

# **Preparation of Tri- and Tetrasubstituted Allenes via Regioselective Lateral Metalation of Benzylic (Trimethylsilyl)alkynes Using TMPZnCl·LiCl**

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**General information:** All reactions were carried out under an argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Yields refer to isolated yields of compounds estimated to be > 95 % pure as determined by  $^1\text{H}$  NMR (25 °C) and capillary GC. Chemical shifts are reported as  $\delta$ -values in ppm relative to the solvent peak. NMR spectra were recorded in a solution of  $\text{CDCl}_3$  (residual chloroform:  $\delta = 7.27$  ppm for  $^1\text{H}$  NMR and  $\delta = 77.0$  ppm for  $^{13}\text{C}$  NMR). Column chromatography was performed using  $\text{SiO}_2$  (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck if not indicated. All reagents were obtained from commercial sources.

**Starting materials:** Commercially available starting materials were purchased from commercial sources and used without further purification. TMPH was distilled under argon prior to use.

### **General procedures for the preparation of various metal salt solutions:**

#### **ZnCl<sub>2</sub> (1M solution in THF):**

A *Schlenk*-flask was charged with ZnCl<sub>2</sub> (27.2 g, 0.20 mol) and dried for 6 h at 150 °C under high vacuum ( $5 \cdot 10^{-2}$  mbar, dry stirring). After cooling, careful addition of THF (200 mL) under an argon atmosphere and stirring overnight furnishes a clear, colorless solution which is kept over molecular sieves (4 Å).

#### **CuCN·2LiCl (1M solution in THF):**

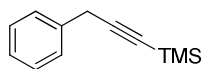
A *Schlenk*-flask was charged with LiCl (16.96 g, 0.40 mol), predried under high vacuum ( $5 \cdot 10^{-2}$  mbar; dry stirring). CuCN (17.95 g, 0.20 mol) was added and the mixture was dried for 6 h at 150 °C under high vacuum ( $5 \cdot 10^{-2}$  mbar; dry stirring). After cooling, careful addition of THF (200 mL) under an argon atmosphere and stirring overnight furnishes a slightly yellowish to greenish solution. A dark green to black color indicates the presence of Cu(II), this solution should not be used.

#### **TMPZnCl·LiCl**

A dry and argon-flushed *Schlenk*-flask was charged with TMPH (10.2 mL, 60 mmol) and THF (60 mL). The solution was cooled to – 40 °C and *n*BuLi-solution (2.3 M in hexanes; 26 mL, 60 mmol) was added dropwise at this temperature. The solution was slowly warmed to – 10 °C over 1 h before the addition of a ZnCl<sub>2</sub>-solution (1.0 M in THF; 66 mL, 66 mmol). The solution was maintained at this temperature for 30 min and warmed to 25 °C for another 30 min. All the volatiles were removed under high vacuum before the addition of THF (30-35 mL) and stirring overnight furnishes a slightly yellowish solution. **The solution was titrated prior to use at 25 °C in THF with benzoic acid using 4-(phenylazo)diphenylamine as indicator.**

## Synthesis of starting materials:

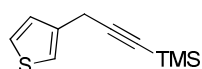
### Trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**)



A dry and argon flushed *Schlenk*-flask was charged with TMS-acetylene (4.26 mL, 30 mmol) and THF (60 mL). The solution was cooled to 0 °C and *i*PrMgCl·LiCl (25.4 mL, 32 mmol; 1.26 M in THF) was added. The resulting solution was stirred at 25 °C for 2 h and added to a solution of benzyl chloride (2.23 mL, 20 mmol) and Co(acac)<sub>3</sub> (200 mg, 0.56 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 5 h and quenched with aq. sat. NH<sub>4</sub>Cl (20 mL). The aqueous layer was extracted with EtOAc (3 x 40 mL). The combined organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (*i*-hexane) to yield compound **2a** (3.23 g, 86 %) as a brown liquid.

The analytical data matches the reported one in the literature.<sup>1</sup>

### Trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**2b**)



A dry and argon-flushed *Schlenk*-flask was charged with TMS-acetylene (4.26 mL, 30 mmol) and THF (60 mL). The solution was cooled to 0 °C and *i*PrMgCl·LiCl (25.4 mL, 32 mmol; 1.26 M in THF) was added. The resulting solution was stirred at 25 °C for 2 h and added to a solution of 3-(chloromethyl)thiophene<sup>2</sup> (2.13 mL, 20 mmol) and Co(acac)<sub>3</sub> (200 mg, 0.56 mmol) in THF (20 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 5 h and quenched with aq. sat. NH<sub>4</sub>Cl (20 mL). The aqueous layer was extracted with EtOAc (3 x 40

<sup>1</sup> Kuno, A.; Saino, N.; Kamachi, T.; Okamoto, S. *Tetrahedron Lett.* **2006**, 47, 2591

<sup>2</sup> Shang, R.; Huang, Z.; Xiao, X.; Lu, X.; Fu, Y.; Liu, L. *Adv. Synth. Catal.* **2012**, 354, 2465 – 2472

mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the solvents *in vacuo* and purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **2b** (3.4 g, 88 %) as a brown liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ/ppm = 7.27 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.15 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.00 (dd, *J* = 4.8, 1.5 Hz, 1H), 3.62 (s, 1H), 3.61 (s, 1H), 0.19 (s, 9H).

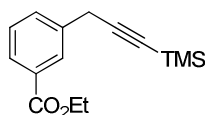
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ/ppm = 136.8, 127.7, 126.0, 121.4, 104.2, 86.5, 21.5, 0.2 (3C).

**IR** (Diamond-ATR, neat)  $\tilde{\nu}$ /cm<sup>-1</sup> = 2950, 2174, 1248, 1024, 832.

**MS** (EI, 70 eV) *m/z* (%) = 42 (100), 73 (80), 179 (21), 194 (7).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>10</sub>H<sub>14</sub>SSi: calc. 194.0585; found 194.0563.

### Ethyl 3-(3-(trimethylsilyl)prop-2-yn-1-yl)benzoate (**2c**)



A dry and argon-flushed 2-necked round-bottom flask equipped with a condenser was charged with ethyl 3-(chloromethyl)benzoate<sup>3</sup> (990 mg, 5.0 mmol), TMS-acetylene (3.55 mL, 25 mmol), cesium carbonate (1.95 g, 5.5 mmol), Pd(OAc)<sub>2</sub> (30 mg, 0.125 mmol), X-Phos (150 mg, 0.30 mmol) and THF (10 mL). The resulting mixture was refluxed for 5 h and quenched with aq. sat. NH<sub>4</sub>Cl (20 mL). The aqueous layer was extracted with EtOAc (3 x 40 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the solvents *in vacuo* and purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane / EtOAc = 50:1) afforded the desired product **2c** (825 mg, 63 %) as a brown liquid.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ/ppm = 8.03 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.42 - 7.38 (dd, 1H), 4.38 (q, *J* = 7.5 Hz, 2H), 3.70 (s, 2H), 1.40 (t, *J* = 7.5 Hz, 3H), 0.20 (s, 9H).

<sup>3</sup> Duez, S.; Bernhardt, S.; Heppekausen, J.; Fleming, F. F.; Knochel, P. *Org. Lett.* **2011**, *13*, 1690

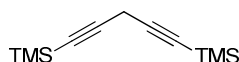
$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 166.6, 136.8, 132.4, 130.9, 129.1, 128.6, 128.0, 103.7, 87.8, 61.1, 26.1, 14.5, 0.2 (3C).

IR (Diamond-ATR, neat)  $\tilde{\nu}/\text{cm}^{-1}$  = 2957, 2177, 1717, 1276, 1248, 837.

MS (EI, 70 eV)  $m/z$  (%) = 201 (100), 215 (12), 245 (35), 260 (13).

HRMS (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Si}$ : calc. 260.1233; found 260.1216.

### 1,5-bis(trimethylsilyl)penta-1,4-diyne (**6**)



A dry and argon-flushed 2-necked round-bottom flask equipped with a condenser was charged with THF (20 mL) and  $\text{CH}_3\text{MgCl}$  (6.04 mL, 16.5 mmol; 2.73 M in THF). TMS-acetylene (2.83 mL, 20 mmol) was added dropwise over a period of 15 min, just fast enough to keep the solution at reflux. The catalyst  $\text{CuCl}$  (50 mg, 0.51 mmol) was added and the mixture was refluxed for 1 h. A solution of propargyl chloride<sup>4</sup> (1.06 g, 1.03 mL, 14.25 mmol) in THF (2.5 mL) was added to the refluxing solution and the mixture was heated for 1 h. The reaction mixture was poured into 25 mL ice water and acidified with 1.25 mL of concentrated  $\text{H}_2\text{SO}_4$ , extracted with  $\text{Et}_2\text{O}$  (3 x 15 mL), and the organic phase was neutralized with sat.  $\text{NaHCO}_3$  solution, washed with water, and dried over  $\text{Na}_2\text{SO}_4$ . Vacuum fractional distillation under argon gave compound **6** (2.00 g, 67 %) as a colorless liquid.

The analytical data matches the reported one in the literature.<sup>5</sup>

<sup>4</sup> Verkruijsse, H.D., Brandsma, L. *Synth. Commun.* **1990** 20, 3375.

<sup>5</sup> Du, B.; Faron, M.F. *Tetrahedron* **1995**, 51, 4359.

### Typical Procedure for the Preparation of Allenylzinc Reagents and Subsequent Allylation (TP1):

A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with alkynes **2a-c** (1.0 mmol), followed by dry THF (2 mL). A freshly titrated solution of TMPZnCl·LiCl in THF (**1**, 1.2 equiv) was added dropwise at 25 °C. After 1 h stirring, a solution of CuCN·2LiCl (0.3 equiv; 1M in THF) was added at 25 °C and the resulting solution was stirred 15 min at this temperature before addition of allyl bromide (1.5 equiv). The solution was stirred at 25 °C for 1 h and quenched with aq. ammonia solution (NH<sub>4</sub>Cl/NH<sub>3</sub> 25 %, 4:1; 2 mL). The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the solvents *in vacuo* and purification by flash column chromatography (Al<sub>2</sub>O<sub>3</sub>) afforded the expected trisubstituted allenes.

### Typical Procedure for Direct Cross-Coupling of Allenylzinc Reagents (TP2):

A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with alkynes **2a-c** (1.0 mmol), followed by dry THF (2 mL). A freshly titrated solution of TMPZnCl·LiCl in THF (**1**, 1.2 equiv) was added dropwise at 25 °C. After 1 h stirring, electrophile (1.0 equiv) was added, followed by a mixture of Pd(OAc)<sub>2</sub> (0.02 equiv) and DPE-Phos (0.02 equiv) or Pd(OAc)<sub>2</sub> (0.02 equiv) and S-Phos (0.04 equiv) or PEPPSI-iPr (0.02 equiv). The reaction mixture was stirred at 25 or 50 °C until the GC analysis of hydrolyzed reaction aliquots (quenched with aq. sat. NH<sub>4</sub>Cl) showed complete conversion of the alkyne (> 98 %). After complete conversion the reaction mixture was quenched with aq. sat. NH<sub>4</sub>Cl (2 mL). The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the solvents *in vacuo* and purification by flash column chromatography (SiO<sub>2</sub>) afforded the expected trisubstituted allenes.

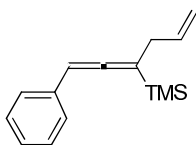
### Typical Procedure for the One-Pot Double Direct Cross-Coupling of Allenylzinc Reagents (TP3):

A dry and argon-flushed *Schlenk*-tube, equipped with a magnetic stirring bar and a rubber septum, was charged with alkyne **2a** (1.0 mmol), followed by dry THF (2 mL). A freshly titrated solution of TMPZnCl.LiCl in THF (1.2 equiv) was added dropwise at 25 °C. After 1 h stirring, electrophile (1.0 equiv) was added, followed by a mixture of Pd(OAc)<sub>2</sub> (0.02 equiv) and DPE-Phos (0.02 equiv) or Pd(OAc)<sub>2</sub> (0.02 equiv) and S-Phos (0.04 equiv). The reaction mixture was stirred at 25 or 50 °C until the GC analysis of hydrolyzed reaction aliquots (quenched with aq. sat. NH<sub>4</sub>Cl) showed complete conversion of the alkyne (> 98 %). After complete conversion, a freshly titrated solution of TMPZnCl.LiCl in THF (1.2 equiv) was added dropwise at 25 °C. After 1 h stirring, electrophile (1.0 equiv) was added, followed by a mixture of Pd(OAc)<sub>2</sub> (0.02 equiv) and DPE-Phos (0.02 equiv) or Pd(OAc)<sub>2</sub> (0.02 equiv) and S-Phos (0.04 equiv). The reaction mixture was stirred at 25 or 50 °C until the GC analysis of hydrolyzed reaction aliquots (quenched with aq. sat. NH<sub>4</sub>Cl) showed complete conversion of the tri-substituted allene (> 98 %). After complete conversion the reaction mixture was quenched with aq. sat. NH<sub>4</sub>Cl (2 mL). The aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and filtered. Evaporation of the solvents *in vacuo* and purification by flash column chromatography (SiO<sub>2</sub>) afforded the expected tetrasubstituted allenes.



## Preparation of Allenyl Allylation Products

### Trimethyl(1-phenylhexa-1,2,5-trien-3-yl)silane (**3a**)



According to **TP1**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), THF (2 mL) and freshly titrated TMPZnCl.LiCl (**1**, 1.02 mL, 1.2 equiv; 1.18 M in THF) were used. After stirring the reaction mixture for 1 h at 25 °C, a solution of CuCN.2LiCl (0.30 mL, 0.30 equiv; 1M in THF) was added at 25 °C and the reaction mixture was stirred 15 min at this temperature, followed by the addition of allyl bromide (181 mg, 0.13 mL, 1.50 equiv). The reaction mixture was stirred for 1 h at 25 °C. Purification by flash chromatography (Al<sub>2</sub>O<sub>3</sub>, *i*-hexane) afforded the desired product **3a** (176 mg, 77 %) as a colourless oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 7.34-7.25 (m, 4H), 7.20-7.14 (m, 1H), 6.00-5.87 (m, 1H), 5.95 (t, *J* = 3.0 Hz, 1H), 5.17-5.10 (m, 1H), 5.07-5.03 (m, 1H), 2.96-2.91 (m, 2H), 0.20 (s, 9H).

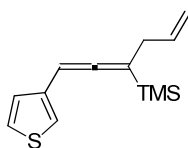
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 206.4, 137.1, 136.0, 128.7 (2C), 126.0 (3C), 115.6, 99.8, 90.2, 34.4, -1.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu$ /cm<sup>-1</sup> = 2956, 1922, 1598, 1249, 832.

**MS** (EI, 70 eV) *m/z* (%) = 43 (100), 45 (15), 61 (18), 70 (12), 73 (29), 228 (3).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>15</sub>H<sub>20</sub>Si: calc. 228.1334; found 228.1338.

### Trimethyl(1-(thiophen-3-yl)hexa-1,2,5-trien-3-yl)silane (**3b**)



According to **TP1**, trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**2b**, 194 mg, 1.00 mmol), THF (2 mL) and freshly titrated TMPZnCl.LiCl (**1**, 1.02 mL, 1.2 equiv; 1.18 M in

THF) were used. After stirring the reaction mixture for 1 h at 25 °C, a solution of CuCN.2LiCl (0.30 mL, 0.30 equiv; 1M in THF) was added at 25 °C and the reaction mixture was stirred 15 min at this temperature, followed by the addition of allyl bromide (181 mg, 0.13 mL, 1.50 equiv). The reaction mixture was stirred for 1 h at 25 °C. Purification by flash chromatography (Al<sub>2</sub>O<sub>3</sub>, *i*-hexane) afforded the desired product **3b** (166 mg, 71 %) as a colourless oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ/ppm = 7.22 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.99 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.94 (dd, *J* = 3.0, 1.2 Hz, 1H), 5.98 (t, *J* = 3.0 Hz, 1H), 5.95-5.81 (m, 1H), 5.12-4.98 (m, 2H), 2.88-2.85 (m, 2H), 0.14 (s, 9H).

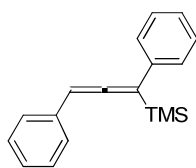
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ/ppm = 207.1, 137.1, 137.0, 126.2, 125.7, 118.6, 115.5, 99.1, 84.9, 34.5, -1.1 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2954, 1922, 1637, 1246, 832.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 165 (18), 234 (20).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>13</sub>H<sub>18</sub>SSi: calc. 234.0898, found 234.0881.

### (1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (**3c**)



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 0.96 mL, 1.2 equiv; 1.25 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 4 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **3c** (180 mg, 68 %) as a white solid.

**M.p.** (°C): 79.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.38-7.28 (m, 8H), 7.23-7.16 (m, 2H), 6.21 (s, 1H), 0.30 (s, 9H).

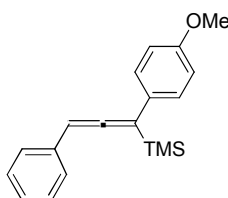
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.6, 136.8, 134.9, 128.8 (2C), 128.7 (2C), 127.0 (2C), 126.7, 126.5, 126.3 (2C), 107.8, 91.5, 0.0 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2966, 1910, 1488, 1242, 833.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 189 (9), 264 (6).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>18</sub>H<sub>20</sub>Si: calc. 264.1334, found 264.132.

**(1-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3d)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 0.96 mL, 1.2 equiv; 1.25 M in THF), 4-iodoanisole (234 mg, 1.00 mmol) and the catalytic system [PEPPSI-*i*Pr (13.6 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 5 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **3d** (223 mg, 76 %) as a yellow solid.

**M.p.** (°C): 96.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm = 7.31-7.27 (m, 6H), 7.18-7.14 (m, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 3.79 (s, 3H), 0.29 (s, 9H).

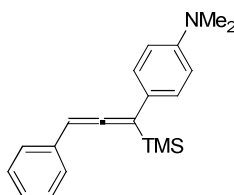
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm = 209.2, 158.6, 135.1, 129.0 (2C), 128.9 (2C), 128.7, 126.4, 126.3 (2C), 114.2 (2C), 104.0, 91.5, 55.4, 0.0 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2959, 1905, 1508, 1245, 828.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 178 (14), 221 (21), 279 (100), 294 (14).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>19</sub>H<sub>22</sub>OSi: calc. 294.1440, found 294.1429.

***N,N*-dimethyl-4-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)aniline (3e)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 4-bromo-*N,N*-dimethylaniline (200 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (9.0 mg, 0.04 mmol) / DPE-Phos (21.5 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 4 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 100:1) afforded the desired product **3e** (203 mg, 66 %) as a yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.30-7.26 (m, 6H), 7.17-7.14 (m, 1H), 6.70 (d, *J* = 8.4 Hz, 2H), 6.20 (s, 1H), 2.94 (s, 6H), 0.30 (s, 9H).

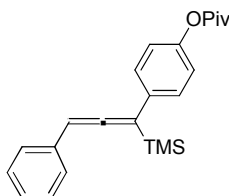
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.0, 149.6, 135.6, 128.77 (2C), 128.75 (2C), 126.24 (2C), 126.20 (2C), 123.8, 112.9, 104.0, 91.6, 40.7 (2C), 0.1 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2952, 1904, 1606, 1515, 1247, 833.

**MS** (EI, 70 eV) *m/z* (%) = 73 (54), 189 (12), 218 (24), 234 (100), 307 (26).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>20</sub>H<sub>25</sub>NSi: calc. 307.1756, found 307.1737.

**4-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)phenyl pivalate (3f)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 4-bromophenylpivalate<sup>6</sup> (257 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 6 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 100:2) afforded the desired product **3f** (208 mg, 57 %) as yellowish oil.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.34 (d, *J* = 9.0 Hz, 2H), 7.31-7.27 (m, 4H), 7.19-7.16 (m, 1H), 6.99 (d, *J* = 9.0 Hz, 2H), 6.21 (s, 1H), 1.35 (s, 9H), 0.29 (s, 9H).

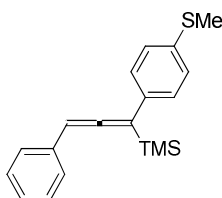
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.7, 177.2, 149.9, 134.8, 134.1, 128.9 (2C), 128.8 (2C), 126.6, 126.3 (2C), 121.7 (2C), 104.1, 91.6, 39.2, 27.3 (3C), -0.1 (3C).

IR (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2961, 1911, 1751, 1108, 835.

MS (EI, 70 eV) *m/z* (%) = 57 (53), 73 (100), 190 (44), 279 (77), 364 (5).

HRMS (EI): *m/z* (M<sup>+</sup>) for C<sub>23</sub>H<sub>28</sub>O<sub>2</sub>Si: calc. 364.1859, found 364.1854.

### Trimethyl(1-(4-(methylthio)phenyl)-3-phenylpropa-1,2-dienyl)silane (**3g**)



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.11 mL, 1.2 equiv; 1.08 M in THF), 4-bromothioanisole (203 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 6 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 100:1) afforded the desired product **3g** (233 mg, 75 %) as yellowish oil.

<sup>6</sup> Lee, J.-s.; Velarde-Ortiz, R.; Guijarro, A.; Wurst, J. R.; Rieke, R. D. *J. Org. Chem.* **2000**, *65*, 5428

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ/ppm = 7.29-7.24 (m, 6H), 7.17-7.13 (m, 3H), 6.20 (s, 1H), 2.45 (s, 3H), 0.27 (s, 9H).

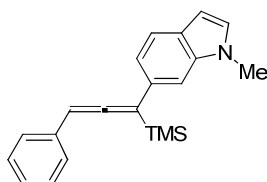
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ/ppm = 209.7, 136.7, 134.8, 133.5, 128.9 (2C), 128.4 (2C), 127.1 (2C), 126.6, 126.3 (2C), 104.2, 91.7, 16.2, 0.0 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2954, 1907, 1486, 1248, 835.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 295 (13), 310 (18).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>19</sub>H<sub>22</sub>SSi: calc. 310.1211, found 310.1206.

**1-methyl-5-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)-1*H*-indole (3h)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 5-bromo,*N*-methylindole (230 mg, 1.10 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 3 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 100:2) afforded the desired product **3h** (202 mg, 64 %) as yellow solid.

**M.p.** (°C): 77.

**<sup>1</sup>H NMR** (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ/ppm = 8.00 (d, *J* = 1.6 Hz, 1H), 7.60 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 2H), 7.22-7.17 (m, *J* = 1.6 Hz, 4H), 6.57 (d, *J* = 2.8 Hz, 1H), 6.50 (dd, *J* = 3.2, 0.8 Hz, 1H), 6.28 (s, 1H), 2.94 (s, 3H), 0.40-0.4 (s, 9H).

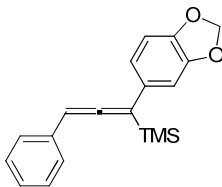
**<sup>13</sup>C NMR** (75 MHz, C<sub>6</sub>D<sub>6</sub>) δ/ppm = 209.6, 136.4, 135.9, 129.7, 129.11 (2C), 129.08, 128.2, 126.6 (2C), 126.6 (2C), 120.5, 109.8, 105.8, 101.6, 91.7, 32.0, 0.2 (3C).

**IR** (Diamond-ATR, neat) ν / cm<sup>-1</sup> = 2922, 1909, 1488, 1244, 834.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 244 (54), 317 (29).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $C_{21}H_{23}NSi$ : calc. 317.1600, found: 317.1575.

**(1-(benzo[*d*][1,3]dioxol-5-yl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3i)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.11 mL, 1.2 equiv; 1.08 M in THF), 3-iodobenzodioxole (248 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 4 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 50:1) afforded the desired product **3i** (290 mg, 94 %) as yellowish oil.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 7.28-7.24 (m, 4H), 7.18-7.13 (m, 1H), 6.85 (d,  $J$  = 1.8 Hz, 1H), 6.80 (dd,  $J$  = 7.8, 1.8 Hz, 1H), 6.74 (d,  $J$  = 7.8 Hz, 1H), 6.18 (s, 1H), 5.91 (s, 2H), 0.27 (s, 9H).

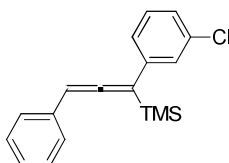
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 209.3, 148.0, 146.6, 134.9, 130.5, 128.9 (2C), 126.5, 126.3 (2C), 121.2, 108.4 (2C), 104.5, 101.1, 91.7, 0.0 (3C).

**IR** (Diamond-ATR, neat)  $\nu$ /cm<sup>-1</sup> = 2954, 2892, 1907, 1479, 1236, 1037, 833.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 276 (15), 278 (11), 308 (15).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $C_{19}H_{20}O_2Si$ : calc. 308.1233, found 308.1237.

**(1-(3-chlorophenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3j)**



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 3-chlorobromobenzene (191 mg, 0.12 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 4 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc, 100:0.5) afforded the desired product **3j** (180 mg, 60 %) as yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.32-7.28 (m, 5H), 7.24-7.18 (m, 4H), 6.24 (s, 1H), 0.30 (s, 9H).

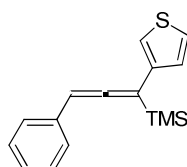
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.9, 138.9, 134.6, 134.4, 129.8, 128.9 (2C), 127.9, 126.8 (2C), 126.4 (2C), 126.0, 104.1, 91.8, -0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2955, 1914, 1588, 1249, 835.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 189 (23), 285/283 (5), 298 (5).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for **C<sub>18</sub>H<sub>19</sub>ClSi**: calc. 298.0945, found 298.0948.

### Trimethyl(3-phenyl-1-(thiophen-3-yl)propa-1,2-dien-1-yl)silane (**3k**)



According to **TP2**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.02 mL, 1.2 equiv; 1.18 M in THF), 3-bromothiophene (163 mg, 0.09 mL, 1.00 mmol) and the catalytic system [PEPPSI-*i*Pr (13.6 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **3k** (197 mg, 73 %) as yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.30-7.27 (m, 4H), 7.26-7.25 (m, 1H) 7.19-7.16 (m, 1H), 7.14-7.13 (m, 1H), 7.12 (dd,  $J$  = 5.4, 1.8 Hz, 1H), 6.19 (s, 1H), 0.31 (s, 9H).



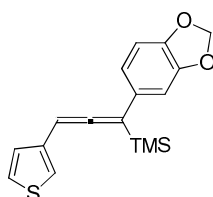
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.9, 136.4, 134.9, 128.8 (2C), 128.0, 126.5, 126.4 (2C), 125.3, 120.8, 99.5, 91.4, -0.2 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2960, 1907, 1245, 830.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 197 (5), 270 (7).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>16</sub>H<sub>18</sub>SSi: calc. 270.0898, found: 270.0887.

**(1-(benzo[d][1,3]dioxol-5-yl)-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (3l)**



According to **TP2**, trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**2b**, 194 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.11 mL, 1.2 equiv; 1.08 M in THF), 3-bromobenzodioxole (0.12 mL, 207.2 mg, 1 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 12 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:1) afforded the desired product **3l** (203 mg, 65 %) as an orange oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm = 7.27 (dd, *J* = 0.39, 7.80 Hz, 1H), 7.05 (s, 1 H), 7.05 - 7.04 (m, 1 H), 6.87 (d, *J* = 1.75 Hz, 1 H), 6.83 - 6.81 (ddd, *J* = 0.39, 1.75, 7.99 Hz, 1 H), 6.78 - 6.76 (dd, *J* = 0.39, 7.99 Hz, 1H), 6.29 (s, 1H), 5.94 (d, *J* = 0.78 Hz, 2H), 0.29 (s, 9H).

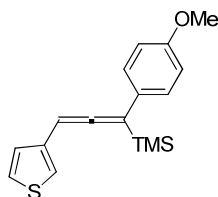
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.8, 147.9, 146.4, 135.7, 130.5, 125.9 (2C), 121.0, 119.4, 108.2 (2C), 103.7, 101.0, 86.3, -0.21 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2957, 2893, 1910, 1482, 1237, 1038, 836.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 283 (12), 285 (10), 313 (12), 314 (31).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>SSi: calc. 314.0797, found 314.0792.

**(1-(4-methoxyphenyl)-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (3m)**



According to **TP2**, trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**2b**, 190 mg, 0.98 mmol), TMPZnCl·LiCl (**1**, 1.02 mL, 1.2 equiv; 1.18 M in THF), 4-iodoanisole (229 mg, 0.98 mmol) and the catalytic system and the catalytic system [Pd(OAc)<sub>2</sub> (4.4 mg, 0.02 mmol) / DPE-Phos (10.6 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:1) afforded the desired product **3m** (233 mg, 78 %) as an orange solid.

**M.p.** (°C): 45.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 (ddd, *J* = 4.8, 3.0, 0.6 Hz, 1H), 7.05 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.04 (ddd, *J* = 3.0, 1.2, 0.6 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 2H), 6.28 (s, 1H), 3.80 (s, 3H), 0.29 (s, 9H).

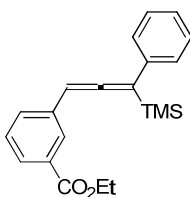
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.6, 158.4, 135.9, 128.9 (2C), 128.7, 126.0, 125.8, 119.2, 114.0 (2C), 103.2, 86.1, 55.3, -0.2 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2953, 1909, 1505, 1244, 830.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 227 (14), 285 (50), 300 (18).

**HRMS** (EI): *m/z* (*M*<sup>+</sup>) for C<sub>17</sub>H<sub>20</sub>OSSi: calc. 300.1004, found 300.1000.

**Ethyl 3-(3-phenyl-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (3n)**



According to **TP2**, ethyl 3-(3-(trimethylsilyl)prop-2-yn-1-yl)benzoate (**2c**, 215 mg, 0.83 mmol), TMPZnCl·LiCl (**1**, 1.11 mL, 1.2 equiv; 1.08 M in THF), iodobenzene (169 mg, 0.09 mL, 0.83 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (3.7 mg, 0.02 mmol) / S-Phos (13.6 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:2) afforded the desired product **3n** (145 mg, 52 %) as yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.94 (t, *J* = 1.8 Hz, 1H), 7.84 (dt, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.47 (dt, *J* = 7.8, 1.8 Hz, 1H), 7.37-7.30 (m, 5H), 7.22 (dt, *J* = 7.2, 1.8 Hz, 1H), 6.24 (s, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.30 (s, 9H).

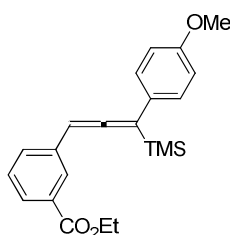
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.4, 166.7, 136.4, 135.5, 131.2, 130.3, 128.8 (3C), 128.0 (2C), 127.6, 127.4, 126.7, 105.2, 90.8, 61.1, 14.5, -0.1 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2956, 1911, 1716, 1276, 1248, 834.

**MS** (EI, 70 eV) *m/z* (%) = 73 (58), 190 (100), 218 (75), 307 (96), 336 (34).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>21</sub>H<sub>24</sub>O<sub>2</sub>Si: calc. 336.1546, found 336.1528.

### Ethyl 3-(3-(4-methoxyphenyl)-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (**3o**)



According to **TP2**, ethyl 3-(3-(trimethylsilyl)prop-2-yn-1-yl)benzoate (**2c**, 200 mg, 0.77 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 4-iodoanisole (162 mg, 0.77 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (3.4 mg, 0.02 mmol) / S-Phos (12.6 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:2) afforded the desired product **3o** (165 mg, 59 %) as yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.93 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.23 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 3H), 1.39 (t, *J* = 7.2 Hz, 3H), 0.03 (s, 9H).

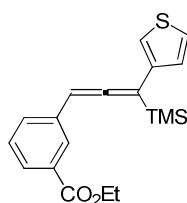
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.0, 166.7, 158.7, 135.2, 131.1, 130.3, 129.1 (2C), 128.8, 128.3, 127.5, 127.3, 114.3 (2C), 104.4, 90.9, 61.1, 55.4, 14.5, 0.0 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2955, 1909, 1715, 1506, 1277, 1244, 834.

**MS** (EI, 70 eV) *m/z* (%) = 73 (30), 220 (61), 248 (41), 293 (9), 337 (100), 366 (19).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>22</sub>H<sub>26</sub>O<sub>3</sub>Si: calc. 366.1651, found 336.1639.

**Ethyl 3-(3-(thiophen-3-yl)-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (3p)**



According to **TP2**, ethyl 3-(3-(trimethylsilyl)prop-2-yn-1-yl)benzoate (**2c**, 260 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.18 mL, 1.2 equiv; 1.02 M in THF), 3-bromothiophene (163 mg, 0.09 mL, 1.00 mmol) and the catalytic system [PEPPSI-*i*Pr (13.6 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:2) afforded the desired product **3p** (252 mg, 74 %) as yellowish oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm = 7.91 (t, *J* = 1.6 Hz, 1H), 7.84 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.45 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.26 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.15-7.14 (m, 1H), 7.10 (dd, *J* = 4.8, 1.6 Hz, 1H), 6.22 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 0.30 (s, 9H).

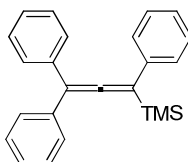
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ/ppm = 209.7, 166.7, 136.0, 135.4, 131.1, 130.4, 128.8, 127.9, 127.6, 127.5, 125.5, 121.1, 99.9, 90.7, 61.1, 14.5, -0.3 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2957, 1907, 1716, 1275, 1248, 832.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (36), 196 (67), 224 (56), 313 (100), 342 (34).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $C_{19}H_{22}O_2SSi$ : calc. 342.1110, found 342.1109.

**Trimethyl(1,3,3-triphenylpropa-1,2-dienyl)silane (4a)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 184 mg, 0.98 mmol), TMPZnCl·LiCl (**1**, 1.05 mL, 1.18 mmol, 1.2 equiv; 1.12 M in THF), iodobenzene (200 mg, 0.11 mL, 0.98 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.4 mg, 0.02 mmol) / S-Phos (16.1 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 4 h at 25 °C. Then, TMPZnCl·LiCl (**1**, 1.05 mL, 1.18 mmol, 1.2 equiv; 1.12 M in THF), iodobenzene (200 mg, 0.11 mL, 0.98 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.4 mg, 0.02 mmol) / S-Phos (16.1 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **4a** (216 mg, 65 %) as a white solid.

**M.p.** (°C): 79.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 7.42-7.30 (m, 12H), 7.27-7.26 (m, 1H), 7.25-7.19 (m, 2H), 0.31 (s, 9H).

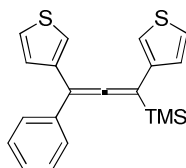
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 209.6, 136.9, 136.8, 128.8 (2C), 128.6 (4C), 128.2 (4C), 128.0 (2C), 126.9, (2C), 126.8 (2C), 106.7, 103.8, 0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu$ /cm<sup>-1</sup> = 2956, 1898, 1489, 1246, 835.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 165 (12), 267 (12), 340 (9).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $C_{24}H_{24}Si$ : calc. 340.1647, found 340.1638.

**Trimethyl(3-phenyl-1,3-di(thiophen-3-yl)propa-1,2-dien-1-yl)silane (4b)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-bromothiophene (164 mg, 0.09 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Then, TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-bromothiophene (164 mg, 0.09 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **4b** (180 mg, 51 %) as a yellow solid.

**M.p.** (°C): 72.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>) δ/ppm = 7.48-7.12 (m, 11H), 0.34 (s, 9H).

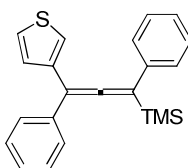
**<sup>13</sup>C NMR** (75 MHz, CDCl<sub>3</sub>) δ/ ppm = 210.1, 137.2, 136.8, 136.4, 128.5 (2C), 127.9, 127.8 (2C), 127.7, 127.0, 125.4, 125.3, 121.4, 120.9, 102.3, 98.5, -0.3 (3C).

**IR (Diamond-ATR, neat)** ν/cm<sup>-1</sup> = 2951, 1898, 1490, 1247, 829.

**MS (EI, 70 eV)** *m/z* (%) = 73 (100), 279 (11), 352 (14).

**HRMS (EI):** *m/z* (M<sup>+</sup>) for C<sub>20</sub>H<sub>20</sub>S<sub>2</sub>Si: calc. 352.0776, found: 352.0767.

**(1,3-diphenyl-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (4c)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 4 h at 25 °C. Then, TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-bromothiophene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **4c** (219 mg, 63 %) as a yellow solid.

**M.p.** (°C): 83.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.47-7.46 (m, 2H), 7.43-7.41 (m, 2H), 7.38-7.32 (m, 5H), 7.29-7.27 (m, 1H), 7.24-7.22 (m, 1H), 7.15-7.12 (m, 2H), 0.33 (s, 9H).

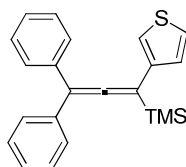
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.8, 137.3, 136.9, 136.7, 128.8 (2C), 128.6 (2C), 128.0 (2C), 127.9 (2C), 127.8, 127.1, 126.8, 125.6, 121.5, 103.6, 102.4, -0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2952, 1900, 1489, 1247.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 273 (13), 346 (18).

**HRMS** (EI):  $m/z$  (M<sup>+</sup>) for C<sub>22</sub>H<sub>22</sub>SSi: calc. 346.1211, found 346.1205.

**(3,3-diphenyl-1-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (4d)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 145 mg, 0.77 mmol), TMPZnCl·LiCl (**1**, 0.82 mL, 0.92 mmol, 1.2 equiv; 1.12 M in THF), 3-bromothiophene (126 mg, 0.07 mL, 0.77 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (3.5 mg, 0.02 mmol) / S-Phos (12.6 mg, 0.03 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Then, TMPZnCl·LiCl (**1**, 0.82 mL, 0.92 mmol, 1.2 equiv; 1.12 M in THF), iodobenzene (157 mg,

0.08 mL, 0.77 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (3.5 mg, 0.02 mmol) / S-Phos (12.6 mg, 0.03 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **4d** (125 mg, 47 %) as a yellow solid.

**M.p.** (°C): 74.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.38-7.33 (m, 8H), 7.28-7.25 (m, 3H), 7.22-7.20 (m, 1H), 7.18-7.17 (m, 1H), 0.33 (s, 9H).

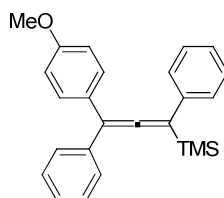
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 210.0, 136.9, 136.6, 128.6 (4C), 128.2 (4C), 128.0 (2C), 127.0 (2C), 125.4, 120.9, 106.5, 98.6, 0.1 (3C).

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2950, 1897, 1490, 1248, 829.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 165 (9), 273 (9), 346 (6).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>22</sub>H<sub>22</sub>SSi: calc. 346.1211, found 346.1205.

**(3-(4-methoxyphenyl)-1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4e)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 4 h at 25 °C. Then, TMPZnCl·LiCl (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 4-iodoanisole (234 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / S-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane) afforded the desired product **4e** (251 mg, 68 %) as yellowish oil.



**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 7.41-7.39 (m, 2H), 7.38-7.36 (m, 2H), 7.34-7.28 (m, 6H), 7.26-7.23 (m, 1H), 7.22-7.19 (m, 1H), 6.88 (d,  $J$  = 9.0 Hz, 2H), 3.82 (s, 3H), 0.30 (s, 9H).

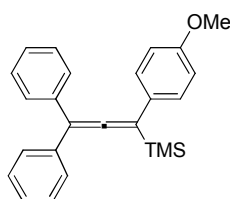
**$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 209.7, 158.8, 137.2, 137.0, 129.3 (2C), 129.1, 128.7 (2C), 128.6 (2C), 128.1 (2C), 128.0 (2C), 126.9, 126.7, 114.1 (2C), 106.3, 103.6, 55.4, 0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2952, 1901, 1506, 1244, 832.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (40), 252 (19), 297 (24), 355 (100), 370 (7).

**HRMS** (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{25}\text{H}_{26}\text{OSi}$ : calc. 370.1753, found 370.1744.

**(1-(4-methoxyphenyl)-3,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4f)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 162 mg, 0.86 mmol),  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 0.92 mL, 1.03 mmol, 1.2 equiv; 1.12 M in THF), 4-iodoanisole (201 mg, 0.86 mmol) and the catalytic system  $[\text{Pd}(\text{OAc})_2$  (3.9 mg, 0.02 mmol) / S-Phos (14.1 mg, 0.03 mmol)] were used. The reaction mixture was stirred for 5 h at 25 °C. Then,  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 0.92 mL, 1.03 mmol, 1.2 equiv; 1.12 M in THF), iodobenzene (175 mg, 0.09 mL, 1.86 mmol) and the catalytic system  $[\text{Pd}(\text{OAc})_2$  (3.9 mg, 0.02 mmol) / S-Phos (14.1 mg, 0.03 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography ( $\text{SiO}_2$ , *i*-hexane/EtOAc = 100:1) afforded the desired product **4f** (213 mg, 67 %) as a yellow solid.

**M.p.** (°C): 104.

**<sup>1</sup>H NMR** (200 MHz, CDCl<sub>3</sub>) δ/ppm = 7.40-7.24 (m, 12H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 0.30 (s, 9H).

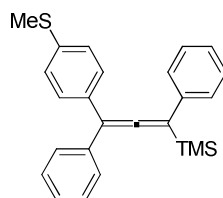
**<sup>13</sup>C NMR** (150 MHz, CDCl<sub>3</sub>) δ/ppm = 209.3, 158.7, 137.1 (2C), 129.1 (2C), 128.7, 128.6 (4C), 128.2 (4C), 126.9 (2C), 114.3 (2C), 106.8, 103.0, 55.4, 0.1 (3C)

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 2960, 1895, 1507, 1244, 833.

**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 165 (14), 252 (23), 297 (32), 355 (91), 370 (12).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>25</sub>H<sub>26</sub>OSi: calc. 370.1753, found 370.1740.

**Trimethyl(3-(4-(methylthio)phenyl)-1,3-diphenylpropa-1,2-dien-1-yl)silane (4g)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol), TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 50 °C. Then, TMPZnCl·LiCl (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 4-bromothioanisole (203 mg, 1.00 mmol) and the catalytic system [Pd(OAc)<sub>2</sub> (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 50 °C. Purification by flash chromatography (SiO<sub>2</sub>, *i*-hexane/EtOAc = 100:1) afforded the desired product **4g** (247 mg, 64 %) as yellowish oil.

**<sup>1</sup>H NMR** (600 MHz, CDCl<sub>3</sub>) δ/ppm = 7.41-7.27 (m, 11H), 7.25-7.21 (m, 3H), 2.50 (s, 3H), 0.31 (s, 9H).

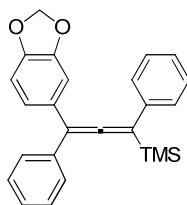
**$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 209.6, 136.9, 136.8, 136.7, 133.8, 128.8 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 128.0 (2C), 127.0, 126.9 (2C), 126.8, 106.3, 103.9, 16.1, 0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2953, 1899, 1487, 1247, 832, 693.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 265 (14), 313 (14), 371 (16), 386 (13).

**HRMS** (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{25}\text{H}_{26}\text{SSi}$ : calc. 386.1524, found 386.1508.

**(3-(benzo[d][1,3]dioxol-5-yl)-1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4h)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol),  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 50 °C. Then,  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-iodobenzodioxole (248 mg, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 3 h at 50 °C. Purification by flash chromatography ( $\text{SiO}_2$ , *i*-hexane/EtOAc = 100:1) afforded the desired product **4h** (268 mg, 70 %) as yellowish oil.

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 7.43-7.39 (m, 4H), 7.37-7.32 (m, 4H), 7.28-7.22 (m, 2H), 6.90 (d,  $J$  = 1.8 Hz, 1H), 6.85 (dd,  $J$  = 8.4, 1.8 Hz, 1H), 6.81 (d,  $J$  = 8.4 Hz, 1H), 5.98 (A of AB system,  $J$  = 1.8 Hz, 1H), 5.97 (B of AB system,  $J$  = 1.8 Hz, 1H), 0.34 (s, 9H).

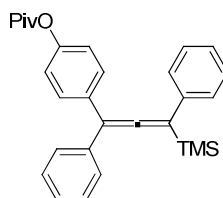
**$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 209.5, 147.9, 146.7, 137.0, 136.8, 130.8, 128.8 (2C), 128.6 (2C), 128.1 (2C), 128.0 (2C), 127.0, 126.8, 121.7, 108.6, 108.4, 106.5, 103.8, 101.2, 0.1 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 1955, 1901, 1438, 1224, 1037, 833.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 252 (31), 311 (22), 356 (18), 384 (14).

**HRMS** (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{25}\text{H}_{24}\text{O}_2\text{Si}$ : calc. 384.1546, found 384.1551.

#### 4-(1,3-diphenyl-3-(trimethylsilyl)propa-1,2-dien-1-yl)phenyl pivalate (**4i**)



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol),  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), iodobenzene (204 mg, 0.11 mL, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 2 h at 50 °C. Then,  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 4-bromophenylpivalate (257 mg, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 12 h at 50 °C. Purification by flash chromatography ( $\text{SiO}_2$ , *i*-hexane/EtOAc = 100:2) afforded the desired product **4i** (287 mg, 65 %) as yellowish oil.

**$^1\text{H}$  NMR** (600 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 7.40-7.36 (m, 6H), 7.34-7.31 (m, 4H), 7.27-7.21 (m, 2H), 7.03 (d,  $J$  = 8.4 Hz, 2H), 1.36 (s, 9H), 0.30 (s, 9H).

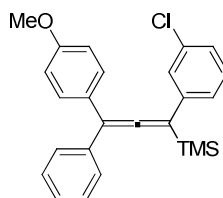
**$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 209.5, 177.3, 150.1, 136.8, 136.7, 134.3, 129.1 (2C), 128.8 (2C), 128.6 (2C), 128.1 (2C), 128.0 (2C), 127.0, 126.8, 121.6 (2C), 106.0, 104.0, 39.2, 27.3 (3C), 0.0 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2959, 1901, 1752, 1108, 834.

**MS** (EI, 70 eV)  $m/z$  (%) = 57 (73), 73 (100), 266 (44), 355 (82), 440 (4).

**HRMS** (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{29}\text{H}_{32}\text{O}_2\text{Si}$ : calc. 440.2172, found 440.2170.

**(1-(3-chlorophenyl)-3-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane**  
**(4j)**



According to **TP3**, trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**, 188 mg, 1.00 mmol),  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 3-chlorobromobenzene (191 mg, 0.12 mL, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 4 h at 50 °C. Then,  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.07 mL, 1.2 equiv; 1.12 M in THF), 4-iodoanisole (234 mg, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / DPE-Phos (10.8 mg, 0.02 mmol)] were used. The reaction mixture was stirred for 12 h at 50 °C. Purification by flash chromatography ( $\text{SiO}_2$ , *i*-hexane/EtOAc = 100:1) afforded the desired product **4j** (170 mg, 42 %) as yellowish oil.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 7.36-7.16 (m, 11H), 6.89 (d,  $J$  = 9.2 Hz, 2H), 3.81 (s, 3H), 0.29 (s, 9H).

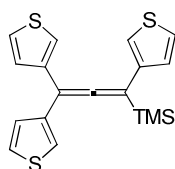
**$^{13}\text{C}$  NMR** (150 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 209.9, 158.9, 139.1, 136.8, 134.6, 129.9, 129.3 (2C), 128.65 (2C), 128.59, 128.1 (2C), 127.9, 127.1, 126.7, 126.1, 114.2 (2C), 106.7, 102.9, 55.4, 0.0 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2954, 1907, 1507, 1245, 830.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (50), 252 (13), 296 (19), 331 (14), 389 (100), 391 (35), 404 (11).

**HRMS** (EI):  $m/z$  ( $\text{M}^+$ ) for  $\text{C}_{25}\text{H}_{25}\text{ClOSi}$ : calc. 404.1363, found 404.1362.

**Trimethyl(1,3,3-tri(thiophen-3-yl)propa-1,2-dien-1-yl)silane (4k)**



According to **TP3**, trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (**2b**, 194 mg, 1.00 mmol),  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-bromothiophene (164 mg, 0.09 mL, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / *S*-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 2 h at 25 °C. Then,  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.14 mL, 1.2 equiv; 1.05 M in THF), 3-bromothiophene (164 mg, 0.09 mL, 1.00 mmol) and the catalytic system [ $\text{Pd}(\text{OAc})_2$  (4.5 mg, 0.02 mmol) / *S*-Phos (16.4 mg, 0.04 mmol)] were used. The reaction mixture was stirred for 12 h at 25 °C. Purification by flash chromatography ( $\text{SiO}_2$ , *i*-hexane) afforded the desired product **4k** (233 mg, 65 %) as white solid.

**M.p.** (°C): 71.

**$^1\text{H}$  NMR** (300 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 7.30 (dd,  $J$  = 5.1, 3.0 Hz, 2H), 7.27-7.25 (m, 1H), 7.22 (dd,  $J$  = 3.0, 1.2 Hz, 2H), 7.16-7.12 (m, 4H), 0.31 (s, 9H).

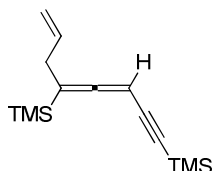
**$^{13}\text{C}$  NMR** (75 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 210.5, 137.1 (2C), 136.3, 128.0, 127.6 (2C), 125.4 (2C), 125.3, 121.1 (2C), 121.0, 98.7, 98.0, -0.3 (3C).

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 2955, 1900, 1248, 829.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 285 (13), 358 (19).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $\text{C}_{18}\text{H}_{18}\text{S}_3\text{Si}$ : calc. 358.0340, found 358.0331.

**octa-3,4,7-trien-1-yne-1,5-diylbis(trimethylsilane) (7)**



According to **TP1**, 1,5-bis(trimethylsilyl)penta-1,4-diyne (**6**, 208 mg, 1.00 mmol), THF (2 mL) and  $\text{TMPZnCl}\cdot\text{LiCl}$  (**1**, 1.10 mL, 1.2 equiv; 1.09 M in THF) were used. After stirring the reaction mixture for 1 h at 25 °C, a solution of  $\text{CuCN}\cdot 2\text{LiCl}$  (0.30 mL, 0.30 equiv, 1M in THF) was added at 25 °C and the reaction mixture was stirred 15 min at this temperature, followed by the addition of allyl bromide (181 mg, 0.13 mL, 1.50 equiv). The reaction mixture was stirred for 1 h at 25 °C. Purification by flash chromatography ( $\text{Al}_2\text{O}_3$ , *i*-hexane) afforded the desired product **7** (149 mg, 60 %) as an orange oil.

**$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 5.82 (ddt,  $J$  = 6.5, 10.2, 17.2 Hz, 1H), 5.08 (t,  $J$  = 2.9 Hz, 1H), 5.08-4.99 (ddt,  $J$  = 1.8 Hz, 2H), 2.83 (A of AB system,  $J$  = 1.2, 6.9, 15.9 Hz, 1H), 2.75 (B of AB system,  $J$  = 1.2, 6.9, 15.9 Hz, 1H), 0.14 (s, 9H), 0.12 (s, 9H).

**$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = 211.8, 136.2, 115.8, 99.1, 97.3, 94.3, 70.4, 33.6, 0.07 (3C), -1.5 (3C).

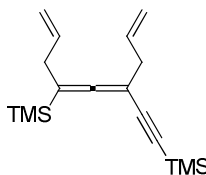
**$^{29}\text{Si}$  NMR** (79 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$  = -1.65, -18.5.

**IR** (Diamond-ATR, neat)  $\nu/\text{cm}^{-1}$  = 3080, 2959, 2899, 2151, 1924, 1639, 1407, 1370, 1248, 1044.

**MS** (EI, 70 eV)  $m/z$  (%) = 73 (100), 159 (11), 160 (47), 248 (7).

**HRMS** (EI):  $m/z$  ( $M^+$ ) for  $\text{C}_{14}\text{H}_{24}\text{Si}_2$ : calc. 248.1417, found 248.1409.

**(3-allylocta-3,4,7-trien-1-yne-1,5-diyl)bis(trimethylsilane) (8)**



According to **TP1**, octa-3,4,7-trien-1-yne-1,5-diylbis(trimethylsilane) (**7**, 124 mg, 0.50 mmol), THF (1 mL) and TMPZnCl·LiCl (**1**, 0.55 mL, 0.60 mmol 1.2 equiv; 1.09 M in THF) were used. After stirring the reaction mixture for 1 h at 25 °C, a solution of CuCN·2LiCl (0.15 mL, 0.30 equiv; 1M in THF) was added at 25 °C and the reaction mixture was stirred 15 min at this temperature, followed by the addition of allyl bromide (91 mg, 0.07 mL, 1.50 equiv). The reaction mixture was stirred for 1 h at 25 °C. Purification by flash chromatography (Al<sub>2</sub>O<sub>3</sub>, *i*-hexane) afforded the desired product **8** (193 mg, 67 %) as an orange oil.

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ/ppm = 5.66 (tdd, *J* = 6.4, 6.8, 10.1, 17.0 Hz, 1H), 5.63 (tdd, *J* = 6.9, 10.1, 17.0 Hz, 1H), 4.90 (d, *J* = 17.0 Hz, 2H), 4.85(d, *J* = 10.1 Hz, 2H), 2.66 (A of AB system, *J* = 1.4, 6.9, 15.8 Hz, 1H), 2.64-2.62 (m, 2H), 5.59 (B of AB system, *J* = 1.4, 6.4, 15.8 Hz, 1H), 0.00 (s, 9H), - 0.05 (s, 9H).

**<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>) δ/ppm = 210.1, 136.6, 135.2, 116.0, 115.5, 101.8, 98.3, 95.8, 83.9, 37.8, 34.0, 0.10 (3C), -1.31 (3C).

**<sup>29</sup>Si NMR** (79 MHz, CDCl<sub>3</sub>) δ/ppm = -1.65, -18.5.

**IR** (Diamond-ATR, neat) ν/cm<sup>-1</sup> = 3080, 2958, 2899, 2143, 1923, 1639, 1432, 1409, 1360, 1248, 1162, 1014, 990.

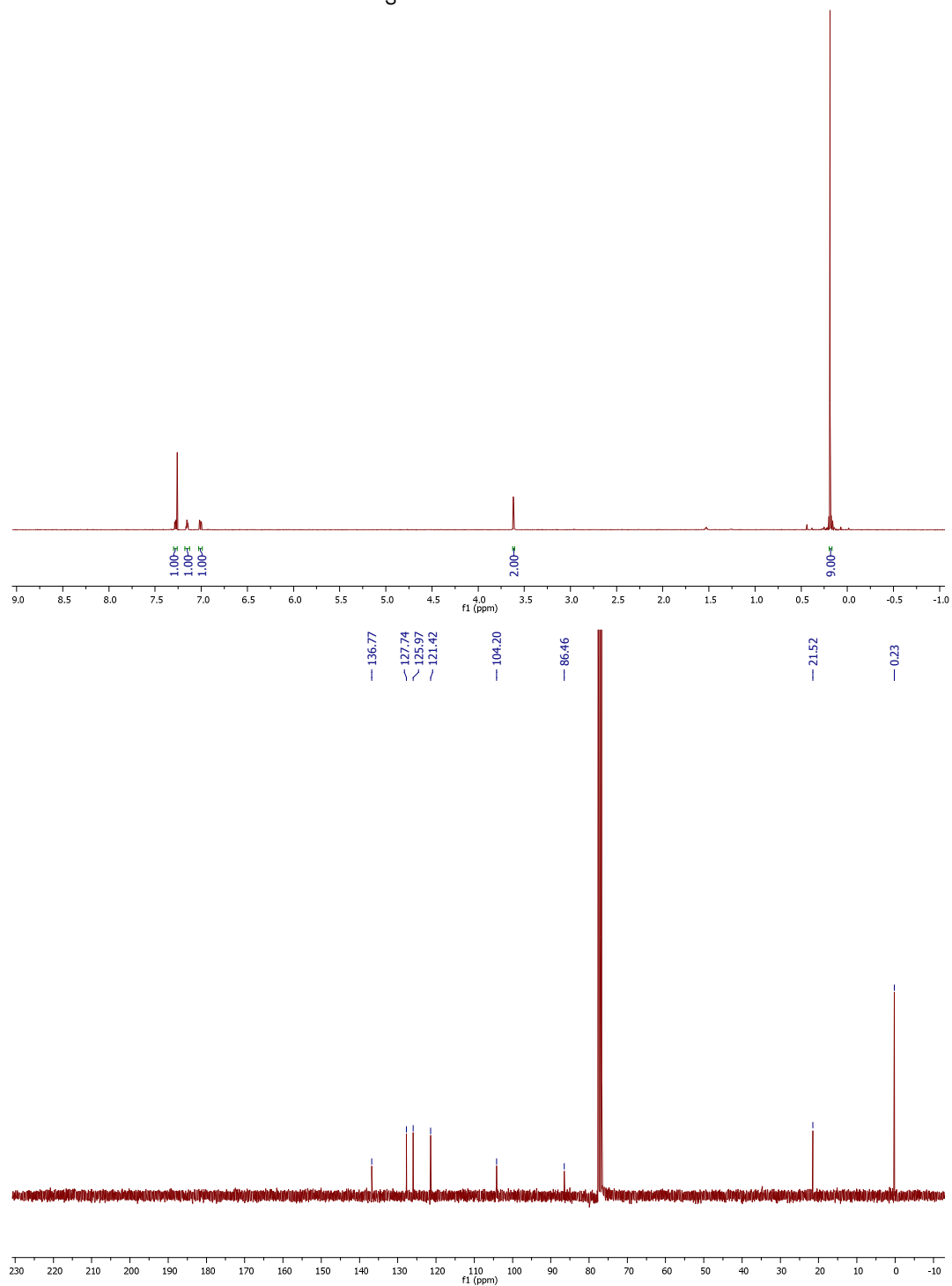
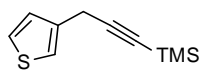
**MS** (EI, 70 eV) *m/z* (%) = 73 (100), 159 (9), 200 (11), 288 (2).

