

Supporting Information for:

Acyl silane directed Cp^{*}Rh(III)-catalysed alkylation/annulation reactions

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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. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian MR-400 (400 MHz) or an Agilent DD2 NMR (500 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 (δ), multiplicity, coupling constant (J Hz) number of protons, assignment. Each carbon resonance was assigned according to the following convention: chemical shift (δ), multiplicity and coupling constants (J Hz). Multiplicity is quoted as br (broad), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet).

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. Each scan or data point on the total ion chromatogram (TIC) is an average of 2247 transients per spectrum, producing four spectra every second. Acquisition was performed using the Agilent Mass Hunter data acquisition software ver. B.10.1 build 10.1.48, and analysis was performed using Mass Hunter Qualitative Analysis ver. B.10.0 build 10.0.10305.0. Acquisition parameters: mode, ESI; drying gas flow, 11 L min $^{-1}$; nebulizer pressure, 25 psi; drying gas temperature, 250 °C. Voltages: capillary, 4000 V; fragmentor, 180 V; skimmer, 45 V; octapole RF, 750 V; scan range, 100–1700 m/z; positive ion mode internal reference ions, m/z 121.050873 and 922.009798. LC conditions: Agilent Zorbax C18 Eclipse Plus (2.1 mm \times 50 mm, 1.8 mm column), 30 °C; sample (2 μL) was eluted using a binary gradient (solvent A, 0.1% aq formic acid; solvent B, acetonitrile; 80–100% B [2 min], 0.4 mL min $^{-1}$).

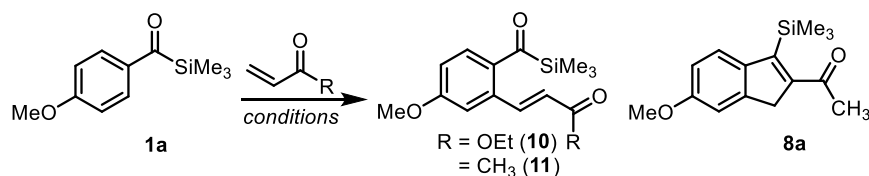
Compounds **8a** and **9a** were recrystallized from *n*-hexanes by heating in a minimal amount of solvent until all solids were dissolved and then allowing this sample to cool slowly. Single crystal X-ray diffraction data was collected on the MX2 beamline at the Australian Synchrotron.¹ In general, single crystals were transferred directly from the mother liquor into immersion oil and placed under a stream of nitrogen at 100 K. Crystal structures were solved by direct methods using the program SHELXT² and refined using a full matrix least-squares procedure based on F^2 (SHELXL),³ within the Olex2⁴ GUI program. In structures containing disordered solvent molecules that could not be satisfactorily modelled, the solvent mask routine within the Olex2 GUI was used.⁴

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 pathway⁵ and the measured spectroscopic data compared well with that previously reported for (4-methoxybenzoyl)trimethylsilane (**1a**)⁶; (4-methoxybenzoyl)triethylsilane (**1b**)⁷; (4-methoxybenzoyl)-*tri*-isopropylsilane (**1c**)⁶; (4-methoxybenzoyl)-*tert*-butyldimethylsilane (**1d**)⁶; benzoyl trimethylsilane (**1e**)⁶; (4-methylbenzoyl)trimethylsilane (**1f**)⁶; (3,4-dimethoxybenzoyl) trimethylsilane (**1g**)⁸; (3,4,5-trimethoxybenzoyl) trimethylsilane (**1h**)⁹; (4-*tert*-butylbenzoyl)trimethylsilane (**1i**)⁶; (3-methoxybenzoyl)trimethylsilane (**1j**)¹⁰; (3-methylbenzoyl)trimethylsilane (**1k**)⁶; (4-trifluoromethoxybenzoyl)trimethylsilane (**1l**)⁶; (4-chlorobenzoyl)trimethylsilane (**1m**)⁶ and (2-hydroxybenzoyl)trimethylsilane (**12**).¹¹ Phenethyl vinyl ketone was prepared according to a literature method.¹²

Table S1. Optimisation of reaction conditions

Entry	Catalyst	Silver Salt	Additive	Solvent	Conversion (%) ^b
1	[RhCp*Cl ₂] ₂ ^a	AgSbF ₆	Cu(OAc) ₂	1,2-DCE	33%
2	[RhCp*Cl ₂] ₂	AgSbF ₆	Cu(OAc) ₂	1,2-DCE	83%
3	[RhCp*Cl ₂] ₂	AgNTf ₂	Cu(OAc) ₂	1,2-DCE	77%
4	[RhCp*Cl ₂] ₂	AgOTf	Cu(OAc) ₂	1,2-DCE	84%
5	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂	1,2-DCE	99% (92%)
6	[RhCp*Cl ₂] ₂	-	Cu(OAc) ₂	1,2-DCE	0%
7	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂ ^d	1,2-DCE	20%
8	[RhCp*Cl ₂] ₂	AgBF ₄	NaOAc	1,2-DCE	15%
9	[RhCp*Cl ₂] ₂	AgBF ₄	KOAc	1,2-DCE	18%
10	[RhCp*Cl ₂] ₂	AgBF ₄	KOPiv	1,2-DCE	10%
11	[RhCp*Cl ₂] ₂	AgBF ₄	AcOH	1,2-DCE	70%
12	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂	CHCl ₃	67%
13	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂	Dioxane	26%
14	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂	THF	28%
15	[RhCp*Cl ₂] ₂	AgBF ₄	Cu(OAc) ₂	PhMe	0%
16	[RhCp*Cl ₂] ₂	AgBF ₄	AgOAc ^e	1,2-DCE	77%
17	[RhCp*Cl ₂] ₂	AgBF ₄	AgOAc ^f	1,2-DCE	71%
18	Cp*Co(CO)I ₂ ^c	AgBF ₄	Cu(OAc) ₂	1,2-DCE	16%
19	[Cp*Rh(MeCN) ₃](SbF ₆) ₂ ^c	-	Cu(OAc) ₂	1,2-DCE	0%
20	[Cp*Rh(MeCN) ₃](SbF ₆) ₂ ^c	-	AgOAc ^e	1,2-DCE	37%
21	[Cp*Rh(MeCN) ₃](SbF ₆) ₂ ^c	-	AgOAc ^f	1,2-DCE	69%

Reaction Conditions: acyl silane (0.2 mmol), methyl vinyl ketone (0.4 mmol), [RhCp*Cl₂]₂ (2.5 mol%), silver salt (10 mol%), additive (1.0 equiv.) in 1.0 mL solvent heated to 80 °C for 16 h unless stated otherwise. ^aReaction conducted at 60 °C. ^bConversion determined by ¹H NMR employing dimethyl sulfone as an internal standard. Isolated yield in parentheses. ^c 5 mol% catalyst used, ^d 0.5 equivalents employed ^e 1.0 equivalents employed ^f 2.0 equivalents employed

Table S2: Comparison of Reaction Outcomes for Acyl Silane Directed C-H Functionalisation

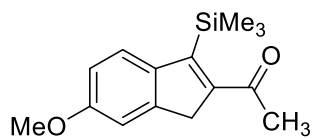
Entry	Reaction Conditions	% Conversion of 1a to 10 or 11	% Conversion of 1a to 8a
1	2.0 equiv. Ethyl Acrylate, 2.5 mol% [Cp*RhCl ₂] ₂ , 10 mol% AgOTf, 1.2 equiv. Cu(OAc) ₂ , 1,2-DCE, 60 °C, 24 h. (adapted from Ref. 13)	100% (10)	0%
2	2.0 equiv. Methyl Vinyl Ketone, 2.5 mol% [Cp*RhCl ₂] ₂ , 10 mol% AgBF ₄ , 1.0 equiv. Cu(OAc) ₂ , 1,2-DCE, 60 °C, 16 h.	0% (11)	33% ^a
3	2.0 equiv. Methyl Vinyl Ketone, 2.5 mol% [Cp*RhCl ₂] ₂ , 10 mol% AgBF ₄ , 1.0 equiv. Cu(OAc) ₂ , 1,2-DCE, 80 °C, 16 h.	0% (11)	100%
4	2.0 equiv. Methyl Vinyl Ketone, 5.0 mol% [Ru(<i>p</i> -cymene)Cl ₂] ₂ , 10 mol% AgSbF ₆ , 1.0 equiv. Cu(OAc) ₂ , 1,2-DCE, 60 °C, 4 h. (adapted from Ref. 14)	100% (11)	0%
5	2.0 equiv. Methyl Vinyl Ketone, 5.0 mol% [Ru(<i>p</i> -cymene)Cl ₂] ₂ , 10 mol% AgSbF ₆ , 1.0 equiv. Cu(OAc) ₂ , 1,2-DCE, 80 °C, 16 h.	75% (11)	25%

^a Only 33% conversion to **8a** with remaining 67% being unreacted starting material **1a**.

SPECIFIC EXPERIMENTAL DETAILS:

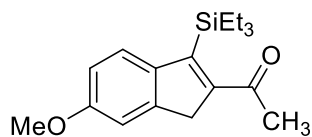
General Procedure: To an oven dried vial containing a stirrer bar was added AgBF₄ (6.0 mg, 10 mol%), [RhCp*Cl₂]₂ (4.6 mg, 2.5 mol%), Cu(OAc)₂ (65 mg, 0.3 mmol) and 1,2-dichloroethane (1.0 mL). After stirring for 5 minutes, acyl silane **1** (0.3 mmol, dissolved in an additional 0.5 mL 1,2-dichloroethane) and alkene (0.6 mmol) were added, the vial sealed and heated at 80°C for 16h. After this time, the reaction mixture was loaded directly onto a silica gel column and subject to flash chromatography to afford the silyl indene product.

1-(6-methoxy-3-(trimethylsilyl)-1H-inden-2-yl)ethanone (**8a**)



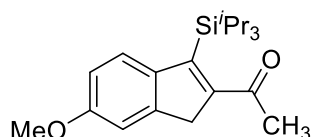
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a white solid in 92% yield (72 mg). MP = 129.1 – 130.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, *J* = 8.6 Hz, 1H), 7.07 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 2H), 2.42 (s, 3H), 0.37 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.1, 159.6, 156.0, 150.6, 146.6, 141.3, 126.2, 112.8, 109.6, 55.5, 41.7, 29.2, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₂₁O₂Si 261.1305, found 261.1306.

1-(6-methoxy-3-(triethylsilyl)-1H-inden-2-yl)ethanone (**8b**)



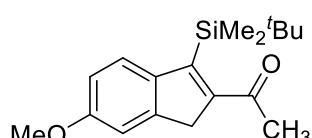
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 86% yield (78 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 2H), 2.43 (s, 3H), 0.94 (s, 15H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 159.4, 153.1, 151.9, 146.3, 141.9, 126.2, 112.8, 109.4, 55.4, 42.1, 29.4, 8.0, 4.1 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₈H₂₇O₂Si 303.1775, found 303.1774.

1-(6-methoxy-3-(triisopropylsilyl)-1H-inden-2-yl)ethanone (**8c**)



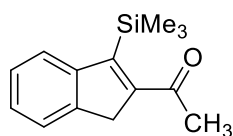
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 31% yield (32 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 2.5 and 8.7 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 2H), 2.44 (s, 3H), 1.66 (dt, *J* = 7.5 and 15.0 Hz, 3H), 1.12 (s, 9H), 1.10 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 199.3, 158.8, 154.3, 148.0, 145.5, 142.1, 126.2, 112.6, 109.1, 55.4, 43.1, 30.1, 19.4, 12.4 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₂₁H₃₃O₂Si 345.2244, found 345.2242.

1-(6-methoxy-3-(*tert*-butyldimethylsilyl)-1H-inden-2-yl)ethanone (**8d**)



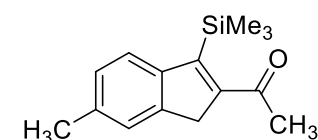
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 89% yield (81 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.6 Hz, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 2H), 2.41 (s, 3H), 1.01 (s, 9H), 0.30 (s, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.0, 159.1, 152.8, 151.0, 145.7, 141.8, 126.6, 112.6, 109.3, 55.5, 42.6, 29.9, 27.8, 18.6, -2.2 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₈H₂₇O₂Si 303.1775, found 303.1775.

1-(3-(trimethylsilyl)-1H-inden-2-yl)ethanone (**8e**)



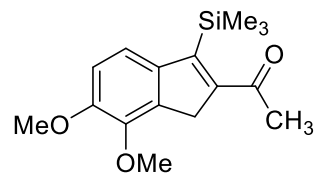
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a white solid in 59% yield (41 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.85 – 7.82 (m, 1H), 7.54 – 7.52 (m, 1H), 7.32 (dd, *J* = 3.0 and 5.4 Hz, 2H), 3.76 (s, 2H), 2.45 (s, 3H), 0.39 (s, 9H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 197.1, 155.3, 152.8, 148.0, 144.0, 127.0, 126.7, 125.4, 124.0, 41.8, 29.5, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₉O₂Si 231.1200, found 231.1198.

1-(6-methyl-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8f)



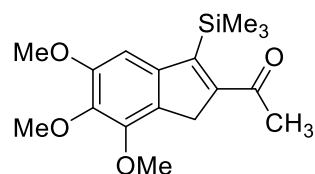
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 86% yield (63 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.34 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 2H), 2.43 (s, 3H), 2.42 (s, 3H), 0.38 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 196.8, 155.6, 151.8, 145.5, 144.6, 137.3, 127.7, 125.1, 124.7, 41.6, 29.4, 21.5, 0.6 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₂₁OSi 245.1356, found 245.1357.

1-(6,7-dimethoxy-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8g)



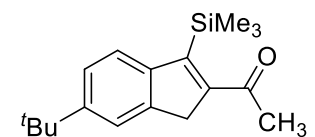
Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (10% EtOAc/hexanes) afforded the title compound as a colorless oil in 91% yield (79 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 10.5 Hz, 1H), 6.91 (d, *J* = 10.5 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.75 (s, 2H), 2.43 (s, 3H), 0.37 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 196.3, 155.8, 152.0, 151.1, 144.7, 142.5, 136.9, 121.4, 111.6, 60.2, 56.1, 39.0, 29.3, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₆H₂₃O₃Si 291.1411, found 291.1410.

1-(5,6,7-trimethoxy-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8h)



Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (20% EtOAc/hexanes) afforded the title compound as a colorless oil in 96% yield (92 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.19 (s, 1H), 3.99 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.71 (s, 2H), 2.43 (s, 3H), 0.38 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 196.2, 155.5, 153.3, 152.7, 148.9, 143.8, 141.7, 128.8, 104.8, 61.1, 60.4, 56.2, 39.2, 29.2, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₇H₂₅O₄Si 321.1517, found 321.1516.

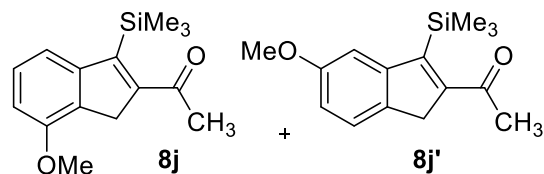
1-(6-*tert*-butyl-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8i)



Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a pale yellow solid in 92% yield (79 mg). MP = 121.1 – 123.9 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 1.1 Hz, 1H), 7.40 (dd, *J* = 1.9 and 8.3 Hz, 1H), 3.76 (s, 2H), 2.45 (s, 3H), 1.37 (s, 9H), 0.39 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 196.8, 155.6, 151.8, 145.5, 144.6, 137.3, 127.7, 125.1, 124.7, 41.6, 29.4, 21.5, 0.6 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₈H₂₇OSi 287.1826, found 287.1825.

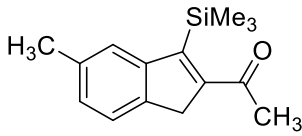
1-(7-methoxy-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8j)

1-(5-methoxy-3-(trimethylsilyl)-1*H*-inden-2-yl)ethanone (8j')

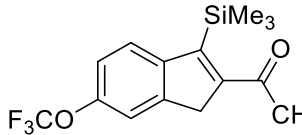


Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 74% yield (58 mg, 8j/8j' 4:1). ¹H NMR (500 MHz, CDCl₃) 8j = δ 7.46 (d, *J* = 7.8 Hz, 0.8H), 7.31 (t, *J* = 8.0 Hz, 0.8H), 6.87 (d, *J* = 8.0 Hz, 0.8H), 3.92 (s, 2.4H), 3.70 (s, 1.6H), 2.46 (s, 2.4H), 0.37 (s, 7.2H) ppm; 8j' = δ 7.40 (d, *J* = 8.2 Hz, 0.2H), 7.38 (d, *J* = 2.4 Hz, 0.2H), 6.92 (dd, *J* = 2.4 and 8.2 Hz, 0.2H), 3.84 (s, 0.6H), 3.70 (s, 0.4H), 2.44 (s, 0.6H), 0.39 (s, 1.8H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 197.1, 155.3, 155.2, 153.1, 149.7, 131.3, 128.3, 124.3, 118.3, 113.6, 110.5, 108.9, 55.3, 41.1, 39.2, 29.4, 26.9, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₂₁O₂Si 261.1305, found 261.1306.

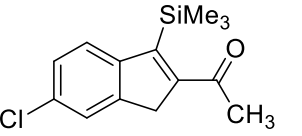
1-(5-methyl-3-(trimethylsilyl)-1H-inden-2-yl)ethanone (8k)

 Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 57% yield (42 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (s, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 3.71 (s, 2H), 2.44 (s, 3H), 2.41 (s, 3H), 0.38 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 197.2, 155.3, 153.2, 148.4, 141.2, 136.3, 128.1, 126.0, 123.7, 41.5, 29.4, 21.8, 0.6 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₂₁OSi 245.1356, found 245.1357.

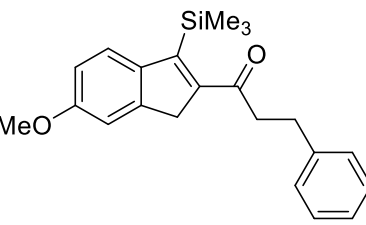
1-(6-trifluoromethoxy-3-(trimethylsilyl)-1H-inden-2-yl)ethanone (8l)

 Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 47% yield (44 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, *J* = 8.5 Hz, 1H), 7.37 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 3.77 (s, 2H), 2.45 (s, 3H), 0.38 (s, 9H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 196.8, 154.2, 153.7, 148.5, 146.7, 145.8, 126.1, 122.3 (q, ¹*J*_{CF} = 255 Hz), 119.7, 116.8, 41.9, 29.5, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₁₈F₃O₂Si 315.1023, found 315.1023.

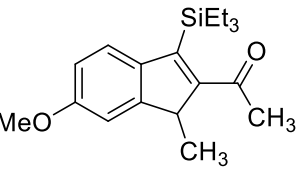
1-(6-chloro-3-(trimethylsilyl)-1H-inden-2-yl)ethanone (8m)

 Prepared according to the General Procedure using methyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 27% yield (21 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.4 Hz, 1H), 7.49 (s, 1H), 7.29 (dd, *J* = 1.7 and 8.4 Hz, 1H), 3.74 (s, 2H), 2.44 (s, 3H), 0.37 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 196.8, 154.5, 152.9, 146.5, 145.7, 133.2, 127.1, 126.1, 124.2, 41.6, 29.4, 0.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₈ClOSi 265.0810, found 265.0811.

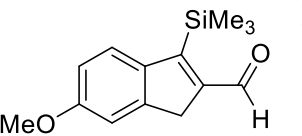
1-(6-methoxy-3-(trimethylsilyl)-1H-inden-2-yl)-3-phenylpropan-1-one (8n)

 Prepared according to the General Procedure using phenethyl vinyl ketone. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 79% yield (83 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.6 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.24 (s, 1H), 7.22 (d, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.88 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 2H), 3.04 (d, *J* = 1.7 Hz, 4H), 0.40 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 197.5, 159.6, 156.1, 150.4, 146.5, 141.4, 141.2, 128.5, 128.4, 126.2, 126.1, 112.8, 109.6, 55.5, 43.1, 41.2, 30.2, 0.6 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₂₂H₂₇O₂Si 351.1775, found 351.1776.

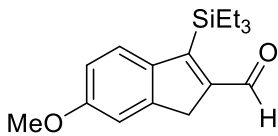
1-(6-methoxy-3-(triethylsilyl)-1-(methyl)inden-2-yl)ethanone (8o)

 Prepared according to the General Procedure using 3-penten-2-one. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 54% yield (51 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 2.2 Hz, 1H), 6.88 (dd, *J* = 2.5 and 8.5 Hz, 1H), 3.85 (s, 3H), 3.78 (q, *J* = 7.4 Hz, 1H), 2.42 (s, 3H), 1.35 (d, *J* = 7.4 Hz, 2H), 0.87 – 0.95 (m, 15H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 199.9, 160.2, 159.2, 151.7, 147.2, 139.8, 125.6, 112.4, 108.9, 55.5, 47.2, 30.5, 17.0, 7.8, 4.2 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₉H₂₉O₂Si 317.1931, found 317.1929.

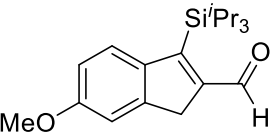
6-methoxy-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (9a)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a white solid in 91% yield (67 mg). MP = 121.7 – 123.9 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.16 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.09 (s, 1H), 6.90 (dd, *J* = 2.4 and 8.6 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 2H), 0.49 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.1, 162.4, 160.4, 153.0, 147.3, 140.6, 126.2, 113.4, 109.8, 55.5, 38.4, 1.4 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₉O₂Si 247.1149, found 247.1150.

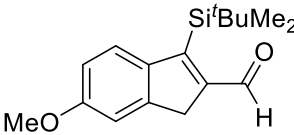
6-methoxy-3-(triethylsilyl)-1H-indene-2-carbaldehyde (9b)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 91% yield (79 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.09 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.09 (s, 1H), 6.89 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 2H), 1.0 (s, 15H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.5, 160.4, 160.2, 154.6, 147.3, 140.9, 126.2, 113.4, 109.7, 55.5, 38.5, 7.5, 5.2 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₁₇H₂₅O₂Si 289.1618, found 289.1618.

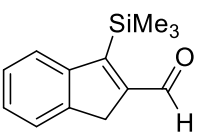
6-methoxy-3-(triisopropylsilyl)-1H-indene-2-carbaldehyde (9c)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 23% yield (23 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.10 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.08 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H), 3.76 (s, 2H), 1.68 – 1.59 (m, 3H), 1.15 (d, *J* = 7.5 Hz, 18H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 190.3, 160.2, 158.2, 155.1, 147.4, 127.1, 113.4, 109.3, 55.5, 39.0, 19.0, 13.4 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₂₀H₃₁O₂Si 331.2088, found 331.2089.

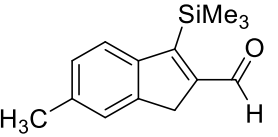
6-methoxy-3-(*tert*-butyldimethylsilyl)-1H-indene-2-carbaldehyde (9d)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 78% yield (67 mg). MP = 106.7 – 108.2 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.12 (s, 1H), 7.64 (d, *J* = 8.6 Hz, 1H), 7.08 (s, 1H), 6.88 (dd, *J* = 2.5 and 8.6 Hz, 1H), 3.85 (s, 3H), 3.72 (s, 2H), 0.98 (s, 9H), 0.50 (s, 6H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.7, 160.3, 154.5, 147.2, 141.4, 127.1, 113.3, 109.5, 55.5, 38.6, 26.8, 17.3, -1.3 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₁₇H₂₅O₂Si 289.1618, found 289.1617.

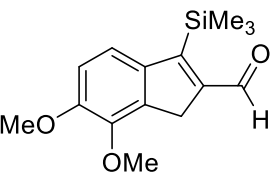
3-(trimethylsilyl)-1H-indene-2-carbaldehyde (9e)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a white solid in 48% yield (31 mg). MP = 123.4 – 125.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 10.25 (s, 1H), 7.78 – 7.72 (m, 1H), 7.56 (s, 1H), 7.40 – 7.33 (m, 2H), 3.72 (s, 2H), 0.51 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 162.0, 154.7, 147.4, 144.7, 128.2, 126.7, 125.4, 124.6, 38.4, 1.4 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₁₃H₁₇OSi 217.1043, found 217.1041.

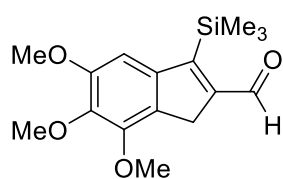
6-methyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (9f)

 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 80% yield (55 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.22 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 2H), 2.43 (s, 3H), 0.50 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.7, 162.2, 153.9, 145.1, 144.9, 138.6, 127.7, 125.4, 125.1, 38.1, 21.7, 1.3 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₁₄H₁₉OSi 231.1200, found 231.1195.

6,7-dimethoxy-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (9g)

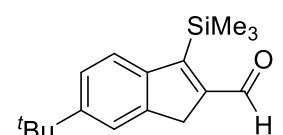
 Prepared according to the General Procedure using acrolein. Purification by flash chromatography (10% EtOAc/hexanes) afforded the title compound as a colorless oil in 87% yield (72 mg). ¹H NMR (400 MHz, CDCl₃) δ 10.17 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.76 (s, 2H), 0.48 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.2, 162.0, 153.3, 152.8, 145.3, 142.0, 136.8, 121.2, 111.5, 60.0, 56.2, 36.0, 1.4 ppm; HRMS (*m/z*) [*M*+H]⁺ Calcd. for C₁₅H₂₁O₃Si 277.1254, found 277.1254.

5,6,7-trimethoxy-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9h)



Prepared according to the General Procedure using acrolein. Purification by flash chromatography (20% EtOAc/hexanes) afforded the title compound as a colorless oil in 92% yield (85 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.18 (s, 1H), 7.05 (s, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 3.90 (s, 3H), 3.71 (s, 2H), 0.50 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.0, 161.7, 154.8, 153.3, 149.5, 143.3, 142.5, 129.2, 104.6, 61.2, 60.2, 56.3, 36.3, 1.4 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₆H₂₃O₄Si 307.1360, found 307.1361.

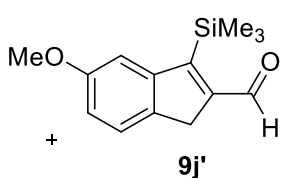
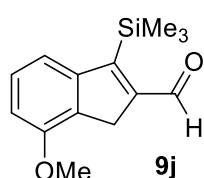
6-*tert*-butyl-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9i)



Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 85% yield (69 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.23 (s, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.60 (s, 1H), 7.41 (dd, *J* = 1.7 and 8.2 Hz, 1H), 3.72 (s, 2H), 1.37 (s, 9H), 0.50 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.7, 162.2, 154.3, 151.9, 144.9, 144.8, 124.9, 124.0, 121.6, 38.4, 35.0, 31.4, 1.4 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₇H₂₅O₂Si 273.1669, found 273.1670.

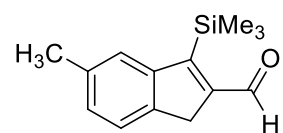
7-methoxy-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9j)

5-methoxy-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9j')



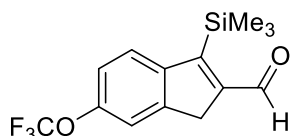
Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 81% yield (60 mg, **9j/9j'** 3:1). ¹H NMR (500 MHz, CDCl₃) **9j** = δ 10.24 (s, 0.75H), 7.37 (dt, *J* = 0.9 and 7.7 Hz, 0.75H), 7.33 (t, *J* = 7.8 Hz, 0.75H), 3.90 (s, 2.25H), 3.67 (s, 1.5H), 0.49 (s, 6.75H) ppm; **9j'** = δ 10.23 (s, 0.25H), 7.45 (d, *J* = 8.3 Hz, 0.25H), 7.27 (d, *J* = 2.3 Hz, 0.25H), 3.85 (s, 0.75H), 3.66 (s, 0.5H), 0.51 (s, 2.25H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.7, 161.8, 155.9, 155.0, 149.0, 132.1, 128.3, 124.9, 118.1, 114.2, 110.8, 110.0, 55.4, 37.6, 36.0, 1.4 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₉O₂Si 247.1149, found 247.1149.

5-methyl-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9k)



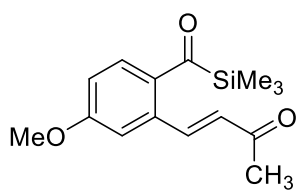
Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 43% yield (30 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.24 (s, 1H), 7.54 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 3.68 (s, 2H), 2.43 (s, 3H), 0.51 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.8, 162.1, 155.1, 147.8, 141.8, 136.3, 129.3, 125.9, 124.3, 38.0, 21.7, 1.5 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₉O₂Si 231.1200, found 231.1192.

6-trifluoromethoxy-3-(trimethylsilyl)-1*H*-indene-2-carbaldehyde (9l)



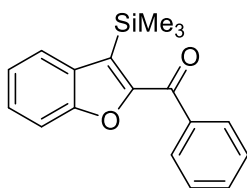
Prepared according to the General Procedure using acrolein. Purification by flash chromatography (5% EtOAc/hexanes) afforded the title compound as a colorless oil in 63% yield (57 mg). ¹H NMR (500 MHz, CDCl₃) δ 10.23 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 3.74 (s, 2H), 0.51 (s, 9H) ppm; ¹³C NMR (126 MHz, CDCl₃) δ 189.4, 160.6, 155.5, 149.3, 146.6, 146.0, 126.1, 122.2 (q, ¹*J*_{CF} = 255 Hz), 119.7, 117.4, 38.7, 1.3 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₄H₁₆F₃O₂Si 301.0866, found 301.0865.

