Supporting Information

Syntheses, characterizations and catalytic properties of three zinc complexes and one lithium compound chelated by β-diketiminate ligands

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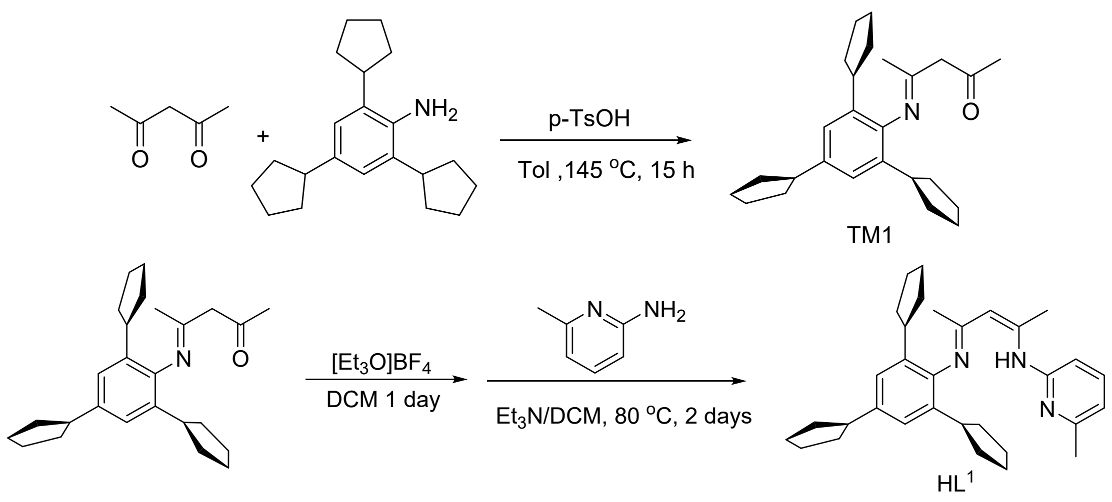
Content

1. General methods

All reactions were carried out in a Vigor glove box filled with N_2 to isolate moisture and oxygen. $ZnEt_2$ and ^nBuLi were purchased from J&K Scientific and directly used as received. Tetrahydrofuran, n-hexane, and toluene were dried with KOH in advance and then were distilled under nitrogen protection using benzophenone as indicator. Collected distillates and added 4 Å molecular sieves for storage. The deuterogenation reagents were dried overnight with CaH_2 and then were distilled under vacuum. NMR spectra were determined on Bruker Avance-III 400 MHz, Agilent 400 MHz instruments and Bruker Avance-III 600 MHz NMR spectrometer. Elemental analyses for carbon, hydrogen and nitrogen were obtained on PerkinElmer 2400 analyzer.

2. Syntheses of the ligands

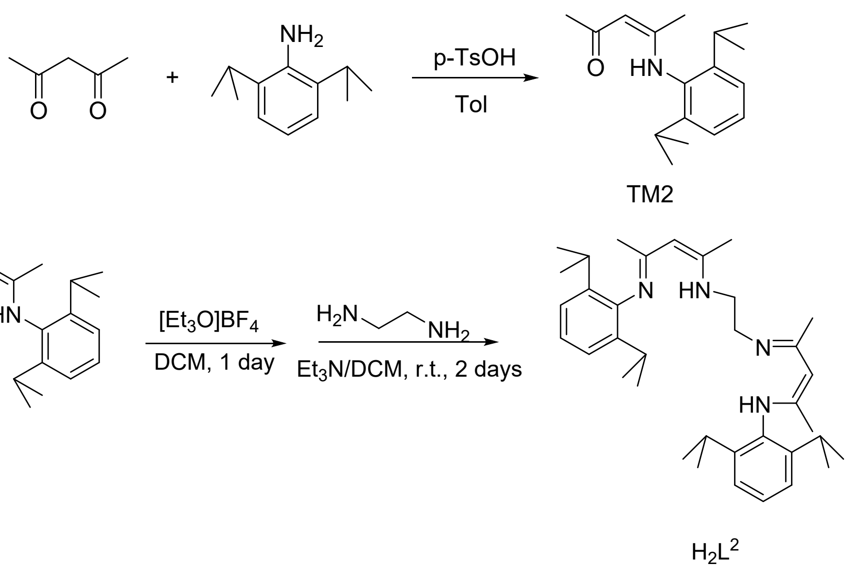
Synthesis of HL^1



Scheme S1. Synthesis of HL^1

A mixture of 2, 4, 6-tricyclopentyl aniline (23.31 g, 78.3 mmol), acetylacetone (7.84 g, 78.3 mmol), and *p*-toluenesulfonic acid (0.14 g, 1 mol%) was placed in a round bottom flask (250 mL). The mixture was dissolved in toluene, and refluxed at 145 °C for 15 hours. After which time, toluene was removed by rotary evaporation to obtain a brown oily substance. The brown oily substance was recrystallized in anhydrous ethanol to obtain 4-((2,4,6-tricyclopentylphenyl)imino)pentan-2-one as a light yellow powder (TM1). Yield: 17.38 g (58.5 %). In a Vigor glove box, 4-((2,4,6-tricyclopentylphenyl)imino)pentan-2-one (3.79 g, 10 mmol), triethyloxyonium tetrafluoroboric acid (1.90 g, 10 mmol), ultra-dry dichloromethane (10 mL) were added in a 100 mL Schlenk flask. The Schlenk flask was removed from the glove box and allowed to stir at room temperature for one day. Then three droppers of triethylamine were added in the Schlenk flask. The Schlenk flask was continuously stirred at 80 °C for another two days. The volatiles were removed and the solid was dissolved in saturated sodium hydroxide solution. The resultant mixture was extract with dichloromethane (50 mL × 3). The organic layers were combined, dried with sodium sulfate and then the solvent was removed under vacuum. The crude product was recrystallized in ethyl acetate to obtain the pure product as a yellow powder. Yield: 2.97 g (63.2 %). Anal. Calcd for $C_{32}H_{43}N_3$: C, 81.06; H, 9.46; N, 8.47. Found: C, 81.15; H, 9.65; N, 8.95.

Synthesis of H_2L^2

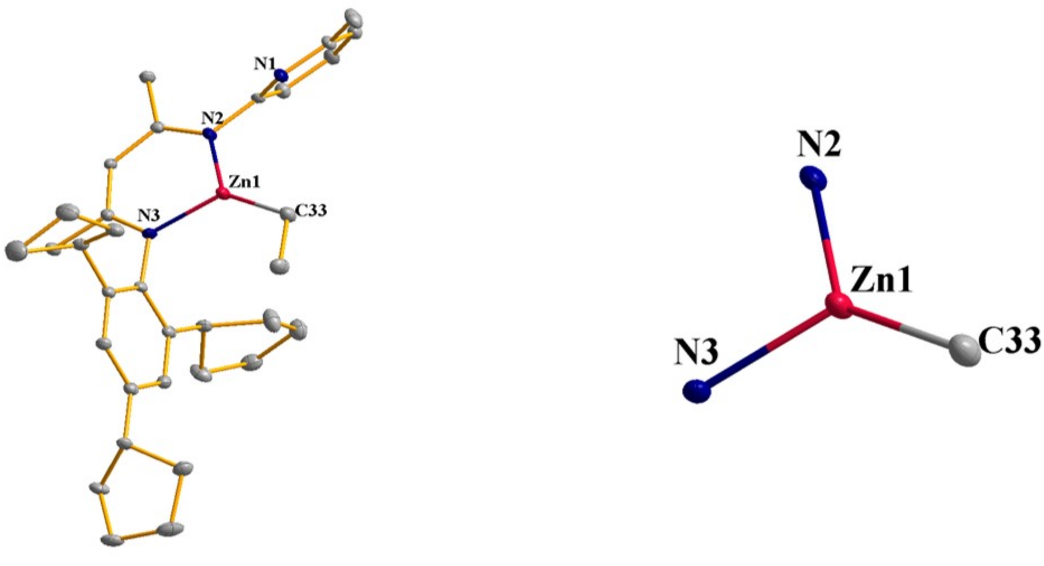


Scheme S2. Synthesis of H_2L^2

To a solution of 2-Hydroxy-4-(2,6-diisopropylphenyl)imino-2-pentene (5.184 g, 20 mmol) in dichloromethane (10 mL), was added the solution of triethyloxonium tetrafluoroborate (3.8 g, 20 mmol) in dichloromethane under a nitrogen atmosphere.

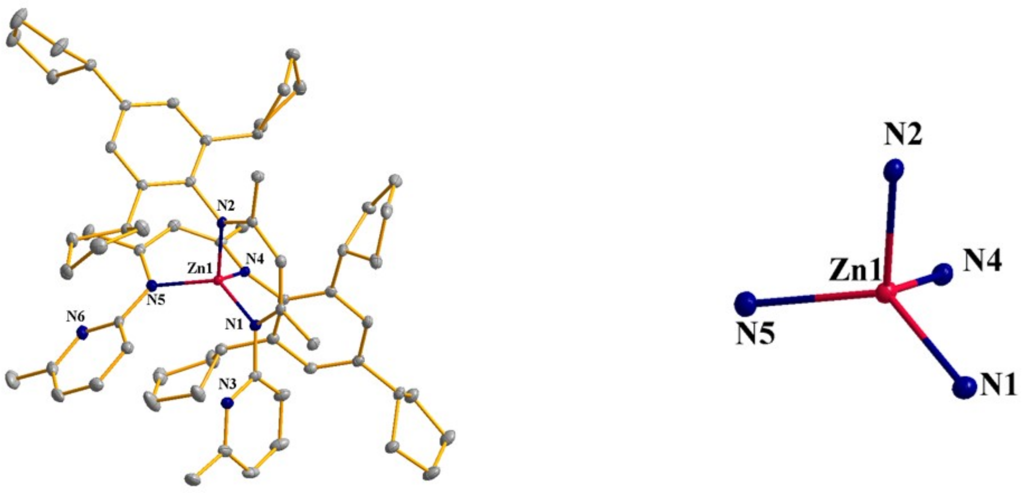
The mixture was stirred at room temperature for 1 day. Then ethane-1,2-diamine (0.60 g 10 mmol) and triethylamine were added. The resulted mixture was continuously stirred at room temperature for another 2 days. Volatiles were removed under vacuum to give an orange oil. The product was obtained by recrystallizing yellow oil in ethanol at -15 °C overnight. Yield: 3.16 g (58 %). Anal. Calcd for $C_{36}H_{54}N_4$: C, 79.65; H, 10.03; N, 10.32. Found: C, 79.82; H, 10.09; N, 10.31.

3. Structures and crystallographic data of the compounds



(a) (b)

Figure S1. (a) Molecular structure of **1** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Core structure of complex **1.**



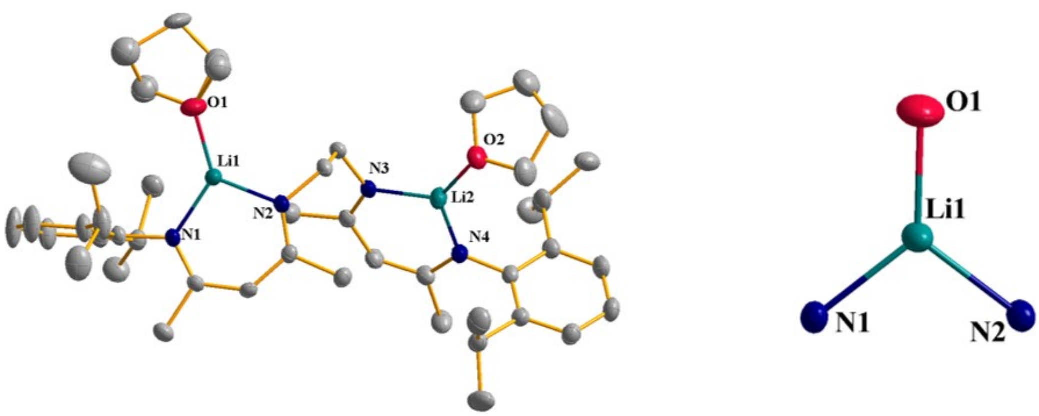
(a) (b)

Figure S2. (a) Molecular structure of **2** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Core structure of complex **2.**

Table S1. Crystallographic Data and Structure Refinement for Compounds 1 and 2

	compound **1**	compound **2**
Empirical formula	$C_{34}H_{47}N_3Zn$	$C_{64}H_{84}N_6Zn$
Formula weight	563.11	1002.74
Temperature [K]	120(2)	120(2)
Crystal system	triclinic	monoclinic
Space group	*P***Error!**	$P2_1/c$
a/Å	9.7865(5)	22.4873(12)
b/Å	10.9488(6)	10.3091(5)
c/Å	14.5720(7)	23.5539(13)
α/°	87.784(2)	90
β/°	74.010(2)	97.174(2)
γ/°	88.444(2)	90
Volume/Å^3	1499.64(13)	5417.6(5)
Z	2	4
ρ_{calc}/g cm^{-3}	1.247	1.229
μ/mm^{-1}	0.845	0.606
F(000)	604	2160
Crystal size/mm^3	0.20 × 0.20 × 0.10	0.04 × 0.03 × 0.02

Radiation	MoKα (λ = 0.71073)	GaKα (λ = 1.34138)
2Θ range for data collection/°	3.724 to 49.998	6.894 to 107.7
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$	$-27 \leq h \leq 26$, $-12 \leq k \leq 11$, $-28 \leq l \leq 28$
Reflections collected	45444	54230
Independent reflections	5223 [R_{int} = 0.1173]	9897 [R_{int} = 0.0559]
Data/restraints/parameters	5223/0/347	9897/0/654
Goodness−of−fit on F^2	1.074	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.0913	R_1 = 0.0400, wR_2 =0.0983
Final R indexes [all data]	R_1 = 0.0759, wR_2 = 0.1020	R_1= 0.0527, wR_2 = 0.1052
Largest diff. peak/hole / e Å^{-3}	0.533/-0.529	0.407/-0.748



(a) (b)

Figure S3. (a) Molecular structure of **3** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Core structure of complex **3.**

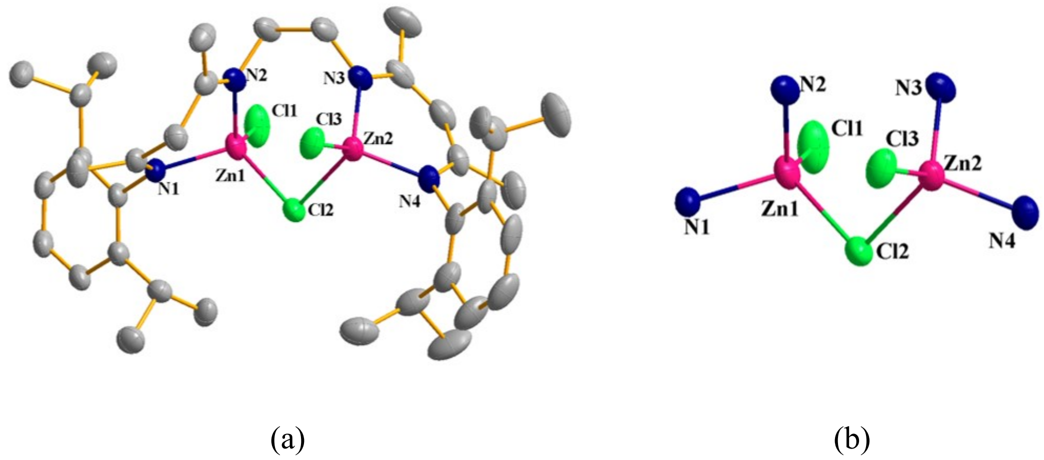


Figure S4. (a) Molecular structure of **4**·Tol from X-ray diffraction. Hydrogen atoms and solvent molecule are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Core structure of complex **4.**

Table S2. Crystallographic Data and Structure Refinement for Compounds 3 and 4·Tol

	compound **3**	compound **4·Tol**
Empirical formula	$C_{44}H_{68}Li_2N_4O_2$	$C_{43}H_{61}Cl_3N_4Zn_2$
Formula weight	698.90	871.04
Temperature [K]	296.15	120.00
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	13.8703(9)	32.1803(15)
b/Å	32.080(2)	12.7041(5)
c/Å	9.7935(7)	23.3535(10)
α/°	90	90
β/°	93.450(2)	110.407(3)
γ/°	90	90
Volume/Å^3	4349.8(5)	8948.2(7)
Z	4	8
ρ_{calc}g/cm^3	1.067	1.293

μ/mm^{-1}	0.064	2.041
F(000)	1528	3664
Crystal size/mm^3	0.22 × 0.08 × 0.04	0.02 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)	GaKα (λ = 1.34138)
2Θ range for data collection/°	4.814 to 55.034	5.098 to 108.37
Index ranges	$-17 \leq h \leq 18$, $-38 \leq k \leq 41$, $-12 \leq l \leq 12$	$-38 \leq h \leq 38$, $-15 \leq k \leq 15$, $-28 \leq l \leq 28$
Reflections collected	54099	84405
Independent reflections	9882 [R_{int} = 0.1136]	8265 [R_{int} = 0.0996]
Data/restraints/parameters	9882/164/531	8265/393/546
Goodness−of−fit on F^2	1.018	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0787, wR_2 = 0.1770	R_1 = 0.0616, wR_2 = 0.1645
Final R indexes [all data]	R_1 = 0.1947, wR_2 = 0.2224	R_1 = 0.1120, wR_2 = 0.1956
Largest diff. peak/hole / e Å^{-3}	0.450/−0.392	0.812/-0.490

4. Characterization data

4.1. Characterization data of the ligands and compounds.

[HL^1]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 13.02 (s, 1H), 7.34 (s, 1H), 7.00 (s, 2H), 6.67 (s, 1H), 6.43 (d, J = 7.4 Hz, 1H), 4.89 (s, 1H), 2.97 (s, 3H), 2.42 (d, J = 10.7 Hz, 6H), 1.64 (d, J = 28.5 Hz, 27H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.82, 156.65, 155.99, 154.38, 142.84, 141.32, 137.33, 137.10, 121.93, 115.67, 111.20, 98.80, 45.90, 40.21, 34.59, 34.41, 33.66, 25.72, 25.61, 25.30, 24.23, 22.16, 21.55.