**HRMS** (EI): *m/z* (M<sup>+</sup>) for C<sub>17</sub>H<sub>28</sub>Si<sub>2</sub>: calc. 288.1730, found 288.1703.

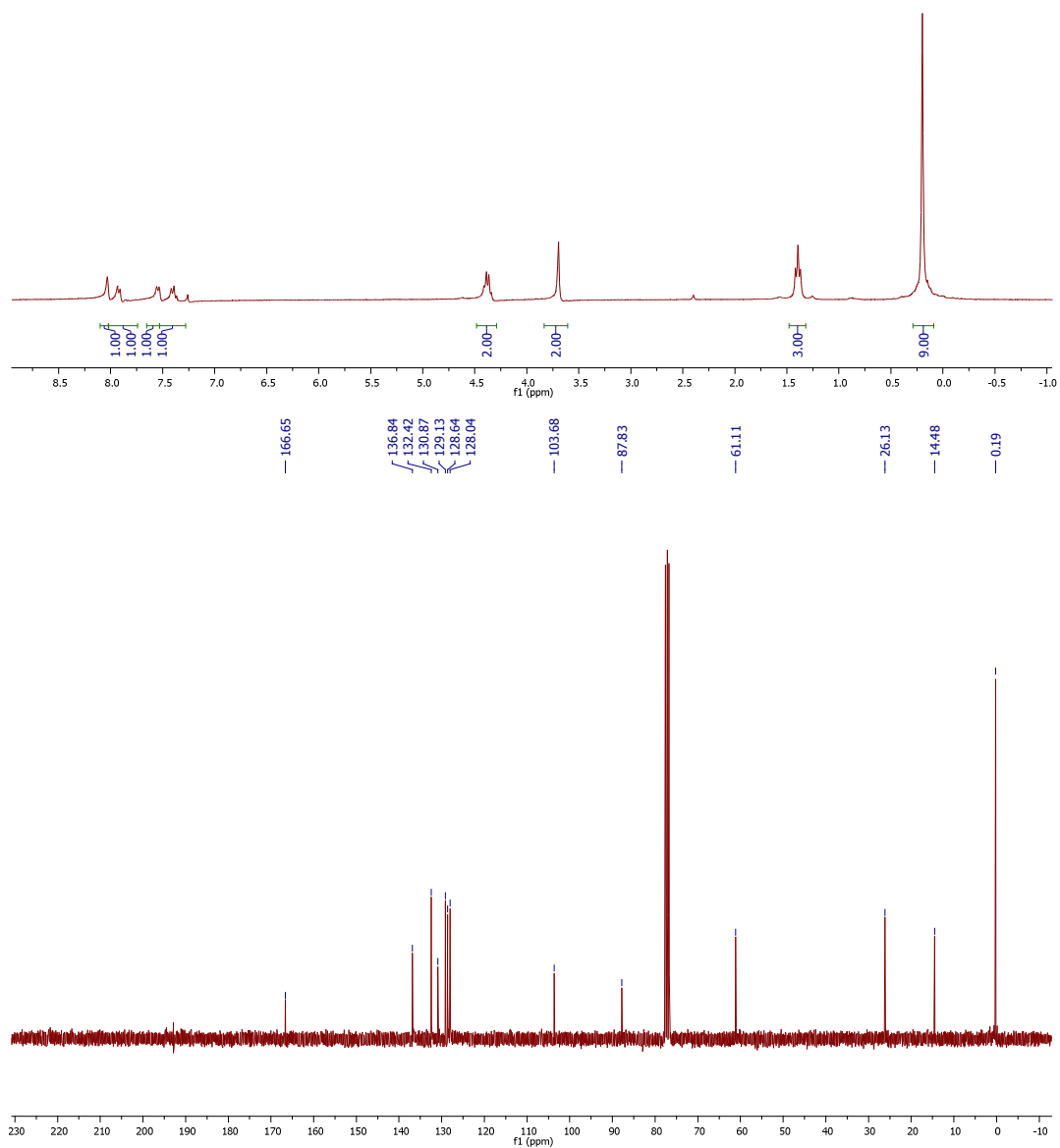
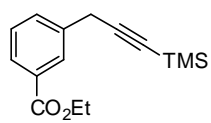


## NMR spectra

### Trimethyl(3-(thiophen-3-yl)prop-1-yn-1-yl)silane (2b)

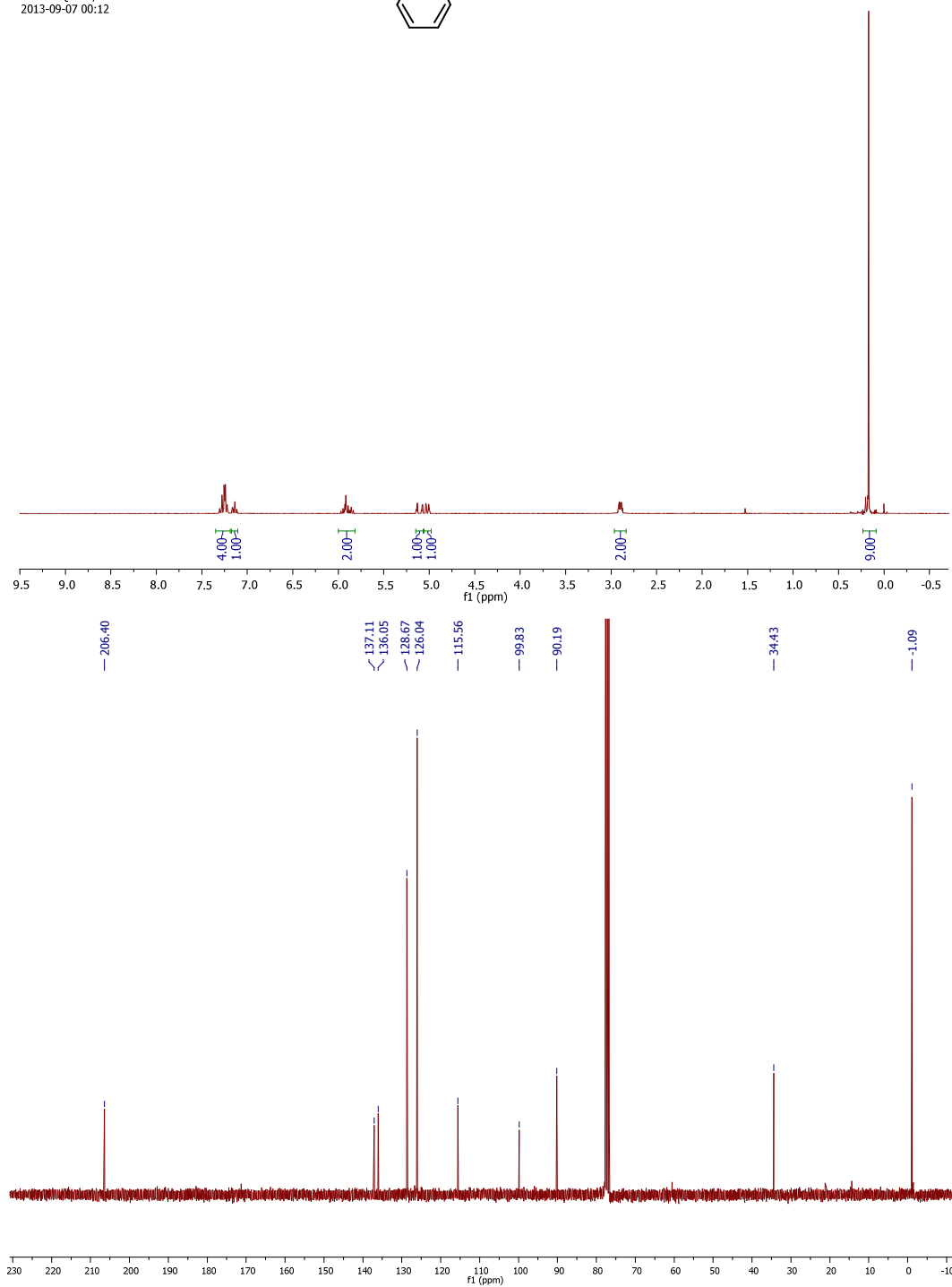
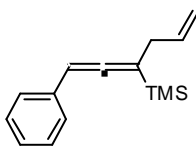


**Ethyl 3-(3-(trimethylsilyl)prop-2-yn-1-yl)benzoate (2c)**

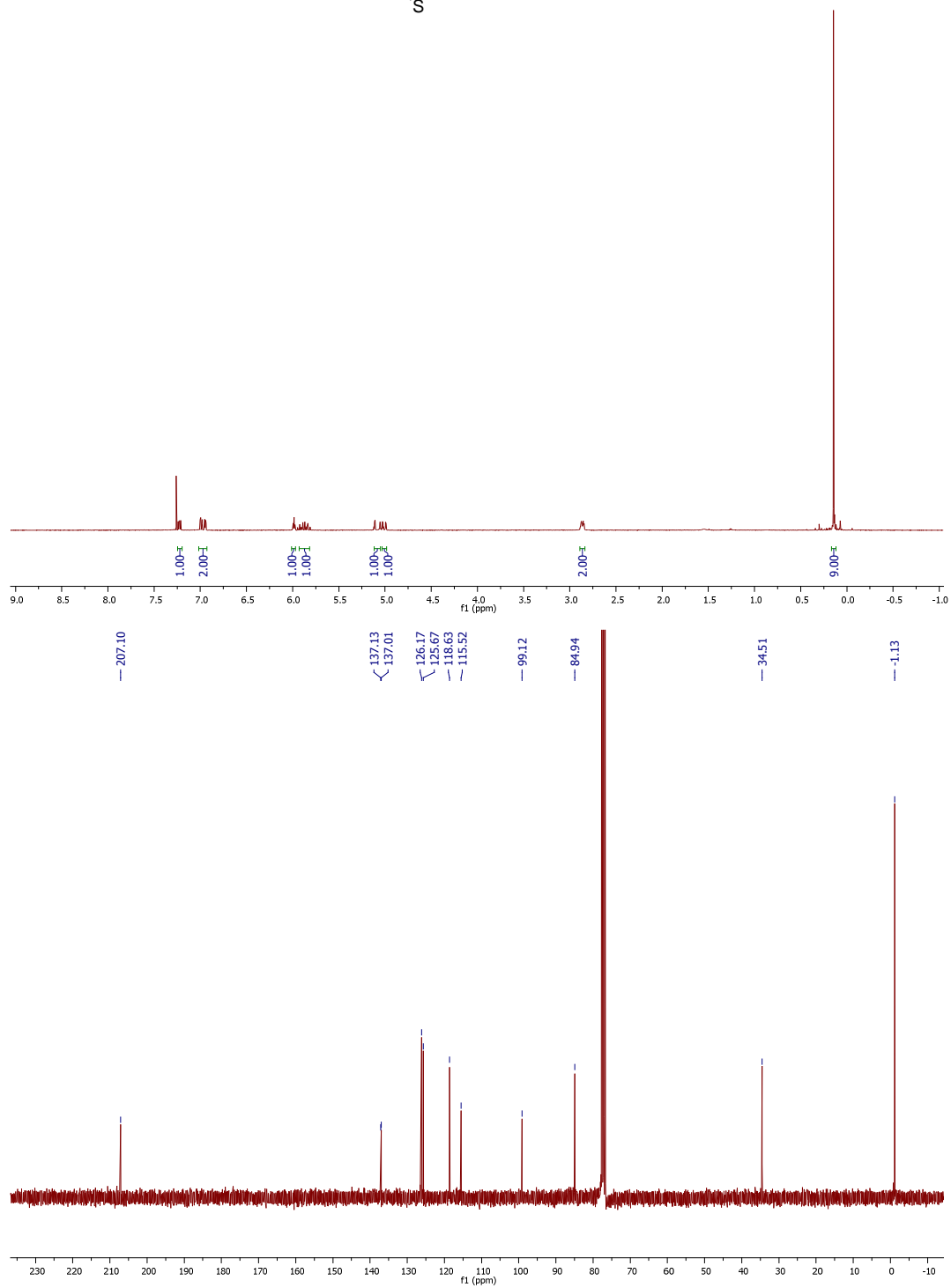
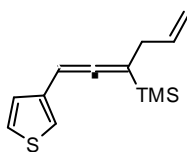


# Trimethyl(1-phenylhexa-1,2,5-trien-3-yl)silane (3a)

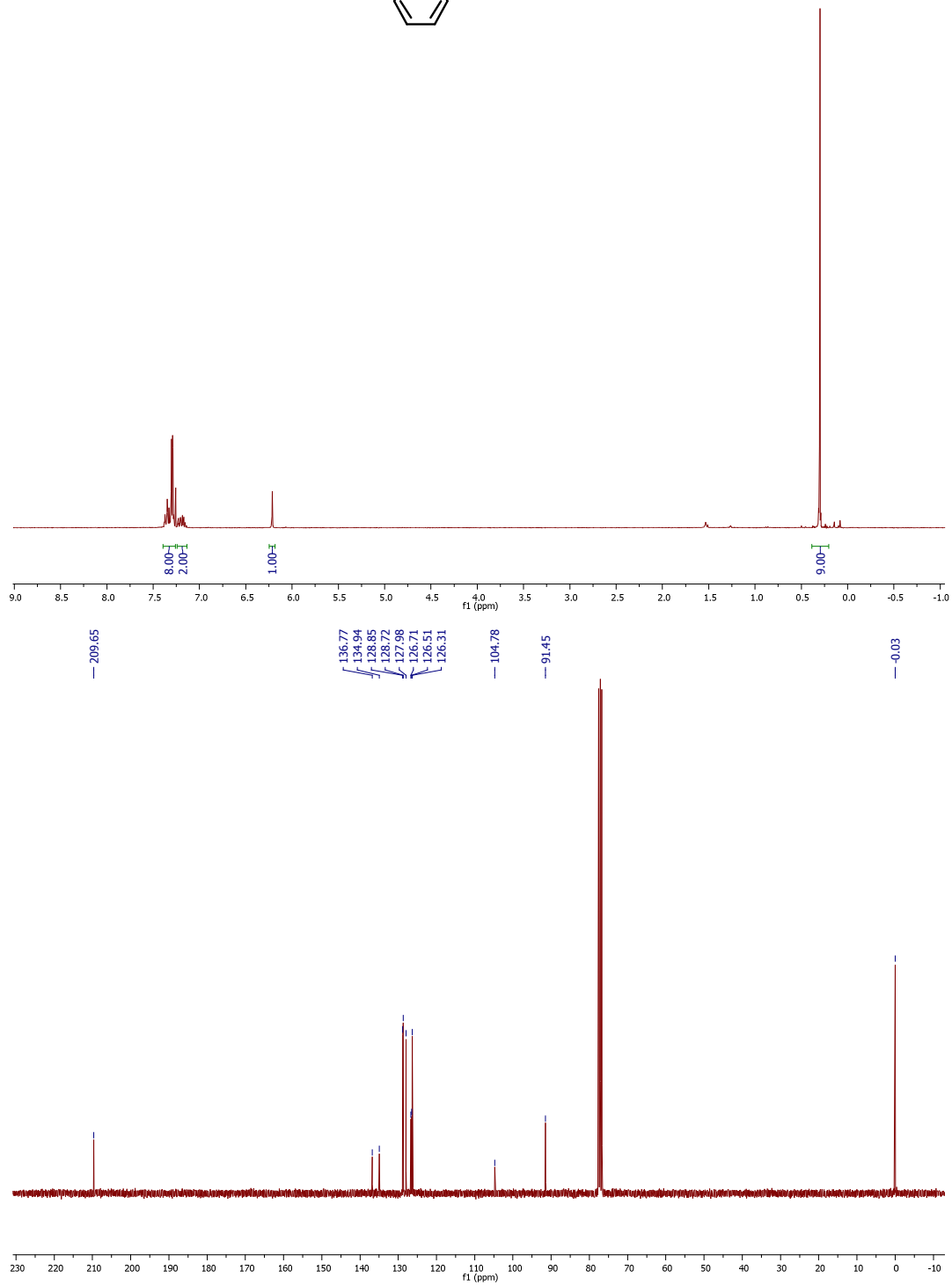
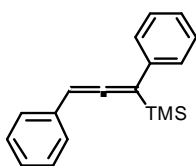
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Pauline Quinio, AK Knochel  
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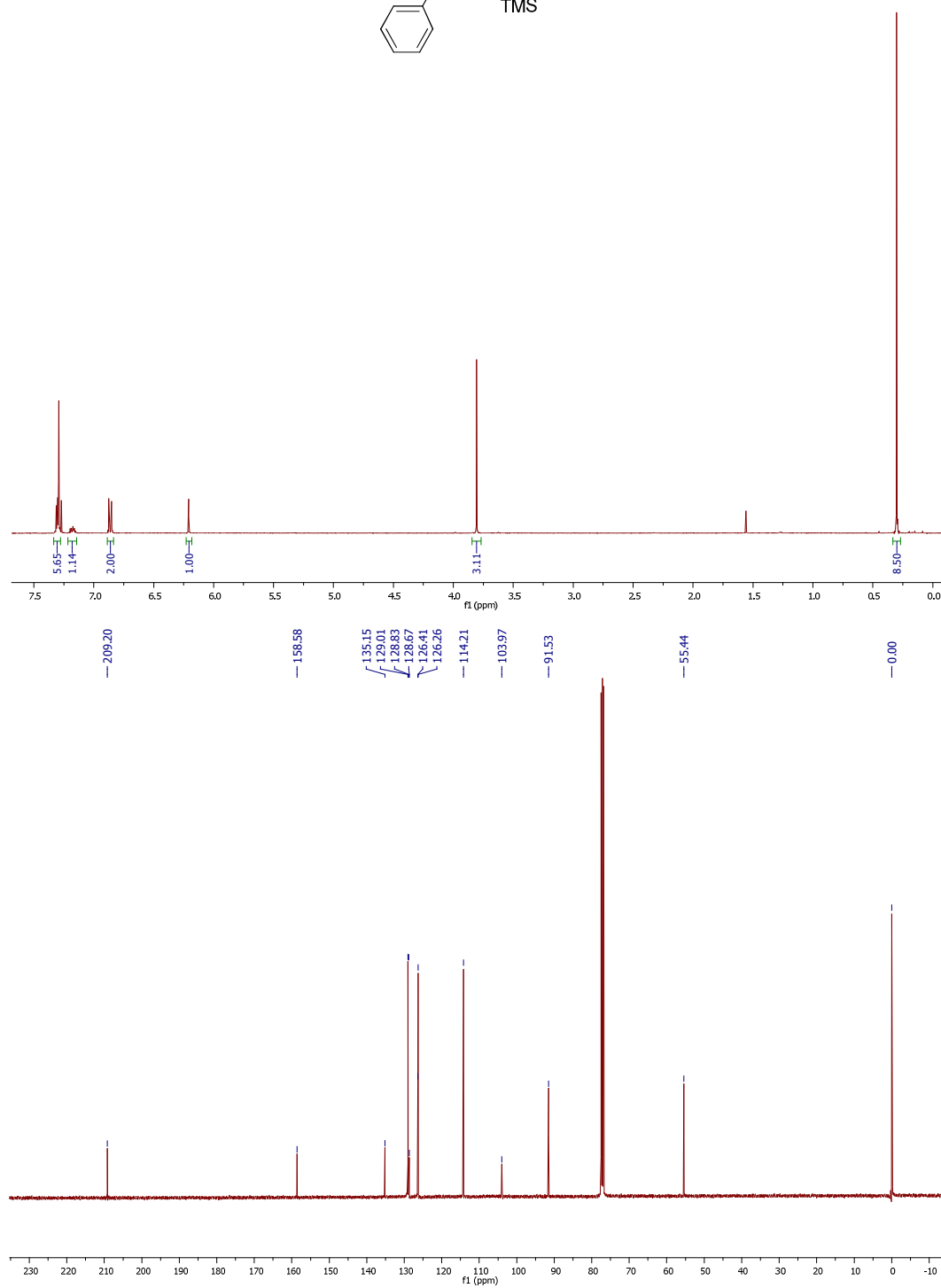
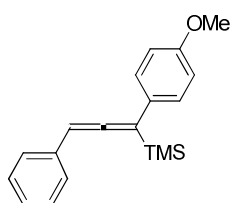
**Trimethyl(1-(thiophen-3-yl)hexa-1,2,5-trien-3-yl)silane (3b)**



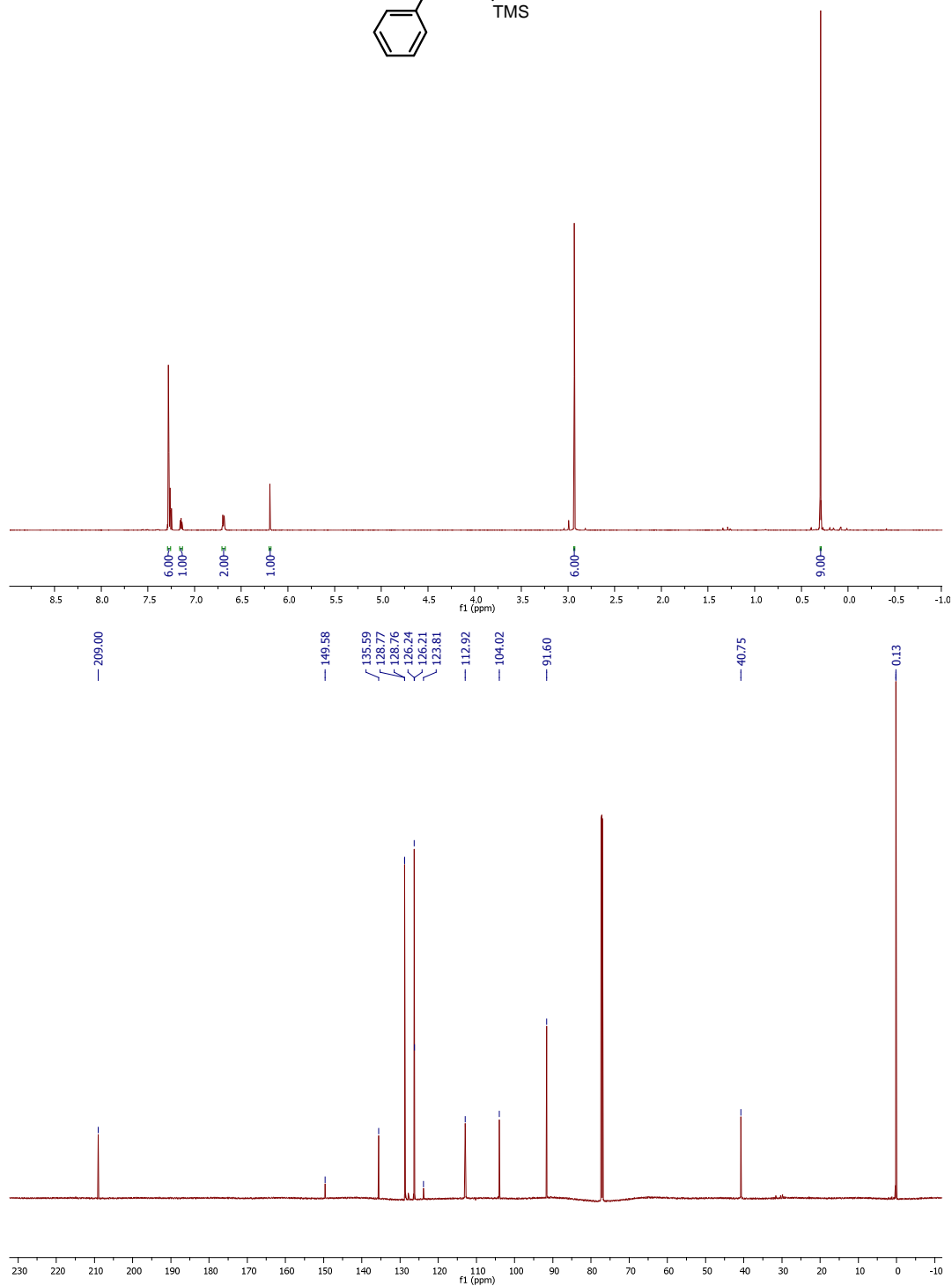
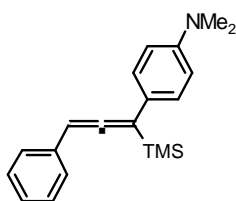
**(1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (3c)**



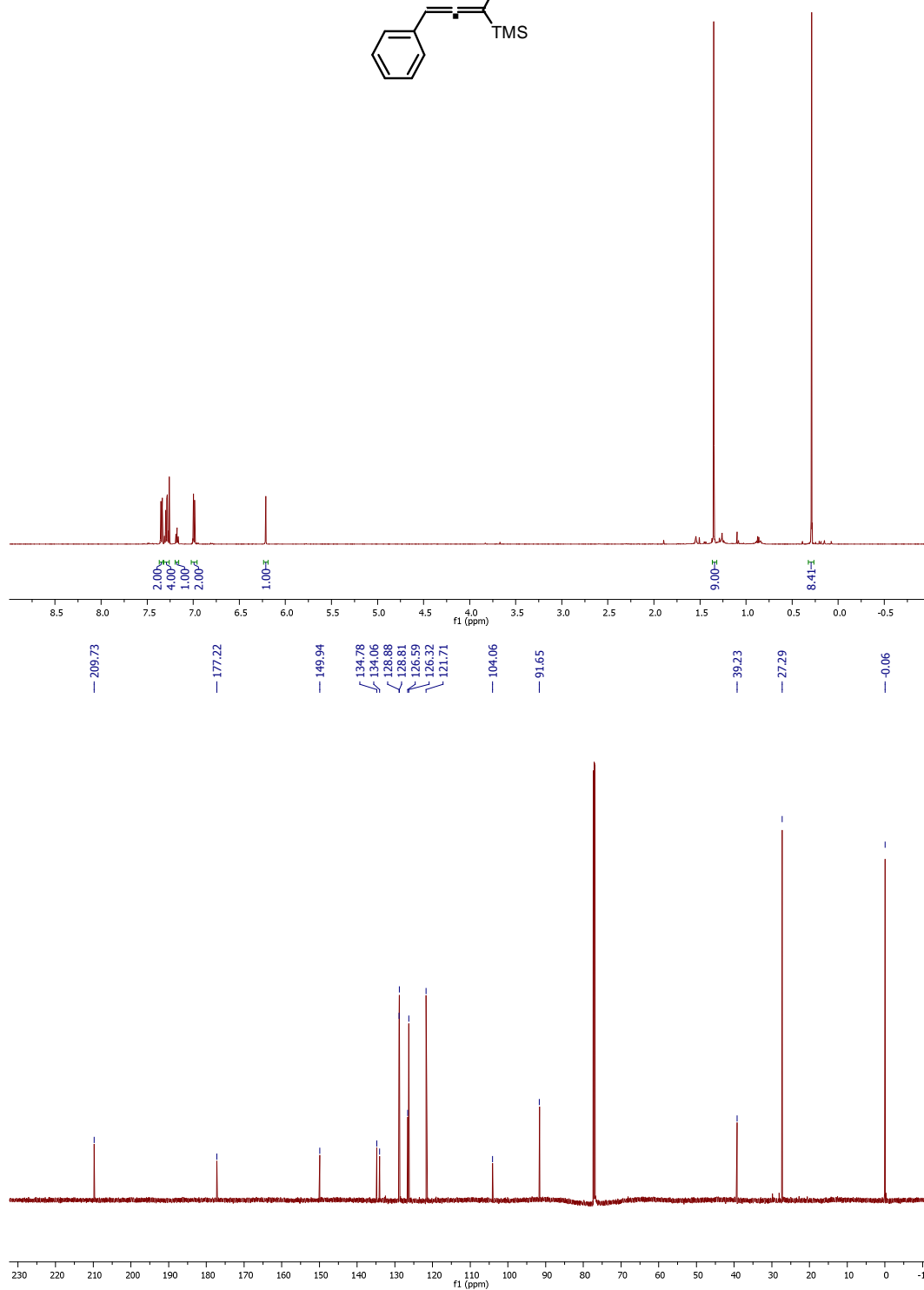
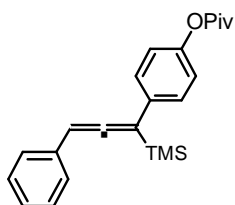
**(1-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3d)**



***N,N*-dimethyl-4-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)aniline (3e)**

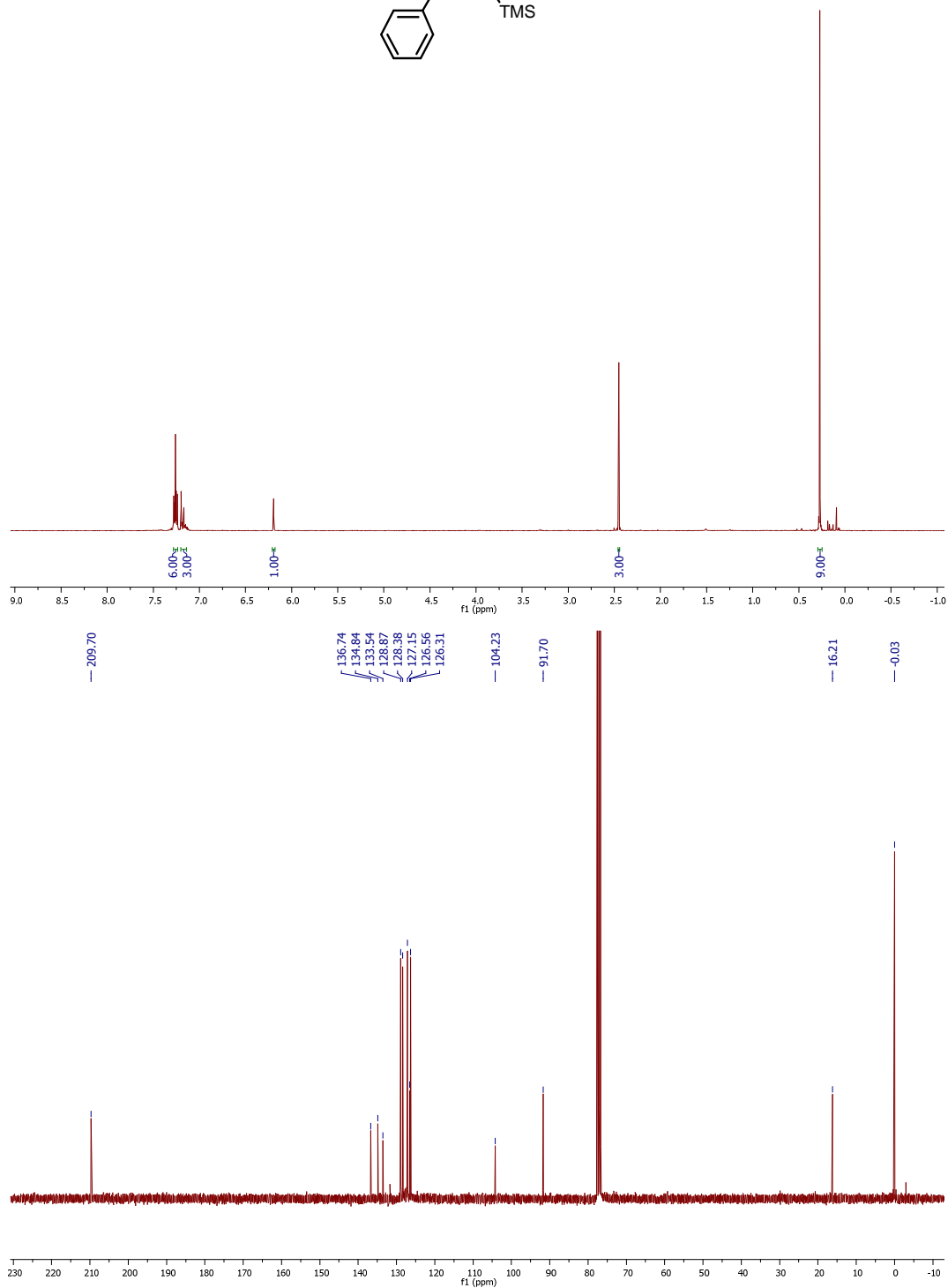
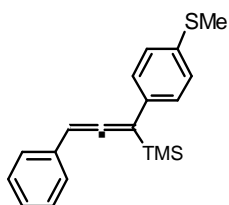


**4-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)phenyl pivalate (3f)**

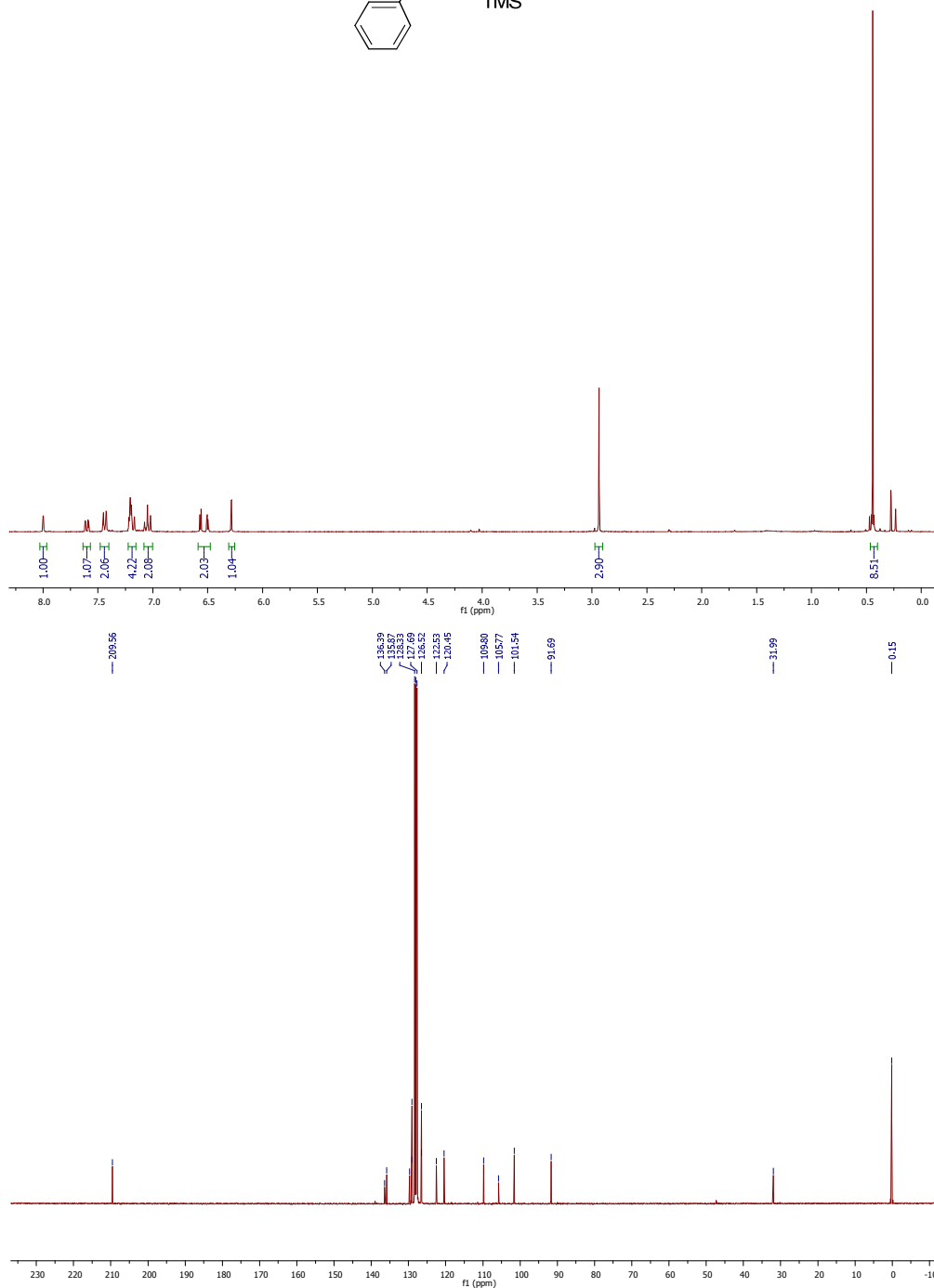
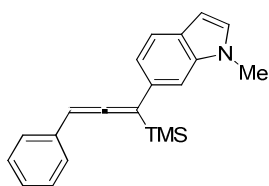




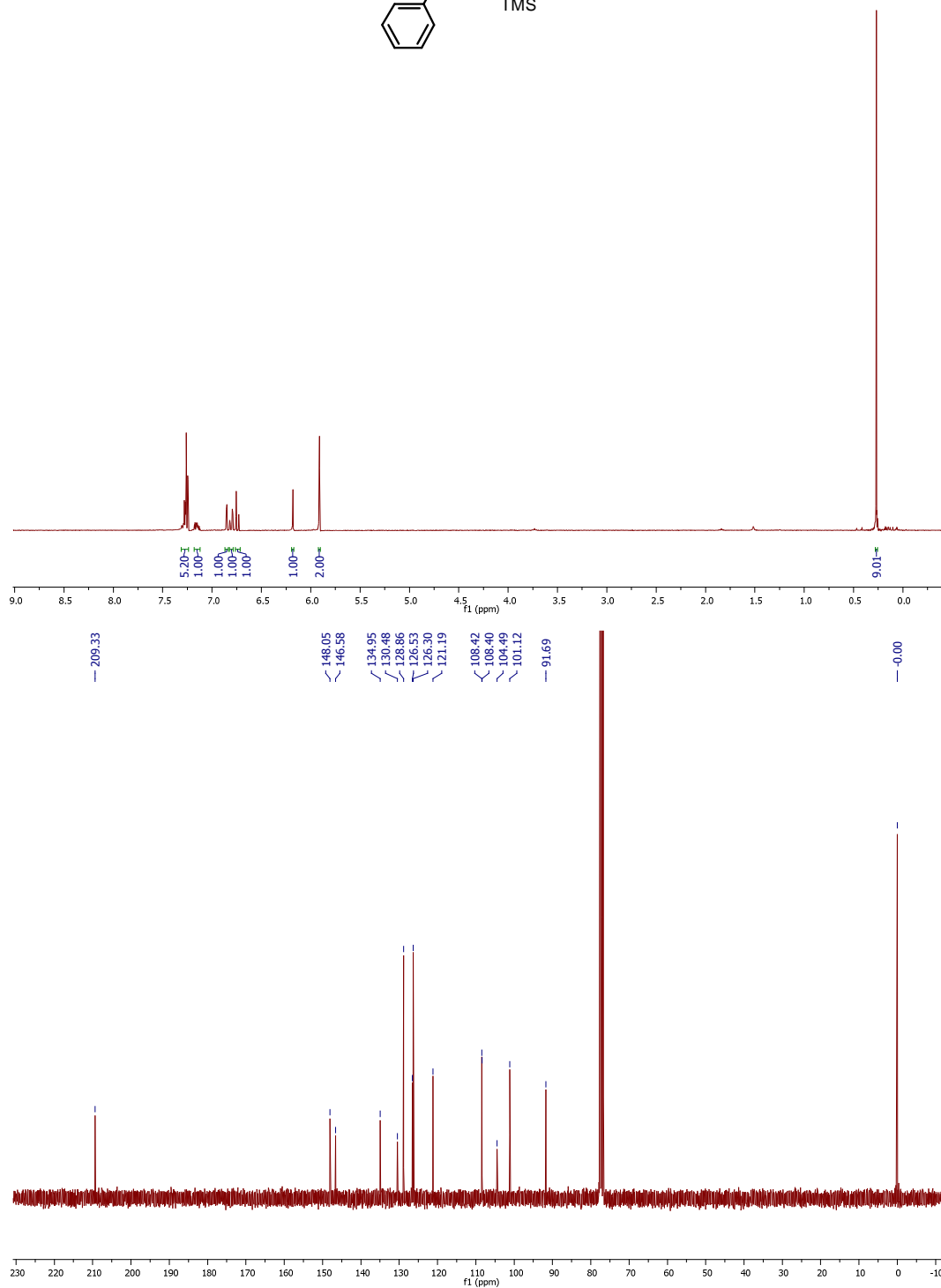
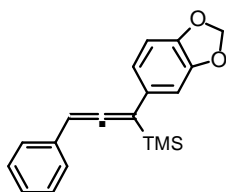
**Trimethyl(1-(4-(methylthio)phenyl)-3-phenylpropa-1,2-dienyl)silane (3g)**



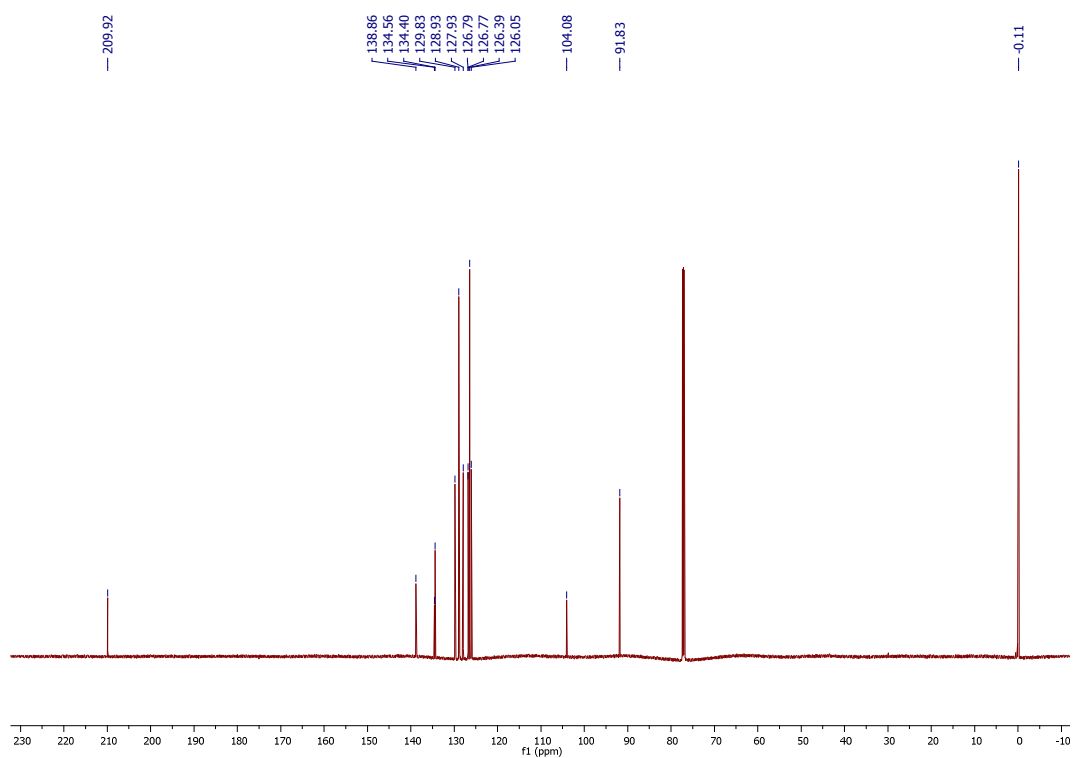
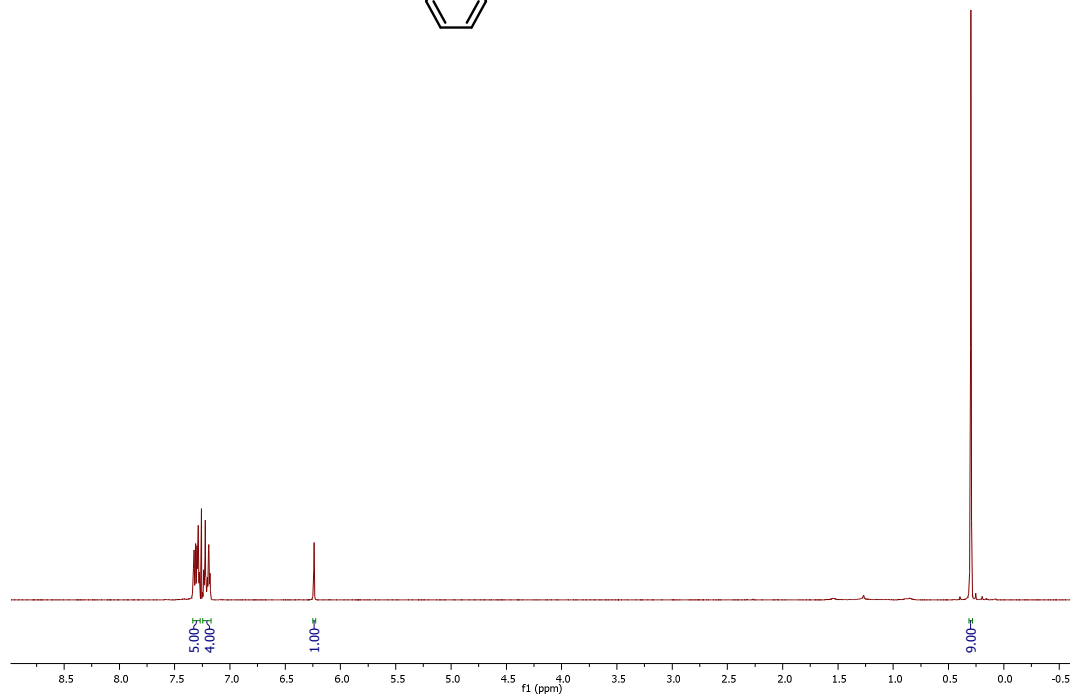
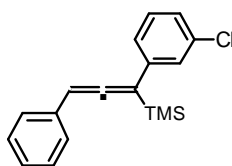
**1-methyl-5-(3-phenyl-1-(trimethylsilyl)propa-1,2-dien-1-yl)-1*H*-indole (3h)**



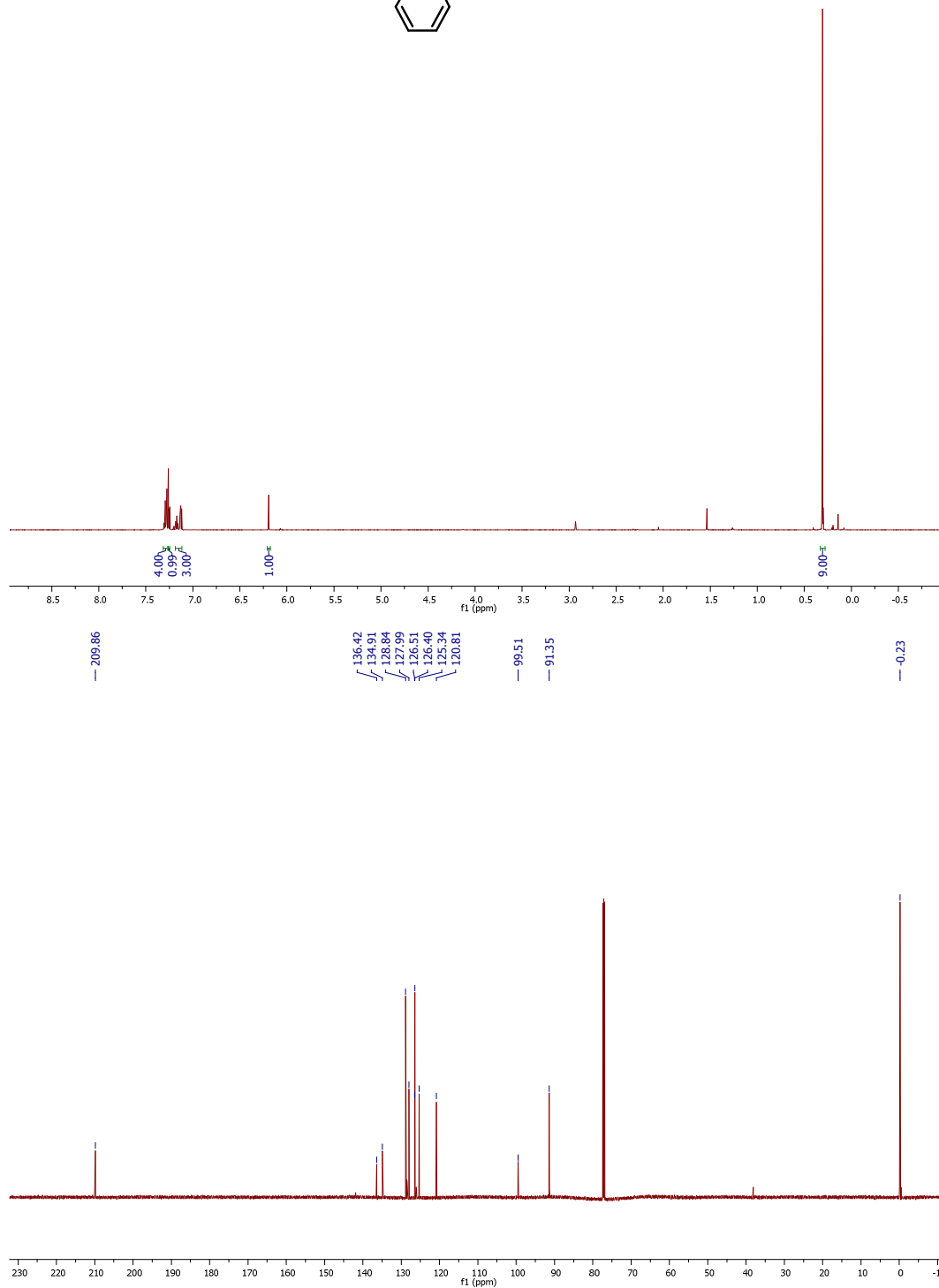
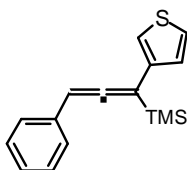
**(1-(benzo[d][1,3]dioxol-5-yl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3i)**



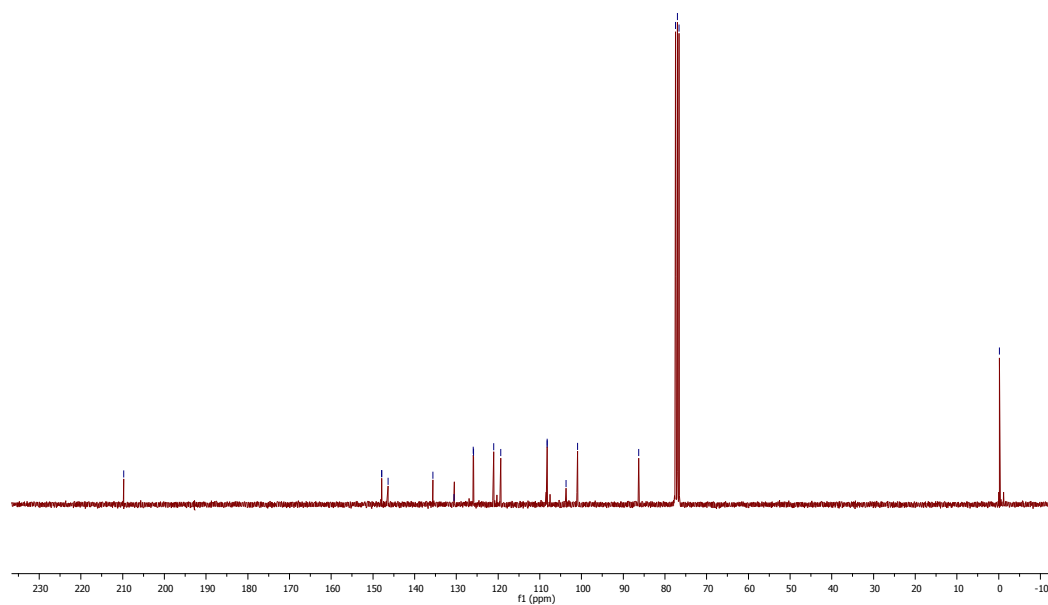
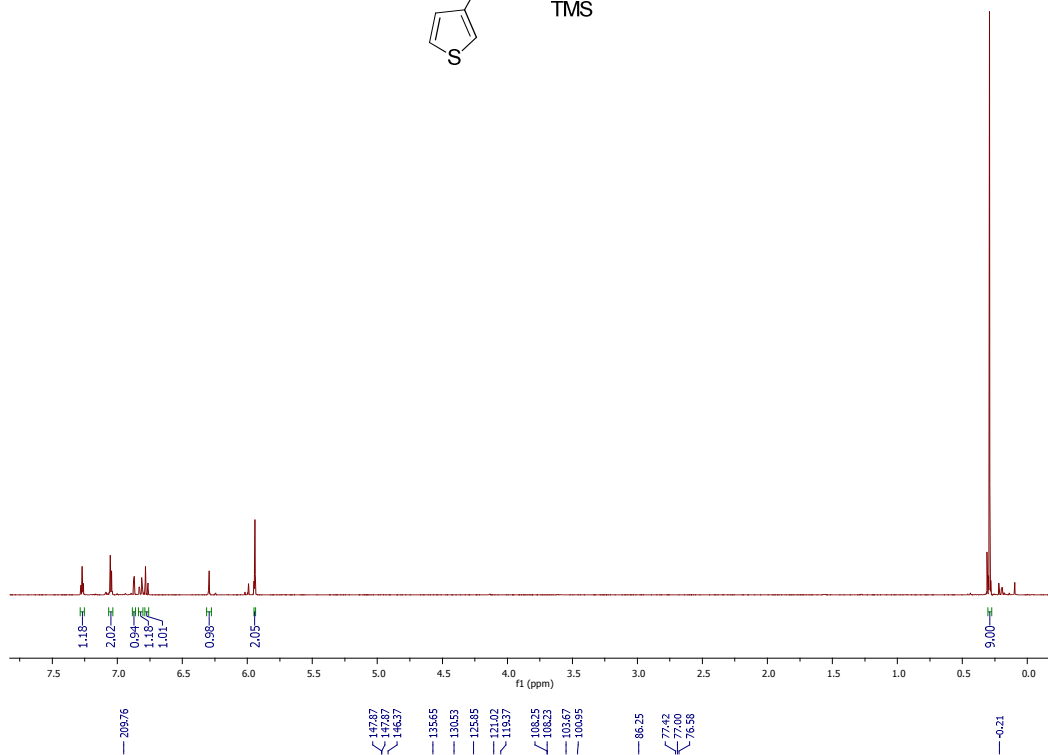
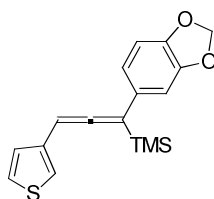
**(1-(3-chlorophenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane (3j)**



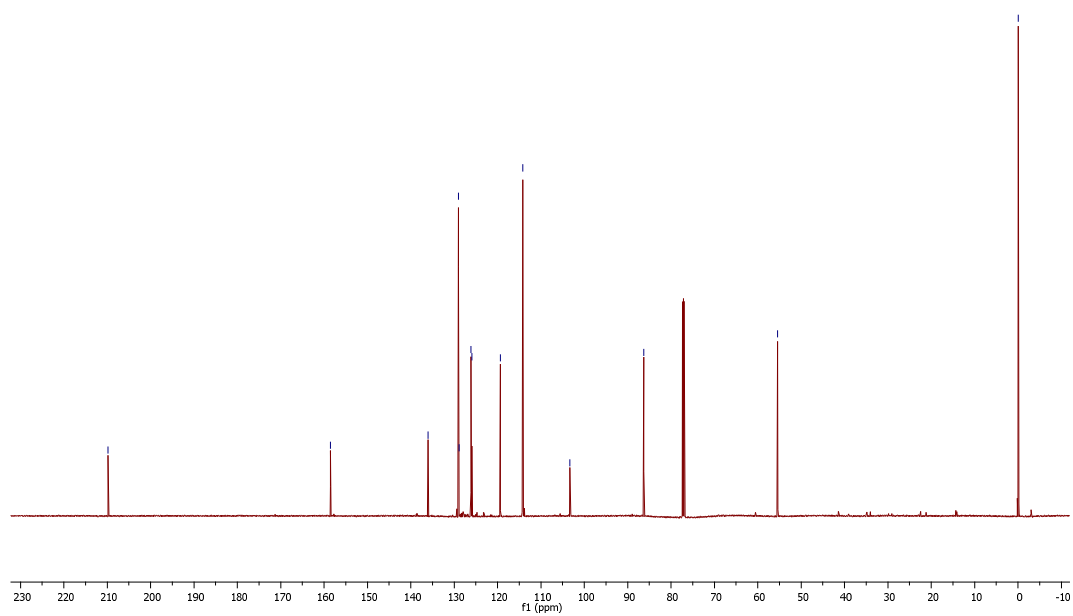
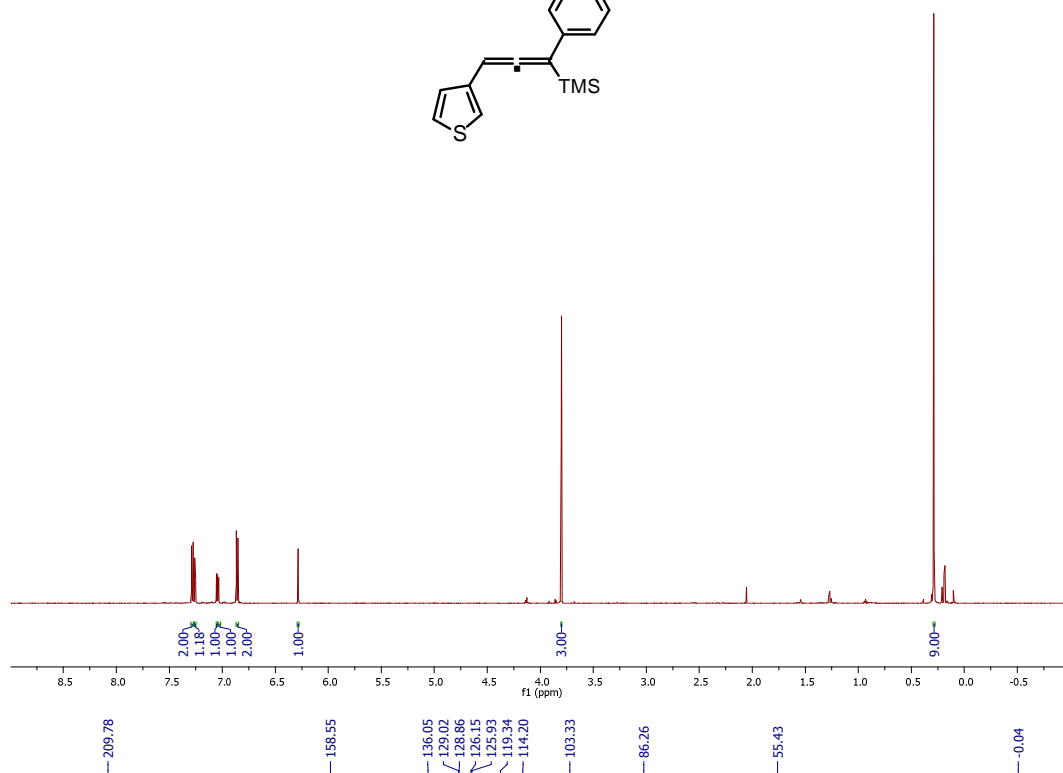
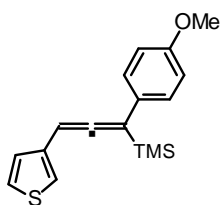
**Trimethyl(3-phenyl-1-(thiophen-3-yl)propa-1,2-dien-1-yl)silane (3k)**



