Electronic Supplementary Information for Stereoselective Synthesis of Vinylsilanes via Copper-Catalyzed Silylation of Styrenes with Silanes

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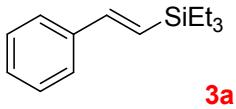
1. General Information

All chemical reagents are obtained from commercial suppliers and used without further purification. All known compounds are characterized by ^{1}H NMR, ^{13}C NMR , and compared with previously reported data. Analytical thin-layer chromatography are performed on glass plates precoated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates are visualized by exposure to ultraviolet light. Mass spectra are taken on a Thermo Scientific ISQ LT GC-MS instrument in the electron ionization (EI) mode. ^{1}H NMR and ^{13}C NMR spectra are recorded on an AVANCE 500 Bruker spectrometer operating at 500 MHz and 125 MHz in $CDCl_3$, respectively, and chemical shifts are reported in ppm.

2. General Procedure

General Procedure for the Synthesis of Vinylsilanes: A mixture of alkenyls or Heteroaromatics (0.5 mmol), silanes (2.5 mmol), $Cu(OAc)_2$ (0.1 mmol), TBP (1 mmol) in *t*BuOH (3.0 mL) under Ar was stirred at 110°C for 24 h. Upon completion, the reaction mixture was diluted with EtOAc (4.0 mL), filtered through a bed of silica gel layer. The volatiles were removed under vacuum to afford the crude product. The crude product was purified by column chromatography on silica gel and eluted with hexanes to afford the desired pure product.

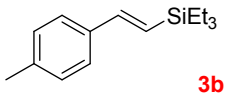
3. Characterization Data



3a

(*E*)-triethyl(styryl)silane
Chemical Formula: $C_{14}H_{22}Si$
Exact Mass: 218.15
Molecular Weight: 218.41
m/z: 218.15 (100.0%), 219.15 (20.2%), 220.15 (4.1%), 220.16 (1.1%)
Elemental Analysis: C, 76.99; H, 10.15; Si, 12.86

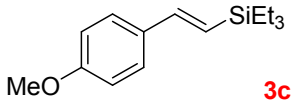
(E)-triethyl(styryl)silane **3a**[1], colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 5.4 Hz, 1H), 6.90 (d, *J* = 19.3 Hz, 1H), 6.43 (d, *J* = 19.3 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.94 (s), 138.66 (s), 128.62 (s), 128.00 (s), 126.44 (s), 126.09 (s), 7.52 (s), 3.66 (s). MS (EI) *m/z*: 218 [M^+].



3b

(*E*)-triethyl(4-methylstyryl)silane
Chemical Formula: $C_{15}H_{24}Si$
Exact Mass: 232.16
Molecular Weight: 232.44
m/z: 232.16 (100.0%), 233.17 (16.5%), 233.16 (5.1%), 234.16 (3.3%), 234.17 (2.1%)
Elemental Analysis: C, 77.51; H, 10.41; Si, 12.08

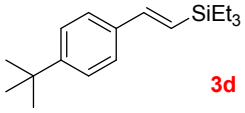
(E)-triethyl(4-methylstyryl)silane **3b** [2], light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.86 (d, *J* = 19.3 Hz, 1H), 6.35 (d, *J* = 19.3 Hz, 1H), 2.34 (s, 3H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.83 (s), 137.88 (s), 136.02 (s), 129.33 (s), 126.37 (s), 124.67 (s), 21.35 (s), 7.56 (s), 3.70 (s). MS (EI) *m/z*: 232 [M^+].



3c

(*E*)-triethyl(4-methoxystyryl)silane
Chemical Formula: $C_{15}H_{24}OSi$
Exact Mass: 248.16
Molecular Weight: 248.44
m/z: 248.16 (100.0%), 249.16 (21.3%), 250.16 (4.4%), 250.17 (1.3%)
Elemental Analysis: C, 72.52; H, 9.74; O, 6.44; Si, 11.30

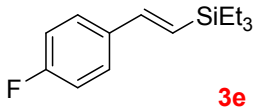
(E)-diethyl 2,4,6-trimethylstyrylphosphonate **3c**[3], light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 6.91 – 6.81 (m, 3H), 6.26 (d, *J* = 19.3 Hz, 1H), 3.83 (s, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) 159.51 (s), 144.36(s), 131.34(s), 127.58 (s), 122.92(s), 113.95 (s), 55.35 (s), 7.46 (s), 3.62 (s). MS (EI) *m/z*: 248 [M^+].



3d

(*E*)-(4-*tert*-butylstyryl)triethylsilane
Chemical Formula: $C_{18}H_{30}Si$
Exact Mass: 274.21
Molecular Weight: 274.52
m/z: 274.21 (100.0%), 275.22 (19.8%), 275.21 (5.1%), 276.21 (4.3%), 276.22 (1.9%)
Elemental Analysis: C, 78.75; H, 11.02; Si, 10.23

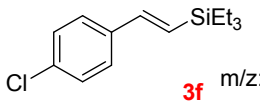
(E)-(4-tert-butylstyryl)triethylsilane **3d**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (q, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 19.3 Hz, 1H), 6.39 (d, *J* = 19.3 Hz, 1H), 1.33 (s, 9H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.18 (s), 144.71 (s), 135.98 (s), 126.15 (s), 125.55 (s), 124.98(s), 34.72 (s), 31.43 (s), 7.53 (s), 3.68 (s). MS (EI) *m/z*: 274 [M^+].



3e

(*E*)-triethyl(4-fluorostyryl)silane
Chemical Formula: $C_{14}H_{21}FSi$
Exact Mass: 236.14
Molecular Weight: 236.40
m/z: 236.14 (100.0%), 237.14 (20.2%), 238.14 (4.1%), 238.15 (1.1%)
Elemental Analysis: C, 71.13; H, 8.95; F, 8.04; Si, 11.88

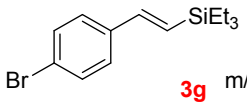
(E)-triethyl(4-fluorostyryl)silane **3e**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.02 (t, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 19.3 Hz, 1H), 6.34 (d, *J* = 19.3 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.66 (s), 161.70 (s), 143.62 (s), 134.91 (s), 127.98 (s), 125.81 (s), 115.38 (s), 7.51 (s), 3.63 (s). MS (EI) *m/z*: 236 [M^+].



3f

(*E*)-(4-chlorostyryl)triethylsilane
Chemical Formula: $C_{14}H_{21}ClSi$
Exact Mass: 252.11
Molecular Weight: 252.86
m/z: 252.11 (100.0%), 254.11 (36.1%), 253.11 (20.2%), 255.11 (7.1%), 254.12 (1.1%), 256.10 (1.1%)
Elemental Analysis: C, 66.50; H, 8.37; Cl, 14.02; Si, 11.11

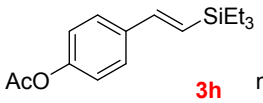
(E)-(4-chlorostyryl)triethylsilane **3f**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 19.3 Hz, 1H), 6.41 (d, *J* = 19.3 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.67 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.54 (s), 137.12 (s), 133.61 (s), 128.76 (s), 127.64 (s), 127.10 (s), 7.52 (s), 3.59 (s). MS (EI) *m/z*: 252 [M^+].



3g

(*E*)-(4-bromostyryl)triethylsilane
Chemical Formula: $C_{14}H_{21}BrSi$
Exact Mass: 296.06
Molecular Weight: 297.31
m/z: 298.06 (100.0%), 296.06 (98.6%), 299.06 (20.1%), 297.06 (19.9%), 300.05 (3.2%), 300.06 (1.8%), 298.07 (1.1%)
Elemental Analysis: C, 56.56; H, 7.12; Br, 26.88; Si, 9.45

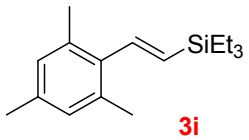
(E)-(4-bromostyryl)triethylsilane **3g**[3], light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 19.3 Hz, 1H), 6.41 (d, *J* = 19.3 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.09 (s), 131.70 (s), 130.73 (s), 127.97 (s), 127.33 (s), 7.50 (s), 3.58 (s). MS (EI) *m/z*: 296 [M^+].



3h

(*E*)-4-(2-(triethylsilyl)vinyl)phenyl acetate
Chemical Formula: $C_{16}H_{24}O_2Si$
Exact Mass: 276.15
Molecular Weight: 276.45
m/z: 276.15 (100.0%), 277.16 (17.7%), 277.15 (5.1%), 278.15 (3.3%), 278.16 (2.8%)
Elemental Analysis: C, 69.51; H, 8.75; O, 11.58; Si, 10.16

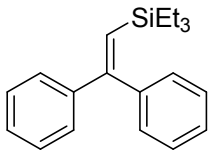
(E)-4-(2-(triethylsilyl)vinyl)phenyl acetate **3h,** light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 19.3 Hz, 1H), 6.37 (d, *J* = 19.3 Hz, 1H), 2.29 (s, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.59 (s), 150.40 (s), 143.84 (s), 136.50 (s), 127.39 (s), 126.45 (s), 121.72 (s), 121.13 (s), 21.27 (s), 7.52 (s), 3.62 (s). MS (EI) *m/z*: 276 [M^+].



3i

(*E*)-triethyl(2,4,6-trimethylstyryl)silane
Chemical Formula: $C_{17}H_{28}Si$
Exact Mass: 260.20
Molecular Weight: 260.49
m/z: 260.20 (100.0%), 261.20 (23.8%), 262.19 (3.3%), 262.20 (2.5%)
Elemental Analysis: C, 78.38; H, 10.83; Si, 10.78

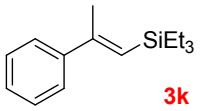
(E)-triethyl(2,4,6-trimethylstyryl)silane **3i**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 – 6.87 (m, 3H), 5.84 (d, *J* = 19.8 Hz, 1H), 2.30 (s, 3H), 2.28 (s, 6H), 1.02 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.97 (s), 135.29 (s), 132.08 (s), 128.65 (s), 119.16 (s), 21.05(s), 20.84 (s), 7.57 (s), 3.68 (s). MS (EI) *m/z*: 260 [M^+].



3j

(2,2-diphenylvinyl)triethylsilane
Chemical Formula: $C_{20}H_{26}Si$
Exact Mass: 294.18
Molecular Weight: 294.51
m/z: 294.18 (100.0%), 295.18 (26.7%), 296.18 (4.4%), 296.19 (2.3%)
Elemental Analysis: C, 81.57; H, 8.90; Si, 9.54

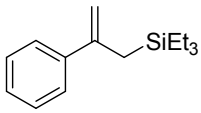
(2,2-diphenylvinyl)triethylsilane **3j**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 3H), 7.31 – 7.26 (m, 4H), 7.23 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.27 (s, 1H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.39 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.19 (s), 143.78 (s), 143.01 (s), 129.68 (s), 128.14 (s), 127.91 (s), 127.69 (s), 127.53 (s), 127.41(s), 126.87 (s), 7.70 (s), 4.60 (s). MS (EI) *m/z*: 294 [M^+].



3k

(*E*)-triethyl(2-phenylprop-1-enyl)silane
Chemical Formula: $C_{15}H_{24}Si$
Exact Mass: 232.16
Molecular Weight: 232.44
m/z: 232.16 (100.0%), 233.17 (16.5%), 233.16 (5.1%), 234.16 (3.3%), 234.17 (2.1%)
Elemental Analysis: C, 77.51; H, 10.41; Si, 12.08

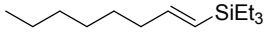
(E)-triethyl(2-phenylprop-1-enyl)silane **3k,** light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 5.86 (s, 1H), 2.22 (s, 3H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.71 (q, *J* = 7.9 Hz, 6H). MS (EI) *m/z*: 232 [M^+].



3k'

triethyl(2-phenylallyl)silane
Chemical Formula: $C_{15}H_{24}Si$
Exact Mass: 232.16
Molecular Weight: 232.44
m/z: 232.16 (100.0%), 233.17 (16.5%), 233.16 (5.1%), 234.16 (3.3%), 234.17 (2.1%)
Elemental Analysis: C, 77.51; H, 10.41; Si, 12.08

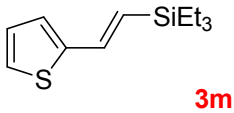
triethyl(2-phenylallyl)silane **3k'**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 7.4 Hz, 1H), 5.10 (d, *J* = 1.6 Hz, 1H), 4.90 (d, *J* = 0.6 Hz, 1H), 2.04 (s, 2H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.42 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.21 (s), 127.38 (s), 126.46 (s), 125.66 (s), 124.15 (s), 110.44 (s), 7.77 (s), 4.83 (s), 3.47 (s). MS (EI) *m/z*: 232 [M^+].



3l

(*E*)-triethyl(oct-1-enyl)silane
Chemical Formula: $C_{14}H_{30}Si$
Exact Mass: 226.21
Molecular Weight: 226.47
m/z: 226.21 (100.0%), 227.22 (15.5%), 227.21 (5.1%), 228.21 (4.1%), 228.22 (1.1%)
Elemental Analysis: C, 74.25; H, 13.35; Si, 12.40

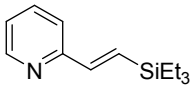
(E)-triethyl(oct-1-enyl)silane **3l**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.04 (dt, *J* = 18.7, 6.3 Hz, 1H), 5.54 (d, *J* = 18.7 Hz, 1H), 2.12 (dd, *J* = 13.9, 6.9 Hz, 2H), 1.29 (dd, *J* = 9.6, 5.2 Hz, 8H), 0.93 (t, *J* = 7.9 Hz, 12H), 0.55 (dd, *J* = 15.8, 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.97 (s), 125.62 (s), 37.19 (s), 31.85 (s), 28.91 (s), 22.75 (s), 14.19 (s), 7.49 (s), 3.68 (s). MS (EI) *m/z*: 226 [M^+].



3m

(*E*)-triethyl(2-(thiophen-2-yl)vinyl)silane
Chemical Formula: $C_{12}H_{20}SSi$
Exact Mass: 224.11
Molecular Weight: 224.44
m/z: 224.11 (100.0%), 225.11 (18.3%), 226.10 (7.9%), 226.11 (1.5%)
Elemental Analysis: C, 64.22; H, 8.98; S, 14.29; Si, 12.51

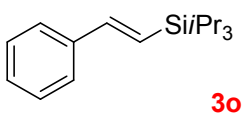
(E)-triethyl(2-(thiophen-2-yl)vinyl)silane **3m**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.12 (m, 1H), 6.98 (dd, *J* = 11.3, 7.7 Hz, 3H), 6.17 (d, *J* = 19.0 Hz, 1H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.54 (s), 137.33 (s), 127.45 (s), 125.85 (s), 125.42 (s), 124.64 (s), 7.42 (s), 3.50 (s). MS (EI) *m/z*: 224 [M^+].



3n

(*E*)-2-(2-(triethylsilyl)vinyl)pyridine
Chemical Formula: $C_{13}H_{21}NSi$
Exact Mass: 219.14
Molecular Weight: 219.40
m/z: 219.14 (100.0%), 220.15 (14.3%), 220.14 (5.4%), 221.14 (3.4%), 221.15 (1.7%)
Elemental Analysis: C, 71.17; H, 9.65; N, 6.38; Si, 12.80

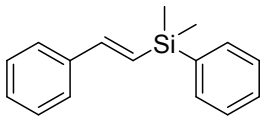
(E)-2-(2-(triethylsilyl)vinyl)pyridine **3n**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 4.3 Hz, 1H), 7.66 (t, *J* = 8.6 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.19 – 7.12 (m, 1H), 6.98 (q, *J* = 19.2 Hz, 2H), 1.00 (t, *J* = 7.9 Hz, 9H), 0.69 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.12 (s), 149.59 (s), 144.65 (s), 136.67 (s), 131.68 (s), 122.54 (s), 121.41 (s), 7.50 (s), 3.52 (s). MS (EI) *m/z*: 219 [M^+].



3o

(*E*)-triisopropyl(styryl)silane
Chemical Formula: $C_{17}H_{28}Si$
Exact Mass: 260.20
Molecular Weight: 260.49
m/z: 260.20 (100.0%), 261.20 (23.8%), 262.19 (3.3%), 262.20 (2.5%)
Elemental Analysis: C, 78.38; H, 10.83; Si, 10.78

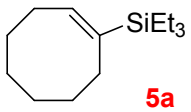
(E)-triisopropyl(styryl)silane **3o**, light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 1H), 6.96 (d, *J* = 19.4 Hz, 1H), 6.42 (d, *J* = 19.4 Hz, 1H), 1.27 – 1.17 (m, 3H), 1.12 (d, *J* = 7.0 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.72 (s), 138.85 (s), 128.64 (s), 127.98 (s), 126.41 (s), 124.12 (s), 18.82 (s), 11.16 (s). MS (EI) *m/z*: 260 [M^+].



3p

(*E*)-dimethyl(phenyl)(styryl)silane
Chemical Formula: $C_{16}H_{18}Si$
Exact Mass: 238.12
Molecular Weight: 238.40
m/z: 238.12 (100.0%), 239.12 (22.6%), 240.11 (3.3%), 240.12 (2.3%)
Elemental Analysis: C, 80.61; H, 7.61; Si, 11.78

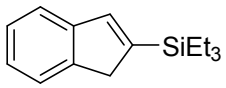
(E)-dimethyl(phenyl)(styryl)silane **3p**[4]**,** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 6.4, 3.0 Hz, 1H), 7.55 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.36 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 19.1 Hz, 1H), 6.59 (d, *J* = 19.1 Hz, 1H), 0.44 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.44 (s), 134.06 (s), 133.13 (s), 129.37 (s), 129.17 (s), 128.65 (s), 128.28 (s), 127.95 (s), 127.83 (s), 127.27 (s), 126.63(s), -2.39 (s). MS (EI) *m/z*: 238 [M^+].



5a

(*E*)-cyclooctenyltriethylsilane
Chemical Formula: $C_{14}H_{28}Si$
Exact Mass: 224.20
Molecular Weight: 224.46
m/z: 224.20 (100.0%), 225.20 (20.5%), 226.19 (3.3%), 226.20 (1.8%)
Elemental Analysis: C, 74.91; H, 12.57; Si, 12.51

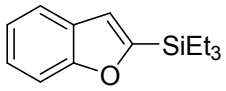
(E)-cyclooctenyltriethylsilane **5a,** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.65 (ddd, *J* = 26.1, 18.5, 9.8 Hz, 1H), 1.35 – 1.22 (m, 4H), 0.98 – 0.90 (m, 14H), 0.61 – 0.50 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 30.06 (s), 26.51 (s), 7.94 (s), 7.61 (s), 3.69 (s), 3.34 (s), 3.23 (d, *J* = 28.8 Hz), 2.94 (dd, *J* = 71.4, 44.3 Hz). MS (EI) *m/z*: 224 [M^+].



