Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

A Free-Radical-Promoted Stereospecific Denitor Silylation of *β*-Nitroalkenes with Silanes

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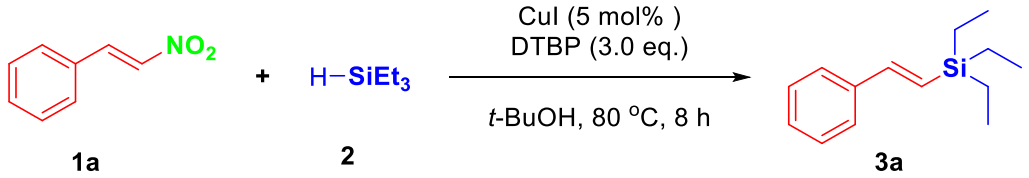
1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. ^{1}H NMR and ^{13}C NMR data analyses were performed with a Varian Mercury plus-400 and Agilent 600 MHz DD2 instruments $CDCl_3$ and DMSO-*d*6 as solvent and tetramethylsilane (TMS) as the internal standard were employed. Chemical shifts were reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm. The data of 1H NMR was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (J values) in Hz and integration. Chemical shift for ^{13}C NMR spectra were recorded in ppm from TMS using the central peak of $CDCl_3$ (77.0 ppm) as the internal standard. ^{19}F NMR spectra were recorded on a Varian Mercury 400 plus instrument. Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Melting points were measured with an XT-4 apparatus. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltonics APEX II 47e and Orbitrap Elite mass spectrometer. Column chromatography was generally performed on silica gel (200-300 mesh) and TLC analyses were conducted on silica gel GF254 plates. All reagents were directly used from purchased without any further purification unless otherwise specified.

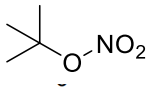
2. Typical Procedure for the Synthesis of 3

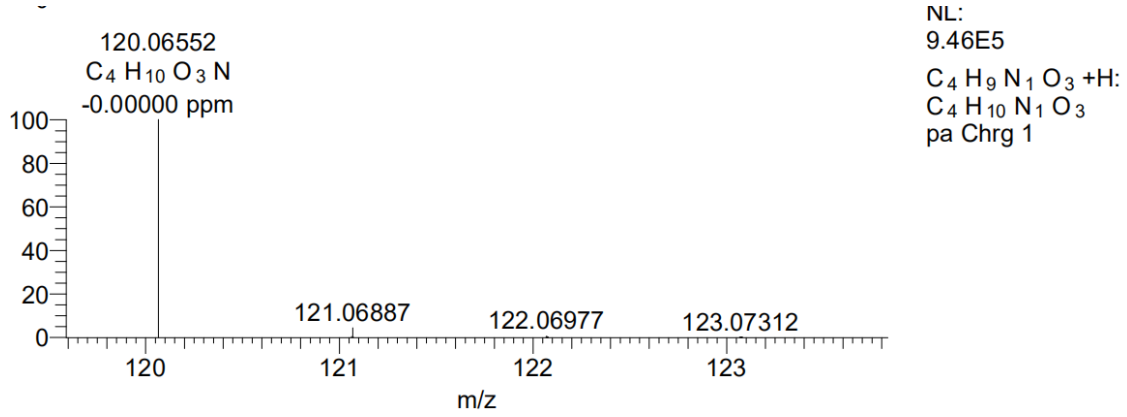


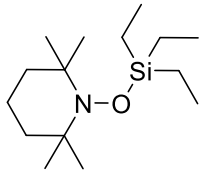
1a **2** **3a**

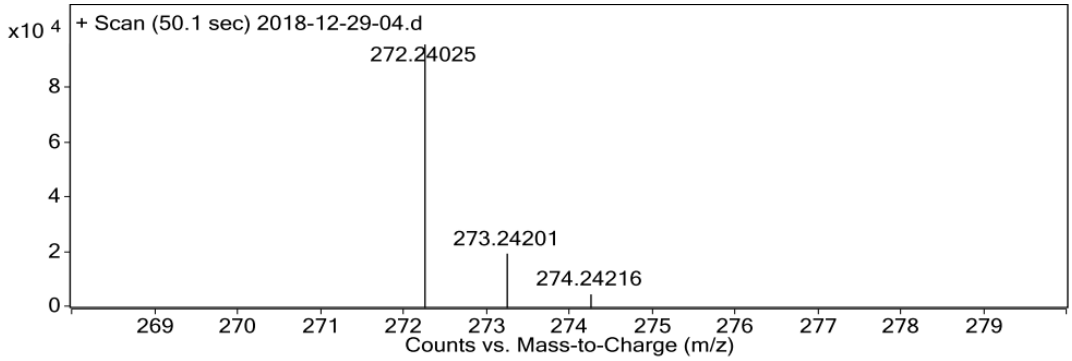
The mixture of (E)-(2-nitrovinyl)benzene **1a** (0.2 mmol), triethylsilane **2a** (1.0 mmol), CuI (5mol%) and DTBP(3.0 eq.) in *t*-BuOH (2 mL) was stirred at 80℃ for 8 hours under air atmosphere. After the reaction completed (monitored by TLC analysis), saturated aq. Na_2SO_3 was added to the mixture to quench the reaction and extracted with ethyl acetate (3×25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and the volatiles were removed in vacuum. The mixture was purified by using silica gel column chromatography (petroleum ether). The corresponding product **3a** was obtained as a colorless liquid (77 mg, 74% yield).

3. Mechanism supplemental data material.







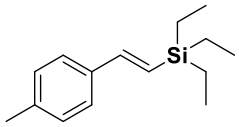


Peak List

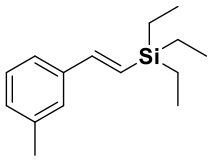
m/z	z	Abund	Formula	Ion
121.05088	1	94516.1		
126.12782	1	79775.9		
142.15859	1	994209		
143.16202	1	96963.7		
149.02282	1	63314.4		
158.15347	1	63827.9		
272.24025	1	95912.8	C15 H34 N O Si	(M+H)+

4. Spectroscopic Data of Compounds

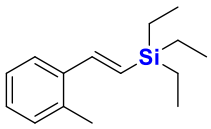
(*E*)-triethyl(styryl)silane (3a). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.89 (d, *J* = 19.2 Hz, 1H), 6.43 (dd, *J* = 19.2, 1.2 Hz, 1H), 0.99 (t, *J* = 7.2 Hz, 9H), 0.66 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 144.78, 138.50, 128.46, 127.85, 126.28, 125.93, 7.38, 3.51. HRMS (ESI) m/z: Calcd for $C_{14}H_{22}Si$: 305.1107 $[M+H]^+$, Found 305.1110.



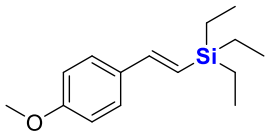
(*E*)-triethyl(4-methylstyryl)silane (3b). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 19.2 Hz, 1H), 6.37 (d, *J* = 19.2 Hz, 1H), 2.35 (s, 3H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.67 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 144.67, 137.70, 135.86, 129.15, 126.20, 124.51, 21.18, 7.39, 3.55. HRMS (ESI) m/z: Calcd for $C_{15}H_{24}Si$: 305.1107 $[M+H]^+$, Found 305.1111.



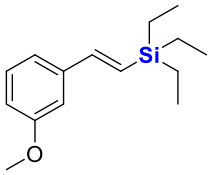
(*E*)-triethyl(3-methylstyryl)silane (3c). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.26 (s, 1H), 7.25 – 7.20 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 19.2 Hz, 1H), 6.40 (d, *J* = 19.2 Hz, 1H), 2.35 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.65 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 144.89, 138.45, 138.00, 128.63, 128.36, 126.95, 125.60, 123.47, 7.37, 3.51. HRMS (ESI) m/z: Calcd for $C_{15}H_{24}Si$: 305.1107 $[M+H]^+$, Found 305.1105.



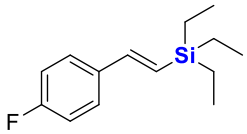
(*E*)-triethyl(2-methylstyryl)silane (3d). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.51 (dd, *J* = 7.2, 1.8 Hz, 1H), 7.19 – 7.11 (m, 4H), 6.29 (d, *J* = 19.2 Hz, 1H), 2.37 (s, 3H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 142.74, 138.00, 135.10, 130.20, 127.76, 127.59, 126.03, 125.27, 19.59, 7.38, 3.56. HRMS (ESI) m/z: Calcd for $C_{15}H_{24}Si$: 305.1107 $[M+H]^+$, Found 305.1110.



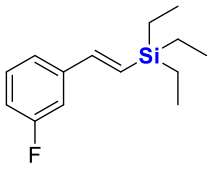
(*E*)-triethyl(4-methoxystyryl)silane (3e). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 9.0 Hz, 2H), 6.87 – 6.84 (m, 2H), 6.81 (s, 1H), 6.24 (d, *J* = 19.2 Hz, 1H), 3.81 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.64 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.47, 144.15, 131.56, 127.48, 123.02, 113.84, 55.29, 7.39, 3.57. HRMS (ESI) m/z: Calcd for $C_{15}H_{24}OSi$: 305.1107 $[M+H]^+$, Found 305.1110.



(*E*)-triethyl(3-methoxystyryl)silane (3f). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.23 (d, *J* = 8.4 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.97 (m, 1H), 6.86 (d, *J* = 19.2 Hz, 1H), 6.81 (dd, *J* = 7.8, 2.4 Hz, 1H), 6.41 (d, *J* = 19.2 Hz, 1H), 3.83 (s, 3H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.83, 144.61, 139.99, 129.41, 126.31, 119.04, 113.69, 111.33, 55.22, 7.37, 3.49. HRMS (ESI) m/z: Calcd for $C_{15}H_{24}OSi$: 305.1107 $[M+H]^+$, Found 305.1110.

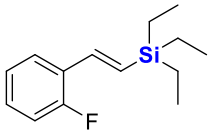


(*E*)-triethyl(4-fluorostyryl)silane (3g). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.42 – 7.38 (m, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 19.2 Hz, 1H), 6.32 (d, *J* = 19.2 Hz, 1H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.65 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 162.51 (m, *J* = 245.9 Hz), 143.46, 134.75 (d, *J* = 3.0 Hz), 127.78 (d, *J* = 8.0 Hz), 125.65 (d, *J* = 2.3 Hz), 115.30 (d, *J* = 21.4 Hz), 7.35, 3.48. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}FSi$: 237.1469 $[M+H]^+$, Found 237.1466.

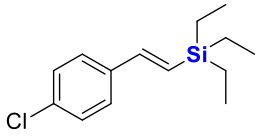


(*E*)-triethyl(3-fluorostyryl)silane (3h). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30 – 7.26 (m, 1H), 7.20 – 7.18 (m, 1H), 7.17 – 7.13 (m, 1H), 6.96 – 6.92 (m, 1H), 6.85 (d, *J* = 19.2 Hz, 1H), 6.45 (d, *J* = 19.2 Hz, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 163.18 (d, *J* = 243.8 Hz), 143.49 (d, *J* = 2.6 Hz), 140.90 (d, *J* = 7.1 Hz), 129.85(d, *J* = 8.1 Hz), 127.83, 122.24 (d, *J* = 2.7 Hz), 114.58 (d, *J* = 21.5 Hz), 112.56 (d, *J* = 21.3 Hz), 7.34, 3.43. HRMS (ESI) m/z: Calcd for

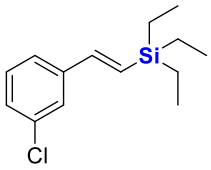
$C_{14}H_{21}FSi$: 237.1469 $[M+H]^+$, Found 237.1464.



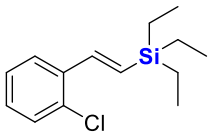
(*E*)-triethyl(2-fluorostyryl)silane (3i). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.57 – 7.53 (m, 1H), 7.23 – 7.18 (m, 1H), 7.13 – 7.08 (m, 2H), 7.04 – 7.00 (m, 1H), 6.48 (d, *J* = 20.4 Hz, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 160.12 (d, *J* = 247.8 Hz), 136.40 (d, *J* = 4.7 Hz), 129.03 (d, *J* = 8.4 Hz), 128.97 (d, *J* = 3.3 Hz), 126.62 (d, *J* = 3.6 Hz), 126.34 (d, *J* = 11.6 Hz), 123.92 (d, *J* = 3.8 Hz), 115.63 (d, *J* = 22.2 Hz), 7.34, 3.45. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}FSi$: 237.1469 $[M+H]^+$, Found 237.1472.



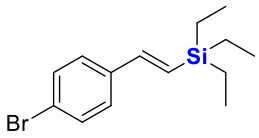
(*E*)-(4-chlorostyryl)triethylsilane (3j). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.37 – 7.34 (m, 2H), 7.30 – 7.27 (m, 2H), 7.24 (d, *J* = 10.0 Hz, 1H), 6.82 (d, *J* = 19.3 Hz, 1H), 6.39 (d, *J* = 19.2 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.65 (q, *J* = 7.9 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.38, 136.96, 133.44, 128.59, 127.47, 126.94, 7.35, 3.44. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}ClSi$: 253.1174 $[M+H]^+$, Found 253.1177



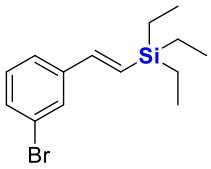
(*E*)-(3-chlorostyryl)triethylsilane (3k). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.43 (t, *J* = 1.9 Hz, 1H), 7.30 – 7.28 (m, 1H), 7.27 – 7.23 (m, 1H), 7.22 – 7.20 (m, 1H), 6.82 (d, *J* = 19.2 Hz, 1H), 6.45 (d, *J* = 19.2 Hz, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.28, 140.37, 134.53, 129.64, 128.10, 127.70, 126.18, 124.54, 7.32, 3.44. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}ClSi$: 253.1174 $[M+H]^+$, Found 253.1179



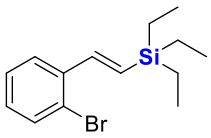
(*E*)-(2-chlorostyryl)triethylsilane (3l). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.60 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.23 (m 1H), 7.17 (m, 1H), 6.42 (d, *J* = 19.2 Hz, 1H), 1.00 (t, *J* = 7.8 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 140.75, 136.60, 133.02, 129.66, 129.59, 128.69, 126.72, 126.62, 7.35, 3.49. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}ClSi$: 253.1174 $[M+H]^+$, Found 253.1172



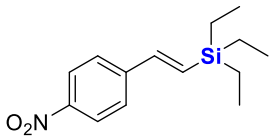
(*E*)-(4-bromostyryl)triethylsilane (3m). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.42 (m, 2H), 7.32 – 7.28 (m, 2H), 6.82 (d, *J* = 19.2 Hz, 1H), 6.42 (d, *J* = 19.2 Hz, 1H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.65 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.43, 137.39, 131.54, 127.80, 127.16, 121.65, 7.36, 3.43. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}BrSi$: 297.0669 $[M+H]^+$, Found 297.0674.



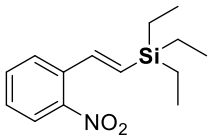
(*E*)-(3-bromostyryl)triethylsilane (3n). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (t, *J* = 1.6 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 19.2 Hz, 1H), 6.45 (d, *J* = 19.2 Hz, 1H), 1.00 (t, *J* = 8.0 Hz, 9H), 0.67 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.14, 140.61, 130.61, 129.96, 129.13, 128.17, 124.99, 122.77, 7.34, 3.41. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}BrSi$: 297.0669 $[M+H]^+$, Found 297.0674.



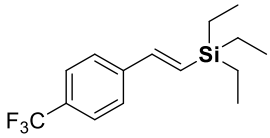
(*E*)-(2-bromostyryl)triethylsilane (3o). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.57 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.27 (m, 1H), 7.22 (s, 1H), 7.11 – 7.07 (m, 1H), 6.36 (d, *J* = 19.2 Hz, 1H), 1.00 (t, *J* = 7.8 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 143.49, 138.36, 132.80, 129.89, 128.93, 127.36, 126.90, 123.61, 7.33, 3.50. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}BrSi$: 297.0669 $[M+H]^+$, Found 297.0673.



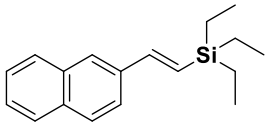
(*E*)-triethyl(4-nitrostyryl)silane (3p). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.21 – 8.17 (m, 2H), 7.57 – 7.53 (m, 2H), 6.93 (d, *J* = 19.2 Hz, 1H), 6.66 (d, *J* = 19.2 Hz, 1H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.13, 132.13, 130.52, 129.34, 122.30, 120.82, 7.33, 3.35. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}NO_2Si$: 263.1342 $[M+H]^+$, Found 263.1344.



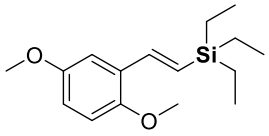
(*E*)-triethyl(2-nitrostyryl)silane (3q). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.89 (d, *J* = 9.0 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 19.2 Hz, 1H), 6.44 (d, *J* = 19.2 Hz, 1H), 1.00 (t, *J* = 7.8 Hz, 9H), 0.68 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.76, 133.14, 132.88, 128.53, 128.08, 124.20, 7.29, 3.36. HRMS (ESI) m/z: Calcd for $C_{14}H_{21}NO_2Si$: 263.1342 $[M+H]^+$, Found 263.1343.



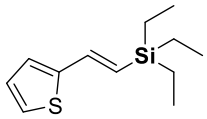
(*E*)-triethyl(4-(trifluoromethyl)styryl)silane (3r). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 7.2 Hz, 2H), 6.90 (d, *J* = 19.2 Hz, 1H), 6.54 (d, *J* = 19.2 Hz, 1H), 0.98 (t, *J* = 8.4 Hz, 9H), 0.67 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.23, 141.72, 129.72, 126.41, 125.41 (q, *J* = 3.9 Hz), 123.28, 109.99, 7.32, 3.39. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.88. HRMS (ESI) m/z: Calcd for $C_{15}H_{21}F_3Si$: 287.1437 $[M+H]^+$, Found 287.1439.



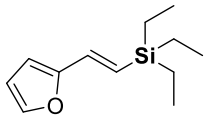
(*E*)-triethyl(2-(naphthalen-2-yl)vinyl)silane (3w). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.75 (m, 4H), 7.68 (dd, *J* = 9.6, 1.6 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.06 (d, *J* = 19.2 Hz, 1H), 6.55 (d, *J* = 19.2 Hz, 1H), 1.01 (t, *J* = 7.6 Hz, 9H), 0.69 (q, *J* = 7.6 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 144.79, 135.92, 133.59, 133.23, 128.12, 128.05, 127.62, 126.47, 126.15, 125.87, 123.29, 7.42, 3.55. HRMS (ESI) m/z: Calcd for $C_{18}H_{24}Si$: 269.1720 $[M+H]^+$, Found 269.1724.



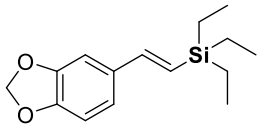
(*E*)-(2,5-dimethoxystyryl)triethylsilane (3s). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.27 (d, *J* = 19.8 Hz, 1H), 7.10 (d, *J* = 3.0 Hz, 1H), 6.81 – 6.76 (m, 2H), 6.37 (d, *J* = 19.2 Hz, 1H), 3.80 (d, *J* = 2.4 Hz, 6H), 0.99 (t, *J* = 7.8 Hz, 9H), 0.67 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 153.78, 151.11, 138.83, 128.59, 126.51, 114.05, 112.60, 111.28, 56.41, 55.76, 7.41, 3.58. HRMS (ESI) m/z: Calcd for $C_{16}H_{26}O_2Si$: 279.1775 $[M+H]^+$, Found 279.1779.



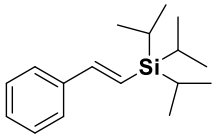
(*E*)-triethyl(2-(thiophen-2-yl)vinyl)silane (3t). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.29 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.26 – 7.25 (m, 1H), 7.19 (dd, *J* = 3.0, 1.2 Hz, 1H), 6.89 (d, *J* = 19.2 Hz, 1H), 6.19 (d, *J* = 19.2 Hz, 1H), 0.98 (t, *J* = 7.8 Hz, 9H), 0.64 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 142.33, 138.60, 125.79, 125.58, 124.85, 122.32, 7.37, 3.48. HRMS (ESI) m/z: Calcd for $C_{12}H_{20}SSi$: 225.1128 $[M+H]^+$, Found 225.1131.



