Supporting Information

Magnesium(II) complexes supported by indole- and pyrrole-containing Schiff-base ligands: syntheses, structures, and applications as precatalysts in the hydroboration of nitriles and alkynes

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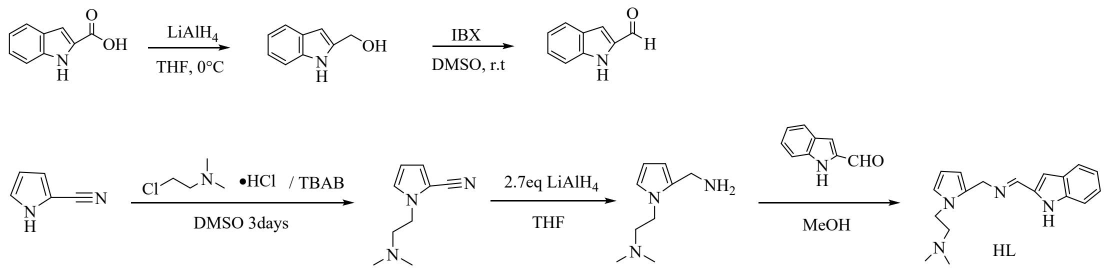
Content

1. General methods

All the reactions were carried out in a Vigor glove box filled with N_2. Grignard reagents were purchased from J&K and Macklin Chemical Company. $CDCl_3$ and C_6D_6 were dried with CaH_2 for 24 h, followed by vacuum distillation under reduced pressure. Tetrahydrofuran, toluene, and hexane were obtained by drying over sodium filaments first and then using benzophenone as an indicator for distillation under nitrogen protection. They are stored with 4 Å molecular sieves. NMR spectra were recorded by a Vnmrs-300 MHz instrument and an Agilent 600 MHz DD2 NMR spectrometer. Elemental analyses for C, H and N were performed on a PerkinElmer 2400 analyser. Crystal determinations were performed with a Bruker SMART APEX II CCDC diffractometer equipped with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) and Ga Kα radiation (λ = 1.34139).

2. Syntheses of the HL ligand



Scheme S1. Synthesis of HL

2.1 Synthesis of 1*H*-indole-2-acetaldehyde

$LiAlH_4$ (1.58 g, 41.4 mmol) was slowly added to a THF solution of 1*H*-indole-2-carboxylic acid (3.22 g, 20 mmol) at 0 °C and stirred for 15 minutes. After the mixture was warmed to room temperature, it was stirred for 3 hours, and the reaction process was monitored by TLC. Then the reaction was quenched with 2M NaOH at 0 °C, and extracted with ethyl acetate. The organic phase was dried with anhydrous sodium sulfate, and the solvent was removed under vacuum to obtain (1*H*-indol-2-yl)methanol as a brown solid. (1*H*-indol-2-yl)methanol (2.03 g, 13.8 mmol) was dissolved in 30 mL of dimethyl sulfoxide. 2-Iodoxybenzoic acid (4.637 g, 16.6 mmol) was added to the mixture, and the reaction was stirred at 25 °C for 10 hours. The reaction process was monitored by TLC. Then, a large amount of water was added. The resultant mixture was extracted with ethyl acetate and dried with anhydrous sodium sulfate. After vacuum removal of the volatile substances, the crude product was purified via column chromatography using EA/PE as the eluent (PE/EA = 20:1). The product was obtained as a white solid.

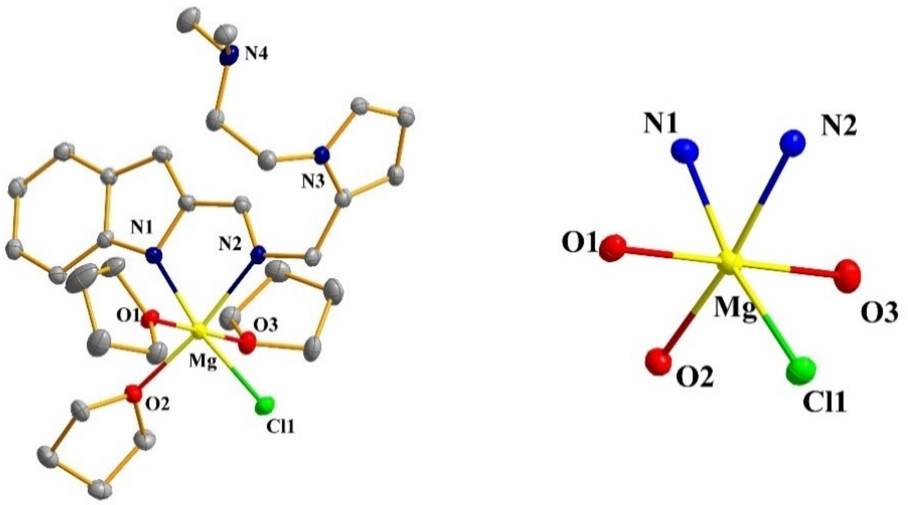
2.2 Synthesis of IN

Compound **IN** (**IN** = 2-(2-(aminomethyl)-1*H*-pyrrol-1-yl)-*N*,*N*-dimethylethan-1 -amine) was prepared following the reported procedure.[S1]

2.3 Synthesis of the HL ligand

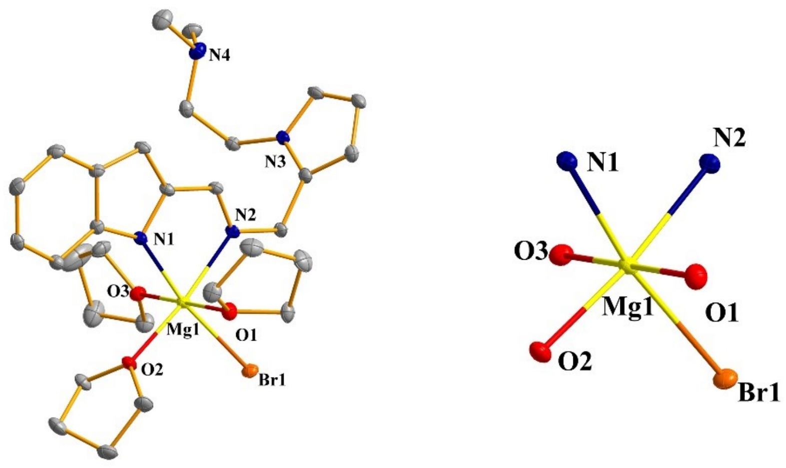
A MeOH solution of **IN** (0.8357 g, 5 mmol) was added to a MeOH (20 mL) solution of 1*H*-indole-2-carbaldehyde (0.7258 g, 5 mmol) at room temperature. After the reaction mixture was stirred for 24 h (Scheme 1), the volatiles were removed by vacuum distillation to obtain a brown oily crude product. The crude product was washed with hexane and ethyl acetate to give a brown powder. The yield was 1.36 g (93%). Anal. Calcd for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03. Found: C, 72.81; H, 7.71; N, 18.93.

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. Selected Bond Lengths [Å] and Angles [°] for Complex 1

	Selected Bond Length(Å)		
Cl1–Mg1	2.4052(18)	Mg1–N2	2.205(4)
Mg1–O3	2.152(3)	N1–C1	1.373(5)
Mg1–O2	2.192(3)	N1–C8	1.375(5)
Mg1–O1	2.110(3)	N2–C9	1.285(5)
Mg1–N1	2.137(4)	N2–C10	1.478(5)
	Selected Angles(°)		
O3–Mg1–Cl1	92.13(10)	N1–Mg1–O1	94.20(14)
O3–Mg1–O1	89.15(13)	N1–Mg1–N2	78.21(14)
O3–Mg1–N2	89.28(14)	N2–Mg1–Cl1	93.48(11)
O2–Mg1–Cl1	89.06(10)	C8–N1–Mg1	111. 1(3)
O2–Mg1–O3	178.72(13)	C9–N2–Mg1	111.7(3)
O2–Mg1–O1	90.28(13)	C9–N2–C10	120.6(4)
O2–Mg1–N1	87.72(14)	C10–N2–Mg1	127.6(3)
O2–Mg1–N2	91.14(14)	N1–C8–C9	118.6(4)
O1–Mg1–Cl1	94.20(11)	C7–C8–N1	113.5(4)
O1–Mg1–N2	172.21(14)	C7–C8–C9	127.8(4)
N1–Mg1–Cl1	171.02(12)	N2–C9–C8	119.7(4)
N1–Mg1–O3	91.18(4)		

Table S2. Selected Bond Lengths [Å] and Angles [°] for Complex 2

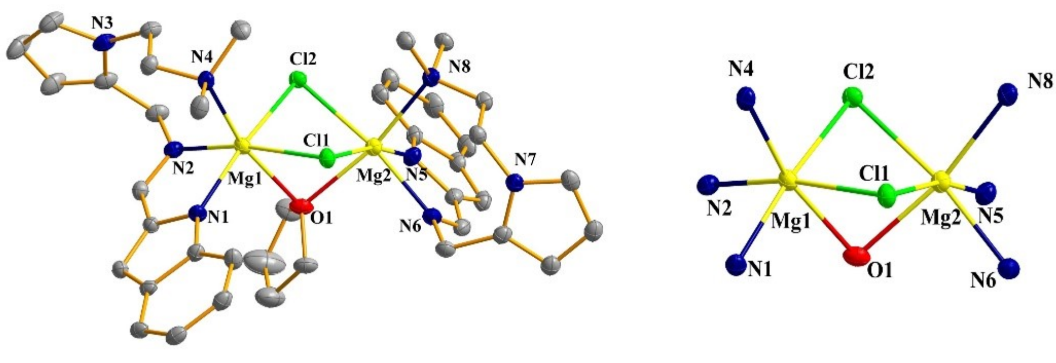
Selected Bond Length(Å)

Br1–Mg1	2.5867(15)	Mg1–N2	2.202(4)
Mg1–O3	2.192(3)	N1–C1	1.368(5)
Mg1–O2	2.107(4)	N1–C8	1.377(6)
Mg1–O1	2.164(3)	N2–C9	1.281(6)
Mg1–N1	2.116(4)	N2–C10	1.473(6)
	Selected Angles(°)		
O3–Mg1–Br1	88.10(10)	N1–Mg1–O1	91.82(14)
O3–Mg1–O1	179.34(15)	N1–Mg1–N2	78.53(14)
O3–Mg1–N2	90.96(15)	N2–Mg1–Br1	93.51(11)
O2–Mg1–Br1	93.02(10)	C8–N1–Mg1	111.4(3)
O2–Mg1–O3	90.44(14)	C9–N2–Mg1	111.6(3)
O2–Mg1–O1	89.63(14)	C9–N2–C10	120.4(4)
O2–Mg1–N1	95.05(14)	C10–N2–Mg1	127.9(3)
O2–Mg1–N2	173.36(15)	N1–C8–C9	118.5(4)
O1–Mg1–Br1	92.55(10)	N1–C8–C7	113.3(4)
O1–Mg1–N2	88.90(14)	C7–C8–C9	128.3(4)
N1–Mg1–Br1	170.84(12)	N2–C9–C8	119.5(4)
N1–Mg1–O3	87.51(14)		

Table S3. Crystallographic Data and Structure Refinement for Compounds 1 and 2

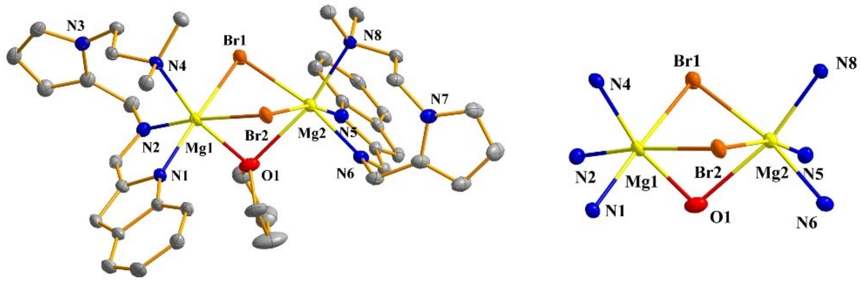
	1	**2**
Empirical formula	$C_{30}H_{45}ClMgN_4O_3$	$C_{30}H_{45}BrMgN_4O_3$
Formula weight	569.46	613.92
Temperature [K]	223.0	223.0
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	17.8805(6)	18.0348(7)
b [Å]	10.8261(4)	10.8915(4)
c [Å]	17.4012(6)	17.4378(6)
α [°]	90	90
β [°]	113.5430(10)	113.6190(10)
γ [°]	90	90
Volume [Å^3]	3088.07(19)	3138.3(2)
Z	4	4

ρ_{calc} [gcm^{-3}]	1.225	1.299
μ [mm^{-1}]	0.180	1.366
F(000)	1224	1296
Crystal size [mm^3]	0.40×0.20×0.16	0.20×0.16×0.10
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2θ range [°]	4.55 to 55.00 (0.77 Å)	4.53 to 50.70 (0.83 Å)
Index ranges	$-23 \le h \le 23$ $-14 \le k \le 13$ $-22 \le l \le 22$	$-21 \le h \le 21$ $-13 \le k \le 13$ $-21 \le l \le 21$
Reflections collected	39925	32043
Independent reflections	7071 R_{int} = 0.0816 R_{sigma} = 0.0584	5733 R_{int} = 0.0933 R_{sigma} = 0.0626
Data / Restraints / Parameters	7071/31/391	5653/0/355
Goodness-of-fit on F^2	1.004	0.964
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0817 wR_2 = 0.1939	R_1 = 0.0487 wR_2 = 0.1215
Final R indexes [all data]	R_1 = 0.1713 wR_2 = 0.2839	R_1 = 0.1091 wR_2 = 0.1835
Largest peak/hole [eÅ^{-3}]	0.48/−0.47	0.86/−0.55



(a) (b)

Figure S3. (a) Molecular structure of **3**·0.2Tol 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**·0.2Tol.



(a) (b)

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

Table S4. Selected Bond Lengths [Å] and Angles [°] for Complex 3·0.2Tol

	Selected Bond Length(Å)		
Cl2–Mg1	2.5013(17)	Mg2–N6	2.195(4)
Cl2–Mg2	2.4916(16)	Mg2–N8	2.267(4)
Cl1–Mg1	2.4797(16)	N1–C8	1.389(5)
Cl1–Mg2	2.4730(17)	N1–C1	1.373(5)
Mg1–O1	2.317(3)	N2–C9	1.284(5)
Mg1–N4	2.304(4)	N2–C10	1.487(5)
Mg1–N1	2.096(4)	N5–C26	1.383(5)
Mg1–N2	2.213(4)	N5–C19	1.374(5)
Mg2–O1	2.452(3)	N6–C27	1.288(5)
Mg2–N5	2.082(3)	N6–C28	1.490(5)
	Selected Angles(°)		
Mg2–Cl2–Mg1	81.11(5)	N5–Mg2–N6	78.97(13)
Mg2–Cl1–Mg1	81.91(5)	N5–Mg2–N8	97.15(13)
Cl1–Mg1–Cl2	86.99(5)	N6–Mg2–Cl2	93.40(10)
O1–Mg1–Cl2	78.50(8)	N5–Mg2–Cl2	165.46(12)
O1–Mg1–Cl1	79.08(8)	N5–Mg2–Cl1	97.66(11)
N4–Mg1–Cl2	92.56(10)	N5–Mg2–O1	91.57(12)
N4–Mg1–Cl1	92.35(9)	N6–Mg2–Cl1	168.38(11)
N4–Mg1–O1	167.84(13)	N6–Mg2–O1	92.18(12)
N1–Mg1–Cl2	100.79(11)	N6–Mg2–N8	98.31(13)
N1–Mg1–Cl1	167.43(12)	N8–Mg2–Cl2	96.19(10)
N1–Mg1–O1	92.70(13)	N8–Mg2–Cl1	93.13(10)
N1–Mg1–N4	97.10(13)	N8–Mg2–O1	167.45(12)
N1–Mg1–N2	78.47(14)	Mg1–O1–Mg2	85.75(10)
N2–Mg1–Cl2	171.26(11)	C27–N6–Mg2	111.2(3)
N2–Mg1–Cl1	92.34(11)	C27–N6–C28	116.1(3)
N2–Mg1–O1	92.81(12)	C28–N6–Mg2	132.6(3)
N2–Mg1–N4	96.17(13)	C9–N2–Mg1	110.9(3)

Cl1–Mg2–Cl2	87.35(5)	C9–N2–C10	115.8(4)
O1–Mg2–Cl2	76.23(8)	C10–N2–Mg1	133.0(3)
O1–Mg2–Cl1	76.71(8)		

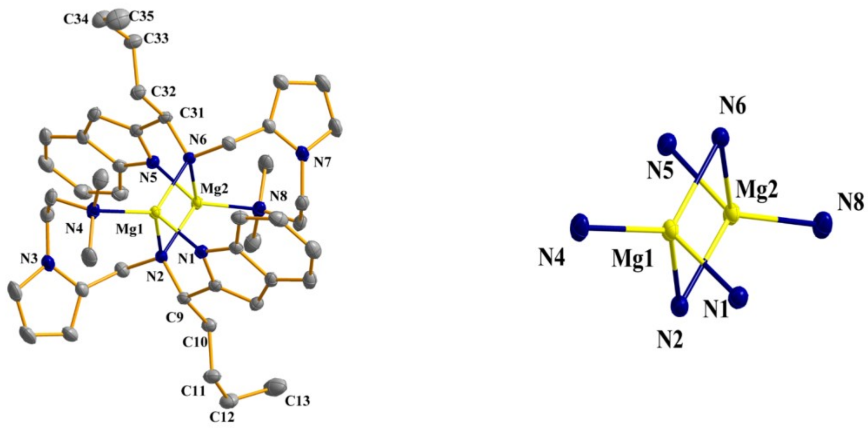
Table S5. Selected Bond Lengths [Å] and Angles [°] for Complex 4

Selected Bond Length(Å)			
Br2–Mg1	2.6791(8)	Mg2–N5	2.100(2)
Br2–Mg2	2.6823(8)	Mg2–N6	2.207(2)
Br1–Mg1	2.6359(8)	N1–C1	1.374(3)
Br1–Mg2	2.6582(8)	N1–C8	1.379(3)
Mg1–O1	2.552(2)	N2–C9	1.284(3)
Mg1–N4	2.261(2)	N2–C10	1.490(3)
Mg1–N2	2.193(2)	N5–C26	1.383(3)
Mg1–N1	2.085(2)	N5–C19	1.372(3)
Mg2–O1	2.3227(19)	N6–C27	1.289(3)
Mg2–N8	2.322(2)	N6–C28	1.491(3)
Selected Angles(°)			
Mg2–Br2–Mg1	79.20(2)	N8–Mg2–Br2	91.74(6)
Mg2–Br1–Mg1	80.41(2)	N8–Mg2–Br1	91.77(5)
Br1–Mg1–Br2	87.53(2)	N8–Mg2–O1	167.68(8)
O1–Mg1–Br2	75.57(4)	N5–Mg2–Br2	100.26(6)
O1–Mg1–Br1	76.01(5)	N5–Mg2–Br1	168.13(7)
O1–Mg1–N4	166.52(7)	N5–Mg2–O1	93.08(8)
N4–Mg1–Br2	95.98(6)	N5–Mg2–N8	96.88(8)
N4–Mg1–Br1	93.45(6)	N5–Mg2–N6	78.76(8)
N2–Mg1–Br2	92.36(6)	N6–Mg2–Br2	172.66(6)
N2–Mg1–Br1	167.97(6)	N6–Mg2–Br1	92.36(6)
N2–Mg1–O1	92.44(7)	N6–Mg2–O1	93.44(7)
N2–Mg1–N4	98.47(8)	N6–Mg2–N8	95.60(8)
N1–Mg1–Br2	164.76(7)	Mg1–O1–Mg2	88.91(6)
N1–Mg1–Br1	97.65(6)	C9–N2–Mg1	111.28(16)
N1–Mg1–O1	92.03(7)	C9–N2–C10	115.3(2)
N1–Mg1–N4	97.76(8)	C10–N2–Mg1	133.36(16)
N1–Mg1–N2	79.13(8)	C27–N6–Mg2	110.75(16)
Br1–Mg2–Br2	87.53(2)	C27–N6–C28	115.3(2)
O1–Mg2–Br2	79.33(5)	C28–N6–Mg2	133.71(16)
O1–Mg2–Br1	79.48(5)		

Table S6. Crystallographic Data and Structure Refinement for Complexes 3·0.2Tol and 4

	3·0.2Tol	**4**
Empirical formula	$C_{41.40}H_{51.60}Cl_2Mg_2N_8O$	$C_{40}H_{50}Br_{1.86}Mg_2N_8O$
Formula weight [g mol^{-1}]	796.82	855.73
Temperature [K]	100.0	150.0
Crystal system	monoclinic	monoclinic
Space group	$P2_1$/c (14)	$P2_1$/c (14)
a/Å	9.4870(4)	9.4766(4)
b/Å	13.7899(7)	13.9573(5)
c/Å	31.3556(14)	31.4956(11)
α/°	90	90
β/°	95.8020(10)	95.9610(10)
γ/°	90	90
Volume/Å^3	4081.1(3)	4143.1(3)
Z	4	4
ρ_{calc}g/cm^3	1.267	1.372
μ/mm^{-1}	0.232	1.888
F(000)	1648	1772
Crystal size/mm^3	0.04×0.03×0.02	0.04×0.03×0.02
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	4.81 to 52.74 (0.80 Å)	5.22 to 53.07 (0.77 Å)
Index ranges	$-10 \leq h \leq 11$ $-17 \leq k \leq 17$ $-34 \leq l \leq 39$	$-11 \leq h \leq 11$ $-17 \leq k \leq 17$ $-39 \leq l \leq 39$
Reflections collected	56481	117735
Independent reflections	8320 R_{int} = 0.1186 R_{sigma} = 0.0757	8523 R_{int} = 0.0919 R_{sigma} = 0.0367
Data/restraints/parameters	8320/6/485	8523/14/502

Goodness-of-fit on F^2	1.049	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0749 wR_2 = 0.1662	R_1 = 0.0332 wR_2 = 0.0734
Final R indexes [all data]	R_1 = 0.1209 wR_2 = 0.1943	R_1 = 0.0503 wR_2 = 0.0816
Largest diff. peak/hole / e Å^{-3}	1.08/−0.70	0.39/−0.31



(a) (b)

Figure S5. (a) Molecular structure of **5** from X-ray diffraction. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) Core structure of complex **5**.

Table S7. Selected Bond Lengths [Å] and Angles [°] for Complex 5

Selected Bond Length(Å)			
Mg1–N6	2.086(2)	Mg2–N8	2.126(3)
Mg1–N2	2.107(2)	N6–C31	1.497(3)
Mg1–N1	2.020(2)	N6–C32	1.481(3)
Mg1–N4	2.133(3)	N2–C9	1.491(3)
Mg2–N6	2.094(2)	N2–C14	1.485(4)
Mg2–N2	2.079(2)	C9–C10	1.533(4)
Mg2–N5	2.017(2)	C31–C32	1.536(4)
Selected Angles(°)			
N6–Mg1–N2	95.64(9)	Mg1–N6–Mg2	84.13(9)
N6–Mg1–N4	125.24(10)	C31–N6–Mg1	123.13(17)
N2–Mg1–N4	122.21(10)	C31–N6–Mg2	105.79(17)
N1–Mg1–N6	109.04(10)	C36–N6–Mg1	111.27(17)
N1–Mg1–N2	86.37(10)	C32–N6–Mg2	120.85(14)
N1–Mg1–N4	111.19(10)	C36–N6–Mg2	121.29(18)

N6–Mg2–N8	119.76(10)	Mg2–N2–Mg1	83.97(9)
N2–Mg2–N6	96.24(9)	C9–N2–Mg1	106.03(17)
N2–Mg2–N8	127.51(10)	C9–N2–Mg2	122.63(17)
N5–Mg2–N6	86.27(10)	C14–N2–Mg1	120.59(18)
N5–Mg2–N2	107.56(10)	C14–N2–Mg2	112.55(17)
N5–Mg2–N8	111.36(10)	C14–N2–C9	109.6(2)

Table S8. Crystallographic Data and Structure Refinement for Complex 5

Empirical formula	$C_{44}H_{60}Mg_2N_8$
Formula weight [g mol^{-1}]	749.62
Temperature [K]	223.00(10)
Crystal system	monoclinic
Space group	$P2_1$/n (14)
a/Å	13.0809(6)
b/Å	15.1297(7)
c/Å	20.6694(10)
α/°	90
β/°	92.944(2)
γ/°	90
Volume/Å^3	4085.3(3)
Z	4
ρ_{calc}g/cm^3	1.219
μ/mm^{-1}	0.101
F(000)	1616
Crystal size/mm^3	0.15×0.13×0.12
Radiation	MoK_α (λ=0.71073 Å)
2Θ range for data collection/°	4.50 to 55.08 (0.83 Å)
Index ranges	$-17 \le h \le 17$ $-19 \le k \le 19$ $-26 \le l \le 26$
Reflections collected	89160
Independent reflections	9397 R_{int} = 0.0955 R_{sigma} = 0.0557
Data/restraints/parameters	9397/83/522
Goodness-of-fit on F^2	1.113

Final *R* indexes [I>=2σ (I)]	R_1 = 0.0832 wR_2 = 0.1505
Final *R* indexes [all data]	R_1 = 0.1402 wR_2 = 0.1759
Largest diff. peak/hole / e Å^{-3}	0.34/−0.24

4. SHAPE program details for 1, 2, 3·0.2Tol, 4, and 5

Table S9 . Shape analysis of the six-coordinate Mg^{II} ions of complexes 1, 2, 3·0.2Tol, and 4.

Agreement factor for Mg^{II} ions in complexes	*HP*-6	*PPY*-6	*OC*-6	*TPR*-6	*JPPY*-6
Mg^{II} in **1**	32.181	27.071	0.546	14.694	30.672
Mg^{II} in **2**	32.378	26.878	0.864	14.857	30.279
Mg1^{II} in **3**·0.2Tol	31.338	25.294	1.098	14.777	29.271
Mg2^{II} in **3**·0.2Tol	31.339	25.296	1.096	14.777	29.273
Mg1^{II} in **4**	31.698	25.264	1.308	14.845	29.697
Mg2^{II} in **4**	31.818	25.391	1.412	14.437	29.898

HP-6(D_{6h})= hexagon, *PPY*-6(C_{5v})= pentagonal pyramid, *OC*-6(O_h)= octahedron, *TPR*-6(D_{3h})= trigonal prism, *JPPY*-6(C_{5v})= Johnson pentagonal pyramid.

Table S10 .Shape analysis of the four-coordinate Mg^{II} ions in complex 5

Agreement factor for Mg^{II} ions in complexes	*SP*-4	*T*-4	*SS*-4
Mg1^{II} in **5**	27.476	2.433	7.347
Mg2^{II} in **5**	28.914	2.371	7.377

SP-4(D_{4h})= square, *T*-4(T_d)= tetrahedron, *SS*-4(C_{2v})= seesaw or sawhorse.

5. Characterization data

5.1. Characterization data of the ligand and compounds.

[HL]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.25 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 7.1 Hz, 1H), 7.09 (t, J = 7.3 Hz, 1H), 6.75 (s, 1H), 6.70 (s, 1H), 6.12 (s, 2H), 4.78 (s, 2H), 4.08 (t, J = 7.1 Hz, 2H), 2.62 (t, J = 7.1 Hz, 2H), 2.24 (s, 6H).^{13}C NMR (151 MHz, $CDCl_3$) δ 152.93, 137.09, 135.23, 129.35, 128.08, 124.42, 121.79, 121.65, 120.10, 77.27, 77.06, 76.85, 60.51, 55.48, 45.76, 45.43. Anal. Calcd for $C_{18}H_{22}N_4$: C, 73.44; H, 7.53; N, 19.03.

[(L)MgCl(THF)$_3$] (1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (s, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.61-7.53 (m, 1H), 7.18-7.11 (m, 1H), 6.90 (t, *J*=7.3 Hz, 1H), 6.80 (s, 1H), 6.56 (s, 1H), 6.12 (s, 1H), 6.06 (s, 1H), 4.85 (s, 2H), 4.48 (s, 2H), 3.69 (s, 12H), 2.47 - 2.38 (m, 2H), 2.31 (s, 6H), 1.71 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.10, 148.03, 141.64, 131.51, 131.07, 123.16, 121.53, 121.08, 117.80, 117.52, 109.37, 108.07, 107.65, 68.22, 61.68, 49.99, 46.97, 44.85, 25.29. Anal. Calcd for $C_{30}H_{45}ClMgN_4O_3$: C, 63.27; H, 7.97; N, 9.84. Found: C, 76.15; H, 9.10; N, 8.43.

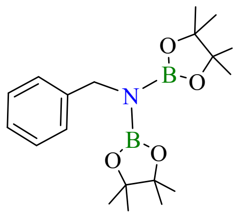
[(L)MgBr(THF)$_3$](2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.91 (s, 1H), 6.83 (s, 1H), 6.58 (s, 1H), 6.13 - 5.98 (m, 2H), 4.89 (s, 2H), 4.46 (s, 2H), 3.79 (s, 12H), 2.55 (t, *J* = 5.5 Hz, 2H), 2.32 (s, 6H), 1.79 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.73, 147.45, 141.97, 131.57, 130.51, 123.10, 121.70, 121.13, 117.83, 116.77, 109.38, 108.34, 107.81, 68.46, 61.40, 50.83, 46.74, 45.06, 25.36. Anal. Calcd for $C_{30}H_{45}BrMgN_4O_3$: C, 58.69; H, 7.39; N, 9.13. Found: C, 58.43; H, 7.43; N, 9.76.

[(L)$_2$Mg$_2$Cl$_2$THF] (3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.84 (s, 1H), 6.54 (s, 1H), 6.11 (s, 1H), 6.07 (t, *J* = 3.1 Hz, 1H), 4.82 (s, 2H), 4.43 (s, 2H), 3.58 (s, 2H), 2.46 (t, *J* = 6.3 Hz, 2H), 2.24 (s, 6H), 1.43 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ 156.59, 137.02, 132.48, 130.56, 126.15, 122.95, 122.09, 121.20, 117.00, 114.29, 109.43, 108.28, 105.23, 67.98, 58.77, 58.11, 45.72, 44.84, 25.63. Anal. Calcd for $C_{40}H_{50}Cl_2Mg_2N_8O$: C, 61.72; H, 6.47; N, 14.4. Found: C, 61.54; H, 6.78; N, 14.42.

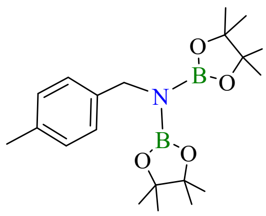
[(L)$_2$Mg$_2$Br$_2$THF] (4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.98 (s, 1H), 7.62 (s, 1H), 7.17 (s, 1H), 6.88 (d, *J* = 13.8 Hz, 2H), 6.55 (s, 1H), 6.10 (d, *J* = 9.2 Hz, 2H), 4.83 (s, 2H), 4.42 (s, 2H), 3.63 (s, 2H), 2.48 (s, 2H), 2.23 (s, 6H), 1.57 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.61, 137.07, 132.50, 130.60, 126.21, 122.97, 122.14, 121.22, 117.03, 114.36, 109.46, 108.31, 105.28, 68.00, 58.80, 58.13, 45.73, 44.86, 25.65. Anal. Calcd for $C_{40}H_{50}Br_2Mg_2N_8O$: C, 55.39; H, 5.81; N, 12.92. Found: C, 55.75; H, 5.86; N, 12.69.

$[(L1)_2Mg_2]$ (5). ^1H NMR (300 MHz, DMSO-d_6) δ 7.51 (d, J = 42.5 Hz, 1H), 7.26 (s, 1H), 6.70 (s, 1H), 6.62 (s, 2H), 6.04 (s, 1H), 5.90 (d, J = 8.6 Hz, 2H), 3.90 (s, 2H), 3.68-3.47 (m, 2H), 2.30 (s, 1H), 2.13 (s, 2H), 1.96 (d, J = 31.1 Hz, 6H), 1.56 (s, 2H), 1.05 (s, 4H), 0.80 - 0.60 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 136.49, 128.40, 121.34, 120.92, 119.91, 119.11, 110.93, 108.15, 106.81, 101.07, 61.16, 57.31, 45.83, 45.64, 43.43, 37.06, 28.44, 22.61, 13.96. Anal. Calcd for $C_{44}H_{60}Mg_2N_8$: C, 70.50; H, 8.07; N, 14.95. Found: C, 70.56; H, 8.54; N, 14.70.

