

Supporting Information

For the article entitled

Synthesis of silyl indenenes by ruthenium catalyzed aldehyde and acylsilane enabled C–H alkylation/cyclization

Tao Zhang,^{a,b} Cheng Zhang,^b Xiunan Lu,^b Chengxing Peng,^b Yawei Zhang,^b Xiong Zhu,^{a*} Guofu Zhong,^{b,c*} and Jian Zhang^{b*}

^a School of Engineering, China Pharmaceutical University, No. 24, Tongjiaxiang, Nanjing 210009, Jiangsu Province, PR China.

^b College of Material, Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education, Hangzhou Normal University, Hangzhou, 311121 Zhejiang, China.

^c Department of Chemistry, Eastern Institute for Advanced Study, Ningbo 315200, Zhejiang, China.

E-mail: cpuzx@foxmail.com; guofuzhong@eias.ac.cn; zhangjian@hznu.edu.cn

Supporting Information

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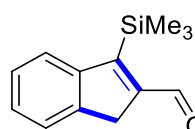
General Considerations

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F 254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^1H NMR) were recorded on Bruker AMX 500 spectrophotometer (CDCl_3 as solvent). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe_4 (δ 0.0) and relative to the signal of chloroform-d (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr plates on a Bio-Rad FTS165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$, AgSbF_6 and $\text{Cu}(\text{OAc})_2$ were purchased from TCI and used directly. Other reagents, unless otherwise noted below, are commercially available from TCI, Energy Chemical, Alfa Aesar (China) Chemical Co. Ltd. and used without further purification. Aroylsilanes were prepared by reported methods.

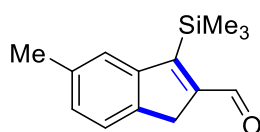
General Procedure for the Ru-Catalyzed Synthesis of Sily Indenes 3

A screw-cap vial was charged with [Ru(*p*-cymene)Cl₂]₂ (5 mol%, 0.01 mmol), AgSbF₆ (20 mol%, 0.04 mmol), Cu(OAc)₂ (1.3 equiv, 0.26 mmol) and DCM (1.0 mL). Then, aroylsilane **1** (1.0 equiv, 0.2 mmol) and acrolein **2** (3.0 equiv, 0.6 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography for separation (EtOAc/petroleum ether mixtures).

Characterization Data

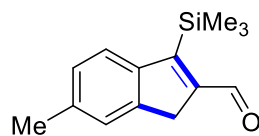


3-(Trimethylsilyl)-1H-indene-2-carbaldehyde (3aa) Following the general procedure, **3aa** was obtained as a white solid, m.p.: 60.5-62.8 °C, yield = 73%. ¹H NMR (500 MHz, CDCl₃): δ = 10.26 (s, 1H), 7.77-7.73 (m, 1H), 7.56-7.54 (m, 1H), 7.38-7.33 (m, 2H), 3.72 (s, 2H), 0.51 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.56, 160.80, 153.59, 146.31, 143.54, 127.03, 125.57, 124.24, 123.48, 37.26, 0.21. HRMS (ESI): m/z for C₁₃H₁₆OSi [M+H]⁺: 217.1043, found: 217.1042. FTIR (KBr, cm⁻¹): 3450.19, 3410.97, 2956.89, 1643.81, 1658.52, 1538.35, 1402.49, 844.89.

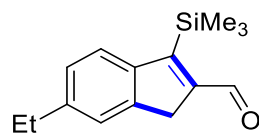


5-Methyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ba)

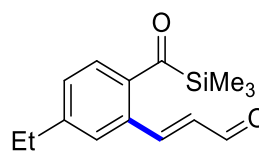
Following the general procedure, **3ba** was obtained as a yellow solid, m.p.: 57.3-59.9 °C, yield = 68%. ¹H NMR (500 MHz, CDCl₃): δ = 10.24 (s, 1H), 7.54 (s, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 3.68 (s, 2H), 2.44 (s, 3H), 0.51 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.55, 160.84, 153.81, 146.54, 140.59, 135.09, 128.02, 124.68, 123.05, 36.76, 20.46, 0.21. HRMS (ESI): m/z for C₁₄H₁₈OSi [M+H]⁺: 231.1200, found: 231.1211. FTIR (KBr, cm⁻¹): 3444.57, 3176.13, 1659.72, 1651.56, 1455.14, 1402.44, 1253.81, 1015.45, 840.67, 802.07.



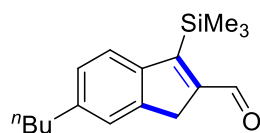
6-Methyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ca) Following the general procedure, **3ca** was obtained as a yellow solid, m.p.: 77.4-78.2 °C, yield = 52%. ¹H NMR (500 MHz, CDCl₃): δ = 10.22 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.38 (s, 1H), 7.17 (d, *J* = 8.0 Hz, 1H), 3.68 (s, 2H), 2.42 (s, 3H), 0.49 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.54, 161.08, 152.83, 143.99, 143.80, 137.50, 126.55, 124.24, 123.96, 36.97, 20.53, 0.21. HRMS (ESI): *m/z* for C₁₄H₁₈OSi [M+H]⁺: 231.1200, found: 231.1199. FTIR (KBr, cm⁻¹): 3507.43, 3441.30, 3175.56, 3144.15, 1651.19, 1644.34, 1402.01, 1247.33, 844.90.



6-Ethyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3da) Following the general procedure, **3da** was obtained as a yellow solid, m.p.: 60.0-60.8 °C, yield = 62%. ¹H NMR (500 MHz, CDCl₃): δ = 10.22 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 2H), 2.74-2.69 (q, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.5 Hz, 3H), 0.50 (s, 1H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.50, 161.09, 152.95, 144.06, 144.04, 143.94, 125.46, 124.09, 123.02, 37.02, 27.93, 14.64, 0.21. HRMS (ESI): *m/z* for C₁₅H₂₀OSi [M+H]⁺: 245.1356, found: 245.1360. FTIR (KBr, cm⁻¹): 3444.29, 3417.44, 3168.01, 2966.48, 1651.10, 1402.79, 1246.27, 843.90.

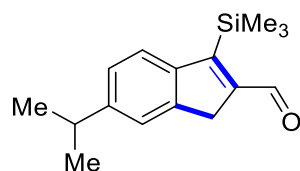


(E)-3-(5-Ethyl-2-((trimethylsilyl) carbonyl) phenyl) acrylaldehyde (5da) Following the general procedure, **3da** was obtained as a brown liquid, yield = 8%. ¹H NMR (500 MHz, CDCl₃): δ = 9.74 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 16.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.45 (s, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 6.57 (q, *J* = 8.0 Hz, 1H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H), 1.26 (s, 2H), 0.36 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 195.97, 154.26, 150.21, 141.07, 134.17, 132.82, 132.38, 131.25, 129.73, 30.53, 16.77, 0.21. HRMS (ESI): *m/z* for C₁₅H₂₀O₂Si [M+H]⁺: 261.1305, found: 261.1310. FTIR (KBr, cm⁻¹): 3444.47, 3416.34, 3171.24, 2923.44, 2358.73, 1643.03, 1632.00, 1401.94.



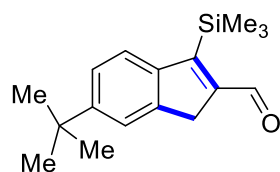
6-Butyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ea) Following

the general procedure, **3ea** was obtained as a yellow liquid, yield = 65%. ^1H NMR (500 MHz, CDCl_3): δ = 10.22 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.38 (s, 1H), 7.17 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 3.69 (s, 2H), 2.67 (t, J = 7.5 Hz, 2H), 1.66-1.60 (m, 2H), 1.41-1.35 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H), 0.50 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.51, 161.14, 152.89, 144.02, 143.93, 142.62, 125.98, 123.98, 123.54, 36.98, 34.67, 32.64, 21.26, 12.82, 0.21. HRMS (ESI): m/z for $\text{C}_{17}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 295.1489, found: 295.1498. FTIR (KBr, cm^{-1}): 3472.50, 3444.54, 3417.37, 3175.09, 1651.34, 1644.55, 1504.69, 1402.46.



6-Isopropyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3fa)

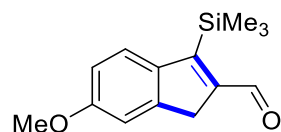
Following the general procedure, **3fa** was obtained as a yellow solid, m.p.: 50.2-52.4 °C, yield = 67%. ^1H NMR (500 MHz, CDCl_3): δ = 10.23 (d, J = 3.5 Hz, 1H), 7.68 (dd, J = 8.5 Hz, J = 3.0 Hz, 1H), 7.43 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 3.70 (d, J = 2.0 Hz, 2H), 3.02-2.93 (m, 1H), 1.29 (dd, J = 7.0 Hz, J = 2.0 Hz, 6H), 0.50 (d, J = 2.5 Hz, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.47, 161.06, 153.04, 148.56, 144.23, 144.01, 124.10, 124.08, 121.50, 37.07, 33.19, 22.92, 0.21. HRMS (ESI): m/z for $\text{C}_{16}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 281.1332, found: 281.1332. FTIR (KBr, cm^{-1}): 3452.60, 3417.27, 2958.38, 1658.87, 1402.63, 1384.70, 1251.86, 841.72.



6-(Tert-butyl)-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ga)

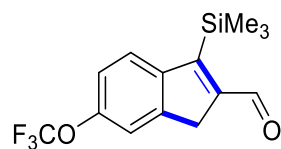
Following the general procedure, **3ga** was obtained as a yellow liquid, yield = 61%. ^1H NMR (500 MHz, CDCl_3): δ = 10.23 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 0.5 Hz, 1H), 7.41 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 3.71 (s, 2H), 1.36 (s, 9H), 0.50 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.49, 161.01, 153.21, 150.79, 143.79, 143.73, 123.80, 122.90, 120.45, 37.22, 33.85, 30.30, 0.21. HRMS (ESI): m/z for $\text{C}_{17}\text{H}_{24}\text{OSi}$ $[\text{M}+\text{H}]^+$: 273,1669, found: 273.1673. FTIR (KBr, cm^{-1}): 3444.53,

3417.81, 3174.82, 1659.95, 1651.53, 1455.12, 1398.33, 840.03.



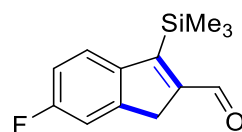
6-Methoxy-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ha)

Following the general procedure, **3ha** was obtained as a yellow solid, m.p.: 121.8-123.1 °C, yield = 51%. ¹H NMR (500 MHz, CDCl₃): δ = 10.17 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.91 (dd, *J* = 8.5 Hz, *J* = 2.5 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 2H), 0.49 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 187.98, 161.23, 159.31, 151.83, 146.17, 139.4, 125.07, 112.26, 108.63, 54.39, 37.22, 0.21. HRMS (ESI): *m/z* for C₁₄H₁₈O₂Si [M+H]⁺: 247.1149, found: 247.1148. FTIR (KBr, cm⁻¹): 3584.82, 3472.65, 3444.32, 3175.42, 1659.84, 1644.79, 1402.44, 1182.43.



6-(Trifluoromethoxy)-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ia)

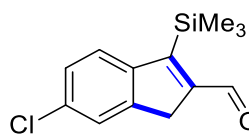
Following the general procedure, **3ia** was obtained as a white solid, m.p.: 75.6-76.9 °C, yield = 62%. ¹H NMR (500 MHz, CDCl₃): δ = 10.24 (s, 1H), 7.74 (d, *J* = 11.0 Hz, 1H), 7.41 (s, 1H), 7.22 (dd, *J* = 8.5 Hz, *J* = 1.0 Hz, 1H), 3.75 (s, 2H), 0.51 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.25, 159.46, 154.47, 148.24 (d, *J*_{C-F} = 1.6 Hz), 145.56, 144.97, 125.07, 119.49 (q, *J*_{C-F} = 255.9 Hz), 118.62, 116.34, 37.66, 0.22. HRMS (ESI): *m/z* for C₁₄H₁₅F₃O₂Si [M+Na]⁺: 323.0686, found: 323.0694. FTIR (KBr, cm⁻¹): 3473.08, 3416.85, 3384.55, 3225.49, 1659.96, 1402.54, 1254.56, 1158.41, 840.66.



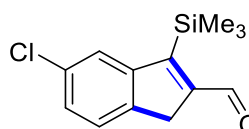
6-Fluoro-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ja)

Following the general procedure, **3ja** was obtained as a white solid, m.p.: 98.4-105.1 °C, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 10.21 (s, 1H), 7.68 (dd, *J* = 8.5 Hz, *J* = 5.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.06 (td, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 3.71 (s, 2H), 0.50 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.13, 162.07 (d, *J*_{C-F} = 247.4 Hz), 160.02, 153.51 (d, *J*_{C-F} = 3.9 Hz), 146.16 (d, *J*_{C-F} = 9.1 Hz), 142.44 (d, *J*_{C-F} = 2.3 Hz), 125.30 (d, *J*_{C-F} = 9.1 Hz), 113.08 (d, *J*_{C-F} = 23 Hz), 110.92 (d, *J*_{C-F} = 22.8 Hz), 37.49 (d, *J*_{C-F} = 2.5 Hz), 0.21. HRMS (ESI): *m/z* for C₁₃H₁₅FOSi [M+H]⁺:

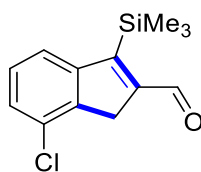
235.0949, found: 235.0954. FTIR (KBr, cm^{-1}): 3472.65, 3444.32, 3175.42, 1659.84, 1651.59, 1402.44, 1182.43, 841.78.



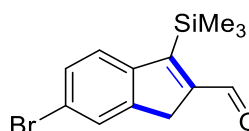
6-Chloro-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ka) Following the general procedure, **3ka** was obtained as a white solid, m. p.: 92.7-93.2 °C, yield = 58%. ^1H NMR (500 MHz, CDCl_3): δ = 10.23 (s, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.53 (s, 1H), 7.33 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H), 3.70 (s, 2H), 0.50 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.40, 159.80, 153.72, 145.29, 144.89, 133.37, 126.09, 125.03, 123.92, 37.32, 0.22. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{15}\text{ClOSi}$ $[\text{M}+\text{Na}]^+$: 273.0473, found: 273.0471. FTIR (KBr, cm^{-1}): 3443.88, 3417.49, 3175.63, 1660.84, 1402.39, 1241.12, 845.57, 818.75.



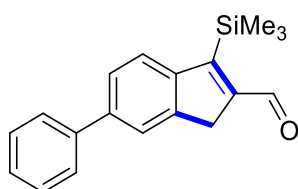
5-Chloro-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3la) Following the general procedure, **3la** was obtained as a yellow liquid, yield = 28%. ^1H NMR (500 MHz, CDCl_3): δ = 10.25 (s, 1H), 7.68 (d, J = 1.5 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.33 (dd, J = 8.0 Hz, J = 1.5 Hz, 1H), 3.69 (s, 2H), 0.51 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.48, 159.60, 154.91, 148.01, 147.70, 131.64, 126.98, 124.43, 124.16, 37.06, 0.21. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{15}\text{ClOSi}$ $[\text{M}+\text{Na}]^+$: 273.0473, found: 273.0475. FTIR (KBr, cm^{-1}): 3452.07, 3423.13, 3385.24, 2922.98, 2359.82, 1651.58, 1399.27, 841.79.



7-Chloro-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3la') Following the general procedure, **3la'** was obtained as a yellow liquid, yield = 17%. ^1H NMR (500 MHz, CDCl_3): δ = 10.26 (s, 1H), 7.64 (dd, J = 7.5 Hz, J = 1.5 Hz, 1H), 7.35-7.30 (m, 2H), 3.75 (s, 2H), 0.51 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): δ = 188.38, 160.08, 153.69, 147.83, 141.54, 129.72, 127.34, 127.05, 122.67, 37.39, 0.21. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{15}\text{ClOSi}$ $[\text{M}+\text{Na}]^+$: 273.0473, found: 273.0476. FTIR (KBr, cm^{-1}): 3474.76, 3449.87, 3424.16, 2985.53, 2956.17, 2354.39, 1644.84, 1633.64, 1402.65.

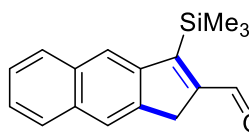


6-Bromo-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ma) Following the general procedure, **3ma** was obtained as a yellow solid, m.p.: 118.1-121.0 °C, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 10.24 (s, 1H), 7.68 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 3.69 (s, 2H), 0.50 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.38, 159.75, 153.64, 145.53, 145.30, 128.94, 126.85, 125.35, 121.66, 37.33, 0.22. HRMS (ESI): *m/z* for C₁₃H₁₅BrOSi [M+Na]⁺: 316.9968, found: 316.9952. FTIR (KBr, cm⁻¹): 3452.10, 3417.62, 3209.15, 1657.27, 1652.02, 1402.74, 844.84, 817.34.



6-Phenyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3na)

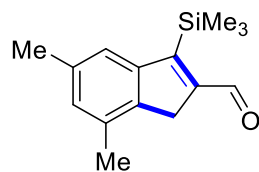
Following the general procedure, **3na** was obtained as a yellow solid, m.p.: 138.5-140.7 °C, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 10.28 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 3.80 (s, 2H), 0.55 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.42, 160.59, 153.70, 145.53, 144.32, 140.19, 139.68, 127.74, 126.45, 126.11, 124.79, 124.45, 122.15, 37.33, 0.21. HRMS (ESI): *m/z* for C₁₉H₂₀OSi [M+H]⁺: 293.1356, found: 293.1362. FTIR (KBr, cm⁻¹): 3472.61, 3444.42, 3175.51, 1651.32, 1645.16, 1402.35, 1247.68, 849.32, 769.88.



3-(Trimethylsilyl)-1H-cyclopenta[b]naphthalene-2-carbaldehyde (3oa)

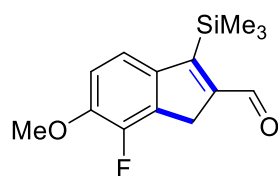
Following the general procedure, **3oa** was obtained as a yellow solid, m.p.: 141.9-143.0 °C, yield = 64%. ¹H NMR (500 MHz, CDCl₃): δ = 10.32 (s, 1H), 8.17 (s, 1H), 7.91 (d, *J* = 8 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.51-7.45 (m, 2H), 3.82 (s, 2H), 0.58 (t, *J* = 1.0 Hz, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.76, 160.11, 154.21, 145.15, 139.85, 132.05, 131.31, 127.47, 126.36, 125.26, 124.23, 123.47, 121.55, 36.12, 0.21. HRMS (ESI): *m/z* for C₁₇H₁₈OSi [M+H]⁺: 267.1200, found: 267.1192. FTIR (KBr, cm⁻¹): 3472.65, 3444.32, 3175.42, 1651.59, 1644.79, 1402.44, 1182.43,

841.78.



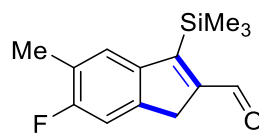
5,7-Dimethyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3pa)

Following the general procedure, **3pa** was obtained as a white solid, m.p.: 106.0-107.8 °C, yield = 25%. ¹H NMR (500 MHz, CDCl₃): δ = 10.24 (s, 1H), 7.39 (s, 1H), 7.02 (s, 1H), 3.57 (s, 2H), 2.40 (s, 3H), 2.34 (s, 3H), 0.50 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.57, 161.27, 153.1, 146.19, 139.46, 135.50, 132.37, 129.14, 122.34, 35.74, 20.35, 17.62, 0.21. HRMS (ESI): m/z for C₁₅H₂₀OSi [M+H]⁺: 245.1356, found: 245.1358. FTIR (KBr, cm⁻¹): 3444.57, 3417.72, 3175.22, 1651.17, 1645.31, 1633.64, 1455.08, 1402.27.



5-Fluoro-6-methoxy-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3qa)

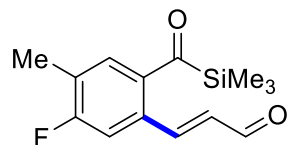
Following the general procedure, **3ra** was obtained as a white solid, m.p.: 173.4-173.8 °C, yield = 74%. ¹H NMR (500 MHz, CDCl₃): δ = 10.18 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 6.98 (t, *J* = 8.0 Hz, 1H), 3.94 (s, 3H), 3.72 (s, 2H), 1.25 (s, 3H), 0.49 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 187.91, 160.26, 152.43 (d, *J*_{C-F} = 1.0 Hz), 147.6 (d, *J*_{C-F} = 247.4 Hz), 147.06 (d, *J*_{C-F} = 10.4 Hz), 141.33 (d, *J*_{C-F} = 4.0 Hz), 130.27 (d, *J*_{C-F} = 14.3 Hz), 120.23 (d, *J*_{C-F} = 3.6 Hz), 111.34, 55.54, 33.90, 0.21. HRMS (ESI): m/z for C₁₄H₁₇FO₂Si [M+H]⁺: 265.1055, found: 265.1060. FTIR (KBr, cm⁻¹): 3416.48, 1682.17, 1634.67, 1620.57, 803.56, 618.45, 480.91.



6-Fluoro-5-methyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3ra)

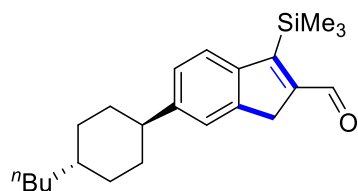
Following the general procedure, **3sa** was obtained as a white solid, m.p.: 105.1-105.7 °C, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 10.19 (s, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.19 (d, *J* = 7.19 Hz, 1H), 3.67 (s, 2H), 2.34 (s, 3H), 0.51 (d, *J* = 1.0 Hz, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.06, 160.58 (d, *J*_{C-F} = 246.5 Hz), 160.17, 153.48 (d, *J*_{C-F} = 3.9 Hz), 143.38 (d, *J*_{C-F} = 11.3 Hz), 142.22 (d, *J*_{C-F} = 2.5 Hz), 126.55 (d, *J*_{C-F} = 6.3 Hz), 122.38 (d, *J*_{C-F} = 18.8 Hz), 110.31 (d, *J*_{C-F} =

23.8 Hz), 37.15 (d, $J_{C-F} = 2.5$ Hz), 13.92 (d, $J_{C-F} = 3.8$ Hz), 0.21. HRMS (ESI): m/z for $C_{14}H_{17}FOSi$ $[M+Na]^+$: 271.0925, found: 271.0919. FTIR (KBr, cm^{-1}): 3416.49, 1651.53, 1634.53, 1615.59, 838.39, 618.38, 469.84.

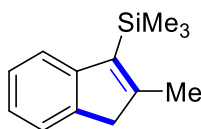


(E)-3-(5-Fluoro-4-methyl-2-((trimethylsilyl)carbonyl) phenyl) acrylaldehyde (5ra) Following the general procedure, **5ra** was obtained as a yellow solid, m.p.:

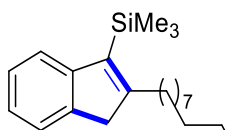
88.3-89.1 °C, yield = 6%. 1H NMR (500 MHz, $CDCl_3$): $\delta = 9.72$ (d, $J = 7.5$ Hz, 1H), 7.90 (d, $J = 16.0$ Hz, 1H), 7.60 (d, $J = 7.0$ Hz, 1H), 6.52 (q, $J = 8.0$ Hz, 1H), 2.39 (s, 3H), 0.37 (s, 9H). ^{13}C NMR (125 Hz, $CDCl_3$): $\delta = 241.23$, 195.54, 164.2 (d, $J_{C-F} = 251.4$ Hz), 152.10 (d, $J_{C-F} = 1.8$ Hz), 139.95 (d, $J_{C-F} = 3.4$ Hz), 135.87 (d, $J_{C-F} = 6.6$ Hz), 134.23 (d, $J_{C-F} = 8.3$ Hz), 132.63, 129.08 (d, $J_{C-F} = 17.9$ Hz), 116.57 (d, $J_{C-F} = 23.6$ Hz), 16.52 (d, $J_{C-F} = 2.9$ Hz), 0.21. HRMS (ESI): m/z for $C_{14}H_{17}FO_2Si$ $[M+H]^+$: 265.1055, found: 265.1057. FTIR (KBr, cm^{-1}): 3441.64, 3418.32, 2900.10, 2359.36, 2329.81, 1682.78, 1402.63, 845.11.



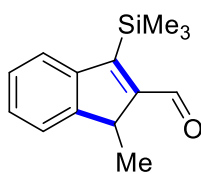
6-((1s,4r)-4-Butylcyclohexyl)-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (3sa) Following the general procedure, **3ta** was obtained as a yellow solid, m.p.: 49.6-55.2 °C, yield = 6%. 1H NMR (500 MHz, $CDCl_3$): $\delta = 10.22$ (d, $J = 2.0$ Hz, 1H), 7.66 (dd, $J = 8.0$ Hz, $J = 1.5$ Hz, 1H), 7.42 (s, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 3.69 (s, 2H), 2.53 (t, $J = 12.0$ Hz, 1H), 1.90 (t, $J = 10.5$ Hz, 4H), 1.53-1.45 (m, 2H), 1.31 (d, $J = 3.0$ Hz, 4H), 1.25 (d, $J = 6.5$ Hz, 3H), 1.10-1.03 (m, 2H), 0.92-0.91 (m, 3H), 0.49 (d, $J = 2.0$ Hz, 9H). ^{13}C NMR (125 Hz, $CDCl_3$): $\delta = 188.44$, 161.09, 153.00, 147.59, 144.24, 143.95, 124.50, 124.05, 121.92, 43.72, 37.06, 36.13, 35.94, 33.26, 32.42, 28.09, 21.87, 13.03, 0.21. HRMS (ESI): m/z for $C_{23}H_{34}OSi$ $[M+Na]^+$: 377.2271, found: 377.2277. FTIR (KBr, cm^{-1}): 3452.48, 3417.55, 2955.86, 2921.81, 2851.66, 1659.70, 1393.30, 840.93.



Trimethyl (2-methyl-1H-inden-3-yl) silane (4ab) Following the general procedure, **4ab** was obtained as a brown liquid, yield = 71%. ¹H NMR (500 MHz, CDCl₃): δ = 7.42-7.37 (dd, *J* = 17.0 Hz, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 3.36 (s, 2H), 2.22 (s, 3H), 0.35 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 155.43, 149.71, 142.82, 135.16, 125.55, 122.77, 122.63, 120.83, 45.95, 17.08, 0.21. HRMS (ESI): *m/z* for C₁₃H₁₈Si [M+Na]⁺: 225.1070, found: 225.1078. FTIR (KBr, cm⁻¹): 3473.09, 3453.12, 3225.51, 1651.59, 1644.80, 1633.88, 1402.39, 1385.06.

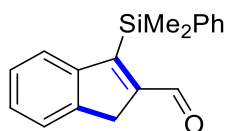


(2-Decyl-1H-inden-3-yl)trimethylsilane (4ac) Following the general procedure, **4ad** was obtained as a yellow liquid, yield = 51%. ¹H NMR (500 MHz, CDCl₃): δ = 7.44-7.41 (m, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.22-7.19 (m, 1H), 7.10-7.06 (m, 1H), 3.39 (s, 2H), 2.58-2.54 (m, 2H), 1.53 (s, 2H), 1.31-1.26 (m, 14H), 0.89-0.86 (m, 3H), 0.35 (d, *J* = 4.5 Hz, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 160.55, 149.31, 142.80, 134.82, 125.33, 122.59, 122.58, 120.87, 31.32, 31.19, 30.51, 29.25, 29.04, 28.75, 22.10, 13.53, 0.21. HRMS (ESI): *m/z* for C₂₂H₃₆Si [M+Na]⁺: 351.2478, found: 351.2479. FTIR (KBr, cm⁻¹): 3444.37, 3417.69, 3224.58, 1651.39, 1644.67, 1633.68, 1402.64, 1384.98.

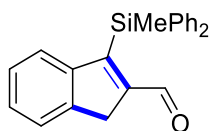


1-Methyl-3-(trimethylsilyl)-1H-indene-2-carbaldehyde (4ad)

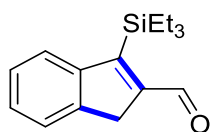
Following the general procedure, **4ae** was obtained as a yellow liquid, yield = 68%. ¹H NMR (500 MHz, CDCl₃): δ = 10.25 (s, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 32.0 Hz, 1H), 7.40-7.32 (m, 2H), 3.82 (q, *J* = 7.5 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H), 0.50 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 188.58, 159.88, 158.13, 150.21, 144.48, 127.13, 125.61, 124.23, 122.34, 43.64, 15.61, 0.21. HRMS (ESI): *m/z* for C₁₄H₁₈OSi [M+H]⁺: 231.1200, found: 231.1208. FTIR (KBr, cm⁻¹): 3444.57, 3417.74, 3159.92, 2358.08, 1651.59, 1402.60, 1251.77, 841.25.



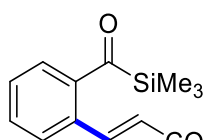
3-(Dimethyl(phenyl)silyl)-1H-indene-2-carbaldehyde (3ua) Following the general procedure, **3ua** was obtained as a yellow liquid, yield = 55%. ^1H NMR (500 MHz, CDCl_3): δ = 9.96 (s, 1H), 7.58-7.57 (m, 1H), 7.55(d, J = 7.5 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.41-7.37 (m, 2H), 7.33 (t, J = 7.0 Hz, 1H), 7.25-7.22 (m, 1H), 3.75 (s, 2H), 0.75 (s, 6H). ^{13}C NMR (125 Hz, CDCl_3): δ = 189.92, 159.70, 155.75, 147.43, 144.57, 137.29, 133.86, 129.86, 128.39, 128.16, 126.70, 125.71, 124.51, 38.58, 0.22. HRMS (ESI): m/z for $\text{C}_{18}\text{H}_{18}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 301.1019, found: 301.1027. FTIR (KBr, cm^{-1}): 3456.29, 3417.61, 2935.88, 2851.09, 2361.94, 2339.90, 1658.84, 1402.23.



3-(Methyldiphenylsilyl)-1H-indene-2-carbaldehyde (3va) Following the general procedure, **3va** was obtained as a yellow liquid, yield = 68%. ^1H NMR (500 MHz, CDCl_3): δ = 9.54 (s, 1H), 7.58-7.54 (m, 5H), 7.45-7.42 (m, 2H), 7.39-7.36 (m, 4H), 7.32-7.29 (m, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 3.79 (s, 2H), 1.02 (s, 3H). ^{13}C NMR (125 Hz, CDCl_3): δ = 191.80, 159.17, 158.23, 149.01, 145.96, 136.80, 136.44, 131.67, 129.97, 129.67, 128.17, 127.65, 125.91, 40.30, 0.22. HRMS (ESI): m/z for $\text{C}_{23}\text{H}_{20}\text{OSi}$ $[\text{M}+\text{Na}]^+$: 363.1176, found: 363.1168. FTIR (KBr, cm^{-1}): 3443.58, 3416.79, 1682.25, 1659.24, 1651.52, 1634.20, 1634.20, 1402.54.

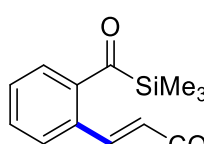


3-(Triethylsilyl)-1H-indene-2-carbaldehyde (3wa) Following the general procedure, **3wa** was obtained as a yellow liquid, yield = 68%. ^1H NMR (500 MHz, CDCl_3): δ = 10.18 (d, J = 2.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 6.5 Hz, 1H), 7.38-7.33 (m, 2H), 3.75 (s, 2H), 1.02 (d, J = 2.0 Hz, 15H). ^{13}C NMR (125 Hz, CDCl_3): δ = 185.12, 154.79, 151.36, 142.79, 139.69, 123.15, 121.73, 120.34, 119.53, 33.57, 2.49, 0.21. HRMS (ESI): m/z for $\text{C}_{16}\text{H}_{22}\text{OSi}$ $[\text{M}+\text{H}]^+$: 259.1513, found: 259.1512. FTIR (KBr, cm^{-1}): 3455.33, 3433.69, 3206.49, 1679.61, 1649.52, 1642.94, 1537.47.



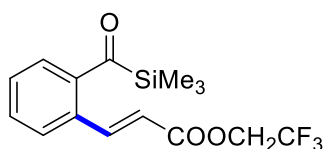
(E)-1-(2-((trimethylsilyl) carbonyl) phenyl) pent-1-en-3-one (5af)

Following the general procedure, **5af** was obtained as a yellow liquid, yield = 19%. ¹H NMR (500 MHz, CDCl₃): δ = 7.68 (d, *J* = 16.5 Hz, 1H), 7.65-7.61 (m, 2H), 7.51-7.47 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 2.73 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H), 0.33 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 243.67, 203.10, 144.54, 143.48, 134.69, 133.15, 131.34, 131.29, 131.02, 130.10, 35.21, 10.07, 0.21.



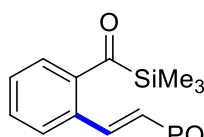
Methyl (E)-3-(2-((trimethylsilyl) carbonyl) phenyl) acrylate (5ag)

Following the general procedure, **5ag** was obtained as a yellow liquid, yield = 31%. ¹H NMR (500 MHz, CDCl₃): δ = 7.95 (d, *J* = 16.0 Hz, 1H), 7.60-7.57 (m, 2H), 7.50-7.46 (m, 2H), 6.28 (d, *J* = 16.0 Hz, 1H), 3.81 (d, *J* = 1.5 Hz, 3H), 0.32 (d, *J* = 1.0 Hz, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 243.90, 168.98, 145.76, 145.09, 134.36, 133.08, 131.46, 130.84, 130.17, 122.53, 53.77, 0.21.



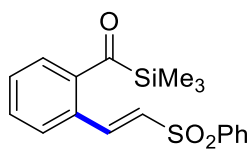
2,2,2-Trifluoroethyl(E)-3-(2-((trimethylsilyl) carbonyl) phenyl) acrylate (5ah)

Following the general procedure, **5ah** was obtained as a yellow liquid, yield = 66%. ¹H NMR (500 MHz, CDCl₃): δ = 8.03 (d, *J* = 16.0 Hz, 1H), 7.61-7.59 (m, 2H), 7.52-7.47 (m, 2H), 6.31 (dd, *J* = 16.0 Hz, *J* = 1.0 Hz, 1H), 4.58 (q, *J* = 8.5 Hz, 2H), 0.31 (d, *J* = 1.0 Hz, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 243.67, 166.80, 148.41, 145.20, 133.91, 133.24, 131.96, 131.10, 130.35, 125.13 (q, *J*_{C-F} = 275.6 Hz), 120.39, 62.43 (q, *J*_{C-F} = 36.4 Hz), 0.21. HRMS (ESD): *m/z* for C₁₅H₁₇F₃O₃Si [M+H]⁺: 331.0972, found: 331.0974. FTIR (KBr, cm⁻¹): 3441.26, 3423.74, 3199.39, 2921.62, 2851.15, 1633.67, 1539.48, 1402.81.

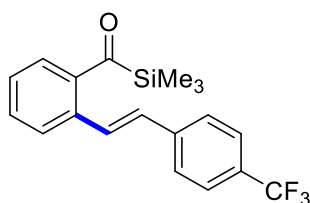


Diethyl (E)-2-((trimethylsilyl) carbonyl) styryl phosphonate

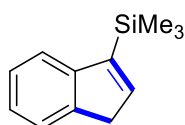
(5ai) Following the general procedure, **5ai** was obtained as a yellow solid, m.p.: 74.2 °C, yield = 69%. ¹H NMR (500 MHz, CDCl₃): δ = 7.71-7.64 (dd, *J* = 22.5 Hz, *J* = 17.5 Hz, 1H), 7.59-7.54 (m, 2H), 7.48-7.46 (m, 2H), 6.15-6.07 (m, 1H), 4.20-4.14 (m, 4H), 1.38-1.35 (td, *J* = 7.0 Hz, *J* = 1.5 Hz, 6H), 0.32-0.31 (m, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 243.86, 149.25 (d, *J*_{C-P} = 7.1 Hz), 144.81, 134.99 (d, *J*_{C-P} = 23.8 Hz), 133.05, 131.32, 130.74, 130.02 (d, *J*_{C-P} = 1.3 Hz), 119.69, 118.18, 64.07 (d, *J*_{C-P} = 5.5 Hz), 18.43 (d, *J*_{C-P} = 6.5 Hz), 0.21.



