Supporting Information

A Chemoselective Radical Cascade Polarity-Mismatched Silylarylation of Unactivated Alkenes

Liang Liu, [a, b] Xiao Yang, [a] Jinghui Tong, [a] Huajie Zhu, [a] Lu Ouyang, [a] Renshi Luo, *[b] Jianhua Liao, *[a]

[a] *School of Pharmacy, Gannan Medical University, Ganzhou, 341000, China.*

[b] *College of Chemistry and Environmental Engineering, Shaoguan University, Shaoguan, 512005, China.*

E-mail: liaojianhua715@163.com

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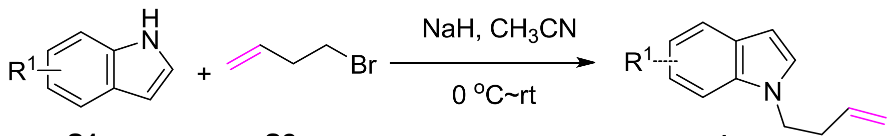
1. Experimental Section

General Information. The starting materials of alkenyl indole (**1**) and silanes (**2**) were purchased and used without further purification.

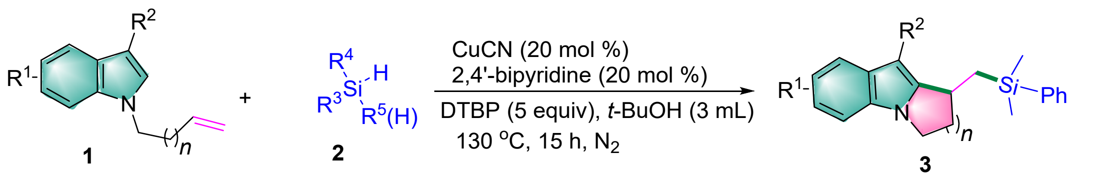
Melting points were measured using a melting point instrument and are uncorrected. ^{1}H and ^{13}C NMR spectra were acquired on a 400 MHz NMR spectrometer. Chemical shifts were reported in ppm from the $CDCl_3$ resonance as the internal reference ($CDCl_3$ 7.26 ppm, δ_C = 77.16 ppm). Multiplicities are reported as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. GC-MS was conducted using electron ionization. HRMS analysis was performed on an EI-ion trap High Resolution mass spectrometer. Thin-layer chromatography (TLC) was performed using commercially prepared 100-400 Mesh silica gel plates and visualization was monitored at 254 nm. X-ray structural analysis was recorded on an X-ray analysis instrument.

2. General Procedures for Synthesis of Indole Alkenes 1.[1]



The indole S**1** (10.0 mmol, 1.0 equiv.) were added to a 150.0 mL round-bottom flask and dissolved in 30.0 mL of CH_3CN. The mixtures were then immersed in an ice bath, sodium hydride (40.0 mmol, 4.0 equiv.) was added slowly at 0°C. Subsequently, 4-bromo-1-butene S**2** (40.0 mmol, 4.0 equiv.) was added slowly, stirring overnight at room temperature. After completion and quenched by H_2O at 0°C, the mixture was extracted with ethyl acetate (3 × 10.0 mL). The combined ethyl acetate layer was then dried over Na_2SO_4 and concentrated in vacuum. Further purification by flash column chromatography on silica gel (PE/EA = 50:1) afforded the desired indole alkenes **1**.

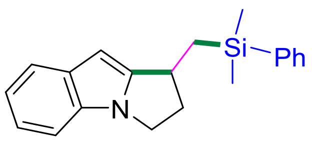
3. General Procedures for Synthesis of Silyated Pyrrolo[1,2-a]indoles.



A dry 25.0 mL Schlenk tube containing a straight condensing tube capped with a balloon was charged with indole alkenes **1** (0.2 mmol, 1.0 equiv.), silanes **2** (2.0 mmol, 10.0 equiv.), CuCN (0.04 mmol, 20.0 mol%), 2,4'-bipyridine (0.04 mmol, 20.0 mol%), DTBP (1.0 mmol, 5.0 equiv.), and 3 mL of *t*-BuOH. The mixtures were vigorously stirred together at 130 ^{o}C for 15 h under nitrogen atmosphere. After completion, the reaction was quenched by saturated brine and then extracted with dichloromethane (3 × 15.0 mL). The combined dichloromethane layer was then dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (PE/EA = 50:1) afforded the desired silyated pyrrolo[1,2-a]indoles **3**.

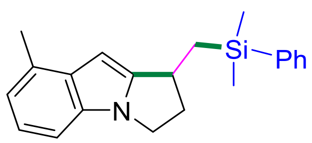
4. Analytical Data of Radical Polarity-Mismatched Silylarylation Products.

1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3aa)



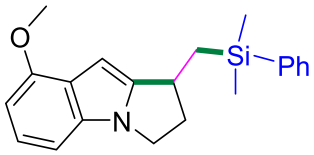
40.3 mg, 66% yield; black solid, m.p. 85-86 ^{o}C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.31-7.29 (m, 3H), 7.14-7.10 (m, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 1H), 5.99 (s, 1H), 4.00-3.95 (m, 1H), 3.82-3.75 (m, 1H), 3.27 (ddd, *J* = 4.5 Hz, *J* = 8.2 Hz, *J* = 12.2 Hz, 1H), 2.52 (qd, *J* = 3.0 Hz, *J* = 7.4 Hz, 1H), 1.97 (dq, *J* = 8.4 Hz, *J* = 12.5 Hz, 1H), 1.46 (dd, *J* = 4.3 Hz, *J* = 14.9 Hz, 1H), 1.02 (dd, *J* = 10.2 Hz, *J* = 14.8 Hz, 1H), 0.31 (d, *J* = 5.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 138.9, 133.6 (2C), 132.8, 132.4, 129.1, 127.9 (2C), 120.4, 120.1, 119.0, 109.2, 91.4, 43.2, 37.5, 33.6, 21.6, -2.2, -2.3. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{24}NSi$, 306.1678; found, 306.1671.

1-((dimethyl(phenyl)silyl)methyl)-8-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ab)



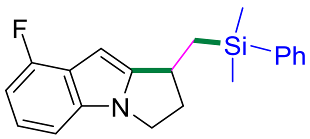
40.2 mg, 63% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.45 (m, 2H), 7.32-7.27 (m, 3H), 6.93 (q, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 6.3 Hz, 1H), 5.97 (s, 1H), 3.98-3.92 (m, 1H), 3.76 (dd, *J* = 8.4 Hz, *J* = 8.8 Hz, 1H), 3.31-3.23 (m, 1H), 2.54-2.48 (m, 1H), 2.41 (s, 3H), 1.95 (td, J = 8.4 Hz, J = 3.9 Hz, 1H), 1.47 (dd, J = 4.2 Hz, J = 14.9 Hz, 1H), 1.05-0.99 (m, 1H), 0.31 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 138.9, 133.6, 132.6, 132.0, 129.7, 129.1, 127.9, 120.3, 119.2, 106.8, 89.9, 43.2, 37.5, 33.6, 21.8, 18.7, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1839.

1-((dimethyl(phenyl)silyl)methyl)-8-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ac)



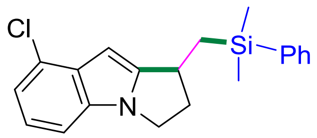
33.5 mg, 50% yield; grey solid, m.p.111-112 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.37 (d, J = 4.0 Hz, 3H), 7.02 (t, J = 7.9 Hz, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.48 (d, J = 7.7 Hz, 1H), 6.19 (s, 1H), 4.06-4.00 (m, 1H), 3.93 (s, 3H), 3.85 (q, J = 8.2 Hz, 1H), 3.33 (dt, J = 6.1 Hz, J = 11.9 Hz, 1H), 2.62-2.55 (m, 1H), 2.04 (dq, J = 8.3 Hz, J = 12.4 Hz, 1H), 1.53 (dd, J = 4.2 Hz, J = 15.0 Hz, 1H), 1.09 (dd, J = 10.2 Hz, J = 14.9 Hz, 1H), 0.38 (d, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 149.1, 138.9, 133.7 ,133.5, 129.0, 127.9, 122.9, 120.9, 102.9, 99.3, 88.6, 55.3, 43.3, 37.6, 33.5, 21.7, -2.1, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NOSi$, 336.1784; found, 336.1791.

1-((dimethyl(phenyl)silyl)methyl)-8-fluoro-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ad)



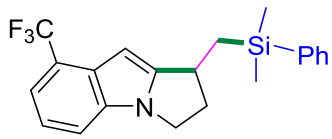
45.2 mg, 70% yield; grey solid, m.p. 82-83 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.39-7.37 (m, 3H), 6.98 (dt, J = 8.0 Hz, J = 13.9 Hz, 2H), 6.71 (dd, J = 7.5 Hz, J = 10.5 Hz, 1H), 6.15 (s, 1H), 4.04 (td, J = 2.9 Hz, J = 9.8 Hz, 1H), 3.87 (dd, J = 8.3 Hz, J = 17.3 Hz, 1H), 3.38-3.30 (m, 1H), 2.64-2.56 (m, 1H), 2.11-2.03 (m, 1H), 1.53 (dd, J = 4.2 Hz, J = 14.8 Hz, 1H), 1.10 (dd, J = 10.2 Hz, J = 14.8 Hz, 1H), 0.39 (d, J = 6.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.7, 133.5 (2C), 129.1, 127.9 (2C), 120.5, 120.4, 105.4 (2C), 104.0, 103.8, 87.6, 43.4, 37.5, 33.6, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.0 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}FNSi$, 324.1584; found, 324.1582.

8-chloro-1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ae)



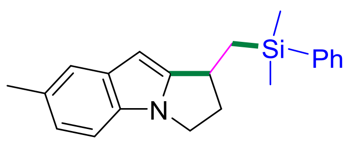
48.1 mg, 71% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.38-7.37 (m, 3H), 7.02 (tt, J = 7.7 Hz, J = 15.3 Hz, 3H), 6.17 (s, 1H), 4.02 (td, J = 2.8 Hz, J = 10.0 Hz, 1H), 3.84 (dd, J = 8.4 Hz, J = 17.2 Hz, 1H), 3,34 (q, J = 11.4 Hz, 1H), 2.61-2.55 (m, 1H), 2.03 (dq, J = 8.4 Hz, J = 12.5 Hz, 1H), 1.55 (dd, J = 4.1 Hz, J = 4.8 Hz, 1H), 1.09 (dd, J = 10.4 Hz, J = 14.8 Hz, 1H), 0.39 (d, J = 4.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 138.7, 133.5, 133.1, 131.2, 129.2, 127.9, 125.2, 120.6, 118.7, 107.8, 90.3, 43.5, 37.3, 33.7, 21.6, -2.3(2C); HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{23}ClNSi$, 340.1288; found, 340.1290.

1-((dimethyl(phenyl)silyl)methyl)-8-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3af)



44.8mg, 60% yield; brown solid, m.p. 79-80 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 2.7 Hz, J = 6.0 Hz, 2H), 7.38-7.37 (m, 3H), 7.31 (t, J = 6.9 Hz, 2H), 7.10 (t, J = 7.8 Hz, 1H), 6.25 (s, 1H), 4.05 (td, J = 2.9 Hz, J = 9.9 Hz, 1H), 3.85 (dd, J = 8.7 Hz, J = 17.0 Hz, 1H), 3.36 (qd, J = 4.4 Hz, J = 8.5 Hz, 1H), 2.63-2.56 (m, 1H), 2.09-2.00 (m, 1H), 1.56 (dd, J = 4.1 Hz, J = 14.9 Hz, 1H), 1.10 (dd, J = 10.4 Hz, J = 14.8 Hz, 1H), 0.39 (d, J = 3.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 138.6, 133.5 (2C), 132.9, 129.2, 127.9 (2C), 121.1 (q, J = 31.7 Hz), 119.2, 116.6 (q, J = 5.0 Hz), 116.5 (d, J = 4.9 Hz), 112.8, 90.8, 43.4, 37.2, 33.8, 21.6, -2.3, -2.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.5 (s, 3F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{23}F_3NSi$, 374.1522; found, 374.1522.

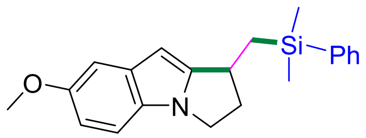
1-((dimethyl(phenyl)silyl)methyl)-7-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ag)



38.9 mg, 61% yield; black solid, m.p. 49-50 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v):

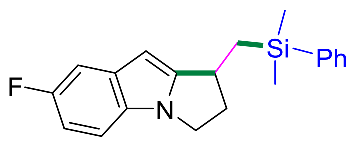
R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 2.8 Hz, J = 6.1 Hz, 2H), 7.38-7.37 (m, 3H), 7.30 (s, 1H), 7.07 (d, J = 8.2 Hz, 1H), 6.91 (d, J = 8.1 Hz, 1H), 5.98 (s, 1H), 4.02 (td, J = 3.0 Hz, J = 9.7 Hz, 1H), 3.83 (dd, J = 8.1 Hz, J = 17.3 Hz, 1H), 3.37-3.29 (m, 1H), 2.62-2.54 (m, 1H), 2.41 (s, 3H), 2.03 (dq, J = 8.3 Hz, J = 12.4 Hz, 1H), 1.52 (dd, J = 4.2 Hz, J = 14.9 Hz, 1H), 1.09 (dd, J = 10.2 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 5.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7, 138.9, 133.6, 133.2, 130.8, 129.1, 128.1, 127.9, 121.6, 120.1, 108.8, 90.8, 43.2, 37.4, 33.6, 21.7, 21.5, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1835.

1-((dimethyl(phenyl)silyl)methyl)-7-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ah)



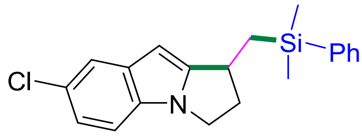
43.6 mg, 65% yield; black solid, m.p. 69-70 ^{o}C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.38 (s, 3H), 7.08-7.01 (m, 2H), 6.75 (d, J = 8.5 Hz, 1H), 6.00 (s, 1H), 4.02 (t, J = 8.8 Hz, 1H), 3.87-3.82 (m, 4H), 3.33 (d, J = 5.7 Hz, 1H), 2.58 (d, J = 8.9 Hz, 1H), 2.08-1.99 (m, 1H), 1.58-1.50 (m, 1H), 1.12-1.06 (m, 1H), 0.38 (d, J = 4.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 151.4, 138.9, 133.6, 133.2, 129.1, 127.9, 127.8, 110.1, 109.8, 102.7, 91.1, 55.9, 43.3, 37.4, 33.8, 21.7, -2.2, -2.3; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{21}H_{26}NOSi$, 336.1784; found, 336.1783.

1-((dimethyl(phenyl)silyl)methyl)-7-fluoro-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ai)



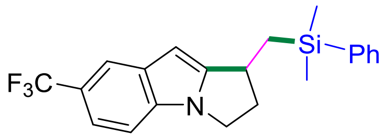
43.9mg, 68% yield; black solid, m.p. 53-54 ^{o}C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 2.8 Hz, 2H), 7.38 (d, J = 1.0 Hz, 3H), 7.16 (d, J = 10.0 Hz, 1H), 7.06 (dd, J = 4.1 Hz, J = 8.3 Hz, 1H), 6.82 (t, J = 9.0 Hz, 1H), 6.02 (s, 1H), 4.03 (t, J = 9.1 Hz, 1H), 3.87-3.81 (m, 1H), 3.35-3.33 (m, 1H), 2.60-2.58 (m, 1H), 2.09-2.00 (m, 1H), 1.54-1.49 (m, 1H), 1.09 (dd, J = 10.5 Hz, J = 14.6 Hz, 1H), 0.38 (d, J = 4.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 138.9, 133.6 (2C), 132.8, 132.4, 129.1, 127.9 (2C), 120.4, 120.1, 119.0, 109.2, 91.4, 43.2, 37.5, 33.6, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -125.8 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}FNSi$, 324.1584; found, 324.1582.

7-chloro-1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3aj)



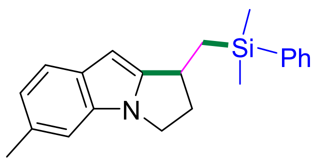
48.8 mg, 72% yield; grey solid, m.p. 60-61 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 2.9 Hz, J = 6.4 Hz, 2H), 7.39 (d, J = 1.5 Hz, 1H), 7.31-7.30 (m, 3H), 6.96 (dt, J = 5.1 Hz, J = 8.6 Hz, 2H), 5.92 (s, 1H), 3.95 (td, J = 3.0 Hz, J = 9.9 Hz, 1H), 3.80-3.74 (m, 1H), 3.30-3.22 (m, 1H), 2.56-2.48 (m, 1H), 2.02-1.93 (m, 1H), 1.44 (dd, J = 4.3 Hz, J = 14.9 Hz, 1H), 1.02 (dd, J = 10.2 Hz, J = 14.9 Hz, 1H), 0.31 (d, J = 4.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 138.7, 133.8, 133.5, 130.8, 129.1, 127.9, 124.6, 120.3, 119.7, 110.1, 91.3, 43.4, 37.3, 33.8, 21.6, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}ClNSi$, 340.1288; found, 340.1292.

1-((dimethyl(phenyl)silyl)methyl)-8-(trifluoromethyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ak)



41.0mg, 55% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.56 (dd, J = 3.0 Hz, J = 6.4 Hz, 2H), 7.38 (dd, J = 3.4 Hz, J = 6.4 Hz, 3H), 7.31 (d, J = 8.4 Hz, 1H), 7.25-7.21 (m, 1H), 6.13 (s, 1H), 4.11-4.06 (m, 1H), 3.94-3.87 (m, 1H), 3.41-3.33 (m, 1H), 2.66-2.59 (m, 1H), 2.12-2.03 (m, 1H), 1.53 (dd, J = 4.2 Hz, J = 14.9 Hz, 1H), 1.11 (dd, J = 10.1 Hz, J = 14.9 Hz, 1H), 0.39 (d, J = 5.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 138.6, 133.6, 132.9, 129.2, 128.0, 125.2 (q, J = 270.0 Hz), 121.1 (q, J = 31.8 Hz), 119.2, 116.5 (q, J = 5.0 Hz), 112.8, 90.8, 43.4, 37.4, 33.7, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.1 (s, 3F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{23}F_3NSi$, 374.1552; found, 374.1548.

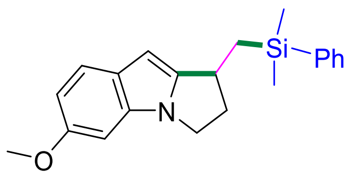
1-((dimethyl(phenyl)silyl)methyl)-6-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3al)



38.9mg, 61% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR

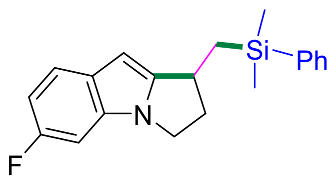
(400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.38 (dd, J = 6.5 Hz, J = 7.5 Hz, 4H), 6.99 (s, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.01 (s, 1H), 4.05-3.99 (m, 1H), 3.83 (dd, J = 8.3 Hz, J = 17.0 Hz, 1H), 3.37-3.29 (m, 1H), 2.61-2.55 (m, 1H), 2.44 (s, 3H), 2.08-1.98 (m, 1H), 1.50 (d, J = 4.3 Hz, 1H), 1.09 (dd, J = 10.2 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 5.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 139.0, 133.6, 132.8, 130.6, 129.8, 129.1, 127.9, 120.6, 120.0, 109.3, 91.2, 43.0, 37.5, 33.5, 21.7, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1833.

1-((dimethyl(phenyl)silyl)methyl)-6-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3am)



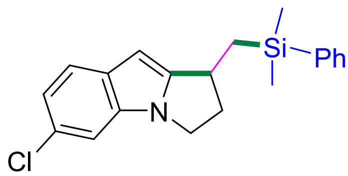
40.2mg, 60% yield; black solid, m.p. 75-76 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 3.1 Hz, 2H), 7.38-7.37 (m, 4H), 6.72-6.69 (m, 2H), 5.99 (s, 1H), 4.03-3.98 (m, 1H), 3.86-3.82 (m, 4H), 3.33 (q, J = 3.3 Hz, 1H), 2.62-2.55 (m, 1H), 2.08-1.99 (m, 1H), 1.51 (dd, J = 4.2 Hz, J = 14.9 Hz, 1H), 1.09 (dd, J = 10.1 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 5.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 149.5, 138.9, 133.6, 132.9, 129.1, 127.9, 127.0, 120.9, 108.6, 93.2, 91.1, 55.8, 43.0, 37.5, 33.5, 21.7, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NOSi$, 336.1784; found, 336.1786.

1-((dimethyl(phenyl)silyl)methyl)-6-fluoro-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3an)



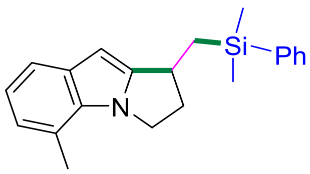
45.9 mg, 71% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.40-7.33 (m, 4H), 6.85-6.73 (m, 2H), 6.00 (d, J = 10.1 Hz, 1H), 3.99-3.90 (m, 1H), 3.82-3.73 (m, 1H), 3.32-3.28 (m, 1H), 2.60-2.50 (m, 1H), 2.07-1.95 (m, 1H), 1.52-1.45 (m, 1H), 1.12-1.03 (m, 1H), 0.38-0.34 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (d, J = 3.6 Hz), 138.8, 133.5 (2C), 129.1 (d, J = 9.0 Hz), 127.9 (2C), 120.8, 120.7, 107.5, 107.4, 95.8, 95.5, 91.5, 43.2, 37.4, 33.6, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.9 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}FNSi$, 324.1584; found, 324.1588.

6-chloro-1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ao)



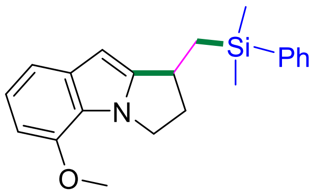
50.2 mg, 74% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 7.39 (d, J = 8.5 Hz, 4H), 7.16 (s, 1H), 6.98 (d, J = 8.4 Hz, 1H), 6.02 (s, 1H), 3.99 (t, J = 9.1 Hz, 1H), 3.81 (dd, J = 8.4 Hz, J = 17.1 Hz, 1H), 3.32 (q, J = 11.9 Hz, 1H), 2.60-2.54 (m, 1H), 2.07-1.98 (m, 1H), 1.50 (dd, J = 4.1 Hz, J = 14.9 Hz, 1H), 1.09 (dd, J = 10.3 Hz, J = 14.7 Hz, 1H), 0.38 (d, J = 4.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 138.7, 133.5, 132.7, 131.3, 129.1, 127.9, 125.9, 121.1, 119.5, 109.2, 91.7, 43.2, 37.3, 33.6, 21.5, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}ClNSi$, 340.1288; found, 340.1289.

1-((dimethyl(phenyl)silyl)methyl)-5-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ap)



52.3 mg, 82% yield; brown solid, m.p. 67-68 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.55 (m, 2H), 7.36 (dd, J = 5.1 Hz, J = 15.6 Hz, 4H), 6.90 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 7.0 Hz, 1H), 6.05 (s, 1H), 4.42-4.37 (m, 1H), 4.15 (dd, J = 8.4 Hz, J = 16.9 Hz, 1H), 3.32-3.24 (m, 1H), 2.61 (s, 4H), 2.06-1.97 (m, 1H), 1.53 (dd, J = 4.0 Hz, J = 14.7 Hz, 1H), 1.08 (dd, J = 10.3 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 5.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 138.9, 133.6, 133.0, 132.0, 129.1, 127.9, 121.7, 120.2, 119.2, 118.2, 91.7, 46.1, 37.5, 33.0, 21.6, 18.0, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1839.

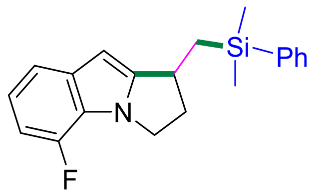
1-((dimethyl(phenyl)silyl)methyl)-5-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3aq)



40.2 mg, 60% yield; black solid, m.p. 53-54 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J = 2.8 Hz, J = 6.1 Hz, 2H), 7.38-7.37 (m, 3H), 7.11 (d, J = 7.9 Hz, 1H), 6.90 (t, J = 7.8 Hz, 1H), 6.51 (d, J = 7.7 Hz, 1H), 6.02 (s, 1H), 4.41-4.46

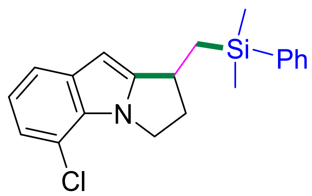
(m, 1H), 4.13-4.06 (m, 1H), 3.88 (s, 3H), 3.32-3.25 (m, 1H), 2.58-2.51 (m, 1H), 2.06-1.97 (m, 1H), 1.54-1.49 (m, 1H), 1.08 (dd, J = 10.3 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 3.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 146.8,141.5,135.4, 133.6, 129.1, 127.9, 122.8, 119.4, 113.4, 100.9, 91.6, 55.4, 46.2, 37.7, 33.3, 21.7, -2.1, -2.2; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NOSi$, 336.1784; found, 336.1780.

1-((dimethyl(phenyl)silyl)methyl)-5-fluoro-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ar)



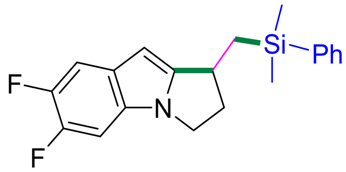
42.0 mg, 65% yield; brown solid, m.p. 59-60 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.38 (s, 4H), 6.89 (dd, J = 7.4 Hz, J = 12.6Hz, 1H), 6.77-6.72 (m, 1H), 6.06 (s, 1H), 4.28 (t, J = 8.9 Hz, 1H), 4.06 (dd, J = 8.5 Hz, J = 17.4 Hz, 1H), 3.31 (q, J = 11.3 Hz, 1H), 2.61-2.55 (m, 1H), 2.10-2.00 (m, 1H), 1.51 (dd, J = 3.9 Hz, J = 14.9 Hz, 1H), 1.10 (dd, J = 10.3 Hz, J = 14.7 Hz, 1H), 0.39-0.36 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 138.7, 133.5 (2C), 129.1, 127.9 (2C), 119.1, 119.0, 116.1 (2C), 105.4, 105.2, 92.2, 45.4, 37.6, 33.3, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.5 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}FNSi$, 324.1584; found, 324.1586.

5-chloro-1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3as)



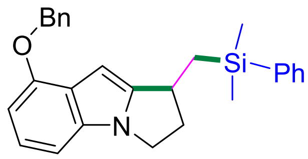
45.4 mg, 67% yield; brown solid, m.p. 57-58 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 3.4 Hz, 2H), 7.37 (d, J = 7.7 Hz, 4H), 7.01 (d, J = 7.6 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 6.07 (s, 1H), 4.57-4.52 (m, 1H), 4.19 (dd, J = 8.1 Hz, J =18.2 Hz, 1H), 3.28 (q, J = 11.9 Hz, 1H), 2.59-2.52 (m, 1H), 2.07-1.97 (m, 1H), 1.51 (dd, J = 4.0 Hz, J = 14.9 Hz, 1H), 1.09 (dd, J = 10.4 Hz, J = 14.7 Hz, 1H), 0.39 (d, J = 3.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 138.7, 134.9, 133.5, 129.1, 127.9, 120.5, 119.7, 119.0, 116.1, 92.3, 46.1, 37.3, 33.1, 21.5, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{23}ClNSi$, 340.1288; found, 340.1281.

1-((dimethyl(phenyl)silyl)methyl)-6,7-difluoro-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3at)



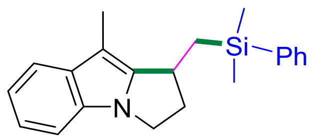
38.0 mg, 56% yield; yellow solid, m.p. 50-51 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 2.9 Hz, J = 6.3 Hz, 2H), 7.37 (dd, J = 3.2 Hz, J = 6.4 Hz, 3H), 7.22 (dd, J = 4.7 Hz, 1H), 6.93 (dd, J = 10.5 Hz, J = 6.8 Hz, 1H), 5.98 (s, 1H), 4.01-3.96 (m, 1H), 3.82 (dd, J = 8.1 Hz, J = 17.4 Hz, 1H), 3.37-3.29 (m, 1H), 2.63-2.56 (m, 1H), 2.10-2.01 (m, 1H), 1.55-1.51 (m, 1H), 1.09 (dd, J = 10.1 Hz, J = 14.9 Hz, 1H), 0.38 (d, J = 4.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1 (d, J = 3.6 Hz), 138.7, 133.5 (2C), 129.2, 127.9 (2C), 127.7 (d, J = 8.4 Hz), 127.5 (d, J = 10.2 Hz), 106.9, 106.7, 97.2, 97.0, 91.7, 43.5, 37.4, 33.9, 21.6, -2.2, -2.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -146.1 (d, J = 21.0 Hz, 2F), δ -149.1 (d, J = 21.0 Hz, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{22}F_2NSi$, 342.1490; found, 342.1492.

8-(benzyloxy)-1-((dimethyl(phenyl)silyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3au)



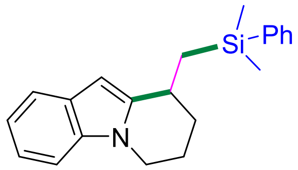
50.1 mg, 61% yield; grey solid, m.p. 94-95 ºC; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.50 (d, J = 7.5 Hz, 2H), 7.40 (s, 1H), 7.38-7.37 (m, 4H), 7.32 (d, J = 7.2 Hz, 1H), 6.99 (t, J = 7.9 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 7.8 Hz, 1H), 6.24 (s, 1H), 5.21 (s, 2H), 4.07-4.02 (m, 1H), 3.89-3.83 (m, 1H), 3.34 (q, J = 11.7 Hz, 1H), 2.61-2.57 (m, 1H), 2.09-2.00 (m, 1H), 1.57-1.53 (m, 1H), 1.10 (dd, J = 10.3 Hz, J = 14.8 Hz, 1H), 0.38 (d, J = 2.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 149.4, 139.1, 138.1, 134.0, 133.7, 129.2, 128.6, 128.1, 127.7, 127.4, 123.5, 121.0, 103.3, 101.1, 89.1, 70.0, 43.5, 37.7, 33.7, 21.9, -2.1; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{27}H_{29}NNaOSi$, 434.1911; found, 434.1911.

1-((dimethyl(phenyl)silyl)methyl)-9-methyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3av)



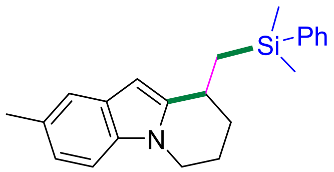
45.9 mg, 72% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 2H), 7.46 (d, J = 7.7 Hz, 1H), 7.38 (d, J = 1.7 Hz, 3H), 7.14 (d, J = 7.8 Hz, 1H), 7.10-7.02 (m, 2H), 4.02-3.96 (m, 1H), 3.83 (dd, J = 7.9 Hz, J = 16.0 Hz, 1H), 3.42-3.36 (m, 1H), 2.62-2.54 (m, 1H), 2.27 (s, 3H), 2.08-1.99 (m, 1H), 1.57-1.54 (m, 1H), 1.11 (dd, J = 12.0 Hz, J = 14.6 Hz, 1H), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 139.0, 133.6, 133.3, 131.9, 129.1, 127.9, 120.0, 118.3, 109.0, 100.0, 42.6, 36.6, 32.8, 21.2, 8.5, -2.2, -2.3; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1836.

9-((dimethyl(phenyl)silyl)methyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (3aw)



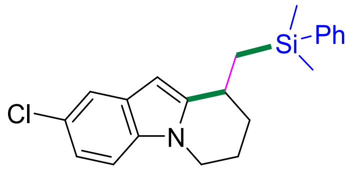
38.9 mg, 61% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.51 (m, 3H), 7.37 (s, 3H), 7.22 (d, J = 7.9 Hz, 1H), 7.09 (dt, J = 6.8 Hz, J = 21.6 Hz, 2H), 6.27 (s, 1H), 4.14-4.12 (m, 1H), 3.82-3.76 (m, 1H), 3.08 (s, 1H), 2.10 (d, J = 7.9 Hz, 1H), 1.93 (dd, J = 9.6 Hz, J = 28.0 Hz, 2H), 1.62-1.54 (m, 2H), 1.22-1.15 (m, 1H), 0.37 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 139.4, 136.3, 133.5, 129.0, 128.1, 127.8, 120.3, 119.7, 119.5, 108.7, 96.9, 42.1, 31.7, 29.9, 22.6, 22.3, -1.8, -1.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{26}NSi$, 320.1835; found, 320.1834.

9-((dimethyl(phenyl)silyl)methyl)-2-methyl-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (3ax)



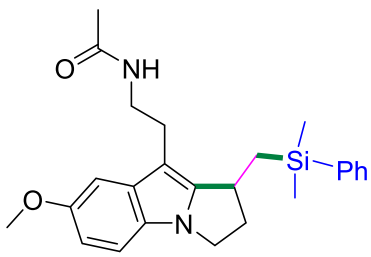
38.6 mg, 58% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.27-7.26 (m, 3H), 7.22 (s, 1H), 7.00 (d, J = 8.2 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.09 (s, 1H), 4.00-3.95 (m, 1H), 3.67-3.61 (m, 1H), 2.00-2.93 (m, 1H), 2.33 (s, 3H), 2.02-1.95 (m, 1H), 1.89-1.75 (m, 2H), 1.51-1.47 (m, 1H), 1.31-1.22 (m, 1H), 1.11-1.05 (m, 1H), 0.27 (d, J = 3.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 141.3, 136.6, 135.4, 130.8, 130.5, 130.3, 129.7, 123.7, 121.3, 110.2, 98.3, 44.0, 33.6, 31.8, 24.5, 24.2, 23.4, 0.1, 0.0; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{22}H_{28}NSi$, 334.1991; found, 334.1993.

