

Supporting Information to the *New Journal of Chemistry*

Synthesis and property of [PCP] pincer silyene cobalt(I) complexes

Yonghui Li,^a Qingqing Fan,^a Haiquan Yang,^a Shangqing Xie,^a Wei Huang,^a Xiaoyan Li,^a Hongjian Sun^{*a}, Olaf Fuhr,^b and 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, 250100 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*

Correspondence author: hjsun@sdu.edu.cn

Contents

1. Crystallographic Data of complexes 2 , 3 , 4 and 6	S2
2. IR and NMR spectra of ligand L2	S4
3. IR and NMR spectra of complexes 2 , 3 , 4 and 6	S6
4. ¹ H and ¹³ C NMR spectra of the catalytic products	S15

1. Crystallographic Data of complexes **2**, **3**, **4** and **6**

Table 1. Crystallographic Data for Complexes **2** and **3**

	2	3
formula	C ₄₅ H ₅₇ ClCoN ₂ O ₂ P ₃ Si	C ₄₆ H ₅₉ ClCoN ₂ O ₂ P ₃ Si
M	873.30	887.33
crystal system	monoclinic	orthorhombic
space group	P2 ₁ /n	Pbca
a/Å	10.1744(3)	13.6916(5)
b/Å	9.3902(2)	13.9509(8)
c/Å	46.7097(14)	47.3618(11)
α/°	90	90
β/°	94.478(2)	90
γ/°	90	90
V [Å ³]	4449.0(2)	9046.6(6)
Z	4	8
M [mm ⁻¹]	3.468	3.416
F(000)	1840.0	3744.0
2θ range for data collection/°	7.634 to 124.998	6.488 to 125.134
reflections collected	25053	31022
independent reflections	10346 [R _{int} = 0.0350, R _{sigma} = 0.0366]	10660 [R _{int} = 0.0264, R _{sigma} = 0.0263]
indep. refl. with I ≥ 2σ (I)	8106	8488
data/restraints/parameters	10346/0/505	10660/0/515
goodness-of-fit on F ²	1.081	1.050
final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0620, wR ₂ = 0.1557	R ₁ = 0.0364, wR ₂ = 0.0963
final R indexes [all data]	R ₁ = 0.0792, wR ₂ = 0.1649	R ₁ = 0.0488, wR ₂ = 0.1016

Table 2. Crystallographic Data for Complexes **4** and **6**

	4	6
formula	C ₄₃ H ₄₈ ClCoN ₂ O ₃ P ₂ Si	C ₃₀ H ₃₄ CoIO ₂ P ₃
M	825.24	705.31
crystal system	monoclinic	orthorhombic
space group	P21/c	Pbca
a/Å	16.7134(2)	21.4260(11)
b/Å	12.4172(2)	15.1726(7)
c/Å	22.7388(3)	18.2179(8)
α /°	90	90
β /°	90.7763(13)	90
γ /°	90	90
V [Å ³]	4718.64(13)	5922.4(5)
Z	4	8
M [mm ⁻¹]	4.561	9.750
F(000)	1826.0	2840.0
2 θ range for data collection/°	5.288 to 152.902	7.51 to 115.172
Index ranges	-21 ≤ h ≤ 21, -15 ≤ k ≤ 14, -23 ≤ l ≤ 28	-26 ≤ h ≤ 26, -8 ≤ k ≤ 19, -22 ≤ l ≤ 19
Reflections collected	26561	30142
Independent reflections	9309 [R _{int} = 0.0426, R _{sigma} = 0.0460]	6138 [R _{int} = 0.0719, R _{sigma} = 0.0502]
Data/restraints/parameters	9309/0/531	6138/0/337
Goodness-of-fit on F ²	1.060	0.916
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0600, wR ₂ = 0.1731	R ₁ = 0.0344, wR ₂ = 0.0740
Final R indexes [all data]	R ₁ = 0.0808, wR ₂ = 0.2176	R ₁ = 0.0618, wR ₂ = 0.0793