(E)-2-(2-(phenylsulfonyl) vinyl) phenyl (trimethylsilyl) methanone (5aj) Following the general procedure, **5aj** was obtained as a yellow liquid, yield = 79%. ¹H NMR (500 MHz, CDCl₃): δ = 8.05-8.03 (m, 2H), 7.97 (d, *J* = 15 Hz, 1H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.62-7.48 (m, 6H), 6.69 (d, *J* = 15.0 Hz, 1H), 0.34 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 242.56, 144.68, 144.66, 142.56, 135.27, 133.30, 132.38, 132.04, 131.49, 131.23, 131.13, 130.63, 129.72, 0.21.

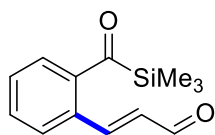


(E)-2-(4-(Trifluoromethyl) styryl) phenyl (trimethylsilyl) methanone (5ak) Following the general procedure, **5ak** was obtained as a yellow solid, m.p.: 62.5 °C, yield = 53%. ¹H NMR (500 MHz, CDCl₃): δ = 7.67 (d, *J* = 8.0 Hz, 1H), 7.61-7.58 (m, 5H), 7.56-7.54 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 6.91 (d, *J* = 16.0 Hz, 1H), 0.30 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 244.76, 143.98, 142.67, 136.50, 132.90, 132.32, 131.81, 131.38 (q, *J*_{C-F} = 32.3 Hz), 130.92, 129.71, 129.41, 128.82, 127.57 (q, *J*_{C-F} = 3.8 Hz), 126.17 (q, *J*_{C-F} = 270.1 Hz)



(1H-Inden-3-yl)trimethylsilane (4aa) Following the general procedure, **4aa** was obtained as a yellow liquid, yield = 3%. ¹H NMR (500 MHz, CDCl₃): δ = 7.39-7.36 (m, 2H),

7.18-7.14 (m, 1H), 7.08-7.04 (m, 1H), 6.65-6.63 (m, 1H), 3.29 (d, $J = 2.5$ Hz, 2H), 0.22-0.19 (m, 9H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 149.35, 146.51, 145.96, 145.36, 127.39, 125.55, 125.07, 123.27, 42.03, 0.21$ (d, $J = 3.0$ Hz). HRMS (ESI): m/z for $\text{C}_{12}\text{H}_{16}\text{Si}$ $[\text{M}+\text{Na}]^+$: 211.0913, found: 211.0910. FTIR (KBr, cm^{-1}): 3493.29, 3416.36, 3300.24, 2367.89, 2289.63, 1658.81, 1643.78, 1632.84.



(E)-3-(2-((Trimethylsilyl) carbonyl) phenyl) acrylaldehyde (5aa)

Following the general procedure, **5aa** was obtained as a yellow liquid, yield = 2%. ^1H NMR (500 MHz, CDCl_3): $\delta = 9.73$ (d, $J = 8.0$ Hz, 1H), 7.93 (d, $J = 16.0$ Hz, 1H), 7.76-7.74 (m, 1H), 7.66-7.65 (m, 1H), 7.58-7.52 (m, 2H), 6.58 (q, $J = 8.0$ Hz, 1H), 0.36 (s, 9H). ^{13}C NMR (125 Hz, CDCl_3): $\delta = 243.15, 195.95, 153.60, 143.86, 133.85, 133.41, 132.71, 131.97, 131.97, 130.29, 0.22$. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$: 233.0992, found: 233.0997. FTIR (KBr, cm^{-1}): 3443.12, 3422.59, 2923.97, 2850.63, 2354.42, 1643.25, 1632.39, 1402.04.

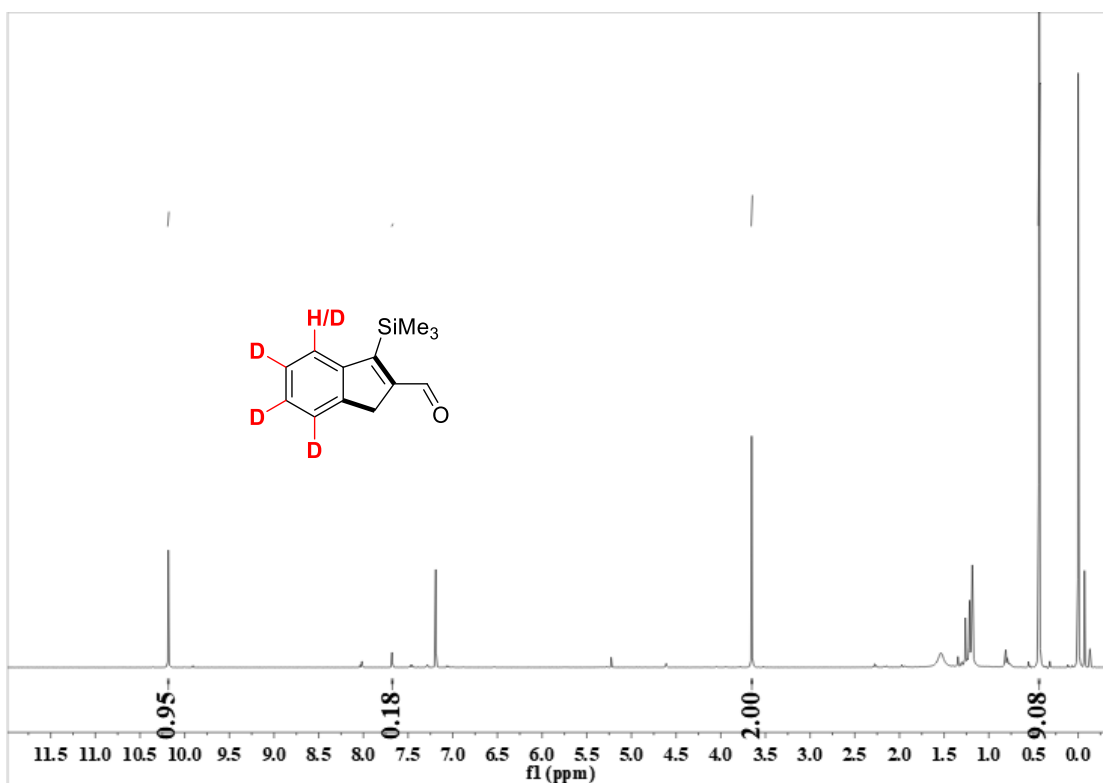
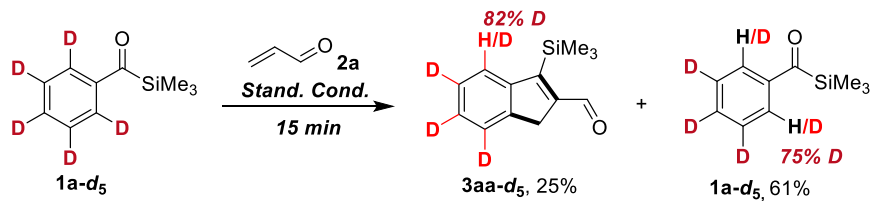
Competition Experiments with **1k** and **1h**:

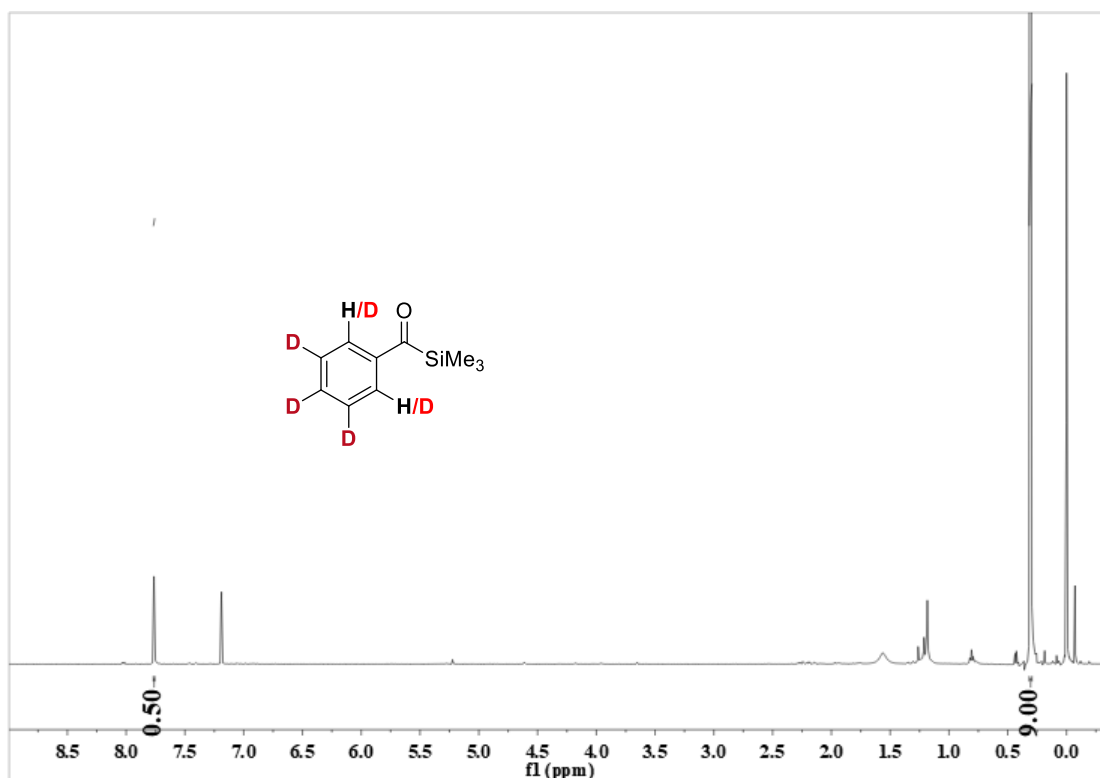
A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (5 mol%, 0.005 mmol, 3.1 mg), AgSbF_6 (20 mol%, 0.02 mmol, 6.9 mg), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.13 mmol, 23.6 mg) and DCM (0.5 mL). Then, aroylsilanes **1k** (1.0 equiv, 0.1 mmol, 21.2 mg), **1h** (1.0 equiv, 0.1 mmol, 20.8 mg) and **2a** (3.0 equiv, 0.3 mmol, 16.8 mg) were added into the solution in sequence. The vial was sealed under argon and heated to 60 °C with stirring for 1 h. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), only leading to product **3ha** (8.4 mg, 32%).

H/D Exchange Experiment

A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (5 mol%, 0.005 mmol), AgSbF_6 (20 mol%, 0.02 mmol), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.13 mmol) and DCM (0.5 mL). Then, **1a-d5** (1.0 equiv, 0.1 mmol) and **2a** (3.0 equiv, 0.3 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 °C with stirring for 15 min. After cooling down, the mixture was

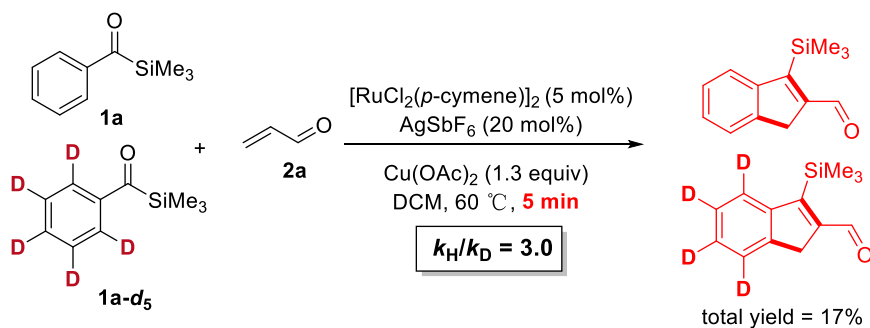
directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), affording **3aa-d₅** (5.9 mg, 25% yield) and **1a-d₅** (11.1 mg, 61% yield). The deuterium incorporation was determined by ¹H NMR.

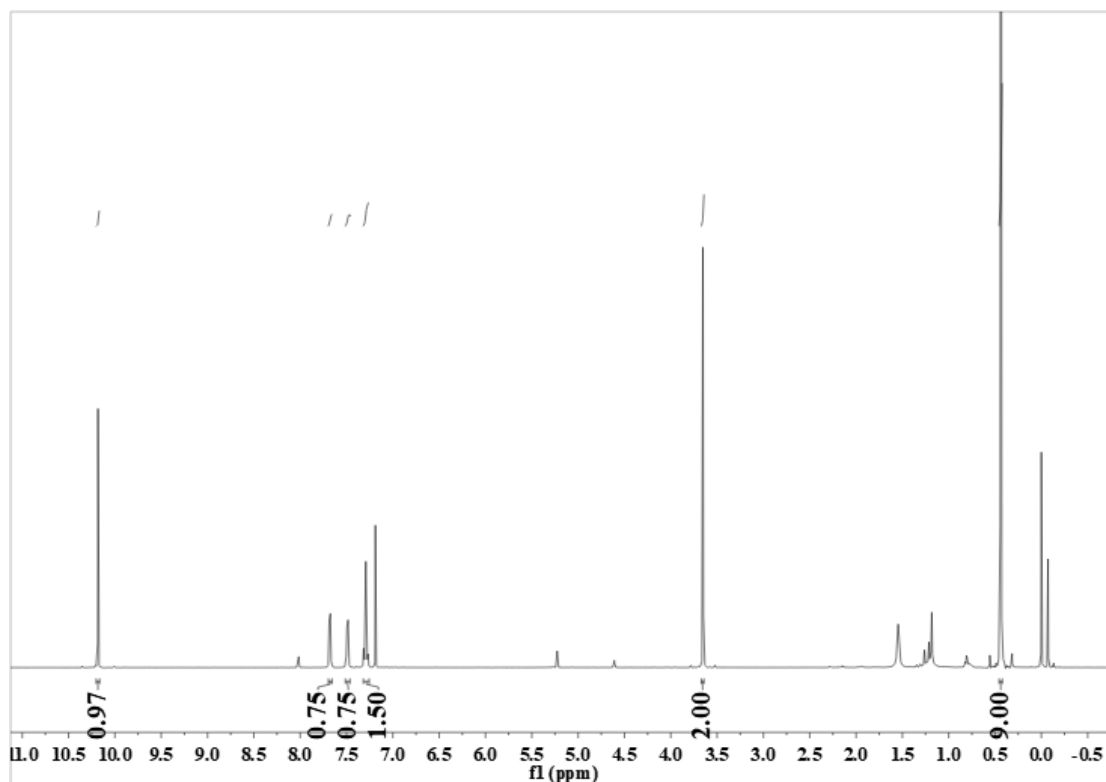




Intermolecular KIE Experiment

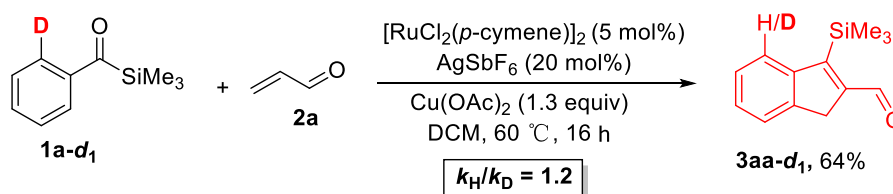
A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (5 mol%, 0.01 mmol), AgSbF_6 (20 mol%, 0.04 mmol), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.26 mmol) and DCM (1.0 mL). Then, **1a** (1.0 equiv, 0.1 mmol), **1a-d₅** (1.0 equiv, 0.1 mmol) and **2a** (3.0 equiv, 0.6 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 °C with stirring for 5 min. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), affording the product as a light yellow solid (7.9 mg, 17% total yield). KIE was determined by ^1H NMR to be 3.0.

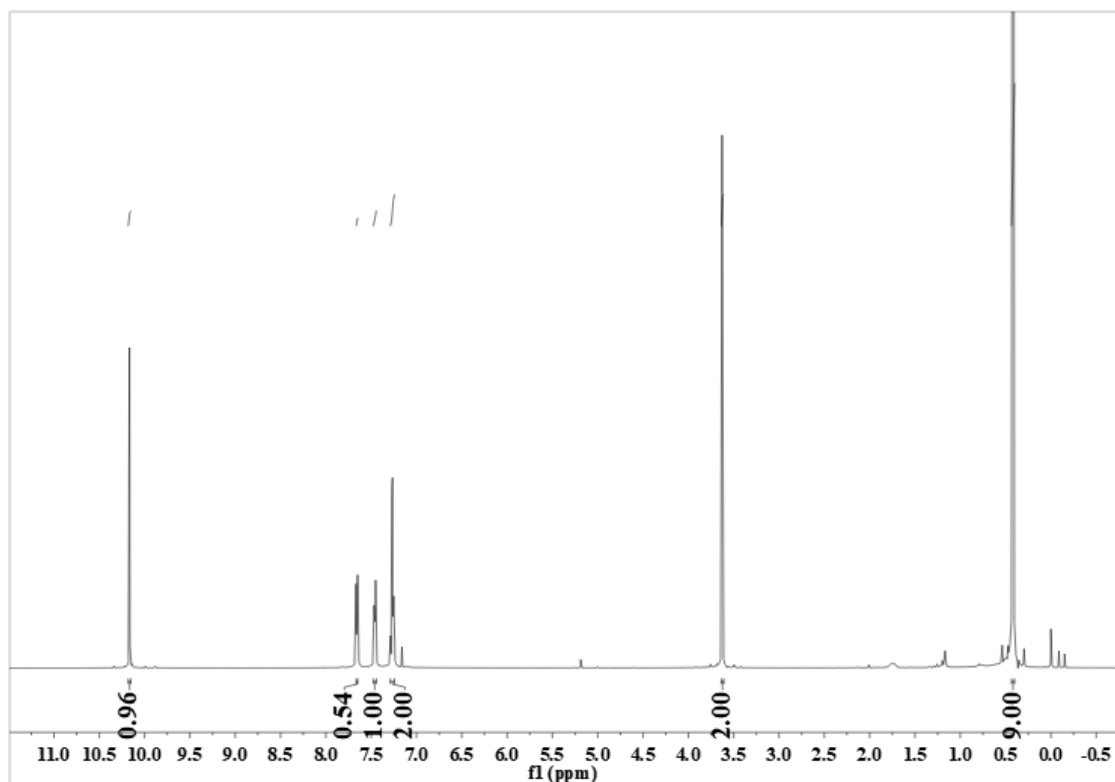




Intramolecular KIE Experiment

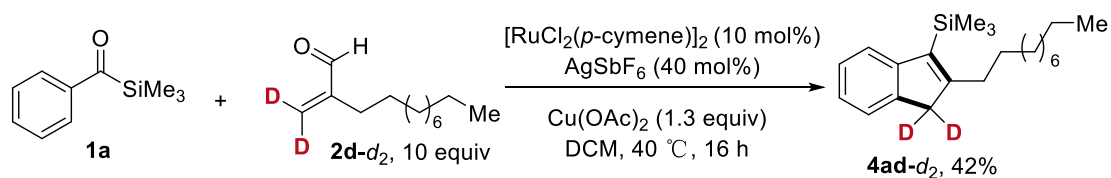
A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (5 mol%, 0.01 mmol), AgSbF_6 (20 mol%, 0.04 mmol), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.26 mmol) and DCM (1.0 mL). Then, **1a-d₁** (1.0 equiv, 0.2 mmol) and **2a** (3.0 equiv, 0.6 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 60 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), affording the product **3aa-d₁** as a light yellow solid (30 mg, 64% yield). KIE was determined by ^1H NMR to be 1.2.

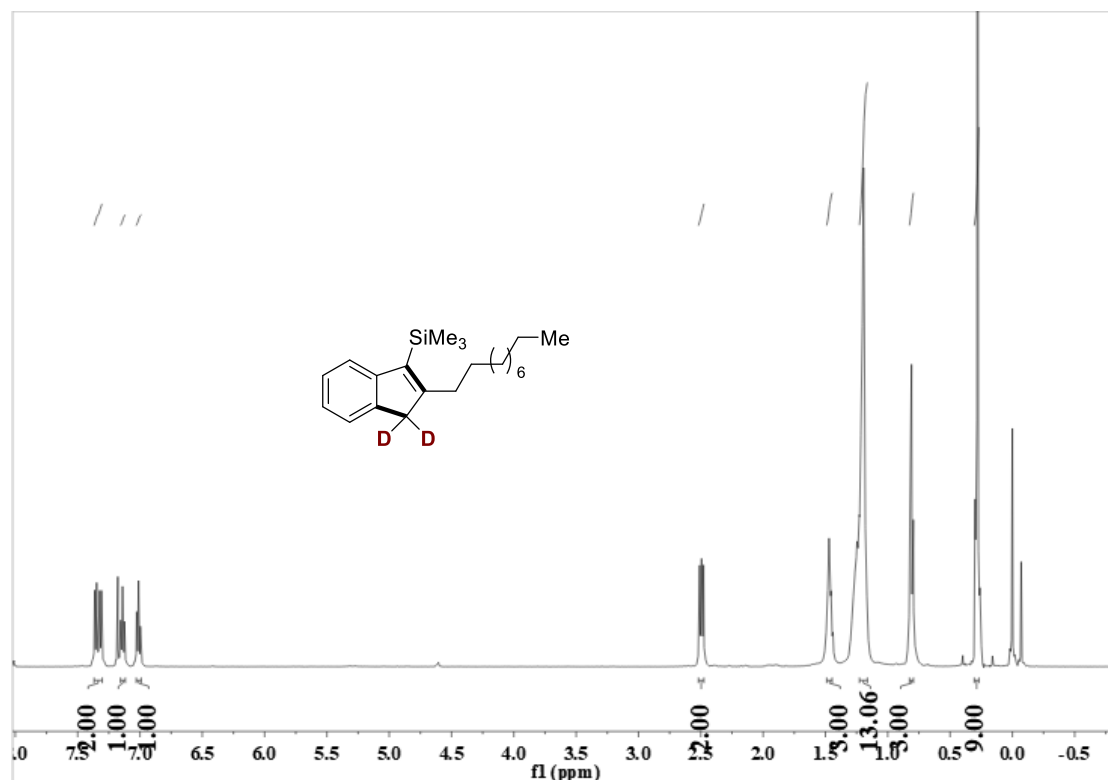




Deuterium Labelling Experiment with 2d-d₂

A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (10 mol%, 0.01 mmol), AgSbF_6 (40 mol%, 0.04 mmol), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.13 mmol) and DCM (0.5 mL). Then, **1a** (17.8 mg, 0.1 mmol) and **2d-d₂** (10.0 equiv, 1.0 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), affording **4ad-d₂** as a light yellow oil (14.5 mg, 42% yield).

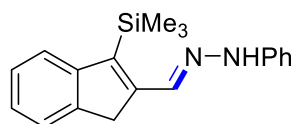




Deuterium Labelling Experiment with 2d-d

A screw-cap vial was charged with $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$ (10 mol%, 0.01 mmol), AgSbF_6 (40 mol%, 0.04 mmol), $\text{Cu}(\text{OAc})_2$ (1.3 equiv, 0.13 mmol) and DCM (0.5 mL). Then, **1a** (17.8 mg, 0.1 mmol) and **2d-d** (10.0 equiv, 1.0 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 40 °C with stirring for 16 h. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures), affording **4ad** as a yellow liquid (13.4 mg, 39% yield).

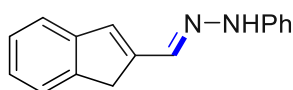
Synthesis of 8



A screw-cap vial was charged with NaOAc (1.0 equiv, 0.1 mmol), AcOH (0.2 mL), KF (0.1 equiv, 0.01 mmol). Then **3aa** (23.2 mg, 0.1 mmol) and PhNHNH_2 (1.1 equiv, 0.11 mmol) were added in sequence. The vial was sealed under argon and stirring in room temperature for 1 h. The mixture was quenched with saturated aqueous NaHCO_3 to pH 8. After the mixture was allowed to warm to ambient temperature, then taken up in EtOAc and washed three times with brine. The combined organic layers were dried over Na_2SO_4 , then concentrated in

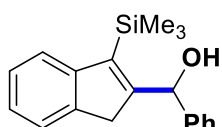
vacuo. The arylsilanes products were purified by flash chromatography (EtOAc/petroleum ether mixtures). Compound **8** was obtained as a brown liquid (31.9 mg, yield = 99%). ¹H NMR (500 MHz, CDCl₃): δ = 7.98 (s, 1H), 7.64 (s, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.23-7.20 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.14-7.12 (m, 2H), 6.94-6.91 (m, 1H), 3.94 (s, 2H), 0.49 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 152.15, 148.24, 143.47, 142.43, 141.17, 134.83, 125.22, 123.97, 122.65, 121.50, 119.25, 111.86, 39.40, 0.21. HRMS (ESI): *m/z* for C₁₉H₂₂N₂Si [M+Na]⁺: 329.1444, found: 329.1444. FTIR (KBr, cm⁻¹): 3451.80, 3416.80, 2954.62, 2922.40, 1642.85, 1602.16, 1503.41, 1401.52, 1251.64.

Synthesis of 9



A screw-cap vial was charged with NaOAc (1.0 equiv, 0.1 mmol), AcOH (0.2 mL), KF (0.1 equiv, 0.01 mmol). Then **3aa** (23.2 mg, 0.1 mmol) and PhNHNH₂ (1.1 equiv, 0.11 mmol) were added in sequence. The vial was sealed under argon and stirring in room temperature for 1 h, then heated to 60 °C with stirring overnight. After the mixture was allowed to warm to ambient temperature, the mixture was quenched with saturated aqueous NaHCO₃ to pH 8, then taken up in EtOAc and washed three times with brine. The combined organic layers were dried over Na₂SO₄, then concentrated in vacuo. The arylsilanes products were purified by flash chromatography (EtOAc/petroleum ether mixtures). Compound **9** was obtained as a brown liquid (21.3 mg, yield = 91%). ¹H NMR (500 MHz, CDCl₃): δ = 7.75 (s, 1H), 7.58 (s, 1H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.33-7.28 (m, 3H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.93-6.89 (m, 2H), 3.83 (s, 2H). ¹³C NMR (125 Hz, CDCl₃): δ = 144.66, 144.55, 144.50, 143.30, 135.21, 131.56, 129.36, 126.60, 125.42, 123.91, 121.17, 120.17, 112.76. HRMS (ESI): *m/z* for C₁₇H₁₆N₂ [M+H]⁺: 249.1386, found: 249.1386. FTIR (KBr, cm⁻¹): 3454.68, 3422.99, 3093.24, 2921.38, 2850.15, 1651.17, 1633.00, 1402.54, 987.09.

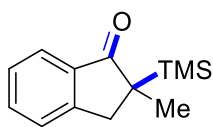
Synthesis of 10



PhMgBr (1 M in THF, 0.12 mmol) was dissolved in THF (0.25 mL) and

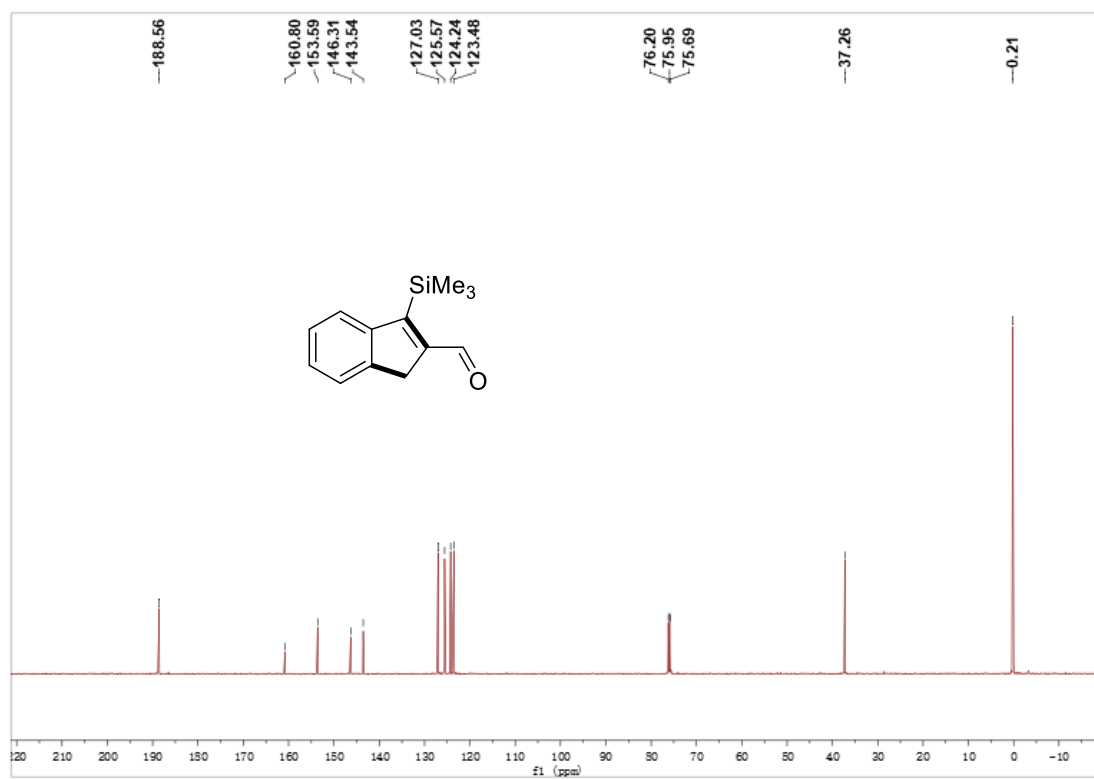
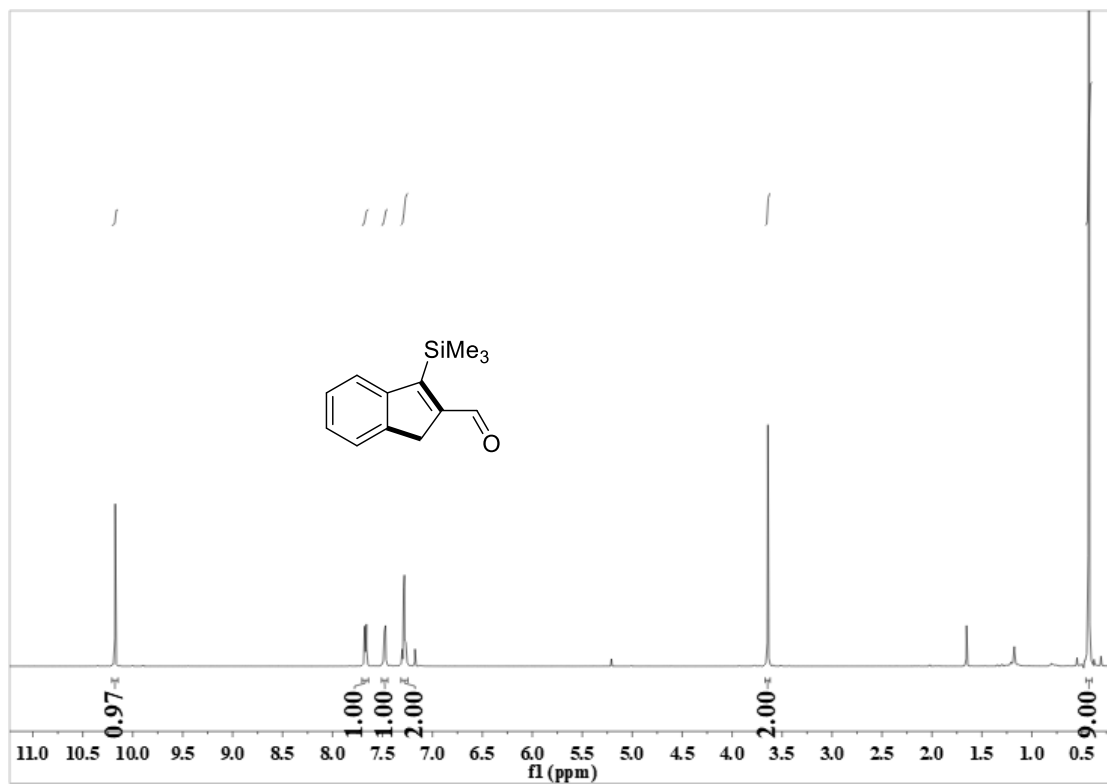
3aa (23.2 mg, 0.1 mmol) was dissolved in THF (0.25 mL) were added at 0 °C. After warming up to rt the mixture was stirred for 3 h. The mixture was quenched with saturated aqueous NH₄Cl. After the mixture was allowed to warm to ambient temperature, then taken up in EtOAc and washed three times with brine. The combined organic layers were dried over Na₂SO₄, concentrated in vacuo, and purified by flash chromatography (EtOAc/petroleum ether mixtures). Compound **10** was obtained as a yellow liquid (25.8 mg, yield = 83%). ¹H NMR (500 MHz, CDCl₃): δ = 7.53 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.36-7.30 (m, 3H), 7.26-7.22 (m, 2H), 7.14-7.11 (m, 1H), 6.10 (s, 1H), 3.60 (d, *J* = 23.5 Hz, 1H), 3.10 (d, *J* = 23.5 Hz, 1H), 0.45 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 158.80, 147.67, 143.03, 142.31, 139.10, 127.64, 126.46, 125.30, 124.85, 123.73, 122.96, 121.88, 70.55, 38.05, 0.23. HRMS (ESI): *m/z* for C₁₉H₂₂O₂Si [M+H]⁺: 295.1513, found: 311.1460. FTIR (KBr, cm⁻¹): 3451.61, 3421.72, 2966.31, 2359.56, 2333.63, 1658.81, 1632.69, 1402.41.