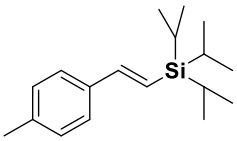
(*E*)-triethyl(2-(furan-2-yl)vinyl)silane (3u). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36 (d, *J* = 2.0 Hz, 1H), 6.68 (d, *J* = 19.6 Hz, 1H), 6.38 (dd, *J* = 3.2, 2.0 Hz, 1H), 6.29 (d, *J* = 13.6 Hz, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 0.97 (t, *J* = 7.8 Hz, 9H), 0.63 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 154.22, 142.06, 132.26, 124.23, 111.34, 107.72, 7.33, 3.41. HRMS (ESI) m/z: Calcd for $C_{12}H_{20}OSi$: 209.1356 $[M+H]^+$, Found 209.1359.



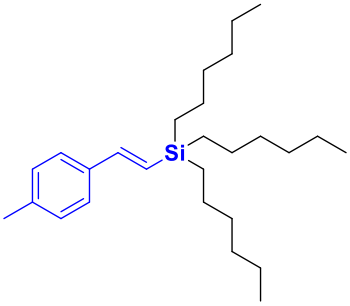
(*E*)-(2-(benzo[d][1,3]dioxol-5-yl)vinyl)triethylsilane (3v). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (d, *J* = 1.6 Hz, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.76 (d, *J* = 4.0 Hz, 1H), 6.21 (d, *J* = 19.2 Hz, 1H), 5.95 (s, 2H), 0.98 (t, *J* = 8.0 Hz, 9H), 0.64 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.04, 147.43, 144.14, 133.34, 123.58, 121.26, 108.10, 105.40, 101.03, 7.38, 3.54. HRMS (ESI) m/z: Calcd for $C_{15}H_{22}O_2Si$: 263.1462 $[M+H]^+$, Found 263.1465.



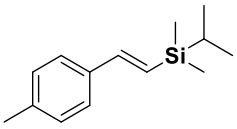
(*E*)-triisopropyl(styryl)silane (3aa). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 6.6 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 3.6 Hz, 1H), 6.94 (d, *J* = 19.2 Hz, 1H), 6.39 (d, *J* = 19.2 Hz, 1H), 1.21 – 1.16 (m, 3H), 1.09 (d, *J* = 7.2 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.54, 138.68, 128.46, 127.80, 126.24, 123.96, 18.66, 11.00. HRMS (ESI) m/z: Calcd for $C_{17}H_{28}Si$: 260.1960 $[M+H]^+$, Found 260.1965.



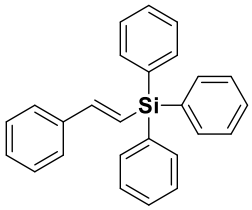
(*E*)-triisopropyl(4-methylstyryl)silane (3x). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 19.6 Hz, 1H), 6.33 (d, *J* = 19.6 Hz, 1H), 2.35 (s, 3H), 1.23 – 1.12 (m, 3H), 1.09 (d, *J* = 6.8 Hz, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.41, 137.68, 136.04, 129.15, 126.15, 122.53, 21.17, 18.67, 11.02. HRMS (ESI) m/z: Calcd for $C_{18}H_{30}Si$: 275.2190 $[M+H]^+$, Found 275.2194.



(*E*)-trihexyl(4-methylstyryl)silane (3z). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 19.2 Hz, 1H), 6.40 (d, *J* = 19.2 Hz, 1H), 2.38 (s, 3H), 1.37 – 1.31 (m, 23H), 0.95 – 0.91 (m, 10H), 0.73 – 0.63 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 144.21, 129.13, 126.18, 125.63, 33.47, 31.54, 23.81, 22.61, 21.17, 14.11, 12.65. HRMS (ESI) m/z: Calcd for $C_{27}H_{48}Si$: 401.3598 $[M+H]^+$, Found 401.3601.



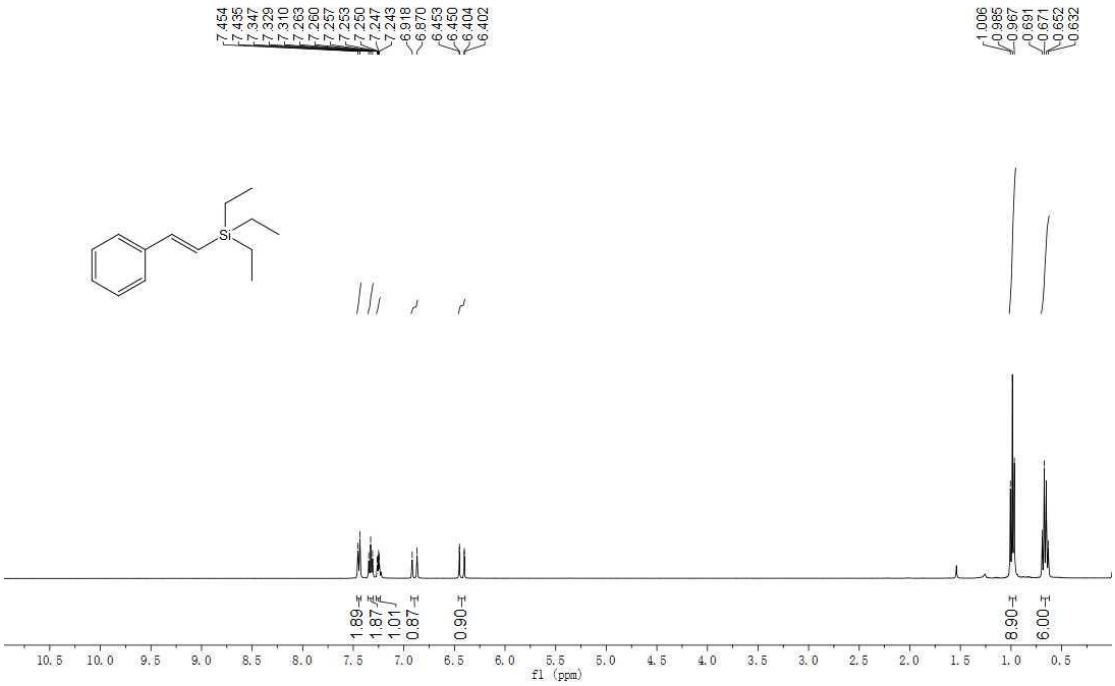
(*E*)-isopropyldimethyl(4-methylstyryl)silane (3y). Colourless Oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 19.2 Hz, 1H), 6.41 (d, *J* = 19.2 Hz, 1H), 2.34 (s, 3H), 0.91 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 144.71, 137.76, 135.75, 129.15, 126.23, 125.37, 26.48, 21.18, 16.77, -0.03, -6.08. HRMS (ESI) m/z: Calcd for $C_{14}H_{22}Si$: 219.1564 $[M+H]^+$, Found 219.1566.

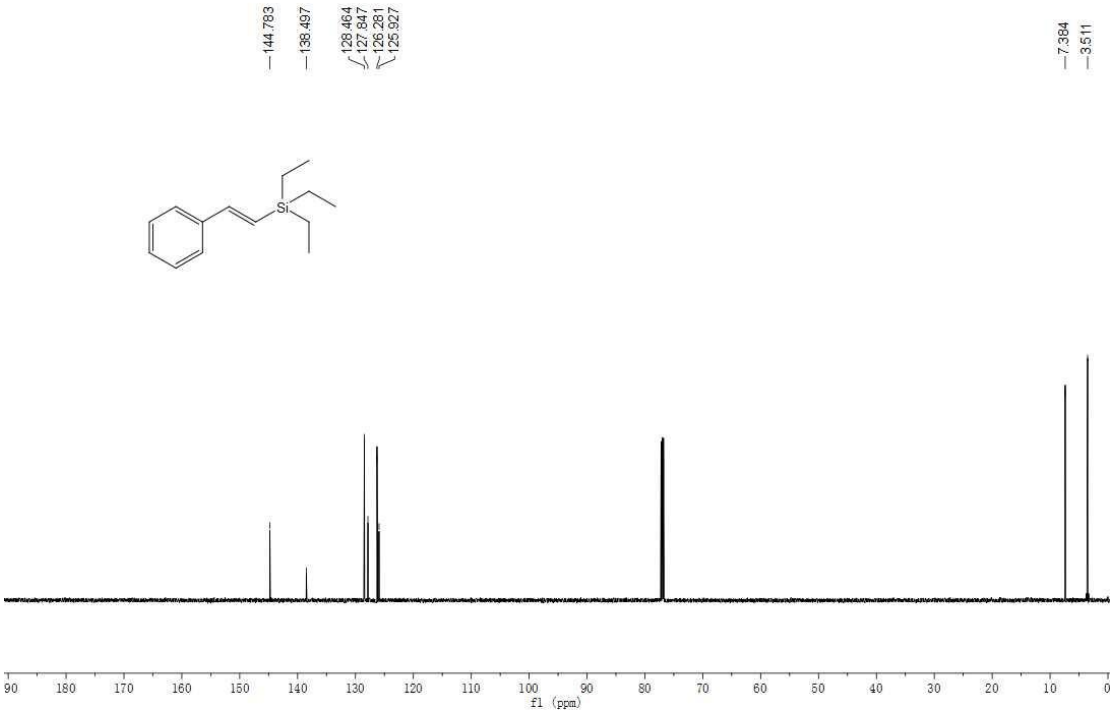


(*E*)-triphenyl(styryl)silane (3ab). Colourless Oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.61 (dd, *J* = 7.8, 1.2 Hz, 6H), 7.52 – 7.49 (m, 2H), 7.46 – 7.44 (m, 2H), 7.42 – 7.39 (m, 7H), 7.38 – 7.34 (m, 2H), 7.31 – 7.28 (m, 1H), 7.01 (d, *J* = 4.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.88, 138.02, 136.03, 135.49, 134.47, 129.60, 128.56, 128.51, 127.92, 127.62, 122.93. HRMS (ESI) m/z: Calcd for $C_{26}H_{22}Si$: 363.1564 $[M+H]^+$, Found 363.1569.

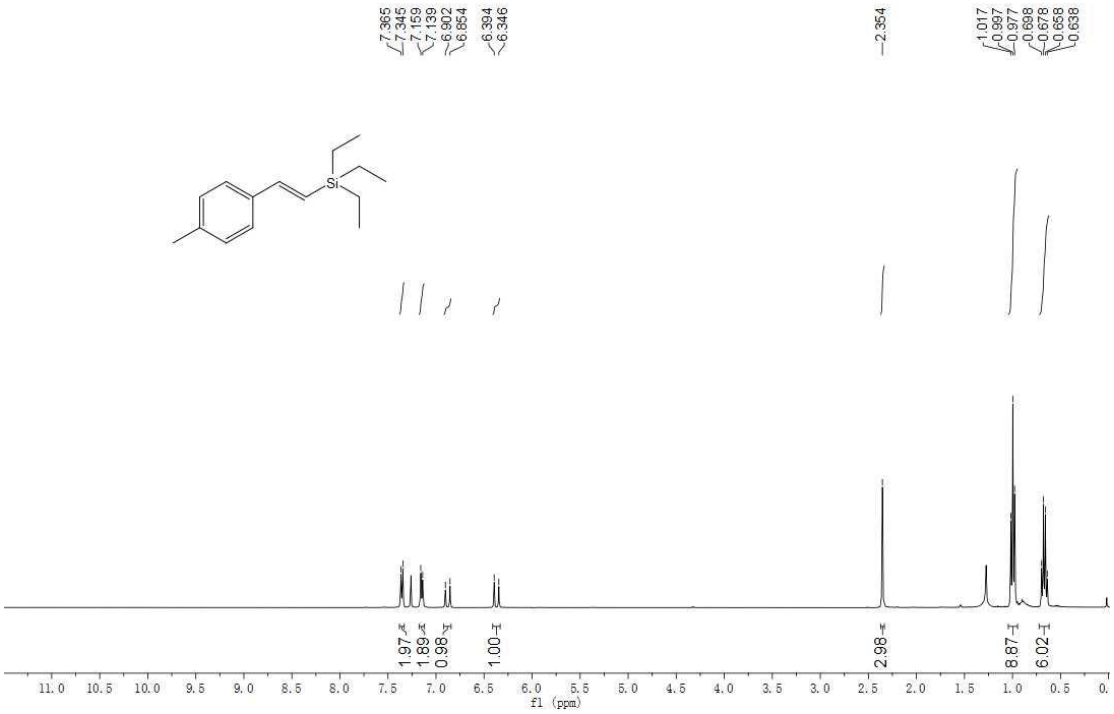
5. Copies of ^{1}H NMR and ^{13}C NMR Spectra for Compound

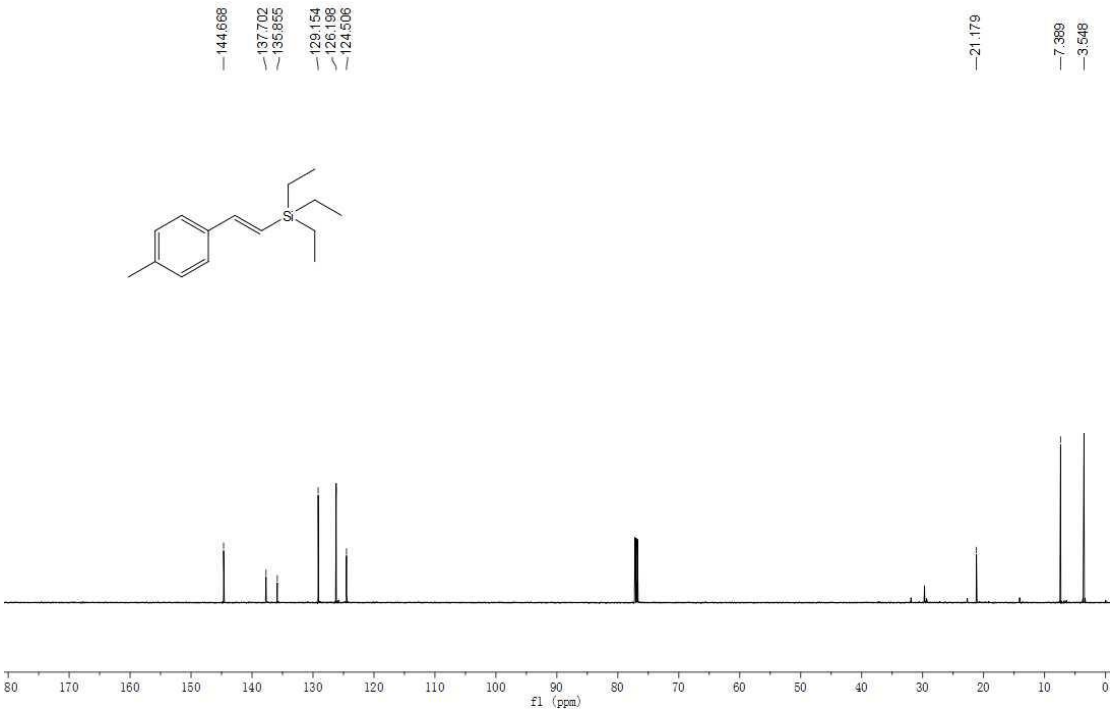
^{1}H and ^{13}C Spectra of compound 3a ($CDCl_3$)



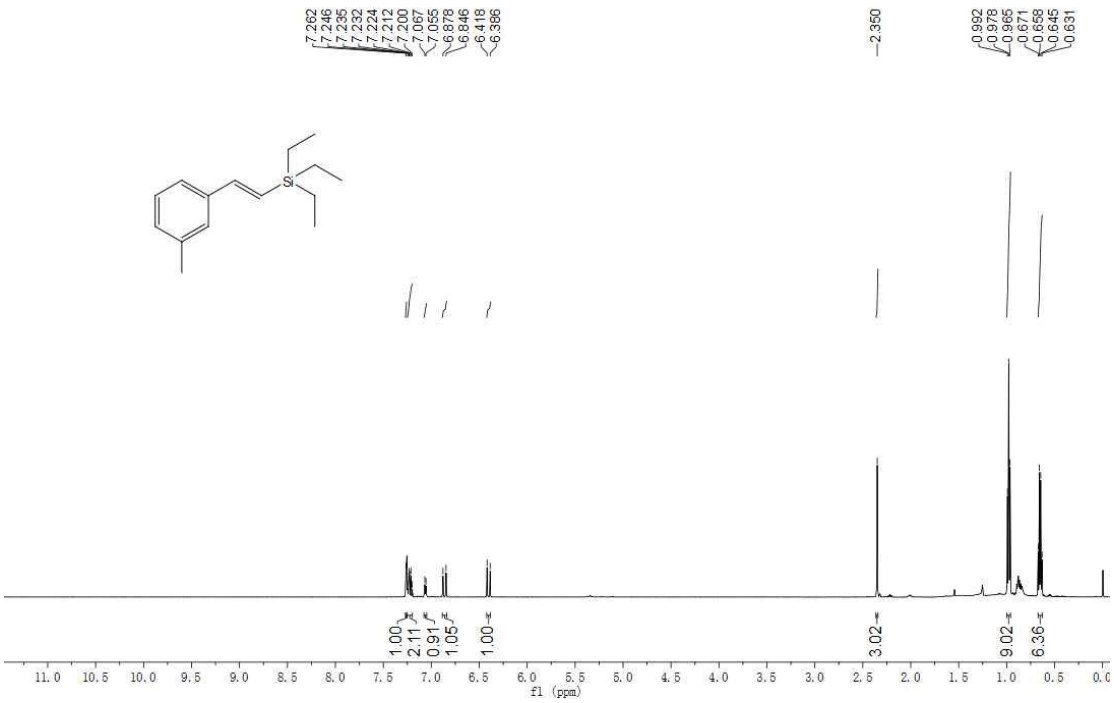


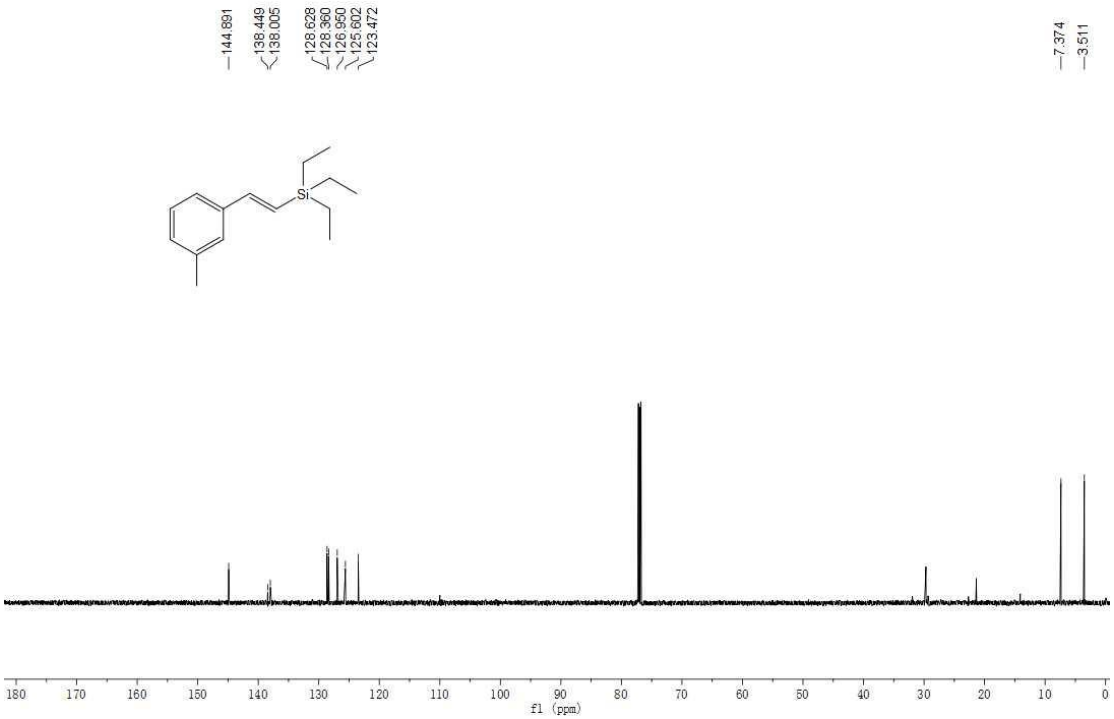
^{1}H and ^{13}C Spectra of compound 3b ($CDCl_3$)