[H_2L^2]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93 (s, 2H), 7.13 (d, J = 8.0 Hz, 4H), 7.04 (t, J = 7.0 Hz, 2H), 4.66 (s, 2H), 3.32 (s, 4H), 2.91−2.79 (m, 4H), 1.97 (s, 6H), 1.64 (s, 6H), 1.14 (dd, J = 18.0, 7.0 Hz, 24H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.15, 155.26, 146.54, 138.00, 122.60, 93.70, 44.42, 27.97, 23.74, 22.69, 21.55, 19.01.

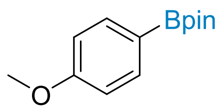
[(L^1)ZnEt] (1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (t, J = 7.7 Hz, 1H), 6.96 (s, 2H), 6.86 (d, J = 7.3 Hz, 1H), 6.74 (d, J = 7.9 Hz, 1H), 4.94 (s, 1H), 3.01 – 2.90 (m, 3H), 2.52 (s, 3H), 2.07 (s, 6H), 1.71 (t, J = 24.2 Hz, 24H), 0.58 (t, J = 8.0 Hz, 3H), -0.14 (q, J = 8.0 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.59, 143.59, 138.66, 137.67, 122.24, 118.25, 116.14, 97.17, 45.90, 39.97, 35.01, 26.15, 25.99, 25.45, 24.38, 23.66, 23.51, 11.62, -2.28.

[(L^1)$_2$Zn] (2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (s, 4H), 6.78 (s, 2H), 6.43 (s, 2H), 5.99 (s, 2H), 4.58 (s, 2H), 3.04 – 2.72 (m, 6H), 2.41 (s, 2H), 2.26 (s, 4H), 2.04 (t, J = 10.3 Hz, 12H), 1.86 – 1.44 (m, 48H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.68, 165.21, 155.59, 142.26, 141.58, 136.57, 122.55, 122.04, 116.04, 115.39, 100.52, 46.06, 39.55, 39.48, 35.29, 35.17, 35.06, 34.71, 34.65, 26.97, 25.72, 25.47, 24.38, 24.24, 24.06.

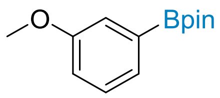
[(L^2)Li_2(THF)$_2$] (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 4H), 7.18 – 7.09 (m, 2H), 4.95 (s, 2H), 3.77 (s, 4H), 3.43 (s, 4H), 3.38 (s, 9H), 2.20 (s, 6H), 1.96 (s, 6H), 1.35 – 1.24 (m, 24H), 1.17 (s, 9H). 13C NMR (101 MHz, C_6D_6) δ 165.56, 161.92, 150.12, 140.95, 122.92, 122.53, 93.20, 68.05, 54.77, 27.76, 25.19, 24.23, 23.50, 23.28, 21.72.

[(HL^2)Zn_2Cl_3] (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (s, 6H), 4.62 (s, 3H), 3.81 (s, 4H), 3.11-3.02 (m, 4H), 2.06 (s, 6H), 1.62 (s, 6H), 1.12 (t, J = 6.8 Hz, 24H).^{13}C NMR (151 MHz, $CDCl_3$) δ 168.60, 165.95, 145.16，142.40, 124.71, 123.11, 93.04, 65.89, 52.50, 38.25, 27.55, 23.93, 23.85, 23.51, 22.29,18.62,13.93.

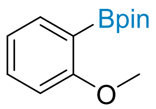
4.2. ^{1}H NMR data of the aryl borates



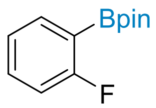
2-(4-methoxyphenyl)-4,4,5,5- tetramethyl-1,3,2-dioxaborolane (6a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 2H), 6.90 (d, J = 8.2 Hz, 2H), 3.82 (s, 3H), 1.34 (s, 12H).



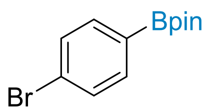
2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.33 (s, 2H), 7.01 (d, J = 7.7 Hz, 1H), 3.82 (s, 3H), 1.34 (s, 12H).



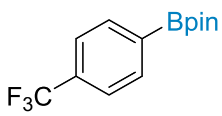
2-(2-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 – 7.64 (m, 1H), 7.43 – 7.35 (m, 1H), 6.93 (t, J = 7.3 Hz, 1H), 6.84 (d, J = 8.3 Hz, 1H), 3.71 (s, 4H), 1.34 (s, 12H).



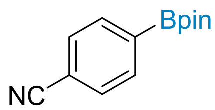
2-(2-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.41 (s, 1H), 7.14 (d, J = 7.2 Hz, 1H), 7.02 (t, J = 8.7 Hz, 1H), 1.36 (s, 12H).



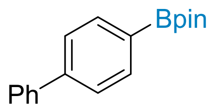
2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (t, J = 7.7 Hz, 2H), 7.52 (t, J = 7.9 Hz, 2H), 1.34 (t, J = 6.2 Hz, 12H).



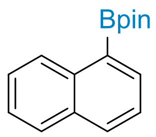
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (6f). ^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.91 (d, J = 11.3 Hz, 2H), 7.61 (d, J = 5.2 Hz, 2H), 1.36 (s, 12H).



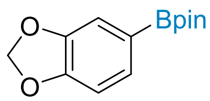
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (6g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 1H), 7.81 (s, 1H), 7.64 (d, J = 7.7 Hz, 1H), 7.33 – 7.15 (m, 1H), 1.35 (s, 12H).



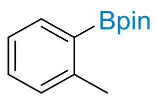
2-([1, 1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6h**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.69 (t, J = 8.5 Hz, 2H), 7.61 (d, J = 7.7 Hz, 2H), 7.51 (d, J = 8.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 1.44 (s, 3H), 1.41 (s, 3H), 1.35 (s, 6H).



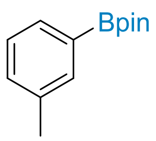
4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (**6i**). ^{1}H NMR (300 MHz, $CDCl_3$)) δ 8.77 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 6.8 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 7.9 Hz, 2H), 7.48 (dt, J = 13.9, 7.7 Hz, 3H), 1.41 (s, 12H).



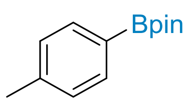
2-(benzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6j**). ^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.36 (d, J = 7.7 Hz, 1H), 7.24 (s, 1H), 6.83 (d, J = 7.7 Hz, 1H), 5.95 (s, 2H), 1.33 (s, 12H).



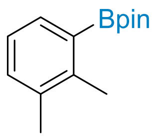
4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (**6k**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 6.7 Hz, 1H), 7.31 (s, 1H), 7.21 – 7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H).



4,4,5,5-tetramethyl-2-(m-tolyl)-1,3,2-dioxaborolane (**6l**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 6.8 Hz, 2H), 7.27 (s, 2H), 2.35 (s, 3H), 1.34 (s, 12H).

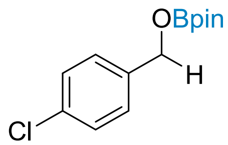


4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (6m). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.17 (s, 2H), 2.36 (s, 3H), 1.33 (s, 12H).

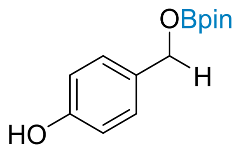


2-(2,3-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6n). ^{1}H NMR (300 MHz, $CDCl_3$)) δ 7.67 (s, 1H), 6.98 (s, 2H), 2.51 (s, 3H), 2.31 (s, 3H), 1.32 (s, 12H).

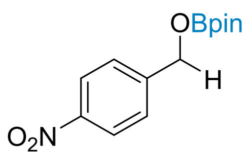
4.3 ^{1}H NMR data of the hydroboration products



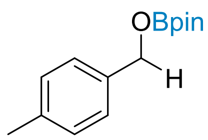
2-((4-chlorobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8a). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 4H), 4.88 (s, 2H), 1.25 (s, 12H).



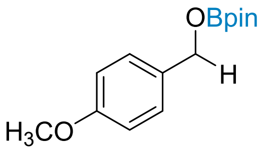
4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)phenol (8b). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 1H), 7.19 (s, 1H), 7.06 (s, 1H), 6.81 (s, 1H), 4.83 (s, 2H), 1.26 (s, 12H).



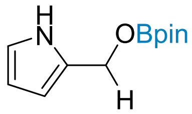
4,4,5,5-tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (8c). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 7.8 Hz, 2H), 5.00 (s, 2H), 1.25 (s, 12H).



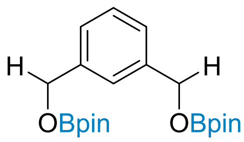
4,4,5,5-tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (8d). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (d, J = 7.0 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 4.88 (s, 2H), 2.32 (s, 3H), 1.25 (s, 12H).



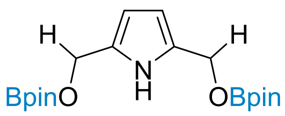
2-((4-methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8e). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 2H), 6.85 (d, J = 8.3 Hz, 2H), 4.84 (s, 2H), 3.77 (s, 3H), 1.25 (s, 12H).



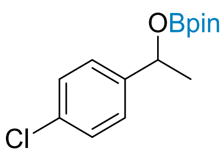
2-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-1H-pyrrole (8f). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 6.75 (s, 1H), 6.13 (s, 1H), 4.84 (s, 2H), 1.27 (s, 12H).



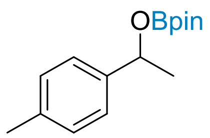
1,3-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzene (8g). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 20.3 Hz, 4H), 4.92 (s, 4H), 1.26 (s, 24H).



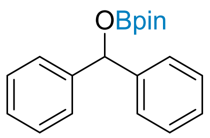
2,5-bis(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)-1H-pyrrole (8h). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.87 (s, 1H), 6.00 (d, J = 2.6 Hz, 2H), 4.79 (s, 4H), 1.26 (s, 24H).



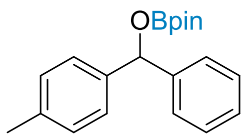
2-(1-(4-chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8i). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 4H), 5.21 (d, *J* = 6.4 Hz, 1H), 1.46 (d, *J* = 6.4 Hz, 3H), 1.24 (s, 12H).



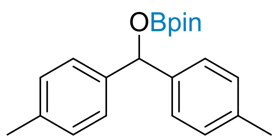
4,4,5,5-tetramethyl-2-(1-(p-tolyl)ethoxy)-1,3,2-dioxaborolane (**8j**). [1]H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.5 Hz, 2H), 5.22 (d, J = 6.3 Hz, 1H), 2.32 (s, 3H), 1.48 (d, J = 6.2 Hz, 3H), 1.24 (s, 12H).



2-(benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8k**). [1]H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 4H), 7.27 (t, J = 7.7 Hz, 4H), 7.22 – 7.17 (m, 2H), 6.17 (s, 1H), 1.18 (s, 12H).



4,4,5,5-tetramethyl-2-(phenyl(p-tolyl)methoxy)-1,3,2-dioxaborolane (**8l**). [1]H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 4H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.15 (s, 1H), 2.28 (s, 3H), 1.18 (s, 12H).



2-(di-p-tolylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8m**). [1]H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 8H), 6.11 (s, 1H), 1.20 (s, 12H).

5. NMR spectra

5.1 NMR spectra of the ligands and compounds

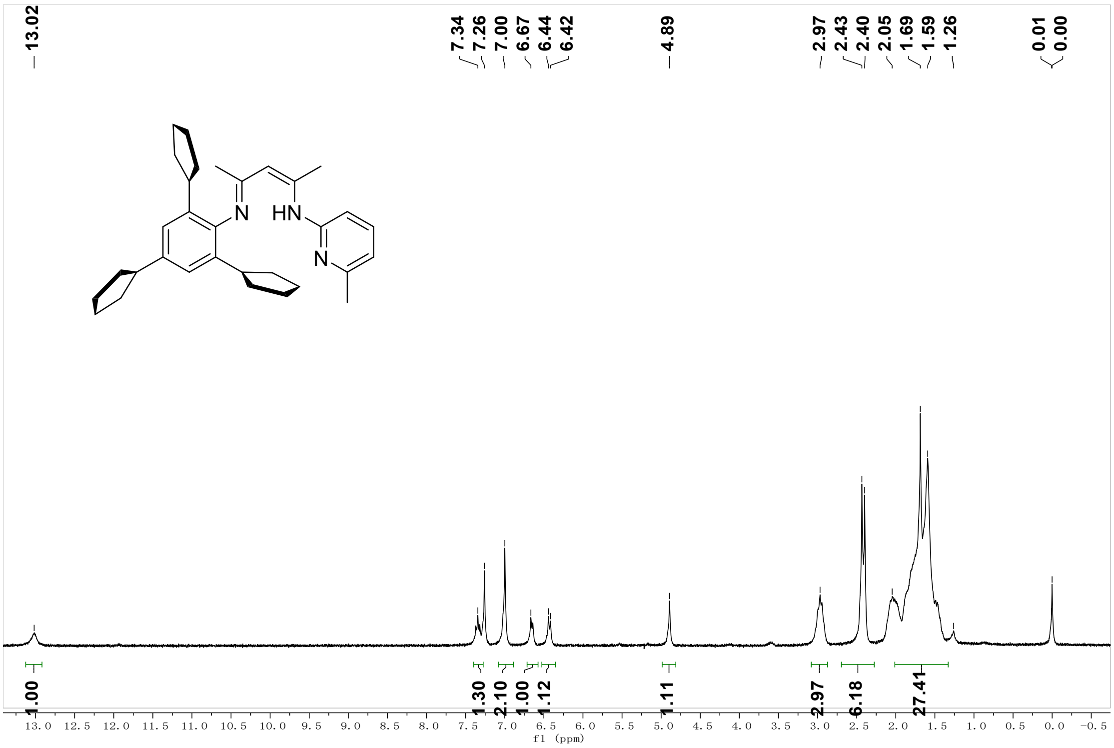


Figure S5. ^{1}H-NMR spectrum of HL^1

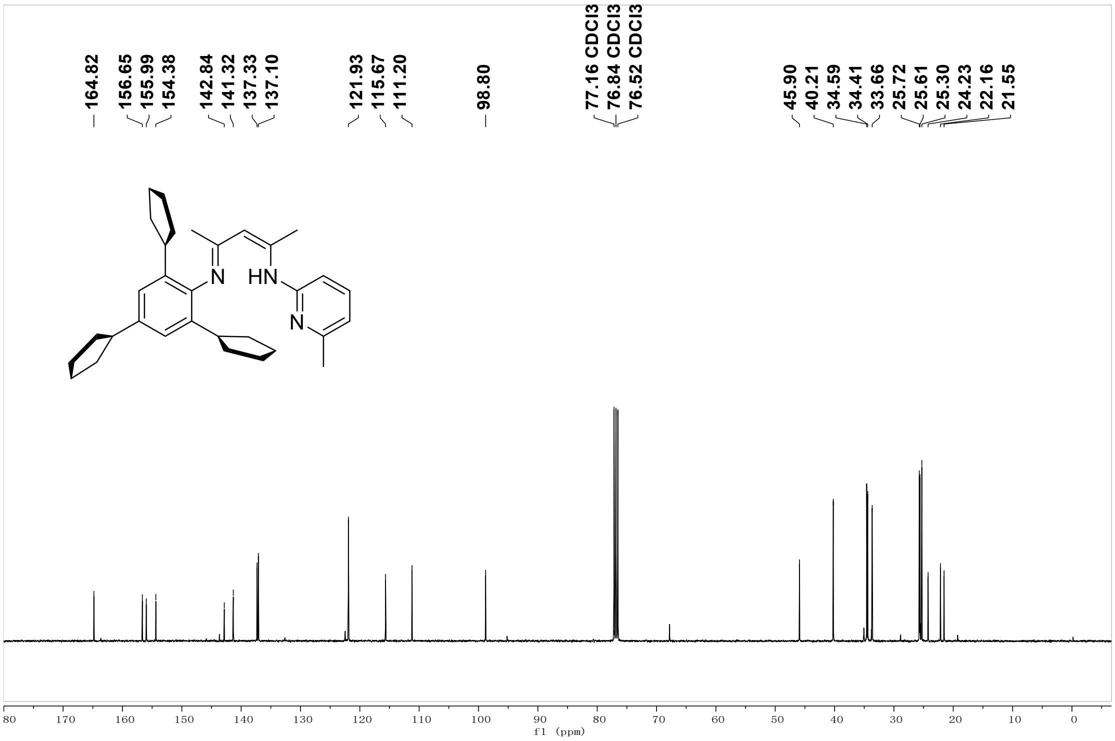


Figure S6. ^{13}C-NMR spectrum of HL[1]

