

Supporting Information for:

## Cobalt-Catalysed Acyl Silane Directed Ortho C-H Functionalisation of Benzoyl Silanes

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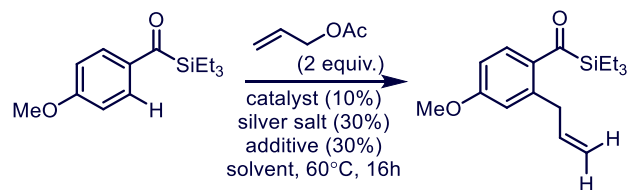
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## General Experimental

Analytical Thin Layer Chromatography (TLC) was carried out using aluminium-backed Merck Kieselgel KG60 F254 silica plates. The plates were visualized by irradiation with short-wave ultraviolet light. Flash chromatography was performed on SiliaFlashR P60 R12030B 40-63 micron silica gel. High-resolution mass spectrometry (HRMS) was performed with an Agilent 6546 LC-QToF coupled to an Agilent 1290 Infinity LC. All data were acquired, and reference mass corrected via a dual-spray electrospray ionization (ESI) source.

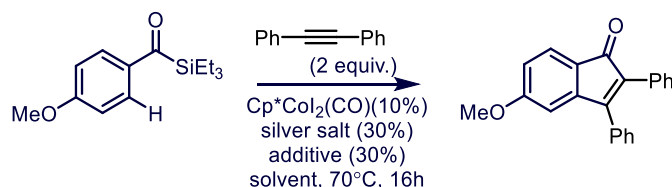
$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Agilent DD2 (500 MHz) or a Bruker (400 MHz). Chemical shifts are expressed in parts per million (PPM) and are referenced to the internal solvent peaks. Solvents used for NMR studies were purchased from Cambridge Isotope Laboratories. Each proton resonance was assigned according to the following convention: chemical shift ( $\delta$ ), multiplicity, coupling constant ( $J$  Hz) number of protons. Each carbon resonance was assigned according to the following convention: chemical shift ( $\delta$ ), multiplicity and coupling constants ( $J$  Hz). Multiplicity is quoted as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

Unless otherwise stated, catalysts, reagents and solvents were purchased from commercial sources and used without further purification. Acyl silanes were prepared using established methods from the corresponding aldehydes via the dithiane pathway<sup>1</sup> and the measured spectroscopic data compared well with that previously reported for (4-methoxybenzoyl)trimethylsilane (**4a**)<sup>2</sup>; (4-methoxybenzoyl) triethylsilane (**4b**)<sup>3</sup>; (4-methoxybenzoyl)-*tri*-isopropylsilane (**4c**)<sup>2</sup>; (4-methoxybenzoyl)-*tert*-butyldimethylsilane (**4d**)<sup>2</sup>; benzoyl triethylsilane (**4e**)<sup>2</sup>; (3,4-dimethoxybenzoyl) trimethylsilane (**4f**)<sup>4</sup>; (4-chlorobenzoyl)triethylsilane (**4g**)<sup>2</sup>; (4-methylbenzoyl)trimethylsilane (**4h**)<sup>2</sup>; (4-*tert*-butylbenzoyl)trimethylsilane (**4i**)<sup>2</sup>. The 1,4,2-dioxazol-5-ones<sup>5</sup> and *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide<sup>6</sup> were prepared using established methods and spectroscopic data compared well with that previously reported.

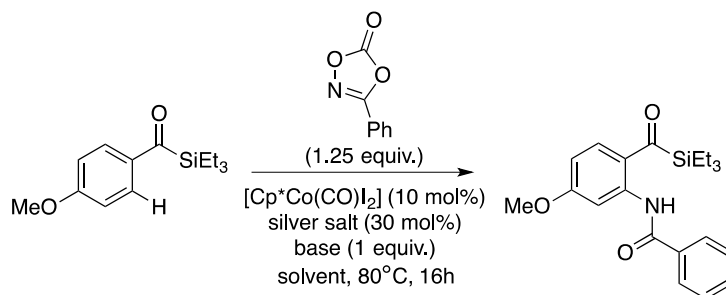
**Table S1. Optimisation of Allylation Reaction**


Entry	Catalyst <sup>a</sup>	Silver Salt	Additive	Solvent	Yield (%)
1	Rh(III) <sup>b,c</sup>	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	34%
2	Rh(III) <sup>c</sup>	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	57%
3	Co(III) <sup>b,c</sup>	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	82%
4	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	80%
5	Co(III) <sup>b</sup>	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	40%
6	Co(III) <sup>c</sup>	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	63%
7	Co(III)	AgSbF <sub>6</sub>	AgOAc	1,2-DCE	33%
8	Co(III)	AgSbF <sub>6</sub>	NaOAc	1,2-DCE	<10%
9	Co(III)	AgSbF <sub>6</sub>	KOAc	1,2-DCE	<10%
10	Co(III)	AgSbF <sub>6</sub>	-	1,2-DCE	0%
11	Co(III)	AgBF <sub>4</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	35%
12	Co(III)	AgNTf <sub>2</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	80%
13	Co(III)	AgOTf	Cu(OAc) <sub>2</sub>	1,2-DCE	26%
14	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	80%
15	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	CHCl <sub>3</sub>	15%
16	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	THF	0%
17	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,4-dioxane	31%
18	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	MeOH	<10%
19	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	MeCN	0%
20	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	50%
21	Co(III)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	47%
22	Co(III)	AgNTf <sub>2</sub>	Cu(OAc) <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	59%
<b>23</b>	<b>Co(III)<sup>f</sup></b>	<b>AgSbF<sub>6</sub></b>	<b>Cu(OAc)<sub>2</sub></b>	<b>1,2-DCE</b>	<b>87%</b>
<b>24</b>	<b>Co(III)<sup>f,g</sup></b>	<b>AgSbF<sub>6</sub></b>	<b>Cu(OAc)<sub>2</sub></b>	<b>1,2-DCE</b>	<b>87%</b>
25	Co(III)	AgSbF <sub>6</sub>	Na <sub>2</sub> CO <sub>3</sub>	1,2-DCE	22%
26	Co(III)	AgSbF <sub>6</sub>	K <sub>2</sub> CO <sub>3</sub>	1,2-DCE	16%
27	Co(III)	AgSbF <sub>6</sub>	Cs <sub>2</sub> CO <sub>3</sub>	1,2-DCE	18%
28	Co(III)	AgSbF <sub>6</sub>	Ag <sub>2</sub> CO <sub>3</sub>	1,2-DCE	67%
29	Co(III)	AgSbF <sub>6</sub>	AgOAc <sup>e,f</sup>	1,2-DCE	36%
30	Ru(II)	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	74%

<sup>a</sup>Rh(III) = 2.5 mol% [Cp\*RhCl<sub>2</sub>]<sub>2</sub>; Co(III) = 10 mol% of [Cp\*Co(CO)I<sub>2</sub>]; Ru(II) = 5 mol% of [(p-cymene)RuCl<sub>2</sub>]<sub>2</sub>; <sup>b</sup>ethyl allyl carbonate used instead of allyl acetate; <sup>c</sup>reaction conducted at 80°C, partial hydrolysis of product to 2-allyl-4-methoxybenzaldehyde occurred at temperatures of 80°C or higher; <sup>d</sup>60 mol% used; <sup>e</sup>120 mol% used; <sup>f</sup>reaction conducted at 70°C; <sup>g</sup>using 5 mol% of [Cp\*Co(CO)I<sub>2</sub>] and 15 mol% of AgSbF<sub>6</sub>.

**Table S2. Optimisation of Alkenylation/Annulation Reaction**


Entry	Silver Salt	Additive	Solvent	Yield (%)
<b>1</b>	<b>AgSbF<sub>6</sub></b>	<b>Cu(OAc)<sub>2</sub></b>	<b>1,2-DCE</b>	<b>89%</b>
2	AgSbF <sub>6</sub>	AgOAc	1,2-DCE	31%
3	AgSbF <sub>6</sub>	NaOAc	1,2-DCE	47%
4	AgSbF <sub>6</sub>	KOAc	1,2-DCE	22%
5	AgSbF <sub>6</sub>	-	1,2-DCE	0%
6	AgBF <sub>4</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	61%
7	AgNTf <sub>2</sub>	Cu(OAc) <sub>2</sub>	1,2-DCE	77%
8	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	THF	13%
9	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	MeOH	0%
10	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub>	MeCN	0%

**Table S3. Optimisation of Amidation Reaction**


Entry	Silver Salt	Additive (equiv.)	Solvent	Temperature	Yield (%) <sup>e</sup>
1	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE	80°C	22%
2	AgOTf	NaOAc (1 equiv.)	1,2-DCE	80°C	19%
3	AgBF <sub>4</sub>	NaOAc (1 equiv.)	1,2-DCE	80°C	0%
4	AgNTf <sub>2</sub>	NaOAc (1 equiv.)	1,2-DCE	80°C	53%
5	-	NaOAc (1 equiv.)	1,2-DCE	80°C	0%
6	-	NaOAc <sup>a</sup>	1,2-DCE	80°C	8%
7	AgSbF <sub>6</sub>	Cu(OAc) <sub>2</sub> (1 equiv.)	1,2-DCE	80°C	42%
8	AgSbF <sub>6</sub>	AgOAc (1 equiv.)	1,2-DCE	80°C	34%
9	AgSbF <sub>6</sub>	Zn(OAc) <sub>2</sub> (1 equiv.)	1,2-DCE	80°C	50%
10	AgSbF <sub>6</sub>	KOAc (1 equiv.)	1,2-DCE	80°C	0%
11	AgSbF <sub>6</sub>	LiOAc (1 equiv.)	1,2-DCE	80°C	35%
12	AgSbF <sub>6</sub>	KOPiv (1 equiv.)	1,2-DCE	80°C	0%
13	AgSbF <sub>6</sub>	AcOH (1 equiv.)	1,2-DCE	80°C	41%
13	AgSbF <sub>6</sub>	-	1,2-DCE	80°C	22%
14	AgSbF <sub>6</sub>	NaOAc <sup>b</sup> (1 equiv.)	1,2-DCE	80°C	0%
16	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,4-dioxane	80°C	8%
17	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	Toluene	80°C	0%
18	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	MeCN	80°C	0%
19	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE	70°C	45%
20	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE <sup>c</sup>	80°C	50%
21	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE <sup>d</sup>	80°C	55%
22	AgSbF <sub>6</sub>	NaOAc (2 equiv.)	1,2-DCE	80°C	0%
23	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE	60°C	11%
24	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	CH <sub>2</sub> Cl <sub>2</sub>	60°C	0%
25	AgSbF <sub>6</sub>	NaOAc (30 mol%)	1,2-DCE	80°C	32%
26	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	Dry 1,2-DCE	80°C	39%
27	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	Dry CH <sub>2</sub> Cl <sub>2</sub>	60°C	27%
28	AgSbF <sub>6</sub>	NaOAc (1 equiv.)	1,2-DCE	90°C	41%
29	AgSbF <sub>6</sub>	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	80°C	31%
30	AgSbF <sub>6</sub>	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	90°C	55% (42%)
31	AgNTf <sub>2</sub>	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	90°C	15%
32	AgSbF <sub>6</sub>	NaOAc (15 mol%)	Dry 1,2-DCE <sup>c,d</sup>	80°C	46%
33	AgSbF <sub>6</sub>	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	100°C	38%
34	AgSbF <sub>6</sub> (20 mol% Co(III) catalyst)	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	80°C	50%
35	AgSbF <sub>6</sub>	NaOAc (30 mol%)	Dry 1,2-DCE <sup>c,d</sup>	80°C, 48h	46%

<sup>a</sup>Reaction conducted with [Cp\*Co(MeCN)<sub>3</sub>](SbF<sub>6</sub>)<sub>2</sub> catalyst. <sup>b</sup>Reaction conducted in absence of [Co] catalyst. <sup>c</sup>Reaction conducted in degassed 1,2-DCE with N<sub>2</sub>. <sup>d</sup>Reaction conducted with 2 equiv. dioxazolone. <sup>e</sup>Yield determined by <sup>1</sup>H NMR using 1,3,5-mesitylene as an internal standard, isolated yield in parentheses.

### General Method A:

[Cp\*Co<sub>2</sub>(CO)] (10 mg, 0.020 mmol, 10 mol%), AgSbF<sub>6</sub> (21 mg, 0.060 mmol, 30 mol%), Cu(OAc)<sub>2</sub> (11 mg, 0.060 mmol, 30 mol%) and 1,2-DCE (1.0 mL) were combined and stirred at room temperature for 5 mins. Benzoyl silane (0.2 mmol, 1.0 equiv.) was then added, followed by allyl acetate (0.4 mmol, 2.0 equiv.) and the reaction was stirred at 70°C for 16h. After this time, the reaction mixture was cooled to room temperature and the crude mixture was filtered through a silica plug (washing with 1:1 EtOAc/hexane). The solvent was removed under reduced pressure and the crude material was purified by column chromatography (0-10% Et<sub>2</sub>O in hexane).

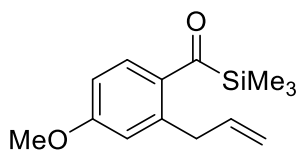
### General Method B:

[Cp\*Co<sub>2</sub>(CO)] (10 mg, 0.020 mmol, 10 mol%), AgSbF<sub>6</sub> (21 mg, 0.060 mmol, 30 mol%), Cu(OAc)<sub>2</sub> (11 mg, 0.060 mmol, 30 mol%) and 1,2-DCE (1.0 mL) were combined and stirred at room temperature for 5 mins. Benzoyl silane (0.2 mmol, 1.0 equiv.) was then added, followed by alkyne (0.4 mmol, 2.0 equiv.) and the reaction was stirred at 70°C for 16h. After this time, the reaction mixture was cooled to room temperature and the crude mixture was filtered through a silica plug (washing with 1:1 EtOAc/hexane). The solvent was removed under reduced pressure and the crude material was purified by column chromatography (10-20% EtOAc in hexane).

### General Method C:

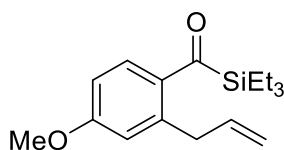
[Cp\*Co<sub>2</sub>(CO)] (15 mg, 0.030 mmol, 10 mol%), AgSbF<sub>6</sub> (31 mg, 0.090 mmol, 30 mol%), NaOAc (7.4 mg, 0.090 mmol, 30 mol%) and 1,2-DCE (1.5 mL) were combined and stirred at room temperature for 5 mins. Benzoyl silane (0.3 mmol, 1 equiv.) was then added, followed by 1,4,2-dioxazol-5-one (0.6 mmol, 2 equiv.) and the reaction was stirred at 80°C for 16h. After this time, the reaction mixture was cooled to room temperature and the crude mixture was filtered through a silica plug (1:1 EtOAc/hexane). The solvent was removed under reduced pressure and the crude material was purified by column chromatography (0-10% Et<sub>2</sub>O in hexane).

### (2-allyl-4-methoxyphenyl)(trimethylsilyl)methanone (5a)



Prepared according to General Method A using (4-methoxybenzoyl)trimethylsilane and allyl acetate to afford the title compound as a yellow oil (44 mg, 89%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.79 (d, *J* = 2.3 Hz, 1H), 5.96 (ddt, *J* = 16.8, 10.3, 6.5 Hz, 1H), 5.05 – 5.01 (m, 1H), 4.98 (dd, *J* = 11.2, 1.5 Hz, 1H), 3.86 (s, 3H), 3.62 (d, *J* = 6.4 Hz, 2H), 0.31 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 239.8, 162.8, 142.5, 138.8, 136.0, 134.7, 118.3, 116.9, 111.7, 56.6, 39.1, 0.0 ppm; HR-MS (*m/z*) [C<sub>14</sub>H<sub>20</sub>O<sub>2</sub>Si + H]<sup>+</sup> calcd. for 249.1305, found 249.1304.

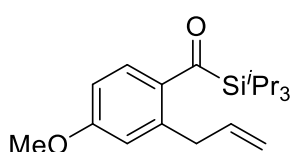
### (2-allyl-4-methoxyphenyl)(triethylsilyl)methanone (5b)



Prepared according to General Method A using (4-methoxybenzoyl)triethylsilane and allyl acetate to afford the title compound as a yellow oil (51 mg, 87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 8.5 Hz, 1H), 6.82 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.77 (d, *J* = 2.5 Hz, 1H), 5.95 (ddt, *J* = 17.0, 10.6, 6.5 Hz, 1H), 5.01 (s, 1H), 4.99 – 4.96 (m, 1H), 3.84 (s, 3H), 3.61 (d, *J* = 6.5 Hz, 2H), 1.00 – 0.93 (m, 9H), 0.88 – 0.79 (m, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

δ 238.7, 161.3, 140.7, 137.5, 135.8, 133.0, 116.9, 115.6, 110.4, 55.3, 37.7, 7.5, 3.7 ppm; HR-MS (*m/z*) [C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>Si + H]<sup>+</sup> calcd. for 291.1775, found 291.1777.

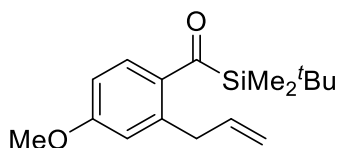
### (2-allyl-4-methoxyphenyl)(triisopropylsilyl)methanone (5c)



Prepared according to General Method A using (4-methoxybenzoyl)triisopropylsilane and allyl acetate to afford the title compound as a yellow oil (55 mg, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.78 (d, *J* = 2.4 Hz, 1H), 5.97 (ddt, *J* = 17.7, 9.5, 6.6 Hz, 1H), 5.04 (dd, *J* = 3.9, 1.5 Hz, 1H), 5.00 (s, 1H), 3.84 (s, 3H), 3.59 (d, *J* = 6.6 Hz, 2H), 1.42 (dt, *J* = 14.9, 7.5 Hz, 3H), 1.10 (d, *J* = 7.5 Hz, 18H) ppm; <sup>13</sup>C NMR

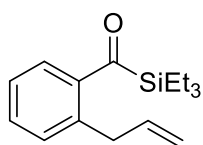
(100 MHz, CDCl<sub>3</sub>) δ 239.2, 161.1, 140.4, 137.6, 137.1, 132.2, 116.8, 115.7, 110.3, 55.2, 37.5, 18.8, 12.3 ppm; HR-MS (*m/z*) [C<sub>20</sub>H<sub>32</sub>O<sub>2</sub>Si + H]<sup>+</sup> calcd. for 333.2244, found 333.2241.

#### (2-allyl-4-methoxyphenyl)(*tert*-butyldimethylsilyl)methanone (5d)



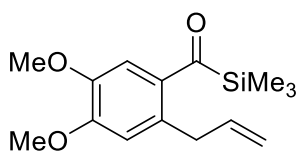
Prepared according to General Method A using (4-methoxybenzoyl)-*tert*-butyldimethylsilane and allyl acetate to afford the title compound as a yellow oil (53 mg, 91%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (d,  $J = 8.4$  Hz, 1H), 6.80 (d,  $J = 8.8$  Hz, 1H), 6.78 (s, 1H), 6.04 – 5.89 (m, 1H), 5.02 (s, 1H), 4.98 (d,  $J = 9.1$  Hz, 1H), 3.83 (s, 3H), 3.58 (d,  $J = 6.4$  Hz, 2H), 0.95 (s, 9H), 0.29 (s, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  238.8, 161.3, 140.7, 137.6, 136.2, 133.2, 116.9, 115.7, 110.3, 55.3, 37.7, 26.9, 17.2, -4.6 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{17}\text{H}_{26}\text{O}_2\text{Si} + \text{H}$ ] $^+$  calcd. for 291.1775, found 291.1773.