(E)-4-(5-methoxy-2-((trimethylsilyl)carbonyl)phenyl)but-3-en-2-one (11)



To an oven dried vial containing a stirrer bar was added AgSbF₆ (10.3 mg, 10 mol%), [Ru(*p*-cymene)Cl₂]₂ (9.2 mg, 5.0 mol%), Cu(OAc)₂ (65 mg, 0.3 mmol) and 1,2-dichloroethane (1.0 mL). After stirring for 5 minutes, acyl silane **1a** (0.3 mmol, dissolved in an additional 0.5 mL 1,2-dichloroethane) and methyl vinyl ketone (0.050 mL, 0.6 mmol) were added, the vial sealed and heated at 60°C for 4 h. After this time, the reaction mixture was loaded directly onto a silica gel column and subject to flash chromatography (15% EtOAc/hexanes) to afford the title compound as a bright yellow oil in 83% yield (69 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 16.3 Hz, 1H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.03 (dd, *J* = 5.5 and 15.2 Hz, 2H), 6.45 (d, *J* = 16.2 Hz, 1H), 3.90 (s, 3H), 2.43 (s, 3H), 0.36 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 237.4, 199.2, 161.9, 144.3, 136.0, 134.6, 133.8, 130.3, 114.3, 113.8, 55.6, 26.8, -1.3 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₅H₂₁O₃Si 277.1254, found 277.1254.

1-[3-(trimethylsilyl)benzofuran-2-yl]acetophenone (13)



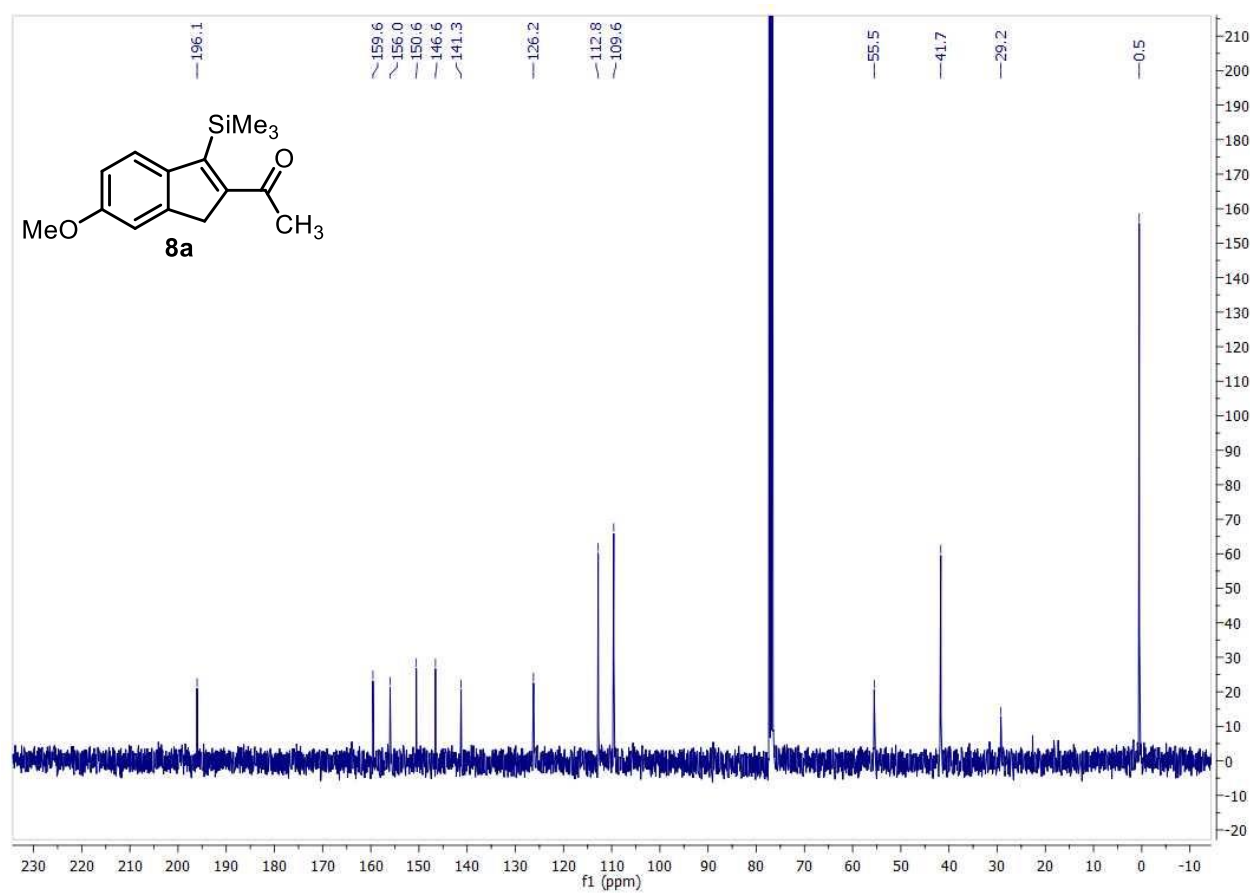
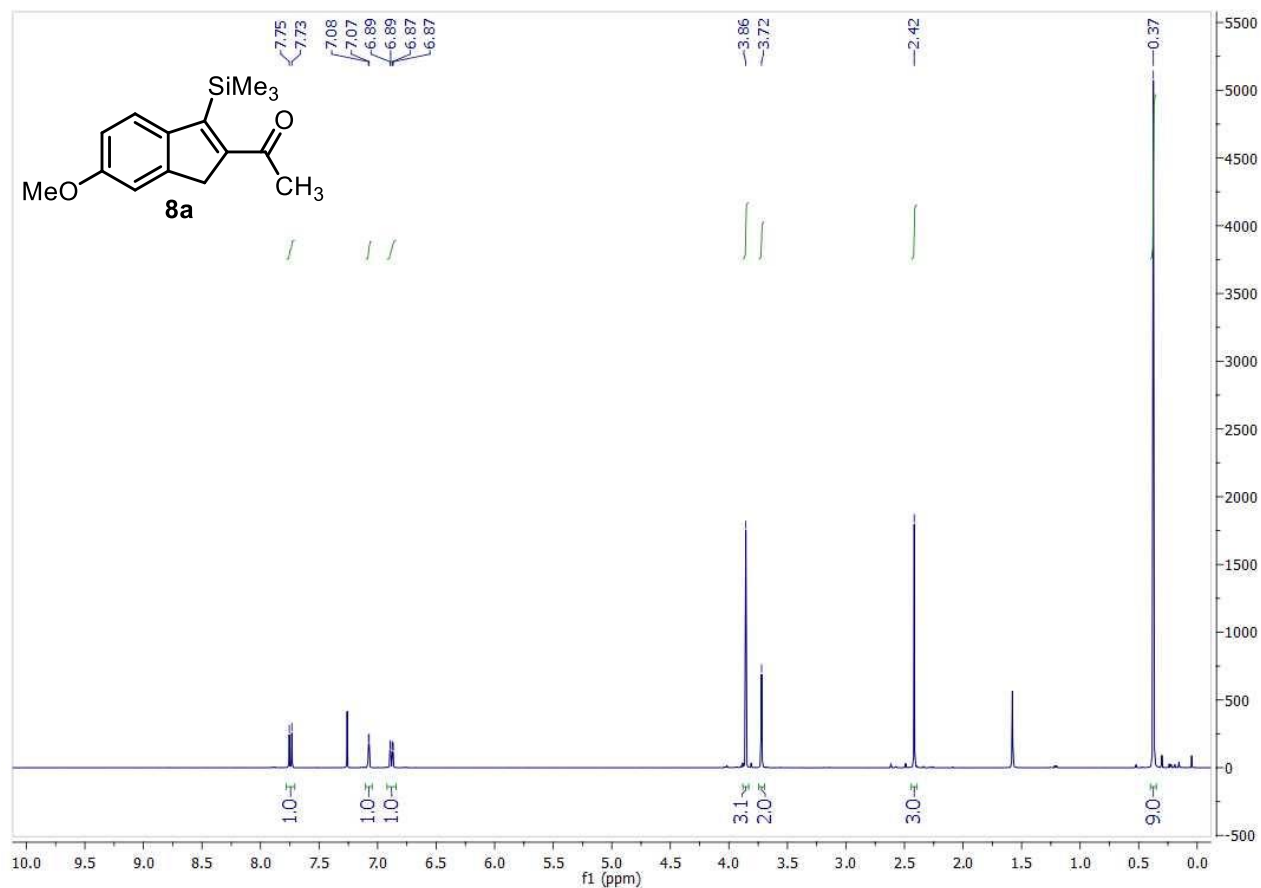
To a stirred solution of (2-hydroxybenzoyl)trimethylsilane (58 mg, 0.3 mmol), and Cs₂CO₃ (195 mg, 0.6 mmol) in acetone (10 mL) was added 2-bromoacetophenone (90 mg, 0.45 mmol) and the resultant solution stirred at room temperature for 16h. After this time, the reaction mixture was diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic fractions were washed with brine, dried over MgSO₄, filtered and the solvent removed *in vacuo*. Purification by flash chromatography (10%

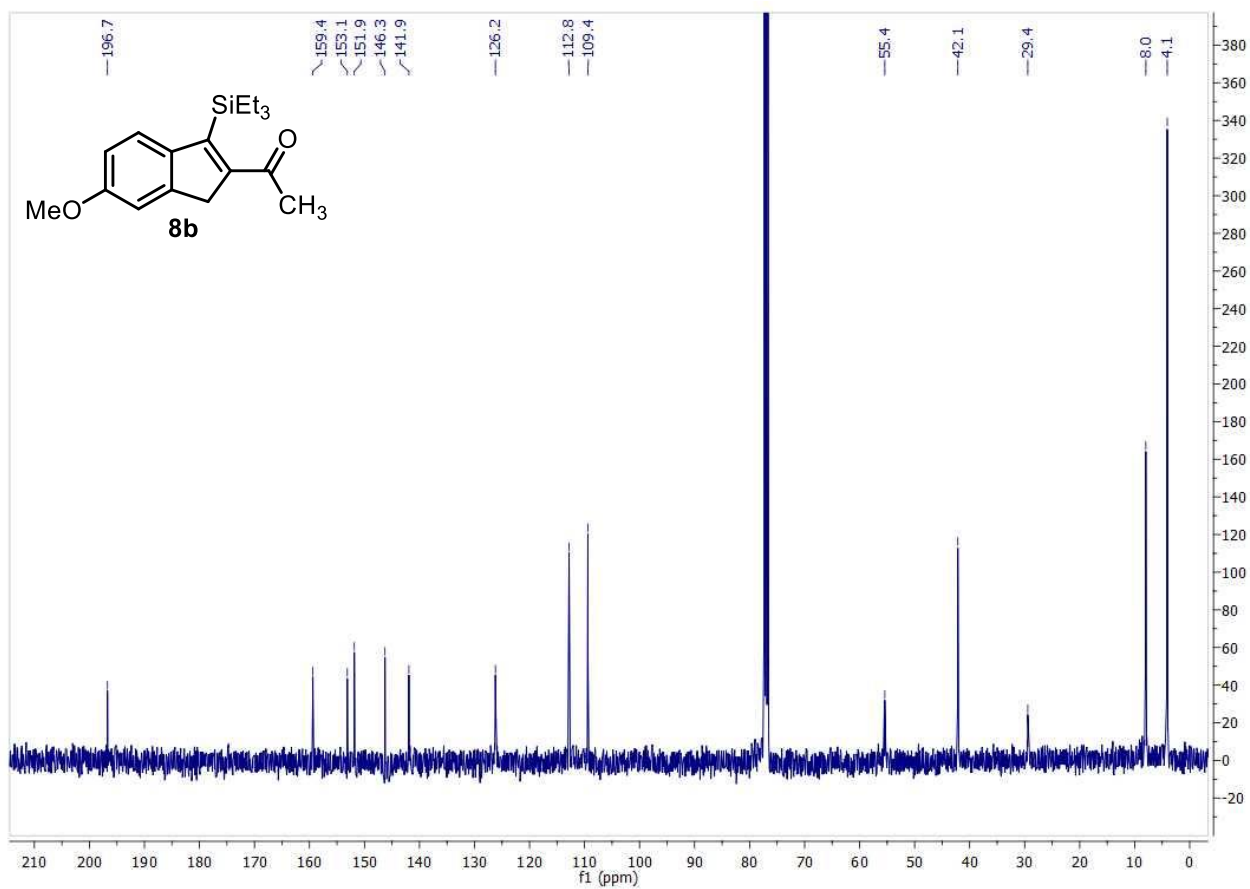
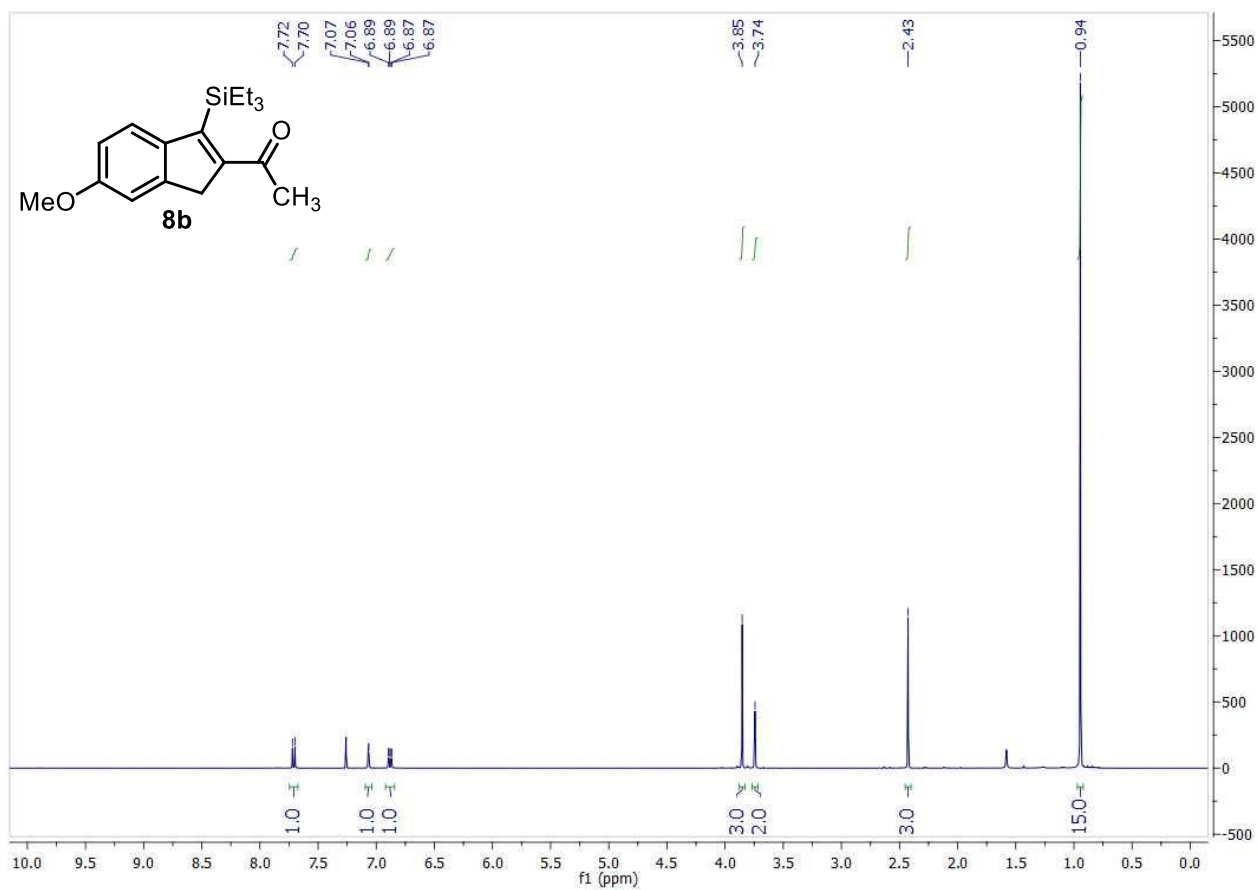
EtOAc/hexanes) afforded the title compound as a pale-yellow oil in 77% yield (68 mg). ¹H NMR (500 MHz, CDCl₃) δ 8.11 (dd, *J* = 1.3 and 8.4 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.68 – 7.50 (m, 4H), 7.46 (ddd, *J* = 1.3, 7.2, and 8.4 Hz, 1H), 7.36 – 7.28 (m, 1H), 0.50 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 185.8, 157.1, 155.3, 137.3, 132.9, 132.1, 130.1, 128.3, 127.2, 124.7, 124.5, 123.4, 112.2, 0.1 ppm; HRMS (*m/z*) [M+H]⁺ Calcd. for C₁₈H₁₉O₂Si 295.1149, found 295.1148.

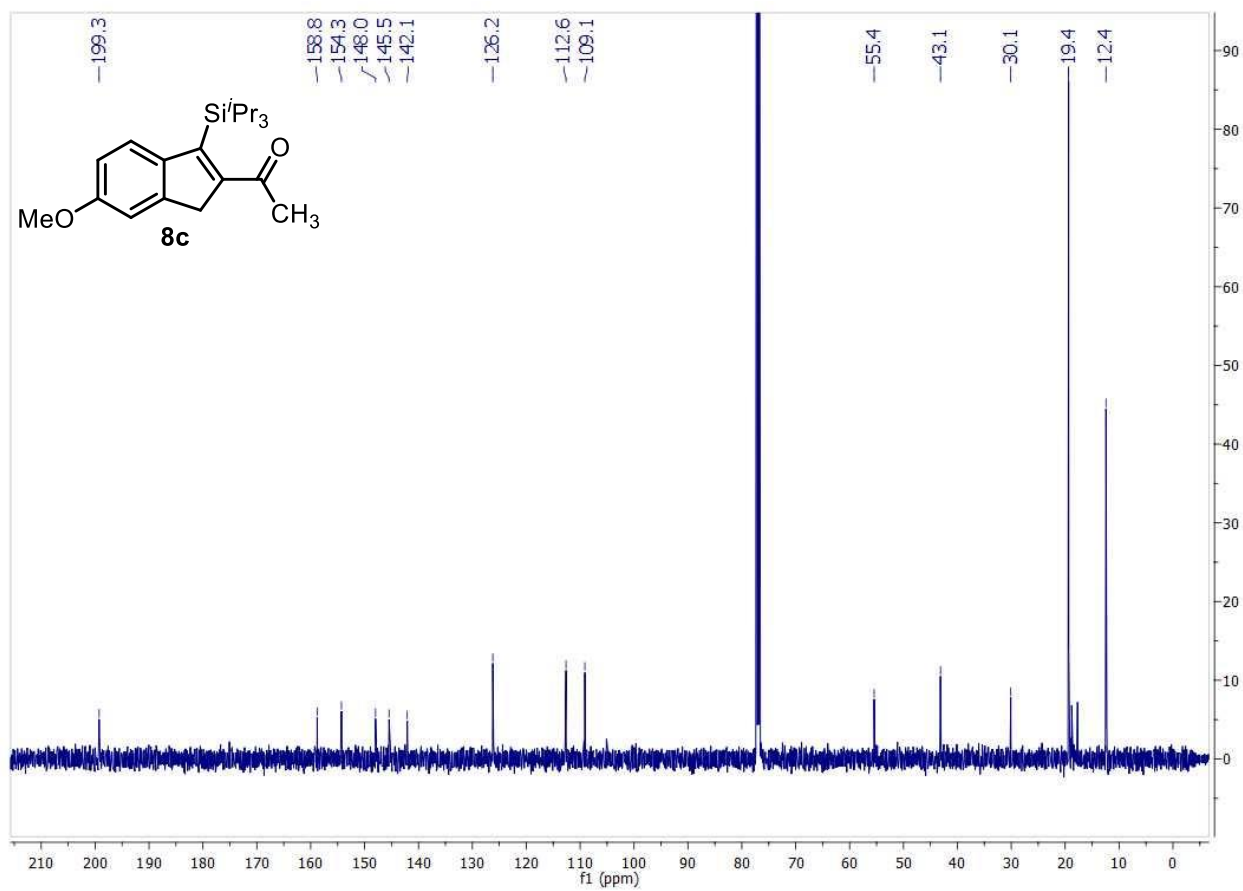
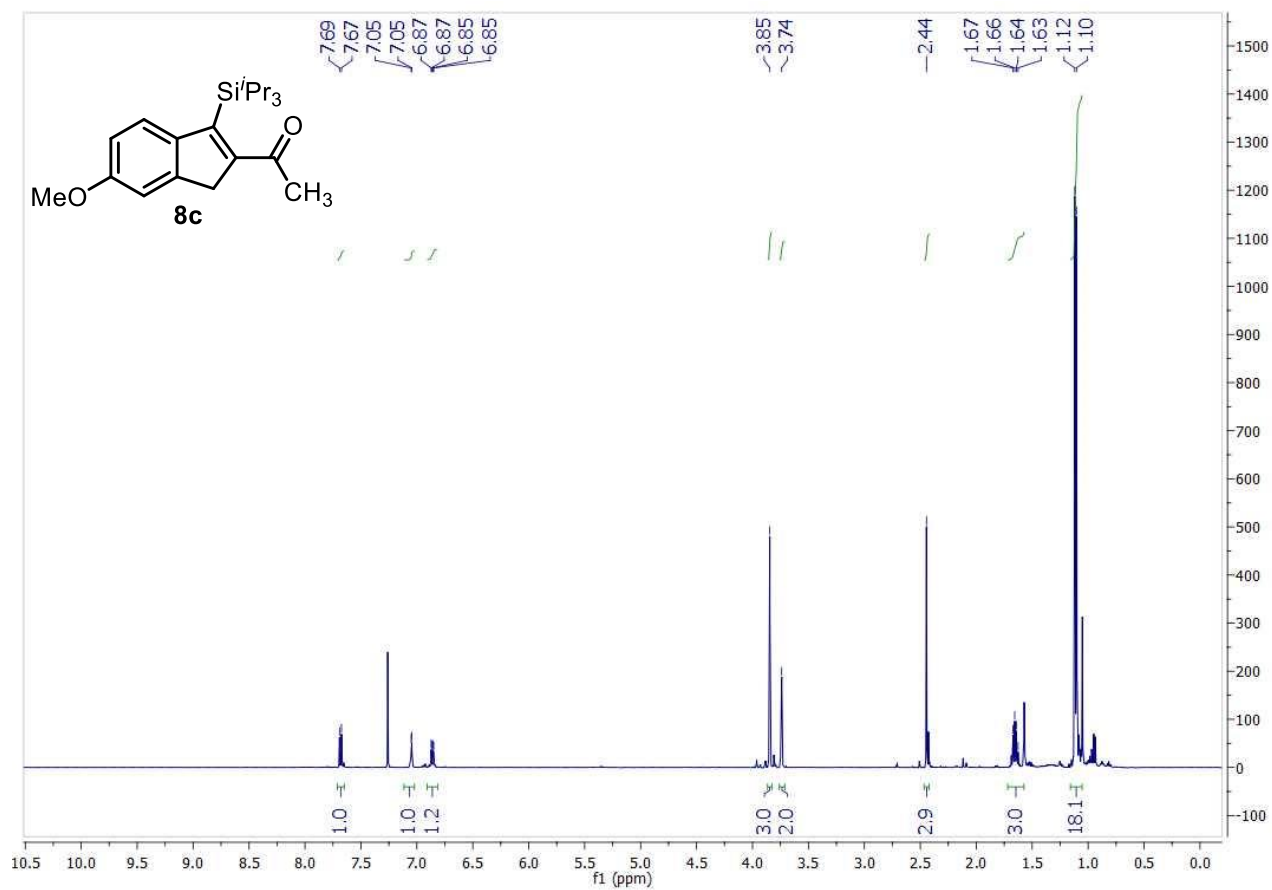
REFERENCES