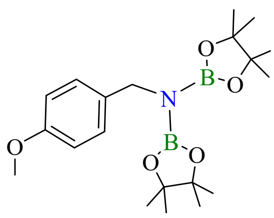
5.2. NMR spectroscopic data of diborylamines **7a**-**7s**.



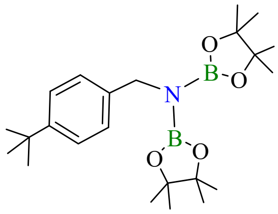
Yield: 99% (**7a**)[S2]. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 7.4 Hz, 2H), 7.12 (d, J = 7.5 Hz, 2H), 7.06 (d, J = 7.1 Hz, 1H), 4.14 (s, 2H), 1.09 (s, 24H).



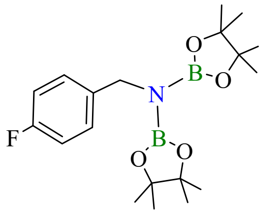
Yield: 72% (**7b**)[S2]. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.10 (m, 2H), 6.95 (d, J = 7.5 Hz, 2H), 4.11 (s, 2H), 2.20 (s, 3H), 1.10 (s, 24H).



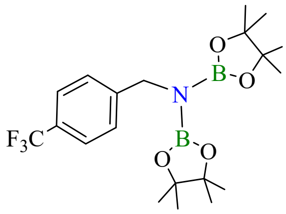
Yield: 99% (**7c**). ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.3 Hz, 2H), 6.77 (d, J = 8.3 Hz, 2H), 4.15 (s, 2H), 3.76 (s, 3H), 1.19 (s, 24H).



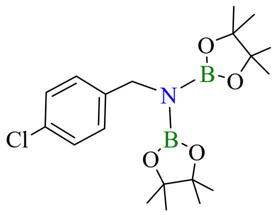
Yield: 99% (**7d**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 4H), 4.10 (s, 2H), 1.20 (d, *J* = 4.1 Hz, 12H), 1.10 (s, 24H).



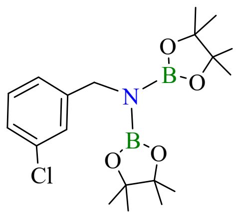
Yield: 99% (**7e**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 8.2, 5.4 Hz, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 4.16 (s, 2H), 1.18 (s, 24H).



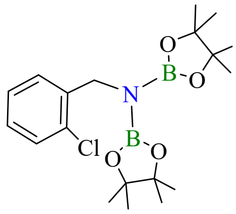
Yield: 99% (**7f**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 2H), 7.43 (s, 2H), 4.29 (s, 2H), 1.20 (s, 24H).



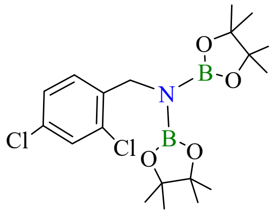
Yield: 99% (**7g**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14 (s, 4H), 4.09 (s, 2H), 1.09 (s, 24H).



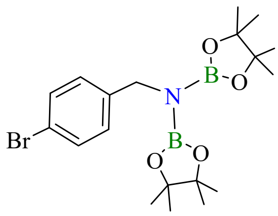
Yield: 99% (**7h**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.07 (s, 3H), 4.10 (s, 2H), 1.10 (s, 24H).



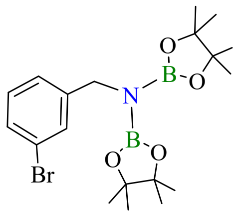
Yield: 99% (**7i**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.6 Hz, 1H), 4.25 (s, 2H), 1.07 (s, 24H).



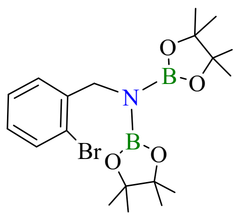
Yield: 99% (**7j**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.10 (s, 2H), 4.20 (s, 2H), 1.10 (s, 24H).



Yield: 99% (**7k**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.08 (s, 2H), 1.10 (s, 24H).

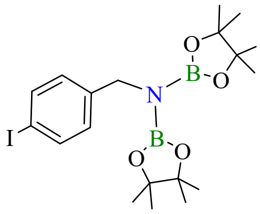


Yield: 99% (**7l**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.25 – 7.07 (m, 2H), 7.00 (t, *J* = 7.9 Hz, 1H), 4.07 (d, *J* = 9.4 Hz, 2H), 1.08 (d, *J* = 9.7 Hz, 24H).

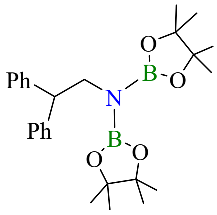


Yield: 99% (**7m**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.25-7.07 (m, 2H), 7.00 (t, *J* = 7.9 Hz, 1H), 4.07 (d, *J* = 9.4 Hz, 2H), 1.08 (d, *J* = 9.7 Hz, 24H). δ 7.42 (dd,

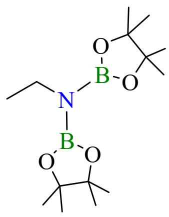
J = 19.0, 7.8 Hz, 1H), 7.20 (d, J = 22.3 Hz, 2H), 7.08 – 6.92 (m, 1H), 4.28 (d, J = 8.2 Hz, 2H), 1.15 (d, J = 8.7 Hz, 24H).



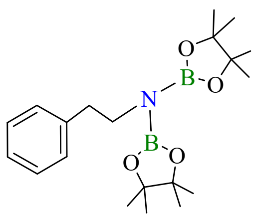
Yield: 99% (**7n**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 – 7.39 (m, 2H), 6.98 (s, 2H), 4.07 (s, 2H), 1.10 (s, 24H).



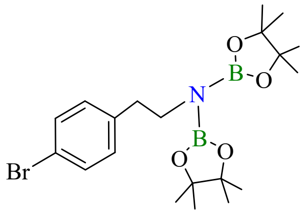
Yield: 65% (**7o**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.31 (m, 10H), 4.37 (t, J = 8.0 Hz, 1H), 3.84 (d, J = 8.0 Hz, 2H), 1.26 (s, 24H).



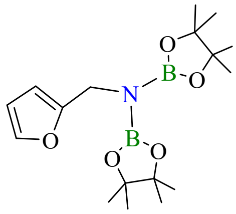
Yield: 67% (**7p**)[S4]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (t, J = 6.7 Hz, 2H), 1.16 (d, J = 5.4 Hz, 24H), 0.95 (t, J = 6.8 Hz, 3H).



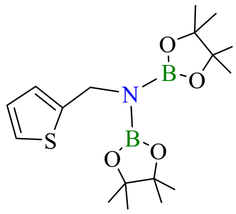
Yield: 99% (**7q**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (t, J = 7.2 Hz, 2H), 7.10 (s, 1H), 7.06 (d, J = 8.0 Hz, 2H), 3.21 (t, J = 7.0 Hz, 2H), 2.63 (t, J = 7.2 Hz, 2H), 1.08 (s, 24H).



Yield: 54% (**7r**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 6.9 Hz, 2H), 1.25 (s, 24H).

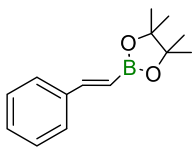


Yield: 99% (**7s**)[S3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (s, 1H), 6.20 (s, 1H), 6.10 – 5.96 (m, 1H), 4.19 (d, *J* = 8.8 Hz, 2H), 1.20 (d, *J* = 11.4 Hz, 24H).

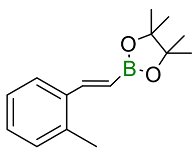


Yield: 99% (**7t**)[S2]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 5.0 Hz, 1H), 6.90 – 6.65 (m, 2H), 4.28 (s, 2H), 1.13 (d, *J* = 8.8 Hz, 24H).

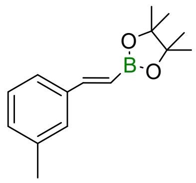
5.3. NMR spectroscopic data of vinylboranes **9a-9s.**



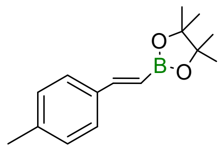
Yield: 99% (**9a**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.73 (d, *J* = 18.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 6.8 Hz, 3H), 6.43 (d, *J* = 18.3 Hz, 1H), 1.12 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.53, 137.47, 128.91, 128.58, 127.06, 83.32, 24.82.



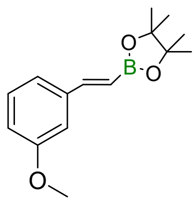
Yield: 81% (**9b**). ^{1}H NMR (300 MHz, C_6D_6) δ 8.03 (d, *J* = 18.3 Hz, 1H), 7.56 (d, *J* = 4.4 Hz, 1H), 7.04 – 6.95 (m, 2H), 6.89 (d, *J* = 4.9 Hz, 1H), 6.42 (d, *J* = 18.3 Hz, 1H), 2.11 (s, 3H), 1.12 (s, 12H).^{13}C NMR (151 MHz, C_6D_6) δ 147.36, 136.69, 136.07, 130.33, 128.48, 126.13, 125.67, 82.82, 24.58, 19.18.



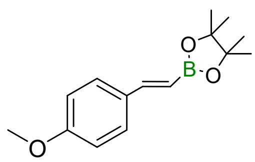
Yield: 83% (**9c**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.74 (d, *J* = 18.3 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 18.3 Hz, 1H), 2.02 (s, 3H), 1.13 (s, 12H).^{13}C NMR (151 MHz, C_6D_6) δ 150.10, 137.78, 137.67, 129.51, 128.39, 127.81, 124.28, 82.78, 24.59, 20.83.



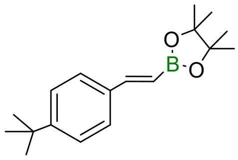
Yield: 80% (**9d**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.77 (d, *J* = 18.3 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.3 Hz, 2H), 6.43 (d, *J* = 18.3 Hz, 1H), 2.01 (s, 3H), 1.13 (s, 12H).^{13}C NMR (151 MHz, C_6D_6) δ 149.90, 138.45, 135.08, 129.22, 127.65, 127.49, 127.05.



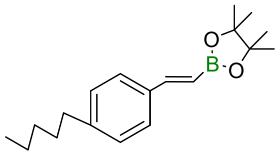
Yield: 79% (**9e**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.74 (d, *J* = 18.3 Hz, 1H), 7.01 (s, 3H), 6.71 (d, *J* = 9.3 Hz, 1H), 6.46 (d, *J* = 18.4 Hz, 1H), 3.25 (s, 3H), 1.13 (s, 12H).^{13}C NMR (151 MHz, C_6D_6) δ 160.07, 149.91, 139.71, 129.47, 119.66, 115.09, 111.76, 82.84, 54.26, 24.57.



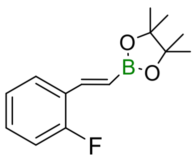
Yield: 85% (**9f**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.76 (d, *J* = 18.3 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.34 (d, *J* = 18.3 Hz, 1H), 3.22 (s, 3H), 1.14 (s, 12H).^{13}C NMR (151 MHz,C_6D_6) δ 189.53, 160.40, 150.00, 131.50, 130.53, 128.46, 113.97, 82.74, 54.35, 24.59.



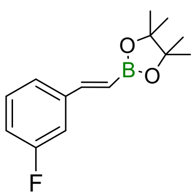
Yield: 75% (**9g**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.87 (d, *J* = 18.3 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 4.4 Hz, 2H), 6.54 (d, *J* = 18.4 Hz, 1H), 1.18 (d, *J* = 2.9 Hz, 21H). ^{13}C NMR (151 MHz, C_6D_6) δ 151.60, 149.87, 135.07, 127.65, 127.49, 126.91, 125.46, 82.77, 34.21, 30.89, 24.62.



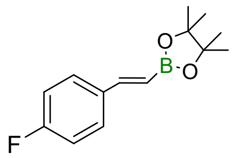
Yield: 70% (**9h**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.76 (d, *J* = 18.3 Hz, 1H), 7.33 (d, *J* = 5.2 Hz, 2H), 6.93 (d, *J* = 5.3 Hz, 2H), 6.43 (d, *J* = 18.3 Hz, 1H), 2.39 (s, 2H), 1.41 (s, 2H), 1.13 (s, 15H), 0.82 (s, 4H). ^{13}C NMR (151 MHz, C_6D_6) δ 149.89, 143.56, 135.32, 132.02, 128.59, 128.32, 127.07, 82.73, 35.62, 31.36, 30.90, 24.59, 22.48, 13.84.



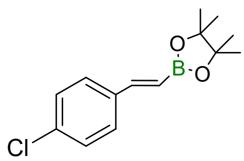
Yield: 70% (**9i**). ^{1}H NMR (300 MHz, C_6D_6) δ 8.08 (d, *J* = 18.7 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 6.83 – 6.61 (m, 3H), 6.51 (d, *J* = 18.5 Hz, 1H), 1.09 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 161.60, 141.30, 129.89, 127.25, 123.96, 115.66, 115.51, 82.96, 24.51.



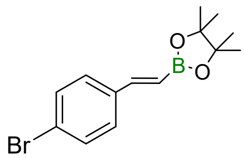
Yield: 72% (**9j**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.57 (d, *J* = 18.3 Hz, 1H), 7.01 (d, *J* = 9.9 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.76 (q, *J* = 7.3 Hz, 1H), 6.71 – 6.59 (m, 1H), 6.32 (d, *J* = 18.5 Hz, 1H), 1.11 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 164.00, 148.28, 140.05, 129.91, 122.82, 115.41, 113.34, 82.94, 24.54.



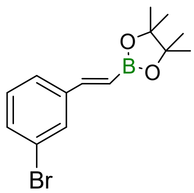
Yield: 73% (**9k**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.58 (d, J = 18.4 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.66 (t, J = 8.5 Hz, 2H), 6.24 (d, J = 18.3 Hz, 1H), 1.13 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 163.91, 162.26, 148.43, 133.79, 128.71, 115.40, 115.25, 82.87, 24.56.



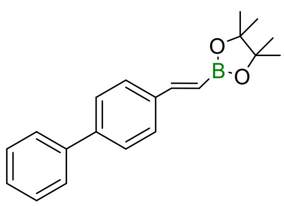
Yield: 73% (**9l**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.54 (d, J = 18.3 Hz, 1H), 6.98 (d, J = 9.4 Hz, 4H), 6.28 (d, J = 19.5 Hz, 1H), 1.12 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 150.60, 138.33, 136.69, 130.97, 130.52, 126.62, 120.04, 85.28, 26.89.



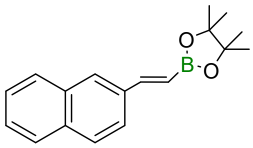
Yield: 76% (**9m**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.80 (d, J = 24.7 Hz, 1H), 7.44 (s, 1H), 7.40 (s, 1H), 7.37 (s, 1H), 7.19 (s, 1H), 6.56 (d, J = 18.4 Hz, 1H), 1.40 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 148.37, 136.38, 131.61, 128.45, 127.66, 127.50, 122.72, 82.95, 24.23.



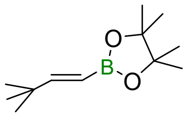
Yield: 80% (**9n**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.52 – 7.40 (m, 2H), 7.11 (d, J = 7.1 Hz, 1H), 7.01 (d, J = 7.7 Hz, 1H), 6.63 (t, J = 7.9 Hz, 1H), 6.24 (d, J = 18.4 Hz, 1H), 1.11 (s, 12H).^{13}C NMR (151 MHz, C_6D_6) δ 147.92, 139.76, 131.39, 129.96, 129.88, 125.30, 122.81, 82.93, 24.55.



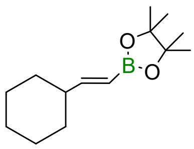
Yield: 75% (**9o**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.79 (d, *J* = 18.2 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 3H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.18 (s, 1H), 7.13 (s, 3H), 6.49 (d, *J* = 18.3 Hz, 1H), 1.12 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 149.47, 141.55, 140.66, 136.66, 128.63, 127.82, 127.66, 127.56, 127.50, 127.25, 127.20, 126.93, 82.87, 24.61.



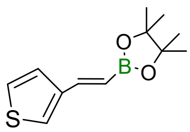
Yield: 65% (**9p**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 – 7.76 (m, 4H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 18.4 Hz, 1H), 7.47 (d, *J* = 9.5 Hz, 2H), 6.33 (d, *J* = 18.4 Hz, 1H), 1.36 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.55, 135.01, 133.75, 133.46, 128.43, 128.28, 128.05, 127.71, 126.43, 126.31, 123.41, 83.39, 24.86.



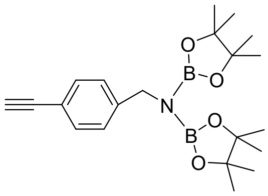
Yield: 99% (**9q**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.64 (d, *J* = 18.3 Hz, 1H), 5.35 (d, *J* = 18.2 Hz, 1H), 1.27 (s, 12H), 1.02 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.25, 82.85, 34.85, 28.66, 24.66, 24.45.



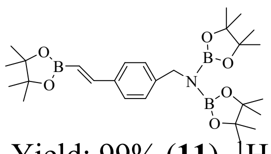
Yield: 80% (**9r**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.57 (d, *J* = 18.2 Hz, 1H), 5.37 (d, *J* = 18.1 Hz, 1H), 2.01 (s, 1H), 1.71 (s, 6H), 1.27 (s, 12H), 1.16 – 1.00 (m, 4H). ^{13}C NMR (151 MHz, C_6D_6) δ 159.61, 82.49, 43.20, 31.92, 26.00, 25.76, 24.57, 24.24.



Yield: 80% (**9s**). ^{1}H NMR (300 MHz, C_6D_6) δ 7.65 (d, *J* = 18.3 Hz, 1H), 7.03 (d, *J* = 4.5 Hz, 1H), 6.82 (d, *J* = 2.0 Hz, 1H), 6.76 – 6.69 (m, 1H), 6.19 (d, *J* = 18.3 Hz, 1H), 1.12 (s, 12H). ^{13}C NMR (151 MHz, C_6D_6) δ 143.49, 141.32, 125.83, 124.91, 124.67, 82.76, 24.57.



Yield: 99% (**10**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.22 (s, 2H), 3.11 (s, 1H), 1.19 (s, 24H).



Yield: 99% (**11**). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 3H), 7.26 (d, *J* = 7.7 Hz, 2H), 6.11 (d, *J* = 18.5 Hz, 1H), 4.21 (s, 2H), 1.31 (s, 12H), 1.18 (s, 24H).^{13}C NMR (101 MHz, $CDCl_3$) δ 149.76, 144.19, 135.41, 131.71, 127.68, 126.96, 126.70, 82.36, 47.09, 24.81, 24.50. HRMS (EI) Calcd for: $C_{27}H_{44}B_3NO_6$: 511.3448, Found: 511.3456.