#### (2-allylphenyl)(triethylsilyl)methanone (5e)



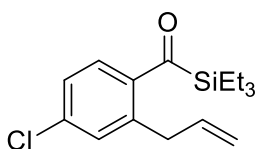
Prepared according to General Method A using benzoyl triethylsilane and allyl acetate to afford the title compound as a yellow oil (34 mg, 65%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (dd,  $J = 7.4$ , 1.1 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.26 (d,  $J = 7.3$  Hz, 1H), 5.94 (ddt,  $J = 16.8$ , 10.1, 6.5 Hz, 1H), 5.03 – 4.93 (m, 2H), 3.52 (d,  $J = 6.5$  Hz, 2H), 0.97 (t,  $J = 7.7$  Hz, 9H), 0.86 – 0.80 (m, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  242.9, 143.4, 137.7, 137.0, 131.2, 130.5, 128.5, 125.8, 115.6, 37.0, 7.3, 3.4 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{16}\text{H}_{24}\text{OSi} + \text{H}$ ] $^+$  calcd. for 261.1669, found 261.1666.

#### (2-allyl-4,5-dimethoxyphenyl)(trimethylsilyl)methanone (5f)



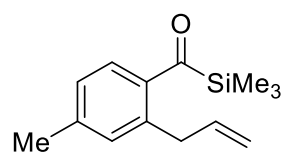
Prepared according to General Method A using (3,4-dimethoxybenzoyl)trimethylsilane and allyl acetate to afford the title compound as a yellow oil (40 mg, 71%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (s, 1H), 6.74 (s, 1H), 5.95 (ddt,  $J = 16.7$ , 10.2, 6.4 Hz, 1H), 5.04 – 4.93 (m, 2H), 3.92 (s, 6H), 3.57 (d,  $J = 6.4$  Hz, 2H), 0.33 (s, 9H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  239.8, 152.3, 147.8, 139.2, 135.5, 133.6, 116.6, 115.4, 115.3, 57.4, 57.3, 38.5, 0.0 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{15}\text{H}_{22}\text{O}_3\text{Si} + \text{H}$ ] $^+$  calcd. for 279.1411, found 279.1414.

#### (2-allyl-4-chlorophenyl)(triethylsilyl)methanone (5g)



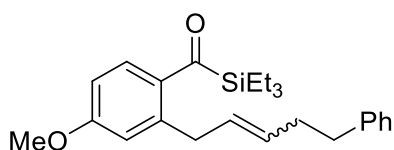
Prepared according to General Method A using (4-chlorobenzoyl)triethylsilane and allyl acetate to afford the title compound as a yellow oil (21 mg containing 7.5% of starting material **4g**, 32% yield of **5g**).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (d,  $J = 8.1$  Hz, 1H), 7.31 – 7.27 (m, 1H), 7.26 (s, 1H), 5.90 (ddt,  $J = 16.7$ , 10.0, 6.5 Hz, 1H), 5.05 (d,  $J = 10.0$  Hz, 1H), 5.00 (d,  $J = 17.1$  Hz, 1H), 3.50 (d,  $J = 6.5$  Hz, 2H), 0.96 (q,  $J = 7.8$  Hz, 9H), 0.83 (t,  $J = 7.8$  Hz, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  241.6, 141.5, 139.3, 136.7, 136.5, 131.2, 130.0, 126.0, 116.4, 36.8, 7.3, 3.4 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{16}\text{H}_{23}\text{ClOSi} + \text{H}$ ] $^+$  calcd. for 295.1279, found 295.1280.

#### (2-allyl-4-methylphenyl)(trimethylsilyl)methanone (5h)



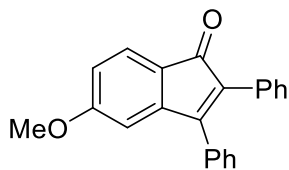
Prepared according to General Method A using (4-methylbenzoyl)trimethylsilane and allyl acetate to afford the title compound as a yellow oil (32 mg, 69%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 7.8$  Hz, 1H), 7.12 (d,  $J = 7.8$  Hz, 1H), 7.07 (s, 1H), 5.94 (ddd,  $J = 16.8$ , 10.2, 6.5 Hz, 1H), 4.96 (m, 2H), 3.54 (d,  $J = 6.4$  Hz, 2H), 2.36 (s, 3H), 0.30 (s, 9H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) 242.9, 142.8, 141.0, 139.4, 139.3, 133.6, 131.6, 127.9, 116.9, 38.9, 23.0, 0.0 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{14}\text{H}_{20}\text{OSi} + \text{H}$ ] $^+$  calcd. for 233.1356, found 233.1353.

#### (2-allyl-4-methoxyphenyl)(triethylsilyl)methanone (5i)



Prepared according to General Method A using (4-methoxybenzoyl)triethylsilane and 5-phenylpent-1-en-3-yl acetate to afford the title compound as a yellow oil (43 mg, 54%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ) Mixture of E/Z isomers:  $\delta$  7.54 (d,  $J = 8.5$  Hz, 1H), 7.24 – 7.06 (m, 5H), 6.76 – 6.70 (m, 1H), 6.67 (dd,  $J = 7.5$ , 2.5 Hz, 1H), 5.58 – 5.38 (m, 2H), 3.76 (d,  $J = 6.9$  Hz, 3H), 3.49 (dd,  $J = 18.9$ , 6.0 Hz, 2H), 2.68 – 2.52 (m, 2H), 2.38 (dt,  $J = 13.0$ , 6.4 Hz, 1H), 2.23 (dd,  $J = 15.0$ , 7.0 Hz, 1H), 0.90 (t,  $J = 7.6$  Hz, 9H), 0.84 – 0.68 (m, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ) Mixture of E/Z isomers:  $\delta$  238.9, 161.4, 142.0, 141.7, 136.0, 136.0, 132.9, 132.8, 129.9, 128.7, 128.5, 128.4, 128.3, 128.2, 125.8, 125.7, 116.8, 116.5, 110.2, 110.1, 55.3, 36.5, 36.0, 35.9, 34.4, 31.2, 29.3, 7.5, 3.8 ppm. **HR-MS** ( $m/z$ ) [ $\text{C}_{25}\text{H}_{34}\text{O}_2\text{Si} + \text{H}$ ] $^+$  calcd. for 395.2401, found 395.2406.

### 5-methoxy-2,3-diphenyl-1H-inden-1-one (6a)



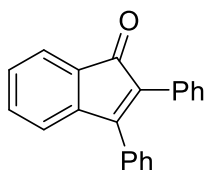
Prepared according to General Method B using (4-methoxybenzoyl)trimethylsilane and diphenylacetylene to afford the title compound as an orange solid (57 mg, 92%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.8$  Hz, 1H), 7.45 – 7.30 (m, 5H), 7.30 – 7.20 (m, 5H), 6.68 – 6.65 (m, 2H), 3.82 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.1, 164.4, 153.1, 147.9, 132.6, 130.0, 129.1, 128.8, 128.5, 128.0, 127.7, 124.9, 123.4, 110.2, 55.8 ppm; **HR-MS**

( $m/z$ ) [ $\text{C}_{22}\text{H}_{16}\text{O}_2 + \text{H}$ ] $^+$  calcd. for 313.1223, found 313.1224. This data correlates well with that previously reported for this compound.<sup>7</sup>

The above reaction was repeated using

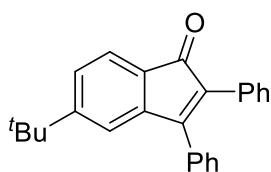
- (4-methoxybenzoyl)triethylsilane to afford the title compound as a yellow oil (56 mg, 89%).
- (4-methoxybenzoyl)triisopropylsilane to afford the title compound as a yellow oil (46 mg, 73%).
- (4-methoxybenzoyl)-*tert*-butyldimethylsilane to afford the title compound as a yellow oil (55 mg, 88%).

### 2,3-diphenyl-1H-inden-1-one (6b)



Prepared according to General Method B using benzoyltriethylsilane and diphenylacetylene to afford the title compound as an orange solid (46 mg, 81%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.0$  Hz, 1H), 7.41 – 7.34 (m, 6H), 7.29 (d,  $J = 7.0$  Hz, 1H), 7.25 (brs, 5H), 7.14 (d,  $J = 7.2$  Hz, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.5, 155.3, 145.2, 133.4, 132.7, 132.4, 130.7, 129.9, 129.3, 128.9, 128.8, 128.5, 128.0, 127.7, 123.0, 121.2 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{21}\text{H}_{14}\text{O} + \text{H}$ ] $^+$  calcd. for 283.1117, found 283.1118. This data correlates well with that previously reported for this compound.<sup>7</sup>

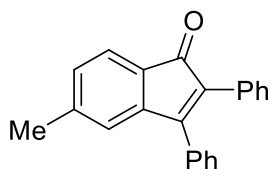
### 5-*tert*-butyl-2,3-diphenyl-1H-inden-1-one (6c)



Prepared according to General Method B using (4-*tert*-butylbenzoyl)trimethylsilane and diphenylacetylene to afford the title compound as an orange solid (51 mg, 76%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.5$  Hz, 1H), 7.47 – 7.44 (m, 2H), 7.41 (dd,  $J = 6.8, 2.9$  Hz, 2H), 7.32 (dd,  $J = 7.6, 1.3$  Hz, 1H), 7.29 (s, 3H), 7.27 (s, 3H), 7.20 (s, 1H), 1.34 (s, 9H) ppm;  $^{13}\text{C NMR}$

(100 MHz,  $\text{CDCl}_3$ )  $\delta$  196.2, 157.7, 155.2, 145.4, 133.0, 132.9, 131.0, 130.0, 129.2, 128.8, 128.6, 128.4, 128.0, 127.6, 125.2, 122.9, 119.0, 35.5, 31.1 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{25}\text{H}_{22}\text{O} + \text{H}$ ] $^+$  calcd. for 339.1743, found 339.1745. This data correlates well with that previously reported for this compound.<sup>7</sup>

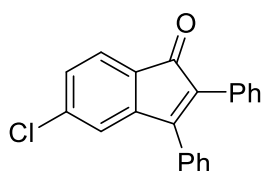
### 5-methyl-2,3-diphenyl-1H-inden-1-one (6d)



Prepared according to General Method B using (4-methylbenzoyl)trimethylsilane and diphenylacetylene to afford the title compound as a yellow oil (42 mg, 71%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 7.3$  Hz, 1H), 7.45 (dd,  $J = 5.0, 1.7$  Hz, 3H), 7.42 – 7.38 (m, 2H), 7.28 (s, 5H), 7.11 (d,  $J = 7.3$  Hz, 1H), 6.97 (s, 1H), 2.38 (s, 3H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )

$\delta$  196.2, 154.9, 145.8, 144.4, 132.9, 132.8, 130.9, 130.0, 129.1, 128.9, 128.8, 128.5, 128.4, 128.0, 127.7, 123.1, 122.5, 22.1 ppm; **HR-MS** ( $m/z$ ) [ $\text{C}_{22}\text{H}_{16}\text{O} + \text{H}$ ] $^+$  calcd. for 297.1274, found 313.1274. This data correlates well with that previously reported for this compound.<sup>7</sup>

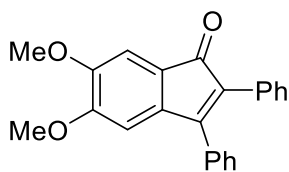
### 5-chloro-2,3-diphenyl-1H-inden-1-one (6e)



Prepared according to General Method B using (4-chlorobenzoyl)triethylsilane and diphenylacetylene to afford the title compound as an orange solid (27 mg, 43%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.6$  Hz, 1H), 7.46 (brm, 3H), 7.42 – 7.37 (brm, 2H), 7.30 (s, 6H), 7.15 (s, 1H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  195.0, 154.0, 147.3, 139.8, 133.6, 132.2, 130.3, 130.0, 129.6, 129.0, 128.9, 128.5, 128.4, 128.1, 128.1, 123.9, 122.0 ppm; **HR-MS** ( $m/z$ )

[ $\text{C}_{21}\text{H}_{13}\text{OCl} + \text{H}$ ] $^+$  calcd. for 317.0728, found 317.0726. This data correlates well with that previously reported for this compound.<sup>7</sup>

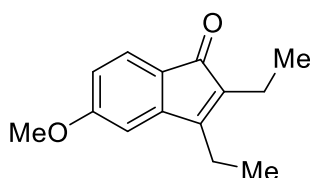
### 5,6-dimethoxy-2,3-diphenyl-1*H*-inden-1-one (6f)



Prepared according to General Method B using (3,4-dimethoxybenzoyl)trimethylsilane and diphenylacetylene to afford the title compound as a red solid (44 mg, 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38 – 7.33 (m, 3H), 7.32 – 7.28 (m, 2H), 7.19 – 7.15 (m, 6H), 6.62 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.0, 154.0, 152.8, 149.2, 139.7, 133.0, 131.0, 129.8, 129.2, 128.9, 128.4, 128.0, 127.5, 107.7, 106.0, 56.5, 56.4 ppm;

HR-MS (*m/z*) [C<sub>23</sub>H<sub>18</sub>O<sub>3</sub> + H]<sup>+</sup> calcd. for 343.1329, found 343.1328.

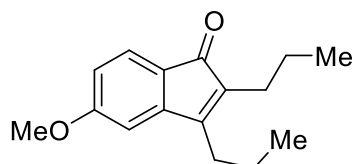
### 5-methoxy-2,3-diethyl-1*H*-inden-1-one (6g)



Prepared according to General Method B using (4-methoxybenzoyl)triethylsilane and 3-hexyne to afford the title compound as a yellow oil (33 mg, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 (d, *J* = 7.9 Hz, 1H), 6.61 (d, *J* = 2.0 Hz, 1H), 6.53 (dd, *J* = 7.9, 2.1 Hz, 1H), 3.84 (s, 3H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.27 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.6 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.1, 164.4, 156.1, 148.1, 137.2, 124.0, 123.5, 108.7, 108.4, 55.6, 19.1, 16.1, 14.0, 12.8 ppm; HR-MS (*m/z*) [C<sub>14</sub>H<sub>16</sub>O<sub>2</sub> + H]<sup>+</sup> calcd.

for 217.1223, found 217.1219.

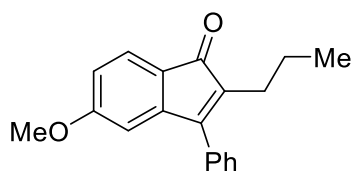
### 5-methoxy-2,3-dipropyl-1*H*-inden-1-one (6h)



Prepared according to General Method B using (4-methoxybenzoyl)triethylsilane and 4-octyne to afford the title compound as a yellow oil (41 mg, 84%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 (d, *J* = 7.9 Hz, 1H), 6.63 (d, *J* = 1.9 Hz, 1H), 6.56 (dd, *J* = 7.9, 1.9 Hz, 1H), 3.87 (s, 3H), 2.54 – 2.43 (m, 2H), 2.34 – 2.22 (m, 2H), 1.66 (dd, *J* = 15.1, 7.5 Hz, 2H), 1.51 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm;

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.2, 164.4, 155.2, 148.4, 136.5, 124.0, 123.4, 108.6, 55.6, 28.1, 25.1, 22.5, 21.5, 14.3, 14.2 ppm; HR-MS (*m/z*) [C<sub>16</sub>H<sub>20</sub>O<sub>2</sub> + H]<sup>+</sup> calcd. for 245.1536, found 245.1534.

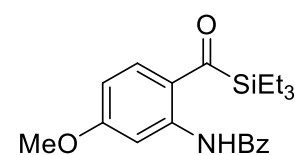
### 5-methoxy-3-phenyl-2-propyl-1*H*-inden-1-one (6i)



Prepared according to General Method B using (4-methoxybenzoyl)triethylsilane and 1-phenyl-1-pentyne to afford the title compound as a yellow oil (38 mg, 68%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 – 7.40 (m, 6H), 6.62 – 6.53 (m, 2H), 3.81 (s, 3H), 2.31 (dd, *J* = 8.7, 6.8 Hz, 2H), 1.51 (dd, *J* = 15.2, 7.6 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 195.9, 163.3, 152.0, 147.7, 136.1, 131.9, 127.9,

126.9, 123.2, 122.7, 108.9, 108.4, 54.7, 24.5, 21.6, 13.2 ppm; HR-MS (*m/z*) [C<sub>19</sub>H<sub>18</sub>O<sub>2</sub> + H]<sup>+</sup> calcd. for 279.1380, found 279.1378.

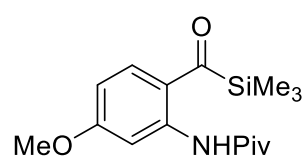
### *N*-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)benzamide (7a)



Prepared according to General Method C using (4-methoxybenzoyl)triethylsilane and 3-phenyl-1,4,2-dioxazol-5-one to afford the title compound as a yellow oil (46 mg, 42%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 13.26 (s, 1H), 8.63 (d, *J* = 2.6 Hz, 1H), 8.12-8.10 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.58-7.53 (m, 3H), 6.72 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.94 (s, 3H), 1.04-0.99 (m, 9H), 0.96-0.91 (m, 6H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 237.2, 166.7, 164.3, 141.7, 136.0,

134.8, 132.0, 128.8, 127.6, 122.3, 109.7, 103.9, 55.7, 7.5, 4.1 ppm; HR-MS (*m/z*) calc. for C<sub>21</sub>H<sub>28</sub>NO<sub>3</sub>Si [M+H]<sup>+</sup>: 370.1839; found 370.1845.

### *N*-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)pivalamide (7b)

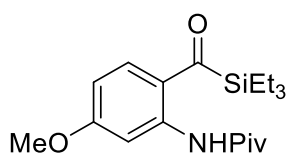


Prepared according to General Method C using (4-methoxybenzoyl)triethylsilane and 3-*tert*-butyl-1,4,2-dioxazol-5-one to afford the title compound as an amorphous colourless solid (44 mg, 48%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 12.48 (s, 1H), 8.50 (d, *J* = 2.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 6.65 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.89 (s, 3H), 1.36 (s, 9H), 0.37 (s, 9H) ppm; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 236.5, 179.2, 164.3, 142.2, 136.0, 121.1, 109.5, 103.6, 55.6,

40.5, 27.6, -0.8 ppm; HRMS (ESI) calc. for C<sub>16</sub>H<sub>25</sub>NNaO<sub>3</sub>Si [M+Na]<sup>+</sup>: 330.1501; found 330.1505.



### N-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)pivalamide (7c)

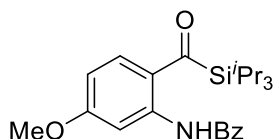


Prepared according to General Method C using (4-methoxybenzoyl)triethylsilane and 3-*tert*-butyl-1,4,2-dioxazol-5-one to afford the title compound as a yellow oil (62 mg, 59%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.46 (s, 1H), 8.48 (d,  $J = 2.6$  Hz, 1H), 7.79 (d,  $J = 8.8$  Hz, 1H), 6.65 (dd,  $J = 8.8, 2.6$  Hz, 1H), 3.88 (s, 3H), 1.35 (s, 9H), 1.01-0.97 (m, 9H), 0.92-0.88 (m, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  236.8, 179.3, 164.3, 141.8, 135.8, 122.4, 109.7, 103.7,

55.7, 40.6, 27.8, 7.6, 4.3 ppm; **HRMS** (ESI) calc. for  $\text{C}_{19}\text{H}_{32}\text{NO}_3\text{Si}$   $[\text{M}+\text{H}]^+$ : 350.2146; found 350.2147.