5b

triethyl(1*H*-inden-2-yl)silane
Chemical Formula: $C_{15}H_{22}Si$
Exact Mass: 230.15
Molecular Weight: 230.42
m/z: 230.15 (100.0%), 231.15 (21.3%), 232.15 (4.2%), 232.16 (1.3%)
Elemental Analysis: C, 78.19; H, 9.62; Si, 12.19

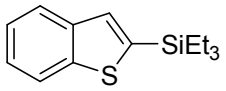
triethyl(1H-inden-2-yl)silane **5b,** light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.15 (s, 1H), 3.47 (s, 2H), 1.01 (t, *J* = 7.9 Hz, 9H), 0.76 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.90 (s), 146.59(s), 145.78 (s), 141.78 (s), 126.34 (s), 124.72 (s), 123.66 (s), 120.80 (s), 43.31 (s), 7.63 (s), 3.78 (s). MS (EI) *m/z*: 230 [M^+].



5c

benzofuran-2-yltriethylsilane
Chemical Formula: $C_{14}H_{20}OSi$
Exact Mass: 232.13
Molecular Weight: 232.39
m/z: 232.13 (100.0%), 233.13 (20.5%), 234.13 (4.3%), 234.14 (1.1%)
Elemental Analysis: C, 72.36; H, 8.67; O, 6.88; Si, 12.09

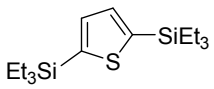
benzofuran-2-yltriethylsilane **5c,** light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.23 (dd, *J* = 6.1, 0.8 Hz, 1H), 7.00 (s, 1H), 1.01 (d, *J* = 7.4 Hz, 9H), 0.86-0.91 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.90 (s), 150.51 (s), 124.09 (s), 122.56 (s), 122.33 (s), 120.98 (s), 117.31 (s), 111.40 (s), 7.59 (s), 3.91 (s). MS (EI) *m/z*: 232 [M^+].



5d

benzo[*b*]thiophen-2-yltriethylsilane
Chemical Formula: $C_{14}H_{20}SSi$
Exact Mass: 248.11
Molecular Weight: 248.46
m/z: 248.11 (100.0%), 249.11 (20.4%), 250.10 (7.9%), 250.11 (2.0%)
Elemental Analysis: C, 67.68; H, 8.11; S, 12.91; Si, 11.30

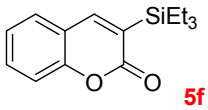
benzo[b]thiophen-2-yltriethylsilane **5d**[5], light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 8.3 Hz, 1H), 7.47 (s, 1H), 7.36 – 7.28 (m, 2H), 1.03 (t, *J* = 7.8 Hz, 9H), 0.87 (q, *J* = 7.4 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.73(s), 141.16 (s), 139.13(s), 131.69 (s), 124.15 (s), 124.00(s), 123.45 (s), 122.23 (s), 7.46 (s), 4.38 (s).MS (EI) *m/z*: 248 [M^+].



5e

2,5-bis(triethylsilyl)thiophene
Chemical Formula: $C_{16}H_{32}SSi_2$
Exact Mass: 312.18
Molecular Weight: 312.66
m/z: 312.18 (100.0%), 313.18 (28.6%), 314.17 (11.2%), 314.18 (3.7%), 315.18 (2.2%)
Elemental Analysis: C, 61.46; H, 10.32; S, 10.26; Si, 17.97

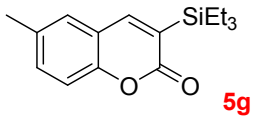
2,5-bis(triethylsilyl)thiophene **5e**[5]**,** colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 2H), 1.01 (t, *J* = 7.9 Hz, 18H), 0.81 (q, *J* = 7.9 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.38 (s), 135.54 (s), 7.54 (s), 4.71 (s). MS (EI) *m/z*: 312 [M^+].



5f

3-(triethylsilyl)-2*H*-chromen-2-one
Chemical Formula: $C_{15}H_{20}O_2Si$
Exact Mass: 260.12
Molecular Weight: 260.40
m/z: 260.12 (100.0%), 261.13 (16.5%), 261.12 (5.1%), 262.12 (3.3%), 262.13 (2.5%)
Elemental Analysis: C, 69.19; H, 7.74; O, 12.29; Si, 10.79

3-(triethylsilyl)-2H-chromen-2-one **5f**, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.51 – 7.43 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 0.98 (t, *J* = 7.7 Hz, 9H), 0.88 (dd, *J* = 11.2, 4.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.95 (s), 154.85 (s), 151.33 (s), 131.77 (s), 127.72 (s), 127.54(s), 124.10 (s), 119.45 (s), 116.75 (s), 7.48 (s), 2.63 (s). MS (EI) *m/z*: 260 [M^+].



5g

6-methyl-3-(triethylsilyl)-2*H*-chromen-2-one
Chemical Formula: $C_{16}H_{22}O_2Si$
Exact Mass: 274.14
Molecular Weight: 274.43
m/z: 274.14 (100.0%), 275.14 (22.5%), 276.14 (4.7%), 276.15 (1.5%)
Elemental Analysis: C, 70.03; H, 8.08; O, 11.66; Si, 10.23

6-methyl-3-(triethylsilyl)-2H-chromen-2-one **5g**, white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.33 – 7.25 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 2.39 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.91 – 0.84 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.21 (s), 152.96 (s), 151.34 (s), 133.70 (s), 132.73 (s), 127.59 (s), 127.21 (s), 119.17 (s), 116.41 (s), 20.82 (s), 7.46 (s), 2.65 (s). MS (EI) *m/z*: 274 [M^+].

[1] Shore. G, Organ. M. G, *Chem. Eur. J.* 2008, **14**, 9641 – 9646

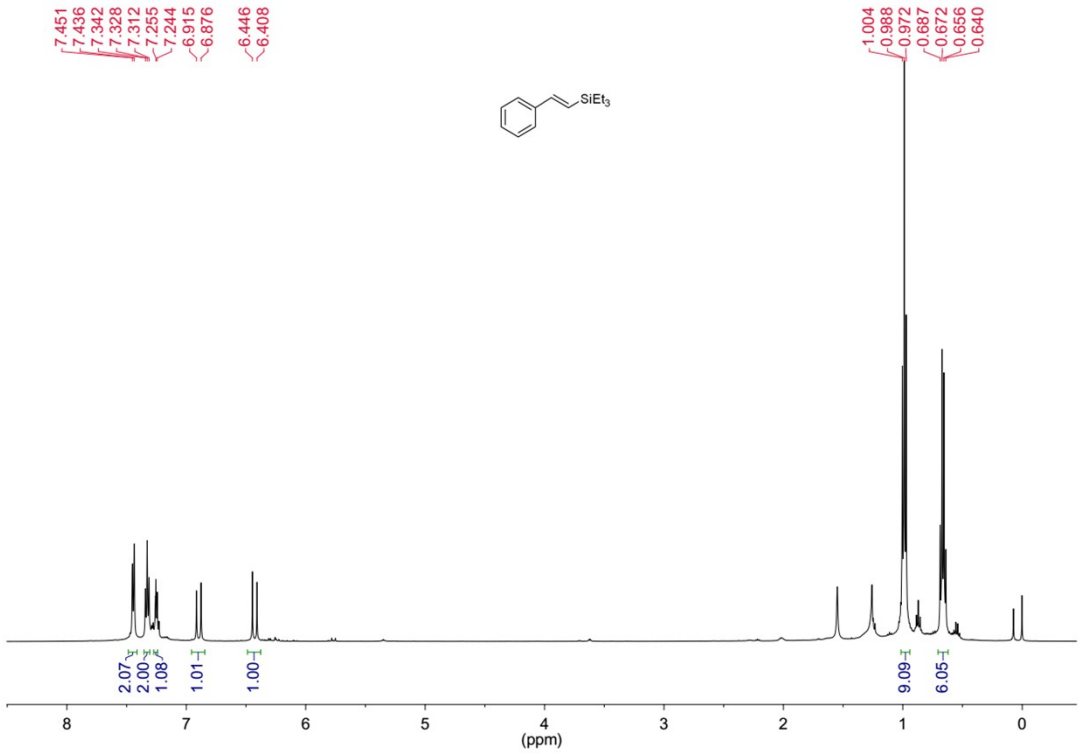
[2] Zhang. L, Hang. Z, Liu. Z.Q. *Angew. Chem. Int. Ed.* 2016, **55**, 236 –239.

[3] Hamze. A, Provot. O, Brion. J. D, Alami. M, *J. Organometallic. Chem,* 2008, **693**, 2789-2797

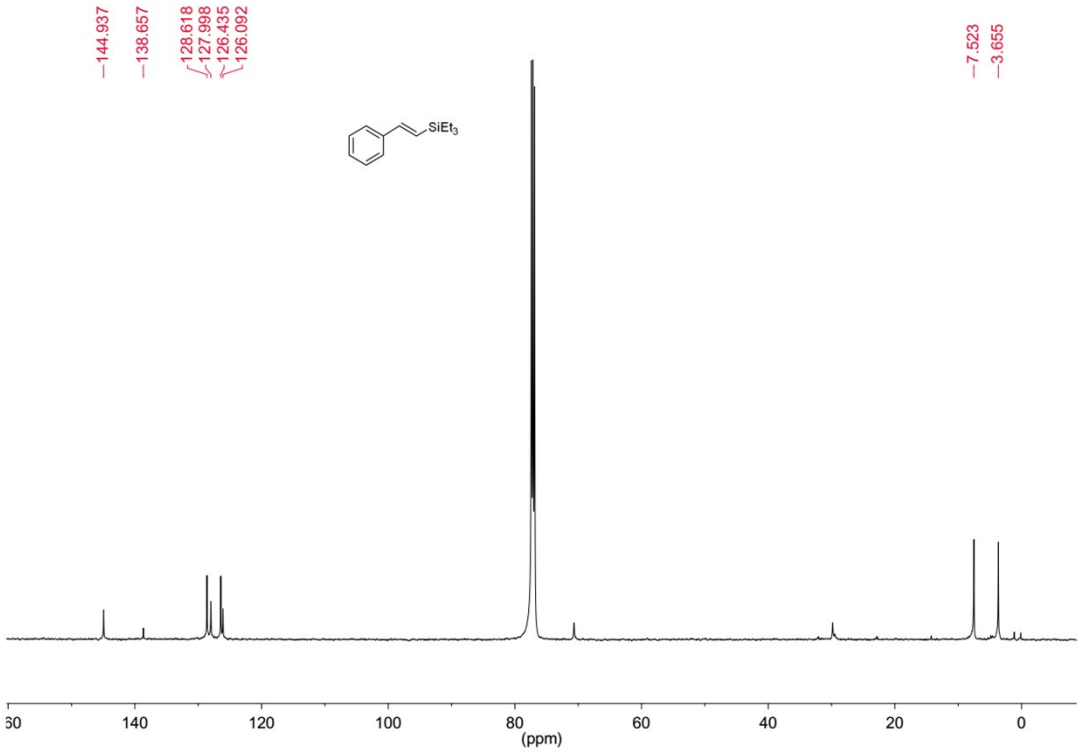
[4] Biffis. A, Conte. L, Tubaro. C, Basato. M, Aronica. L. A, Cuzzola. A, Caporusso. A. M, *J. Organometallic. Chem,* 2010, **695**, 792-798

[5] Toutov. A. A, Liu. W, Betz. K, Fedorov. A, Stoltz. B, Grubbs. R, *Nature*, 2015, **518**, 80-84

