Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

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1. General Information

a. Materials

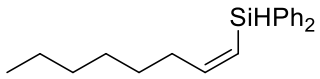
All manipulations were carried out using standard Schlenk, high-vacuum and glovebox techniques. Tetrahydrofuran (THF) was distilled from sodium benzophenoneketyl prior to use. The following chemicals were purchased and used as received: $Pd(OAc)_2$ (J&K), $Pd(PPh_3)_4$ (Alfa Aesar), $PdCl_2$ (J&K), Pd_2dba_3 (J&K), $(Pd\text{-}\eta^2\text{-}C_3H_5Cl)_2$ (Strem), $NaBEt_3H$ (1.0 M in THF, Aldrich), TBAF (1.0 M in THF, TCI), $PhSiH_3$ (TCI), Ph_2SiH_2 (J&K), $(EtO)_3SiH$ (TCI), MD'M (TCI). The following compounds, $(P^CNN)FeCl_2$ (**1a-b**),[1] $(P^CNN)CoCl_2$ (**2a-b**),[1] *tert*-butyl(hept-6-yn-1-yloxy)dimethylsilane (**3l**),[2] *tert*-butyl(hept-6-yn-1-yloxy)diphenylsilane (**3m**),[2] hept-6-yn-1-yl 4-methylbenzenesulfonate (**3n**)[3] were prepared according to procedures previously reported. All other chemicals were purchased from TCI, Alfa Aesar, Aldrich or J&K, Chemical Co., and used as received unless otherwise noted.

b. Analytical Methods

NMR spectra were recorded on Agilent 400 MHz, 600 MHz or Varian Mercury 400 MHz. ^1H NMR chemical shifts were referenced to residual protio solvent peaks or tetramethylsilane signal (0 ppm), and ^{13}C NMR chemical shifts were referenced to the solvent resonance. ^{31}P NMR chemical shifts were referenced to an external H_3PO_4 standard. Data for ^1H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, coupling constant (s) in Hz, integration). Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). Elemental analysis and high resolution mass spectrometer (HR-MS) were carried out by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS).

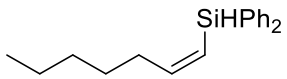
2. Procedure for Co-catalyzed Hydrosilylation of Alkynes

General procedure for hydrosilylation using cobalt complex 2b. In a nitrogen filled glovebox, the coblat complex **2b** (3.2 mg, 1 mol %), Ph_2SiH_2 (0.6 mmol, 1 equiv) and alkene **3** (0.9 mmol, 1.5 equiv) were added to a 5 mL tube equipped with a magnetic stir bar. The reaction mixture was chilled in the freezer to −38 °C and $NaBEt_3H$ (12 μL, 2 mol %) was then added to the reaction mixture. The reaction was stirred at 25 ºC for 24 h and was quenched by exposing the solution to air. The resulting solution was concentrated in vacuum and the residue was purified by chromatography on silica gel.



(Z)-oct-1-en-1-yldiphenylsilane 4a

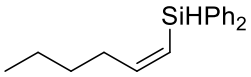
The reaction was carried out according to the typical procedure by using **3a** (99.2 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (155 mg, 88%, *Z/E* = 99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 4H), 7.43 – 7.33 (m, 6H), 6.67 (dt, *J* = 14.5, 7.3 Hz, 1H), 5.84 (dd, *J* = 13.7, 5.4 Hz, 1H), 5.27 (d, *J* = 5.3 Hz, 1H), 2.20 (dd, *J* = 14.9, 7.5 Hz, 2H), 1.37 – 1.30 (m, 2H), 1.29 – 1.18 (m, 6H), 0.85 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 135.4, 134.7, 129.6, 128.1, 121.5, 33.9, 31.8, 29.4, 29.0, 22.7, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{20}H_{26}Si$+], 294.1804; found: 294.1798.



(Z)-hept-1-en-1-yldiphenylsilane 4b

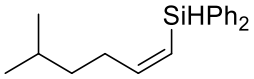
The reaction was carried out according to the typical procedure by using **3b** (86.6 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %)

and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (148 mg, 88%, *Z/E* = 98:2).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.43 – 7.33 (m, 6H), 6.67 (dt, J = 14.5, 7.5 Hz, 1H), 5.84 (dd, J = 13.6, 5.1 Hz, 1H), 5.27 (d, J = 5.3 Hz, 1H), 2.20 (q, J = 7.3 Hz, 2H), 1.39 – 1.31 (m, 2H), 1.27 – 1.17 (m, 4H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 135.4, 134.7, 129.6, 128.1, 121.5, 33.9, 31.5, 29.1, 22.6, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{19}H_{24}Si$+], 280.1647; found: 280.1651.



(Z)-hex-1-en-1-yldiphenylsilane 4c

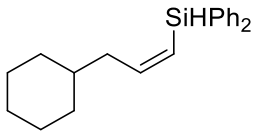
The reaction was carried out according to the typical procedure by using **3c** (73.9 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (145 mg, 91%, *Z/E* = 99:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.42 – 7.33 (m, 6H), 6.67 (dt, *J* = 14.3, 7.4 Hz, 1H), 5.84 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.28 (d, *J* = 5.4 Hz, 1H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.36 – 1.29 (m, 2H), 1.28 – 1.21 (m, 2H), 0.82 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 135.4, 134.7, 129.6, 128.1, 121.5, 33.6, 31.6, 22.4, 14.1. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{22}Si$+], 266.1491; found: 266.1493.



(Z)-(5-methylhex-1-en-1-yl)diphenylsilane 4d

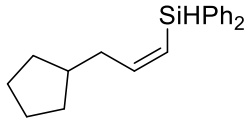
The reaction was carried out according to the typical procedure by using **3d** (86.6 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (103 mg, 61%, *Z/E* = 93:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.5 Hz, 4H), 7.41 – 7.34 (m, 6H), 6.66 (dt, *J* = 14.3, 7.4 Hz, 1H), 5.83 (dd, *J* = 13.8, 5.4 Hz, 1H), 5.28 (d, *J* = 5.3 Hz, 1H), 2.19

(q, *J* = 7.7 Hz, 2H), 1.50 – 1.43 (m, 1H), 1.27 – 1.19 (m, 2H), 0.79 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 135.4, 134.7, 129.6, 128.1, 121.3, 38.5, 31.9, 27.8, 22.6. HRMS-EI (*m/z*): Calcd for [$C_{19}H_{24}Si$+], 280.1647; found: 280.1650.



(Z)-(3-cyclohexylprop-1-en-1-yl)diphenylsilane 4e

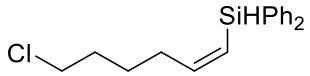
The reaction was carried out according to the typical procedure by using **3e** (110.0 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (152 mg, 83%, *Z/E* = 91:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 4H), 7.44 – 7.33 (m, 6H), 6.69 (dt, *J* = 14.5, 7.4 Hz, 1H), 5.87 (dd, *J* = 13.7, 5.6 Hz, 1H), 5.28 (d, *J* = 5.5 Hz, 1H), 2.12 (t, *J* = 7.2 Hz, 2H), 1.70 – 1.58 (m, 5H), 1.36 – 1.29 (m, 1H), 1.23 – 1.07 (m, 3H), 0.91 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 135.4, 134.7, 129.6, 128.1, 122.3, 41.4, 38.3, 33.1, 26.6, 26.5. HRMS-EI (*m/z*): Calcd for [$C_{21}H_{26}Si$+], 306.1804; found: 306.1805.



(Z)-(3-cyclopentylprop-1-en-1-yl)diphenylsilane 4f

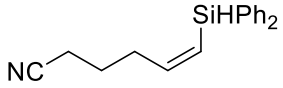
The reaction was carried out according to the typical procedure by using **3f** (97.4 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (102 mg, 58%, *Z/E* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 4H), 7.43 – 7.35 (m, 6H), 6.71 (dt, *J* = 14.4, 7.4 Hz, 1H), 5.87 (dd, *J* = 13.8, 5.5 Hz, 1H), 5.30 (d, *J* = 5.5 Hz, 1H), 2.25 (t, *J* = 7.3 Hz, 2H), 1.86 (p, *J* = 7.7 Hz, 1H), 1.74 – 1.66 (m, 2H), 1.61 – 1.43 (m, 4H),

1.17 – 1.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 135.3, 134.6, 129.5, 128.0, 121.6, 39.9, 39.7, 32.1, 25.0. HRMS-EI (*m/z*): Calcd for [$C_{20}H_{24}Si$+], 292.1647; found: 292.1645.



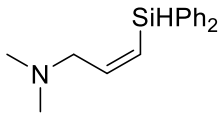
(Z)-(6-chlorohex-1-en-1-yl)diphenylsilane 4g

The reaction was carried out according to the typical procedure by using **3g** (104.9 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex 2**b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (152 mg, 83%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 4H), 7.38 (q, *J* = 7.7, 6.7 Hz, 6H), 6.64 (dt, *J* = 14.3, 7.4 Hz, 1H), 5.90 (dd, *J* = 13.8, 5.1 Hz, 1H), 5.26 (d, *J* = 5.3 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.23 (q, *J* = 7.4 Hz, 2H), 1.67 (p, *J* = 6.9 Hz, 2H), 1.49 (p, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 135.3, 134.3, 129.6, 128.1, 122.5, 44.8, 32.9, 31.9, 26.4. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{21}ClSi$+], 300.1101; found: 300.1093.



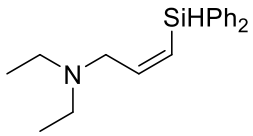
(Z)-6-(diphenylsilyl)hex-5-enenitrile 4h

The reaction was carried out according to the typical procedure by using **3h** (88.3 mg, 1.2 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 30/1 as eluenas eluent) afforded the title compound as a colorless oil (113 mg, 68%, *Z*−β/α = 84:16). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.44 – 7.35 (m, 6H), 6.59 (dt, *J* = 14.4, 7.4 Hz, 1H), 6.00 (dd, *J* = 13.8, 5.1 Hz, 1H), 5.27 (d, *J* = 5.2 Hz, 1H), 2.33 (q, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 7.4 Hz, 2H), 1.69 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 135.3, 134.0, 129.9, 128.2, 124.8, 119.6, 32.5, 25.1, 16.5. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{19}NSi$+], 277.1287; found: 277.1282.



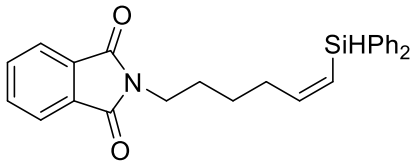
(Z)-3-(diphenylsilyl)-N,N-dimethylprop-2-en-1-amine 4i

The reaction was carried out according to the typical procedure by using **3i** (74.8 mg, 0.9 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 1/1 as eluent) afforded the title compound as a pale yellow oil (150 mg, 92%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 4H), 7.39 – 7.34 (m, 6H), 6.71 (dt, *J* = 13.1, 6.2 Hz, 1H), 6.05 (dd, *J* = 13.9, 5.1 Hz, 1H), 5.28 (d, *J* = 5.1 Hz, 1H), 3.06 (d, *J* = 6.2 Hz, 2H), 2.13 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 135.2, 134.9, 129.6, 128.1, 124.9, 61.2, 45.2. HRMS-EI (*m/z*): Calcd for [$C_{17}H_{21}NSi$+], 267.1443; found: 267.1442.



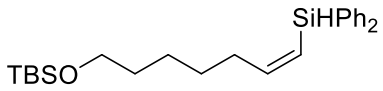
(Z)-3-(diphenylsilyl)-N,N-diethylprop-2-en-1-amine 4j

The reaction was carried out according to the typical procedure by using **3j** (100.1 mg, 0.9 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 1/1 as eluent) afforded the title compound as a pale yellow oil (156 mg, 88%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.55 (m, 4H), 7.42 – 7.34 (m, 6H), 6.75 (dt, *J* = 13.5, 6.5 Hz, 1H), 6.02 (dd, *J* = 14.5, 5.3 Hz, 1H), 5.31 (d, *J* = 5.5 Hz, 1H), 3.23 (d, *J* = 6.3 Hz, 2H), 2.48 (q, *J* = 7.3 Hz, 4H), 0.96 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 135.3, 134.4, 129.7, 128.1, 124.0, 55.4, 46.7, 11.6. HRMS-EI (*m/z*): Calcd for [$C_{19}H_{25}NSi$+], 295.1756; found: 295.1764.



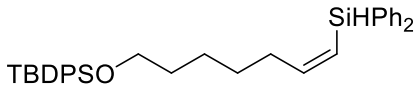
(Z)-2-(6-(diphenylsilyl)hex-5-en-1-yl)isoindoline-1,3-dione 4k

The reaction was carried out according to the typical procedure by using **3k** (205.2 mg, 1.20 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 10/1 as eluent) afforded the title compound as a yellow oil (210 mg, 85%, *Z/E* = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.73 – 7.70 (m, 2H), 7.58 – 7.52 (m, 4H), 7.41 – 7.29 (m, 6H), 6.62 (dt, *J* = 13.8, 7.4 Hz, 1H), 5.86 (dd, *J* = 13.7, 5.4 Hz, 1H), 5.24 (d, *J* = 5.3 Hz, 1H), 3.58 (t, *J* = 7.2 Hz, 2H), 2.23 (q, *J* = 7.3 Hz, 2H), 1.59 – 1.51 (m, 2H), 1.43 – 1.32 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 152.8, 135.3, 134.5, 134.0, 132.2, 129.6, 128.1, 123.3, 122.4, 37.9, 33.3, 28.2, 26.6. HRMS-EI (*m/z*): Calcd for [$C_{26}H_{25}NO_2Si$+], 411.1655; found: 411.1649.



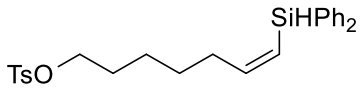
(Z)-tert-butyl((7-(diphenylsilyl)hept-6 -en-1-yl)oxy)dimethylsilane 4l

The reaction was carried out according to the typical procedure by using **3l** (204.3 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 50/1 as eluent) afforded the title compound as a colorless oil (222 mg, 90%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.43 – 7.31 (m, 6H), 6.66 (dt, *J* = 14.4, 7.4 Hz, 1H), 5.84 (dd, *J* = 13.7, 5.4 Hz, 1H), 5.26 (d, *J* = 5.3 Hz, 1H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.20 (q, *J* = 7.4 Hz, 2H), 1.47 – 1.31 (m, 4H), 1.29 – 1.21 (m, 2H), 0.89 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.6, 135.4, 134.7, 129.6, 128.1, 121.7, 63.3, 33.9, 32.8, 29.2, 26.1, 25.5, 18.5, -5.1. HRMS-EI (*m/z*): Calcd for [$C_{21}H_{29}OSi_2$+], 353.1757; found: 353.1760.



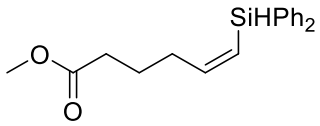
(Z)-tert-butyl((7-(diphenylsilyl)hept-6-en-1-yl)oxy)diphenylsilane 4m

The reaction was carried out according to the typical procedure by using **3m** (316.1 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 50/1 as eluent) afforded the title compound as a colorless oil (300 mg, 93%, *Z/E* = 98/2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 4H), 7.60 – 7.54 (m, 4H), 7.43 – 7.33 (m, 12H), 6.64 (dt, *J* = 14.4, 7.4 Hz, 1H), 5.83 (dd, *J* = 13.8, 5.2 Hz, 1H), 5.26 (d, *J* = 5.3 Hz, 1H), 3.58 (t, *J* = 6.5 Hz, 2H), 2.18 (q, *J* = 7.1 Hz, 2H), 1.52 – 1.44 (m, 2H), 1.37 – 1.22 (m, 4H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 135.7, 135.4, 134.7, 134.3, 129.6, 128.1, 127.7, 121.7, 64.0, 33.9, 32.5, 29.1, 27.0, 25.5, 19.4. HRMS-EI (*m/z*): Calcd for [$C_{31}H_{33}OSi_2$+], 477.2070; found: 477.2062.



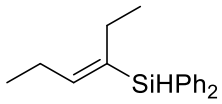
(Z)-7-(diphenylsilyl)hept-6-en-1-yl 4-methylbenzenesulfonate 4n

The reaction was carried out according to the typical procedure by using **3n** (240.0 mg, 0.9 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 5/1 as eluent) afforded the title compound as a colorless oil (237 mg, 88%, *Z/E* = 99:1).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.60 – 7.53 (m, 4H), 7.41 – 7.30 (m, 8H), 6.58 (dt, *J* = 14.3, 7.4 Hz, 1H), 5.85 (dd, *J* = 13.8, 5.3 Hz, 1H), 5.23 (d, *J* = 5.3 Hz, 1H), 3.93 (t, *J* = 6.5 Hz, 2H), 2.44 (s, 3H), 2.14 (q, *J* = 7.3 Hz, 2H), 1.57 – 1.49 (m, 2H), 1.33 – 1.17 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 144.7, 135.3, 134.4, 133.2, 129.9, 129.7, 128.1, 127.9, 122.1, 70.6, 33.5, 28.6, 28.5, 24.9, 21.7. HRMS-ESI (*m/z*): Calcd for [($C_{26}H_{30}O_3SSi$+NH_4)+], 468.2023; found: 468.2021.



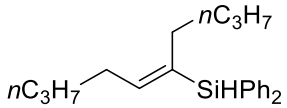
methyl (Z)-6-(diphenylsilyl)hex-5-enoate 4o

The reaction was carried out according to the typical procedure by using **3o** (113.5 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (6.4 mg, 2 mol %) and $NaBEt_3H$ (24 μL, 4 mol %). Purification by silica gel chromatography (*n*-hexane/ethyl acetate = 50/1 as eluent) afforded the title compound as a colorless oil (148 mg, 80%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 4H), 7.45 – 7.32 (m, 6H), 6.62 (dt, *J* = 14.3, 7.4 Hz, 1H), 5.90 (dd, *J* = 14.0, 5.4 Hz, 1H), 5.25 (d, *J* = 5.4 Hz, 1H), 3.62 (s, 3H), 2.23 (q, *J* = 7.2 Hz, 4H), 1.70 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 152.1, 135.3, 134.3, 129.7, 128.1, 123.0, 51.6, 33.4, 33.0, 24.5. HRMS-EI (*m/z*): Calcd for [$C_{19}H_{22}O_2Si$+], 310.1389; found: 310.1393.



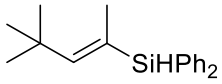
(E)-hex-3-en-3-yldiphenylsilane 4p

The reaction was carried out according to the typical procedure by using **3p** (49.3 mg, 0.60 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %, *Z/E* = 99:1). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (134 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 4H), 7.44 – 7.33 (m, 6H), 5.89 (t, *J* = 6.9 Hz, 1H), 5.08 (s, 1H), 2.29 – 2.16 (m, 4H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.90 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 136.1, 135.9, 134.3, 129.6, 128.0, 23.4, 22.1, 14.7, 14.2. These spectroscopic data correspond to reported data.[4]



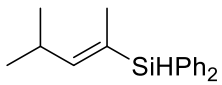
(E)-dec-5-en-5-yldiphenylsilane 4q

The reaction was carried out according to the typical procedure by using **3q** (124.4 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (138 mg, 71%, *Z/E* = 99:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 4H), 7.44 – 7.34 (m, 6H), 5.92 (t, *J* = 6.9 Hz, 1H), 5.10 (s, 1H), 2.28 – 2.16 (m, 4H), 1.40 – 1.22 (m, 8H), 0.93 (t, *J* = 6.9 Hz, 3H), 0.82 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 135.8, 135.1, 134.4, 129.5, 128.0, 32.1, 31.7, 30.3, 28.7, 23.0, 22.7, 14.2, 14.0. These spectroscopic data correspond to reported data.[4]



(E)-(4,4-dimethylpent-2-en-2-yl)diphenylsilane 4r

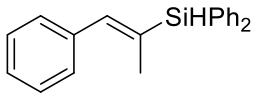
The reaction was carried out according to the typical procedure by using **3r** (86.6 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (139 mg, 82%, regioselectivity 99:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H), 7.44 – 7.34 (m, 6H), 6.01 (s, 1H), 4.98 (s, 1H), 1.91 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 135.8, 134.2, 129.6, 129.0, 128.0, 35.3, 30.8, 16.5. These spectroscopic data correspond to reported data.[5]



(E)-(4-methylpent-2-en-2-yl)diphenylsilane 4s

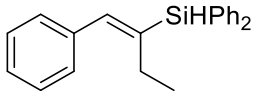
The reaction was carried out according to the typical procedure by using **3s** (73.9 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (127 mg, 80%,

regioselectivity 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 4H), 7.43 – 7.33 (m, 6H), 5.83 (d, *J* = 8.9 Hz, 1H), 5.01 (s, 1H), 2.79 (dq, *J* = 13.5, 6.7 Hz, 1H), 1.78 (s, 3H), 0.98 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 135.8, 134.0, 129.6, 128.0, 127.2, 27.8, 22.6, 15.4. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{22}Si$+], 266.1491; found: 266.1500.



(E)-diphenyl(1-phenylprop-1-en-2-yl)silane 4t

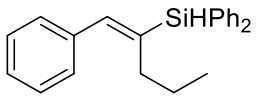
The reaction was carried out according to the typical procedure by using **3t** (104.5 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (169 mg, 94%, regioselectivity 91:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.61 (m, 4H), 7.46 – 7.38 (m, 6H), 7.37 – 7.33 (m, 4H), 7.26 – 7.22 (m, 1H), 6.96 (s, 1H), 5.18 (s, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 138.0, 135.9, 134.2, 133.3, 129.9, 129.2, 128.2, 128.2, 127.1, 17.7. HRMS-EI (*m/z*): Calcd for [$C_{21}H_{20}Si$+], 300.1334; found: 300.1331.



(E)-diphenyl(1-phenylbut-1-en-2-yl)silane 4u

The reaction was carried out according to the typical procedure by using **3u** (117.2 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (175 mg, 93%, regioselectivity 88:12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 4H), 7.45 – 7.37 (m, 6H), 7.35 – 7.28 (m, 4H), 7.26 – 7.21 (m, 1H), 6.86 (s, 1H), 5.24 (s, 1H), 2.52 (q, *J* = 7.5 Hz, 2H), 1.05 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

142.8, 141.0, 138.0, 136.0, 133.7, 129.8, 128.8, 128.3, 128.1, 127.1, 24.6, 14.6. HRMS-EI (*m/z*): Calcd for [$C_{22}H_{22}Si$+], 314.1491; found: 314.1493.



(E)-diphenyl(1-phenylpent-1-en-2-yl)silane 4v

The reaction was carried out according to the typical procedure by using **3v** (129.8 mg, 0.90 mmol), Ph_2SiH_2 (110.6 mg, 0.60 mmol), cobalt complex **2b** (3.2 mg, 1 mol %) and $NaBEt_3H$ (12 μL, 2 mol %). Purification by silica gel chromatography (*n*-hexane as eluent) afforded the title compound as a colorless oil (179 mg, 91%, regioselectivity 91:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.46 – 7.29 (m, 10H), 7.25 – 7.21 (m, 1H), 6.87 (s, 1H), 5.23 (s, 1H), 2.50 – 2.41 (m, 2H), 1.47 (q, *J* = 7.8 Hz, 2H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 139.6, 138.1, 135.9, 133.7, 129.8, 128.9, 128.3, 128.1, 127.1, 33.8, 23.2, 14.5. HRMS-EI (*m/z*): Calcd for [$C_{23}H_{24}Si$+], 328.1647; found: 328.1642.

we determined the stereochemistry of the C=C bond by using NOSEY (**Figure S1**). For example, if the reaction of prop-1-yn-1-ylbenzene (**3t**) with Ph_2SiH_2 formed the *Z*-product, there will be a signal resulting from the interaction between "C*H*$_3$" and the olefinic H "Ph-C*H*=" moiety. However, we did not observe such a signal in the NOSEY spectrum.

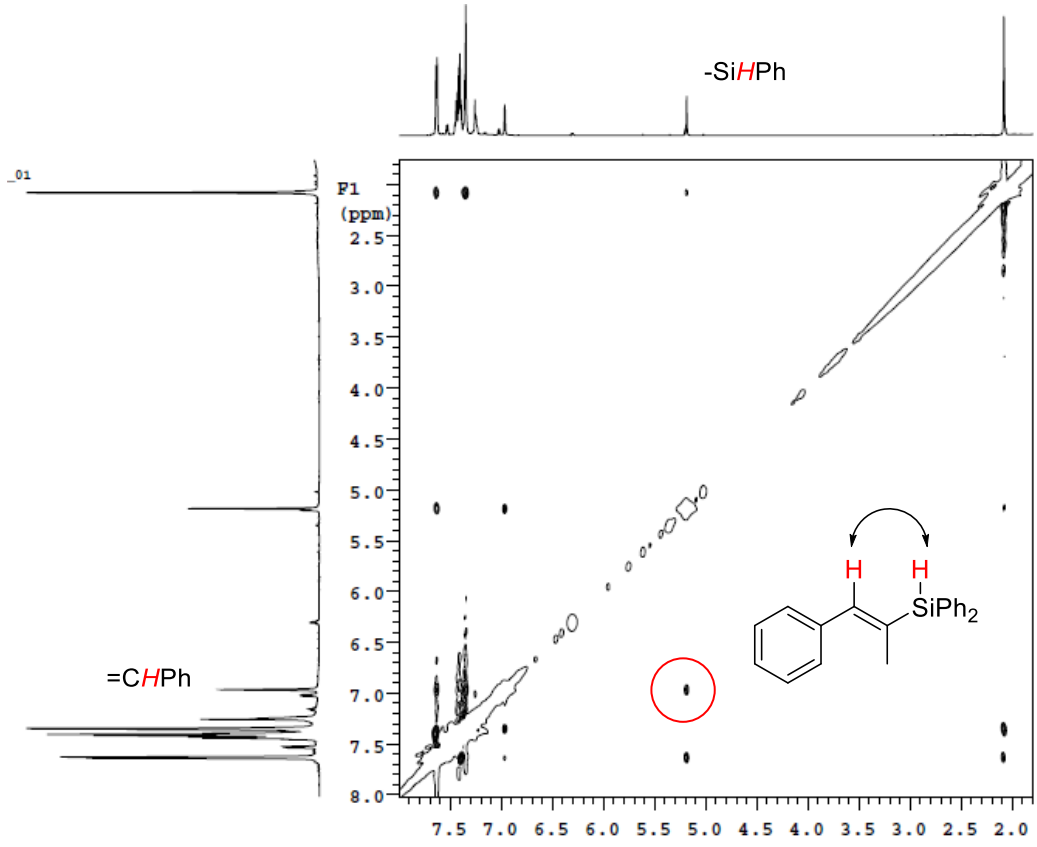
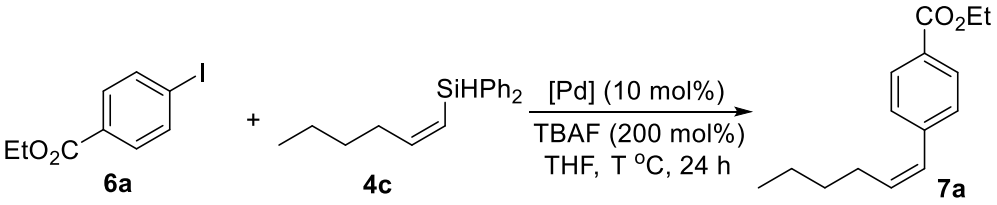


Figure S1. NOESY for compound **4t**

3. Optimizations for Pd-catalyzed Hiyama-Denmark cross-coupling reaction

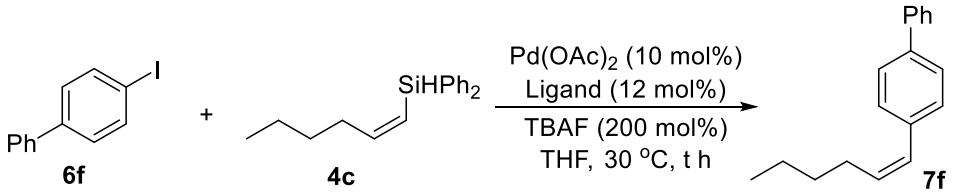
Table S1. Screening of Pd catalysts



Entry	[Pd]	T (°C)	Yield (%)[a]
1	Pd_2dba_3	35	92(84)
2	$Pd(PPh_3)_4$	35	51
3	$(Pd\text{-}\eta^2\text{-}C_3H_5Cl)_2$	35	82
4	$PdCl_2$	35	70
5	$Pd(OAc)_2$	35	88
6	$Pd(OAc)_2$	25	89

[a] Conditions: **4c** (0.24 mmol), **5a** (0.2 mmol), TBAF (0.4 mmol) in THF (0.4 mL). The yield were determined by H^1 NMR with mesitylene as an internal standard.

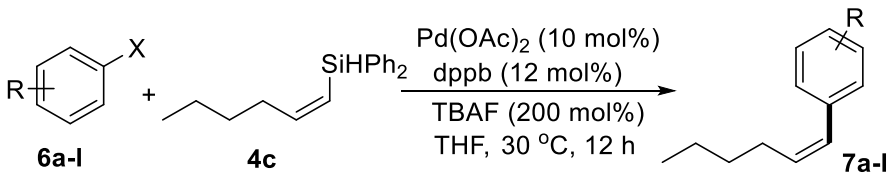
Table S2. Screening of Ligands



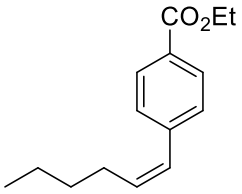
Entry	Ligand	t (h)	Yield (%)[a]	*E*/*Z*[b]
1	--	24	80(71)	70:30
2	JohnPhos	24	67	84:16
3	X-Phos	24	79	85:15
4	S-Phos	24	69	80:20
5	RuPhos	24	74	88:12
6	$Pd(PtBu_3)_2$	24	--	--
7	dppb	24	98(93)[c]	91:9
8	dppf	24	98	85:15
9	BINAP	24	79	91:19
10	L1	24	91	85:15
11	L2	24	96	86:14
12	dppb	12	98	94:6
13	dppb	6	96	94:6
14	dppb	3	87	94:6

[a] Conditions: **4c** (0.24 mmol), **5f** (0.2 mmol), TBAF (0.4 mmol) and Ligand (0.024 mol) in THF (0.4 mL). The yield were determined by H^1 NMR with mesitylene as an internal standard. [b] Determined by GC. [c] isolated yield.

