**Supporting Information**

# [CNC]-Pincer Cobalt Hydride Catalysed Distinct Selective Hydrosilylation of Aryl Alkene and Alkyl Alkene

Shangqing Xie,[a] Xiaoyan Li, [a,*] Hongjian Sun,[a,*] Olaf Fuhr,[b] Dieter Fenske[b]

[a]*School of Chemistry and Chemical Engineering, Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, Shandong University, Shanda Nanlu 27, 250199 Jinan, People's Republic of China*
[b]*Institut für Nanotechnologie (INT) und Karlsruher Nano-Micro-Facility (KNMF), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

corresponding author: xli63@sdu.edu.cn；hjsun@sdu.edu.cn

## Table of Contents

## 1. Crystallographic Data for Complexes 3b, 4a and 4b

**Table S1** Crystallographic Data for **3b**

| | **3b** |
|---|---|
| Empirical formula | $C_{26}H_{34}CoN_3P_2$ |
| Formula weight | 509.43 |
| Temperature/K | 150.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 14.2089(2) |
| b/Å | 12.0651(2) |
| c/Å | 15.0485(2) |
| α/° | 90 |
| β/° | 104.0750(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 2502.34(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.352 |
| μ/mm$^{-1}$ | 4.637 |
| F(000) | 1072.0 |
| Crystal size/mm$^3$ | 0.2 × 0.06 × 0.04 |
| Radiation | GaKα (λ = 1.34143) |
| 2Θ range for data collection/° | 5.578 to 124.99 |
| Reflections collected | 26605 |
| Independent reflections | 5984 [$R_{int}$ = 0.0139, $R_{sigma}$ = 0.0098] |
| Data/restraints/parameters | 5609 |
| Goodness-of-fit on $F^2$ | 5984/0/300 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0263, w$R_2$ = 0.0715 |
| Final R indexes [all data] | $R_1$ = 0.0289, w$R_2$ = 0.0732 |

**Table S2** Crystallographic Data for **4a** and **4b**

| | **4a** | **4b** |
|---|---|---|
| Empirical formula | $C_{46}H_{44}CoN_6$ | $C_{42}H_{37}CoN_6O_{0.5}$ |
| Formula weight | 739.80 | 692.70 |
| Temperature/K | 150.15 | 150.15 |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | C2/c |
| a/Å | 12.3251(6) | 28.6899(16) |
| b/Å | 13.7981(7) | 13.5418(8) |
| c/Å | 14.1475(8) | 23.9052(19) |
| α/° | 62.572(4) | 90 |
| β/° | 70.605(4) | 132.036(4) |
| γ/° | 63.850(4) | 90 |
| Volume/Å$^3$ | 1891.6(2) | 6898.0(8) |
| Z | 2 | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.299 | 1.334 |
| μ/mm$^{-1}$ | 2.653 | 2.894 |
| F(000) | 778.0 | 2896.0 |
| Crystal size/mm$^3$ | 0.2 × 0.18 × 0.04 | 0.28 × 0.27 × 0.25 |
| Radiation | GaKα (λ = 1.34143) | GaKα (λ = 1.34143) |
| 2Θ range for data collection/° | 6.206 to 117.986 | 6.564 to 120.326 |
| Reflections collected | 18854 | 20983 |
| Independent reflections | 8065 [$R_{int}$ = 0.0805, $R_{sigma}$ = 0.0623] | 7597 [$R_{int}$ = 0.0636, $R_{sigma}$ = 0.0822] |
| Data/restraints/parameters | 8065/0/480 | 7597/11/430 |
| Goodness-of-fit on $F^2$ | 1.422 | 1.029 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1132, $wR_2$ = 0.2935 | $R_1$ = 0.0867, $wR_2$ = 0.2367 |
| Final R indexes [all data] | $R_1$ = 0.1299, $wR_2$ = 0.3060 | $R_1$ = 0.1578, $wR_2$ = 0.2677 |