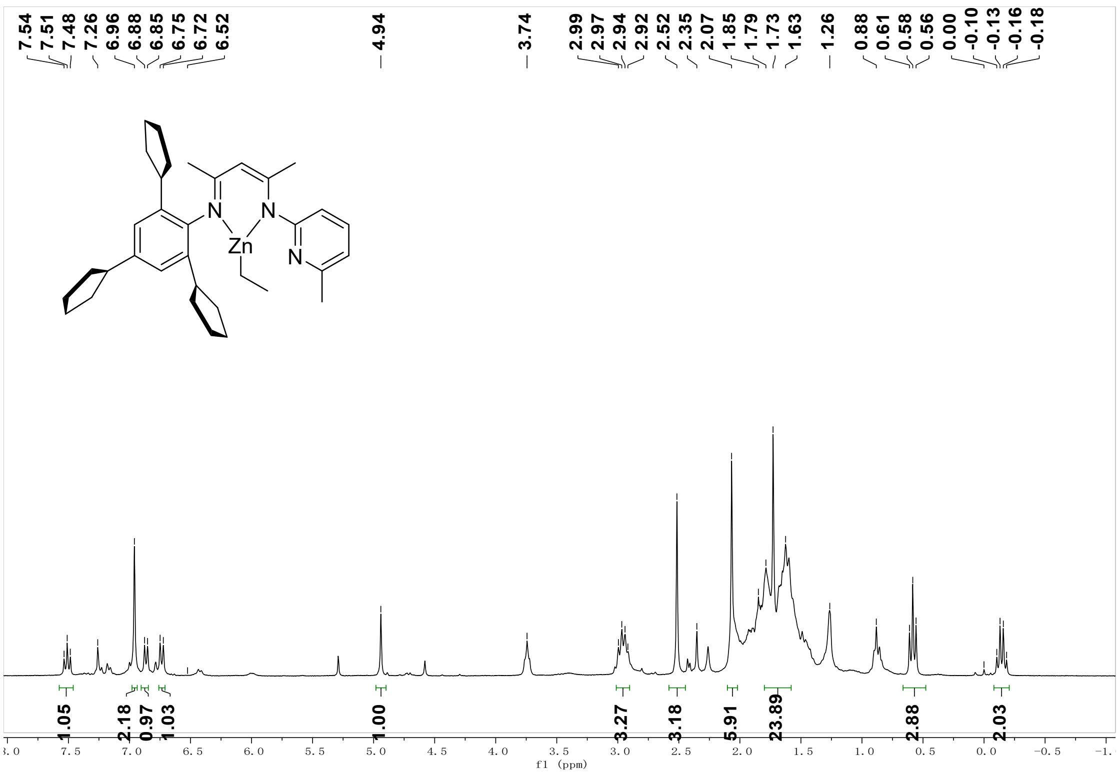


Figure S7. ^{1}H-NMR spectrum of **1**

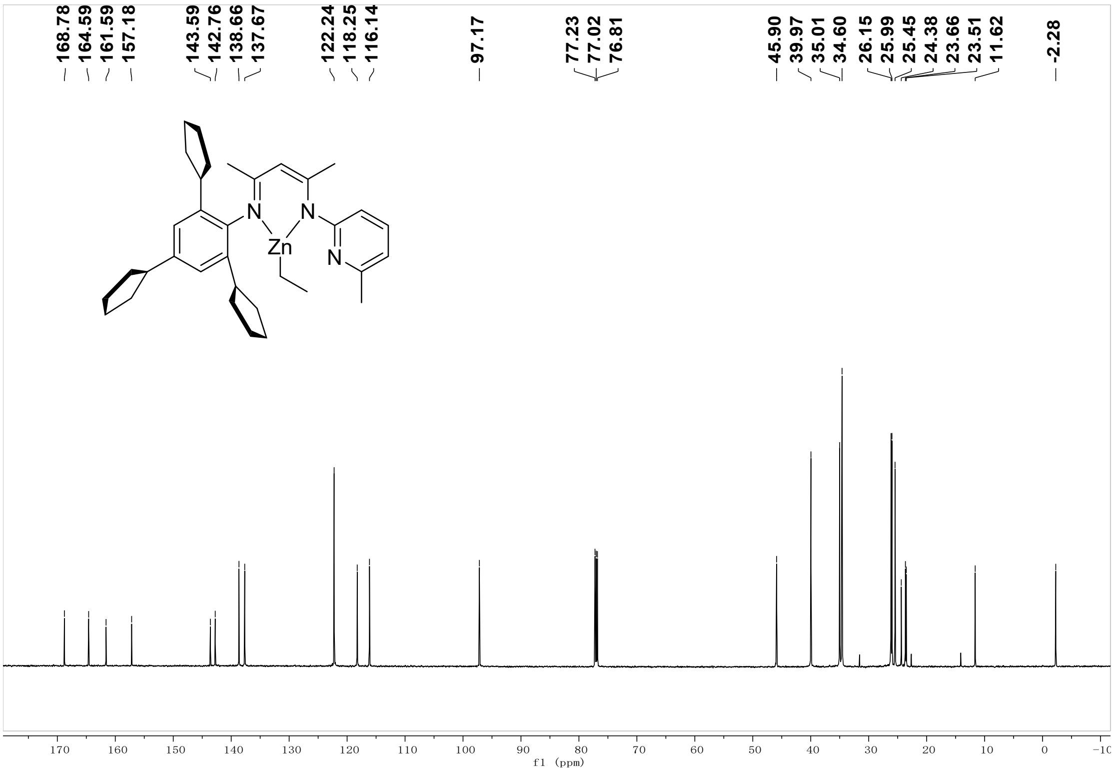


Figure S8. ^{13}C-NMR spectrum of **1**

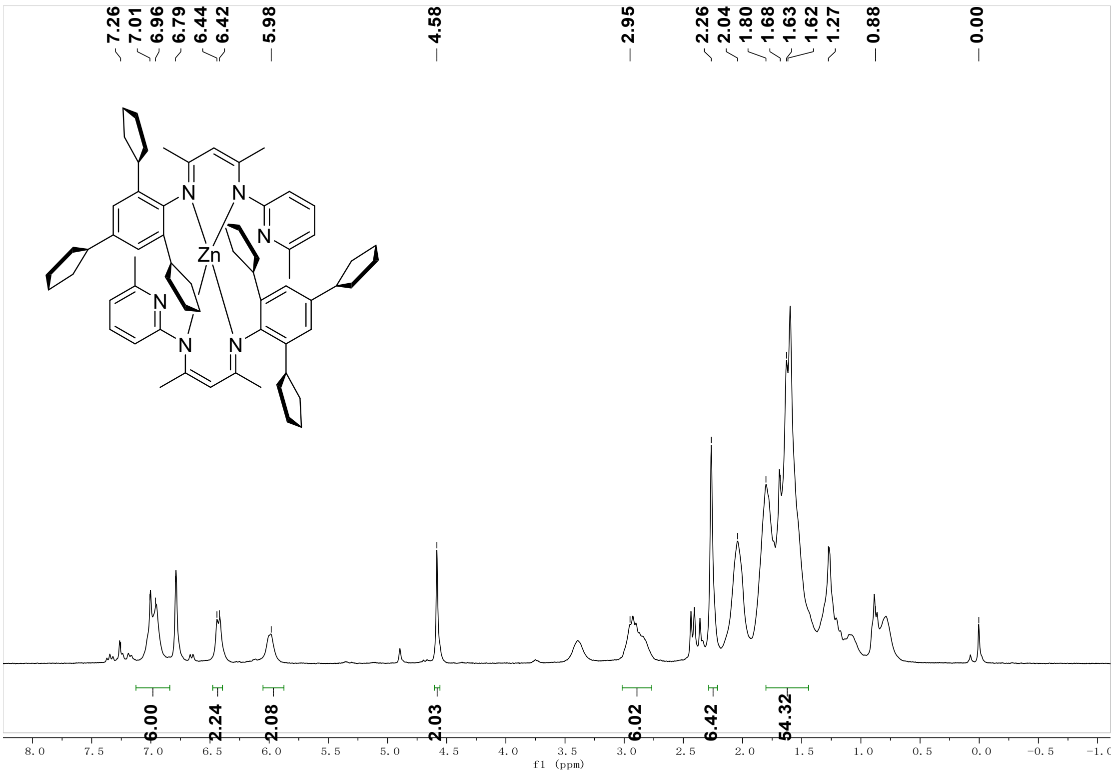


Figure S9. ^{1}H-NMR spectrum of **2**

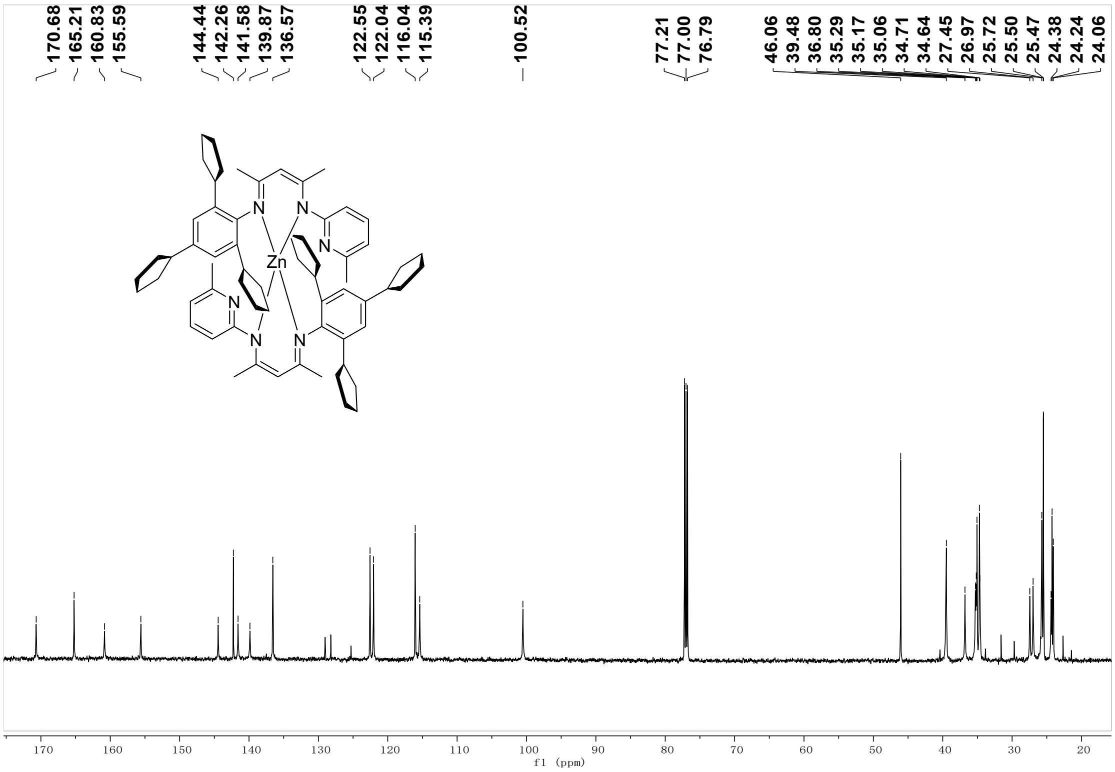


Figure S10. ^{13}C-NMR spectrum of **2**

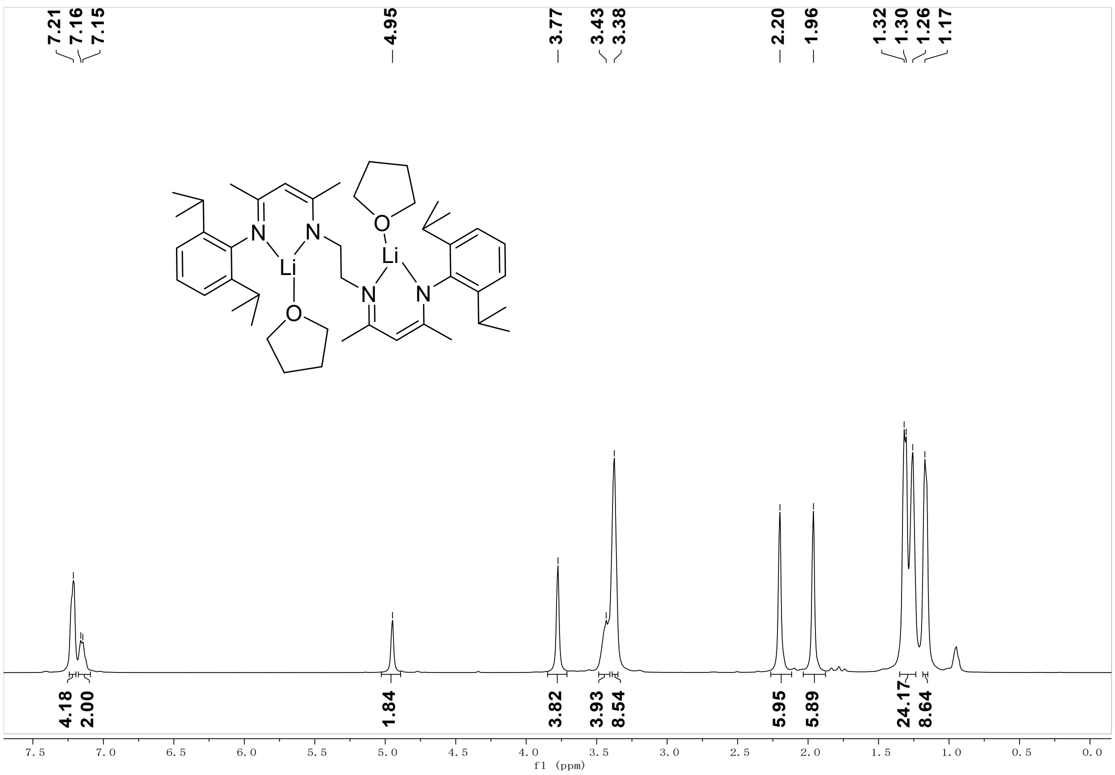


Figure S11. ^{1}H-NMR spectrum of **3**

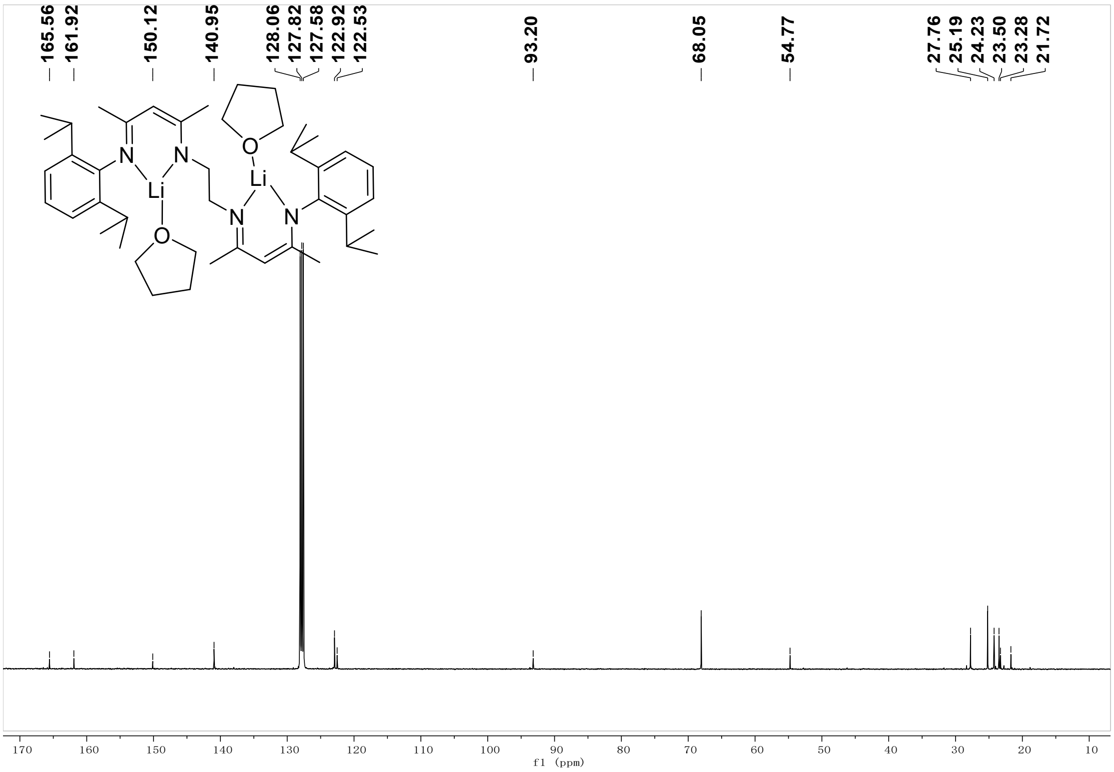


Figure S12. ^{13}C-NMR spectrum of **3**

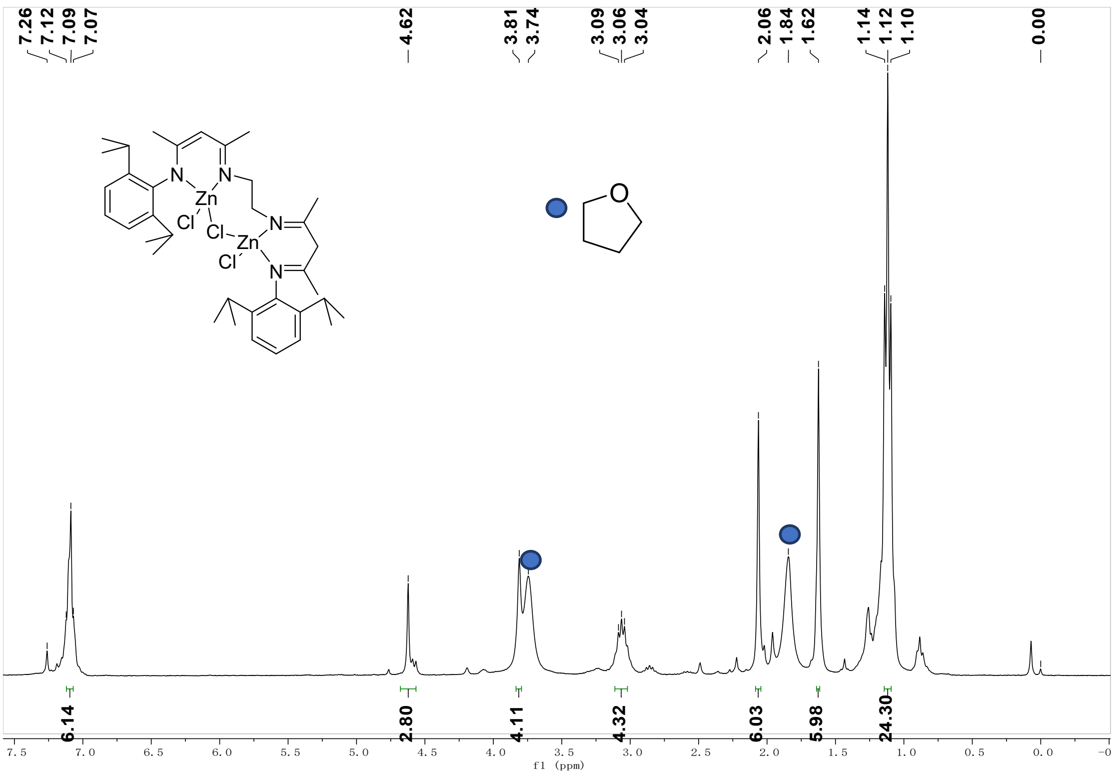


Figure S13. ^{1}H-NMR spectrum of **4**

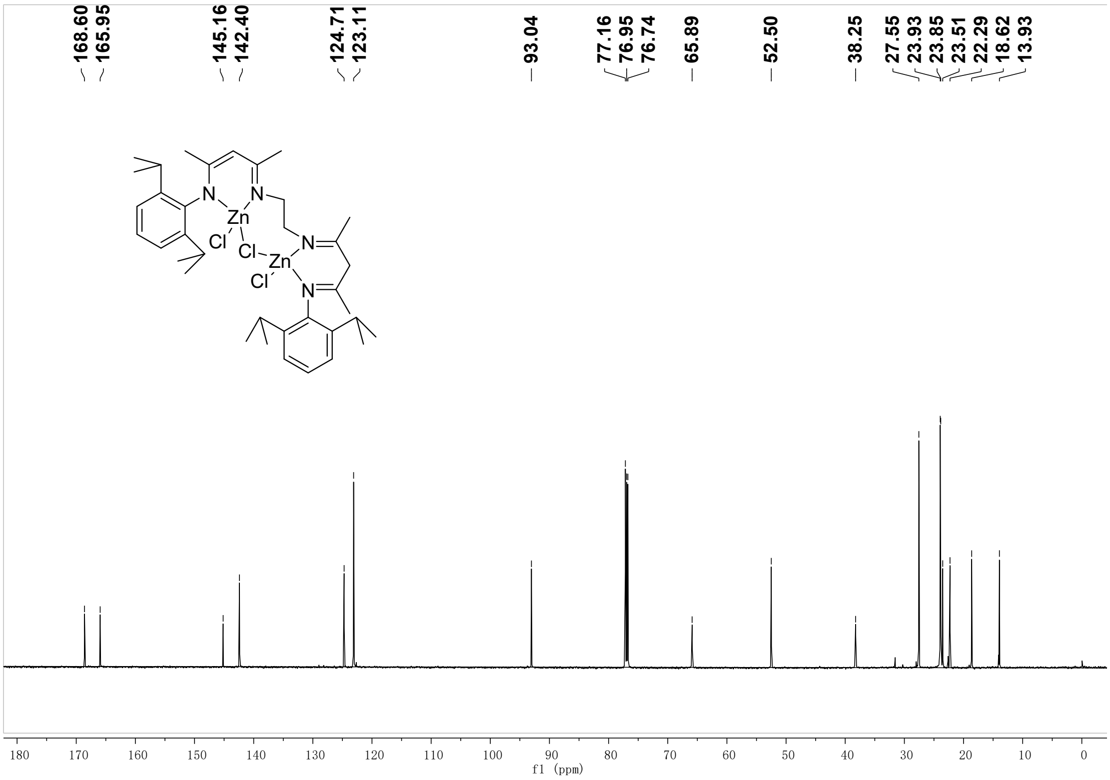