1. IR and NMR spectra of ligand L2

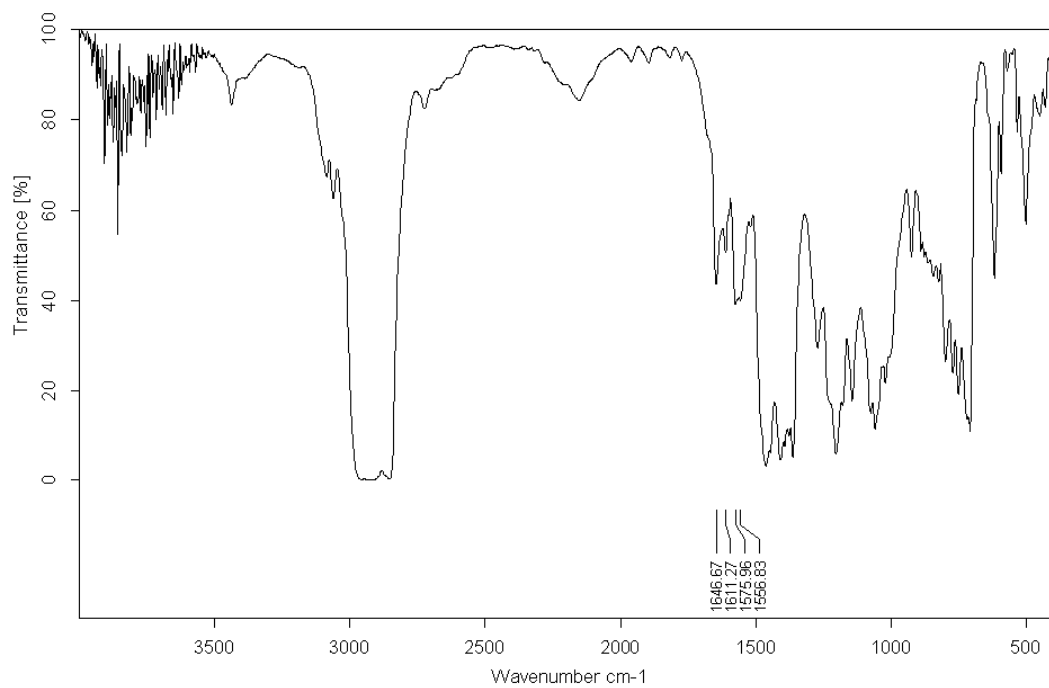


Figure S1. IR of L2

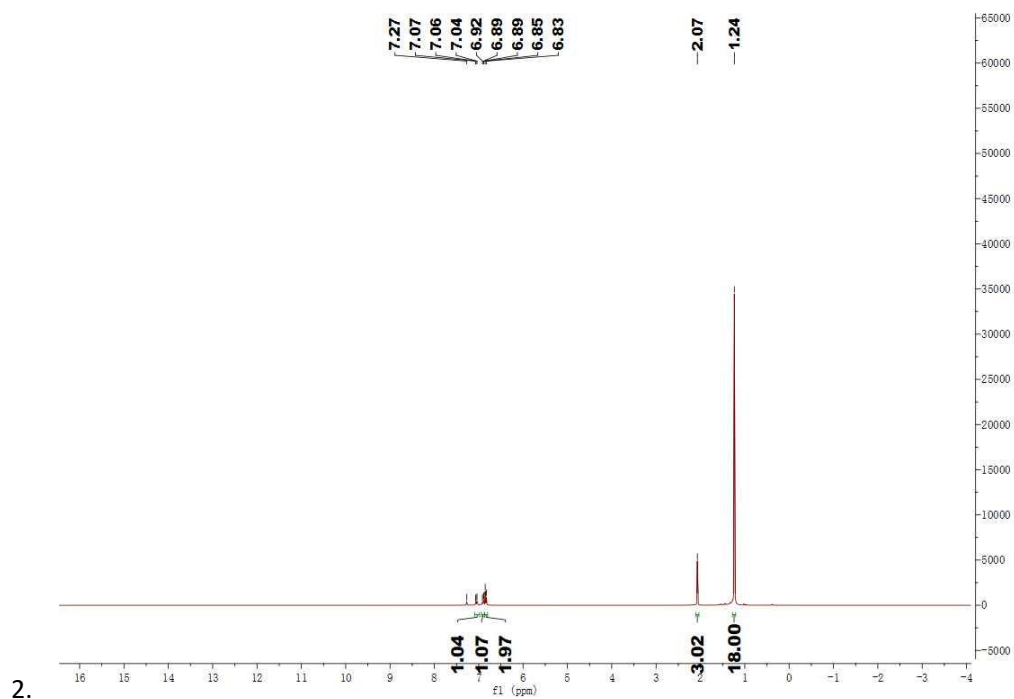


Figure S2. ¹H NMR of L2 in C₆D₆

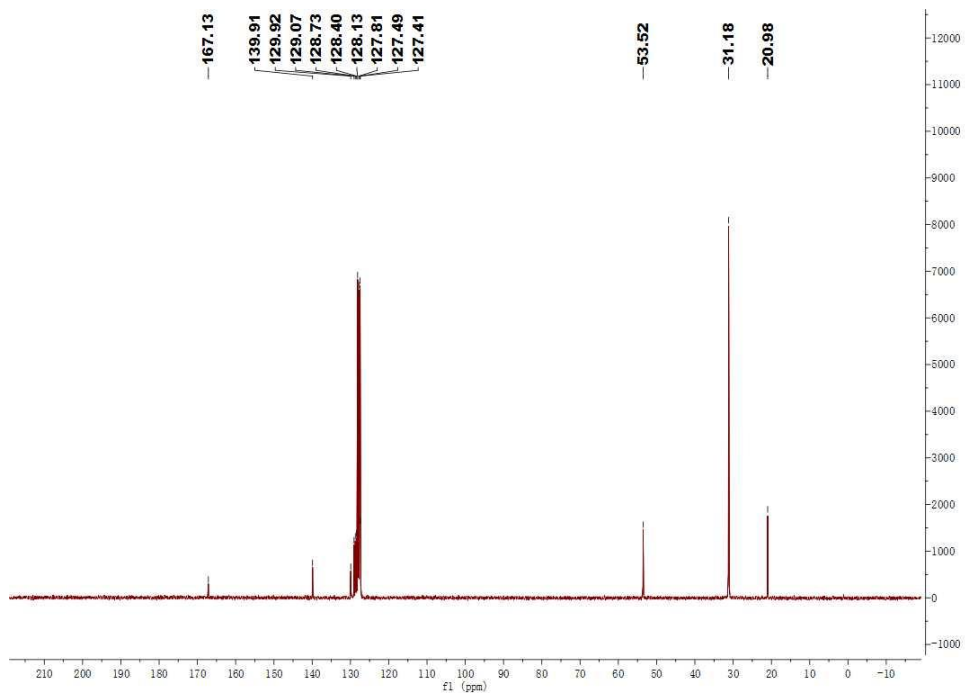


Figure S3. ^{13}C NMR of **L2** in C_6D_6

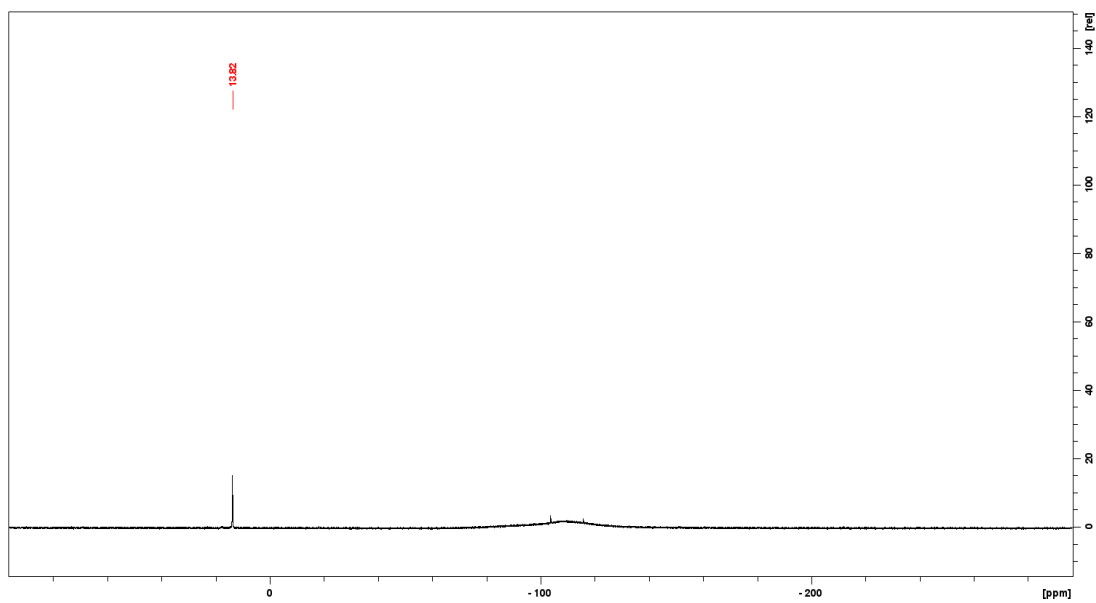


Figure S4. ^{29}Si NMR of **L2** in C_6D_6

3. IR and NMR spectra of complexes 2, 3, 4 and 6

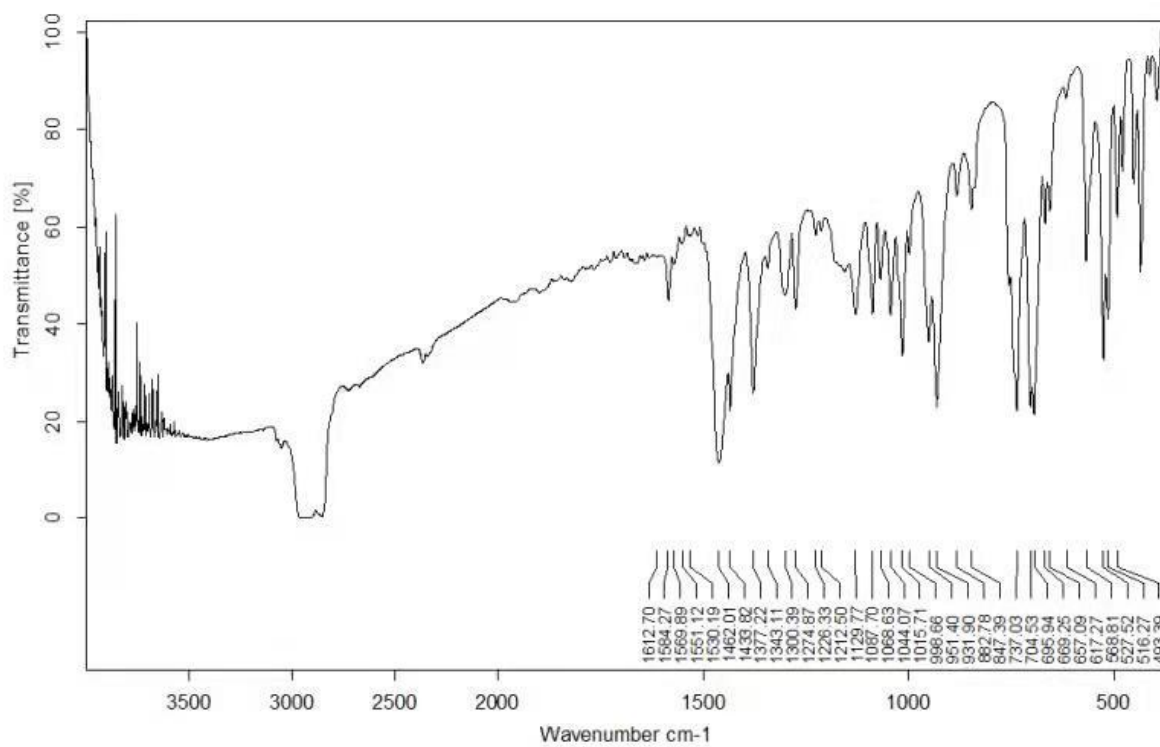


Figure S5. IR of 2

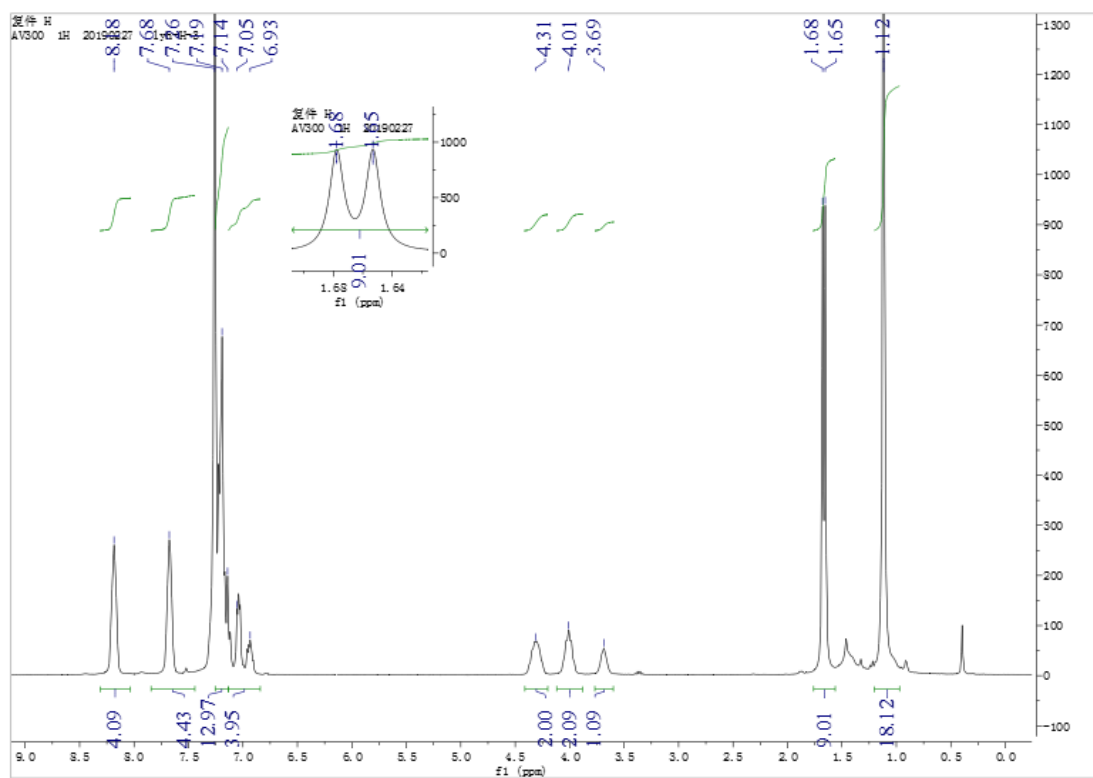


Figure S6. ¹H NMR of 2 in C₆D₆

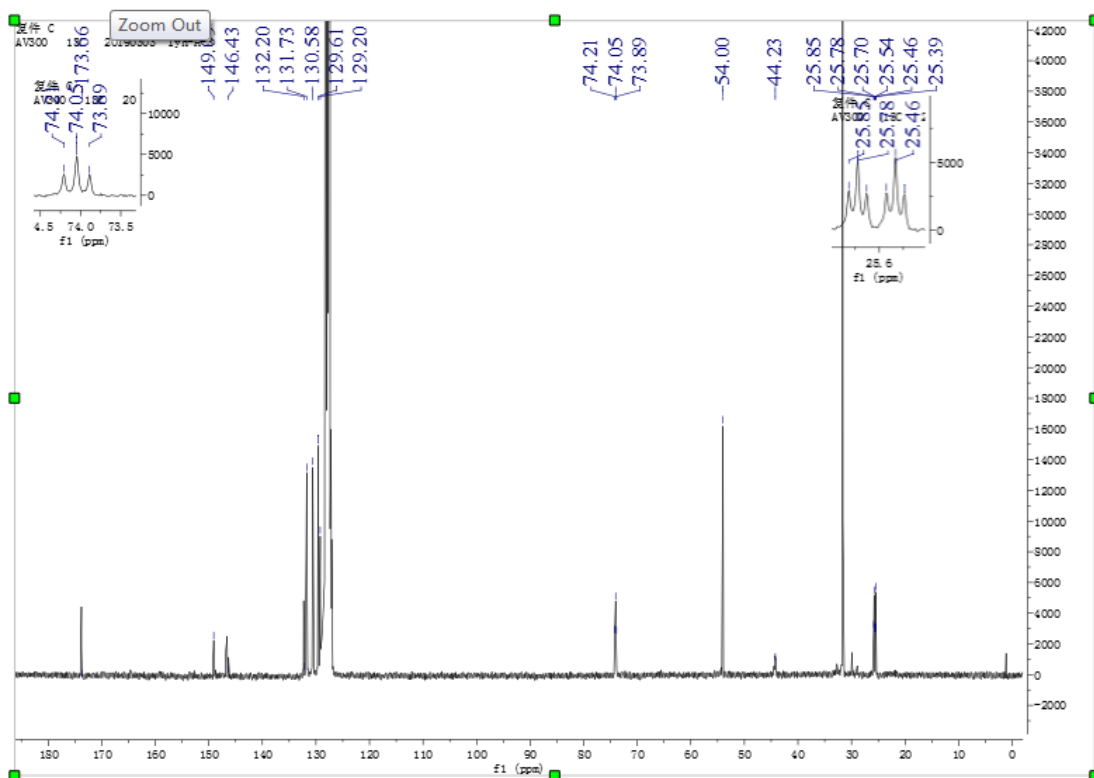


Figure S7. ^{13}C NMR of **2** in C_6D_6

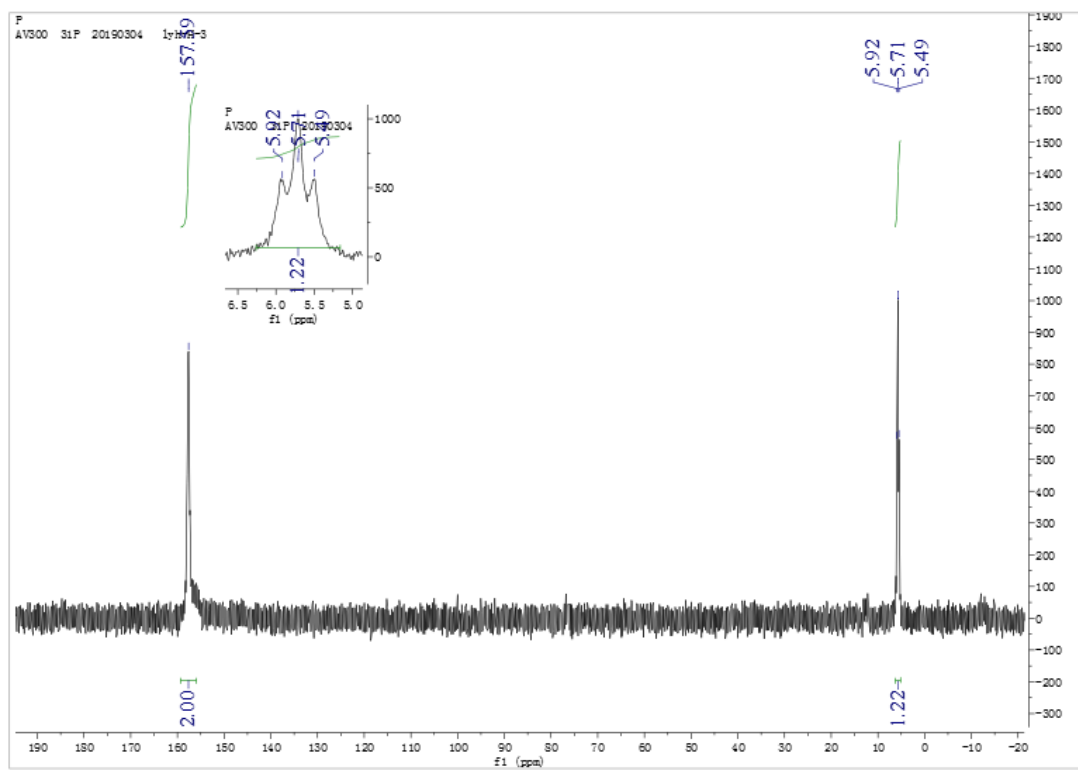


Figure S8. ^{31}P NMR of **2** in C_6D_6

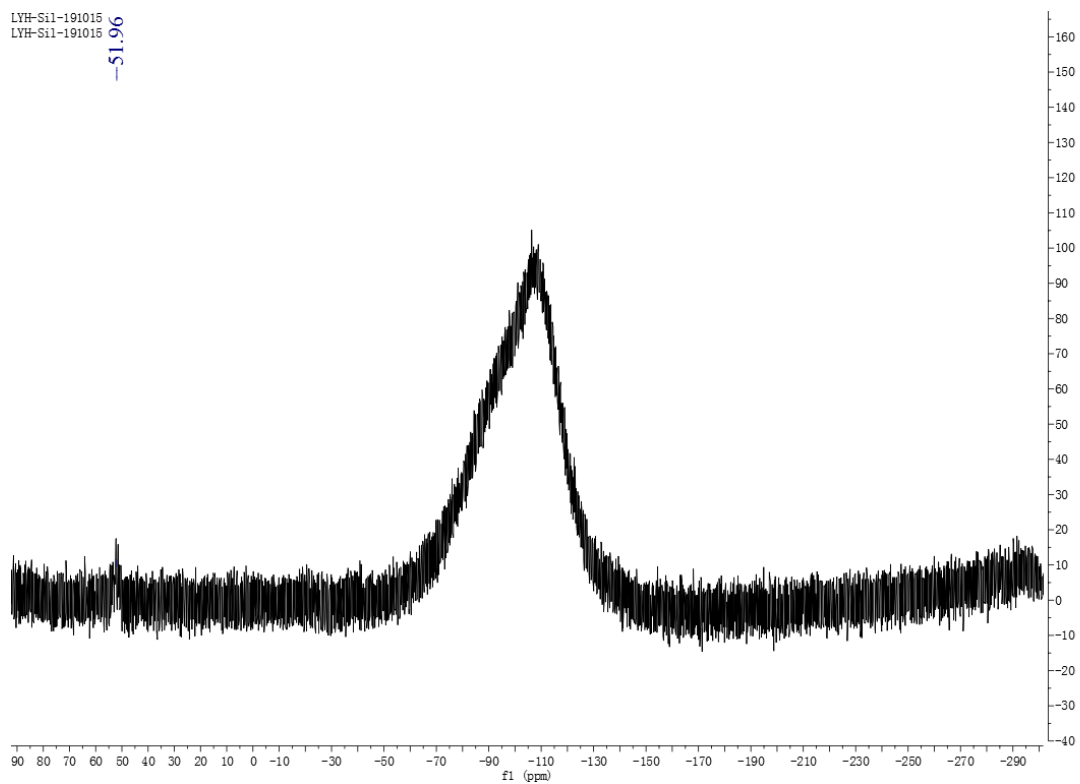


Figure S9. ^{29}Si NMR of **2** in C_6D_6

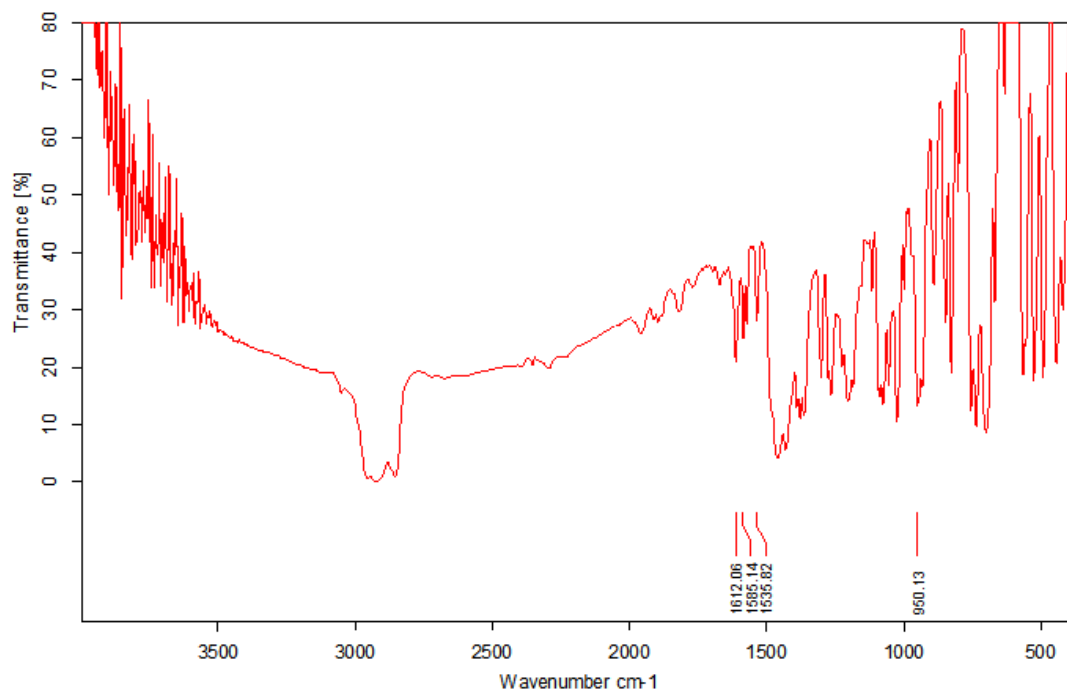


Figure S10. IR of **3**

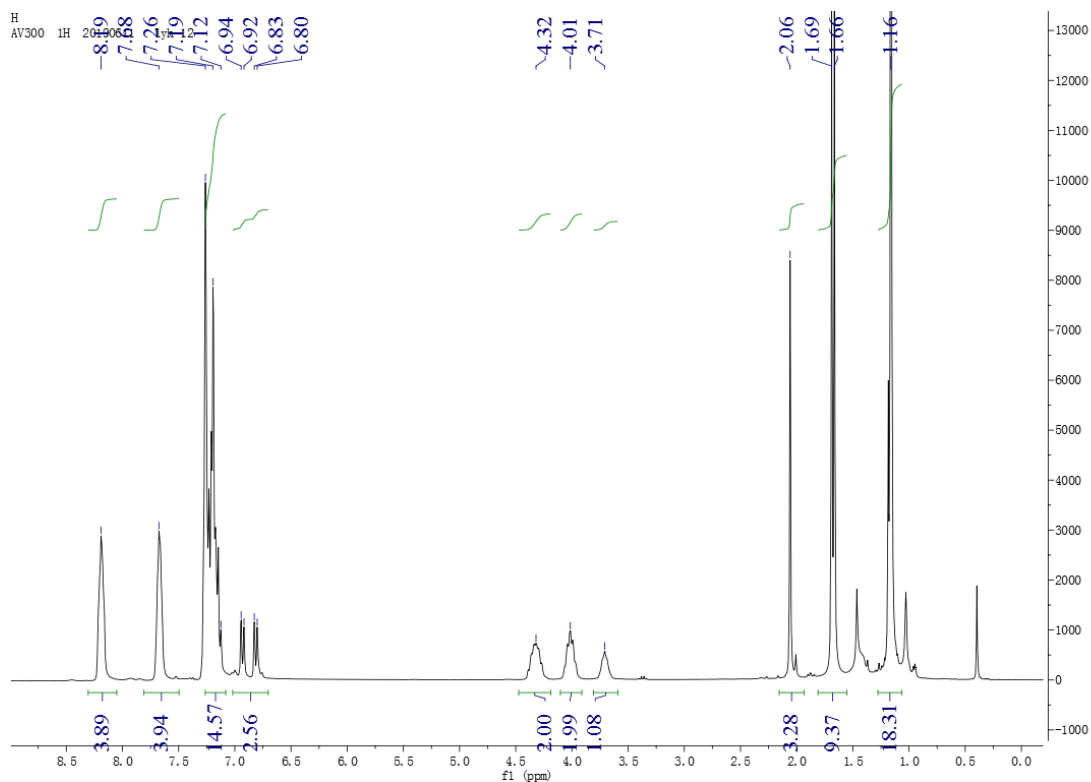


Figure S11. ¹H NMR of 3 in C₆D₆

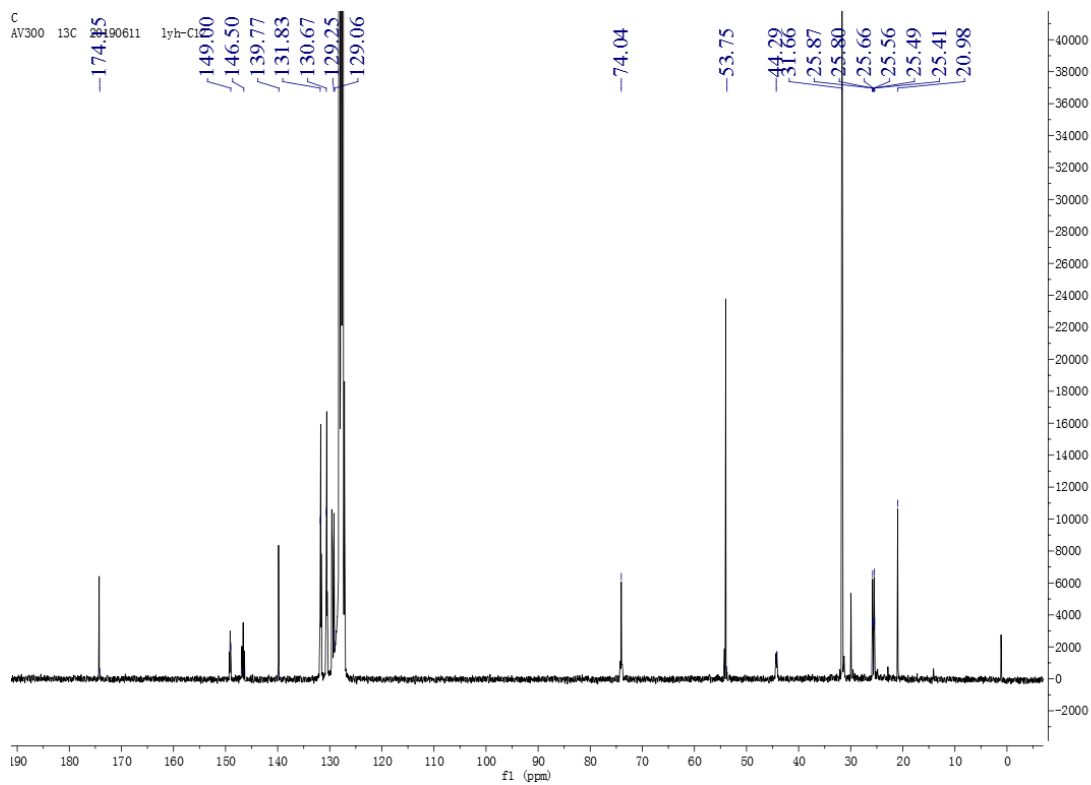


Figure S12. ¹³C NMR of 3 in C₆D₆

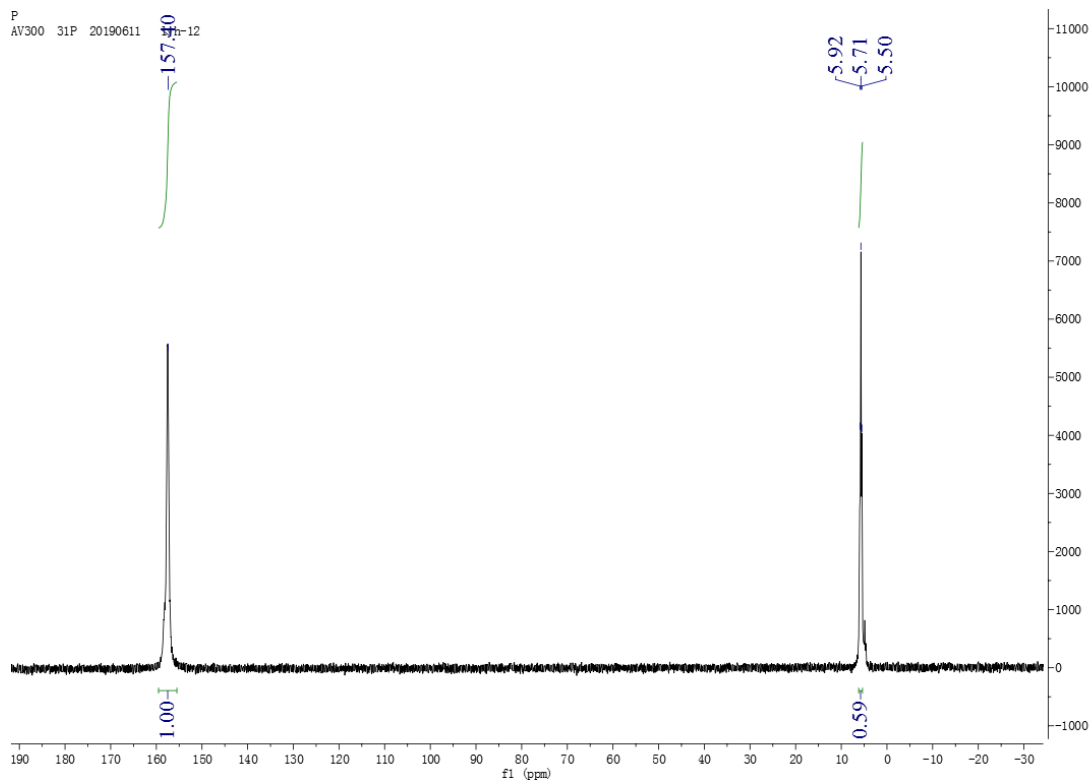


Figure S13. ^{31}P NMR of **3** in C_6D_6