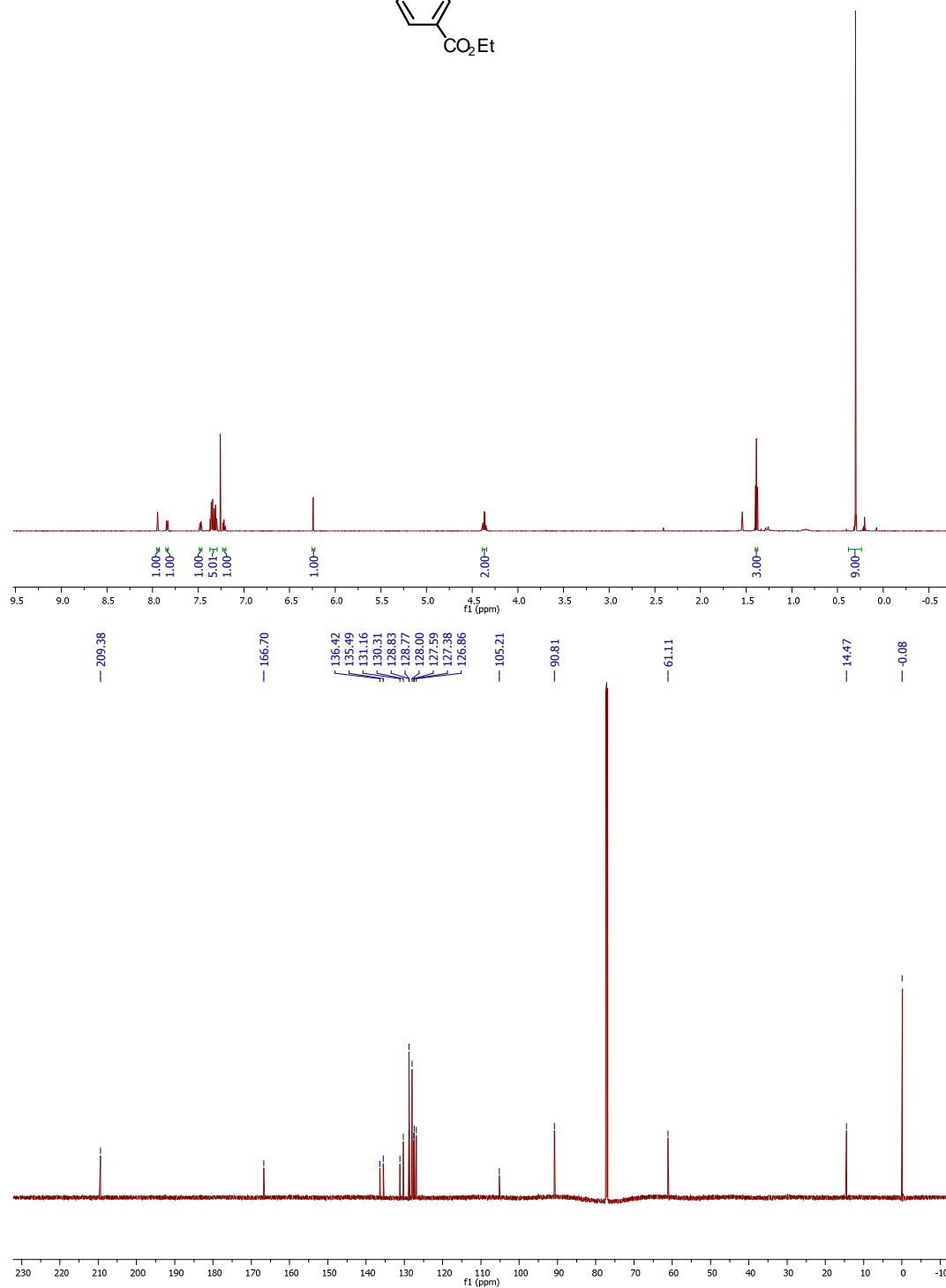
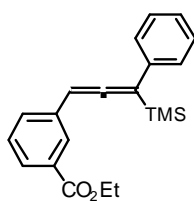
**(1-(benzo[d][1,3]dioxol-5-yl)-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (3l)**



**(1-(4-methoxyphenyl)-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (3m)**

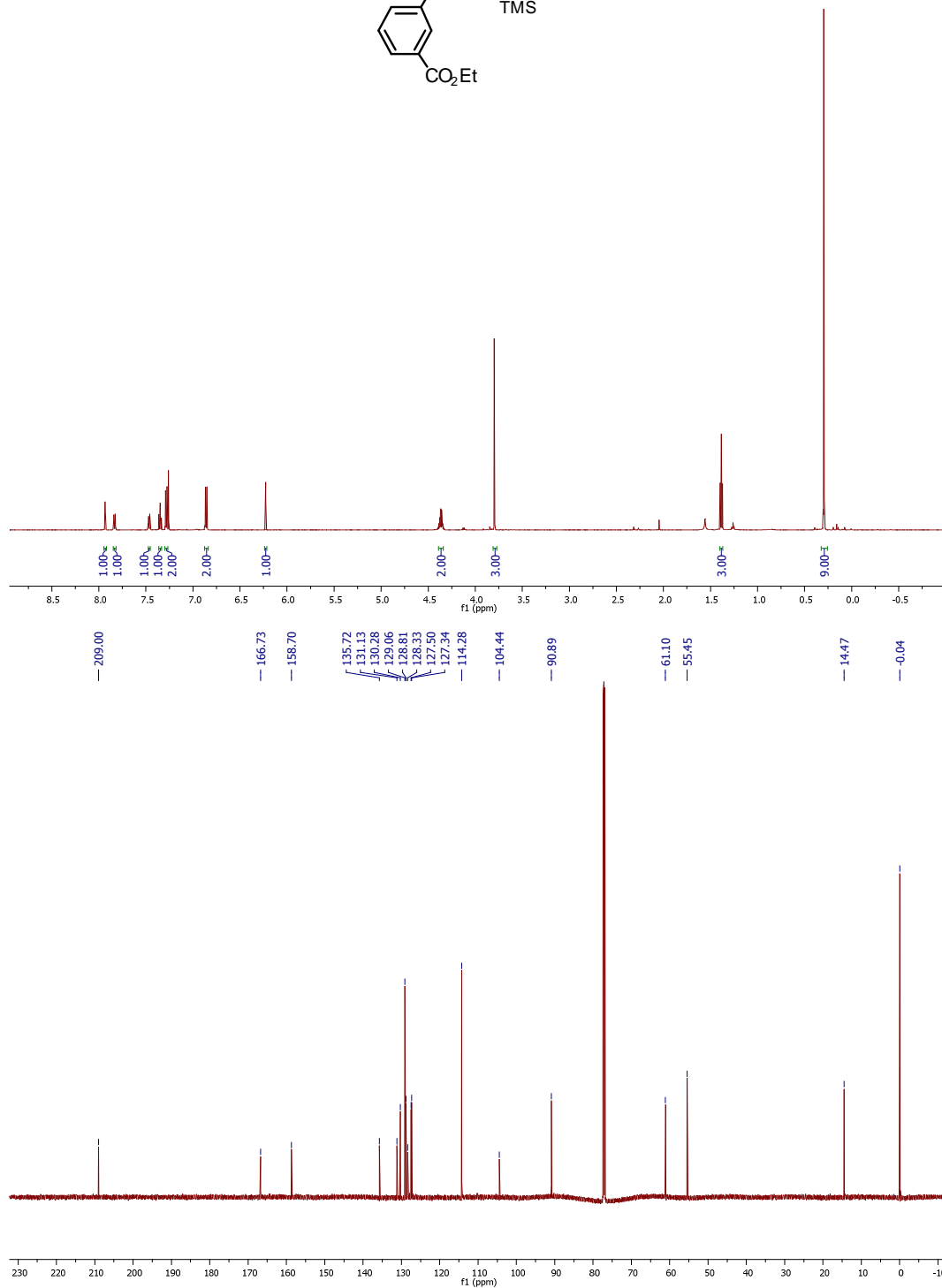
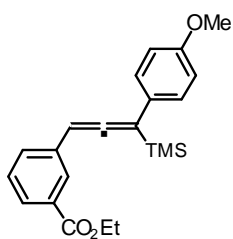


# **Ethyl 3-(3-phenyl-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (3n)**

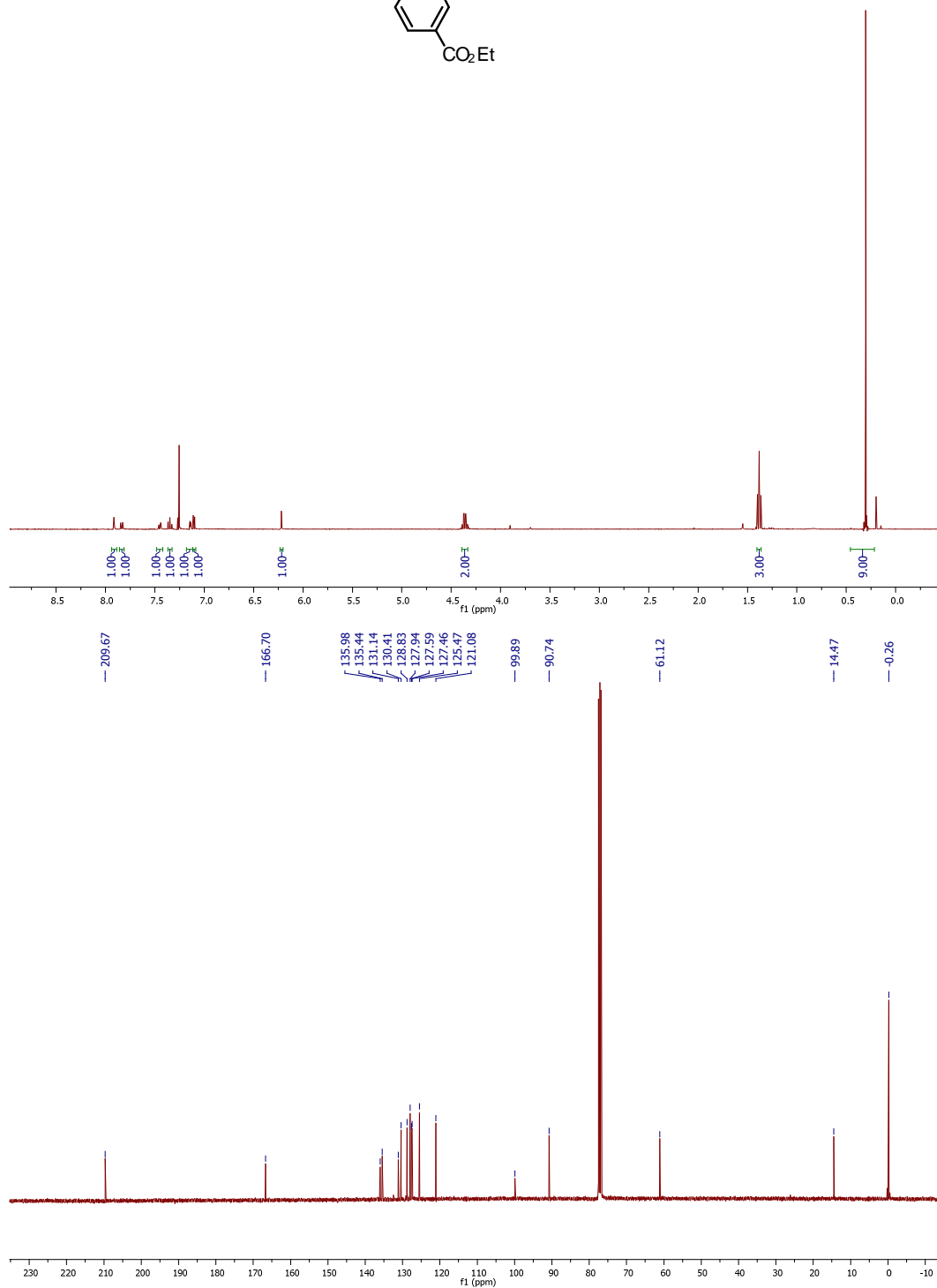
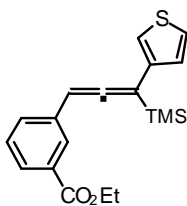




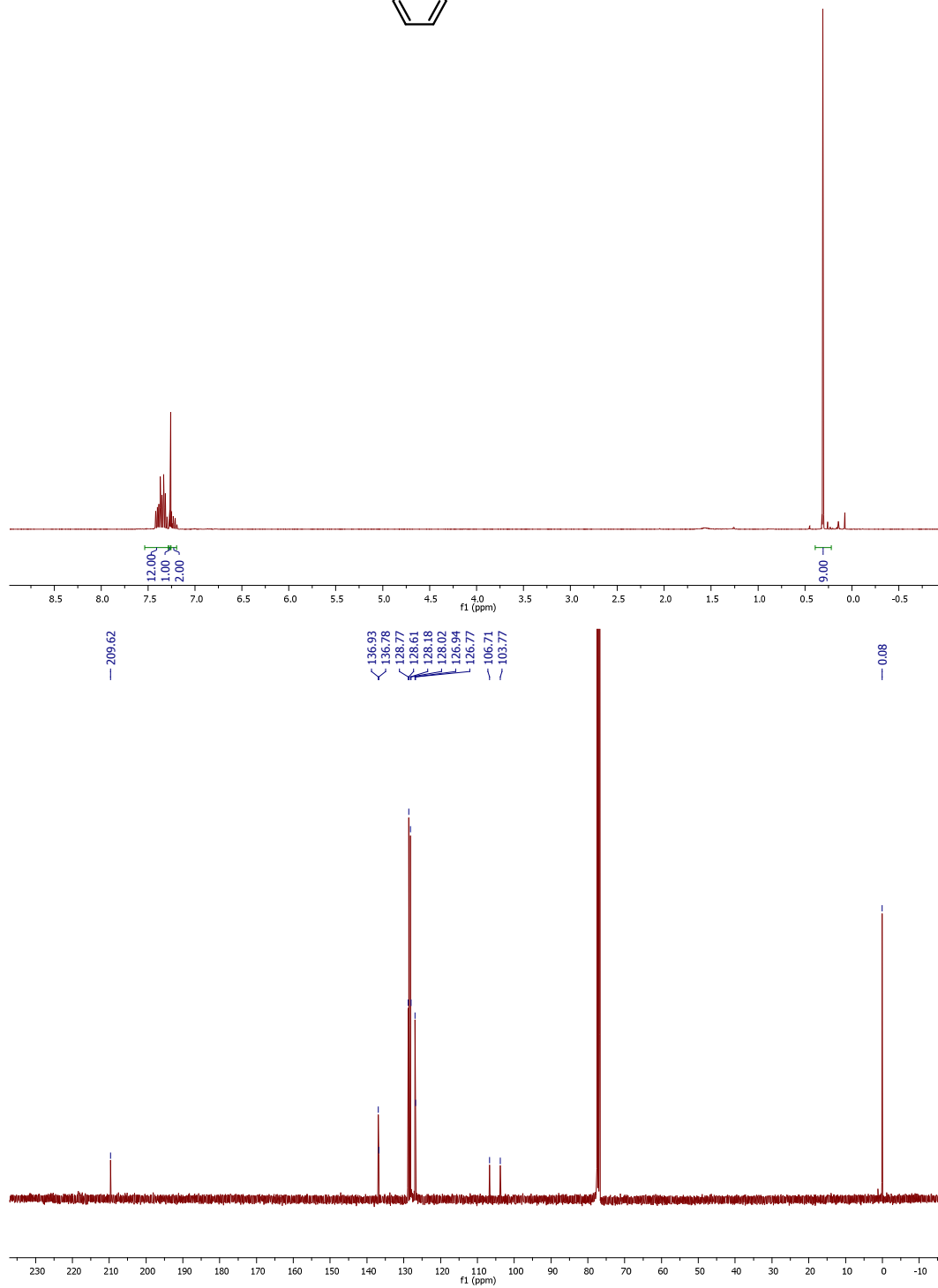
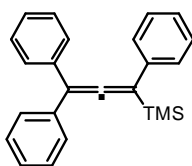
**Ethyl 3-(3-(4-methoxyphenyl)-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (3o)**



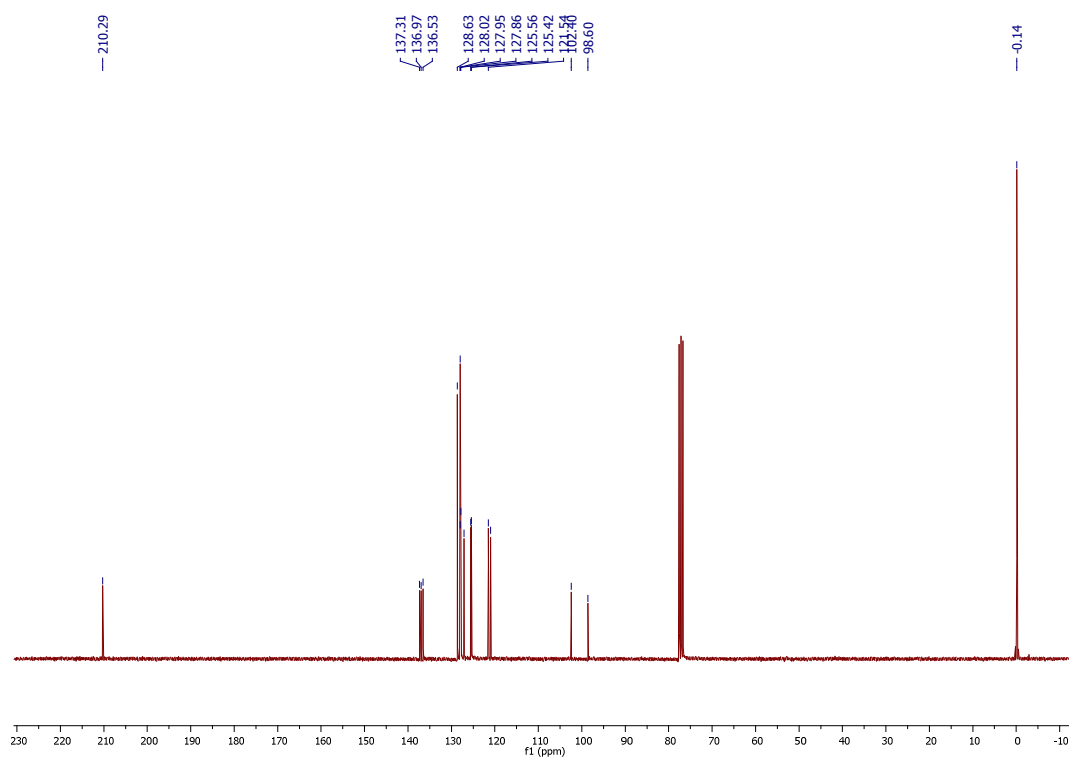
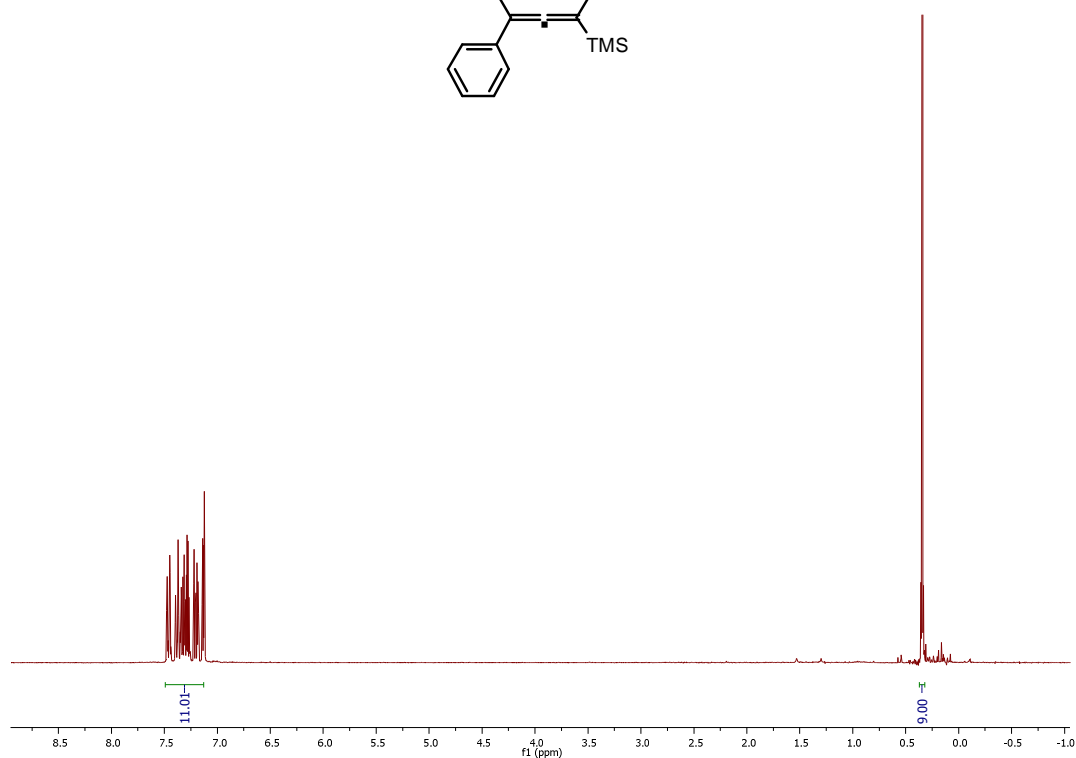
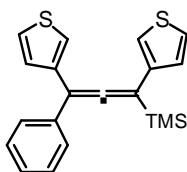
**Ethyl 3-(3-(thiophen-3-yl)-3-(trimethylsilyl)propa-1,2-dien-1-yl)benzoate (3p)**



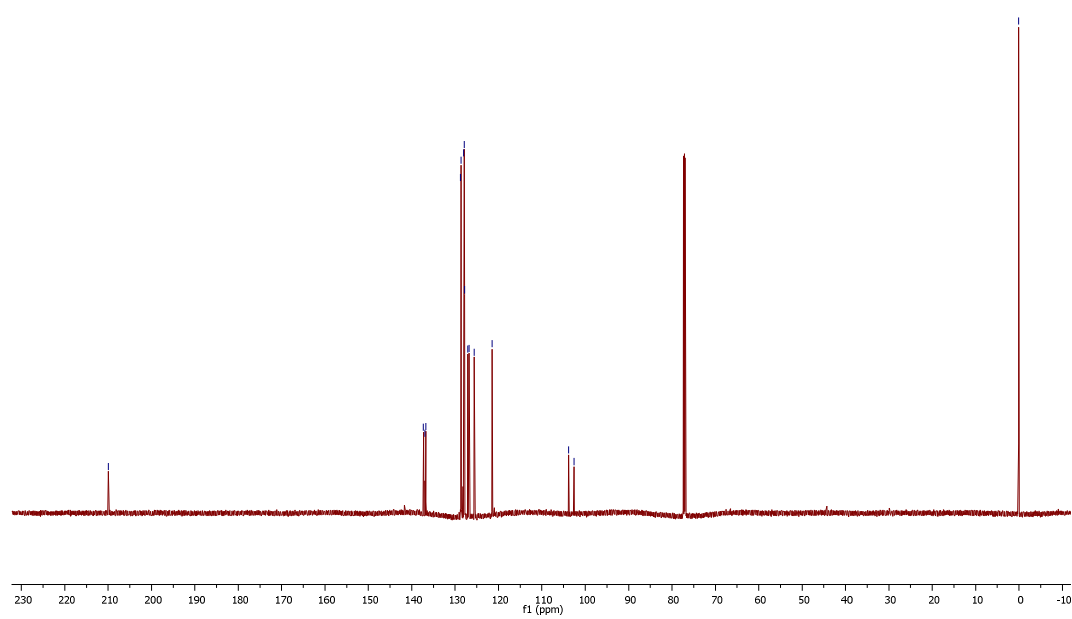
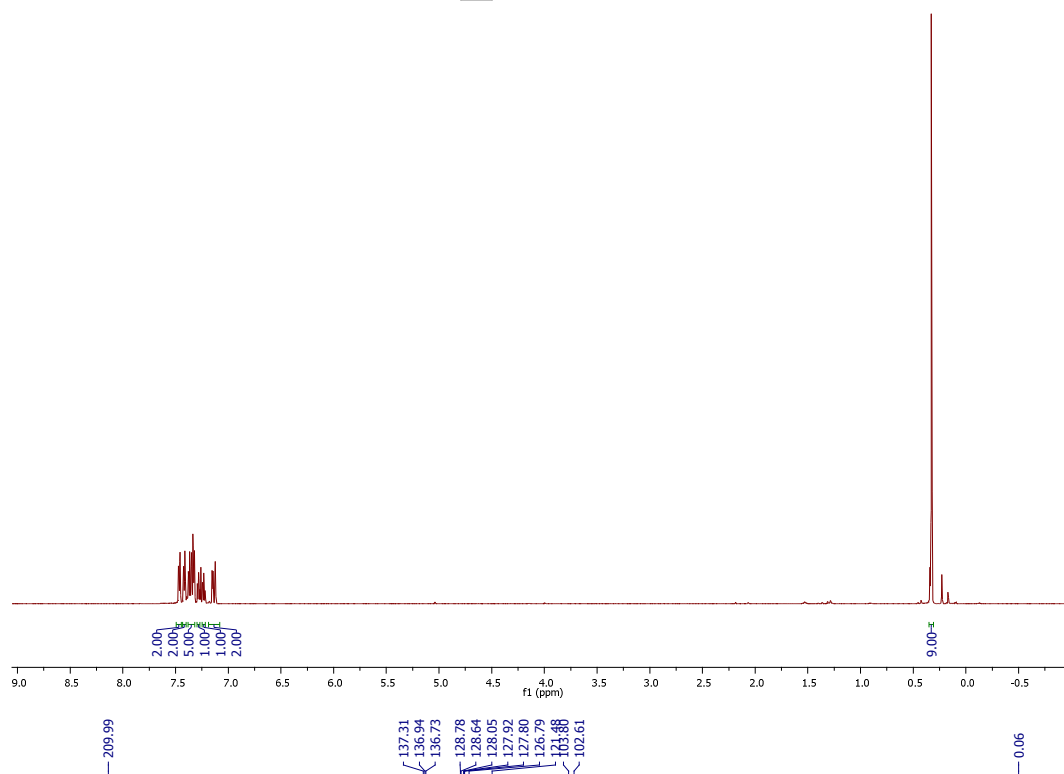
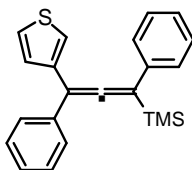
**Trimethyl(1,3,3-triphenylpropa-1,2-dienyl)silane (4a)**



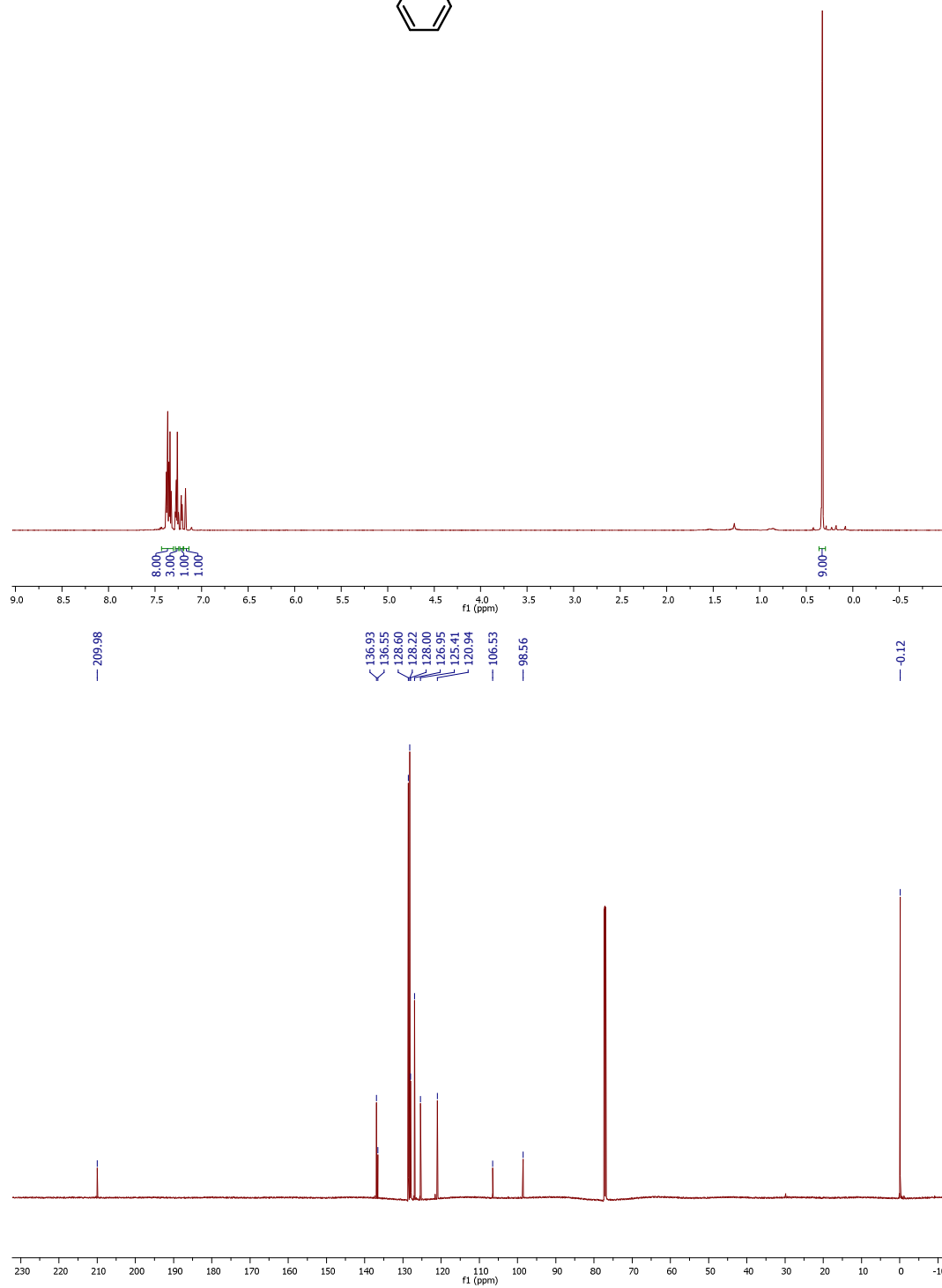
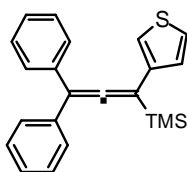
**Trimethyl(3-phenyl-1,3-di(thiophen-3-yl)propa-1,2-dien-1-yl)silane (4b)**



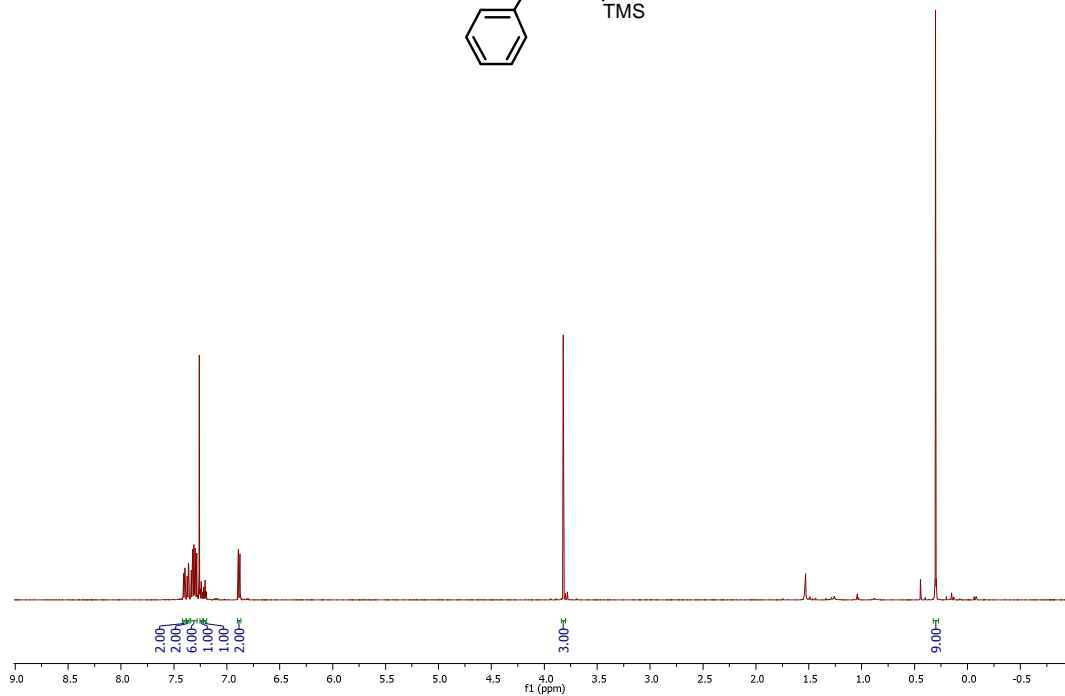
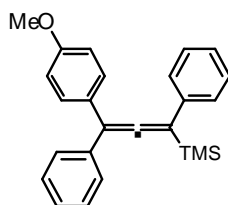
**(1,3-diphenyl-3-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (4c)**



**(3,3-diphenyl-1-(thiophen-3-yl)propa-1,2-dien-1-yl)trimethylsilane (4d)**

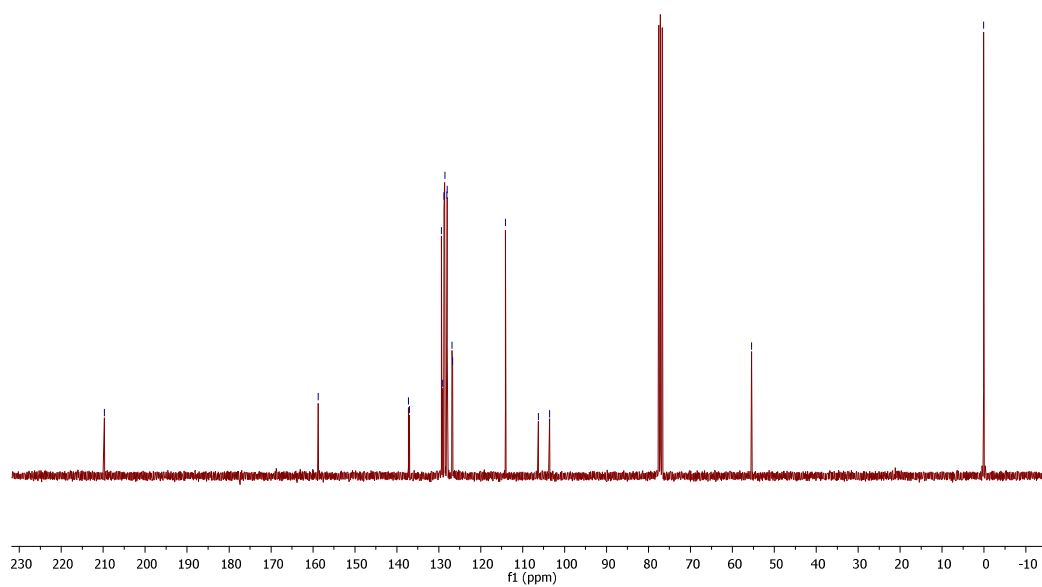


**(3-(4-methoxyphenyl)-1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4e)**

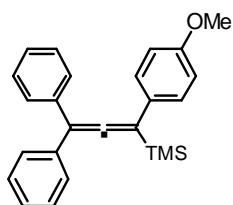


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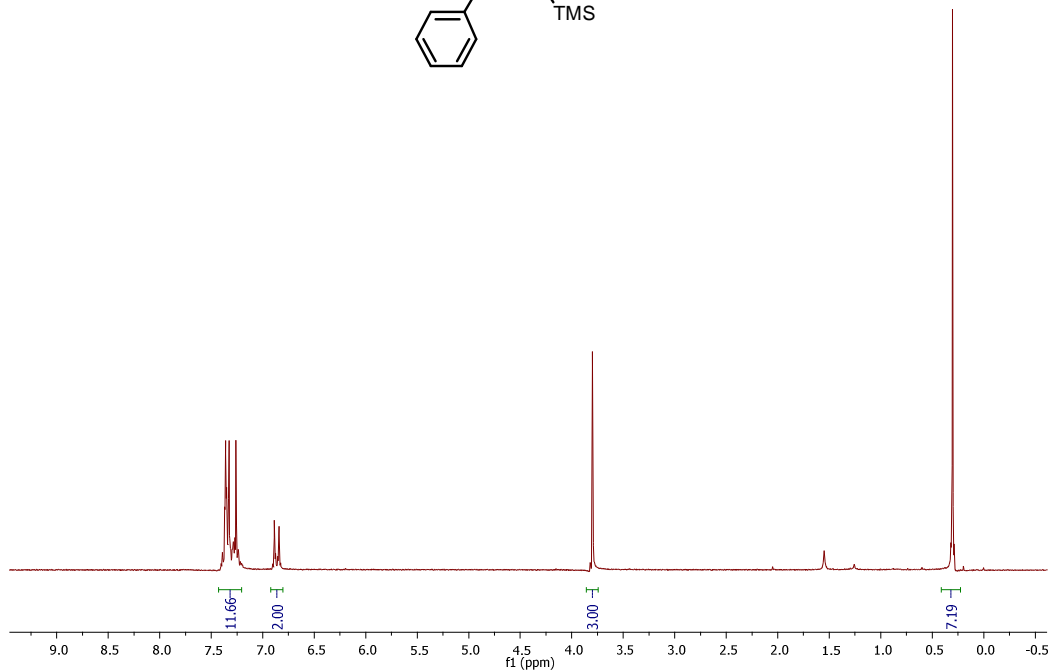
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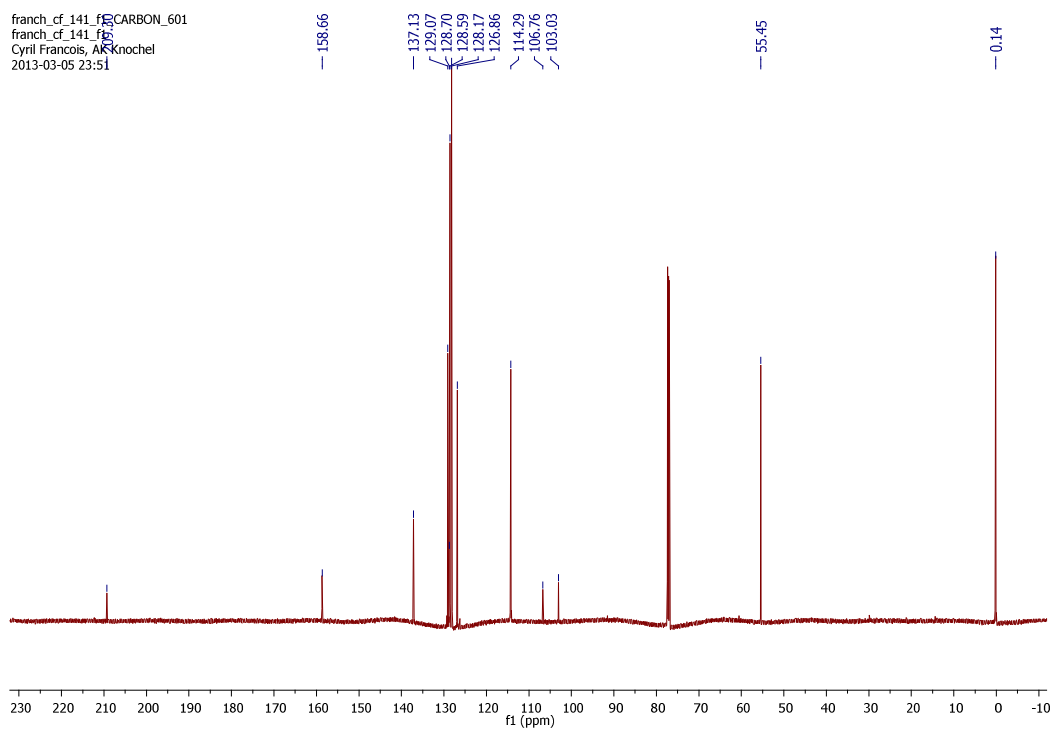
**(1-(4-methoxyphenyl)-3,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4f)**



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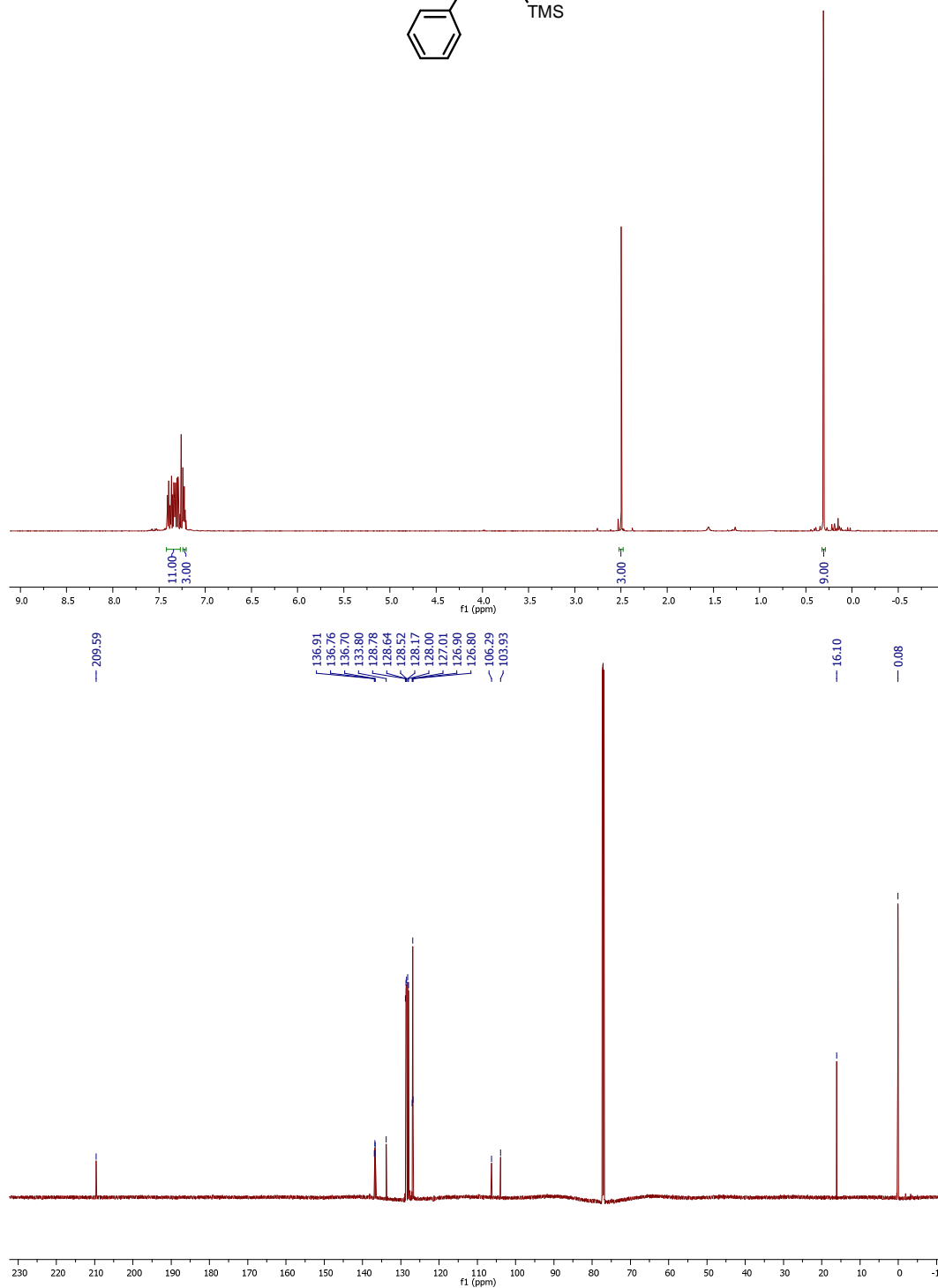
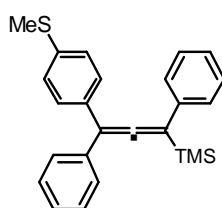


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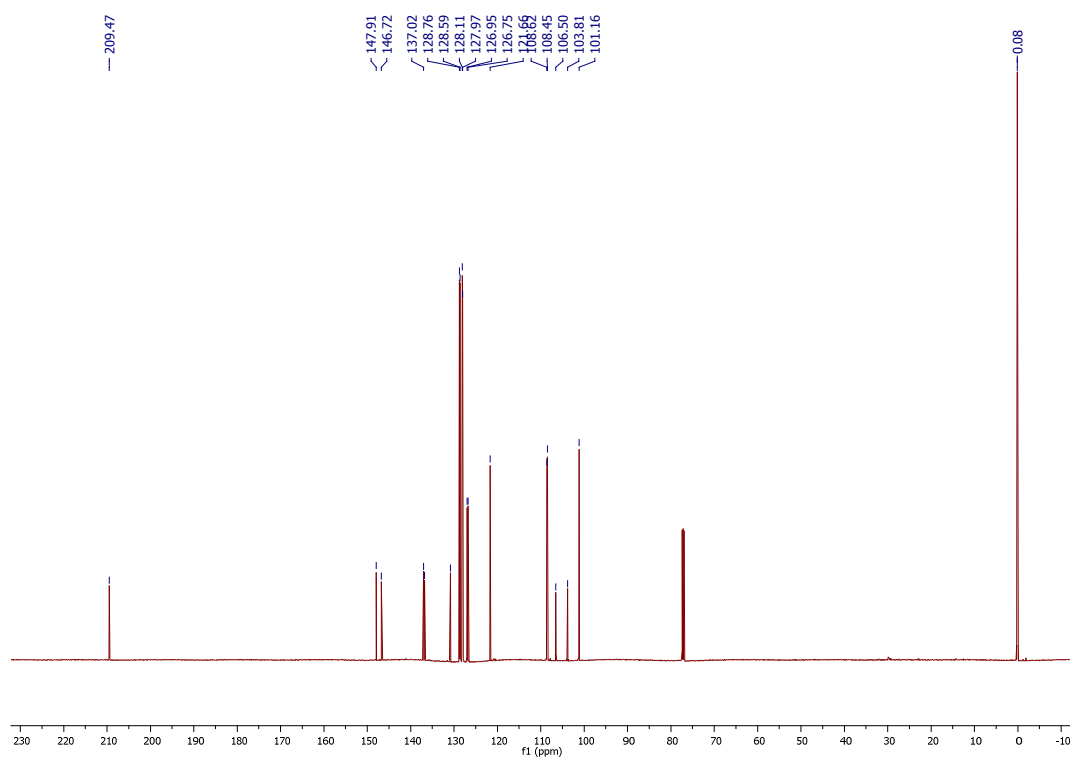
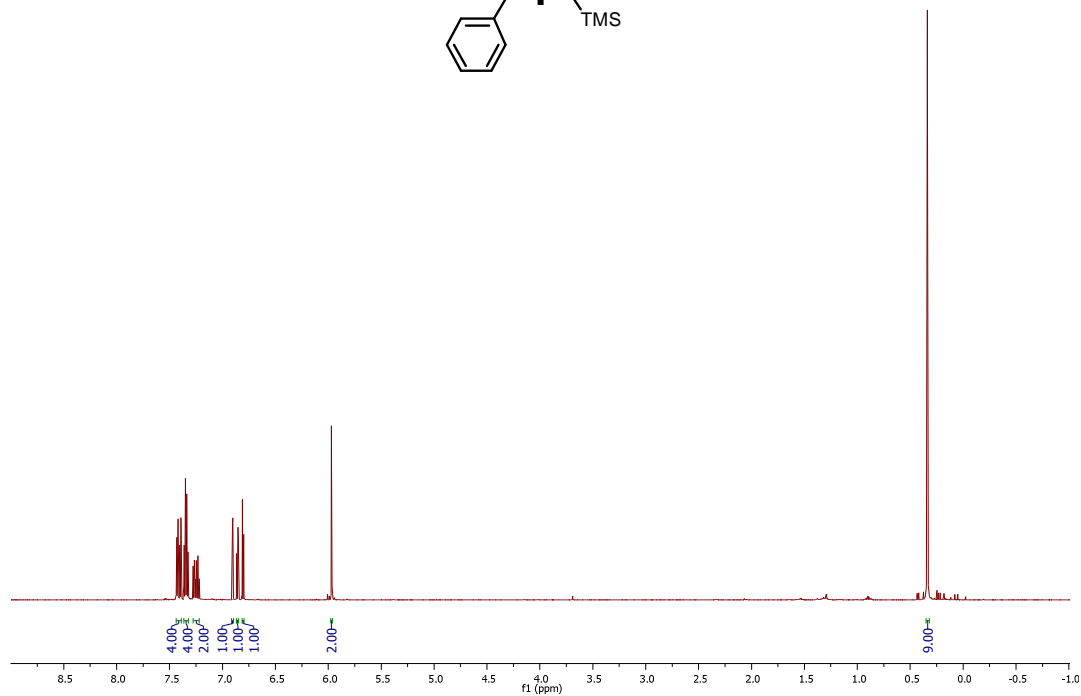
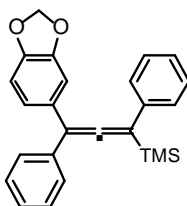




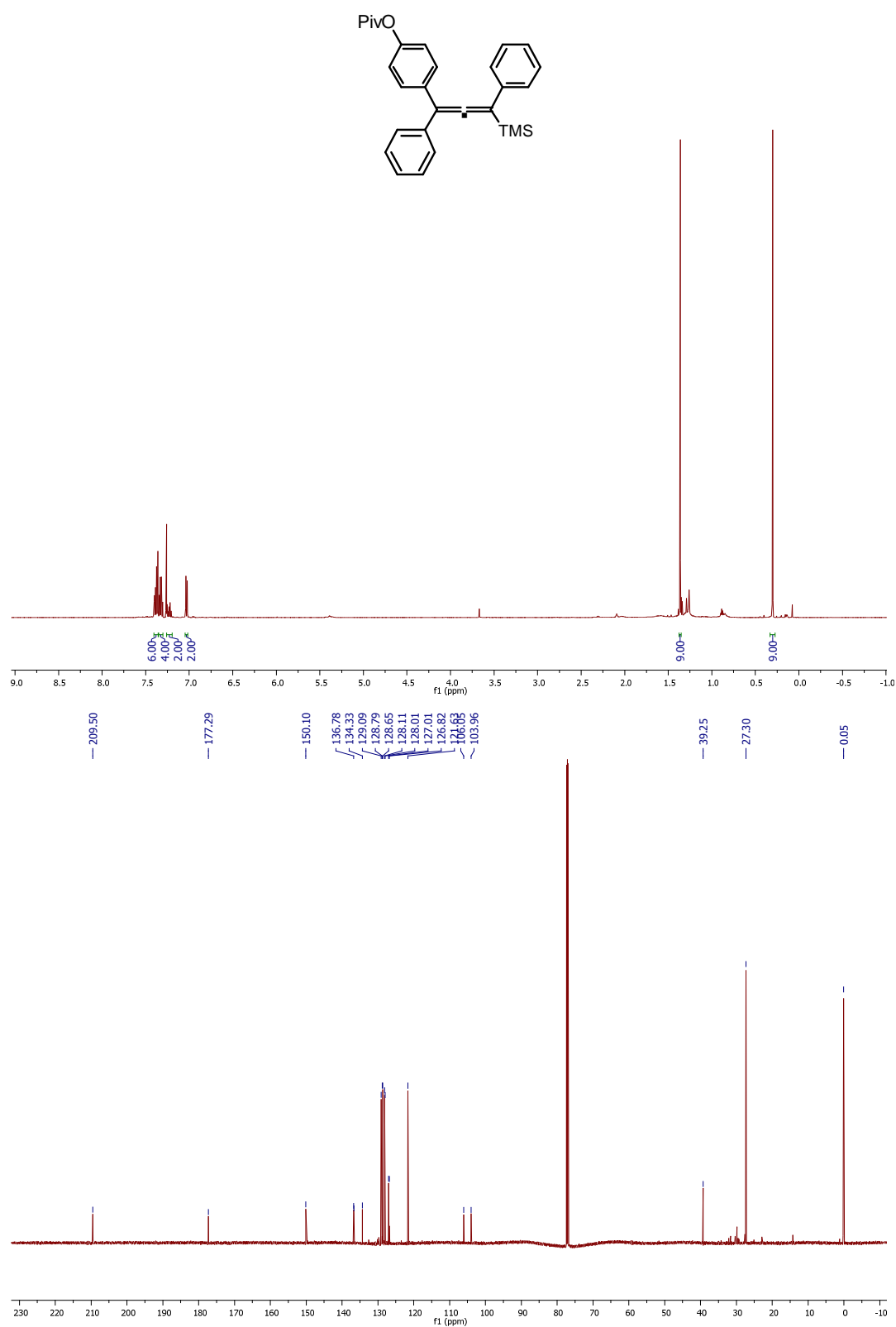
**Trimethyl(3-(4-(methylthio)phenyl)-1,3-diphenylpropa-1,2-dien-1-yl)silane (4g)**



**(3-(benzo[d][1,3]dioxol-5-yl)-1,3-diphenylpropa-1,2-dien-1-yl)trimethylsilane (4h)**

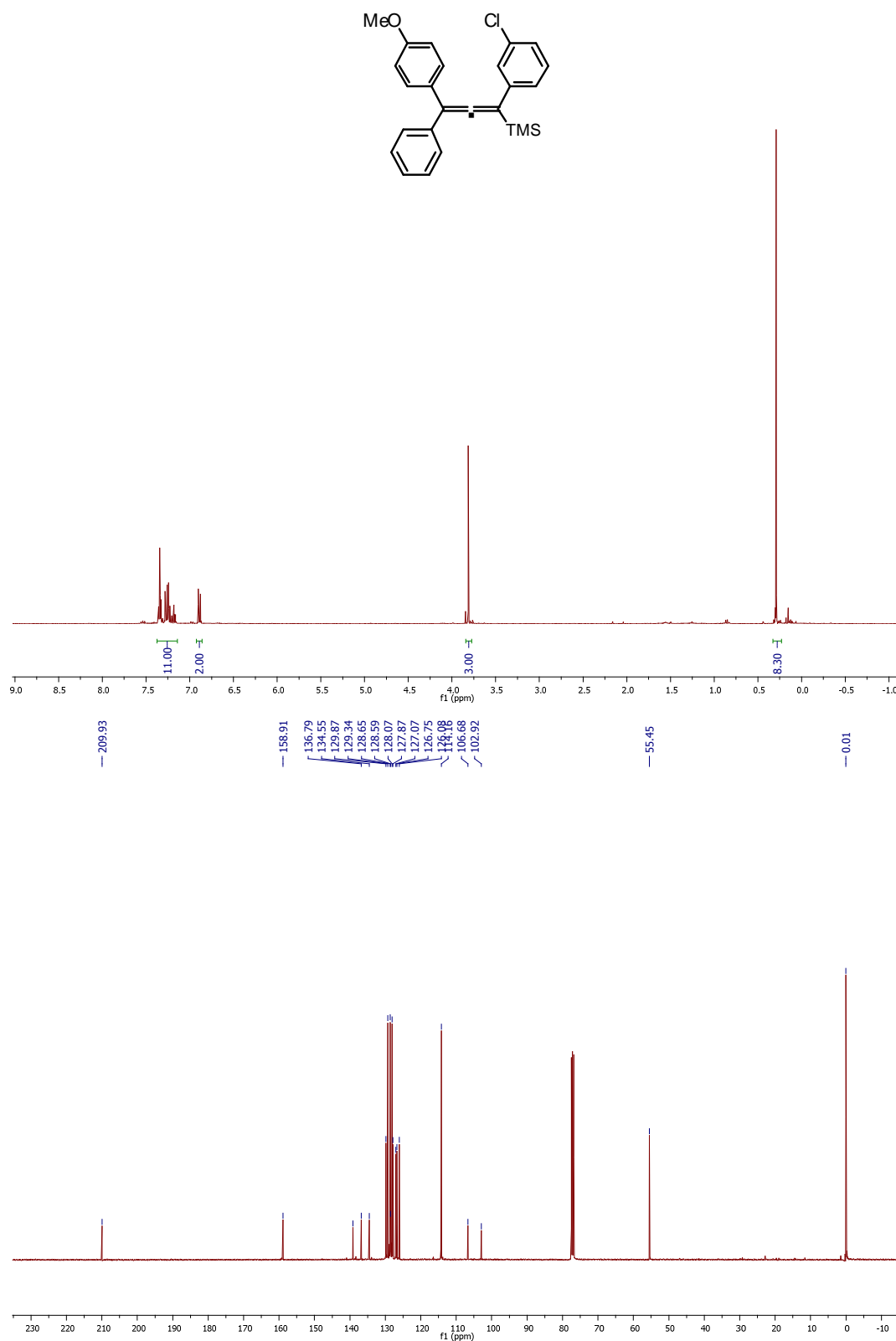


**4-(1,3-diphenyl-3-(trimethylsilyl)propa-1,2-dien-1-yl)phenyl pivalate (4i)**

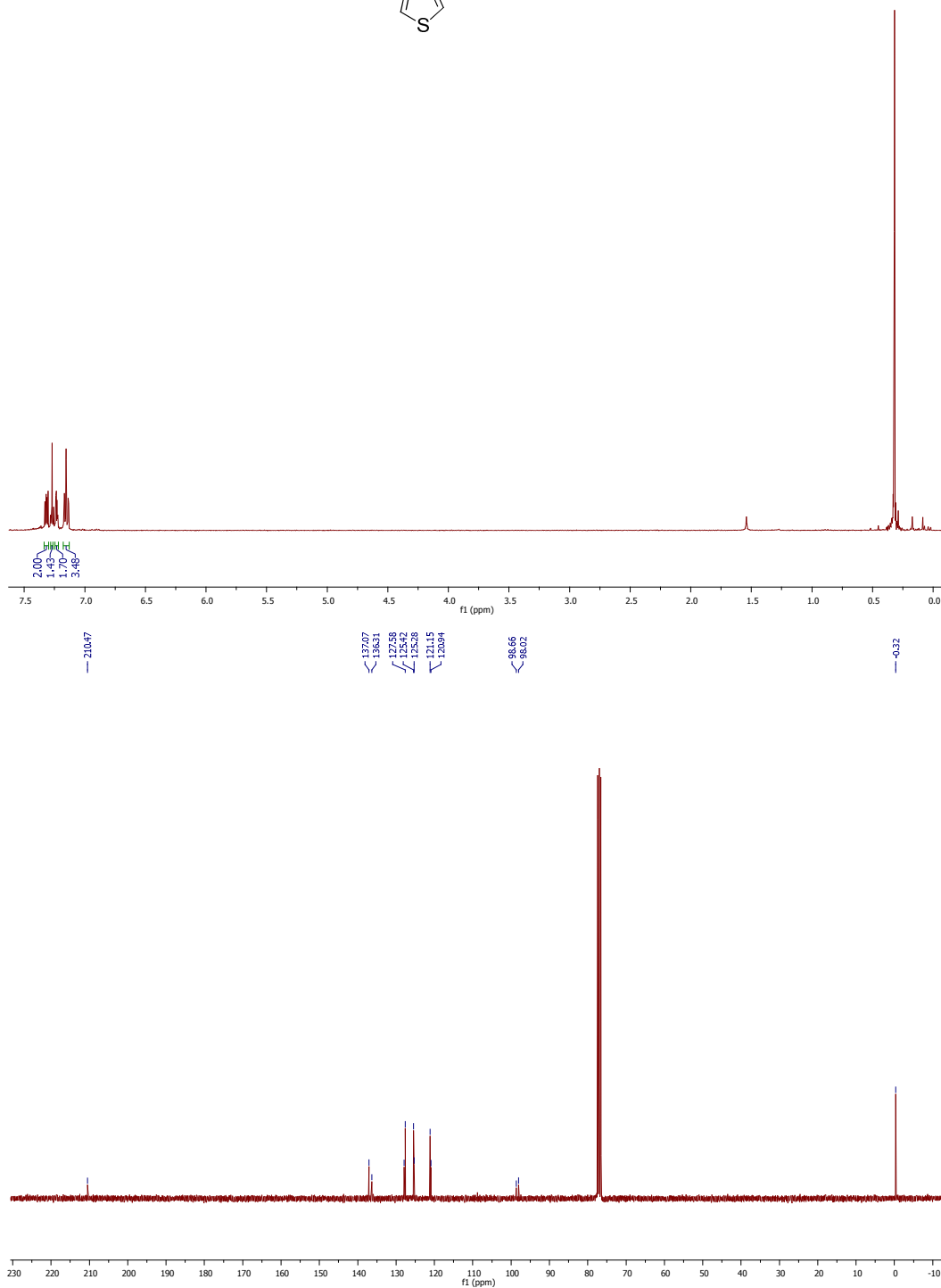
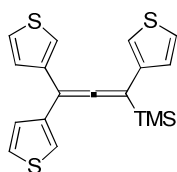