### N-(5-methoxy-2-((triisopropylsilyl)carbonyl)phenyl)benzamide (7d)

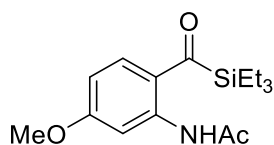


Prepared according to General Method C using (4-methoxybenzoyl)triisopropylsilane and 3-phenyl-1,4,2-dioxazol-5-one to afford the title compound as a yellow oil (45.2 mg, 37%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  13.30 (s, 1H), 8.63 (d,  $J = 2.6$  Hz, 1H), 8.11 (dd,  $J = 7.6, 2.0$  Hz, 2H), 7.81 (d,  $J = 8.8$  Hz, 1H), 7.58-7.53 (m, 3H), 6.71 (dd,  $J = 8.8, 2.6$  Hz, 1H), 3.94 (s, 3H),

1.50 (dt,  $J = 15.0, 7.5$  Hz, 3H), 1.49 (d,  $J = 7.5$  Hz, 18H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  237.1, 166.7, 164.2, 141.6, 136.2, 134.9, 131.9, 128.8, 127.6, 122.9, 109.5, 103.9, 55.6, 18.9, 12.7 ppm; **HRMS** (ESI) calc. for  $\text{C}_{24}\text{H}_{34}\text{NO}_3\text{Si}$   $[\text{M}+\text{H}]^+$ : 412.2308; found 412.2315.

### N-(5-methoxy-2-((triethylsilyl)carbonyl)phenyl)acetamide (7e)

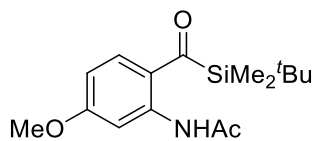


Prepared according to General Method C using (4-methoxybenzoyl)triethylsilane and 3-methyl-1,4,2-dioxazol-5-one to afford the title compound as a yellow oil (46.9 mg, 51%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.29 (s, 1H), 8.38 (d,  $J = 2.6$  Hz, 1H), 7.80 (d,  $J = 8.8$  Hz, 1H), 6.66 (dd,  $J = 8.8, 2.6$  Hz, 1H), 3.88 (s, 3H), 2.23 (s, 3H), 1.01-0.97 (m, 9H), 0.92-0.86 (m, 6H) ppm;

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  237.0, 170.1, 164.3, 141.5, 135.9, 121.7, 109.2, 103.9, 55.6, 25.6, 7.4, 4.1 ppm; **HRMS** (ESI) calc. for  $\text{C}_{16}\text{H}_{25}\text{NNaO}_3\text{Si}$   $[\text{M}+\text{Na}]^+$ : 330.1501; found 330.1509.

### N-(2-((*tert*-butyldimethylsilyl)carbonyl)-5-methoxyphenyl)acetamide (7f)

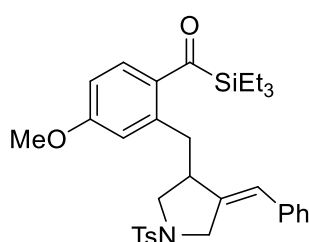


Prepared according to General Method C (0.1 mmol scale) using (4-methoxybenzoyl)*tert*-butyldimethylsilane and 3-methyl-1,4,2-dioxazol-5-one to afford the title compound as an amorphous brown solid (12 mg, 31%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  12.28 (s, 1H), 8.38 (d,  $J = 2.6$  Hz, 1H), 7.82 (d,  $J = 8.8$  Hz, 1H), 6.65 (dd,  $J = 8.8,$

2.6 Hz, 1H), 3.88 (s, 3H), 2.23 (s, 3H), 0.96 (s, 9H), 0.37 (s, 6H) ppm;  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  236.7, 170.1, 164.2, 141.6, 136.9, 122.0, 109.0, 103.8, 55.6, 26.9, 25.7, 17.2, -3.9 ppm; **HRMS** (ESI) calc. for  $\text{C}_{16}\text{H}_{26}\text{NO}_3\text{Si}$   $[\text{M}+\text{Na}]^+$ : 308.1676; found 308.1678.

### (Z)-(2-((4-benzylidene-1-tosylpyrrolidin-3-yl)methyl)-4-methoxyphenyl)(triethylsilyl)methanone (8)

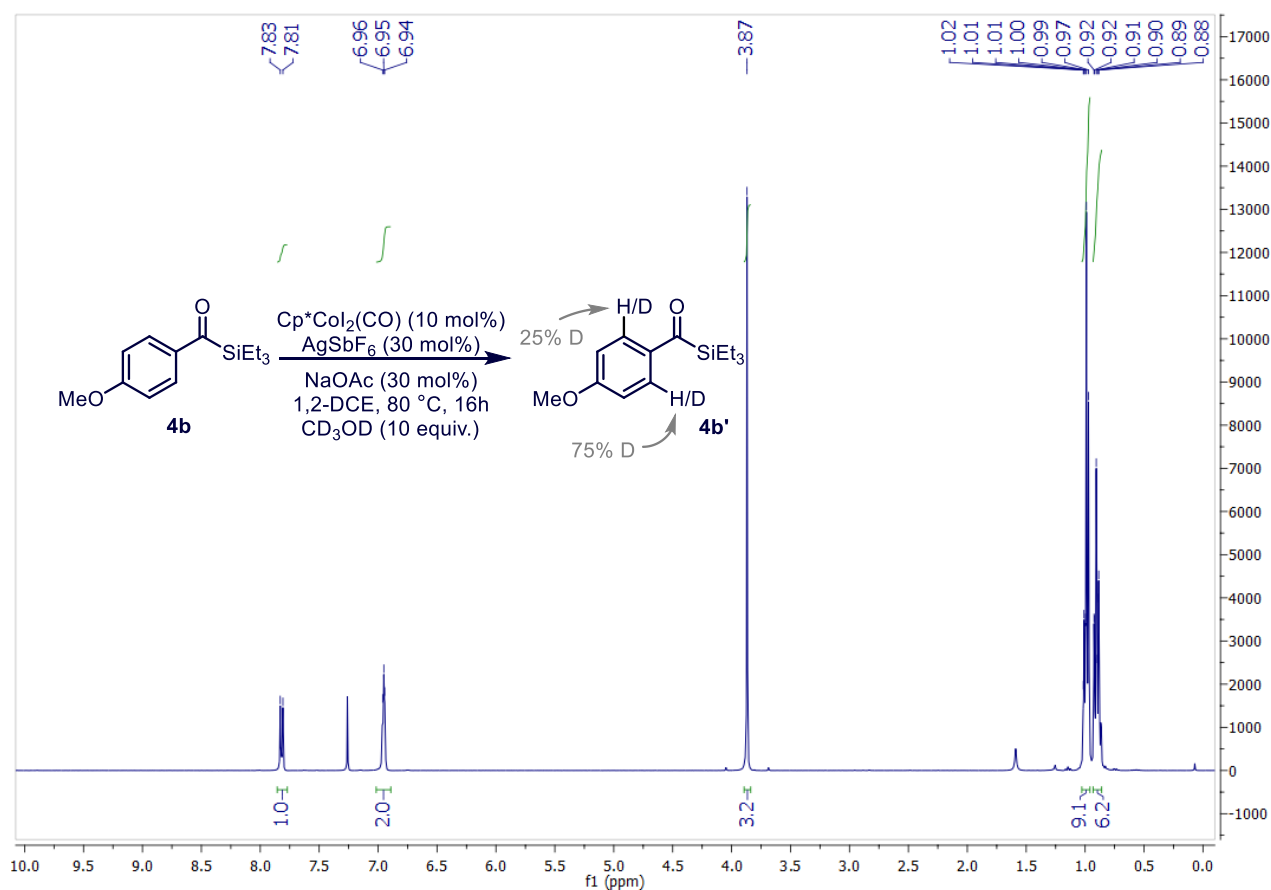


To a vial containing  $\text{CoBr}_2$  (3.3 mg, 0.015 mmol), dppp (6.3 mg, 0.015 mmol), Zn (2.0 mg, 0.030 mmol),  $\text{ZnI}_2$  (9.6 mg, 0.030 mmol) was added *N*-allyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (98 mg, 0.30 mmol) and the vial purged with nitrogen gas three times. (4-Methoxybenzoyl)triethylsilane (75mg, 0.30 mmol) and anhydrous dichloromethane (1.5 mL) were added via syringe. The reaction mixture was heated at 40 °C for 16h, after which time the mixture was cooled, diluted with dichloromethane and filtered through a pad of Celite. The solvent was removed *in vacuo* and purification via column chromatography afforded the title compound as a yellow oil (102 mg, 59%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73 (d,  $J = 8.6$  Hz, 1H), 7.69 (d,  $J = 8.2$  Hz, 2H), 7.36 – 7.27 (m, 4H), 7.22 (t,  $J = 7.4$  Hz, 1H), 7.13 (d,  $J = 7.4$  Hz, 2H), 6.87 (dd,  $J = 8.5, 2.5$  Hz, 1H), 6.68 (d,  $J = 2.4$  Hz, 1H), 6.30 (s, 1H), 4.31 (d,  $J = 14.7$  Hz, 1H), 4.00 (dd,  $J = 14.8, 2.0$  Hz, 1H), 3.85 (s, 3H), 3.29 (dd,  $J = 12.5, 5.7$  Hz, 1H), 3.19 (dd,  $J = 9.1, 4.2$  Hz, 1H), 3.12 (s, 1H), 3.00 (dd,  $J = 9.0, 6.4$  Hz, 1H), 2.77 (dd,  $J = 12.5, 9.3$  Hz, 1H), 2.40 (s, 3H), 0.97 (t,  $J = 7.6$  Hz, 9H), 0.87 (t,  $J = 7.8$  Hz, 6H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  238.0, 161.4, 143.6, 140.2, 140.0, 136.7, 135.4, 134.2, 133.0, 129.7, 128.5, 128.1, 127.8, 126.9, 123.6, 118.0, 111.5, 55.4, 51.4, 50.7, 46.2, 38.1, 21.5, 7.5, 3.9 ppm; **HR-MS** ( $m/z$ )  $[\text{C}_{33}\text{H}_{41}\text{NO}_4\text{Si} + \text{H}]^+$  calcd. for 576.2598, found 576.2604.

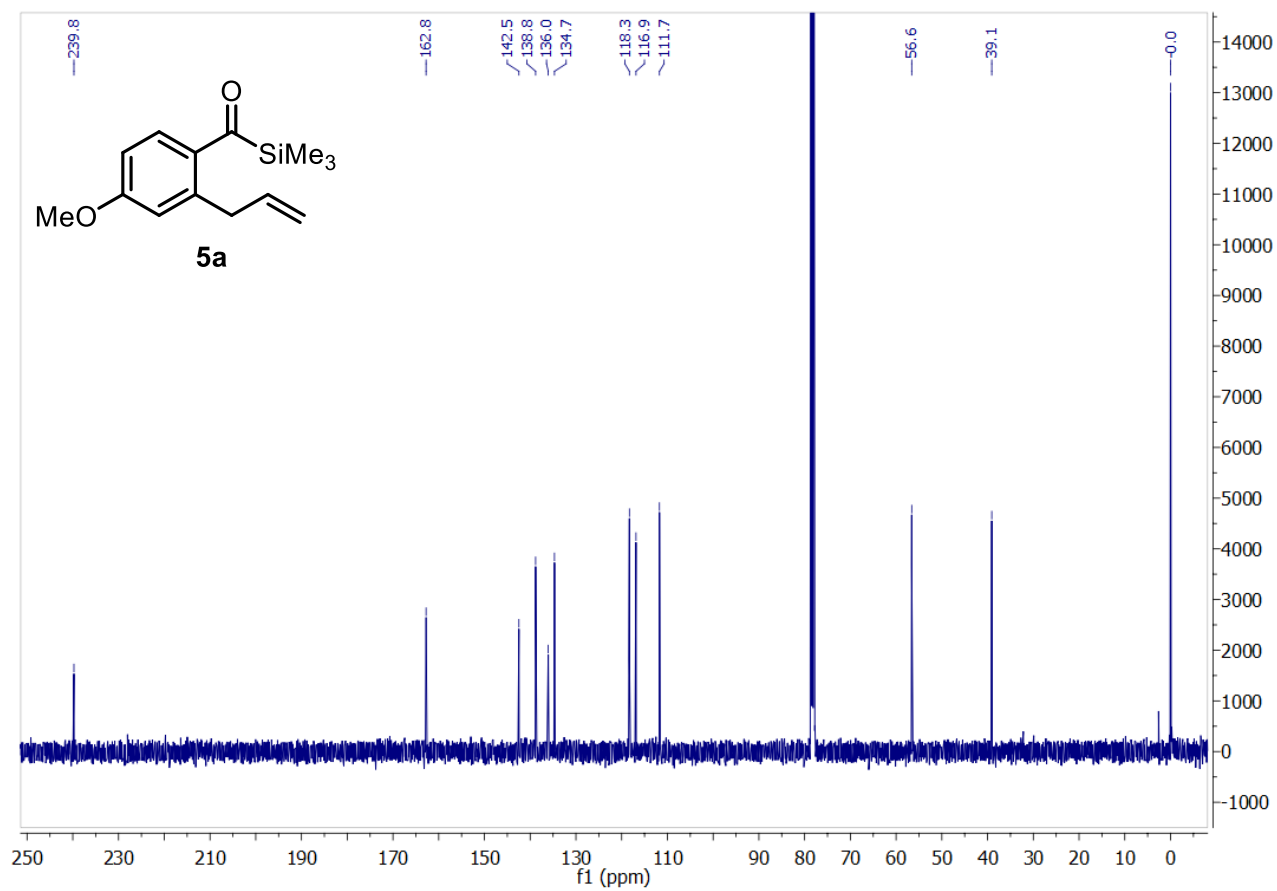
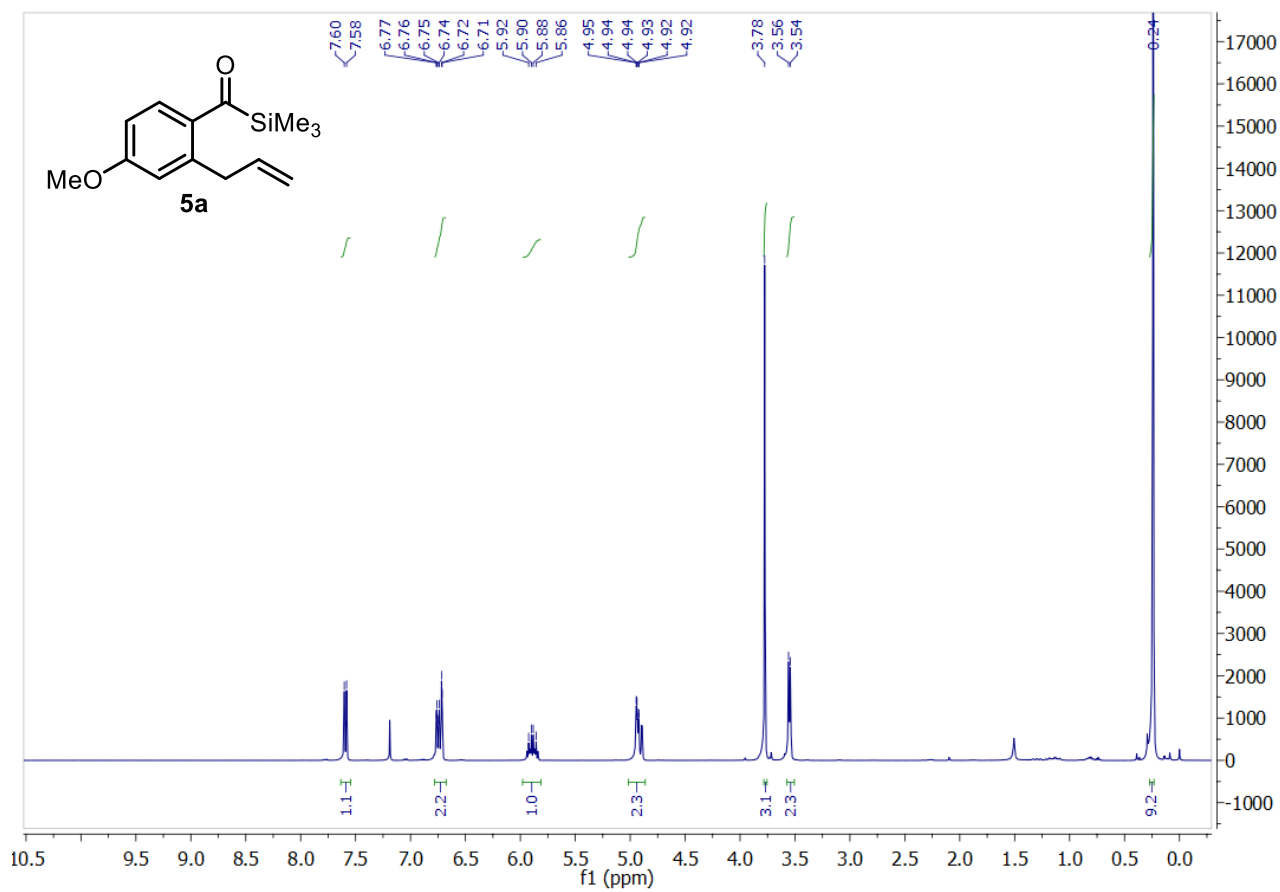
## H/D Scrambling Experiment

