Supporting Information for:

Recyclable and reusable K_2PtCl_4/Xphos-SO_3Na/PEG-400/H_2O system for highly regio- and stereoselective hydrosilylation of terminal alkynes

Caifeng Xu, Bin Huang, Tao Yan and Mingzhong Cai*

Key Laboratory of Functional Small Organic Molecule, Ministry of Education and College of Chemistry & Chemical Engineering, Jiangxi Normal University, Nanchang 330022, P. R. China

E-mail: mzcai@jxnu.edu.cn

Contents:

General remarks

All chemicals were reagent grade and used as purchased. The products were purified by flash chromatography on silica gel. Light petroleum ether or a mixture of EtOAc and light petroleum ether was generally used as eluent. All products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H and ^{13}C NMR spectra were recorded at 400 or 100 MHz with $CDCl_3$ as the solvent and TMS as an internal standard. Chemical shifts are reported in δ (ppm) relative to TMS. HRMS spectra were recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI). Melting points are uncorrected.

General procedure for the platinum-catalyzed hydrosilylation reaction of terminal alkynes in PEG-400/H_2O

Under an argon atmosphere, a mixture of K_2PtCl_4 (0.01 mmol), Xphos-SO_3Na (0.02 mmol), PEG-400 (0.67 mL) and H_2O (0.33 mL) was stirred at 60 ºC for 30 min. Then, terminal alkyne **1** (1.0 mmol) and hydrosilane **2** (1.5 mmol) were successively added via syringe and the resulting mixture was stirred at 60 ºC for 6 h. After being cooled to room temperature, the mixture was extracted three times with cyclohexane (3 × 5 mL). The combined cyclohexane phase was concentrated under reduced pressure, and the residue was purified by flash column chromatography on silica gel (light petroleum ether or light petroleum ether–ethyl acetate) to afford the desired product **3** or **4**.

The residue of the extraction was heated to 60 ºC in vacuum for 20 min to remove the residual cyclohexane, and then subjected to a second run of the hydrosilylation reaction by charging with the same substrates (terminal alkyne **1** and hydrosilane **2**) under the same conditions without further addition of K_2PtCl_4 and Xphos-SO_3Na.

Characterization data of products

(*E*)-Triethyl(styryl)silane (3a).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 19.2 Hz,

1H), 6.42 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 7.8 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 138.6, 128.5, 127.9, 126.3, 126.0, 7.4, 3.6.

(*E*)-Triethyl(4-methylstyryl)silane (3b).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 6.86 (d, J = 19.2 Hz, 1H), 6.35 (d, J = 19.2 Hz, 1H), 2.33 (s, 3H), 0.98 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 137.7, 135.9, 129.2, 126.2, 124.6, 21.2, 7.4, 3.6.

(*E*)-(4-Butylstyryl)triethylsilane (3c). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 19.2 Hz, 1H), 6.36 (d, J = 19.2 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 1.63-1.54 (m, 2H), 1.40-1.30 (m, 2H), 0.98 (t, J = 8.0 Hz, 9H), 0.92 (t, J = 7.4 Hz, 3H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 142.9, 136.1, 128.6, 126.2, 124.6, 35.4, 33.6, 22.3, 13.9, 7.4, 3.6. HRMS calcd for $C_{18}H_{30}Si^+$ [M^+]: 274.2117, found 274.2122.

(*E*)-Triethyl(4-methoxystyryl)silane (3d).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8..4 Hz, 2H), 6.83 (d, J = 19.2 Hz, 1H), 6.24 (d, J = 19.2 Hz, 1H), 3.80 (s, 3H), 0.98 (t, J = 7.8 Hz, 9H), 0.67 (q, J = 7.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 144.2, 131.6, 127.5, 123.1, 113.9, 55.3, 7.4, 3.6.

(*E*)-Triethyl(3-methylstyryl)silane (3e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.19 (m, 3H), 7.06 (d, J = 6.8 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 = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 138.5, 138.0, 128.7, 128.4, 127.0, 125.6, 123.5, 21.4, 7.4, 3.6. HRMS calcd for $C_{15}H_{25}Si^+$ [M + H^+]: 233.1726, found 233.1728.

(*E*)-2-(4-(2-(Triethylsilyl)vinyl)phenyl)acetonitrile (3f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 19.2 Hz, 1H), 6.45 (d, J = 19.2 Hz, 1H), 3.73 (s, 2H), 0.99 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 138.5, 129.2, 128.1, 127.3, 127.0, 117.8, 23.4, 7.4, 3.5. HRMS calcd for $C_{16}H_{23}NSi^+$ [M^+]: 257.1600, found 257.1601.

(*E*)-4-(2-(Triethylsilyl)vinyl)benzonitrile (3g).[1] Colorless oil. ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.61 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 19.2 Hz, 1H), 6.60 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.68 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 142.6, 132.4, 131.6, 126.8, 119.0, 111.0, 7.4, 3.4.

(*E*)-Methyl 4-(2-(triethylsilyl)vinyl)benzoate (3h).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 19.2 Hz, 1H), 6.58 (d, J = 19.2 Hz, 1H), 3.91 (s, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 143.7, 142.7, 129.9, 129.8, 129.2, 126.2, 52.1, 7.4, 3.4.

(*E*)-Triethyl(2-methylstyryl)silane (3i).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 1H), 7.20-7.09 (m, 4H), 6.30 (d, J = 19.2 Hz, 1H), 2.37 (s, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 138.0, 135.2, 130.3, 127.8, 127.6, 126.1, 125.3, 19.6, 7.4, 3.6.

(*E*)-Triethyl(2-methoxystyryl)silane (3j).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J = 7.8, 1.4 Hz, 1H), 7.30 (d, J = 19.2 Hz, 1H), 7.25-7.19 (m, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 6.38 (d, J = 19.2 Hz, 1H), 3.84 (s, 3H), 0.99 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 139.1, 128.9, 127.8, 126.2, 126.1, 120.6, 111.0, 55.6, 7.4, 3.6.

(*E*)-Triethyl(2-(4'-ethylbiphenyl-4-yl)vinyl)silane (3k). White solid, Mp 59–60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 19.4 Hz, 1H), 6.46 (d, J = 19.4 Hz, 1H), 2.69 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H), 1.00 (t, J = 8.0 Hz, 9H), 0.67 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 143.5, 140.6, 138.2, 137.3, 128.3, 127.1, 126.9, 126.7, 125.9, 28.6, 15.6, 7.4, 3.6. HRMS calcd for $C_{22}H_{31}Si^+$ [M + H$^+$]: 323.2195, found 323.2190.

(*E*)-Triethyl(2-(naphthalene-1-yl)vinyl)silane (3l).[2] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 18.4 Hz, 1H), 7.66 (d, J = 5.6 Hz, 1H), 7.54-7.43 (m, 3H), 6.48 (d, J = 18.8 Hz, 1H), 1.05 (t, J = 8.0 Hz, 9H), 0.73 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 136.9, 133.6, 130.9, 130.3, 128.5, 128.1, 126.0, 125.7, 125.6, 123.6, 7.5, 3.7.

(*E*)-2-(2-(Triethylsilyl)vinyl)pyridine (3m).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 4.0 Hz, 1H), 7.68-7.63 (m, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.17-7.13 (m, 1H), 7.01 (d, J = 19.2 Hz, 1H), 6.93 (d, J = 19.2 Hz, 1H), 0.99 (t, J = 8.0 Hz, 9H), 0.69 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 144.6, 136.5, 131.5, 128.8, 122.4, 121.3, 7.4, 3.4.

(*E*)-(2-Cyclohexenylvinyl)triethylsilane (3n).[3] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.54 (d, J = 19.0 Hz, 1H), 5.80 (br, 1H), 5.63 (d, J = 19.0 Hz, 1H), 2.19-2.13 (m, 4H), 1.70-1.58 (m, 4H), 0.94 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 137.5, 130.6, 120.6, 25.9, 24.0, 22.6, 22.5, 7.4, 3.6.

(*E*)-Triethyl(hex-1-enyl)silane (3o).[2] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.03 (dt, J = 18.8, 6.4 Hz, 1H), 5.53 (d, J = 18.8 Hz, 1H), 2.15-2.10 (m, 2H), 1.42-1.28 (m, 4H), 0.95-0.87 (m, 12H), 0.54 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.8, 125.5, 36.7, 31.0, 22.2, 13.9, 7.4, 3.6.

(*E*)-(5-Phenylpent-1-enyl)triethylsilane (3p). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.24 (m, 2H), 7.19-7.15 (m, 3H), 6.04 (dt, J = 18.8, 6.4 Hz, 1H), 5.57 (d, J = 18.8 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 2.20-2.13 (m, 2H), 1.77-1.68 (m, 2H), 0.93 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 142.6, 128.5, 128.3, 126.3, 125.7, 36.5, 35.4, 30.6, 7.4, 3.6. HRMS calcd for $C_{17}H_{29}Si^+$ [M + H^+]: 261.2039, found 261.2035.

(*E*)-(5-Chloropent-1-enyl)triethylsilane (3q).[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (dt, J = 18.8, 6.4 Hz, 1H), 5.62 (d, J = 18.8 Hz, 1H), 3.53 (t, J = 6.6 Hz, 2H), 2.31-2.24 (m, 2H), 1.92-1.84 (m, 2H), 0.92 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 127.7, 44.4, 34.0, 31.6, 7.4, 3.5.

(*E*)-4-(Triethylsilyl)but-3-en-1-ol (3r).[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01 (dt, J = 18.8, 6.4 Hz, 1H), 5.71 (d, J = 18.8 Hz, 1H), 3.69 (t, J = 6.2 Hz, 2H), 2.44-2.38 (m, 2H), 1.47 (br, 1H), 0.93 (t, J = 8.0 Hz, 9H), 0.56 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 130.2, 61.5, 40.3, 7.3, 3.4.

(*E*)-3-(Triethylsilyl)prop-2-en-1-ol (3s).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.21 (dt J = 18.8, 4.4 Hz, 1H), 5.85 (d, J = 18.8 Hz, 1H), 4.21-4.18 (m, 2H),

1.54 (br, 1H), 0.94 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1, 125.7, 65.7, 7.3, 3.4.

(*E*)-4-(Triethylsilyl)but-3-en-2-ol (3t).[4] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.11 (dd, J = 19.2, 5.0 Hz, 1H), 5.76 (d, J = 19.2 Hz, 1H), 4.32-4.27 (m, 1H), 1.60 (br, 1H), 1.27 (d, J = 6.4 Hz, 3H), 0.93 (t, J = 7.8 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.1, 124.2, 70.7, 23.1, 7.3, 3.4.

(*E*)-1-(2-(Triethylsilyl)vinyl)cyclohexanol (3u).[2] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (d, J = 19.0 Hz, 1H), 5.79 (d, J = 19.0 Hz, 1H), 1.70-1.47 (m, 8H), 1.34-1.25 (m, 2H), 0.93 (t, J = 8.0 Hz, 9H), 0.57 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 121.3, 72.7, 37.6, 25.6, 22.1, 7.3, 3.5.

(*E*)-Triethyl(3-phenoxyprop-1-enyl)silane (3v).[2] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (m, 2H), 6.96-6.90 (m, 3H), 6.23 (dt, J = 18.8, 4.6 Hz, 1H), 6.00 (dd, J = 19.2, 1.6 Hz, 1H), 4.59-4.56 (m, 2H), 0.94 (t, J = 8.0 Hz, 9H), 0.59 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 142.0, 129.4, 129.0, 120.7, 114.9, 70.8, 7.3, 3.3.

(*E*)-(3-(Benzyloxy)prop-1-enyl)triethylsilane (3w).[2] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (m, 5H), 6.14 (dt, J = 18.8, 5.0 Hz, 1H), 5.88 (d, J = 18.8 Hz, 1H), 4.52 (s, 2H), 4.08-4.05 (m, 2H), 0.94 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 138.4, 128.6, 128.4, 127.8, 127.6, 73.3, 72.1, 7.3, 3.4.

(*E*)-3-(Triethylsilyl)allyl acetate (3x).[5] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.08 (dt, J = 18.8, 5.2 Hz, 1H), 5.87 (d, J = 18.8 Hz, 1H), 4.60 (dd, J = 5.2, 1.6 Hz, 2H), 2.09 (s, 3H), 0.94 (t, J = 8.0 Hz, 9H), 0.58 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.7, 140.5, 129.8, 67.1, 21.0, 7.3, 3.3.

(*E*)-Dimethyl(phenyl)(styryl)silane (4a).[1] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 2H), 7.44 (d, J = 7.2 Hz, 2H), 7.38-7.23 (m, 6H), 6.94 (d, J = 19.2 Hz, 1H), 6.59 (d, J = 19.2 Hz, 1H), 0.43 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 134.0, 130.9, 129.1, 128.9, 128.6, 128.2, 127.9, 127.1, 126.5, -2.5.

(*E*)-Dimethyl(4-methylstyryl)(phenyl)silane (4b). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.54 (m, 2H), 7.38-7.32 (m, 5H), 7.12 (d, J = 7.6 Hz, 2H), 6.91

(d, J = 19.2 Hz, 1H), 6.51 (d, J = 19.2 Hz, 1H), 2.33 (s, 3H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.2, 138.7, 138.0, 135.5, 133.9, 129.2, 129.0, 127.8, 126.4, 125.7, 21.2, -2.5. HRMS calcd for $C_{17}H_{21}Si^+$ [M + H^+]: 253.1413, found 253.1417.

(*E*)-Methyl 4-(2-(dimethyl(phenyl)silyl)vinyl)benzoate (4c). White solid, Mp 87–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, J = 6.8 Hz, 2H), 7.59-7.54 (m, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.42-7.34 (m, 3H), 6.96 (d, J = 19.2 Hz, 1H), 6.73 (dd, J = 19.2, 1.6 Hz, 1H), 3.91 (s, 3H), 0.46 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 144.1, 142.4, 138.0, 133.9, 130.9, 129.9, 129.5, 129.2, 127.9, 126.4, 52.1, -2.6. HRMS calcd for $C_{18}H_{20}O_2Si^+$ [M^+]: 296.1233, found 296.1235.

(*E*)-(2-Cyclohexenylvinyl)dimethyl(phenyl)silane (4d).[6] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.51 (m, 2H), 7.36-7.32 (m, 3H), 6.59 (d, J = 18.8 Hz, 1H), 5.83 (br, 1H), 5.80 (d, J = 18.8 Hz, 1H), 2.19-2.12 (m, 4H), 1.69-1.56 (m, 4H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.0, 139.2, 137.3, 133.9, 131.6, 128.8, 127.7, 121.9, 26.0, 24.0, 22.6, 22.4, -2.4.

(*E*)-6-(Dimethyl(phenyl)silyl)hex-5-en-1-ol (4e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 2H), 7.36-7.32 (m, 3H), 6.11 (dt, J = 18.4, 6.2 Hz, 1H), 5.77 (d, J = 18.4 Hz, 1H), 3.64 (t, J = 6.4 Hz, 2H), 2.21-2.15 (m, 2H), 1.62-1.45 (m, 4H), 1.35 (br, 1H), 0.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.7, 139.2, 133.8, 128.8, 127.8, 127.7, 62.8, 36.4, 32.2, 24.7, -2.5. HRMS calcd for $C_{14}H_{23}OSi^+$ [M + H^+]: 235.1518, found 235.1513.

(*E*)-6-(Dimethyl(phenyl)silyl)hex-5-enenitrile (4f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.37-7.33 (m, 3H), 6.02 (dt, J = 18.4, 6.0 Hz, 1H), 5.86 (d, J = 18.4 Hz, 1H), 2.34-2.27 (m, 4H), 1.82-1.74 (m, 2H), 0.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 138.7, 133.8, 130.5, 129.0, 127.8, 119.6, 35.3, 24.3, 16.5, -2.5. HRMS calcd for $C_{14}H_{19}NSi^+$ [M^+]: 229.1287, found 229.1288.

(*E*)-4-(Dimethyl(phenyl)silyl)but-3-en-1-ol (4g).[7] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.36-7.33 (m, 3H), 6.10 (dt, J = 18.8, 6.4 Hz, 1H), 5.92 (d, J = 18.8 Hz, 1H), 3.70 (t, J = 6.0 Hz, 2H), 2.46-2.40 (m, 2H), 1.41 (br, 1H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 138.8, 133.8, 131.6, 129.0, 127.8, 61.5, 40.1 -2.5.

(*E*)-3-(Dimethyl(phenyl)silyl)prop-3-en-1-ol (4h).[8] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.37-7.33 (m, 3H), 6.24 (dt, J = 18.8, 4.2 Hz, 1H), 6.05 (d, J = 18.8 Hz, 1H), 4.21-4.18 (m, 2H), 1.57 (br, 1H), 0.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 138.4, 133.8, 129.1, 127.8, 127.2, 65.4, -2.6.

(*E*)-4-(Dimethyl(phenyl)silyl)but-3-en-2-ol (4i).[8] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.36-7.34 (m, 3H), 6.16 (dd, J = 18.8, 4.8 Hz, 1H), 5.96 (d, J = 18.8 Hz, 1H), 4.34-4.28 (m, 1H), 1.63 (br, 1H), 1.27 (d, J = 6.4 Hz, 3H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 138.5, 133.8, 129.0, 127.8, 125.9, 70.4, 22.9, -2.6.

(*E*)-1-(2-(Dimethyl(phenyl)silyl)vinyl)cyclohexanol (4j).[8] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 2H), 7.36-7.33 (m, 3H), 6.21 (d, J = 18.8 Hz, 1H), 6.00 (d, J = 18.8 Hz, 1H), 1.67-1.49 (m, 9H), 1.36 (br, 1H), 1.31-1.22 (m, 1H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.3, 138.8, 133.8, 128.9, 127.7, 123.1, 72.7, 37.4, 25.5, 22.0, -2.5.

(*E*)-2-(3-(Dimethyl(phenyl)silyl)allyloxy)ethanol (4k). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H), 7.37-7.34 (m, 3H), 6.16 (dt, J = 18.8, 4.4 Hz, 1H), 6.06 (d, J = 18.8 Hz, 1H), 4.08 (d, J = 4.4 Hz, 2H), 3.77-3.73 (m, 2H), 3.56 (t, J = 4.6 Hz, 2H), 2.12 (br, 1H), 0.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 138.4, 133.8, 129.9, 129.1, 127.8, 73.9, 71.5, 61.9, -2.7. HRMS calcd for $C_{13}H_{20}O_2Si^+$ [M^+]: 236.1233, found 236.1237.

(*E*)-Dimethyl(3-(oxiran-2-ylmethoxy)prop-1-enyl)(phenyl)silane (4l). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.37-7.34 (m, 3H), 6.16 (dt, J = 18.8, 4.2 Hz, 1H), 6.07 (d, J = 18.8 Hz, 1H), 4.15-4.05 (m, 2H), 3.74 (dd, J = 11.4, 3.0 Hz, 1H), 3.41 (dd, J = 11.4, 5.8 Hz, 1H), 3.20-3.15 (m, 1H), 2.81 (t, J = 4.4 Hz, 1H), 2.64-2.61 (m, 1H), 0.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 138.4, 133.8, 130.0, 129.1, 127.8, 74.1, 71.1, 50.8, 44.4, -2.7. HRMS calcd for $C_{14}H_{21}O_2Si^+$ [$M + H^+$]: 249.1311, found 249.1308.

(*E*)-(1,2-Diphenylvinyl)triethylsilane (6a).[9] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (t, J = 7.4 Hz, 2H), 7.19 (t, J = 7.2 Hz, 1H), 7.10-7.05 (m, 3H), 7.01-6.93 (m, 4H), 6.77 (s, 1H), 0.96 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 8.0 Hz, 6H). ^{13}C

NMR (100 MHz, $CDCl_3$): δ 144.1, 143.2, 138.8, 137.4, 129.5, 128.6, 127.9, 127.3, 127.0, 125.5, 7.3, 2.8.

(*E*)-(1,2-Diphenylvinyl)dimethyl(phenyl)silane (6b).[10] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.38-7.33 (m, 3H), 7.25-7.20 (m, 3H), 7.18-7.14 (m, 3H), 7.08-6.93 (m, 2H), 6.89 (d, J = 7.6 Hz, 2H), 6.82 (s, 1H), 0.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 142.3, 139.2, 137.7, 137.2, 134.3, 129.6, 129.1, 128.5, 127.9, 127.8, 127.7, 127.2, 125.7, -3.1.

(*E*)-Dec-5-en-5-yldimethyl(phenyl)silane (6c).[11] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.48 (m, 2H), 7.35-7.30 (m, 3H), 5.79 (t, J = 6.8 Hz, 1H), 2.15-2.07 (m, 4H), 1.39-1.29 (m, 4H), 1.26-1.13 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H), 0.81 (t, J = 7.0 Hz, 3H), 0.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 139.5, 138.8, 134.0, 128.6, 127.6, 32.4, 31.8, 29.6, 28.3, 23.0, 22.5, 14.0, 13.9, -2.5.

(*E*)-Hex-3-en-3-yldimethyl(phenyl)silane (6d).[12] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.48 (m, 2H), 7.35-7.30 (m, 3H), 5.78 (t, J = 6.8 Hz, 1H), 2.18-2.09 (m, 4H), 0.99 (t, J = 7.4 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H), 0.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 139.8, 139.4, 134.0, 128.7, 127.6, 22.6, 21.7, 14.9, 14.1, -2.6.

(*E*)-Ethyl 2-(dimethyl(phenyl)silyl)-3-phenylacrylate (6e). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.59 (m, 2H), 7.40-7.36 (m, 3H), 7.31-7.25 (m, 5H), 6.79 (s, 1H), 4.11 (q, J = 7.2 Hz, 2H), 1.11 (t, J = 7.2 Hz, 3H), 0.52 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 143.4, 137.0, 136.5, 136.3, 134.2, 129.5, 128.6, 128.3, 127.9, 60.5, 14.0, -2.9. HRMS calcd for $C_{19}H_{22}O_2Si^+$ [M^+]: 310.1389, found 310.1394.

(*E*)-Ethyl 2-(dimethyl(phenyl)silyl)oct-2-enoate (6f). Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.51 (m, 2H), 7.36-7.32 (m, 3H), 6.18 (t, J = 7.2 Hz, 1H), 4.10 (q, J = 7.2 Hz, 2H), 2.42-2.36 (m, 2H), 1.44-1.36 (m, 2H), 1.31-1.25 (m, 4H), 1.18 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 6.8 Hz, 3H), 0.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.1, 154.5, 137.6, 134.2, 134.0, 129.1, 127.7, 59.9, 31.7, 31.5, 28.7, 22.4, 14.2, 14.0, -2.5. HRMS calcd for $C_{18}H_{28}O_2Si^+$ [M^+]: 304.1859, found 304.1857.

(*E*)-Triethyl(1-phenylprop-1-en-2-yl)silane (6g).[9] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.13 (m, 5H), 6.70 (d, J = 1.6 Hz, 1H), 1.93 (d, J = 1.6 Hz, 3H),

0.98 (t, J = 7.8 Hz, 9H), 0.68 (q, J = 7.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 138.4, 137.0, 129.1, 128.0, 126.4, 17.0, 7.5, 2.7.

(*E*)-Triethyl(1-phenylprop-1-enyl)silane (6g').[9] Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.13 (m, 3H), 6.94-6.91 (m, 2H), 6.06 (q, J = 6.4 Hz, 1H), 1.56 (d, J = 6.4 Hz, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.55 (q, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.7, 138.6, 137.5, 128.0, 127.8, 125.2, 16.0, 7.3, 2.9.

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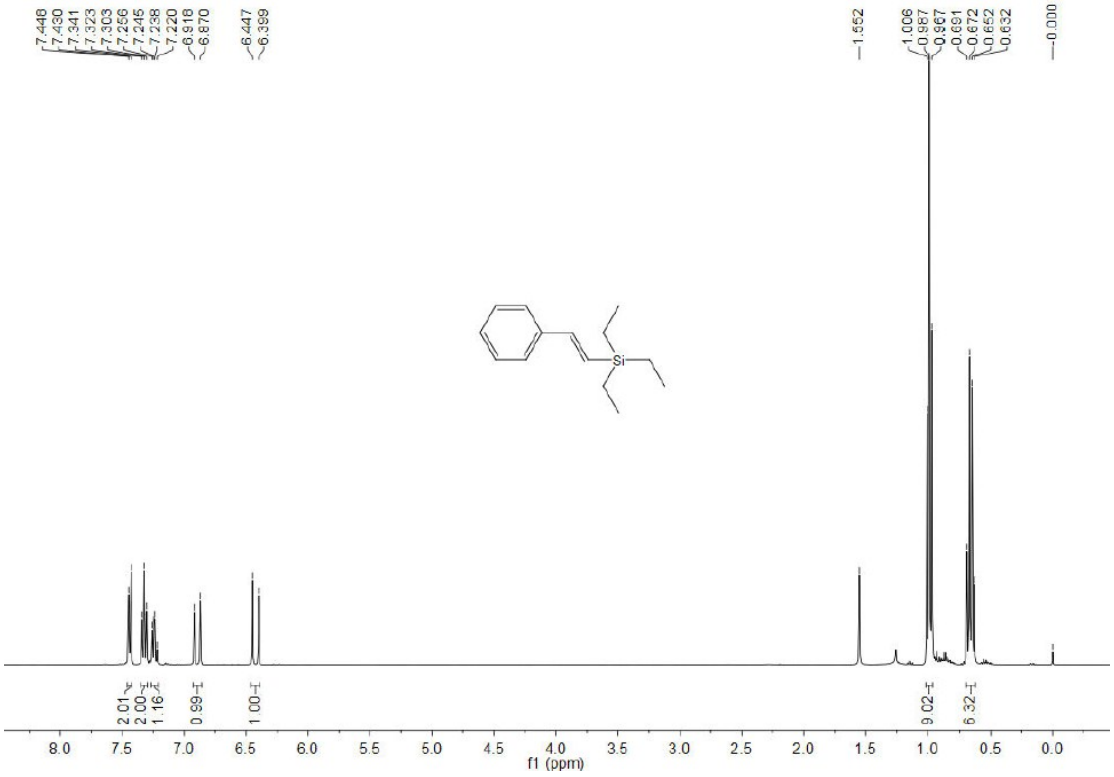
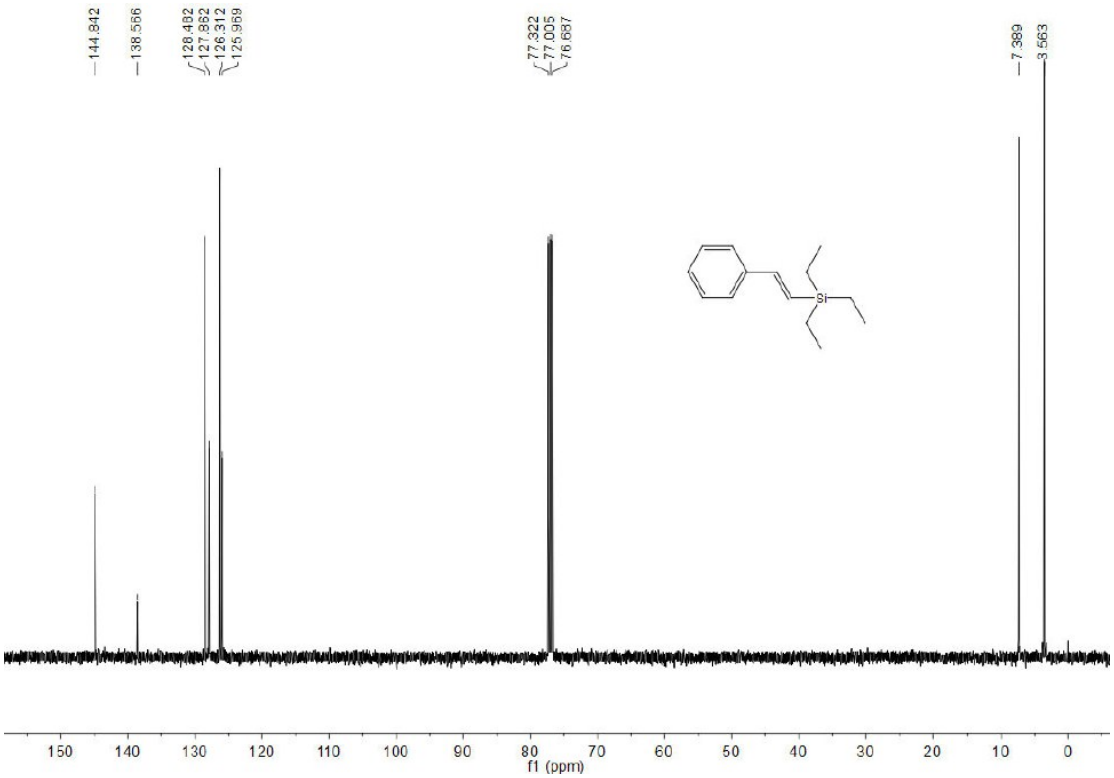
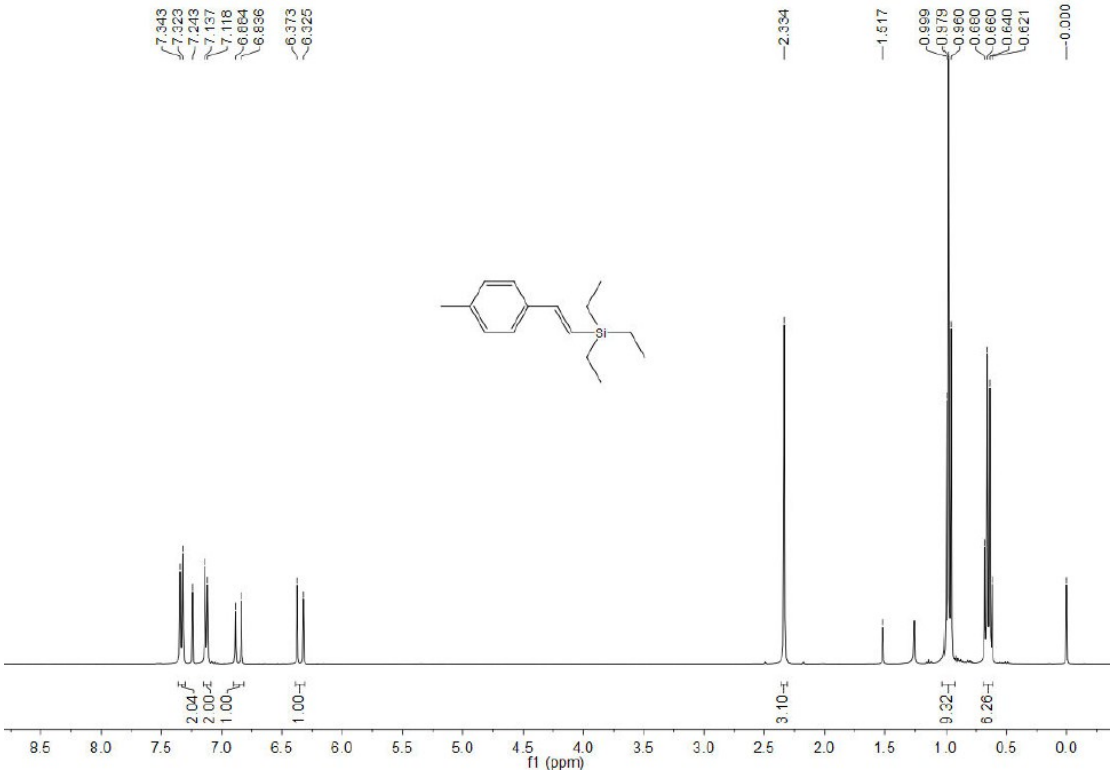
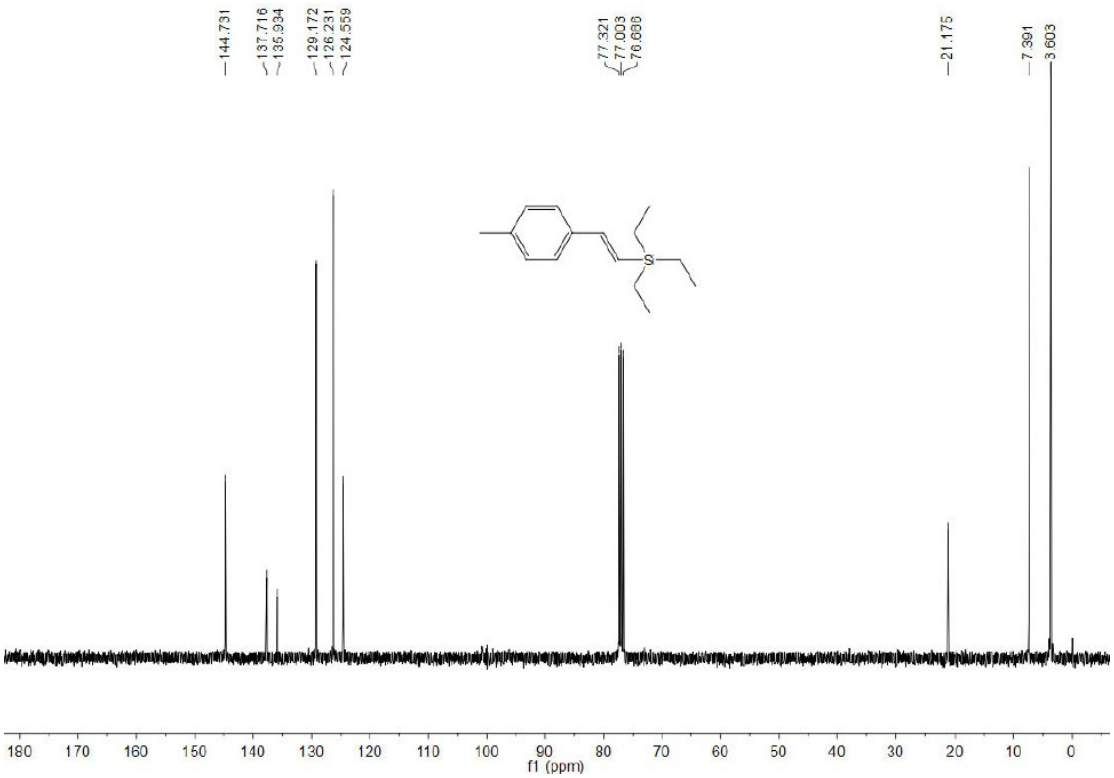
NMR Spectra of products