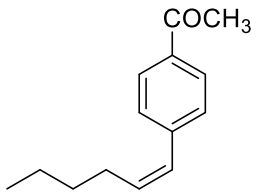
4. Procedure for Pd-catalyzed Hiyama-Denmark cross-coupling reaction



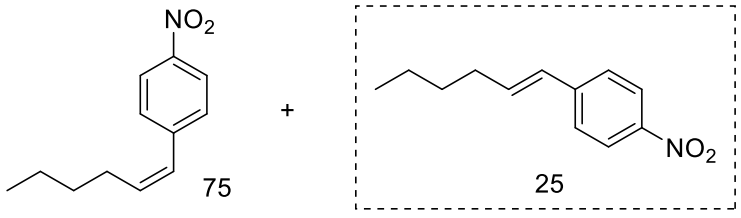
General procedure for Pd-catalyzed Hiyama-Denmark cross-coupling of (Z)-vinylsilanes with aryl halides. In a nitrogen filled glovebox, vinyl silane **4c** (64 mg, 0.24 mmol) was added to a 5 ml tube equipped with a magnetic stir bar. 0.4 ml of TBAF (0.4 mmol, 1.0 M in THF) was added and the solution was stirred for 5 min. Then arylhalides **6** (0.2 mmol), $Pd(OAc)_2$ (4.6 mg, 0.02 mmol) and dppb (10.2 mg, 0.024 mol) were added to the mixture. After that, the sealed tube was removed from the glovebox. The reaction mixture was stirred at 30 °C for 24 h. Then it was quenched by exposing the solution to air. The crude reaction mixture was purified by flash column chromatography.



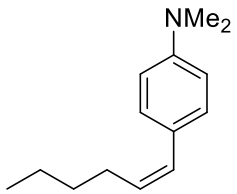
ethyl (Z)-4-(hex-1-en-1-yl)benzoate (7a). The reaction was carried out according to the typical procedure by using **6a** (55 mg, 0.20 mmol). Purification by preparative HPLC afforded the title compound as a colorless oil (41 mg, 89%, *Z/E* = 96:4). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 11.7 Hz, 1H), 5.77 (dt, *J* = 11.7, 7.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.33 (q, *J* = 7.3 Hz, 2H), 1.49 – 1.29 (m, 7H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 142.5, 135.5, 129.5, 128.7, 128.4, 128.1, 61.0, 32.1, 28.6, 22.5, 14.5, 14.1. HRMS-EI (*m/z*): Calcd for [$C_{15}H_{20}O_2$+], 232.1463; found: 232.1465.



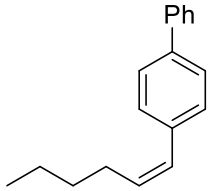
(Z)-1-(4-(hex-1-en-1-yl)phenyl)ethan-1-one (7b). The reaction was carried out according to the typical procedure by using **6b** (49 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the title compound as a pale yellow oil (31 mg, 77%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 12.0 Hz, 1H), 5.79 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.60 (s, 3H), 2.34 (q, *J* = 7.2 Hz, 2H), 1.48 – 1.42 (m, 2H), 1.39 – 1.32 (m, 2H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 142.9, 135.8, 135.2, 129.0, 128.4, 128.0, 32.1, 28.7, 26.7, 22.5, 14.1. HRMS-EI (*m/z*): Calcd for [$C_{14}H_{18}O$+], 202.1358; found: 202.1360.



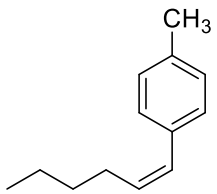
(Z)-1-(hex-1-en-1-yl)-4-nitrobenzene (7c). The reaction was carried out according to the typical procedure by using **6c** (46 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 30/1 as eluent) afforded a mixture of Z and E isomer as a yellow oil (35 mg, 86%, *Z/E* = 75:25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 – 8.12 (m, 2H), 7.47 – 7.38 (m, 2H), 6.46 – 6.43 (m, 1H), 5.87 (dt, *J* = 11.8, 7.5 Hz, 75%, 1H, Z isomer), 2.37 – 2.25 (m, 2H), 1.51 – 1.43 (m, 2H), 1.37 (dt, *J* = 14.4, 7.2 Hz, 2H), 0.92 (dd, *J* = 15.4, 7.6 Hz, 3H). HRMS-EI (*m/z*): Calcd for [$C_{12}H_{15}NO_2$+], 205.1103; found: 205.1102.



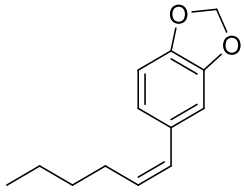
(Z)-4-(hex-1-en-1-yl)-N,N-dimethylaniline (7d). The reaction was carried out according to the typical procedure by using **6d** (50 mg, 0.20 mmol). Purification by preparative HPLC afforded the title compound as a yellow oil (25mg, 62%, *Z/E* = 94:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.7 Hz, 2H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.05 (dt, *J* = 15.7, 6.9 Hz, 1H), 2.97 (s, 6H), 2.21 (q, *J* = 7.1 Hz, 2H), 1.50 – 1.35 (m, 4H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 129.5, 127.3, 127.0, 126.8, 112.9, 40.9, 32.9, 32.0, 22.4, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{14}H_{21}N$+], 203.1674; found: 203.1668.



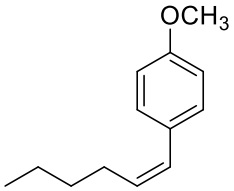
(Z)-4-(hex-1-en-1-yl)-1,1'-biphenyl (7e). The reaction was carried out according to the typical procedure by using **6e** (56 mg, 0.20 mmol). Purification by silica gel chromatography (hexane as eluent) afforded the title compound as a yellow oil (43 mg, 91%, *Z/E* = 94:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 4H), 7.50 – 7.33 (m, 5H), 6.46 (d, *J* = 11.6 Hz, 1H), 5.73 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.42 (q, *J* = 7.4 Hz, 2H), 1.55 – 1.45 (m, 2H), 1.44 – 1.34 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 139.3, 137.0, 133.7, 129.3, 128.9, 128.4, 127.3, 127.1, 126.9, 32.3, 28.7, 22.6, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{20}$+], 236.1565; found: 236.1559.



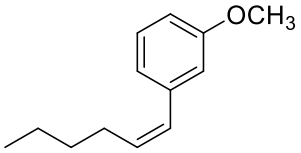
(Z)-1-(hex-1-en-1-yl)-4-methylbenzene (7f). The reaction was carried out according to the typical procedure by using **6f** (44 mg, 0.20 mmol). Purification by silica gel chromatography (hexane as eluent) afforded the title compound as a pale yellow oil (27 mg, 78%, *Z/E* = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.38 (d, *J* = 11.6 Hz, 1H), 5.63 (dt, *J* = 11.5, 7.2 Hz, 1H), 2.36 (s, 3H), 1.49 – 1.33 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.1, 132.7, 128.9, 128.8, 128.6, 32.4, 28.6, 22.6, 21.3, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{13}H_{18}$+], 174.1409; found: 174.1402.



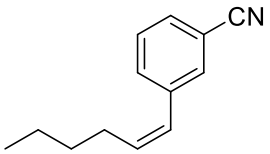
(Z)-5-(hex-1-en-1-yl)benzo[d][1,3]dioxole (7g). The reaction was carried out according to the typical procedure by using **6g** (50 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the title compound as a yellow oil (34 mg, 83%, *Z/E* = 93:7). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 – 6.71 (m, 3H), 6.30 (d, *J* = 11.7 Hz, 1H), 5.95 (s, 2H), 5.57 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.31 (q, *J* = 7.1 Hz, 2H), 1.47 – 1.32 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 146.1, 132.3, 132.1, 128.3, 122.6, 109.1, 108.2, 101.0, 32.3, 28.5, 22.6, 14.1. HRMS-EI (*m/z*): Calcd for [$C_{13}H_{16}O_2$+], 204.1150; found: 204.1153.



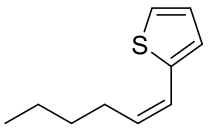
(Z)-1-(hex-1-en-1-yl)-4-methoxybenzene (7h). The reaction was carried out according to the typical procedure by using **6h** (47 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the title compound as a yellow oil (32 mg, 84%, *Z/E* = 97:3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 11.6 Hz, 1H), 5.59 (dt, *J* = 11.6, 7.2 Hz, 1H), 3.82 (s, 3H), 2.34 (q, *J* = 7.1 Hz, 2H), 1.47 – 1.33 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 131.8, 130.6, 130.0, 128.2, 113.6, 55.4, 32.4, 28.5, 22.6, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{13}H_{18}O$+], 190.1358; found: 190.1356.



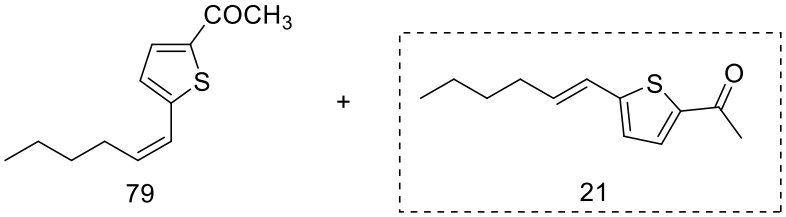
(Z)-1-(hex-1-en-1-yl)-3-methoxybenzene (7i). The reaction was carried out according to the typical procedure by using **6i** (47 mg, 1.00 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the title compound as a yellow oil (26 mg, 70%, *Z/E* = 88:12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.41 (d, *J* = 11.6 Hz, 1H), 5.70 (dt, *J* = 11.7, 7.3 Hz, 1H), 3.84 (s, 3H), 2.37 (q, *J* = 7.8, 7.4 Hz, 2H), 1.51 – 1.36 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 139.3, 133.7, 129.2, 128.7, 121.5, 114.4, 112.0, 55.3, 32.3, 28.6, 22.6, 14.2. HRMS-EI (*m/z*): Calcd for [$C_{13}H_{18}O$+], 190.1358; found: 190.1354.



(Z)-3-(hex-1-en-1-yl)benzonitrile (7j). The reaction was carried out according to the typical procedure by using **6j** (37 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the title compound as a yellow oil (21 mg, 55%, *Z/E* = 91:9). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.36 (m, 4H), 6.36 (d, *J* = 11.7 Hz, 1H), 5.79 (dt, *J* = 11.6, 7.3 Hz, 1H), 2.28 (q, *J* = 6.9 Hz, 2H), 1.46 – 1.31 (m, 4H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 135.9, 133.2, 132.2, 130.0, 129.1, 126.7, 119.1, 112.4, 32.0, 28.4, 22.5, 14.0. HRMS-EI (*m/z*): Calcd for [$C_{13}H_{15}N$+], 185.1204; found: 185.1211.



(Z)-2-(hex-1-en-1-yl)thiophene (7k). The reaction was carried out according to the typical procedure by using **6k** (42 mg, 0.20 mmol). Purification by silica gel chromatography (hexane as eluent) afforded the title compound as a colorless oil (22 mg, 66%, *Z/E* = 90:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 5.4 Hz, 1H), 7.03 – 6.96 (m, 2H), 6.54 (d, *J* = 11.6 Hz, 1H), 5.59 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.42 (q, *J* = 7.1 Hz, 2H), 1.55 – 1.46 (m, 2H), 1.45 – 1.36 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 131.4, 127.1, 126.8, 125.0, 121.8, 31.8, 29.2, 22.6, 14.1. HRMS-EI (*m/z*): Calcd for [$C_{10}H_{14}S$+], 166.0816; found: 166.0812.



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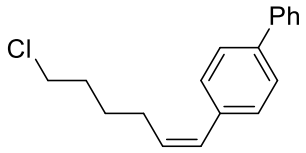
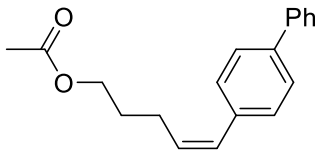
(Z)-1-(5-(hex-1-en-1-yl)thiophen-2-yl)ethan-1-one (7l). The reaction was carried

out according to the typical procedure by using **6l** (51 mg, 0.20 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded a mixture of Z and E isomer as a yellow oil (26 mg, 64%, *Z/E* = 79:21). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 3.4 Hz, 0.79H, Z isomer), 7.52 (d, *J* = 3.5 Hz, 0.21H, E isomer), 6.95 (d, *J* = 3.6 Hz, 79%, 1H, Z isomer), 6.86 (d, *J* = 3.3 Hz, 21%, 1H, E isomer), 6.51 (d, *J* = 12.4 Hz, 79%, 1H, Z isomer), 6.34 – 6.22 (m, 21%, 1H, E isomer), 5.78 (dt, *J* = 11.6, 7.3 Hz, 0.79%, 1H, Z isomer), 2.54 (s, 79%, 3H, Z isomer), 2.50 (s, 21%, 3H, E isomer), 2.44 (q, *J* = 7.1 Hz, 79%, 2H, Z isomer), 2.20 (d, *J* = 7.2 Hz, 21%, 2H, E isomer), 1.53 – 1.34 (m, 4H), 0.97 – 0.88 (m, 3H). HRMS-EI (*m/z*): Calcd for [$C_{12}H_{16}OS$+], 208.0922; found: 208.0924.



(Z)-4-(6-chlorohex-1-en-1-yl)-1,1'-biphenyl (7m). The reaction was carried out according to the typical procedure by using **4g** (36 mg, 0.12 mmol) and **6e** (28 mg, 0.10 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 100/1 as eluent) afforded the tittle compund as a colorless oil (26 mg, 96%, *Z/E* = 94:6). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.33 (m, 3H), 6.49 (d, *J* = 11.7 Hz, 1H), 5.68 (dt, *J* = 11.7, 7.2 Hz, 1H), 3.55 (t, *J* = 6.6 Hz, 2H), 2.43 (qd, *J* = 7.4, 1.8 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.69 – 1.60 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.5, 136.7, 132.5, 129.3, 129.1, 128.9, 127.4, 127.1, 127.0, 45.0, 32.3, 28.0, 27.3. HRMS-EI (*m/z*): Calcd for [$C_{18}H_{19}Cl$+], 270.1175; found: 270.1174.



(Z)-5-([1,1'-biphenyl]-4-yl)pent-4-en-1-yl acetate (7n). The reaction was carried out according to the typical procedure by using **4o** (31 mg, 0.12 mmol) and **6e** (28 mg, 0.10 mmol). Purification by silica gel chromatography (petroleum ether/ethyl acetate = 50/1 as eluent) afforded the tittle compund as a colorless oil (26 mg, 94%, *Z/E* = 98:2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 13.5, 8.0 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 3H), 6.49 (d, *J* = 11.7 Hz, 1H), 5.67 (dt, *J* = 11.7, 7.3 Hz, 1H), 3.65 (s, 3H), 2.43 (q, *J* = 7.5 Hz, 2H), 2.37 (t, *J* = 7.5 Hz, 2H), 1.82 (p, *J* = 7.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 140.9, 139.5, 136.6, 132.0, 129.5, 129.3, 128.9, 127.4, 127.1, 127.0, 51.7, 33.7, 28.2, 25.3. HRMS-EI (*m/z*): Calcd for [$C_{19}H_{20}O_2$+], 280.1463; found: 280.1458.

5. References

[1] X. Du, Y. Zhang, D. Peng, Z. Huang, *Angew. Chem. Int. Ed.* **2016**, *55*, 6671-6675.

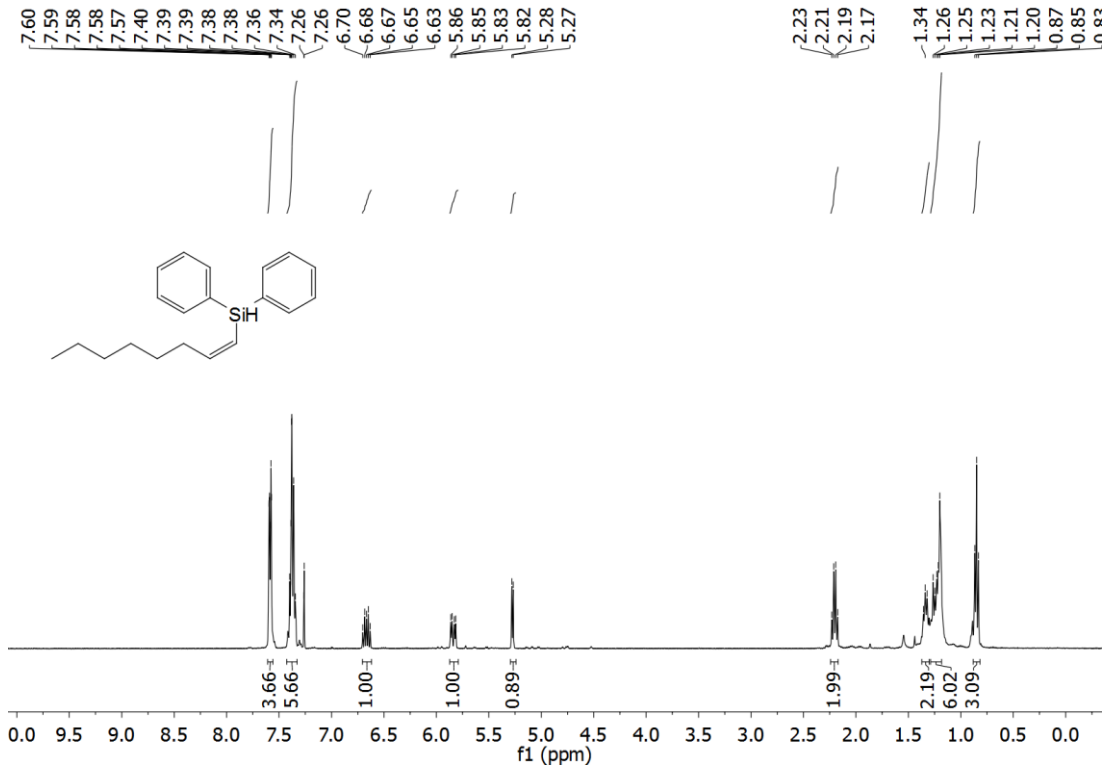
[2] L. Cleary, H. Yoo, K. J. Shea, *Org. Lett.* **2011**, *13*, 1781-1783.

[3] R. G. Iafe, D. G. Chan, J. L. Kuo, B. A. Boon, D. J. Faizi, T. Saga, J. W. Turner, C. A. Merlic, *Org. Lett.* **2012**, *14*, 4282-4285.

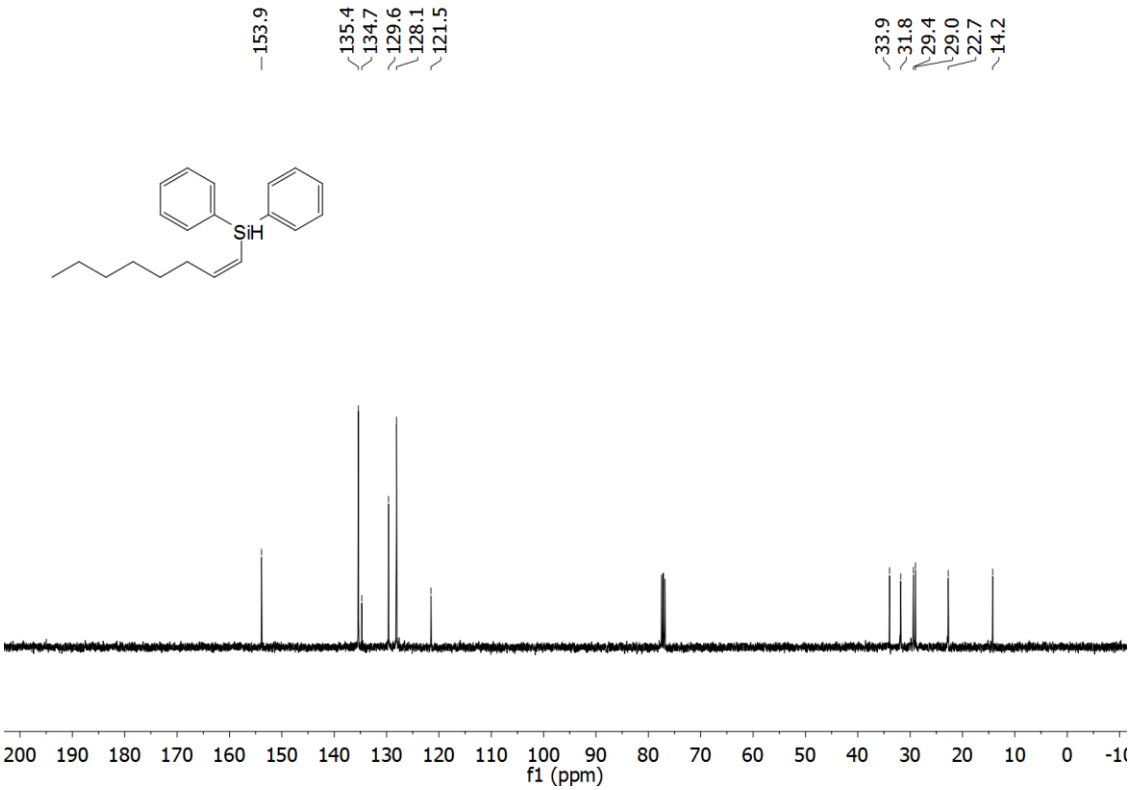
[4] Z. Mo, J. Xiao, Y. Gao, L. Deng, *J. Am. Chem. Soc.* **2014**, *136*, 17414-17417.

[5] J. Guo, Z. Lu, *Angew. Chem. Int. Ed.* **2016**, *55*, 10835-10838.

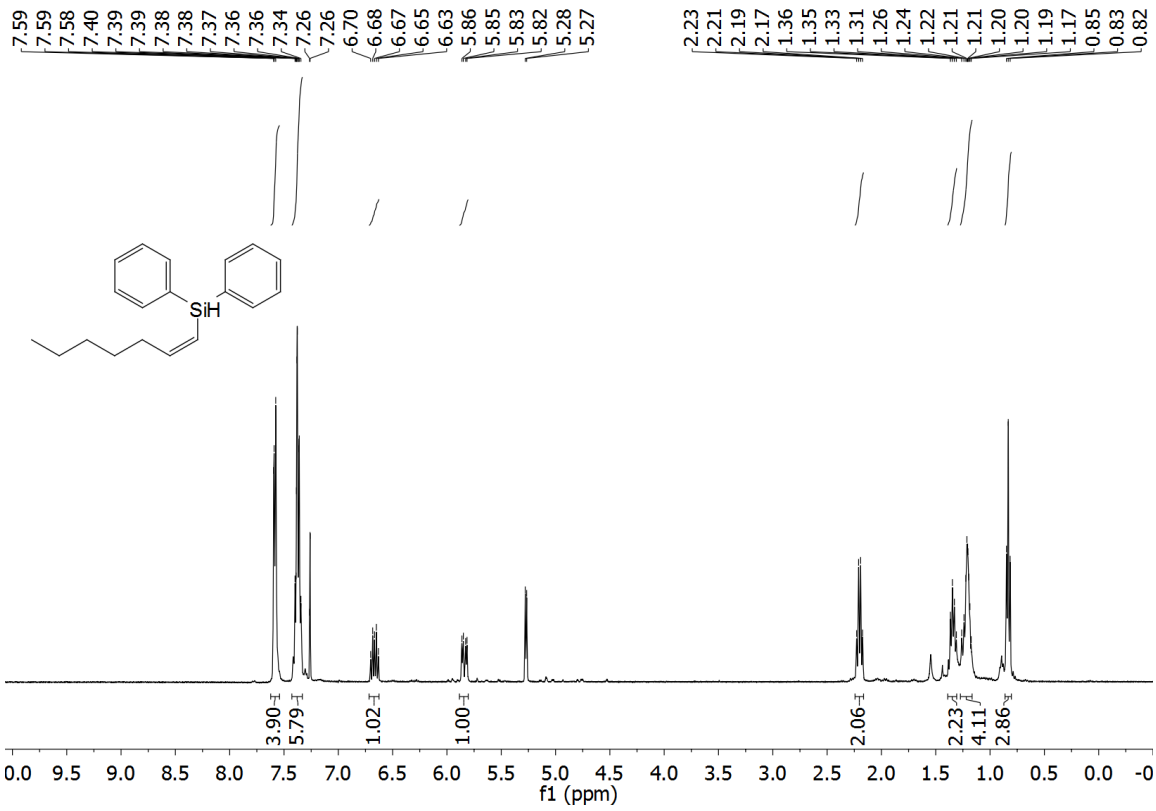
6. NMR Spectra



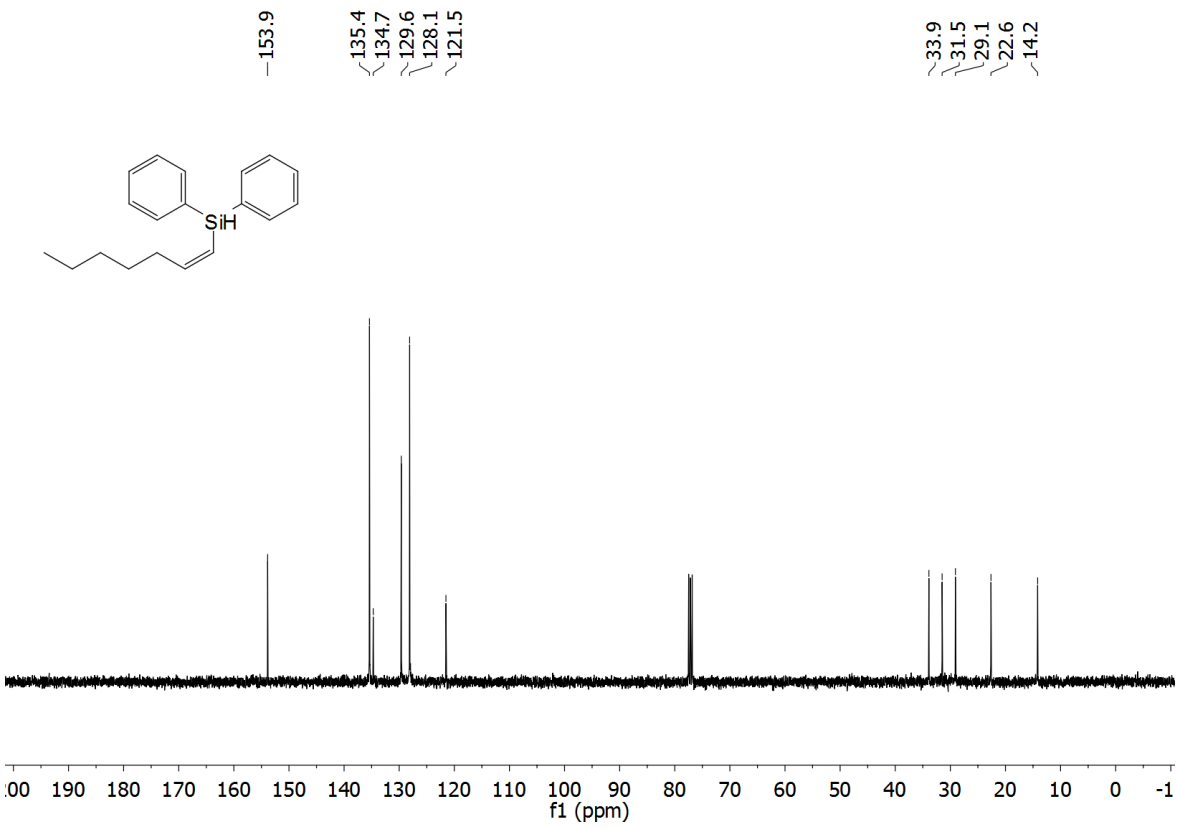
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



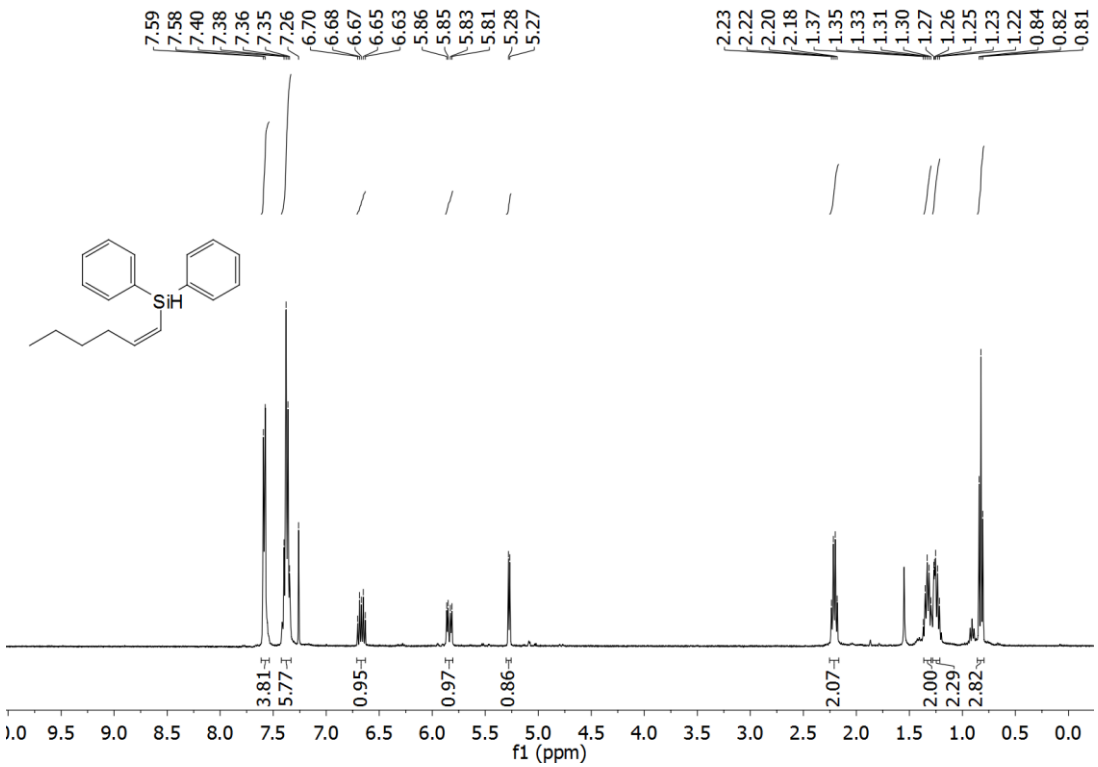
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