6. NMR spectra

6.1 NMR spectra of the ligand and compounds

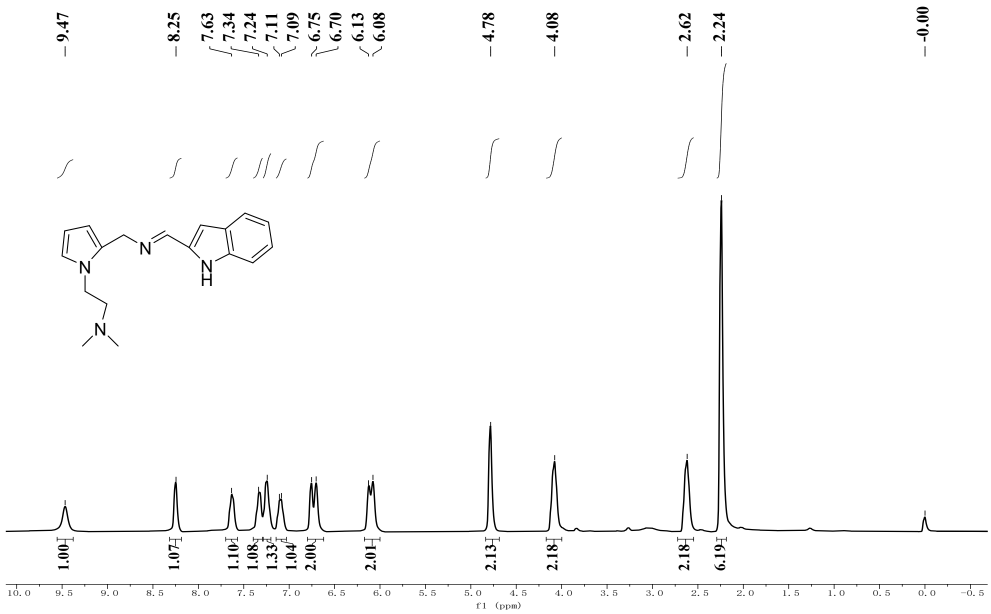


Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **HL.**

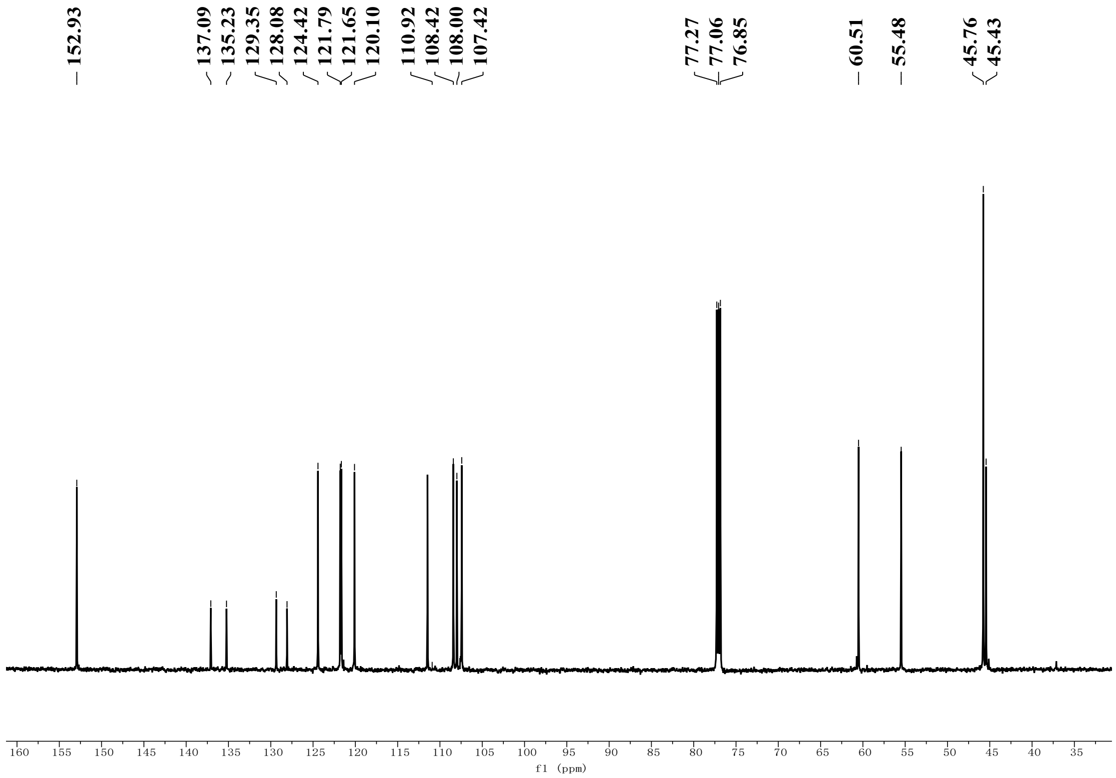


Figure S7. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **HL.**

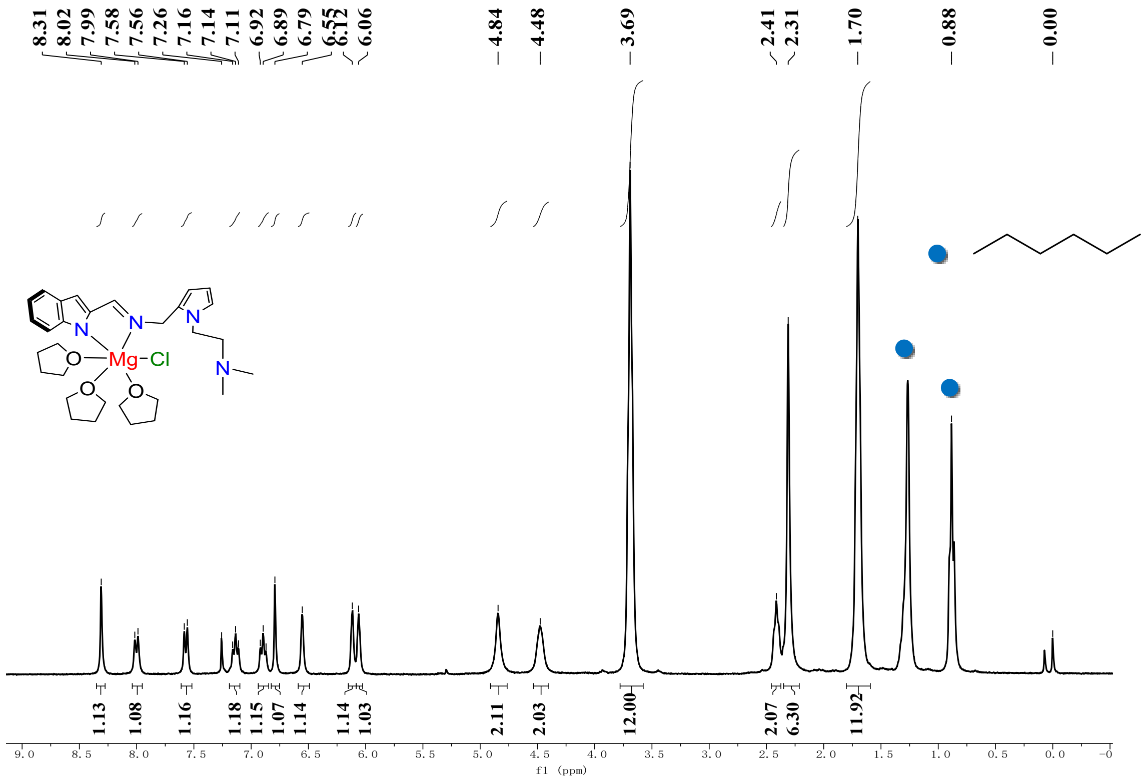


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **1.**

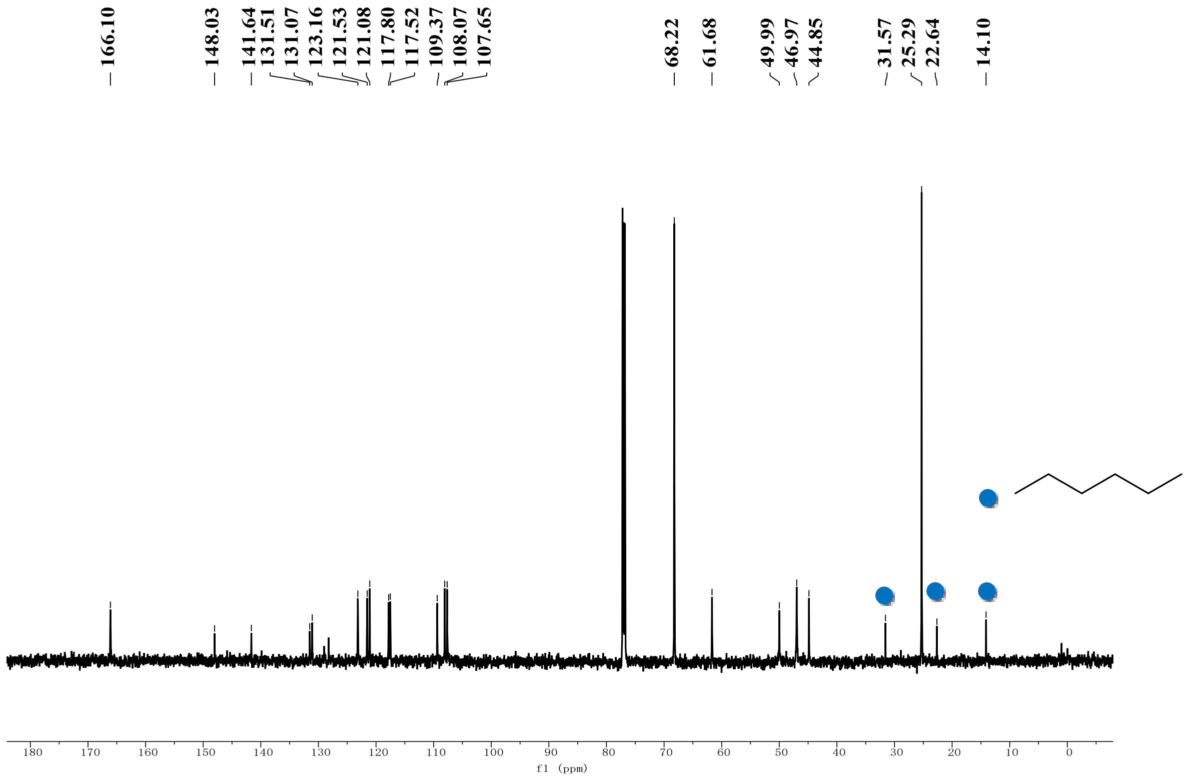


Figure S9. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **1.**

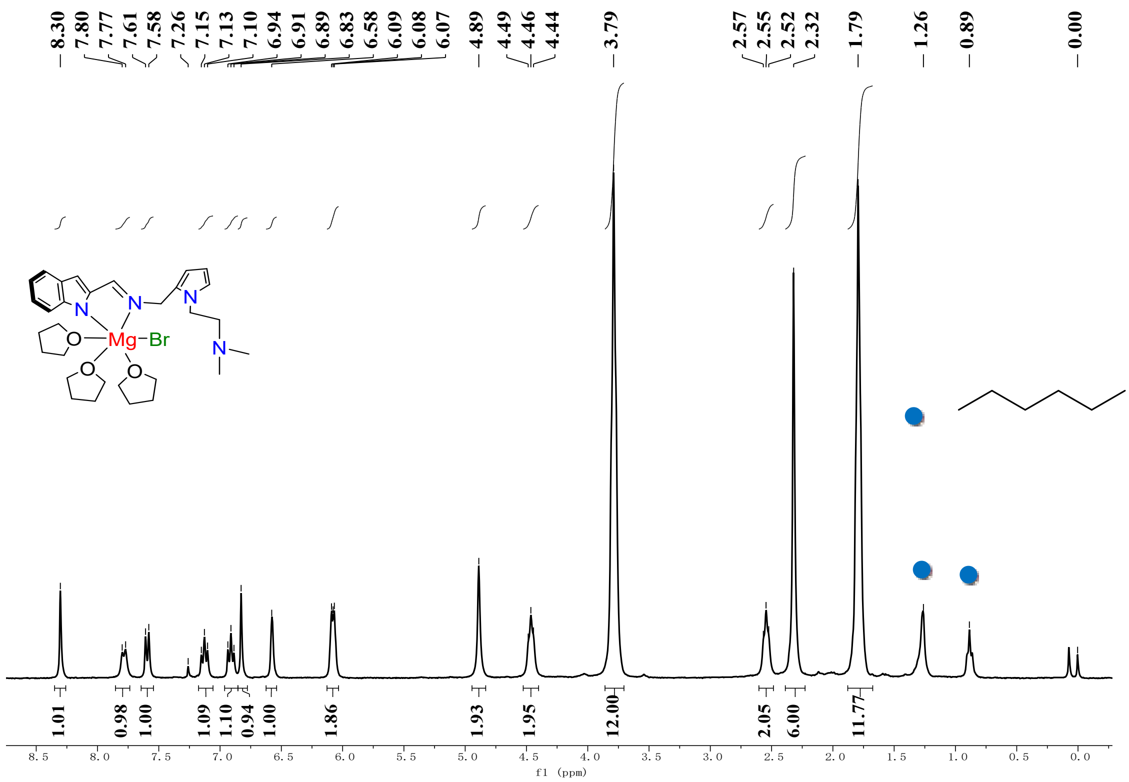


Figure S10. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **2.**

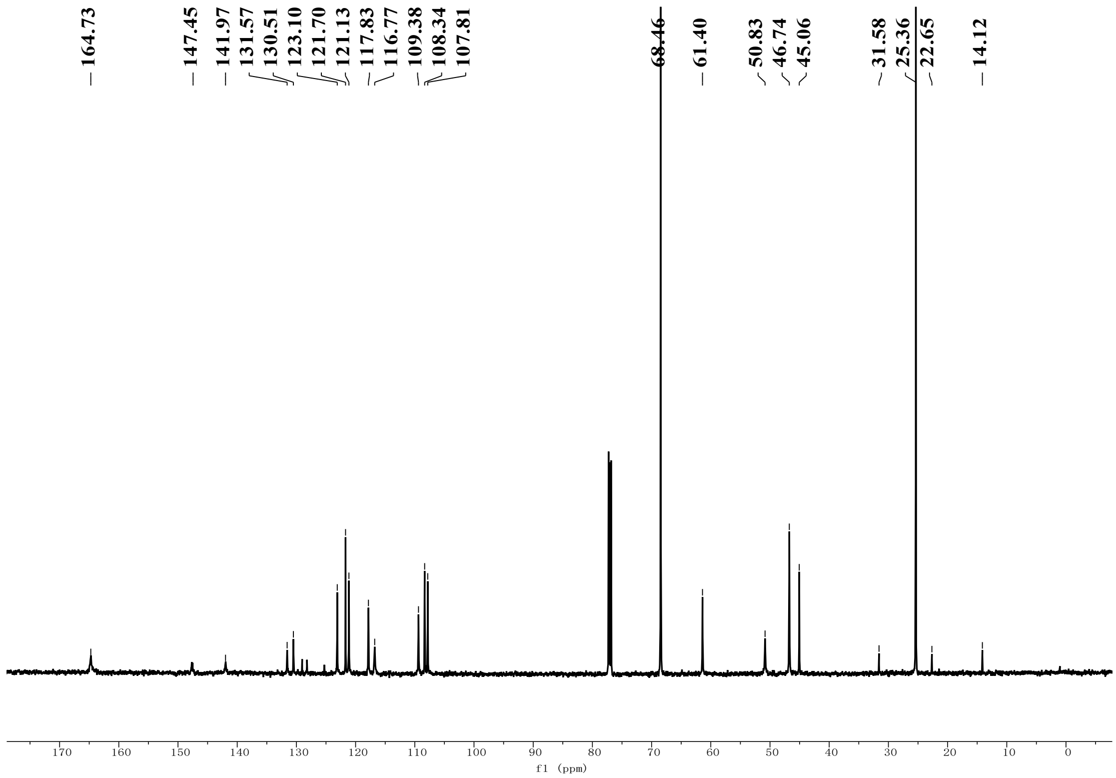


Figure S11. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **2.**

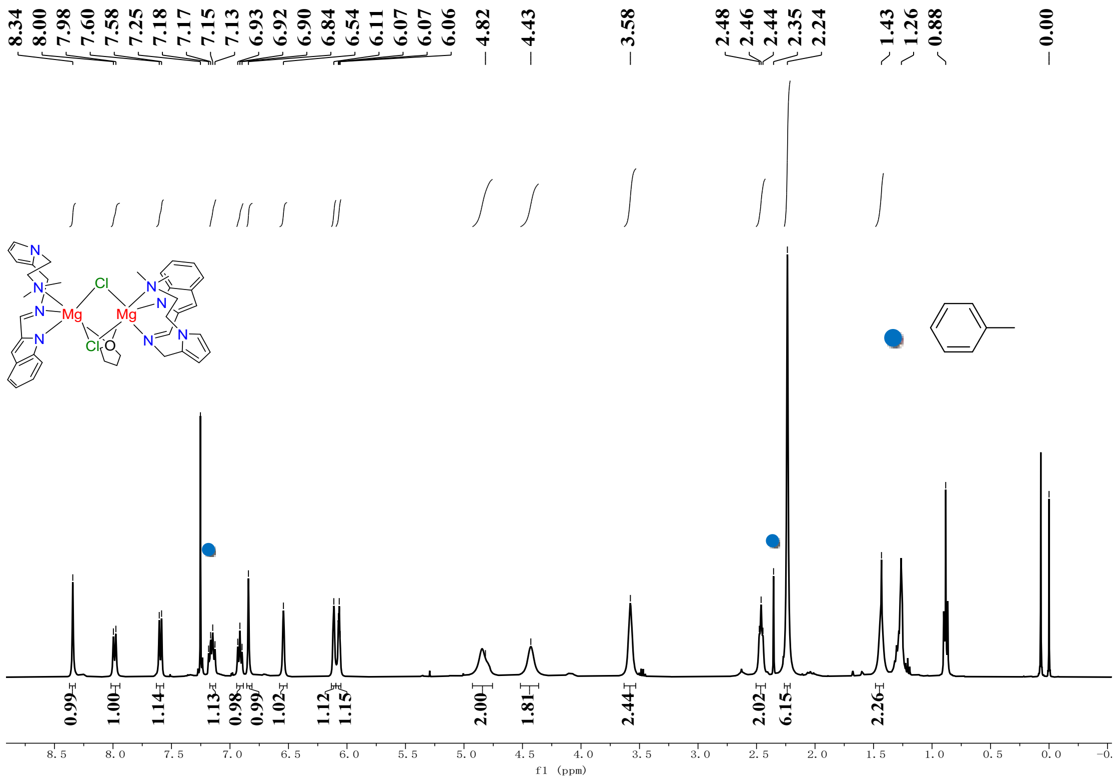


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3.**

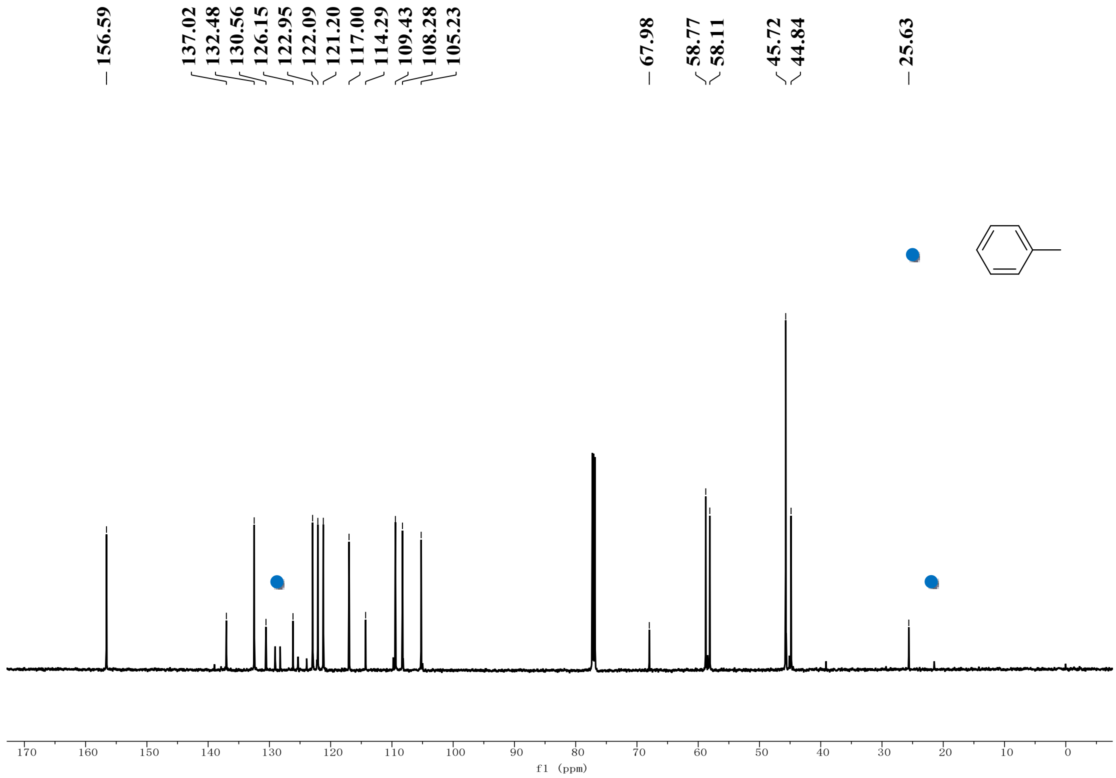


Figure S13. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **3.**

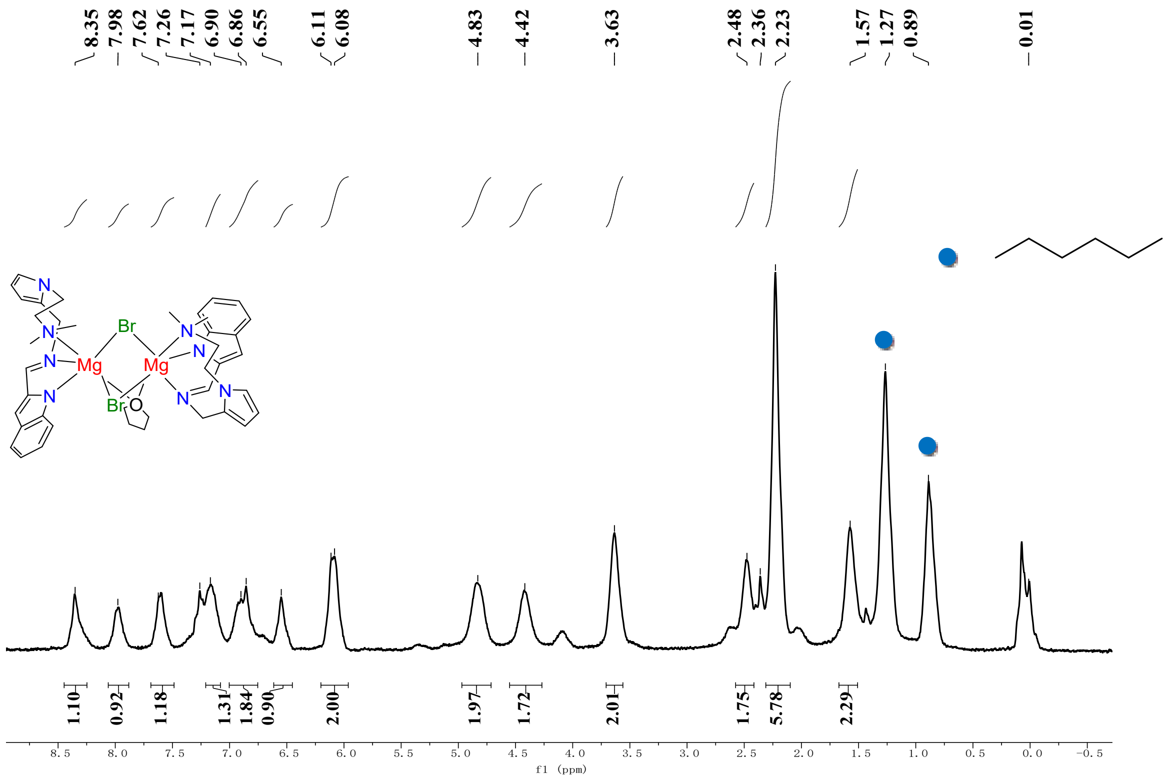


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **4.**

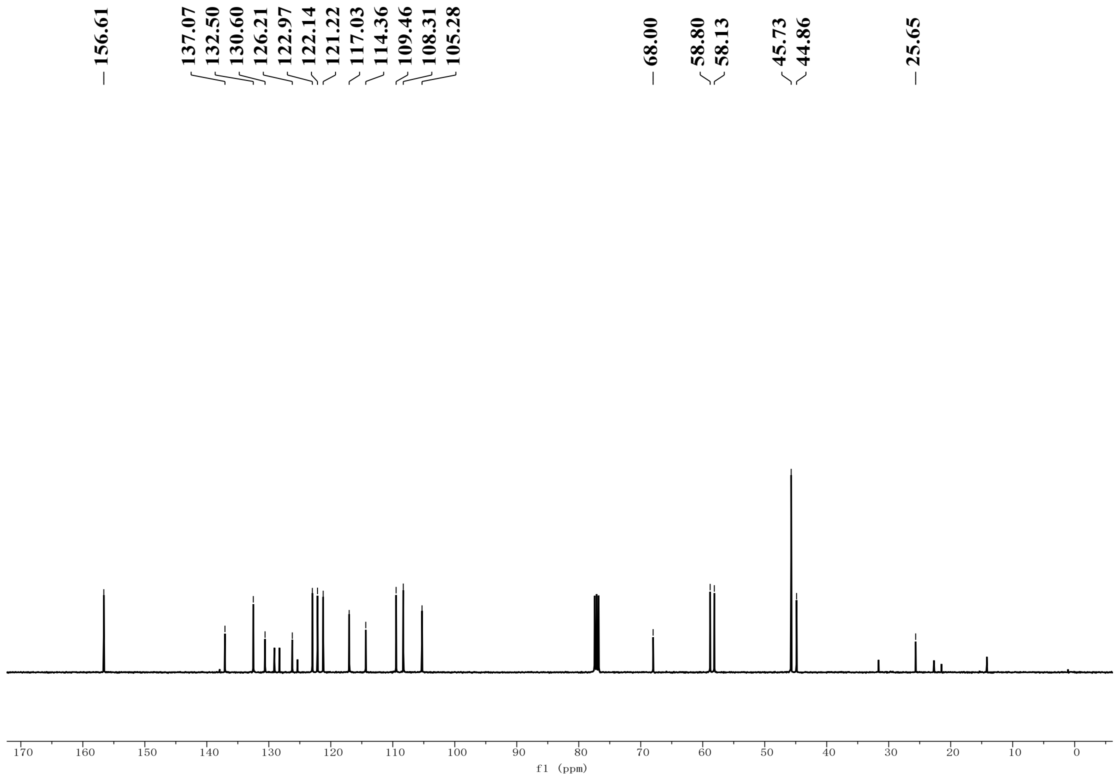


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **4.**

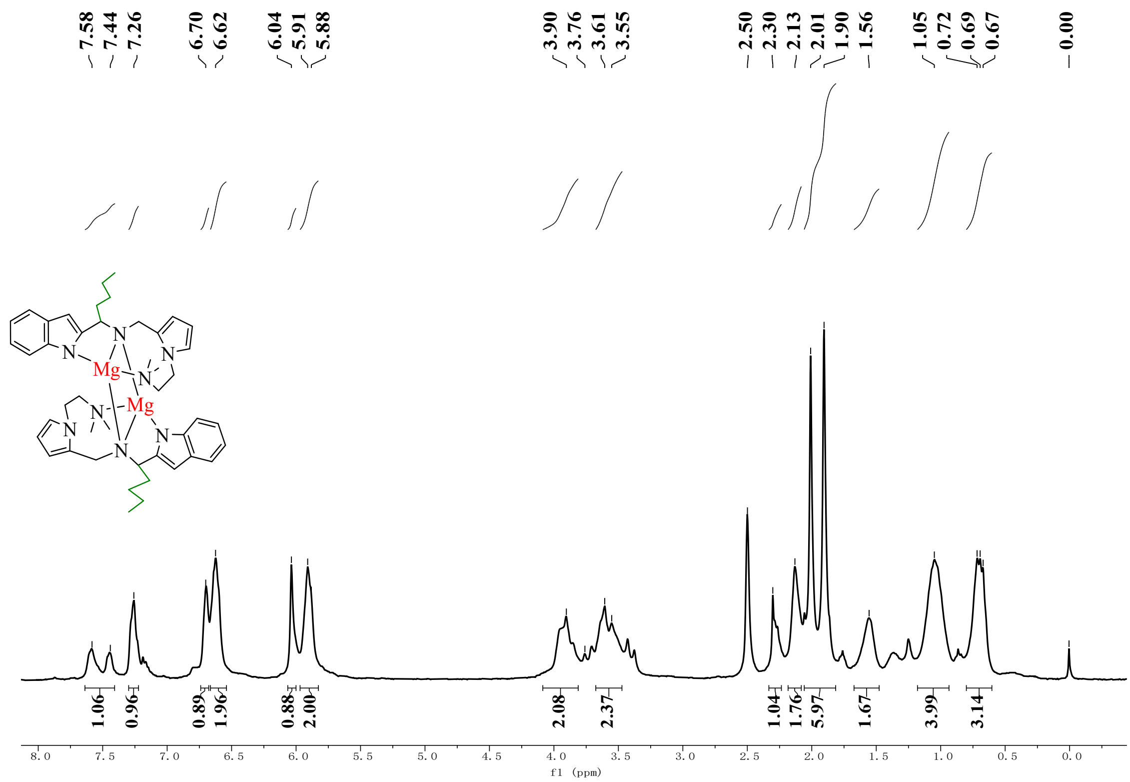


Figure S16. ^{1}H NMR (300 MHz, DMSO-d_6) spectrum of **5.**

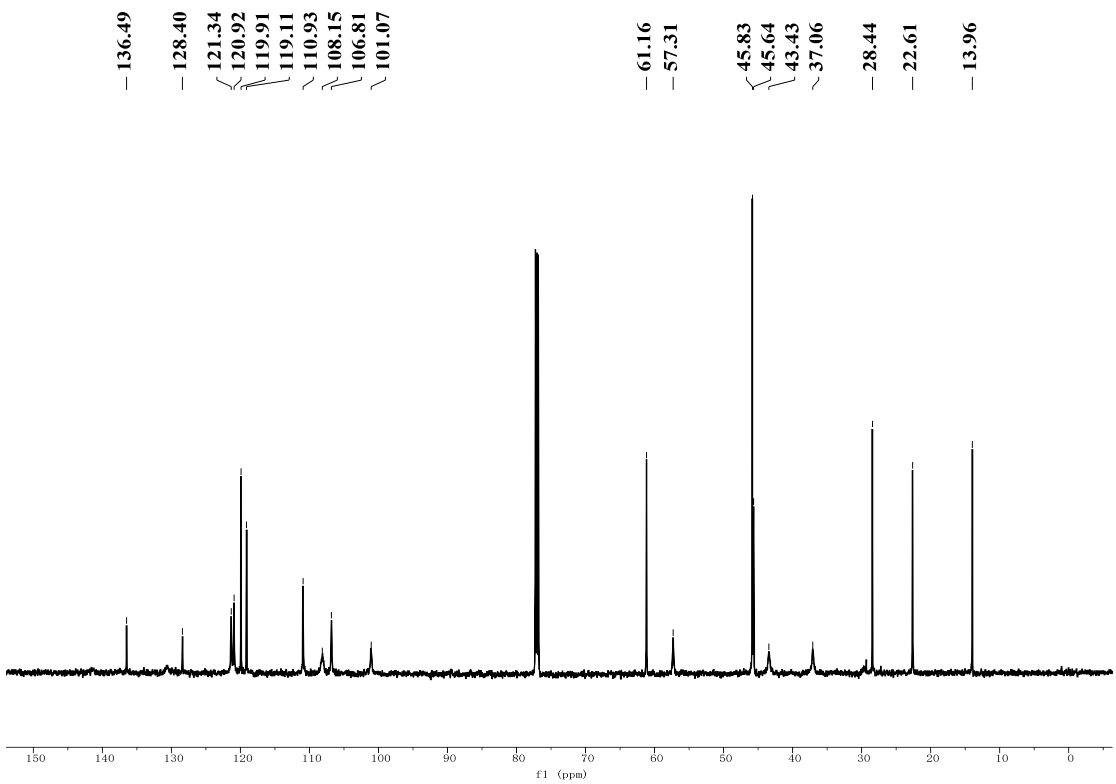


Figure S17. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **5.**

6.2 NMR spectra of diborylamines

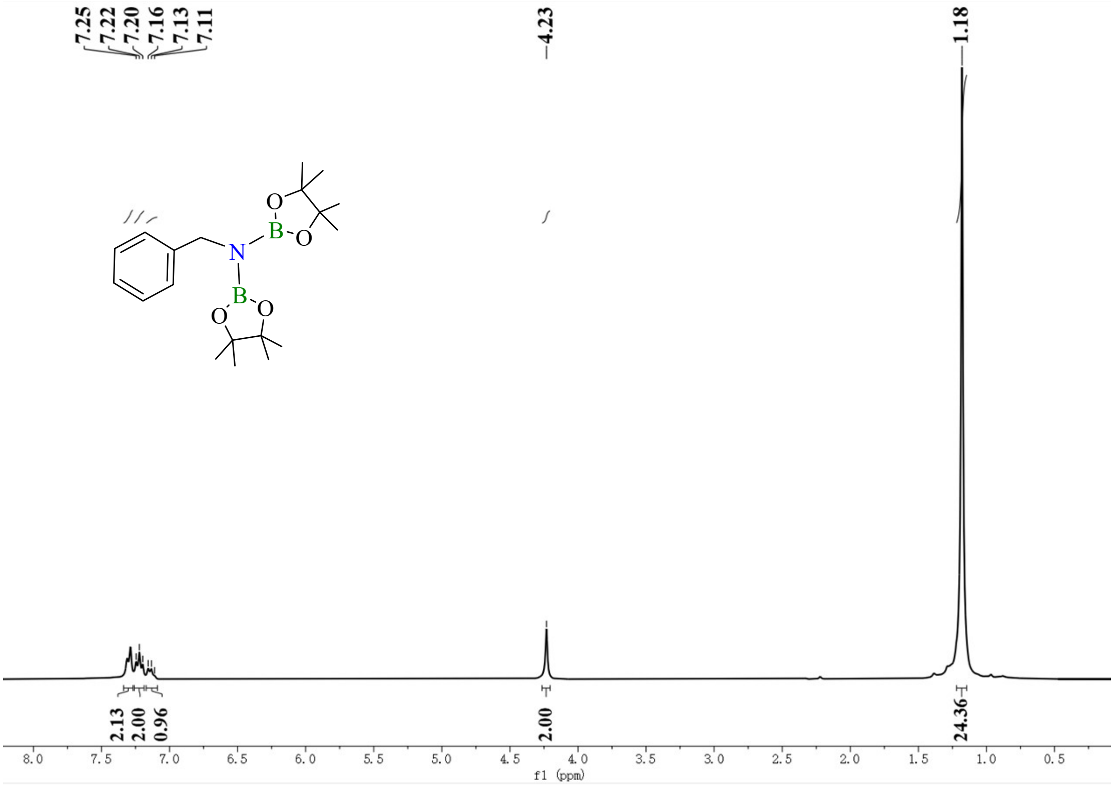


Figure S18. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7a**.

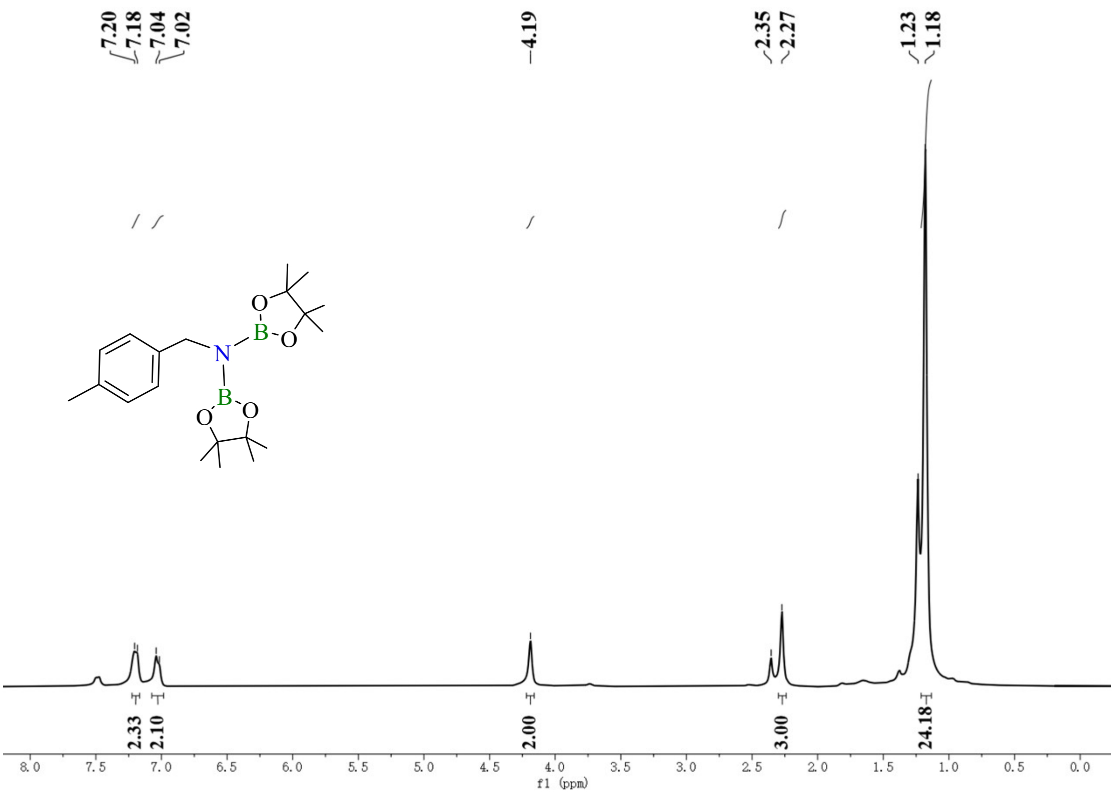


Figure S19. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7b**.

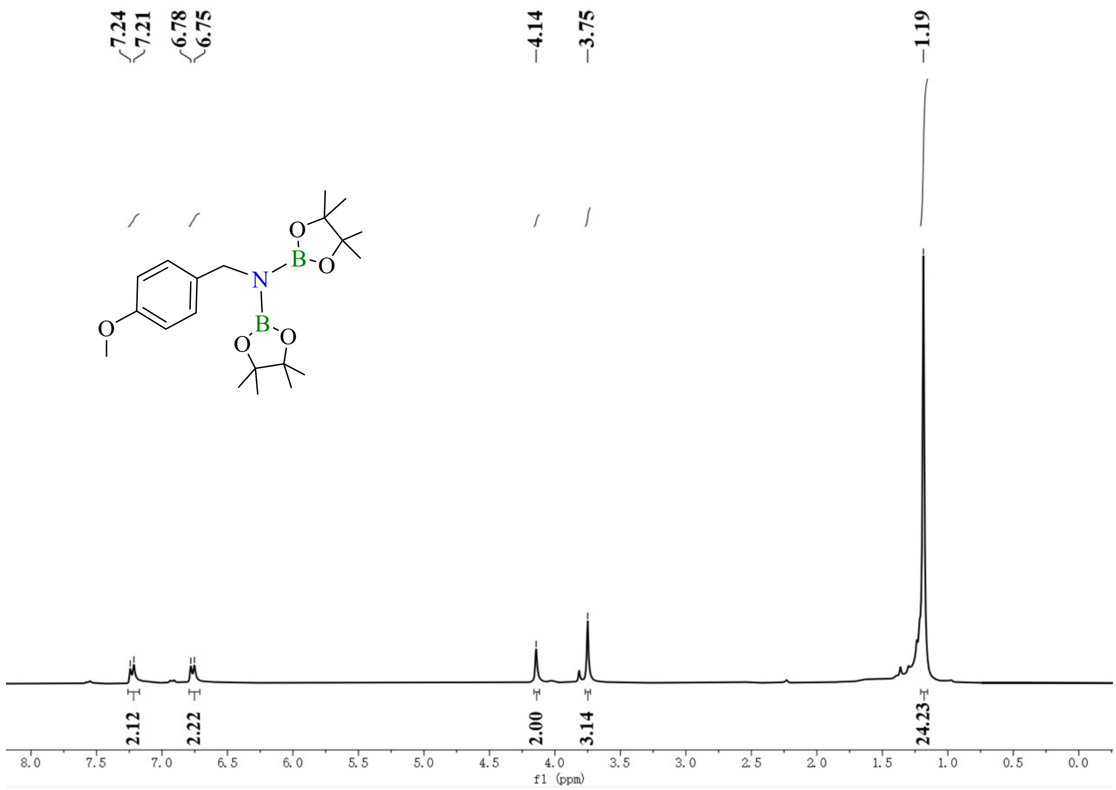


Figure S20. ¹H NMR (300 MHz, $CDCl_3$) spectrum of **7c**.

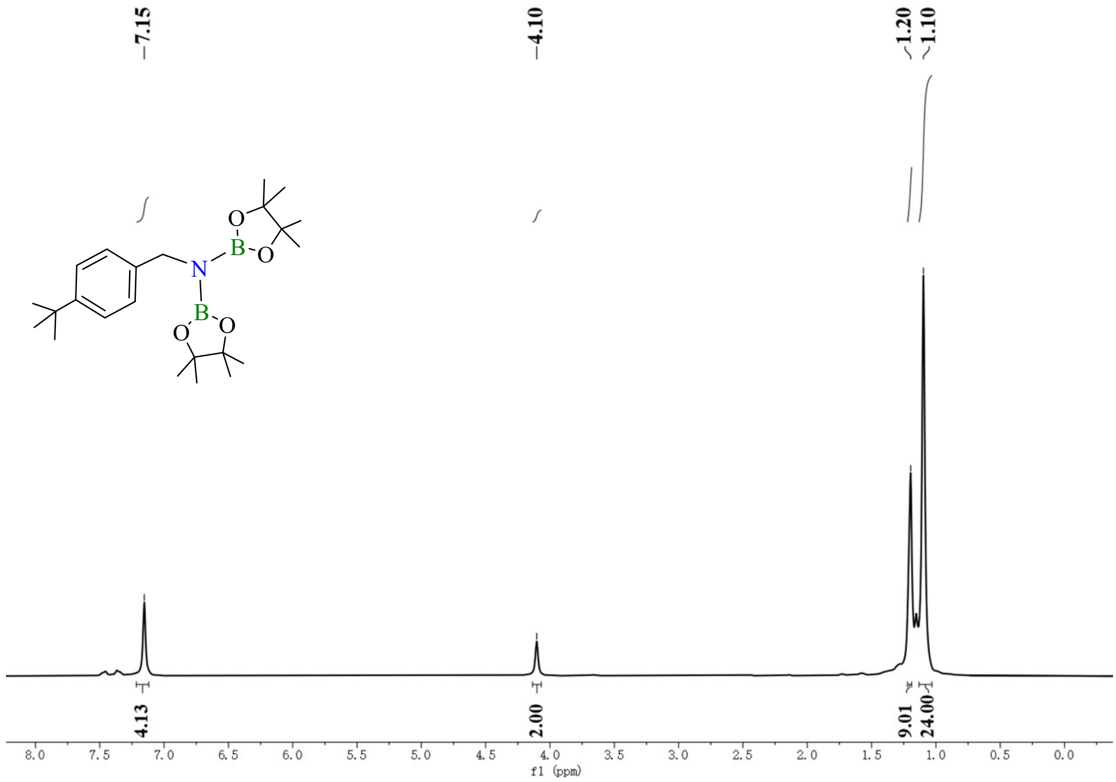


Figure S21. ¹H NMR (300 MHz, $CDCl_3$) spectrum of **7d**.

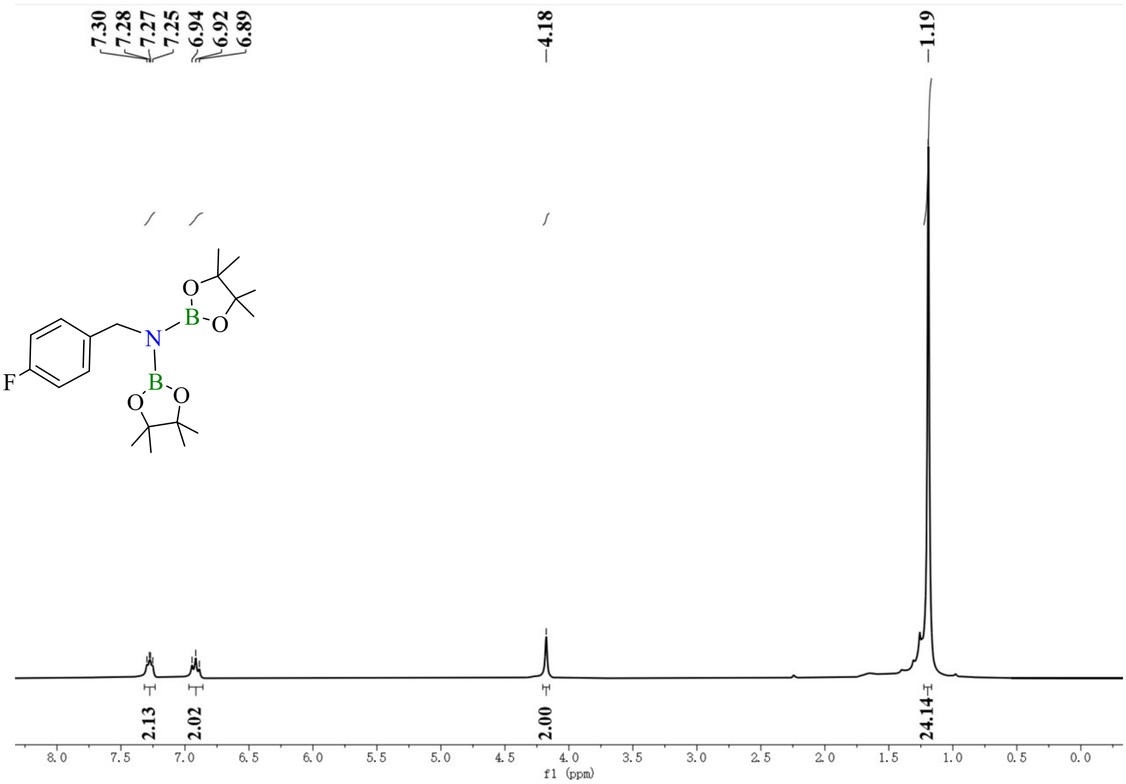


Figure S22. [1]H NMR (300 MHz, $CDCl_3$) spectrum of **7e**.