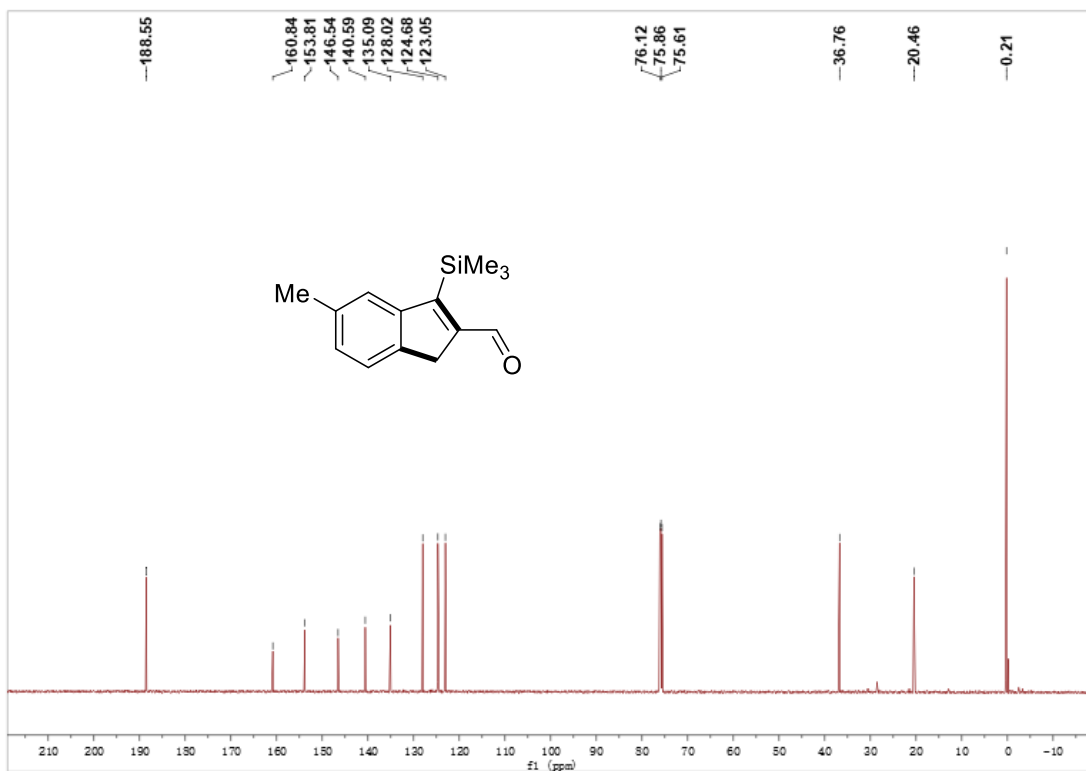
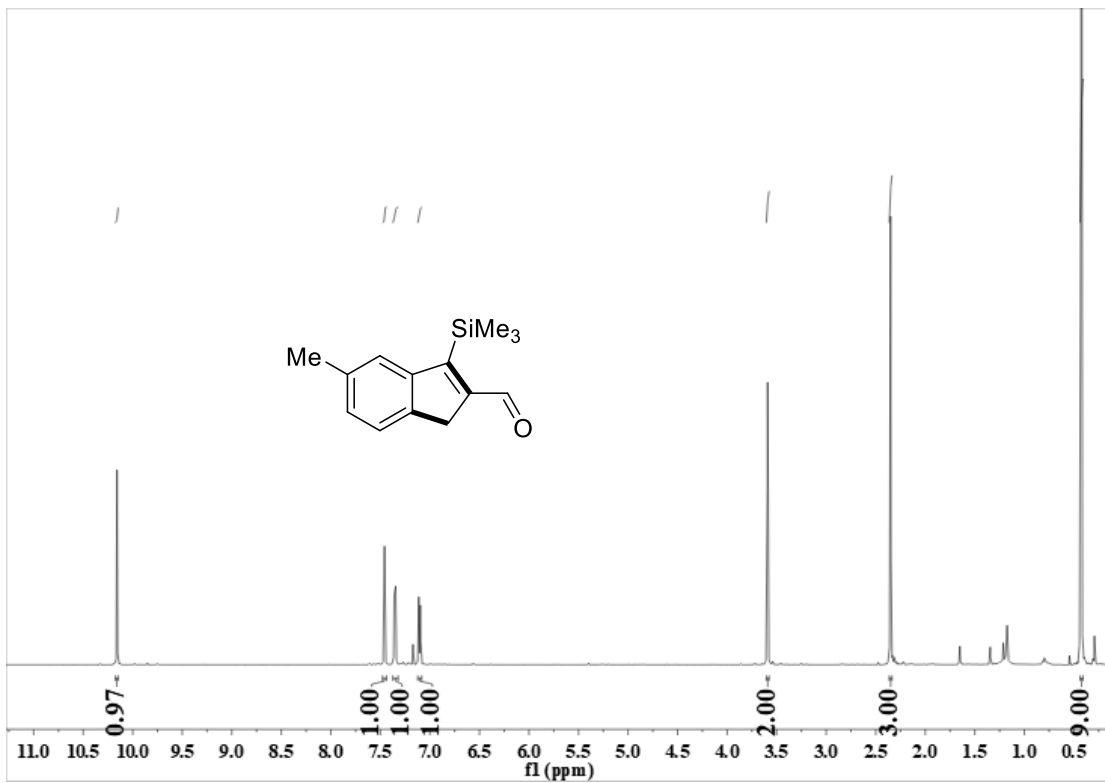
Synthesis of 11

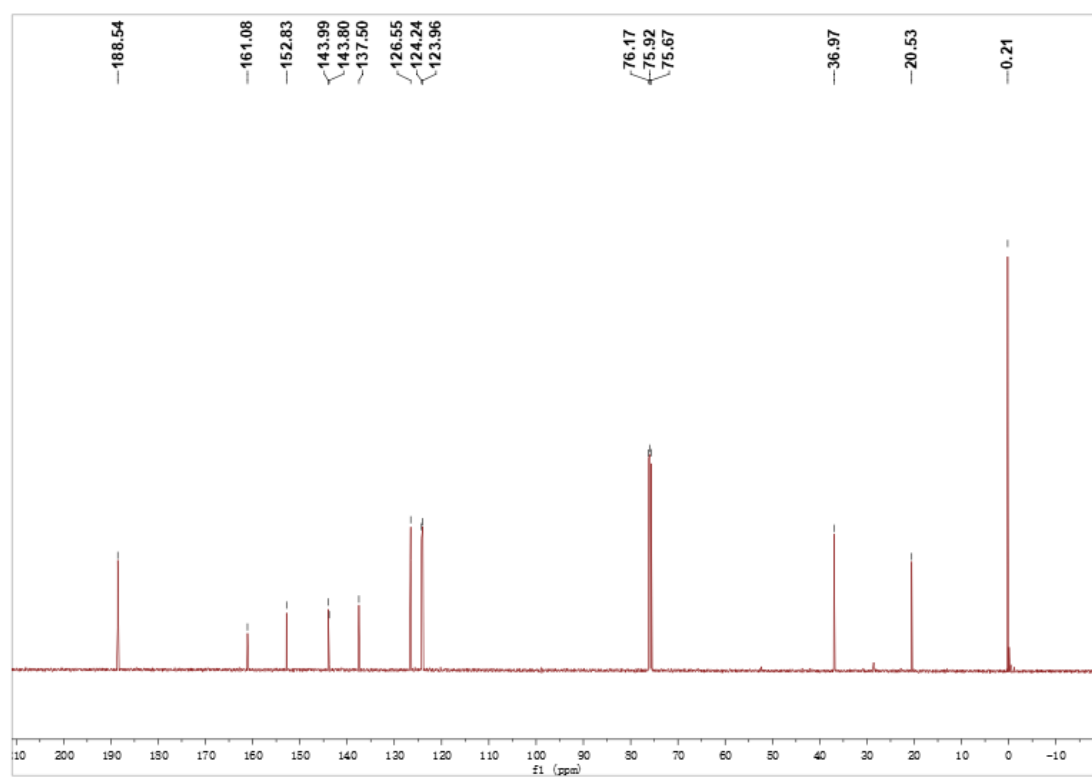
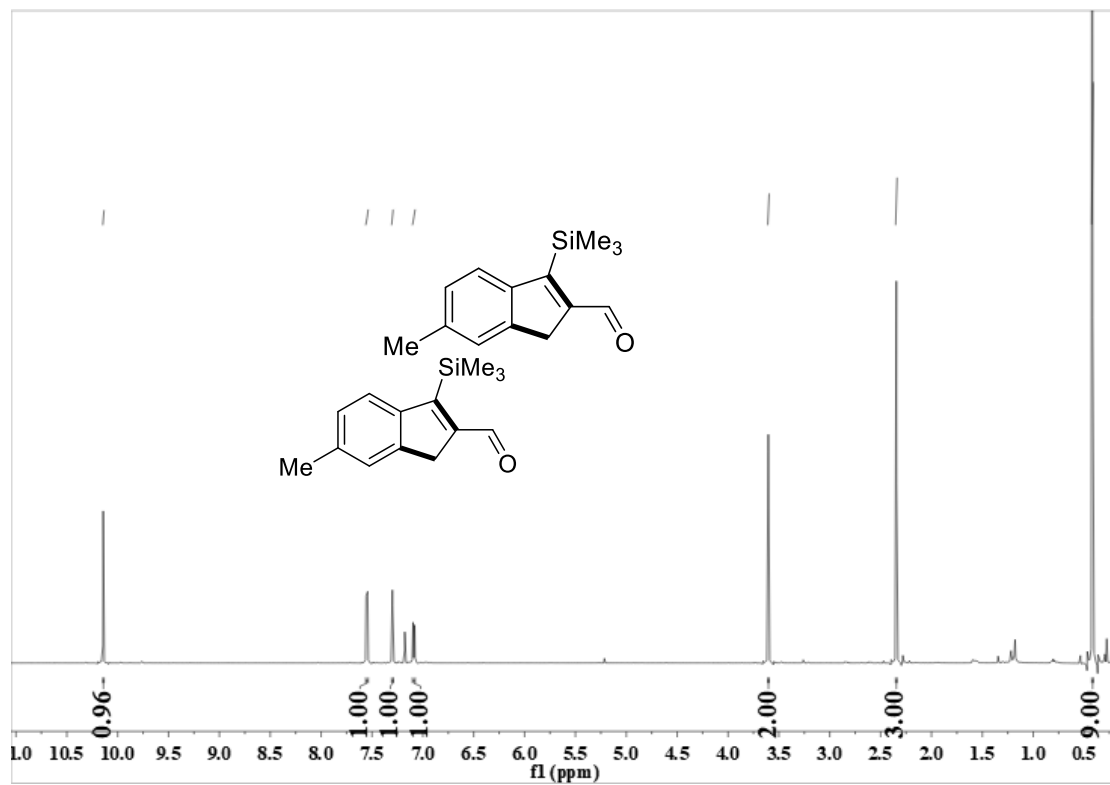


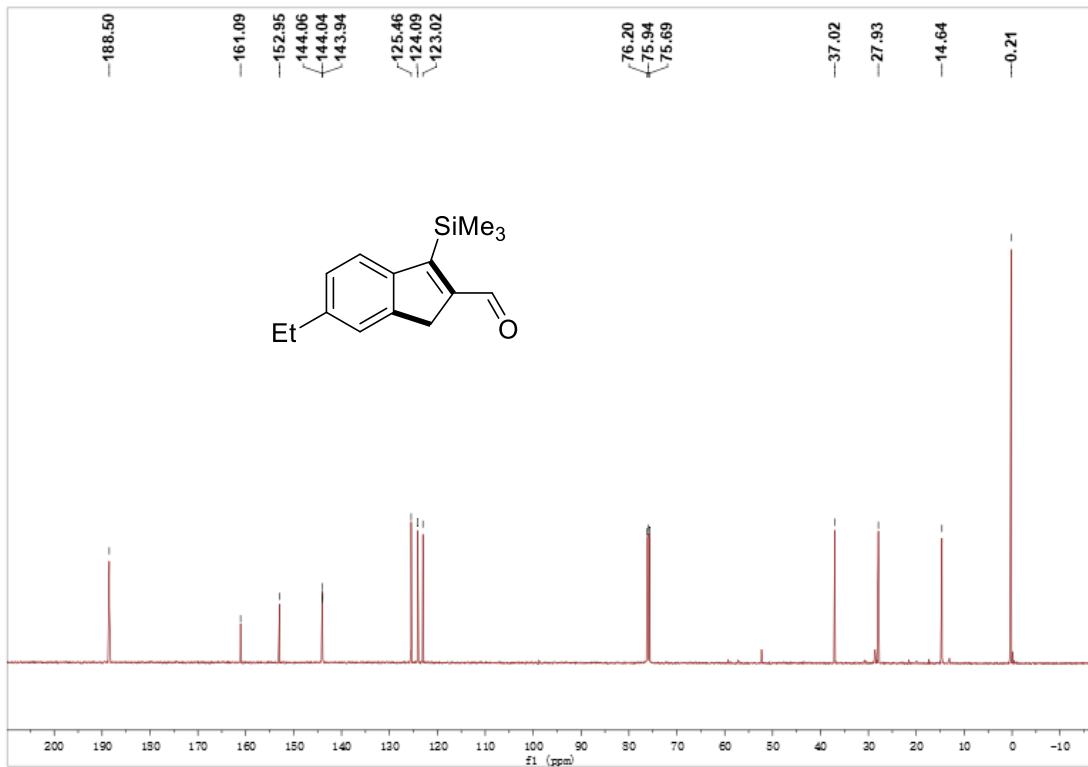
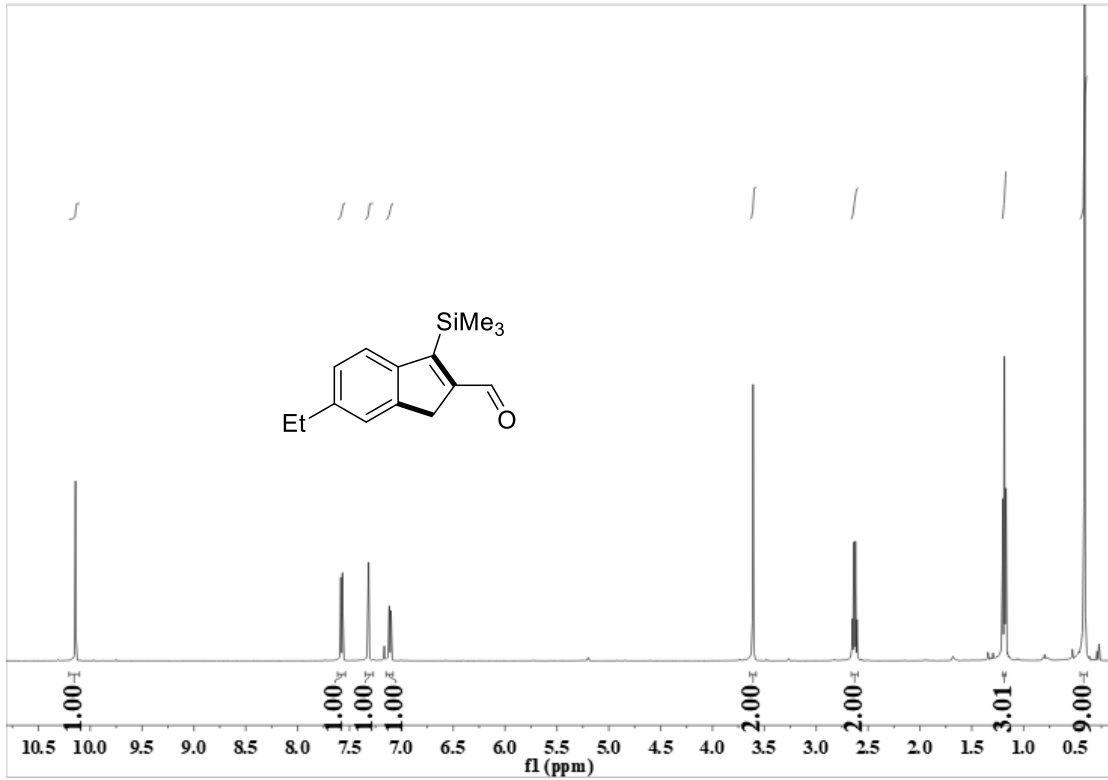
Compound **4ab** (21.8 mg, 0.1 mmol) was dissolved in CH₂Cl₂ (0.5 mL) and *m*-CPBA (0.11 mmol) were added at 0 °C. After warming up to rt the mixture was stirred for 12 h. The mixture was allowed to warm to ambient temperature, then taken up in CH₂Cl₂ and washed three times with brine. The combined organic layers were dried over Na₂SO₄, then concentrated in vacuo. The arylsilanes products were purified by flash chromatography (EtOAc/petroleum ether mixtures). Compound **11** was obtained as a colorless liquid (19.4 mg, yield = 83%). ¹H NMR (500 MHz, CDCl₃): δ = 7.72 (d, *J* = 7.5 Hz, 1H), 7.56-7.53 (td, *J* = 7.5 Hz, *J* = 1.0 Hz, 1H), 7.42 (d, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 1H), 3.29 (d, *J* = 18.0 Hz, 1H), 2.86 (d, *J* = 17.5 Hz, 1H), 1.39 (s, 3H), - 0.05 (s, 9H). ¹³C NMR (125 Hz, CDCl₃): δ = 214.80, 156.70, 142.45, 138.25, 131.69, 130.15, 127.81, 48.75, 42.92, 22.77, 0.21. HRMS (ESI): *m/z* for C₁₃H₁₈O₂Si [M+H]⁺: 219.1200, found: 219.1205. FTIR (KBr, cm⁻¹): 3447.89, 3423.57, 2945.62, 2796.97, 1734.19, 1657.89, 897.63.

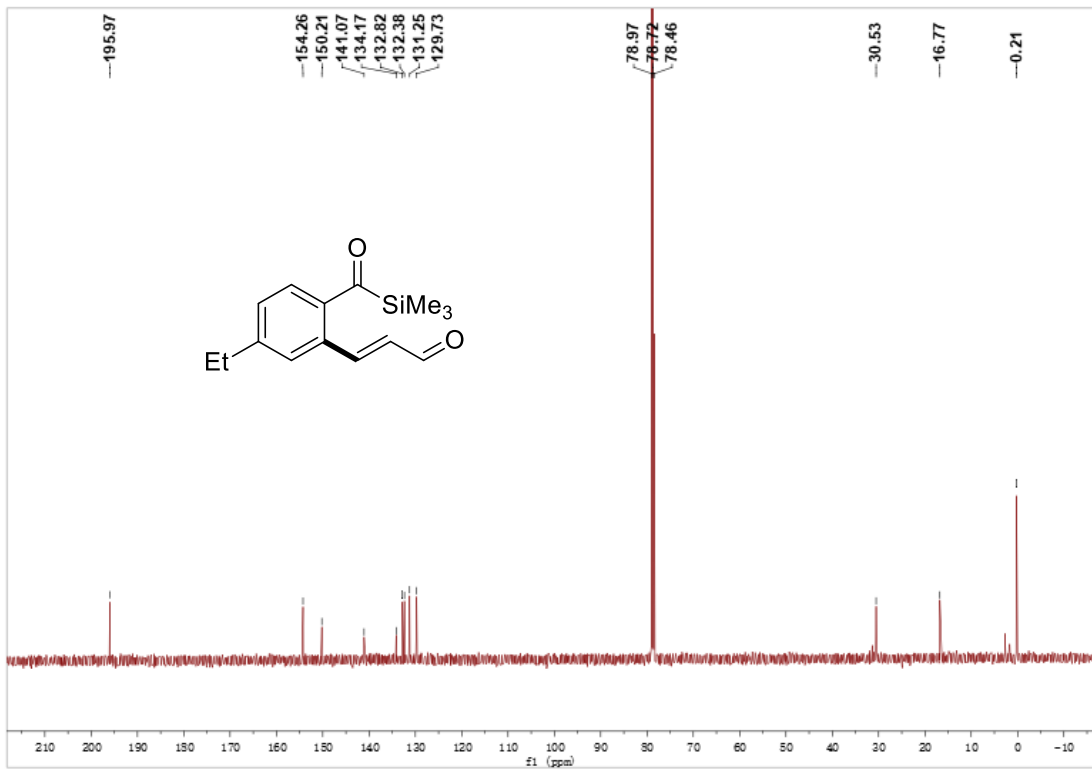
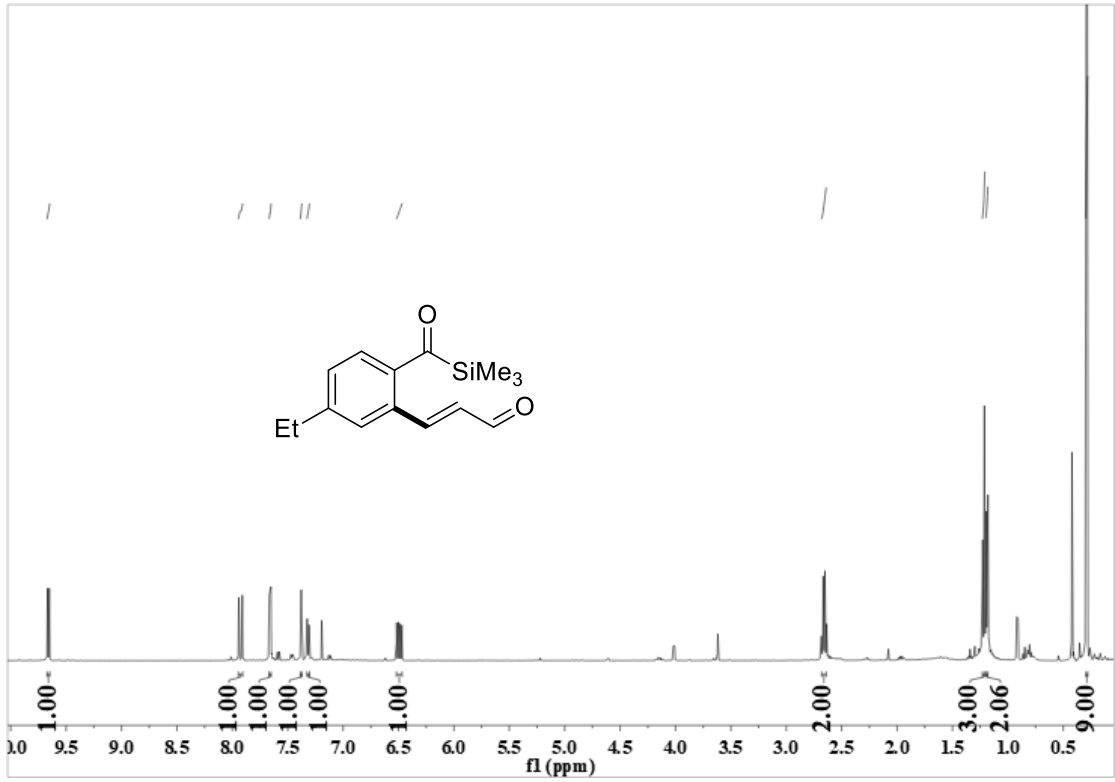
NMR Spectra

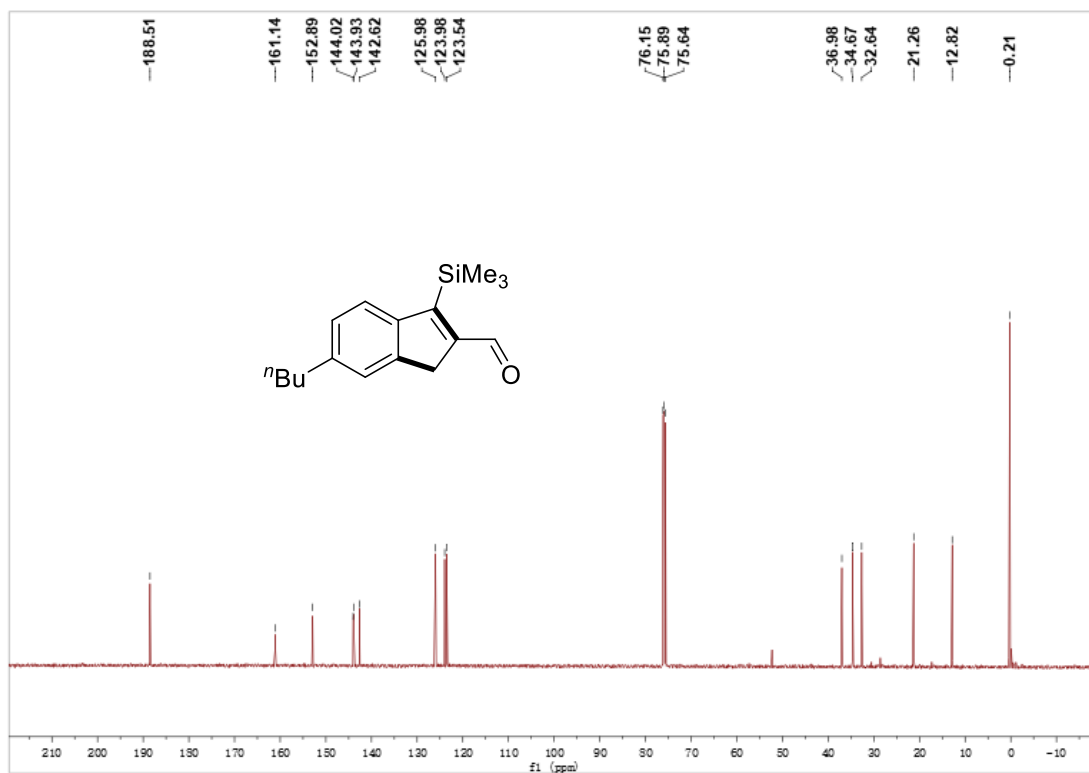
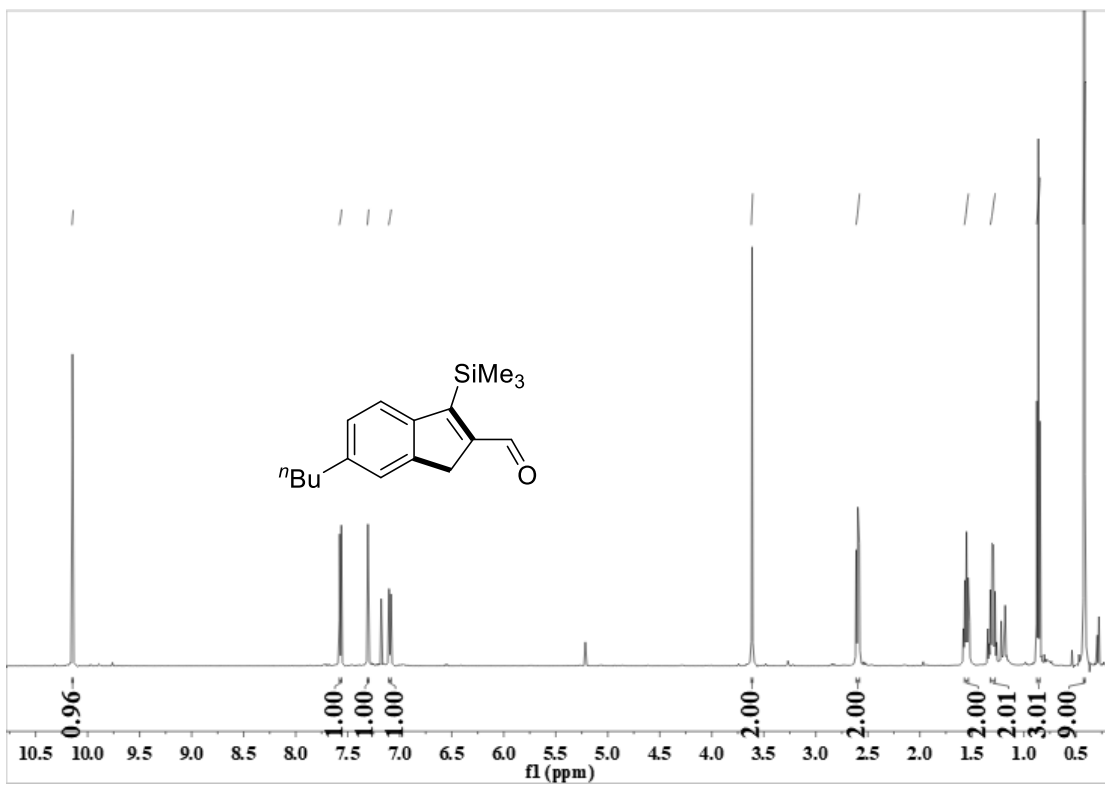


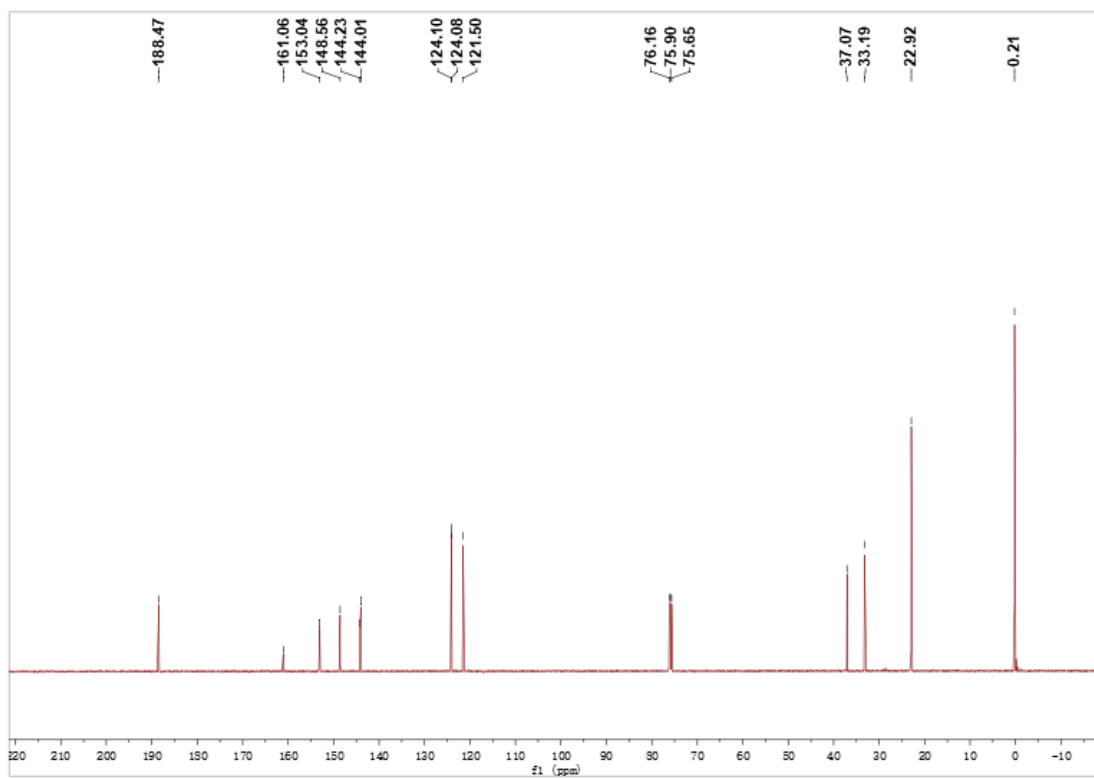
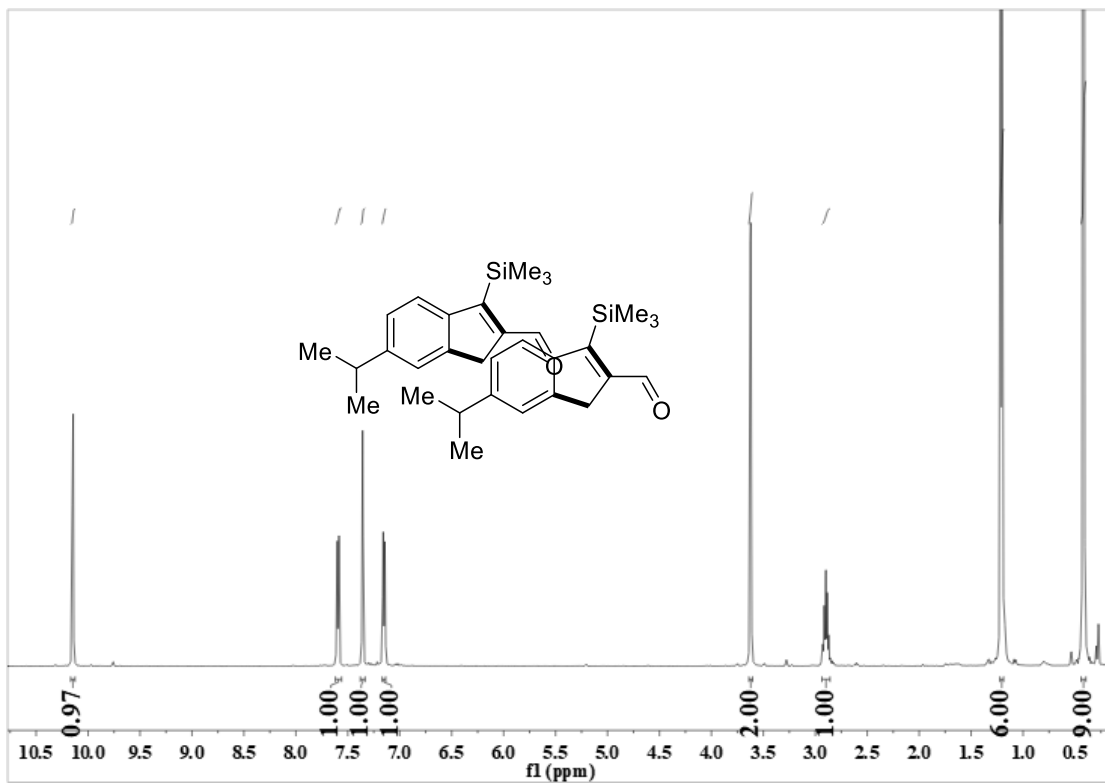


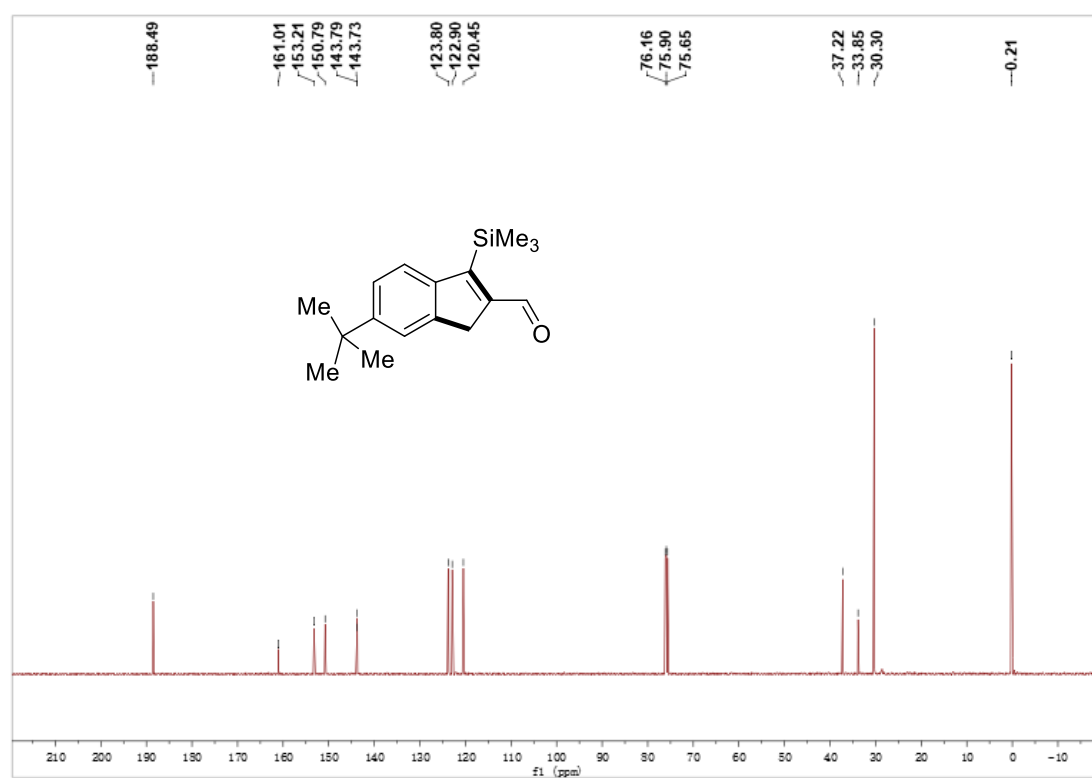
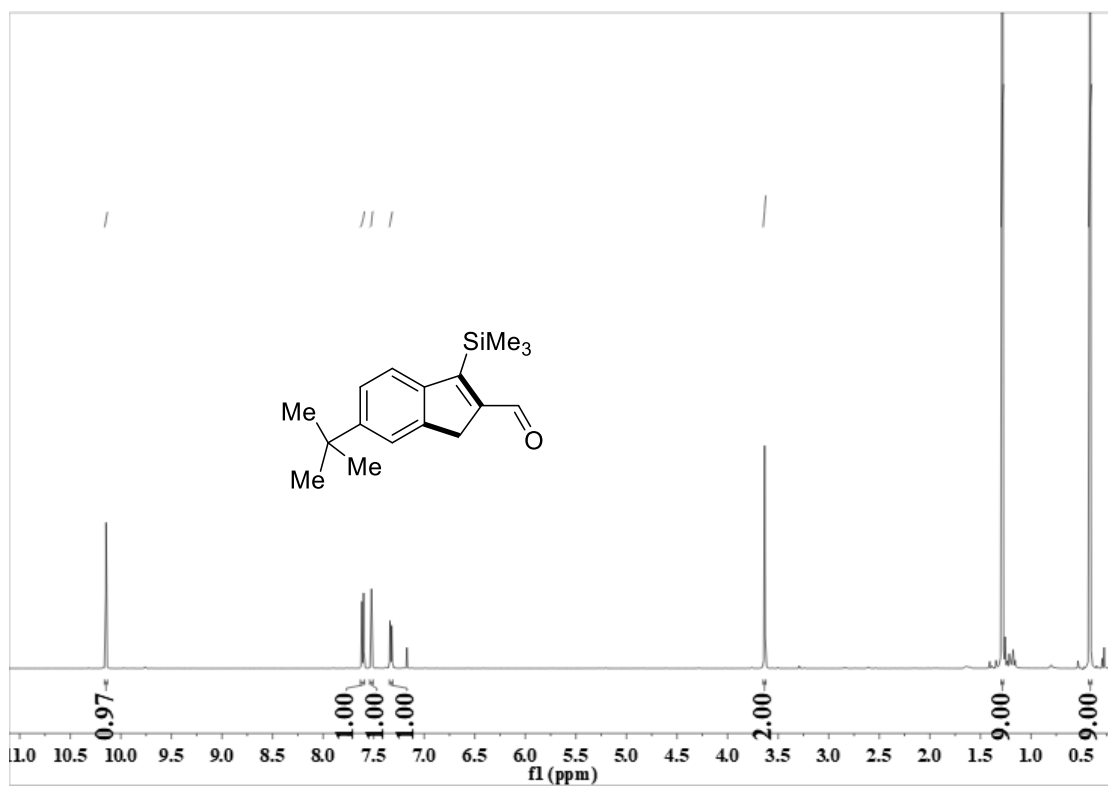