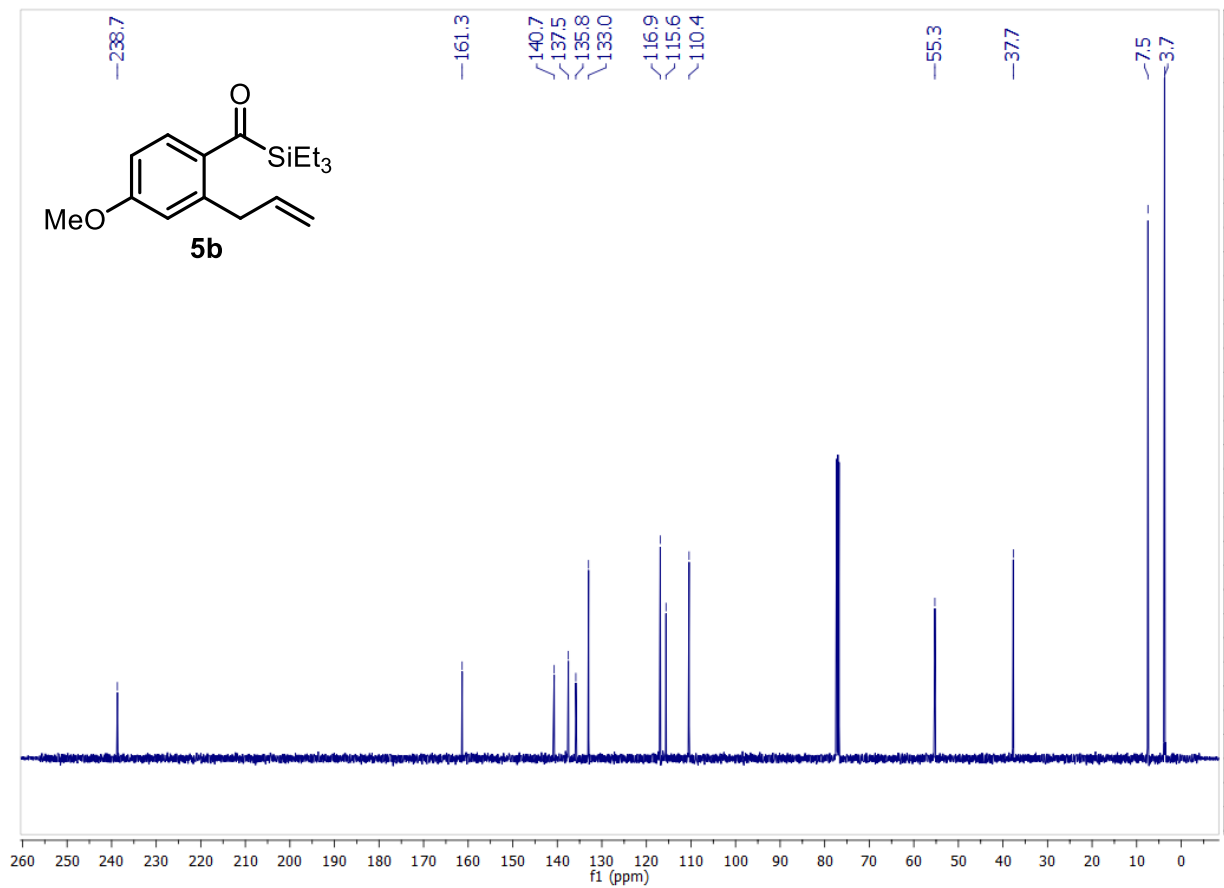
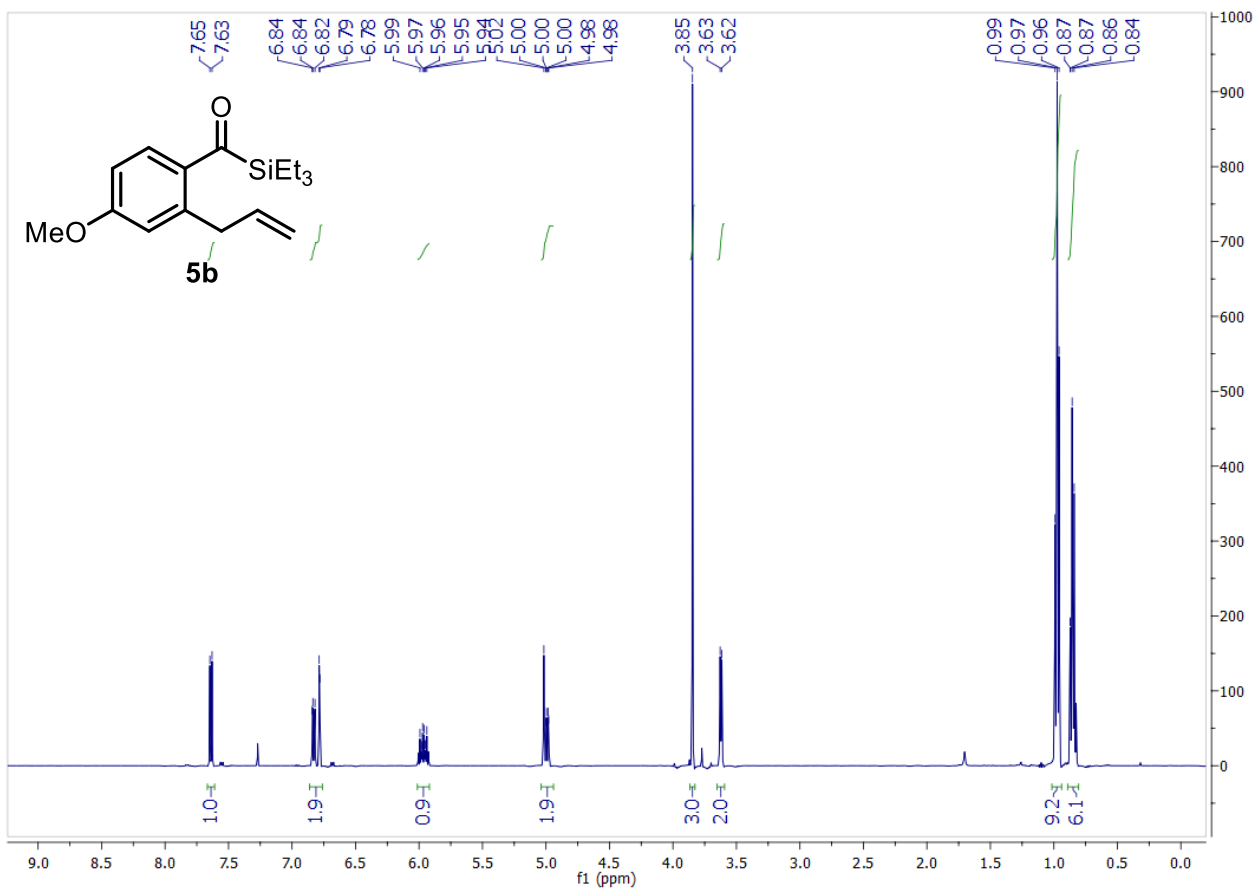
[Cp\*Co<sub>2</sub>(CO)] (10 mg, 0.020 mmol, 10 mol%), AgSbF<sub>6</sub> (21 mg, 0.060 mmol, 30 mol%), Cu(OAc)<sub>2</sub> (11 mg, 0.060 mmol, 30 mol%) and 1,2-DCE (1.0 mL) were combined and stirred at room temperature for 5 mins. 4-methoxybenzoyl triethylsilane (0.2 mmol, 1.0 equiv.) was then added, followed by deuterated methanol (CD<sub>3</sub>OD, 10.0 equiv.) and the reaction was stirred at 80°C for 16h. After this time, the reaction mixture was cooled to room temperature and the crude mixture was filtered through a silica plug (washing with 1:1 EtOAc/hexane) and the solvent removed *in vacuo* affording benzoyl silane **4b'**. NMR analysis revealed the absence of 1 x proton resonance for the peak at 7.82 ppm which for the starting material integrates for 2H, inferring 50% scrambling of H/D at either the 2- and/or 6-positions. HRMS analysis confirmed the presence of isomers in the approximate ratio of 25% (0D – [M+H]<sup>+</sup> 251.1463); 50% (1D – [M+H]<sup>+</sup> 252.1520); 25% (2D – [M+H]<sup>+</sup> 253.1576).

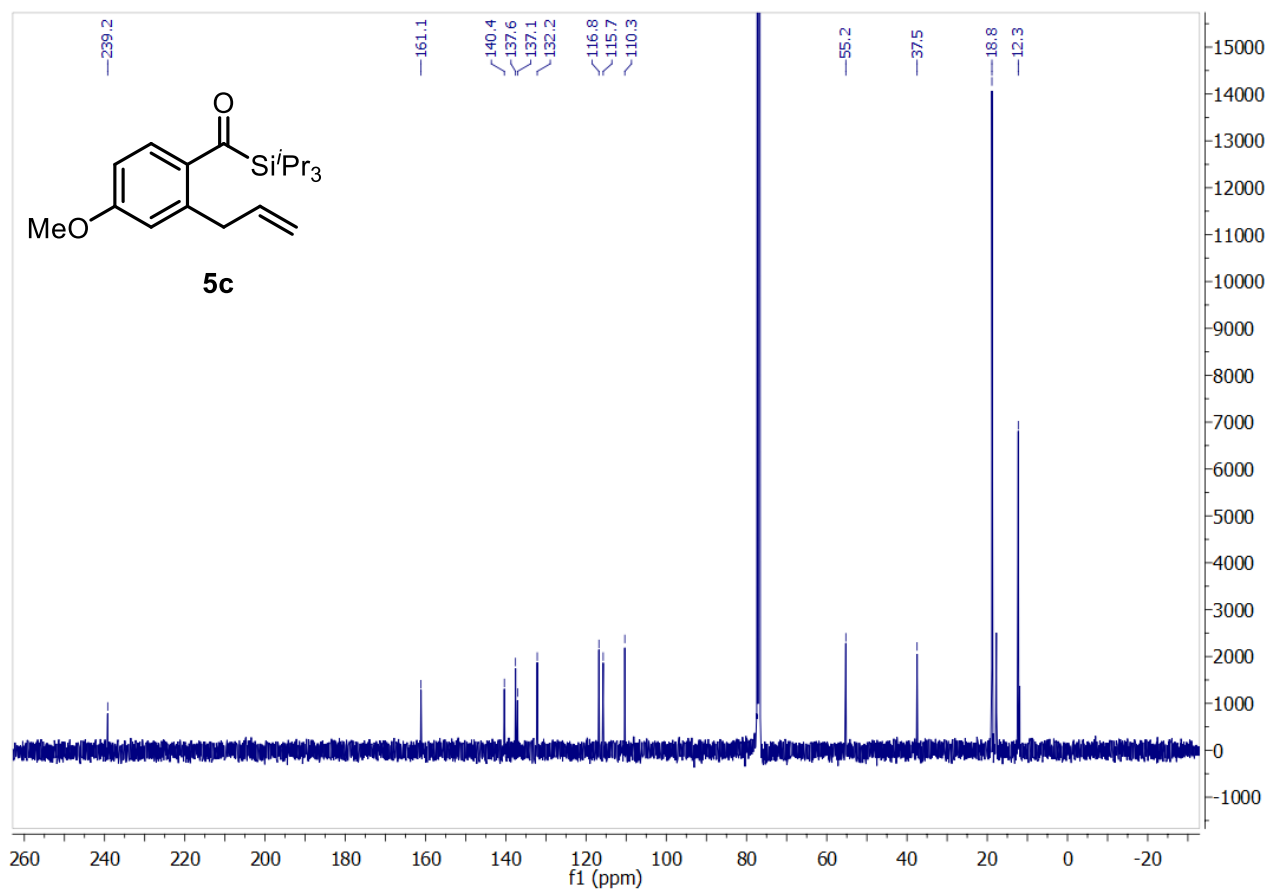
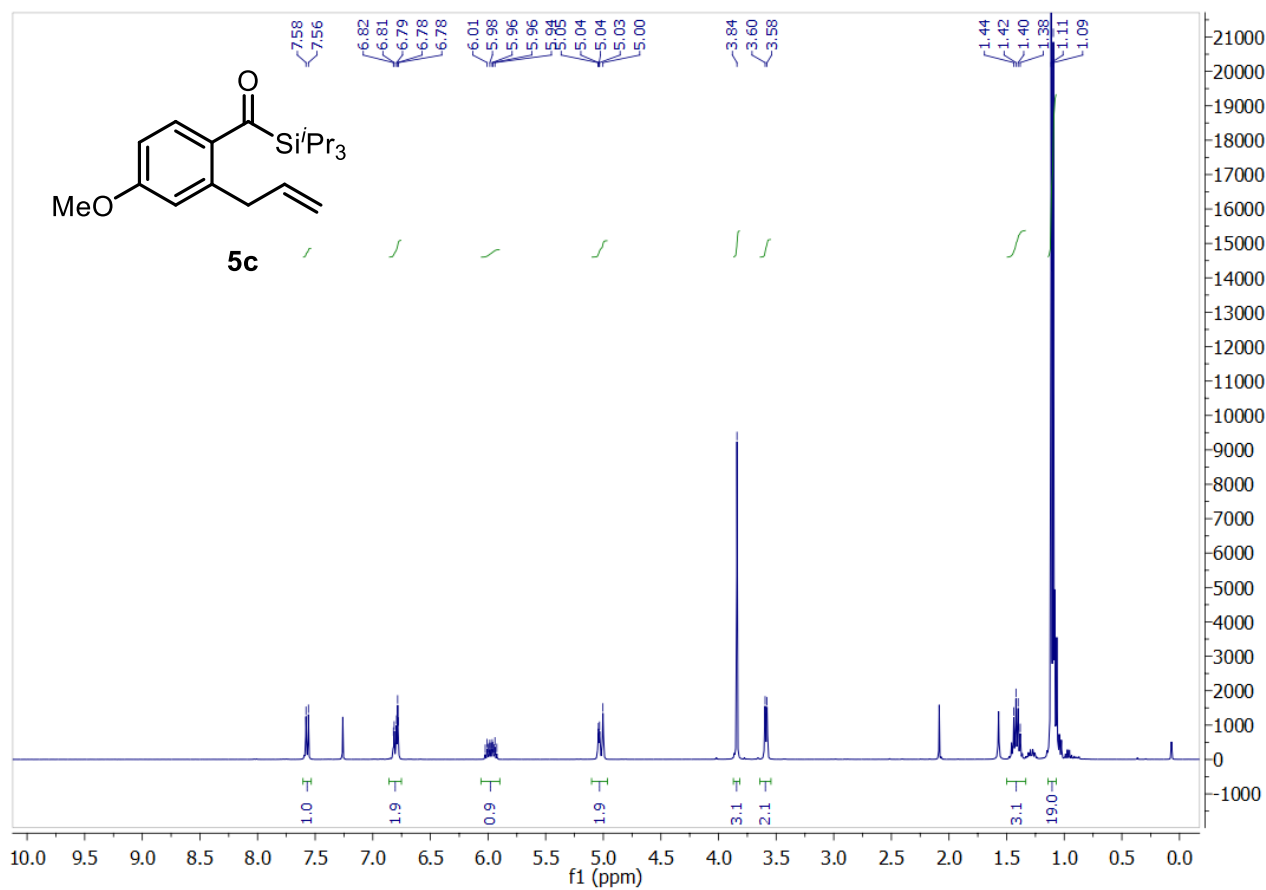


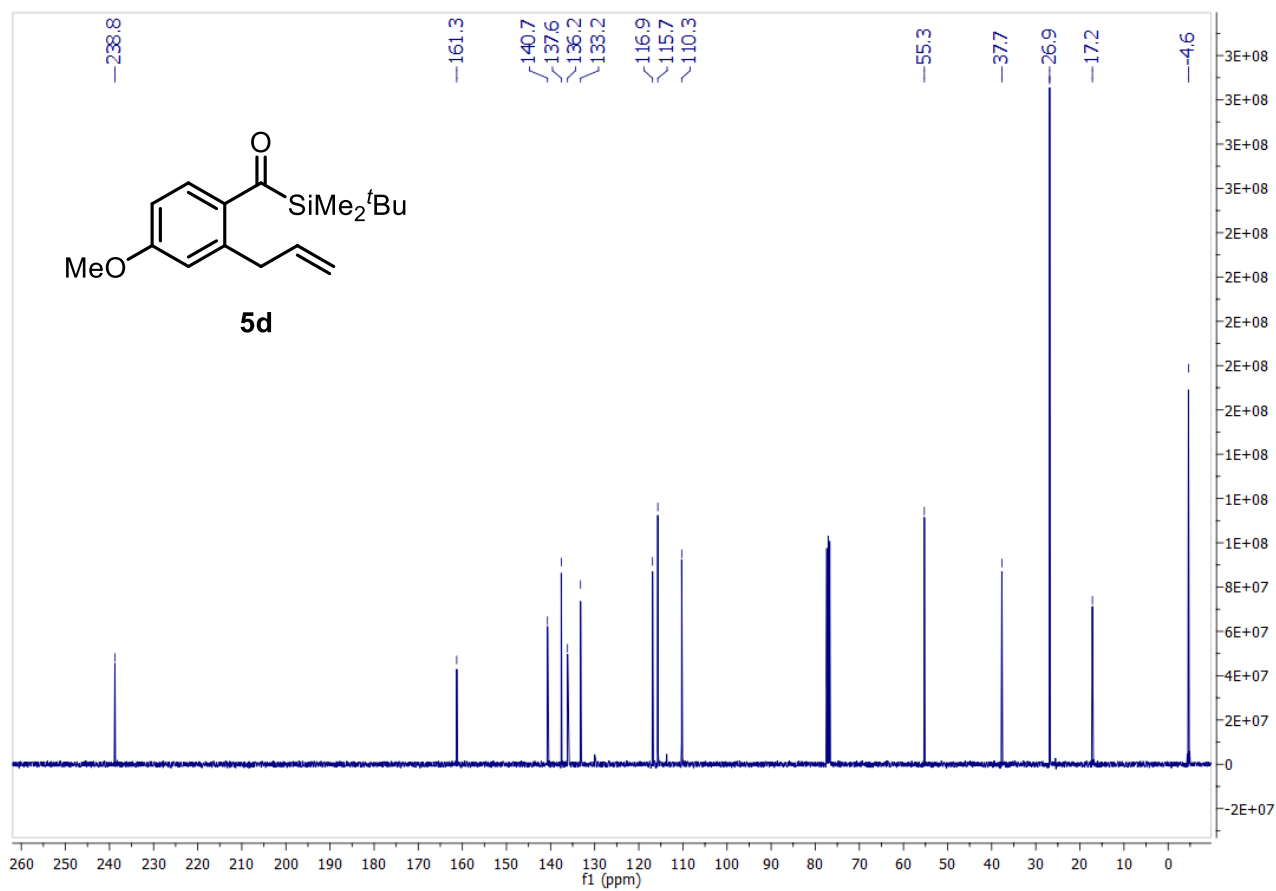
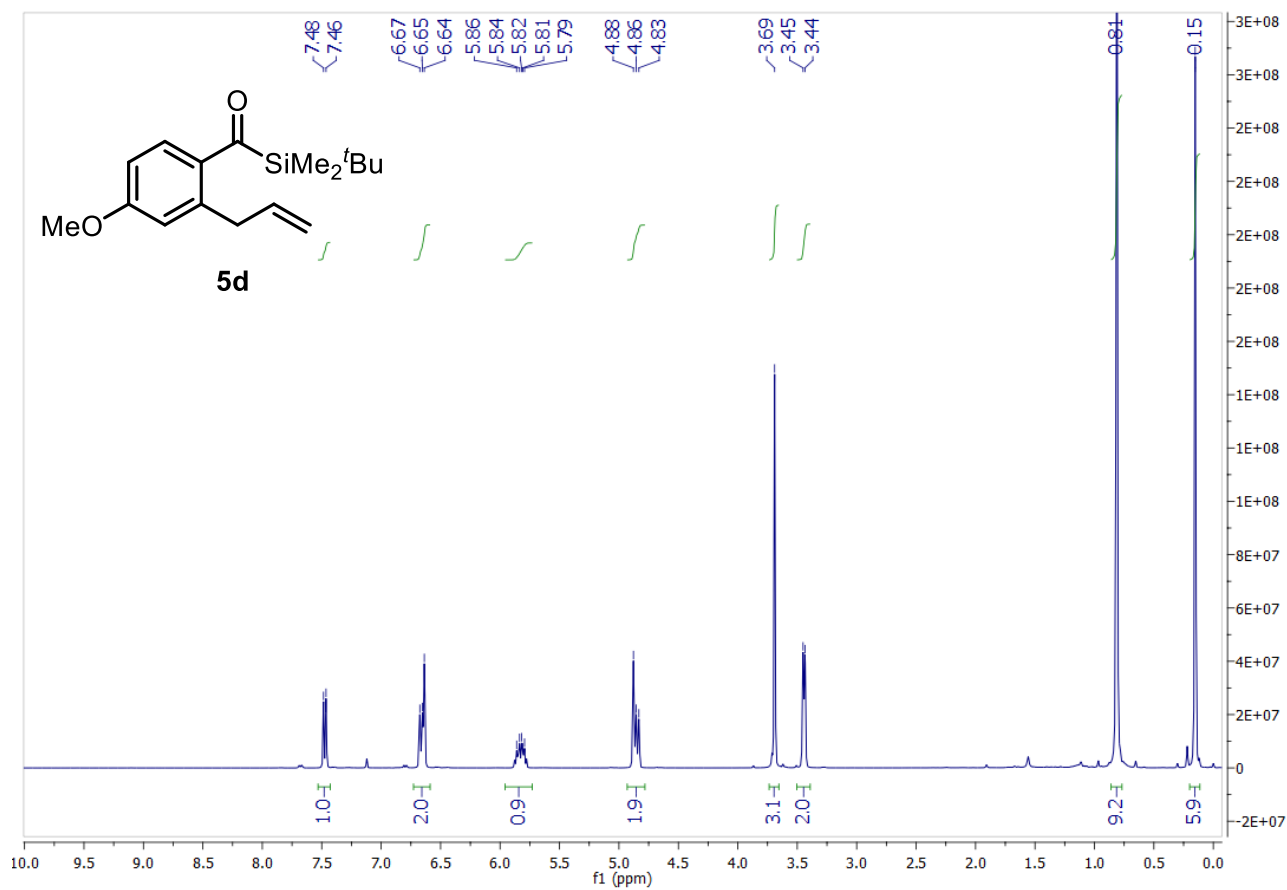
## REFERENCES

