Electronic Supplementary Information

Stannyl phosphaketene as a synthon for phosphorus analogues of β-lactams

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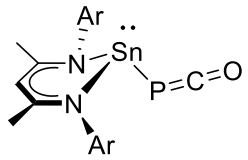
General Information

All manipulations were carried out on a Schlenk line or in an argon atmosphere glovebox. Solvents were dried using a MBraun solvent purification system, and stored over 3 Å sieves. Unless otherwise stated, commercial reagents were used without further purification. CH{(CMe)(2,6-^{i}Pr$_2$C$_6$H$_3$N)}$_2$SnCl[S1] and NaPCO(dioxane)[S2] were synthesized according to the literature methods. ^{1}H, ^{19}F, ^{31}P, ^{11}B and ^{13}C NMR spectra were recorded on a Bruker Ascend 500M or Bruker Advance 400M spectrometer. HRMS were recorded on a Thermo Scientific TM Q-Exactive PlusTM mass spectrometer. Single-crystal X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer using Cu (60W, Diamond, μKα = 12.894 mm^{-1}) micro-focus X-ray sources. Using Olex2,[S3] the structure was solved with the XT[S4] structure solution program using Intrinsic Phasing and refined with the XL[S5] refinement package using Least Squares minimisation.

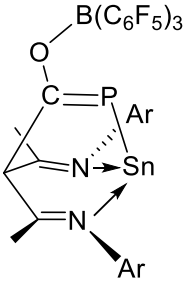
Experimental Section

Synthesis of **1**:



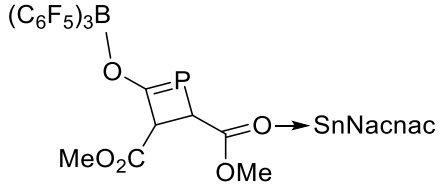
A mixture of NaPCO(dioxane)$_x$ (4 mmol, 30.6% wt., 1071 mg) and toluene (10 mL) was added into a toluene solution (10 mL) of NacNacSnCl (4 mmol, 2287 mg). The resulting orange reaction mixture was stirred at room temperature overnight. After filtration, the solvent was removed under vacuum, and the residues were washed with hexane to give pale yellow powders of **1** (1970 mg, 83% yield). Colorless crystals were obtained by storage a solution of **1** in hexane/toluene at -30 ℃ overnight. ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.14-7.10 (m, 4H, Ar*H*), 7.07-7.04 (m, 2H, Ar*H*), 4.93 (s, 1H, γ-*H*), 3.91-3.85 (m, 2H, ArC*H*Me$_2$), 3.24-3.17 (m, 2H, ArC*H*Me$_2$), 1.53 (s, 6H, β-*Me*), 1.44 (d, *J* = 6.79 Hz, 6H, CH*Me$_2$*), 1.23-1.21 (m, 12H, CH*Me$_2$*, overlapped), 1.05 (d, *J* = 6.80 Hz, 6H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, ppm): δ 189.4 (d, *J* = 91.10 Hz, P*C*O), 167.5 (*C*N), 146.0, 143.1, 141.5, 127.7, 125.4, 124.1 (Ar), 101.8 (γ-*C*), 29.3 (d, *J* = 6.83 Hz, β-*Me*), 28.5 (*C*HMe$_2$), 24.7, 23.9 (CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, ppm) δ -316.8. HRMS (*m/z*): HRMS (m/z): $[M+Na]^+$ Calcd. for $C_{30}H_{41}SnN_2OPNa^+$: 619.1871; Found: 619.1893.

Synthesis of **2**:



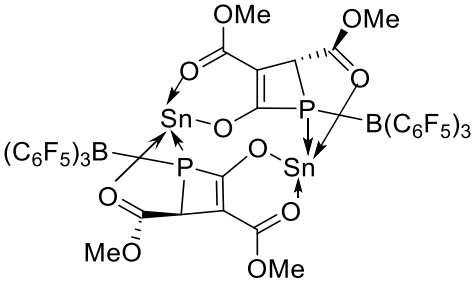
A mixture of **1** (0.1 mmol, 60 mg), $B(C_6F_5)_3$ (51 mg, 0.1 mmol) and toluene (5 mL) was stirred at ambient temperature for 2 h. The resulting yellow solution was storing at -30 °C overnight to afford orange crystals of **2**. The crystals were collected and wash with cool hexane and dry *in vacuo* for 2 hours (40 mg, 47%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 7.32-7.30 (m, 4H, Ar*H*), 7.28-7.26 (m, 2H, Ar*H*), 5.33 (s, 1H, γ-*H*), 3.41 (br, 4H, C*H*Me$_2$), 1.89 (s, 6H, β-*Me*), 1.31 (d, *J* = 6.8 Hz, 12H, CH*Me$_2$*), 1.20 (d, *J* = 6.8 Hz, 12H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, ppm): δ 189.0-187.43 (m, P-*C*-O), 167.2 (*C*N), 144.4, 144.0, 127.3, 124.6 (*Ar*), 101.5 (γ-*C*H), 29.0, 26.4, 24.3, 24.2 (*C*HMe$_2$, β-*Me*, CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$, ppm): δ -320.0. ^{19}F{^{1}H} NMR (471 MHz, $CDCl_3$, ppm) δ -128.1 (6F, *o*-C_6F_5), -143.8 (3F, *p*-C_6F_5), -160.9 (6F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, $CDCl_3$) δ 56.9. HRMS (*m/z*): [M - H]$^-$ Calcd. for $C_{48}H_{40}ON_2BF_{15}PSn^-$: 1107.1759; Found: 1107.1730.

Synthesis of **3**:



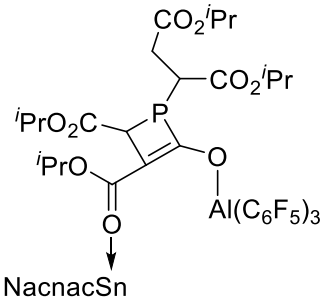
At -30 ℃, a toluene (3 mL) solution of $B(C_6F_5)_3$ (0.1 mmol, 51 mg) was added slowly into a toluene (3 mL) solution of **1** (0.1 mmol, 60 mg) and dimethyl fumarate (0.1 mmol, 14 mg). The reaction mixture was stirred at -30 ℃ for additional 2 hours, and the floccules were filtrated. The resulting brown solution was stored at -30 ℃ for 24 hours till colorless crystals of **3** (42 mg, 61%) were obtained and isolated. ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 7.38 (t, *J* = 7.70 Hz, 2H, Ar*H*), 7.29 (d, *J* = 7.70 Hz, 4H, Ar*H*), 5.85 (s, 1 H, γ-*H*), 4.72 (d, *J* = 5.60 Hz, 1H, P-C*H*-COOMe), 3.82 (s, 3H, O-*Me*), 3.72 (s, 3H, O-*Me*), 3.54 (s, 1H, CO-C*H*-CH-P), 2.72 (sept, *J* = 6.91 Hz, 4H, C*H*Me$_2$), 2.00 (s, 6 H, β-*Me*), 1.14 (t, *J* = 6.66 Hz, 24 H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, ppm): δ 184.5 (P-*C*=O-B), 171.9，171.4 (*C*(O)OMe), 168.9 (*C*N), 163.9 (*C*(O)OMe), 149.6-147.7 (m, C_6F_5), 144.0 (*Ar*), 140.7 (br, C_6F_5), 139.0 (*Ar*), 138.1-136.3 (m, C_6F_5), 129.0 (*Ar*), 125.3 (Ar), 120.1 (br, C_6F_5), 104.2 (γ-*C*), 60.4, 56.0 (C(O)O*Me*), 52.8 (C(O)*C*P), 34.0 (C(O)*C*C=OB), 29.1, 25.8, 24.5, 24.1 (C*H*Me$_2$, β-*Me,* CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, ppm): δ 193.9. ^{19}F{^{1}H} NMR (471 MHz, CD_2Cl_2, ppm) δ -134.8 (br, 6F, *o*-C_6F_5), -162.1 (br, 3F, *p*-C_6F_5), -166.9 (br, 6F, *m*-C_6F_5). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, ppm) δ -2.0. HRMS (*m/z*): $[M + H]^+$ Calcd. for $C_{54}H_{50}SnN_2F_{15}BO_5P^+$: 1253.2328; Found: 1253.2310.

Synthesis of **4**:



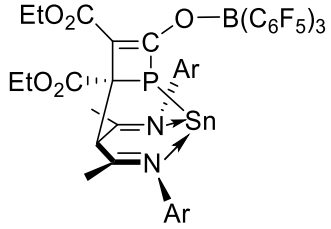
A solution of **1** (0.1 mmol, 60 mg), dimethyl fumarate (0.1 mmol, 14 mg) and $B(C_6F_5)_3$ (0.1 mmol, 51 mg) in toluene (10 mL) was sealed and stirred at 35 ℃ for 48 hours. The reaction mixture was filtrated, and the resulting brown solution was concentrated to about 5 mL. After storing the brown solution at room temperature for 2 hours, colorless crystals of **4** were obtained, collected and washed with cool toluene (35 mg, 42%). ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 3.94 (s, 6H, C*H*$_3$), 3.65 (s, 6H, C*H*$_3$), 3.33 (s, 2H, P-C*H*-CO). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, ppm): δ 180.8 (MeO*C*=O), 163.4 (d, *J* = 14.3 Hz, P-*C*=C-CO), 149.2-147.3, 138.3-136.5 (m, *C*$_6$F$_5$), 106.2-106.0 (d, *J* = 16.0 Hz, P-C-*C*-CO), 55.7, 53.4 (O*Me*), 36.2 (P-*C*-CO). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, ppm): 57.3. ^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, ppm) δ -131.0 (t, *J* = 20.0 Hz, 12F, *o*-C$_6$*F*$_5$), -157.6 (t, *J* = 20.2 Hz, 6F, *p*-C$_6$*F*$_5$), -163.8 (t, *J* = 18.7 Hz, 12F, *m*-C$_6$*F*$_5$). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2) δ -15.2.

Synthesis of **5**:



A solution of $Al(C_6F_5)_3 \cdot 0.5Tol$ (0.1 mmol, 57 mg) in toluene (2 mL) was add dropwise into a solution of **1** (0.1 mmol, 60 mg) and diisopropyl fumarate (0.2 mmol, 34 mg) in toluene (5 mL) at ambient temperature. The resulting yellow reaction mixture was stirred overnight and became orange. The solvent was removed under vacuum to afford yellowish residues. The residues were further washed with hexane and recrystallized in toluene/*n*-hexane to give colorless crystals of **5** (67mg, 52%). ^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.29 (q, *J* = 7.4 Hz, 2H, *Ar*), 7.04 (dd, *J* = 29.6, 7.6 Hz, 4H, *Ar*), 5.09-4.95 (m, 4H, OC*H*Me$_2$), 4.84 (s, 1H, γ-*H*), 3.38 (s, 1H, P*CH*C(O)O), 3.15-3.09 (m, 1H, C=CP*CH*C), 2.90-2.86 (m, 2H, C*H*Me), 2.77-2.71 (m, 1H, C*H*Me), 2.63 (d, *J* = 16.2 Hz, 2H, C=CPC*CH$_2$*), 2.60-2.55 (m, 1H, C*H*Me), 1.57 (d, *J* = 6.6 Hz, 3H, CH*Me*), 1.37 (d, *J* = 18.9 Hz, 6H, β-*Me*), 1.25-0.86 (m, 45H, CH*Me*). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, ppm): δ 194.2 (P-*C*-O-Al), 171.6, 171.1, 170.7, 169.9 (*C*(O)O^{i}Pr), 167.0, 166.1 (*C*N), 162.8 (P-C=*C*), 144.4, 143.7, 142.3, 141.7, 125.4, 124.8, 124.7, 124.4 (*Ar*), 110.2 (γ-C), 70.3, 69.1, 68.5, 68.1 (O*C*H(CH$_3$)$_2$), 49.1, 39.7 (P-*C*), 32.4 (P-C-*C*-C=O), 29.6, 28.6, 28.2, 26.5, 25.9, 24.5, 24.3, 23.7, 23.5, 23.3, 21.9, 21.8, 21.7, 21.6, 21.5, 21.4 (O-CH*Me$_2$*, β-*Me*, *C*HMe$_2$, CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, C_6D_6, ppm): δ 44.5. ^{19}F{^{1}H} NMR (471 MHz, C_6D_6, ppm) δ -120.9 (br, 6F, *o*-C$_6$*F*$_5$), -153.4 (br, 3F, *p*-C$_6$*F*$_5$), -160.8 (br, 6F, *m*-C$_6$*F*$_5$). HRMS (*m/z*): $[M + H]^+$ Calcd. for $C_{68}H_{74}AlF_{15}N_2O_9PSn$:1525.3725; Found: 1525.3724.

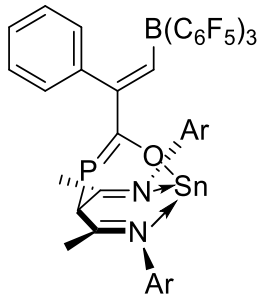
Synthesis of **6**:



A solution of $B(C_6F_5)_3$ (0.1 mmol, 51 mg) in toluene (2 mL) was add dropwise into a solution of **1** (0.1 mmol, 60 mg) and diethyl acetylenedicarboxylate (0.1 mmol, 17 mg) in toluene (5 mL) at -30 ℃. The yellow reaction mixture was allowed to warm to ambient temperature and was stirred for further 2 hours. The resulting brown suspension was filtrated and the residues were washed with hexane to give light yellow powders of **6** (74 mg, 57%). ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 7.38 (q, *J* = 7.7 Hz, 2H, Ar*H*), 7.30 (ddd, *J* = 9.5, 7.9, 1.6 Hz, 2H, Ar*H*), 7.23 (ddd, *J* = 9.0, 7.7, 1.6 Hz, 2H, Ar*H*), 5.77 (d, *J* = 6.8 Hz, 1H, γ-*H*), 4.26-4.20 (m, 1H, OC*H*$_2$Me), 4.19-4.14 (m, 1H, OC*H*$_2$Me), 4.12-4.05 (m, 1H, OC*H*$_2$Me), 4.02-3.96 (m, 1H, OC*H*$_2$Me), 2.65-2.59 (m, 1H, C*H*Me$_2$), 2.55 (s, 3H, β-*Me*), 2.58-2.52 (m, 1H, C*H*Me$_2$), 2.4-2.36 (m, 1H, C*H*Me$_2$), 2.33 (s, 3H, β-*Me*), 2.08-2.04(m, 1H, C*H*Me$_2$), 1.35 (d, *J* = 6.1 Hz, 3H, CH*Me$_2$*), 1.28 (d, *J* = 6.7 Hz, 3H, CH*Me$_2$*), 1.23-1.17 (m, 12H, CH*Me*$_2$), 0.99 (t, *J* = 6.7 Hz, 6H, OCH$_2$*Me*), 0.83 (d, *J* = 6.7 Hz, 3H, CH*Me$_2$*), 0.74 (d, *J* = 6.6 Hz, 3H, CH*Me$_2$*). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, ppm): δ 192.2 (P-*C*-O-BCF), 189.8 (*C*(O)OEt), 179.2, 179.0(*C*N), 176.6 (d, *J* = 5.3 Hz, *C*(O)OEt), 161.5(B-O-C=*C*-C(O)OEt), 150.0-148.0 (m, C_6F_5), 142.6, 141.6, 141.0, 140.4, 138.6, 137.3 (m, C_6F_5), 136.1 (br, C_6F_5), 130.0, 129.6, 126.7, 126.1, 126.0, 125.8 (*Ar*), 110.8 (d, *J* = 15.4 Hz, P-C=*C*C(O)OEt), 62.7, 61.8 (OCH$_2$Me), 59.8 (γ-*C*H), 48.9 (d, *J* = 18.3 Hz, P-*C*-C(O)OEt), 30.3, 30.2, 30.1, 29.8, 29.4, 27.9, 27.8, 26.7, 26.2, 26.1, 26.0, 25.5, 24.8, 24.7, 24.3, 23.5, 14.2, 13.8 (OCH$_2$*Me*, β-*Me*, *C*HMe$_2$, CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, ppm): δ 34.1. ^{19}F{^{1}H} NMR (471 MHz, CD_2Cl_2, ppm) δ -131.6 (br, 6F, *o*-C$_6$*F*$_5$), -160.2 (br,

3F, *p*-C_6F_5), -166.0 (br, 6F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2) δ -1.7. HRMS (*m/z*): [M - H]$^-$ Calcd. for $C_{56}H_{50}O_5N_2BF_{15}PSn^-$: 1277.2338; Found: 1277.2350.

Synthesis of **7**:



A solution of $B(C_6F_5)_3$ (0.1 mmol, 51 mg) in toluene (2 mL) was add dropwise into a solution of **1** (0.1 mmol, 60 mg) and phenylacetylene (0.1 mmol, 10 mg) in in toluene (5 mL) at -30 ℃. The pale-yellow reaction mixture was allowed to warm to ambient temperature and was stirred for further 2 hours. The resulting red suspension was filtrated and the residues were washed with hexane to give orange powders of **7** (53 mg, 42%). ^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 8.06 (br, 1H, C=C-*H*), 7.47-7.32 (m, 6H, Ar*H*), 7.08-6.94 (m, 5H, Ar*H*), 4.17 (br, 1H, γ-*H*), 2.68-2.66 (m, 4H, C*H*Me$_2$), 2.28 (s, 6H, β-*Me*), 1.18-1.34 (m, 24H, CH*Me$_2$, overlapped*). ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, ppm): δ 214.6 (P=CO), 174.0, 173.1 (*C*N), 149.4-147.6 (m, *C*$_6$F$_5$), 144.0, 140.4, 137.9, 130.2, 127.1, 126.9, 126.4., 125.2 (Ar), 111.0 (γ-*C*), 30.3, 28.1, 26.5, 24.7, 24.5 (β-*Me*, C*H*Me$_2$, CH*Me$_2$*). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, ppm): δ 109.6. ^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, ppm) δ -130.8 (br, 6F, *o*-C$_6$*F*$_5$), -164.2 (br, 3F, *p*-C$_6$*F*$_5$), -167.9 (br, 6F, *m*-C$_6$*F*$_5$). ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2) δ -16.4. HRMS (*m/z*): $[M + H]^+$ Calcd. For $C_{56}H_{48}SnN_2F_{15}BOP^+$:1211.2375; Found: 1211.2378.