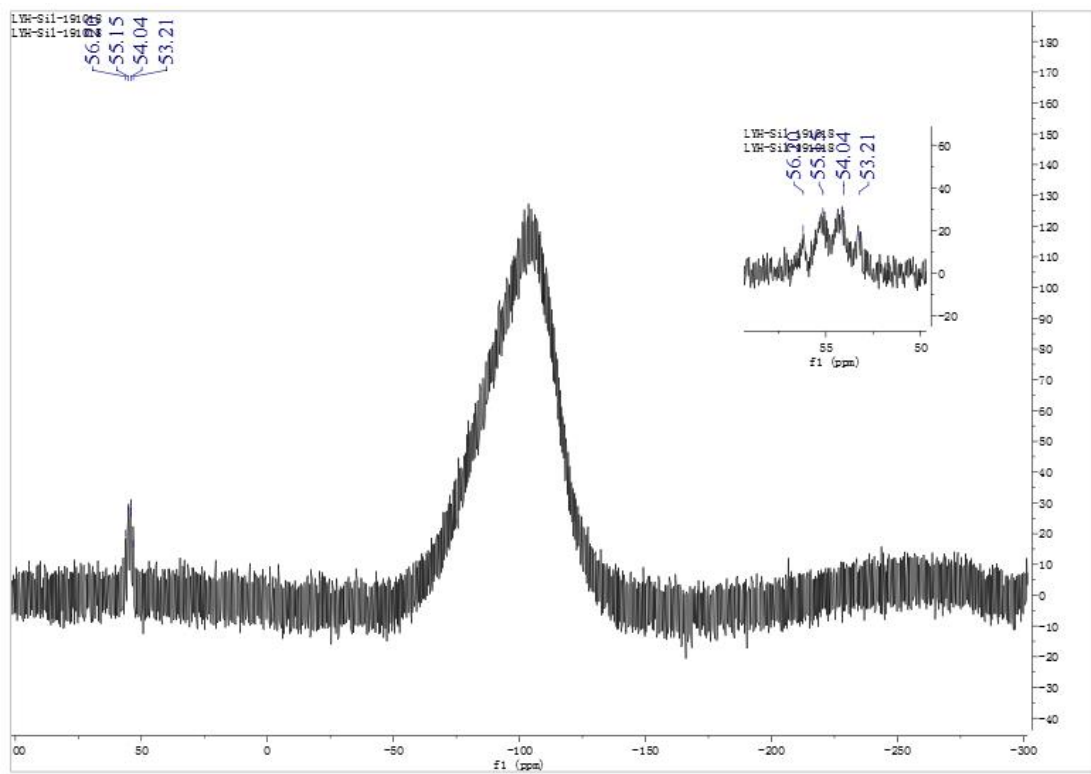


Figure S14. ^{29}Si NMR of **3** in C_6D_6

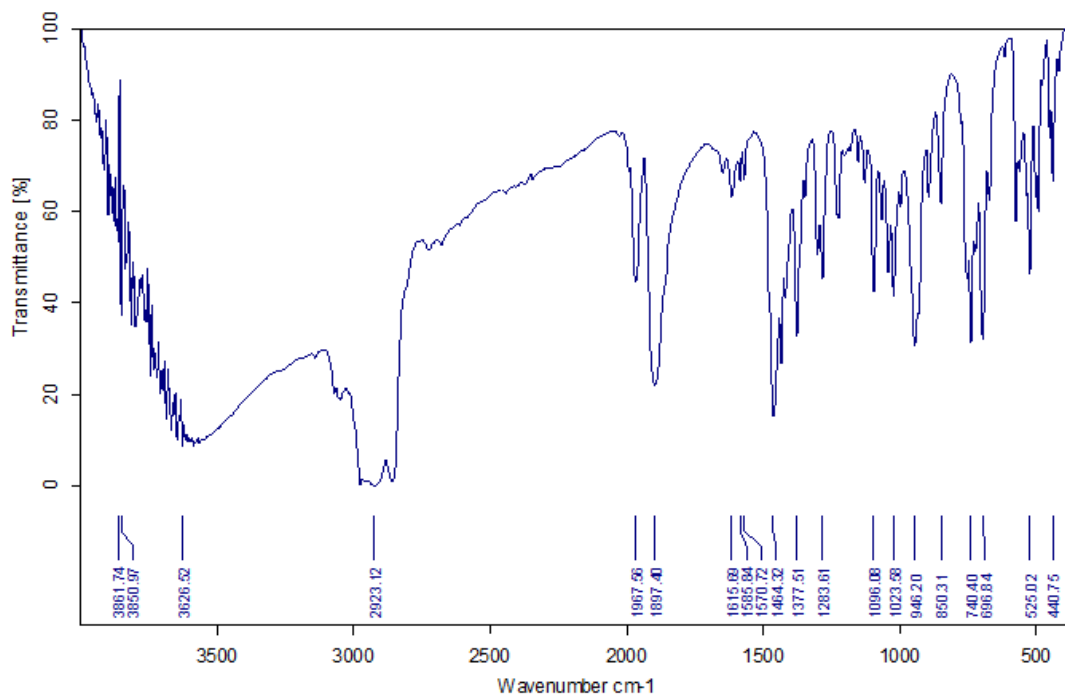


Figure S15. IR of 4

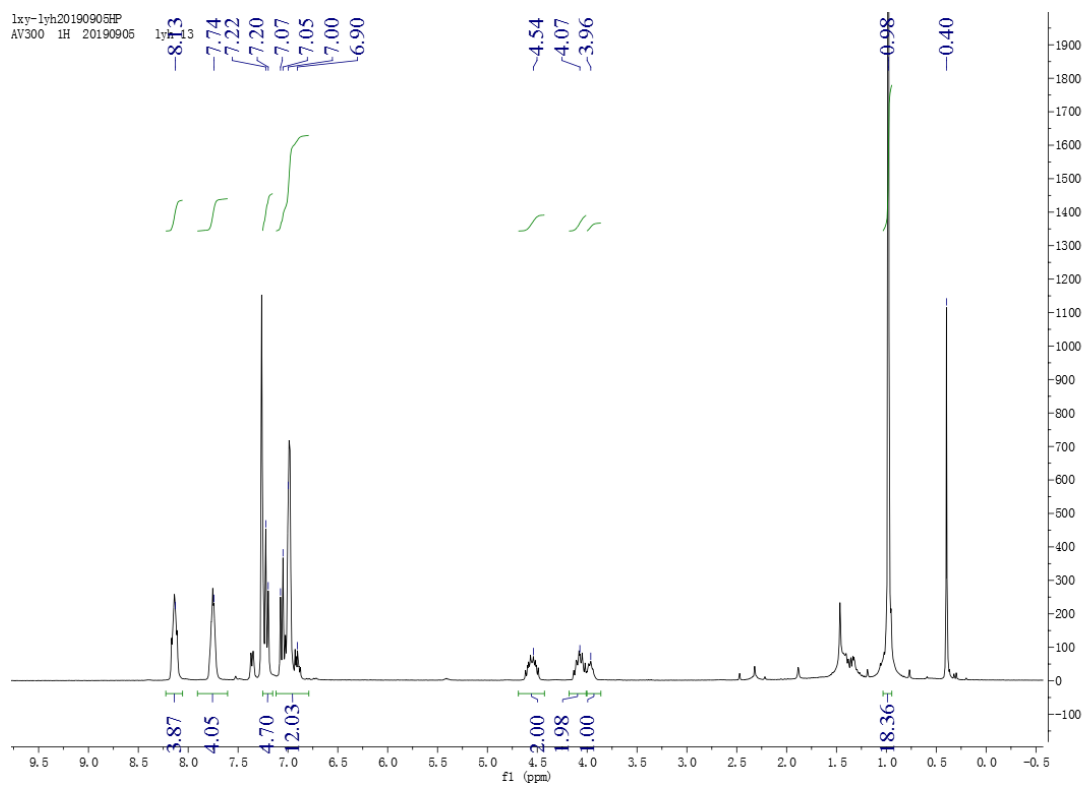


Figure S16. ^1H NMR of 4 in C_6D_6

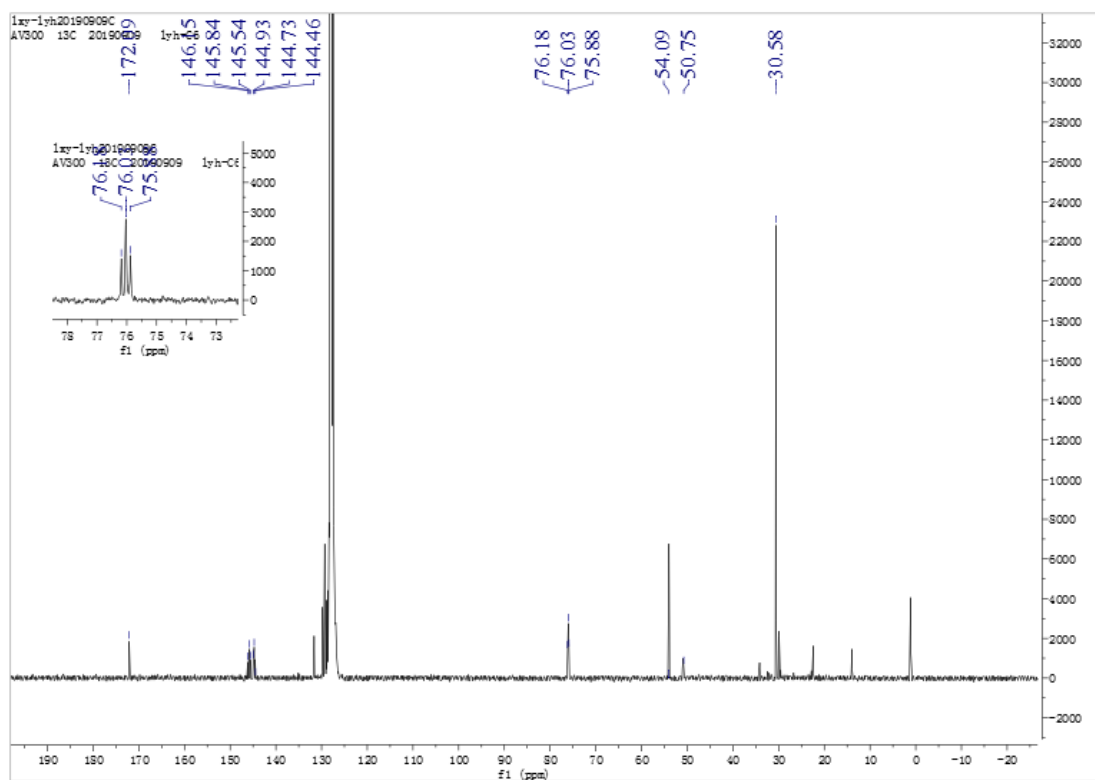


Figure S17. ^{13}C NMR of 4 in C_6D_6

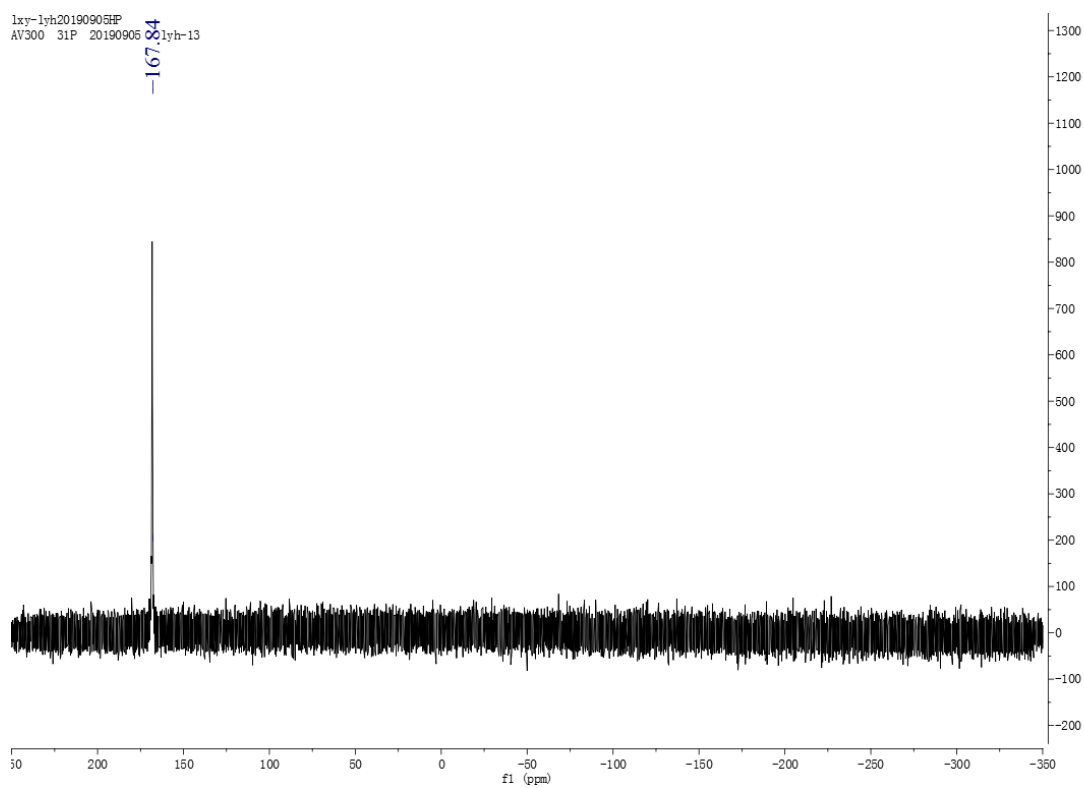


Figure S18. ^{31}P NMR of 4 in C_6D_6

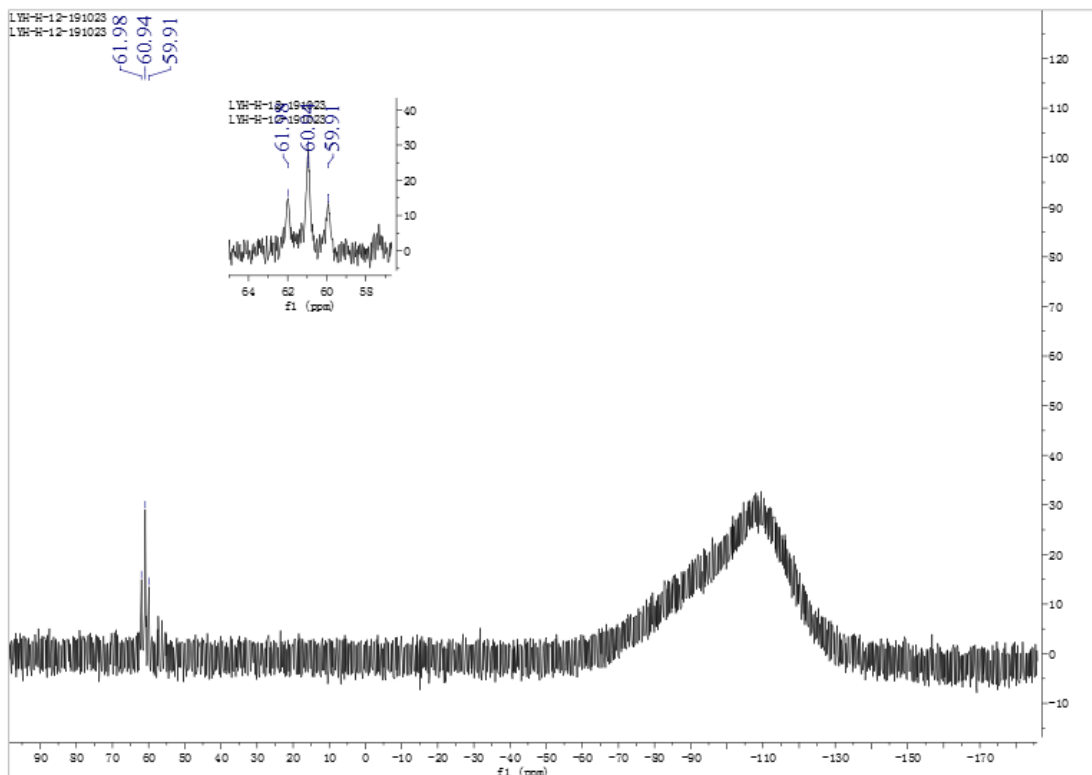


Figure S19. ^{29}Si NMR of 4 in C_6D_6

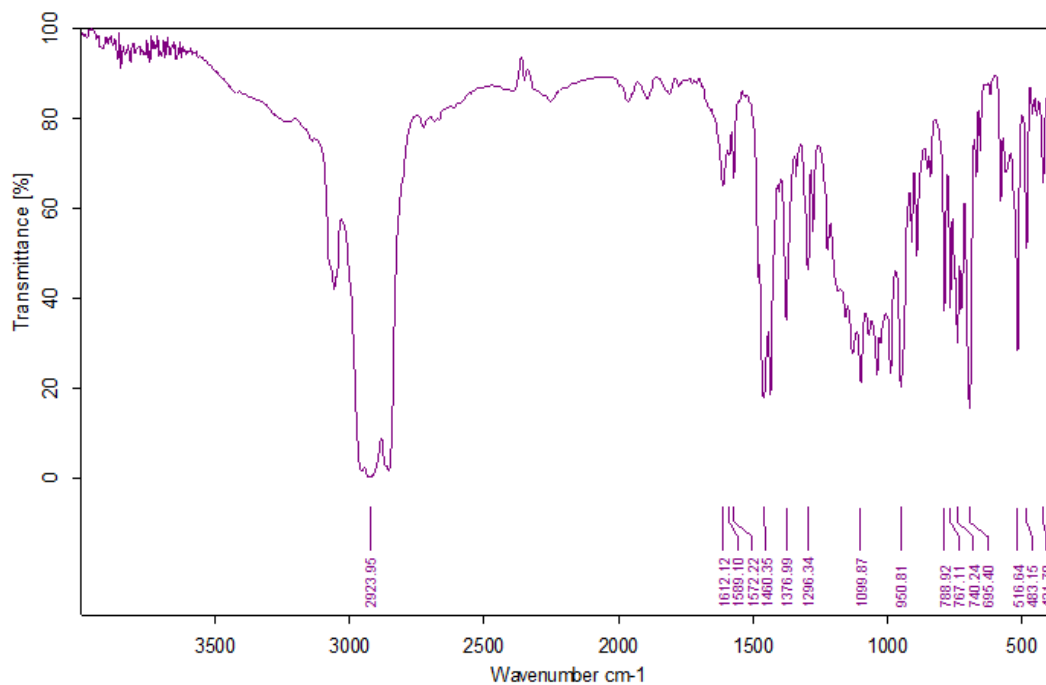


Figure S20. IR of 6

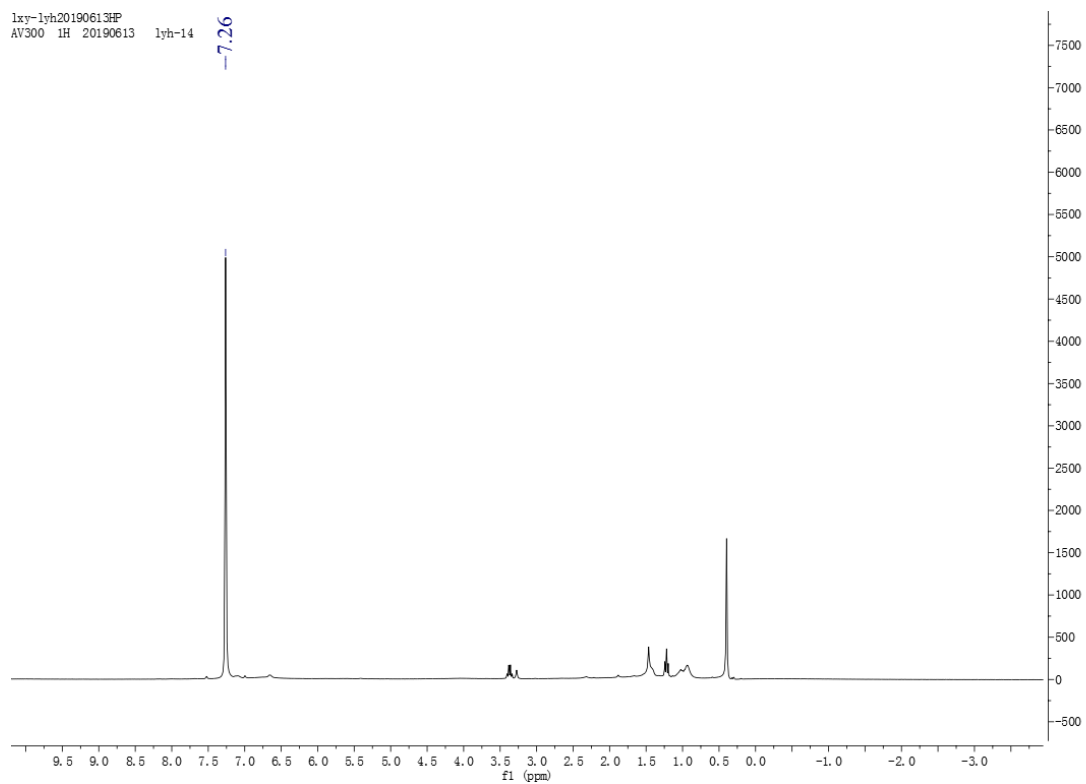


Figure S21. ^1H NMR of **6** in C_6D_6

4. ^1H and ^{13}C NMR spectra of the catalytic products

Diphenyl(1-phenylethyl)silane (2a)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.53 - 7.50 (m, 2H), 7.35-7.30 (m, 6H), 7.26-6.99 (m, 7H), 4.85 (d, $J = 3.3$ Hz, 1H), 2.82 (qd, $J = 7.5, 3.4$ Hz, 1H), 1.46 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 144.46, 135.86, 135.71, 133.15, 129.87, 129.73, 128.32, 128.08, 128.0, 127.89, 127.86, 125.08, 27.11, 16.66.

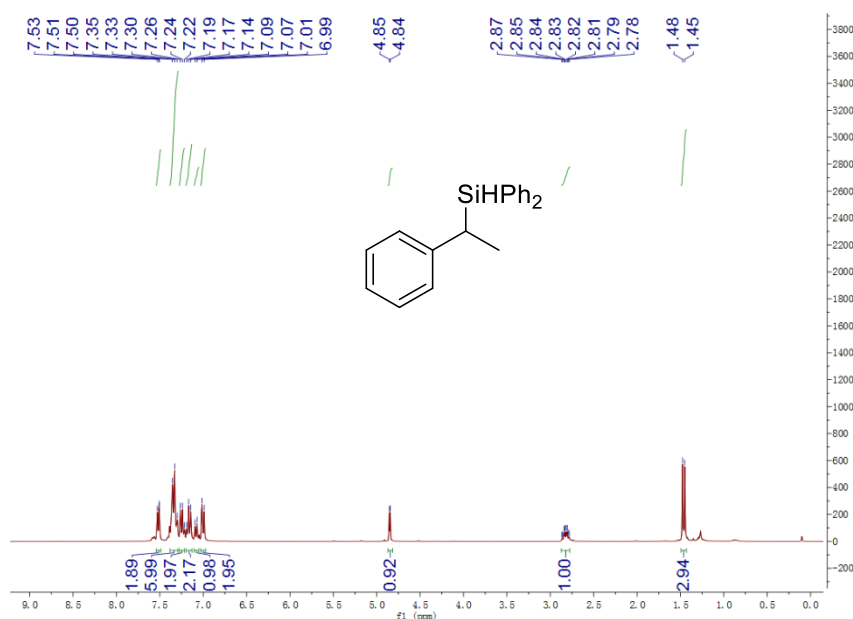