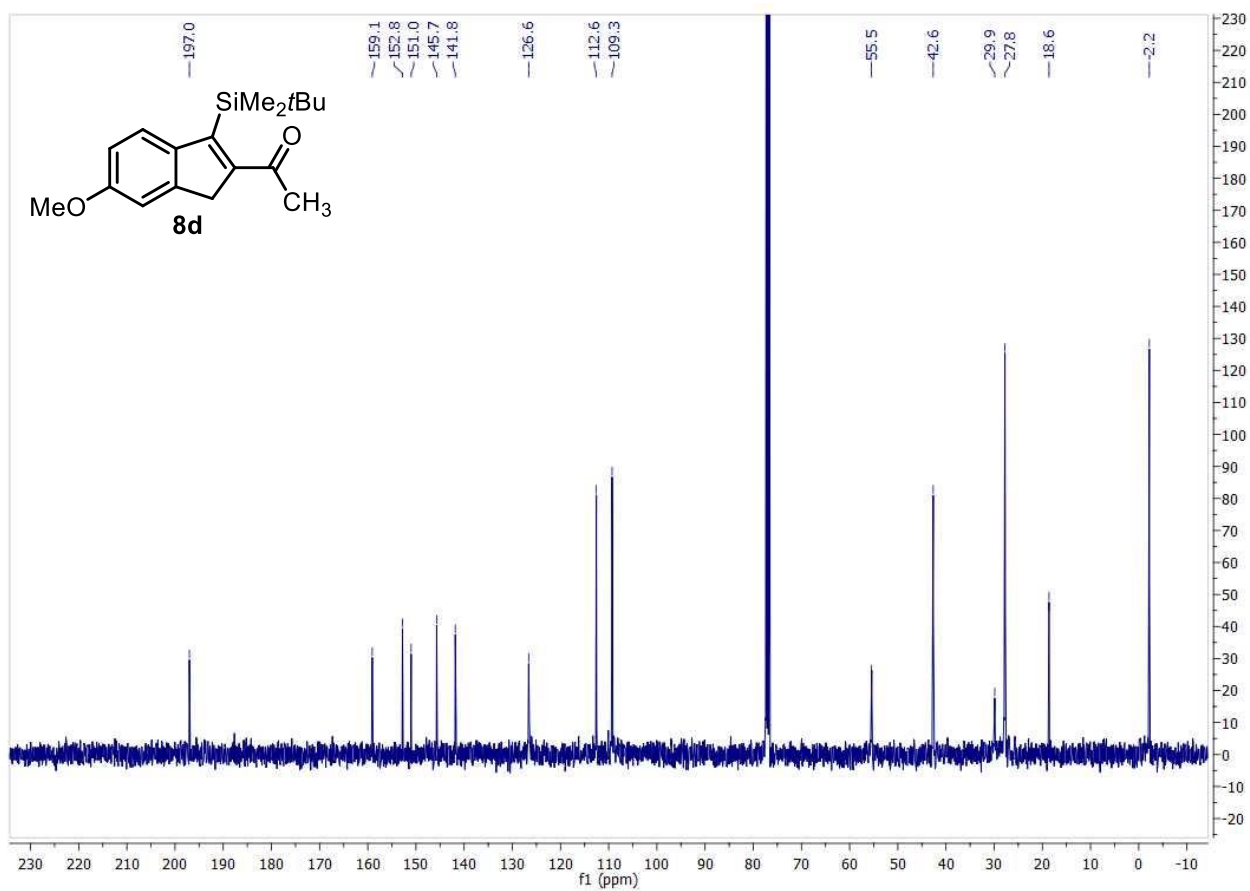
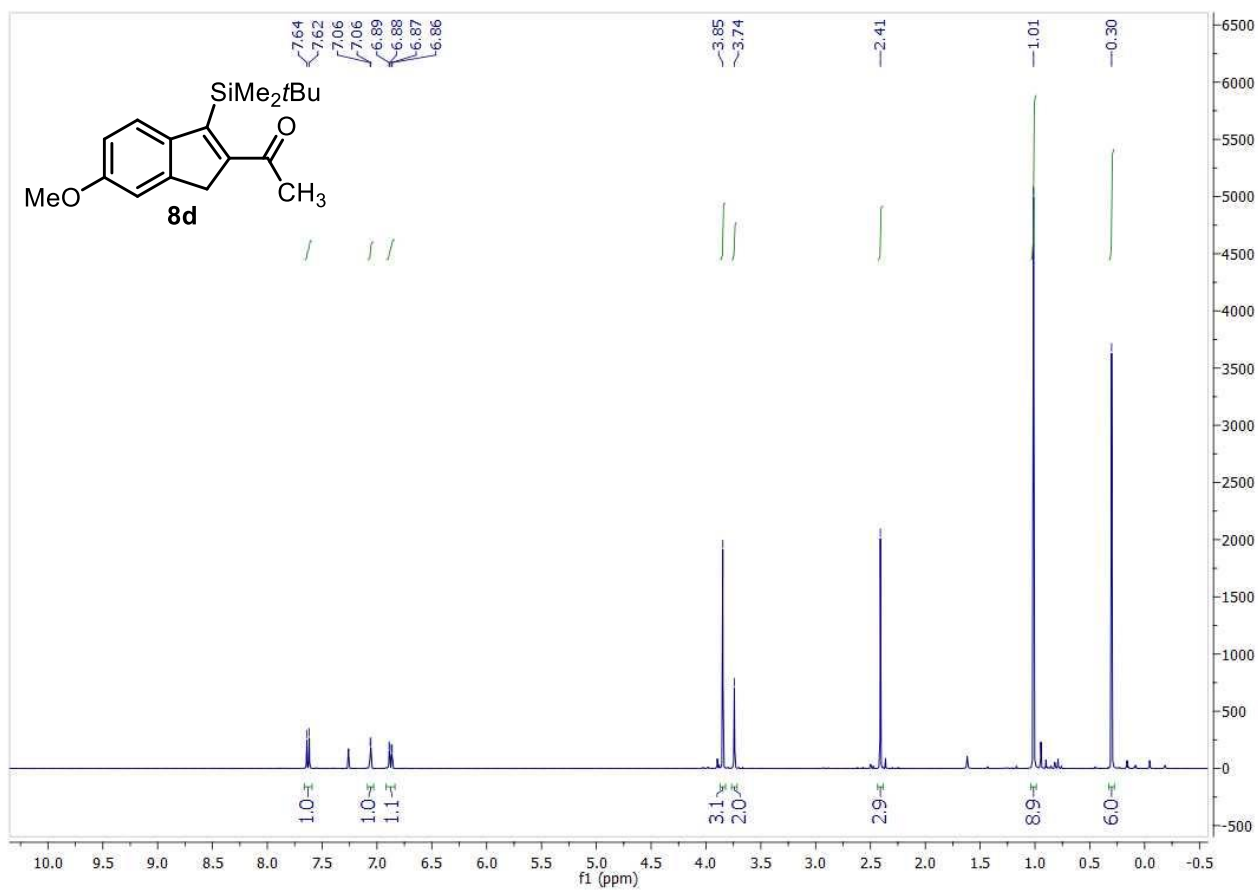
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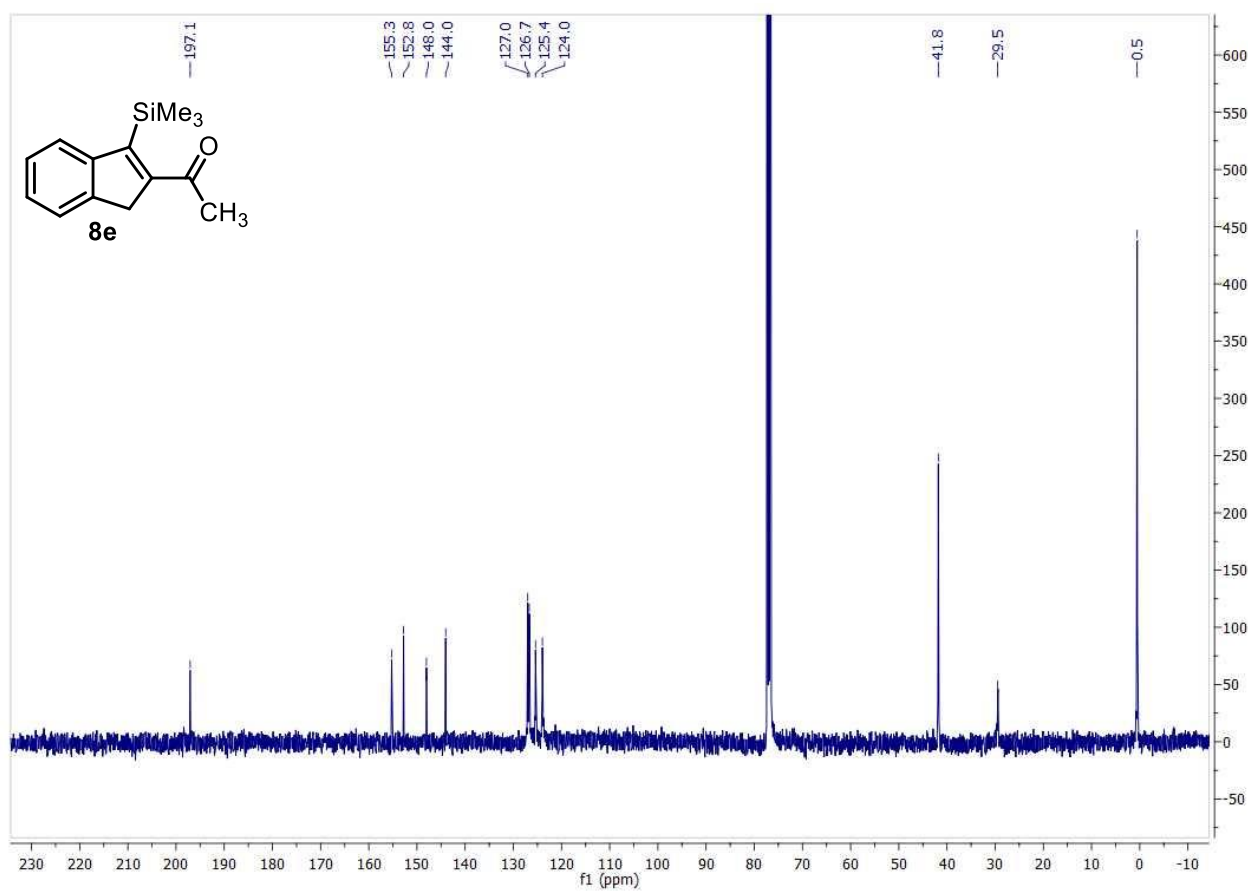
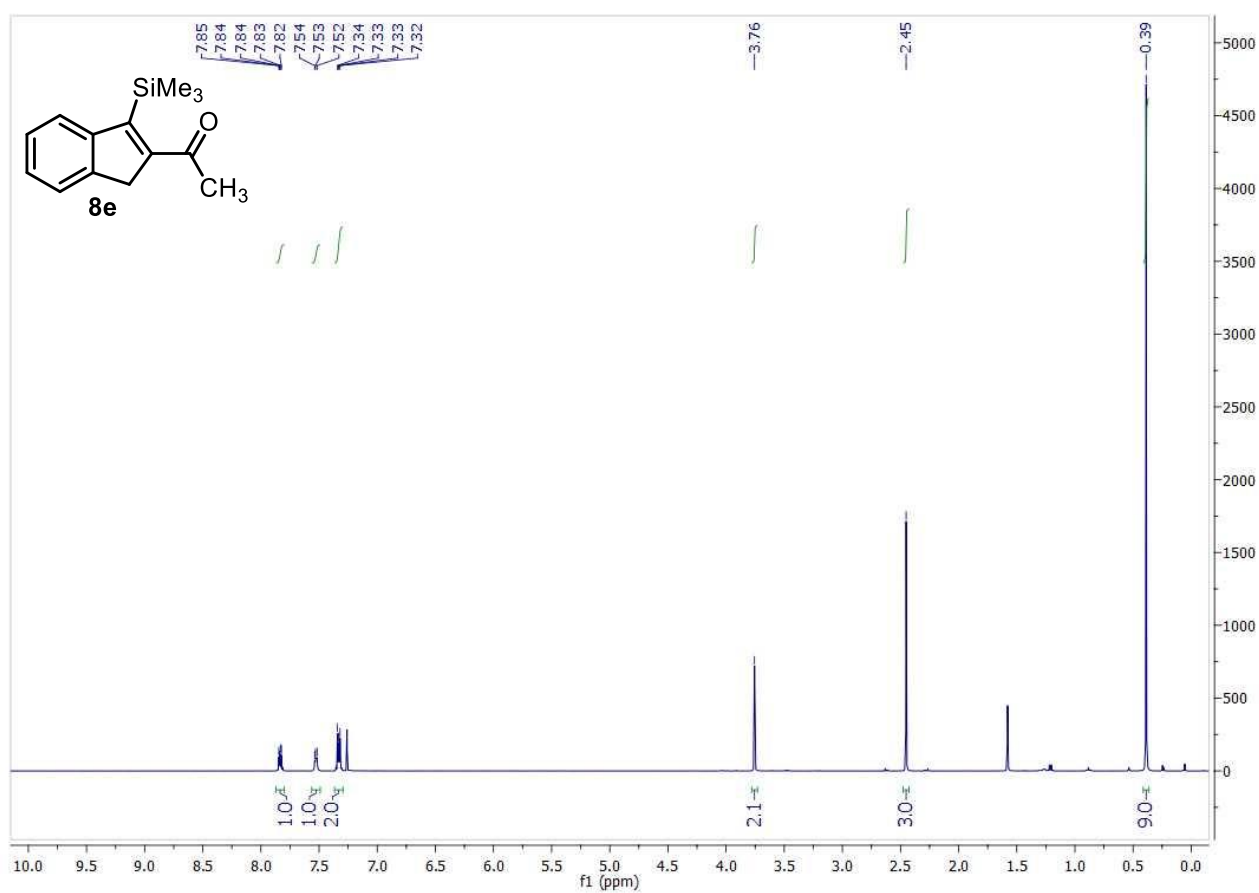
NMR Spectra

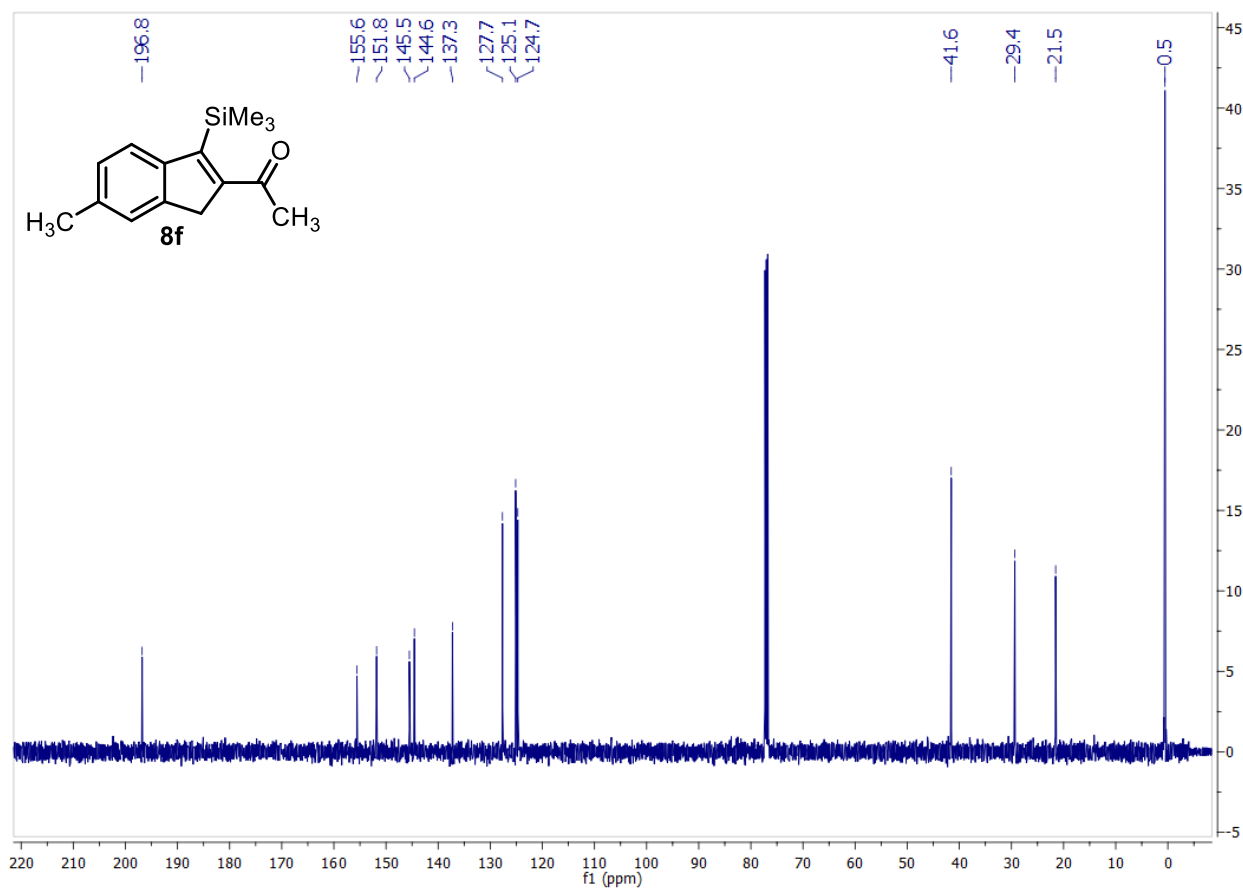
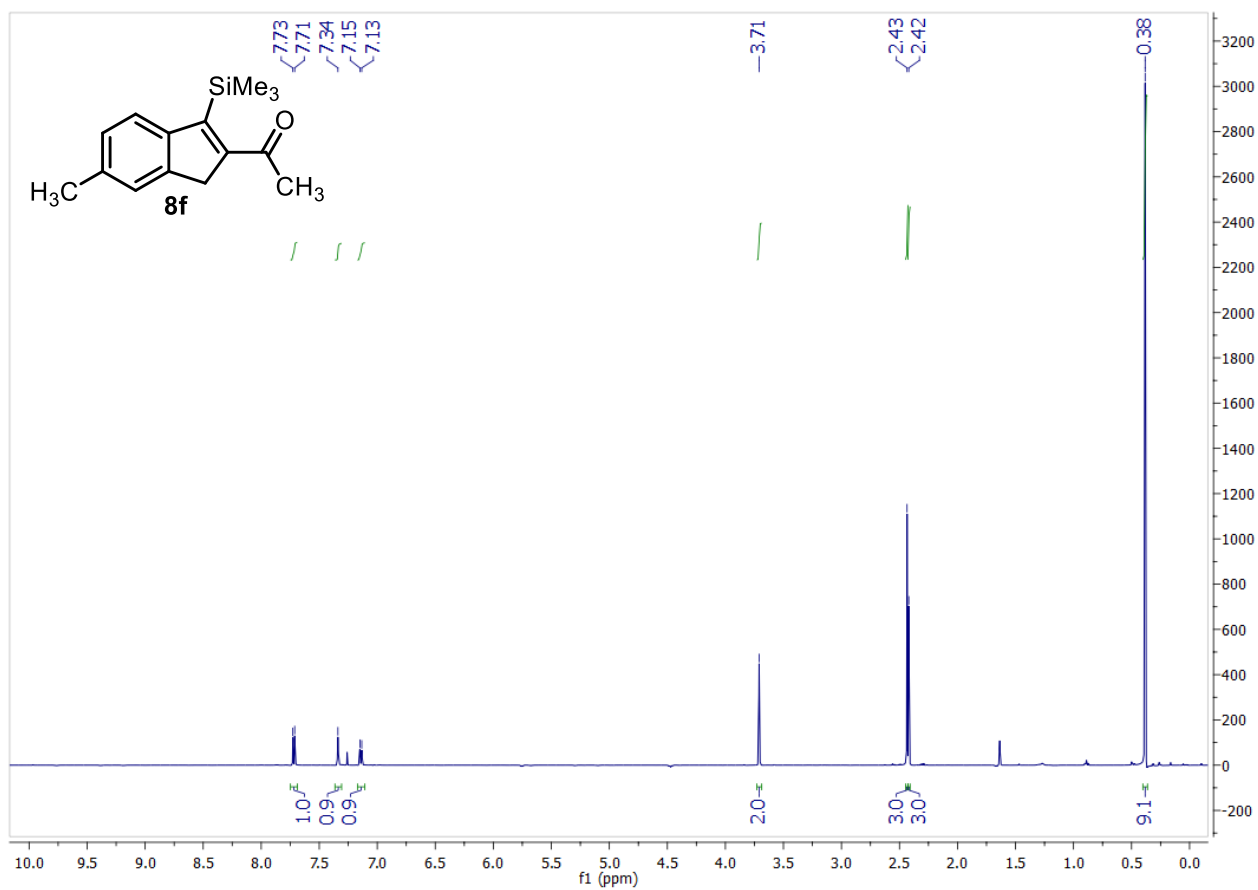


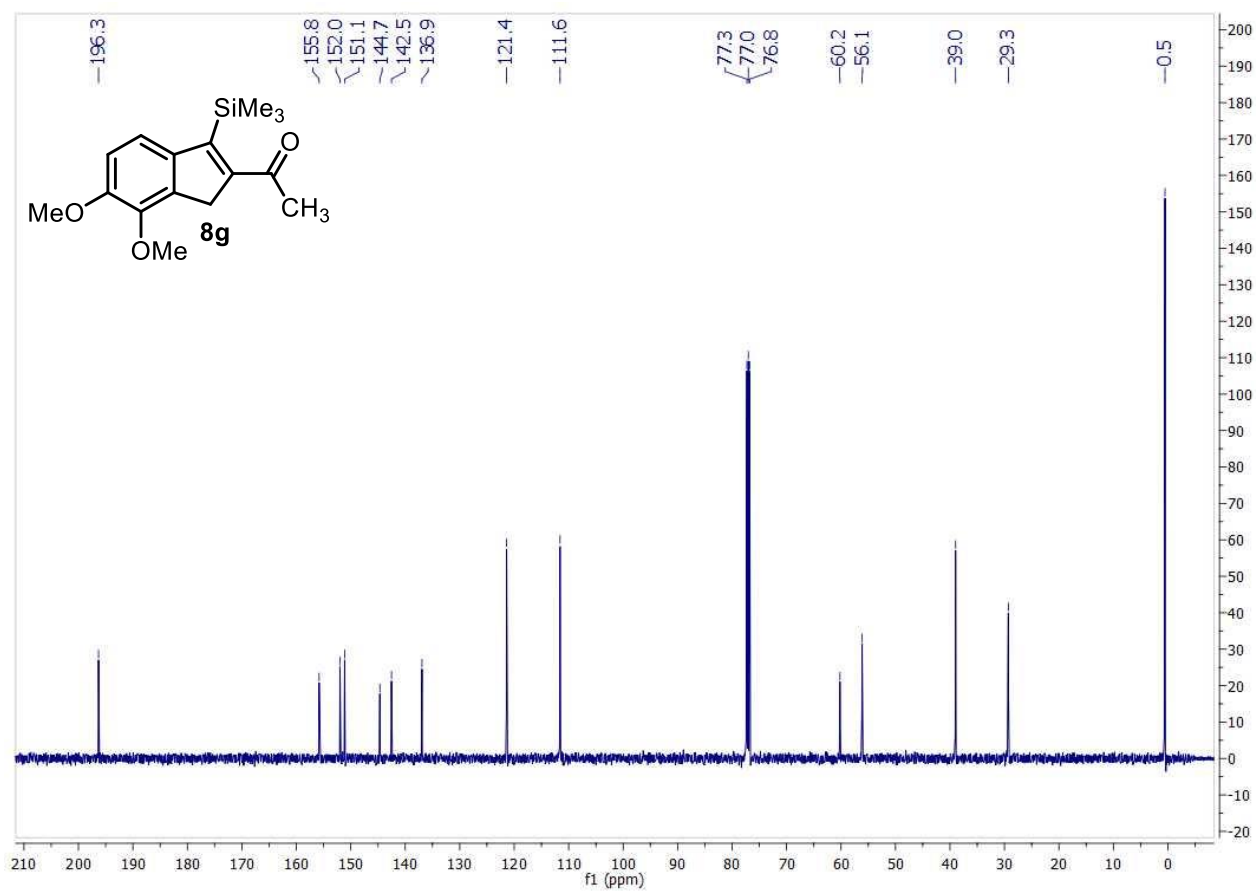
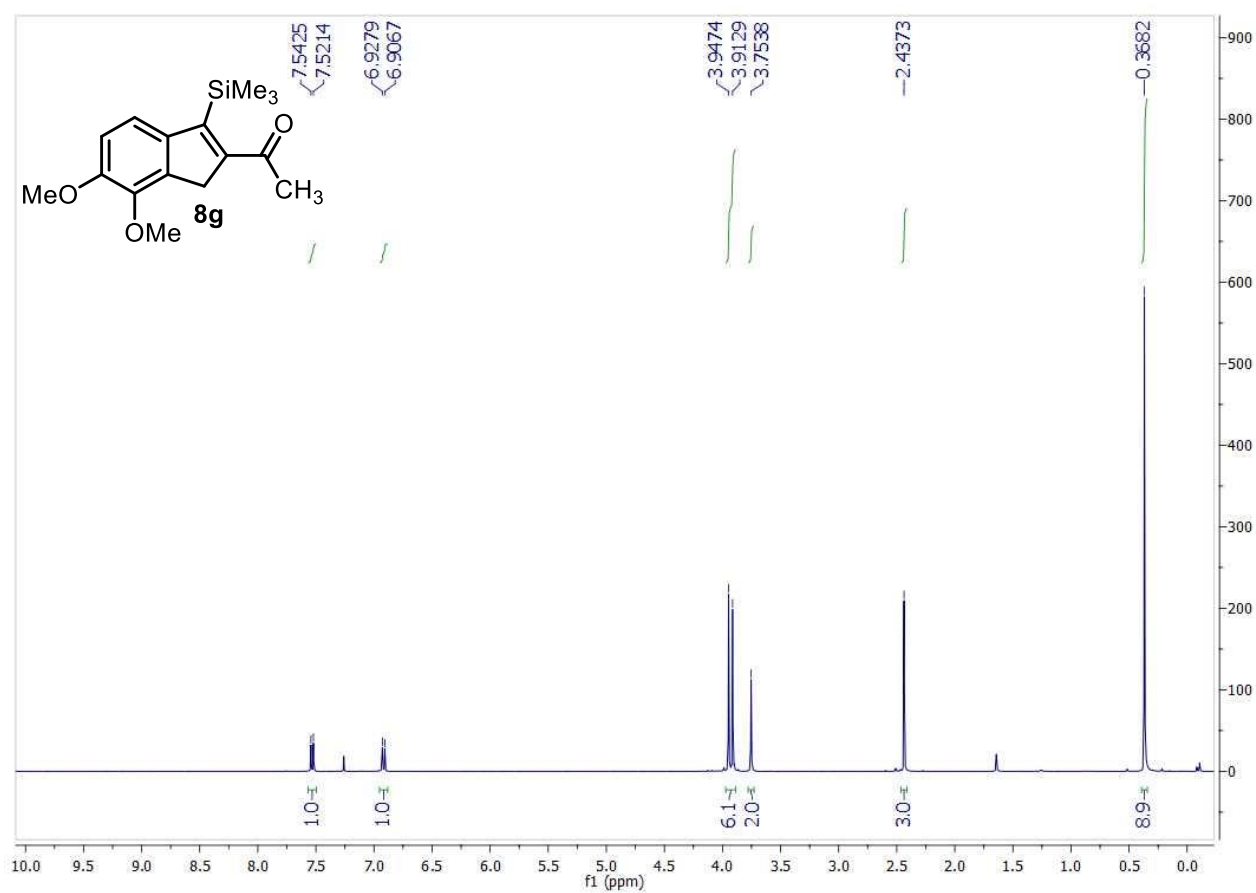


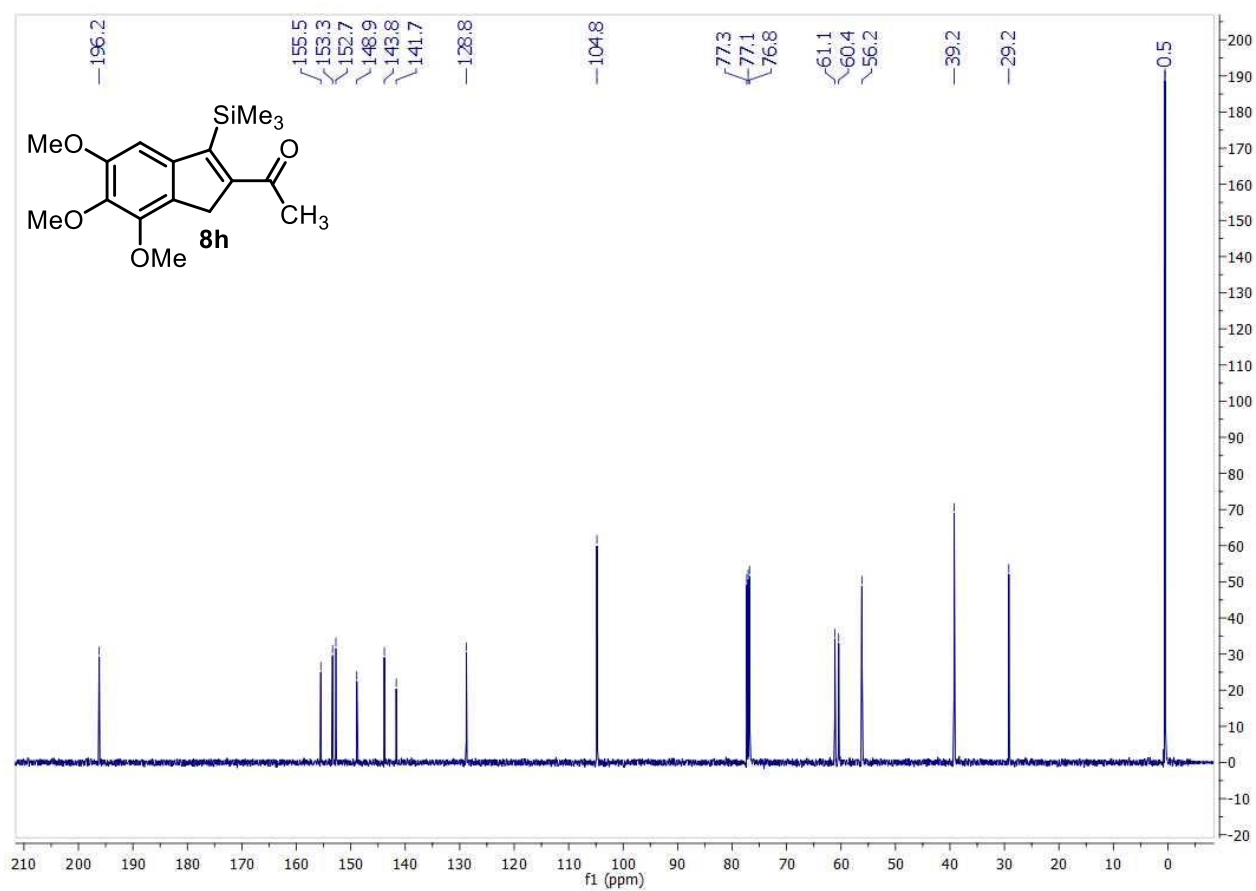
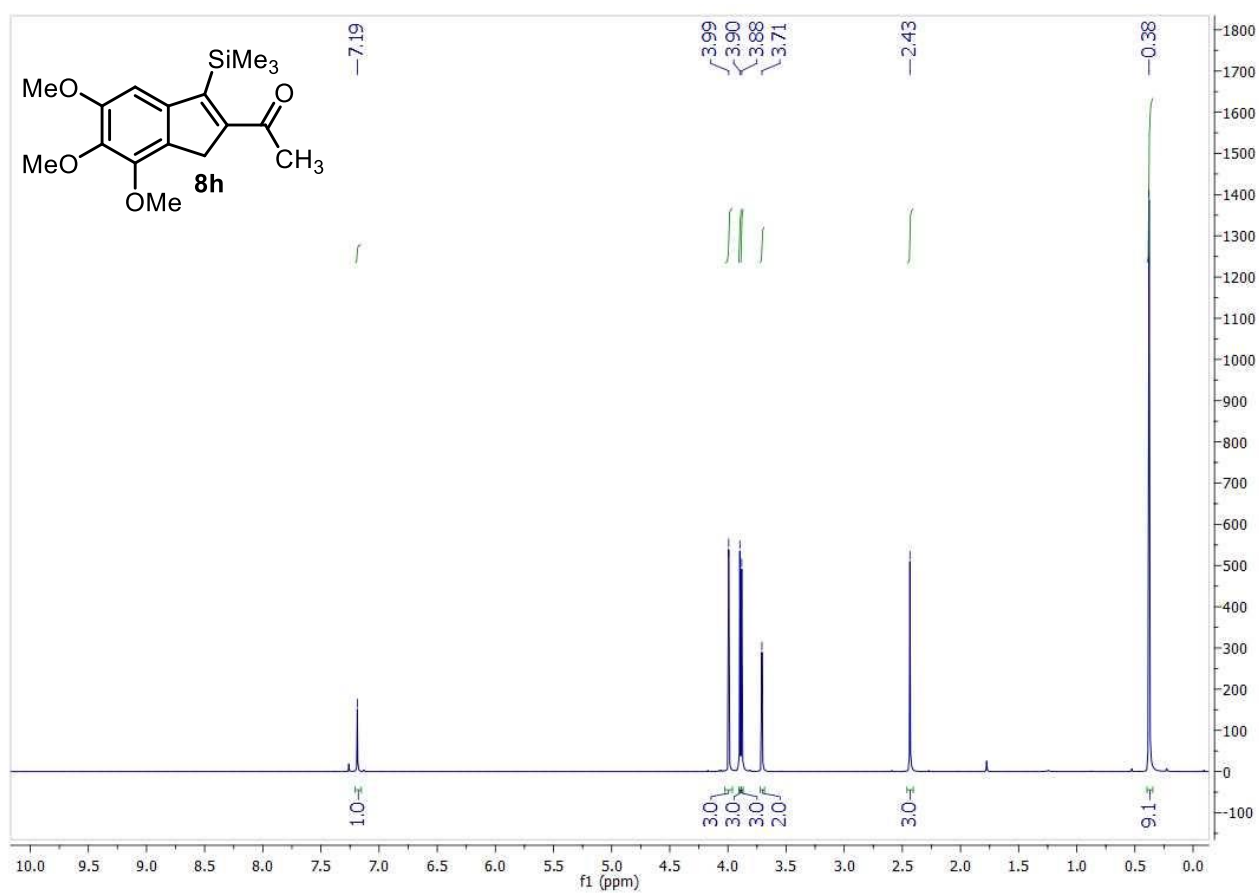