X-ray Crystallography

Table S1. Crystal data and structure refinement details for compounds **1-4**

	1	**2**	**3**	**4**
CCDC	2195054	2263622	2263623	2263624
Empirical formula	$C_{30}H_{41}N_2OPSn$	$C_{65}H_{60}BF_{15}N_2OPSn$	$C_{68.2}H_{64.2}BF_{15}N_2O_5PSn$	$C_{32}H_{15}BF_{15}O_5PSn$
Formula weight	595.31	1330.62	1437.28	924.91
Temperature, K	273	150	150	150
Crystal system	triclinic	monoclinic	triclinic	triclinic
Space group	P-1	$P2_1/n$	P-1	P-1
a, Å	9.076(11)	15.5036(7)	14.6414(9)	11.5863(5)
b, Å	11.89(2)	25.6431(12)	15.4756(10)	12.5598(6)
c, Å	14.910(14)	15.6976(7)	17.6749(14)	13.4404(6)
α, deg	96.70(9)	90	100.891(4)	99.900(3)
β, deg	98.19(9)	91.655(2)	108.982(4)	114.828(2)
γ, deg	110.74(12)	90	111.357(3)	103.138(2)
V, $Å^3$	1465(4)	6238.1(5)	3305.2(4)	1647.63(13)
Z	2	4	2	2
D_{calcd}, g/cm^3	1.350	1.417	1.444	1.864
μ/mm^{-1}	0.951	4.266	4.117	7.817
F(000)	616.0	2708	1465	904
2*θ* range, deg	2.806-51.988	6.604 to 133.184	5.642 to 133.188	7.582 to 136.91
Index ranges	$-11 \le h \le 11$,	$-18 \le h \le 18$,	$-15 \le h \le 17$,	$-13 \le h \le 13$,
	$-14 \le k \le 14$,	$-30 \le k \le 30$,	$-18 \le k \le 18$,	$-15 \le k \le 15$,
	$-18 \le l \le 18$,	$-18 \le l \le 18$	$-21 \le l \le 21$	$-16 \le l \le 16$
Reflections collected	11230	150341	113680	61002
Independent reflections	5633	11017	11672	6035
	[R_{int} = 0.0214,	[R_{int} = 0.0482,	[R_{int} = 0.0929,	[R_{int} = 0.0659,
	R_{sigma} = 0.0331]	R_{sigma} = 0.0187]	R_{sigma} = 0.0424]	R_{sigma} = 0.0287]
Data/restraints/parameters	5633/0/326	11017/440/868	11672/232/896	6035/0/499
Goodness-of-fit on F^2	1.080	1.024	1.078	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0406,	R_1 = 0.0308,	R_1 = 0.0560,	R_1 = 0.0254,
	wR_2 = 0.1014	wR_2 = 0.0809	wR_2 = 0.1462	wR_2 = 0.0653
Final R indexes [all data]	R_1 = 0.0438,	R_1 = 0.0317,	R_1 = 0.0612,	R_1 = 0.0273,
	wR_2 = 0.1031	wR_2 = 0.0816	wR_2 = 0.1498	wR_2 = 0.0662
Largest diff. peak/hole, $e/Å^{-3}$	1.88/-0.54	0.71/-0.55	0.74/-1.33	0.86/-0.51

Table S2. Crystal data and structure refinement details for compounds **5-7**

	5	**6**	**7**
CCDC	2264168	2263625	2263626
Empirical formula	$C_{68}H_{73}AlF_{15}N_2O_9PSn$	$C_{58.6}H_{56.2}BCl_{3.7}F_{15}N_2O_5PSn$	$C_{56}H_{47}BF_{15}N_2OPSn$
Formula weight	1523.92	1445.09	1209.42
Temperature, K	150	200	200
Crystal system	triclinic	monoclinic	triclinic
Space group	P-1	$P2_1/n$	P-1
a, Å	12.7892(4)	13.9857(3)	11.4575(3)
b, Å	21.2487(6)	18.8170(4)	15.5646(4)
c, Å	27.5926(9)	24.5153(6)	16.0433(5)
α, deg	84.417(2)	90	84.280(2)
β, deg	81.544(2)	95.8090(10)	75.467(2)
γ, deg	89.324(2)	90	86.6760(10)
V, Å^3	7381.7(4)	6418.5(2)	2754.08
Z	4	4	2
D_{calcd}, g/cm^3	1.371	1.495	1.458
μ/mm^{-1}	3.870	5.624	4.772
F(000)	3120	2919	1220
2*θ* range, deg	4.178to 133.19	6.988 to 133.18	5.71 to 140.34
Index ranges	$-15 \le h \le 15$,	$-16 \le h \le 16$,	$-13 \le h \le 13$,
	$-25 \le k \le 25$,	$-22 \le k \le 22$,	$-18 \le k \le 18$,
	$-32 \le l \le 32$	$-29 \le l \le 29$	$-19 \le l \le 19$
Reflections collected	305899	113733	67812
Independent reflections	26036	11344	10422
	[R_{int} = 0.0658,	[R_{int} = 0.0959,	[R_{int} = 0.0595,
	R_{sigma} = 0.0266]	R_{sigma} = 0.0412]	R_{sigma} = 0.0332]
Data/restraints/parameters	26036/1/1783	11344/52/879	10422/0/704
Goodness-of-fit on F^2	1.091	1.036	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0445,	R_1 = 0.0541,	R_1 = 0.0289,
	wR_2 = 0.1091	wR_2 = 0.1443	wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0477,	R_1 = 0.0650,	R_1 = 0.0326,
	wR_2 = 0.1107	wR_2 = 0.1528	wR_2 = 0.0722
Largest diff. peak/hole, e/Å^{-3}	1.49/-1.15	1.80/-0.50	0.37/-0.44

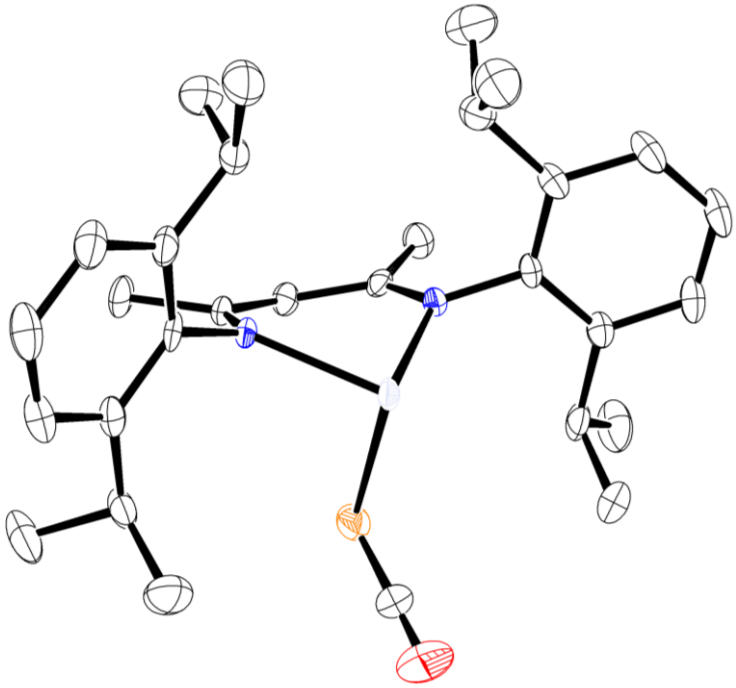


Figure S1. Thermal ellipsoid plot for **1** with the anisotropic displacement parameters depicted at the 50% probability level.

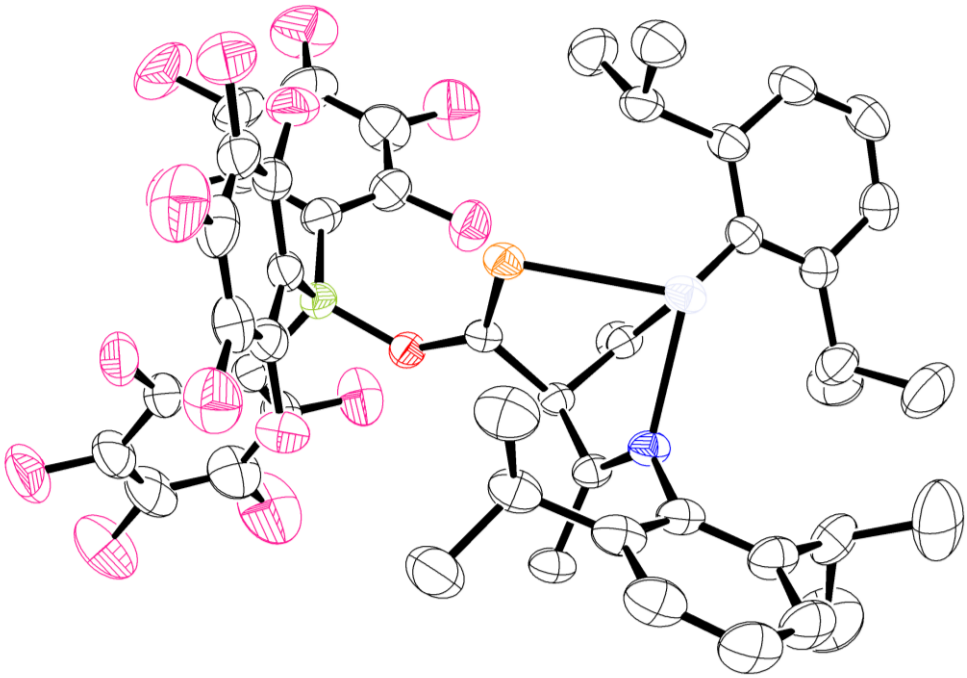


Figure S2. Thermal ellipsoid plot for **2** with the anisotropic displacement parameters depicted at the 50% probability level.

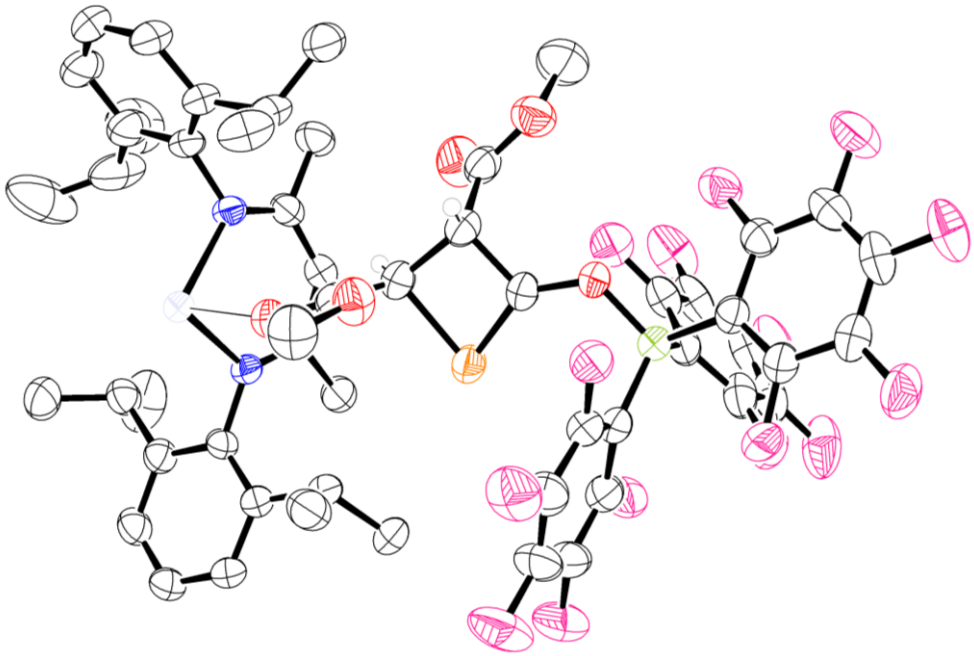


Figure S3. Thermal ellipsoid plot for **3** with the anisotropic displacement parameters depicted at the 50% probability level.

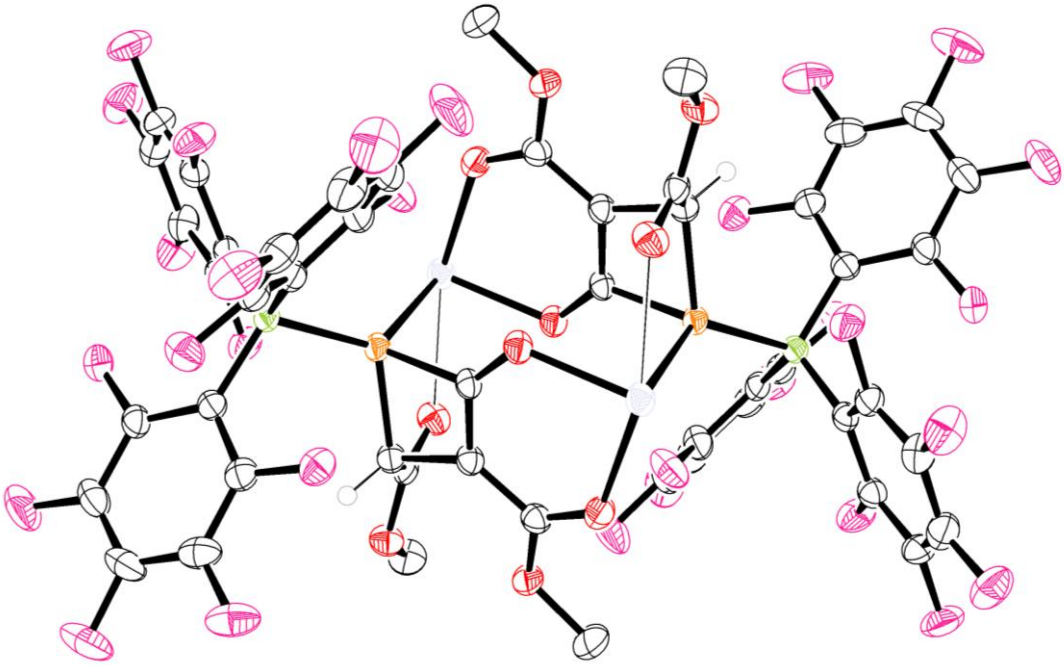


Figure S4. Thermal ellipsoid plot for **4** with the anisotropic displacement parameters depicted at the 50% probability level.

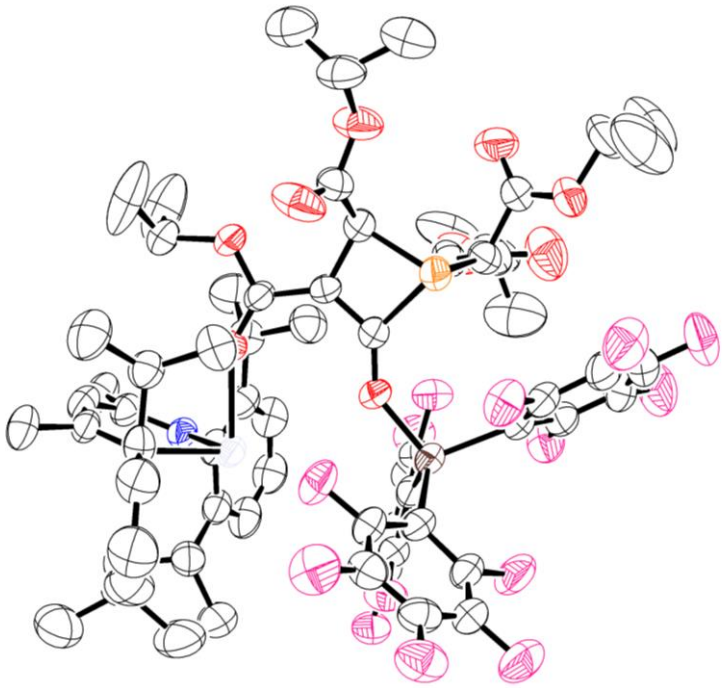


Figure S5. Thermal ellipsoid plot for **5** with the anisotropic displacement parameters depicted at the 50% probability level.

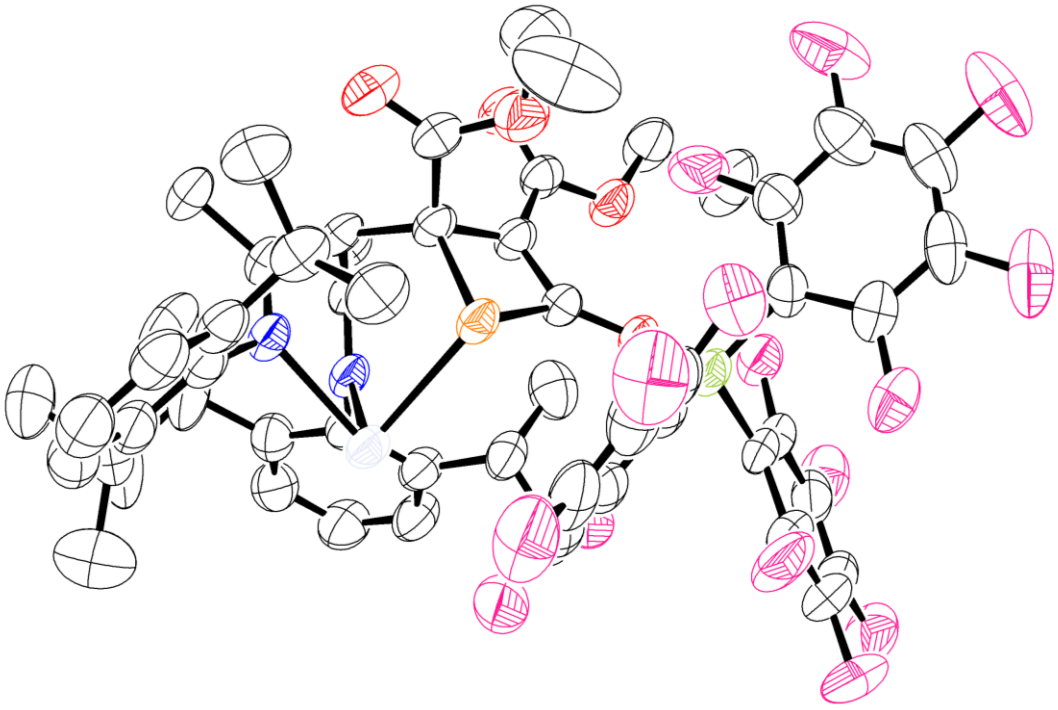


Figure S6. Thermal ellipsoid plot for **6** with the anisotropic displacement parameters depicted at the 50% probability level.

