Supporting Information

Synthesis And Study of An Unprecedented 1- Hydro -1-Lithio -1-Silafluorene Anion.

Dawei Tian,[†] Xiaofei Li,[†] Yuanyuan Liu, [†] Yue Cao, [†] Tianhao, Li,[‡] Hongfan Hu,[‡] Chunming Cui*[,‡]*

[†]College of Chemistry, Tianjin Key Laboratory of Structure and Performance for Functional Molecule,Tianjin Normal University, 393 Binshui West Road, Tianjin 300387, China

[‡]State Key Laboratory of Elemento-Organic Chemistry, Nankai UniVersity, Tianjin 300071, People's Republic of China

hxxytdw@mail.tjnu.edu.cn

cmcui@nankai.edu.cn

Genaral Considerations. All operations were carried out under an atmosphere of dry argon or nitrogen by using modified Schlenk line and glovebox techniques. All solvents were freshly distilled from Na and degassed immediately prior to use. The NMR spectra were recorded at room temperature on Bruker AMX 300, AMX 400 spectrometers. Chemical shifts are referenced against external Me_4Si (^1H, ^{13}C) and $SiCl_4$ (^{29}Si). Elemental analyses were carried out on an Elemental Vario EL analyzer. 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3I$,[1] 1,1-Br_2-2,5-TMS_2-3,4-Ph_2-silole (**7**)[2] 1,3-*i*Pr_2-4,5-Me_2-imidazol-2- ylidene (NHC) [3] were synthesized as described in literature.

Synthesis of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3SiCl_3$ (1). *n*-Butyllithium (5.1 mL, 12.2 mmol, 2.4 M in hexane) was added dropwise via syringe to a suspension of 2,6-(3,5-$Me_2C_6H_3)_2C_6H_3I$ (5.00 g, 12.1 mmol) in ether (50 mL) at -78 °C. The reaction mixture was slowly warmed to room temperature and stirred for 2 hours. The mixture was then added dropwise via cannula to a solution of $SiCl_4$ (2.50 g, 14.7 mmol) in ether (30 mL) at -78 °C and then warmed to room temperature. After stirring overnight, the volatile material was removed under reduced pressure, and the resulting solid was extract with hexane (100 ml) and the extract was then concentrated (ca. 30 mL) and stored at 0 °C overnight to afford colorless crystals of **1**. Yield: 3.20 g, 52%; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (t, Ar-*H*, *J* = 7.6Hz, 1H), 7.43 (d, Ar-*H*, *J* = 7.6 Hz, 2H), 7.17 (s, Ar-*H*, 4H), 7.07 (s, Ar-*H*, 2H), 2.39 (s, Ar-C*H*$_3$, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 151.65, 143.05, 138.12, 131.54, 129.84, 129.42, 128.68, 127.94, 21.27. Anal. Calcd for $C_{22}H_{21}Cl_3Si$: C, 62.94; H, 5.04. Found: C, 62.80; H, 5.15.

Synthesis of [1-(3,5-dimethylphenyl)-6,8-dimethyl-9-silafluorene]$^-$ [Li(thf)$_3$]$^+$ (2). A suspension of **1** (5.00 g, 11.9 mmol), lithium (0.1667 g, 23.8 mmol) and naphthalene (0.10 g, 0.8 mmol) in tetrahydrofuran (50 ml) was stirred at -78 °C overnight. Then lithium (0.1667 g, 23.8 mmol) was added to the reaction mixture and the mixture was stirred at -78 °C until the lithium disappeared. The volatile material was removed under reduced pressure, and the resulting solid was extracted with toulene (70 ml) and the extract was then concentrated (ca. 20 mL) and stored at -35 °C overnight to afford yellow crystals of **2**. Yield: 3.2 g, 50%; ^1H NMR (300 MHz, C_6D_6): δ 8.26 (d, Ar-*H*, *J* = 7.3 Hz, 1H), 8.00 (s, Ar-*H*, 1H), 7.83 (s, Ar-*H*, 2H), 7.62 (d, Ar-*H*, *J* = 6.7 Hz, 1H), 7.52 (t, Ar-*H*, *J* = 7.5 Hz, 1H), 7.08 (s, Ar-*H*, 1H), 6.80 (s, Ar-*H*, 1H), 5.40 (s, Si-*H*, 1H), 3.16 – 3.02 (m, O-C*H*$_2$, 12H), 2.81 (s, Ar-C*H*$_3$, 3H), 2.53 (s, Ar-C*H*$_3$, 3H), 2.32 (s, Ar-C*H*$_3$, 6H), 1.24 – 1.10 (m, $(CH_2)_2CH_2$, 12H). ^{29}Si NMR (79 MHz, C_6D_6): δ -60.12. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 157.05, 155.66, 148.71, 147.51, 147.39, 146.51, 140.78, 136.63, 133.54, 127.37, 127.21, 126.29, 125.23, 124.43, 120.13, 119.58, 67.82, 25.18, 24.04, 22.00, 21.51. IR(KBr, cm^{-1}): *ν*(Si-H) 2135.

Synthesis of 1-(3,5-dimethylphenyl)-6,8-dimethyl-9-diisopropylphosphino-9-silafluorene (5). A solution of **2** (0.20 g, 0.37 mmol) in toluene (10 mL) was added to a stirred solution of chlorobis(isopropyl)phosphine (0.057 g, 0.37 mmol) in toluene (10 mL) at -78 °C. The mixture was kept at -78 °C for 2 h and then slowly warmed to room temperature and stirred overnight. Removal of the solvents afforded white powder which was then extracted with hexane (30 mL). Concentration to ca. 5 mL and storage at -35 °C for 2 days afforded colorless crystals of **5**. Yield: 0.13 g, 82%; ^1H NMR (400 MHz, C_6D_6) δ 7.73 (d, Ar-*H*, *J* = 7.5 Hz, 1H), 7.52 (s, Ar-*H*, 1H), 7.36 – 7.28 (m, Ar-*H*, 2H), 7.24 (s, Ar-*H*, 2H), 6.85 (s, Ar-*H*, 1H), 6.82 (s, Ar-*H*, 1H), 5.73 (d, Si-*H*, *J* = 28.0 Hz, 1H), 2.71 (s, Ar-*H*, 3H), 2.22 (s, Ar-*H*, 3H), 2.19 (s, Ar-*H*, 6H), 1.82 (dt, $(CH_3)_2CH$, *J* = 14.4, 7.1 Hz, 1H), 1.34 (dt, $(CH_3)_2CH$, *J* = 13.6, 6.9 Hz, 1H), 0.93 – 0.83 (m, CH-C*H*$_3$, 6H), 0.77 – 0.66 (m, CH-C*H*$_3$, 6H). ^{31}P NMR (162 MHz, C_6D_6): δ -34.14. $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6): δ 149.78, 149.62, 148.86, 145.53, 144.30, 140.89, 138.29, 136.46, 132.31, 132.20, 131.06, 130.26, 129.14, 128.13, 127.18, 120.62, 120.32, 23.92 (d, J_{CP} = 6.8 Hz), 22.51 (d, J_{CP} = 16.3 Hz), 22.19 (d, J_{CP} = 16.9 Hz), 21.78 (d, J_{CP} = 7.6 Hz), 21.75, 21.62 (d, J_{CP} = 13.2 Hz), 21.37, 19.66 (d, J_{CP} = 13.5 Hz). MS (EI): m/z = 430.1 [M$^+$]. Anal. Calcd for $C_{28}H_{35}PSi$: C, 78.09; H, 8.19. Found: C, 78.13; H, 8.35.

Synthesis of 1-(3,5-dimethylphenyl)-6,8-dimethyl-9-chloro-9-silafluorene (4). Route A: A solution of **5** (0.13 g,

0.30 mmol) in toluene (10 mL) was added to a stirred solution of chlorobis(isopropyl)phosphine (0.045 g, 0.30 mmol) in toluene (10 mL) at room temperature. The mixture was heated to 70 °C for 4 h and then evaporated. The residue was then extracted with hexane (30 mL). Concentration to ca. 5 mL and storage at -35 °C overnight afforded colorless crystals of **4**. Yield: 0.094 g, 90%; **Route B:** A solution of **2** (0.20 g, 0.37 mmol) in toluene (10 mL) was added to a stirred solution of chlorobis(isopropyl)phosphine (0.11 g, 0.74 mmol) in toluene (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and then heated to 70 °C for 4 h. Removal of the solvents afforded white powder which was then extracted with hexane (30 mL). Concentration to ca. 10 mL and storage at -35 °C overnight afforded colorless crystals of **4**. Yield: 0.09 g, 73%; ^{1}H NMR (400 MHz, C_6D_6): δ 7.54 (d, Ar-*H*, *J* = 6.6 Hz, 1H), 7.32 (s, Ar-*H*, 3H), 7.29 (s, Ar-*H*, 1H), 7.27 (d, Ar-*H*, *J* = 7.5 Hz, 1H), 6.87 (s, Ar-*H*, 1H), 6.69 (s, Ar-*H*, 1H), 5.87 (s, Si-*H*, 1H), 2.35 (s, Ar-C*H*$_3$, 3H), 2.24 (s, Ar-C*H*$_3$, 6H), 2.13 (s, Ar-C*H*$_3$, 3H). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 149.65, 149.05, 148.08, 144.17, 143.16, 142.79, 138.21, 132.71, 131.48, 130.48, 129.59, 128.85, 128.61, 126.53, 120.18, 119.93, 22.29, 21.61, 21.27. ^{29}Si NMR (79 MHz, C_6D_6): δ -8.67. MS (EI): m/z = 348.1 [M$^+$]. Anal. Calcd for $C_{22}H_{21}ClSi$: C, 75.73; H, 6.01. Found: C, 76.35; H, 6.75.

Synthesis of 1-(3,5-dimethylphenyl)-6,8-dimethyl-9- (2,2-dimethyl-1-oxopropyl)-9-silafluorene (6). A solution of **2** (0.20 g, 0.37 mmol) in toluene (10 mL) was added slowly to a stirred solution of pivaloyl chloride (0.044 g, 0.37 mmol) in toluene (10 mL) at -78 °C. The mixture was kept at -78 °C for 2 h and then slowly warmed to room temperature and stirred overnight. Removal of the solvents afforded white powder which was then extracted with hexane (30 mL). Concentration to ca. 10 mL and storage at -35 °C for 2 days afforded colorless crystals of **6**. Yield: 0.12 g, 81%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (dd, Ar-*H*, *J* = 7.0, 1.6 Hz, 1H), 7.47 (s, Ar-*H*, 1H), 7.38 (d, Ar-*H*, *J* = 1.8 Hz, 2H), 7.29 (s, Ar-*H*, 2H), 6.77 (d, Ar-*H*, *J* = 12.8 Hz, 2H), 5.46 (s, Si-*H*, 1H), 2.32 (s, Ar-C*H*$_3$, 3H), 2.23 (s, Ar-C*H*$_3$, 6H), 2.18 (s, Ar-C*H*$_3$, 3H), 0.65 (s, C-C*H*$_3$, 9H). ^{13}C NMR{^{1}H} (101 MHz, C_6D_6): δ 241.63, 150.30, 149.33, 148.77, 143.97, 143.87, 141.55, 138.61, 133.67, 131.92, 130.22, 129.48, 127.83, 126.10, 120.50, 120.28, 49.69, 24.74, 23.32, 21.63, 21.21. MS (EI): m/z = 398.0 [M$^+$]. Anal. Calcd for $C_{27}H_{30}OSi$: C, 81.35; H, 7.59. Found: C, 80.95; H, 7.75.

