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**Supporting Information**

# Distinct Selective Alkene Hydrosilylation Catalyzed by Acylenalato Cobalt Hydrides

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**CONTENTS:**

**IR, $^{1}H$, $^{31}P$ NMR Spectra of Complexes 1-3**

Complex **1**: $^{1}H$ NMR (500 MHz, Benzene-$d_6$, ppm): δ 2.70 (t, J = 6.0 Hz, 2H), 2.33 (t, J = 6.1 Hz, 2H), 1.67 (tt, J = 17.4, 6.0 Hz, 4H), 1.17 (t, J = 3.5 Hz, 18H), 1.04 (d, J = 5.8 Hz, 9H), -26.70 (t, J = 61.5 Hz, 1H). $^{31}P$ NMR (202 MHz, Benzene-$d_6$, ppm): δ 8.84 (2P), -2.46 (1P).

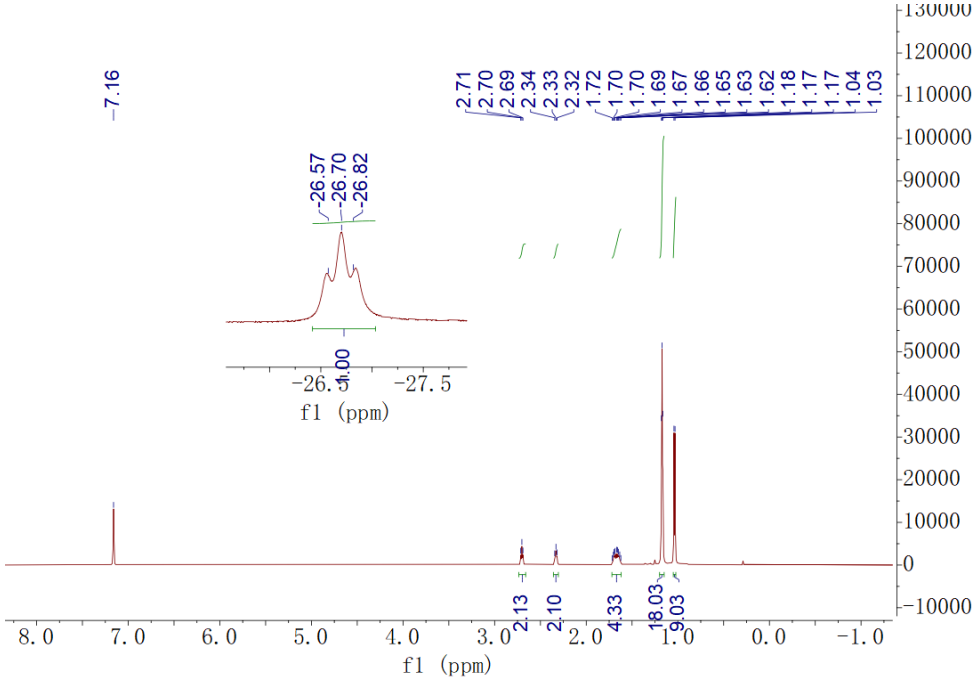


Fig.S1 The $^{1}H$ NMR spectrum of complex **1** ($C_6D_6$)

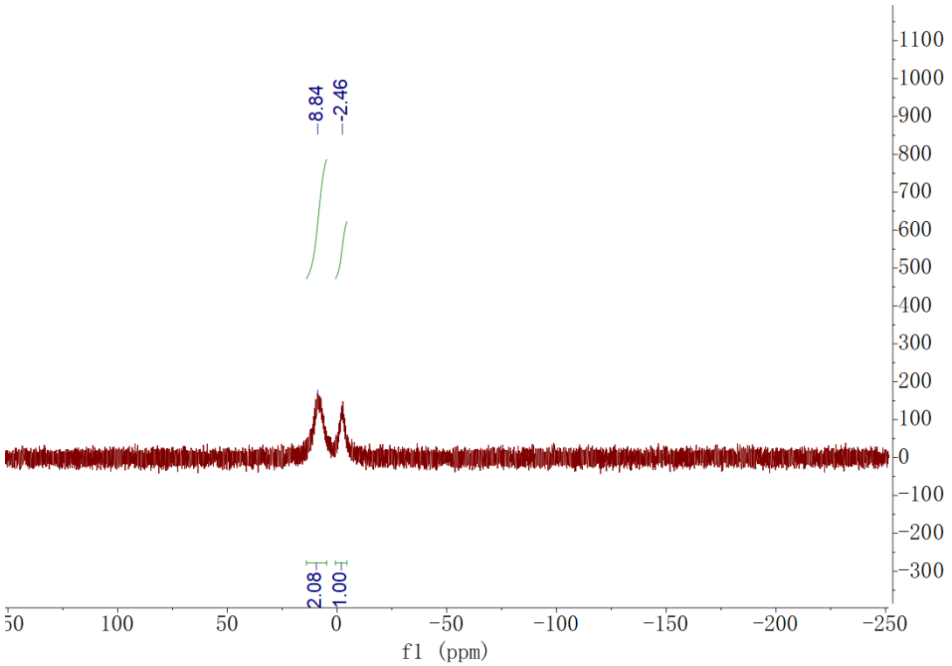


Fig.S2 The $^{31}P$ NMR spectrum of complex **1** ($C_6D_6$)

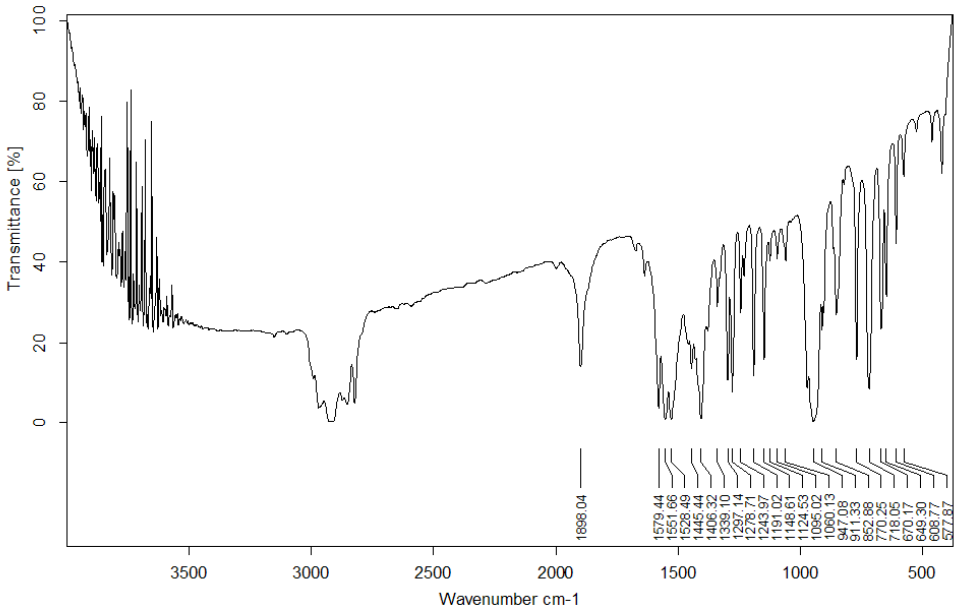


Fig.S3 The IR spectrum of complex **1**

**Complex 2**: $^{1}$H NMR (500 MHz, Benzene-$d_6$, ppm): δ 7.91 (s, 1H), 7.26 (s, 2H), 6.60 (s, 1H), 1.35 (s, 18H), 1.02 (s, 9H), -26.18 (t, $J$ = 63.4 Hz, 1H). $^{31}$P NMR (202 MHz, Benzene-$d_6$, ppm): δ 6.40 (2P), -3.59 (1P).

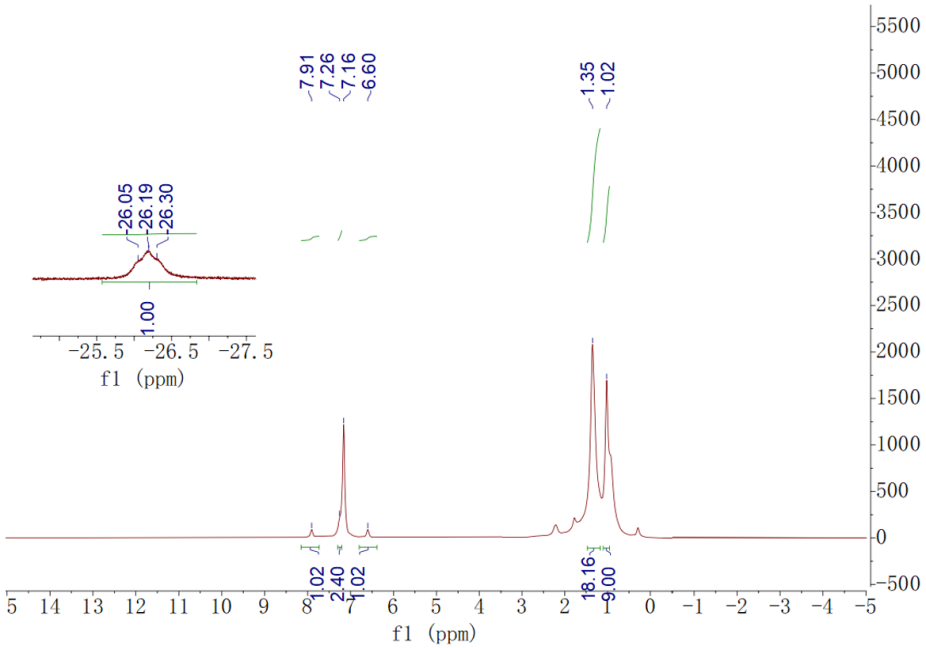


Fig.S4 The $^{1}$H NMR spectrum of complex **2** ($C_6D_6$)

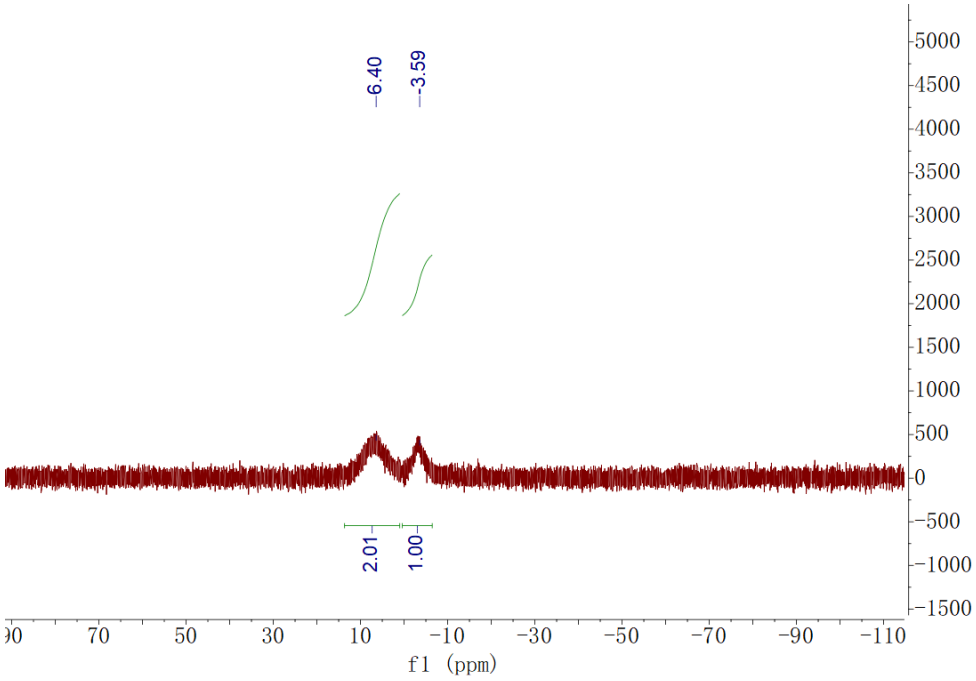


Fig.S5 The $^{31}P$ NMR spectrum of complex **2** ($C_6D_6$)

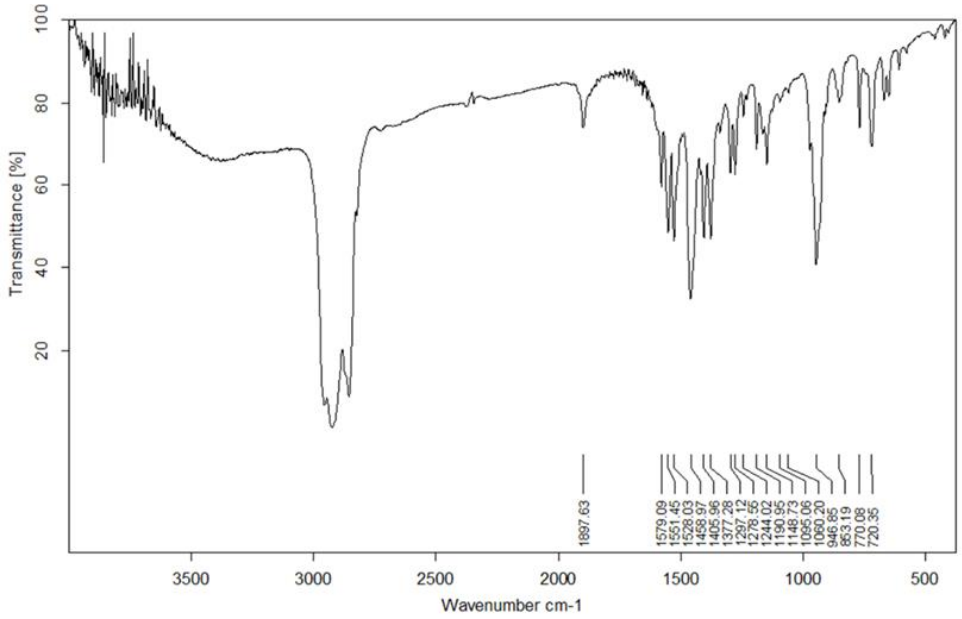


Fig.S6 The IR spectrum of complex **2**

Complex **3**: $^{1}$H NMR (500 MHz, Benzene-$d_6$, ppm): δ 7.63 (s, 1H), 7.20 (s, 1H), 2.36 (s, 3H), 1.69 (s, 9H), 1.07 (d, J = 5.9 Hz, 9H), 1.03 (s, 18H), -25.96 (t, J = 69.8 Hz, 1H). $^{31}$P NMR (202 MHz, Benzene-$d_6$, ppm): δ 7.13 (2P), -3.63 (1P).

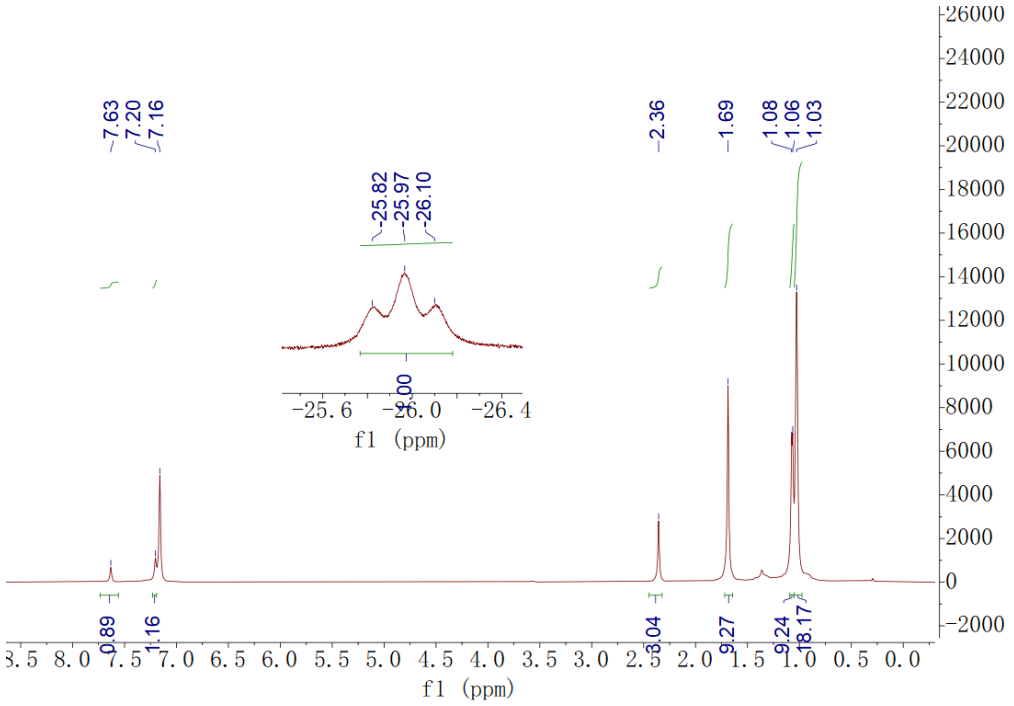


Fig.S7 The $^{1}$H NMR spectrum of complex **3** ($C_6D_6$)

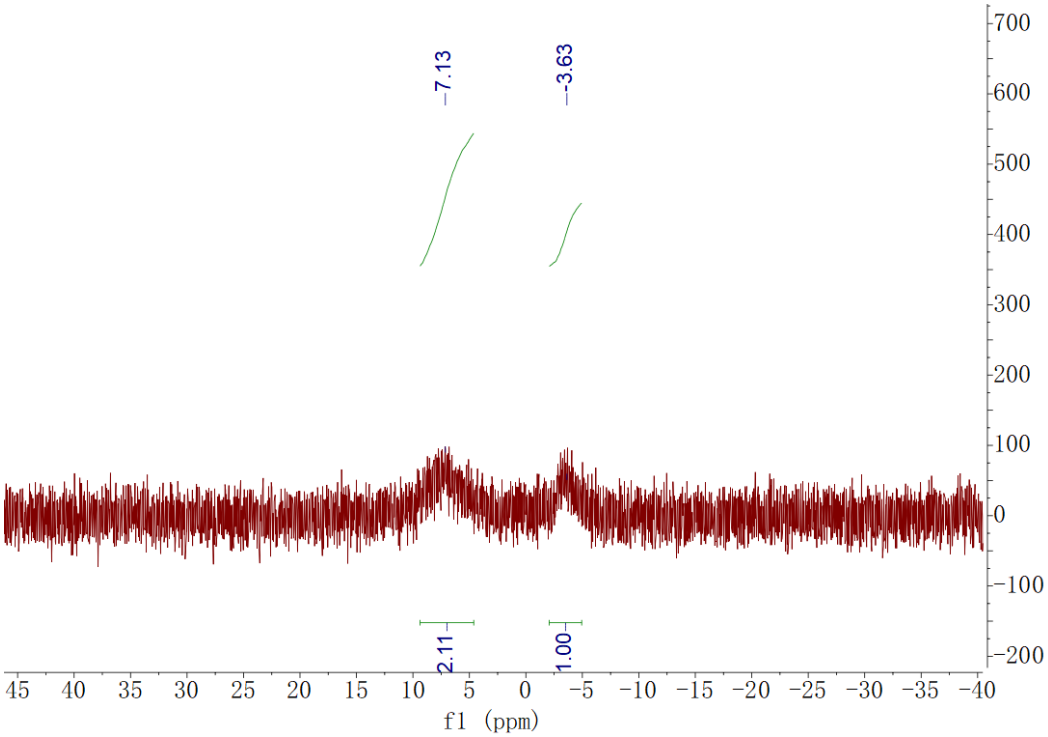


Fig.S8 The $^{31}$P NMR spectrum of complex **3** ($C_6D_6$)