## 2. IR, $^{1}H$,$^{31}P$, and $^{13}C$NMR Spectra of Complexes 1, 2, 3 and 4

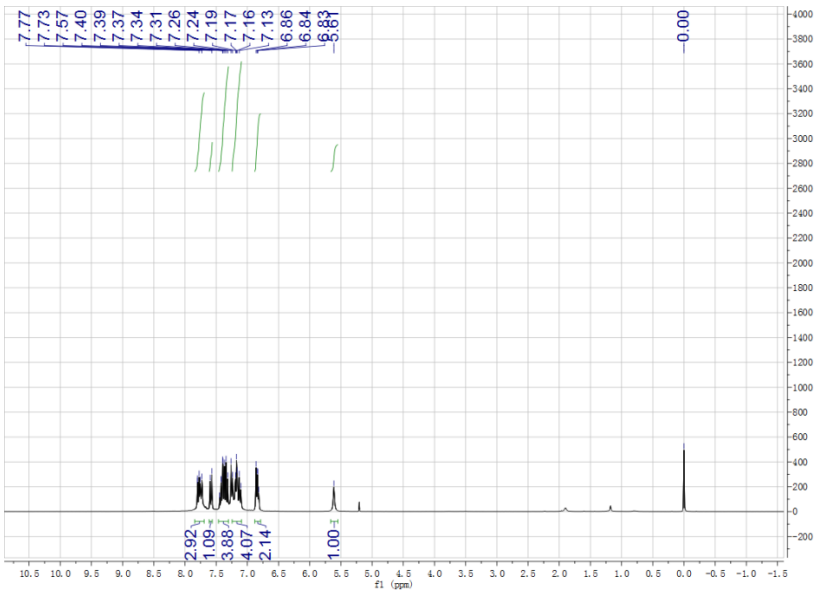



**Figure S1**. $^{1}H$ NMR of **1**

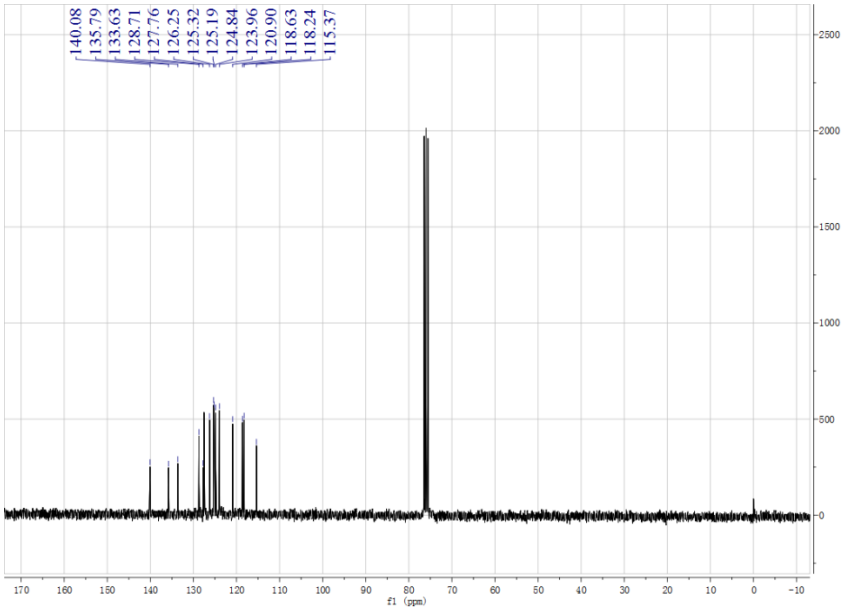



**Figure S2**. $^{13}C$ NMR of **1**

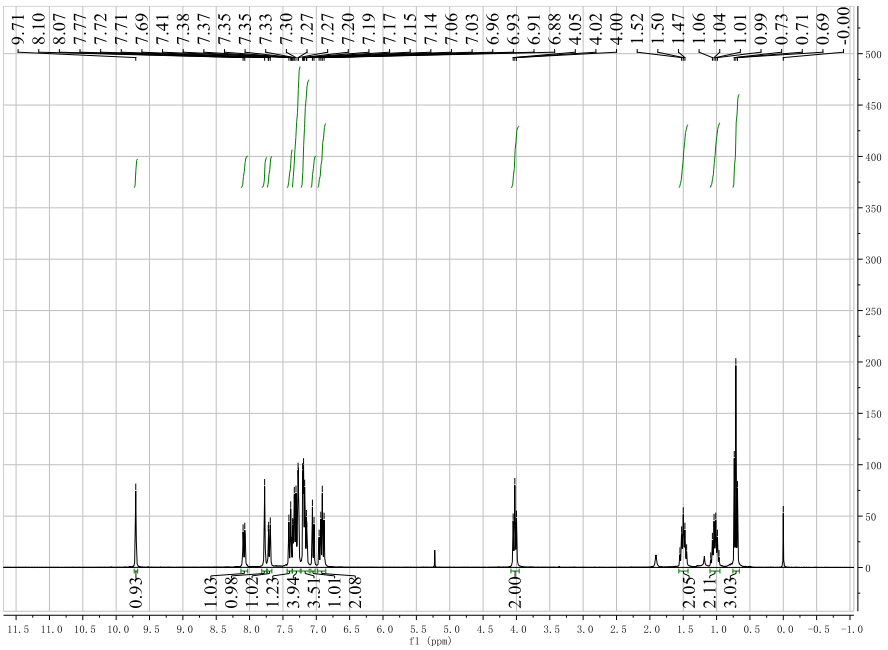


**Figure S3**. $^{1}$H NMR of **2a**

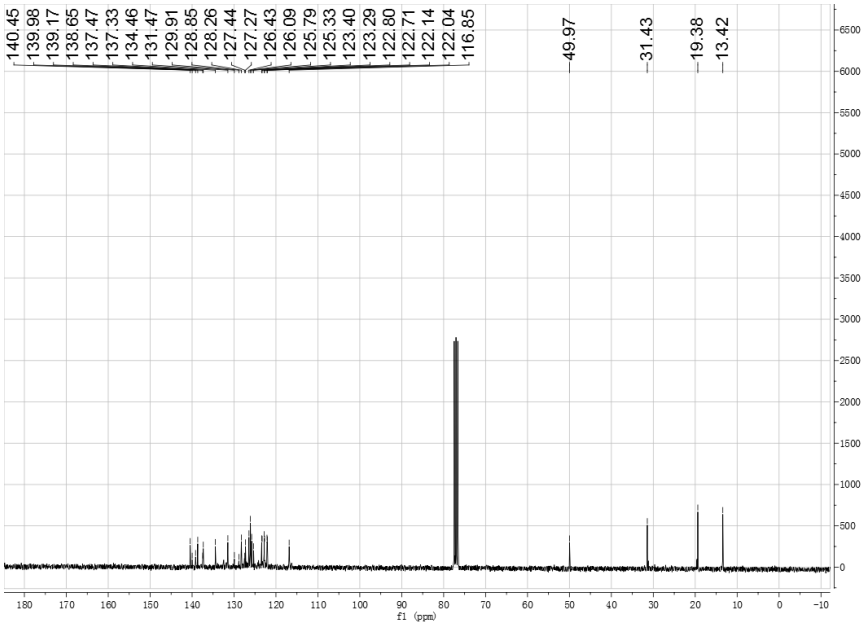


**Figure S4.** $^{13}$C NMR of **2a**

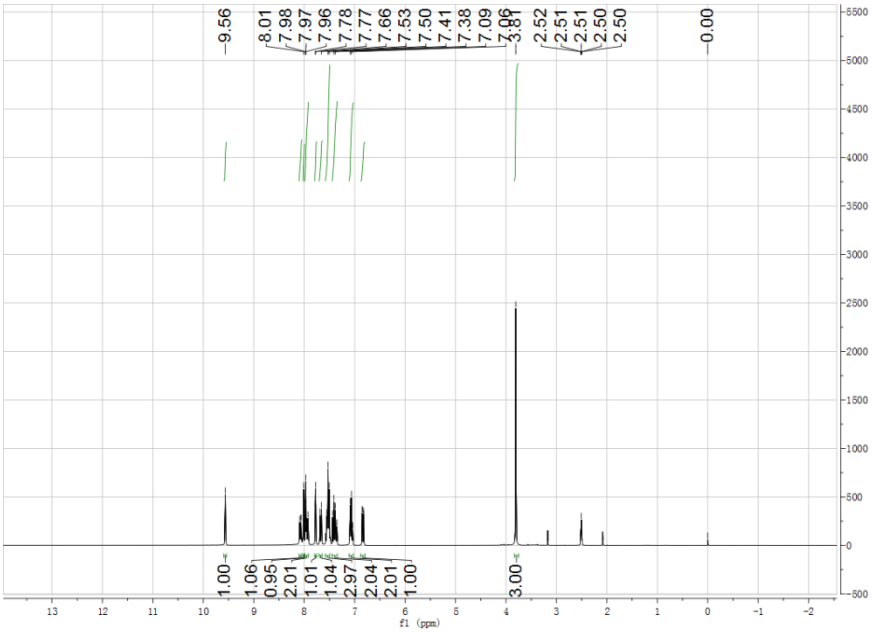



**Figure S5.** $^{1}$H NMR of **2b**

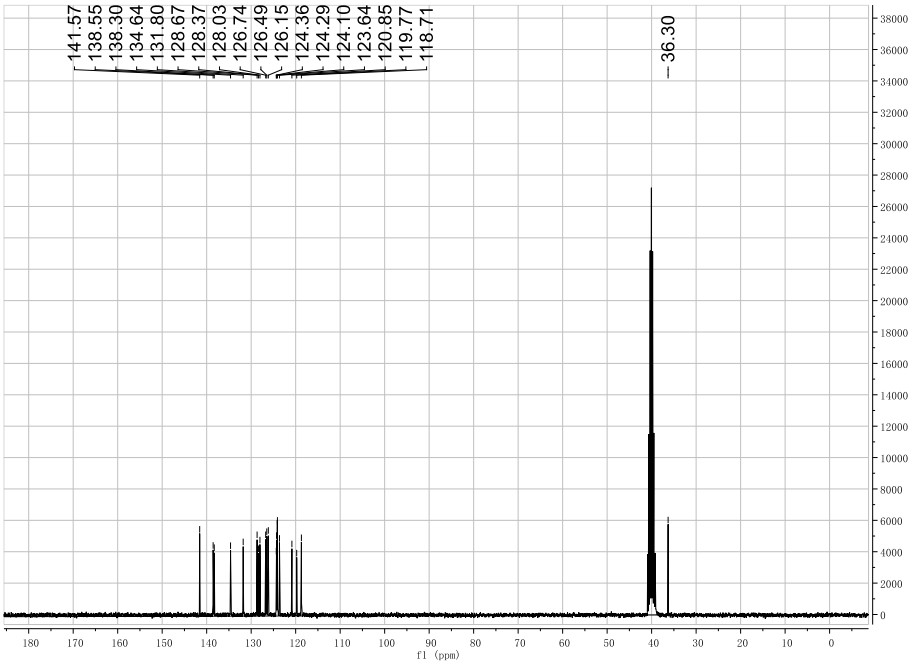



**Figure S6.** $^{13}$C NMR of **2b**

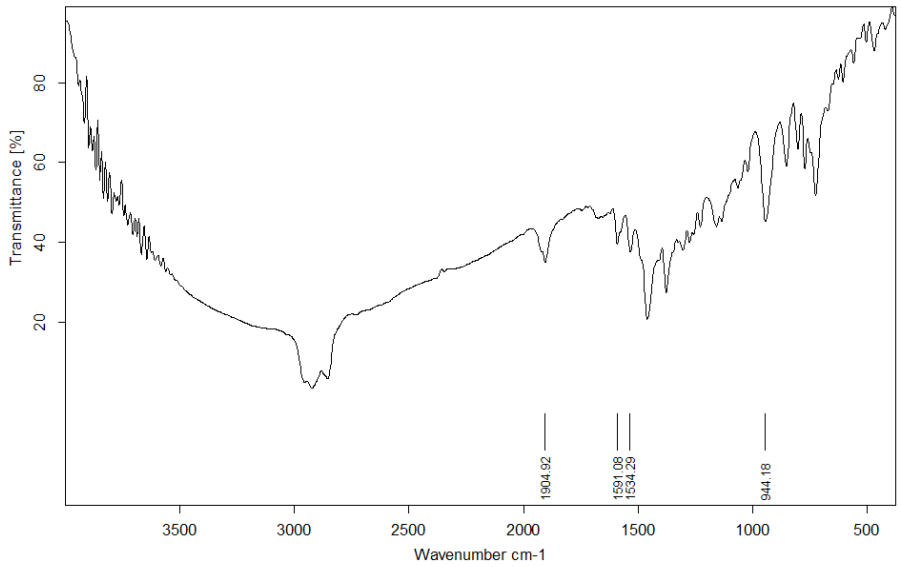



**Figure S7.** IR spectrum of **3a**

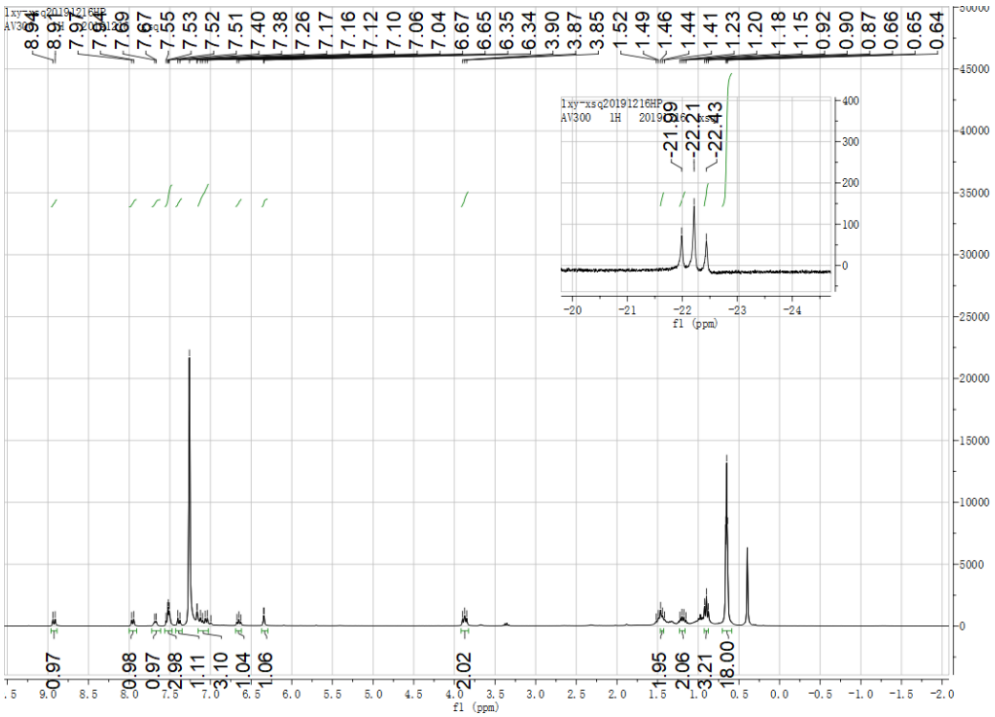



**Figure S8.** $^{1}$H NMR of **3a**

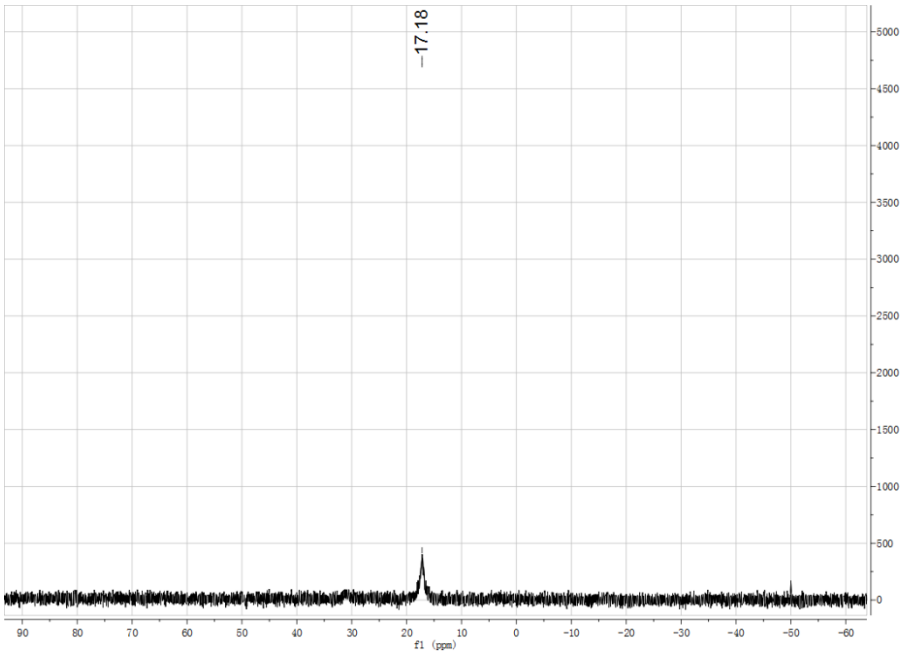



**Figure S9.** $^{31}$P NMR of **3a**

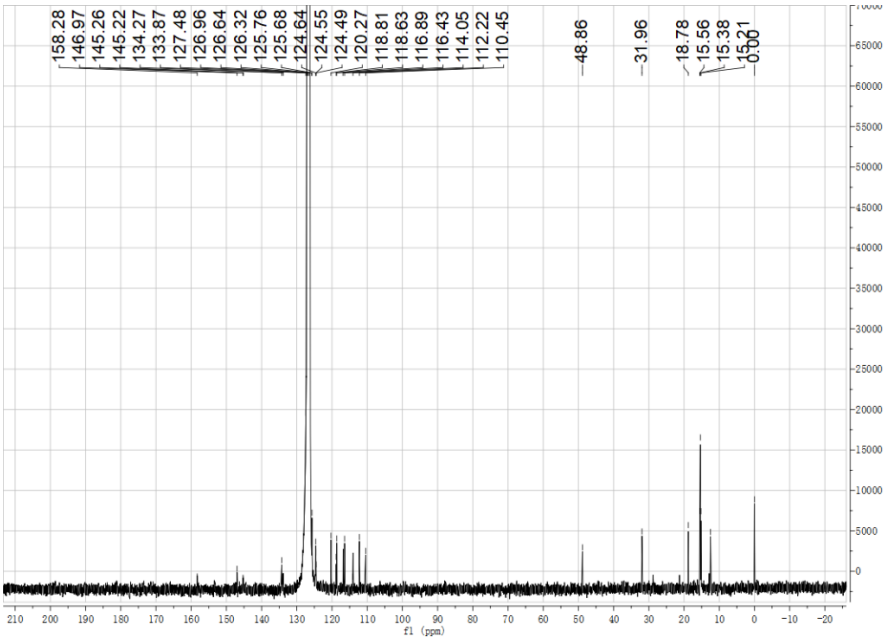



**Figure S10.** $^{13}$C NMR of **3a**

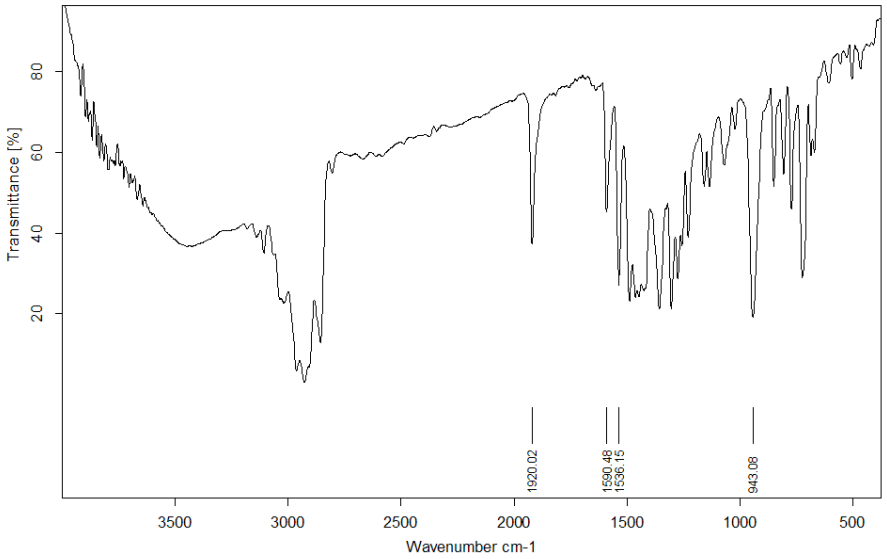



**Figure S11.** IR spectrum of **3b**

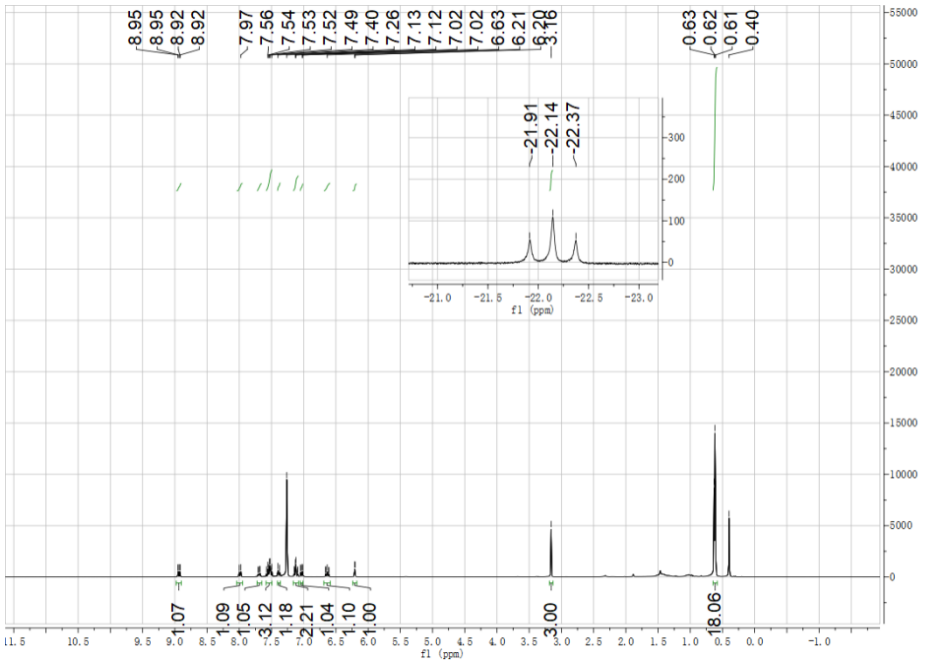



**Figure S12.** $^{1}$H NMR of **3b**

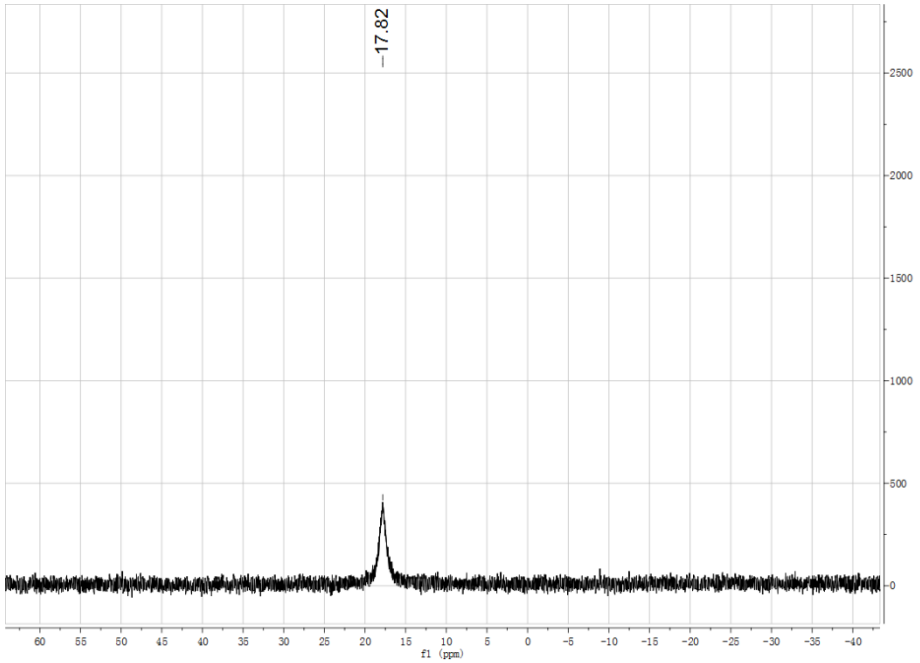



**Figure S13.** $^{31}$P NMR of **3b**

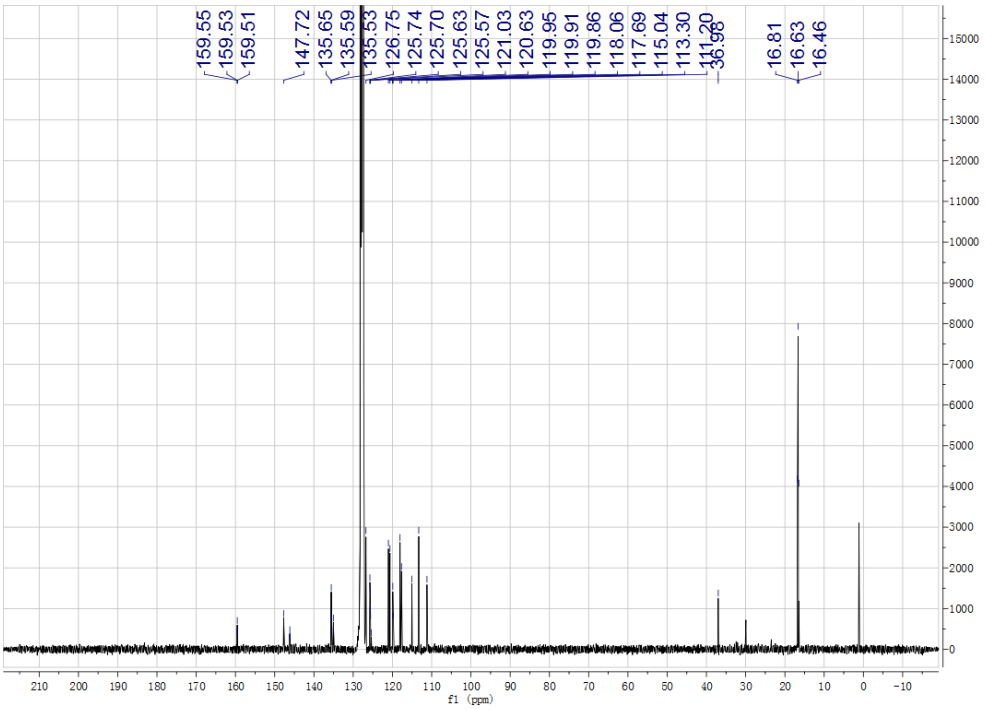



**Figure S14.** $^{13}$C NMR of **3b**

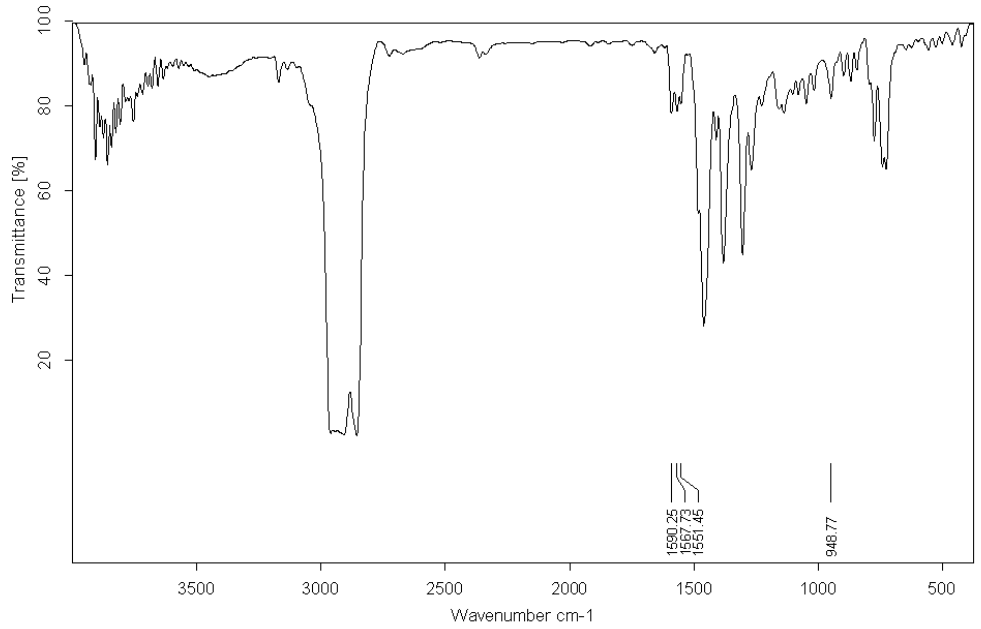



**Figure S15.** IR spectrum of **4a**

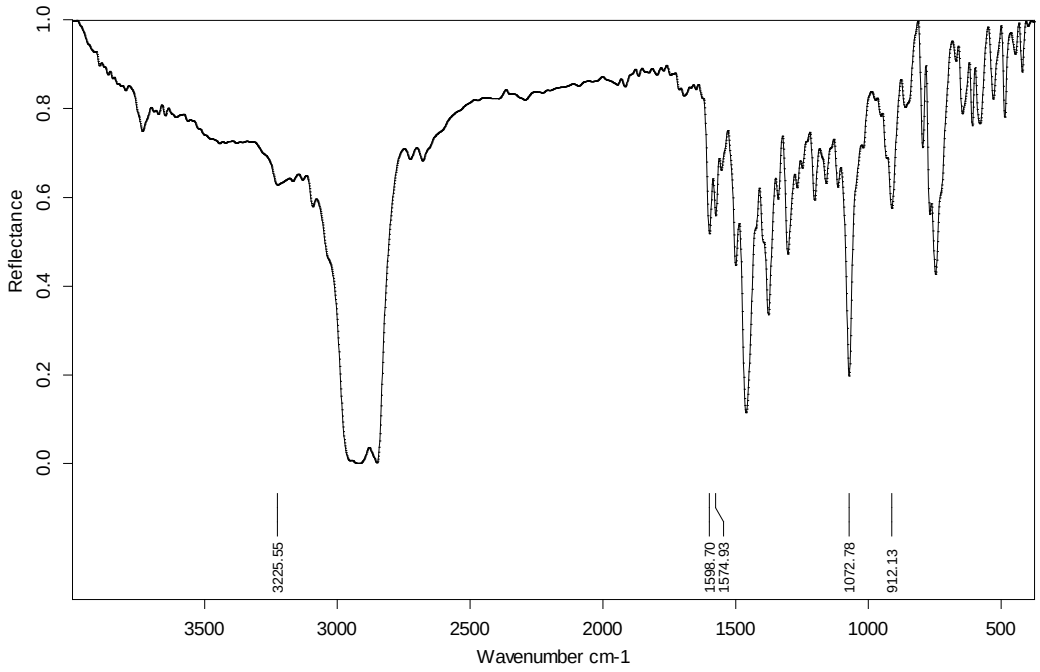
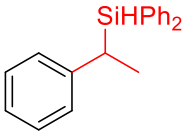