**(1-(3-chlorophenyl)-3-(4-methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl)trimethylsilane**

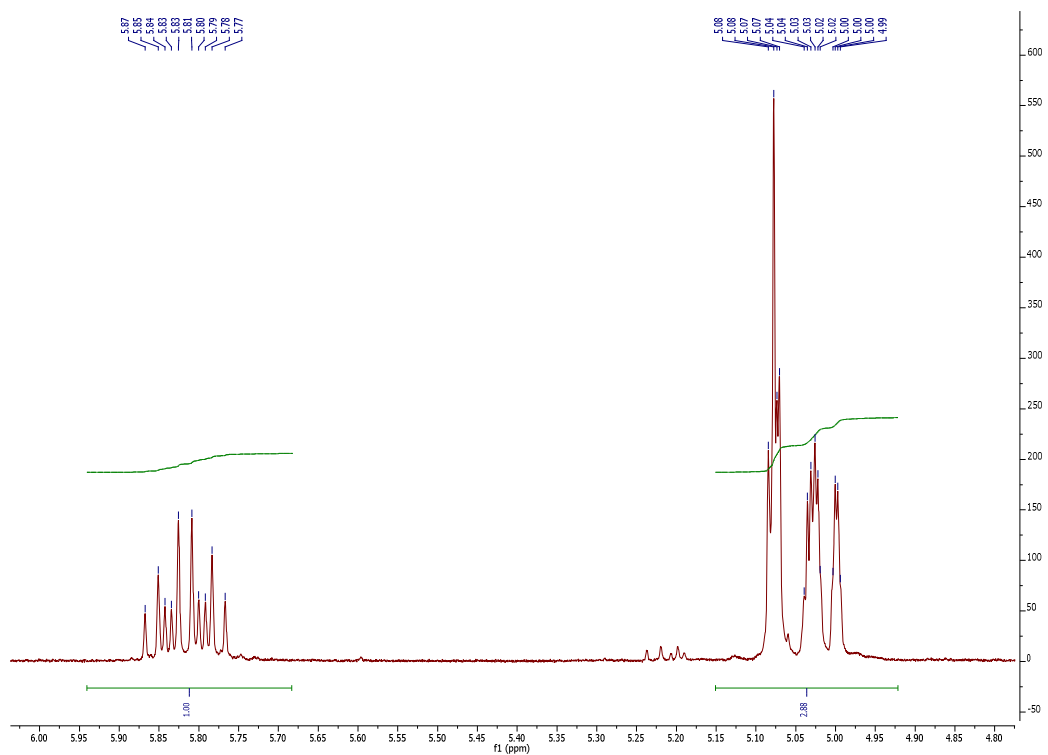
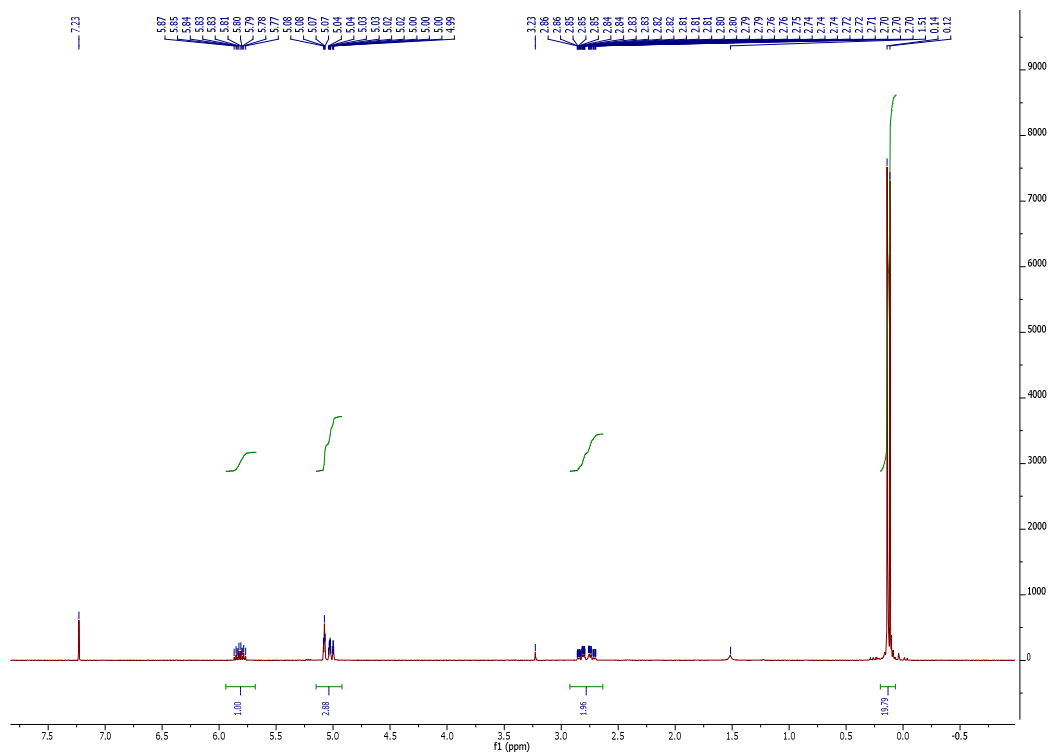
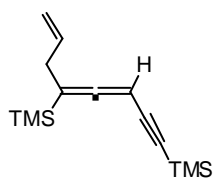
**(4j)**

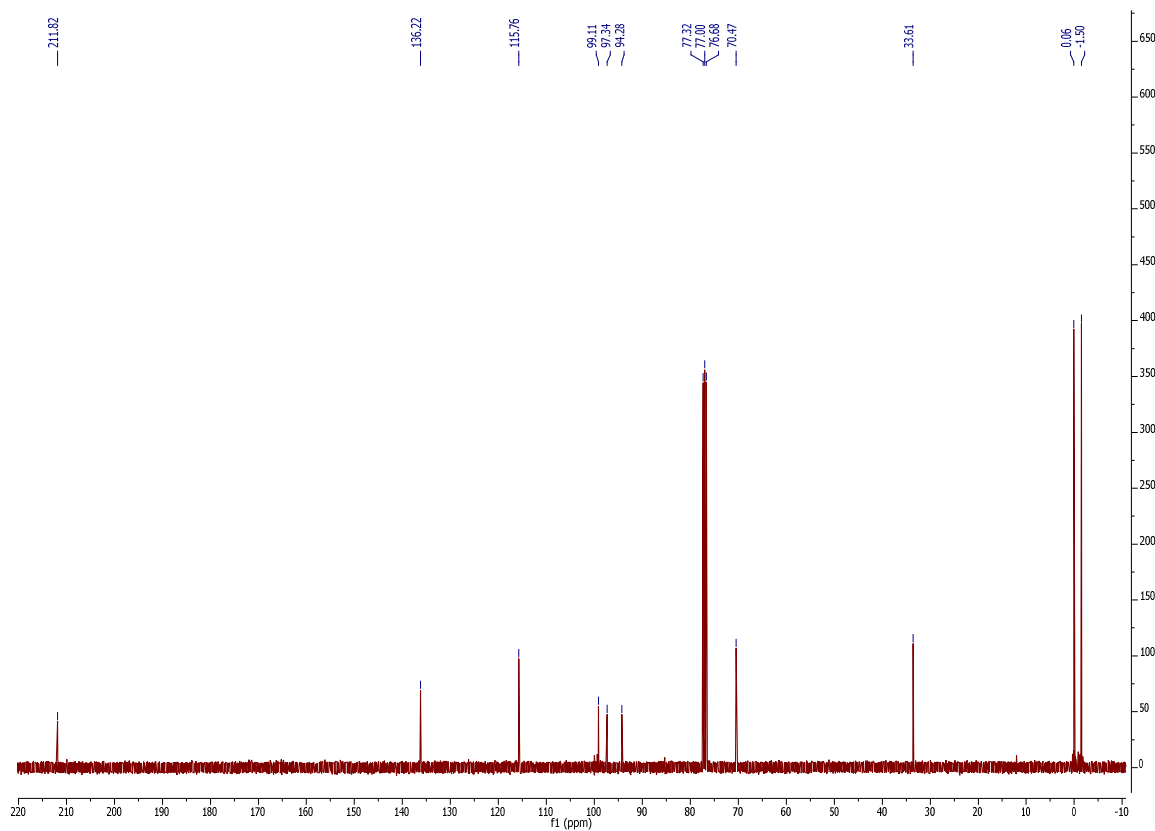
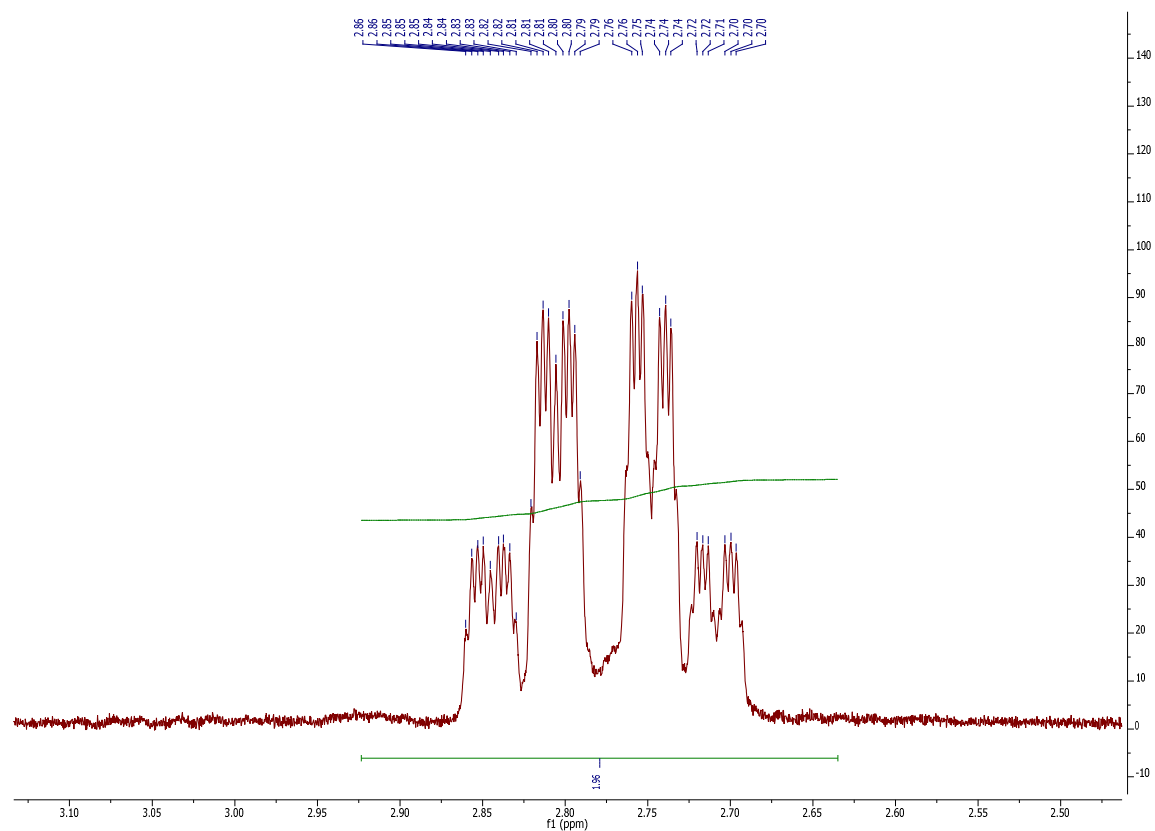


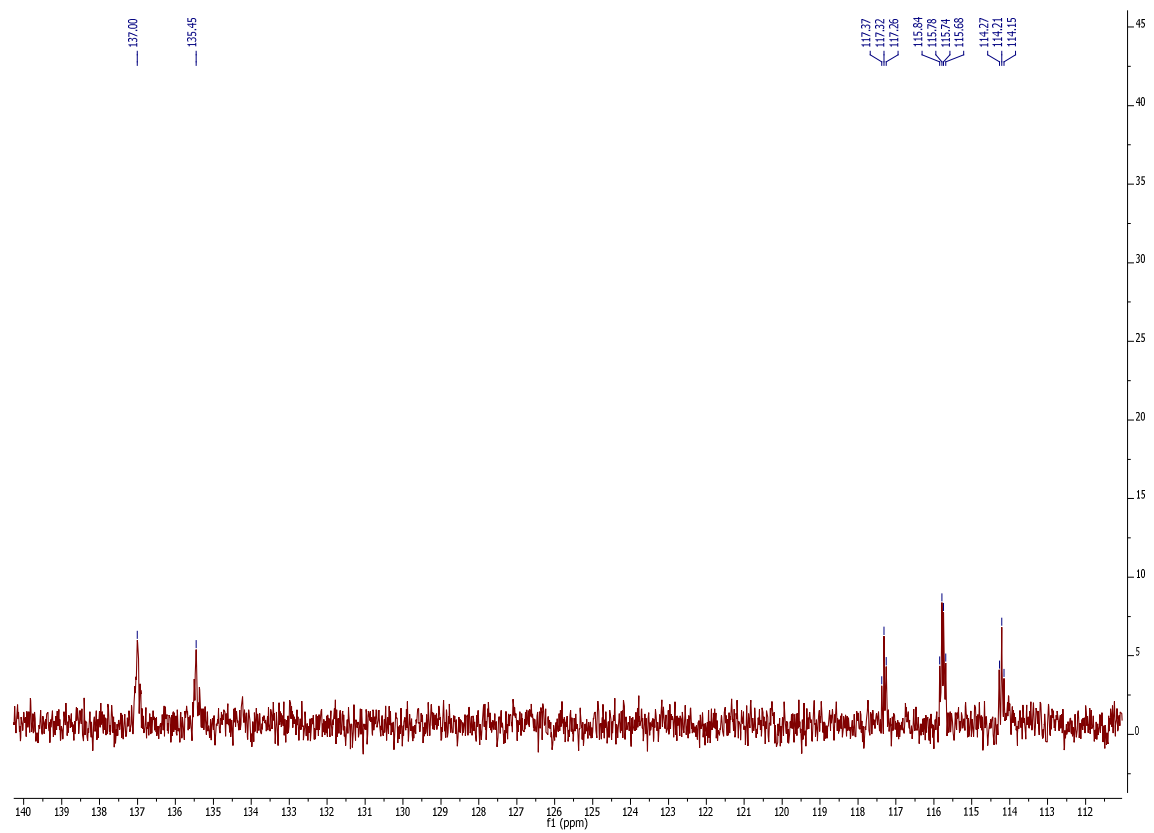
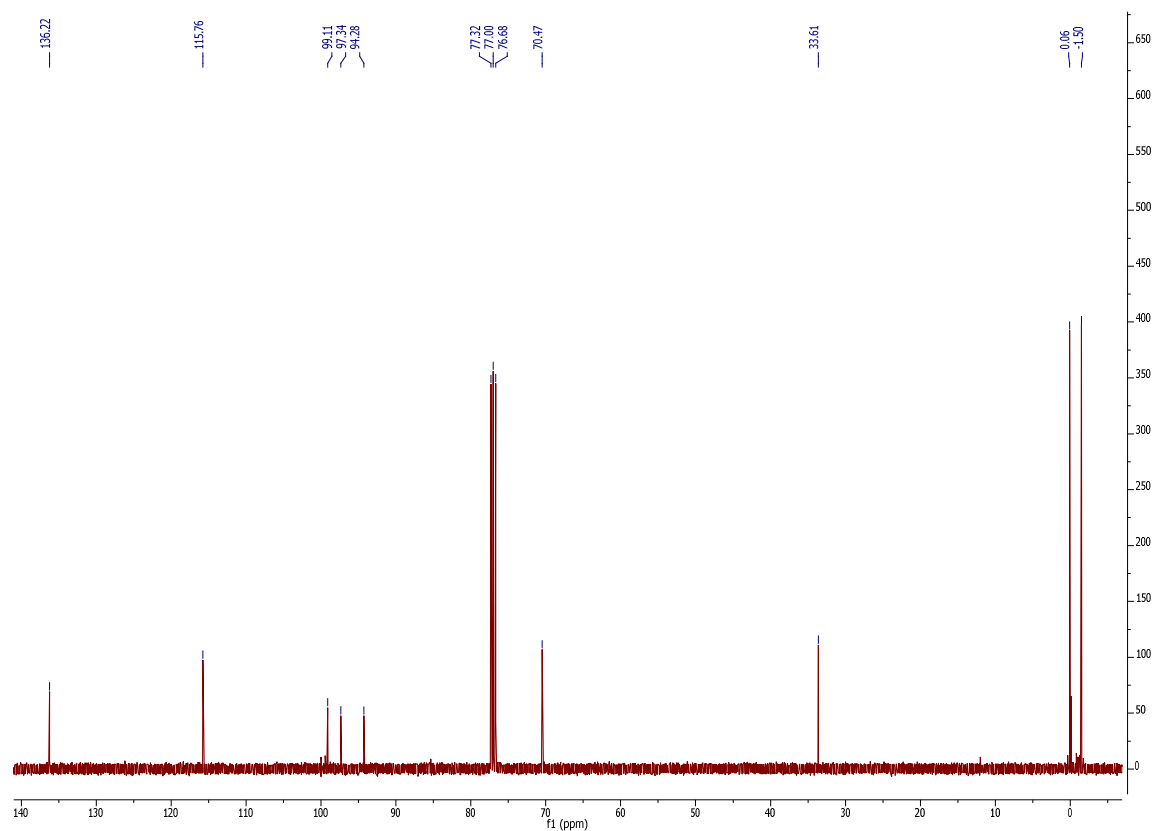
**Trimethyl(1,3,3-tri(thiophen-3-yl)propa-1,2-dien-1-yl)silane (4k)**



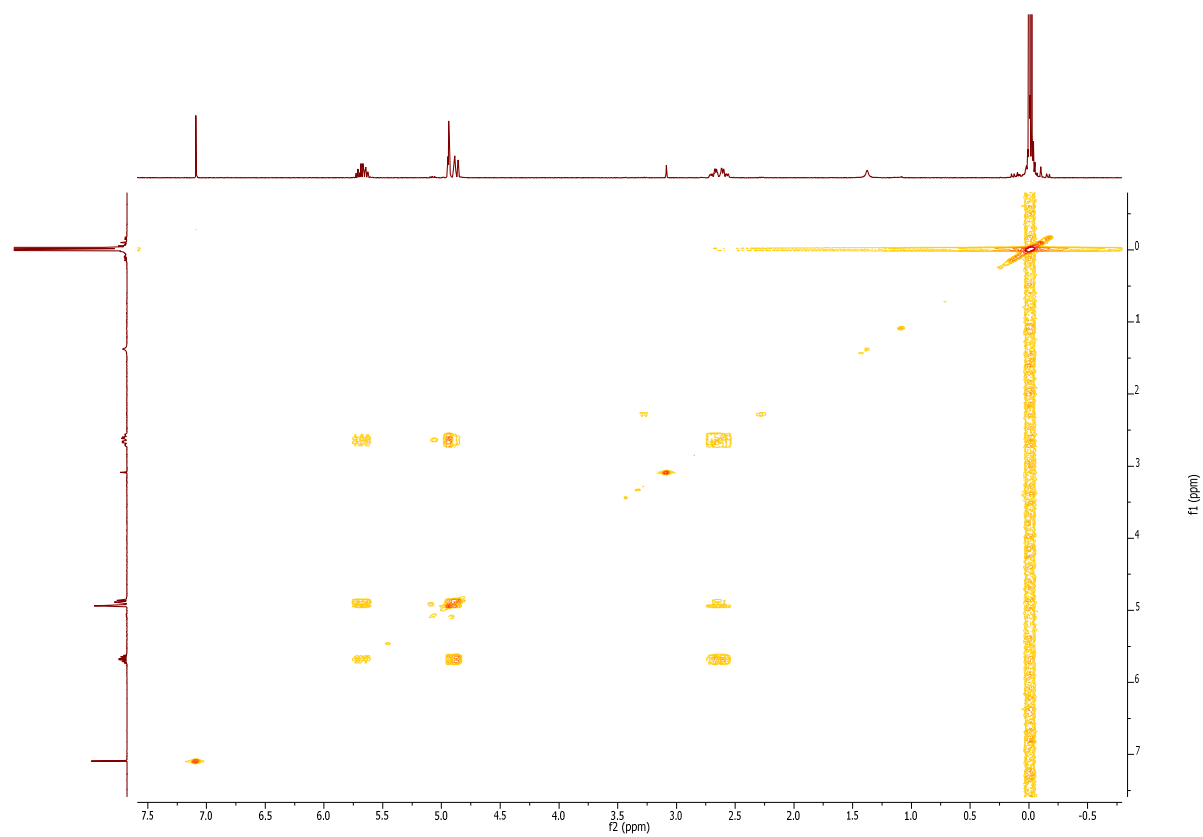
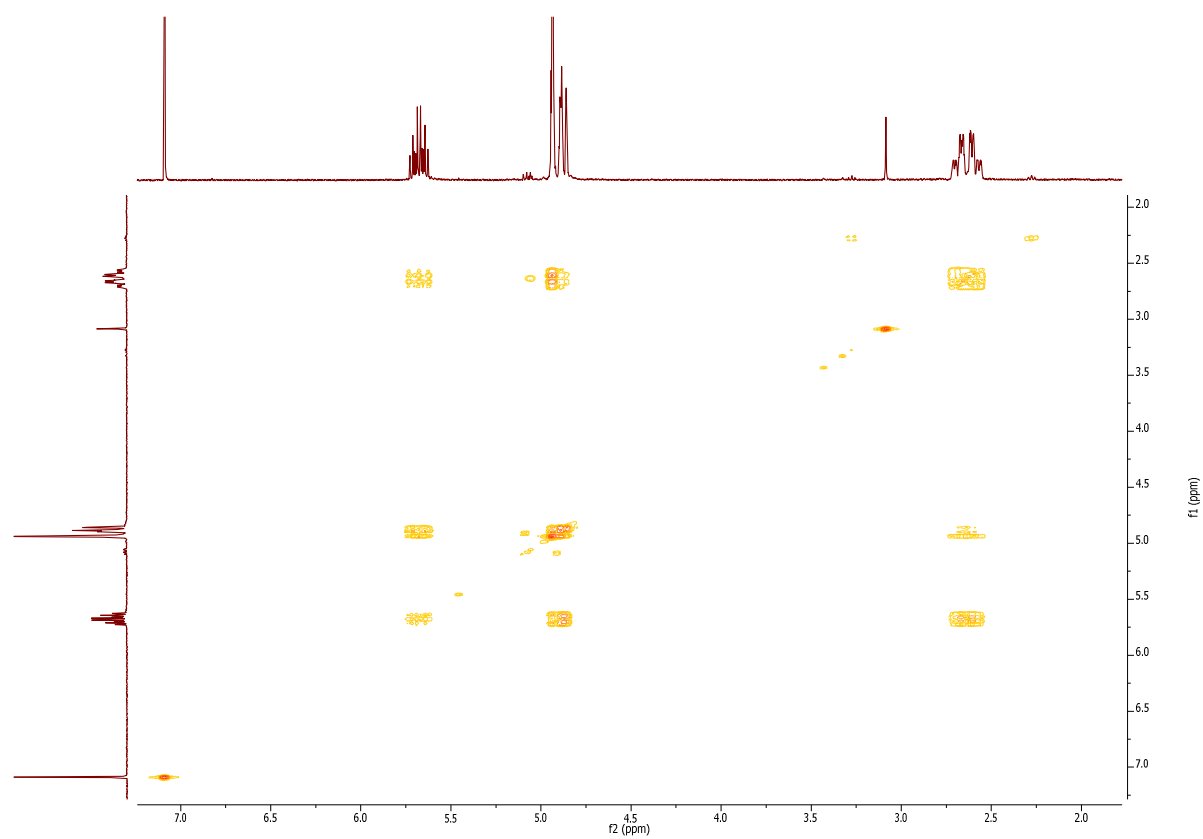
octa-3,4,7-trien-1-yne-1,5-diylbis(trimethylsilane) (7)

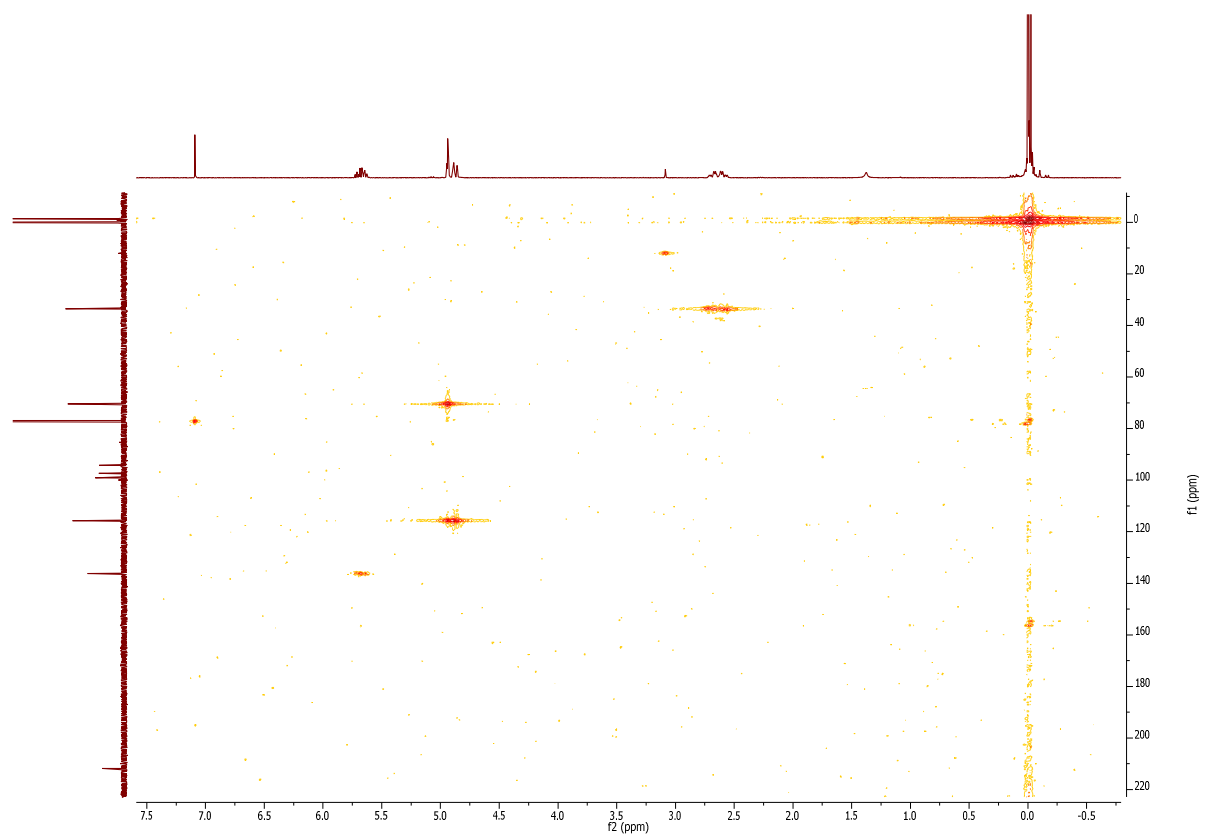
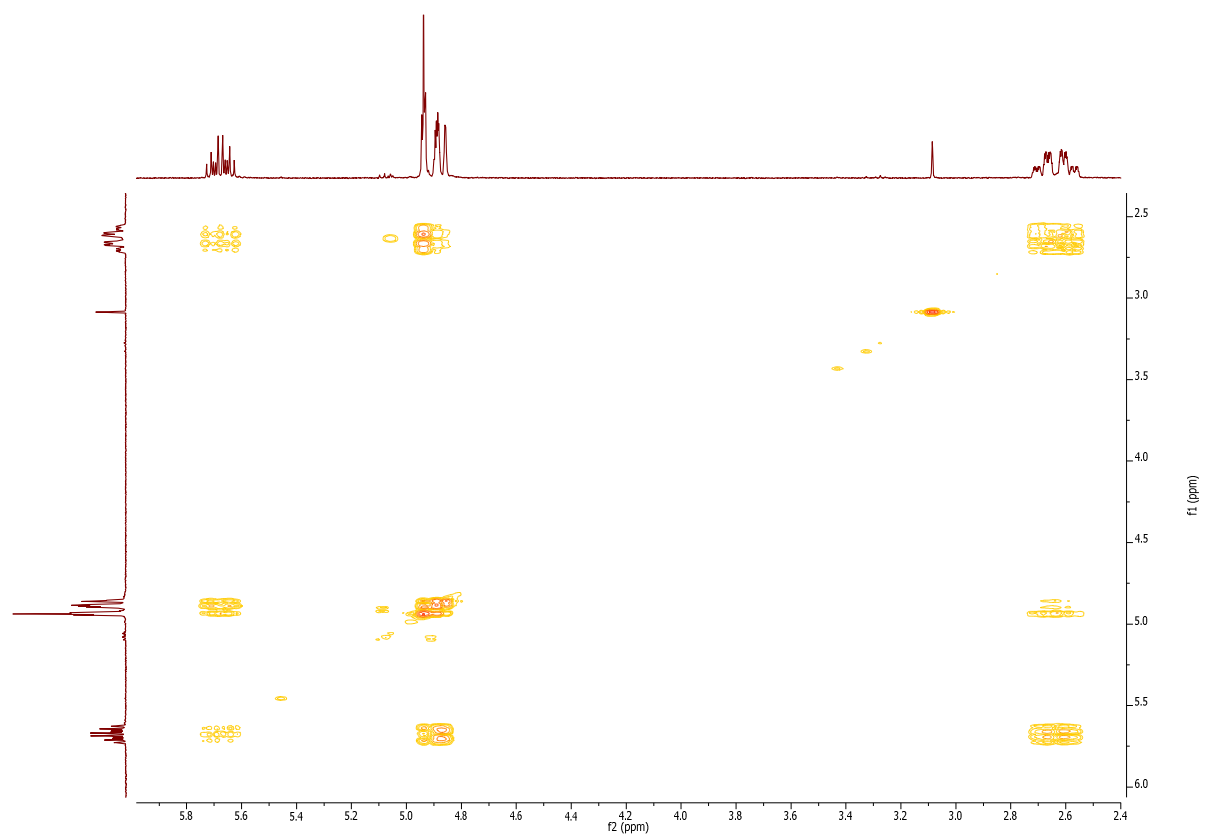


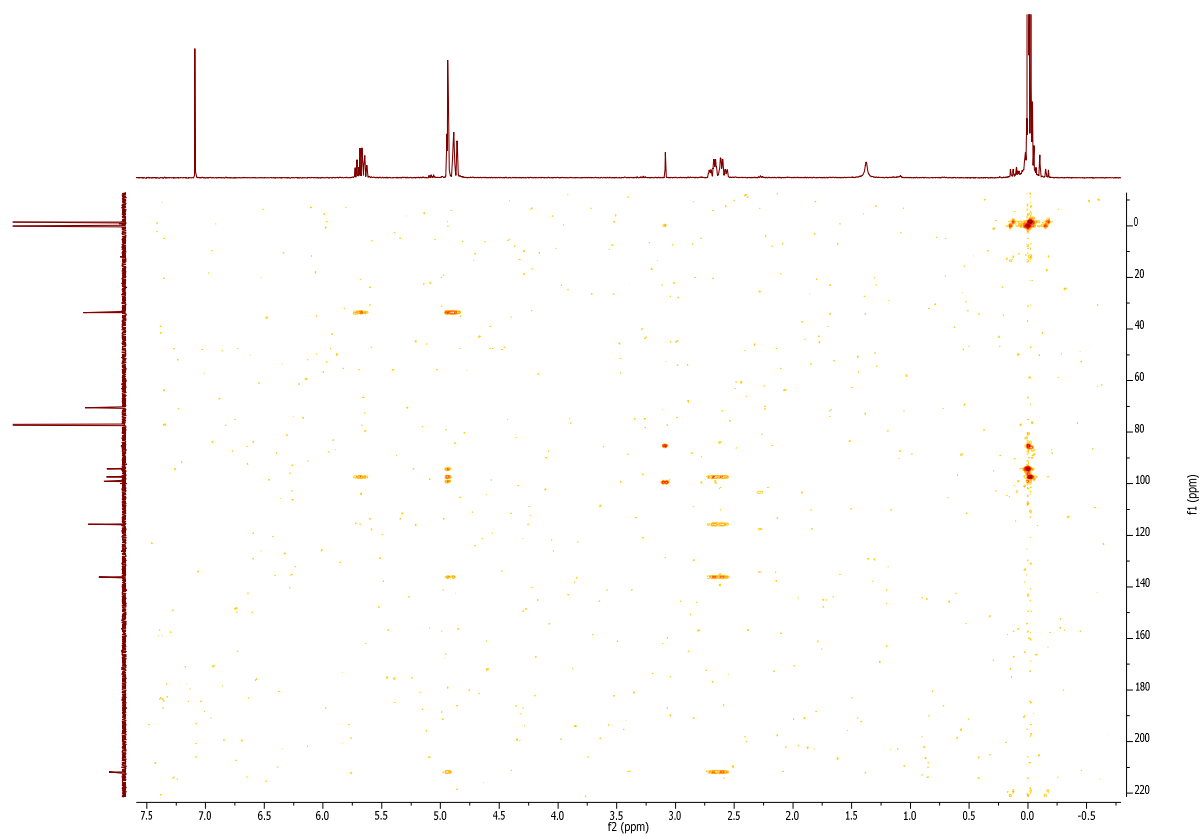
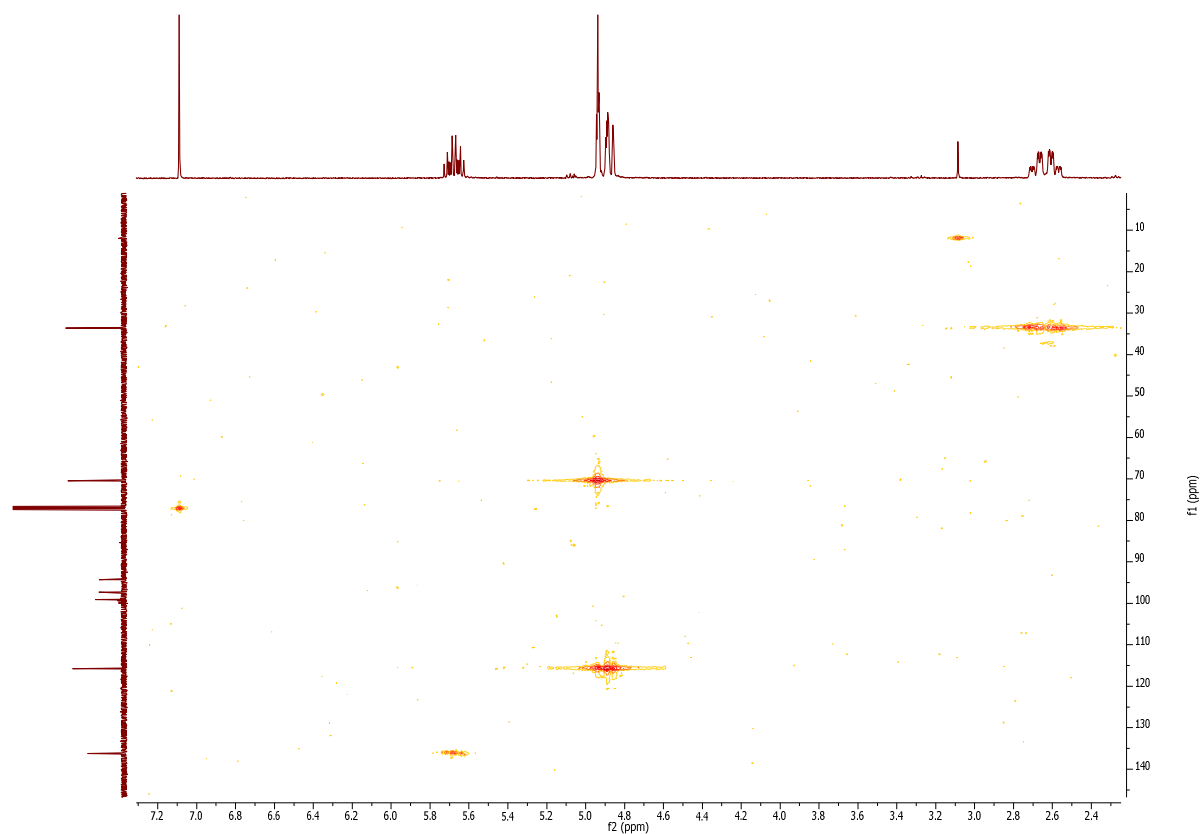


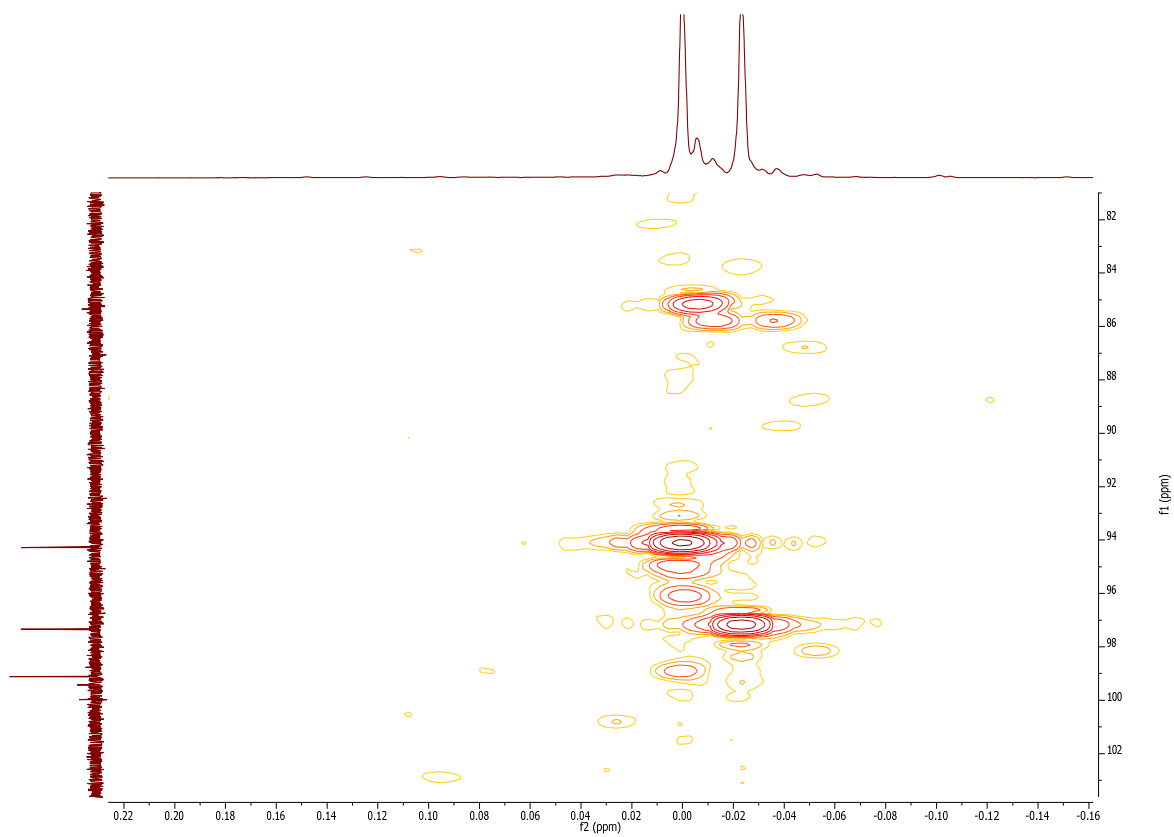
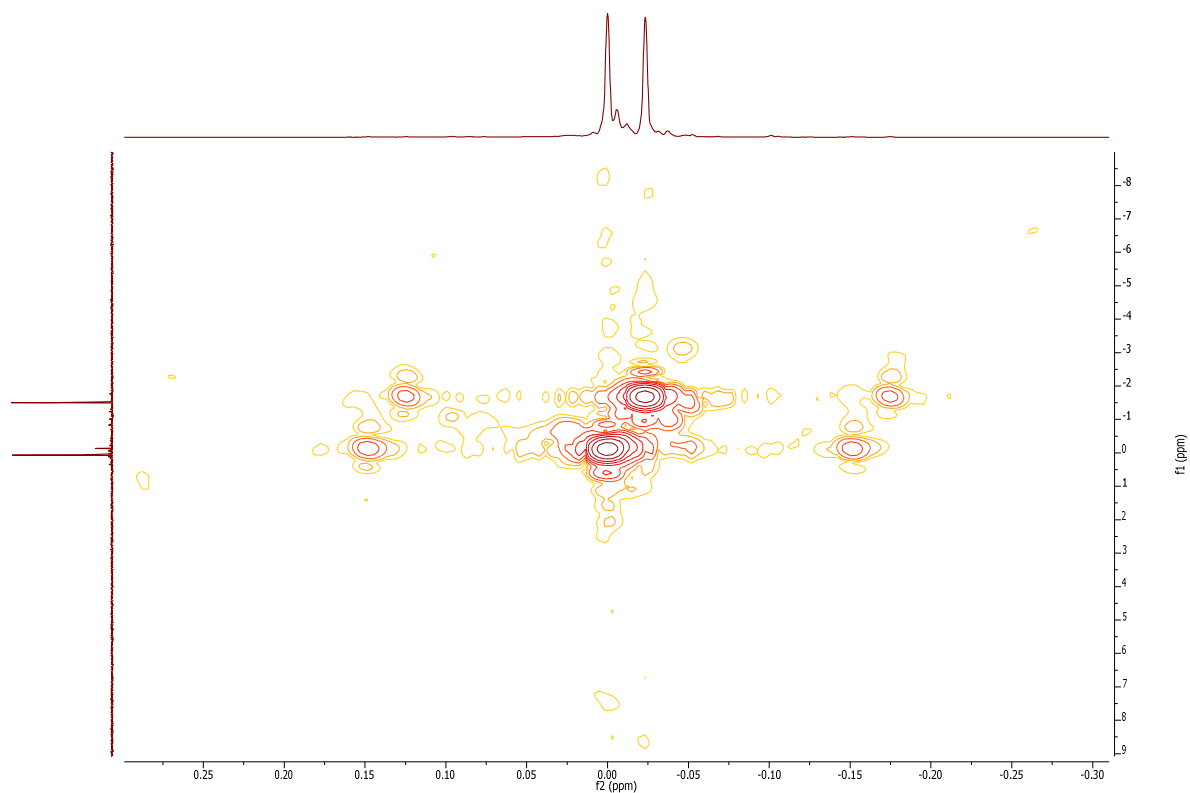


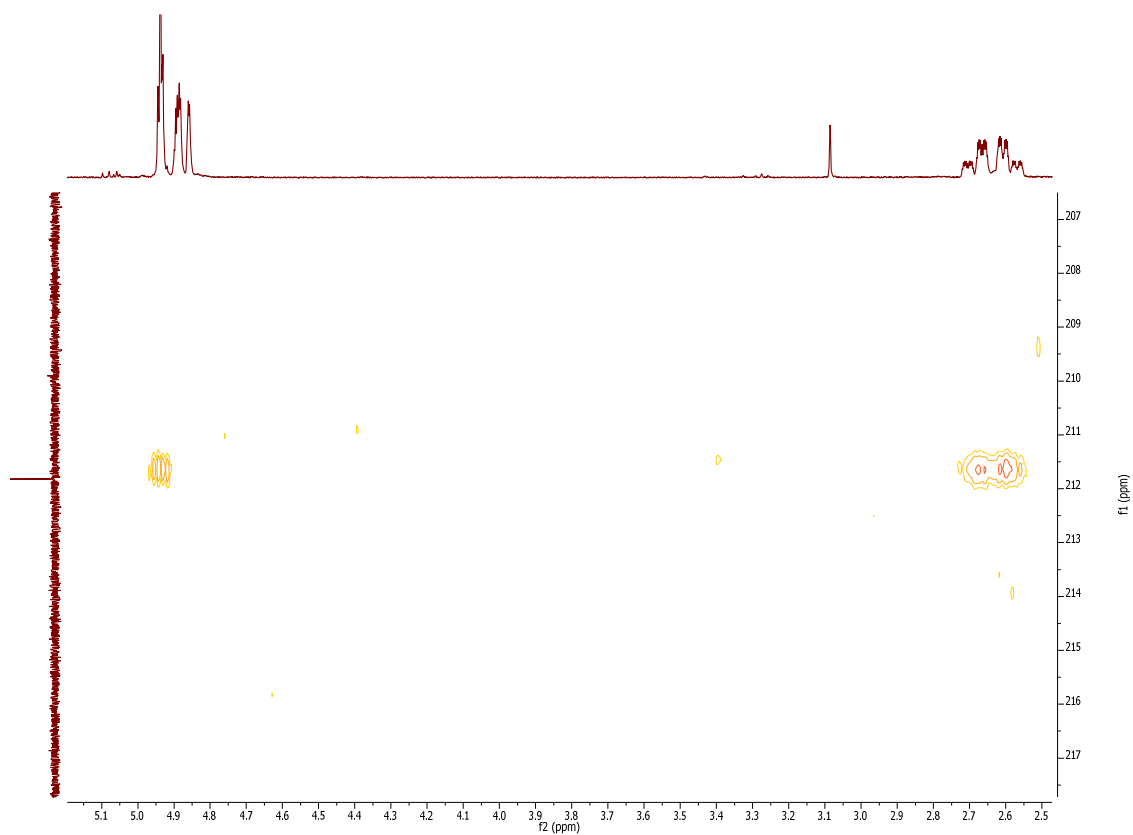
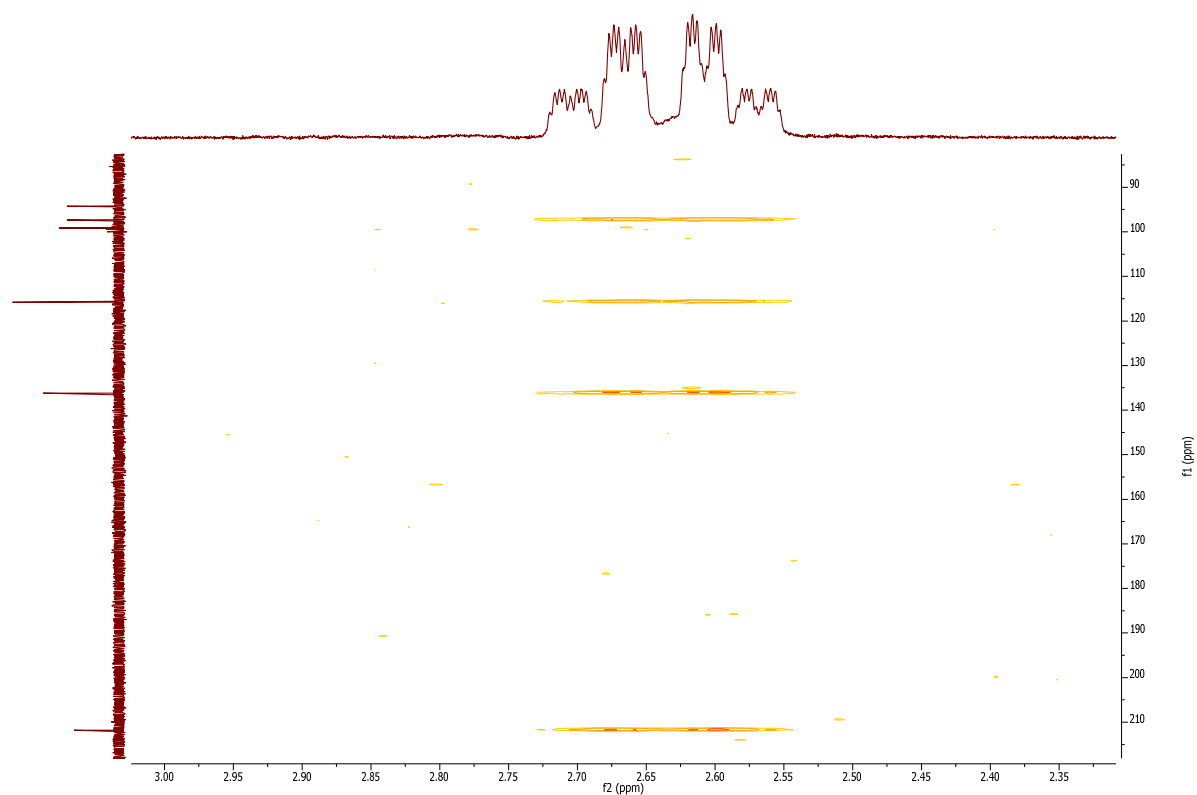


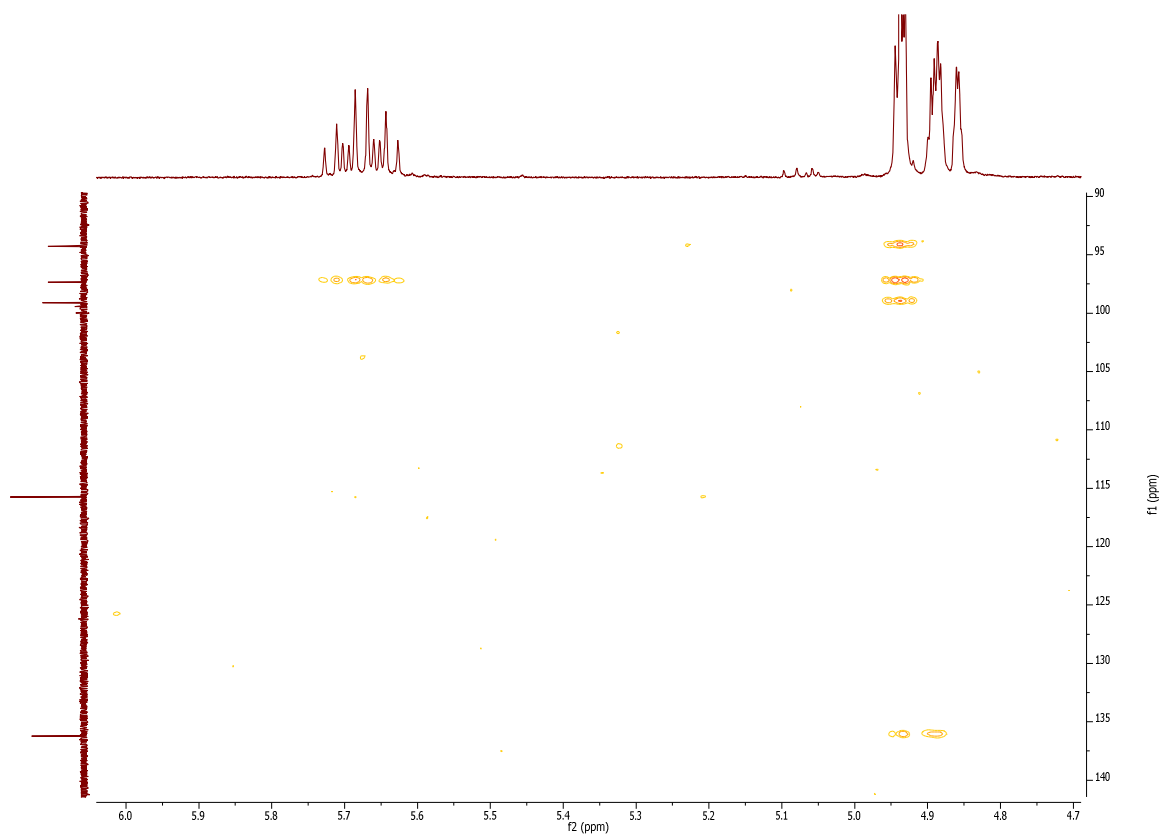
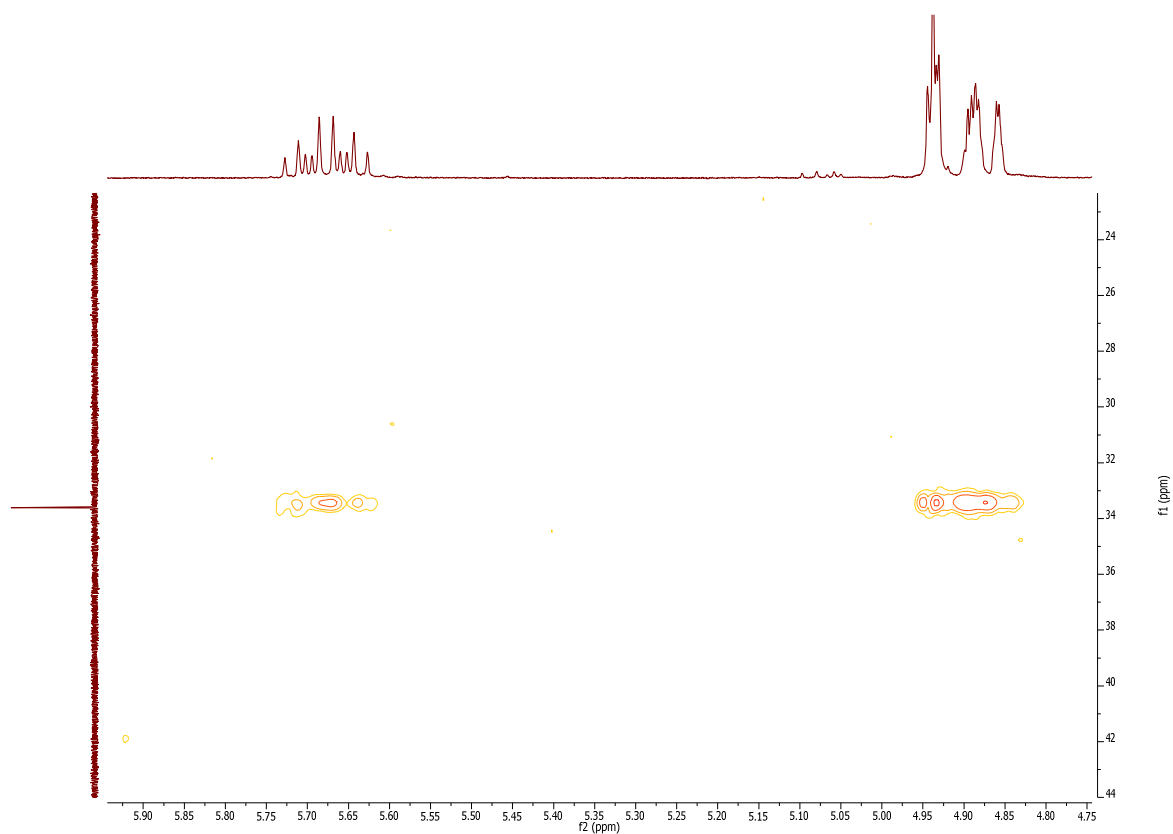




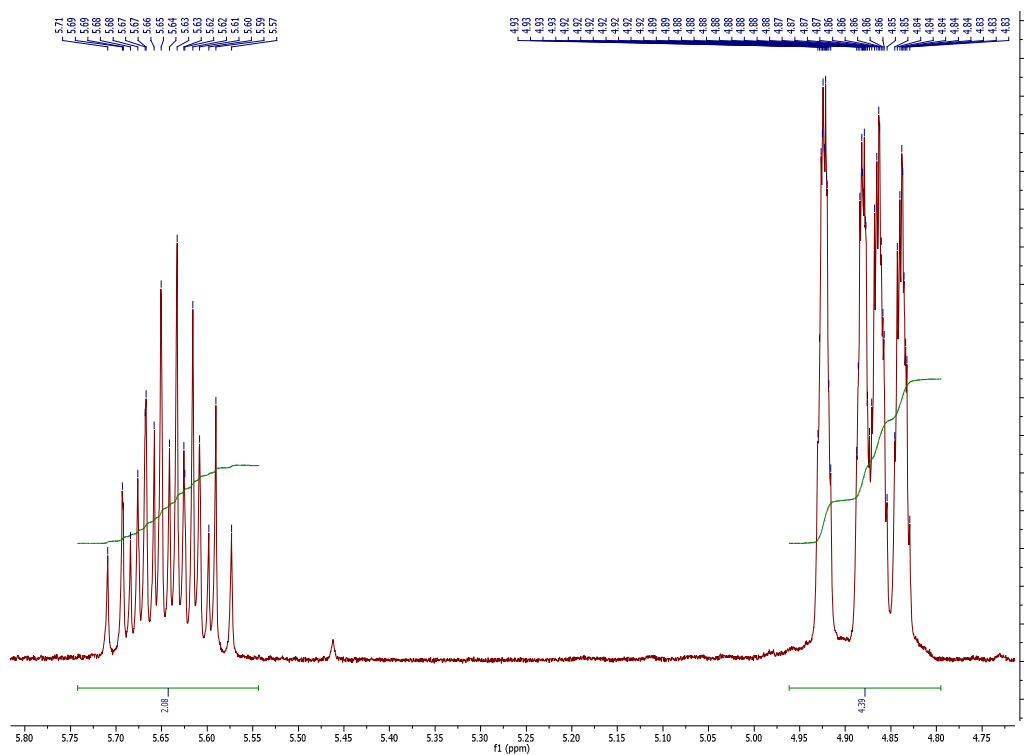
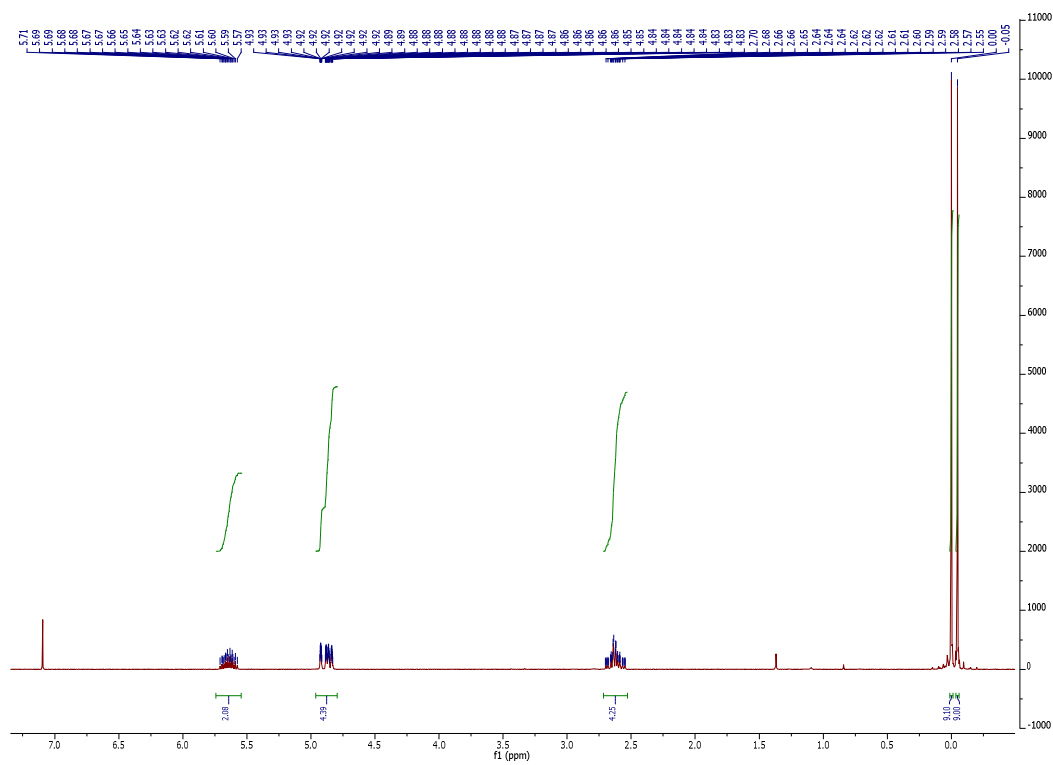
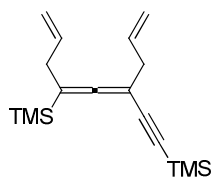


