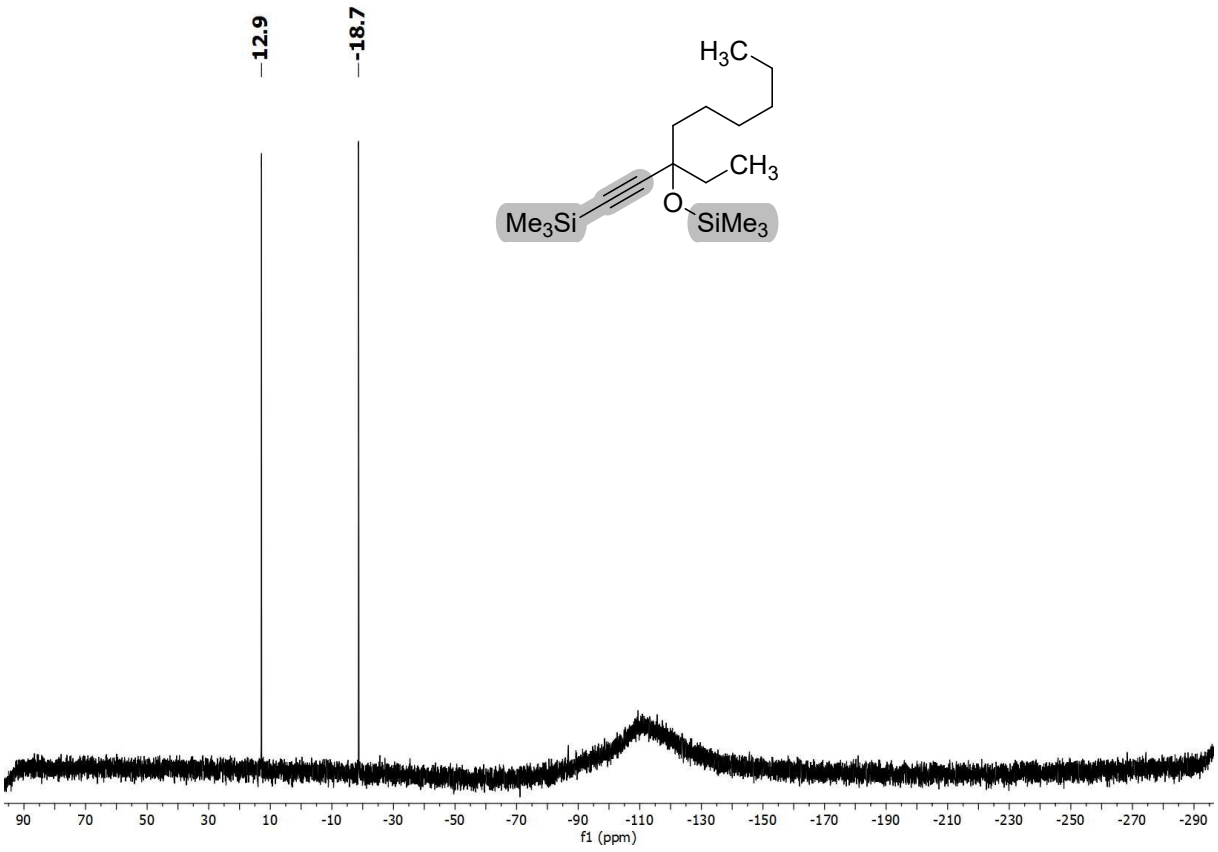



-17.0
-17.6
N
CH3
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

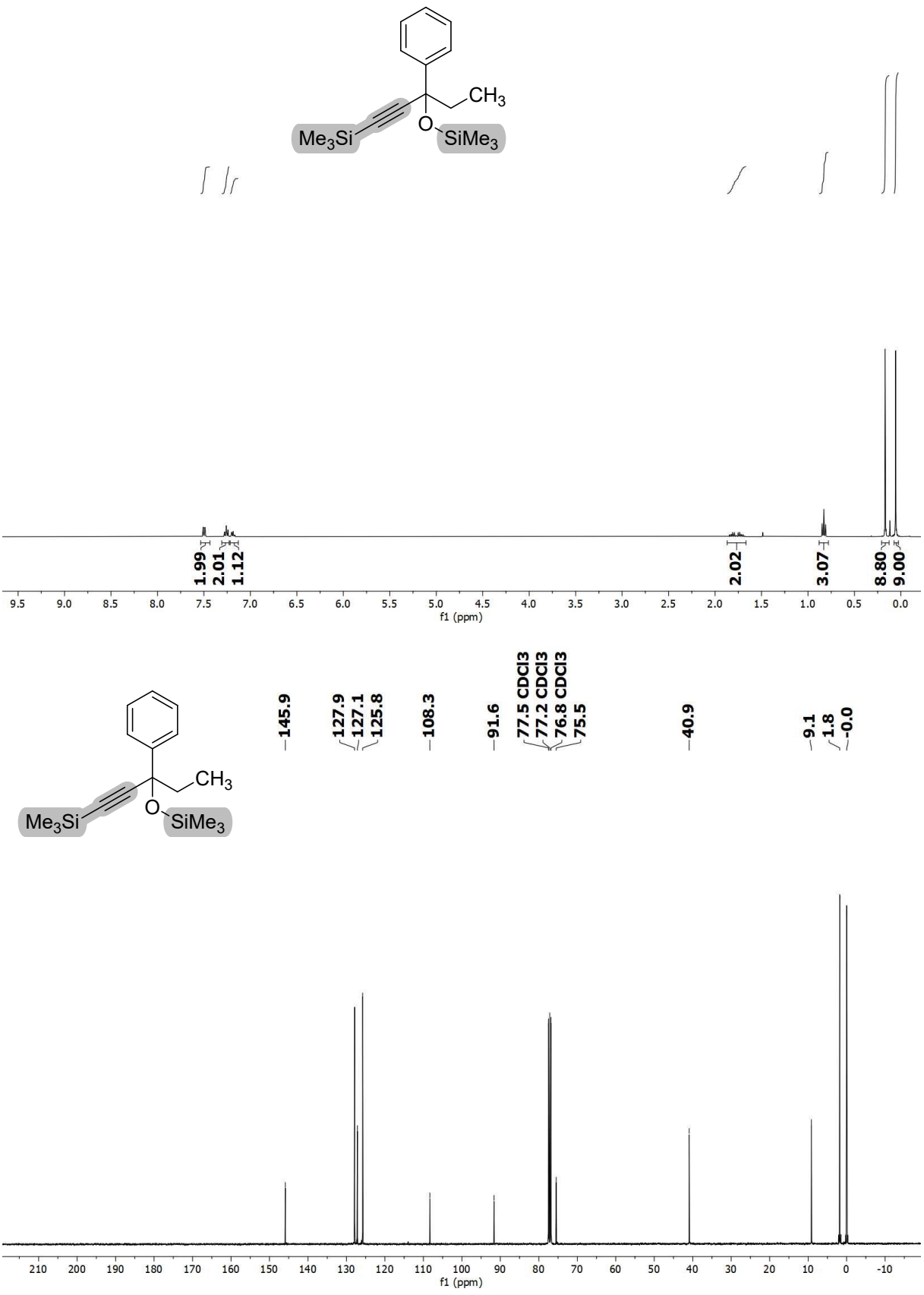
((3-Ethyl-1-(trimethylsilyl)non-1-yn-3-yl)oxy)trimethylsilane (3q)

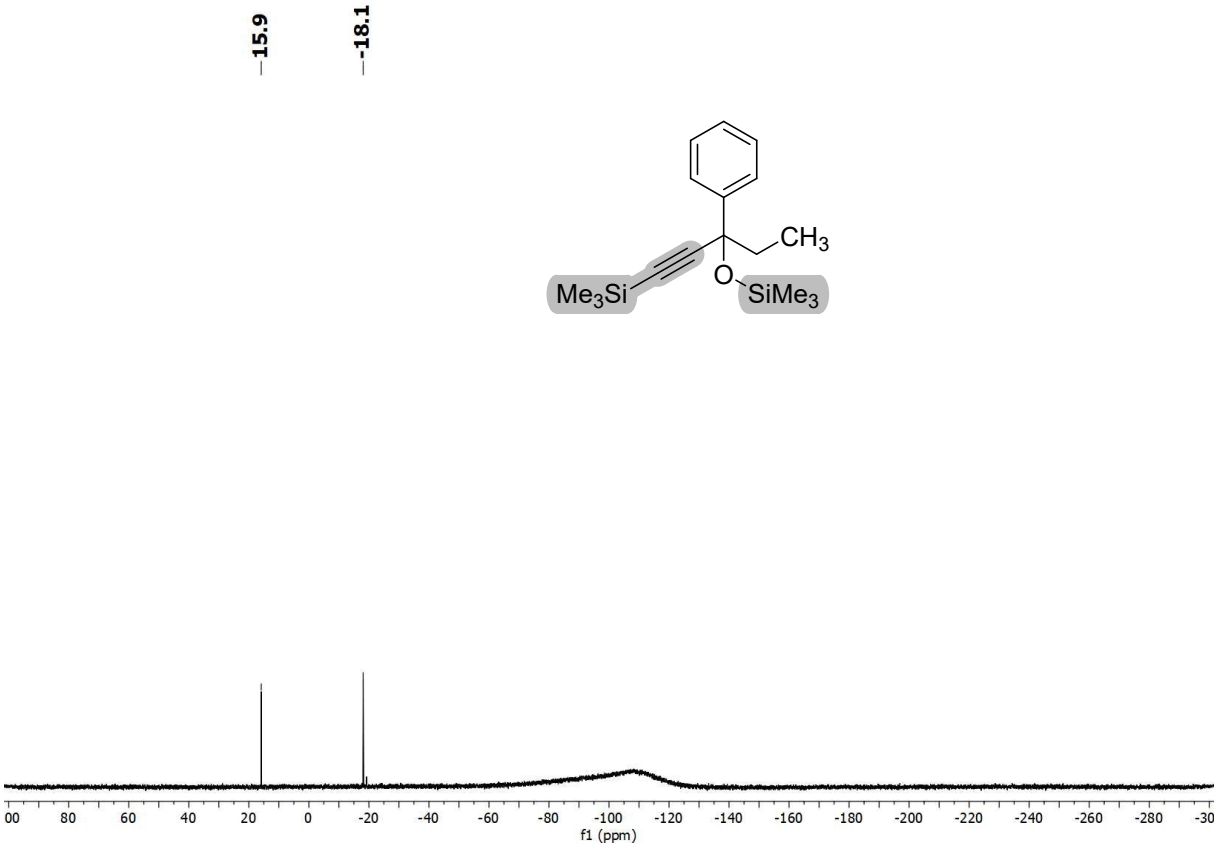




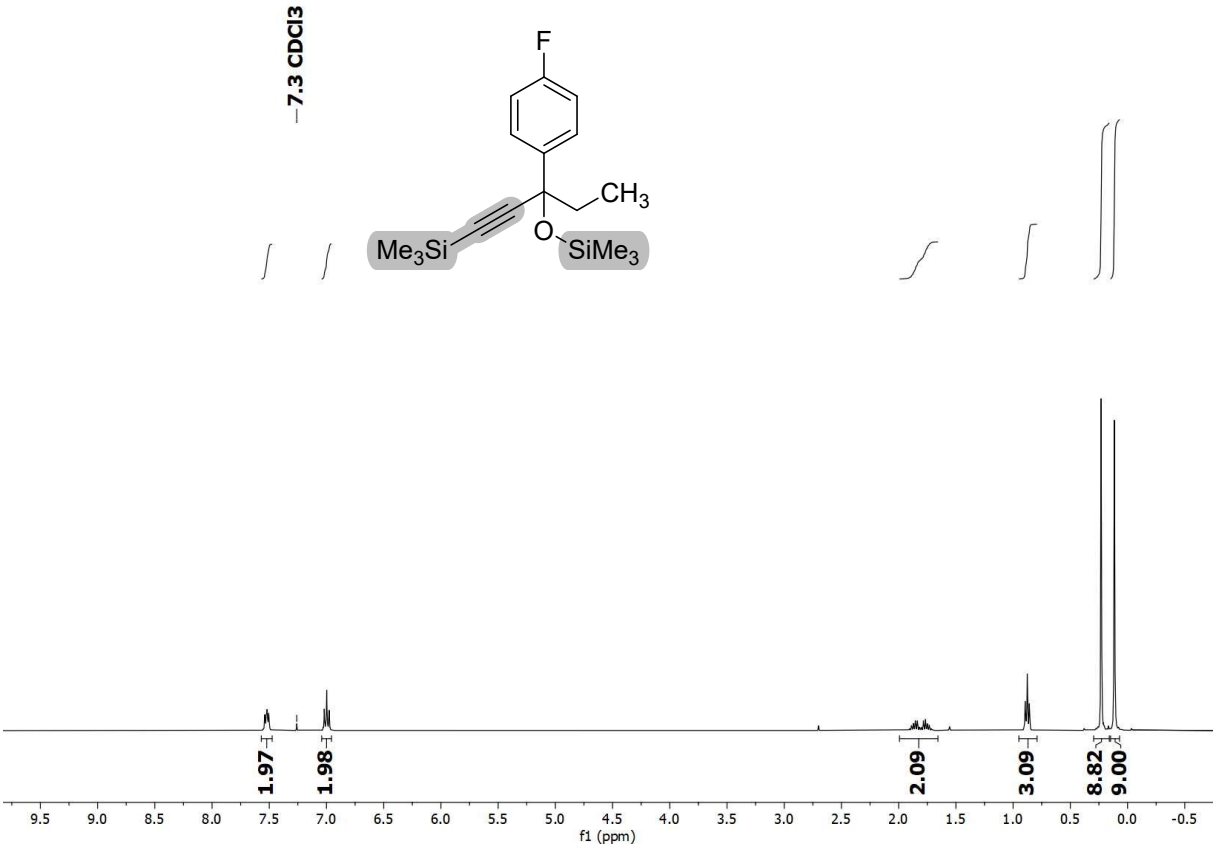

-12.9
-18.7
H3C
CH3
Me3Si
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

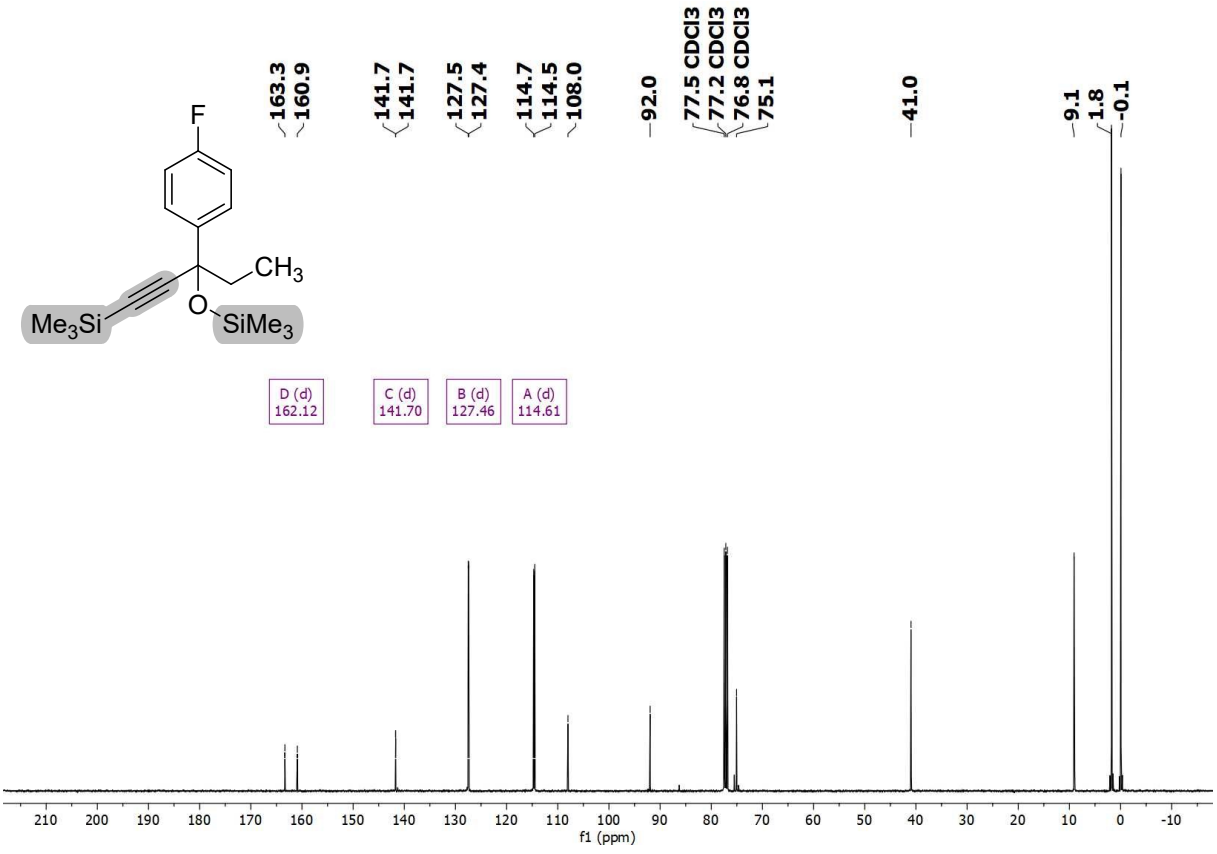
Trimethyl((3-phenyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)silane (3r)

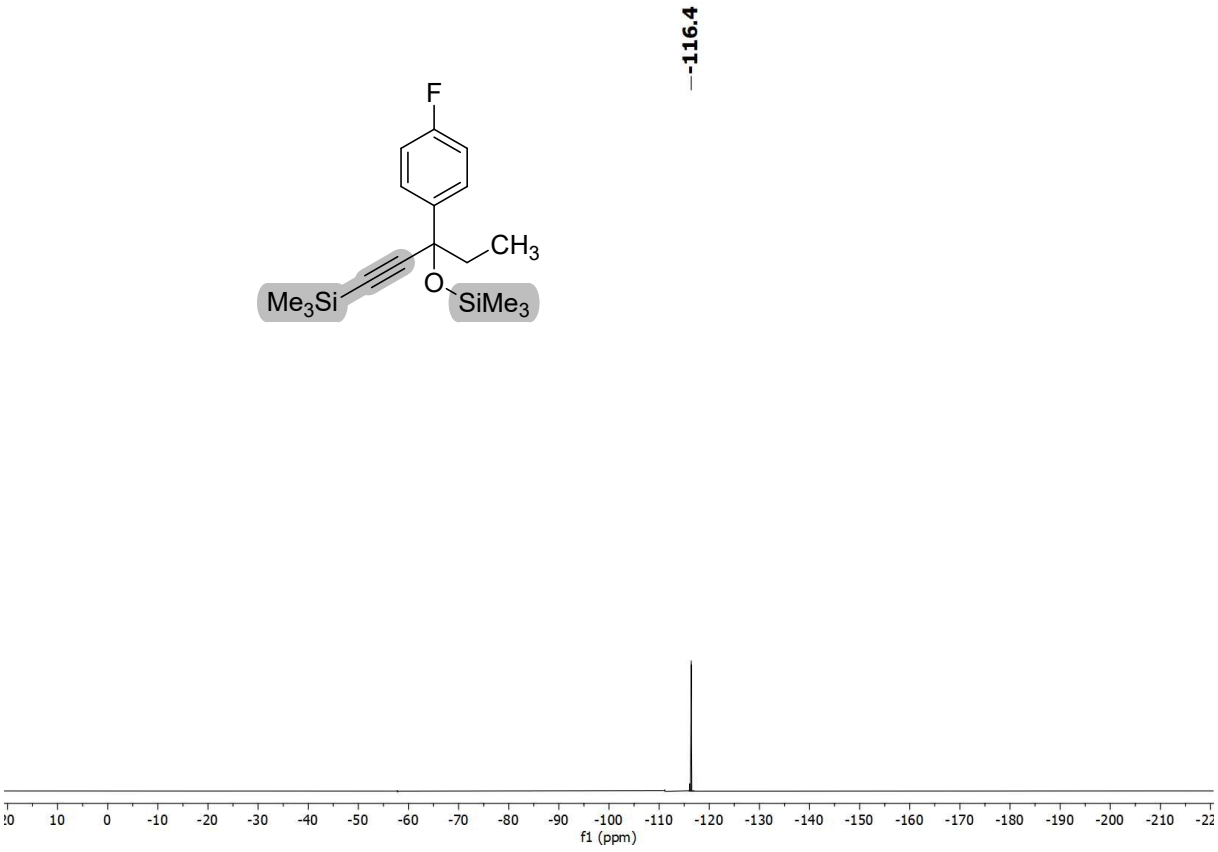


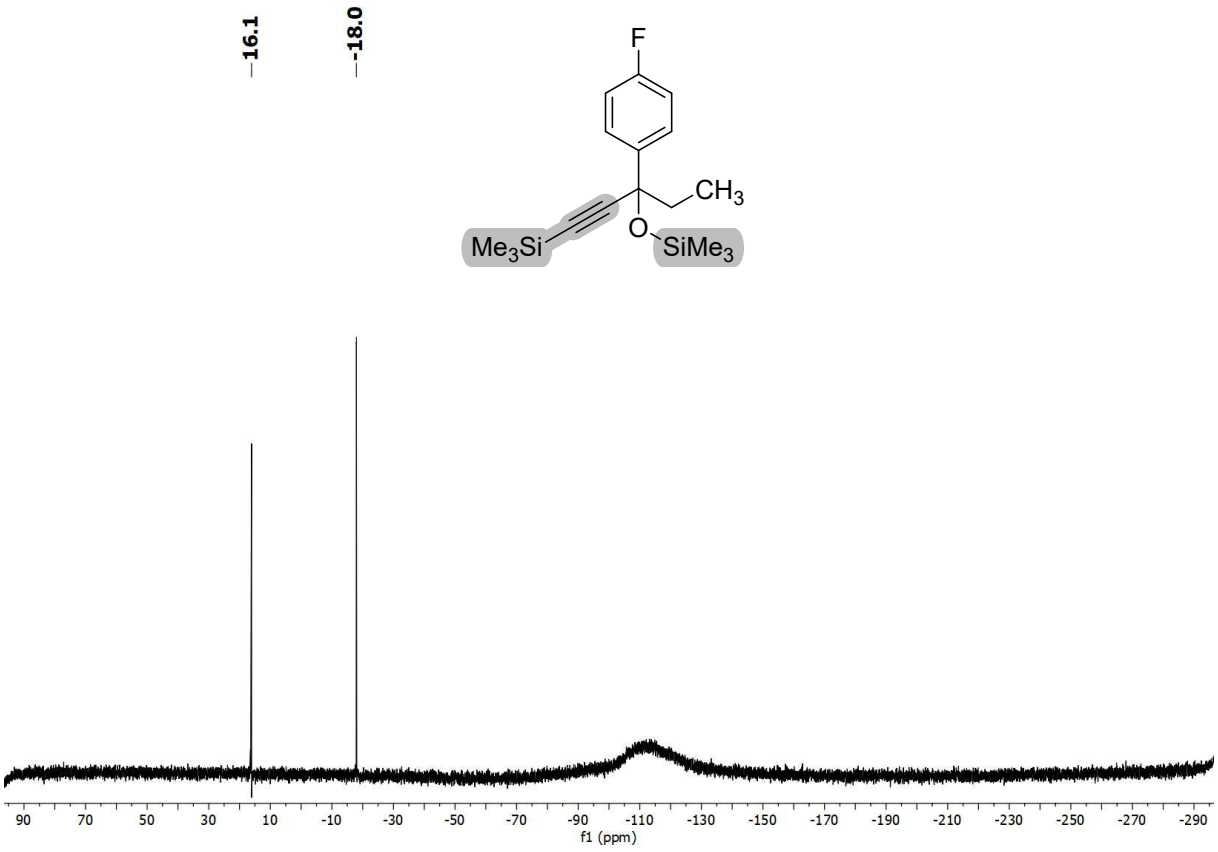

-15.9
-18.1
CH3
Me3Si
O
SiMe3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

((3-(4-Fluorophenyl)-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (3s)

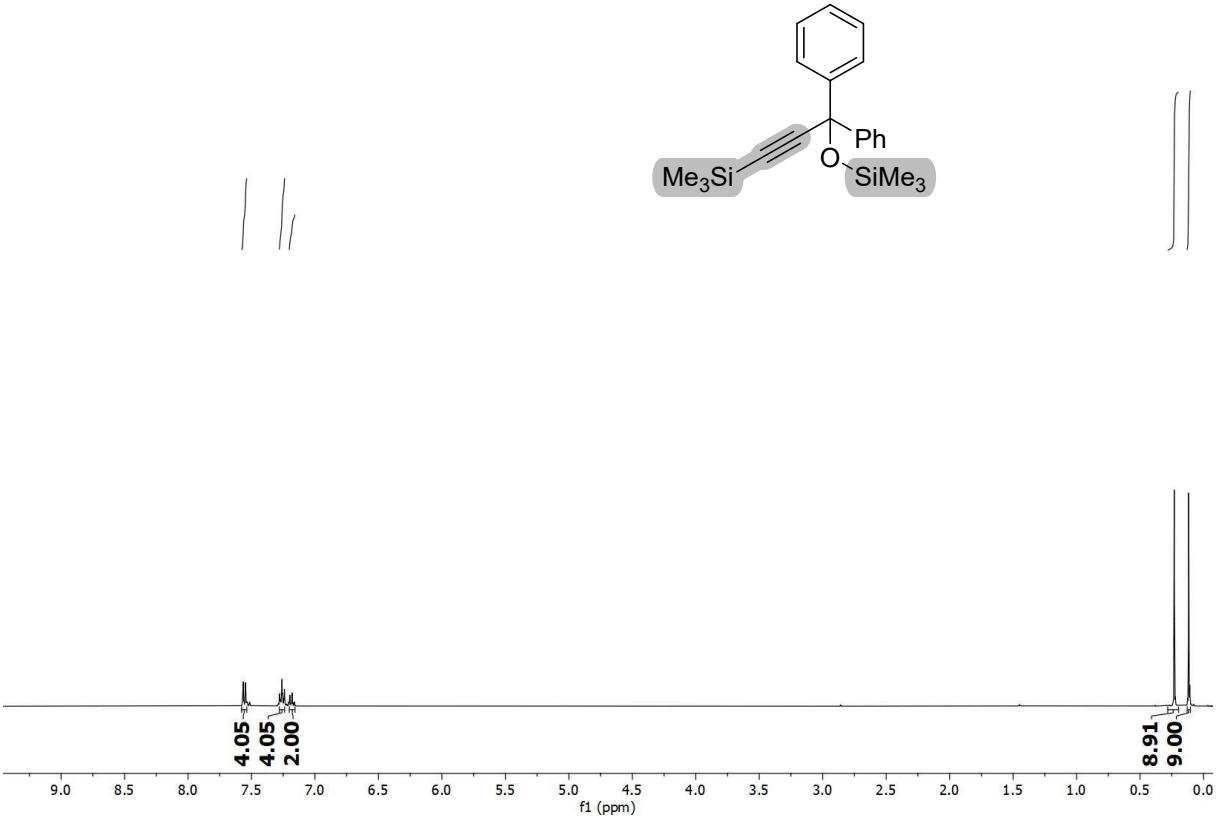


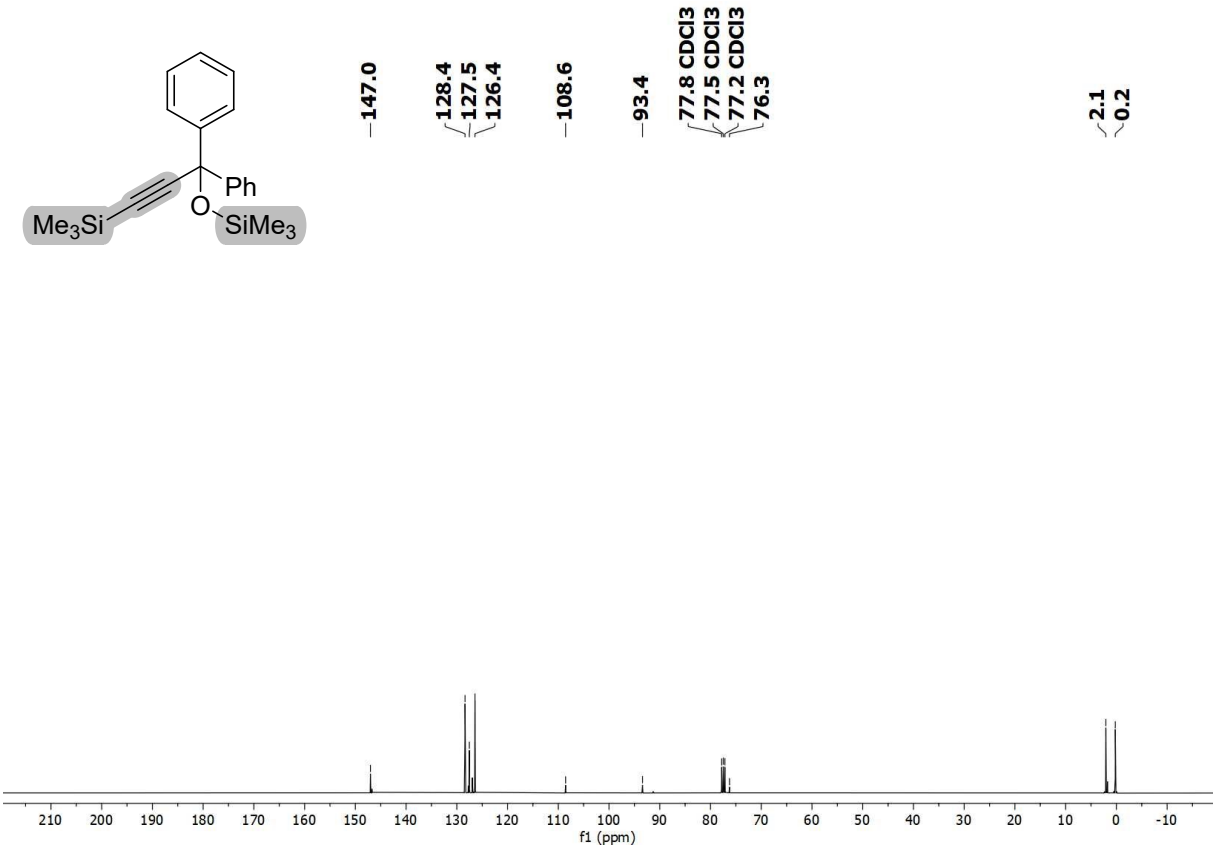


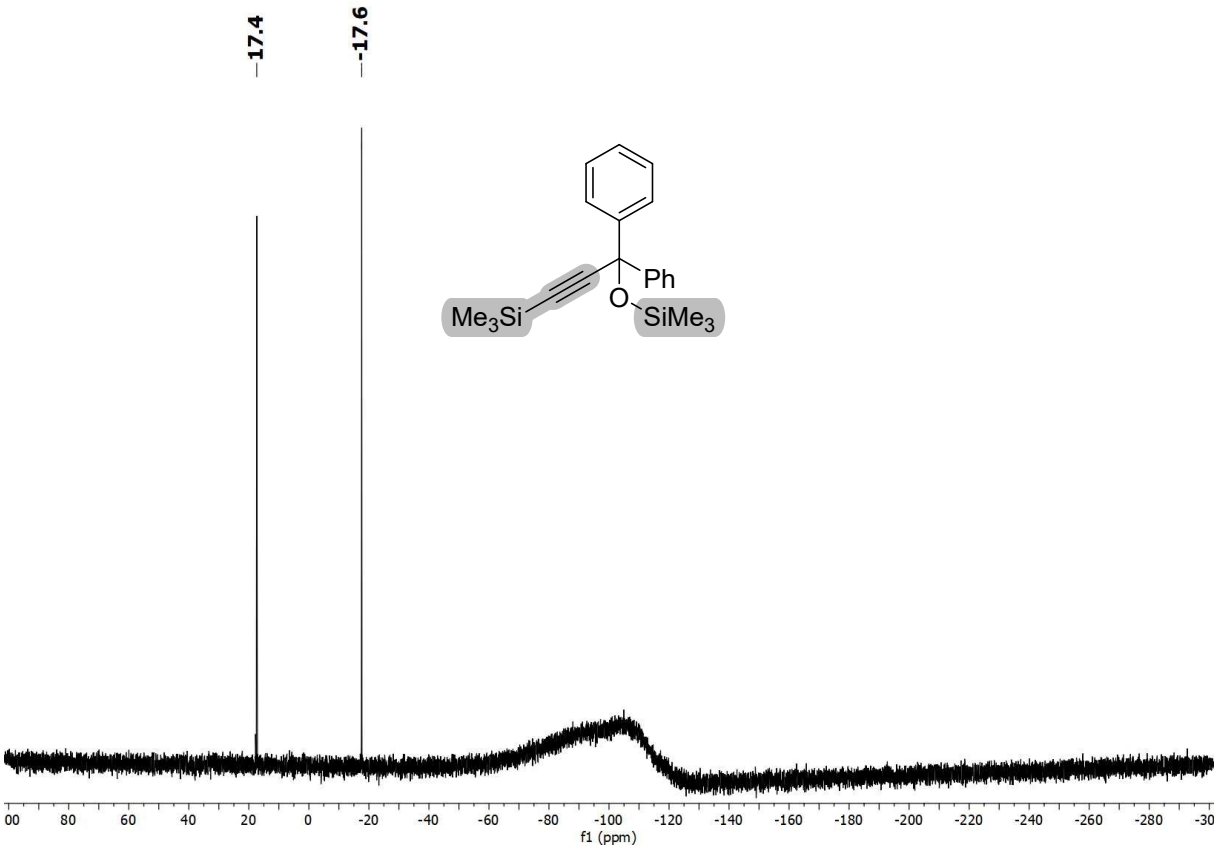

-116.4
F
CH3
Me3Si
O
SiMe3
f1 (ppm)