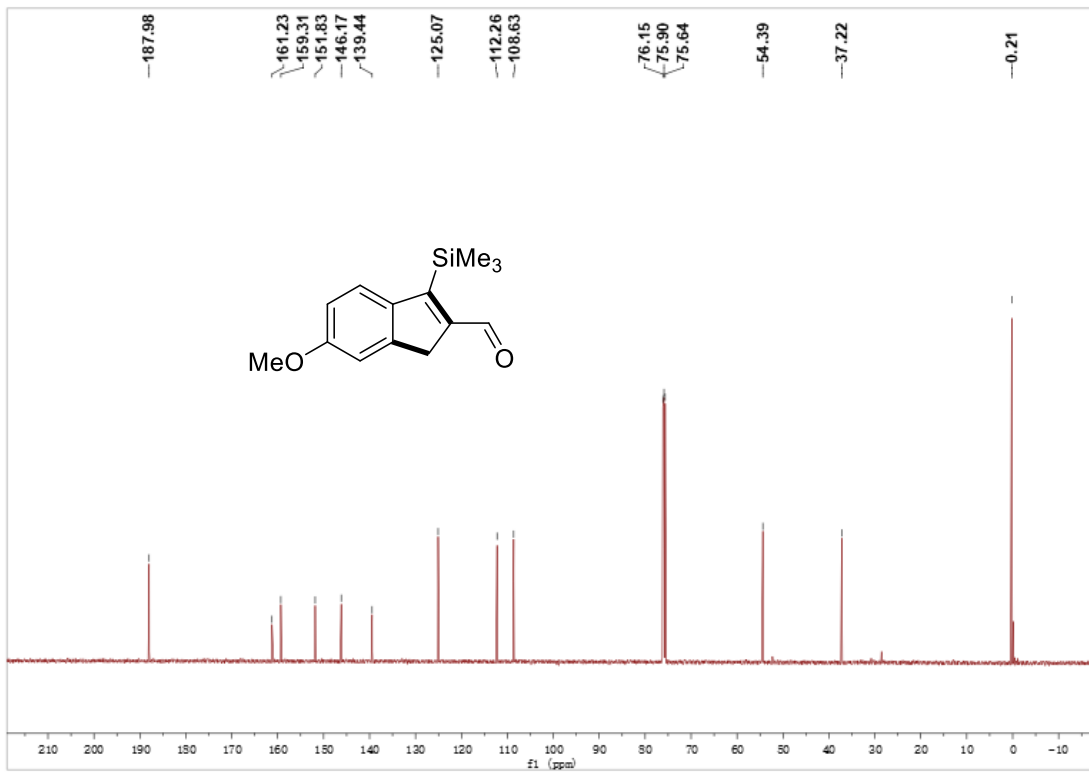
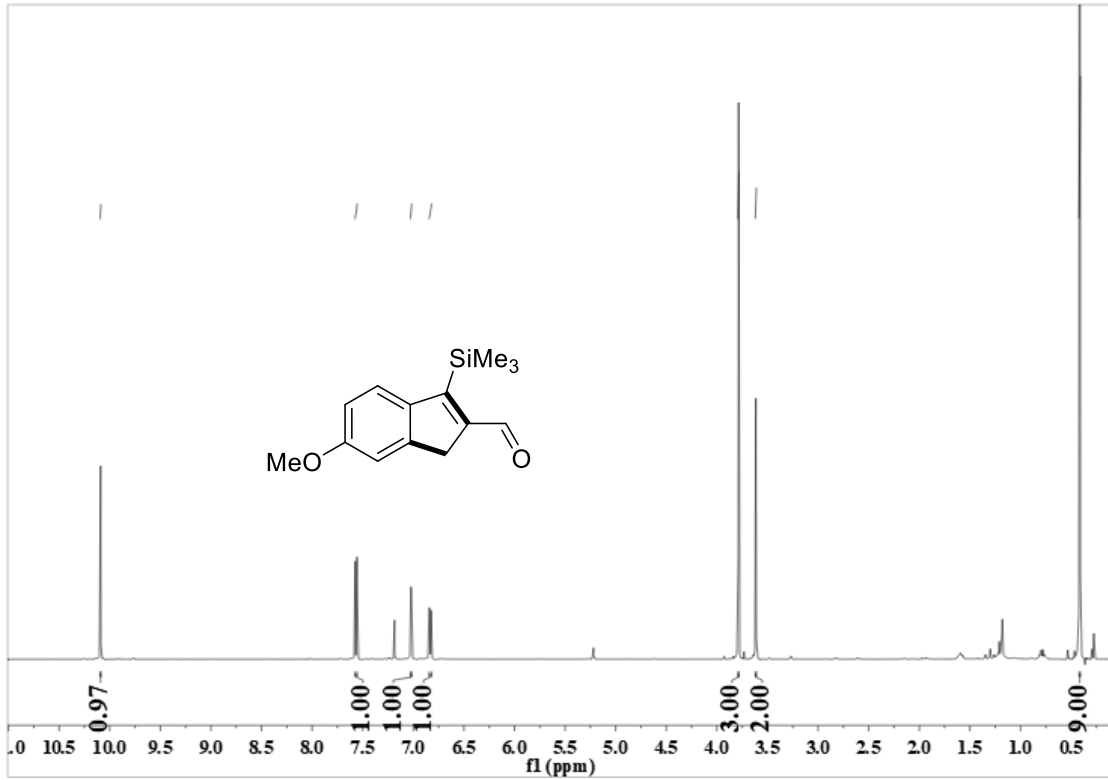


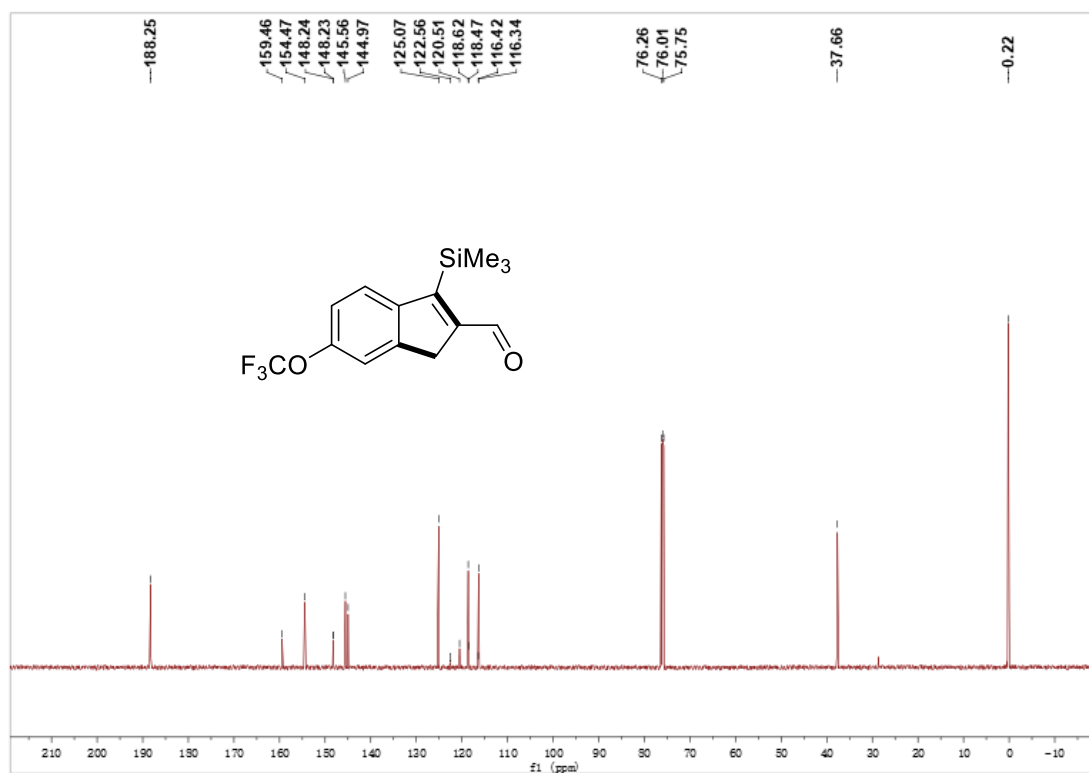
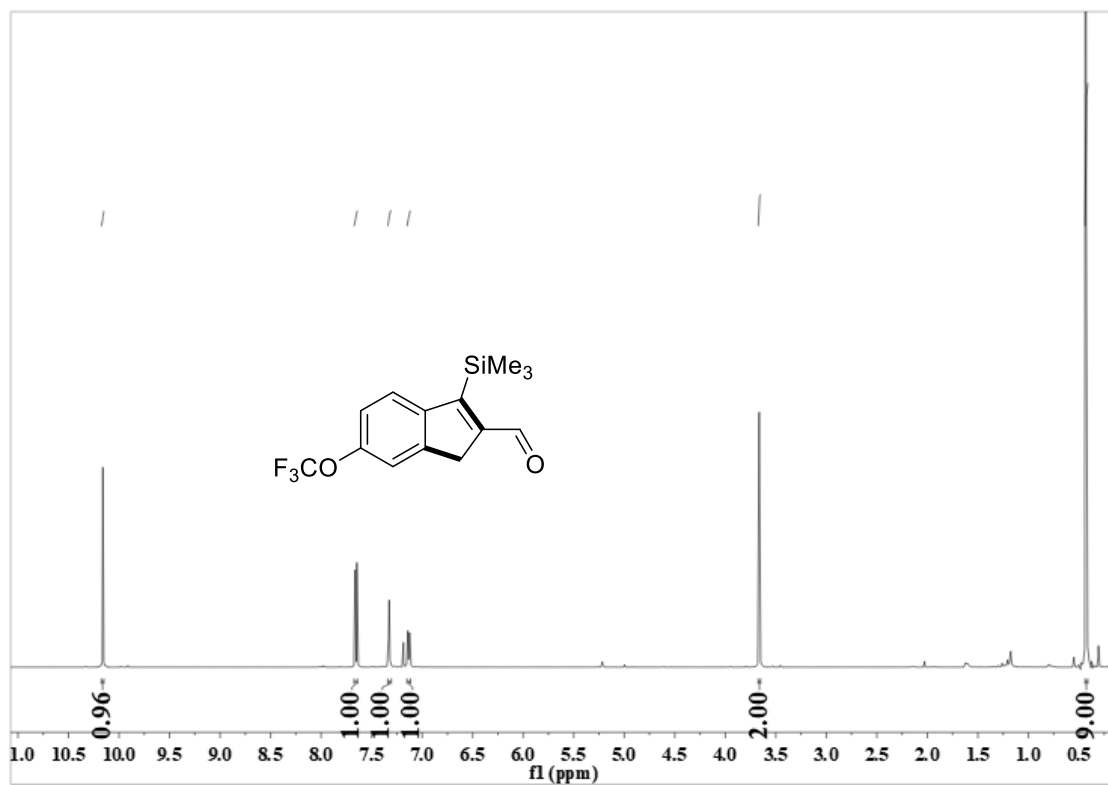


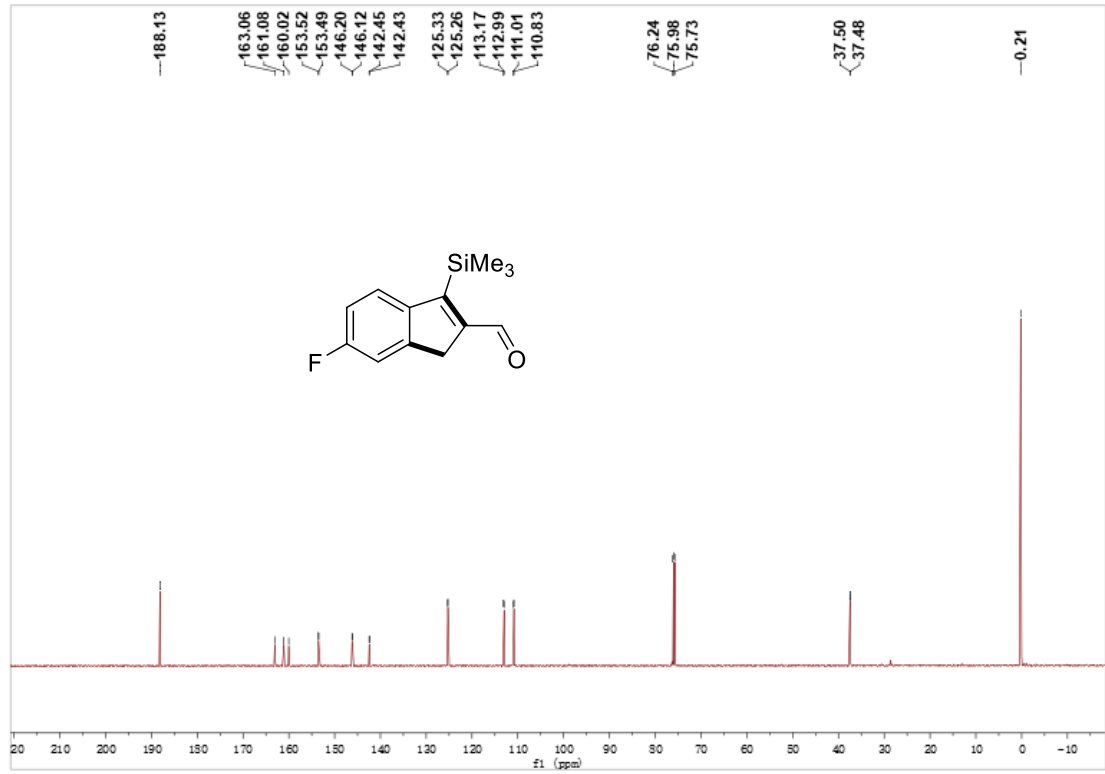
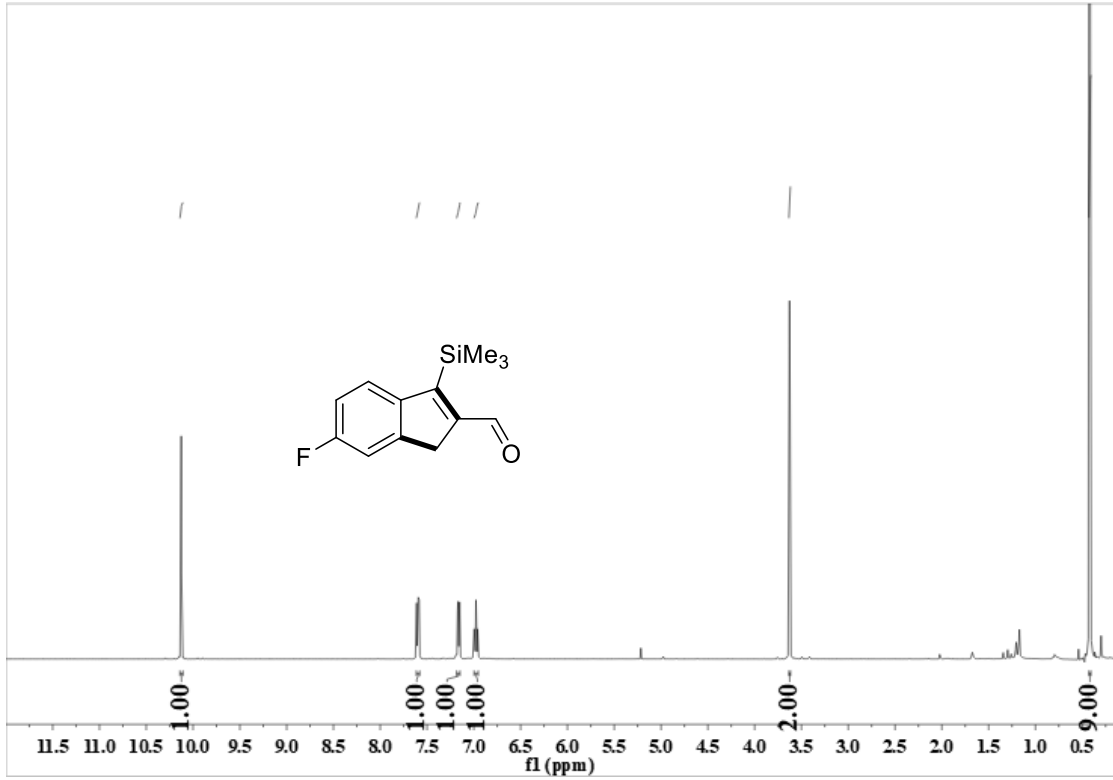


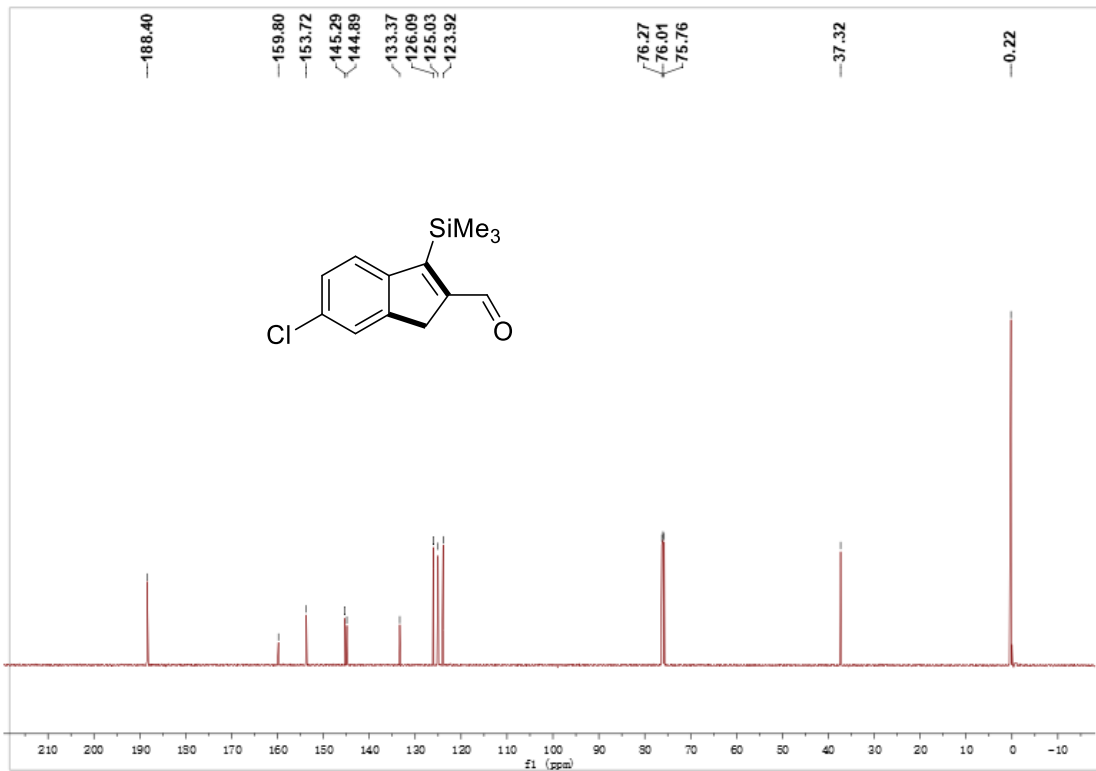
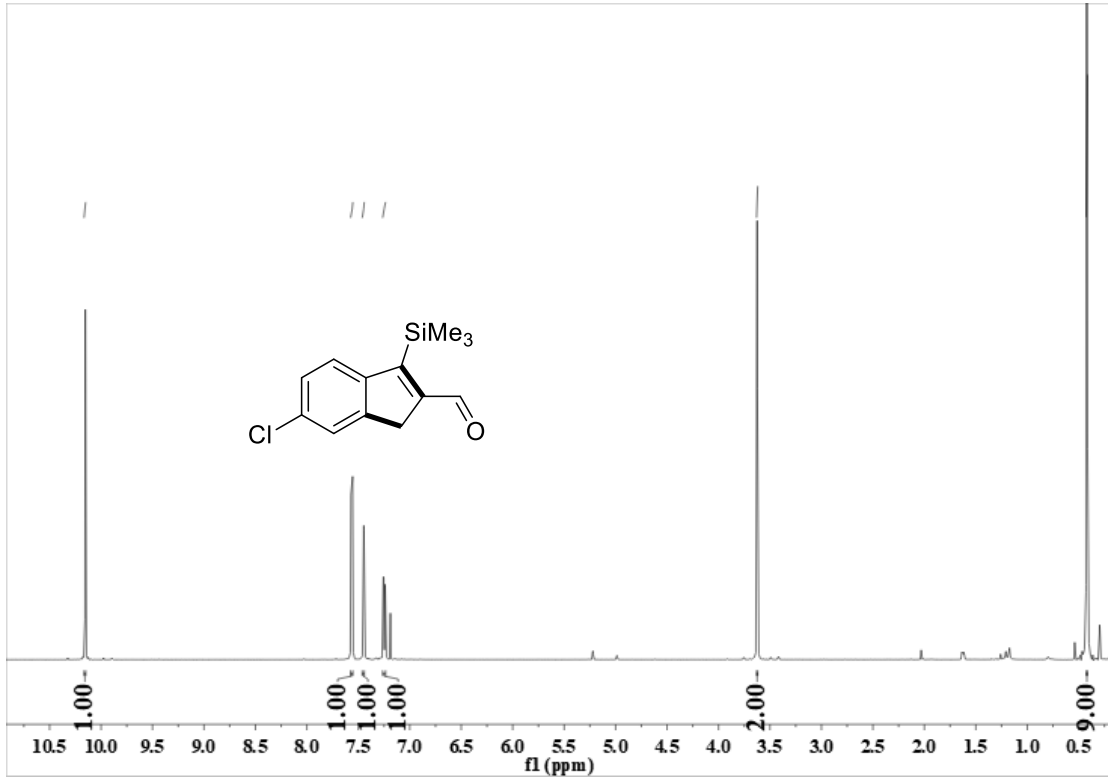


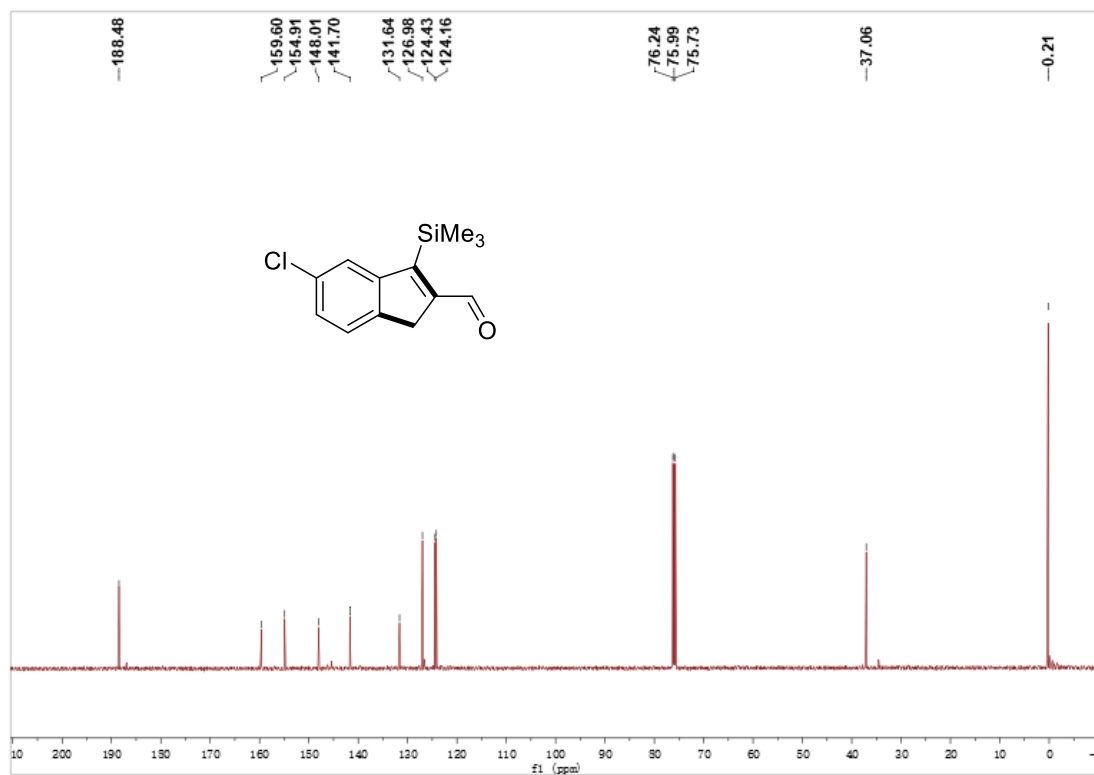
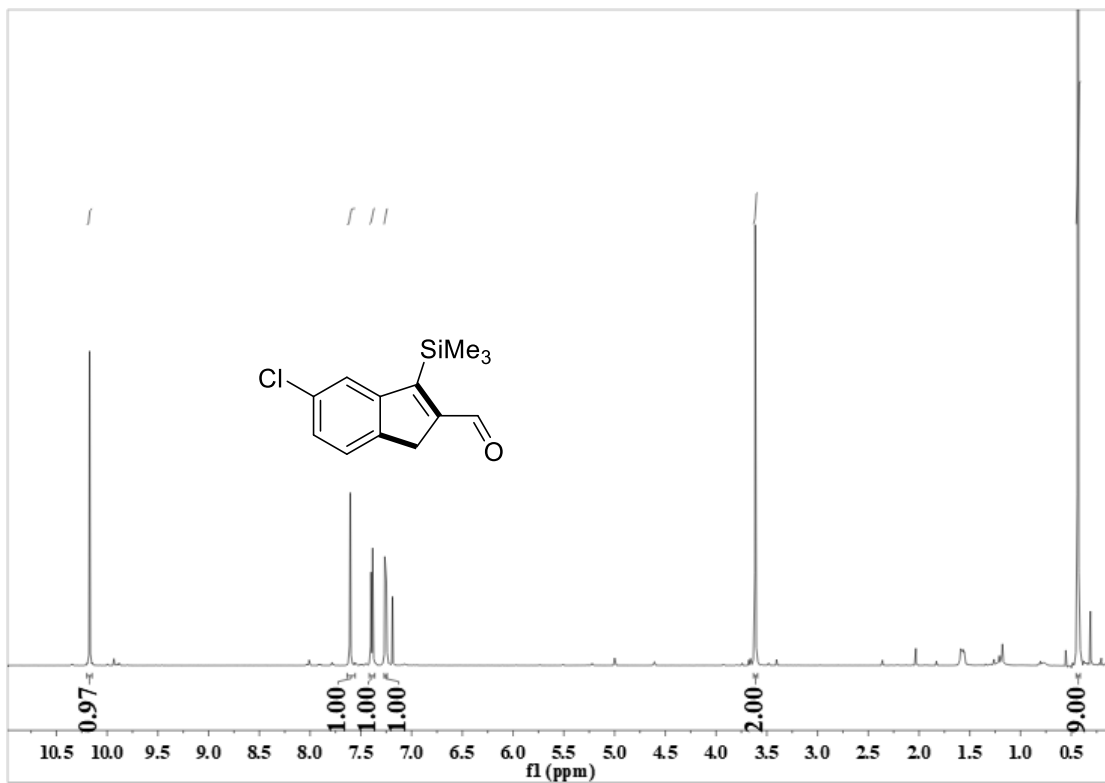


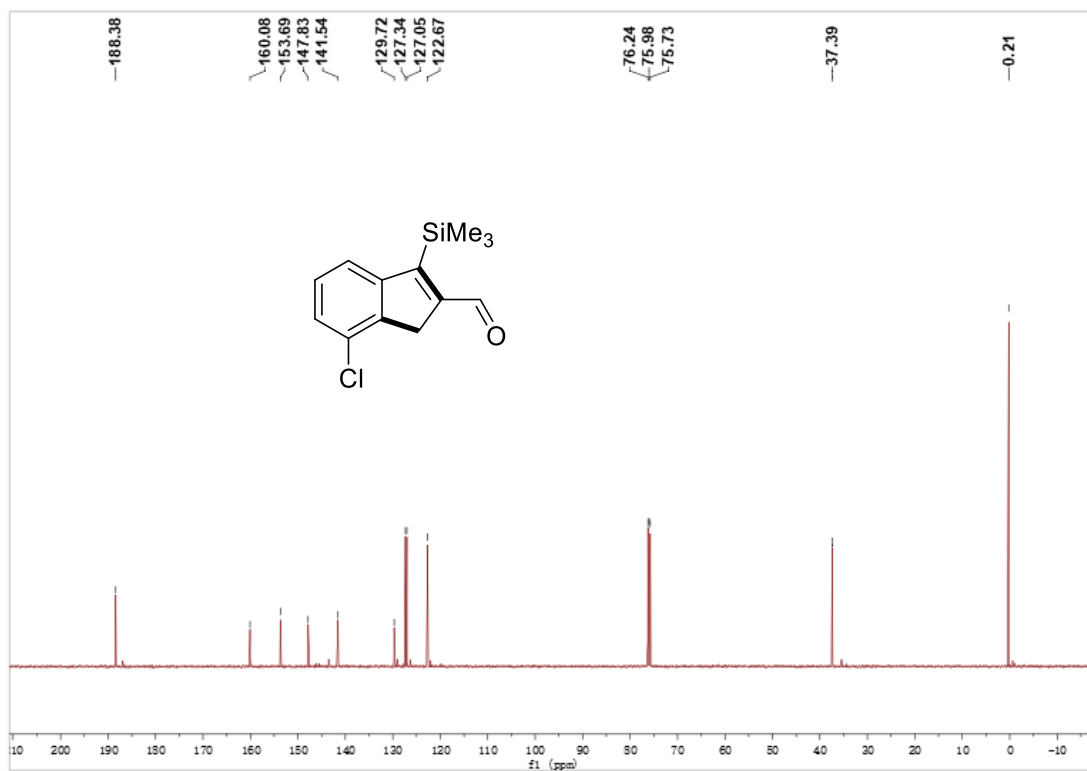
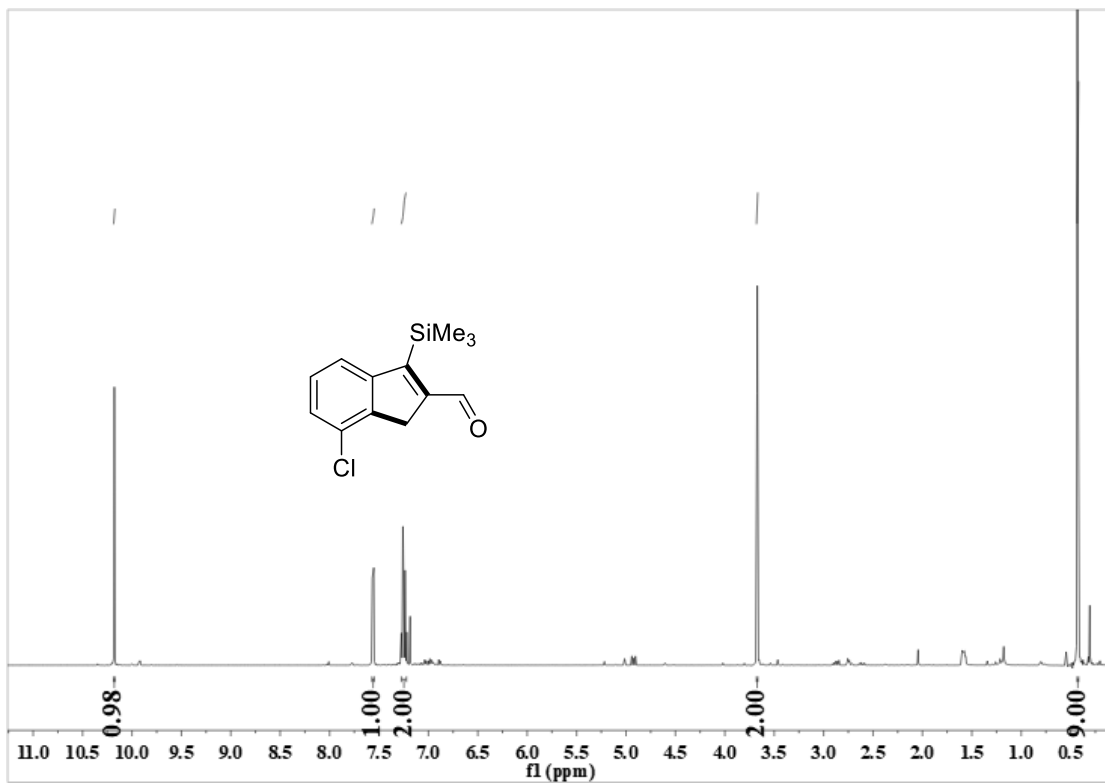


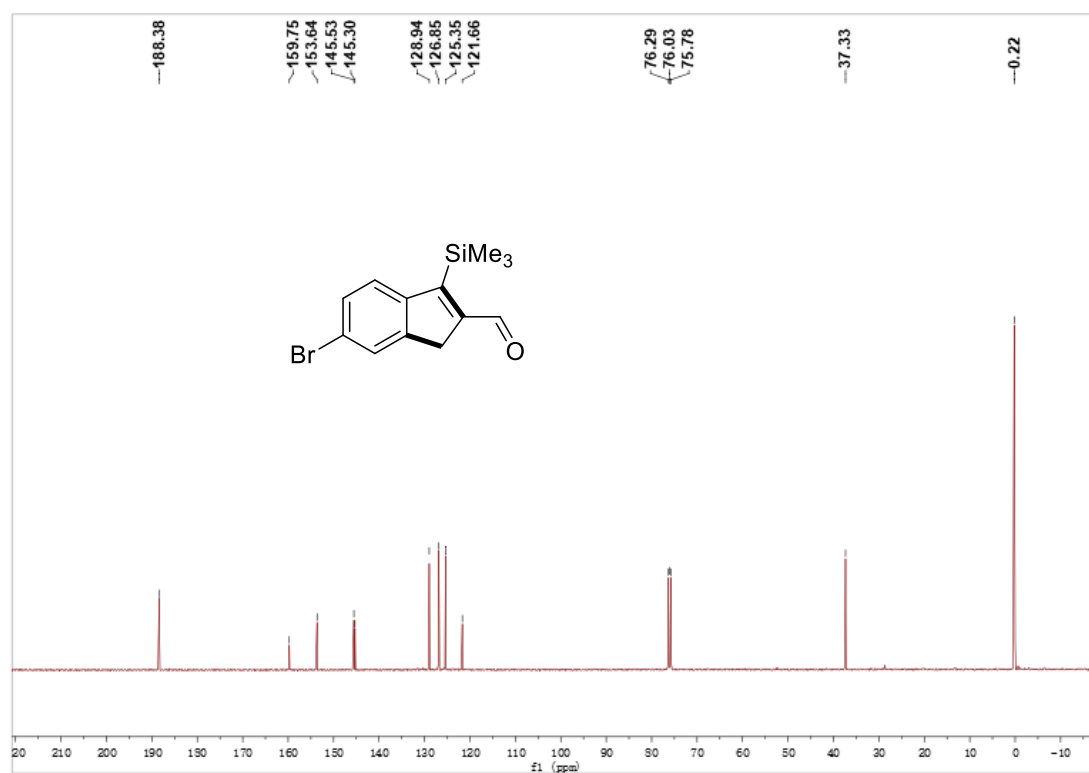
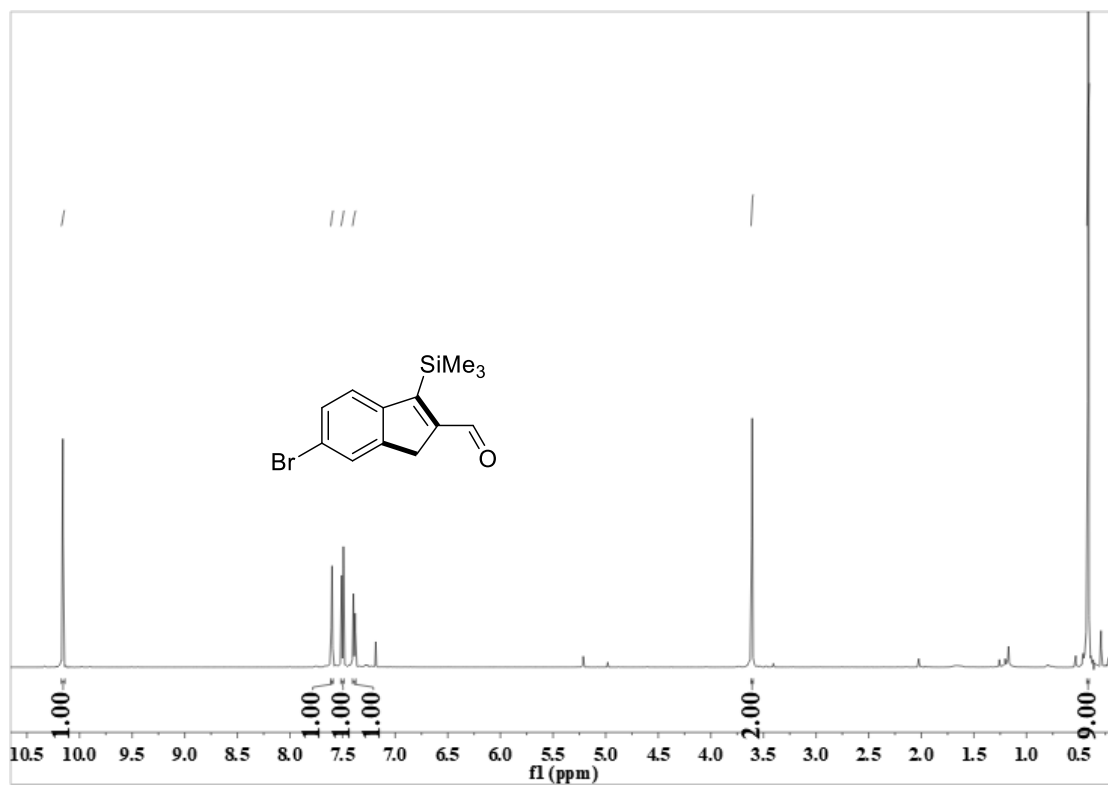