^{1}H NMR and ^{13}C NMR spectra of compound **3a**





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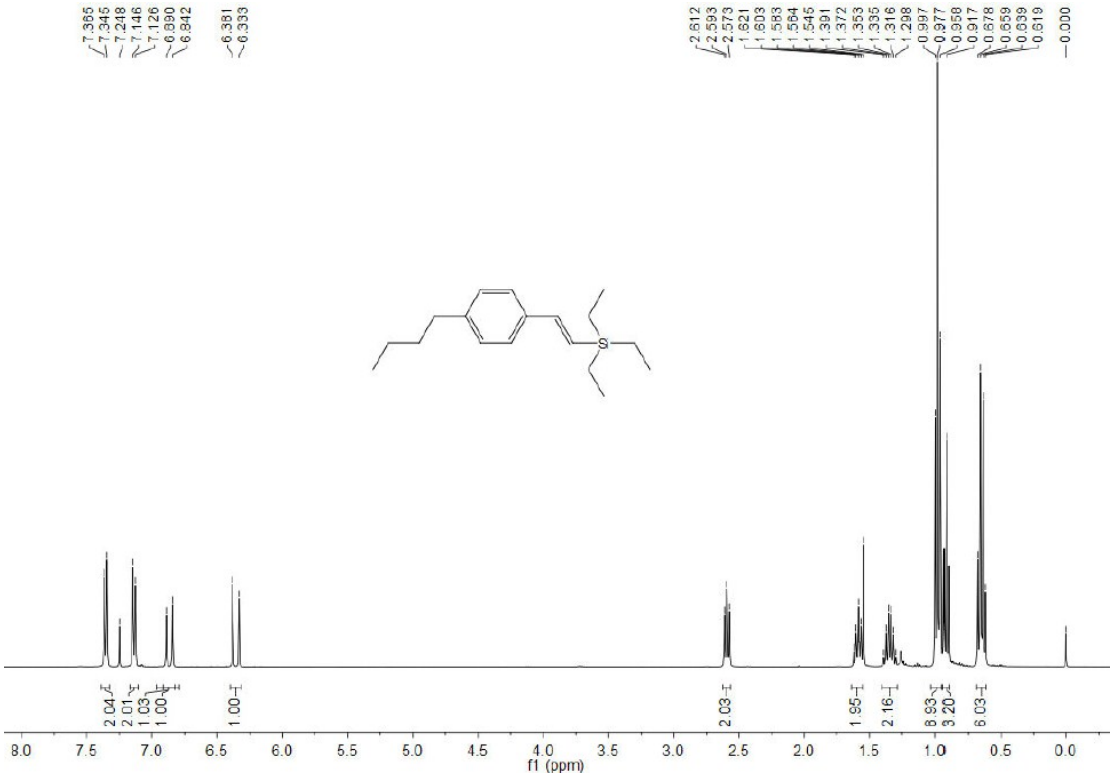
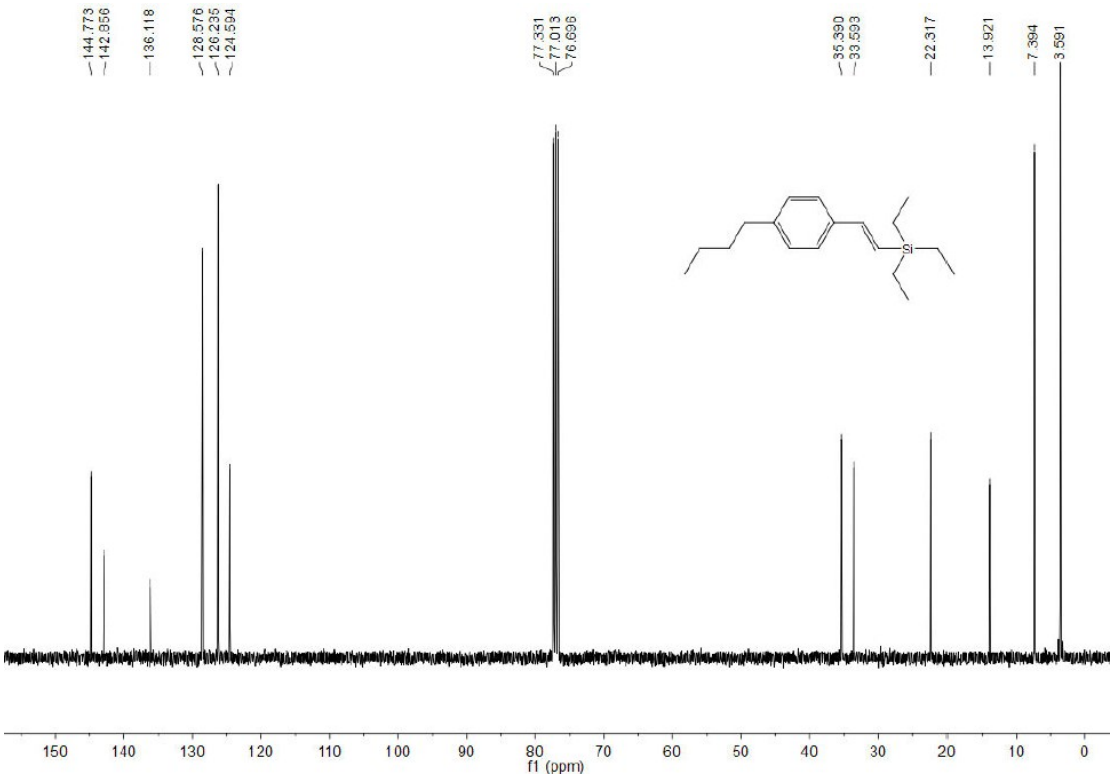
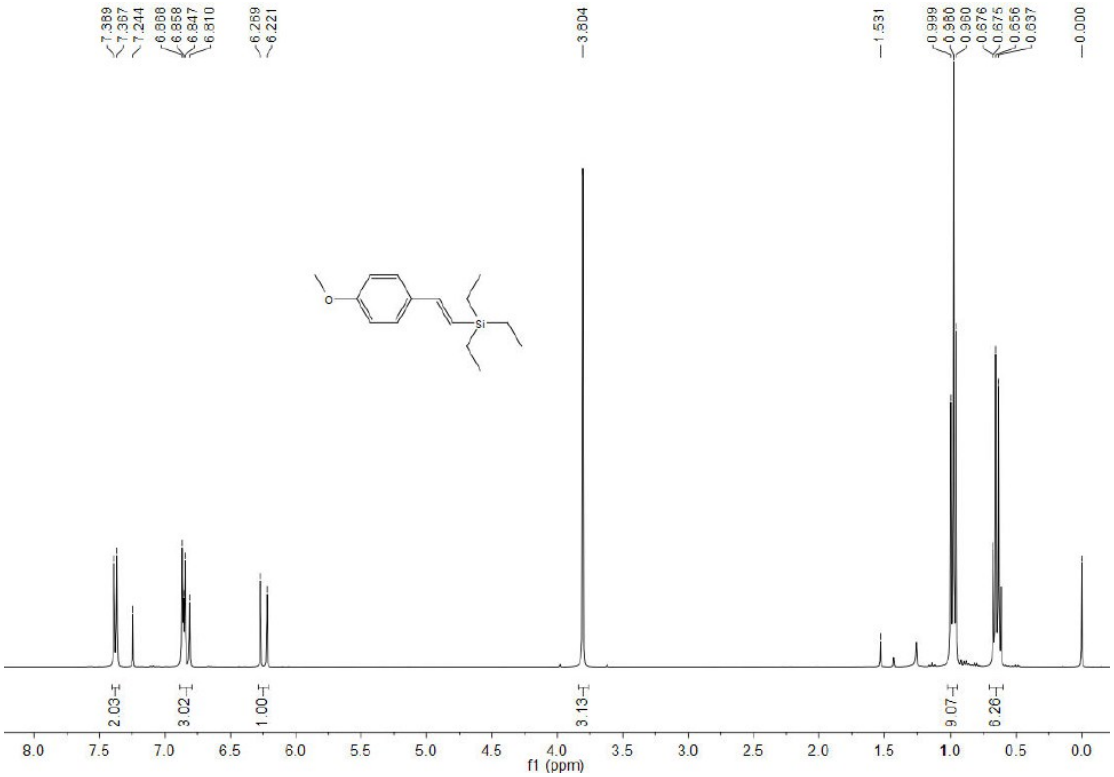
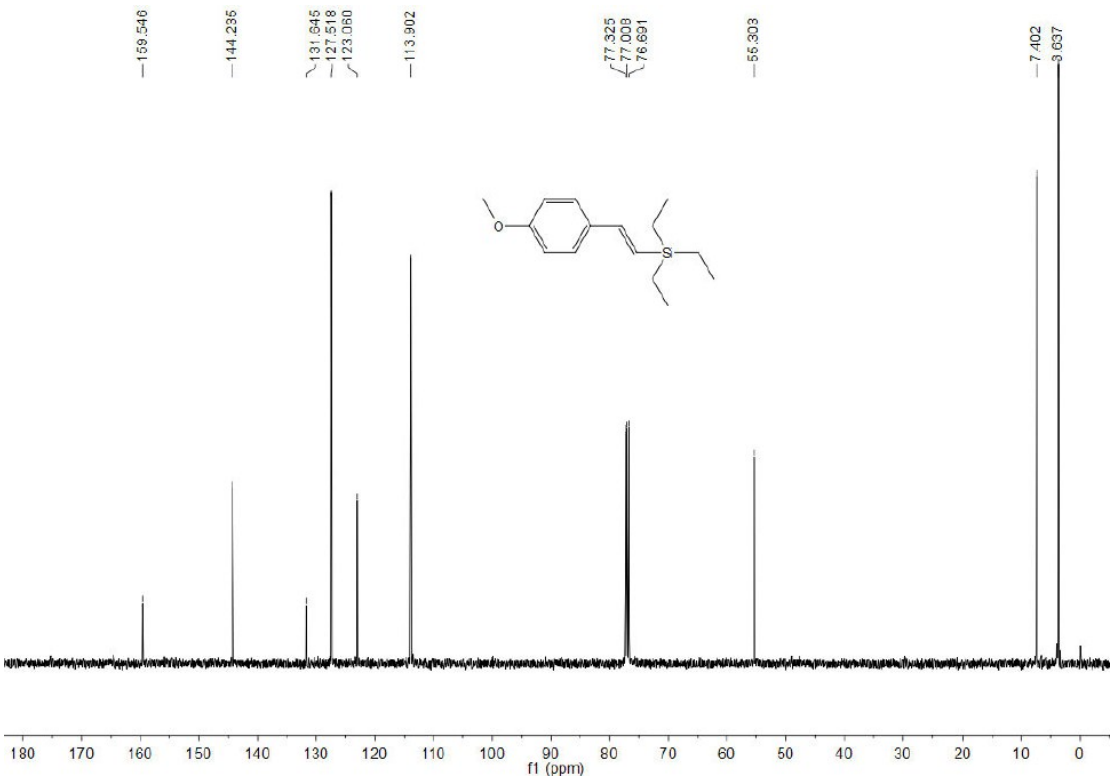




^{1}H NMR and ^{13}C NMR spectra of compound **3c**





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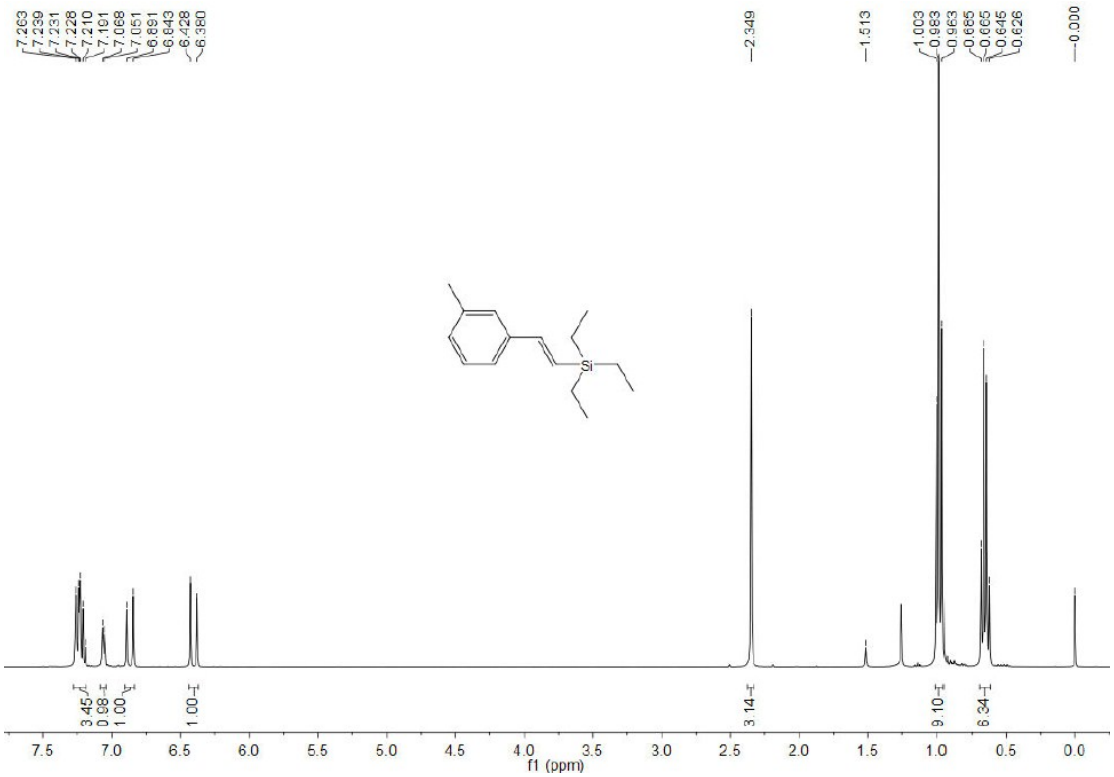
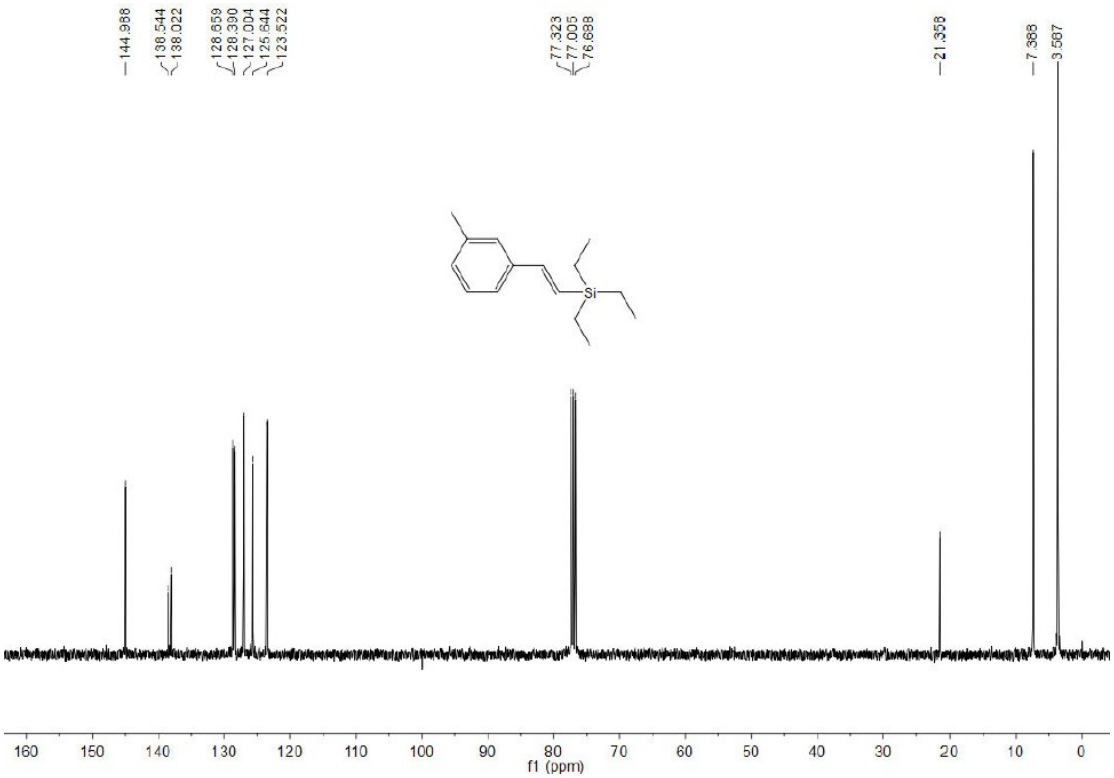
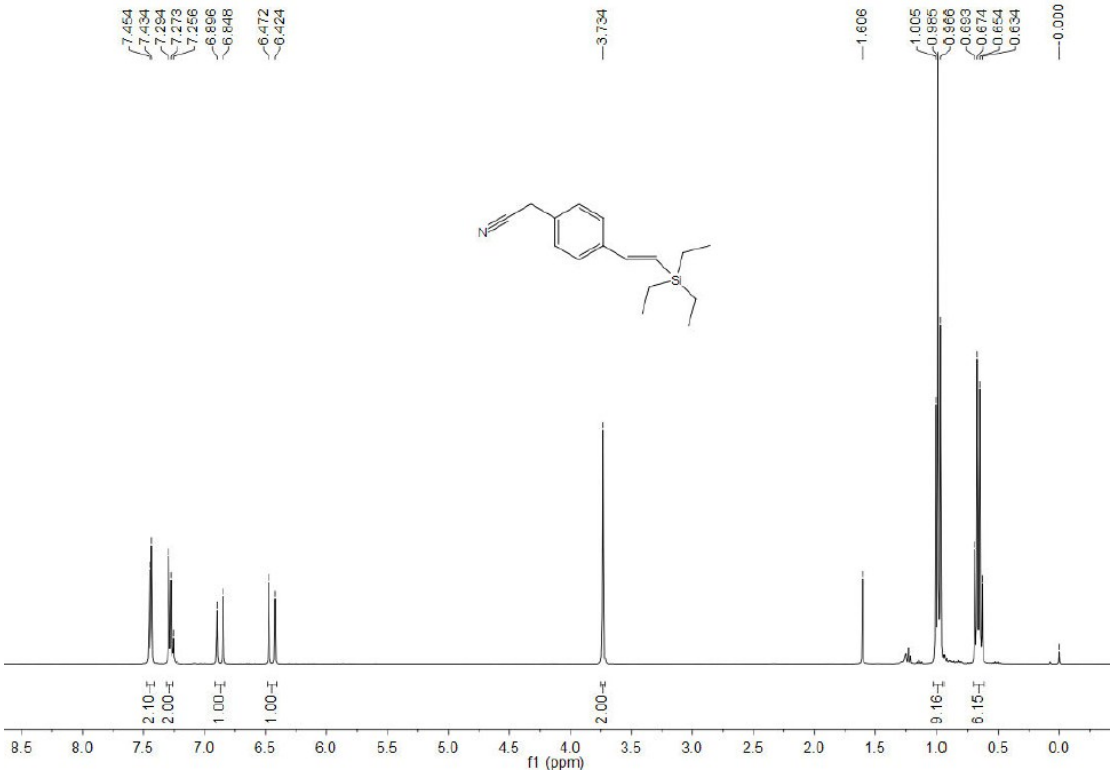
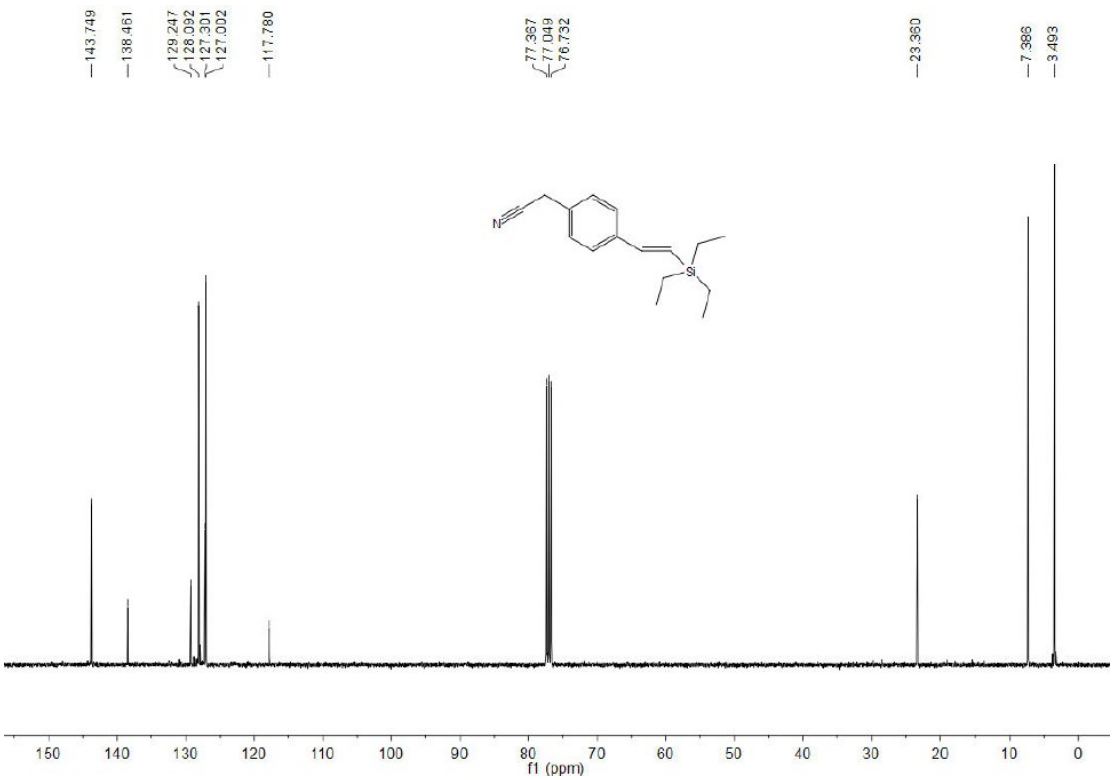


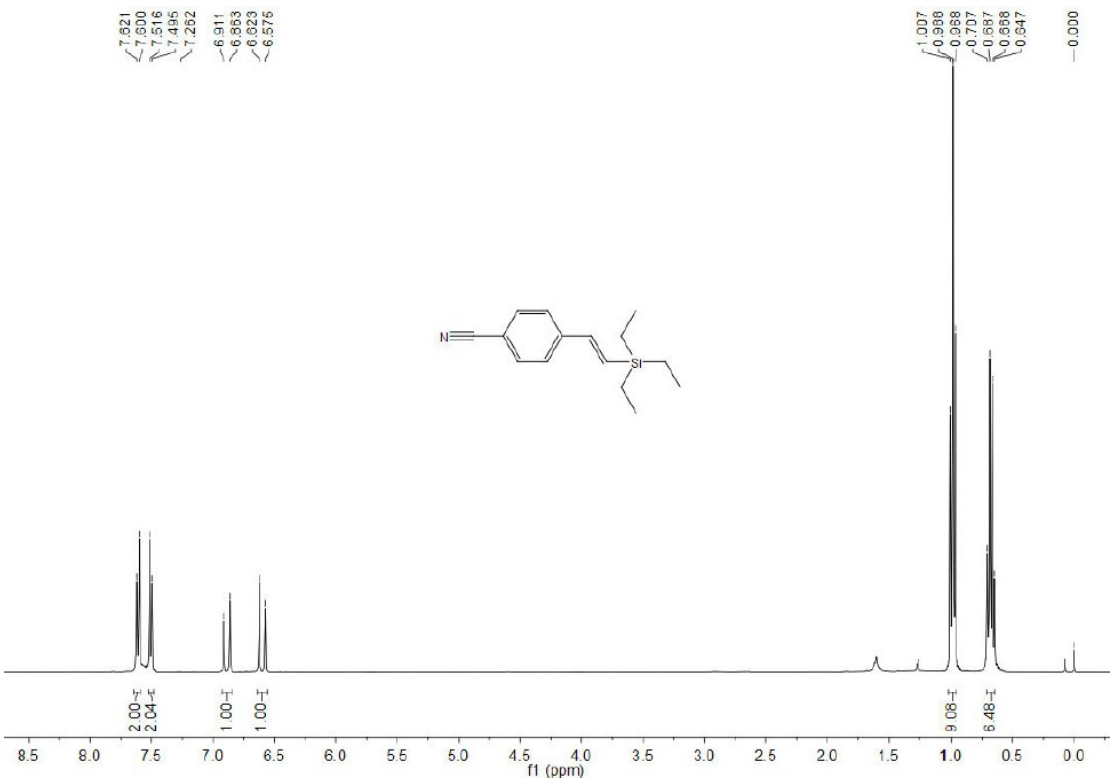


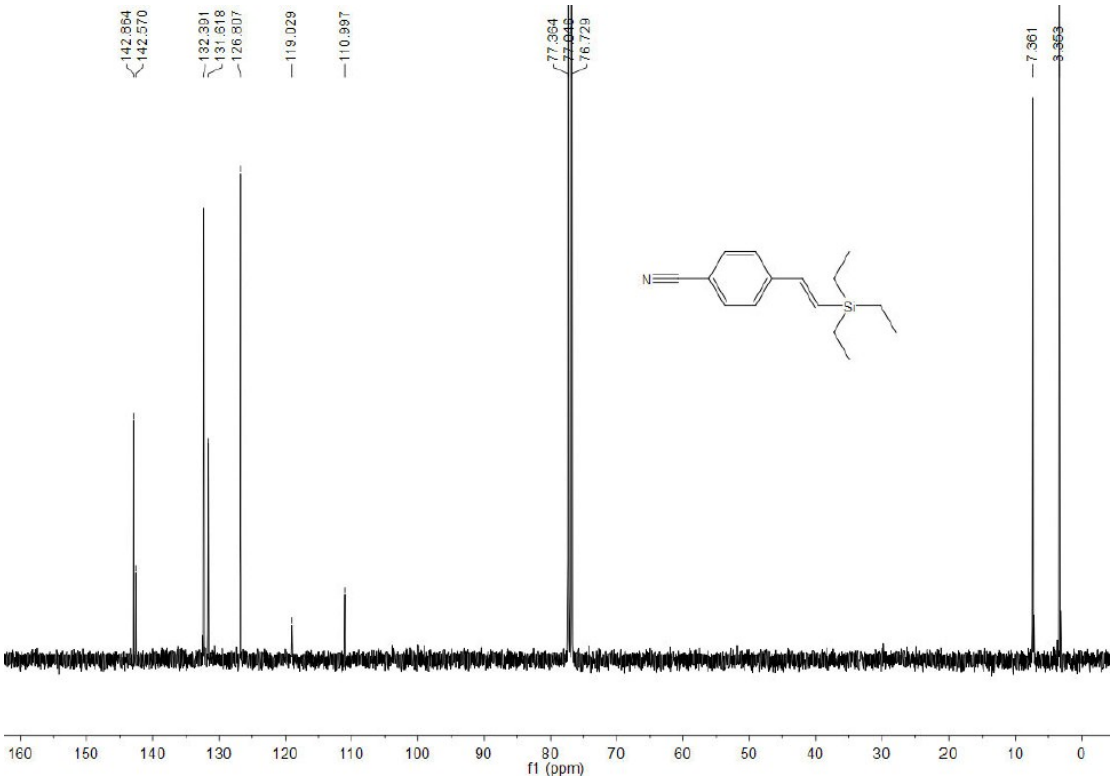
^{1}H NMR and ^{13}C NMR spectra of compound **3e**



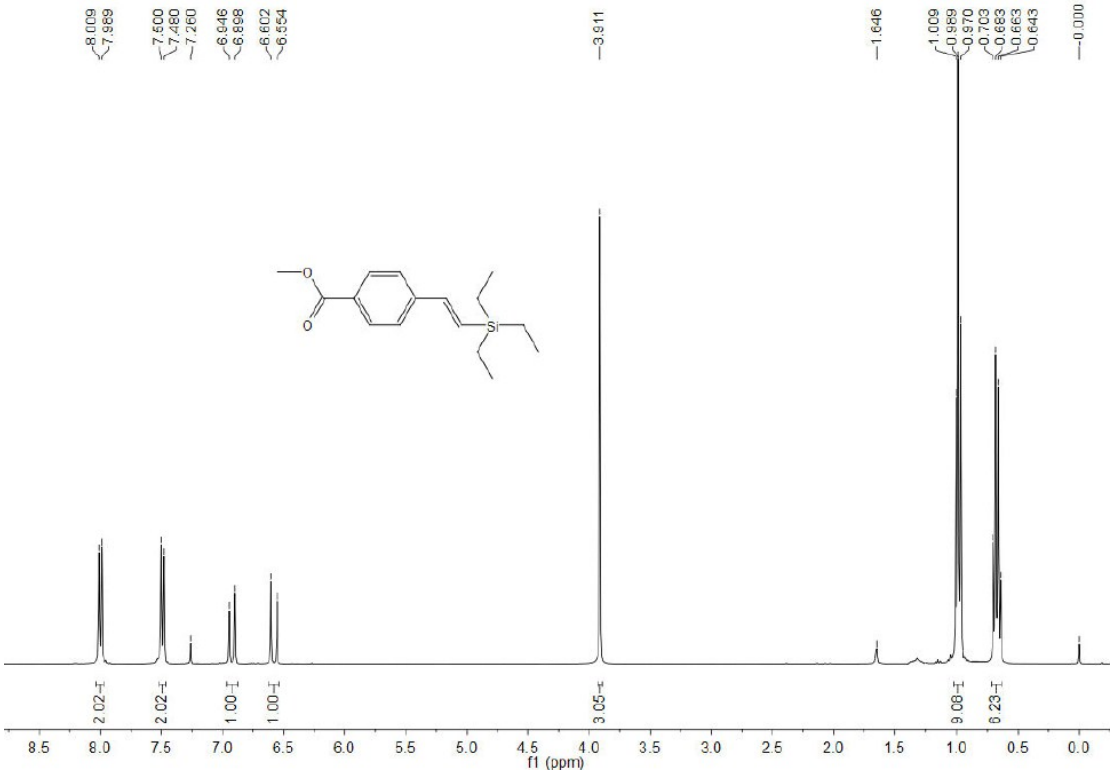


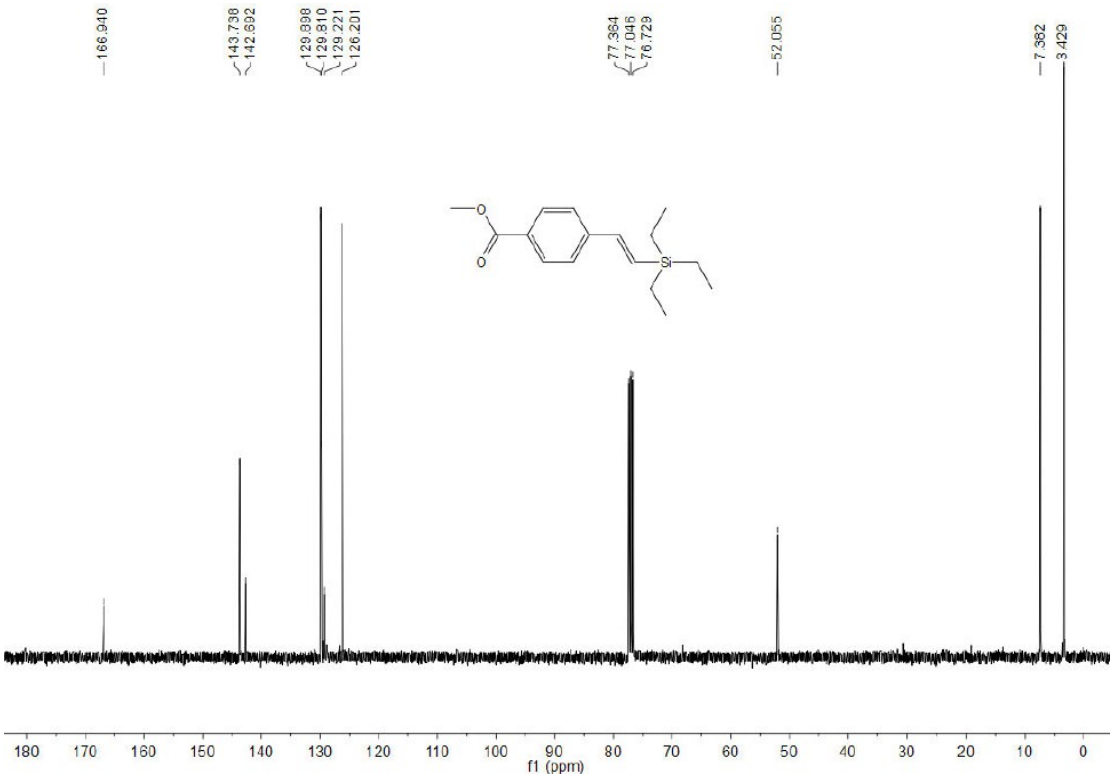
^{1}H NMR and ^{13}C NMR spectra of compound **3f**