-16.1
-18.0
F
CH3
Me3Si
O
SiMe3
f1 (ppm)

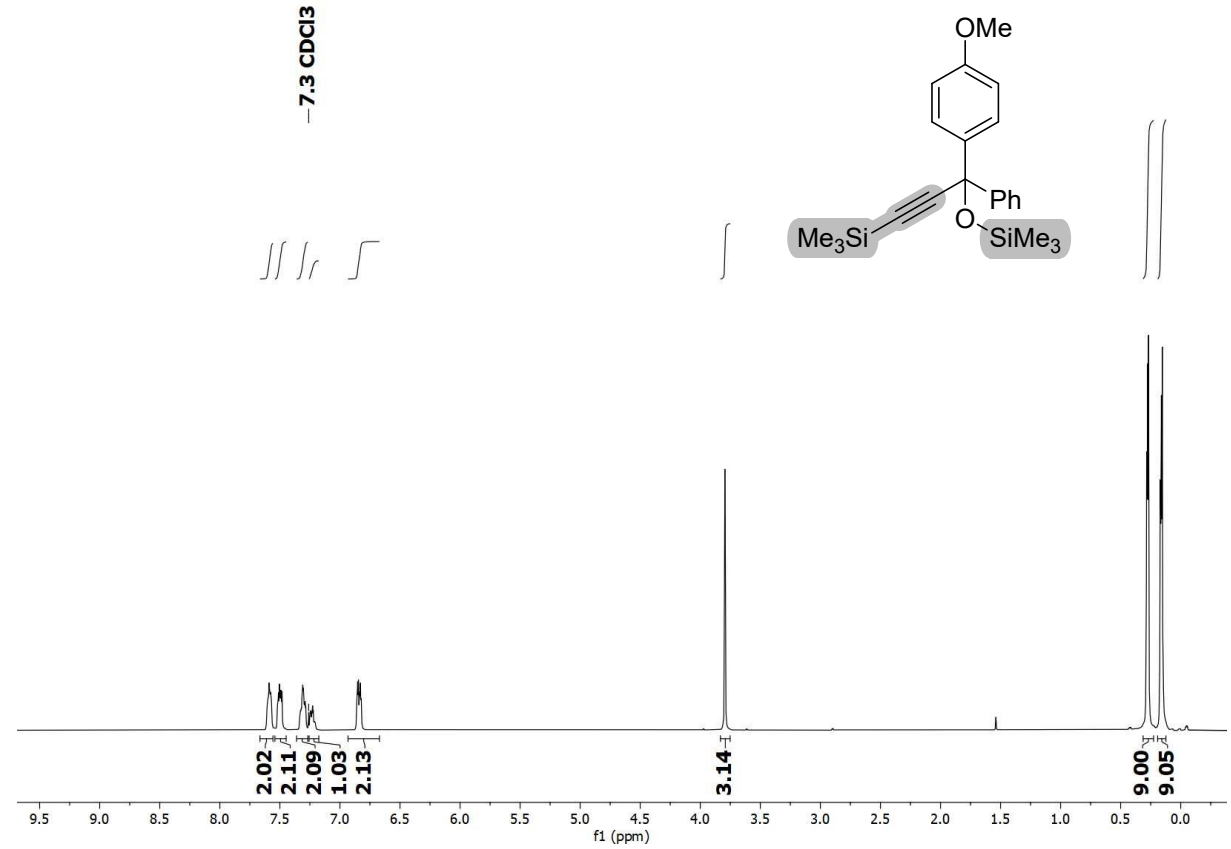
(3,3-Diphenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (3t)

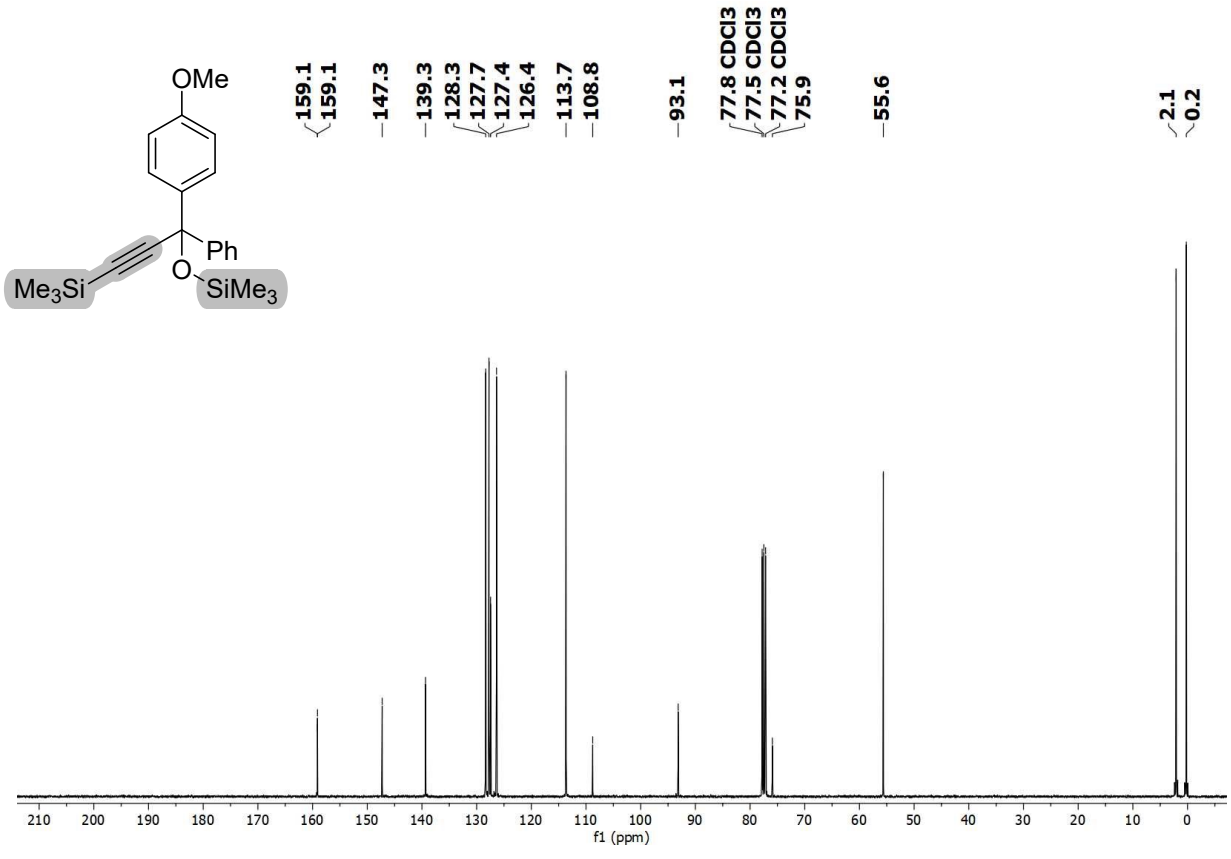


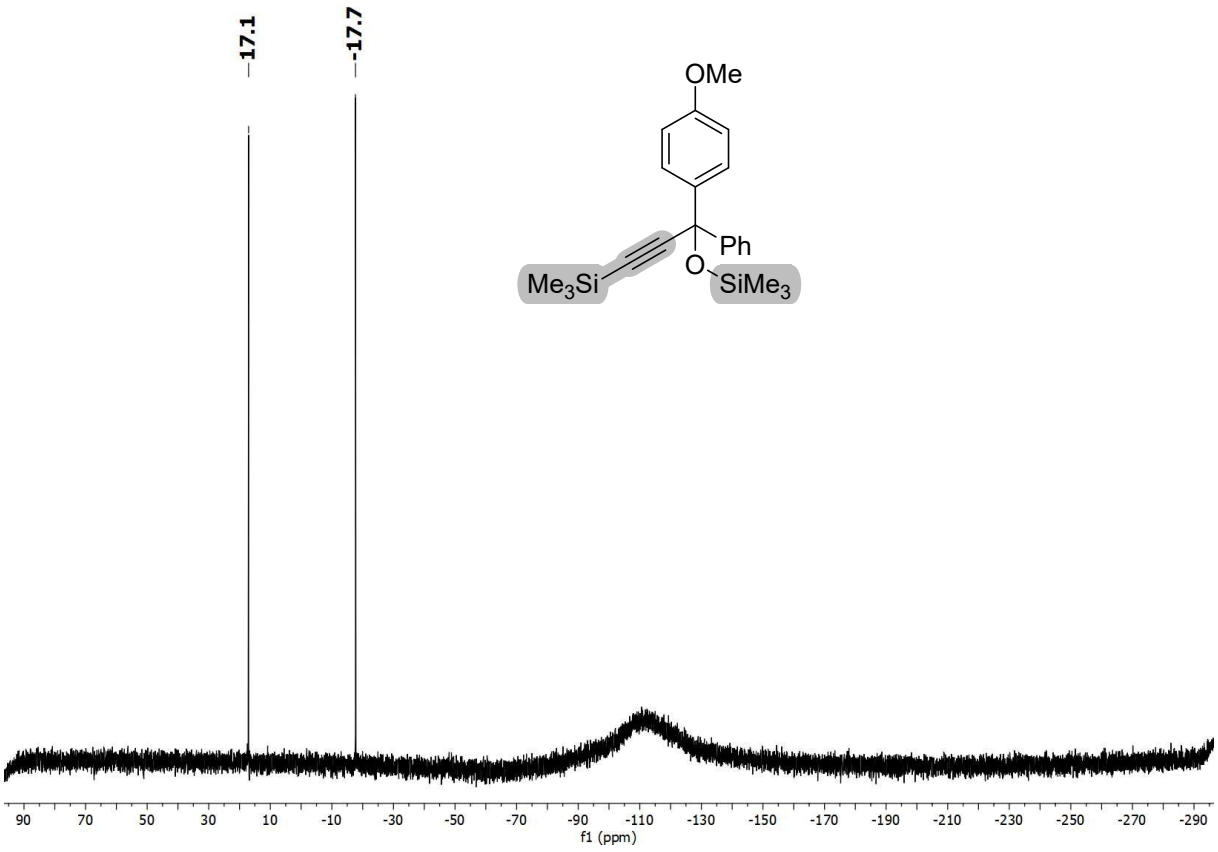



-17.4
-17.6
Ph
O
Me3Si
SiMe3
00 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -30
f1 (ppm)

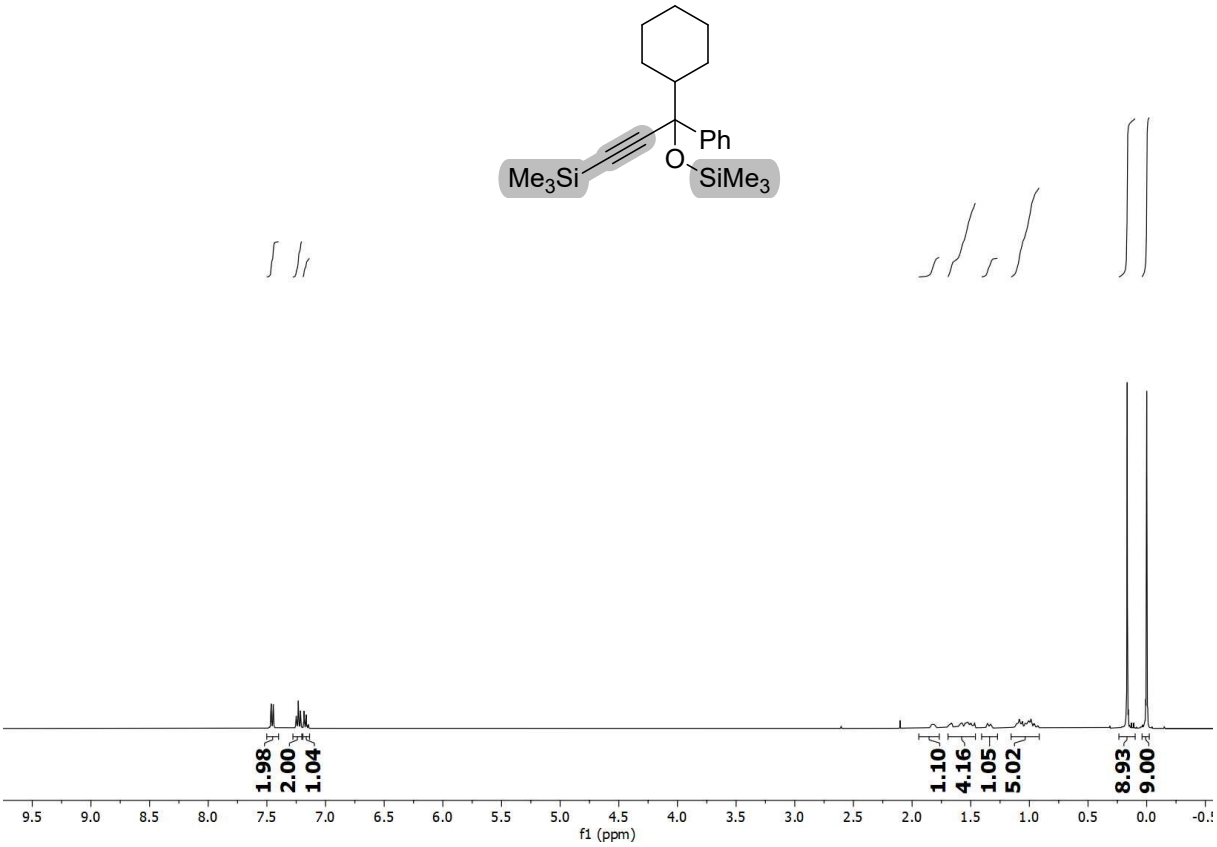
((1-(4-Methoxyphenyl)-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane (3u)

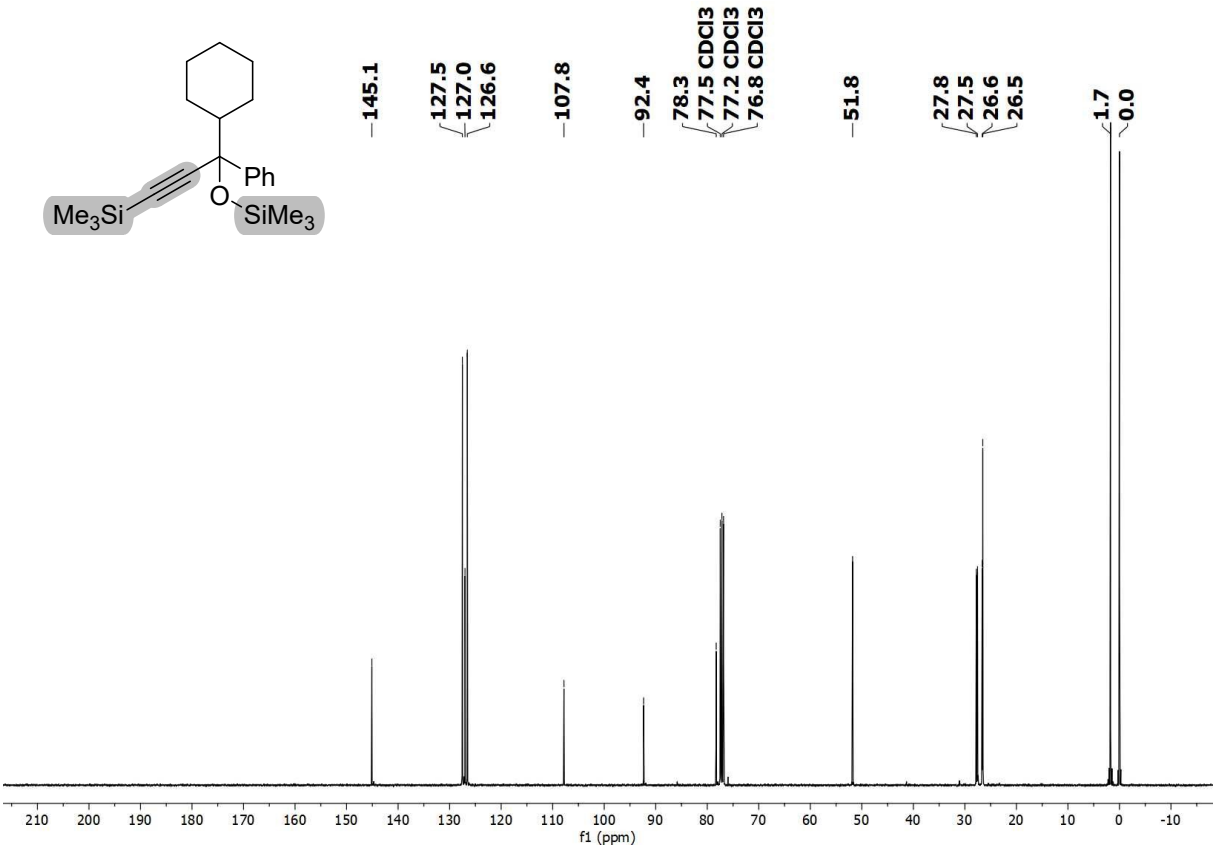


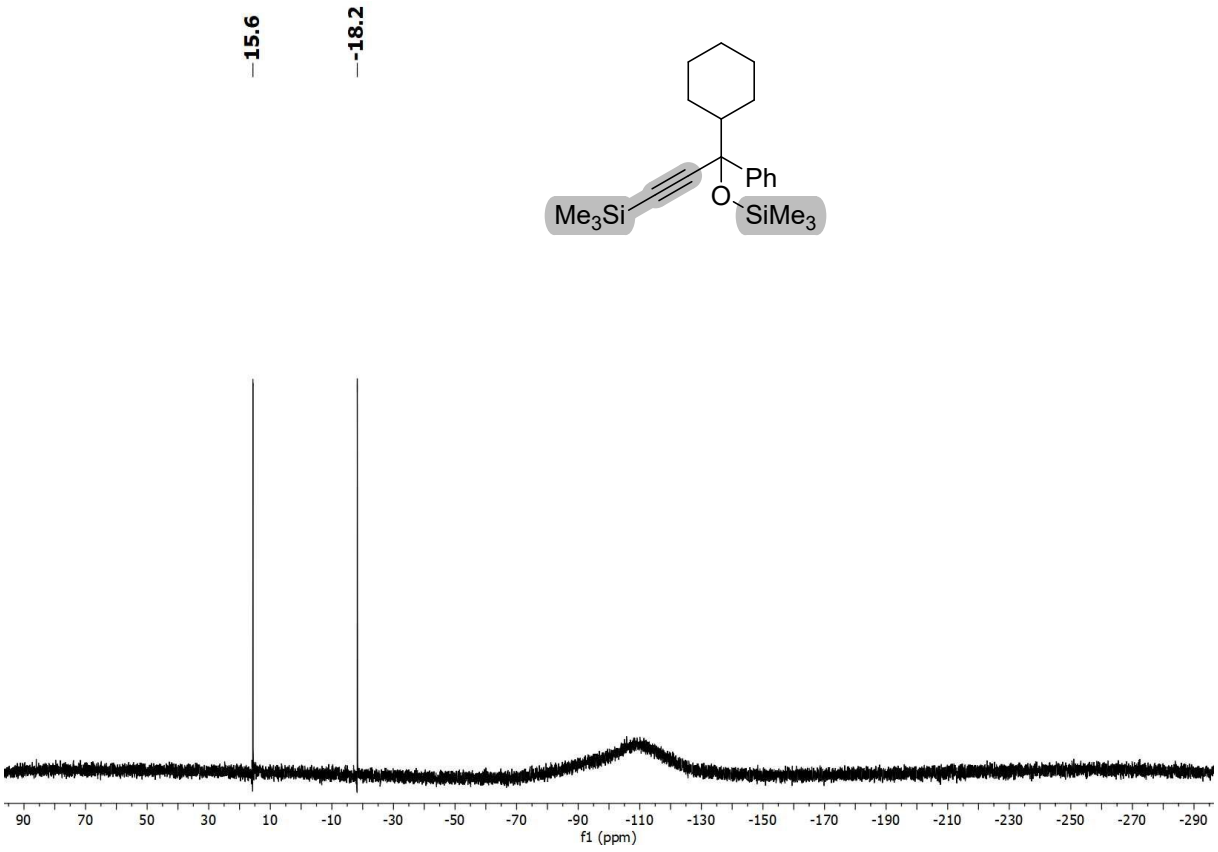



-17.1
-17.7
OMe
Ph
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

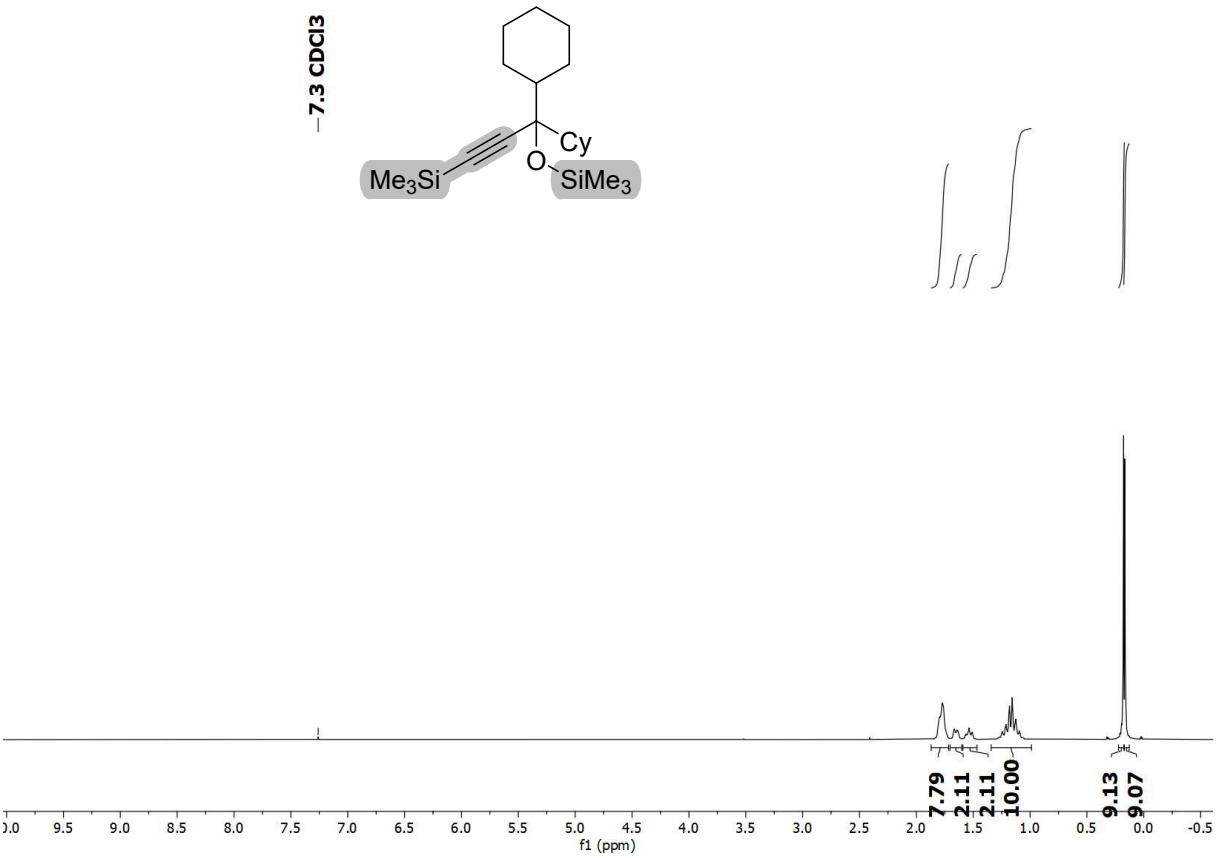
((1-Cyclohexyl-1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)oxy)trimethylsilane (3v)

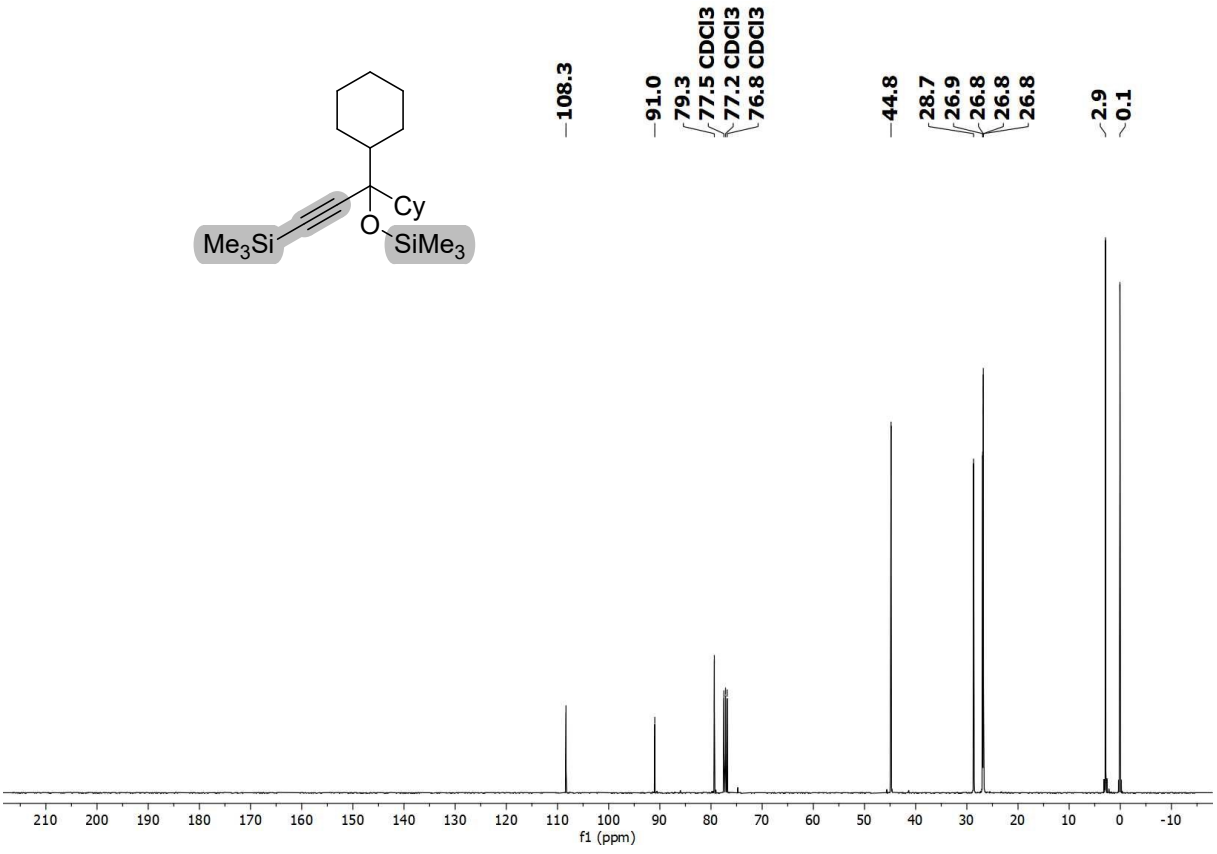


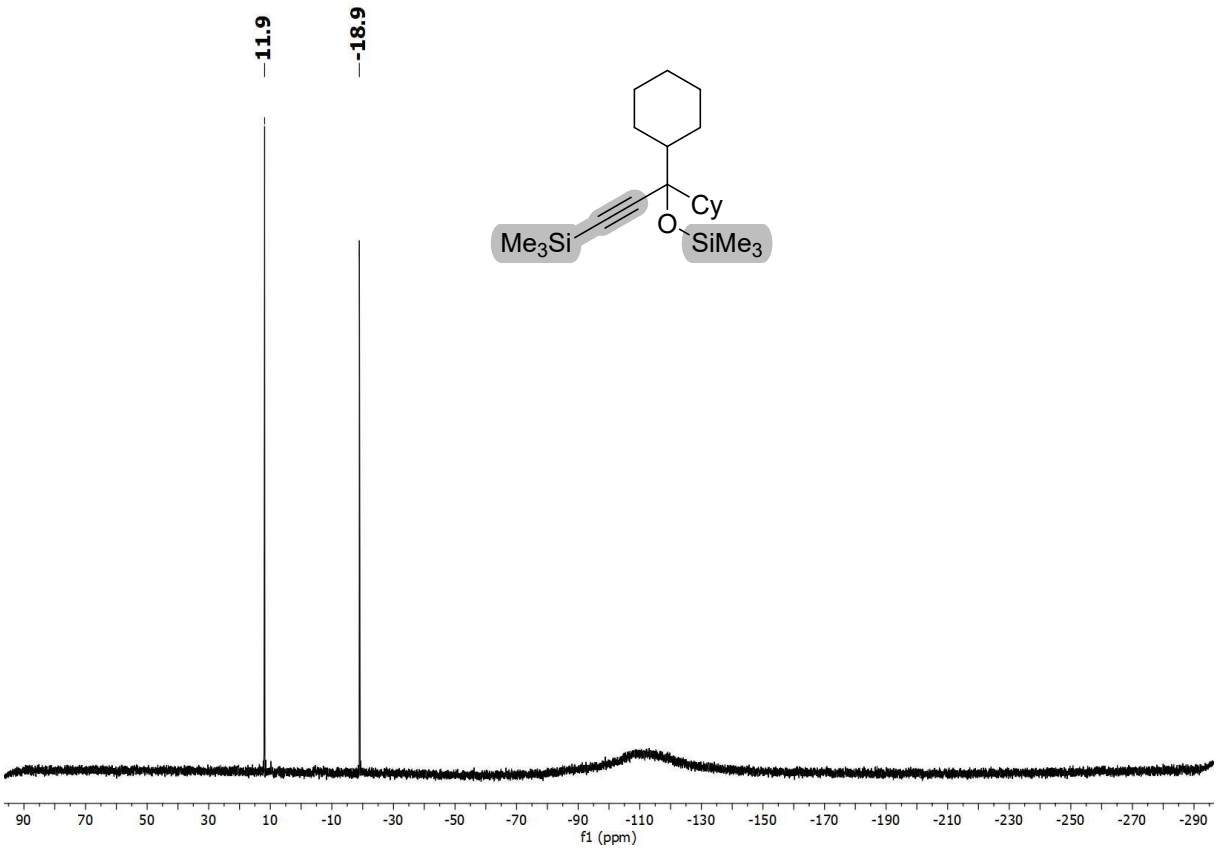



-15.6
-18.2
Ph
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

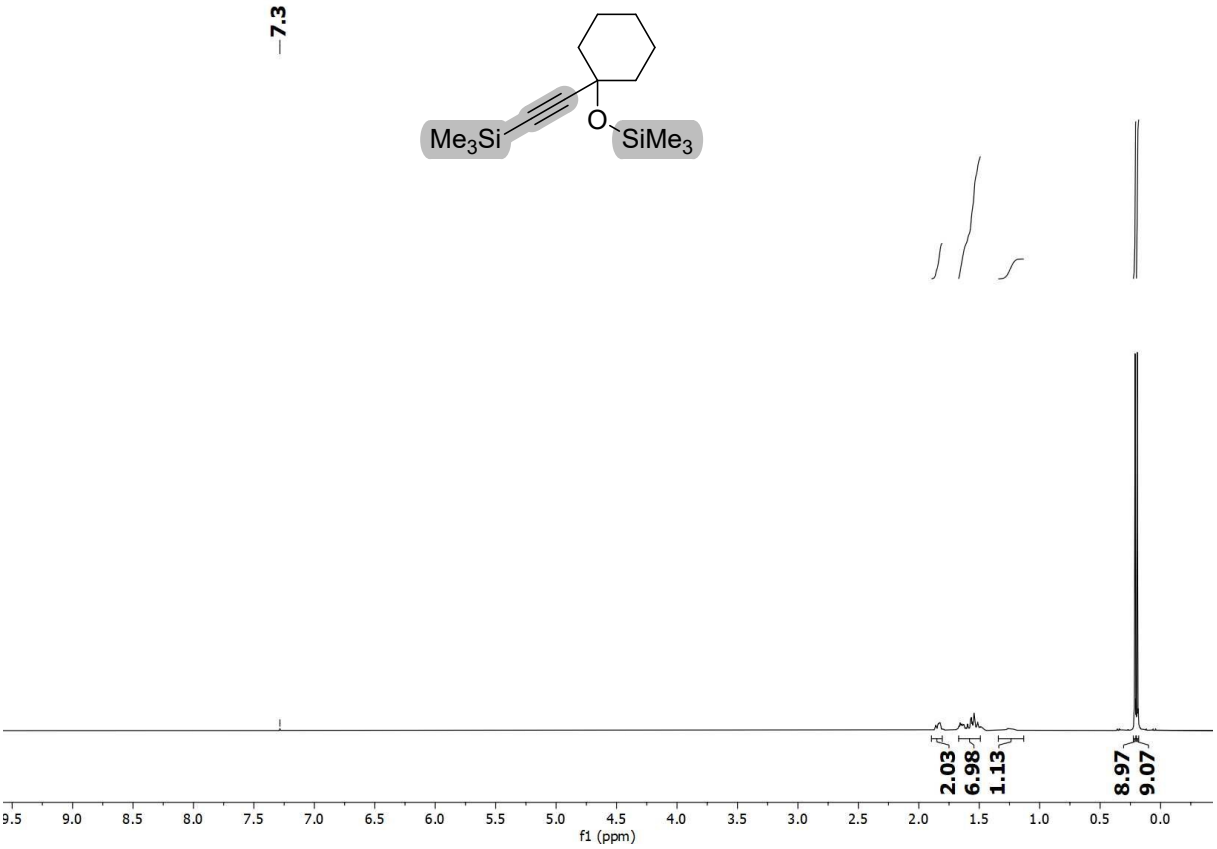
(3,3-Dicyclohexyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (3w)