**Figure S16.** IR spectrum of **4b**

## 3. $^{1}$H NMR and $^{13}$C NMR Spectra of Hydrosilylation Products

**Diphenyl(1-phenylethyl)silane (5a)**[1]




$^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.24-7.15 (m, 6H), 7.13-7.10 (m, 2H), 7.04-7.01 (m, 2H), 6.96-6.94 (m, 1H), 6.90-6.87 (m, 2H), 4.75 (d, *J* = 3.4 Hz, 1H), 2.70 (qd, *J* = 7.5, 3.4 Hz, 1H), 1.34 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.52, 135.92, 135.78, 133.23, 129.93, 129.79, 128.39, 128.15, 127.95, 127.93, 125.15, 27.20, 16.74.

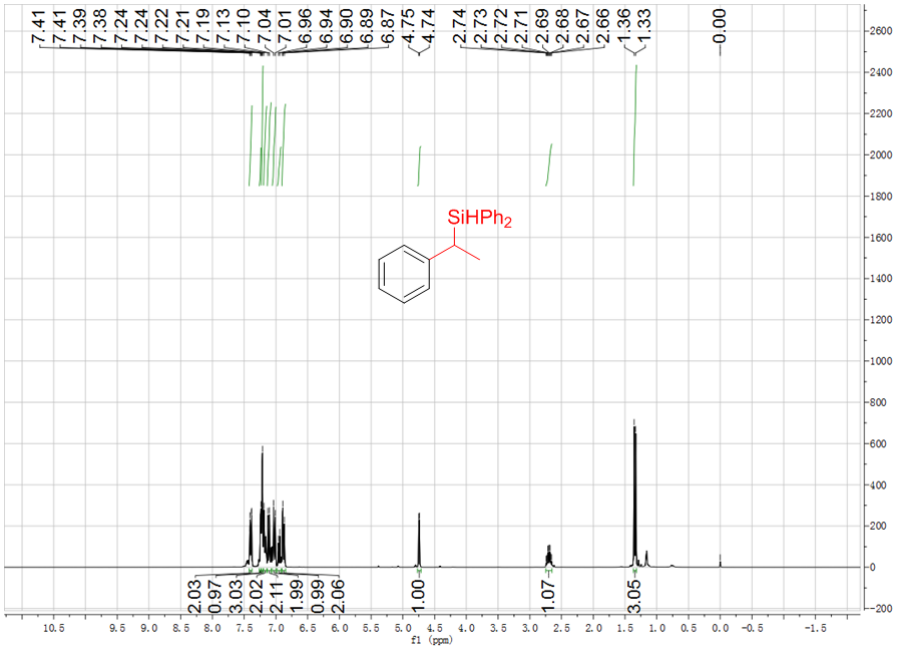



**Figure S17.** $^{1}$H NMR spectrum of **5a**

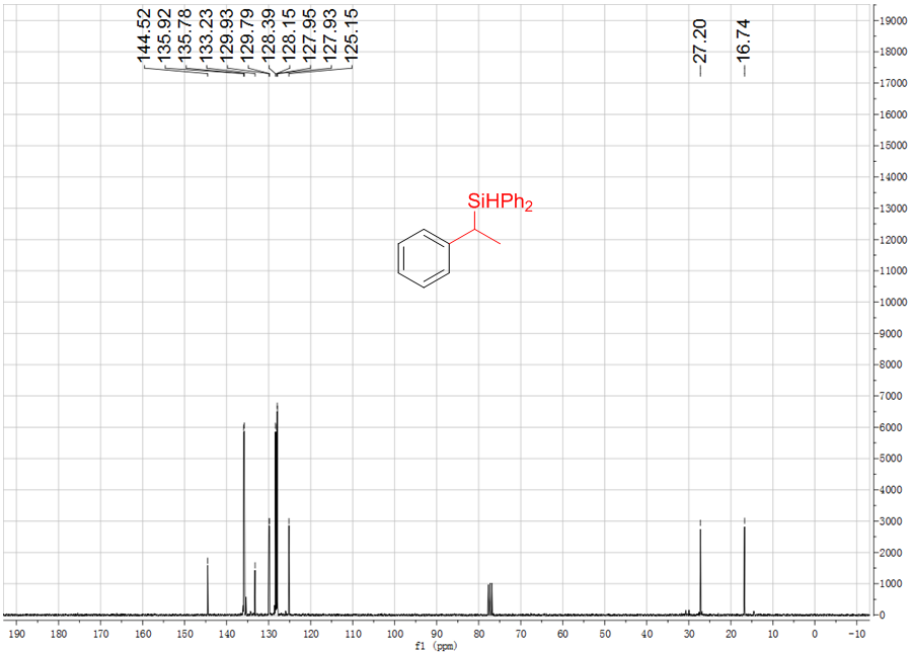
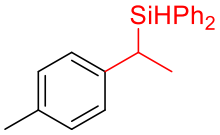



**Figure S18.** $^{13}$C NMR spectrum of **5a**

**Diphenyl(1-(p-tolyl)ethyl)silane(5b)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (dd, *J* = 7.6, 1.5 Hz, 2H) 7.28-7.22 (m, 6H), 7.17-7.14 (m, 2H), 6.90-6.87 (m, 2H), 6.82-6.79 (m, 2H), 4.74 (d, *J* = 3.3 Hz, 1H), 2.95 (qd, *J* = 7.4, 3.8 Hz, 1H), 2.17 (s, 3H), 1.34 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.31, 135.84, 135.70, 134.34, 133.35, 133.32, 129.76, 129.64, 129.01, 128.01, 127.83, 127.71, 26.50, 21.07, 16.84.

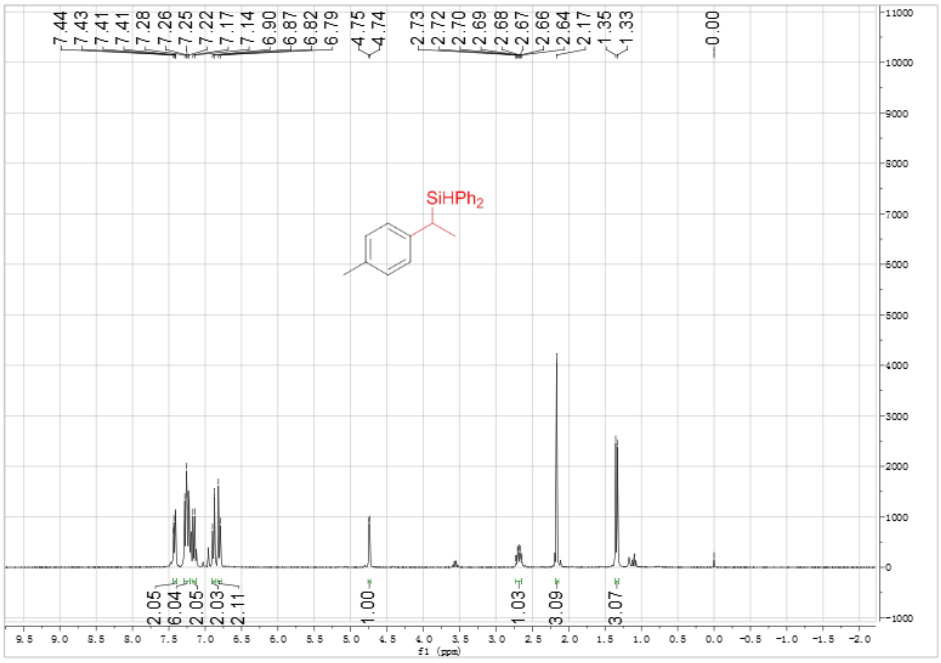



**Figure S19.** $^1$H NMR spectrum of **5b**

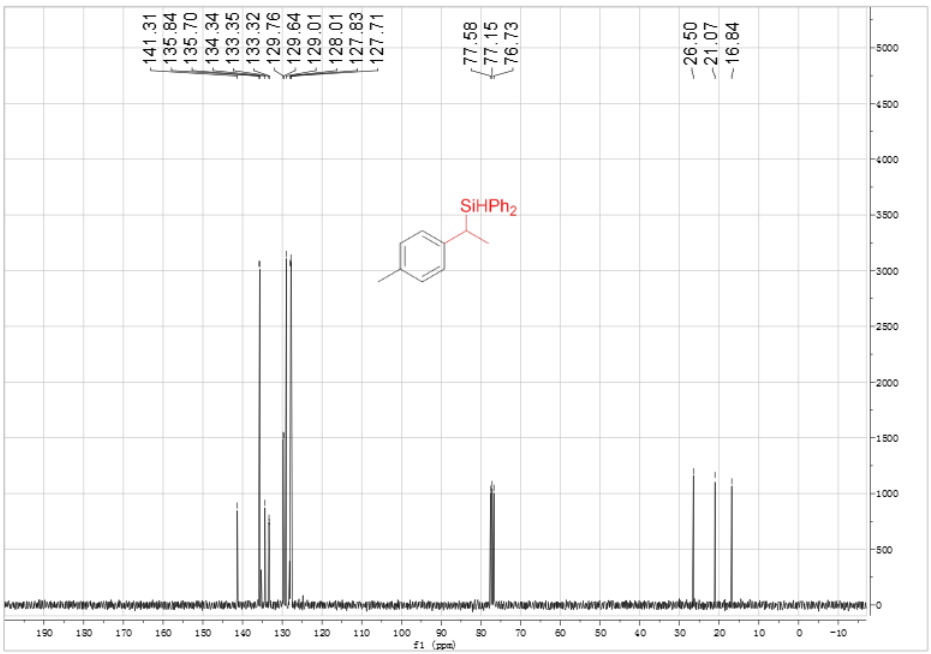
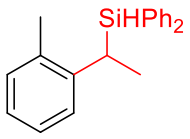



**Figure S20.** $^{13}$C NMR spectrum of **5b**

**Diphenyl(1-(o-tolyl)ethyl)silane (5c)**[2]




$^1$H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.43 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.30 – 7.11 (m, 8H), 7.01 – 6.98 (m, 1H), 6.95 – 6.90 (m, 3H), 4.71 (d, *J* = 3.4 Hz, 1H), 2.90 (qd, J = 7.4, 3.4 Hz, 1H), 1.96 (s, 3H), 1.34 (d, *J* = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ (ppm) 142.96, 135.96, 135.43, 135.27, 133.48, 132.98, 130.22, 129.90, 129.67, 128.08, 127.84, 126.92, 126.20, 124.89, 22.17, 20.23, 16.75.

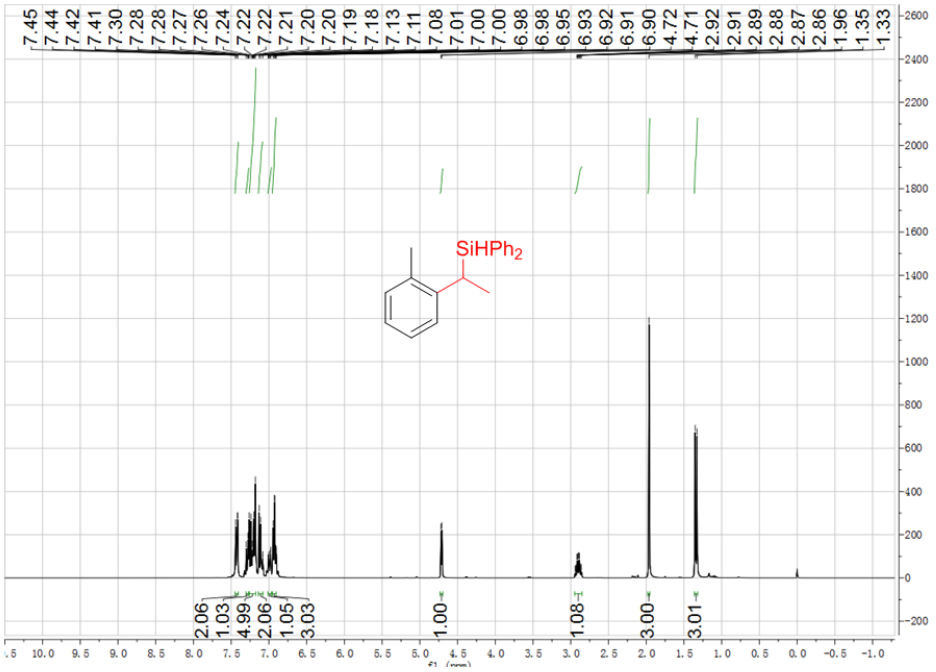



**Figure S21.** $^1$H NMR spectrum of **5c**

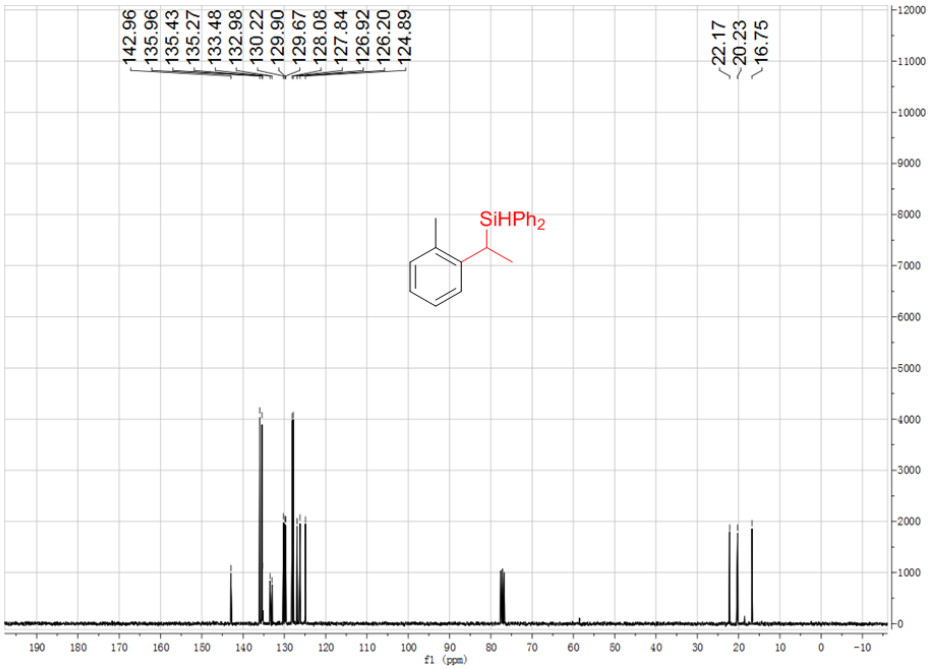
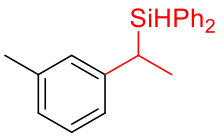



**Figure S22.** $^{13}$C NMR spectrum of **5c**

**Diphenyl(1-(m-tolyl)ethyl)silane (5d)**




$^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, $J$ = 7.7, 1.6 Hz, 2H), 7.26-7.21 (m, 6H), 7.16-7.10 (m, 2H), 6.98-6.93 (m, 1H), 6.79 (d, $J$ = 7.5 Hz, 1H), 6.72-6.68 (m, 2H), 4.74 (d, $J$ = 3.3 Hz, 1H), 2.68 (qd, $J$ = 7.5, 3.3 Hz, 1H), 2.10 (s, 3H), 1.34 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 144.31, 137.67, 135.97, 135.88, 135.75, 133.29, 129.82, 129.69, 128.80, 128.20, 128.03, 127.83, 125.83, 124.87, 26.99, 21.56, 16.65.