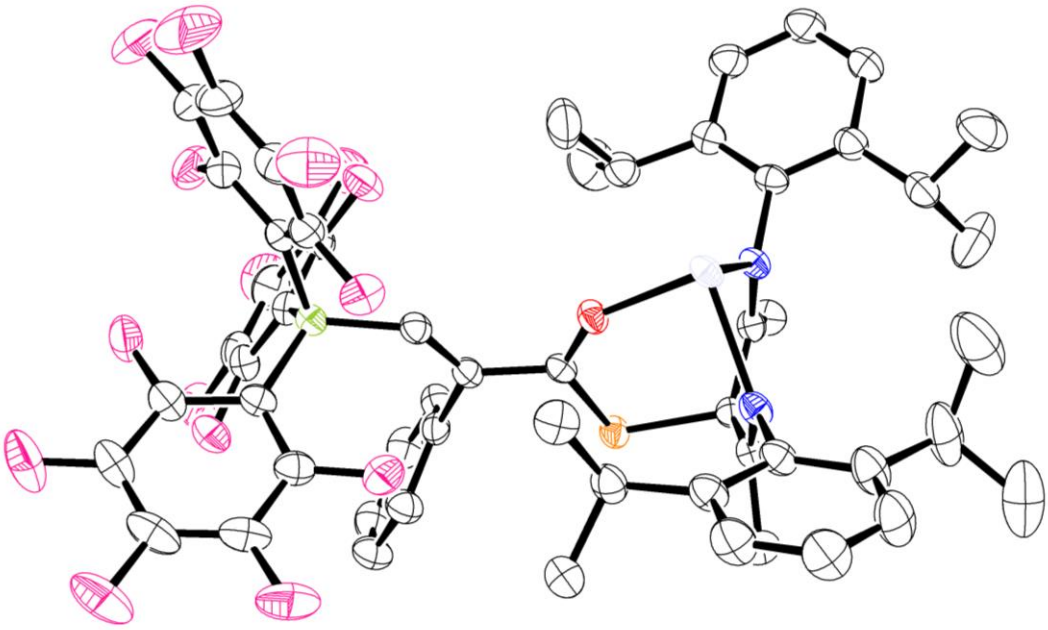


Figure S7. Thermal ellipsoid plot for **7** with the anisotropic displacement parameters depicted at the 50% probability level.