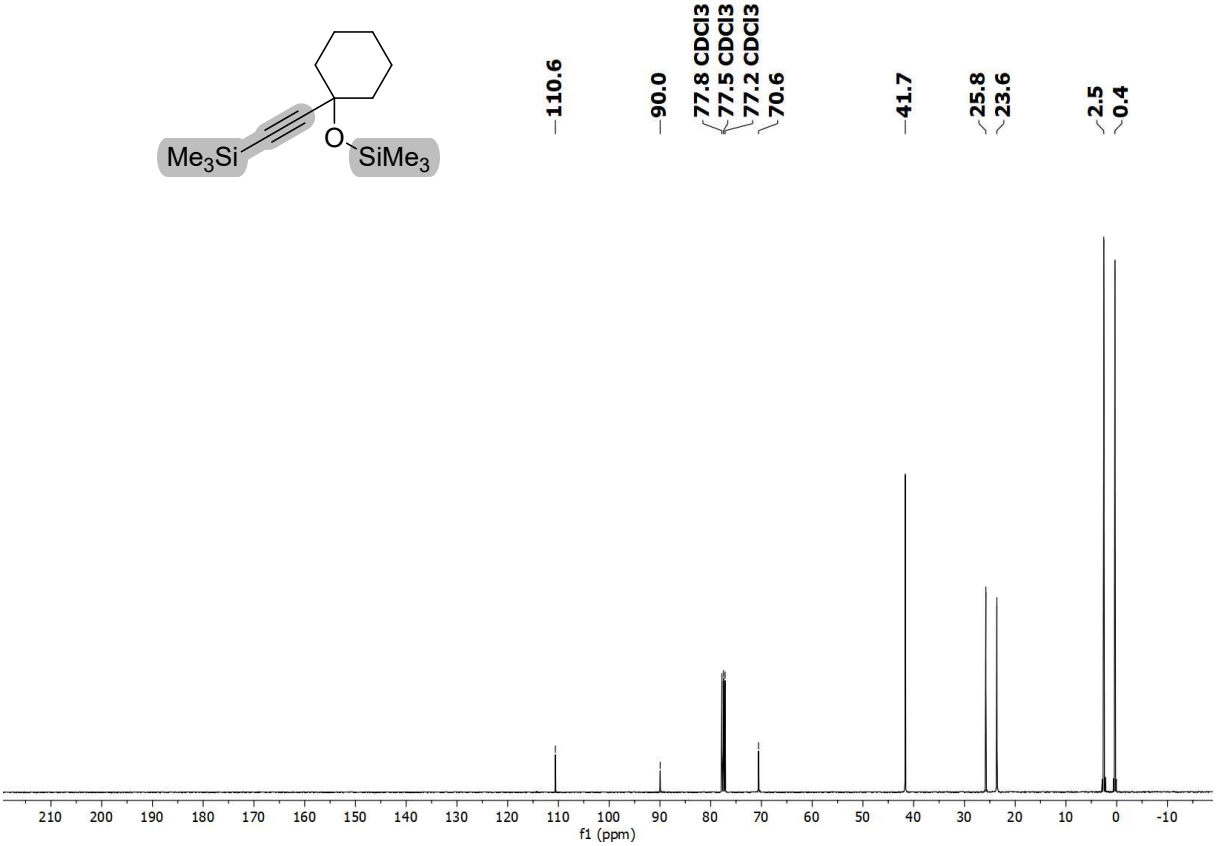


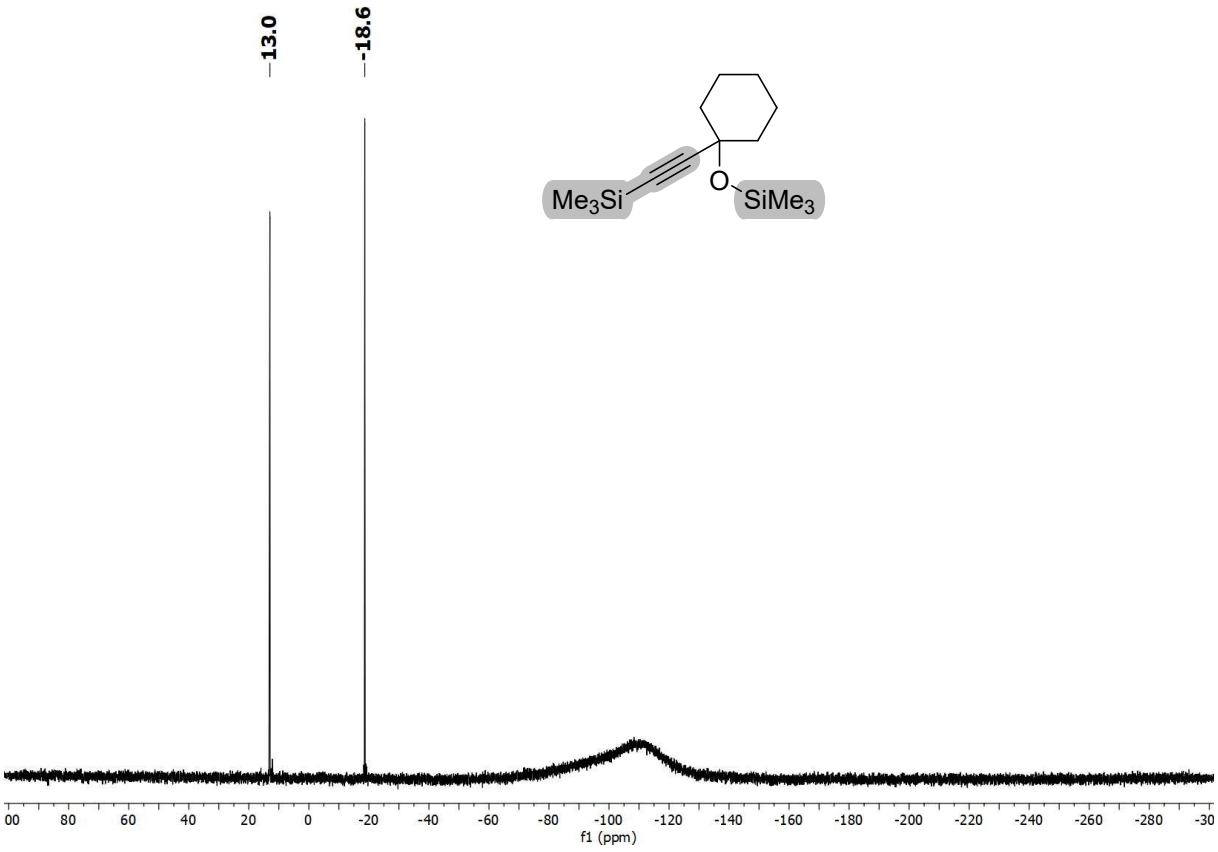



-11.9
-18.9
Cy
O
Me3Si
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

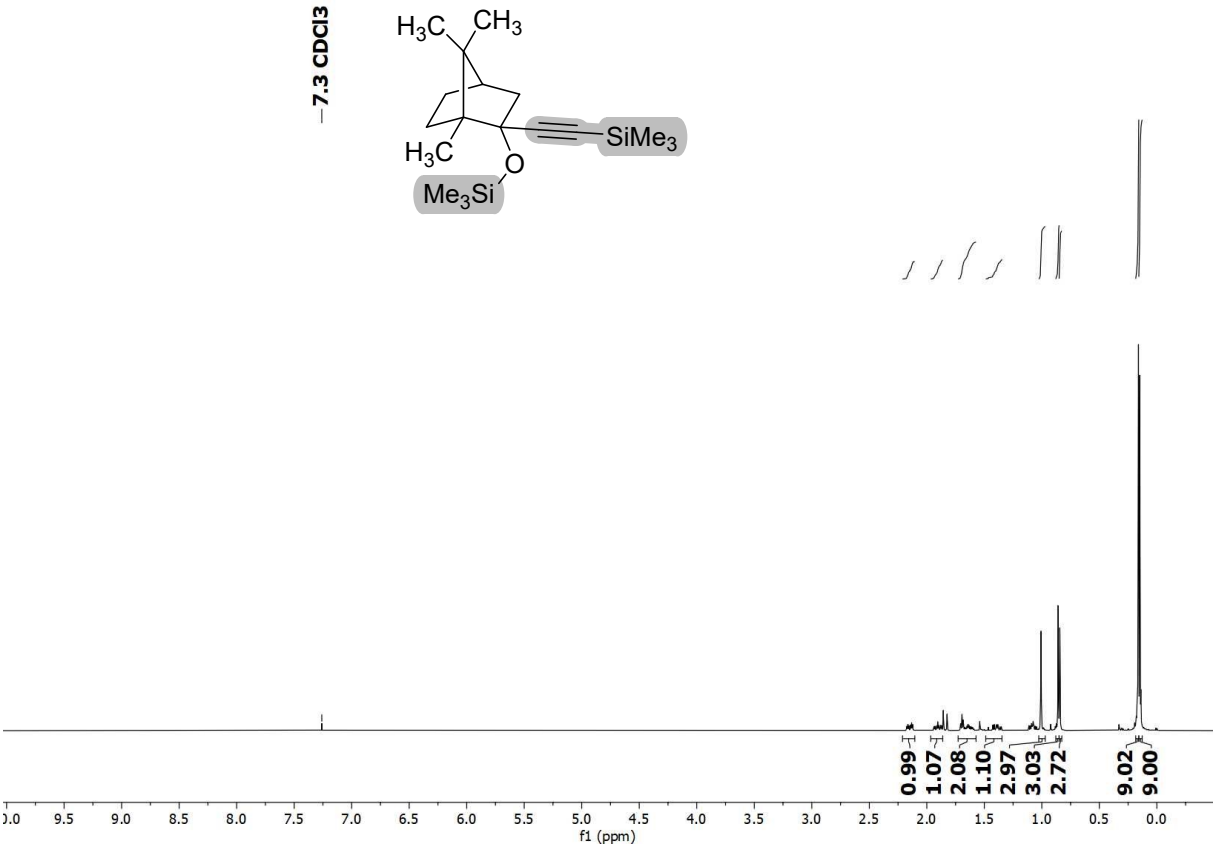
Trimethyl((1-((trimethylsilyl)ethynyl)cyclohexyl)oxy)silane (3x)

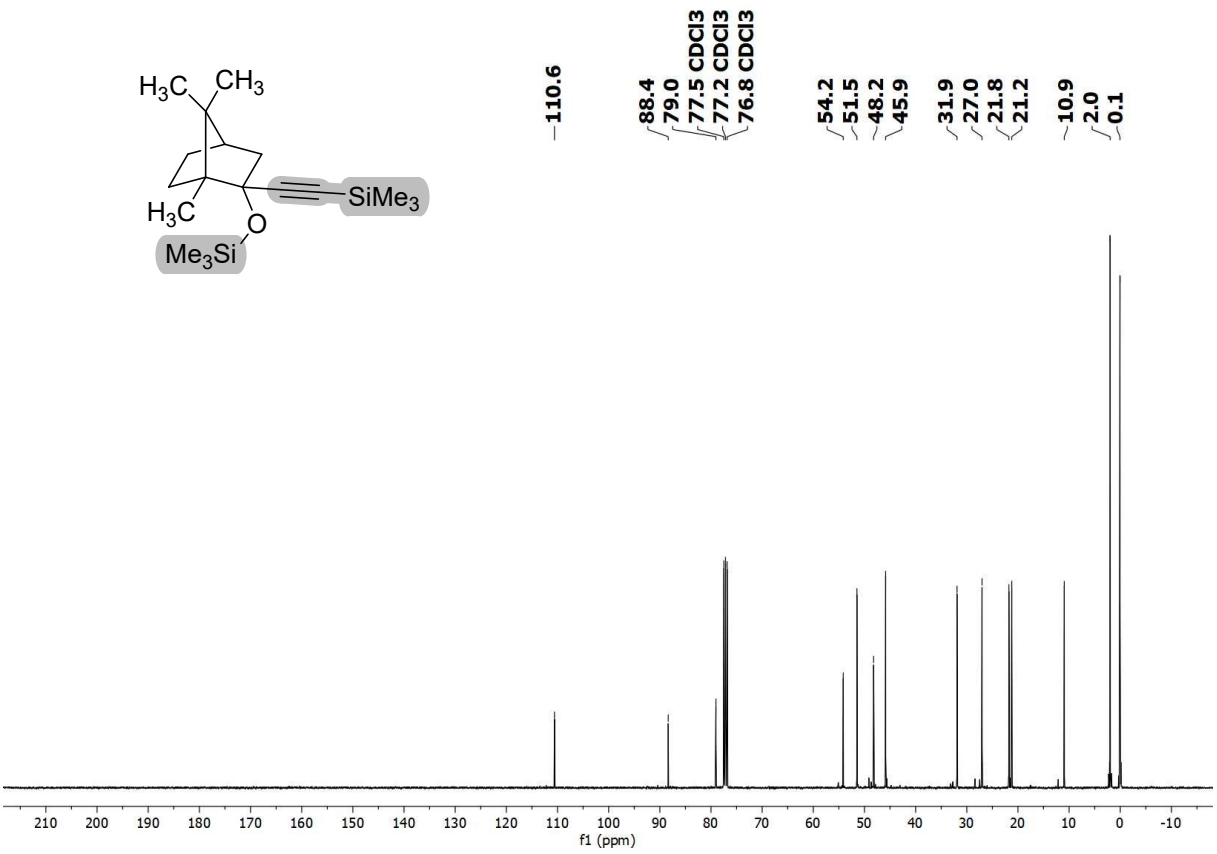


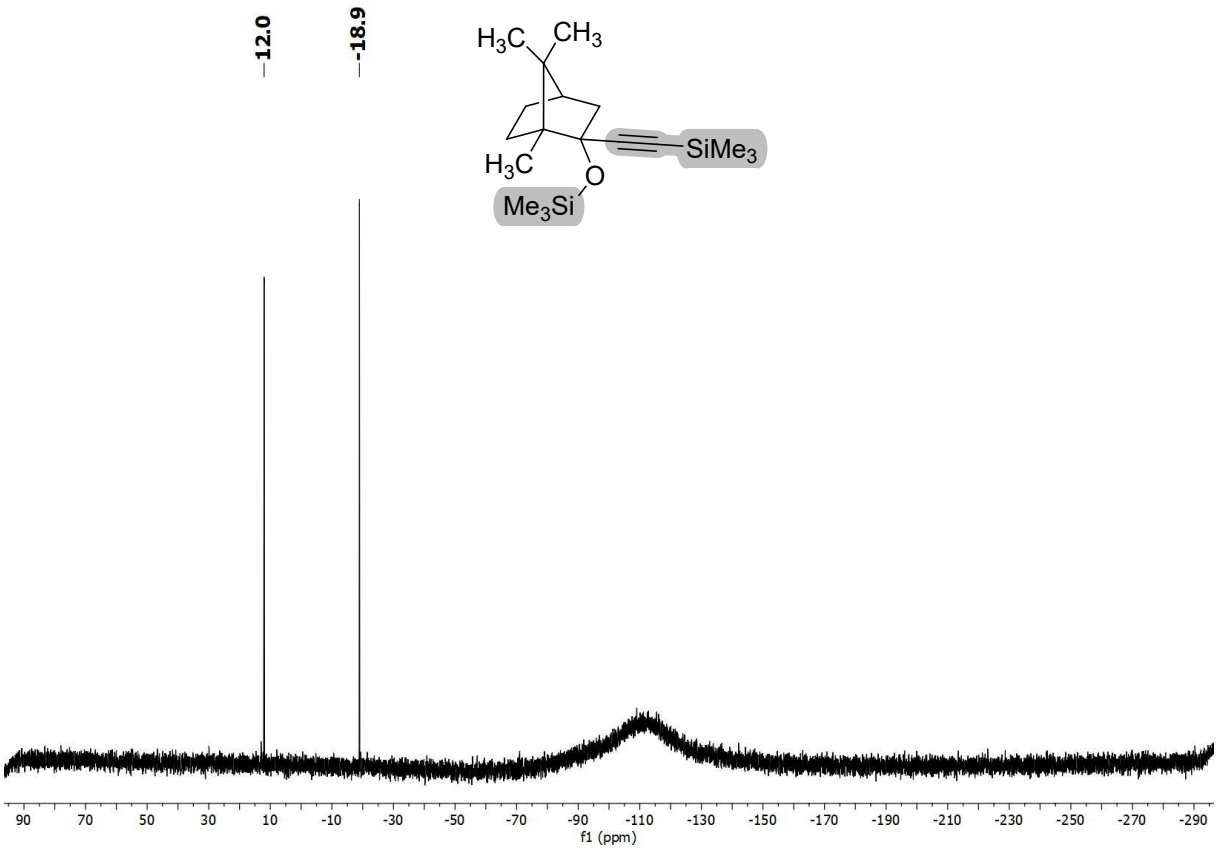



-13.0
-18.6
Me3Si
O
SiMe3
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-30
f1 (ppm)

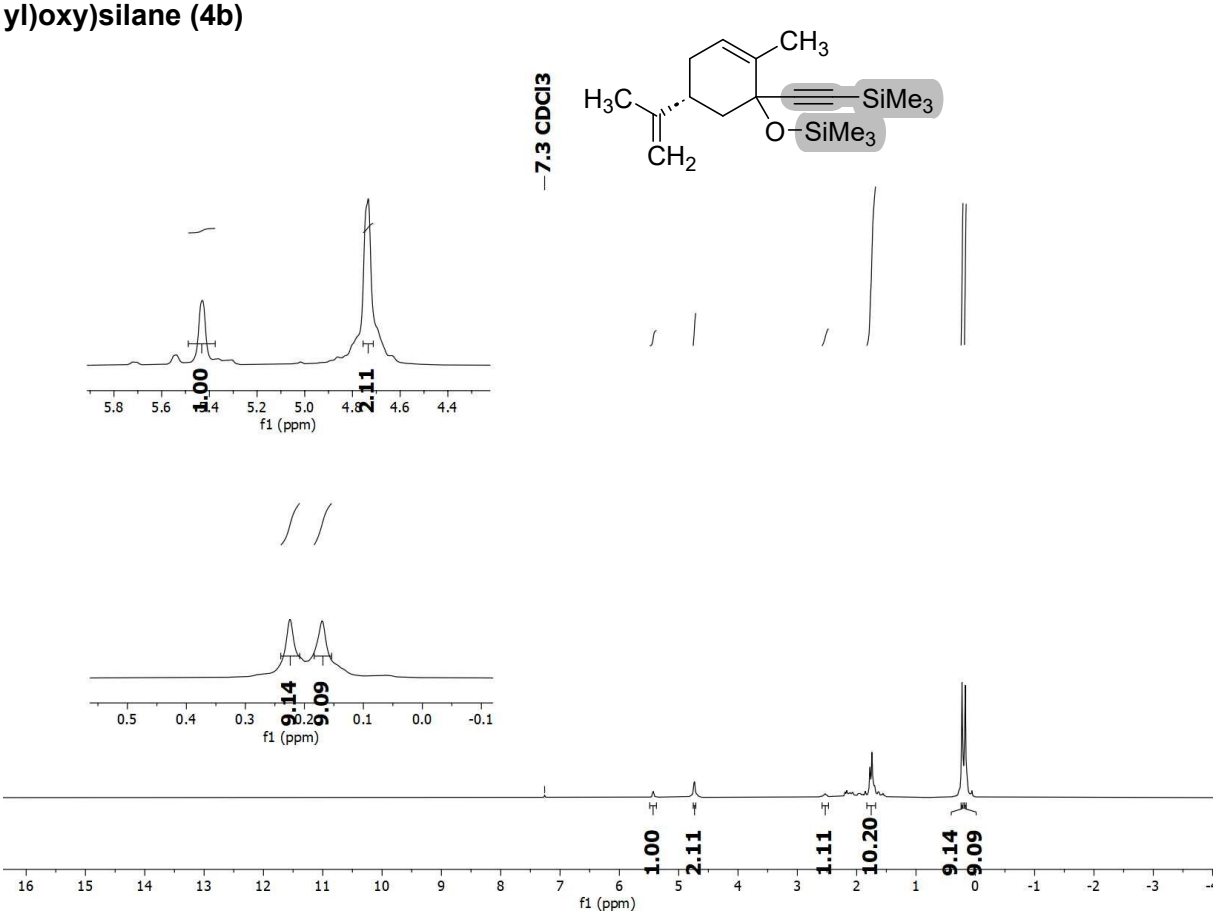
Trimethyl(((1S,2S,4R)-1,7,7-trimethyl-2-((trimethylsilyl)ethynyl)bicyclo[2.2.1]heptan-2-yl)oxy)silane (4a)

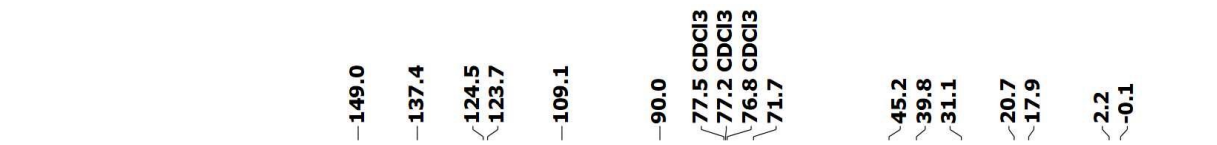


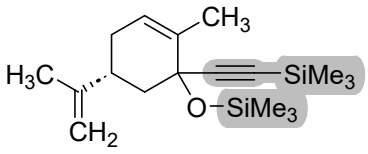


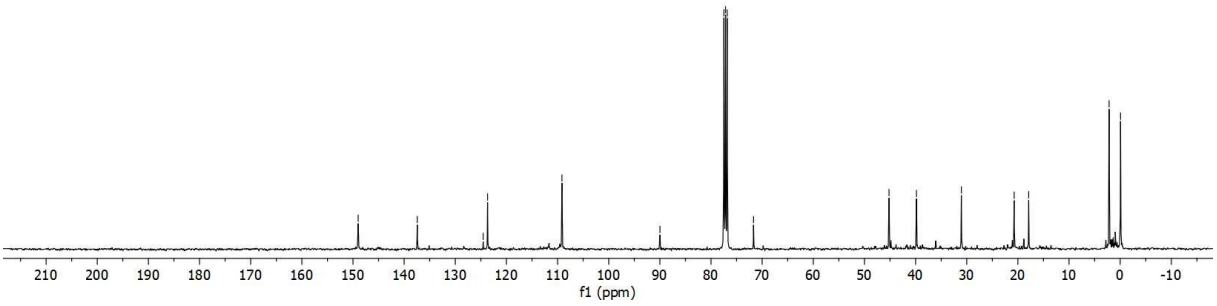

-12.0
-18.9
H3C
CH3
H3C
O
SiMe3
Me3Si
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

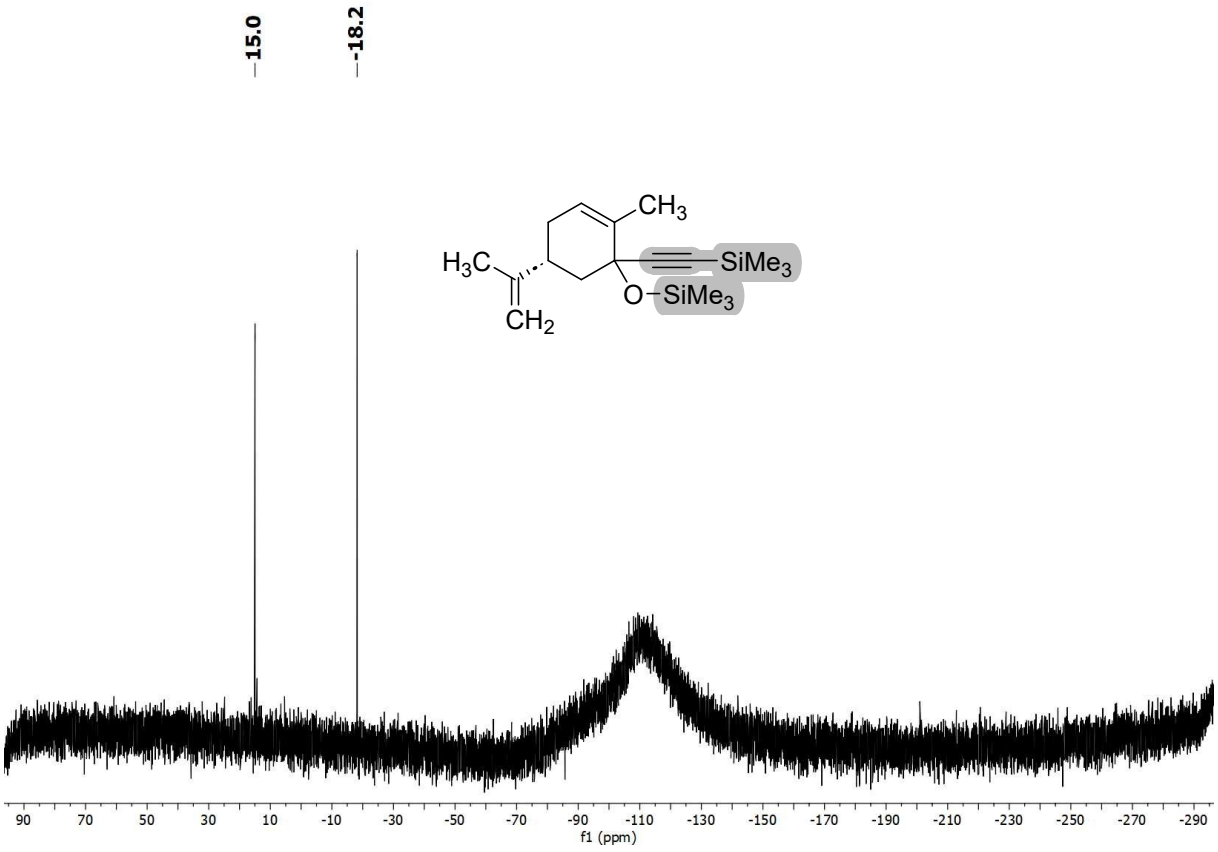
Trimethyl(((5R)-2-methyl-5-(prop-1-en-2-yl)-1-((trimethylsilyl)ethynyl)cyclohex-2-en-1-yl)oxy)silane (4b)