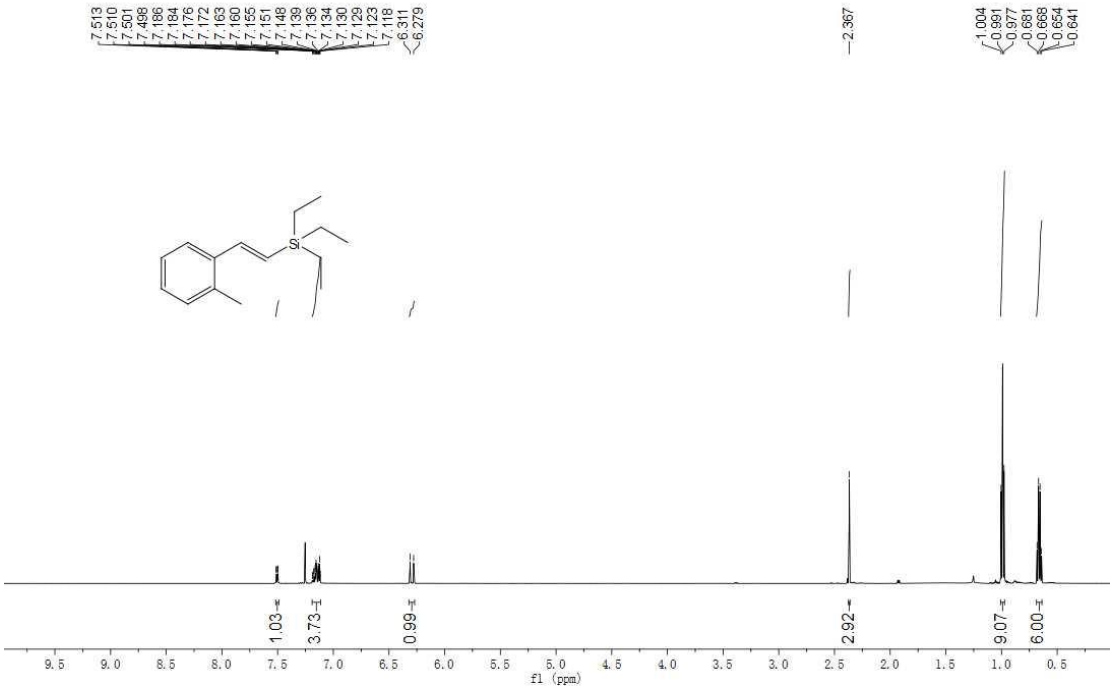


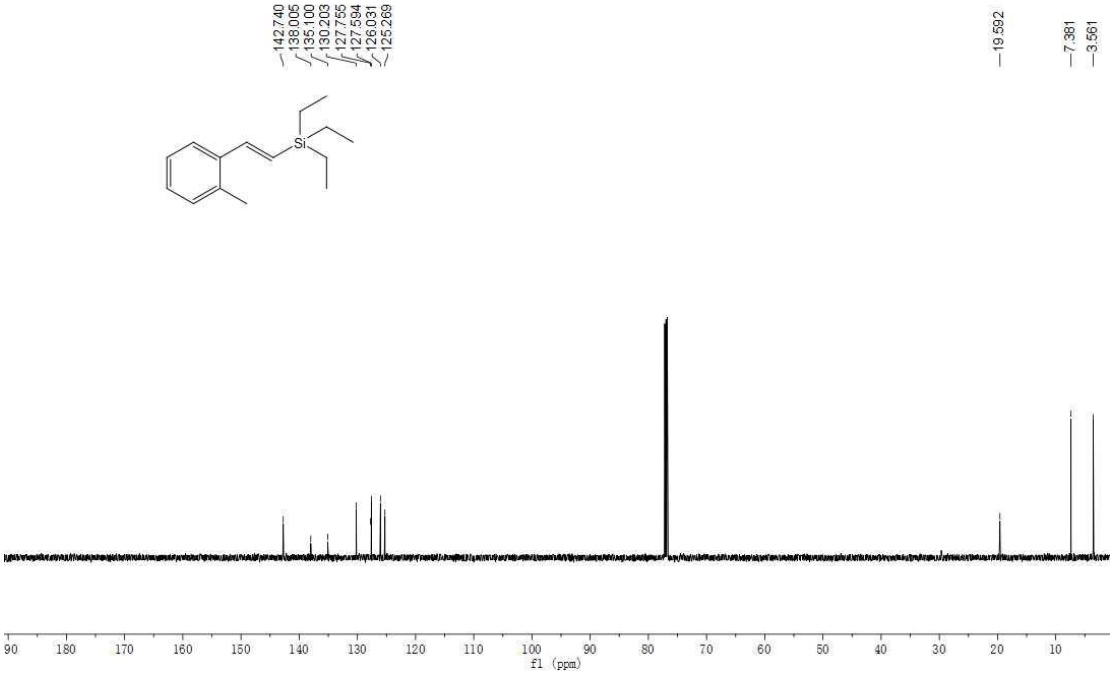
^{1}H and ^{13}C Spectra of compound 3c ($CDCl_3$)



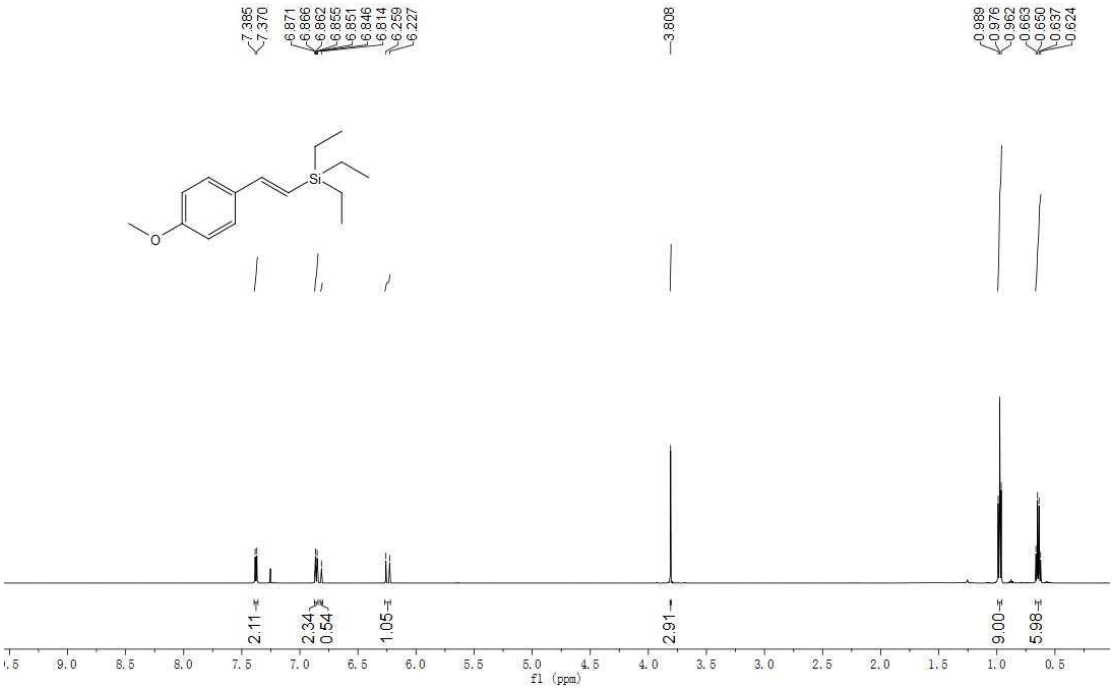


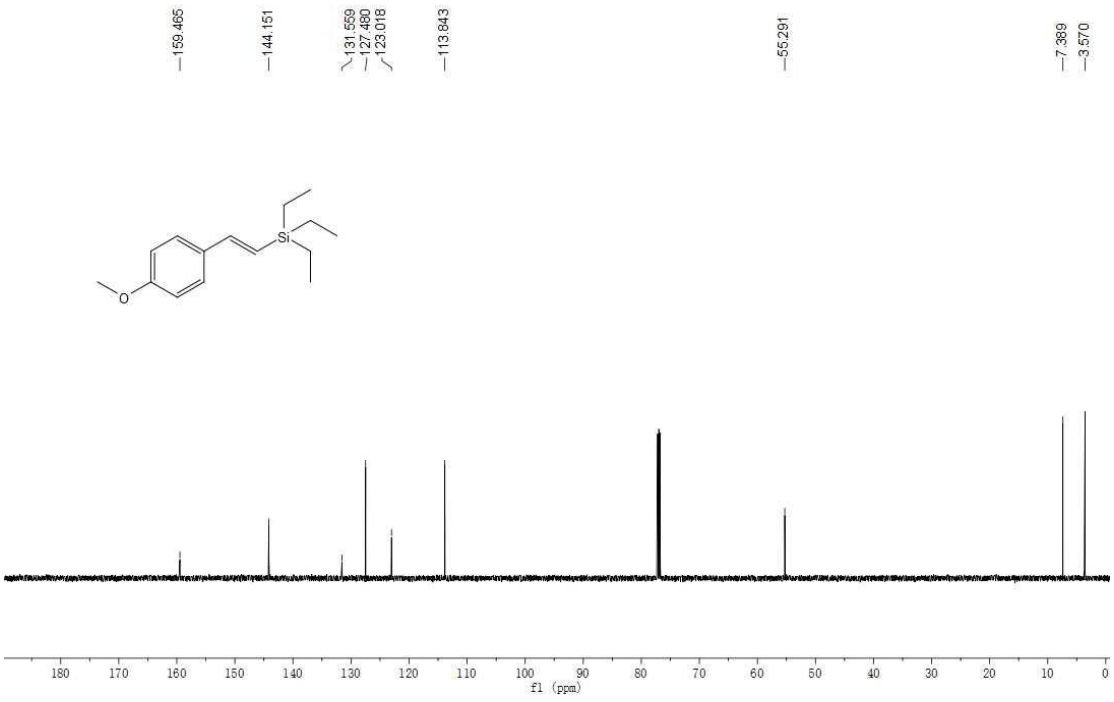
^{1}H and ^{13}C Spectra of compound 3d ($CDCl_3$)



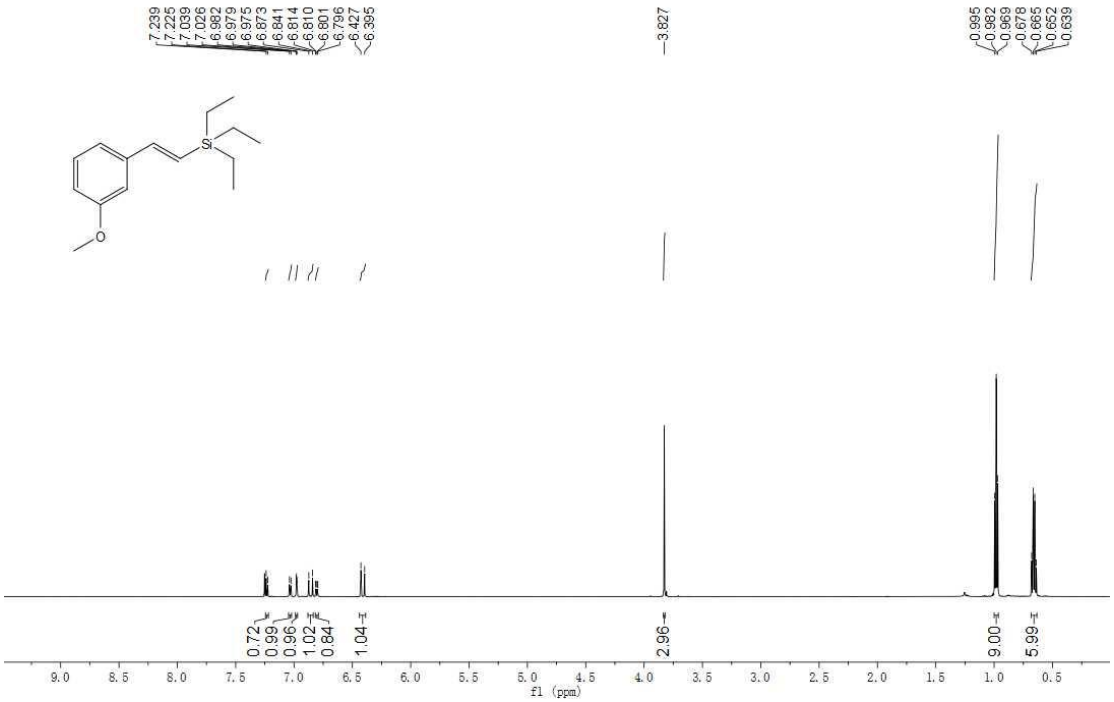


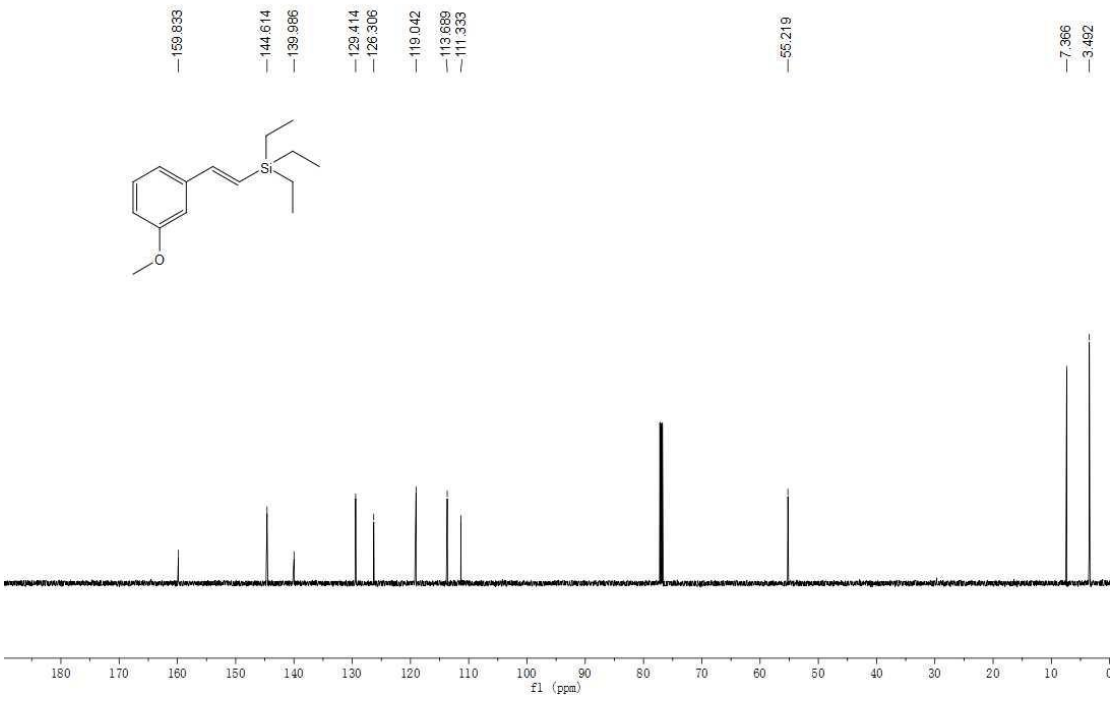
^{1}H and ^{13}C Spectra of compound 3e ($CDCl_3$)



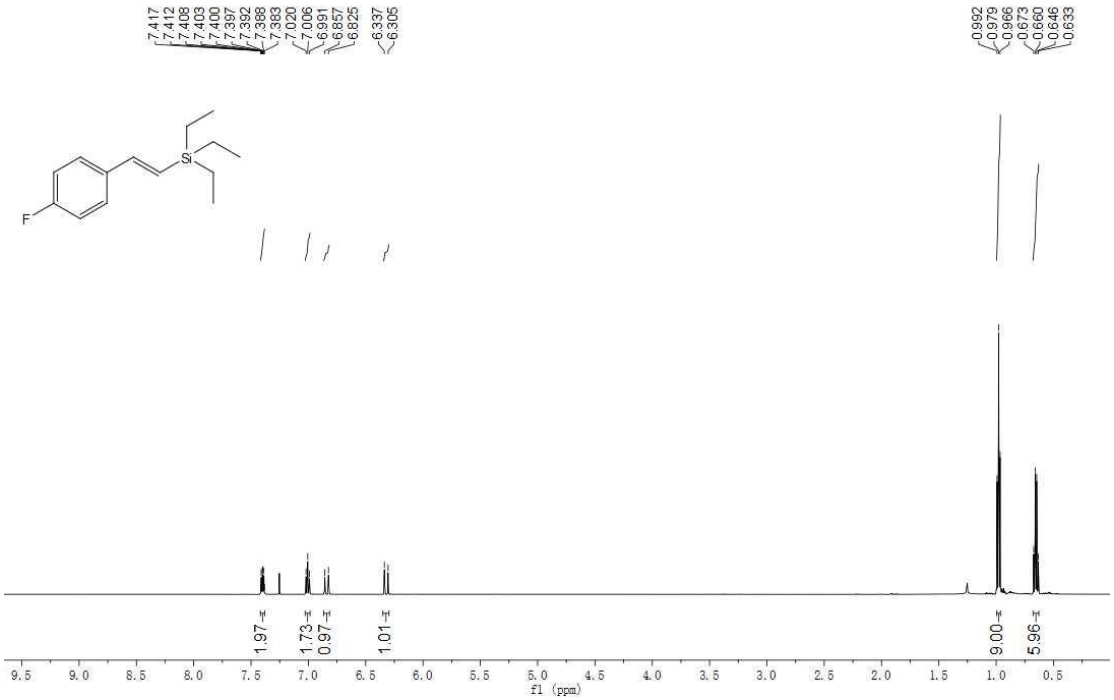


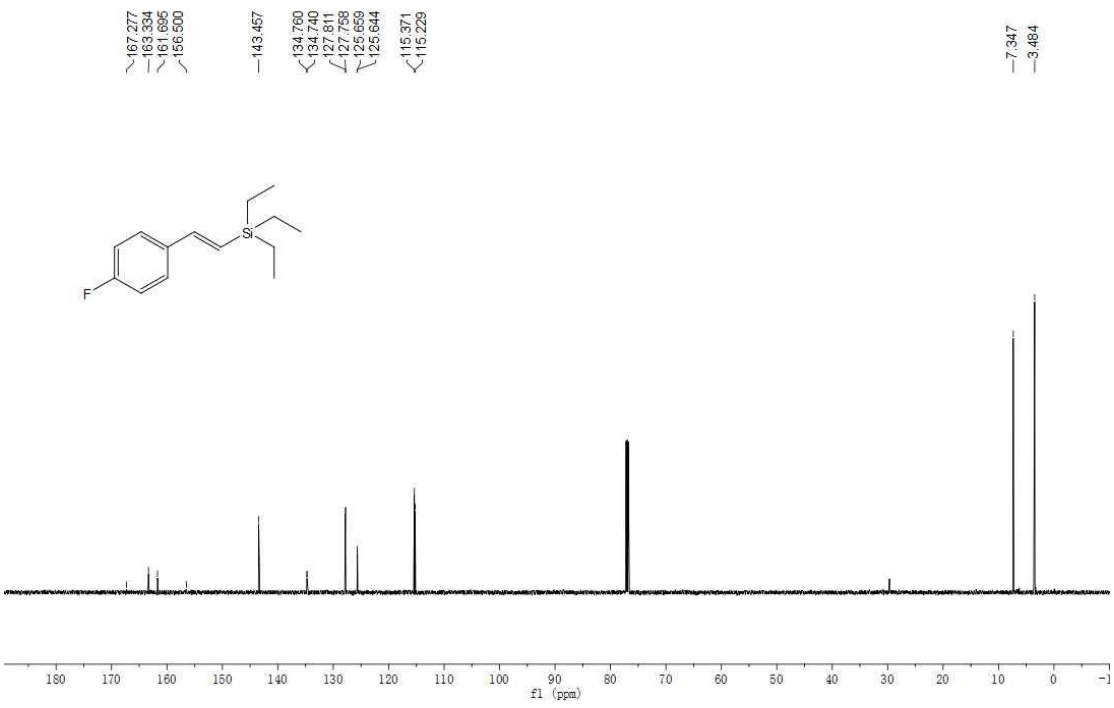
^{1}H and ^{13}C Spectra of compound 3f ($CDCl_3$)