Figure S14. ^{13}C-NMR spectrum of **4**

5.2 NMR spectra of the products

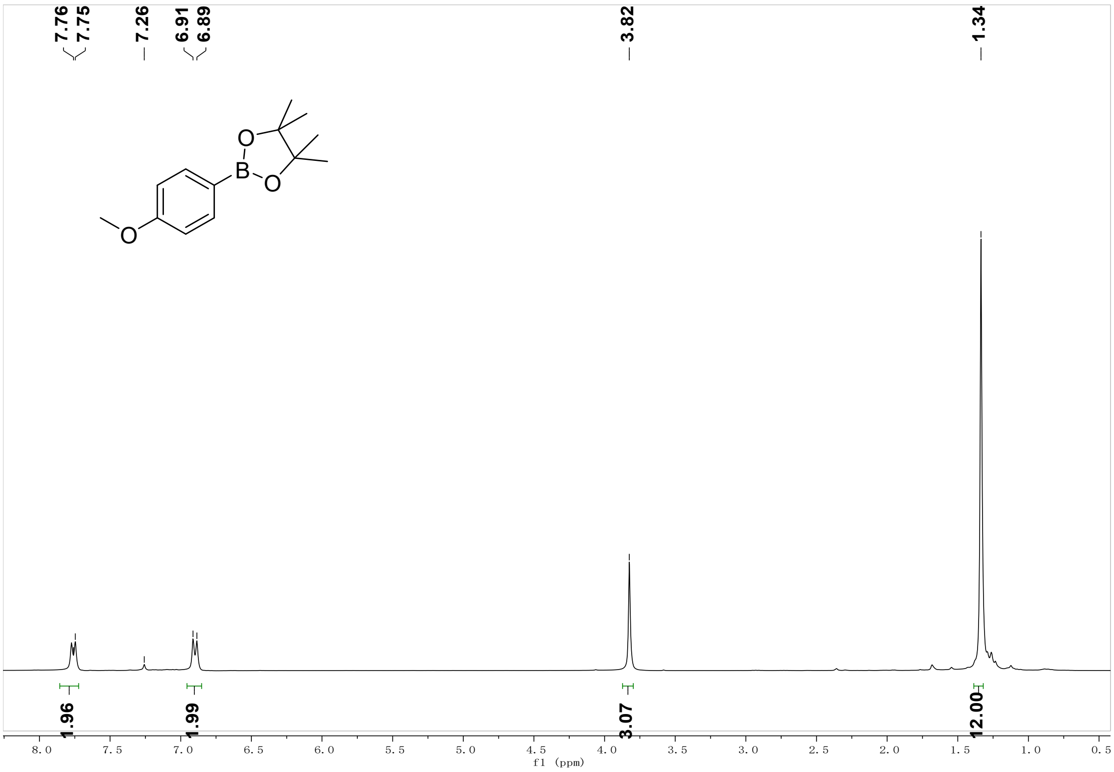


Figure S15. ^{1}H-NMR spectrum of **6a.**

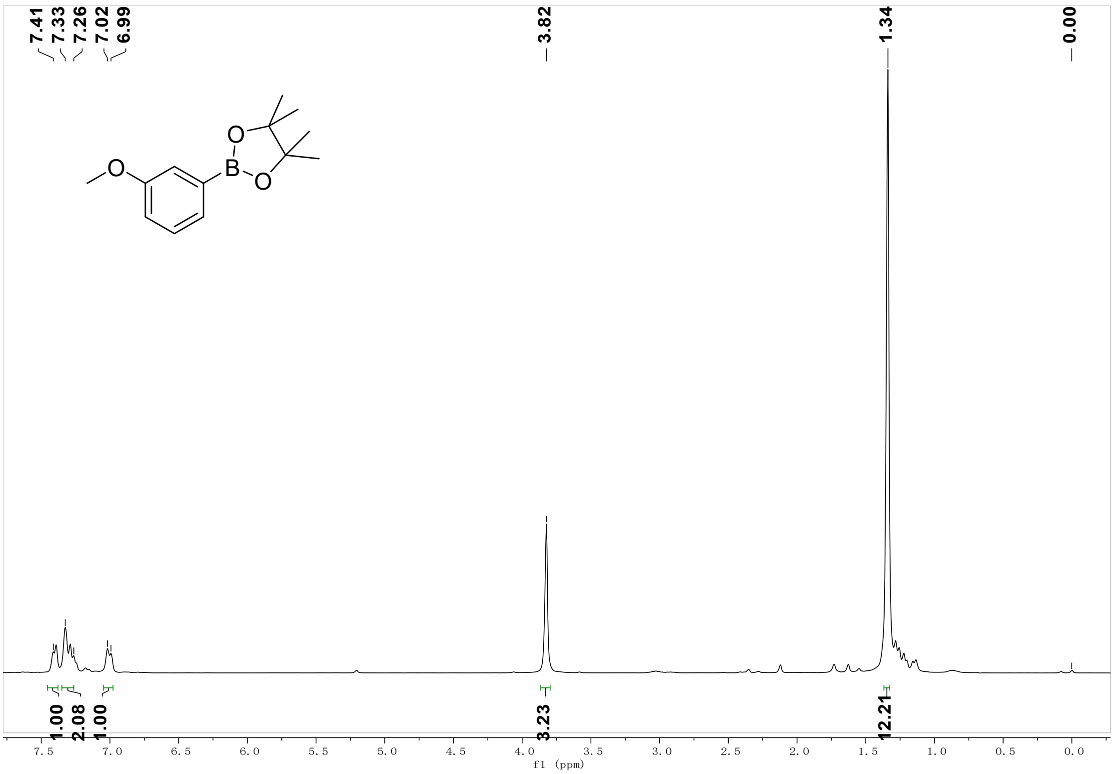


Figure S16. ^{1}H-NMR spectrum of **6b.**

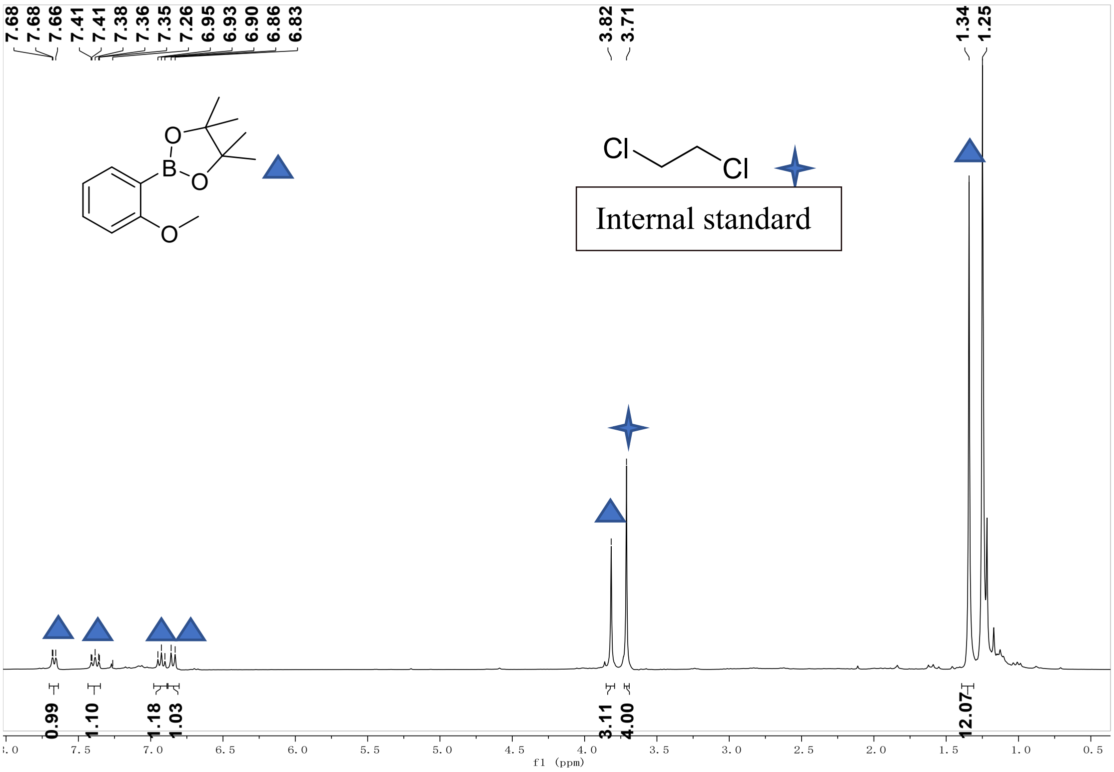


Figure S17. [1]H-NMR spectrum of **6c** (> 99%) in the un-isolated reaction mixture using 1,2-dichloroethane as internal standard.

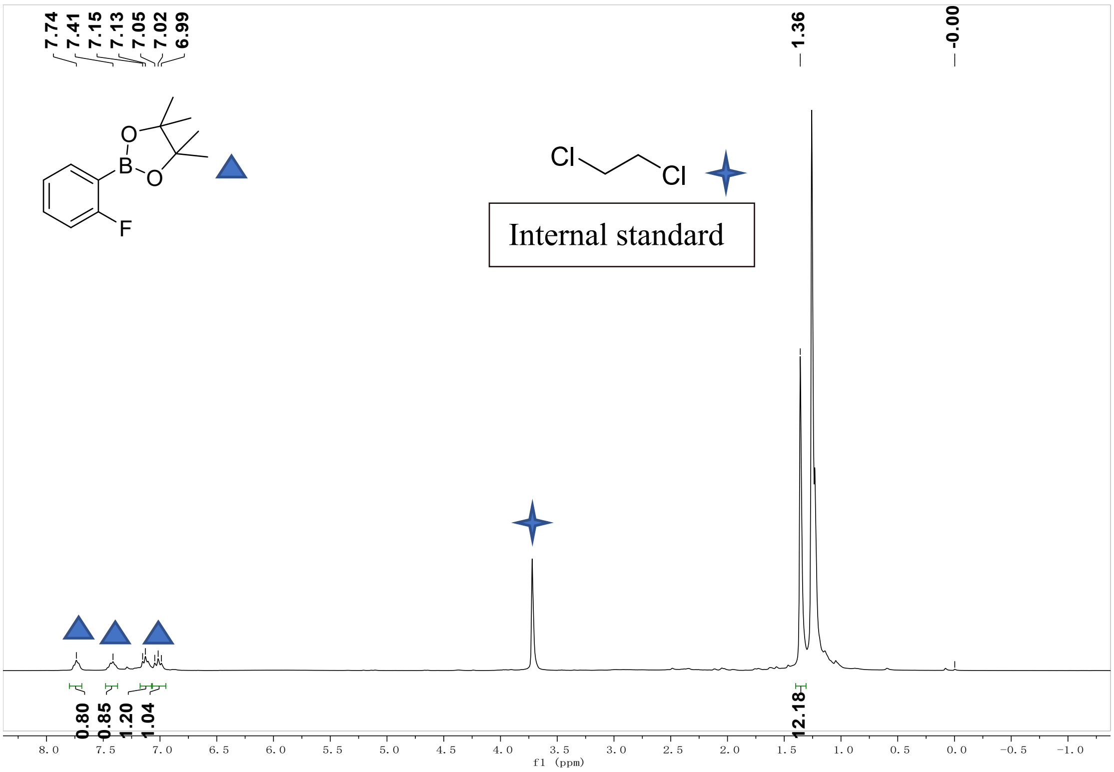


Figure S18. [1]H-NMR spectrum of **6d** (> 99%) in the un-isolated reaction mixture using 1,2-dichloroethane as internal standard.