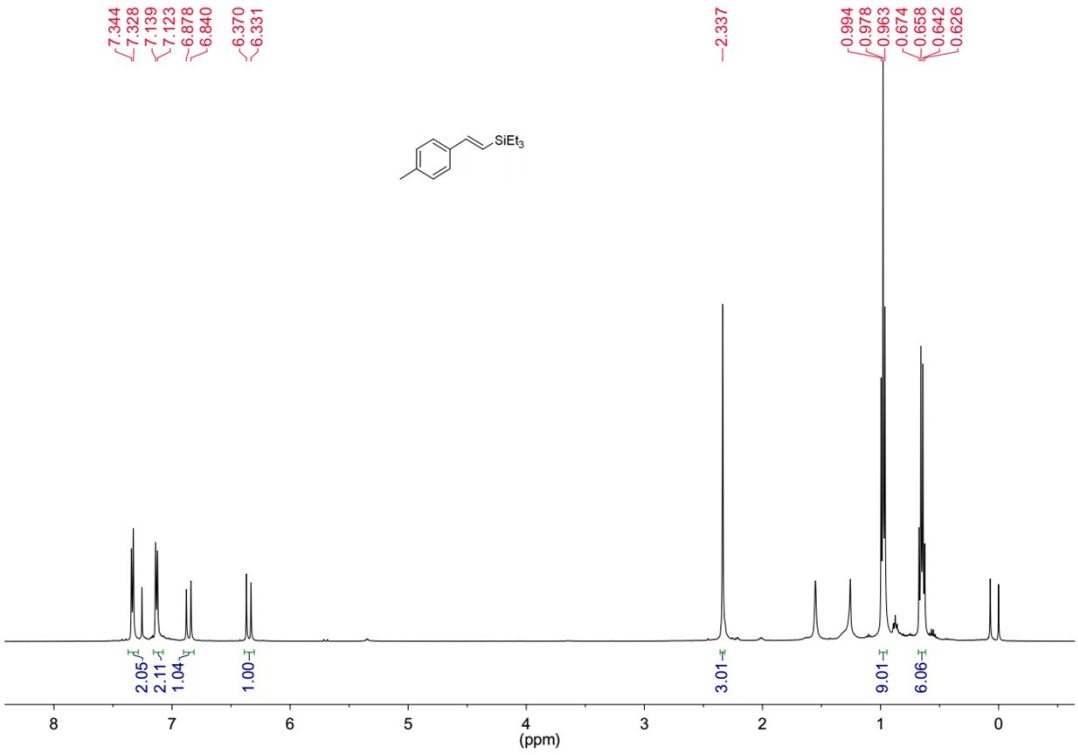
4. NMR Spectra of All Products



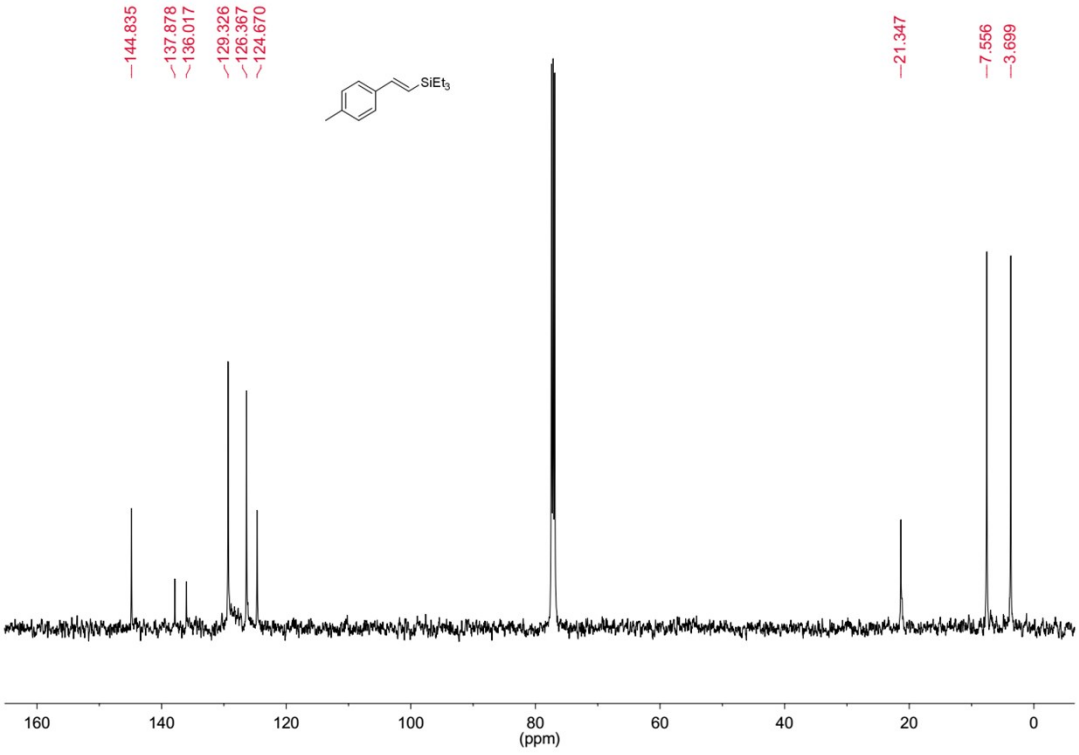
^{1}H NMR **3a**



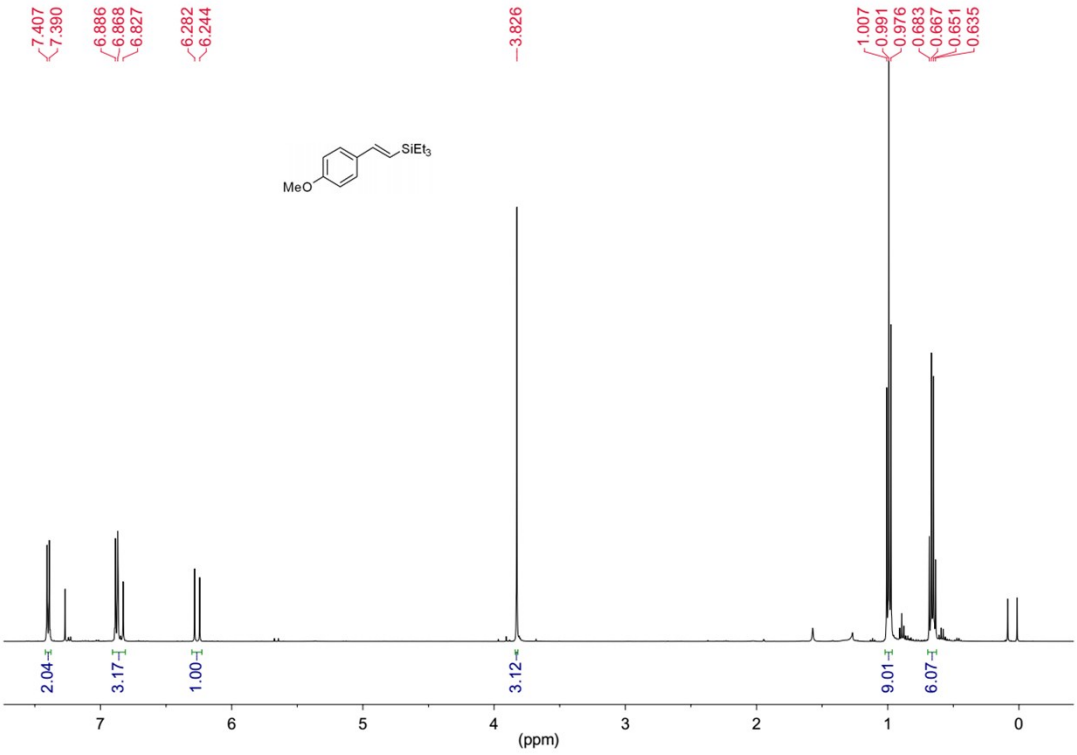
^{13}C NMR **3a**



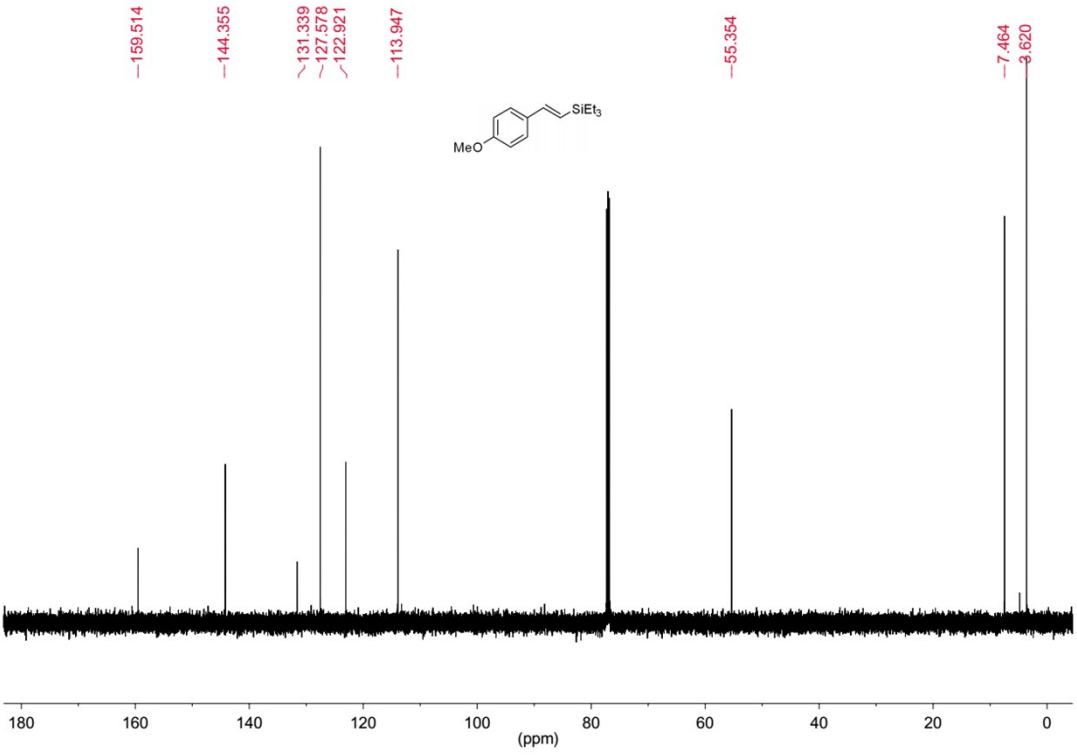
^{1}H NMR **3b**



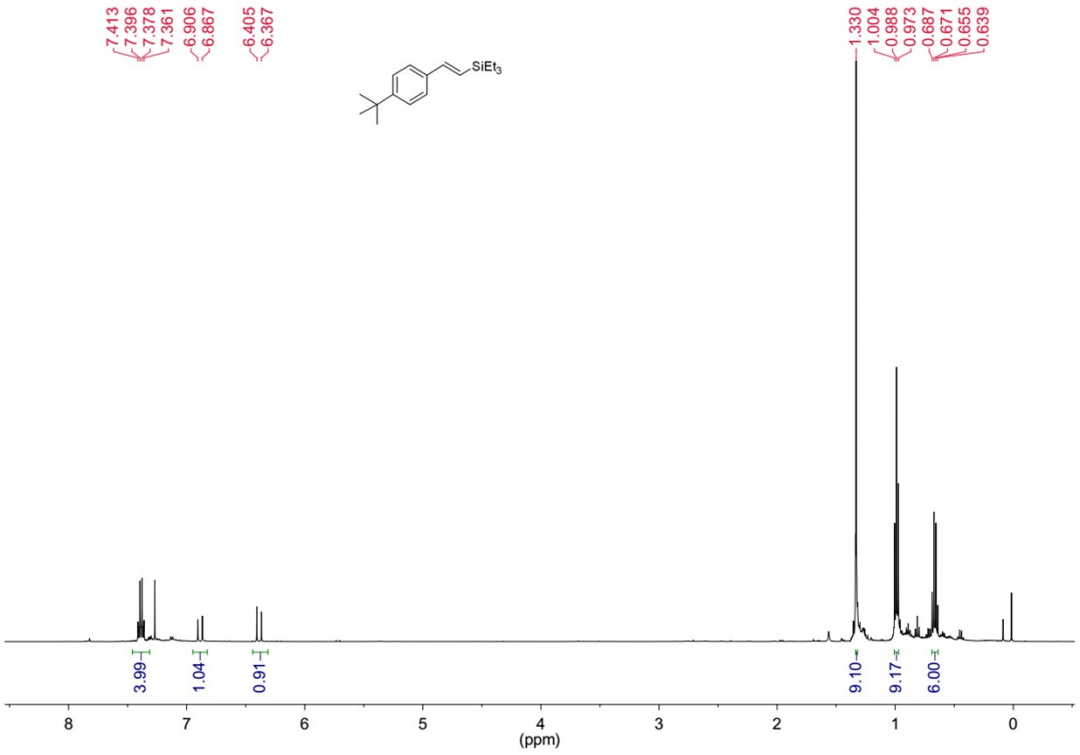
^{13}C NMR **3b**



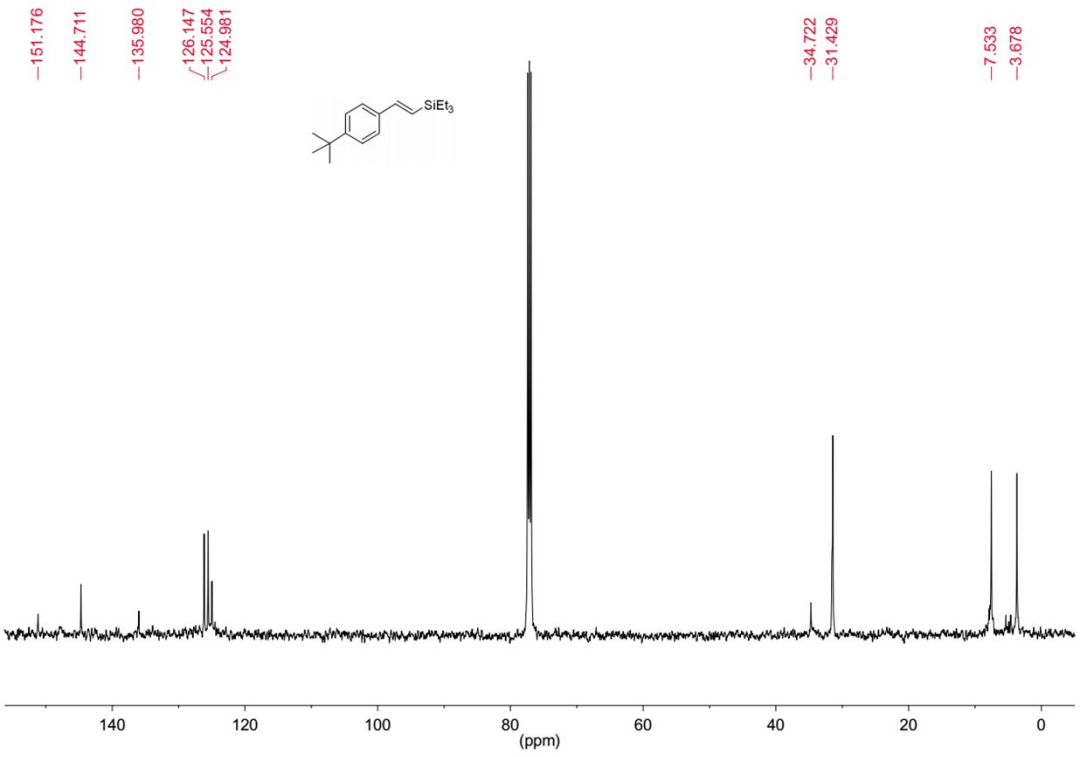
^{1}H NMR **3c**



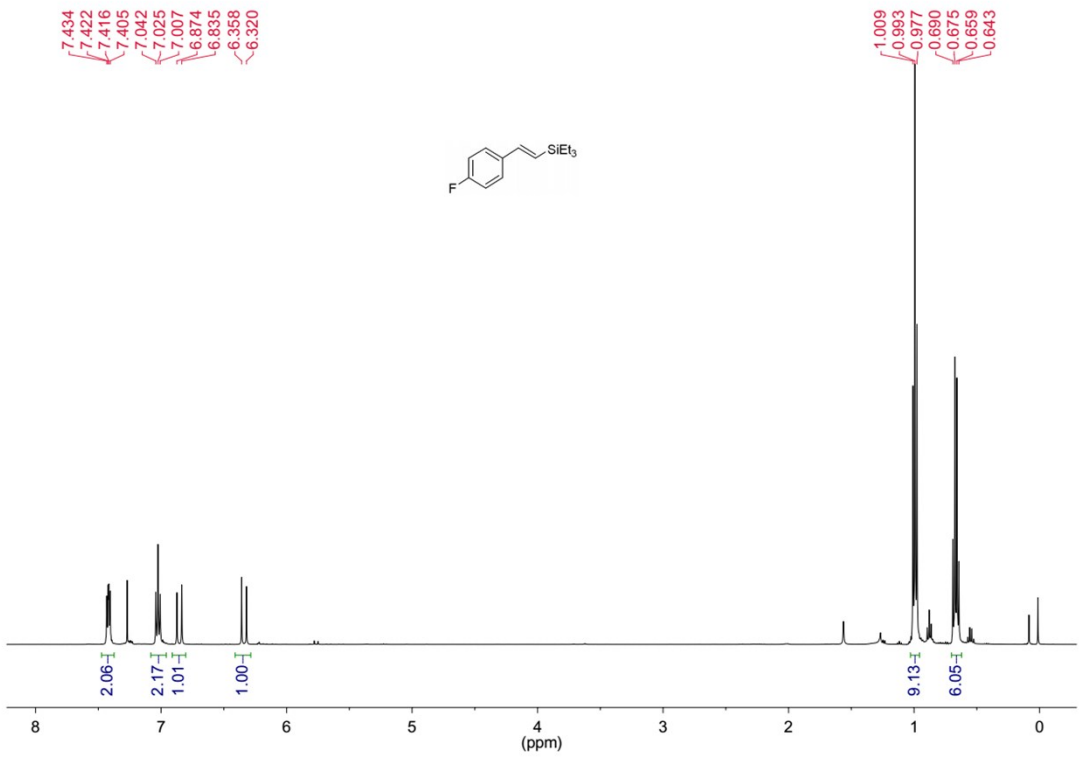
^{13}C NMR **3c**



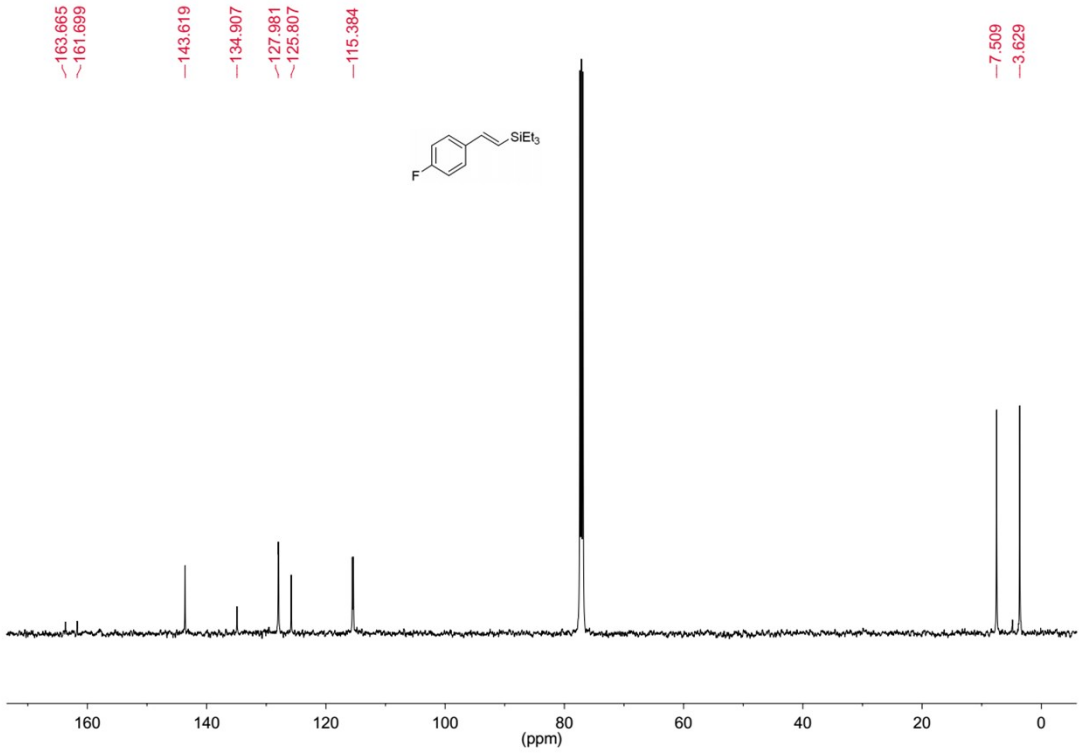