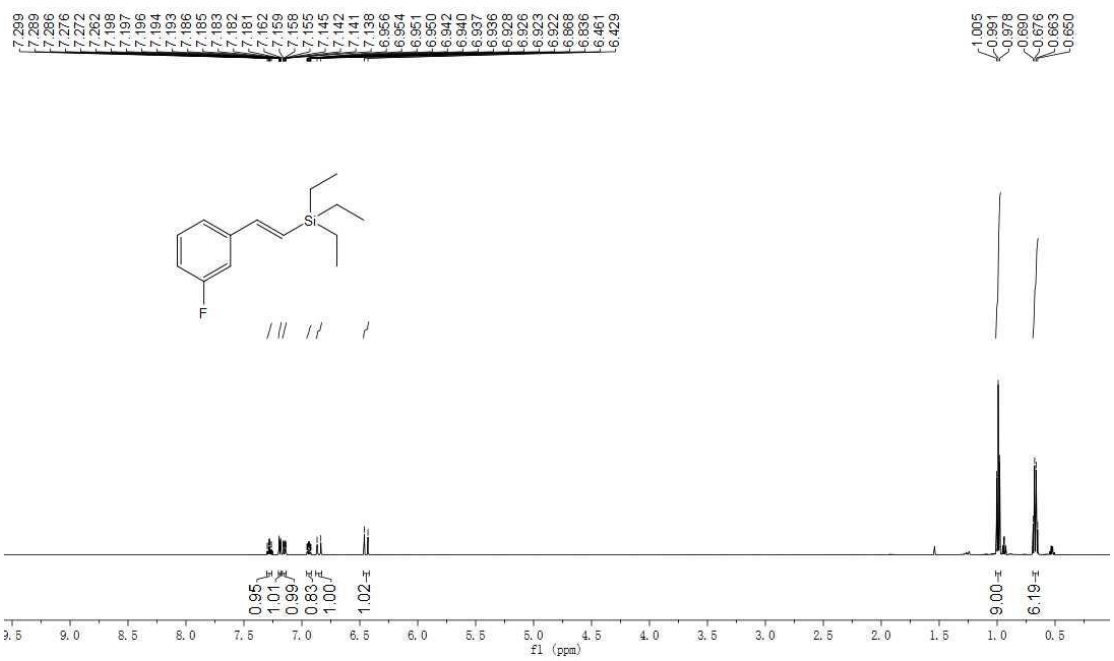


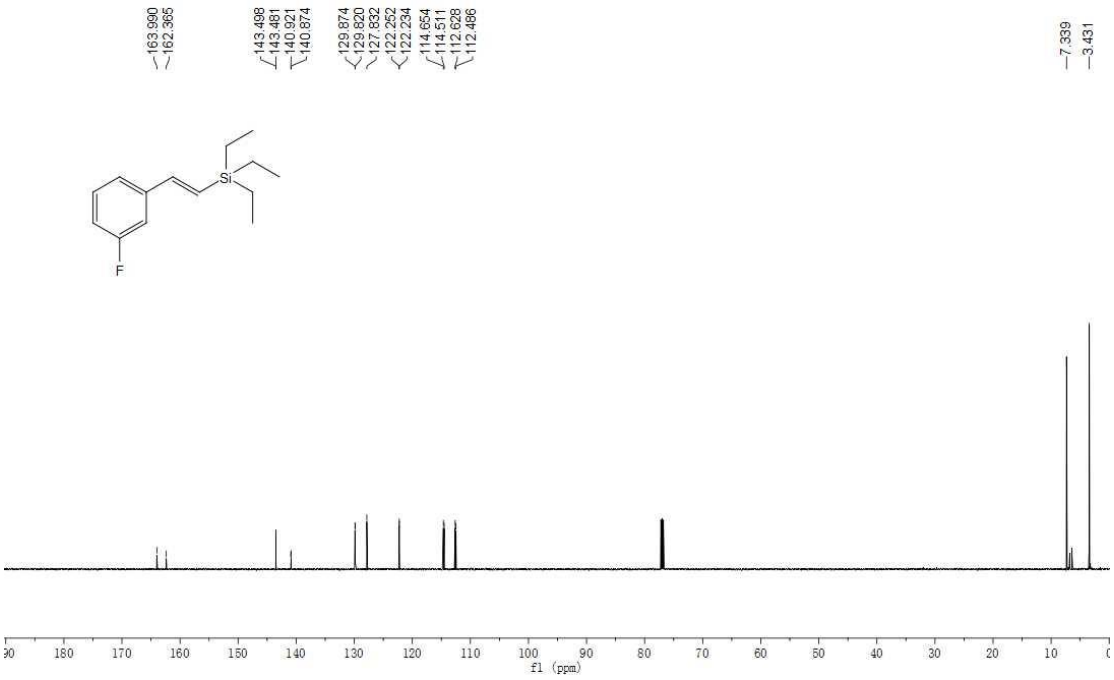
^{1}H and ^{13}C Spectra of compound 3g ($CDCl_3$)



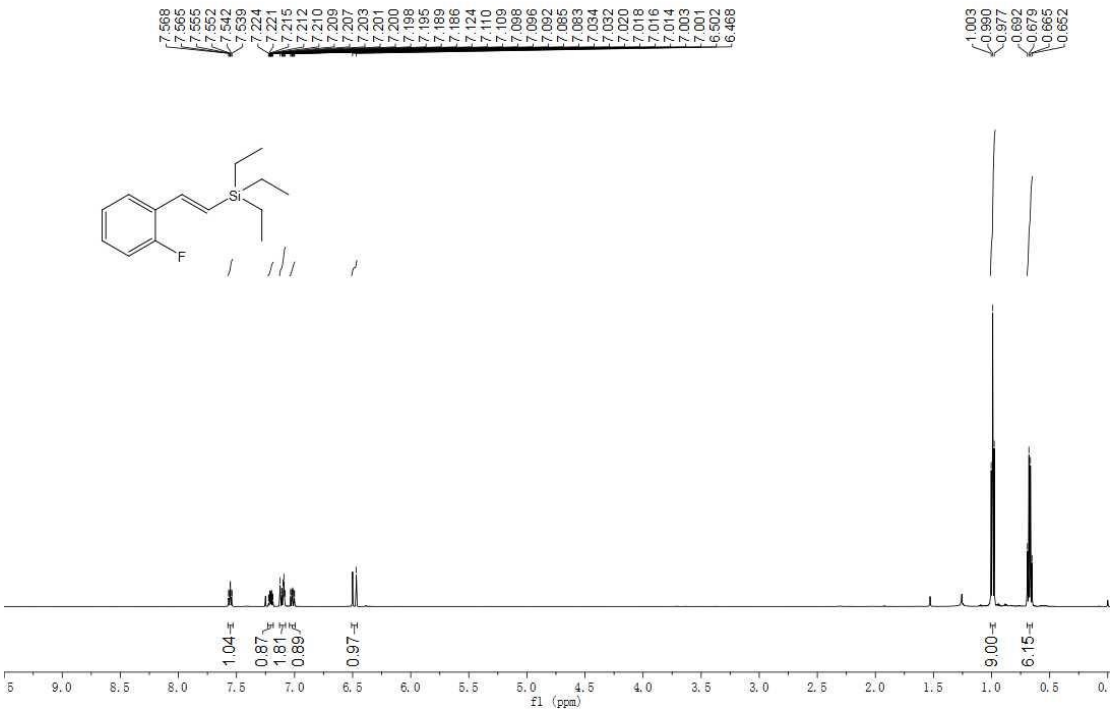


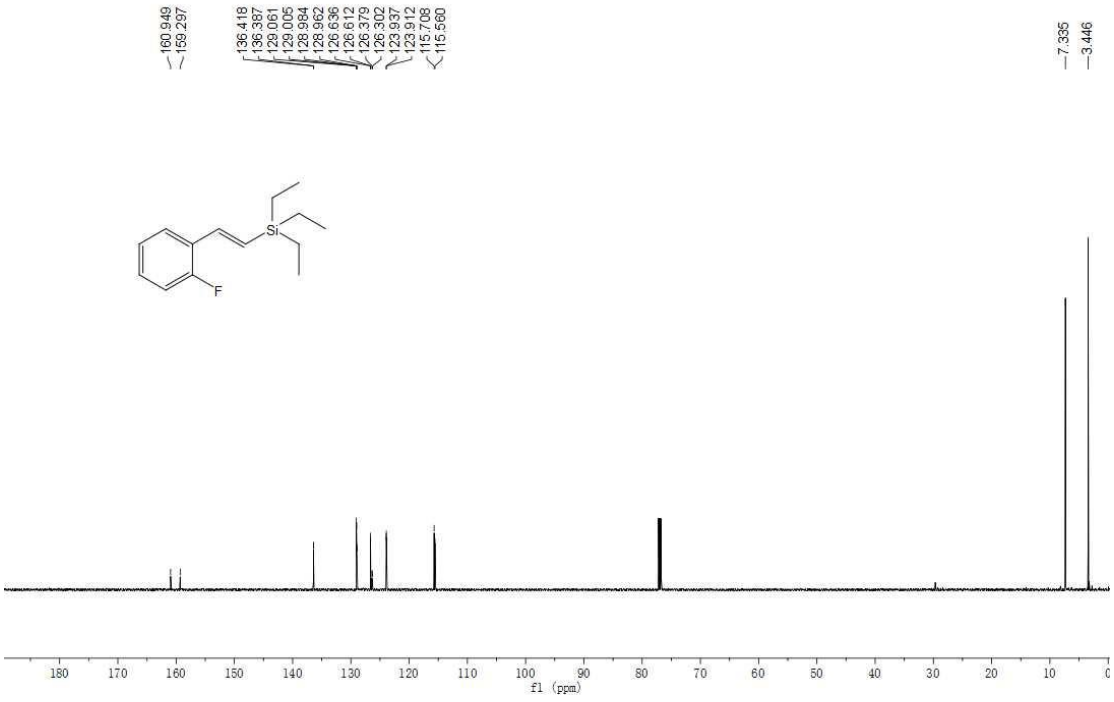
^{1}H and ^{13}C Spectra of compound 3h ($CDCl_3$)



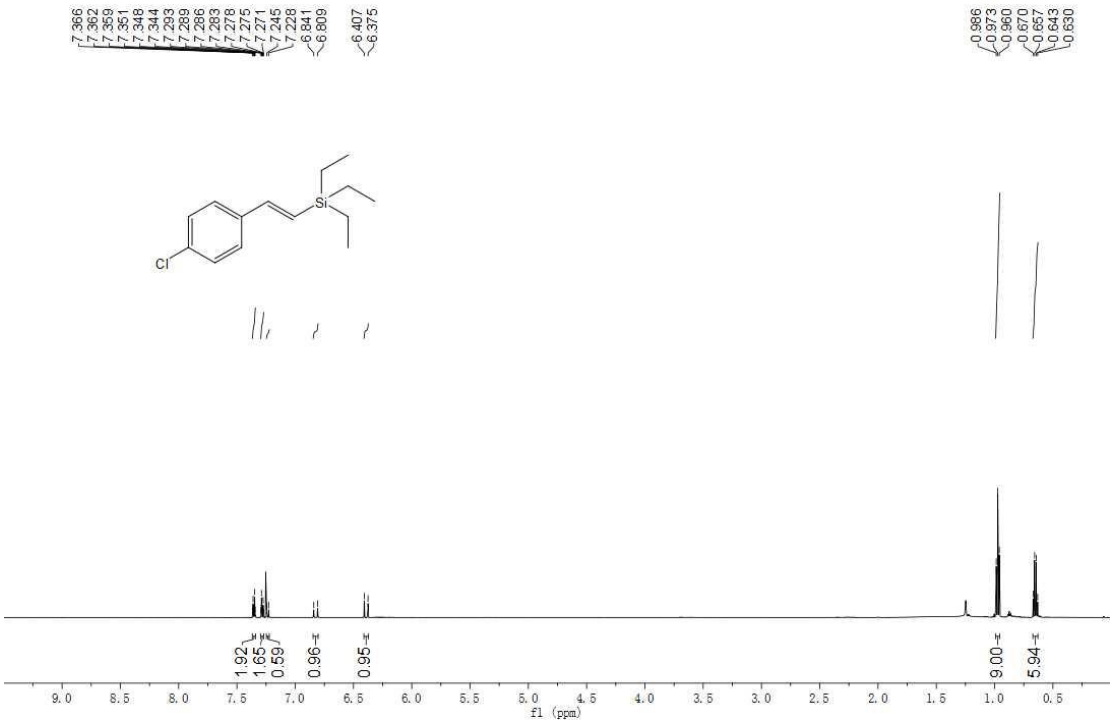


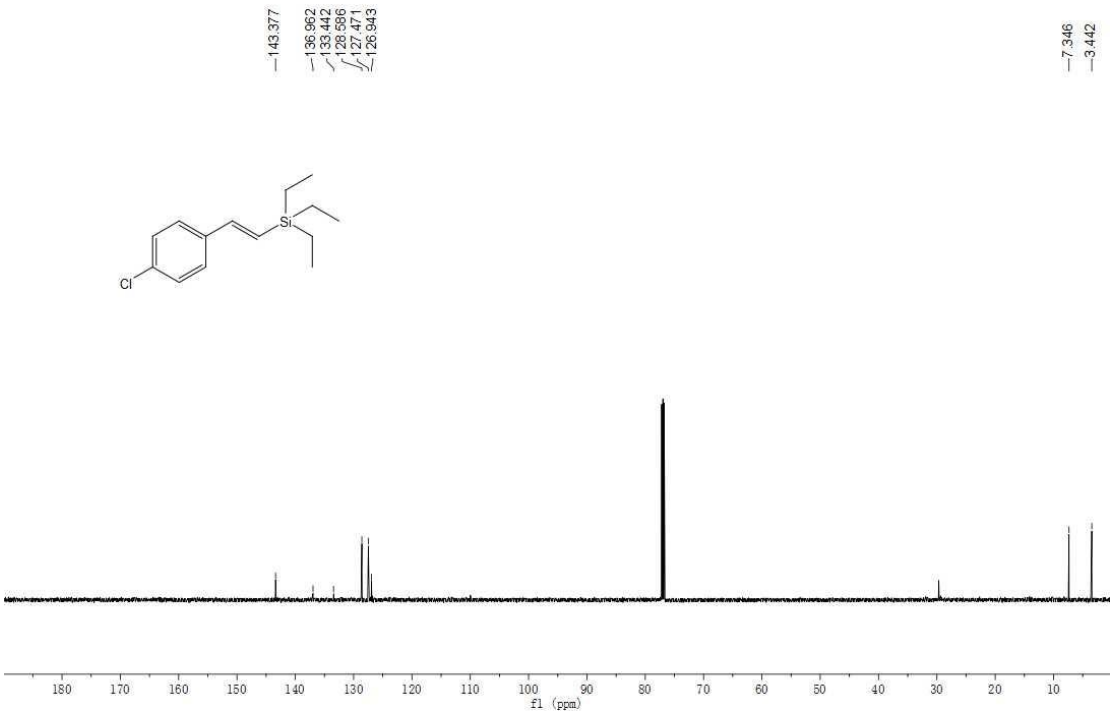
^{1}H and ^{13}C Spectra of compound 3i ($CDCl_3$)



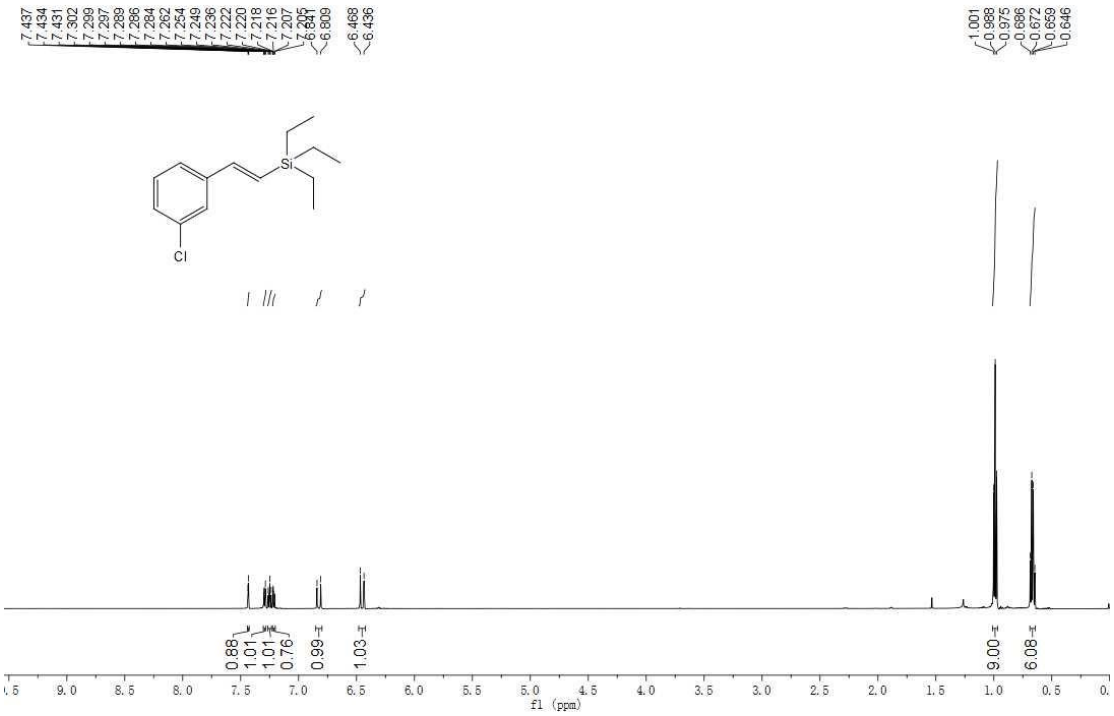


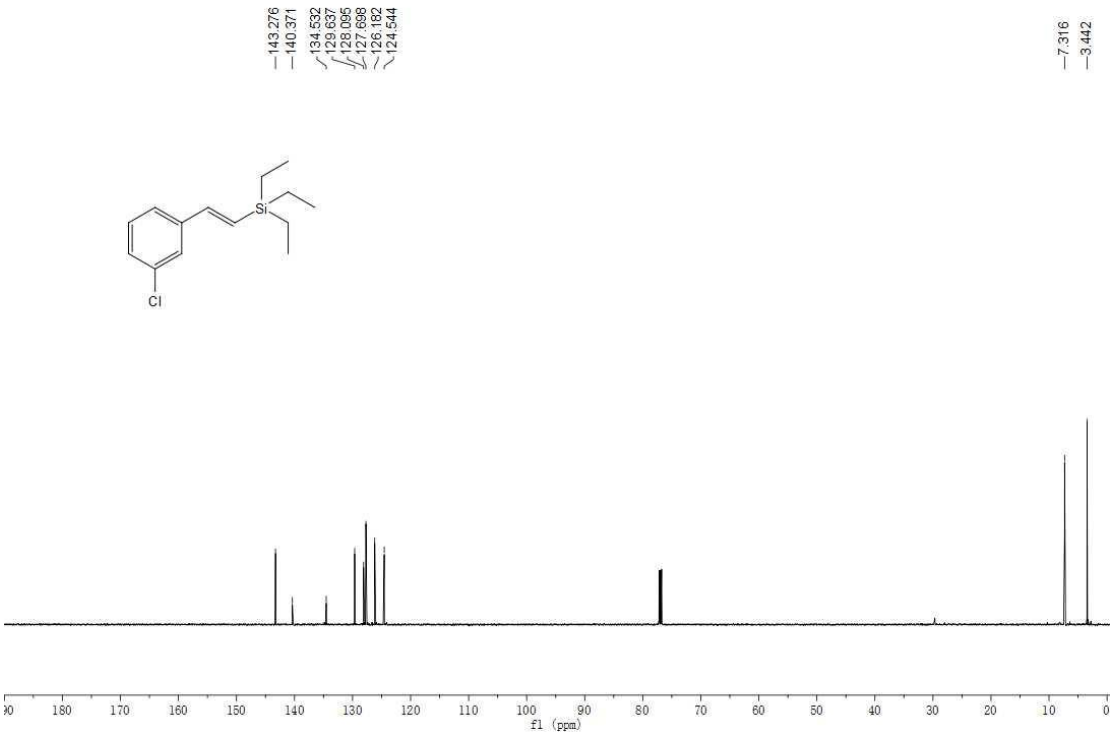
^{1}H and ^{13}C Spectra of compound 3j ($CDCl_3$)