2-chloro-9-((dimethyl(phenyl)silyl)methyl)-6,7,8,9-tetrahydropyrido[1,2-*a*]indole (3ay)



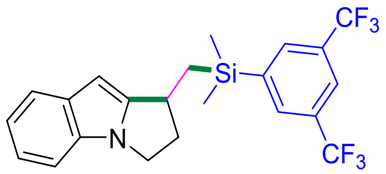
49.4 mg, 70% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.46-7.45 (d, J = 1.9 Hz, 1H), 7.36-7.34 (m, 3H), 7.09-7.02 (m, 2H), 6.18 (s, 1H), 4.07-4.02 (m, 1H), 3.76-3.69 (m, 1H), 3.07-3.00 (m, 1H), 2.10-2.05 (m, 1H), 1.98-1.83 (m, 2H), 1.57-1.53 (m, 1H), 1.40-1.31 (m, 1H), 1.19-1.13 (m, 1H), 0.4 (d, J = 2.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 141.1, 136.6, 135.4, 131.0, 131.0, 129.8, 127.0, 122.3, 121.0, 111.5, 98.7, 44.2, 33.6, 31.5, 24.4, 24.2, 0.1, 0.0; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{25}ClNSi$, 354.1445; found, 354.1443.

***N*-(2-(1-((dimethyl(phenyl)silyl)methyl)-7-methoxy-2,3-dihydro-1*H*-pyrrolo[1,2-a]indol-9-yl)ethyl)acetamide (3az)**



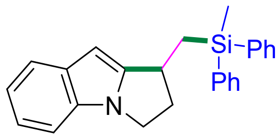
42.0 mg, 50% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 3/1, v/v): R_f = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.52 (m, 2H), 7.36 (q, J = 2.7 Hz, 3H), 7.03 (d, J = 8.7 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.74 (dd, J = 8.7, 2.4 Hz, 1H), 5.75 (s, 1H), 3.96-3.91 (m, 1H), 3.80 (s, 3H), 3.78-3.73 (m, 1H), 3.51-3.42 (m, 2H), 3.36-3.29 (m, 1H), 2.88 (t, J = 6.7 Hz, 2H), 2.58-2.50 (m, 1H), 2.04-1.96 (m, 1H), 1.83 (s, 3H), 1.52 (dd, J = 14.8, 2.6 Hz, 1H), 1.08 (dd, J = 14.7, 11.9 Hz, 1H), 0.38 (d, J = 2.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 156.0, 150.3, 140.9, 135.9, 135.3, 131.5, 130.3, 129.7, 112.5, 112.4, 103.6, 102.9, 58.3, 45.2, 42.5, 38.7, 35.6, 26.6, 25.6, 24.1, 0.0. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{33}N_2O_2Si$, 421.2306; found, 421.2342.

1-(((3,5-bis(trifluoromethyl)phenyl)dimethylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3ba)



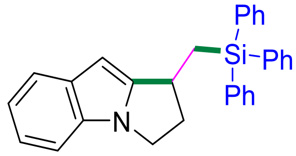
52.0 mg, 59% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.87 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.25-7.19 (m, 1H), 7.07 (dt, J = 7.1 Hz, J = 26.1 Hz, 2H), 6.08 (s, 1H), 4.13-4.08 (m, 1H), 3.92 (dd, J = 7.7 Hz, J = 17.5 Hz, 1H), 3.42-3.34 (m, 1H), 2.69-2.61 (m, 1H), 2.13-2.04 (m, 1H), 1.57 (dd, J = 4.6 Hz, J = 15.0 Hz, 1H), 1.22-1.19 (m, 1H), 0.47 (d, J = 3.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 142.7, 133.2 (2C), 132.6 (q, J = 32.4 Hz), 130.9 (q, J = 32.8 Hz), 124.9, 123.0 (dt, J = 4.0 Hz, J = 7.7 Hz), 122.2, 120.5, 120.4, 119.2, 109.3, 91.7, 43.1, 37.6, 33.4, 21.3, -2.4 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8 (s, 1F); HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{22}H_{22}F_6NSi$, 442.1426; found, 442.1428.

1-((methyldiphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bb)



47.7 mg, 65% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 6.7 Hz, 4H), 7.51 (d, J = 7.6 Hz, 2H), 7.37 (d, J = 5.9 Hz, 5H), 7.17 (d, J = 7.8 Hz, 1H), 7.10-7.01 (m, 2H), 6.06 (s, 1H), 4.04-3.99 (m, 1H), 3.85-3.78 (m, 1H), 3.42 (dd, J = 11.5 Hz, J = 17.9 Hz, 1H), 2.53-2.45 (m, 1H), 2.07-1.98 (m, 1H), 1.88 (dd, J = 2.9 Hz, J = 15.0 Hz, 1H), 1.42 (dd, J = 10.4 Hz, J = 14.9 Hz, 1H), 0.68 (d, J = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 136.9, 136.7, 134.5, 134.4, 132.8, 132.4, 129.4, 128.0, 128.0, 120.4, 120.2, 119.0, 109.2, 91.5, 43.1, 37.4, 33.5, 20.0, -3.6; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{26}NSi$, 368.1835; found, 368.1839.

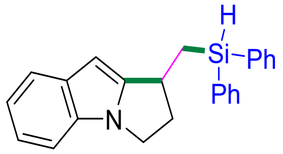
1-((triphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bc)



62.6 mg, 73% yield; black solid, m.p. 61-62 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 6.9 Hz, 6H), 7.49 (d, J = 7.7 Hz, 1H), 7.50-7.36 (m, 9H), 7.15 (d, J = 7.9 Hz, 1H), 7.09-7.00 (m, 2H), 5.98 (s, 1H), 4.01-3.95 (m, 1H), 3.77 (dd,

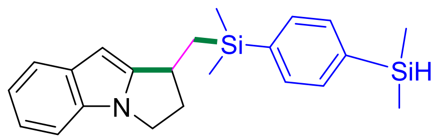
J = 8.2 Hz, J = 17.0 Hz, 1H), 3.55-3.51 (m, 1H), 2.37-2.32 (m, 1H), 2.17 (dd, J = 3.7 Hz, J = 15.1 Hz, 1H), 2.03-1.94 (m, 1H), 1.70 (dd, J = 10.1 Hz, J = 15.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 135.7, 134.7, 132.8, 132.4, 129.7, 128.0, 120.4, 120.2, 119.0, 109.2, 91.6, 43.1, 37.6, 33.4, 19.1; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{30}H_{28}NSi$, 430.1991; found, 430.1994.

1-((diphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bd)



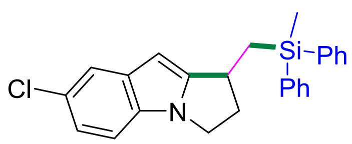
42.4 mg, 60% yield; brown oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 6.8 Hz, 4H), 7.53 (d, J = 7.8 Hz, 1H), 7.43-7.35 (m, 6H), 7.22-7.18 (m, 1H), 7.12-7.02 (m, 2H), 6.17 (s, 1H), 5.07 (t, J = 3.8 Hz, 1H), 4.10-4.05 (m, 1H), 3.87 (dd, J = 7.8 Hz, J = 17.4 Hz, 1H), 3.49-3.41 (m, 1H), 2.71-2.63 (m, 1H), 2.23-2.14 (m, 1H), 1.87-1.81 (m, 1H), 1.56-1.47 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 135.1, 135.1, 133.8, 133.7, 132.8, 132.4, 129.8, 128.1, 128.1, 120.4, 120.2, 119.0, 91.9, 43.0, 37.4, 33.7, 18.3; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{24}H_{24}NSi$, 354.1678; found, 354.1677.

1-(((4-(dimethylsilyl)phenyl)dimethylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3be)



32.7 mg, 45% yield; black solid, m.p. 57-58 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.51 (m, 5H), 7.23-7.18 (m, 1H), 7.11-7.01 (m, 2H), 6.06 (s, 1H), 4.45-4.41 (m, 1H), 4.09-4.04 (m, 1H), 3.91-3.84 (m, 1H), 3.39-3.32 (m, 1H), 2.66-2.59 (m, 1H), 2.11-2.02 (m, 1H), 1.54 (dd, J = 4.3 Hz, J = 14.9 Hz, 1H), 1.11 (dd, J = 10.1 Hz, J = 14.9 Hz, 1H), 0.37 (dd, J = 3.7 Hz, J = 13.5 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 139.9, 138.4, 133.4, 132.9, 132.8, 132.4, 120.4, 120.1, 119.0, 109.2, 91.4, 43.2, 37.5, 33.6, 21.6, -2.3, -3.9; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{22}H_{30}NSi$, 364.1917; found, 364.1914.

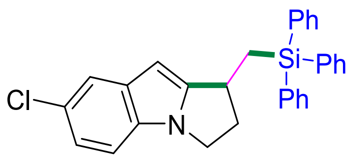
7-chloro-1-((methyldiphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bf)



60.2mg, 75% yield; brown solid, m.p. 63-64 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v):

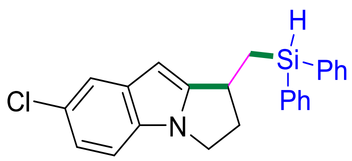
R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 6.1 Hz, 4H), 7.38 (s, 1H), 7.31 (t, J = 6.5 Hz, 6H), 6.99-6.93 (m, 2H), 5.89 (s, 1H), 3.94-3.89 (m, 1H), 3.73 (dd, J = 8.3 Hz, J = 17.2 Hz, 1H), 3.34 (dd, J = 11.5 Hz, J = 17.3 Hz, 1H), 2.46-2.38 (m, 1H), 2.01-1.91 (m, 1H), 1.77 (dd, J = 4.1 Hz, J = 15.0 Hz, 1H), 1.33 (dd, J = 10.2 Hz, J = 14.9 Hz, 1H), 0.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 136.8, 136.5, 134.5, 134.4, 133.8, 130.8, 129.4, 129.4, 128.0, 128.0, 124.7, 120.4, 119.7, 110.1, 91.5, 43.4, 37.3, 33.7, 20.0, -3.6; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{25}ClNSi$, 402.1445; found, 402.1445.

7-chloro-1-((triphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bg)



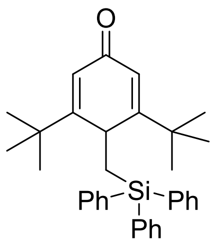
66.7 mg, 72% yield; brown solid, m.p. 109-110 °C; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 6.6 Hz, 6H), 7.35-7.29 (m, 10H), 6.95 (dd, J = 8.2 Hz, J = 14.8 Hz, 2H), 5.80 (s, 1H), 3.88 (dd, J = 6.2 Hz, J = 12.0 Hz, 1H), 3.68 (dd, J = 7.9 Hz, J = 16.1 Hz, 1H), 3.46 (d, J = 5.4 Hz, 1H), 2.32-2.25 (m, 1H), 2.06 (d, J = 10.1 Hz, 1H), 1.97-1.88 (m, 1H), 1.66-1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 135.7, 134.6, 133.7, 130.8, 129.7, 128.0, 124.6, 120.4, 119.7, 110.1, 91.6, 43.3, 37.6, 33.6, 19.0; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{30}H_{27}ClNSi$, 464.1601; found, 464.1602.

7-chloro-1-((diphenylsilyl)methyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indole (3bh)



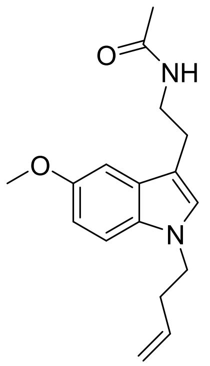
50.3 mg, 65% yield; black oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.1 Hz, 4H), 7.47 (s, 1H), 7.39 (t, J = 7.0 Hz, 6H), 7.08-7.02 (m, 2H), 6.09 (s, 1H), 5.05 (t, J = 3.7 Hz, 1H), 4.06-4.00 (m, 1H), 3.84 (dd, J = 7.9 Hz, J = 17.4 Hz, 1H), 3.48-3.40 (m, 1H), 2.71-2.63 (m, 1H), 2.23-2.14 (m, 1H), 1.84-1.78 (m, 1H), 1.53-1.46 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 135.1, 133.8, 133.7, 133.6, 130.8, 129.9, 129.8, 128.2, 128.1, 124.7, 120.4, 119.8, 110.1, 91.9, 43.3, 37.3, 33.9, 18.2; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{24}H_{23}ClNSi$, 388.1288; found, 388.1289.

3,5-di-*tert*-butyl-4-((triphenylsilyl)methyl)cyclohexa-2,5-dien-1-one (5)



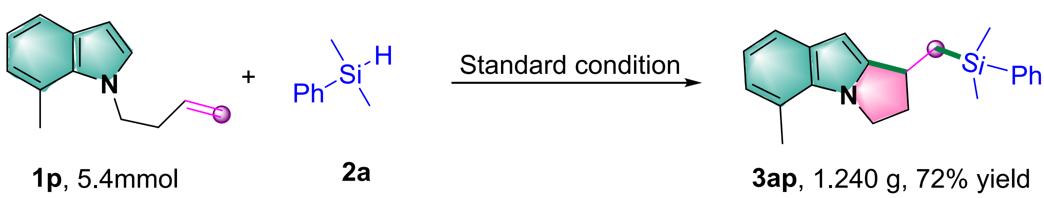
45.9 mg, 48% yield; yellow oil; TLC (petroleum ether/ethyl acetate = 100/1, v/v): R_f = 0.20; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 3H), 7.37 (s, 6H), 7.33-7.29 (m, 6H), 6.59 (s, 2H), 2.81 (s, 1H), 1.43 (s, 2H), 1.22 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 150.9, 136.0, 129.4, 127.6, 125.8, 124.9, 34.1, 30.4, 30.1, 22.8; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{33}H_{39}OSi$, 479.2770; found, 479.2775.

***N*-(2-(1-(but-3-en-1-yl)-5-methoxy-1*H*-indol-3-yl)ethyl)acetamide(1z)**



943.9 mg, 33% yield; white solid, m.p. 63-65 °C; TLC (petroleum ether/ethyl acetate = 5/1, v/v): R_f = 0.60; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.9 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.92-6.86 (m, 2H), 5.76 (m, 1H), 5.61 (s, 1H), 5.09-5.01 (m, 2H), 4.10 (t, J = 7.2 Hz, 2H), 3.86 (s, 3H), 3.56 (q, J = 6.5 Hz, 2H), 2.94-2.89 (m, 2H), 2.54 (q, J = 6.9 Hz, 2H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 153.8, 134.8, 131.7, 128.2, 126.3, 117.4, 112.0, 111.0, 110.3, 100.6, 56.0, 46.0, 39.8, 34.6, 25.2, 23.4. HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{17}H_{23}N_2O_2$, 287.1754; found 287.1749.

5. Procedure for gram-scale experiment



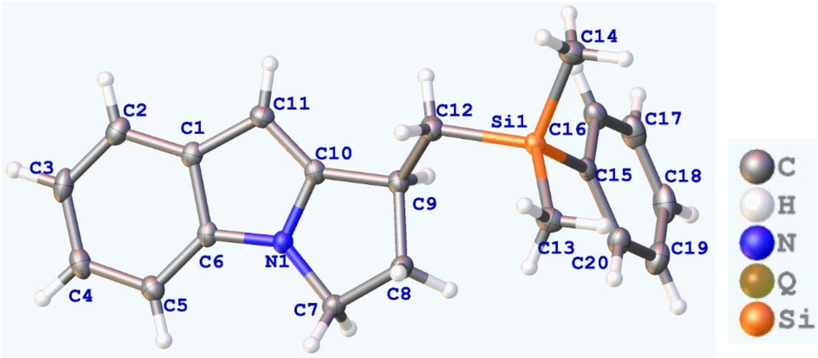
A dry 100 mL flask containing a straight condensing tube capped with a balloon was charged with 1-(but-3-en-1-yl)-7-methyl-1H-indole **1p** (5.4 mmol, 1.00 g), dimethylphenylsilane **2a** (54 mmol, 10.0 equiv.), CuCN (1.08 mmol, 20.0 mol%), 2,4'-bipyridine (1.08 mmol, 20.0 mol%), DTBP (5.0 equiv.) in *t*-BuOH (15.0 mL) successively. The mixture was stirred at 130 ^{o}C for 15 h in a nitrogen atmosphere. After completion, the reaction was quenched by saturated brine and then extracted with dichloromethane (3 × 25.0 mL). The combined dichloromethane layer was then dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (PE/EA = 50:1) afforded the desired silyated pyrrolo[1,2-a]indoles **3ap**.

6. Radical Trapping Experiments

A dry 25 mL Schlenk tube containing a straight condensing tube capped with a balloon was charged with 1-(but-3-en-1-yl)-1H-indole **1a** (0.2 mmol, 1.0 equiv.), triphenylsilane **2b** (2.0 mmol, 10.0 equiv.), CuCN (0.04 mmol, 20 mol%), 2,4'-bipyridine (0.04 mmol, 20.0 mol%), DTBP (1.0 mmol, 5.0 equiv.), radical scavenger (2 equiv.), and *t*-BuOH (3.0 mL). The mixtures were vigorously stirred together at 130 ^{o}C for 15 h. After completion, the reaction was quenched by saturated brine and then extracted with dichloromethane (3 × 15.0 mL). The combined dichloromethane layer was then dried over anhydrous Na_2SO_4 and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel afforded the desired product.

7. X-ray Crystallographic Data

The X-ray crystallographic structures for **3aa**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2264465.



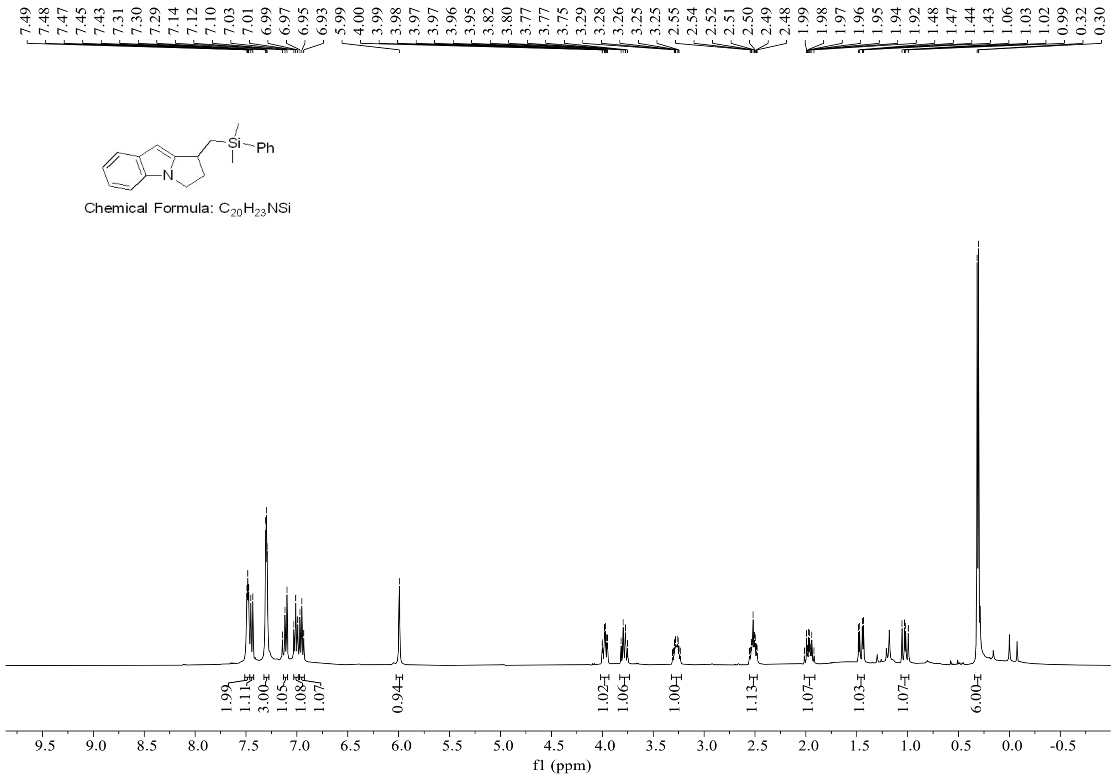
Identification code	**3aa**
Empirical formula	$C_{20}H_{23}NSi$
Formula weight	305.48
Temperature	150(10) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/_C$
Unit cell dimensions	a = 10.1994(8) Å alpha = 90 deg. b = 12.6675(10) Å beta = 98.481(7) deg. c = 13.4020(11) Å gamma = 90 deg.
Volume	1712.6 (2) $Å^3$
Z, Calculated density	4, 1.185 Mg/m^3
Absorption coefficient	0.134 mm^{-1}
F(000)	656.0
Crystal size	0.15×0.13×0.12 mm
Theta range for data collection	4.038 to 49.996 deg.
Limiting indices	$-9 \le h \le 12$, $-15 \le k \le 13$, $-15 \le l \le 15$
Reflections collected / unique	8031 / 3013 [R(int) = 0.0244]
Completeness to theta = 25.00	99.99%

Refinement method	Goodness-of-fit on F^{2-}
Data / restraints / parameters	3013 / 0 / 201
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0418, wR2 = 0.1011
R indices (all data)	R1 = 0.0521, wR2 = 0.1077

8. References

[1] Gerry, C. J.; Hua, B. K.; Wawer, M. J.; Knowles, J. P.; Nelson, Jr S. D.; Boskovic, Z. V. Real-Time Biological Annotation of Synthetic Compounds. *J. Am. Chem. Soc.* **2016**, *138*, 8920-8927.

9. NMR Spectra of New Compounds



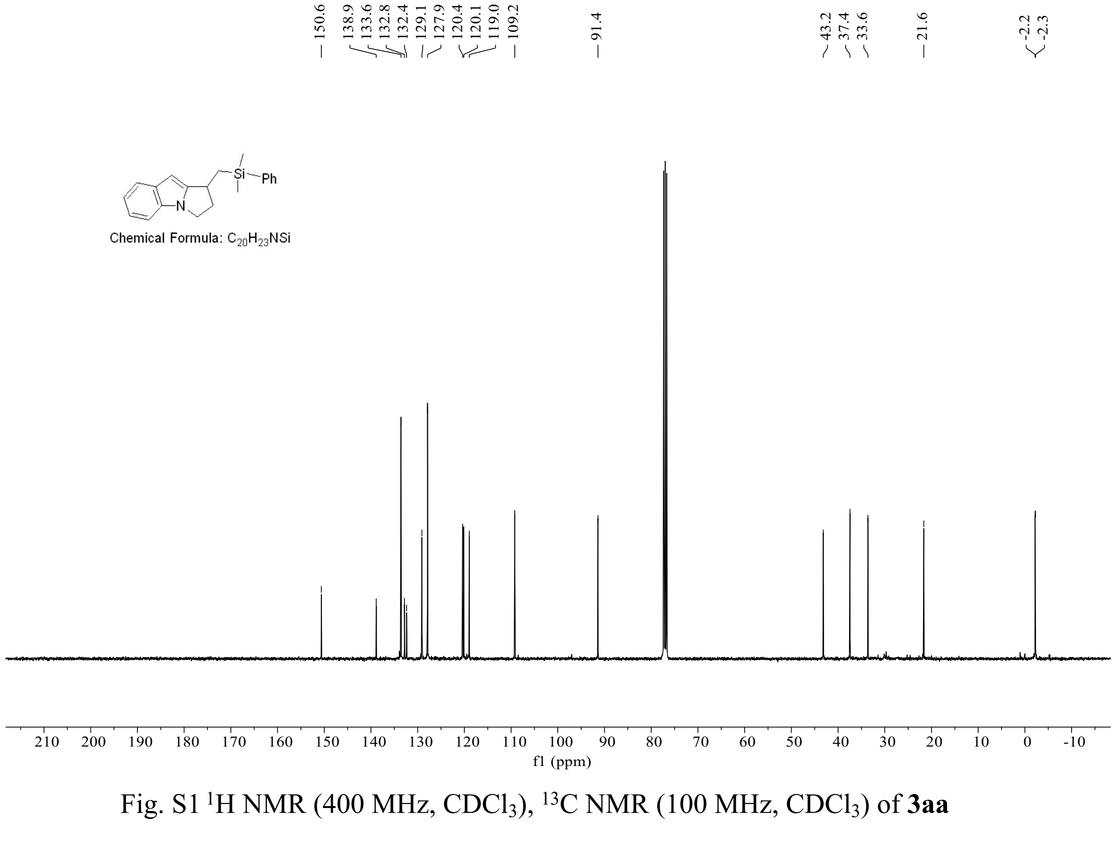
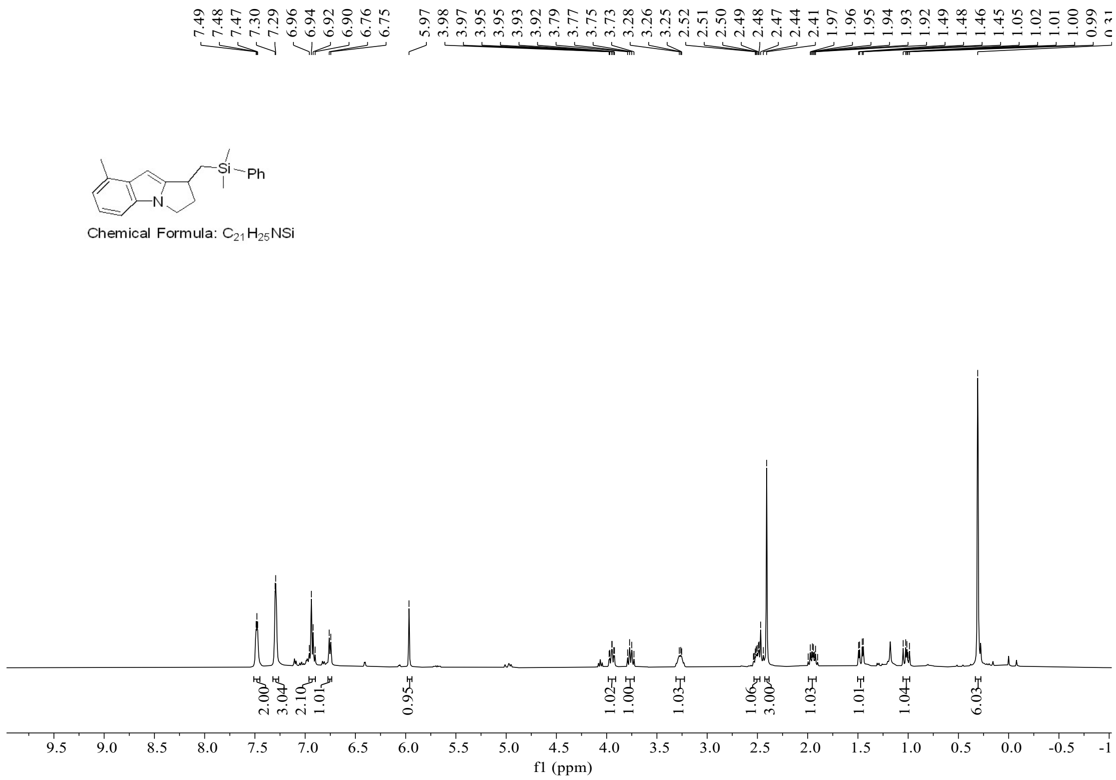


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3aa**



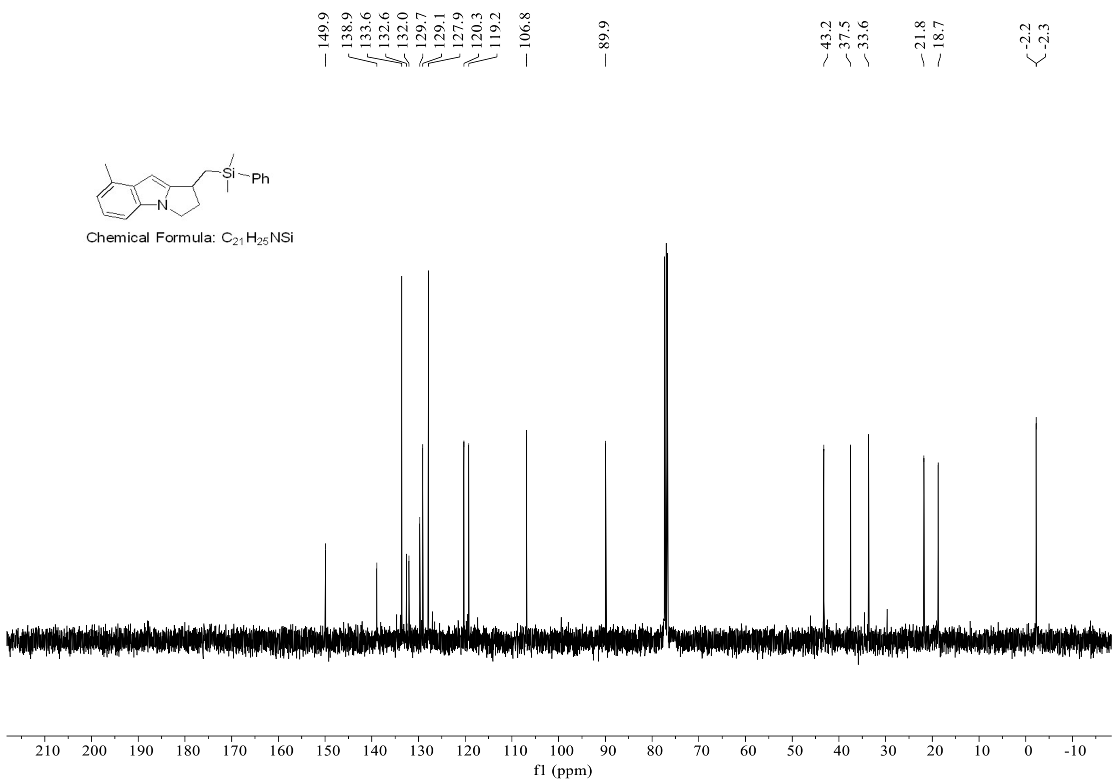
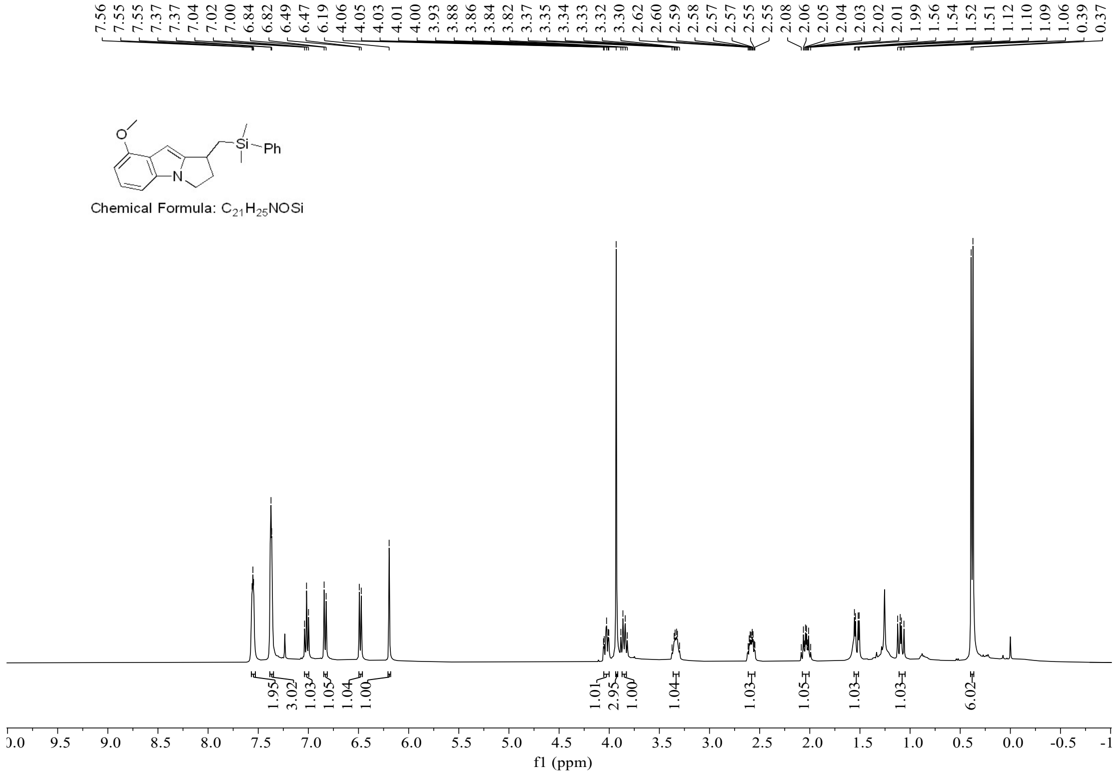