Figure S22. ^1H NMR of 2a (CDCl_3)

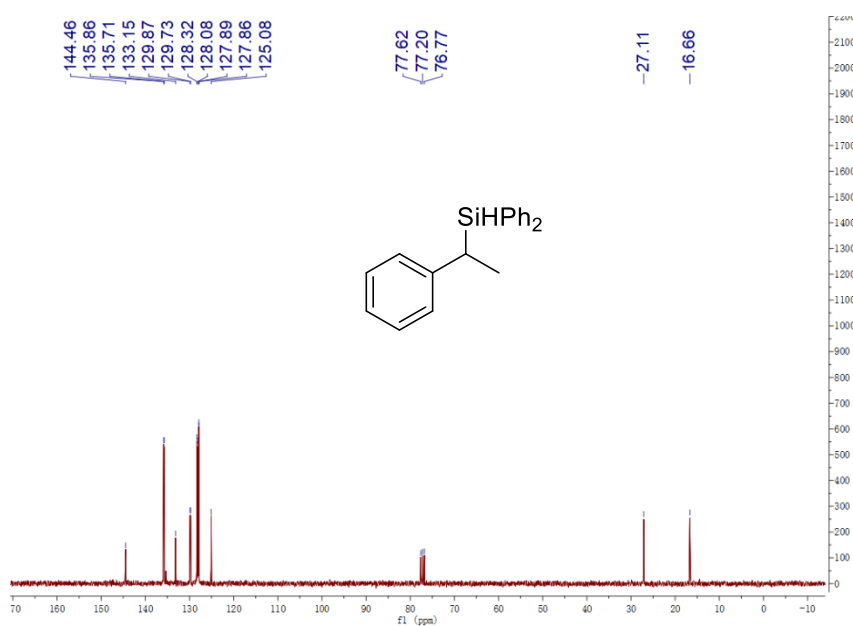


Figure S23. ^{13}C NMR of 2a (CDCl_3)

Diphenyl(1-(*p*-tolyl)ethyl)silane (**2b**)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.44-7.42 (m, 2H) 7.30-7.22 (m, 6H), 7.19-7.17 (m, 2H), 6.92-6.80 (m, 2H), 4.75 (d, $J = 3.3$ Hz, 1H), 2.70 (qd, $J = 7.5, 3.5$ Hz, 1H), 2.19 (s, 3H), 1.35 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 141.29, 135.83, 135.68, 134.34, 133.31, 129.76, 129.63, 129.0, 127.99, 127.82, 127.69, 26.46, 21.07, 16.82.

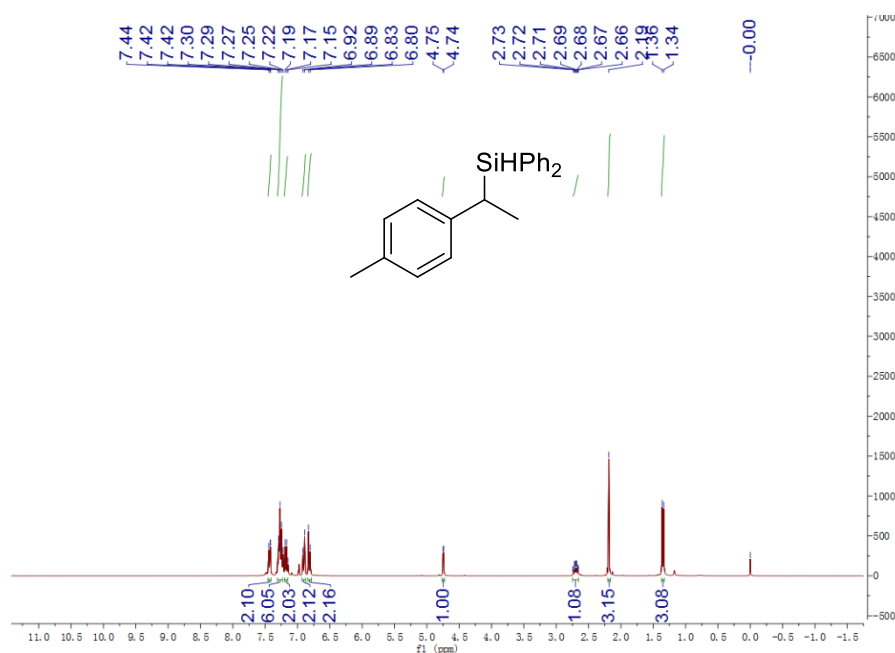


Figure S24. ^1H NMR of **2b** (CDCl_3)

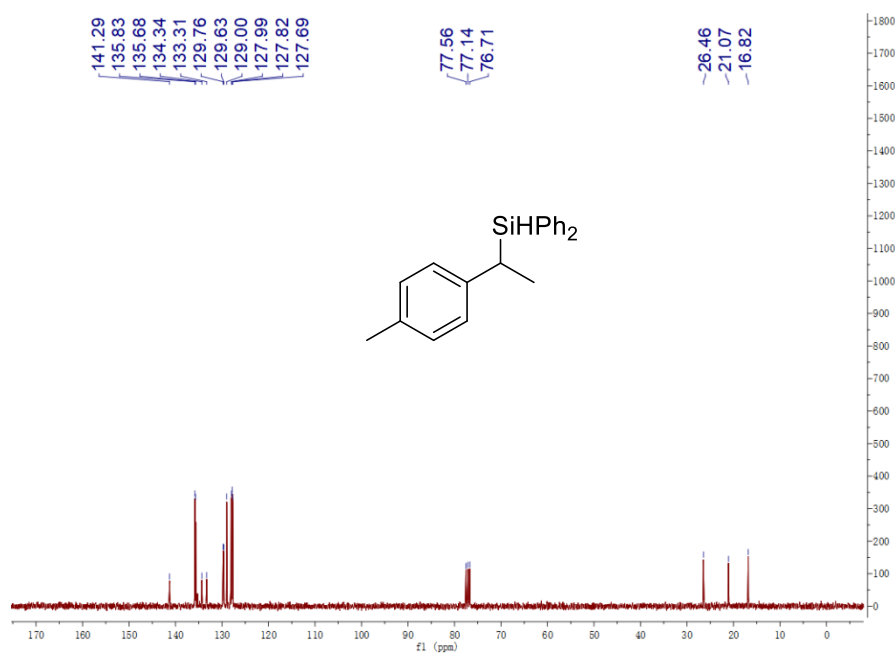


Figure S25. ^{13}C NMR of **2b** (CDCl_3)

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

^1H NMR (300 MHz, CDCl_3) δ (ppm) 7.47–7.44 (m, 2H), 7.31–7.15 (m, 9H), 6.96–6.92 (m, 3H), 4.72 (d, $J = 3.3$ Hz, 1H), 2.92 (qd, $J = 7.4, 3.4$ Hz, 1H), 1.99 (s, 3H), 1.36 (d, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 142.87, 135.86, 135.33, 133.37, 132.84, 130.10, 129.81, 129.57, 127.97, 127.73, 126.80, 126.08, 124.77, 22.03, 20.15, 16.61.