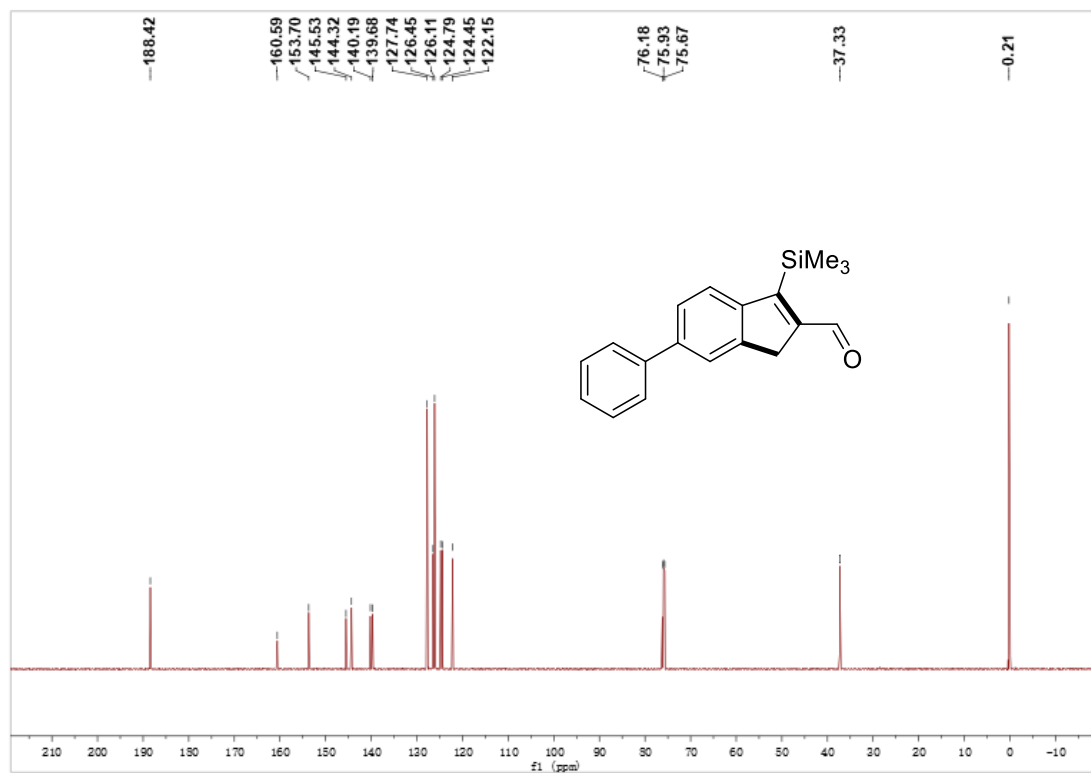
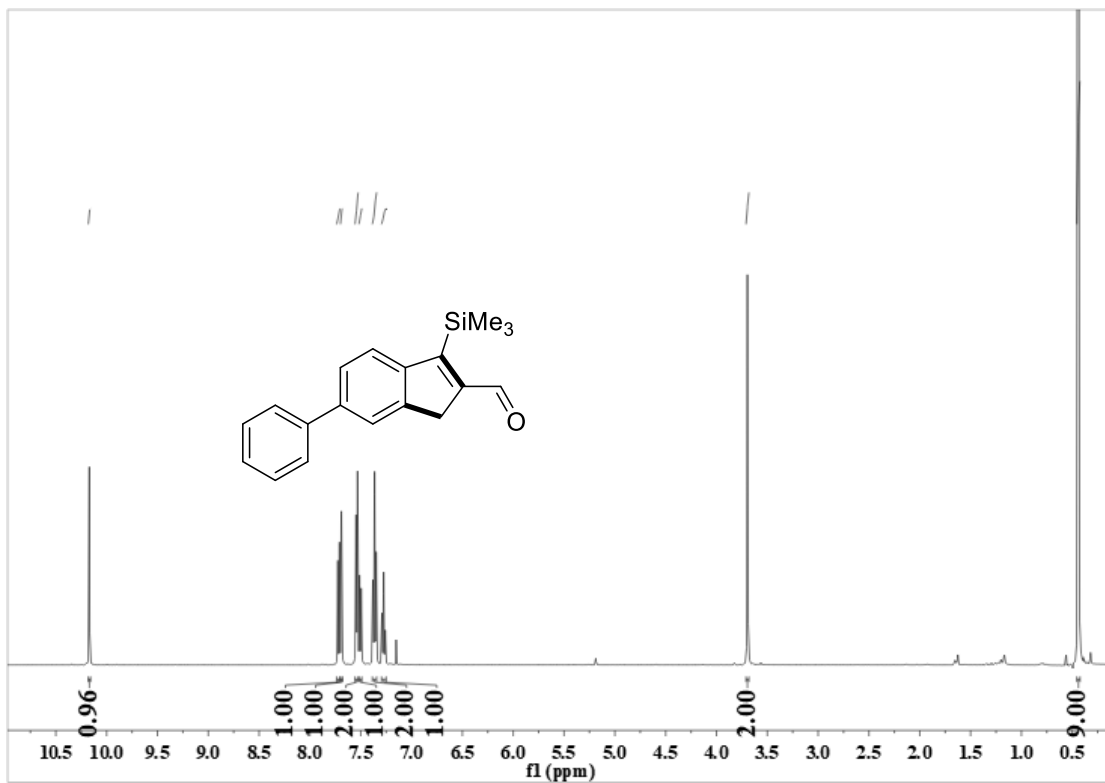


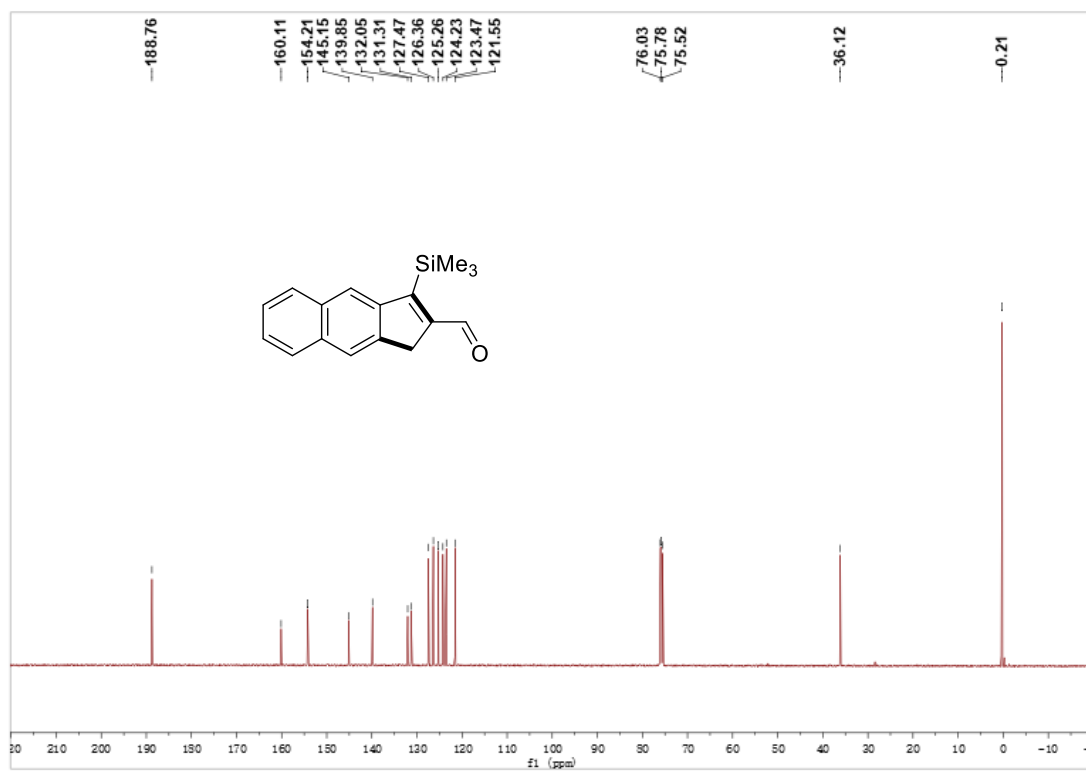
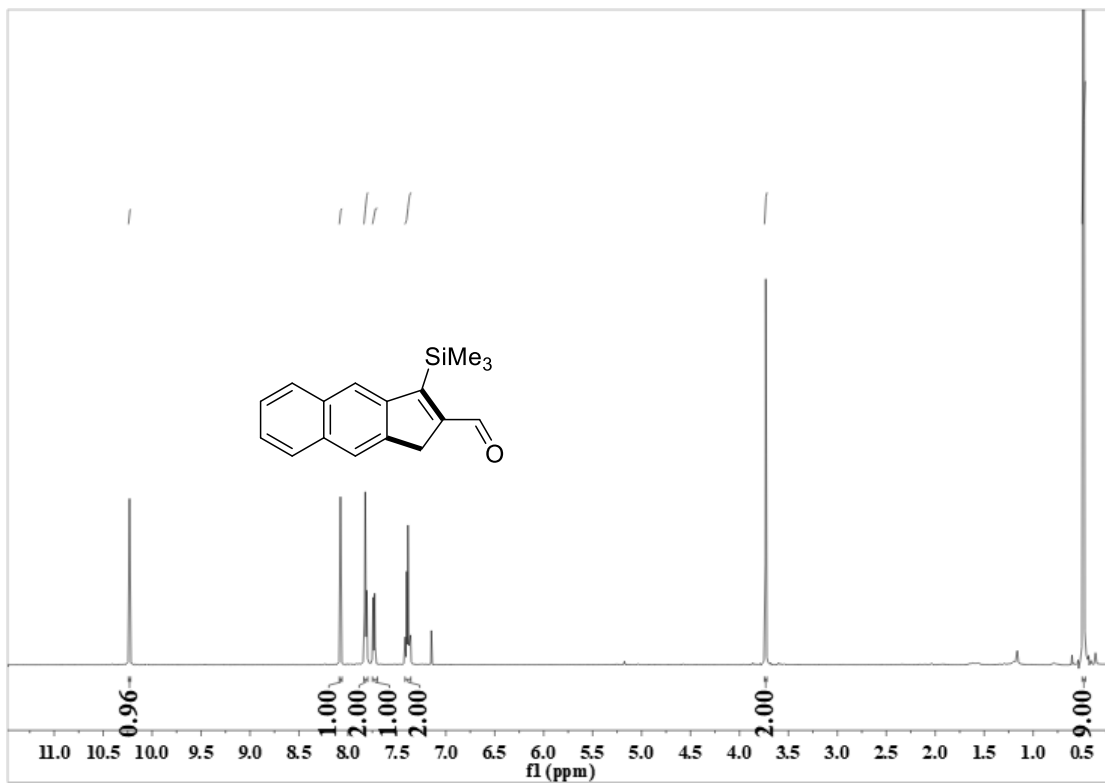


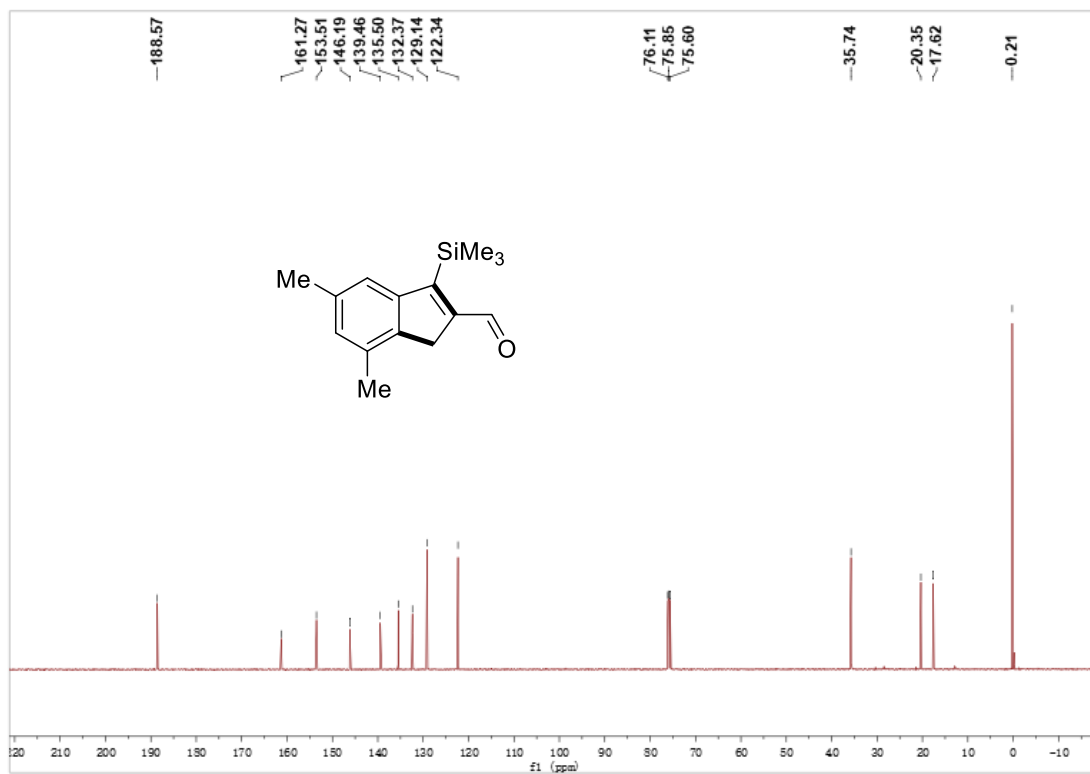
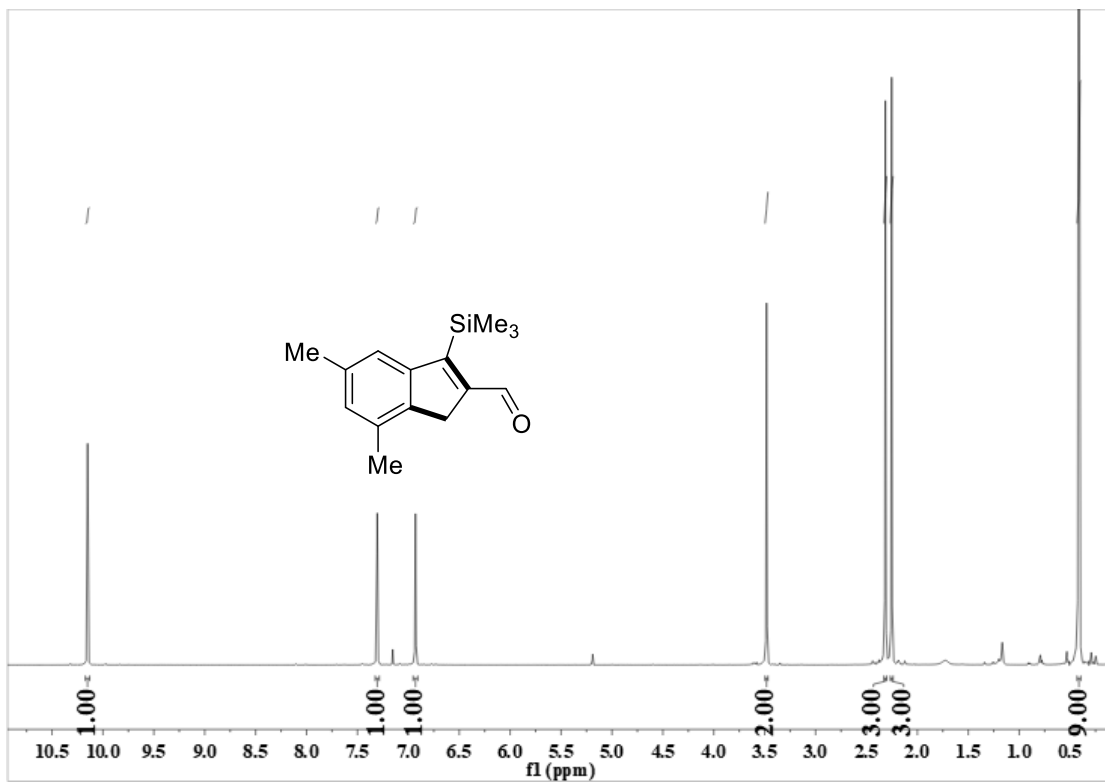


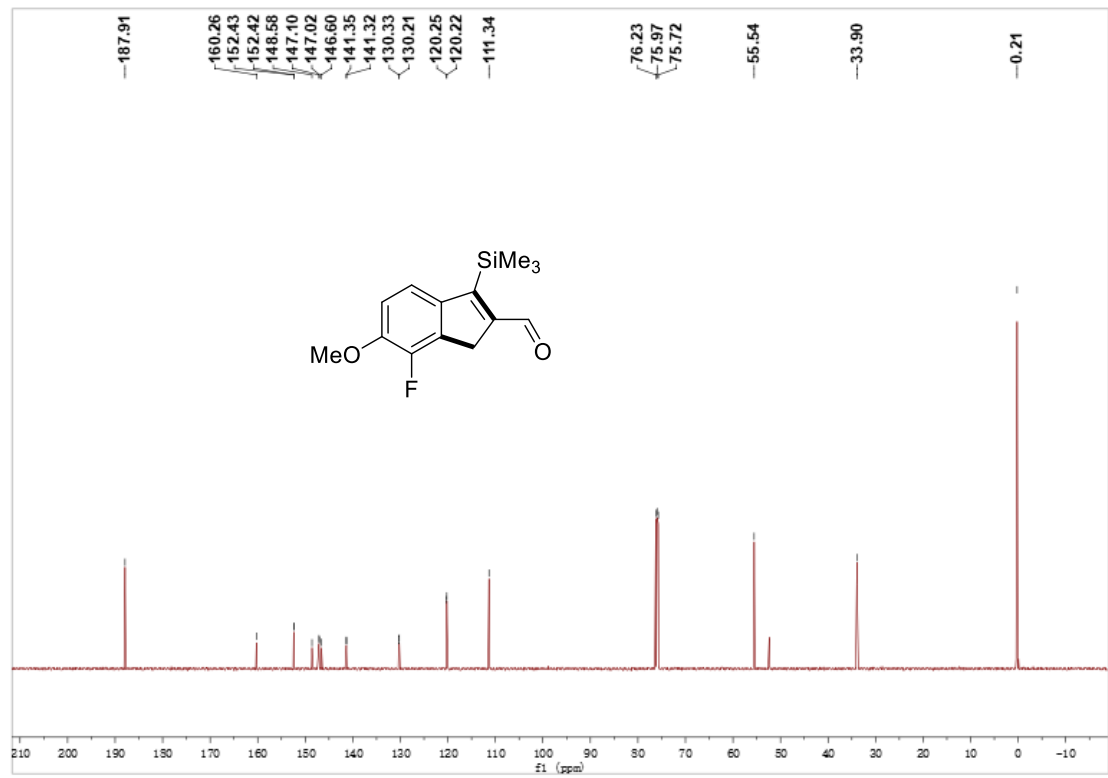
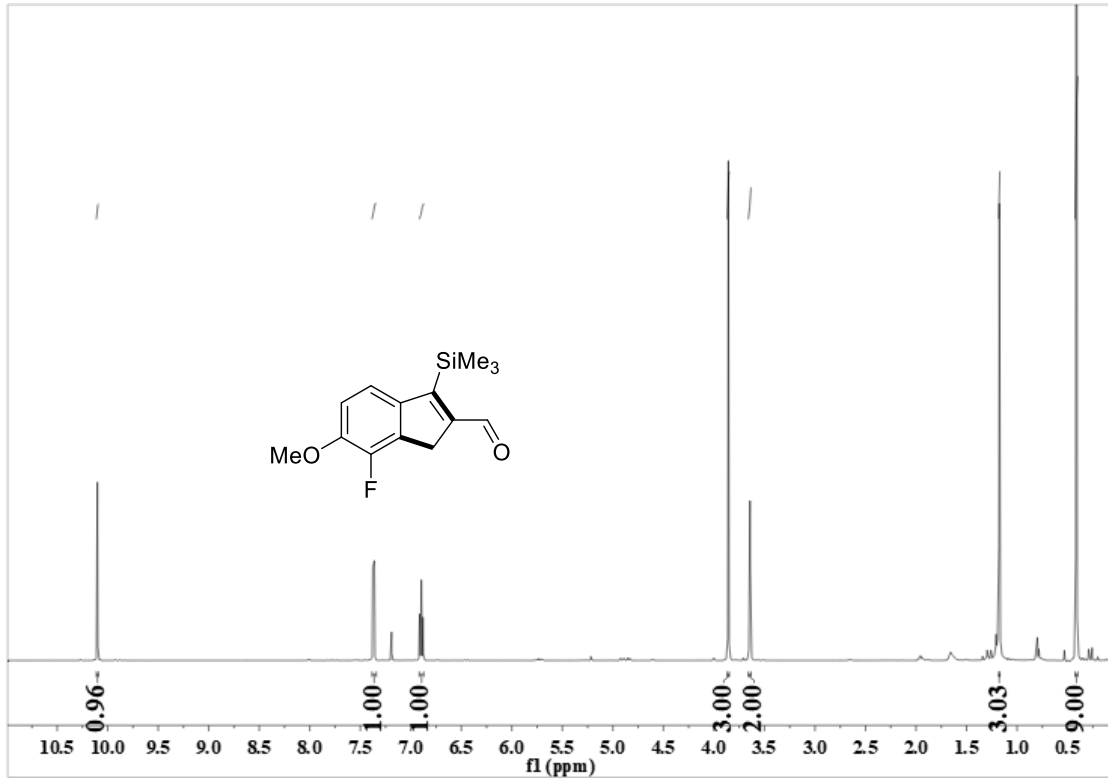


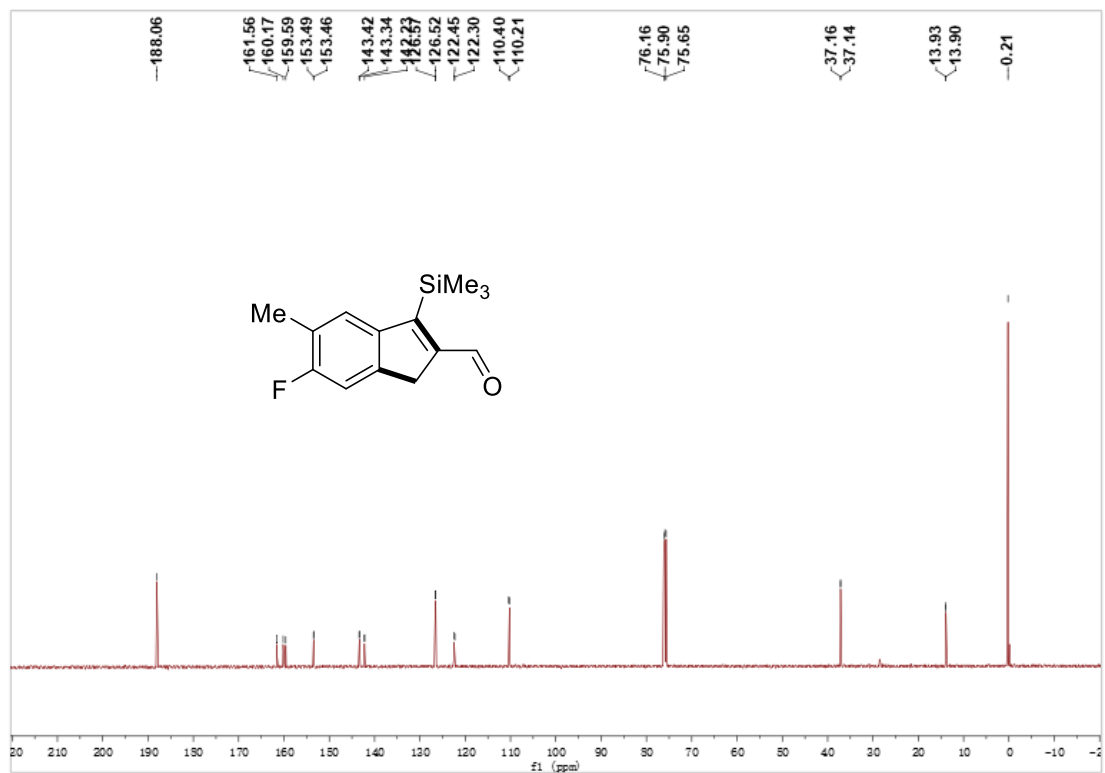
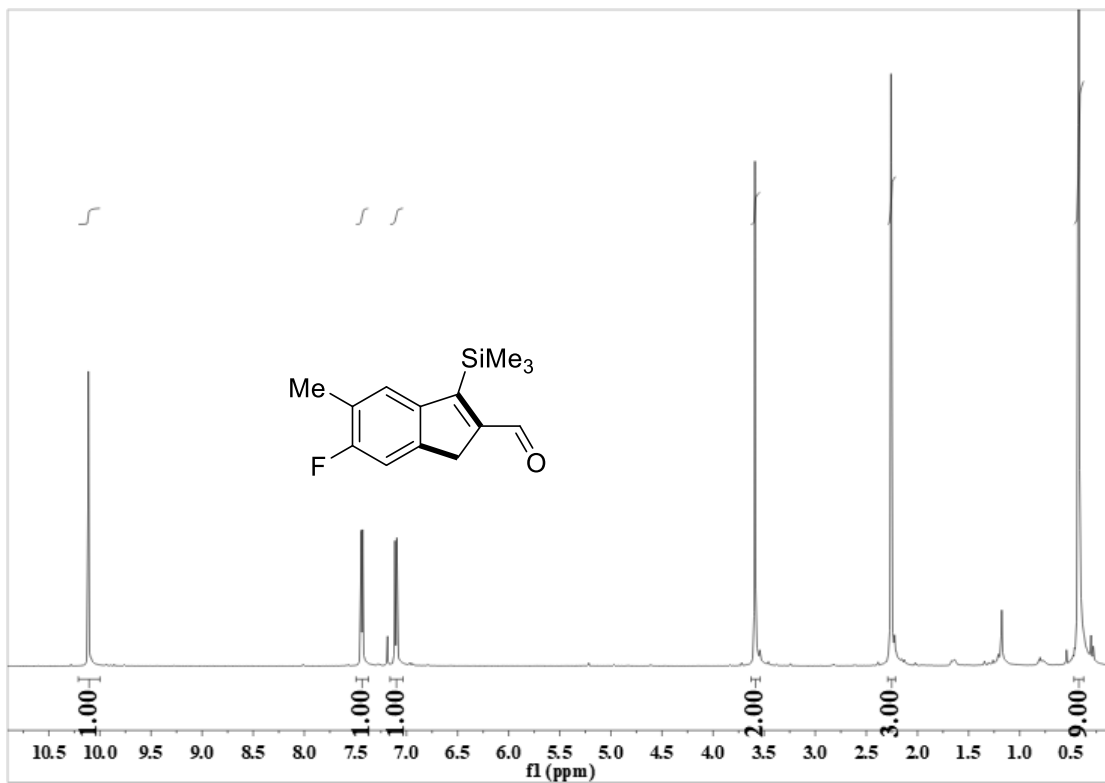


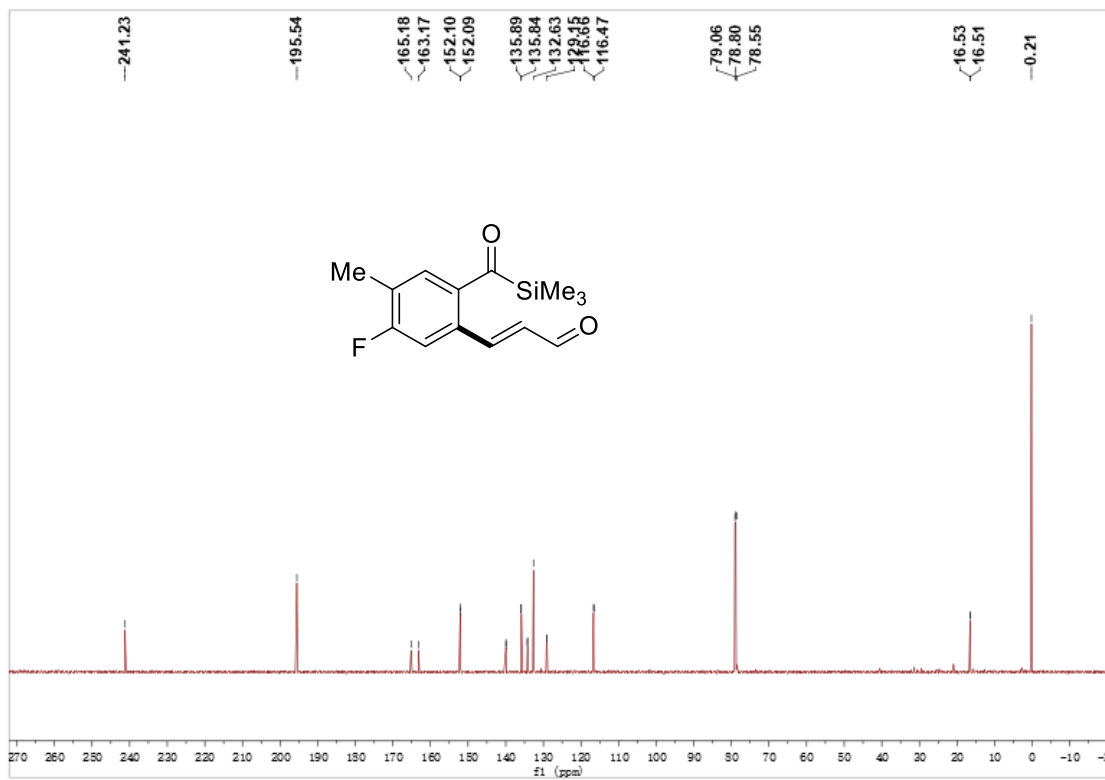
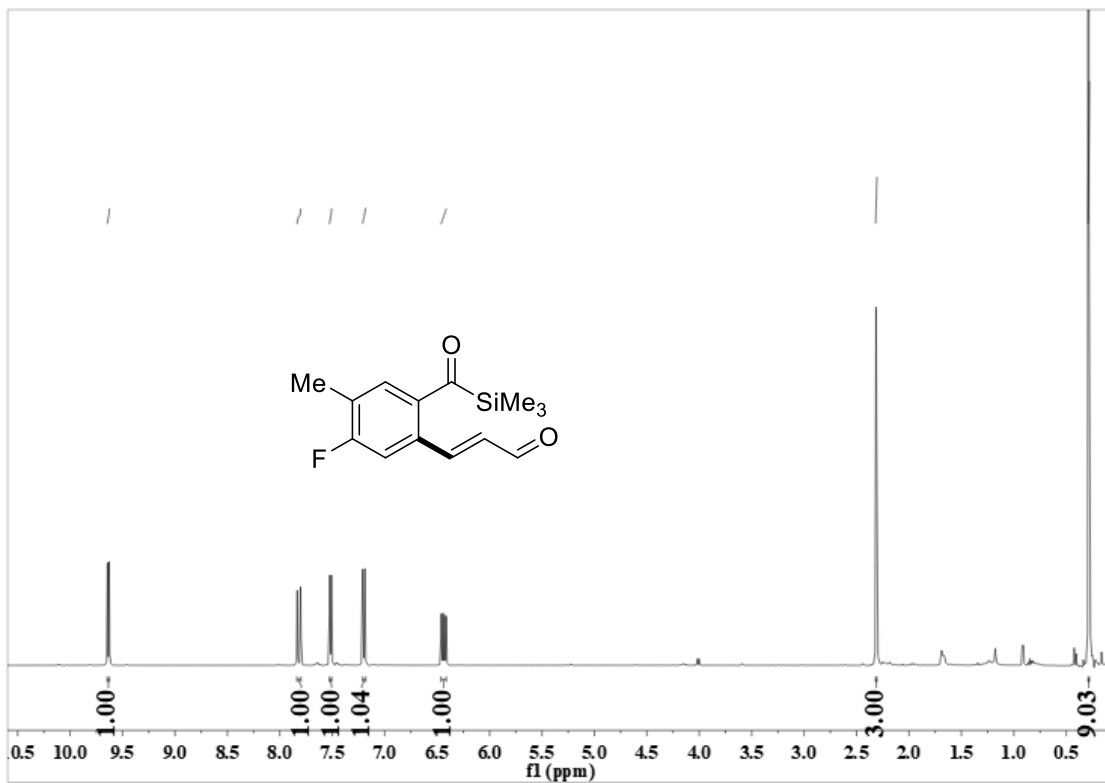


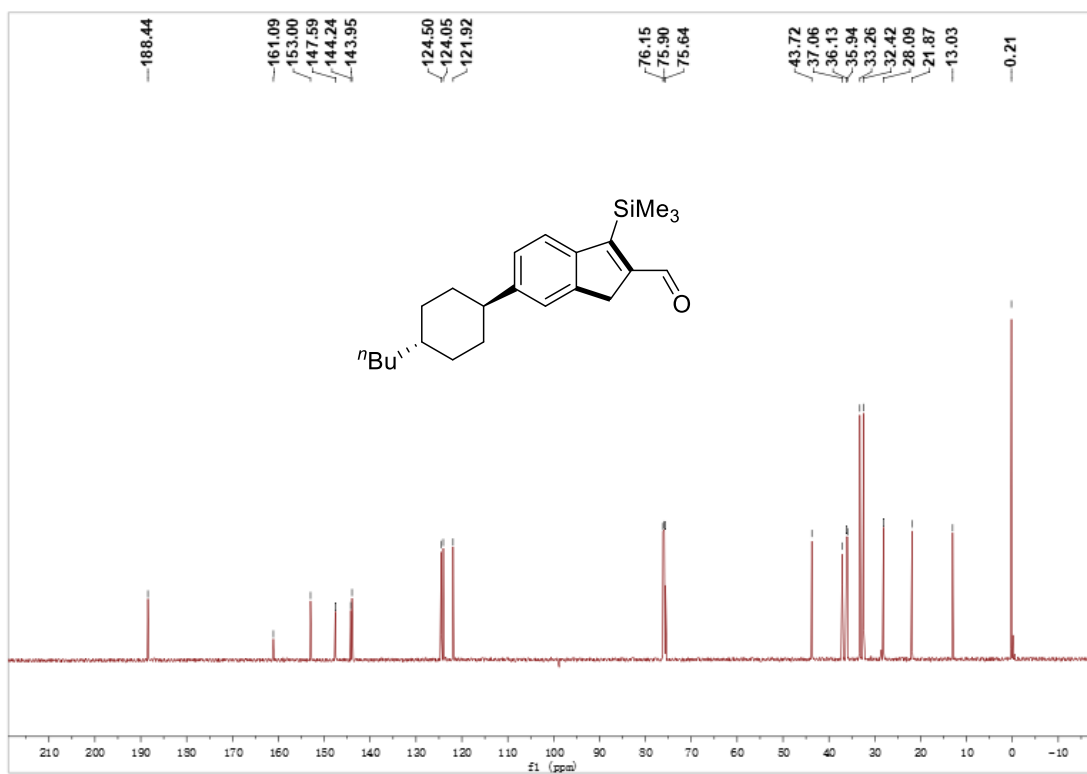
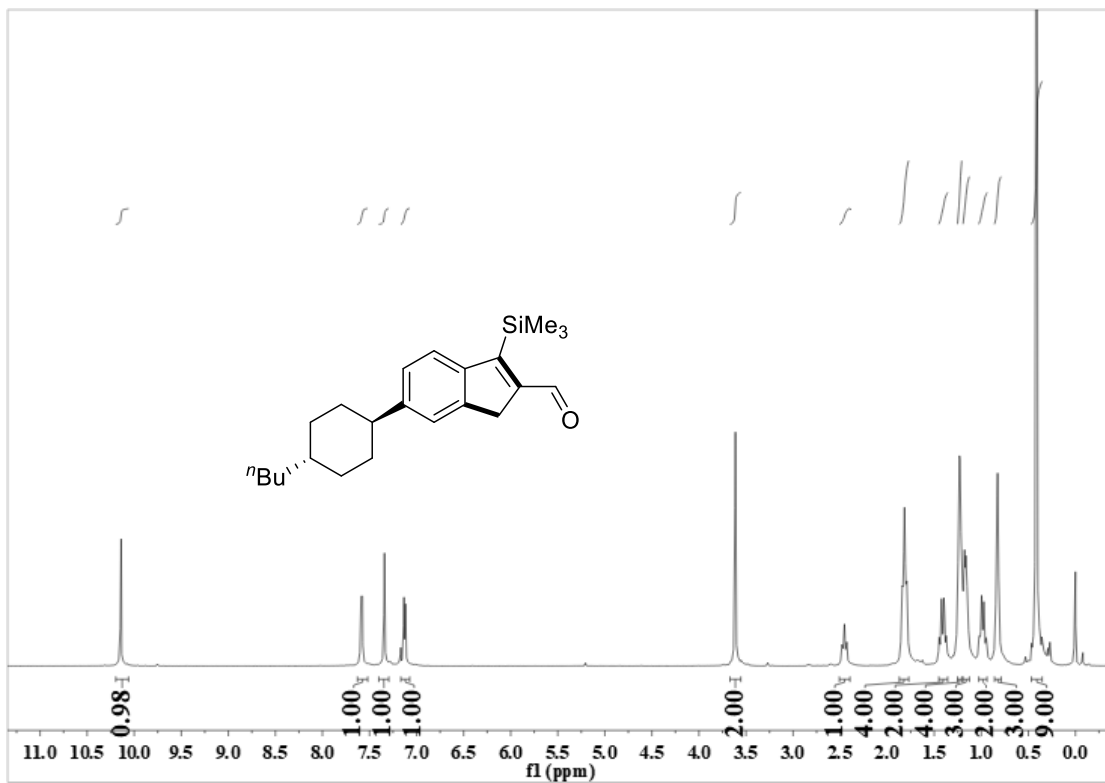


