Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
This journal is © The Royal Society of Chemistry 2023

SUPPORTING INFORMATION

Preparation of Cyclic Alkenyl Boronates from Alkenyl Chlorides and Di-boron reagents via Palladium-Catalysis

Hongru Ou, Xu Zhao and Yunfei Luo*

Anhui Province Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, School of Chemistry and Chemical Engineering Hefei University of Technology, Hefei, 230009, China

*Corresponding authors

Table of contents

1. General Experimental Details

Extra dry solvents such as: tetrahydrofuran, 1,4-dioxane and acetonitrile were purchased from Energy Chemical in anhydrous septum sealed bottles. Other solvents like toluene, N,N-Dimethylformamide and ethanol were dried with anhydrous magnesium sulfate for 12 h before use. All inorganic bases like potassium phosphate, potassium carbonate, potassium acetate and sodium acetate were purchased from commercial suppliers and dried in constant temperature drying oven at 60 ℃ for 2 h prior to use. 3-Chloro-5,5-dimethyl-2-cyclohexen-1-one was purchased from LeYan as received. Bis(pinacolato)diboron was purchased from Lianhetech as received. Other alkenyl chlorides except **1p-1r** received from Xu Zhao in our research group were prepared according to published procedures.[1] All other substrates and reagents were commercially available and used without further purification. The Schlenk tubes and other glassware used for synthesis of alkenyl boronic esters were dried in a constant temperature drying oven at 60 ℃ for 2 h prior to use. All reactions for alkenyl boronic esters were set up using standard Schlenk technique and heated with stirring in temperature controlled oil baths. All yields in optimization reactions were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard. **Note**: The ^{13}C NMR signal for carbons attached to boron atom was not observed likely due to the quadruple splitting of ^{11}B.[2]

2.Instrumentation and Chromatography

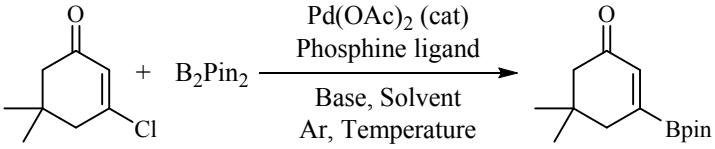
All NMR spectra samples were analyzed in the indicated deuteron-solvent and were recorded at ambient temperatures. ^{1}H NMR spectra were obtained on a Varian VNMRS600 (600 MHz) spectrometer. Chemical shifts were quoted in parts per million downfield of teramethylsilane, using residual protonated solvent as internal standard ($CDCl_3$: δ 7.26 ppm). Abbreviations are reported as follows: chemical shifts (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constant (*J*, Hz). ^{13}C NMR spectra were obtained on a Varian VNMRS600 (151 MHz) spectrometer with carbon and proton decoupling. Chemical shifts are reported in ppm and calibrated using the

residual deuteron-solvent as a standard ($CDCl_3$: δ 77.16 ppm). ^{11}B NMR spectra were obtained on Bruker spectrometer (400 MHz and 600MHz). High resolution mass spectra data was obtained on a Vanquish Q Exactive Plus from Thermo Fisher using electrospray ionization (ESI), and a LCT Premier mass spectrometer using atmospheric pressure chemical ionization (APCI) or electron ionization (EI) from Waters. Thin layer chromatography (TLC) was performed on silica gel 60 GF254 precoated glass plates and visualized by UV light at 254 nm staining with iodone, $KMnO_4$, and alizarin. Column chromatography was carried out using 48-75 μm silica gel (200-300 mesh).

3. Optimization of Reaction Conditions

The borylation reactions of 1a and 1j were evaluated and yields of reactions were determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard. All reactions were set up under inert atmosphere (argon or nitrogen) using standard Schlenk technology. **Note:** The borylation reaction of 1a was performed on 0.3 mmol scale, while the borylation reaction of 1j was performed on 0.15 mmol scale, but concentration of reactions was 0.15 mmol／1 ml.

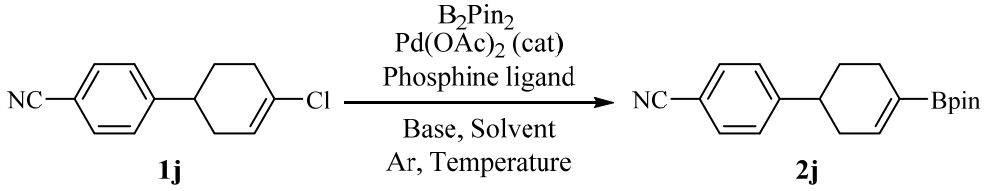
Procedure A (1a as model substrate):



1a **2a**

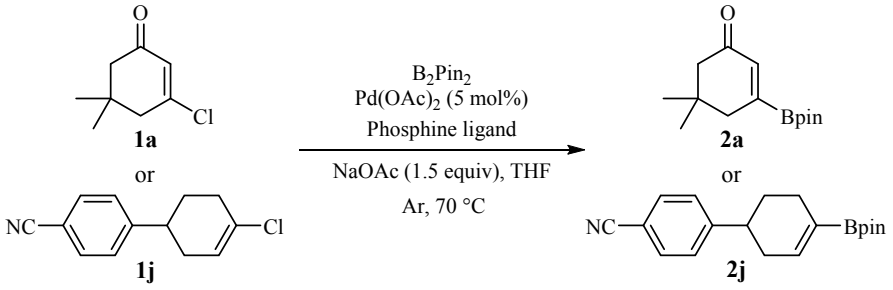
A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with B_2Pin_2 (84 mg, 0.33 mmol, 1.1equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), Phosphine ligand, base and purged with argon or nitrogen before the additional of 2 ml degassed solution of **1a** (0.3 mmol, 1.0 equiv) in solvent. The reaction mixture was stirred for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. 1,3,5-trimethoxybenzene was added to above mixture. The mixture was concentrated under reduced pressure and yield of reaction was determined by ^1H NMR.

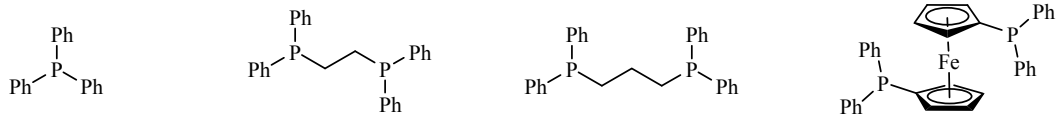
Procedure B (1j as model substrate):

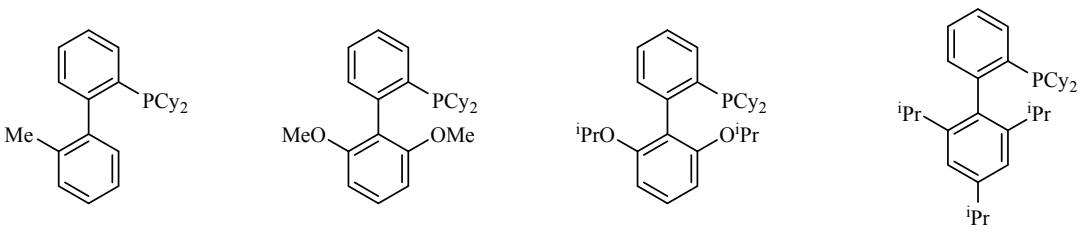


A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with **1j** (0.15 mmol, 1.0 equiv), B_2Pin_2 (42 mg, 0.165 mmol, 1.1equiv), $Pd(OAc)_2$ (1.7 mg, 0.0075 mmol, 5 mol%), Phosphine ligand, base and purged with argon or nitrogen before the additional of 1 ml degassed solvent. The reaction mixture was stirred for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. 1,3,5-trimethoxybenzene was added to above mixture. The mixture was concentrated under reduced pressure and yield of reaction was determined by ^{1}H NMR.

Table S1. Evaluation of ligands [a]





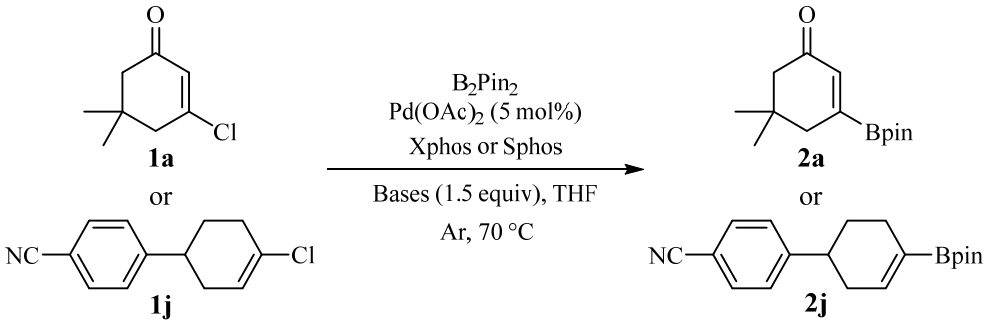


Entry	Ligand	Yield 2a (%)[b]	Yield 2j (%)[b]
1	PPh_3 (20 mol%)	71	N.R
2	DPPE (10 mol%)	N.R	N.R
3	DPPP (10 mol%)	N.R	N.R
4	DPPF (10 mol%)	83	N.R
5	Mephos (20 mol%)	82	73
6	Sphos (20 mol%)	96	89
7	Ruphos (20 mol%)	47	90
8	Xphos (20 mol%)	94	99
9	Xphos (none)		N.R
10	Xphos (10 mol%)		90
11	Xphos (30 mol%)		97
12	Sphos (none)	N.R	
13	Sphos (10 mol%)	84	
14	Sphos (30 mol%)	87	

[a]**1a** was operated according to method A, while**1j** was operated according to method B.