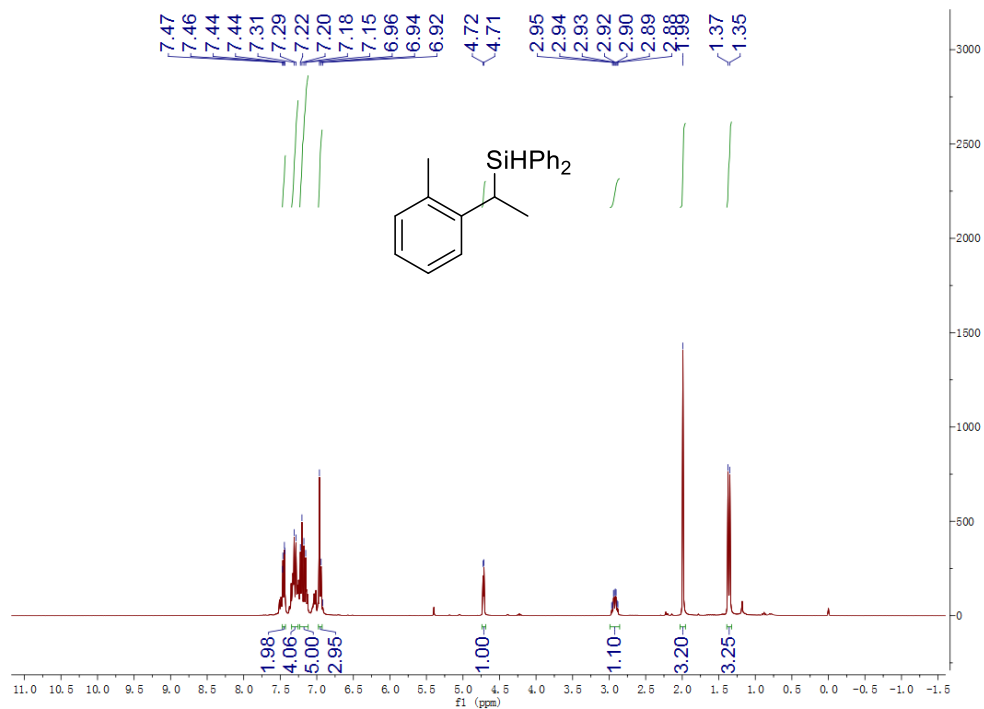


Figure S26. ^1H NMR of 2c (CDCl_3)

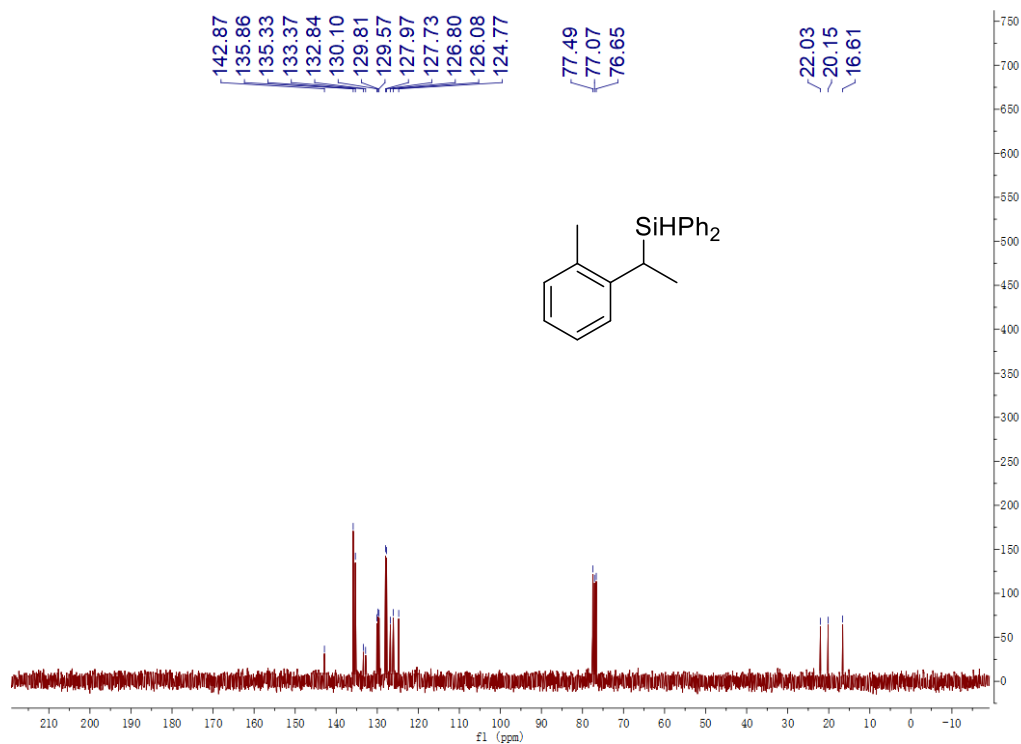


Figure S27. ^{13}C NMR of 2c (CDCl_3)

Diphenyl(1-(*m*-tolyl)ethyl)silane (**2d**)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.45-7.42 (m, 2H), 7.29-7.17 (m, 8H), 7.01-6.96 (m, 1H), 6.82-6.71 (m, 3H), 4.74 (d, $J = 3.3$ Hz, 1H), 2.74-2.65 (m, 1H), 2.13 (s, 3H), 1.36 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 144.24, 137.63, 135.81, 135.68, 133.21, 129.76, 129.63, 128.73, 128.13, 127.95, 127.75, 125.75, 124.79, 26.89, 21.49, 16.56.

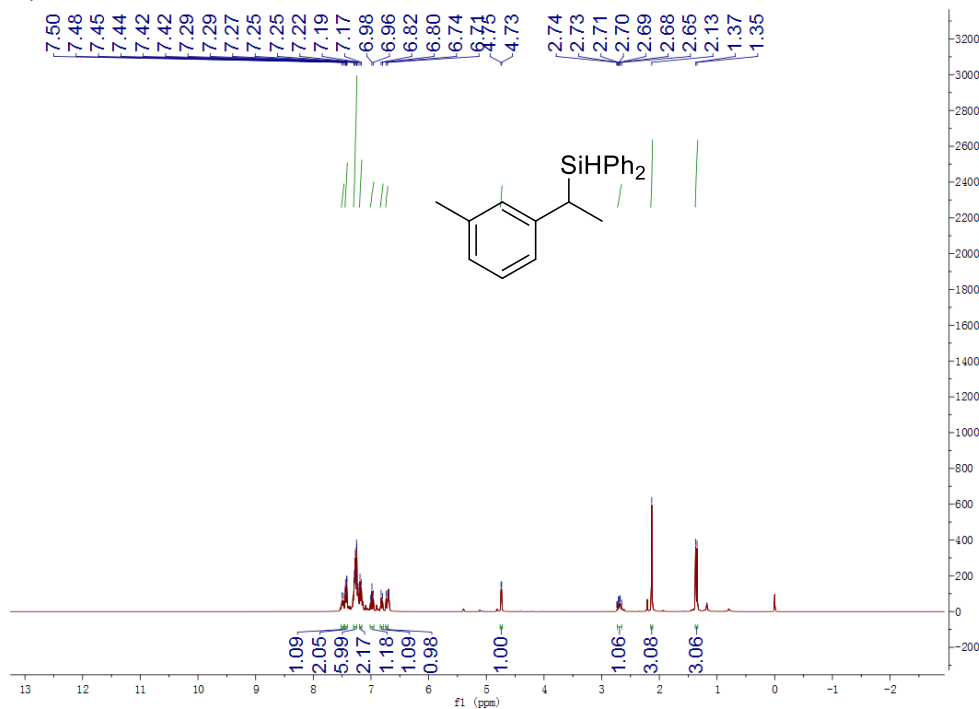


Figure S28. ^1H NMR of **2d** (CDCl_3)

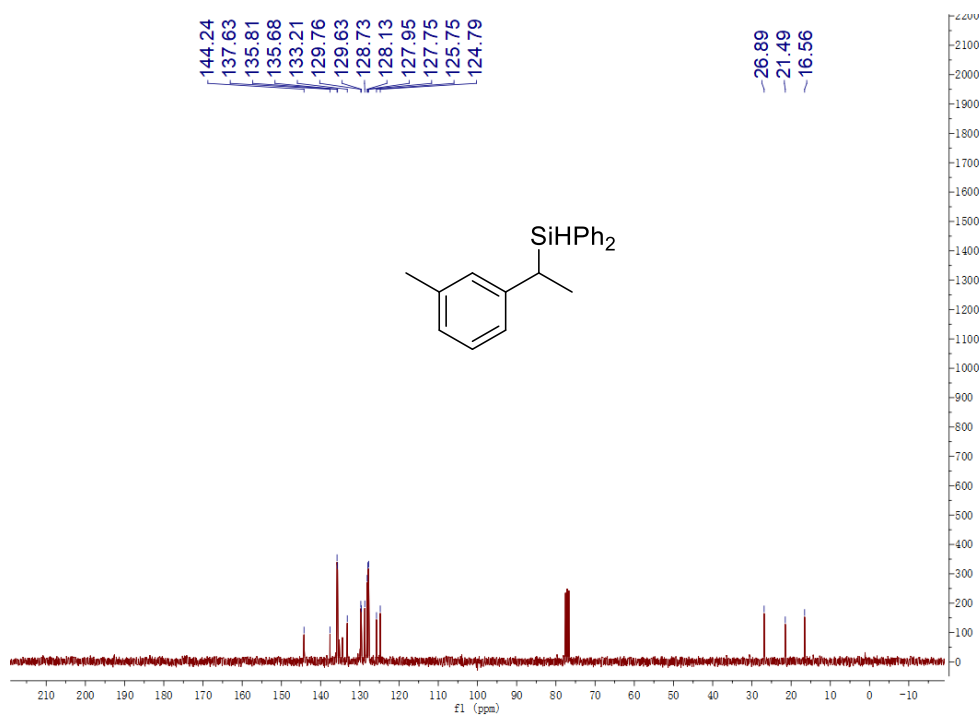


Figure S29. ^{13}C NMR of **2d** (CDCl_3)

(1-(4-(tert-butyl)phenyl)ethyl)diphenylsilane (2e)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.42-7.39 (m, 2H), 7.26-7.17 (m, 6H), 7.13-7.08 (m, 4H), 6.84 (d, $J = 8.3$ Hz, 2H), 4.74 (d, $J = 3.4$ Hz, 1H), 2.69 (qd, $J = 7.4, 3.4$ Hz, 1H), 1.35 (d, $J = 7.5$ Hz, 3H), 1.18 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 147.88, 141.31, 135.96, 135.80, 133.45, 133.41, 129.87, 129.71, 128.11, 127.88, 127.54, 125.25, 34.48, 31.70, 26.48, 16.76.

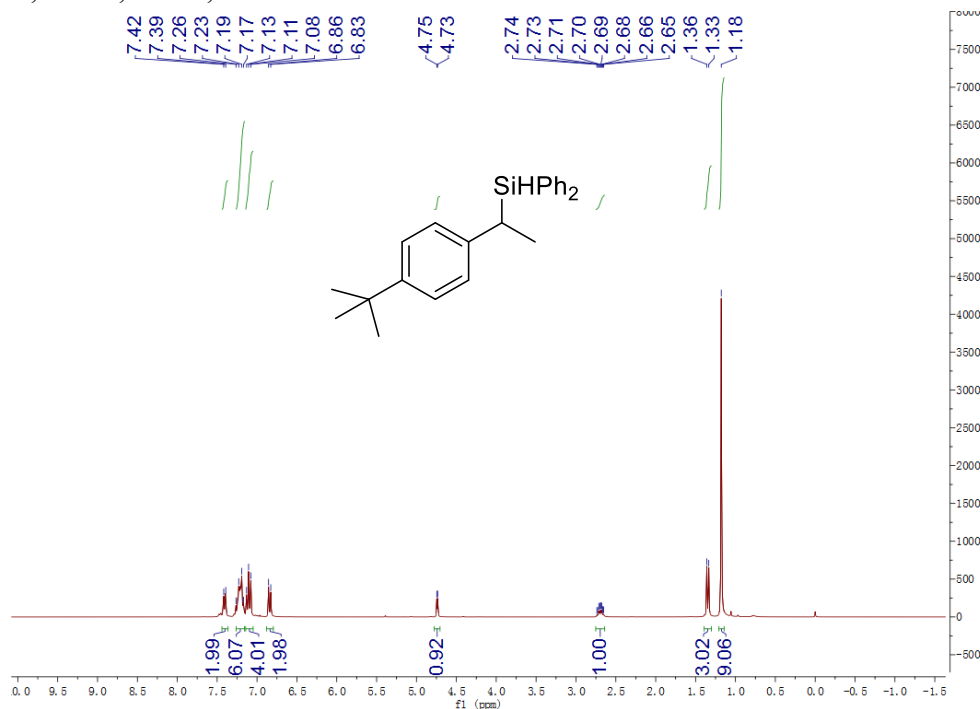


Figure S30. ^1H NMR of 2e (CDCl_3)

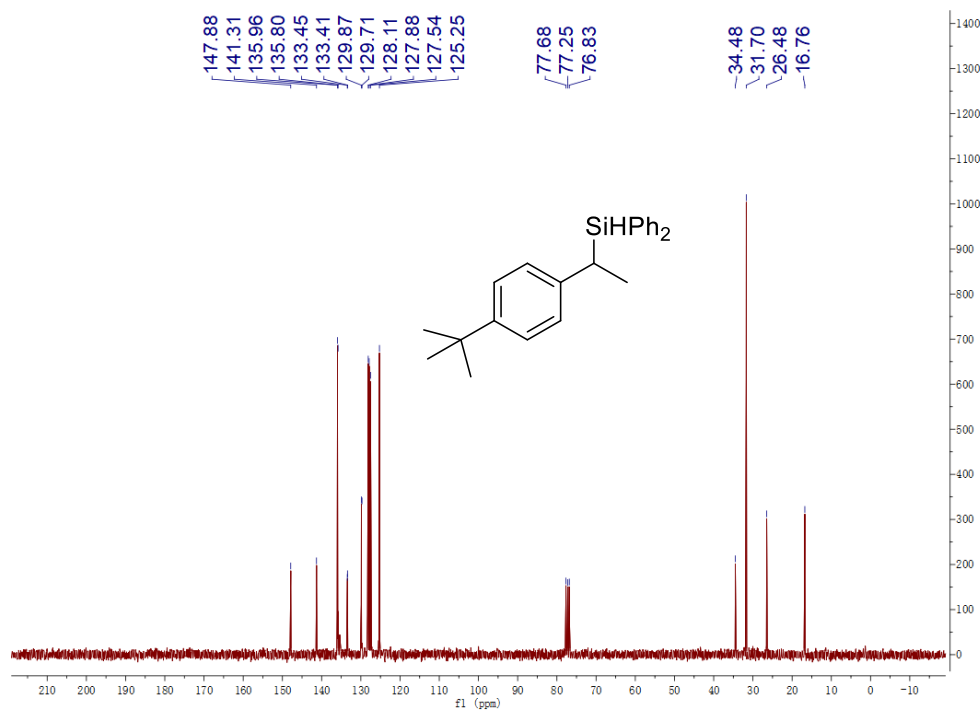


Figure S31. ^{13}C NMR of 2e (CDCl_3)

(1-(4-methoxyphenyl)ethyl)diphenylsilane (2f)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.65-7.63 (m, 2H), 7.50-7.45 (m, 6H), 7.40-7.37 (m, 2H), 7.05 (d, $J = 8.7$ Hz, 2H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.96 (d, $J = 3.3$ Hz, 1H), 3.85 (s, 3H), 2.89 (qd, $J = 7.4, 3.3$ Hz, 1H), 1.56 (d, $J = 7.6$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 157.23, 136.35, 135.80, 135.68, 133.32, 133.26, 129.75, 129.62, 128.64, 128.00, 127.82, 113.74, 55.24, 25.91, 16.95.

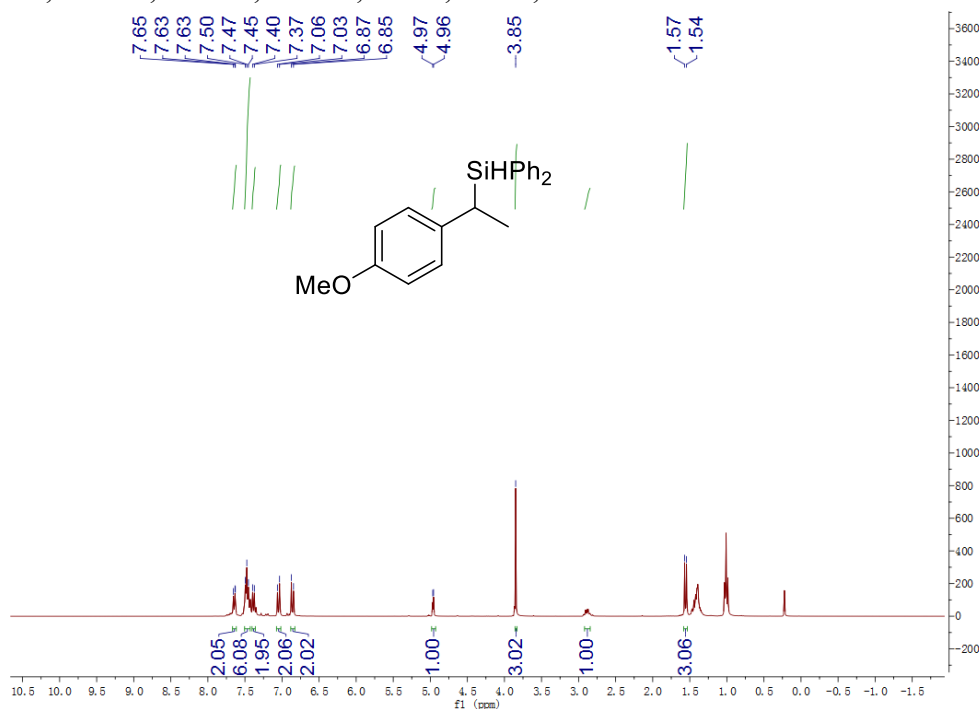


Figure S32. ^1H NMR of 2f (CDCl_3)

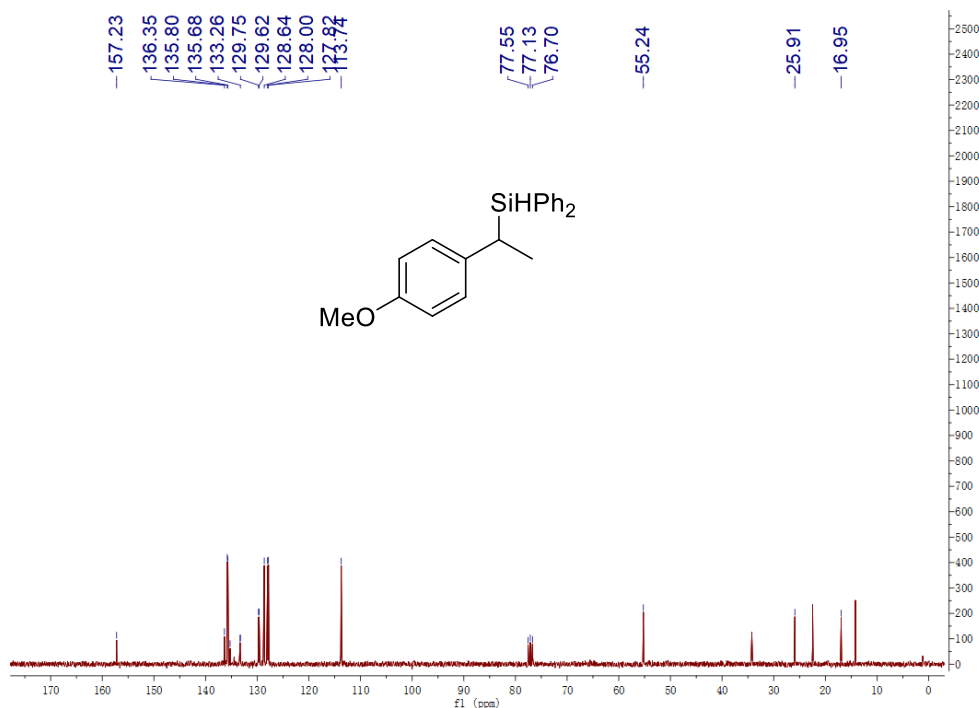


Figure S33. ^{13}C NMR of 2f (CDCl_3)

(1-([1,1'-biphenyl]-4-yl)ethyl)diphenylsilane (2g)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.49-7.43 (m, 4H), 7.35-7.17 (m, 13H), 6.97 (d, $J = 8.2$ Hz, 2H), 4.78 (d, $J = 3.2$ Hz, 1H), 2.78 (qd, $J = 7.4, 3.3$ Hz, 1H), 1.40 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 143.66, 141.15, 137.77, 135.84, 135.70, 133.03, 129.86, 129.74, 128.80, 128.19, 128.05, 127.87, 126.98, 126.95, 126.90, 26.79, 16.56.