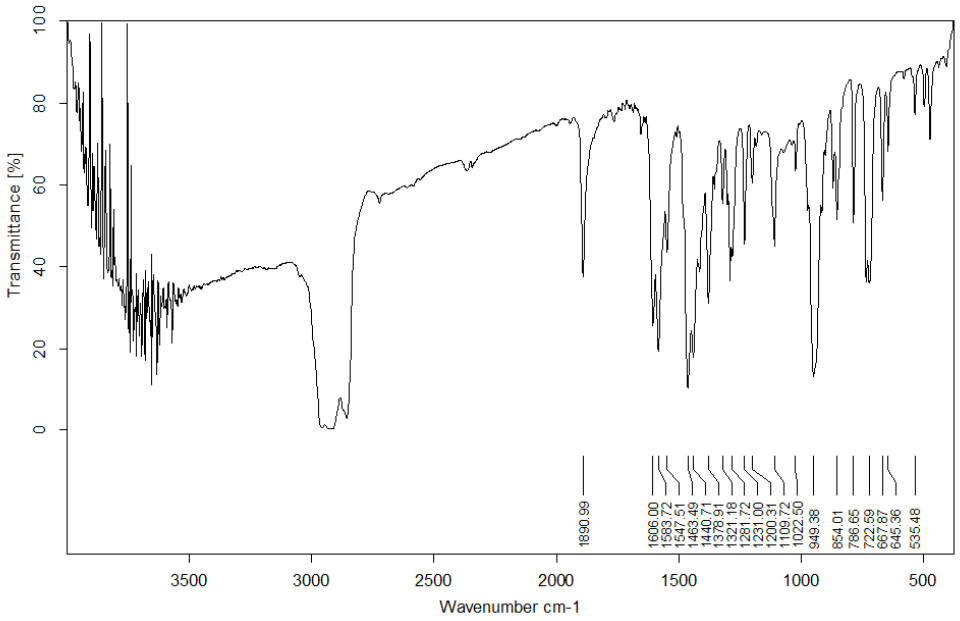


Fig.S9 The IR spectrum of complex **3**

**SII** $^{1}$H and $^{13}$C NMR Spectra of Hydrosilylation Products

**Diphenyl(1-phenylethyl)silane (4a)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.42 – 7.30 (m, 6H), 7.30 – 7.22 (m, 2H), 7.18 (t, $J$ = 7.7 Hz, 2H), 7.08 (t, $J$ = 7.2 Hz, 1H), 7.00 (d, $J$ = 8.3 Hz, 2H), 4.83 (d, $J$ = 3.4 Hz, 1H), 2.82 (qd, $J$ = 7.5, 3.4 Hz, 1H), 1.46 (d, $J$ = 7.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 144.37, 135.73, 135.58, 133.06, 129.73, 129.59, 128.18, 127.94, 127.74, 124.93, 77.47, 77.05, 76.62, 27.00, 16.52.

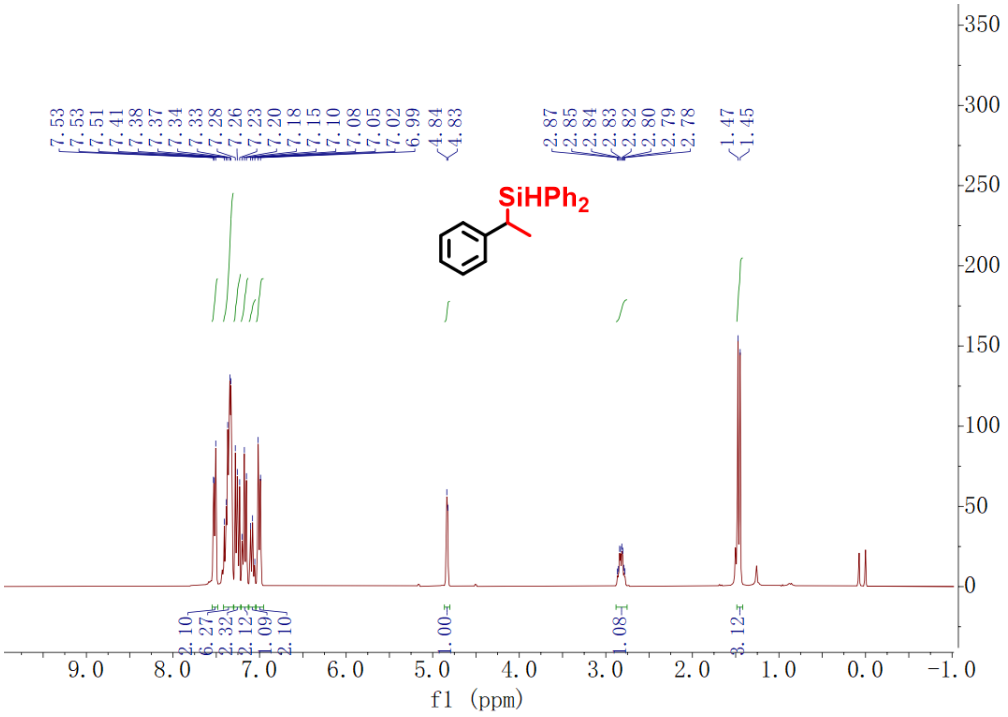


Fig.S10 $^{1}$H NMR of **4a** ($CDCl_3$)

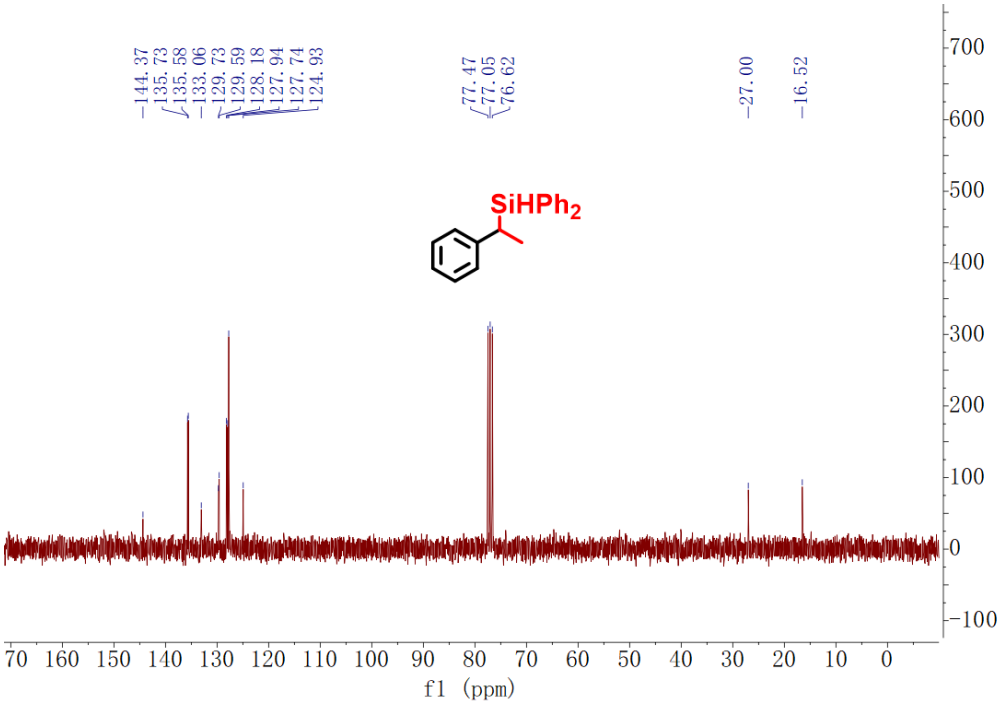


Fig.S11 $^{13}$C NMR of **4a** ($CDCl_3$)

**Diphenyl(1-(o-tolyl)ethyl)silane (4b)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.53 (dd, *J*=7.8, 1.6 Hz, 2H), 7.42–7.27 (m, 6H), 7.25–7.19 (m, 2H), 7.14–7.07 (m, 1H), 7.06–6.99 (m, 3H), 4.80 (d, *J*=3.4 Hz, 1H), 3.00 (qd, *J*=7.4, 3.4 Hz, 1H), 2.07 (s, 3H), 1.44 (d, *J*=7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.89, 135.88, 135.35, 133.41, 132.90, 130.12, 129.81, 129.58, 127.99, 127.74, 126.83, 126.10, 124.79, 77.50, 77.08, 76.65, 22.08, 20.14, 16.65.

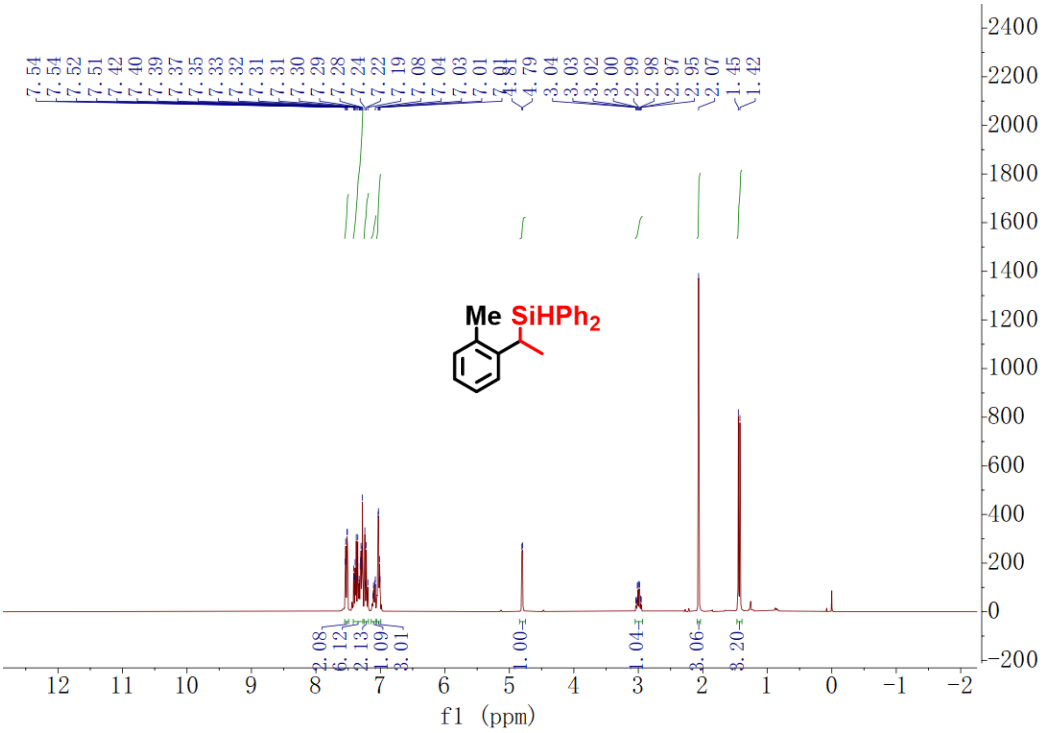


Fig.S12 $^{1}$H NMR of **4b** ($CDCl_3$)

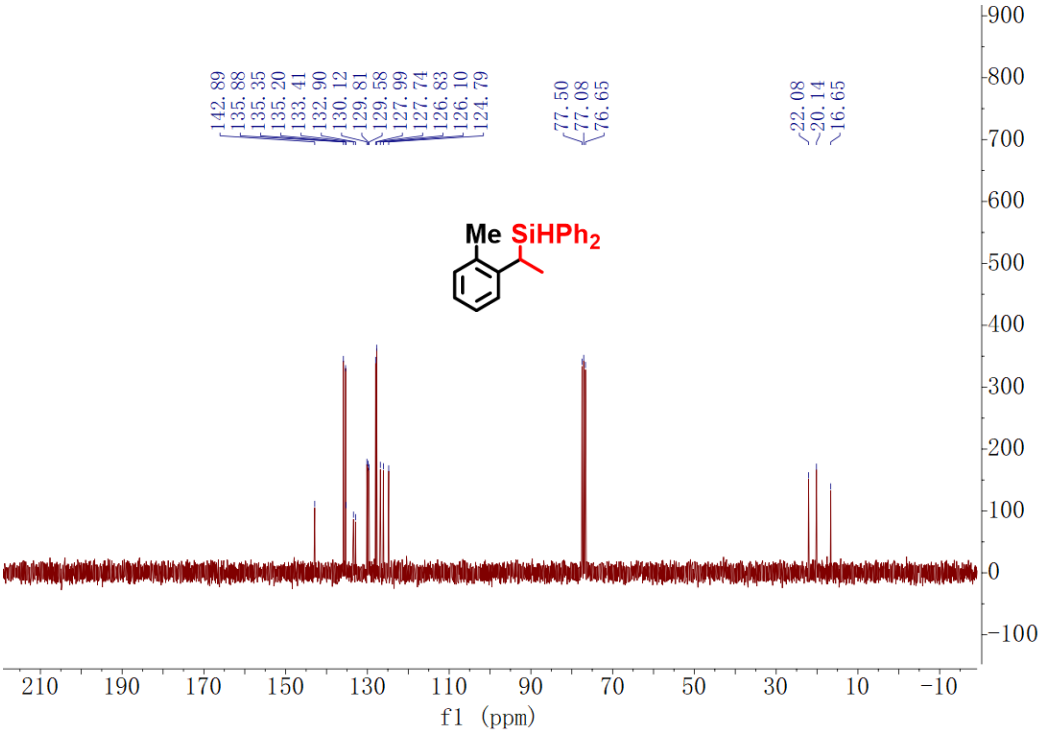


Fig.S13 $^{13}$C NMR of **4b** ($CDCl_3$)

**Diphenyl(1-(m-tolyl)ethyl)silane (4c)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.45 (m, 2H), 7.37 – 7.27 (m, 6H), 7.24 (t, *J* = 7.0 Hz, 2H), 7.05 (td, *J* = 7.5, 3.5 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 1H), 6.83 – 6.74 (m, 2H), 4.83 (d, *J* = 3.2 Hz, 1H), 2.77 (qd, *J* = 7.5, 3.6 Hz, 1H), 2.20 (s, 3H), 1.44 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 144.27, 137.63, 135.83, 135.69, 133.24, 129.77, 129.63, 128.75, 128.14, 127.97, 127.77, 125.78, 124.81, 77.55, 77.12, 76.70, 26.93, 21.50, 16.59.

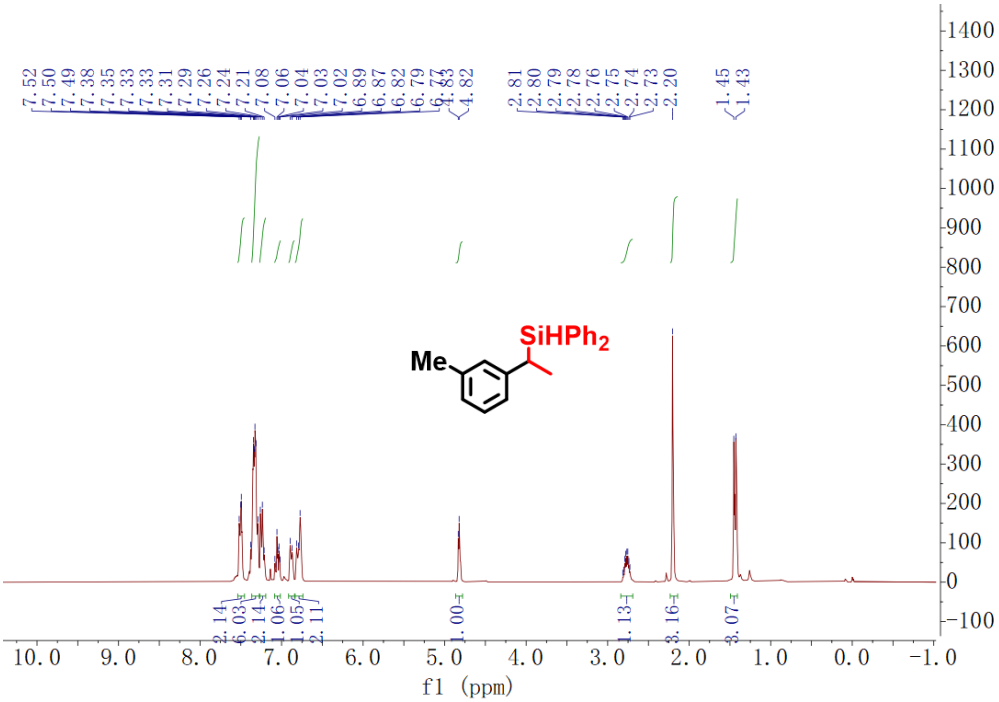


Fig.S14 $^{1}$H NMR of **4c** ($CDCl_3$)

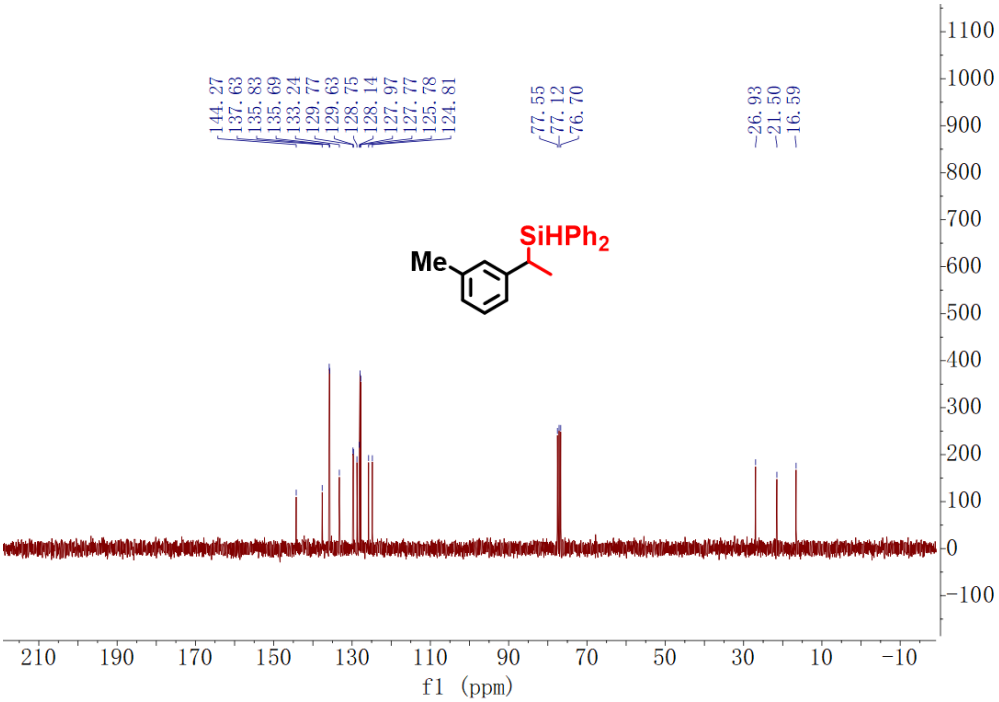


Fig.S15 $^{13}$C NMR of **4c** ($CDCl_3$)

**(1-(4-(tert-butyl)phenyl)ethyl)diphenylsilane (4e)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, $J$ = 7.8, 1.7 Hz, 2H), 7.39 – 7.28 (m, 6H), 7.24 (d, $J$ = 5.9 Hz, 2H), 7.21 – 7.16 (m, 2H), 6.94 (d, $J$ = 8.3 Hz, 2H), 4.83 (d, $J$ = 3.3 Hz, 1H), 2.79 (qd, $J$ = 7.5, 3.4 Hz, 1H), 1.45 (d, $J$ = 7.5 Hz, 3H), 1.28 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 147.77, 141.17, 135.81, 135.65, 133.35, 133.30, 129.71, 129.54, 127.95, 127.72, 127.37, 125.10, 77.93, 77.09, 76.67, 34.34, 31.52, 26.33, 16.58.