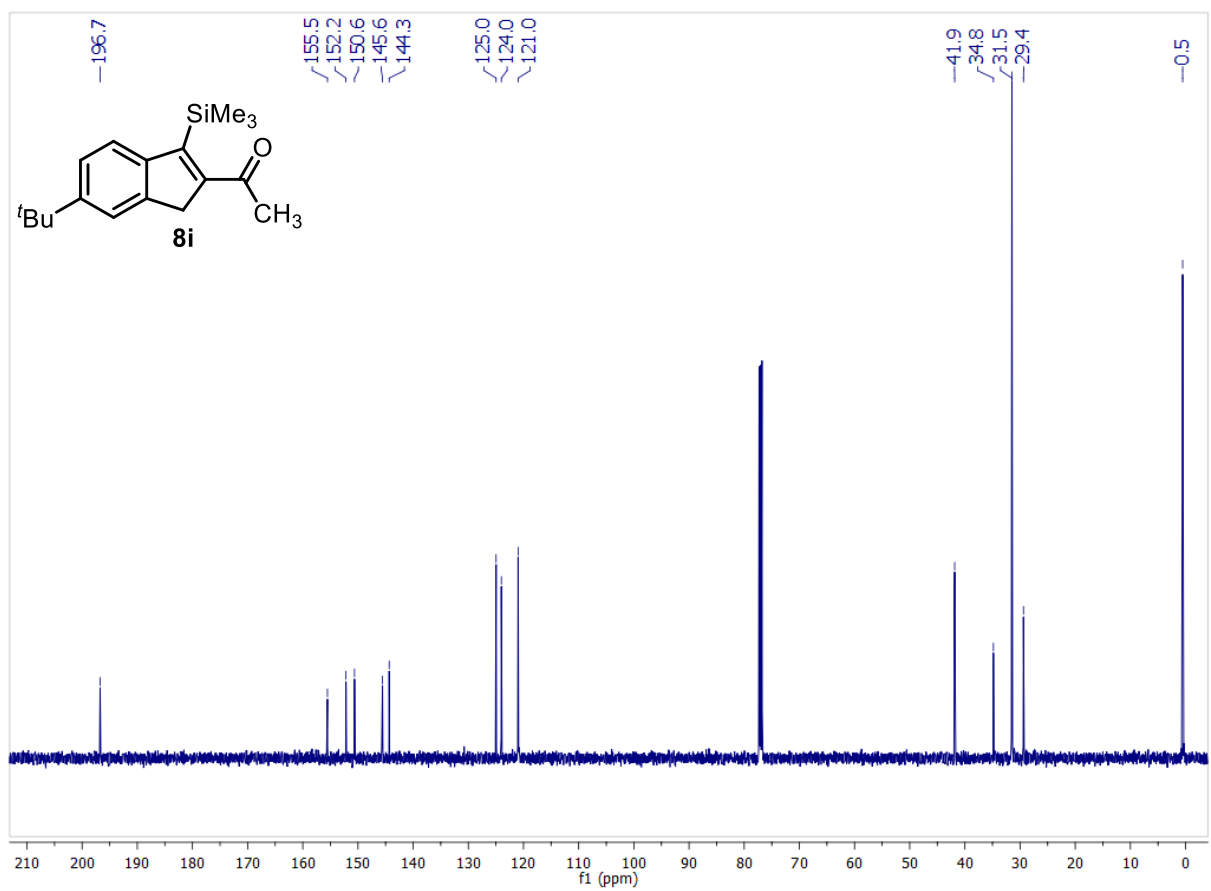
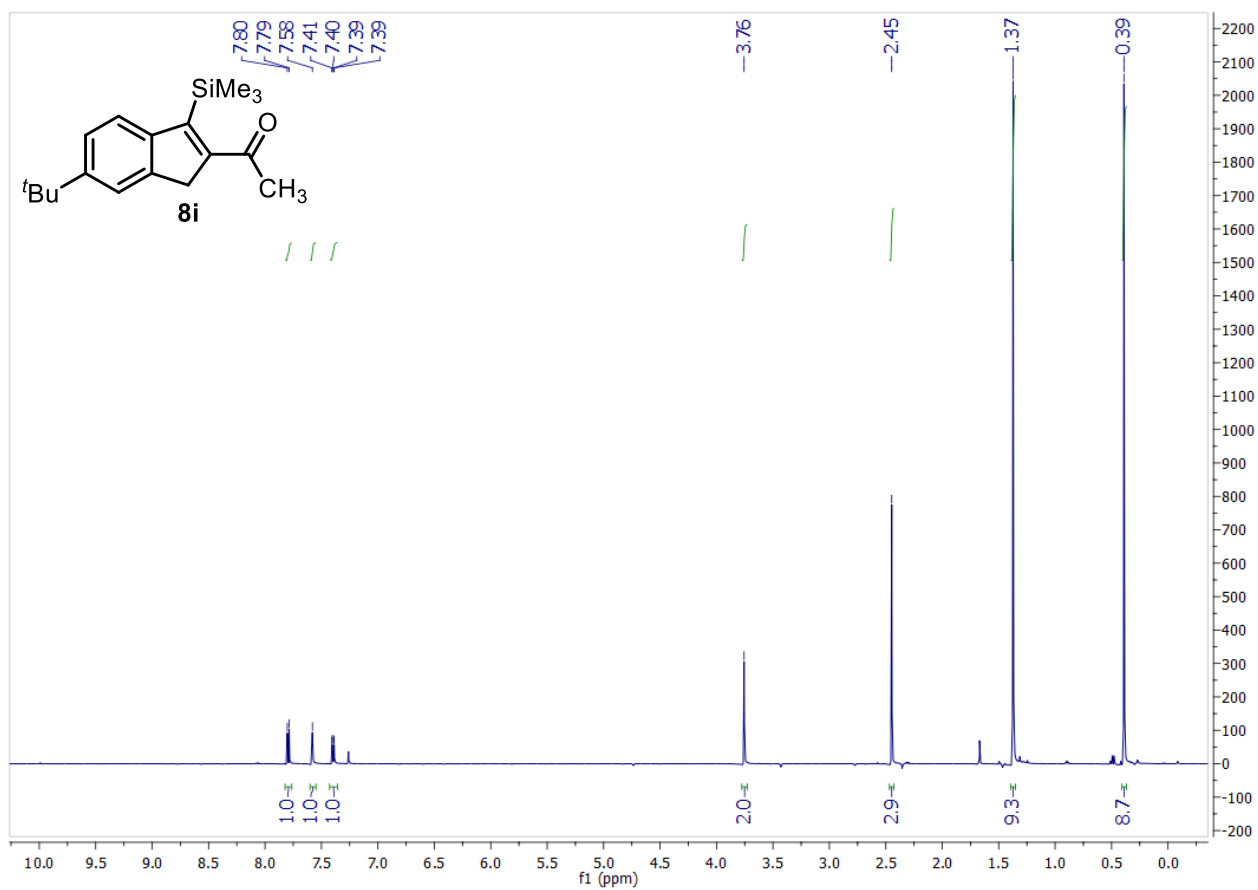


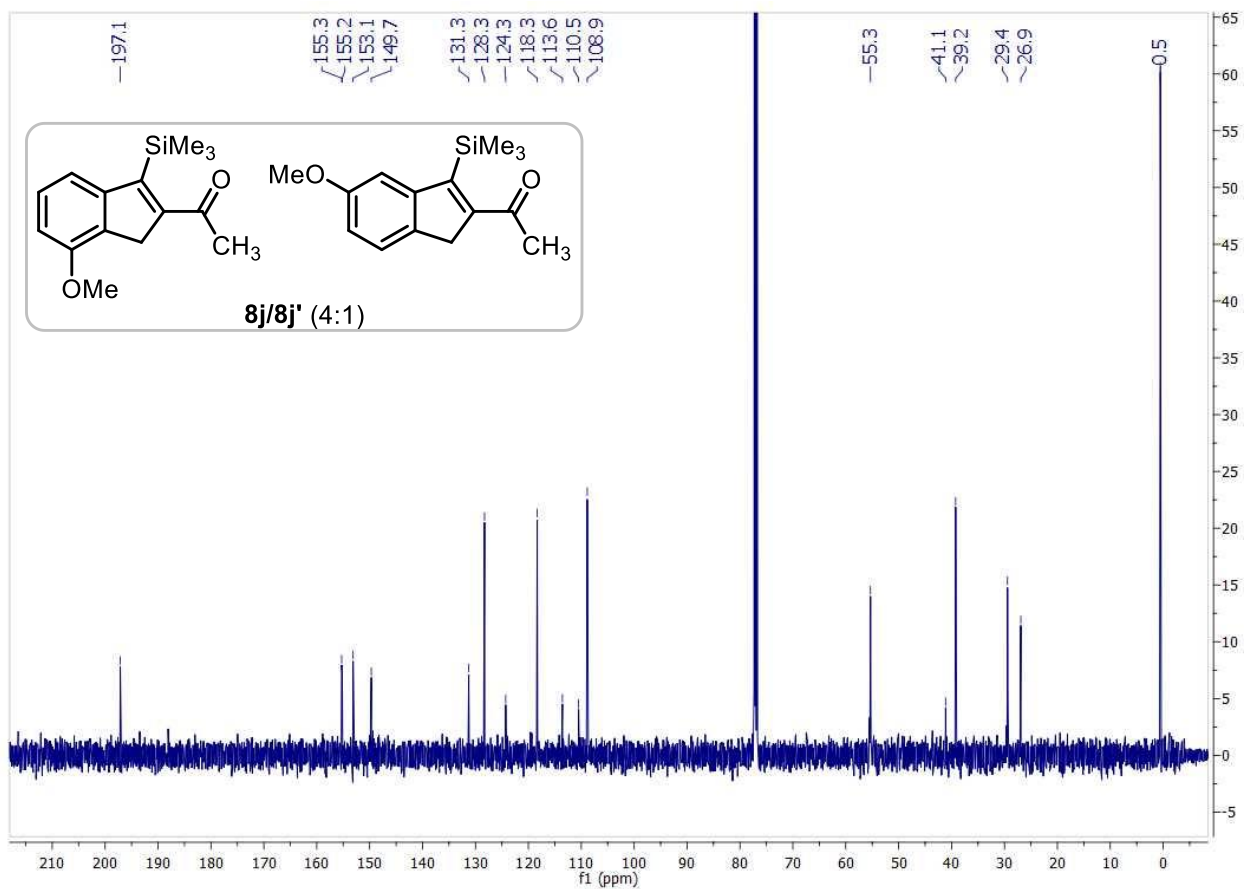
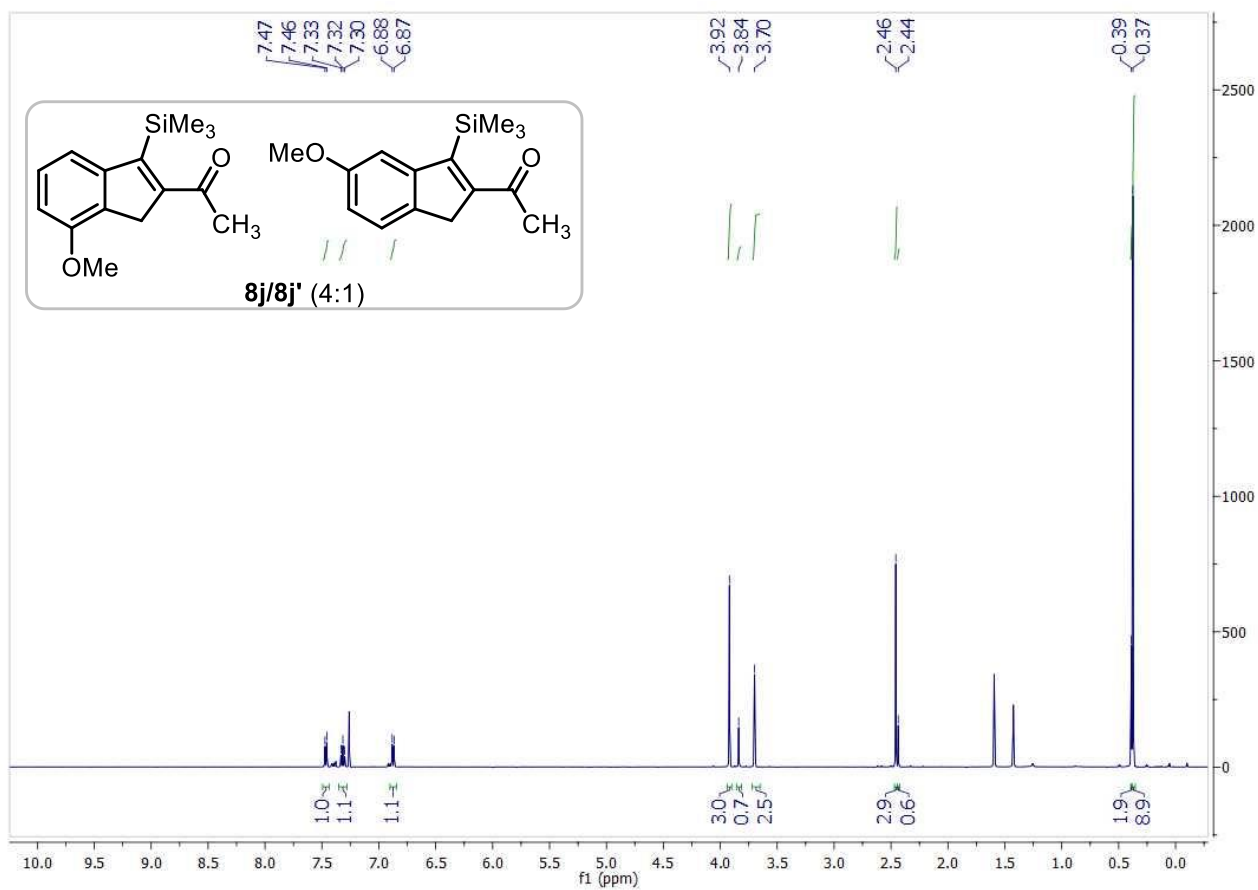


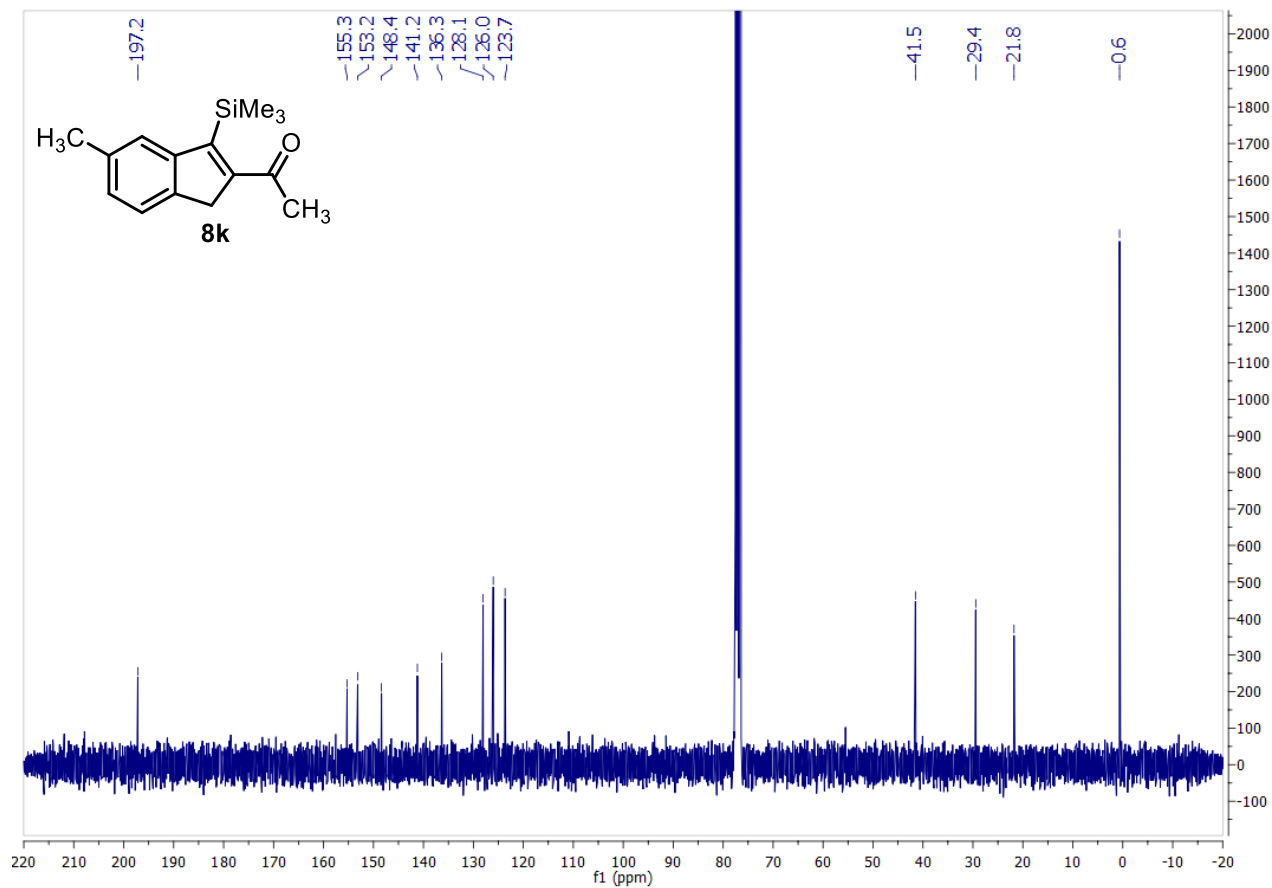
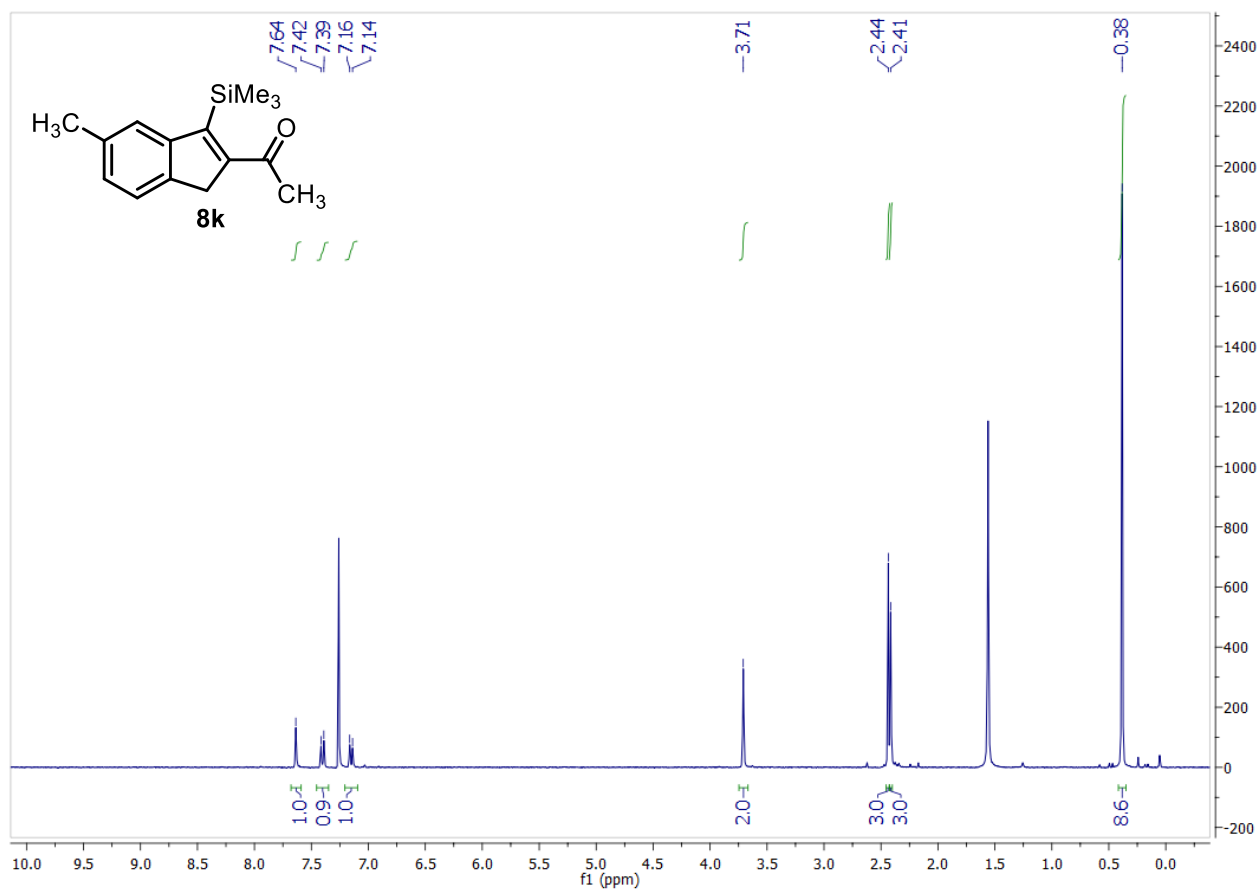


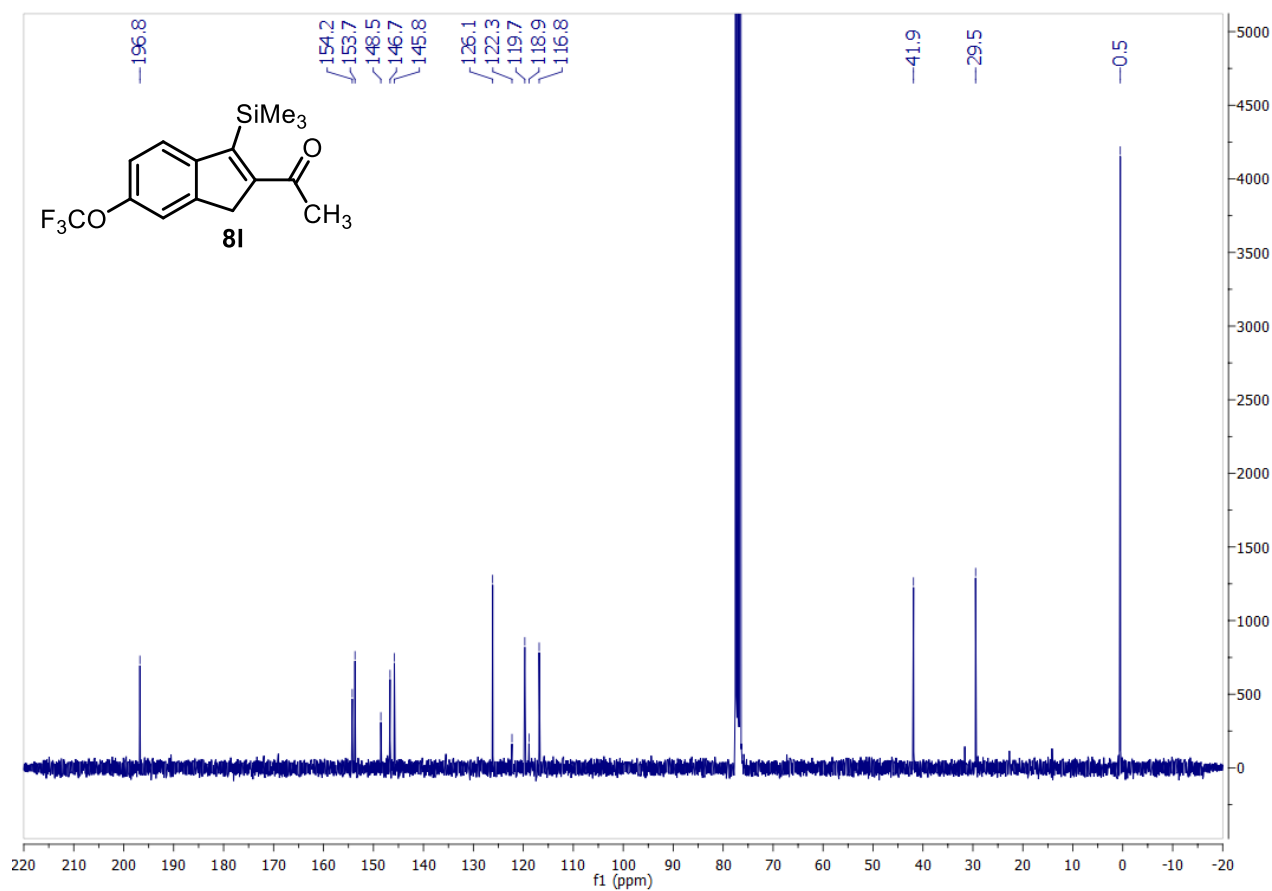
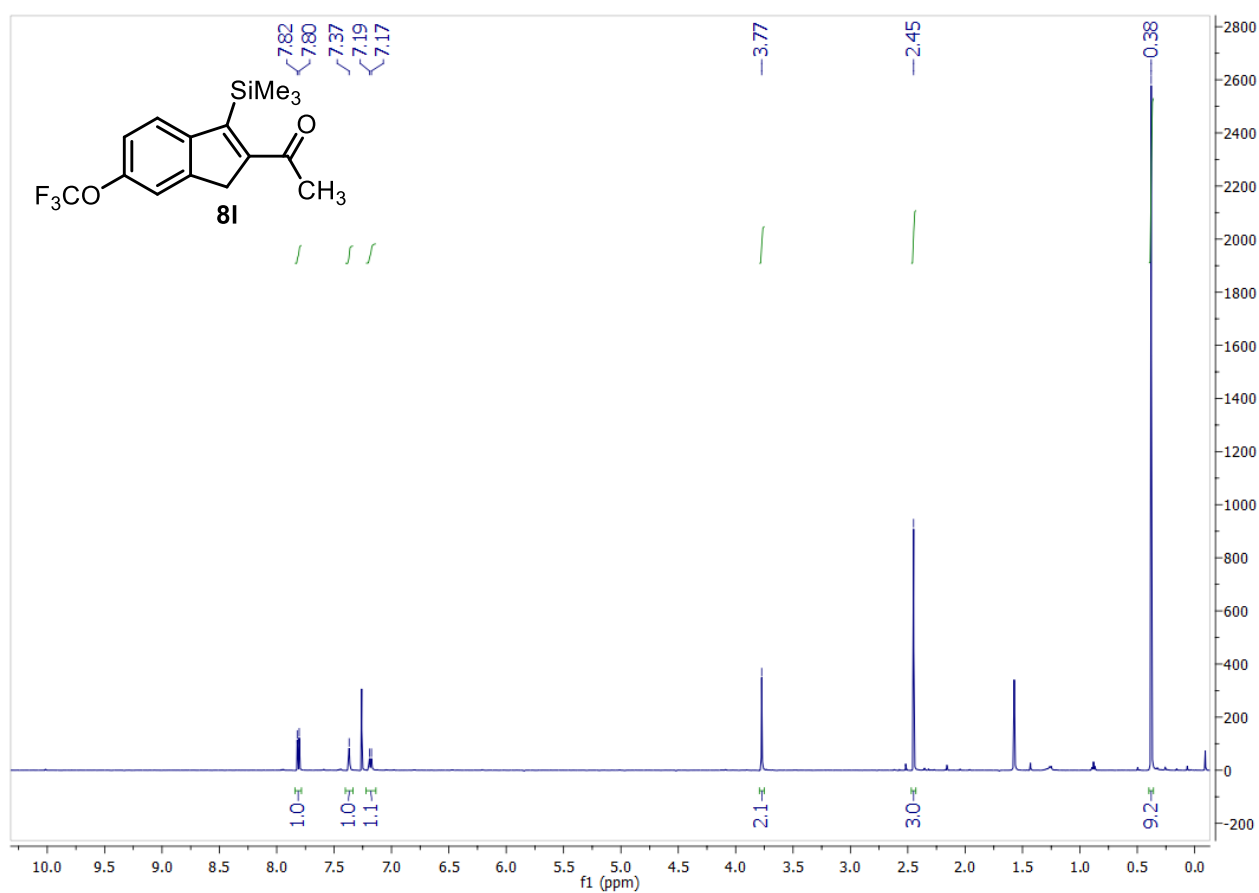