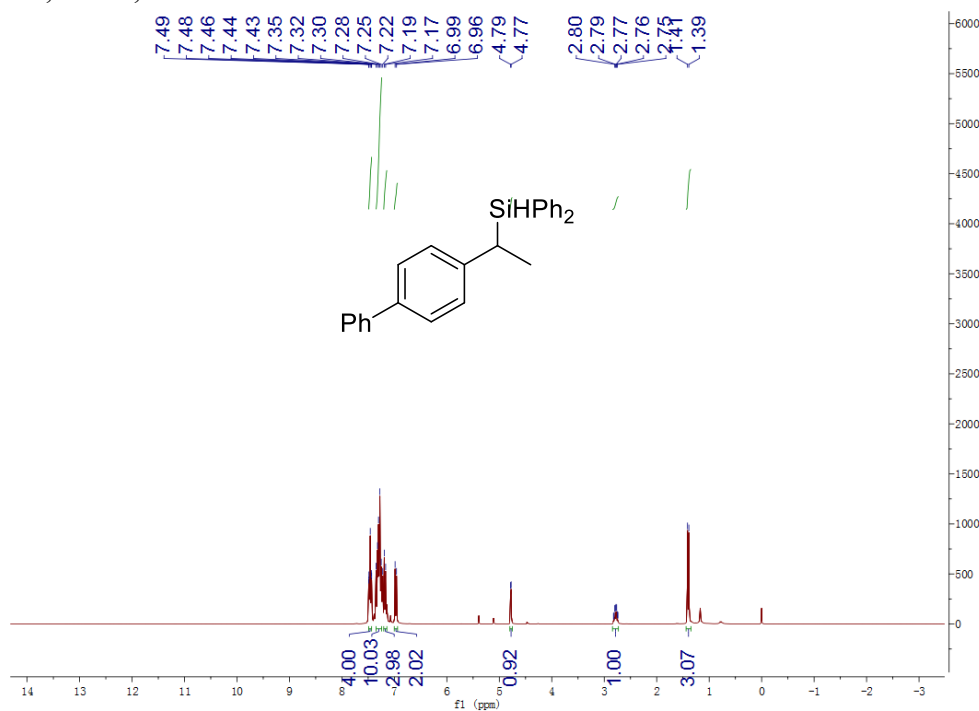


Figure S34. ^1H NMR of 2g (CDCl_3)

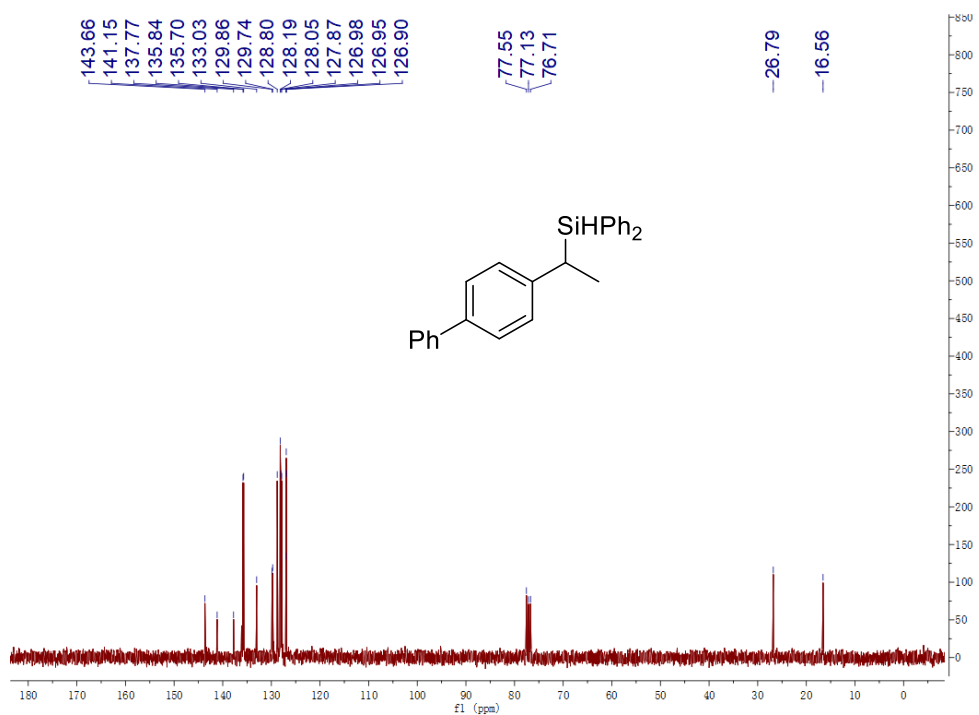


Figure S35. ^{13}C NMR of 2g (CDCl_3)

(1-(3-chlorophenyl)ethyl)diphenylsilane (2h+2h')

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.49-7.46 (m, 4H), 7.44-7.41 (m, 2H), 7.30-7.25 (m, 12H), 7.21-7.19 (m, 2H), 7.07-7.05 (m, 3H), 6.87-6.77 (m, 2H), 4.80 (t, $J = 3.7$ Hz, 1H), 4.73 (d, $J = 3.7$ Hz, 1H), 2.75-2.69 (m, 1H), 2.66-2.61 (m, 1H), 1.43-1.37 (m, 2H), 1.35 (d, $J = 7.4$ Hz, 3H); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm) 146.65, 146.38, 135.88, 135.71, 135.56, 135.19, 133.84, 129.97, 129.82, 129.63, 129.33, 128.17, 128.08, 127.90, 127.74, 126.14, 125.96, 125.09, 30.26, 27.05, 16.27, 14.16.

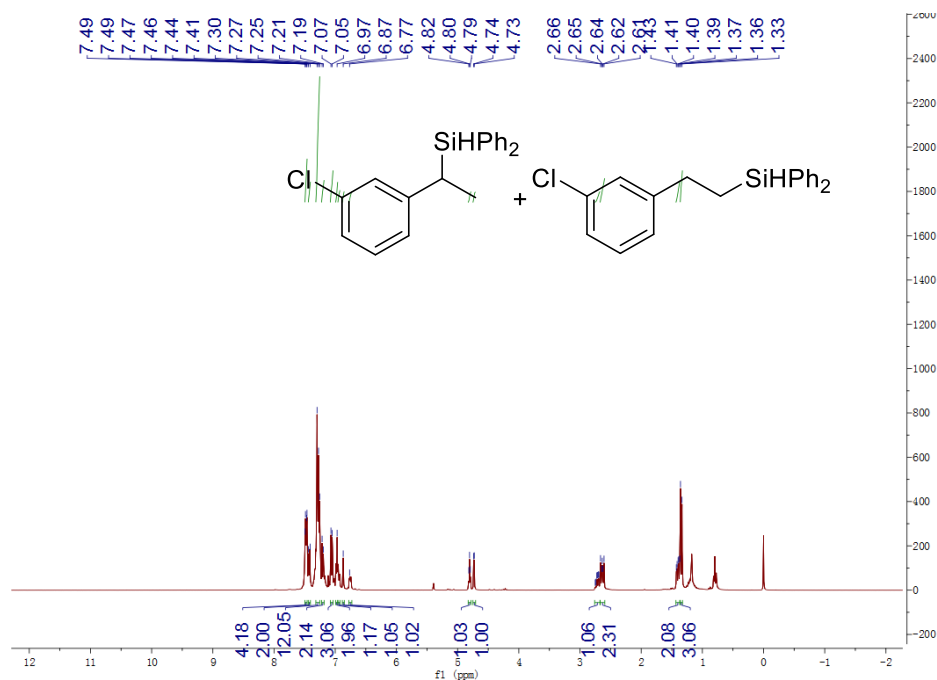


Figure S36. ^1H NMR of 2h+2h' (CDCl_3)

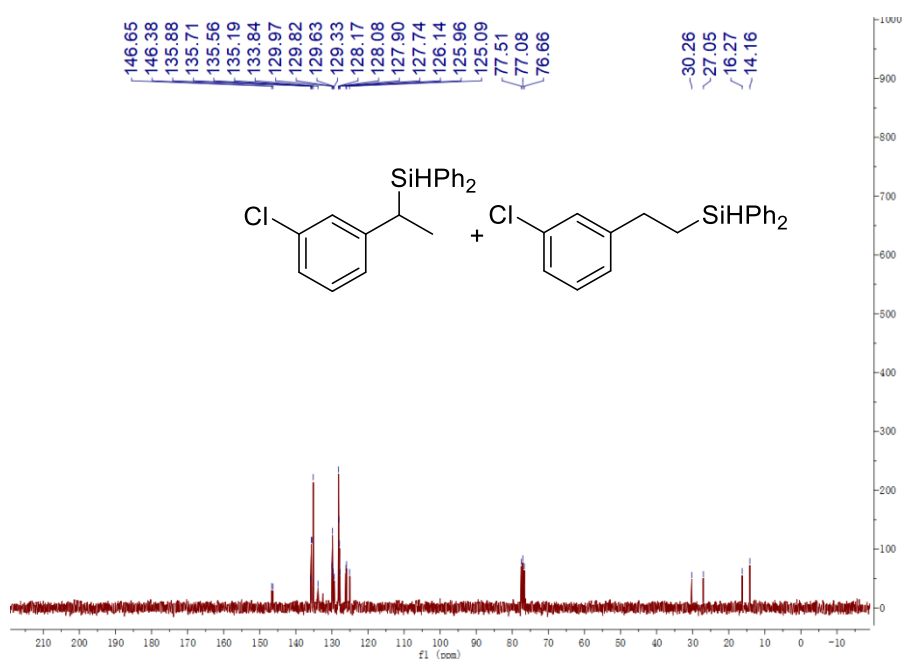


Figure S37. ^{13}C NMR of 2h+2h' (CDCl_3)

(1-(naphthalen-2-yl)ethyl)diphenylsilane (2i)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.65-7.62 (m, 1H), 7.54-7.51 (m, 2H), 7.43-7.41 (m, 2H), 7.28-7.24 (m, 9H), 7.14-7.12 (m, 2H), 7.05-7.02 (m, 1H), 4.81 (d, $J = 3.1$ Hz, 1H), 2.93-2.84 (m, 1H), 1.44 (d, $J = 7.5$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 142.18, 135.87, 135.72, 133.81, 133.05, 133.02, 131.67, 129.89, 129.78, 128.07, 127.91, 127.68, 127.63, 127.47, 127.39, 125.88, 125.40, 124.89, 27.34, 16.71.

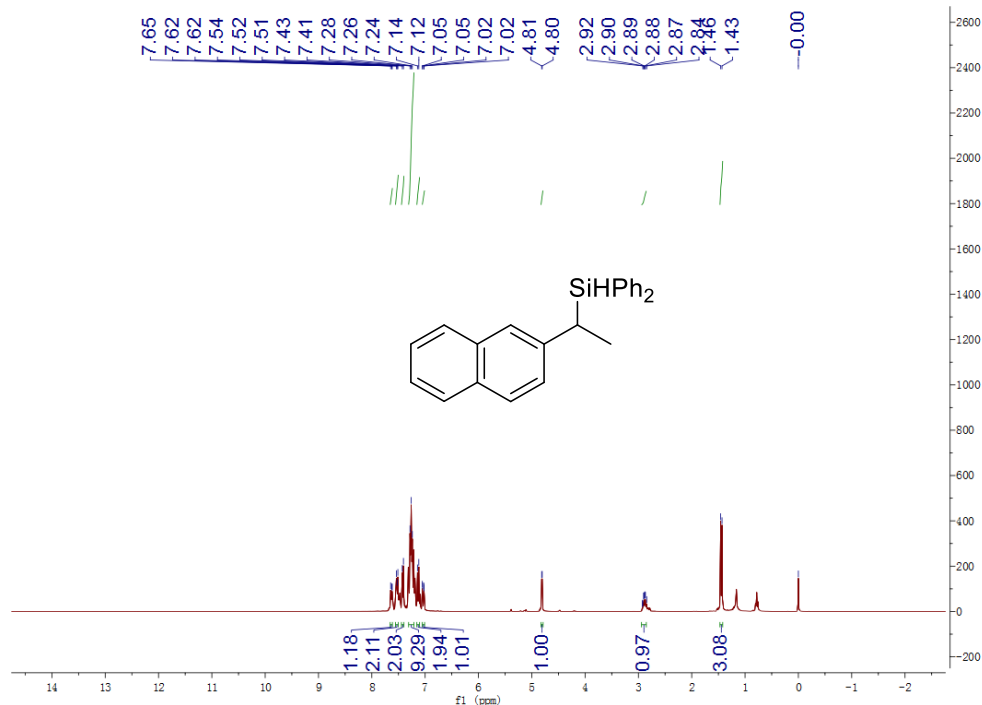


Figure S38. ^1H NMR of 2i (CDCl_3)

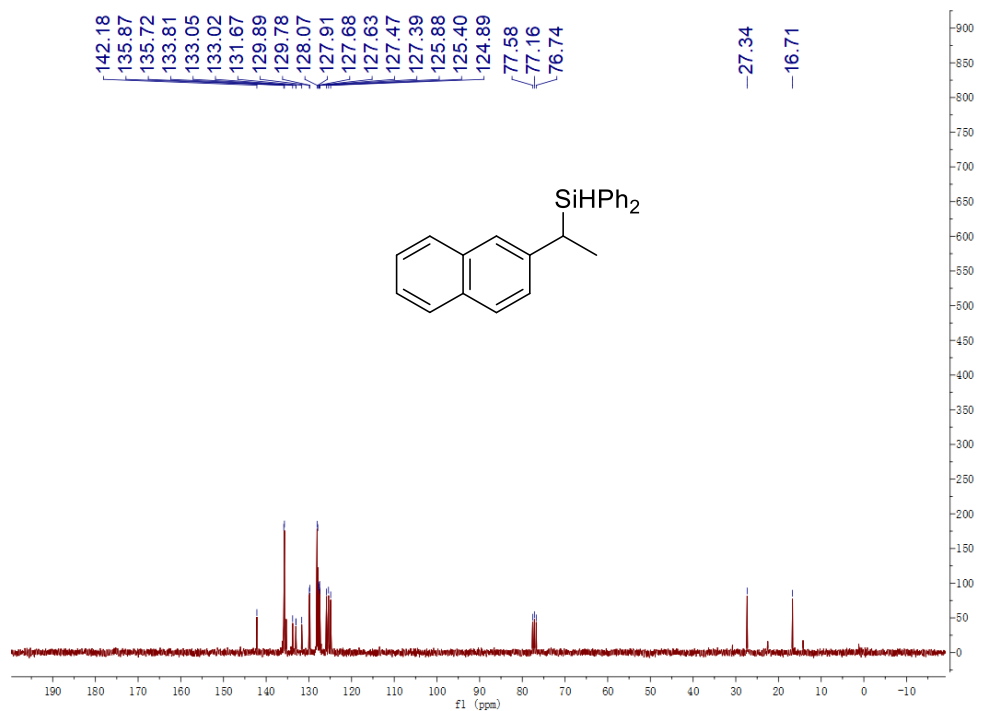


Figure S39. ^{13}C NMR of 2i (CDCl_3)

(1-(4-fluorophenyl)ethyl)diphenylsilane (2k)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.63–7.61 (m, 2H), 7.47–7.45 (m, 6H), 7.39–7.37 (m, 2H), 7.03–6.96 (m, 4H), 4.93 (d, $J = 2.6$ Hz, 1H), 2.95–2.87 (m, 1H), 1.54 (d, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 162.35, 139.99, 135.74, 135.60, 132.84, 129.90, 129.77, 128.97, 128.87, 128.17, 128.07, 127.89, 115.10, 114.82, 26.27, 16.76.