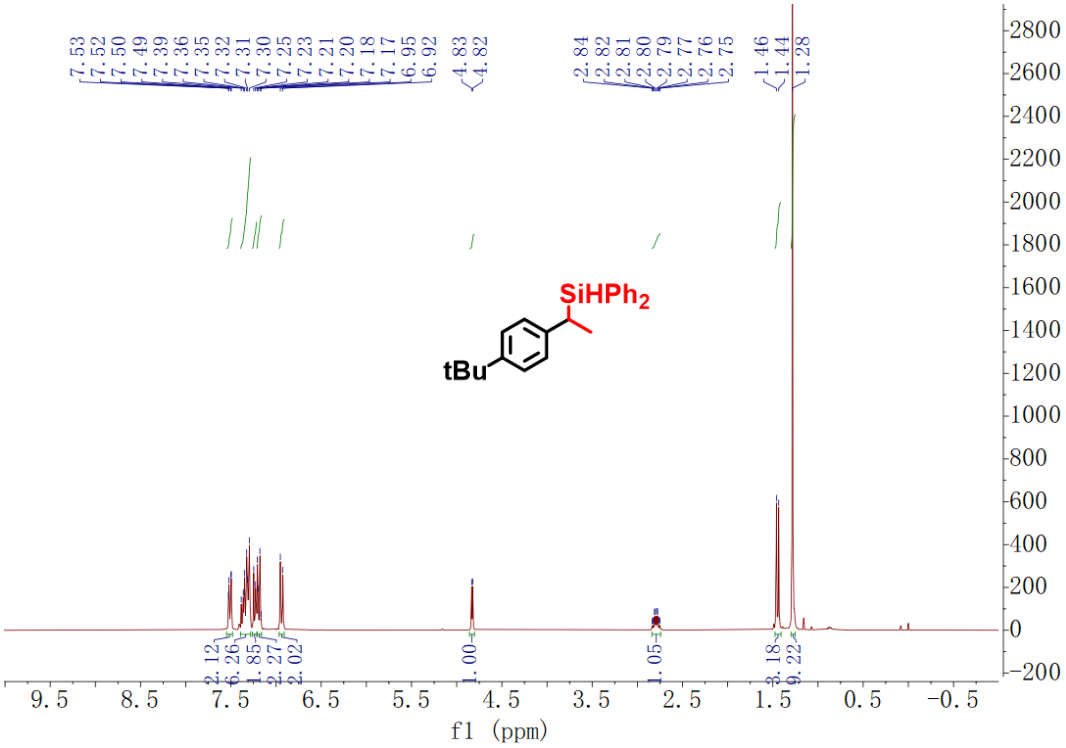


Fig.S16 $^{1}$H NMR of **4e** ($CDCl_3$)

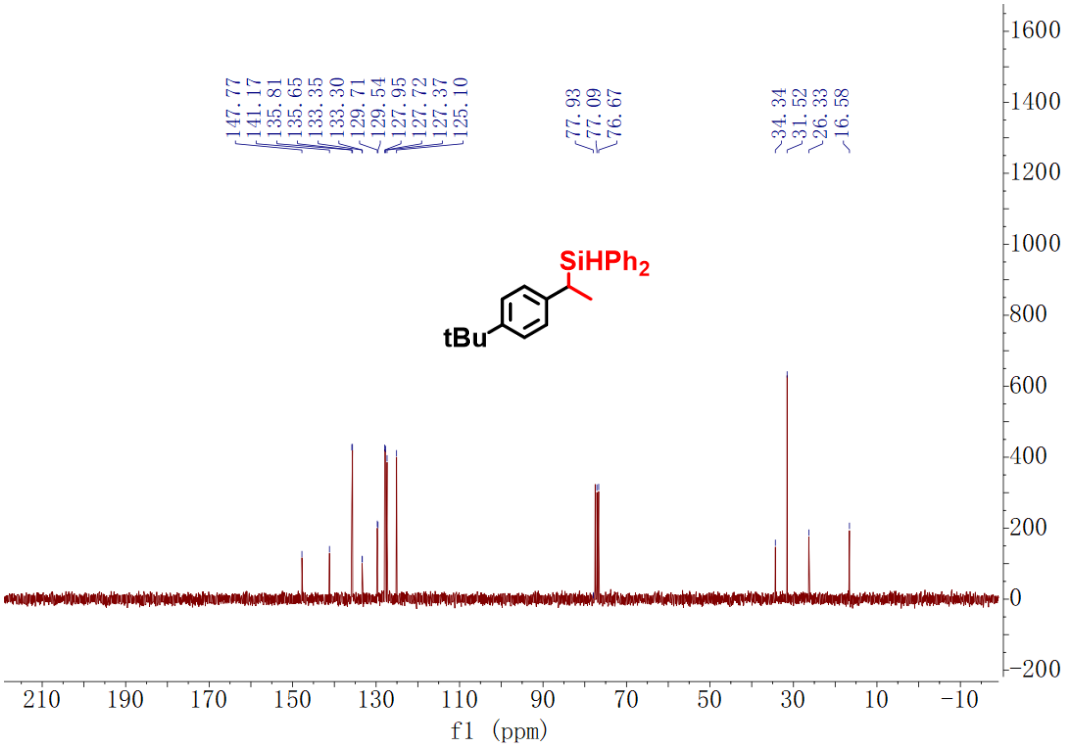


Fig.S17 $^{13}$C NMR of **4e** ($CDCl_3$)

**(1-(4-methoxyphenyl)ethyl)diphenylsilane (4f)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.38 – 7.29 (m, 6H), 7.25 (t, *J* = 6.9 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.7 Hz, 2H), 4.83 (d, *J* = 3.4 Hz, 1H), 3.73 (s, 3H), 2.76 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.42 (d, *J* = 7.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 157.21, 136.36, 135.78, 135.66, 133.31, 133.26, 129.73, 129.60, 128.62, 127.98, 127.80, 113.74, 77.54, 77.11, 76.69, 55.27, 25.89, 16.94.

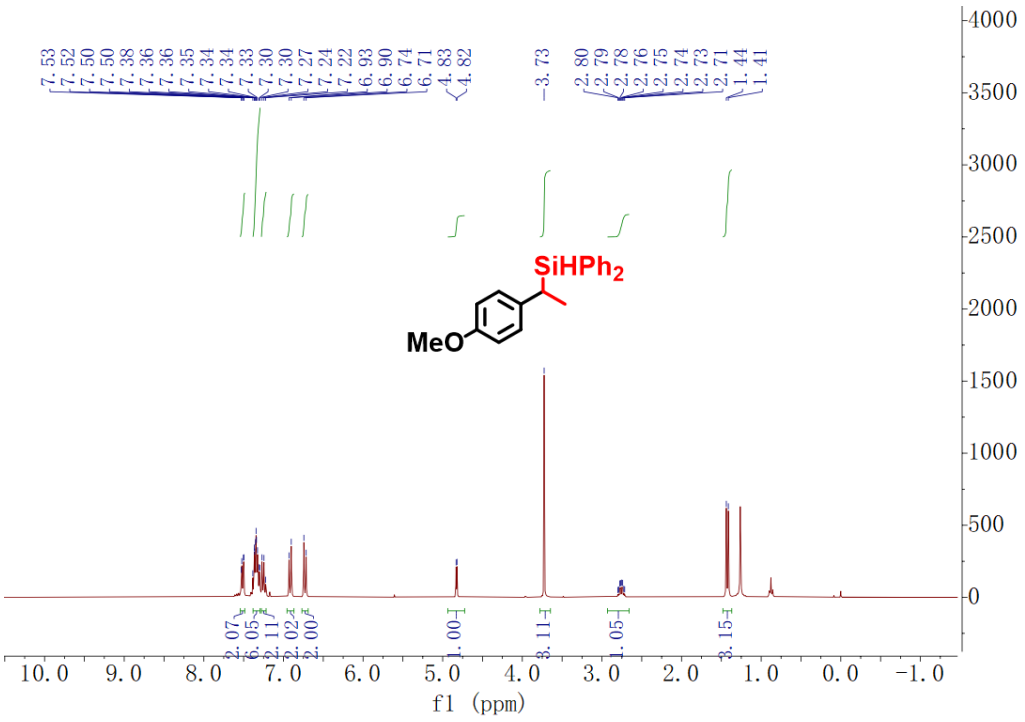


Fig.S18 $^{1}$H NMR of **4f** ($CDCl_3$)

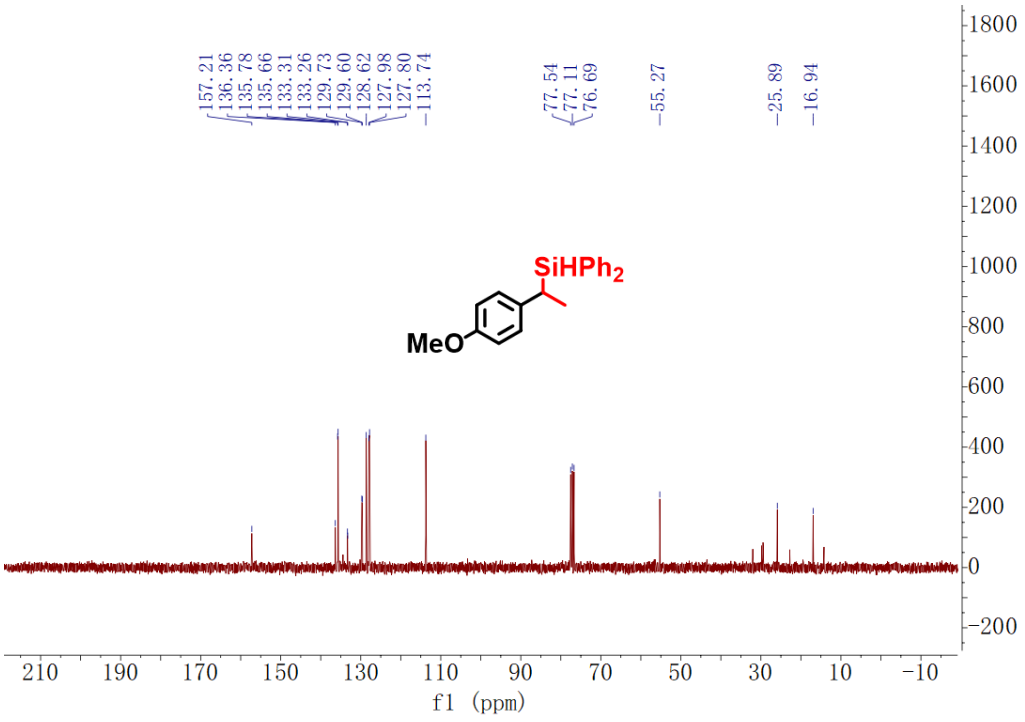


Fig.S19 $^{13}$C NMR of **4f** ($CDCl_3$)

**(1-(3-fluorophenyl)ethyl)diphenylsilane (4g)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.46 – 7.37 (m, 6H), 7.35 – 7.27 (m, 2H), 7.20 – 7.10 (m, 1H), 6.84 – 6.69 (m, 3H), 4.86 (d, *J* = 3.3 Hz, 1H), 2.87 (qd, *J* = 7.5, 3.3 Hz, 1H), 1.48 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.66, 135.50, 132.58, 129.89, 129.77, 129.47, 128.02, 127.84, 114.50, 114.22, 111.84, 77.46, 77.03, 76.61, 27.10, 16.30.

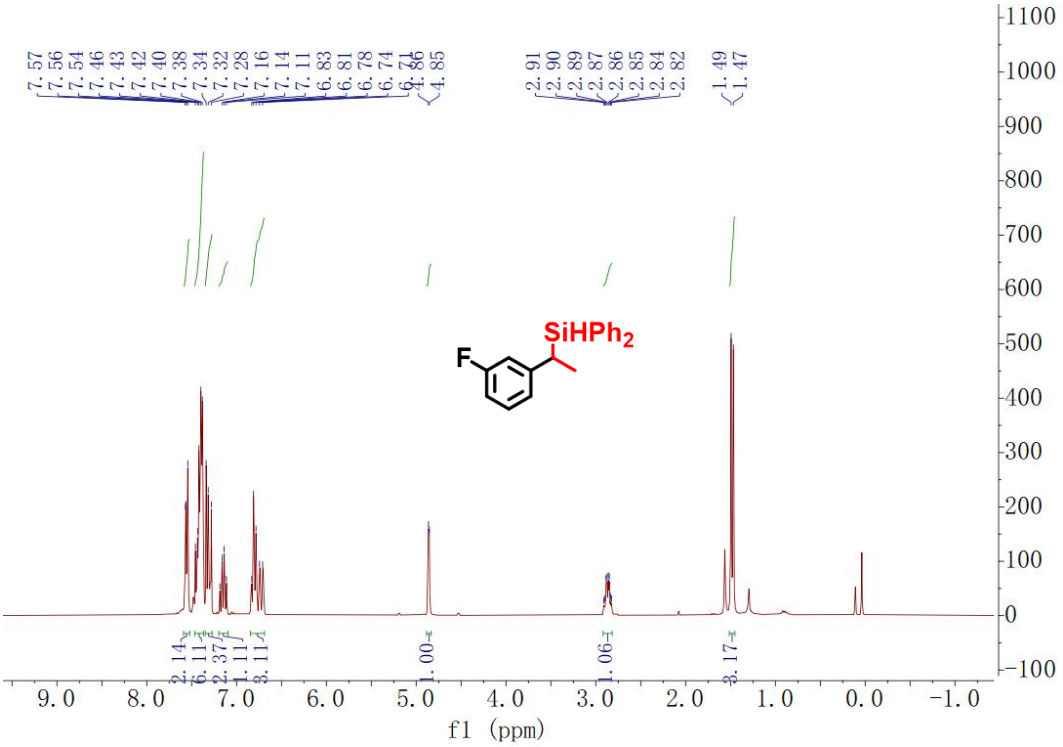


Fig.S20 $^{1}$H NMR of **4g** ($CDCl_3$)

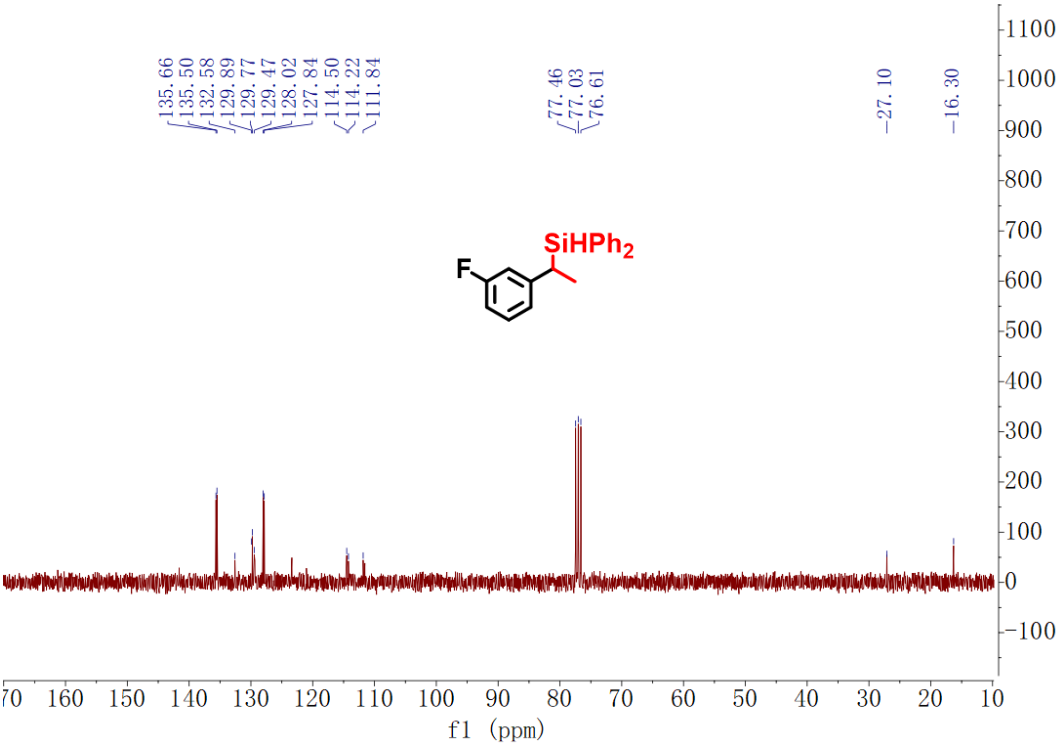


Fig.S21 $^{13}$C NMR of **4g** ($CDCl_3$)

**(1-(4-fluorophenyl)ethyl)diphenylsilane (4h)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.36 (dd, *J* = 12.5, 5.2 Hz, 6H), 7.30 – 7.23 (m, 2H), 6.94 – 6.81 (m, 4H), 4.81 (d, *J* = 3.4 Hz, 1H), 2.80 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.44 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.67, 135.53, 132.79, 129.82, 129.69, 128.90, 128.80, 127.99, 127.81, 115.02, 114.74, 77.45, 77.03, 76.61, 26.22, 16.69.