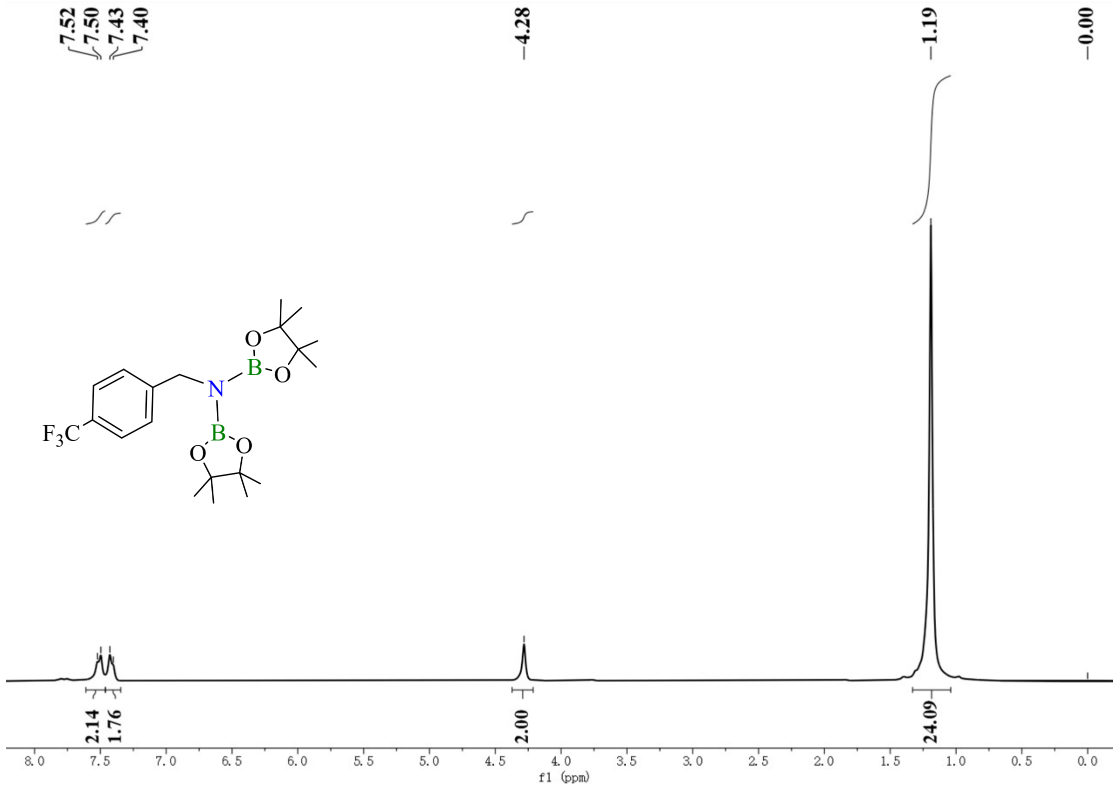


Figure S23. [1]H NMR (300 MHz, $CDCl_3$) spectrum of **7f**

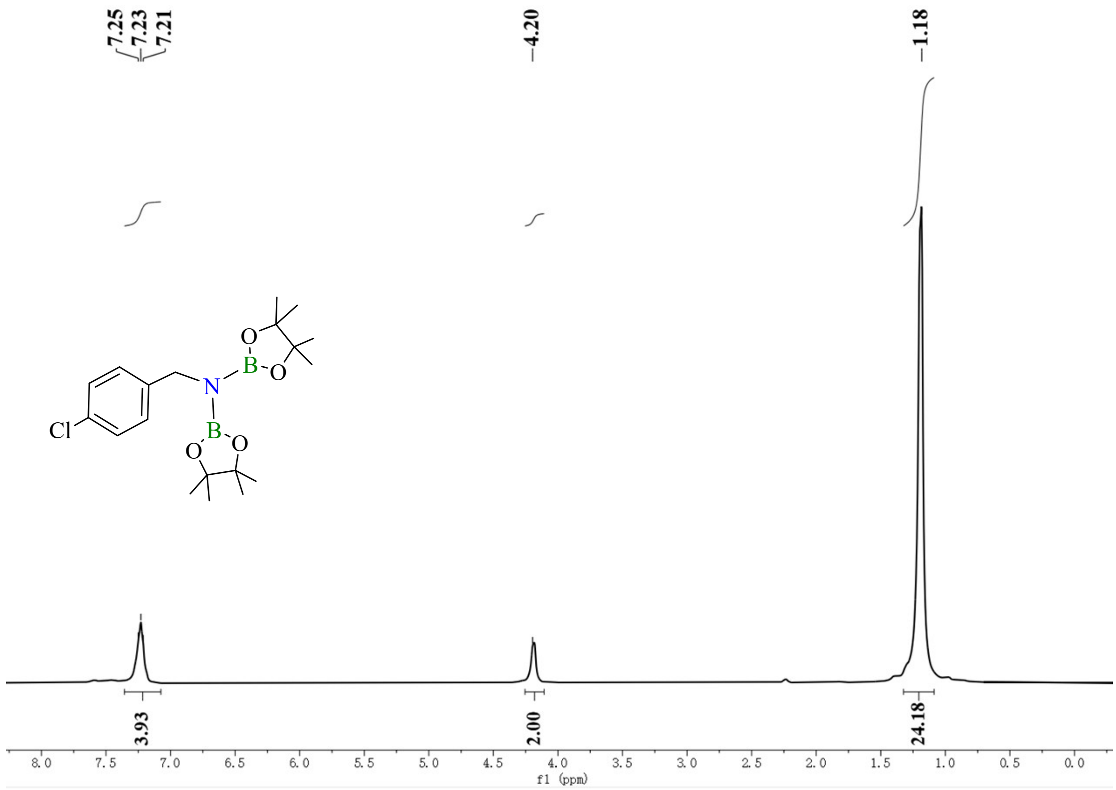


Figure S24. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7g**.

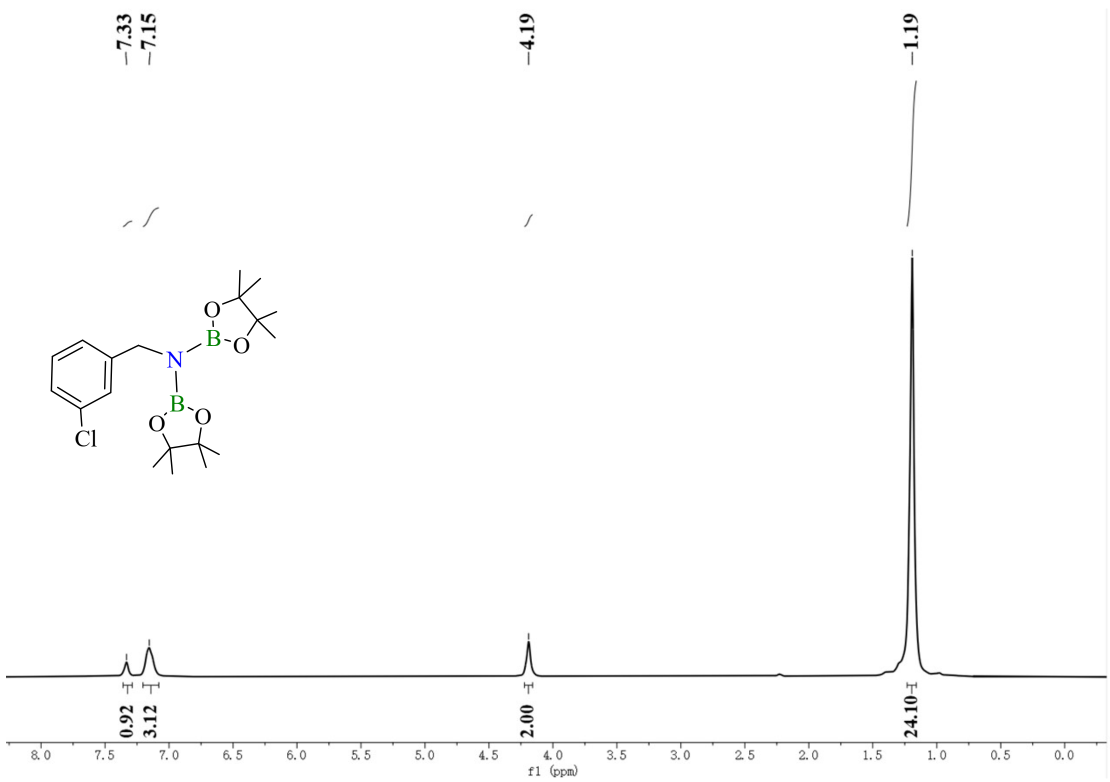


Figure S25. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7h**.

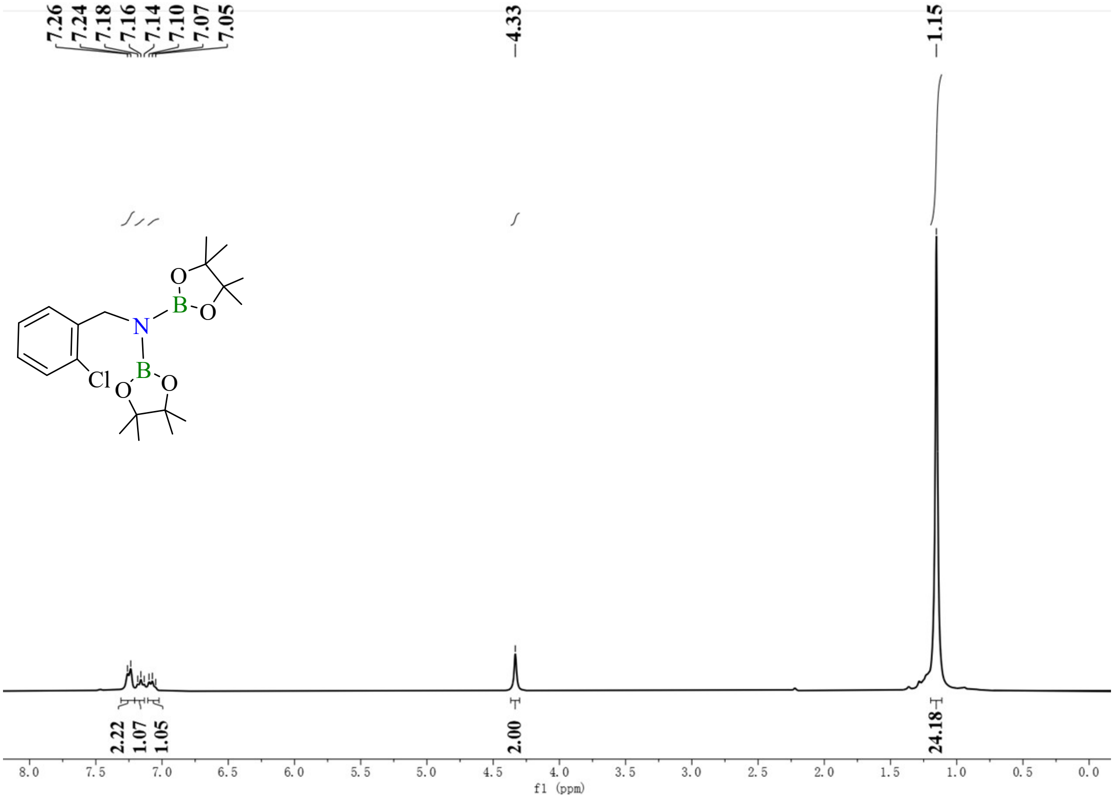


Figure S26. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7i**.

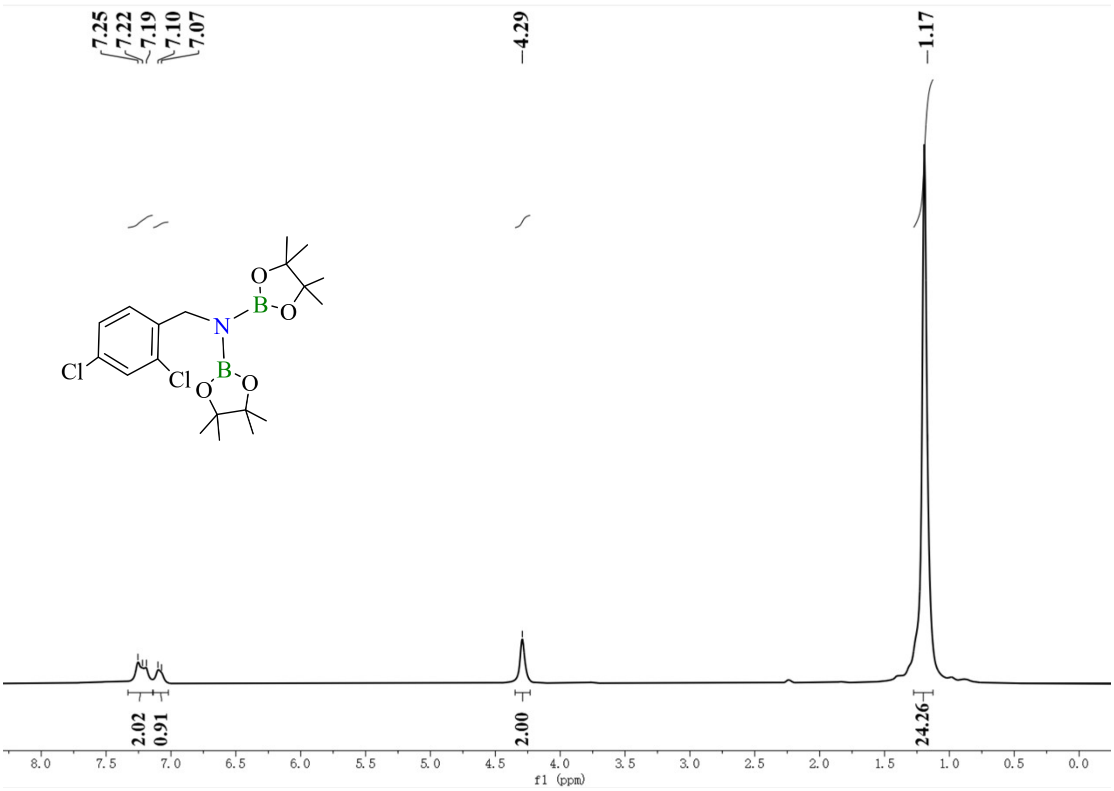


Figure S27. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7j**.

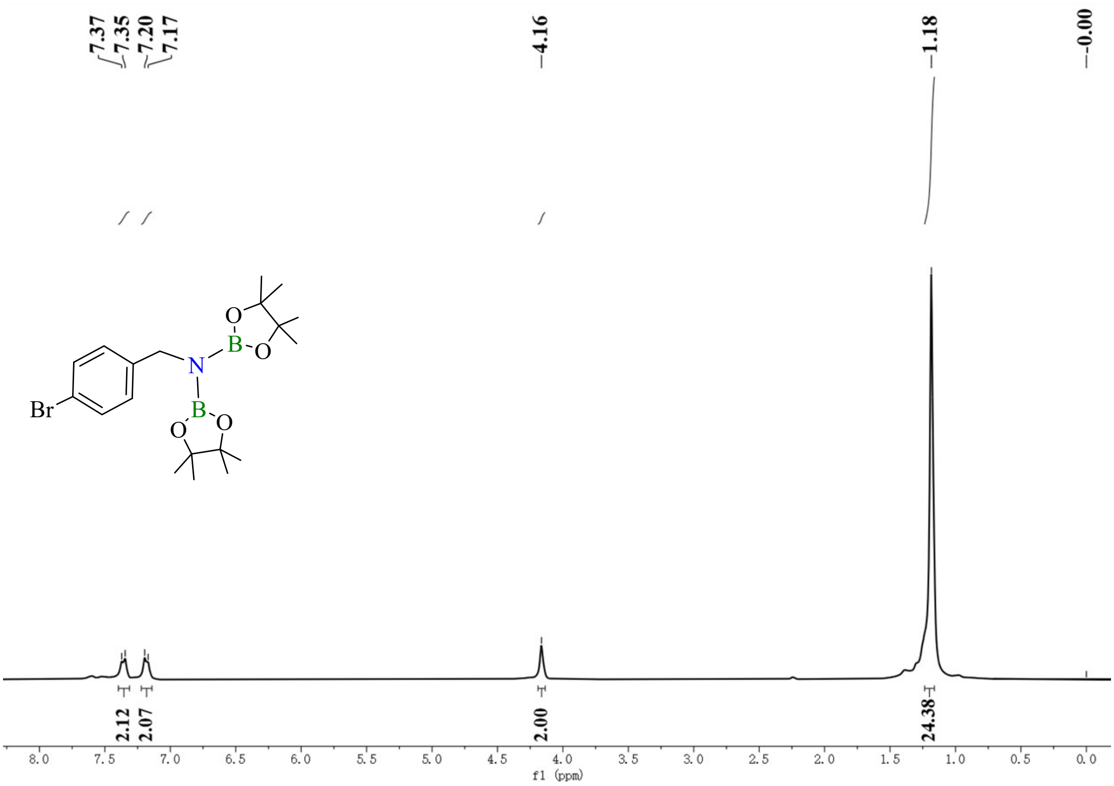


Figure S28. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7k**.

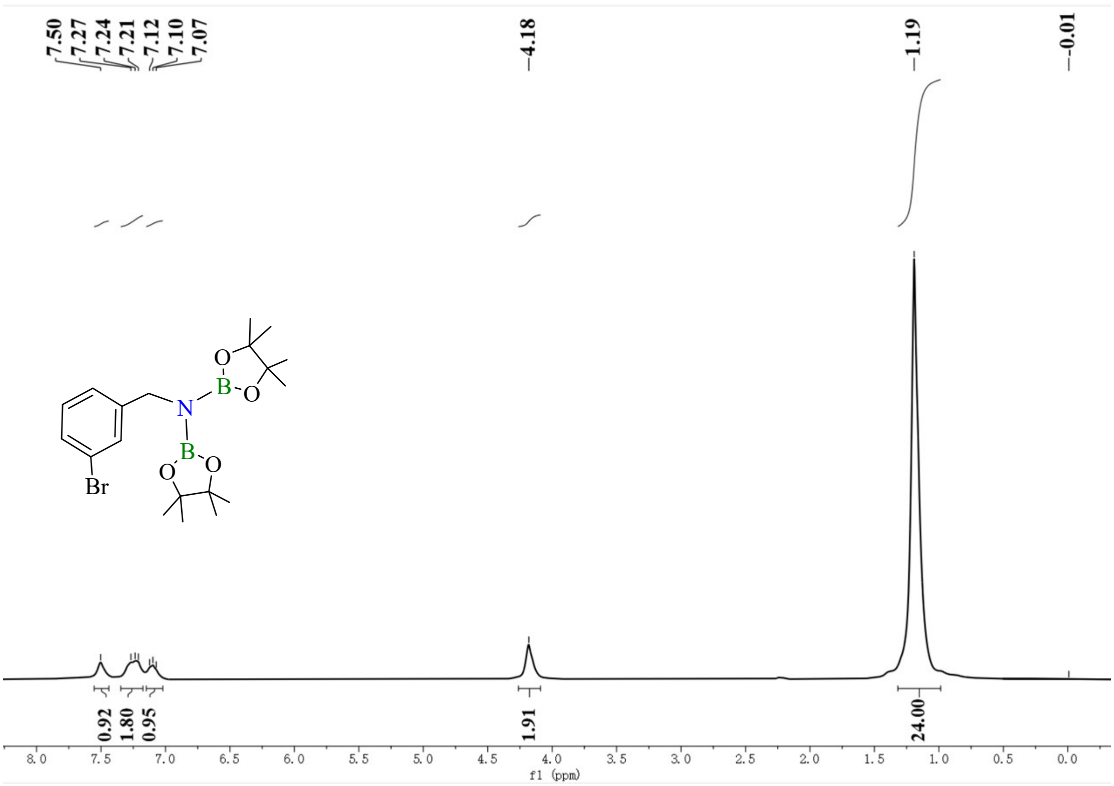


Figure S29. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7l**.

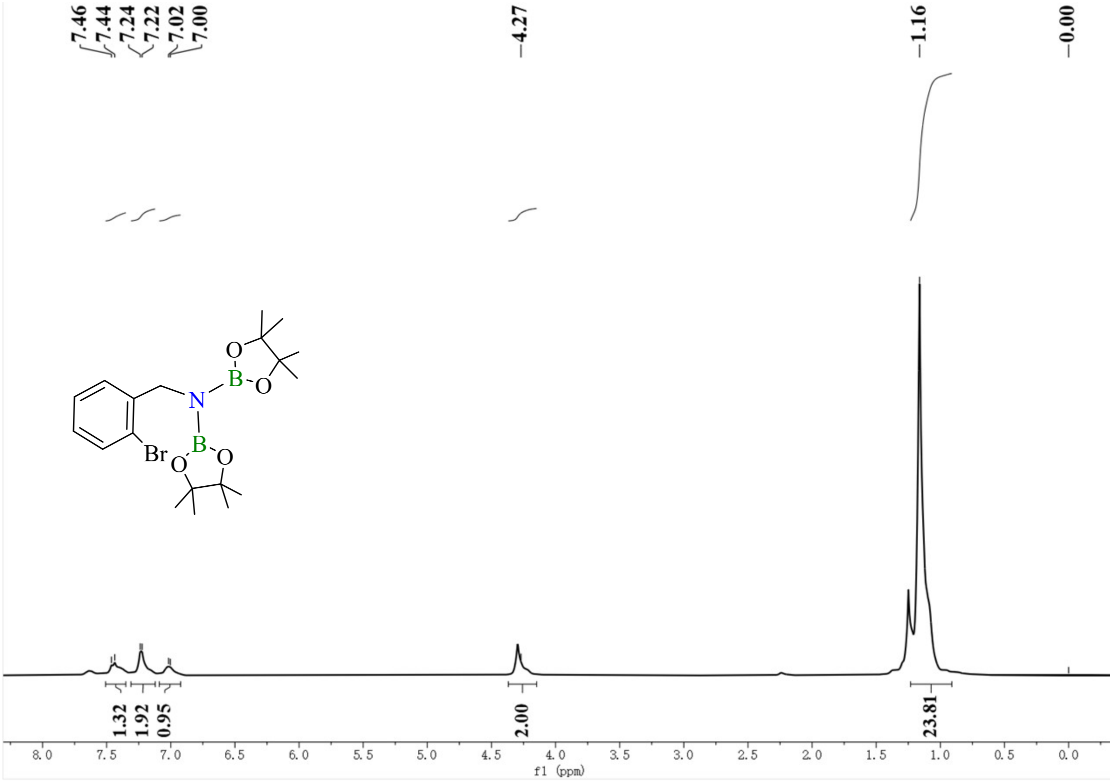


Figure S30. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7m**.

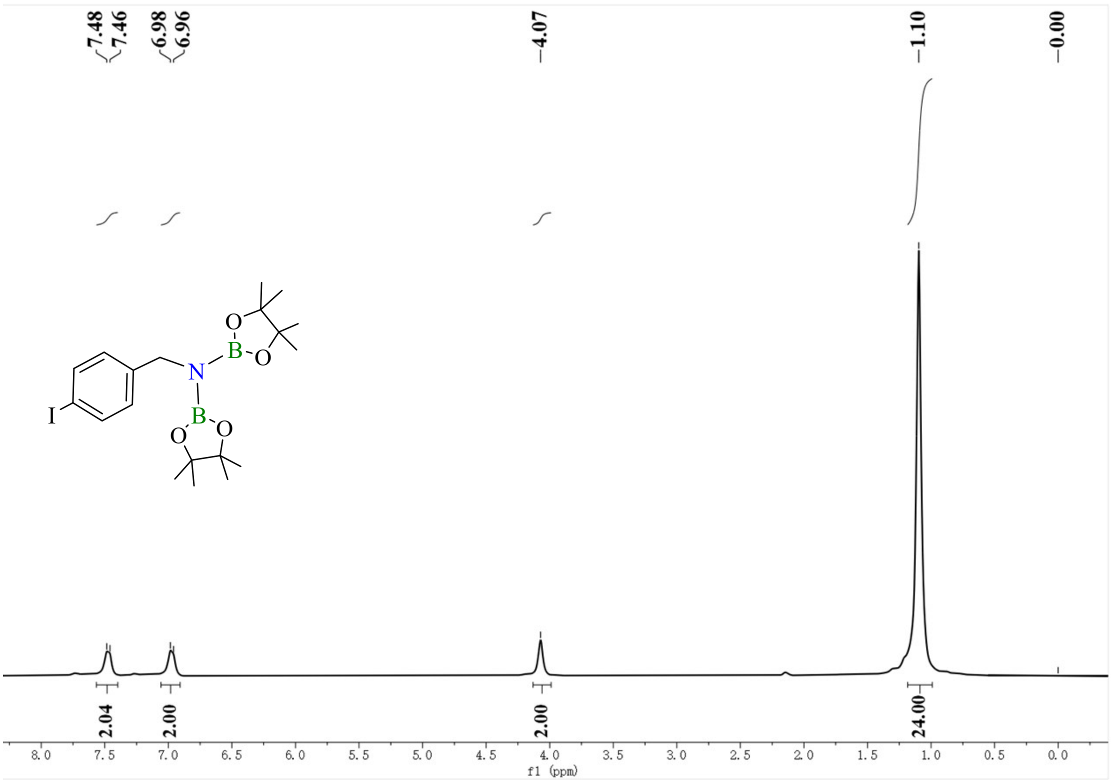


Figure S31. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7n**.

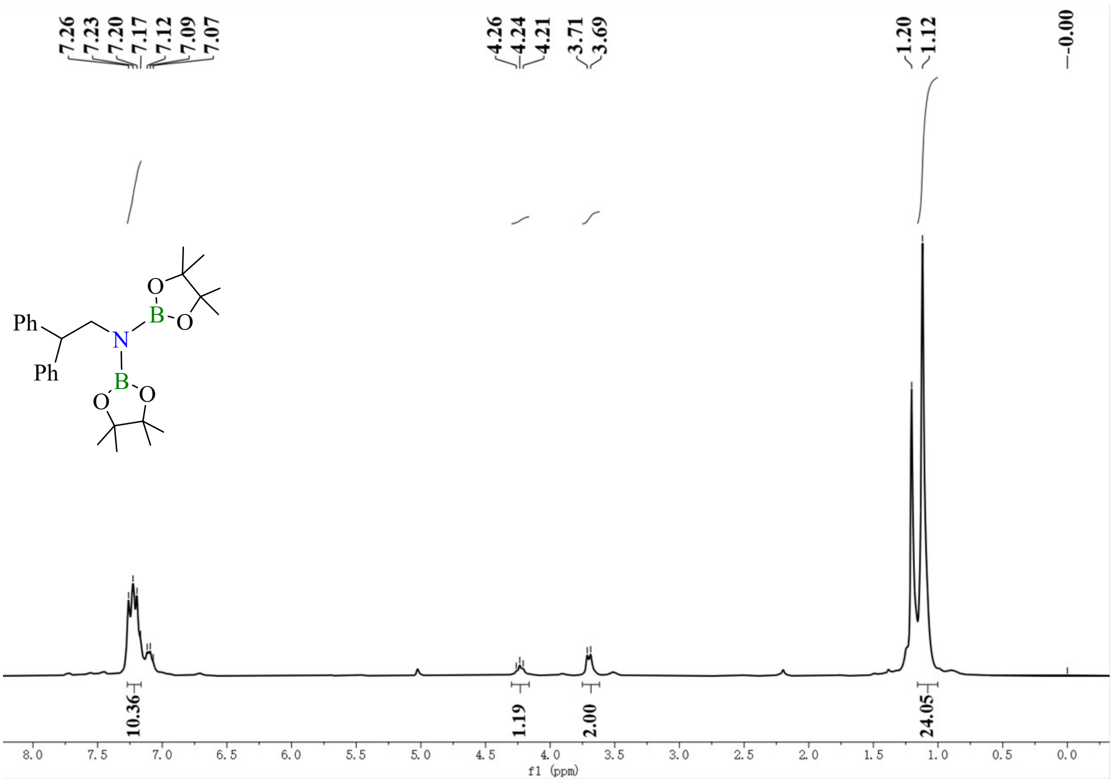


Figure S32. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7o**.

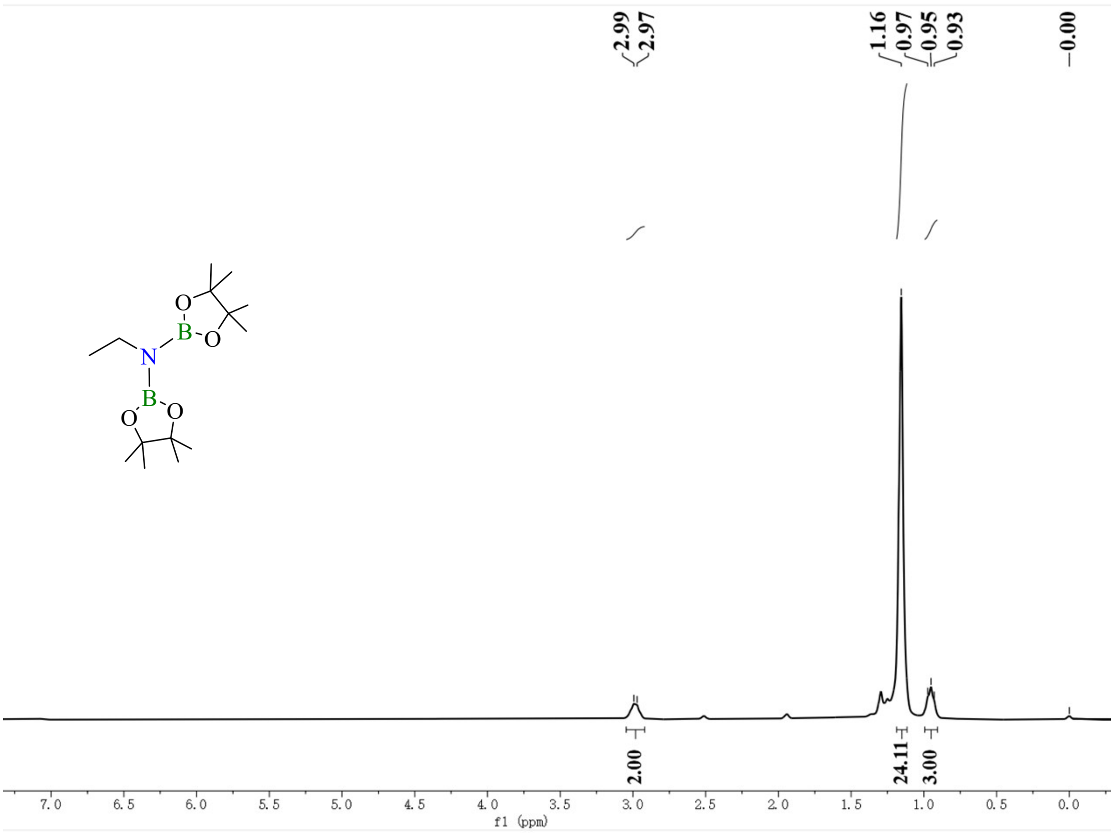


Figure S33. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7p**.