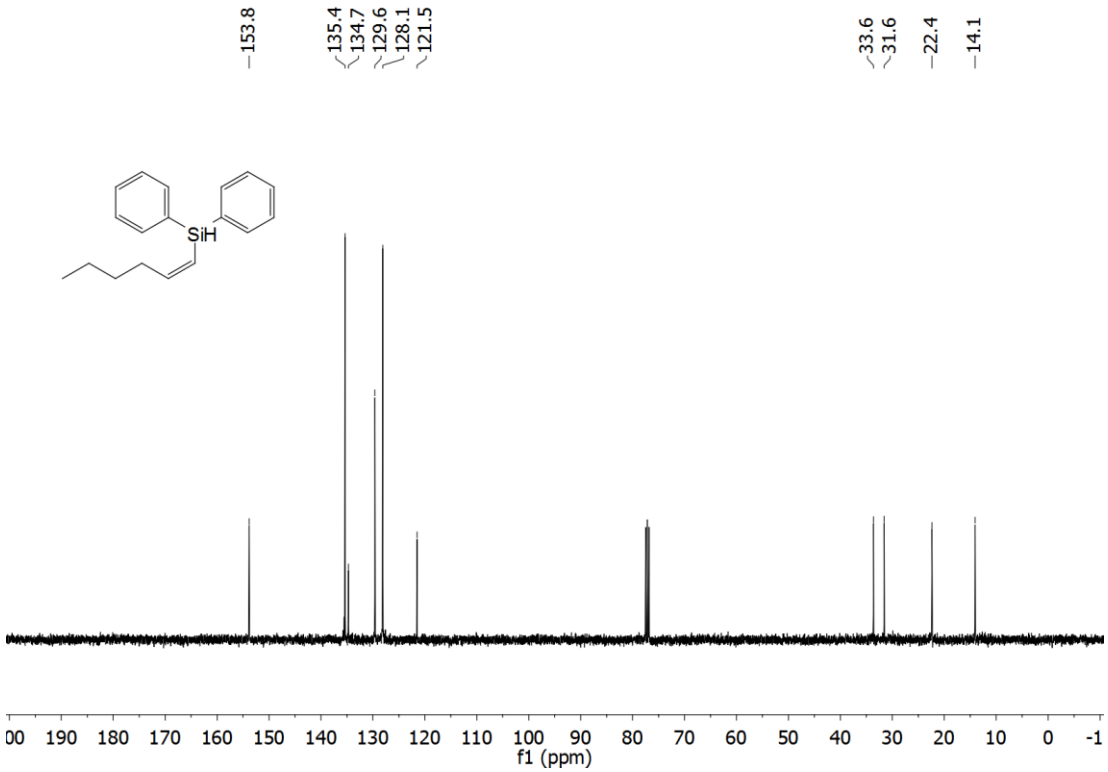
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



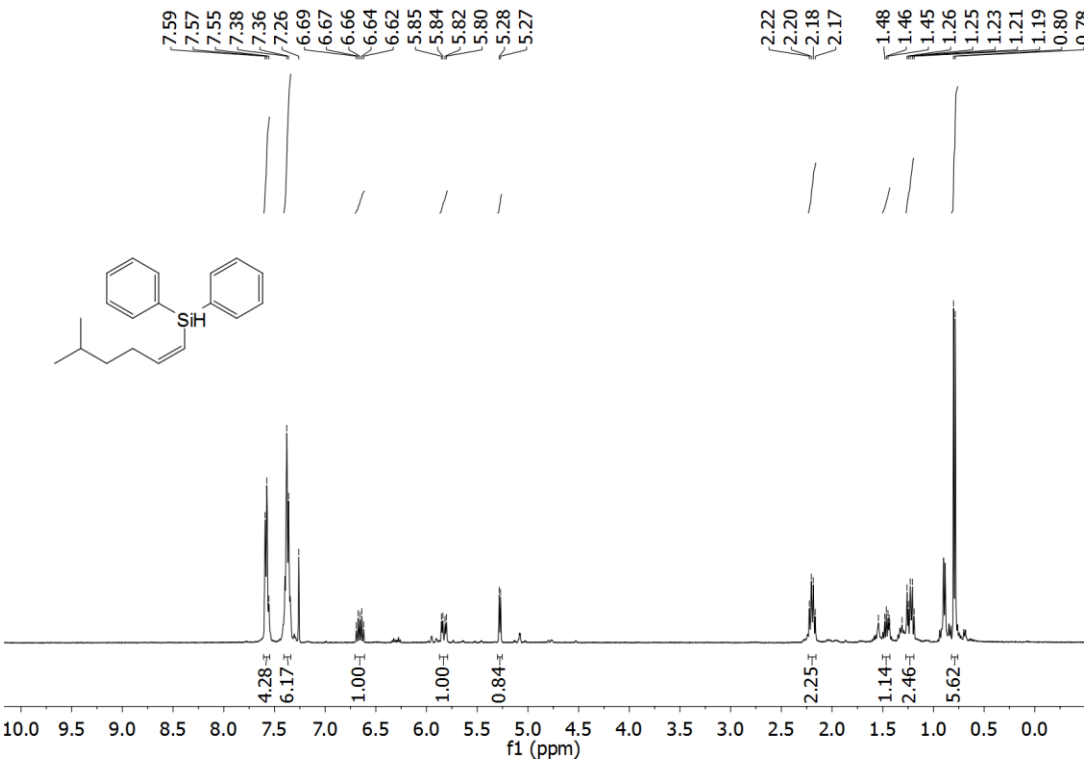
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



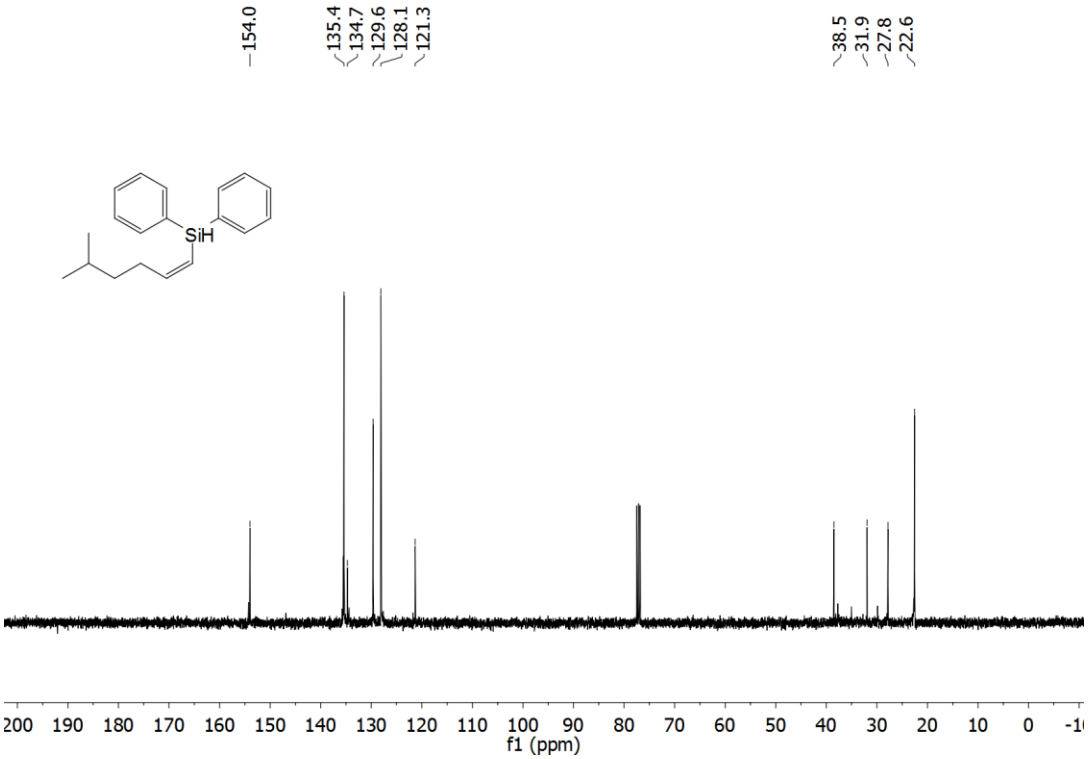
^{1}H NMR (500 MHz, $CDCl_3$) of **4c**



^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



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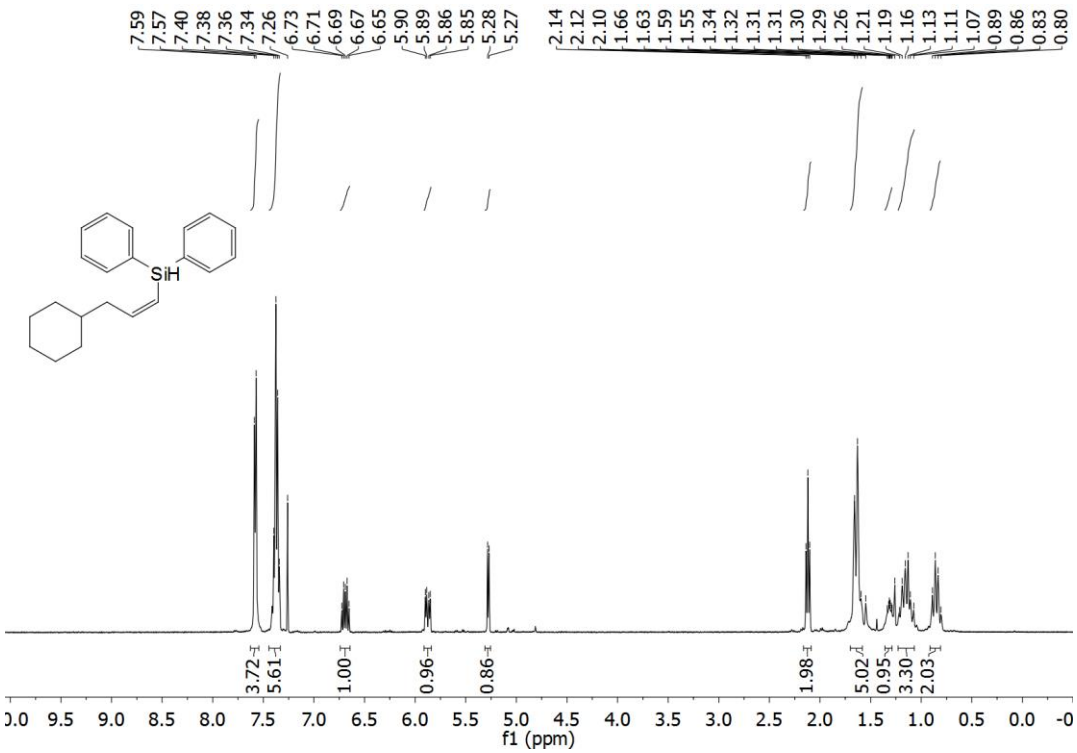
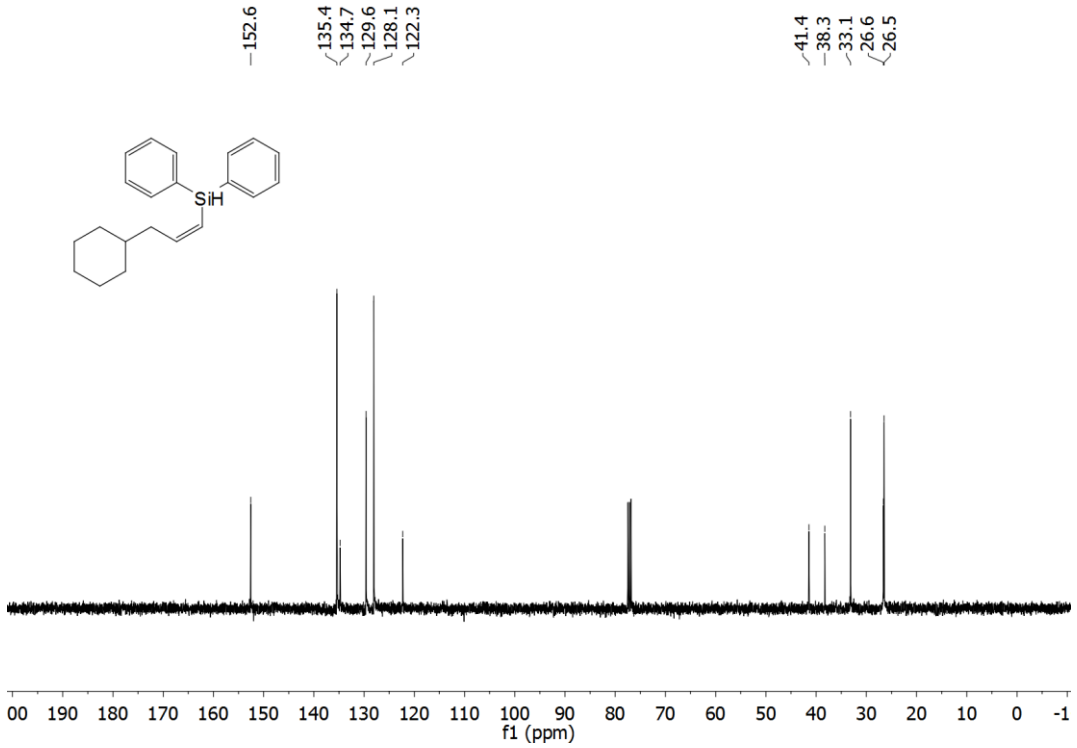


^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



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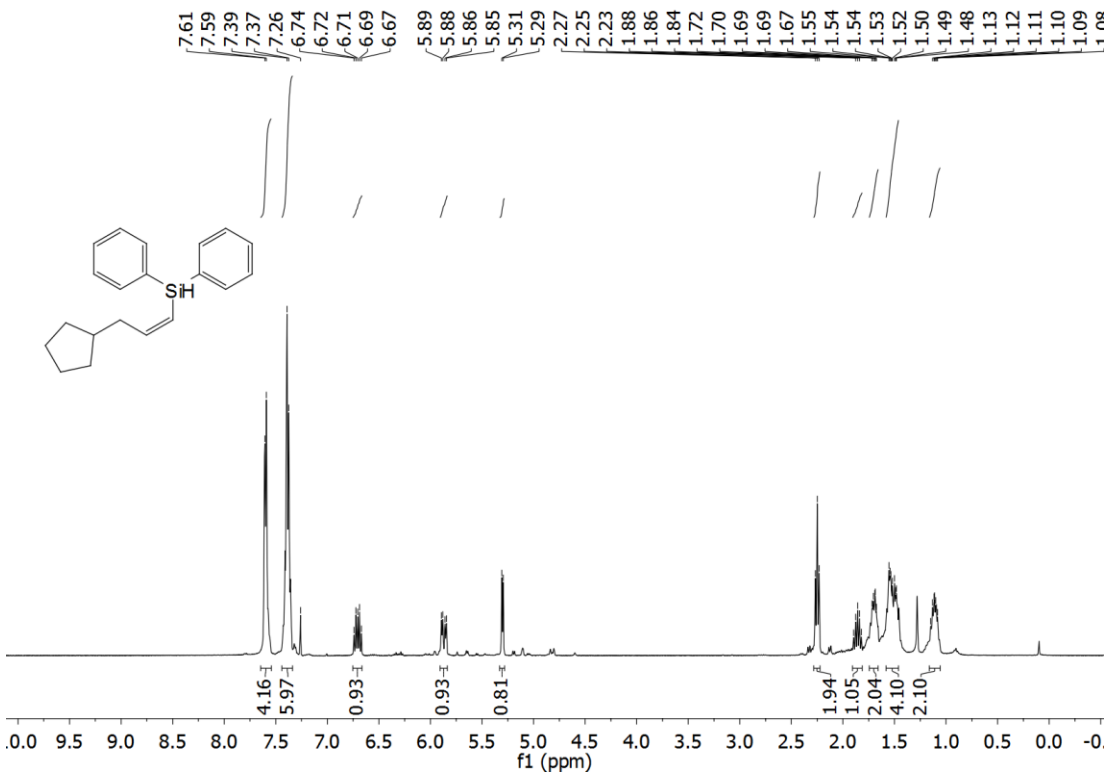

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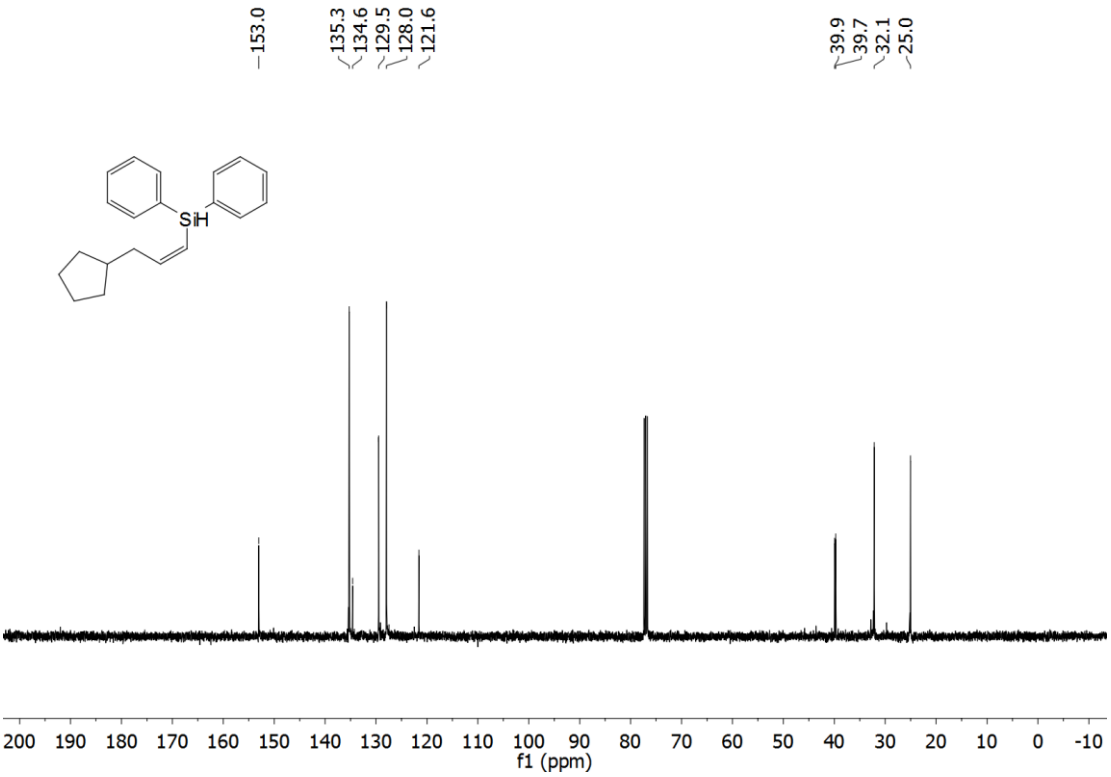

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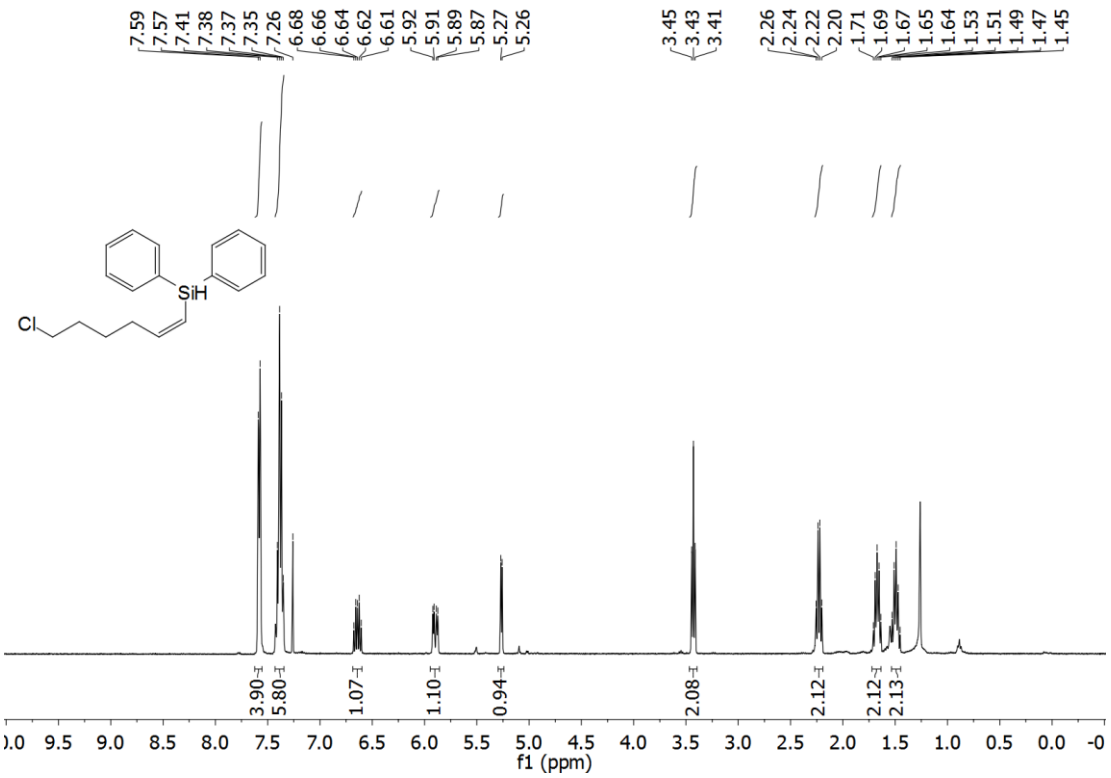
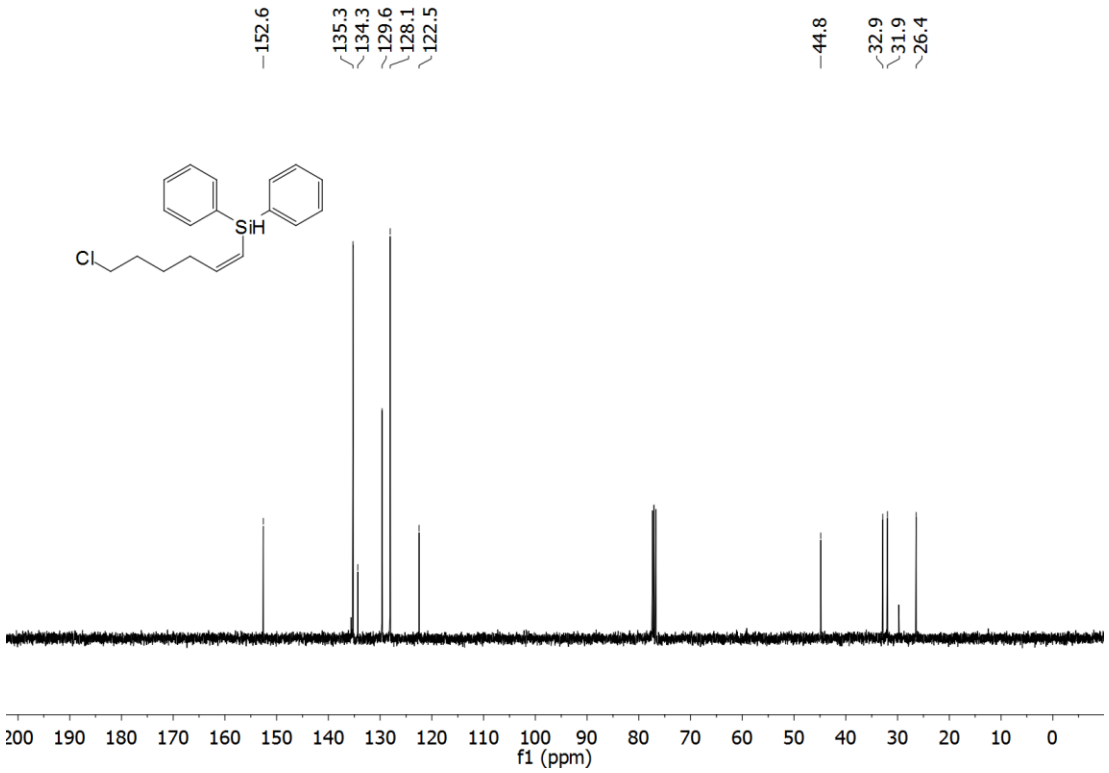
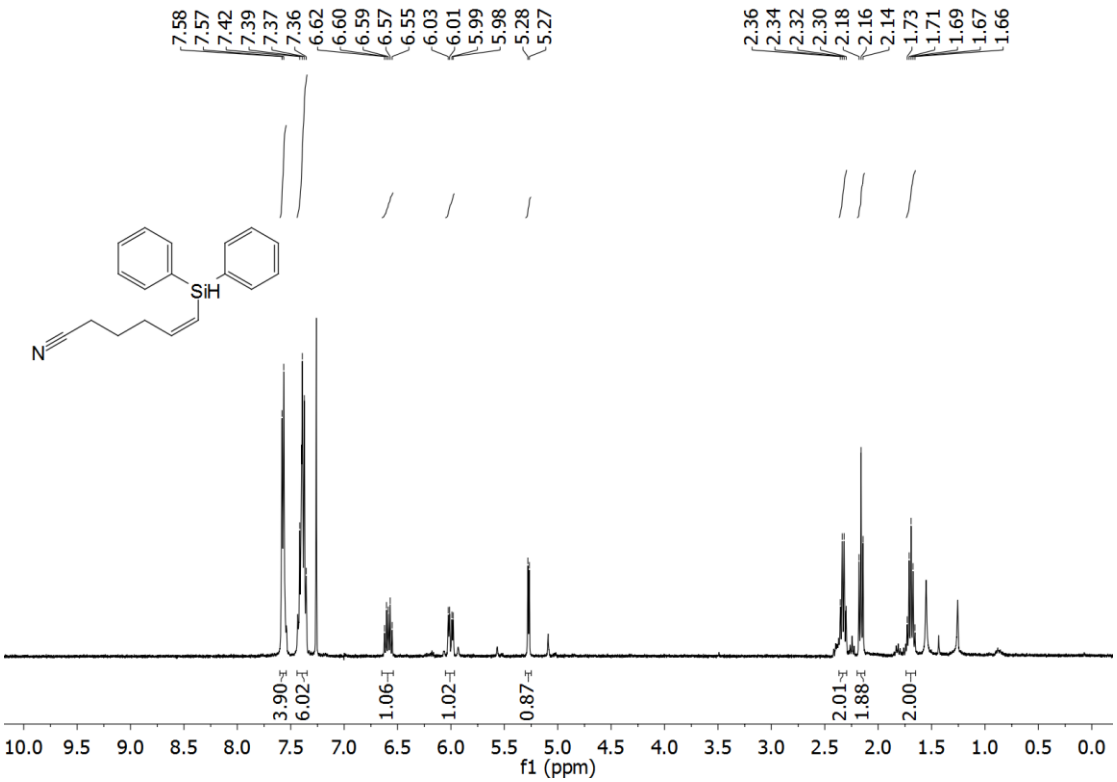


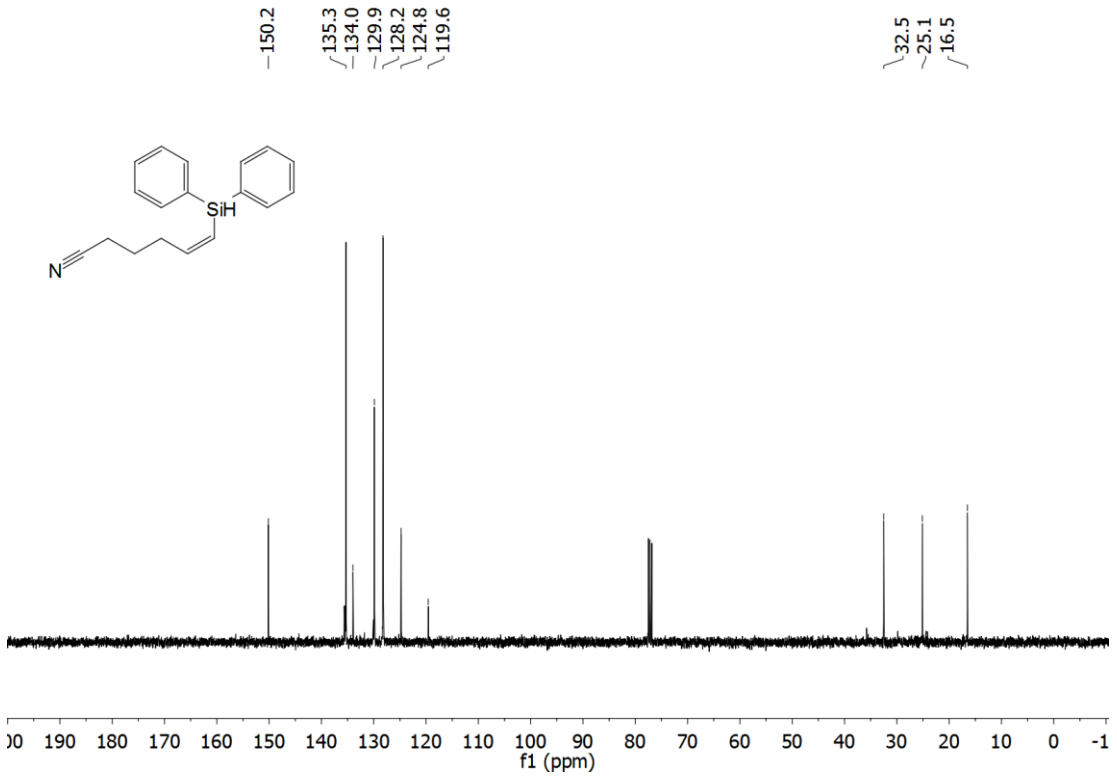
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