Synthesis of 8. A solution of **2** (0.40 g, 0.74 mmol) in toluene (10 mL) was added slowly to a stirred solution of **7** (0.40 g, 0. 74 mmol) in toluene (10 mL) at -78 °C. The mixture was kept at -78 °C for 2 h and then slowly warmed to room temperature and stirred overnight. Removal of the solvents afforded white powder which was then extracted with hexane (30 mL). Concentration to ca. 10 mL and storage at -35 °C overnight afforded colorless crystals of **8**. Yield: 0.49 g, 86%; ^{1}H NMR (300 MHz, C_6D_6): δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.57 (s, 1H), 7.47 (s, 2H), 7.40 (dd, *J* = 14.7, 7.3 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 6H), 6.74 (s, 2H), 6.63 (s, 2H), 5.84 (s, Si-*H*, 1H), 2.60 (s, Ar-C*H*$_3$, 3H), 2.35 (s, Ar-C*H*$_3$, 6H), 2.25 (s, Ar-C*H*$_3$, 3H), 0.10 (s, Si-C*H*$_3$, 9H), -0.31 (s, Si-C*H*$_3$, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.93, 149.54, 148.66, 143.52, 140.52, 140.07, 139.89, 137.05, 131.34, 130.22, 128.48, 127.81, 127.55, 127.17, 126.80, 126.56, 126.19, 125.85, 125.67, 125.58, 119.41, 119.27, 24.03, 20.44, 20.34, 0.00, -0.62. MS (EI): m/z = 770.0 [M$^+$]. Anal. Calcd for $C_{44}H_{49}BrSi_4$: C, 68.42; H, 6.41. Found: C, 68.57; H, 6.47.

Synthesis of [2,5-TMS$_2$-3,4-Ph$_2$-silole]·[(MeCN^{i}Pr)$_2$C] (9). A solution of **8** (0.49 g, 0.64 mmol) in tetrahydrofuran (15 mL) was added slowly to a stirred solution of 1,3-*i*Pr$_2$-4,5-Me$_2$-imidazol-2- ylidene (0.23 g, 1. 28 mmol) in tetrahydrofuran (15 mL) at -78 °C. The mixture was kept at -78 °C for 2 h and then slowly warmed to room temperature and stirred for 2 days. Removal of the solvents afforded light yellow powder which was then extracted with toluene (80 mL). Concentration to ca. 10 mL and storage at -35 °C overnight afforded yellow crystals of **9**. Yield: 0.18 g, 51%; ^{1}H NMR (400 MHz, C_6D_6) δ 7.31 (d, *J* = 6.9 Hz, 4H), 7.09 (t, *J* = 7.6 Hz, 4H), 6.95 (t, *J* = 7.4 Hz, 2H), 5.39 (dt, $(CH_3)_2CH$, *J* = 14.2, 7.1 Hz, 2H), 1.46 (s, C-C*H*$_3$, 12H), 0.19 (s, Si-C*H*$_3$, 18H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 161.66, 157.12, 155.94, 146.82, 130.57, 126.85, 126.72, 125.13, 100.21, 51.74, 21.62, 9.70, 2.91. ^{29}Si NMR (79 MHz, C_6D_6): δ -30.4. Anal. Calcd for $C_{33}H_{48}N_2Si_3$: C, 71.16; H, 8.69; N, 5.03. Found: C, 71.20; H, 8.79; N, 5.31.

X-ray Crystallography

Details of the crystal data and a summary of the intensity data collection parameters for **2** are listed in Table S1. The X-ray data were collected on a Rigaku Saturn CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 113 K. The structure was solved by direct methods (SHELXS-97) [4] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97). [5]

Table S1. Crystallographic data and structure refinement details for **2**

	2
formula	$C_{34}H_{45}LiO_3Si$
fw	536.73
T (K)	113(2)
λ (Å)	0.71073
cryst syst	Monoclinic
space group	P2(1)/c
a, (Å)	8.991(4)
b, (Å)	16.122(7)
c, (Å)	22.047(10)
α, □(deg□)	90
β, □(deg□)	91.154(7)
γ, □(deg□)	90
V, (Å^3)	3195(3)
Z	4
Dcalc, (g / cm^3)	1.116
M(mm^{-1})	0.104
F(000)	1160
cryst size (mm)	0.22 x 0.20 x 0.18
2θ range, (deg□)	1.56-27.92
reflns collected	31556
indep reflns/R_{int}	7536 / 0.0597
params	386
GOF on F^2	1.148
*R*1, w*R*2 [I>2σ(I)]	0.0994, 0.2373
*R*1, w*R*2 (all data)	0.1173, 0.2500