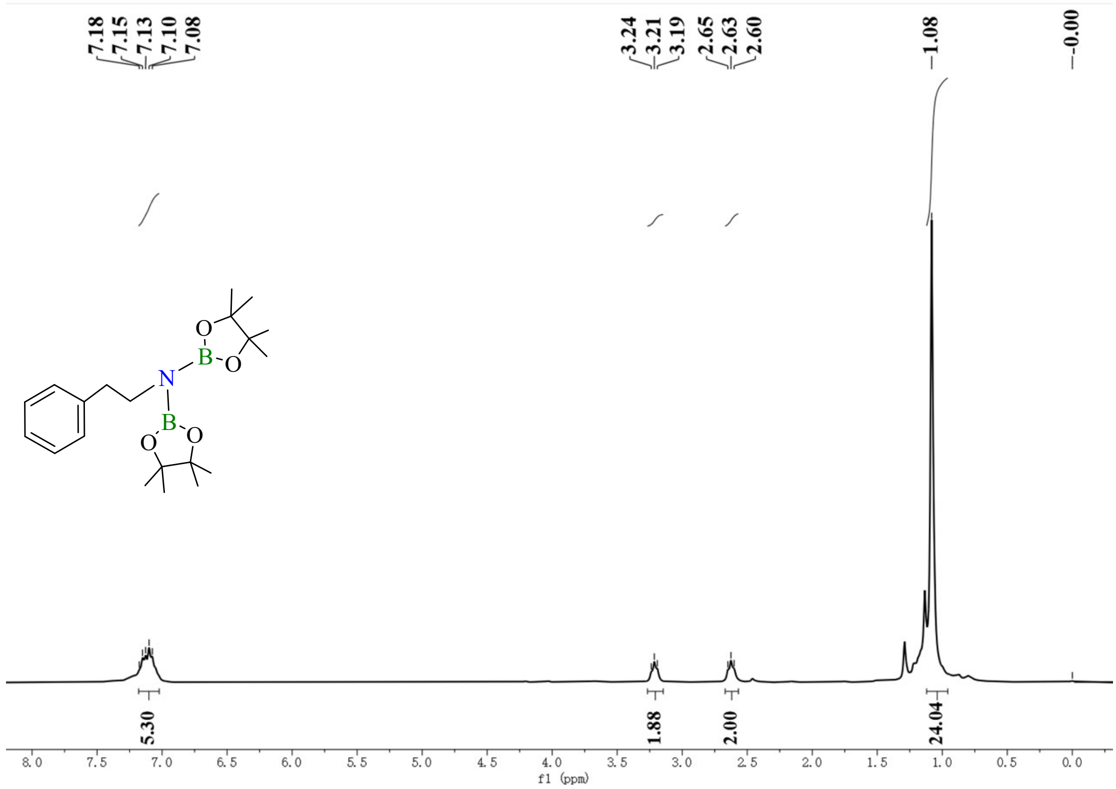


Figure S34. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7q**.

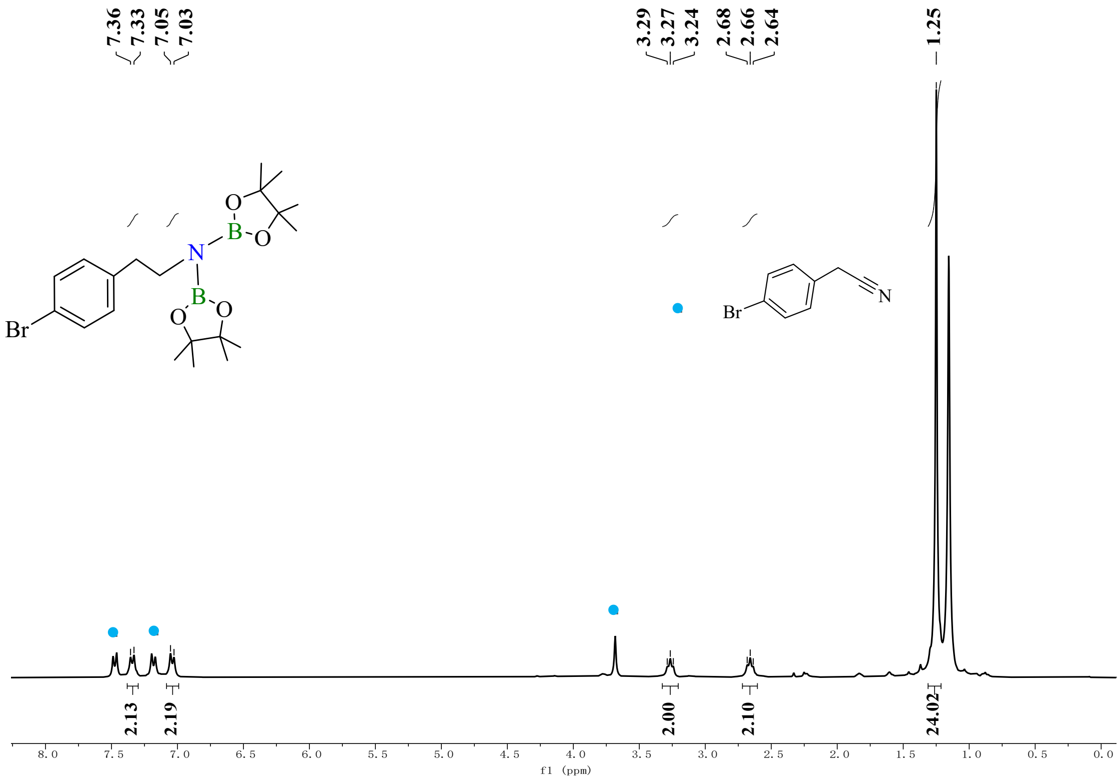


Figure S35. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7r**.

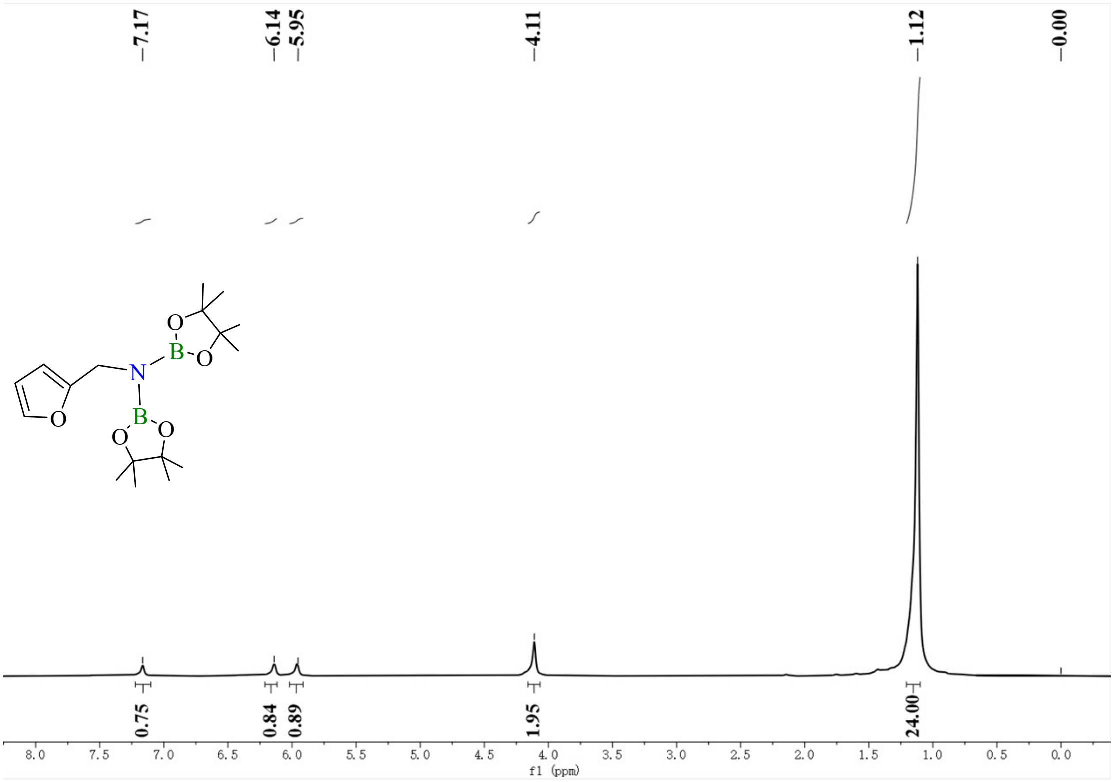


Figure S36. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7s**.

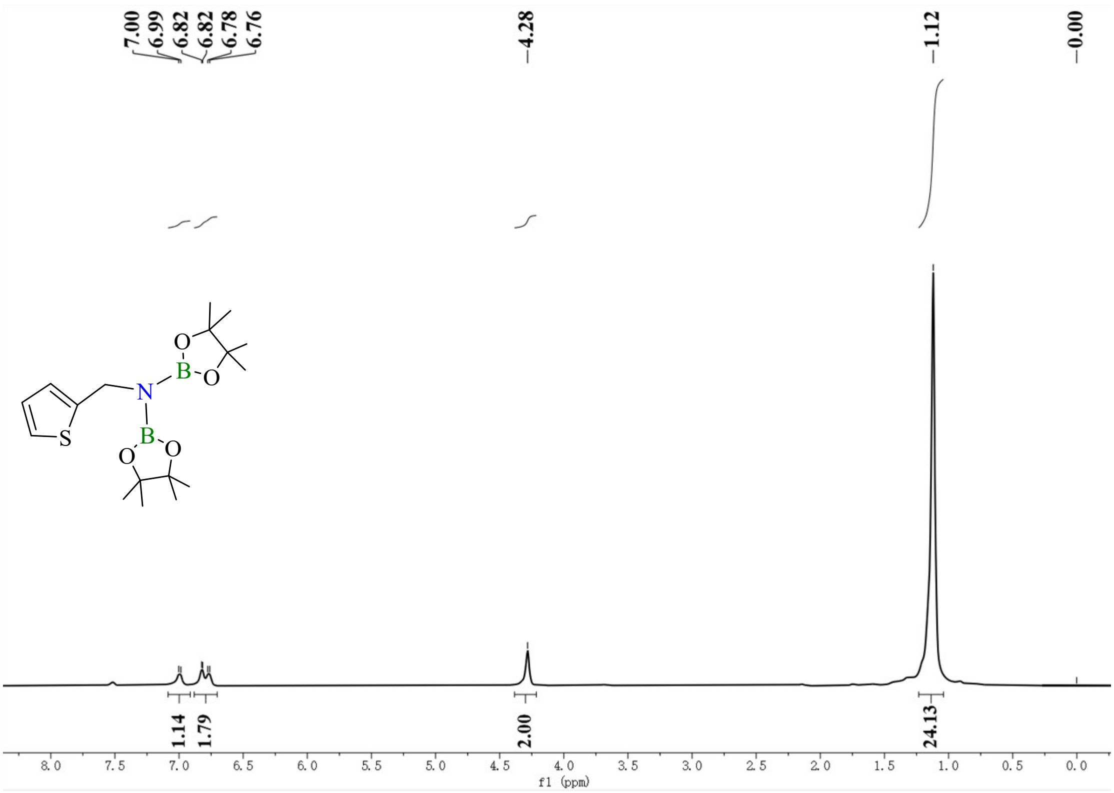


Figure S37. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **7t**.

6.3 NMR spectra of vinylboranes

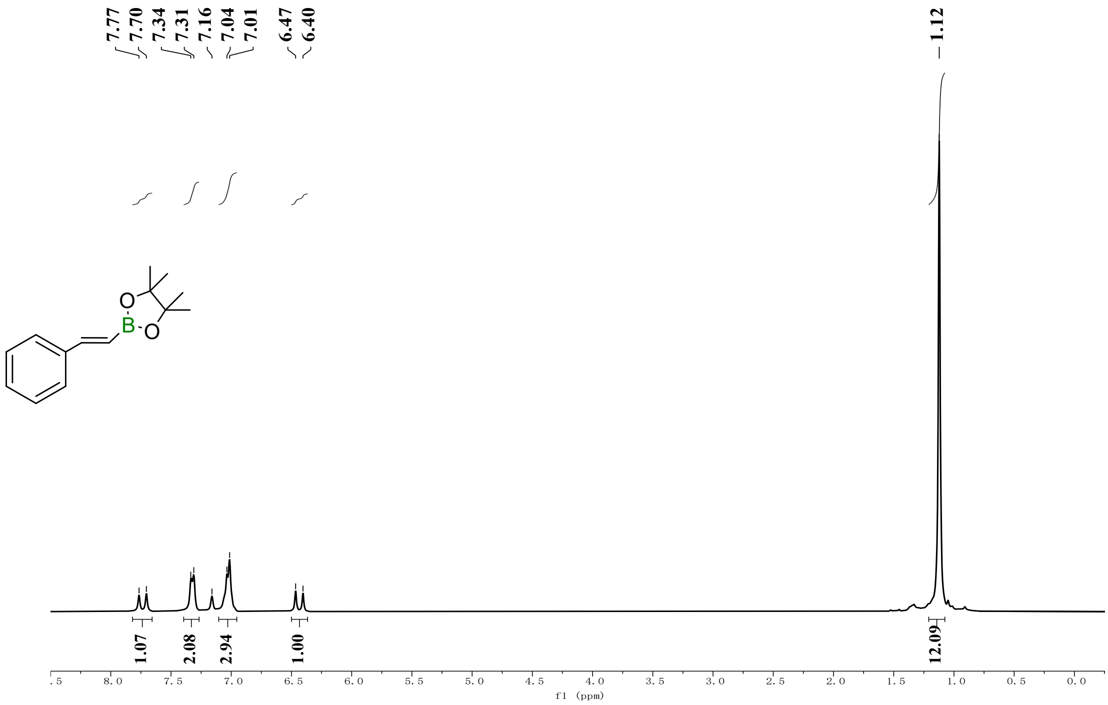


Figure S38. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9a**.

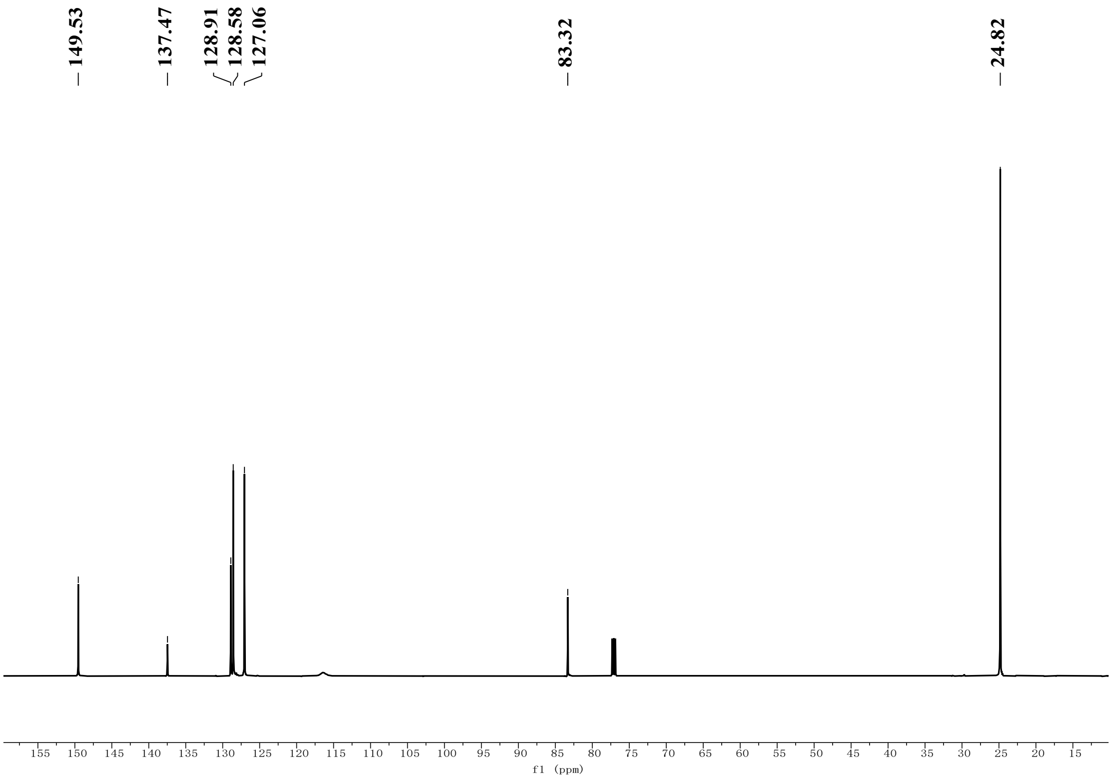


Figure S39. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9a**.

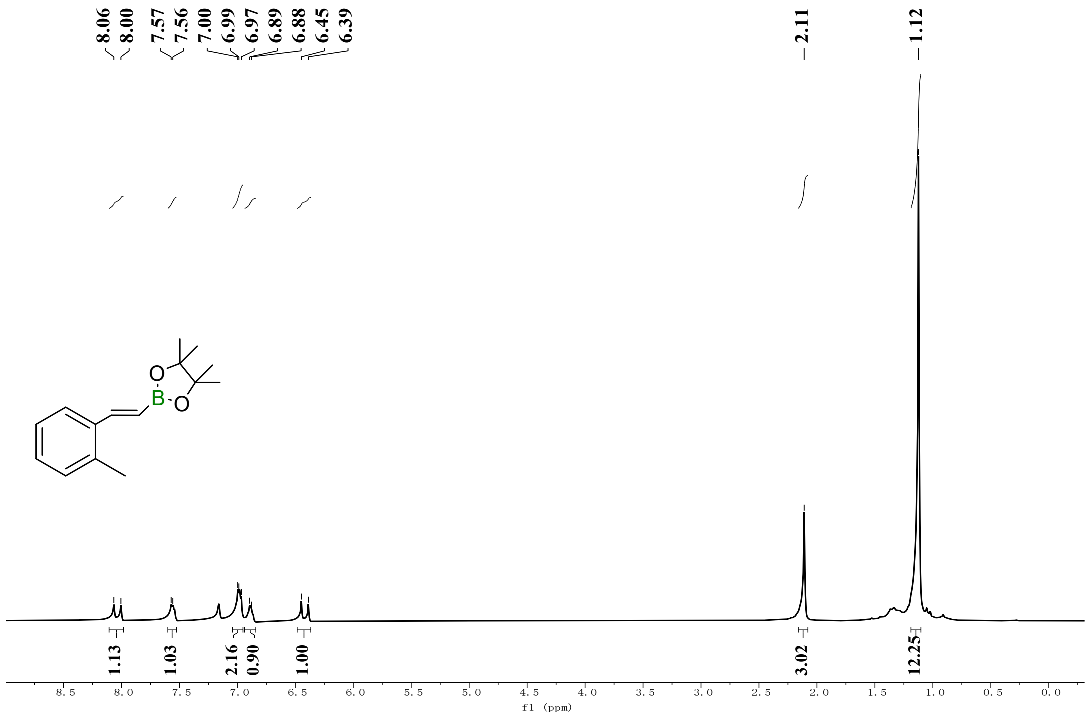


Figure S40. ^{1}H NMR (300 MHz, C_6D_6) spectrum **9b**.

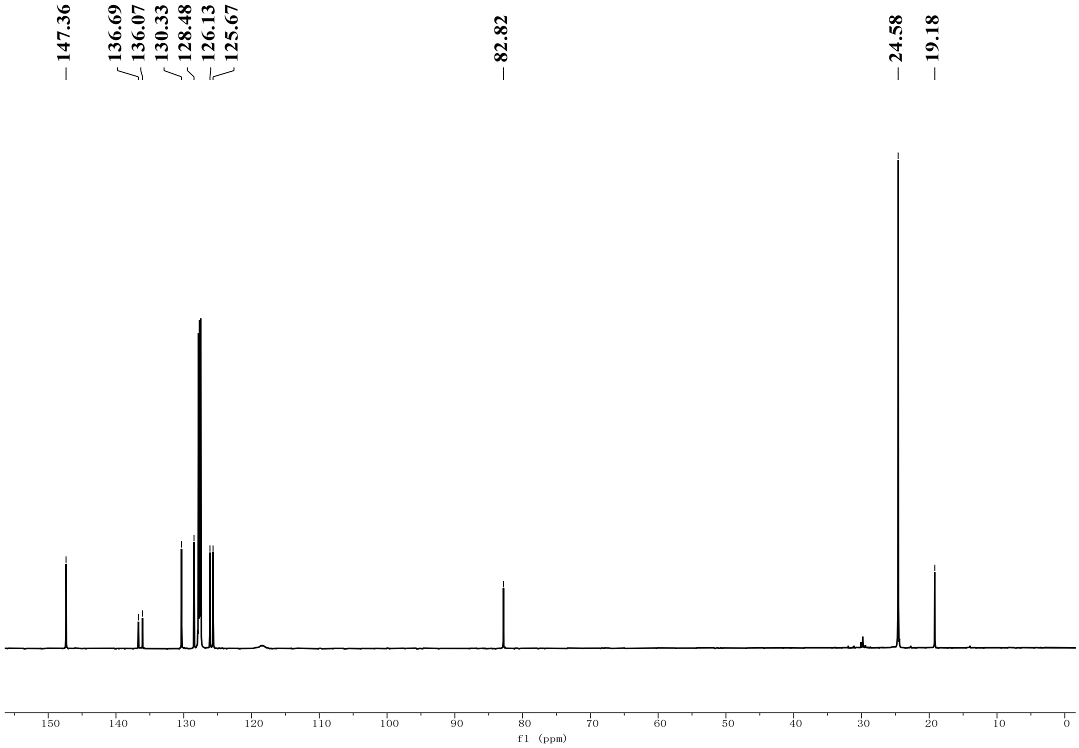


Figure S41. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9b**.

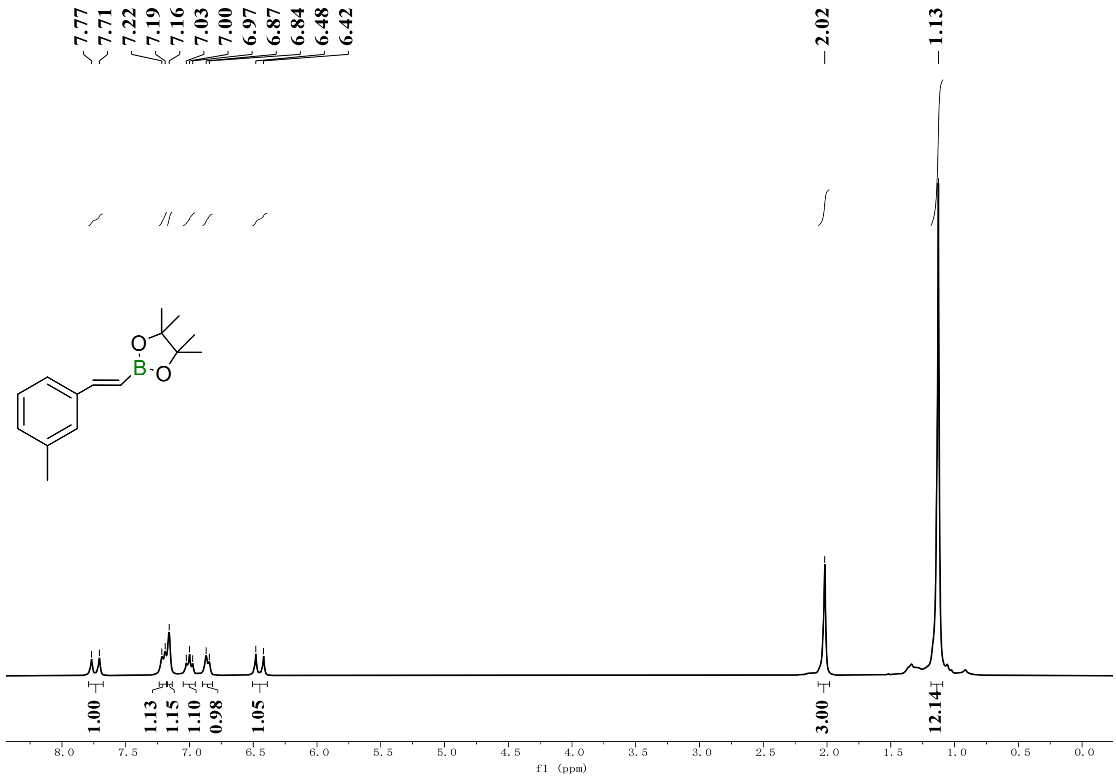


Figure S42. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9c**.

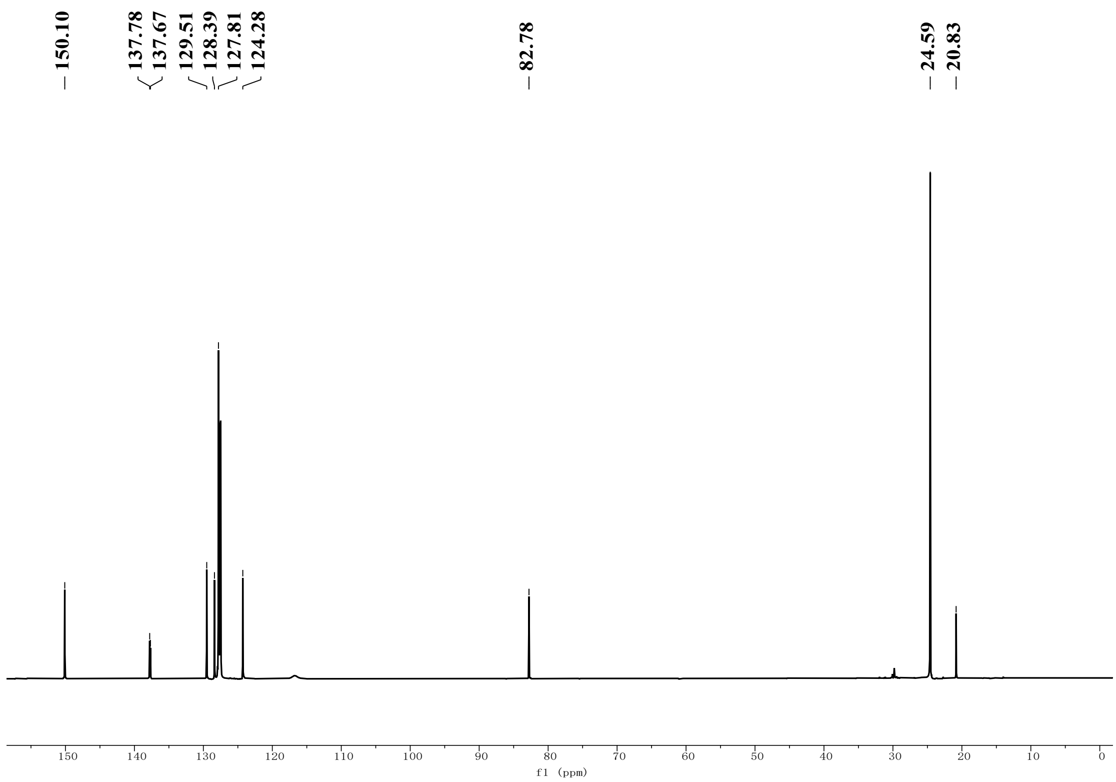


Figure S43. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9c**.

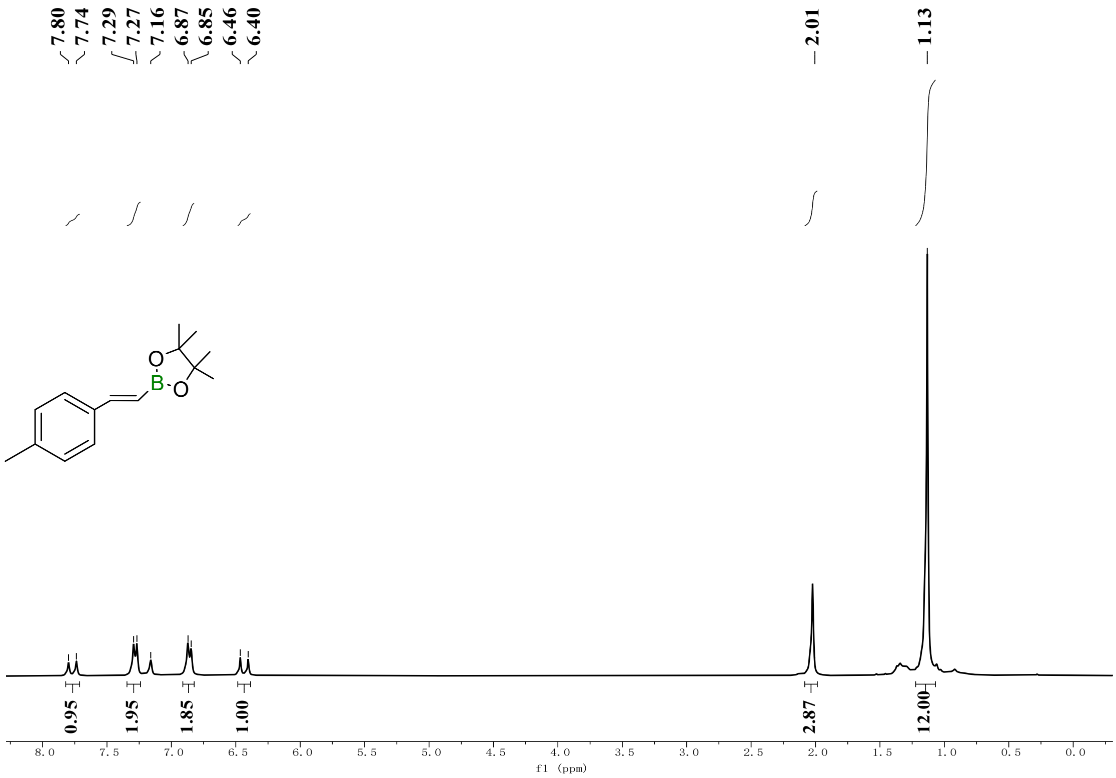


Figure S44. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9d**.

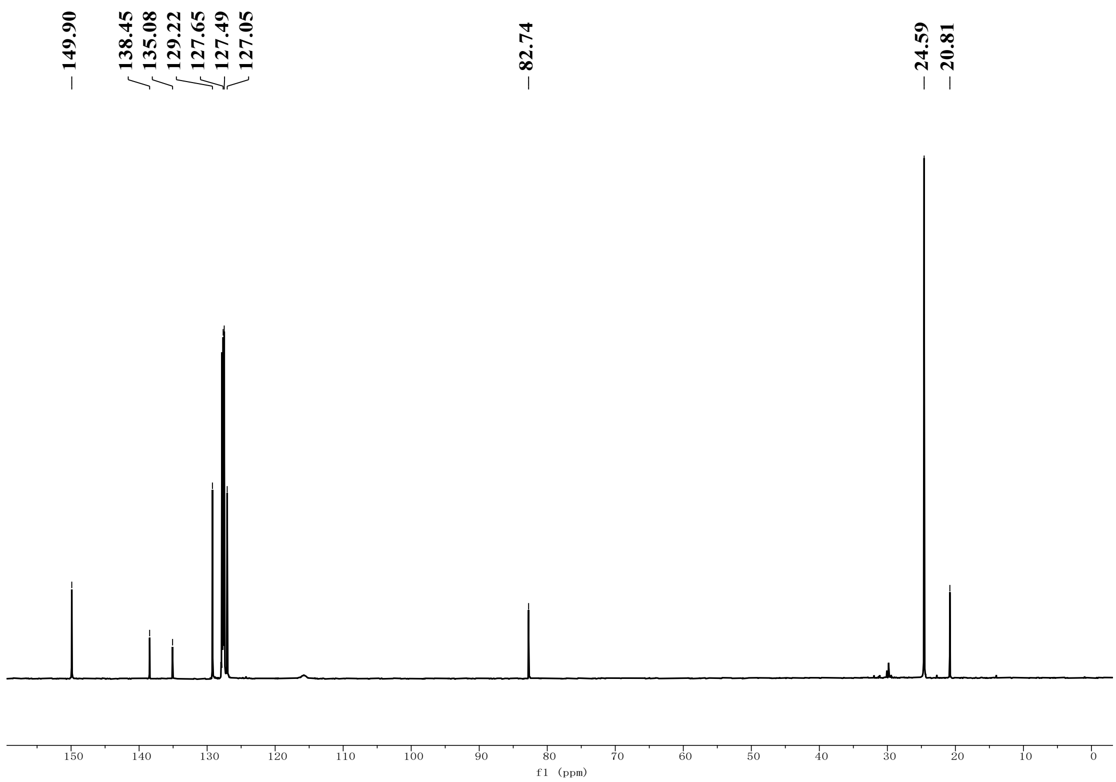


Figure S45. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9d**.