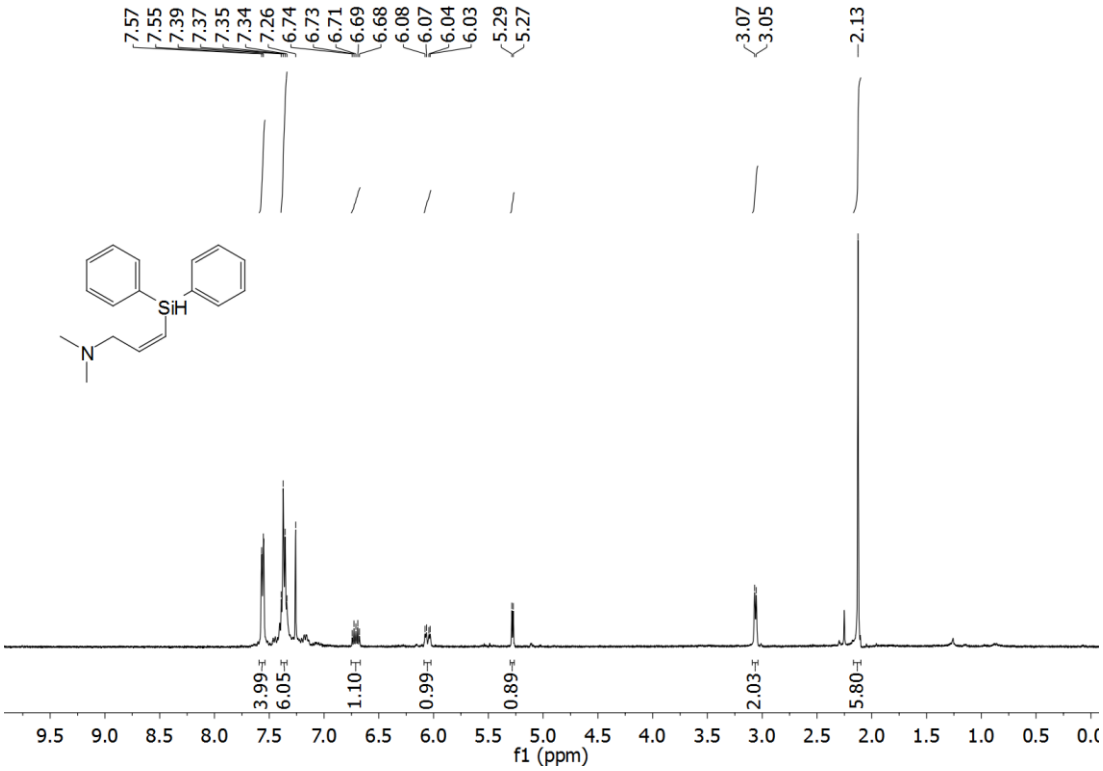
^{13}C NMR (101 MHz, $CDCl_3$) of **4g**



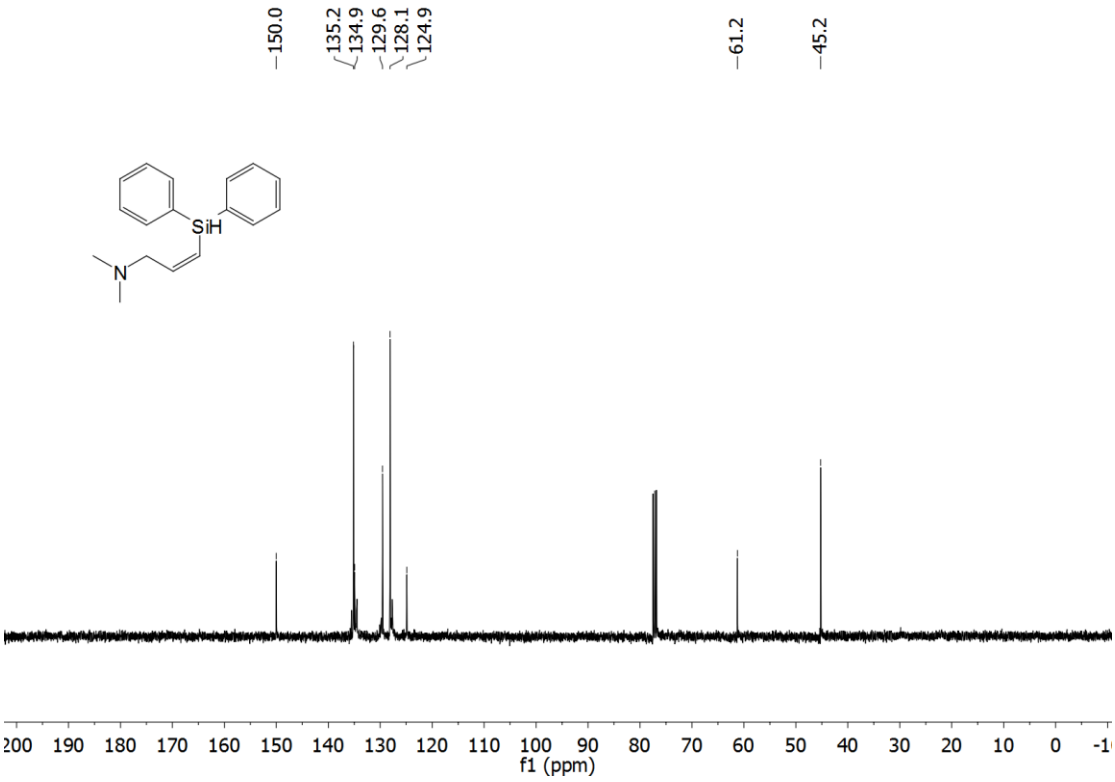
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



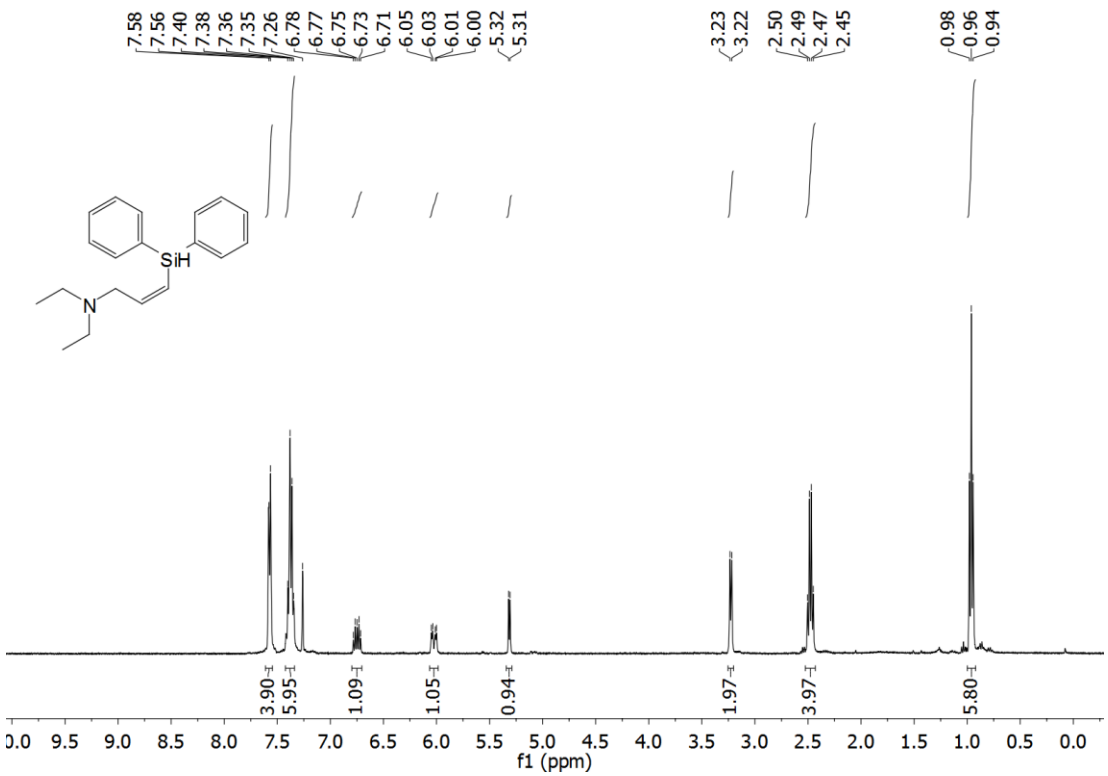
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



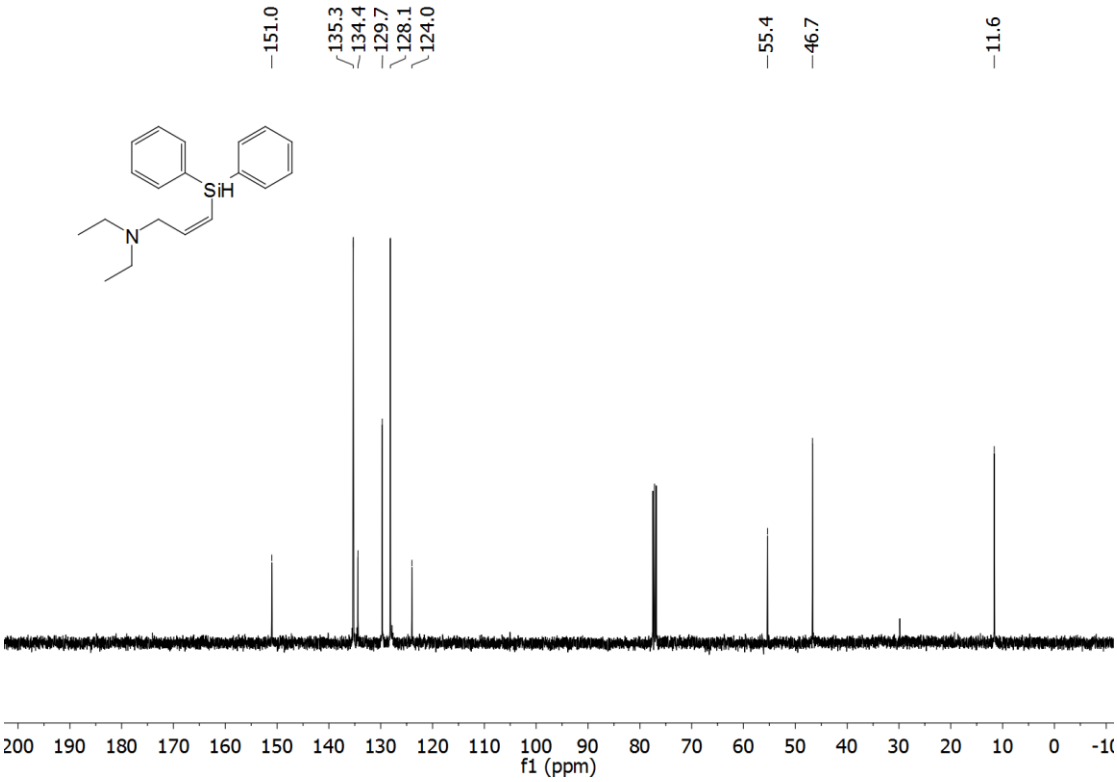
^{1}H NMR (400 MHz, $CDCl_3$) of 4**i**



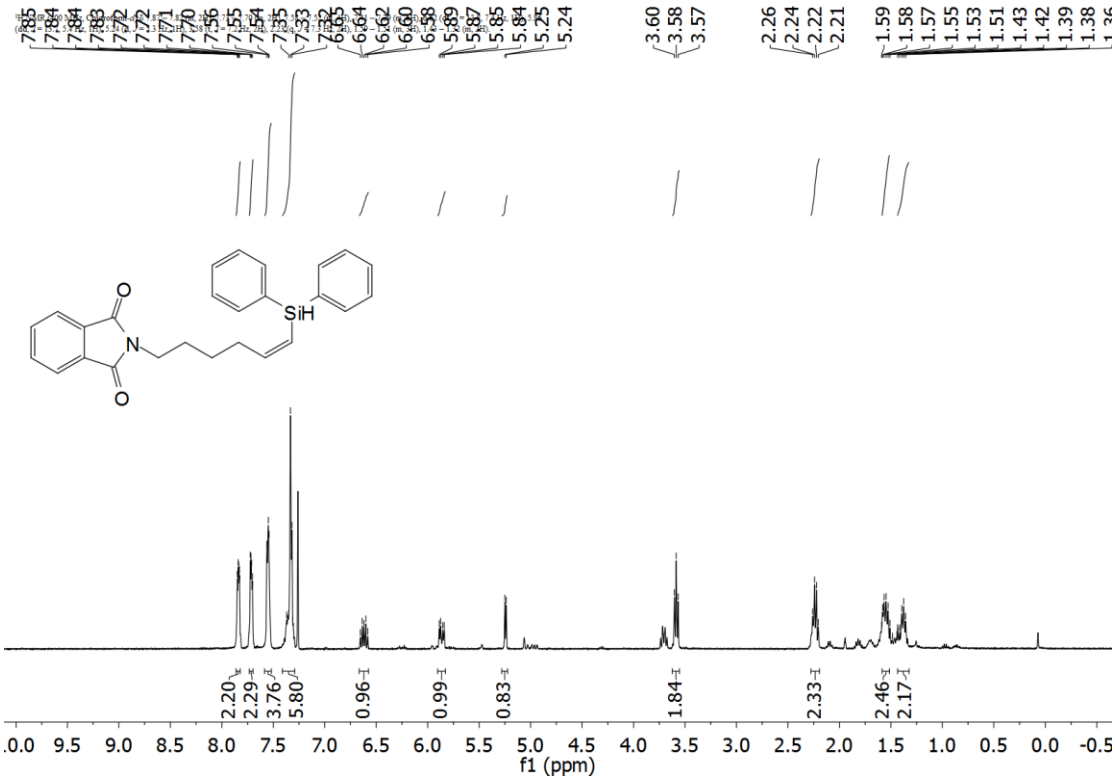
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



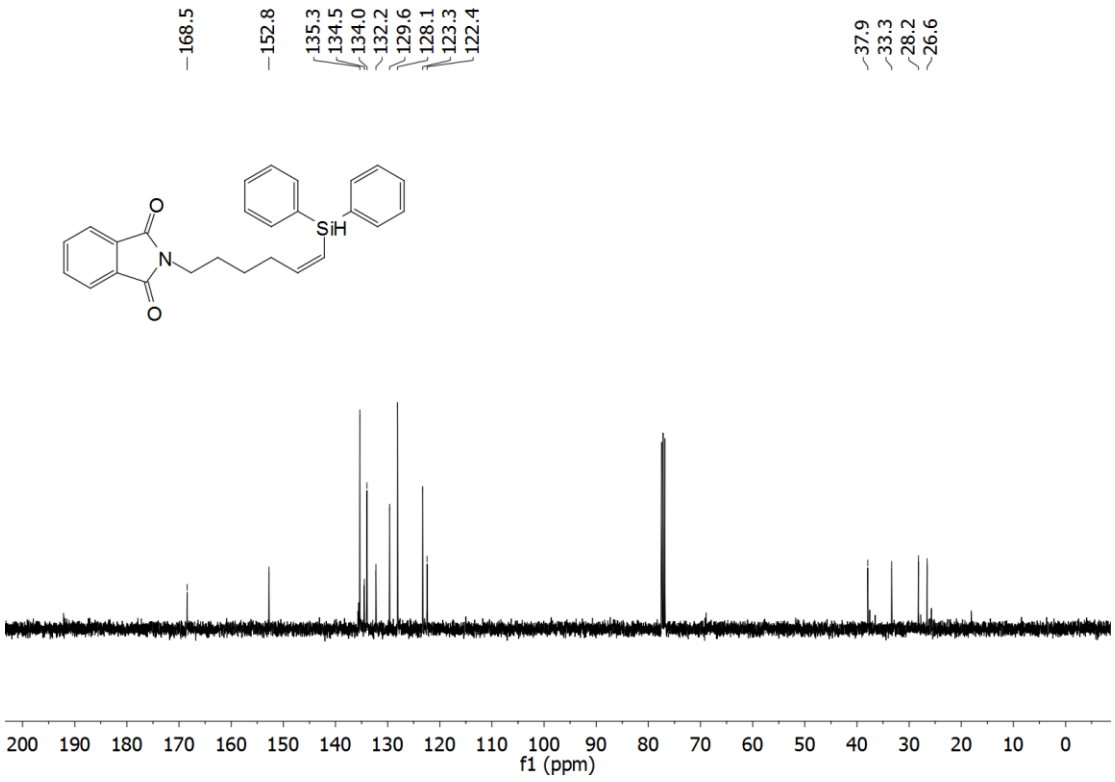
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



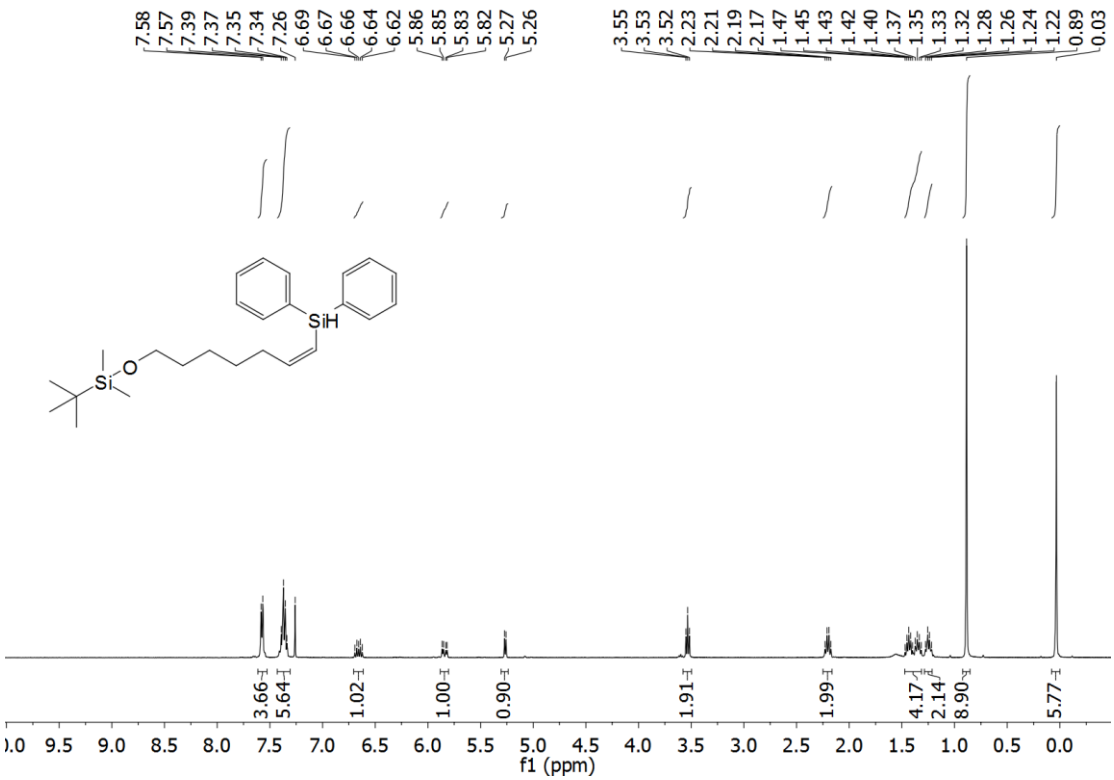
^{13}C NMR (101 MHz, $CDCl_3$) of **4j**



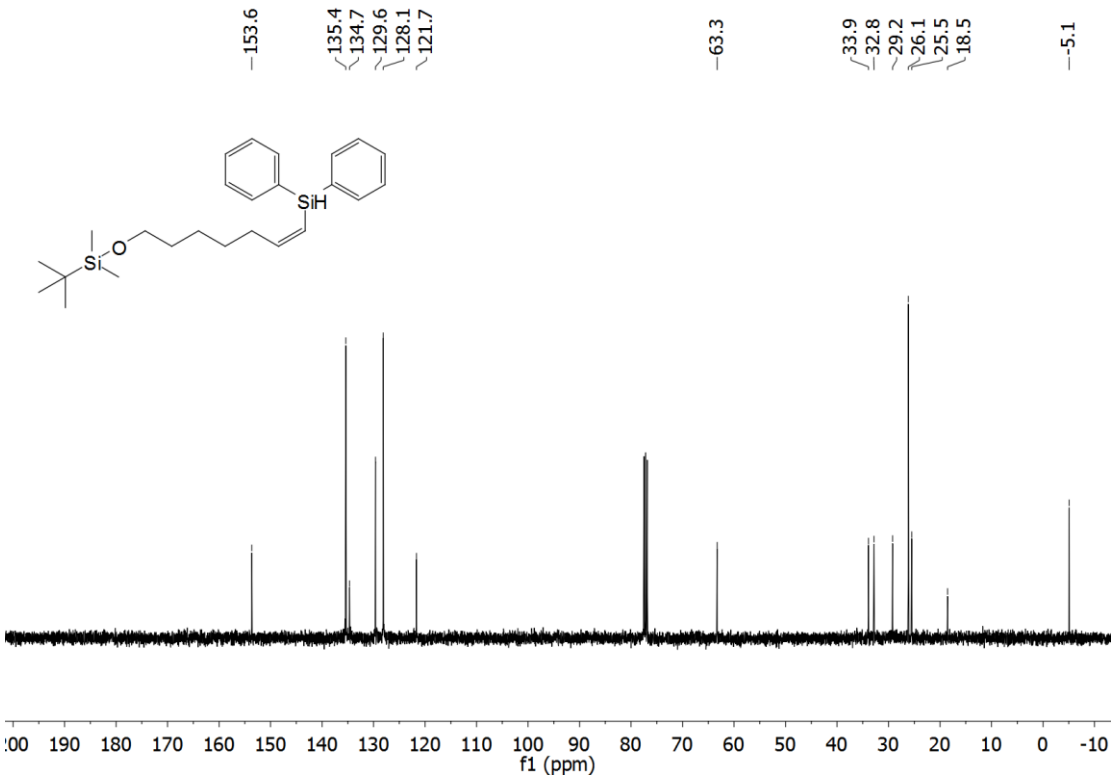
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



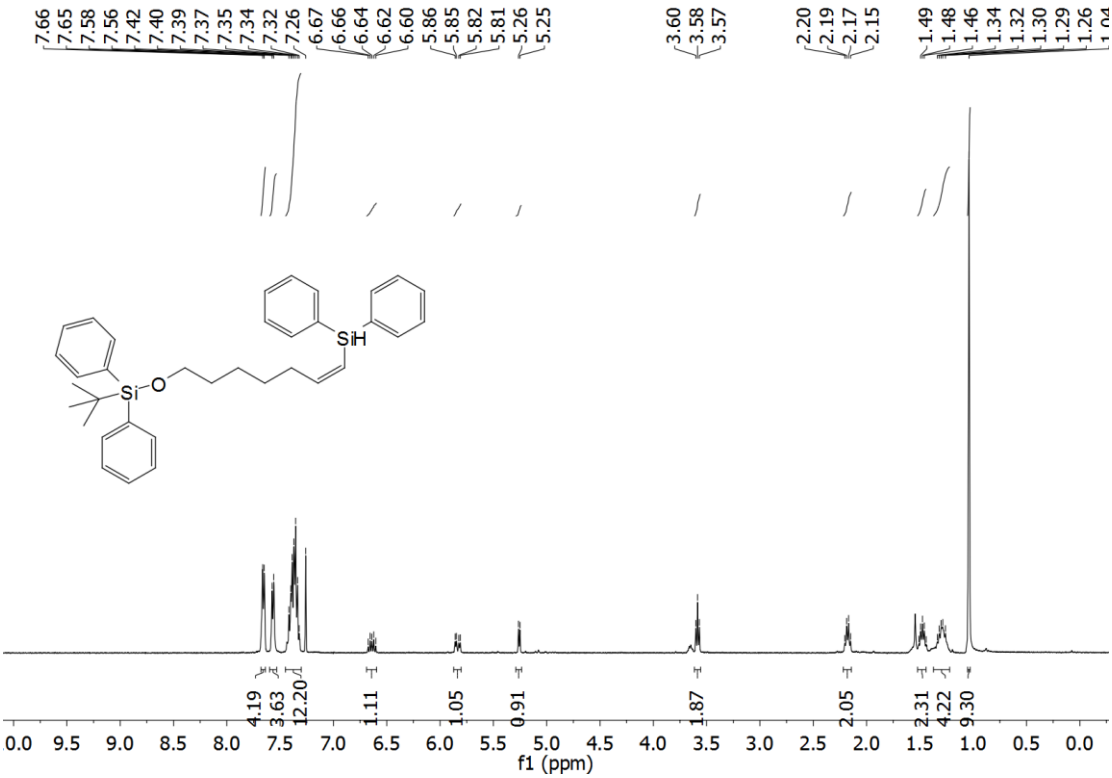
^{13}C NMR (101 MHz, $CDCl_3$) of **4k**



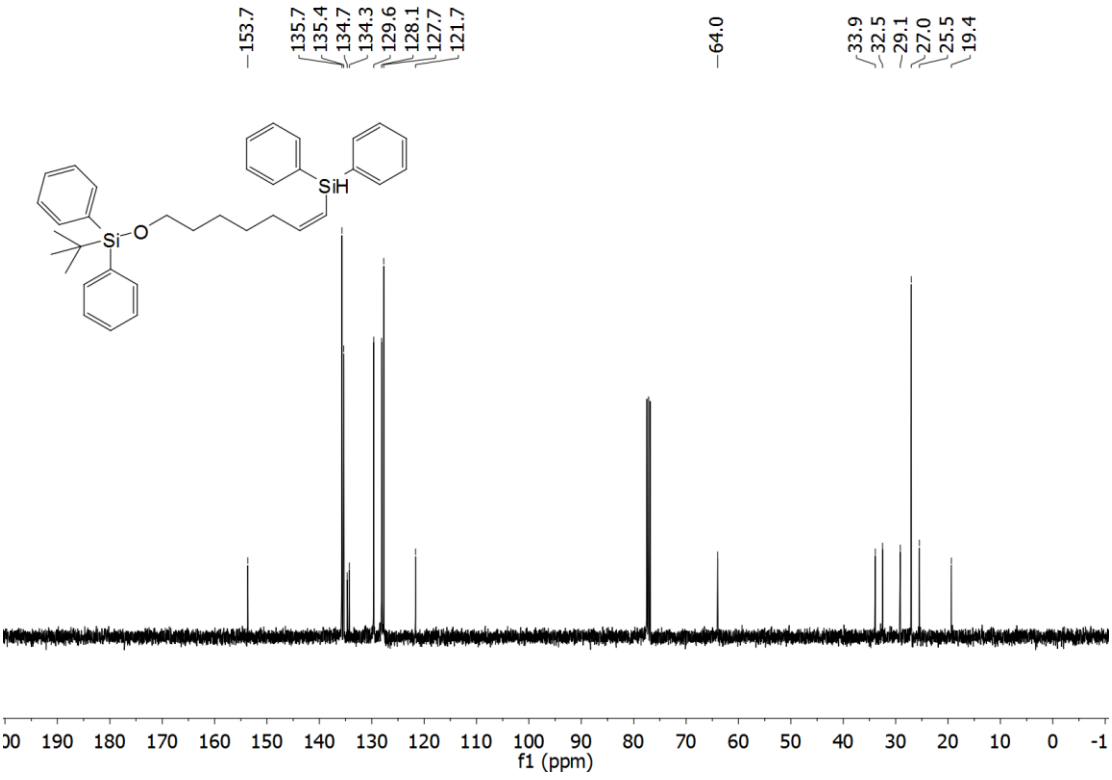
^{1}H NMR (400 MHz, $CDCl_3$) of **4l**



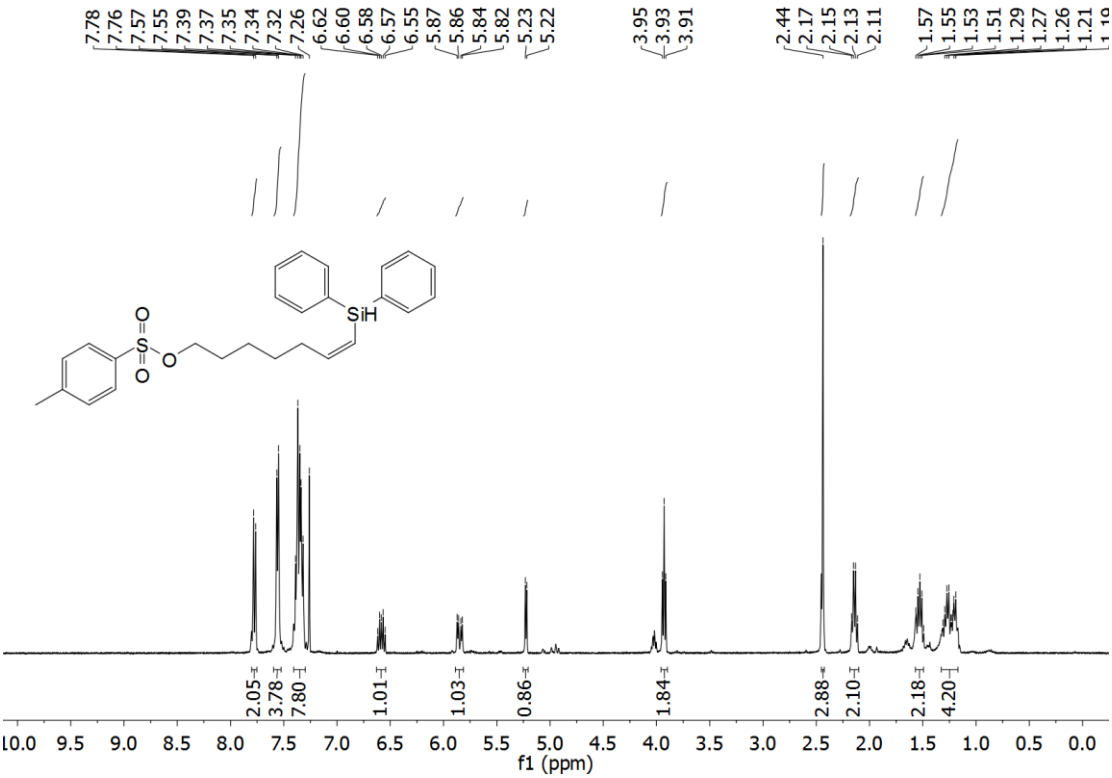
^{13}C NMR (101 MHz, $CDCl_3$) of **4l**