NMR Spectra

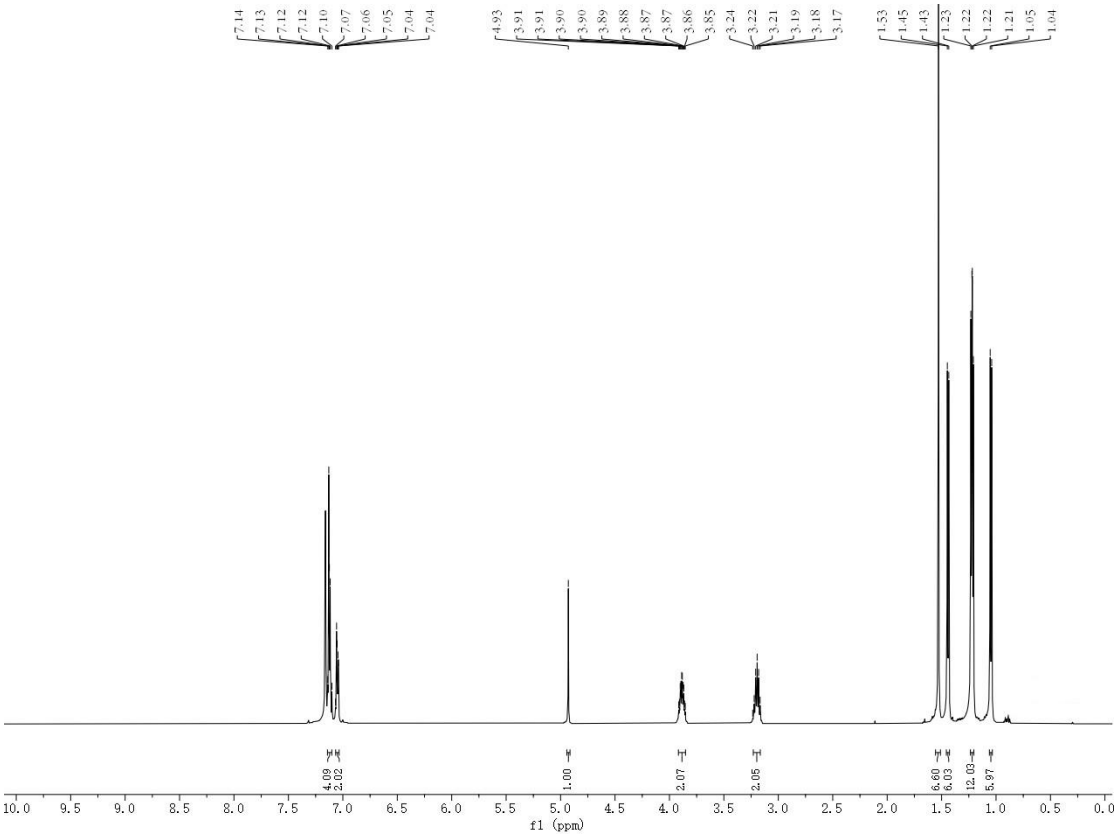


Figure S8. ^{1}H NMR spectrum of **1** in C_6D_6

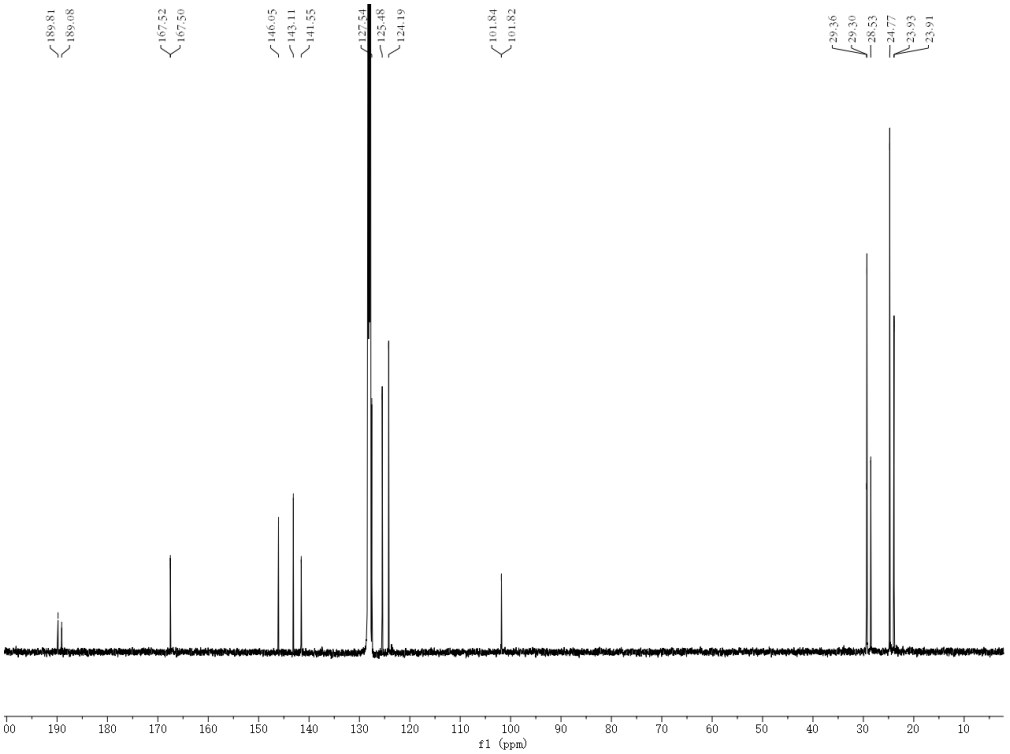


Figure S9. ^{13}C NMR spectrum of **1** in C_6D_6

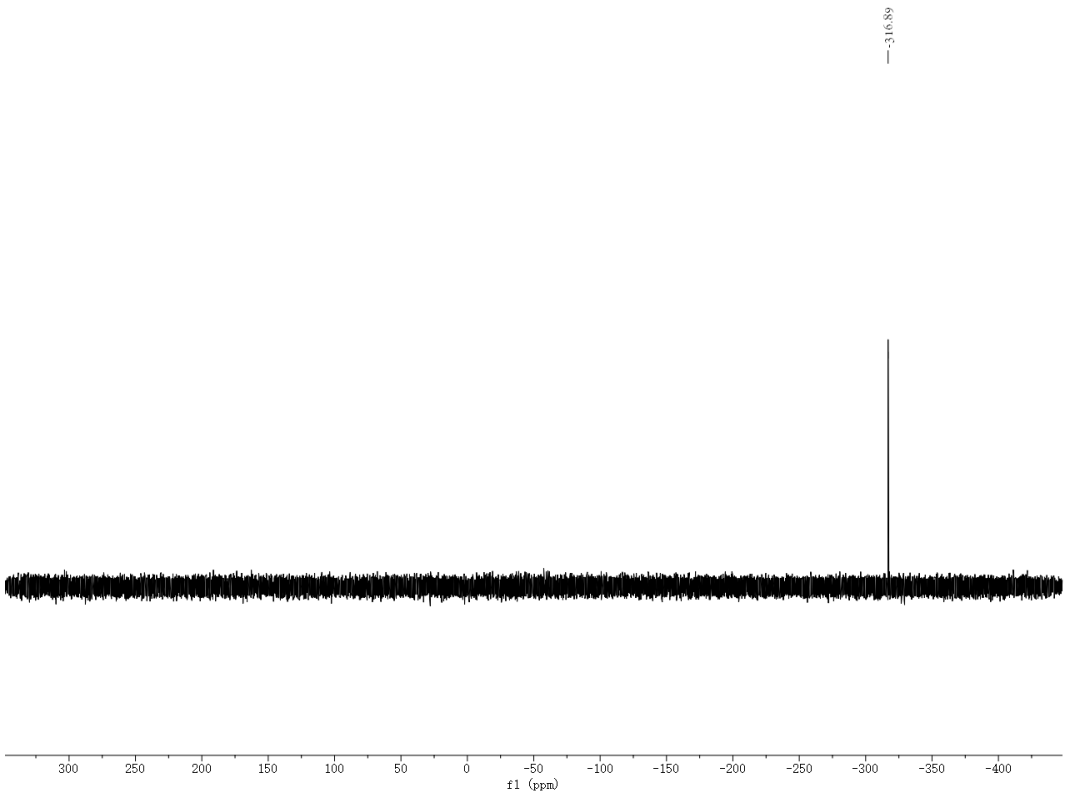


Figure S10. ^{31}P NMR spectrum of **1** in C_6D_6

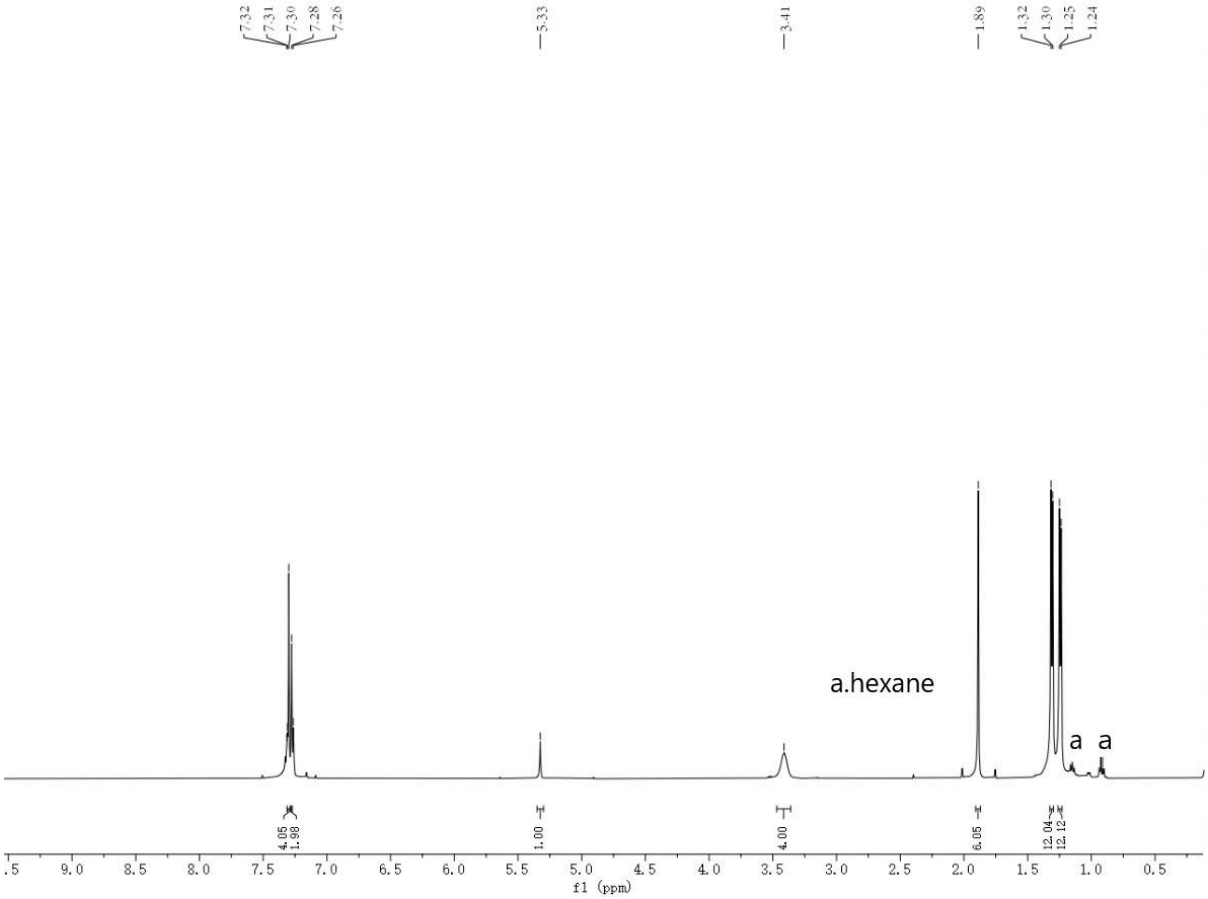


Figure S11. ^{1}H NMR spectrum of **2** in $CDCl_3$

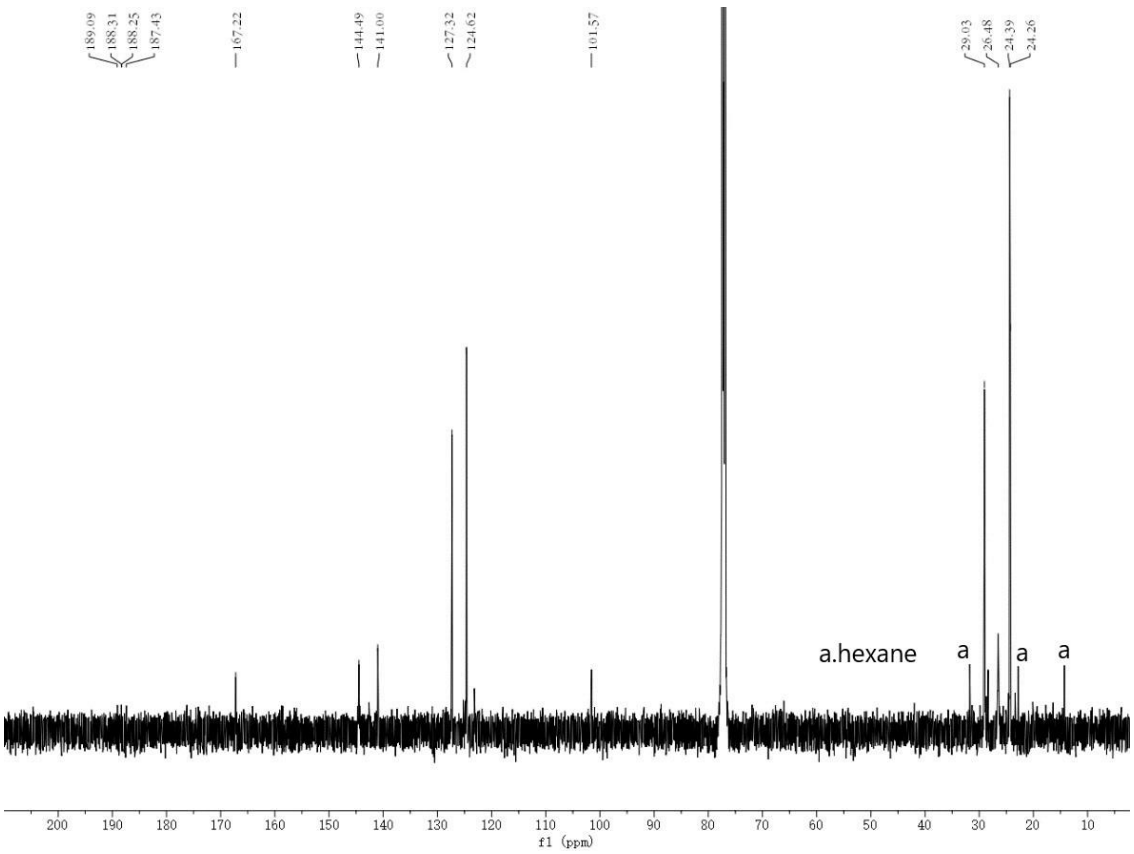


Figure S12. ^{13}C NMR spectrum of **2** in $CDCl_3$

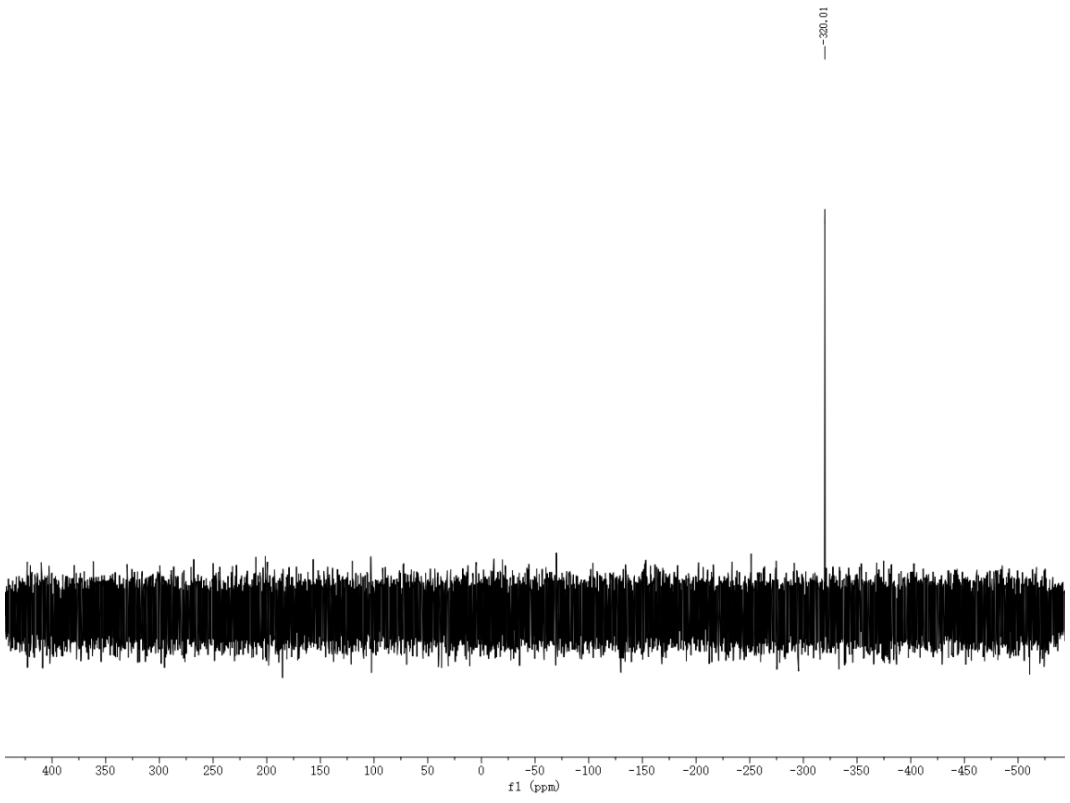


Figure S13. ^{31}P NMR spectrum of **2** in $CDCl_3$

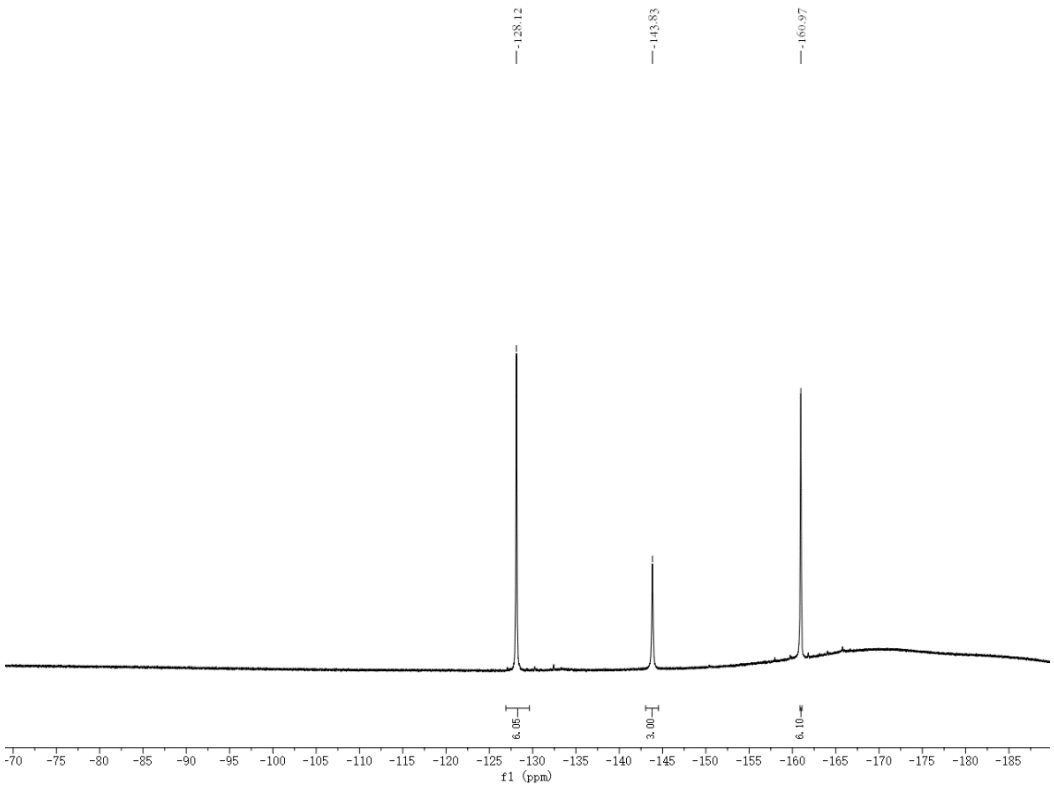


Figure S14. ^{19}F NMR spectrum of **2** in $CDCl_3$

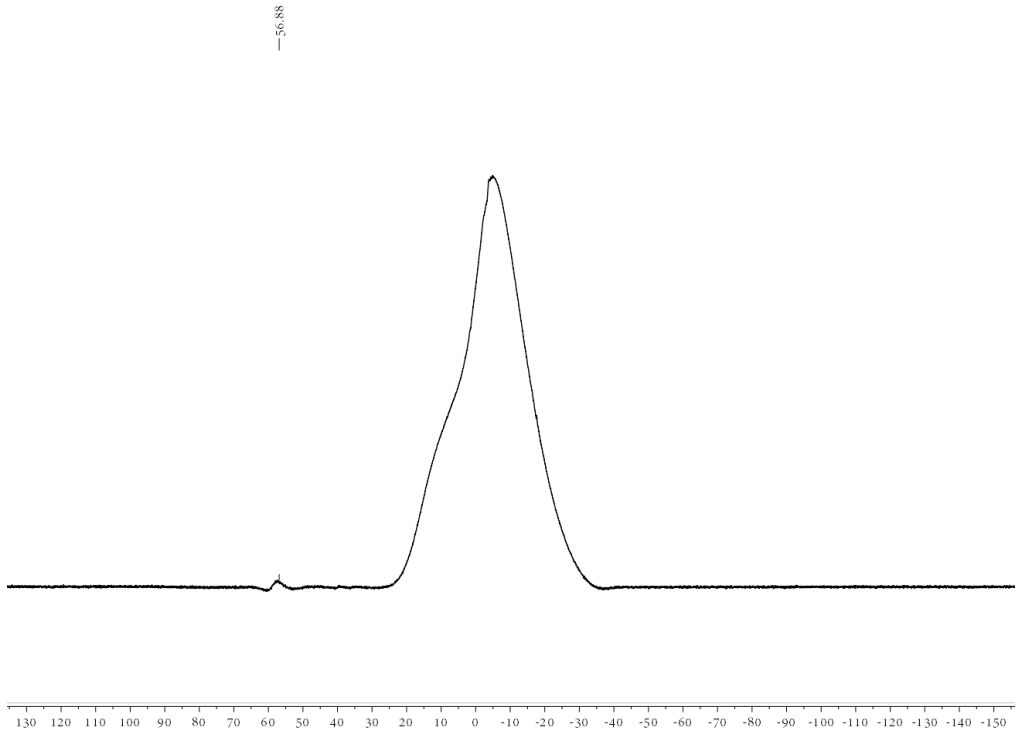


Figure S15. ^{11}B NMR spectrum of **2** in $CDCl_3$

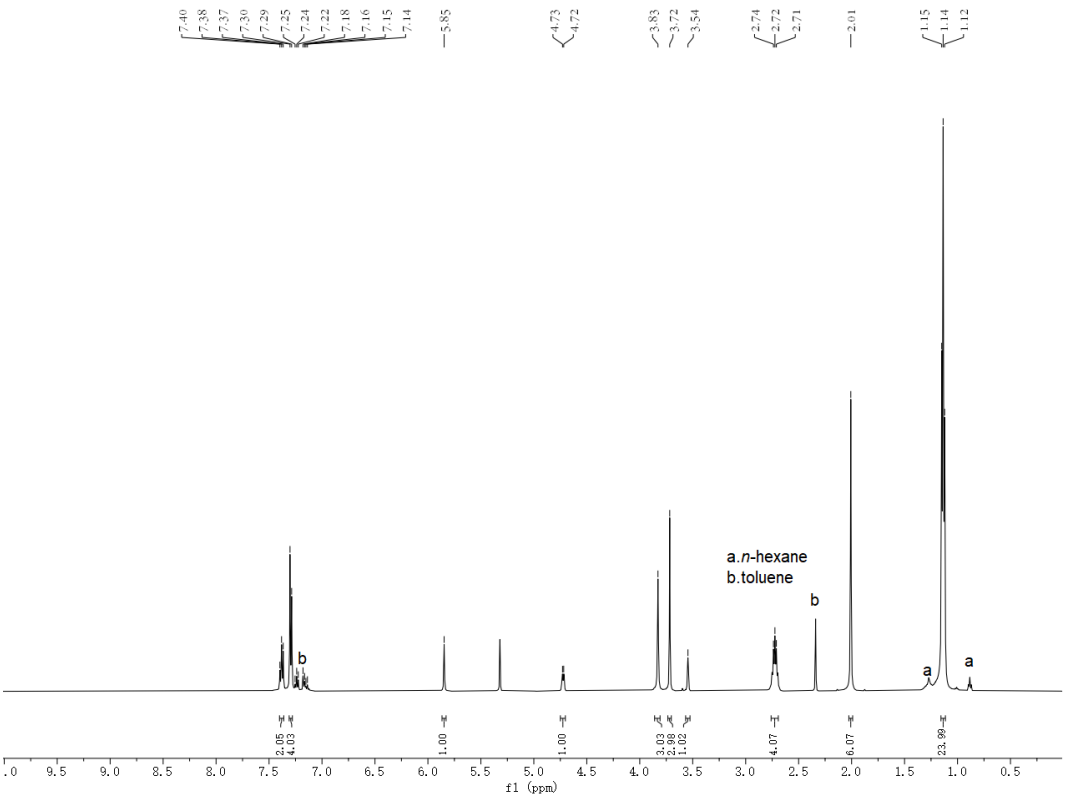