Fig. S2 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ab**



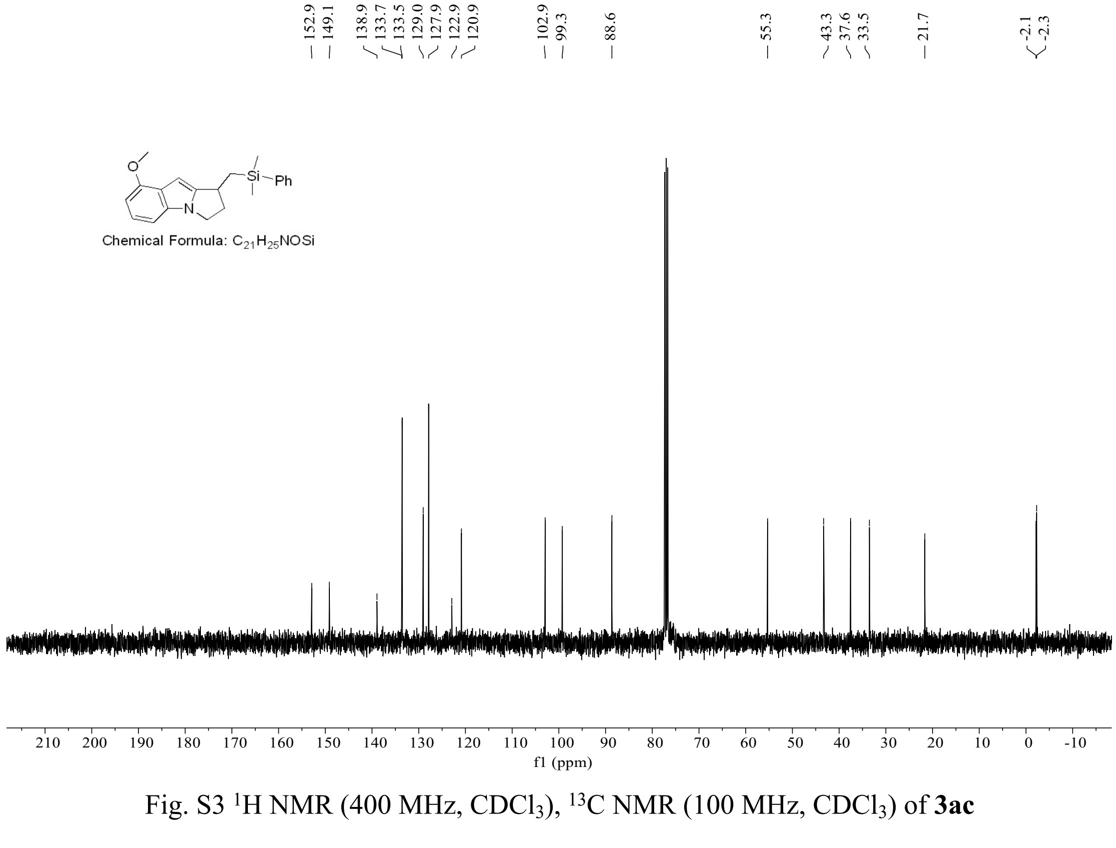
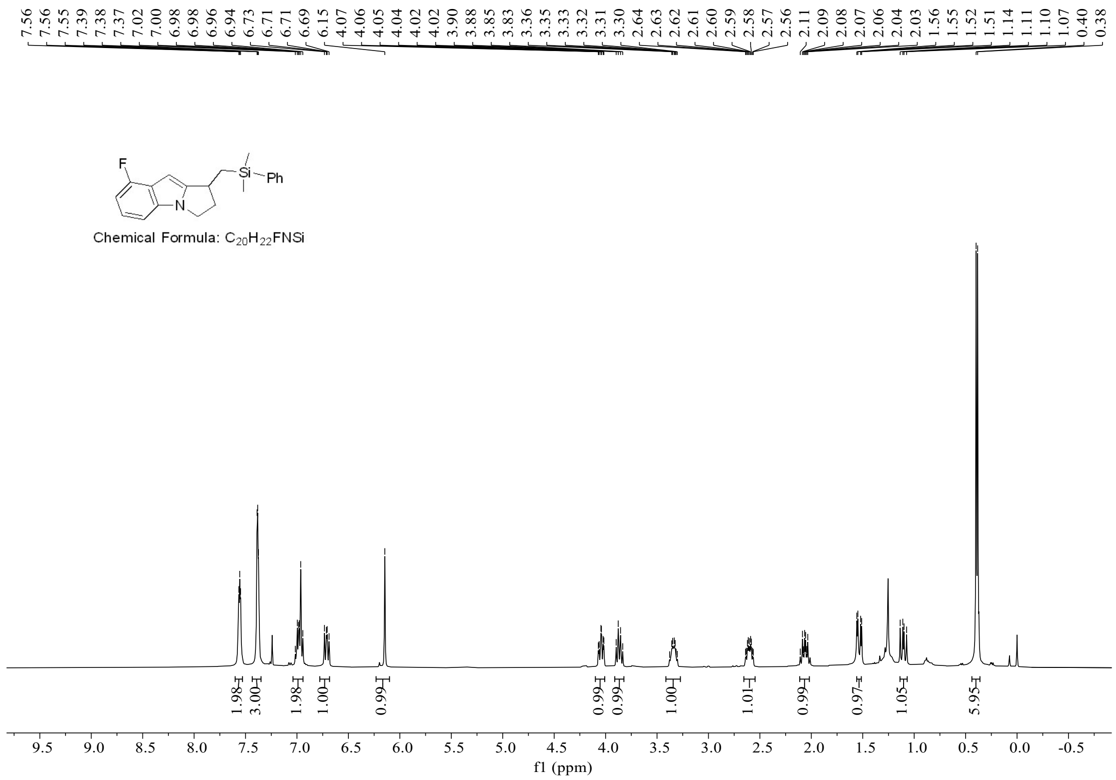
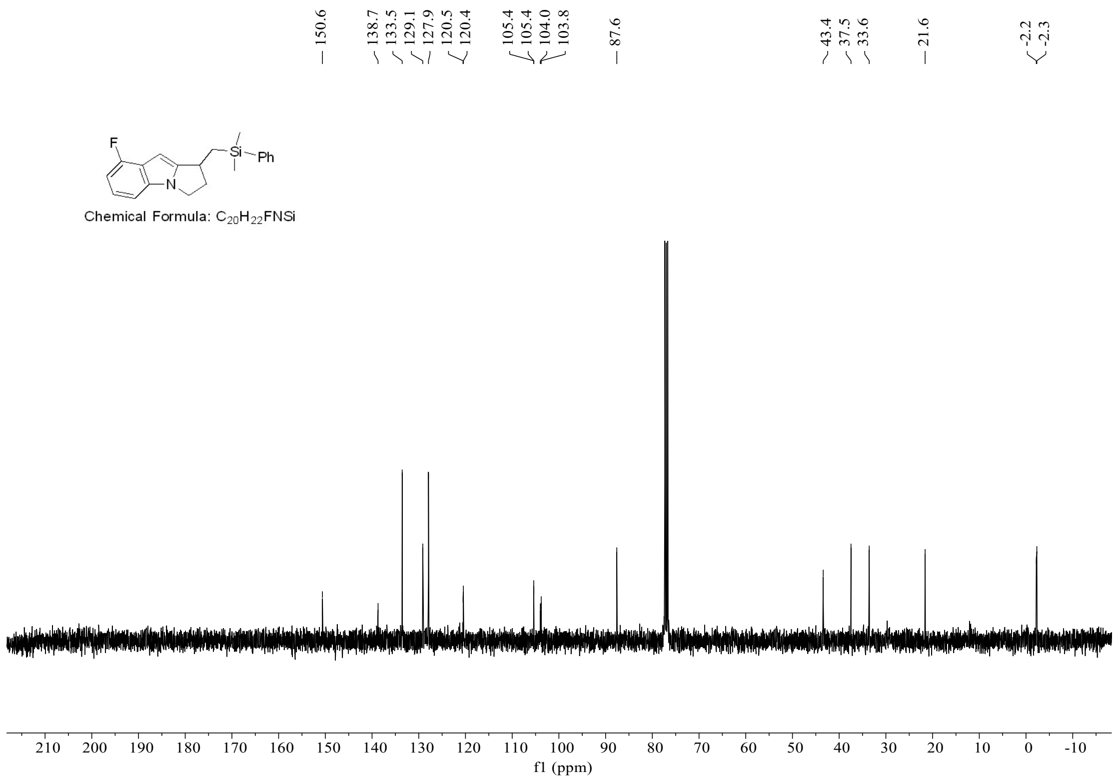


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ac**





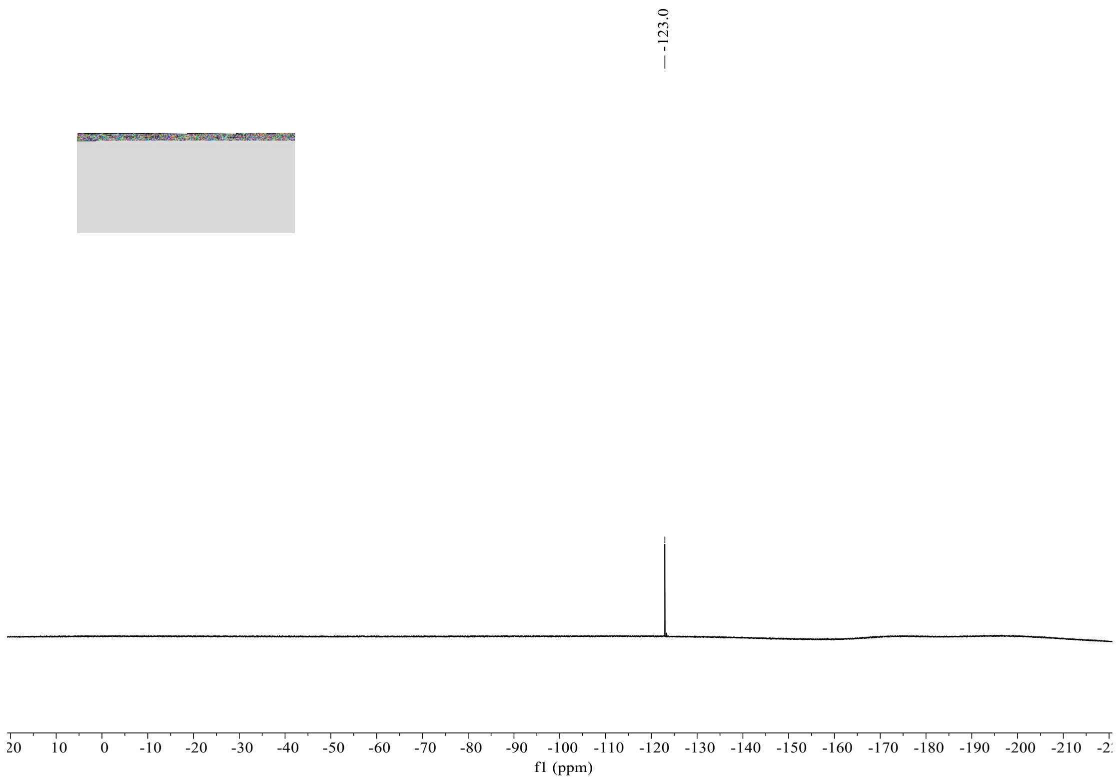
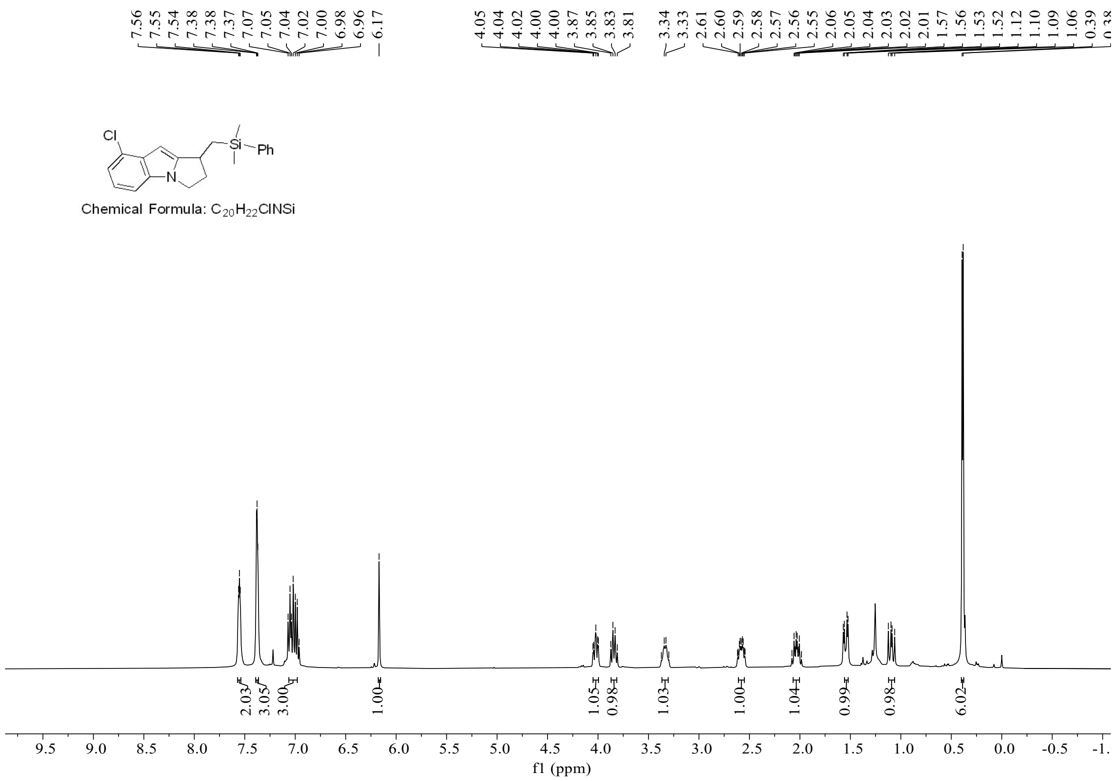


Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3ad**



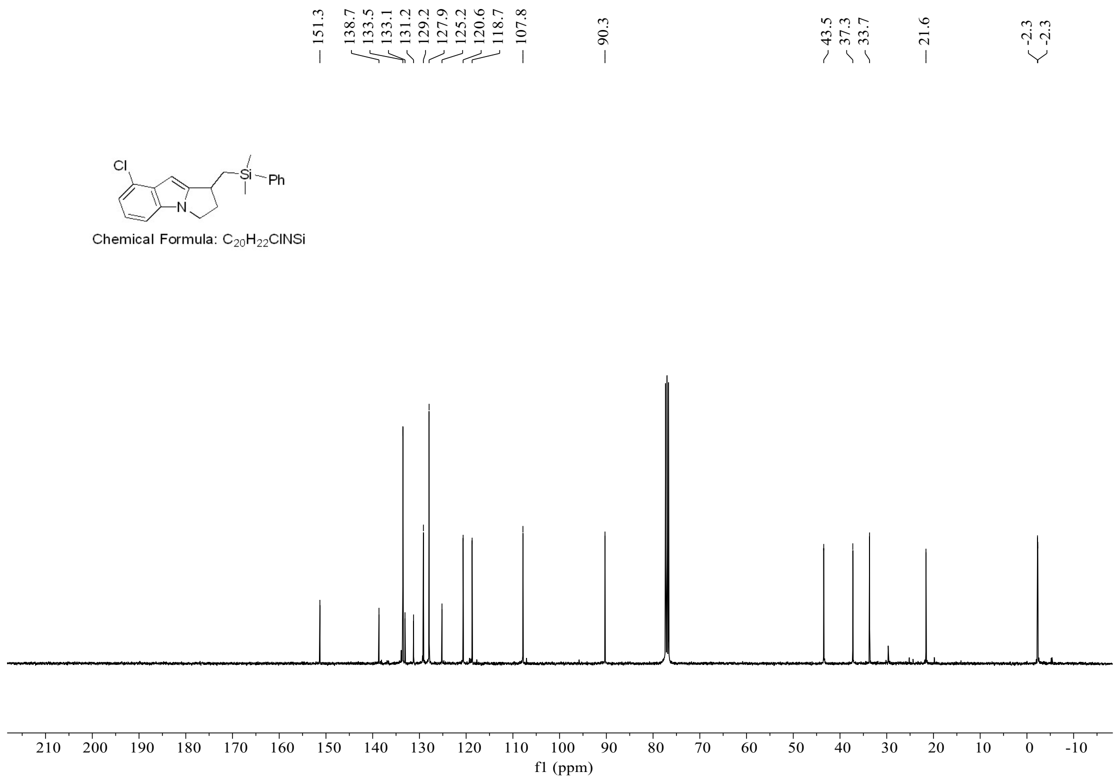
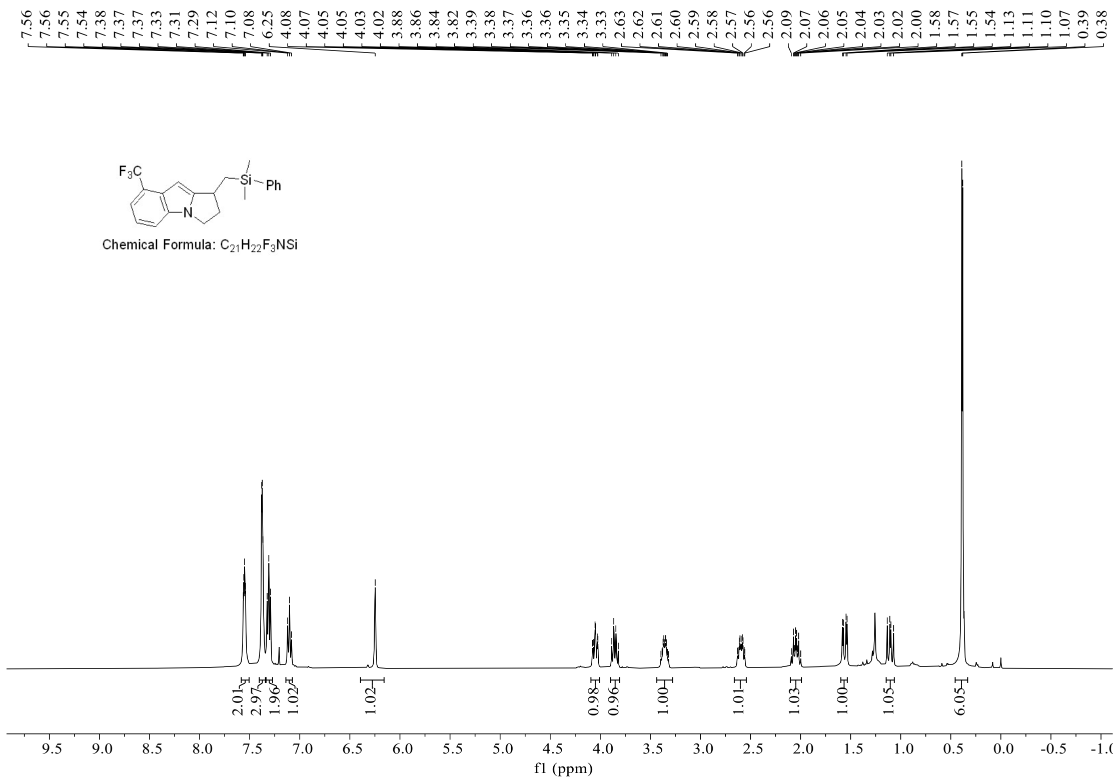
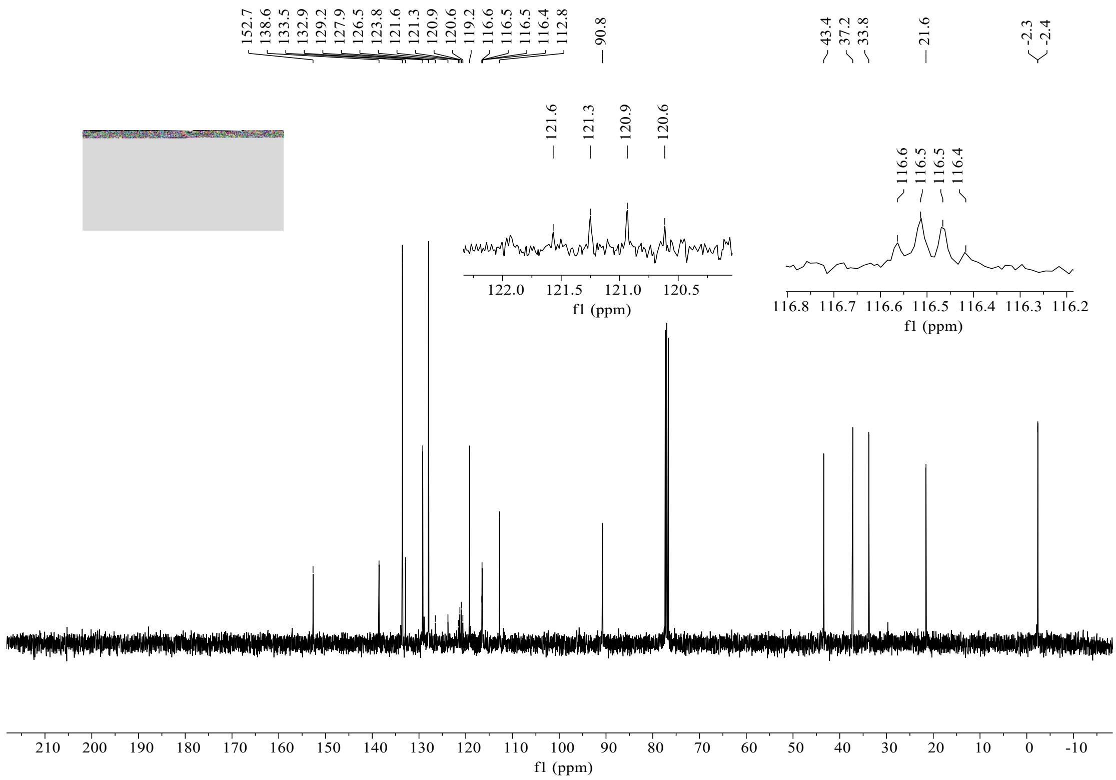


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ae**





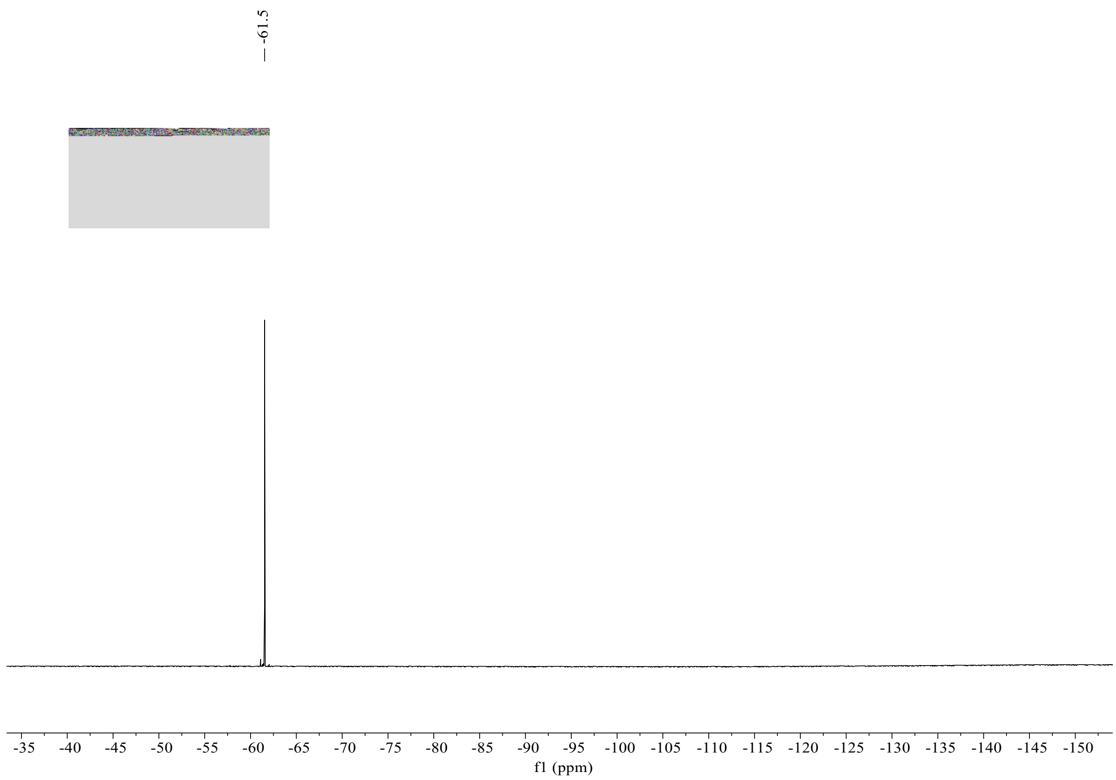
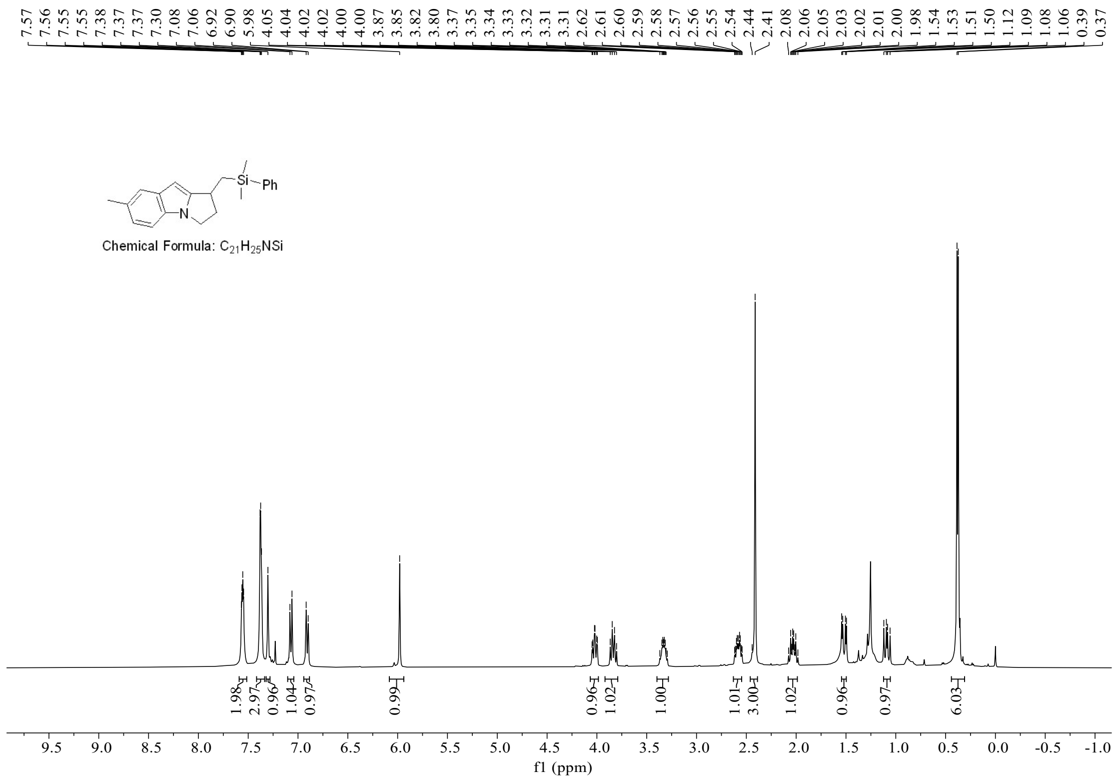


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3af**



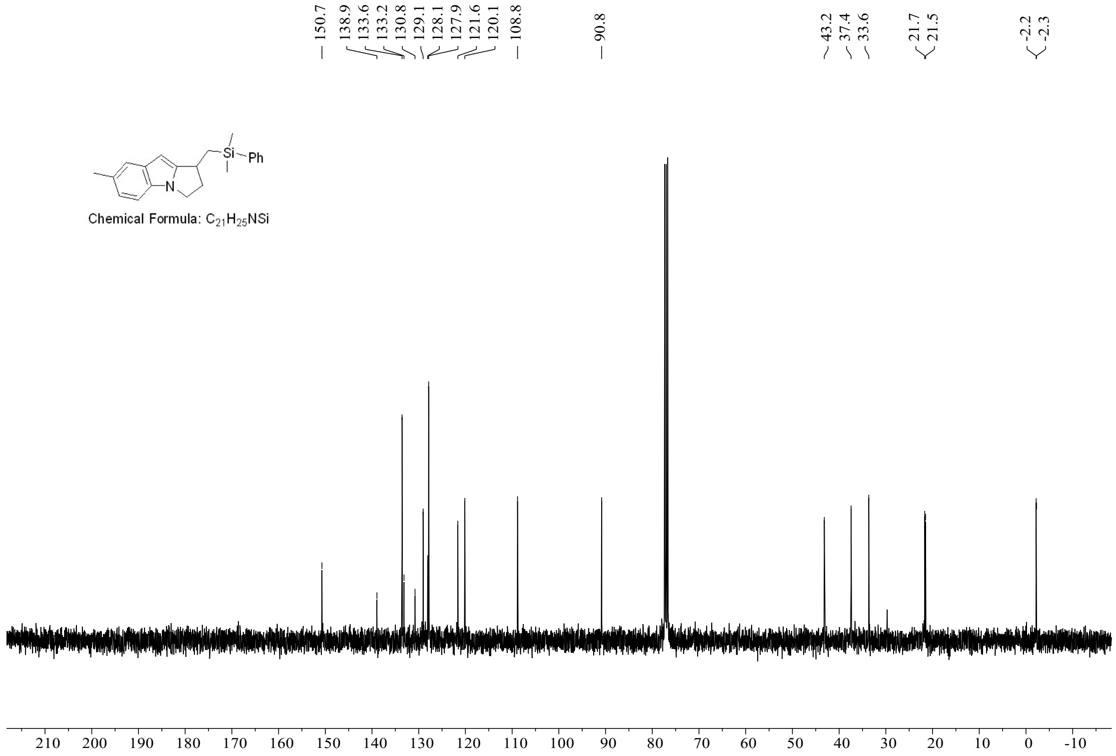
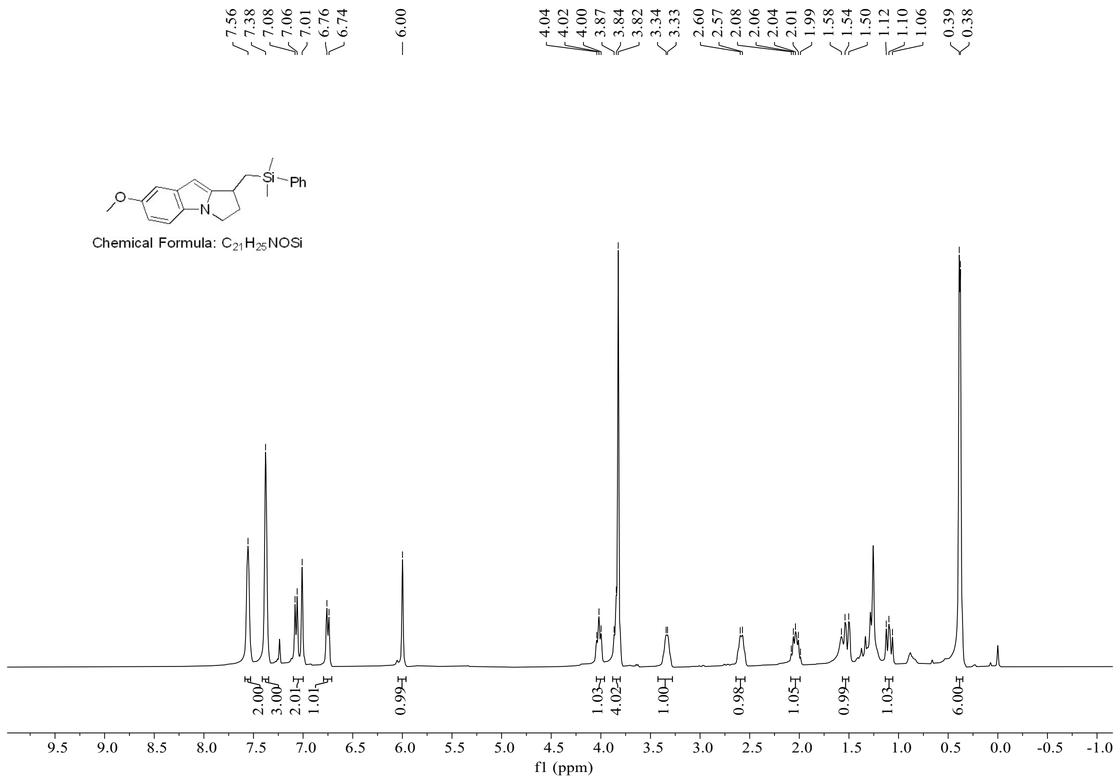