Figure S1. ^{1}H NMR spectrum of 1 in $CDCl_3$

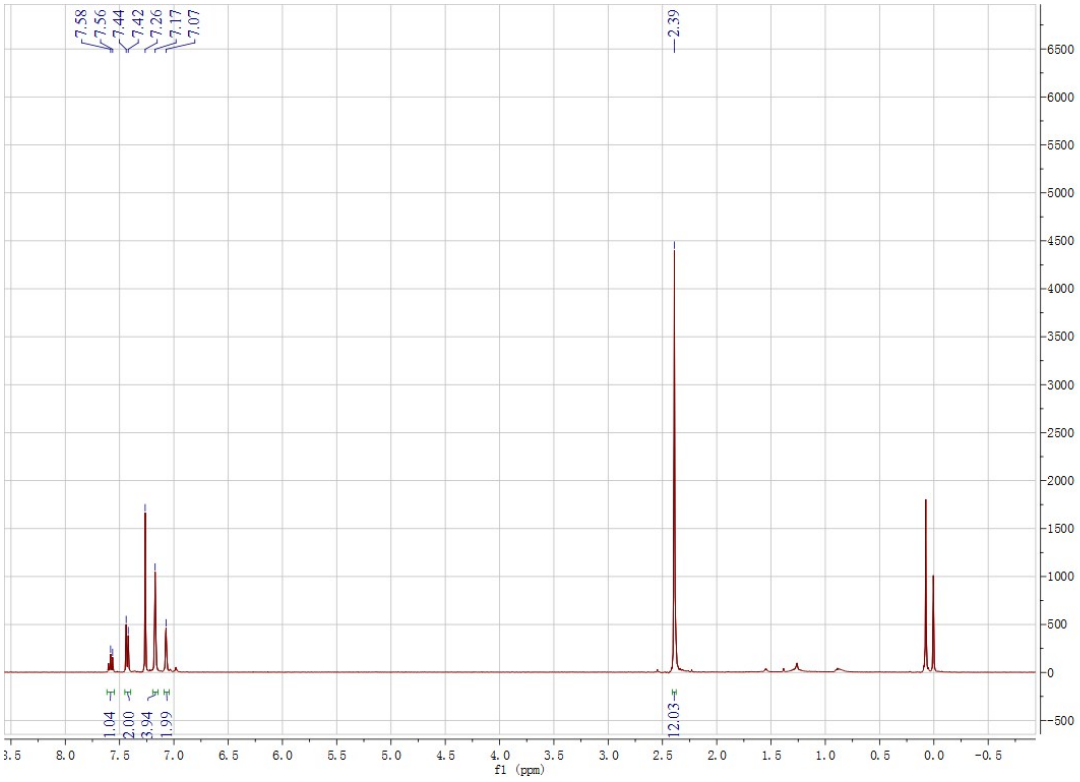


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of 1 in $CDCl_3$

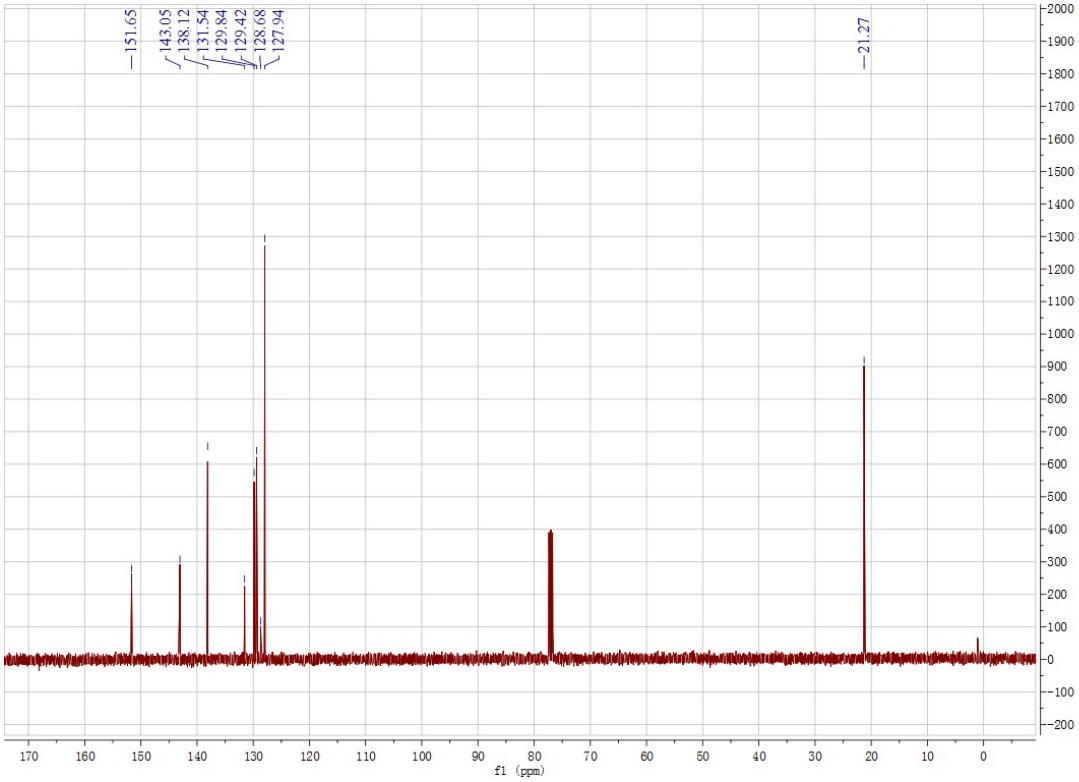


Figure S3. ^{1}H NMR spectrum of 2 in C_6D_6

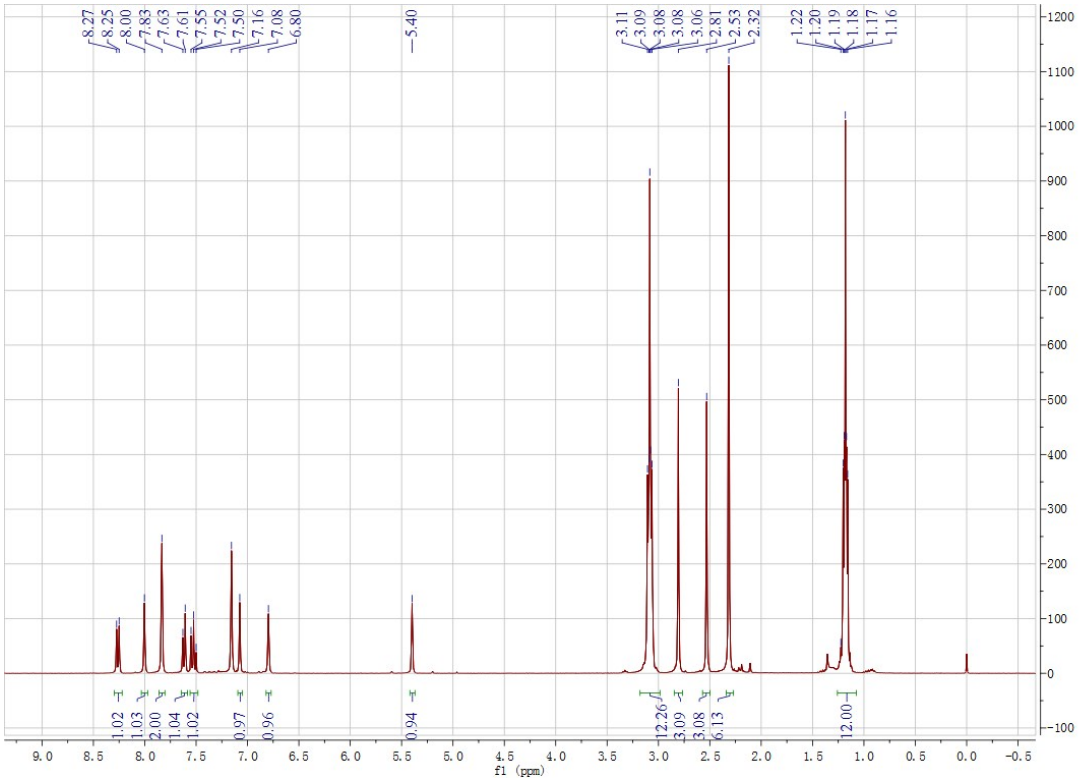


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of 2 in C_6D_6

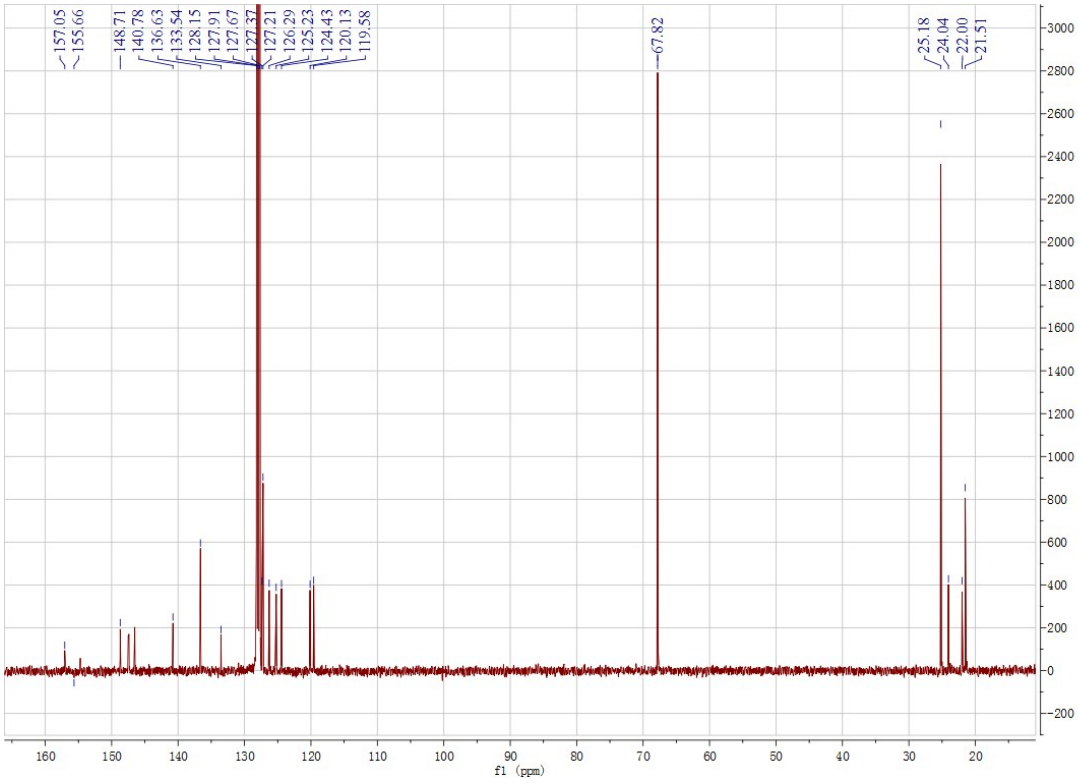


Figure S5.^{29}Si NMR spectrum of 2 in C_6D_6

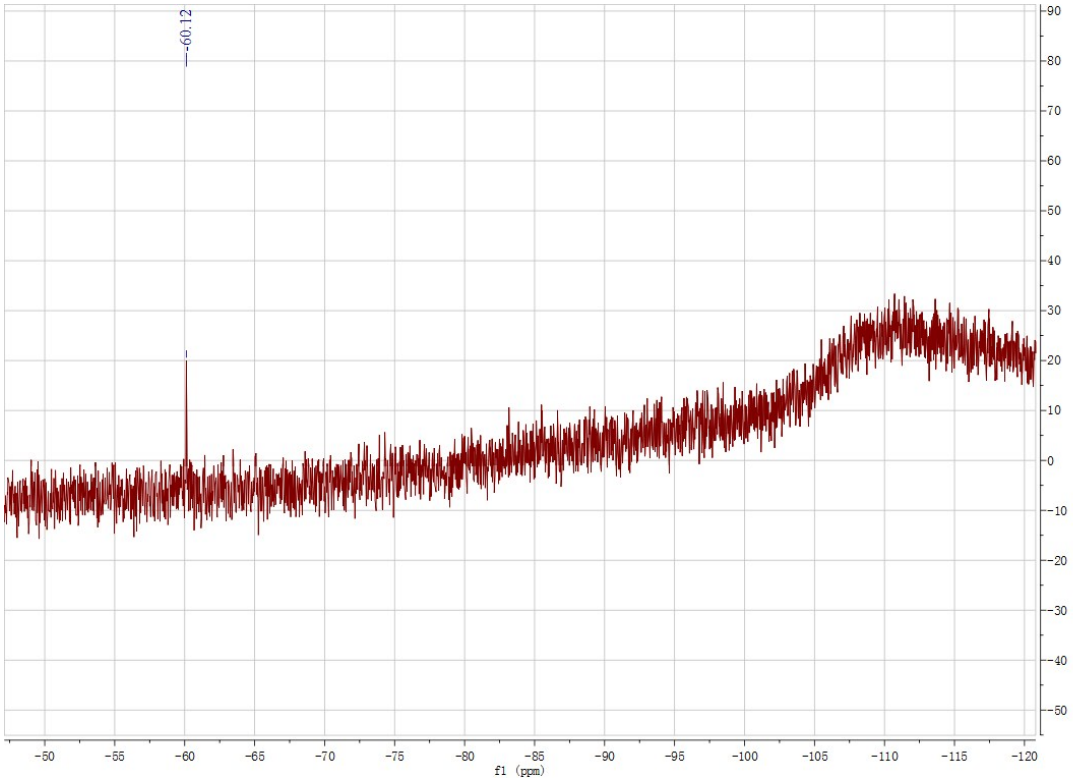