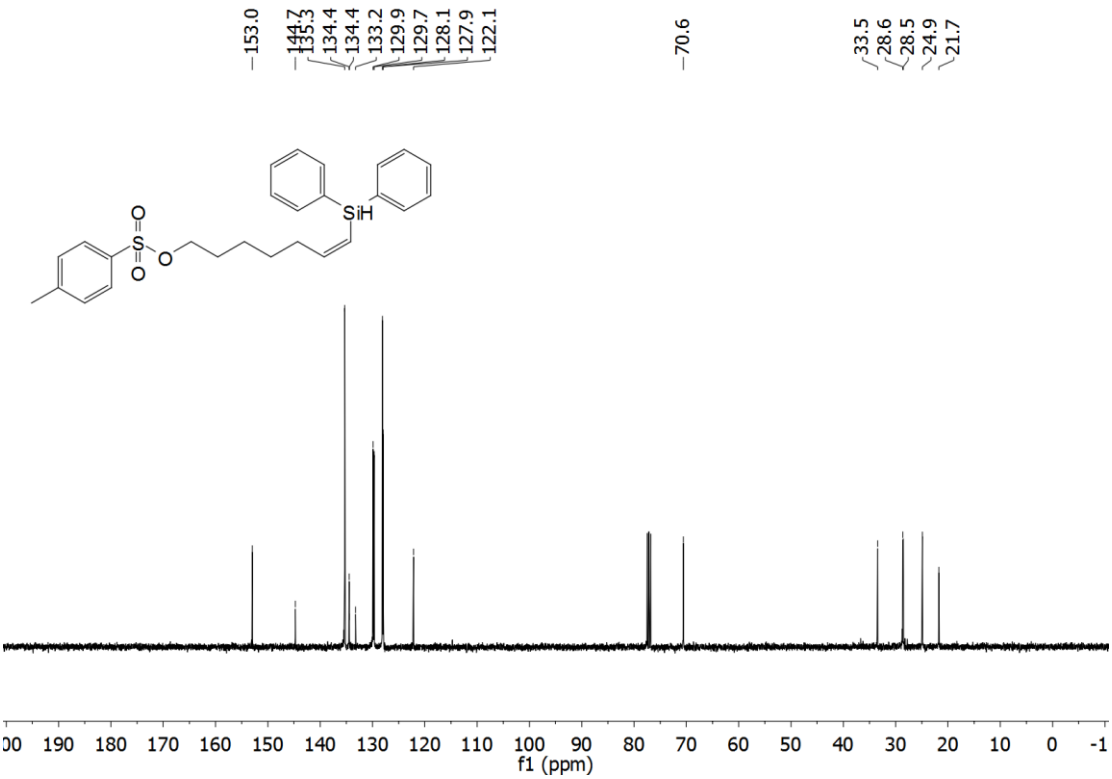
^{1}H NMR (400 MHz, $CDCl_3$) of **4m**



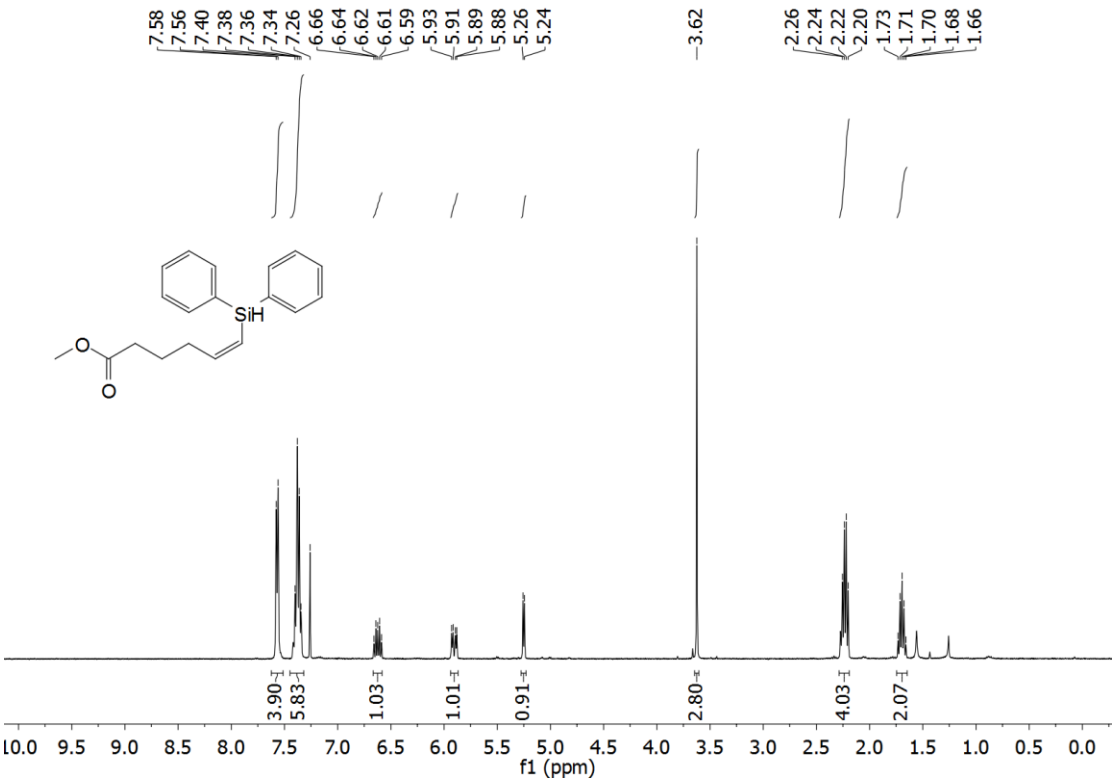
^{13}C NMR (101 MHz, $CDCl_3$) of **4m**



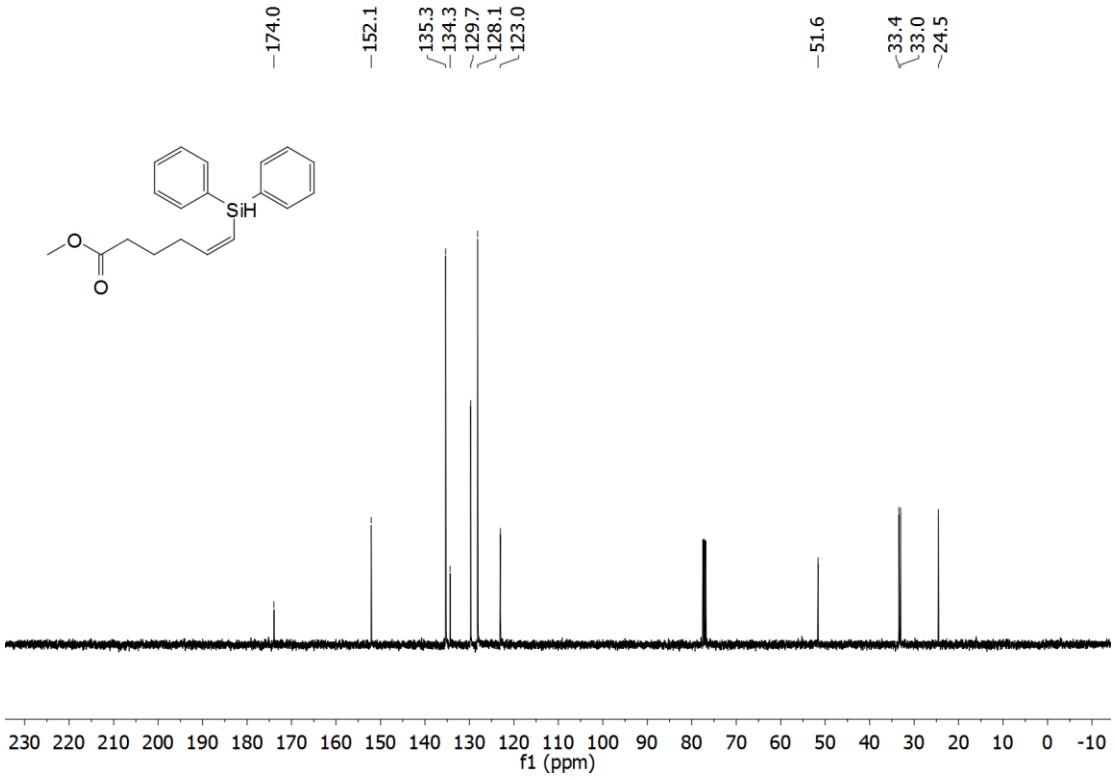
^{1}H NMR (400 MHz, $CDCl_3$) of **4n**



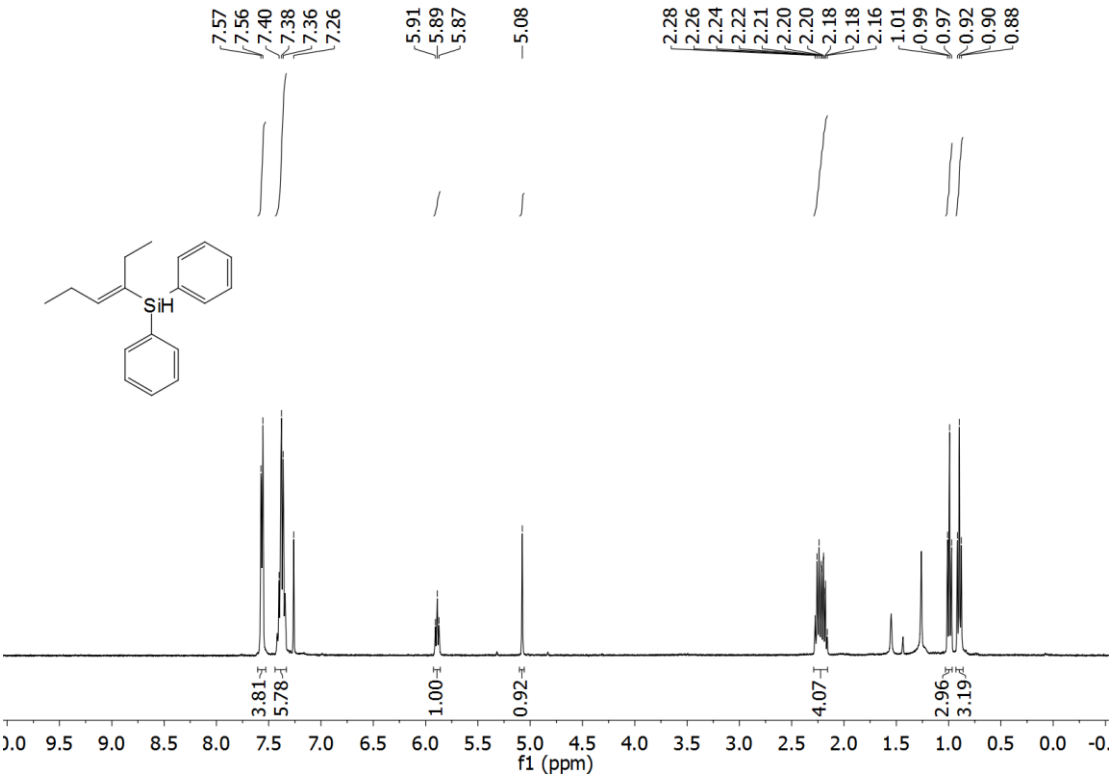
^{13}C NMR (101 MHz, $CDCl_3$) of **4n**



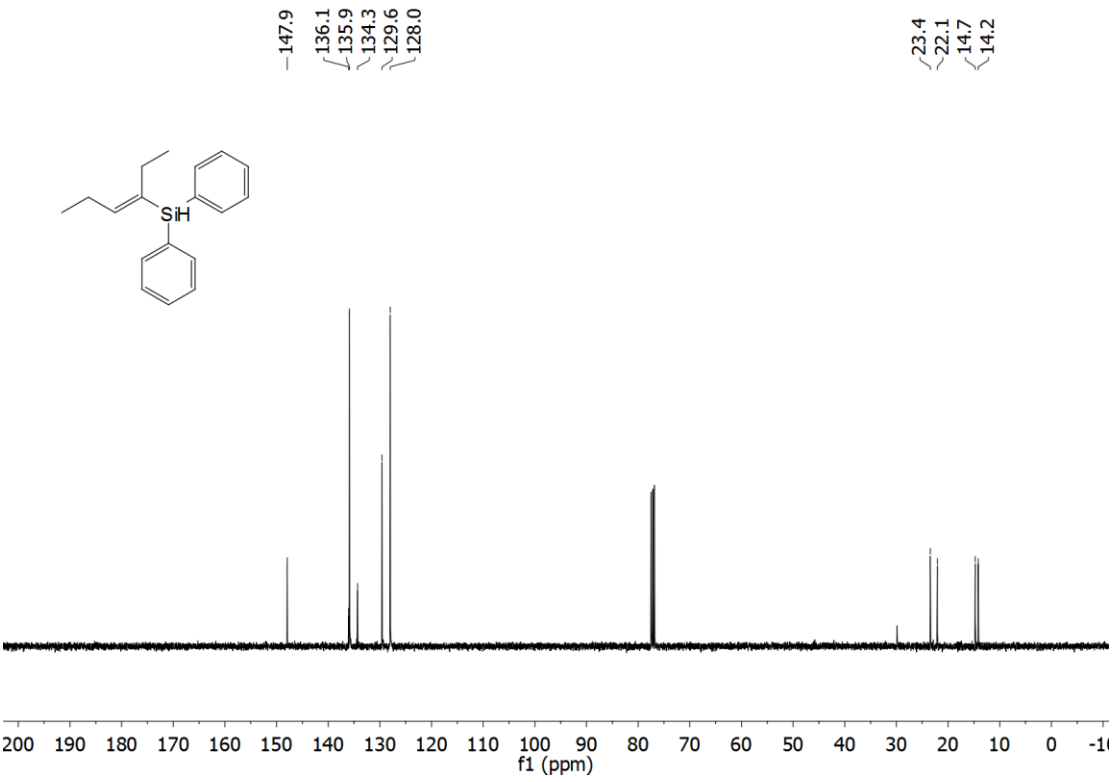
^{1}H NMR (400 MHz, $CDCl_3$) of **4o**



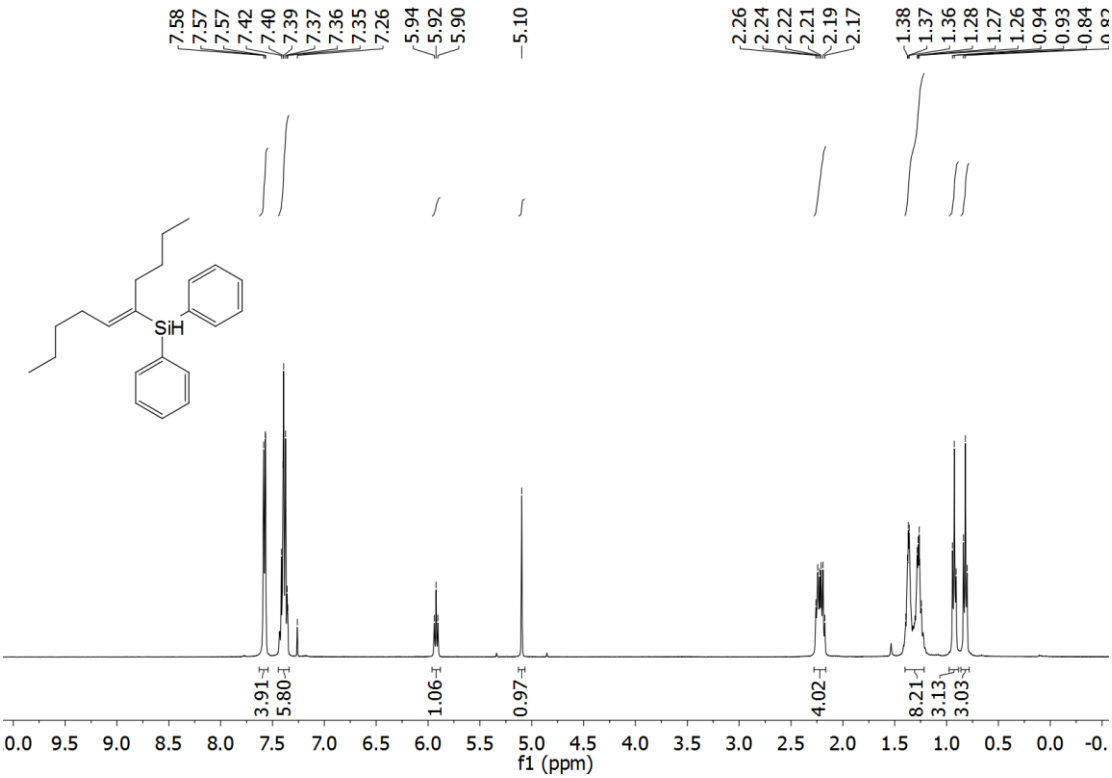
^{13}C NMR (101 MHz, $CDCl_3$) of **4o**



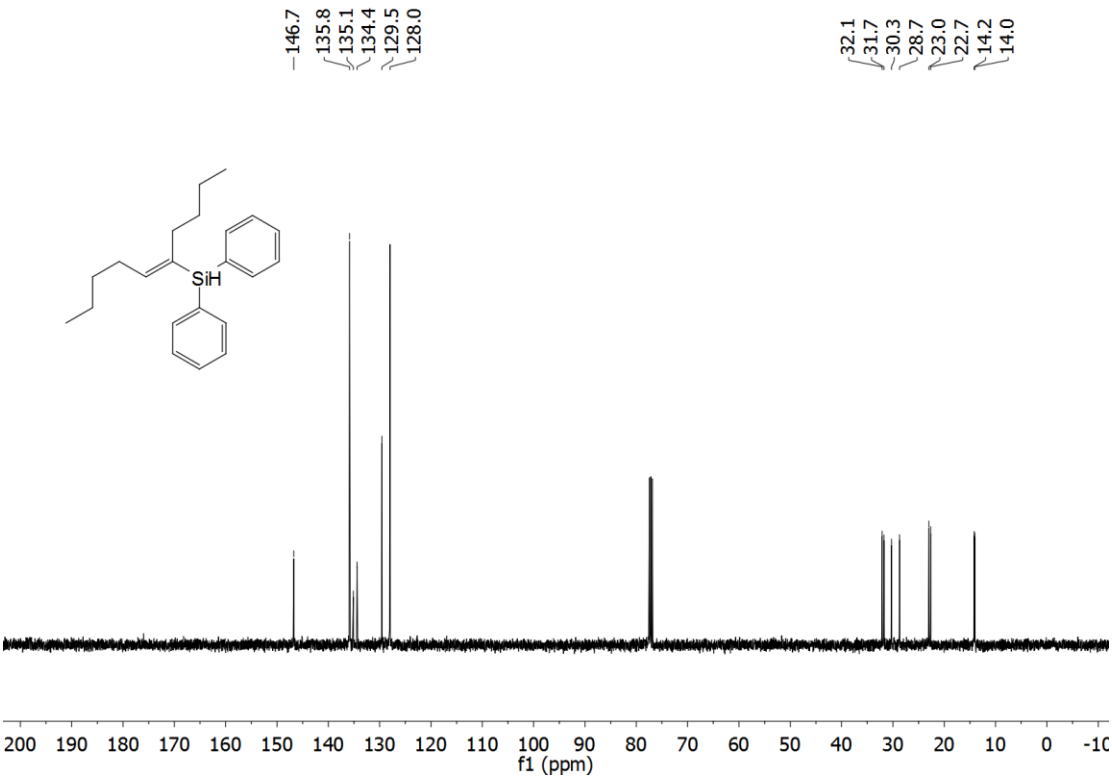
^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



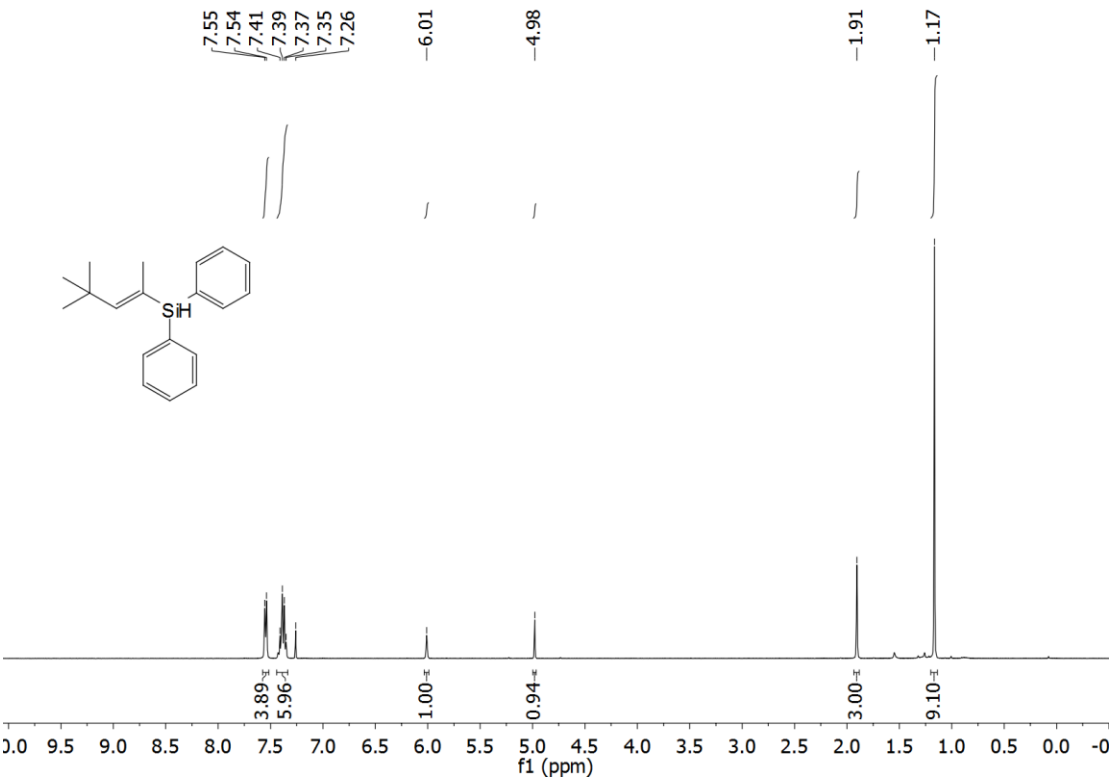
^{1}H NMR (400 MHz, $CDCl_3$) of **4p**



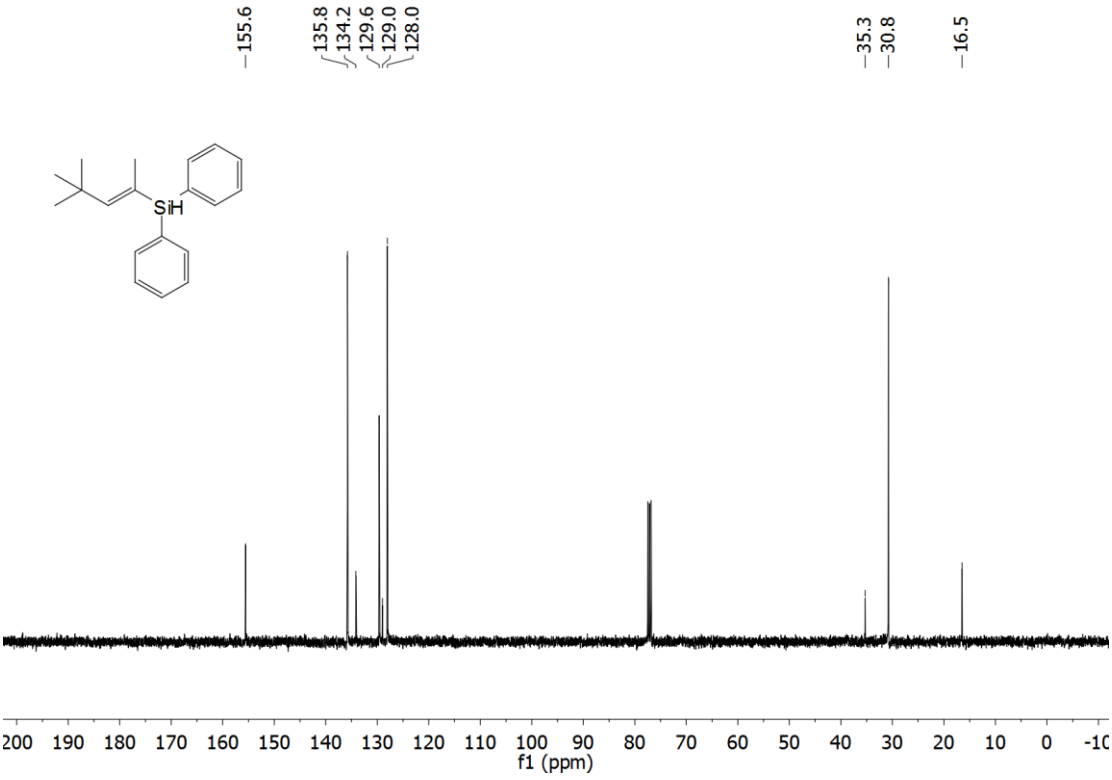
^{1}H NMR (400 MHz, $CDCl_3$) of **4q**



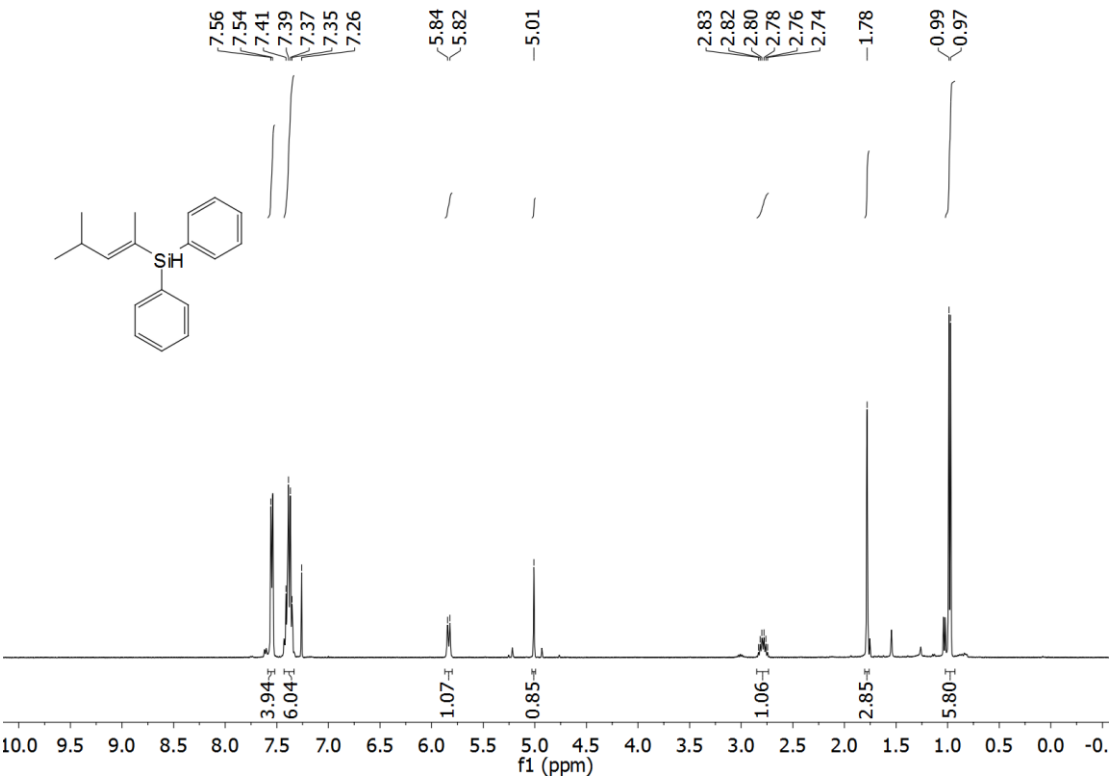
^{13}C NMR (101 MHz, $CDCl_3$) of **4q**