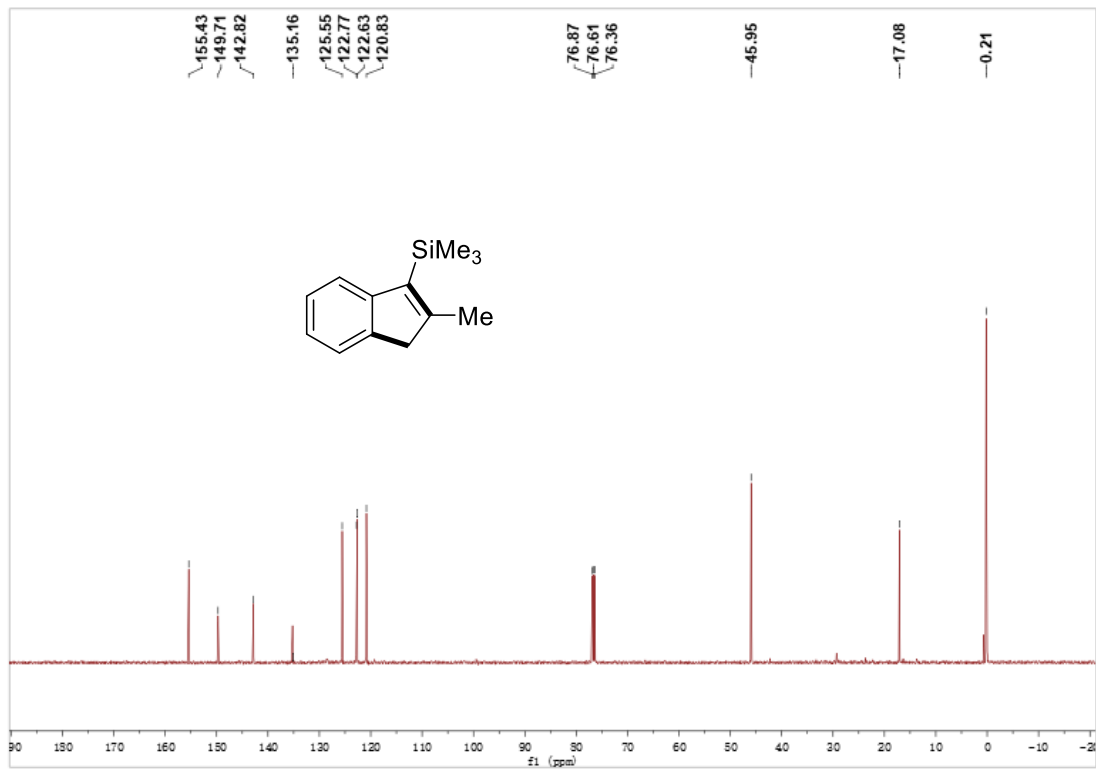
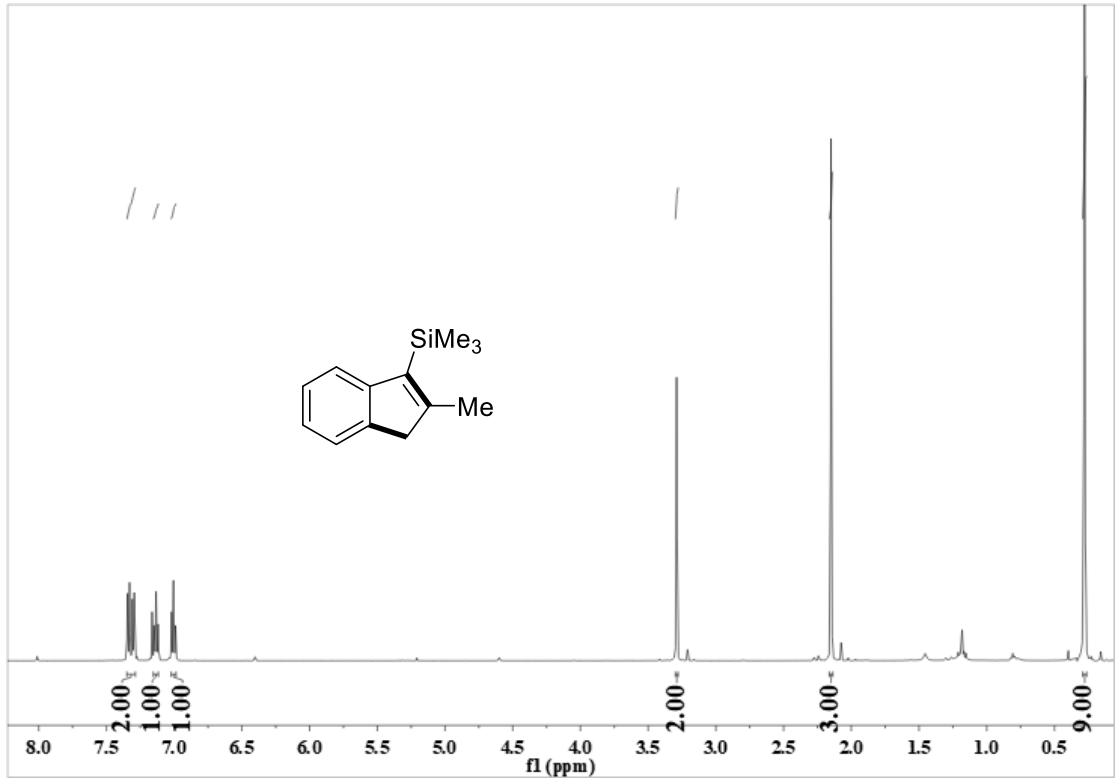


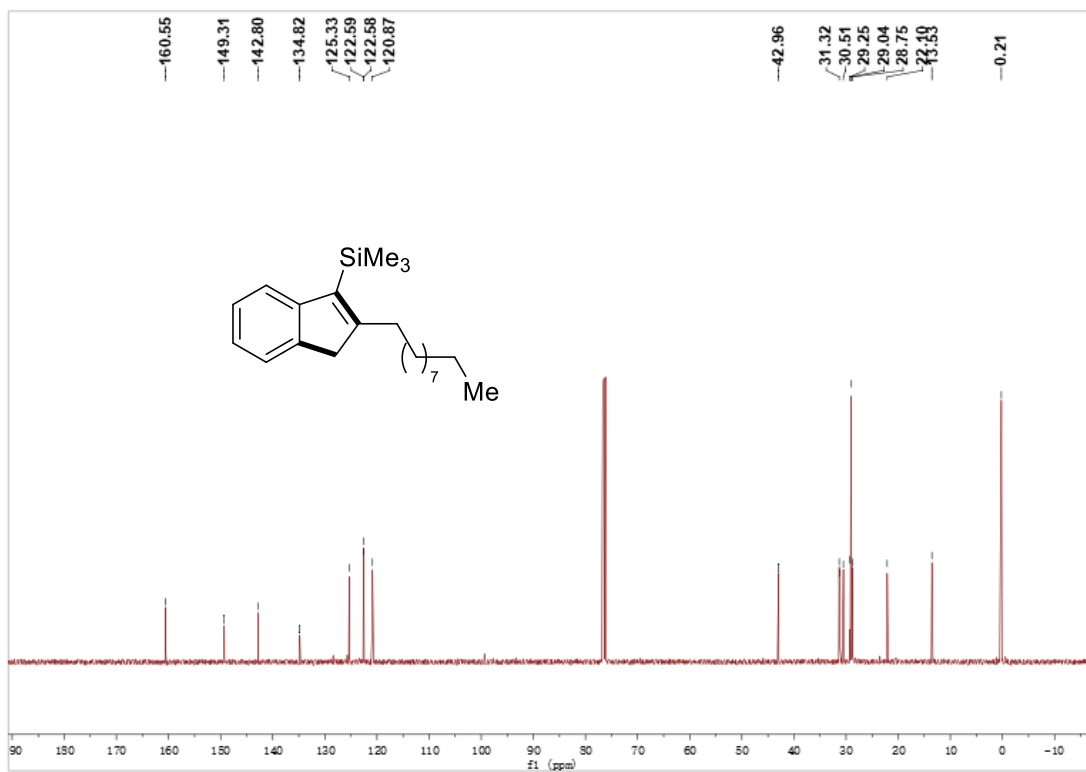
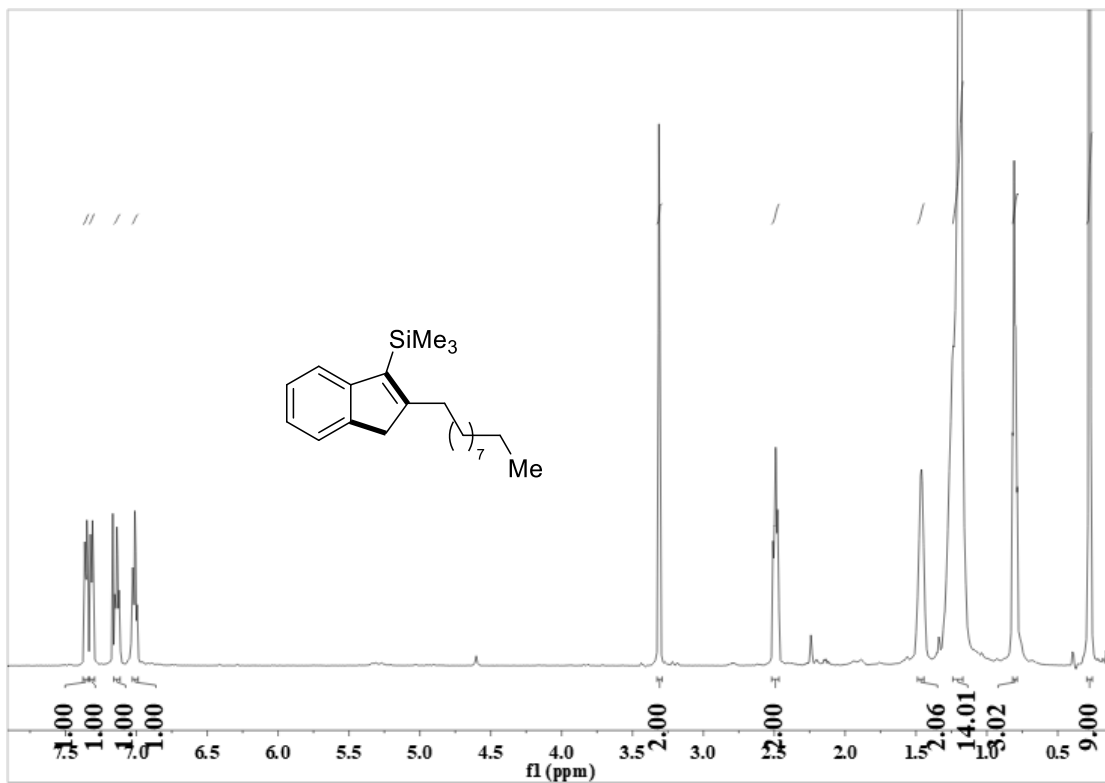


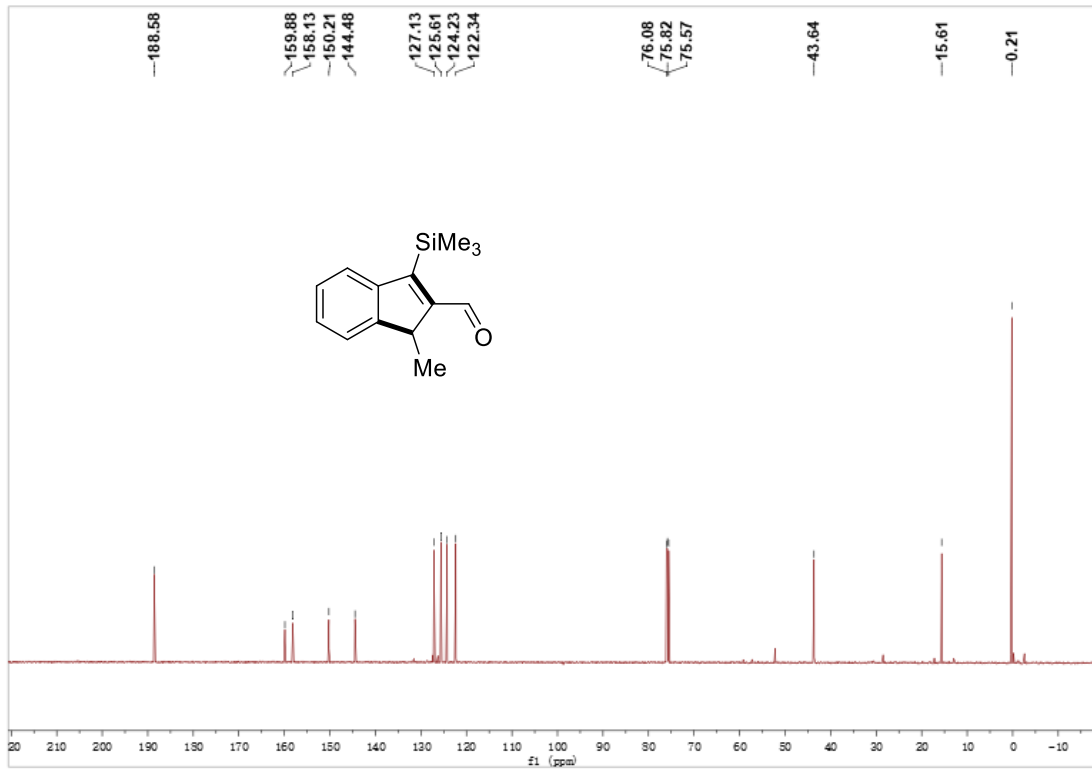
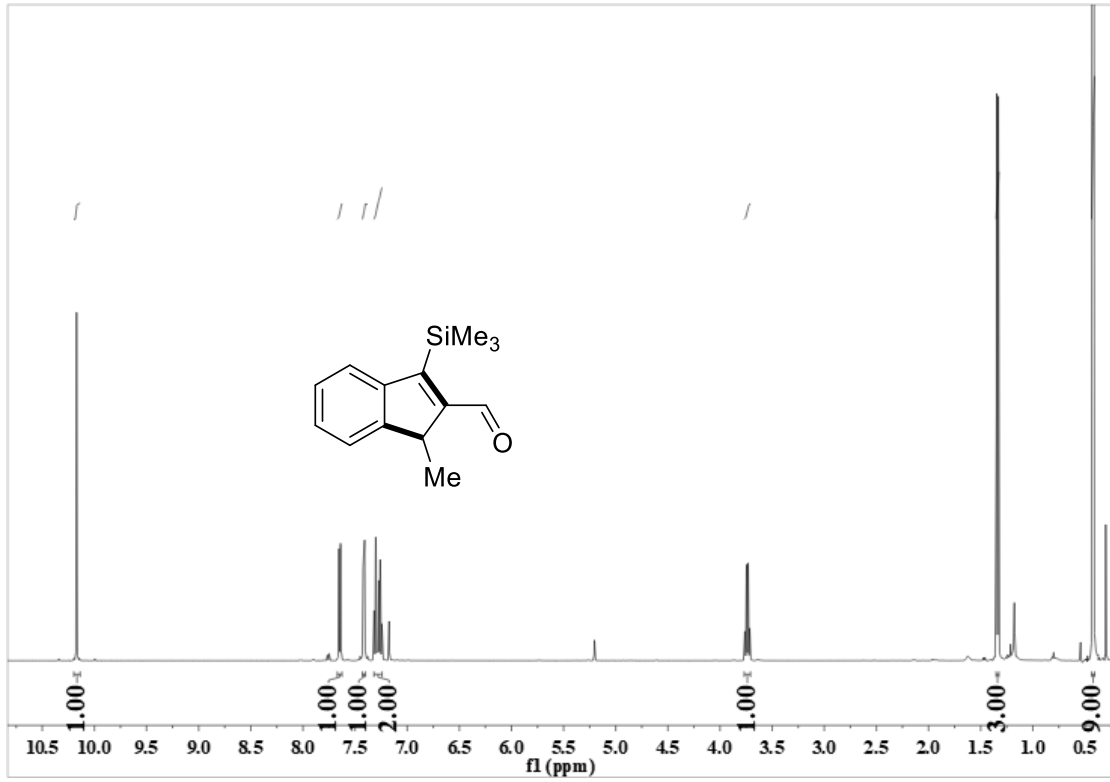


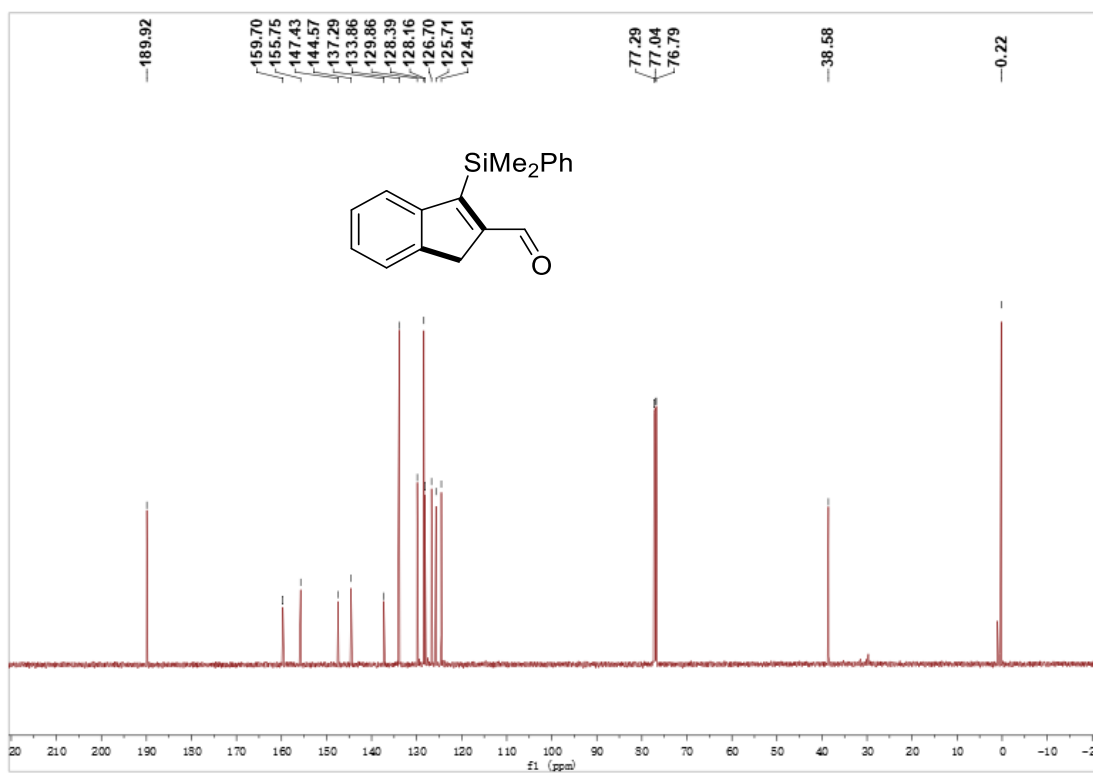
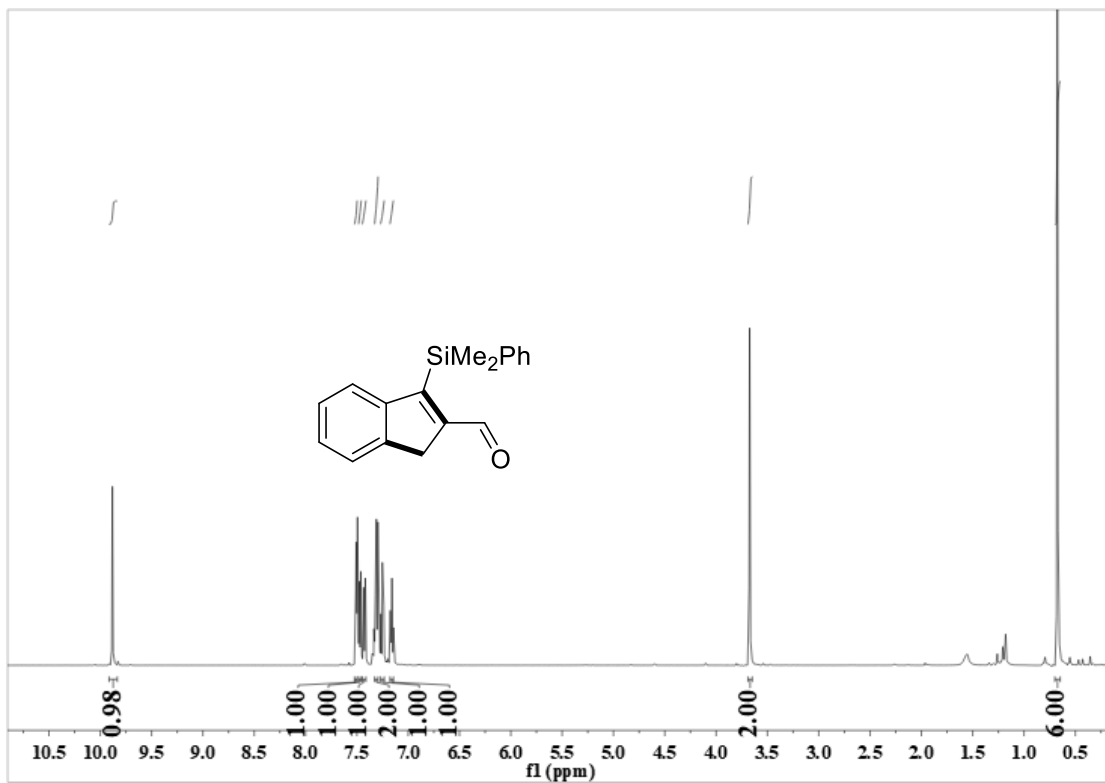


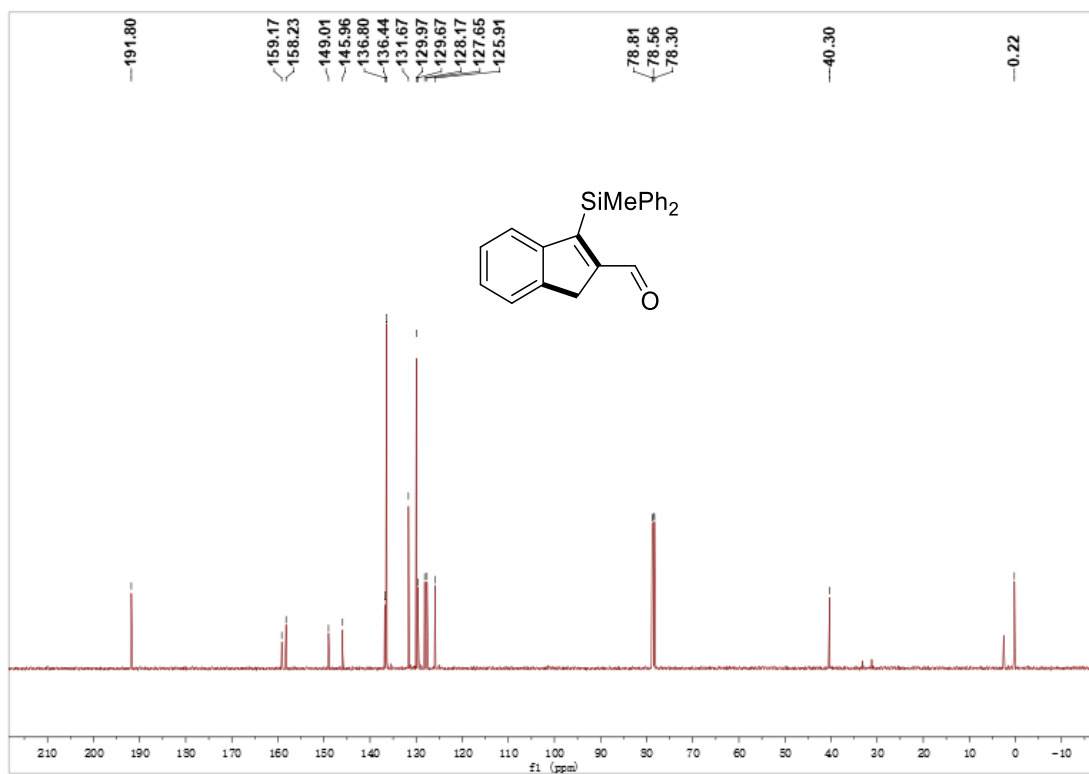
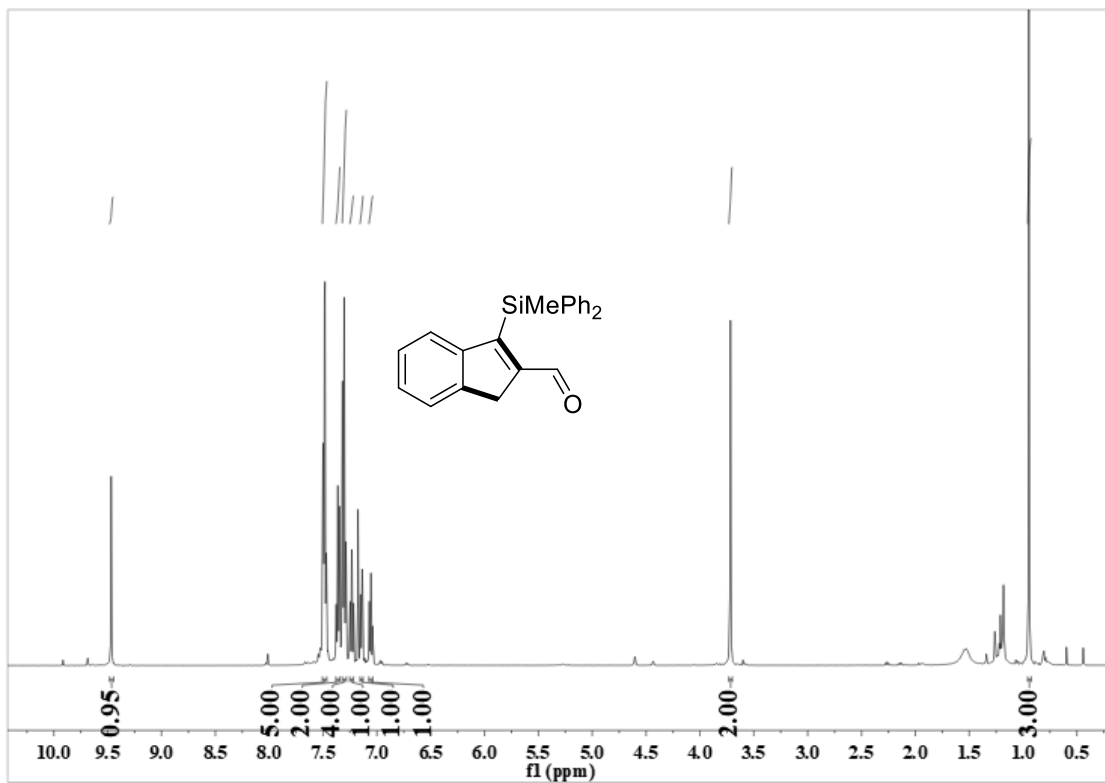


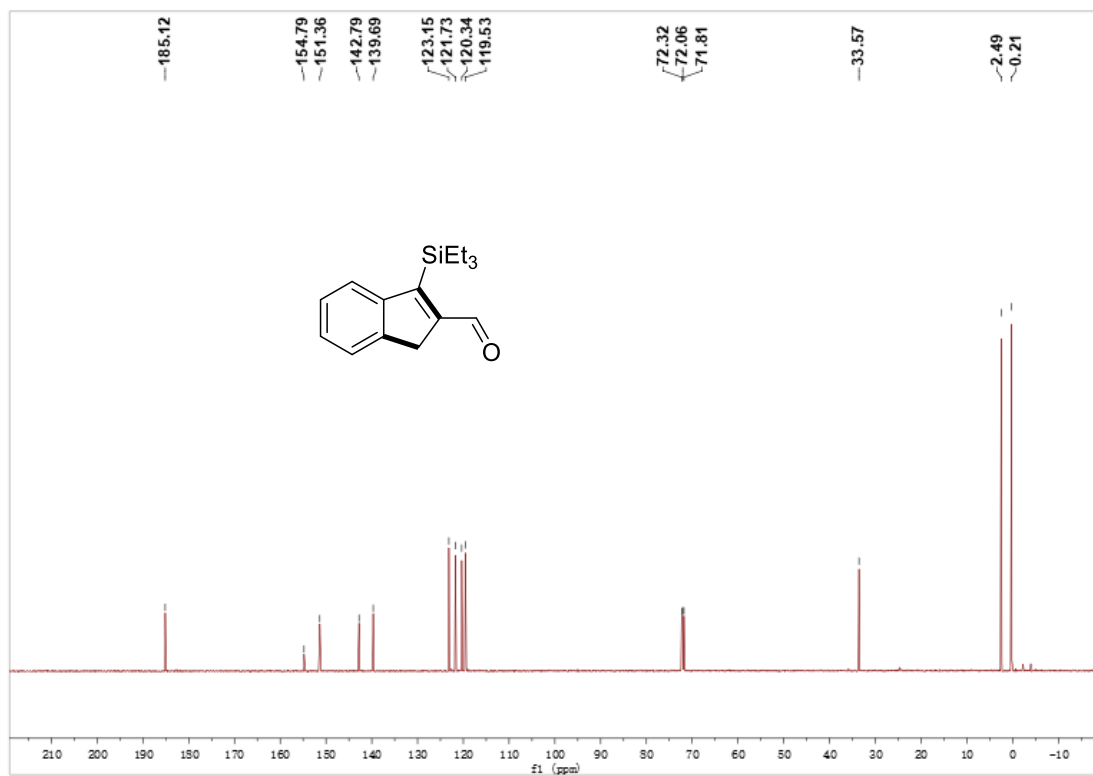
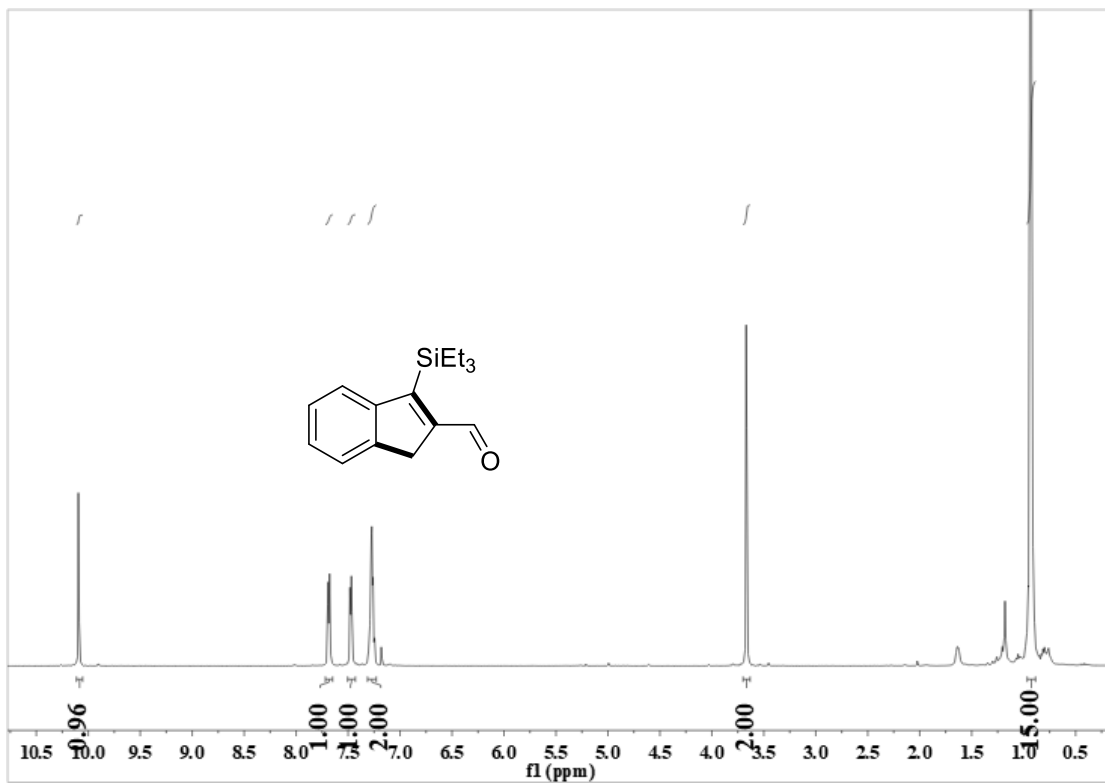