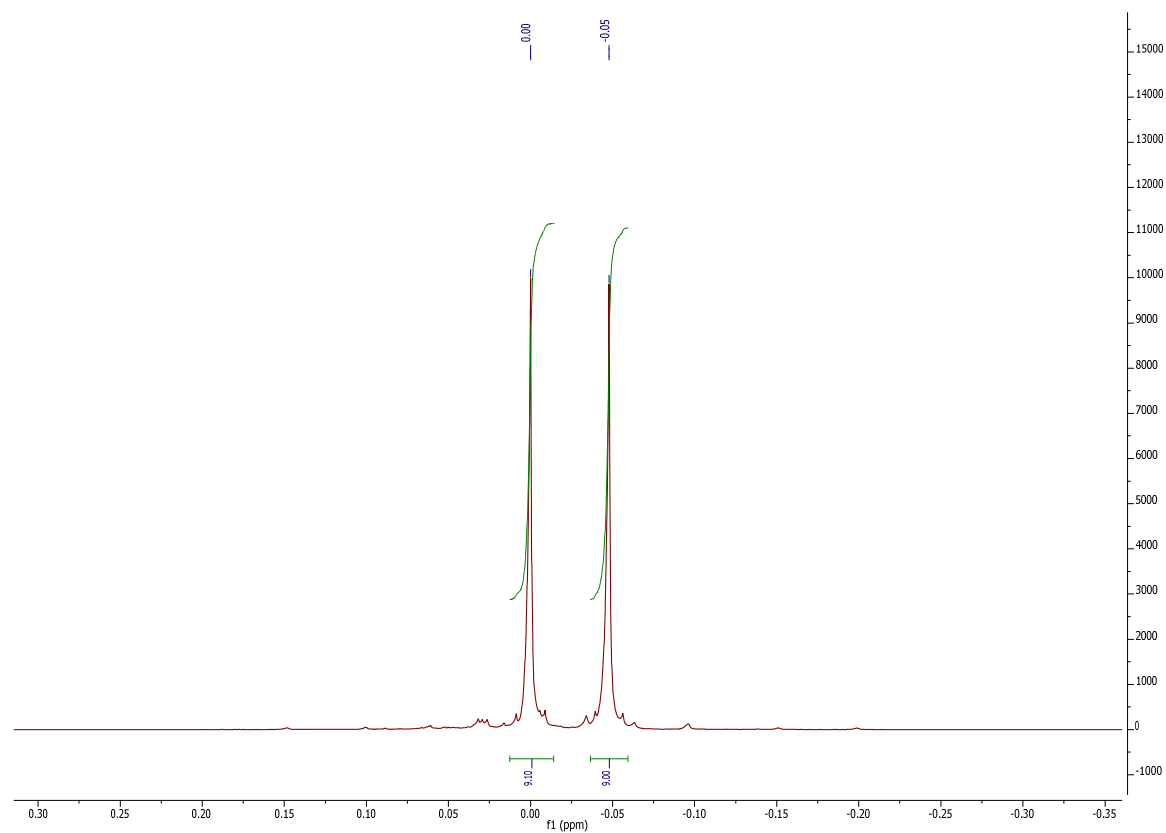
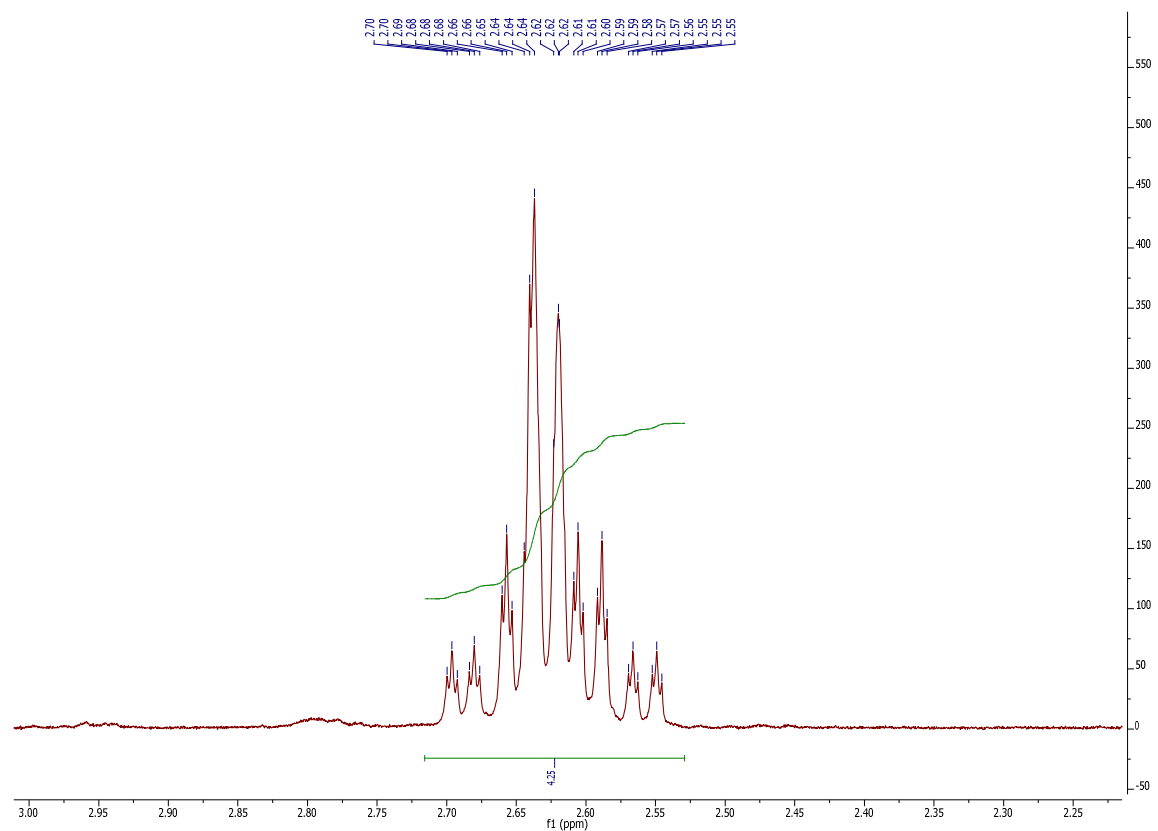




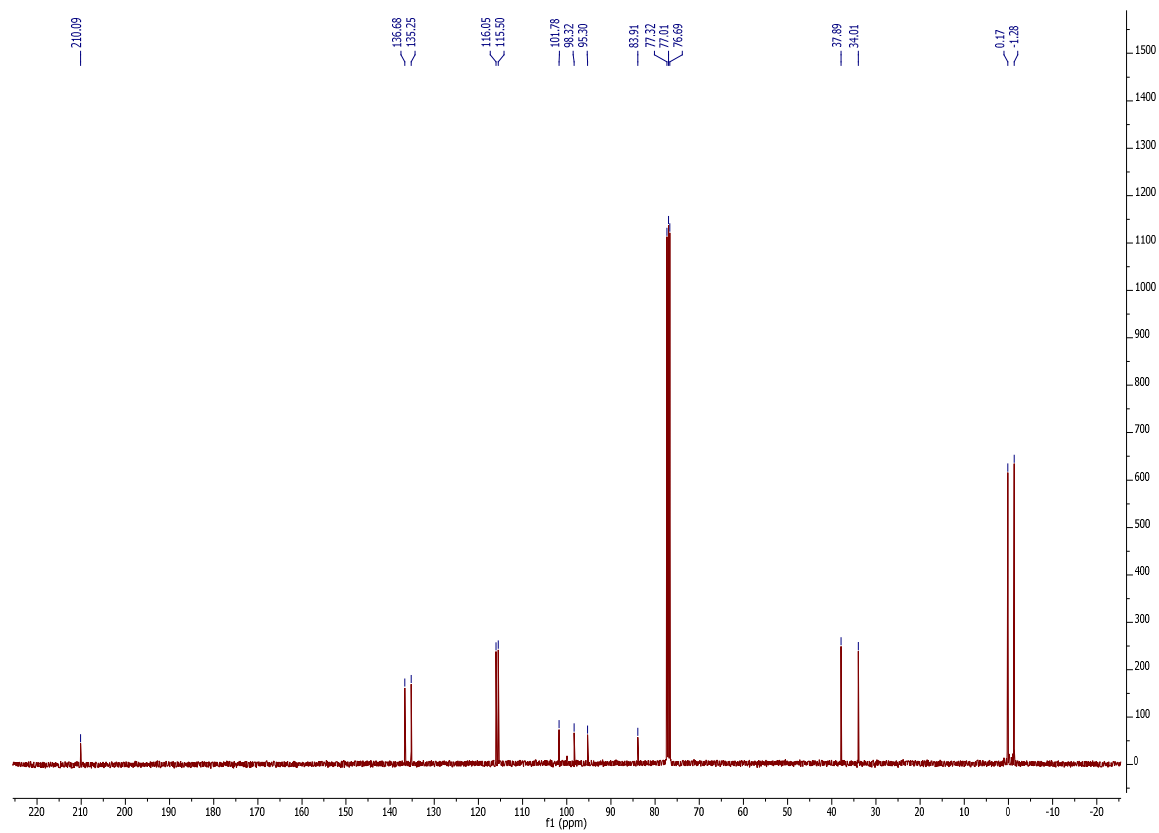
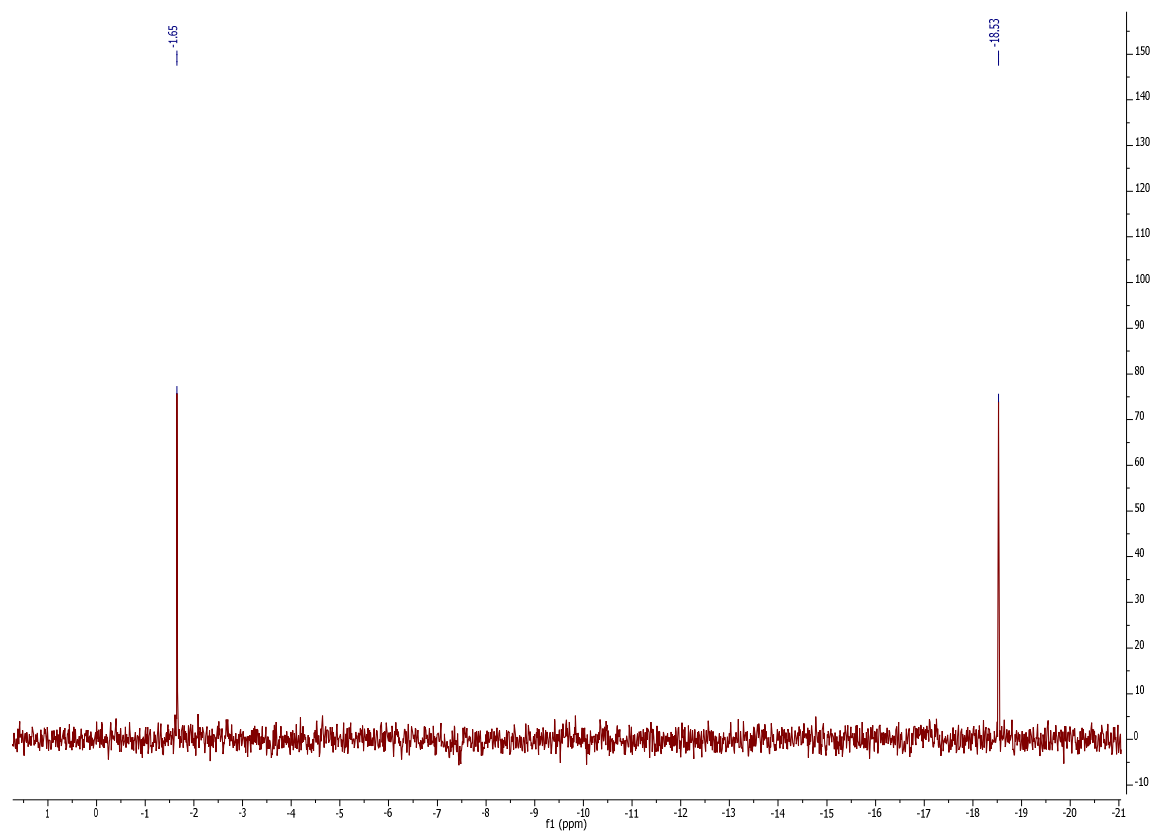


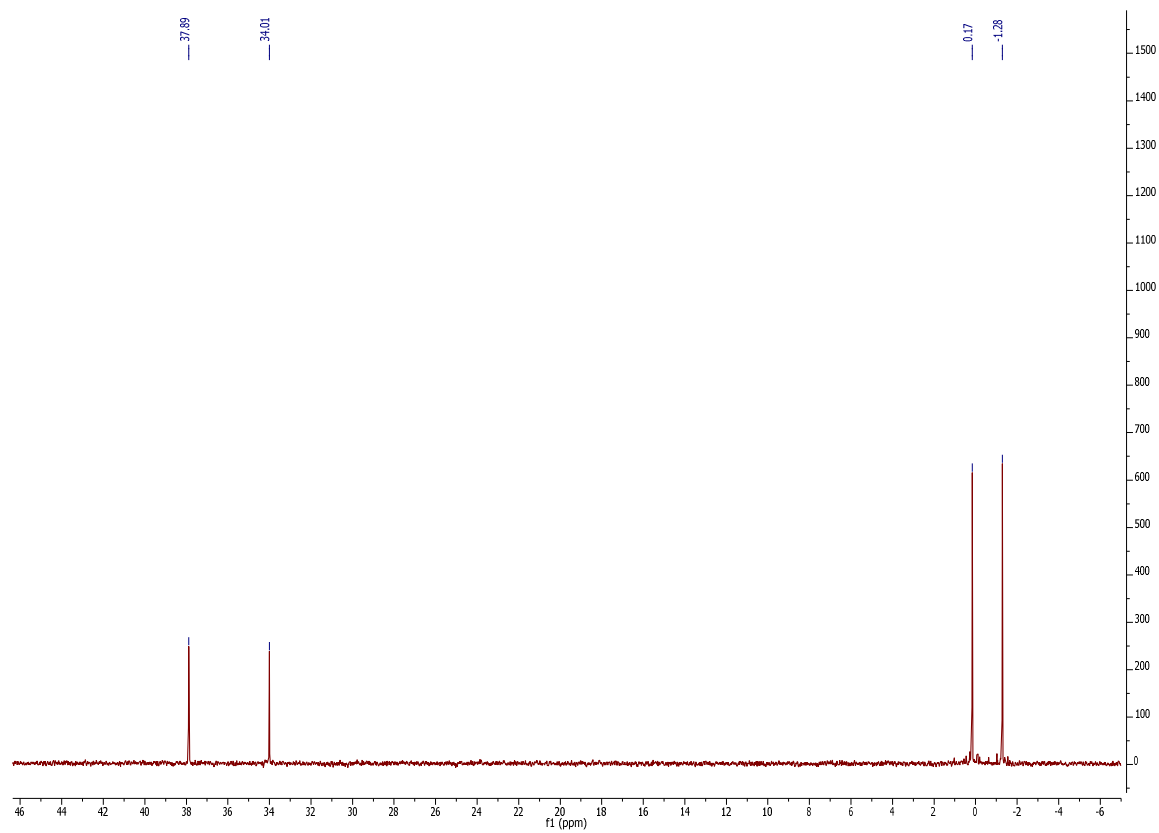
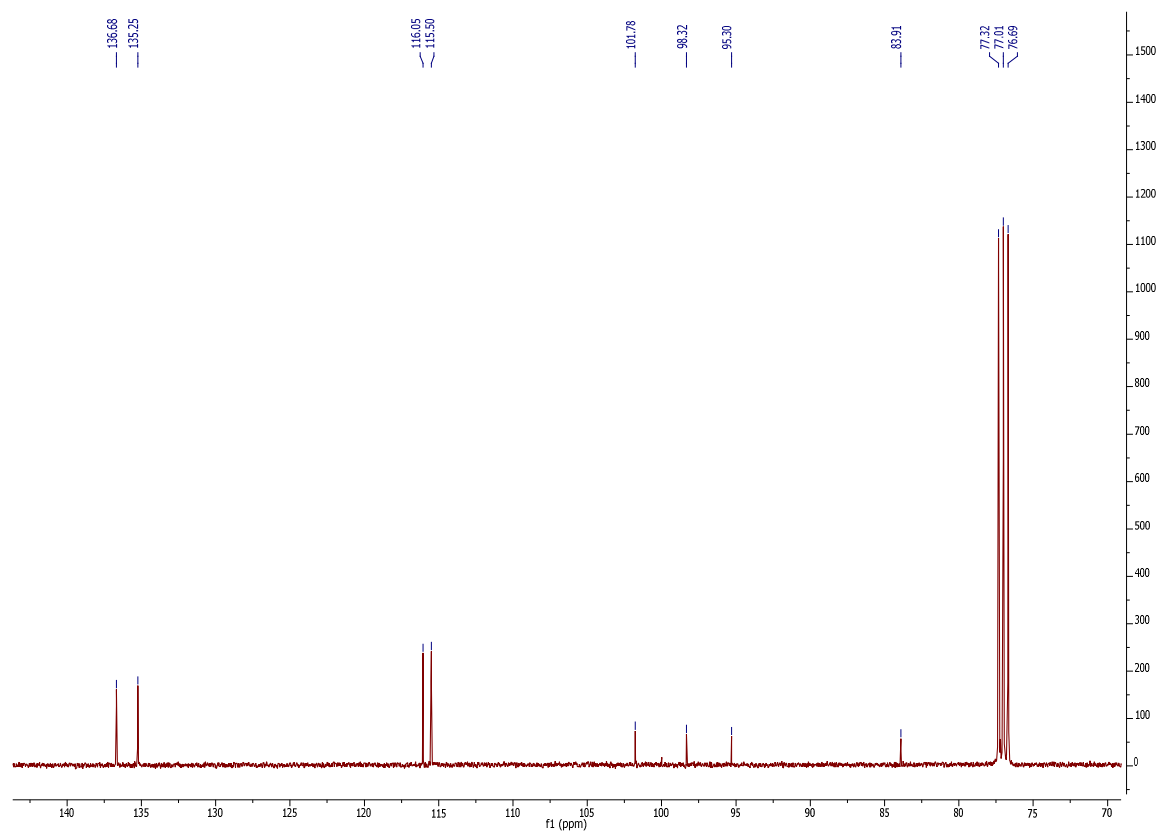
**(3-allylocta-3,4,7-trien-1-yne-1,5-diyl)bis(trimethylsilane) (8)**

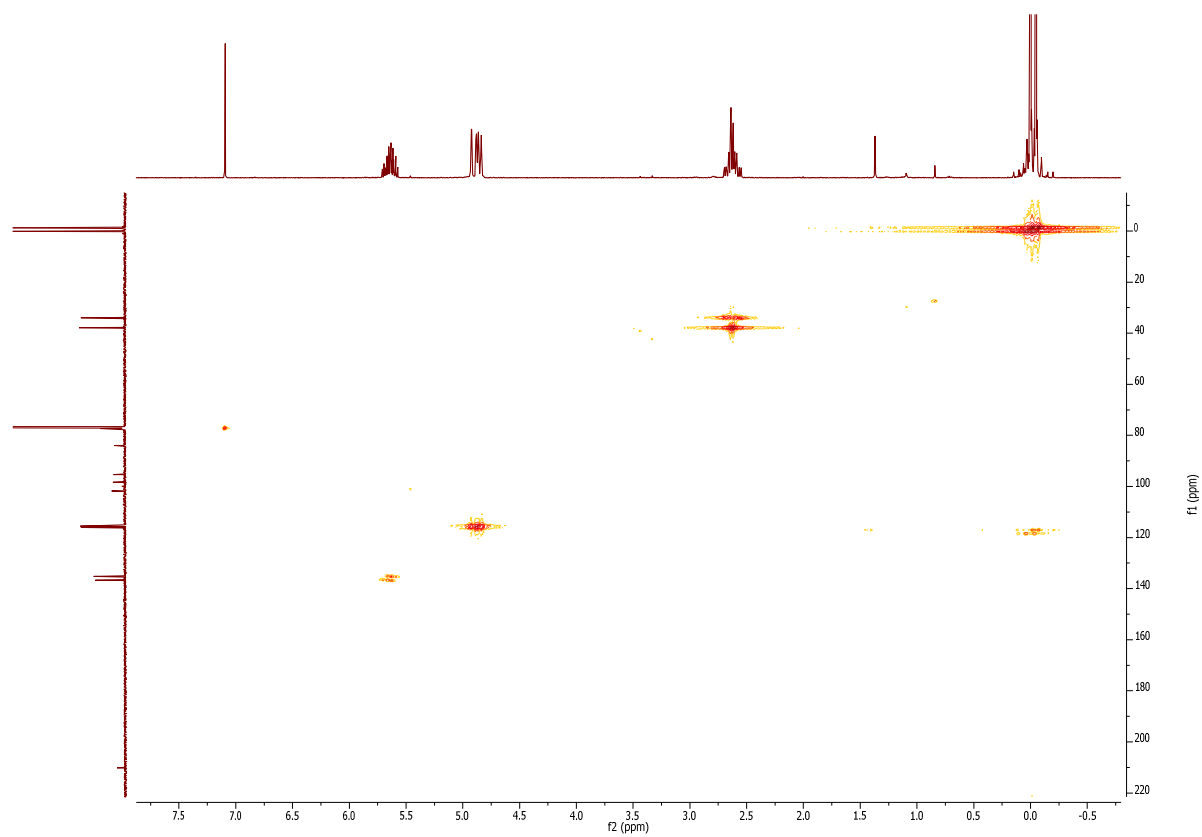
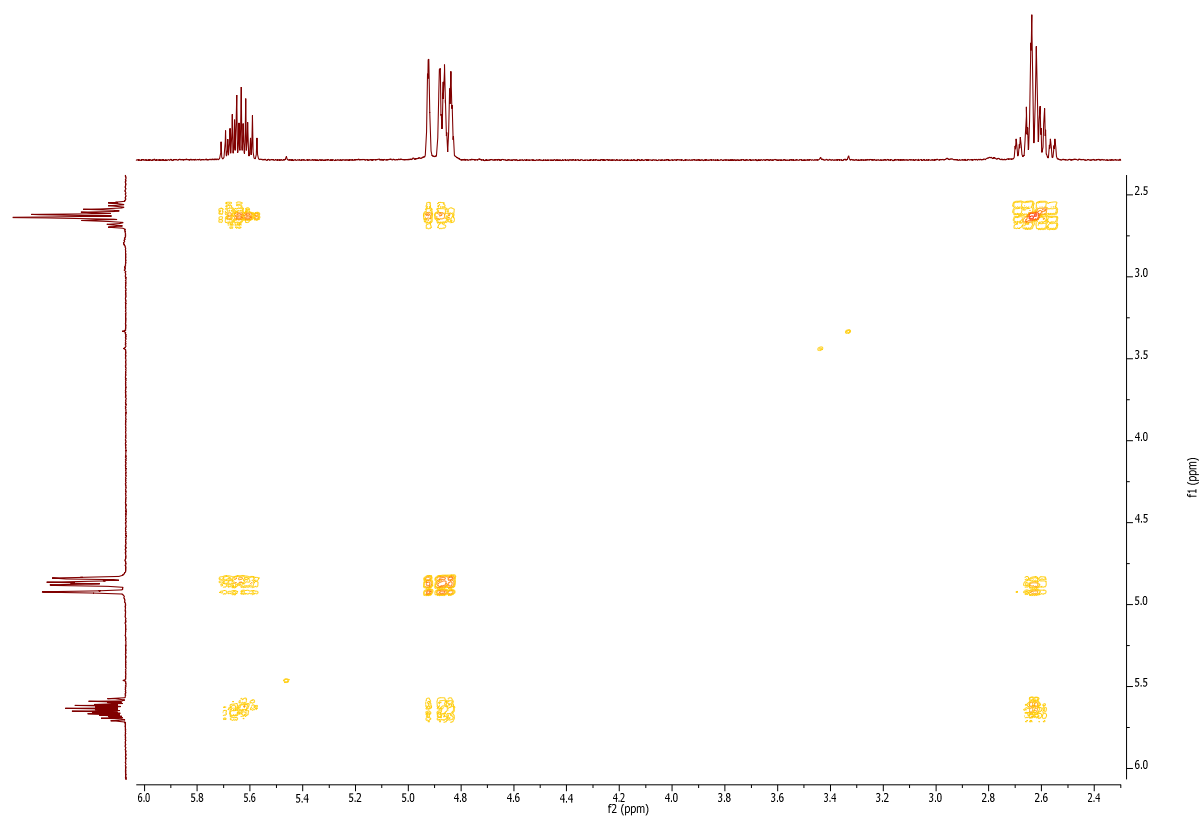


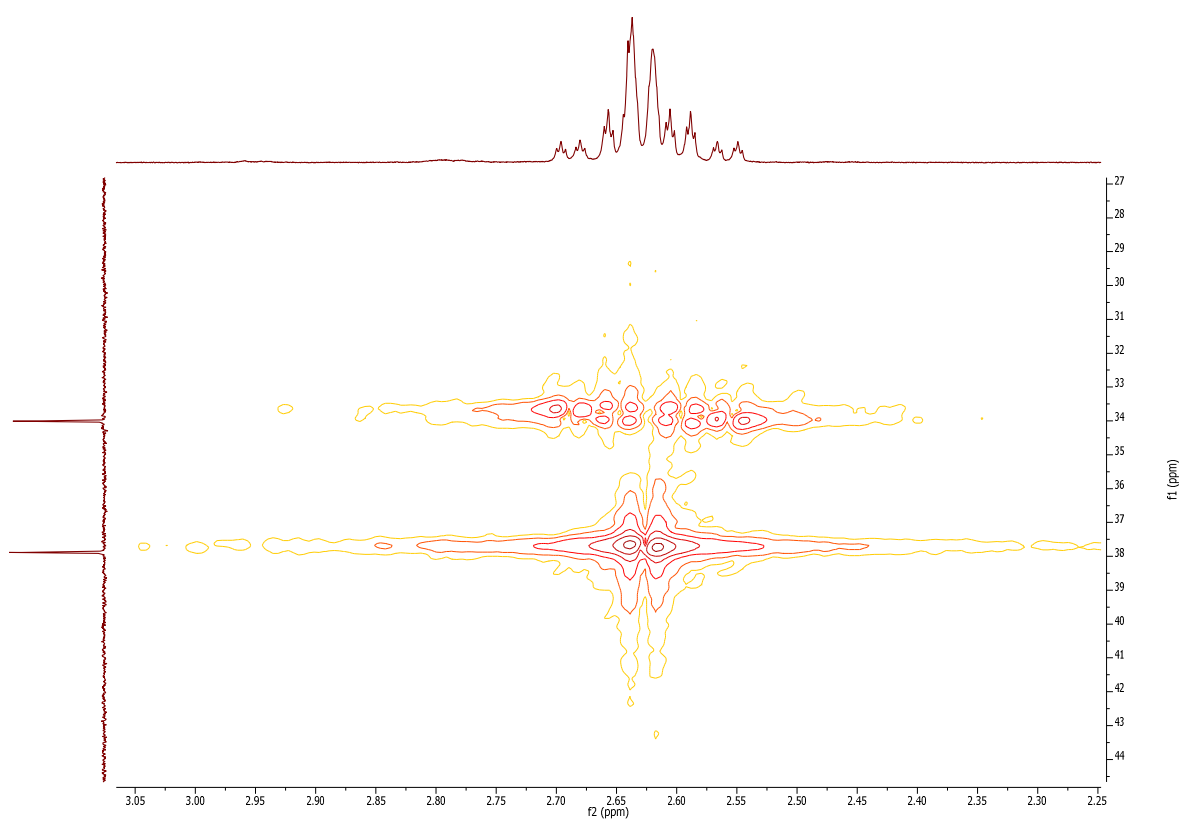
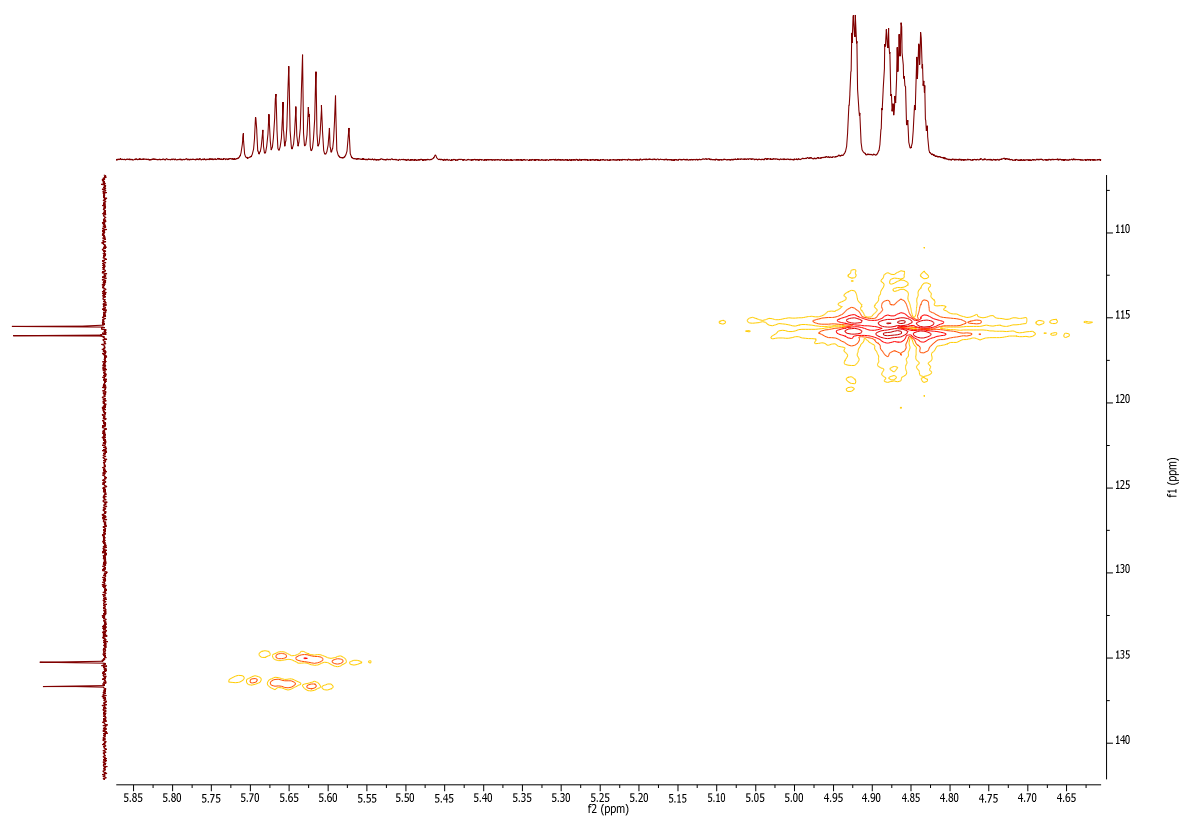


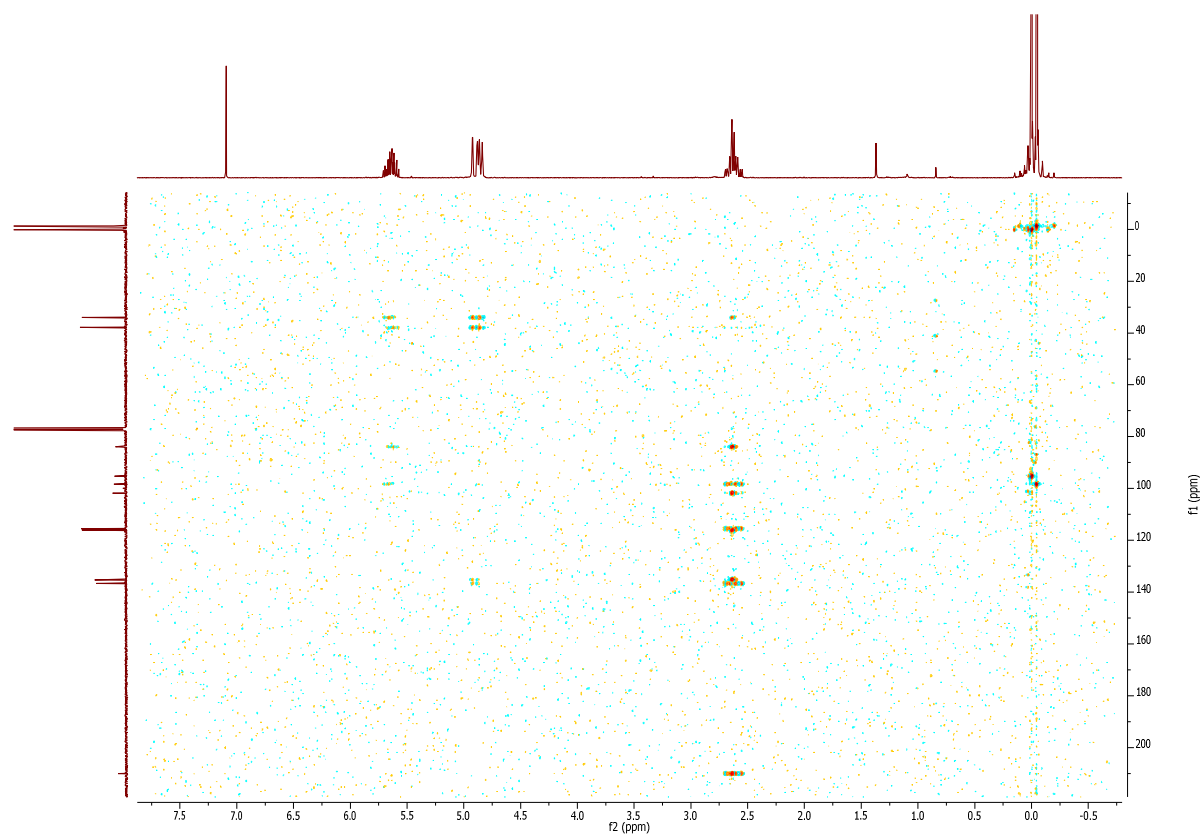
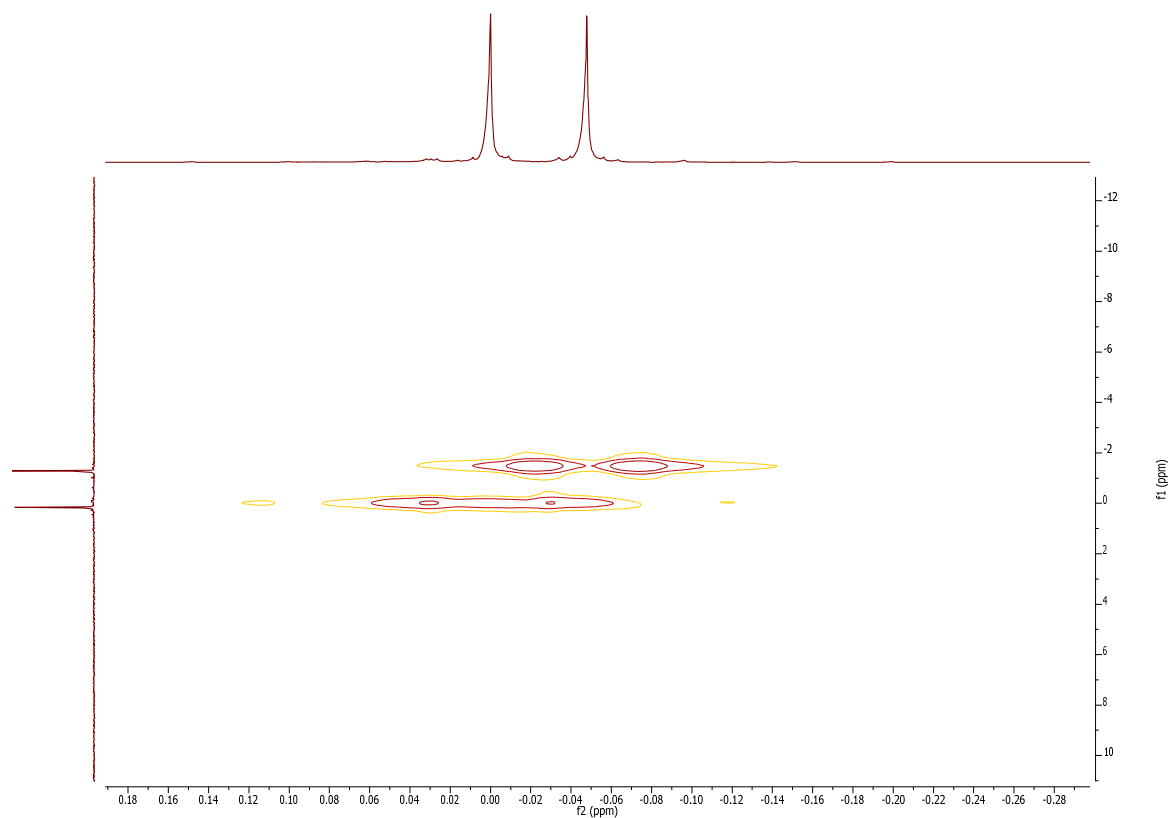


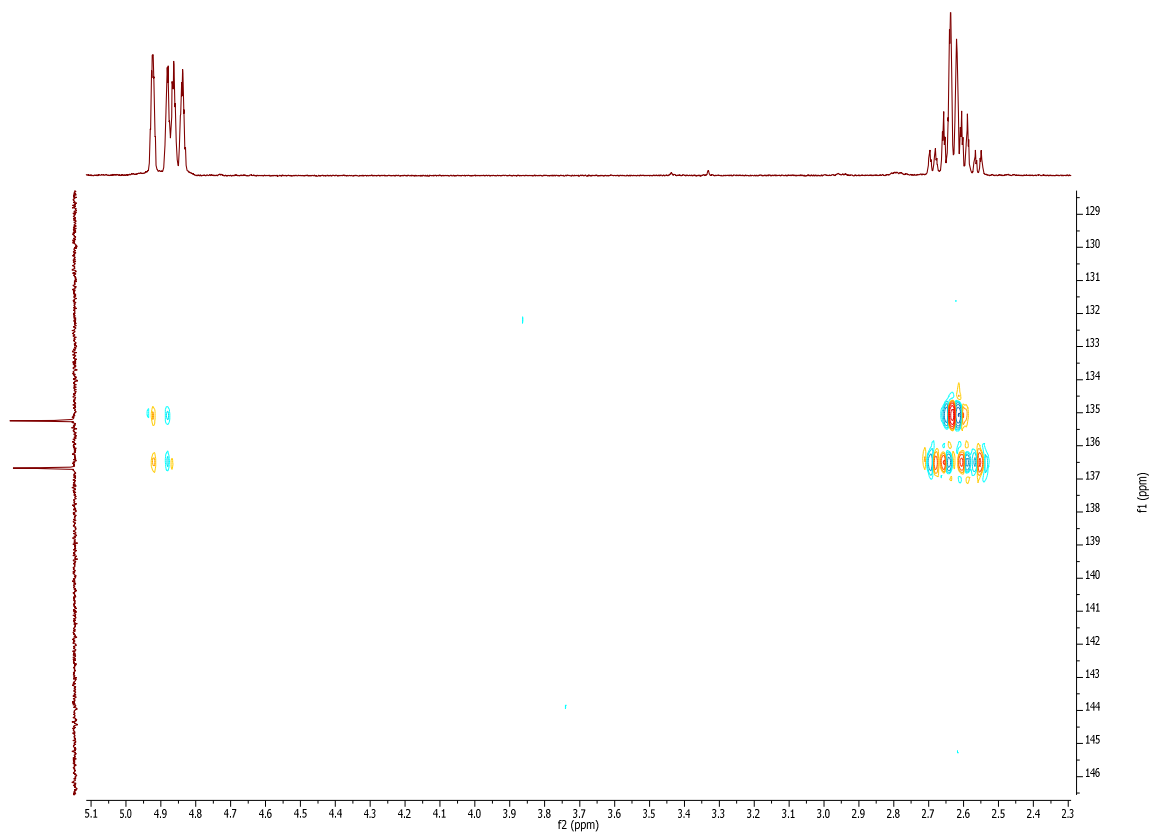
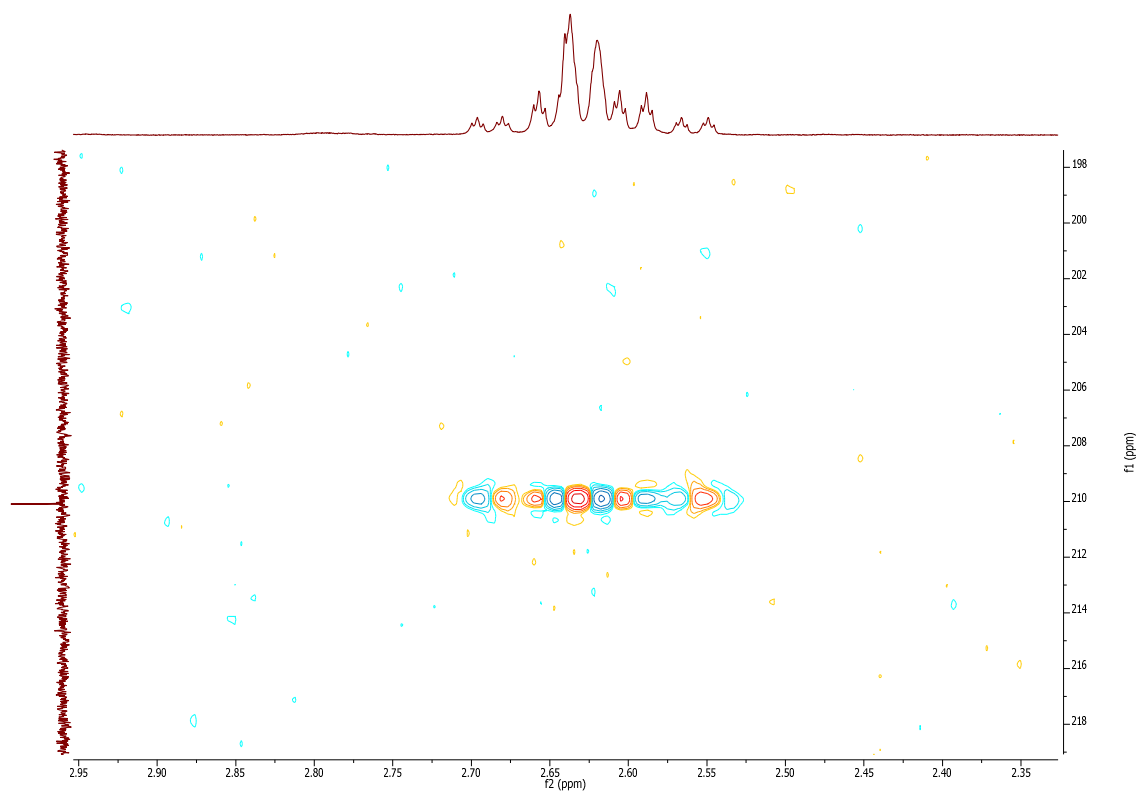


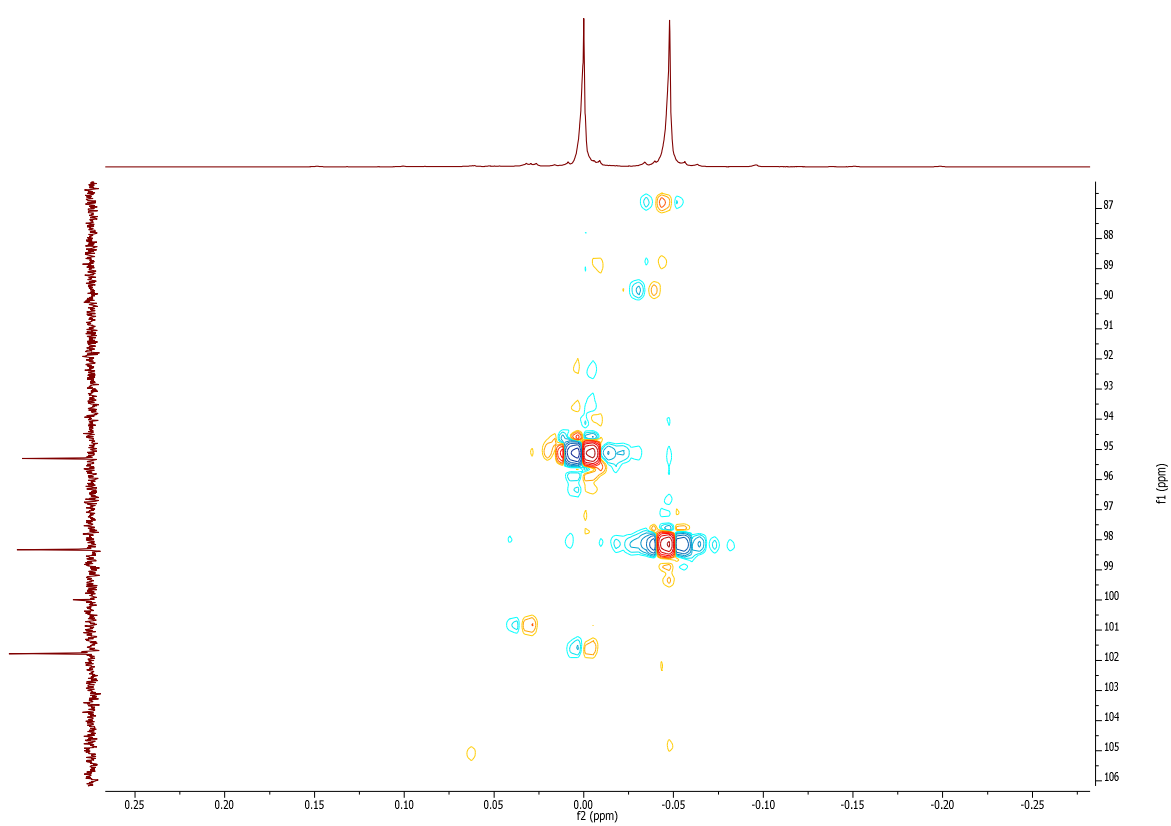
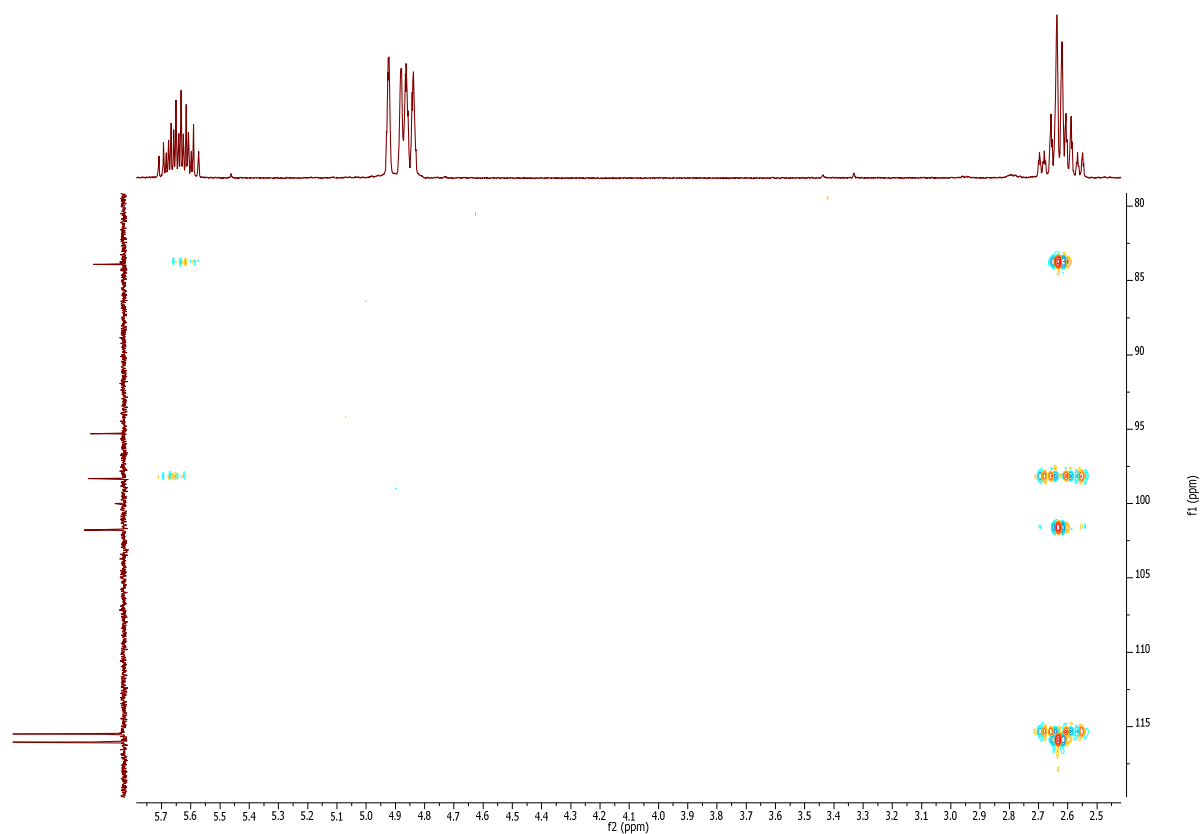


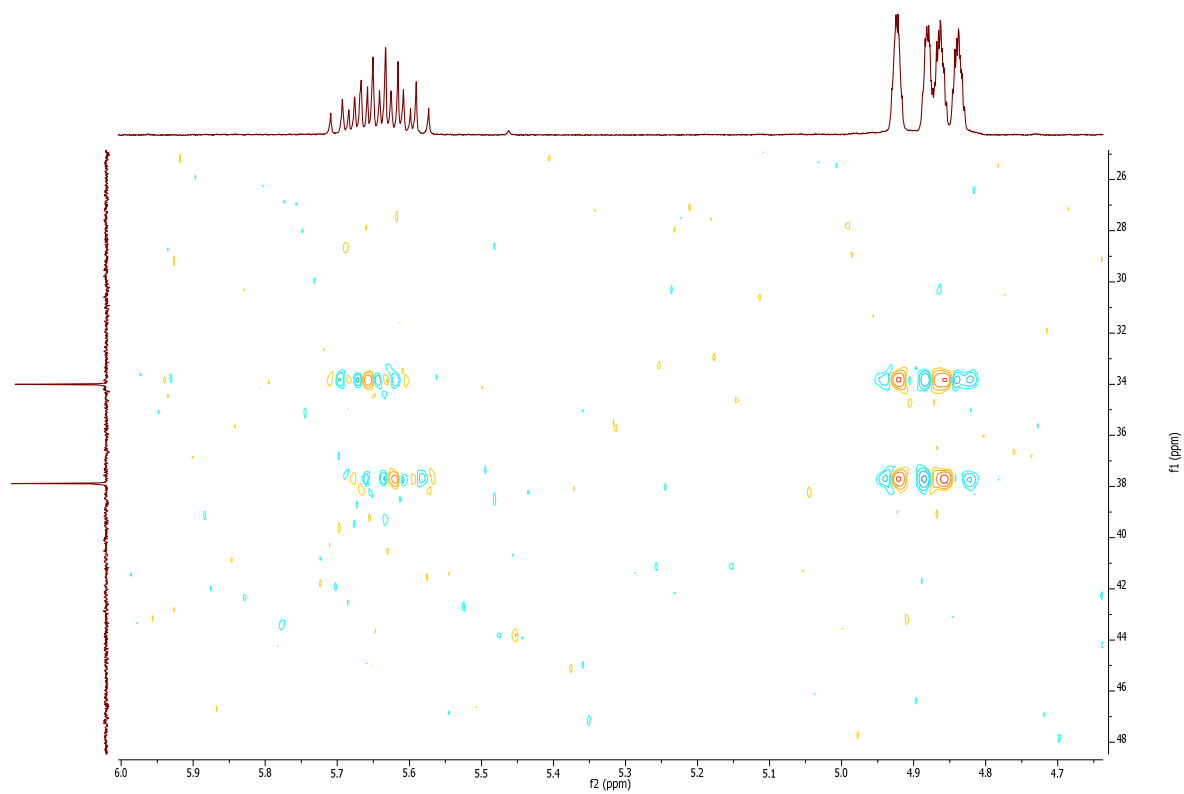














## Single Crystal X-Ray Diffraction Studies

Single crystals of allenes **3c**, **4c**, **4f**, **4k**, suitable for X-ray diffraction, were obtained by slow evaporation of *i*-hexane-ethylacetate solutions. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on the top of a thin glass wire. Data collection was performed with an Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-K $\alpha$  radiation ( $\lambda = 0.71071 \text{ \AA}$ ).

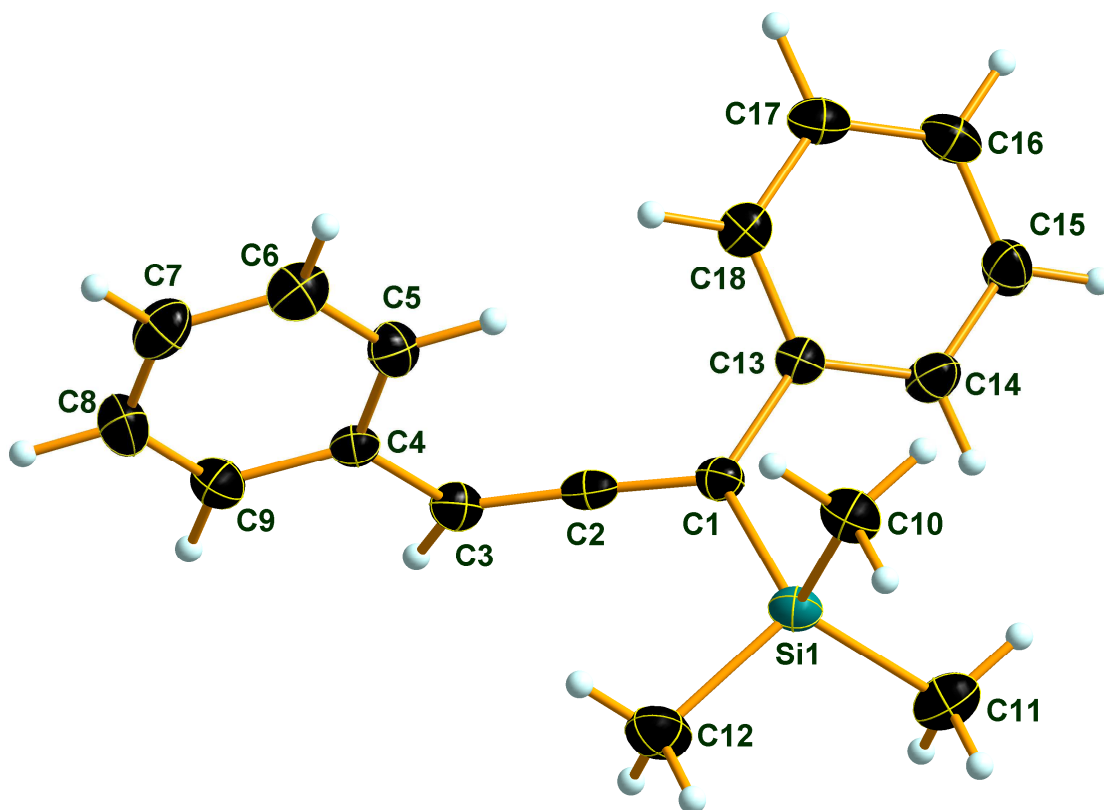
Data collection was performed with the CrysAlis CCD software;<sup>a)</sup> CrysAlis RED software<sup>b)</sup> was used for data reduction. Absorption correction using the SCALE3 ABSPACK multiscan method<sup>c)</sup> was applied. The structures were solved with SHELXS-97,<sup>d)</sup> refined with SHELXL-97<sup>e)</sup> and finally checked using PLATON.<sup>f)</sup> Details for data collection and structure refinement are summarized in Table 1.

CCDC-1038905 (for **3c**), CCDC-1038906 (for **4c**), CCDC-1038907 (for **4f**) and CCDC-1038908 (for **4k**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via*

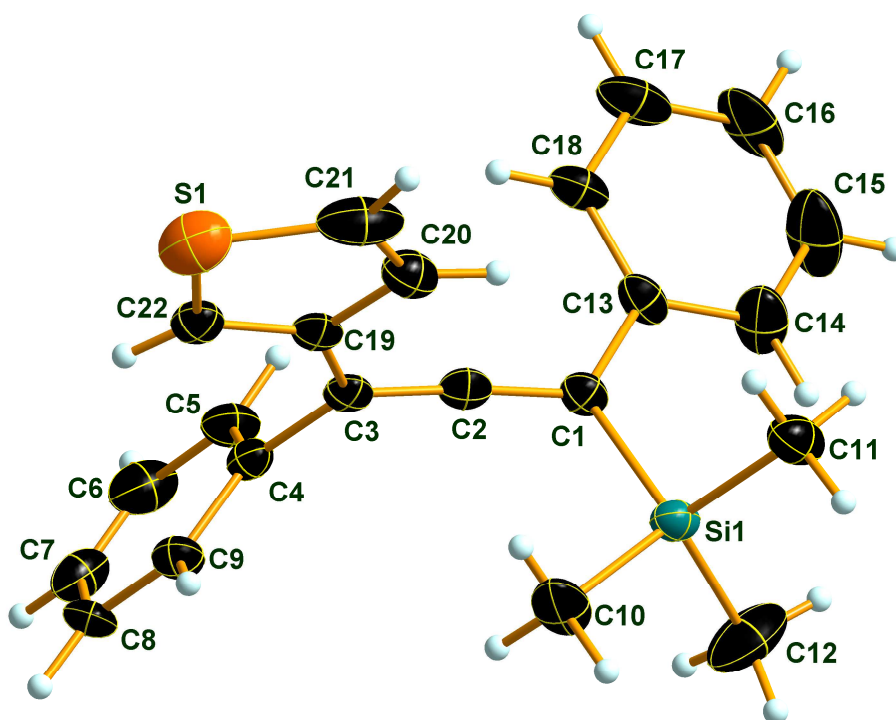
[www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1.** Details for X-ray data collection and structure refinement for allenes **3c**, **4c**, **4f**, **4k**.