Figure S16. ^{1}H NMR spectrum of **3** in CD_2Cl_2

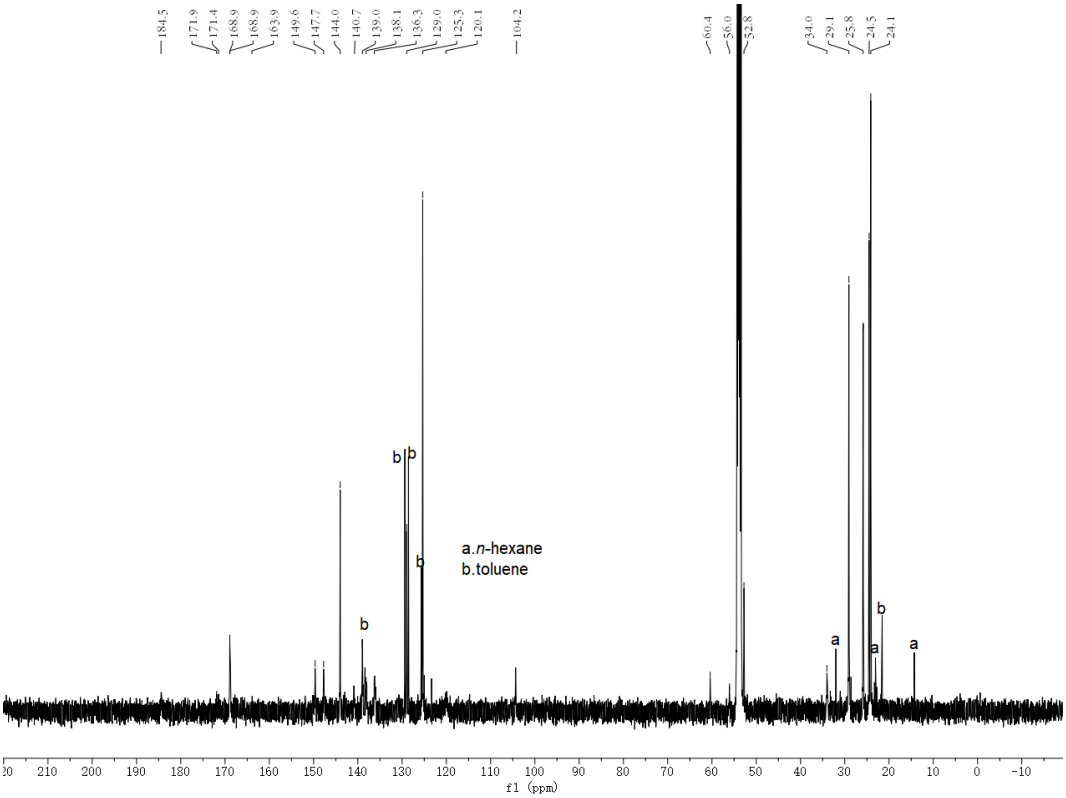


Figure S17. ^{13}C NMR spectrum of **3** in CD_2Cl_2

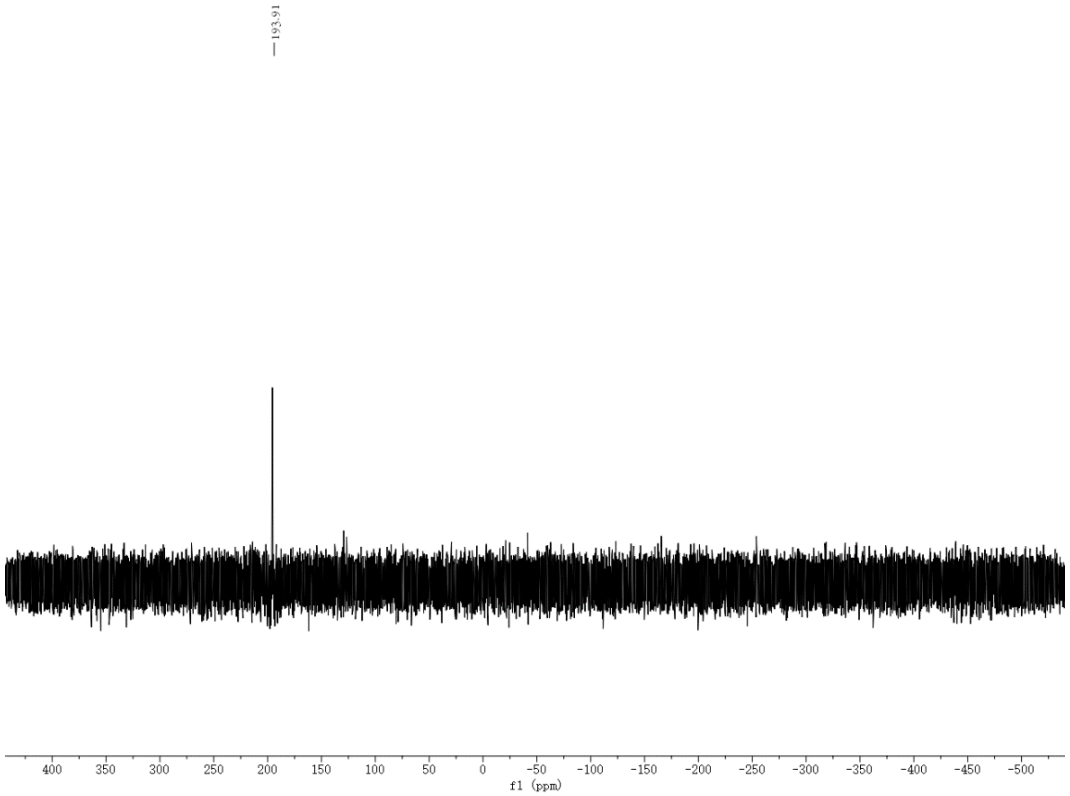


Figure S18. ^{31}P NMR spectrum of **3** in CD_2Cl_2

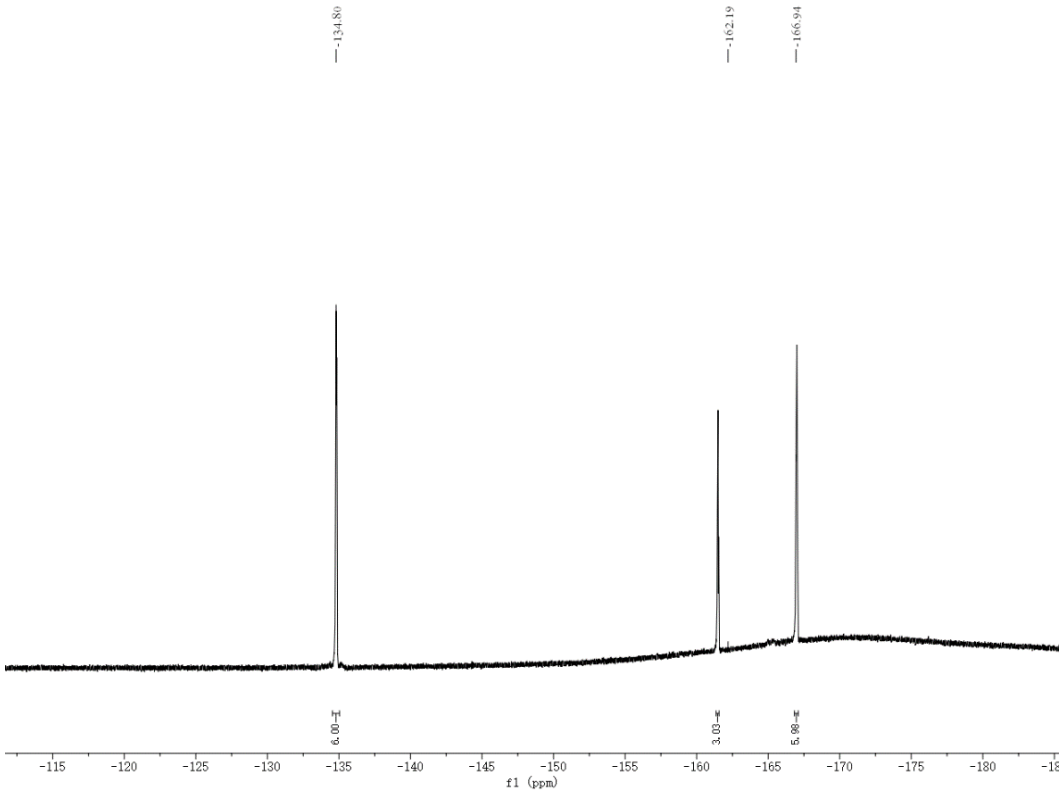


Figure S19. ^{19}F NMR spectrum of **3** in CD_2Cl_2

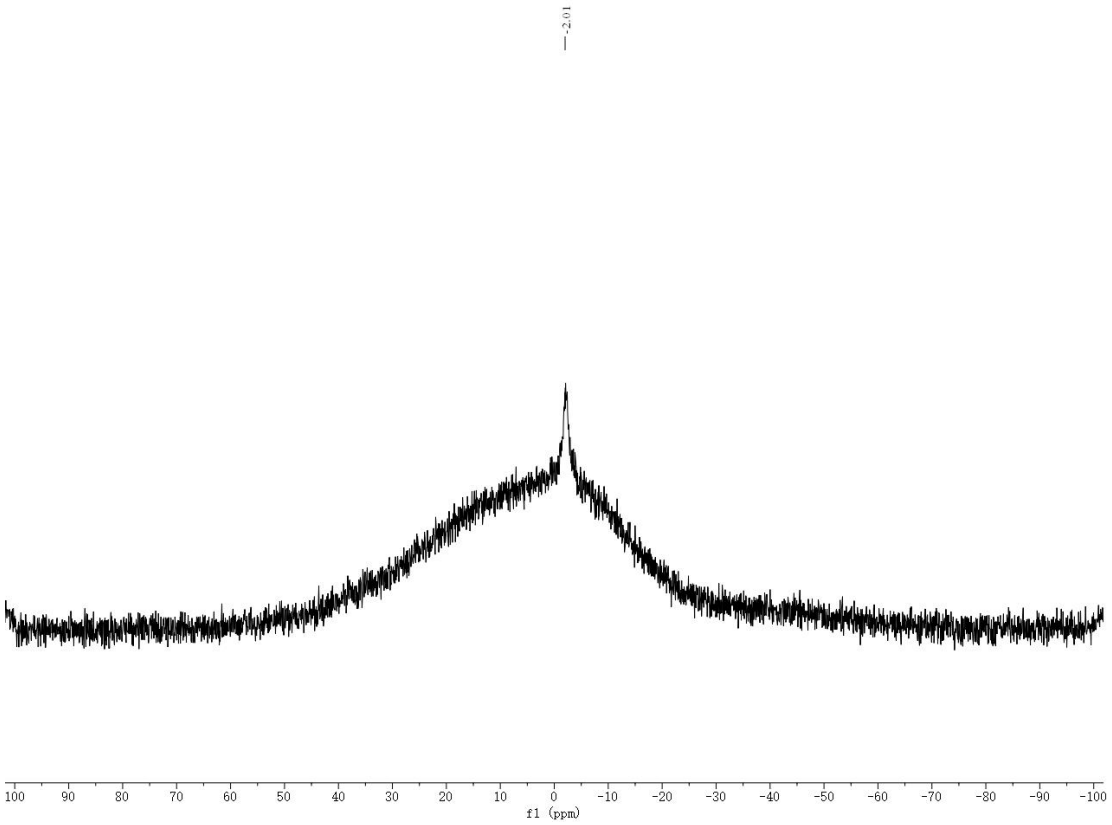


Figure S20. ^{11}B NMR spectrum of **3** in CD_2Cl_2

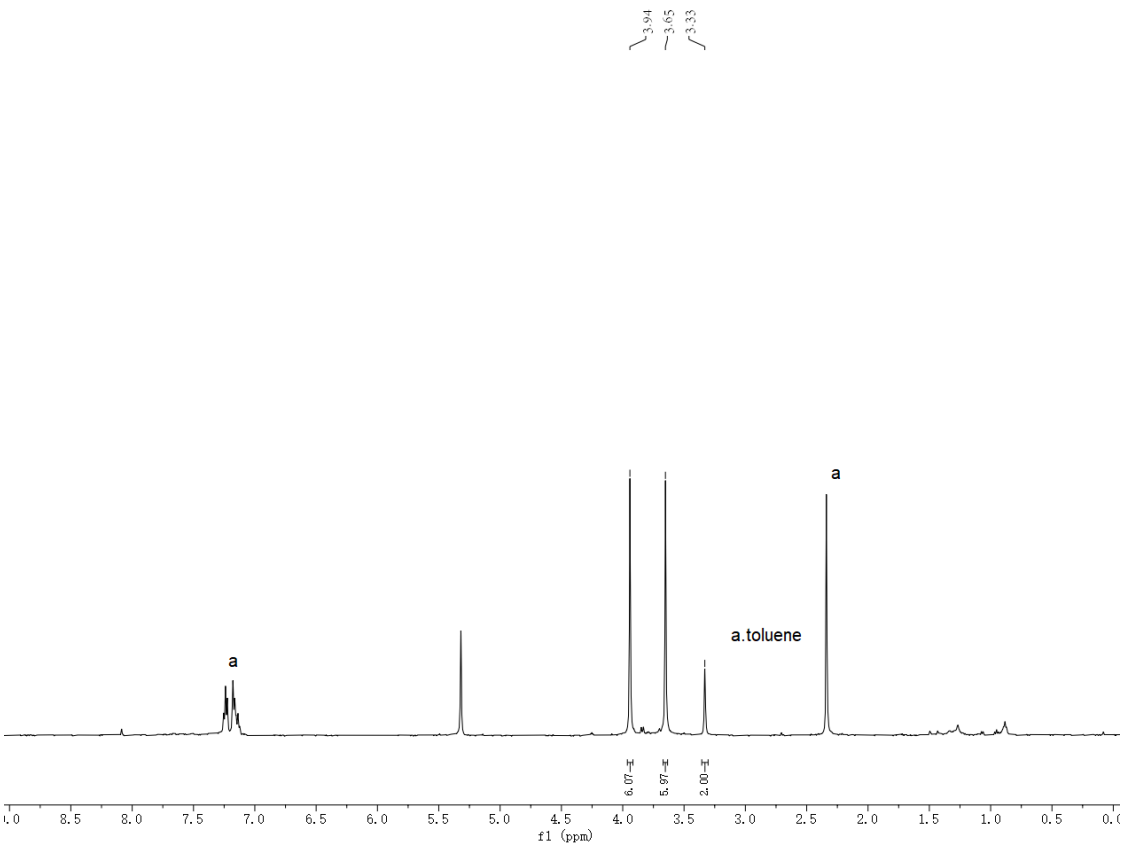


Figure S21. ^{1}H NMR spectrum of **4** in CD_2Cl_2

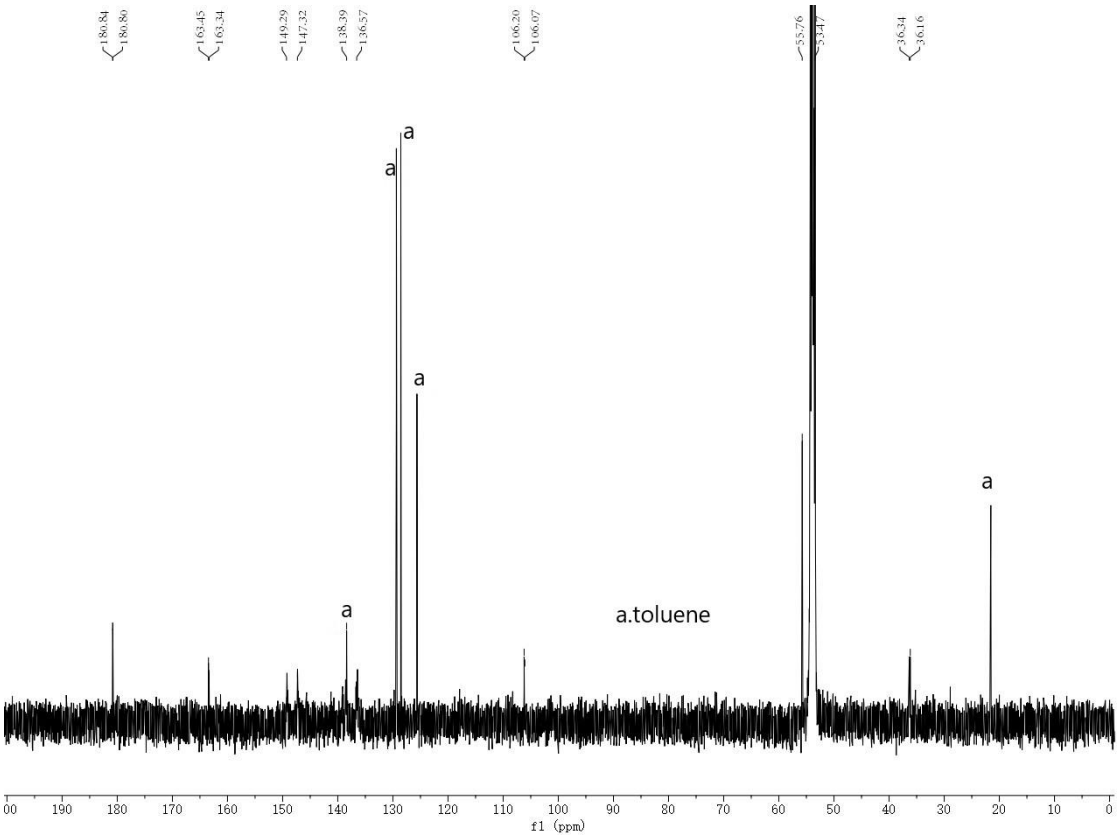


Figure S22. ^{13}C NMR spectrum of **4** in CD_2Cl_2

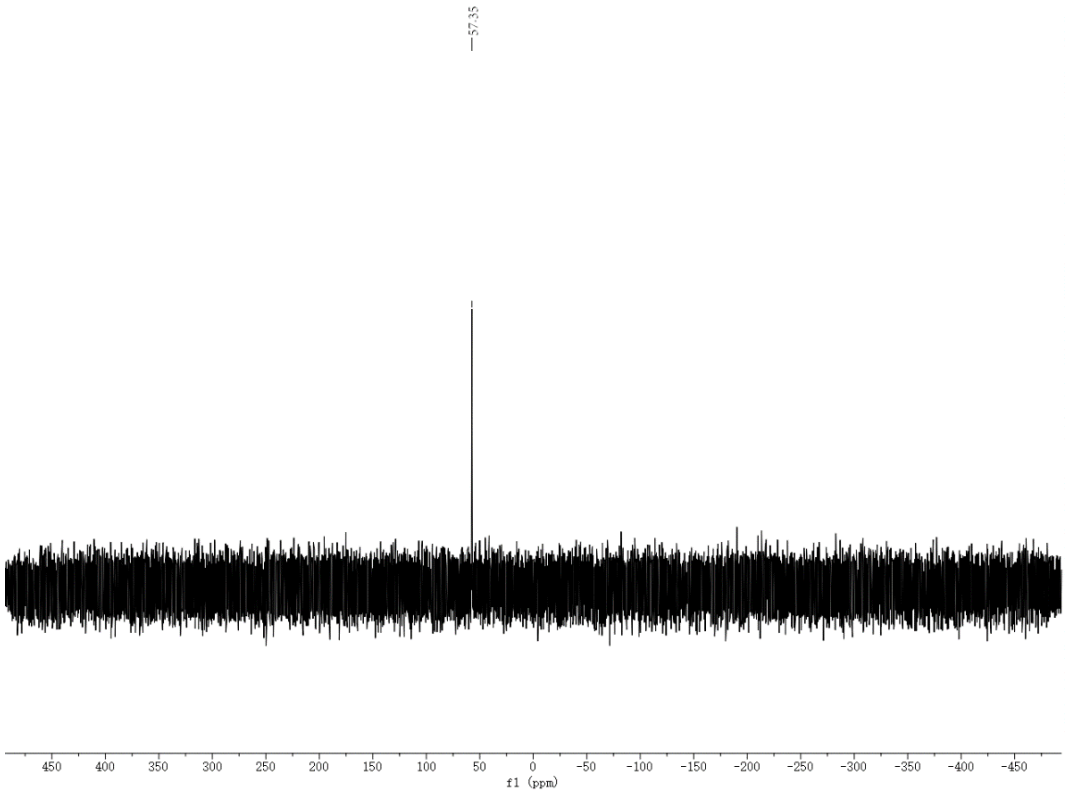


Figure S23. ^{31}P NMR spectrum of **4** in CD_2Cl_2

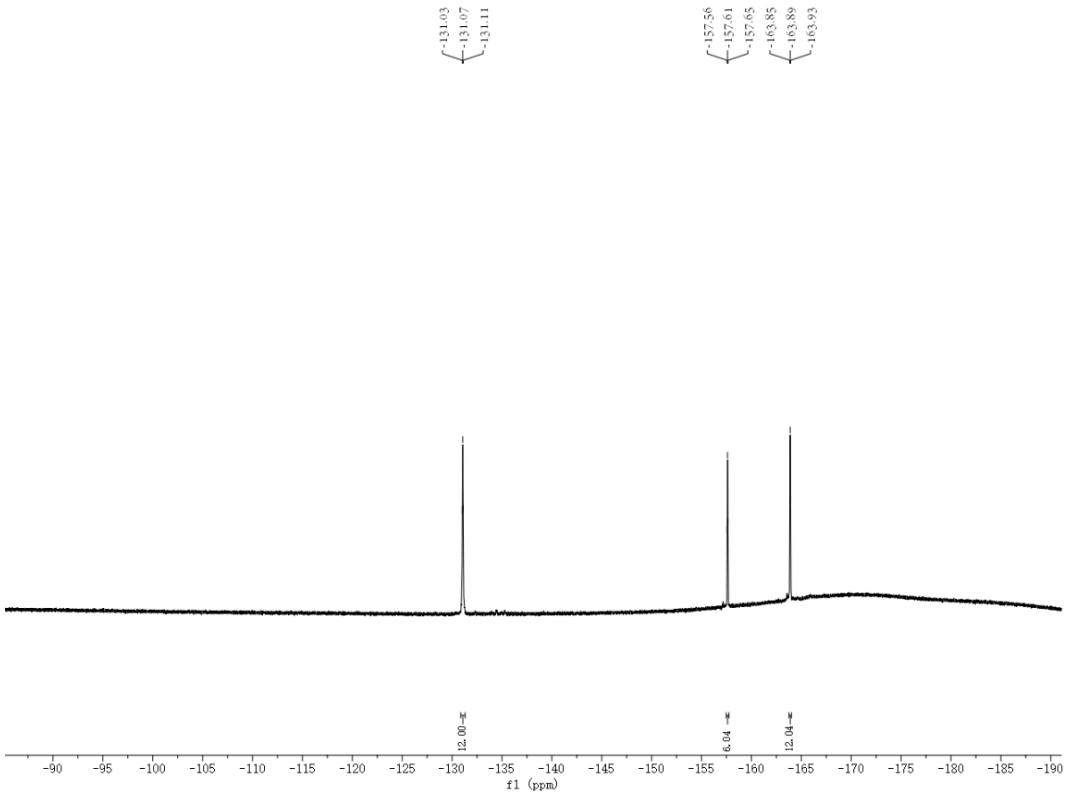


Figure S24. ^{19}F NMR spectrum of **4** in CD_2Cl_2