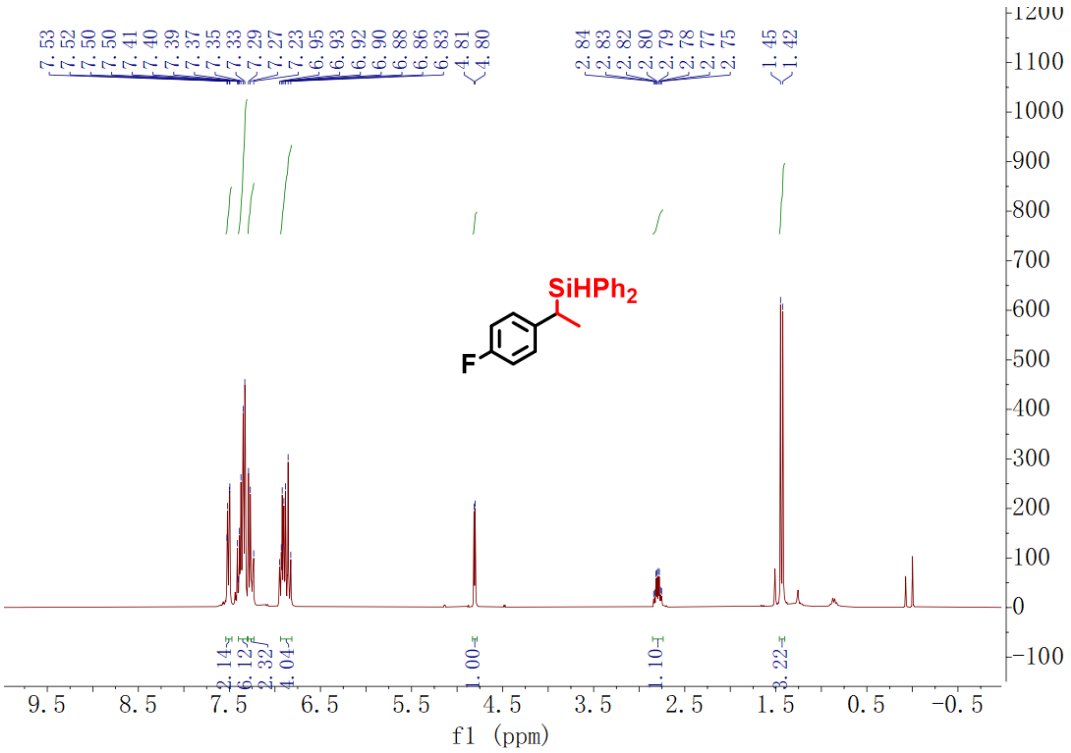


Fig.S22 $^{1}$H NMR of **4h** ($CDCl_3$)

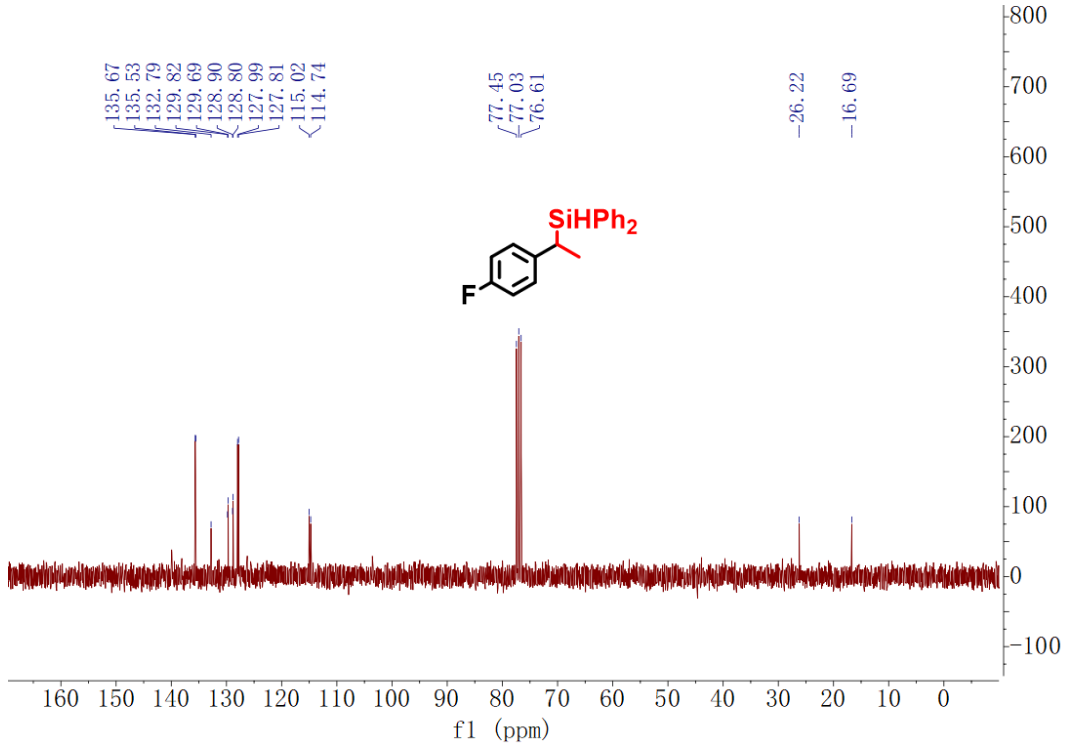


Fig.S23 $^{13}$C NMR of **4h** ($CDCl_3$)

**(1-(3-chlorophenyl)ethyl)diphenylsilane (4i)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.30 (dt, *J* = 24.5, 7.5 Hz, 8H), 7.08 – 7.02 (m, 2H), 6.96 (s, 1H), 6.88 – 6.79 (m, 1H), 4.82 (d, *J* = 2.7 Hz, 1H), 2.78 (qd, *J* = 7.2, 2.7 Hz, 1H), 1.42 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 146.70, 135.74, 135.59, 135.22, 134.06, 132.54, 130.00, 129.89, 129.37, 128.20, 128.11, 127.94, 127.79, 125.96, 125.13, 77.55, 77.13, 76.71, 27.11, 16.32.

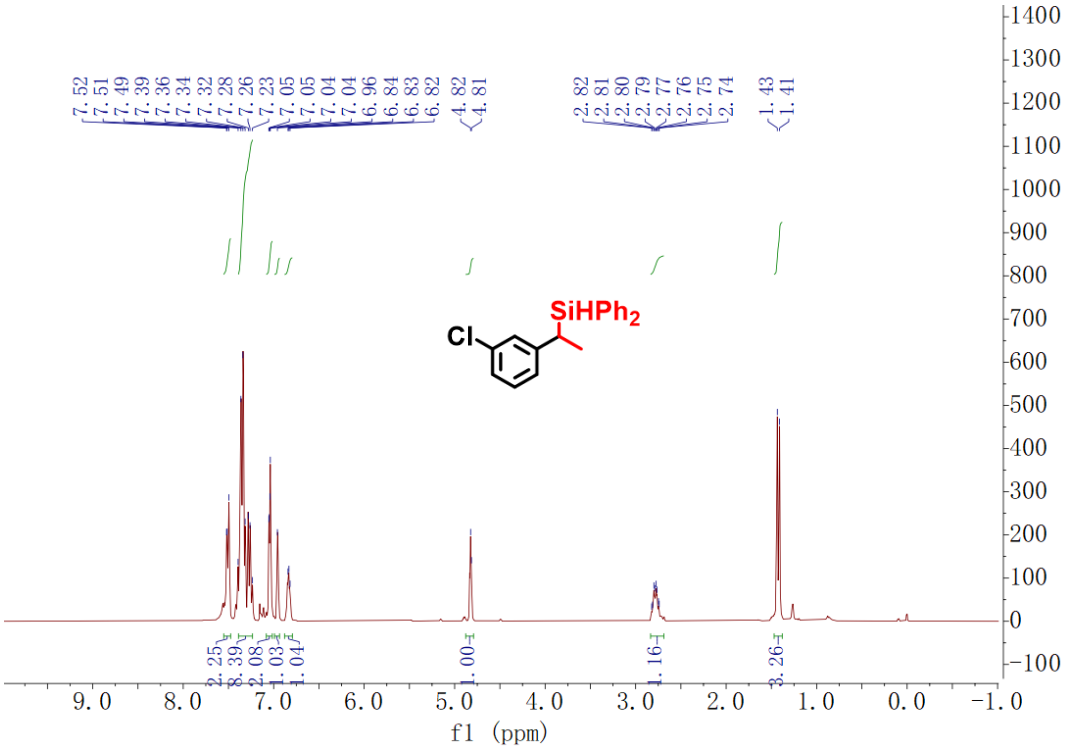


Fig.S24 $^{1}$H NMR of **4i** ($CDCl_3$)

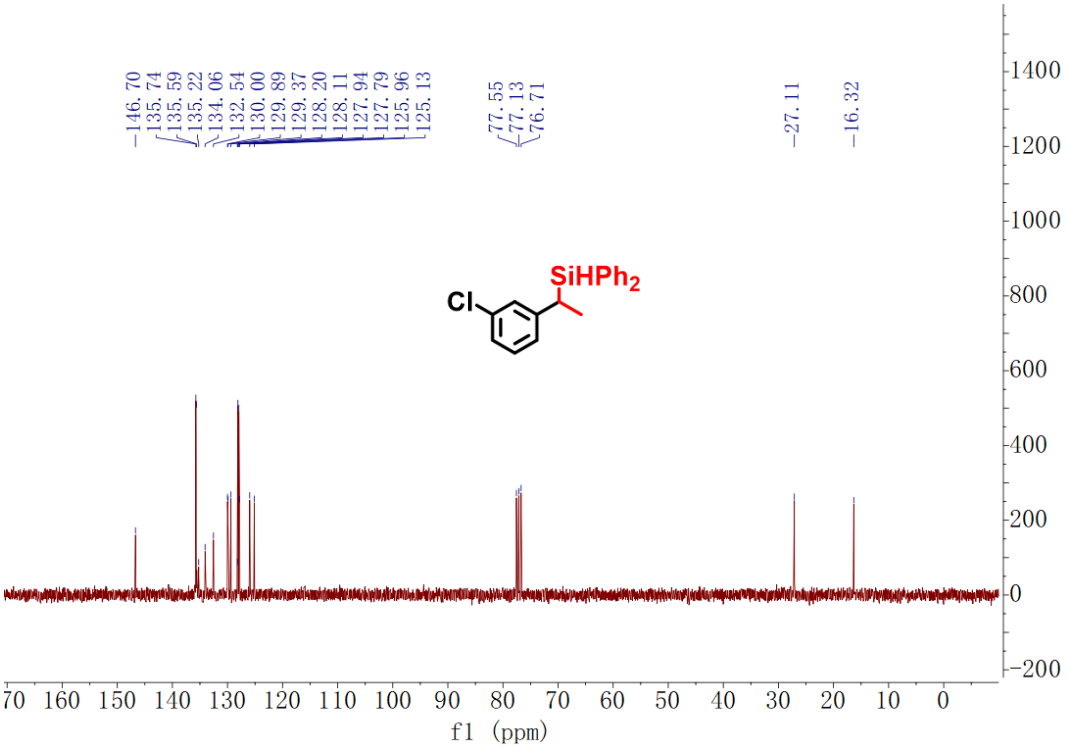


Fig.S25 $^{13}$C NMR of **4i** (CDCl3)

**(1-(4-chlorophenyl)ethyl)diphenylsilane (4j)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.38 – 7.23 (m, 8H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.73 (d, *J* = 3.3 Hz, 1H), 2.72 (tt, *J* = 7.5, 3.7 Hz, 1H), 1.35 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 143.60, 135.66, 135.52, 129.87, 129.76, 128.94, 128.21, 128.01, 127.85, 77.45, 77.03, 76.60, 26.57, 16.41.

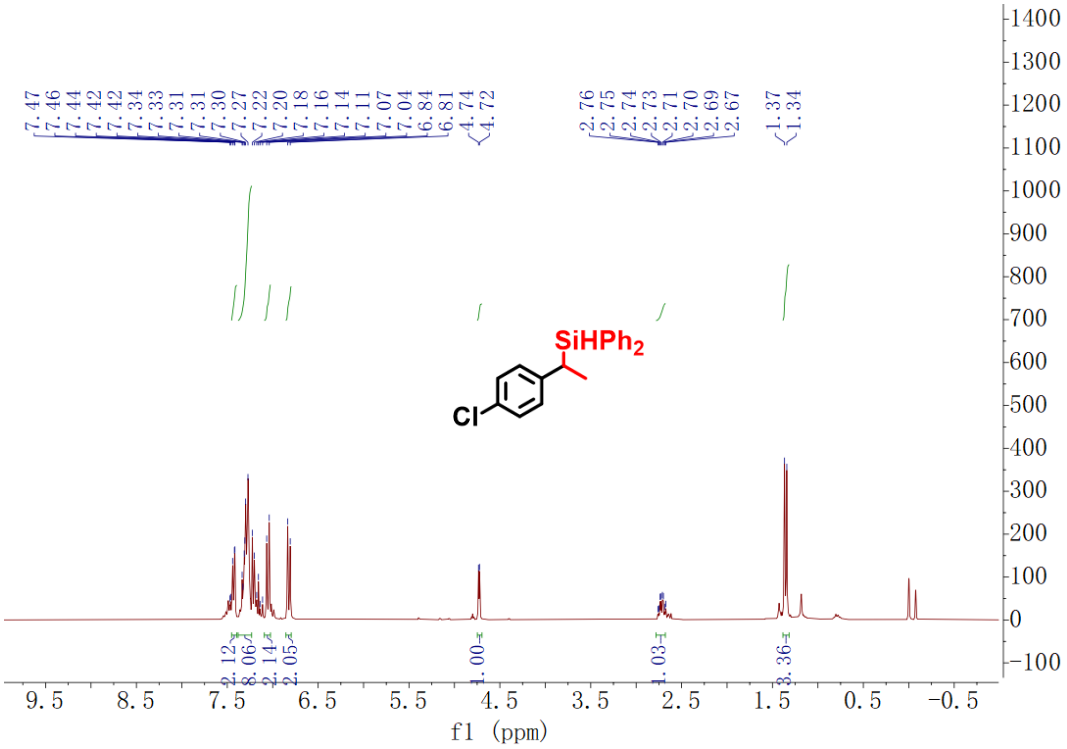


Fig.S26 $^{1}$H NMR of **4j** ($CDCl_3$)

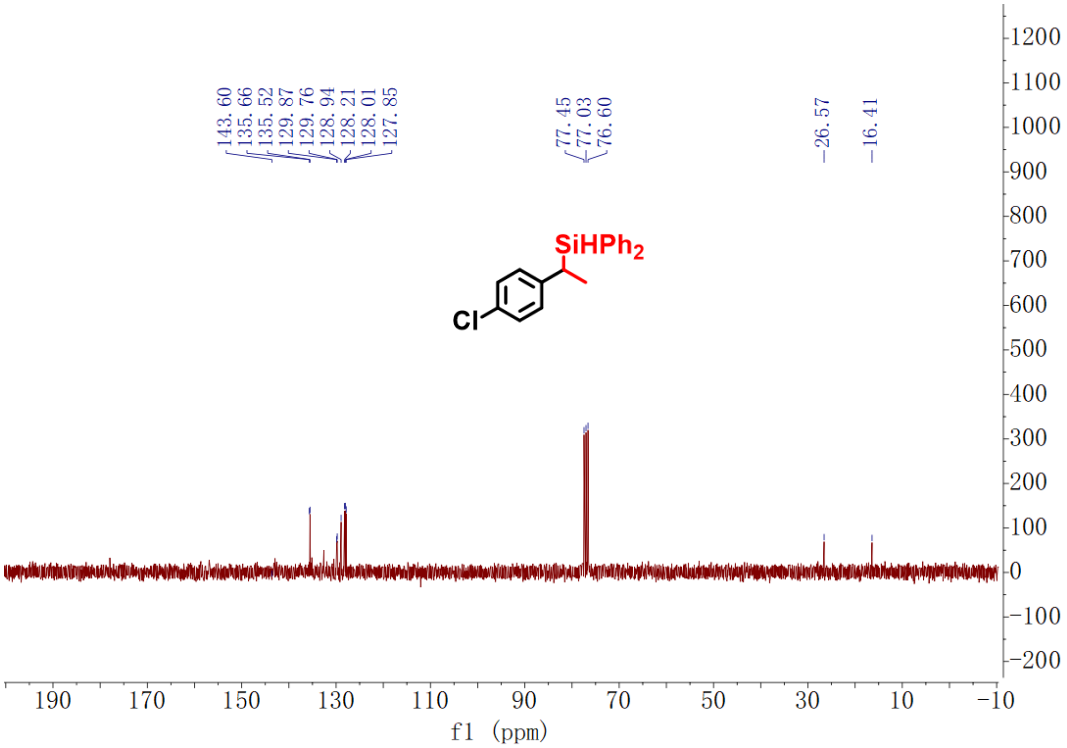


Fig.S27 $^{13}$C NMR of **4j** ($CDCl_3$)

**(1-(4-Bromophenyl)ethyl)diphenylsilane (4k)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.37 – 7.31 (m, 6H), 7.27 (dd, *J* = 7.9, 3.2 Hz, 4H), 6.83 (d, *J* = 8.4 Hz, 2H), 4.81 (d, *J* = 3.3 Hz, 1H), 2.77 (qd, *J* = 7.5, 3.3 Hz, 1H), 1.42 (d, *J* = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 143.53, 135.72, 135.58, 135.20, 132.60, 131.20, 129.94, 129.84, 129.43, 128.08, 127.93, 118.52, 77.53, 77.11, 76.69, 26.70, 16.41.