[b]Yields obtained by ^1H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S2. Examination of bases [a]

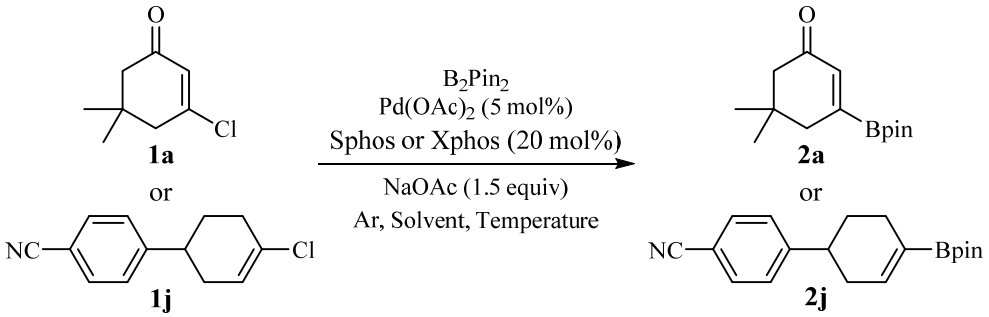


Entry	Base	Yield 2a (%)[b]	Yield 2j (%)[b]
1	NaOAc (1.5 equiv)	95	99
2	KOAc (1.5 equiv)	91	99
3	K_2CO_3 (1.5 equiv)	88	78
4	K_3PO_4 (1.5 equiv)	64	94

5	NEt_3 (1.5 equiv)	12	16
6	NaOAc (0.5 equiv)	43	51
7	NaOAc (3.0 equiv)	96	99

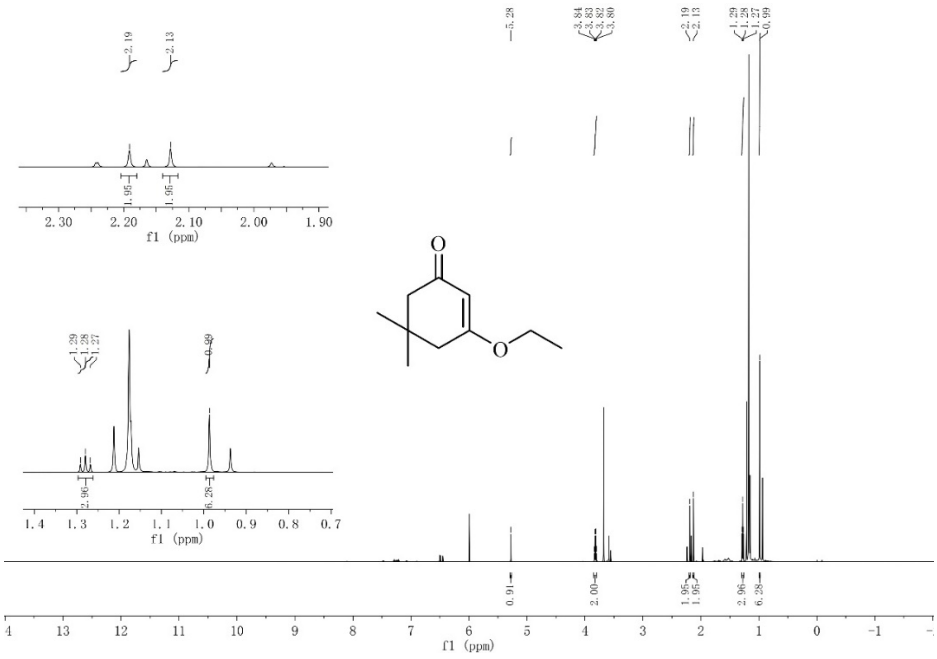
[a] Sphos was used as ligand when reaction of **1a** was set up according to method A while Xphos was used in reaction of **1j** referring to method B. [b]Yields determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard.

Table S3. Optimization of solvents and temperature [a]



Entry	Solvent	Temperature (℃)	Yield 2a (%)[b]	Yield 2j (%)[b]
1	1,4-dioxane	70	99	98
2	Toluene	70	91	79
3	Ethanol	70	25[c]	97
4	THF	70	95	99
5	THF	50	41	81
6	THF	60	86	95
7	THF	80	90	98

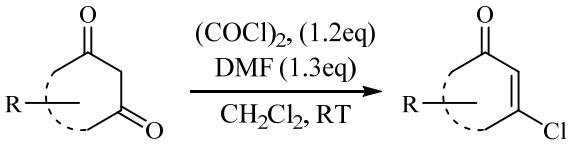
[a] Sphos was used as ligand when reaction of **1a** was set up according to method A while Xphos was used in reaction of **1j** referring to method B. [b] Yields determined by ^{1}H NMR with 1,3,5-trimethoxybenzene as internal standard. [c] 75% product was obtained as 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one in agreement with published literature[3]. The spectrum data was shown below. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.34 (s, 1H), 3.88 (q, J = 7.0 Hz, 2H), 2.25 (s, 2H), 2.19 (s, 2H), 1.34 (t, J = 7.0 Hz, 3H), 1.05 (s, 6H).



4. General Procedure for Non-commercial Alkenyl Chlorides

Alkenyl chlorides **1a-1f**[1a] and **1g-1o**[1b] were prepared referring to known methods. Spectra data of **1a**[4], **1c**[4], **1d**[4], **1g**[5], **1n**[5], **1h**[6], and **1m**[7] are in agreement with literatures. **1p-1r** were obtained from Xu Zhao[8] in our research group and used without further purification.

Procedure A:

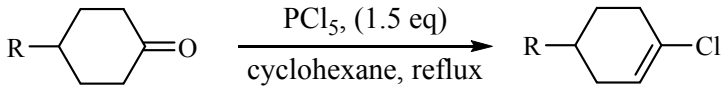


S1–S6 **1a–1f**

1a-1f were prepared according to procedure A. To a 25 ml dried round bottom flask with magnetic stir bar and rubber septum, 0.5 ml DMF (6.5 mmol, 1.3 equiv) dissolved in 10 ml CH_2Cl_2 and the mixture was cooled to 0 ℃. Subsequently, 0.5 ml $(COCl)_2$ (6 mmol, 1.2 equiv) was added slowly via syringe with concurrent gas evolution and β-diketones (5mmol) were added before the flask was sealed. The reaction was allowed to warm to ambient temperature until stirring for approximately 1 h. The reaction was decapped, quenched with water (20 ml), and extracted with EtOAc (3×20 ml). The combined organic layers were washed with water (20 ml) and brine (20 ml), dried with

anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc as eluent).

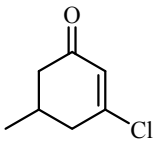
Procedure B:



S7–S15 **1g–1o**

1g-1o were prepared according to procedure B. To a 50 ml dried round bottom flask with magnetic stir bar and reflux condenser tube, PCl_5 (1.5 equiv) was suspended in 30 ml cyclohexane and the suspension was reflux until PCl_5 was dissolved. Then, a solution of corresponding ketone (1 equiv) in 5-10 ml CH_2Cl_2 was added slowly. The reaction was reflux for additional 1 h, subsequently allowed to cool to room temperature, and poured into water (30 ml). The mixture was stirred for 30 min and extracted with petroleum ether. The combined organic layers were washed with water (30 ml) and brine (30 ml), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude oil was purified by flash silica gel chromatography (petroleum ether as eluent).

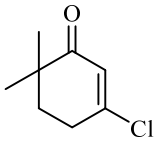
The analytical data of new alkenyl chlorides were listed as following:



1b

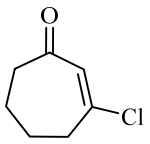
3-chloro-5-methylcyclohex-2-en-1-one (**1b**): According to procedure A, to a 25 ml dried round bottom flask with magnetic stir bar and rubber septum, 0.5 ml DMF (6.5 mmol, 1.3 equiv) dissolved in 10 ml CH_2Cl_2 and the mixture was cooled to 0 ℃. Subsequently, 0.5 ml $(COCl)_2$ (6 mmol, 1.2 equiv) was added slowly via syringe with concurrent gas evolution and 5-methylcyclohexane-1,3-dione (630 mg, 5mmol) was added before the flask was sealed. The reaction was allowed to warm to ambient temperature until stirring for approximately 1 h. The reaction was decapped, quenched with water (20 ml), and extracted with EtOAc (3×20 ml). The combined organic layers were washed with water (20 ml) and brine (20 ml), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 100：1) to afford **1b** as

light yellow liquid (499 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.20 – 6.17 (m, 1H), 2.68 (dd, *J* = 18.3, 4.7 Hz, 1H), 2.48 – 2.38 (m, 2H), 2.36 – 2.26 (m, 1H), 2.07 (dd, *J* = 16.3, 11.9 Hz, 1H), 1.09 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.1, 157.9, 128.0, 44.6, 41.9, 29.9, 20.7. HRMS (APCI) m/z, calcd for $[C_8H_{13}O_2]^+$ (M-Cl+CH_3OH)$^+$: 141.0910; found: 141.0915.



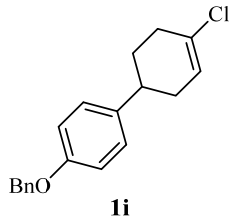
1e

3-chloro-6,6-dimethylcyclohex-2-en-1-one (**1e**): According to procedure A, **1e** was synthesized with 4,4-dimethylcyclohexane-1,3-dione (701 mg, 5 mmol), DMF (0.5 ml, 6.5 mmol, 1.3 equiv), and $(COCl)_2$ (0.5 ml, 6 mmol, 1.2 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether) to afford **1e** as light yellow liquid (381 mg, 48%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.09 (t, J = 1.5 Hz, 1H), 2.66 (td, J = 6.2, 1.5 Hz, 2H), 1.86 (t, J = 6.2 Hz, 2H), 1.09 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.7, 156.3, 126.7, 40.3, 35.9, 31.6, 23.8. HRMS (ESI) m/z, calcd for $[C_8H_{11}O_1Na_1Cl_1]^+$ (M+Na)$^+$: 181.0391; found: 181.0400.



1f

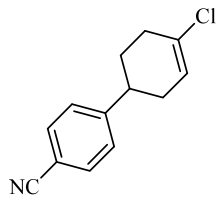
3-chlorocyclohept-2-en-1-one (**1f**): According to procedure A, **1f** was synthesized with cycloheptane-1,3-dione (631 mg, 5 mmol), DMF (0.5 ml, 6.5 mmol, 1.3 equiv), and $(COCl)_2$ (0.5 ml, 6 mmol, 1.2 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 100：1) to afford **1f** as light yellow liquid (485 mg, 77%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.27 (s, 1H), 2.83 (t, *J* = 6.0 Hz, 2H), 2.59 (t, *J* = 6.4 Hz, 2H), 1.91 – 1.85 (m, 2H), 1.84 – 1.77 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 155.1, 131.3, 43.1, 39.5, 25.6, 21.4. HRMS (ESI) m/z, calcd for $[C_8H_{13}O_2]^+$ (M-Cl+CH_3OH)$^+$: 141.0910; found: 141.0909.