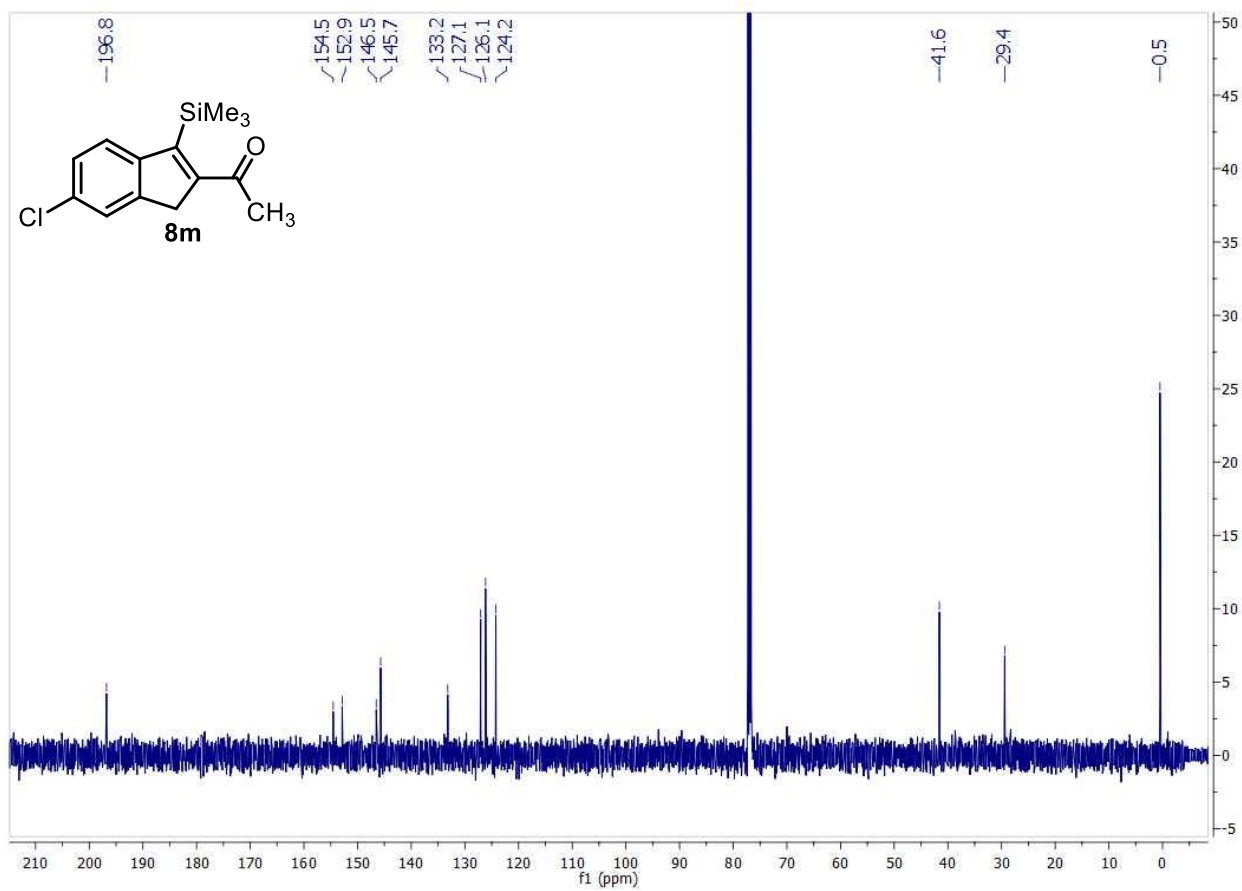
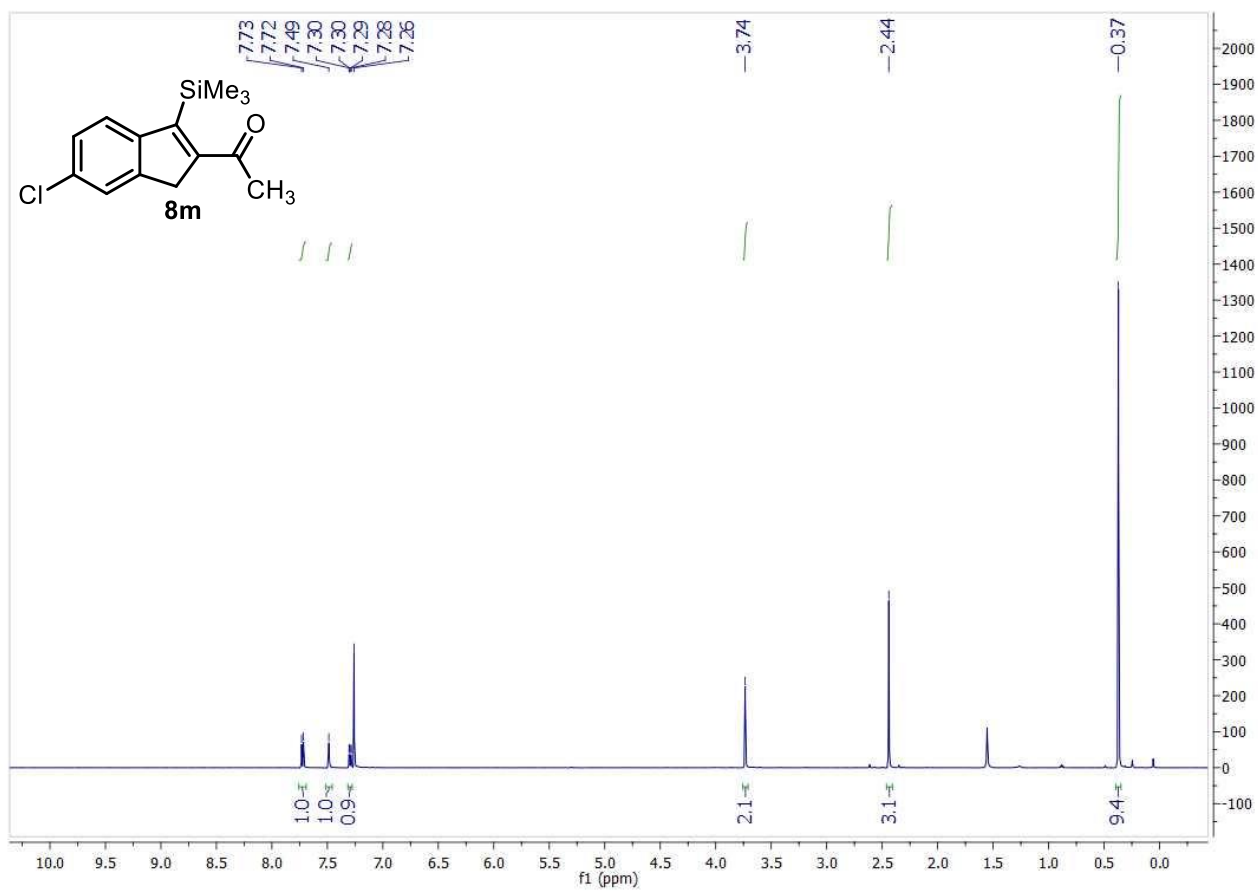


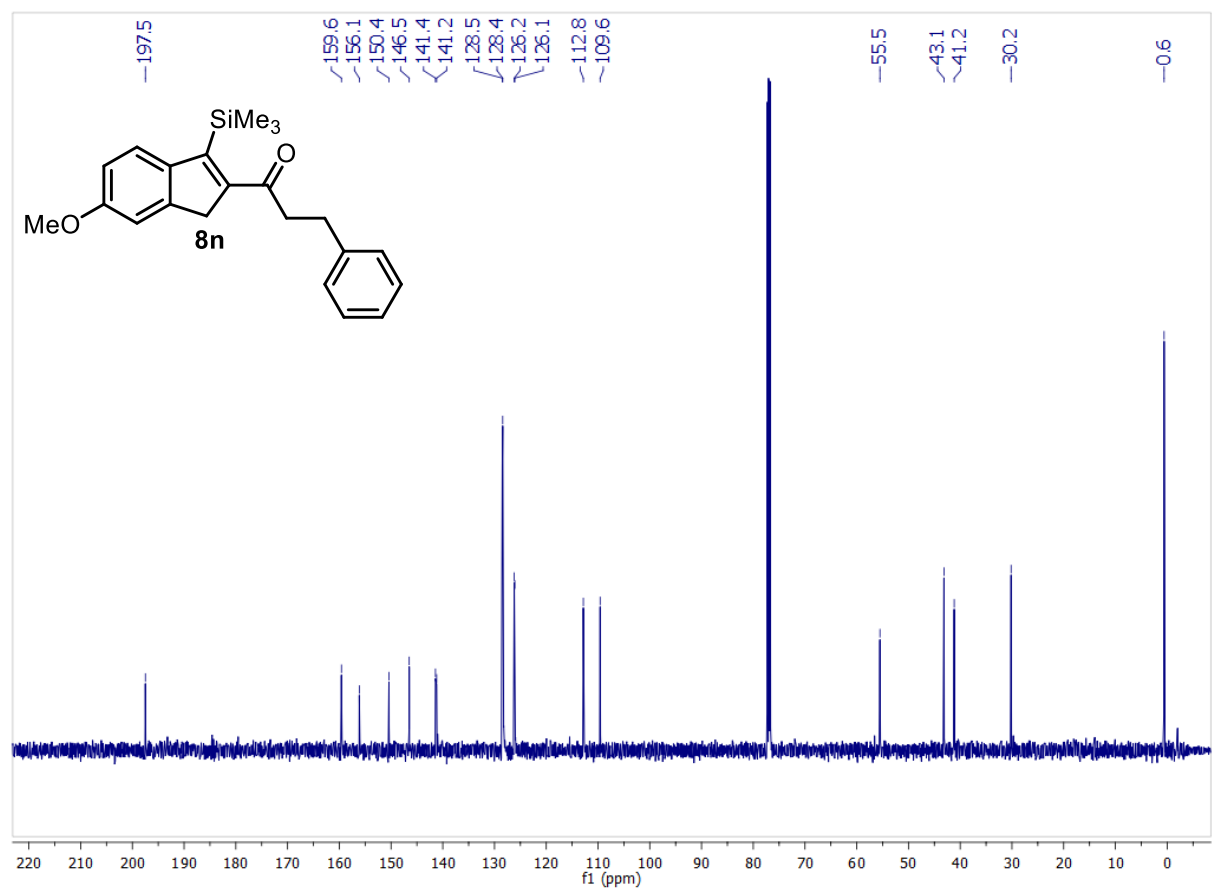
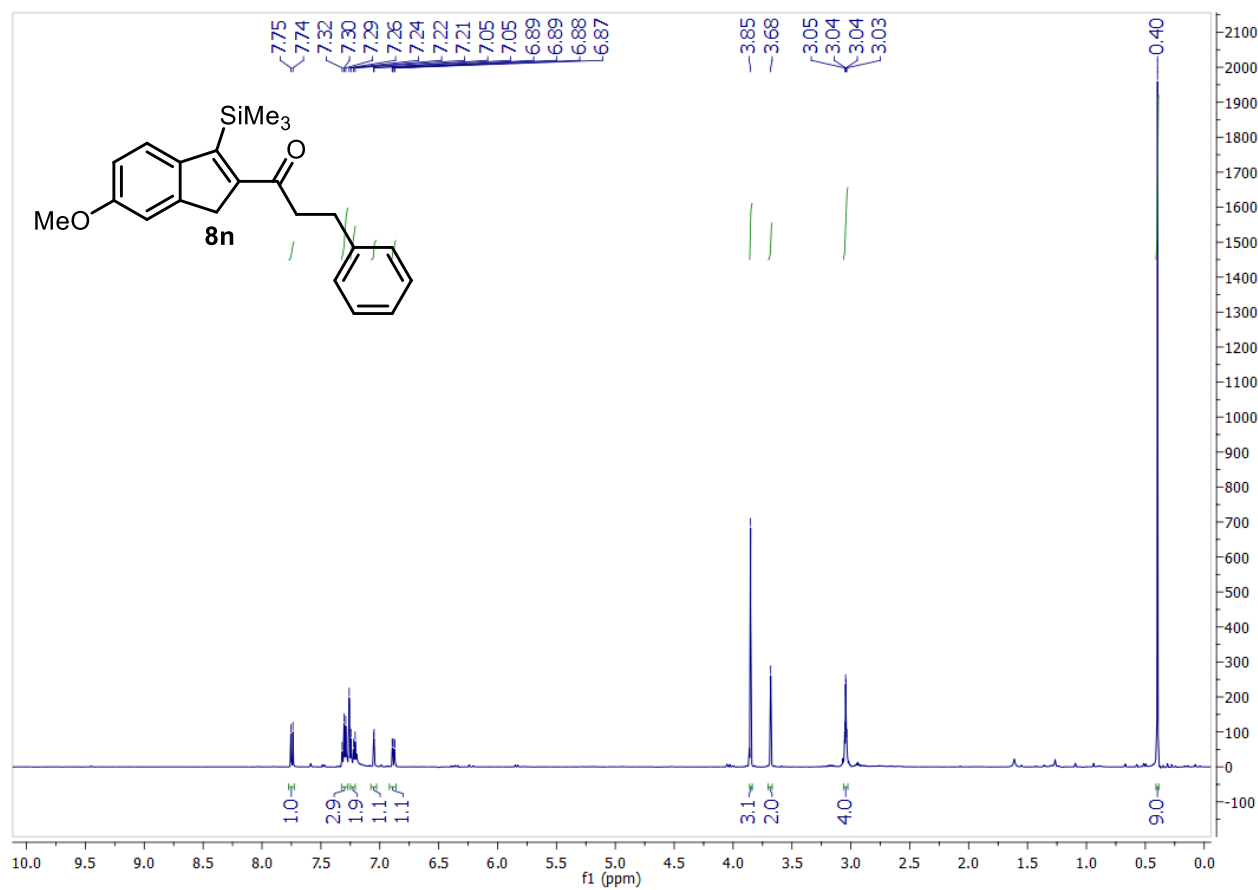


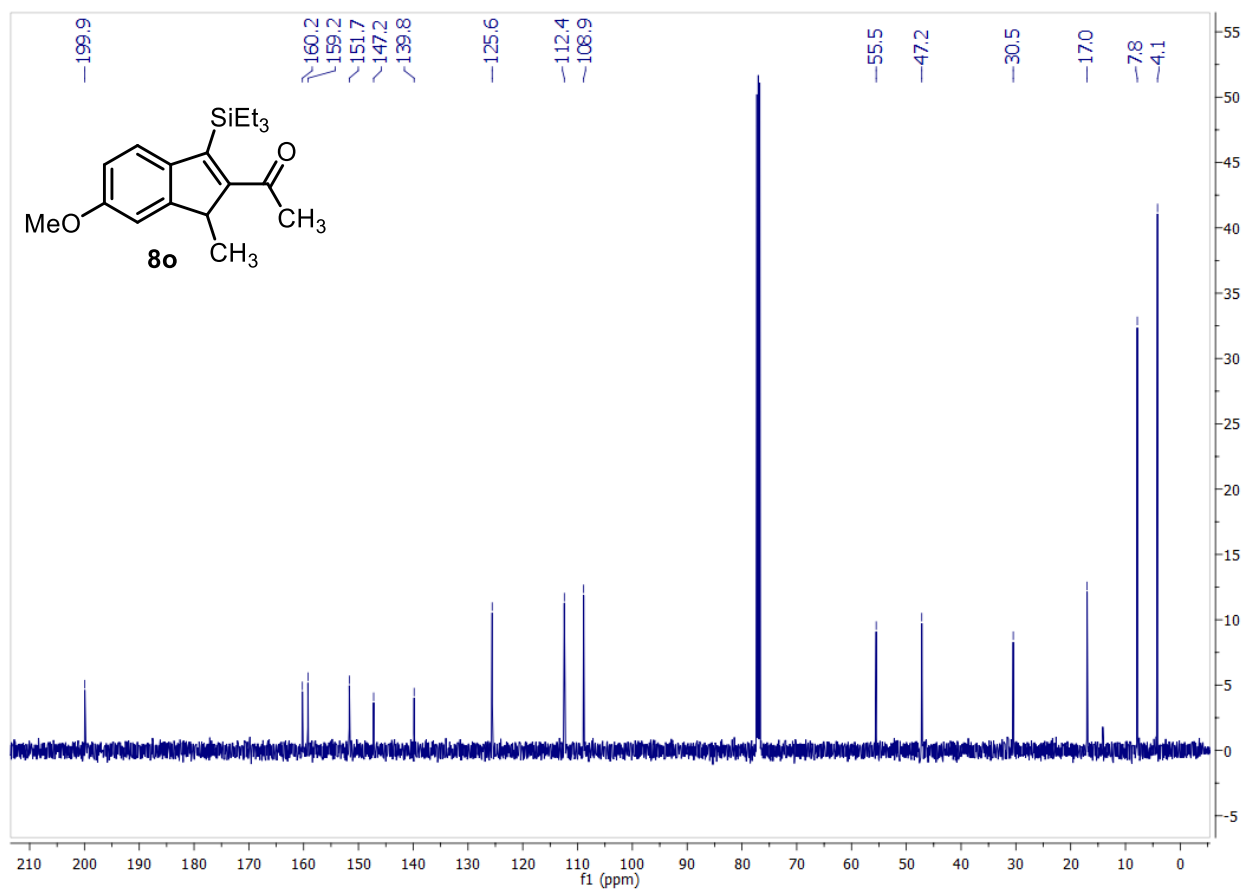
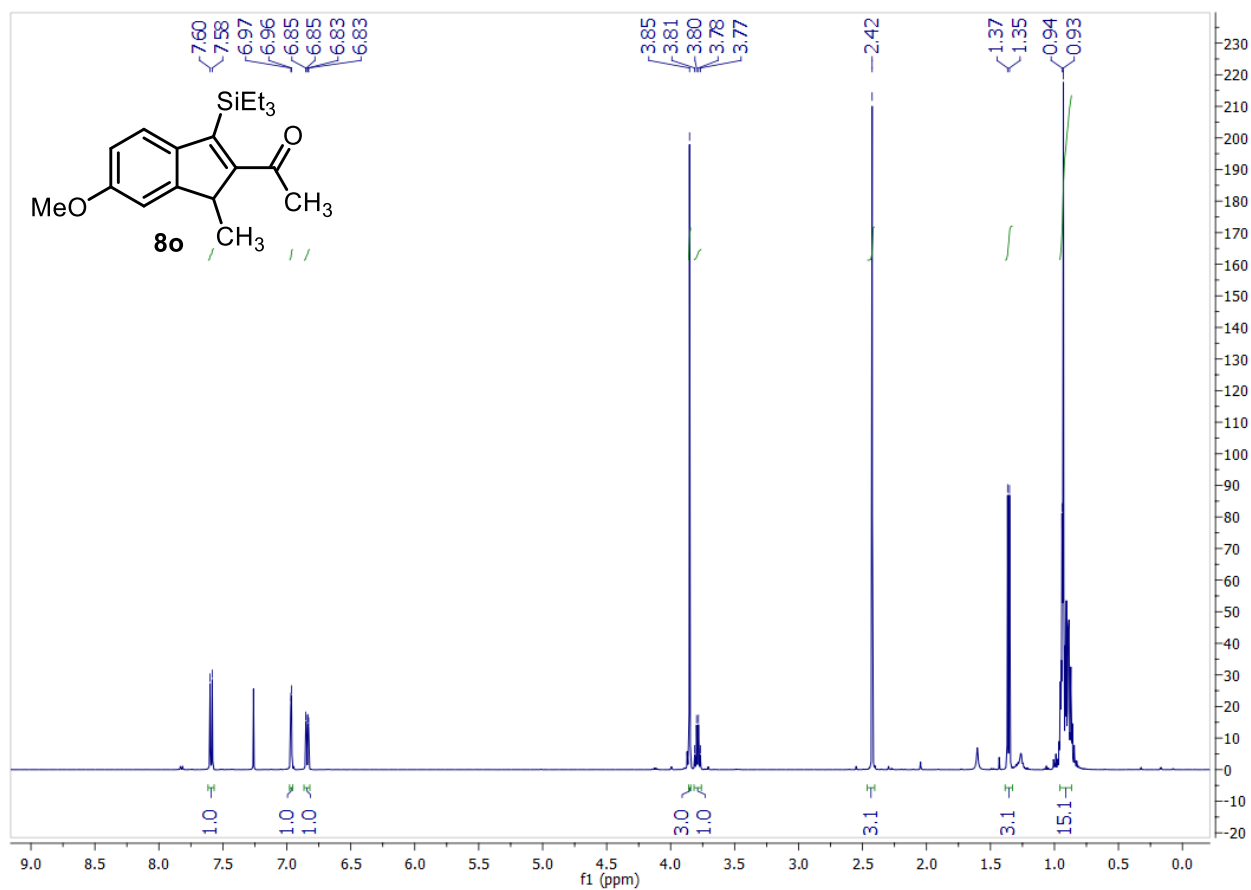


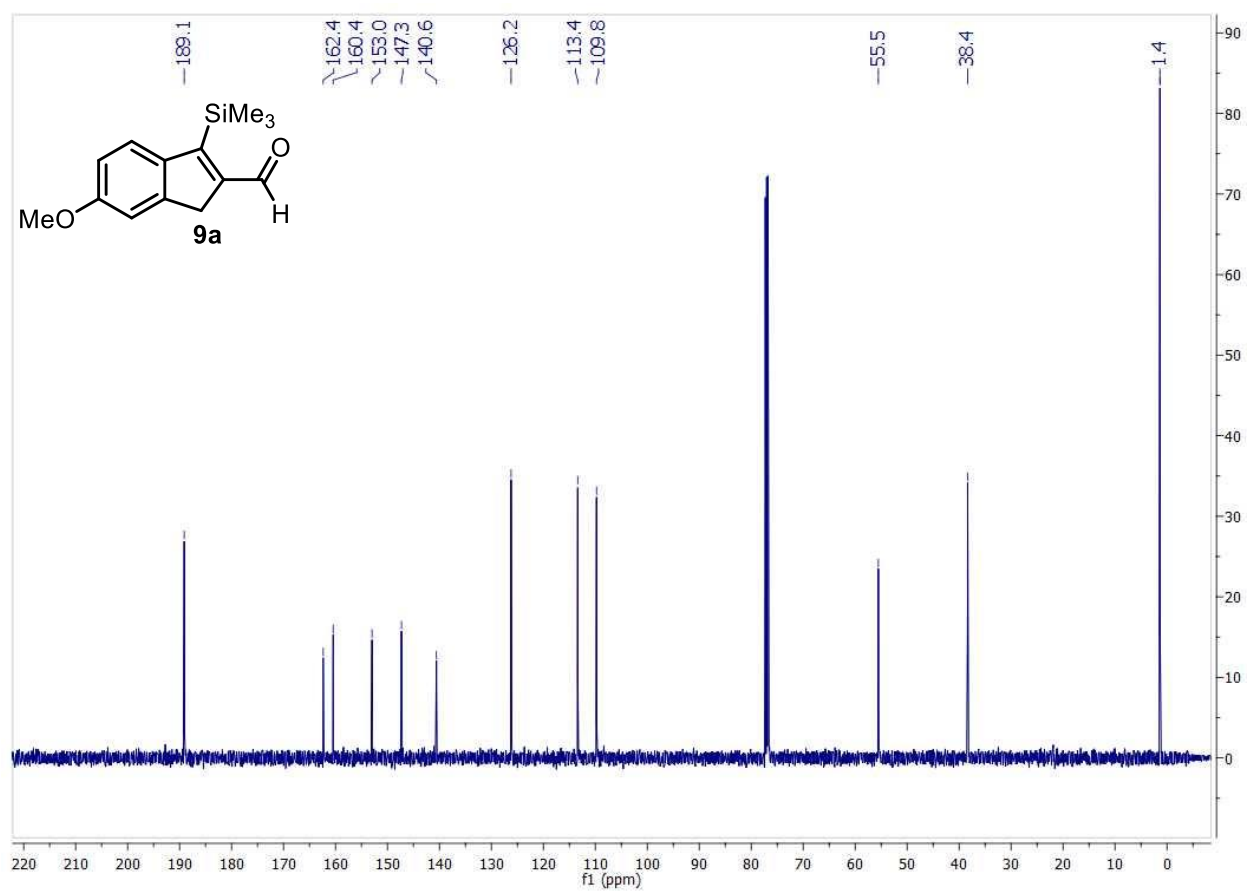
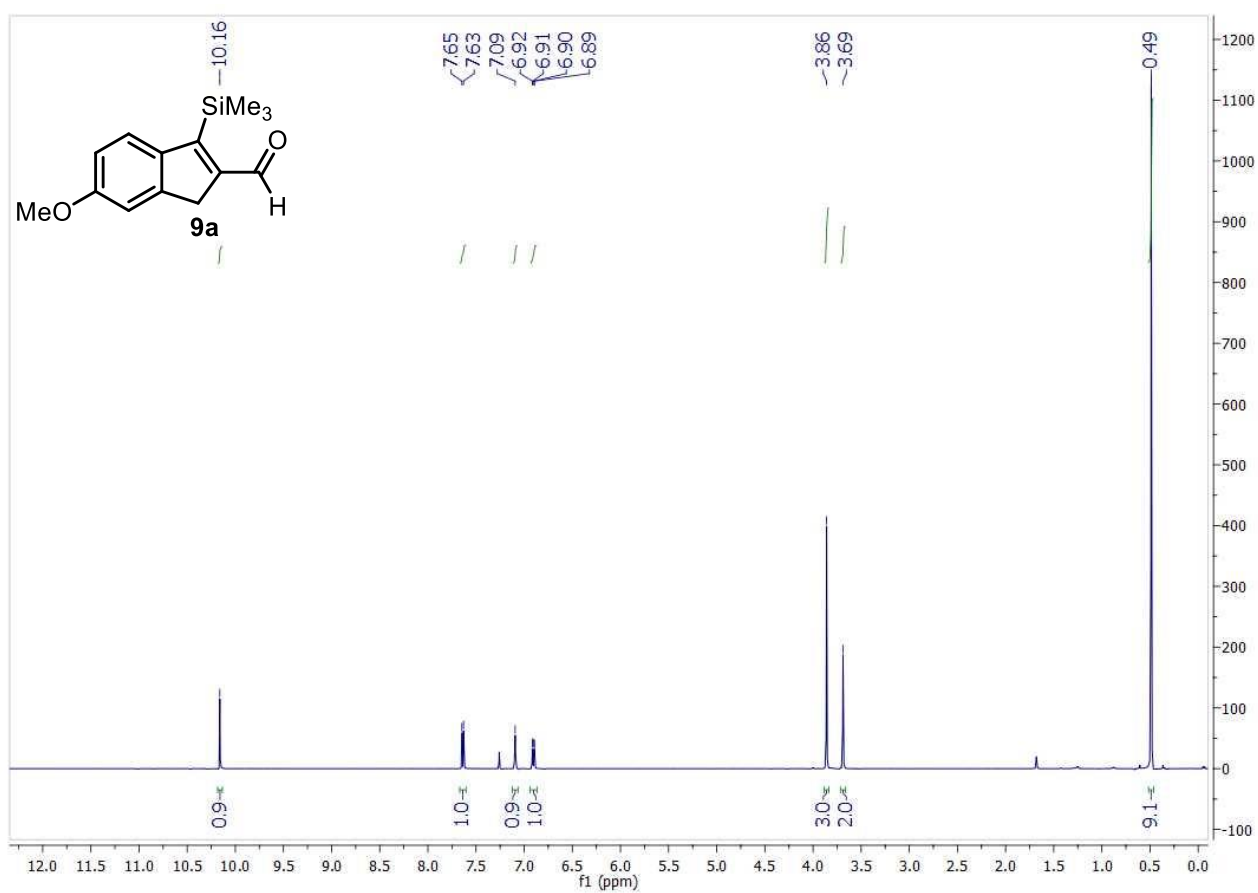


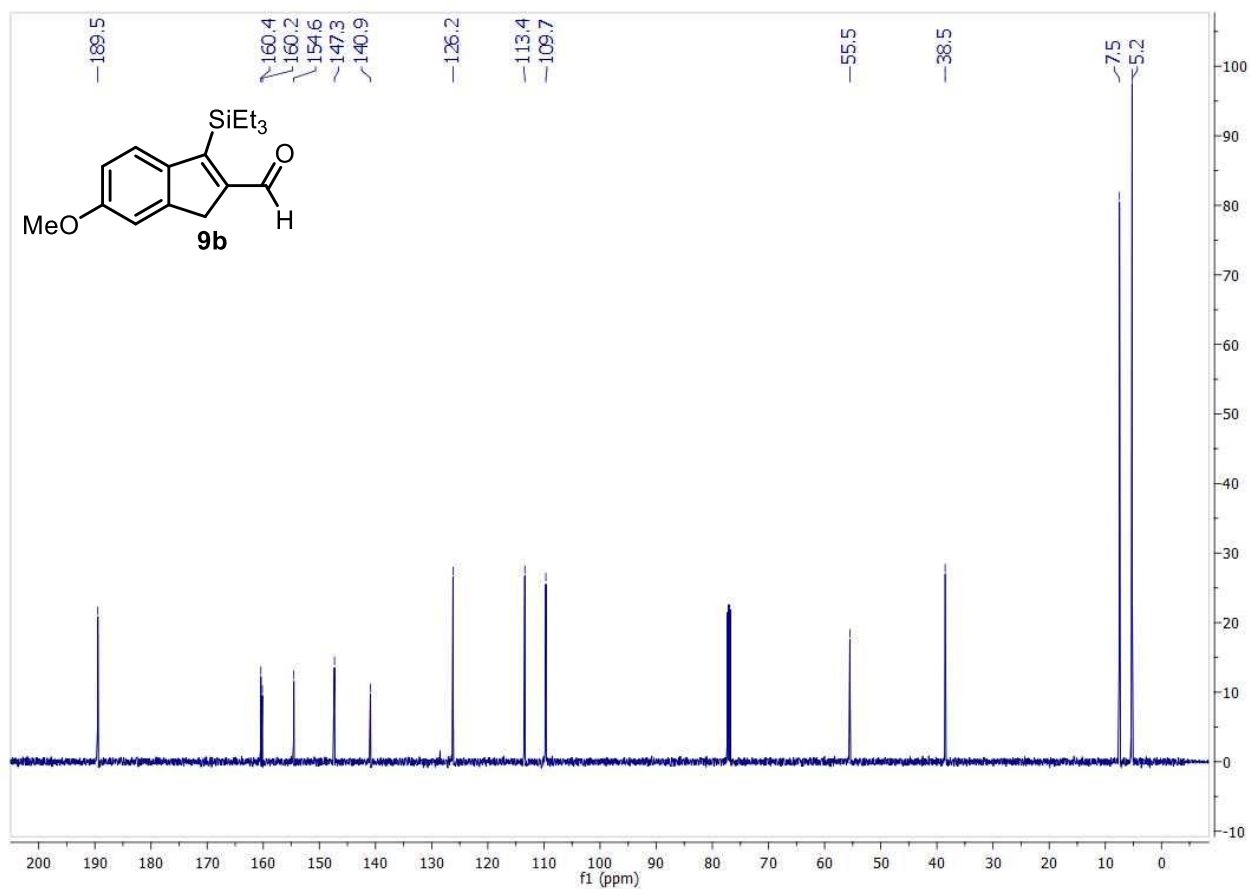
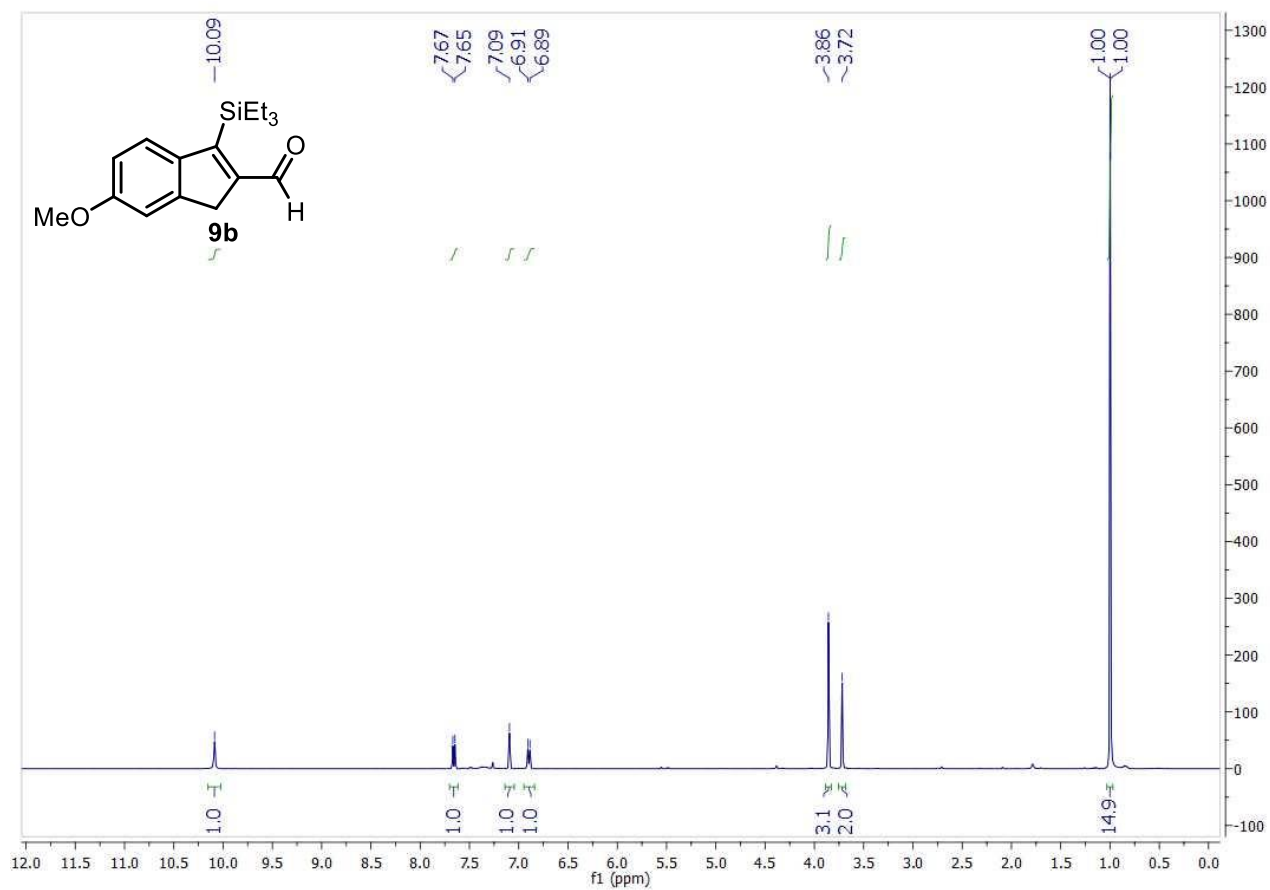