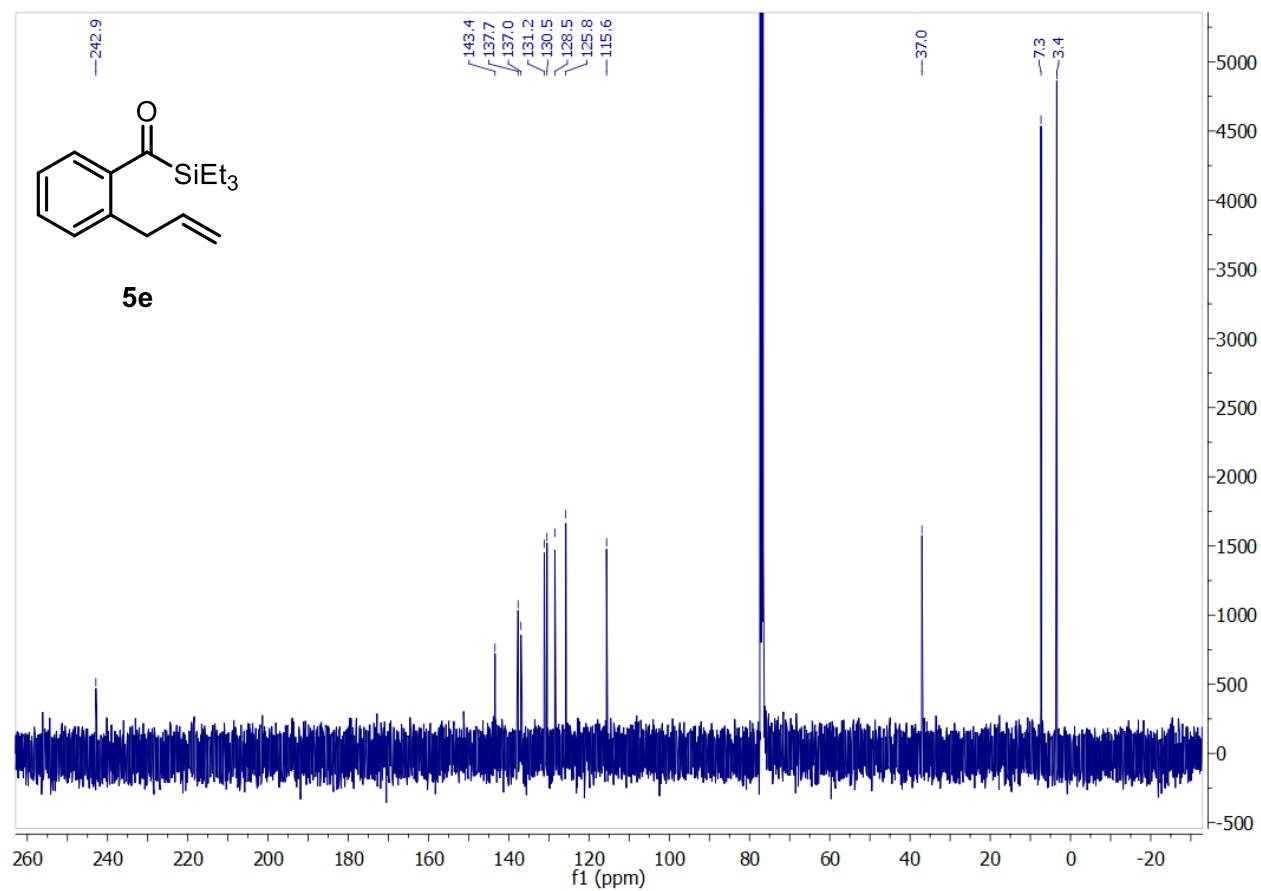
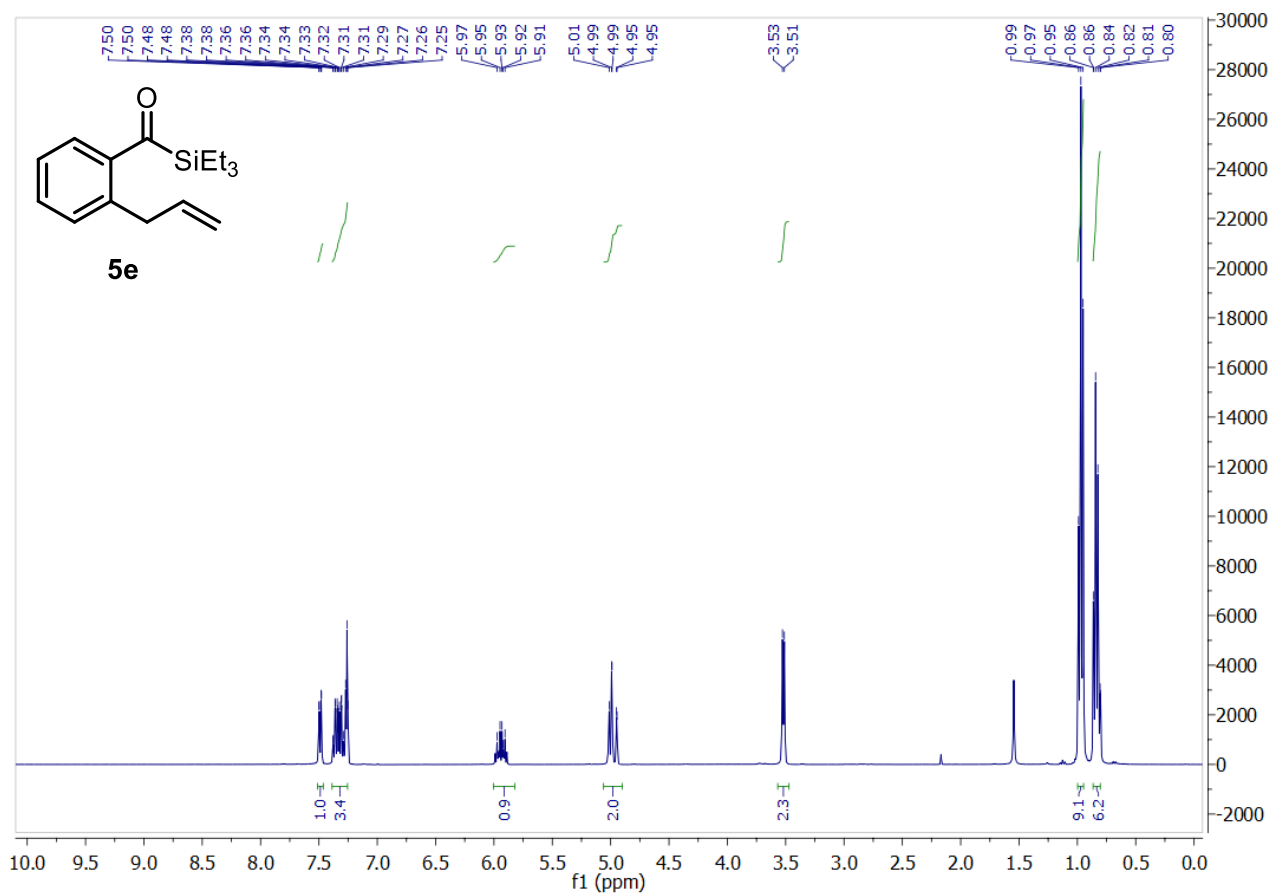
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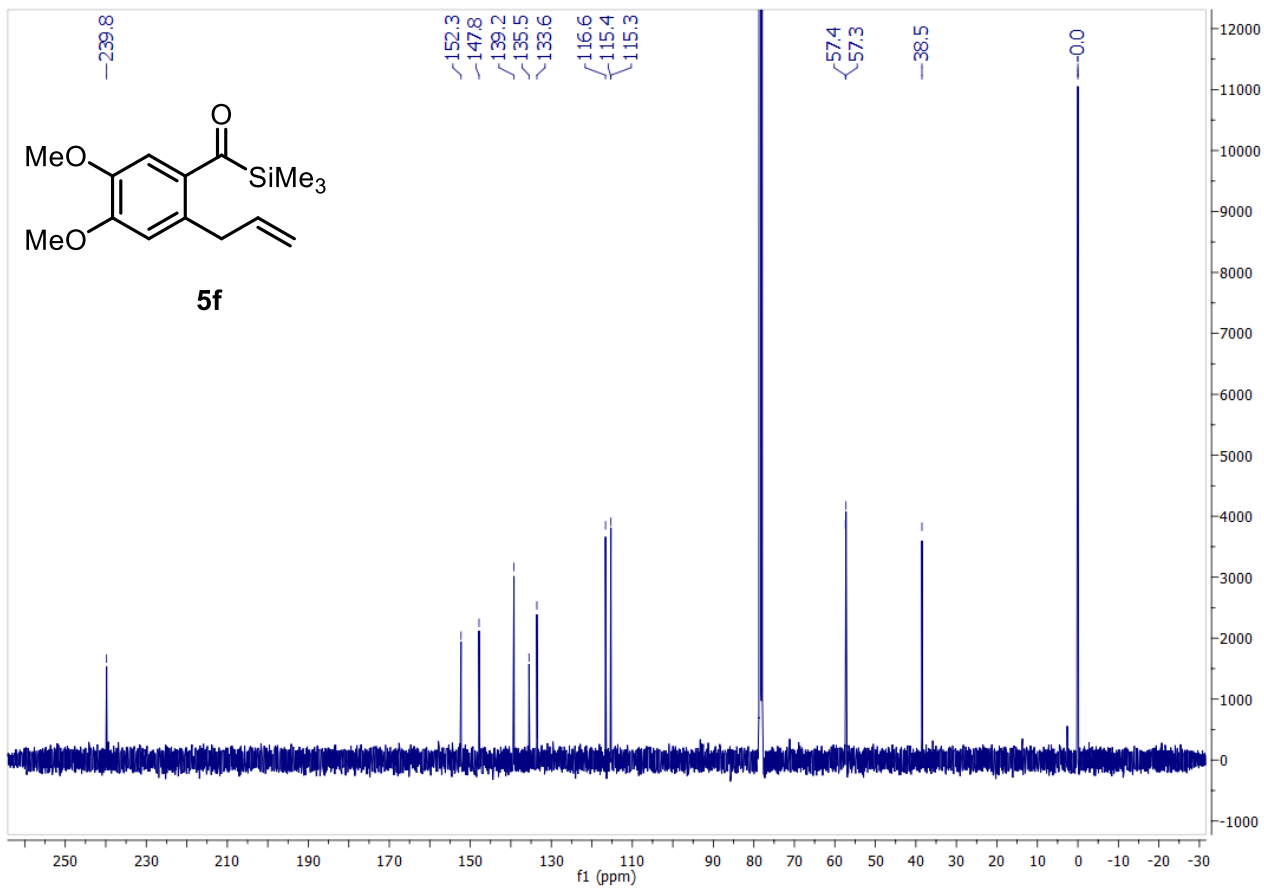
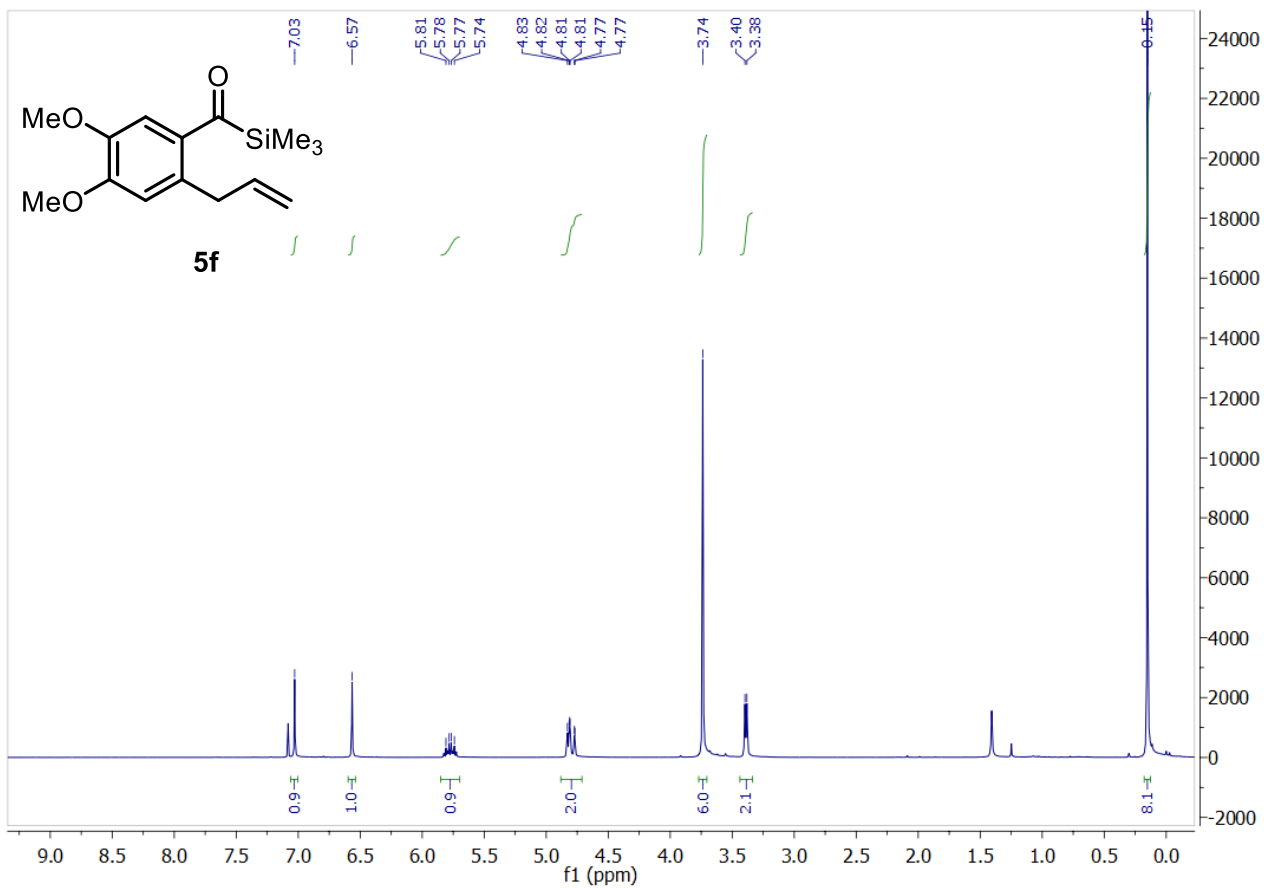