1i

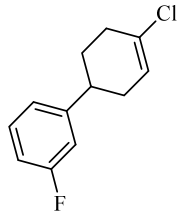
4'-(benzyloxy)-4-chloro-1,2,3,6-tetrahydro-1,1'-biphenyl (**1i**): According to procedure B, to a 50 ml dried round bottom flask with magnetic stir bar and reflux condenser tube, PCl_5 (625 mg, 3 mmol, 1.5 equiv) was suspended in 30 ml cyclohexane and the suspension was reflux until PCl_5 was dissolved. Then, a solution of 4-(4-(benzyloxy)phenyl)cyclohexan-1-one (461 mg, 2 mmol) in 5-10 ml CH_2Cl_2 was added slowly. The reaction was reflux for additional 1 h,

subsequently allowed to cool to room temperature, and poured into water (30 ml). The mixture was stirred for 30 min and extracted with petroleum ether. The combined organic layers were washed with water (30 ml) and brine (30 ml), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude oil was purified by flash silica gel chromatography (petroleum ether as eluent) to afford **1i** as white solid (382 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.15 – 7.11 (m, 2H), 6.96 – 6.91 (m, 2H), 5.88 (dt, J = 5.4, 2.4 Hz, 1H), 5.05 (s, 2H), 2.80 – 2.74 (m, 1H), 2.56 – 2.48 (m, 1H), 2.40 – 2.30 (m, 2H), 2.24 – 2.15 (m, 1H), 2.01 – 1.96 (m, 1H), 1.92 – 1.84 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.3, 138.0, 137.1, 131.7, 128.6, 127.9, 127.7, 127.5, 124.1, 114.8, 70.1, 38.1, 34.1, 33.2, 30.9. HRMS (ESI) m/z, calcd for $[C_{19}H_{20}O_1Cl_1]^+$ $(M+H)^+$: 299.1203; found: 299.1201.



1j

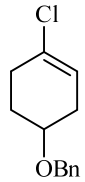
4'-chloro-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**1j**): according to procedure B, **1j** was synthesized with 4-(4-oxocyclohexyl)benzonitrile (997 mg, 5 mmol) and PCl_5 (1560 mg, 3 mmol, 1.5 equiv). The crude oil was purified by flash silica gel chromatography (petroleum ether ∶ EtOAc = 300 ∶ 1) to afford **1j** as white solid (730 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 – 7.58 (m, 2H), 7.33 – 7.30 (m, 2H), 5.90 – 5.87 (m, 1H), 2.92 – 2.85 (m, 1H), 2.57 – 2.48 (m, 1H), 2.41 – 2.34 (m, 2H), 2.26 – 2.19 (m, 1H), 2.03 – 1.98 (m, 1H), 1.96 – 1.88 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0, 132.4, 131.9, 127.7, 123.4, 118.9, 110.3, 39.1, 33.3, 32.8, 30.2. HRMS (ESI) m/z, calcd for $[C_{13}H_{13}N_1Cl_1]^+$ $(M+H)^+$: 218.0737; found: 218.0735.



1k

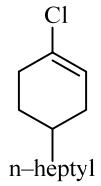
4-chloro-3'-fluoro-1,2,3,6-tetrahydro-1,1'-biphenyl (**1k**): according to procedure B, **1k** was synthesized with 4-(3-fluorophenyl)cyclohexan-1-one (480 mg, 2.5 mmol) and PCl_5 (781 mg, 3.75 mmol, 1.5 equiv). The crude oil was purified by flash silica gel chromatography (petroleum ether) to afford **1k** as colorless liquid (444 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H), 7.01 – 6.98 (m, 1H), 6.94 – 6.88 (m, 2H), 5.90 – 5.86 (m, 1H), 2.86 –

2.79 (m, 1H), 2.57 – 2.49 (m, 1H), 2.41 – 2.34 (m, 2H), 2.26 – 2.18 (m, 1H), 2.04 – 1.98 (m, 1H), 1.94 – 1.86 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0 (d, J = 245.5 Hz), 148.2 (d, J = 6.9 Hz), 131.8, 129.9 (d, J = 8.2 Hz), 123.7, 122.5 (d, J = 2.8 Hz), 113.7 (d, J = 21.1 Hz), 113.2 (d, J = 21.0 Hz), 38.7 (d, J = 1.6 Hz), 33.7, 33.0, 30.5. HRMS (EI) m/z, calcd for $[C_{12}H_{12}Cl_1F_1]^+$ $(M)^+$: 210.0606; found: 210.0600.



1l

(((4-chlorocyclohex-3-en-1-yl)oxy)methyl)benzene (**1l**): according to procedure B, **1l** was synthesized with 4-(benzyloxy)cyclohexan-1-one (408 mg, 2 mmol) and PCl_5 (625 mg, 3 mmol, 1.5 equiv). The crude oil was purified by flash silica gel chromatography (petroleum ether) to afford **1l** as colorless liquid (422 mg, 93%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 5.71 – 5.67 (m, 1H), 4.61 – 4.53 (m, 2H), 3.71 – 3.65 (m, 1H), 2.51 – 2.31 (m, 3H), 2.24 – 2.17 (m, 1H), 2.02 – 1.96 (m, 1H), 1.91 – 1.84 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.6, 131.4, 128.4, 127.6, 127.5, 121.5, 71.8, 70.2, 32.0, 30.8, 28.4. HRMS (APCI) m/z, calcd for $[C_{13}H_{15}O_1]^+$ $(M-Cl)^+$: 187.1117; found: 187.1116.



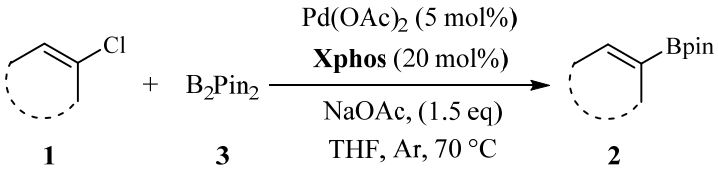
1o

1-chloro-4-heptylcyclohex-1-ene (**1o**): according to procedure B, **1o** was synthesized with 4-heptylcyclohexan-1-one (491 mg, 2.5 mmol) and PCl_5 (781 mg, 3.75 mmol, 1.5 equiv). The crude oil was purified by flash silica gel chromatography (petroleum ether) to afford **1o** as colorless liquid (487 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.77 – 5.73 (m, 1H), 2.39 – 2.31 (m, 1H), 2.29 – 2.23 (m, 1H), 2.20 – 2.13 (m, 1H), 1.83 – 1.77 (m, 1H), 1.74 – 1.67 (m, 1H), 1.55 – 1.47 (m, 1H), 1.39 – 1.20 (m, 13H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.7, 124.0, 35.7, 32.7, 32.6, 32.4, 31.9, 20.0, 29.8, 29.3, 27.1, 22.7, 14.1. HRMS (EI) m/z, calcd for $[C_{13}H_{23}Cl_1]^+$ $(M)^+$: 214.1483; found: 214.1478.

5. General Procedure for Alkenyl Boronic Esters

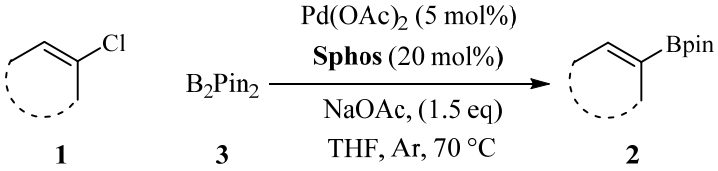
Note: alkenyl chlorides **1a-1f**, **1k-1o** were used as solution of anhydrous THF (0.5 mmol／2ml). Scale of all reactions was 0.5 mmol otherwise mentioned.

Procedure A:



A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with alkenyl chlorides (0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), **Xphos** (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and purged with argon or nitrogen before the additional of 2 ml degassed THF (liquid alkenyl chlorides were added in solution form mentioned in the note above). The reaction mixture was stirred at 70 ℃ for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether／EtOAc as eluent).

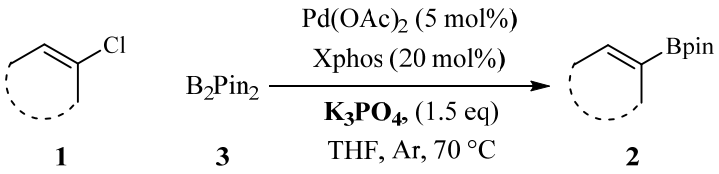
Procedure B:



A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with alkenyl chlorides (0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), **Sphos** (41 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and purged with argon or nitrogen before the additional of 2 ml degassed THF (liquid alkenyl chlorides were added in solution form mentioned in the note above). The reaction mixture was stirred at 70 ℃ for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The

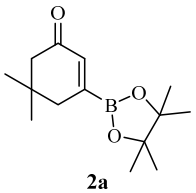
mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc as eluent).

Procedure C:



A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with alkenyl chlorides (0.3 mmol, 1.0 equiv), B_2Pin_2 (84 mg, 0.33 mmol, 1.1equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), Xphos (29 mg, 0.06 mmol, 20 mol%), **K_3PO_4** (96 mg, 0.45 mmol, 1.5 equiv) and purged with argon or nitrogen before the additional of 2 ml degassed THF. The reaction mixture was stirred at 70 ℃ for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc as eluent).

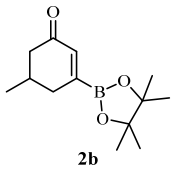
The analytical data of **2a**[9], **2c**[10], **2g**[11], **2h**[11], **2p**[8] were in agreement with published literatures. The spectra data of alkenyl boronates were listed as following:



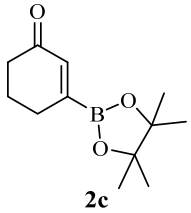
2a

5,5-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one (**2a**): **According to procedure A**, a 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and purged with argon before the additional of 2 ml degassed 3-chloro-5,5-dimethylcyclohex-2-en-1-one (80 mg, 0.5 mmol) in THF. The reaction mixture was stirred at 70 ℃ for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml)

and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2a** as yellow oil (110 mg, 88%). **According to procedure B**, **2a** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 3-chloro-5,5-dimethylcyclohex-2-en-1-one (80 mg, 0.5 mmol). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2a** as yellow oil (111 mg, 89%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.52 (s, 1H), 2.31 (d, *J* = 2.1 Hz, 2H), 2.24 (s, 2H), 1.28 (s, 12H), 1.01 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 137.6, 84.3, 51.7, 41.1, 34.0, 28.2, 24.8. HRMS (APCI) m/z, calcd for $[C_{14}H_{24}B_1O_3]^+$ $(M+H)^+$: 251.1813; found: 251.1820.