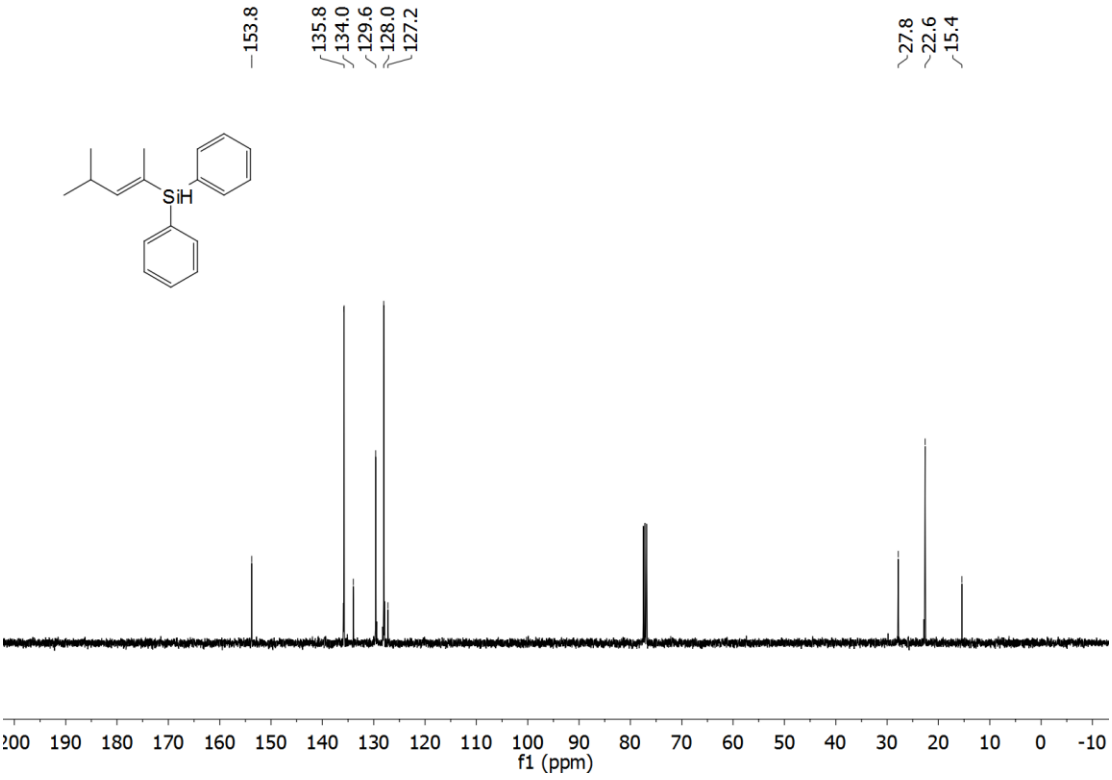
^{1}H NMR (500 MHz, $CDCl_3$) of **4r**



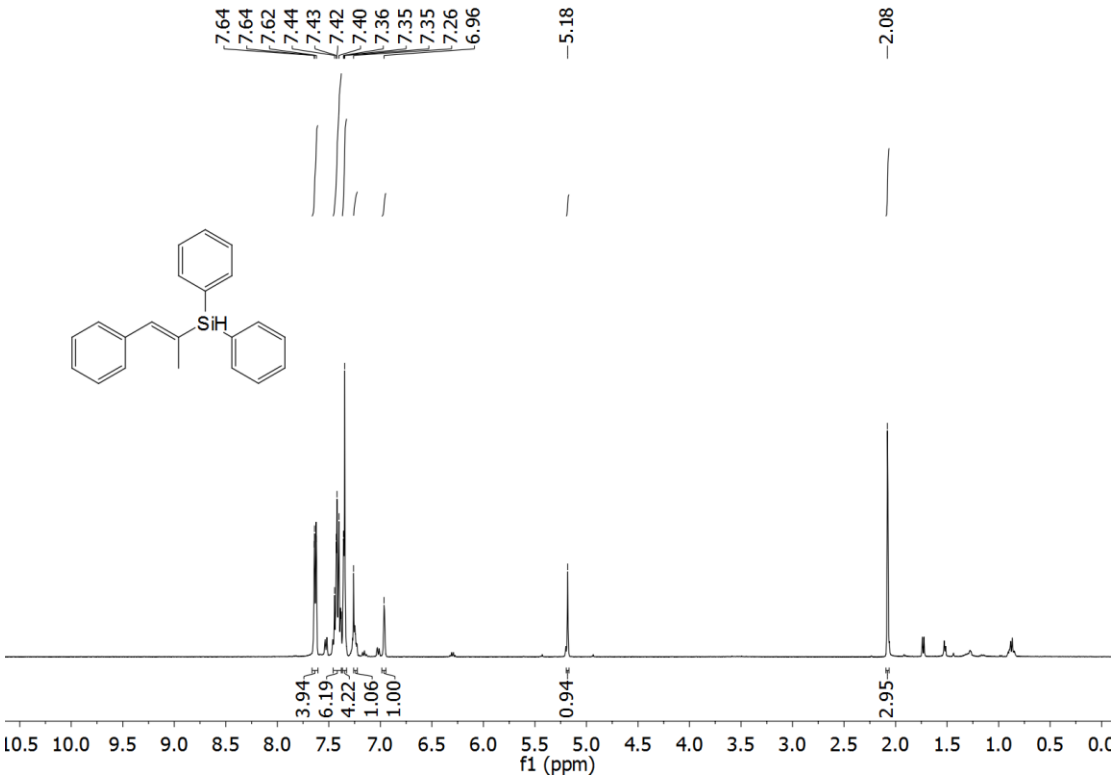
^{13}C NMR (101 MHz, $CDCl_3$) of **4r**



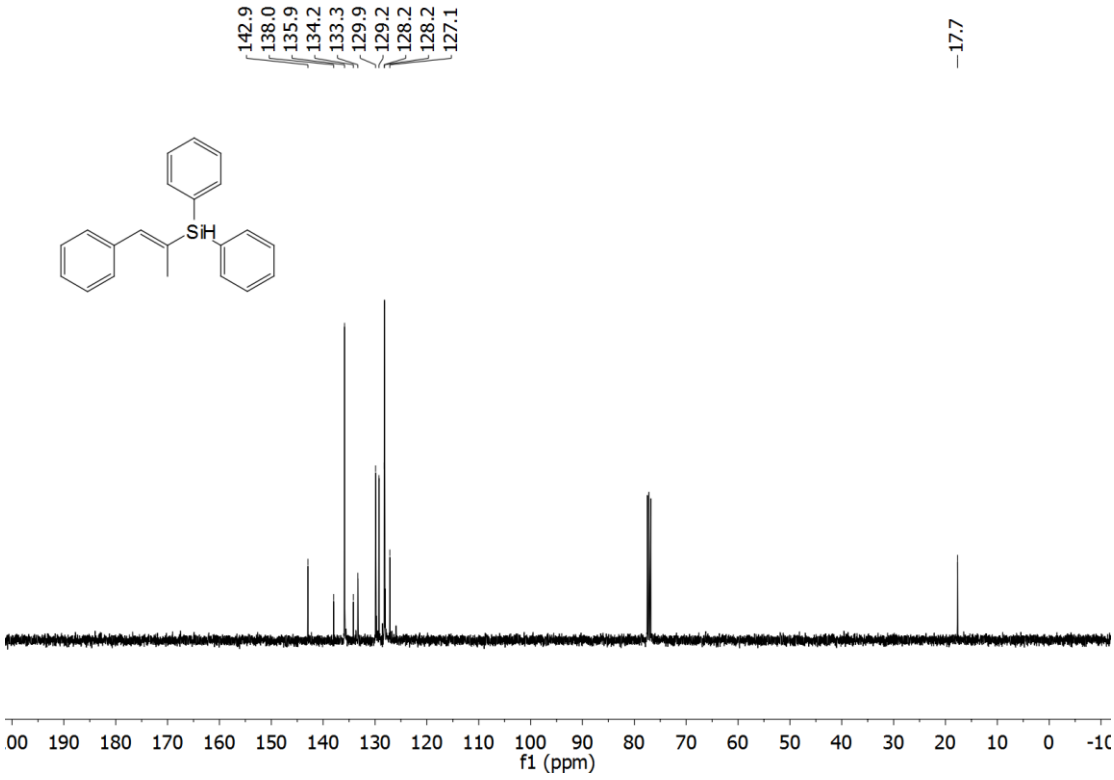
^{1}H NMR (400 MHz, $CDCl_3$) of **4s**



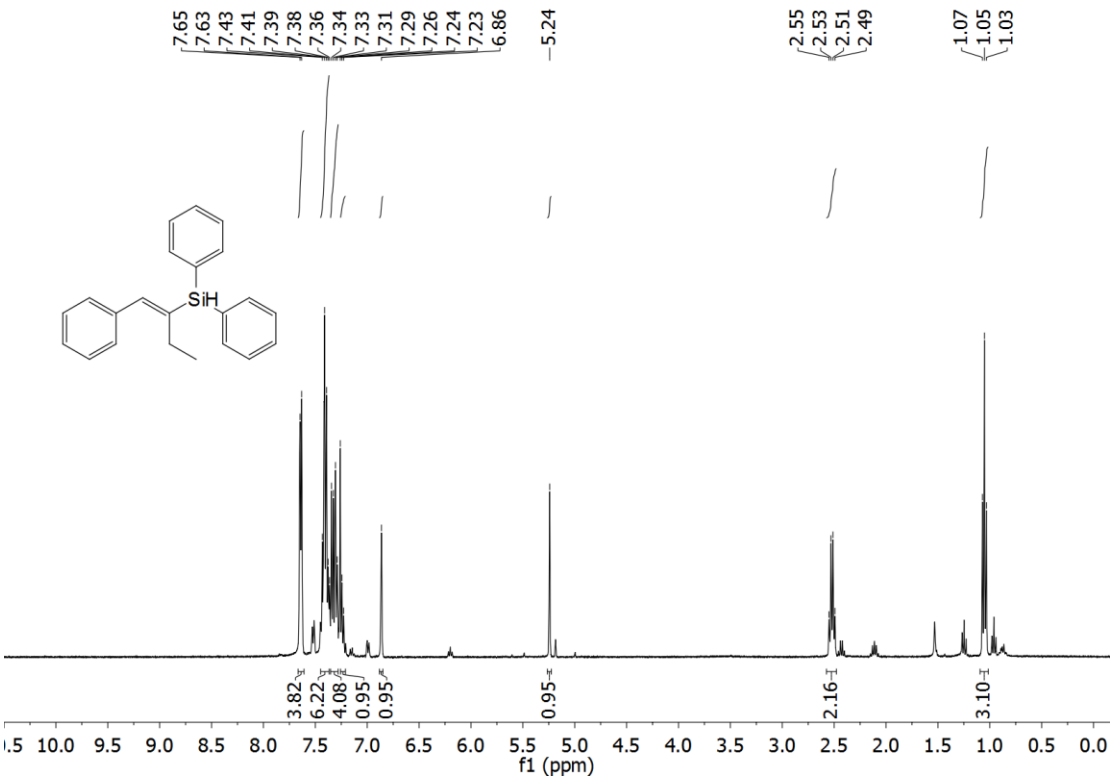
^{13}C NMR (101 MHz, $CDCl_3$) of **4s**



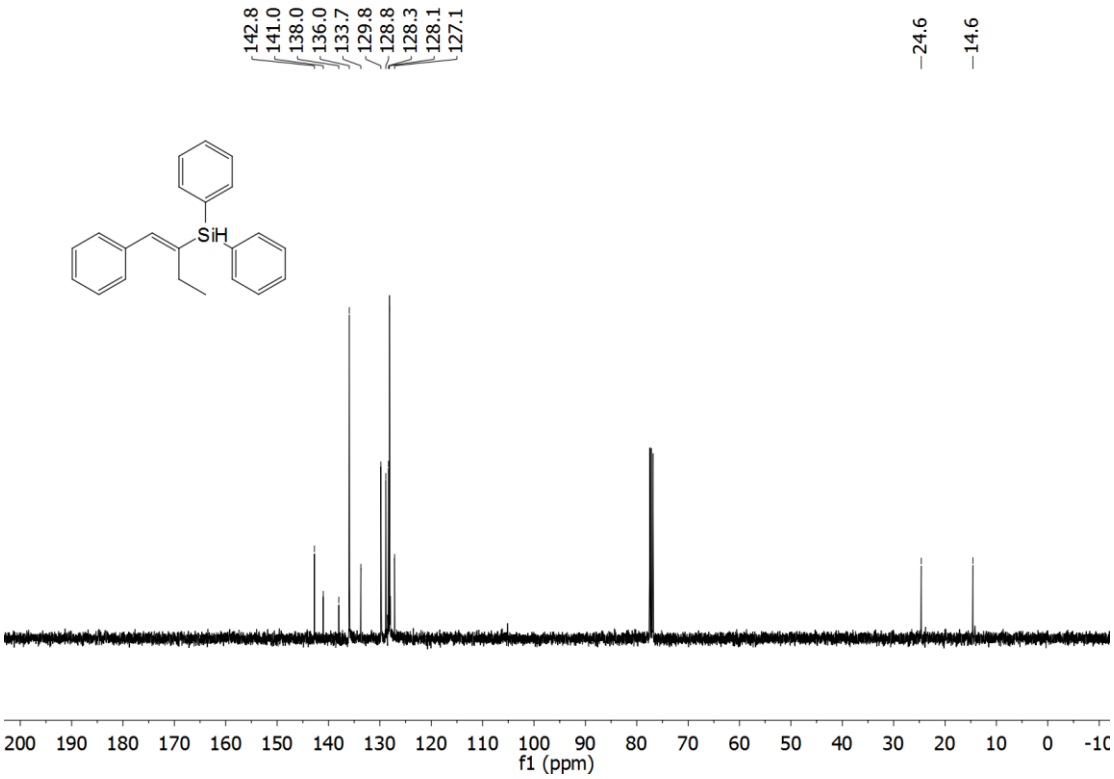
^{1}H NMR (400 MHz, $CDCl_3$) of **4t**



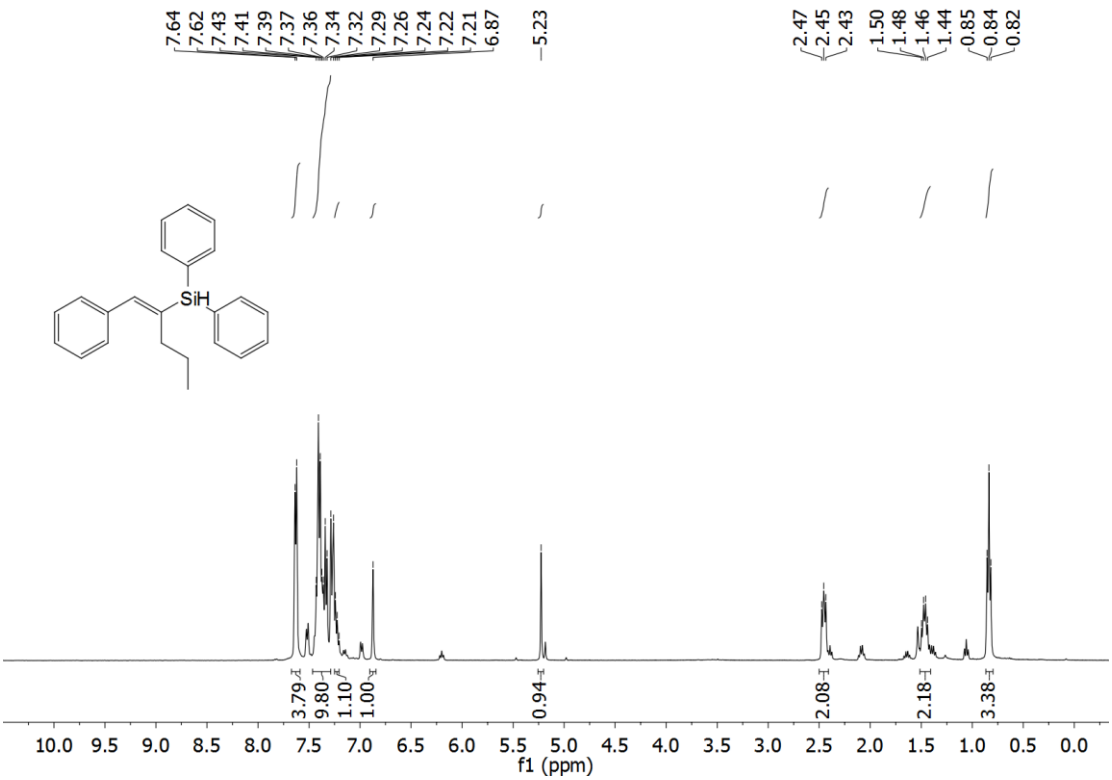
^{13}C NMR (101 MHz, $CDCl_3$) of **4t**



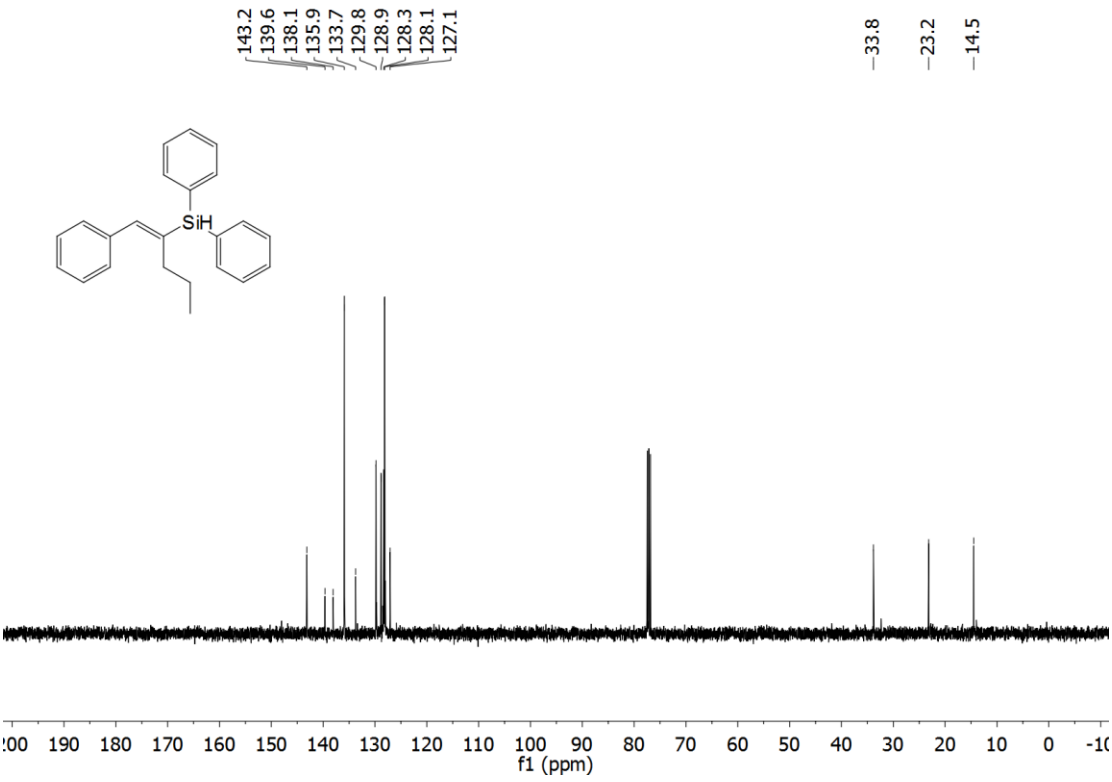
^{1}H NMR (400 MHz, $CDCl_3$) of **4u**



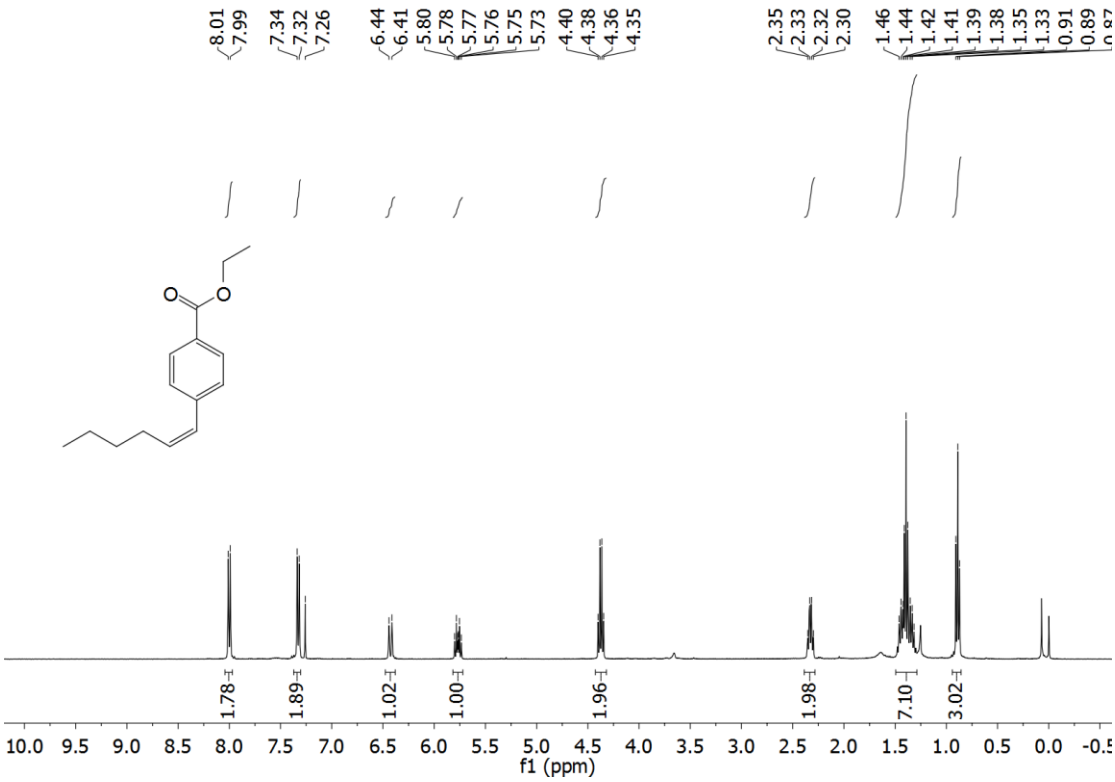
^{13}C NMR (101 MHz, $CDCl_3$) of **4u**



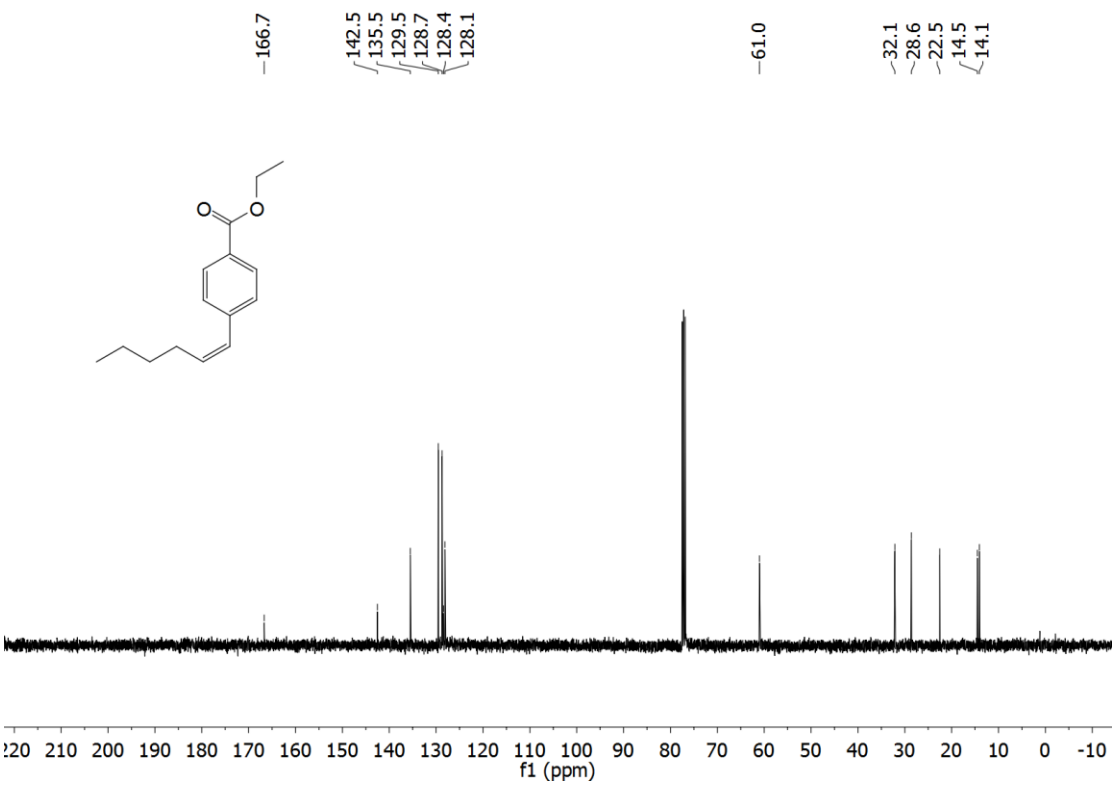
^{1}H NMR (400 MHz, $CDCl_3$) of **4v**



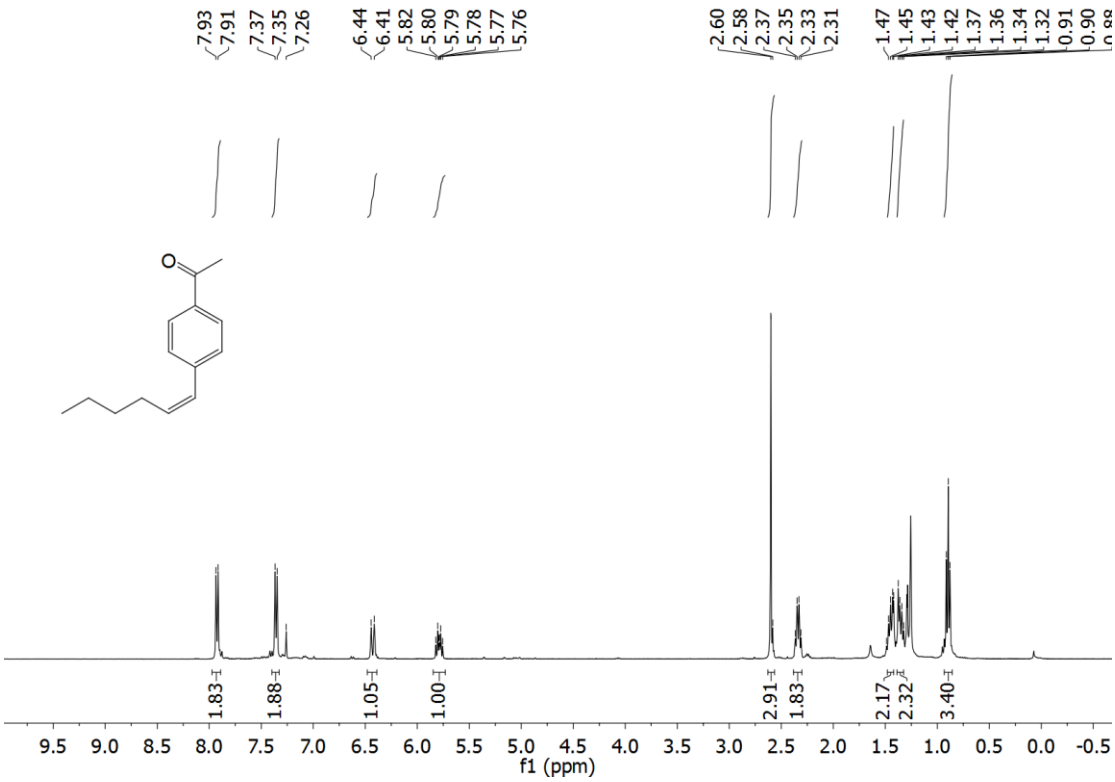
^{13}C NMR (101 MHz, $CDCl_3$) of **4v**



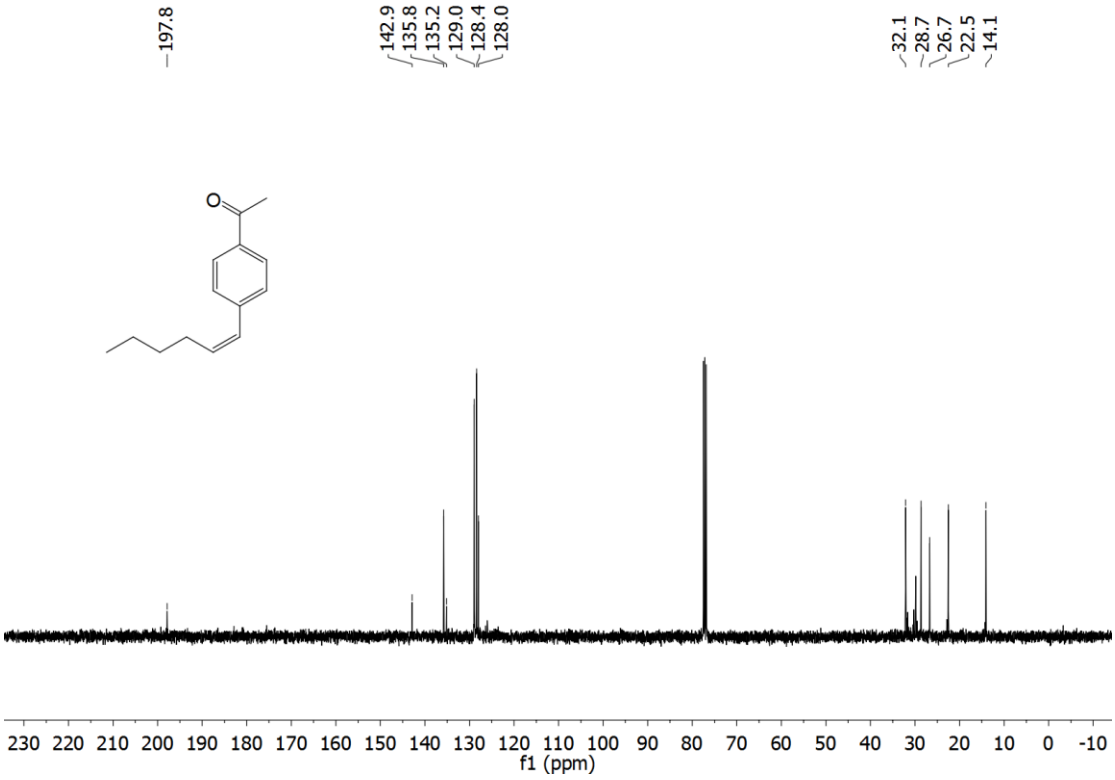
^{1}H NMR (400 MHz, $CDCl_3$) of **7a**



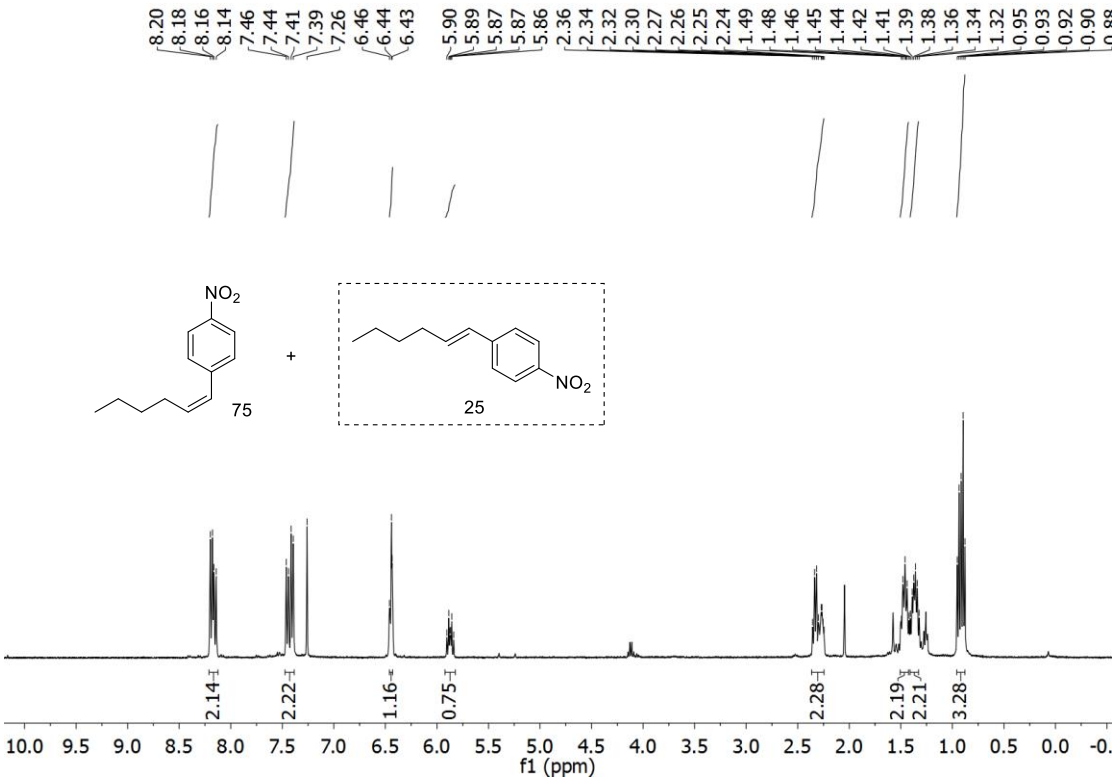
^{13}C NMR (101 MHz, $CDCl_3$) of **7a**