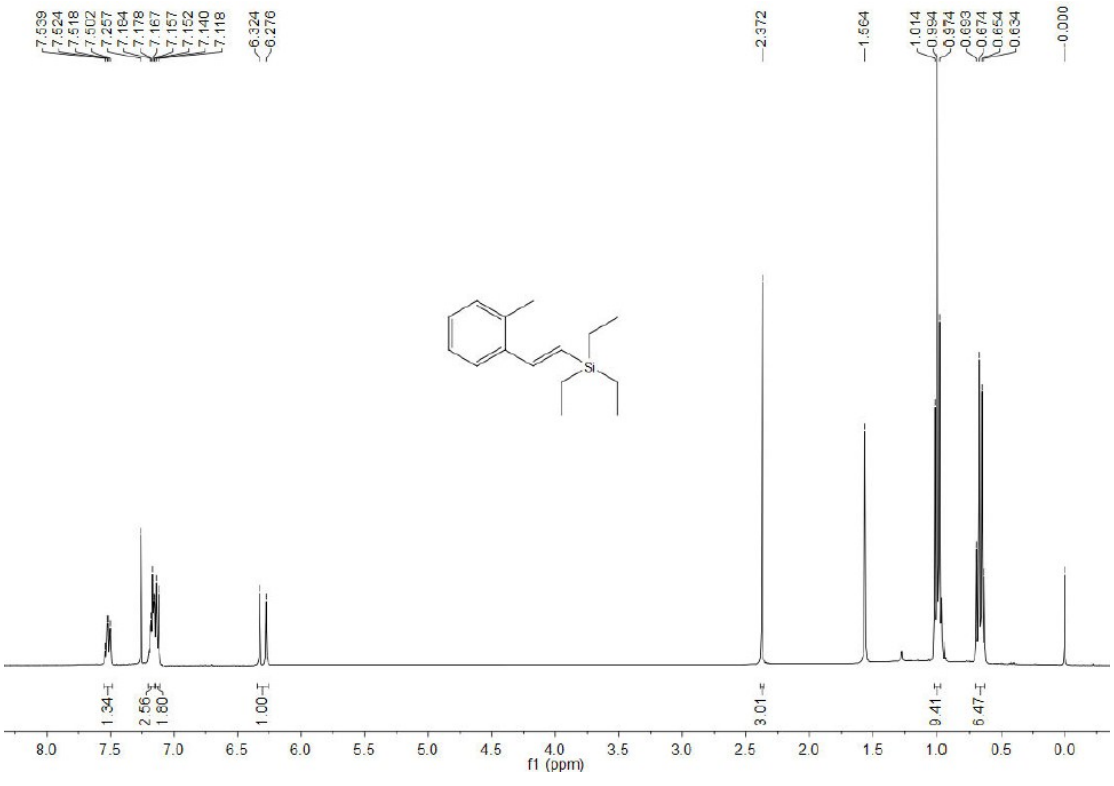


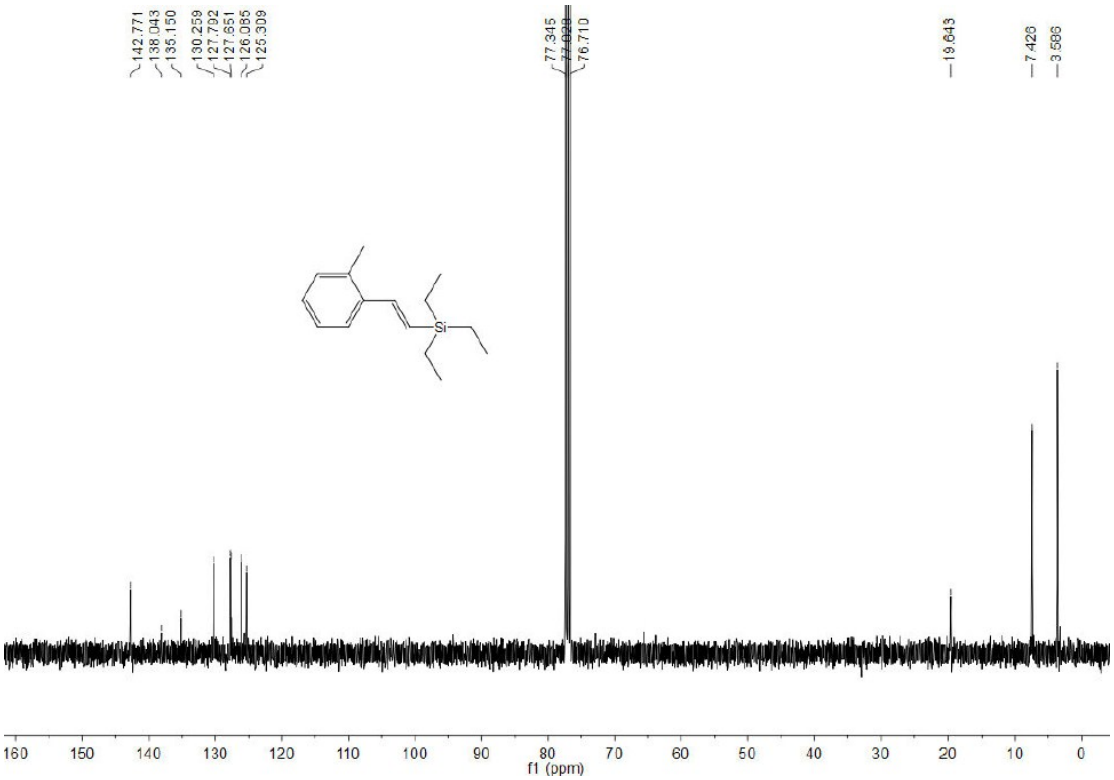
^{1}H NMR and ^{13}C NMR spectra of compound **3g**



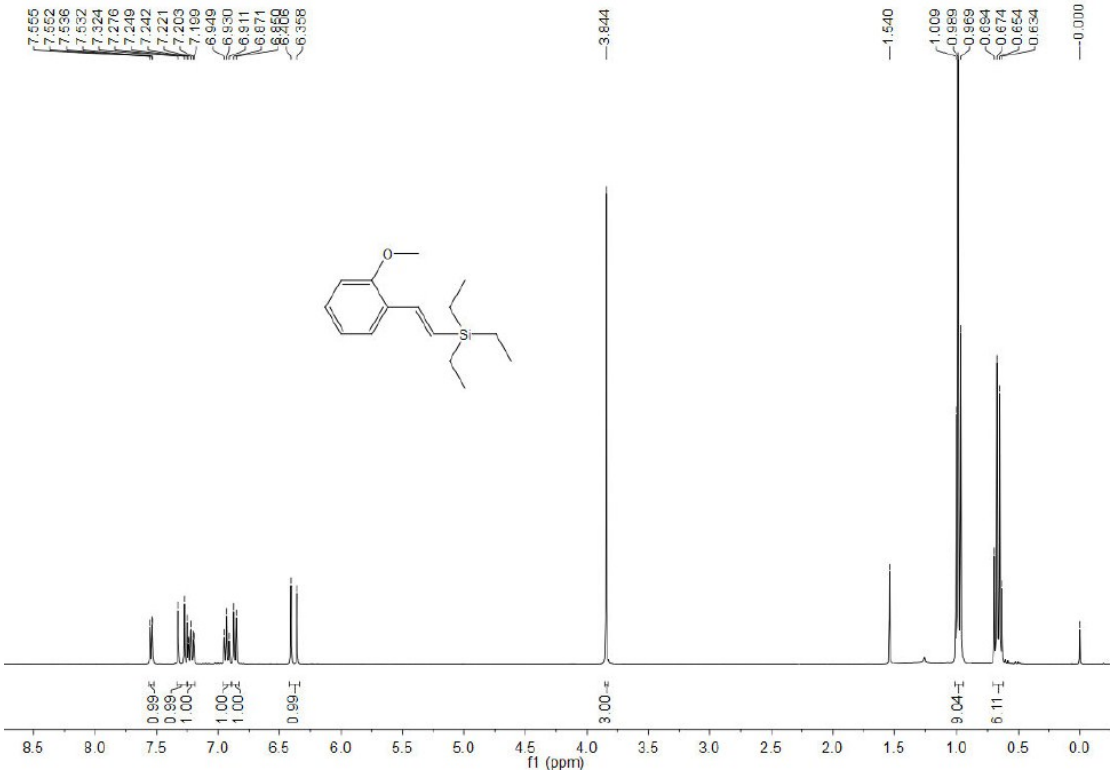


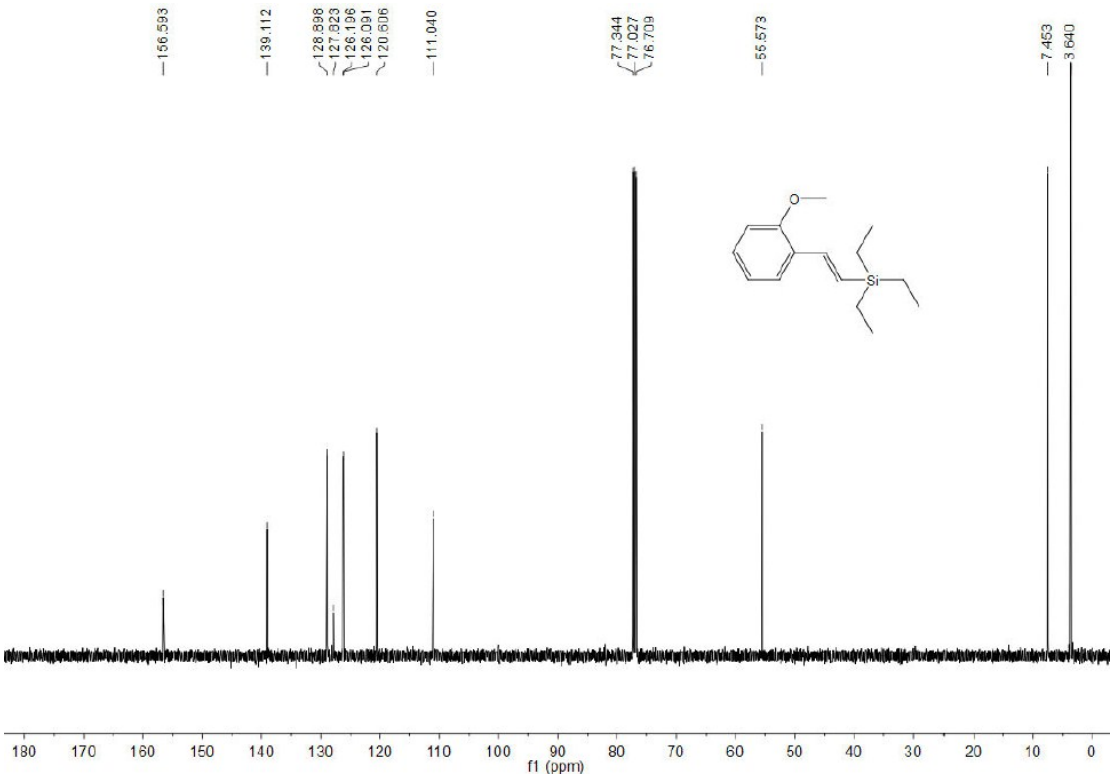
^{1}H NMR and ^{13}C NMR spectra of compound **3h**



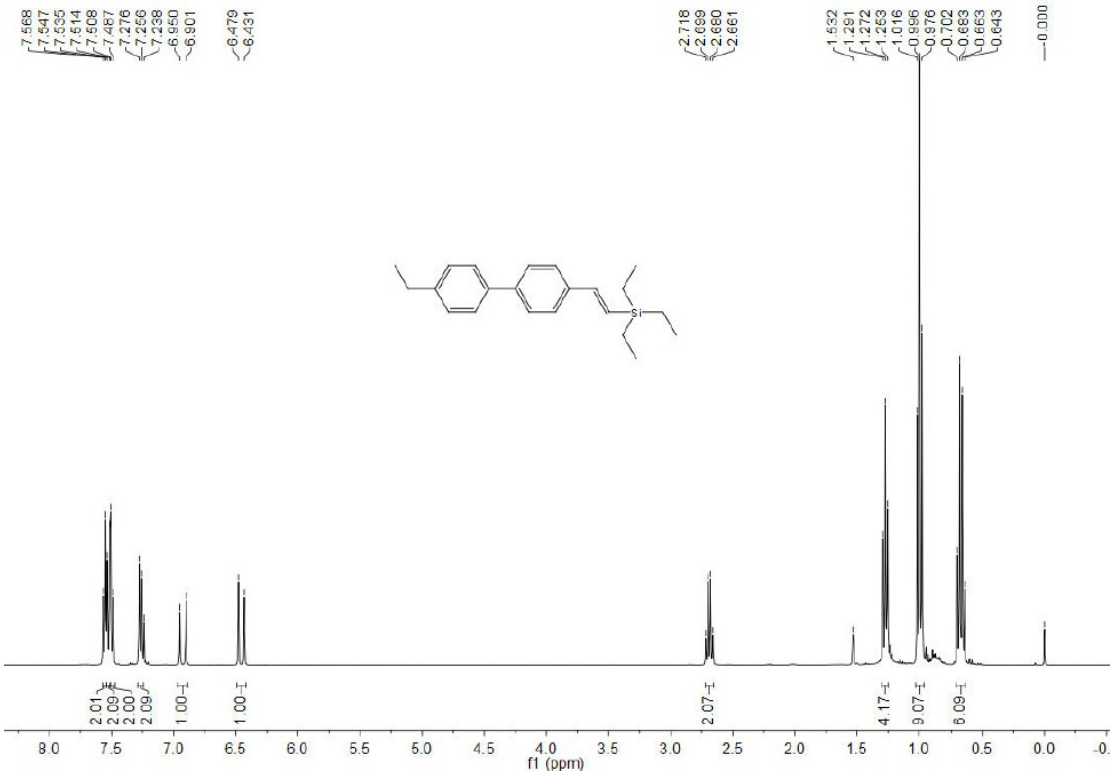


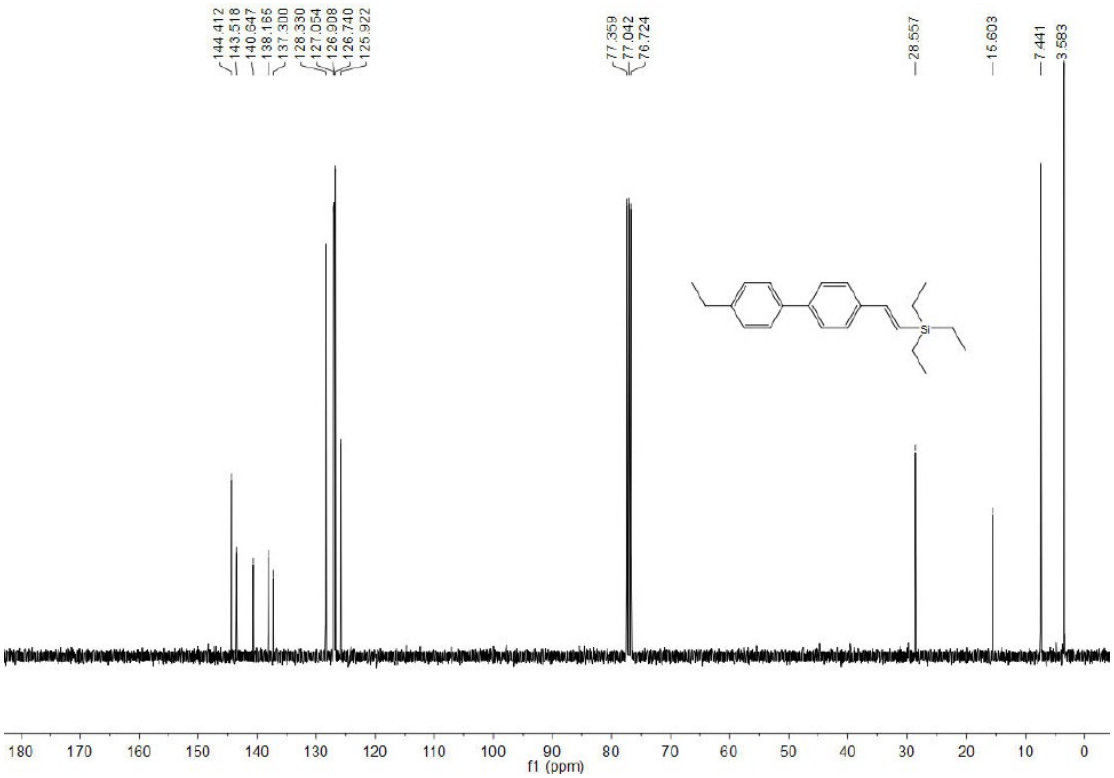
^{1}H NMR and ^{13}C NMR spectra of compound **3i**





^{1}H NMR and ^{13}C NMR spectra of compound **3j**





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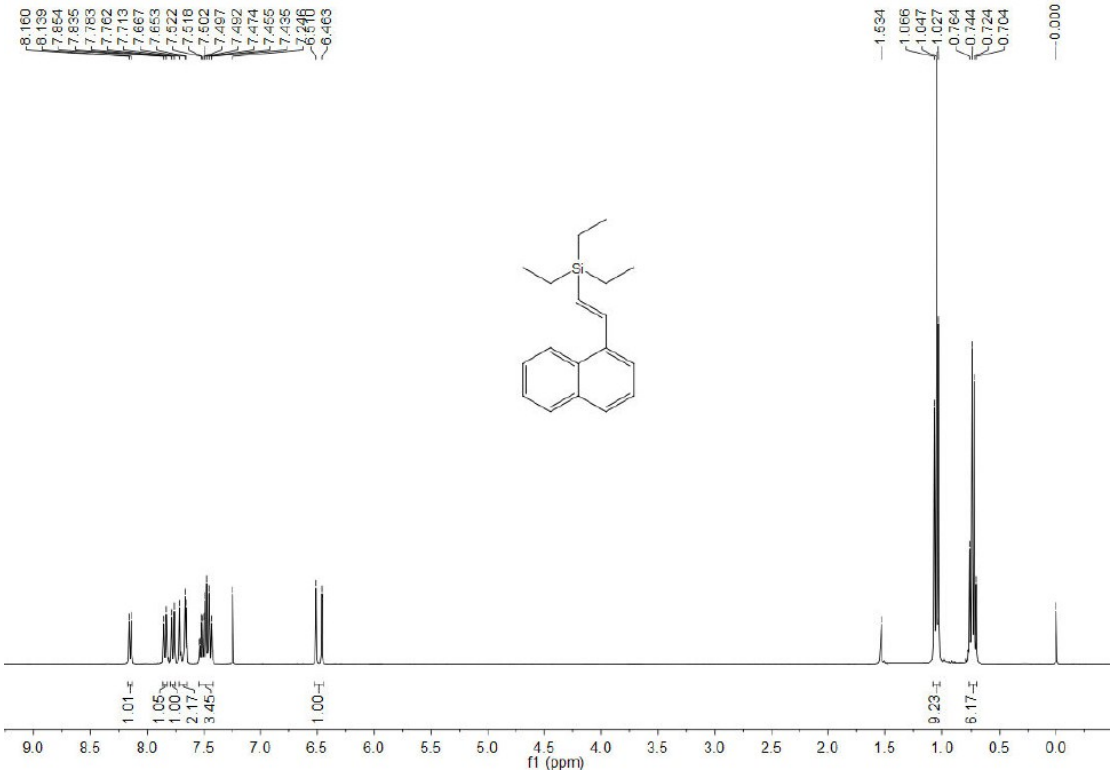
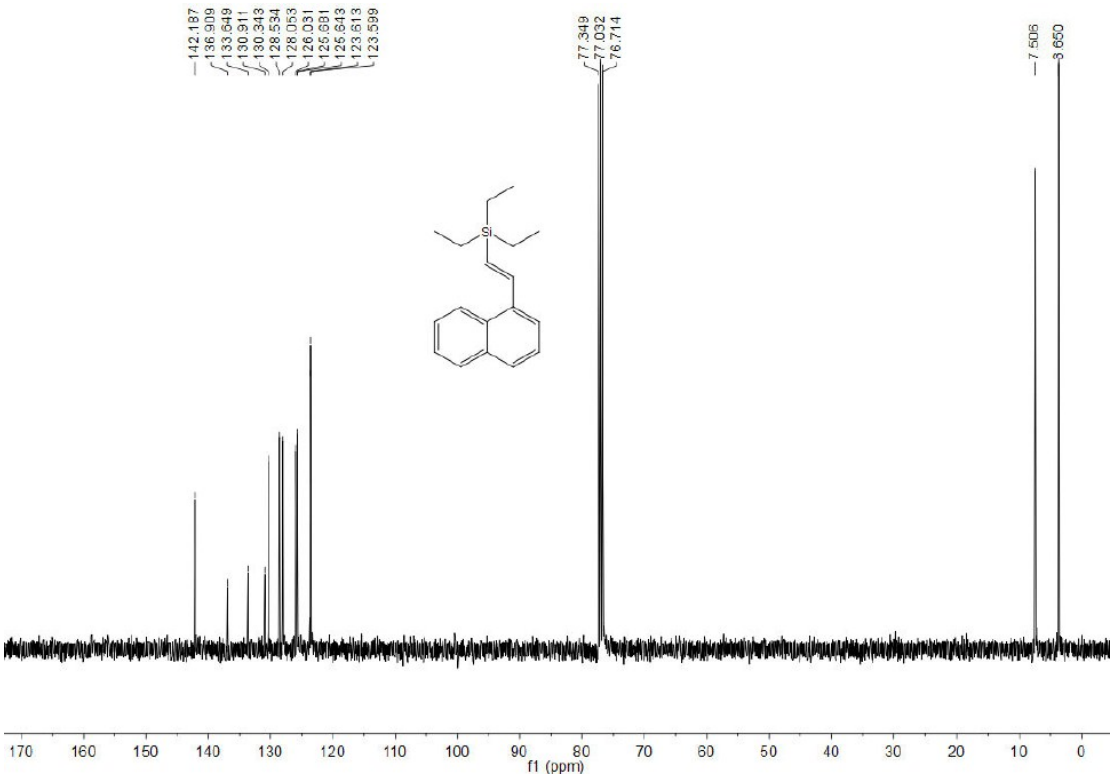
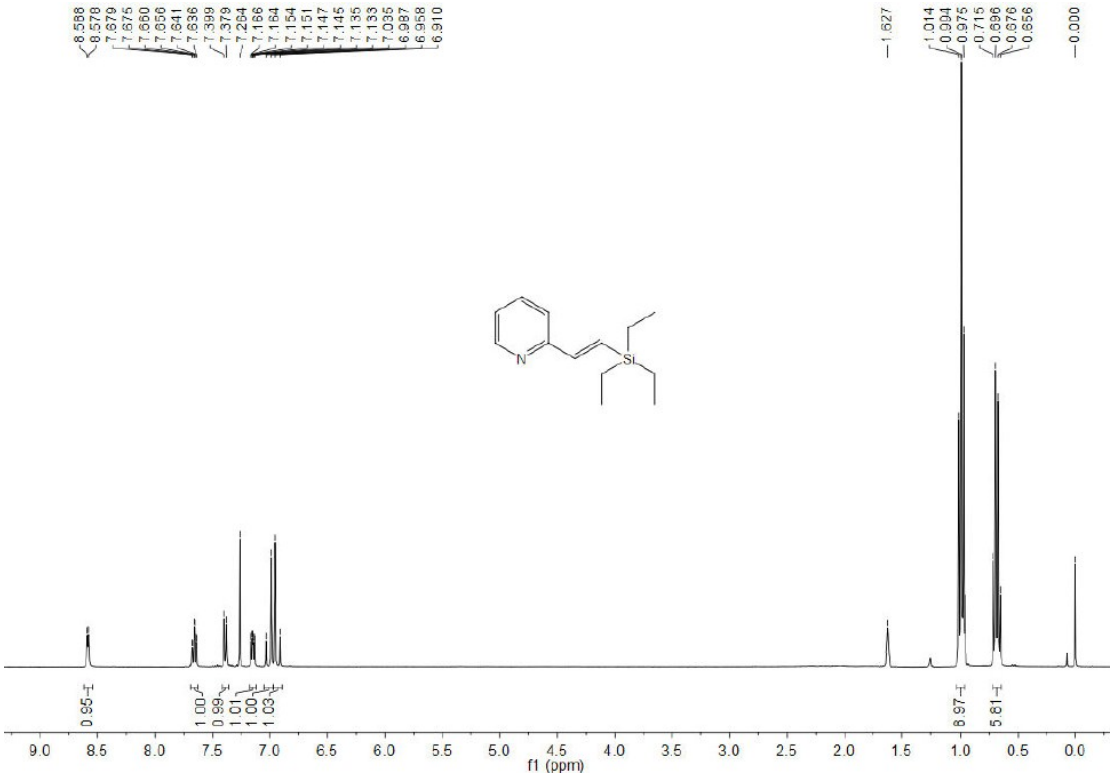
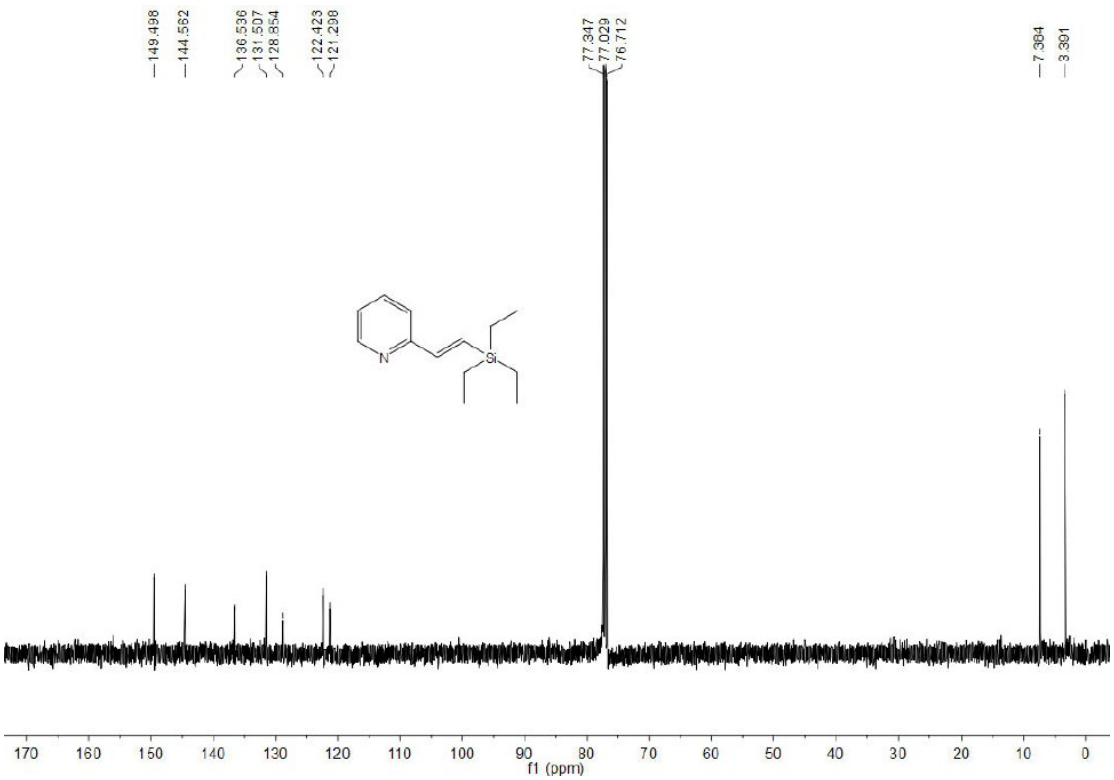