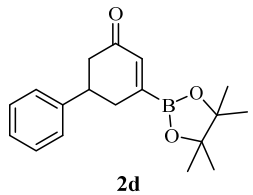

2b

5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one (**2b**): According to procedure A, **2b** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 3-chloro-5-methylcyclohex-2-en-1-one (73 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2b** as colorless oil (96 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.47 (d, *J* = 2.8 Hz, 1H), 2.52 (dd, *J* = 18.4, 4.0 Hz, 1H), 2.43 (dd, *J* = 15.9, 3.3 Hz, 1H), 2.16 – 2.08 (m, 1H), 2.06 – 1.95 (m, 2H), 1.26 (s, 12H), 1.02 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.2, 138.2, 84.3, 46.4, 35.4, 30.7, 24.8, 21.3. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.4. HRMS (ESI) m/z, calcd for $[C_{13}H_{22}B_1O_3]^+$ $(M+H)^+$: 237.1662; found: 237.1657.

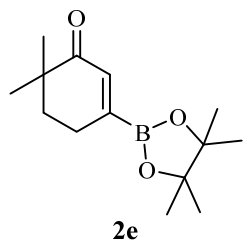

2c

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one (**2c**): According to procedure A, **2c** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 3-chlorocyclohex-2-en-1-one (66 mg, 0.5 mmol). The crude product was purified by flash silica gel

chromatography (petroleum ether：EtOAc = 50：1) to afford **2c** as colorless oil (89 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.49 (s, 1H), 2.40 – 2.36 (m, 4H), 2.00 – 1.93 (m, 2H), 1.26 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.8, 138.4, 84.3, 38.3, 27.0, 24.8, 23.2. HRMS (ESI) m/z, calcd for $[C_{12}H_{19}B_1O_3]^+$ $(M+H)^+$: 223.1500; found: 223.1498.

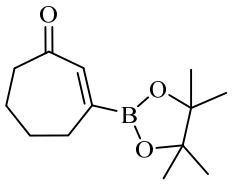

2d

5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (**2d**): **According to procedure A**, **2d** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 5-chloro-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (104 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2d** as yellow gum (106 mg, 71%). **According to procedure B**, **2d** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 5-chloro-1,6-dihydro-[1,1'-biphenyl]-3(2H)-one (104 mg, 0.5 mmol). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2d** as yellow gum (127 mg, 85%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (t, J = 7.6 Hz, 2H), 7.25 – 7.21 (m, 3H), 6.61 (d, J = 2.9 Hz, 1H), 3.31 – 3.24 (m, 1H), 2.79 (dd, J = 18.6, 4.1 Hz, 1H), 2.70 (dd, J = 16.3, 3.6 Hz, 1H), 2.61 (dd, J = 16.2, 13.8 Hz, 1H), 2.55 – 2.46 (m, 1H), 1.28 (d, J = 1.7 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.5, 143.5, 138.2, 128.6, 126.8, 126.7, 84.5, 44.9, 41.3, 35.3, 24.8 (d, J = 11.4 Hz). ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.2. HRMS (ESI) m/z, calcd for $[C_{18}H_{25}B_1O_3]^+$ $(M+H)^+$: 299.1813; found: 299.1807.


2e

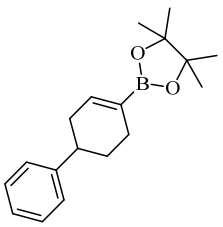
6,6-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-2-en-1-one (**2e**): According to procedure A, **2e** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2

ml degassed solution of 3-chloro-6,6-dimethylcyclohex-2-en-1-one (79 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2e** as yellow oil (104 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.39 (t, *J* = 2.1 Hz, 1H), 2.39 (td, *J* = 6.0, 2.1 Hz, 2H), 1.78 (t, *J* = 6.0 Hz, 2H), 1.26 (s, 12H), 1.06 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.6, 137.2, 84.2, 41.1, 36.7, 24.8, 24.4, 24.0. ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.2. HRMS (ESI) m/z, calcd for $[C_{14}H_{23}B_1O_3Na_1]^+$ $(M+Na)^+$: 273.1632; found: 273.1630.



2f

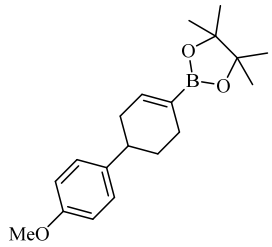
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohept-2-en-1-one (**2f**): **According to procedure A**, **2f** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 3-chlorocyclohept-2-en-1-one (72 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2f** as yellow oil (84 mg, 71%). **According to procedure B**, **2f** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 3-chlorocyclohept-2-en-1-one (72 mg, 0.5 mmol). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2f** as yellow oil (86 mg, 73%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.61 (s, 1H), 2.56 (t, *J* = 6.2 Hz, 2H), 2.52 – 2.48 (m, 2H), 1.79 – 1.71 (m, 4H), 1.26 (s, 12H). 13C NMR (151 MHz, CDCl3) δ 205.1, 142.4, 84.3, 42.7, 29.5, 25.8, 24.8, 21.4. ^{11}B NMR (128 MHz, CDCl3) δ 30.8. HRMS (ESI) m/z, calcd for $[C_{13}H_{22}B_1O_3]^+$ $(M+H)^+$: 237.1657; found: 237.1656.



2g

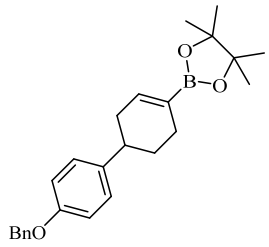
4,4,5,5-tetramethyl-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (**2g**): **According to procedure A**, **2g** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 4-chloro-1,2,3,6-tetrahydro-1,1'-

biphenyl (97 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2g** as colorless oil (115 mg, 81%). **According to procedure B**, **2g** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 4-chloro-1,2,3,6-tetrahydro-1,1'-biphenyl (97 mg, 0.5 mmol. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2g** as colorless oil (75 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.23 – 7.17 (m, 3H), 6.68 – 6.64 (m, 1H), 2.81 – 2.74 (m, 1H), 2.45 – 2.31 (m, 2H), 2.29 – 2.18 (m, 2H), 1.98 – 1.92 (m, 1H), 1.74 – 1.65 (m, 1H), 1.28 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 142.3, 128.3, 126.8, 125.9, 83.1, 39.8, 34.9, 29.8, 27.0, 24.8. HRMS (APCI) m/z, calcd for $[C_{18}H_{26}B_1O_2]^+$ $(M+H)^+$: 285.2020; found: 285.2029.



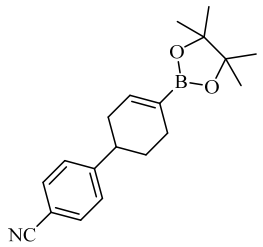
2h

2-(4'-methoxy-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**): According to procedure A, **2h** was synthesized with 4-chloro-4'-methoxy-1,2,3,6-tetrahydro-1,1'-biphenyl (112 mg, 0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2h** as colorless oil (142 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 – 7.11 (m, 2H), 6.87 – 6.82 (m, 2H), 6.68 – 6.64 (m, 1H), 3.79 (s, 3H), 2.77 – 2.69 (m, 1H), 2.42 – 2.31 (m, 2H), 2.29 – 2.14 (m, 2H), 1.95 – 1.90 (m, 1H), 1.70 – 1.61 (m, 1H), 1.28 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 142.4, 139.4, 127.7, 113.7, 83.1, 55.2, 38.9, 35.1, 30.0, 27.1, 24.8 (d, J = 3.3 Hz). HRMS (APCI) m/z, calcd for $[C_{19}H_{28}B_1O_3]^+$ $(M+H)^+$: 315.2126; found: 315.2127.



2i

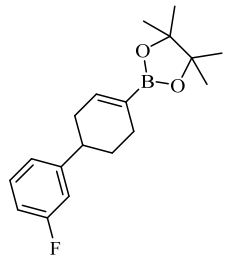
2-(4'-(benzyloxy)-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2i**): According to procedure A, **2i** was synthesized with 4'-(benzyloxy)-4-chloro-1,2,3,6-tetrahydro-1,1'-biphenyl (149 mg, 0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2i** as white solid (171 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.68 – 6.65 (m, 1H), 5.05 (s, 2H), 2.78 – 2.70 (m, 1H), 2.43 – 2.31 (m, 2H), 2.29 – 2.15 (m, 2H), 1.96 – 1.90 (m, 1H), 1.70 – 1.62 (m, 1H), 1.29 (s, 12H).^{13}C NMR (151 MHz, $CDCl_3$) δ 157.05, 142.36, 139.74, 137.24, 128.54, 127.87, 127.72, 127.47, 114.70, 83.13, 70.04, 38.89, 35.08, 30.01, 27.07, 24.83 (d, *J* = 3.2 Hz). ^{11}B NMR (193 MHz, $CDCl_3$) δ 28.6. HRMS (APCI) m/z, calcd for $[C_{25}H_{32}B_1O_3]^+$ $(M+H)^+$: 391.2439; found: 391.2438.



2j

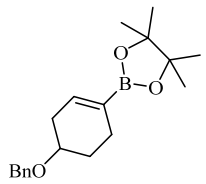
4'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**2j**): **According to procedure A**, **2j** was synthesized with 4'-chloro-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (109 mg, 0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2j** as white solid (147 mg, 95%). **According to procedure B**, **2j** was synthesized with 4'-chloro-1',2',3',6'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (109 mg, 0.5 mmol, 1.0 equiv), B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv). The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2j** as white solid (111 mg, 72%). ^{1}H

NMR (600 MHz, $CDCl_3$) δ 7.59 – 7.55 (m, 2H), 7.31 – 7.28 (m, 2H), 6.64 – 6.60 (m, 1H), 2.87 – 2.79 (m, 1H), 2.42 – 2.28 (m, 2H), 2.27 – 2.14 (m, 2H), 1.95 – 1.89 (m, 1H), 1.73 – 1.63 (m, 1H), 1.27 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.7, 141.2, 132.2, 127.7, 119.1, 109.8, 83.2, 39.9, 34.2, 29.3, 26.5, 24.8 (d, J = 3.3 Hz). ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.3. HRMS (ESI) m/z, calcd for $[C_{19}H_{25}B_1N_1O_2]^+$ $(M+H)^+$: 310.1978; found: 310.1978.