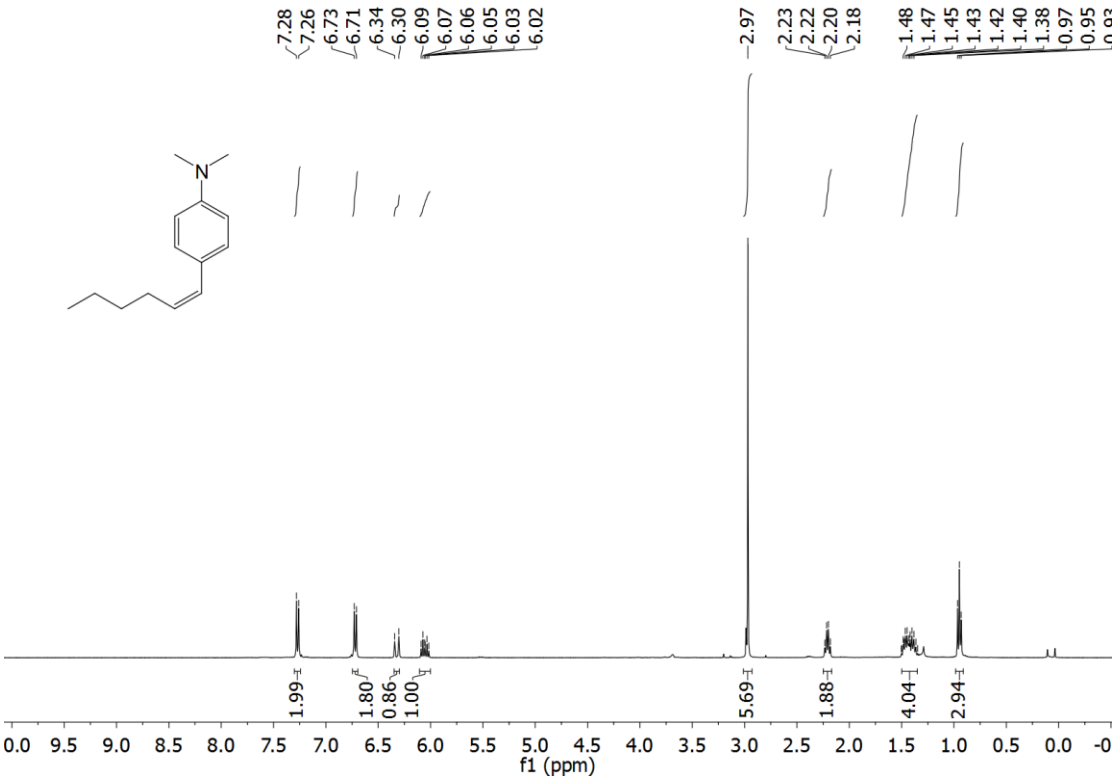
^{1}H NMR (400 MHz, $CDCl_3$) of **7b**



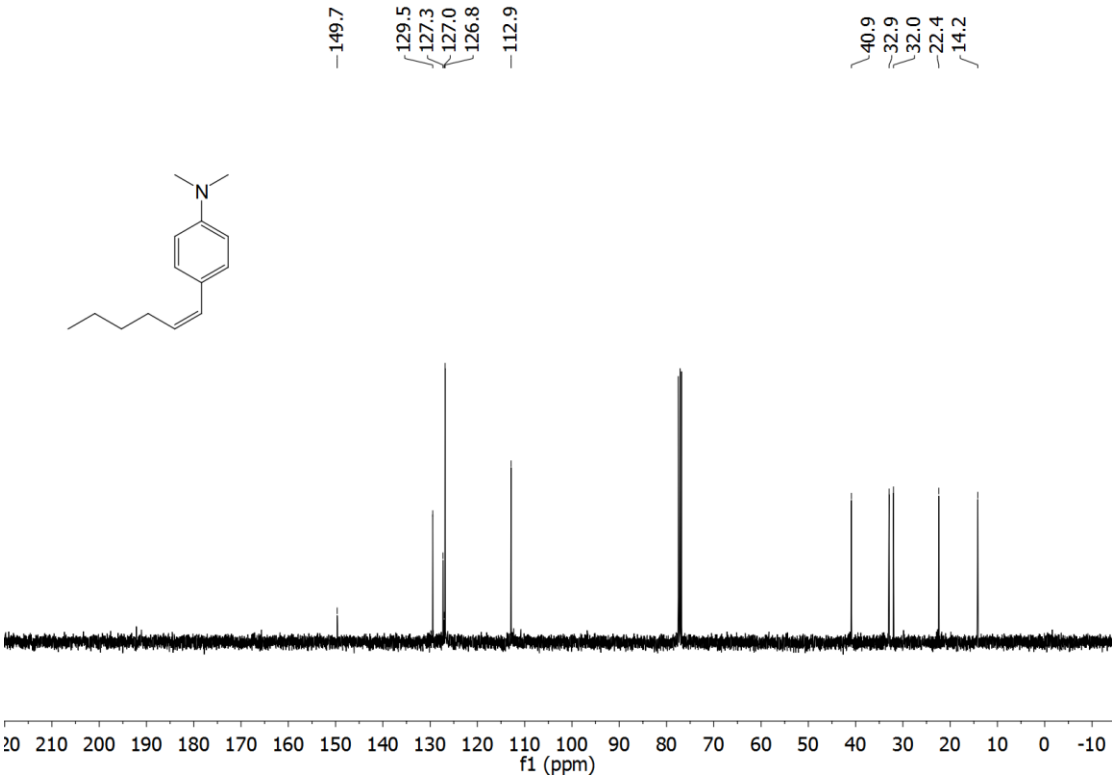
^{13}C NMR (101 MHz, $CDCl_3$) of **7b**



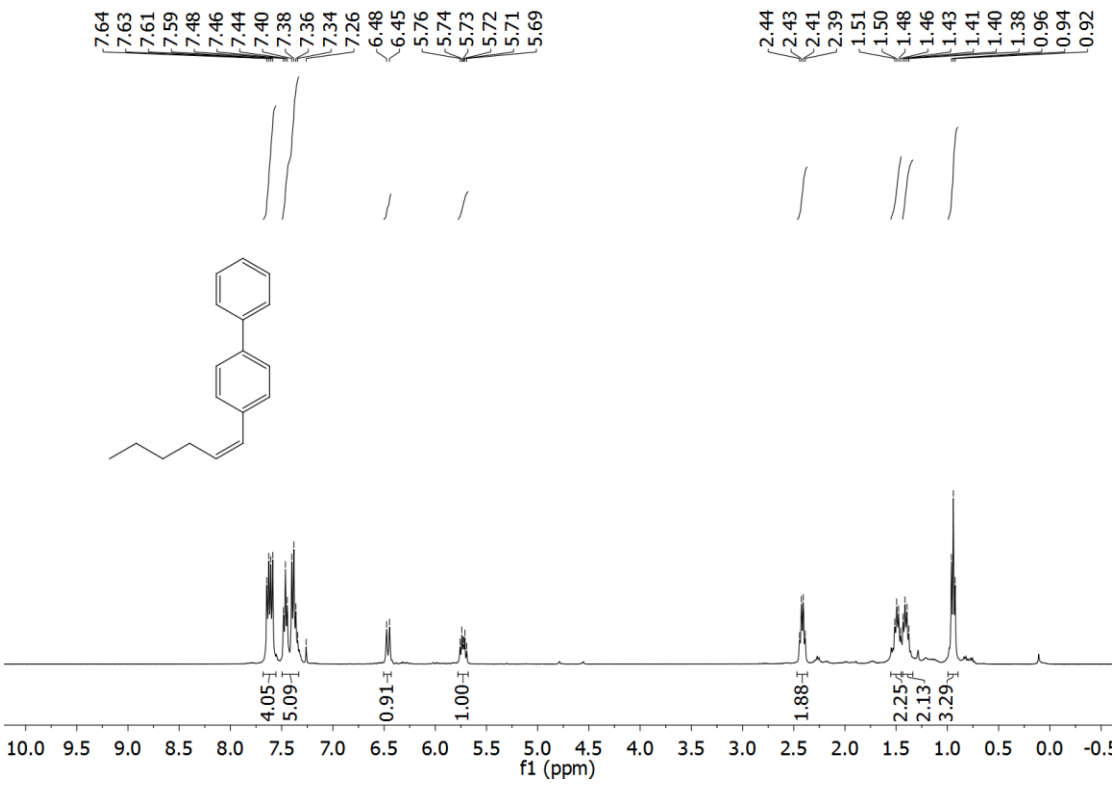
^{1}H NMR (400 MHz, $CDCl_3$) of **7c**



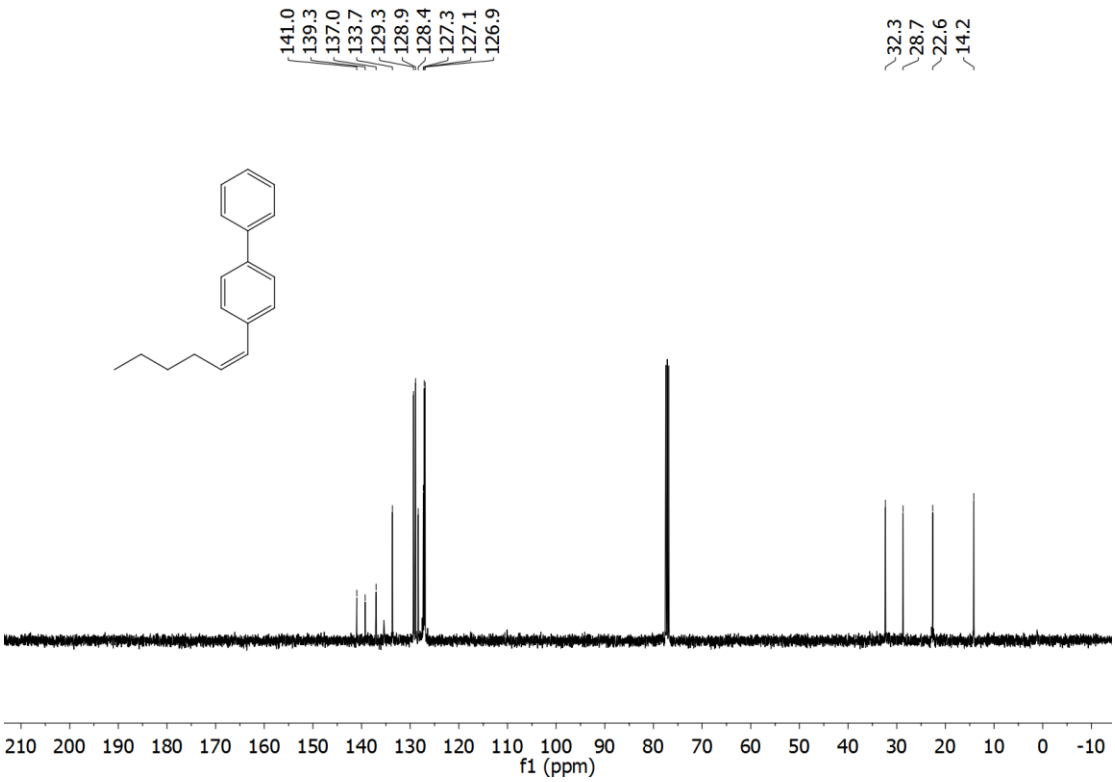
^{1}H NMR (400 MHz, $CDCl_3$) of **7d**



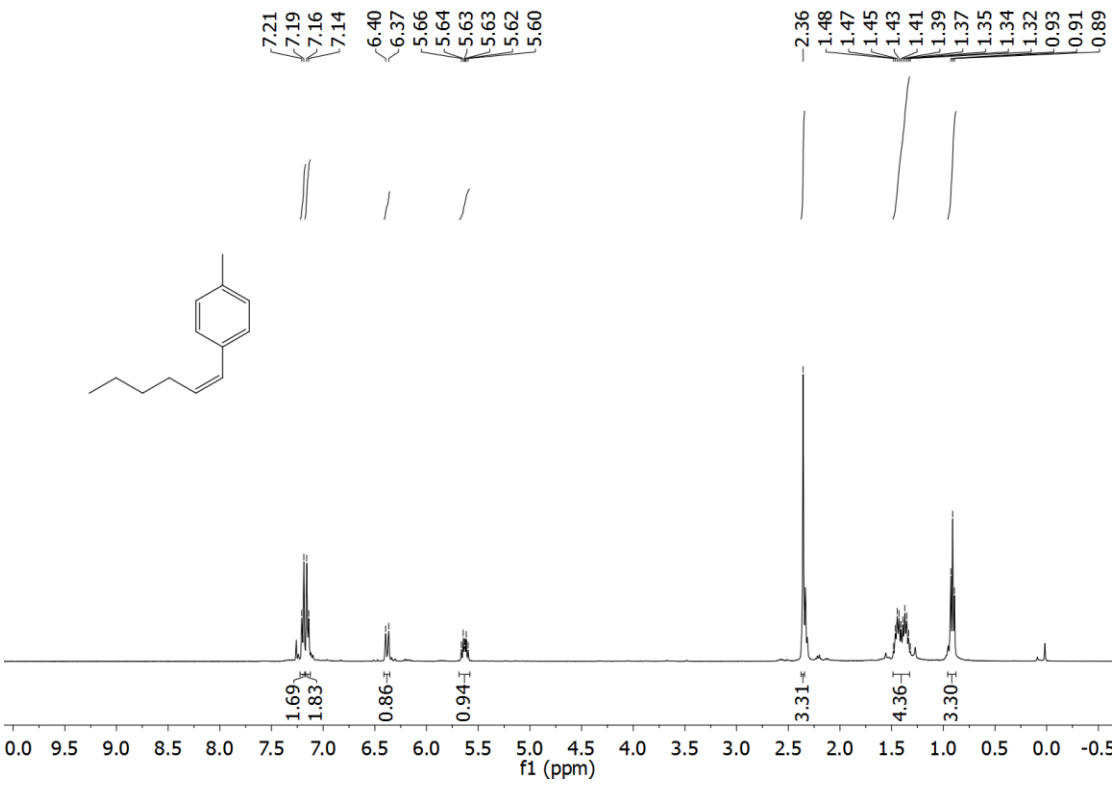
^{13}C NMR (101 MHz, $CDCl_3$) of **7d**



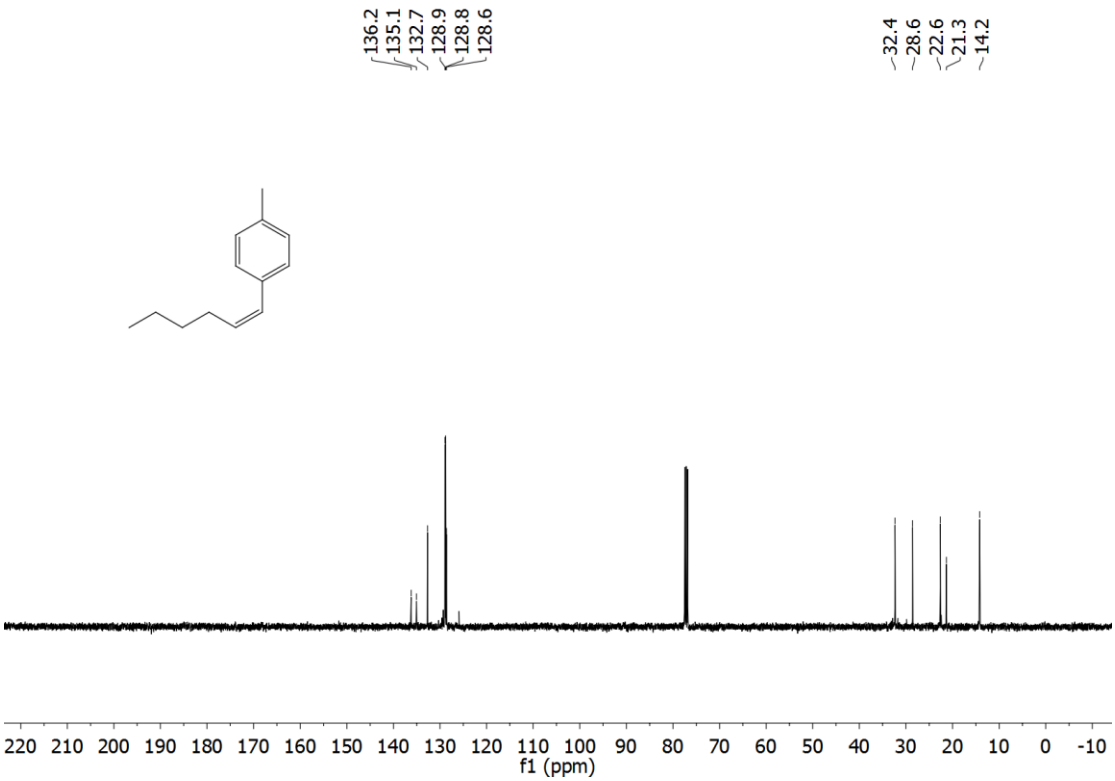
^{1}H NMR (400 MHz, $CDCl_3$) of **7e**



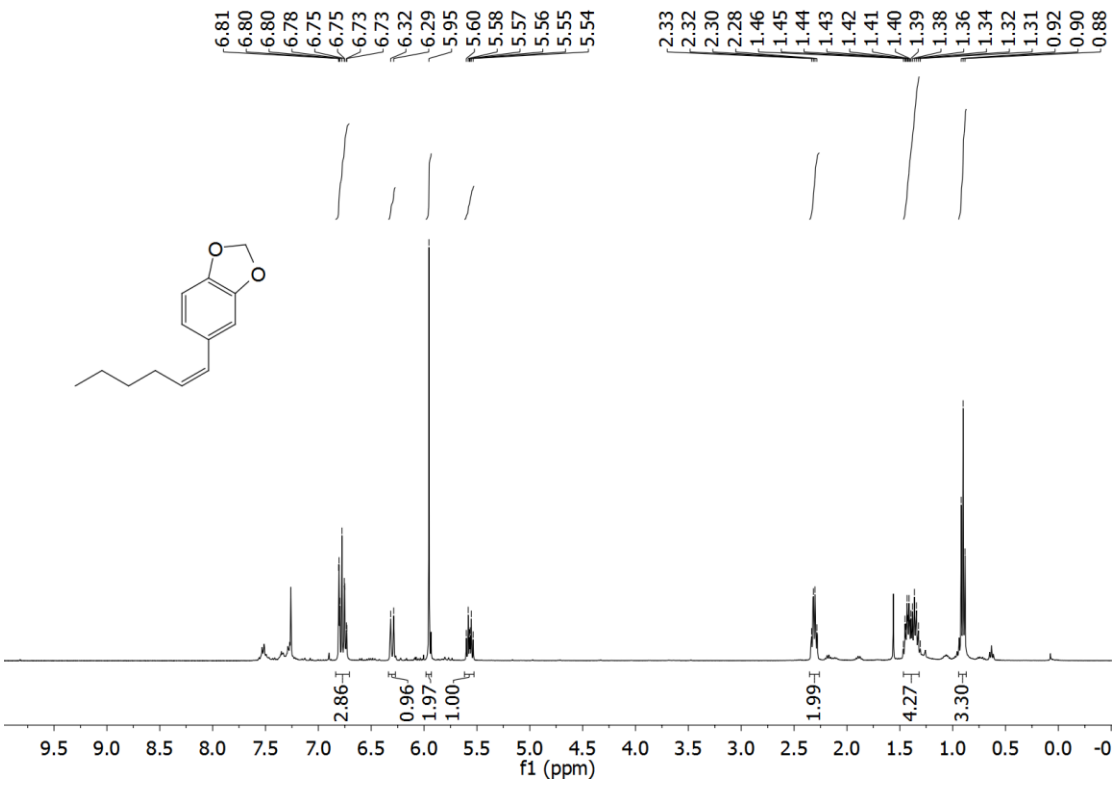
^{13}C NMR (101 MHz, $CDCl_3$) of **7e**



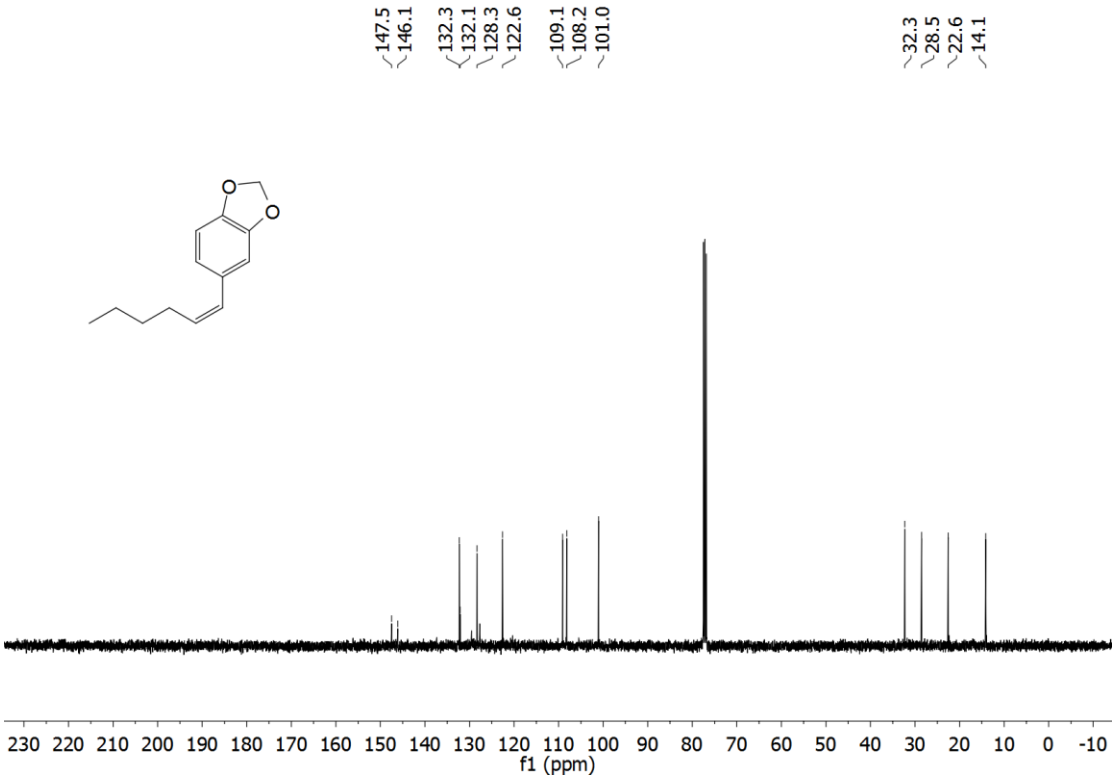
^{1}H NMR (400 MHz, $CDCl_3$) of **7f**



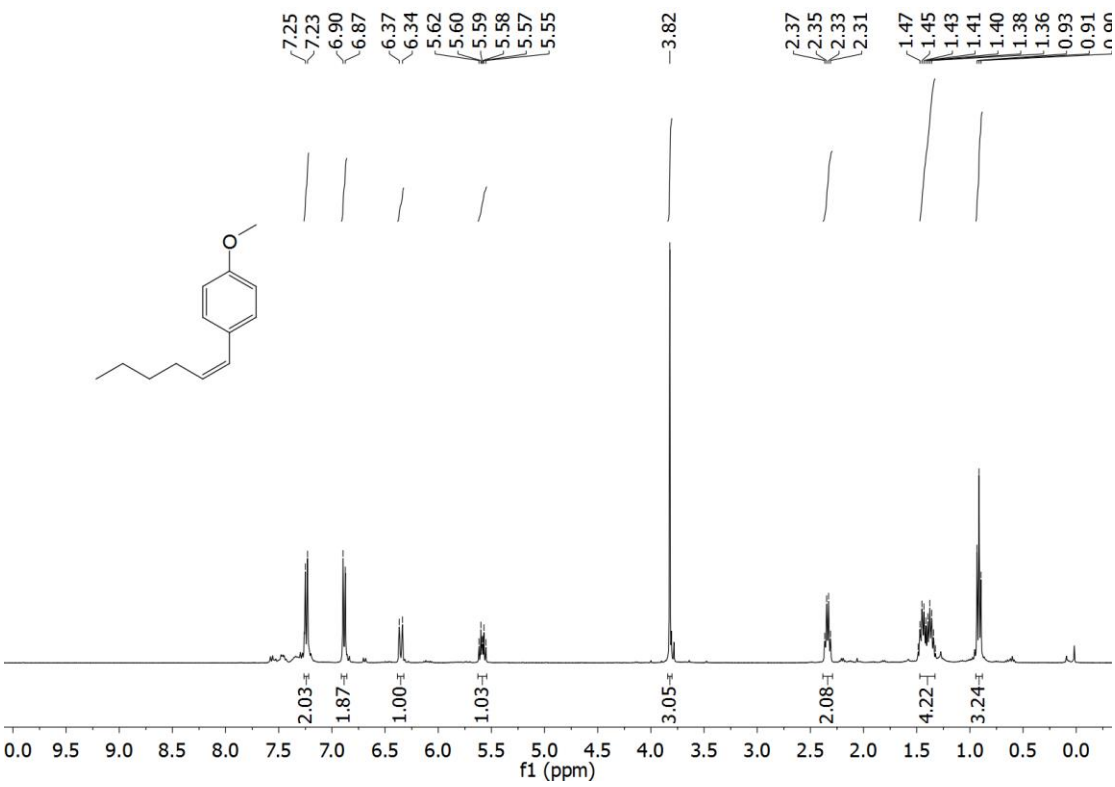
^{13}C NMR (101 MHz, $CDCl_3$) of **7f**



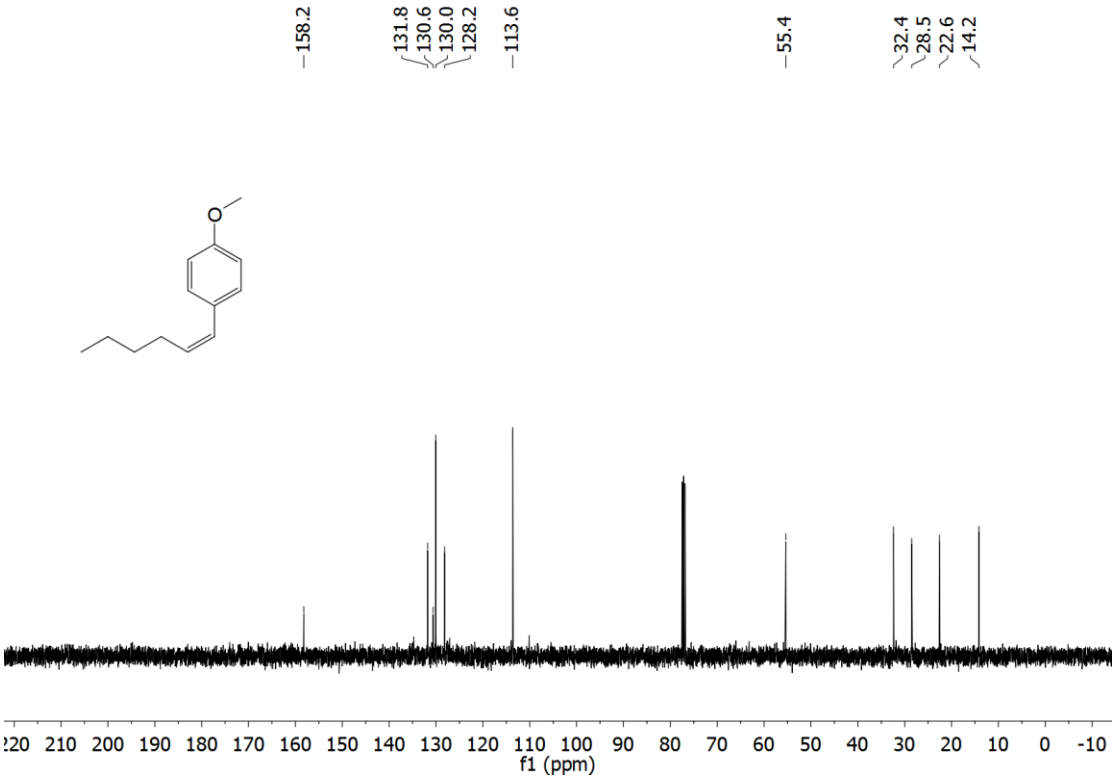
^{1}H NMR (400 MHz, $CDCl_3$) of **7g**



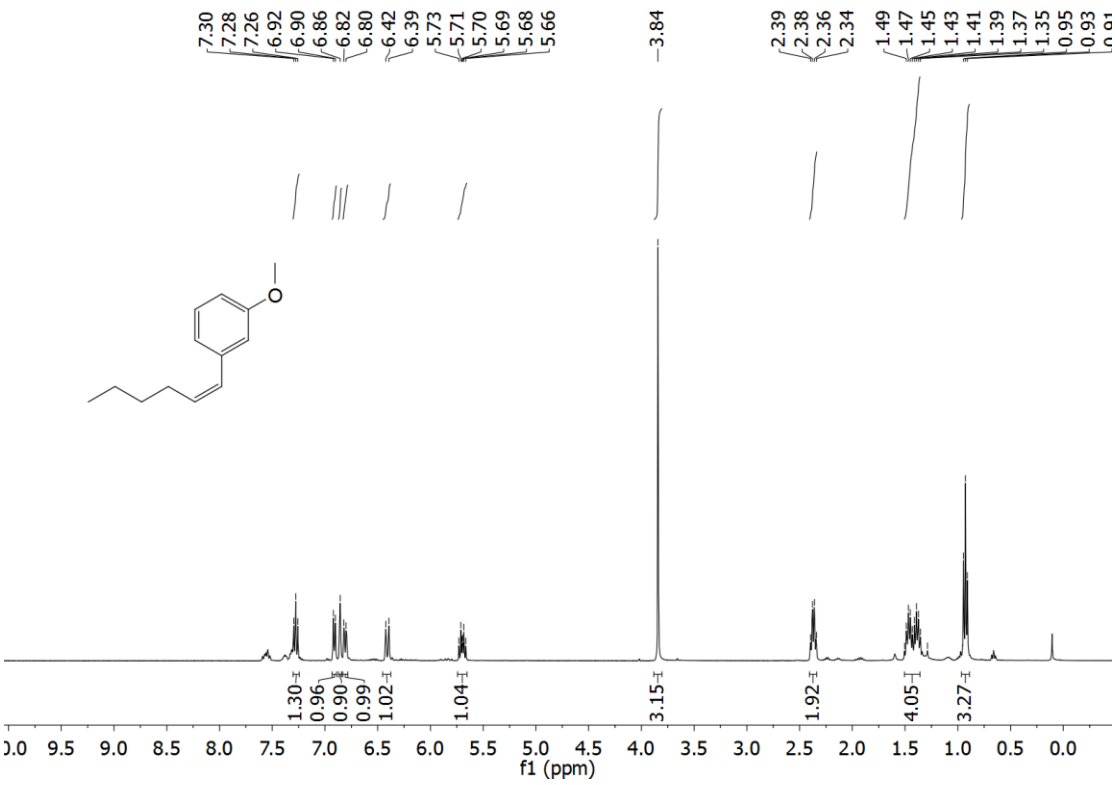
^{13}C NMR (101 MHz, $CDCl_3$) of **7g**