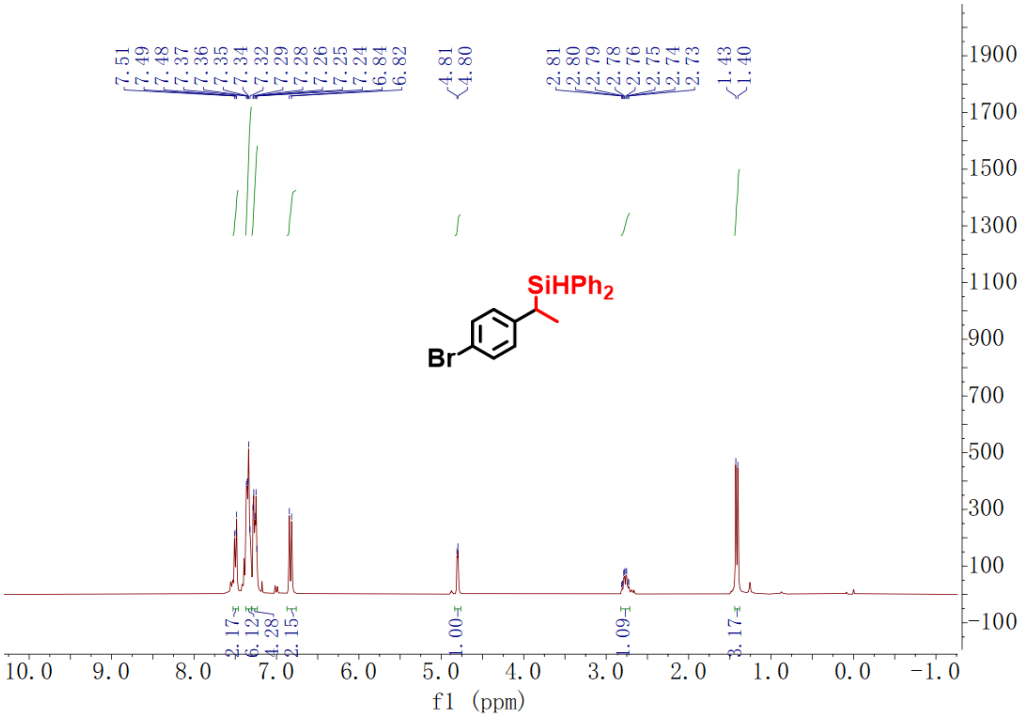


Fig.S28 $^{1}$H NMR of **4k** ($CDCl_3$)

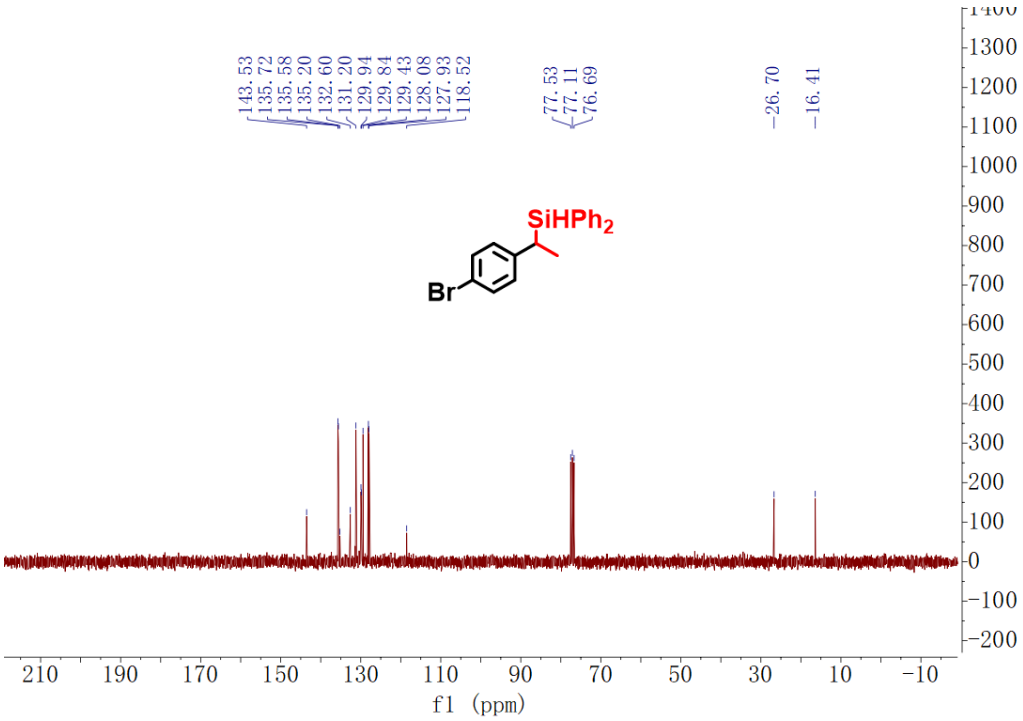


Fig.S29 $^{13}$C NMR of **4k** ($CDCl_3$)

**Diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silane (4l)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.46 (m, 2H), 7.34 (dt, *J* = 7.6, 3.9 Hz, 7H), 7.29 – 7.21 (m, 3H), 7.13 (d, *J* = 8.6 Hz, 2H), 4.82 (d, *J* = 3.1 Hz, 1H), 2.88 (qd, *J* = 7.5, 3.2 Hz, 1H), 1.47 (d, *J* = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 145.43, 135.66, 135.52, 132.25, 130.92, 130.03, 129.92, 128.49, 128.11, 127.94, 124.39, 121.74, 121.69, 78.03, 77.06, 76.64, 27.33, 16.09.

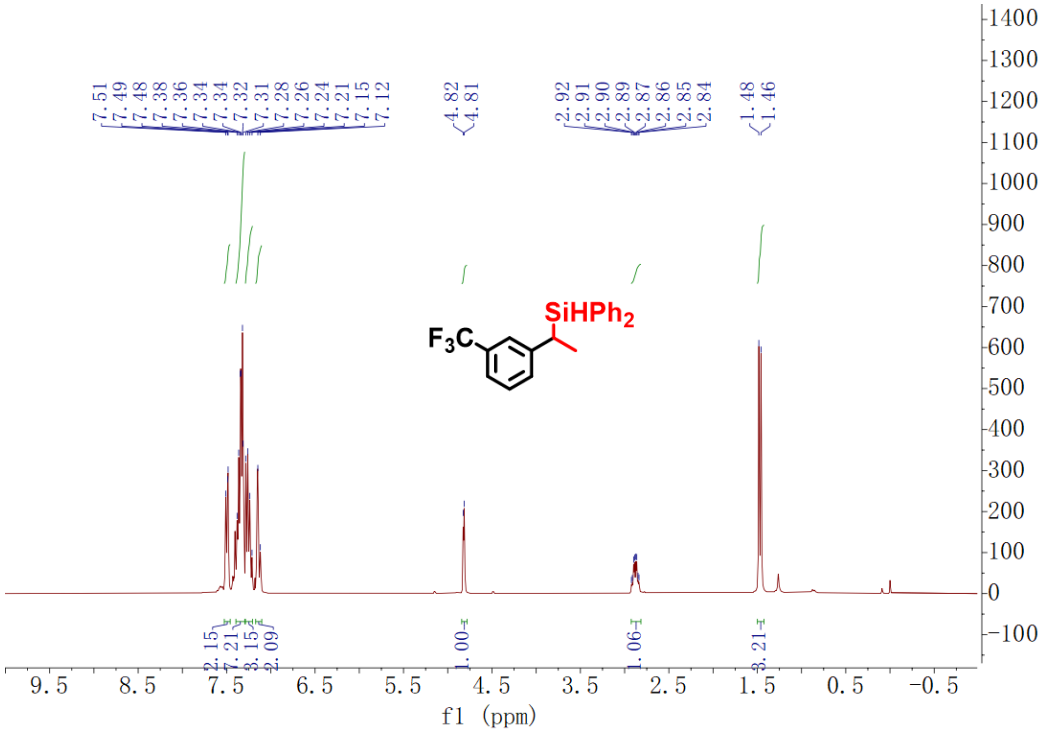


Fig.S30 $^{1}$H NMR of **4l** ($CDCl_3$)

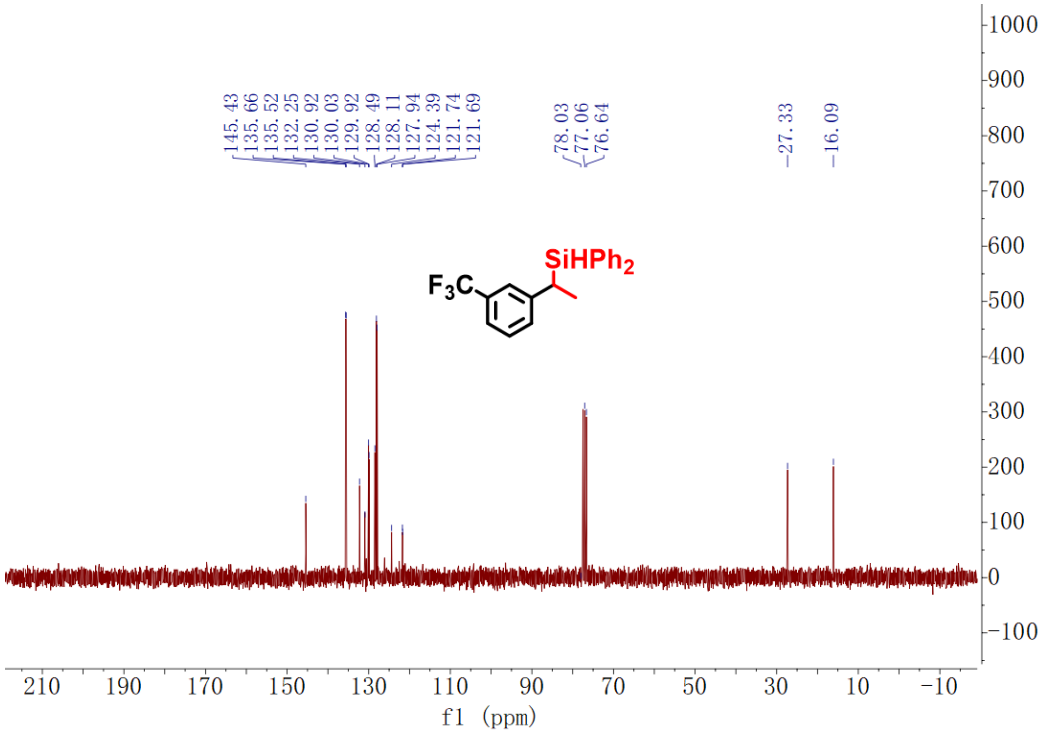


Fig.S31 $^{13}$C NMR of **4l** ($CDCl_3$)

**Diphenyl(1-(4-(trifluoromethyl)phenyl)ethyl)silane (4m)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.51 (dd, $J$ = 7.8, 1.6 Hz, 2H), 7.43 – 7.33 (m, 8H), 7.27 (dd, $J$ = 7.9, 6.5 Hz, 2H), 7.06 (d, $J$ = 8.1 Hz, 2H), 4.82 (d, $J$ = 3.2 Hz, 1H), 2.90 (qd, $J$ = 7.5, 3.2 Hz, 1H), 1.47 (d, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 148.93, 135.72, 135.54, 132.35, 132.31, 130.06, 129.94, 128.13, 127.97, 127.86, 125.11, 125.06, 77.51, 77.09, 76.66, 27.49, 16.17.

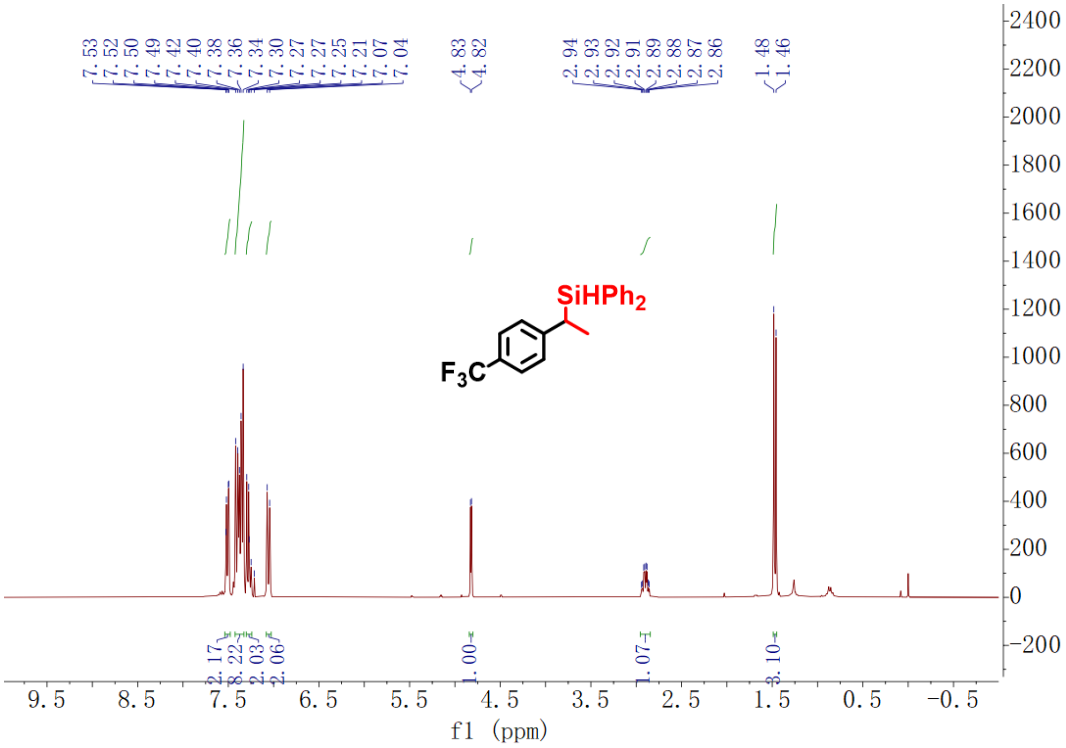


Fig.S32 $^{1}$H NMR of **4m** ($CDCl_3$)

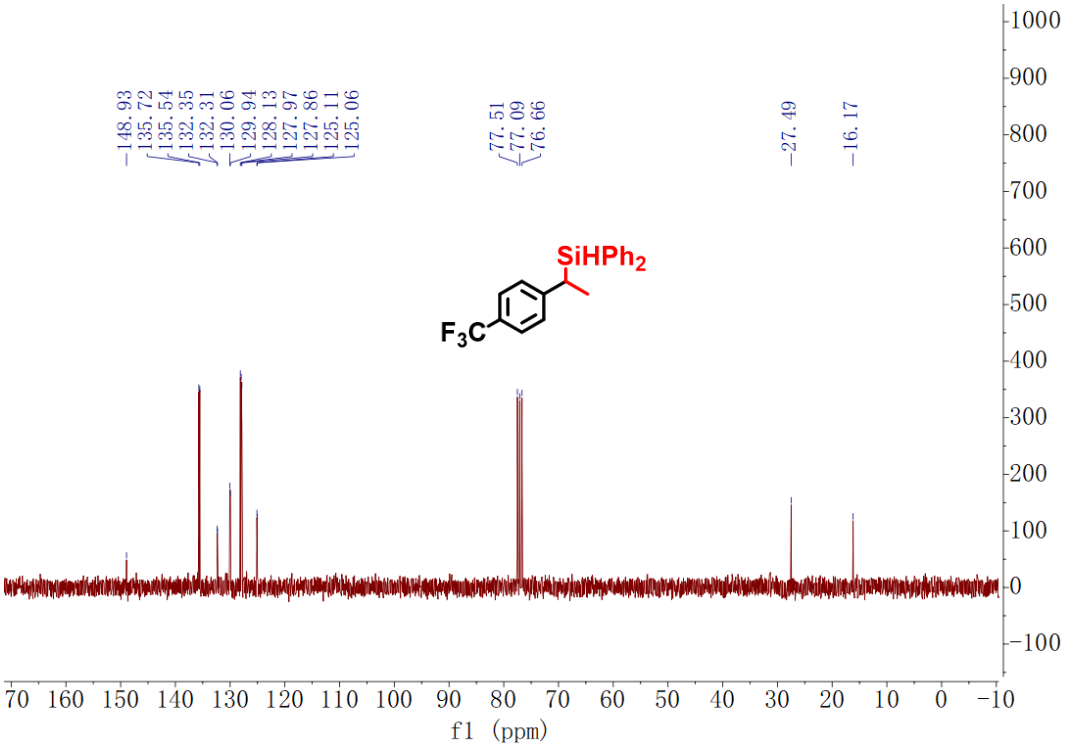


Fig.S33 $^{13}$C NMR of **4m** ($CDCl_3$)

**(1-([1,1'-biphenyl]-4-yl)ethyl)diphenylsilane (3n)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.60 – 7.51 (m, 4H), 7.45 – 7.24 (m, 13H), 7.07 (d, *J* = 8.3 Hz, 2H), 4.86 (d, *J* = 3.3 Hz, 1H), 2.87 (qd, *J* = 7.5, 3.3 Hz, 1H), 1.49 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 143.66, 141.15, 137.77, 135.83, 135.69, 133.02, 129.86, 129.73, 128.79, 128.18, 128.05, 127.87, 126.94, 126.90, 77.56, 77.13, 76.71, 26.79, 16.56.