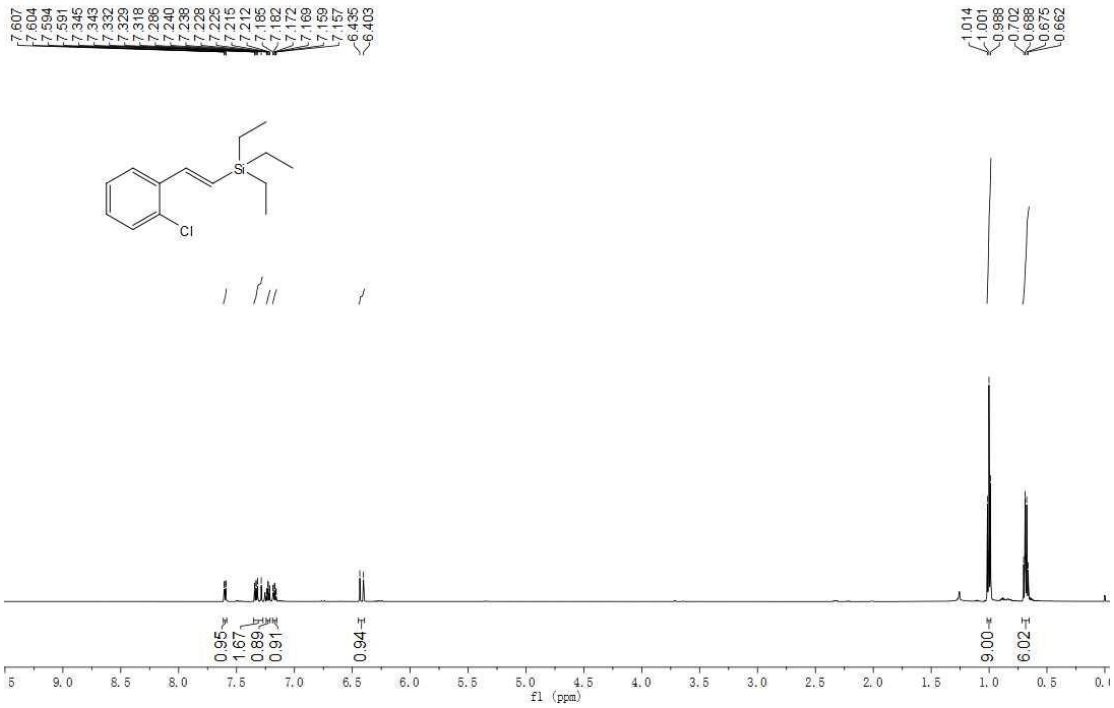


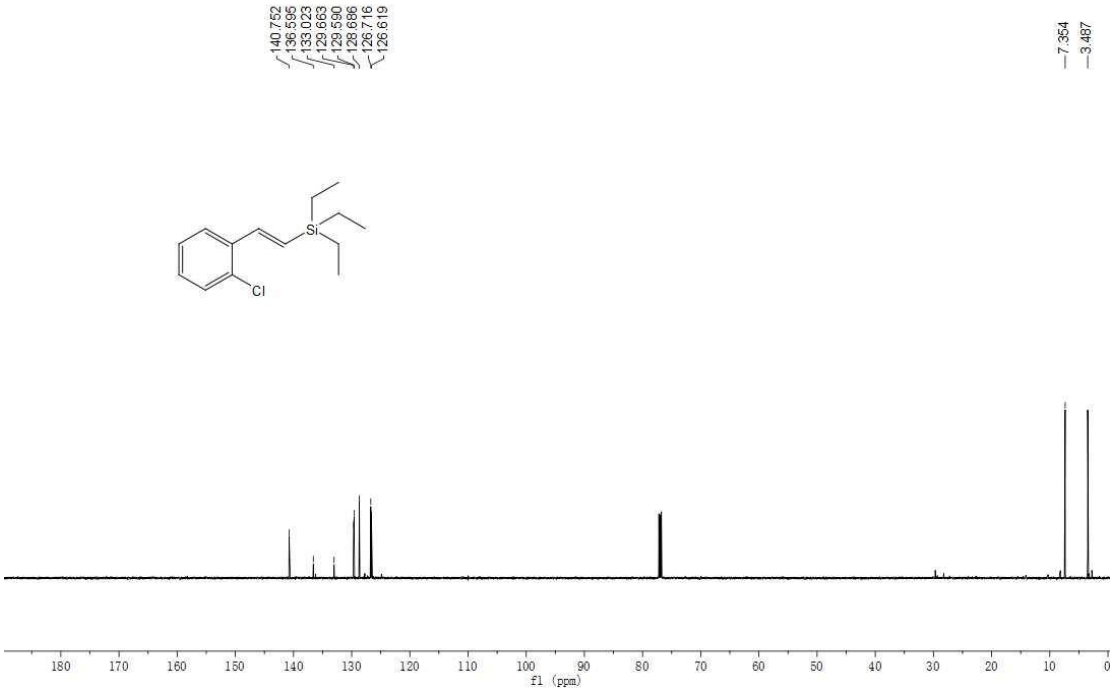
^{1}H and ^{13}C Spectra of compound 3k ($CDCl_3$)



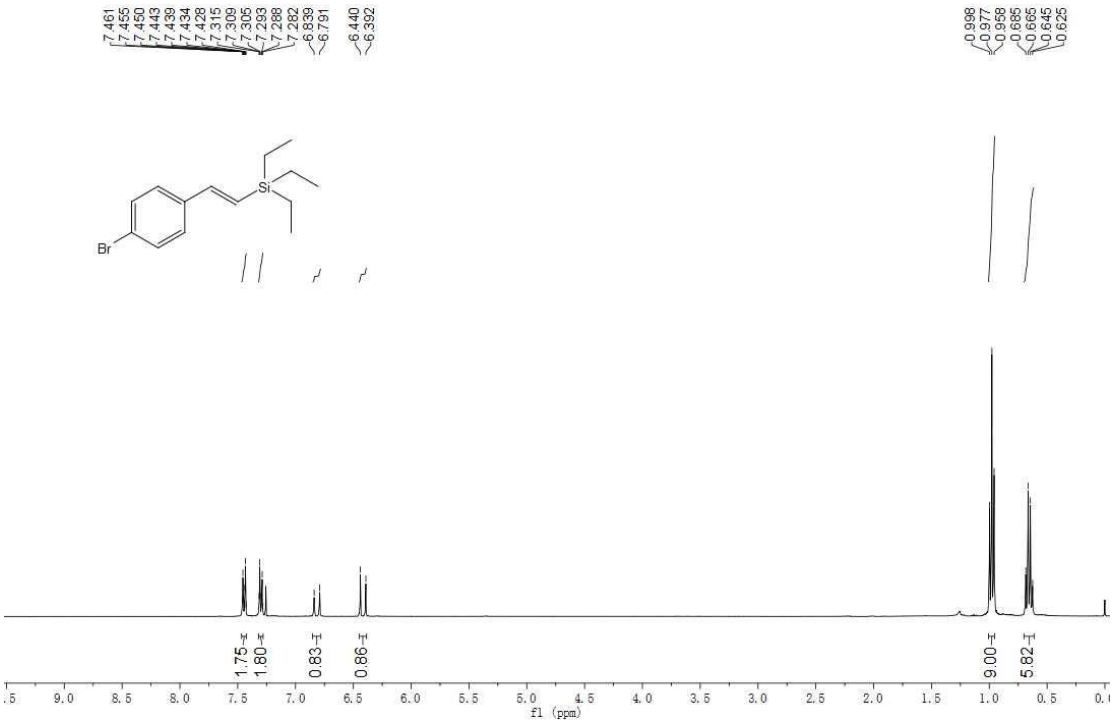


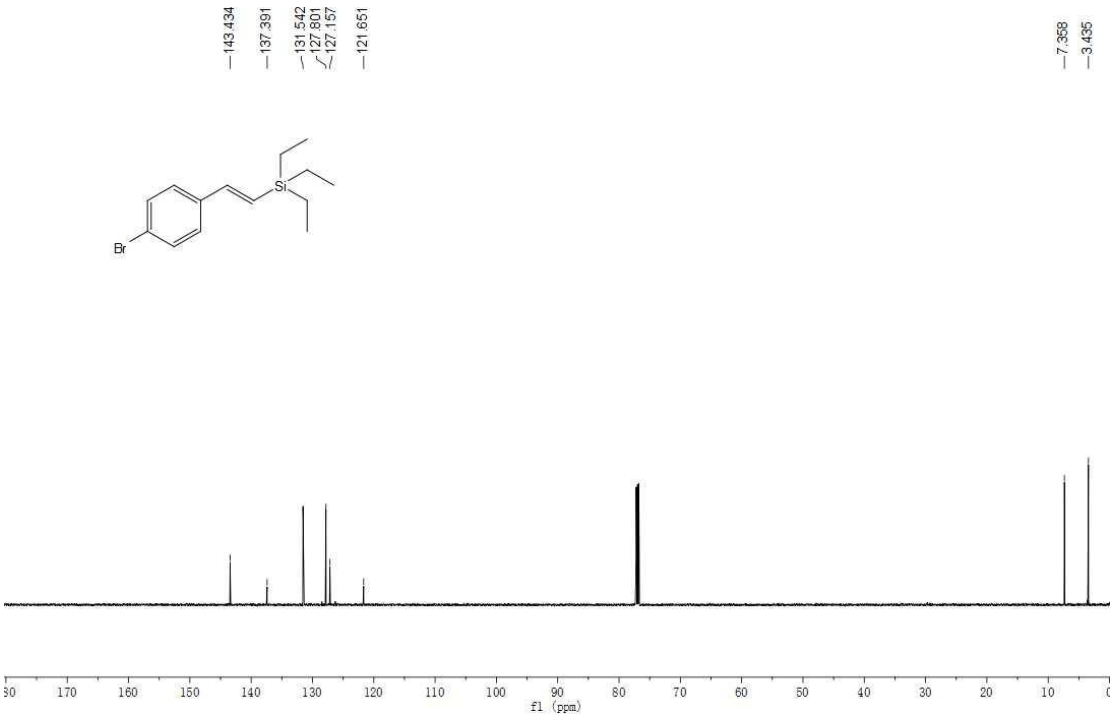
^{1}H and ^{13}C Spectra of compound 3l ($CDCl_3$)



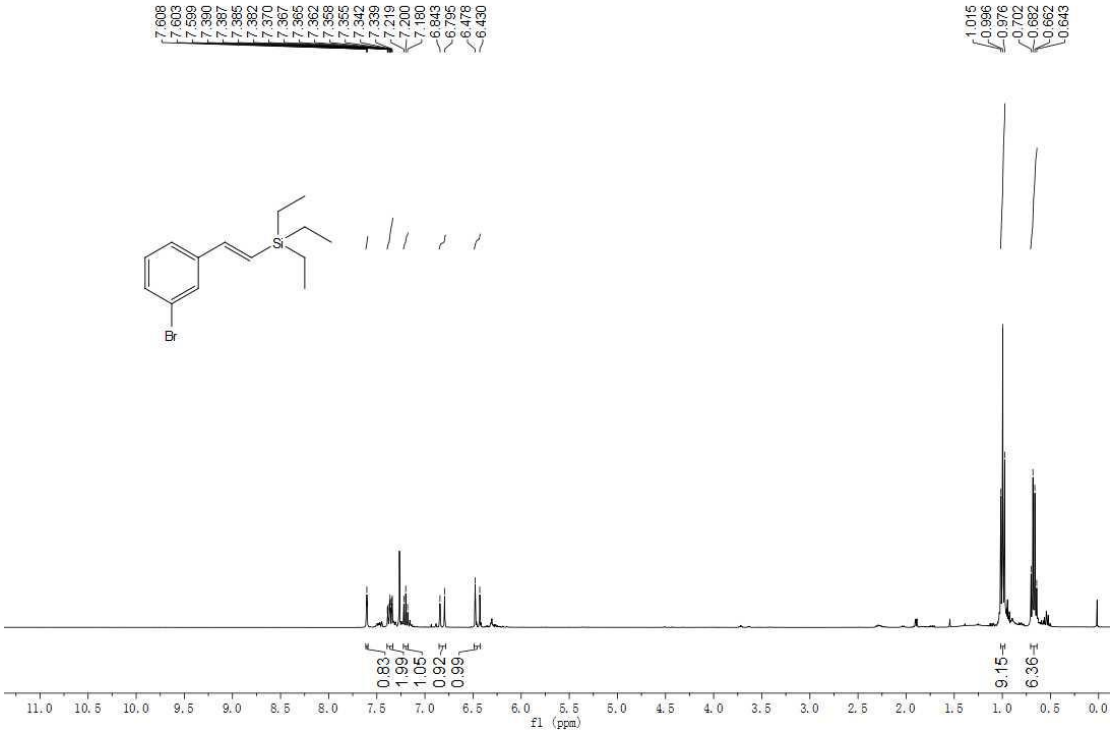


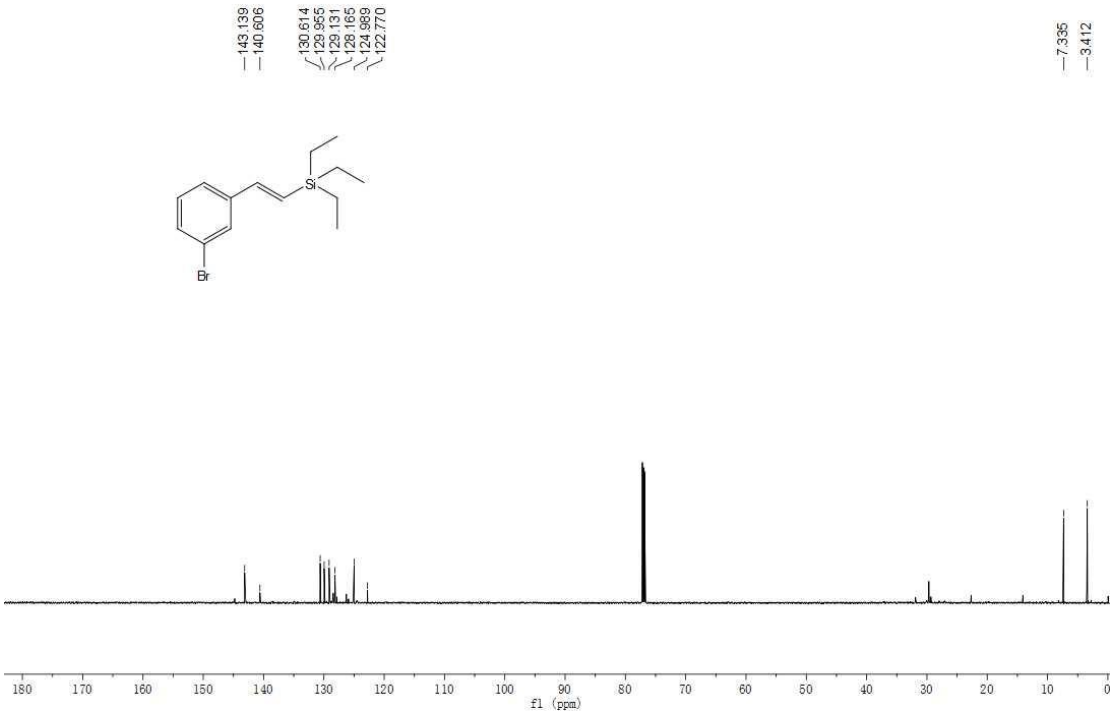
^{1}H and ^{13}C Spectra of compound 3m ($CDCl_3$)



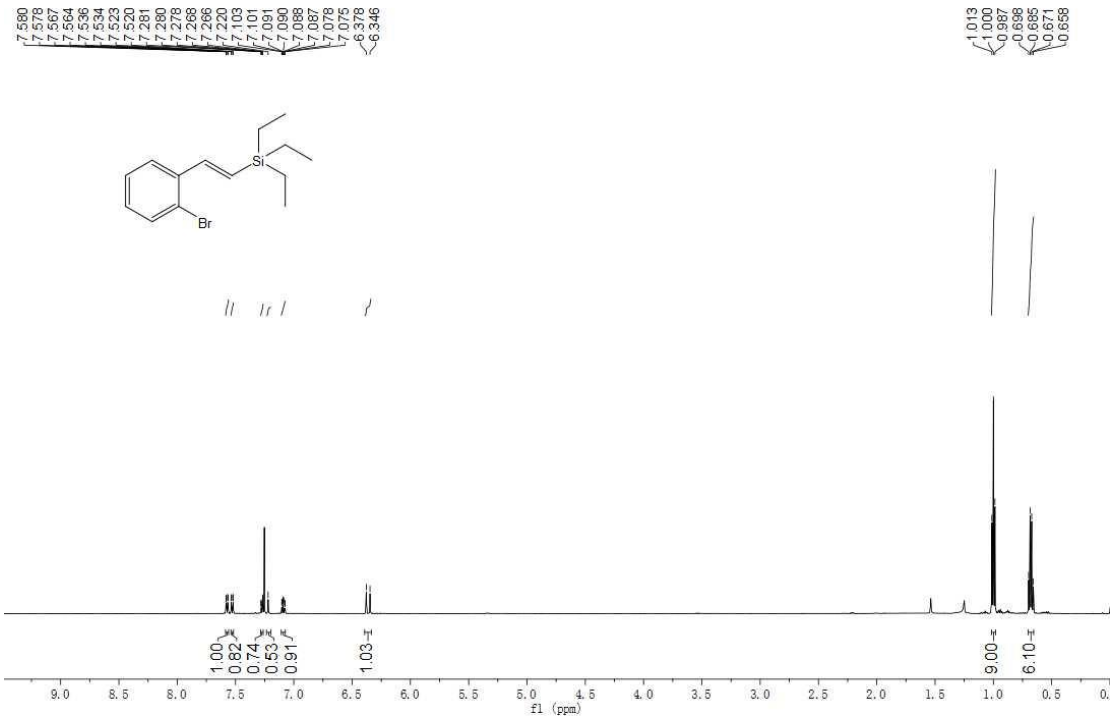


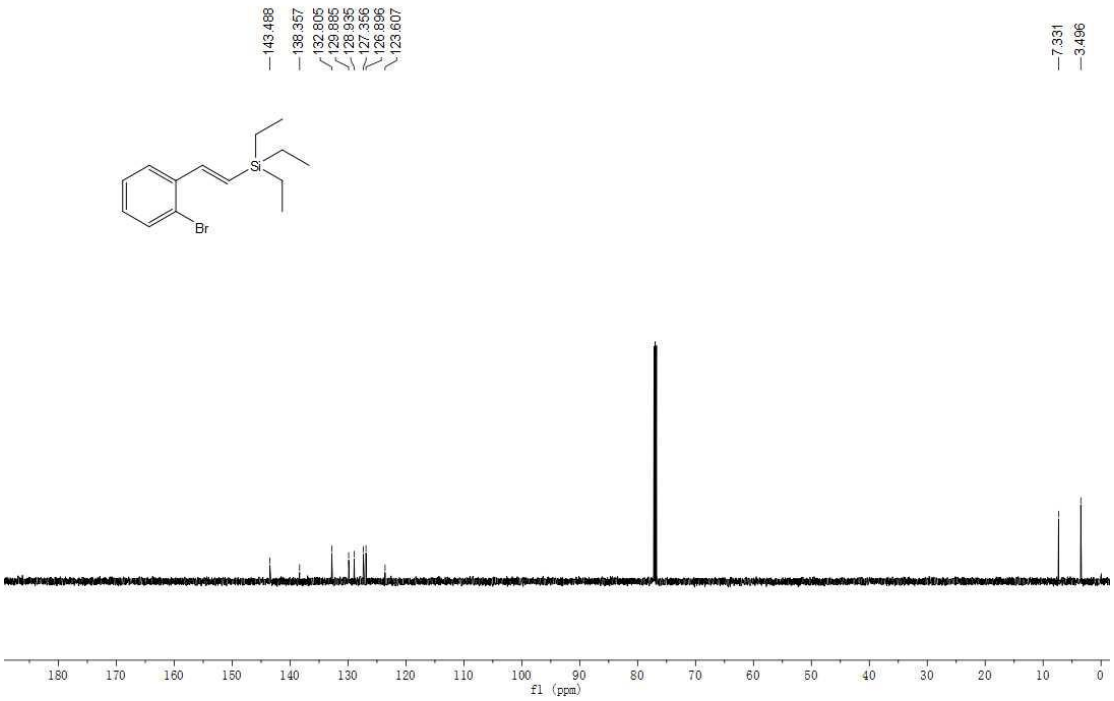
^{1}H and ^{13}C Spectra of compound 3n ($CDCl_3$)