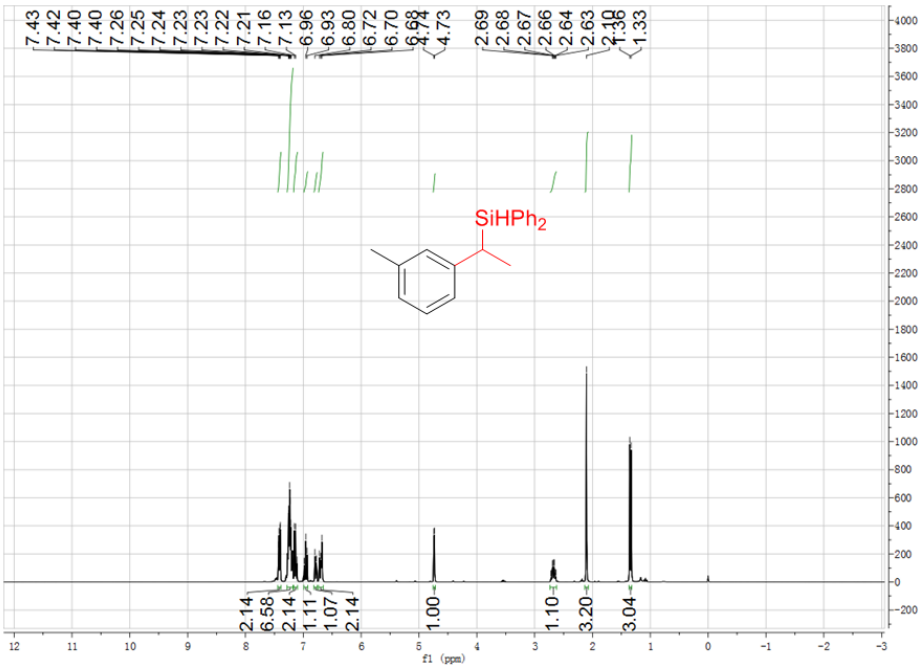



**Figure S23.** $^{1}$H NMR spectrum of **5d**

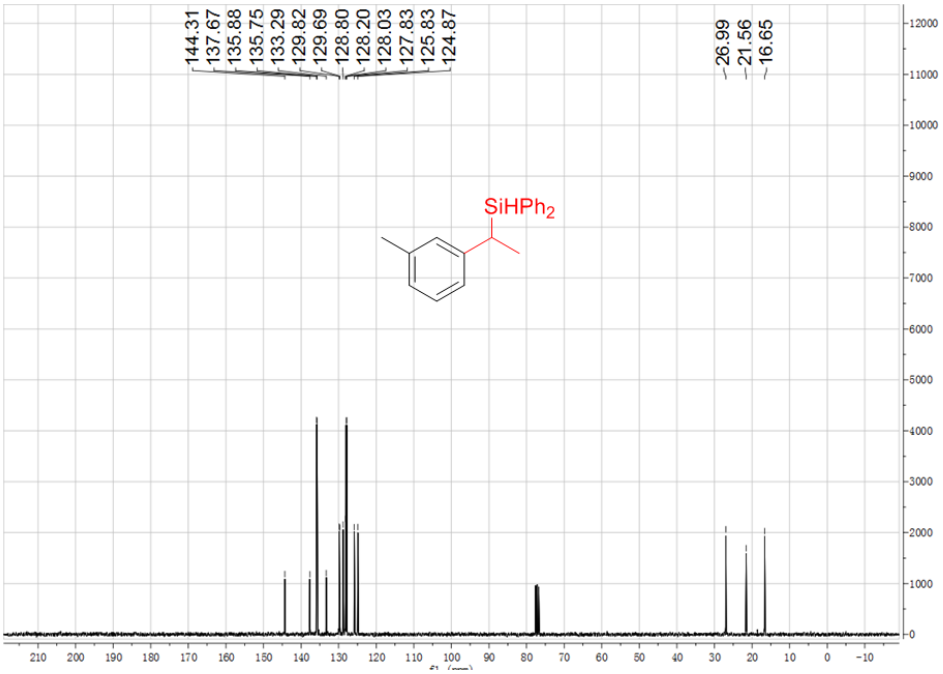
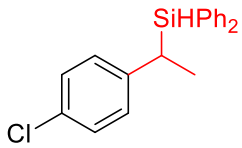



**Figure S24.** $^{13}$C NMR spectrum of **5d**

**(1-(4-chlorophenyl)ethyl)diphenylsilane (5e)**




$^{1}$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.65 (dd, $J$ = 7.7, 1.6 Hz, 2H), 7.53-7.45 (m, 6H), 7.42-7.40 (m, 2H), 7.26 (d, $J$ = 8.5 Hz 2H), 7.03 (d, $J$ = 8.4 Hz, 2H),, 4.97 (d, $J$ = 3.2 Hz, 1H), 2.93 (qd, $J$ = 7.5, 3.3 Hz, 1H), 1.57 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.04, 135.81, 135.67, 135.29, 132.70, 130.63, 130.02, 129.92, 129.39, 129.09, 128.37, 128.26, 128.10, 128.01, 26.71, 16.56.

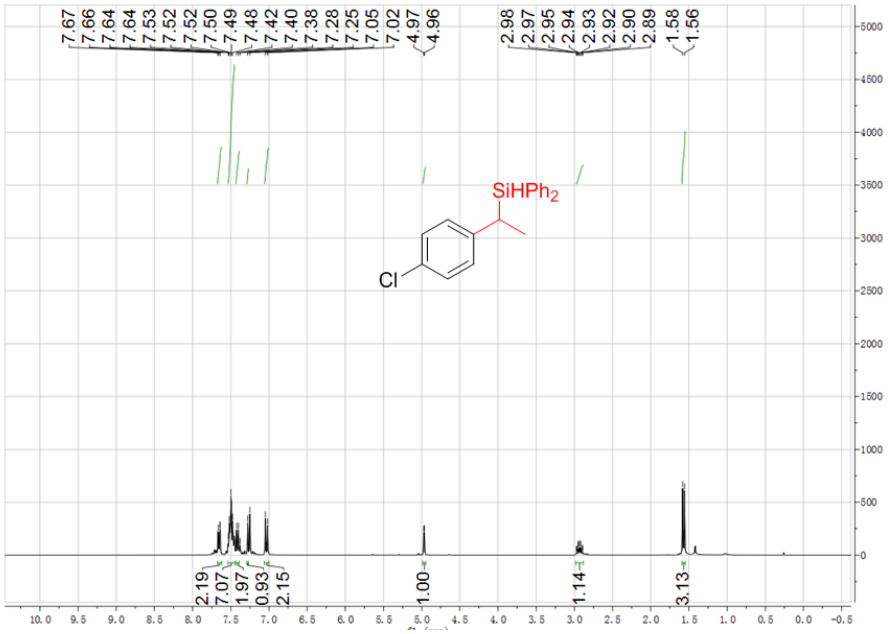



**Figure S25.** $^{1}$H NMR spectrum of **5e**

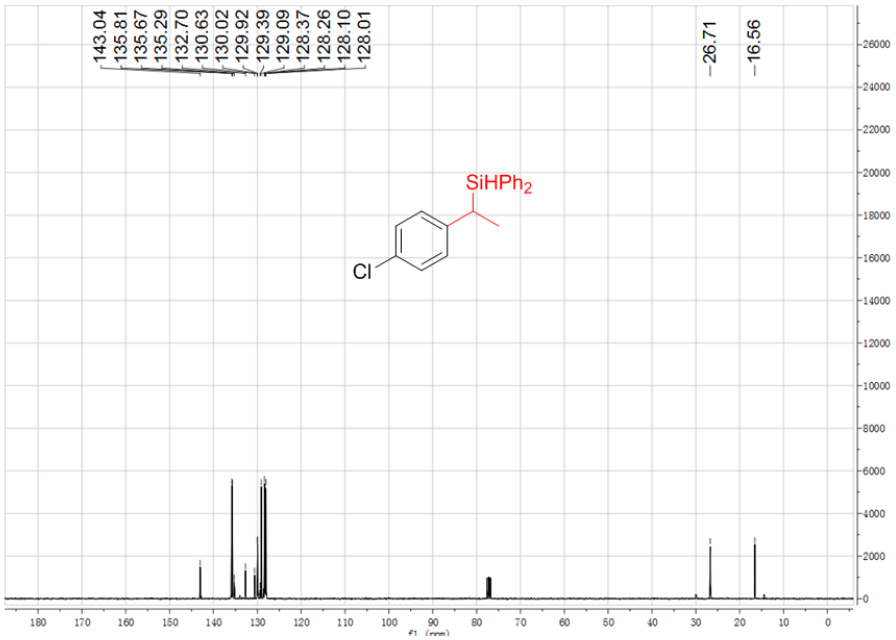
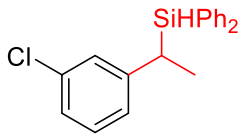



**Figure S26.** $^{13}$C NMR spectrum of **5e**

**(1-(3-chlorophenyl)ethyl)diphenylsilane (5f)**




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.40 (dd, $J$ = 7.7, 1.6 Hz, 2H), 7.28-7.20 (m, 6H), 7.17-7.12 (m, 2H), 6.94-6.92 (m, 2H), 6.85 (s, 1H), 6.74-6.71 (m, 1H), 4.72 (d, $J$ = 3.3 Hz, 1H), 2.68 (qd, $J$ = 7.4, 3.3 Hz, 1H), 1.32 (d, $J$ = 7.5 Hz, 3H); $^{13}$C NMR: (75 MHz, $CDCl_3$) : δ (ppm) 146.74, 135.81, 135.66, 134.13, 132.58, 130.07, 129.96, 129.44, 128.18, 128.01, 127.85, 126.03, 125.20, 27.16, 16.38.

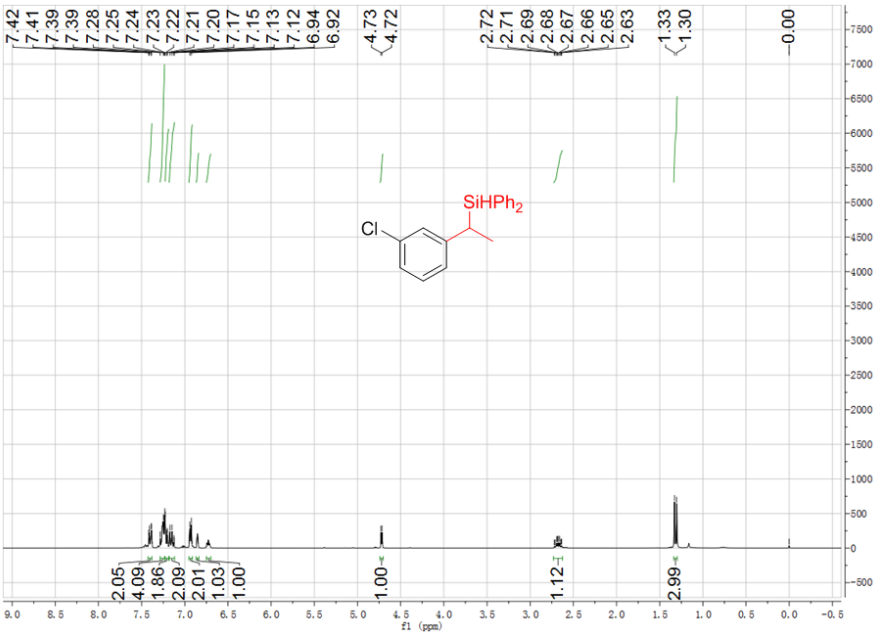



**Figure S27.** $^1$H NMR spectrum of **5f**

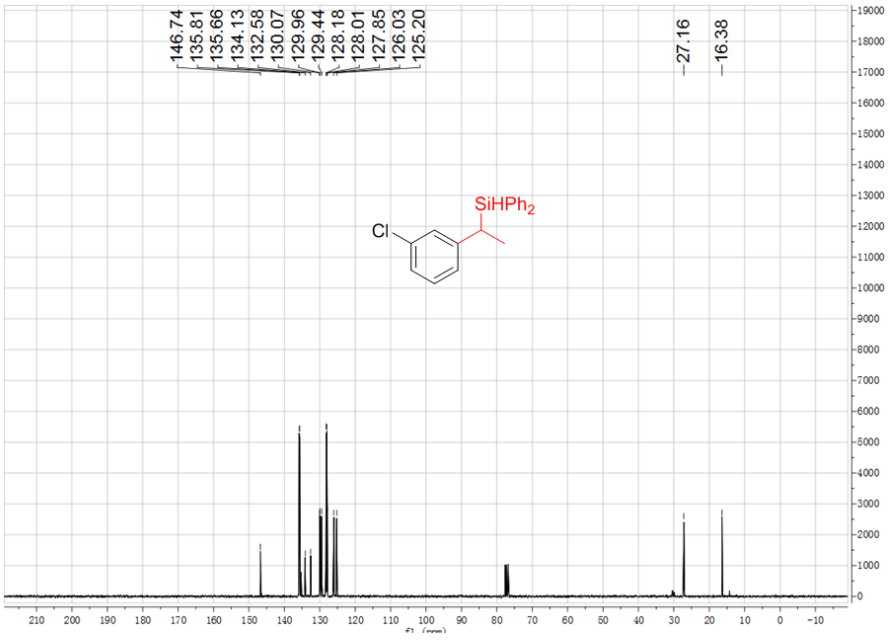
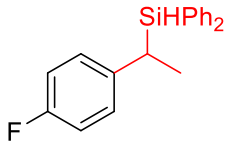



**Figure S28.** $^{13}$C NMR spectrum of **5f**

**(1-(4-fluorophenyl)ethyl)diphenylsilane (5g)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43-7.40 (m, 2H), 7.27-7.22 (m, 6H), 7.18-7.13 (m, 2H), 6.85-6.72 (m, 4H), 4.72 (d, $J$ = 3.4 Hz, 1H), 2.70 (qd, $J$ = 7.3, 3.1 Hz, 1H), 1.34 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 160.77 (d, $J$ = 242.6 Hz), 139.98 (d, $J$ = 3.1 Hz), 135.75, 135.61, 132.86, 132.85, 129.90, 129.78, 128.93 (d, $J$ = 7.6 Hz), 128.08, 127.90, 114.97 (d, $J$ = 21.0 Hz), 26.29, 16.77.