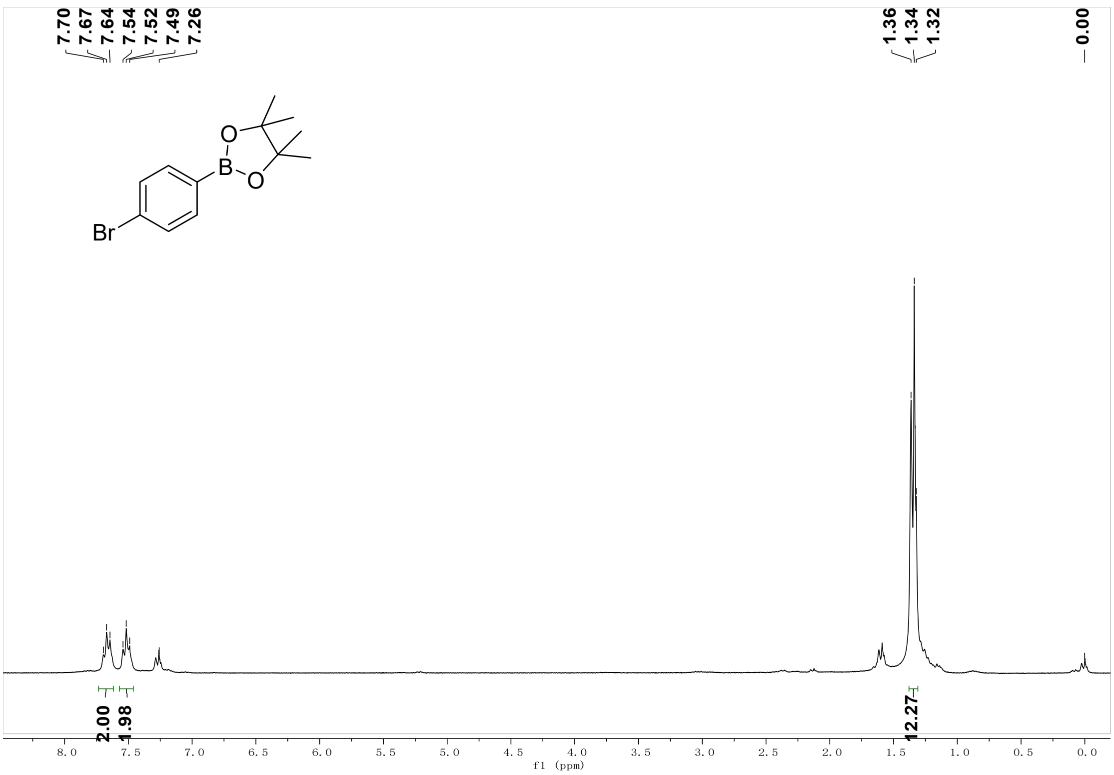


Figure S19. [1]H-NMR spectrum of **6e.**

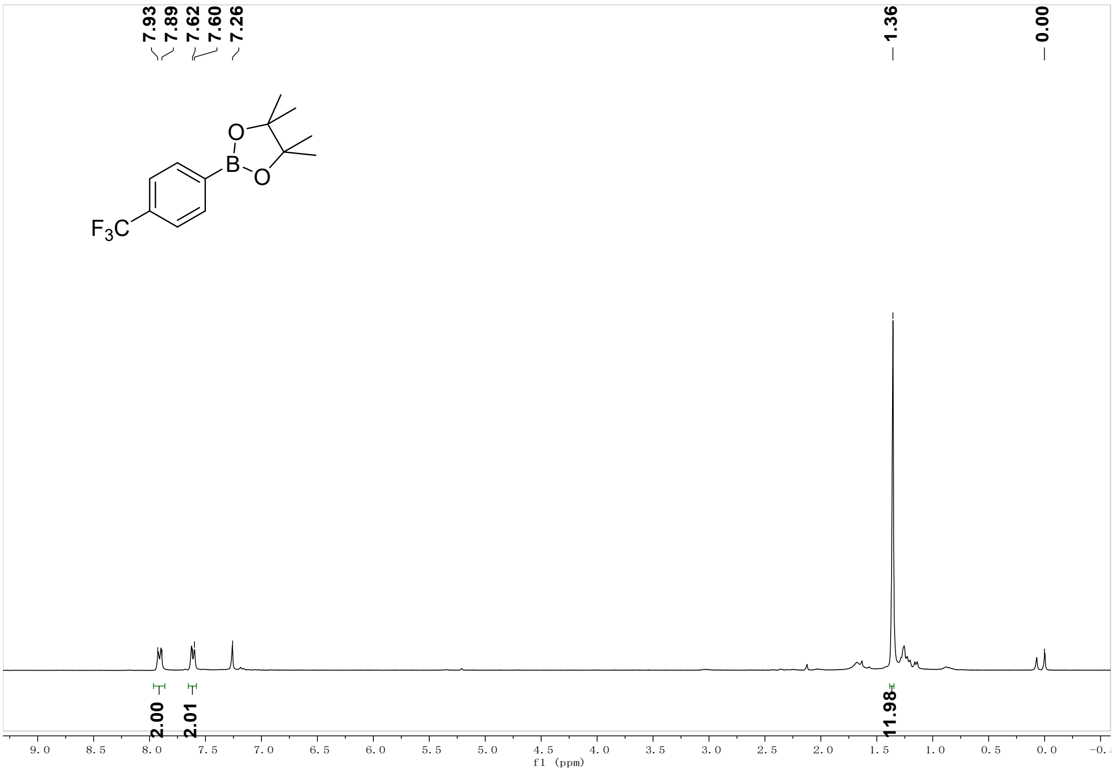


Figure S20. ^{1}H-NMR spectrum of **6f.**

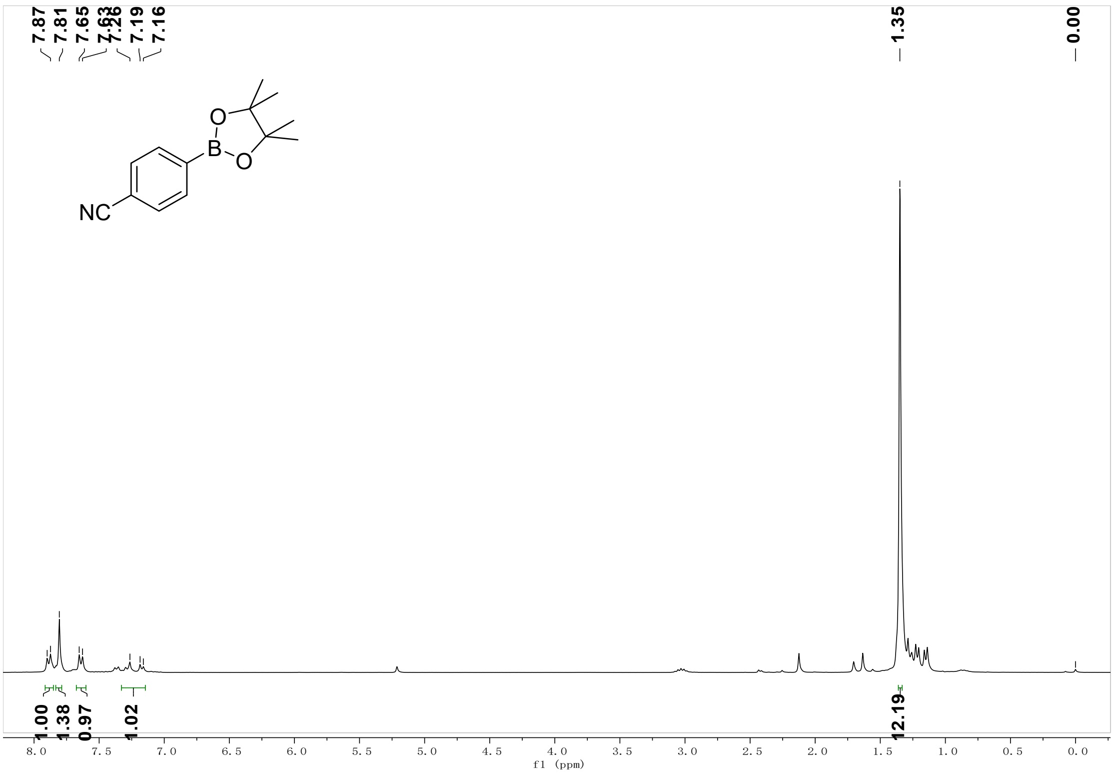


Figure S21. ^{1}H-NMR spectrum of **6g.**

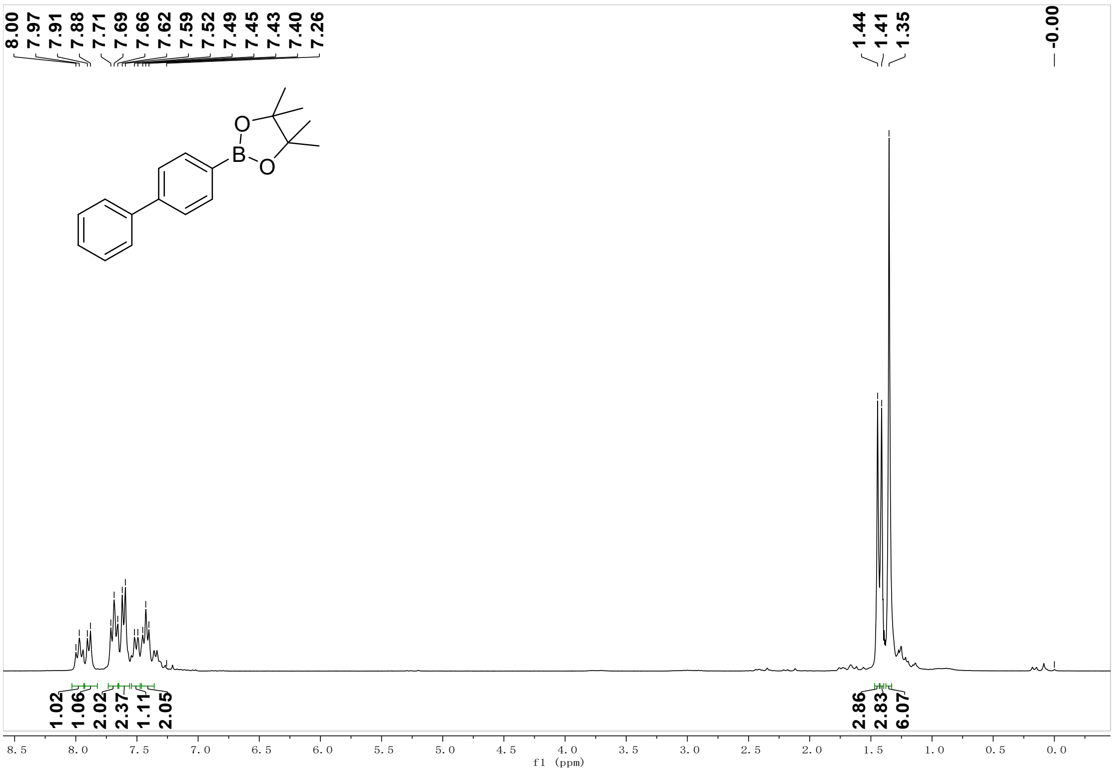


Figure S22. ^{1}H-NMR spectrum of **6h.**

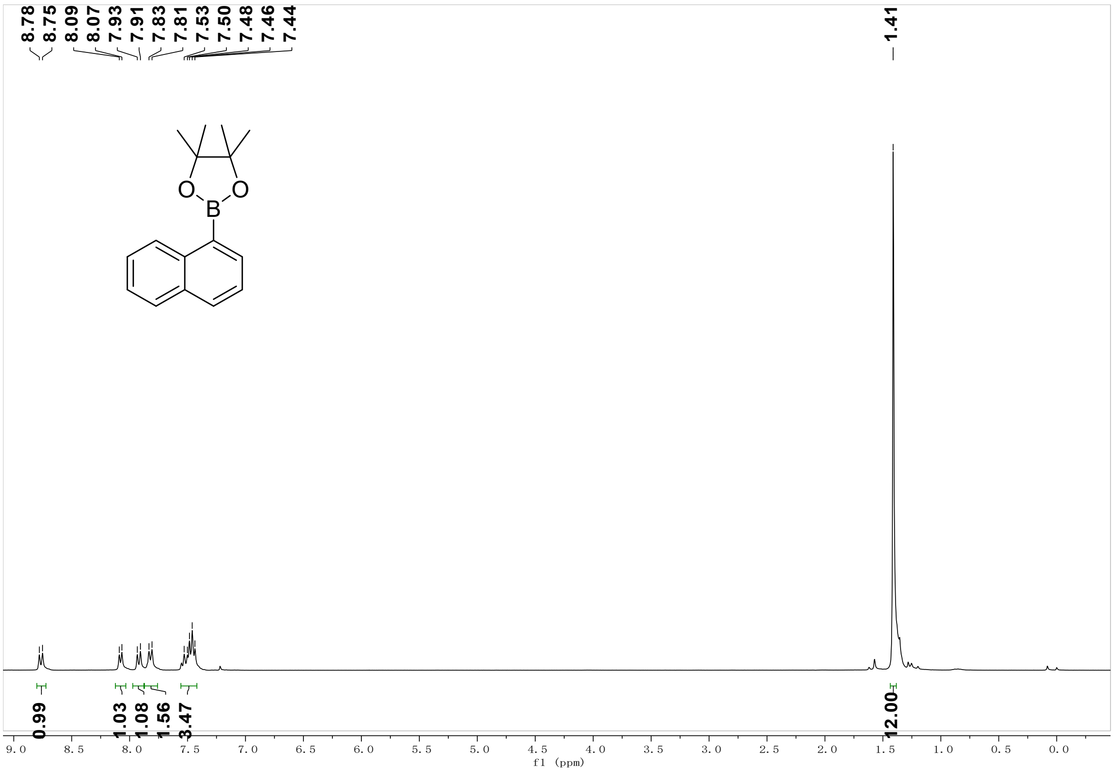


Figure S23. ^{1}H-NMR spectrum of **6i.**

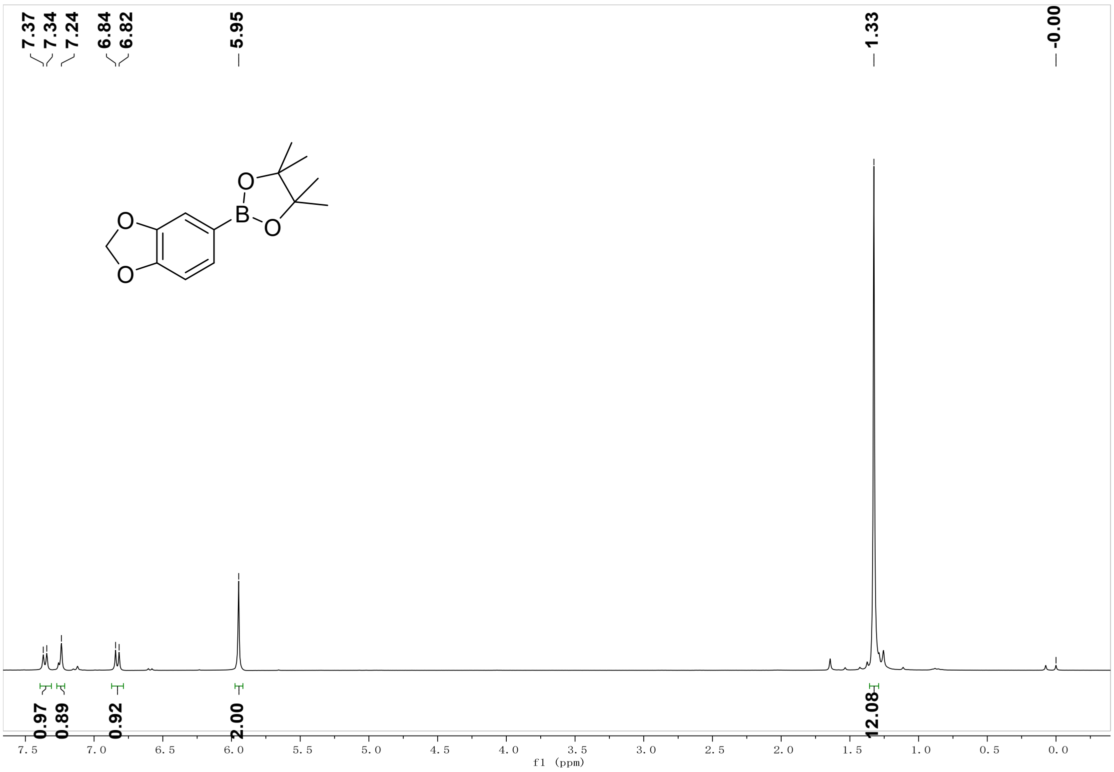


Figure S24. ^{1}H-NMR spectrum of **6j.**

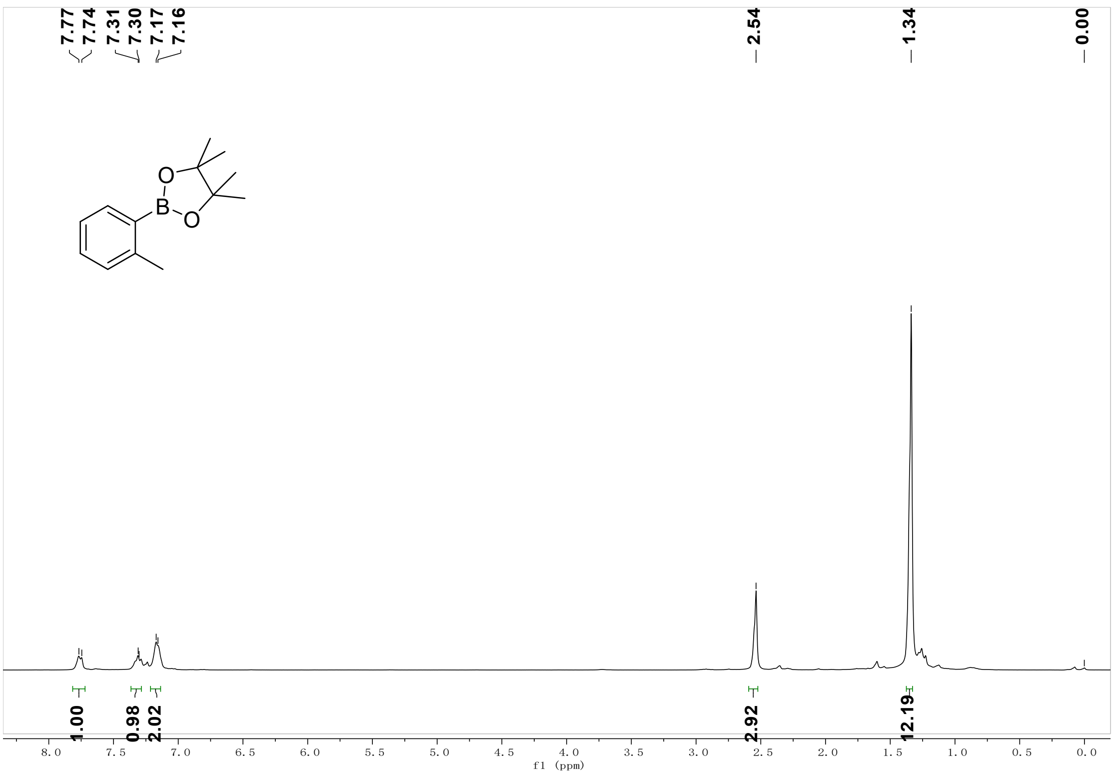


Figure S25. ^{1}H-NMR spectrum of **6k.**

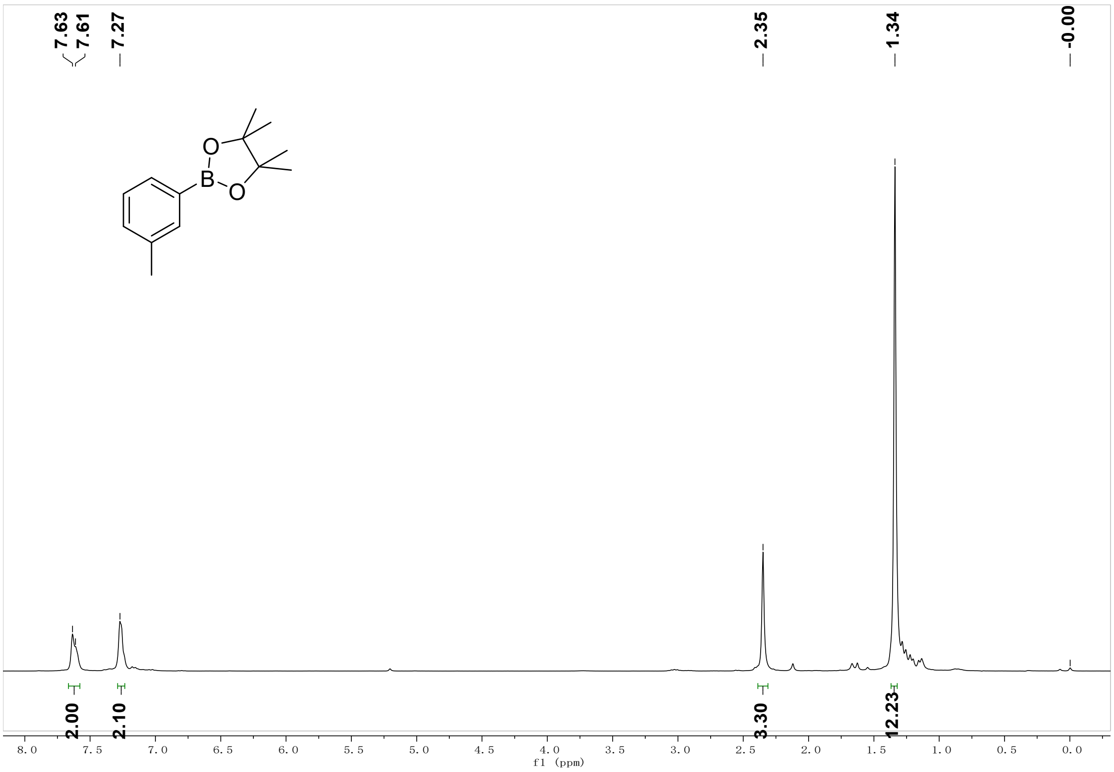