2k

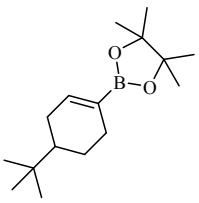
2-(3'-fluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2k**): According to procedure A, **2k** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 4-chloro-3'-fluoro-1,2,3,6-tetrahydro-1,1'-biphenyl (109 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2k** as colorless oil (121 mg, 80%). ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.67 – 6.61 (m, 1H), 2.81 – 2.74 (m, 1H), 2.43 – 2.30 (m, 2H), 2.28 – 2.14 (m, 2H), 1.97 – 1.91 (m, 1H), 1.71 – 1.62 (m, 1H), 1.27 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.0 (d, J = 245.0 Hz), 149.9 (d, J = 6.9 Hz), 141.8, 129.7 (d, J = 8.2 Hz), 122.5 (d, J = 2.7 Hz), 113.6 (d, J = 20.8 Hz), 112.7 (d, J = 21.0 Hz), 83.2, 39.5 (d, J = 1.7 Hz), 34.6, 29.6, 26.8, 24.8 (d, J = 4.1 Hz). ^{11}B NMR (193 MHz, $CDCl_3$) δ 29.5. HRMS (APCI) m/z, calcd for $[C_{18}H_{25}B_1F_1O_2]^+$ $(M+H)^+$: 303.1926; found: 303.1934.



2l

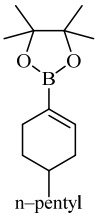
2-(4-(benzyloxy)cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**): According to procedure A, **2l** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of (((4-chlorocyclohex-3-en-1-yl)oxy)methyl)benzene (110mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether： EtOAc = 200：1) to afford **2l** as colorless oil (178 mg, 93%). ^1H NMR (600 MHz,

$CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.28 – 7.24 (m, 1H), 6.49 – 6.45 (m, 1H), 4.63 – 4.53 (m, 2H), 3.67 – 3.61 (m, 1H), 2.53 – 2.46 (m, 1H), 2.39 – 2.32 (m, 1H), 2.21 – 2.09 (m, 2H), 2.01 – 1.95 (m, 1H), 1.65 – 1.58 (m, 1H), 1.25 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 139.9, 139.0, 128.3, 127.6, 127.4, 83.2, 73.6, 69.9, 33.3, 27.9, 25.1, 24.8 (d, J = 6.9 Hz). ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.0. HRMS (APCI) m/z, calcd for $[C_{19}H_{28}B_1O_3]^+$ $(M+H)^+$: 315.2126; found: 315.2132.



2m

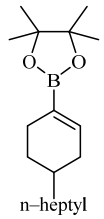
2-(4-(tert-butyl)cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2m**): According to procedure A, **2m** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 4-(tert-butyl)-1-chlorocyclohex-1-ene (86 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2m** as colorless oil (116 mg, 88%). ^1H NMR (600 MHz, $CDCl_3$) δ 6.59 – 6.56 (m, 1H), 2.30 – 2.24 (m, 1H), 2.15 – 2.08 (m, 1H), 2.07 – 1.98 (m, 1H), 1.88 – 1.77 (m, 2H), 1.25 (s, 13H), 1.11 – 1.02 (m, 1H), 0.84 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.4, 83.0, 43.7, 32.2, 28.4, 27.8, 27.1, 24.8 (d, J = 7.5 Hz), 23.9. ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.2. HRMS (APCI) m/z, calcd for $[C_{17}H_{32}B_1O_2]^+$ $(M+H)^+$: 265.2333; found: 265.2340.



2n

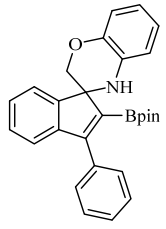
4,4,5,5-tetramethyl-2-(4-pentylcyclohex-1-en-1-yl)-1,3,2-dioxaborolane (**2n**): According to procedure A, **2n** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 1-chloro-4-pentylcyclohex-1-ene (94 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2n** as colorless oil (117 mg, 84%). **According to procedure B**, **2n** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Sphos (41 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 1-chloro-4-pentylcyclohex-1-ene (94 mg, 0.5 mmol) in THF. The crude product was

purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2n** as colorless oil (93 mg, 67%).^{1}H NMR (600 MHz, $CDCl_3$) δ 6.56 – 6.52 (m, 1H), 2.23 – 2.16 (m, 2H), 2.10 – 2.02 (m, 1H), 1.75 – 1.64 (m, 2H), 1.52 – 1.43 (m, 1H), 1.34 – 1.18 (m, 20H), 1.17 – 1.09 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 83.0, 36.7, 33.5, 33.1, 32.1, 29.0, 26.5, 26.3, 24.8 (d, *J* = 3.2 Hz), 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.8. HRMS (APCI) m/z, calcd for $[C_{17}H_{32}B_1O_2]^+$ $(M+H)^+$: 279.2490; found: 279.2497.



2o

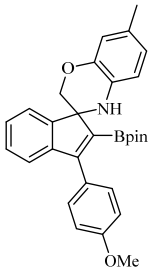
2-(4-heptylcyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2o**): According to procedure A, **2o** was synthesized with B_2Pin_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of 1-chloro-4-heptylcyclohex-1-ene (108 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2o** as colorless oil (124 mg, 81%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.55 – 6.52 (m, 1H), 2.23 – 2.15 (m, 2H), 2.10 – 2.01 (m, 1H), 1.76 – 1.65 (m, 2H), 1.53 – 1.44 (m, 1H), 1.31 – 1.19 (m, 24H), 1.17 – 1.09 (m, 1H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.6, 83.0, 36.8, 33.5, 33.0, 31.9, 30.0, 29.4, 29.0, 26.8, 26.3, 24.8 (d, *J* = 3.0 Hz), 22.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.3. HRMS (APCI) m/z, calcd for $[C_{19}H_{36}B_1O_2]^+$ $(M+H)^+$: 307.2803; found: 307.2796.



2p

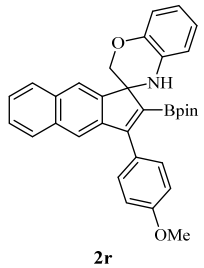
3'-phenyl-2'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-indene] (**2p**): According to procedure C, **2p** was synthesized with 2'-chloro-3'-phenyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-indene] (**1p**) (104 mg, 0.3 mmol), B_2Pin_2 (84 mg, 0.33 mmol, 1.1equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), Xphos (29 mg, 0.06 mmol, 20 mol%), and K_3PO_4 (96 mg, 0.45 mmol, 1.5 equiv) in 1 ml THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 80：1-50：1) to afford **2p** as light yellow solid (88 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.49 (m, 2H), 7.44 – 7.35 (m, 4H), 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 1H), 6.94 (dd, *J* = 8.0,

1.5 Hz, 1H), 6.83 (td, *J* = 7.6, 1.5 Hz, 1H), 6.74 (td, *J* = 7.7, 1.6 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.14 – 3.98 (m, 2H), 1.09 (d, *J* = 20.8 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 150.1, 143.5, 142.4, 135.2, 133.3, 128.7, 128.2, 128.1, 127.2, 123.3, 121.8, 121.4, 118.5, 116.7, 116.0, 83.6, 70.4, 67.8, 24.5 (d, *J* = 60.2 Hz).



2q

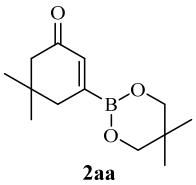
3'-(4-methoxyphenyl)-7-methyl-2'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-indene] (**2q**): According to procedure C, **2q** was synthesized with 2'-chloro-3'-(4-methoxyphenyl)-7-methyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-indene] (**1q**) (116 mg, 0.3 mmol), B_2Pin_2 (84 mg, 0.33 mmol, 1.1equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), Xphos (29 mg, 0.06 mmol, 20 mol%), and K_3PO_4 (96 mg, 0.45 mmol, 1.5 equiv) in 1 ml THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2q** as orange-yellow solid (106 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 (m, 2H), 7.16 (t, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.56 (d, *J* = 7.9 Hz, 1H), 4.58 (d, *J* = 10.4 Hz, 1H), 3.99 (d, *J* = 10.4 Hz, 1H), 3.93 (s, 1H), 3.87 (s, 3H), 2.29 (s, 3H), 1.12 (d, *J* = 11.8 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 154.9, 150.7, 143.5, 142.5, 130.6, 130.1, 128.3, 128.0, 127.6, 127.1, 123.4, 122.3, 121.4, 117.2, 116.3, 113.4, 83.6, 70.3, 67.6, 55.3, 24.8, 24.3, 20.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.0. HRMS (ESI) m/z, calcd for $[C_{30}H_{33}B_1N_1O_4]^+$ $(M+H)^+$: 482.2497; found: 482.2498.



2r

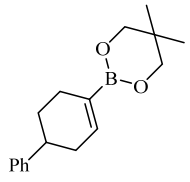
3'-(4-methoxyphenyl)-2'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H,4H - spiro [benzo [b] [1,4]oxazine-3,1'-cyclopenta [b] naphthalene] (**2r**): According to procedure C, **2r** was synthesized with 2'-chloro-3'-(4-methoxyphenyl)-2H,4H-spiro[benzo[b] [1,4] oxazine-3,1'-cyclopenta[b]naphthalene] (**1r**) (128 mg, 0.3 mmol), B_2Pin_2 (84 mg, 0.33 mmol, 1.1equiv), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), Xphos (29 mg, 0.06 mmol, 20 mol%), and K_3PO_4 (96 mg, 0.45 mmol, 1.5 equiv) in 1 ml THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2r** as tan solid

(95 mg, 61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 3H), 7.66 (s, 1H), 7.56 – 7.53 (m, 2H), 7.44 – 7.38 (m, 2H), 7.04 – 6.97 (m, 3H), 6.85 (td, *J* = 7.5, 1.5 Hz, 1H), 6.76 (td, *J* = 7.7, 1.5 Hz, 1H), 6.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 4.57 (d, *J* = 10.5 Hz, 1H), 4.20 – 4.06 (m, 2H), 3.90 (s, 3H), 1.12 (d, *J* = 22.9 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.77, 154.12, 147.17, 143.54, 141.47, 133.79, 133.38, 132.89, 130.10, 128.45, 128.30, 127.65, 125.94, 125.89, 122.05, 121.91, 120.02, 118.39, 116.82, 115.87, 113.58, 83.71, 70.71, 67.07, 55.34, 24.56 (d, *J* = 65.3 Hz). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.6. HRMS (ESI) m/z, calcd for $[C_{33}H_{33}B_1N_1O_4]^+$ $(M+H)^+$: 518. 2509; found: 518.2497.



2aa

3-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)-5,5-dimethylcyclohex-2-en-1-one (**2aa**): According to procedure A, **2aa** was synthesized with B_2neop_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of **1a** (79 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 50：1) to afford **2aa** as colorless oil (109mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.47 (t, *J* = 2.1 Hz, 1H), 3.65 (s, 4H), 2.25 (d, *J* = 2.2 Hz, 2H), 2.20 (s, 2H), 0.97 (s, 6H), 0.95 (s, 6H). ^{13}C NMR (151 MHz, $cdcl_3$) δ 200.7, 135.9, 72.3, 51.7, 40.8, 33.9, 31.7, 28.3, 21.7. ^{11}B NMR (128 MHz, $CDCl_3$) δ 26.6. HRMS (ESI) m/z, calcd for $[C_{13}H_{22}B_1O_3]^+$ $(M+H)^+$: 237.1667; found: 237.1657.