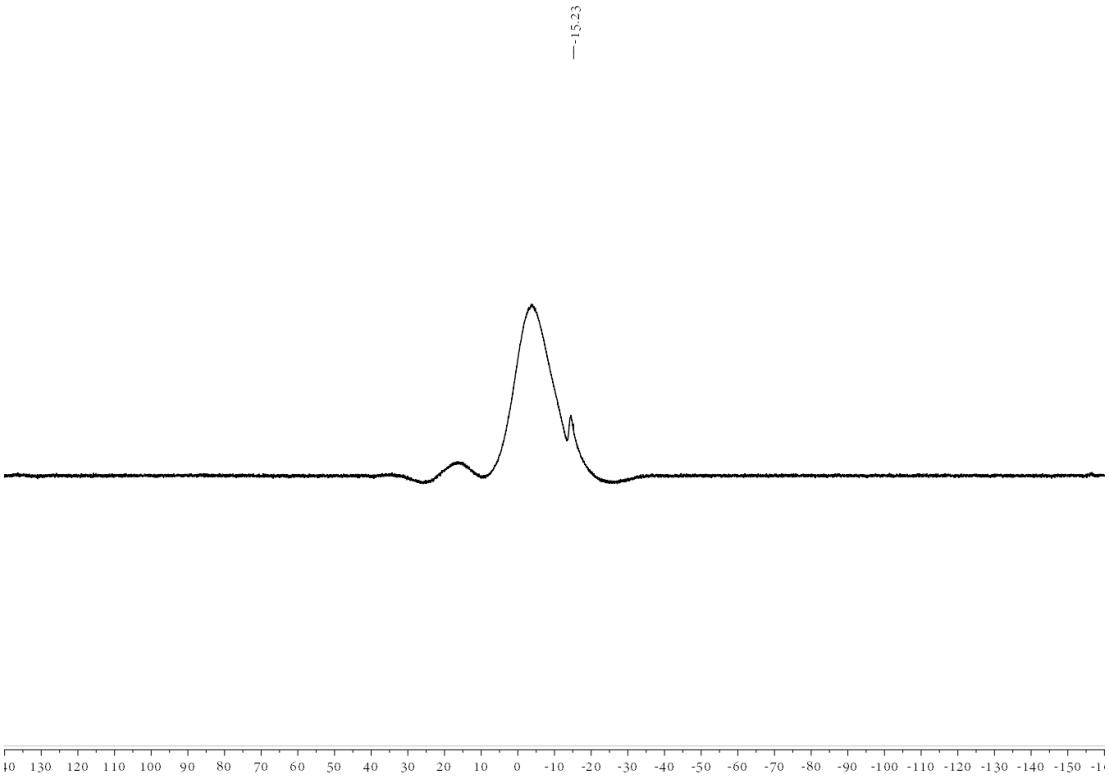


Figure S25. ^{11}B NMR spectrum of **4** in CD_2Cl_2

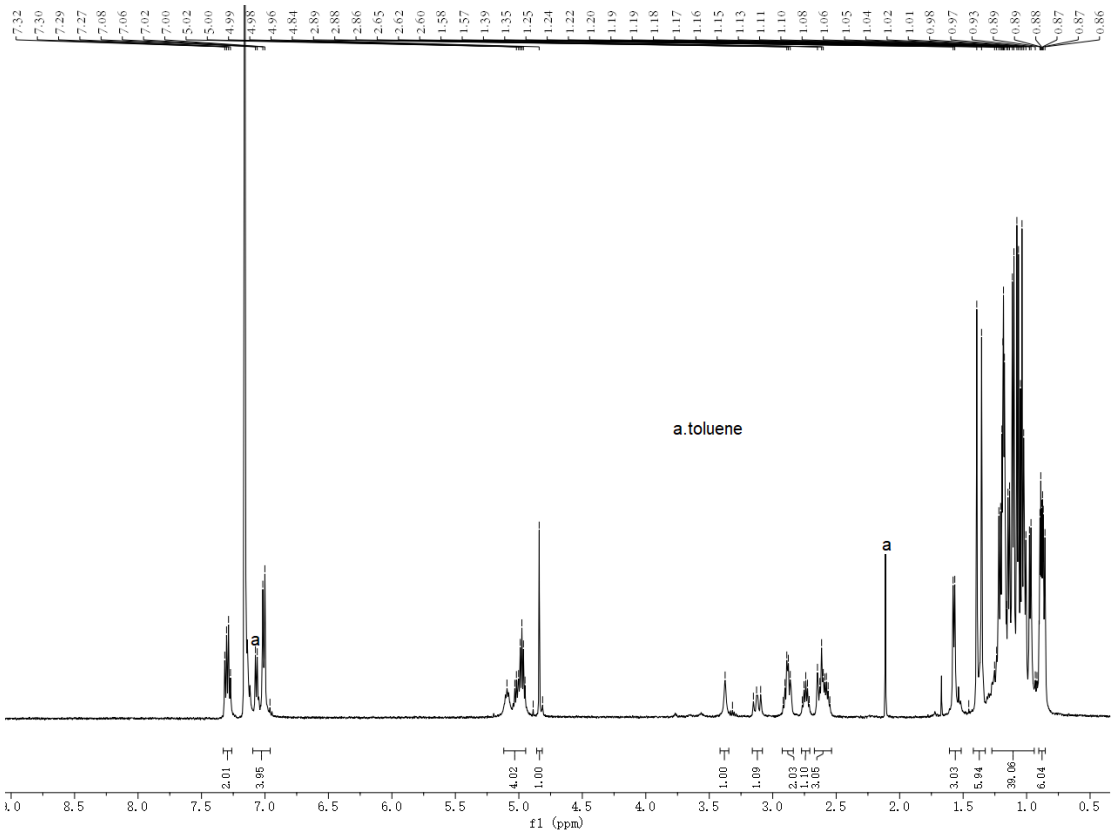


Figure S26. ^{1}H NMR spectrum of **5** in C_6D_6

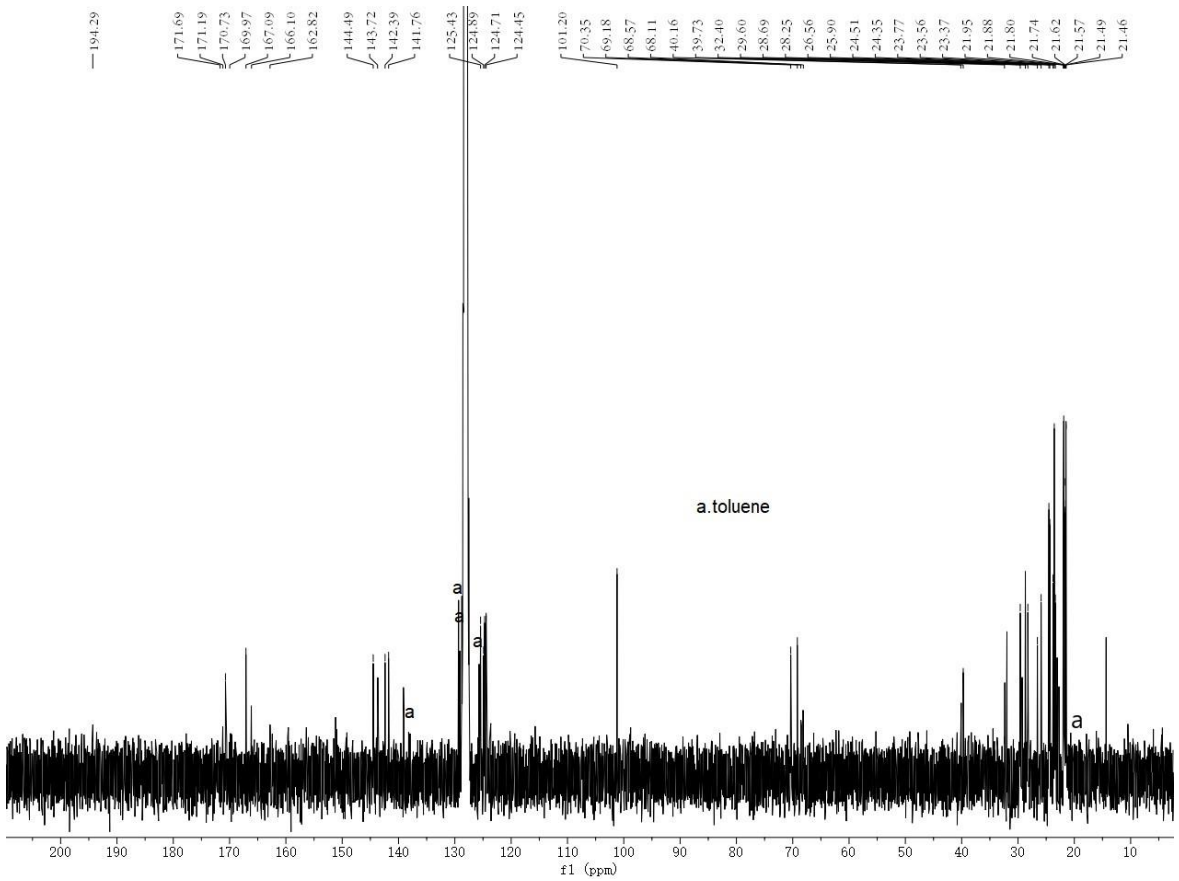


Figure S27. ^{13}C NMR spectrum of **5** in C_6D_6

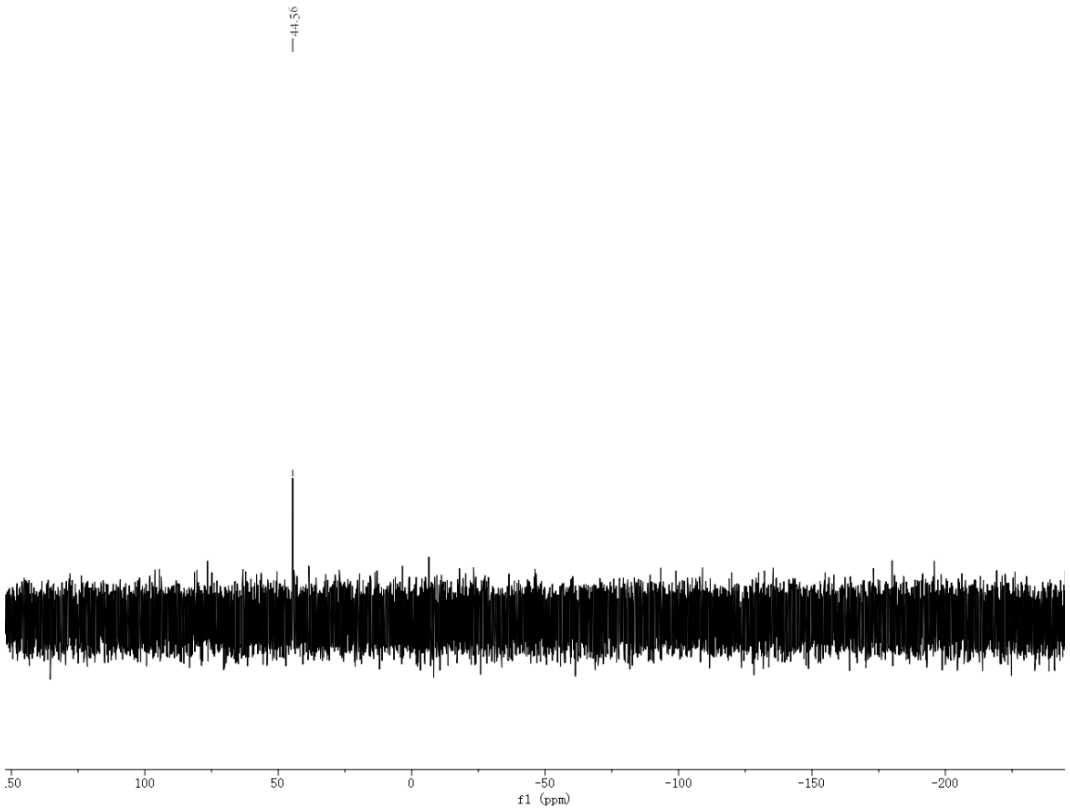


Figure S28. ^{31}P NMR spectrum of **5** in C_6D_6

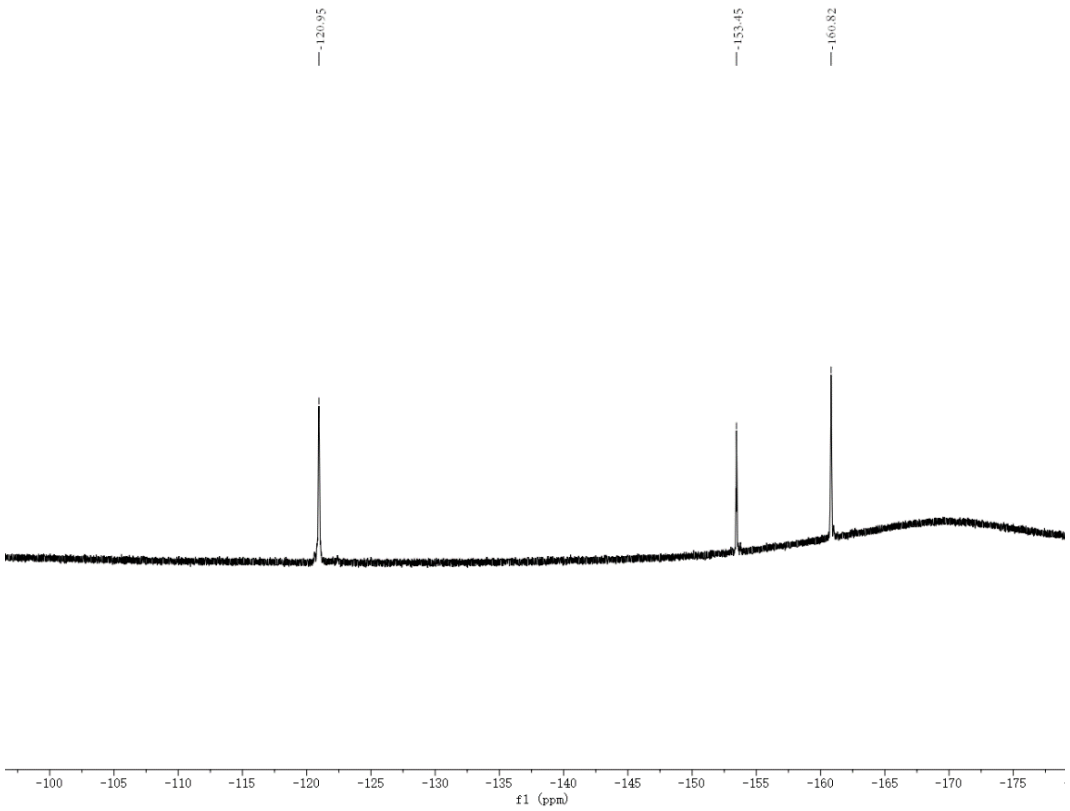


Figure S29. ^{19}F NMR spectrum of **5** in C_6D_6

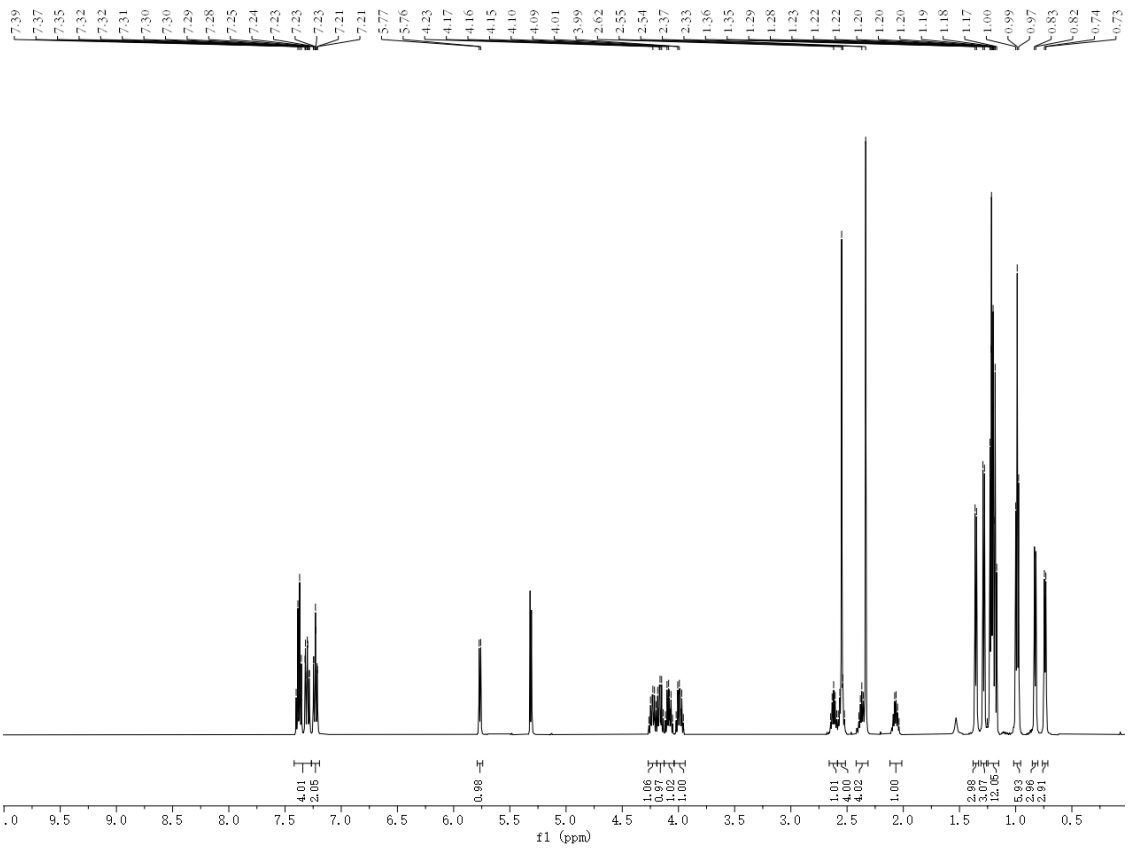


Figure S30. ^{1}H NMR spectrum of **6** in CD_2Cl_2

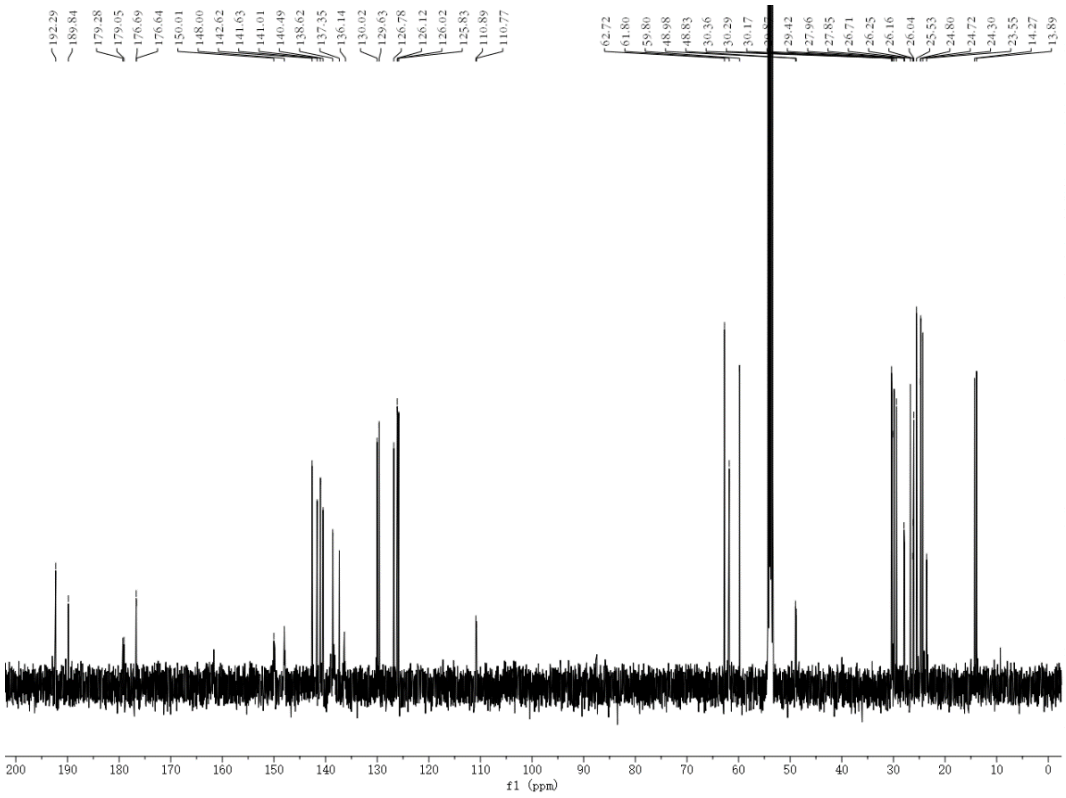


Figure S31. ^{13}C NMR spectrum of **6** in CD_2Cl_2

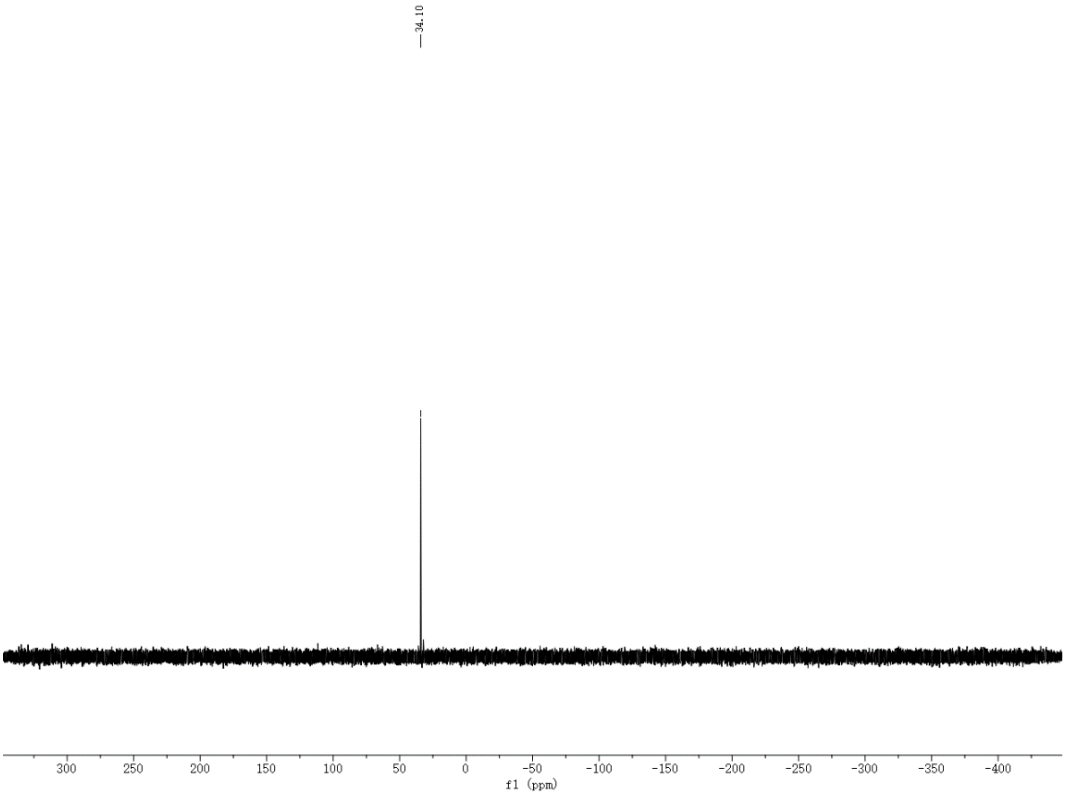


Figure S32. ^{31}P NMR spectrum of **6** in CD_2Cl_2

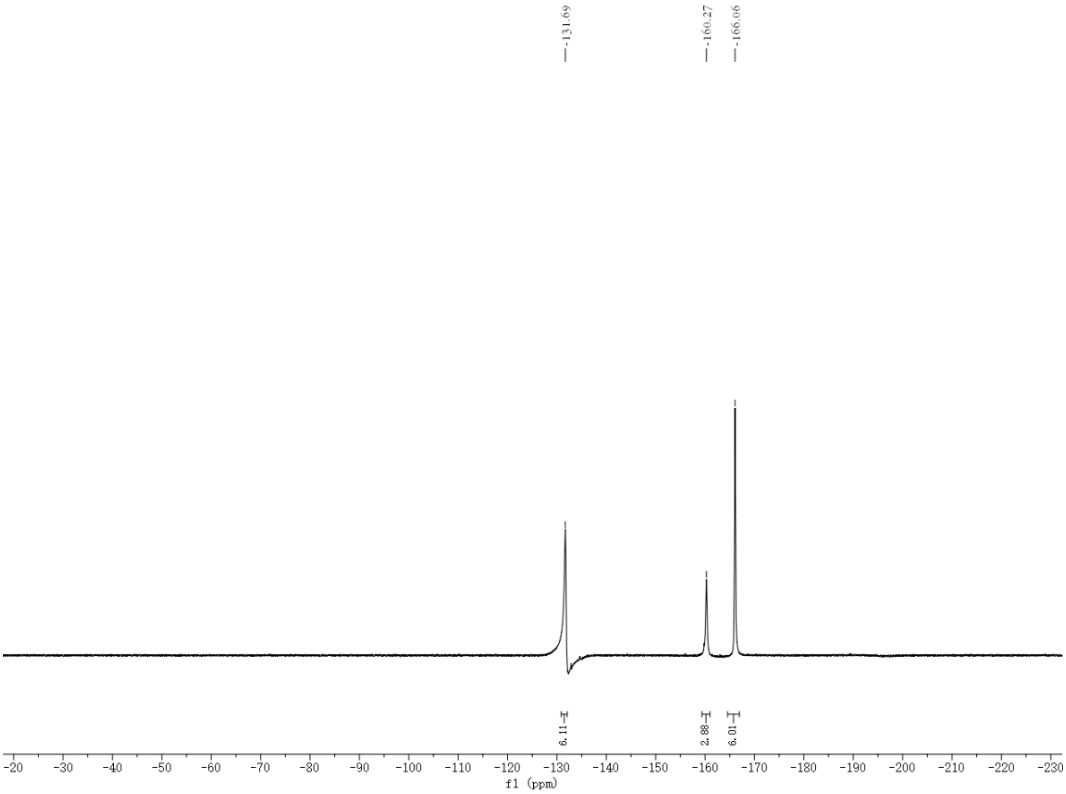


Figure S33. ^{19}F NMR spectrum of **6** in CD_2Cl_2