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ag**



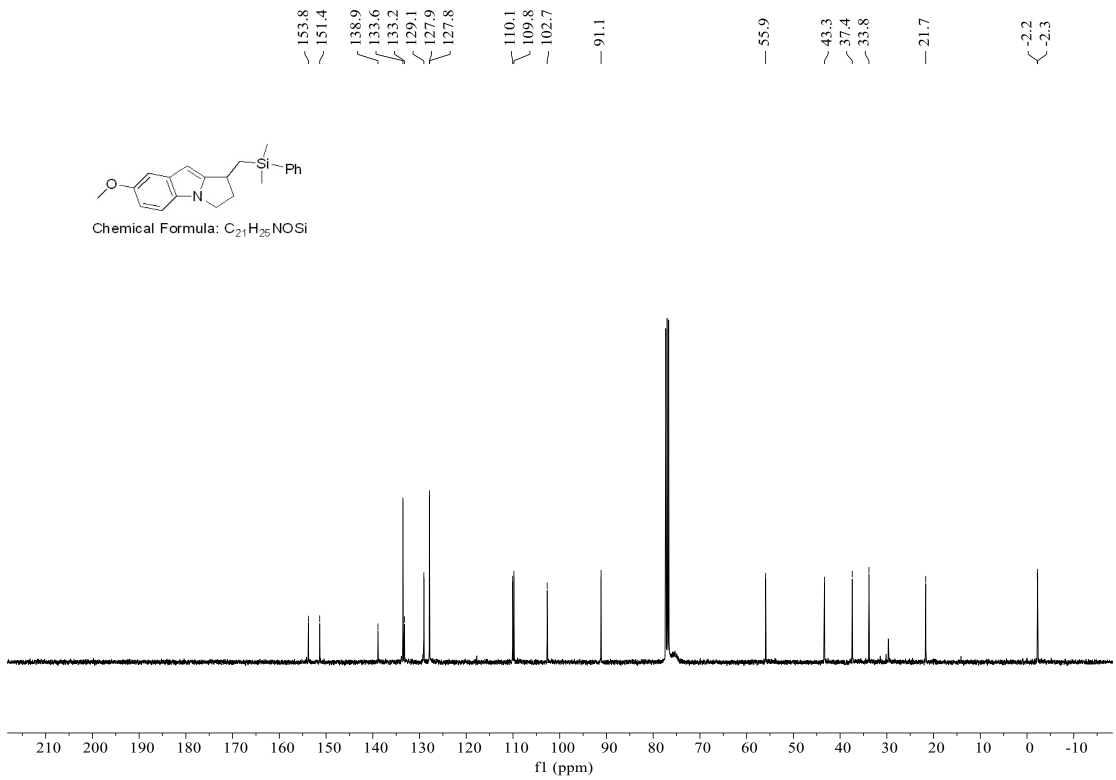
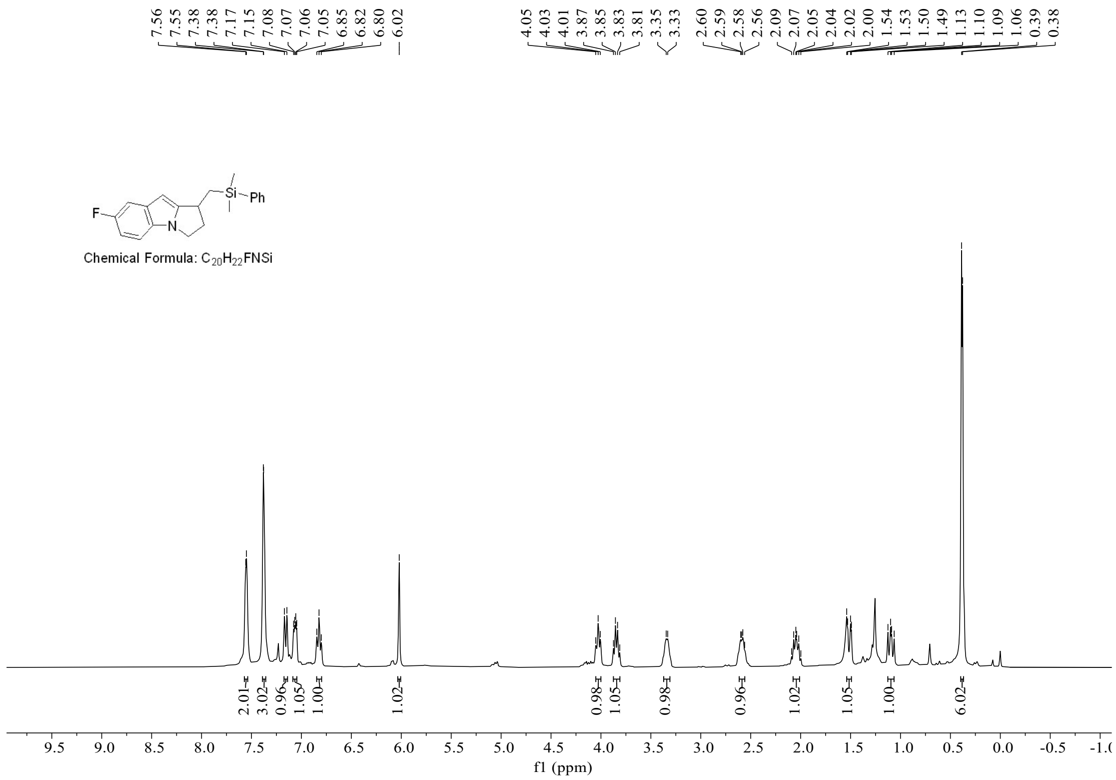
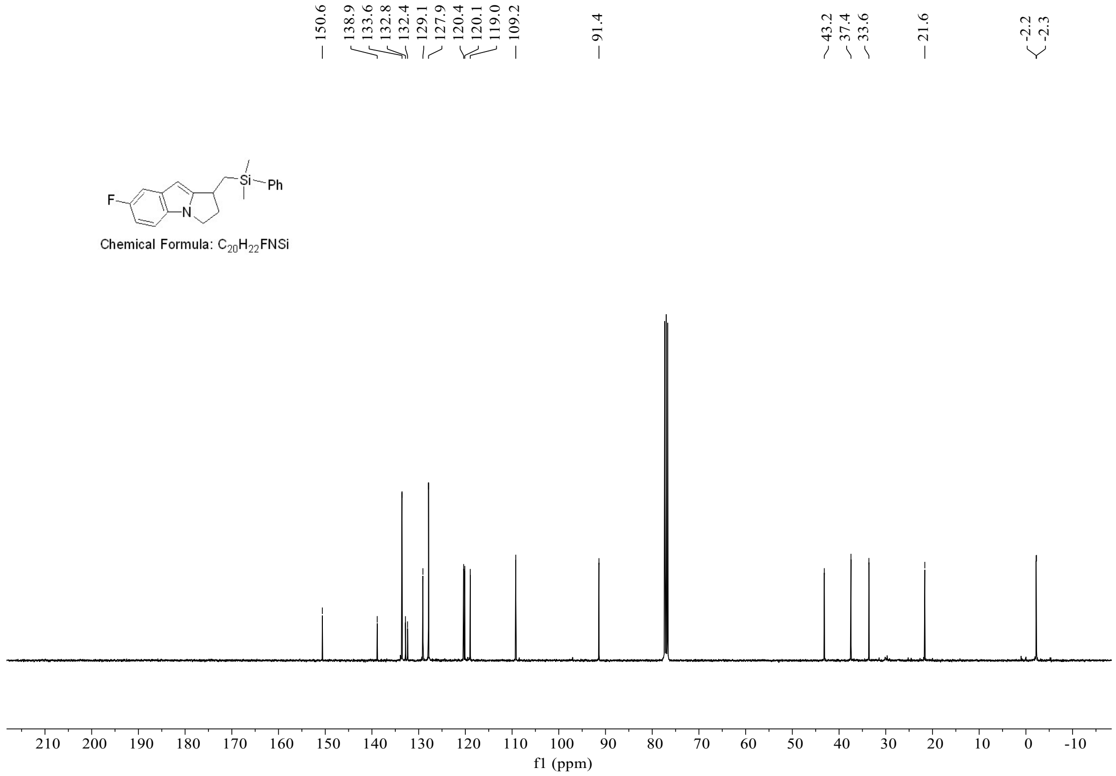


Fig. S8 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ah**


7.56 7.55 7.38 7.38 7.17 7.15 7.08 7.07 7.06 7.05 6.85 6.82 6.80 6.02
4.05 4.03 4.01 3.87 3.85 3.83 3.81 3.35 3.33 2.60 2.59 2.58 2.56 2.09 2.07 2.05 2.04 2.02 2.00 1.54 1.53 1.50 1.49 1.13 1.10 1.09 1.06 0.39 0.38
F
Si
Ph
N
Chemical Formula: C20H22FNSi
2.01 3.02 0.96 1.05 1.00 1.02 0.98 1.05 0.98 0.96 1.02 1.05 1.00 6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.(
f1 (ppm)


150.6 138.9 133.6 132.8 132.4 129.1 127.9 120.4 120.1 119.0 109.2 91.4 43.2 37.4 33.6 21.6 -2.2 -2.3
F
Si
Ph
N
Chemical Formula: C20H22FNSi
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

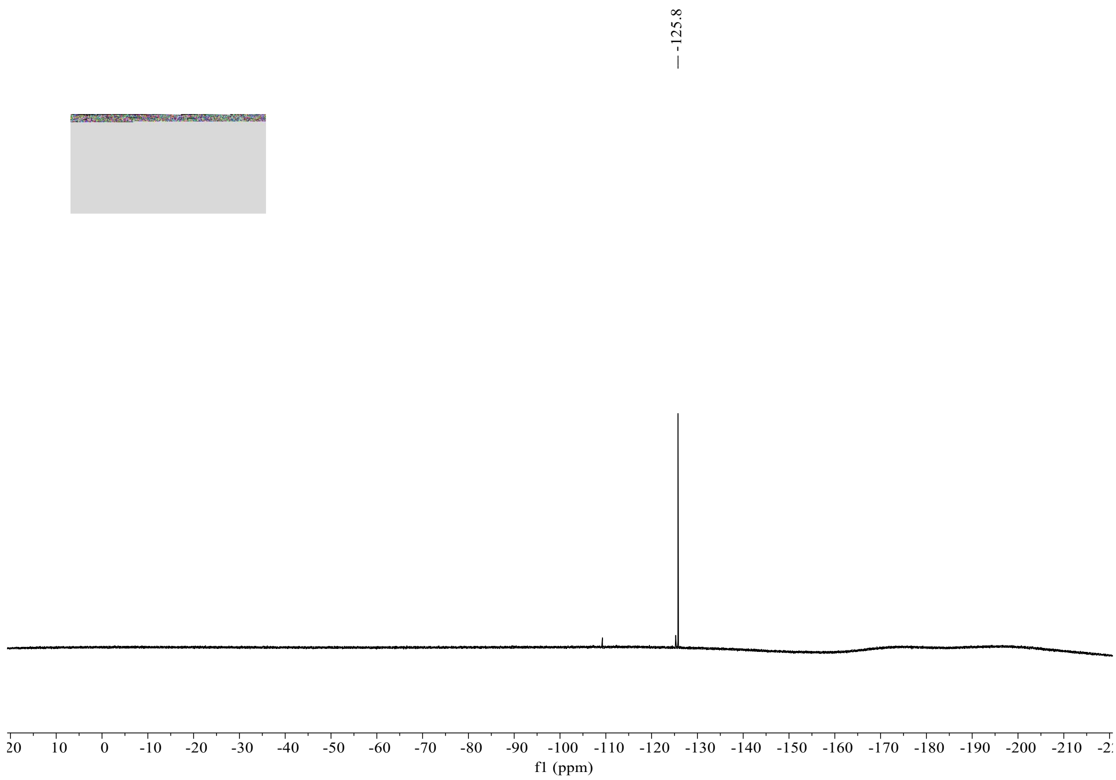
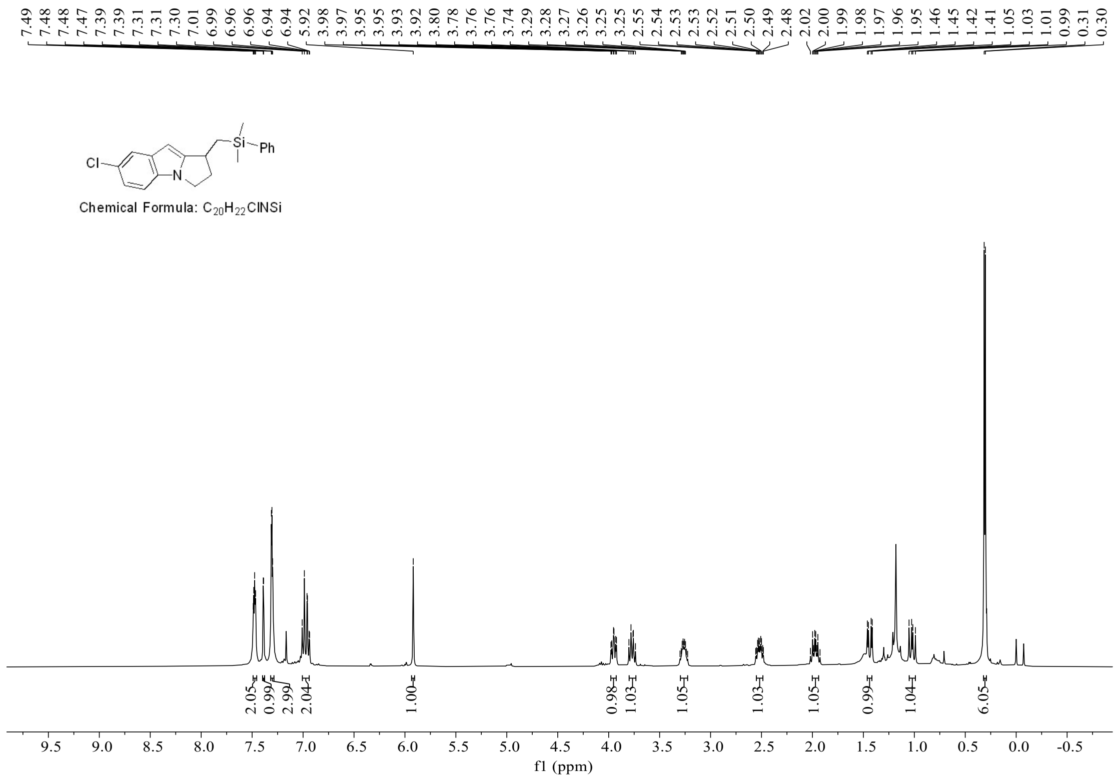


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3ai**



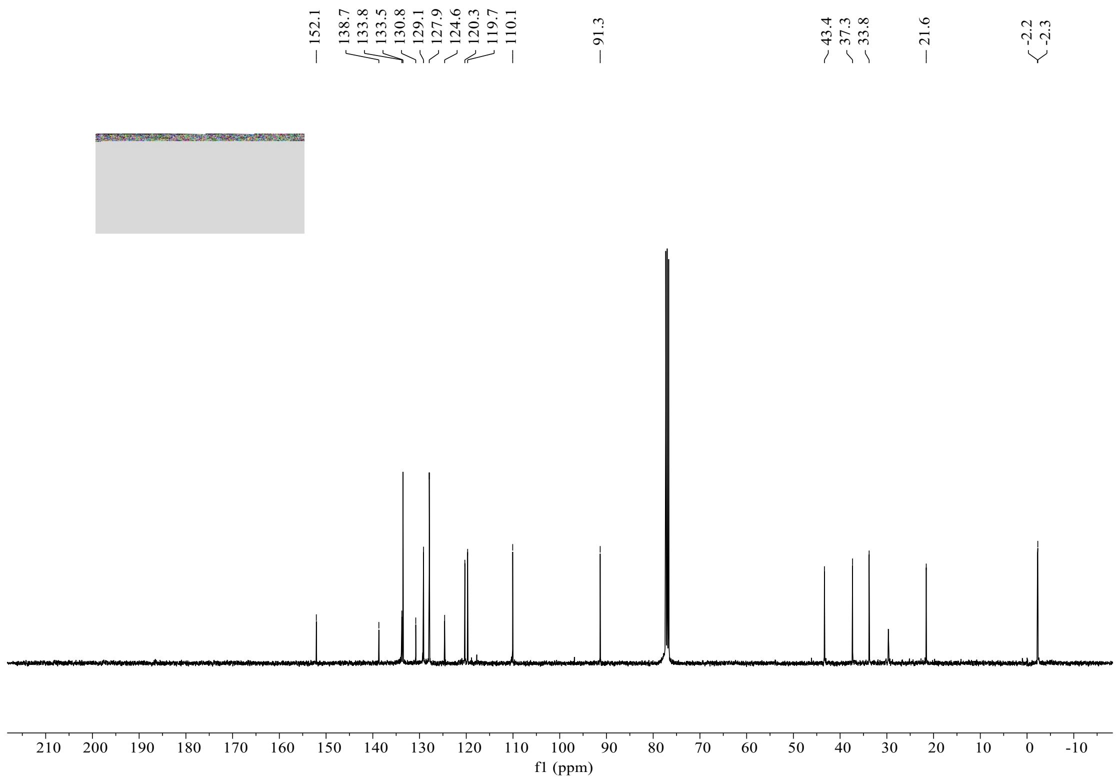
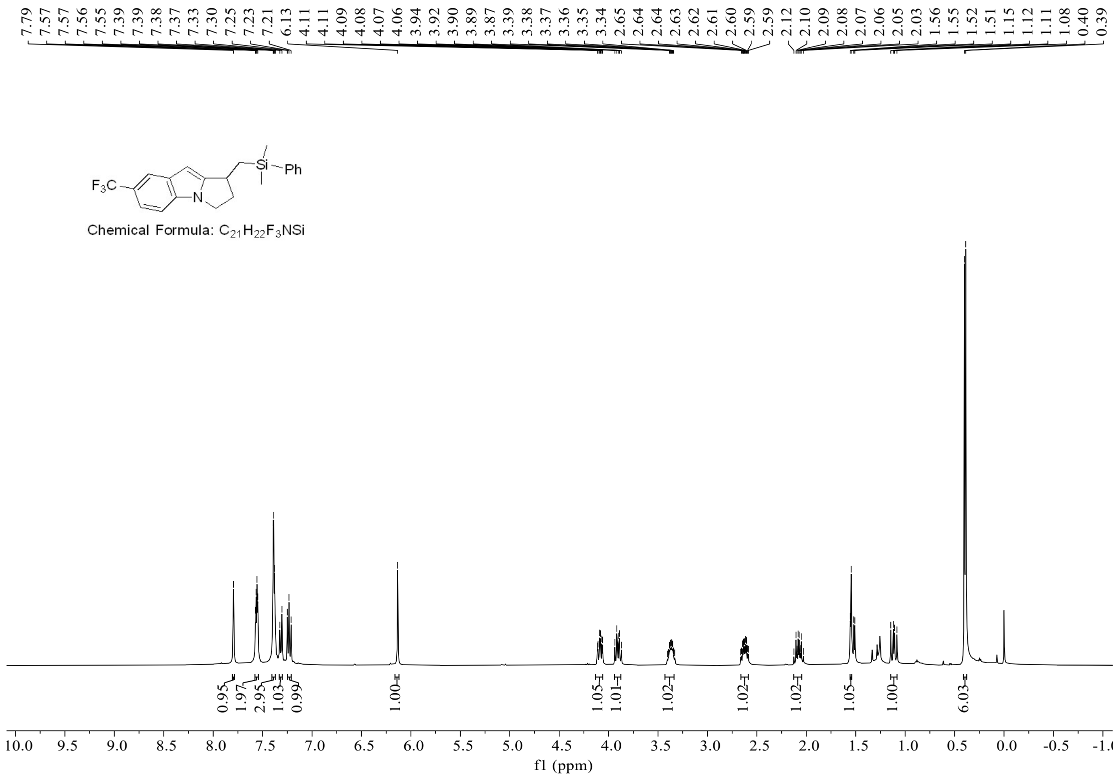
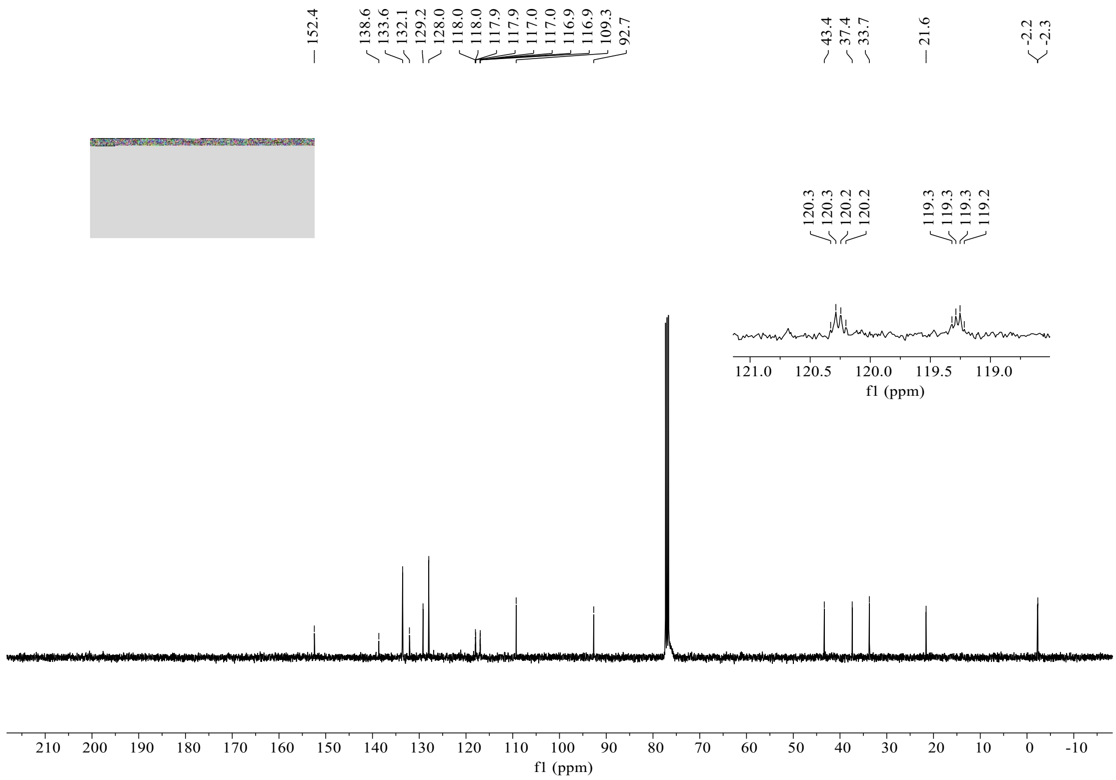


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3aj**





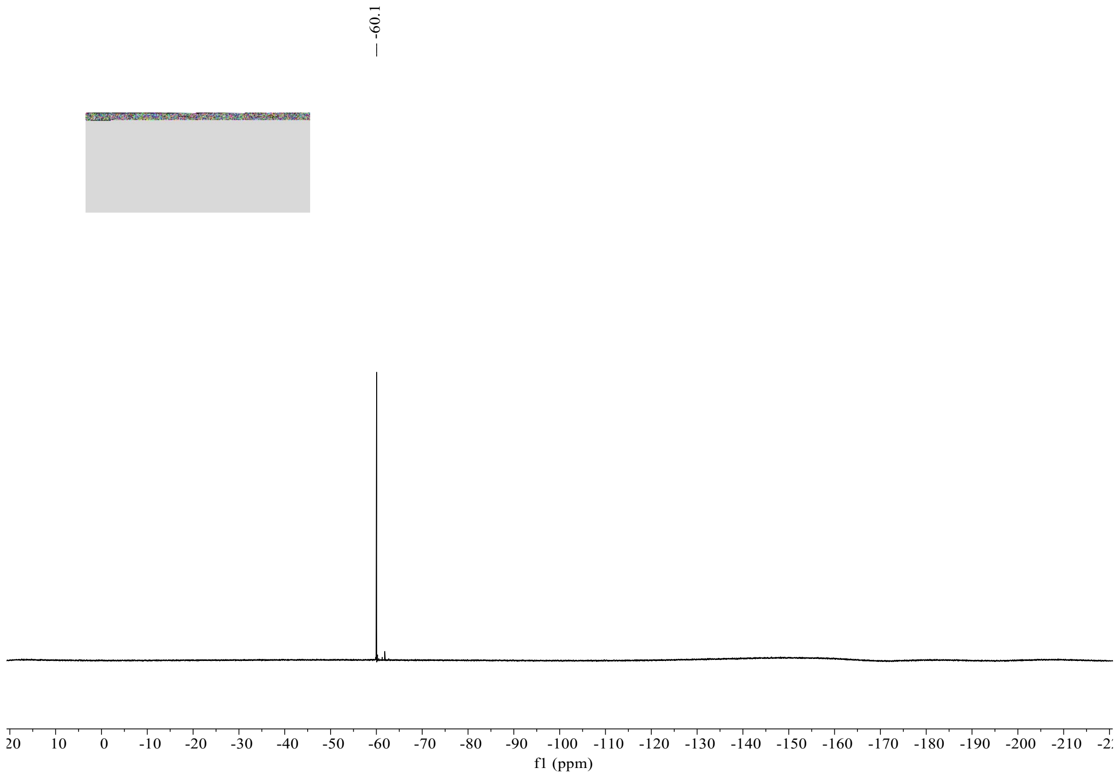
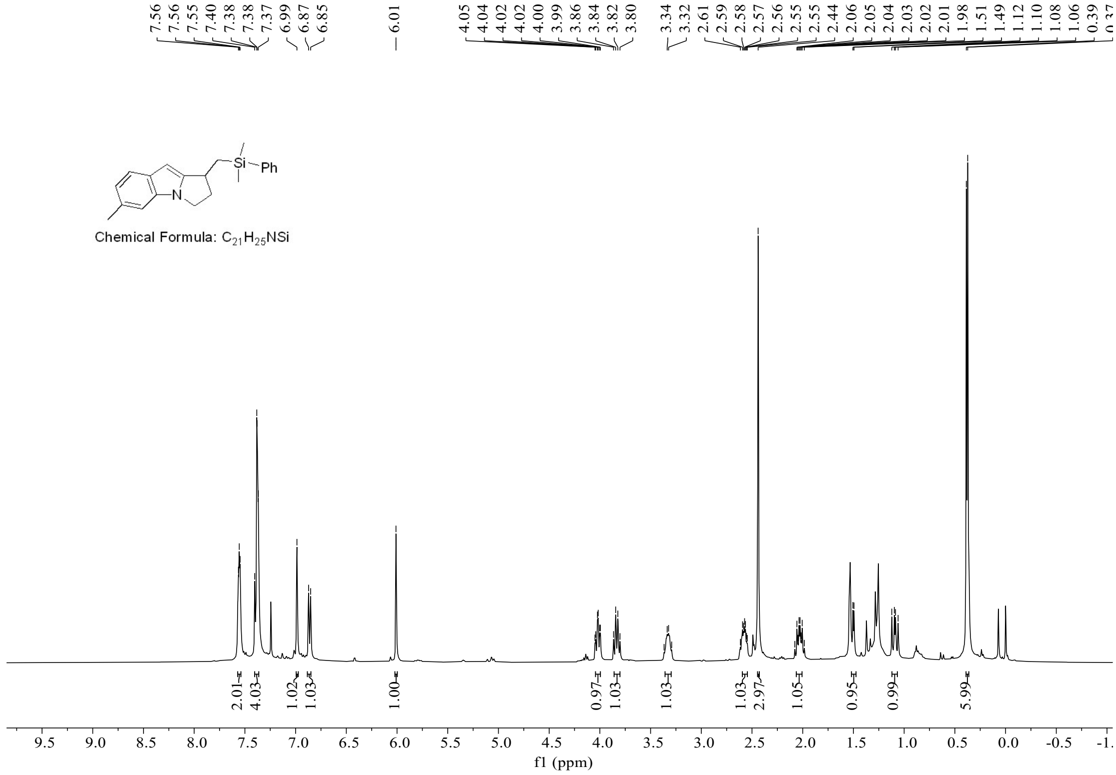


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3ak**



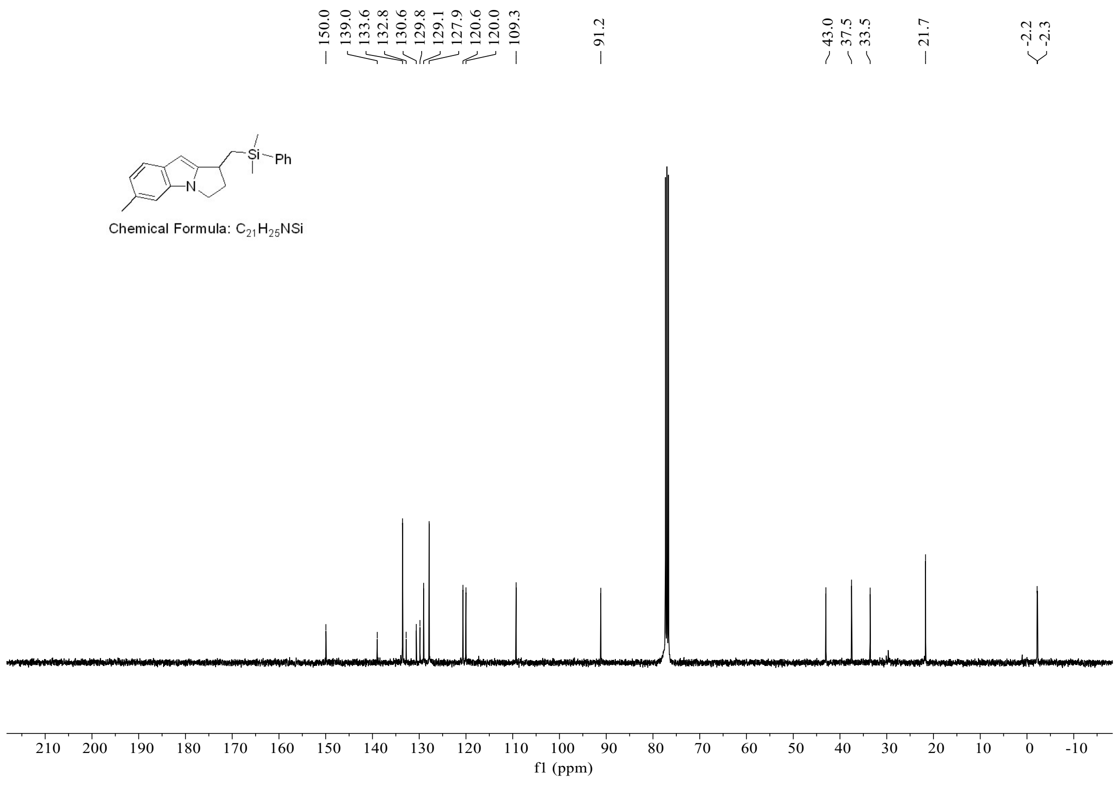
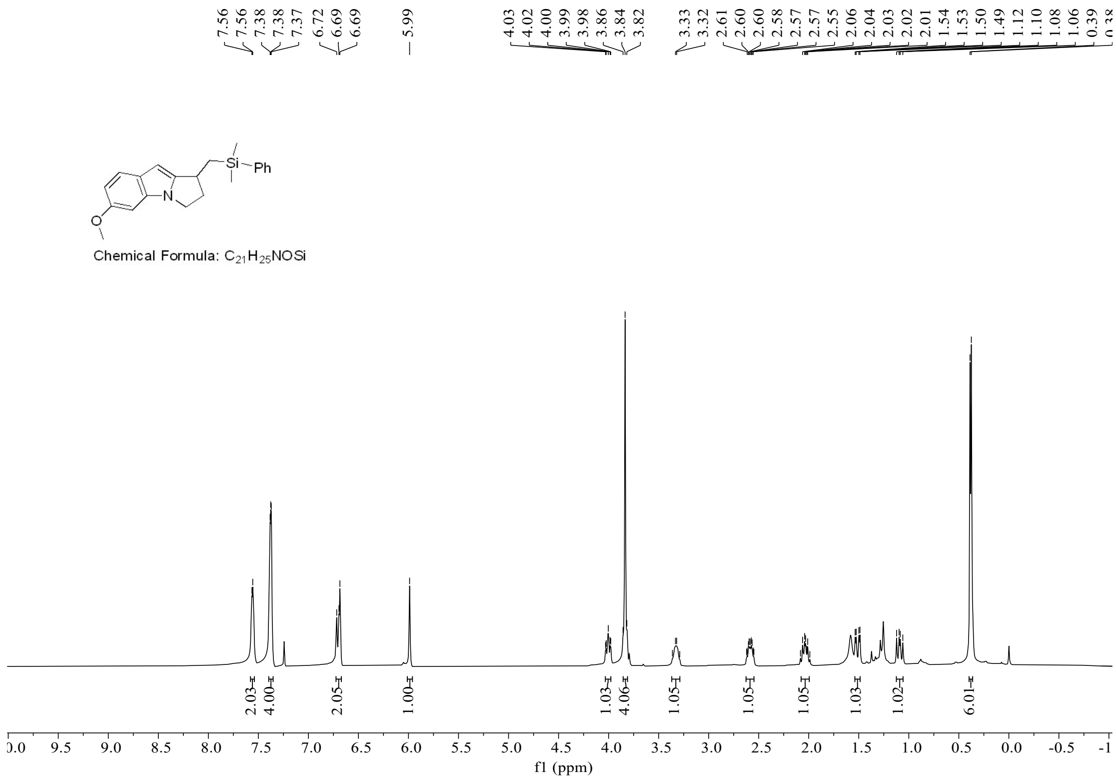