Figure S6.^{29}Si NMR spectrum of 2 in THF-d_8

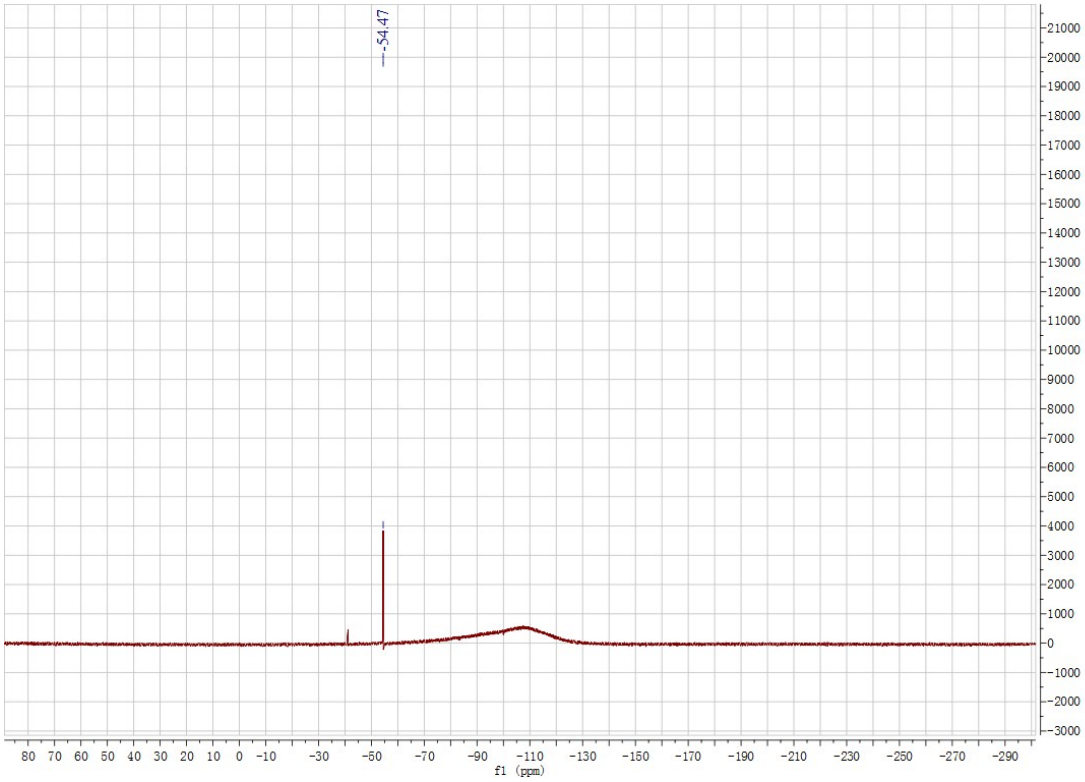


Figure S7.^{1}H NMR spectrum of 5 in C_6D_6

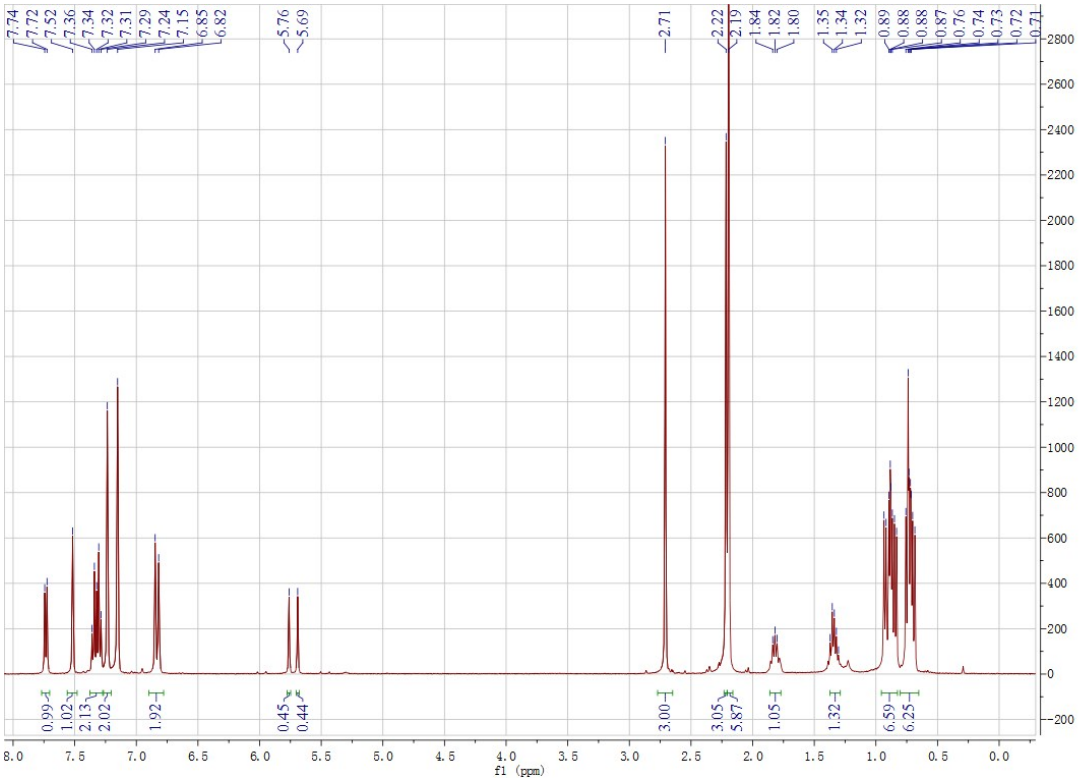


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of 5 in C_6D_6

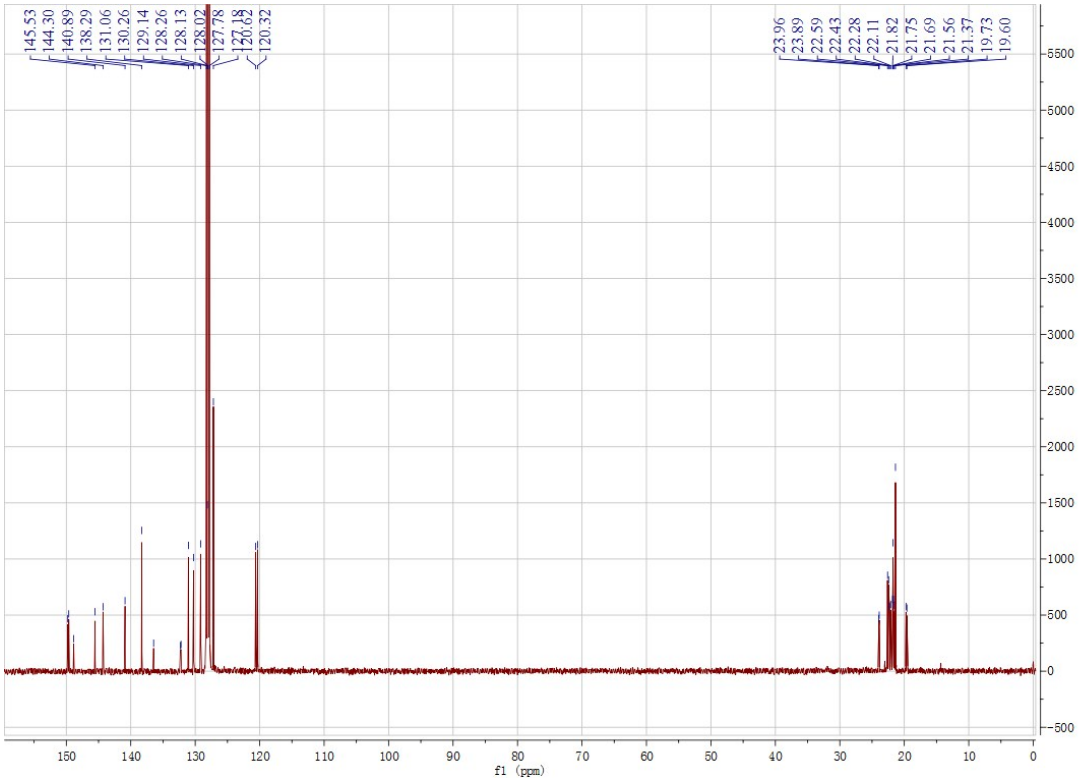


Figure S9. ^{31}P NMR spectrum of 5 in C_6D_6

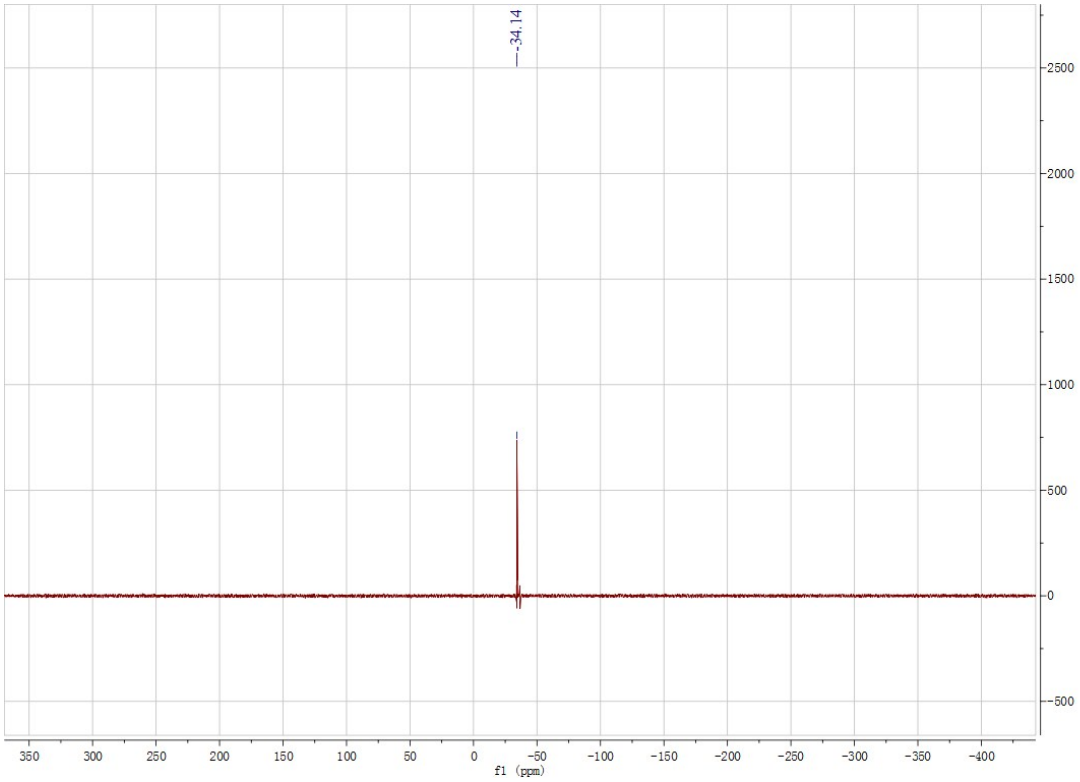


Figure S10. ^{1}H NMR spectrum of 4 in C_6D_6

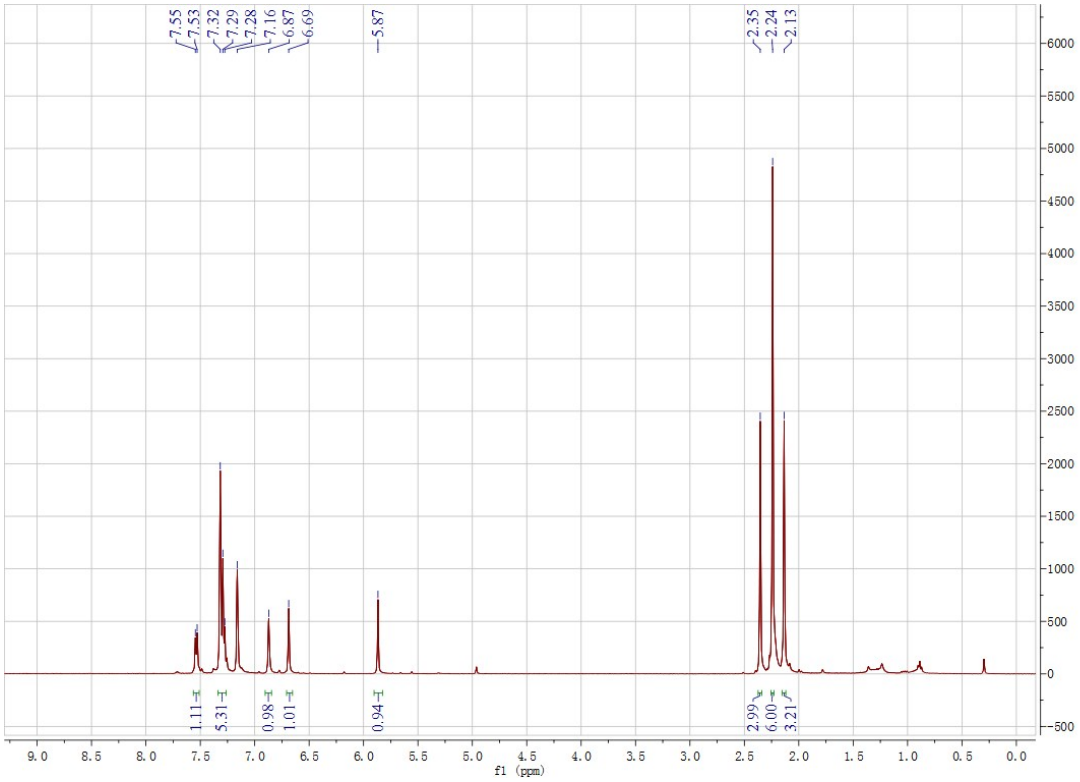


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of 4 in C_6D_6