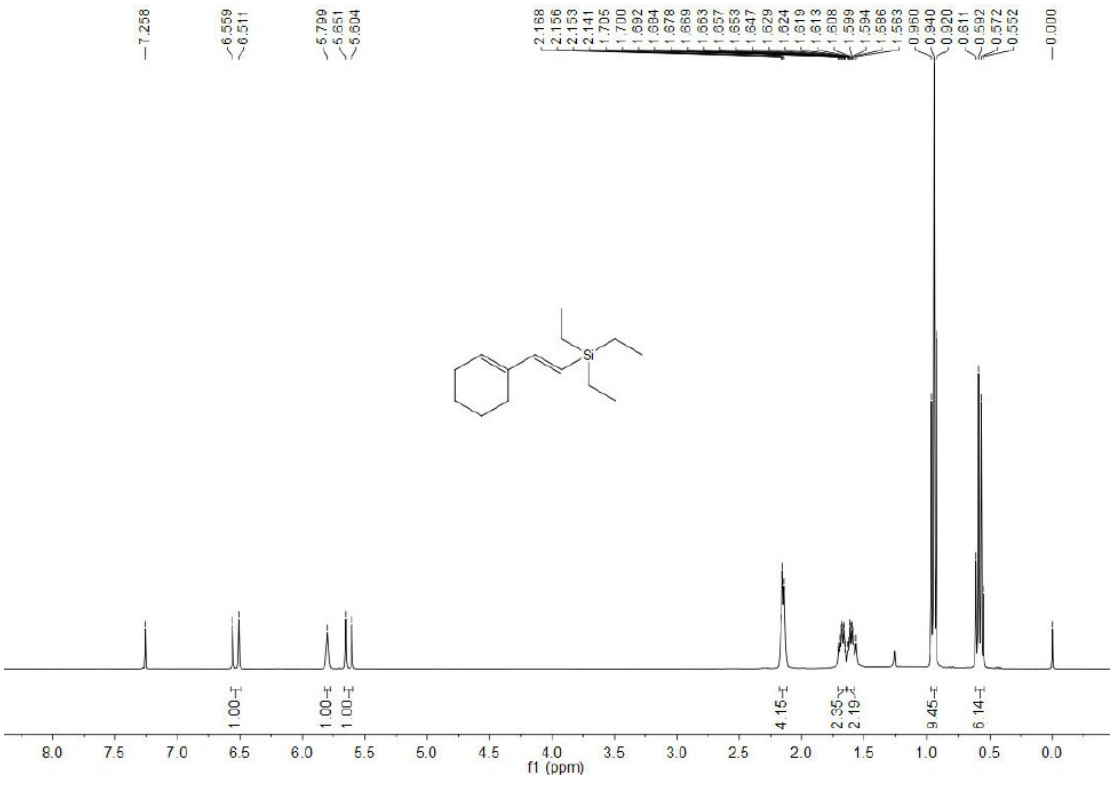


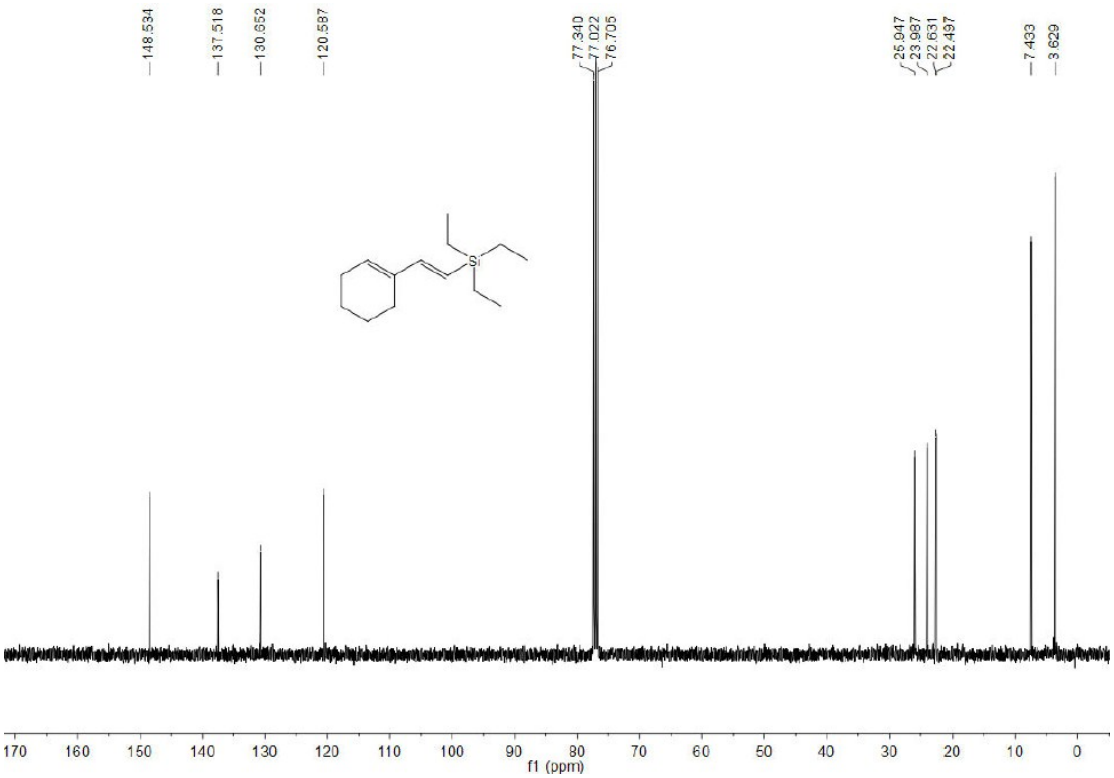
^{1}H NMR and ^{13}C NMR spectra of compound **3l**



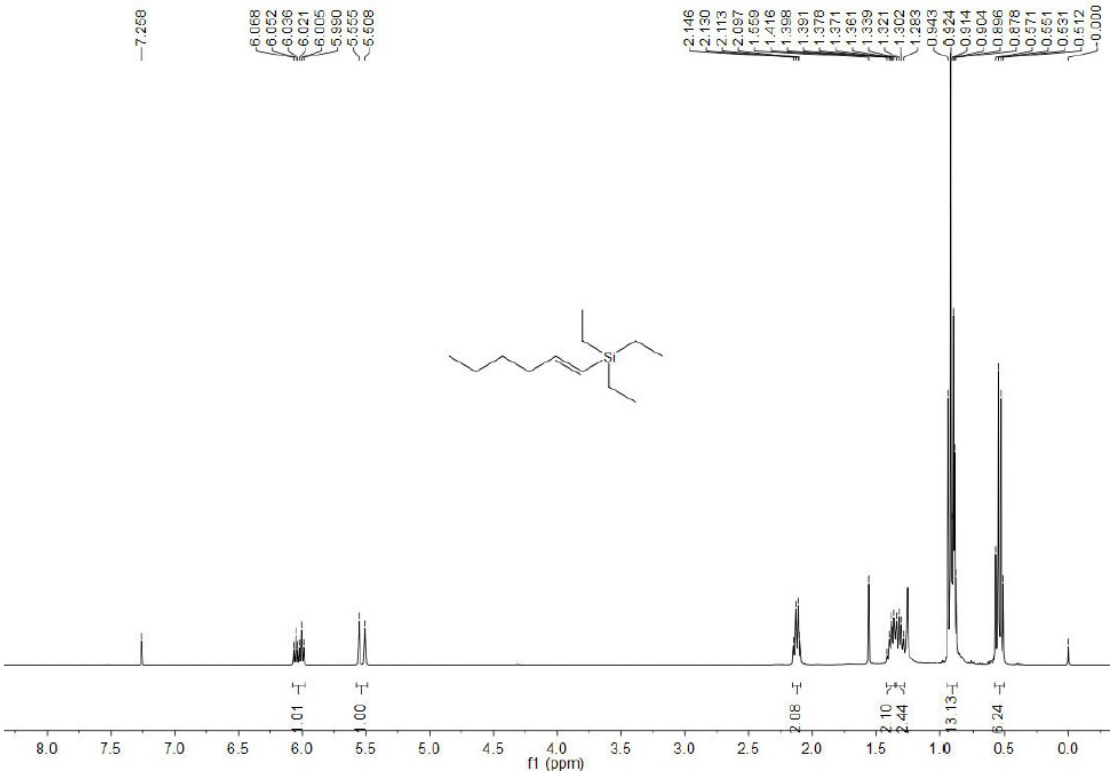


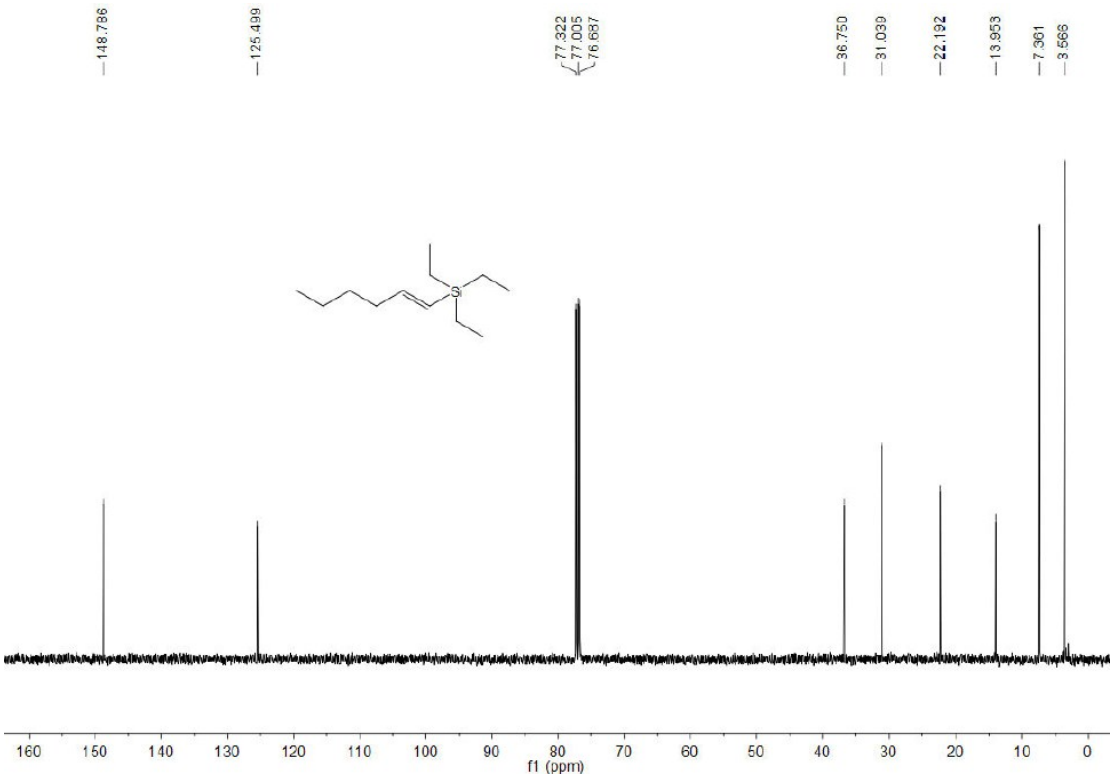
^{1}H NMR and ^{13}C NMR spectra of compound **3m**



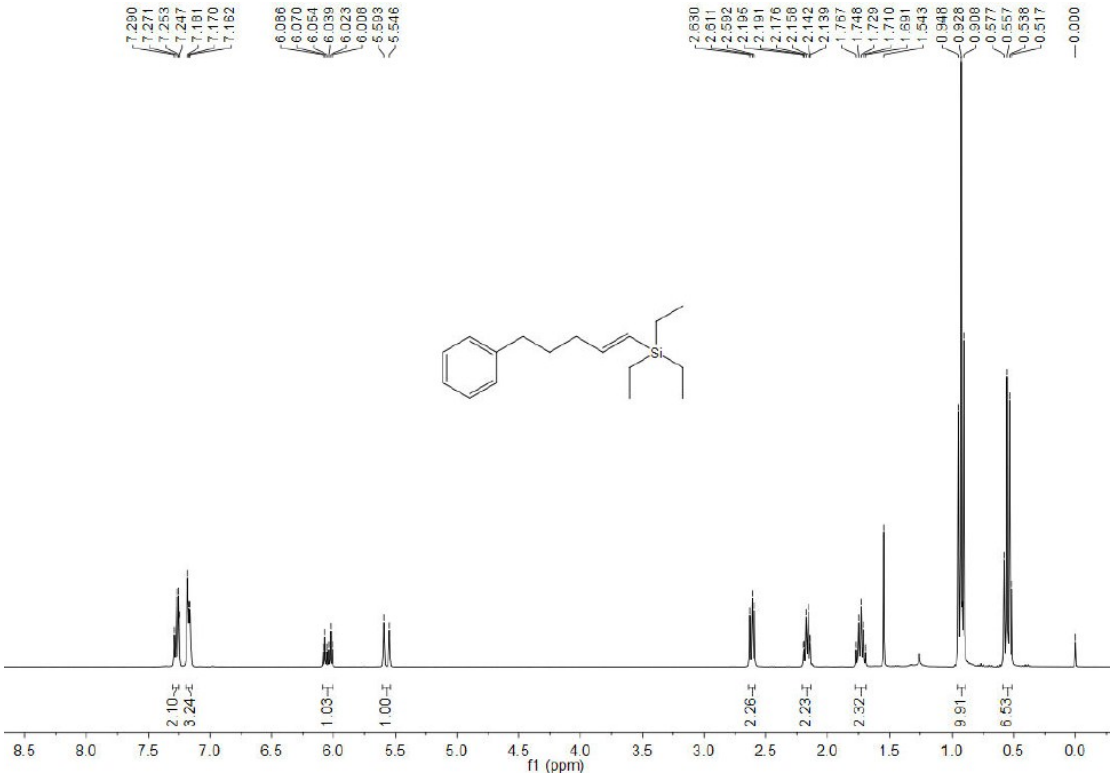


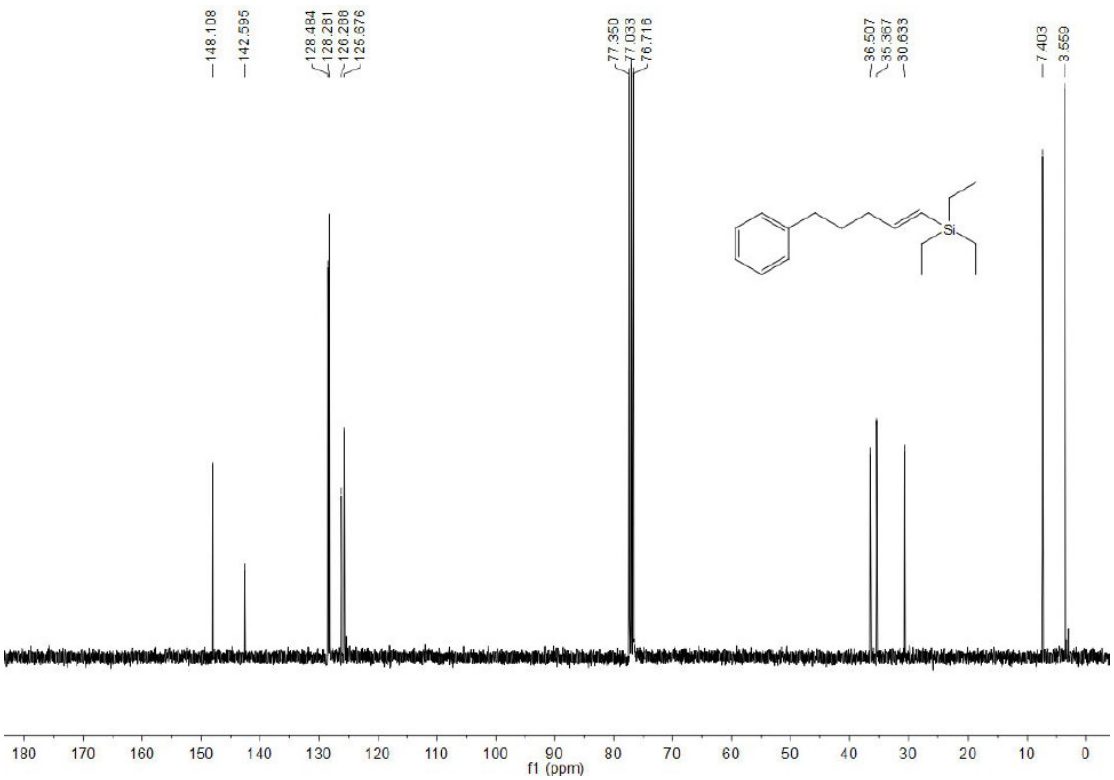
^{1}H NMR and ^{13}C NMR spectra of compound **3n**



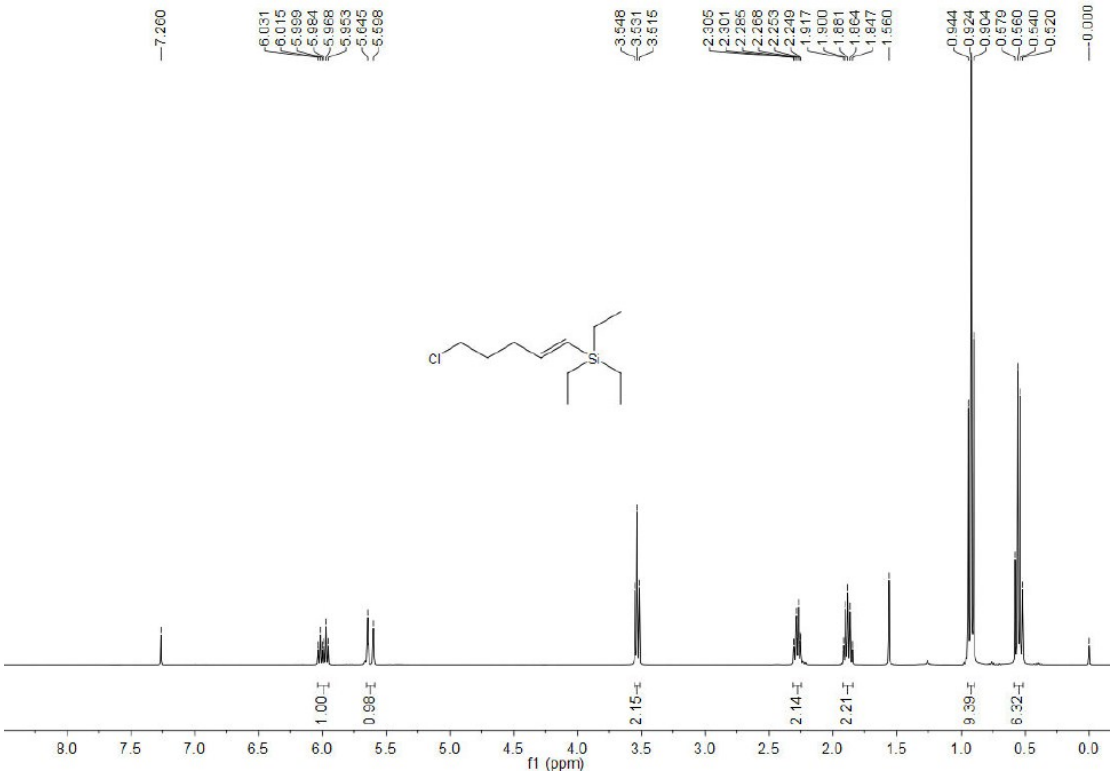


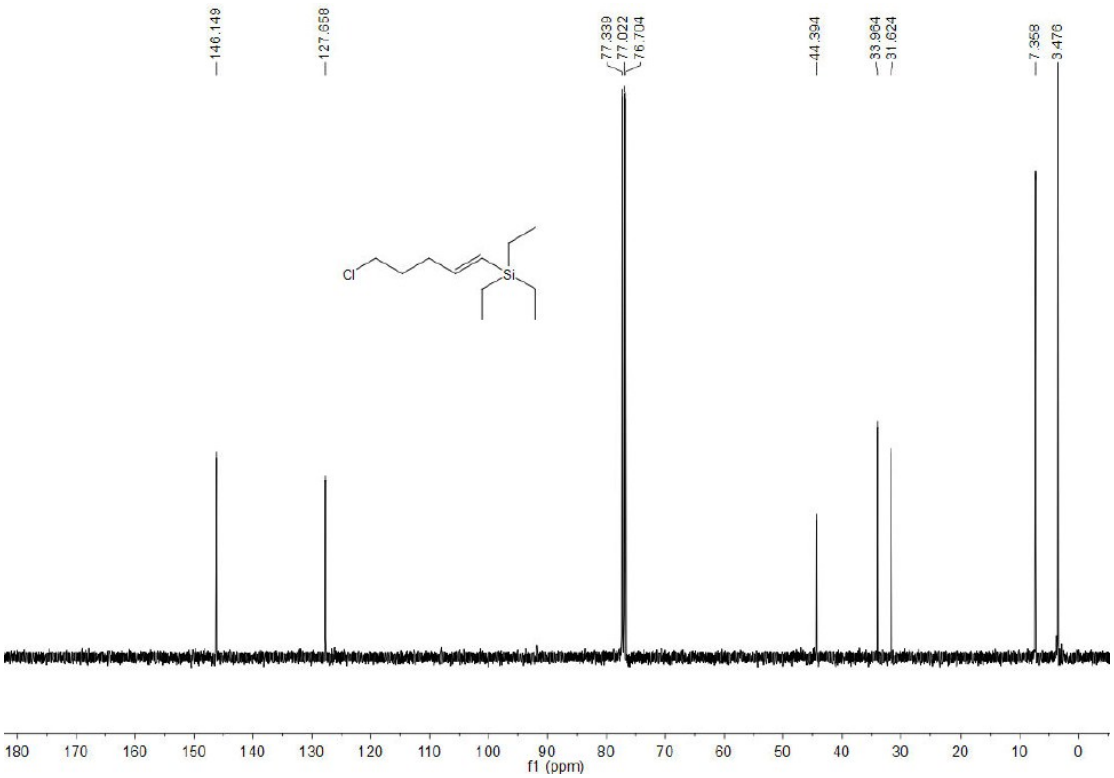
^{1}H NMR and ^{13}C NMR spectra of compound **3o**



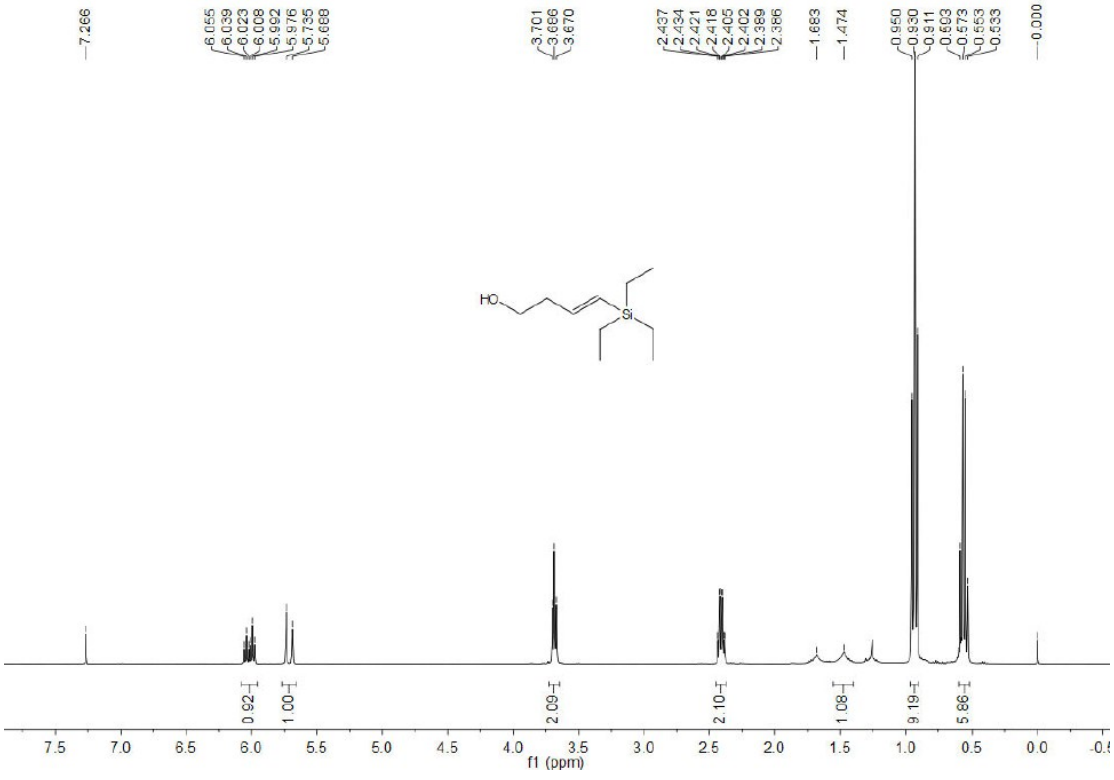


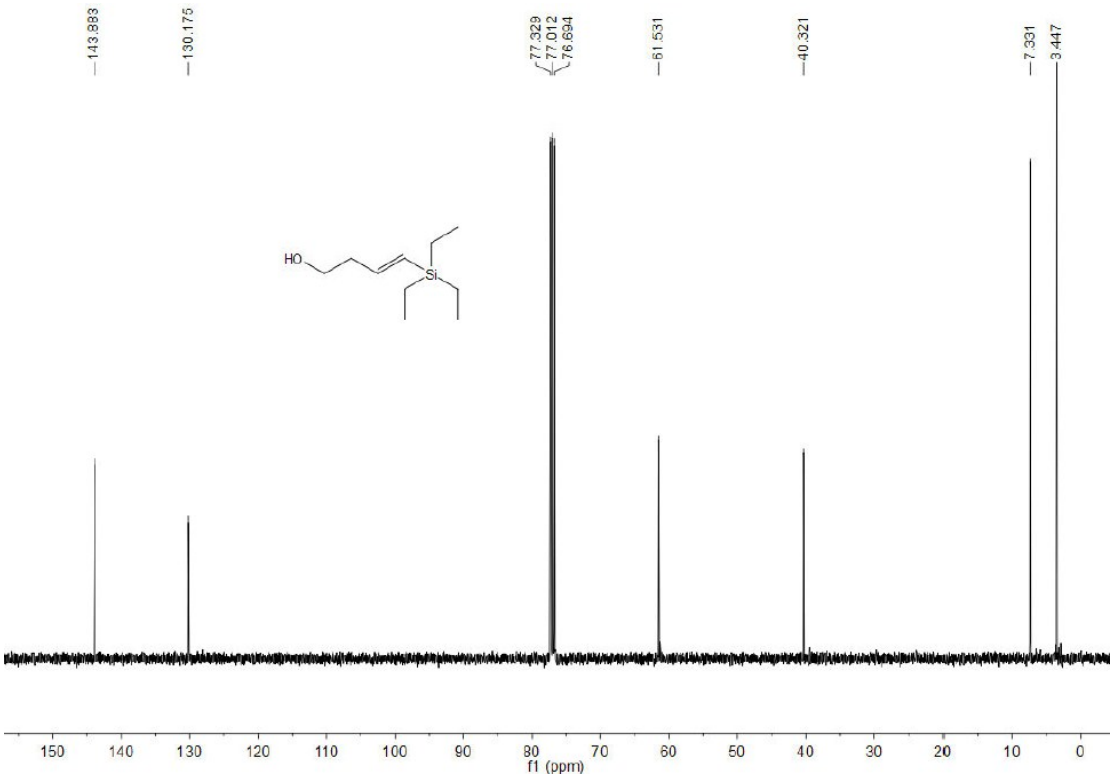
^{1}H NMR and ^{13}C NMR spectra of compound **3p**



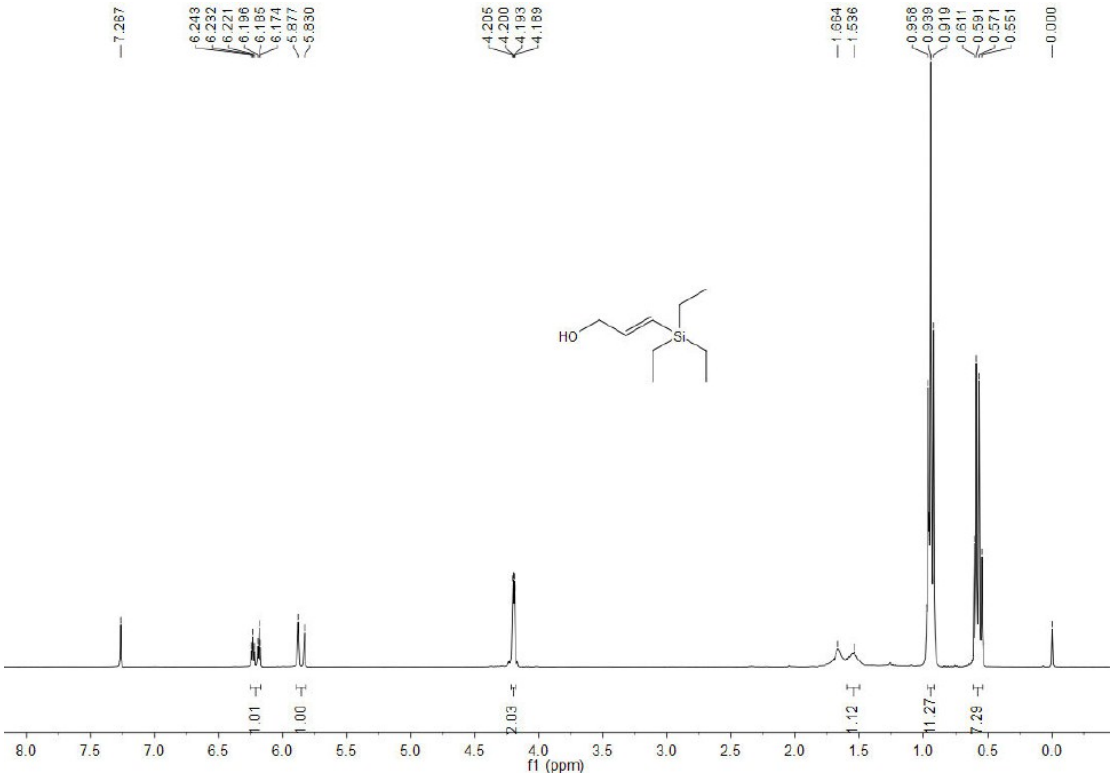


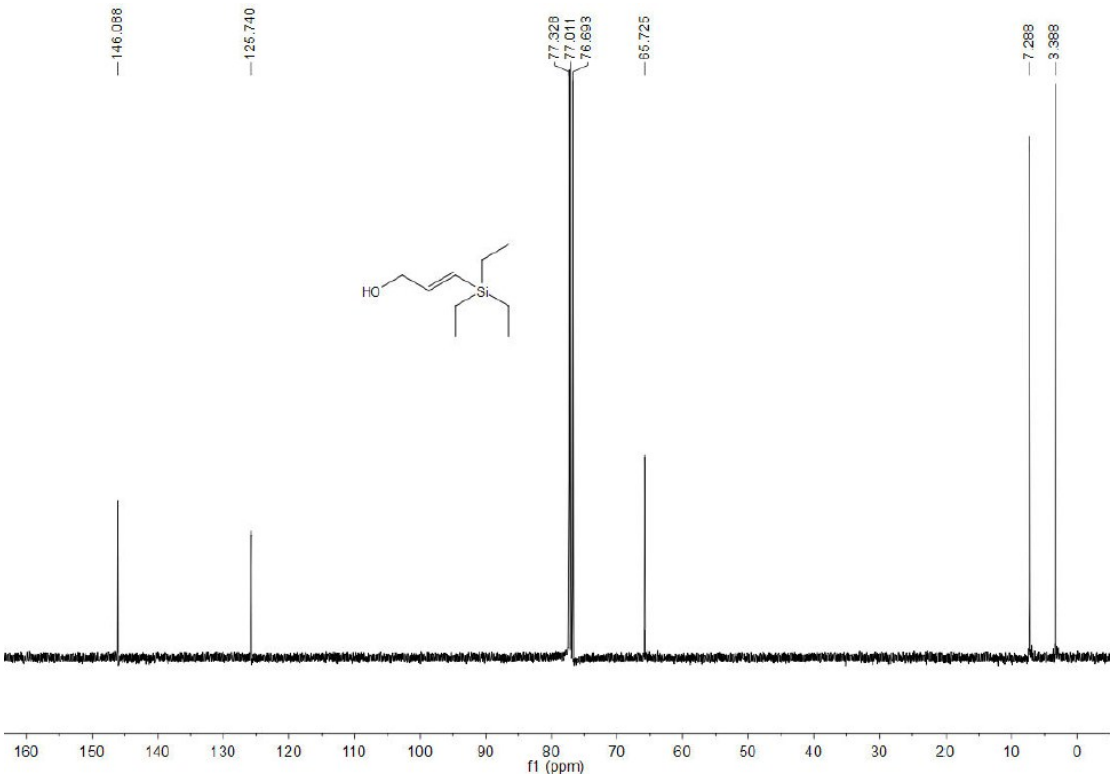
^{1}H NMR and ^{13}C NMR spectra of compound **3q**