^{1}H NMR **3d**



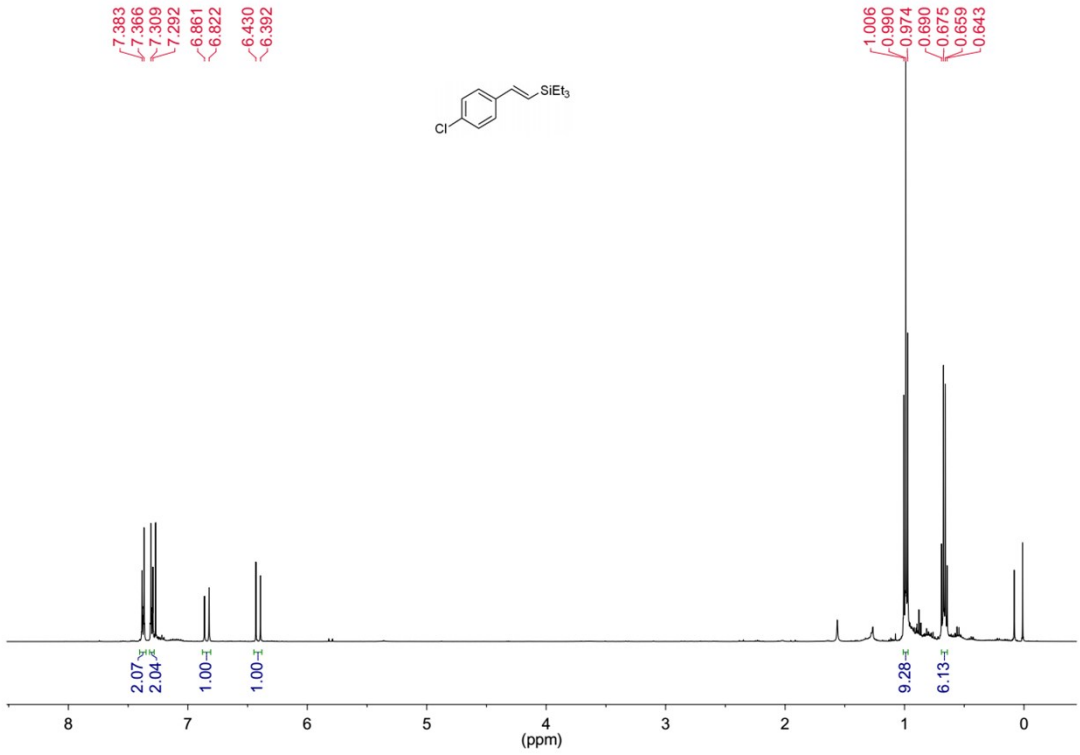
^{13}C NMR **3d**



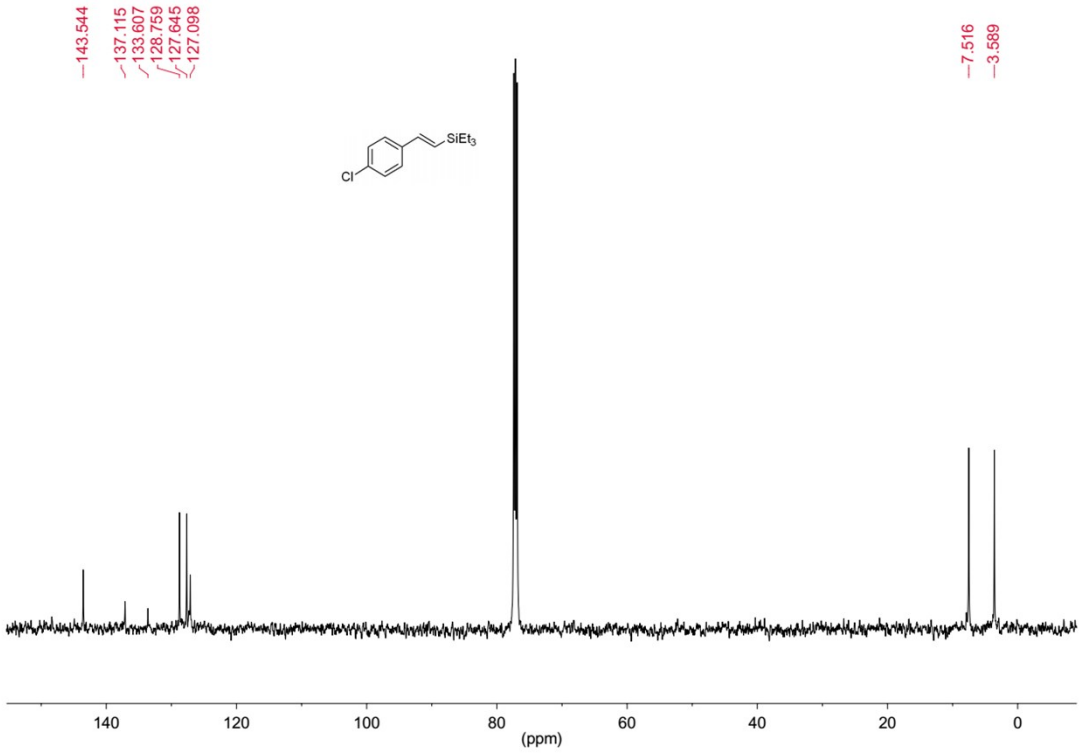
^{1}H NMR **3e**



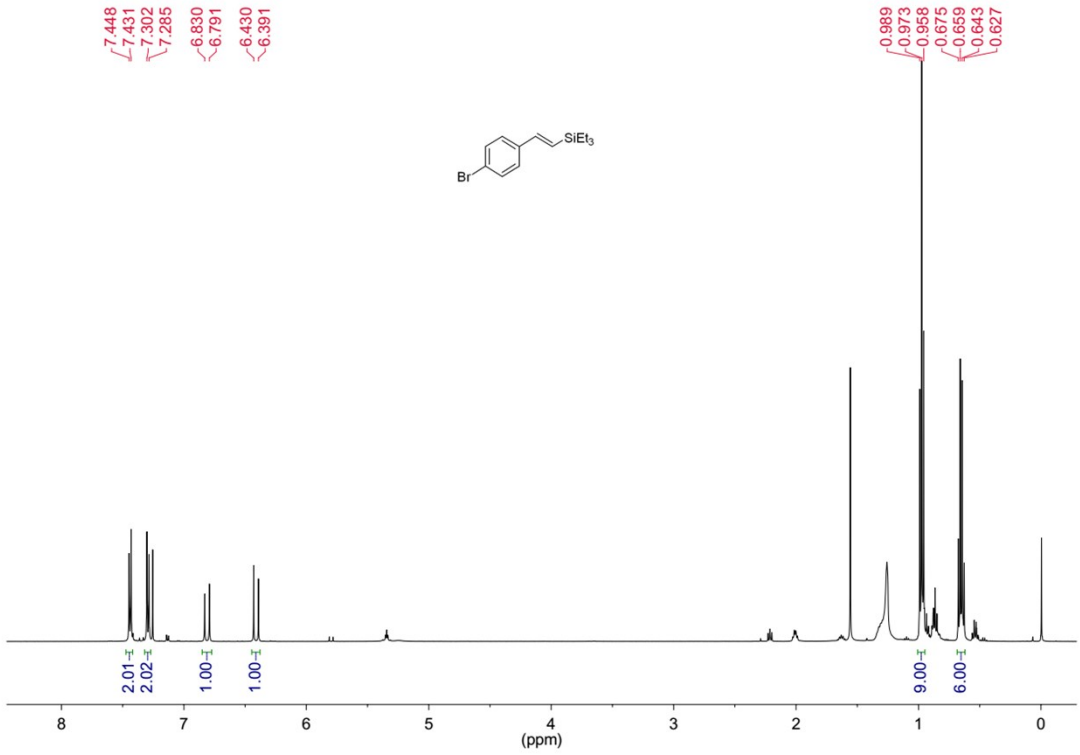
^{13}C NMR **3e**



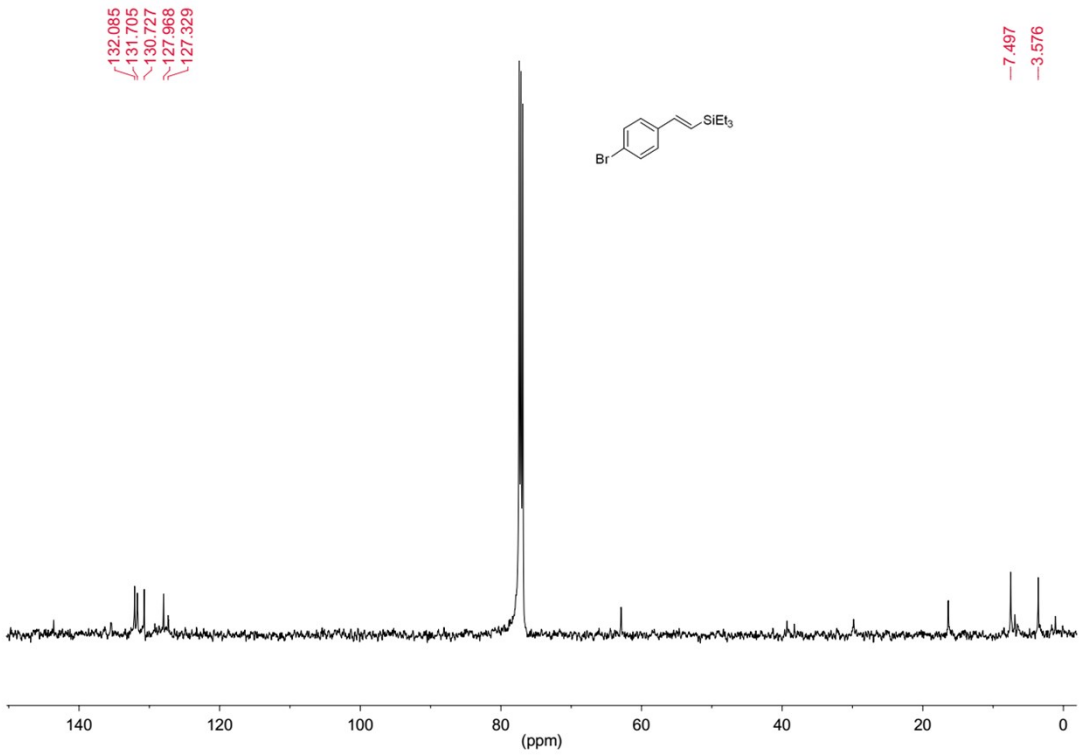
^{1}H NMR **3f**



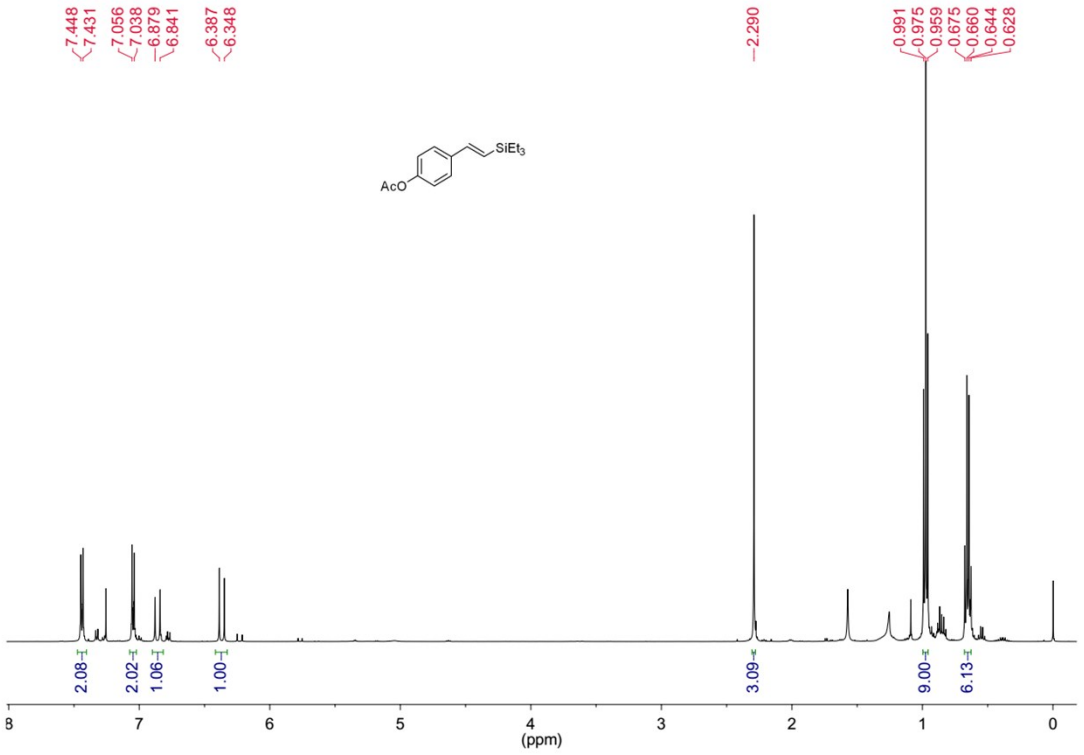
^{13}C NMR **3f**



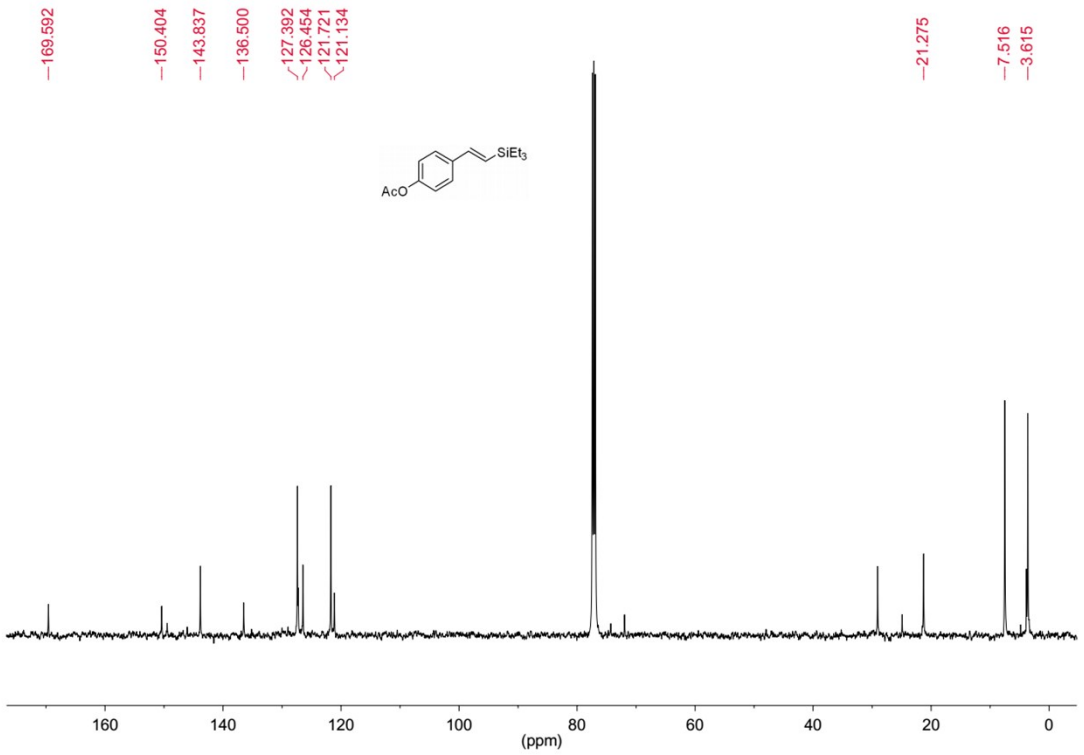
^{1}H NMR **3g**



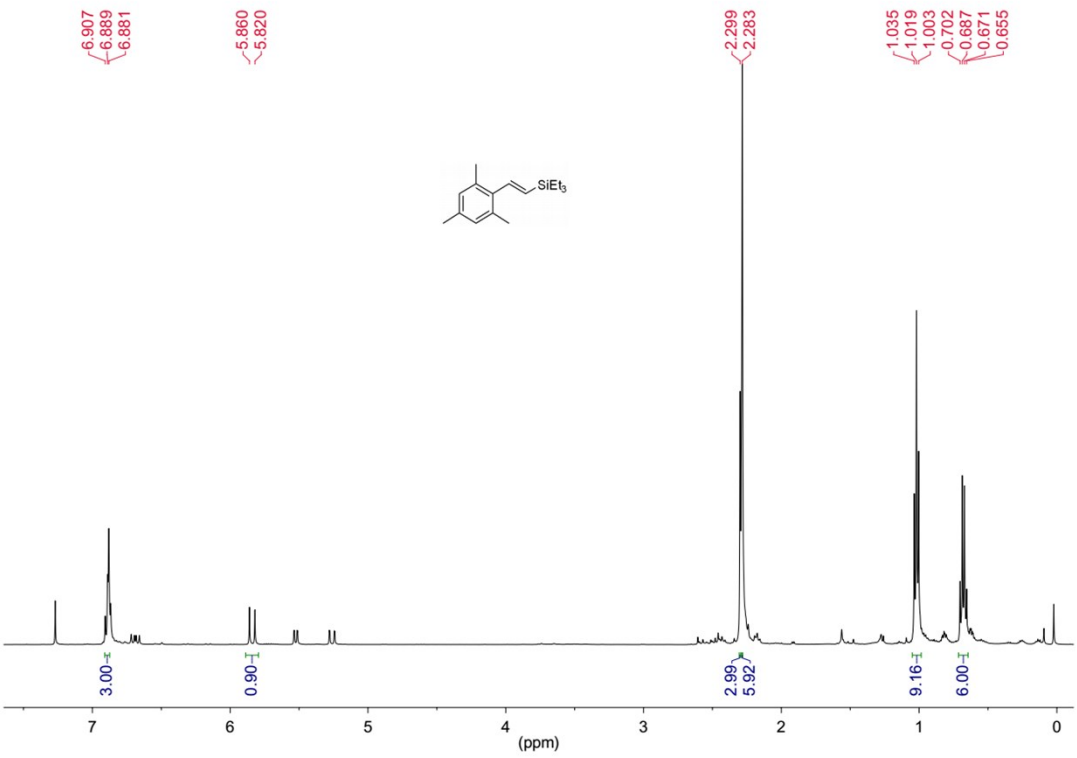
^{13}C NMR **3g**



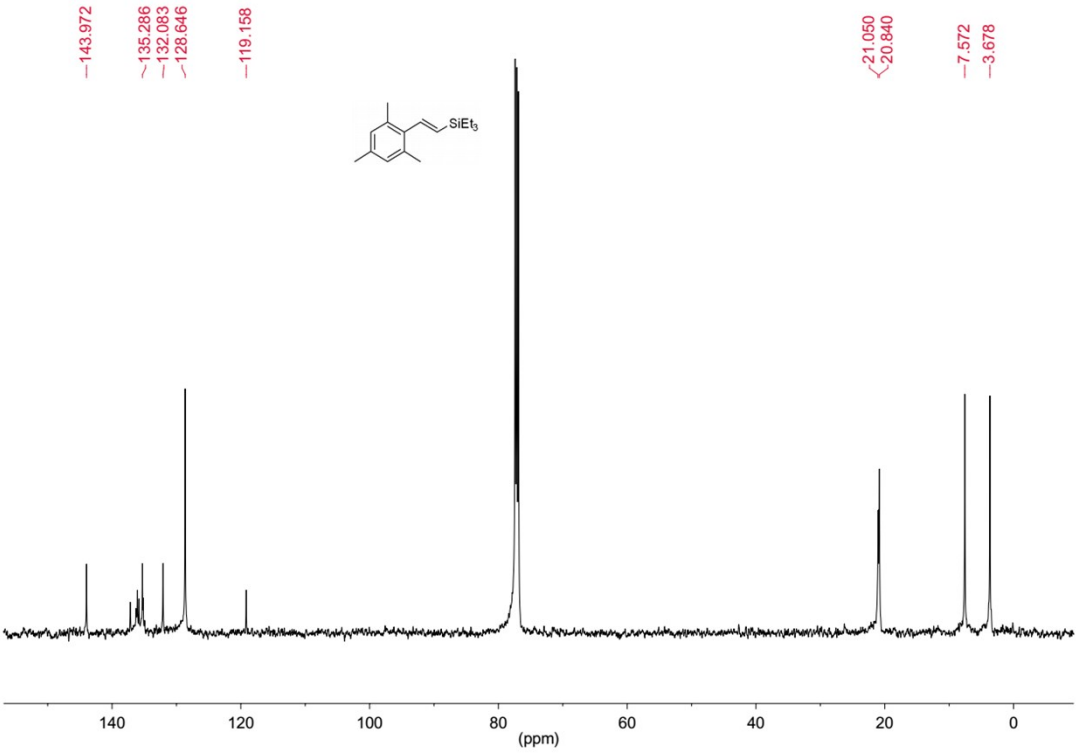