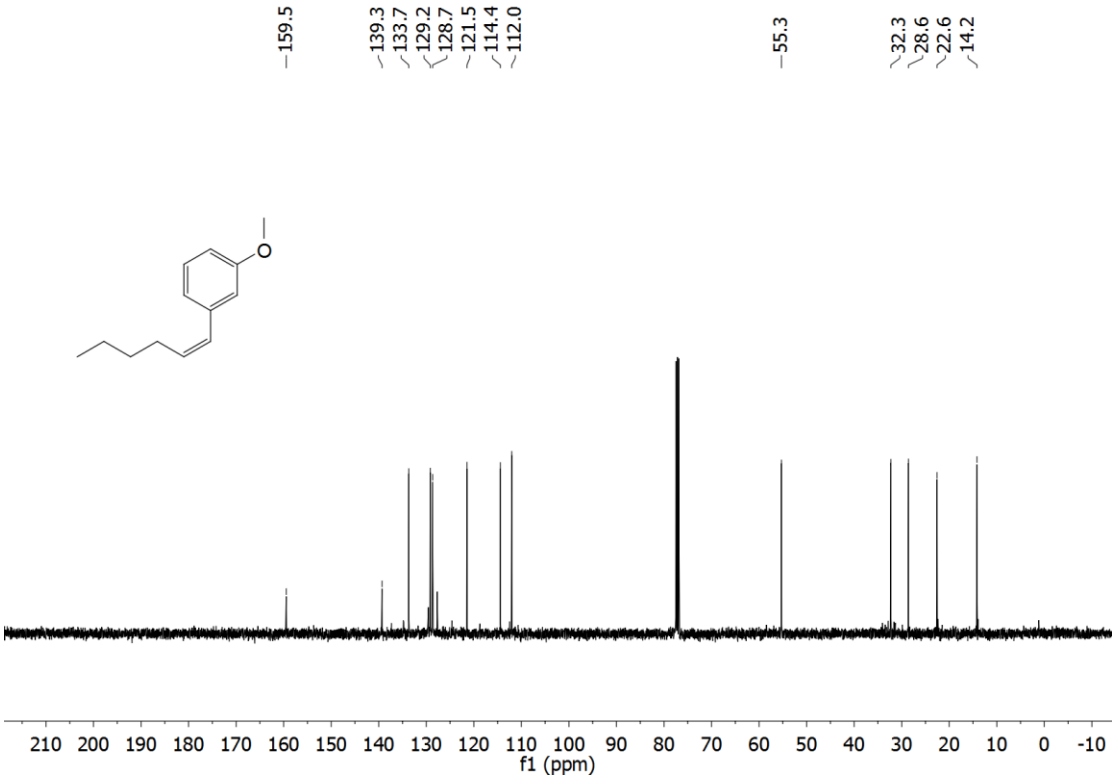
^{1}H NMR (400 MHz, $CDCl_3$) of **7h**



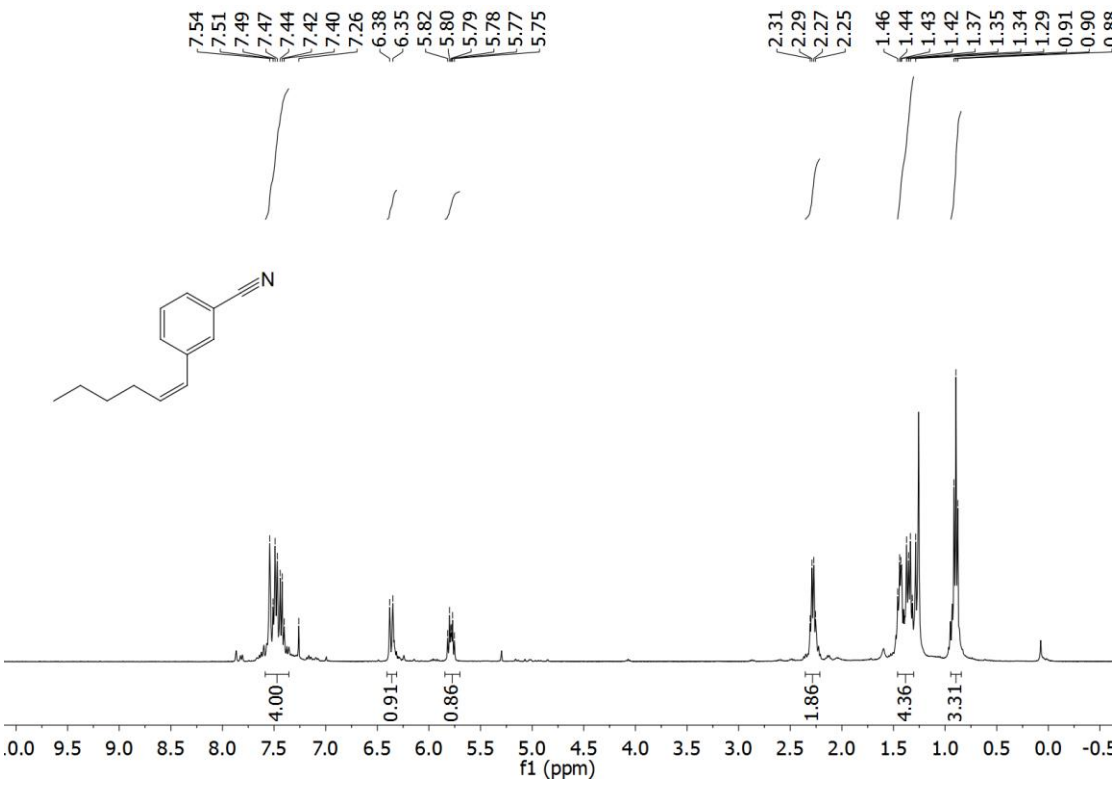
^{13}C NMR (101 MHz, $CDCl_3$) of **7h**



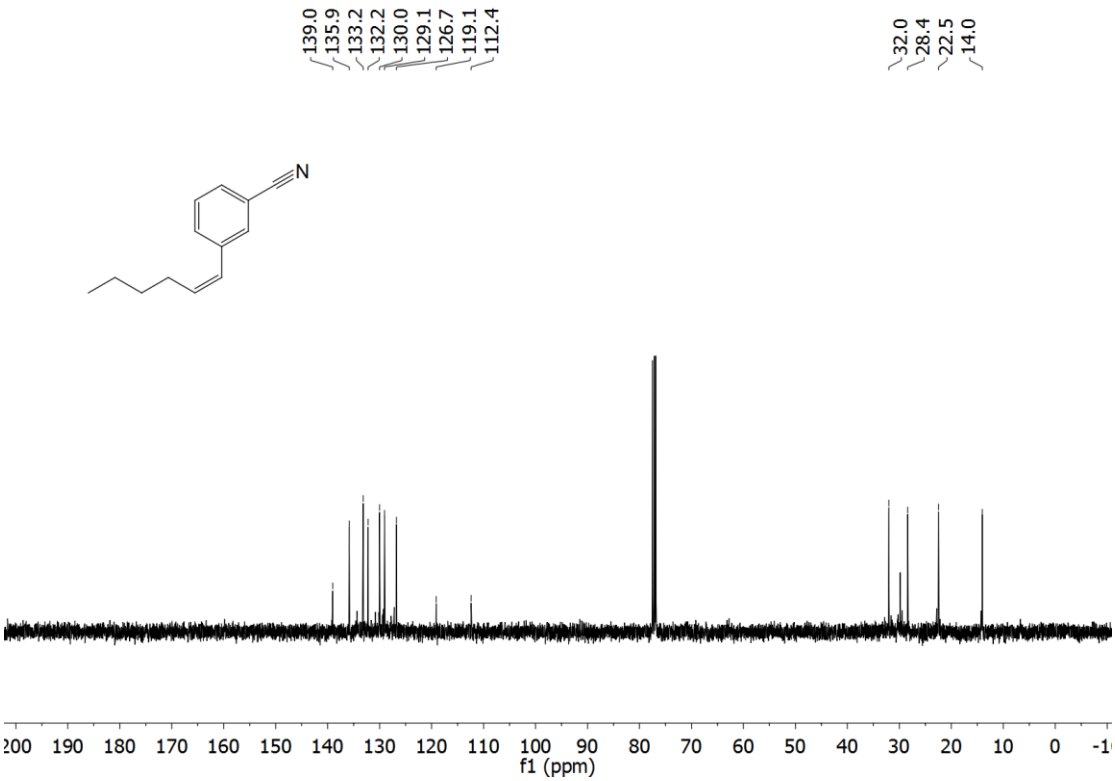
^{1}H NMR (400 MHz, $CDCl_3$) of **7i**



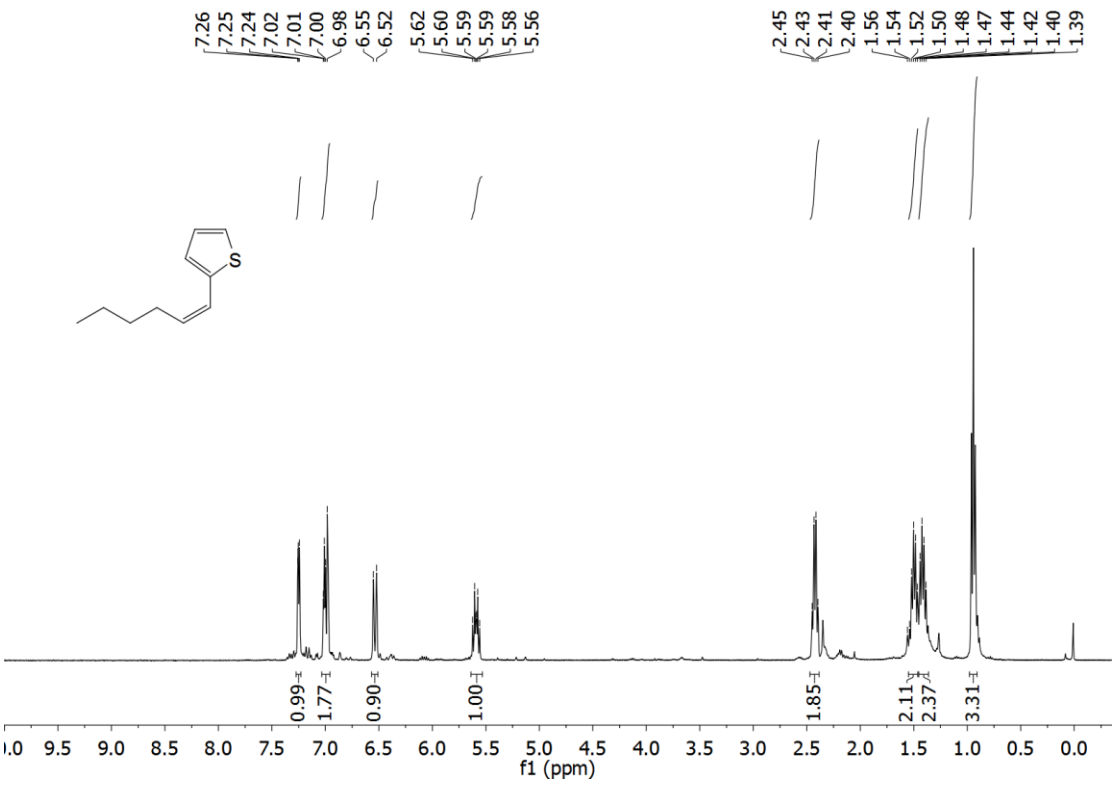
^{13}C NMR (101 MHz, $CDCl_3$) of **7i**



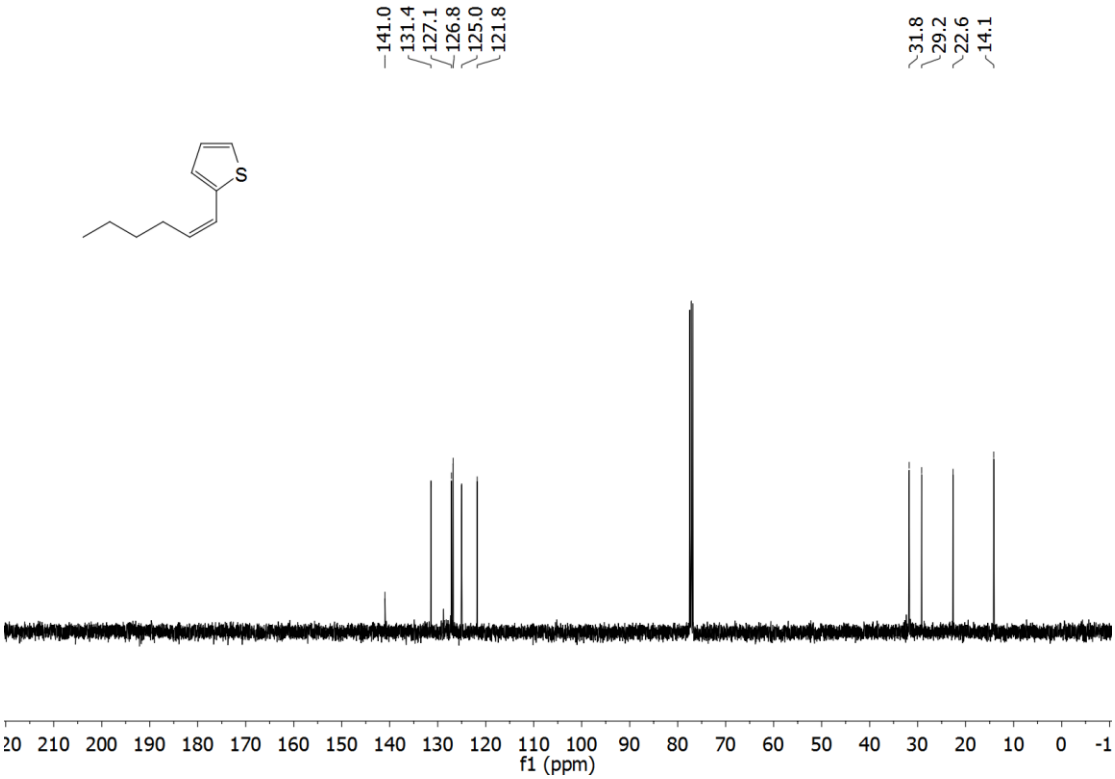
^{1}H NMR (400 MHz, $CDCl_3$) of **7j**



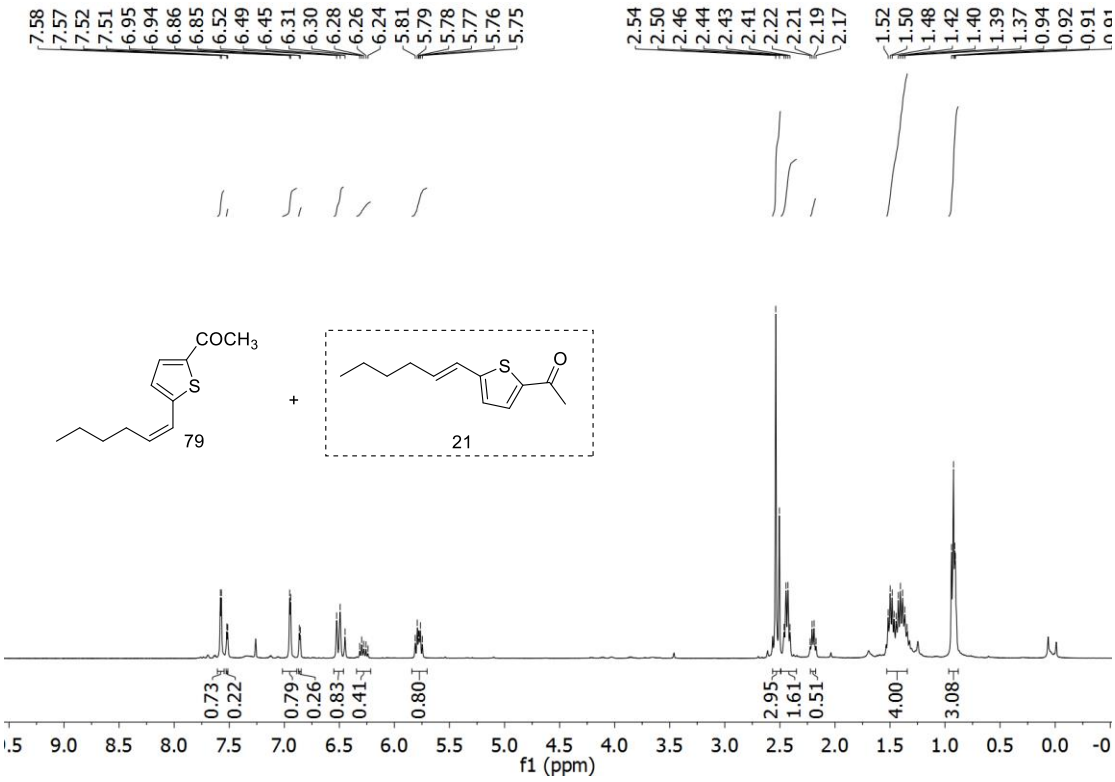
^{13}C NMR (101 MHz, $CDCl_3$) of **7j**



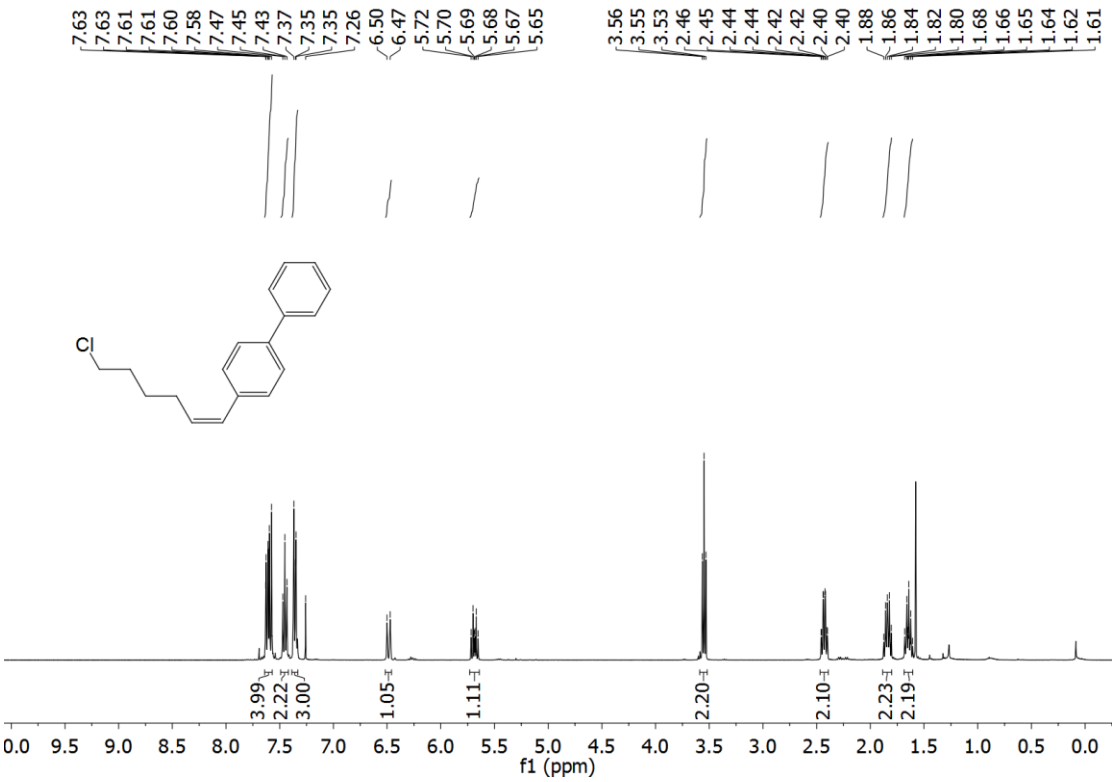
^{1}H NMR (400 MHz, $CDCl_3$) of **7k**



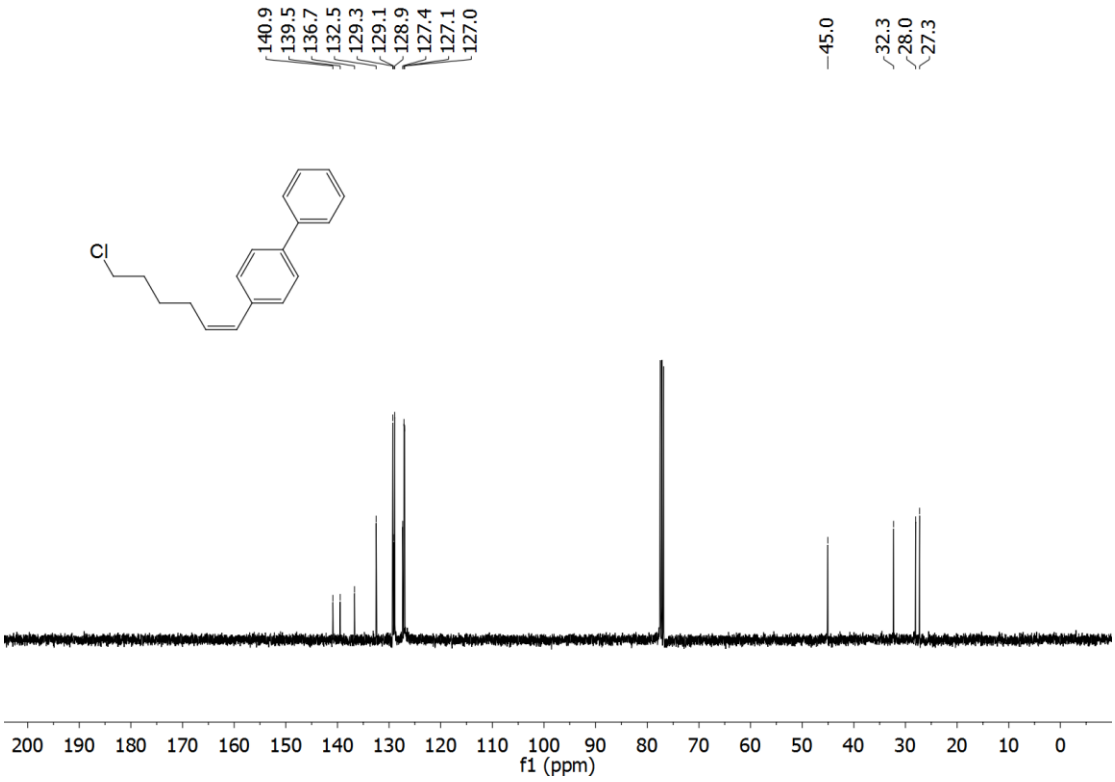
^{13}C NMR (101 MHz, $CDCl_3$) of **7k**



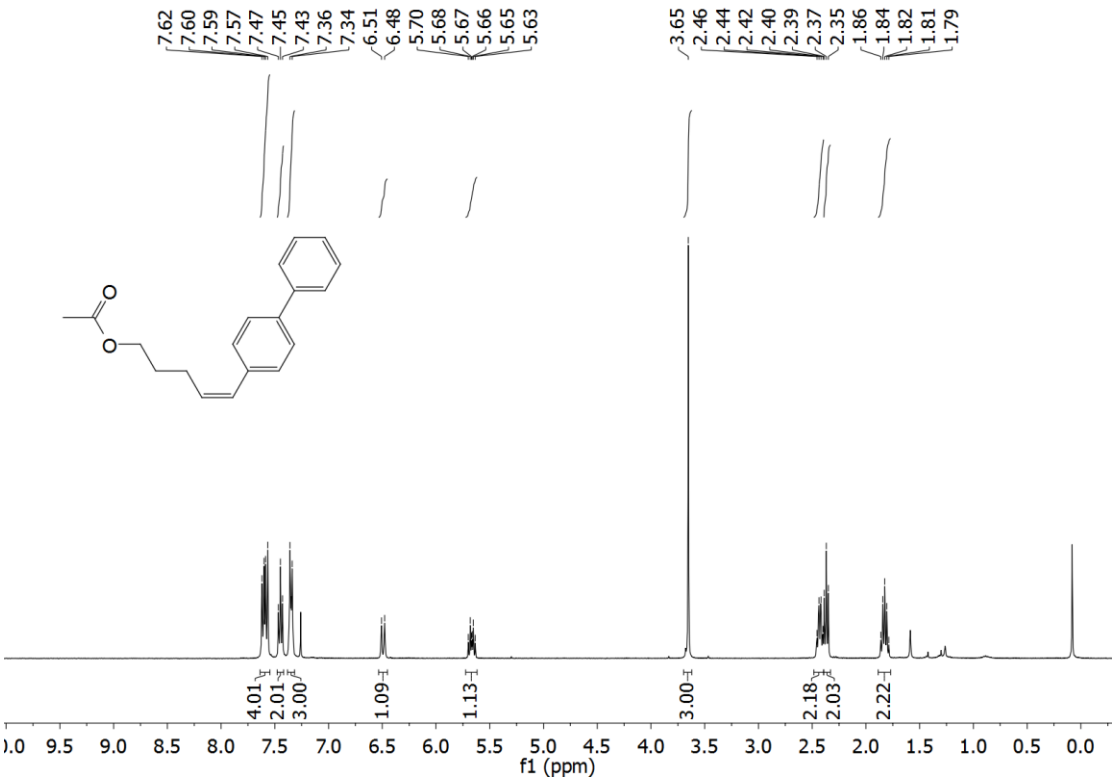
^{1}H NMR (400 MHz, $CDCl_3$) of **7l**



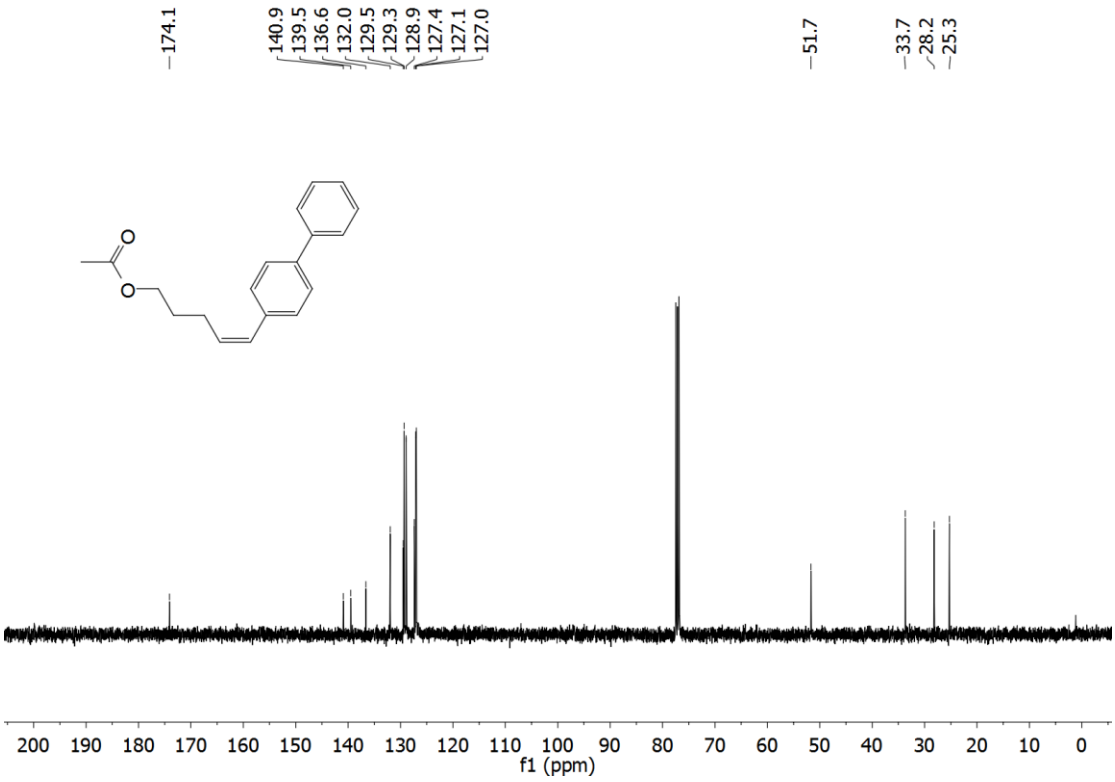
^{1}H NMR (400 MHz, $CDCl_3$) of **7m**



^{13}C NMR (101 MHz, $CDCl_3$) of **7m**



^{1}H NMR (400 MHz, $CDCl_3$) of **7n**



^{13}C NMR (101 MHz, $CDCl_3$) of **7n**