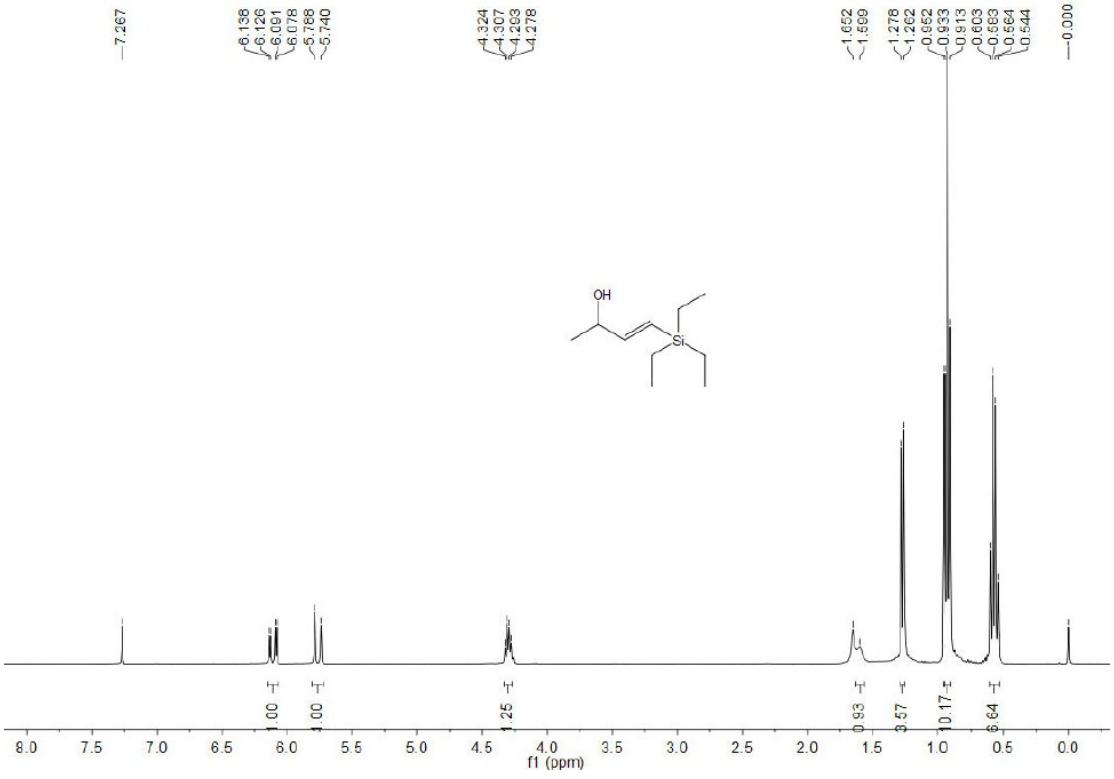


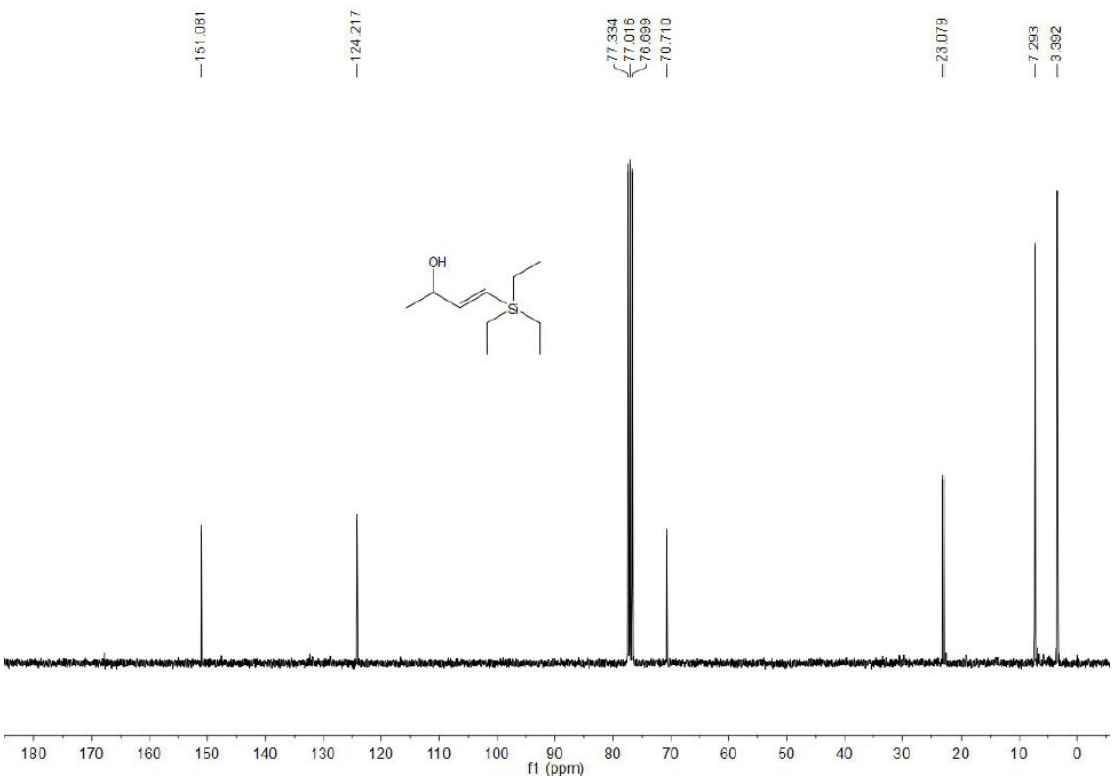
^{1}H NMR and ^{13}C NMR spectra of compound **3r**



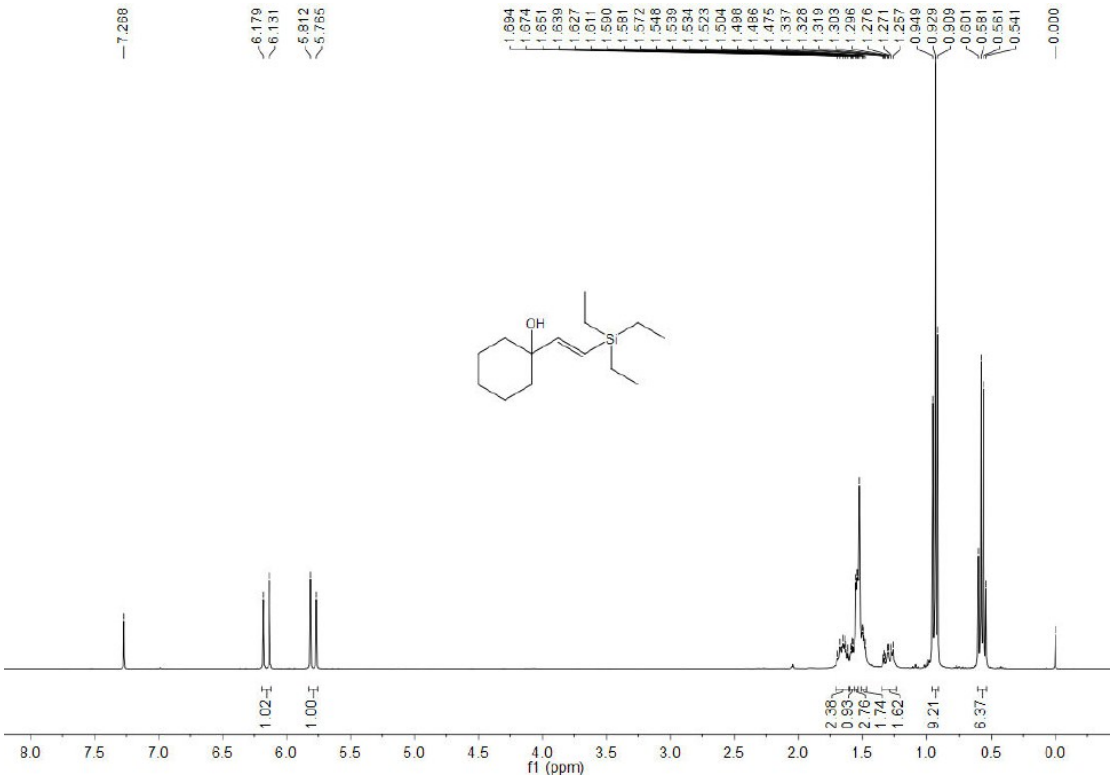


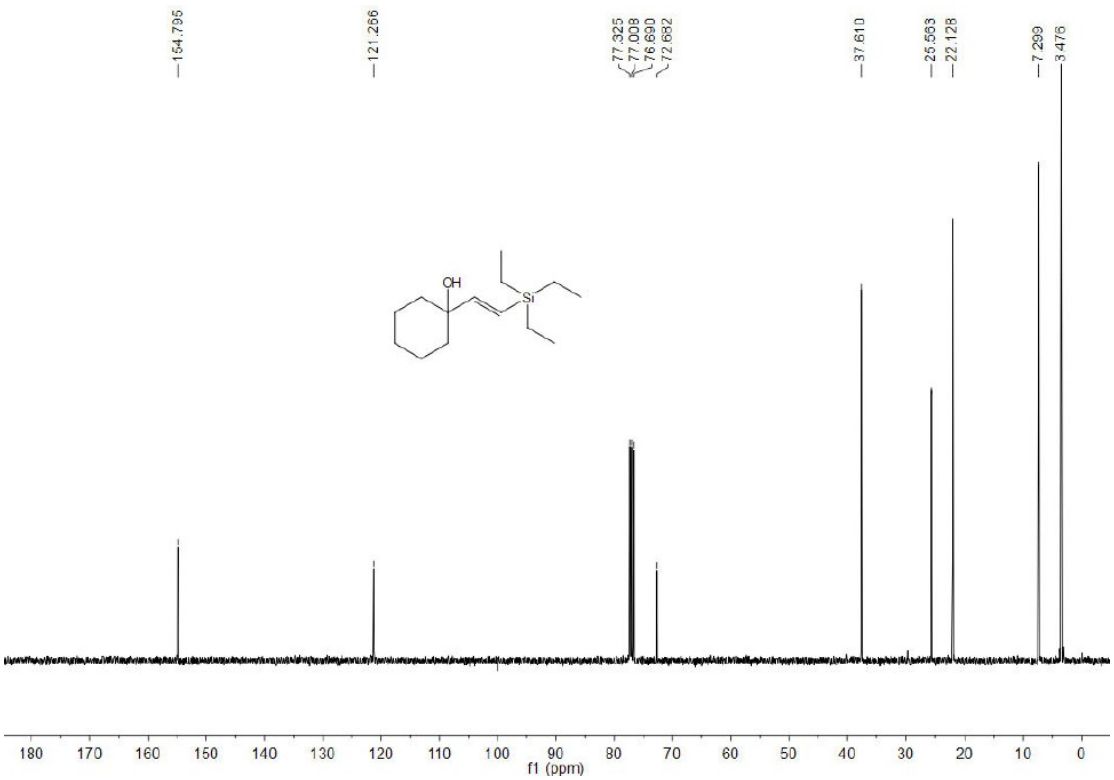
^{1}H NMR and ^{13}C NMR spectra of compound **3s**



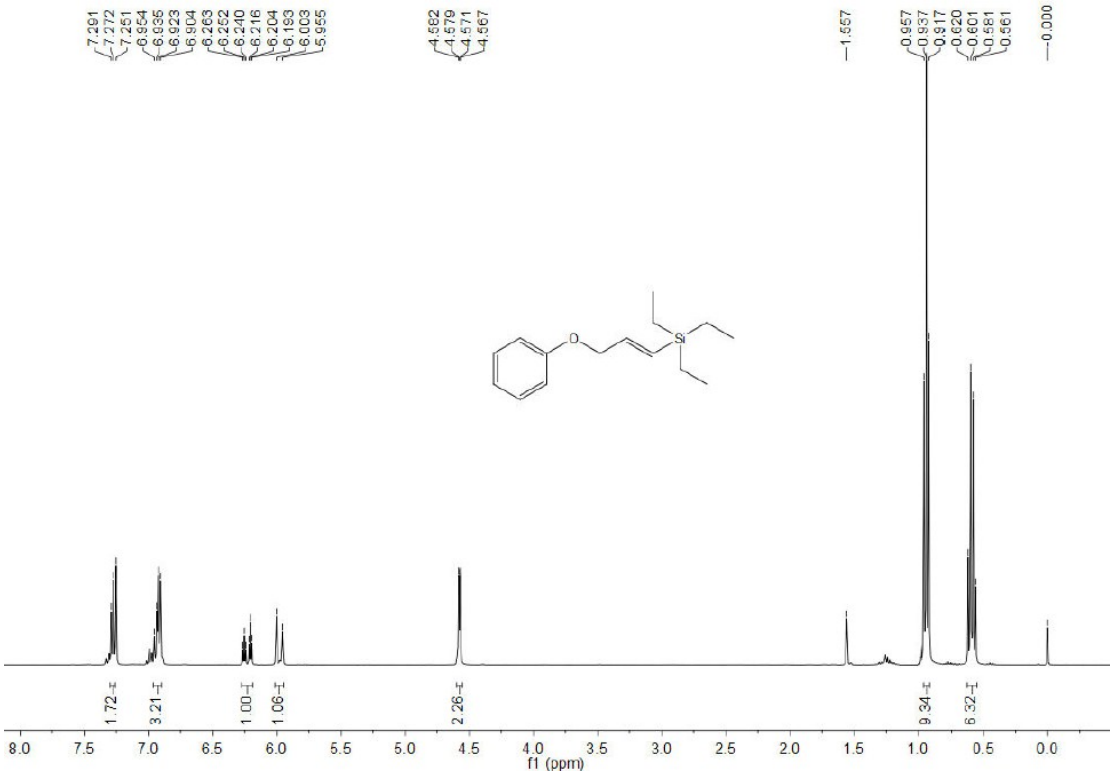


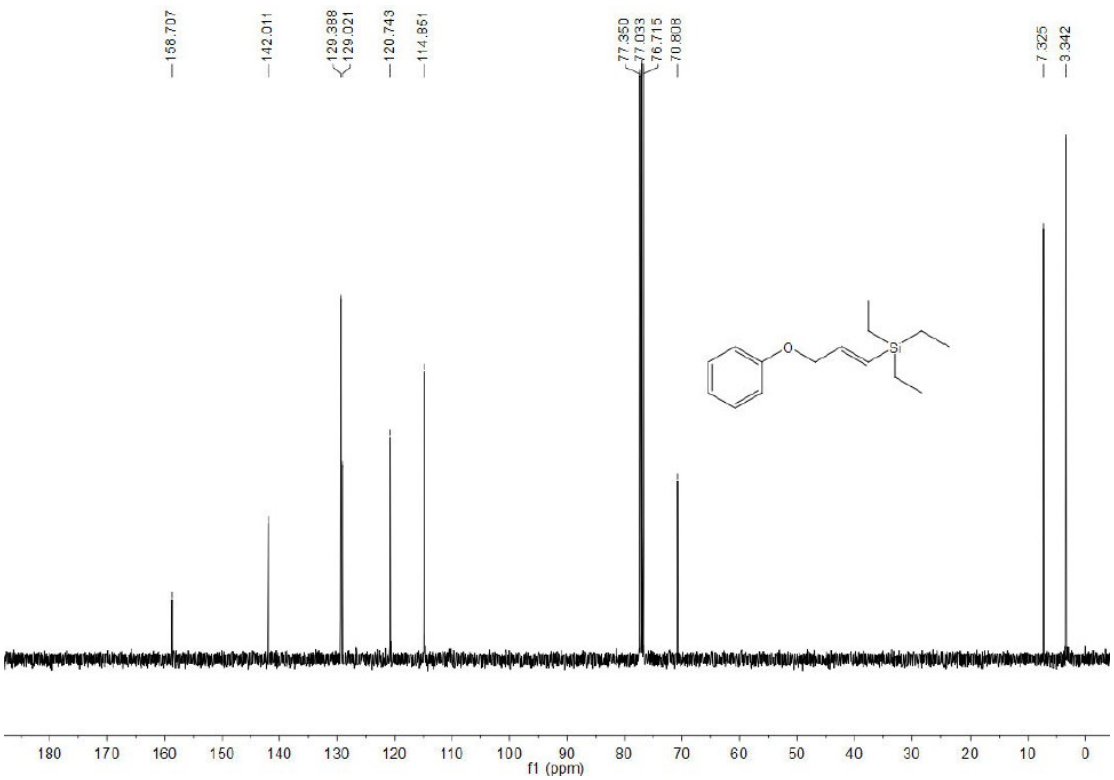
^{1}H NMR and ^{13}C NMR spectra of compound **3t**



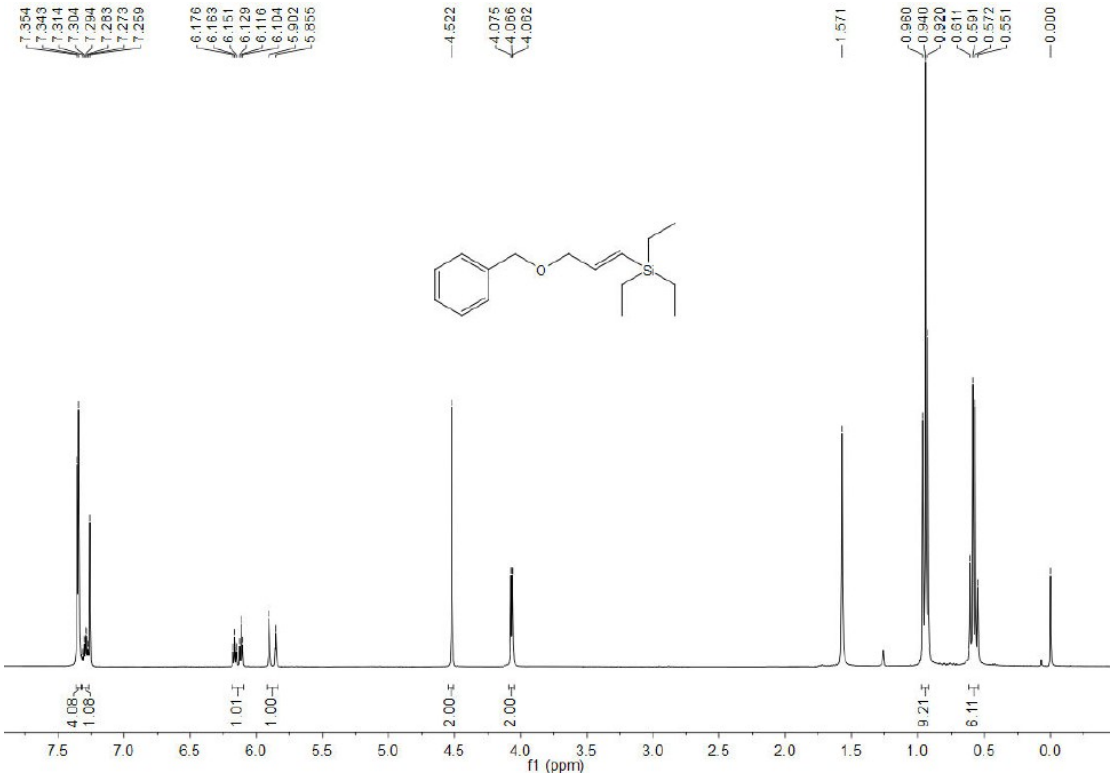


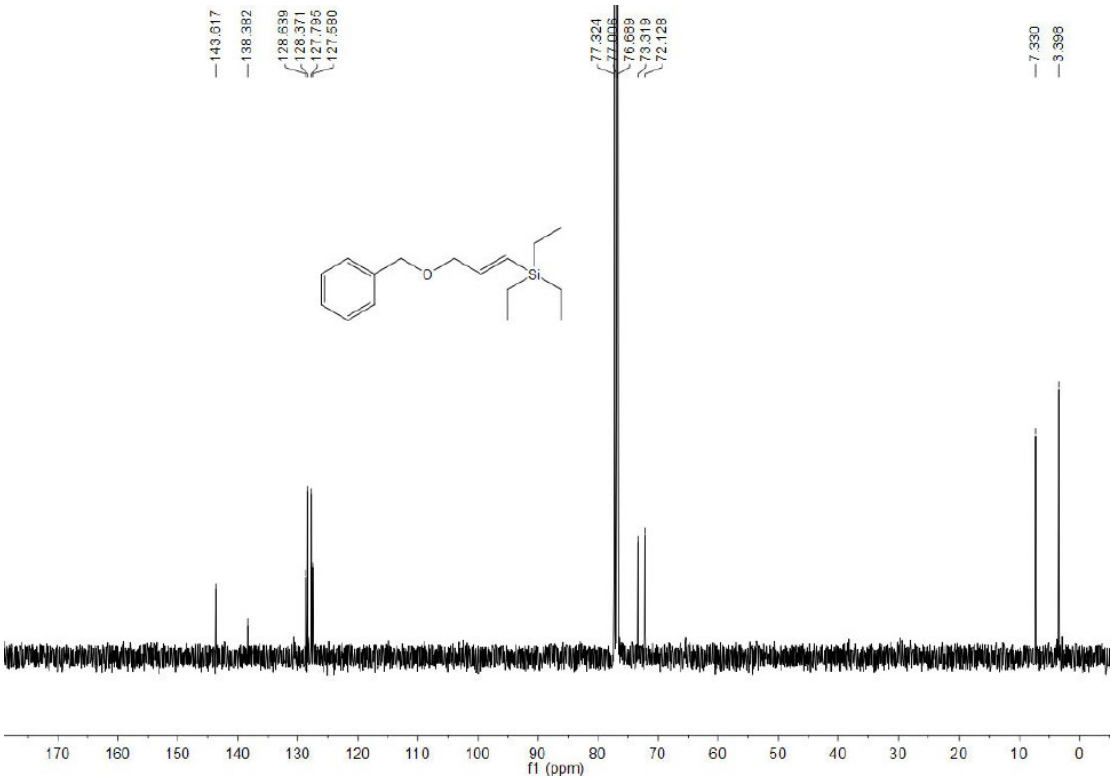
^{1}H NMR and ^{13}C NMR spectra of compound **3u**



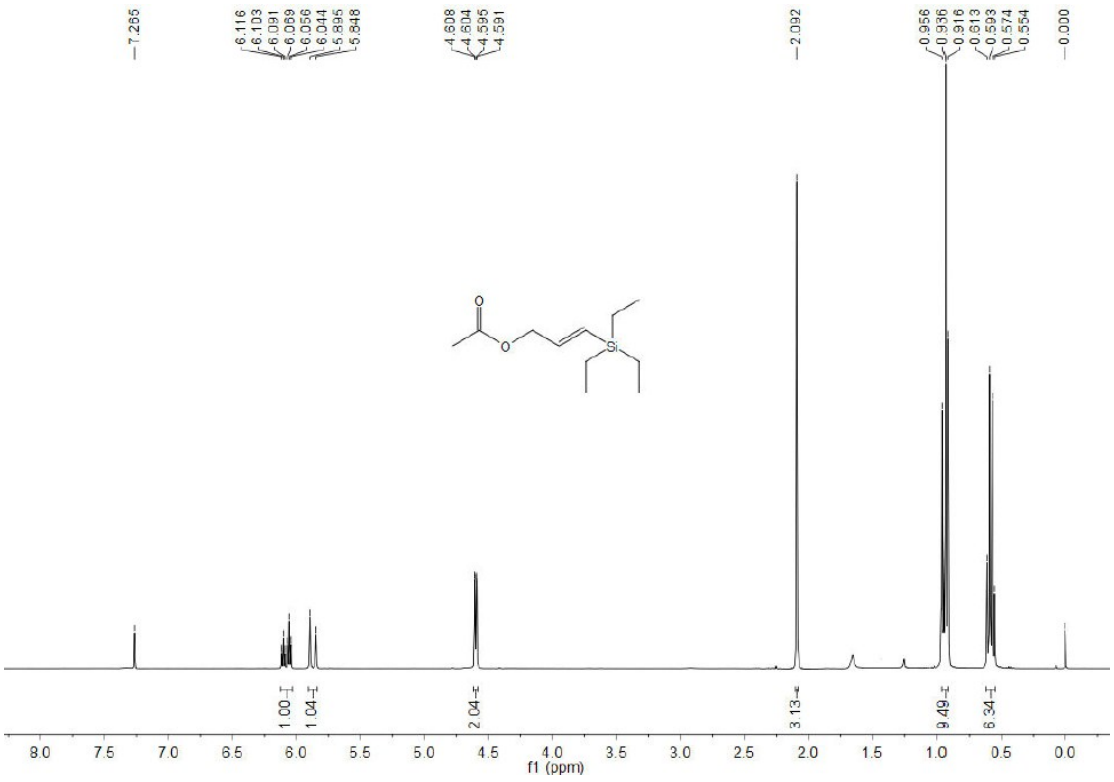


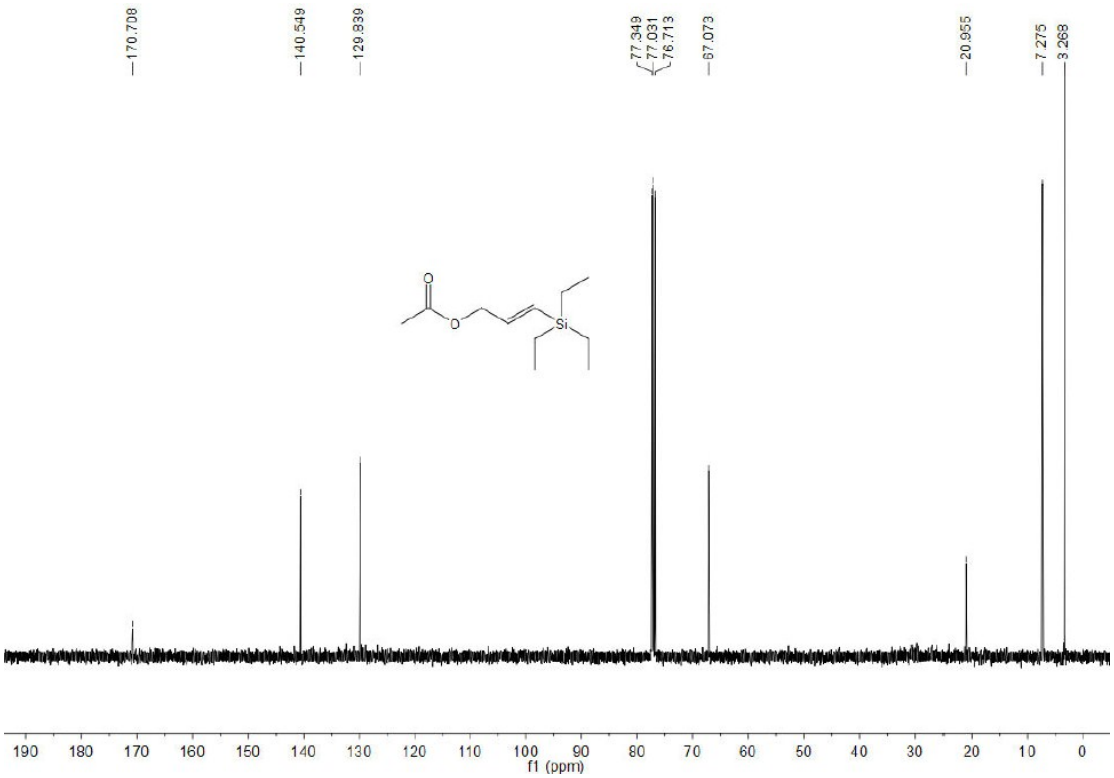
^{1}H NMR and ^{13}C NMR spectra of compound **3v**



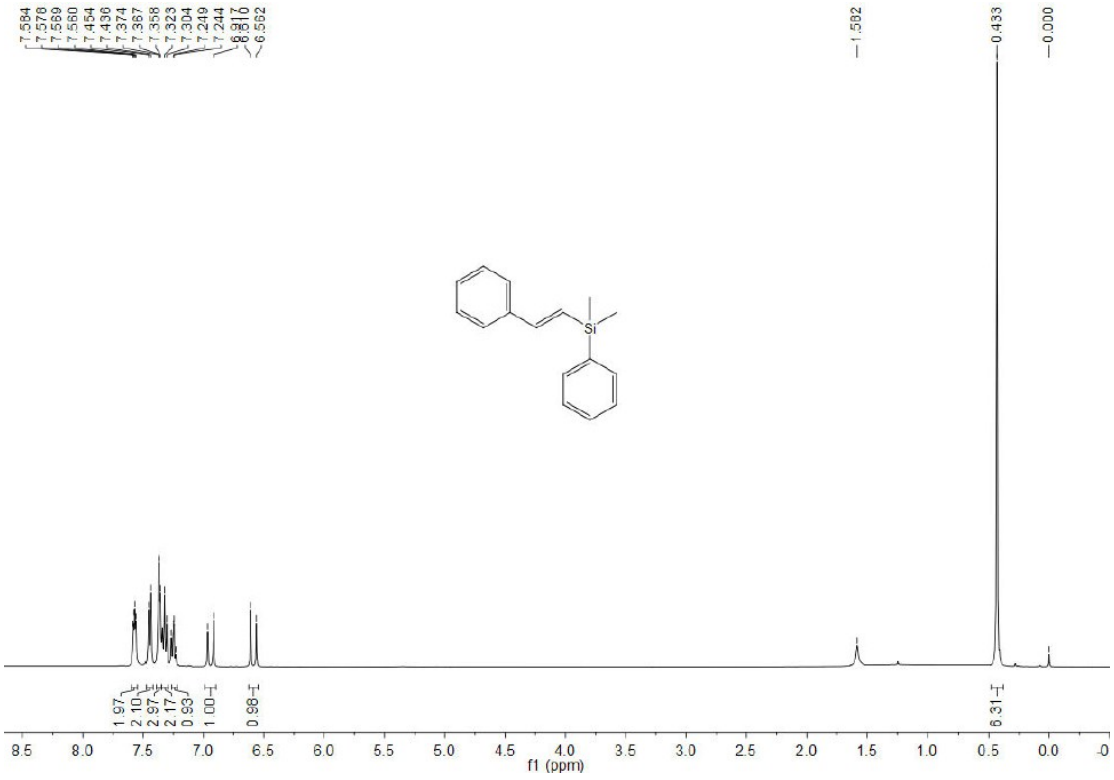


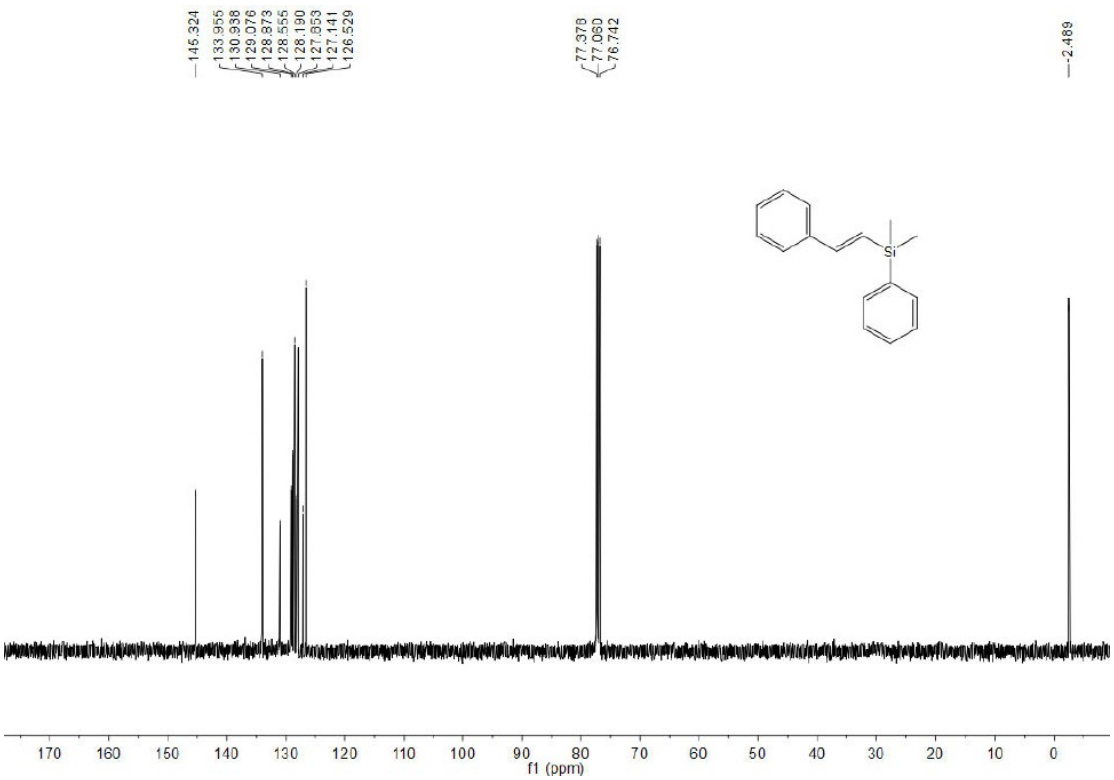
^{1}H NMR and ^{13}C NMR spectra of compound **3w**