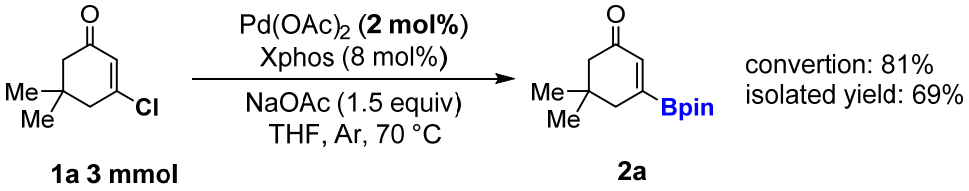


2ga

5,5-dimethyl-2-(1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborinane (**2ga**): According to procedure A, **2ga** was synthesized with B_2neop_2 (140 mg, 0.55 mmol, 1.1equiv), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol, 5 mol%), Xphos (48 mg, 0.1 mmol, 20 mol%), and NaOAc (62 mg, 0.75 mmol, 1.5 equiv) and 2 ml degassed solution of **1g** (96 mg, 0.5 mmol) in THF. The crude product was purified by flash silica gel chromatography (petroleum ether：EtOAc = 200：1) to afford **2ga** as light yellow oil (123mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.23 – 7.19 (m, 1H), 6.64 – 6.61 (m, 1H), 3.67 (s, 4H), 2.83 – 2.76

(m, 1H), 2.45 – 2.32 (m, 2H), 2.27 – 2.17 (m, 2H), 2.00 – 1.95 (m, 1H), 1.75 – 1.67 (m, 1H), 1.00 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$)) δ 147.5, 139.6, 128.33, 126.9, 125.9, 72.1, 40.0, 34.9, 31.7, 30.0, 26.7, 21.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 27.2. HRMS (ESI) m/z, calcd for $[C_{17}H_{23}B_1O_2Na_1]^+$ $(M+Na)^+$: 293.1683; found: 293.1690.

6、3 mmol Scale Borylation of 1a



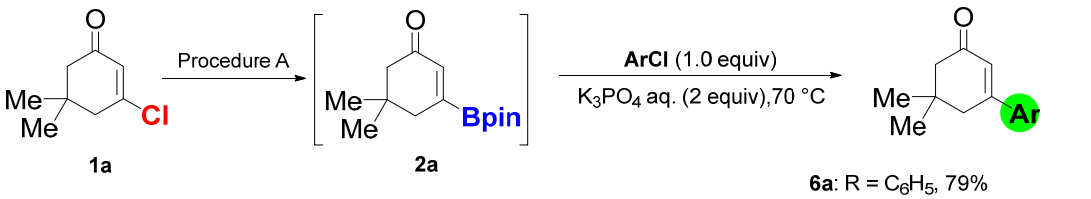
1a 3 mmol **2a**

General procedure:

A 25 ml dried Schlenk tube with Teflon screw cap and magnetic stir bar was charged with B_2Pin_2 (838 mg, 3.3 mmol, 1.1equiv), $Pd(OAc)_2$ (13.5 mg, 0.06 mmol, **2 mol%**), **Xphos** (114 mg, 0.48 mmol, 8 mol%), NaOAc (369 mg, 4.5 mmol, 1.5 equiv) and purged with argon before the additional of 4 ml degassed solution of **1a** (476 mg, **3 mmol**) inTHF. The reaction mixture was stirred at 70 ℃ for 12 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (20 ml) and water (30 ml), extracted with EtOAc (2×20 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. The 81% conversion to corresponding product **2a** was obtained via ^{1}H NMR based on relative intensity of alkene hydrogen. Then, the crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 50∶1) to give **2a** in 69% (518 mg) isolated yield.

7、Transformations for Alkenyl Boronates

A. Procedure of Suzuki-Miyaura Coupling[12]



1a **2a**

6a: R = C_6H_5, 79%
6b: R = p-$CH_3C_6H_5$, 83%
6c: R = p-$COCH_3C_6H_5$, 76%

5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (6a)[13]: 1a (0.5 mmol) was performed according to general procedure A and reacted for 3 h. Then the degassed mixture of chlorobenzene (56 mg, 1mmol, 1 equiv), K_3PO_4 (212 mg, 2 equiv) and 0.75 ml solvent (THF：H_2O = 2：1) were added to above reaction mixture under inert atmosphere and reacted for another 6 h. Then, the flask was removed from oil bath, allowed to cool to room temperature and decapped. The mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 100：1) to give **6a** as colorless liquid (79 mg, 79%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.41 – 7.38 (m, 3H), 6.40 (t, *J* = 1.5 Hz, 1H), 2.63 (d, *J* = 1.6 Hz, 2H), 2.32 (s, 2H), 1.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 157.6, 139.0, 129.9, 128.7, 126.1, 124.3, 50.9, 42.3, 33.7, 28.4.

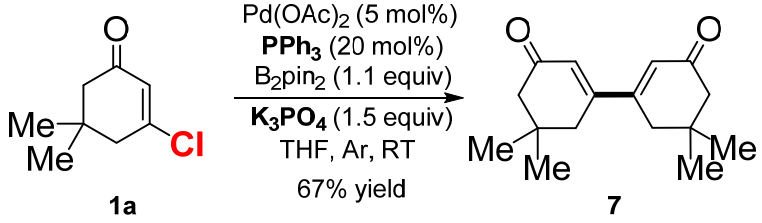
4',5,5-trimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (6b): 1a (0.5 mmol) was performed according to general procedure A and reacted for 3 h. Then the degassed mixture of 1-chloro-4-methylbenzene (63 mg, 0.5 mmol, 1.0 equiv), K_3PO_4 (212 mg, 2 equiv) and 0.75 ml solvent (THF：H_2O = 2：1) were added to above reaction mixture under inert atmosphere and reacted for another 6 h. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 80：1) to give **6b** as yellow liquid (89 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 2H), 7.22 – 7.19 (m, 2H), 6.40 (t, *J* = 1.5 Hz, 1H), 2.62 (d, *J* = 1.6 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 2H), 1.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.1, 157.5, 140.3, 136.0, 129.5, 126.1, 123.5, 50.9, 42.2, 33.7, 28.4, 21.3. HRMS (ESI) m/z, calcd for $[C_{15}H_{19}O_1]^+$ $(M+H)^+$: 215.1430; found: 215.1430.

4'-acetyl-5,5-dimethyl-5,6-dihydro-[1,1'-biphenyl]-3(4H)-one (6c): 1a (0.5 mmol) was performed according to general procedure A and reacted for 3 h. Then the degassed mixture of 1-(4-chlorophenyl)ethan-1-one (77 mg, 0.5 mmol, 1.0 equiv), K_3PO_4 (212 mg, 2 equiv) and 0.75 ml solvent (THF：H_2O = 2：1) were added to above reaction mixture under inert atmosphere and reacted for another 6 h. The crude product was

purified by flash silica gel chromatography (petroleum ether/EtOAc = 10∶1) to give **6c** as orange-yellow solid (92 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1H), 7.60 – 7.56 (m, 2H), 6.40 (t, *J* = 1.6 Hz, 1H), 2.63 (d, *J* = 1.7 Hz, 2H), 2.59 (s, 3H), 2.32 (s, 2H), 1.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.7, 197.3, 156.1, 143.5, 137.8, 128.7, 126.3, 125.7, 50.9, 42.2, 33.8, 28.3, 26.7. HRMS (ESI) m/z, calcd for $[C_{16}H_{18}O_2Na_1]^+$ $(M+Na)^+$: 265.1199; found: 265.1212.

B. Procedure of Homo-Coupling of 1a

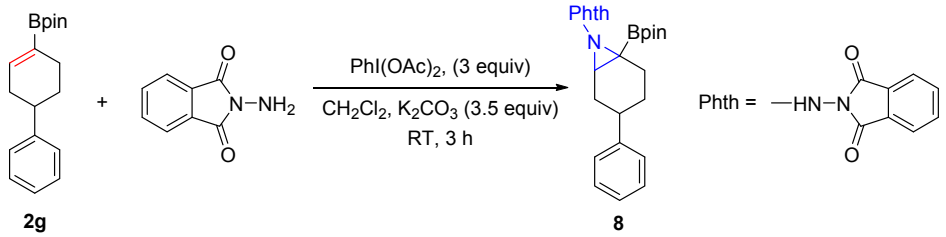
Surprisingly, a homo-coupling reaction not shown in part 3 was found when examination of reaction condition was performed and compound **7** could be obtained directly from **1a**.



To a 25 ml dried Schlenk tube was charged with $Pd(OAc)_2$ (11.2 mg, 0.05mmol, 5 mol%), PPh_3 (53 mg, 0.2 mmol, 20 mol%), K_3PO_4 (320 mg, 1.5 mmol, 1.5 equiv) and purged with argon before the additional of 2 ml degassed solvent of **1a** (159 mg, 1 mmol) in THF. The reaction mixture was stirred at room temperature for 12 h. Then, the flask was decapped, and the mixture was diluted with EtOAc (10 ml) and water (10 ml), extracted with EtOAc (2×10 ml) and combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. The crude product was purified by flash silica gel chromatography (petroleum ether/EtOAc = 25∶1) to give **7** as light yellow solid (83 mg, 67%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.28 (t, *J* = 1.5 Hz, 2H), 2.40 (d, *J* = 1.6 Hz, 4H), 2.29 (s, 4H), 1.06 (s, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.9, 154.5, 126.8, 51.0, 40.1, 33.3, 28.3. HRMS (ESI) m/z, calcd for $[C_{16}H_{23}O_2]^+$ $(M+H)^+$: 247.1693; found: 247.1696.

C. Procedure of Aziridination of 2g[14]

Note: Product **8** will decompose during column chromatography and deactivated silica gel was used.[14] Spectra of product **8** indicates that product is a stereoisomer mixture.