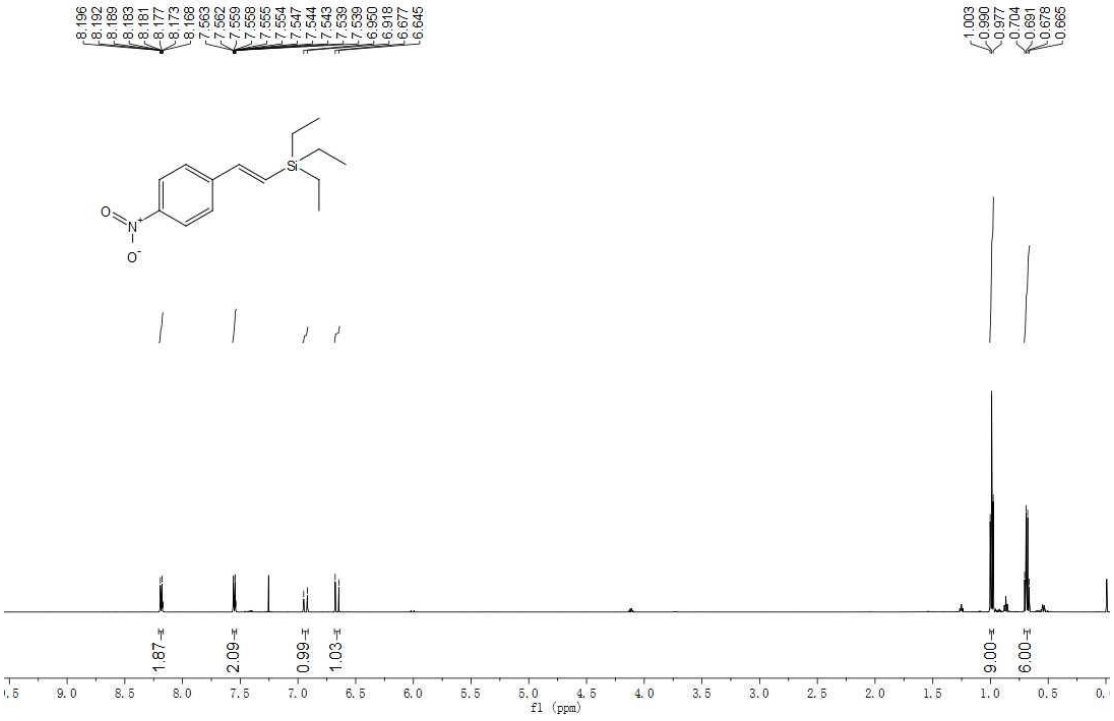


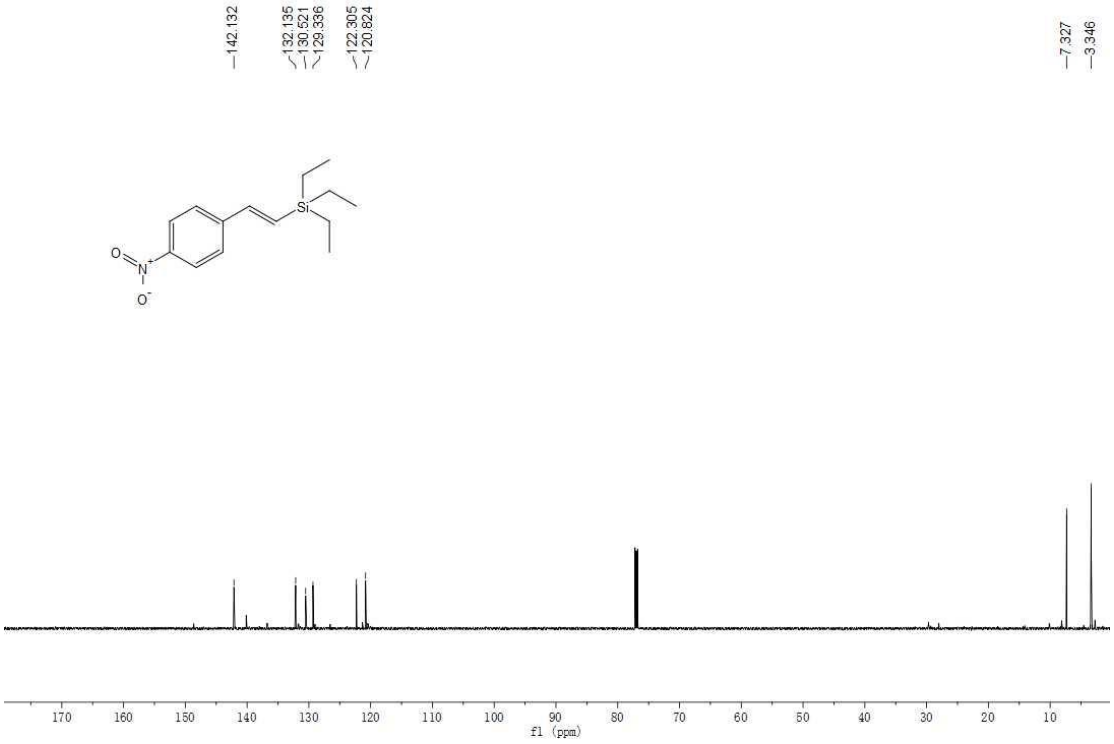
^{1}H and ^{13}C Spectra of compound 3o ($CDCl_3$)



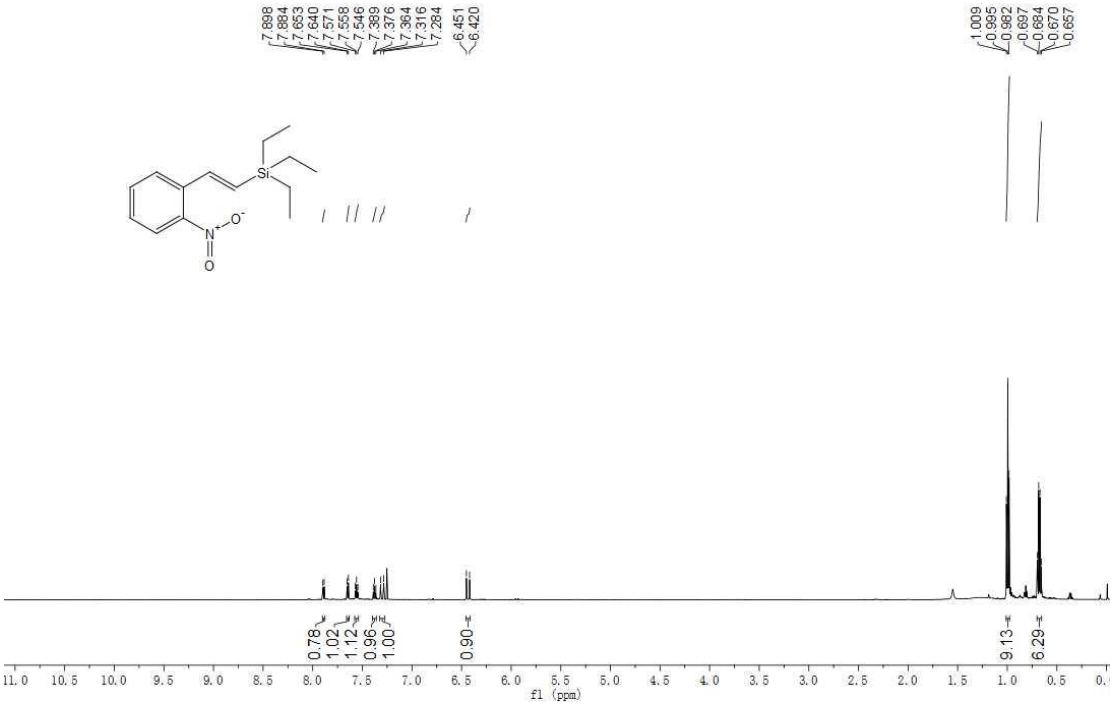


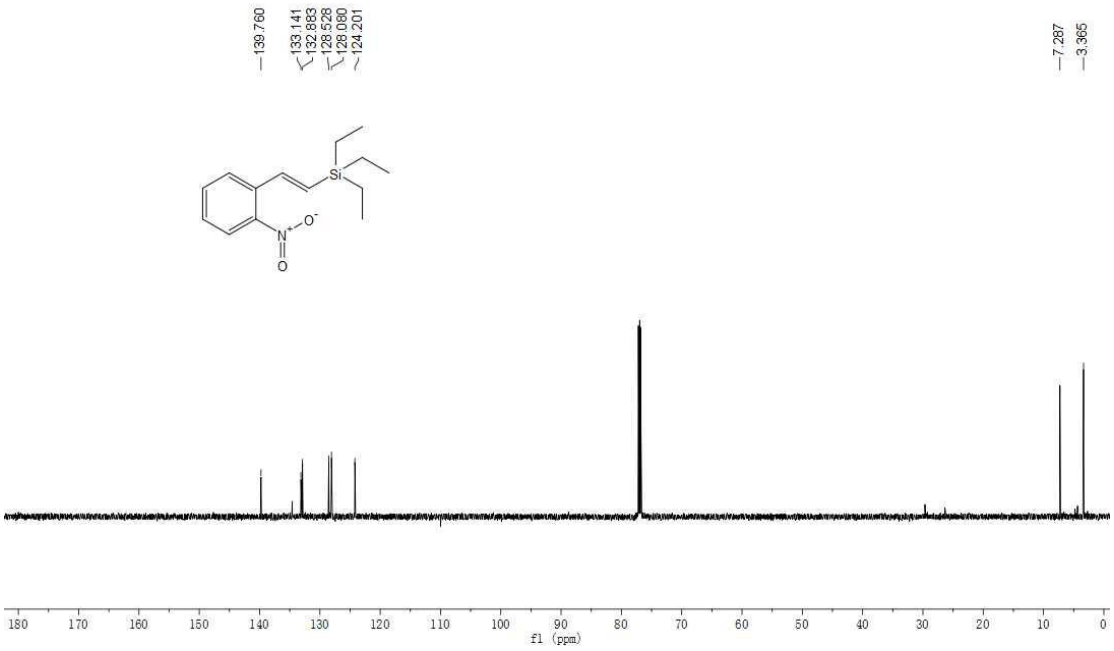
^{1}H and ^{13}C Spectra of compound 3p ($CDCl_3$)



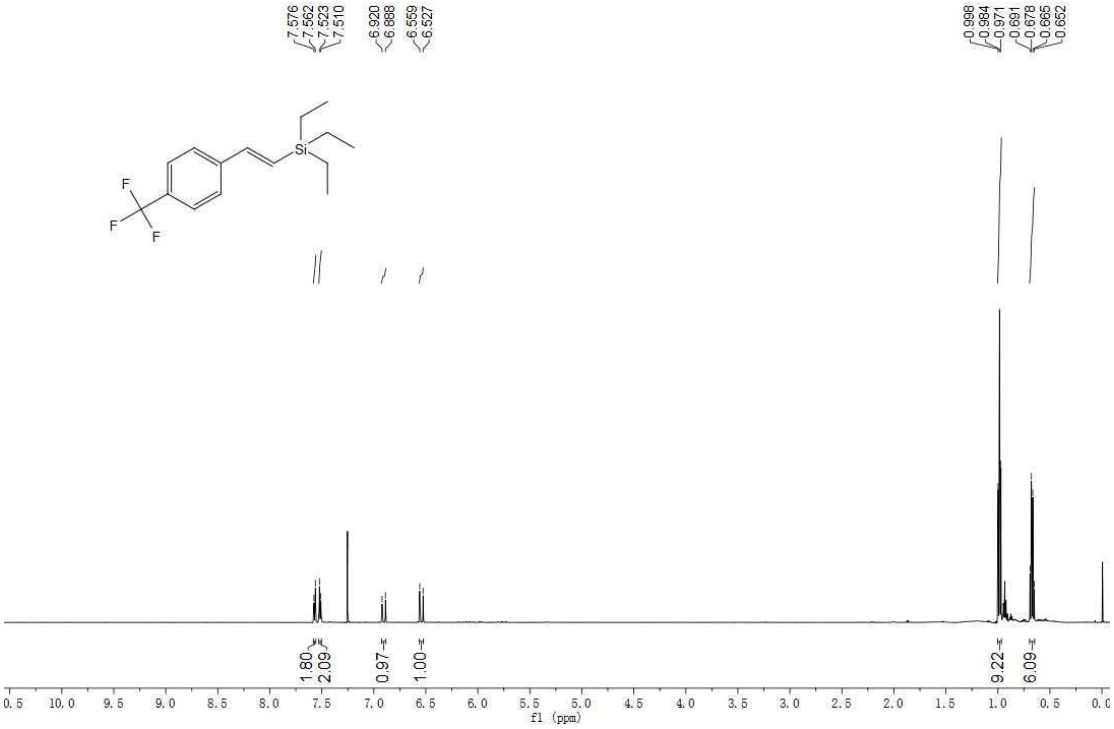

142.132
132.135
130.521
129.336
122.305
120.824
7.327
3.346
Si
O
N+
O-
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

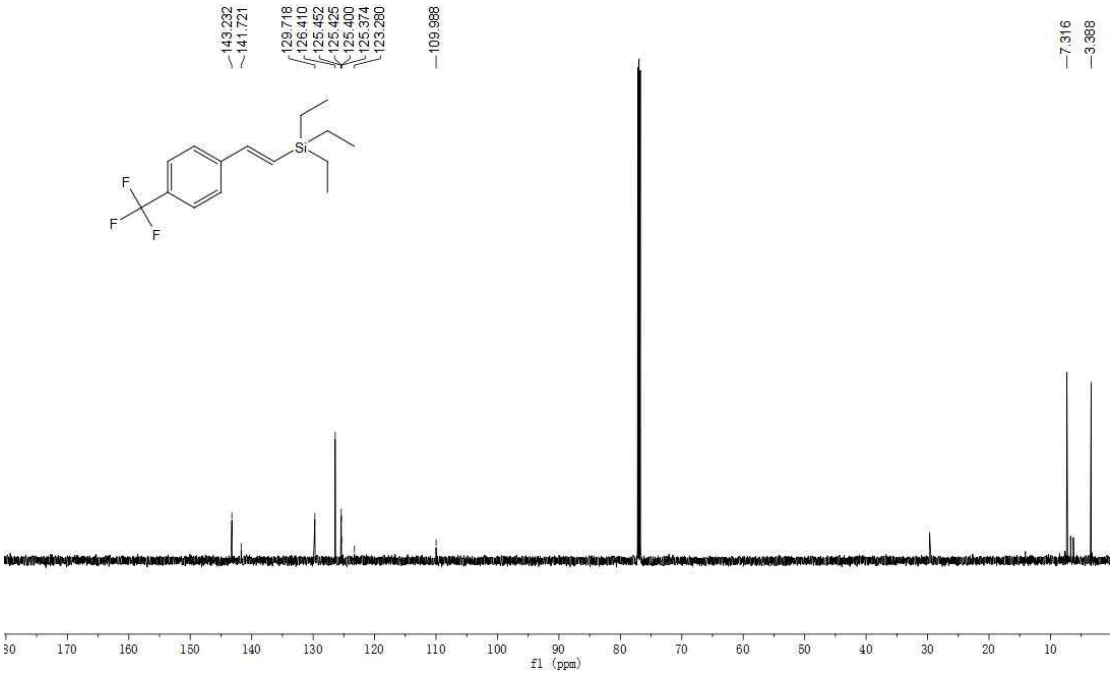
^{1}H and ^{13}C Spectra of compound 3q ($CDCl_3$)

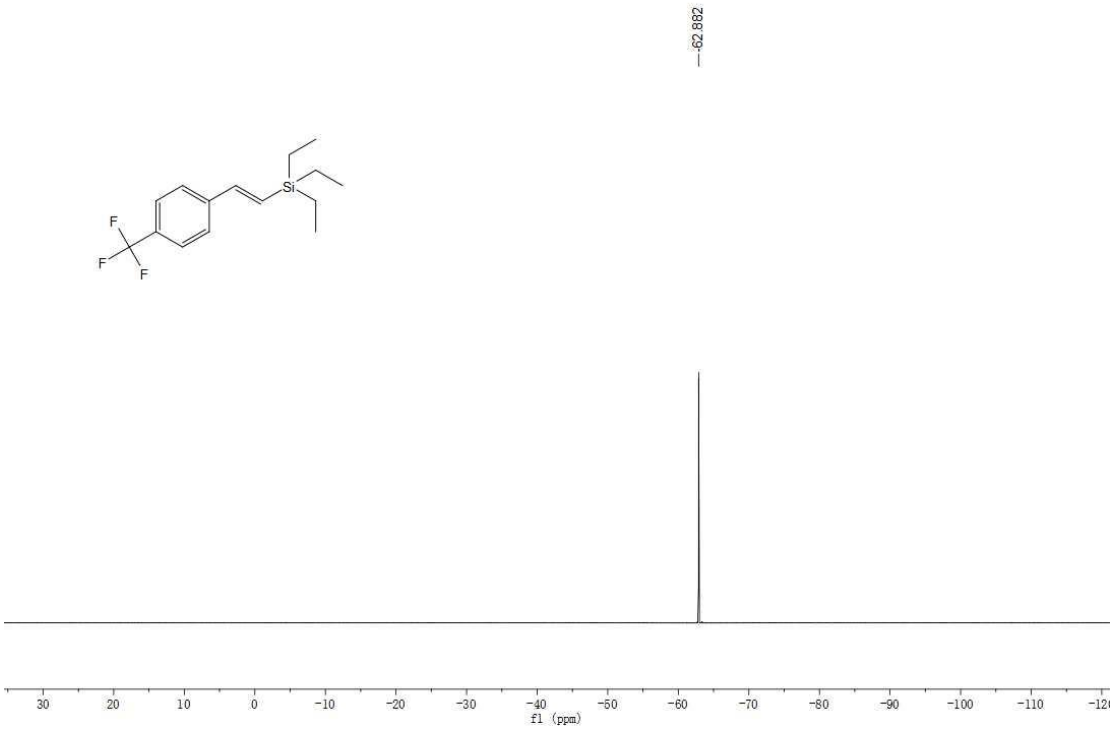




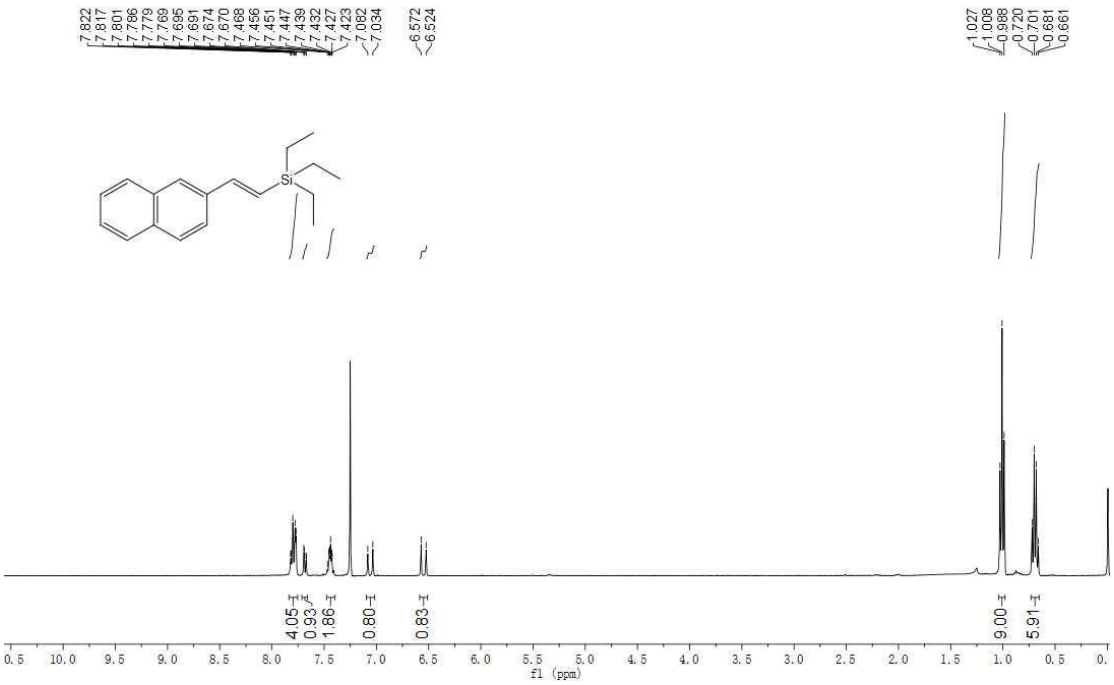
^{1}H and ^{13}C and ^{19}F Spectra of compound 3r ($CDCl_3$)