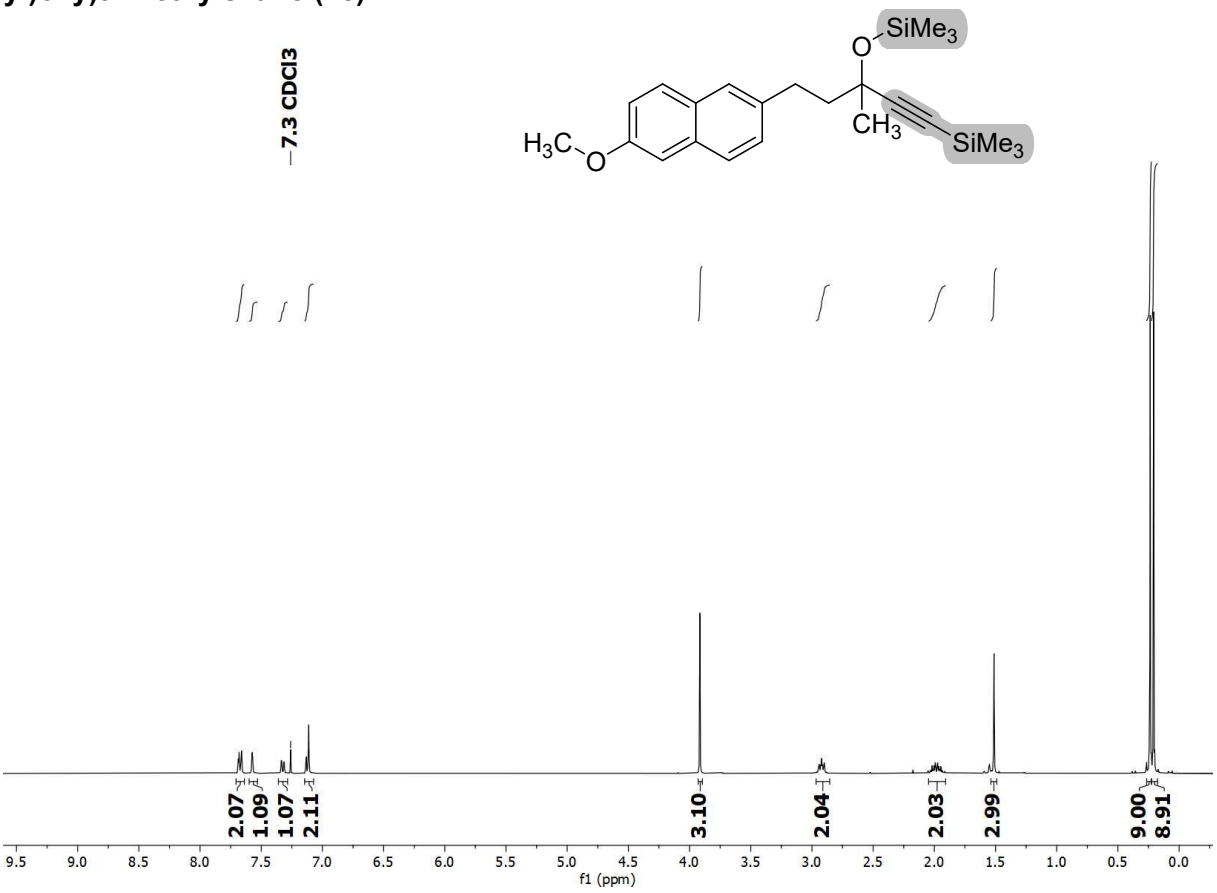


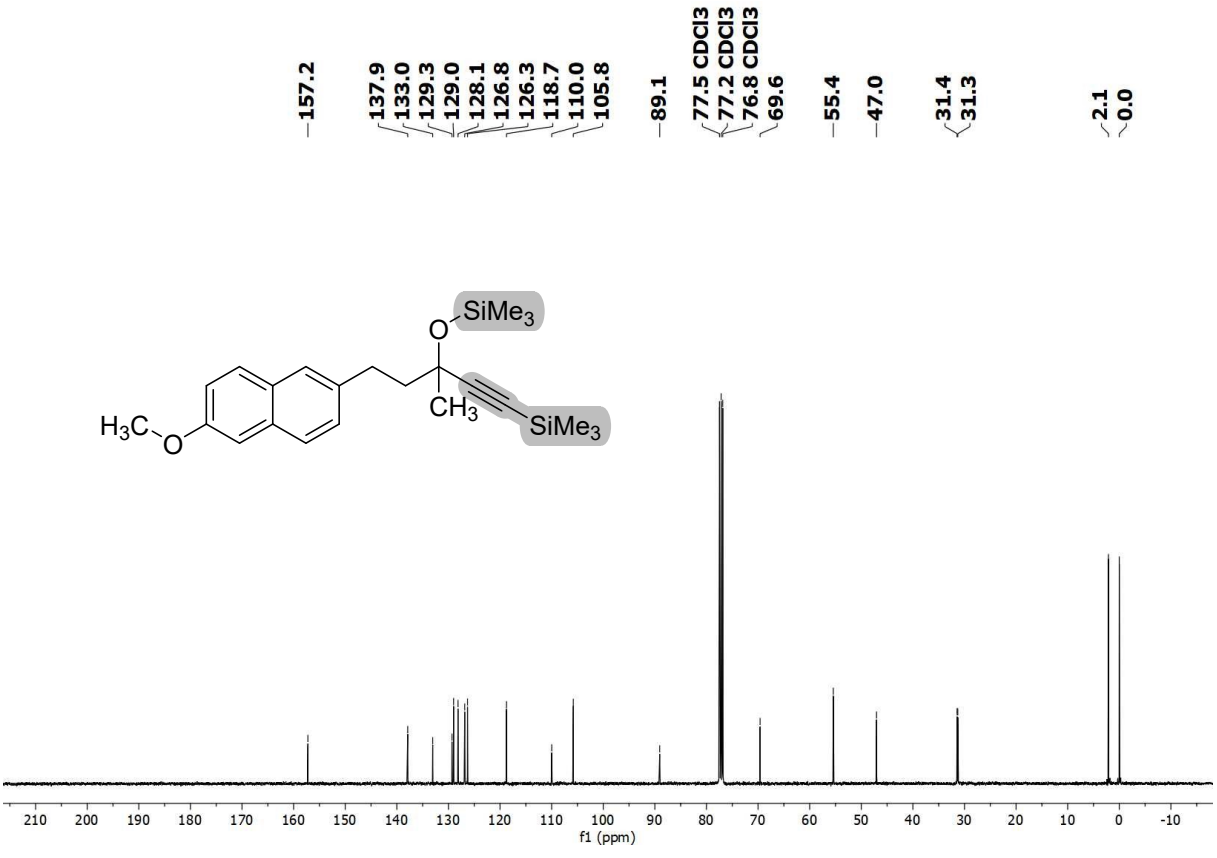


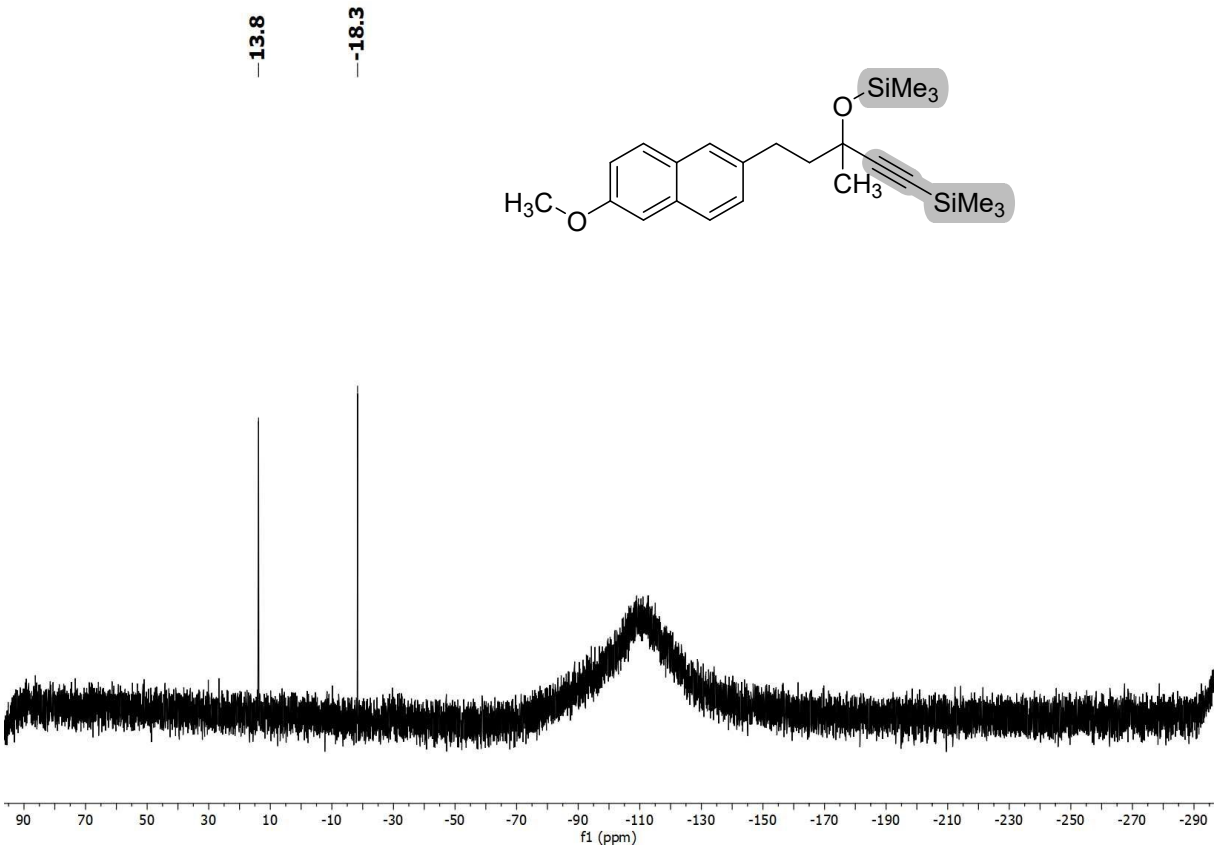



-15.0
-18.2
CH3
H3C
SiMe3
O–SiMe3
CH2
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

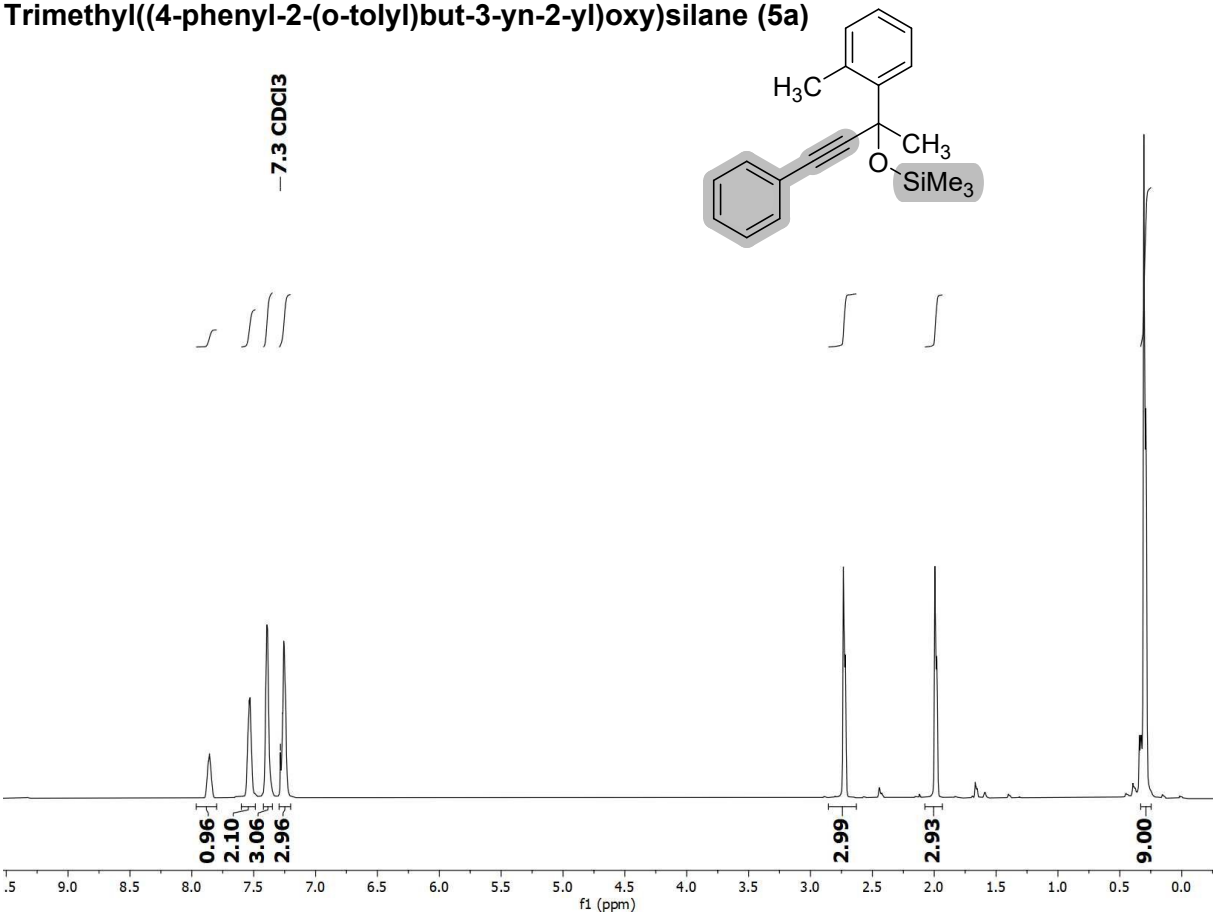
((5-(6-Methoxynaphthalen-2-yl)-3-methyl-1-(trimethylsilyl)pent-1-yn-3-yl)oxy)trimethylsilane (4c)

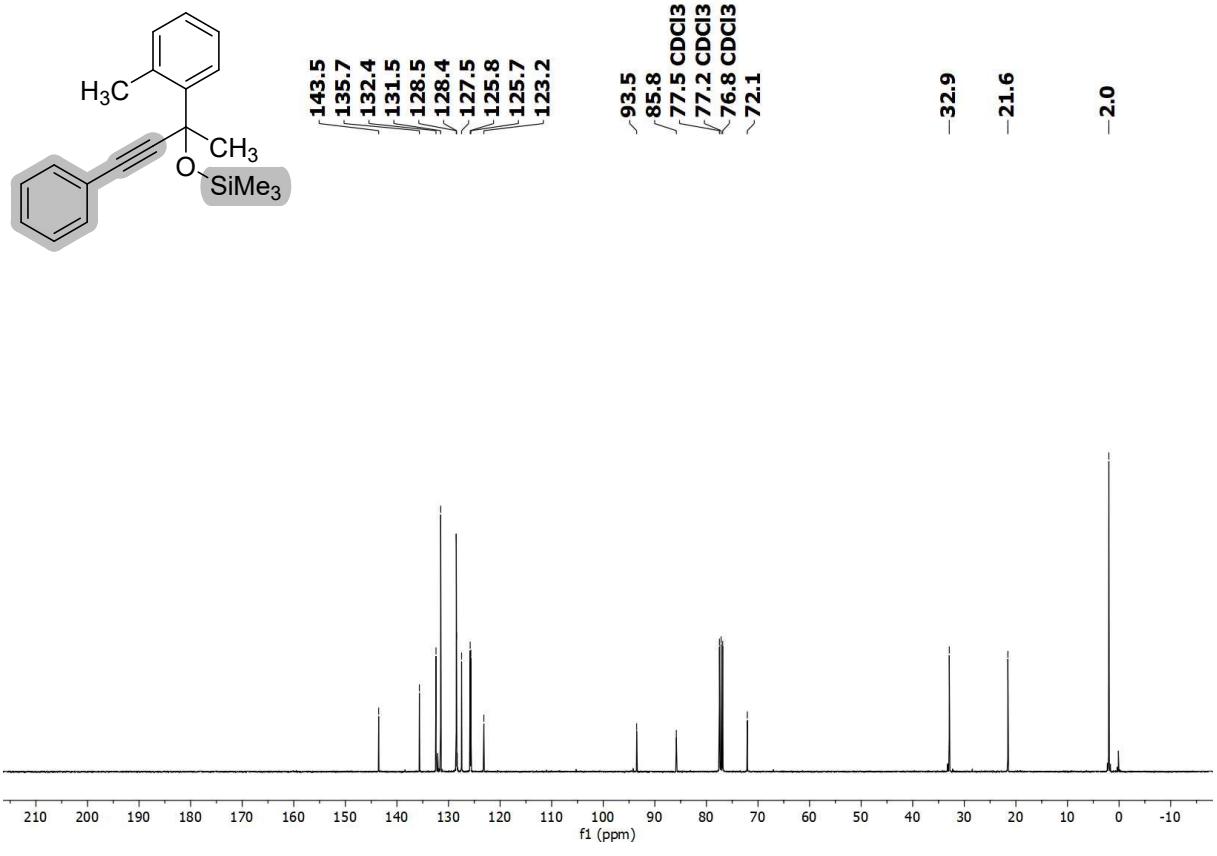


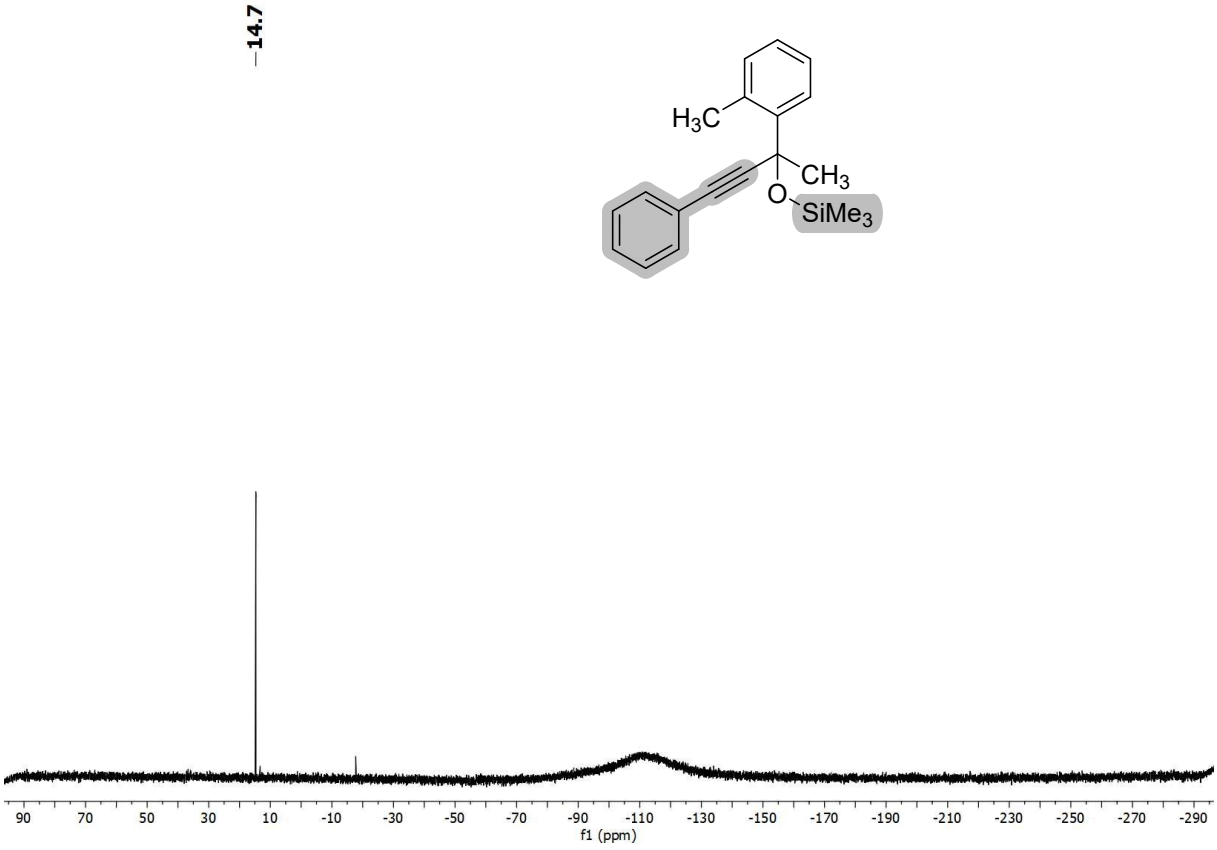



-13.8
-18.3
SiMe3
O
CH3
SiMe3
H3C
O
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

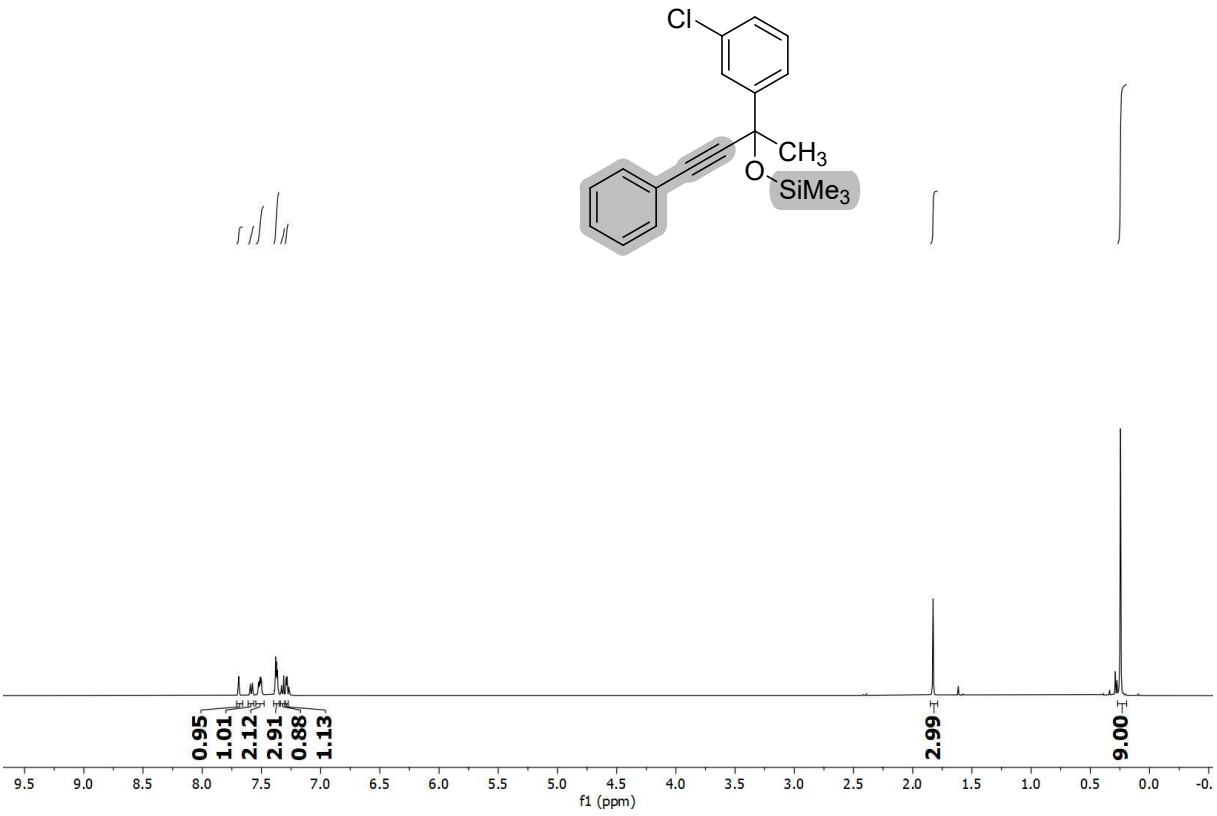
Trimethyl((4-phenyl-2-(o-tolyl)but-3-yn-2-yl)oxy)silane (5a)

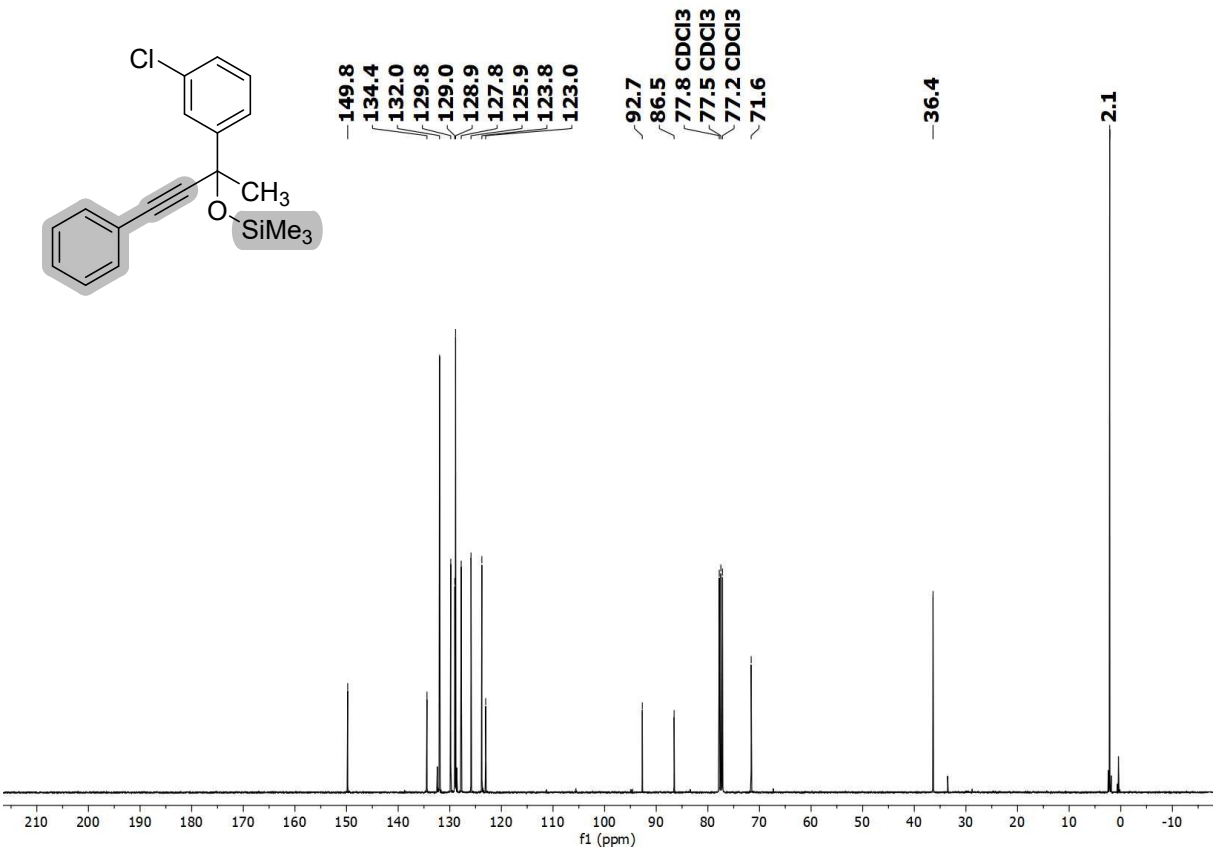


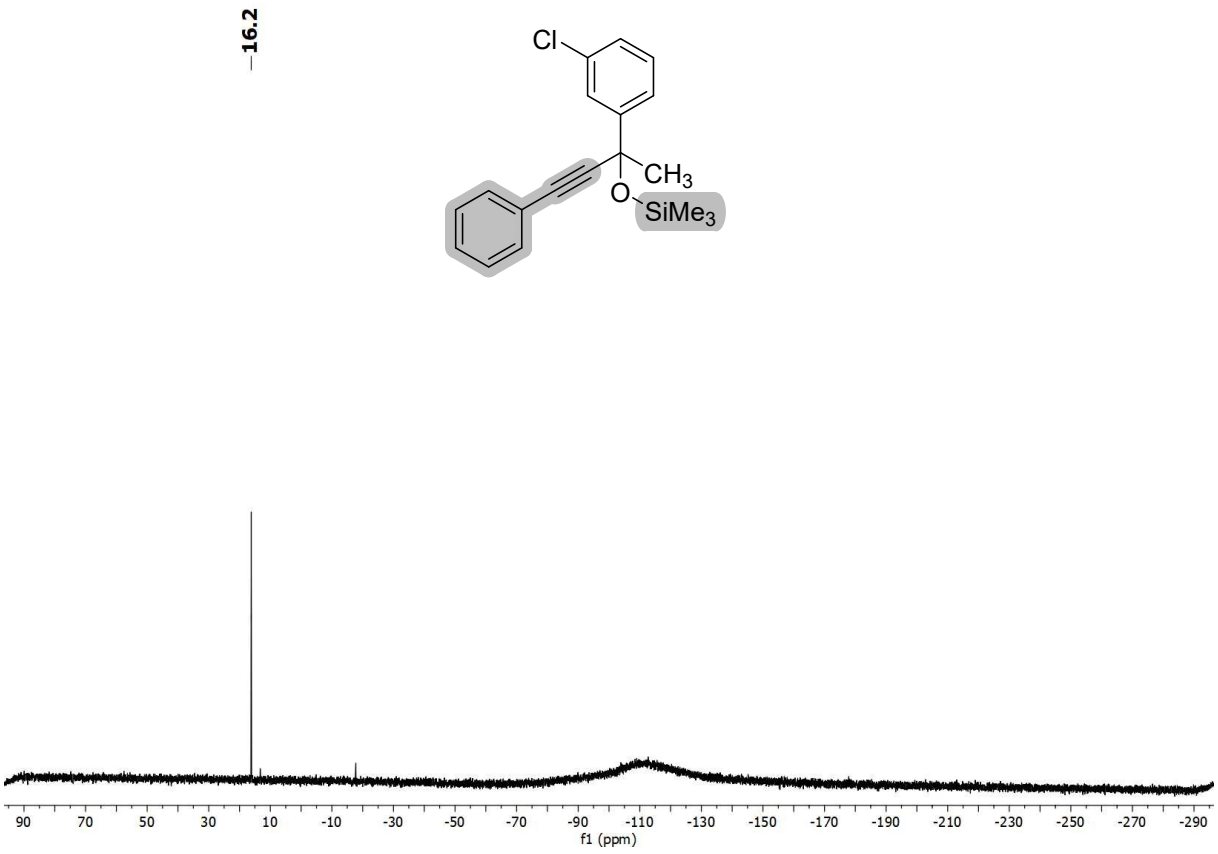



14.7
H3C
CH3
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

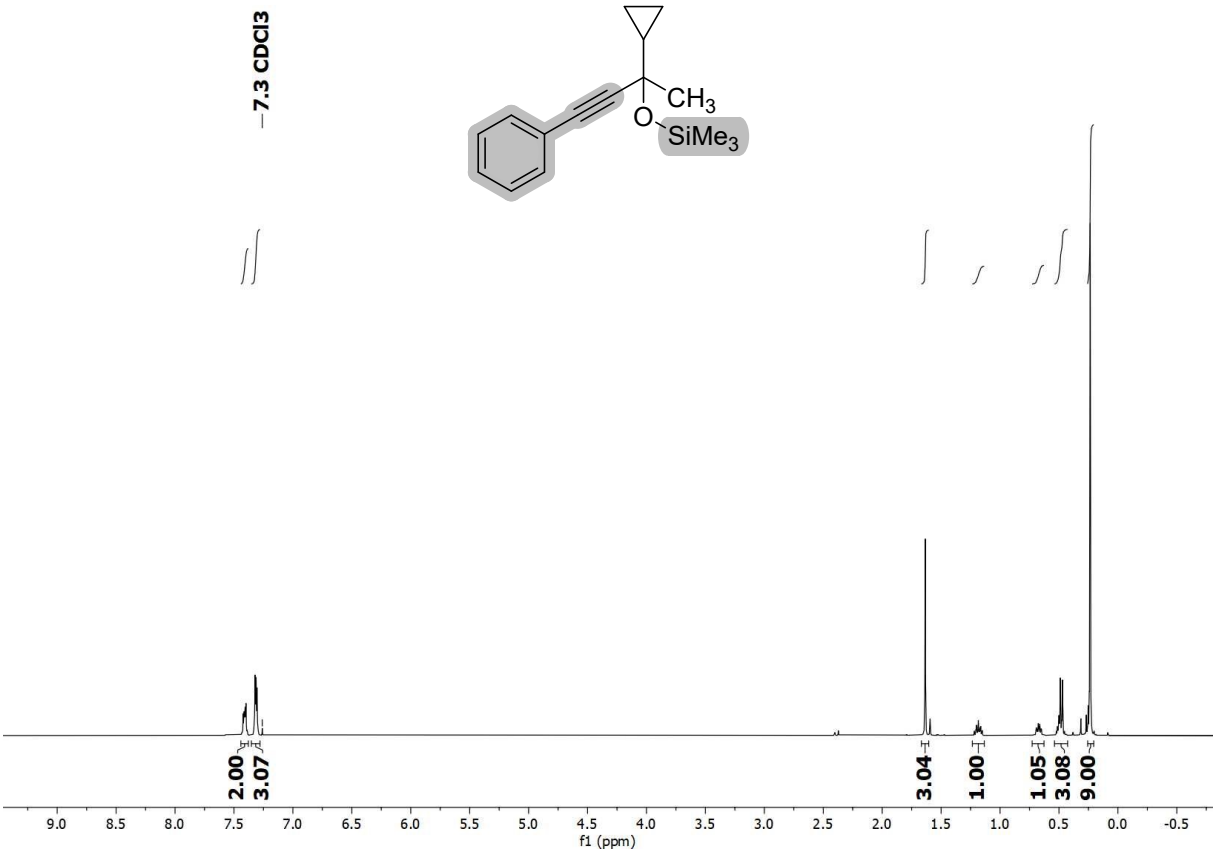
((2-(3-Chlorophenyl)-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane (5b)