Figure S26. ^{1}H-NMR spectrum of **6l.**

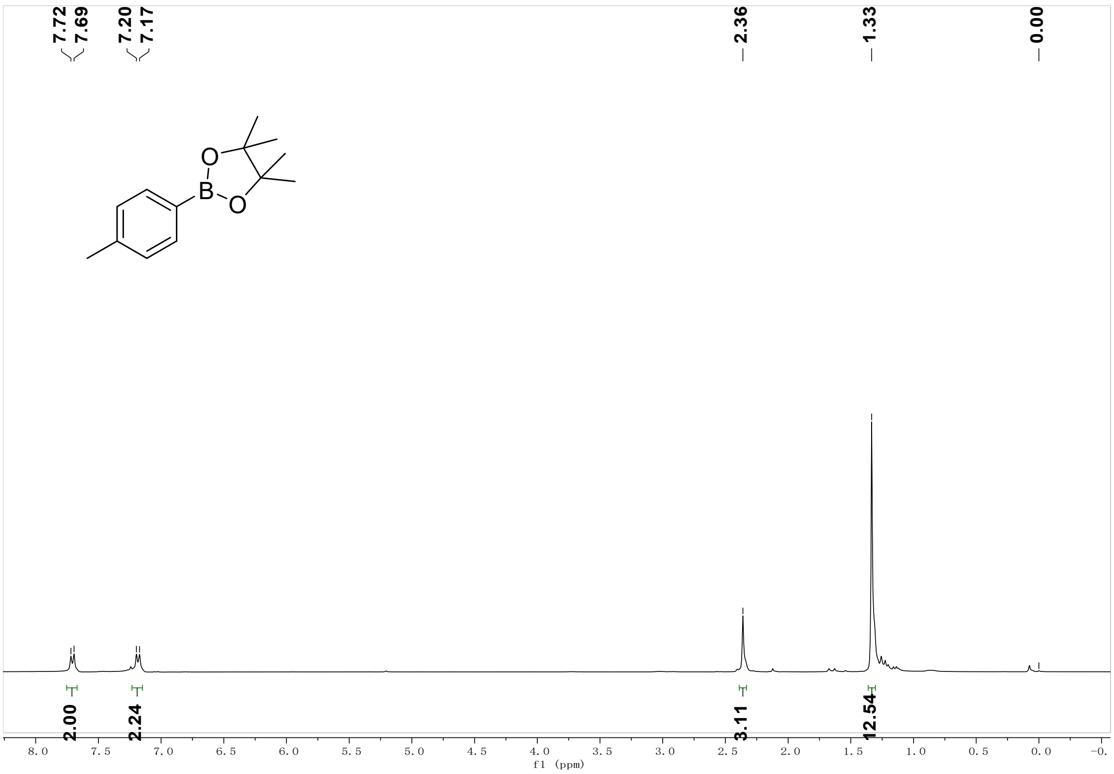


Figure S27. ^{1}H-NMR spectrum of **6m.**

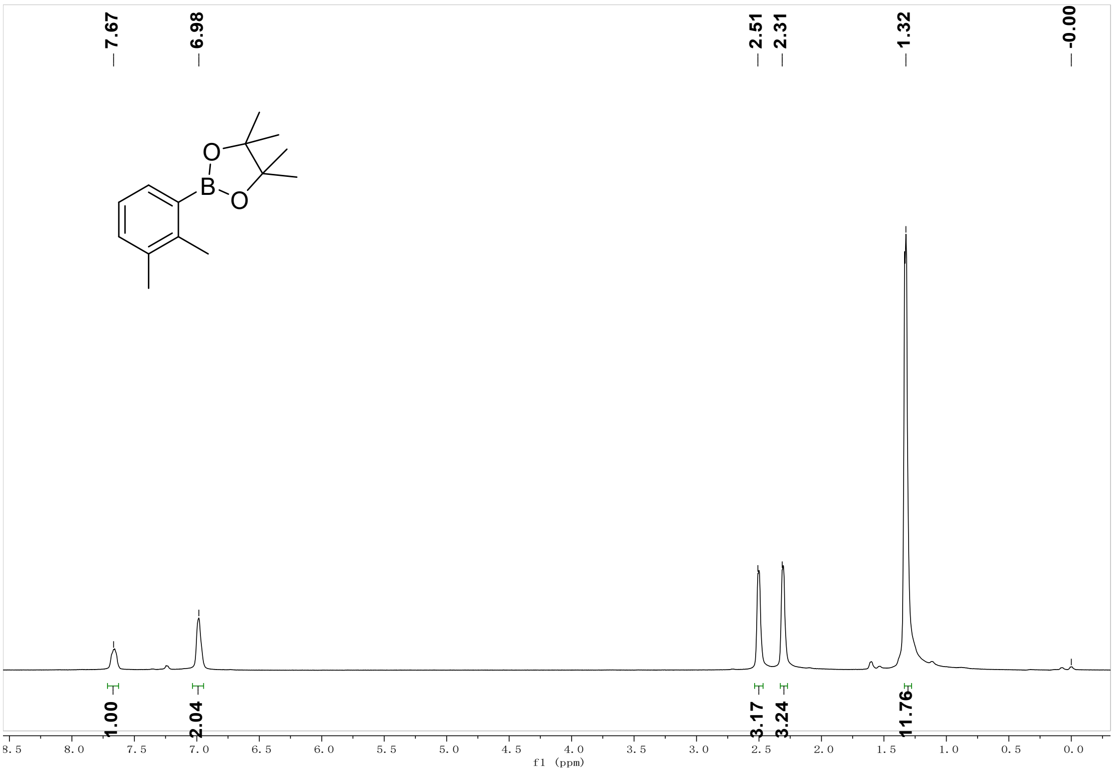


Figure S28. ^{1}H-NMR spectrum of **6n.**

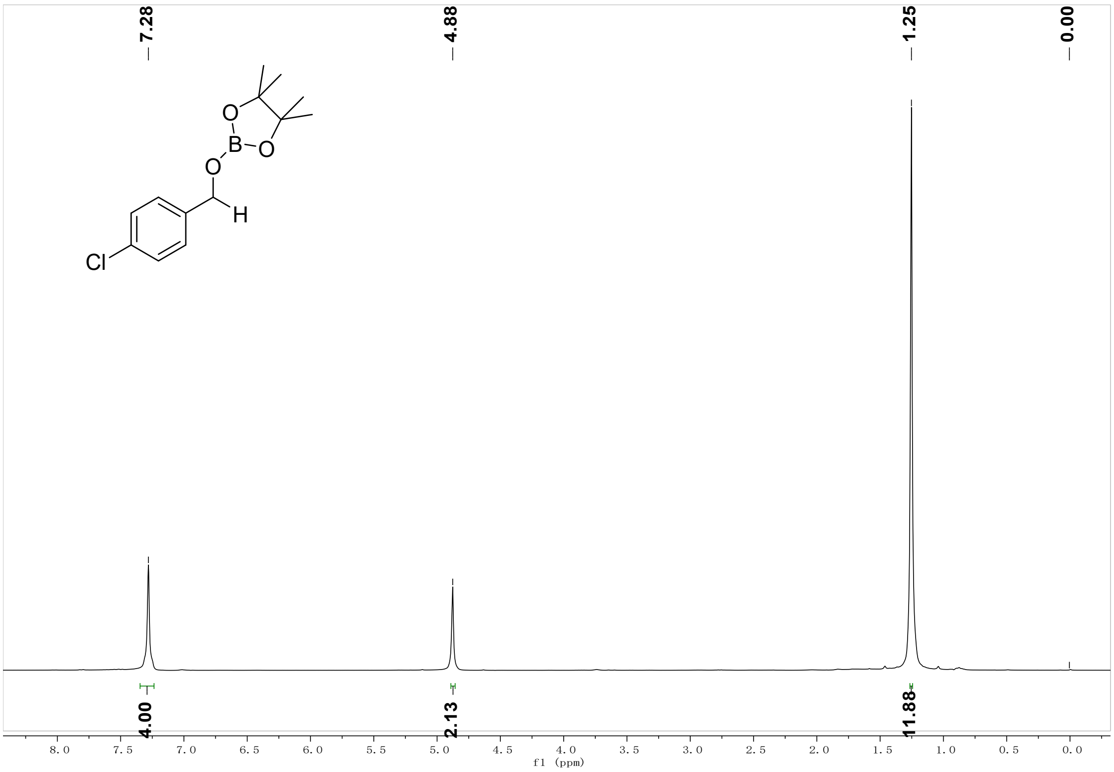


Figure S29. ^{1}H-NMR spectrum of **8a.**

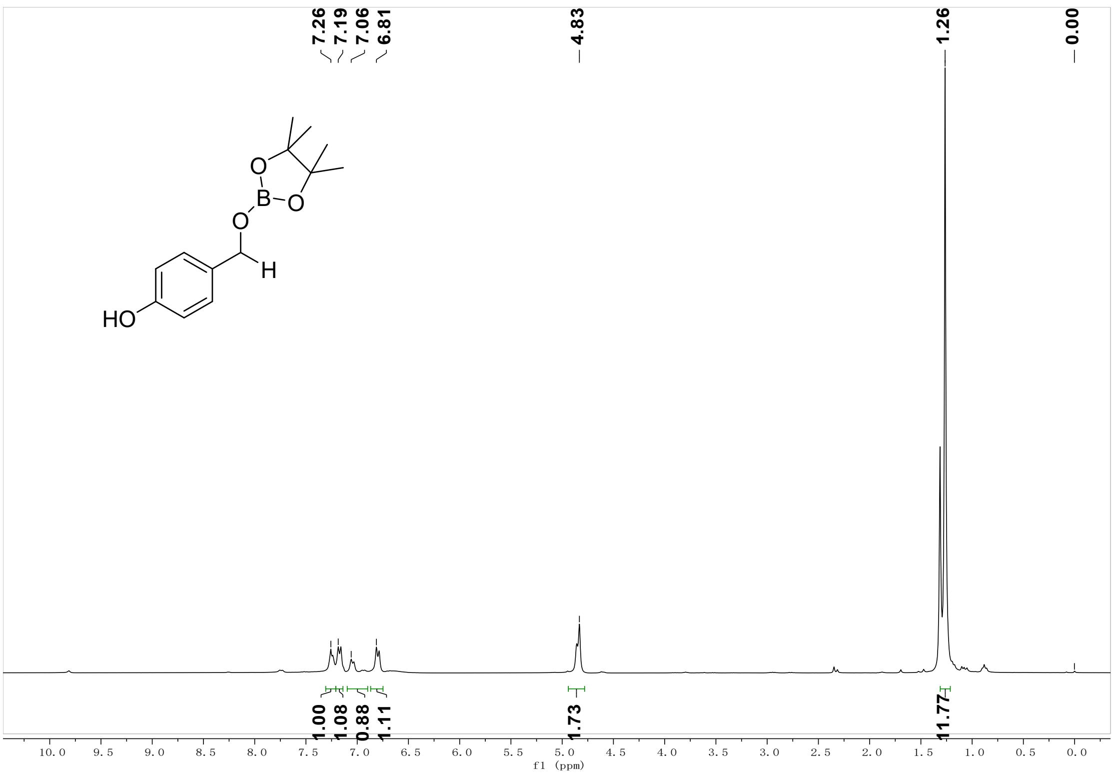


Figure S30. ^{1}H-NMR spectrum of **8b.**

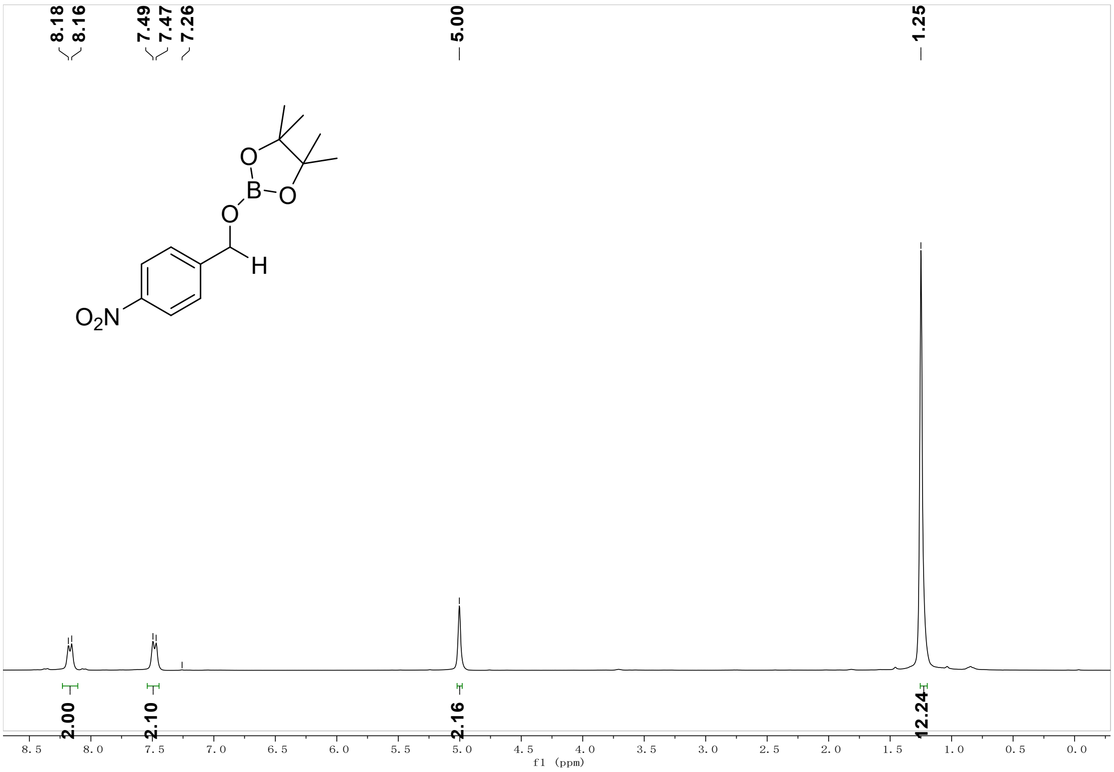


Figure S31. ^{1}H-NMR spectrum of **8c.**

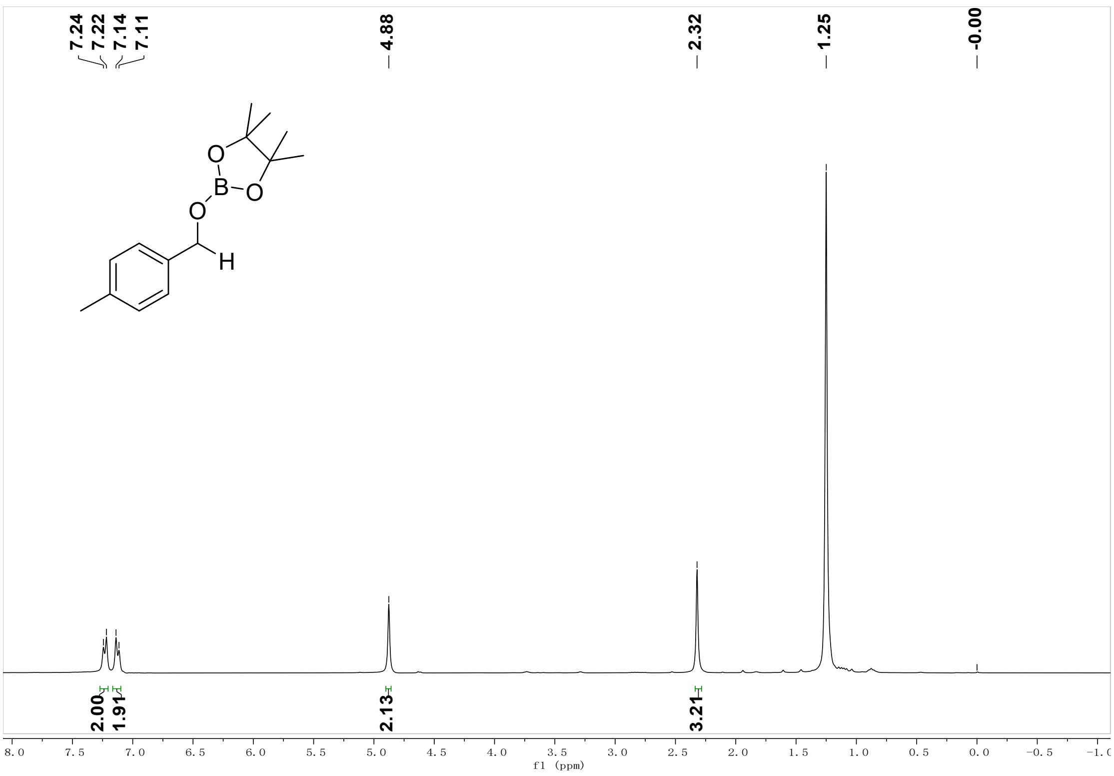


Figure S32. ^{1}H-NMR spectrum of **8d.**

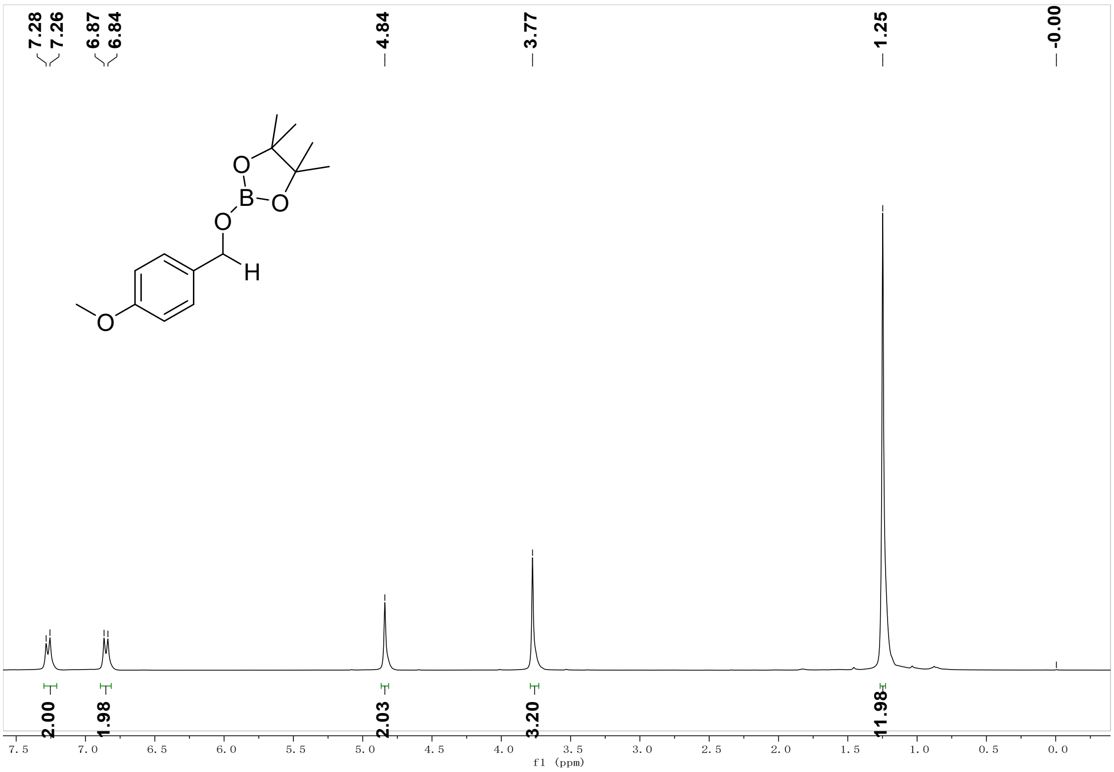


Figure S33. ^{1}H-NMR spectrum of **8e.**