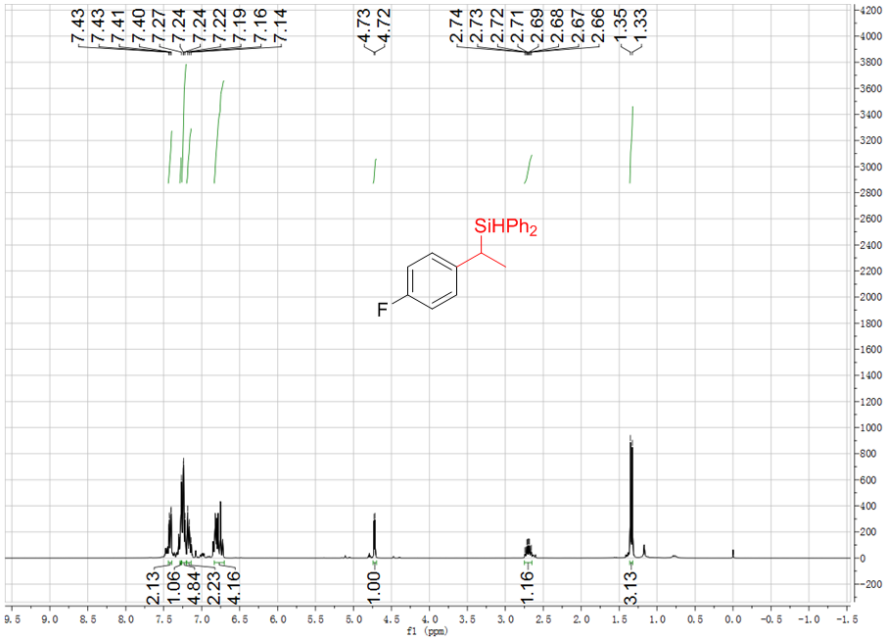



**Figure S29.** $^1$H NMR spectrum of **5g**

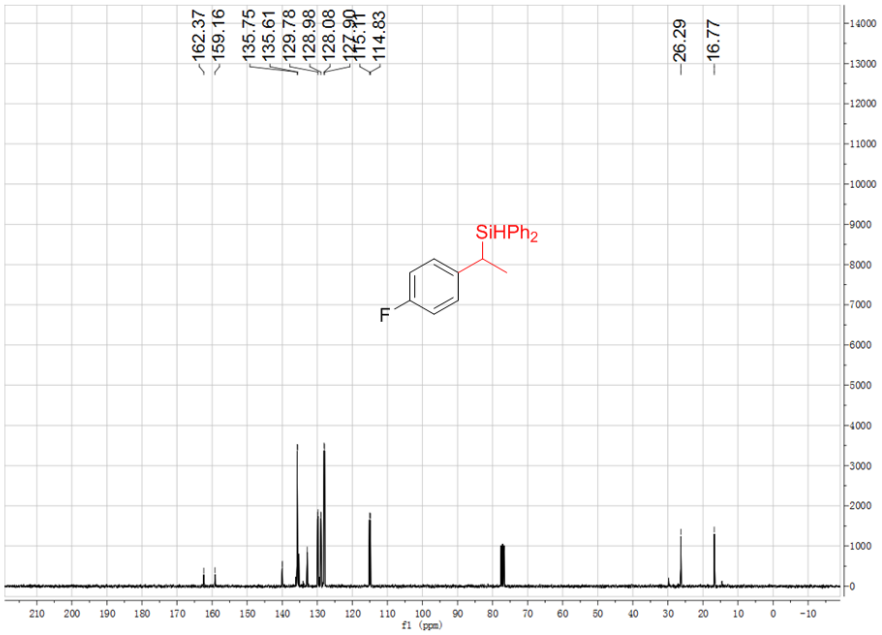
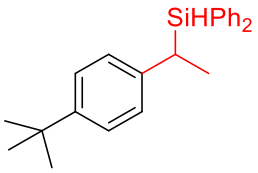



**Figure S30.** $^{13}$C NMR spectrum of **5g**

**(1-(4-(tert-butyl)phenyl)ethyl)diphenylsilane (5h)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (dd, $J$ = 7.7, 1.6 Hz, 2H), 7.29-7.21 (m, 6H), 7.16-7.09 (m, 4H), 6.85 (d, $J$ = 8.3 Hz, 2H), 4.74 (d, $J$ = 3.4 Hz, 1H), 2.71 (qd, $J$ = 7.5, 3.4 Hz, 1H), 1.36 (d, $J$ = 7.5 Hz, 3H), 1.20 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 147.79, 141.19, 135.83, 135.67, 133.36, 133.32, 129.73, 129.56, 127.97 , 127.74, 127.40, 125.12, 34.36, 31.54, 26.35, 16.60.

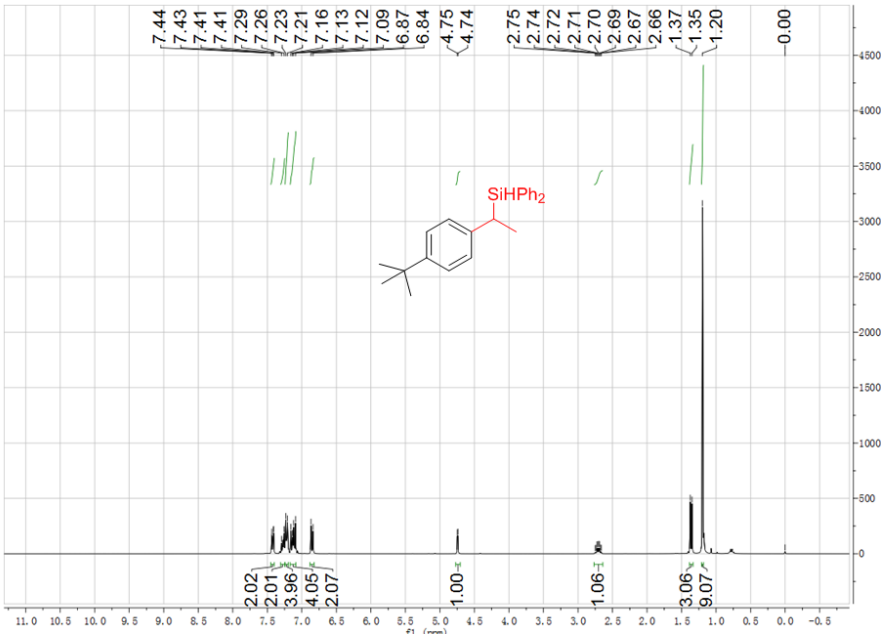



**Figure S31.** $^1$H NMR spectrum of **5h**

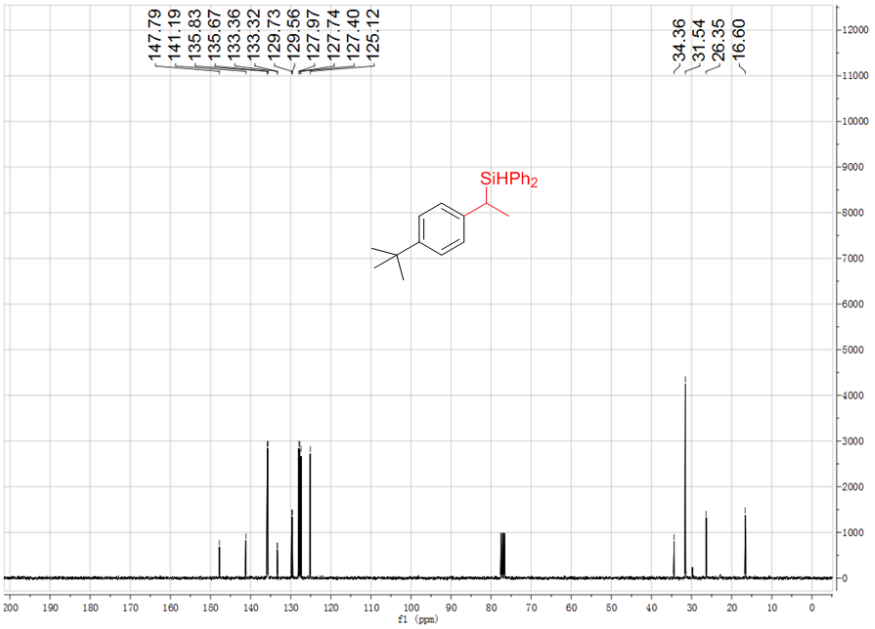
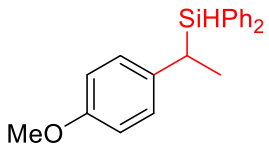



**Figure S32.** $^{13}$C NMR spectrum of **5h**

**(1-(4-methoxyphenyl)ethyl)diphenylsilane (5i)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.39 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.25-7.09 (m, 8H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.59 (d, *J* = 8.7 Hz, 2H), 4.73 (d, *J* = 3.3 Hz, 1H), 3.54 (s, 3H), 2.63 (qd, *J* = 7.6, 3.4 Hz, 1H), 1.30 (d, *J* = 7.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 157.39, 136.45, 135.91, 135.79, 133.45, 133.39, 129.88, 129.76, 128.76, 128.14, 127.96, 113.90, 55.31, 26.04, 17.11.

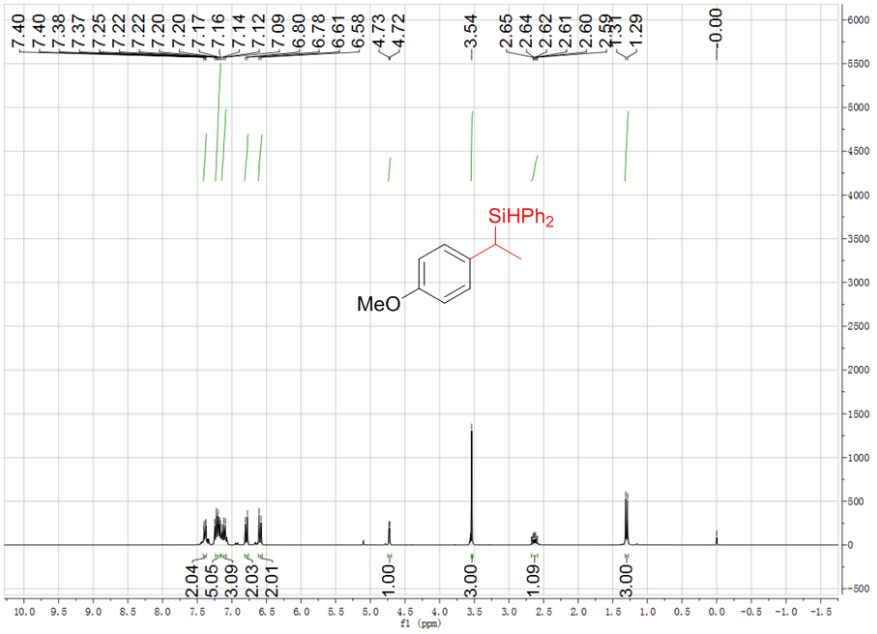



**Figure S33.** $^1$H NMR spectrum of **5i**

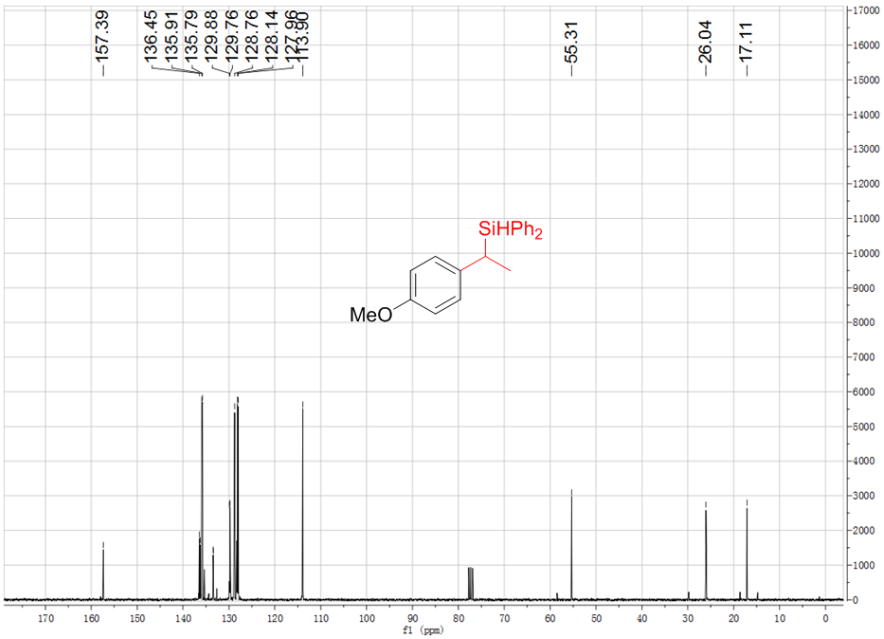
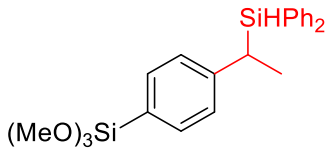



**Figure S34.** $^{13}$C NMR spectrum of **5i**

**(4-(1-(diphenylsilyl)ethyl)phenyl)trimethoxysilane (5j)**




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.42 (dd, $J$ = 7.8, 1.6 Hz, 2H), 7.38 (d, $J$ = 8.1 Hz, 2H), 7.28-7.22 (m, 6H), 7.16-7.11 (m, 2H), 6.95 (d, $J$ = 8 Hz, 2H), 4.74 (d, $J$ = 3.3 Hz, 1H), 3.51 (s, 9H), 2.80-2.71 (m, 1H), 1.38 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 147.33, 135.72, 135.57, 134.74, 129.82, 129.66, 127.98, 127.76, 127.49, 50.83, 27.41, 16.21.

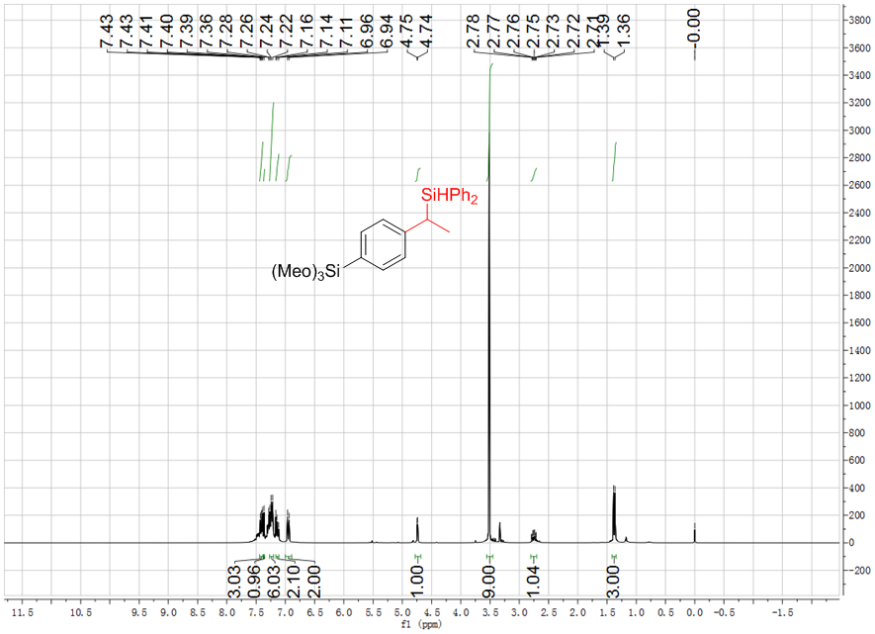



**Figure S35.** $^1$H NMR spectrum of **5j**

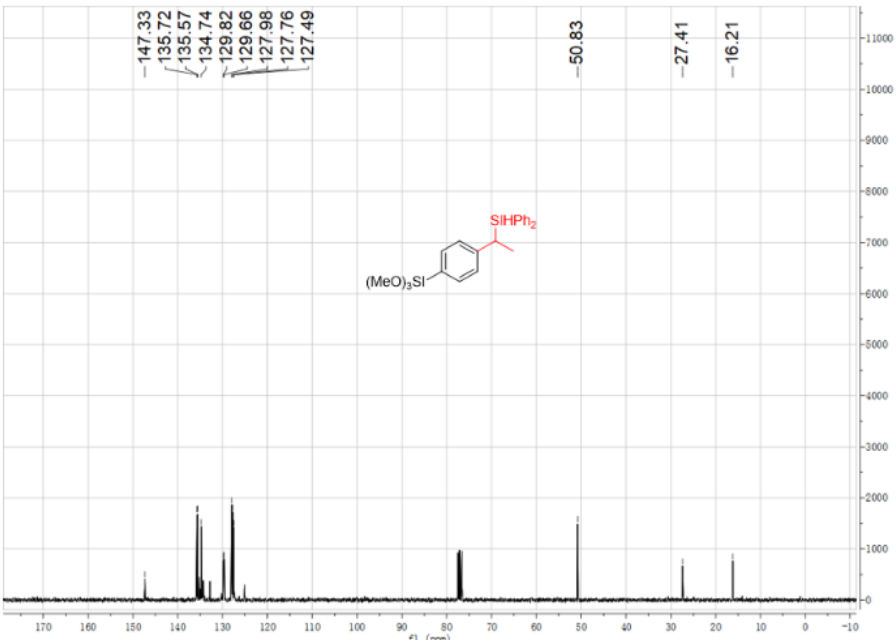
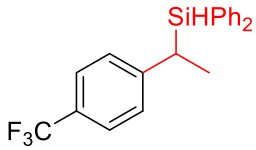



**Figure S36.** $^{13}$C NMR spectrum of **5j**

**Diphenyl(1-(4-(trifluoromethyl)phenyl)ethyl)silane (5k)**[2]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.49-7.41 (m, 3H), 7.34-7.21 (m, 7H), 7.20 (d, $J$ = 6.2 Hz, 2H), 6.98 (d, $J$ = 8.2 Hz, 2H), 4.74 (d, $J$ = 3.2 Hz, 1H), 2.82 (qd, $J$ = 7.4, 3.2 Hz, 1H), 1.39 (d, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 148.87, 135.55, 135.48, 132.27 (d, $J$ = 3.1 Hz), 129.95 (d, $J$ = 8.5 Hz), 128.08, 127.92, 127.80, 125.03 (q, $J$ = 3.8 Hz), 27.43, 16.12.