Fig. S12 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3al**



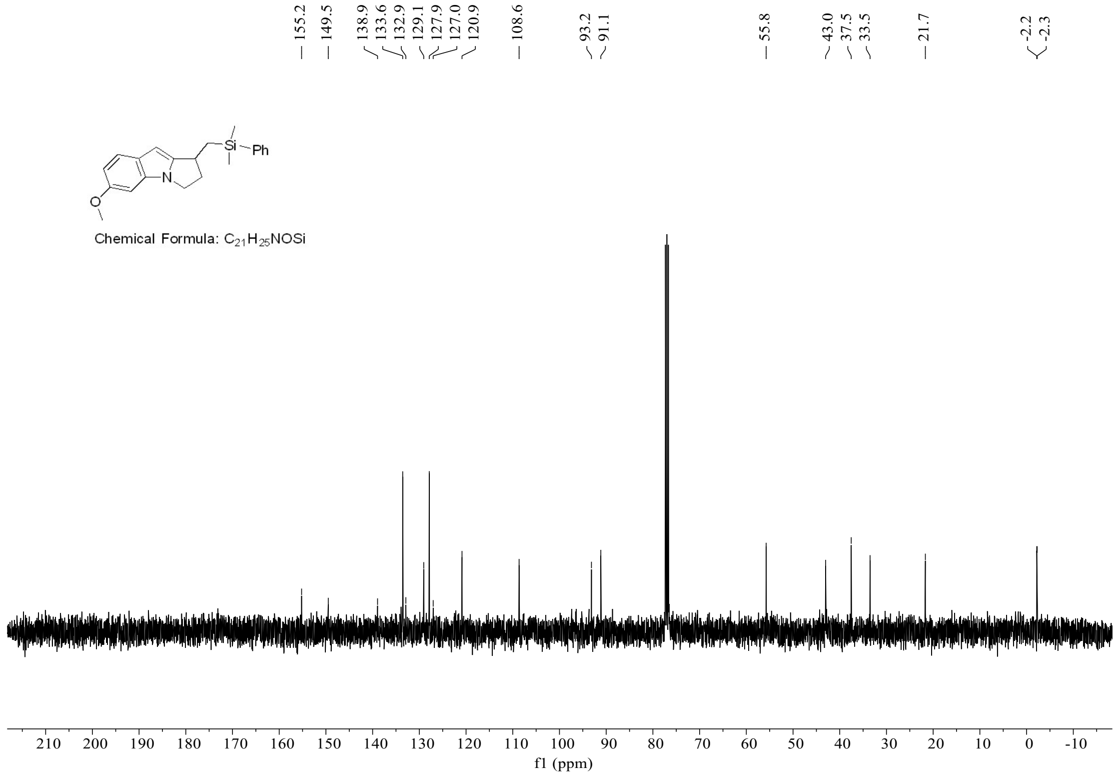
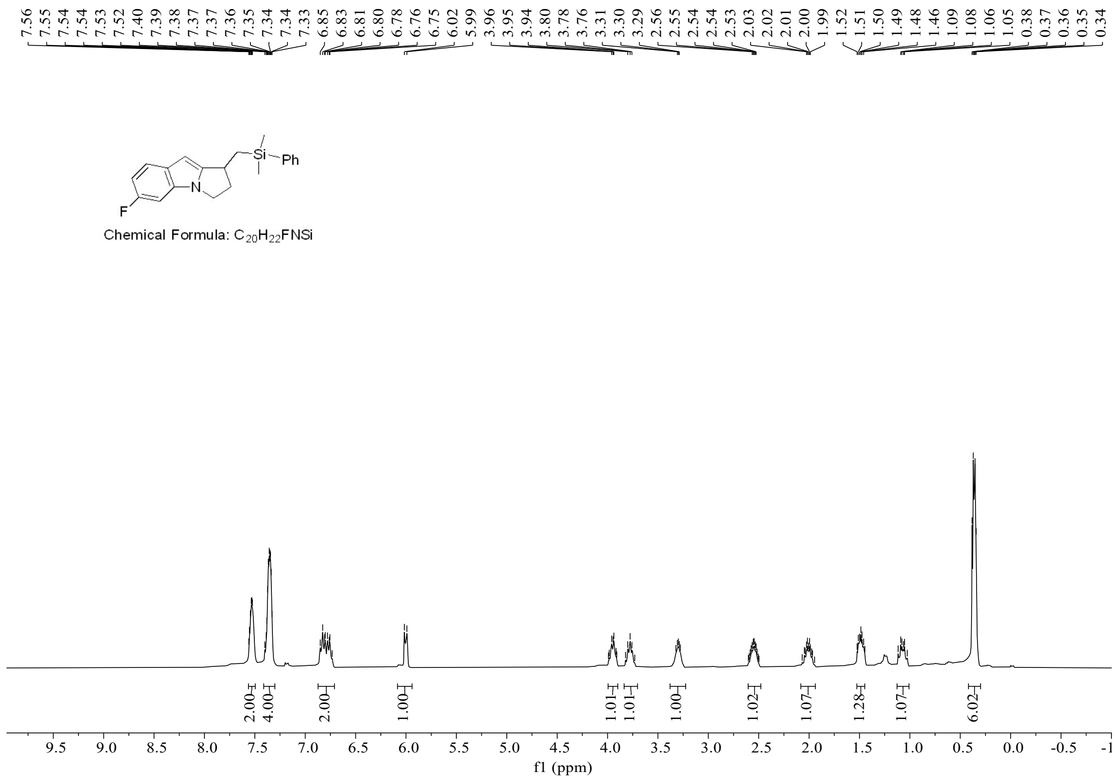
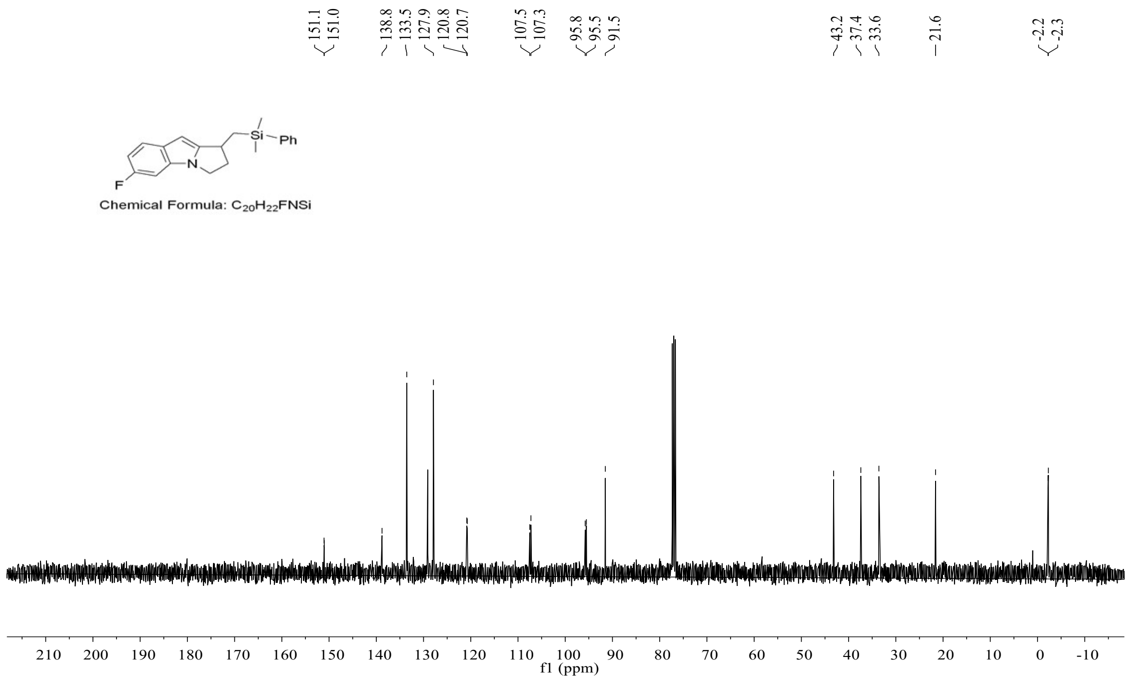


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3am**


Ph
Si
N
F
Chemical Formula: C20H22FNSi
f1 (ppm)


Ph
Si
N
F
Chemical Formula: C20H22FNSi
f1 (ppm)

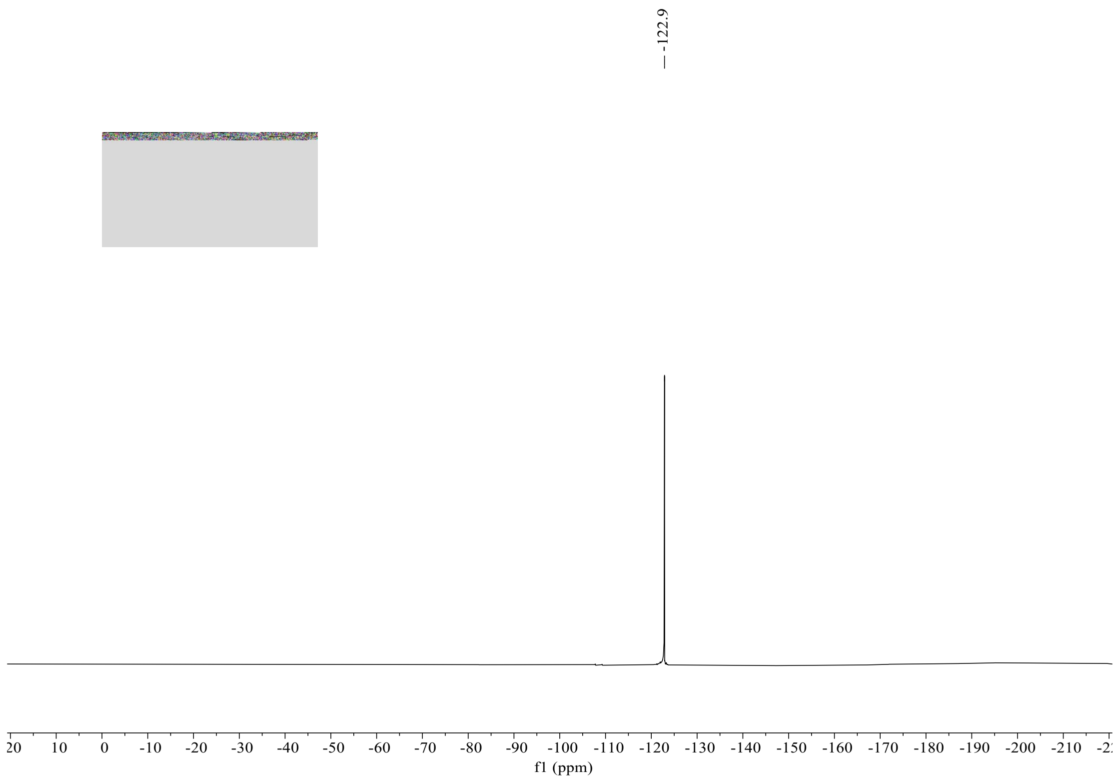
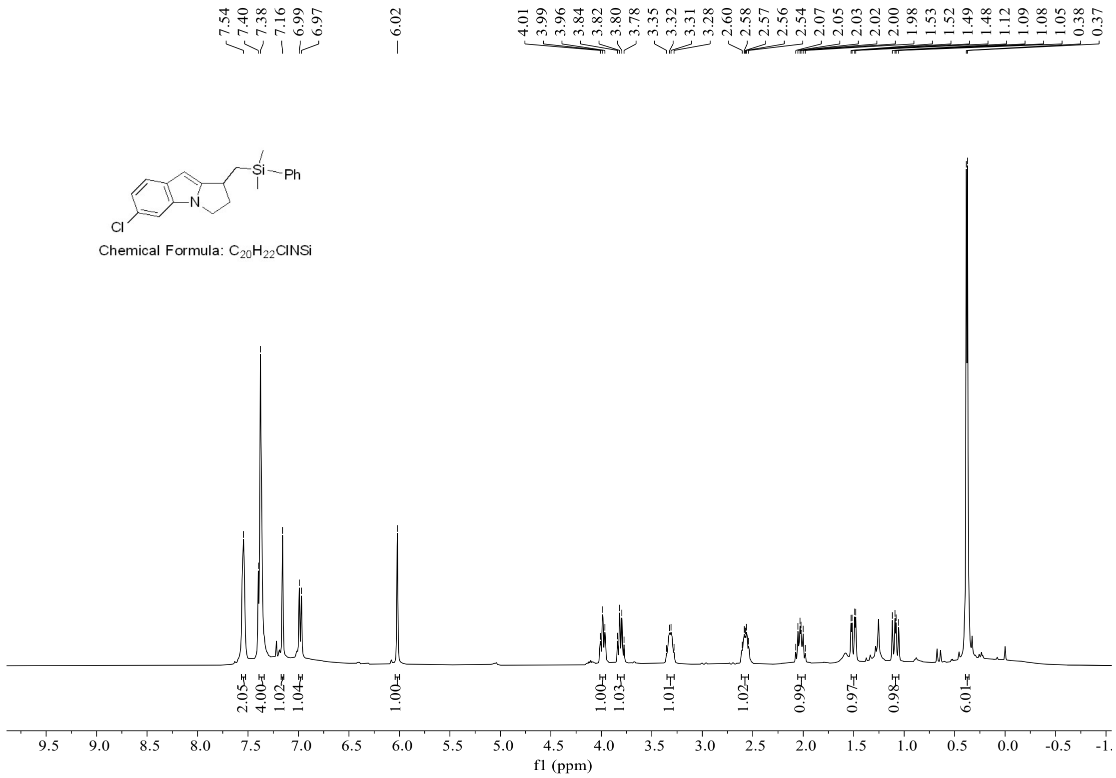


Fig. S14 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3an**



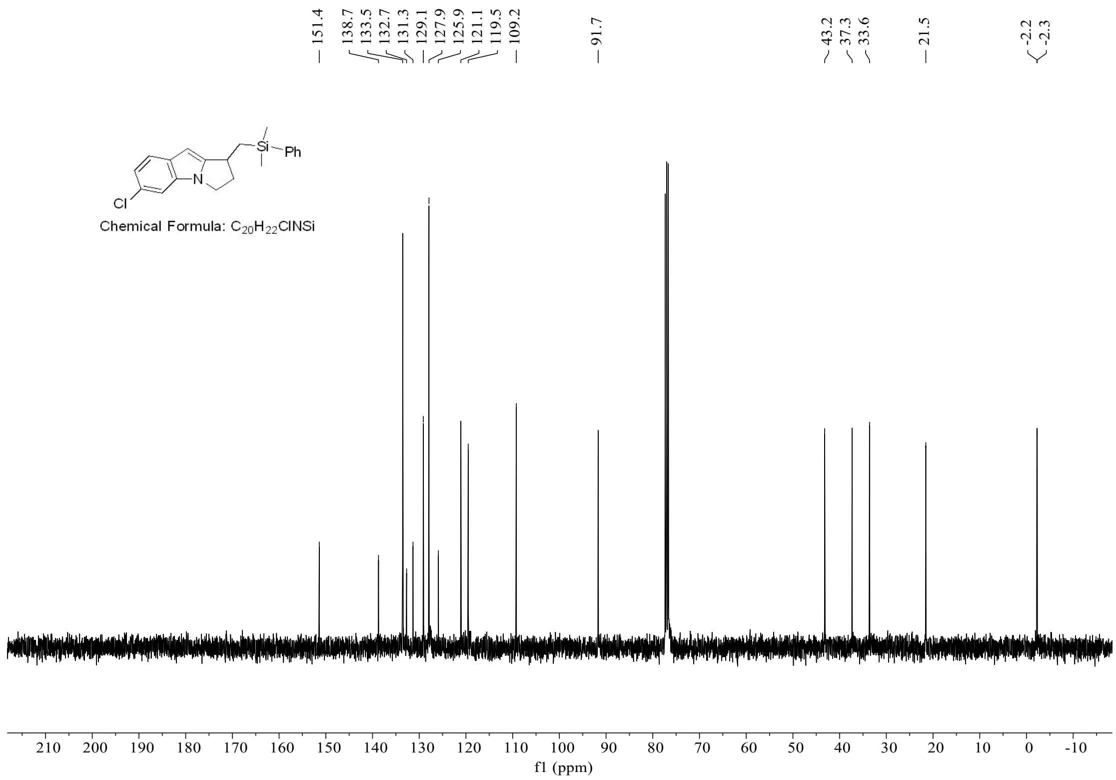
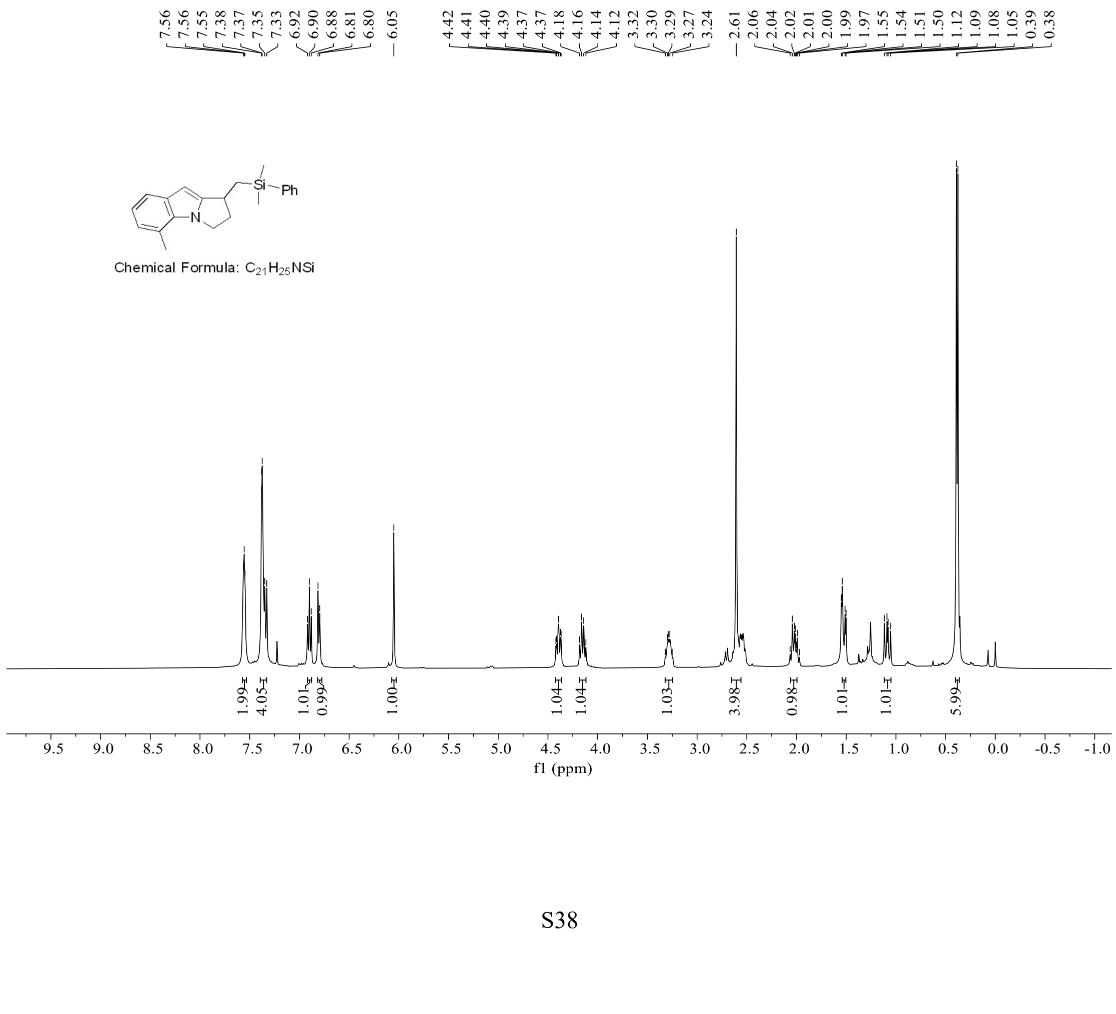


Fig. S15 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ao**



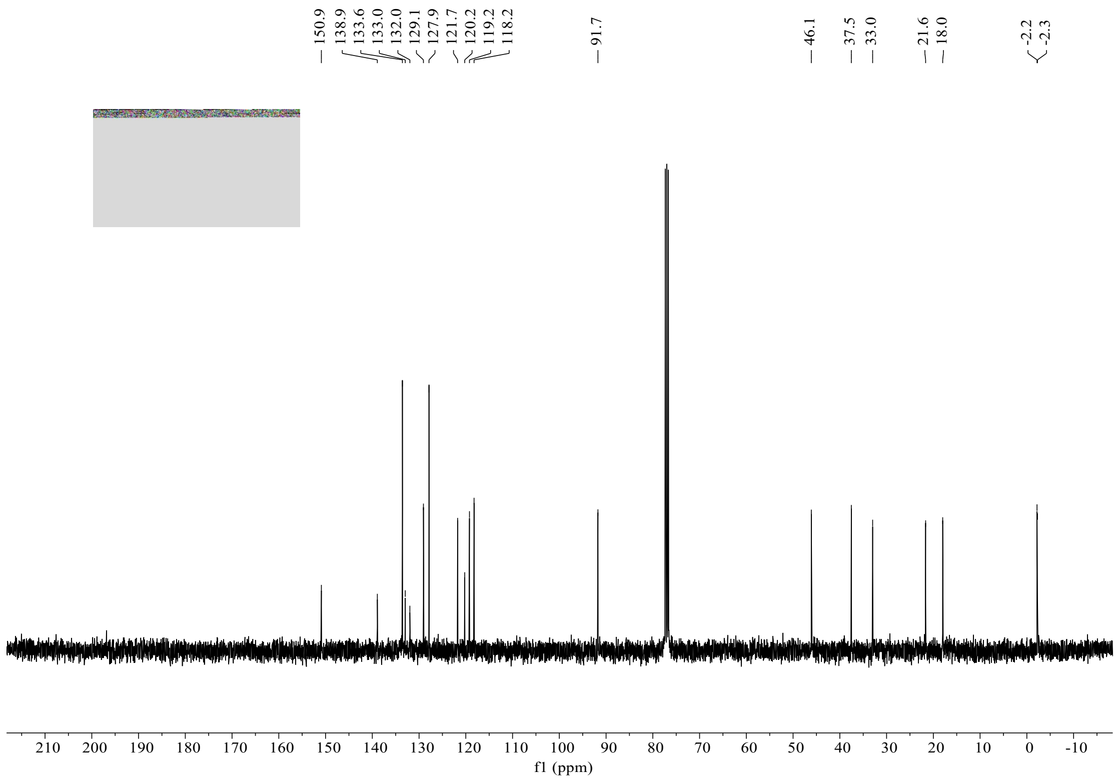
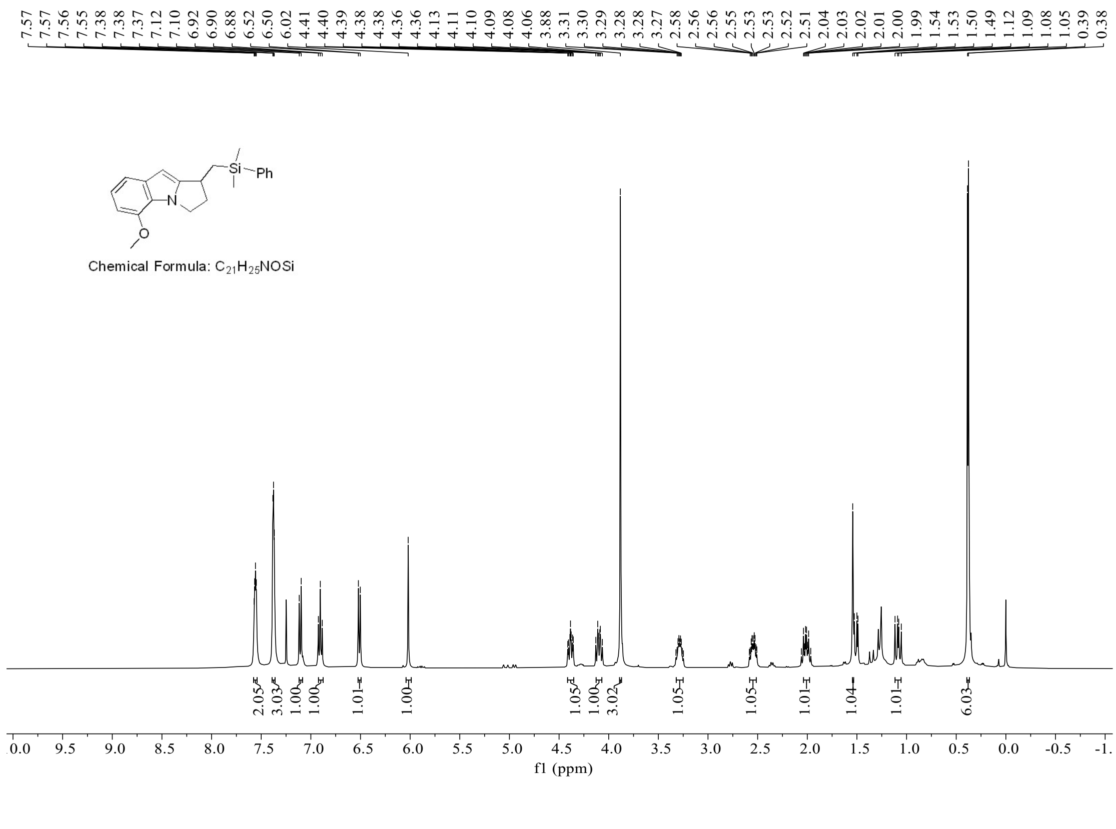


Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ap**



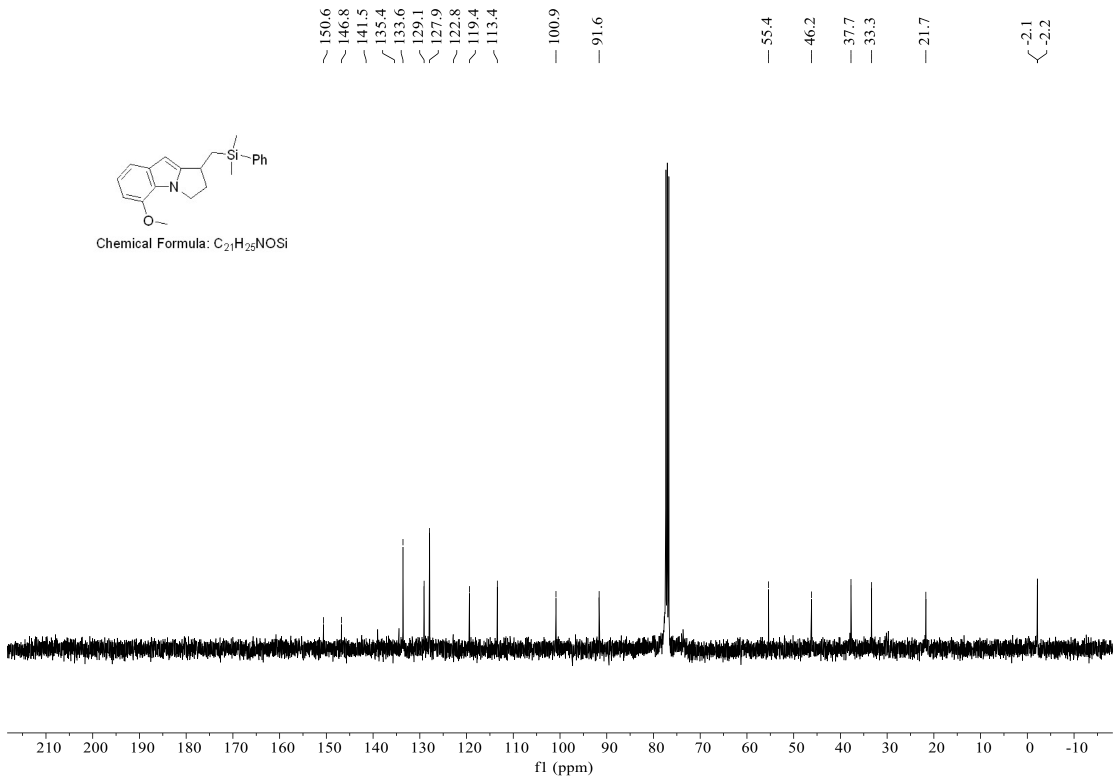
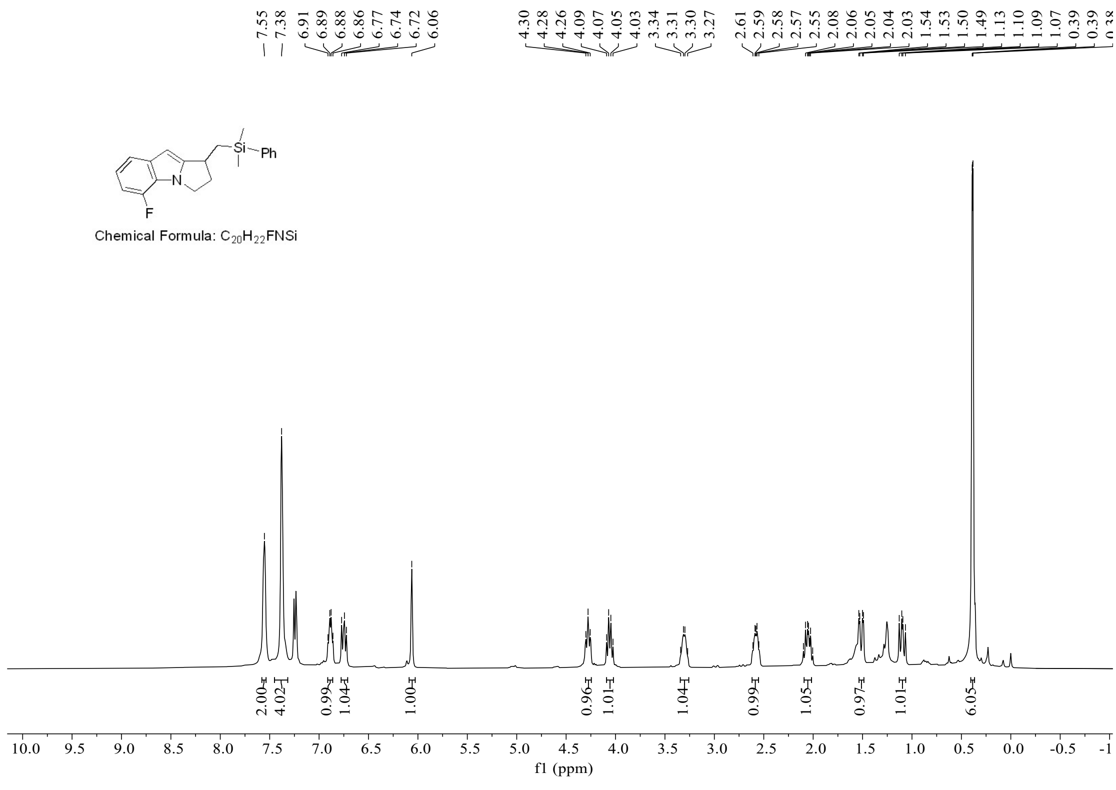
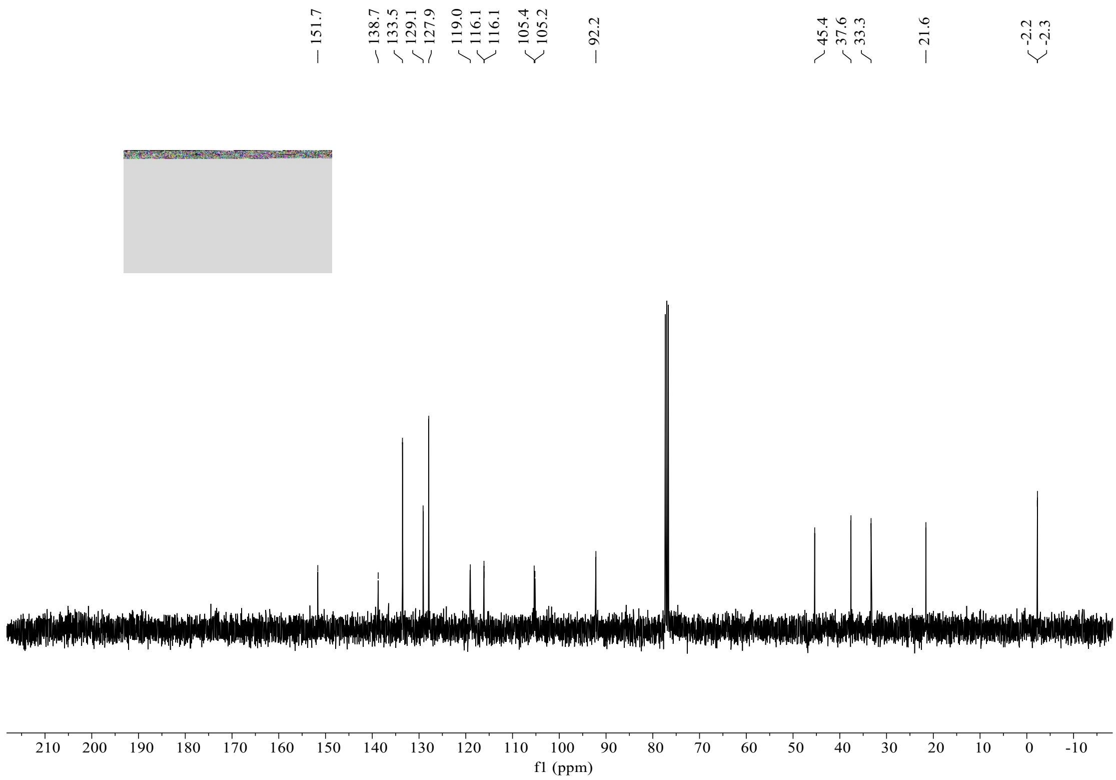


Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3aq**





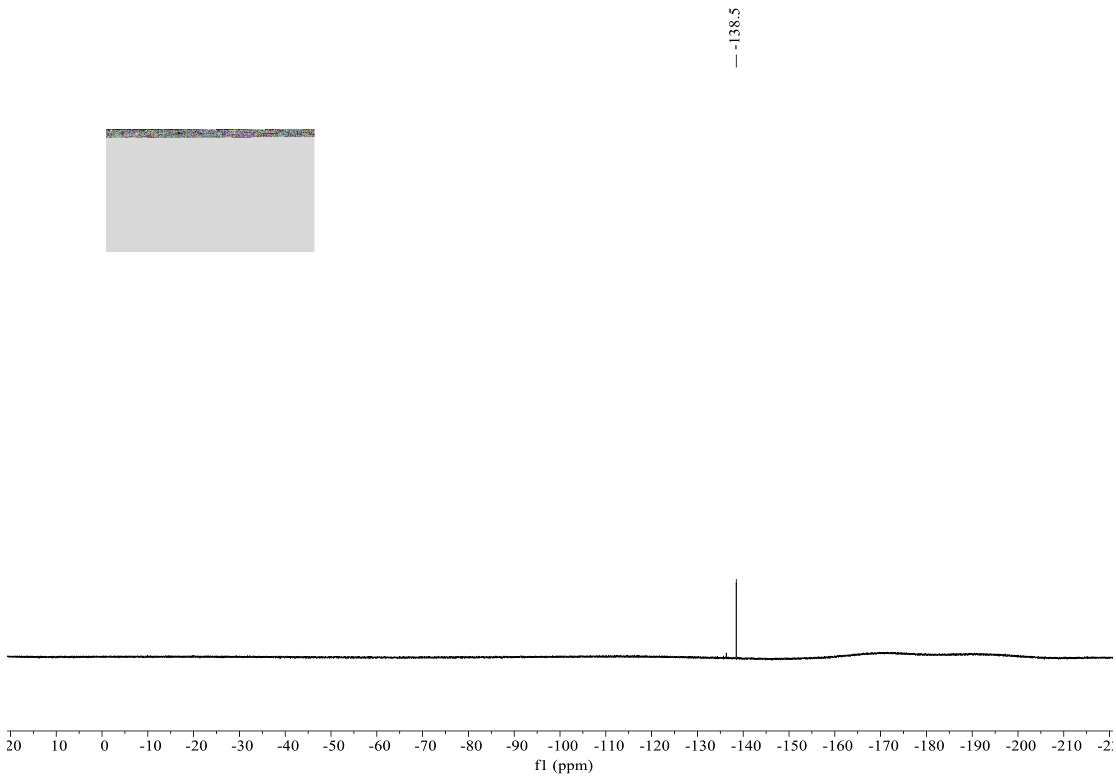
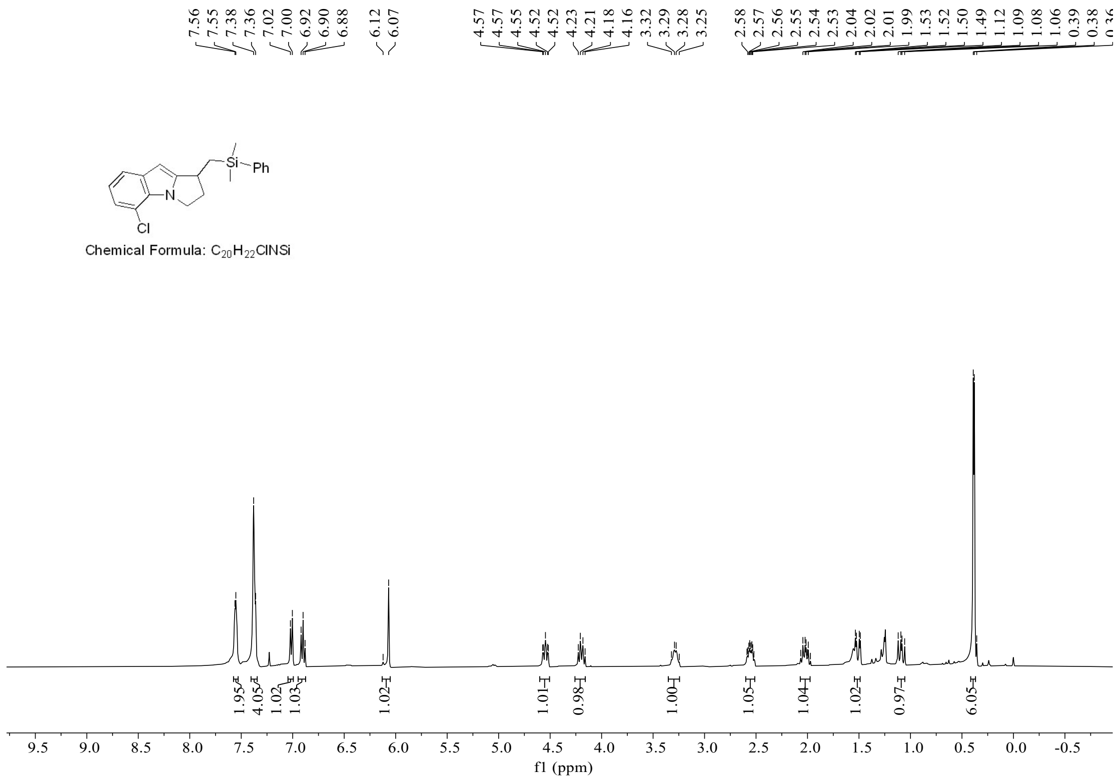


Fig. S18 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3ar**



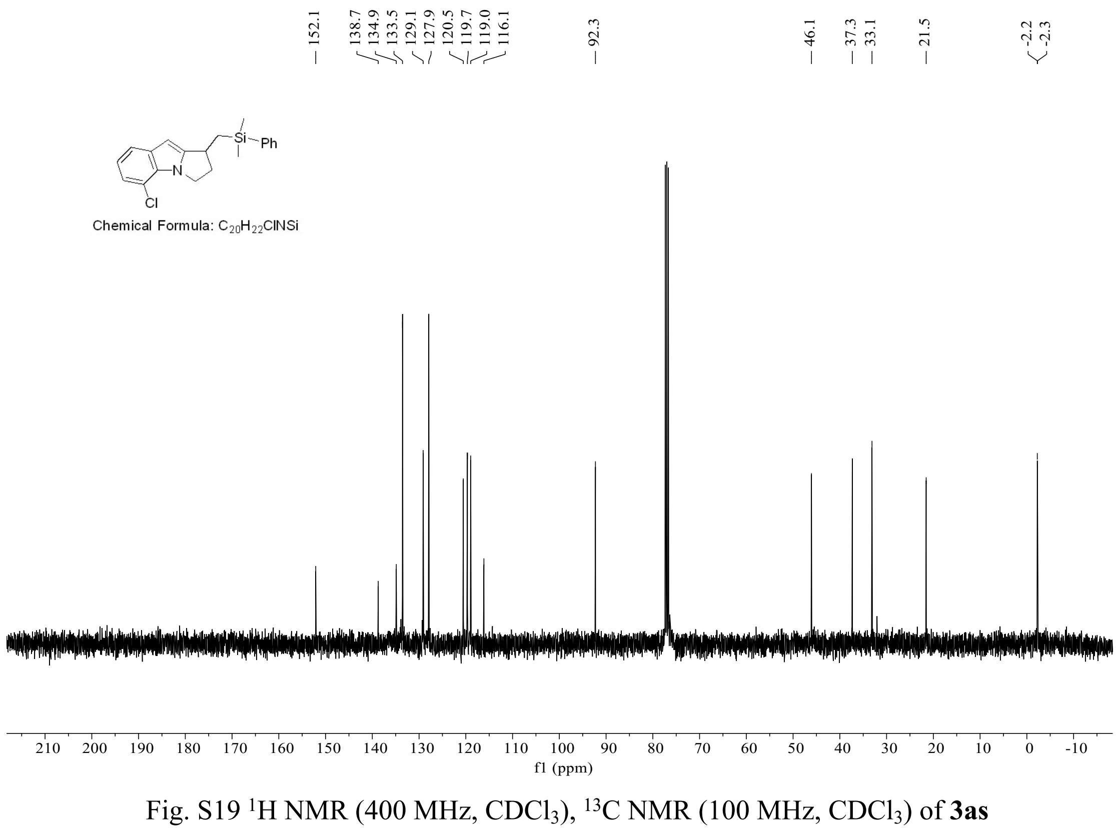
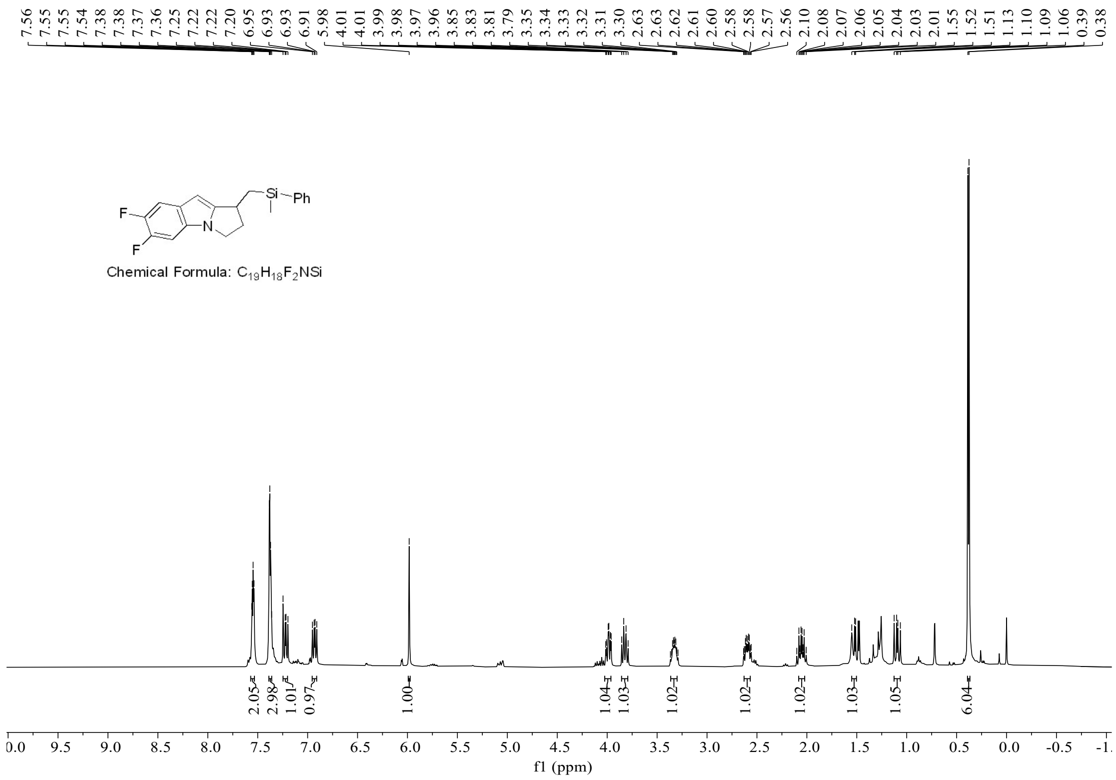
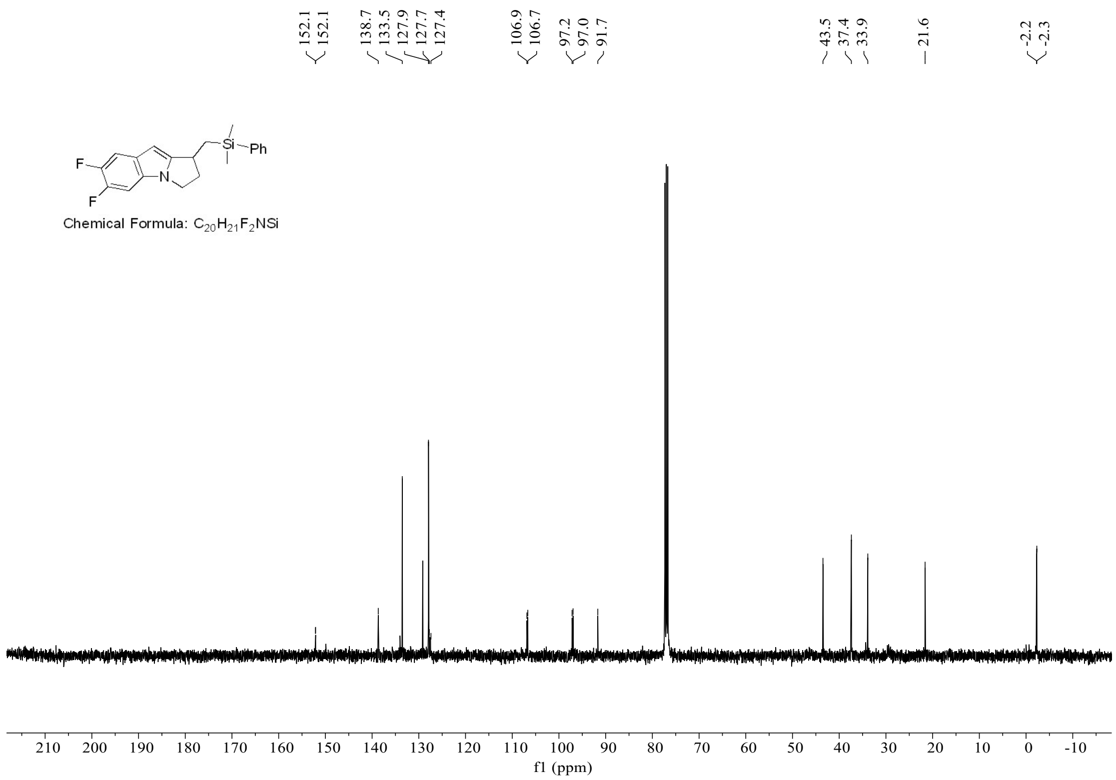


Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3as**


Chemical Formula: $C_{19}H_{18}F_2NSi$
f1 (ppm)


Chemical Formula: $C_{20}H_{21}F_2NSi$
f1 (ppm)

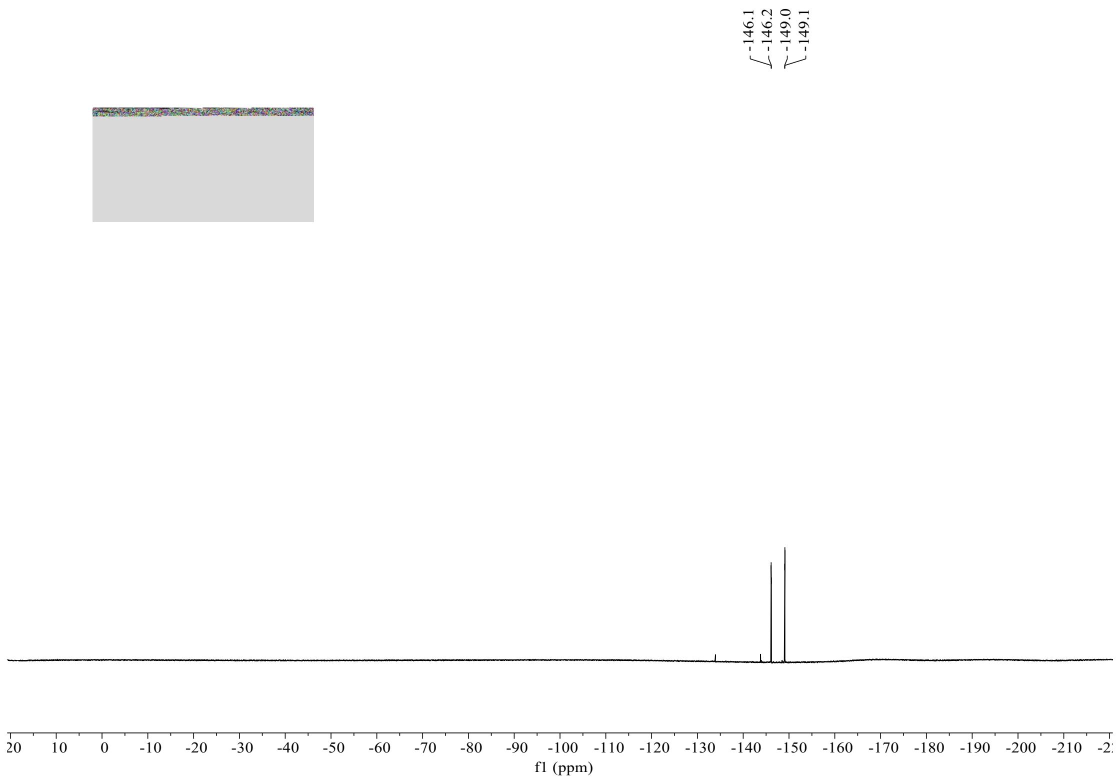
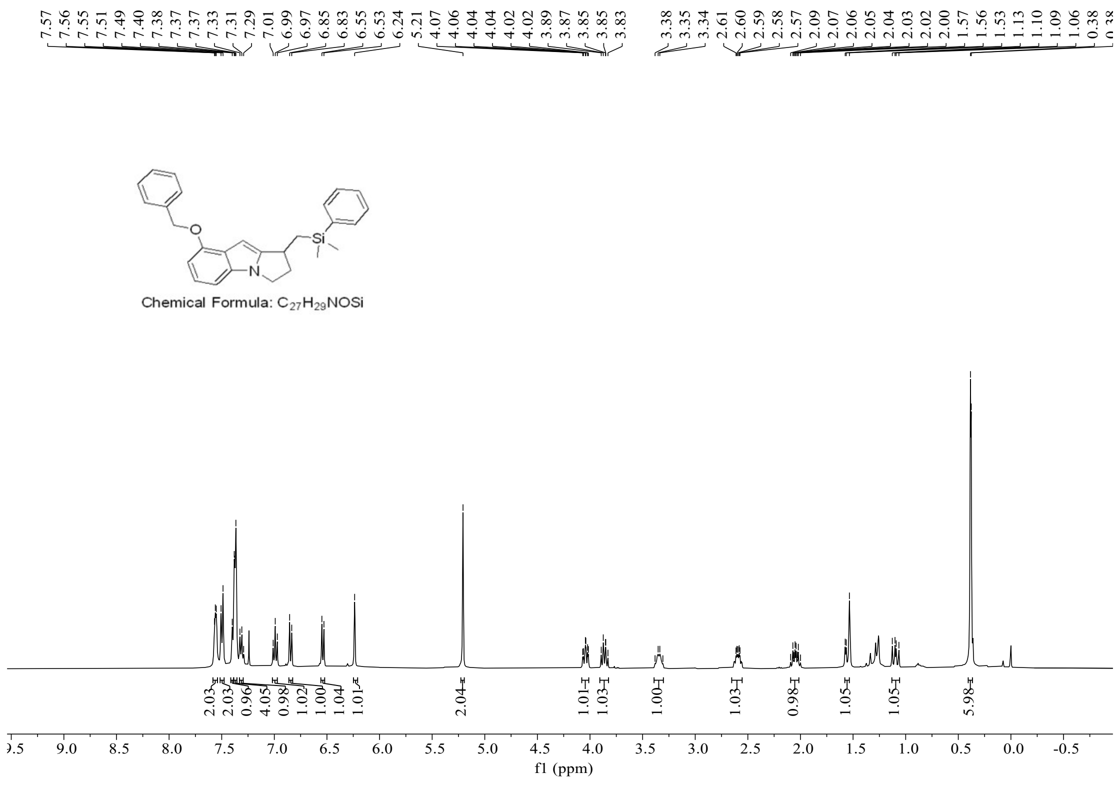


Fig. S20 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3at**



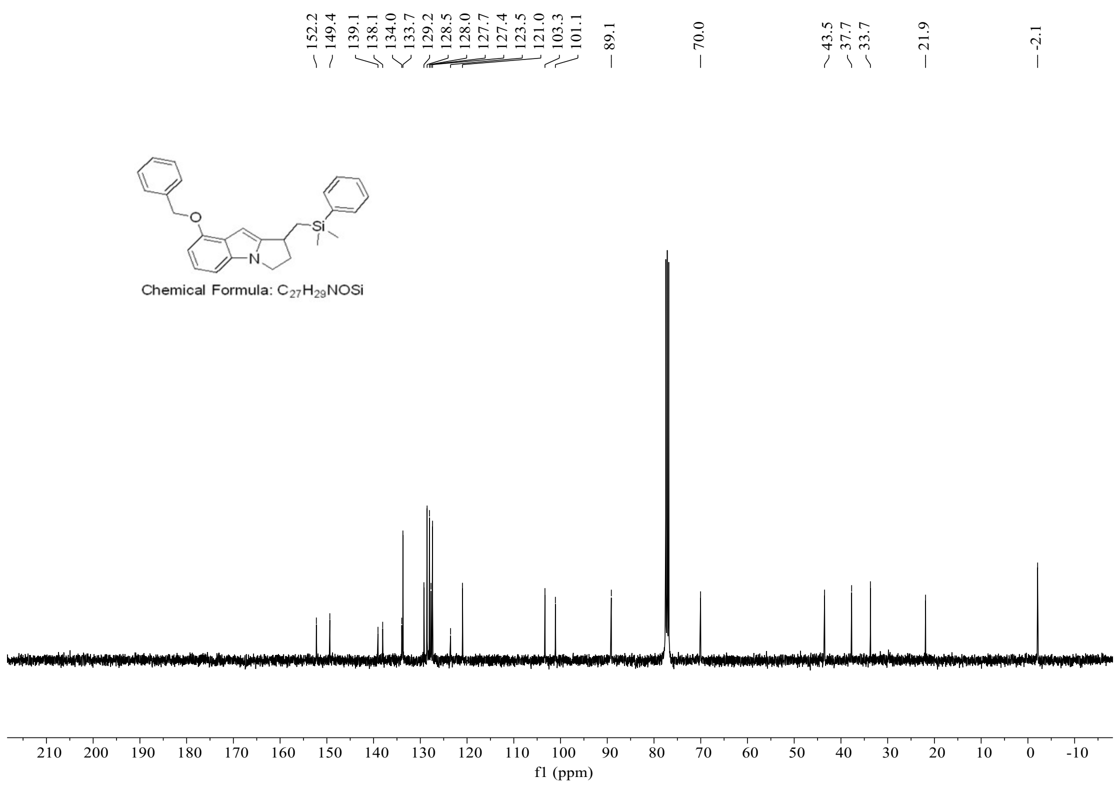
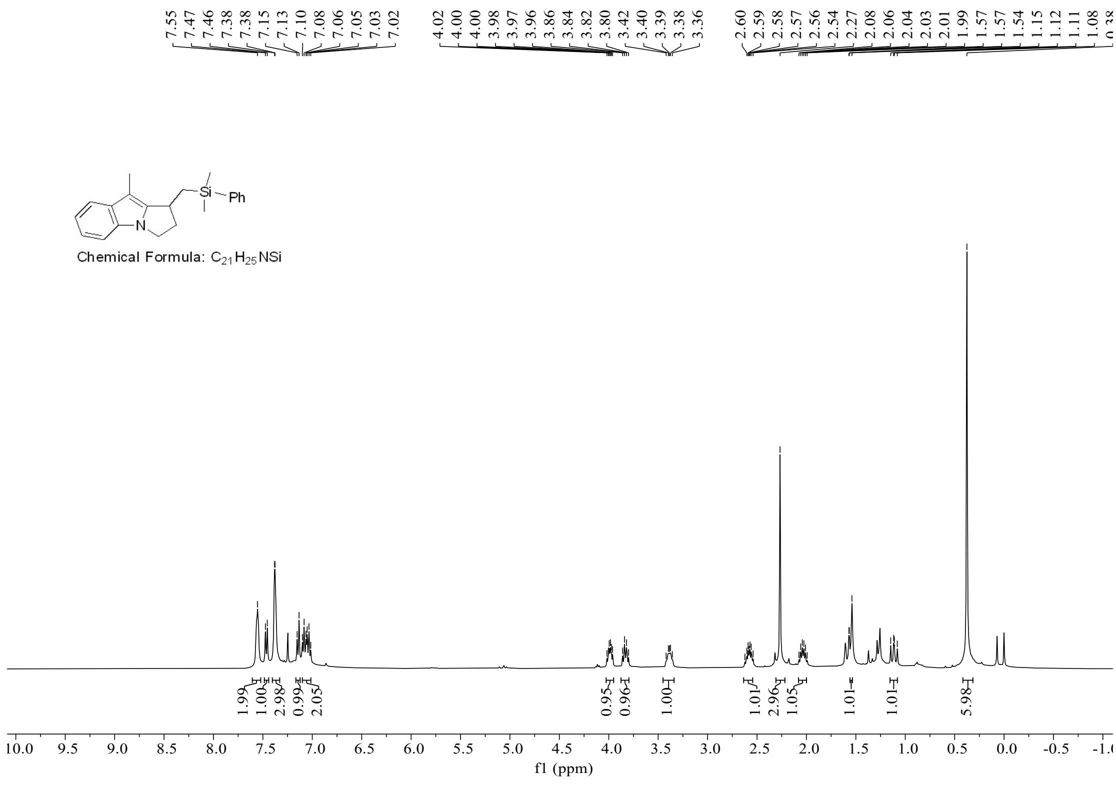


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3au**



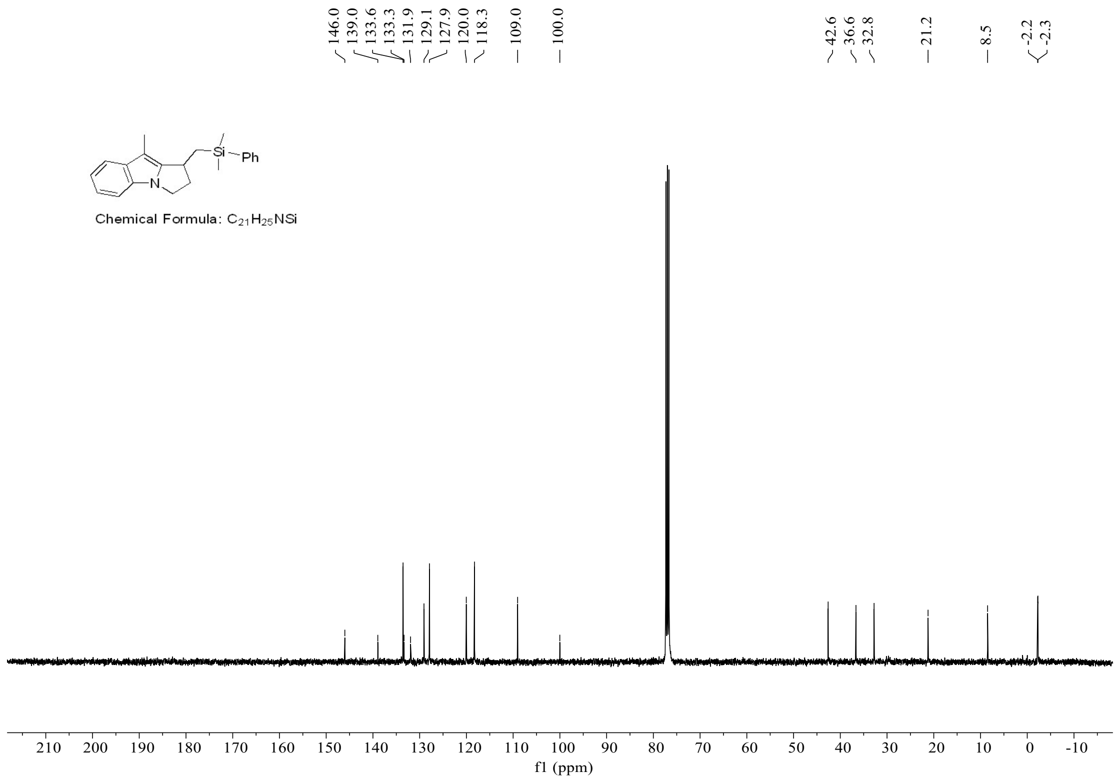
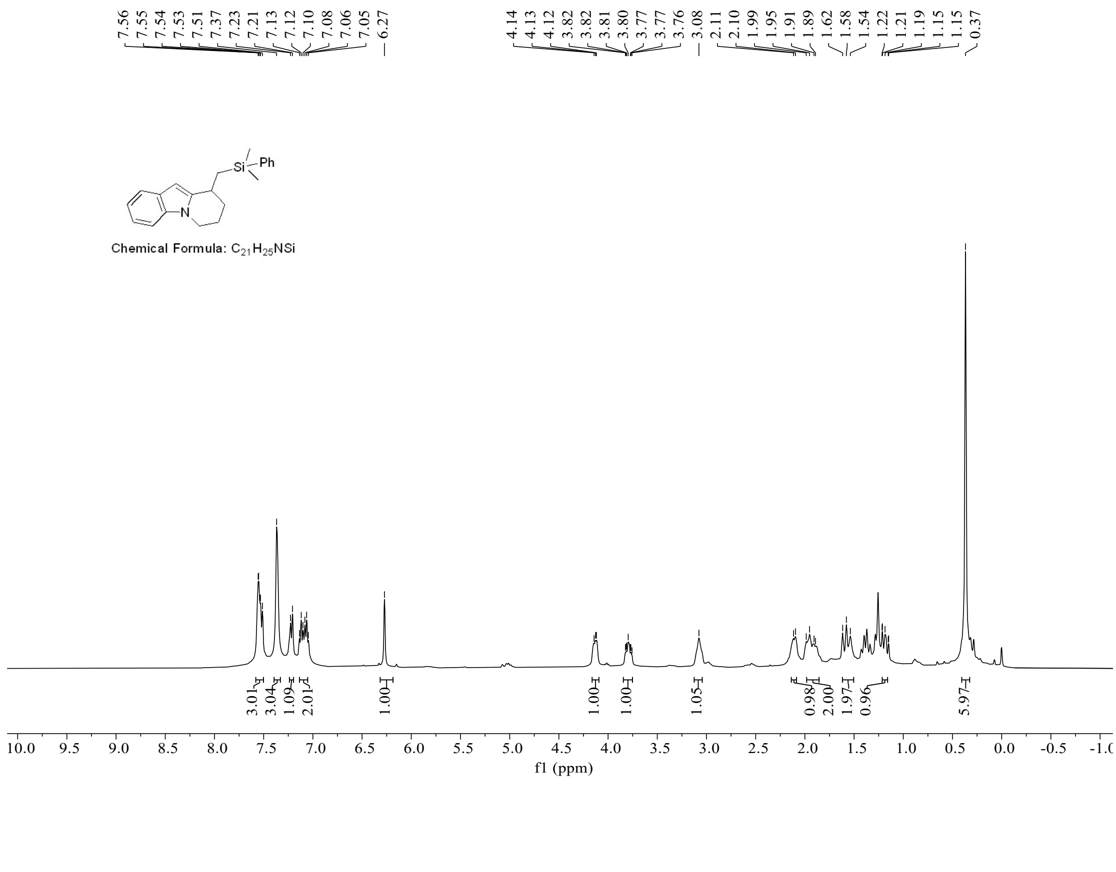


Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3av**



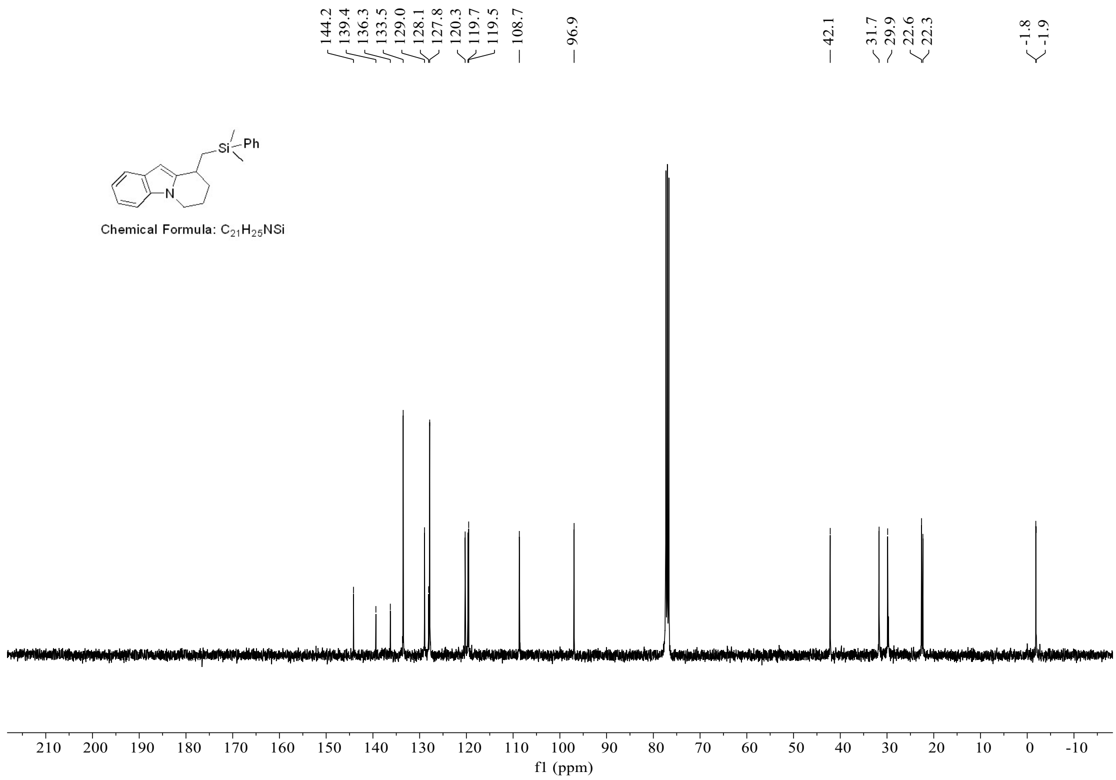
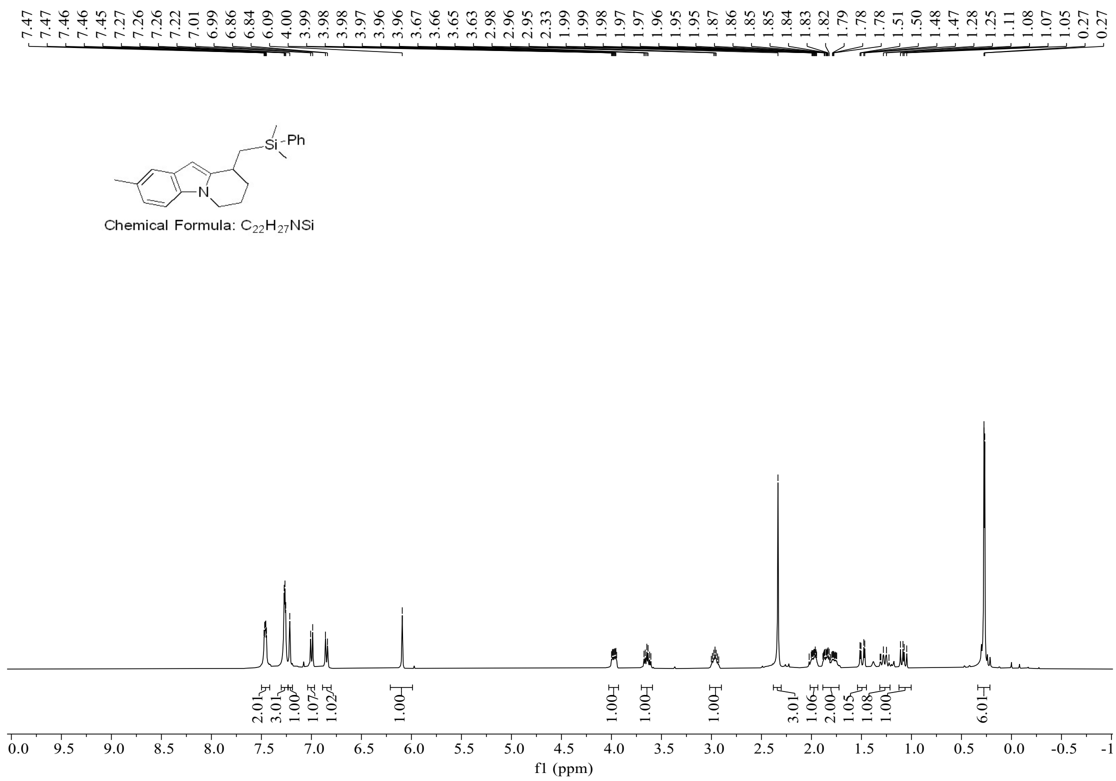


Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3aw**



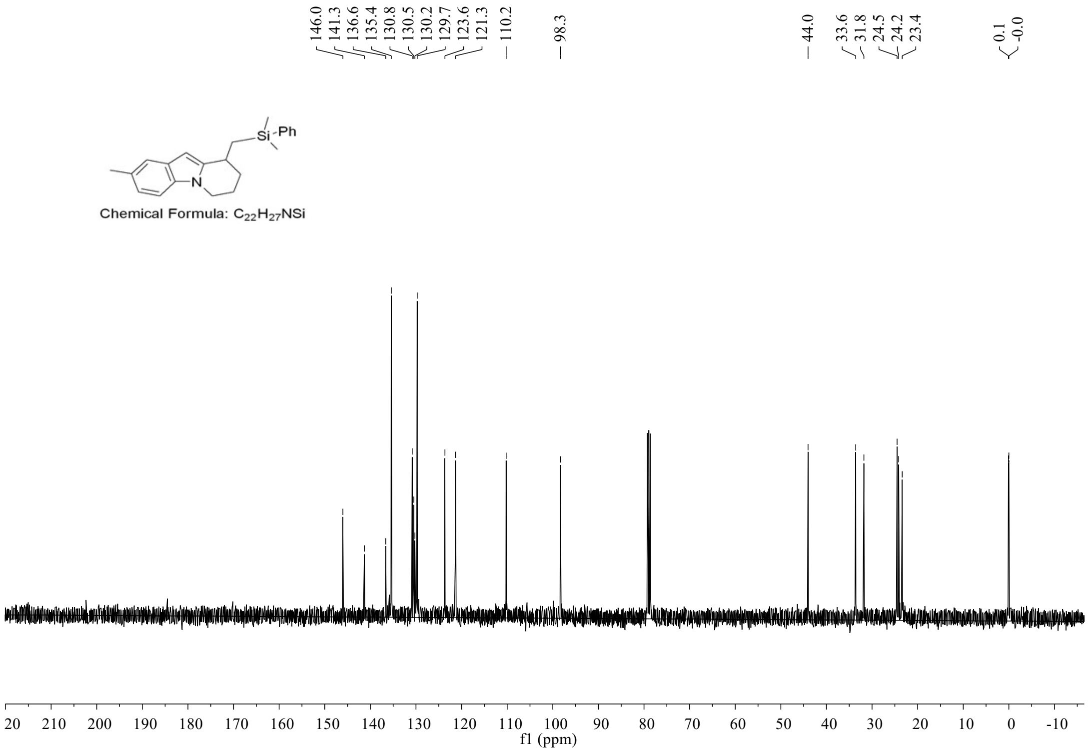
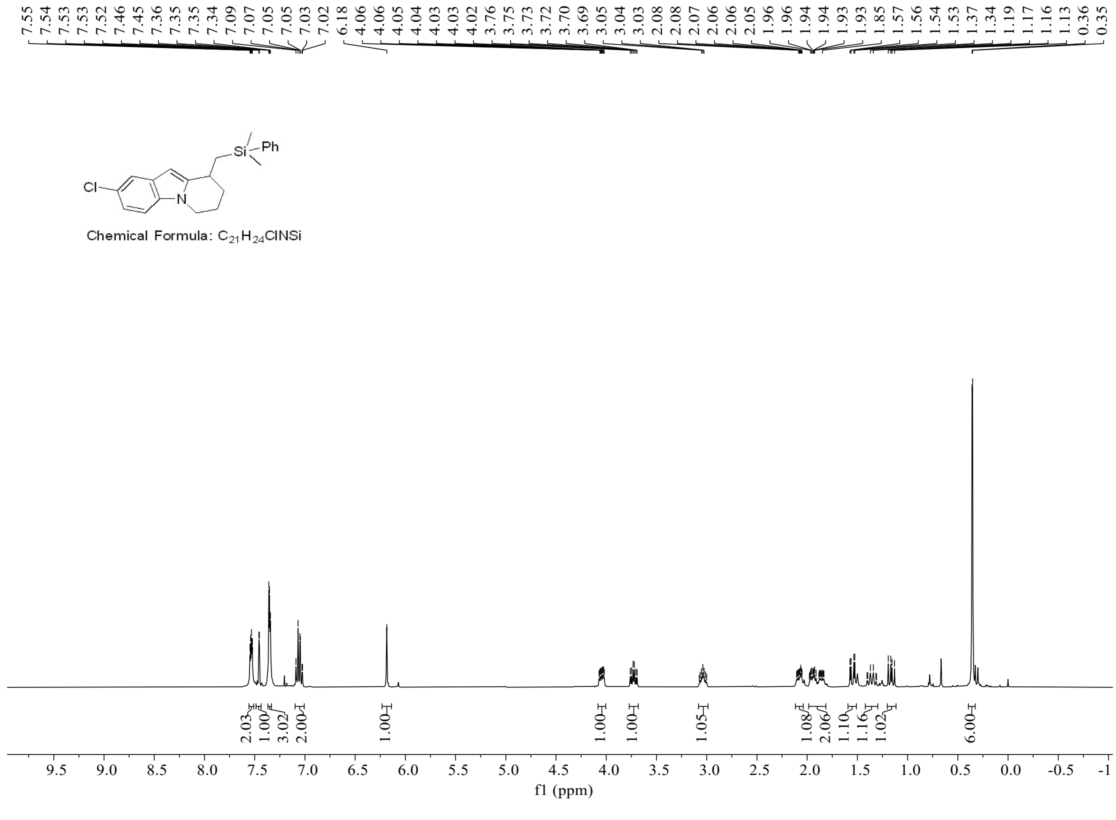


Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ax**



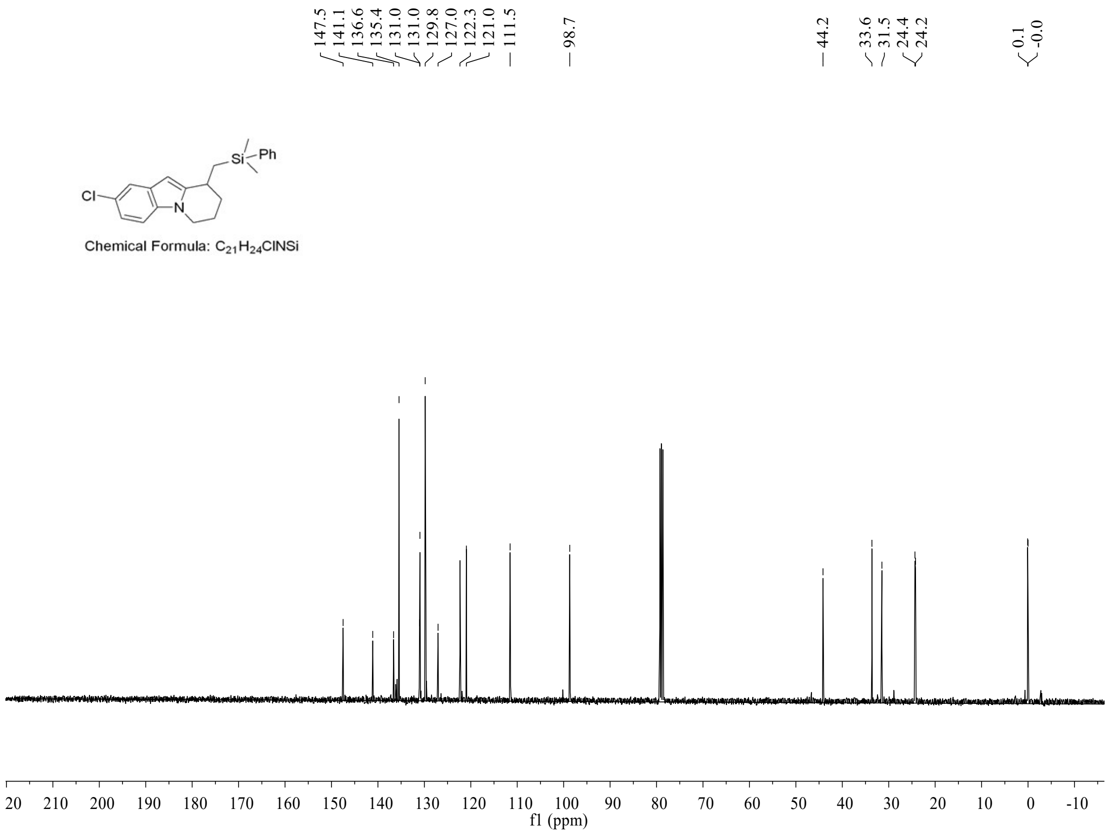
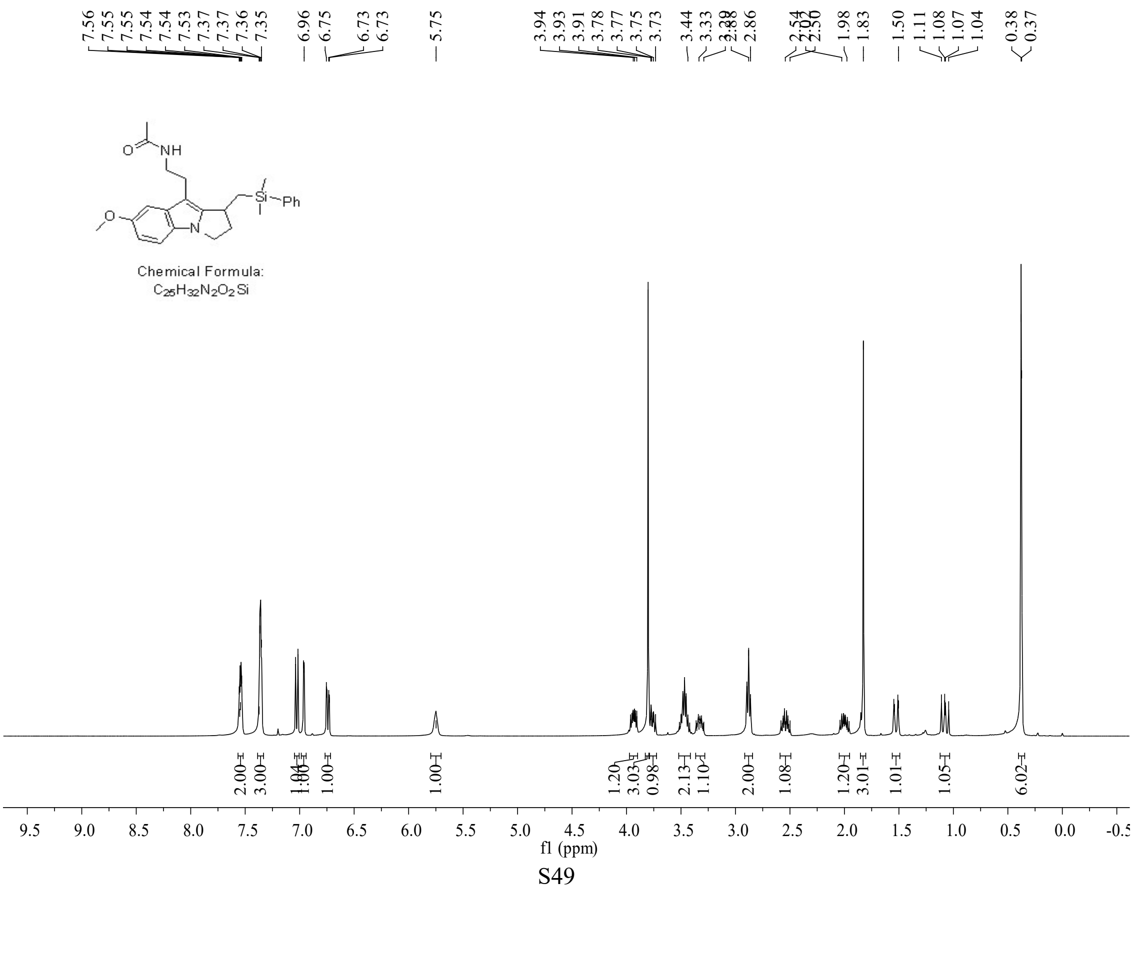


Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3ay**



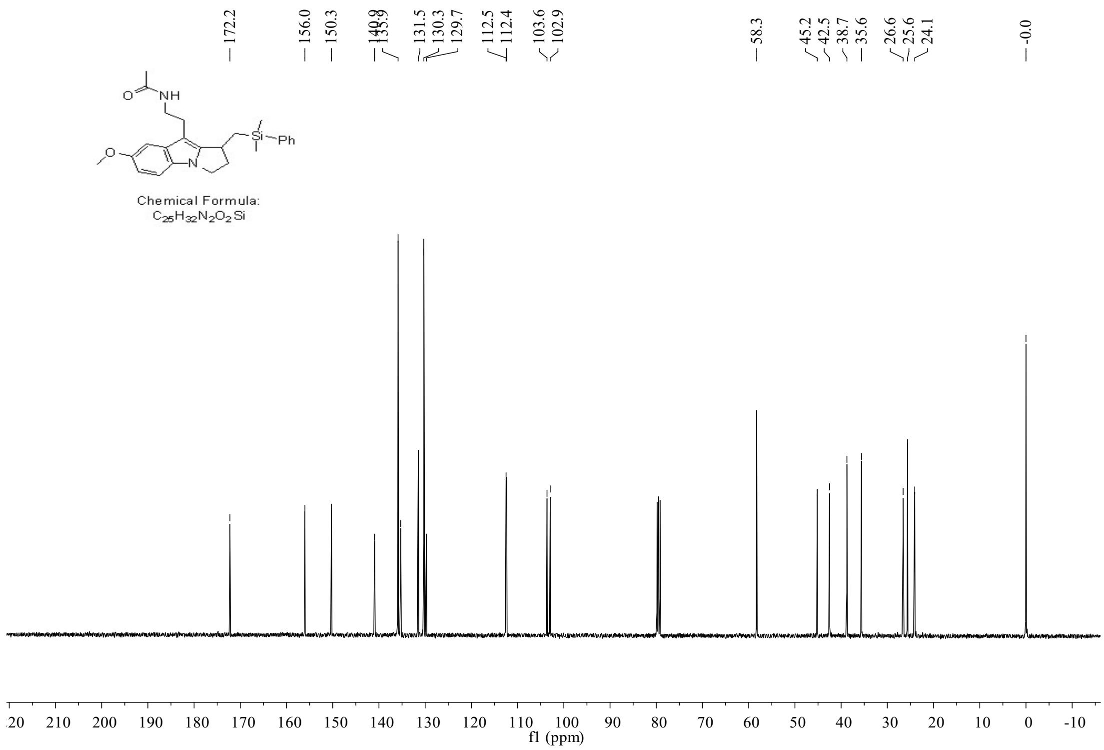
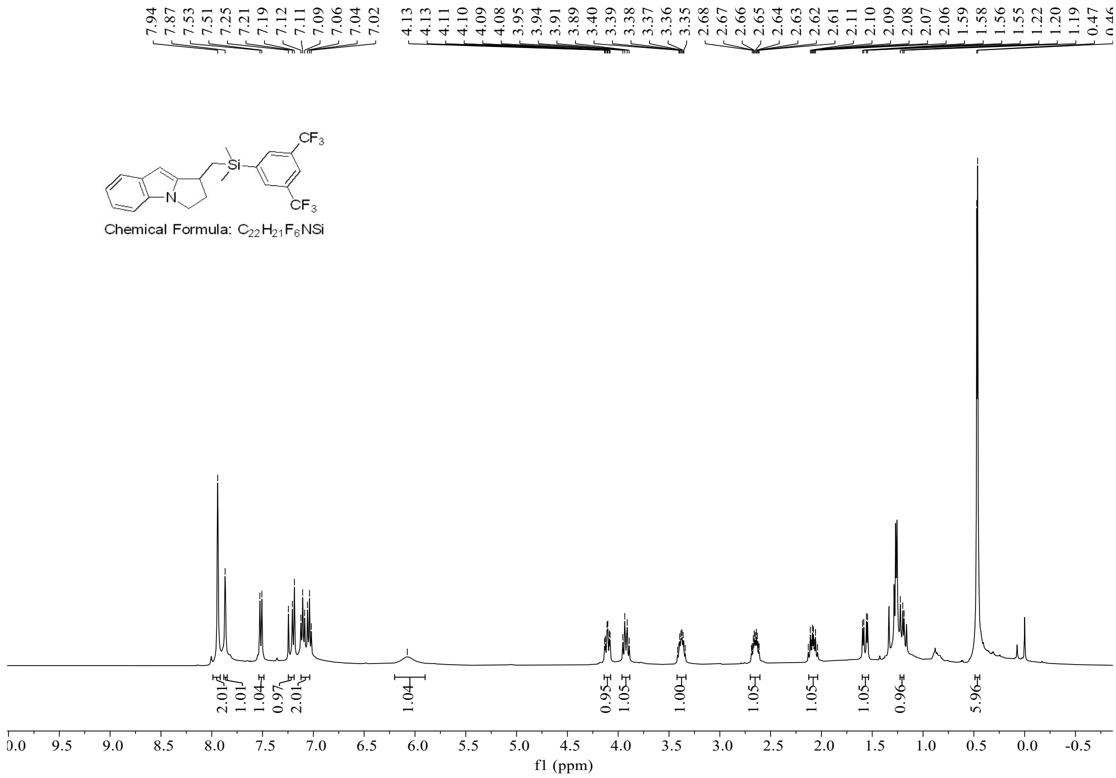
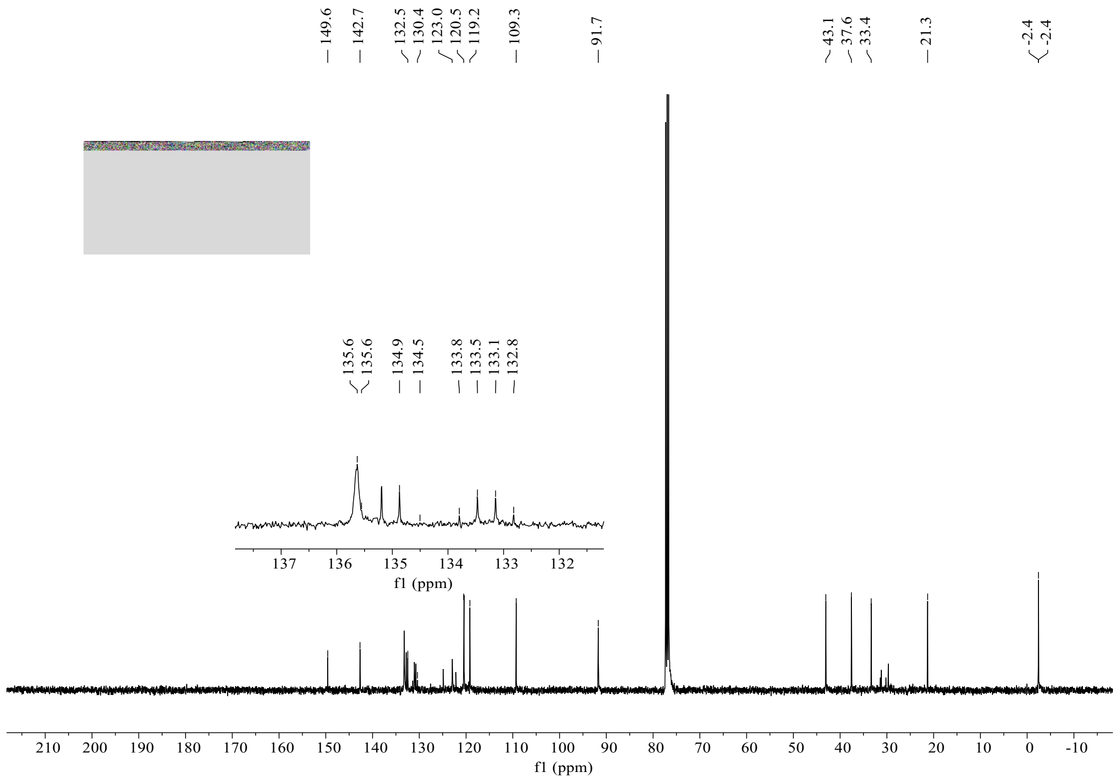


Fig. S26 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3az**





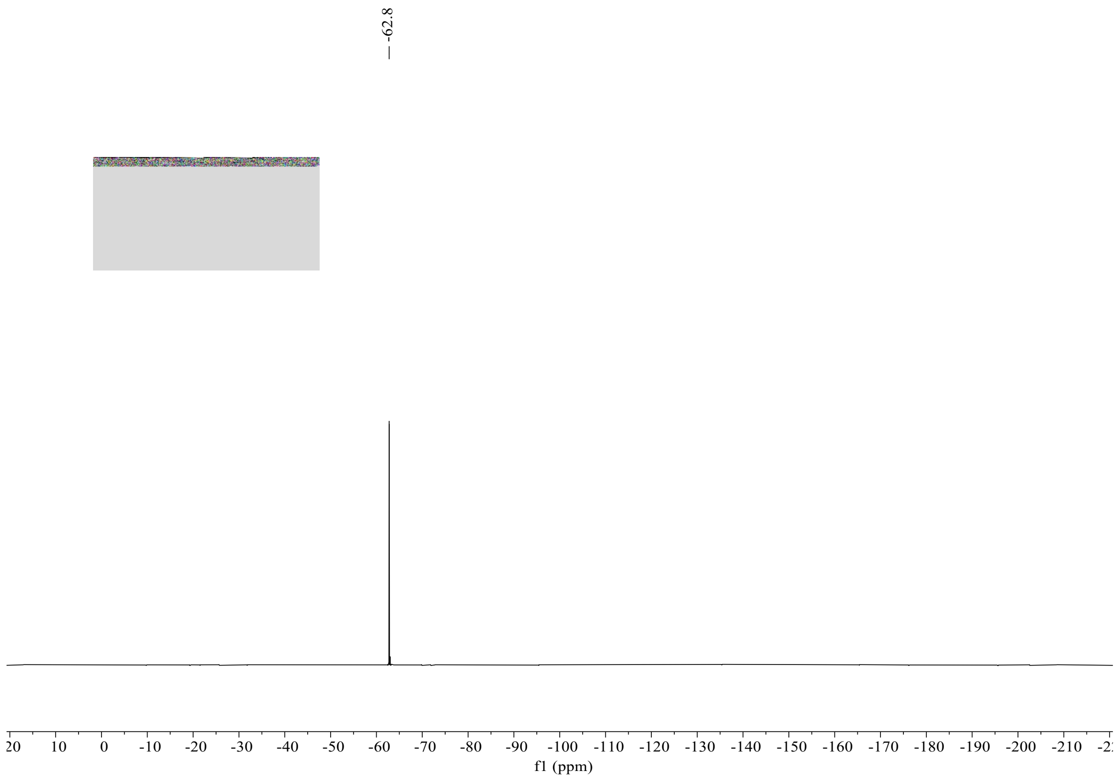


Fig. S27 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$), ^{19}F NMR (376 MHz, $CDCl_3$) of **3ba**

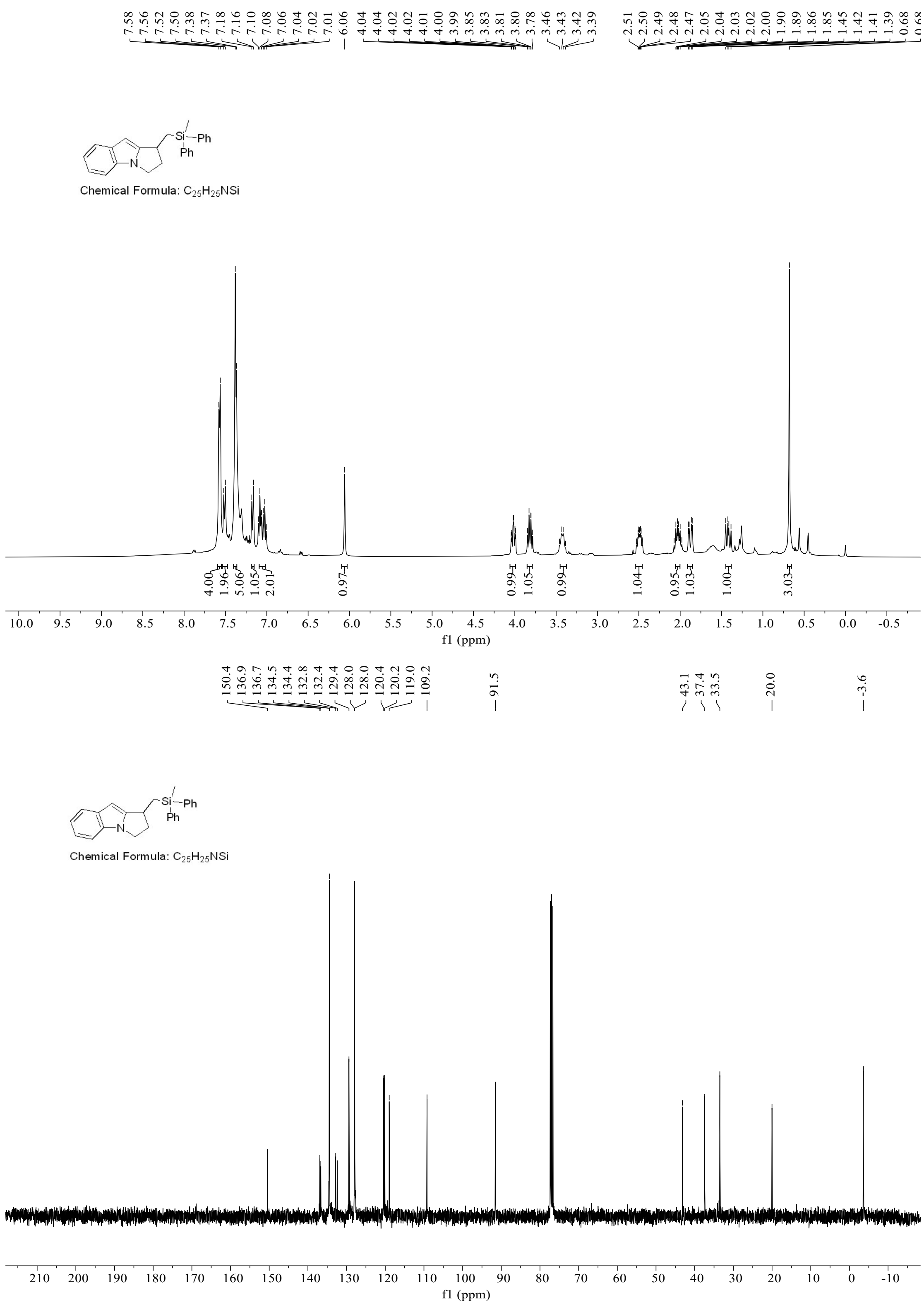
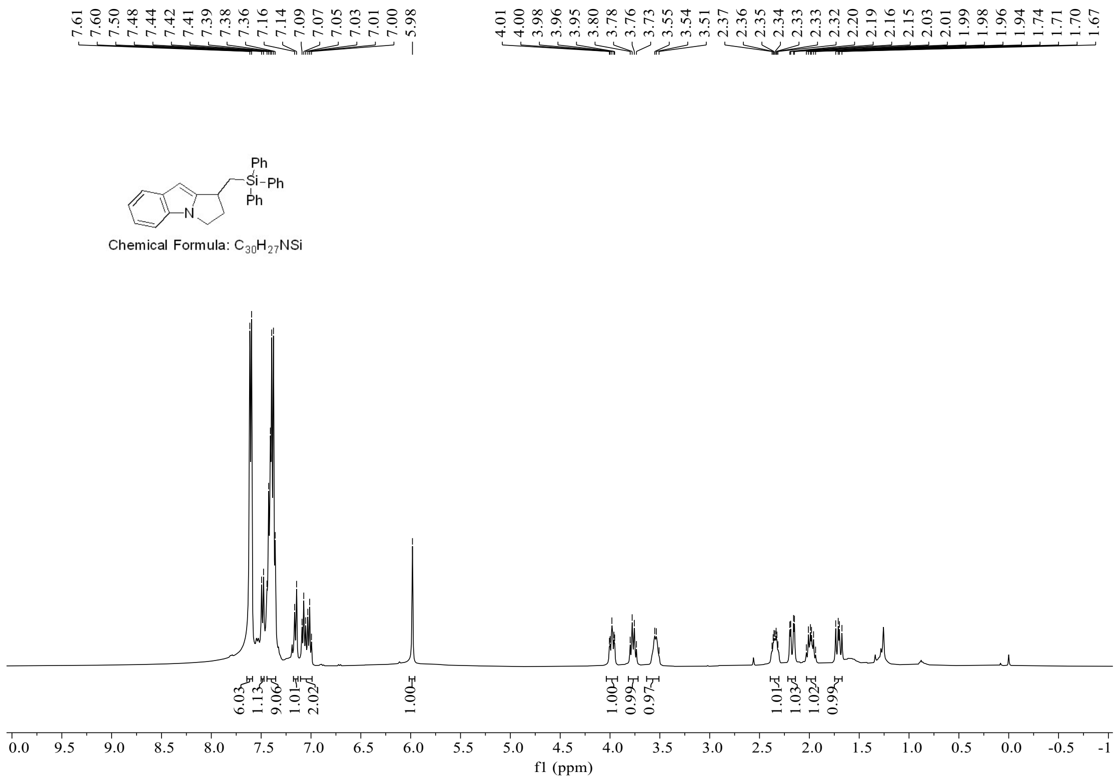


Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bb**



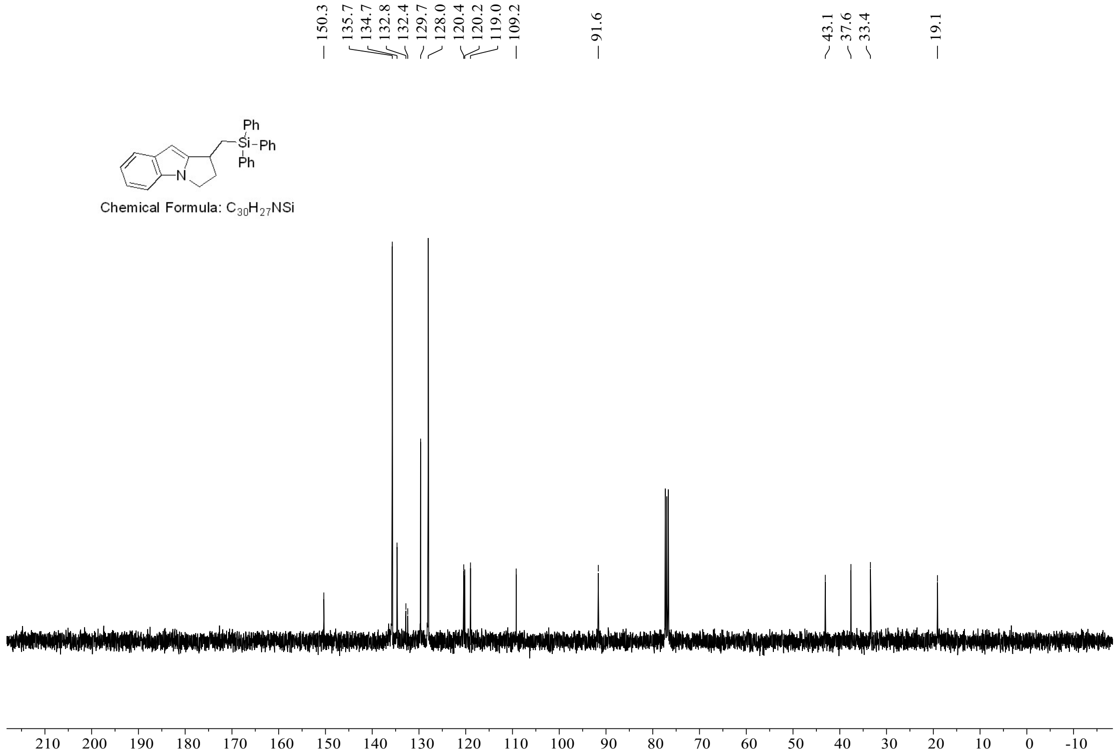
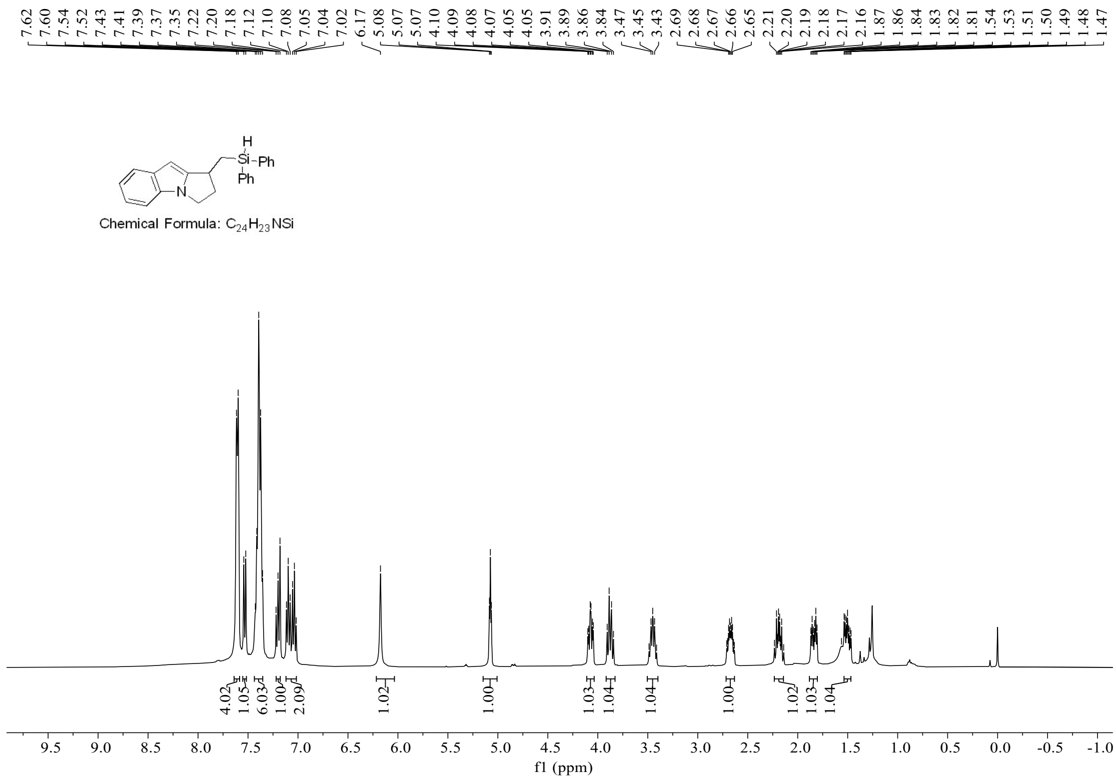