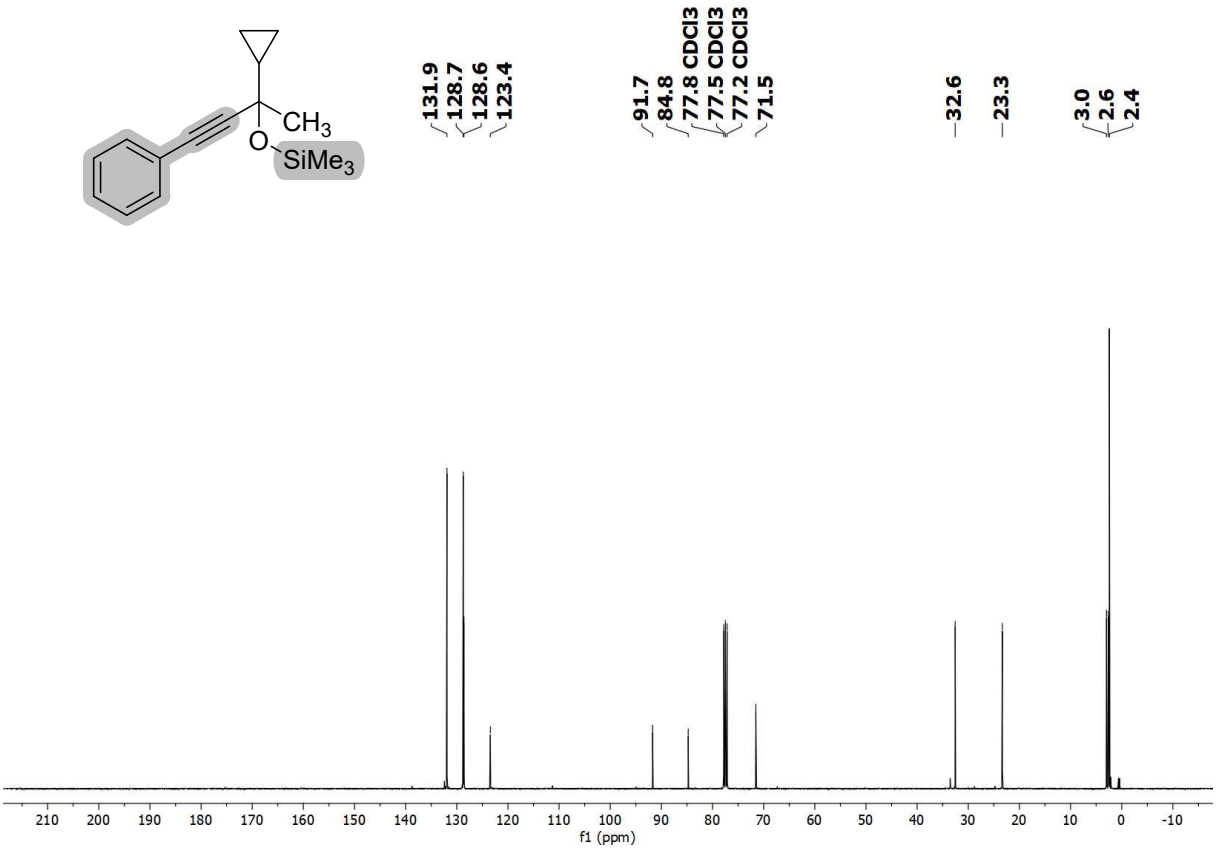


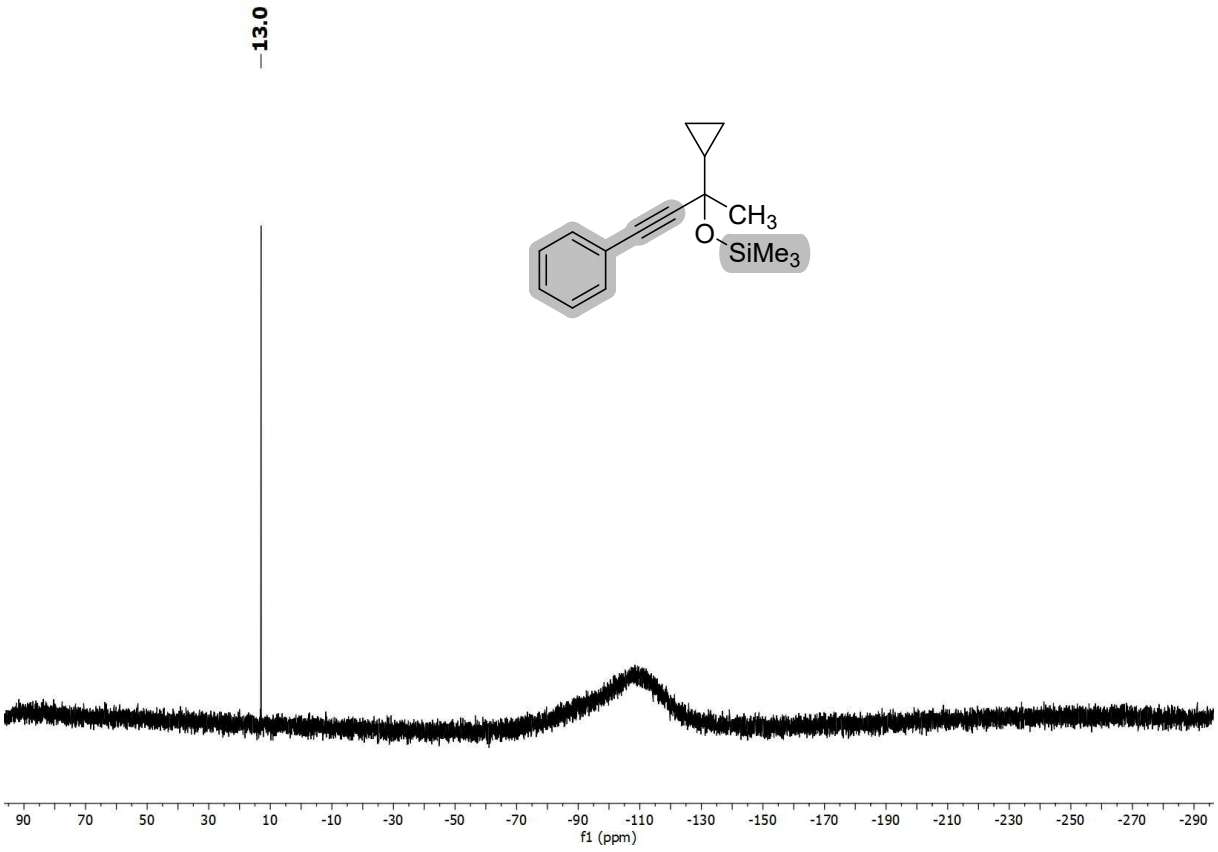



-16.2
Cl
CH3
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

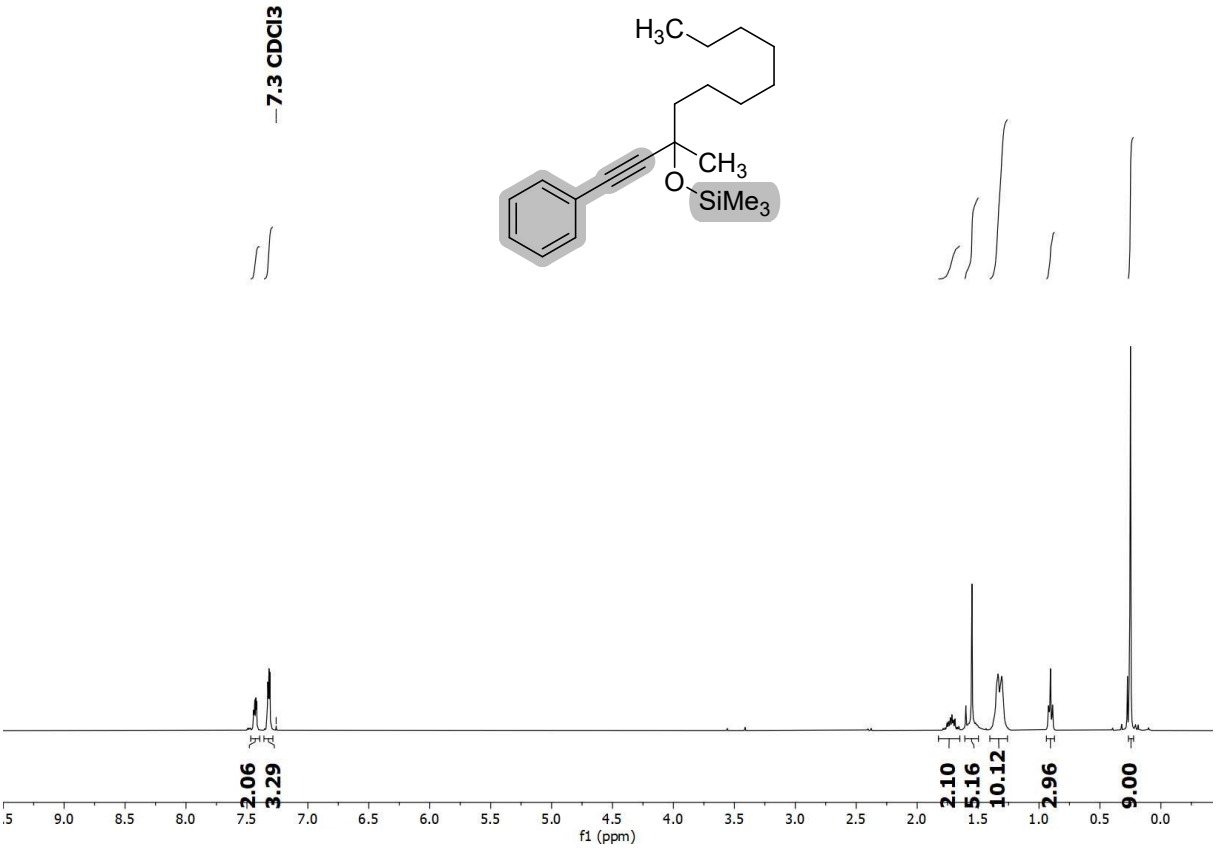
((2-Cyclopropyl-4-phenylbut-3-yn-2-yl)oxy)trimethylsilane (5c)

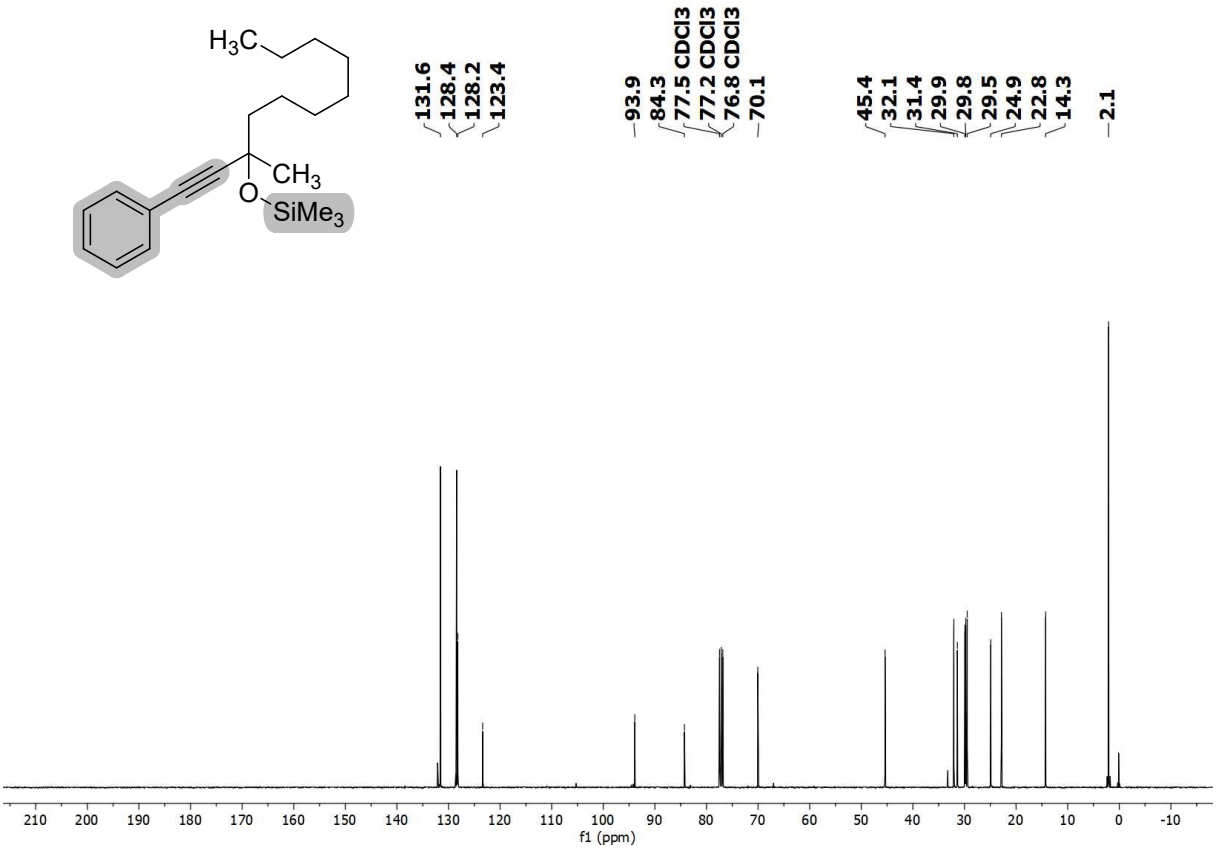


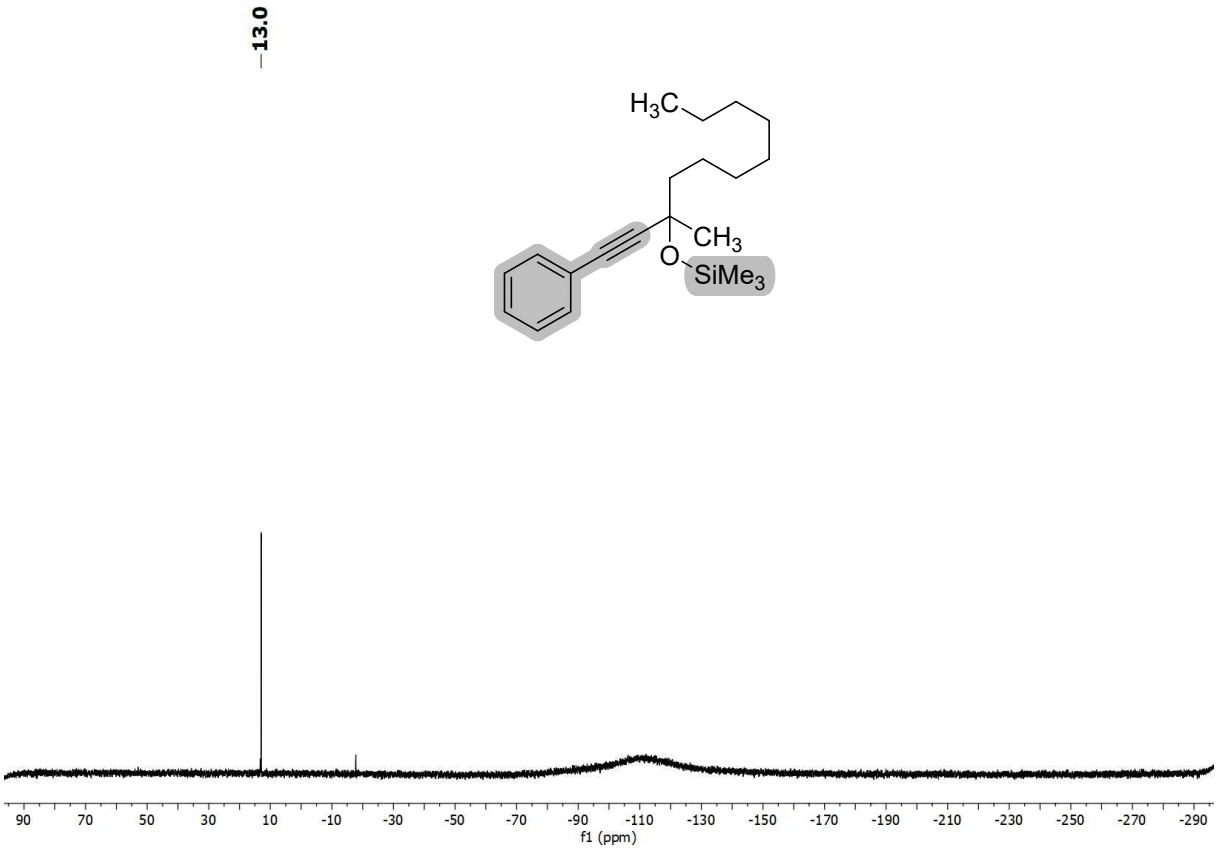



13.0
CH3
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

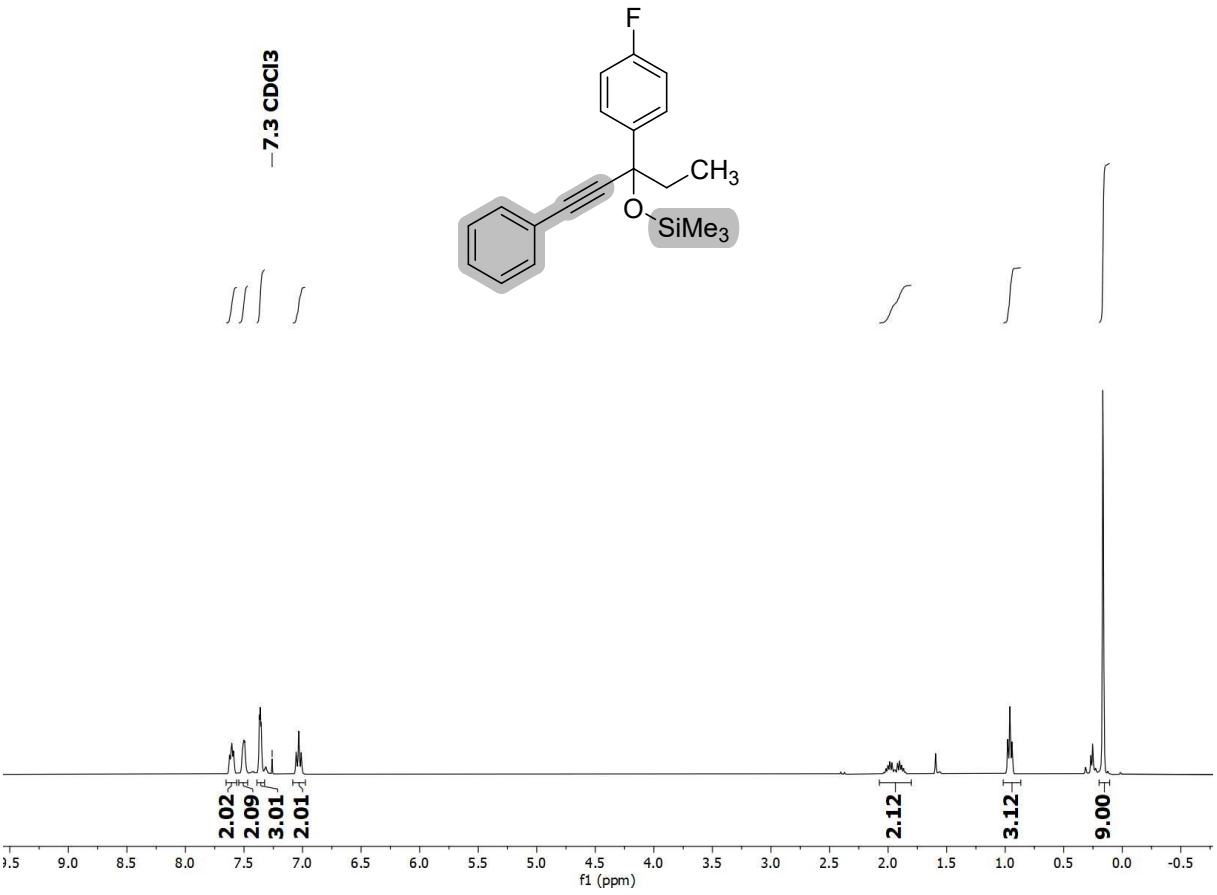
Trimethyl((3-methyl-1-phenylundec-1-yn-3-yl)oxy)silane (5d)

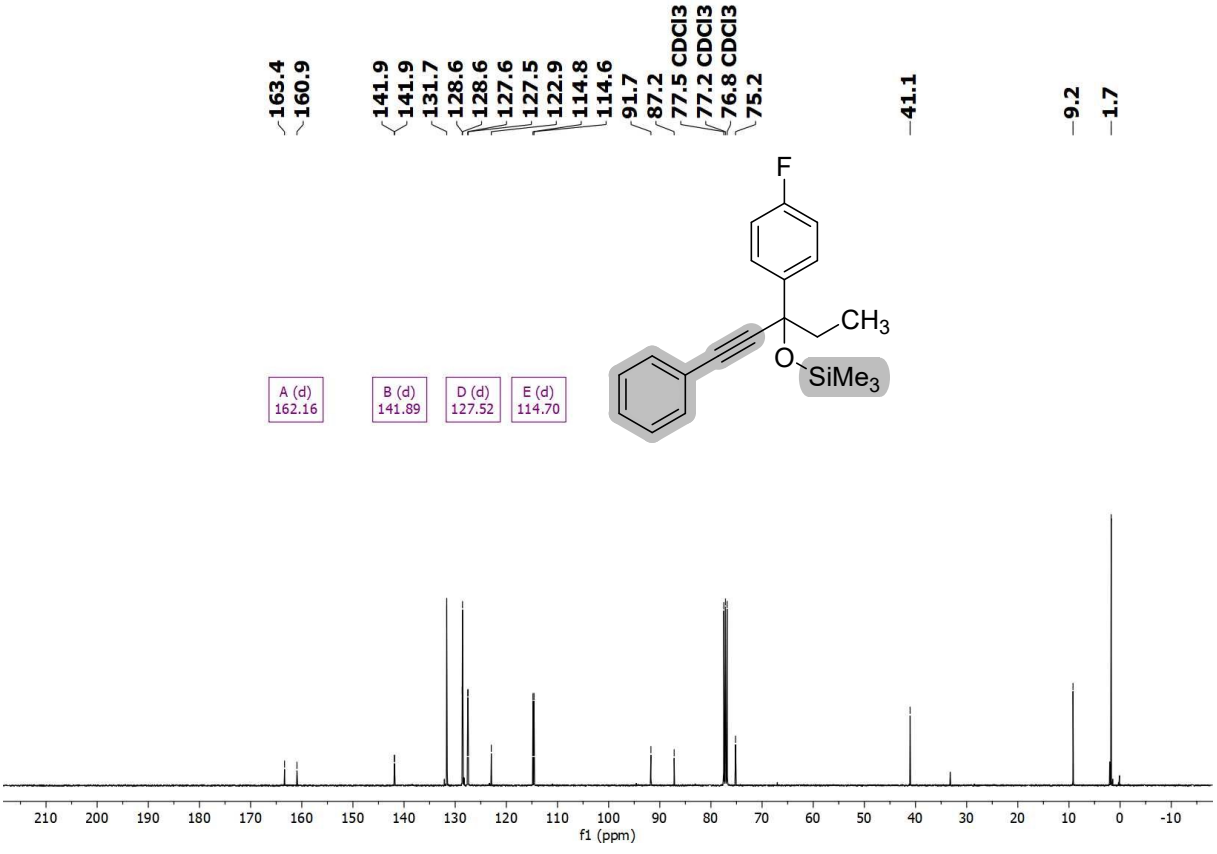


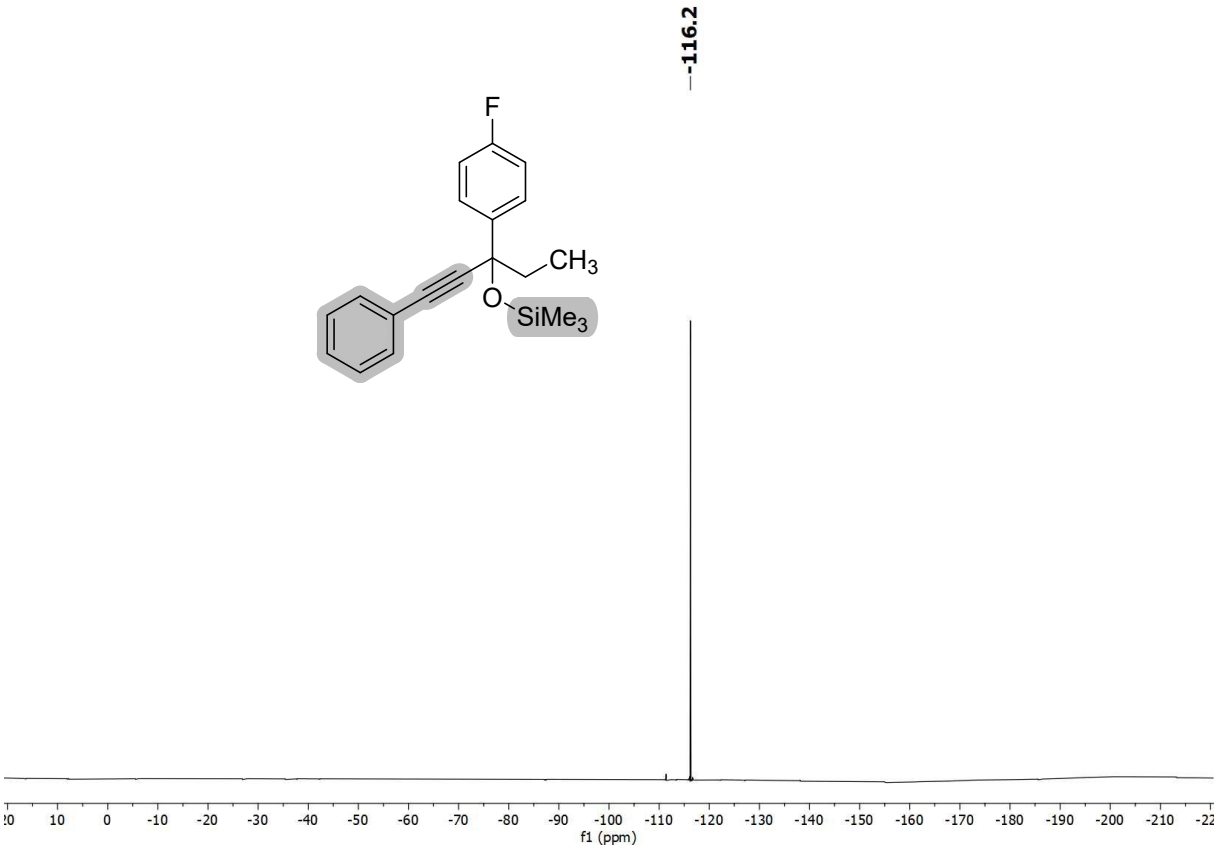


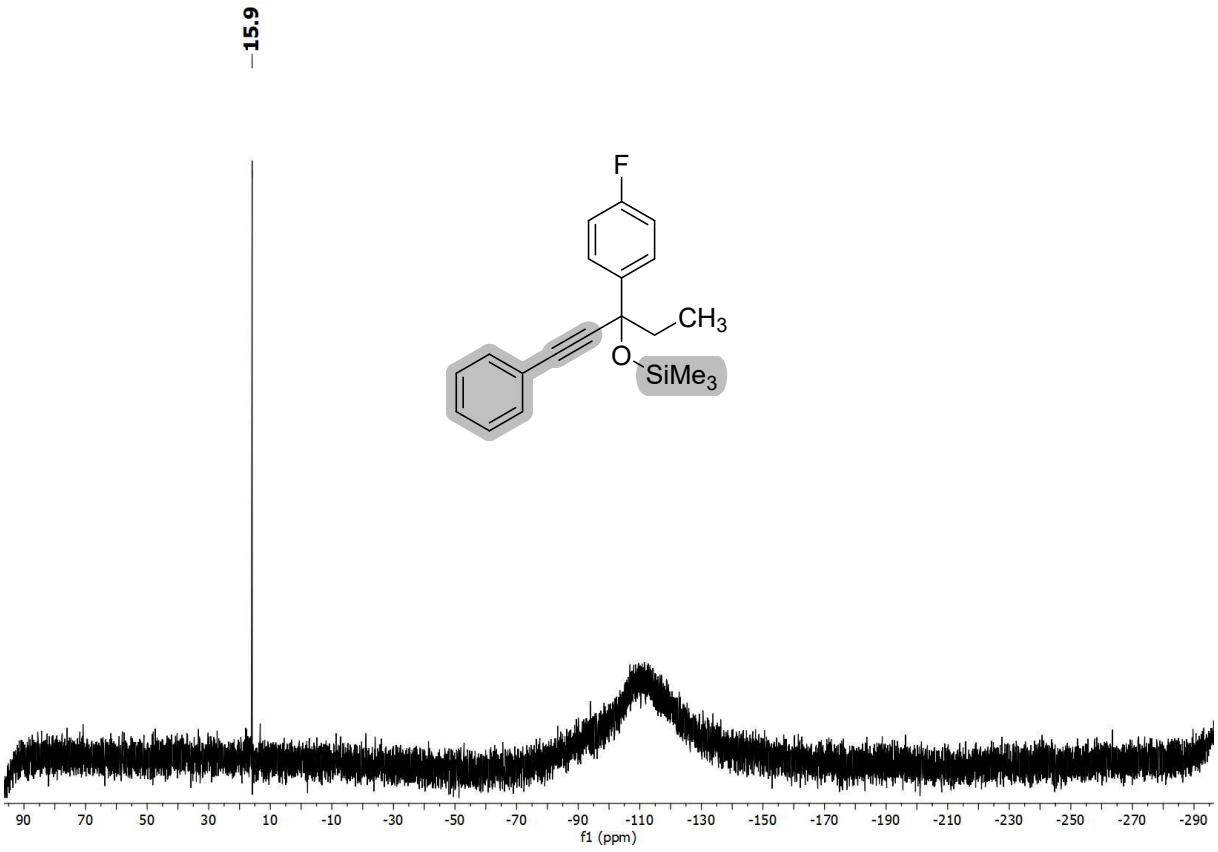

13.0
H3C
CH3
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

((3-(4-Fluorophenyl)-1-phenylpent-1-yn-3-yl)oxy)trimethylsilane (5e)