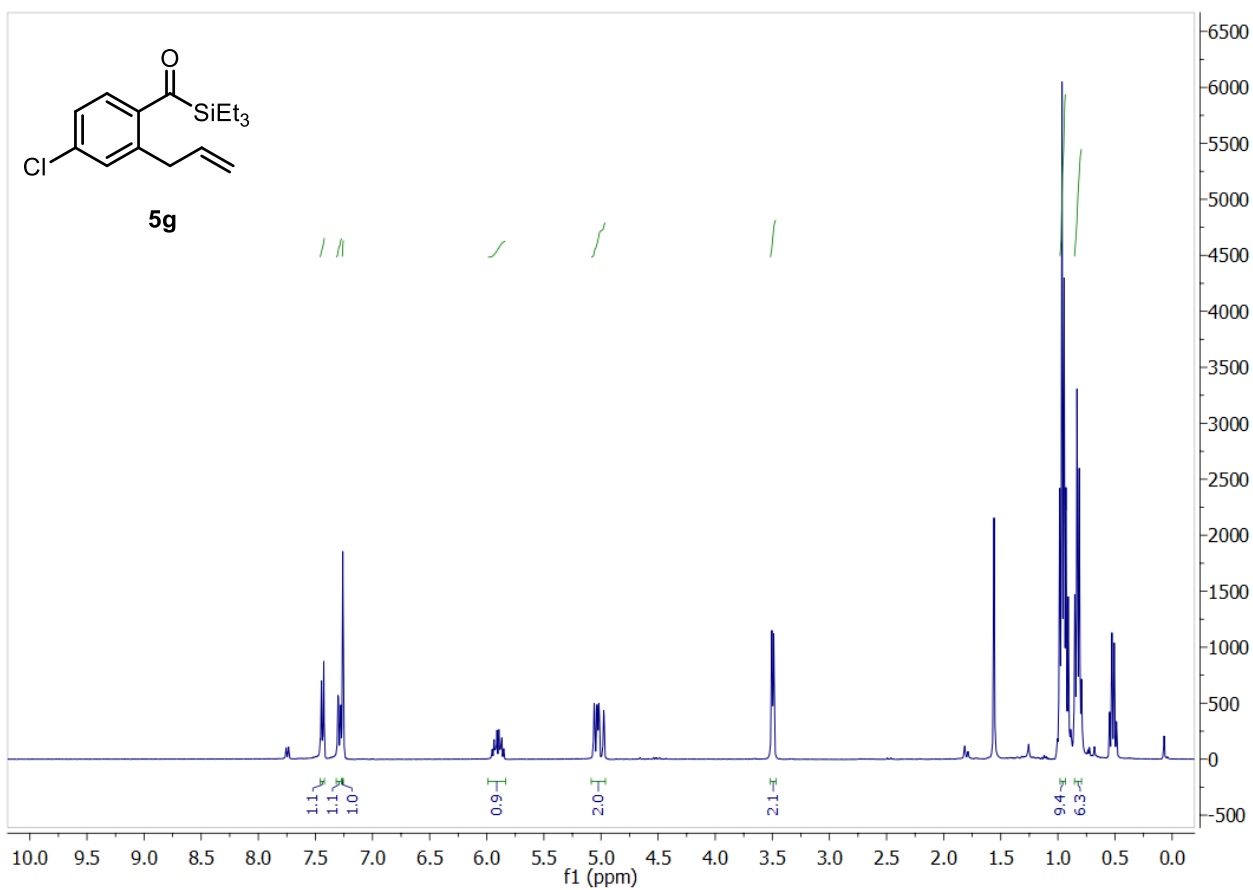




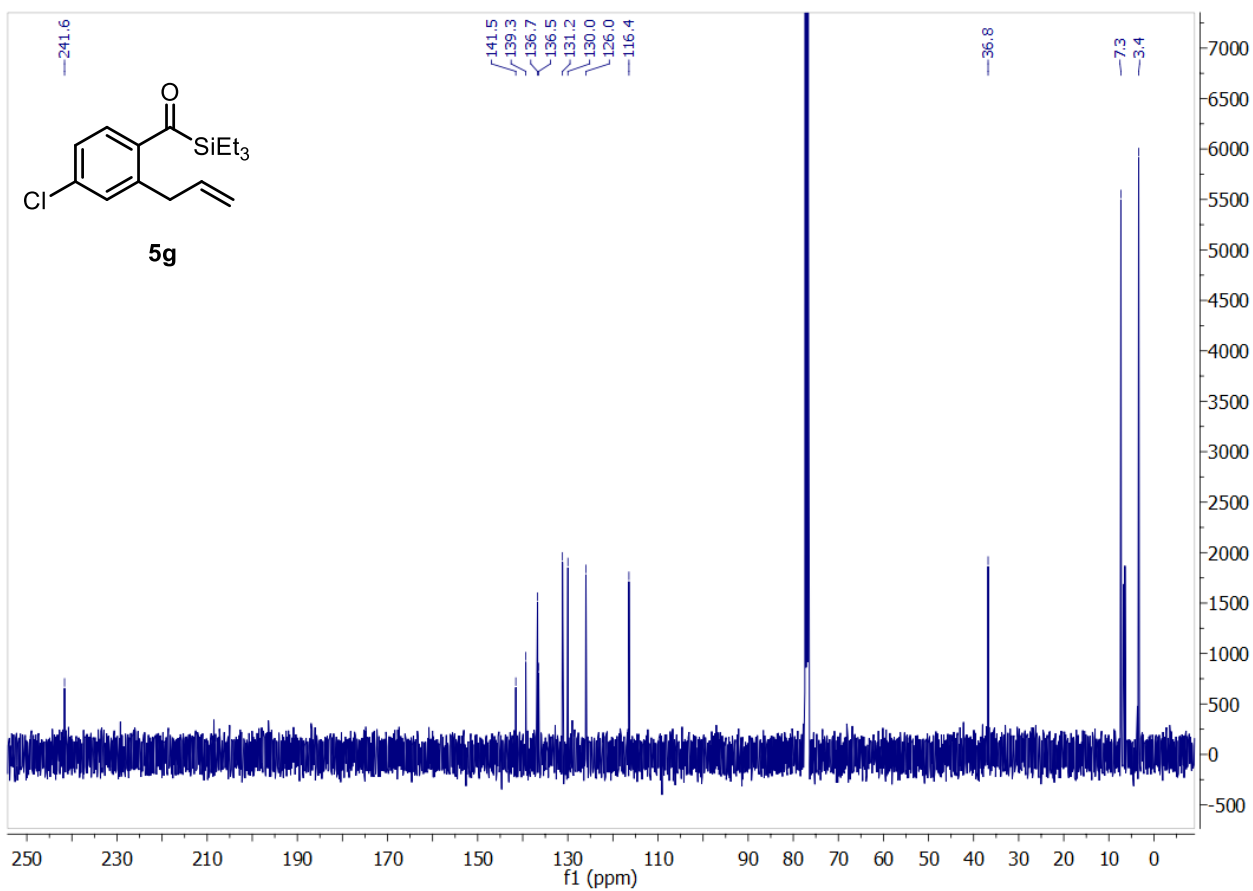


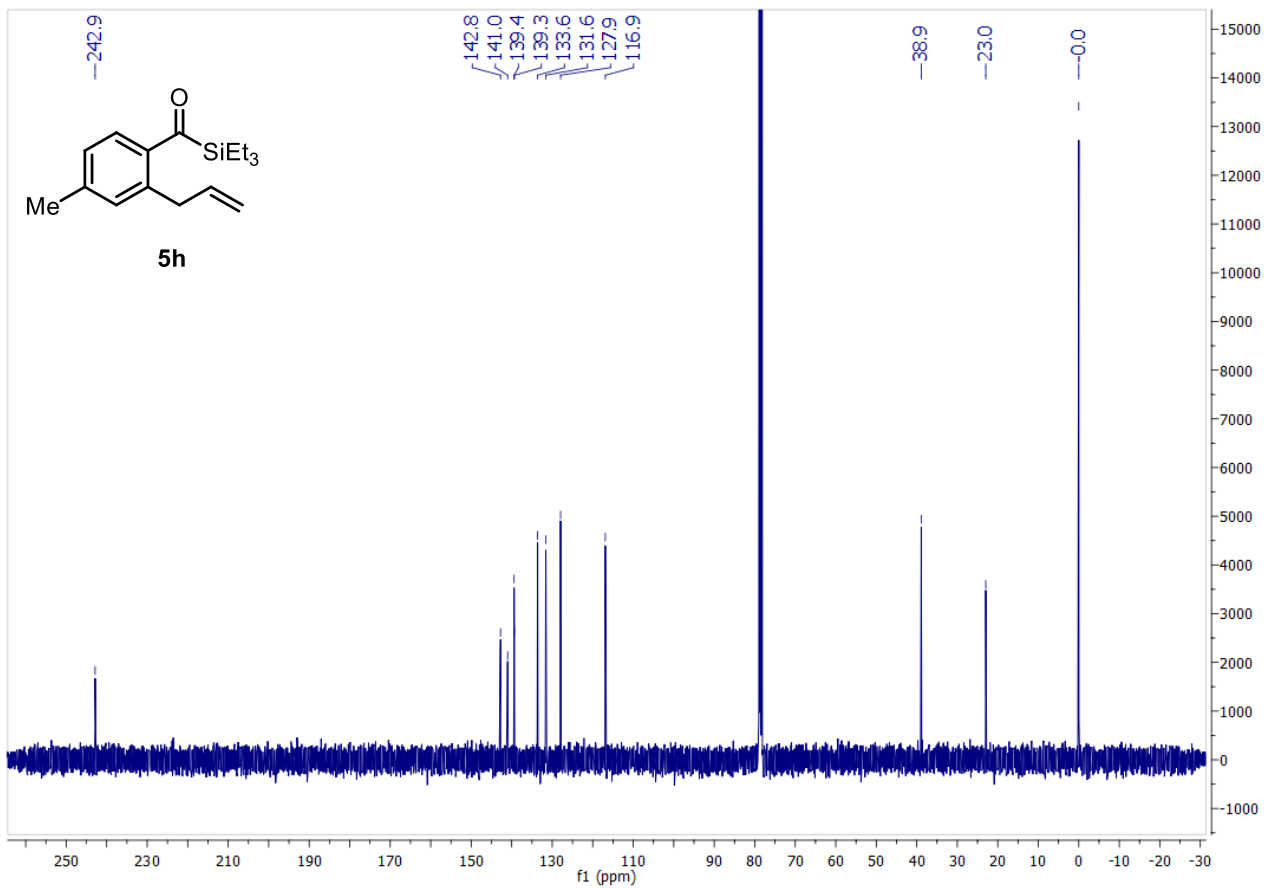
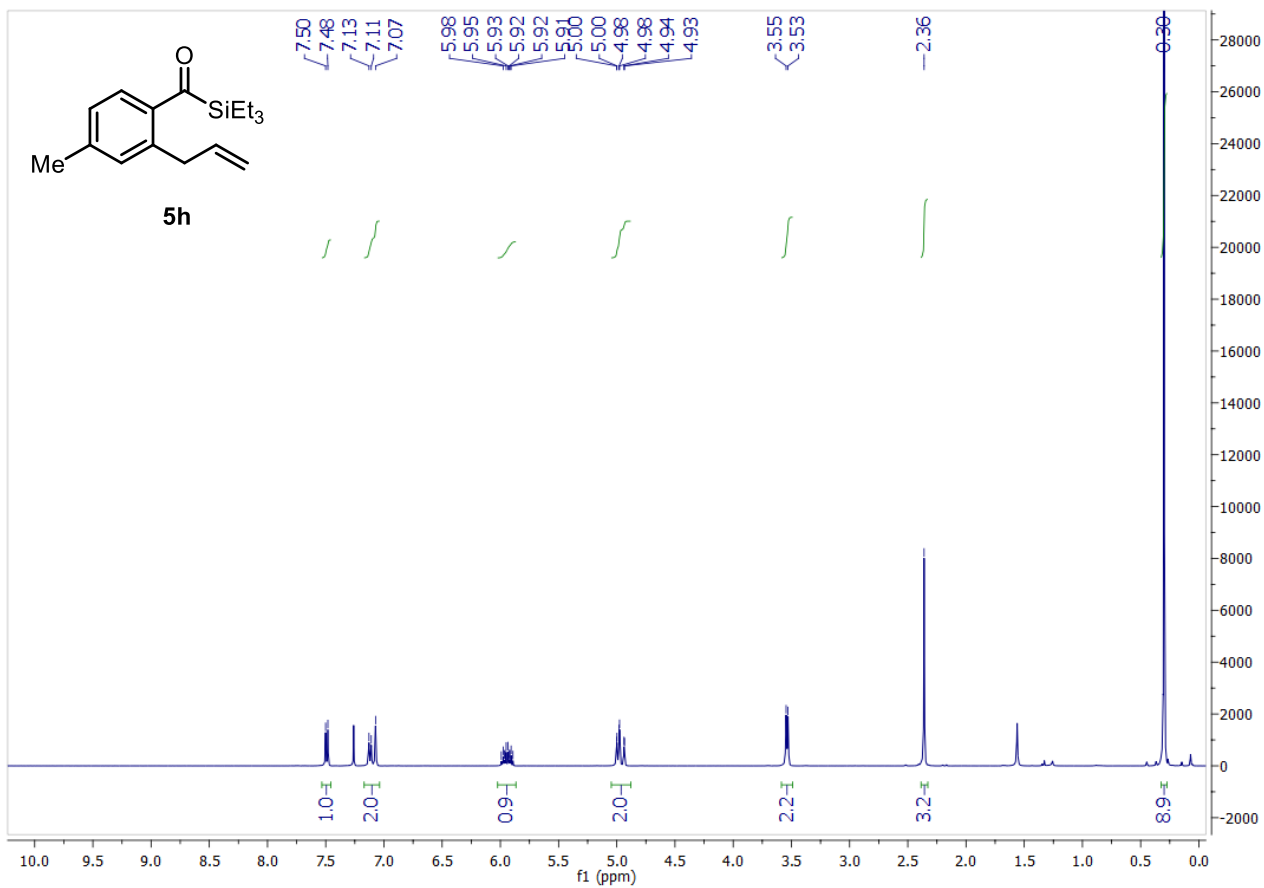


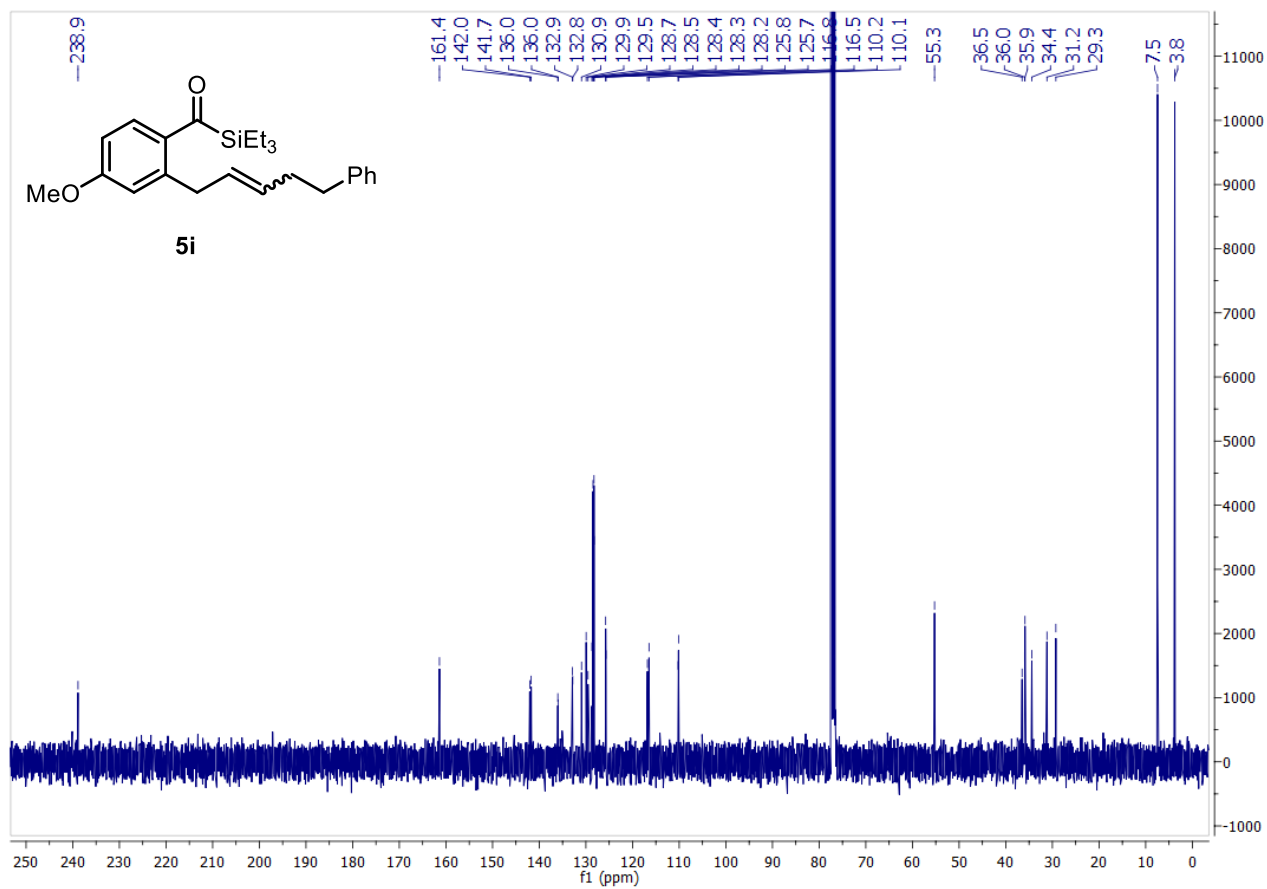
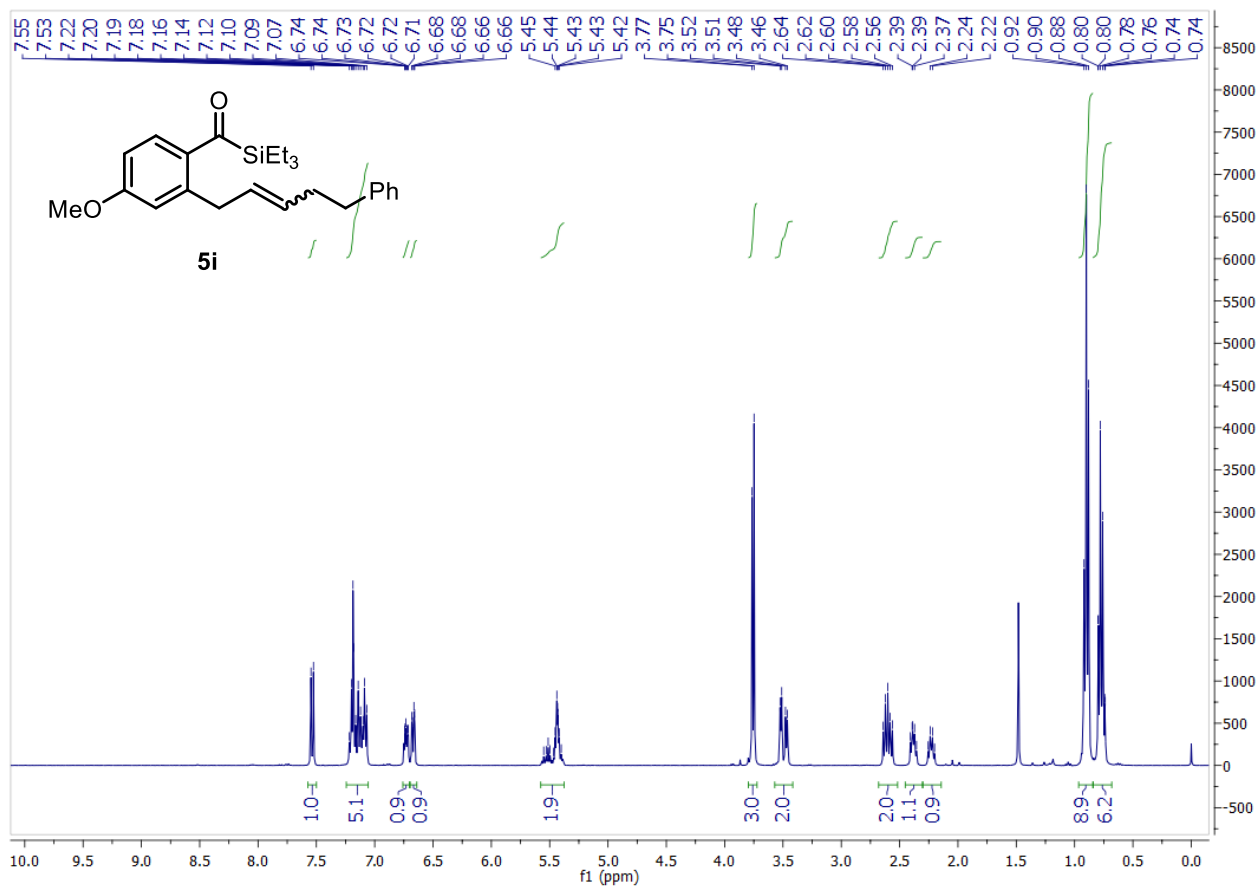