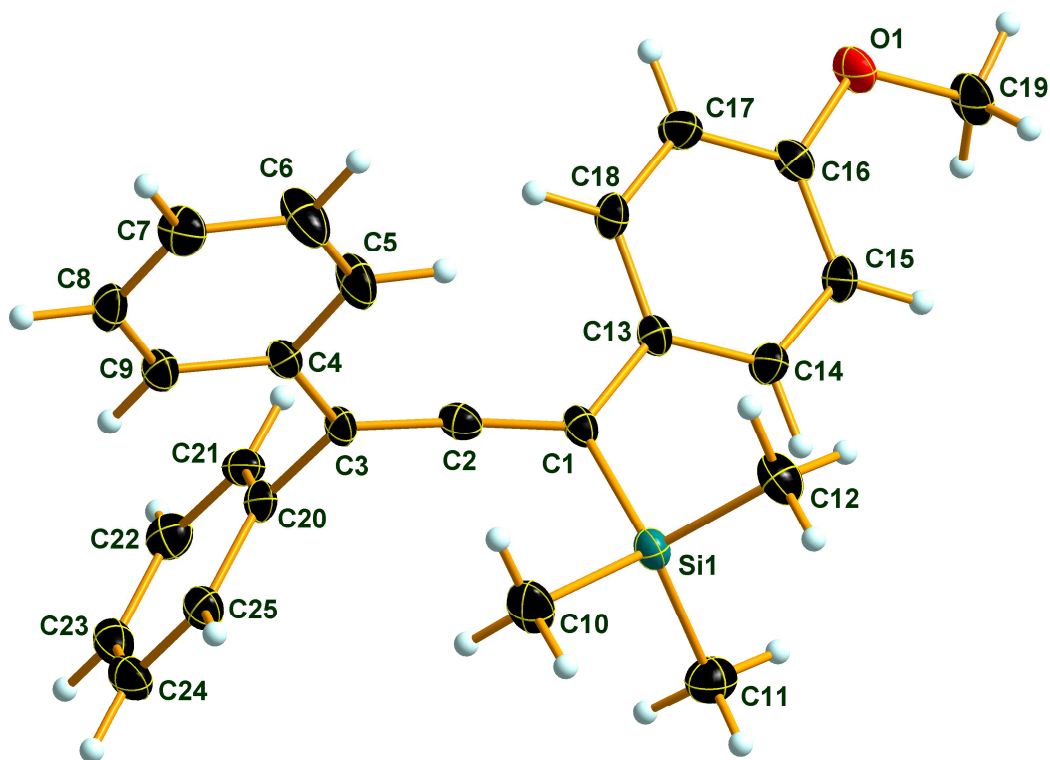
	<b>3c</b>	<b>4c</b>	<b>4f</b>	<b>4k</b>
Empirical formula	C <sub>18</sub> H <sub>20</sub> Si	C <sub>22</sub> H <sub>22</sub> SSi	C <sub>25</sub> H <sub>26</sub> OSi	C <sub>18</sub> H <sub>18</sub> S <sub>3</sub> Si
Formula mass	264.43	346.55	370.55	358.59
T[K]	100(2)	100(2)	100(2)	100(2)
Crystal size [mm]	0.40 × 0.17 × 0.07	0.45 × 0.35 × 0.25	0.34 × 0.28 × 0.21	0.32 × 0.06 × 0.05
Crystal description	colorless platelet	colorless block	colorless block	colorless rod
Crystal system	monoclinic	triclinic	triclinic	orthorhombic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>Pccn</i>
a [Å]	11.7536(9)	9.8470(10)	7.7678(8)	39.103(3)
b [Å]	6.0009(6)	10.6857(12)	11.5078(7)	15.3784(9)
c [Å]	21.9793(19)	10.7187(16)	12.8935(12)	6.1528(4)
α [°]	90	73.657(11)	97.150(7)	90
β [°]	95.951(8)	77.949(11)	105.425(9)	90
γ [°]	90	64.606(11)	108.269(8)	90
V [Å <sup>3</sup> ]	1541.9(2)	972.6(2)	1027.48(2)	3699.9(4)
Z	4	2	2	8
ρ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.139	1.183	1.198	1.288
μ [mm <sup>-1</sup> ]	0.137	0.228	0.126	0.459
<i>F</i> (000)	568	368	396	1504
Θ range [°]	4.17 – 25.68	4.25 – 25.34	4.20 – 25.35	4.27 – 25.35
Index ranges	-14 ≤ <i>h</i> ≤ 12 -5 ≤ <i>k</i> ≤ 7 -26 ≤ <i>l</i> ≤ 26	-11 ≤ <i>h</i> ≤ 11 -12 ≤ <i>k</i> ≤ 12 -12 ≤ <i>l</i> ≤ 12	-9 ≤ <i>h</i> ≤ 9 -11 ≤ <i>k</i> ≤ 13 -15 ≤ <i>l</i> ≤ 15	-46 ≤ <i>h</i> ≤ 47 -17 ≤ <i>k</i> ≤ 18 -7 ≤ <i>l</i> ≤ 7
Reflns. collected	9465	7048	6573	21824
Reflns. obsd.	1868	2786	2727	2474
Reflns. unique	2921 ( <i>R</i> <sub>int</sub> = 0.0778)	3528 ( <i>R</i> <sub>int</sub> = 0.0375)	3633 ( <i>R</i> <sub>int</sub> = 0.0766)	3365 ( <i>R</i> <sub>int</sub> = 0.1120)
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (2σ data)	0.0557, 0.0980	0.0714, 0.1888	0.0476, 0.1096	0.0722, 0.1378
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1005, 0.1169	0.0886, 0.2121	0.0715, 0.1299	0.1034, 0.1525
GOOF on <i>F</i> <sup>2</sup>	0.975	1.046	1.044	1.079
Peak/hole [e Å <sup>-3</sup> ]	0.355 / -0.321	1.508 / -0.647	0.429 / -0.473	0.498 / -0.412



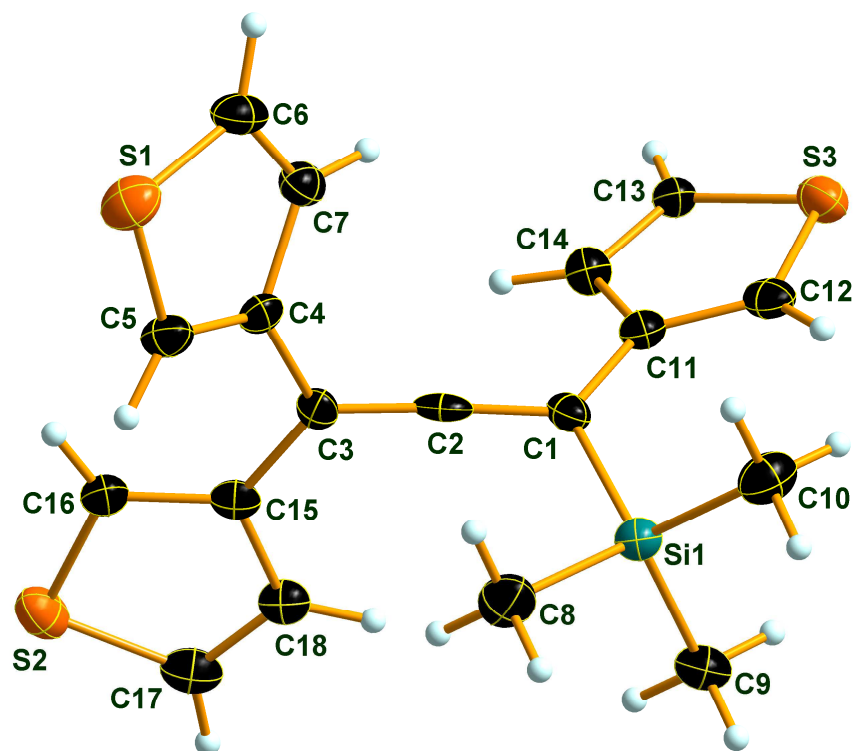
**Figure 1.** Molecular structure of compound **3c** in the crystal, DIAMOND<sup>g)</sup> representation; thermal ellipsoids are drawn at 50 % probability level.



**Figure 2.** Molecular structure of compound **4c** in the crystal, DIAMOND<sup>g)</sup> representation; thermal ellipsoids are drawn at 50 % probability level.



**Figure 3.** Molecular structure of compound **4f** in the crystal, DIAMOND<sup>g)</sup> representation; thermal ellipsoids are drawn at 50 % probability level.



**Figure 4.** Molecular structure of compound **4k** in the crystal, DIAMOND<sup>g)</sup> representation; thermal ellipsoids are drawn at 50 % probability level.

**Table 2.** Selected bond lengths (Å) of compound **1**.

Si1 – C1	1.900(2)	C5 – C6	1.388(4)
Si1 – C10	1.862(3)	C6 – C7	1.382(4)
Si1 – C11	1.860(3)	C7 – C8	1.385(4)
Si1 – C12	1.856(3)	C8 – C9	1.383(4)
C1 – C2	1.305(4)	C13 – C14	1.391(4)
C1 – C13	1.502(3)	C13 – C18	1.395(4)
C2 – C3	1.317(4)	C14 – C15	1.389(4)
C3 – C4	1.481(4)	C15 – C16	1.383(4)
C4 – C5	1.398(4)	C16 – C17	1.388(4)
C4 – C9	1.391(4)	C17 – C18	1.382(4)

**Table 3.** Selected bond angles (°) of compound **1**.

C1 – Si1 – C10	107.3(1)	C4 – C5 – C6	121.1(3)
C1 – Si1 – C11	114.5(1)	C5 – C6 – C7	120.4(3)
C1 – Si1 – C12	107.3(1)	C6 – C7 – C8	118.9(3)
C10 – Si1 – C11	107.6(1)	C7 – C8 – C9	121.0(3)
C10 – Si1 – C12	110.9(1)	C4 – C9 – C8	120.8(3)
C11 – Si1 – C12	109.4(1)	C1 – C13 – C14	121.1(2)
Si1 – C1 – C2	115.9(2)	C1 – C13 – C18	121.0(2)
Si1 – C1 – C13	122.8(2)	C14 – C13 – C18	117.9(2)
C2 – C1 – C13	120.9(2)	C13 – C14 – C15	120.9(3)
C1 – C2 – C3	174.2(2)	C14 – C15 – C16	120.8(3)
C2 – C3 – C4	124.1(2)	C15 – C16 – C17	118.6(3)
C3 – C4 – C5	121.0(2)	C16 – C17 – C18	120.8(3)
C3 – C4 – C9	121.2(2)	C13 – C18 – C17	121.0(3)
C5 – C4 – C9	117.8(2)		

**Table 4.** Selected torsion angles (°) of compound **1**.

C10 – Si1 – C1 – C2	-113.5(2)	C3 – C4 – C9 – C8	-179.3(2)
C10 – Si1 – C1 – C13	60.0(2)	C5 – C4 – C9 – C8	0.3(4)
C11 – Si1 – C1 – C2	127.2(2)	C4 – C5 – C6 – C7	0.4(4)
C11 – Si1 – C1 – C13	-59.3(2)	C5 – C6 – C7 – C8	-0.1(4)
C12 – Si1 – C1 – C2	5.6(2)	C6 – C7 – C8 – C9	0.0(4)
C12 – Si1 – C1 – C13	179.1(2)	C7 – C8 – C9 – C4	-0.1(4)
Si1 – C1 – C13 – C14	44.7(3)	C1 – C13 – C14 – C15	-179.8(2)

Si1 – C1 – C13 – C18	-134.0(2)	C18 – C13 – C14 – C15	-1.1(4)
C2 – C1 – C13 – C14	-142.2(3)	C1 – C13 – C18 – C17	179.9(2)
C2 – C1 – C13 – C18	39.2(4)	C14 – C13 – C18 – C17	1.2(4)
C2 – C3 – C4 – C5	9.7(4)	C13 – C14 – C15 – C16	0.4(4)
C2 – C3 – C4 – C9	-170.6(3)	C14 – C15 – C16 – C17	0.1(4)
C3 – C4 – C5 – C6	179.2(2)	C15 – C16 – C17 – C18	0.0(4)
C9 – C4 – C5 – C6	-0.4(4)	C16 – C17 – C18 – C13	-0.7(4)

**Table 5.** Selected bond lengths (Å) of compound **2**.

Si1 – C21	1.763(4)	C5 – C6	1.389(5)
Si1 – C22	1.703(3)	C6 – C7	1.244(6)
Si1 – C1	1.894(3)	C7 – C8	1.412(6)
Si1 – C10	1.864(5)	C8 – C9	1.414(4)
Si1 – C11	1.864(3)	C13 – C14	1.393(5)
Si1 – C12	1.854(4)	C13 – C18	1.404(5)
C1 – C2	1.306(4)	C14 – C15	1.394(7)
C1 – C13	1.494(5)	C15 – C16	1.378(7)
C2 – C3	1.322(4)	C16 – C17	1.358(6)
C3 – C4	1.495(4)	C17 – C18	1.401(6)
C3 – C19	1.482(4)	C19 – C20	1.435(4)
C4 – C5	1.395(5)	C19 – C22	1.375(4)
C4 – C9	1.398(4)	C20 – C21	1.361(5)

**Table 6.** Selected bond angles (°) of compound **2**.

C21 – Si1 – C22	92.1(2)	C5 – C6 – C7	120.4(5)
C1 – Si1 – C10	107.5(2)	C6 – C7 – C8	124.0(4)
C1 – Si1 – C11	106.7(2)	C7 – C8 – C9	117.6(3)
C1 – Si1 – C12	113.2(2)	C4 – C9 – C8	118.8(3)
C10 – Si1 – C11	110.2(2)	C1 – C13 – C14	121.0(3)
C10 – Si1 – C12	107.4(2)	C1 – C13 – C18	120.4(3)
C11 – Si1 – C12	111.8(2)	C14 – C13 – C18	118.6(3)
Si1 – C1 – C2	113.8(3)	C13 – C14 – C15	120.8(4)
Si1 – C1 – C13	124.1(2)	C14 – C15 – C16	119.1(4)
C2 – C1 – C13	121.8(3)	C15 – C16 – C17	121.7(4)
C1 – C2 – C3	172.6(4)	C16 – C17 – C18	119.8(4)
C2 – C3 – C4	118.9(3)	C13 – C18 – C17	119.9(4)

C2 – C3 – C19	119.8(3)	C3 – C19 – C20	123.1(3)
C4 – C3 – C19	121.4(3)	C3 – C19 – C22	124.6(3)
C3 – C4 – C5	119.5(3)	C20 – C19 – C22	112.3(3)
C3 – C4 – C9	122.4(3)	C19 – C20 – C21	113.3(3)
C5 – C4 – C9	118.2(3)	S1 – C21 – C20	110.2(3)
C4 – C5 – C6	121.1(4)	S1 – C22 – C19	112.1(2)

**Table 7.** Selected torsion angles (°) of compound **2**.

C22 – S1 – C21 – C20	0.3(4)	C9 – C4 – C5 – C6	-0.5(5)
C21 – S1 – C22 – C19	-0.6(3)	C3 – C4 – C9 – C8	-177.8(3)
C10 – Si1 – C1 – C2	1.8(3)	C5 – C4 – C9 – C8	0.4(4)
C10 – Si1 – C1 – C13	175.8(3)	C4 – C5 – C6 – C7	0.3(6)
C11 – Si1 – C1 – C2	-116.4(3)	C5 – C6 – C7 – C8	0.1(6)
C11 – Si1 – C1 – C13	57.6(3)	C6 – C7 – C8 – C9	-0.1(5)
C12 – Si1 – C1 – C2	120.3(3)	C7 – C8 – C9 – C4	-0.1(4)
C12 – Si1 – C1 – C13	-65.7(3)	C1 – C13 – C14 – C15	178.2(4)
Si1 – C1 – C13 – C14	19.8(4)	C18 – C13 – C14 – C15	-0.8(6)
Si1 – C1 – C13 – C18	-161.2(2)	C1 – C13 – C18 – C17	-179.0(3)
C2 – C1 – C13 – C14	-166.6(3)	C14 – C13 – C18 – C17	0.0(5)
C2 – C1 – C13 – C18	12.3(5)	C13 – C14 – C15 – C16	2.7(7)
C2 – C3 – C4 – C5	-54.8(4)	C14 – C15 – C16 – C17	-3.9(7)
C2 – C3 – C4 – C9	123.4(4)	C15 – C16 – C17 – C18	3.1(6)
C19 – C3 – C4 – C5	124.8(3)	C16 – C17 – C18 – C13	-1.1(6)
C19 – C3 – C4 – C9	-56.9(4)	C3 – C19 – C20 – C21	178.7(4)
C2 – C3 – C19 – C20	-4.4(5)	C22 – C19 – C20 – C21	-0.6(5)
C2 – C3 – C19 – C22	174.7(3)	C3 – C19 – C22 – S1	-178.4(3)
C4 – C3 – C19 – C20	175.9(3)	C20 – C19 – C22 – S1	0.8(4)
C4 – C3 – C19 – C22	-4.9(5)	C19 – C20 – C21 – S1	0.1(5)
C3 – C4 – C5 – C6	177.8(3)		

**Table 8.** Selected bond lengths (Å) of compound **3**.

Si1 – C1	1.891(3)	C7 – C8	1.378(3)
Si1 – C10	1.851(2)	C8 – C9	1.388(3)
Si1 – C11	1.850(3)	C13 – C14	1.377(3)
Si1 – C12	1.855(2)	C13 – C18	1.396(3)
O1 – C16	1.365(3)	C14 – C15	1.387(3)
O1 – C19	1.429(3)	C15 – C16	1.387(3)
C1 – C2	1.306(3)	C16 – C17	1.373(3)
C1 – C13	1.487(3)	C17 – C18	1.373(3)
C2 – C3	1.320(3)	C20 – C21	1.382(3)

C3 – C4	1.485(3)	C20 – C25	1.389(3)
C3 – C20	1.500(3)	C21 – C22	1.387(3)
C4 – C5	1.397(3)	C22 – C23	1.374(3)
C4 – C9	1.389(3)	C23 – C24	1.378(3)
C5 – C6	1.380(4)	C24 – C25	1.378(3)
C6 – C7	1.380(3)		

**Table 9.** Selected bond angles (°) of compound **3**.

C1 – Si1 – C10	107.7(1)	C7 – C8 – C9	120.3(2)
C1 – Si1 – C11	111.6(1)	C4 – C9 – C8	121.2(2)
C1 – Si1 – C12	108.6(1)	C1 – C13 – C14	122.2(2)
C10 – Si1 – C11	108.6(1)	C1 – C13 – C18	120.9(2)
C10 – Si1 – C12	110.7(1)	C14 – C13 – C18	116.9(2)
C11 – Si1 – C12	109.7(1)	C13 – C14 – C15	122.8(2)
C16 – O1 – C19	117.4(2)	C14 – C15 – C16	118.6(2)
Si1 – C1 – C2	114.1(2)	O1 – C16 – C15	124.2(2)
Si1 – C1 – C13	123.0(2)	O1 – C16 – C17	116.0(2)
C2 – C1 – C13	122.6(2)	C15 – C16 – C17	119.8(2)
C1 – C2 – C3	171.9(2)	C16 – C17 – C18	120.5(2)
C2 – C3 – C4	121.0(2)	C13 – C18 – C17	121.4(2)
C2 – C3 – C20	119.3(2)	C3 – C20 – C21	121.1(2)
C4 – C3 – C20	119.7(2)	C3 – C20 – C25	121.0(2)
C3 – C4 – C5	120.1(2)	C21 – C20 – C25	117.9(2)
C3 – C4 – C9	122.2(2)	C20 – C21 – C22	121.1(2)
C5 – C4 – C9	117.7(2)	C21 – C22 – C23	120.0(2)
C4 – C5 – C6	120.9(2)	C22 – C23 – C24	119.7(2)
C5 – C6 – C7	120.8(2)	C23 – C24 – C25	120.1(2)
C6 – C7 – C8	119.1(2)	C20 – C25 – C24	121.2(2)

**Table 10.** Selected torsion angles (°) of compound **3**.

C10 – Si1 – C1 – C2	-11.8(2)	C9 – C4 – C5 – C6	-0.1(4)
C10 – Si1 – C1 – C13	162.7(2)	C4 – C5 – C6 – C7	0.9(4)
C11 – Si1 – C1 – C2	107.4(2)	C5 – C6 – C7 – C8	-0.9(4)
C11 – Si1 – C1 – C13	-78.2(2)	C6 – C7 – C8 – C9	0.1(4)
C12 – Si1 – C1 – C2	-131.6(2)	C7 – C8 – C9 – C4	0.7(4)
C12 – Si1 – C1 – C13	42.9(2)	C1 – C13 – C18 – C17	178.4(2)
C19 – O1 – C16 – C17	-178.6(2)	C14 – C13 – C18 – C17	-0.2(3)
C19 – O1 – C16 – C15	0.6(3)	C1 – C13 – C14 – C15	-178.5(2)
Si1 – C1 – C13 – C18	-146.2(2)	C18 – C13 – C14 – C15	0.1(3)
Si1 – C1 – C13 – C14	32.4(3)	C13 – C14 – C15 – C16	0.1(3)



C2 – C1 – C13 – C14	-153.6(2)	C14 – C15 – C16 – C17	-0.3(3)
C2 – C1 – C13 – C18	27.8(3)	C14 – C15 – C16 – O1	-179.5(2)
C2 – C3 – C4 – C5	5.4(4)	O1 – C16 – C17 – C18	179.5(2)
C20 – C3 – C4 – C9	5.0(3)	C15 – C16 – C17 – C18	0.2(3)
C2 – C3 – C20 – C21	-67.1(3)	C16 – C17 – C18 – C13	0.0(3)
C2 – C3 – C20 – C25	111.7(3)	C3 – C20 – C21 – C22	-179.9(2)
C4 – C3 – C20 – C21	113.1(3)	C25 – C20 – C21 – C22	1.4(4)
C4 – C3 – C20 – C25	-68.2(3)	C3 – C20 – C25 – C24	-179.6(2)
C2 – C3 – C4 – C9	-174.8(2)	C21 – C20 – C25 – C24	-0.8(4)
C20 – C3 – C4 – C5	-174.8(2)	C20 – C21 – C22 – C23	-1.4(4)
C3 – C4 – C9 – C8	179.5(2)	C21 – C22 – C23 – C24	0.8(4)
C5 – C4 – C9 – C8	-0.7(4)	C22 – C23 – C24 – C25	-0.3(4)
C3 – C4 – C5 – C6	179.7(2)	C23 – C24 – C25 – C20	0.3(4)

**Table 11.** Selected bond lengths (Å) of compound **4**.

S1 – C5	1.719(5)	C2 – C3	1.325(7)
S1 – C6	1.703(5)	C3 – C4	1.482(6)
S2 – C16	1.715(5)	C3 – C15	1.481(6)
S2 – C17	1.710(5)	C4 – C5	1.363(6)
S3 – C12	1.706(5)	C4 – C7	1.428(7)
S3 – C13	1.732(5)	C6 – C7	1.354(7)
Si1 – C1	1.891(5)	C11 – C12	1.369(6)
Si1 – C8	1.858(5)	C11 – C14	1.432(7)
Si1 – C9	1.869(5)	C13 – C14	1.385(7)
Si1 – C10	1.860(5)	C15 – C16	1.368(6)
C1 – C2	1.314(7)	C15 – C18	1.425(6)
C1 – C11	1.488(6)	C17 – C18	1.362(7)

**Table 12.** Selected bond angles (°) of compound **4**.

C5 – S1 – C6	91.6(2)	C3 – C4 – C7	122.6(4)
C16 – S2 – C17	91.7(2)	C5 – C4 – C7	111.0(4)
C12 – S3 – C13	92.4(2)	S1 – C5 – C4	112.3(4)
C1 – Si1 – C8	107.7(2)	S1 – C6 – C7	111.8(4)
C1 – Si1 – C9	107.1(2)	C4 – C7 – C6	113.3(4)
C1 – Si1 – C10	113.1(2)	C1 – C11 – C12	125.5(4)
C8 – Si1 – C9	110.9(2)	C1 – C11 – C14	123.7(4)
C8 – Si1 – C10	108.1(2)	C12 – C11 – C14	110.9(4)
C9 – Si1 – C10	109.9(2)	S3 – C12 – C11	113.1(4)
Si1 – C1 – C2	113.5(3)	S3 – C13 – C14	109.8(4)
Si1 – C1 – C11	125.6(3)	C11 – C14 – C13	113.9(4)

C2 – C1 – C11	120.7(4)	C3 – C15 – C16	125.4(4)
C1 – C2 – C3	173.1(5)	C3 – C15 – C18	123.6(4)
C2 – C3 – C4	117.9(4)	C16 – C15 – C18	111.0(4)
C2 – C3 – C15	120.9(4)	S2 – C16 – C15	112.4(3)
C4 – C3 – C15	121.1(4)	S2 – C17 – C18	111.5(3)
C3 – C4 – C5	126.4(4)	C15 – C18 – C17	113.4(4)

**Table 13.** Selected torsion angles (°) of compound **4**.

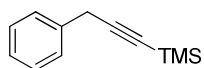
C6 – S1 – C5 – C4	1.2(4)	C2 – C3 – C15 – C16	-168.6(5)
C5 – S1 – C6 – C7	-1.4(4)	C2 – C3 – C15 – C18	9.7(7)
C17 – S2 – C16 – C15	0.2(4)	C4 – C3 – C15 – C16	9.5(7)
C16 – S2 – C17 – C18	0.1(4)	C4 – C3 – C15 – C18	-172.2(4)
C13 – S3 – C12 – C11	-1.0(4)	C3 – C4 – C5 – S1	178.3(4)
C12 – S3 – C13 – C14	0.9(4)	C7 – C4 – C5 – S1	-0.8(5)
C8 – Si1 – C1 – C2	-10.3(4)	C3 – C4 – C7 – C6	-179.4(4)
C8 – Si1 – C1 – C11	174.6(4)	C5 – C4 – C7 – C6	-0.3(6)
C9 – Si1 – C1 – C2	109.0(4)	S1 – C6 – C7 – C4	1.2(5)
C9 – Si1 – C1 – C11	-66.1(4)	C1 – C11 – C12 – S3	-178.6(4)
C10 – Si1 – C1 – C2	-129.7(4)	C14 – C11 – C12 – S3	0.9(5)
C10 – Si1 – C1 – C11	55.1(4)	C1 – C11 – C14 – C13	179.3(4)
Si1 – C1 – C11 – C12	-25.2(7)	C12 – C11 – C14 – C13	-0.2(6)
Si1 – C1 – C11 – C14	155.4(4)	S3 – C13 – C14 – C11	-0.5(5)
C2 – C1 – C11 – C12	160.0(5)	C3 – C15 – C16 – S2	178.1(4)
C2 – C1 – C11 – C14	-19.4(7)	C18 – C15 – C16 – S2	-0.3(5)
C2 – C3 – C4 – C5	-137.6(5)	C3 – C15 – C18 – C17	-178.1(4)
C2 – C3 – C4 – C7	41.4(6)	C16 – C15 – C18 – C17	0.4(6)
C15 – C3 – C4 – C5	44.2(7)	S2 – C17 – C18 – C15	-0.2(5)
C15 – C3 – C4 – C7	-136.8(5)		

## References

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## NMR studies

### Trimethyl(3-phenylprop-1-yn-1-yl)silane (2a)

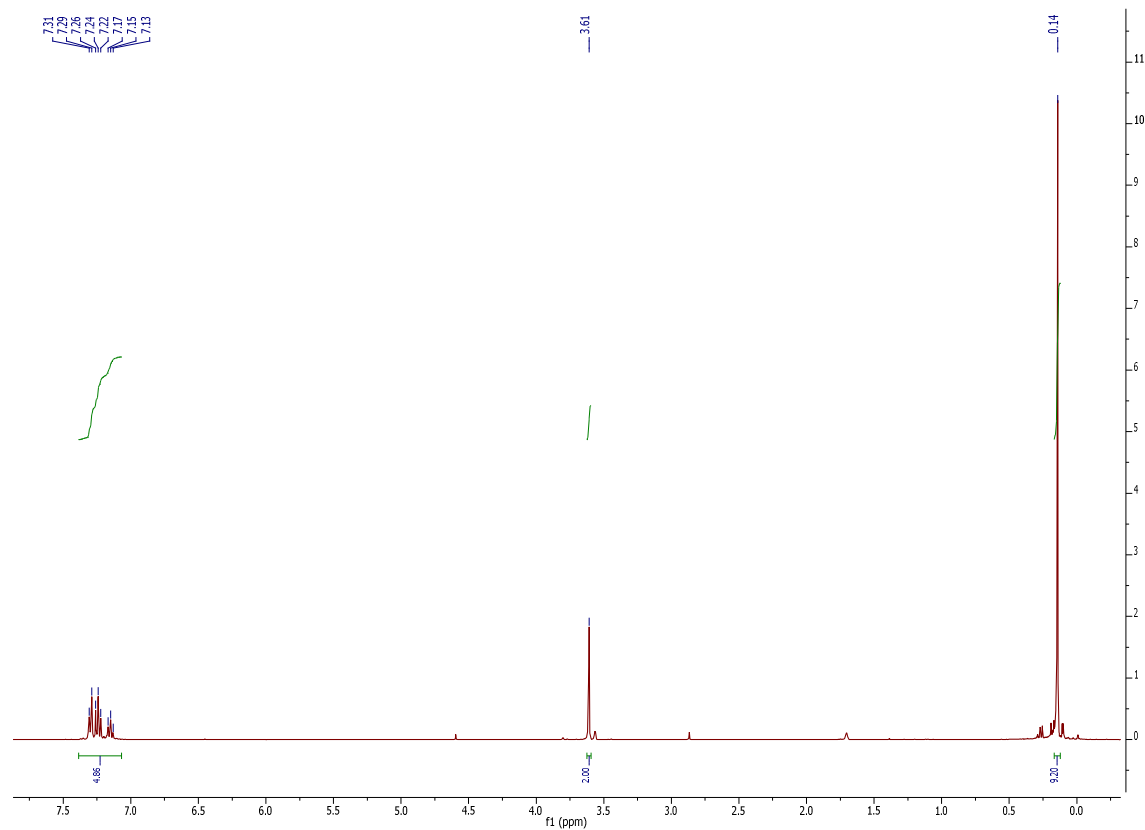


**$^1\text{H}$  NMR** (400 MHz, THF- $d_8$ )  $\delta$ /ppm = 7.30 (2H, dd, 2- $\text{H}_{\text{meta}}$ ), 7.24 (2H, d, 2- $\text{H}_{\text{ortho}}$ ), 7.15 (1H, t, 1- $\text{H}_{\text{para}}$ ), 3.61 (1H, s,  $\text{CH}_2$ ), 0.03 (9H, s,  $\text{CH}_3$ ).

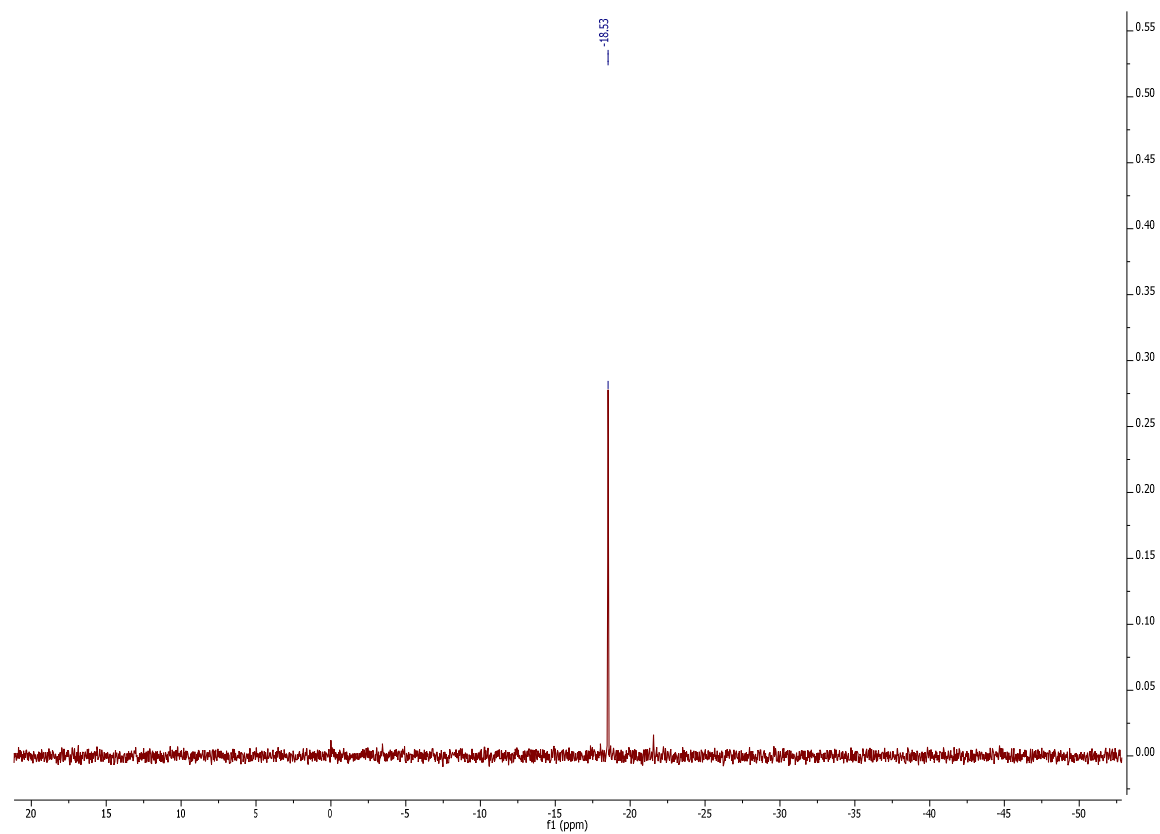
**$^{13}\text{C}$  NMR** (100 MHz, THF- $d_8$ )  $\delta$ /ppm = 104.5 ( $-\text{C}\equiv$ ), 136.6 ( $\text{C}_{\text{ipso}}$ ), 128.2 (2 $\text{C}_{\text{meta}}$ ) 127.7 (2 $\text{C}_{\text{ortho}}$ ), 126.3 ( $\text{C}_{\text{para}}$ ), 85.8 ( $\equiv\text{C}-\text{Si}$ ), 25.5 ( $\text{CH}_2$ ), -0.71 ( $\text{CH}_3$ ).

**$^{29}\text{Si}$  NMR** (79 MHz, THF- $d_8$ )  $\delta$ /ppm = -18.53.

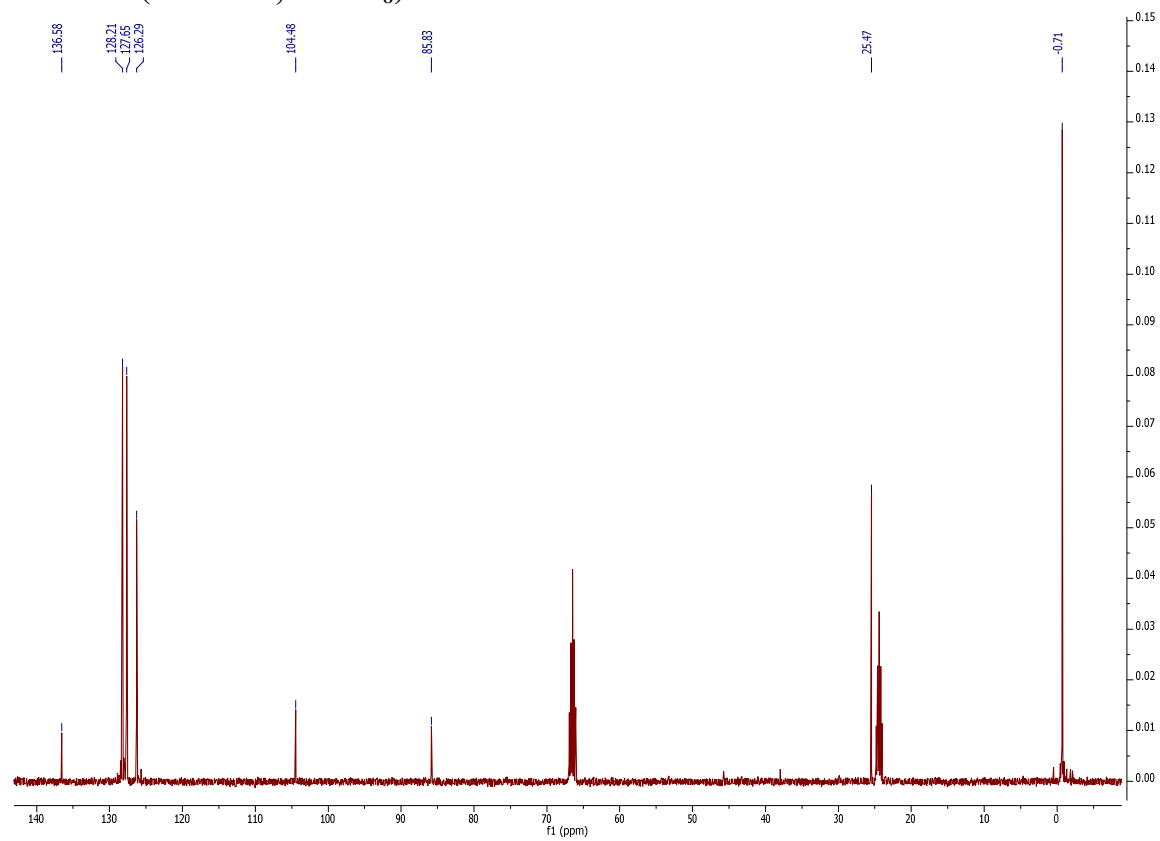
### $^1\text{H}$ NMR (400 MHz, THF- $d_8$ )



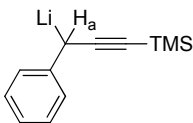
**$^{29}\text{Si}$  NMR (79 MHz, THF- $d_8$ )**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ )**



## NMR studies of the metalated intermediate **9**



In order to provide structural information on the metalated TMS-alkyne of type **9**, we investigated the metalation of trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**) with *n*BuLi at 25°C. Therefore trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**; 0.25 mmol, 47.0 mg) and THF-*d*<sub>8</sub> (0.5 mL) were charged in a dry, argon flushed NMR tube. The NMR tube was cooled to 0°C and *n*BuLi (1.00 equiv, 0.10 mL, 2.45 M in hexanes) was slowly added and the tube was shaken once. The NMR tube was warmed up to 25 °C and NMR studies were performed at 25 °C, including <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si, <sup>7</sup>Li and 2D NMR.

**<sup>1</sup>H NMR** (400 MHz, THF-*d*<sub>8</sub>) δ/ppm = 6.67 (2H, dd, 2-H<sub>meta</sub>), 6.63 (2H, d, 2-H<sub>ortho</sub>), 6.07 (1H, t, 1-H<sub>para</sub>), 3.33 (1H, s, H<sub>a</sub>), 0.03 (9H, s, CH<sub>3</sub>).

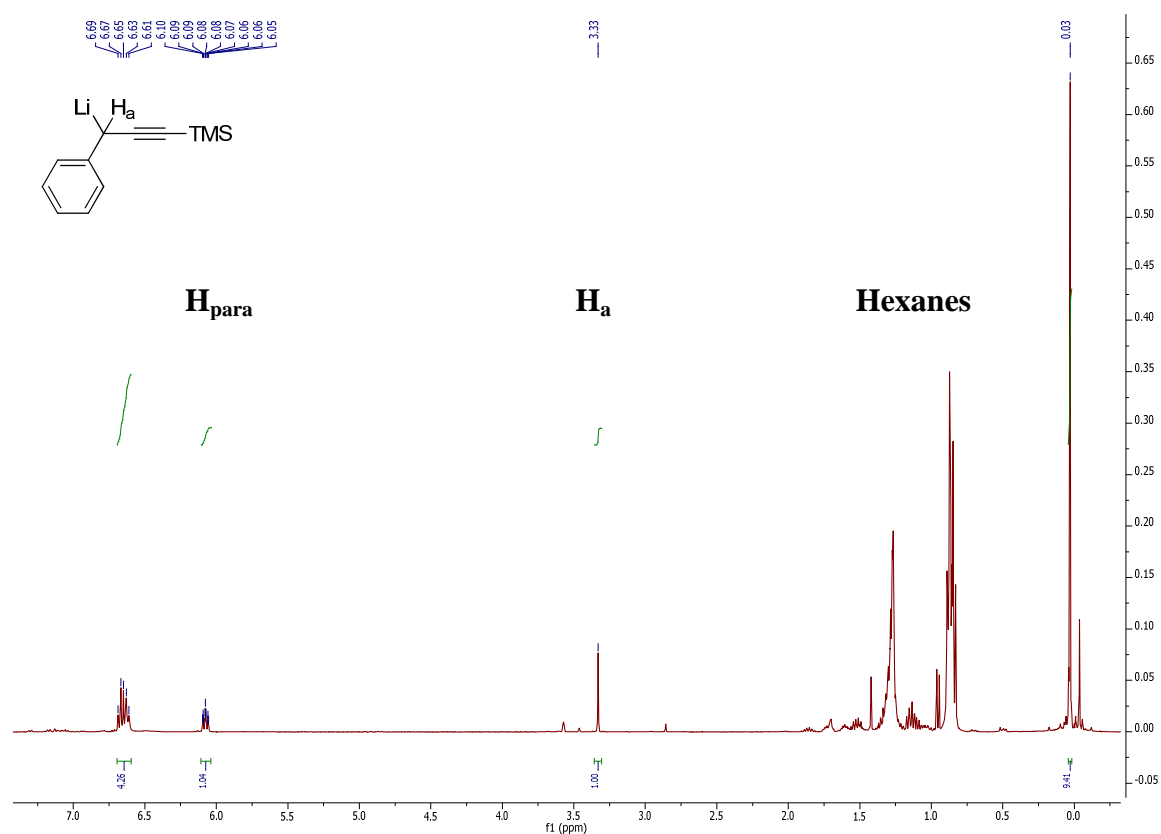
**<sup>13</sup>C NMR** (100 MHz, THF-*d*<sub>8</sub>) δ/ppm = 151.4 (-C≡)\*, 149.9 (C<sub>ipso</sub>), 127.2 (2C<sub>meta</sub>) 118.9 (2C<sub>ortho</sub>), 112.9 (C<sub>para</sub>), 95.0 (≡C-Si), 51.9 (C-H<sub>a</sub>), 1.71 (CH<sub>3</sub>).

**<sup>29</sup>Si NMR** (79 MHz, THF-*d*<sub>8</sub>) δ/ppm = -18.83.

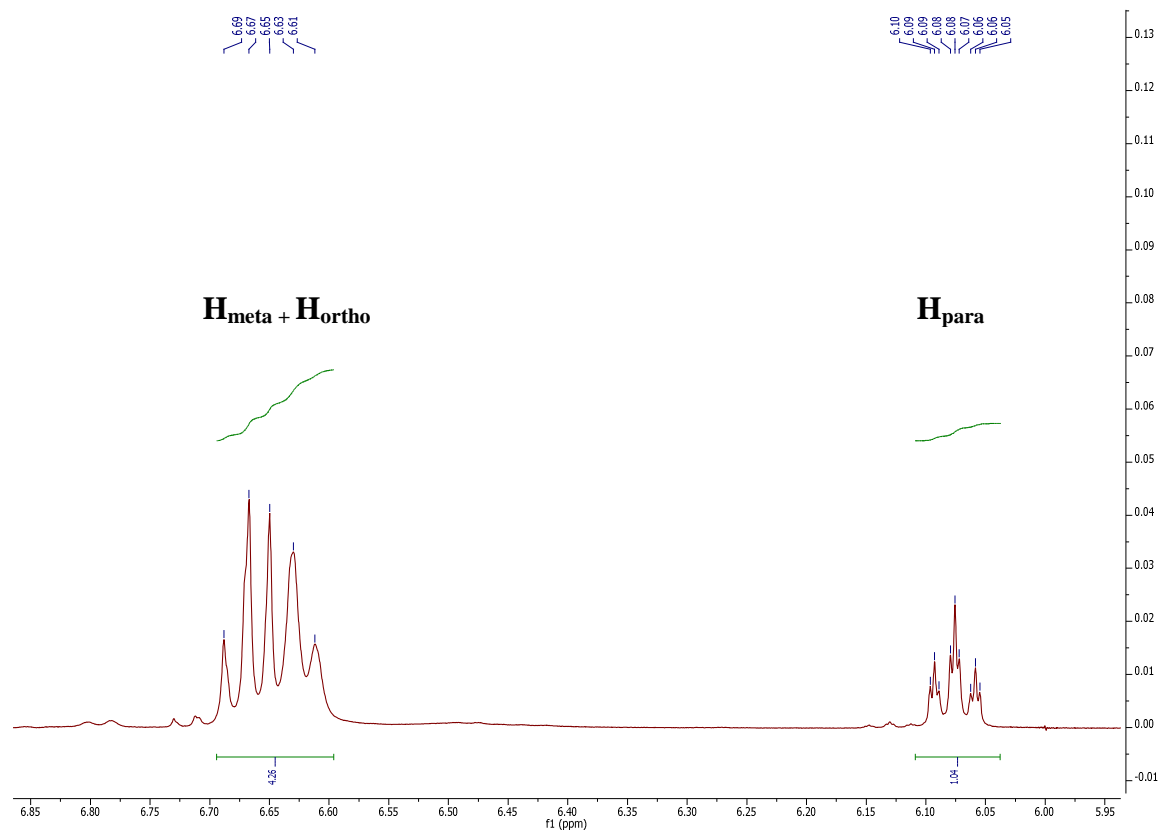
**<sup>7</sup>Li NMR** (155 MHz, THF-*d*<sub>8</sub>) δ/ppm = 2.87.

\* we found surprisingly that the acetylenic carbon directly next to the carbon bearing the Lithium was extremely shifted. Running of <sup>13</sup>C without <sup>1</sup>H decoupling confirmed that the signal was the right one, since it is a singlet.

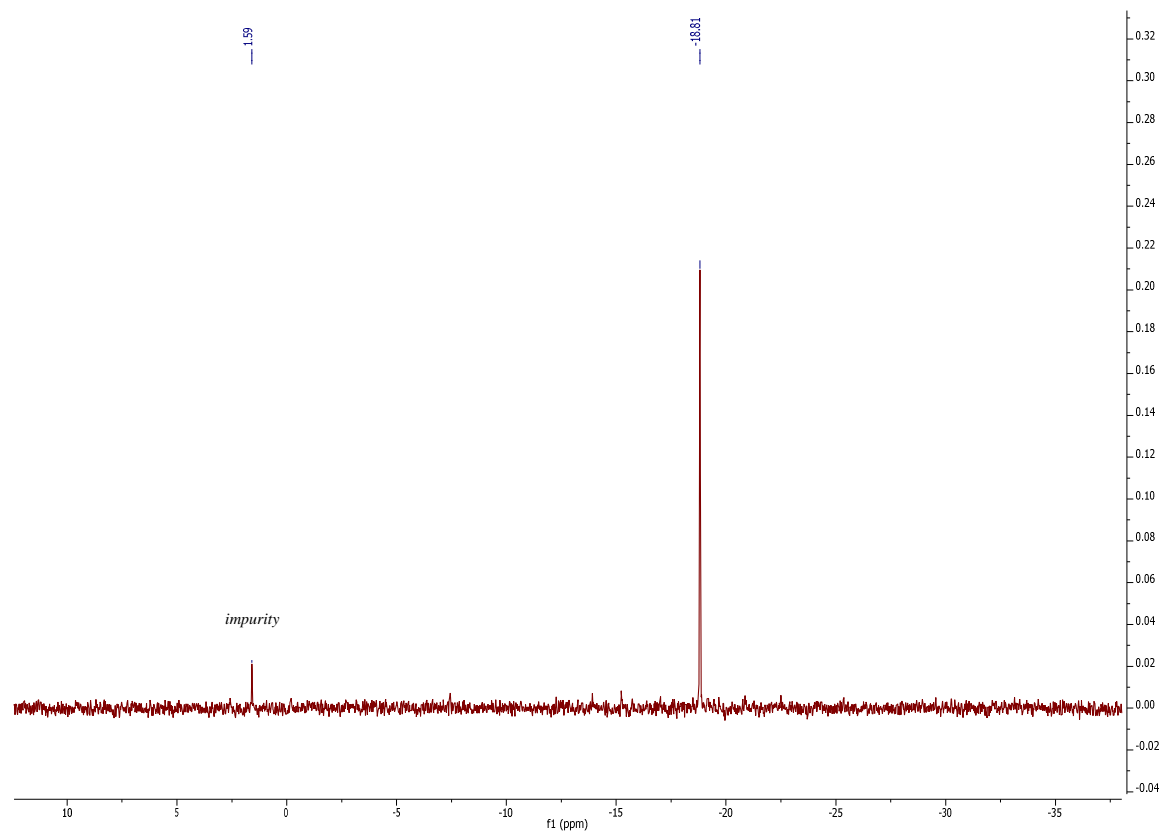
**$^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ )**



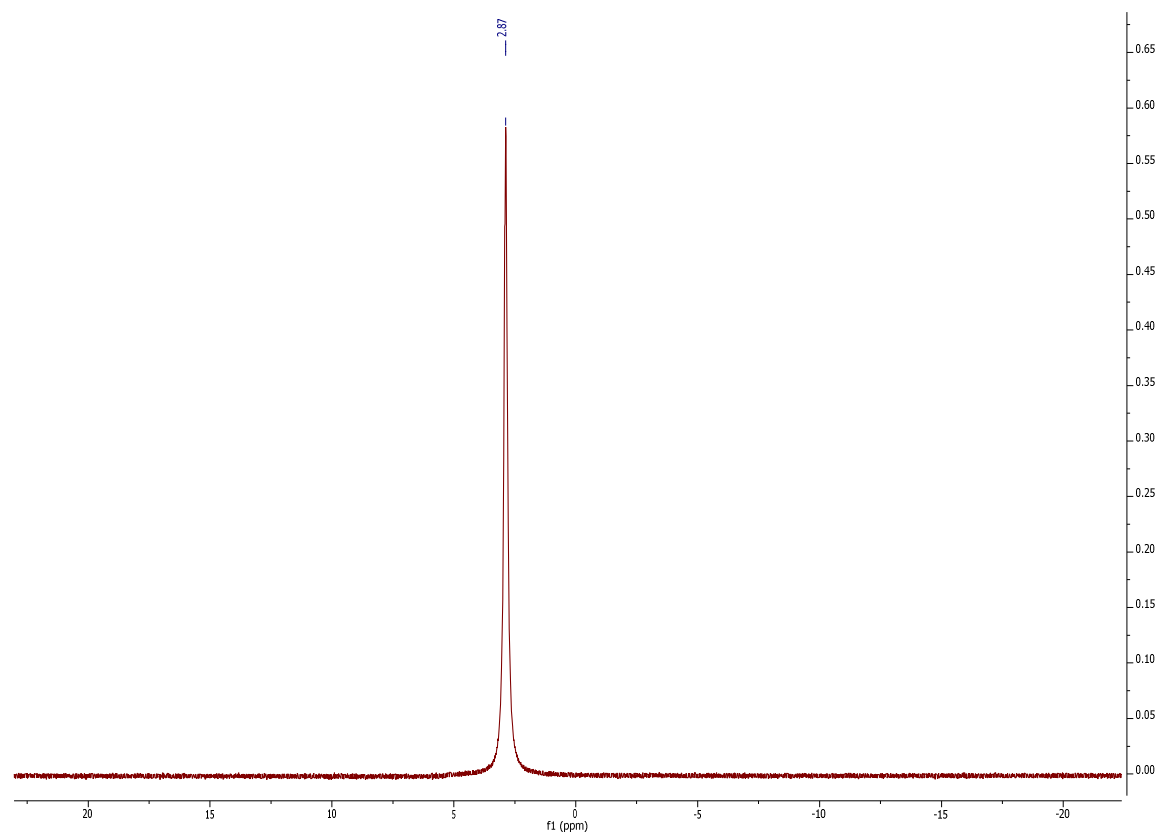
**$^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ), zoom on aromatic region**



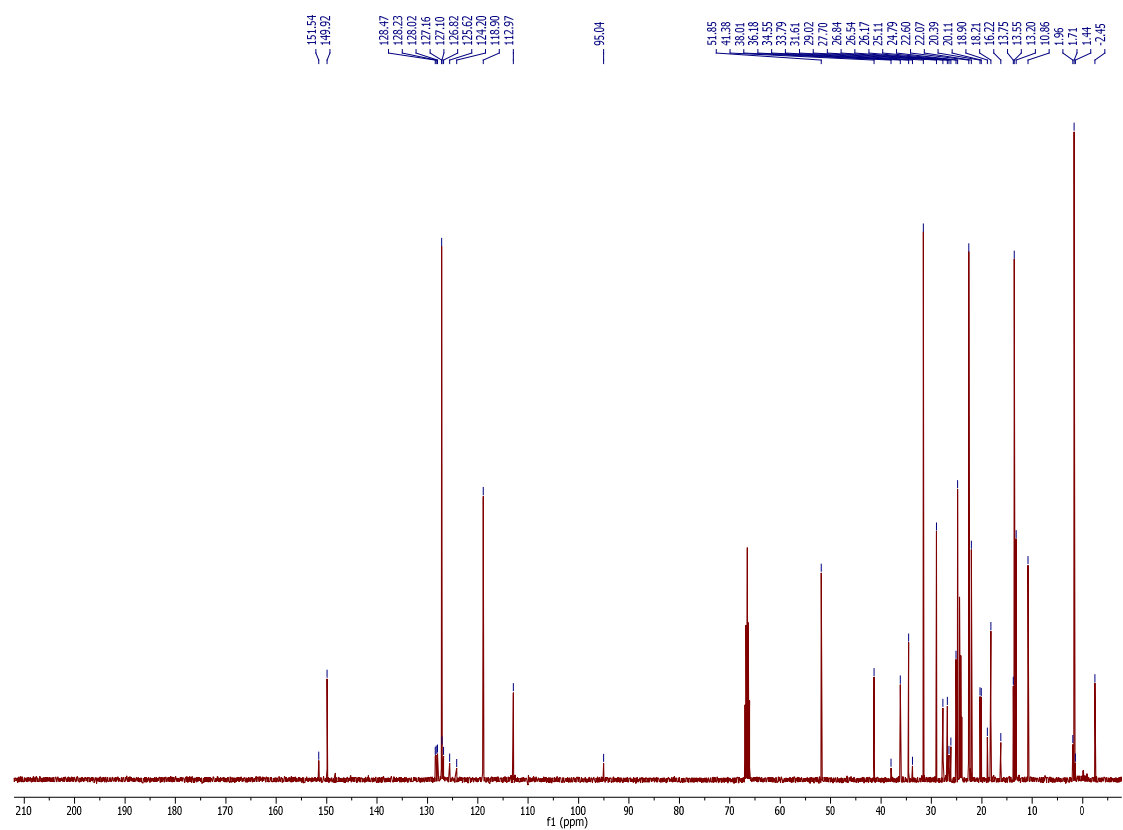
**$^{29}\text{Si}$  NMR (79 MHz, THF- $d_8$ )**



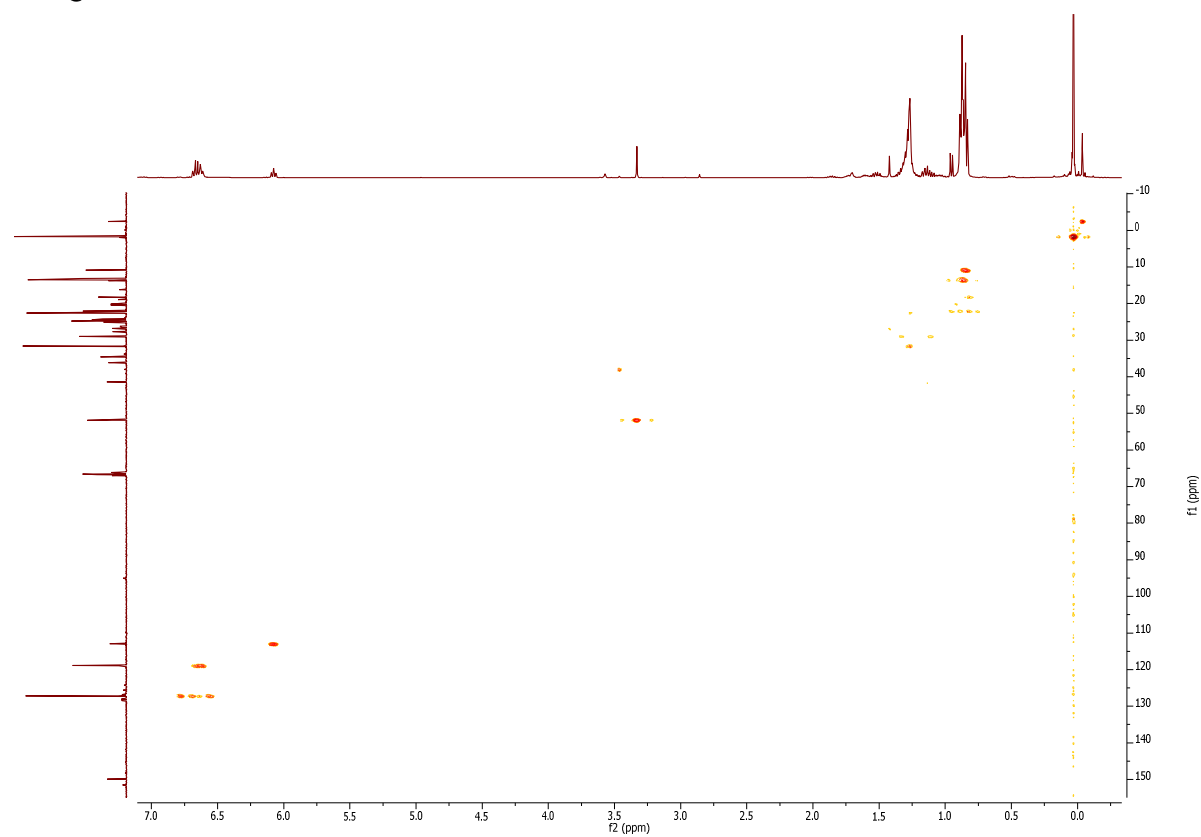
**$^7\text{Li}$  NMR (155 MHz, THF- $d_8$ )**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ )**