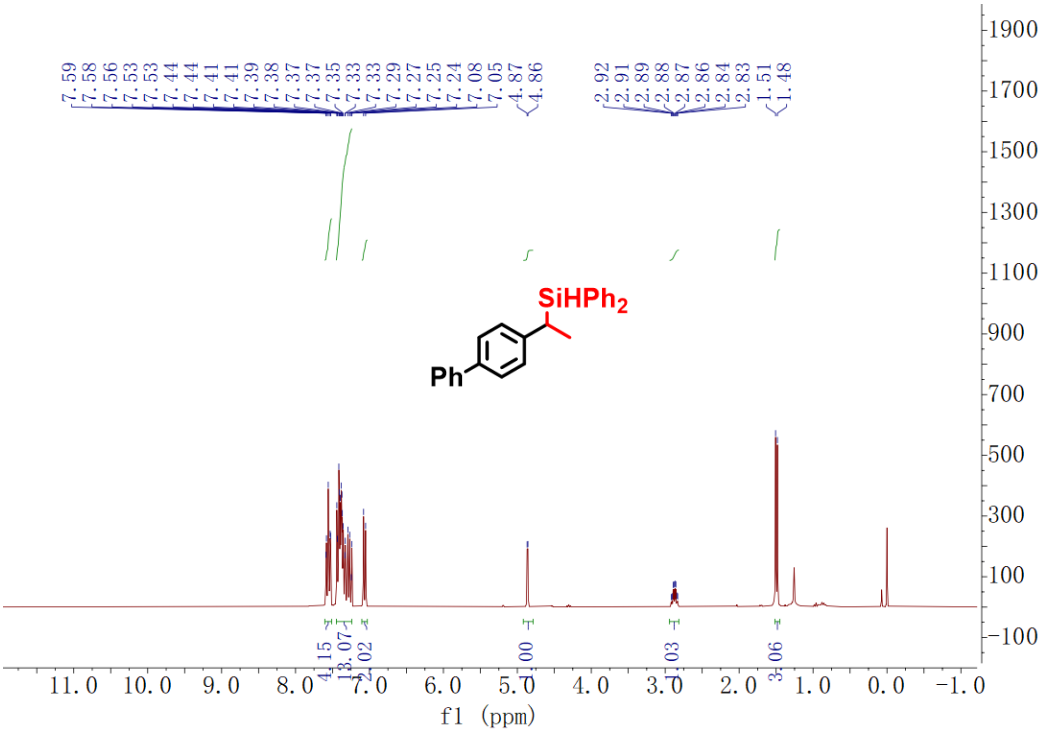


Fig.S34 $^{1}$H NMR of **4n** ($CDCl_3$)

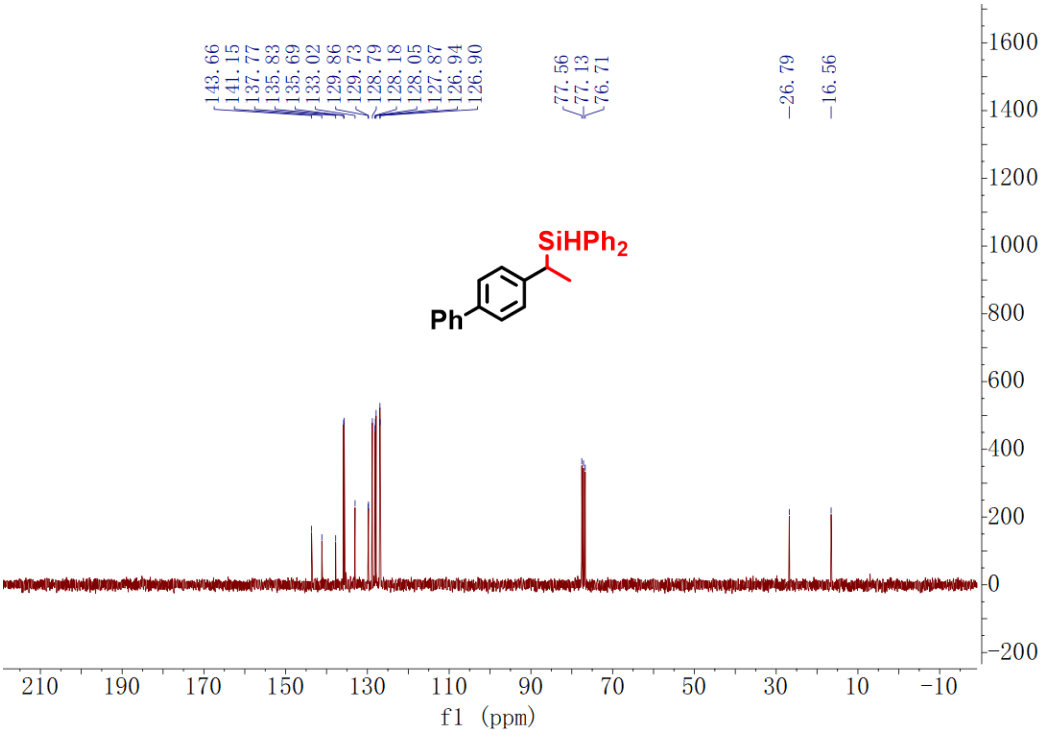


Fig.S35 $^{13}$C NMR of **4n** ($CDCl_3$)

**(1-(naphthalen-2-yl)ethyl)diphenylsilane (4o)**

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 1H), 7.67 – 7.59 (m, 2H), 7.52 (d, *J* = 6.3 Hz, 2H), 7.43 – 7.29 (m, 9H), 7.26 – 7.19 (m, 2H), 7.14 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.90 (d, *J* = 3.2 Hz, 1H), 2.99 (qd, *J* = 7.4, 3.1 Hz, 1H), 1.54 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.14, 135.81, 135.66, 133.76, 133.02, 131.63, 129.82, 129.71, 128.00, 127.84, 127.61, 127.56, 127.40, 127.32, 125.81, 125.35, 124.82, 77.52, 77.10, 76.67, 27.30, 16.66.

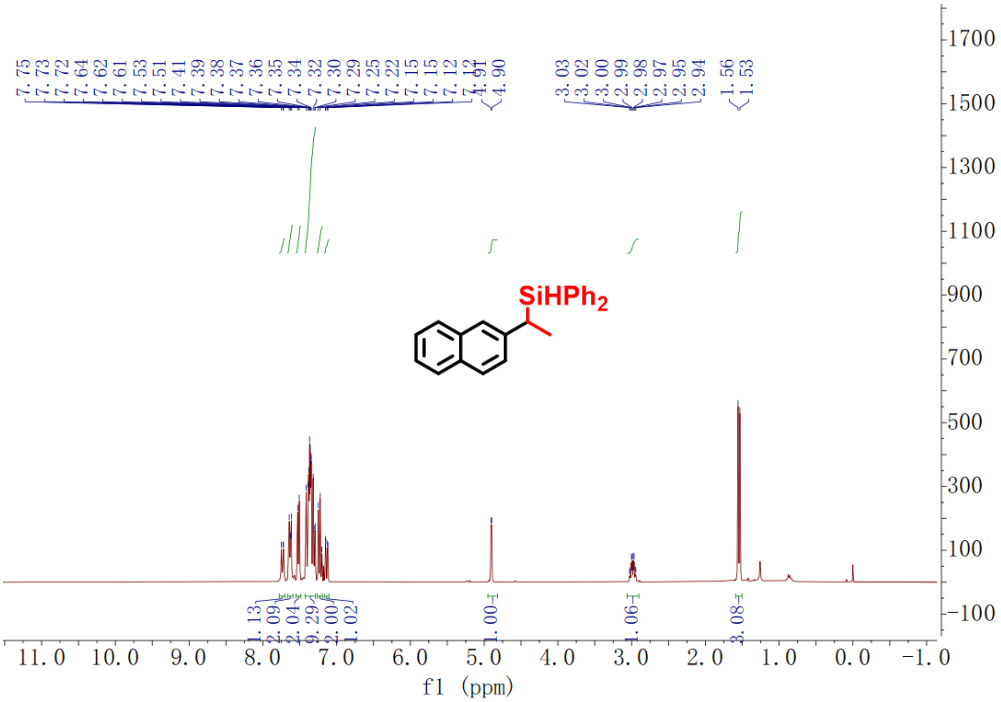


Fig.S36 $^1$H NMR of **4o** ($CDCl_3$)

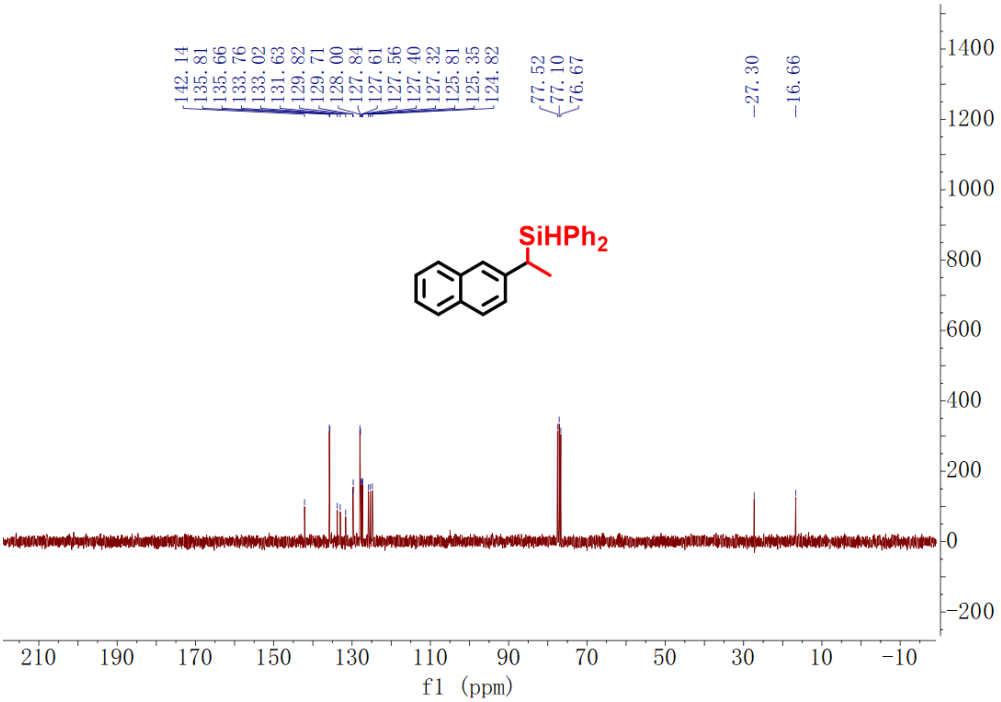


Fig.S37 $^{13}$C NMR of **4o** ($CDCl_3$)

**(1-(thiophen-2-yl) ethyl)diphenylsilane (4p)**

$^1$H NMR (300 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.45 – 7.28 (m, 8H), 6.99 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.84 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.58 (d, *J* = 3.5 Hz, 1H), 4.91 (d, *J* = 3.2 Hz, 1H), 3.12 (ddt, *J* = 10.3, 7.1, 3.2 Hz, 1H), 1.50 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 145.56, 135.69, 135.59, 132.75, 129.88, 129.81, 128.01, 127.87, 126.73, 122.83, 121.81, 77.47, 77.05, 76.63, 22.29, 18.08, 5.72.

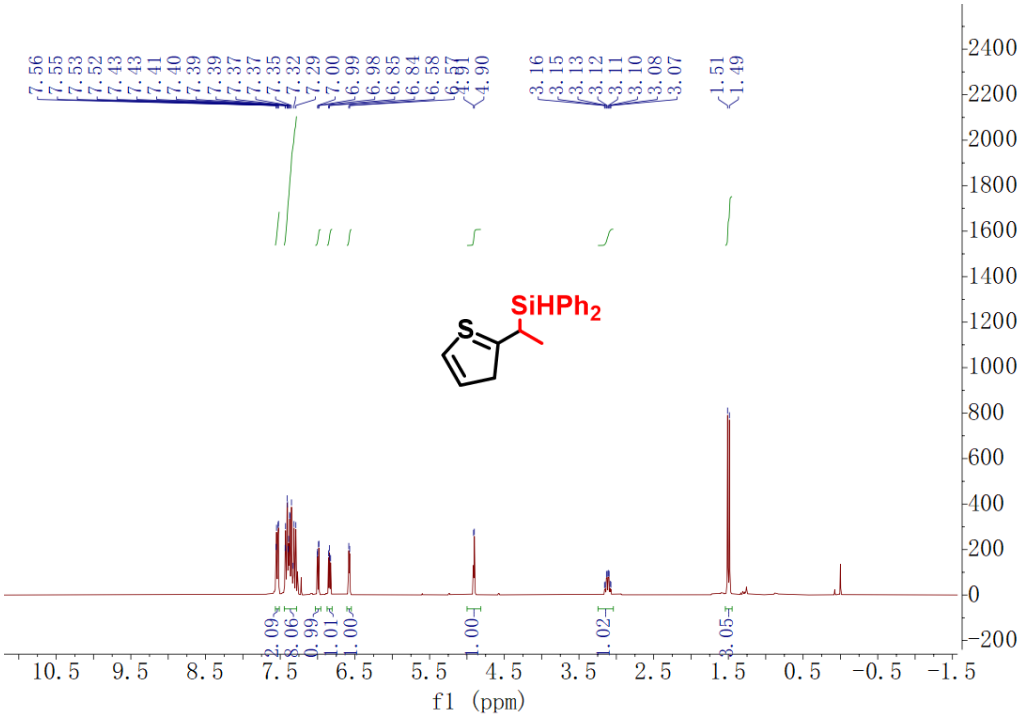


Fig.S38 $^1$H NMR of **4p** ($CDCl_3$)

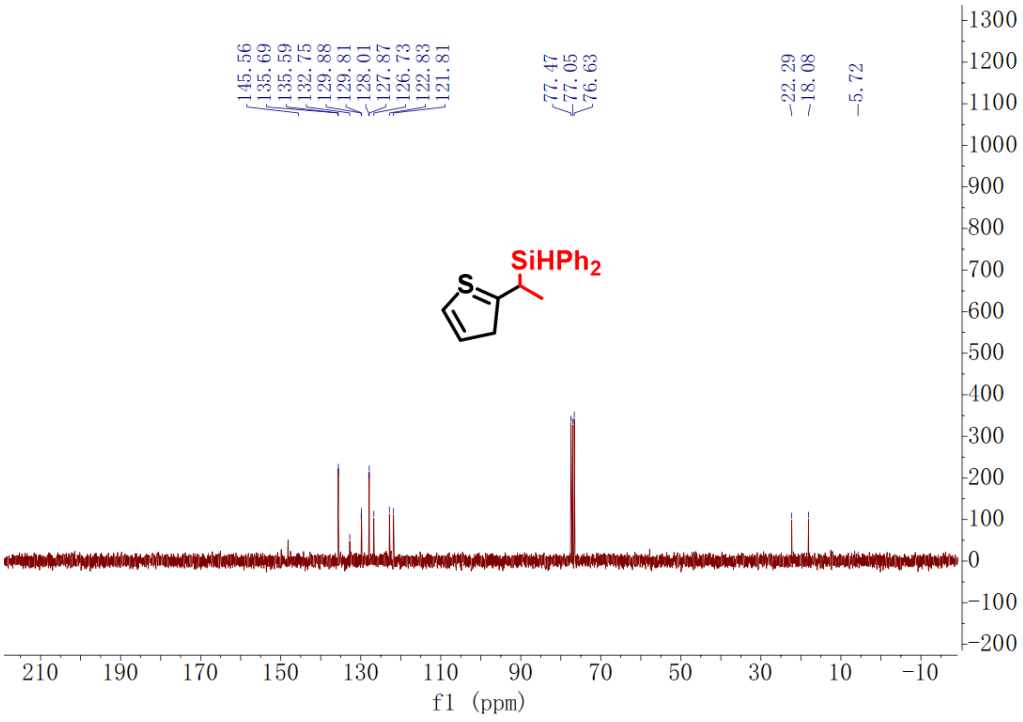


Fig.S39 $^{13}$C NMR of **4p** ($CDCl_3$)

**(n-Octyl)diphenylsilane (4q)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 4H), 7.19 (dd, *J* = 5.7, 1.8 Hz, 6H), 4.77 (t, *J* = 3.7 Hz, 1H), 1.36 (t, *J* = 7.8 Hz, 2H), 1.23 (d, *J* = 7.0 Hz, 2H), 1.16 (s, 8H), 1.06 – 0.99 (m, 2H), 0.76 (d, *J* = 5.8 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.85, 135.31, 134.89, 129.60, 128.28, 128.10, 77.58, 77.16, 76.74, 33.42, 32.19, 29.93, 29.43, 24.63, 22.94, 14.31, 12.40.

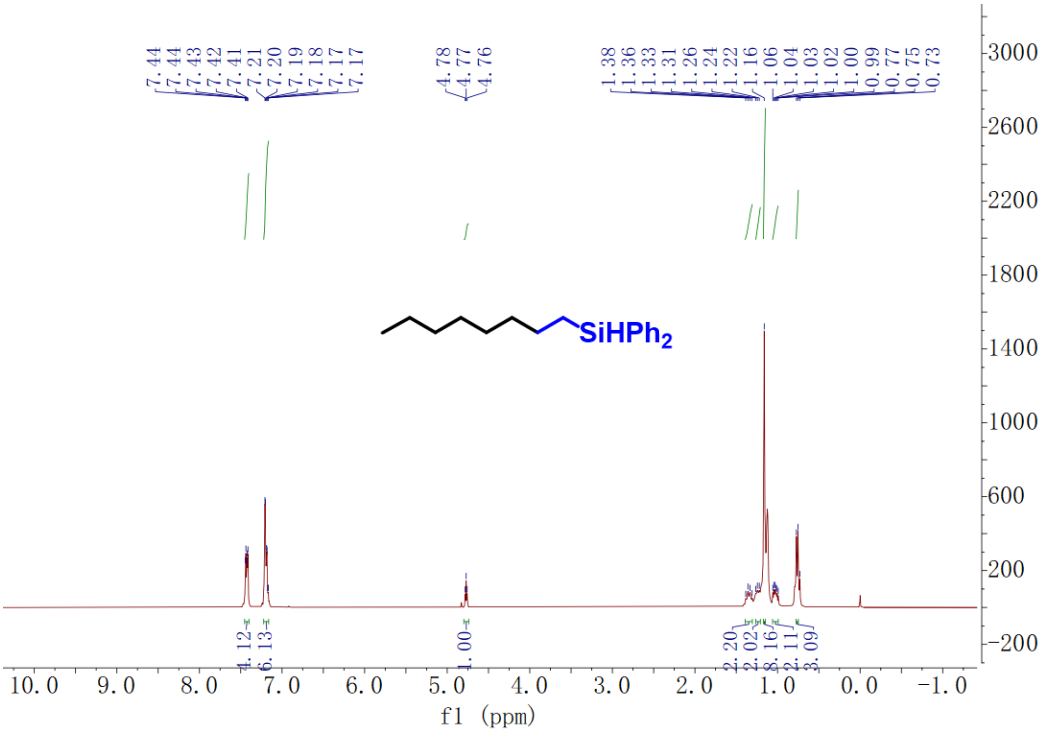


Fig.S40 $^{1}$H NMR of **4q** ($CDCl_3$)

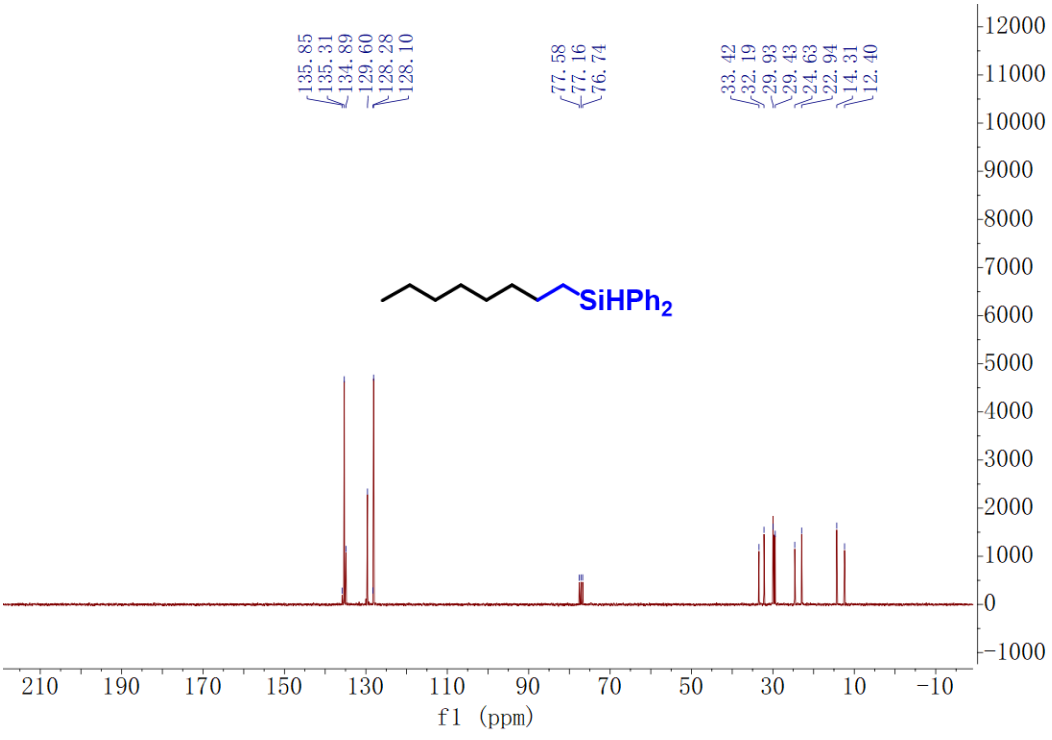


Fig.S41 $^{13}$C NMR of **4q** ($CDCl_3$)

**(6-Chlorohexyl)phenylsilane (4r)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.38 – 7.31 (m, 6H), 4.85 (t, $J$ = 3.7 Hz, 1H), 3.46 (t, $J$ = 6.7 Hz, 2H), 1.70 (p, $J$ = 6.8 Hz, 2H), 1.49 – 1.34 (m, 6H), 1.18 – 1.10 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.18, 134.58, 129.60, 128.05, 77.53, 77.11, 76.69, 45.15, 32.56, 32.37, 26.52, 24.32, 12.14.