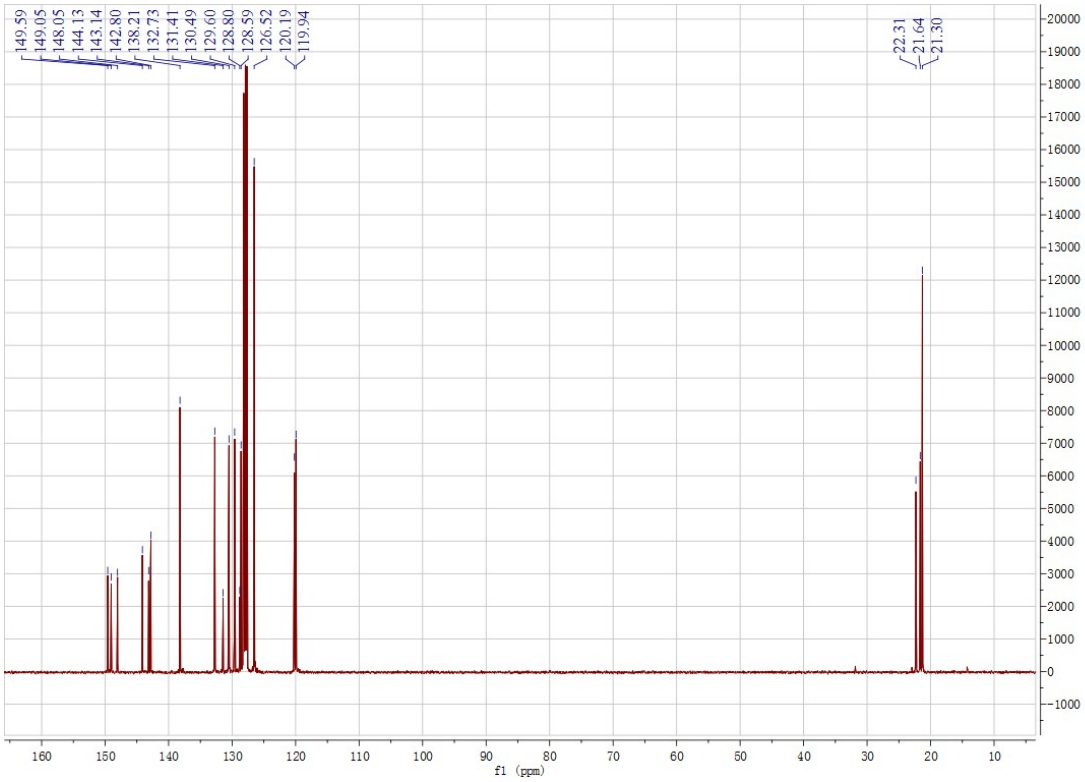


Figure S12. ^{1}H NMR spectrum of 6 in $CDCl_3$

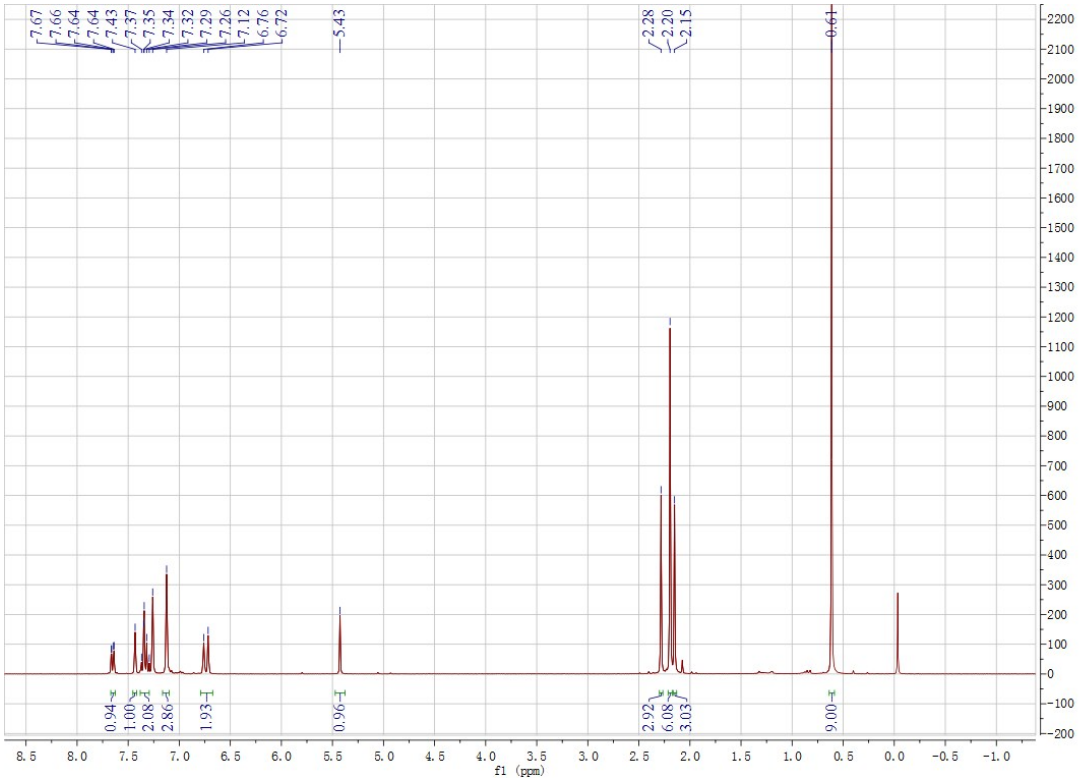


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of 6 in C_6D_6

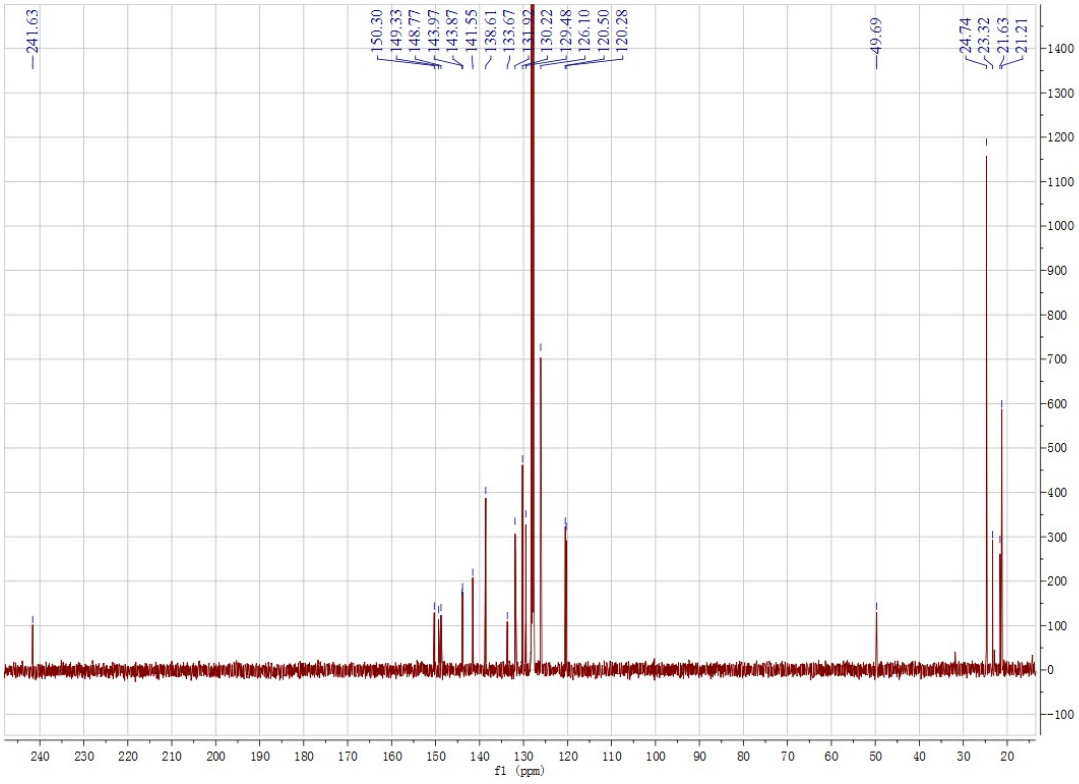


Figure S14. ^{1}H NMR spectrum of 8 in C_6D_6

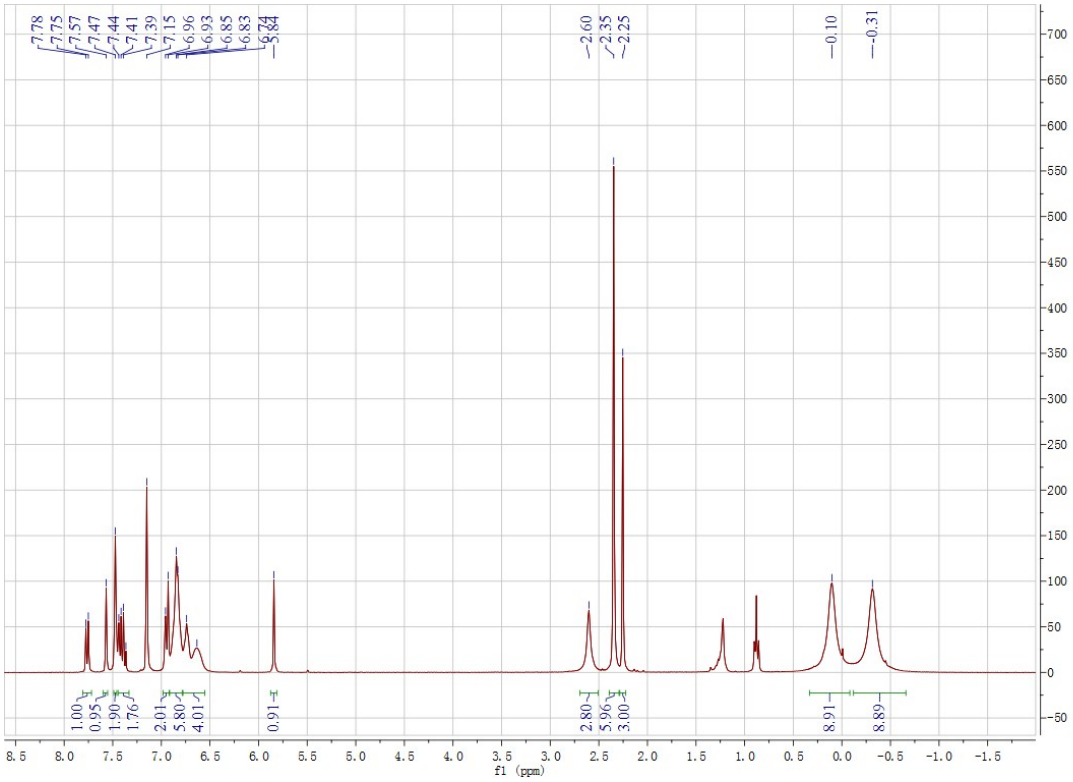


Figure S15 ^{1}H NMR spectrum of 8 in THF-d_8 (20^{o}C)

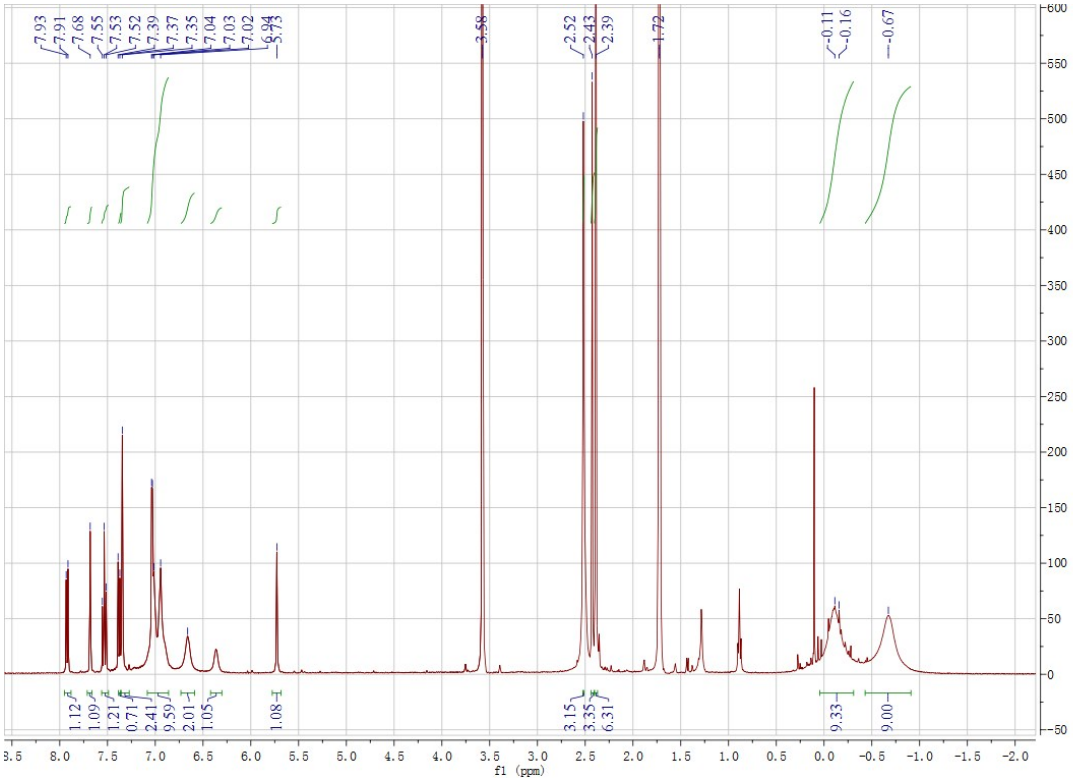


Figure S16. ^{1}H NMR spectrum of 8 in THF-d_8 (10°C)