^{1}H NMR **3h**



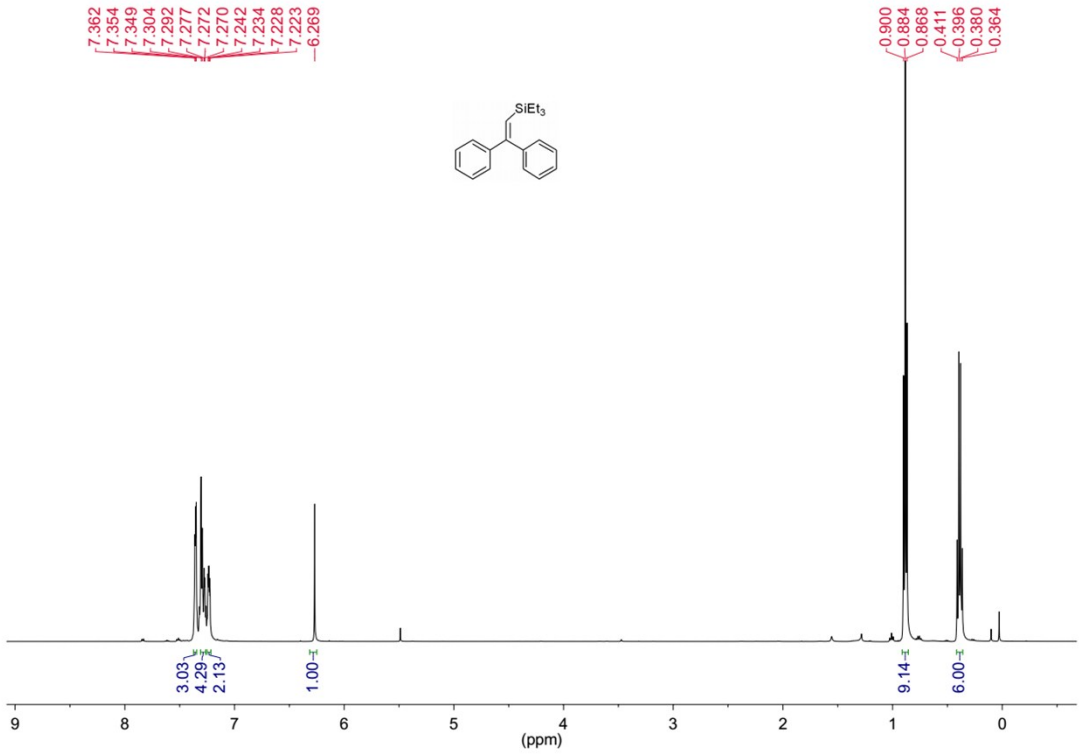
^{13}C NMR **3h**



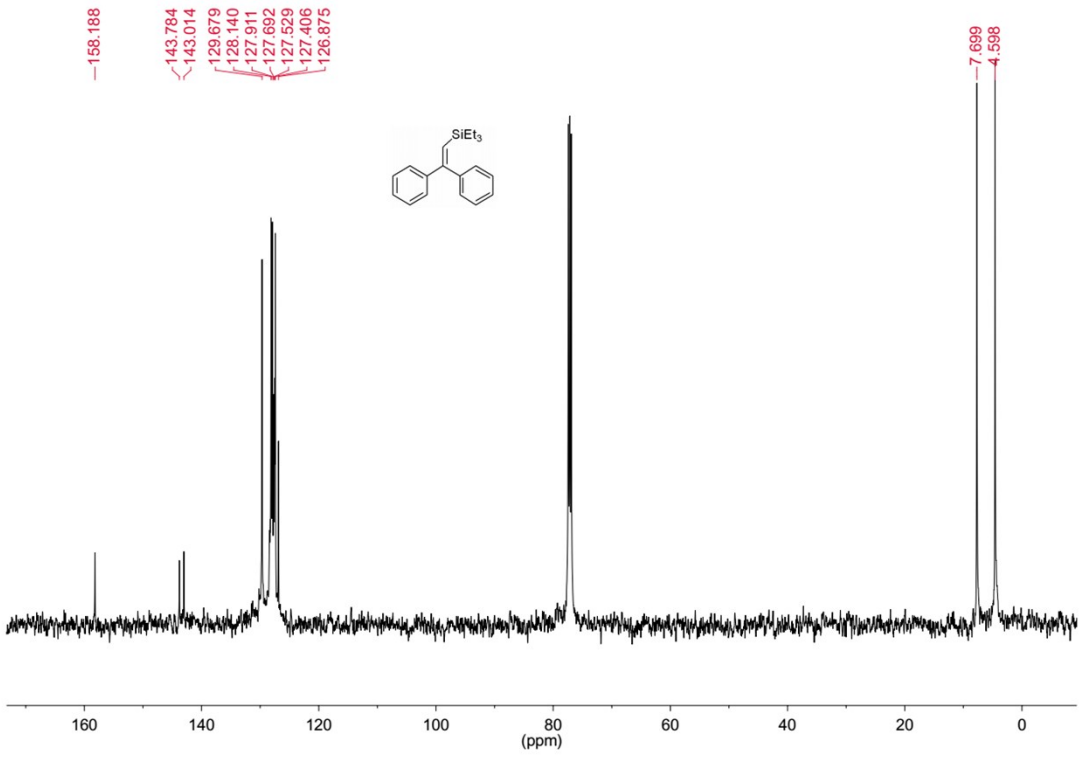
^{1}H NMR **3i**



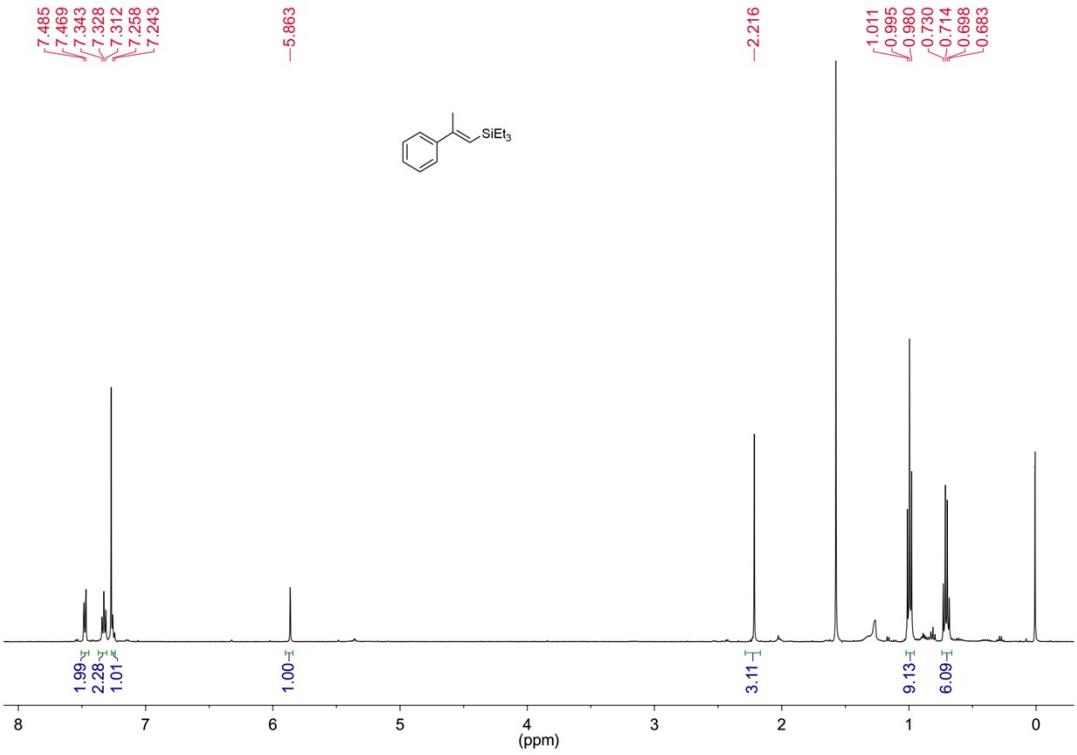
^{13}C NMR **3i**



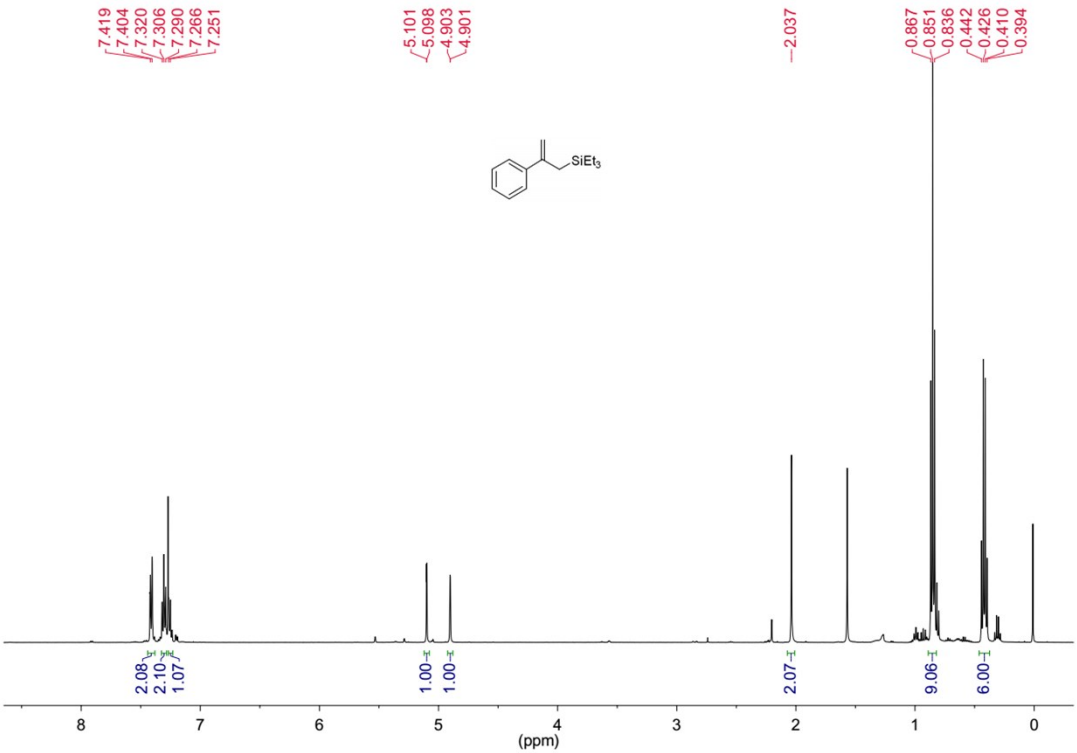
^{1}H NMR **3j**



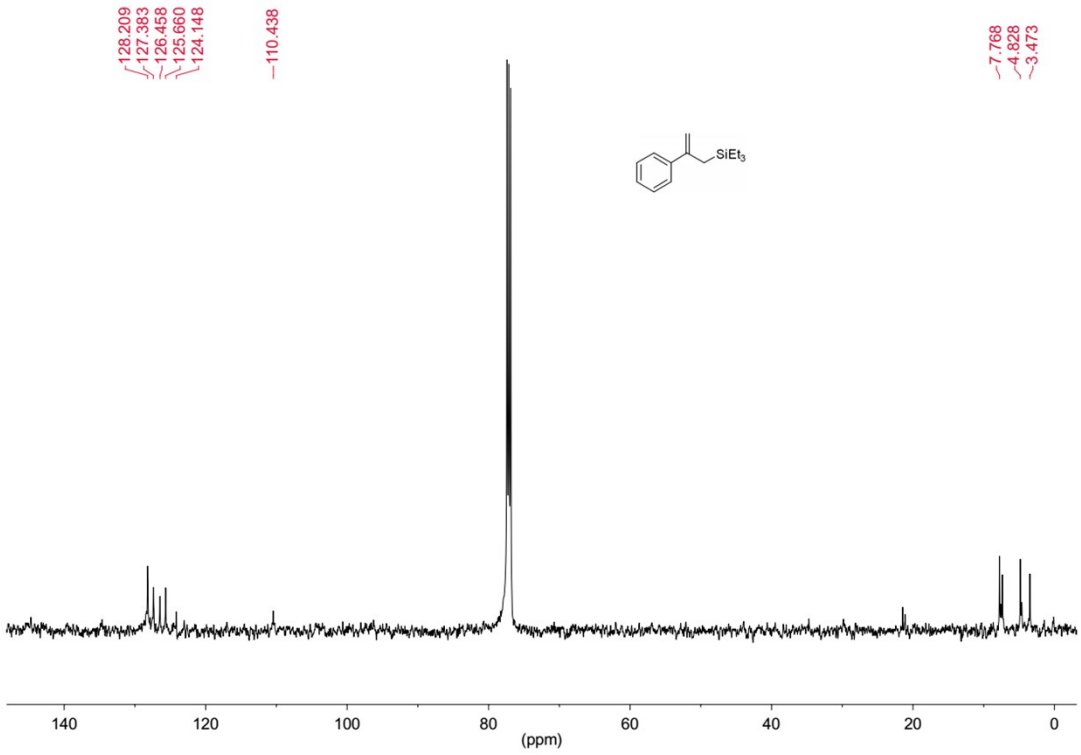
^{13}C NMR **3j**



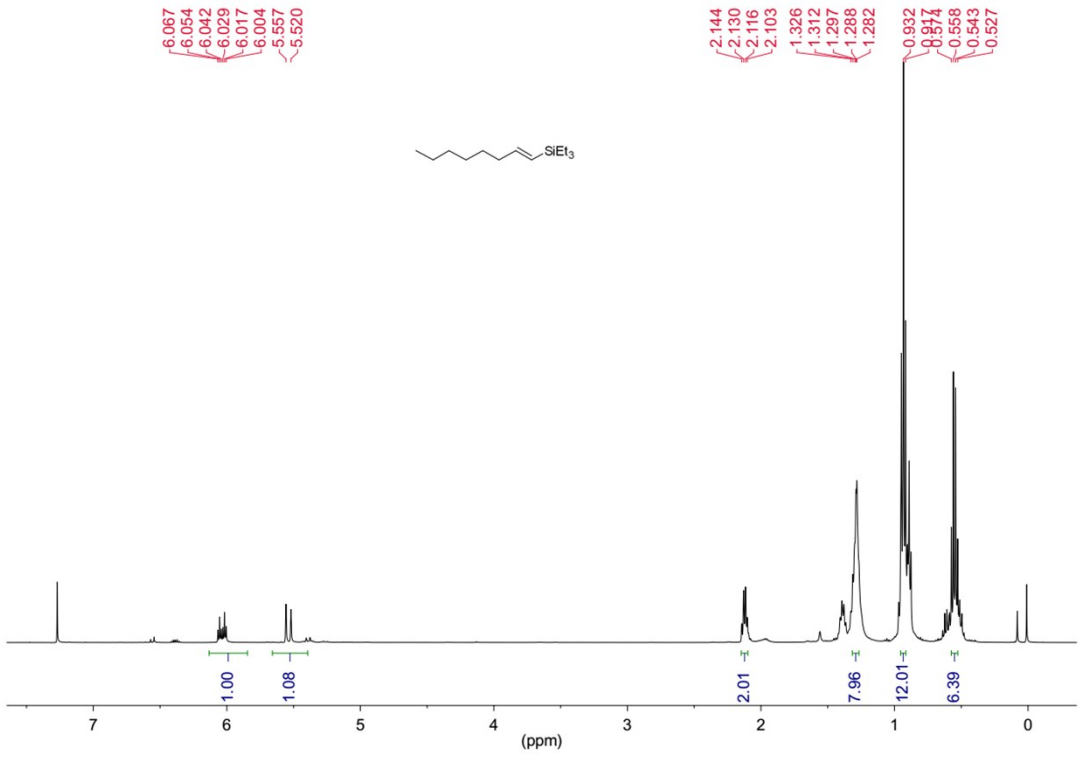
^{1}H NMR **3k**



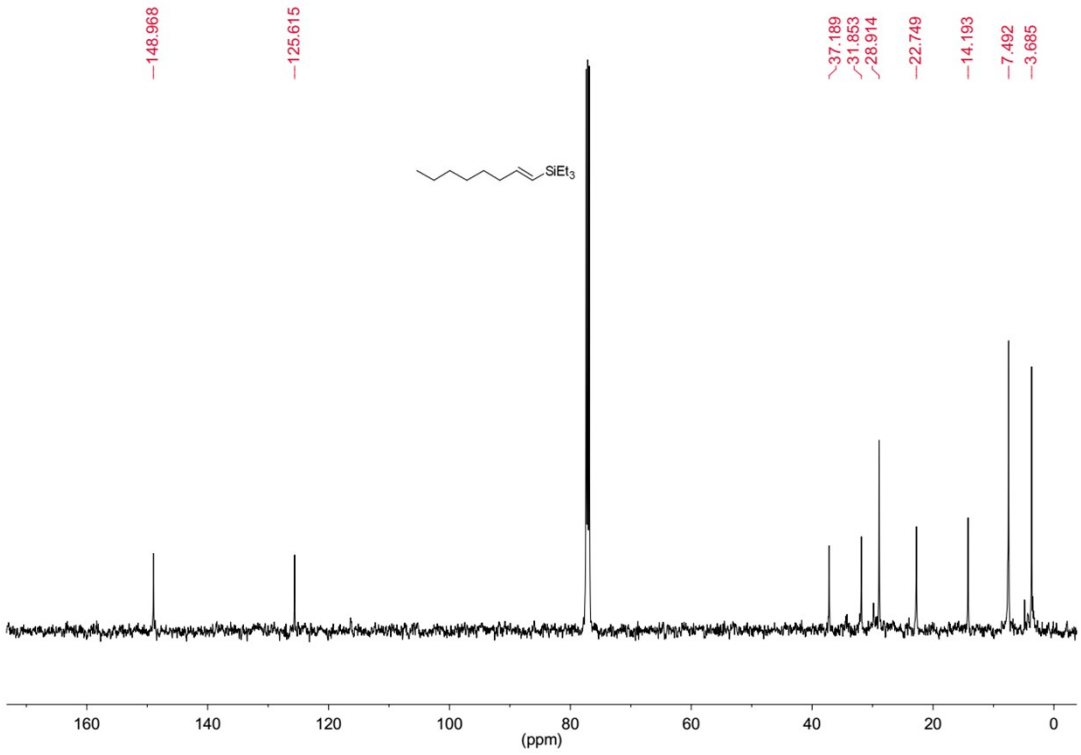
^{1}H NMR **3k'**