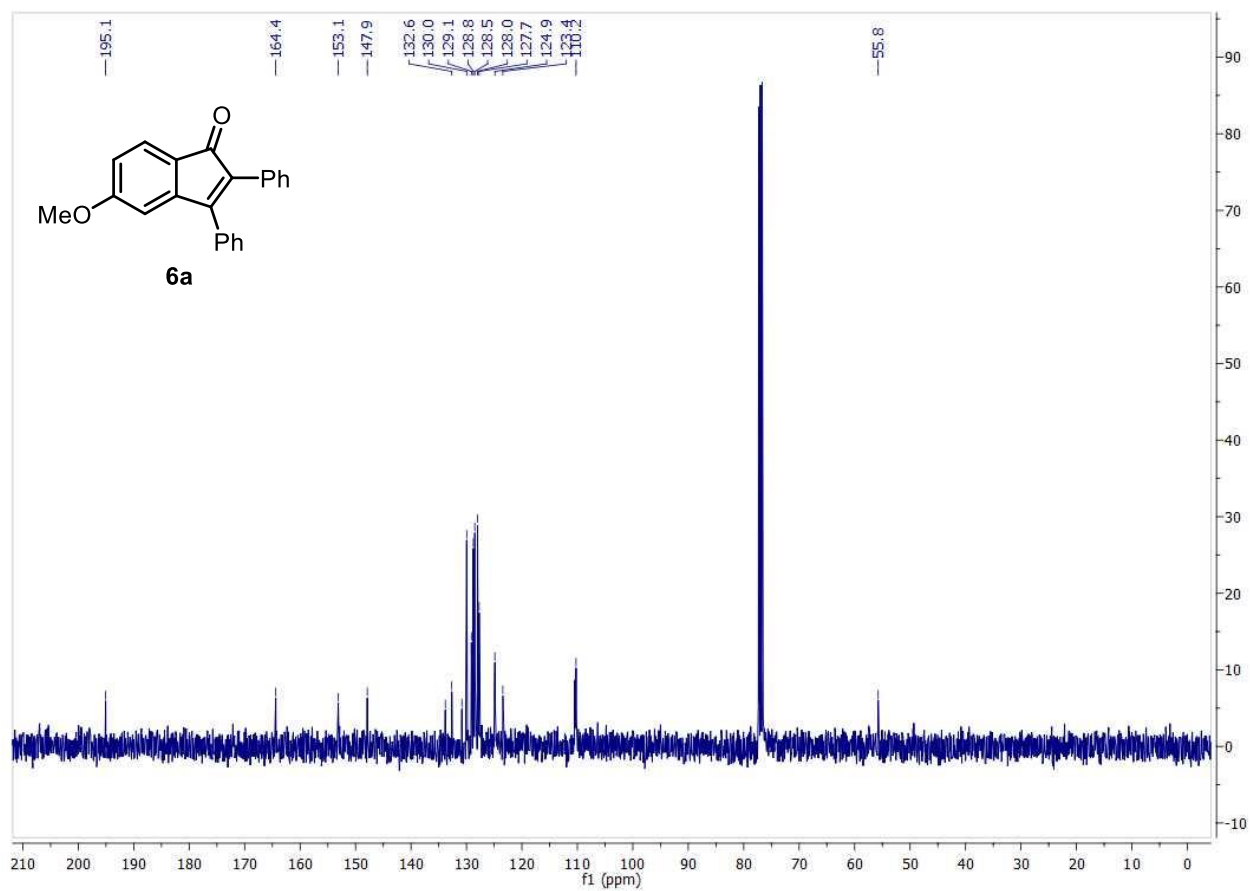
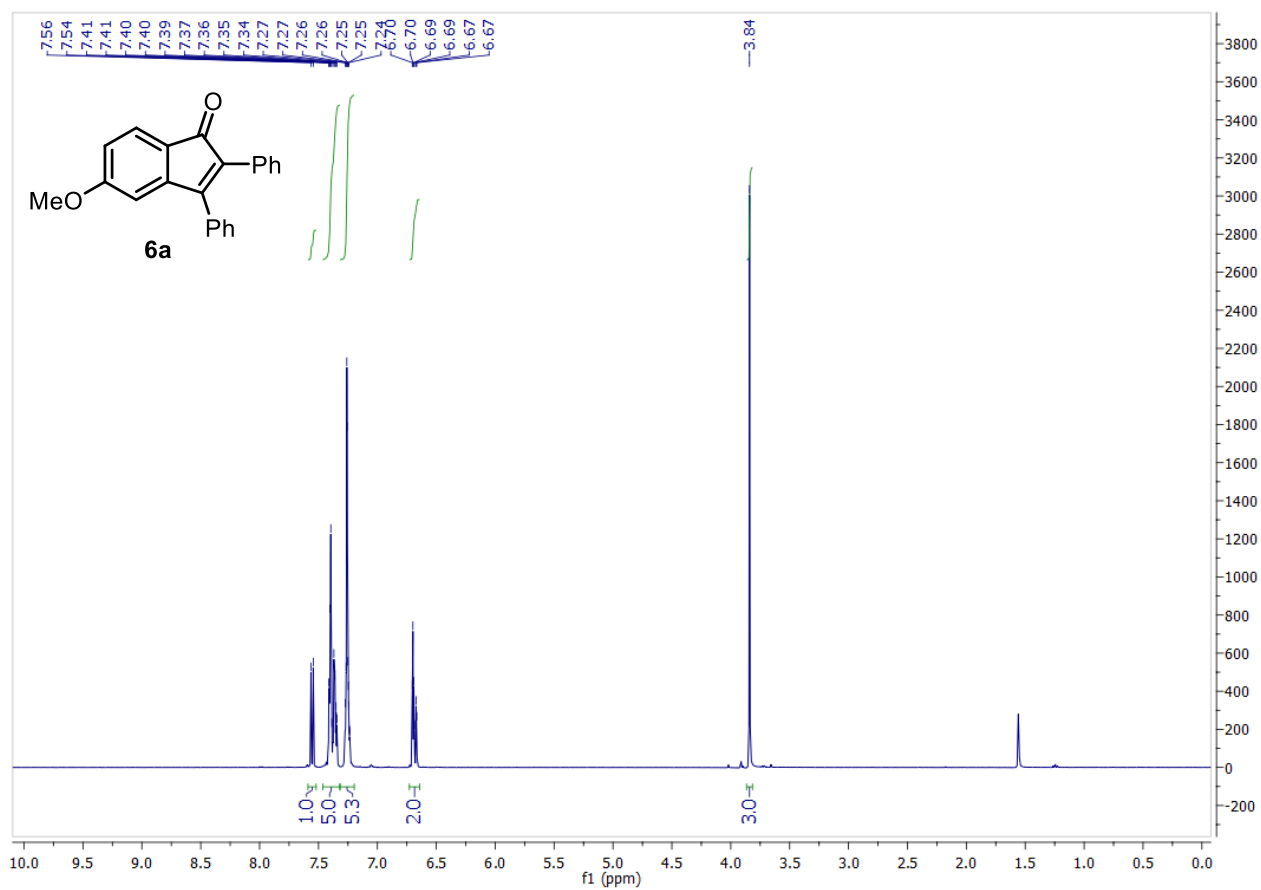


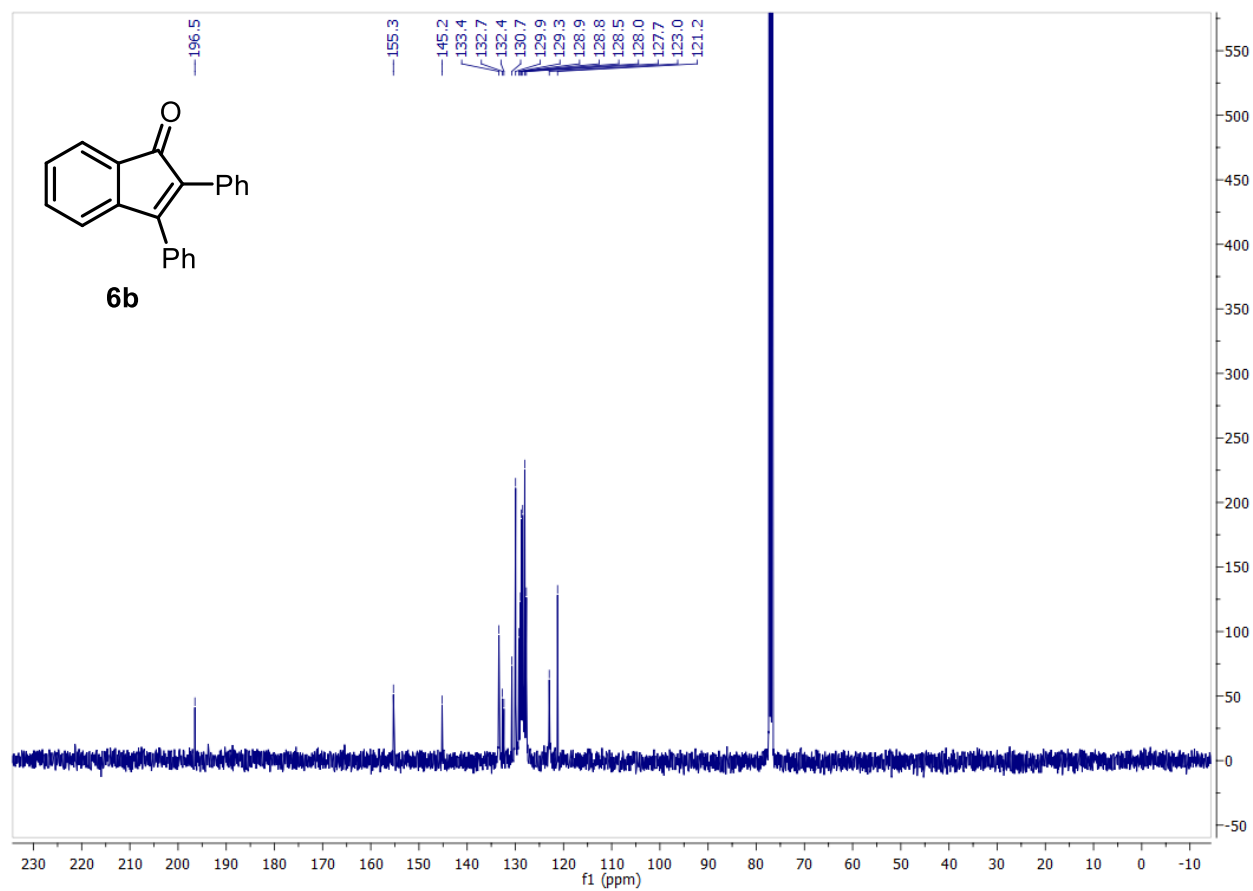
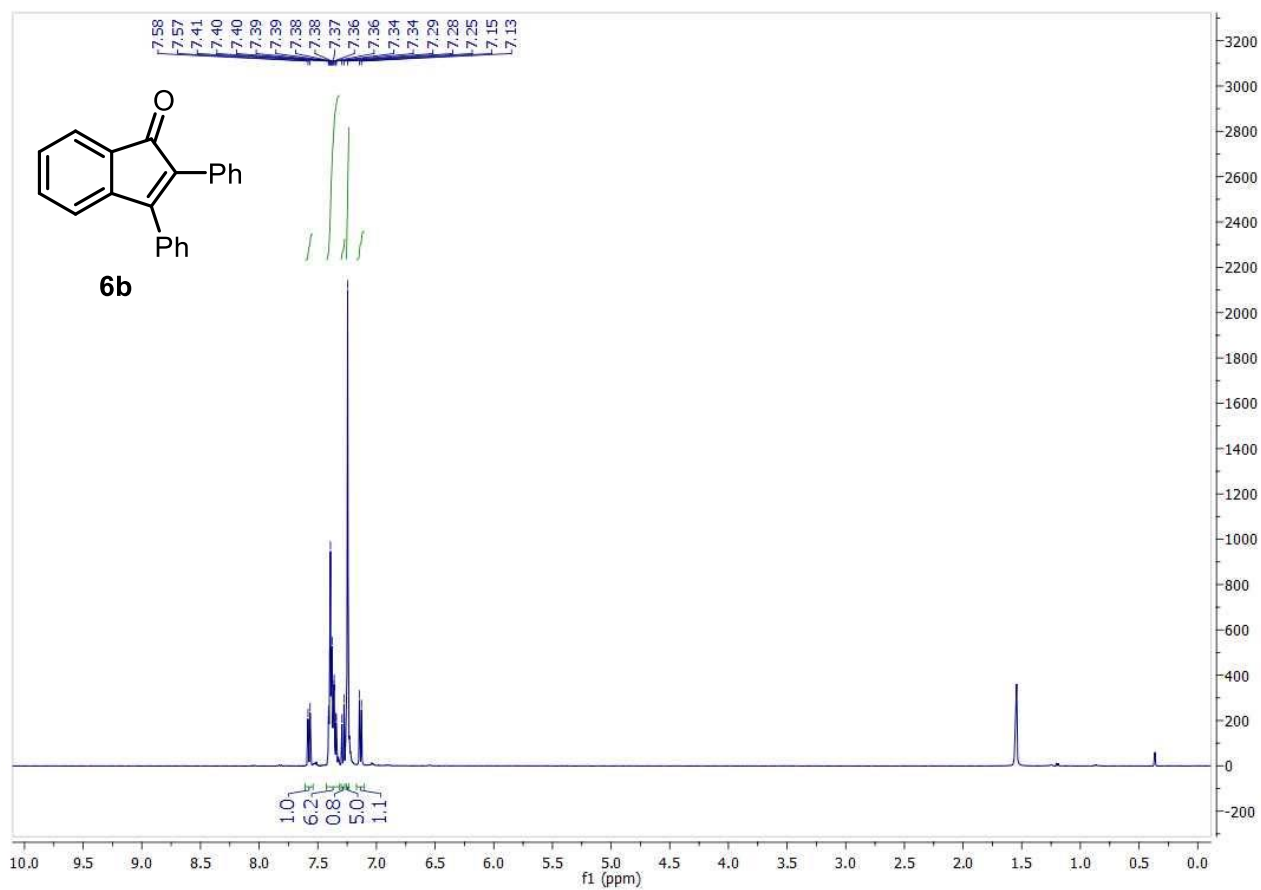
\* The minor peak at 7.75ppm corresponds to (4-chlorobenzoyl)triethylsilane **4g** present in 7.5%

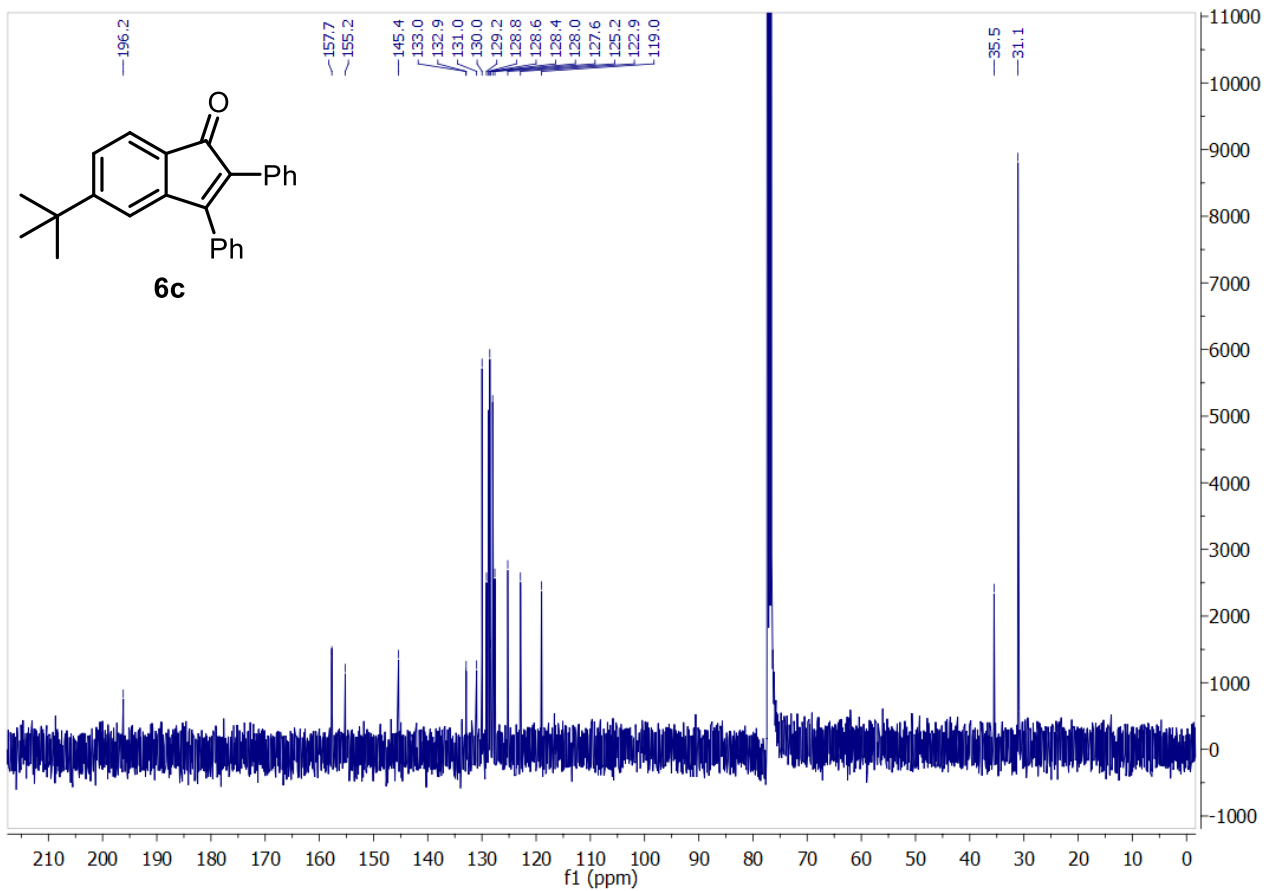
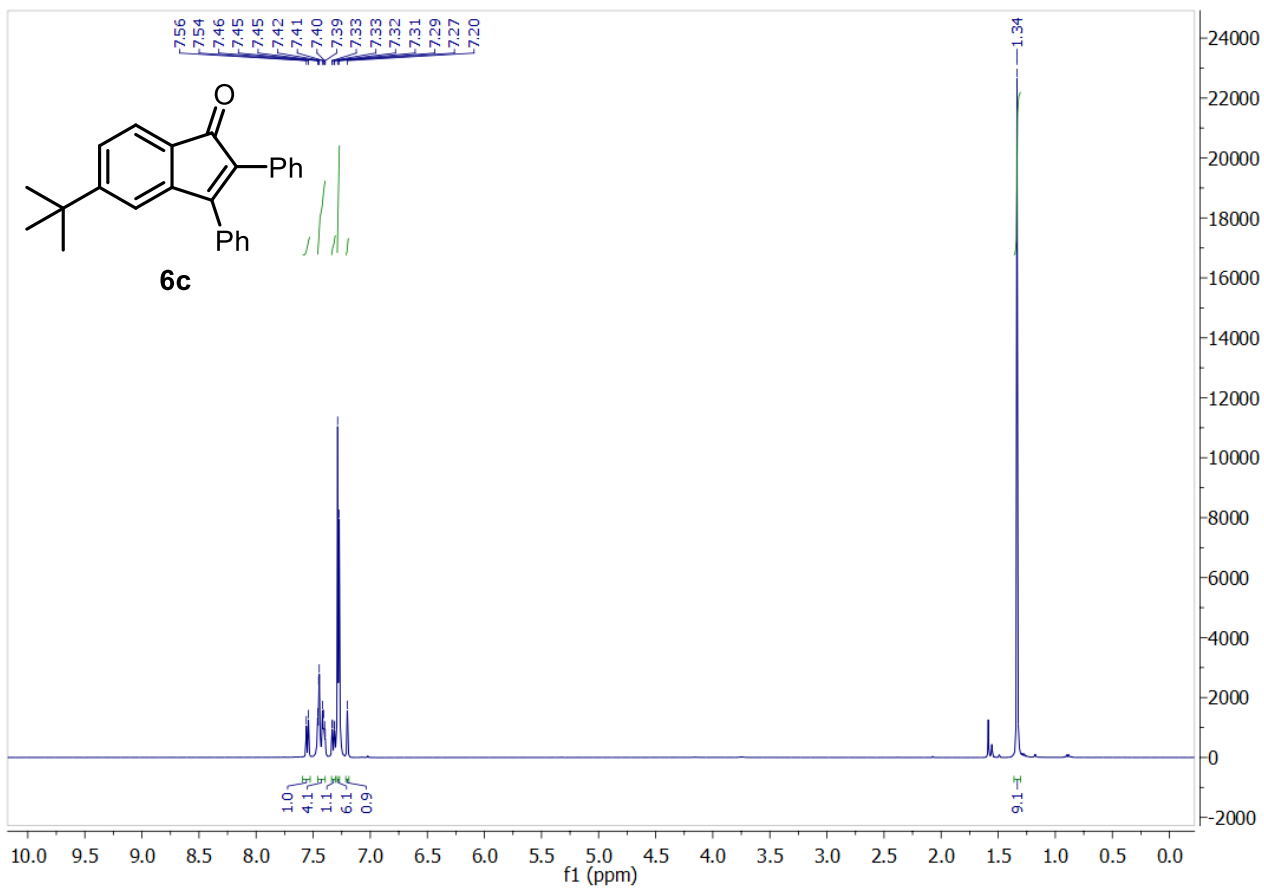