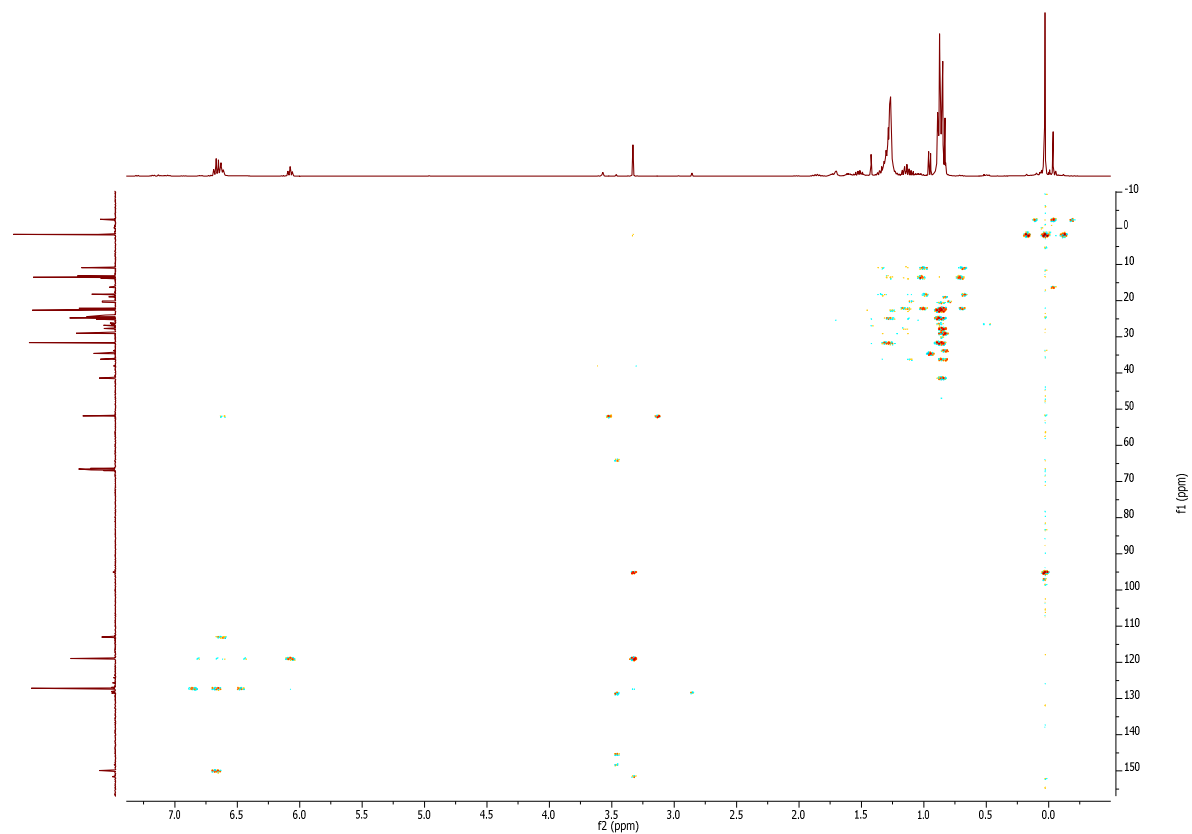


**HMQC**

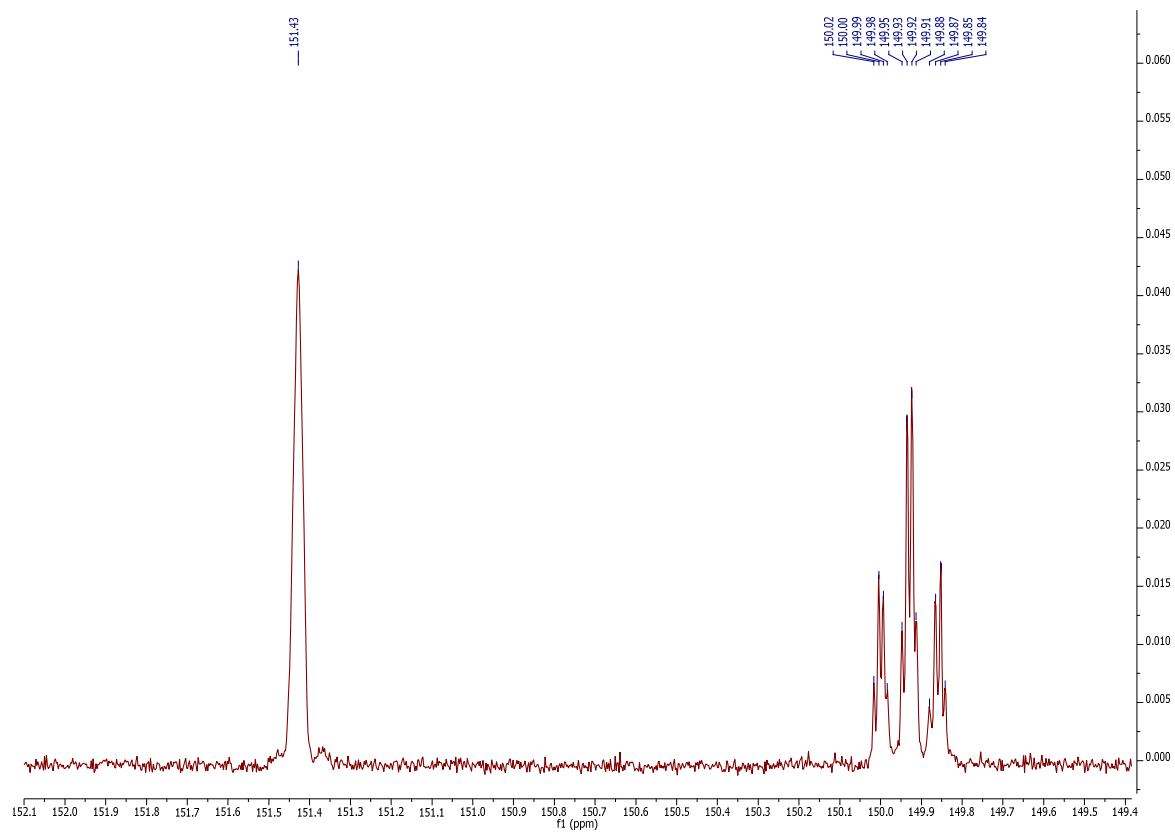




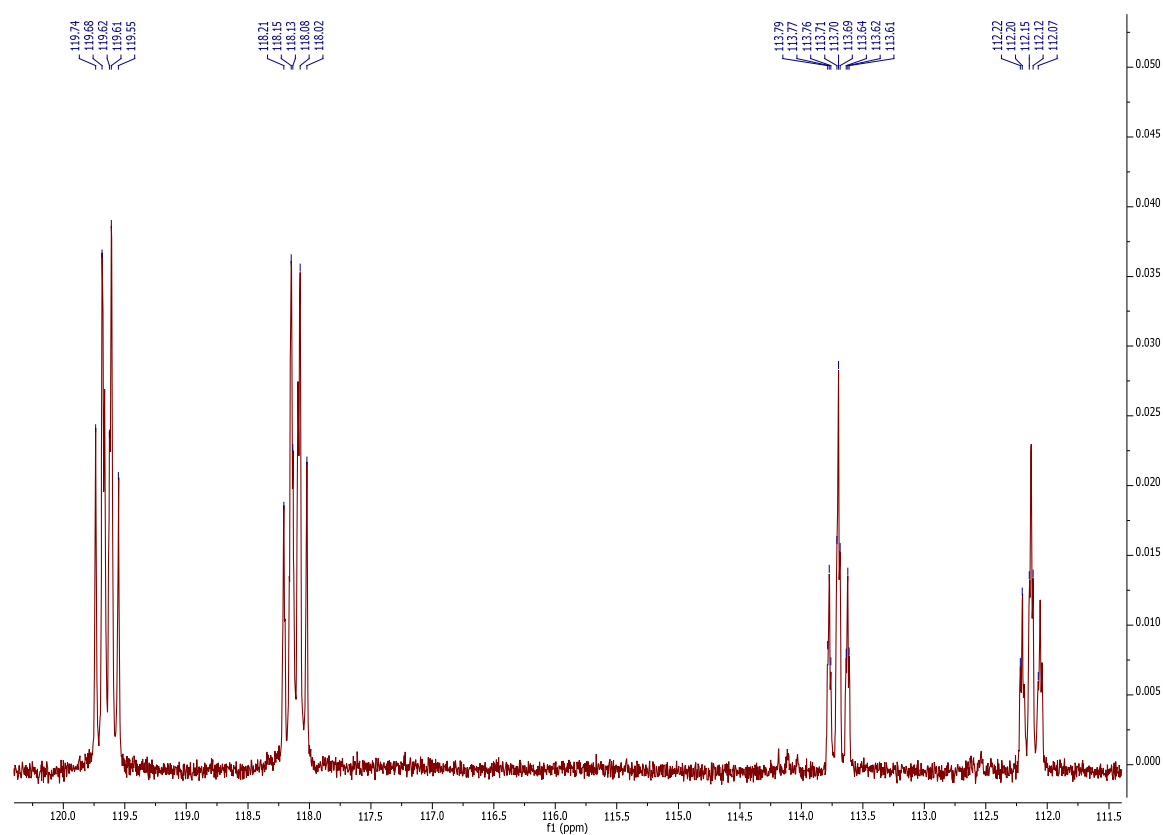
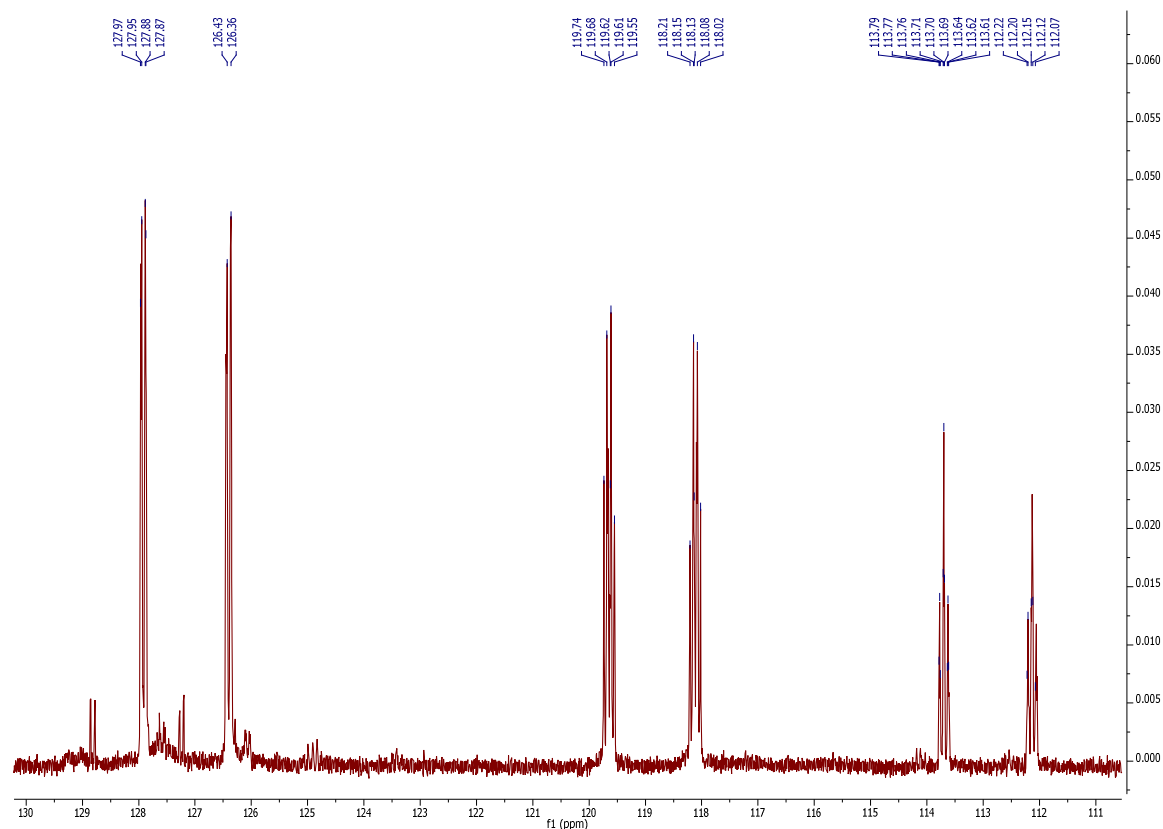
# HMBC



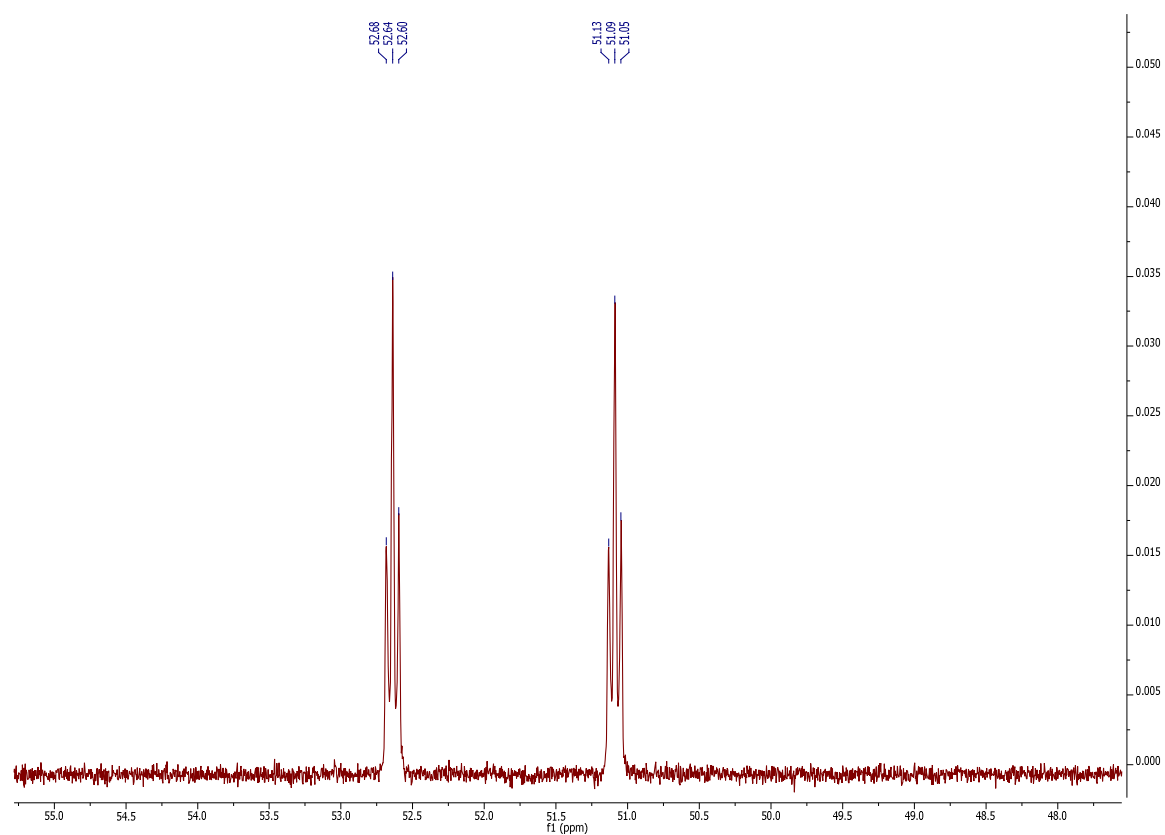
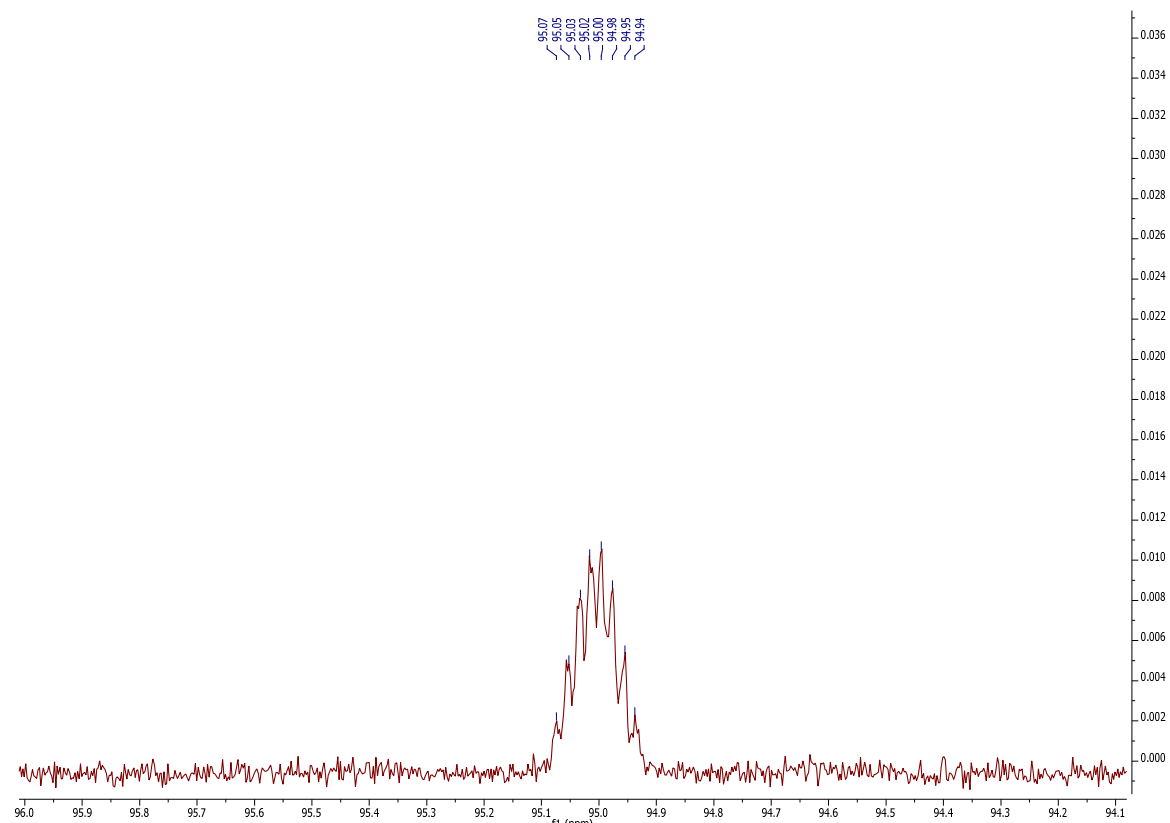
## $^{13}\text{C}$ without $^1\text{H}$ decoupling 1/7



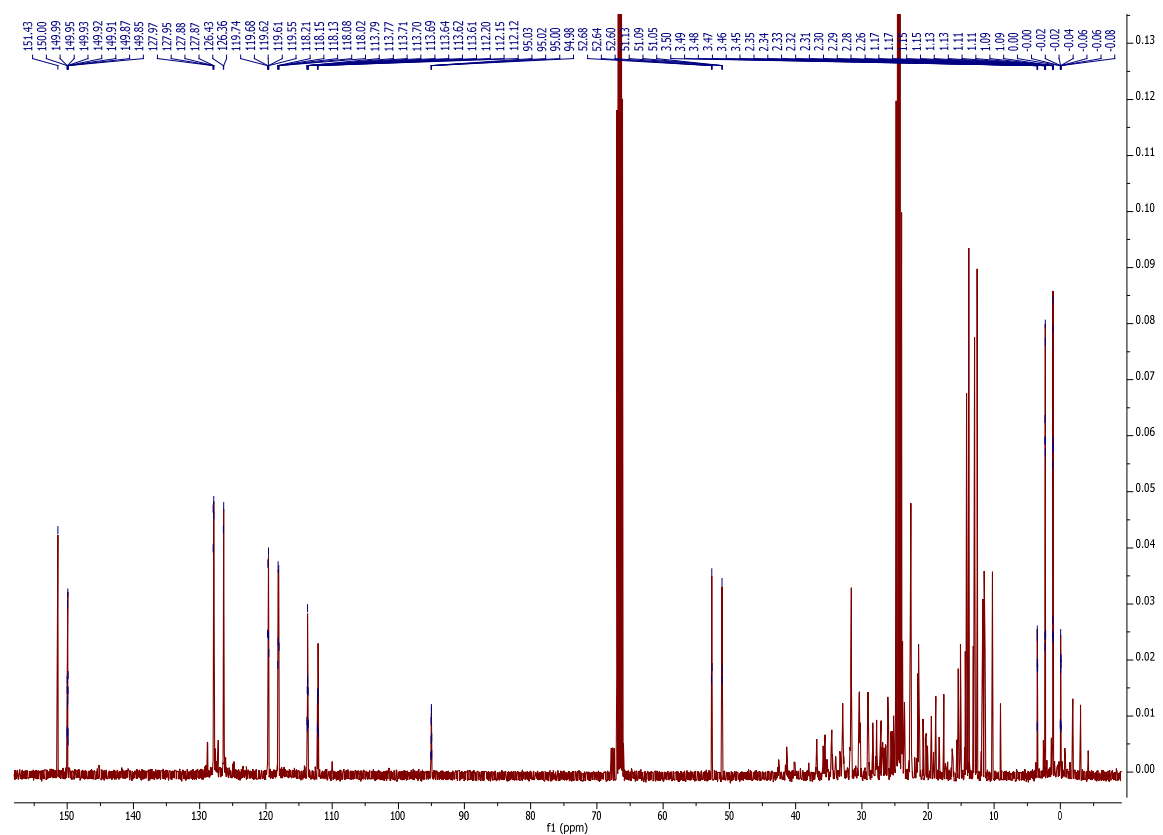
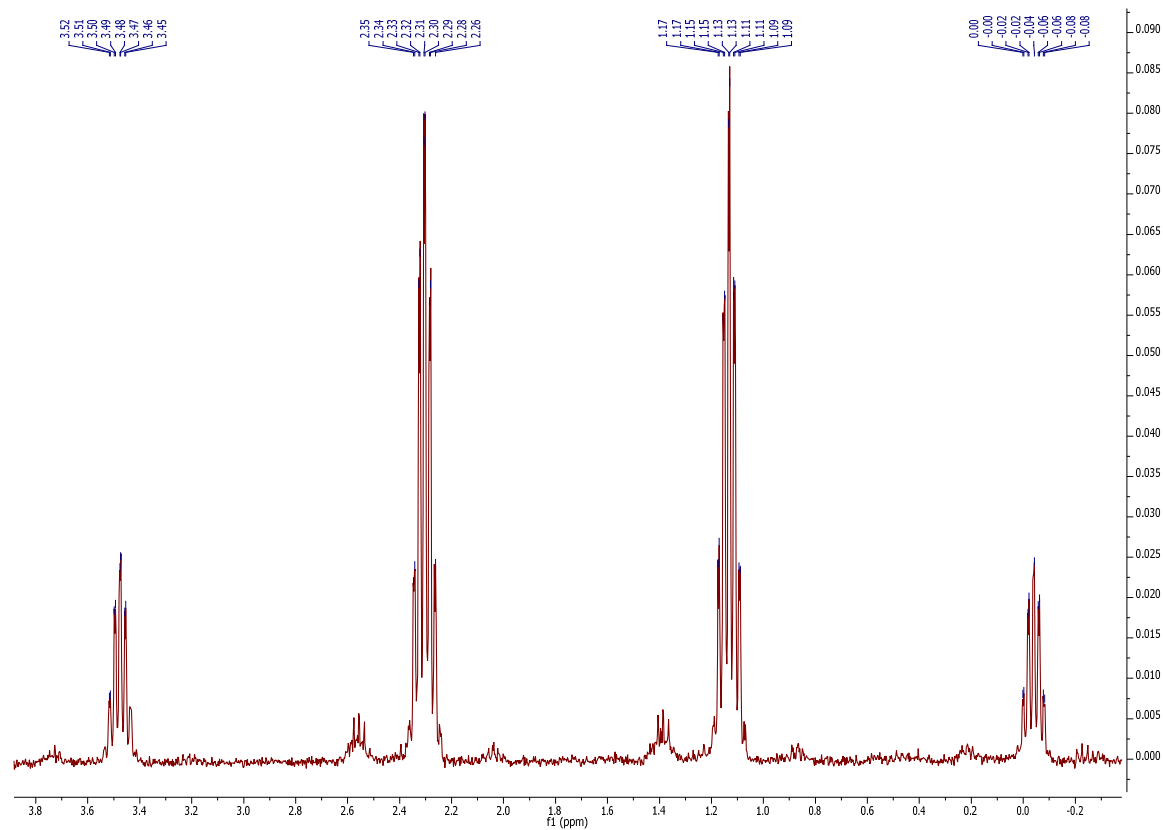
# $^{13}\text{C}$ without $^1\text{H}$ decoupling 2+3/7



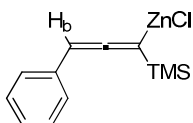
# <sup>13</sup>C without <sup>1</sup>H decoupling 4+5/7



# $^{13}\text{C}$ without $^1\text{H}$ decoupling 6+7/7



## NMR studies of the metalated intermediate **10**



In order to provide structural information on the metalated allene of type **10**, we investigated the metalation of trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**) with TMPZnCl·LiCl at 25°C. Therefore trimethyl(3-phenylprop-1-yn-1-yl)silane (**2a**; 0.25 mmol, 47.0 mg) and THF-*d*<sub>8</sub> (0.5 mL) were charged in a dry, argon flushed NMR tube. TMPZnCl·LiCl (1.2 equiv, 0.27 mL; 1.10 M in THF-*d*<sub>8</sub>) was slowly added and the tube was shaken once. The NMR tube was kept at 25 °C and NMR studies were performed at 25 °C, including <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si and 2D NMR.

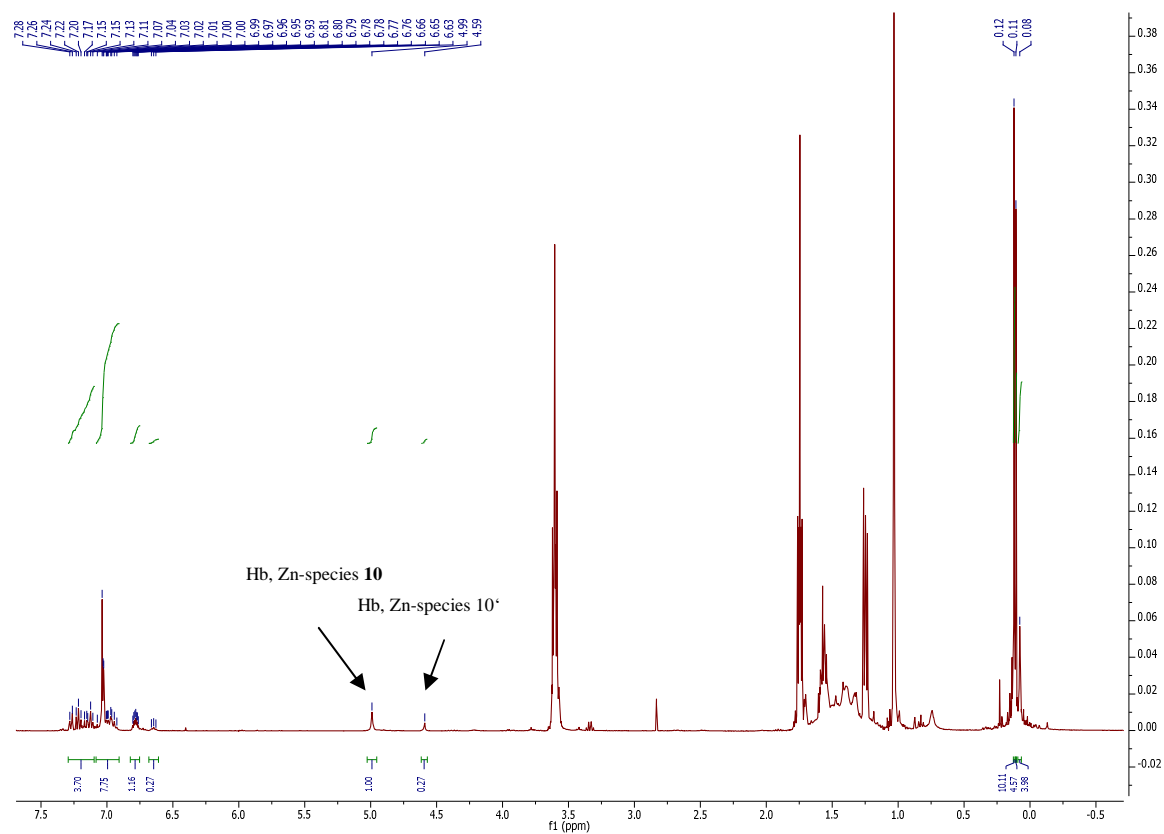
**<sup>1</sup>H NMR** (400 MHz, THF-*d*<sub>8</sub>) δ/ppm = 7.04 (2H, dd, 2-H<sub>ortho</sub>), 7.03 (2H, d, 2-H<sub>meta</sub>), 6.78 (1H, t, 1-H<sub>para</sub>), 4.99 (1H, s, H<sub>b</sub>), 0.12 (9H, s, CH<sub>3</sub>).

**<sup>13</sup>C NMR** (100 MHz, THF-*d*<sub>8</sub>) δ/ppm = 202.8 (=C=), 139.4 (C<sub>ipso</sub>), 127.9 (2C<sub>meta</sub>) 124.0 (2C<sub>ortho</sub>), 122.7 (C<sub>para</sub>), 94.0 (C-Zn), 73.4 (C-H<sub>b</sub>), - 0.13 (CH<sub>3</sub>).

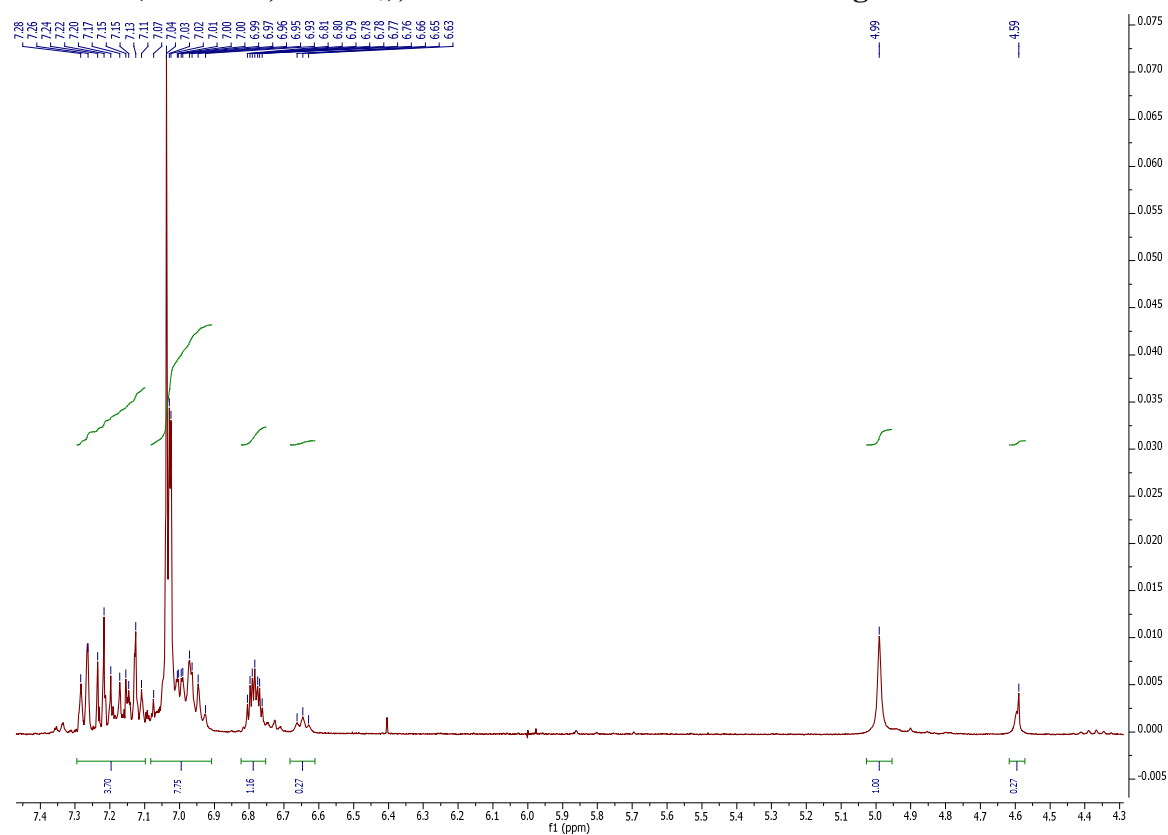
**<sup>29</sup>Si NMR** (79 MHz, THF-*d*<sub>8</sub>) δ/ppm = -4.59.

NMR studies of the metalated intermediate **10** were done again after 3 and 6 days measuring the same NMR tube (under argon) to show that the zinc species **10** equilibrates to another allenylzinc species.

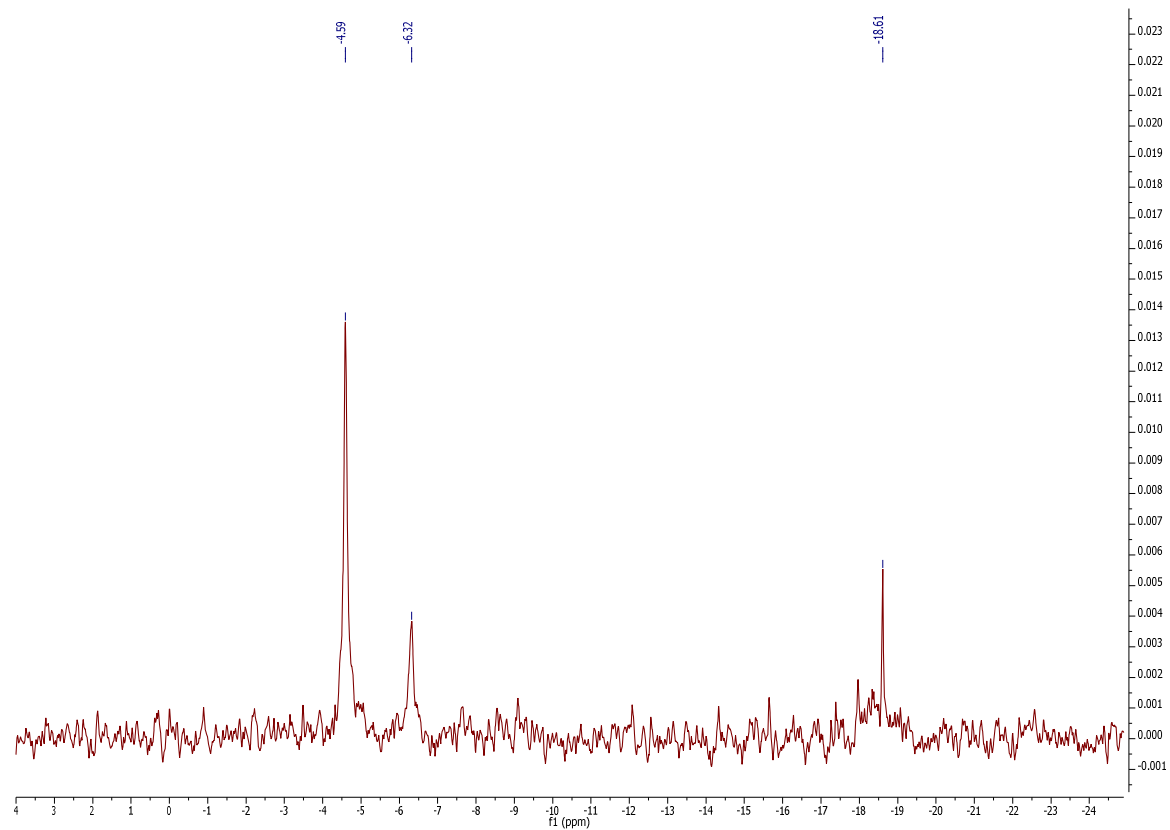
**$^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ )**



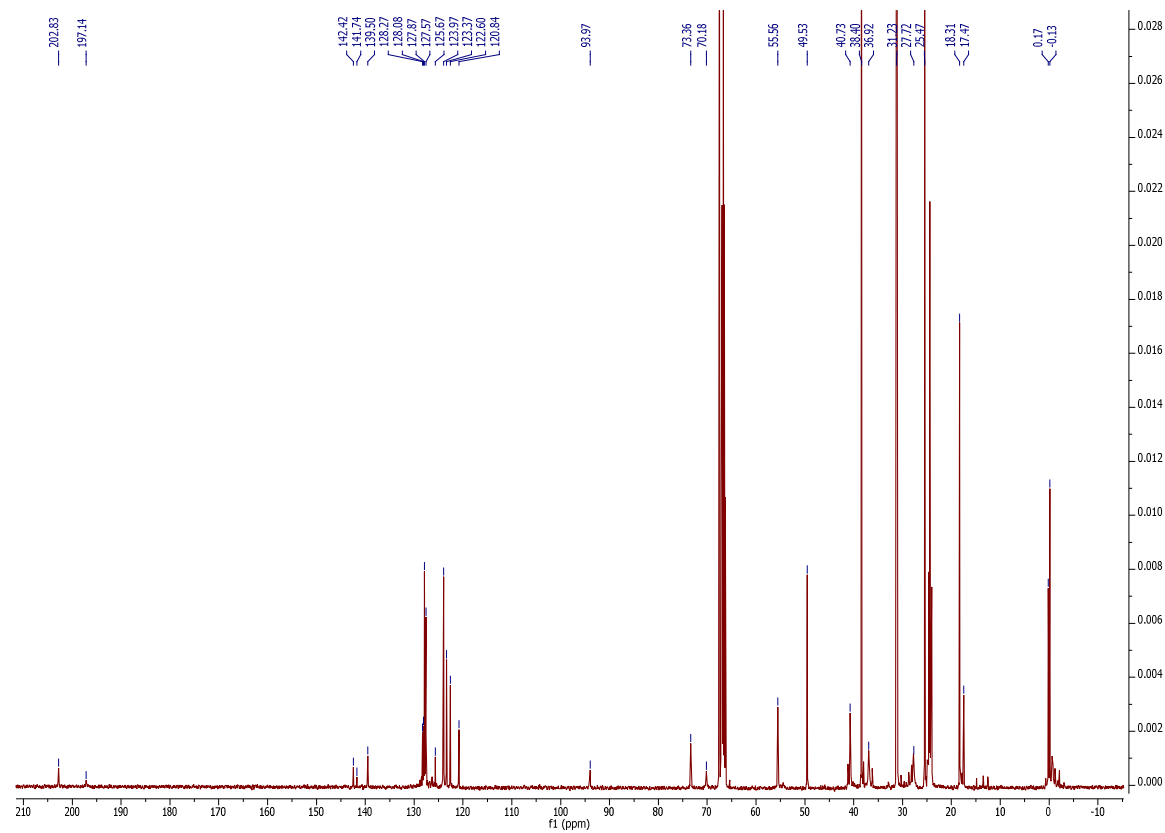
**$^1\text{H}$  NMR (400 MHz,  $\text{THF-d}_8$ ), zoom on aromatic and allenic region**



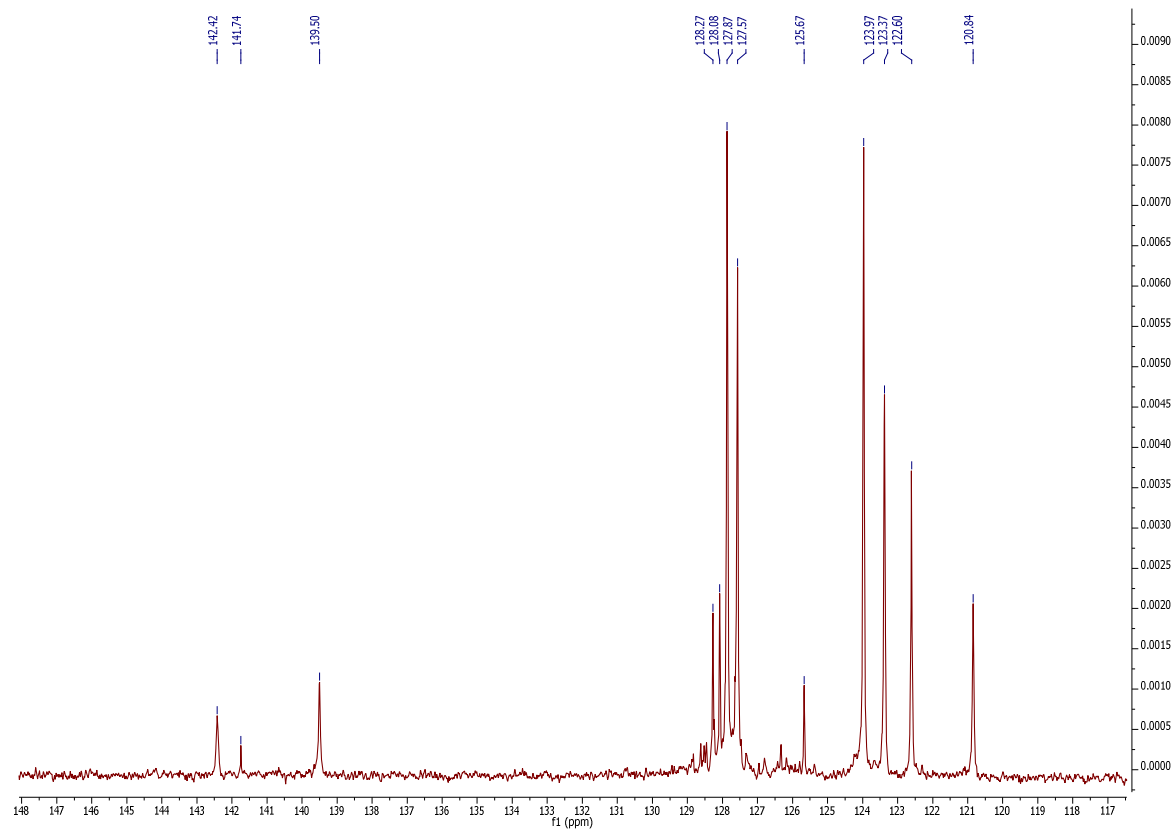
**$^{29}\text{Si}$  NMR (79 MHz, THF- $d_8$ )**



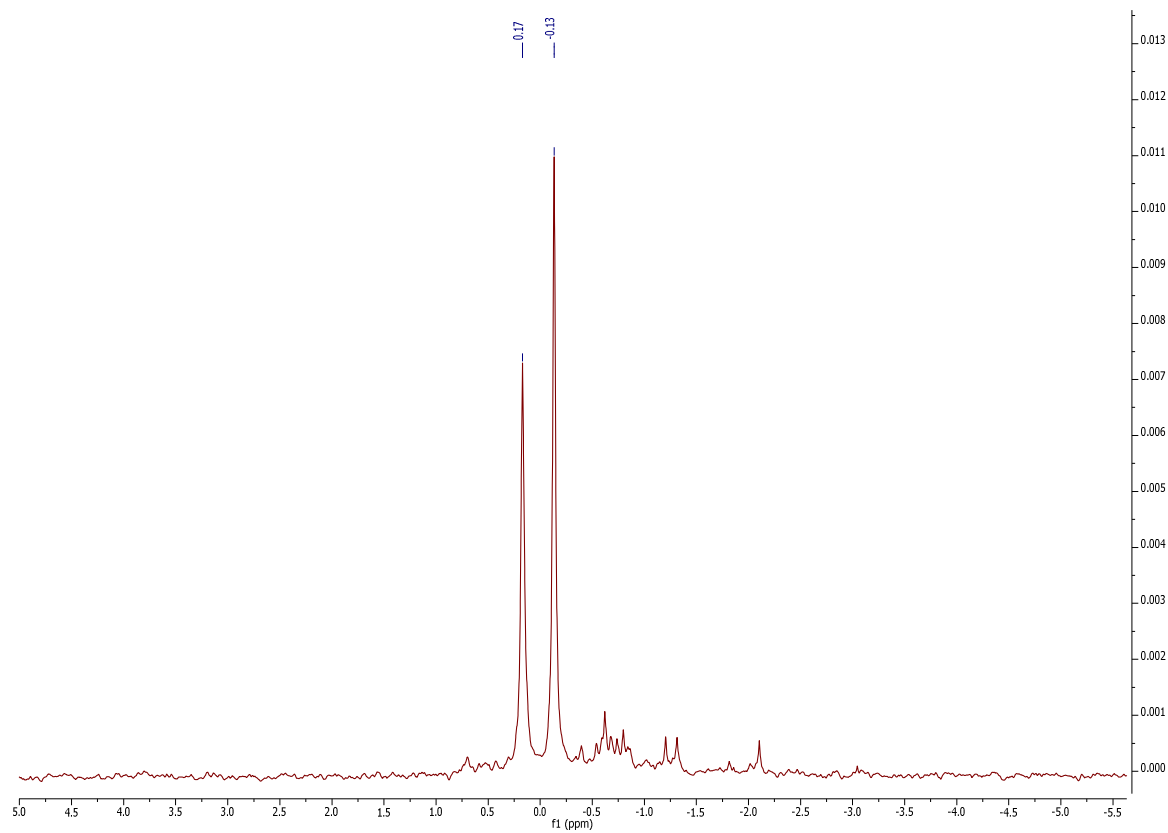
**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ )**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ), zoom**

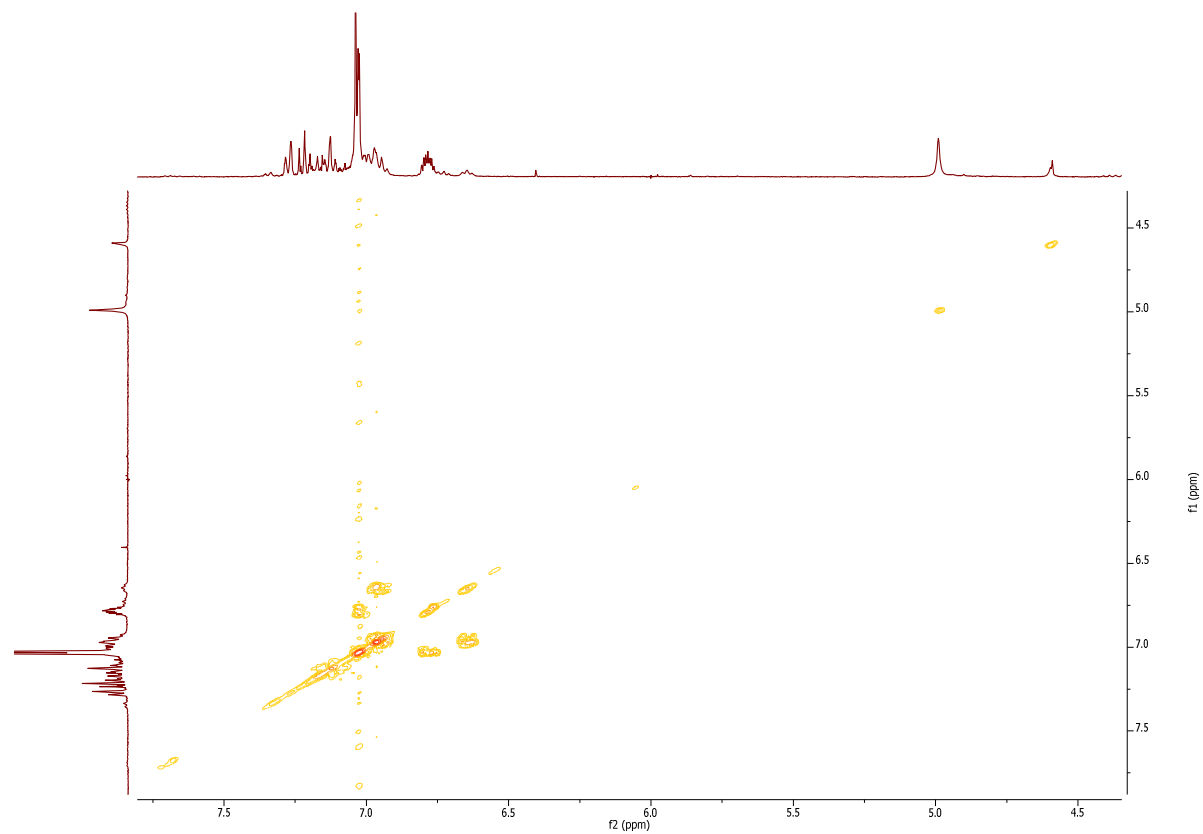


**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ), zoom on  $\text{Si}(\text{CH}_3)_3$  region**

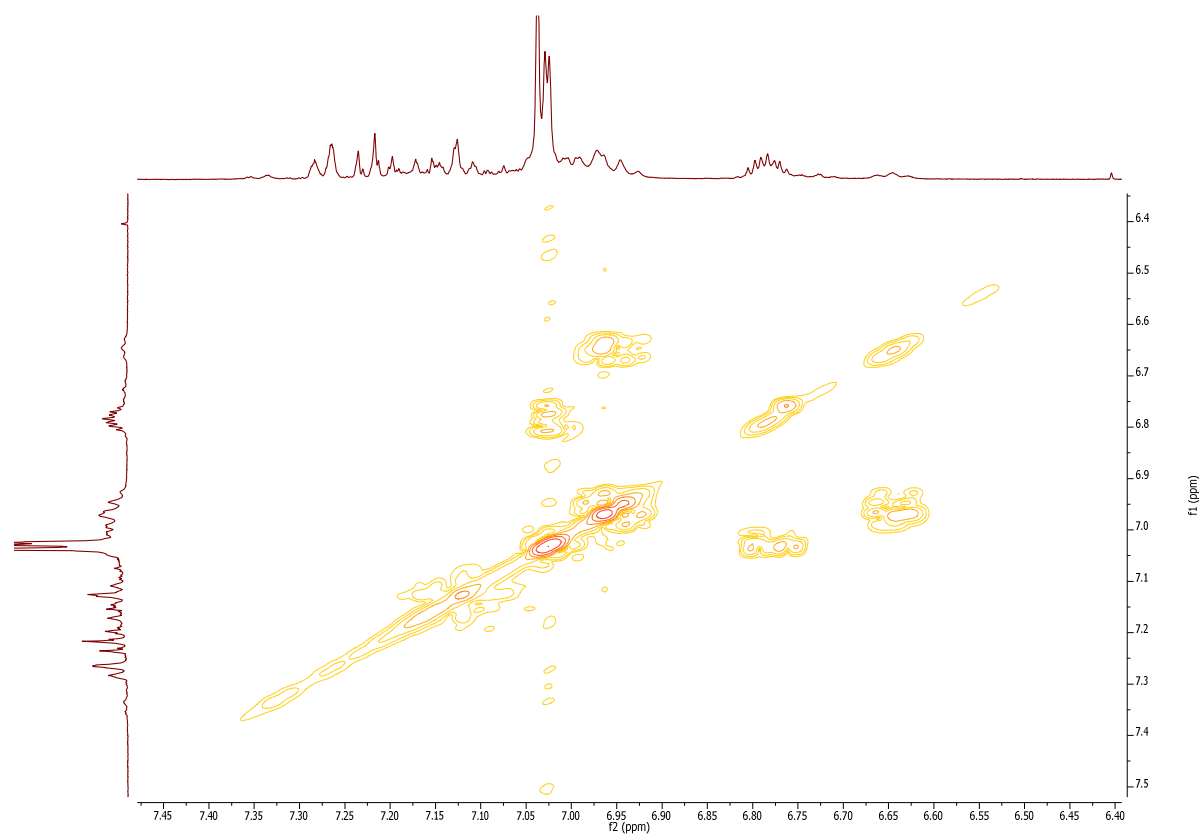




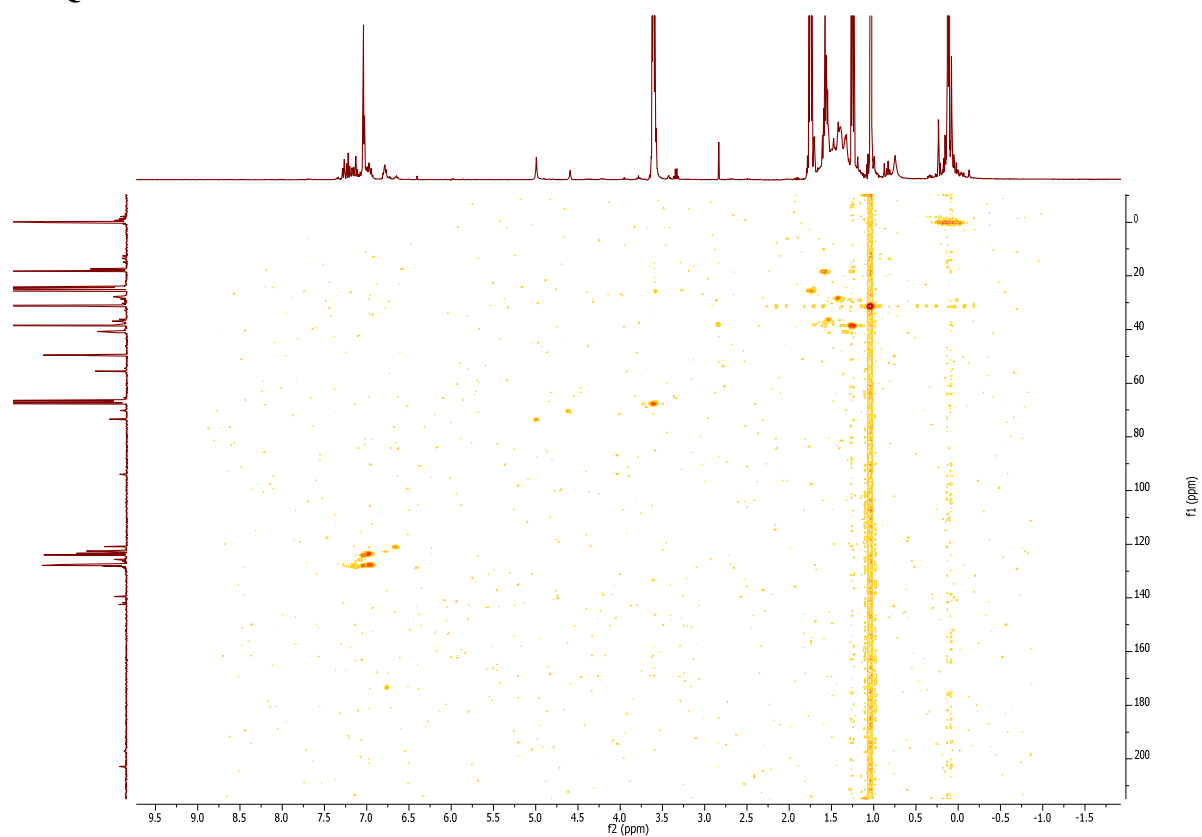
**COSY**



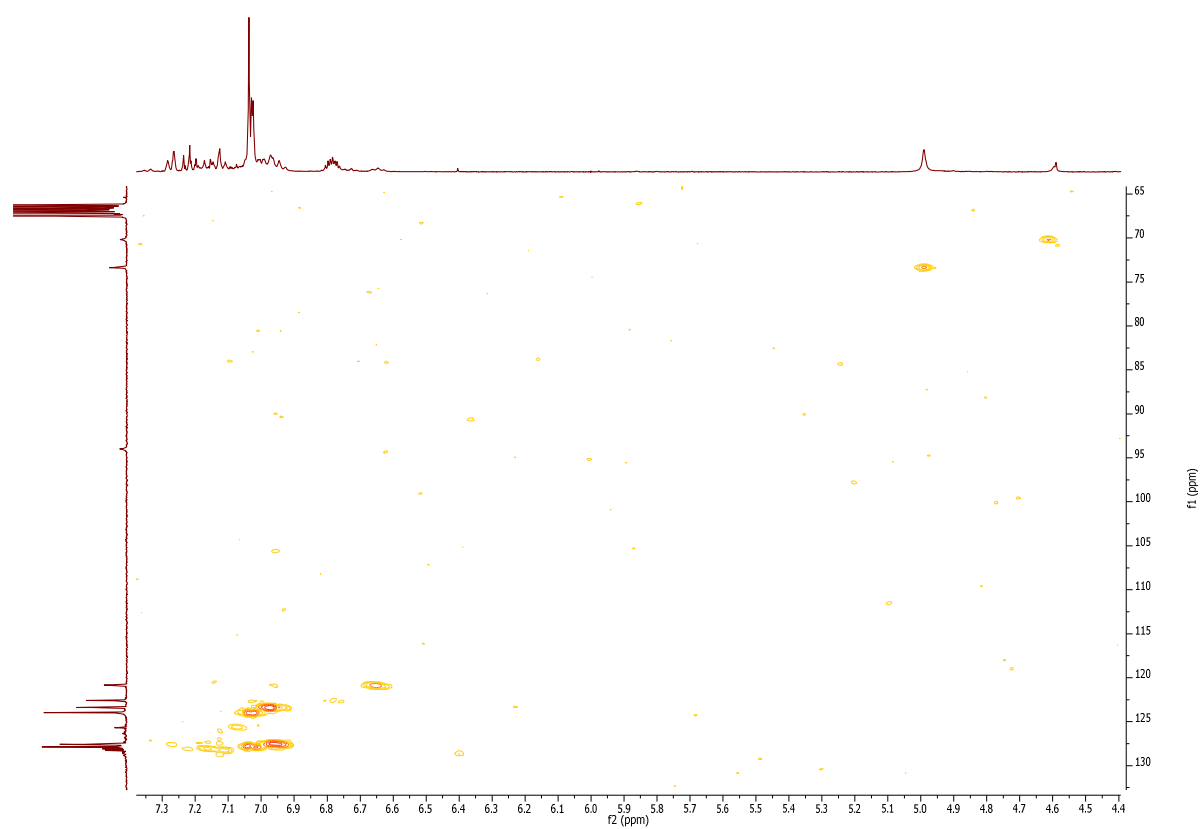
**COSY**



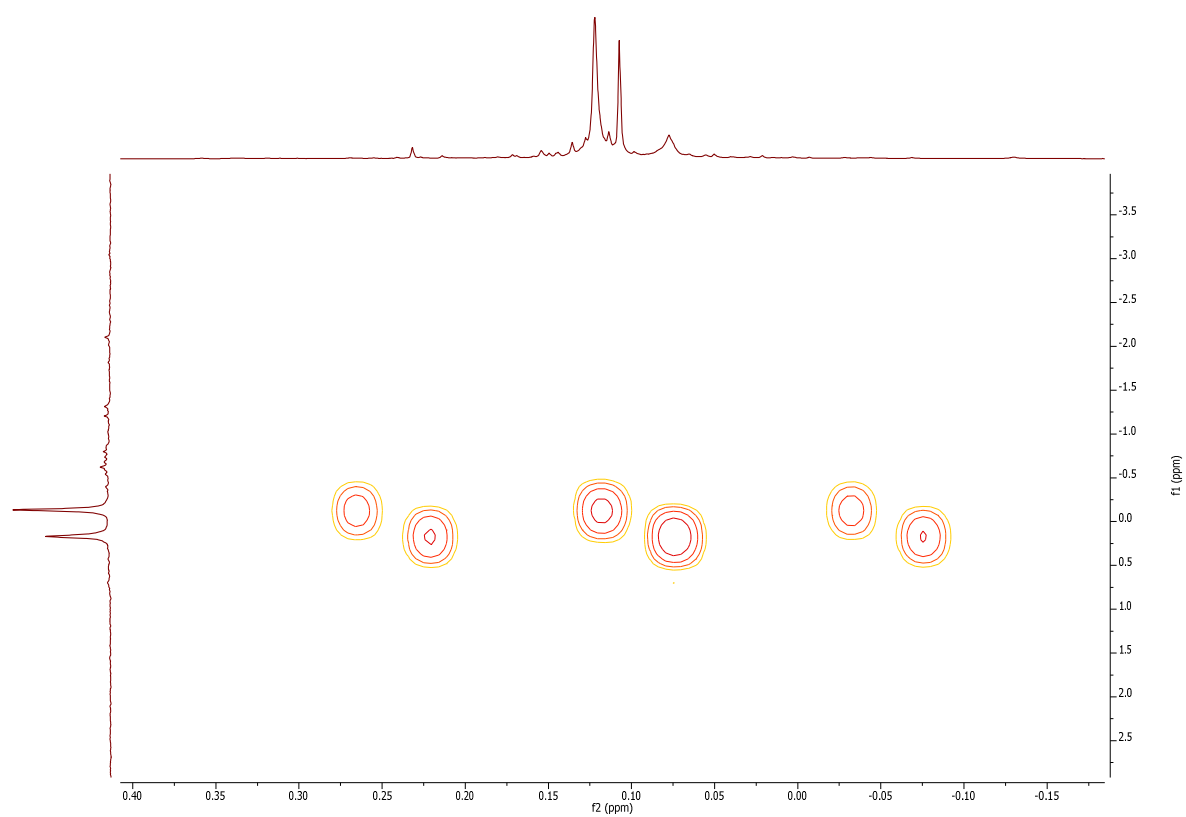
## HMQC



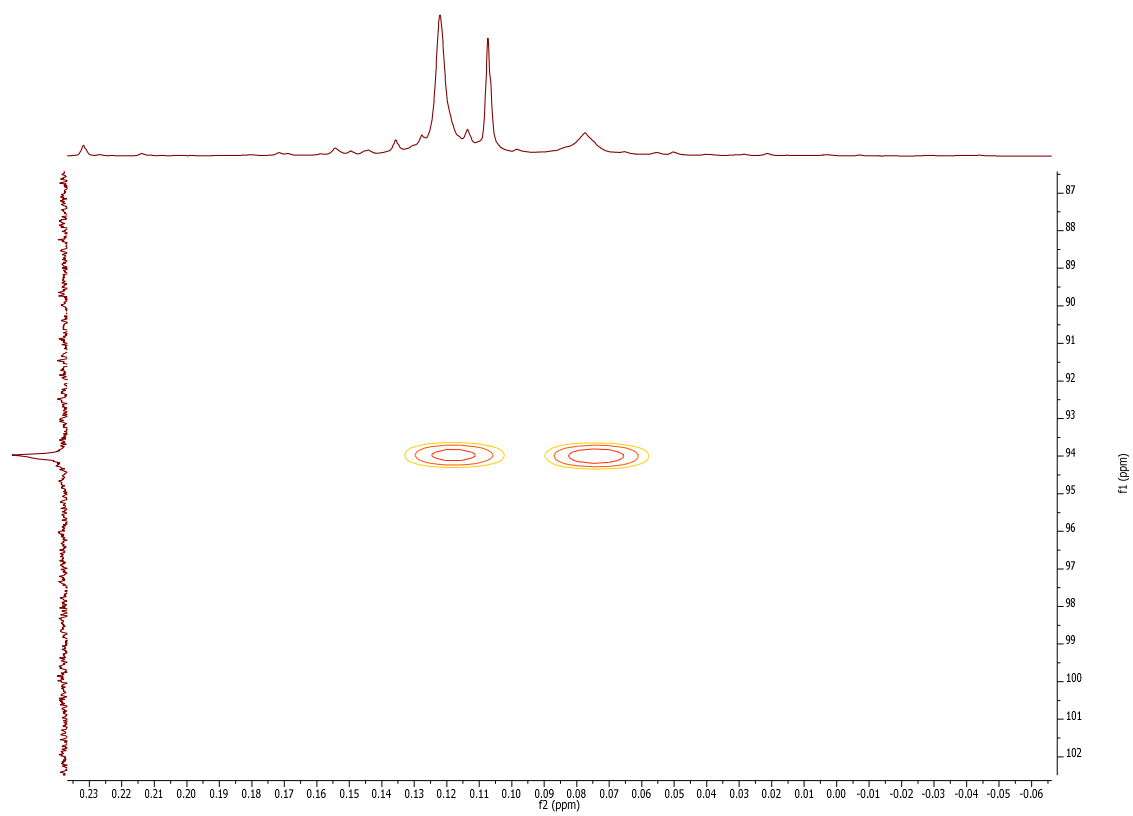
## HMQC, zoom on allenic region



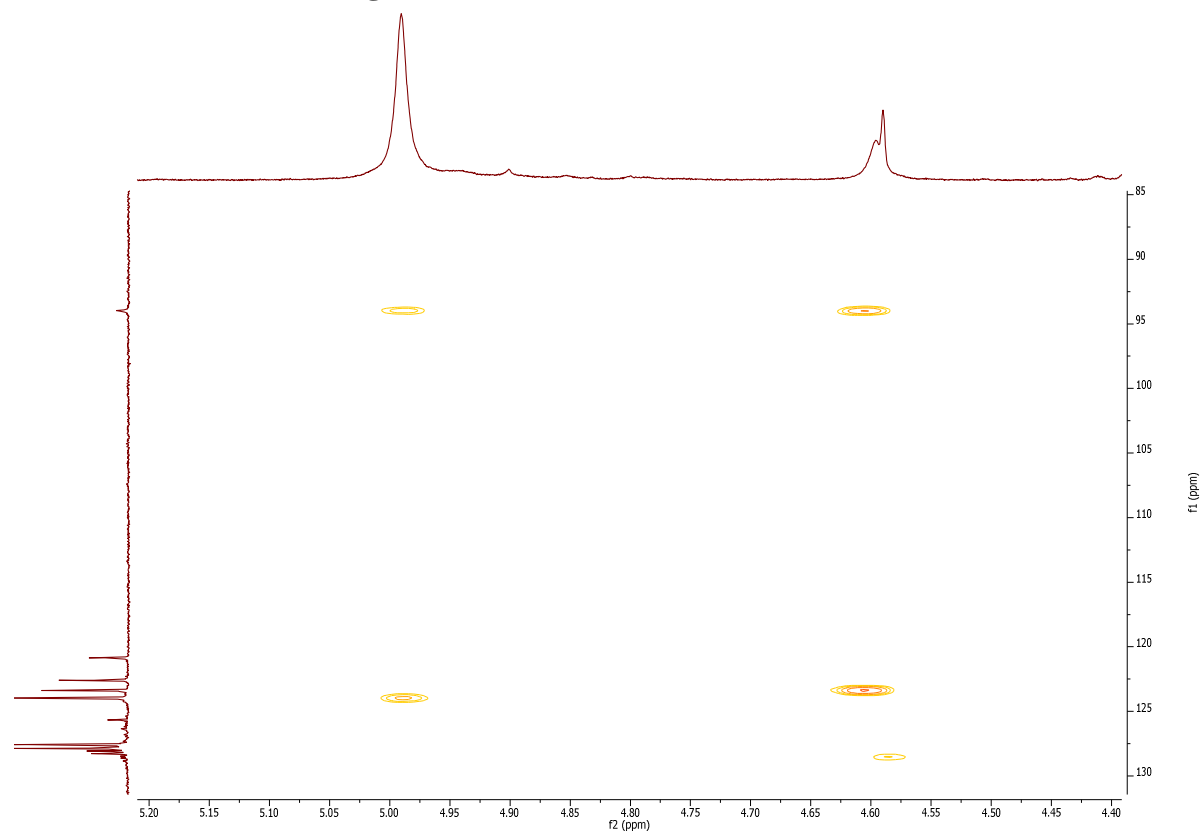
### HMQC, zoom on Si(CH<sub>3</sub>)<sub>3</sub> region