Fig. S29 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bc**



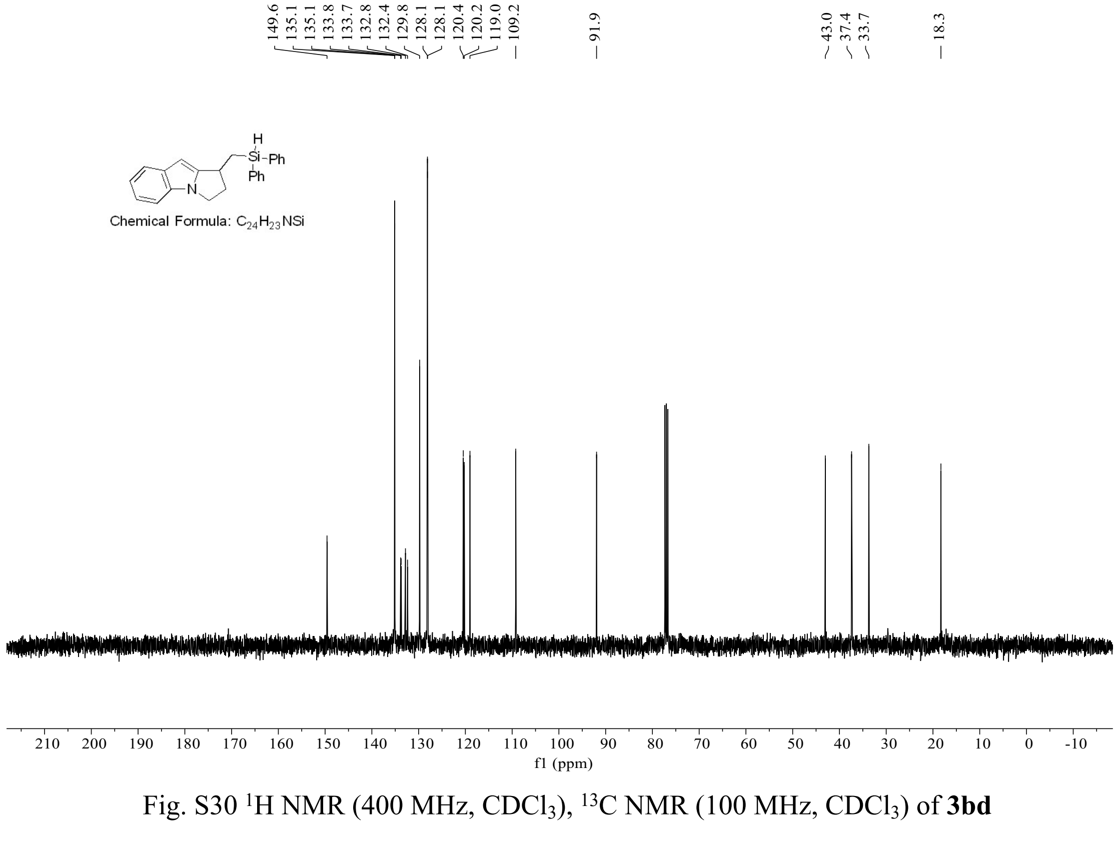
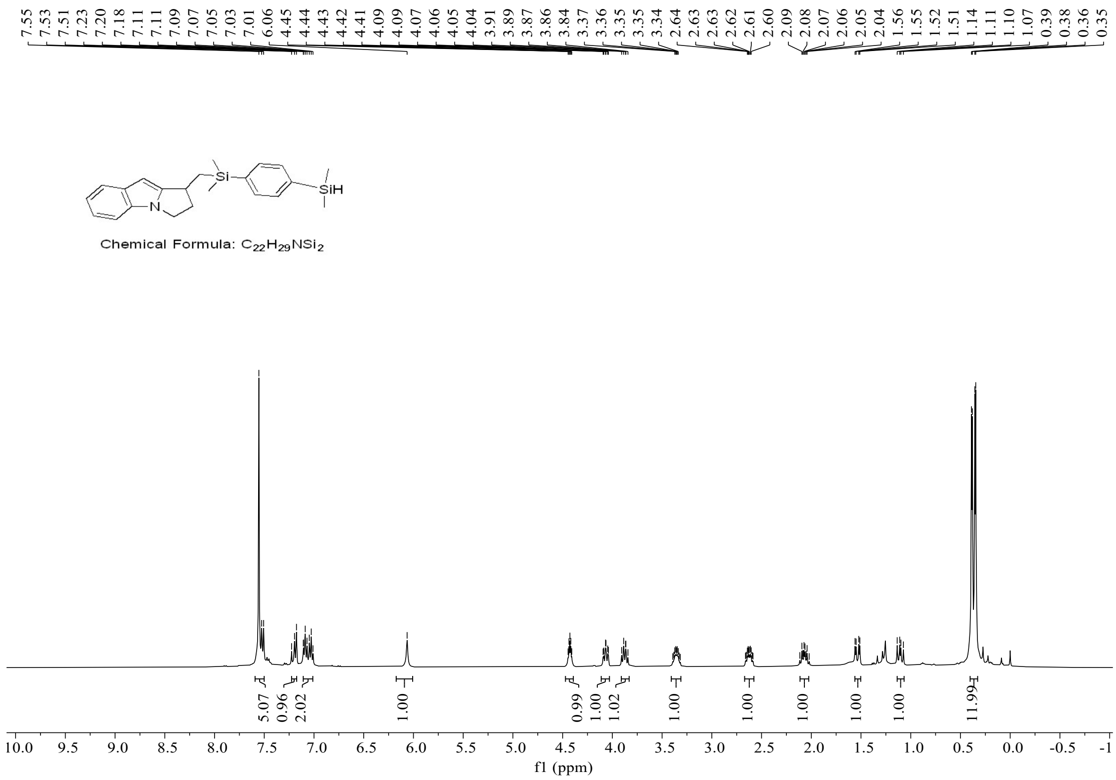


Fig. S30 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bd**



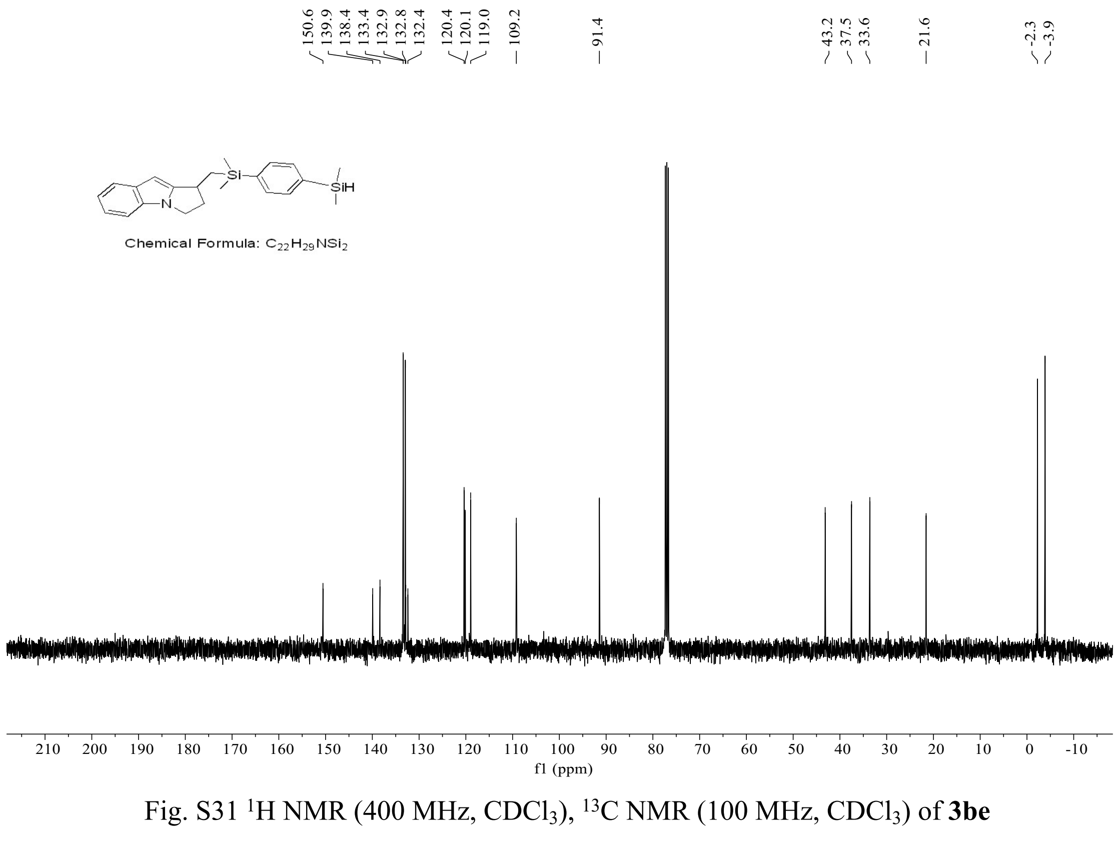


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3be**

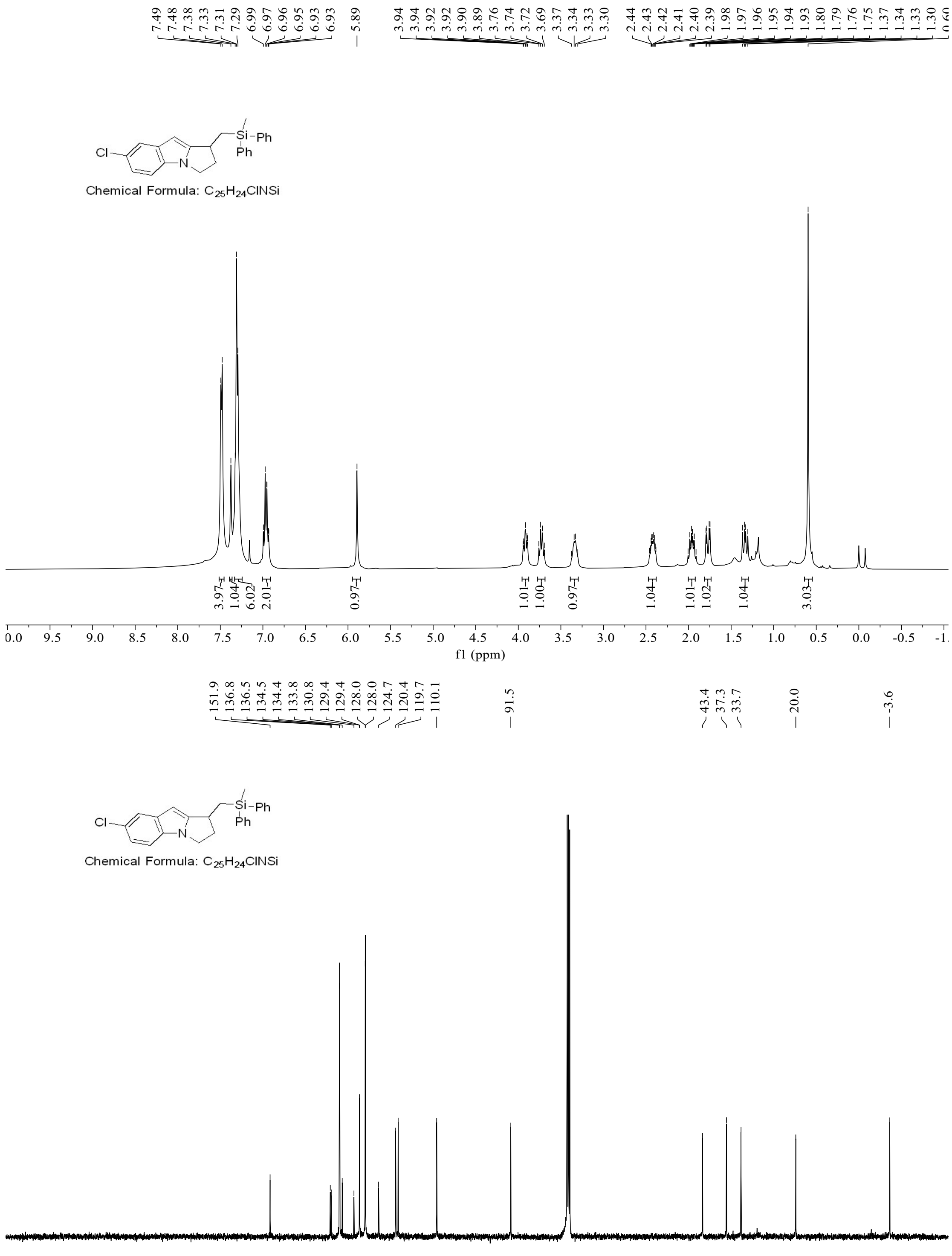
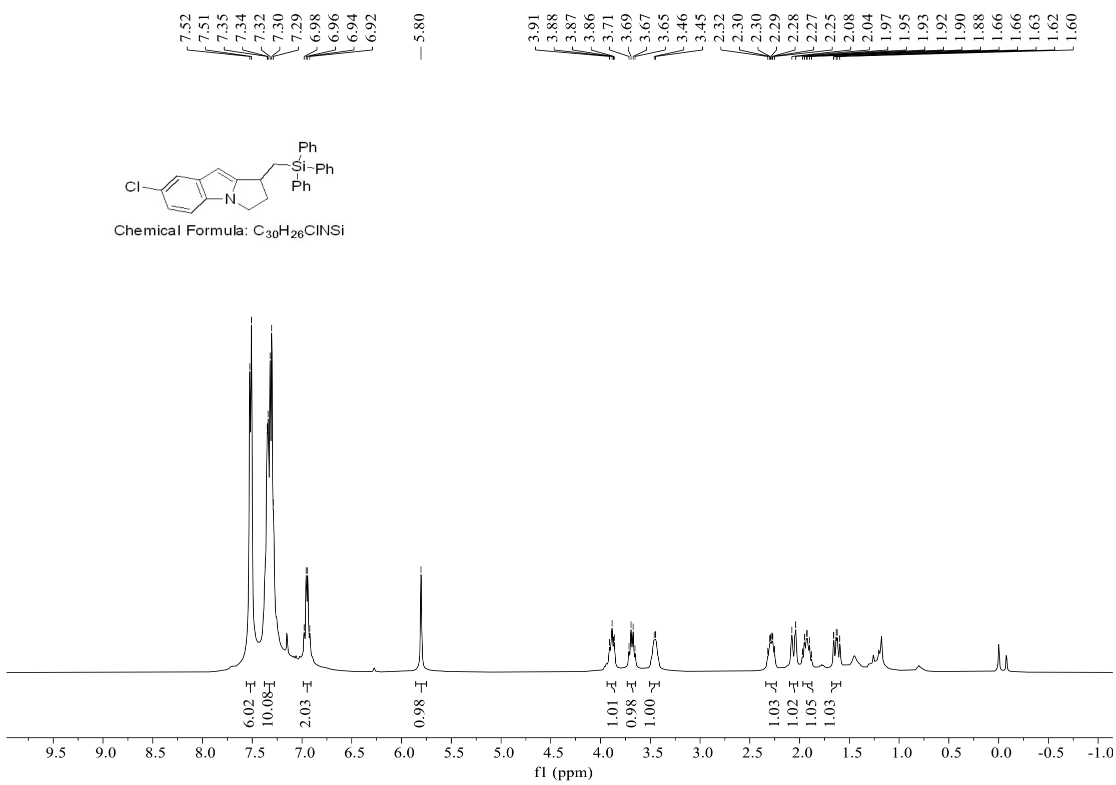


Fig. S32 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bf**



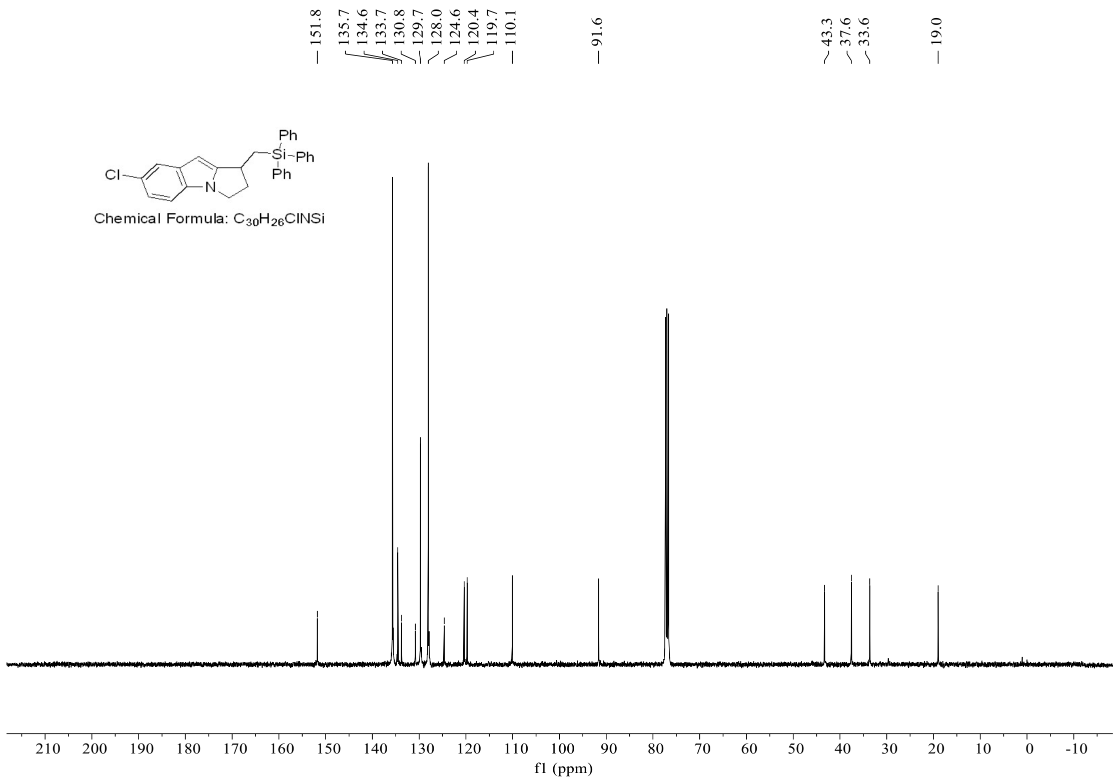
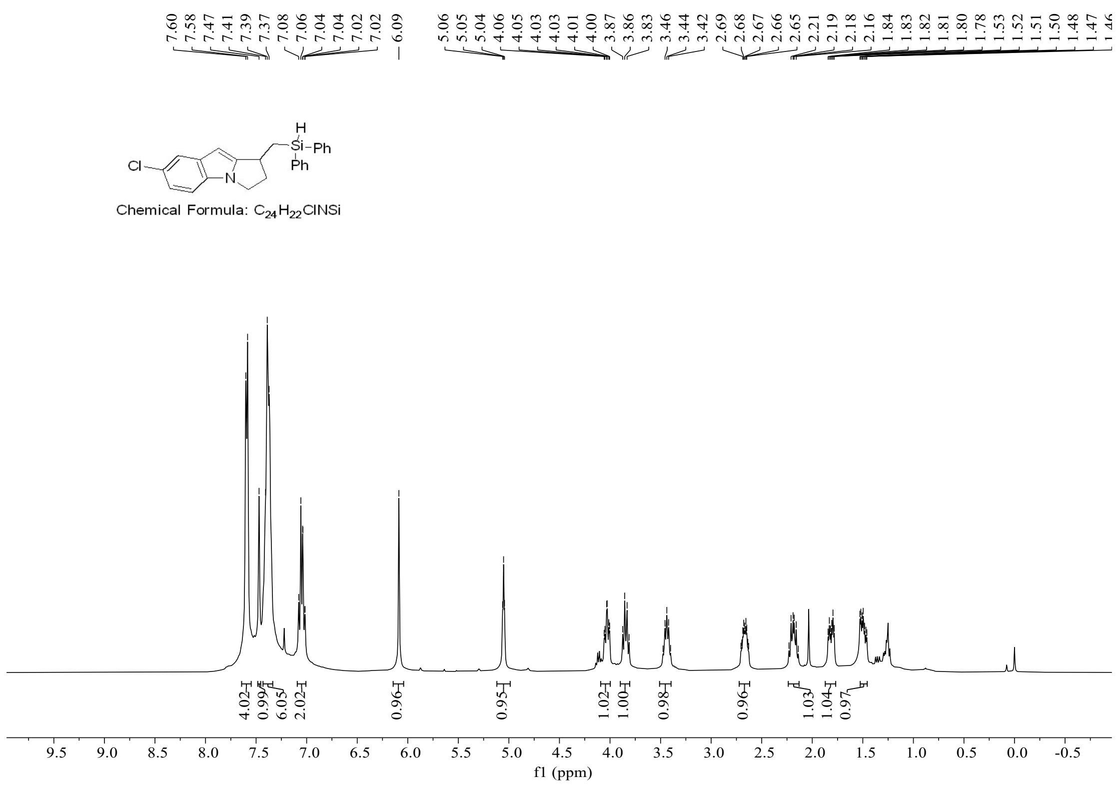


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bg**



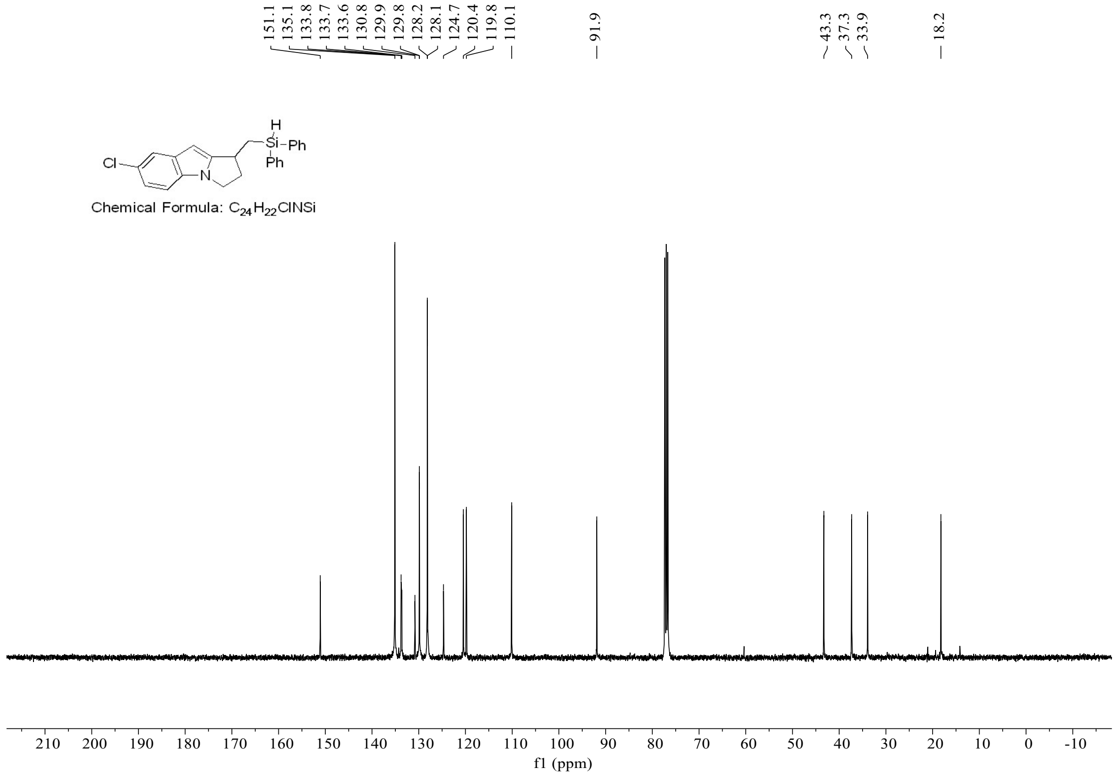


Fig. S34 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **3bh**

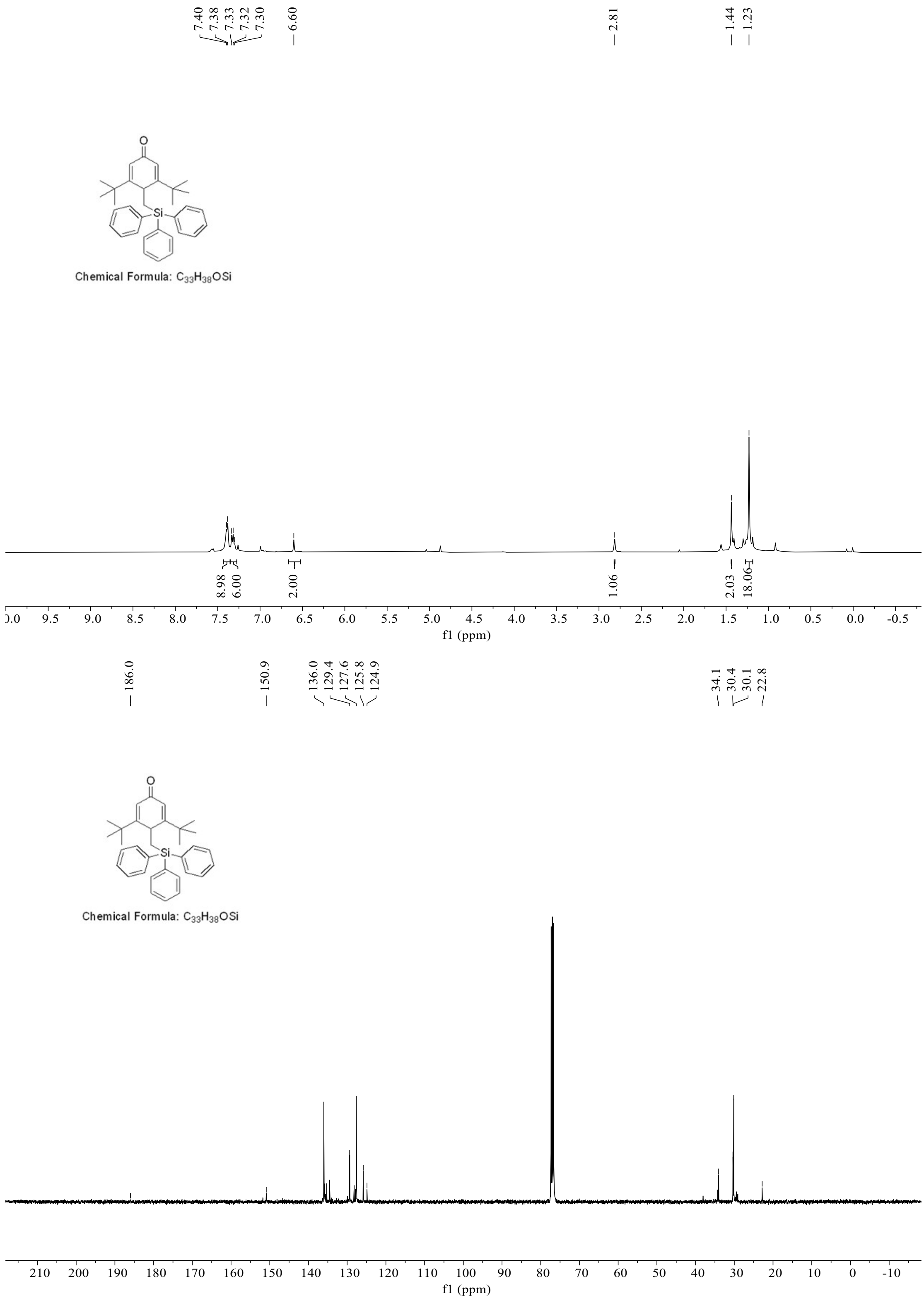


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **5**

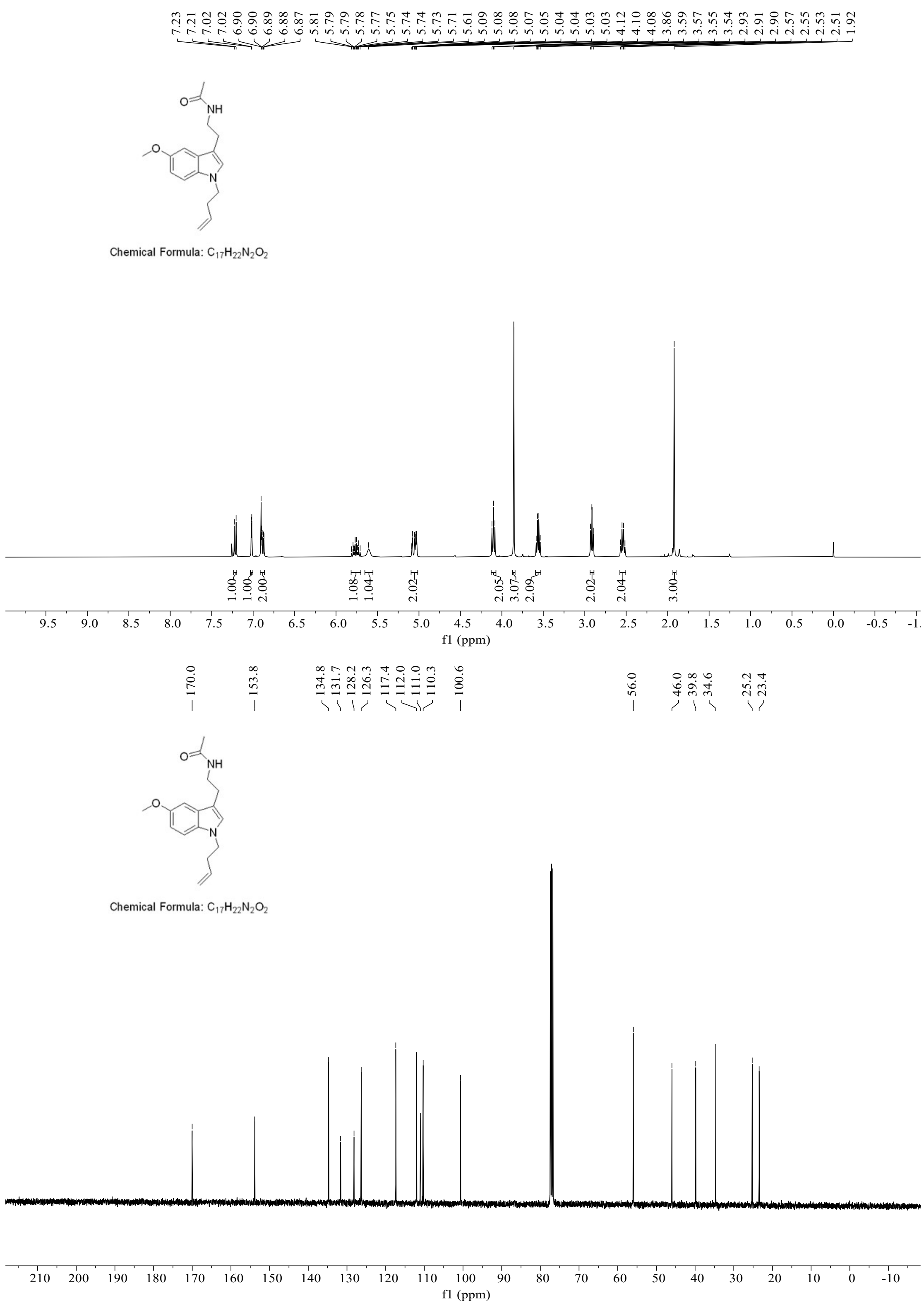


Fig. S36 ^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) of **1z**