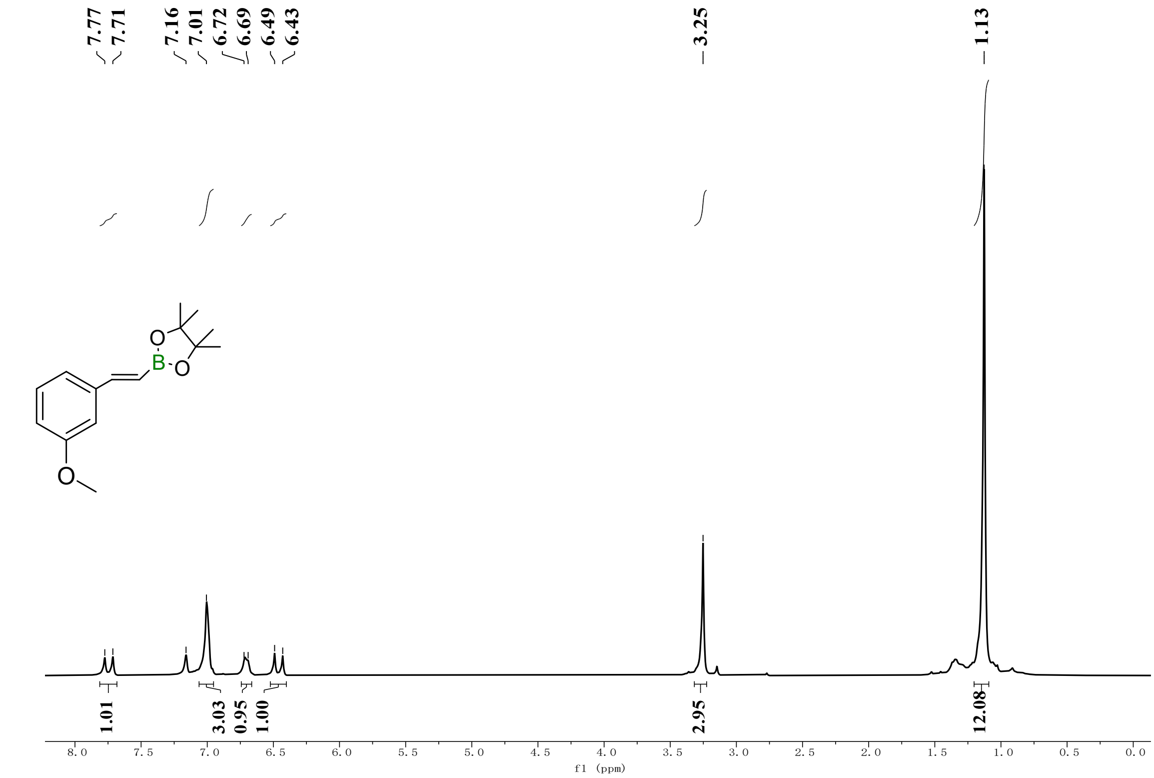


Figure S46. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9e**.

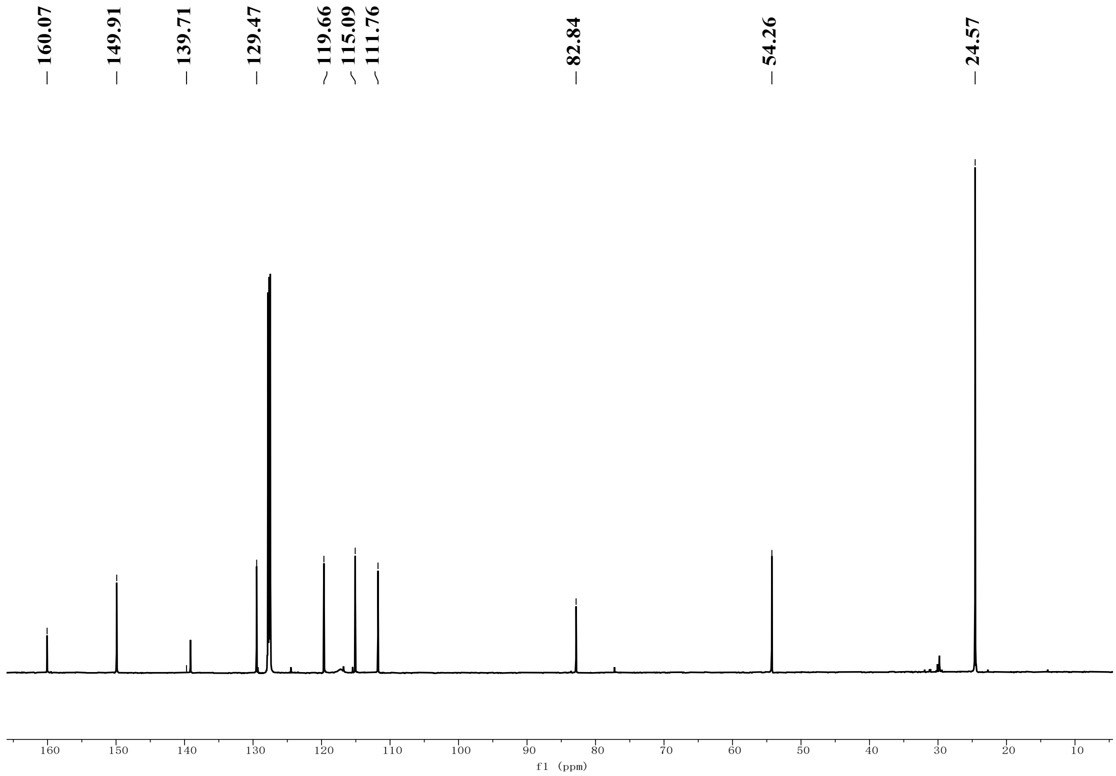


Figure S47. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9e**.

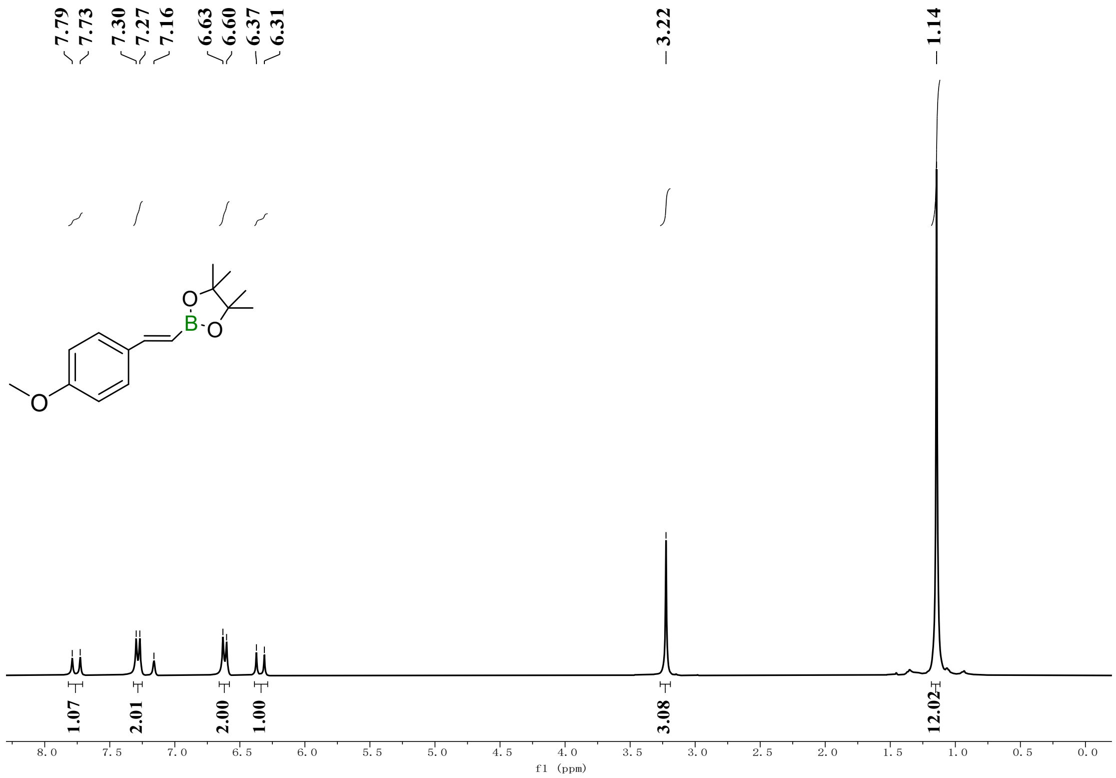


Figure S48. [1]H NMR (300 MHz, C_6D_6) spectrum of **9f**.

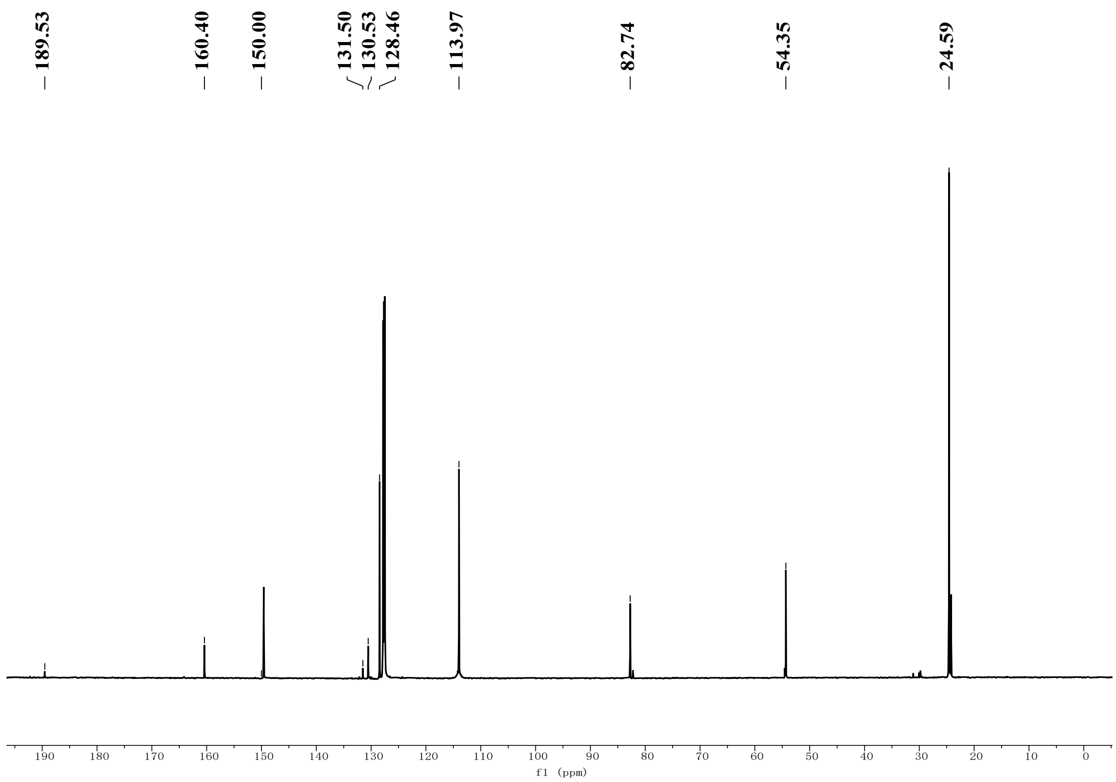


Figure S49. [13]C NMR (151 MHz, C_6D_6) spectrum of **9f**.

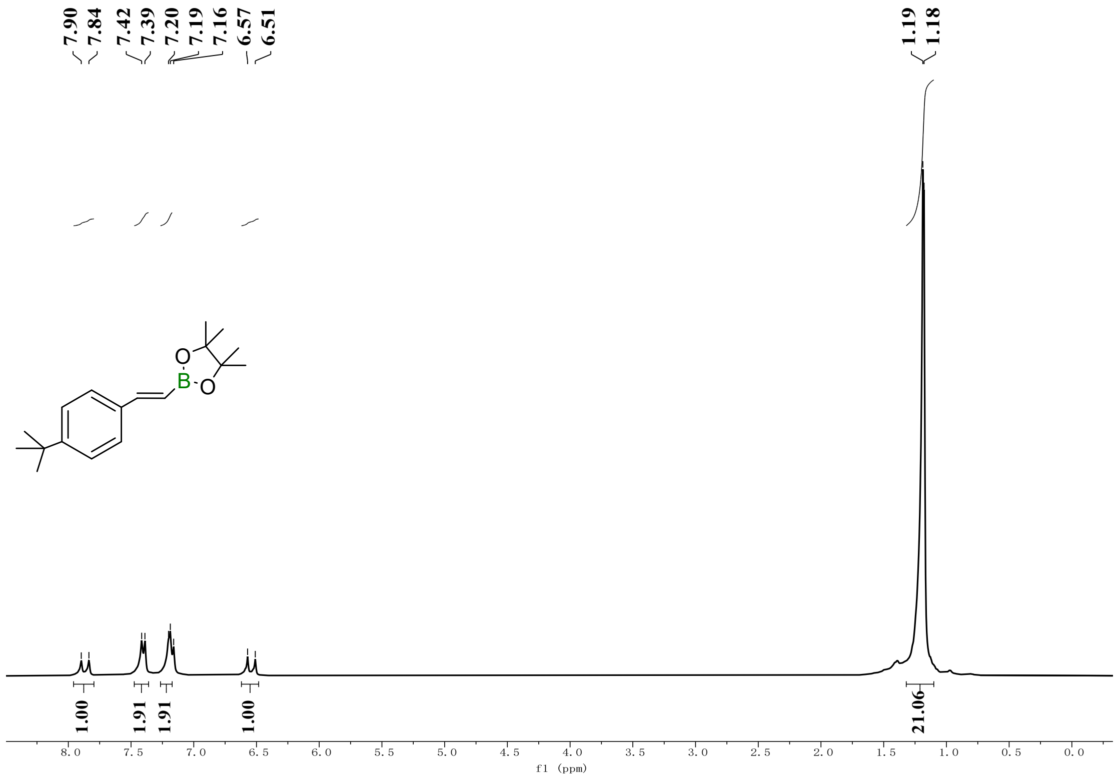


Figure S50. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9g**.

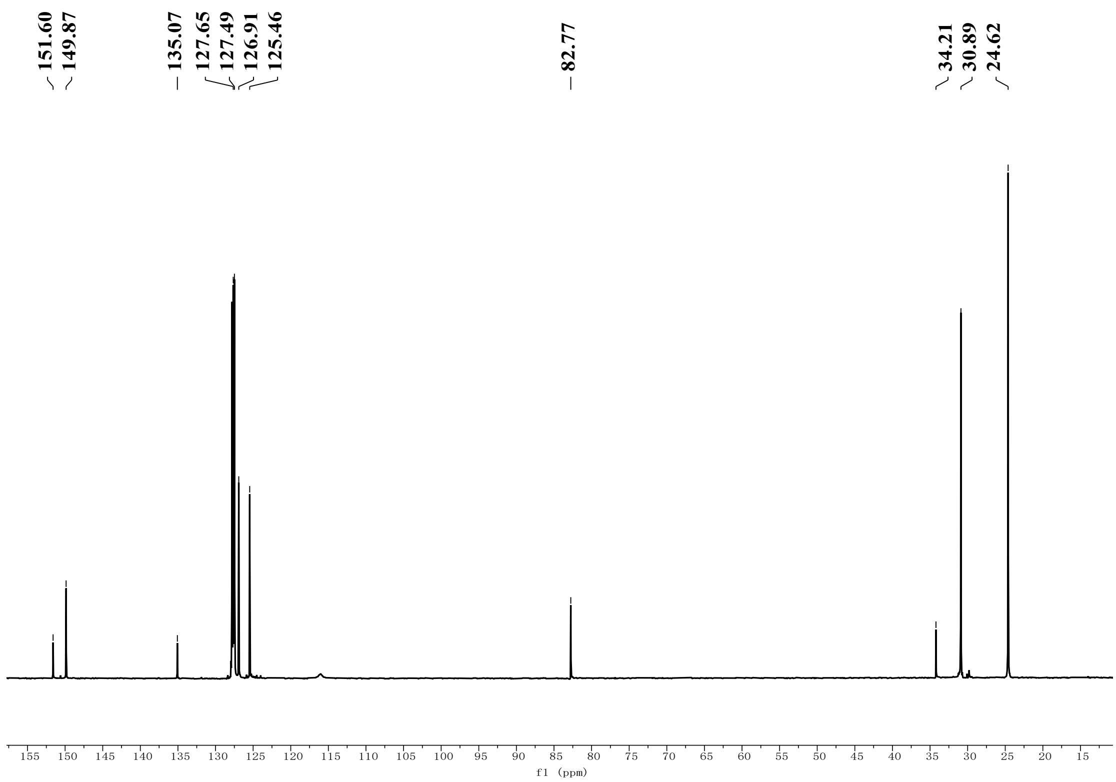


Figure S51. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9g**.

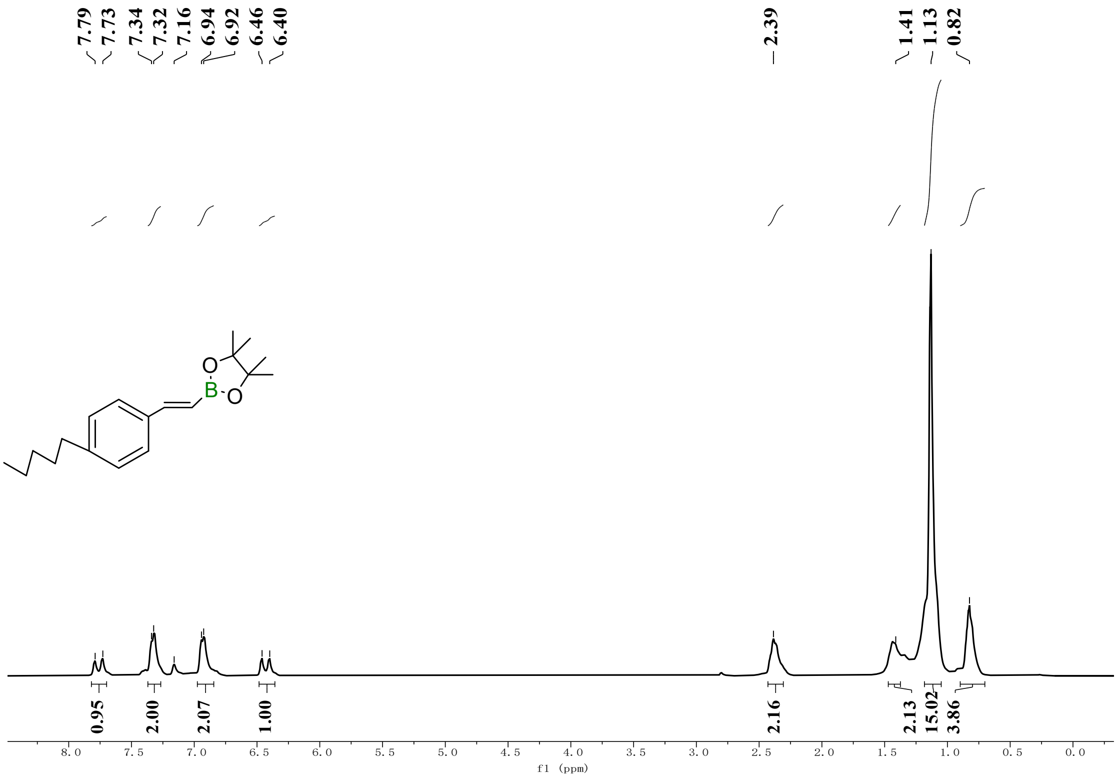


Figure S52. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9h**.

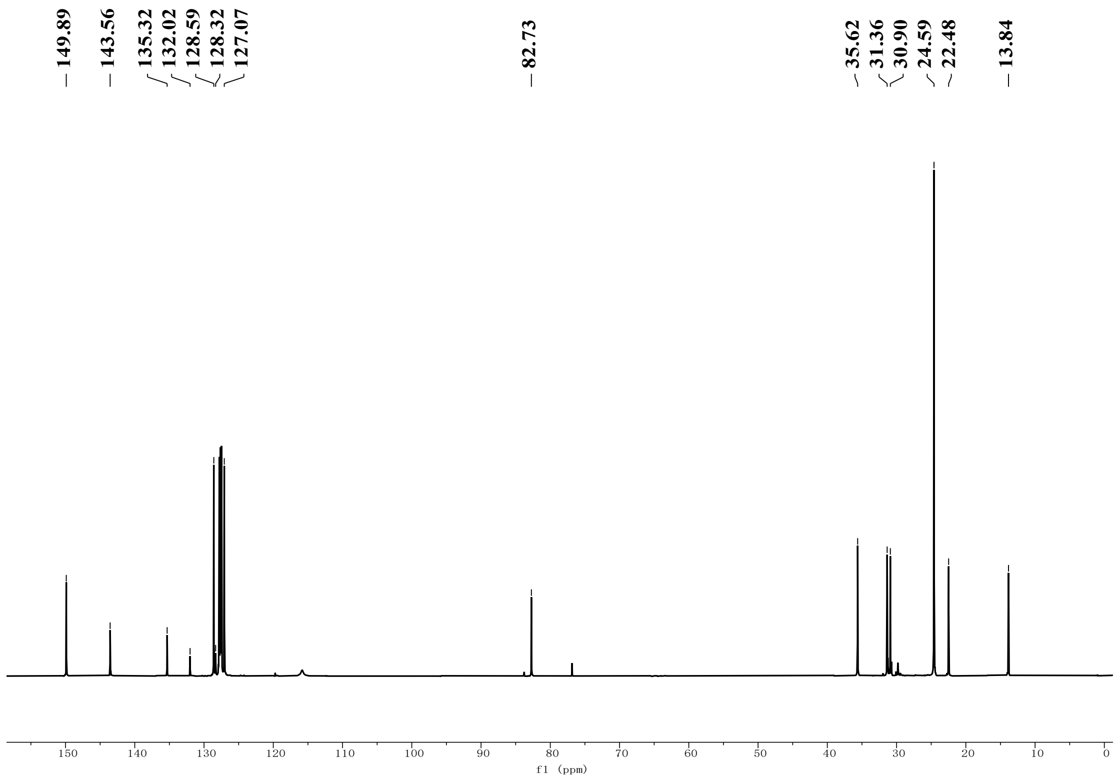


Figure S53. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9h**.

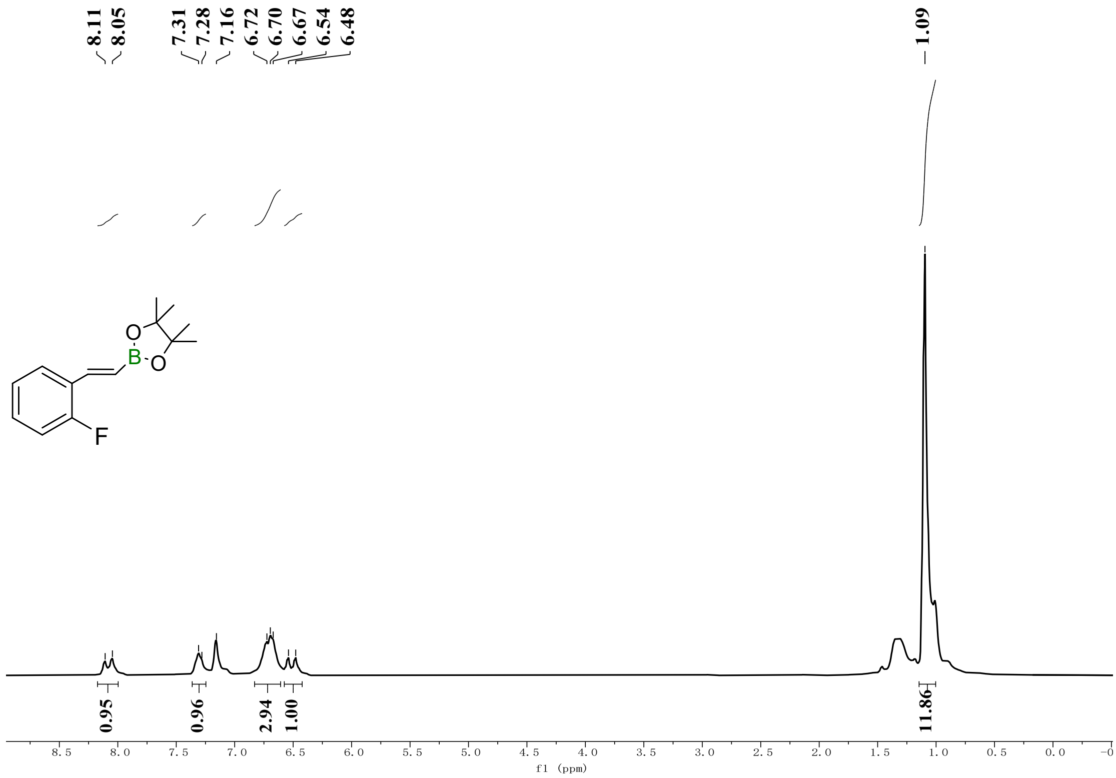


Figure S54. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9i**.

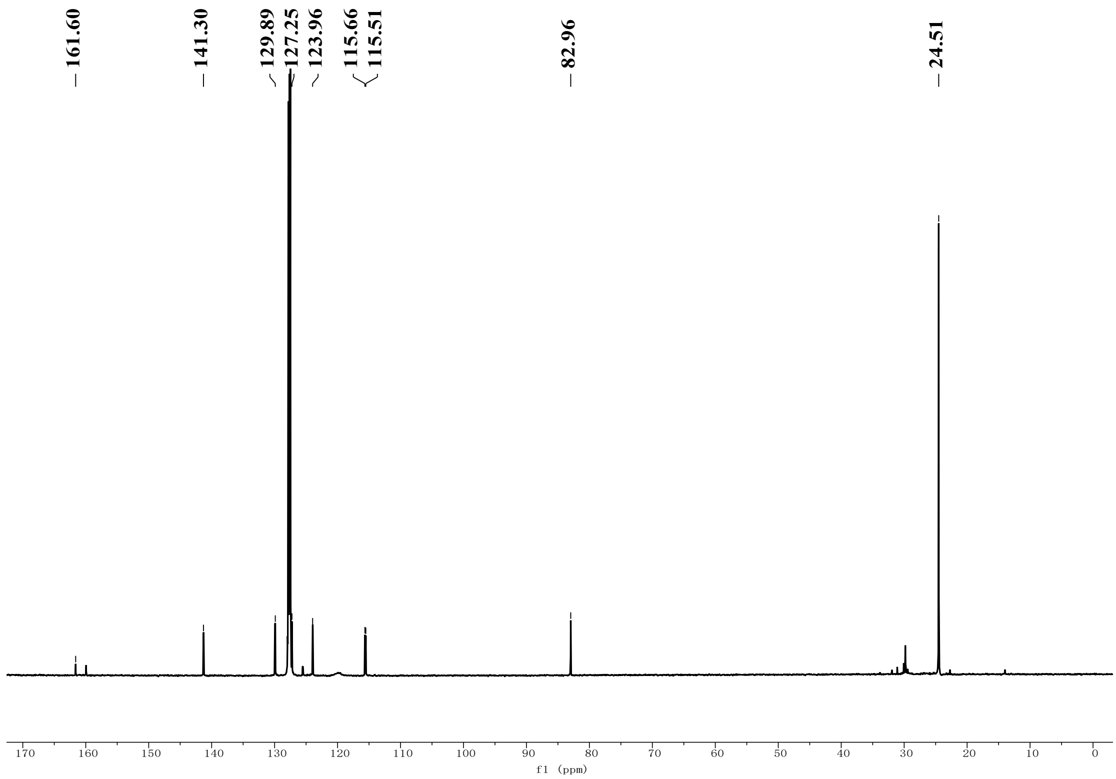


Figure S55. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9i**.

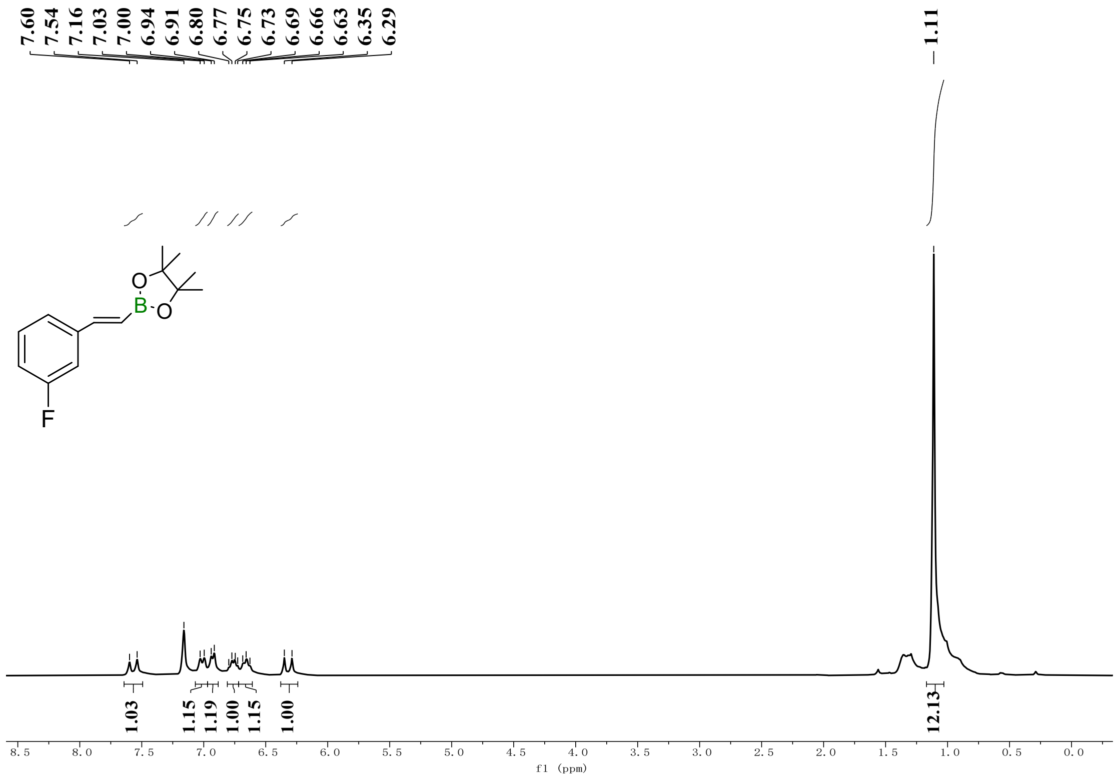


Figure S56. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9j**.

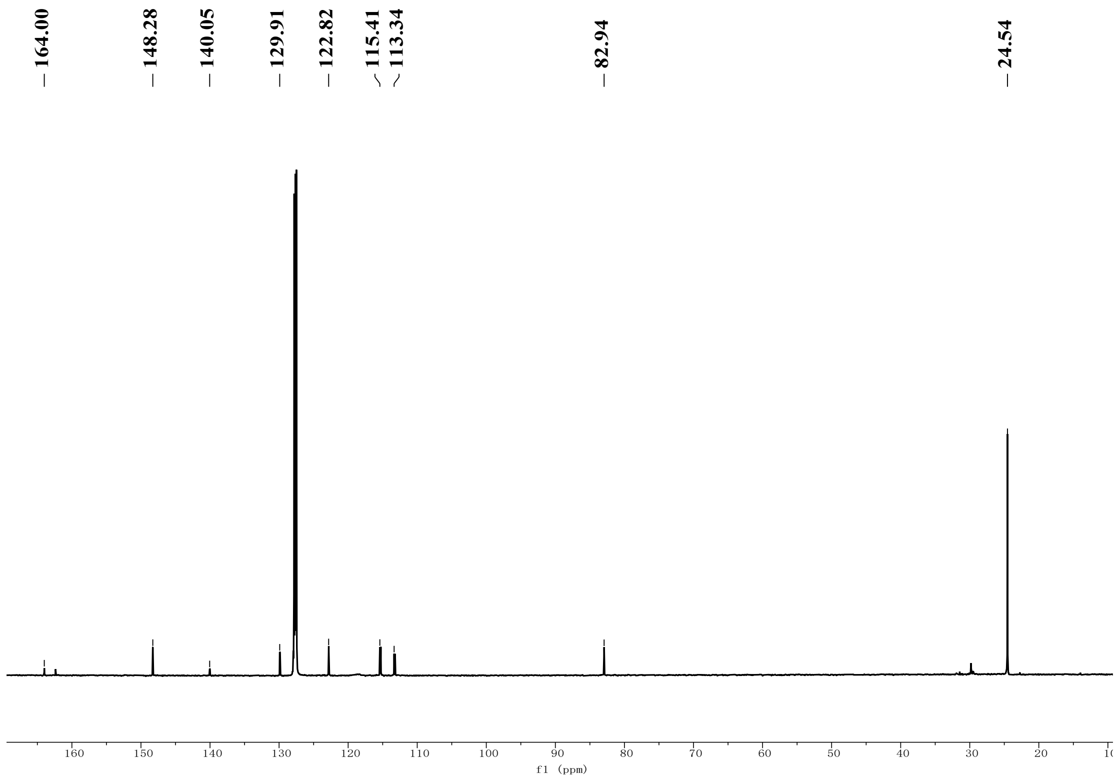


Figure S57. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9j**.