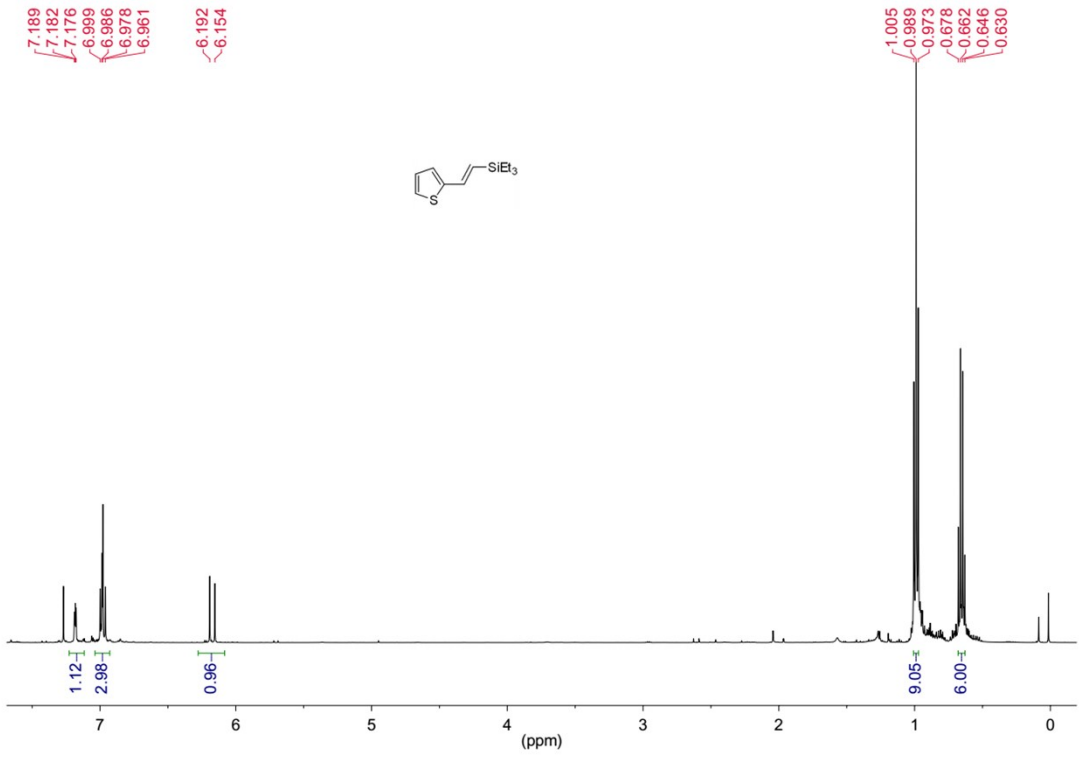
^{13}C NMR **3k'**



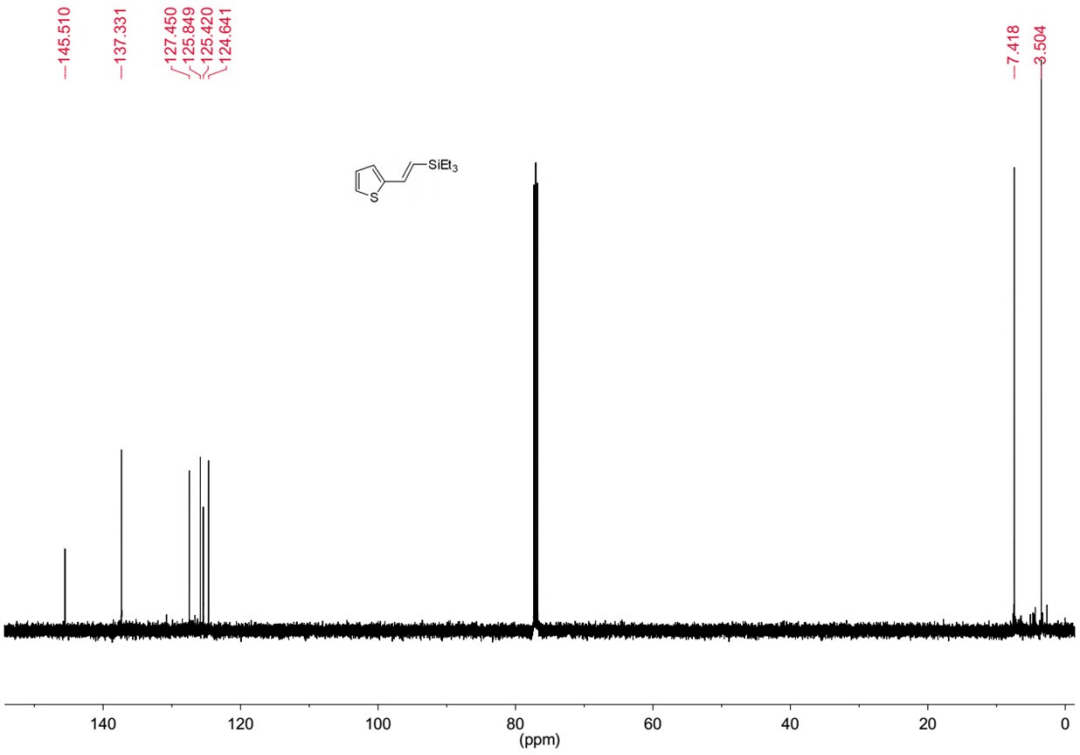
^{1}H NMR **3l**



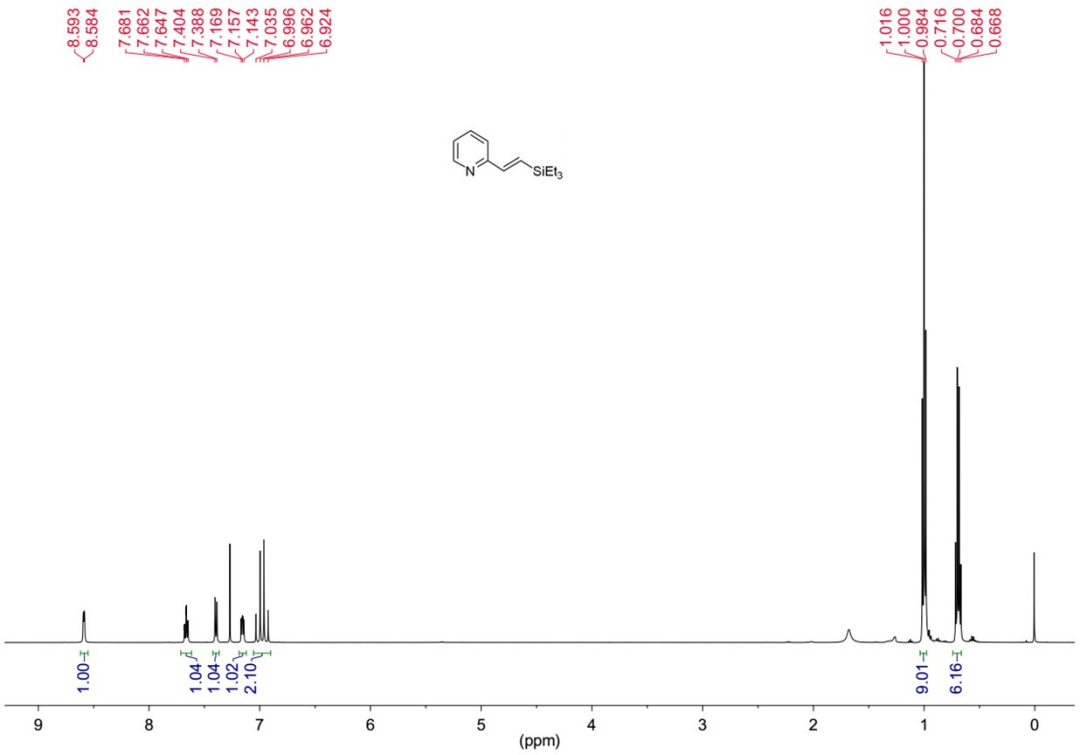
^{13}C NMR **3l**



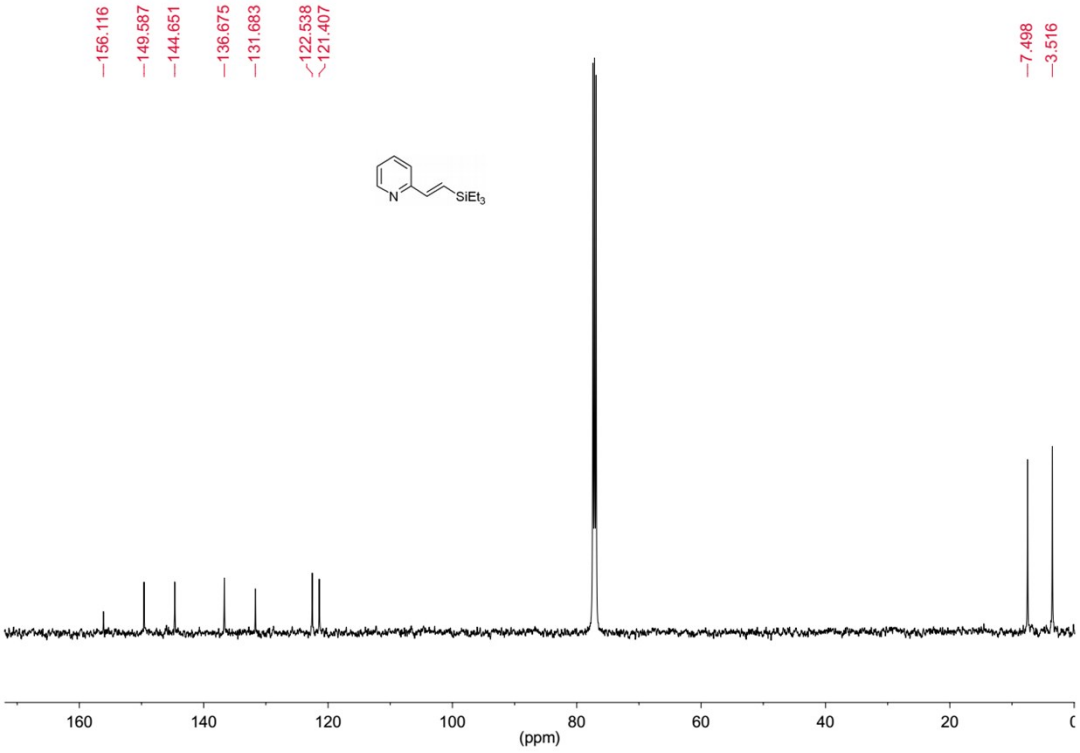
^{1}H NMR **3m**



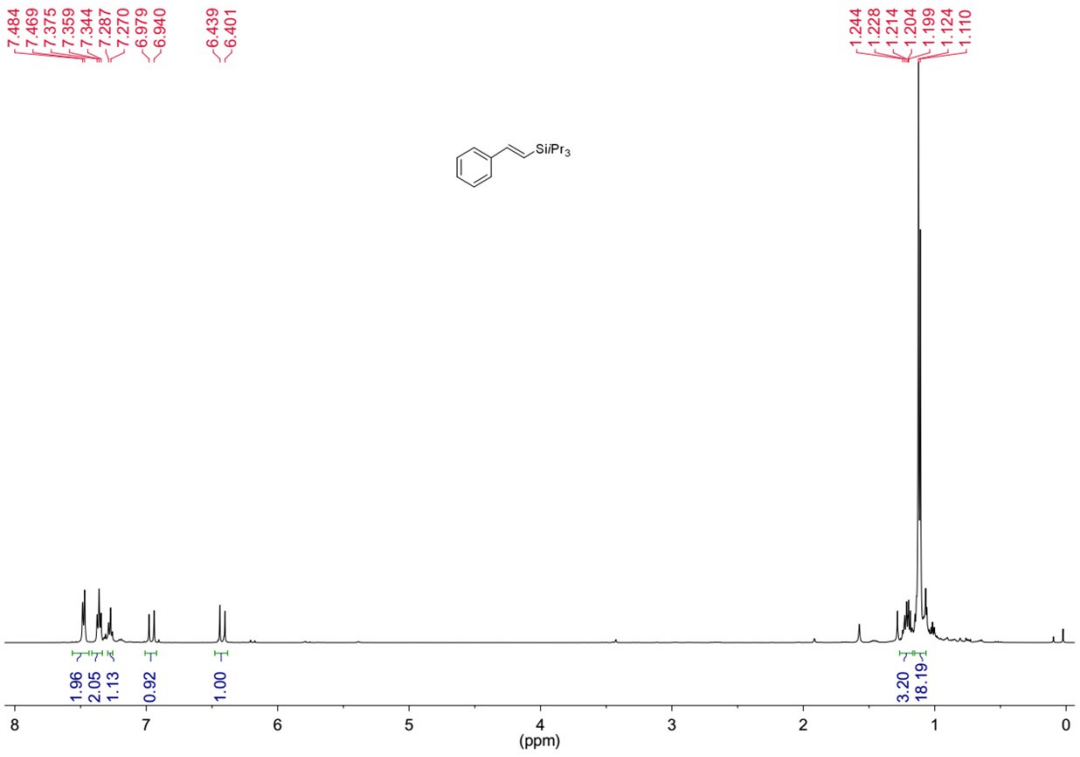
^{13}C NMR **3m**



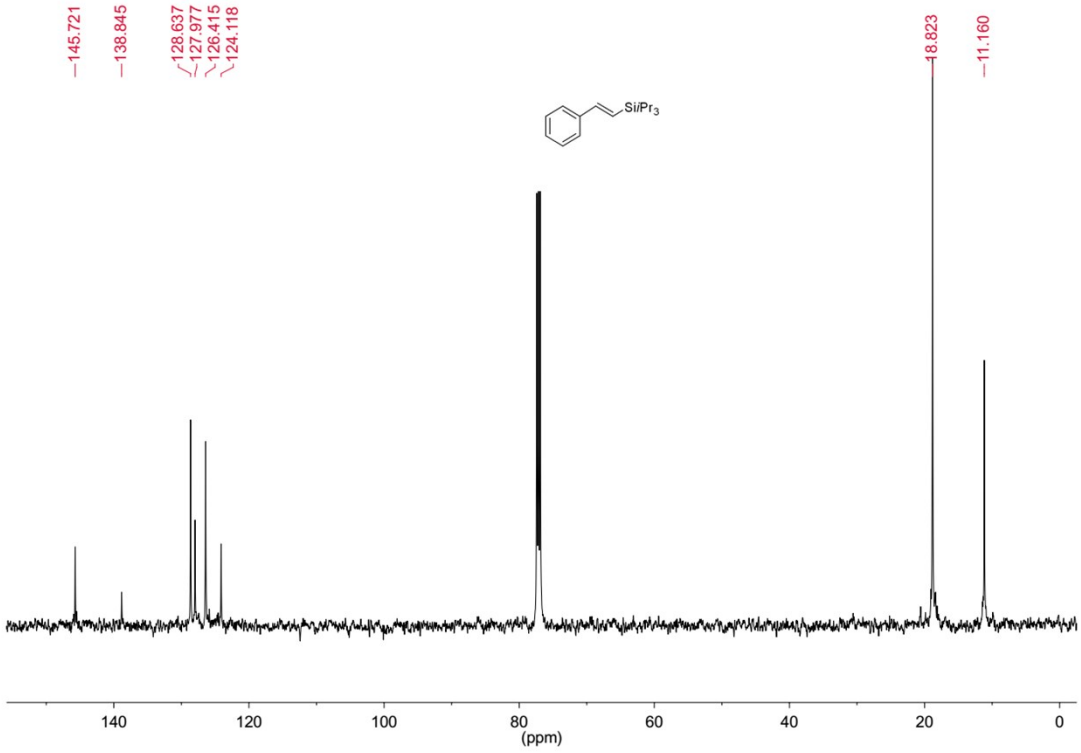
^{1}H NMR **3n**



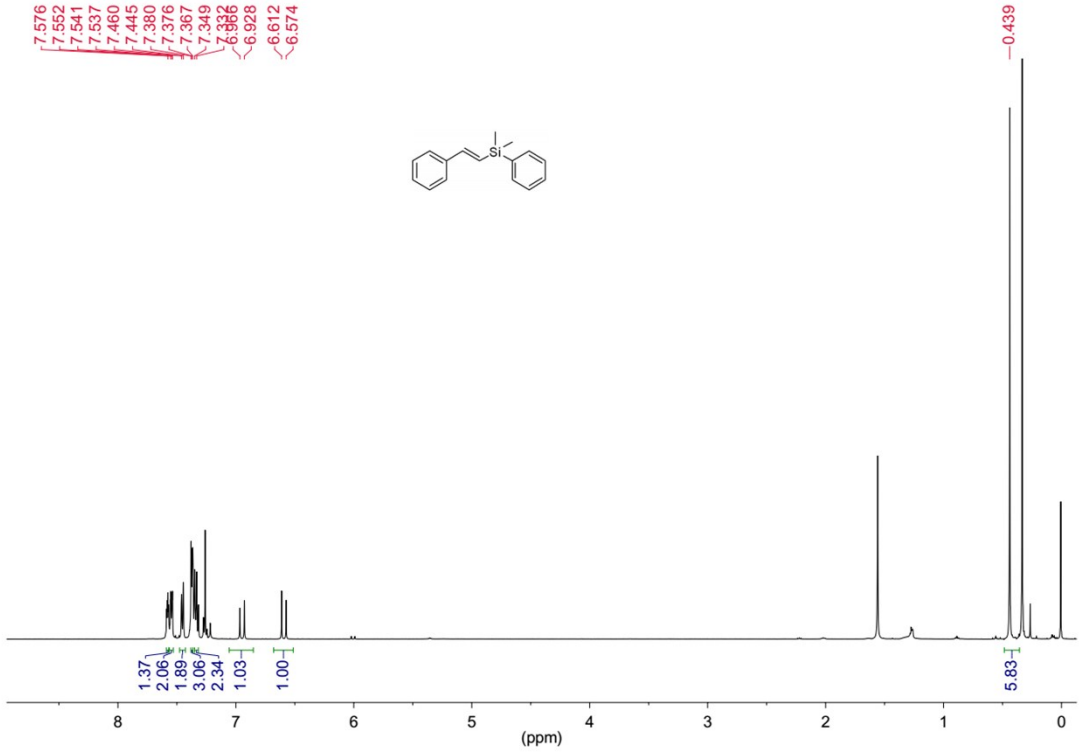
^{13}C NMR **3n**



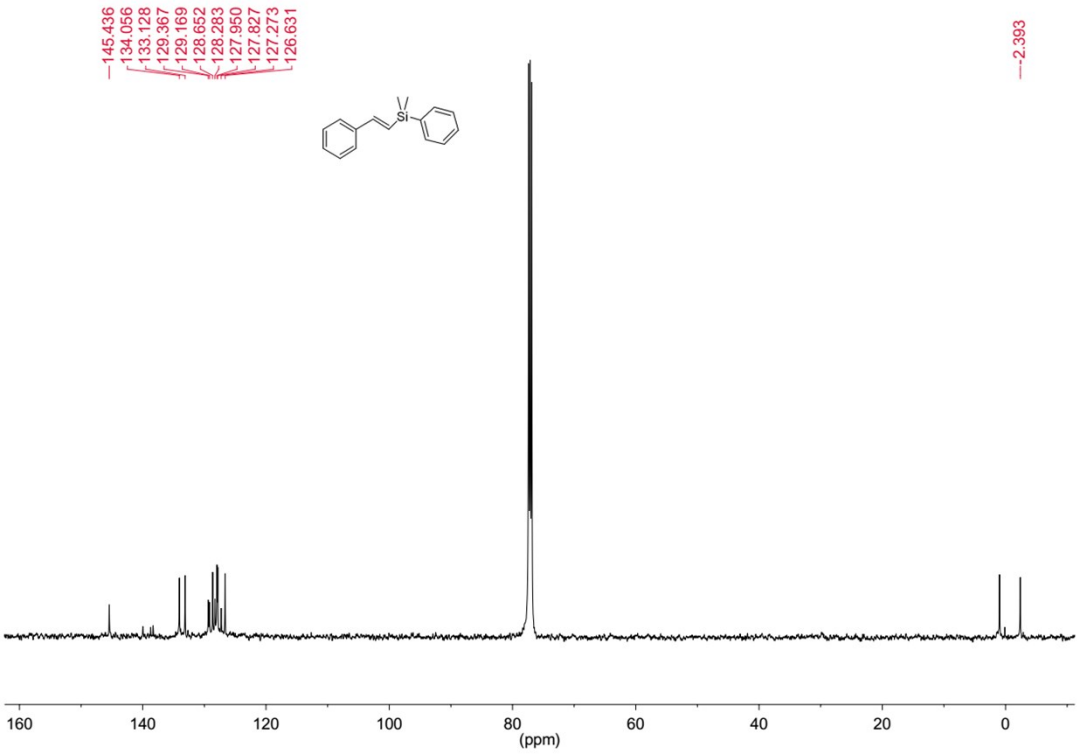
^{1}H NMR **3o**