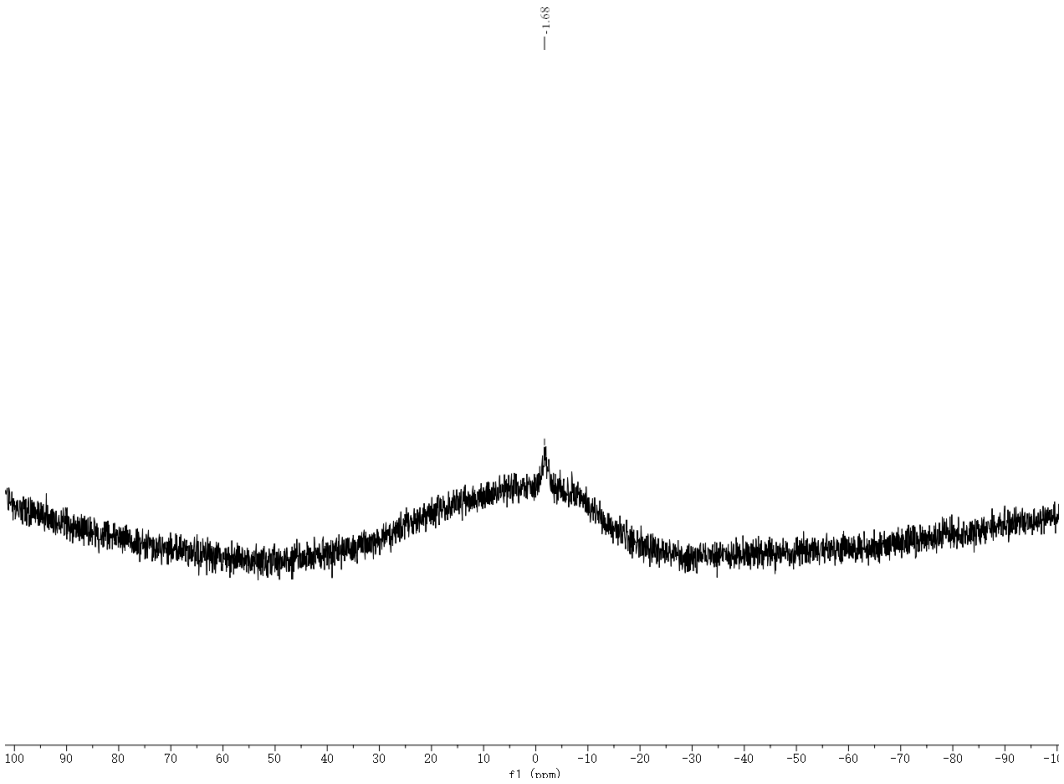


Figure S34. ^{11}B NMR spectrum of **6** in CD_2Cl_2

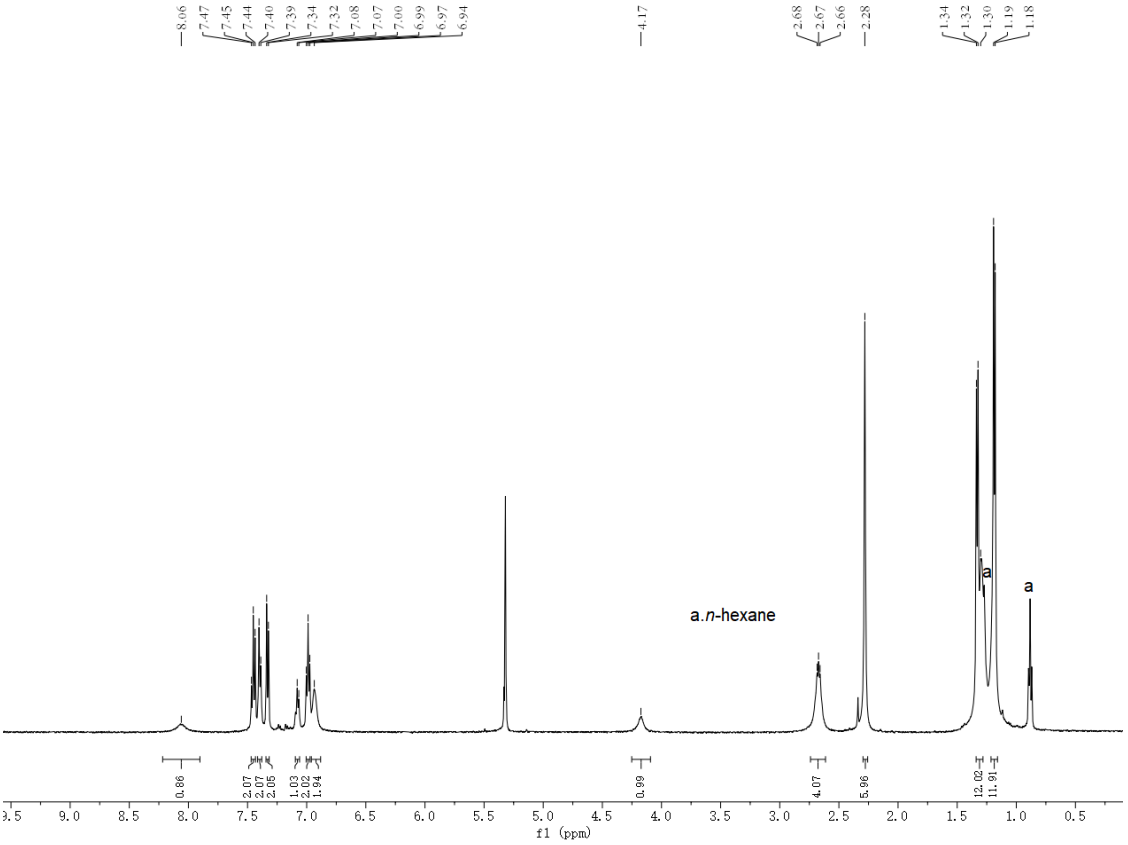


Figure S35. ^{1}H NMR spectrum of **7** in CD_2Cl_2

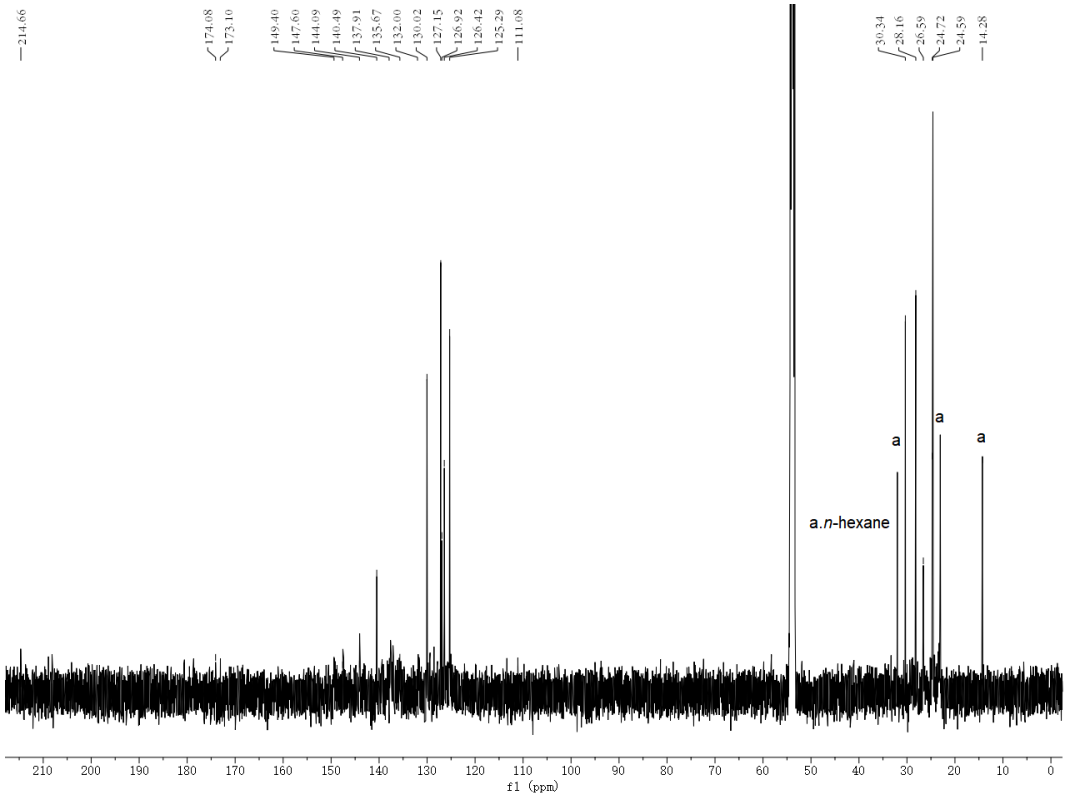


Figure S36. ^{13}C NMR spectrum of **7** in CD_2Cl_2

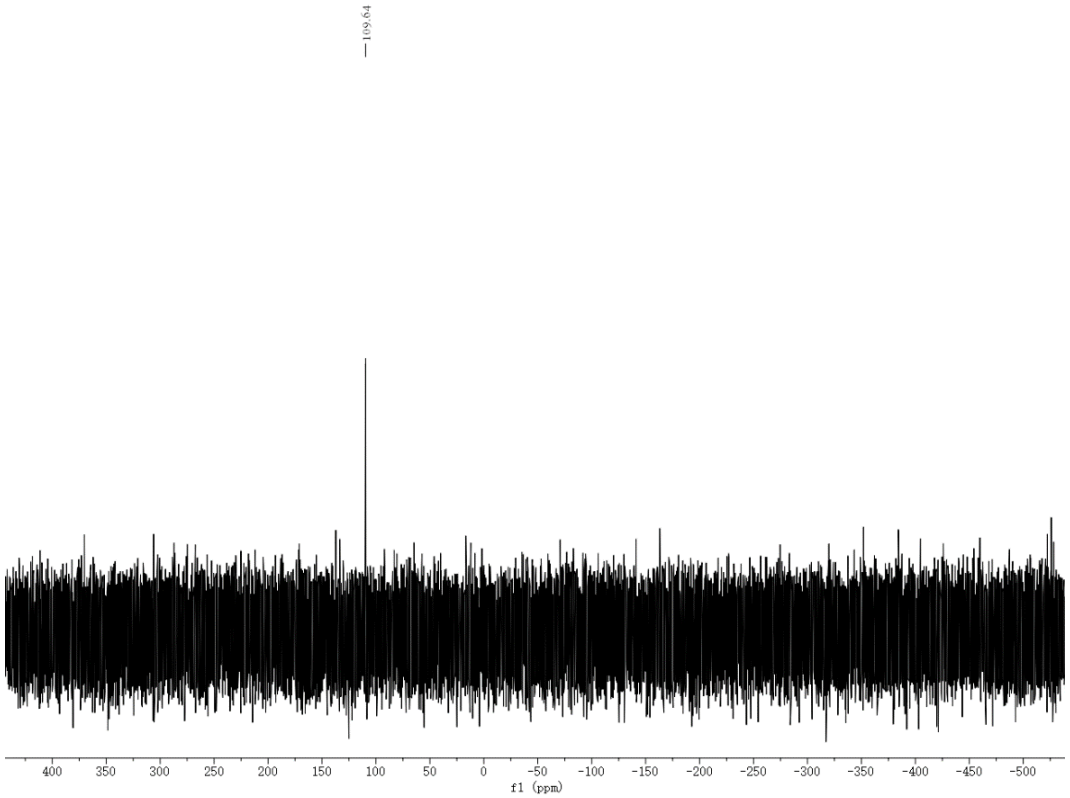


Figure S37. ^{31}P NMR spectrum of **7** in CD_2Cl_2

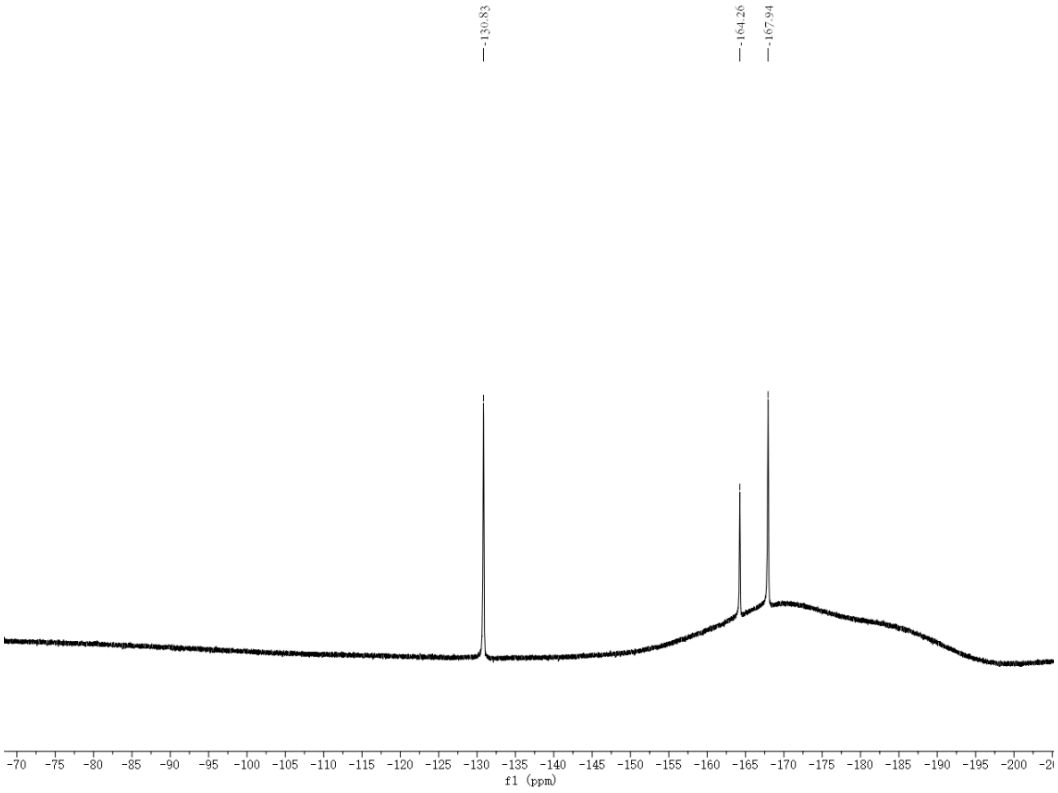


Figure S38. ^{19}F NMR spectrum of **7** in CD_2Cl_2

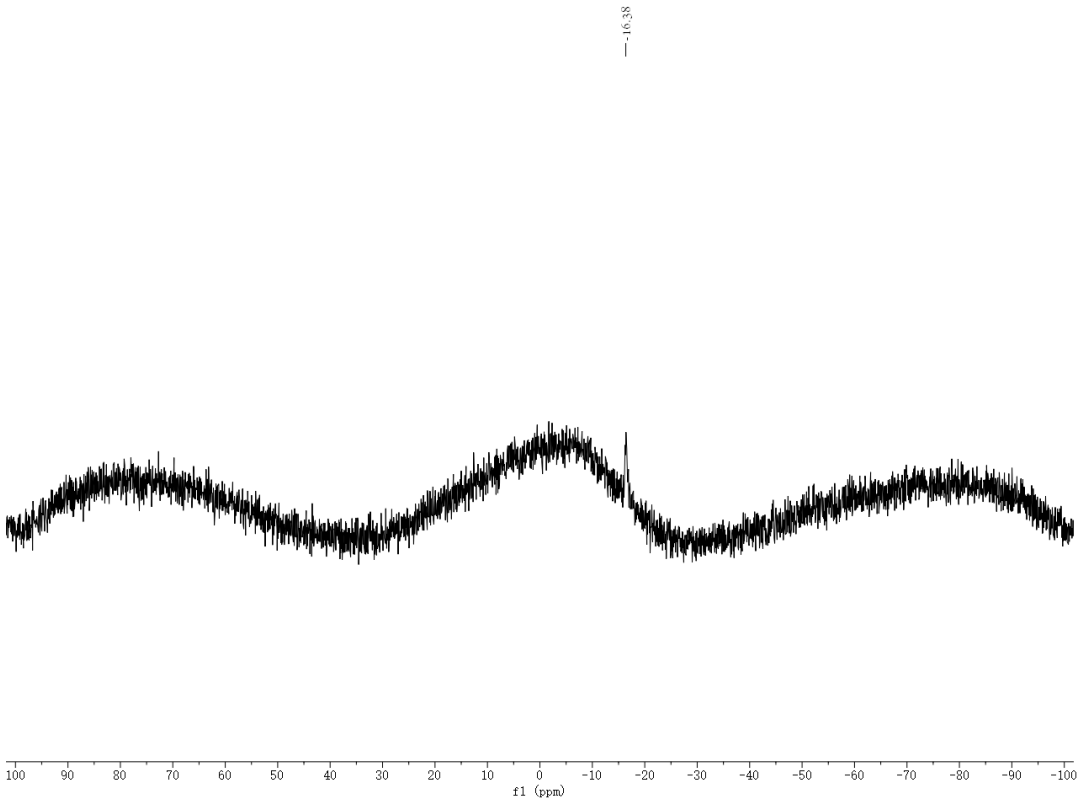


Figure S39. ^{11}B NMR spectrum of **7** in CD_2Cl_2

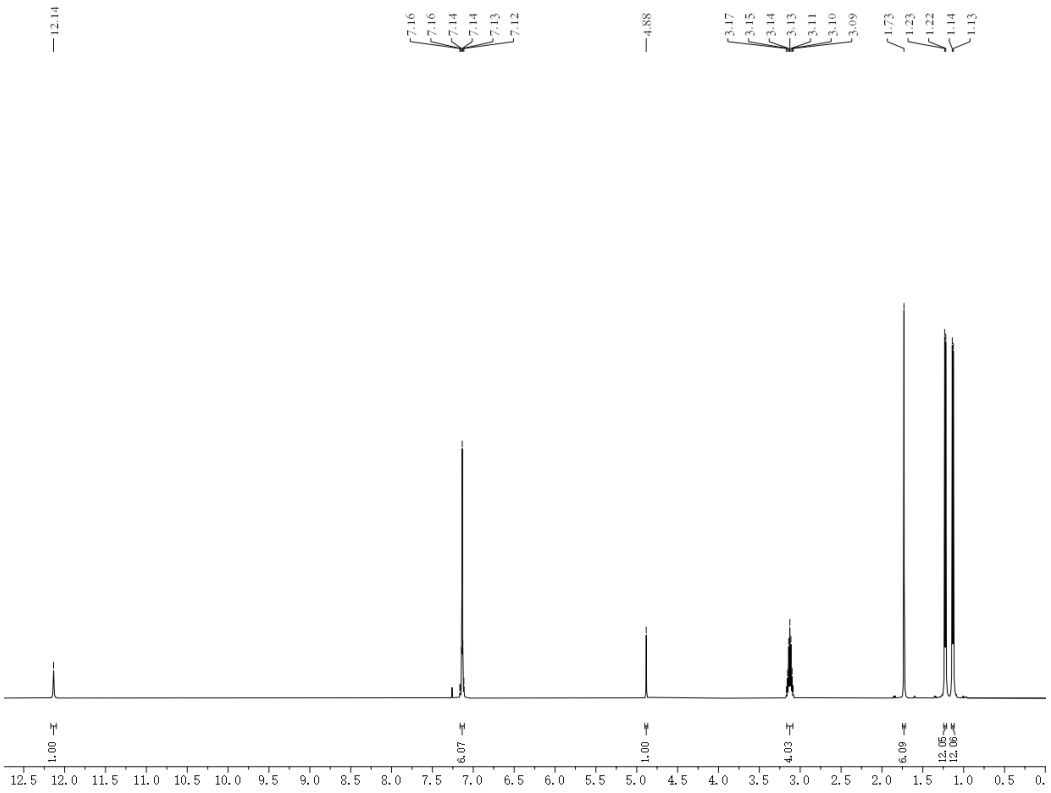


Figure S40. ^{11}H NMR spectrum ($CDCl_3$) of the NacnacH isolated from the reaction of **1** and dimethyl maleate at room temperature

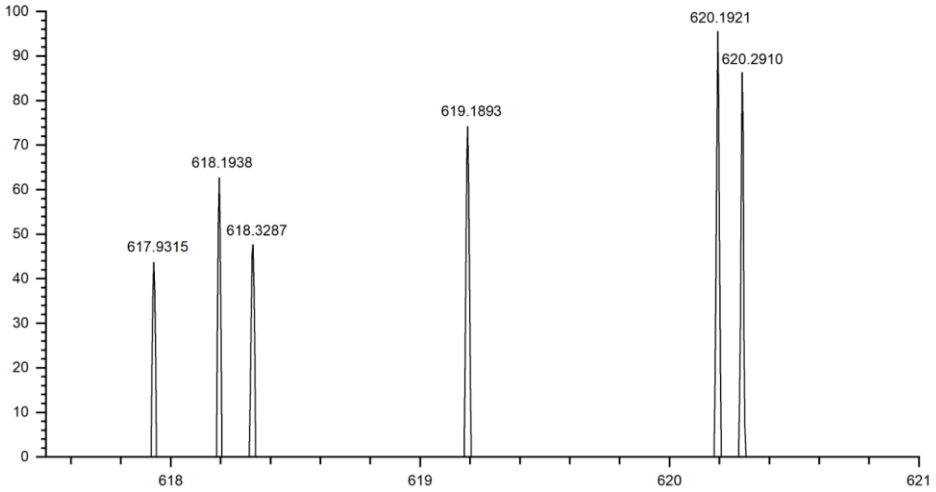