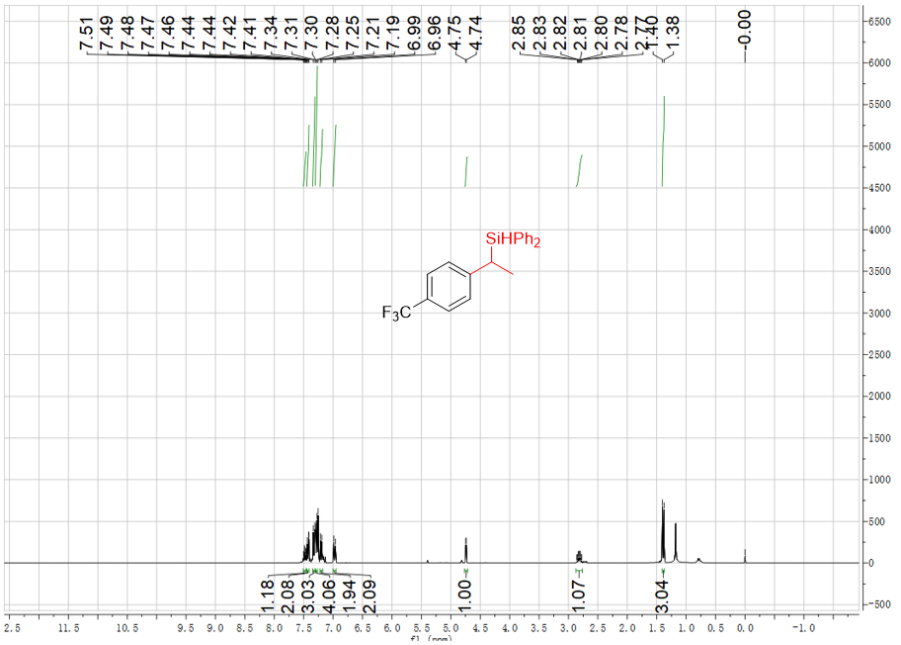



**Figure S37.** $^1$H NMR spectrum of **5k**

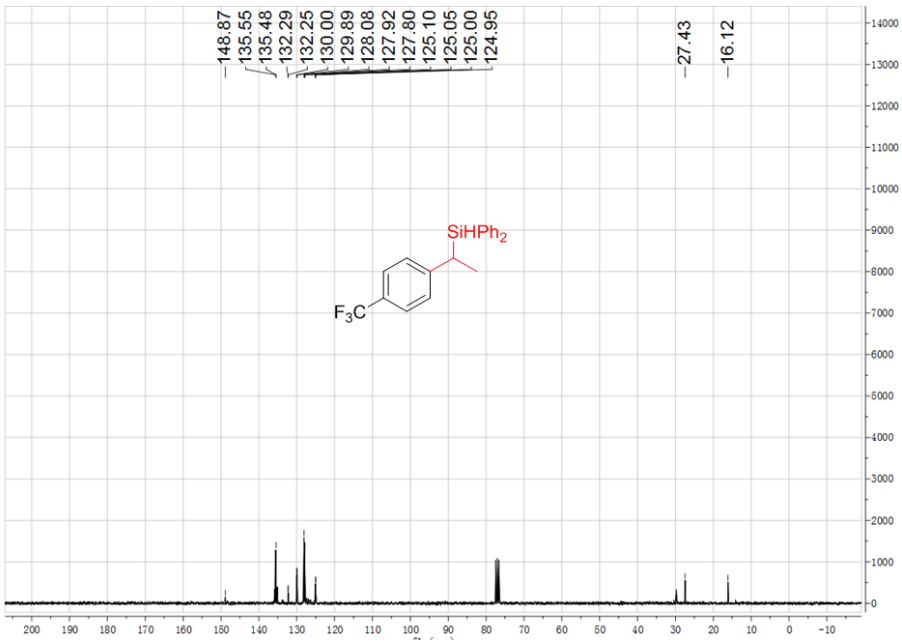
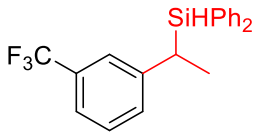



**Figure S38.** $^{13}$C NMR spectrum of **5k**

**Diphenyl(1-(3-(trifluoromethyl)phenyl)ethyl)silane (5l)**[3]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.48-7.44 (m, 1H), 7.40 (dd, $J$ = 7.8, 1.6 Hz, 2H), 7.31-7.22 (m, 6H), 7.18-7.11 (m, 3H), 7.06-7.02 (m, 2H), 4.72 (d, $J$ = 3.2 Hz, 1H), 2.78 (qd, $J$ = 7.5, 3.3 Hz, 1H), 1.37 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 145.45, 135.69, 135.55, 135.21, 132.28, 131.41-131.38(m), 130.95 (d, $J$ = 1.2 Hz), 130.06, 129.95, 129.88, 128.52, 128.22, 128.14, 127.97, 124.44 (q, $J$ = 3.7 Hz), 121.74 (q, $J$ = 3.9 Hz), 27.36, 16.11.

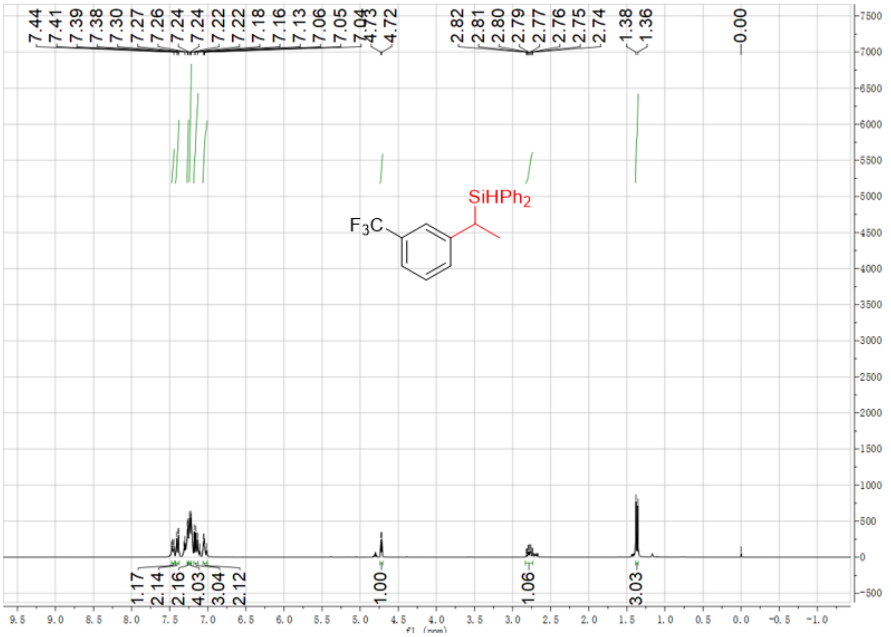



**Figure S39.** $^1$H NMR spectrum of **5l**

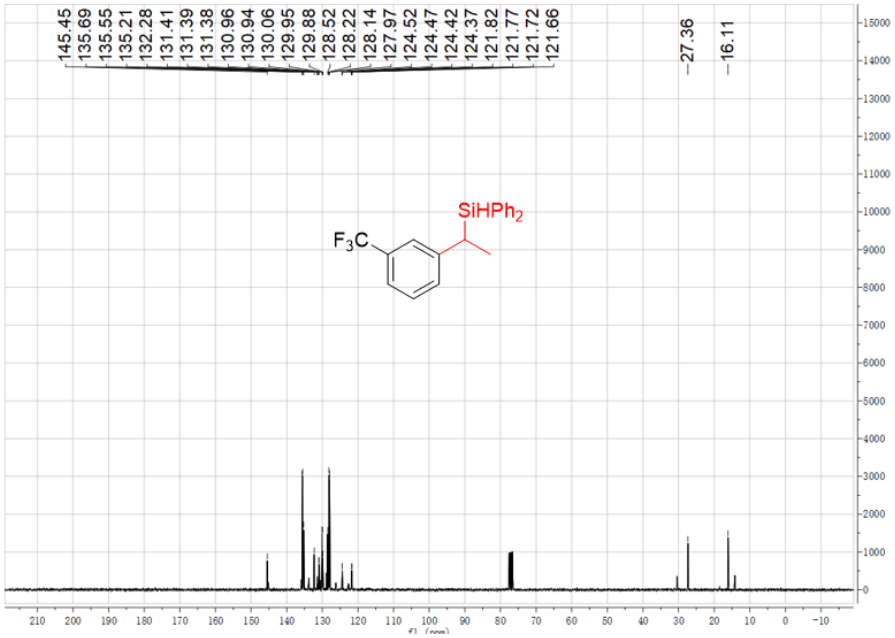
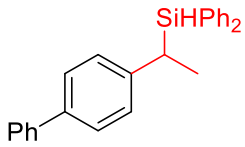



**Figure S40.** $^{13}$C NMR spectrum of **5l**

**(1-([1,1'-biphenyl]-4-yl)ethyl)diphenylsilane (5m)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.46-7.41 (m, 4H), 7.32-7.19 (m, 10H), 7.16-7.13 (m, 3H), 6.95 (d, $J$ = 8.2 Hz, 2H), 4.77 (d, $J$ = 3.2 Hz, 1H), 2.80-2.71 (qd, $J$ = 7.4, 3.2 Hz, 1H), 1.38 (d, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 143.71, 141.20, 137.83, 135.89, 135.75, 133.08, 129.92, 129.80, 128.85, 128.25, 128.11, 127.94, 127.04, 126.99, 126.96, 26.85, 16.63.

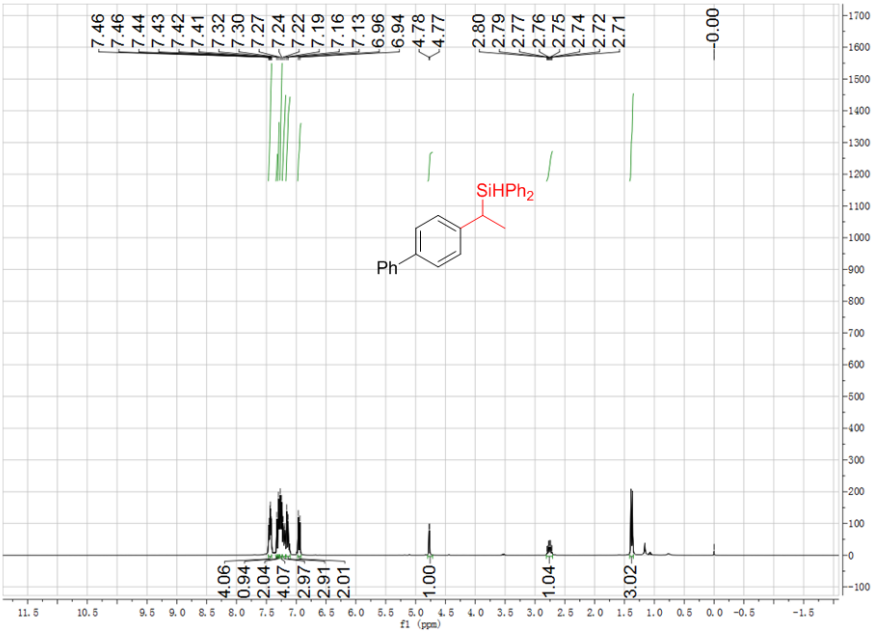



**Figure S41.** $^1$H NMR spectrum of **5m**

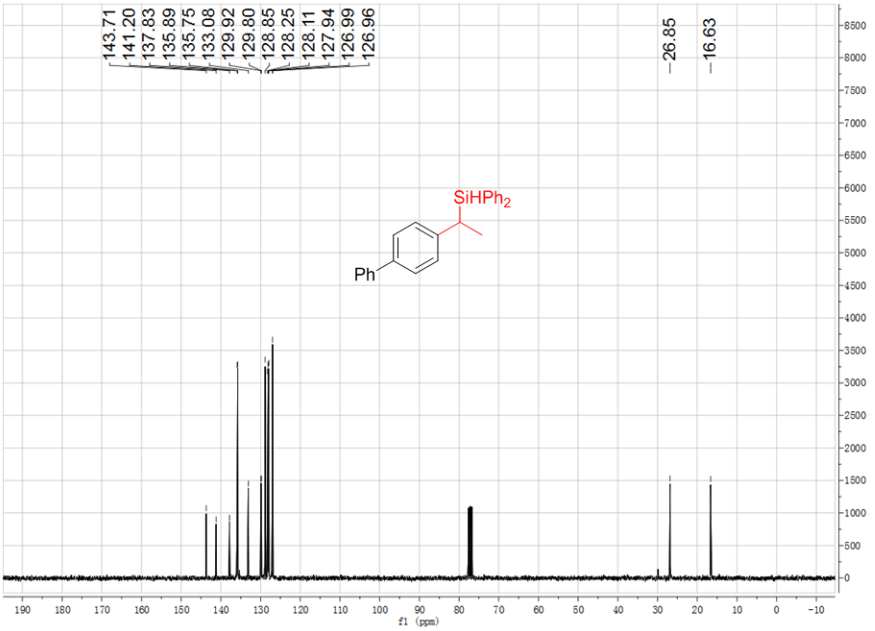
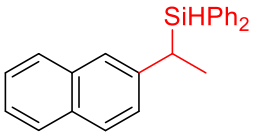



**Figure S42.** $^{13}$C NMR spectrum of **5m**

**(1-(naphthalen-2-yl)ethyl)diphenylsilane (5n)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.59-7.56 (m, 1H), 7.51-7.46 (m, 2H), 7.38 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.28 (s, 1H), 7.25-7.12 (m, 8H), 7.09-7.03 (m, 2H), 7.00 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 2.85 (qd, *J* = 7.4, 3.0 Hz, 1H), 1.41 (d, *J* = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.29, 135.99, 135.85, 133.96, 133.18, 133.15, 131.83, 130.01, 129.90, 128.20, 128.04, 127.81, 127.78, 127.59, 127.49, 126.01, 125.55, 125.02, 27.48, 16.85.

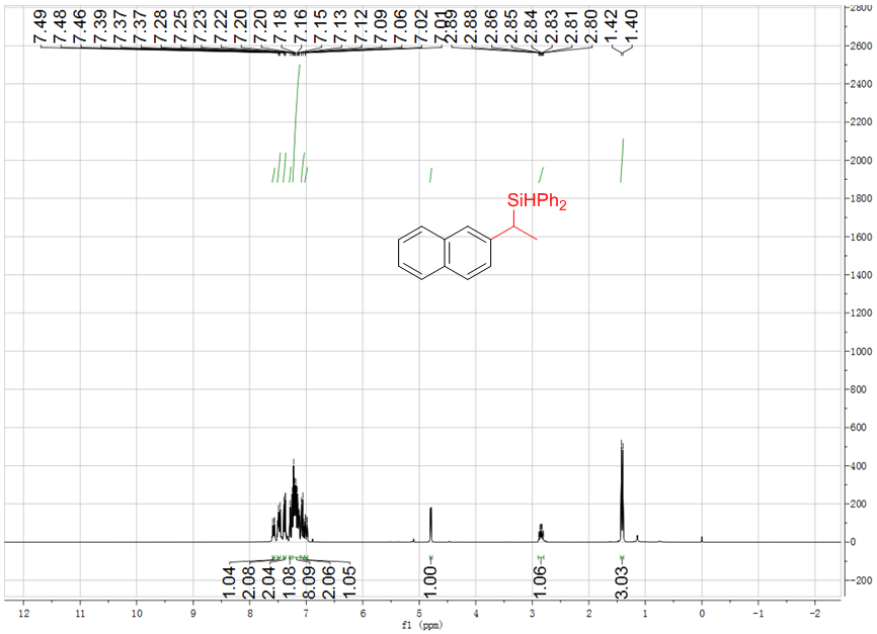



**Figure S43.** $^1$H NMR spectrum of **5n**

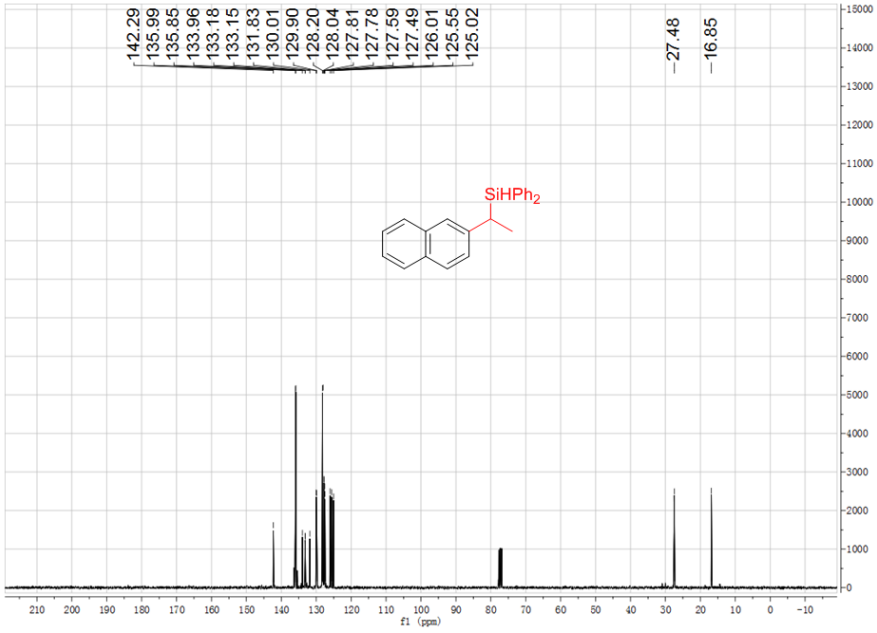
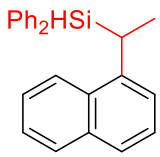



**Figure S44.** $^{13}$C NMR spectrum of **5n**

**(1-(naphthalen-1-yl)ethyl)diphenylsilane (5o)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.92 (d, *J* = 7.8 Hz, 1H), 7.72-6.69 (m, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.37 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.32-7.17 (m, 9H), 7.13-7.06 (m, 3H), 4.80 (d, *J* = 2.6 Hz, 1H), 3.59 (qd, *J* = 7.3, 2.6 Hz, 1H), 1.49 (d, *J* = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 141.17, 136.13, 135.55, 134.10, 133.39, 132.98, 131.66, 129.94, 129.79, 129.02, 128.30 (s), 128.05, 127.99, 125.75, 125.70, 125.52, 125.43, 124.27, 123.76, 21.38, 17.05.