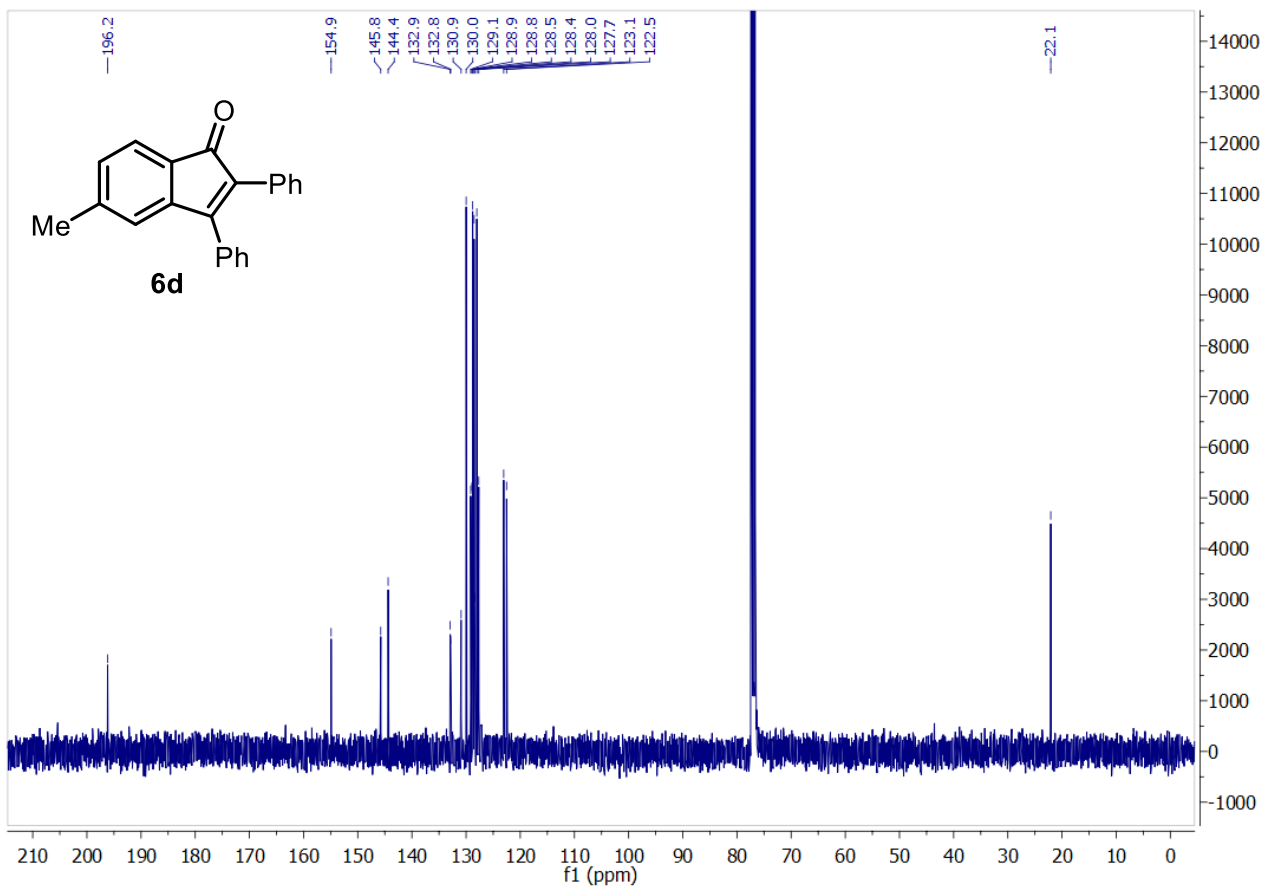
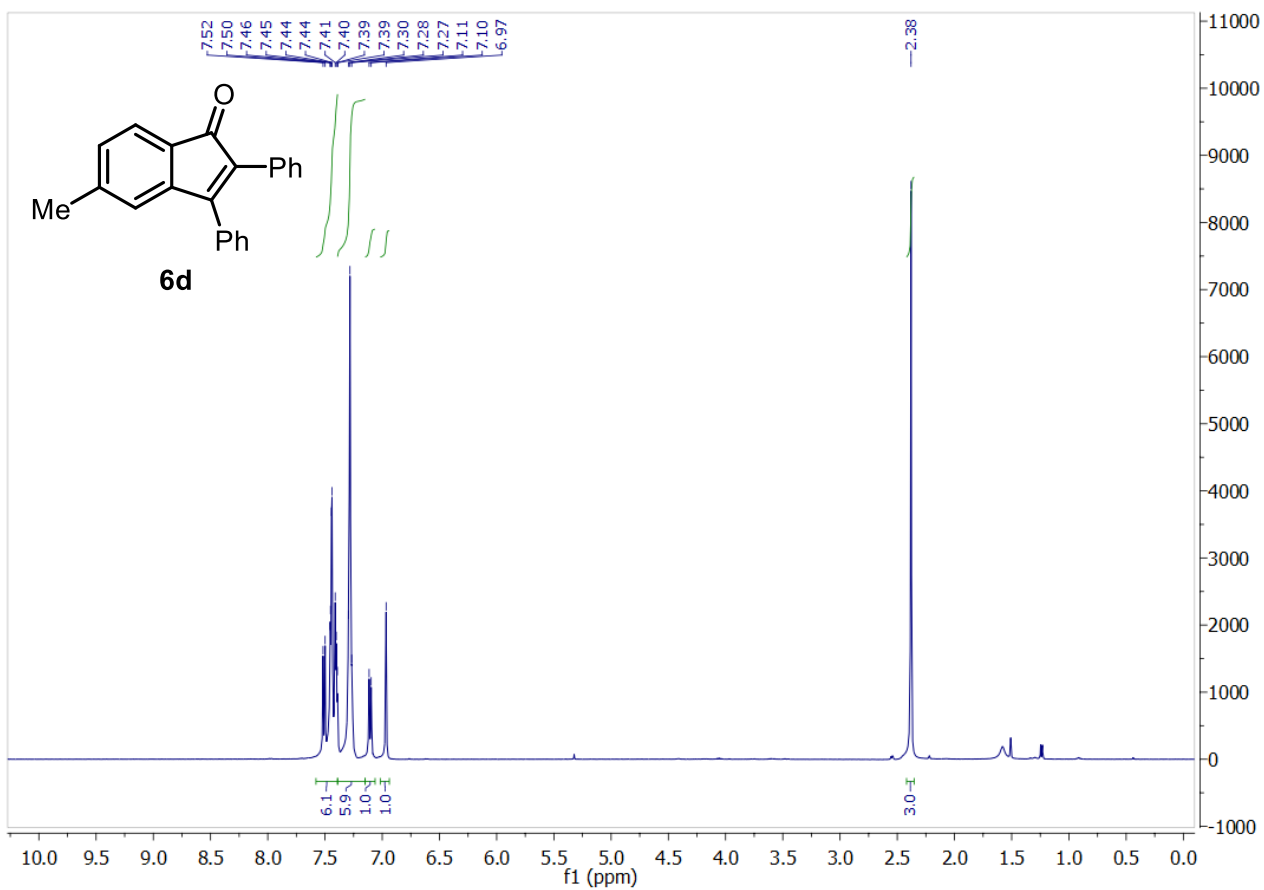


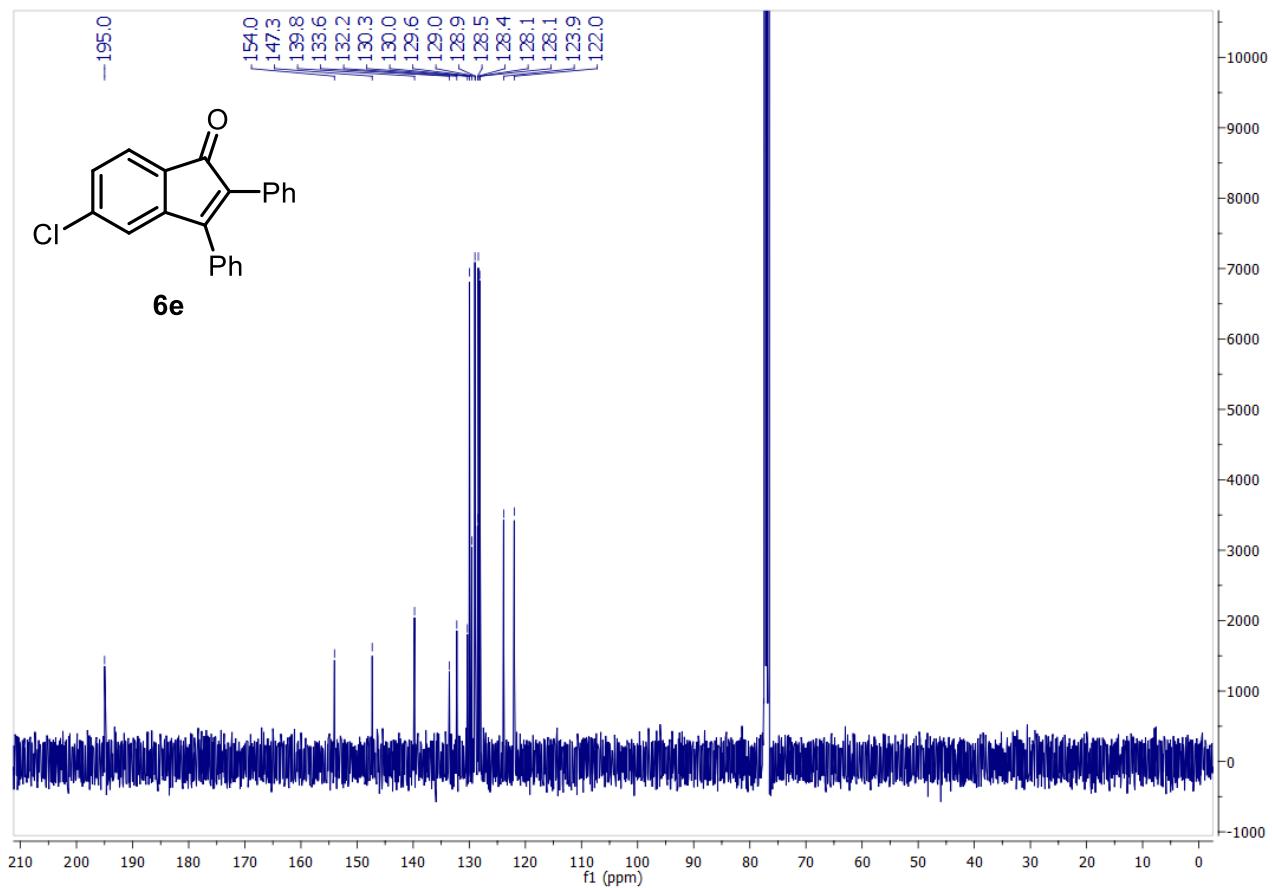
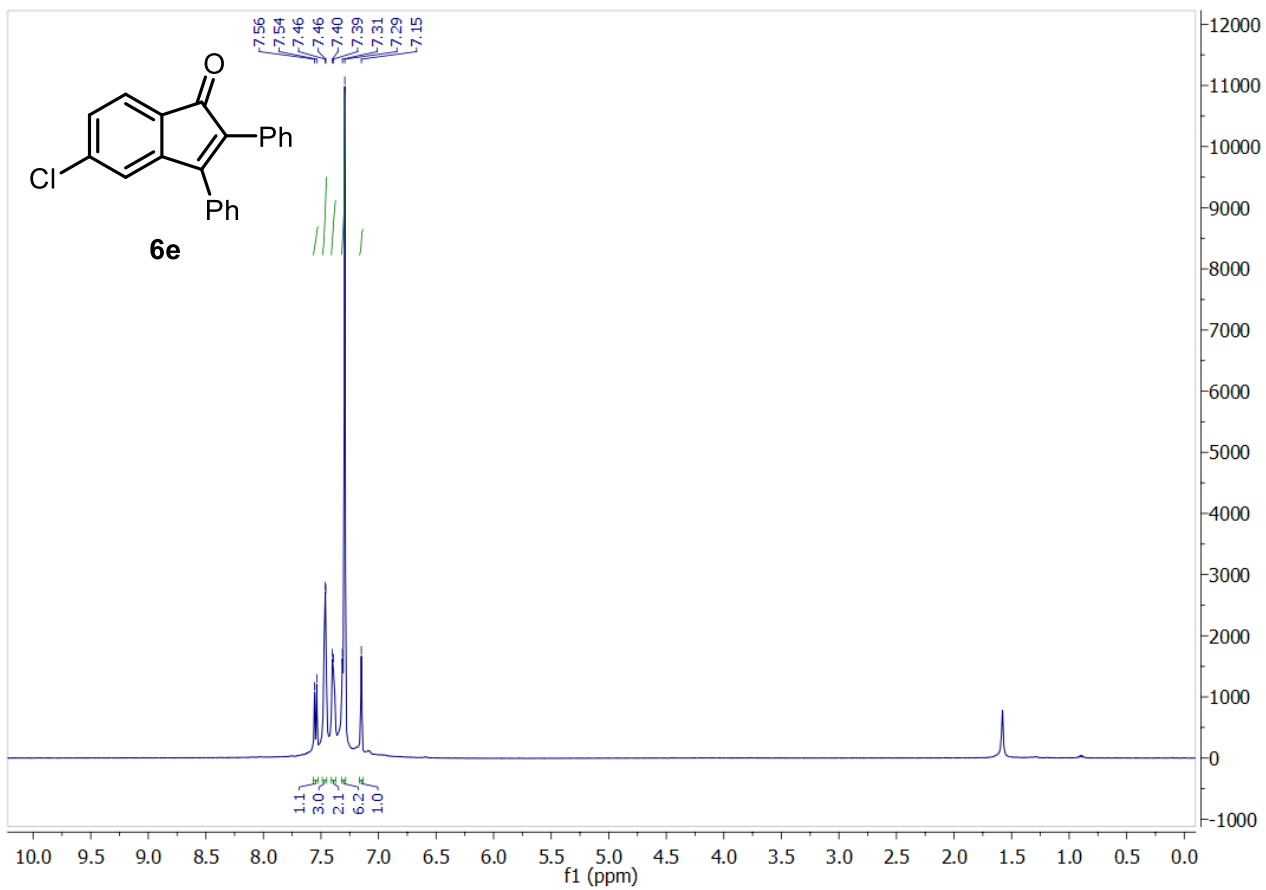




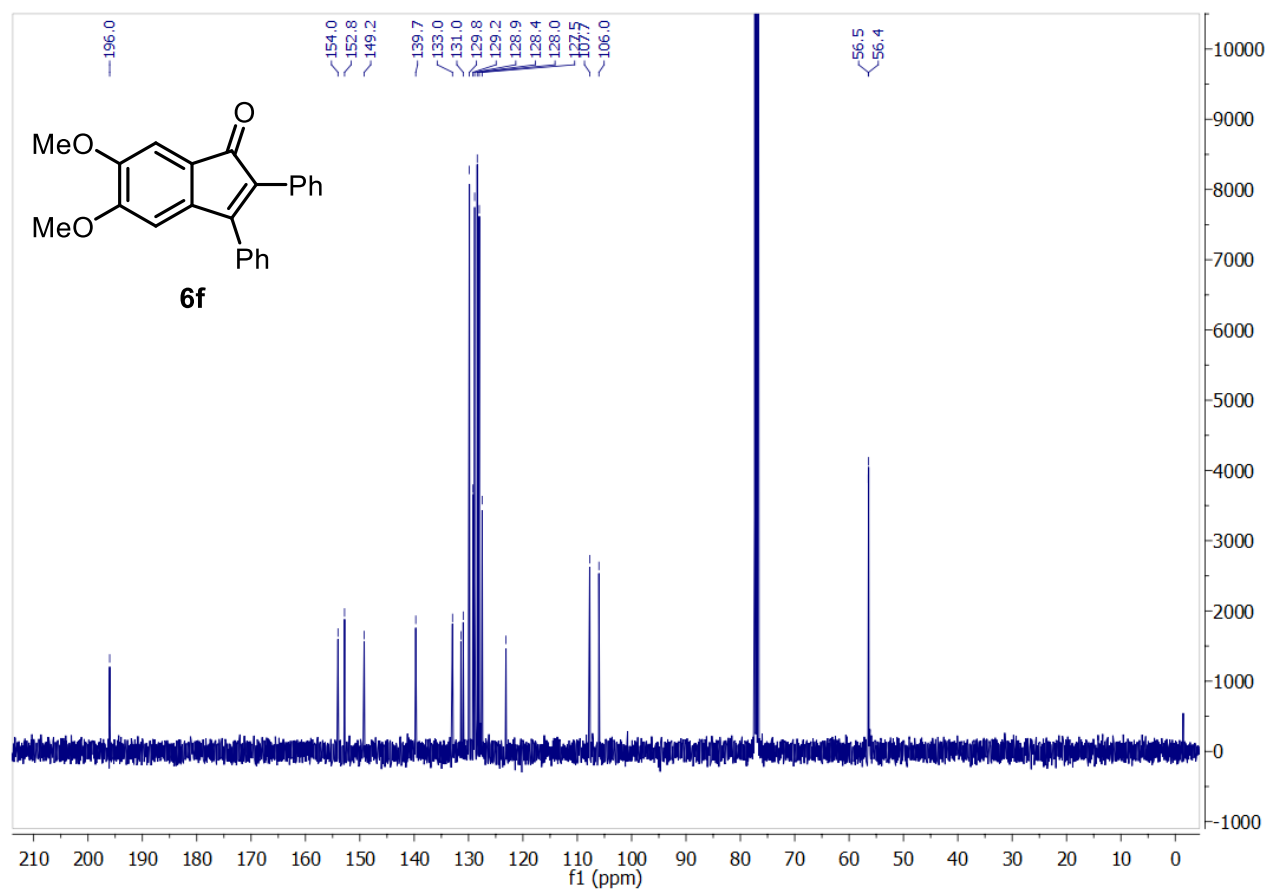
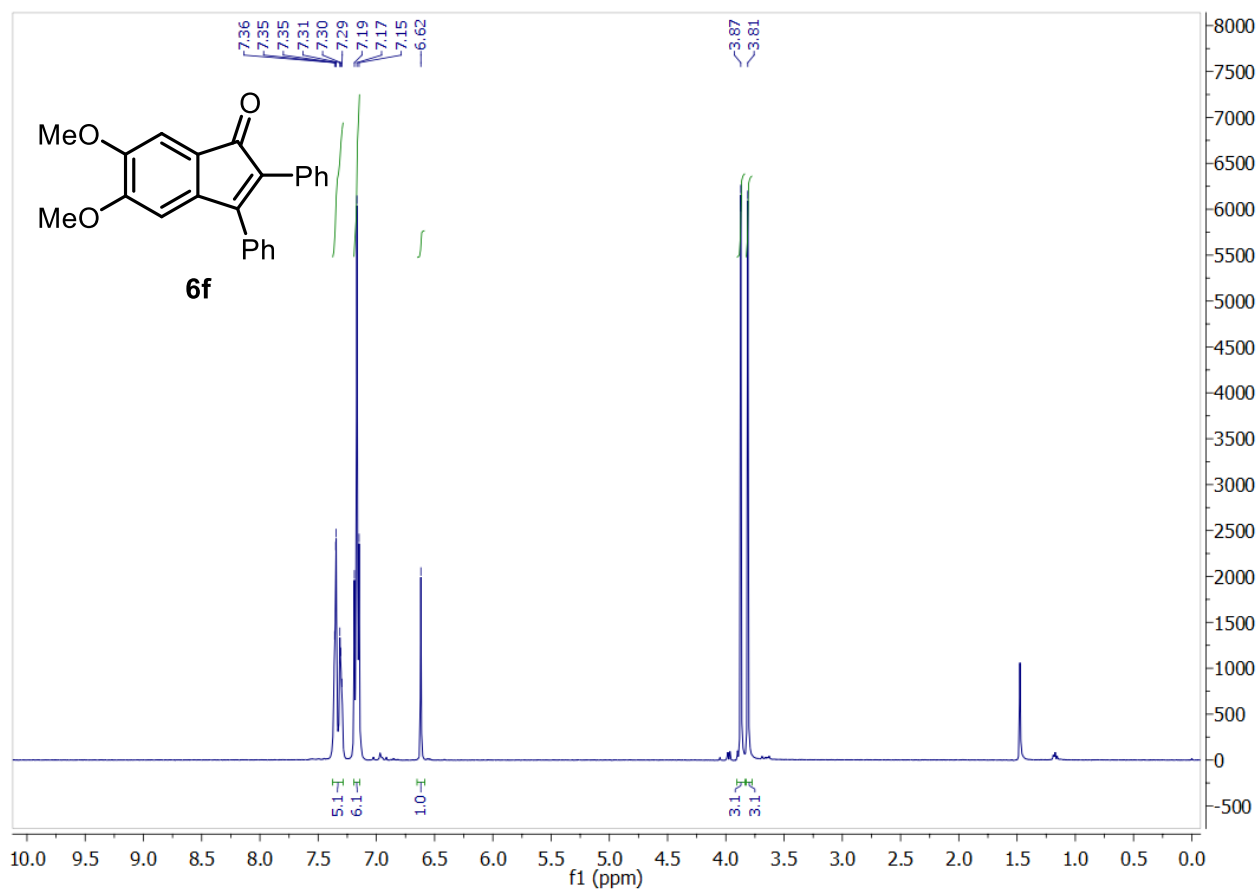












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