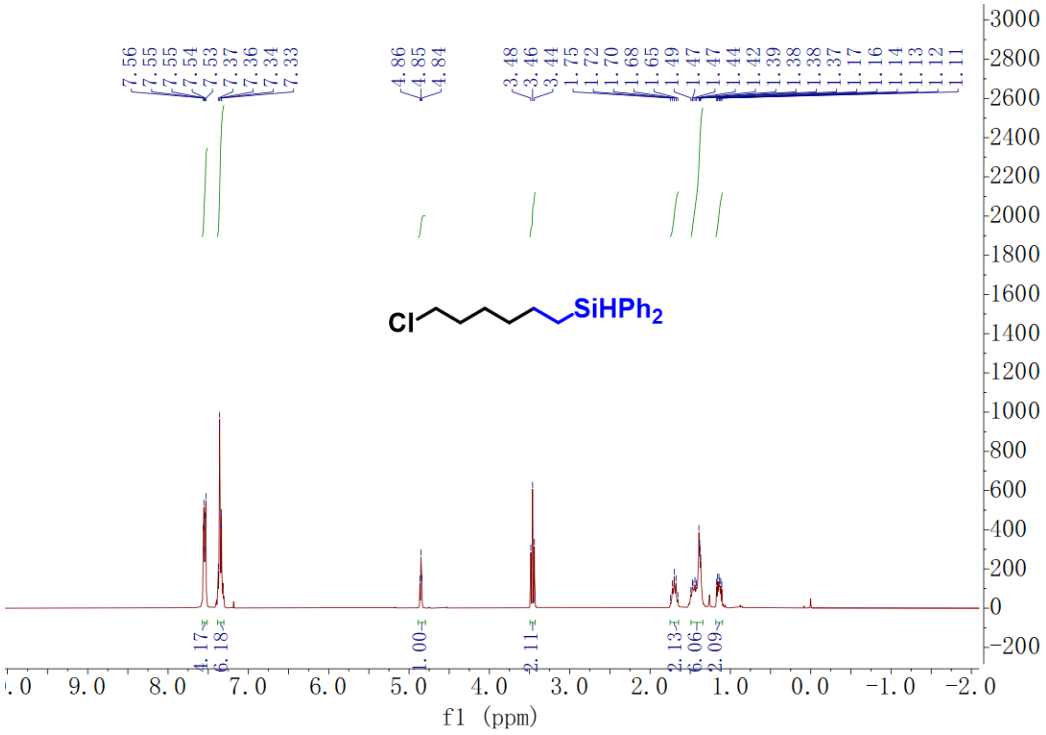


Fig.S42 $^{1}$H NMR of **4r** ($CDCl_3$)

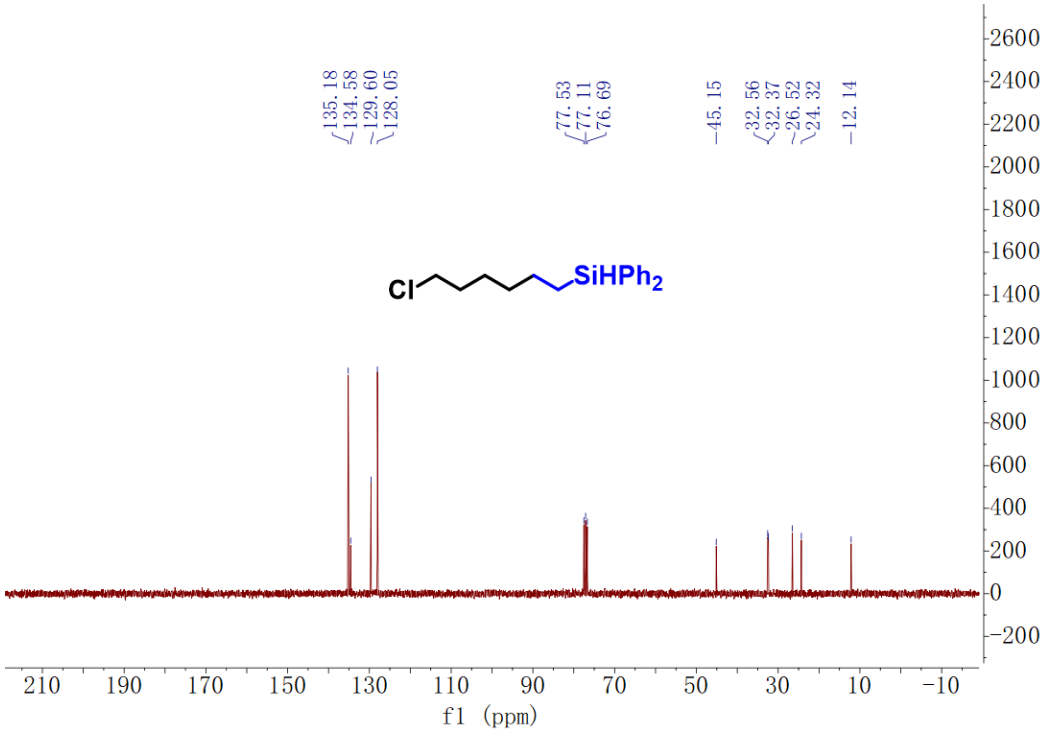


Fig.S43 $^{13}$C NMR of **4r** ($CDCl_3$)

**(2-cyclohexylethyl)diphenylsilane (4t)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.57 – 7.51 (m, 4H), 7.33 (d, *J* = 6.0 Hz, 6H), 4.84 (t, *J* = 3.3 Hz, 1H), 1.69 (t, *J* = 14.9 Hz, 5H), 1.32 (dd, *J* = 8.4, 6.0 Hz, 2H), 1.22 – 1.07 (m, 6H), 0.83 (q, *J* = 11.6, 10.5 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.20, 134.80, 129.52, 128.20, 128.01, 77.51, 77.09, 76.67, 40.55, 32.99, 31.92, 26.83, 26.48, 9.28.

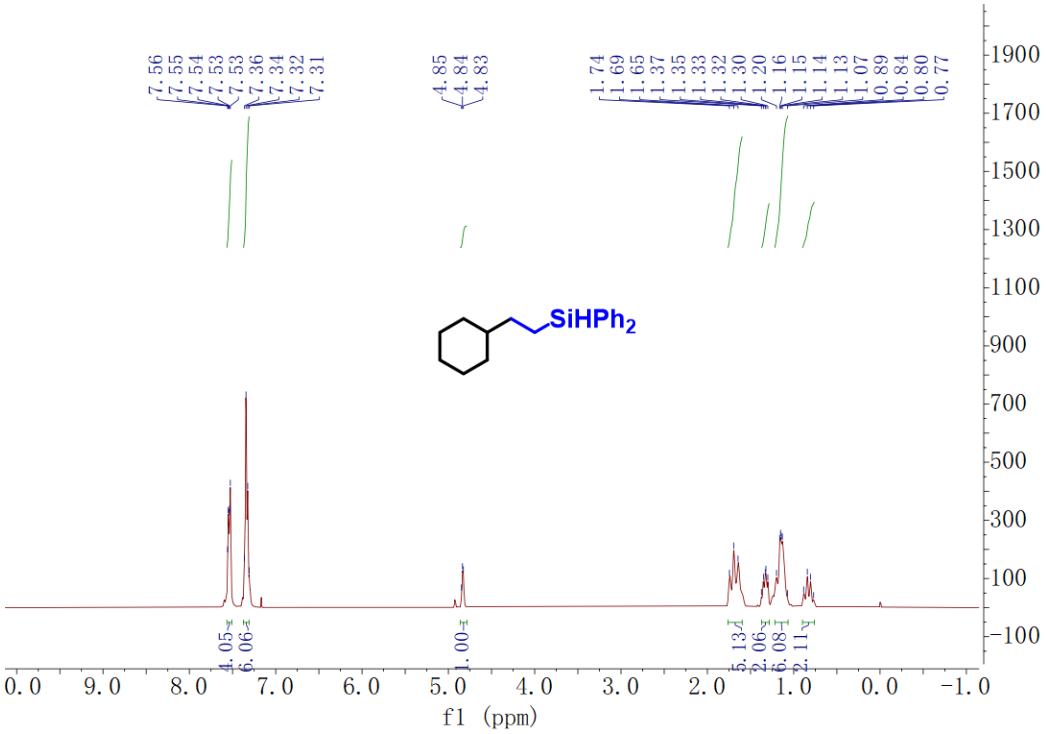


Fig.S44 $^{1}$H NMR of **4t** ($CDCl_3$)

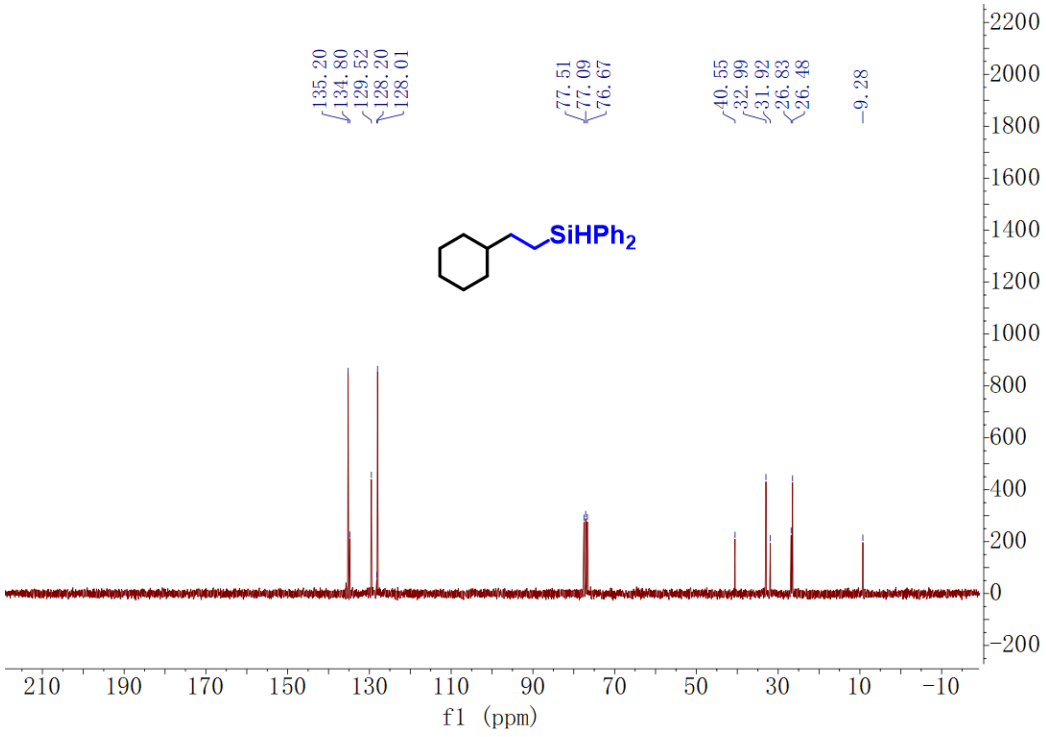


Fig.S45 $^{13}$C NMR of **4t** ($CDCl_3$)

**(2-(cyclohex-3-en-1-yl)ethyl)diphenylsilane (4u)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 4H), 7.34 (d, *J* = 6.1 Hz, 6H), 5.63 (d, *J* = 2.5 Hz, 2H), 4.86 (t, *J* = 3.7 Hz, 1H), 2.17 – 2.06 (m, 1H), 2.00 (d, *J* = 4.0 Hz, 2H), 1.74 (d, *J* = 14.3 Hz, 1H), 1.69 – 1.57 (m, 1H), 1.56 – 1.47 (m, 1H), 1.46 – 1.37 (m, 2H), 1.22 – 1.11 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 135.23, 134.69, 129.61, 128.08, 127.15, 126.66, 77.56, 77.14, 76.72, 36.45, 31.67, 31.21, 28.55, 25.42, 9.37.

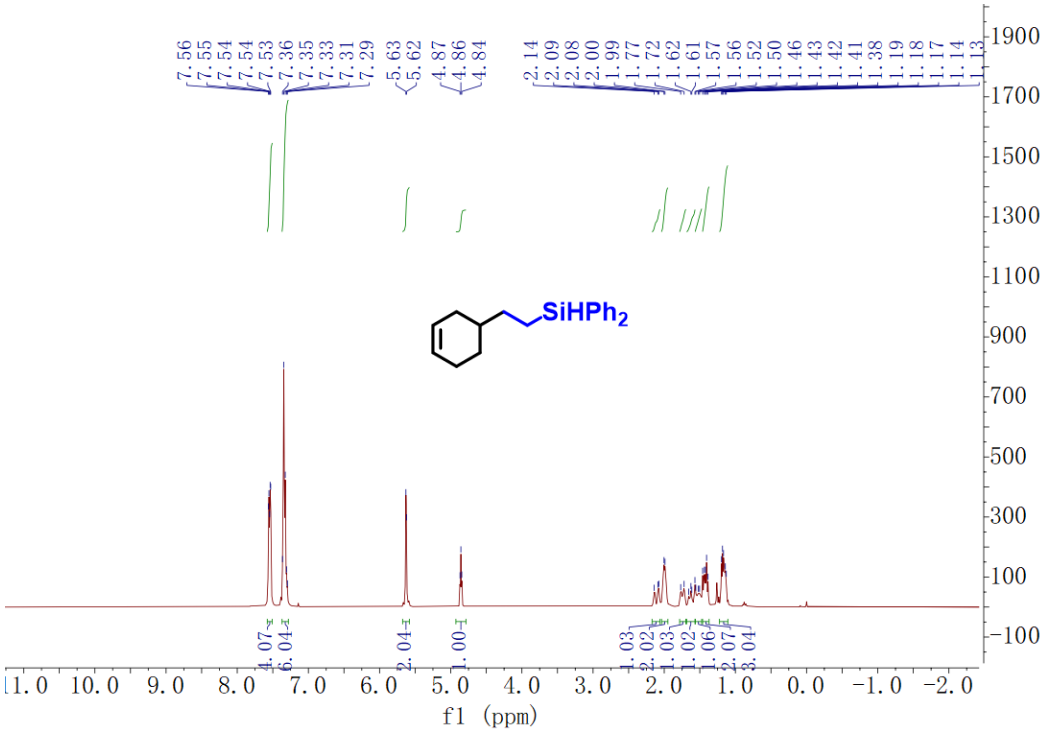


Fig.S46 $^{1}$H NMR of **4u** ($CDCl_3$)

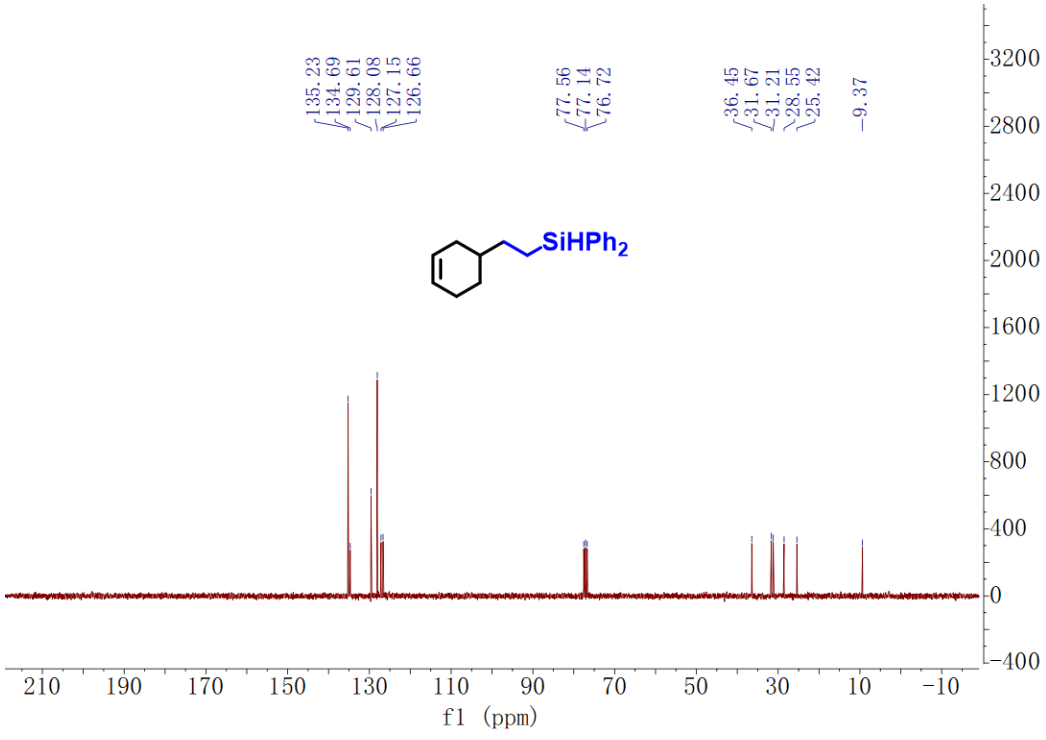


Fig.S47 $^{13}$C NMR of **4u** ($CDCl_3$)

**Diphenyl (4-phenylbutyl)silane (4x)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 4H), 7.20 (d, *J* = 7.1 Hz, 6H), 7.10 (t, *J* = 7.2 Hz, 2H), 7.04 – 6.96 (m, 3H), 4.77 (t, *J* = 3.7 Hz, 1H), 2.48 – 2.39 (m, 2H), 1.57 (p, *J* = 7.2 Hz, 2H), 1.46 – 1.34 (m, 2H), 1.05 (dt, *J* = 11.5, 3.8 Hz, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.80, 135.38, 134.74, 129.77, 128.61, 128.48, 128.23, 125.84, 77.72, 77.29, 76.87, 35.74, 35.09, 24.35, 12.27.