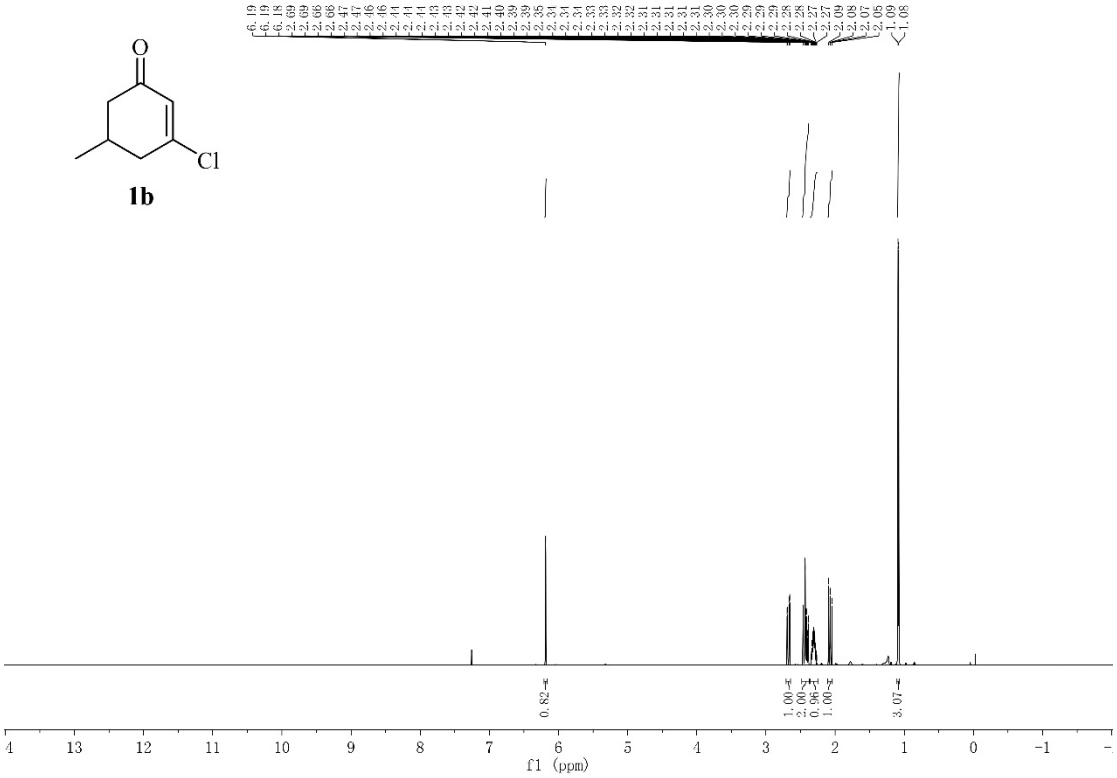
A 10 ml Schlenk tube was charged with **2g** (57 mg, 0.2 mmol), 2-aminoisoindoline-1,3-dione (91 mg, 0.56 mmol, 2.8 equiv), and anhydrous potassium carbonate (97 mg, 0.7 mmol, 3.5 equiv). The tube was evacuated and backfilled with argon for three times. Then 1 ml dichloromethane was added and the mixture was cooled to 0 ℃. After, the $PhI(OAc)_2$ (193 mg, 0.6 mmol, 3 equiv) was added. Finally, the above mixture was warmed to ambient temperature and stirred for 3 h. The reaction mixture was added 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol) as internal standard, filtered over degreased cotton and concentrated. The 60% NMR yield was obtained and the above mixture was purified by flash silica gel chromatography (petroleum ether/EtOAc = 8：1) to give **8** as gelatinous solid (52 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 – 7.71 (m, 4H), 7.65 – 7.63 (m, 4H), 7.31 – 7.26 (m, 4H), 7.22 – 7.16 (m, 6H), 3.35 – 3.32 (m, 1H), 3.17 – 3.13 (m, 1H), 2.77 – 2.71 (m, 2H), 2.65 – 2.58 (m, 2H), 2.51 – 2.40 (m, 2H), 2.30 – 2.24 (m, 1H), 2.16 – 2.09 (m, 1H), 2.04 – 1.98 (m, 1H), 1.91 – 1.85 (m, 1H), 1.71 – 1.62 (m, 2H), 1.59 – 1.54 (m, 1H), 1.43 – 1.35 (m, 1H), 1.14 (d, J = 13.6 Hz, 12H), 1.00 (d, J = 18.8 Hz, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.53, 165.48, 146.71, 146.57, 133.56, 130.77, 130.74, 128.39, 128.38, 126.97, 126.93, 126.09, 126.06, 122.49, 122.48, 84.01, 83.98, 49.31, 47.58, 39.43, 36.64, 31.98, 31.48, 28.80, 26.53, 26.50, 25.28, 24.88, 24.85, 24.61, 24.54. ^{11}B NMR (193 MHz, $CDCl_3$) δ 30.3. HRMS (ESI) m/z, calcd for $[C_{27}H_{33}O_5B_1N_2Na_1]^+$ $(M+Na+CH_3OH)^+$: 499.2375; found: 499.2381.

8. References

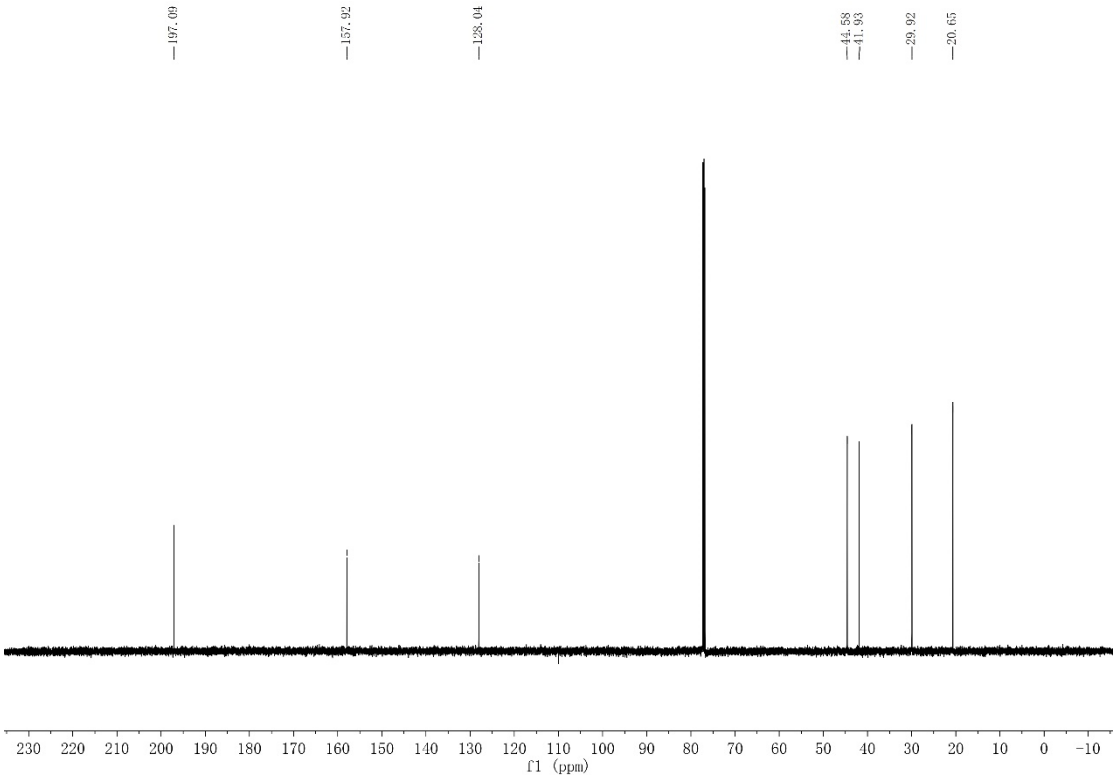
1. (a) R. E. Mewshaw, *Tetrahedron Lett.*, 1989, **30**, 3753-3756.T. (b) Fujihara, K. Nogi, T. Xu, J. Terao and Y. Tsuji, *J. Am. Chem. Soc.*, 2012, **134**, 9106-9109.
2. S. K. Bose and T. B. Marder, *Org. Lett.*, 2014, **16**, 4562-4565.
3. S. Poplata and T. Bach, *J. Am. Chem. Soc.*, 2018, **140**, 3228-3231.
4. G. M. Constantino, L. V. Junior, C. d. S. L. Filho and V. J. d. G. Silva, *Lett. Org. Chem.*, 2004, **1**, 360-364.
5. J. Wang, Y. Ogawa and N. Shibata, *Sci. Rep.*, 2019, **9**, 19113.
6. M. Kuriyama, G. Yano, H. Kiba, T. Morimoto, K. Yamamoto, Y. Demizu and O. Onomura, *Org Process Res Dev*, 2019, **23**, 1552-1557.
7. M. A. Saputra, L. Ngo and R. Kartika, *J. Org. Chem.*, 2015, **80**, 8815-8820.
8. X. Zhao, C. Fan, J. He and Y. Luo, *Org. Lett.*, 2022, **24**, 9169-9173.
9. T. Ishiyama, J. Takagi, A. Kamon and N. Miyaura, *J. Organomet. Chem.*, 2003, **687**, 284-290.
10. C. Feng, H. Wang, L. Xu and P. Li, *Org. Biomol. Chem.*, 2015, **13**, 7136-7139.
11. L. Gong, C. Li, F. Yuan, S. Liu and X. Zeng, *Org. Lett.*, 2022, **24**, 3227-3231.
12. T. E. Barder, S. D. Walker, J. R. Martinelli and S. L. Buchwald, *J. Am. Chem. Soc.*, 2005, **127**, 4685-4696.
13. J. Lee, S. Wang, M. Callahan and P. Nagorny, *Org. Lett.*, 2018, **20**, 2067-2070.
14. J. Hernández-Toribio, M. M. Hussain, K. Cheng, P. J. Carroll and P. J. Walsh, *Org. Lett.*, 2011, **13**, 6094-6097.