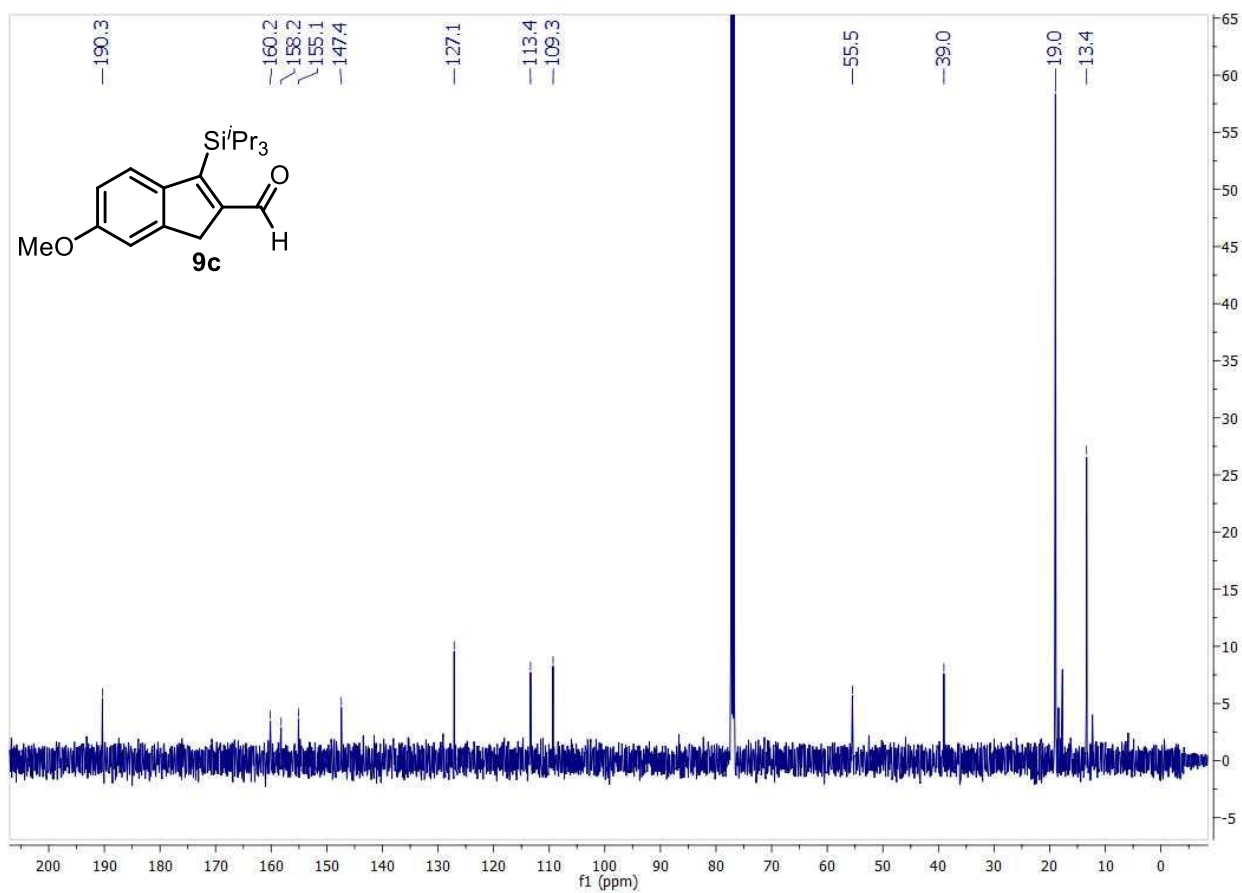
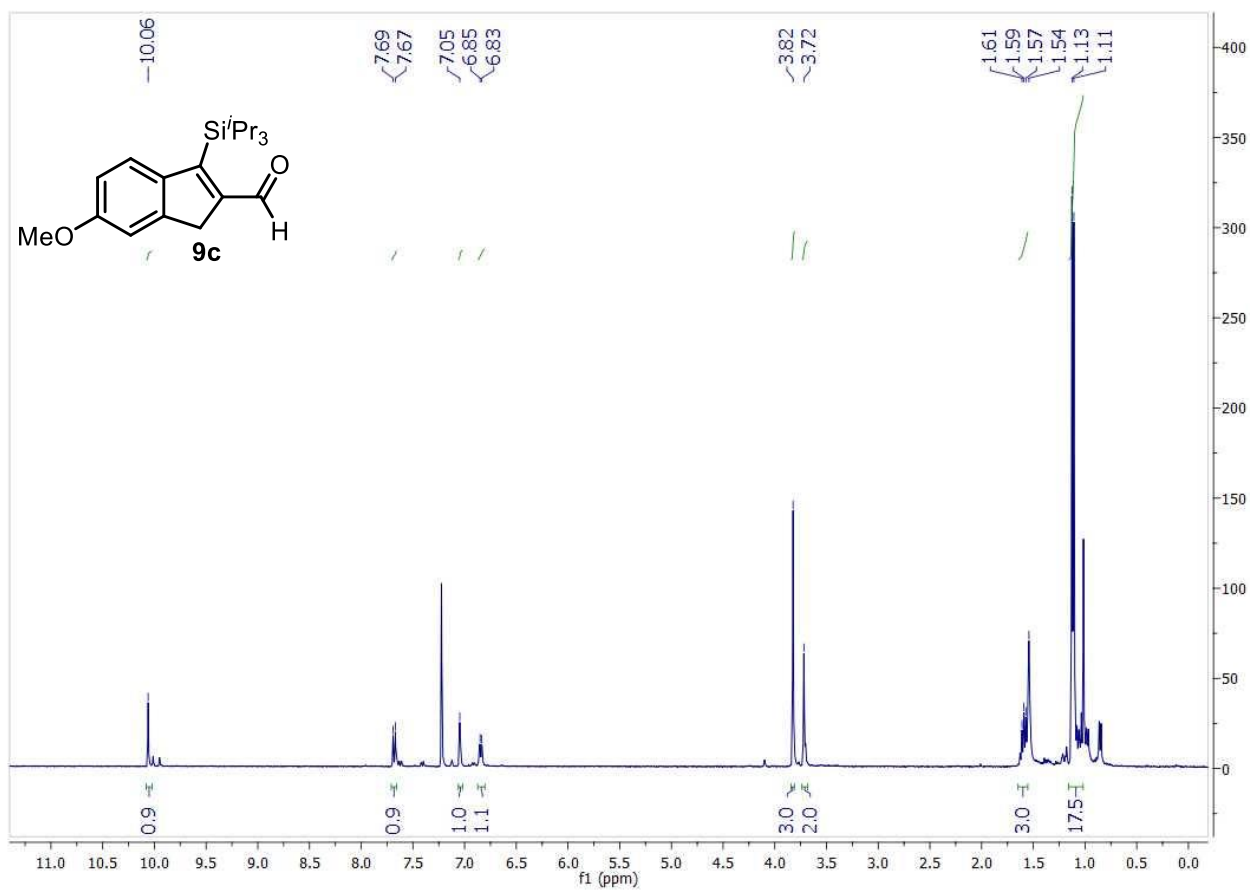


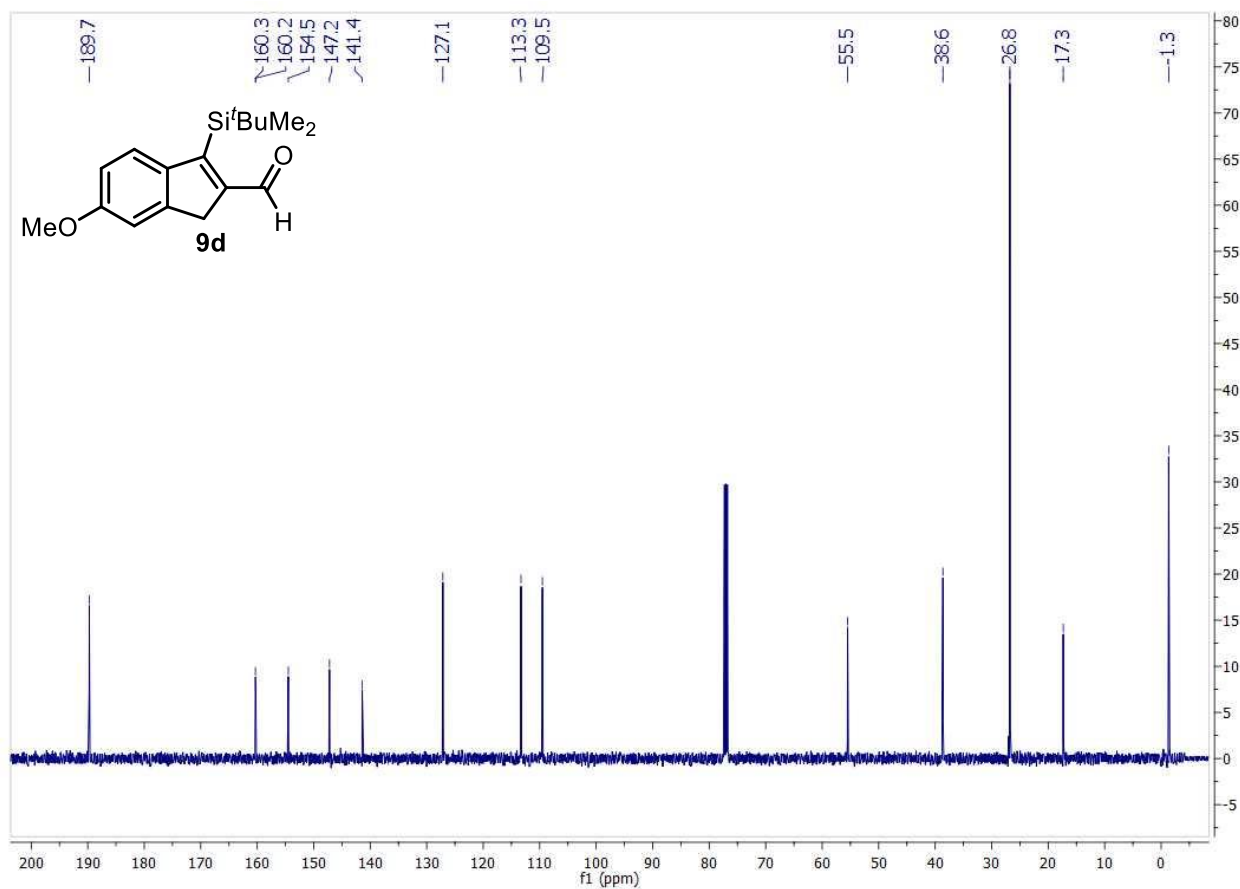
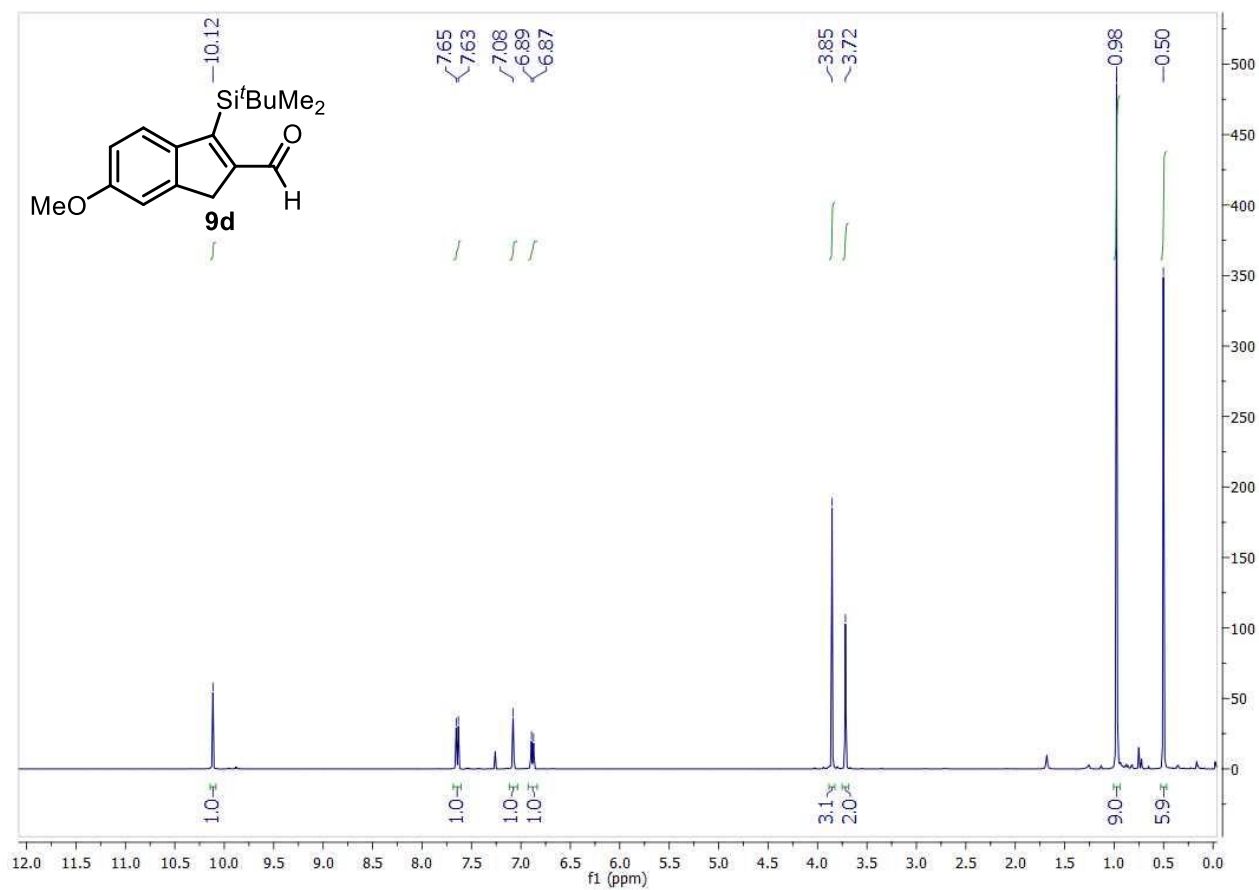


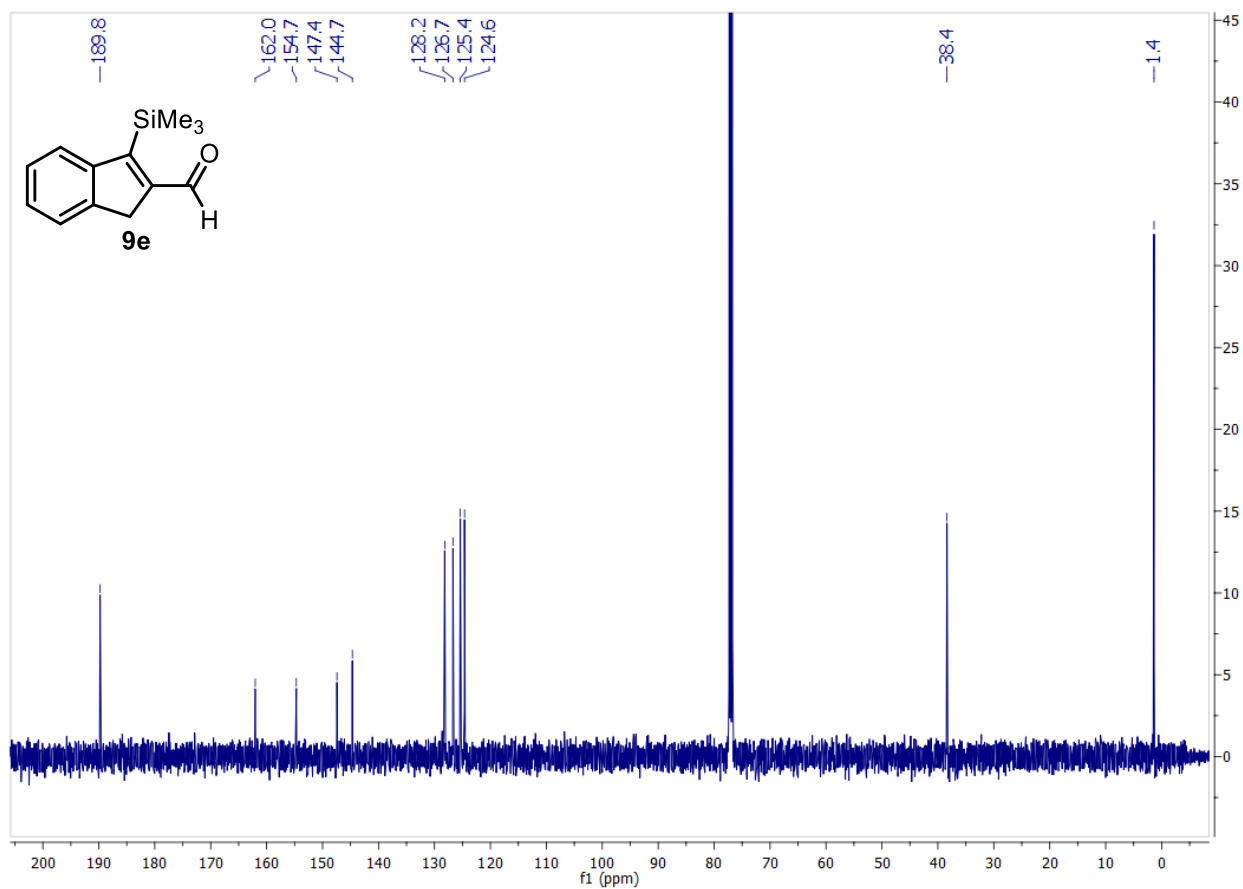
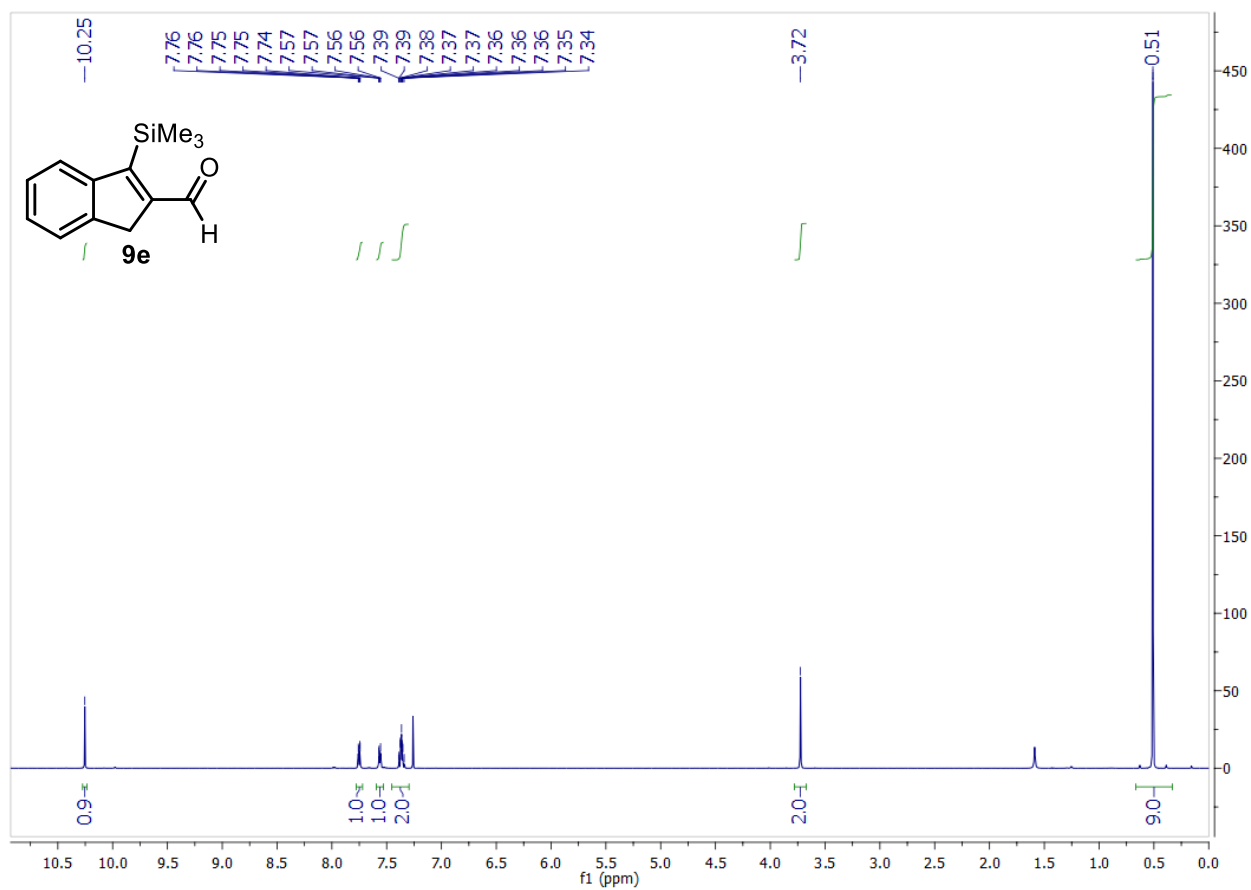


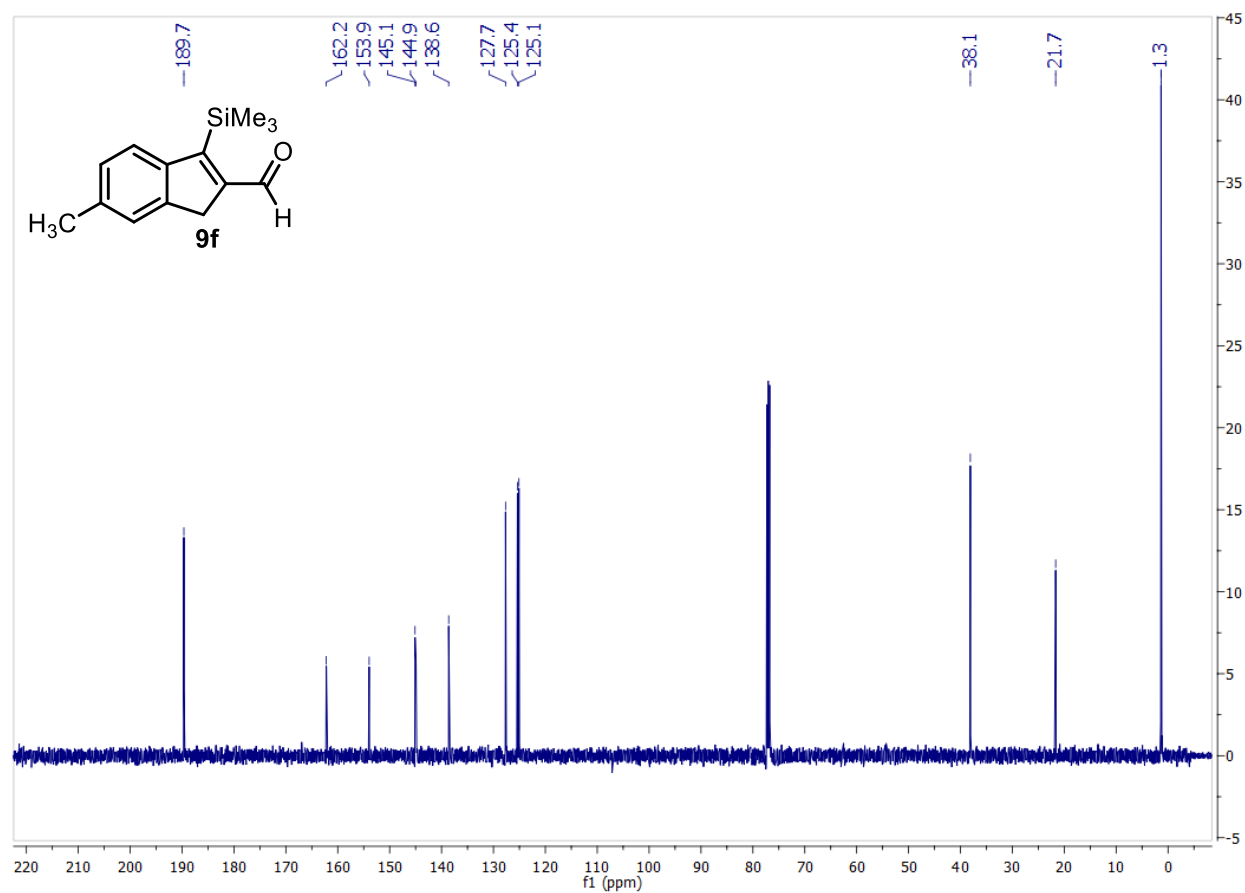
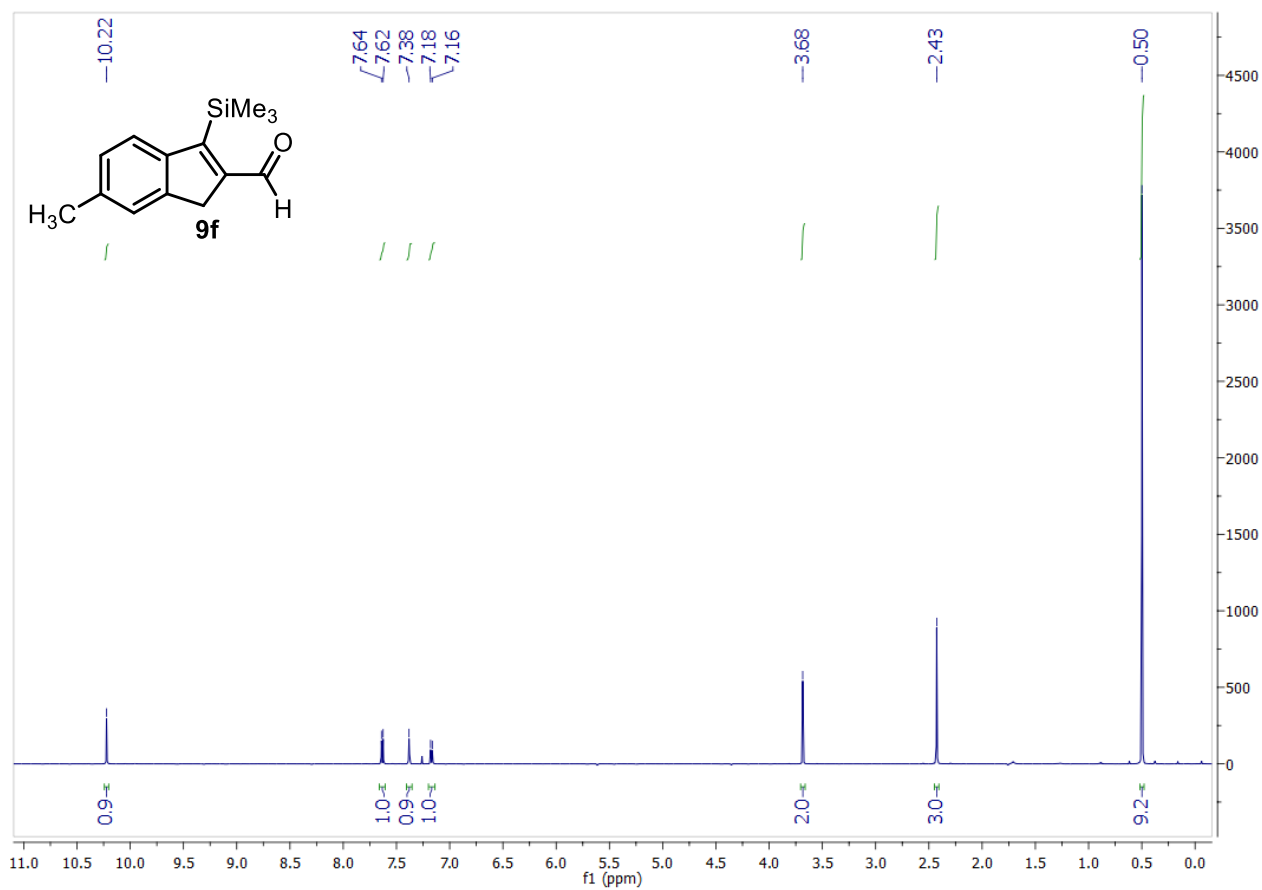