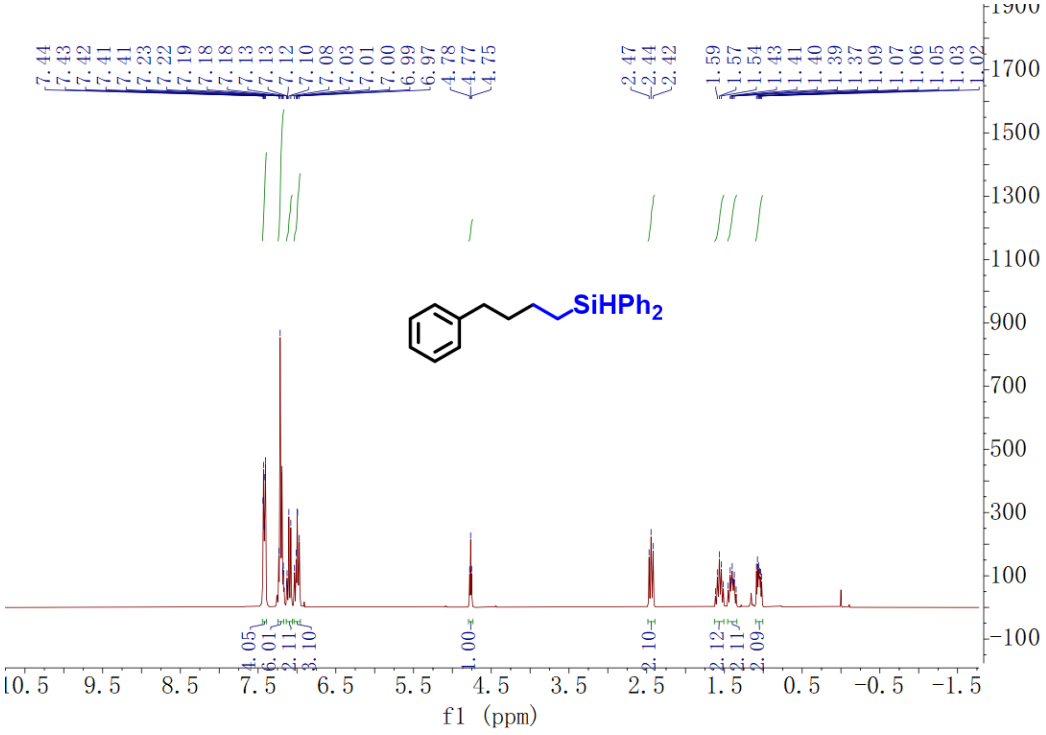


Fig.S48 $^{1}$H NMR of **4x** ($CDCl_3$)

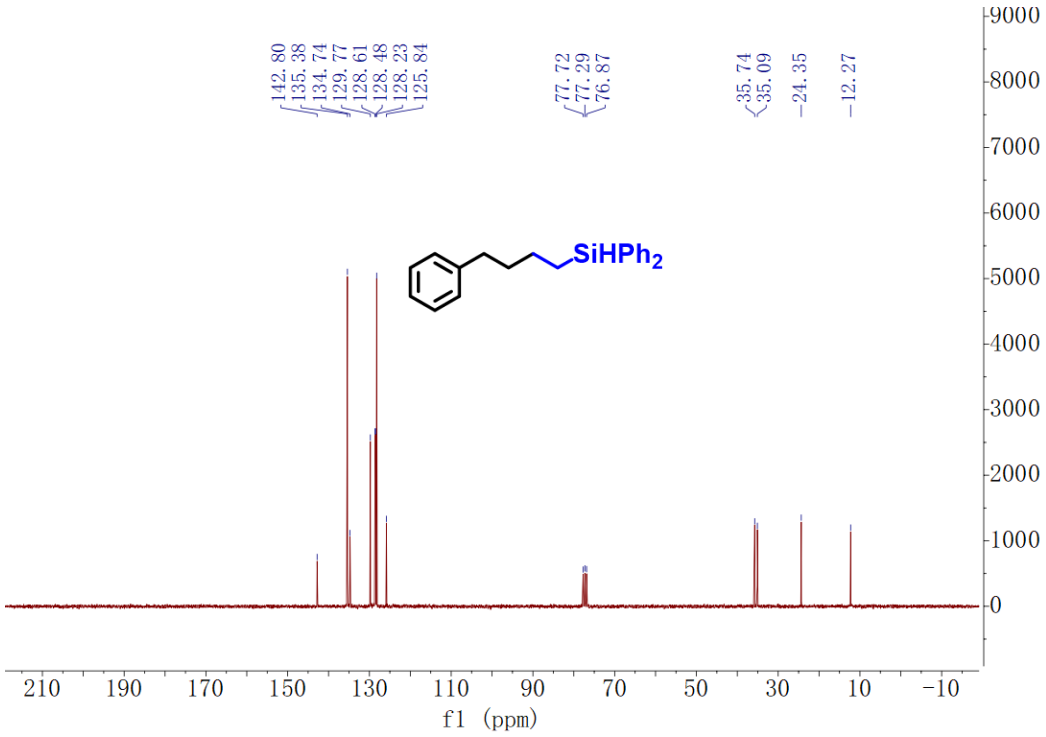


Fig.S49 $^{13}$C NMR of **4x** ($CDCl_3$)

**Diphenyl(3-phenylpropyl)silane (4y)**

$^{1}$H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.3, 1.9 Hz, 4H), 7.37 – 7.29 (m, 6H), 7.23 (t, *J* = 7.1 Hz, 2H), 7.13 (dd, *J* = 13.1, 7.4 Hz, 3H), 4.87 (t, *J* = 3.7 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.78 (p, *J* = 8.7, 8.3 Hz, 2H), 1.20 – 1.11 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 142.26, 135.26, 134.49, 129.67, 128.65, 128.37, 128.11, 125.85, 77.57, 77.15, 76.73, 39.36, 26.43, 11.97.

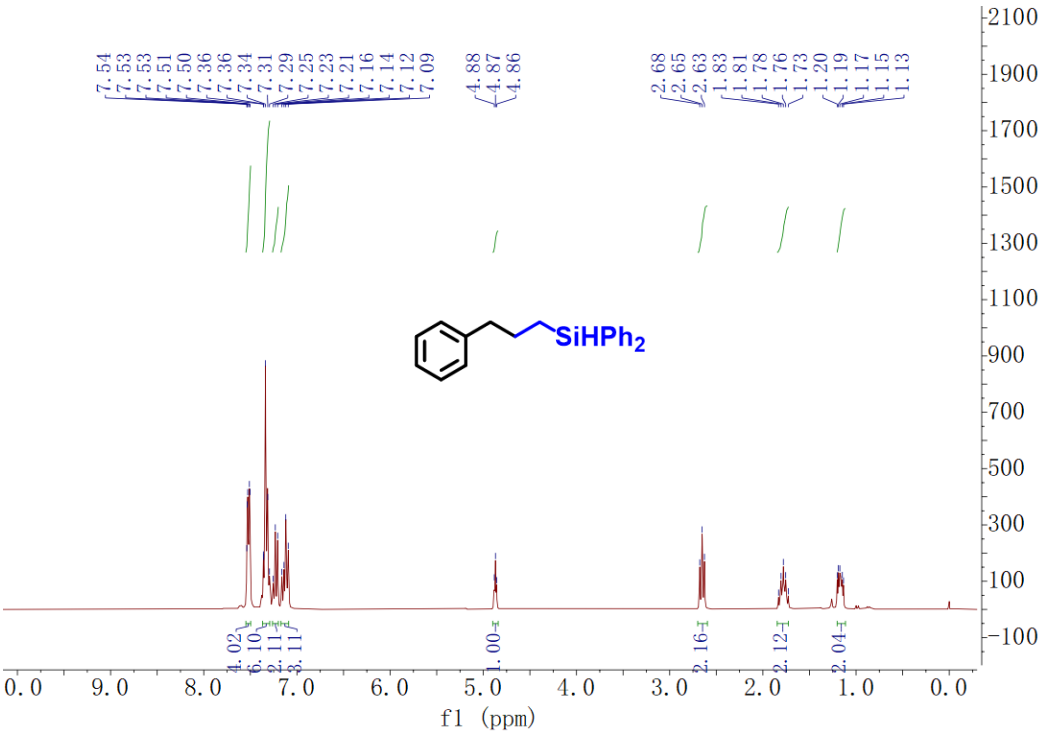


Fig.S50 $^{1}$H NMR of **4y** ($CDCl_3$)

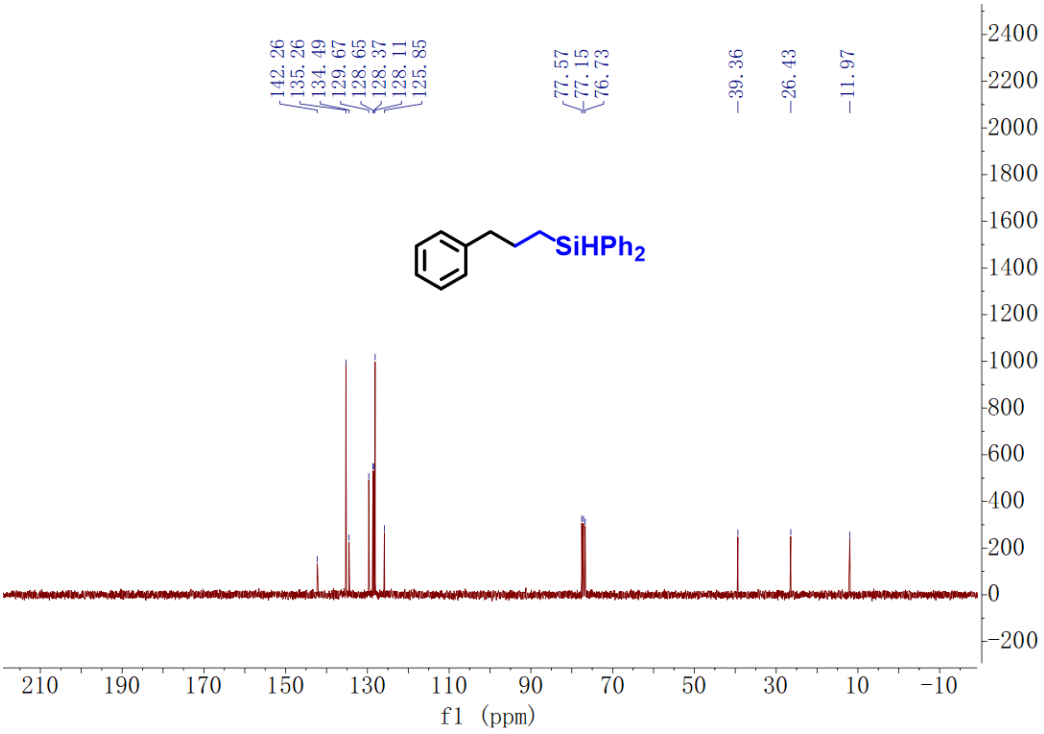


Fig.S51 $^{13}$C NMR of **4y** ($CDCl_3$)

**SIII**. Mechanistic study

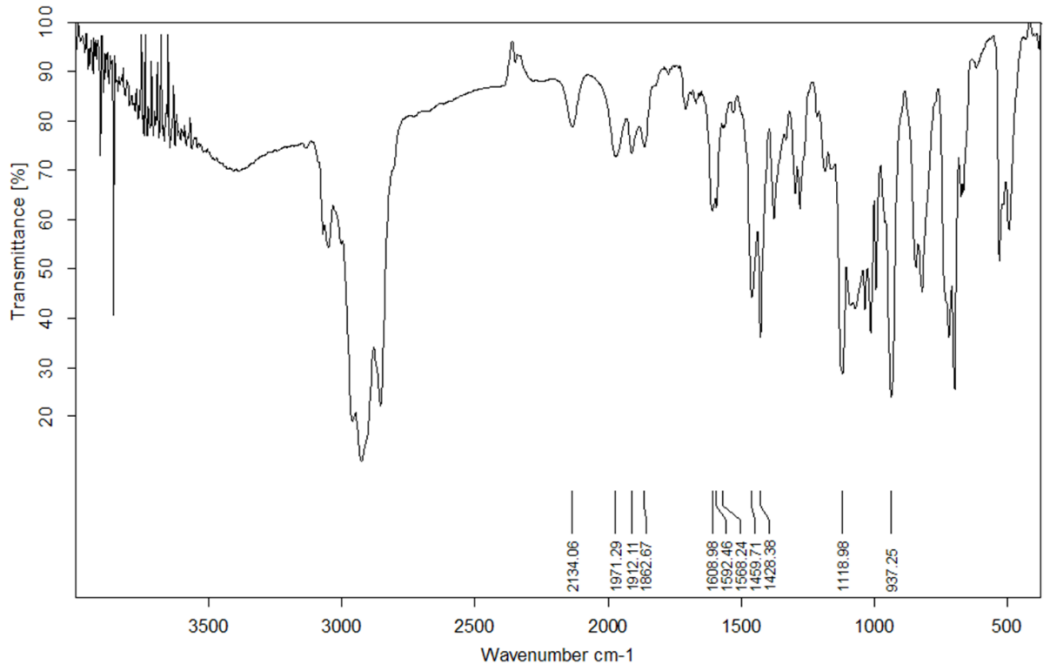


Fig. S52 IR spectrum of the reaction of complex **1** with $SiH_2Ph_2$ for 20 min.

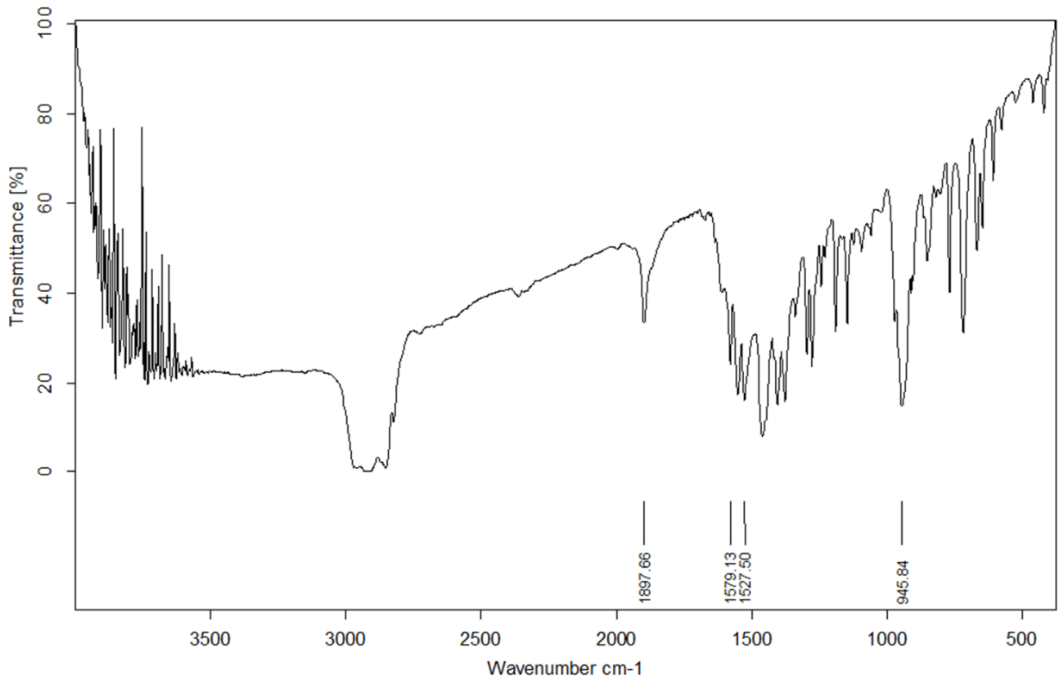


Fig. S53 IR spectrum of the reaction of complex **1** with styrene for 1 h

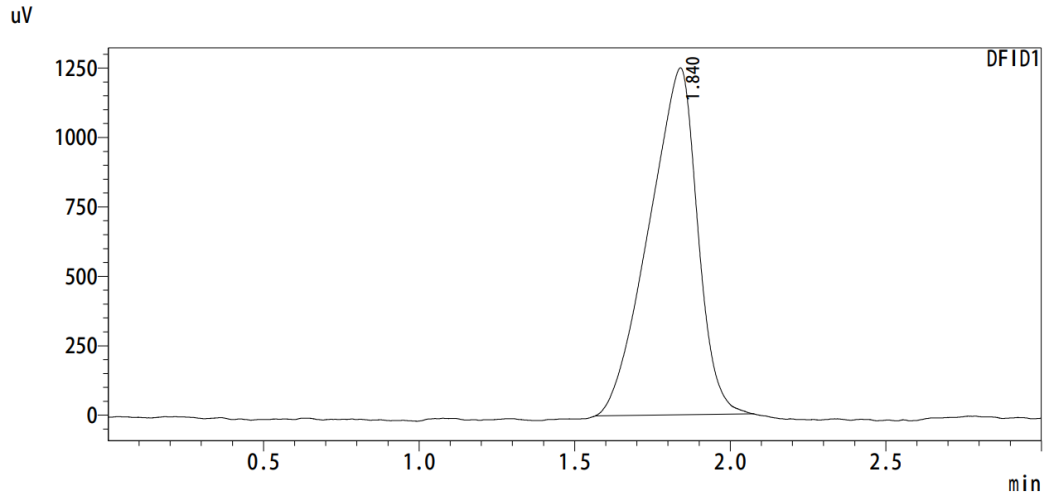


Fig. S54 Formation of dihydrogen in the reaction of complex **1** and $Ph_2SiH_2$ was confirmed by GC.

**SIV** The competitive intermolecular catalytic hydrosilylation of styrene and vinyl cyclohexane

Catalyst **1** (1% mol) was added to a 20mL-Schlenk tube containing a magnetic stirrer under a nitrogen atmosphere. Then styrene (0.104 g, 1.0 mmol), vinyl cyclohexane (0.11 g, 1.0 mmol), diphenylsilane (0.18 g, 1.0 mmol), and *n*-dodecane (0.17 g, 1.0 mmol) were added to the tube in sequence. The mixture was stirred at 50 °C for 1 h. The reaction products were analyzed using GC.

**SV** Gram-Scale Reaction

Under a nitrogen atmosphere catalyst **1** (1% mol) was added to a 20mL-Schlenk tube containing magnetic stirrer. Then styrene (1.04 g, 10.0 mmol) and diphenylsilane (2.21 g, 12.0 mmol) were added to this tube in sequence. The mixture was stirred at 50 °C for 1 h. The generated mixture was quenched with ethyl acetate and the solvents were evaporated. Using petroleum ether as the eluent, 2.65 g (b: l = 99:1) of the product was separated by column chromatography.