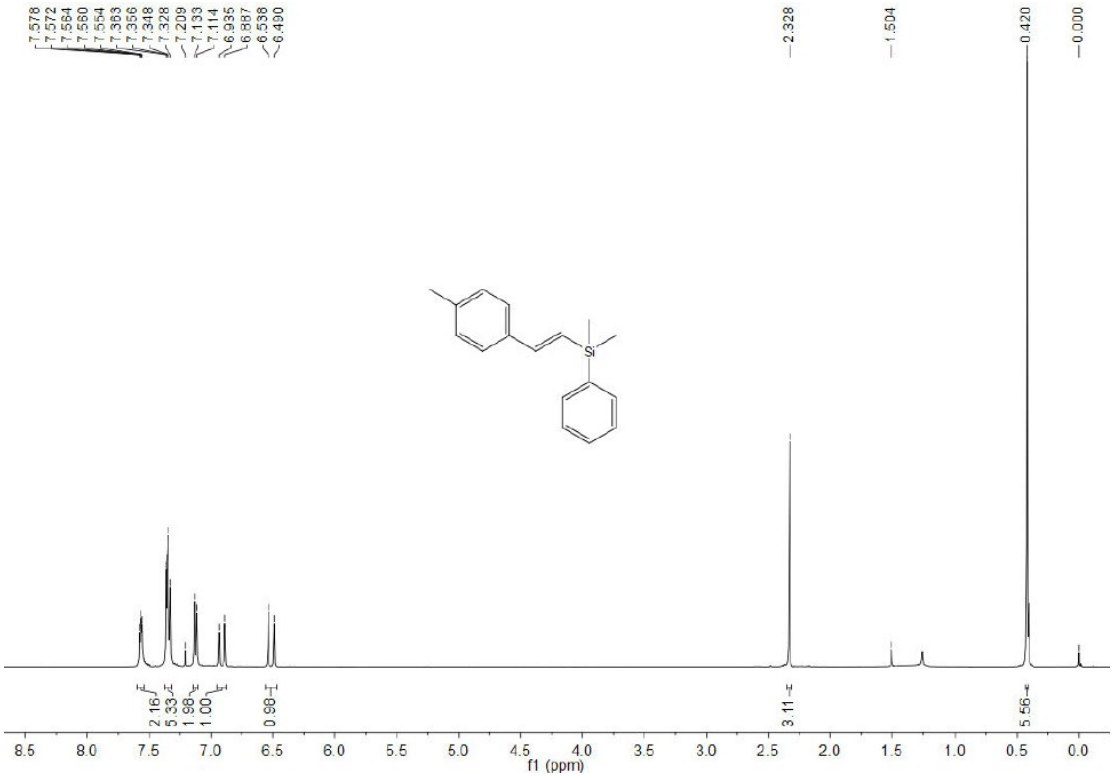


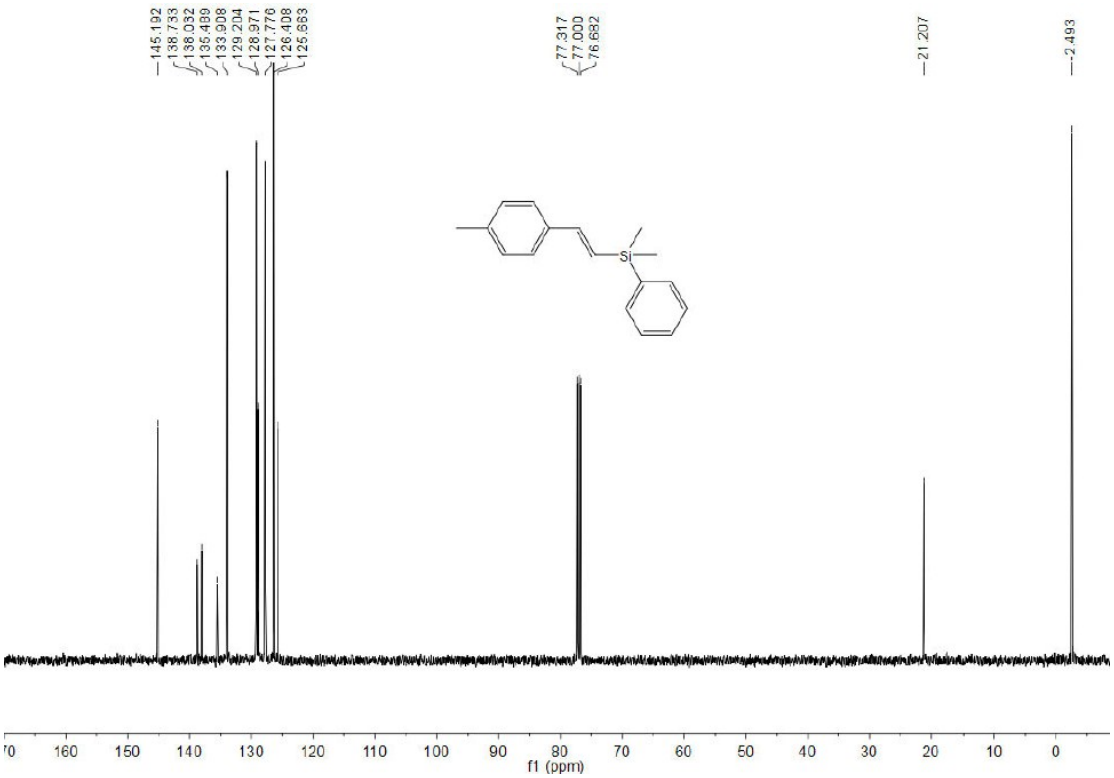
^{1}H NMR and ^{13}C NMR spectra of compound **3x**



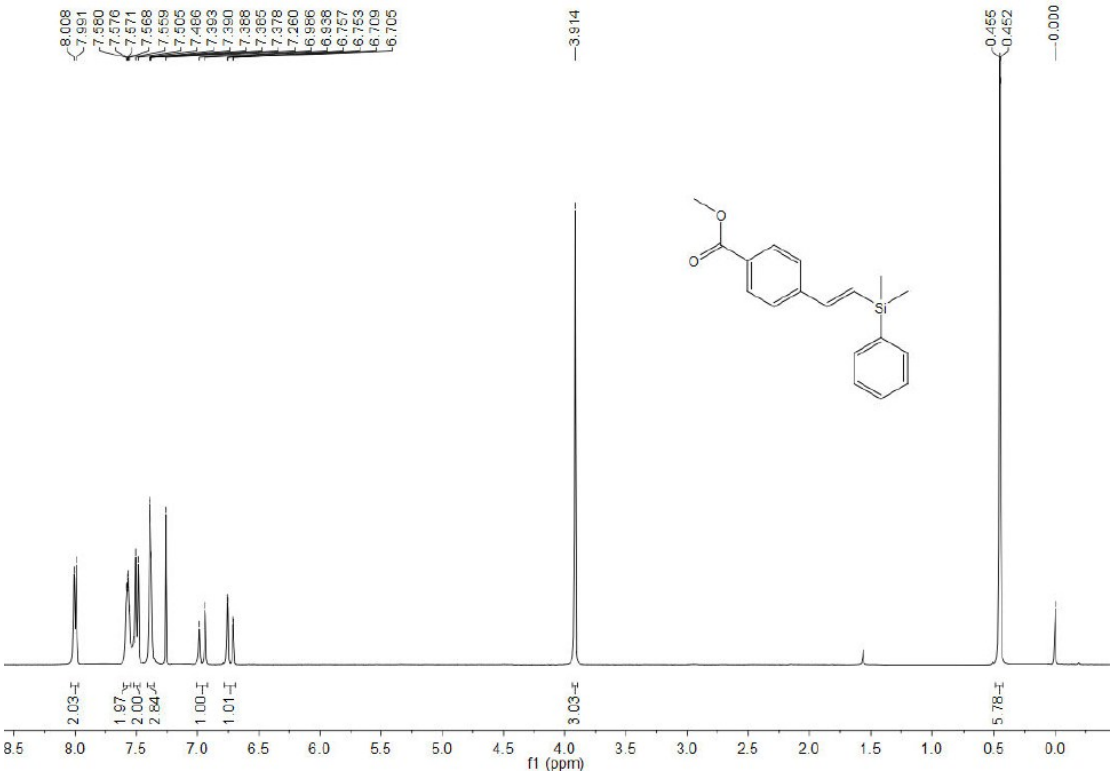


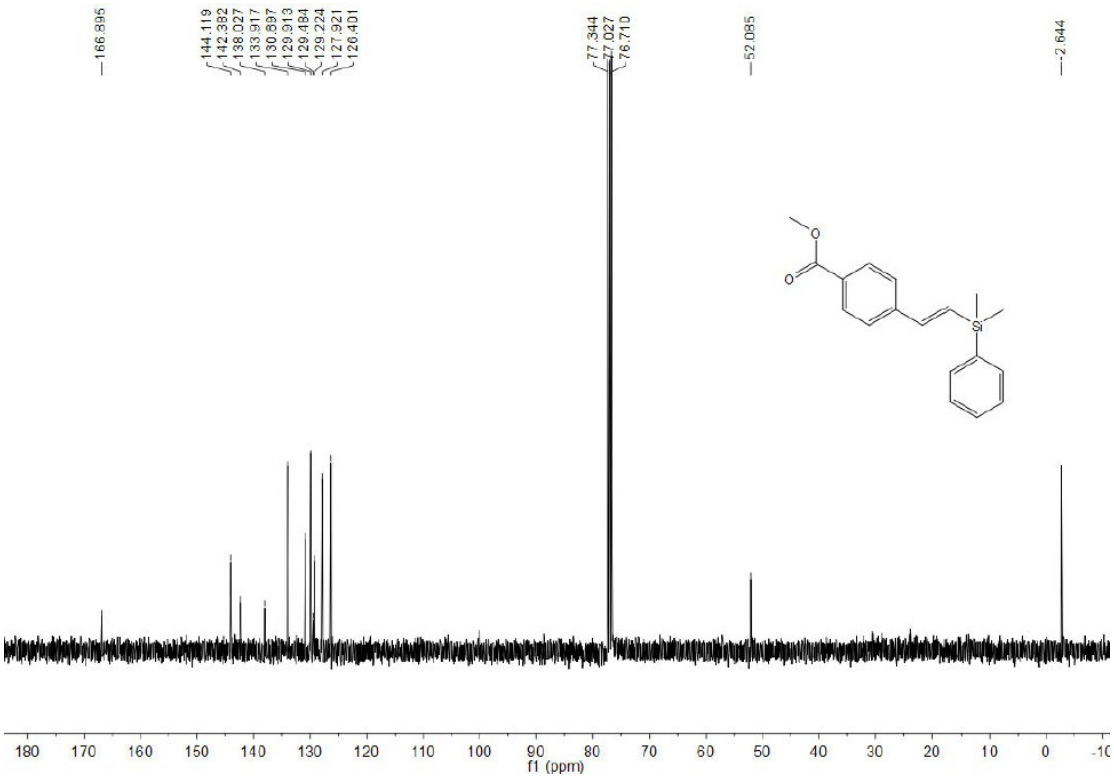
^{1}H NMR and ^{13}C NMR spectra of compound **4a**



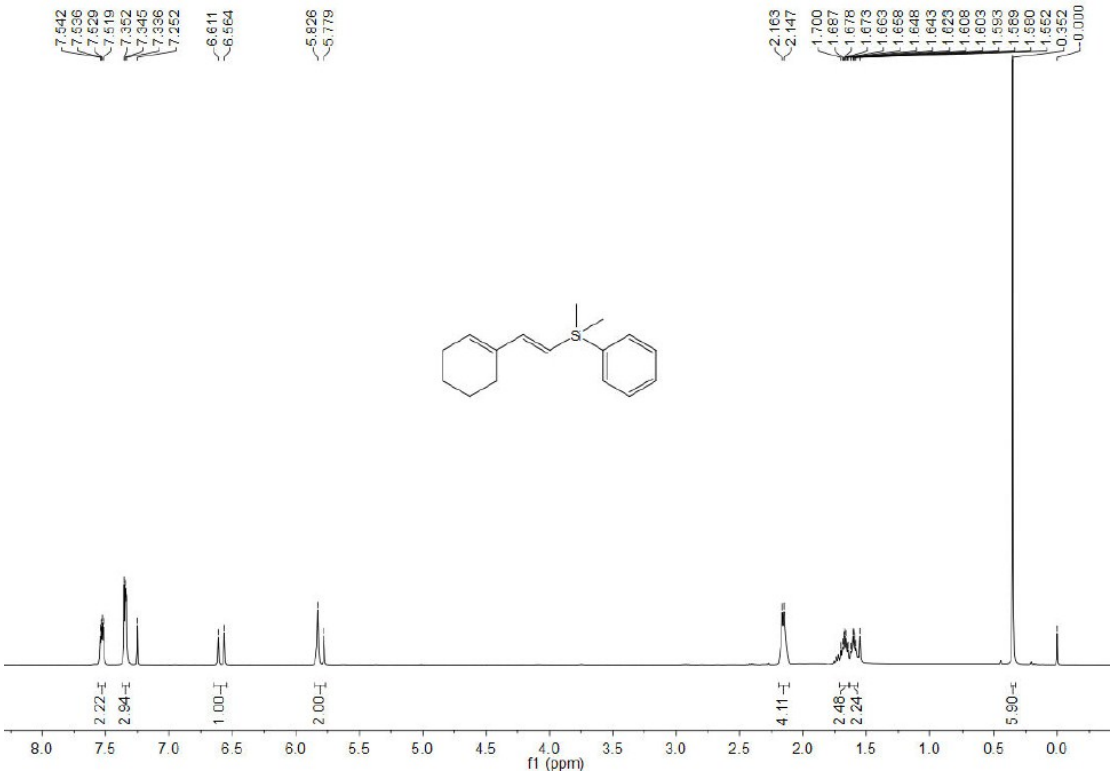


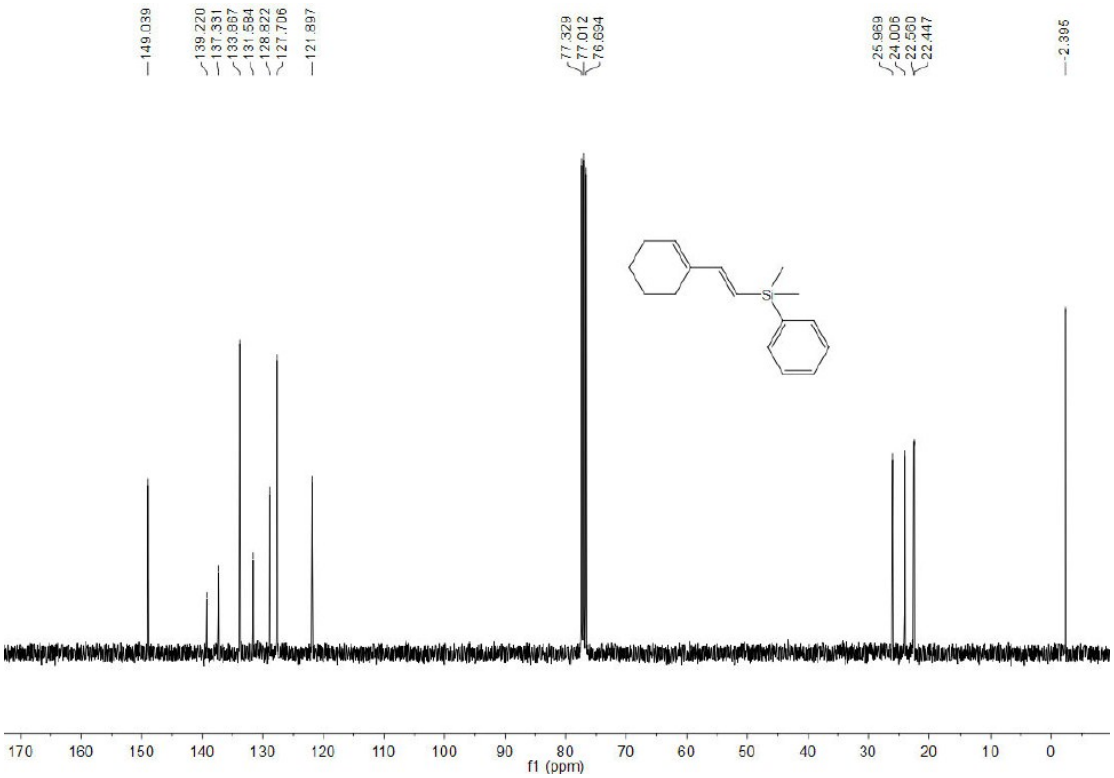
^{1}H NMR and ^{13}C NMR spectra of compound **4b**



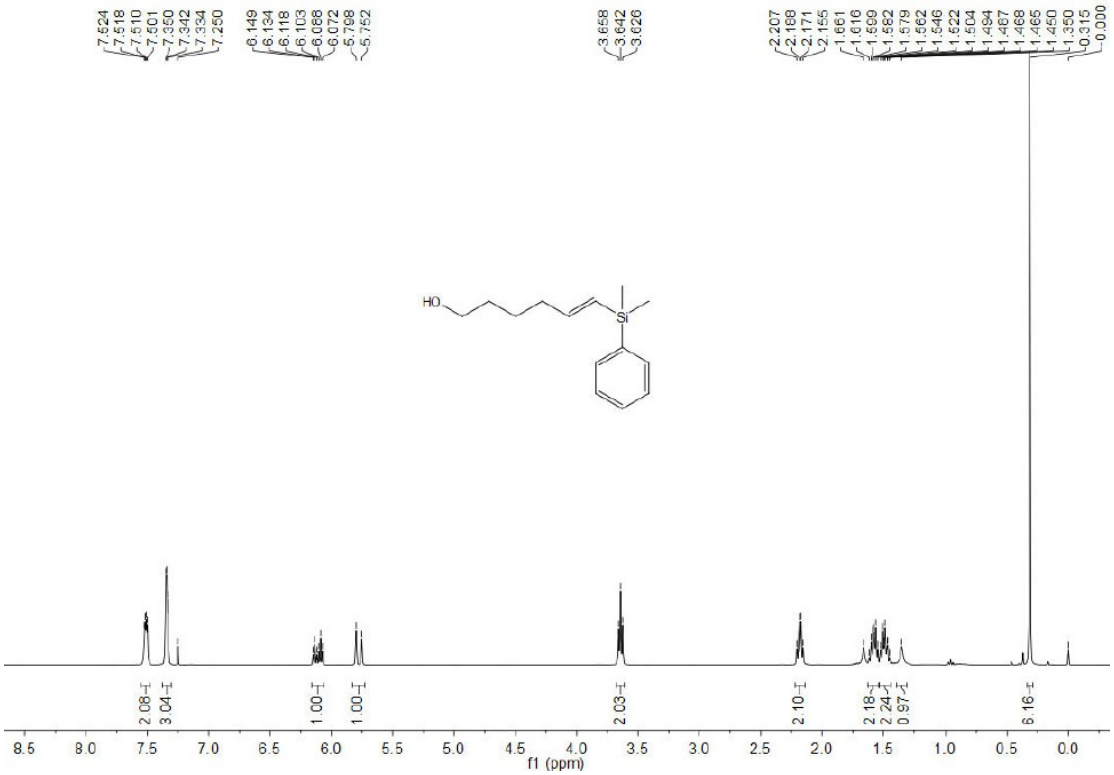


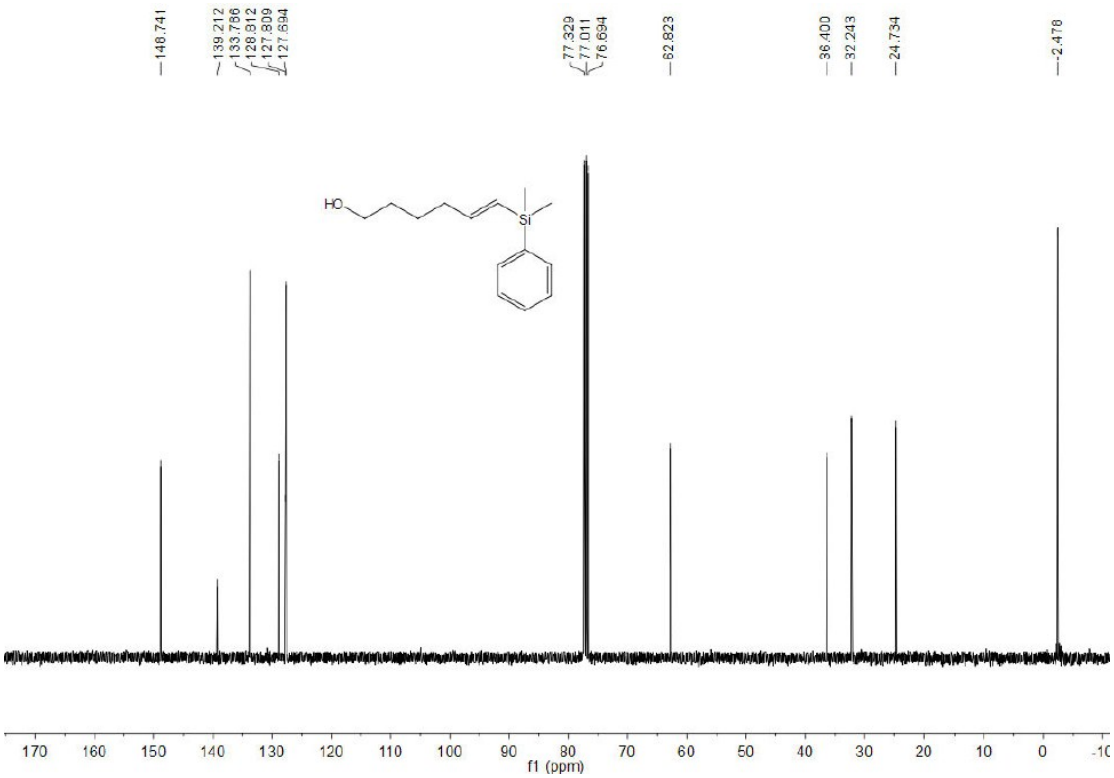
^{1}H NMR and ^{13}C NMR spectra of compound **4c**



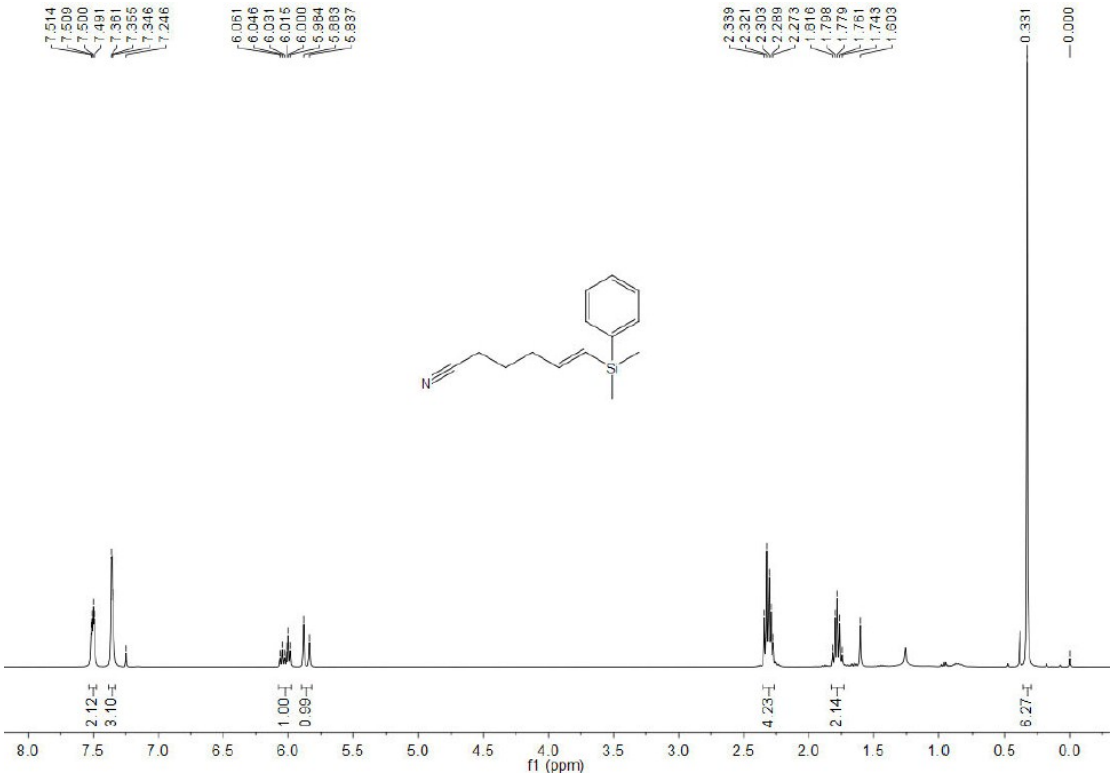


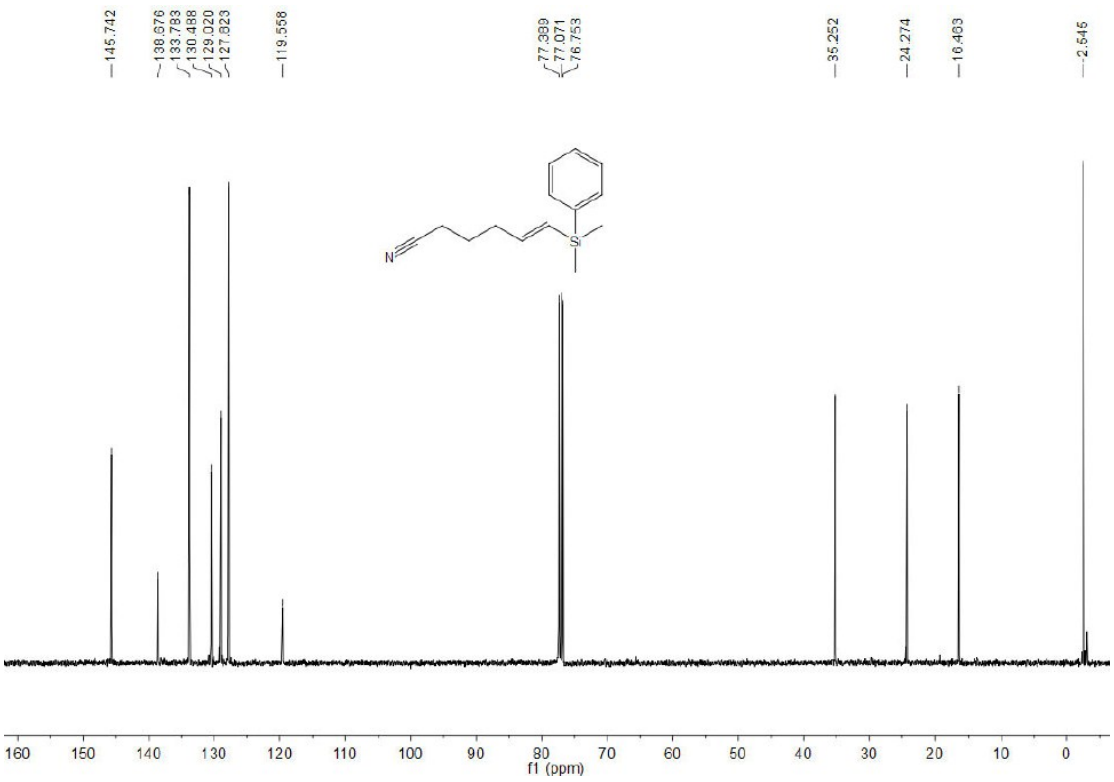
^{1}H NMR and ^{13}C NMR spectra of compound **4d**



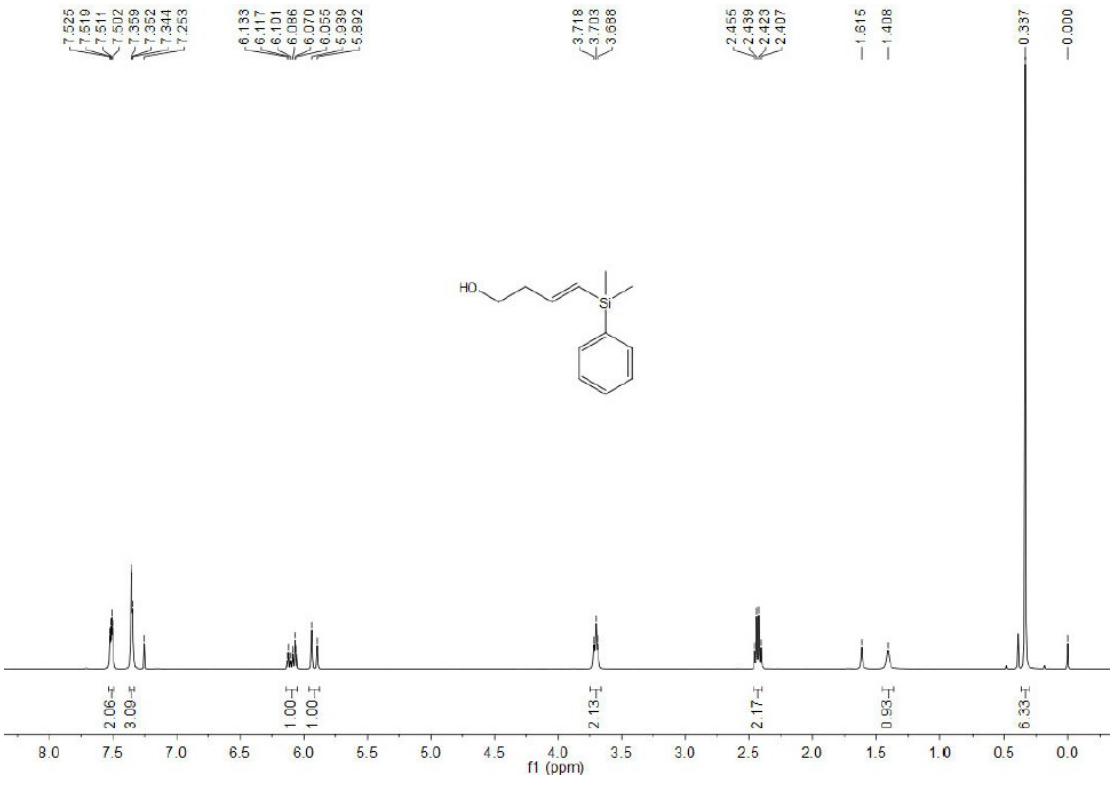


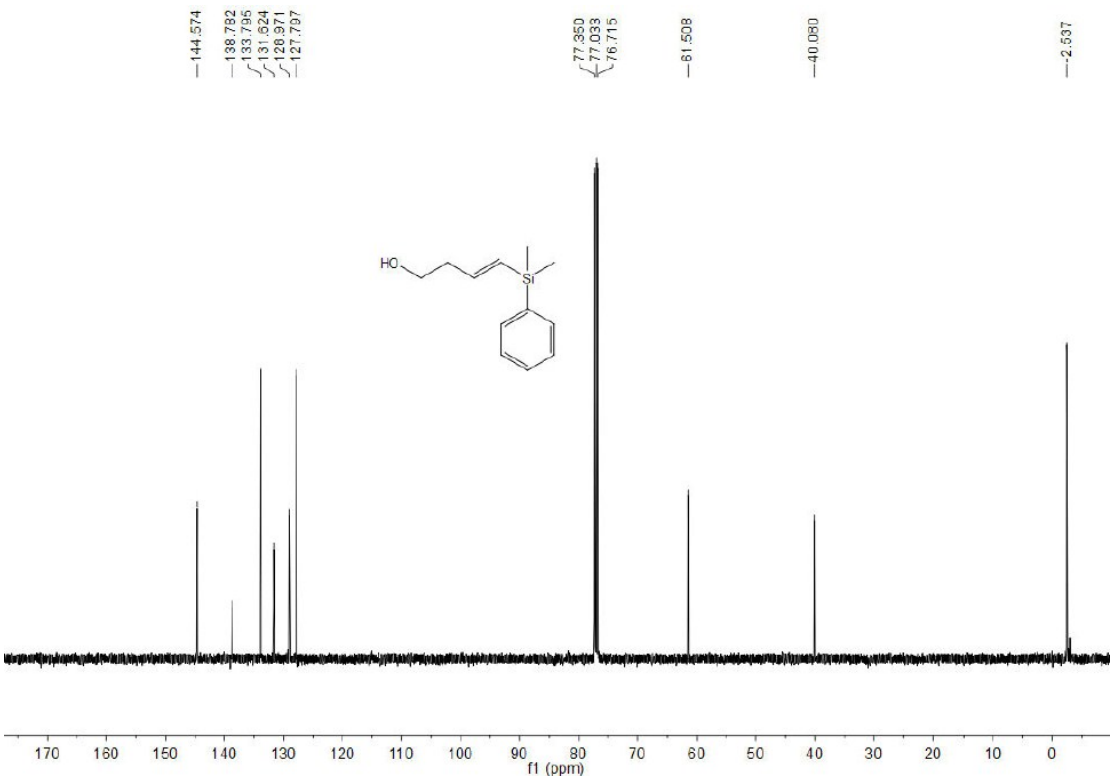
^{1}H NMR and ^{13}C NMR spectra of compound **4e**