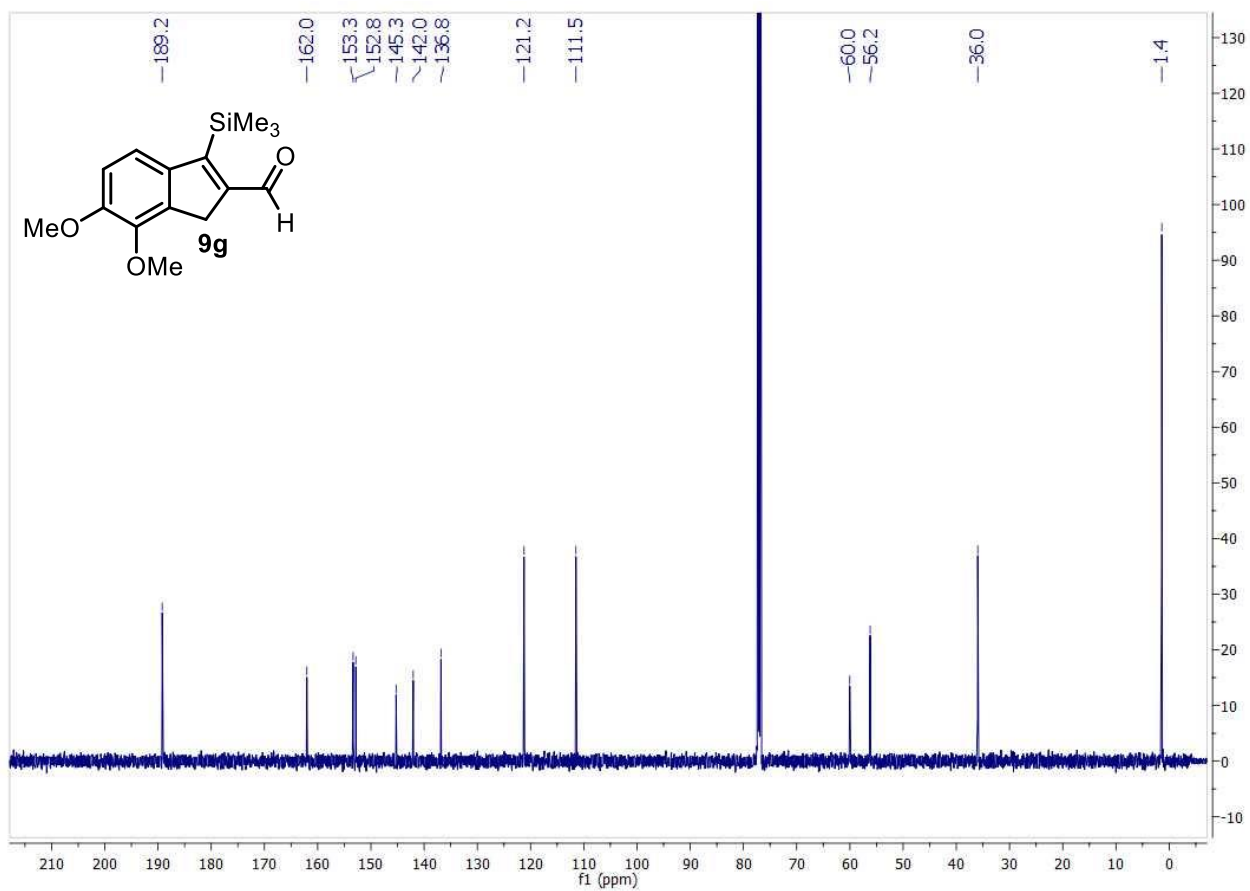
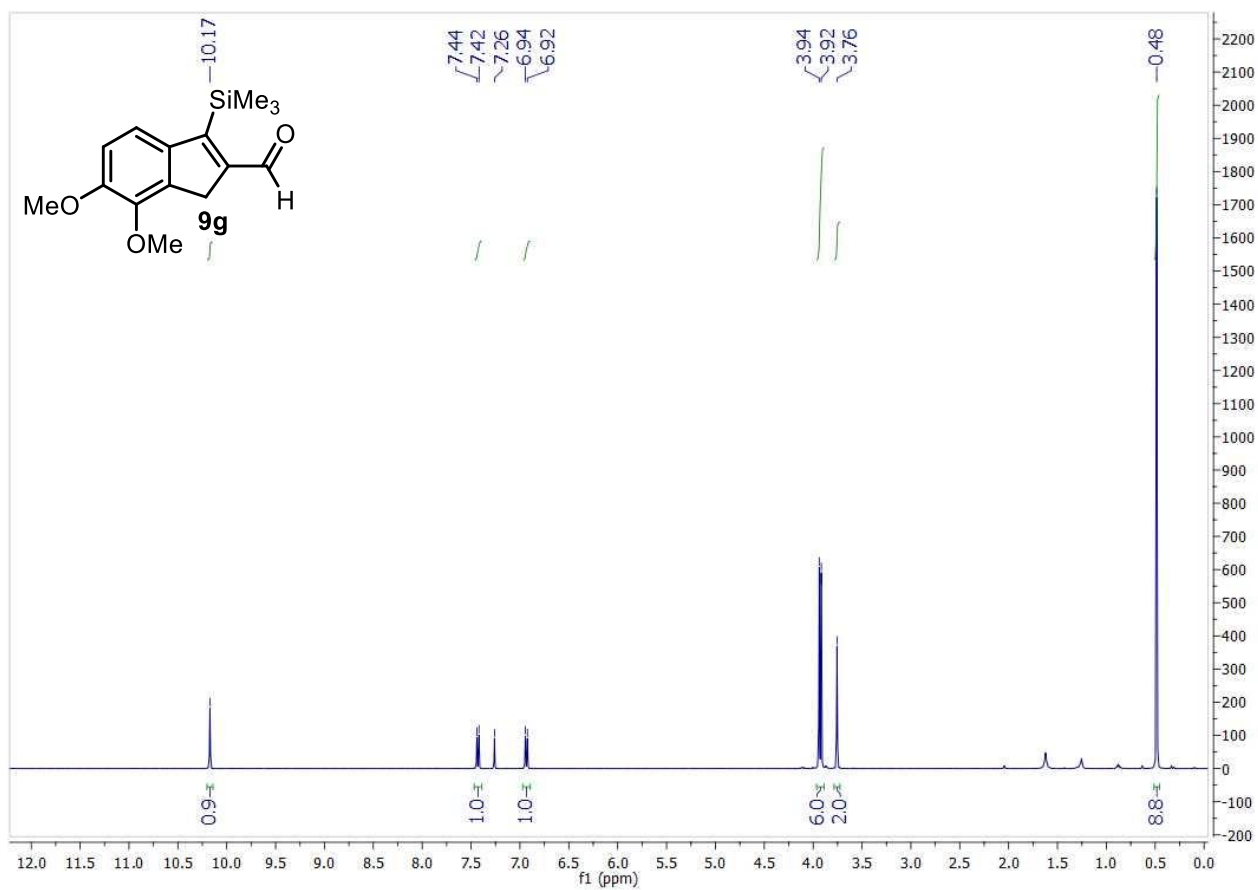


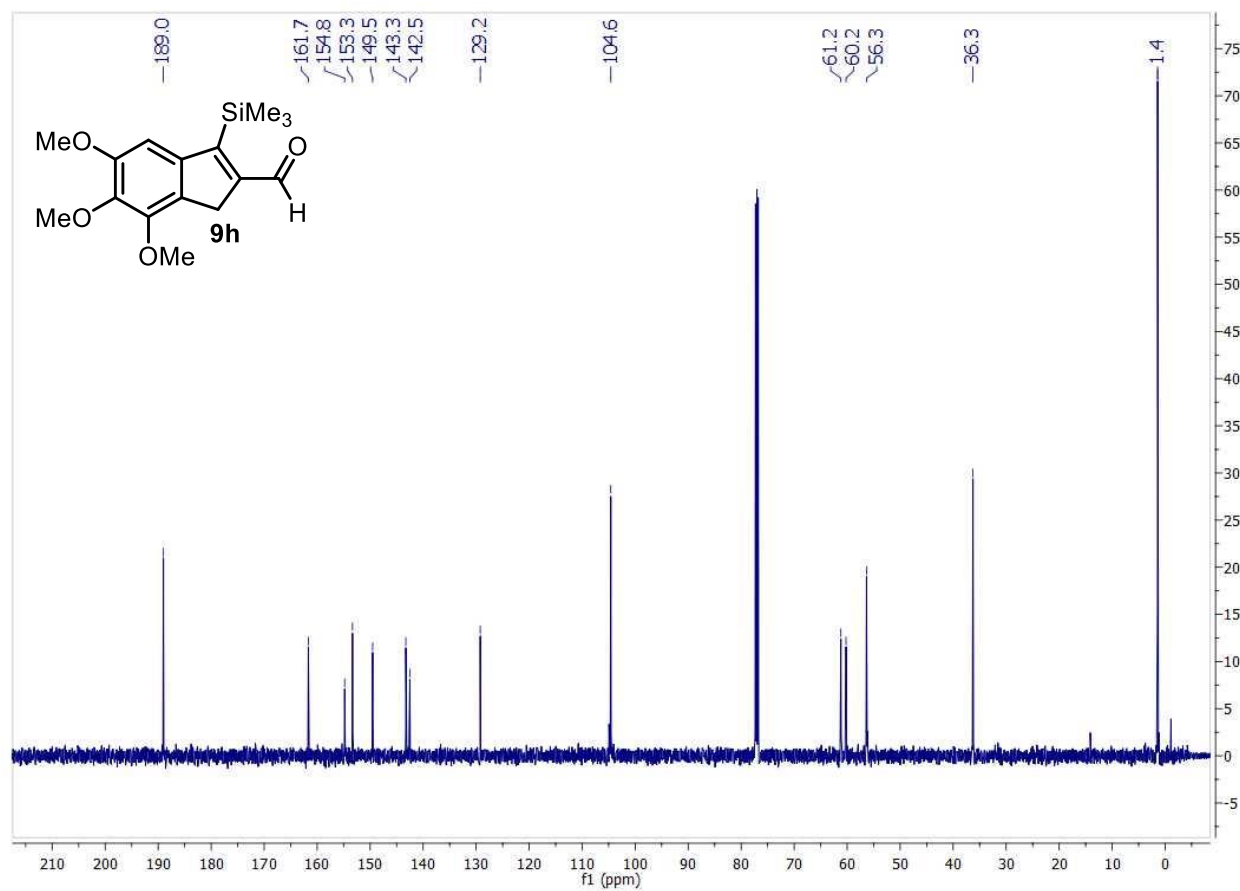
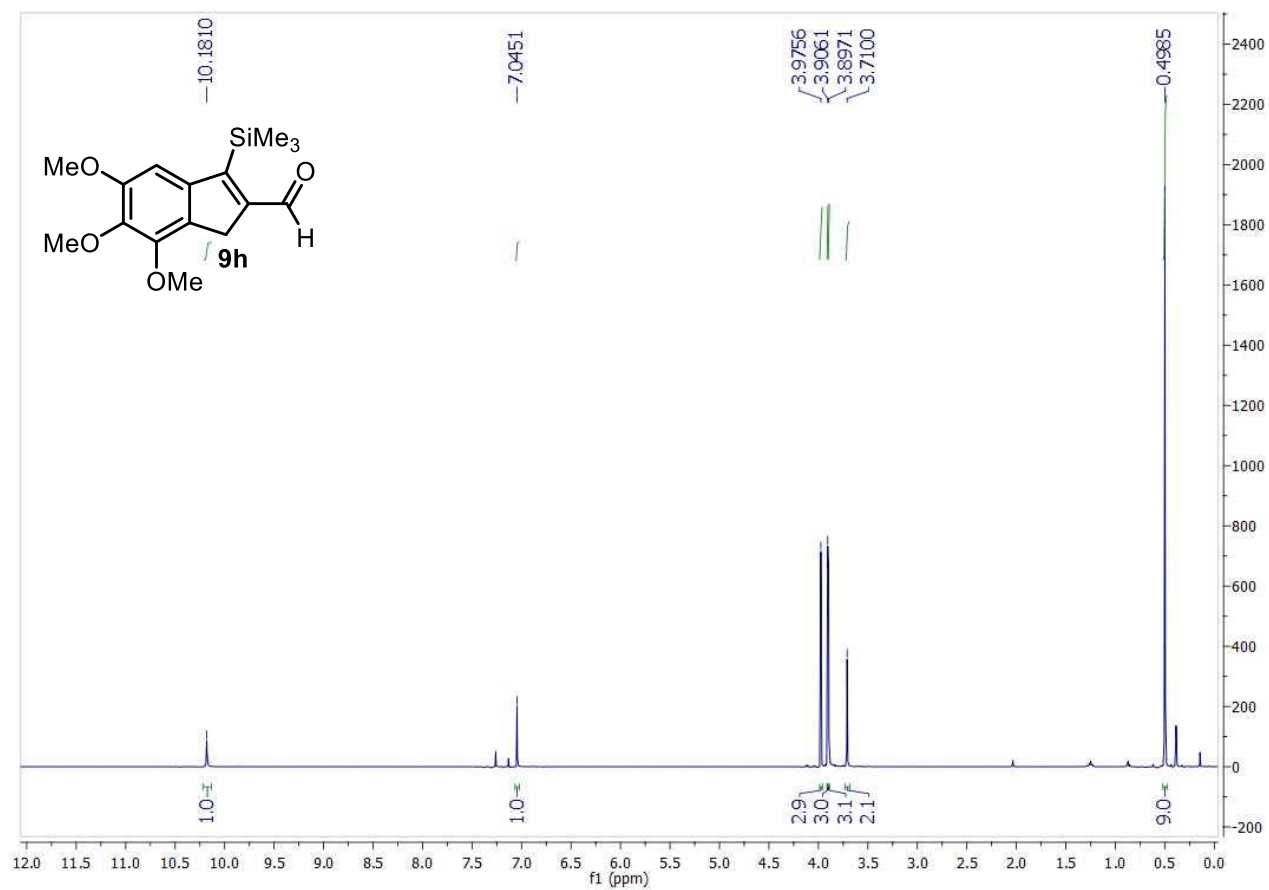


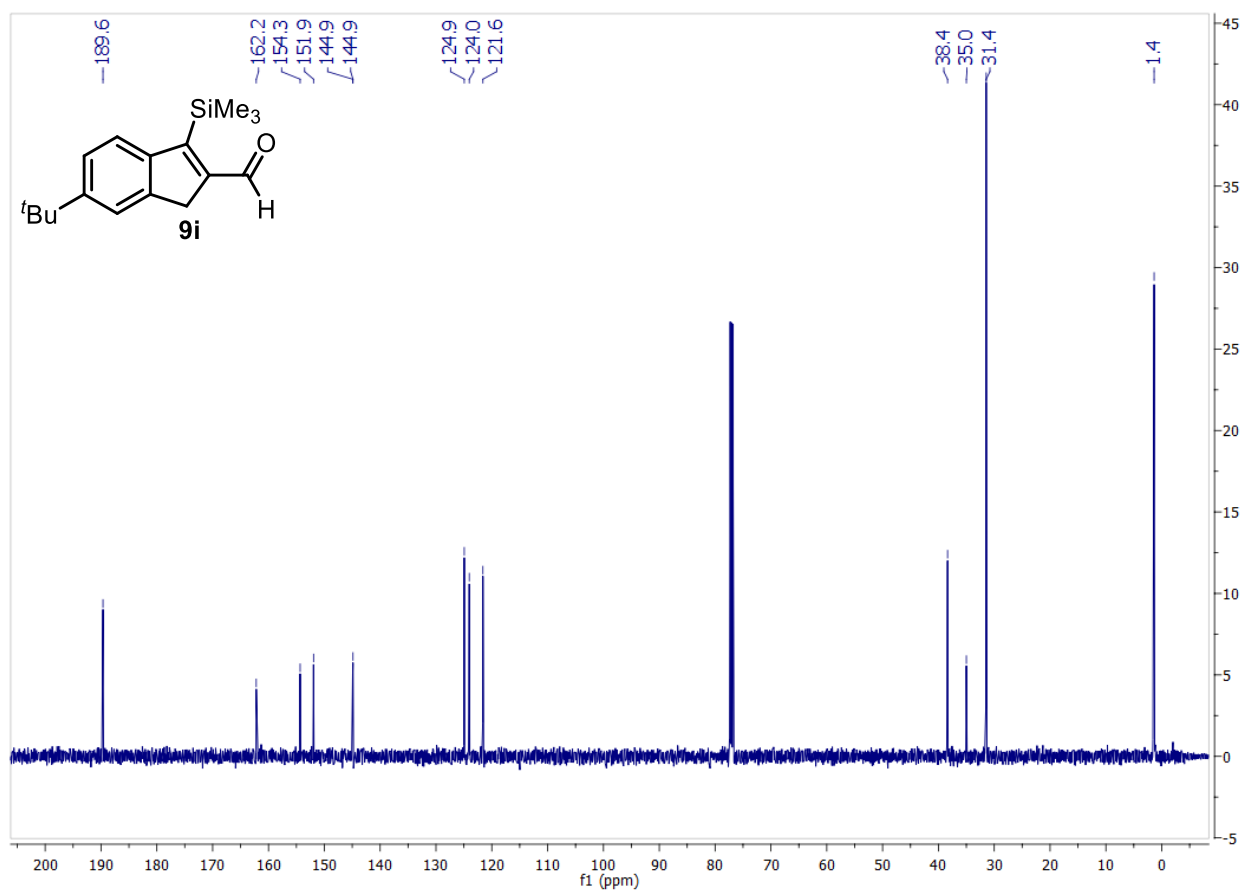
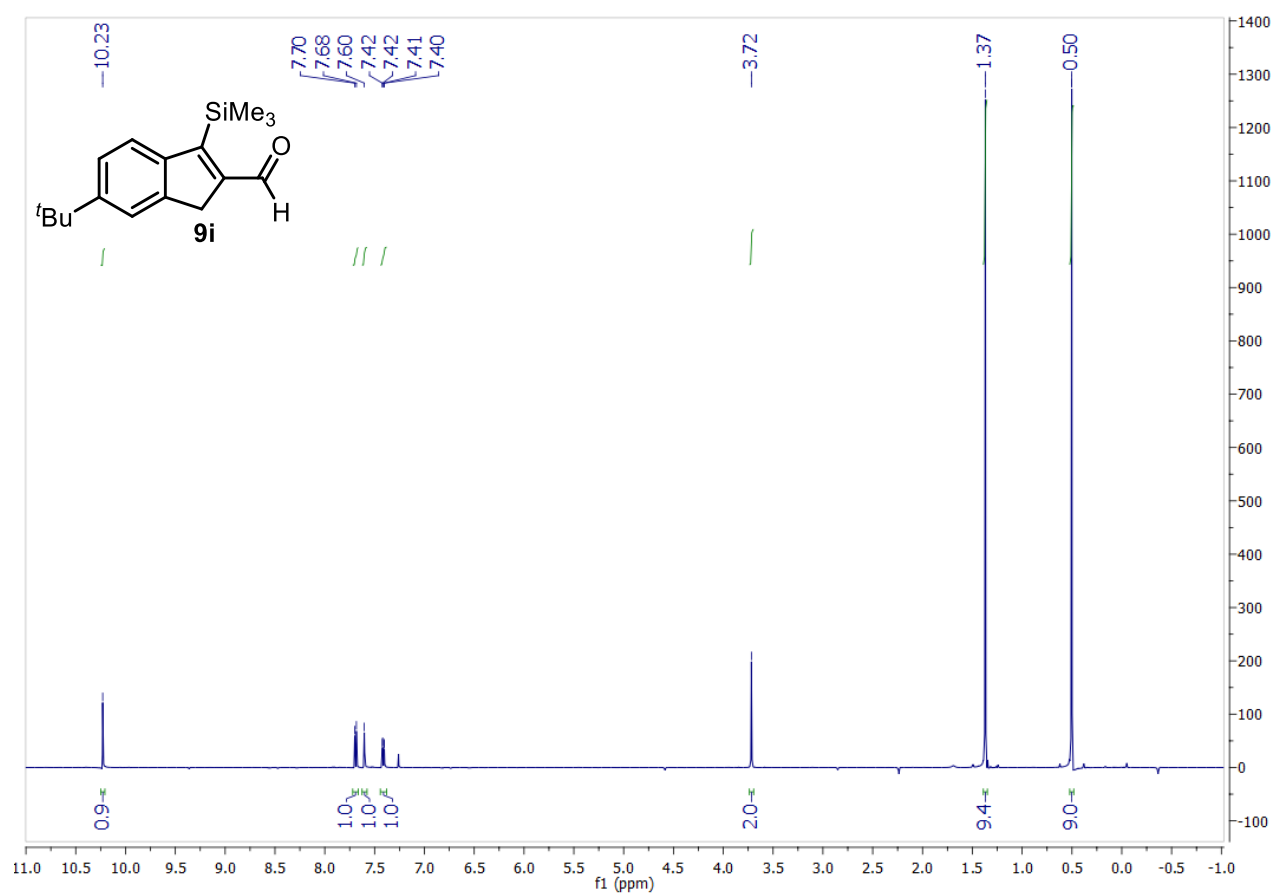


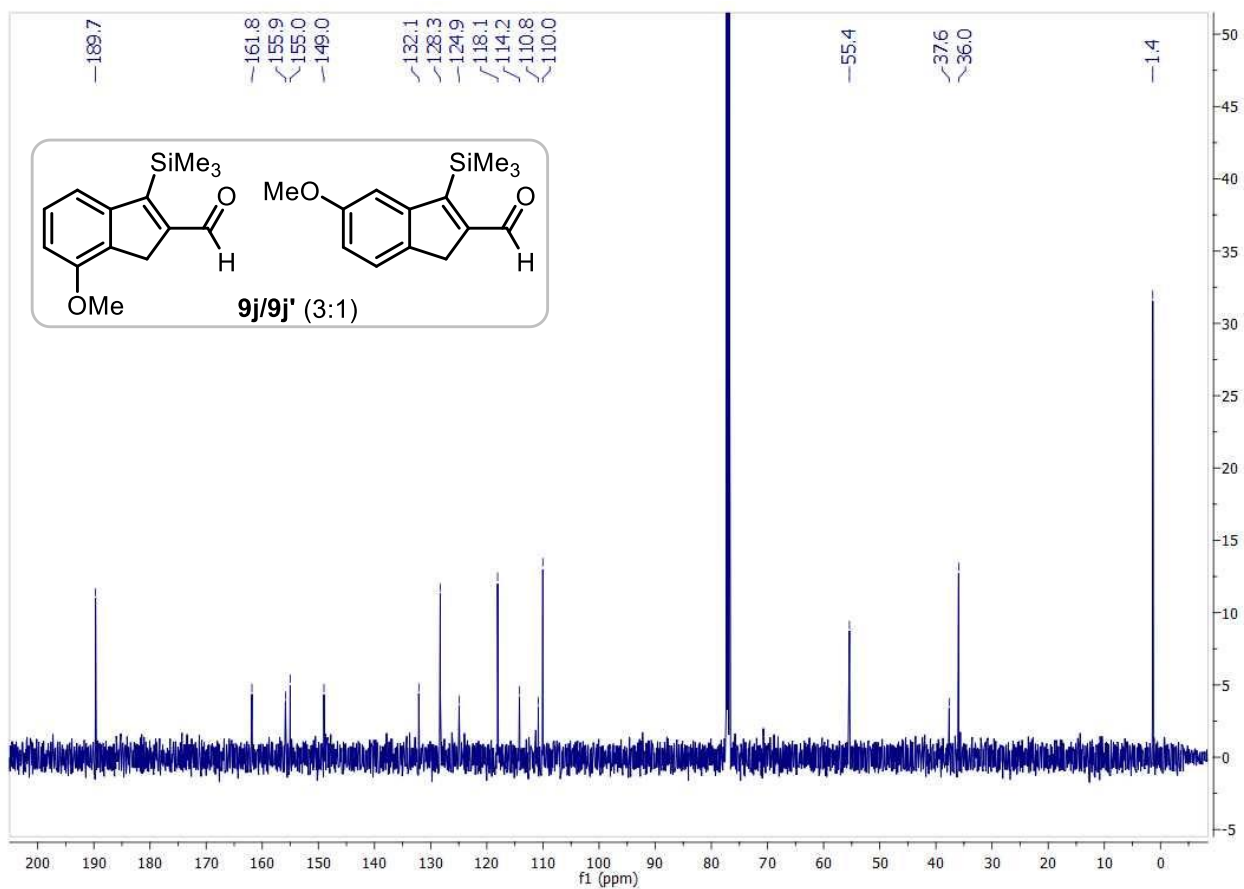
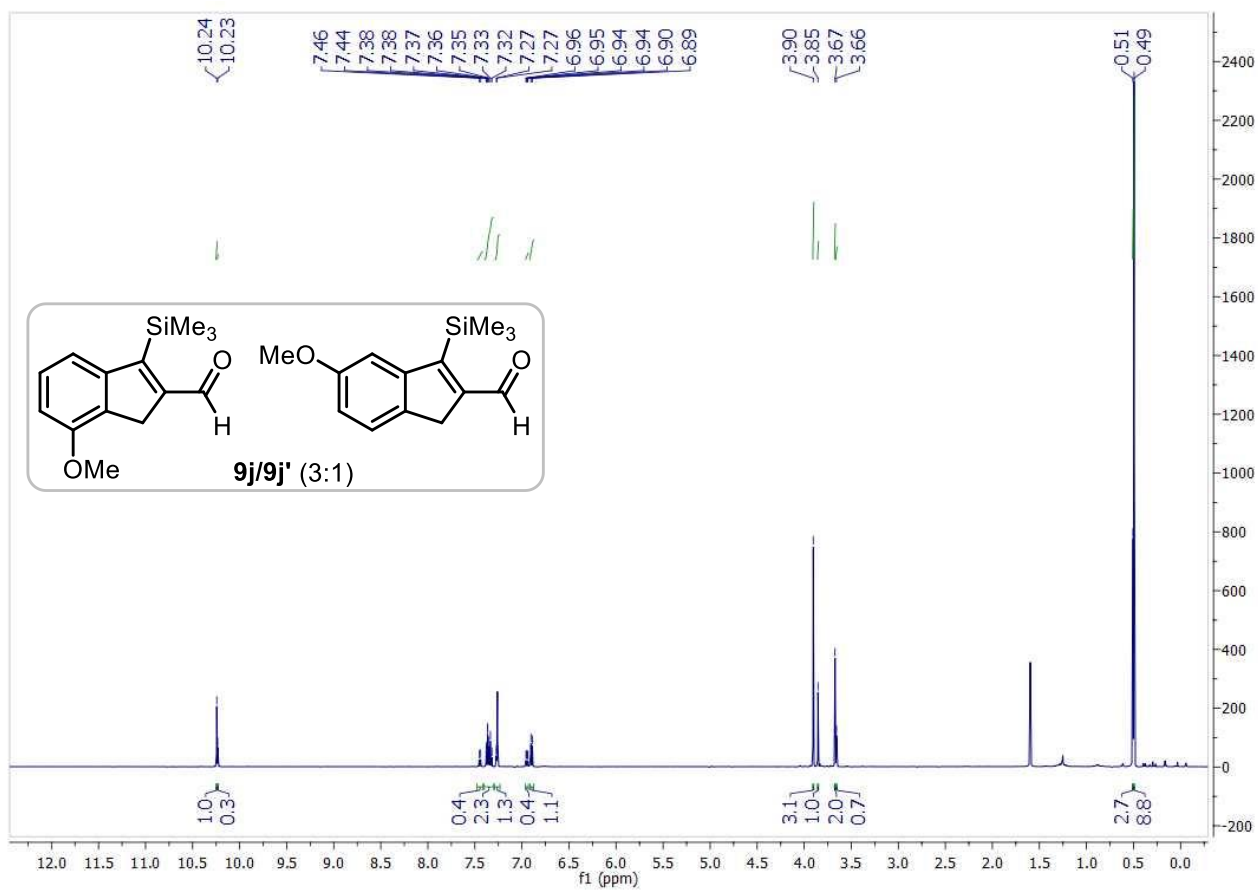