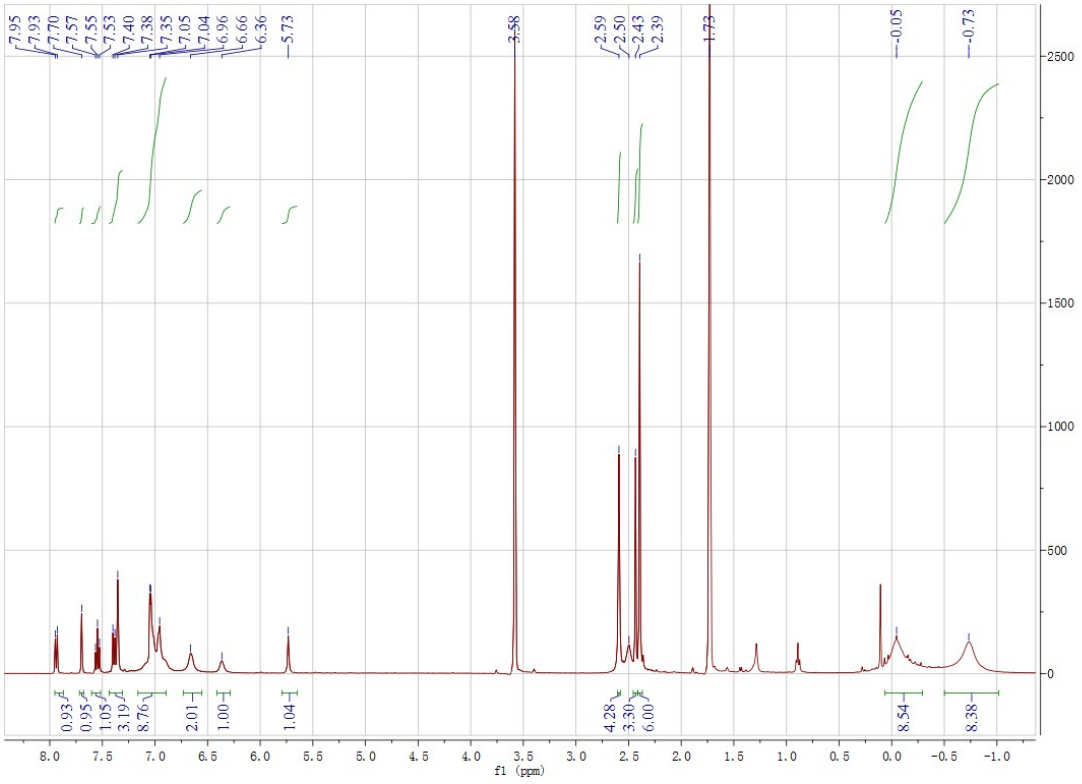


Figure S17. ^{1}H NMR spectrum of 8 in THF-d_8 (0°C)

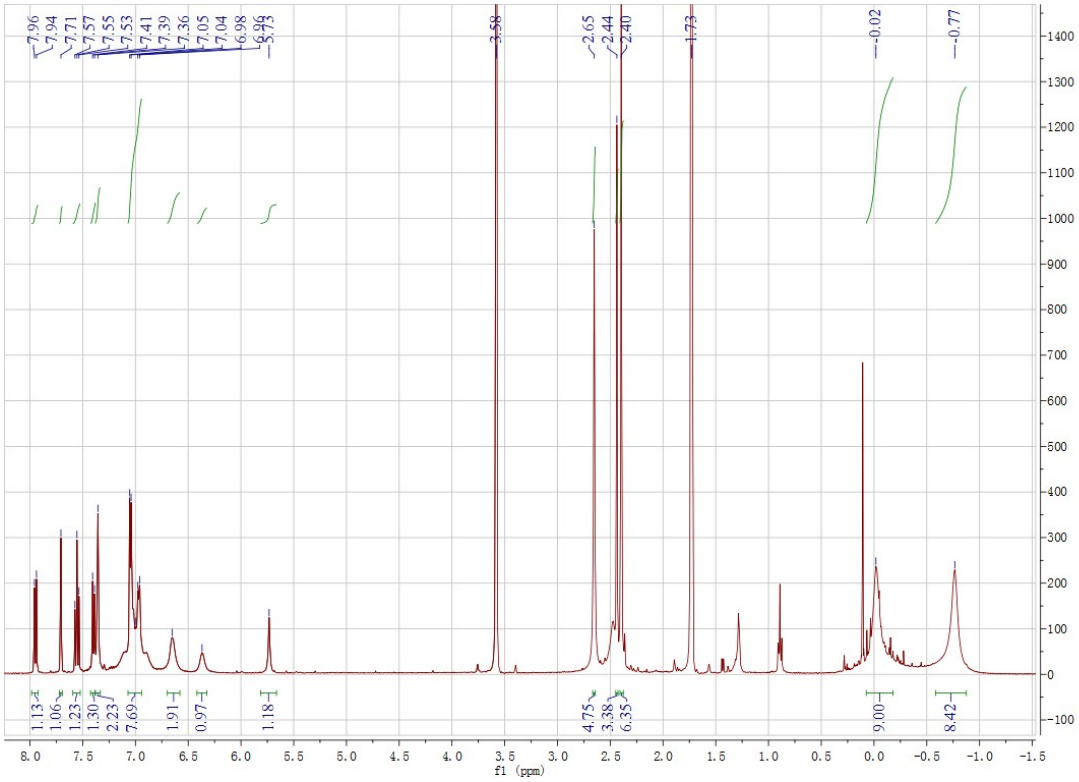


Figure S18. ^{1}H NMR spectrum of 8 in THF-d_8 (-10°C)

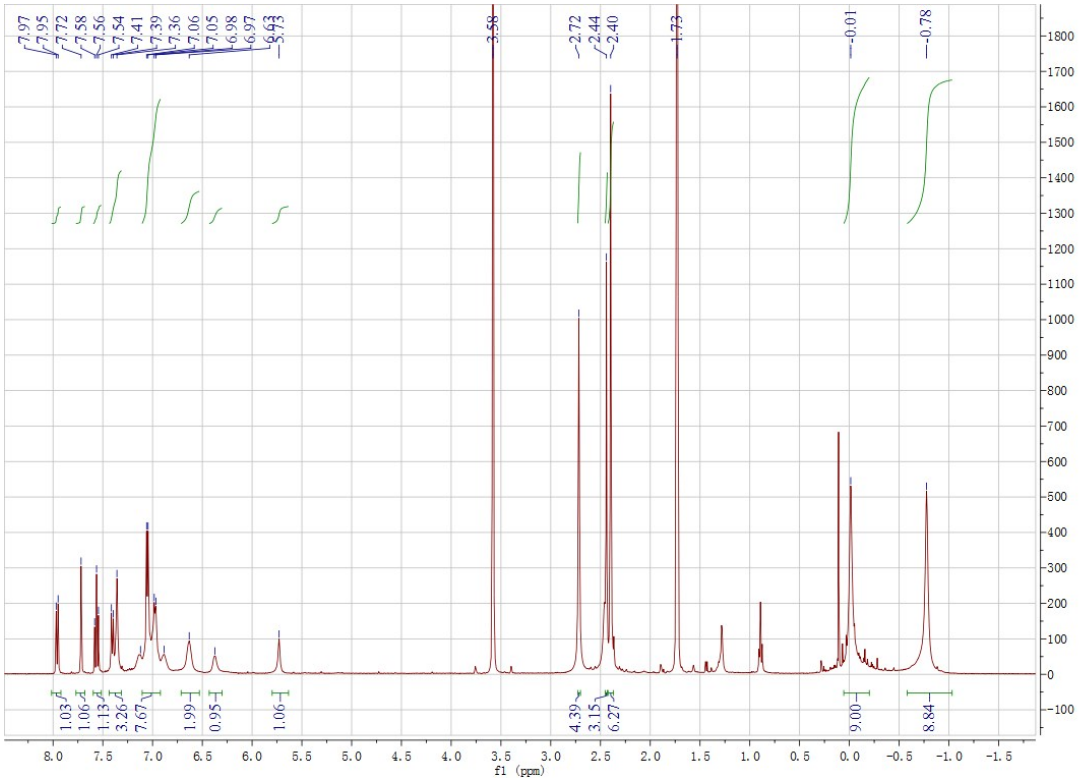


Figure S19. ^{1}H NMR spectrum of 8 in THF-d_8 (-20°C)

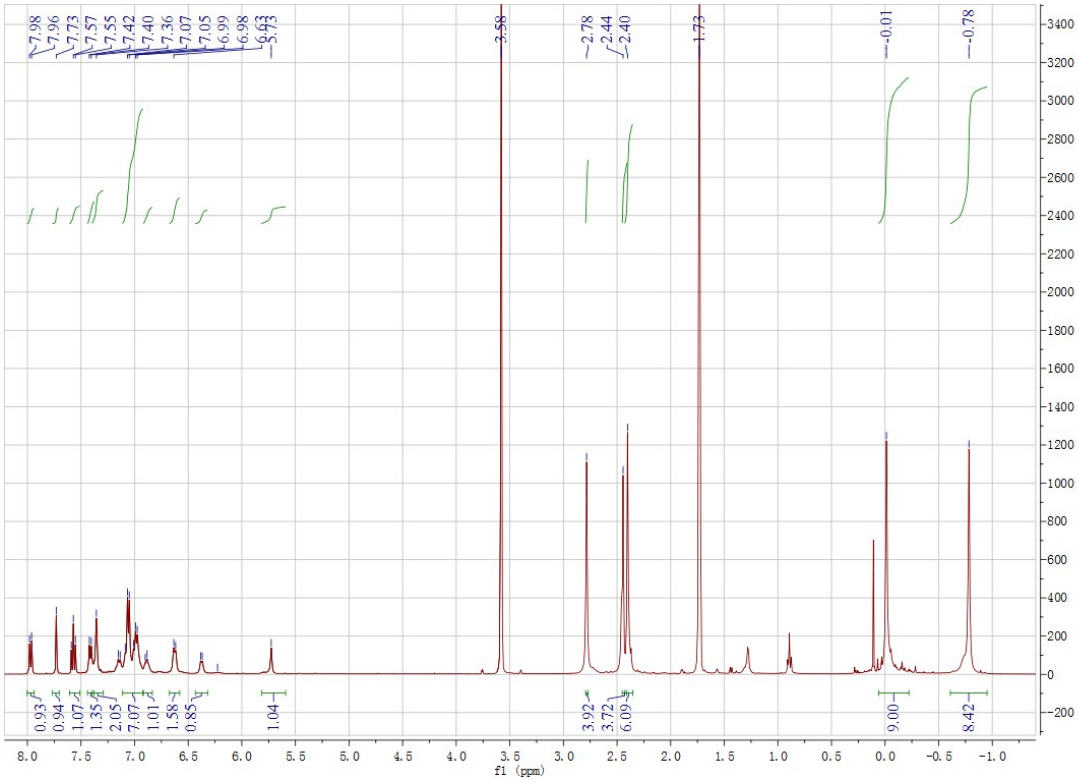


Figure S20. ^{1}H NMR spectrum of 8 in THF-d_8 (-30°C)

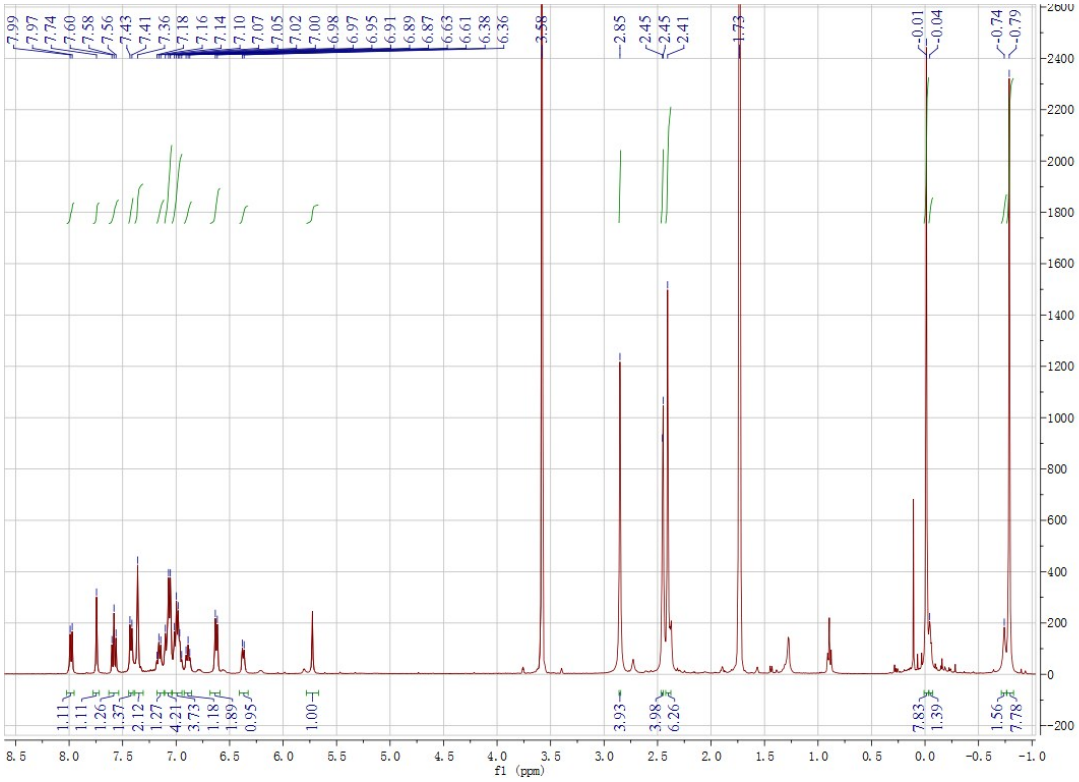


Figure S21. ^{1}H NMR spectrum of 8 in THF-d_8 (-35°C)