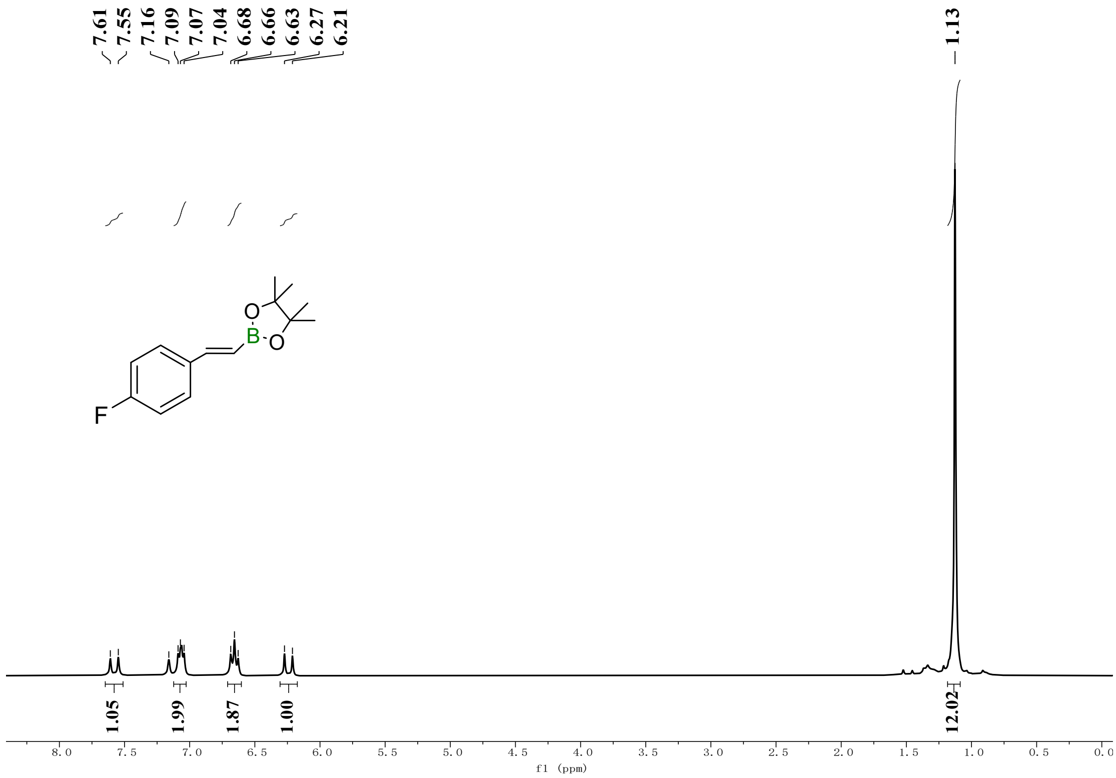


Figure S58. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9k**.

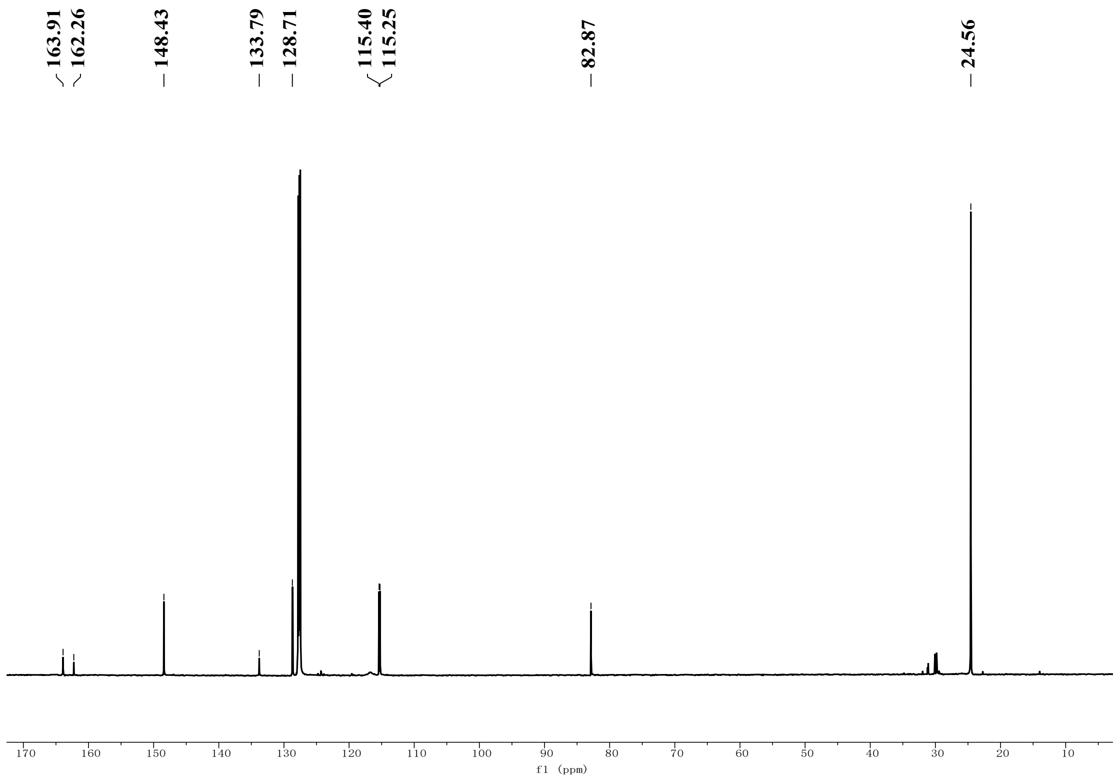


Figure S59. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9k**.

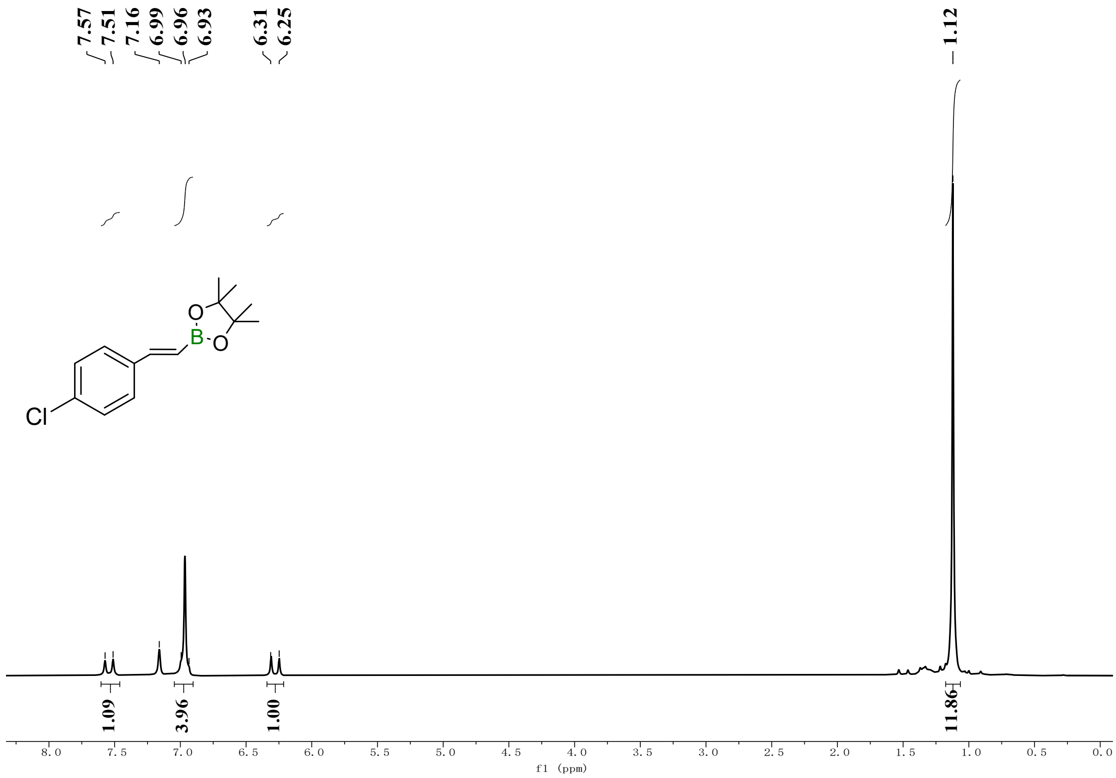


Figure S60. ¹H NMR (300 MHz, C_6D_6) spectrum of **9l**.

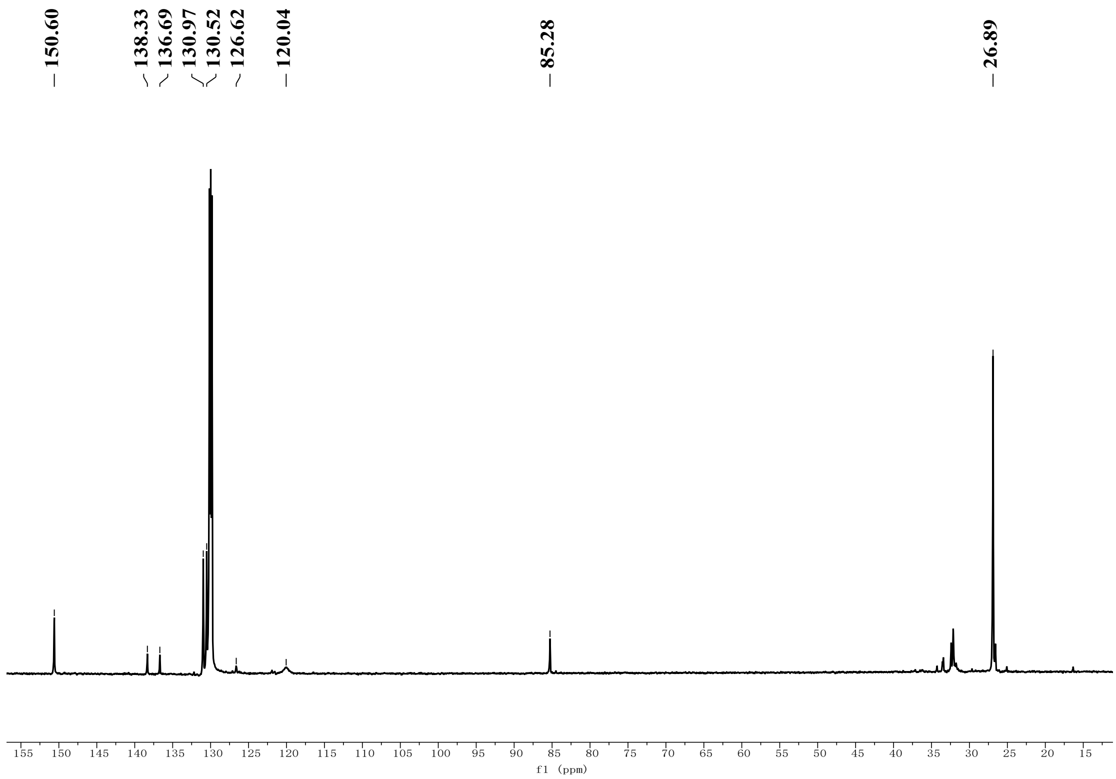


Figure S61. ¹³C NMR (151 MHz, C_6D_6) spectrum of **9l**.

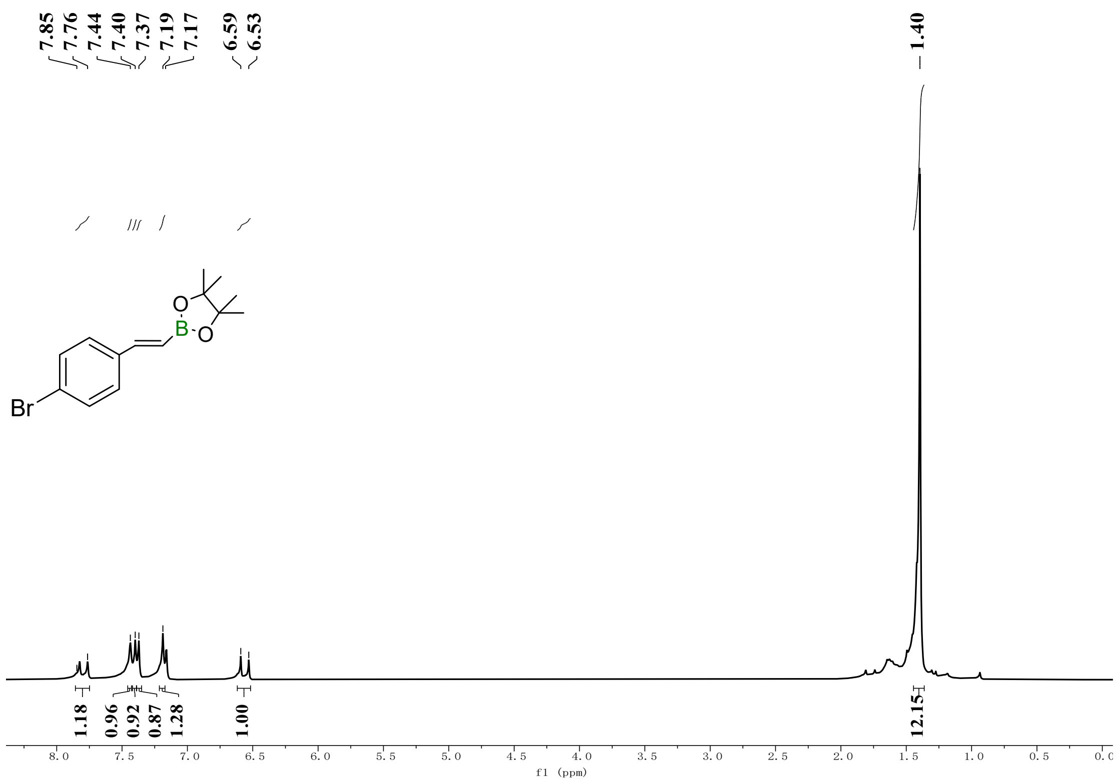


Figure S62. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9m**.

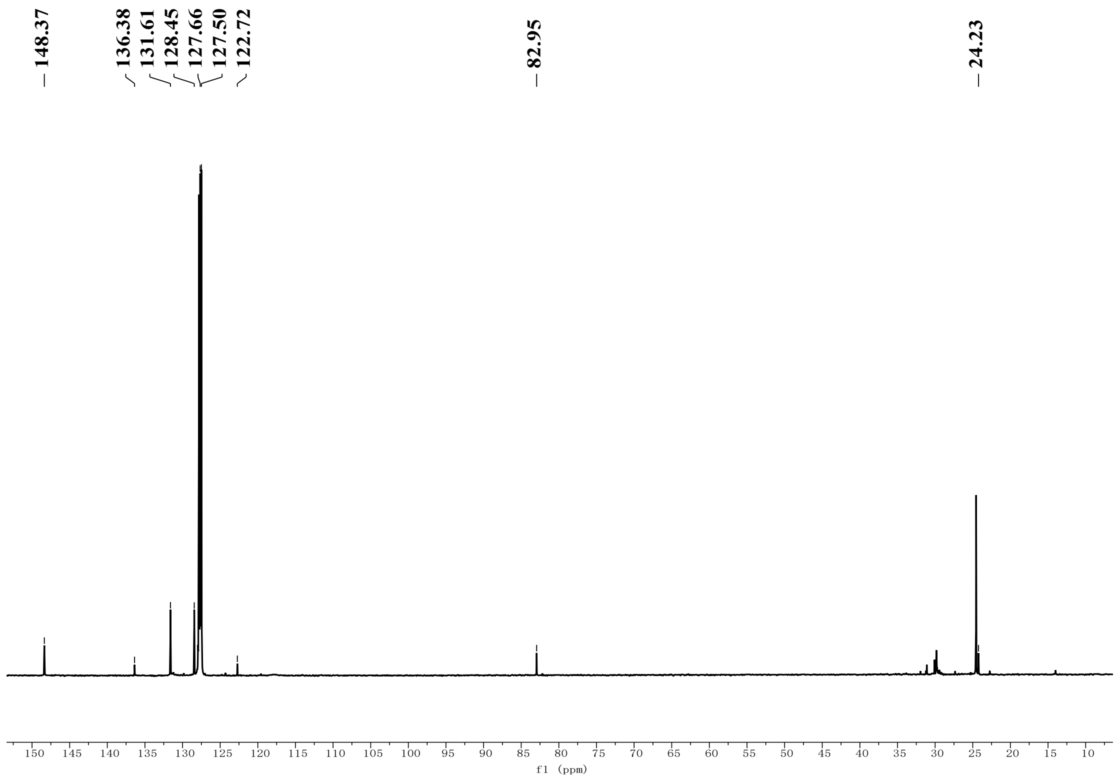


Figure S63. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9m**.

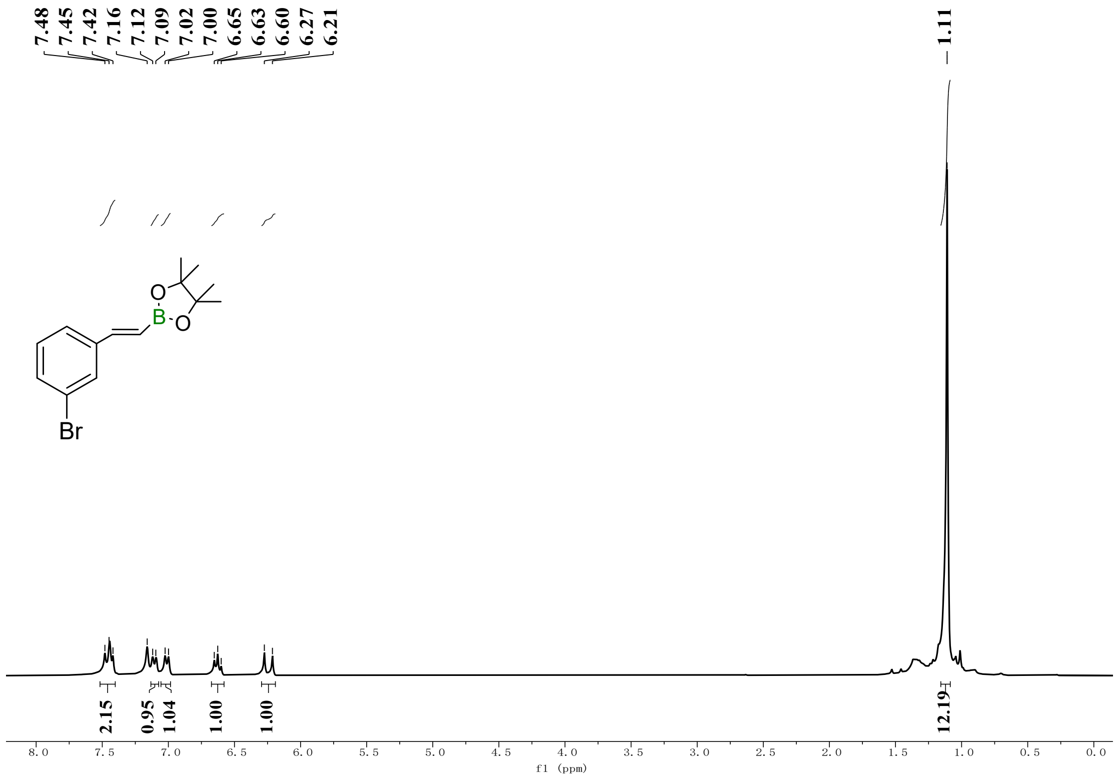


Figure S64. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9n**.

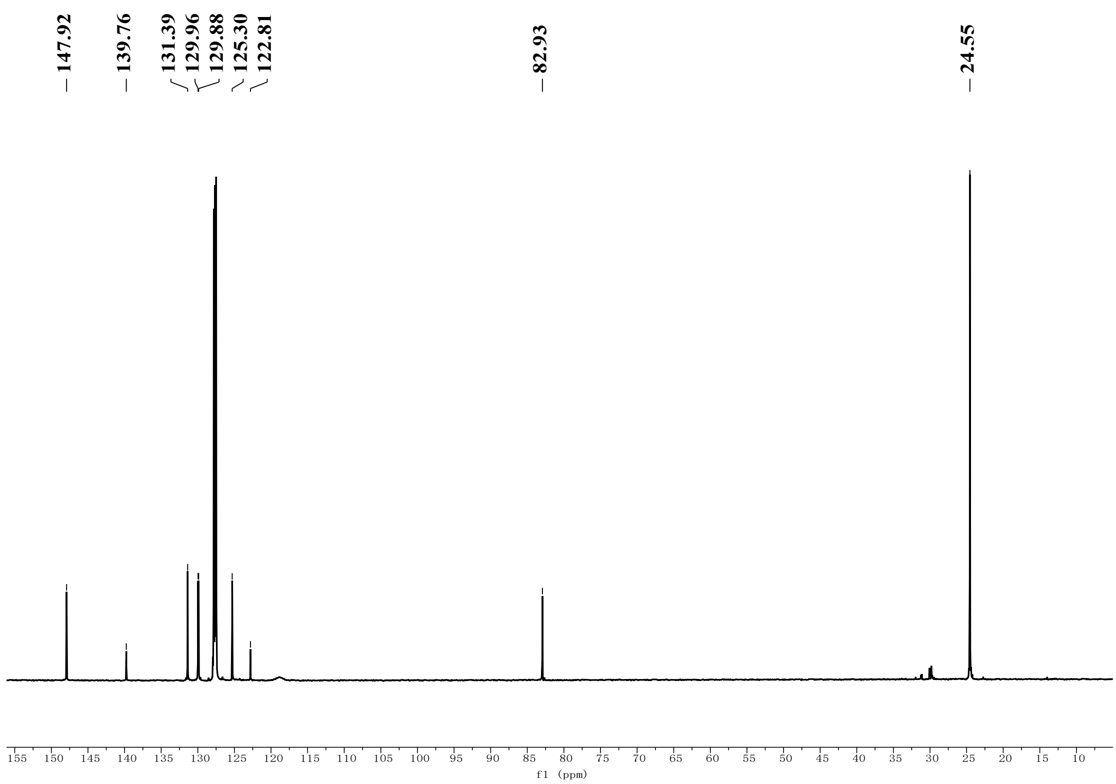


Figure S65. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9n**.

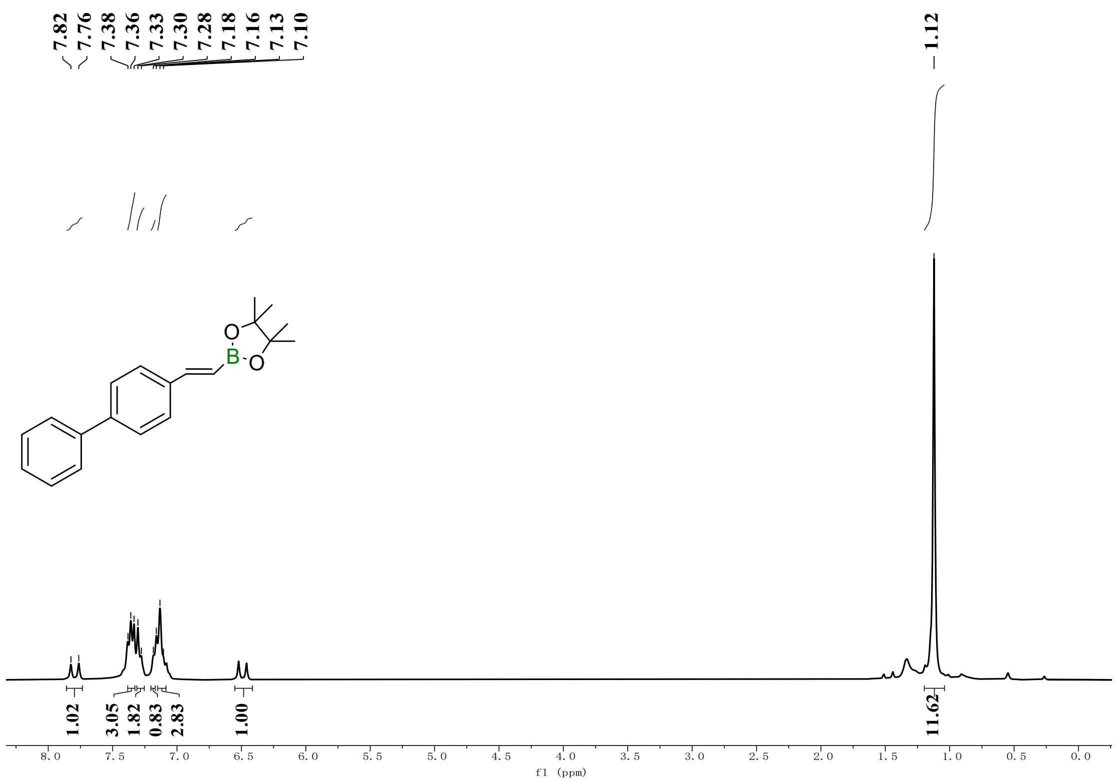


Figure S66. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9o**.

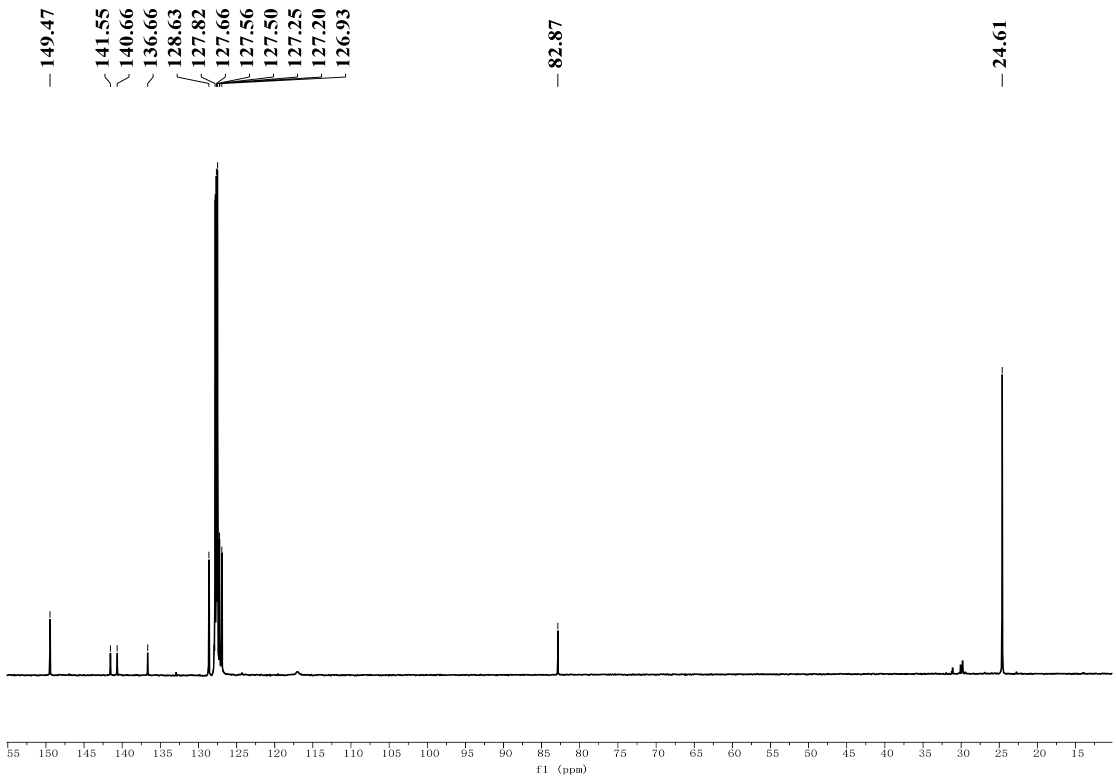


Figure S67. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9o**.

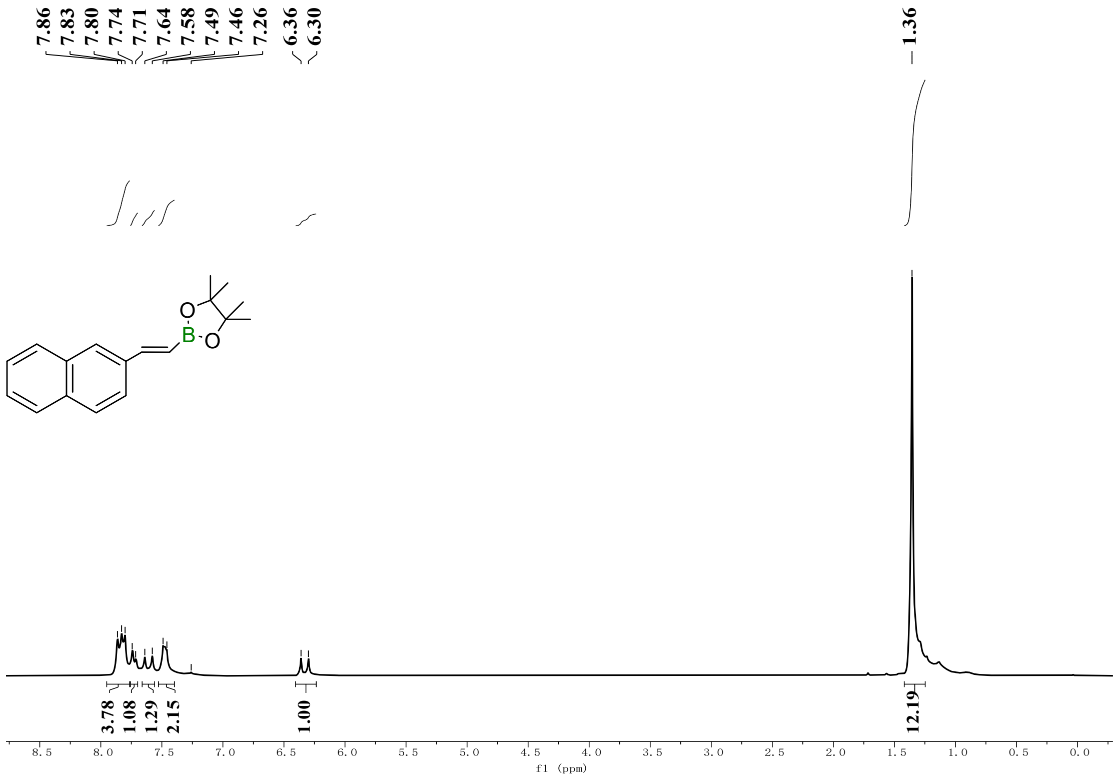


Figure S68. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **9p**.