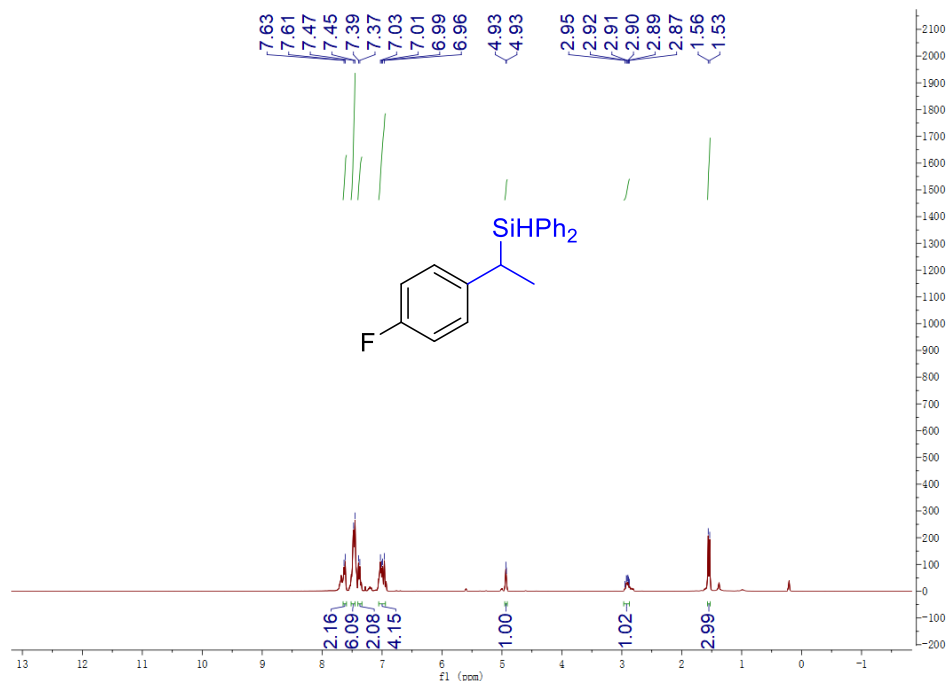


Figure S40. ^1H NMR of **2k** (CDCl_3)

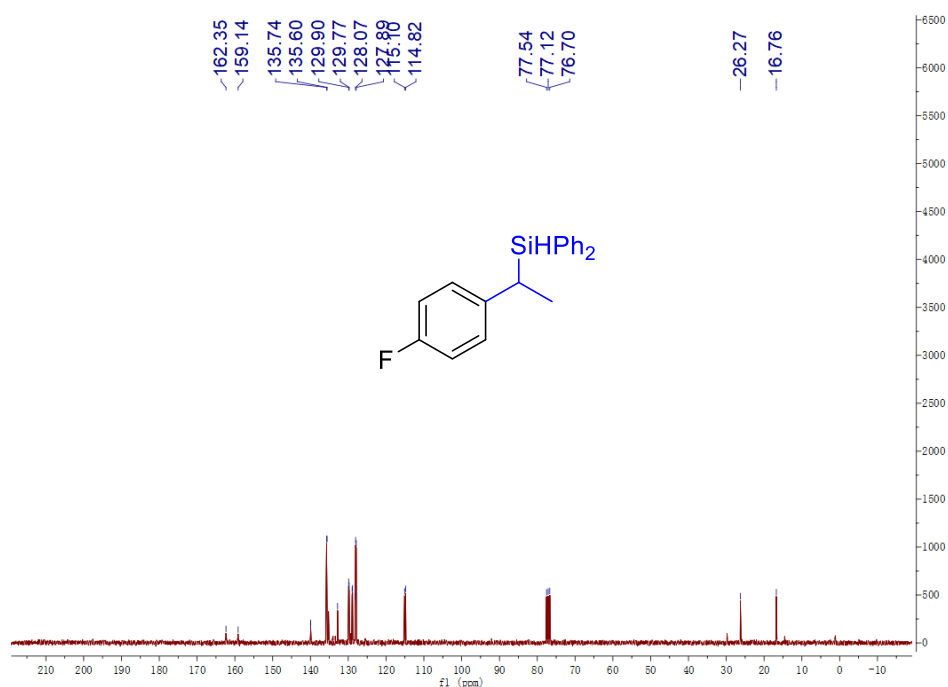


Figure S41. ^{13}C NMR of **2k** (CDCl_3)

(*n*-octyl)diphenylsilane (2l)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.50-7.47 (m, 4H), 7.30-7.28 (m, 6H), 4.77 (t, $J = 3.7$ Hz, 1H), 1.41-1.33 (m, 4H), 1.18-1.10 (m, 8H), 1.09-1.03 (m, 2H), 0.81-0.77 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 134.10, 133.69, 128.42, 126.90, 32.16, 30.85, 28.69, 28.18, 23.36, 21.64, 13.08, 11.10.

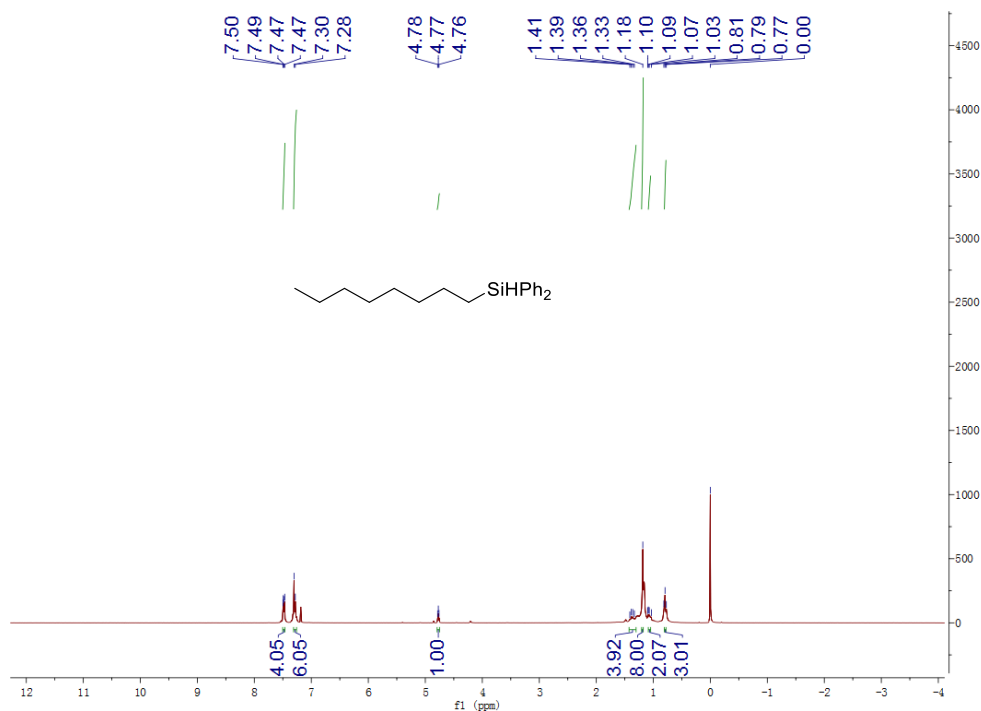


Figure S42. ^1H NMR of **2l** (CDCl_3)

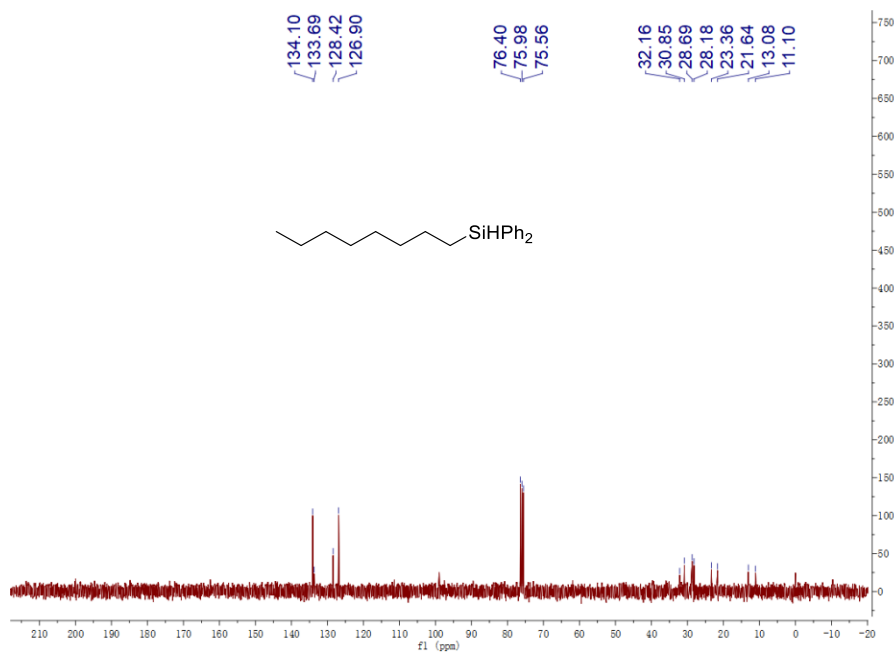


Figure S43. ^{13}C NMR of **2l** (CDCl_3)

(*n*-heptyl)diphenylsilane (2m)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.59-7.54 (m, 4H), 7.40-7.33 (m, 6H), 4.87 (t, $J = 3.0$ Hz, 1H), 1.54-1.46 (m, 4H), 1.28-1.25 (m, 6H), 1.18-1.13 (m, 2H), 0.88 (t, $J = 6.0$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 135.38, 134.83, 129.54, 128.03, 33.27, 31.94, 29.35, 24.53, 22.75, 14.25, 12.09.

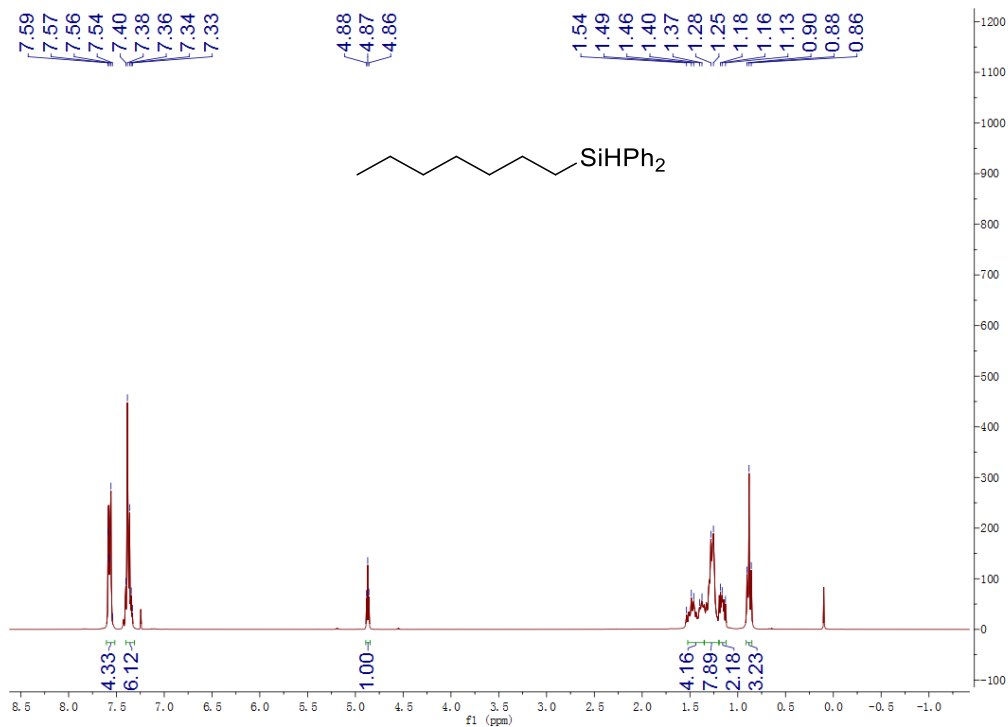


Figure S44. ^1H NMR of **2m** (CDCl_3)

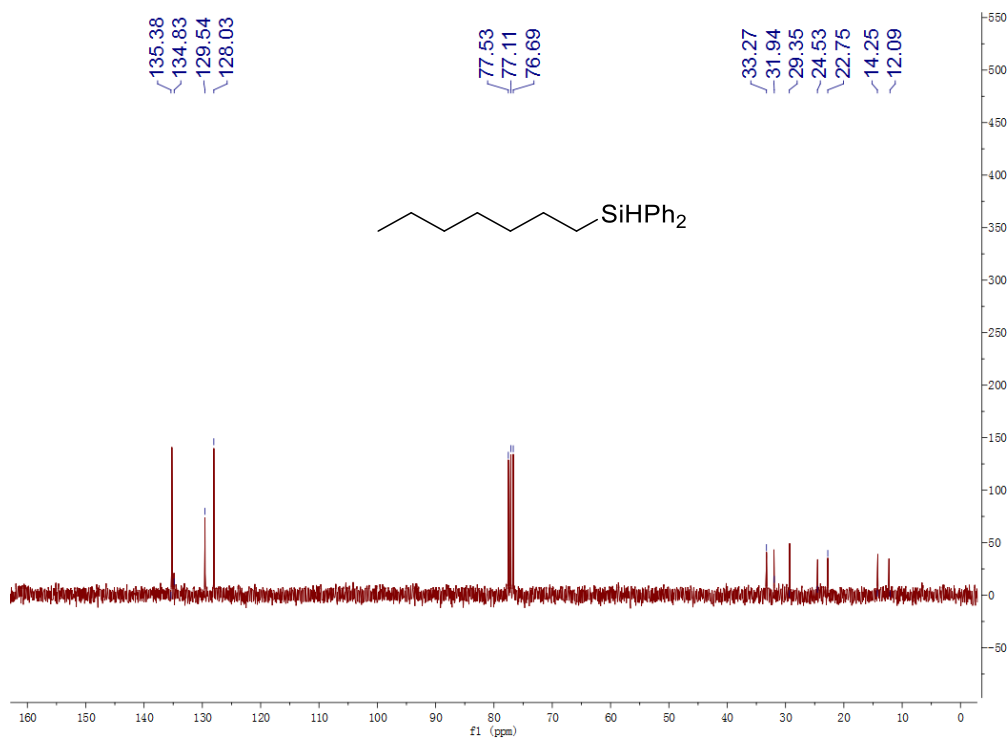


Figure S45. ^{13}C NMR of **2m** (CDCl_3)

(2-cyclohexylethyl)diphenylsilane (2n)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.44-7.41 (m, 4H), 7.29-7.22 (m, 6H), 5.15 (s, 1H), 1.61-1.51 (m, 2H), 1.34-1.22 (m, 6H), 1.22-0.97(m, 5H), 0.85-0.82 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 135.04, 129.60, 128.08, 126.76, 36.51, 31.62, 31.29, 28.55, 25.34, 9.30.

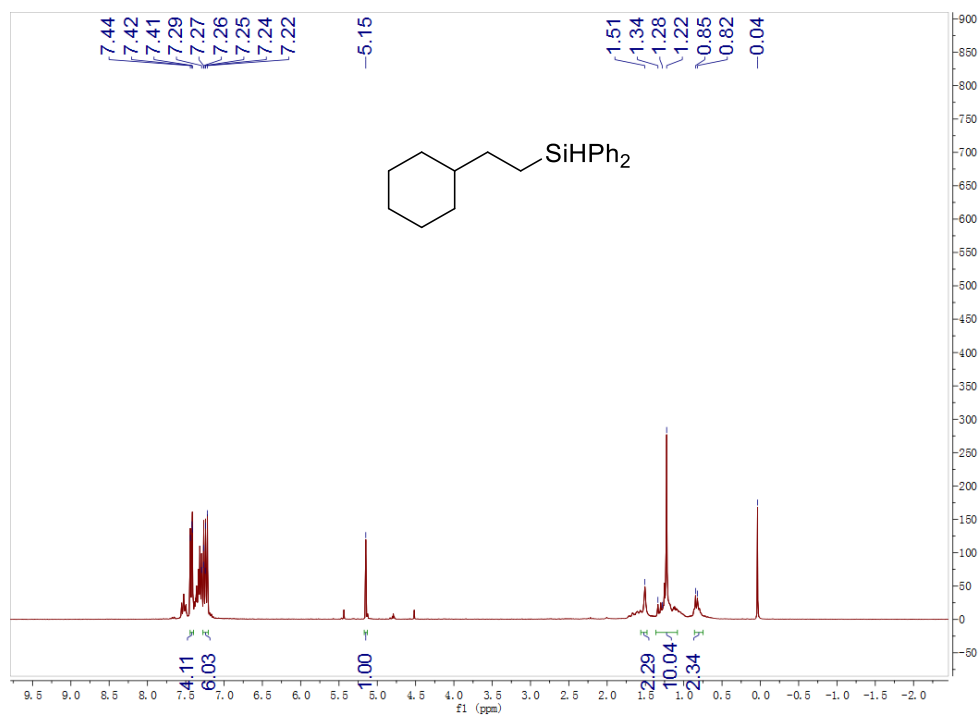


Figure S46. ^1H NMR of 2n (CDCl_3)

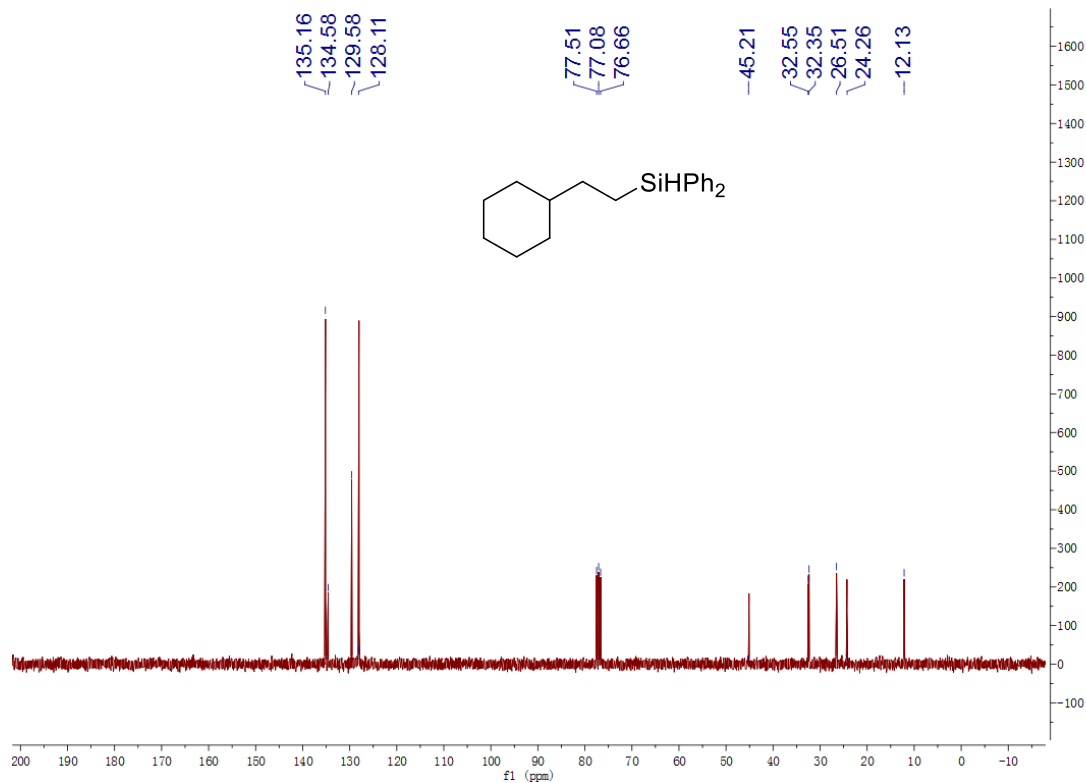


Figure S47. ^{13}C NMR of **2n** (CDCl_3)

(2-(cyclohex-3-en-1-yl)ethyl)diphenylsilane (2o)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.48-7.44 (m, 4H), 7.27-7.24 (m, 6H), 5.54-5.53 (m, 2H), 4.78 (t, $J = 3.0$ Hz, 1H), 2.00-2.00 (m, 1H), 1.99-1.91 (m, 2H), 1.69-1.68 (m, 1H), 1.65-1.63 (m, 1H), 1.54-1.49 (m, 1H), 1.88-1.34 (m, 2H), 1.10-1.05 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 135.38, 134.69, 129.59, 128.15, 127.04, 126.65, 36.35, 31.66, 31.10, 28.54, 25.12, 9.19.