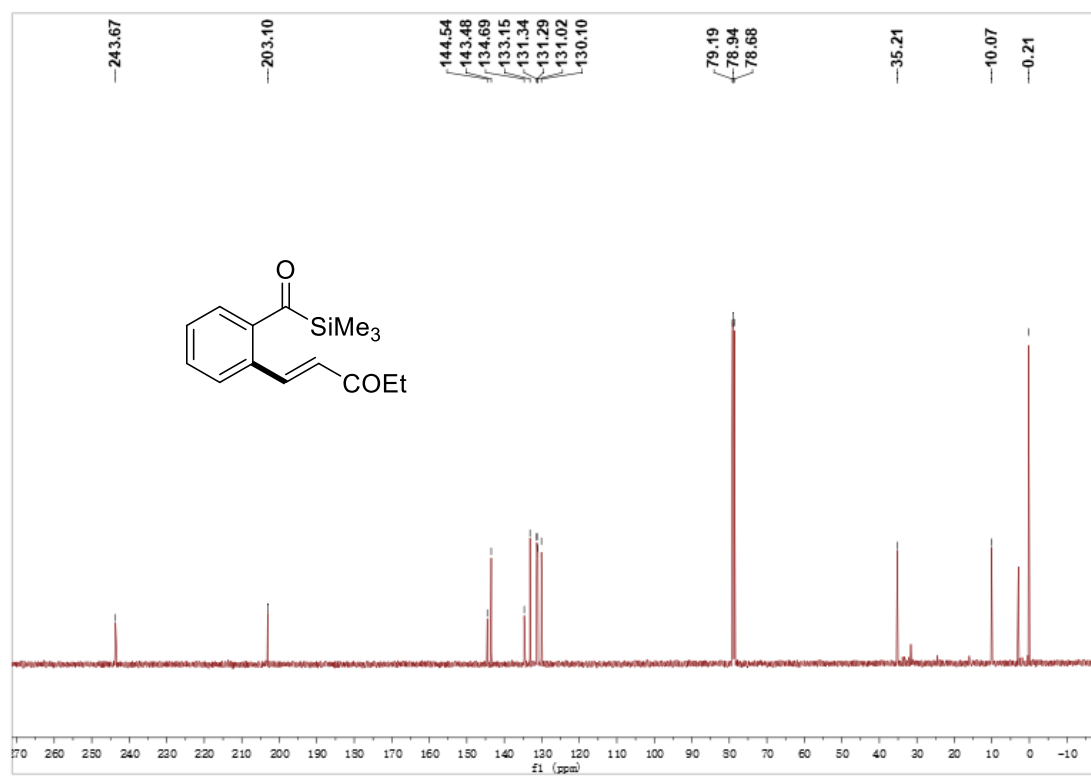
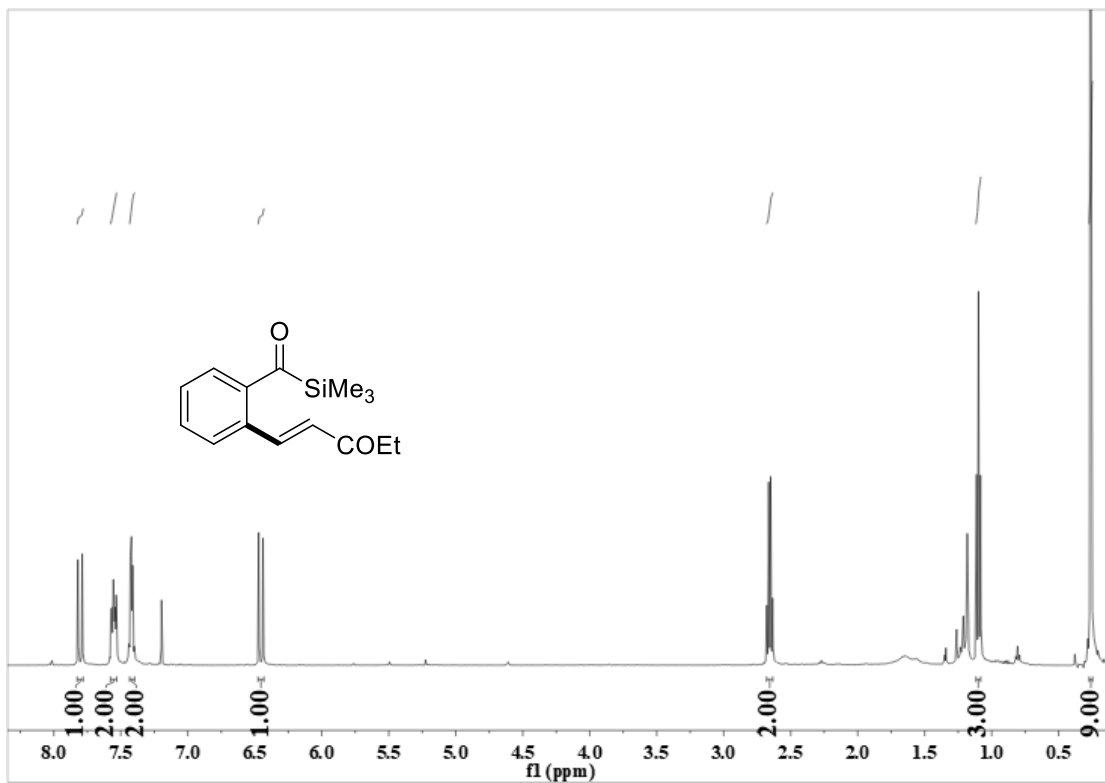


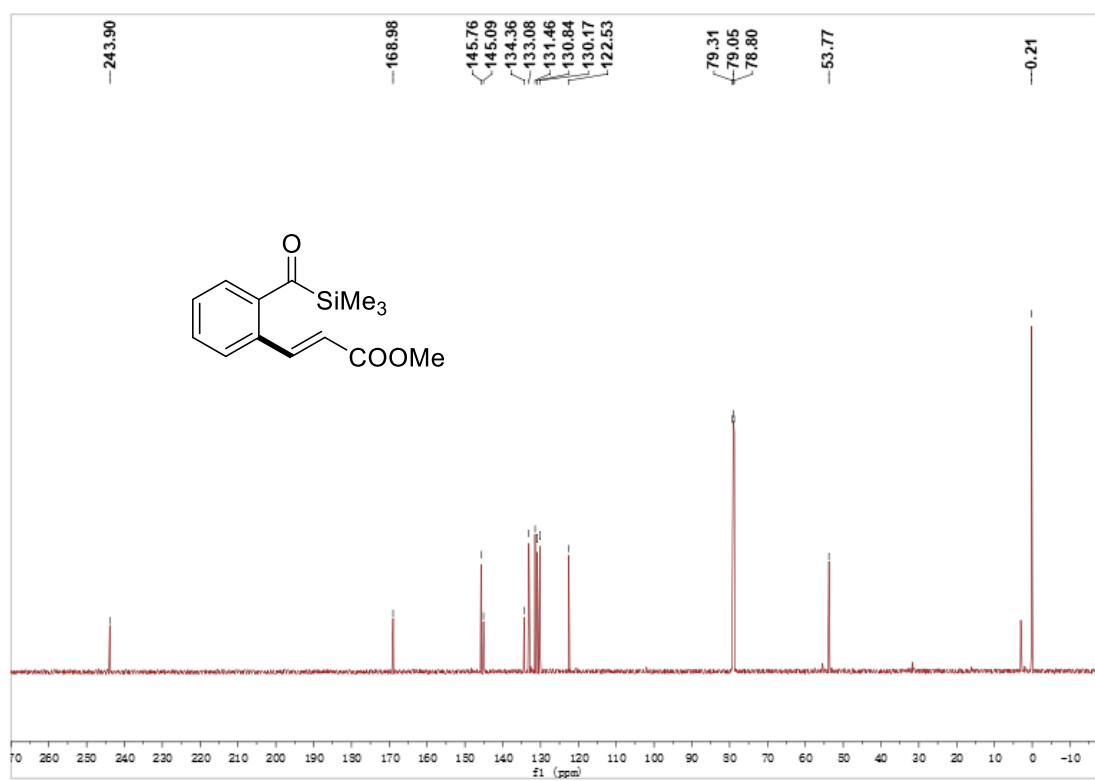
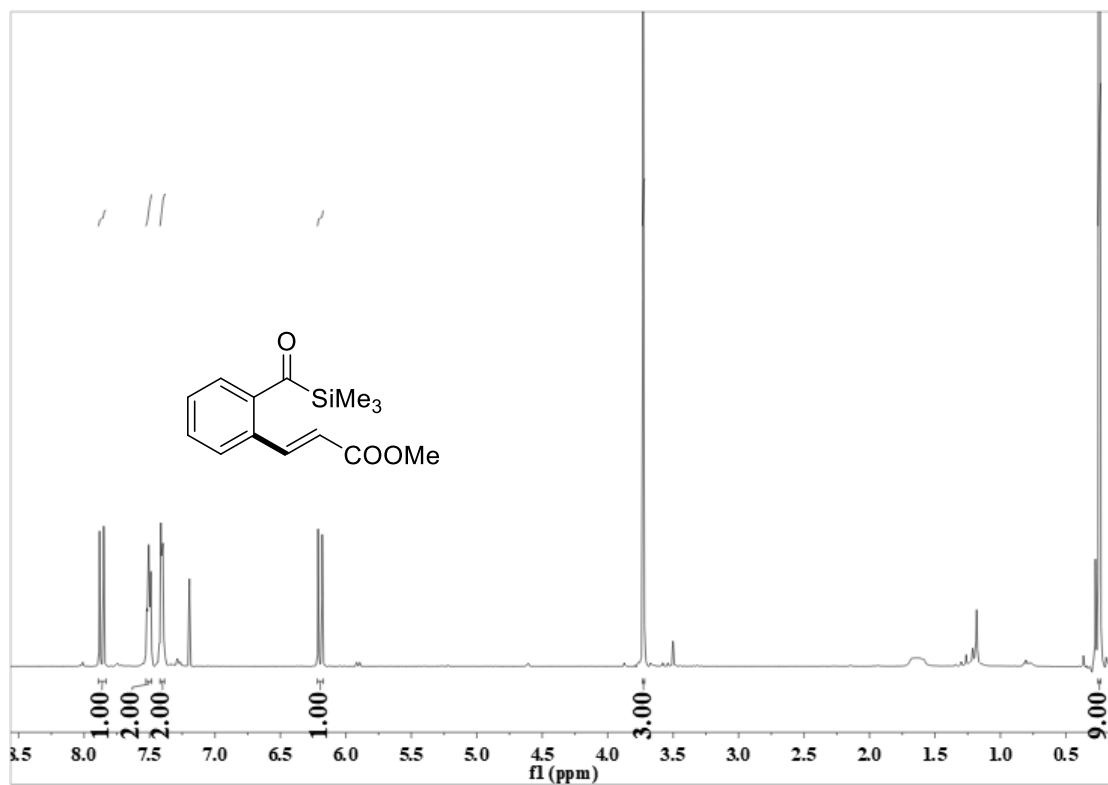


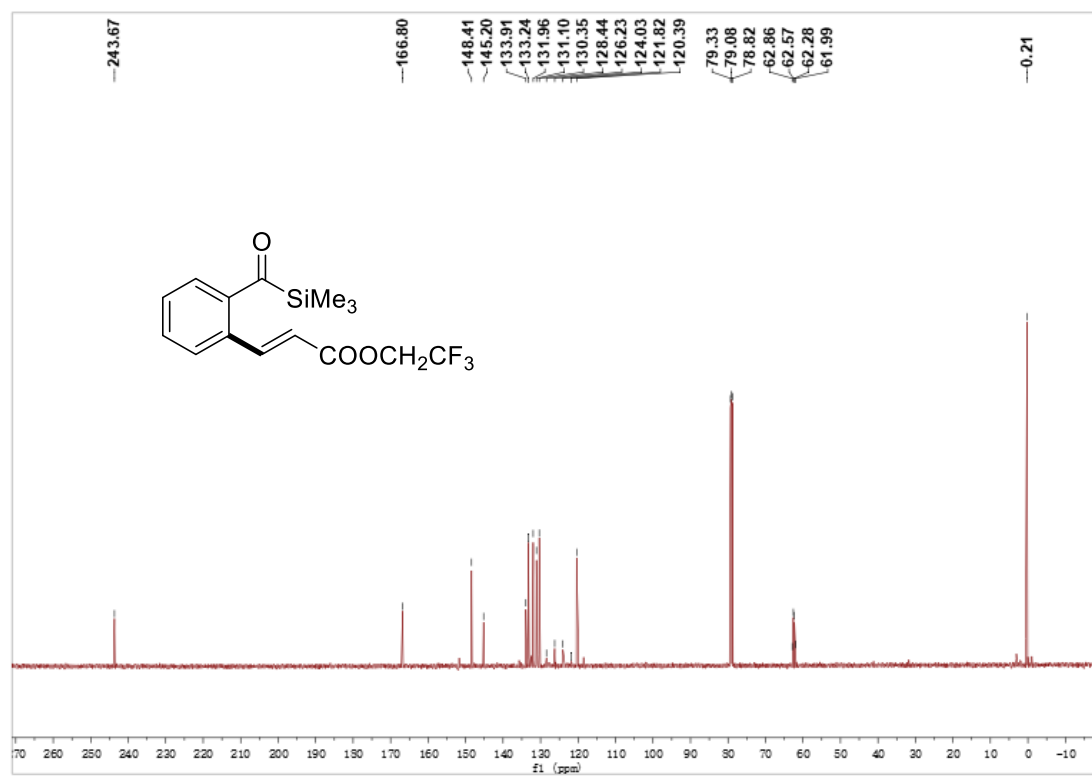
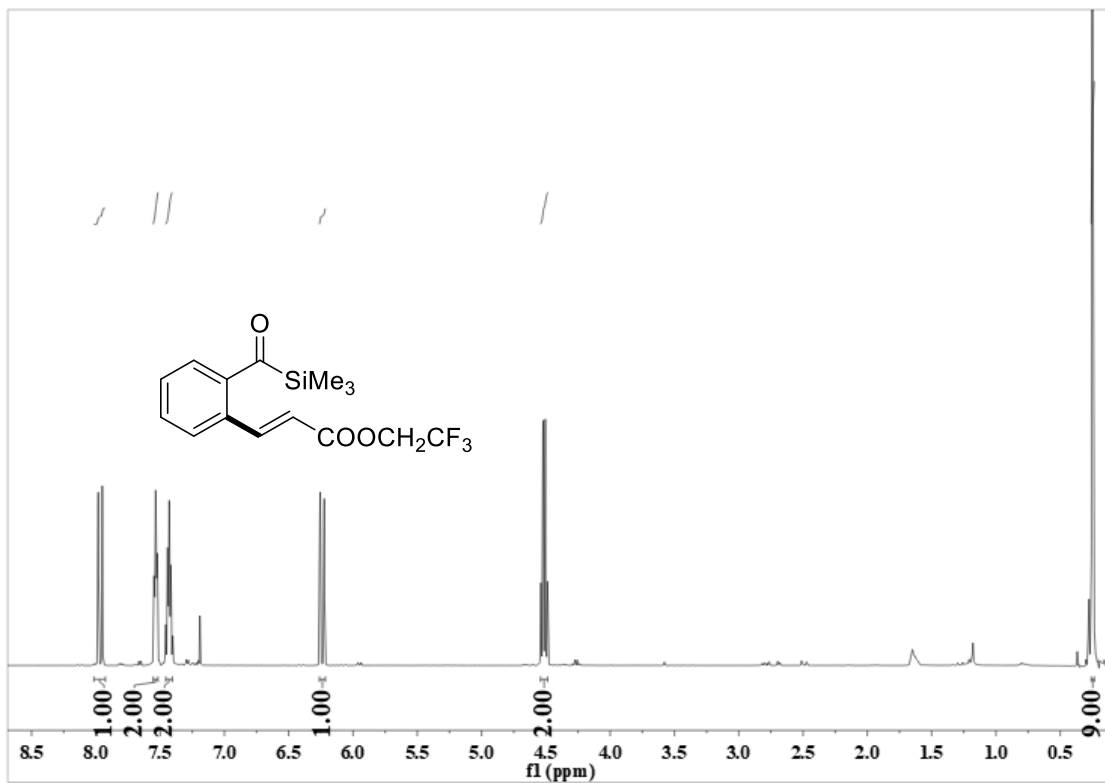


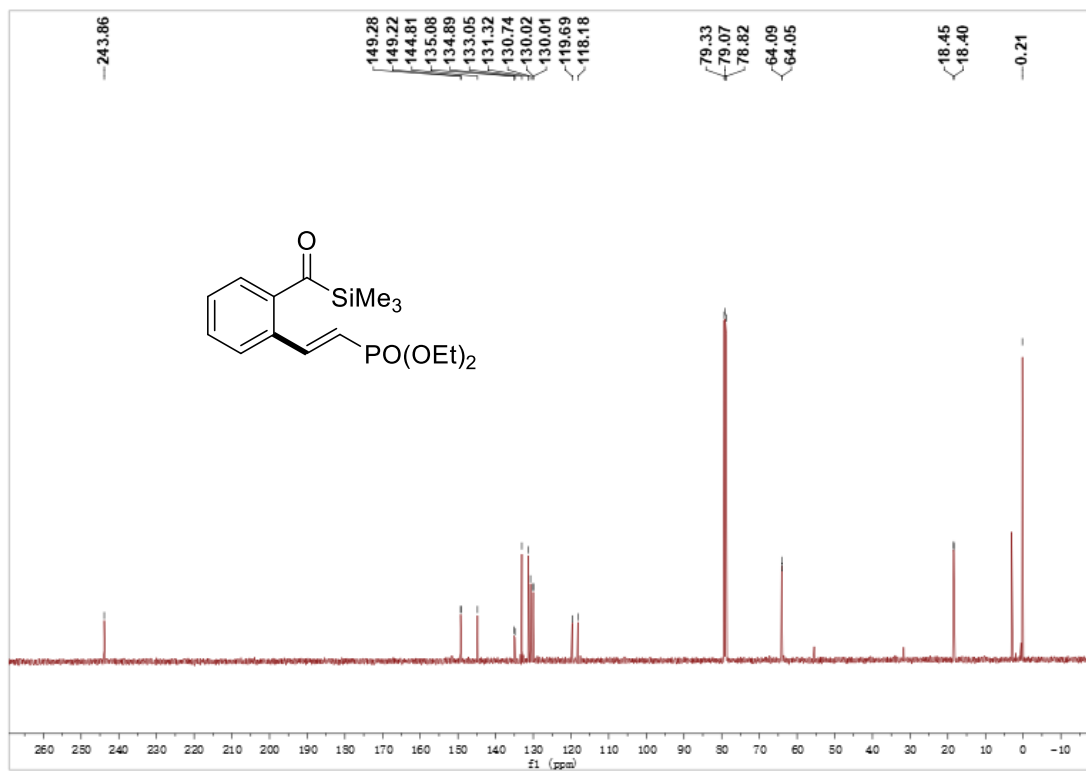
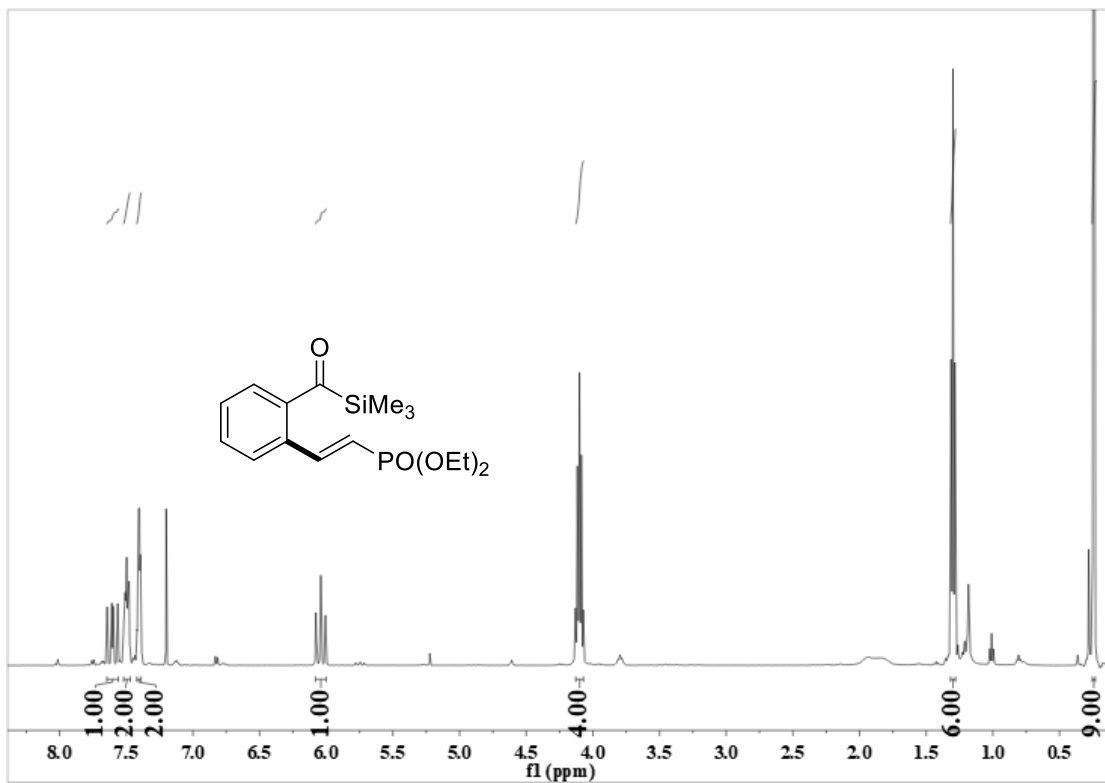


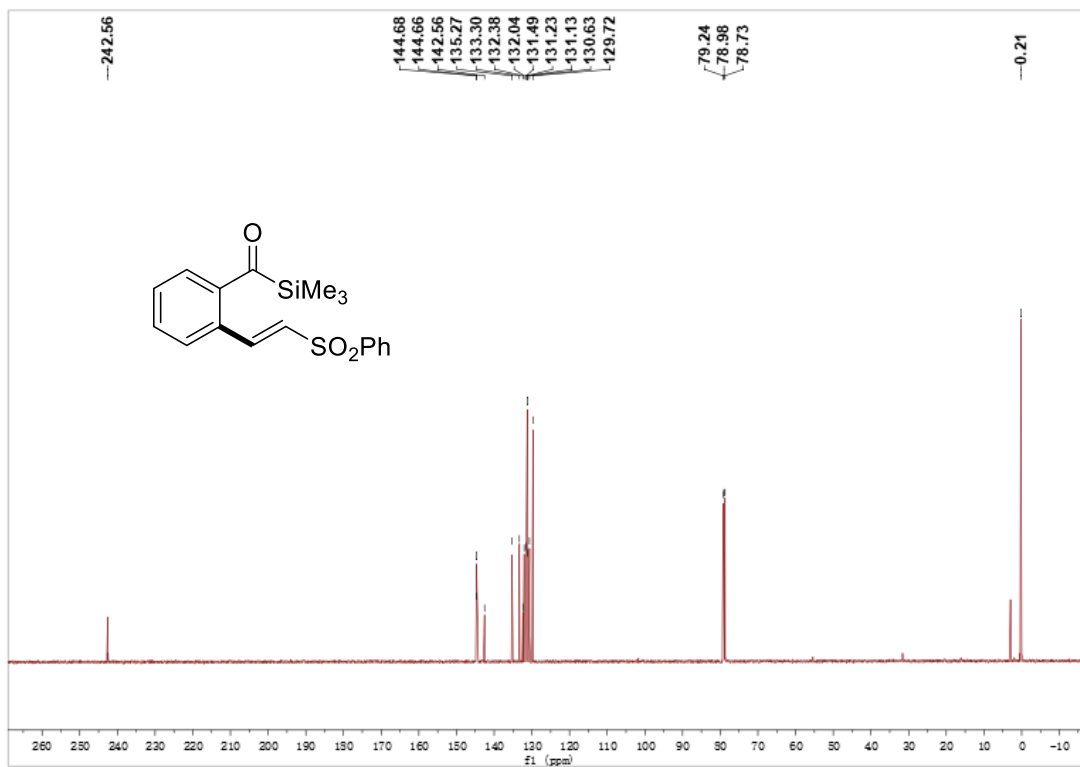
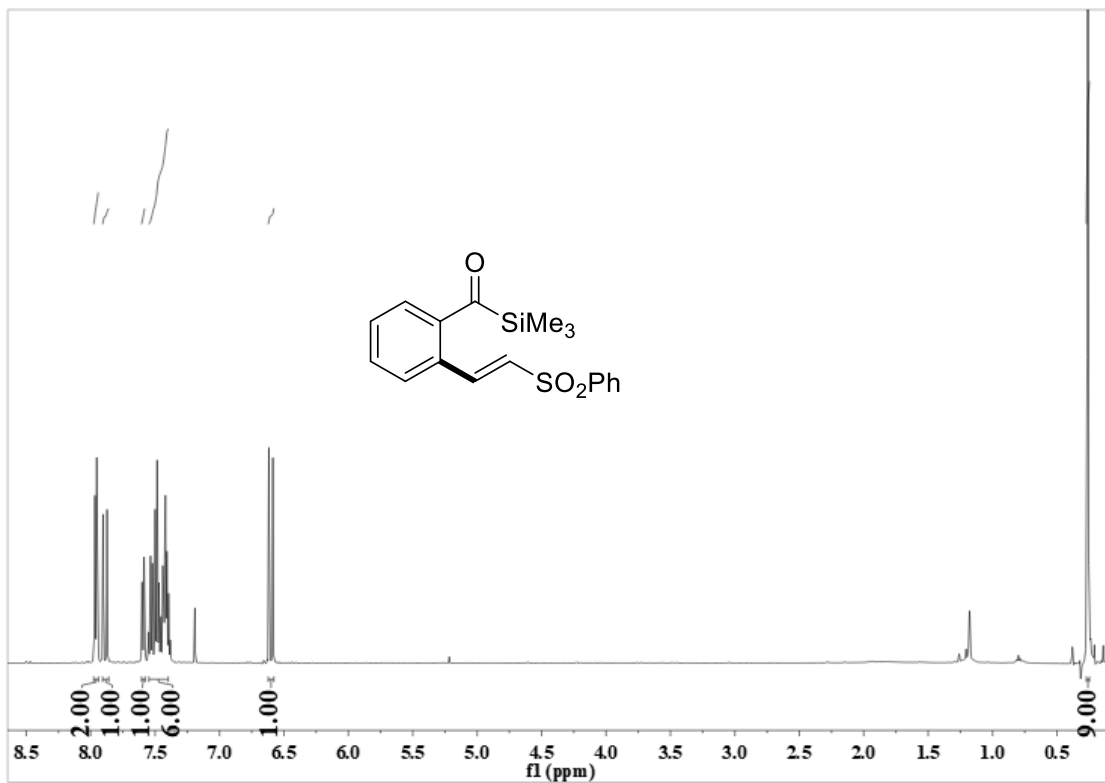


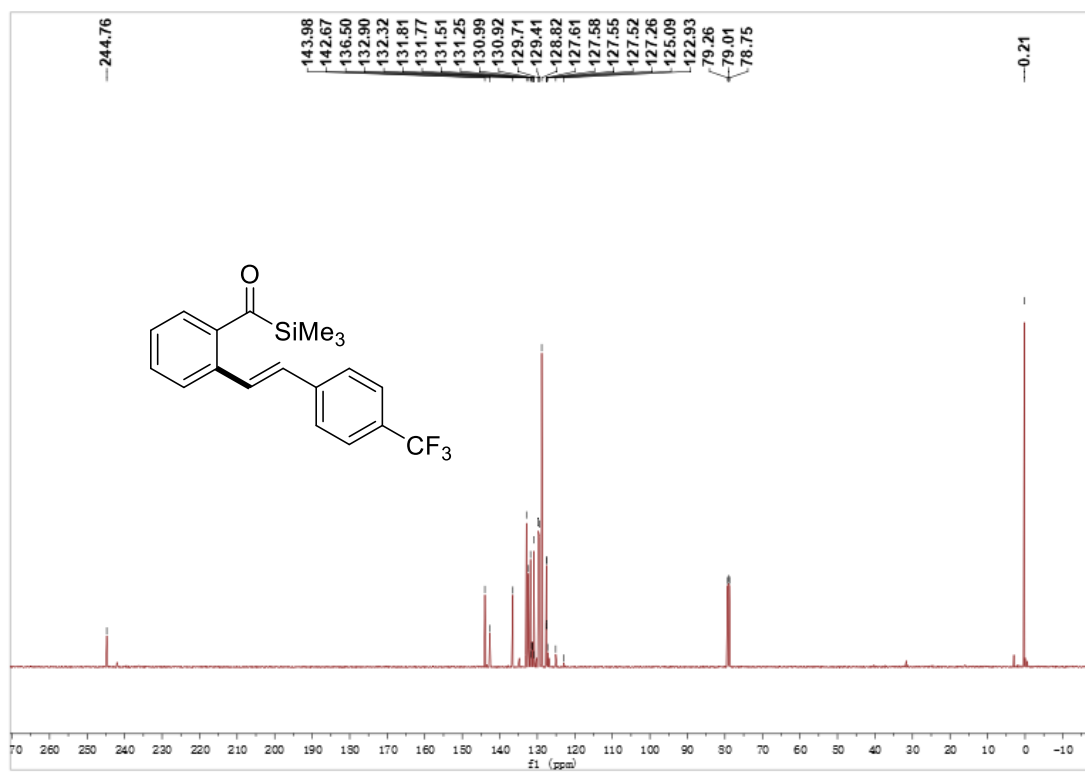
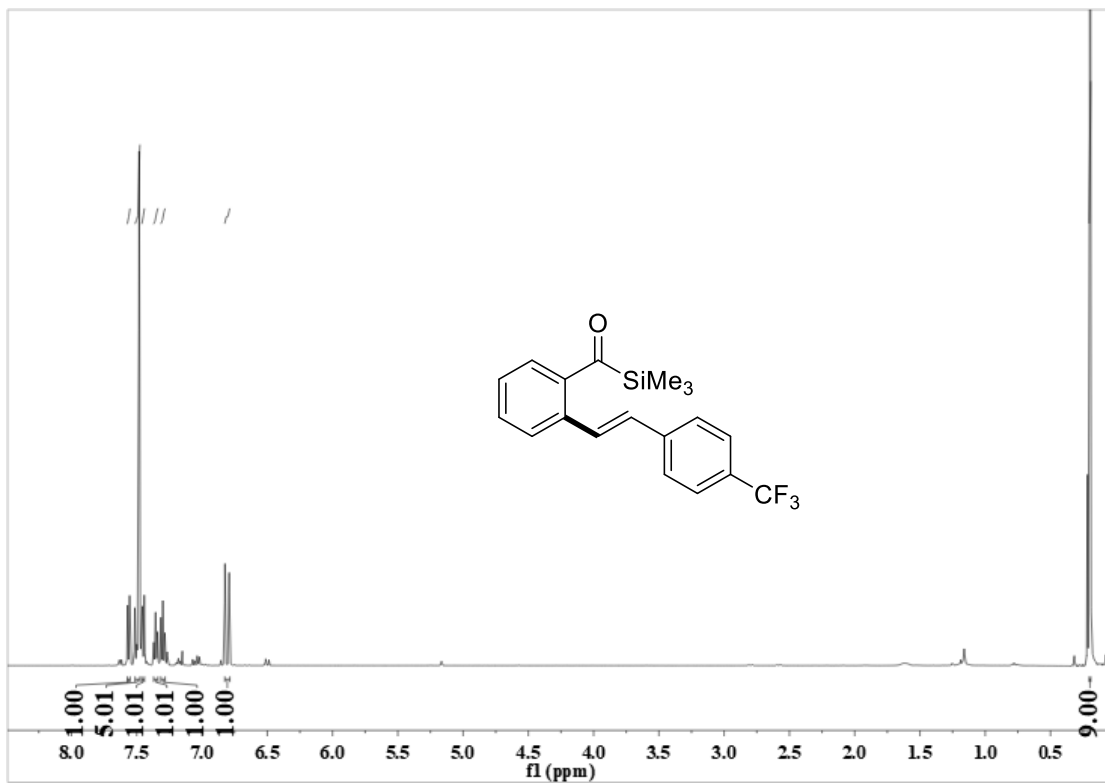


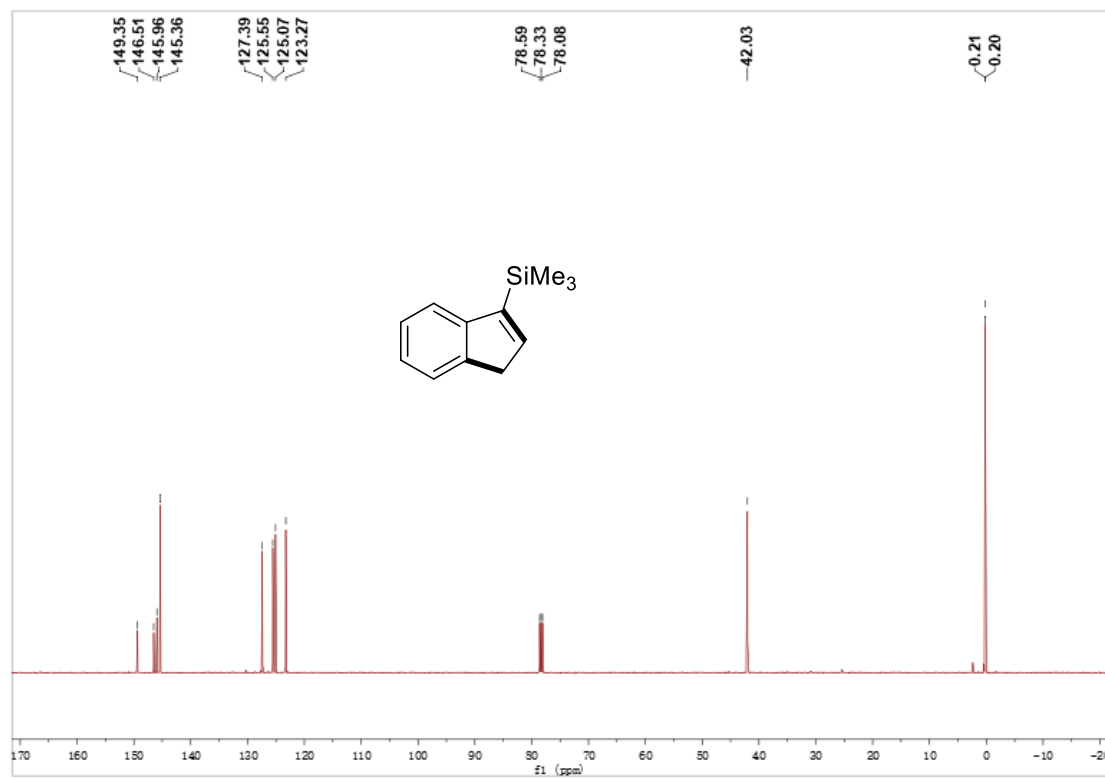
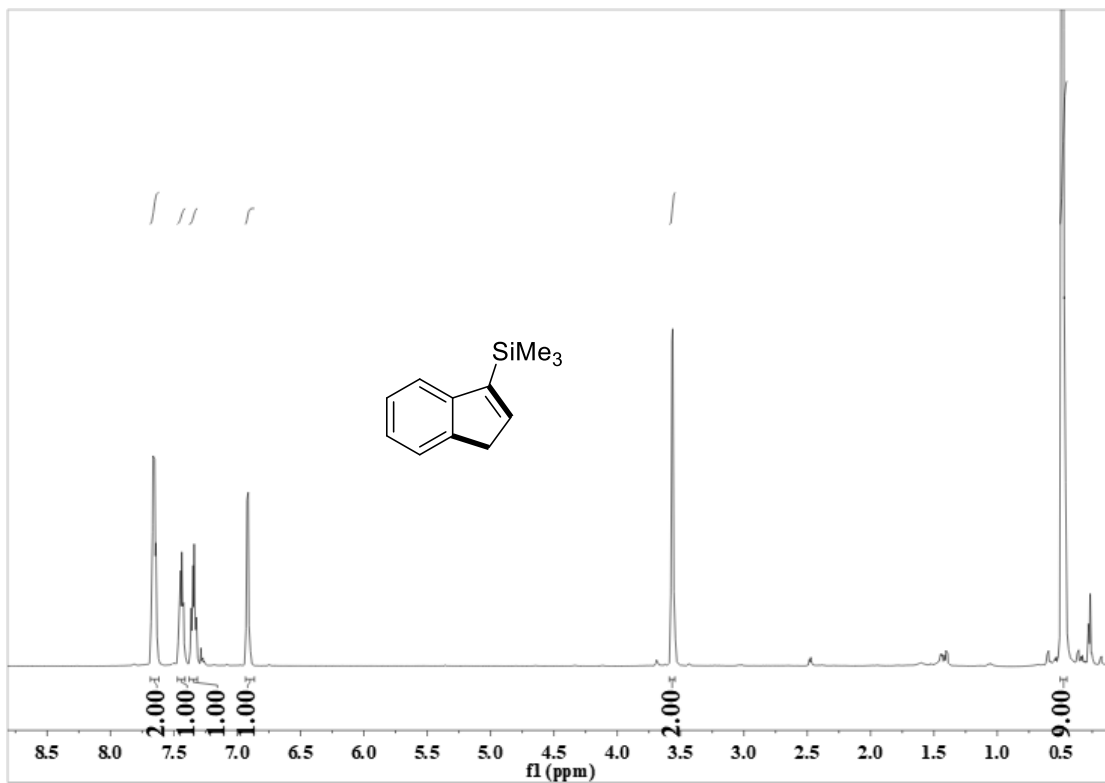