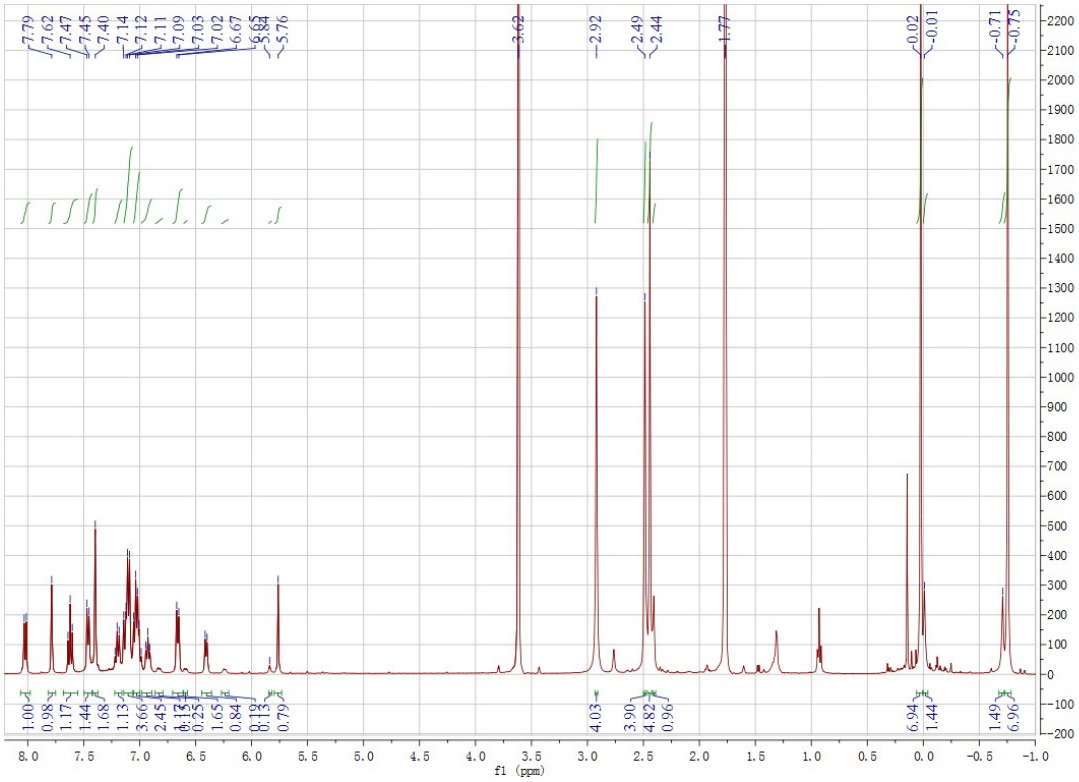


Figure S22. ^{1}H NMR spectrum of 8 in $CDCl_3$ (20°C)

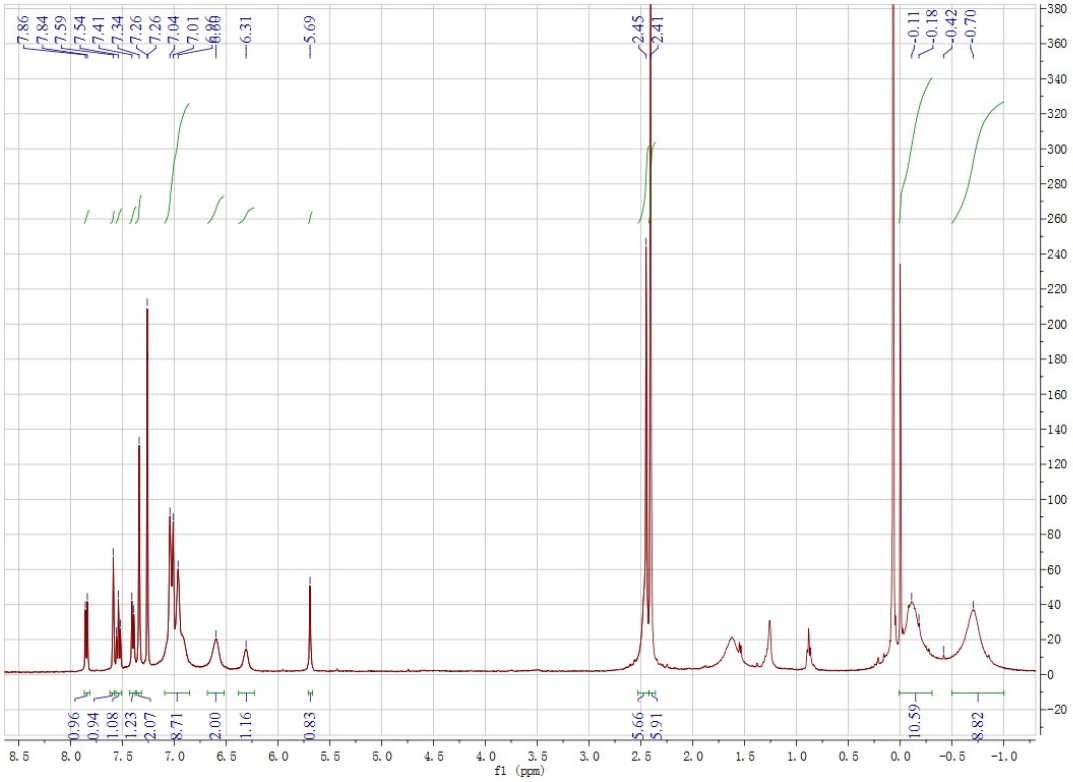


Figure S23. ^{1}H NMR spectrum of 8 in $CDCl_3$ (40°C)

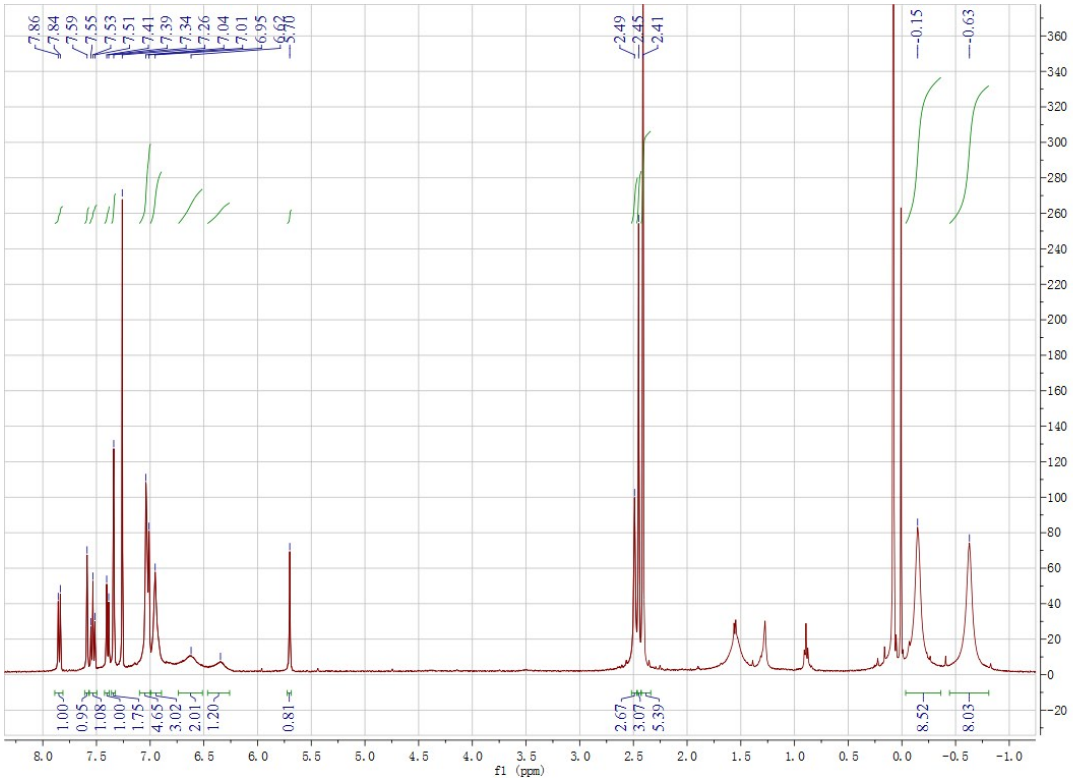


Figure S24. ^{1}H NMR spectrum of 8 in $CDCl_3$ (50°C)