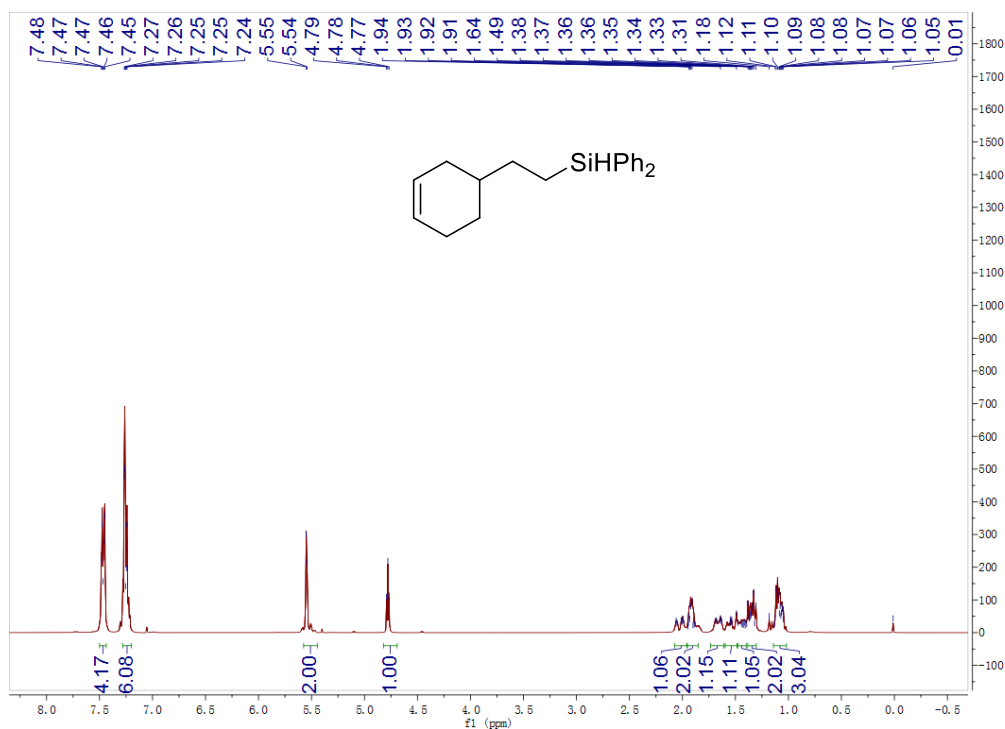


Figure S48. ^1H NMR of **2o** (CDCl_3)

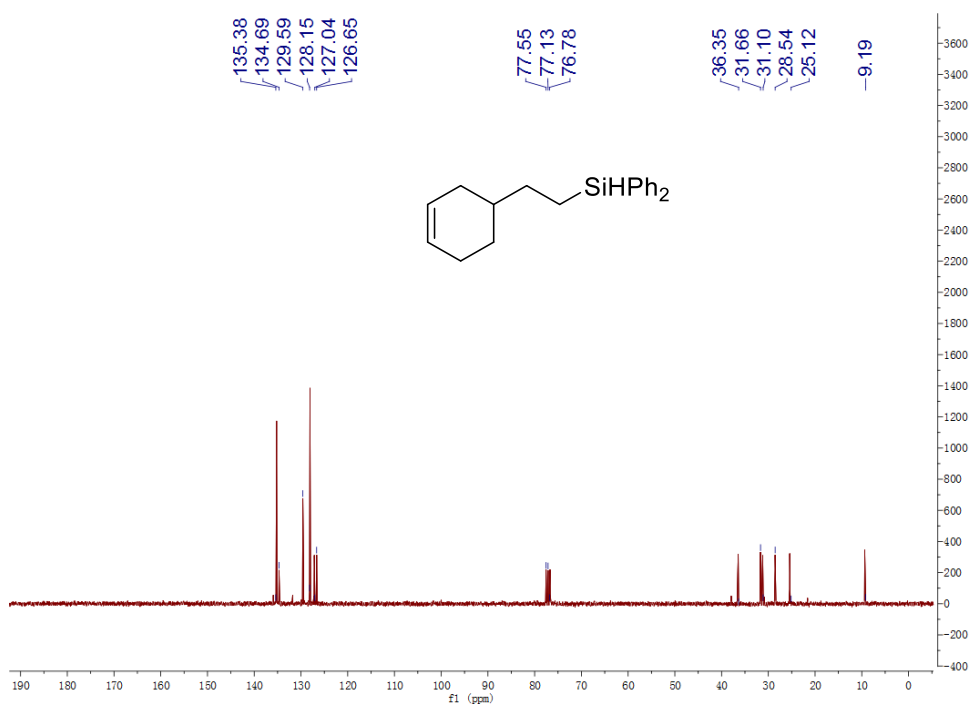


Figure S49. ^{13}C NMR of **2o** (CDCl_3)

Diphenyl(4-phenylbutyl)silane (2p)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.54-7.52 (m, 4H), 7.36-7.29 (m, 6H), 7.25-7.20 (m, 2H), 7.15-7.09 (m, 3H), 4.86 (t, $J = 3.0$ Hz, 1H), 3.11 (t, $J = 9.0$ Hz, 2H), 1.73-1.63 (m, 2H), 1.56-1.46 (m, 2H), 1.19-1.13 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 142.72, 135.27, 134.66, 129.66, 128.51, 128.38, 128.12, 125.73, 35.58, 35.06, 24.17, 12.03.

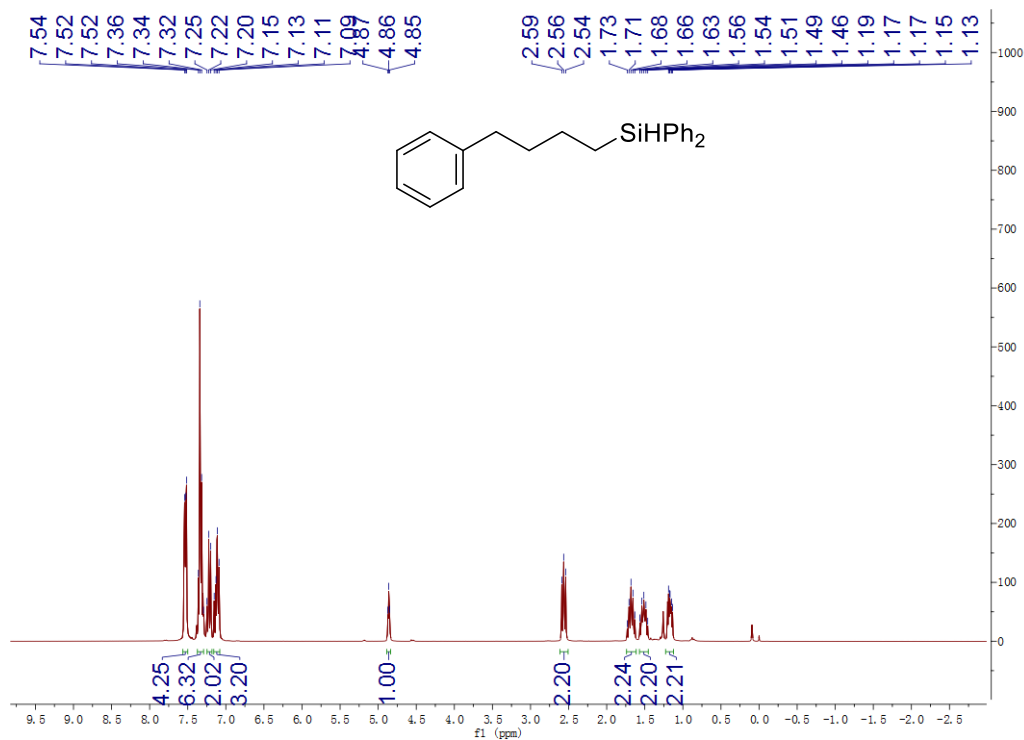


Figure S50. ^1H NMR of **2p** (CDCl_3)

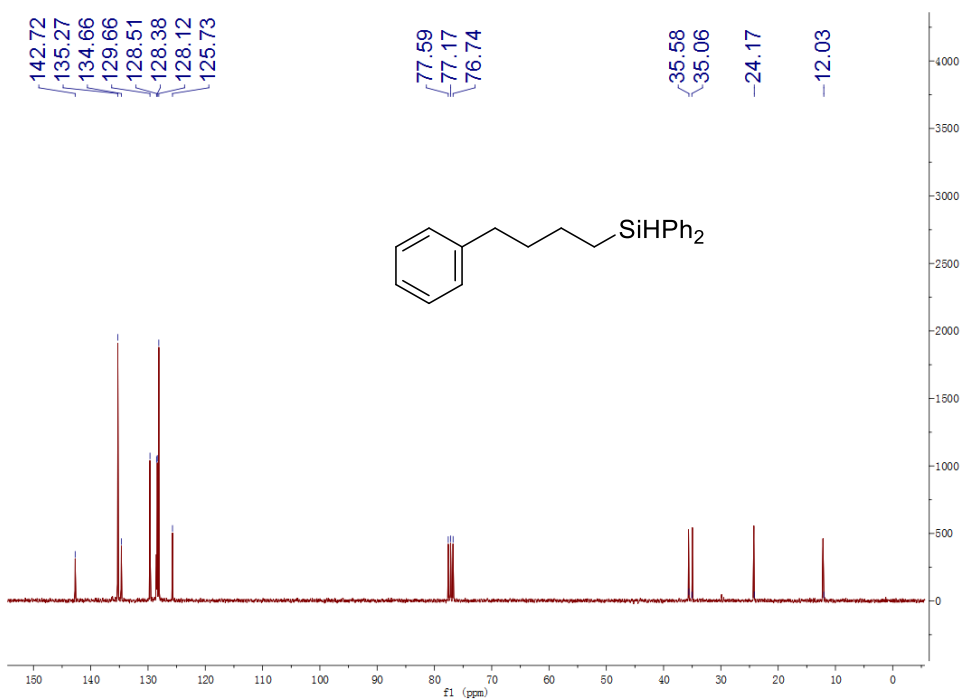


Figure S51. ^{13}C NMR of **2p** (CDCl_3)

(6-chlorohexyl)diphenylsilane(2q)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.66-7.63 (m, 4H), 7.46-7.41 (m, 6H), 4.94 (t, $J = 6.0$ Hz, 1H), 3.56 (t, $J = 6.0$ Hz, 2H), 1.82-1.77(m, 2H), 1.56-1.48 (m, 6H), 1.30-1.23(m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 135.18, 134.58, 129.72, 128.05, 45.21, 31.94, 26.60, 23.59, 11.65.

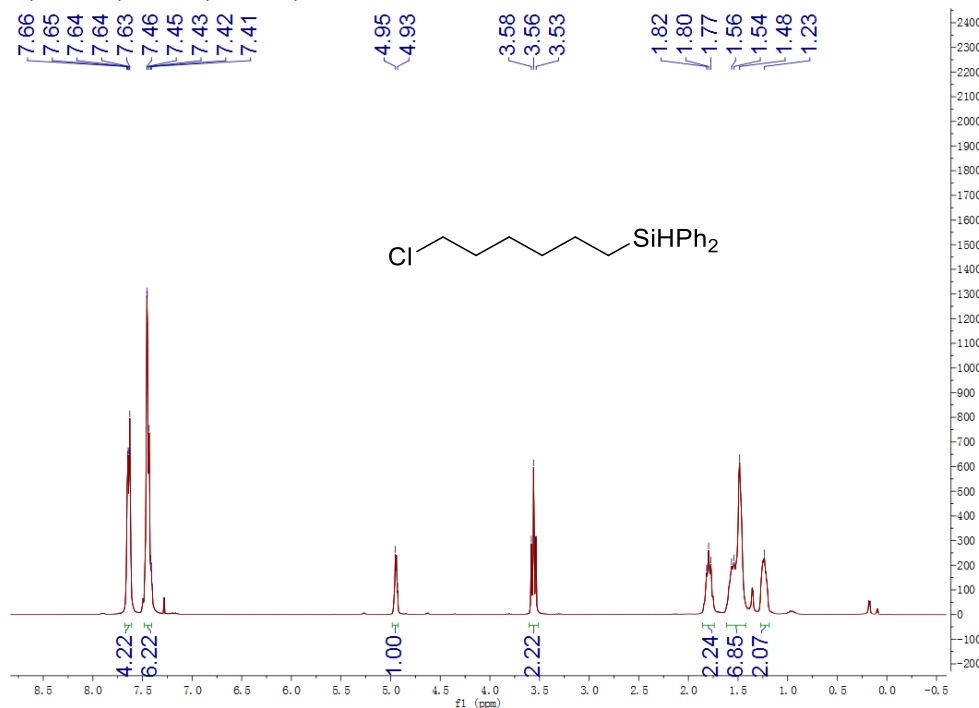


Figure S52. ^1H NMR of **2q** (CDCl_3)

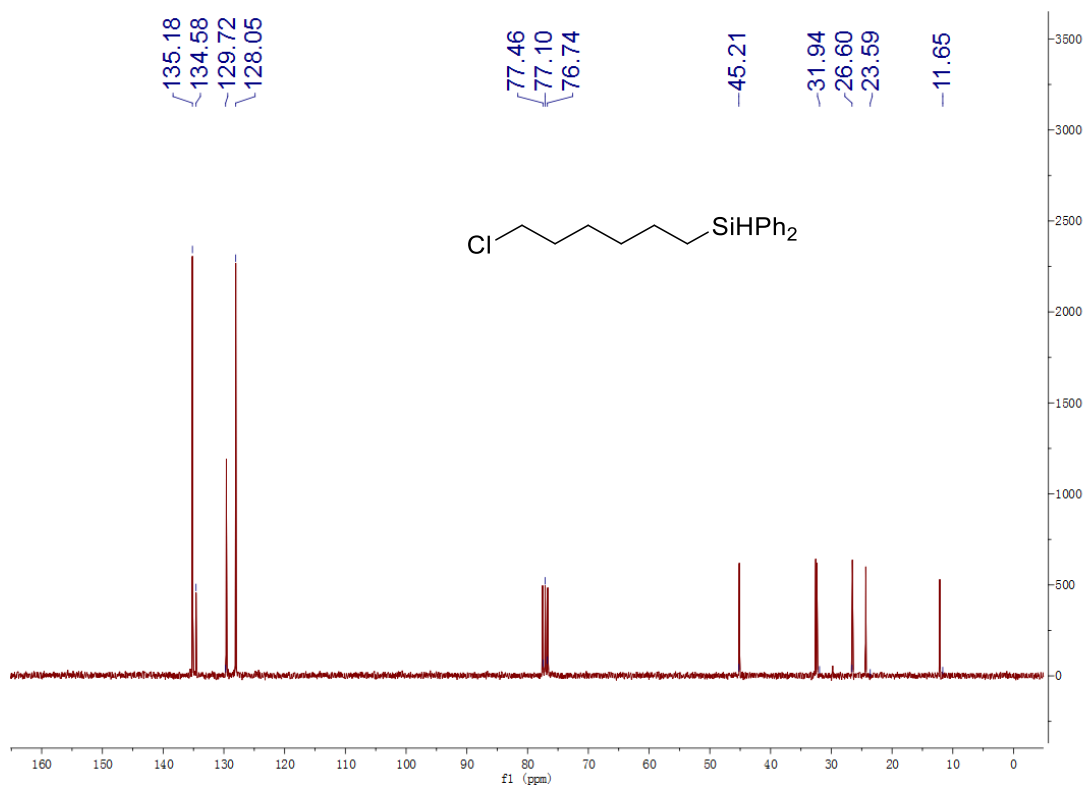


Figure S53. ^{13}C NMR of **2q** (CDCl_3)