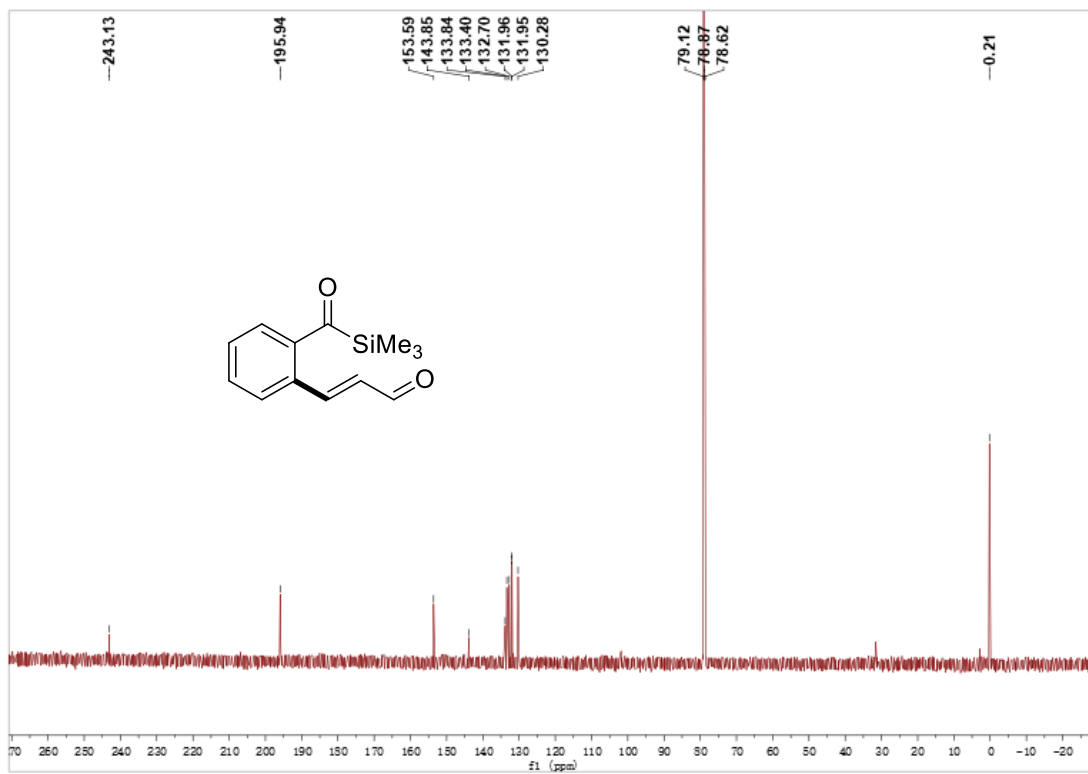
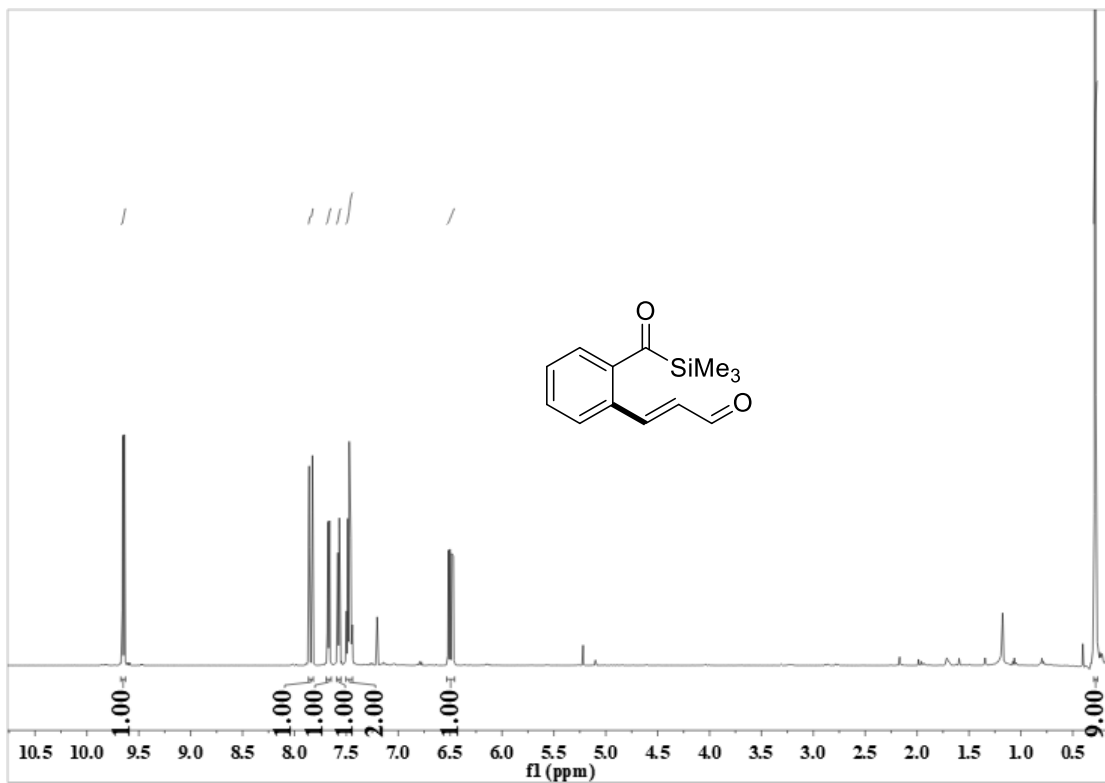


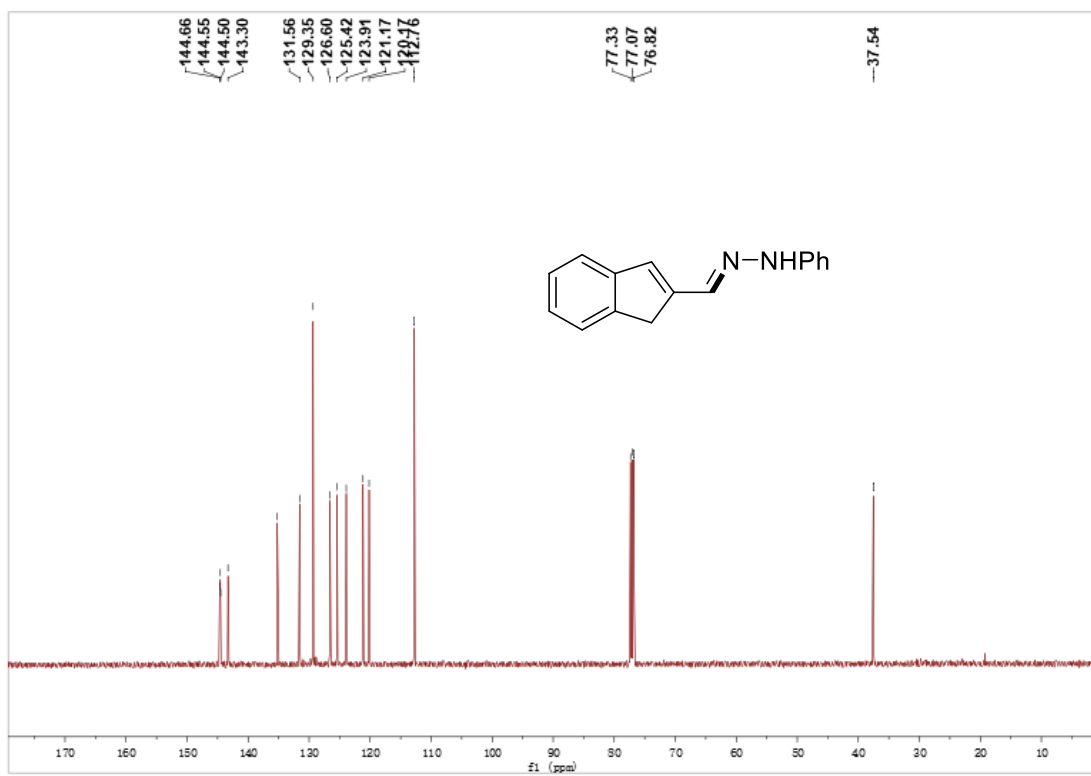
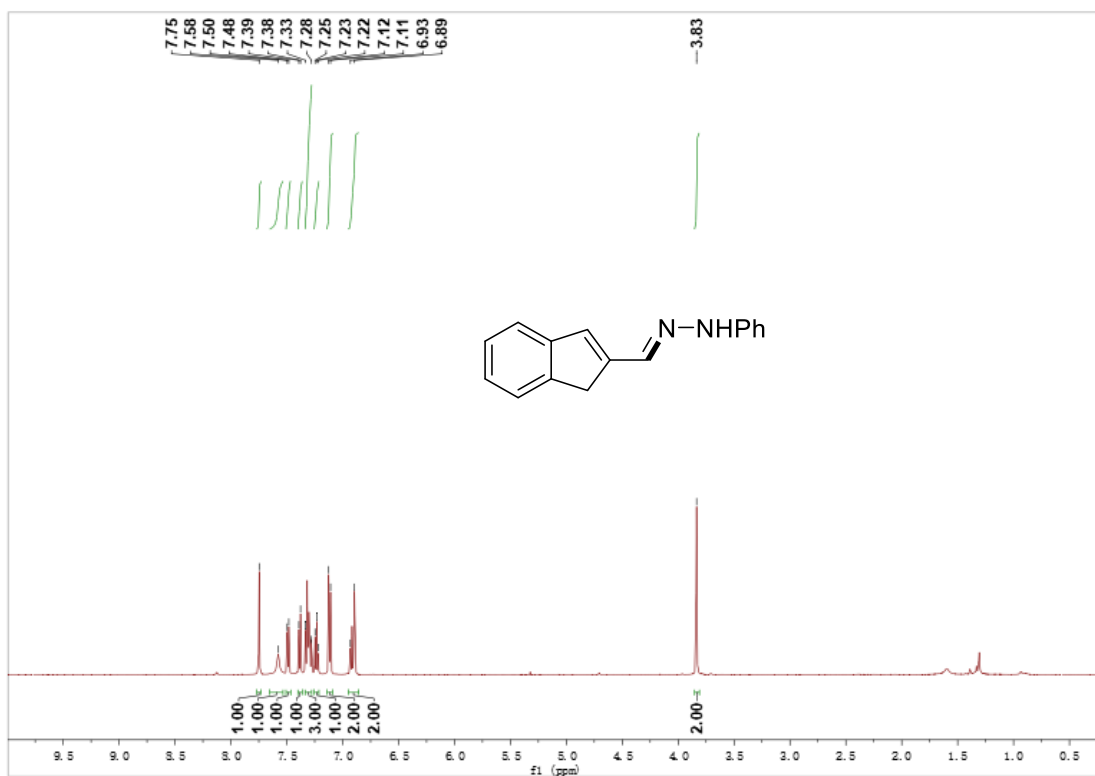


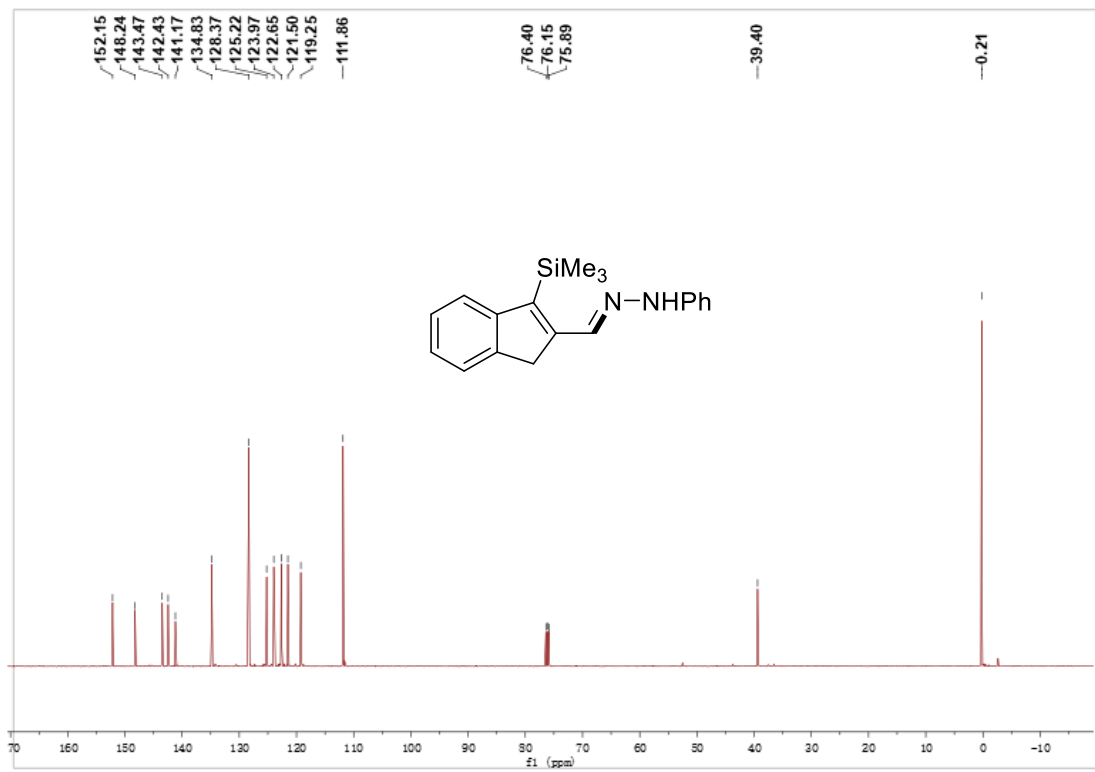
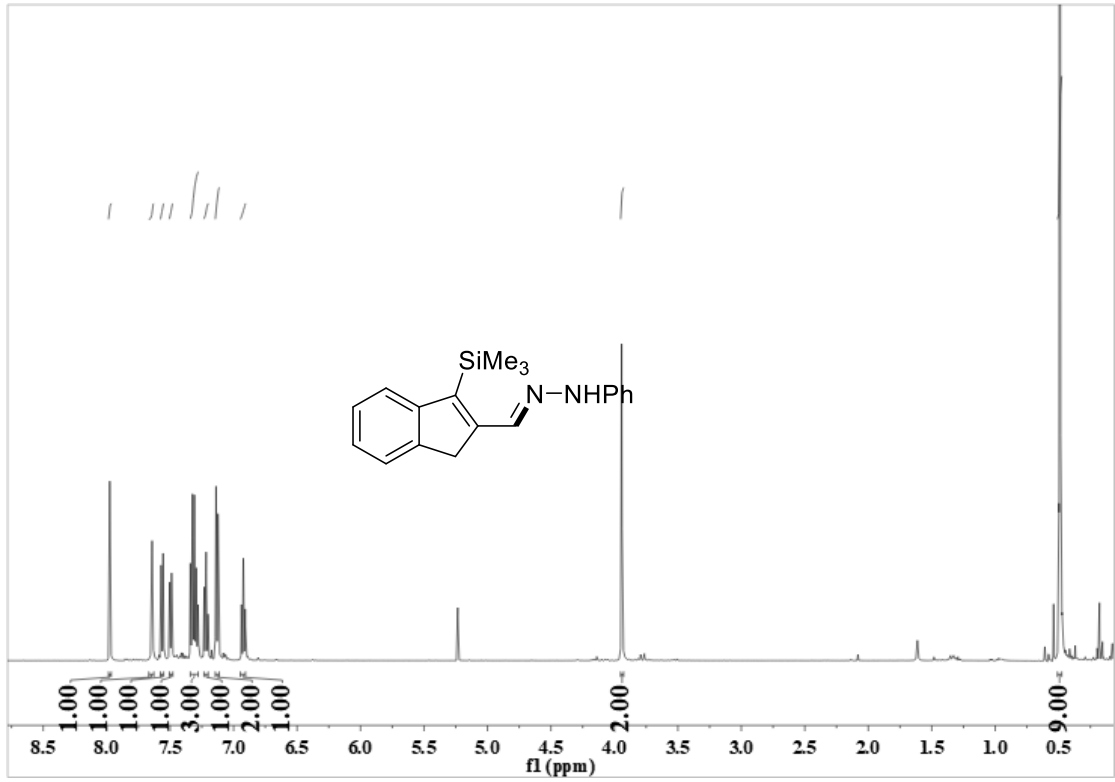


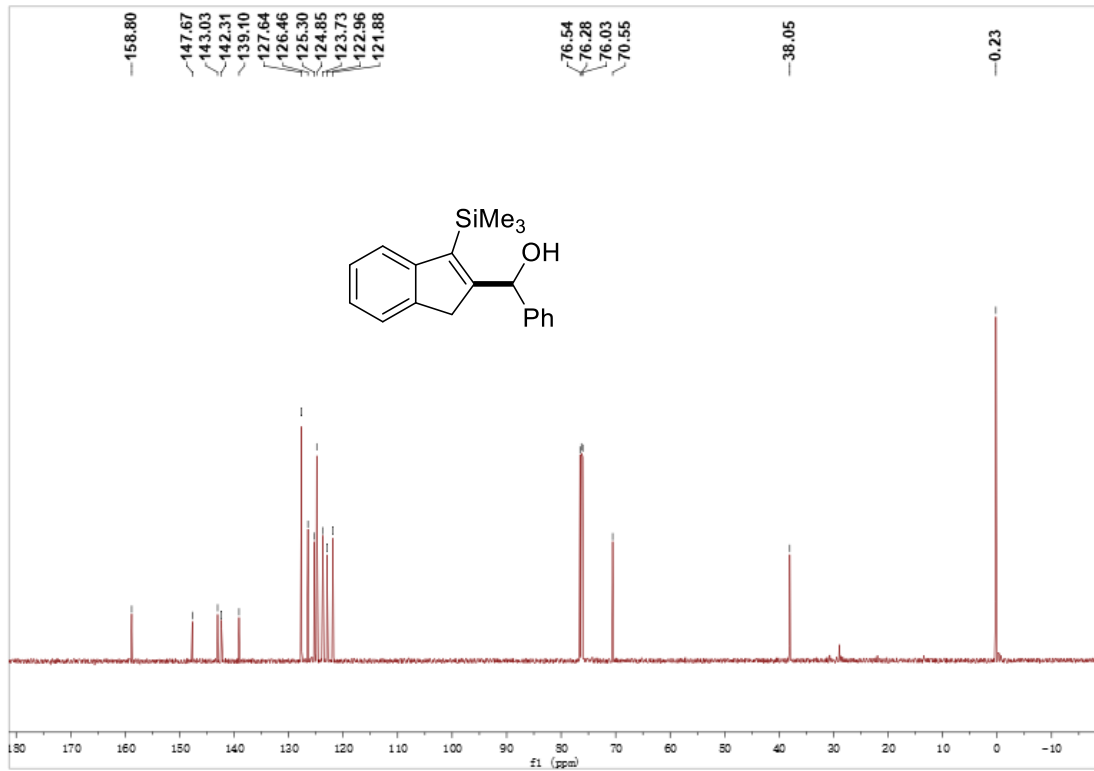
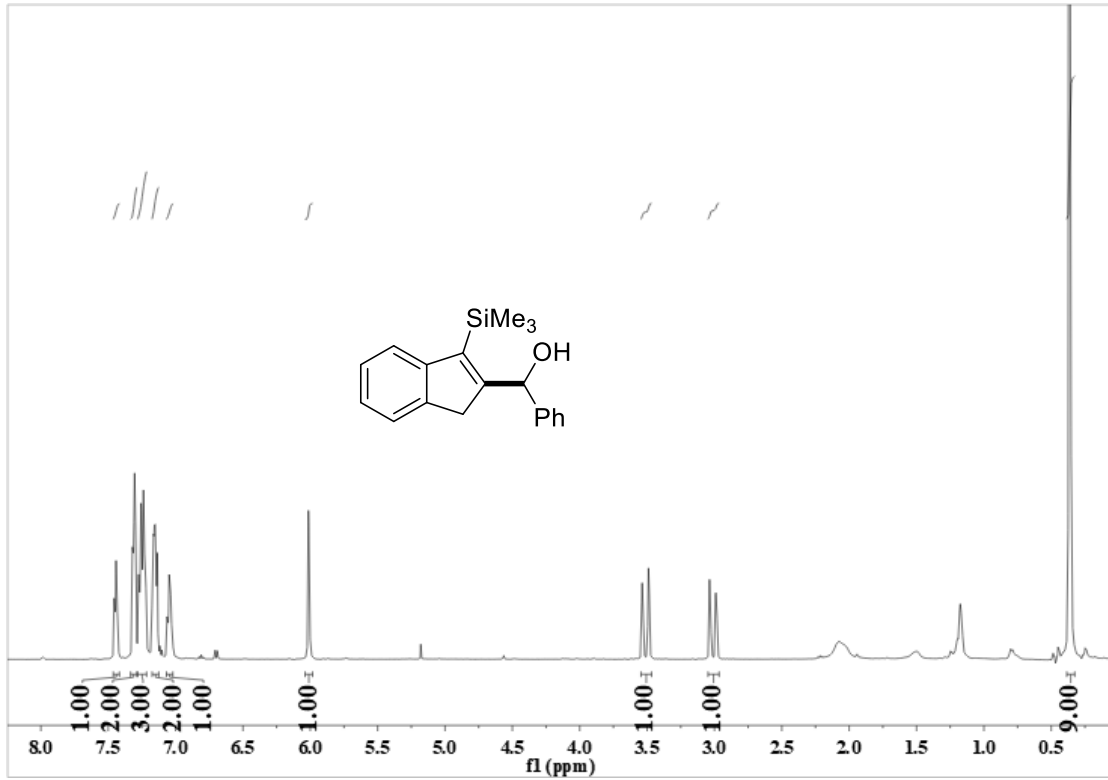


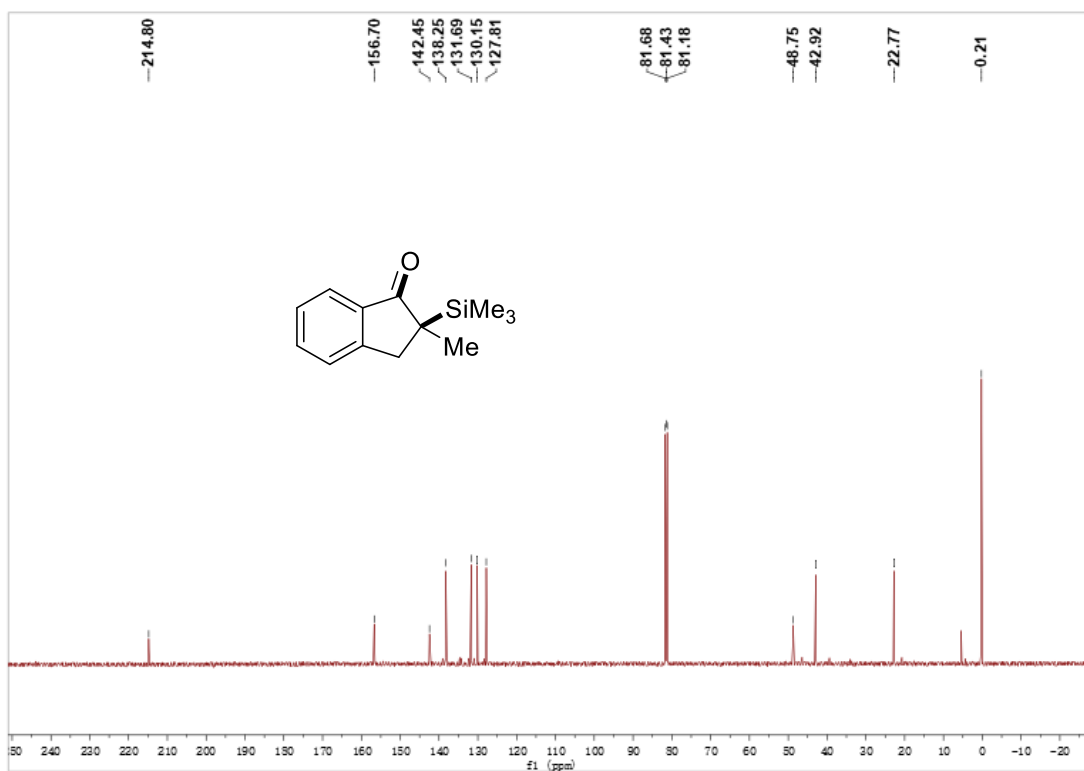
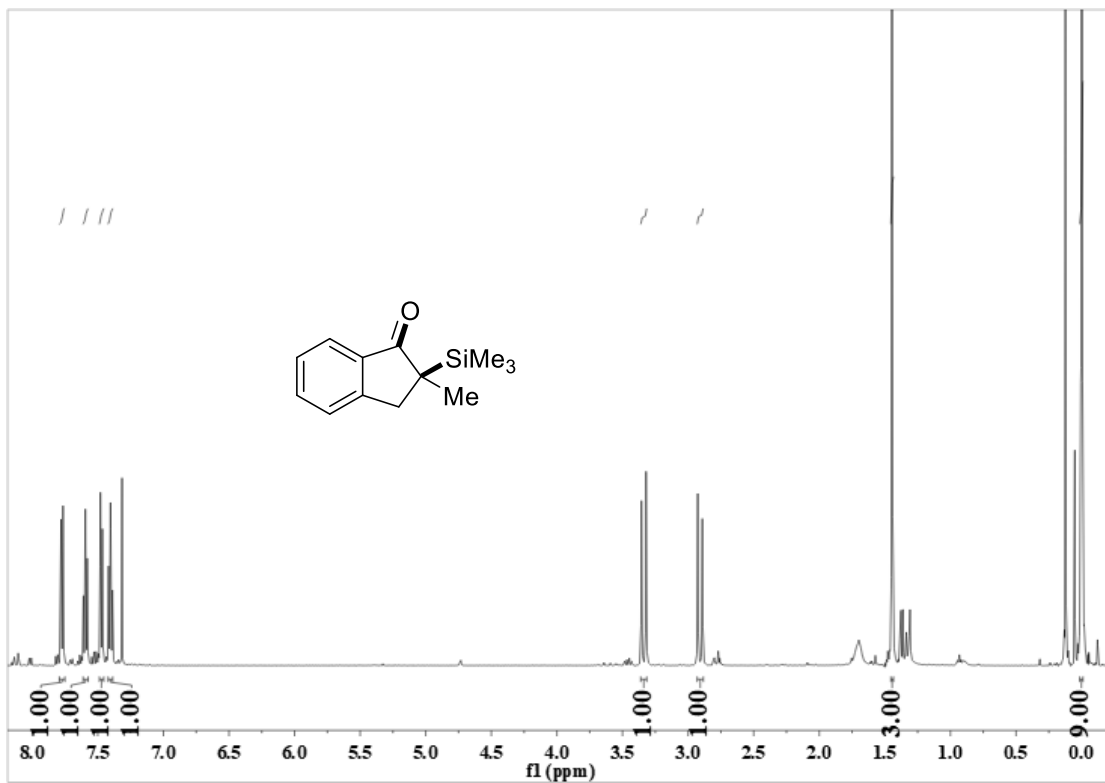


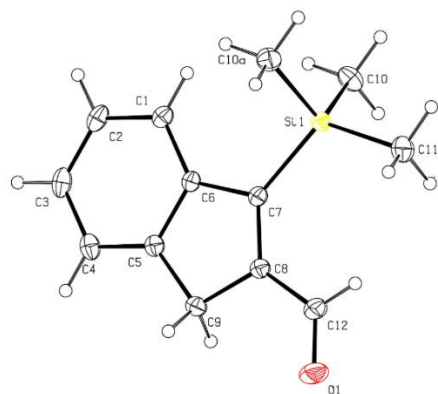












3aa

mo_210617_LXN_3_0m

Table 1 Crystal data and structure refinement for mo_210617_LXN_3_0m.

Identification code	mo_210617_LXN_3_0m
Empirical formula	C ₁₃ H ₁₆ O _{Si}
Formula weight	216.35
Temperature/K	170.0
Crystal system	monoclinic
Space group	P2 ₁ /m
a/Å	8.6562(3)
b/Å	7.0369(2)
c/Å	9.8957(3)
α/°	90
β/°	97.7960(10)
γ/°	90
Volume/Å ³	597.20(3)
Z	2
ρ _{calc} /cm ³	1.203
μ/mm ⁻¹	0.168
F(000)	232.0
Crystal size/mm ³	0.49 × 0.35 × 0.3
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.75 to 54.232
Index ranges	-11 ≤ h ≤ 11, -9 ≤ k ≤ 9, -12 ≤ l ≤ 12
Reflections collected	11768
Independent reflections	1422 [R _{int} = 0.0304, R _{sigma} = 0.0172]
Data/restraints/parameters	1422/0/88
Goodness-of-fit on F ²	1.069
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0338, wR ₂ = 0.0924
Final R indexes [all data]	R ₁ = 0.0362, wR ₂ = 0.0947

Largest diff. peak/hole / e Å⁻³ 0.21/-0.28

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_210617_LXN_3_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	x	y	z	U(eq)
Si1	8422.0(5)	2500	2089.8(4)	23.67(16)
O1	3317.7(17)	2500	-362.1(15)	48.6(4)
C1	7112(2)	2500	5185.5(17)	26.8(4)
C2	6508(2)	2500	6420.7(18)	32.0(4)
C3	4904(3)	2500	6454.7(19)	35.0(4)
C4	3869(2)	2500	5249.9(19)	31.6(4)
C5	4460(2)	2500	4020.3(17)	24.5(3)
C6	6073.0(19)	2500	3974.6(16)	22.3(3)
C7	6366.5(19)	2500	2535.2(16)	22.7(3)
C8	4940.4(19)	2500	1749.9(17)	24.4(3)
C9	3619.8(19)	2500	2595.4(18)	26.9(4)
C10	9368.4(15)	4709(2)	2845.6(15)	36.6(3)
C11	8589(2)	2500	231(2)	40.1(5)
C12	4624(2)	2500	270.7(18)	33.3(4)

Table 3 Anisotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for mo_210617_LXN_3_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+...]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	21.8(2)	26.5(3)	23.1(3)	0	4.30(17)	0
O1	35.2(8)	77.0(12)	30.2(7)	0	-8.5(6)	0
C1	31.3(9)	24.3(8)	23.8(8)	0	0.6(7)	0
C2	49.5(11)	25.0(8)	20.6(8)	0	1.7(7)	0
C3	54.1(12)	28.3(9)	25.3(9)	0	15.3(8)	0
C4	35.8(10)	28.1(9)	33.6(9)	0	14.8(8)	0
C5	26.9(8)	21.1(8)	26.1(8)	0	5.5(6)	0
C6	26.2(8)	19.1(7)	21.8(7)	0	3.7(6)	0
C7	25.0(8)	22.2(8)	20.8(7)	0	2.4(6)	0
C8	23.7(8)	25.8(8)	23.4(8)	0	2.0(6)	0
C9	21.7(8)	30.1(9)	29.0(8)	0	3.6(6)	0

C10	31.3(6)	34.5(7)	44.5(7)	-5.4(6)	7.7(5)	-7.6(5)
C11	38.4(10)	54.8(13)	29.2(9)	0	11.8(8)	0
C12	31.1(9)	43.8(11)	24.0(9)	0	-0.3(7)	0

Table 4 Bond Lengths for mo_210617_LXN_3_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Si1	C7	1.8902(17)	C3	C4	1.391(3)
Si1	C10	1.8656(14)	C4	C5	1.383(2)
Si1	C10 ¹	1.8656(14)	C5	C6	1.403(2)
Si1	C11	1.865(2)	C5	C9	1.496(2)
O1	C12	1.216(2)	C6	C7	1.480(2)
C1	C2	1.393(2)	C7	C8	1.367(2)
C1	C6	1.397(2)	C8	C9	1.505(2)
C2	C3	1.393(3)	C8	C12	1.452(2)

¹+X,1/2-Y,+Z

Table 5 Bond Angles for mo_210617_LXN_3_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10 ¹	Si1	C7	106.41(5)	C6	C5	C9	109.16(14)
C10	Si1	C7	106.41(5)	C1	C6	C5	120.01(16)
C10	Si1	C10 ¹	112.86(9)	C1	C6	C7	130.58(15)
C11	Si1	C7	115.56(8)	C5	C6	C7	109.42(14)
C11	Si1	C10 ¹	107.87(6)	C6	C7	Si1	120.95(12)
C11	Si1	C10	107.87(6)	C8	C7	Si1	132.35(13)
C2	C1	C6	118.53(17)	C8	C7	C6	106.70(14)
C3	C2	C1	121.00(17)	C7	C8	C9	112.30(15)
C4	C3	C2	120.51(17)	C7	C8	C12	127.27(16)
C5	C4	C3	118.81(17)	C12	C8	C9	120.43(15)
C4	C5	C6	121.14(16)	C5	C9	C8	102.42(13)
C4	C5	C9	129.71(16)	O1	C12	C8	123.66(18)

¹+X,1/2-Y,+Z

Table 6 Torsion Angles for mo_210617_LXN_3_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Si1	C7	C8	C9	180.000(0)	C6	C5	C9	C8	0.000(0)
Si1	C7	C8	C12	0.000(0)	C6	C7	C8	C9	0.000(0)
C1	C2	C3	C4	0.000(1)	C6	C7	C8	C12	180.000(0)
C1	C6	C7	Si1	0.000(0)	C7	C8	C9	C5	0.000(0)
C1	C6	C7	C8	180.000(0)	C7	C8	C12	O1	180.000(0)
C2	C1	C6	C5	0.000(0)	C9	C5	C6	C1	180.000(0)
C2	C1	C6	C7	180.000(0)	C9	C5	C6	C7	0.000(0)
C2	C3	C4	C5	0.000(1)	C9	C8	C12	O1	0.000(0)
C3	C4	C5	C6	0.000(1)	C10 ¹	Si1	C7	C6	60.29(5)
C3	C4	C5	C9	180.000(0)	C10	Si1	C7	C6	-60.29(5)
C4	C5	C6	C1	0.000(0)	C10 ¹	Si1	C7	C8	-119.71(5)
C4	C5	C6	C7	180.000(0)	C10	Si1	C7	C8	119.71(5)
C4	C5	C9	C8	180.000(0)	C11	Si1	C7	C6	180.000(0)
C5	C6	C7	Si1	180.000(0)	C11	Si1	C7	C8	0.000(0)
C5	C6	C7	C8	0.000(0)	C12	C8	C9	C5	180.000(0)
C6	C1	C2	C3	0.000(1)					

¹+X,1/2-Y,+Z

Table 7 Hydrogen Atom Coordinates ($\text{\AA}\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2\times 10^3$) for mo_210617_LXN_3_0m.

Atom	x	y	z	U(eq)
H1	8206.73	2500	5166.85	32
H2	7200.08	2500	7252.44	38
H3	4515.12	2500	7307.3	42
H4	2774.87	2500	5271.71	38
H9A	2961.09	3646.64	2416.55	32
H9B	2961.09	1353.36	2416.54	32
H10A	9296	4742.95	3825.06	55
H10B	10467.54	4722.58	2705.4	55
H10C	8838.75	5821.71	2403.39	55
H11A	8099.17	1350.52	-191.38	60
H11B	8063.5	3624.3	-197.99	60
H11C	9692.29	2525.18	104.02	60
H12	5485.36	2500	-230.49	40

Table 8 Atomic Occupancy for mo_210617_LXN_3_0m.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H9A	0.5	H9B	0.5	H11A	0.5
H11B	0.5	H11C	0.5		

Experimental

Single crystals of C₁₃H₁₆OSi [**mo_210617_LXN_3_0m**] were []. A suitable crystal was selected and [] on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of [mo_210617_LXN_3_0m]

Crystal Data for C₁₃H₁₆OSi ($M = 216.35$ g/mol): monoclinic, space group P2₁/m (no. 11), $a = 8.6562(3)$ Å, $b = 7.0369(2)$ Å, $c = 9.8957(3)$ Å, $\beta = 97.7960(10)^\circ$, $V = 597.20(3)$ Å³, $Z = 2$, $T = 170.0$ K, $\mu(\text{MoK}\alpha) = 0.168$ mm⁻¹, $D_{\text{calc}} = 1.203$ g/cm³, 11768 reflections measured ($4.75^\circ \leq 2\theta \leq 54.232^\circ$), 1422 unique ($R_{\text{int}} = 0.0304$, $R_{\text{sigma}} = 0.0172$) which were used in all calculations. The final R_1 was 0.0338 ($I > 2\sigma(I)$) and wR_2 was 0.0947 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups

2. Others

Fixed Sof: H9A(0.5) H9B(0.5) H11A(0.5) H11B(0.5) H11C(0.5)

3.a Secondary CH2 refined with riding coordinates:

C9(H9A,H9B)

3.b Me refined with riding coordinates:

C10(H10A,H10B,H10C), C11(H11A,H11B,H11C)

3.c Aromatic/amide H refined with riding coordinates:

C1(H1), C2(H2), C3(H3), C4(H4), C12(H12)

This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.