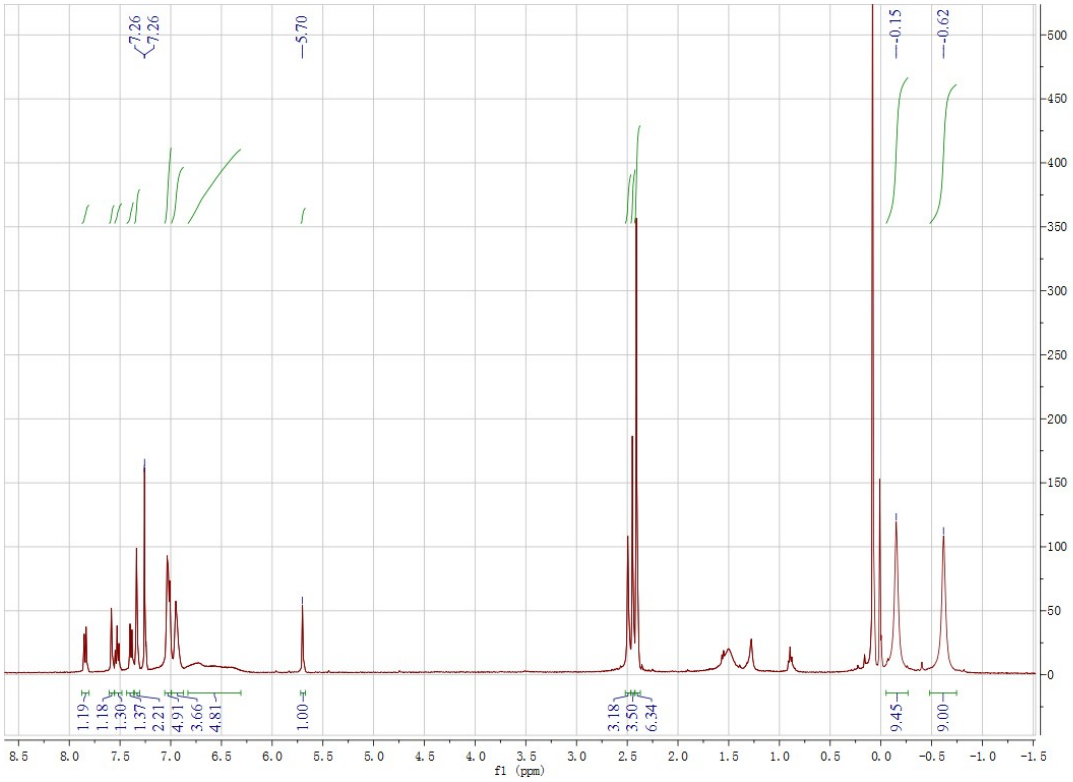


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of 8 in $CDCl_3$

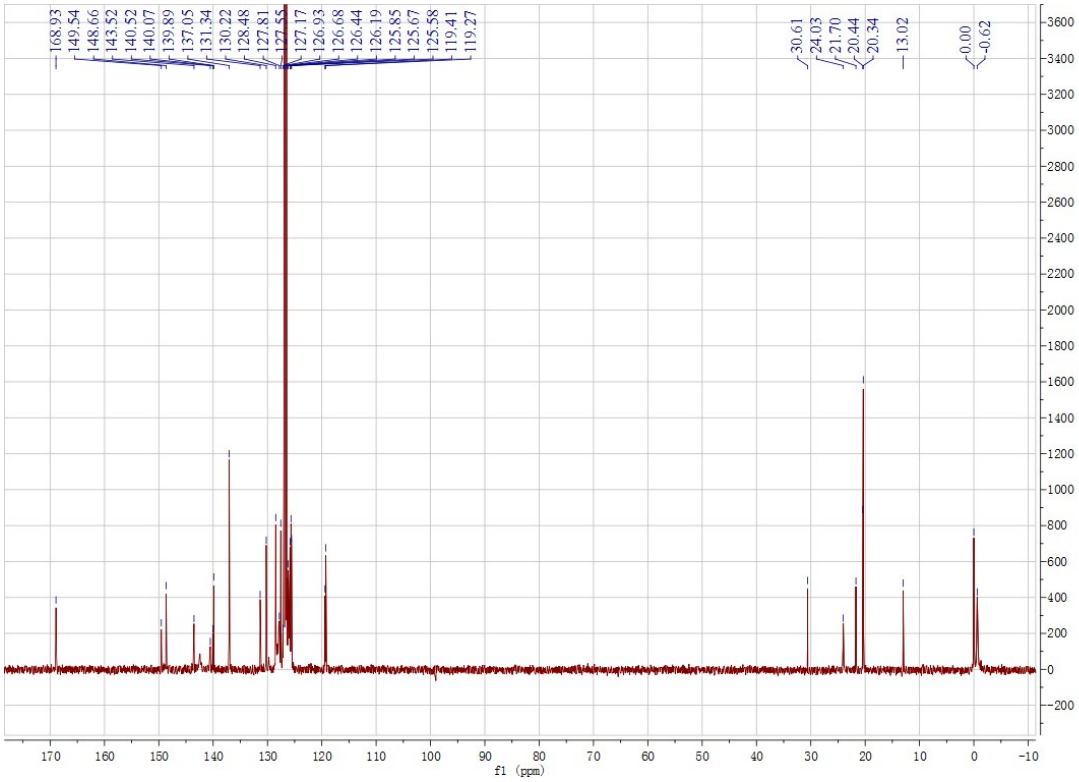


Figure S26. ^{1}H NMR spectrum of 9 in C_6D_6

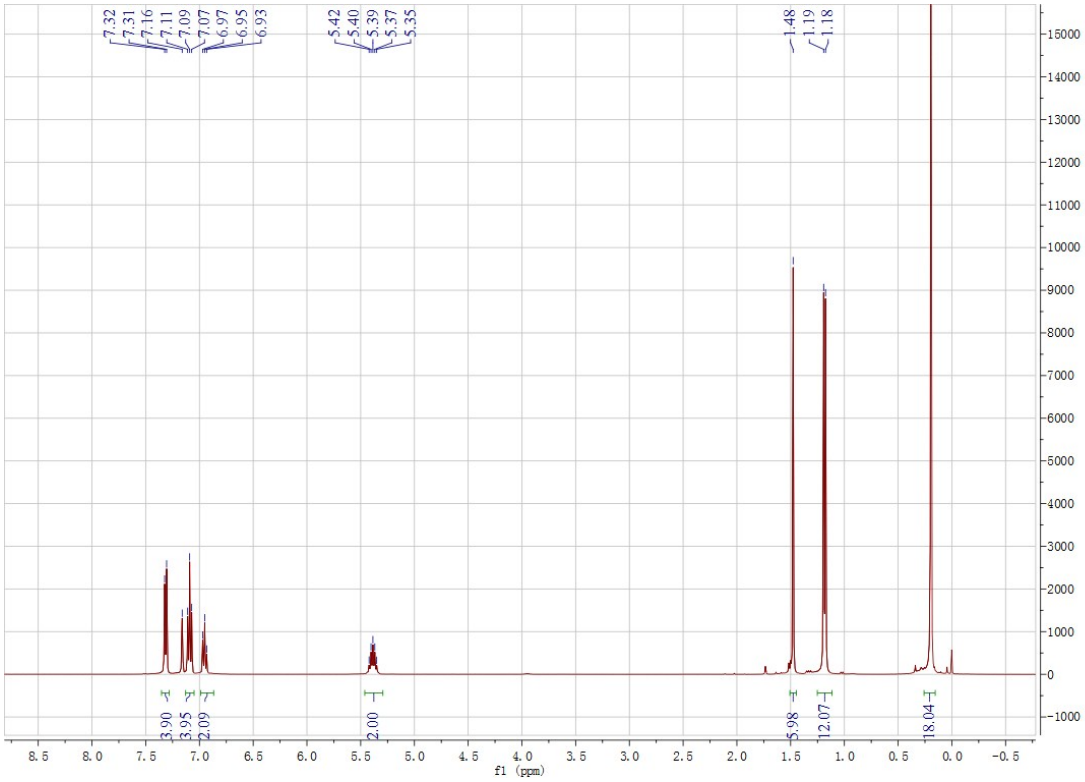


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of 9 in C_6D_6

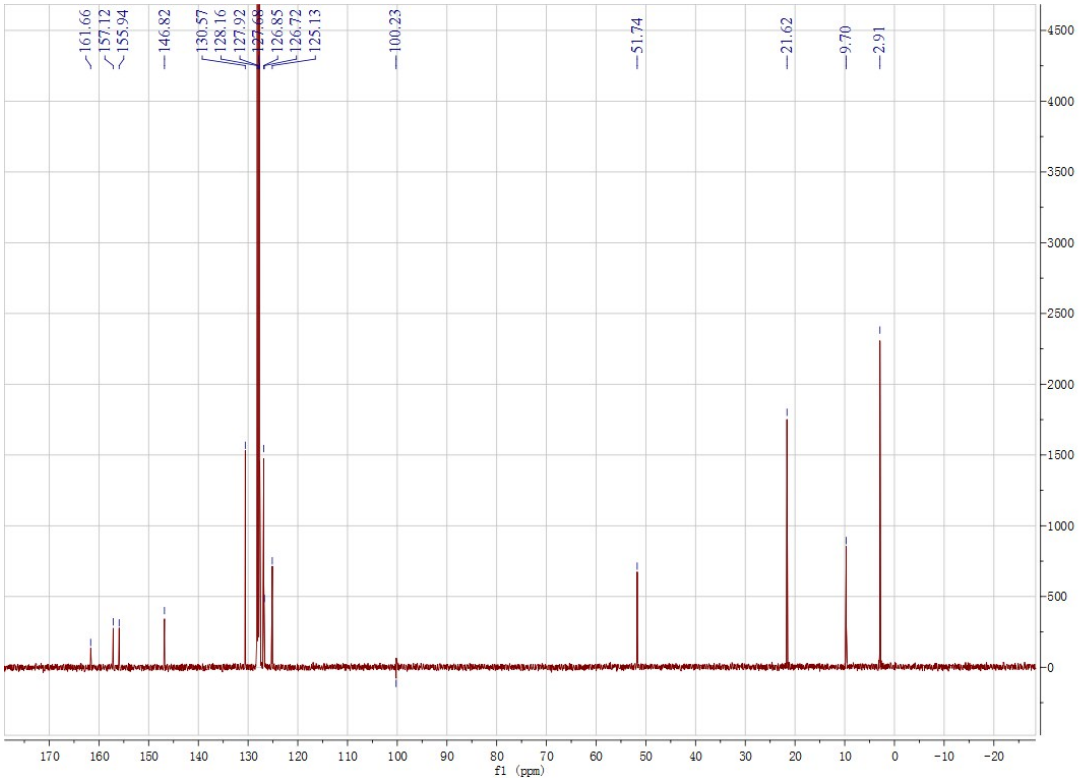
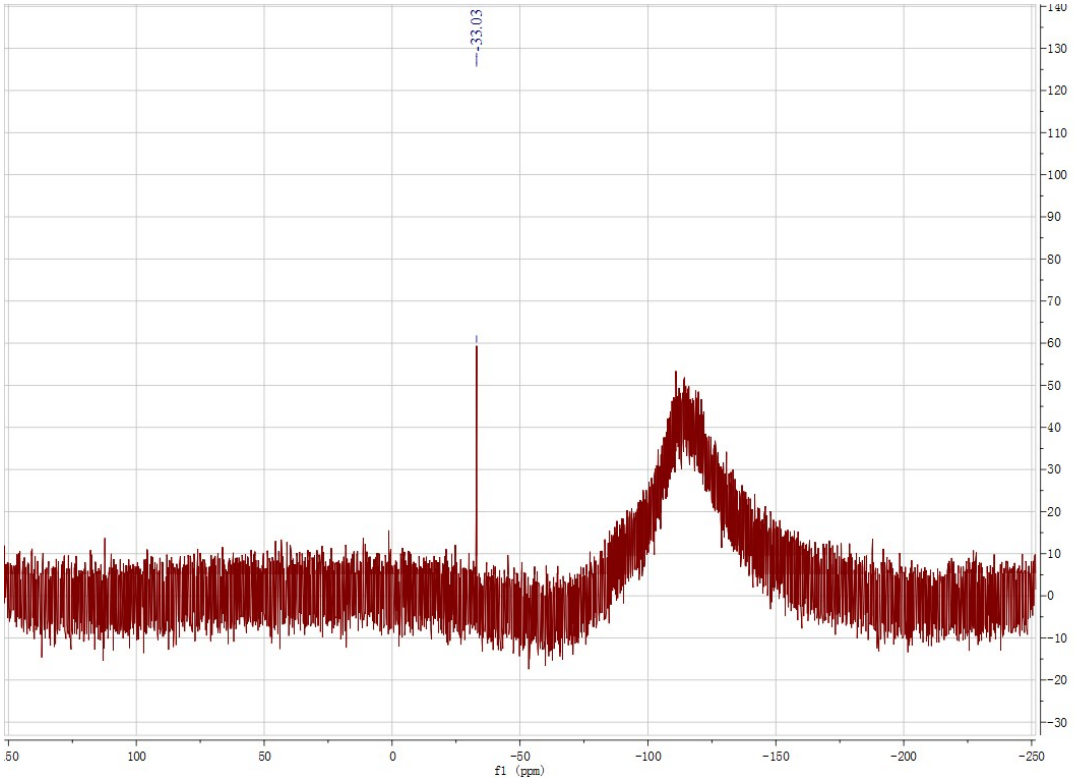


Figure S28. ^{29}Si NMR spectrum of 9 in C_6D_6



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