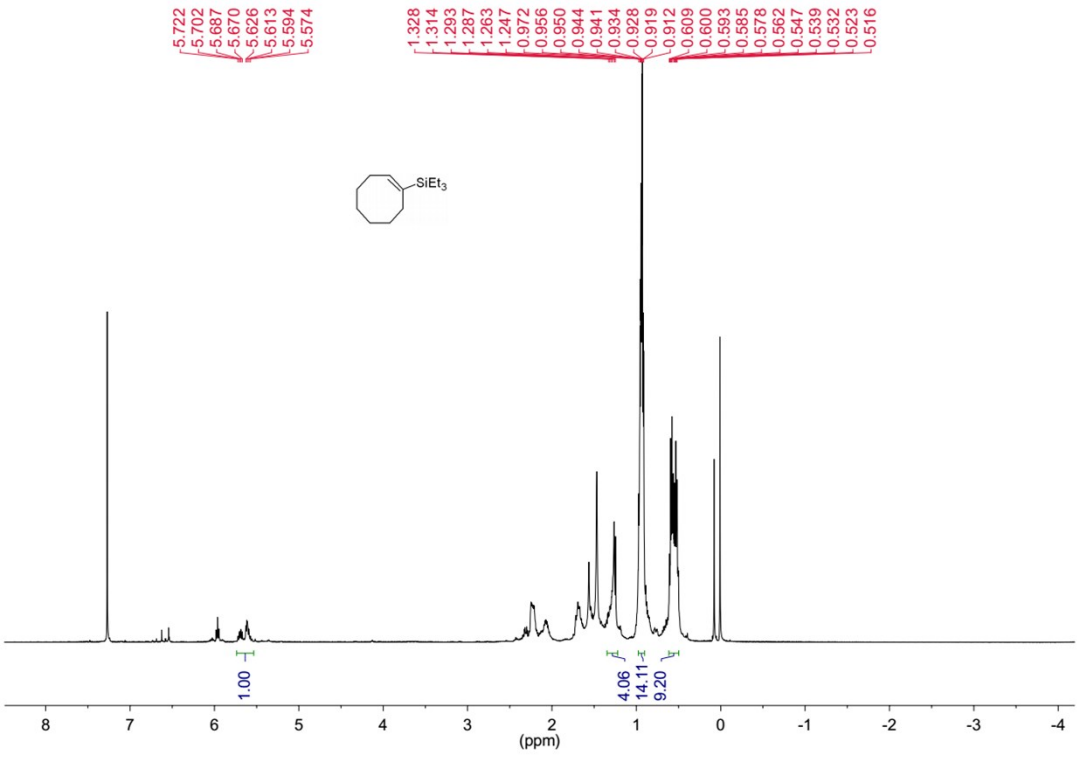
^{13}C NMR **3o**



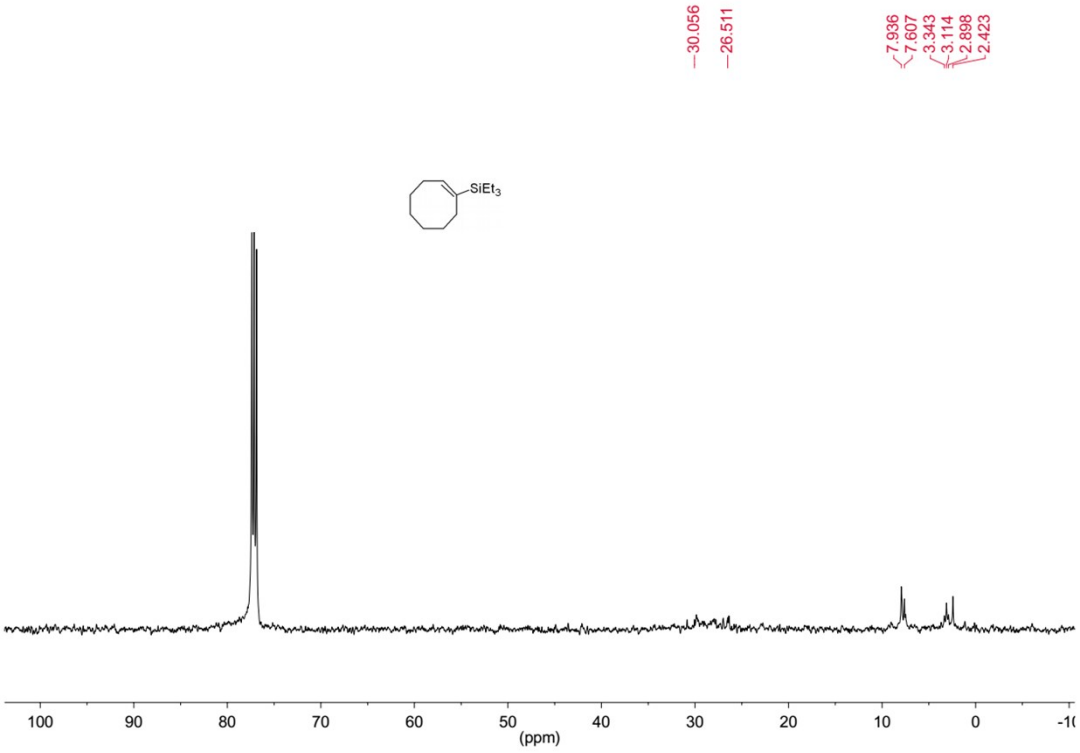
^{1}H NMR **3p**



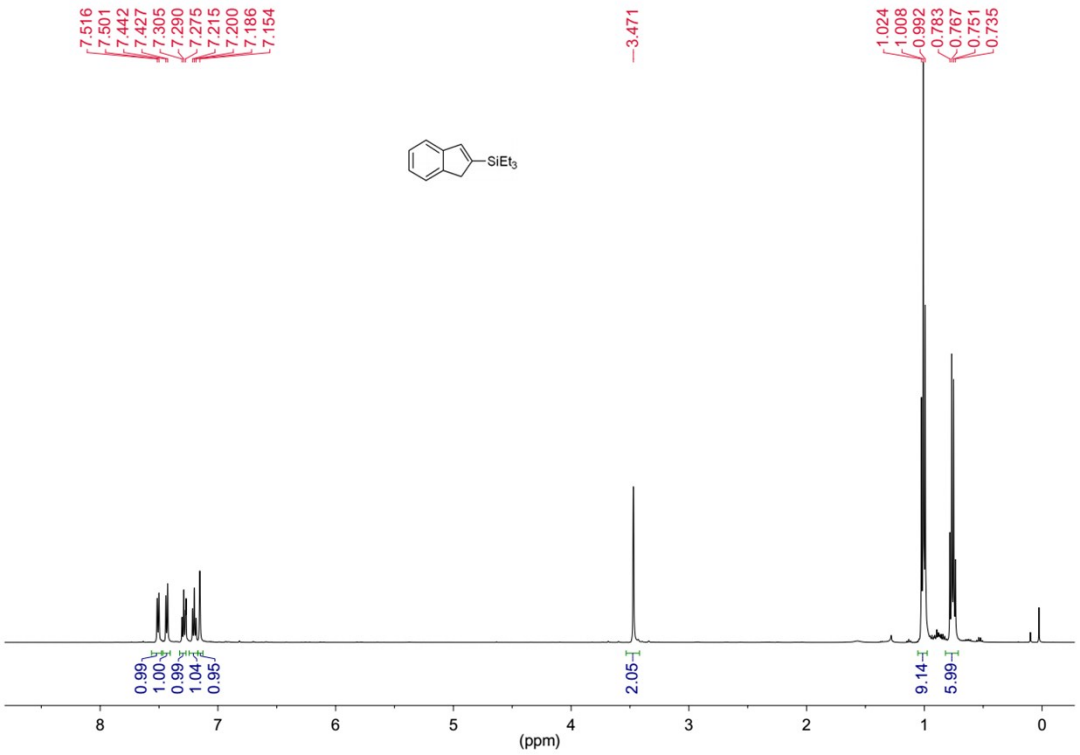
^{13}C NMR **3p**



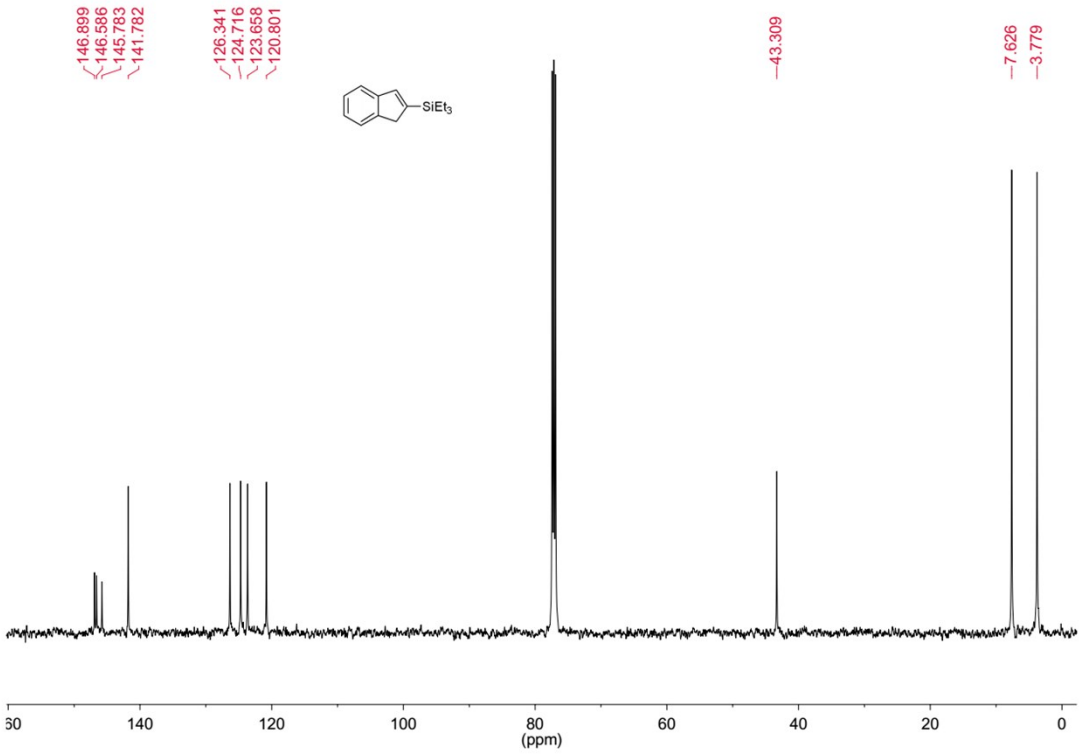
^{1}H NMR **5a**



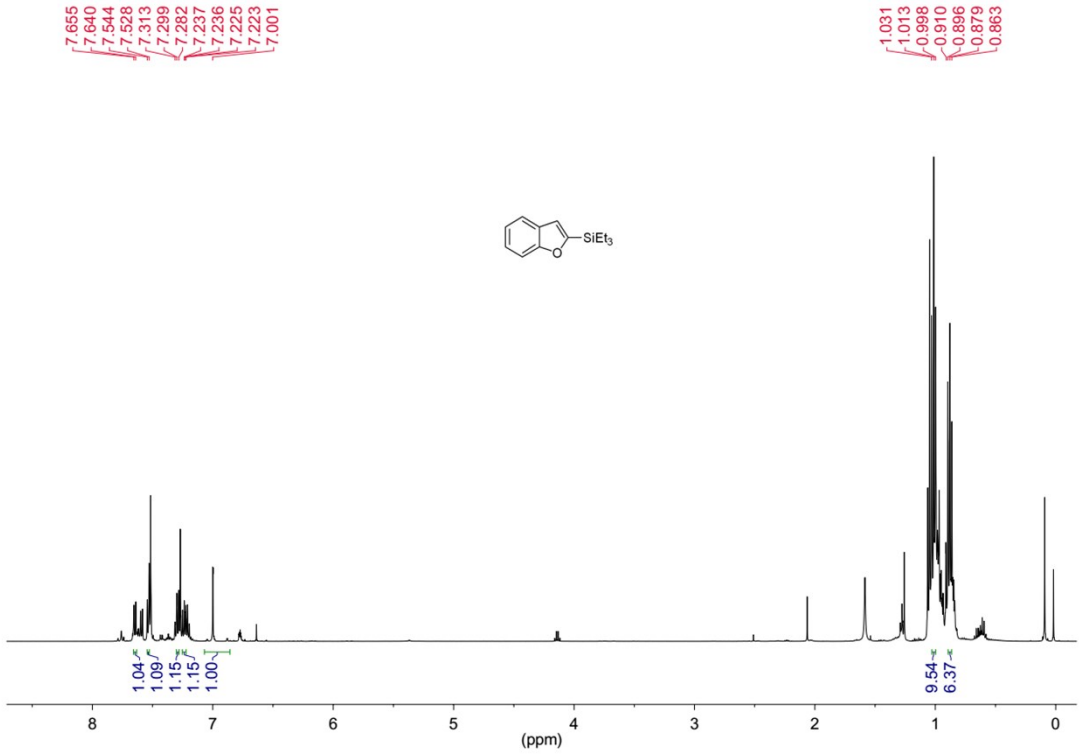
^{13}C NMR **5a**



^{1}H NMR **5b**



^{13}C NMR **5b**



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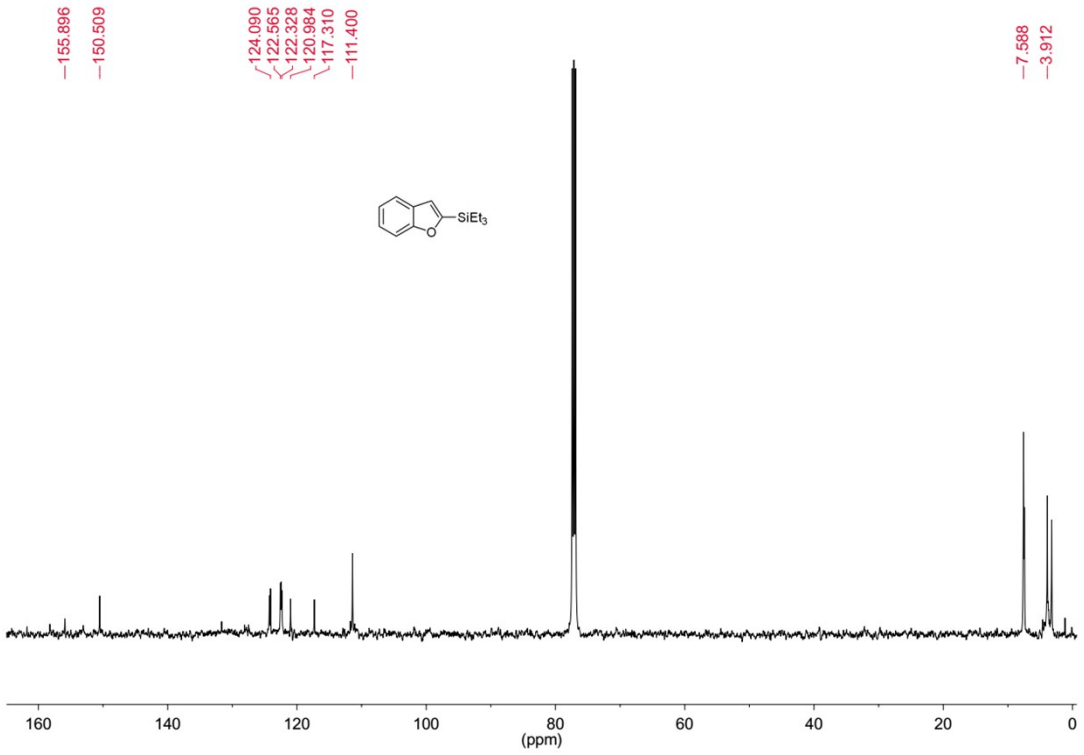
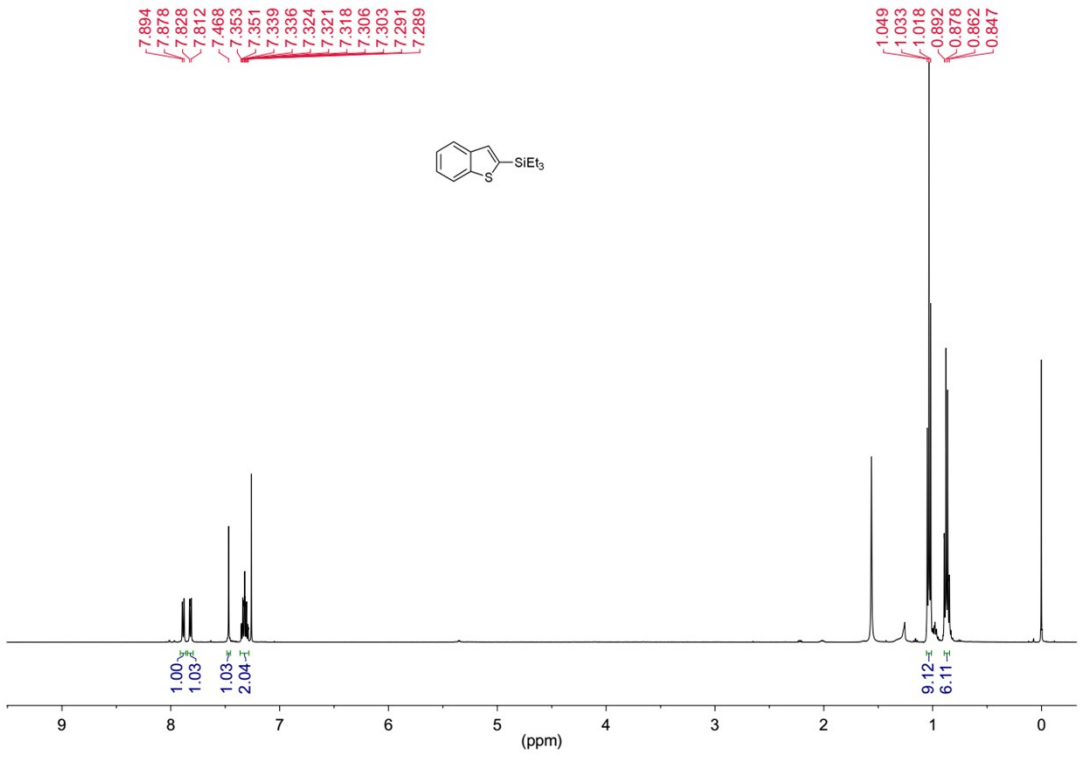