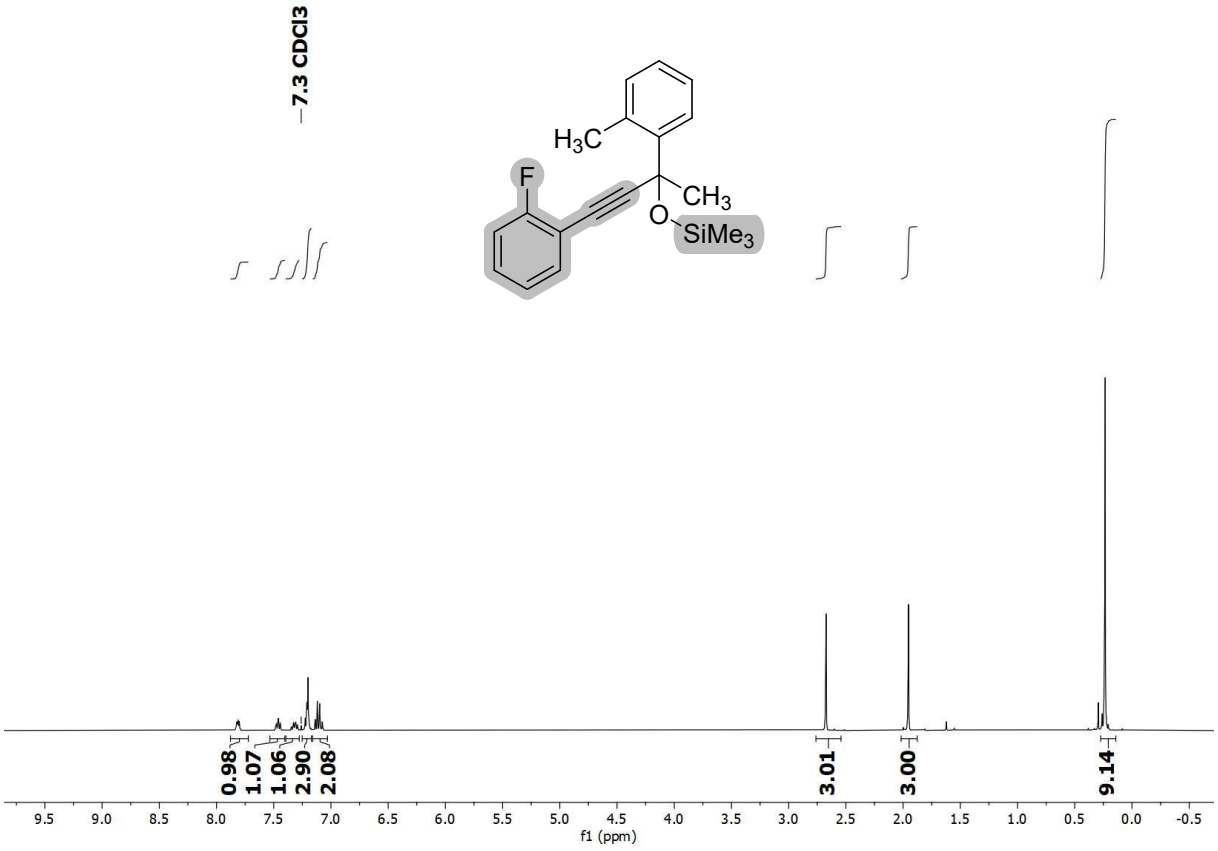


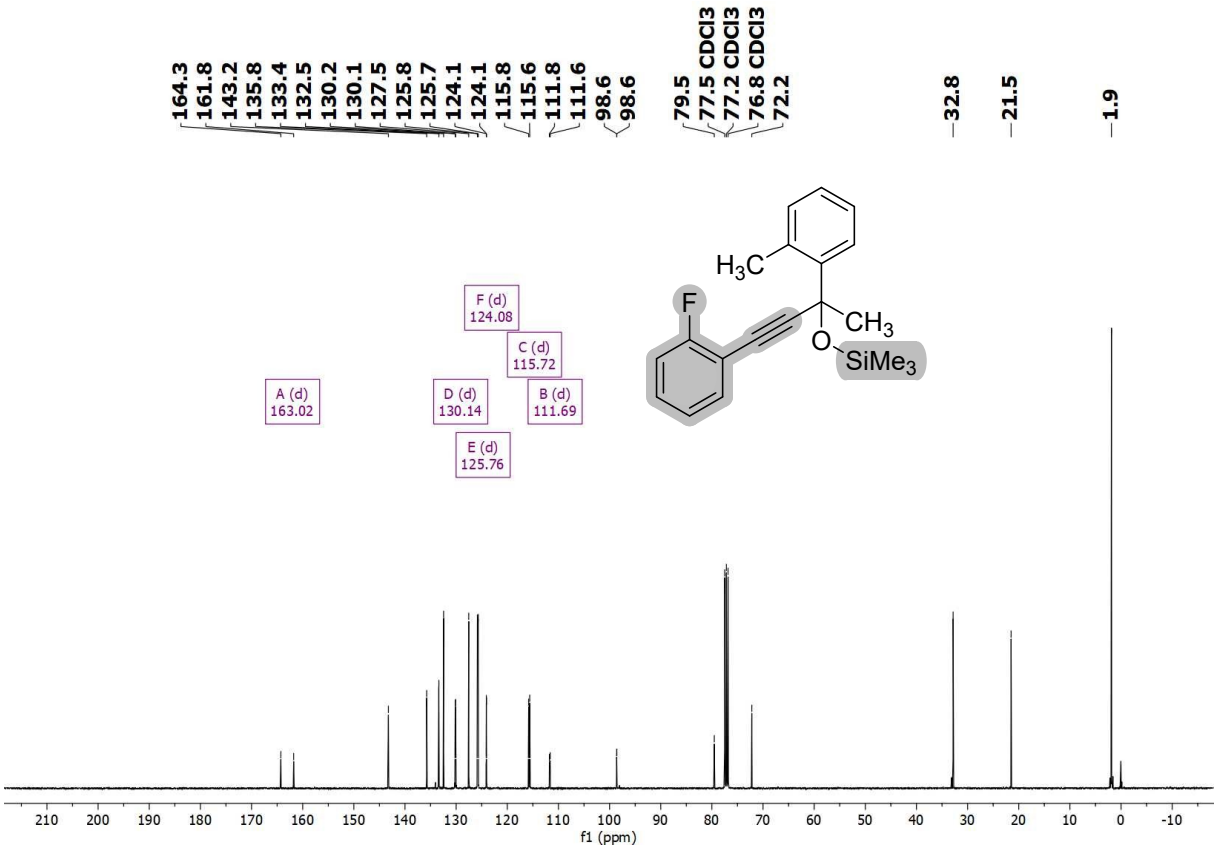


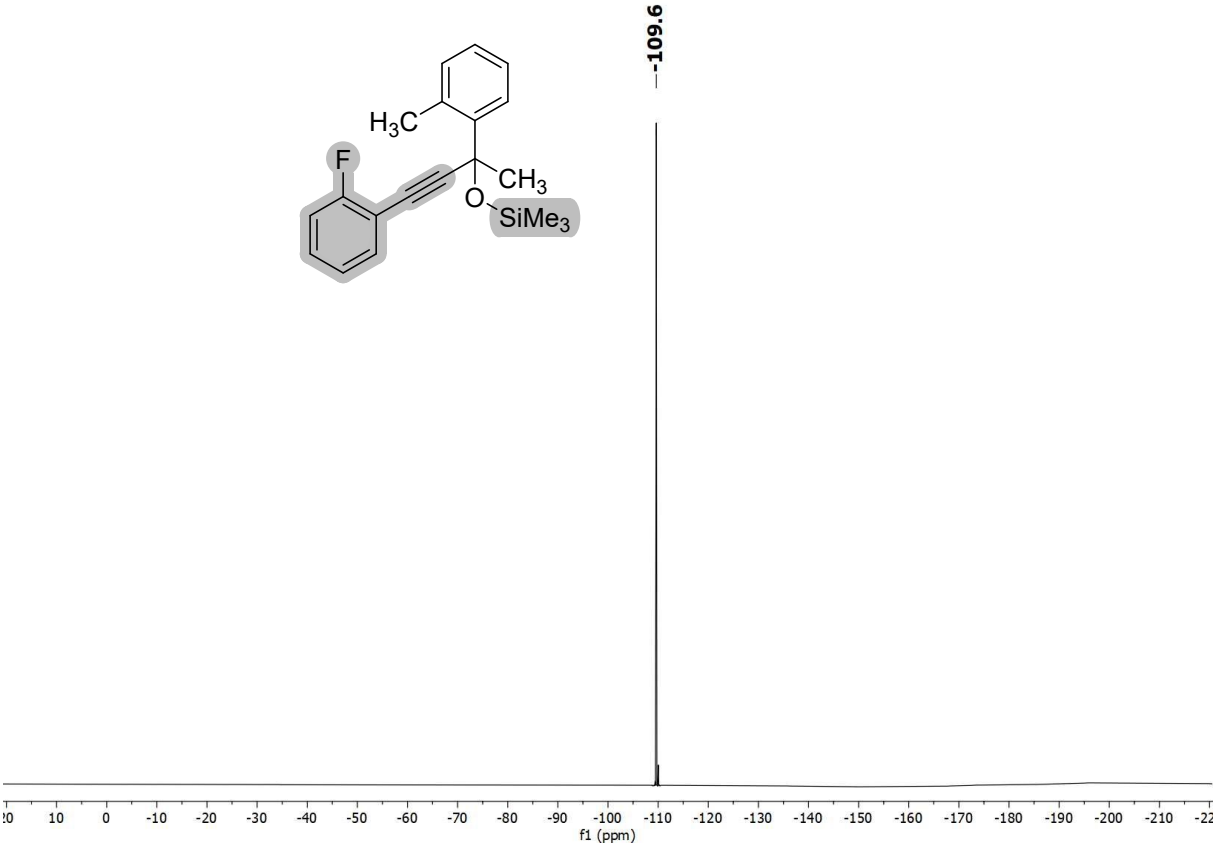

-116.2
F
CH3
O
SiMe3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

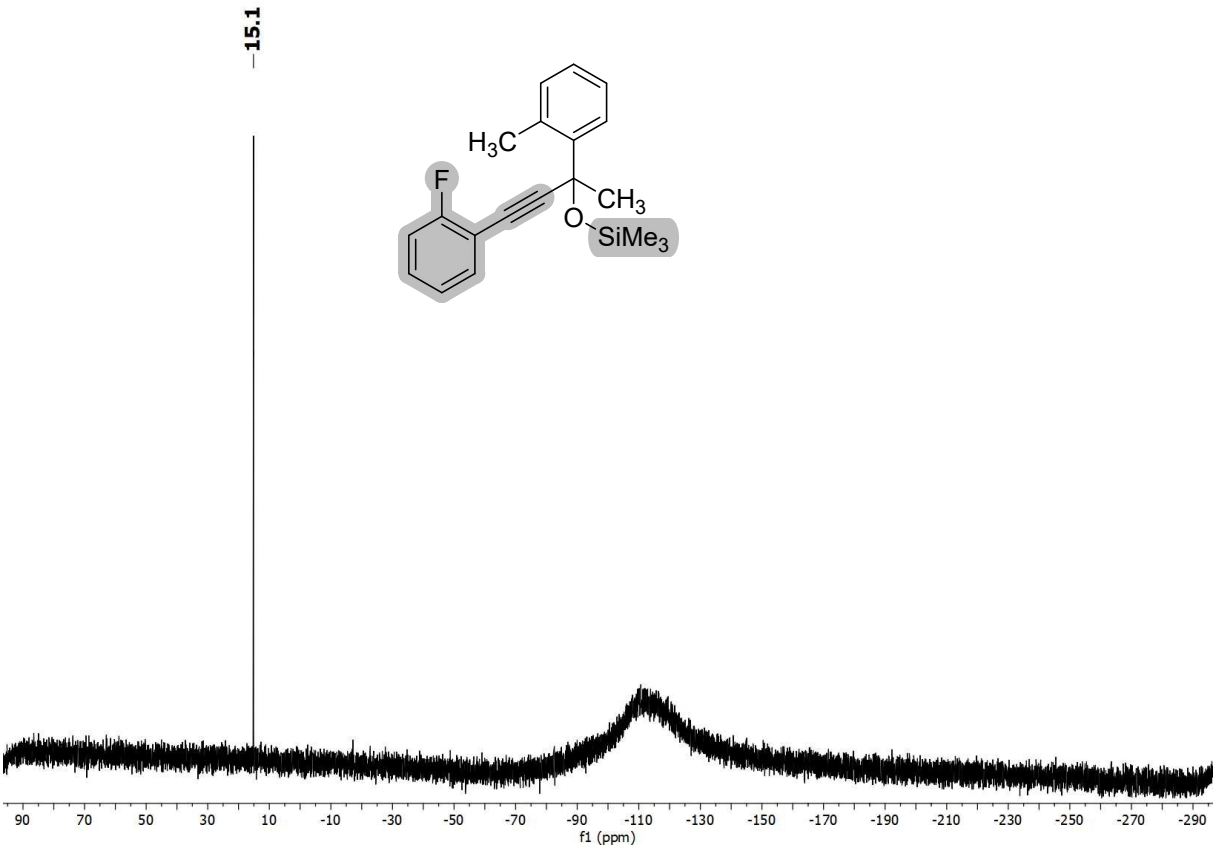

15.9
F
CH3
O
SiMe3
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

((4-(2-Fluorophenyl)-2-(o-tolyl)but-3-yn-2-yl)oxy)trimethylsilane (5f)

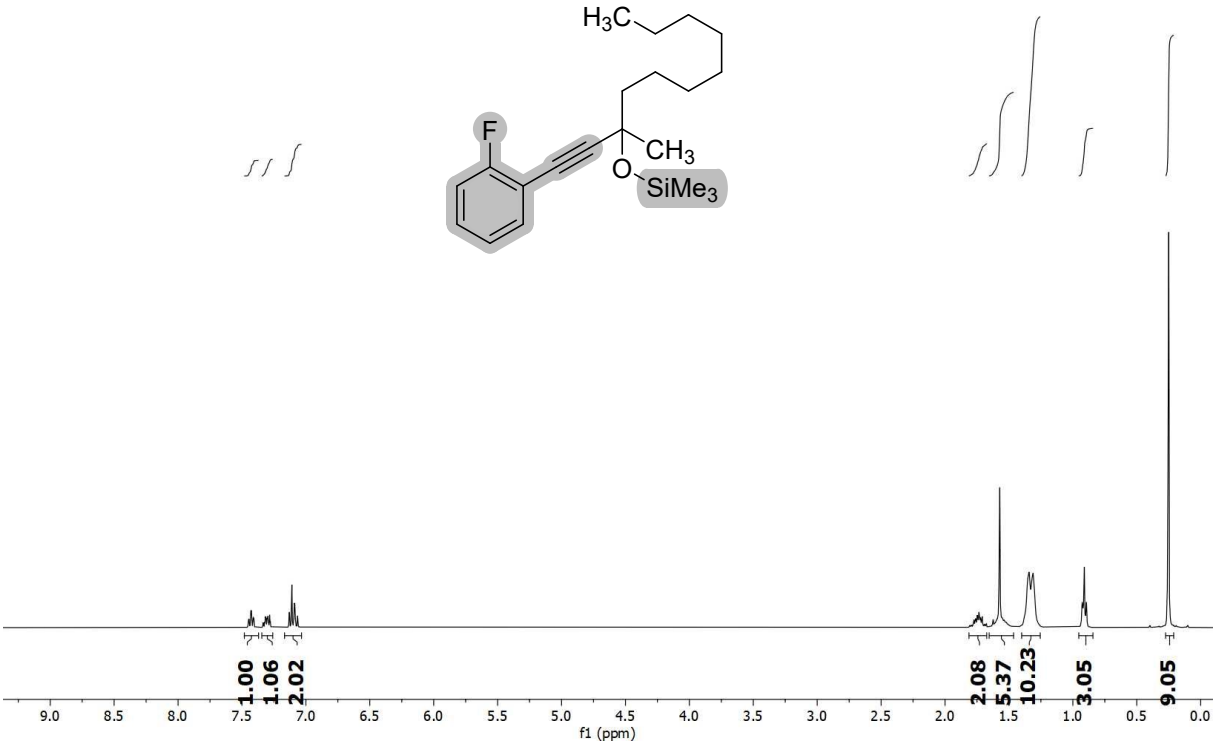


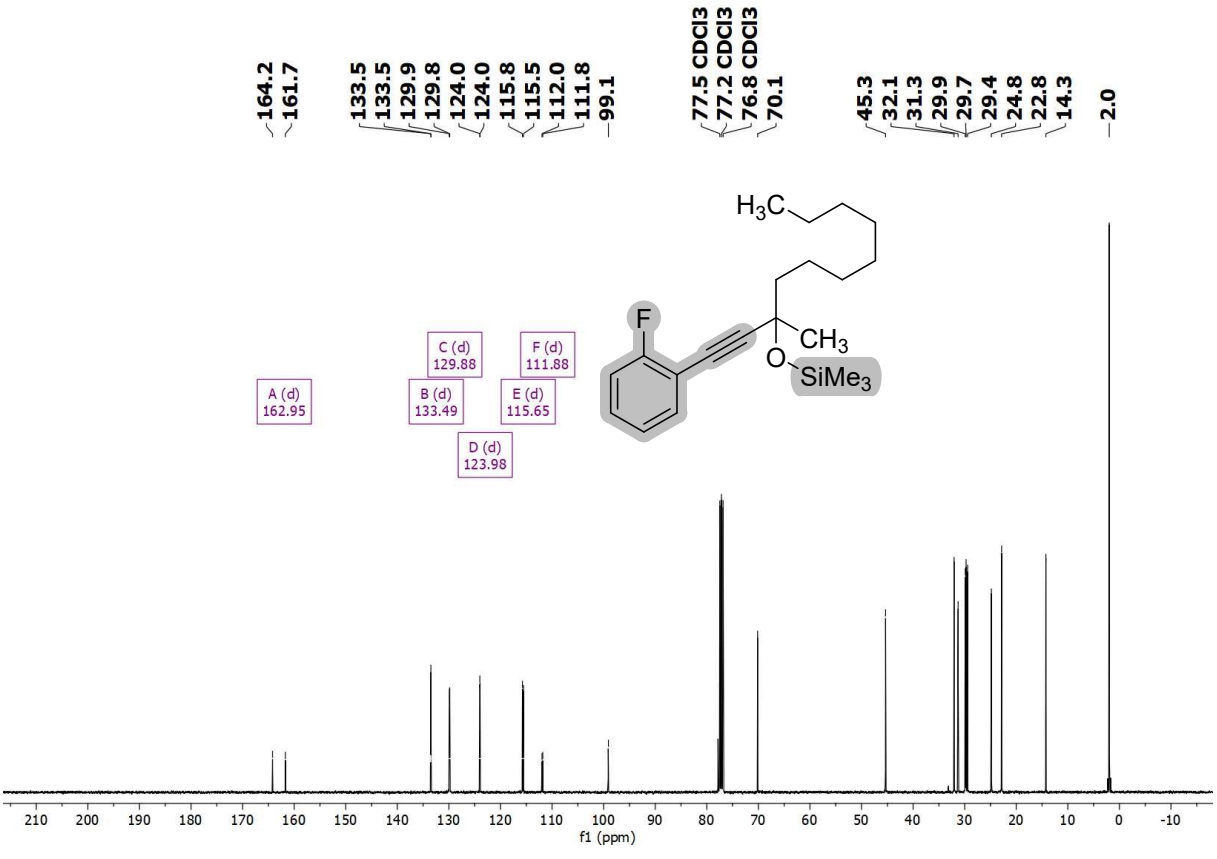


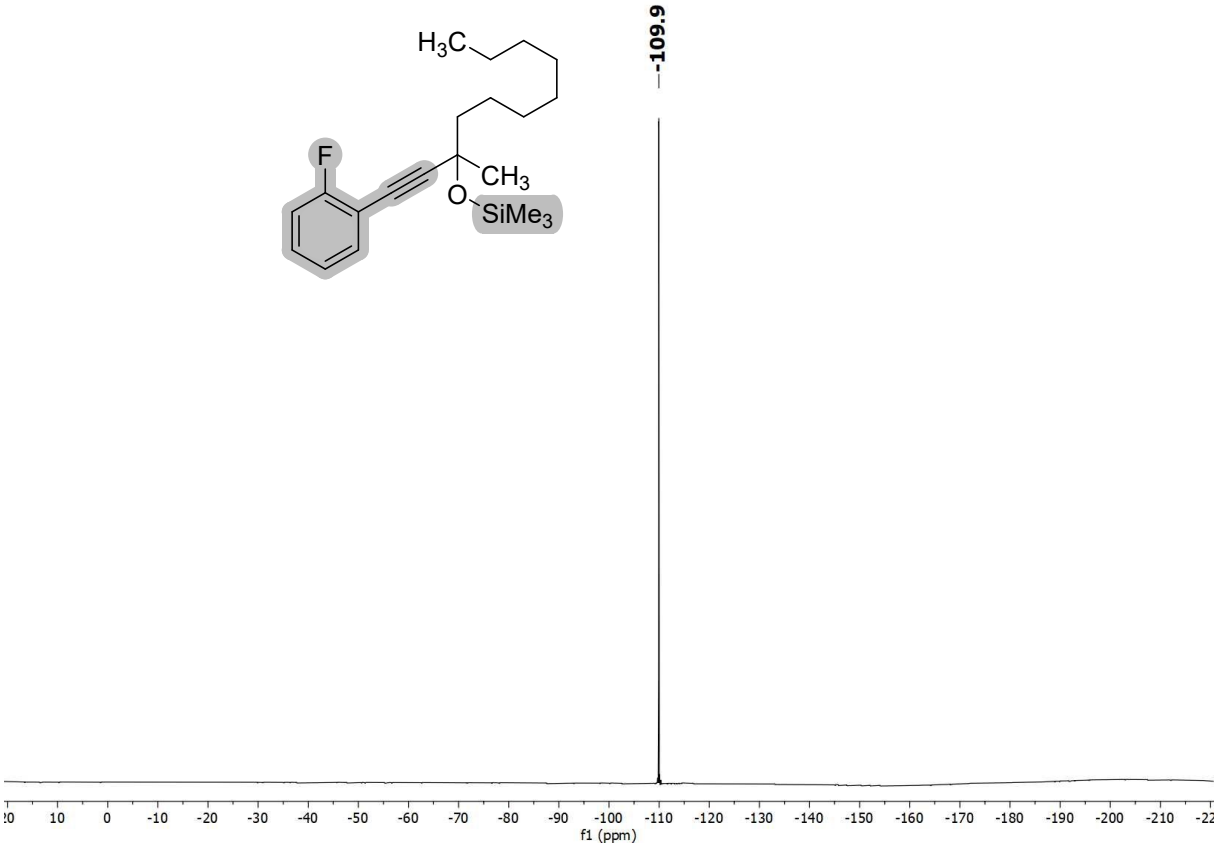

-109.6
H3C
F
CH3
O
SiMe3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

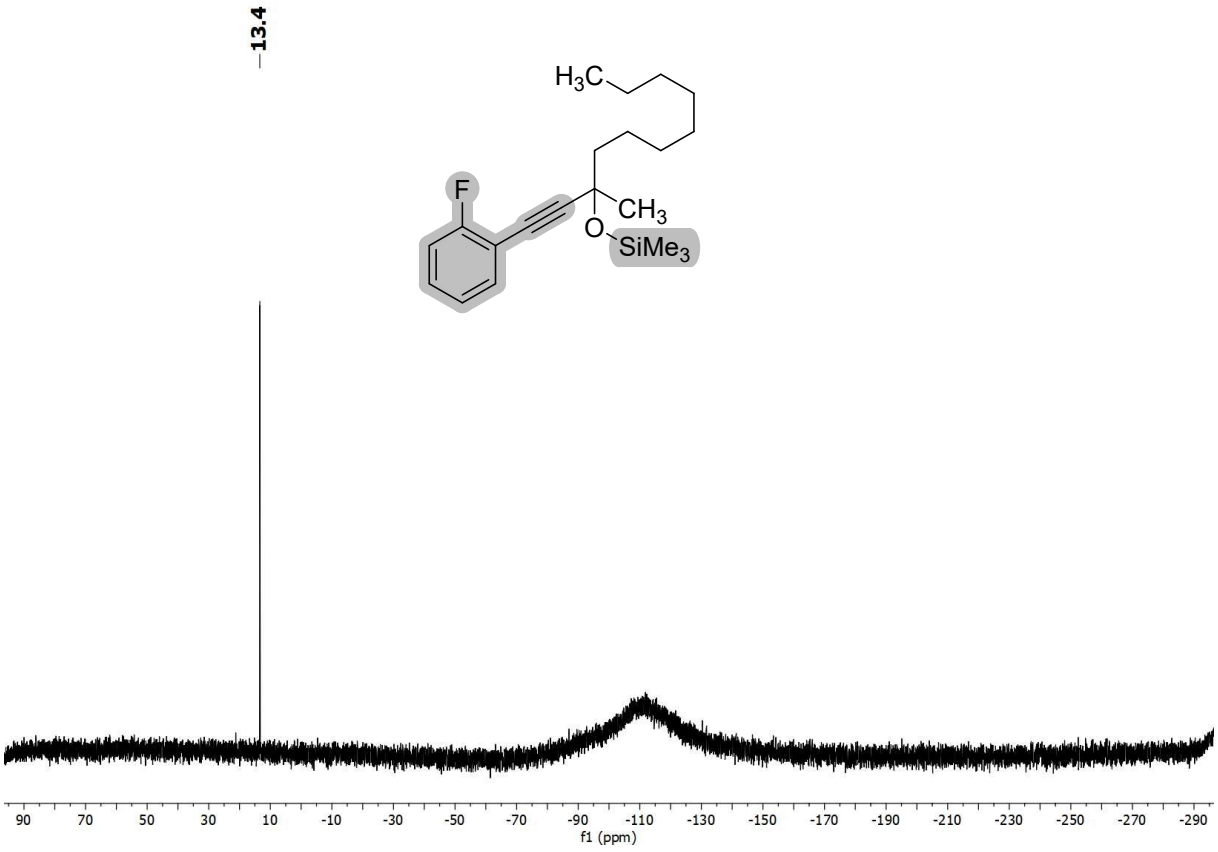

-15.1
H3C
F
CH3
O
SiMe3
90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

((1-(2-Fluorophenyl)-3-methylundec-1-yn-3-yl)oxy)trimethylsilane (5g)

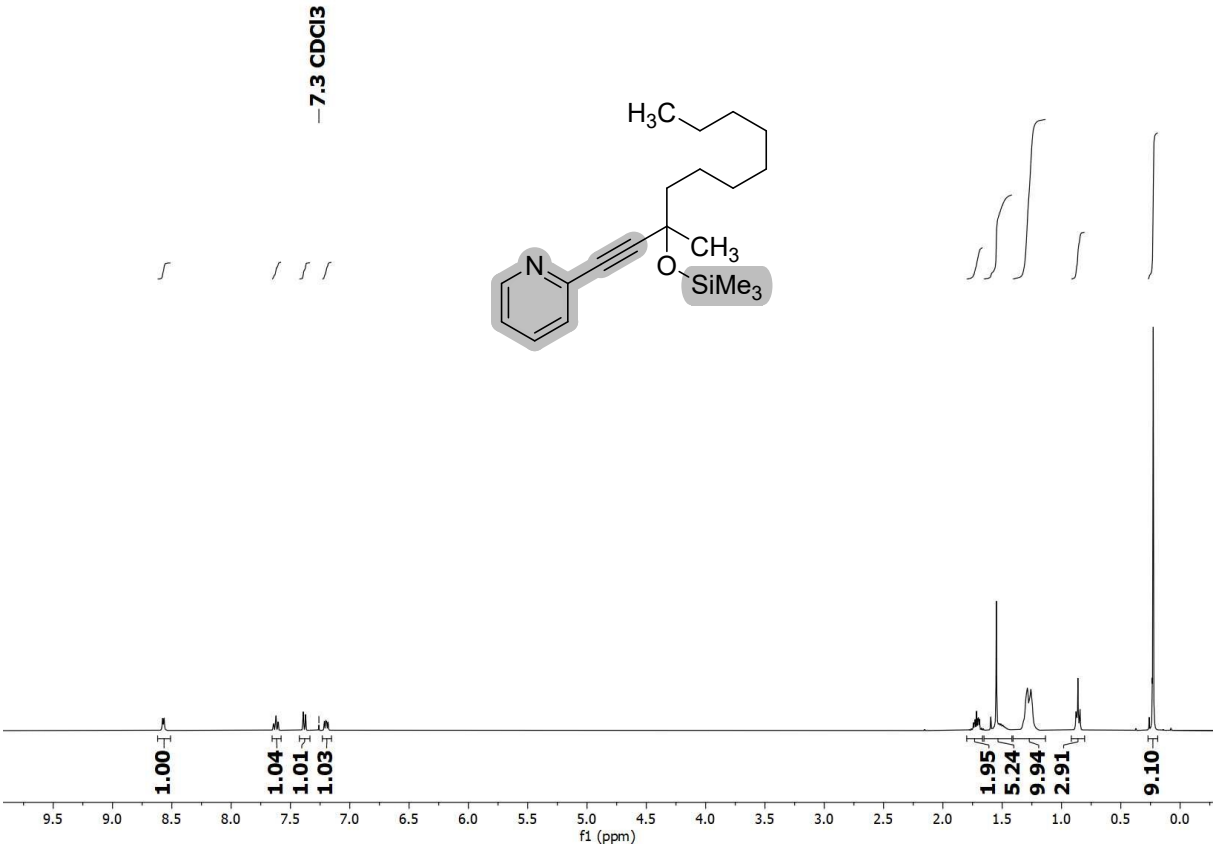


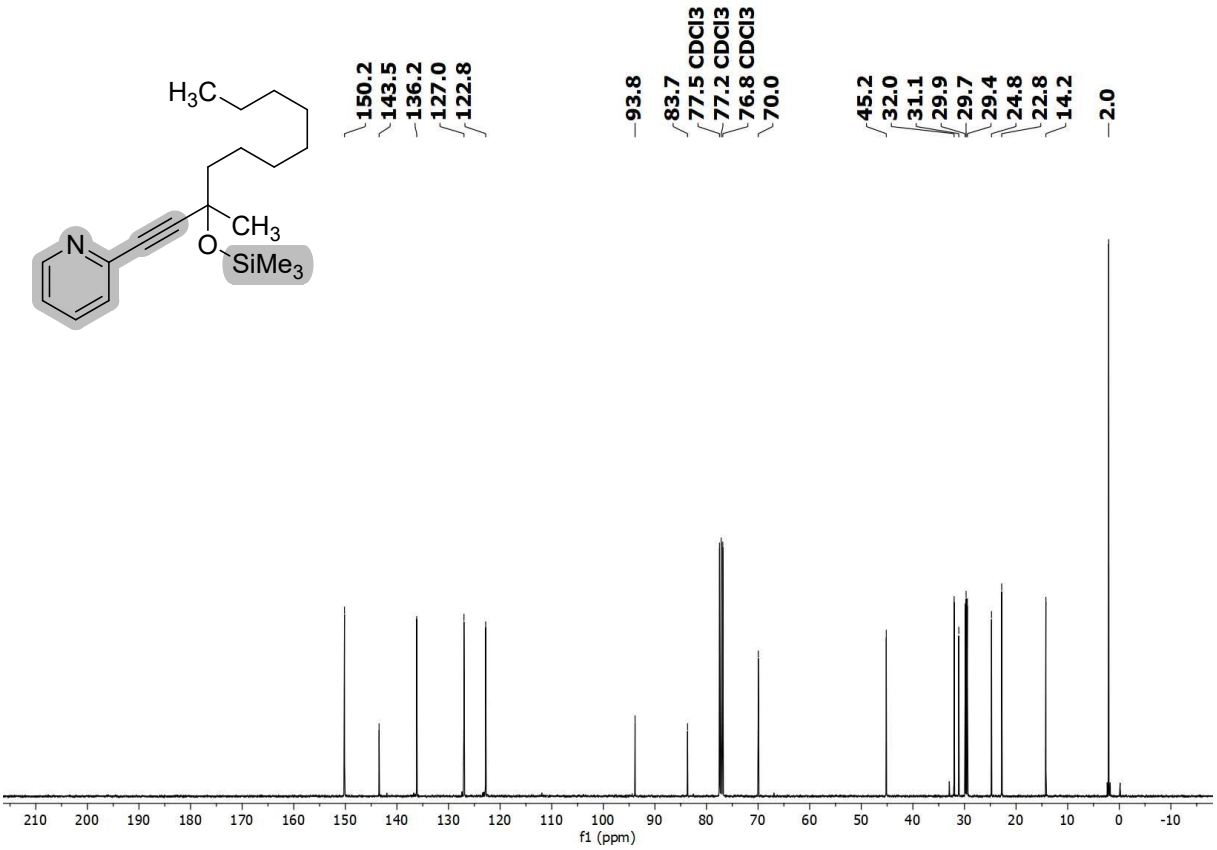


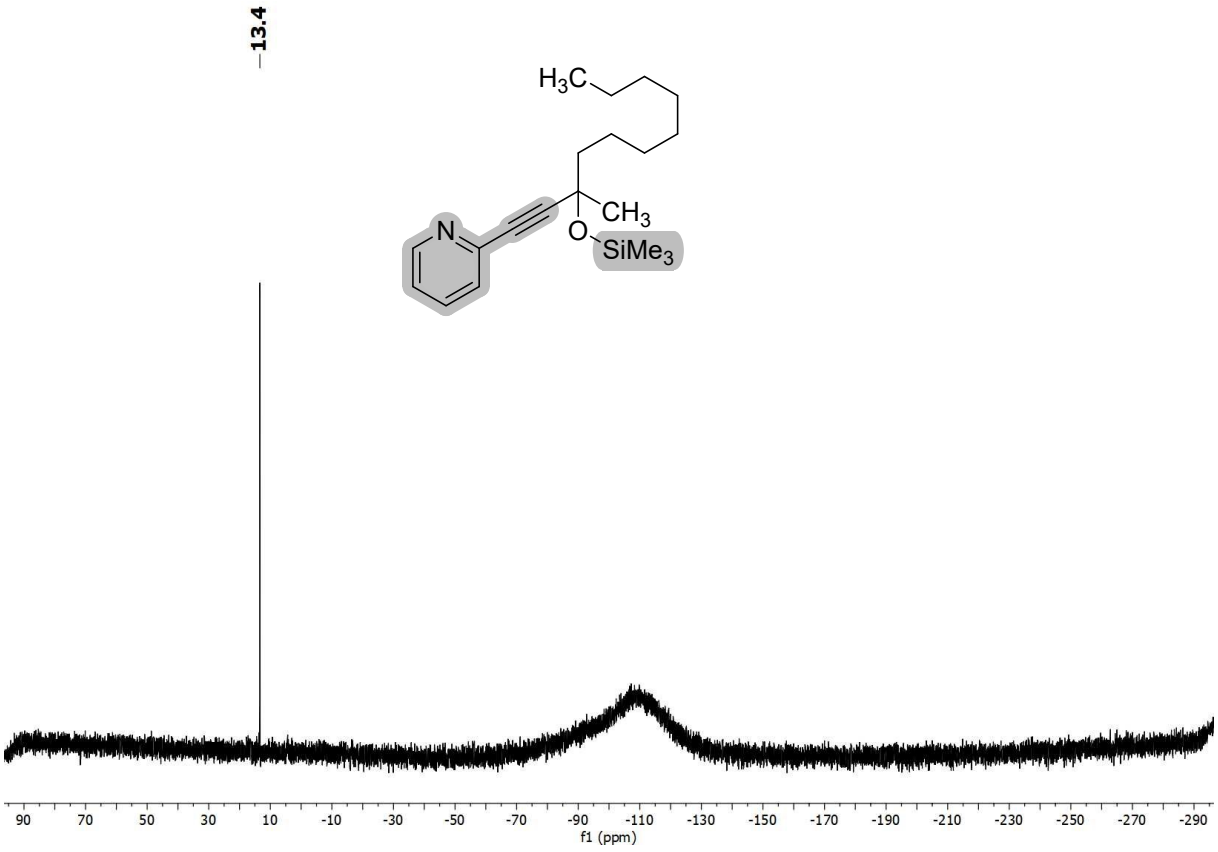

H3C
F
CH3
O
SiMe3
-109.9
f1 (ppm)


H3C
F
CH3
O
SiMe3
13.4
f1 (ppm)

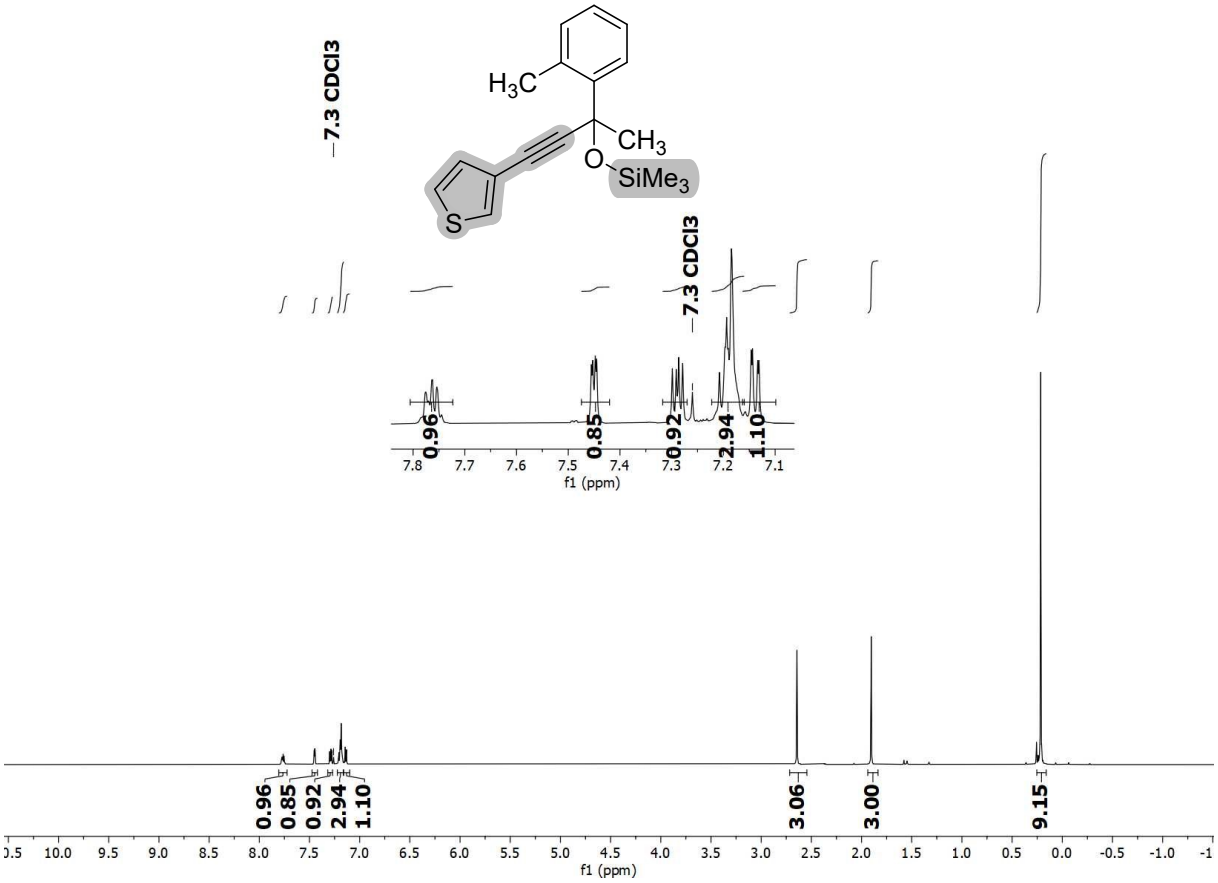
2-(3-Methyl-3-((trimethylsilyl)oxy)undec-1-yn-1-yl)pyridine (5h)