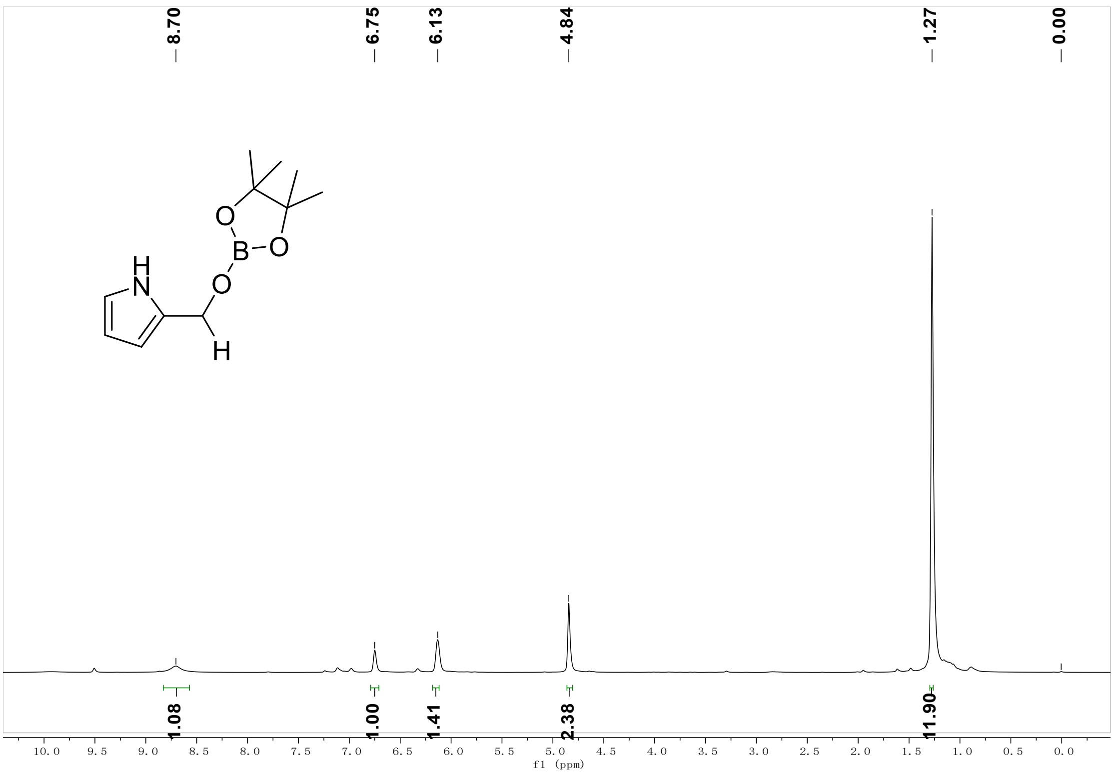


Figure S34. ^{1}H-NMR spectrum of **8f.**

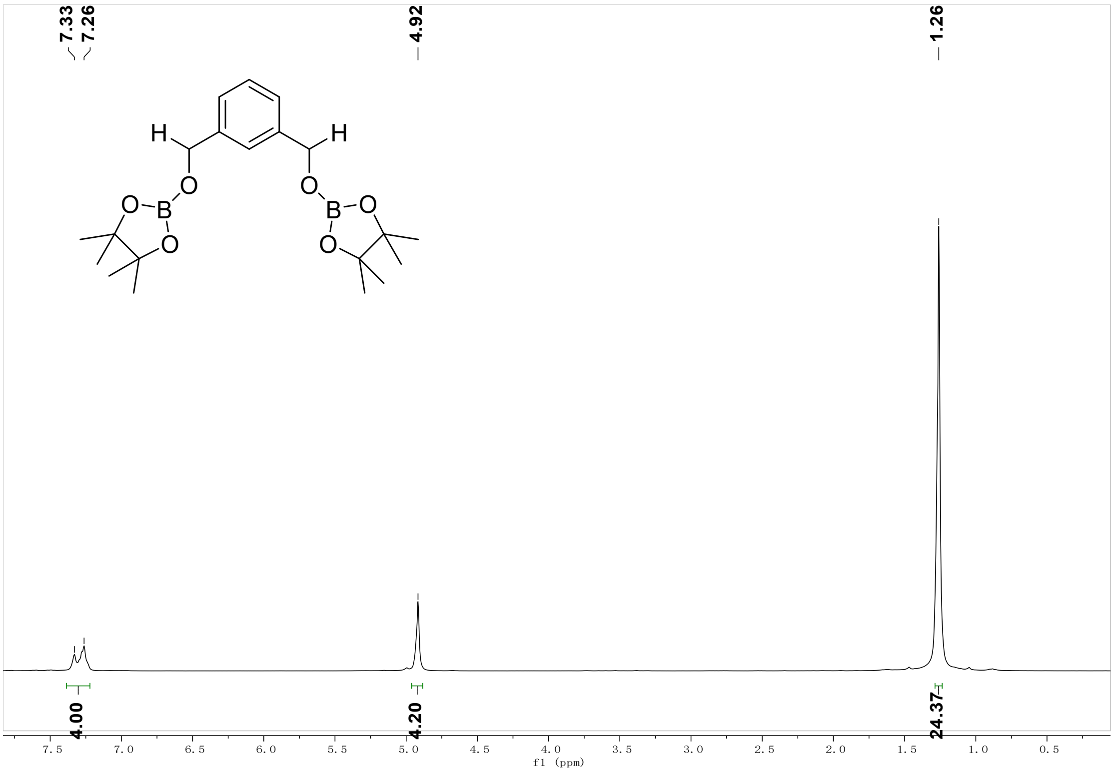


Figure S35. ^{1}H-NMR spectrum of **8g.**

Figure S36. ^{1}H-NMR spectrum of **8h.**

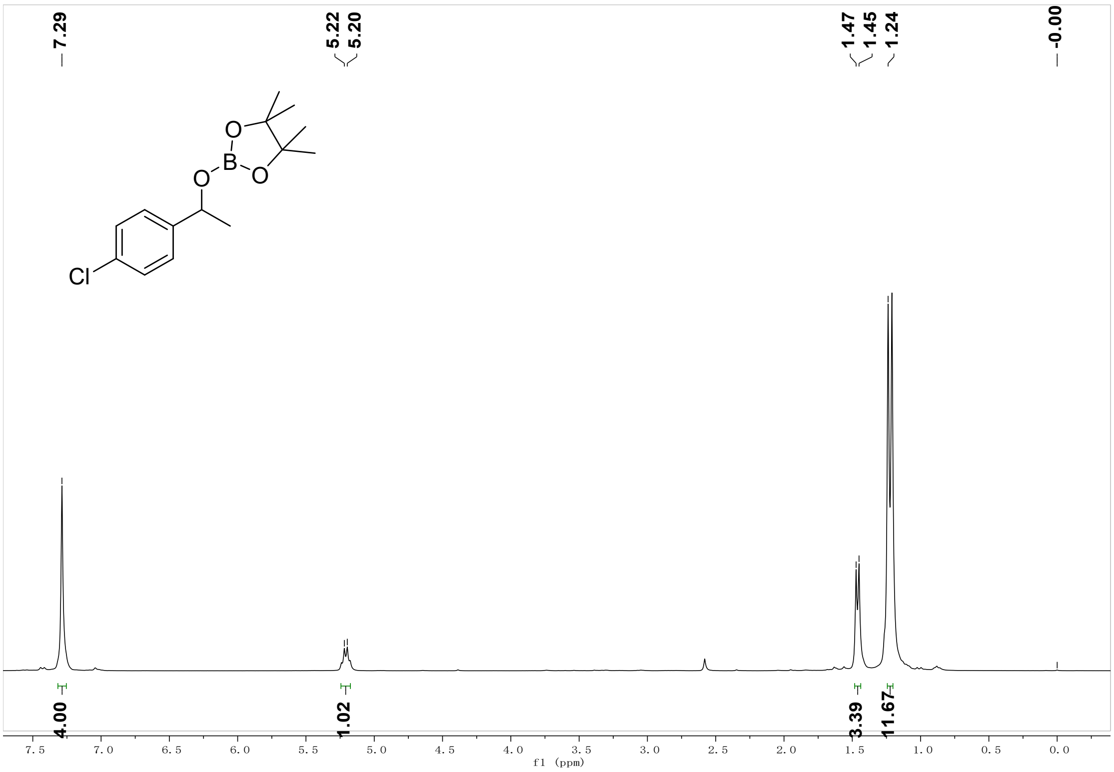


Figure S37. ^{1}H-NMR spectrum of **8i.**

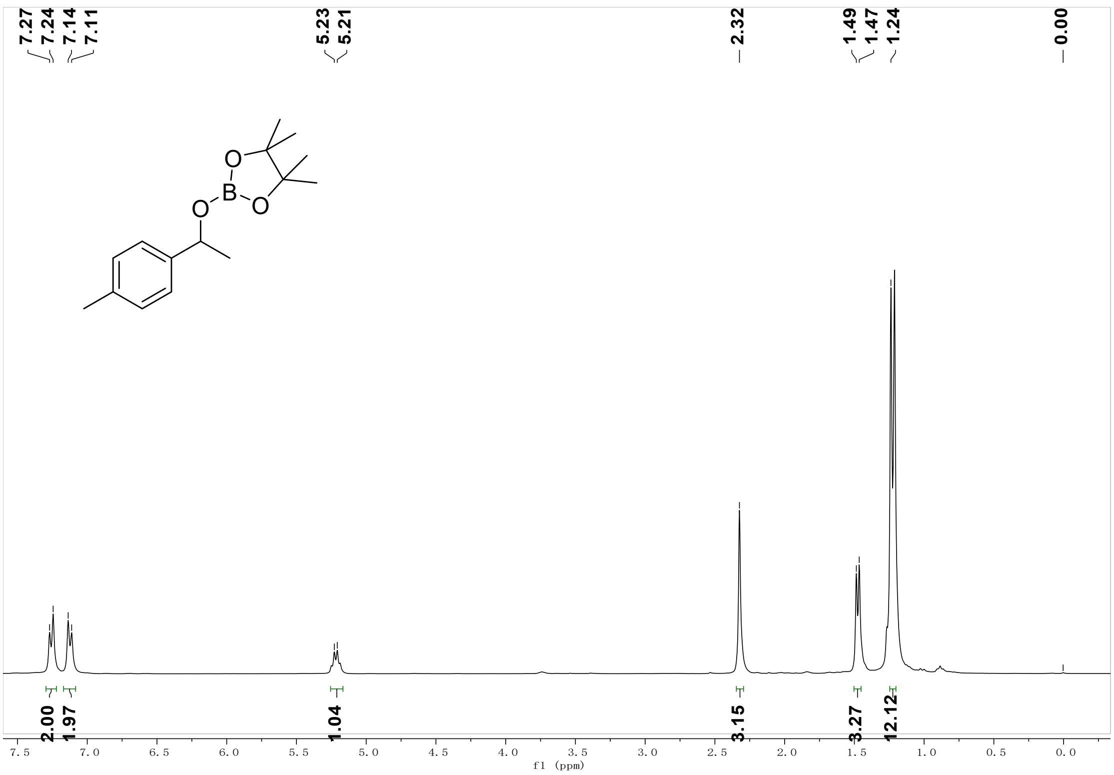


Figure S38. ^{1}H-NMR spectrum of **8j.**

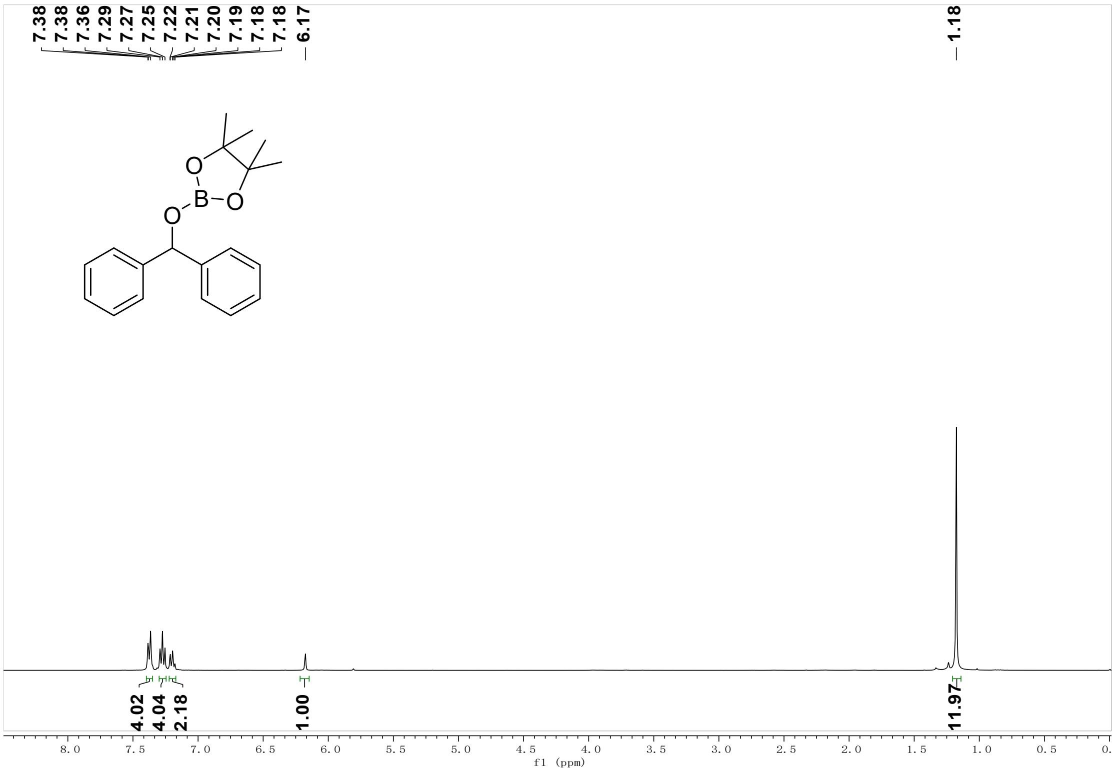


Figure S39. ^{1}H-NMR spectrum of **8k.**

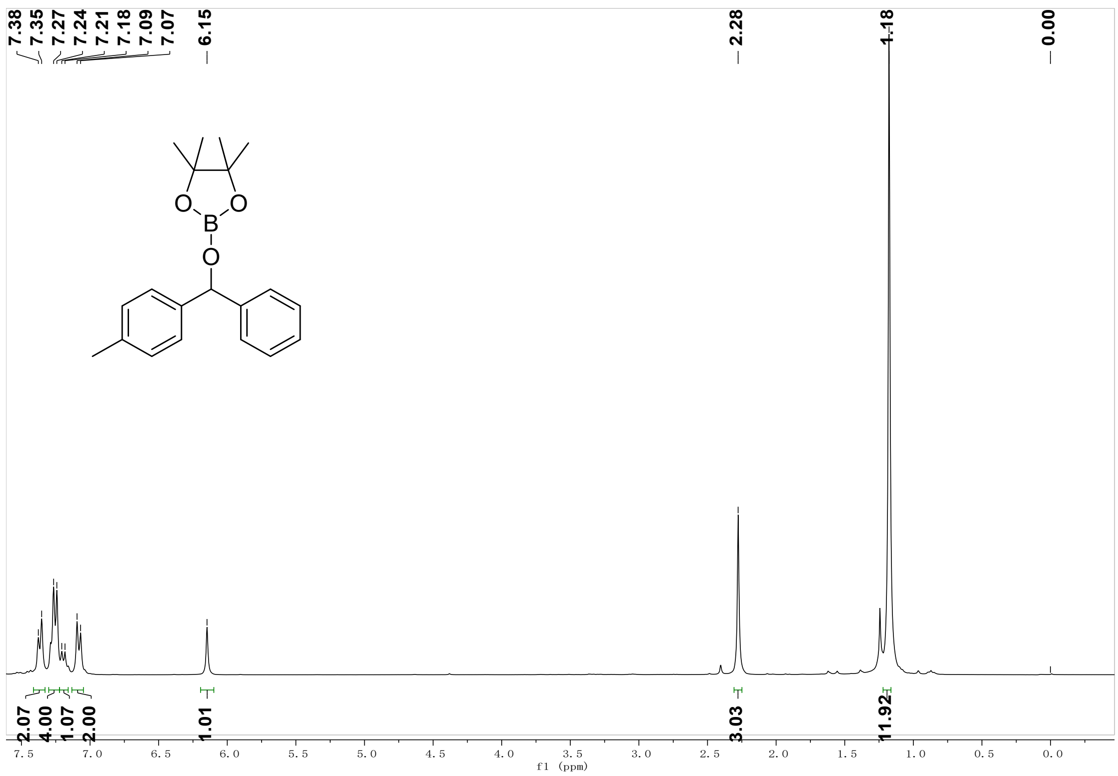


Figure S40. ^{1}H-NMR spectrum of **8l.**

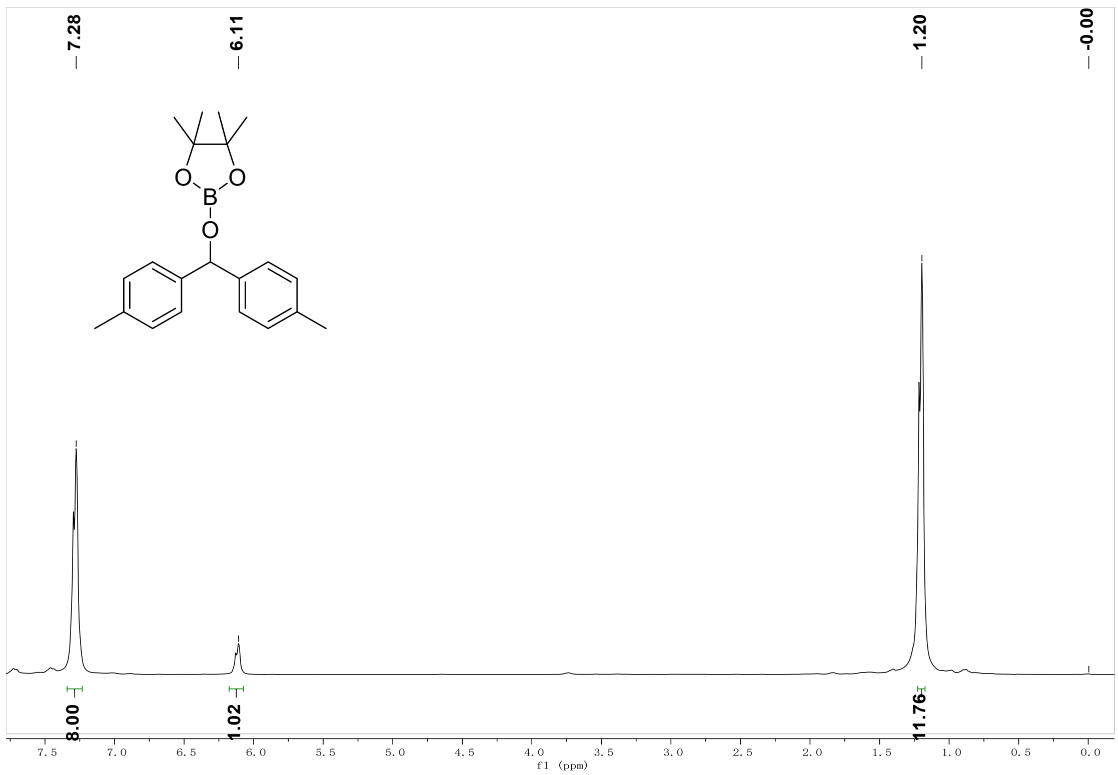


Figure S41. ^{1}H-NMR spectrum of **8m**.