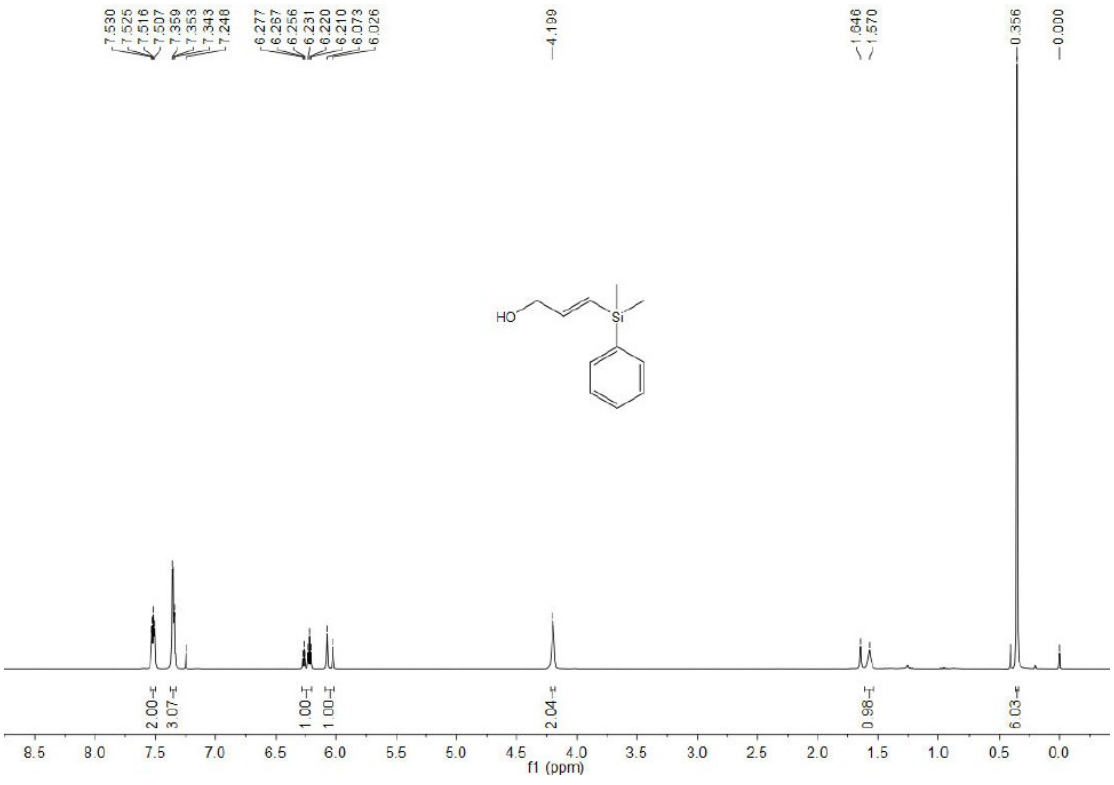


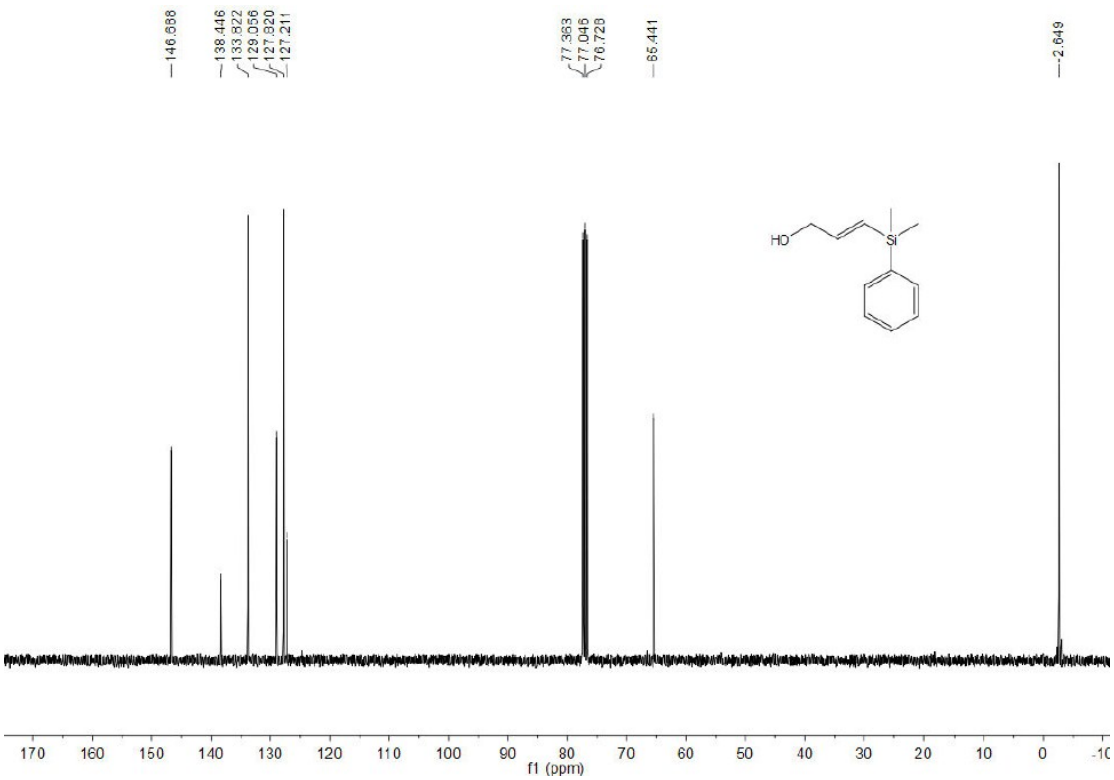
^{1}H NMR and ^{13}C NMR spectra of compound **4f**



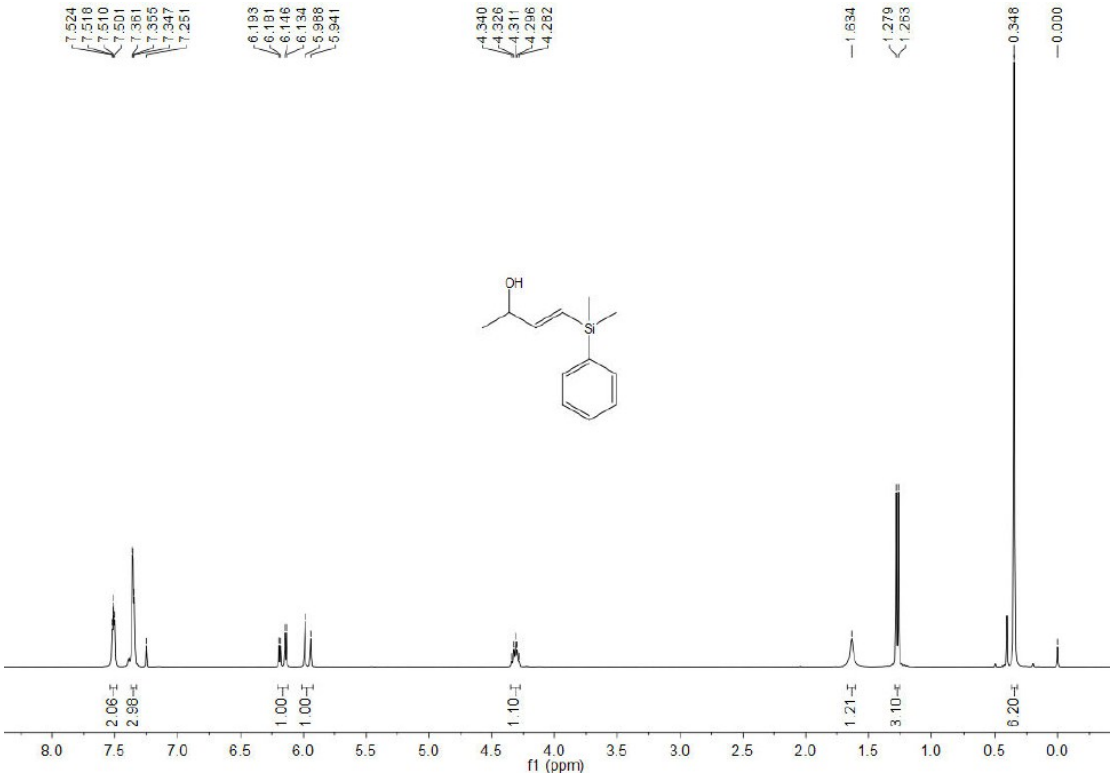


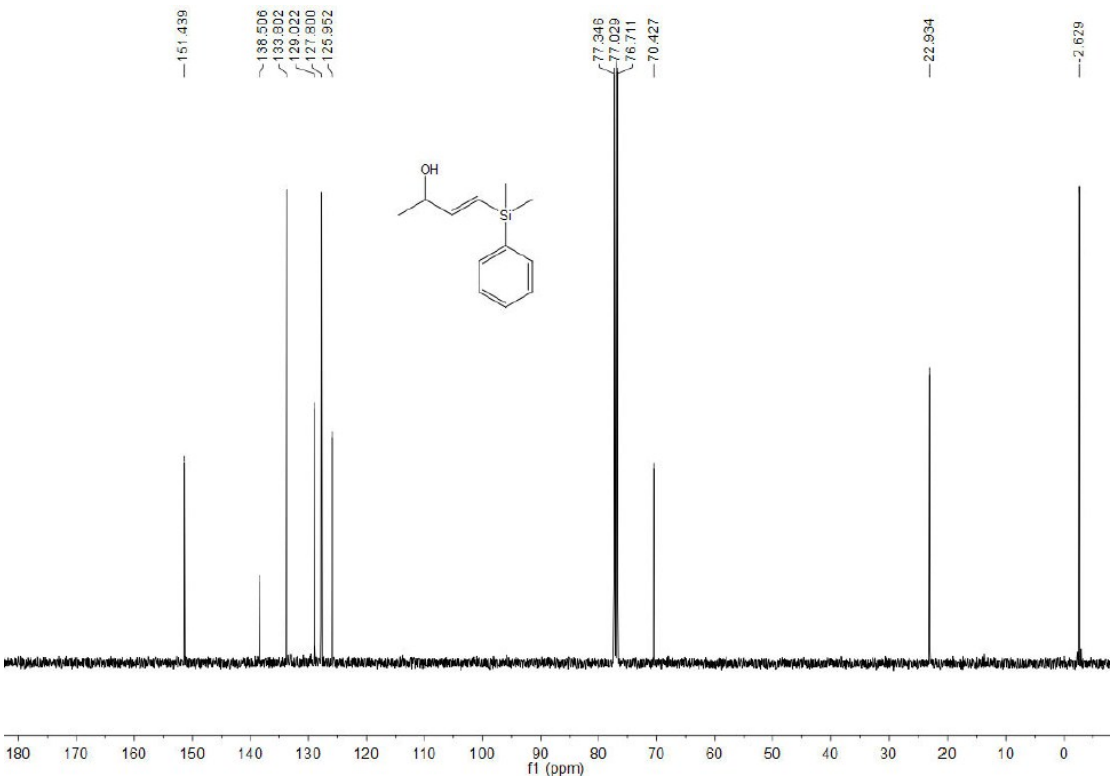
^{1}H NMR and ^{13}C NMR spectra of compound **4g**



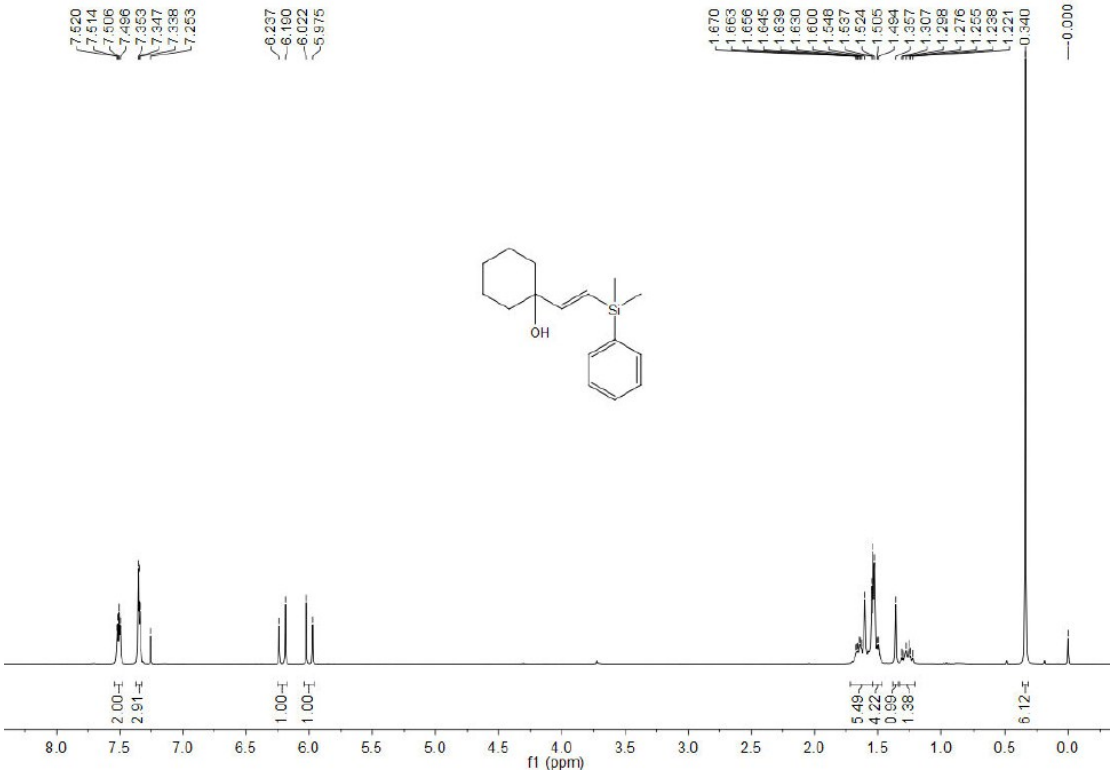


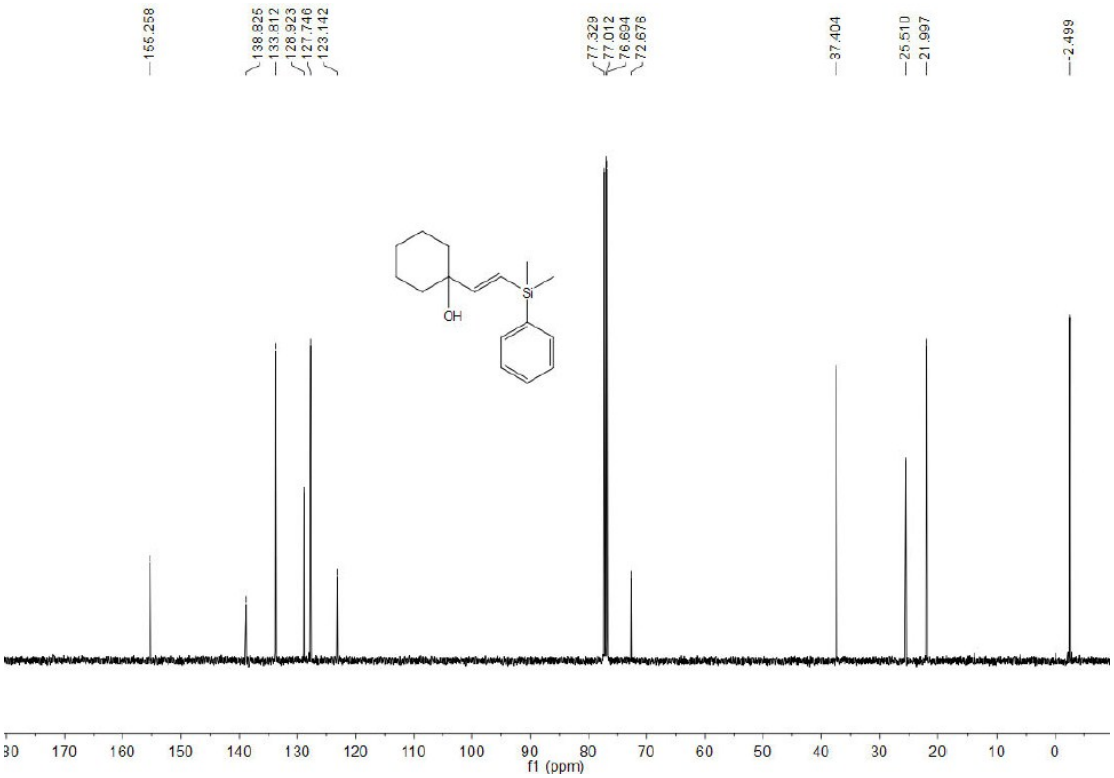
^{1}H NMR and ^{13}C NMR spectra of compound **4h**



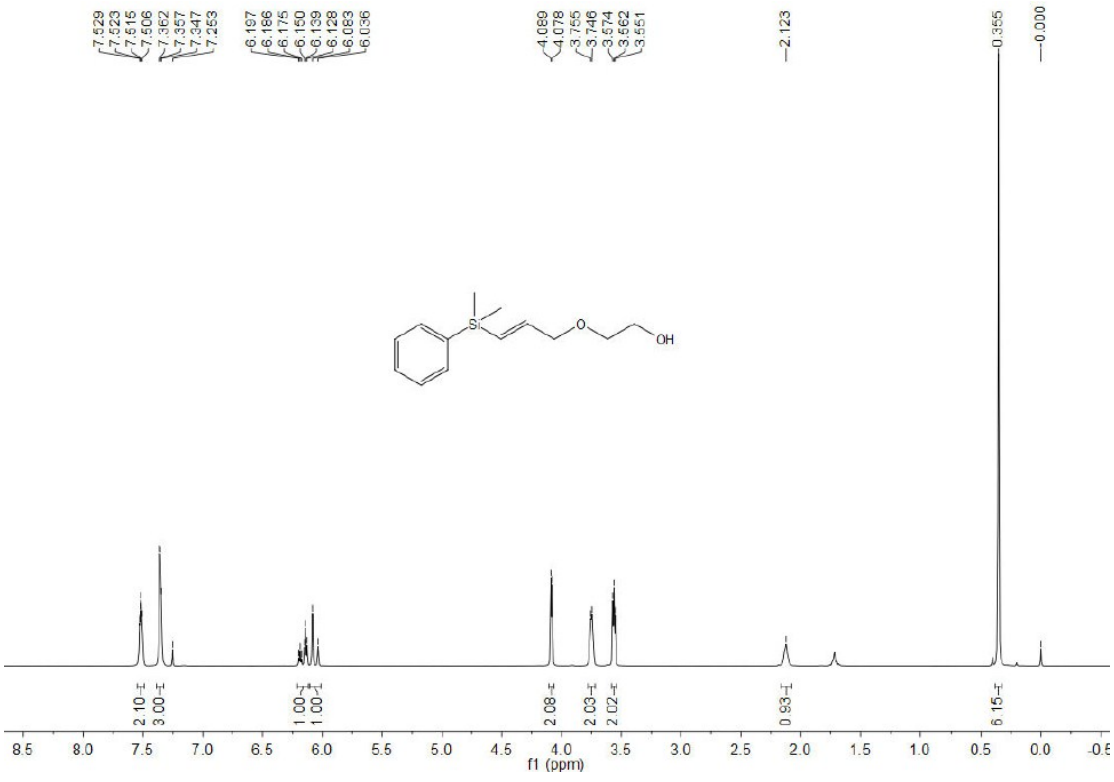


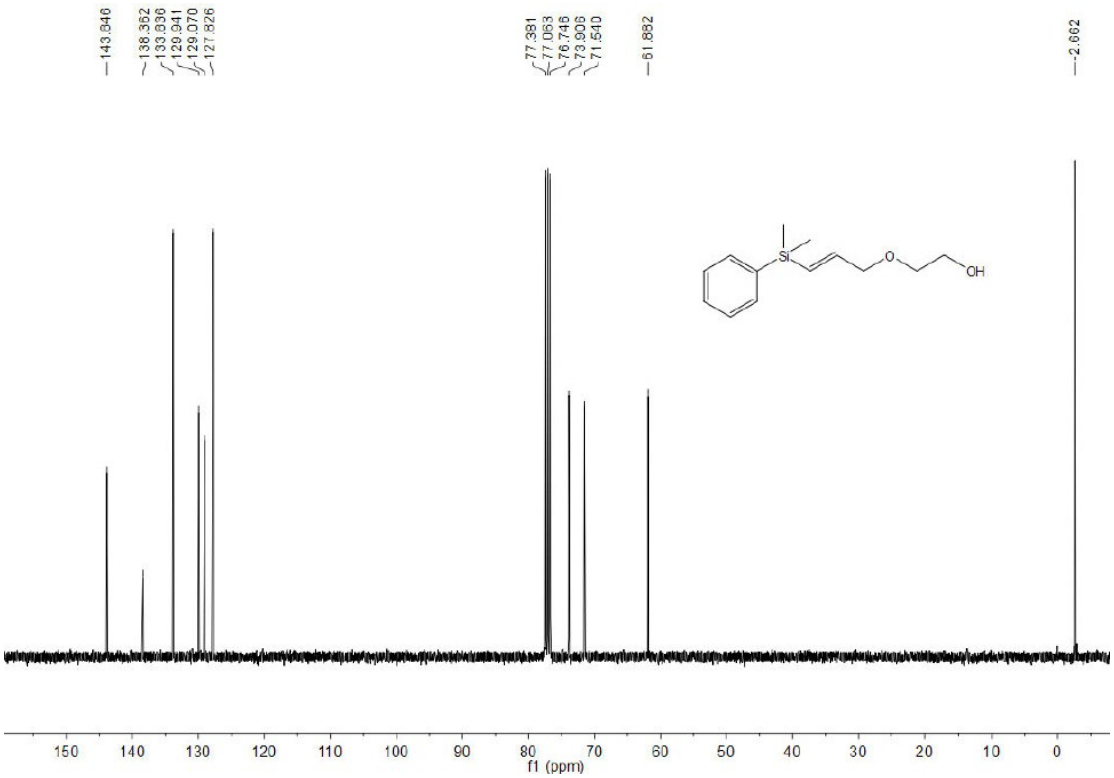
^{1}H NMR and ^{13}C NMR spectra of compound **4i**



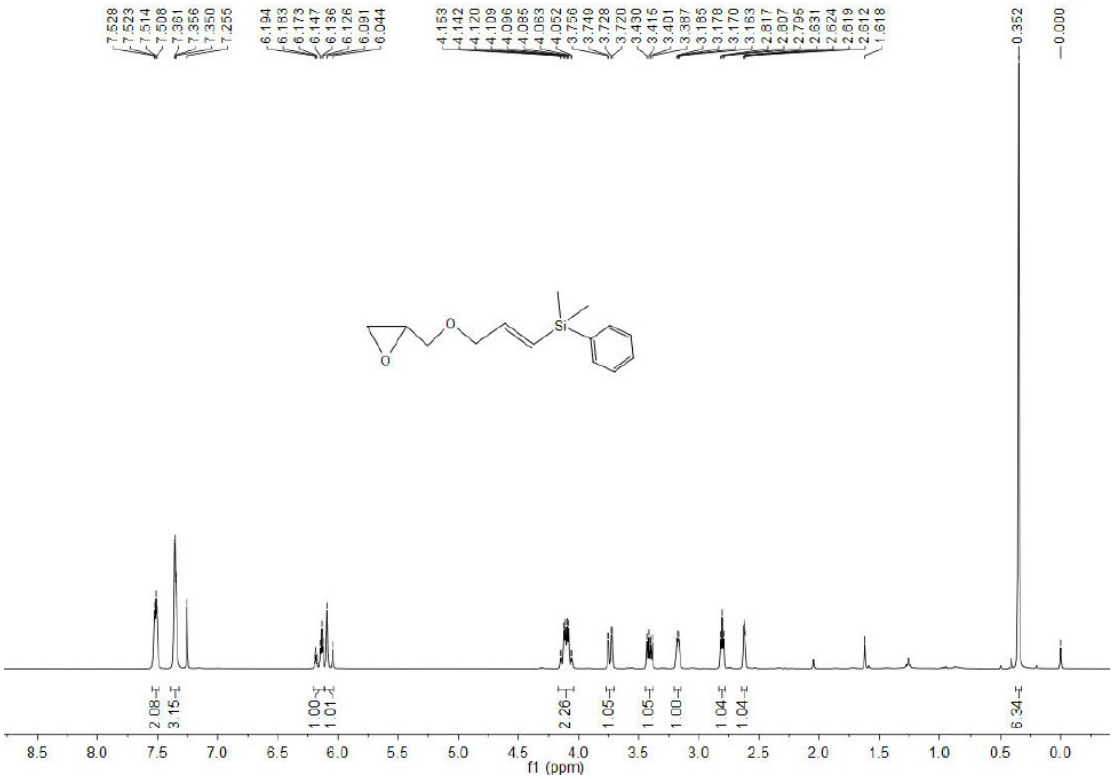


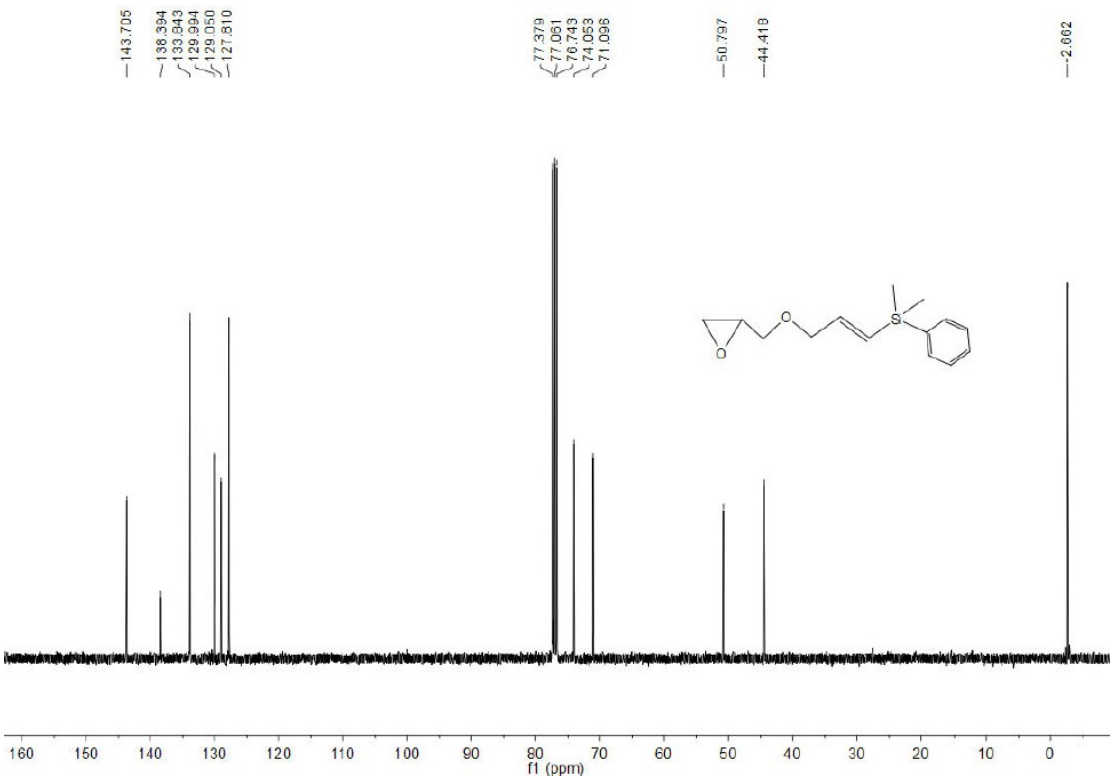
^{1}H NMR and ^{13}C NMR spectra of compound **4j**



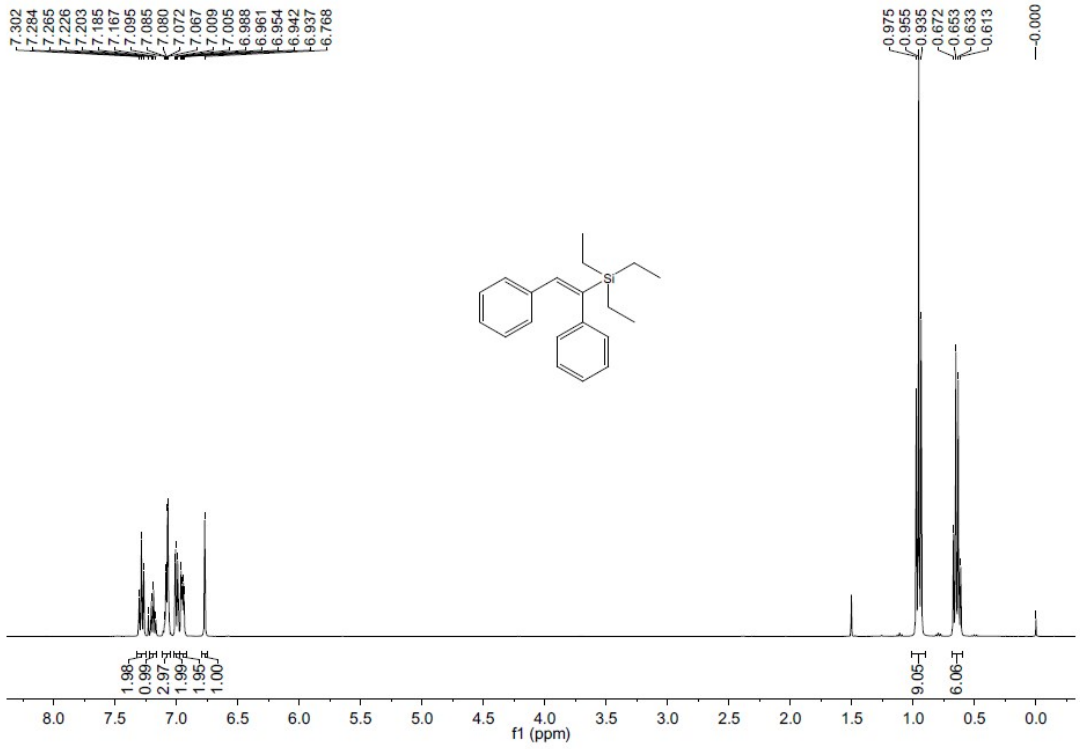


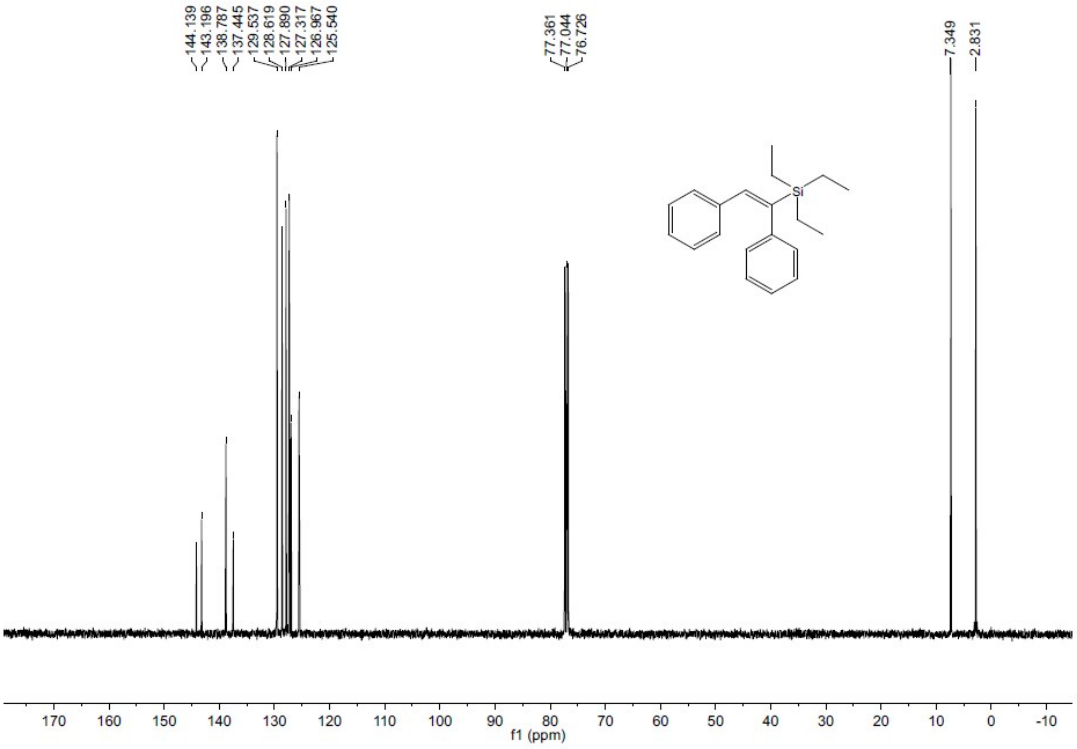
^{1}H NMR and ^{13}C NMR spectra of compound **4k**