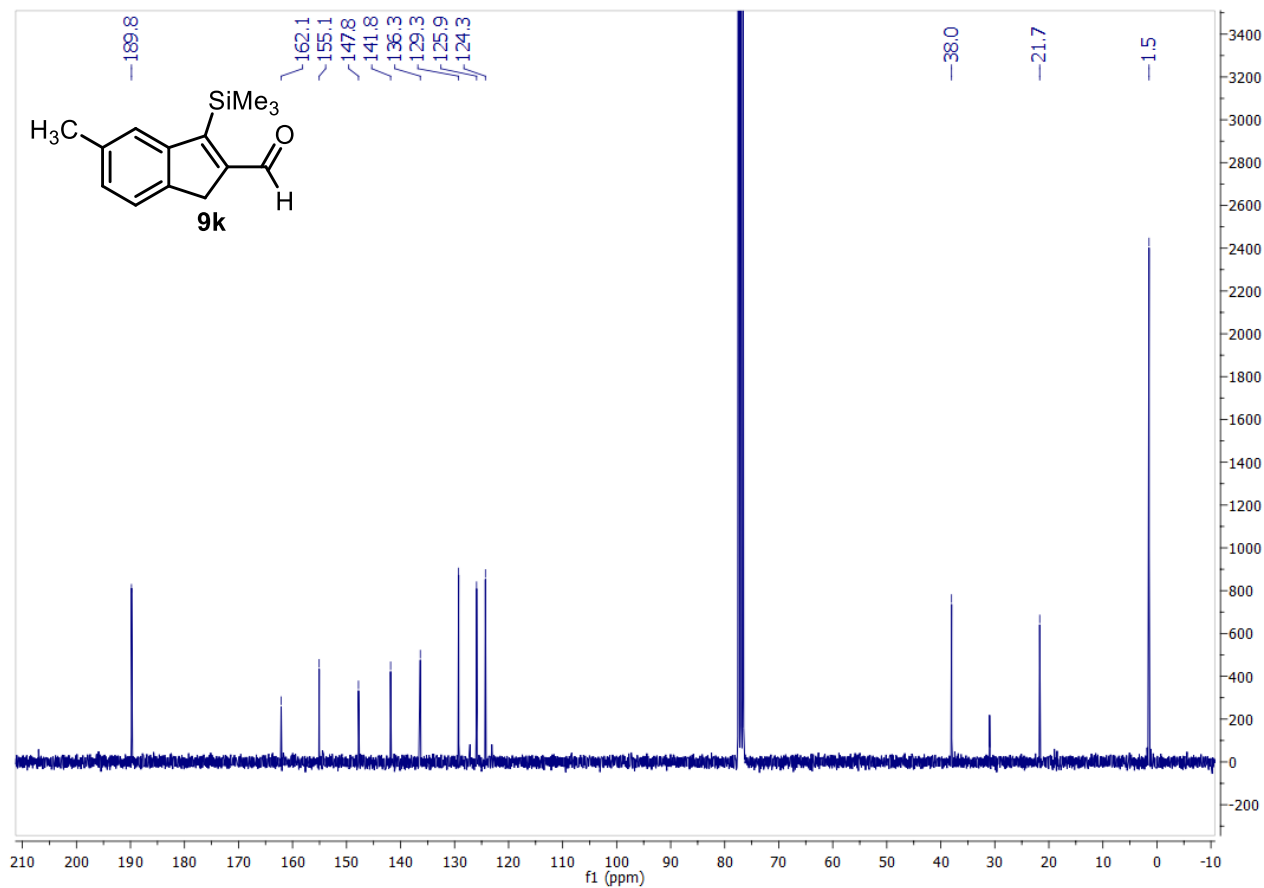
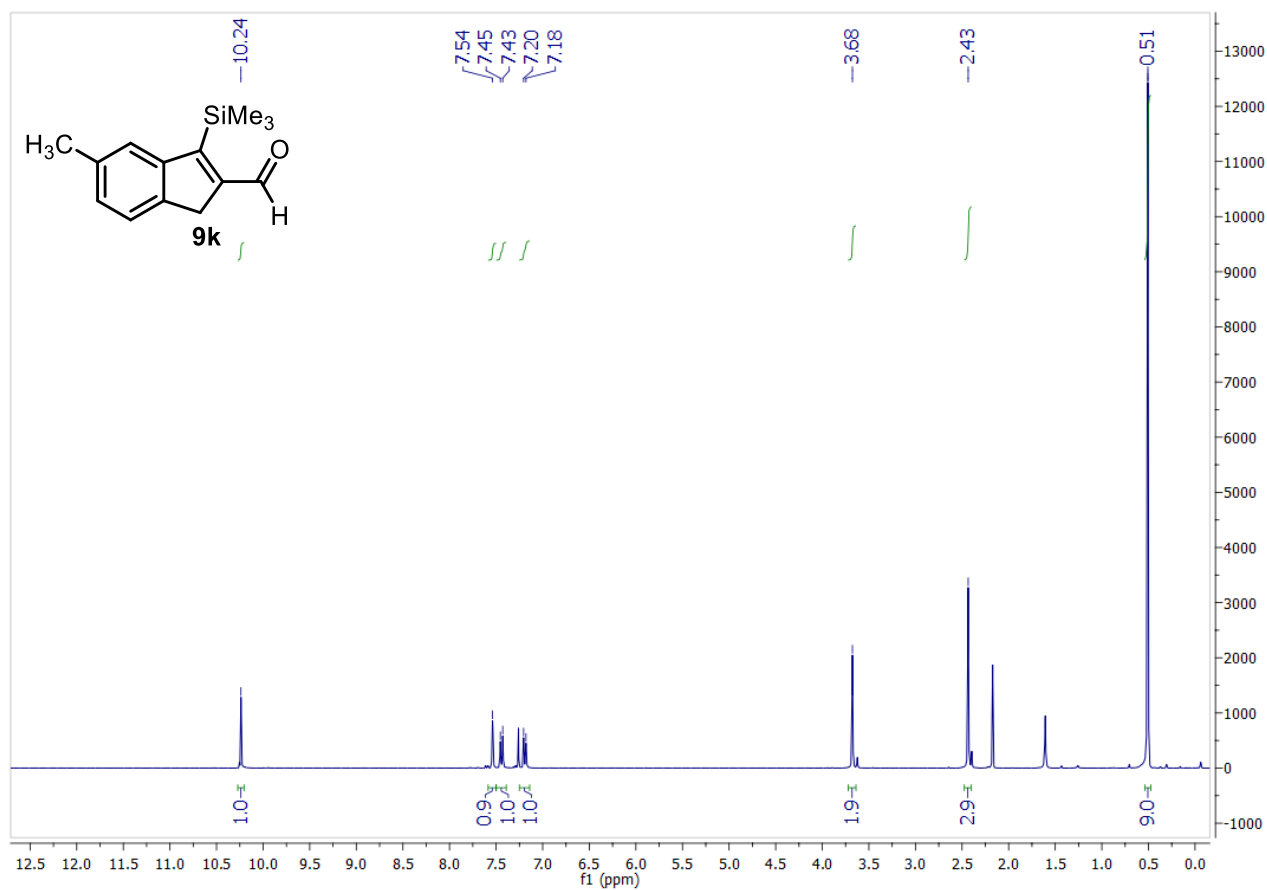


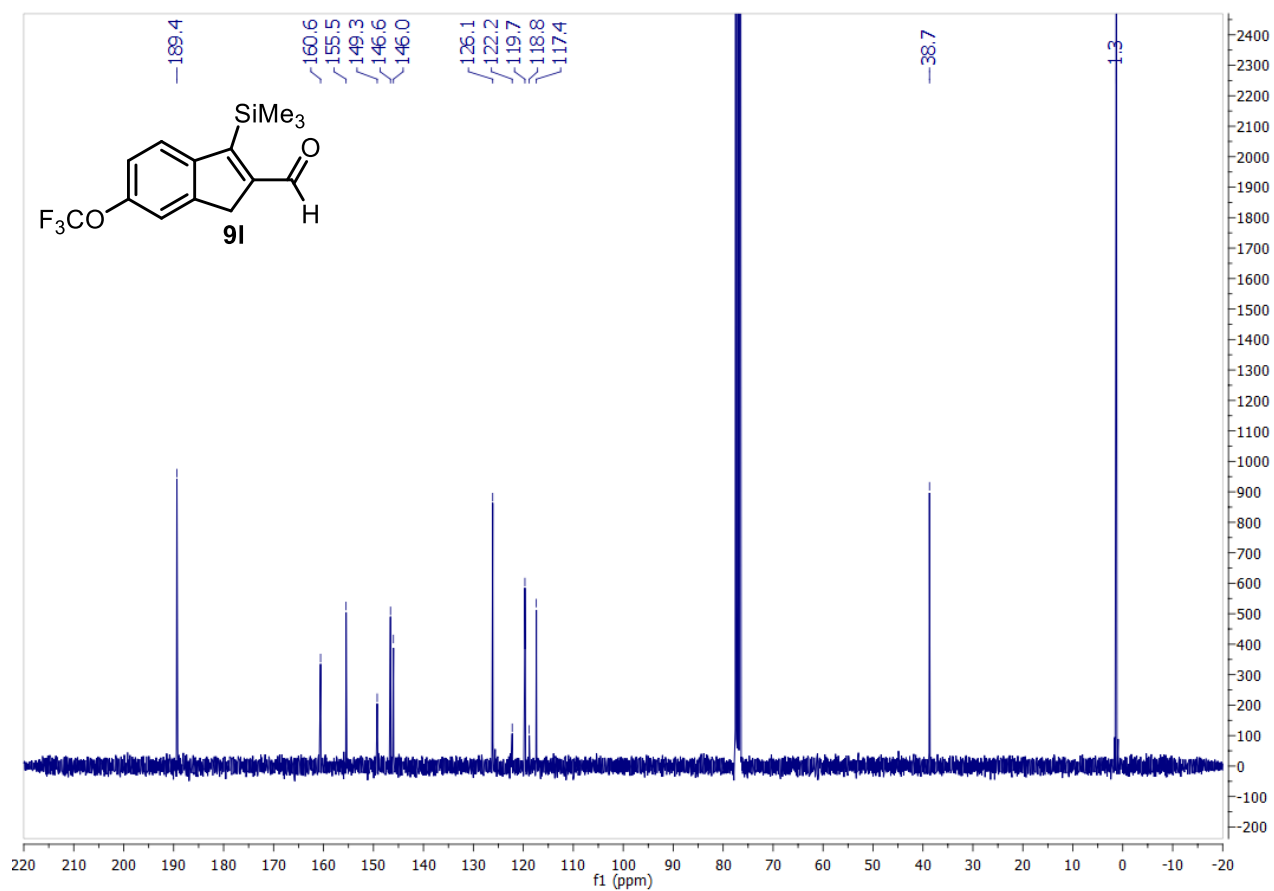
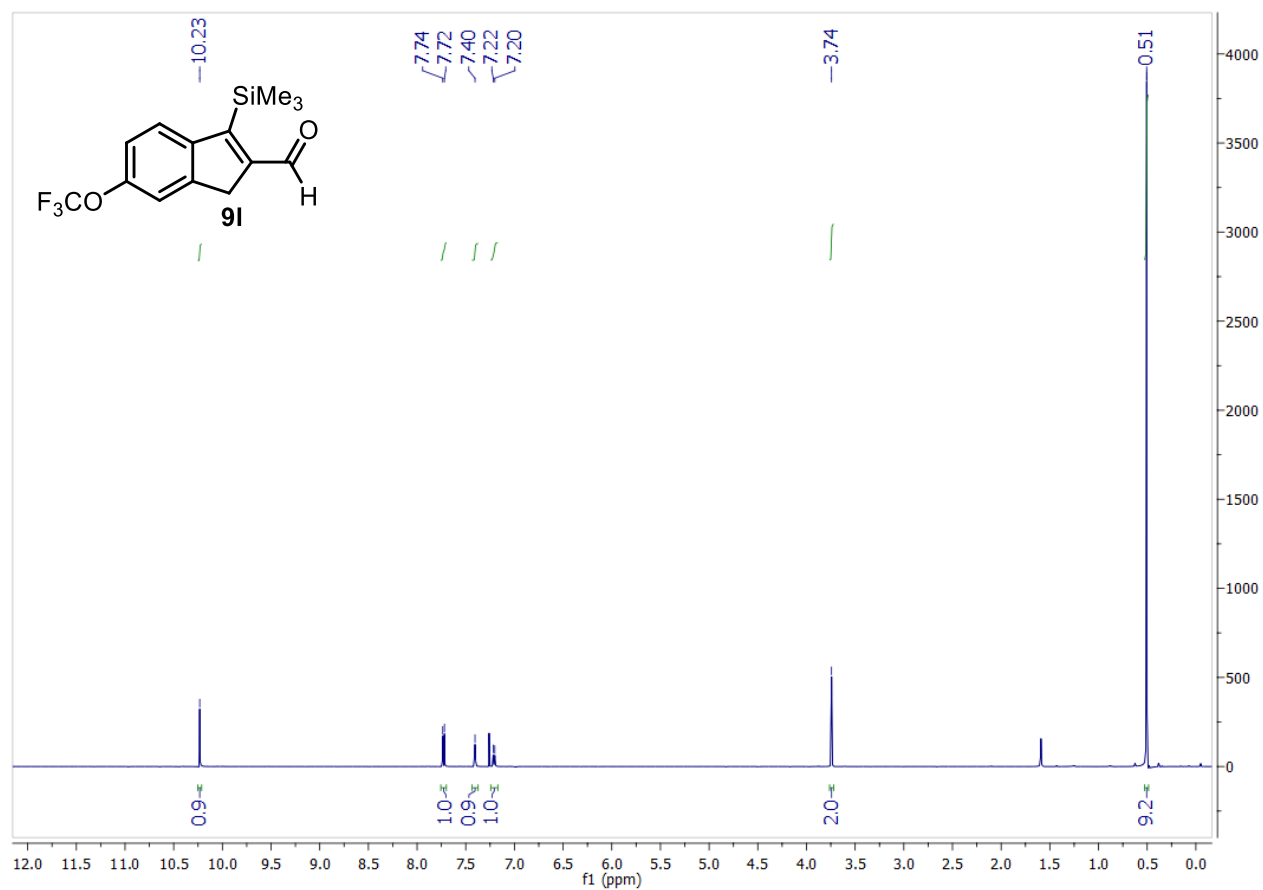


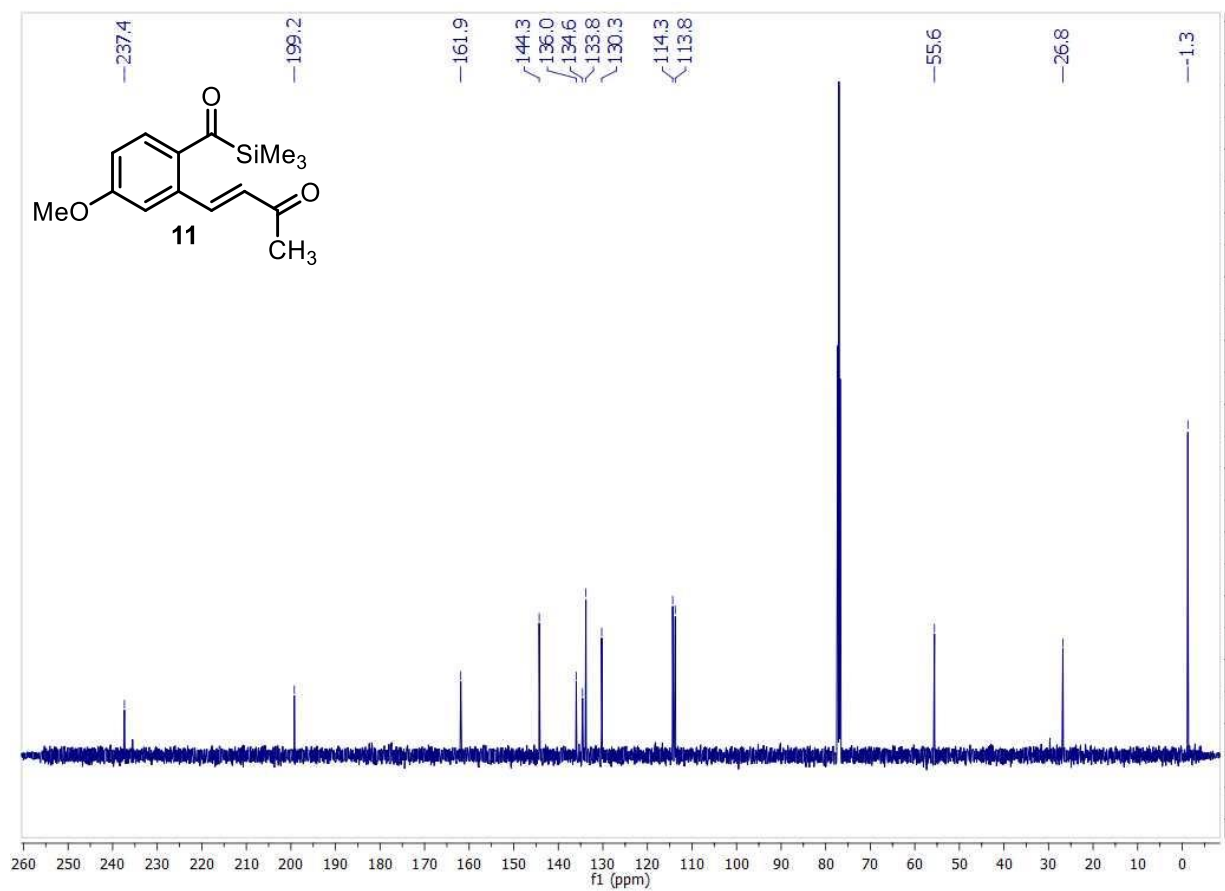
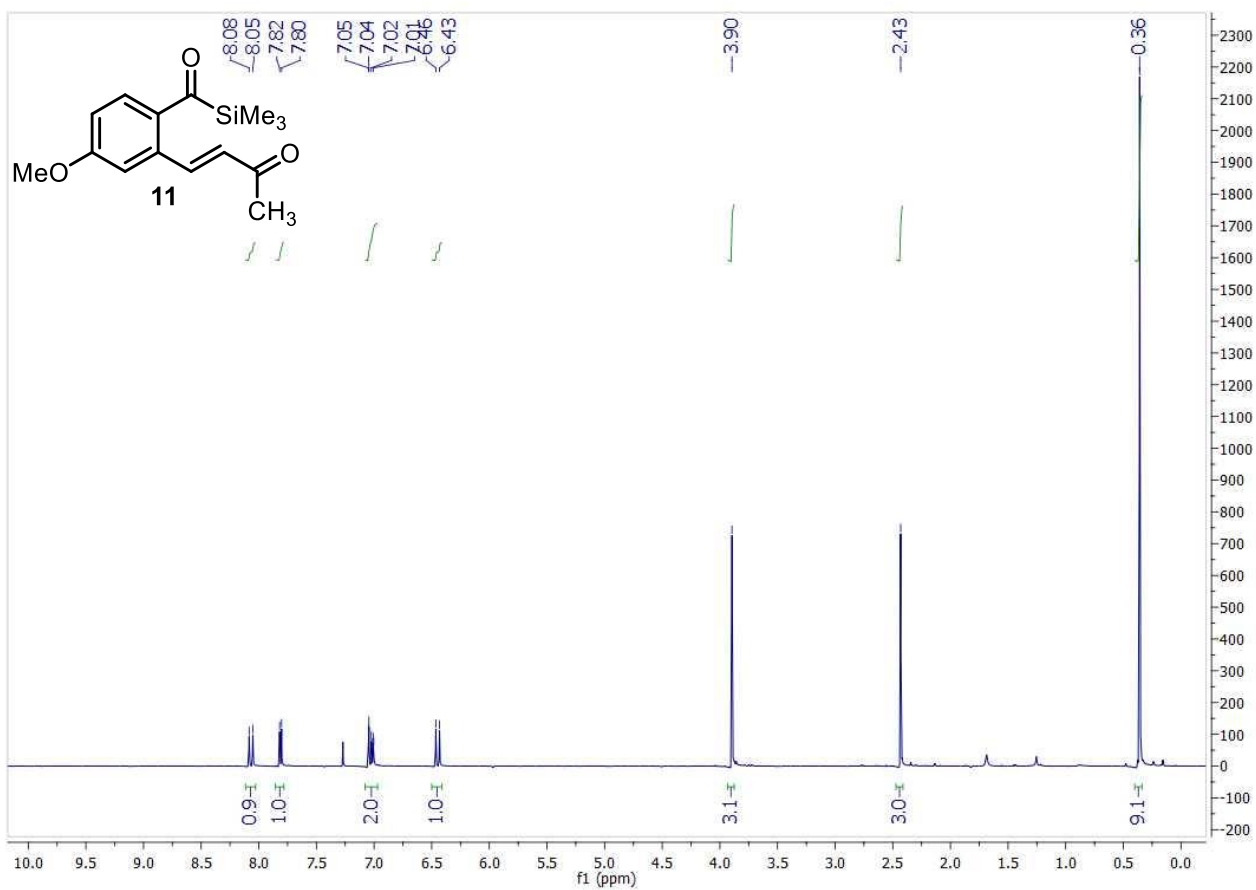


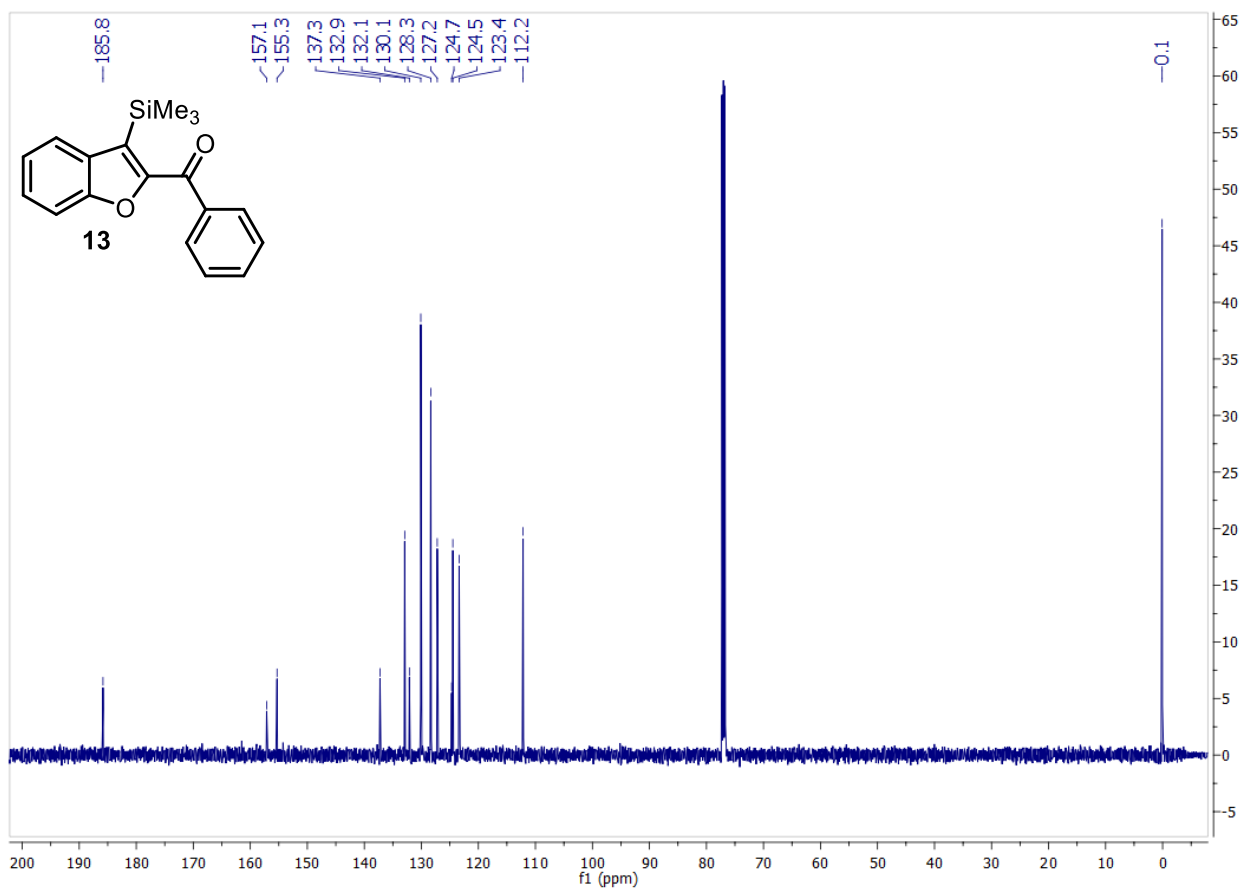
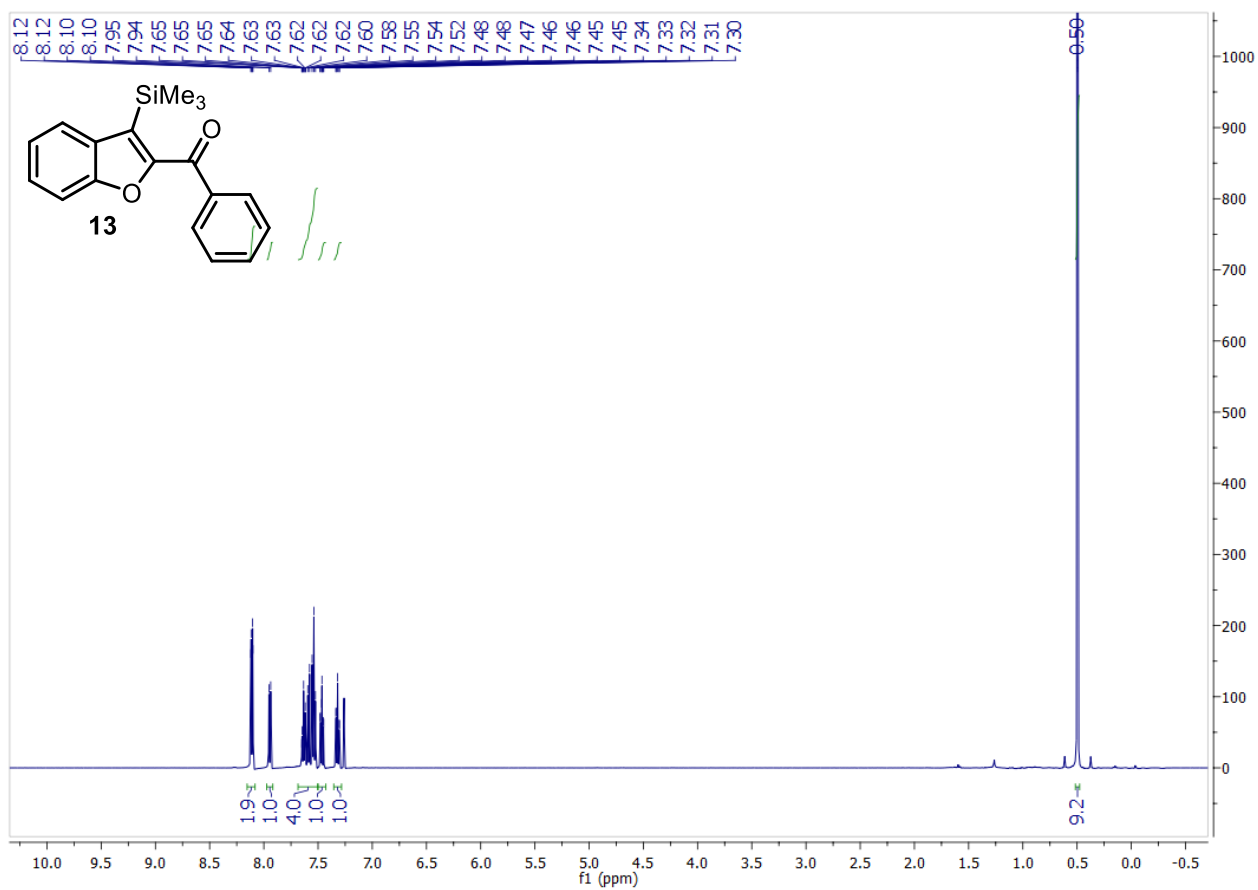












X-Ray Crystallography Data for Compound 8a

The deposition number for **8a** at the Cambridge Crystallographic Data Centre is CCDC 2080244

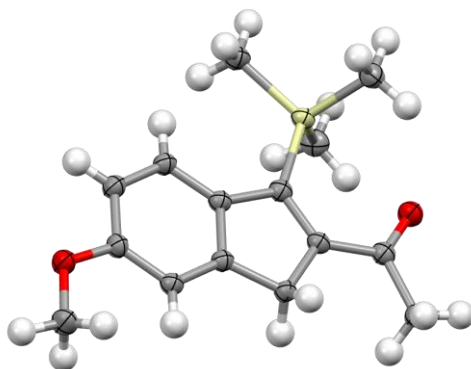


Figure S1. Ortep drawing of compound **8a** with ellipsoids at 50% occupancy

Table S2. Crystal data and structure refinement for 8a.

Identification code	DP_18x
Empirical formula	C ₁₅ H ₂₀ O ₂ Si
Formula weight	260.40
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	Pnma
a/Å	16.140(3)
b/Å	7.0200(14)
c/Å	12.550(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	1422.0(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.216
μ/mm^{-1}	0.158
F(000)	560.0
Crystal size/mm ³	0.2 × 0.05 × 0.02
Radiation	Synchrotron ($\lambda = 0.710755$)
2 θ range for data collection/ $^\circ$	4.112 to 57.256
Index ranges	-21 ≤ h ≤ 21, -9 ≤ k ≤ 9, -16 ≤ l ≤ 16
Reflections collected	33258
Independent reflections	1869 [$R_{\text{int}} = 0.0384$, $R_{\text{sigma}} = 0.0143$]
Data/restraints/parameters	1869/0/110
Goodness-of-fit on F ²	1.176
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0465$, $wR_2 = 0.1530$
Final R indexes [all data]	$R_1 = 0.0587$, $wR_2 = 0.2032$
Largest diff. peak/hole / e Å ⁻³	0.53/-0.76

X-Ray Crystallography Data for Compound 9a

The deposition number for **9a** at the Cambridge Crystallographic Data Centre is CCDC 2080243

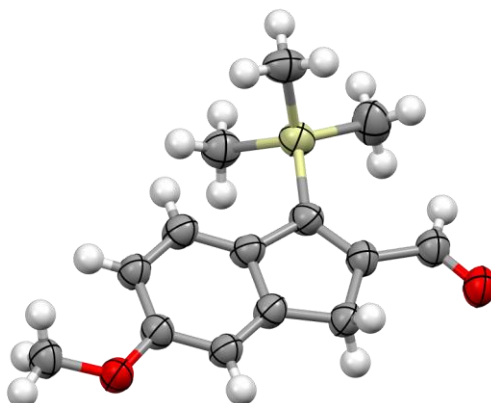


Figure S2. Ortep drawing of compound **9a** with ellipsoids at 50% occupancy

Table S3. Crystal data and structure refinement for **9a**.

Identification code	DP-200A
Empirical formula	C ₁₄ H ₁₈ O ₂ Si
Formula weight	246.37
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.9100(14)
b/Å	16.060(3)
c/Å	12.250(3)
α /°	90
β /°	91.67(3)
γ /°	90
Volume/Å ³	1358.9(5)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.204
μ/mm^{-1}	0.161
F(000)	528.0
Crystal size/mm ³	0.25 × 0.2 × 0.2
Radiation	Synchrotron ($\lambda = 0.71073$)
2 θ range for data collection/°	4.182 to 57.402
Index ranges	$-8 \leq h \leq 9$, $-19 \leq k \leq 21$, $-16 \leq l \leq 15$
Reflections collected	30967
Independent reflections	3127 [$R_{\text{int}} = 0.0557$, $R_{\text{sigma}} = 0.0279$]
Data/restraints/parameters	3127/0/158
Goodness-of-fit on F ²	1.605
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1173$, $wR_2 = 0.3125$
Final R indexes [all data]	$R_1 = 0.1549$, $wR_2 = 0.3950$
Largest diff. peak/hole / e Å ⁻³	1.10/-0.89