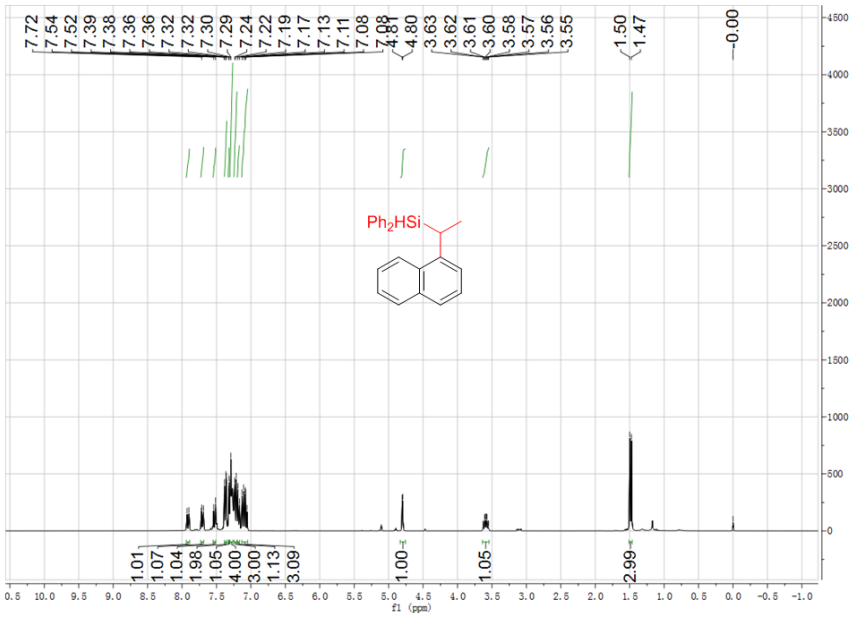



**Figure S45.** $^1$H NMR spectrum of **5o**

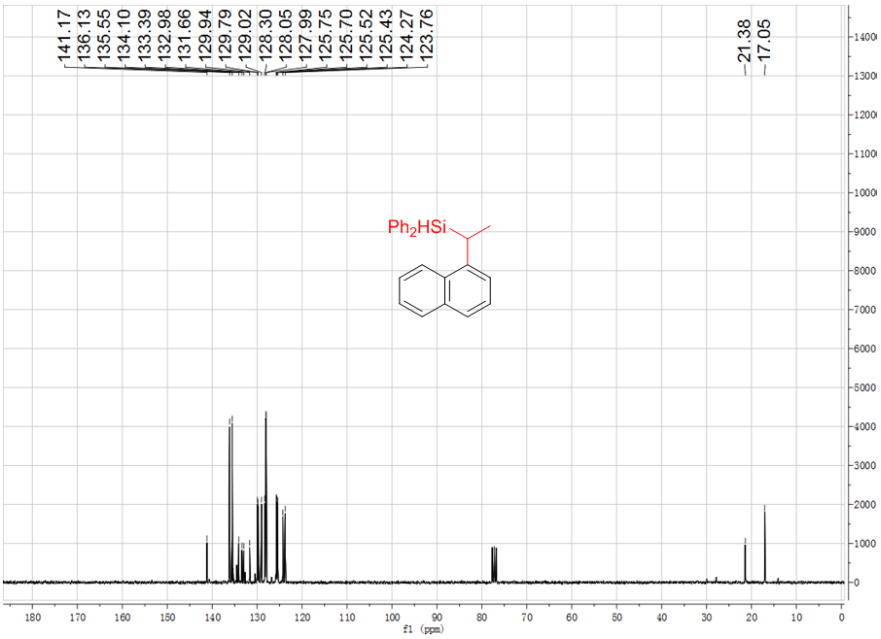
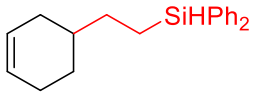



**Figure S46.** $^{13}$C NMR spectrum of **5o**

**(2-(cyclohex-3-en-1-yl)ethyl)diphenylsilane (5q)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.47-7.44 (m, 4H), 7.27-7.23 (m, 6H), 5.53 (d, $J$ = 2.1 Hz, 2H), 4.77 (t, $J$ = 3.6 Hz, 1H), 2.02 (dd, $J$ = 16.0, 2.3 Hz, 1H), 1.92-1.90 (m, 2H), 1.67-1.63 (m, 1H), 1.56-1.17 (m, 4H), 1.10-1.04 (m, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 135.29, 134.74, 129.66, 128.14, 127.19, 126.71, 36.51, 31.73, 31.28, 28.61, 25.48, 9.44.

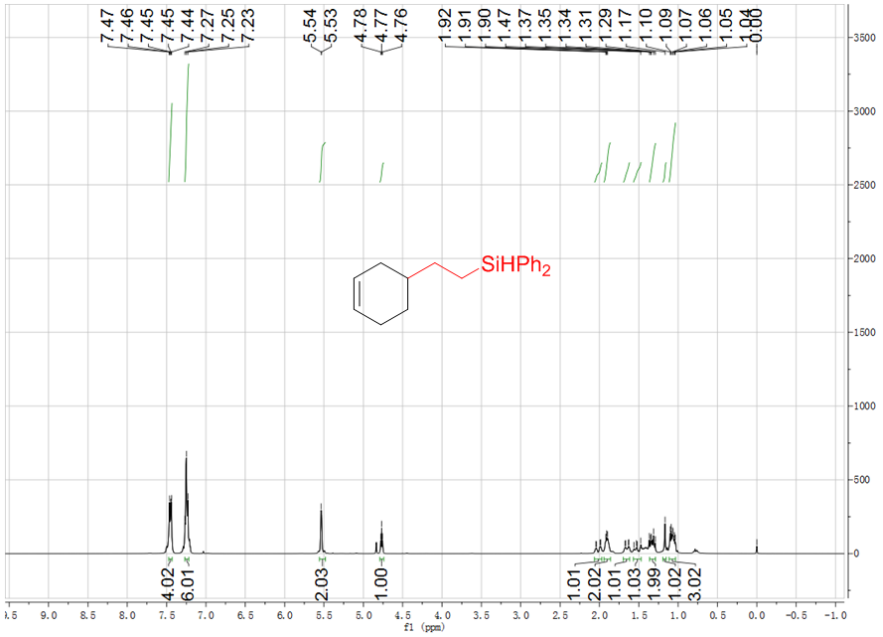



**Figure S47.** $^1$H NMR spectrum of **5q**

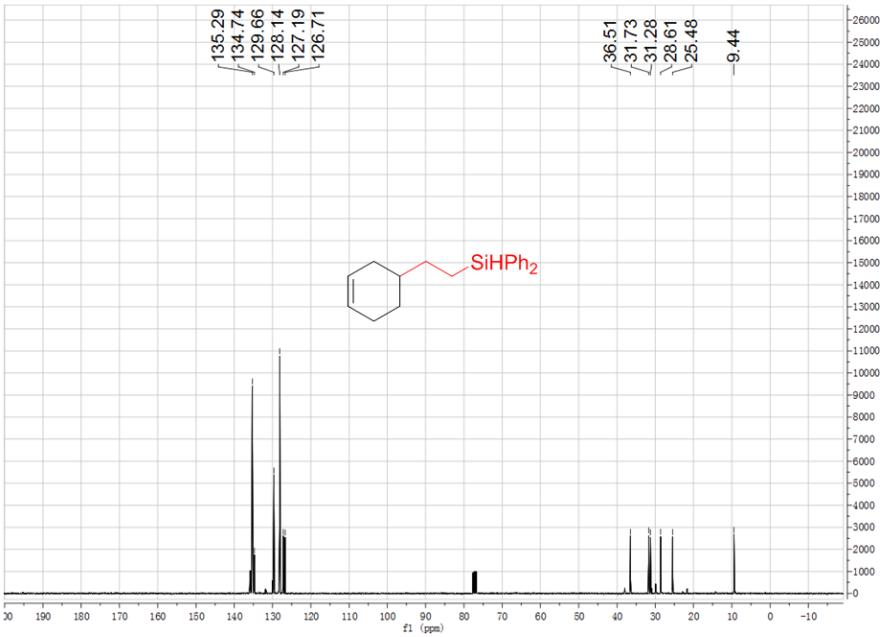
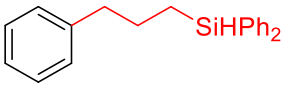



**Figure S48.** $^{13}$C NMR spectrum of **5q**

**Diphenyl(3-phenylpropyl)silane (5r)**[1]




$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.41 (dd, $J$ = 7.4, 2.0 Hz, 4H), 7.24-7.20 (m, 6H), 7.12-7.09 (m, 2H), 7.05-6.98 (m, 3H), 4.78 (t, $J$ = 3.7 Hz, 1H), 2.54 (t, $J$ = 7.5 Hz, 2H), 1.79-1.58 (m, 2H), 1.09-1.03 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 142.36, 135.40, 134.62, 129.81, 128.79, 128.52, 128.26, 126.00, 39.49, 26.58, 12.12.

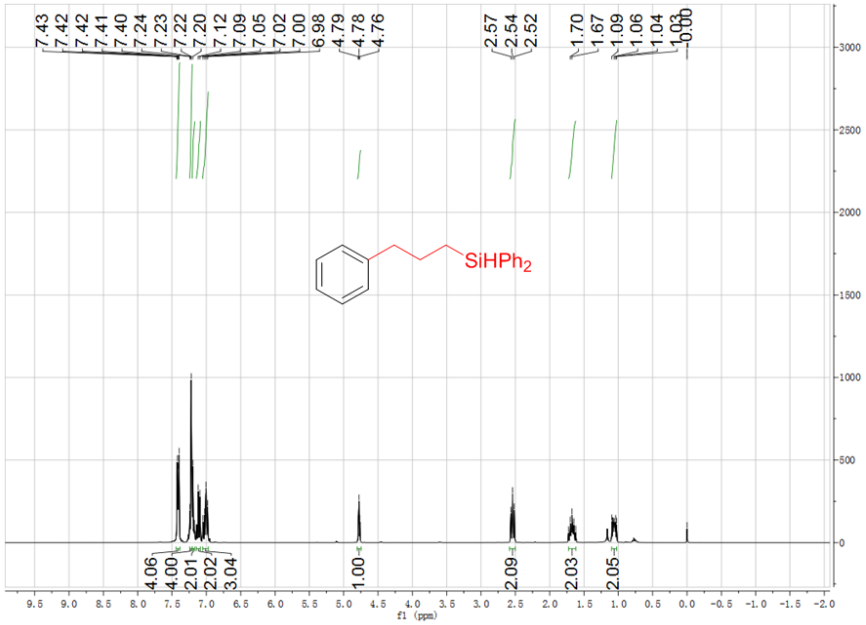



**Figure S49.** $^1$H NMR spectrum of **5r**

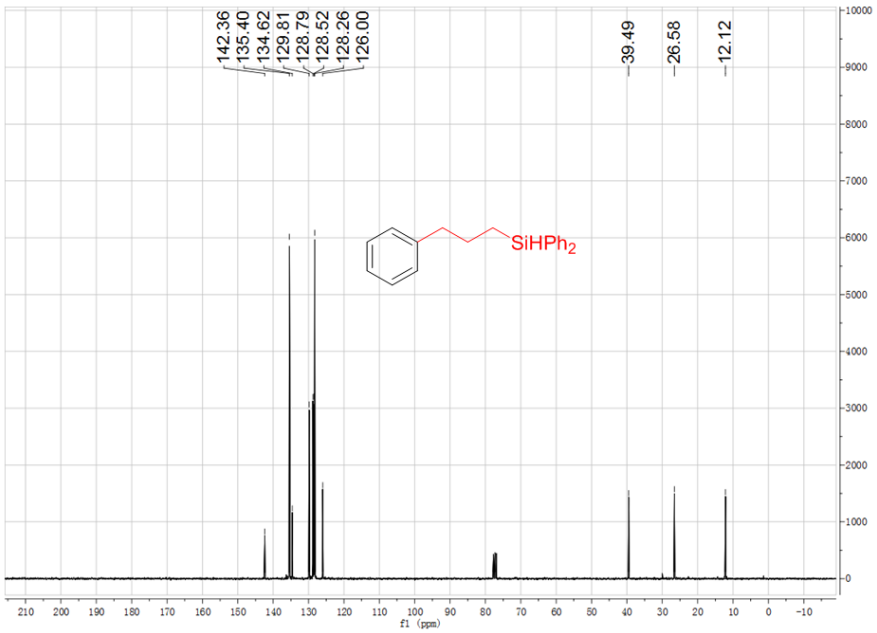
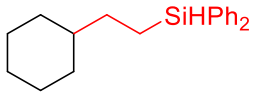



**Figure S50.** $^{13}$C NMR spectrum of **5r**

**(2-cyclohexylethyl)diphenylsilane(5s)**[1]




$^{1}$H NMR (300 MHz, CDCl3): δ (ppm) 7.47 (dd, *J* = 7.3, 2.1 Hz, 4H), 7.30-7.26 (m, 6H), 4.75 (t, *J* = 3.6 Hz, 1H), 1.67-1.57 (m, 5H), 1.30-1.22 (m, 2H), 1.13-1.05 (m, 6H), 0.81-0.73 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 135.17, 134.78, 129.49, 127.98, 40.52, 32.96, 31.89 (s), 26.80, 26.44, 9.25.

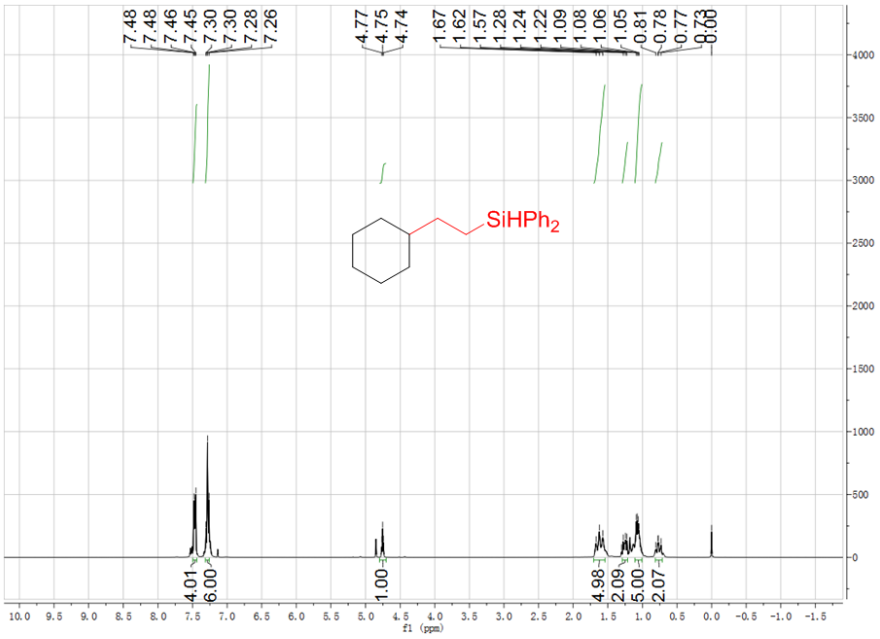



**Figure S51.** $^{1}$H NMR spectrum of **5s**

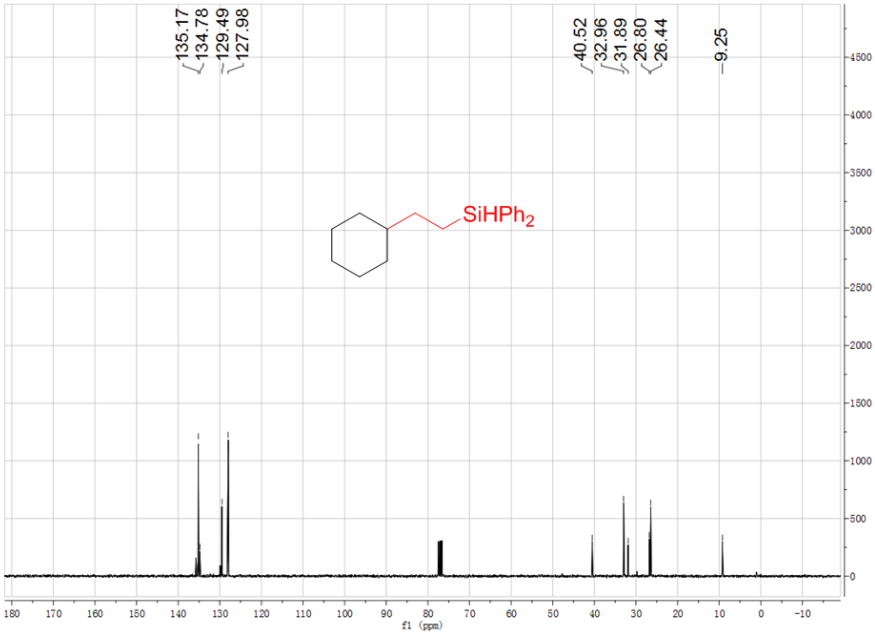



**Figure S52.** $^{13}$C NMR spectrum of **5s**

**(n-octyl)diphenylsilane (5t)**[1]


$^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.48 (dd, $J$ = 7.3, 2.0 Hz, 4H), 7.31-7.24 (m, 6H), 4.77 (t, $J$ = 3.7 Hz, 1H), 1.41-1.33 (m, 2H), 1.30-1.28 (m, 2H), 1.18-1.16 (m, 8H), 1.10-1.03 (m, 2H), 0.79 (t, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 135.14, 134.74, 129.46, 127.94, 33.19, 31.89, 29.22, 29.19, 24.40, 22.67, 14.12, 12.15.