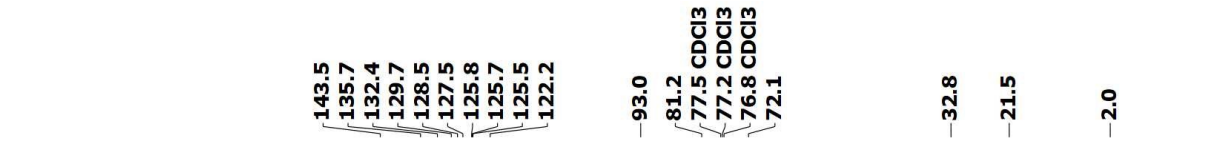


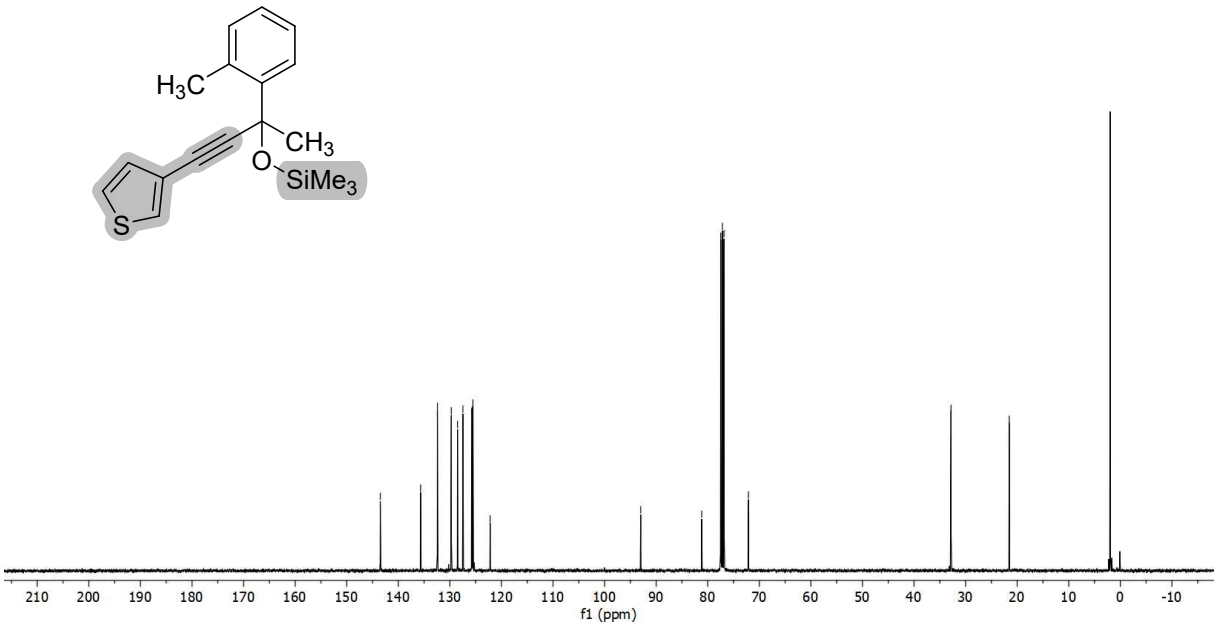


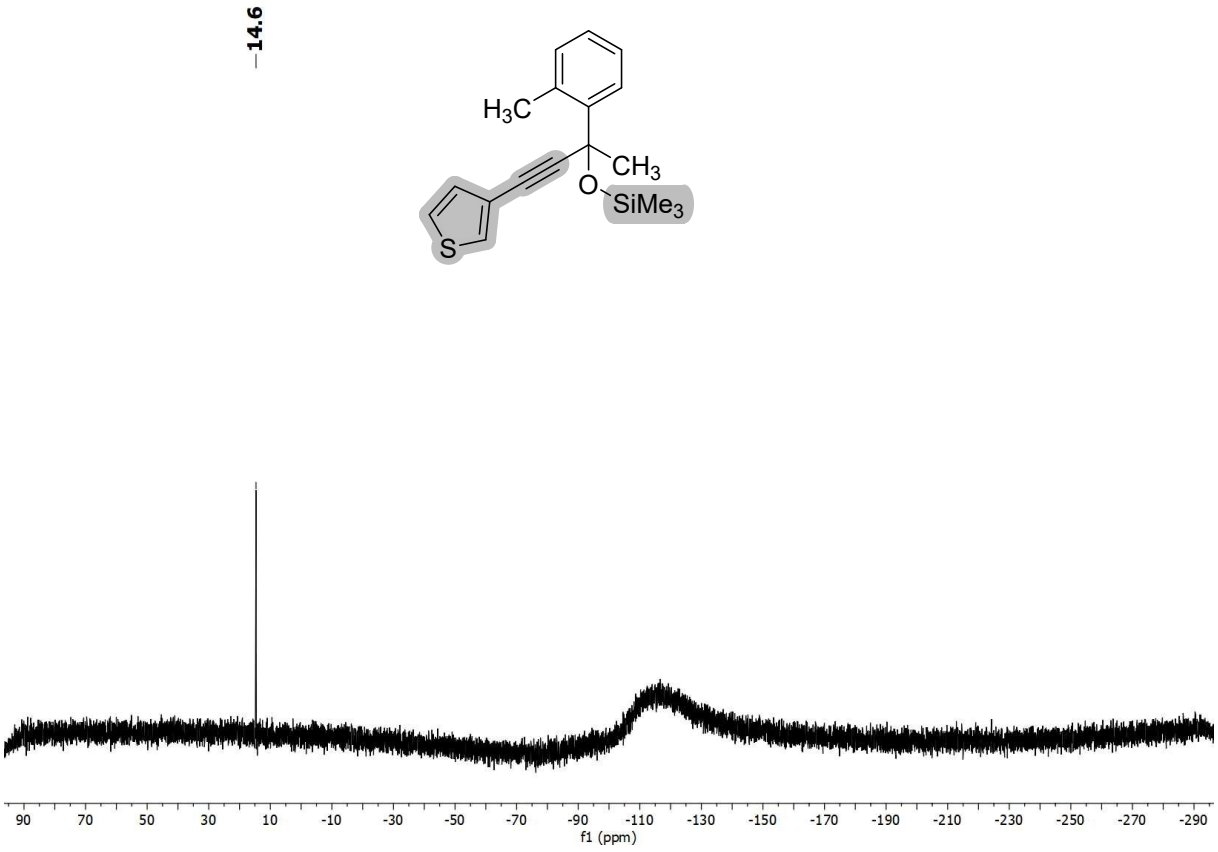

13.4
H3C
CH3
N
O
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

Trimethyl((4-(thiophen-3-yl)-2-(o-tolyl)but-3-yn-2-yl)oxy)silane (5i)

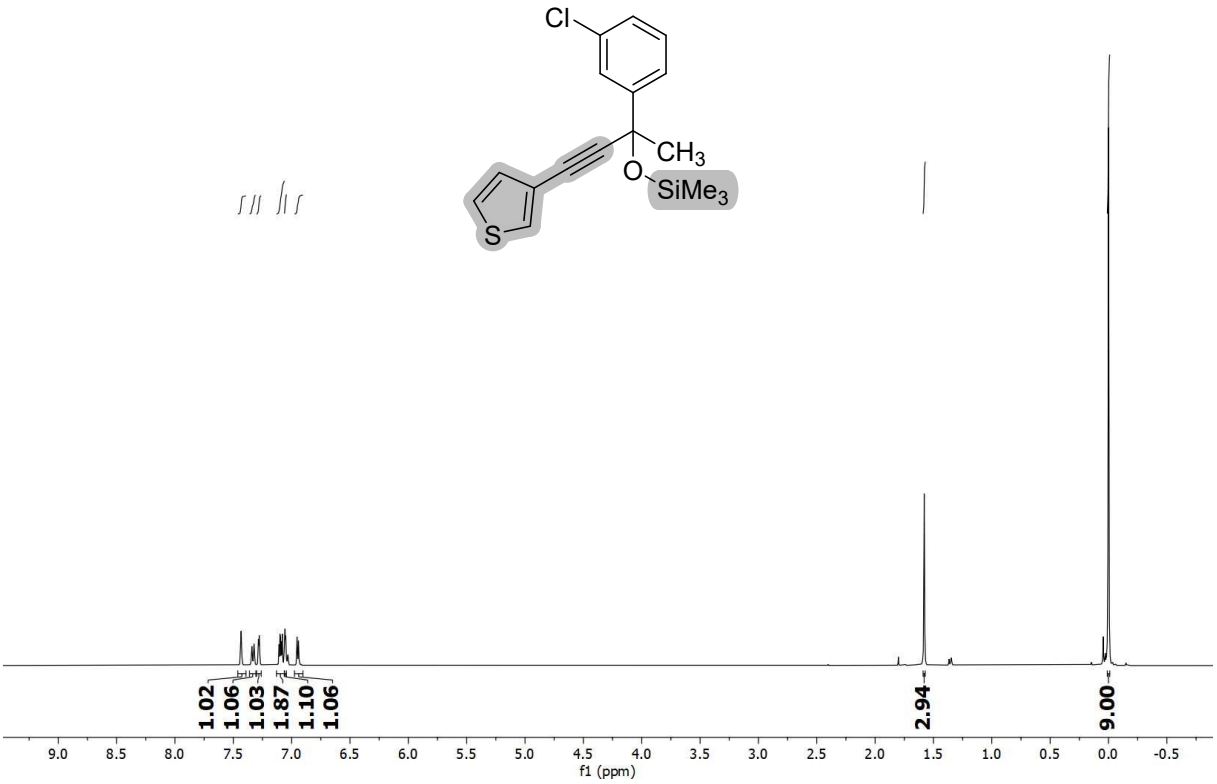


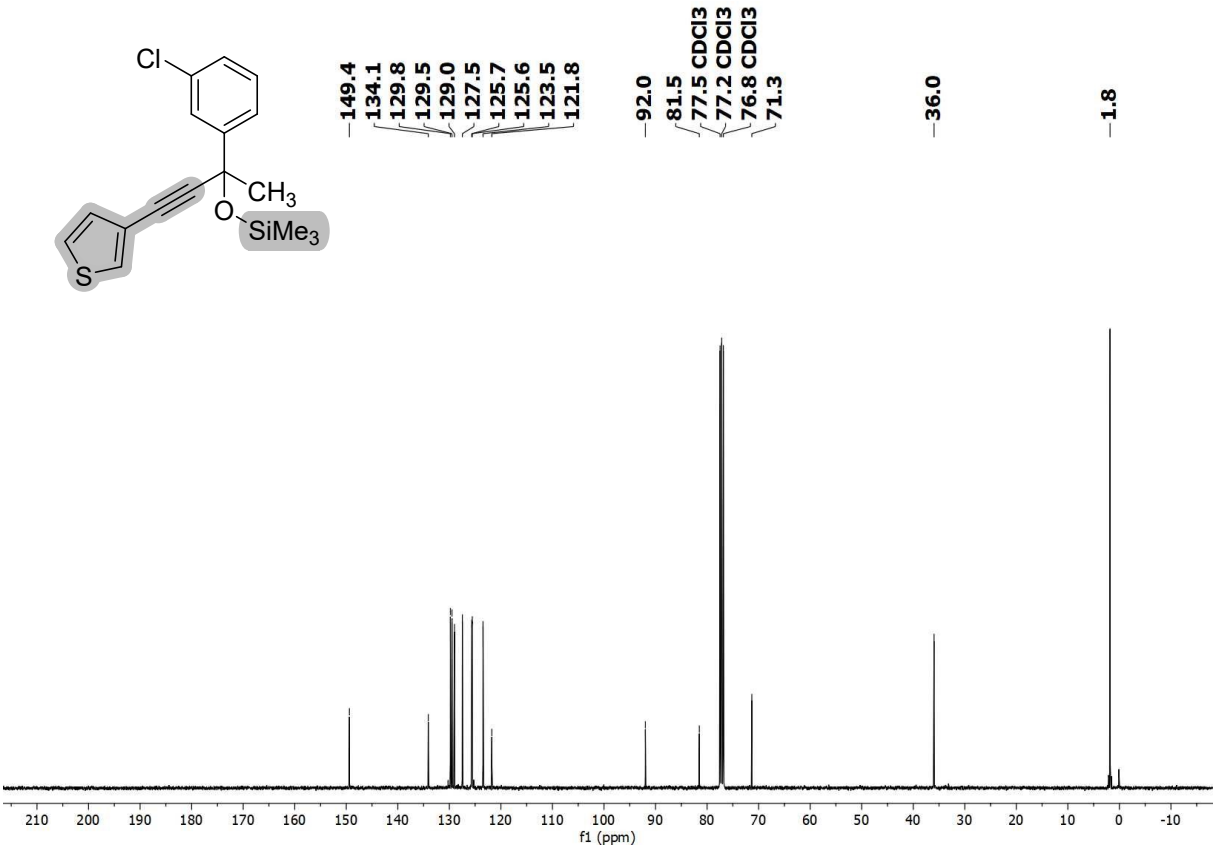


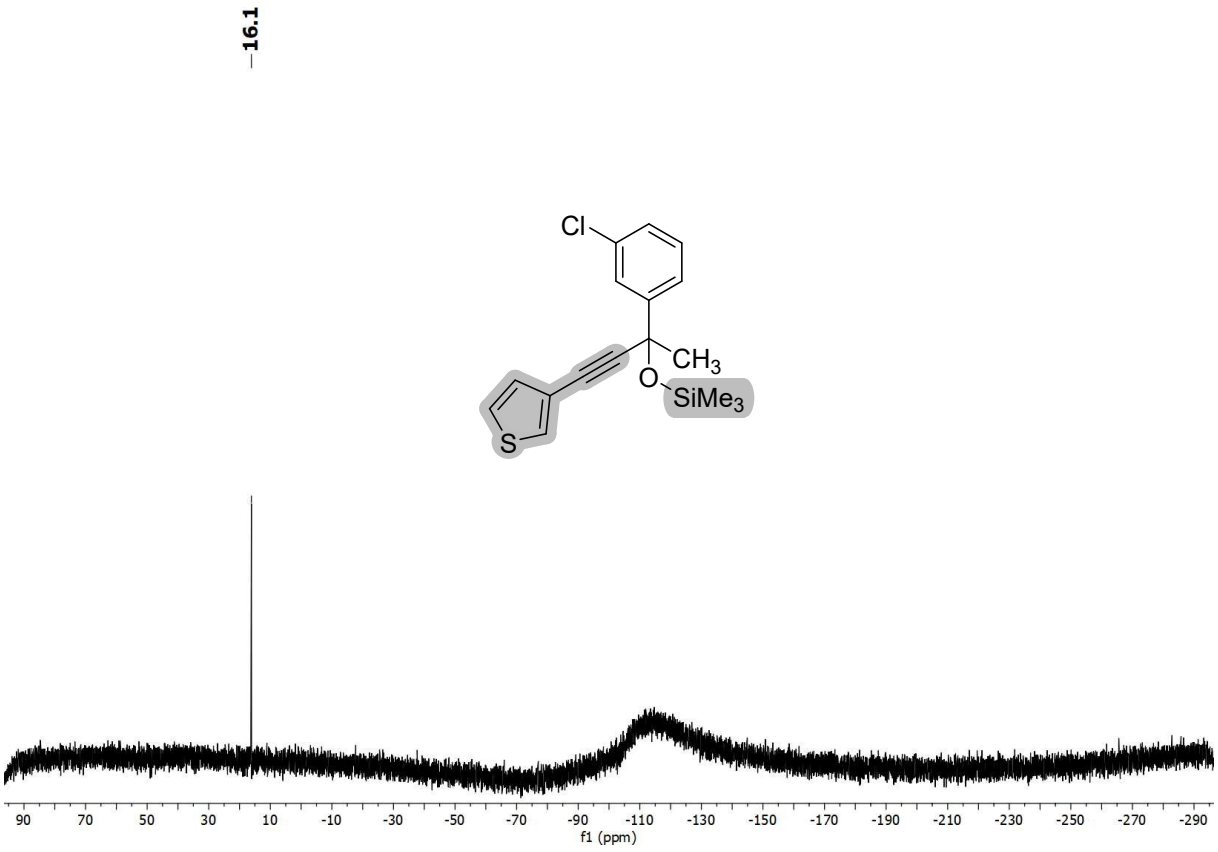



14.6
H3C
CH3
O
SiMe3
S
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

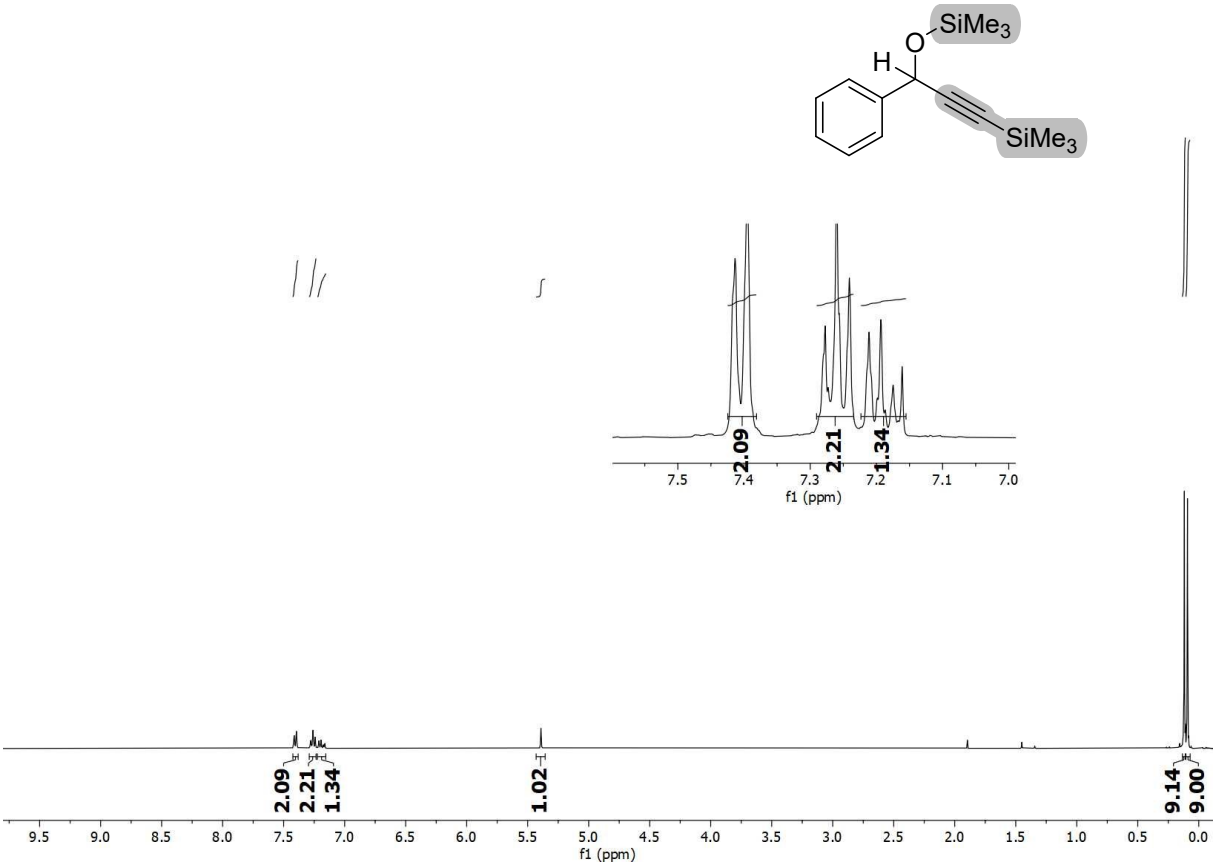
((2-(3-Chlorophenyl)-4-(thiophen-3-yl)but-3-yn-2-yl)oxy)trimethylsilane (5j)

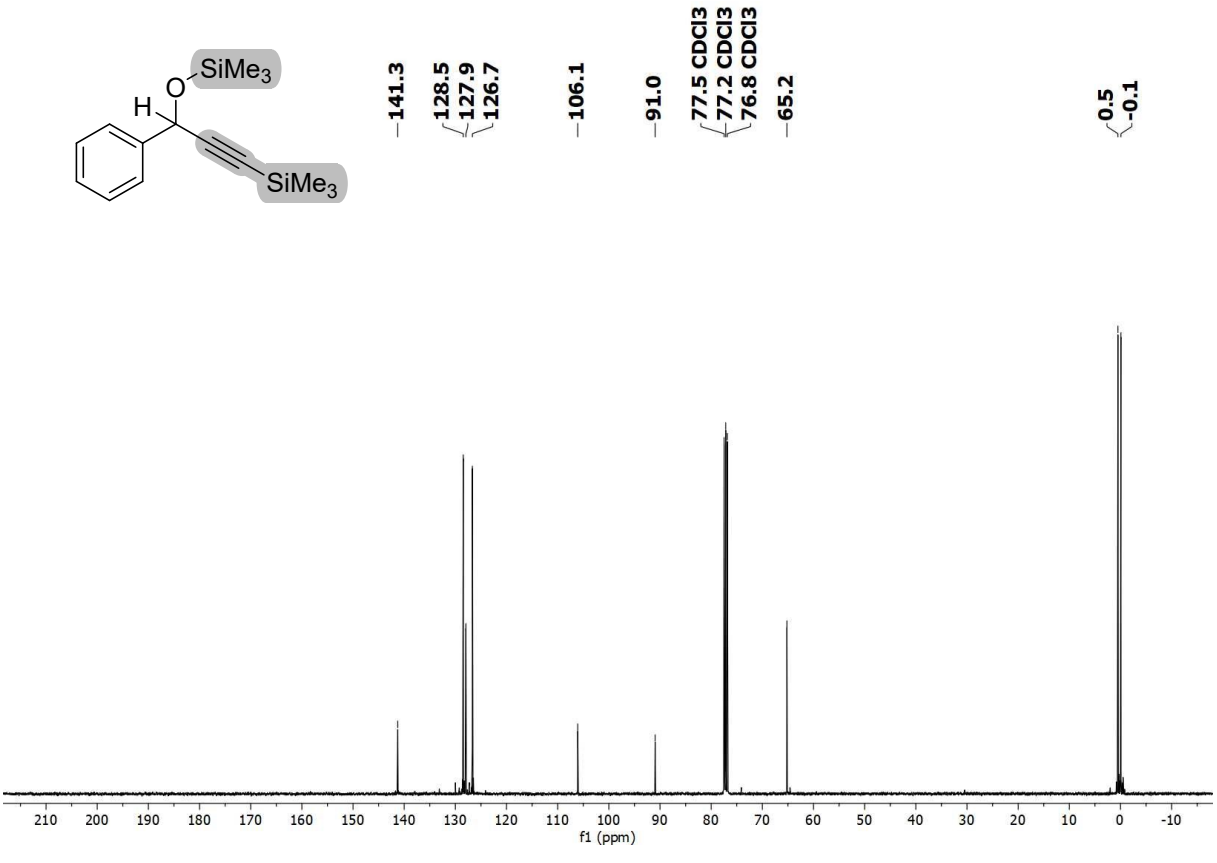


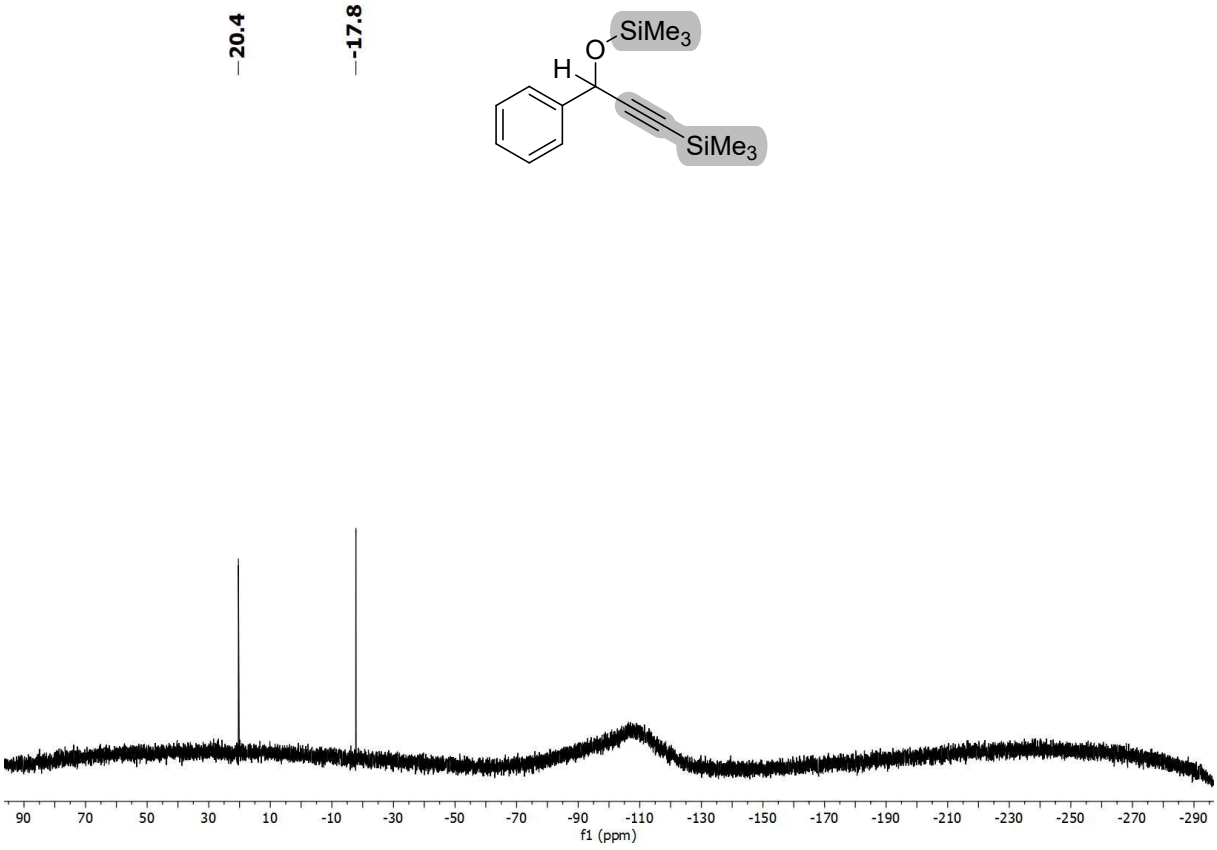



16.1
Cl
CH3
O
SiMe3
S
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

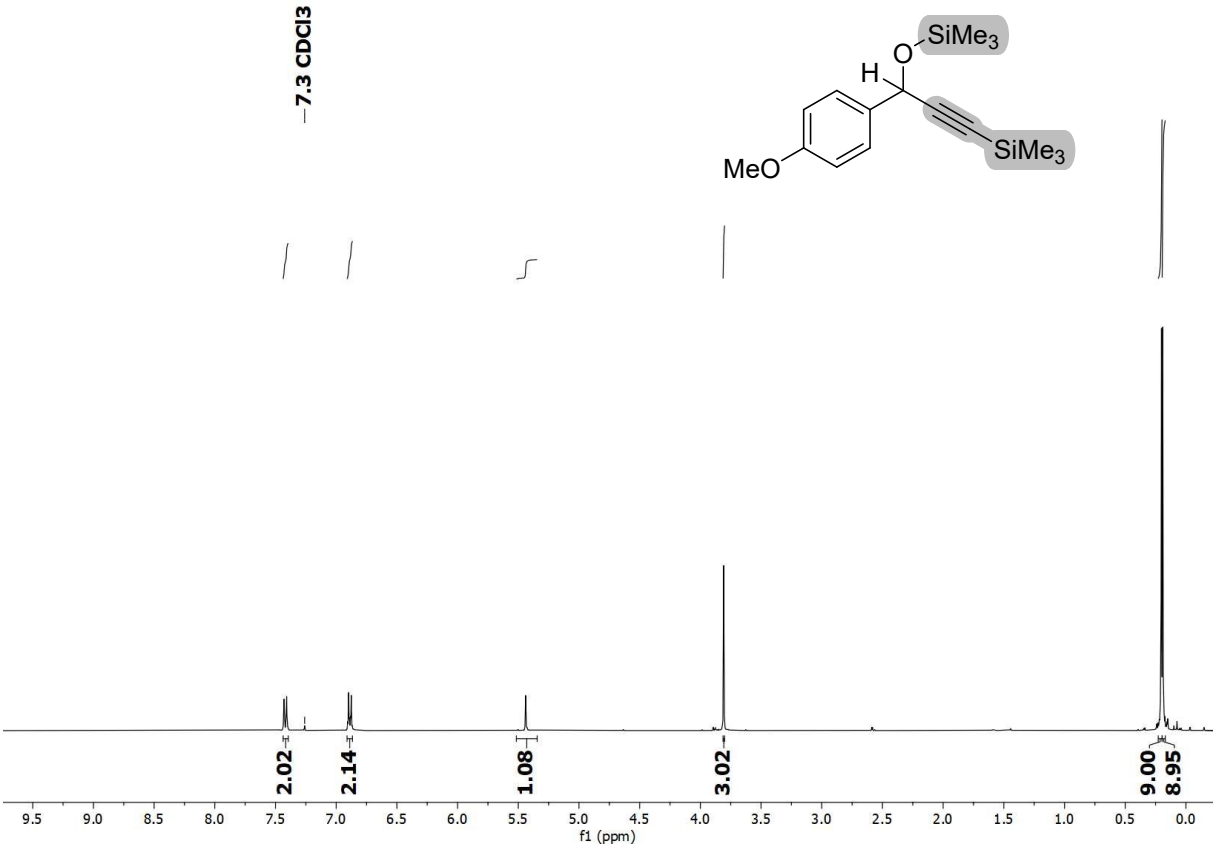
Trimethyl(3-phenyl-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)silane (7a)