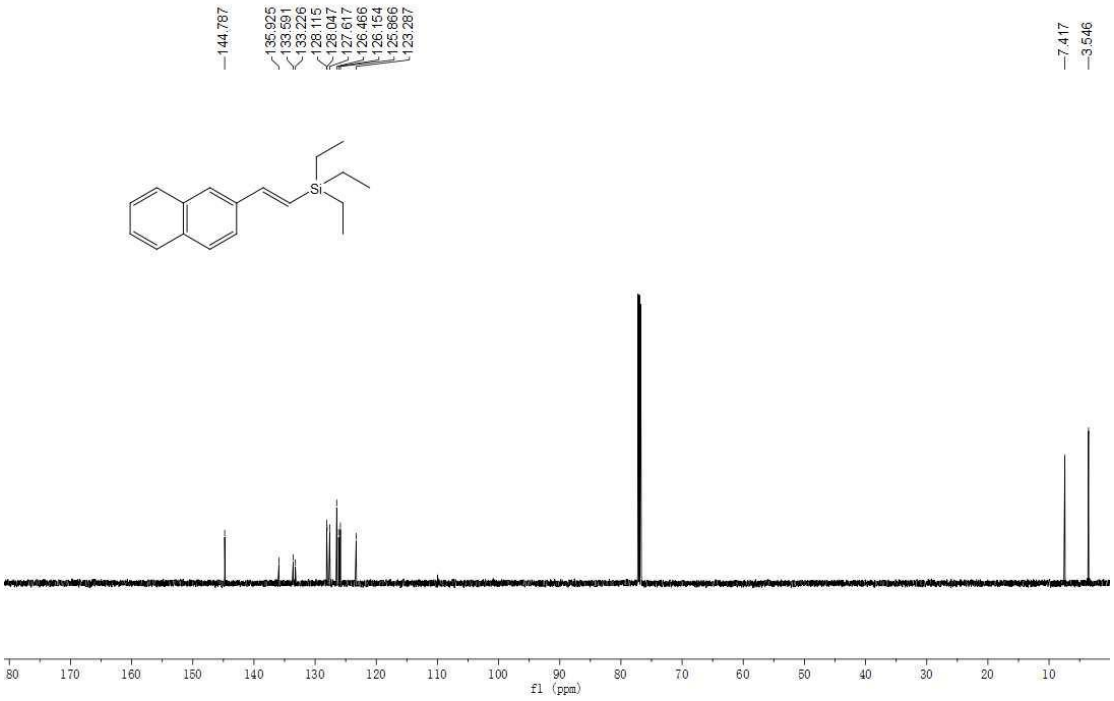




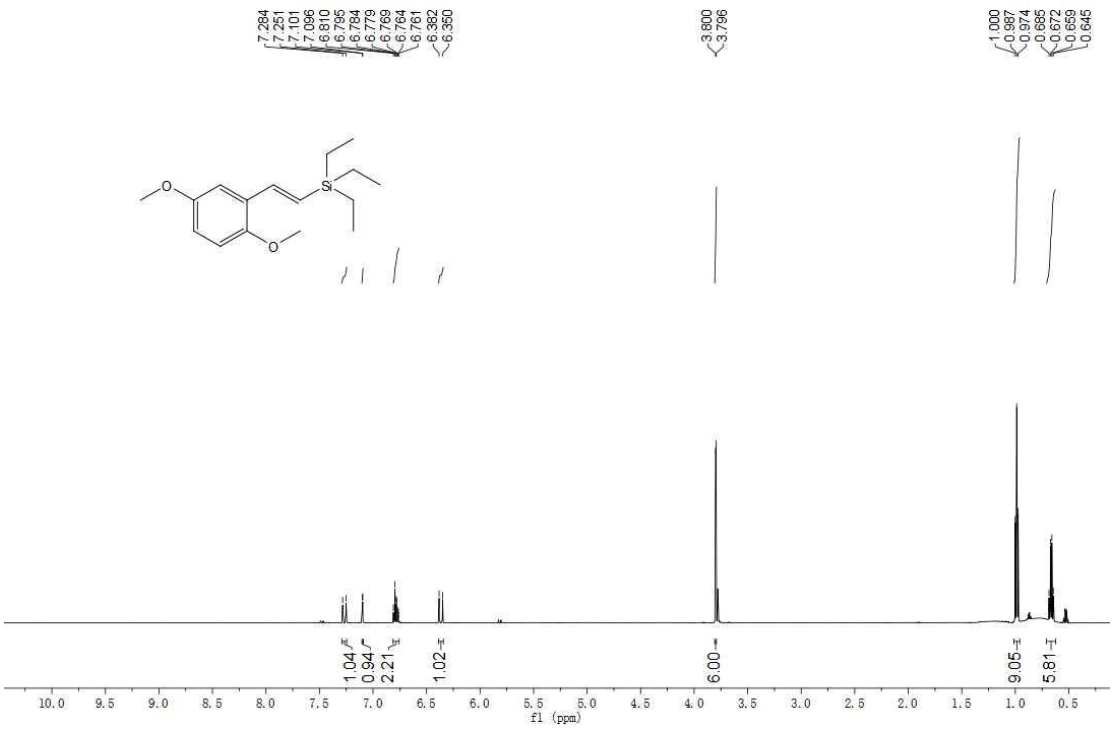

-62.882
Si
F
F
F
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

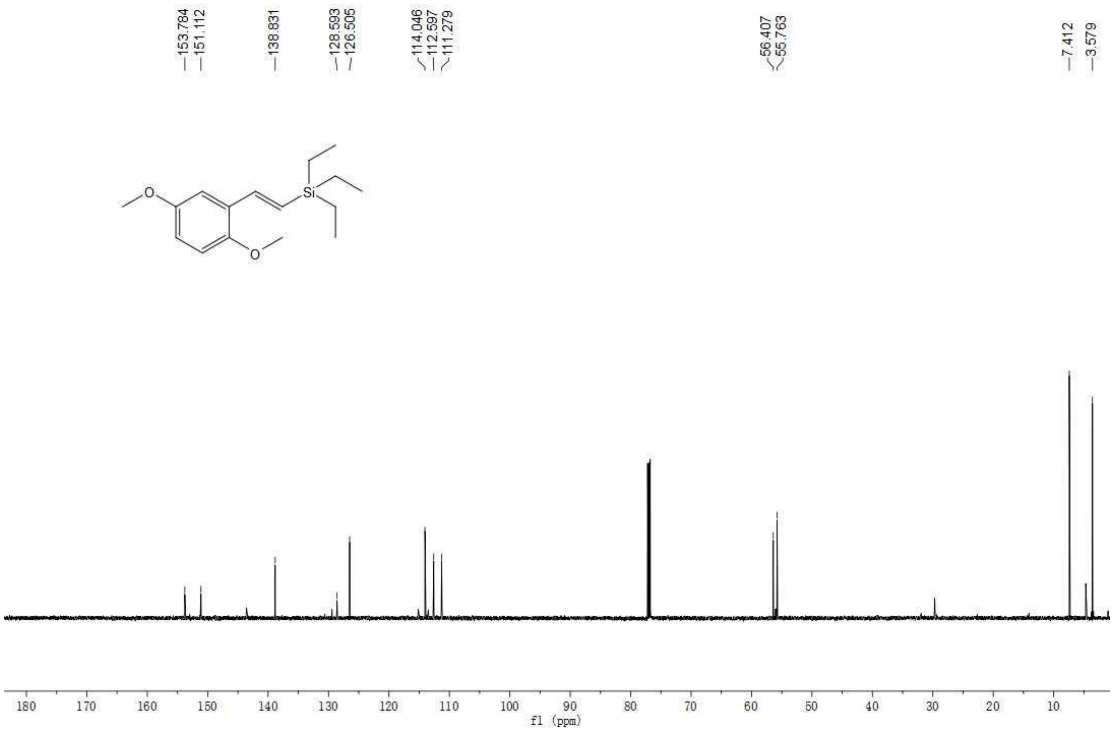
^{1}H and ^{13}C Spectra of compound 3s ($CDCl_3$)



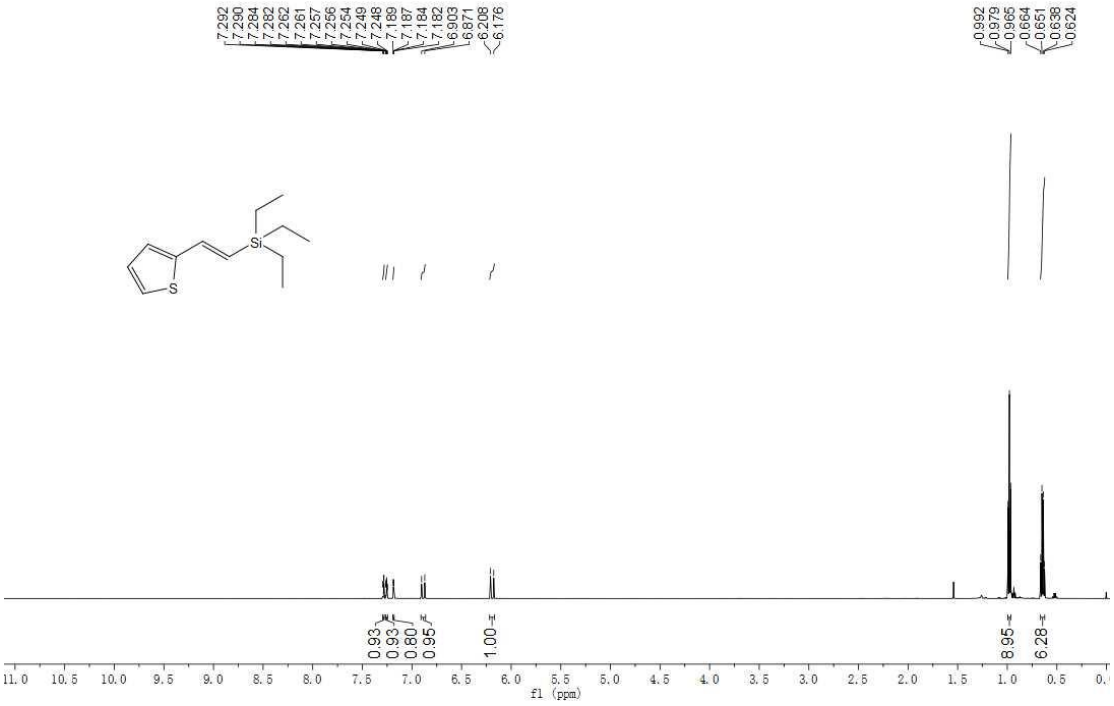


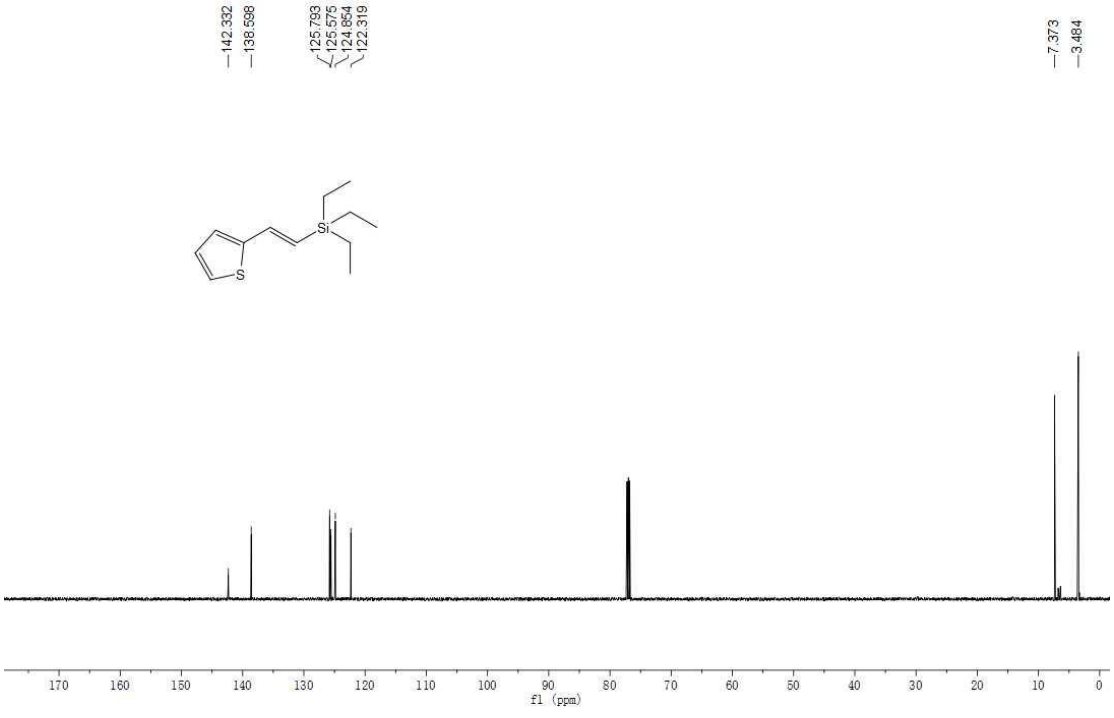
^{1}H and ^{13}C Spectra of compound 3t ($CDCl_3$)



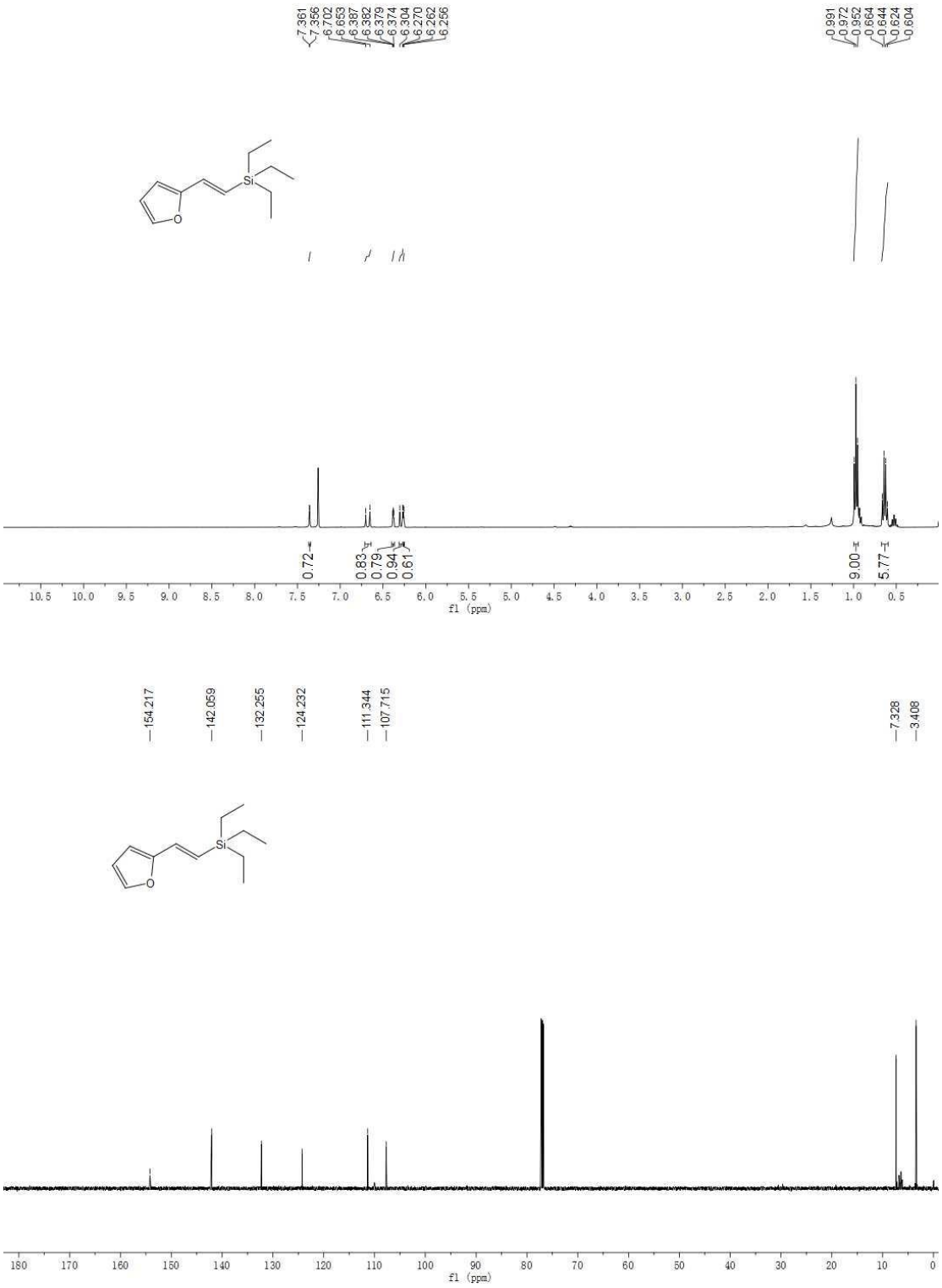


^{1}H and ^{13}C Spectra of compound 3u ($CDCl_3$)

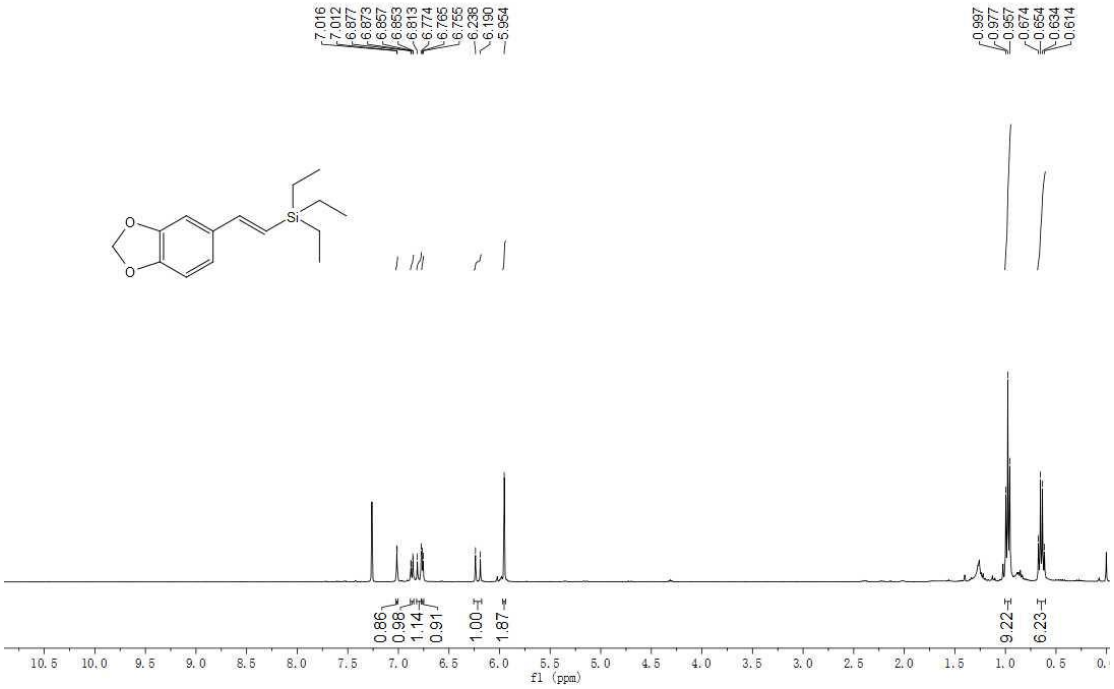


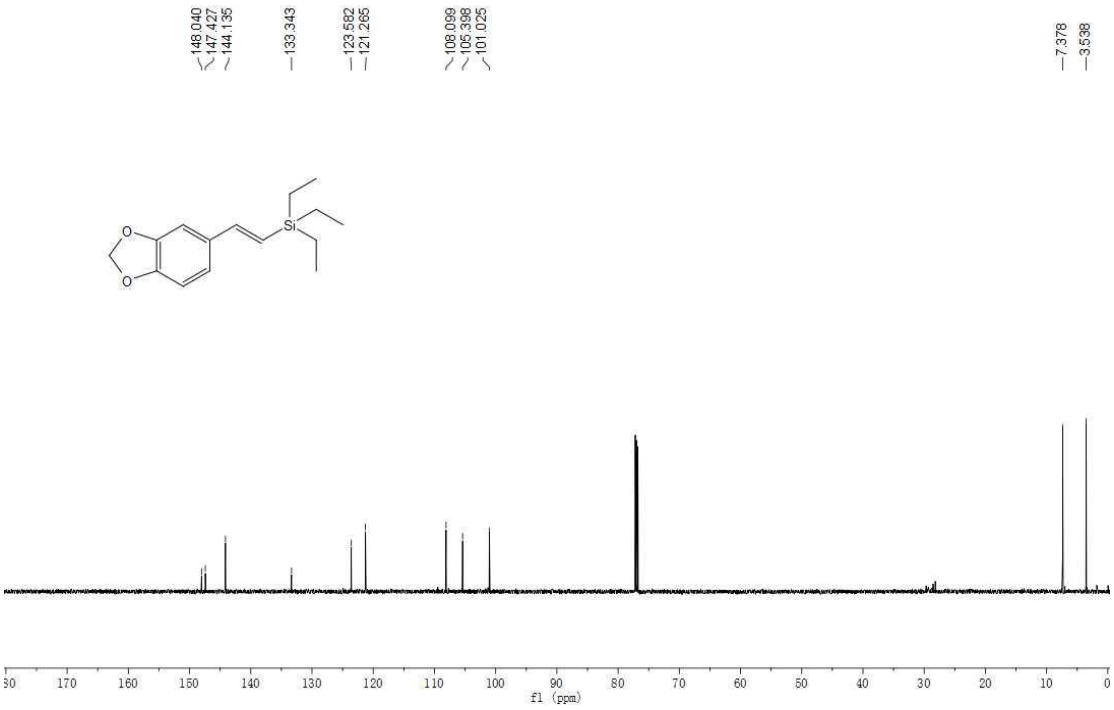


^{1}H and ^{13}C Spectra of compound 3v ($CDCl_3$)