Figure S41. HRMS spectrum of **1**

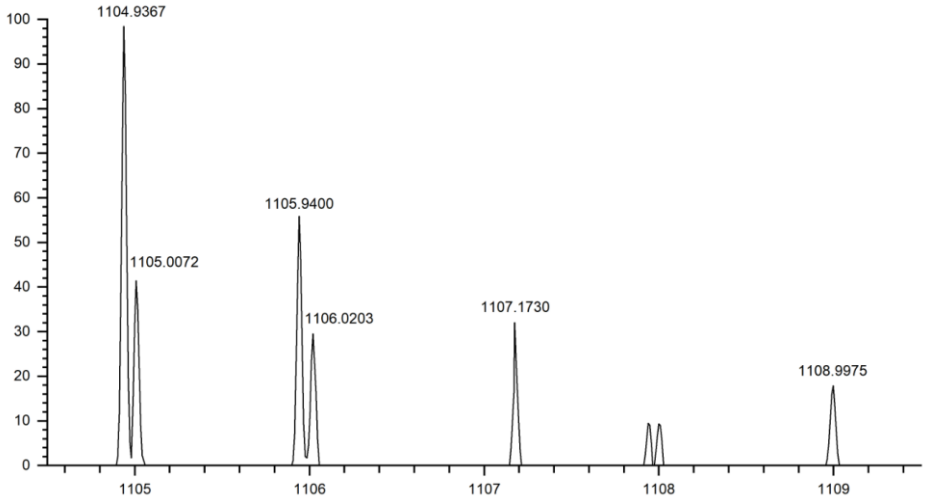


Figure S42. HRMS spectrum of **2**

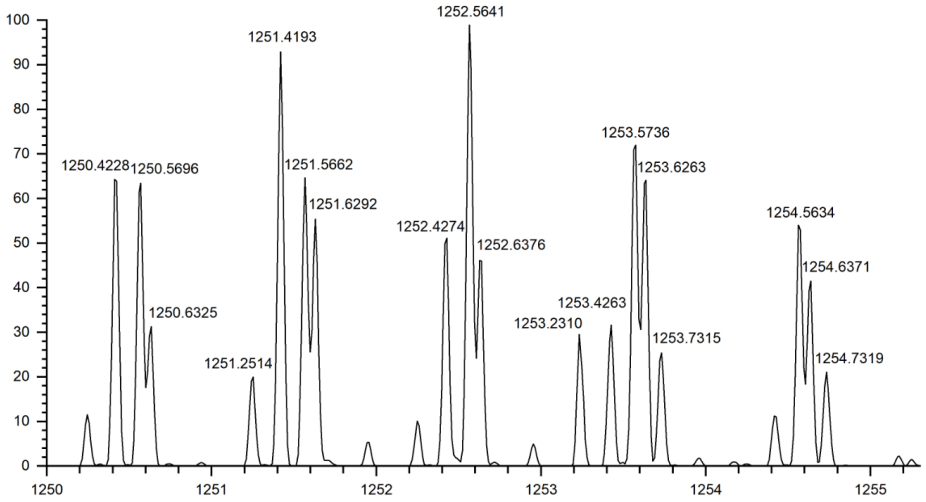


Figure S43. HRMS spectrum of **3**

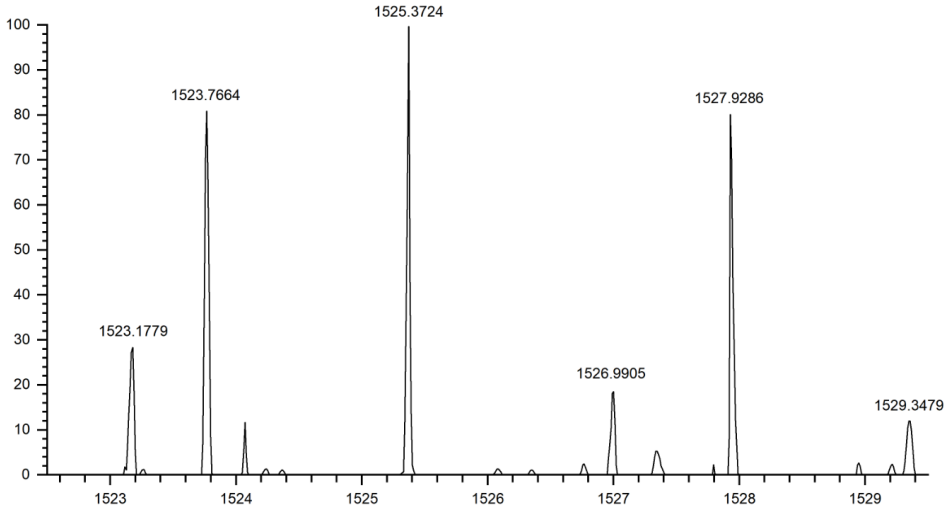


Figure S44. HRMS spectrum of **5**

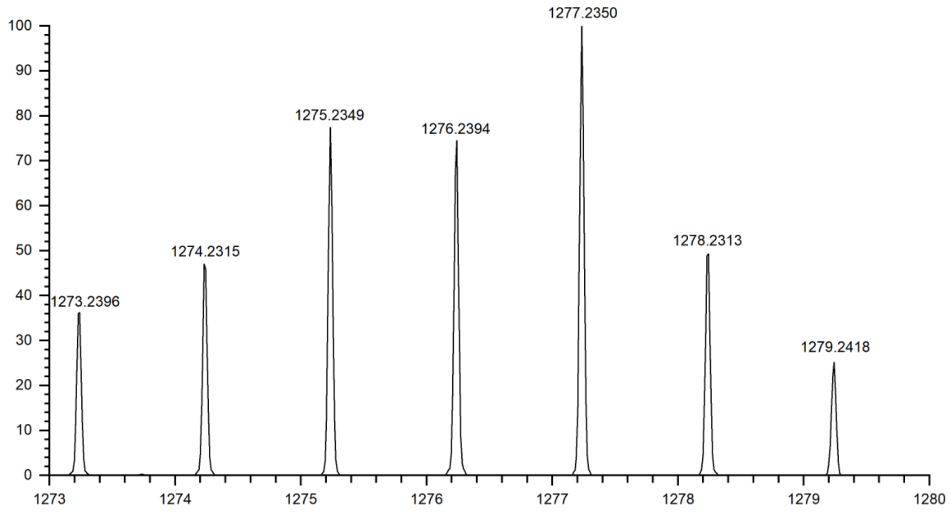


Figure S45. HRMS spectrum of **6**

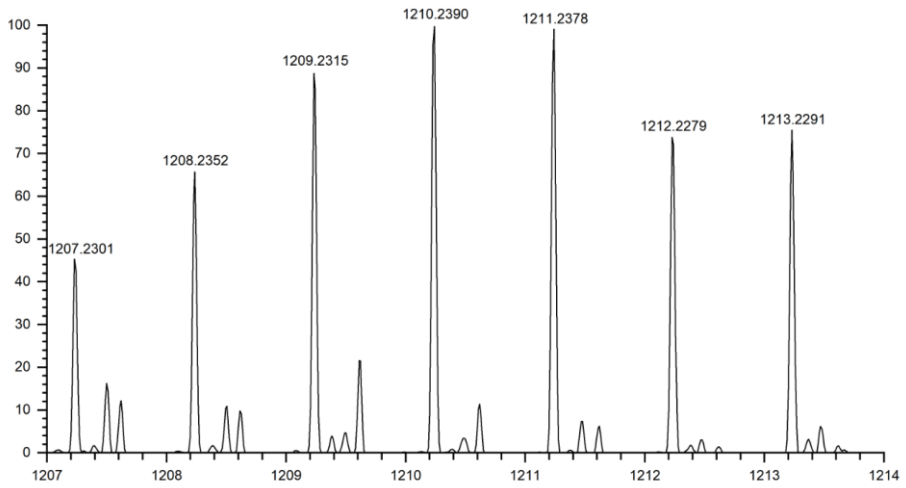


Figure S46. HRMS spectrum of **7**

Reference

[S1] Y. Ding, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, P. P. Power, *Organometallics* **2001**, *20*, 1190-1194.

[S2] D. Heift, Z. Benkő, H. Grützmacher, *Dalton Trans.* **2014**, *43*, 831-840.

[S3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

[S4] G. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3-8.

[S5] G. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112-122.