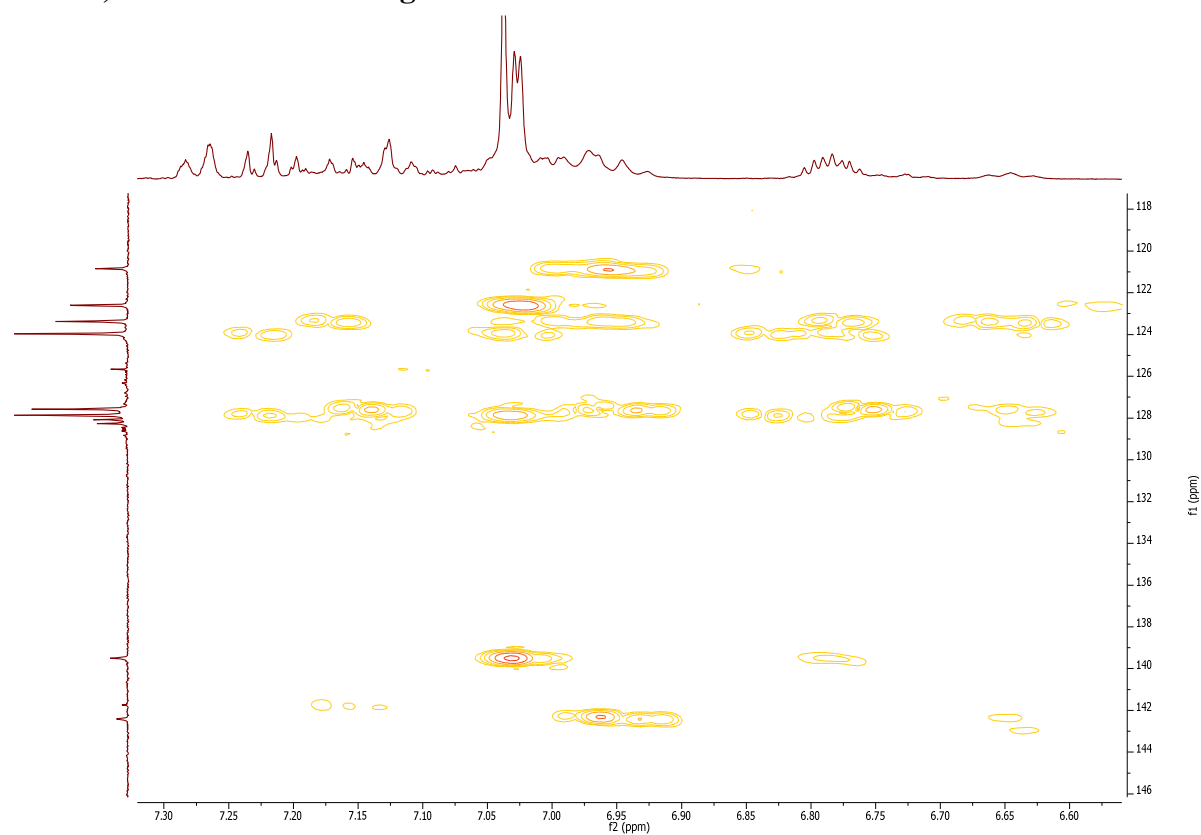
### HMBC, zoom on Si(CH<sub>3</sub>)<sub>3</sub> region



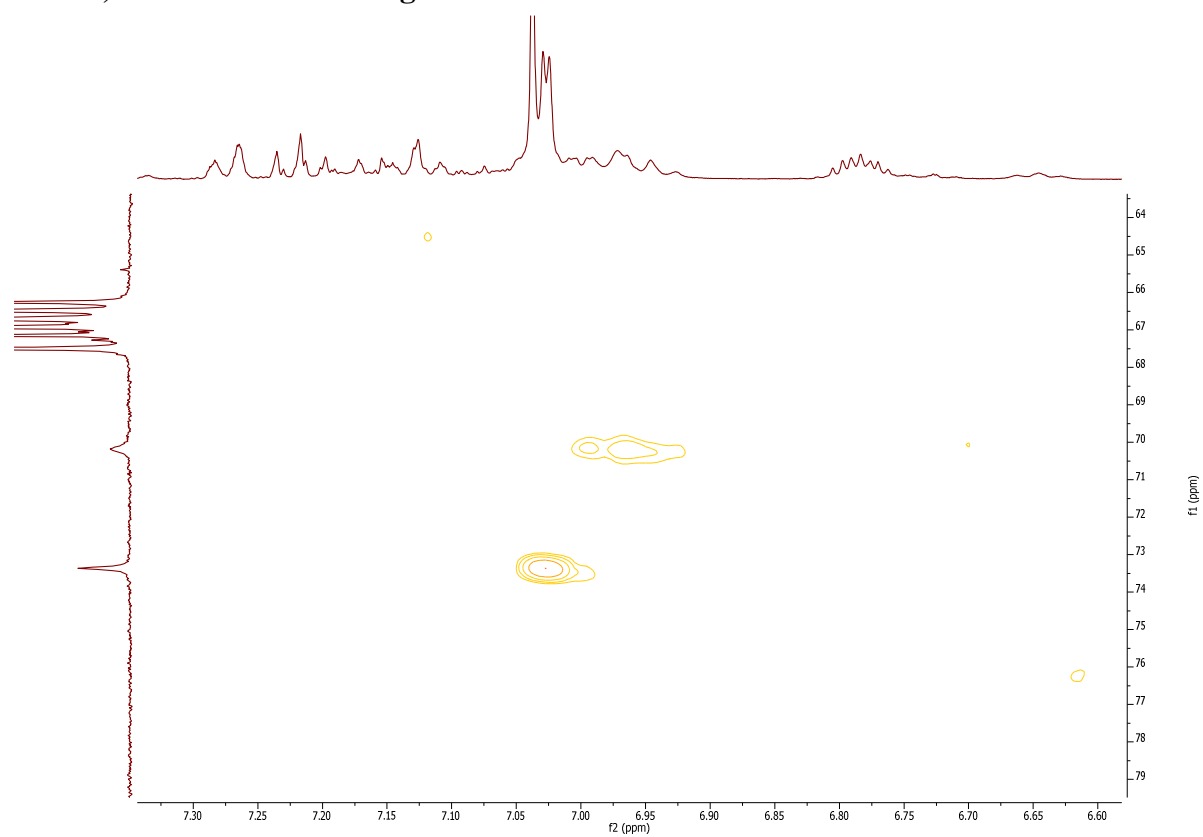
### HMBC, zoom on allenic region



### HMBC, zoom on aromatic region

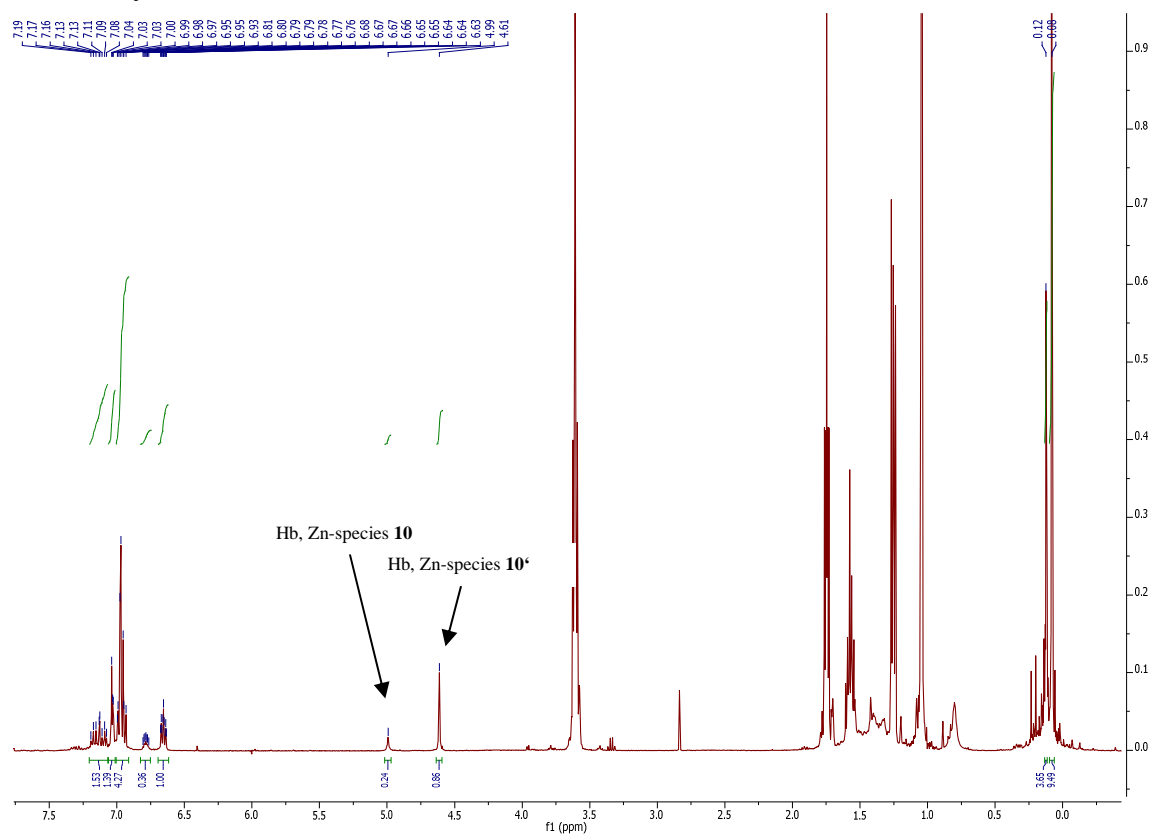


# HMBC, zoom on aromatic region

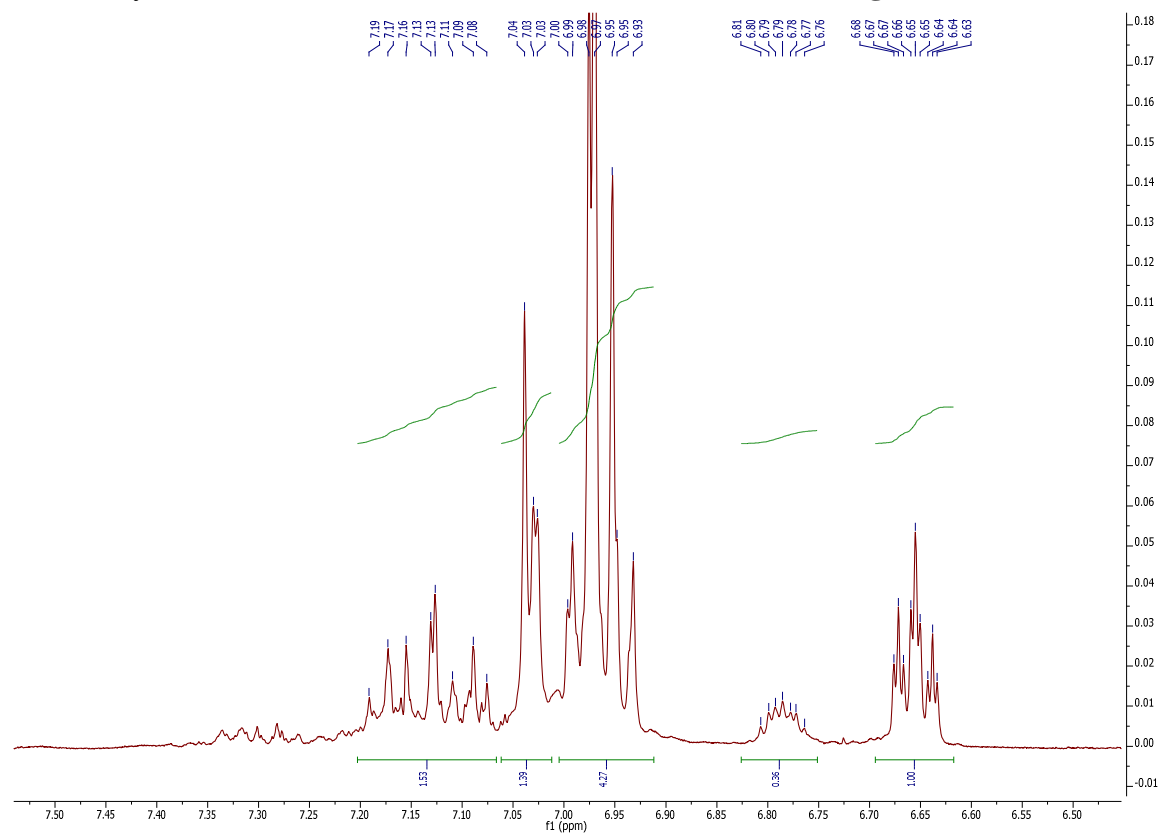


NMR studies of the metalated intermediate **10** after 3 and 6 days at 25°C under argon

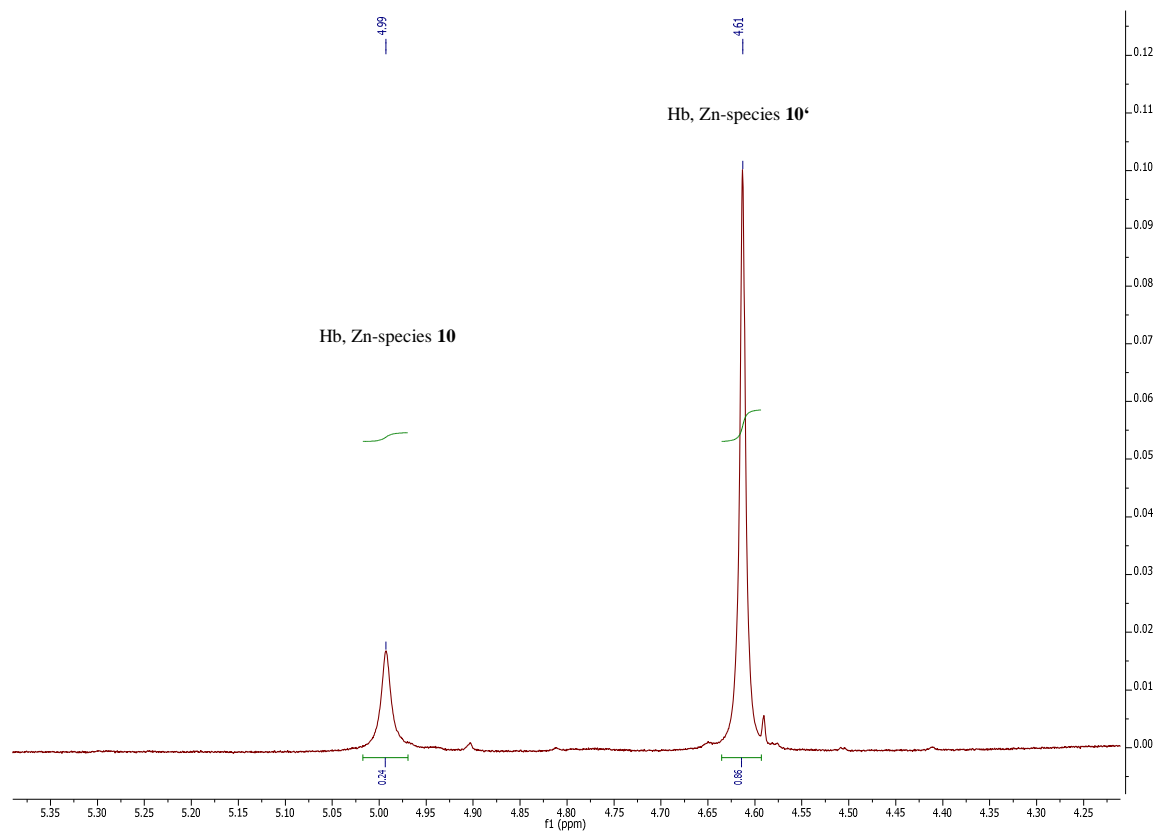
After 3 days,  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ )



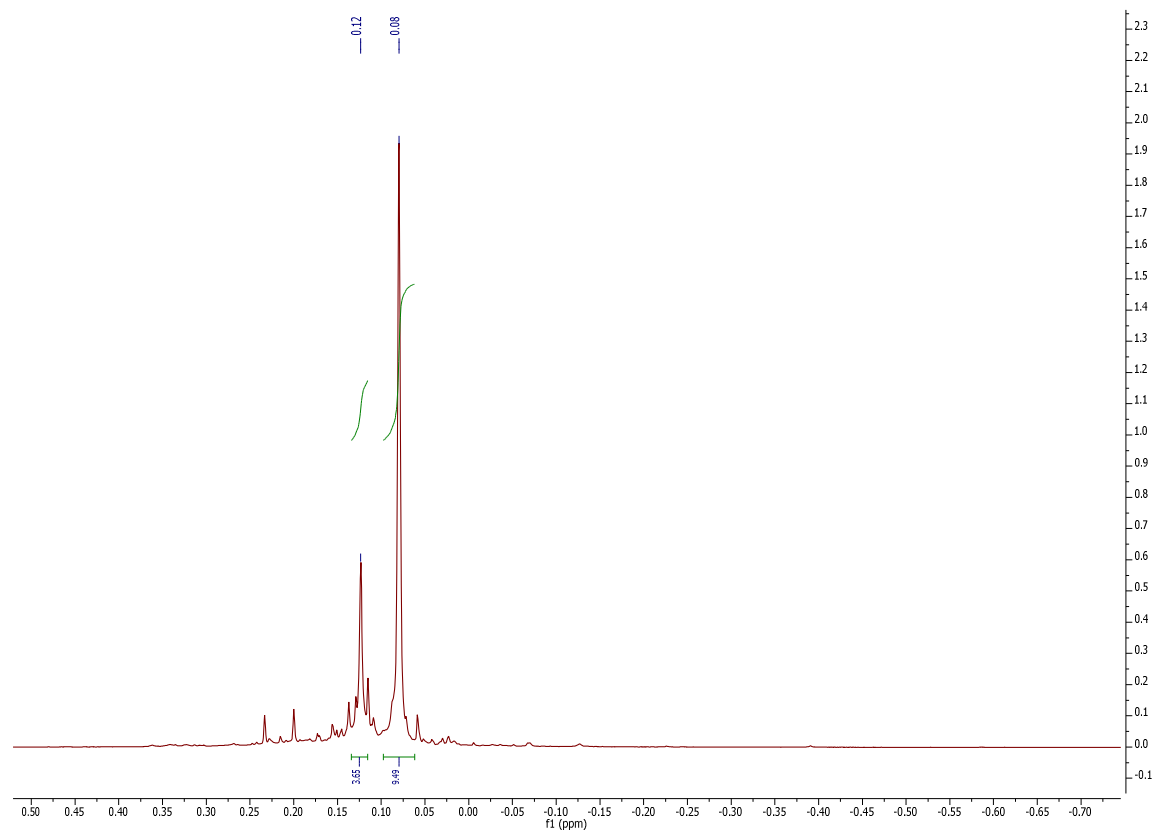
After 3 days,  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ), zoom on aromatic region



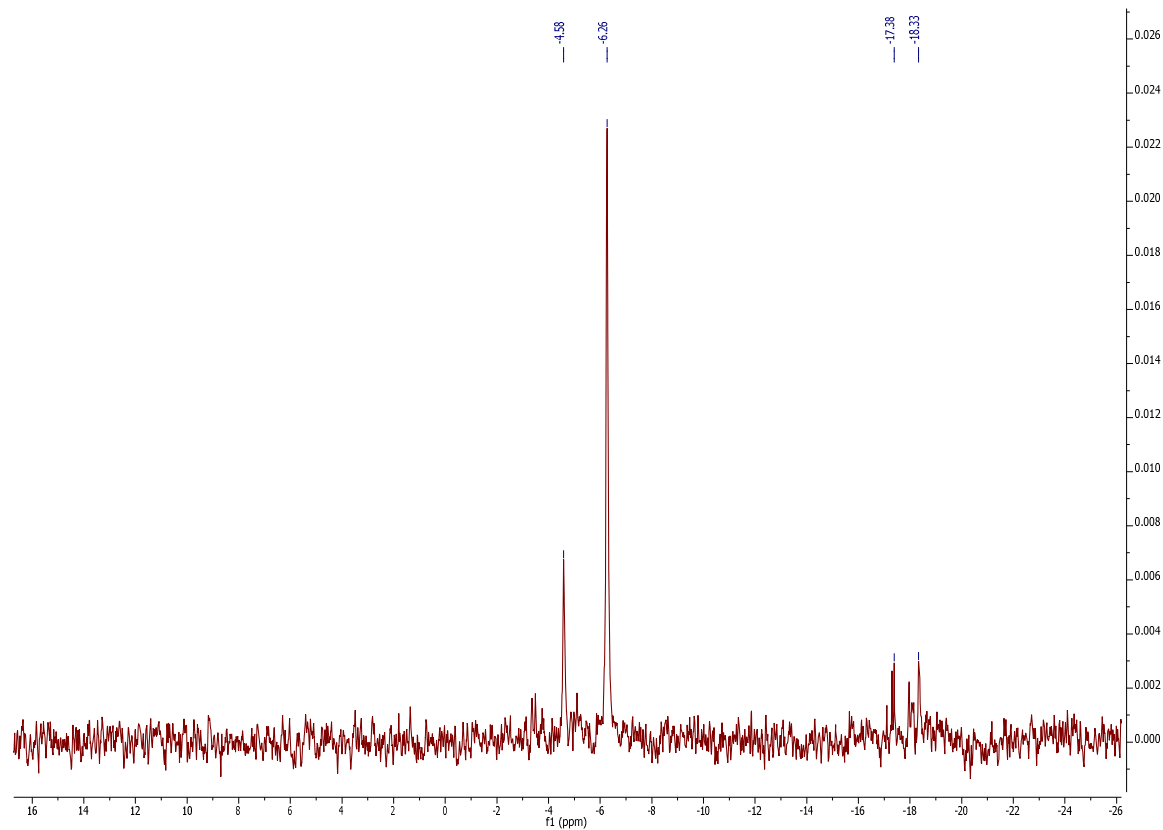
After 3 days,  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ), zoom on allenic region



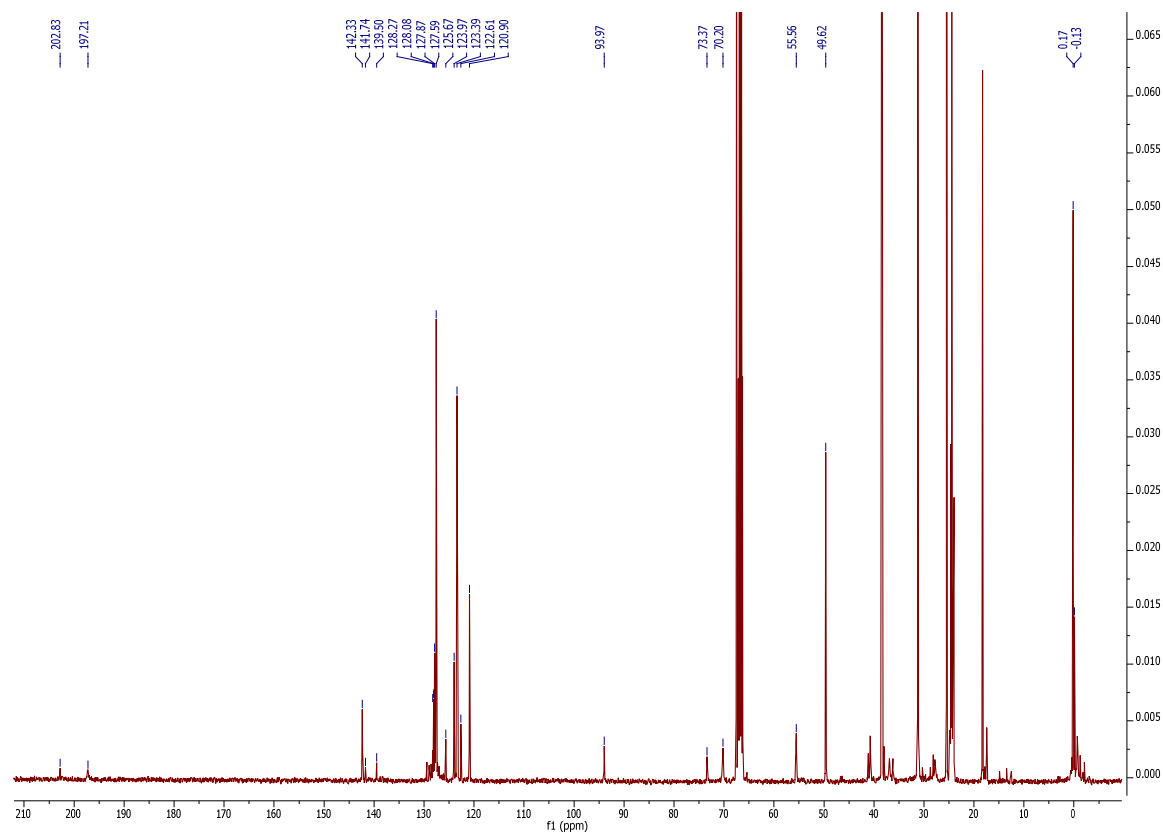
After 3 days,  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ), zoom on  $\text{Si}(\text{CH}_3)_3$  region



After 3 days,  $^{29}\text{Si}$  NMR (79 MHz,  $\text{THF-}d_8$ )

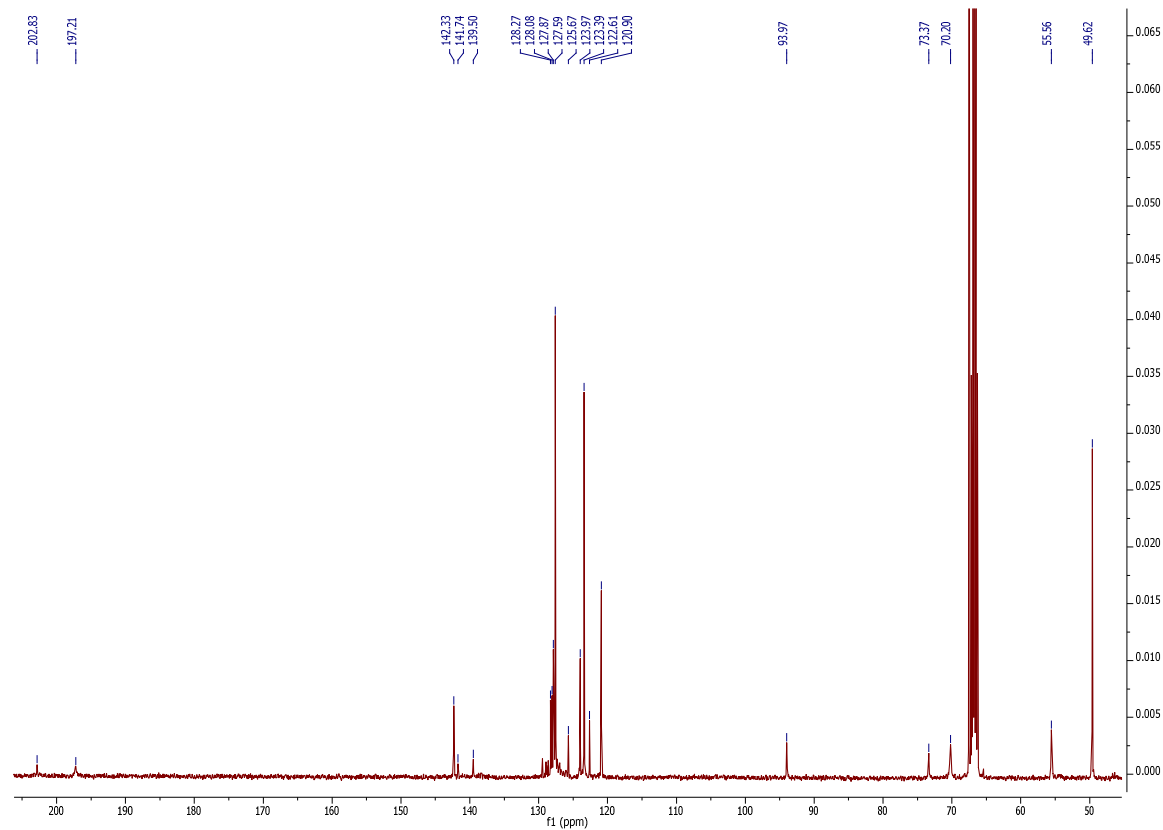


After 3 days,  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF-}d_8$ )

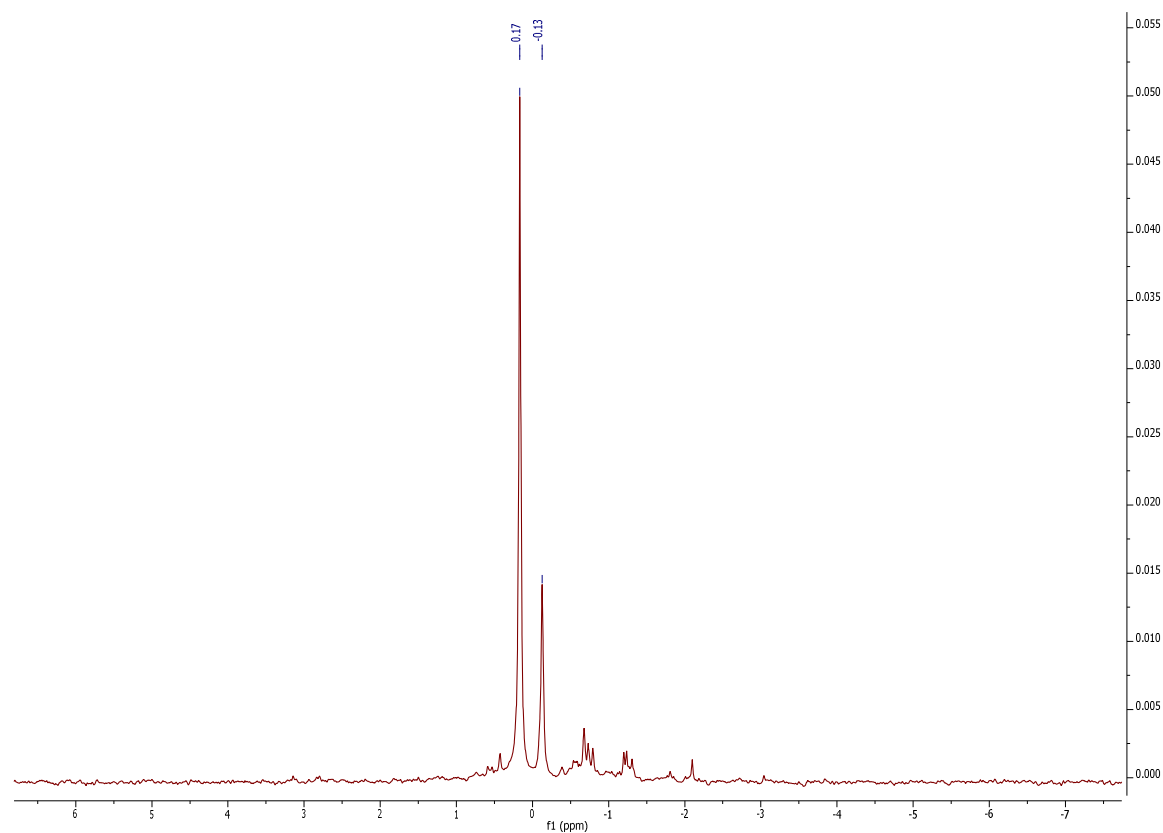




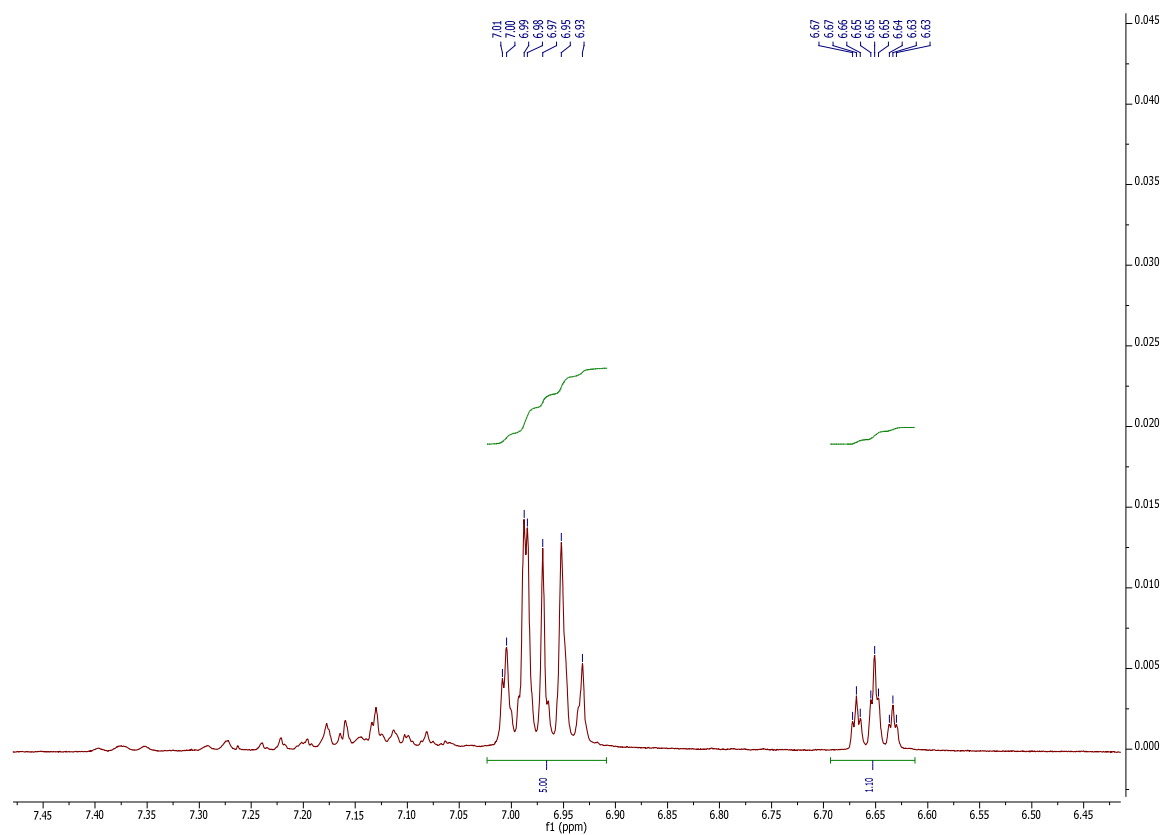
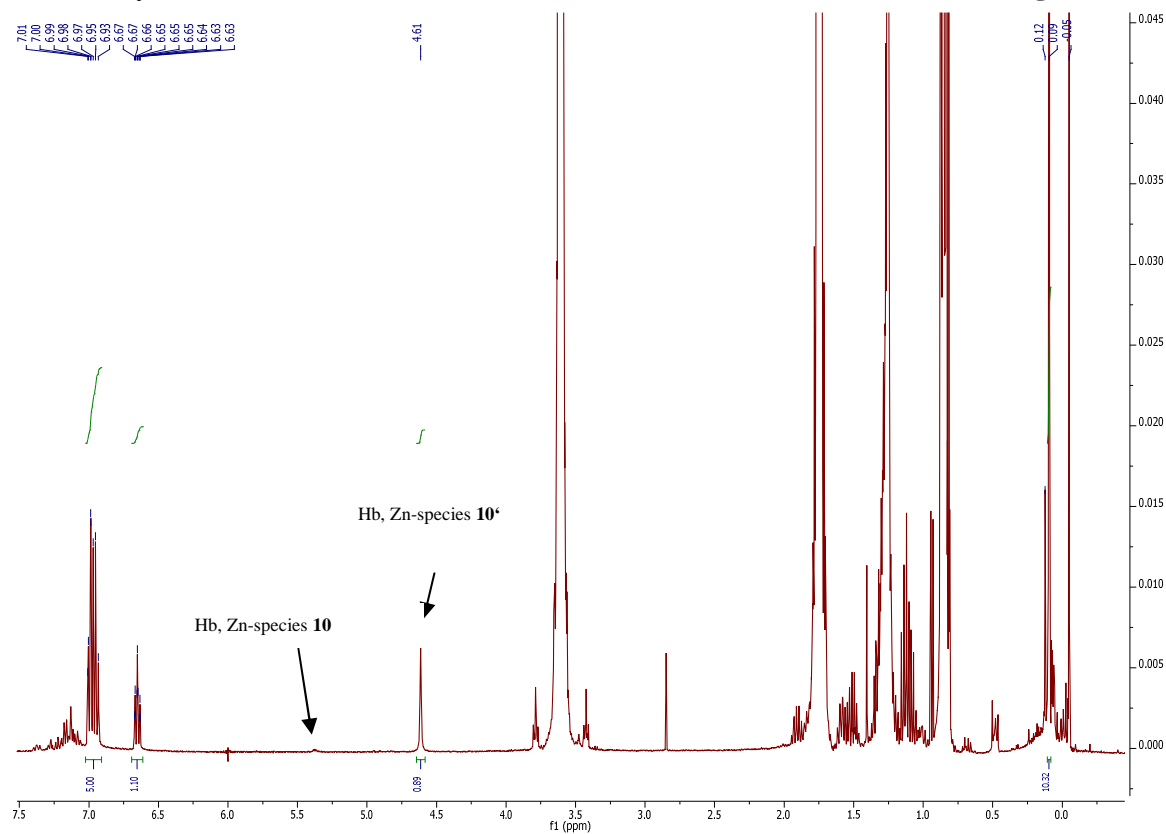
After 3 days,  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF-}d_8$ ) zoom



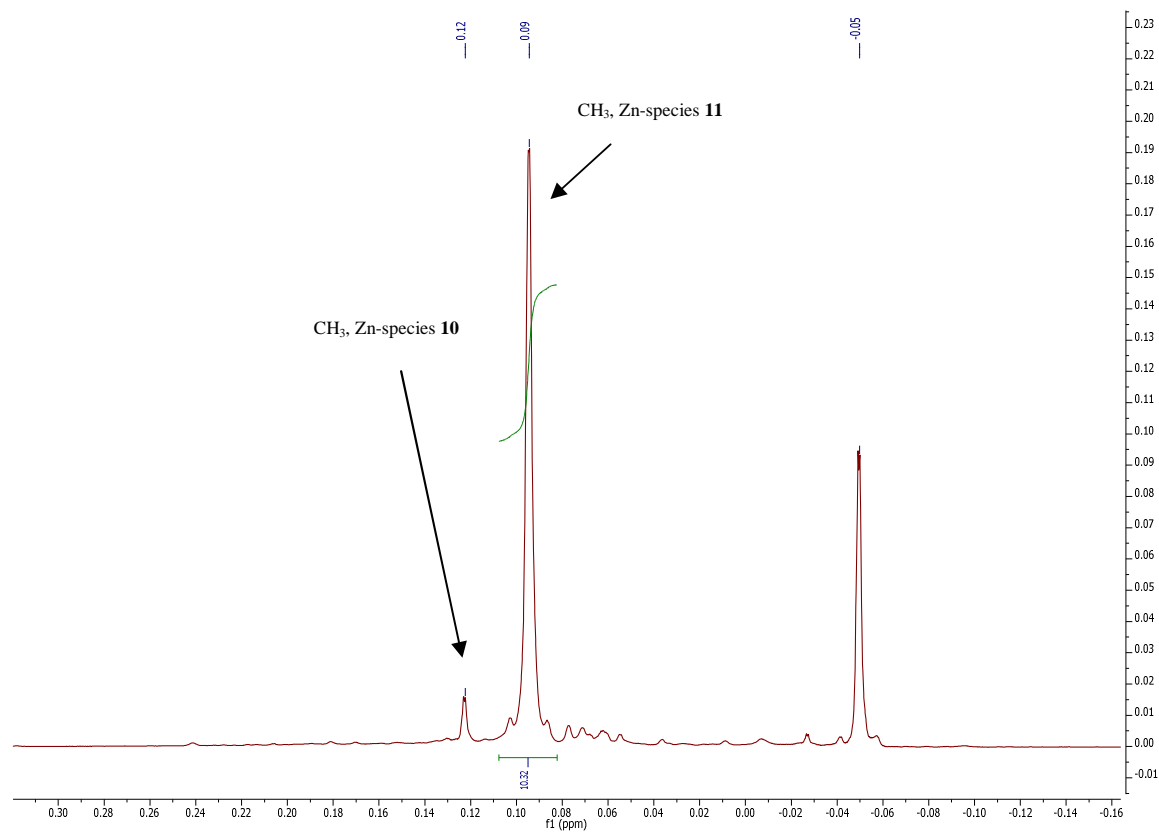
After 3 days,  $^{13}\text{C}$  NMR (100 MHz,  $\text{THF-}d_8$ ) zoom on  $\text{Si}(\text{CH}_3)_3$  region



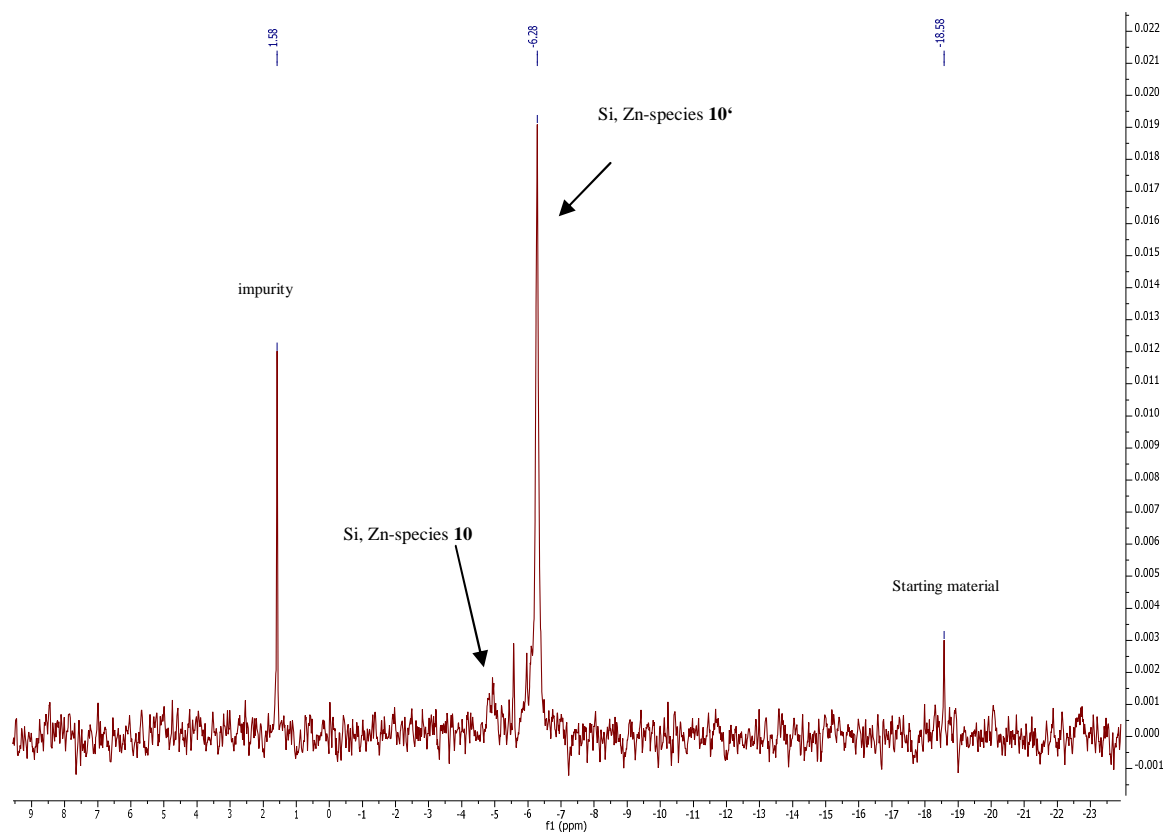
After 6 days,  $^1\text{H}$  NMR (400 MHz,  $\text{THF-}d_8$ ), overall and zoom on aromatic region



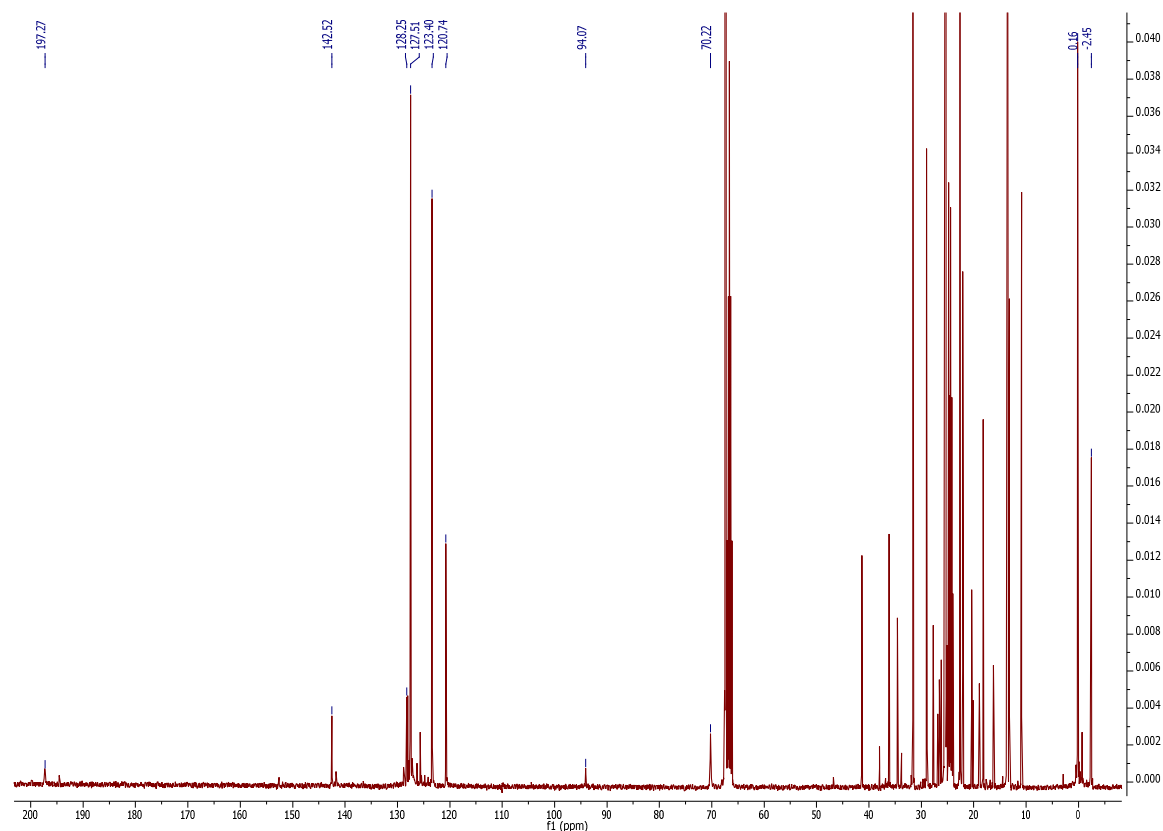
**$^1\text{H}$  NMR (400 MHz, THF- $d_8$ ), zoom on  $\text{Si}(\text{CH}_3)_3$  region**



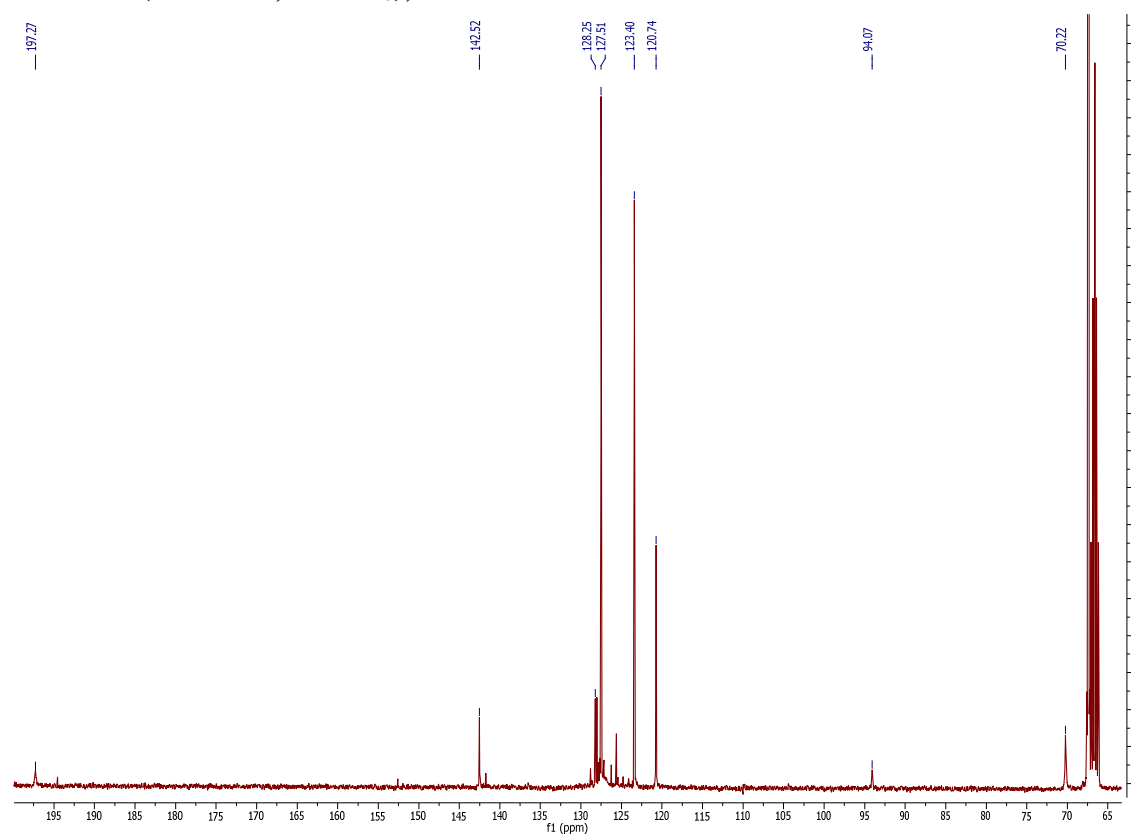
**$^{29}\text{Si}$  NMR (79 MHz, THF- $d_8$ )**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ )**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ), zoom**



**$^{13}\text{C}$  NMR (100 MHz, THF- $d_8$ ), zoom**