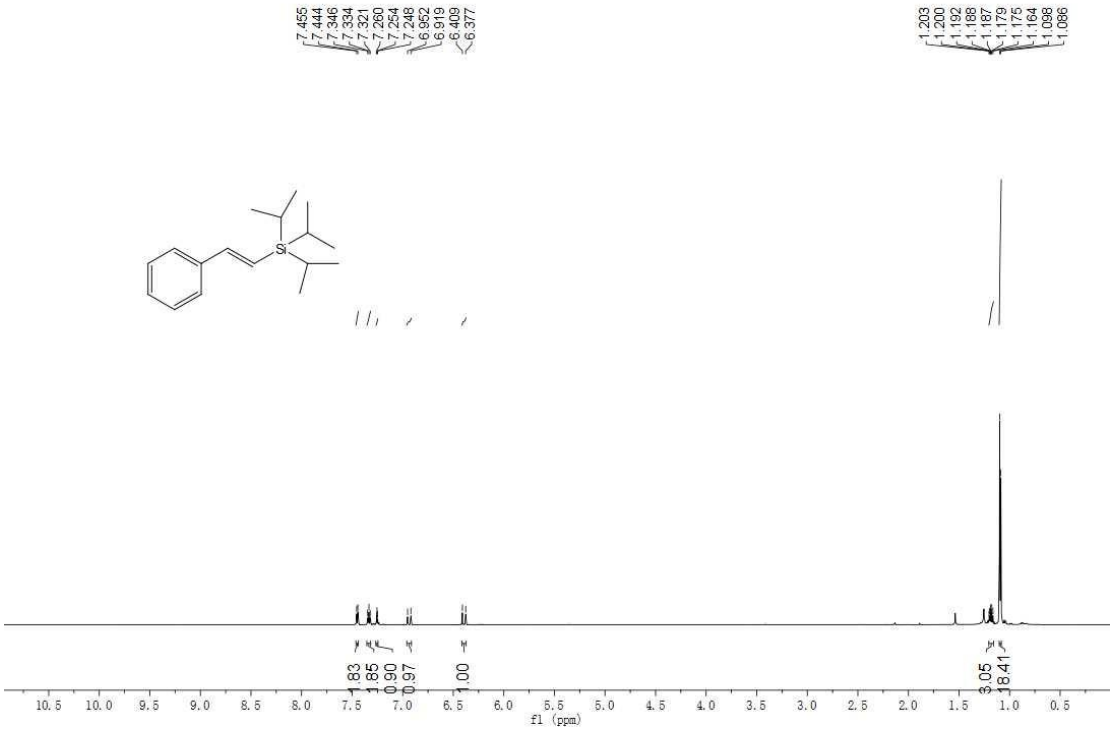


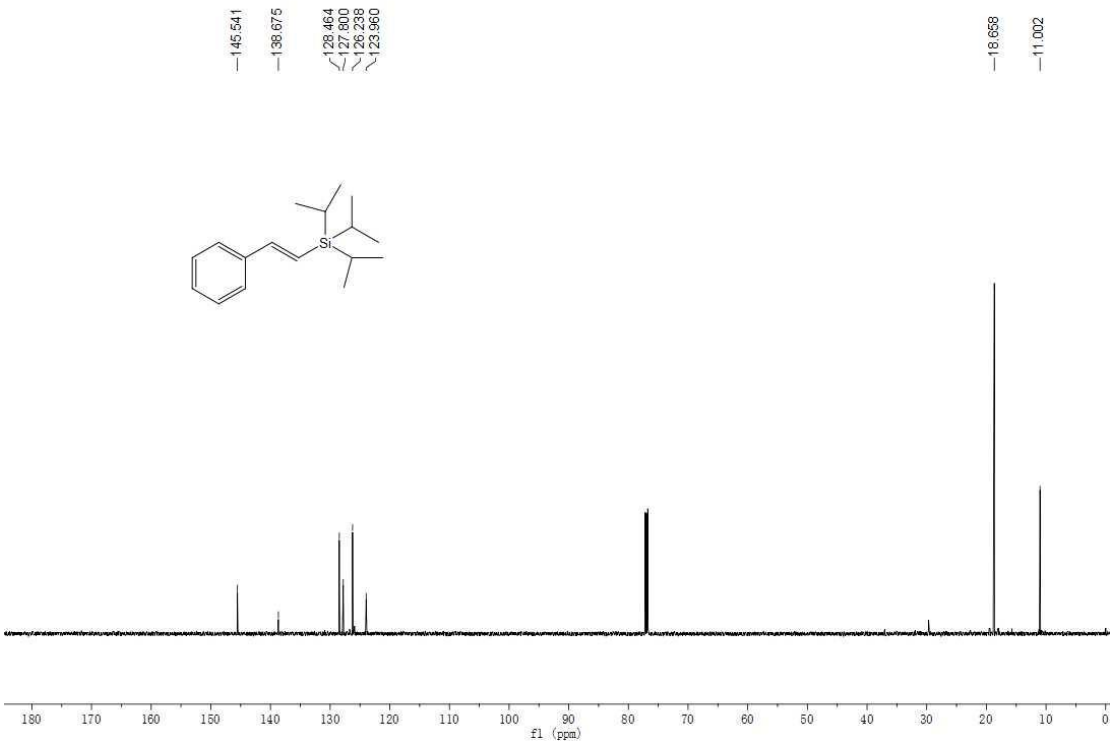
^{1}H and ^{13}C Spectra of compound 3w ($CDCl_3$)



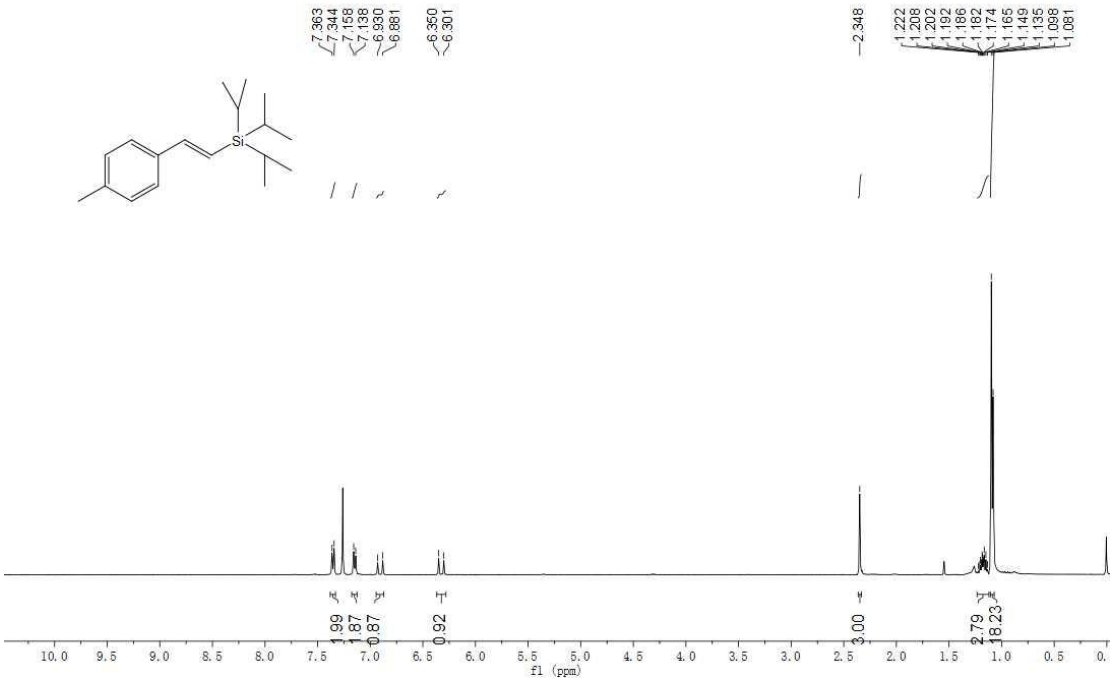


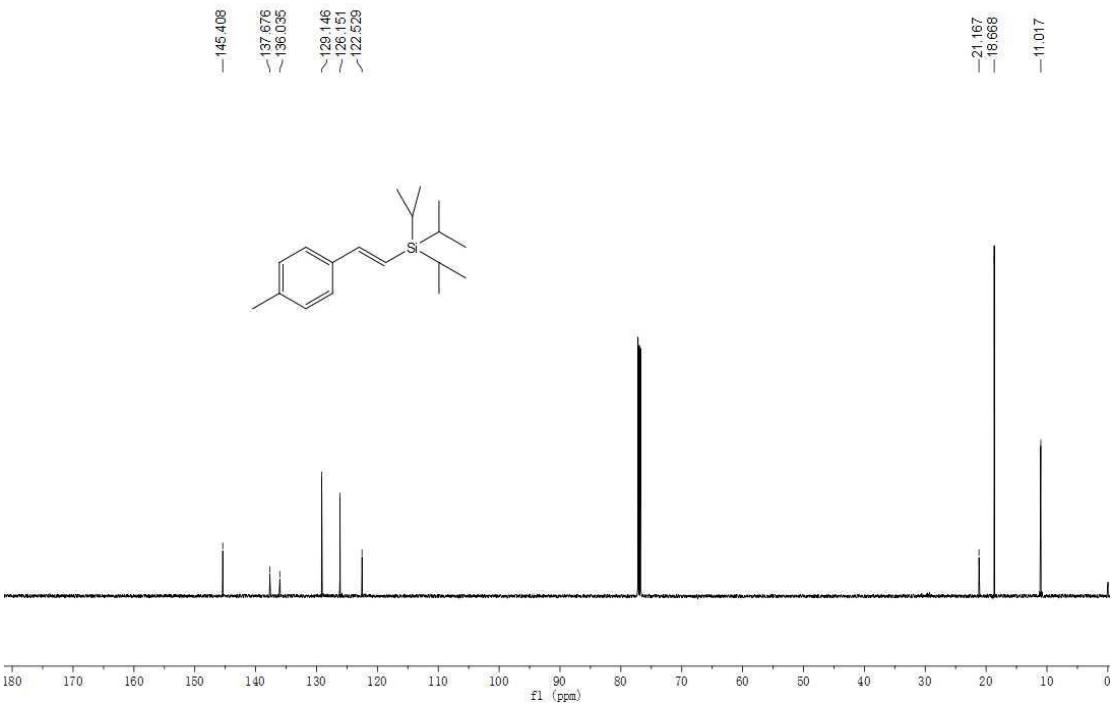
^{1}H and ^{13}C Spectra of compound 3x ($CDCl_3$)



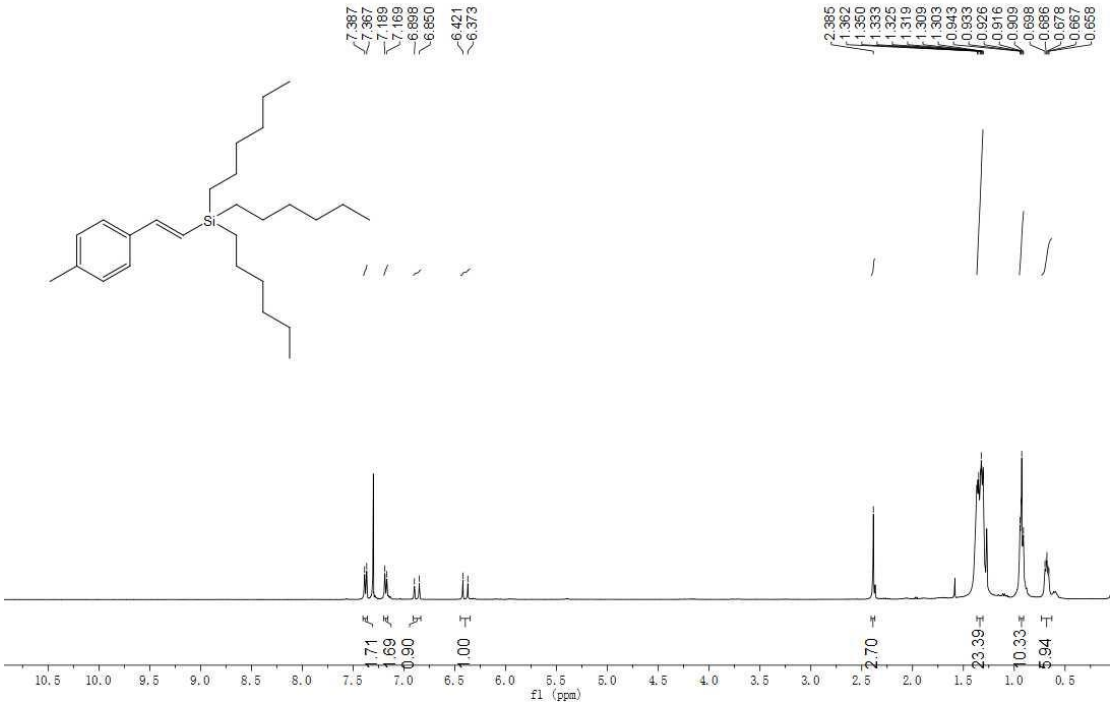


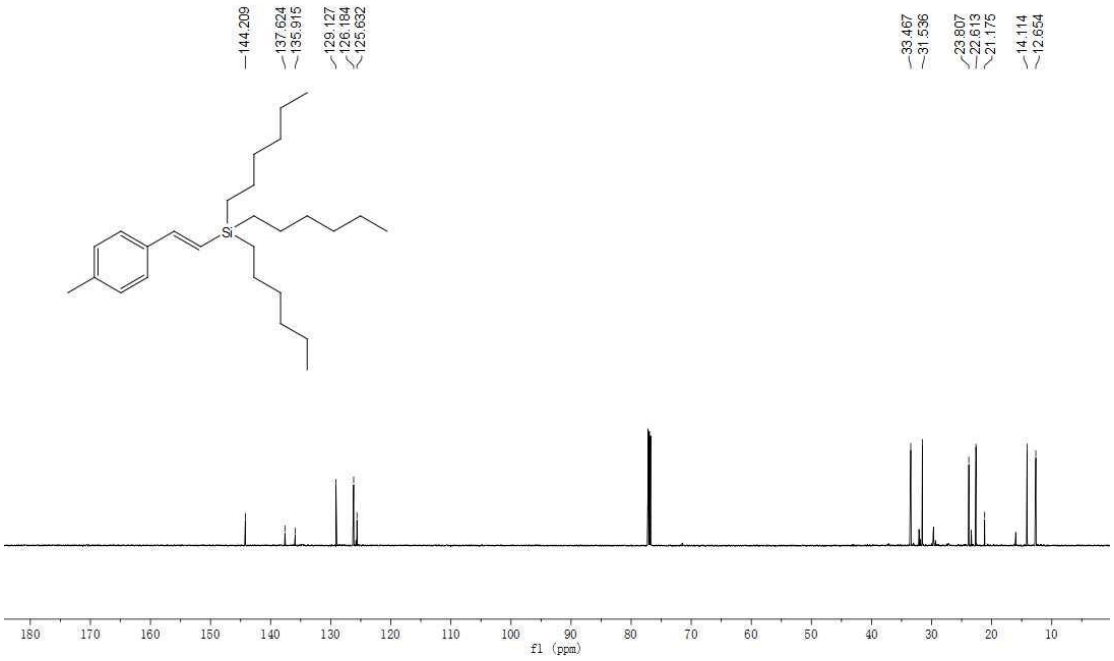
^{1}H and ^{13}C Spectra of compound 3y ($CDCl_3$)



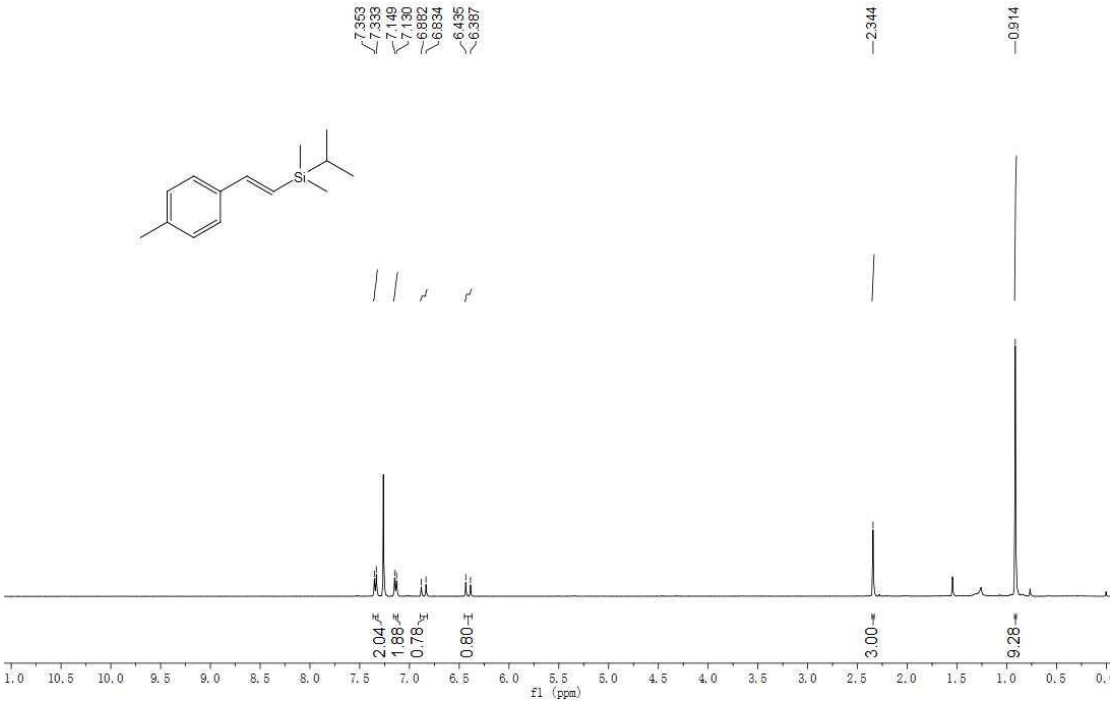


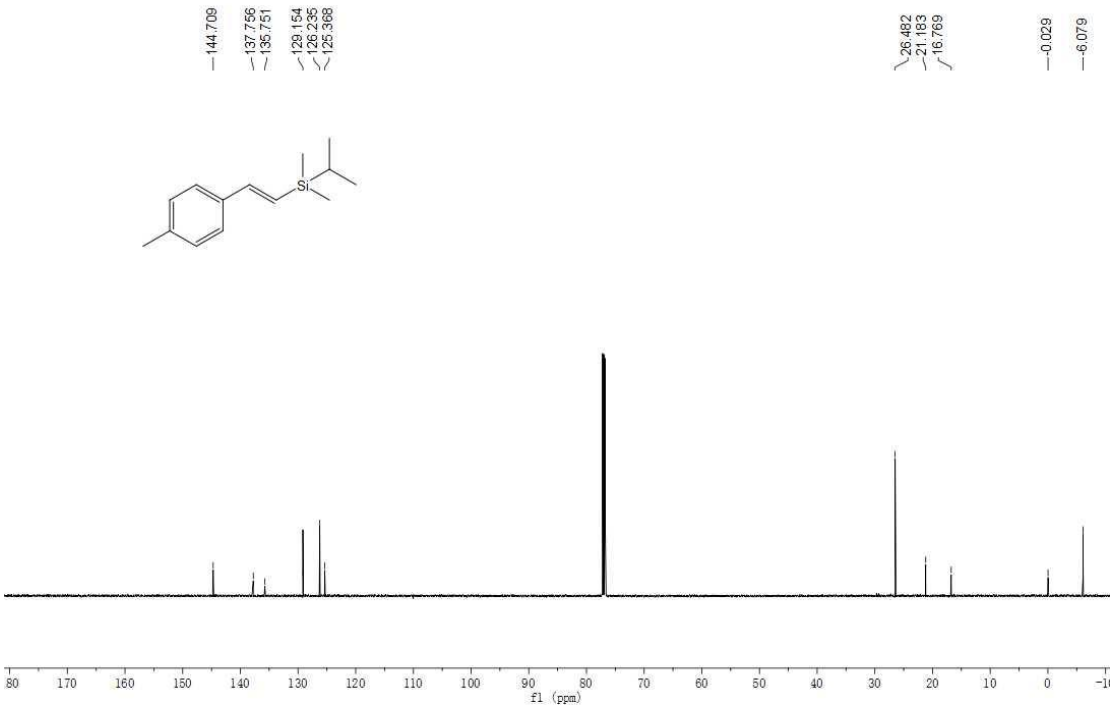
^{1}H and ^{13}C Spectra of compound 3z ($CDCl_3$)





^{1}H and ^{13}C Spectra of compound 3aa ($CDCl_3$)





^{1}H and ^{13}C Spectra of compound 3ab ($CDCl_3$)