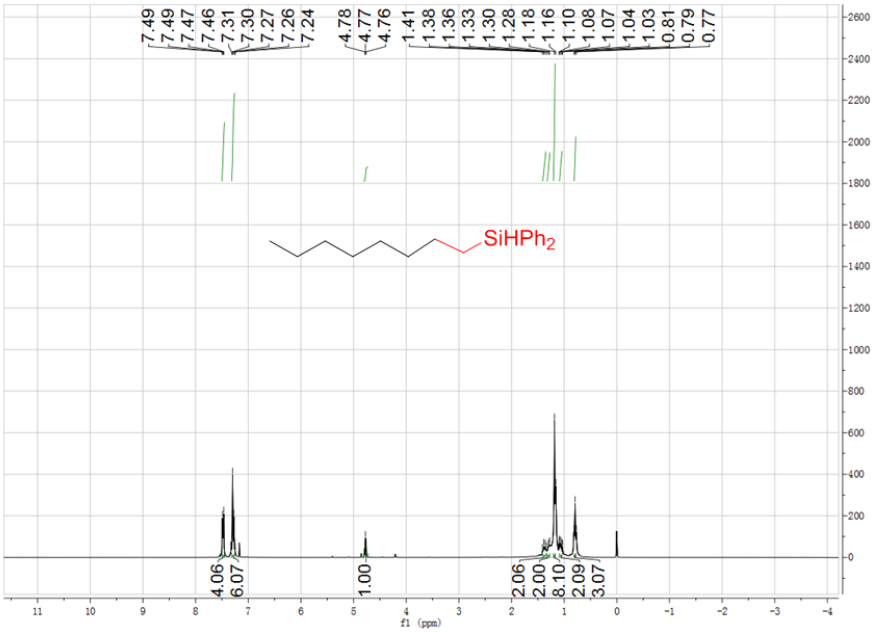



**Figure S53.** $^1$H NMR spectrum of **5t**

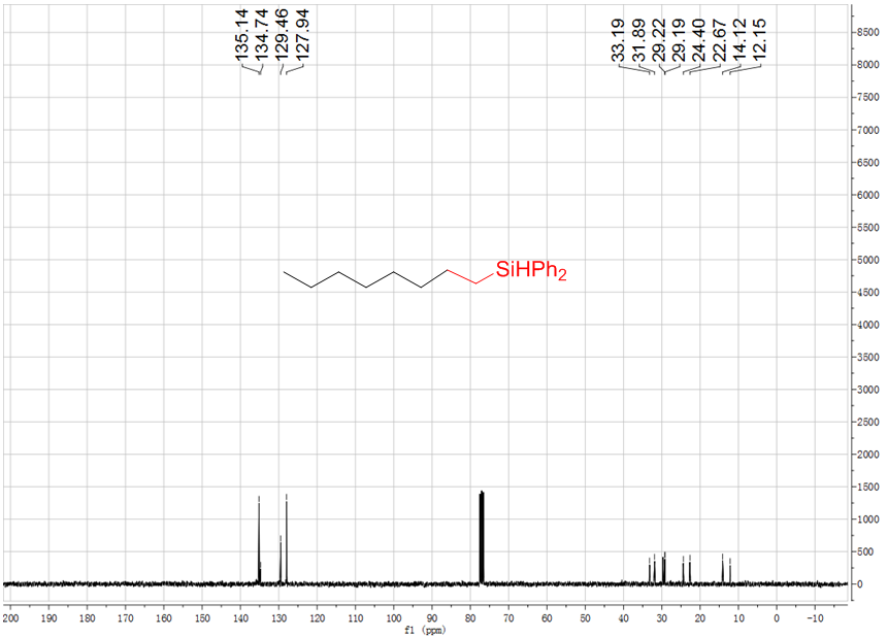



**Figure S54.** $^{13}$C NMR spectrum of **5t**

## 4. $^{1}$H NMR ,$^{31}$P NMR and GC Study on Catalytic Mechanism

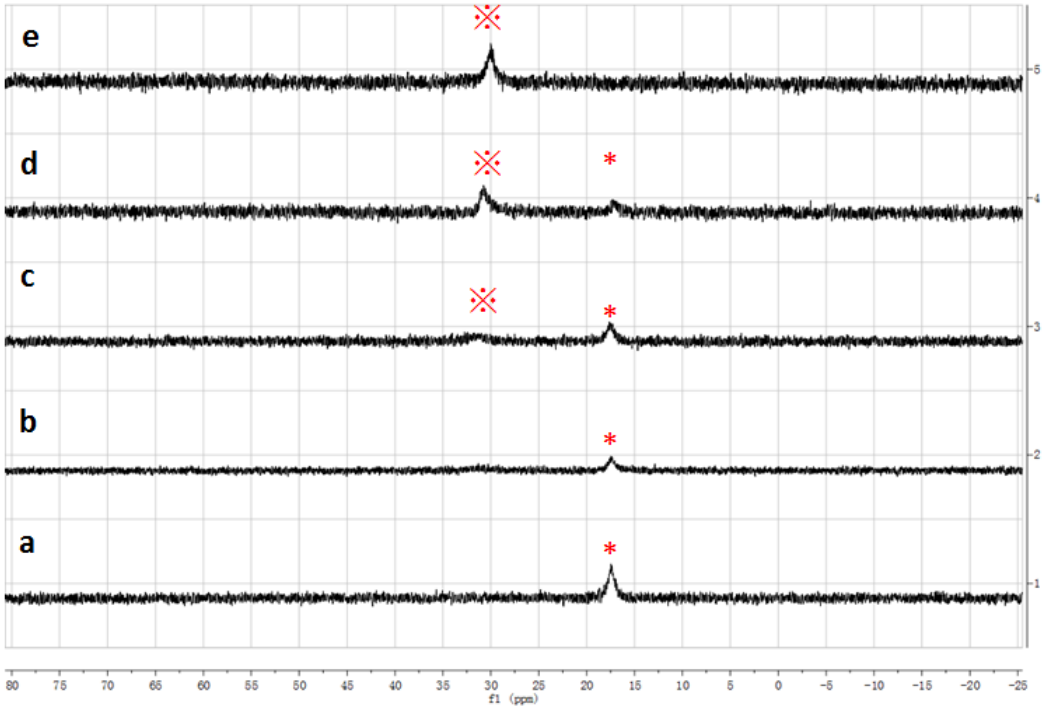



**Figure S55.** *In situ*$^{31}$P NMR of 1 eq. **3a** reacted with 10 eq. 4-*tert*-butylstyrene, (a) 1 h, (b) 2 h, (c)4 h, (d) 10 h, (e)20 h, ***3a**, δ 17.18 ppm;※.The new compound may be the complex **F**, δ30.79 ppm.

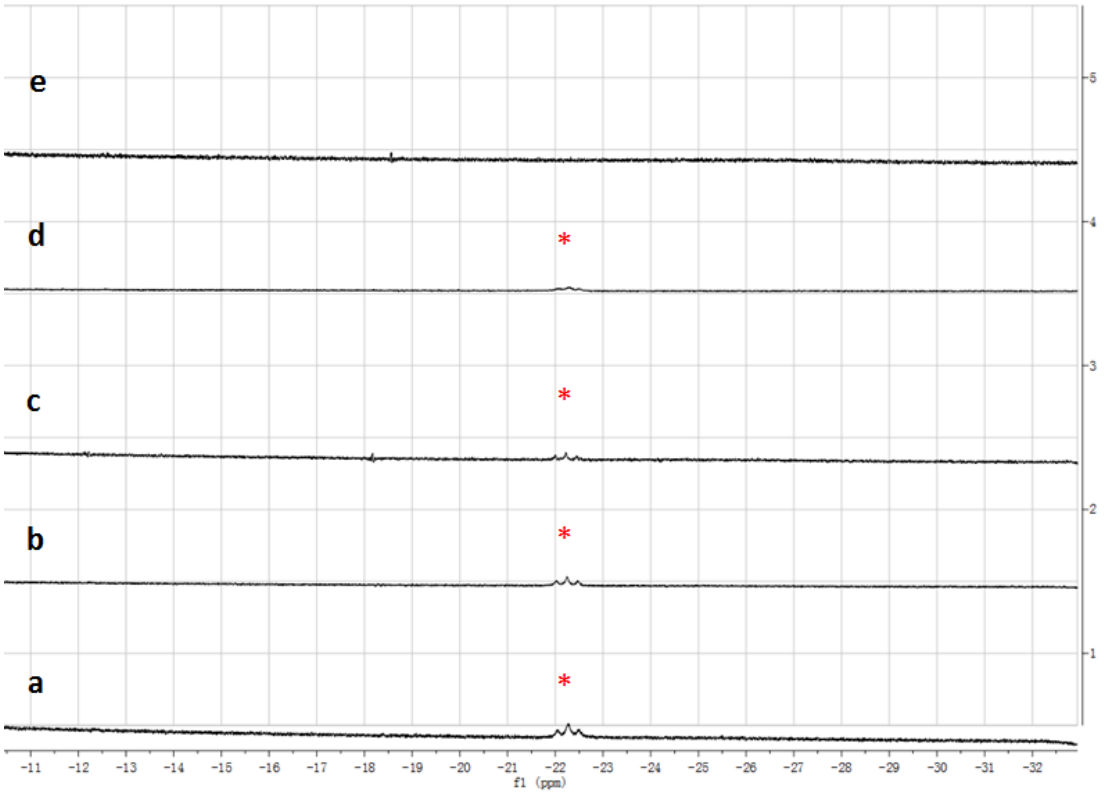



**Figure S56.** *In situ*$^{1}$H NMR of 1 eq. **3a** reacted with 10 eq. 4-*tert*-butylstyrene, (a) 1 h, (b) 2 h, (c)4 h, (d) 10 h, (e)20 h, ***3a**, δ-22.22 ppm.

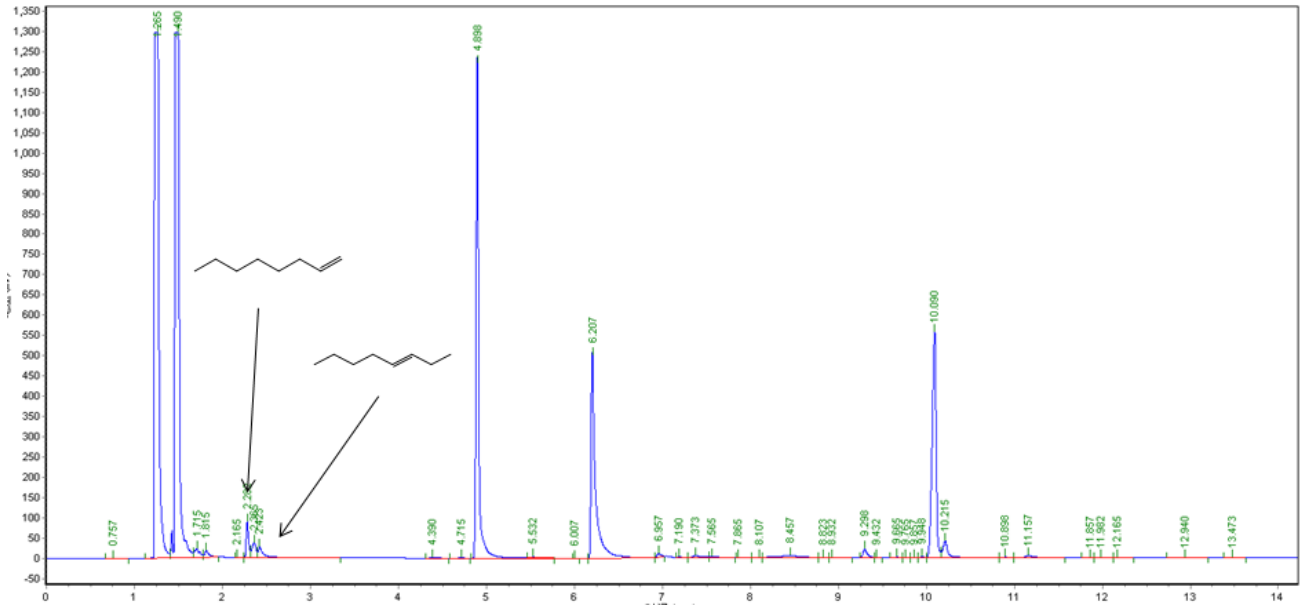


**Figure S57**. GC spectrum of the mixture formed from the reaction of 1-octene with $Ph_2SiH_2$ using **3a** as a catalyst.

**Table S3**. The Effect of the Addition Sequence of the Reactants[a]

| Entry | Catalyst | Loading (mol%) | solvent | silane | Temp (℃) | Time (h) | Conv. (%) | Product ratios (b/l) |
|---|---|---|---|---|---|---|---|---|
| 1[b] | 3a | 1 | neat | $Ph_2SiH_2$ | 70 | 10 | 55 | 72:28 |
| 2[c] | 3a | 1 | neat | $Ph_2SiH_2$ | 70 | 10 | 98 | 94:6 |

[a]Catalytic reaction conditions: Styrene (1.0 mmol), $Ph_2SiH_2$(1.2 mmol), catalyst loading (1.0 mol%), neat, conversions and product ratios were determined by GC analysis using *n*-dodecane as internal standard.

[b]Change the order of addition of the reagents: reacted silane with catalyst at 70 °C for 30 minutes first, then styrene were added and reacted at 70 ° C for 10 hours next.

[c] Change the order of addition of the reagents: reacted styrene with the catalyst at 70 °C for 30 minutes first, silane were added and reacted at 70 ° C for 10 hours next.

## 6. References

1. Gao, Y.; Wang, L.; Deng, L. Distinct Catalytic Performance of Cobalt(I)−N-Heterocyclic Carbene Complexes in Promoting the Reaction of Alkene with Diphenylsilane: Selective 2,1-Hydrosilylation, 1,2-Hydrosilylation, and Hydrogenation of Alkene. *ACS Catal*. **2018**, *8*, 9637−9646.

2. Gribble, M. W.; Pirnot, M. T.; Bandar, J. S.; Liu, R. Y.; Buchwald, S. L. Cobalt-Catalyzed Asymmetric Hydrogenation of Vinylsilanes with a Phosphine−Pyridine−Oxazoline Ligand: Synthesis of Optically Active Organosilanes and Silacycles. *Organometallics.* **2019**, *38*, 3906−3911.

3. Gribble, M.W.; Pirnot, M. T.; Bandar, J. S.; Liu, R. Y.; Buchwald, S. L. Asymmetric Copper Hydride-Catalyzed Markovnikov Hydrosilylation of Vinylarenes and Vinyl Heterocycles. *J. Am. Chem. Soc.* **2017**, *139*, 2192−2195.