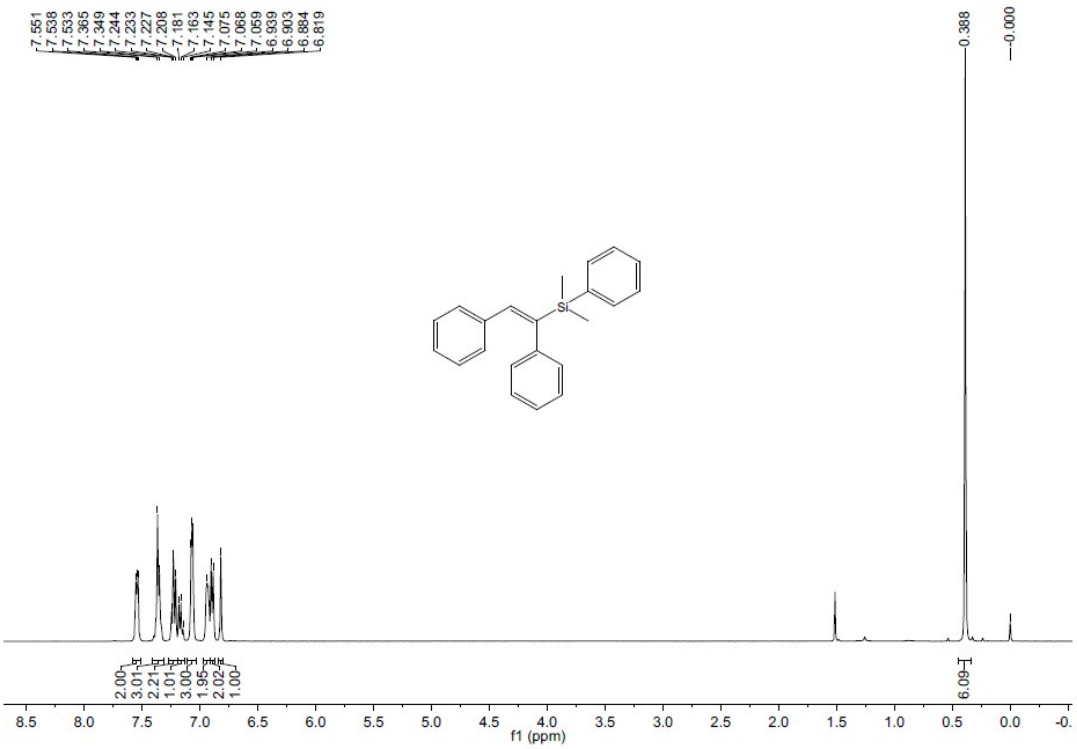


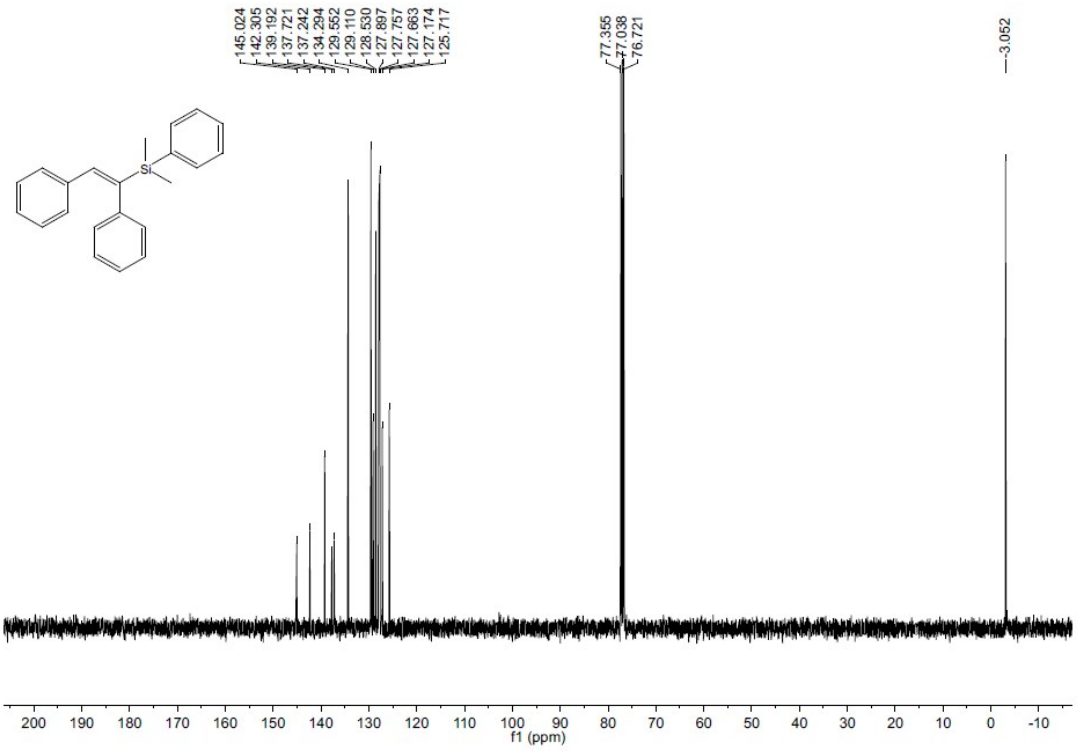
^{1}H NMR and ^{13}C NMR spectra of compound **4l**



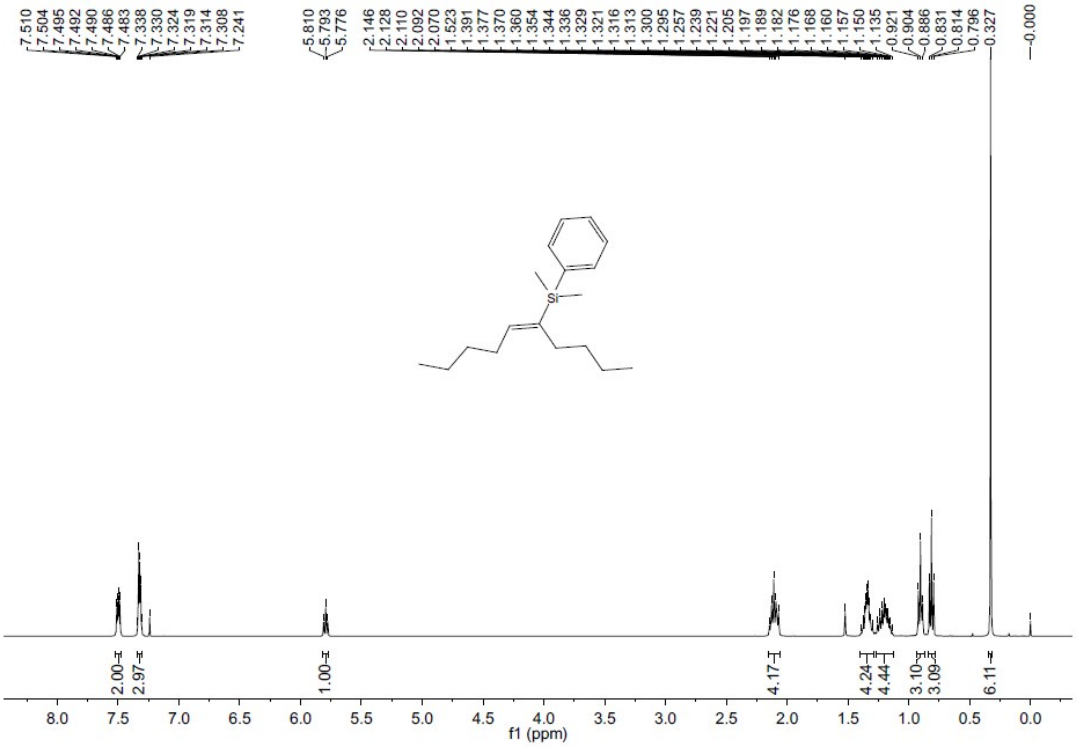


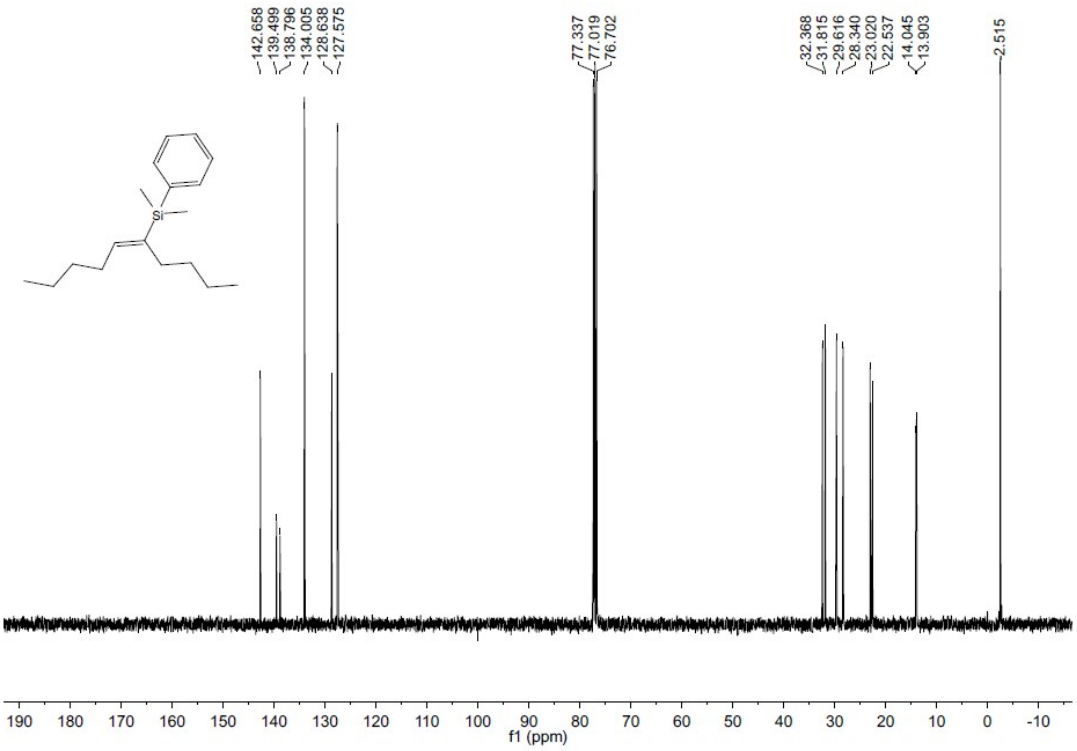
^{1}H NMR and ^{13}C NMR spectra of compound **6a**



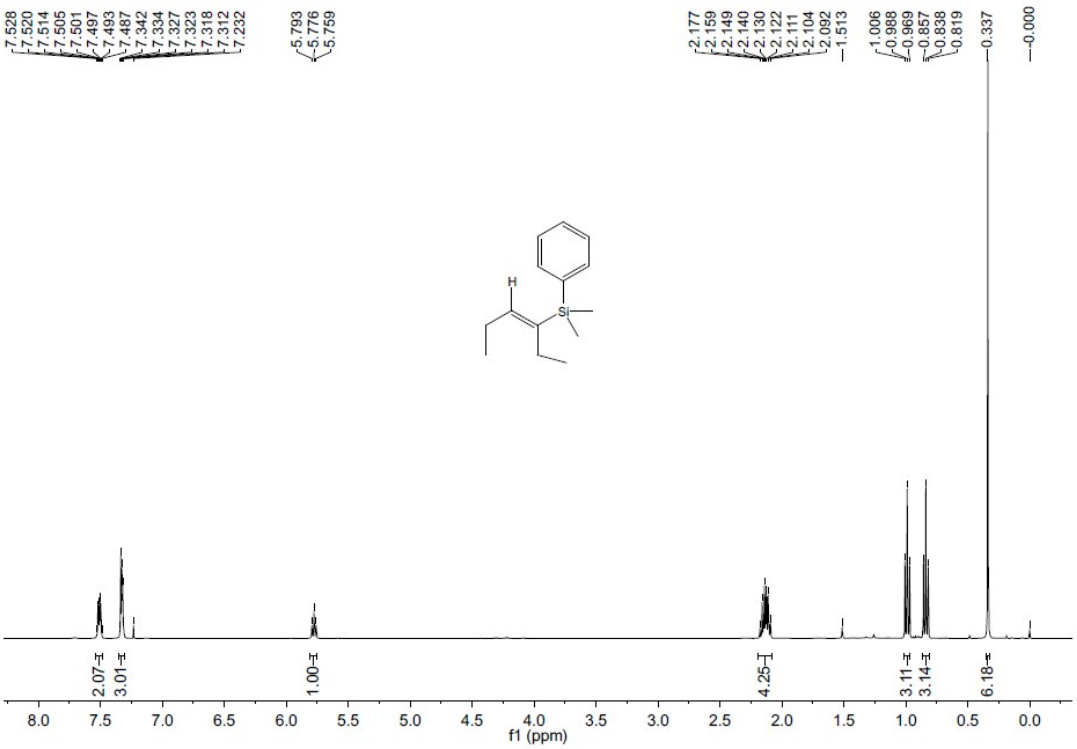


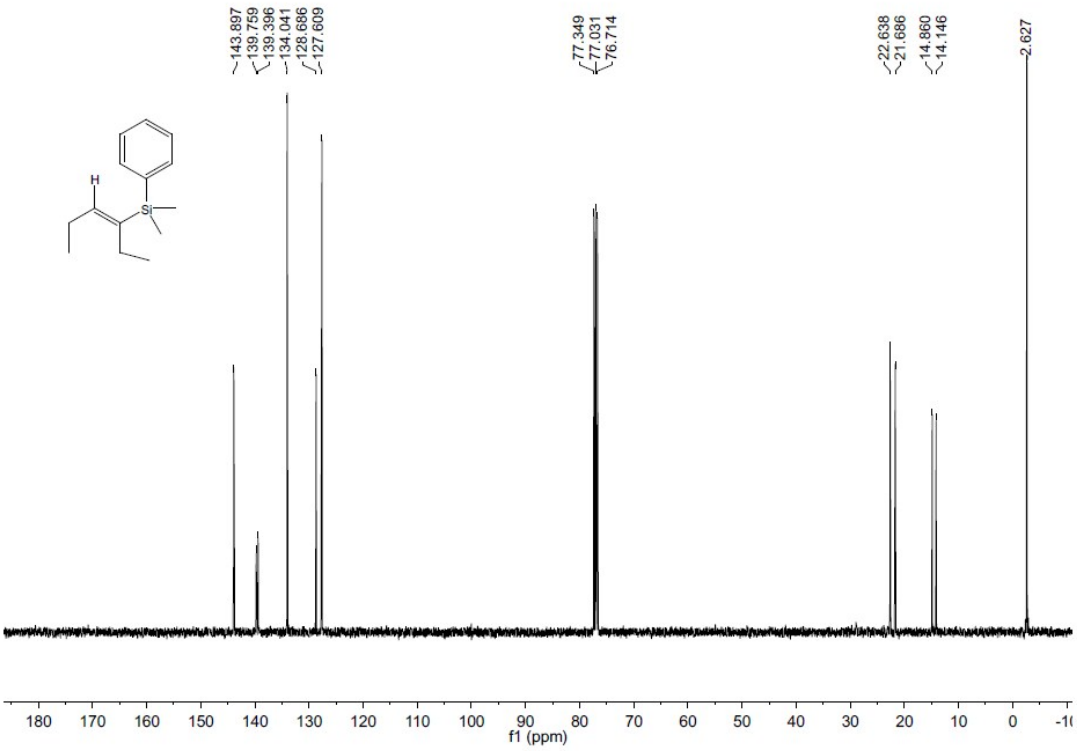
^{1}H NMR and ^{13}C NMR spectra of compound **6b**



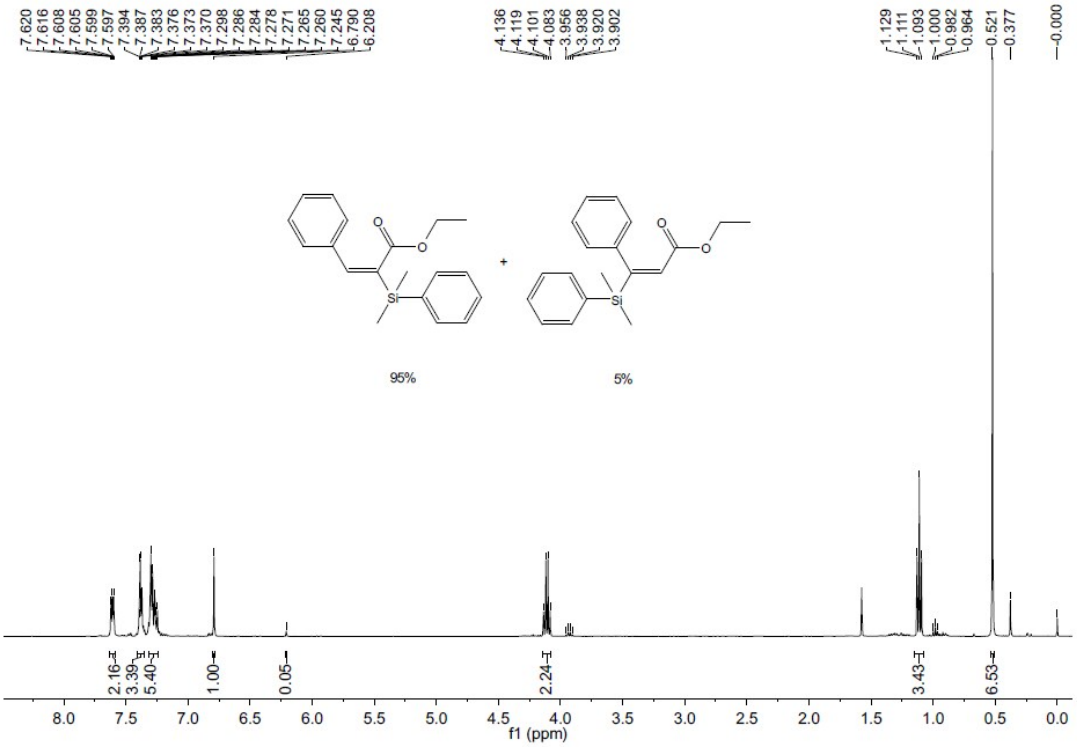


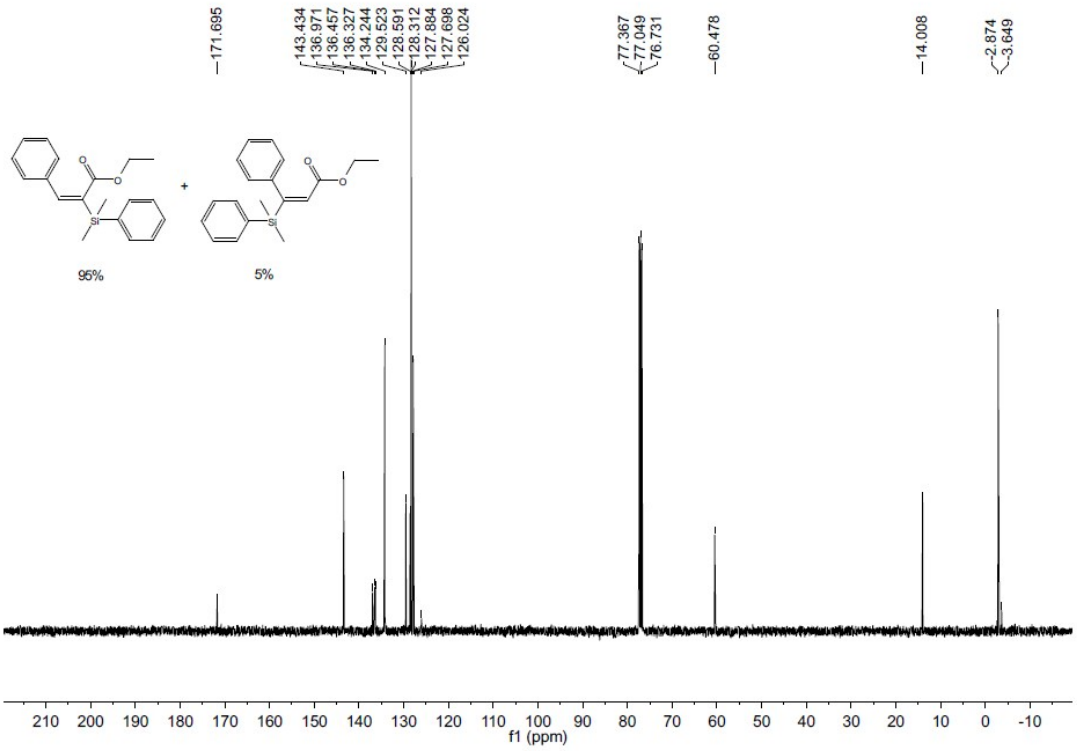
^{1}H NMR and ^{13}C NMR spectra of compound **6c**



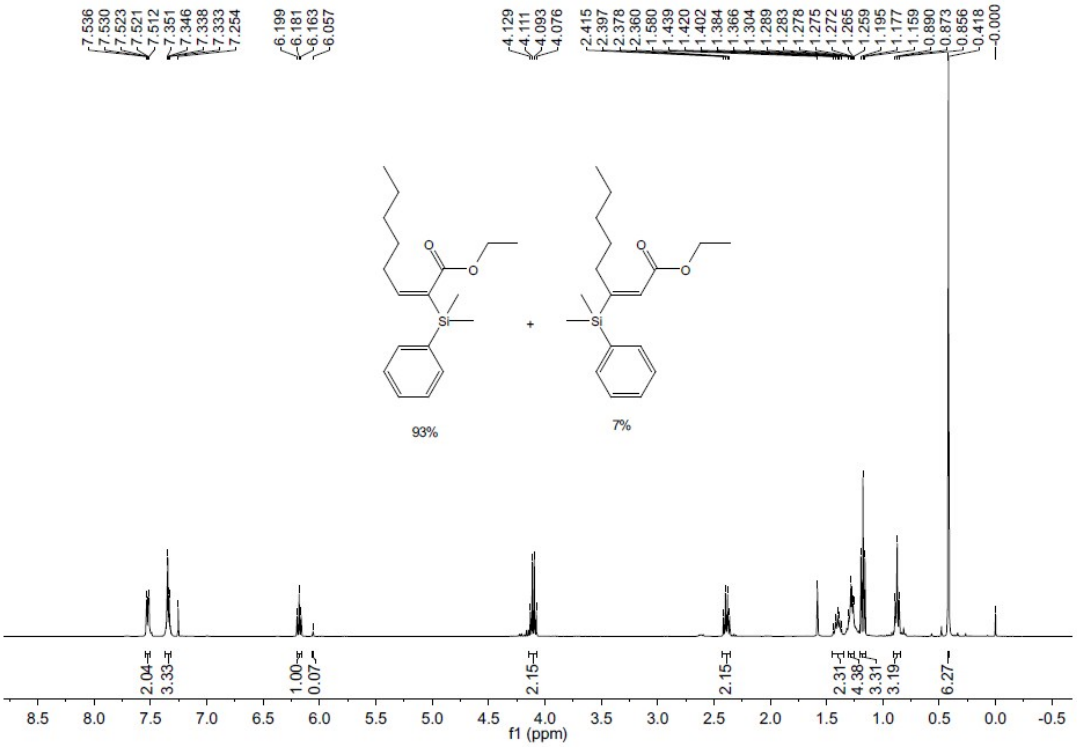


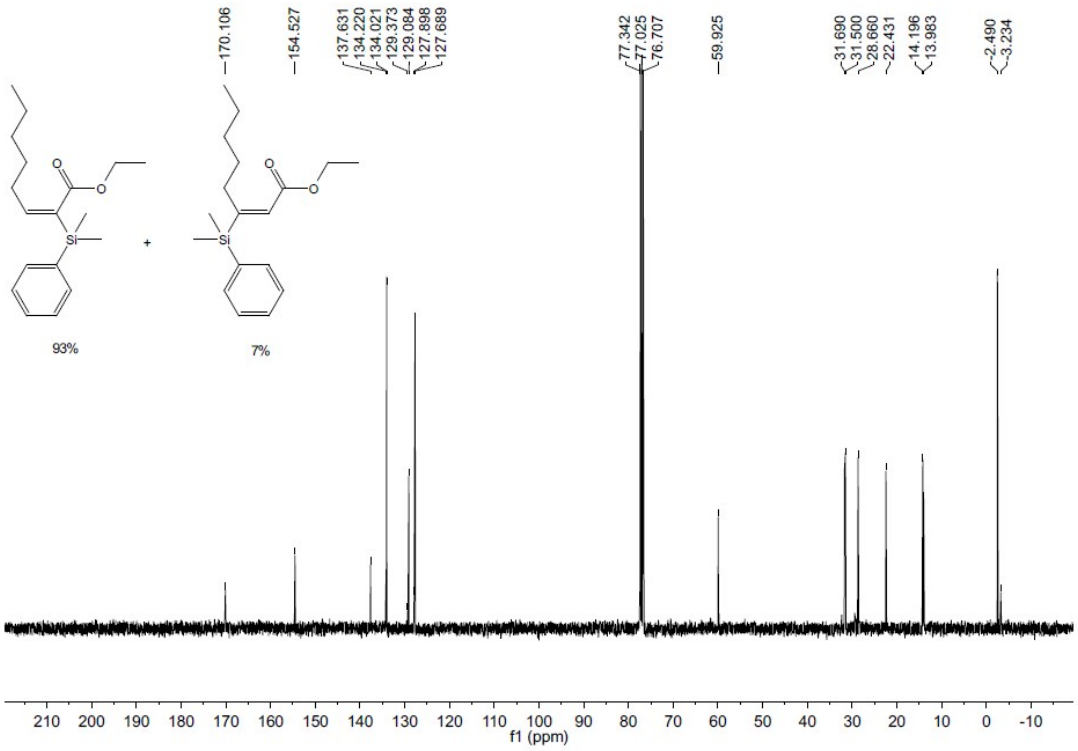
^{1}H NMR and ^{13}C NMR spectra of compound **6d**



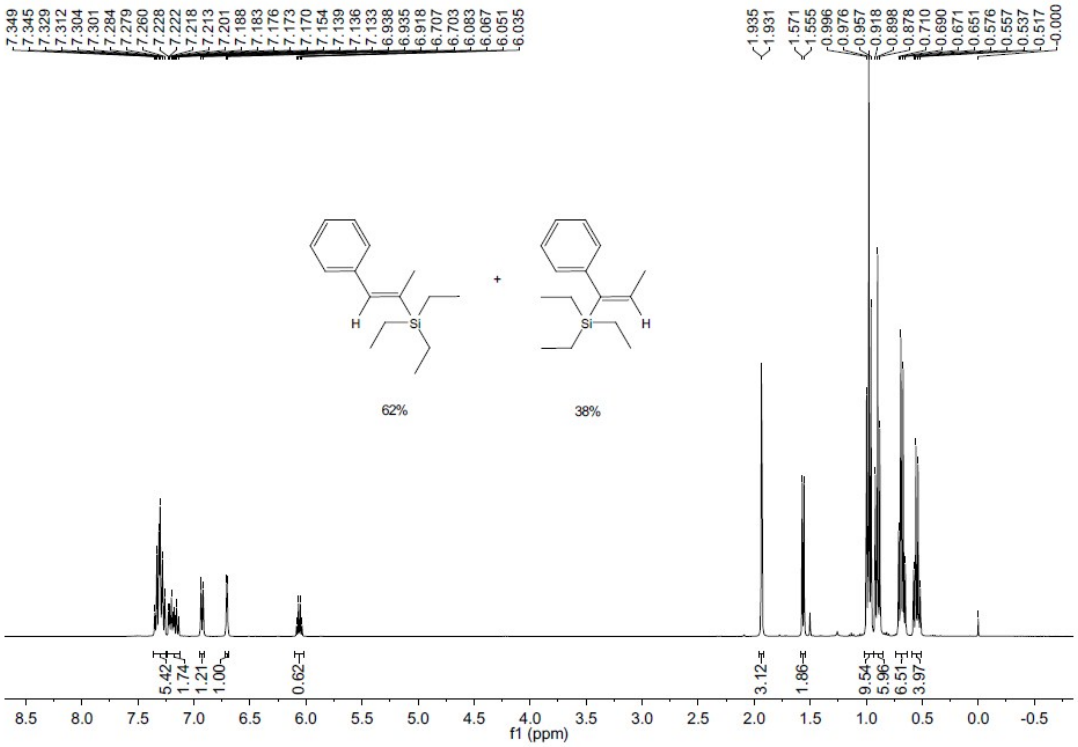


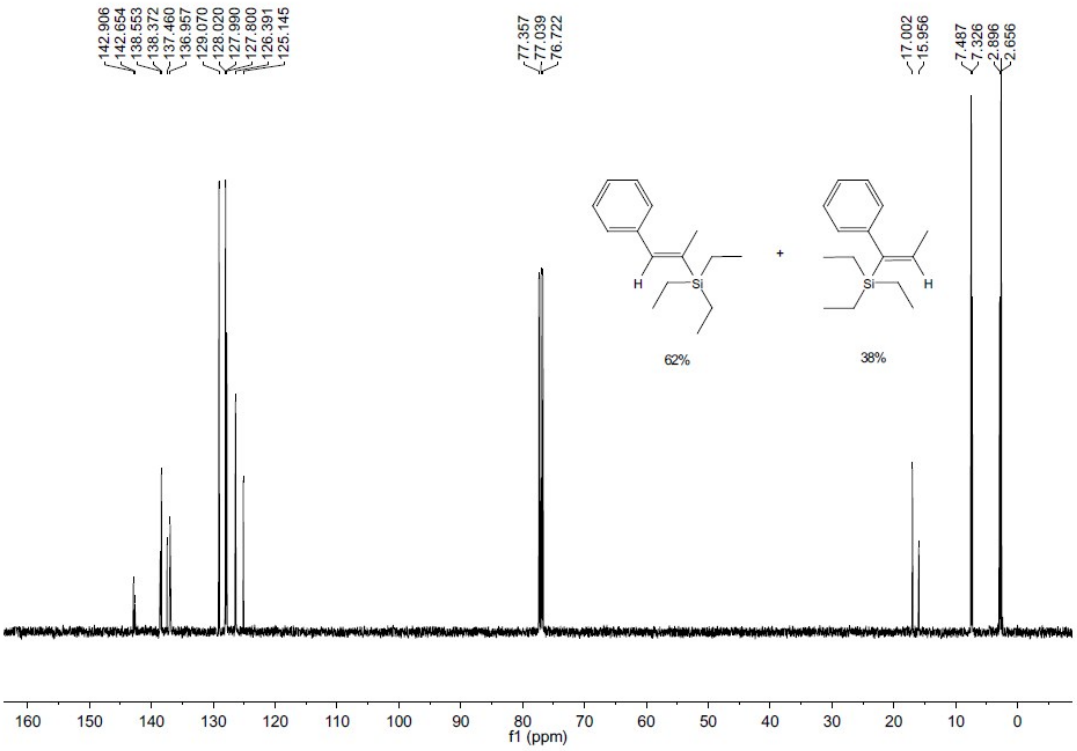
^{1}H NMR and ^{13}C NMR spectra of compound **6e**





^{1}H NMR and ^{13}C NMR spectra of compound **6f**





^{1}H NMR and ^{13}C NMR spectra of compound **6g** and **6g'**