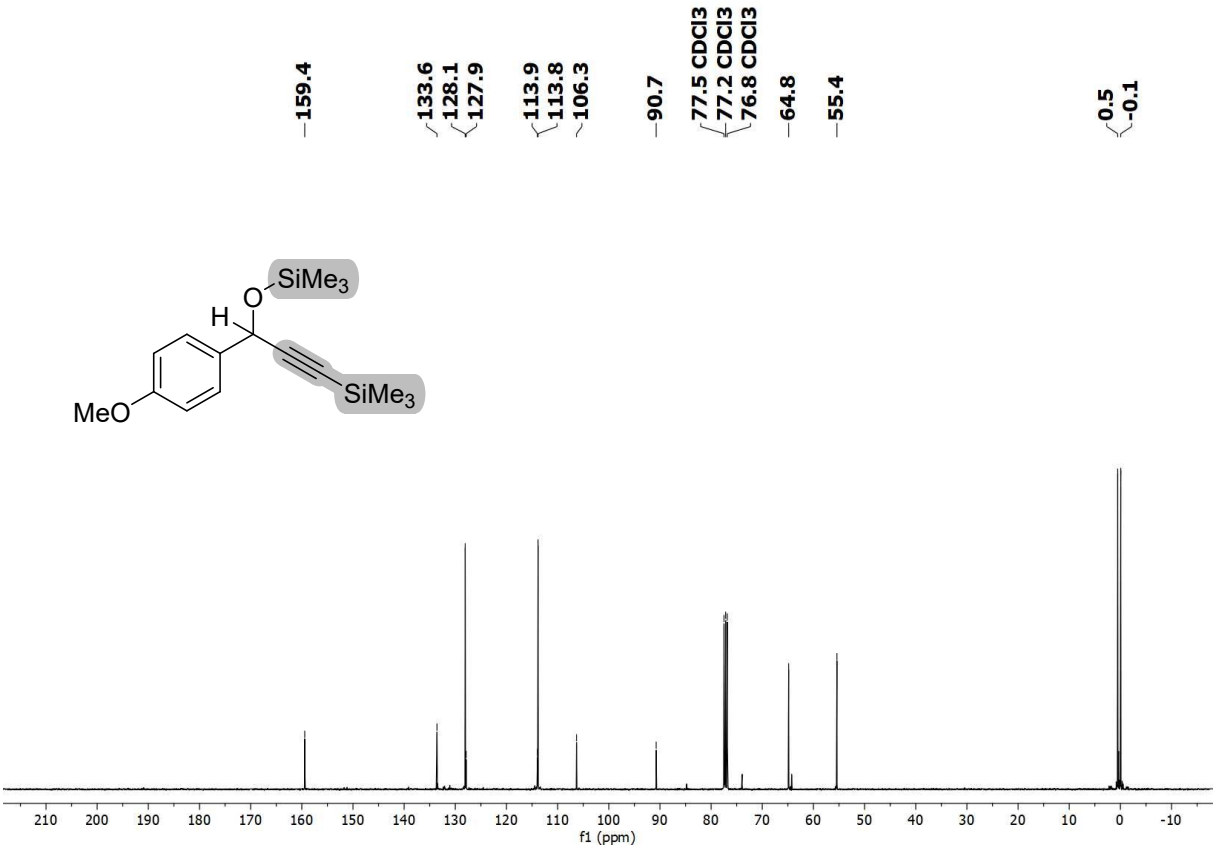


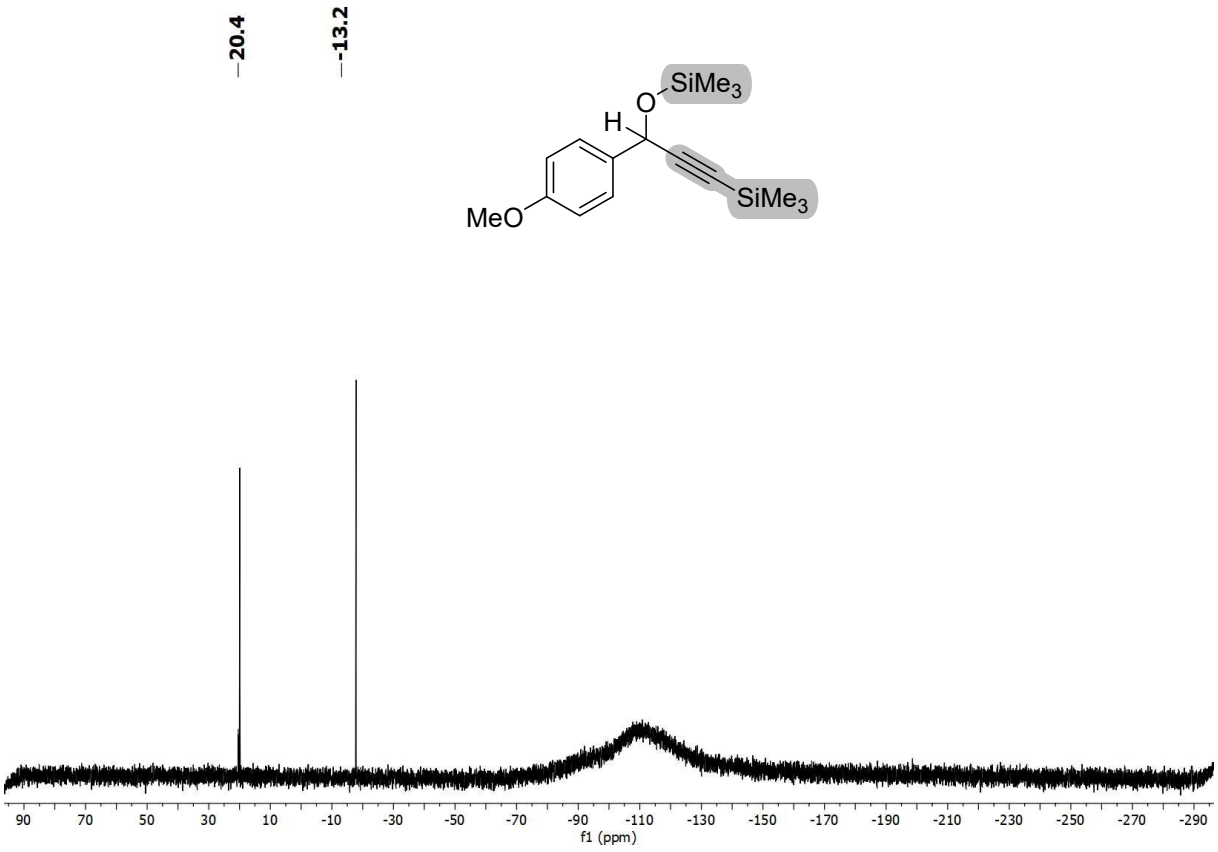



-20.4
-17.8
SiMe3
O
H
SiMe3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

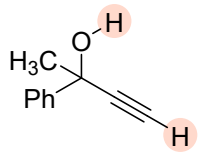
(3-(4-Methoxyphenyl)-3-((trimethylsilyl)oxy)prop-1-yn-1-yl)trimethylsilane (7b)

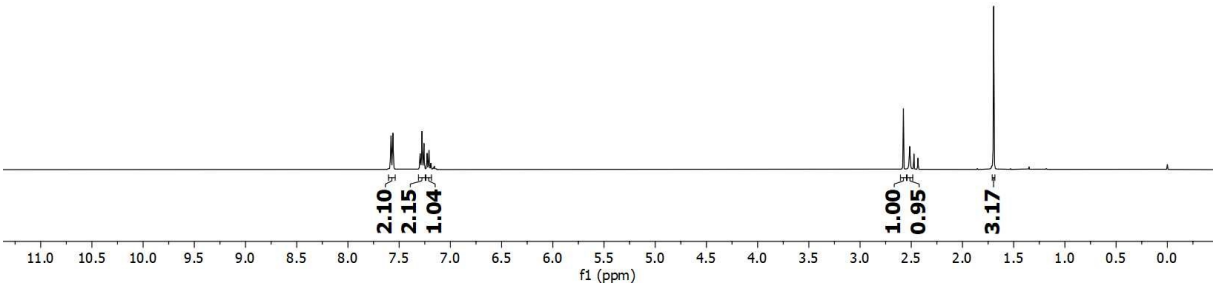


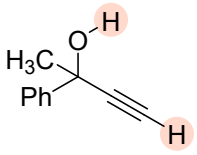


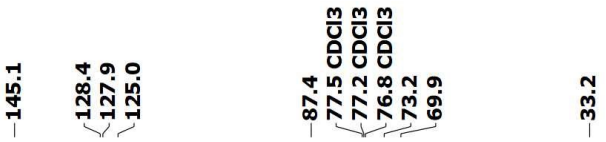

-20.4
-13.2
SiMe3
O
H
SiMe3
MeO
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

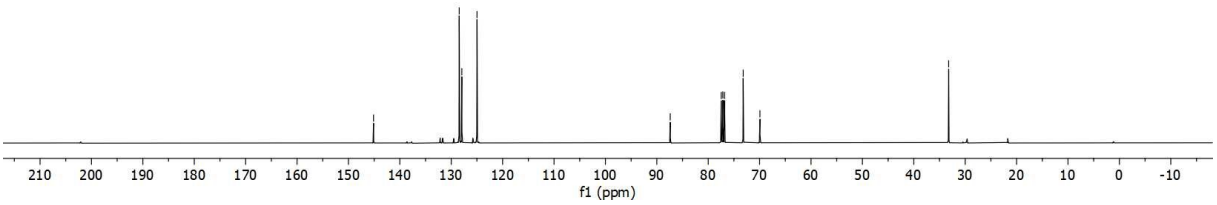
2-Phenylbut-3-yn-2-ol (8a)



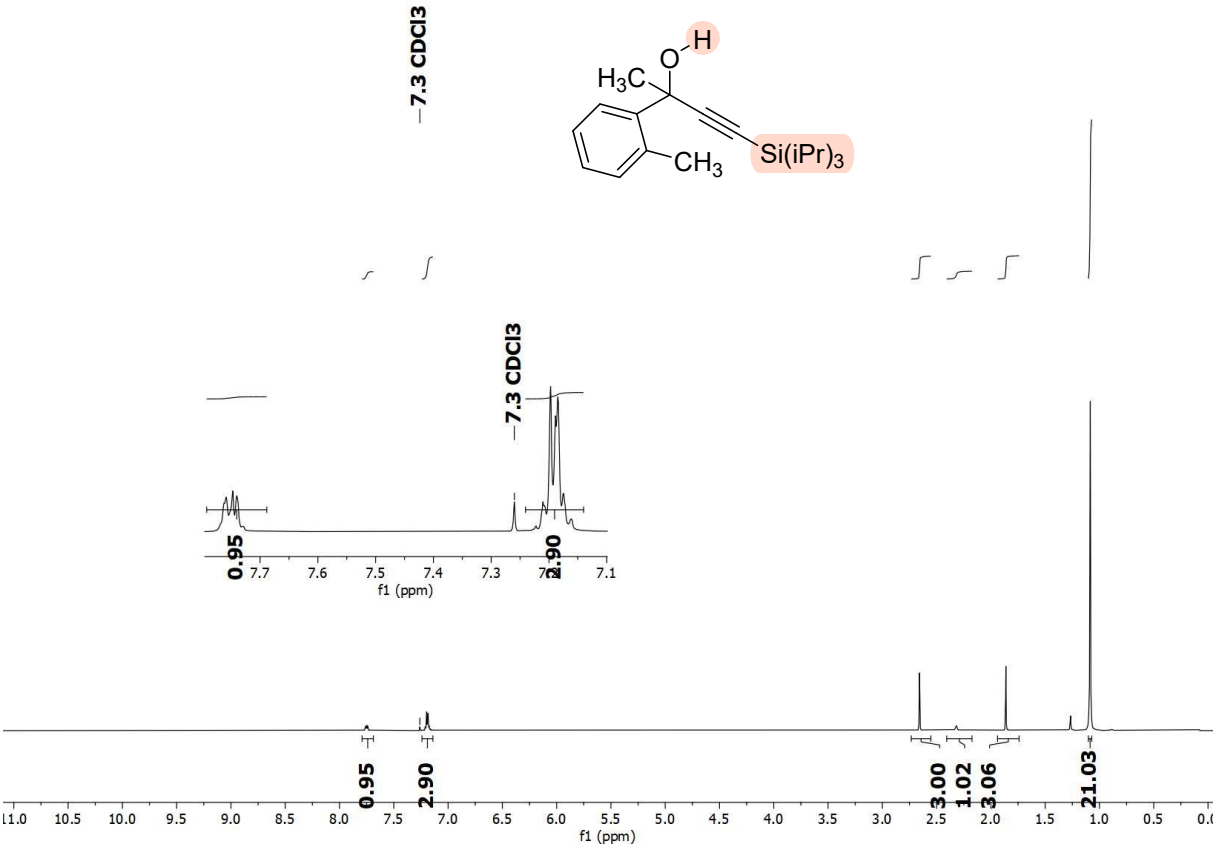


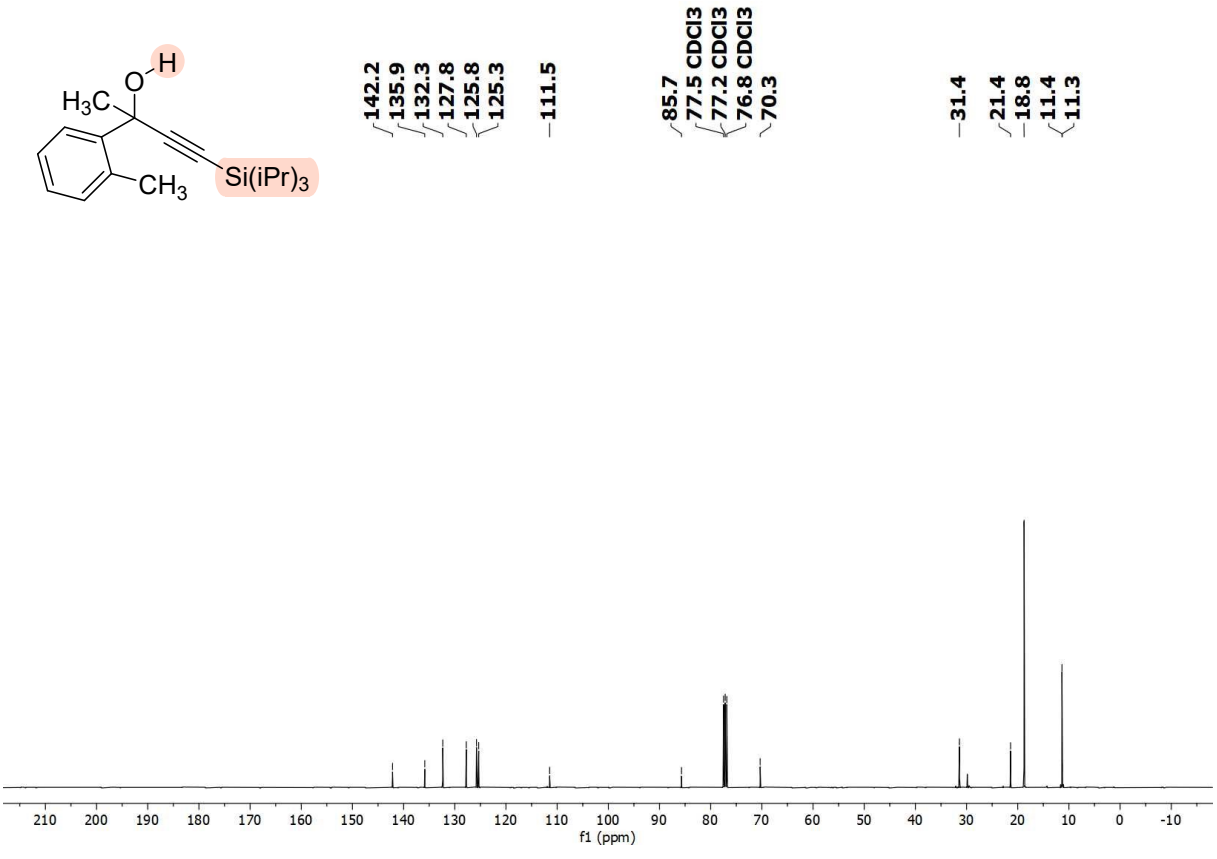


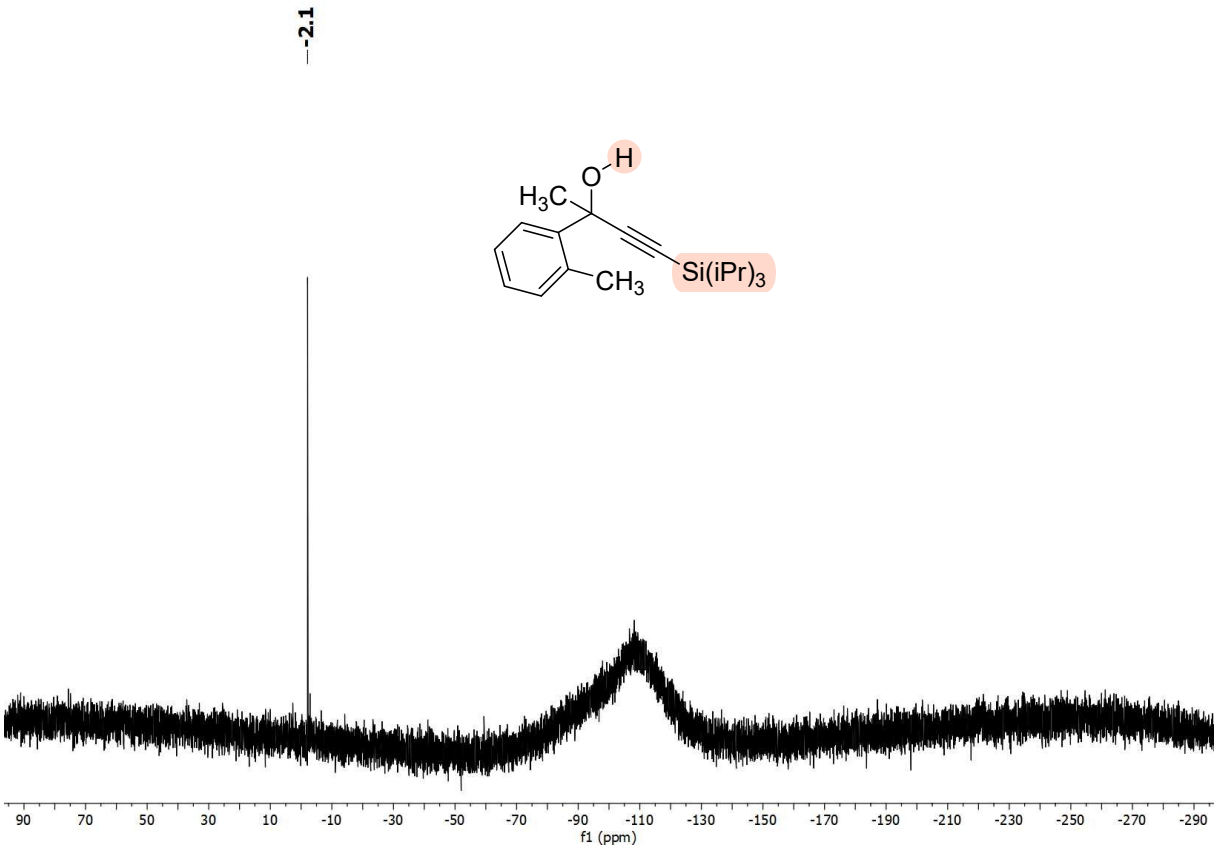




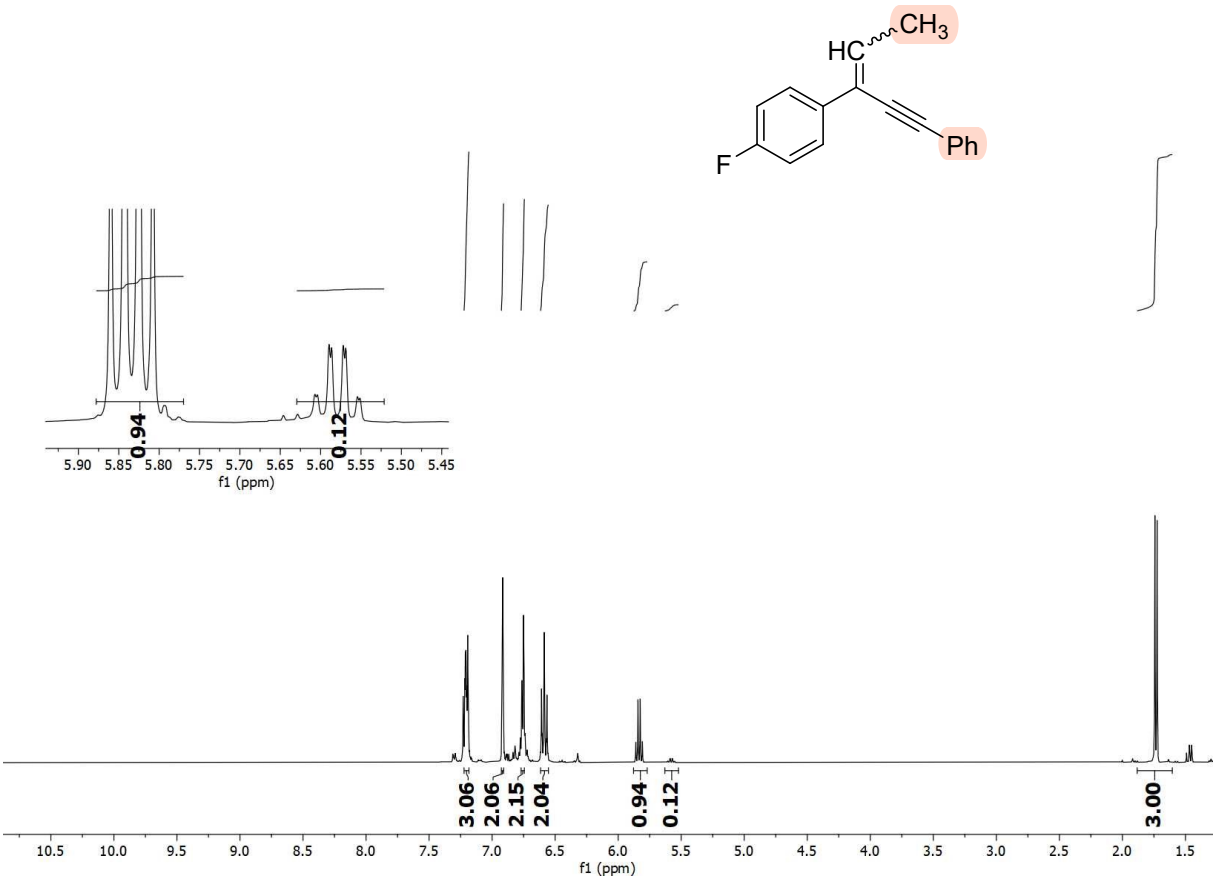
2-(o-Tolyl)-4-(triisopropylsilyl)but-3-yn-2-ol (8b)

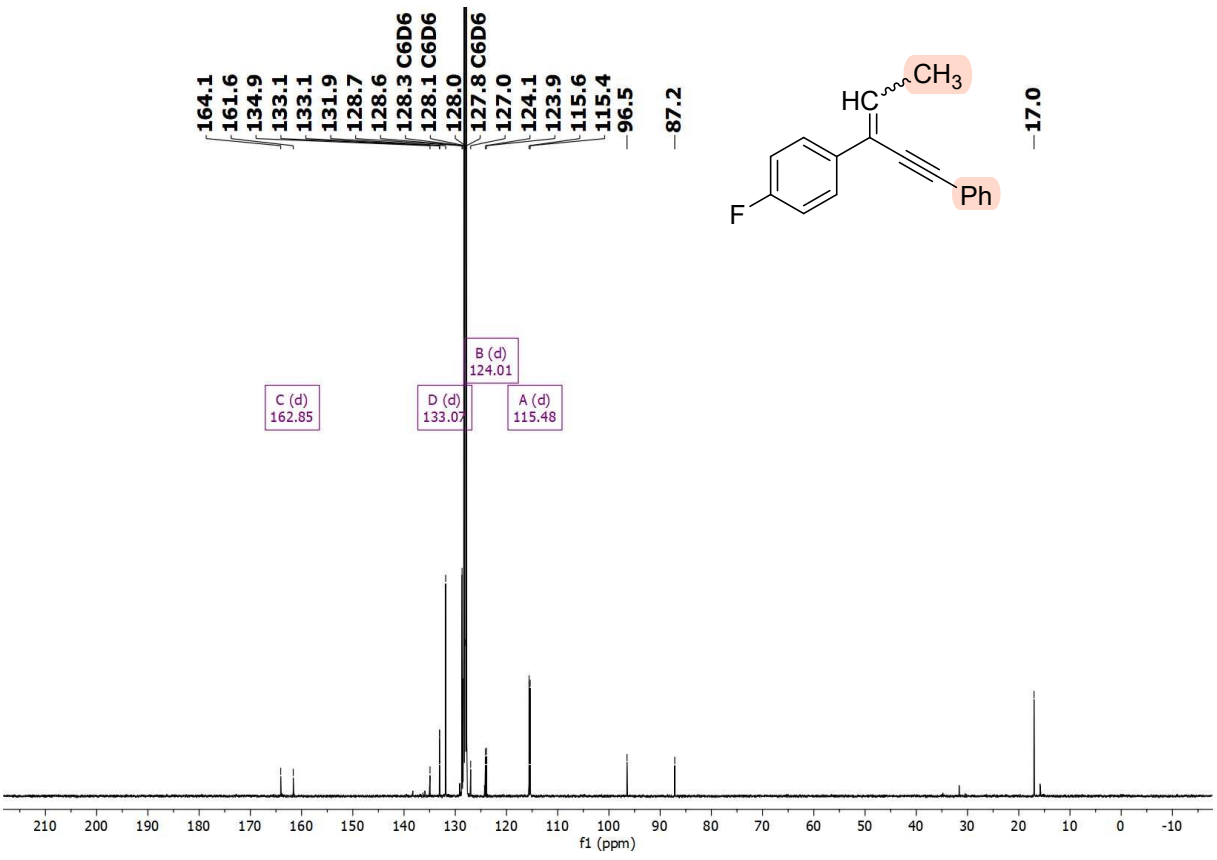


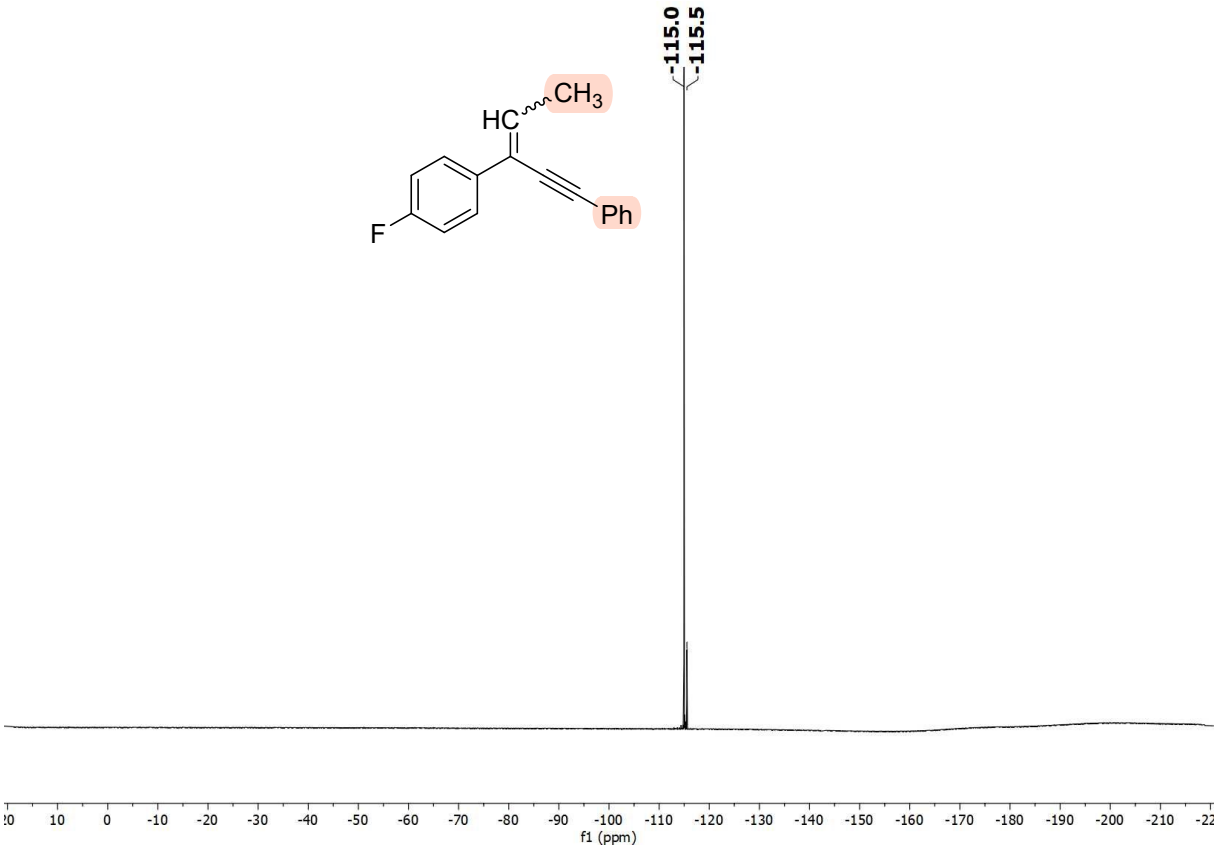



-2.1
H
O
H3C
Si(iPr)3
CH3
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
f1 (ppm)

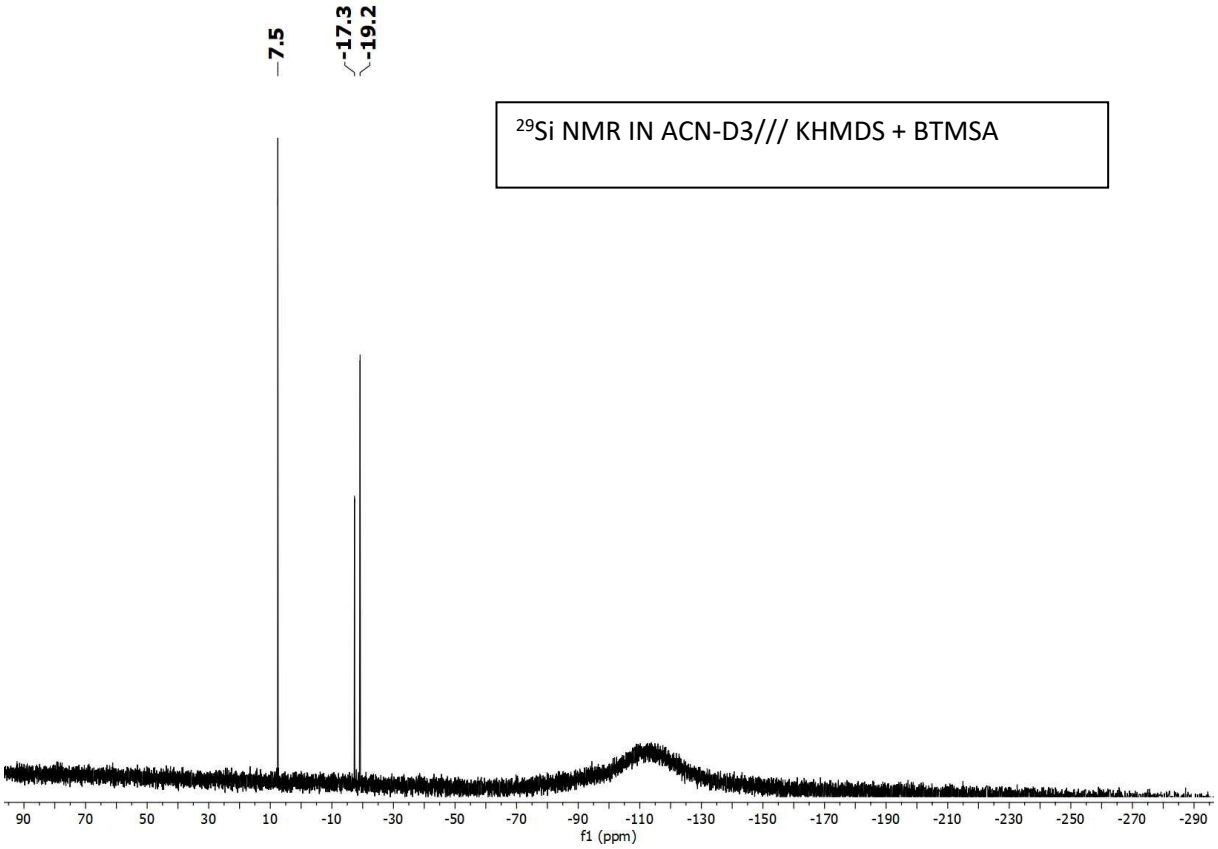
1-Fluoro-4-(1-phenylpent-3-en-1-yn-3-yl)benzene (8c)



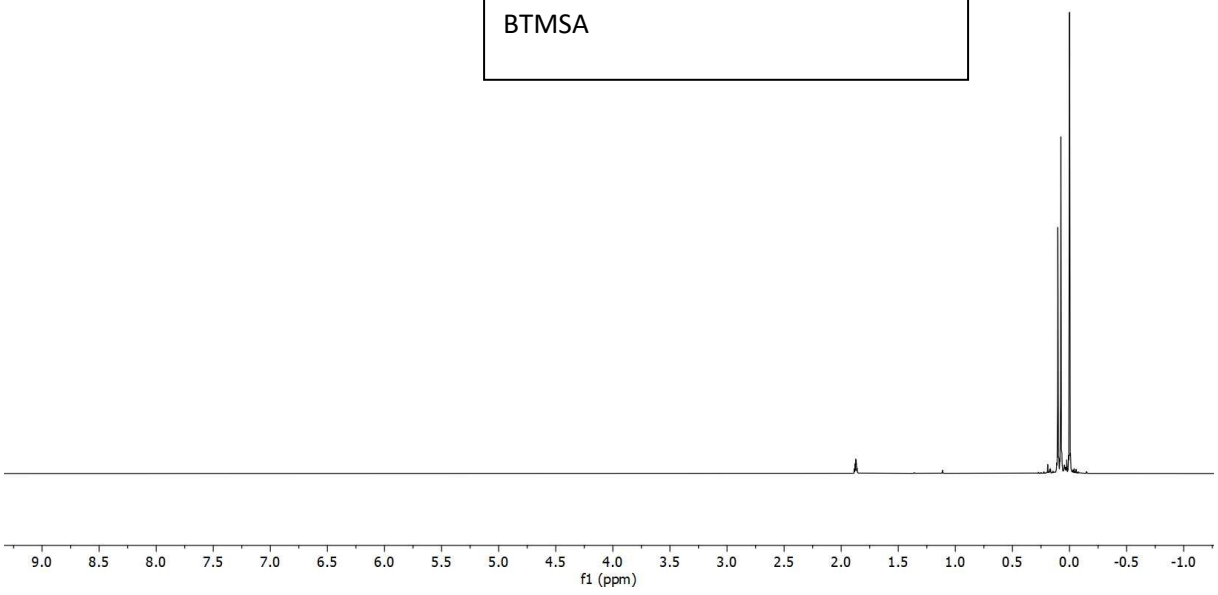



-115.0
-115.5
CH3
HC
Ph
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

MECHANISTIC STUDIES



^{29}Si NMR IN ACN-D3/// KHMDS + BTMSA



^{1}H NMR IN ACN-D3 /// KHMDS + BTMSA

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[1] T. Ishikawa, M. Okano, T. Aikawa, S. Saito, *J. Org. Chem.* **2001**, *66*, 4635–4642.

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