^{13}C NMR **5c**



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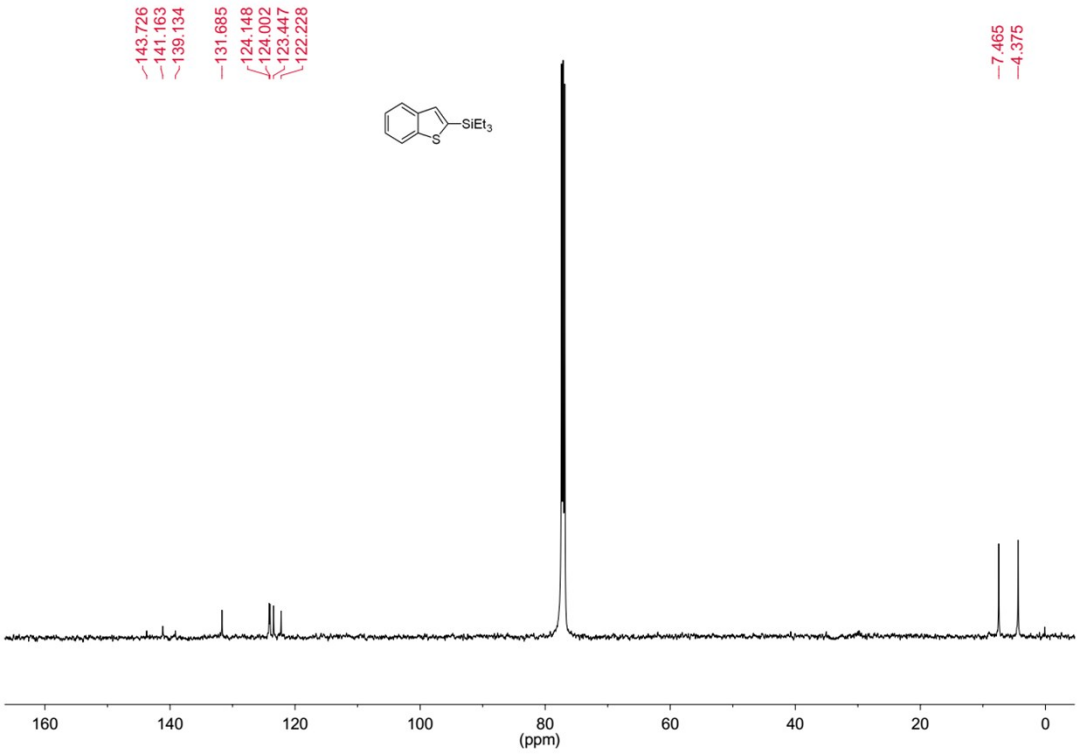
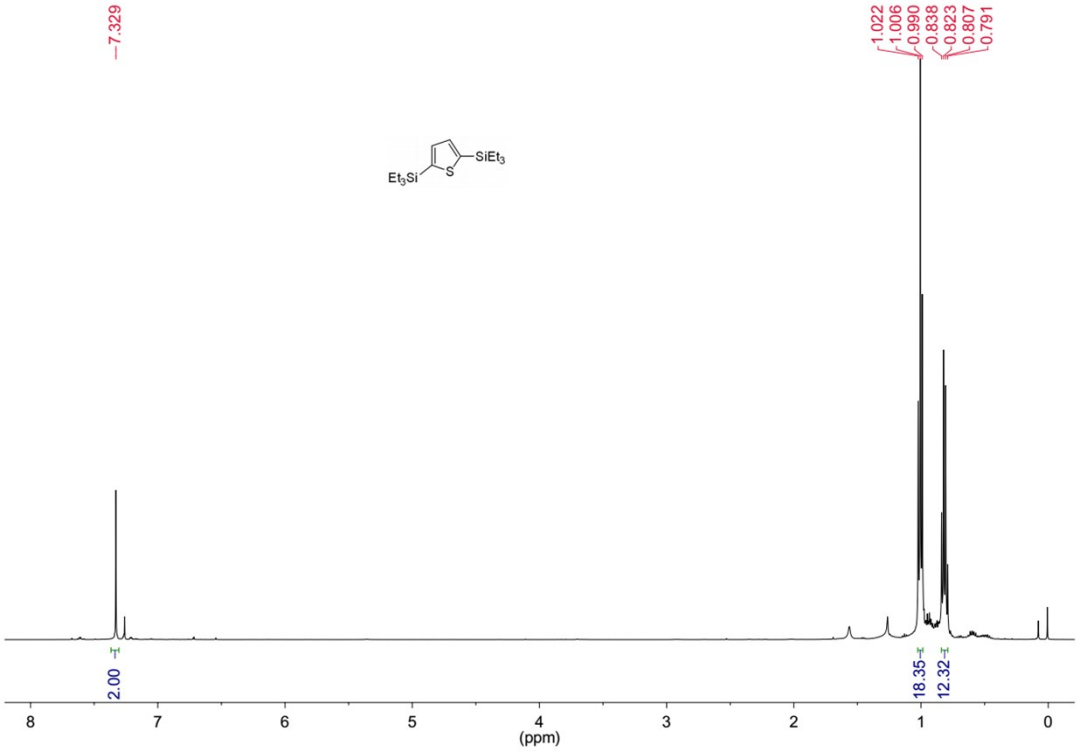
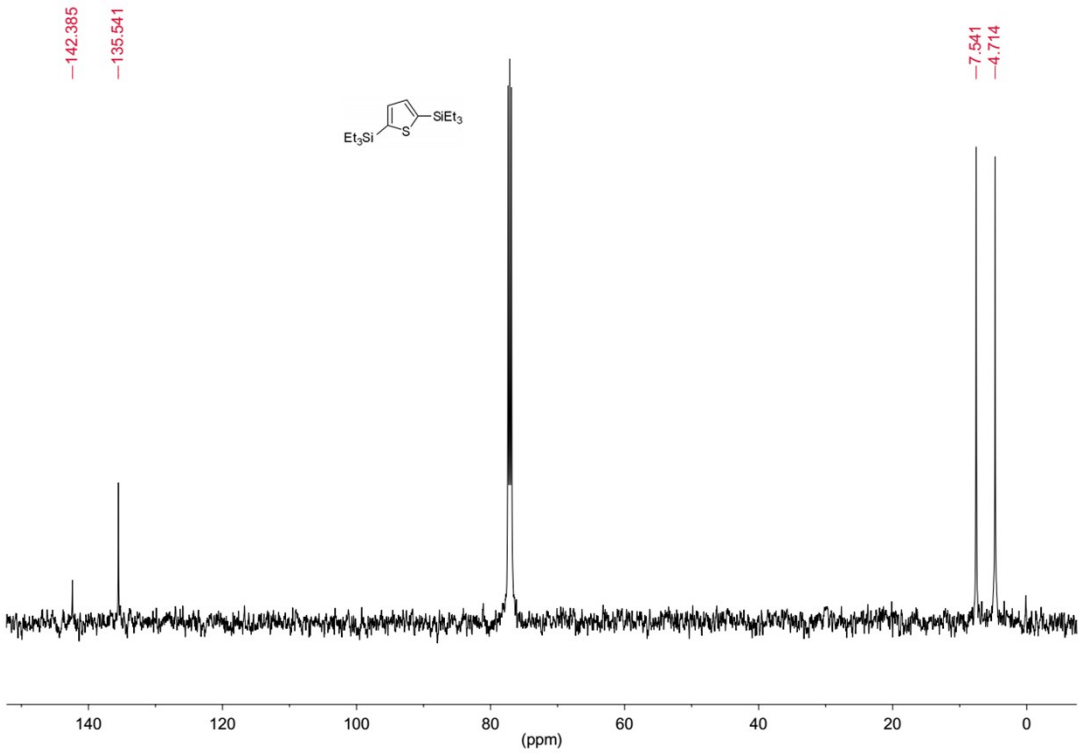


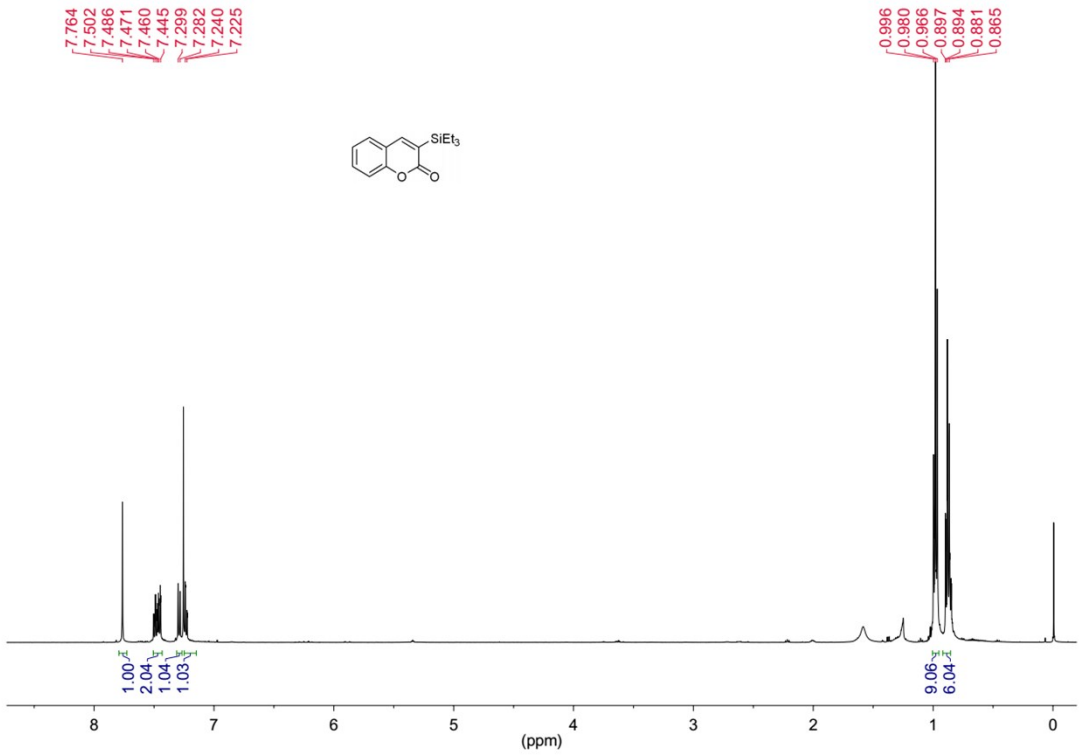
^{13}C NMR **5d**



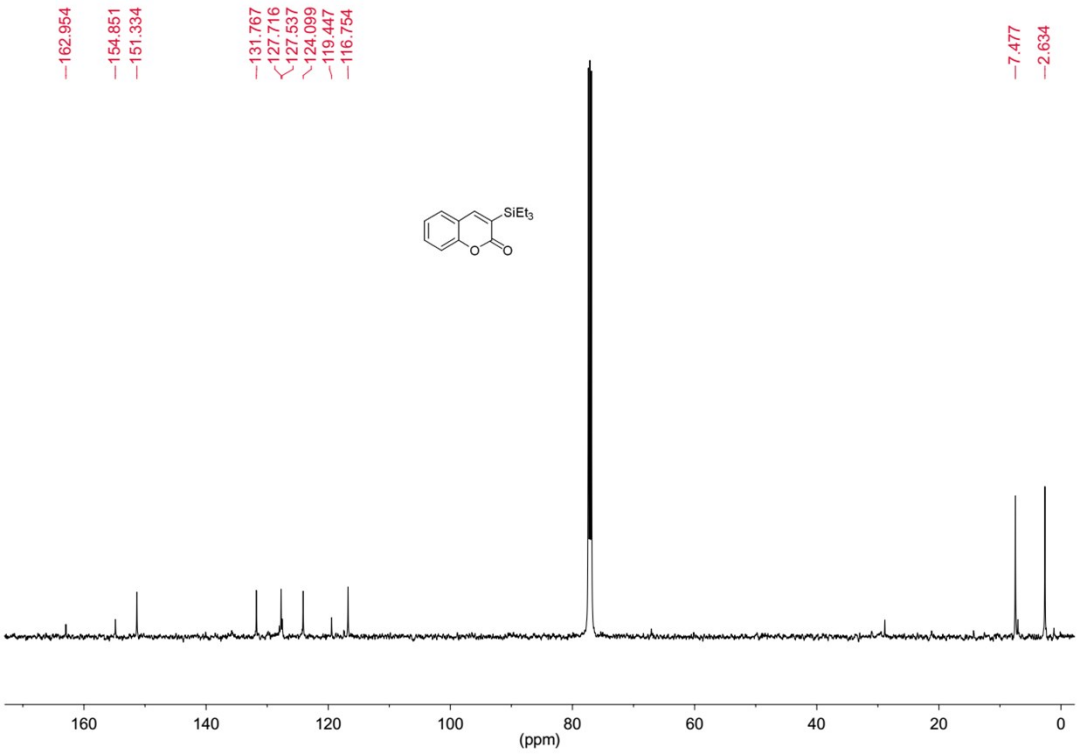
^{1}H NMR **5e**



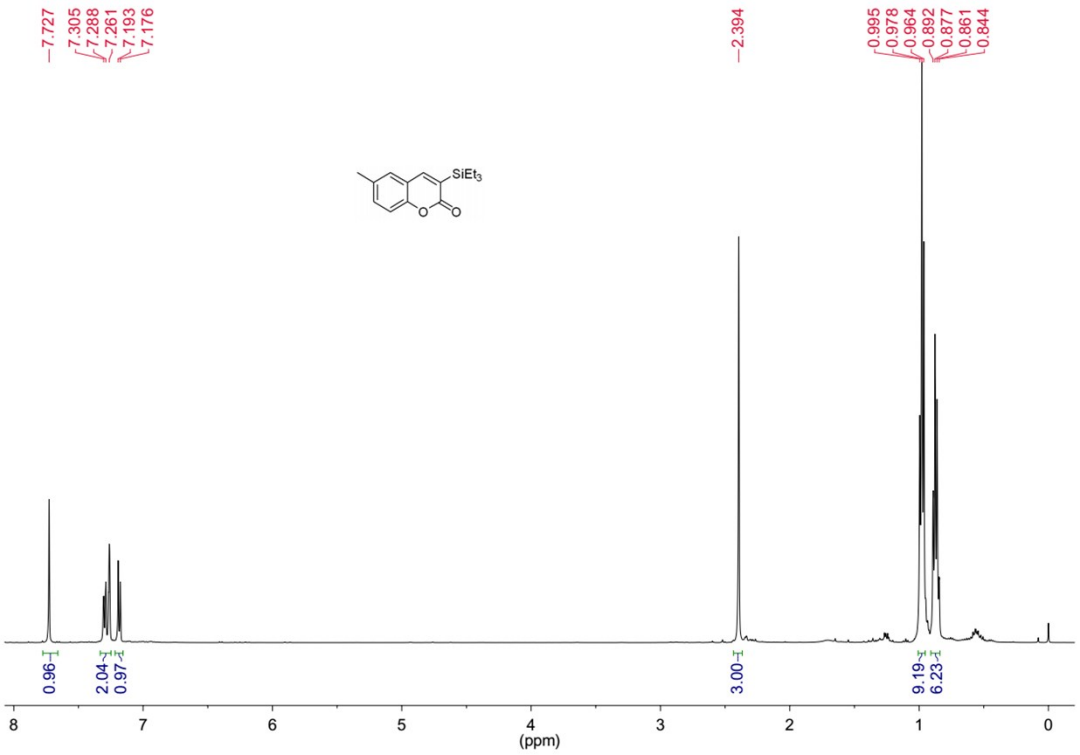
^{13}C NMR **5e**



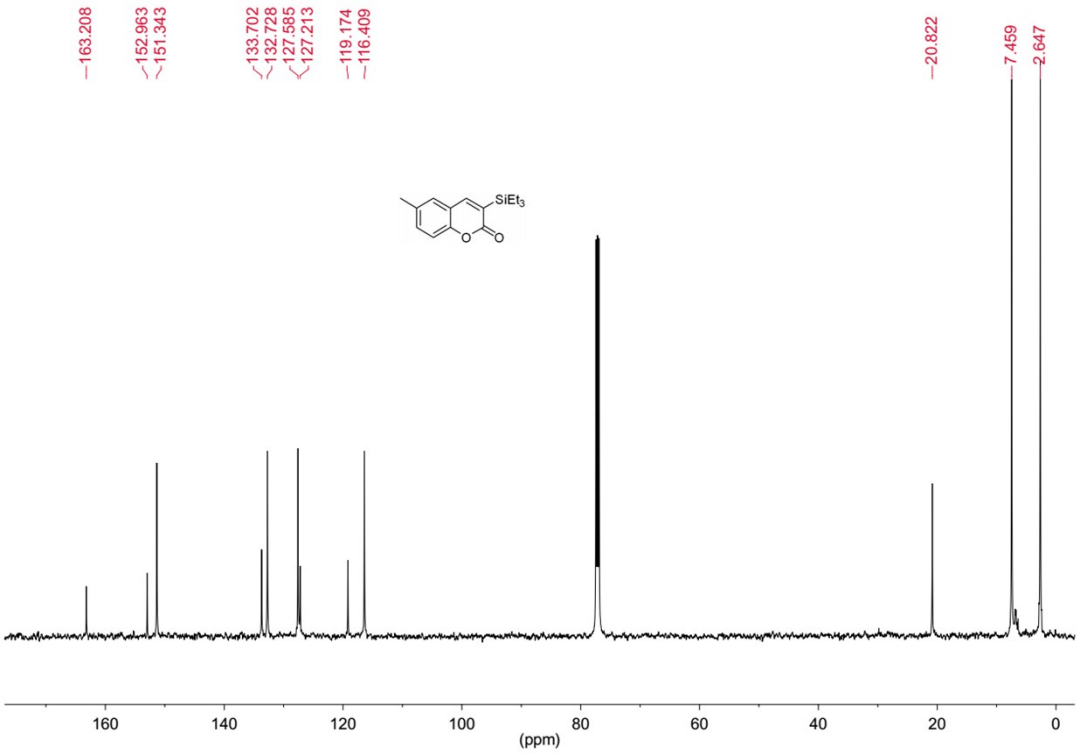
^{1}H NMR **5f**



^{13}C NMR **5f**



^{1}H NMR **5g**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151.343
133.702
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127.585
127.213
119.174
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7.459
2.647
SiEt3
O
O
160
140
120
100
80
60
40
20
0
(ppm)

^{13}C NMR **5g**