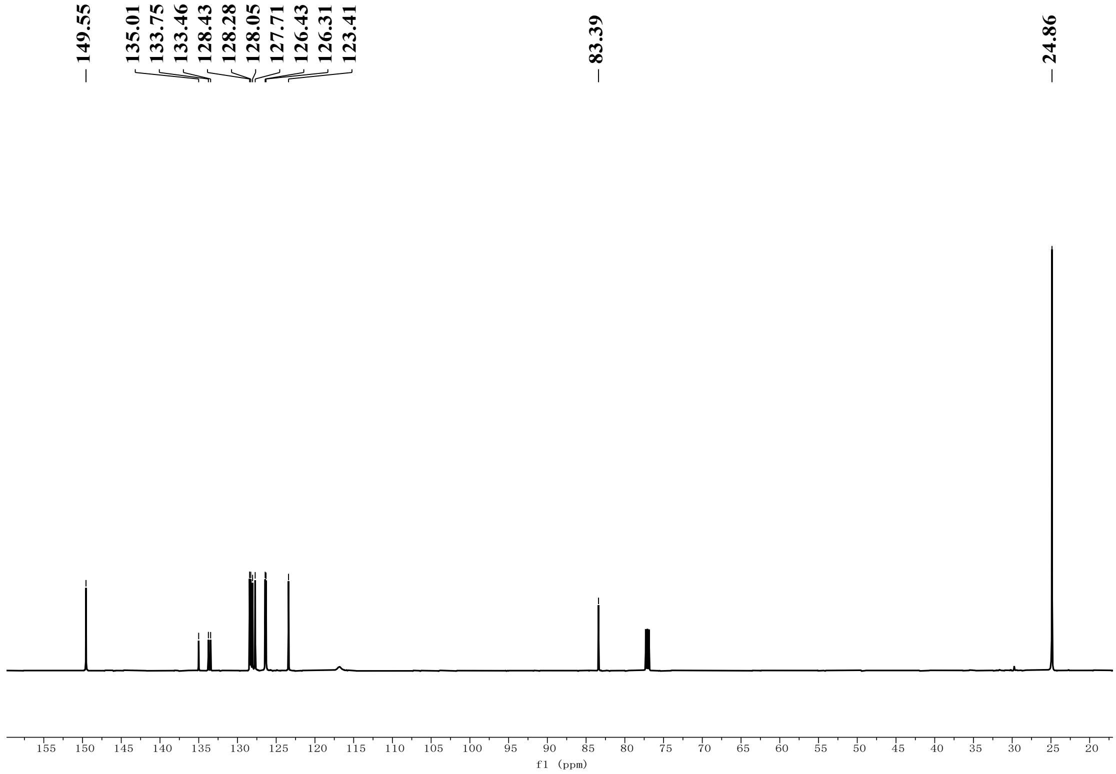


Figure S69. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9p**.

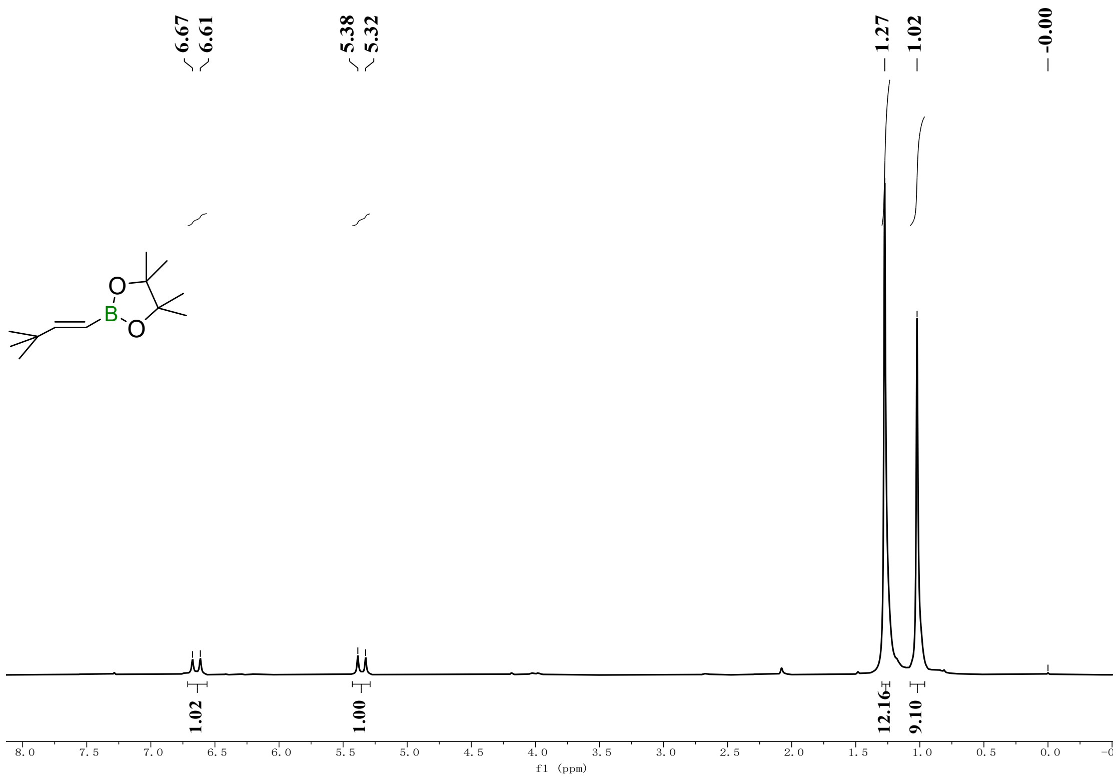


Figure S70. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of **9q**.

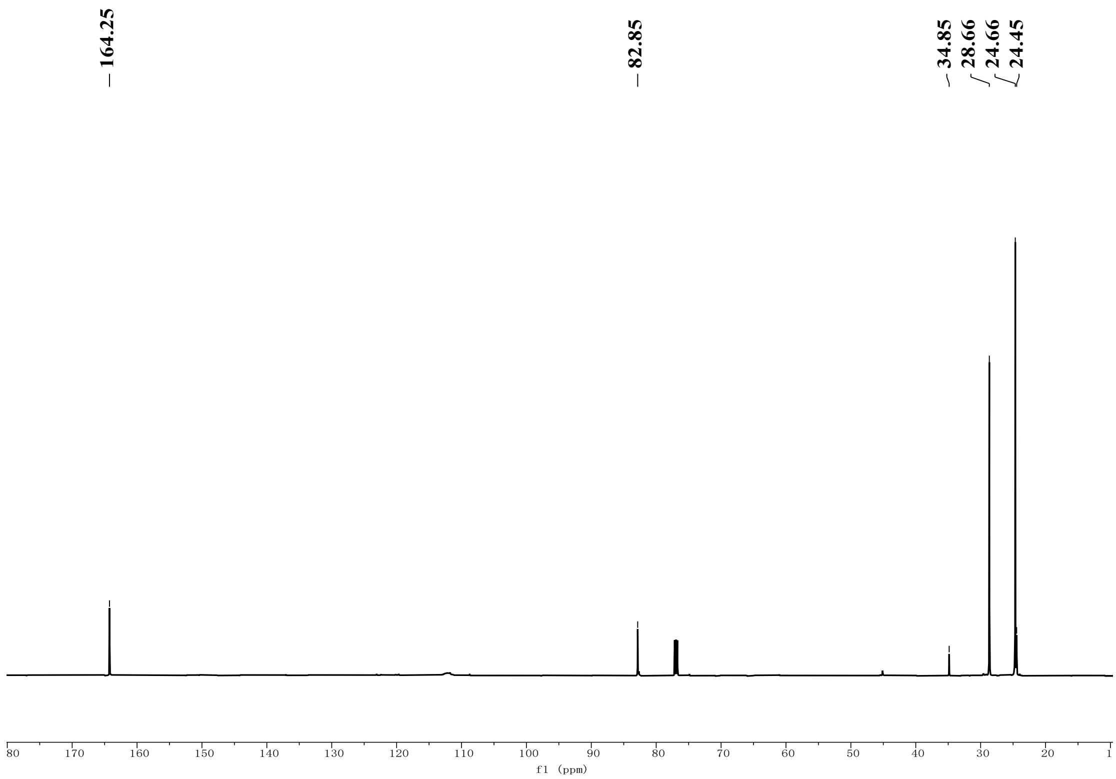


Figure S71. ^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **9q**.

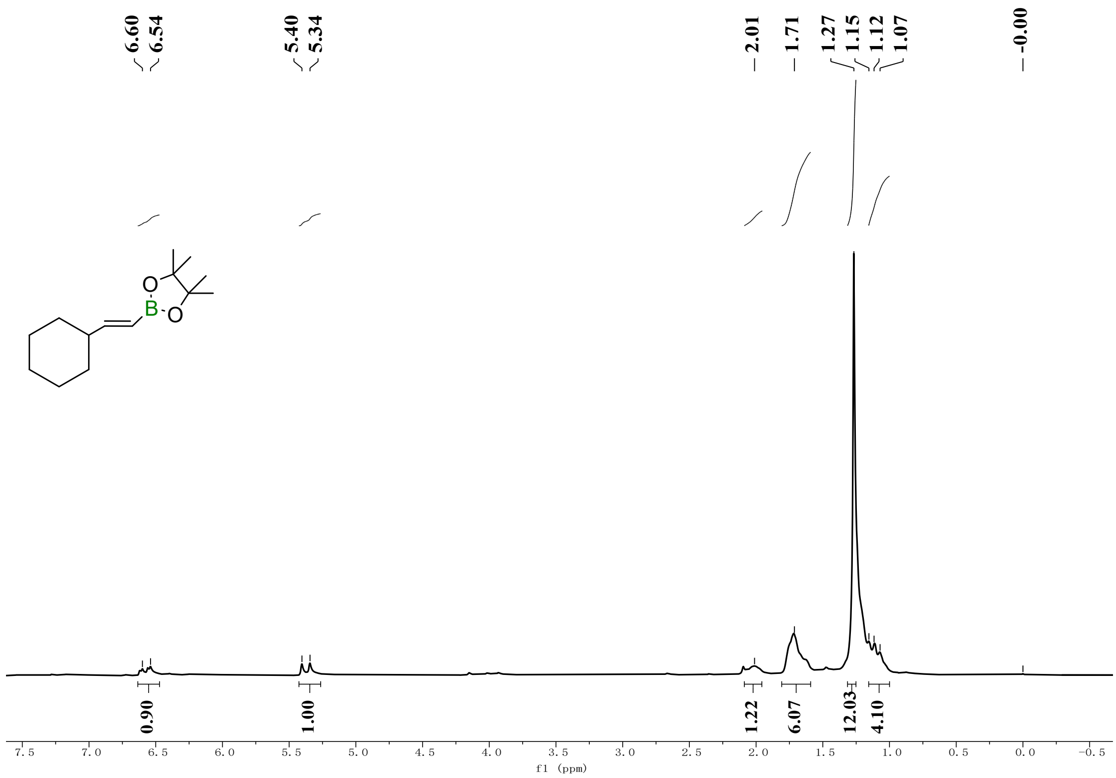


Figure S72. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9r**.

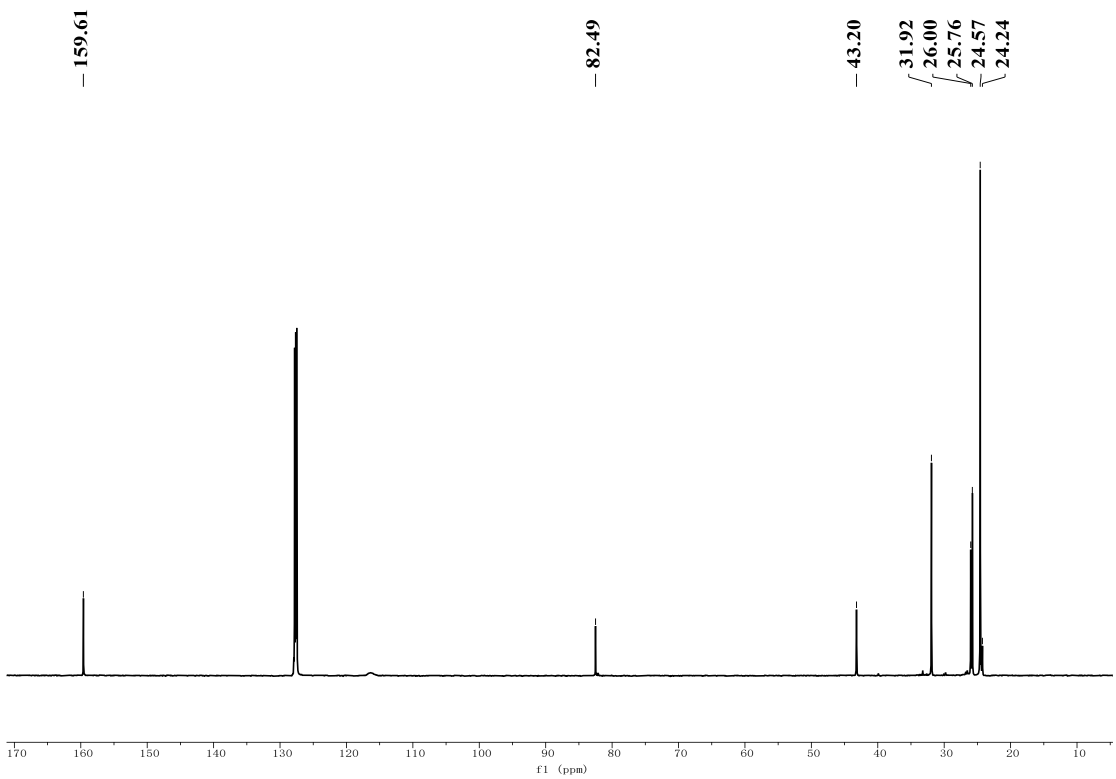


Figure S73. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9r**.

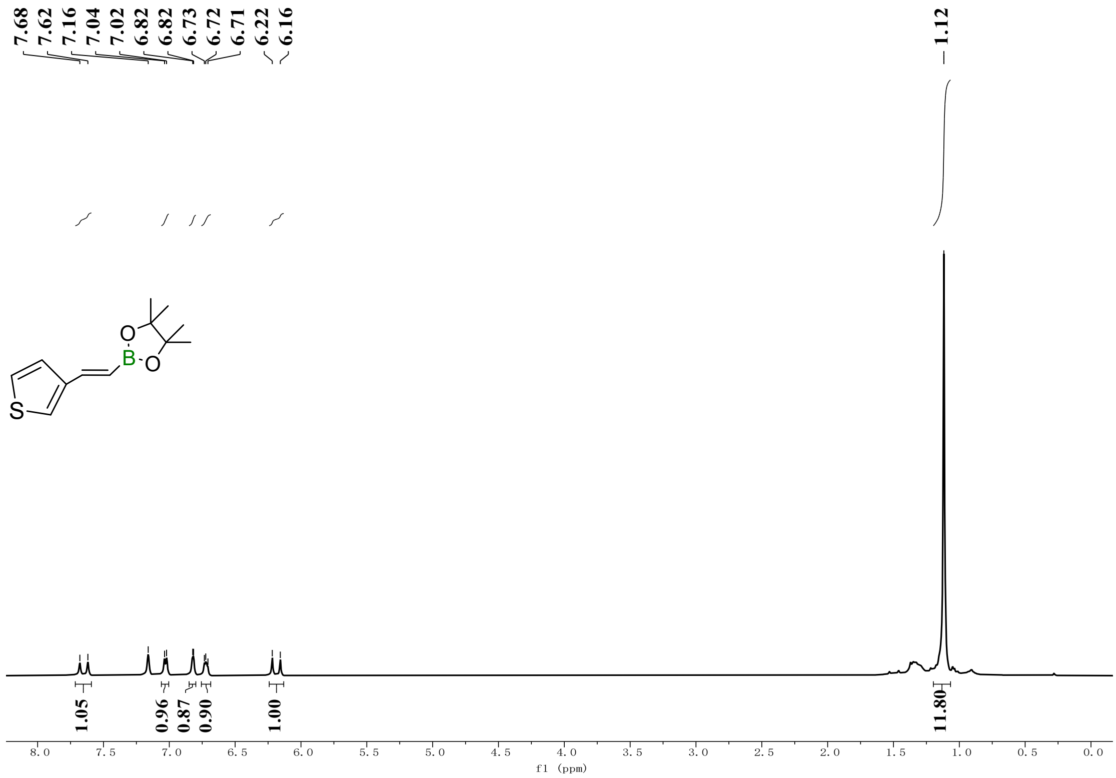


Figure S74. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **9s**.

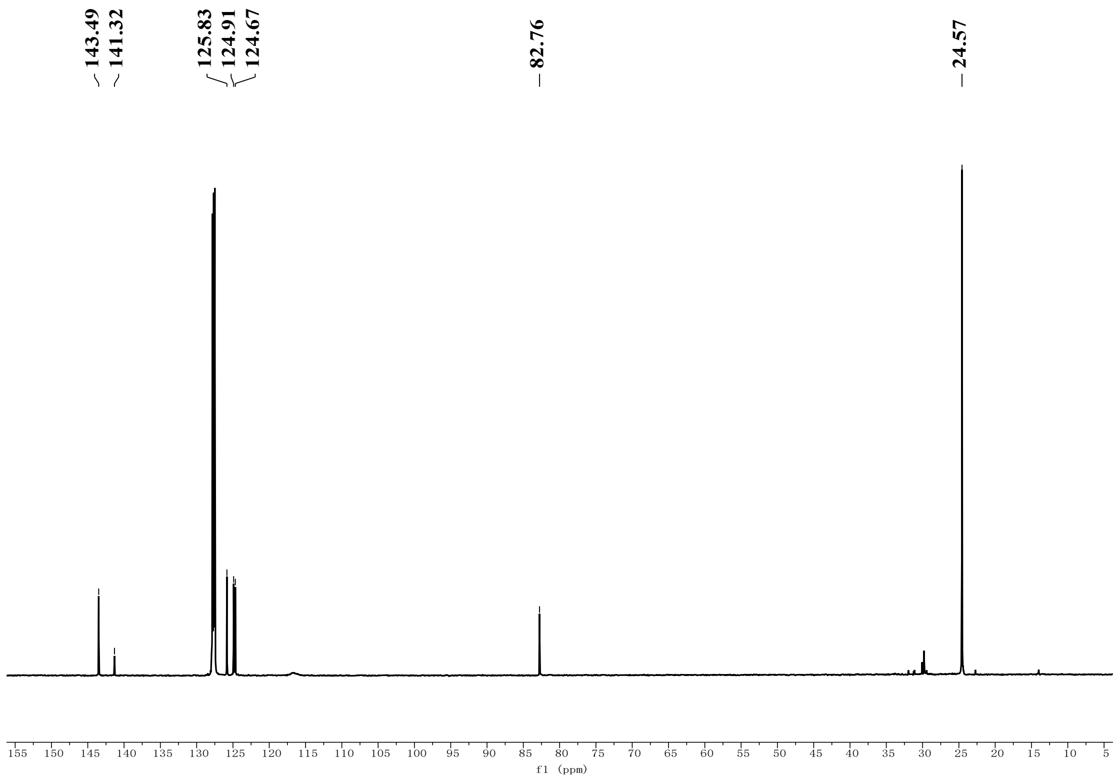


Figure S75. ^{13}C NMR (151 MHz, C_6D_6) spectrum of **9s**.

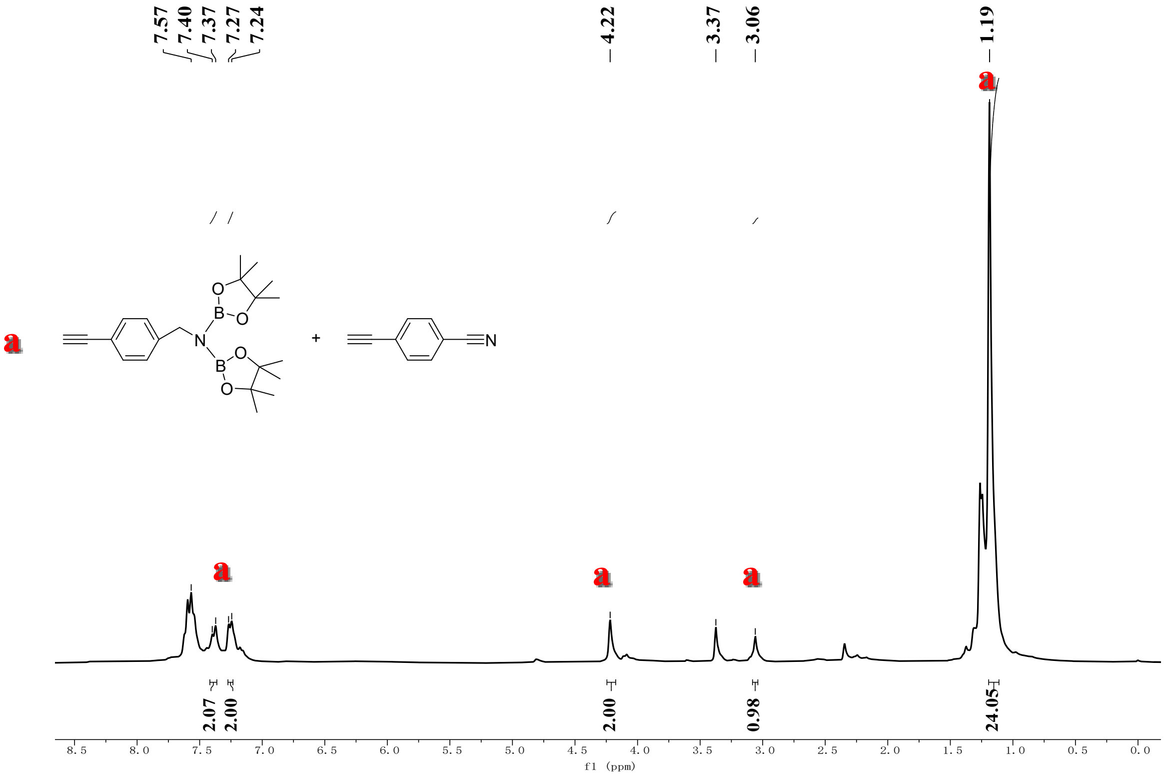


Figure S76. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-ethynylbenzonitrile reacted with HBPin at a 1:1 molar ratio.

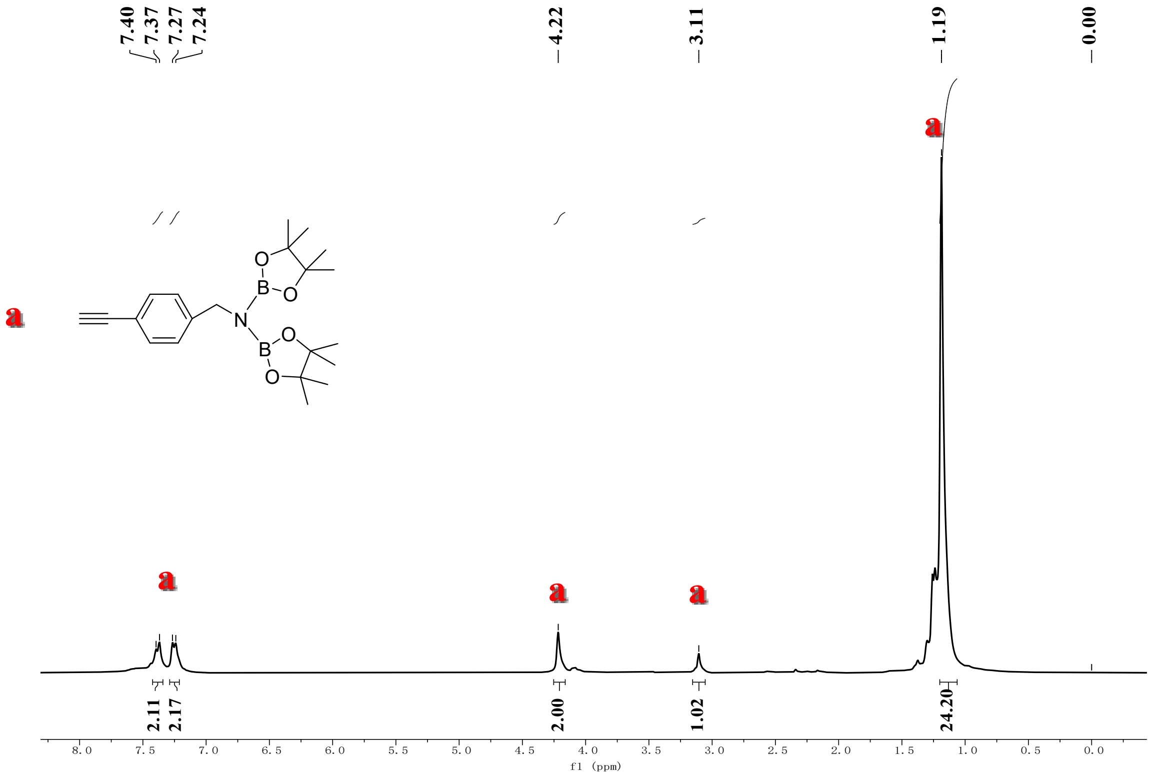


Figure S77. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-ethynylbenzonitrile reacted with HBPin at a 1:2 molar ratio.

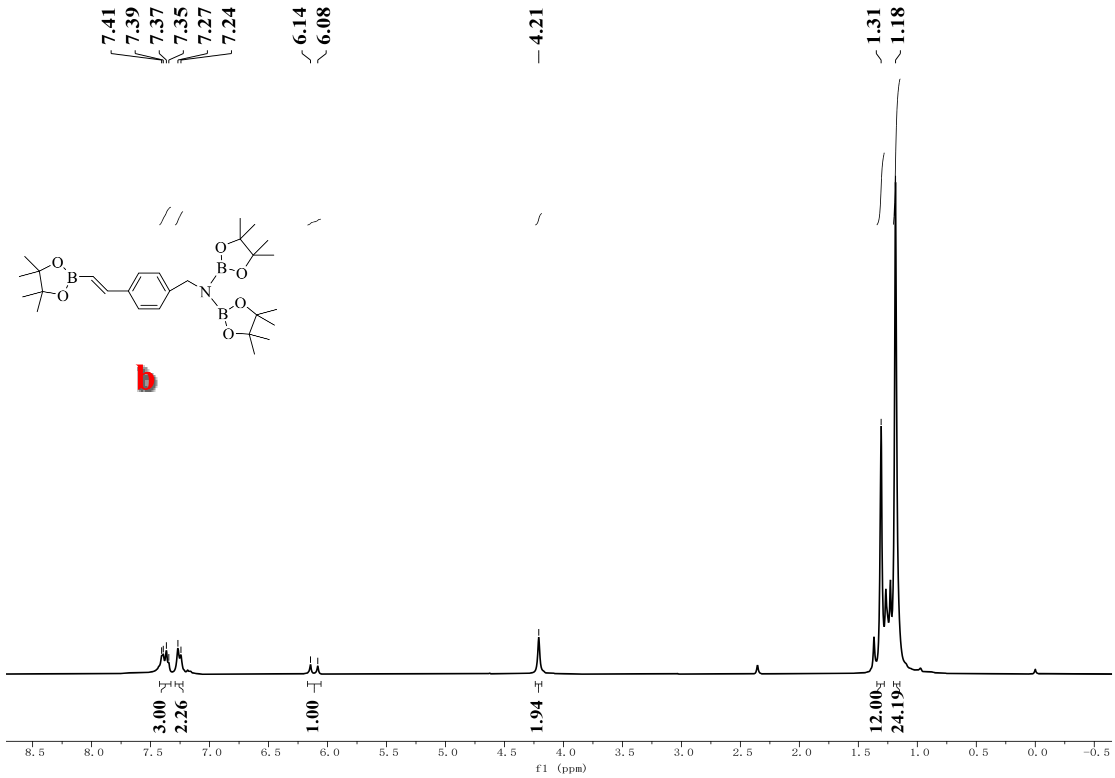


Figure S78. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of 4-ethynylbenzonitrile reacted with HBPin at a 1:3 molar ratio.

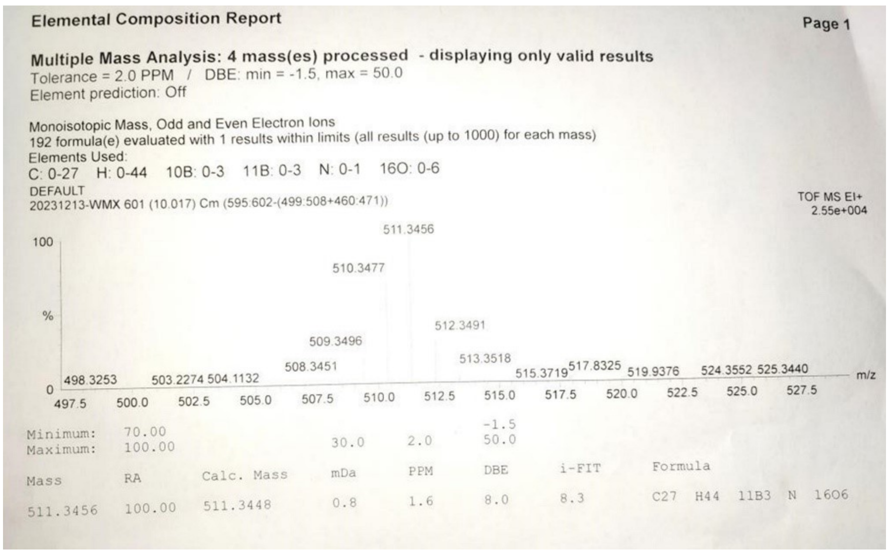
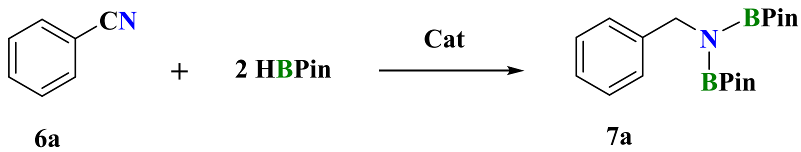


Figure S79. HRMS of compound **11**

7. Comparison of the catalytic performance of different catalysts for the hydroboration of benzonitrile (6a) and ethynylbenzene (8a).

Table S11. Comparison of the catalytic performance of different catalysts for the dihydroboration of benzonitrile (6a)



Cat. loading	Temperature (°C)	Time (h)	Solvent	Yield[a] (%)
5 mol % [(ArN)Mo(H)(Cl) $(PMe_3)_3$]	RT	12	C_6D_6	>99[S5]
1 mol % [^{dpp}BIANFe]	70	3.5	Tol	98[S6]
1 mol % [Mn(S^{Me}NS)$(CO)_3$]	25(hv)	8	THF	>99[S7]
2 mol % [Ni^{II}X(NNN)]	RT	10	Neat	>99[S8]
2 mol % $[L^1ZnH]_2$	60	12	Neat	>99[S9]
5 mol % [$OsH_6(P^iPr_3)_2$]	60	24	C_7D_8	92[S10]
3 mol % [(η^6-cymene){(IMes)P}RuCl]	60	11	Neat	>99[S11]
3 mol % [$L^2Ti(NMe_2)_2$]	60	2	Neat	>99[S12]
2 mol % [L^3Zr $(C_5H_5)_2Cl$]	60	12	Neat	>99[S13]
1 mol % [Mg]	RT	12	$CDCl_3$	>99(This work)

a = ^{1}H-NMR yield
Ar = 2,6-$^i Pr_2C_6H_3$[S5]
BIAN = 1,2-((bis-2,6-diisopropylphenyl)imino)acenaphthene) [S6]
L^1 = {(ArNH)(ArN)−C=N−C=(NAr)(NHAr)}; Ar = 2,6-Et_2-C_6H_3[S9]
IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene[S11]
H_2L^2 = {$Ph_2P(BH_3)NH$}$_2C_6H_4$[S12]
HL^3 = [Ph_2P(S) NH-$(CH_2)_2N(CH_2CH_2)_2O$] [S13]

Table S12. Comparison of the catalytic performance of different catalysts for the hydroboration of ethynylbenzene (6a).

Cat. loading	Temperature	Time	Solvent	Yield[a] (%)

	(°C)	(h)		
3 mol % $Co(acac)_2$ 3 mol % dppp	50	24	THF	41 [S14]
5 mol % $[(IPrCl)Zn\text{-}C_6F_5][B(C_6F_5)_4]$	RT	24	CD_2Cl_2	77[S15]
10 mol % (7-DIPP)ZnPh(NTf_2)	90	36	C_6D_6	73 [S16]
1 mol % (NHC)$CoCl_2$ 1 mol % $LiHBEt_3$	80	12	Neat	>99 [S17]
1 mol % $[L^2Ti(NMe_2)_2]$	RT	1	Tol	>99 [S12]
2 mol % $[L^3Zr\ (C_5H_5)_2Cl]$	60	12	Neat	94 [S13]
5 mol % [Mg-Me]	80	18	Neat	91 [S18]
2 mol % [Mg]	80	12	Tol	>99(This work)

a = ^{1}H-NMR yield
Dppp = 1,3-bis(diphenylphosphino)propane [S14]
7-DIPP = 1,3-bis(2,6-diisopropylphenyl)-4,5,6,7-tetrahydro-1H-1,3-diazepin-3-ium-2-ide) [S16]
H_2L^2 = $\{Ph_2P(BH_3)NH\}_2C_6H_4$[S12]
HL^3 = $[Ph_2P(S)\ NH\text{-}(CH_2)_2N(CH_2CH_2)_2O]$ [S13]

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