6. ^{1}H-NMR spectra of the radical capture experiments

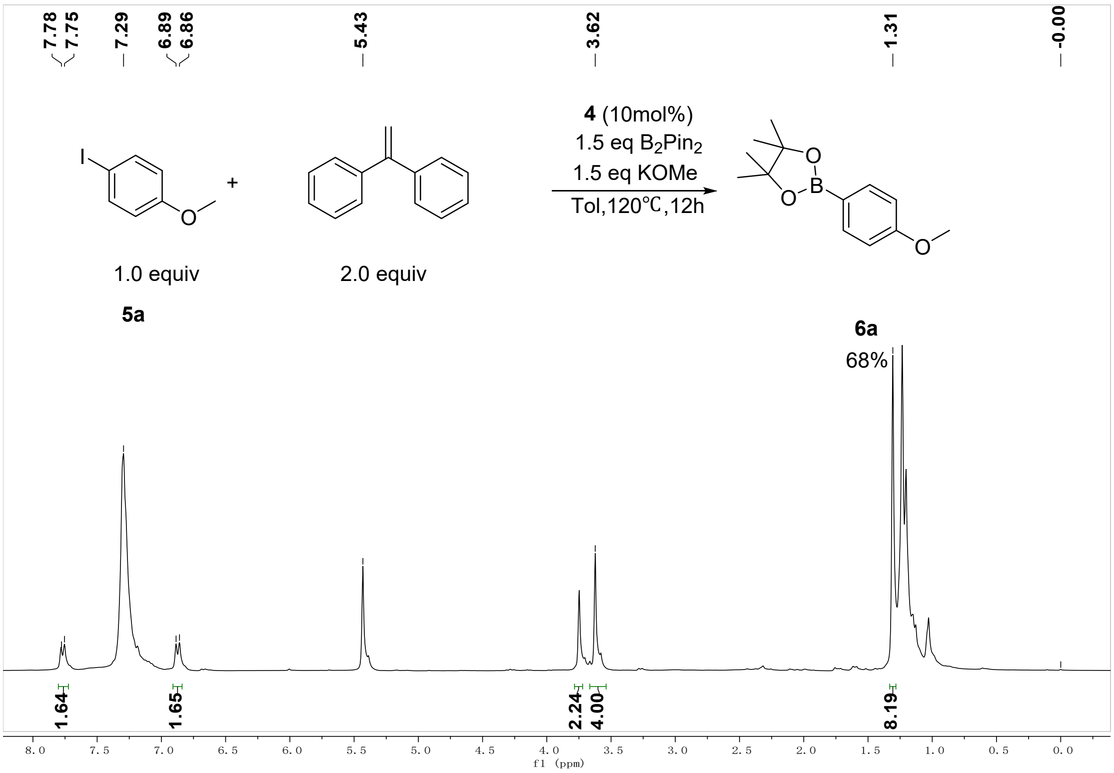


Figure S42. ^{1}H-NMR spectrum of the reaction mixture of **5a** and B_2Pin_2 catalyzed by **4** under the conditions listed in Table 3 with ethene-1,1-diyldibenzene (2 eq) as radical scavenger and using 1,2-dichloroethane as internal standard. The product **6a** was afforded in 68% yield.

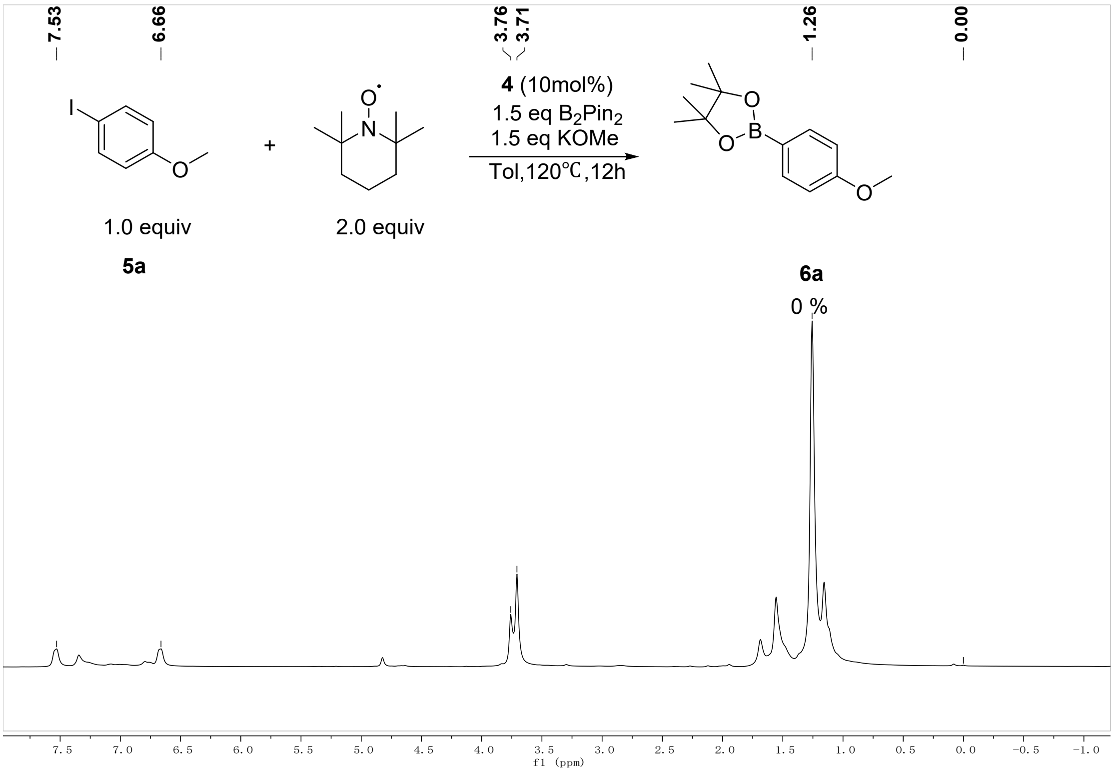
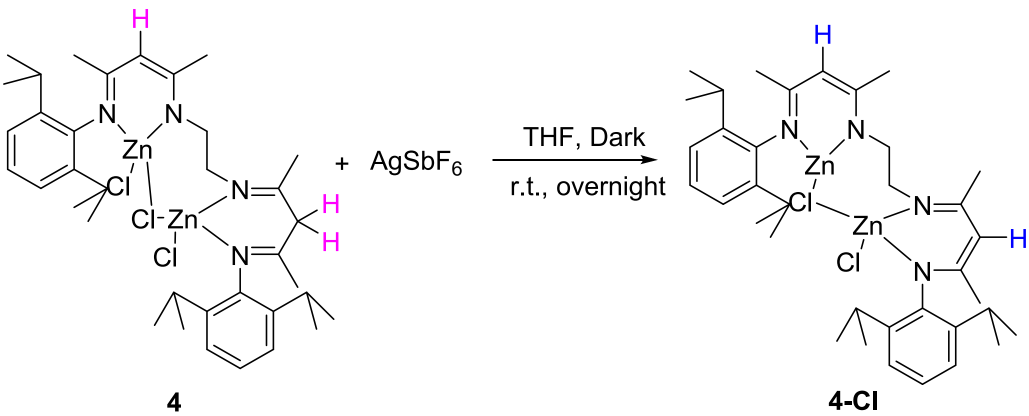


Figure S43. [1]H-NMR spectrum of the reaction mixture of **5a** and B_2Pin_2 catalyzed by **4** under the conditions listed in Table 3 with TEMPO (2 eq) as radical scavenger and using 1,2-dichloroethane as internal standard. The product **6a** was not afforded (0% yield).

7. Synthesis and catalytic performance of 4-Cl



Scheme S3. Synthesis of **4-Cl**

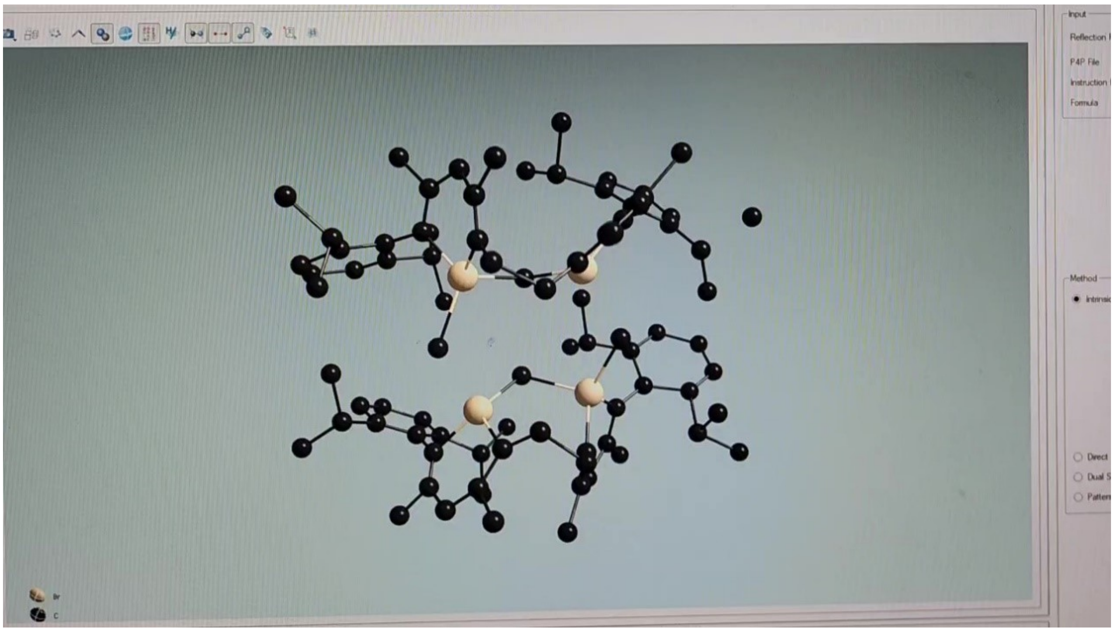


Figure S44. Fast scan structure of **4-Cl** from X-ray single crystal diffraction

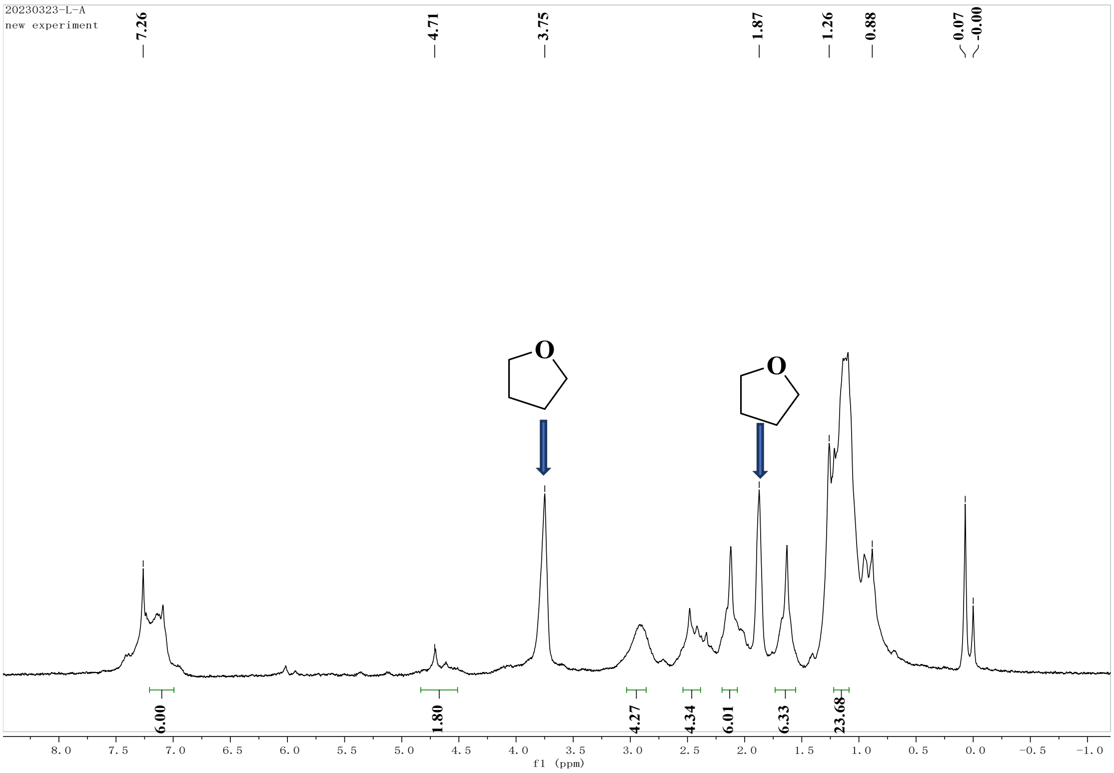


Figure S45. [1]H-NMR spectrum of **4-Cl.**

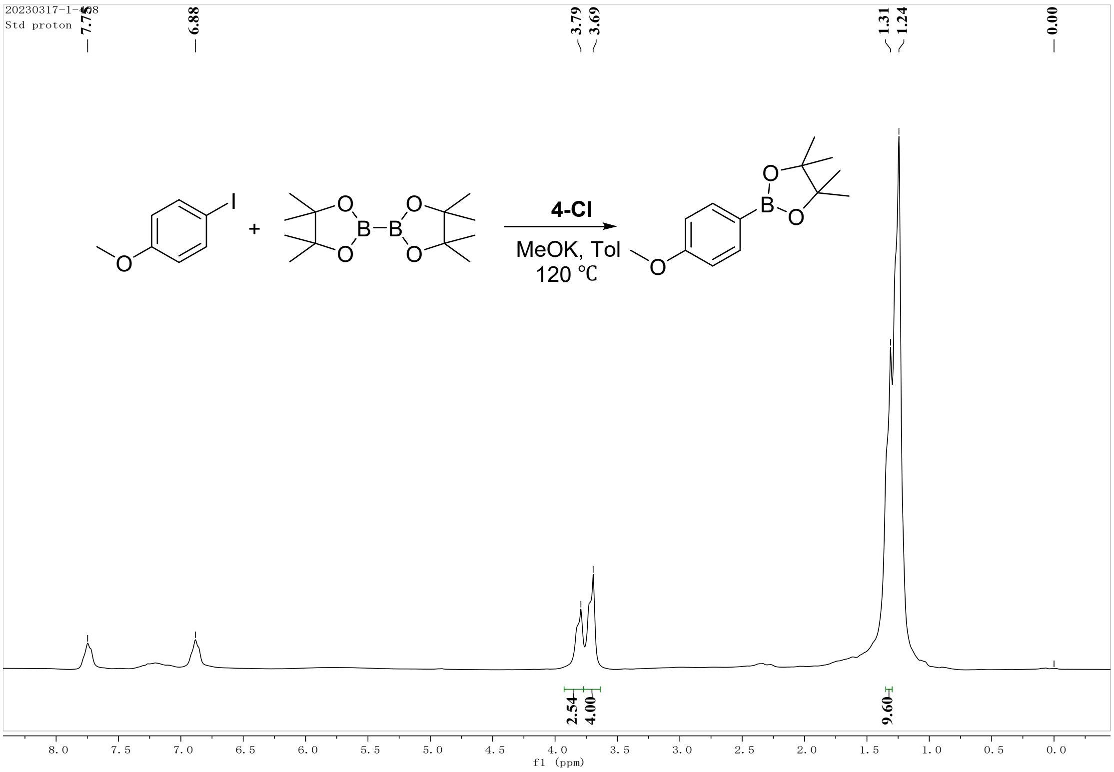
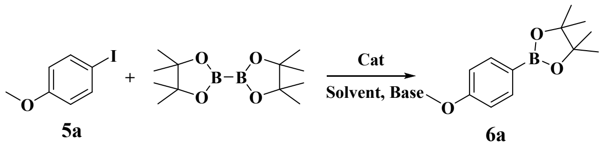


Figure S46. ^{1}H-NMR spectrum of **6a** (80%) in the un-isolated reaction mixture using 1,2-dichloroethane as internal standard.

8. Comparison of the catalytic performance of different catalysts for the hydroboration of 4-iodoanisole (5a)

Table S3. Comparison of the catalytic performance of different catalysts for the hydroboration of 4-iodoanisole (**5a**)



Cat. loading	Temperature (℃)	Time (h)	Yield （%）
10 mol% [Zn-IMes]	r.t.	12	68[1]

10 mol% [Zn- dtbpy]	50	12	48[2]
10 mol% [LZn_2Et]	75	12	82[3]
0.5 mol% [Rh(COD)Cl]$_2$	50	24	73[4]
10 mol% [ZnL^1]/ [ZnL^2]	75	12	99, 54 (^{1}H NMR yield)[5]
2.5 mol% [Co]	50	8	84[6]
10 mol% [Zn]	120	1	72 (this work)

IMes (L^1) = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) [1]
dtbpy =4,4′-di-tert-butyl-2,2′-bipyridine[2]
H_2L =N-(4-((2-((4-((2,6-diisopropylphenyl)imino)pent-2-en-2-yl)amino)ethyl)imino)pent-2-en-2-yl)-2,6-diisopropylaniline[3]
HL^1=2-(2-((((1H-pyrrol-2-yl)methylene)amino)methyl)-1H-pyrrol-1- yl)-N,N-dimethylethan-1-amine [5]
H_2L^2=N-((1H-pyrrol-2-yl)methyl)-1-(1H-pyrrol-2-yl)methanimine [5]
IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene[6]

9. References

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