9. NMR Spectra

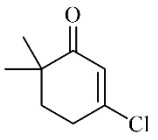
^{1}H NMR of **1b** (600 MHz, $CDCl_3$)



^{13}C NMR of **1b** (151 MHz, $CDCl_3$)

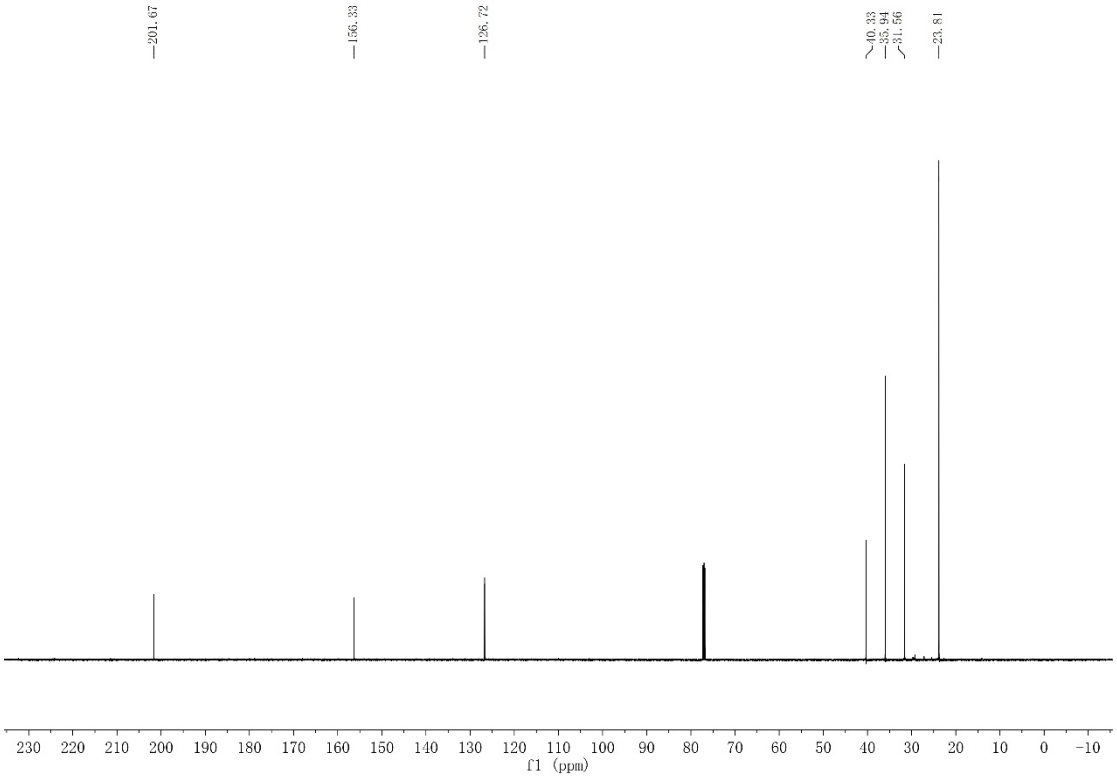


^{1}H NMR of **1e** (600 MHz, $CDCl_3$)

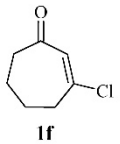


1e

^{13}C NMR of **1e** (151 MHz, $CDCl_3$)

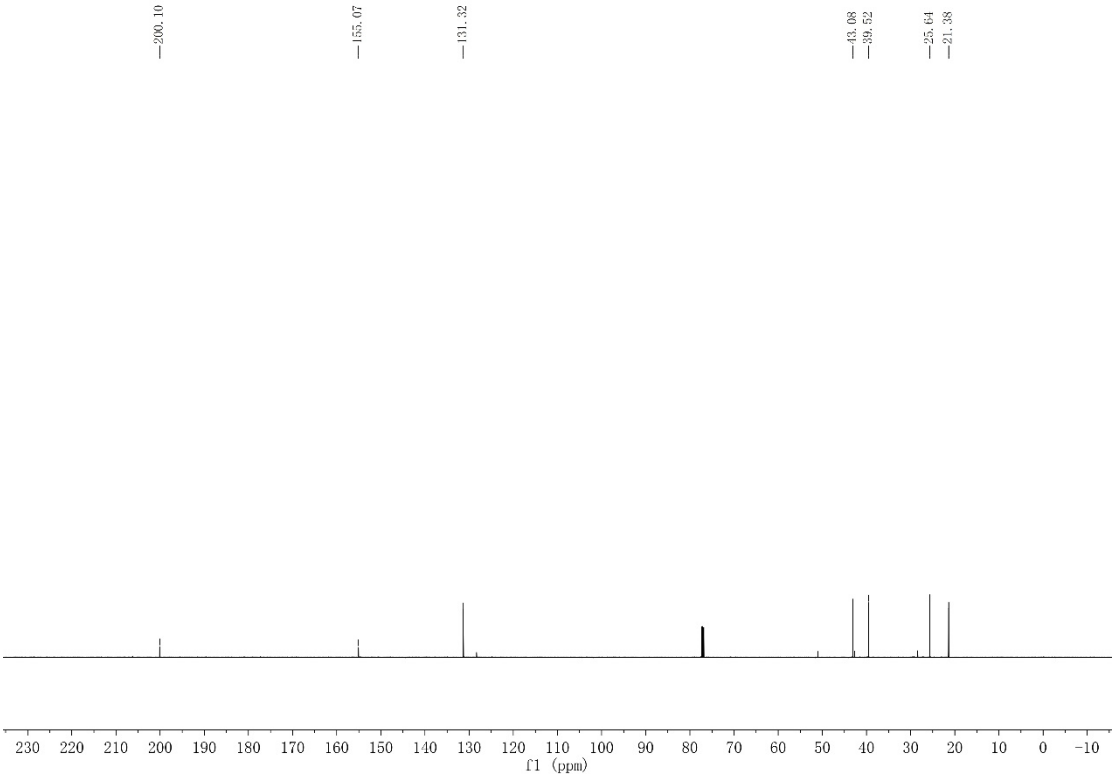


^{1}H NMR of **1f** (600 MHz, $CDCl_3$)

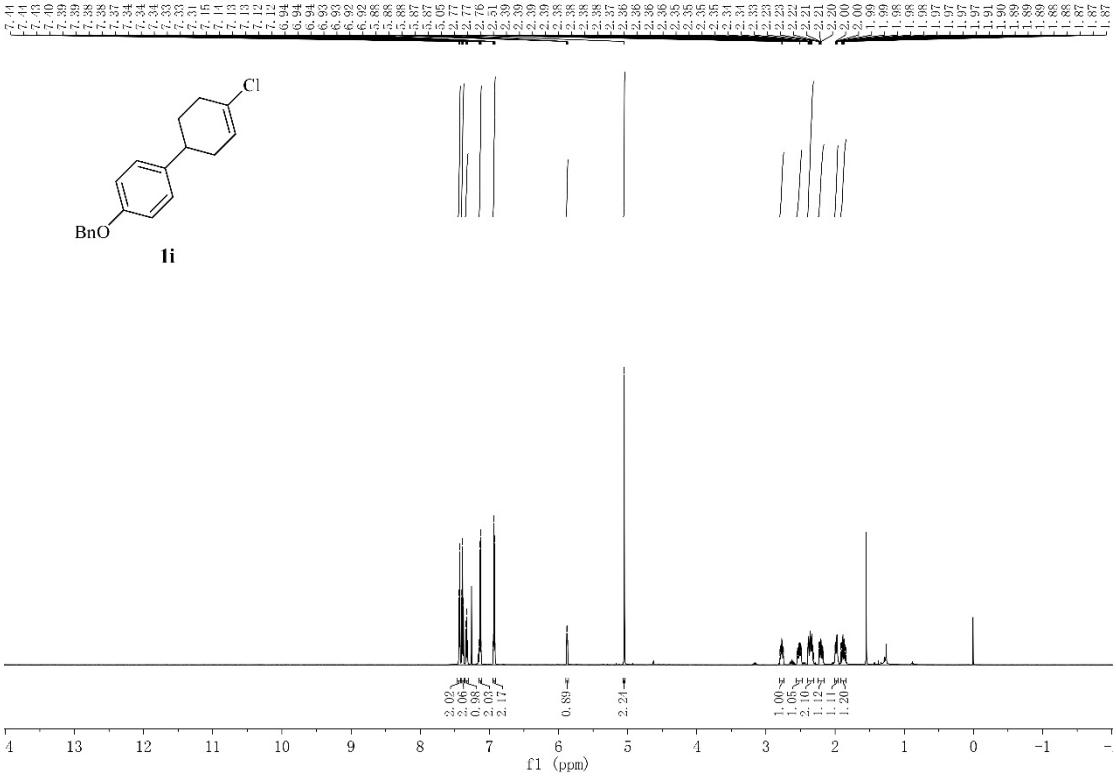


1f

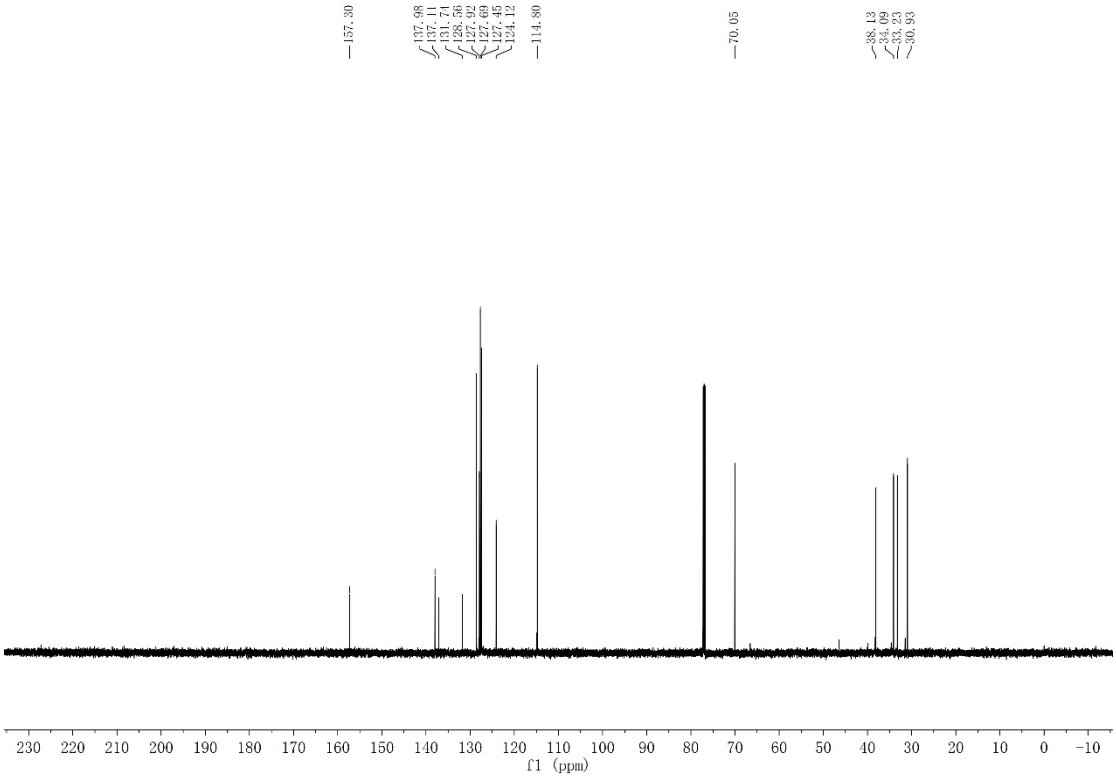
^{13}C NMR of **1f** (151 MHz, $CDCl_3$)



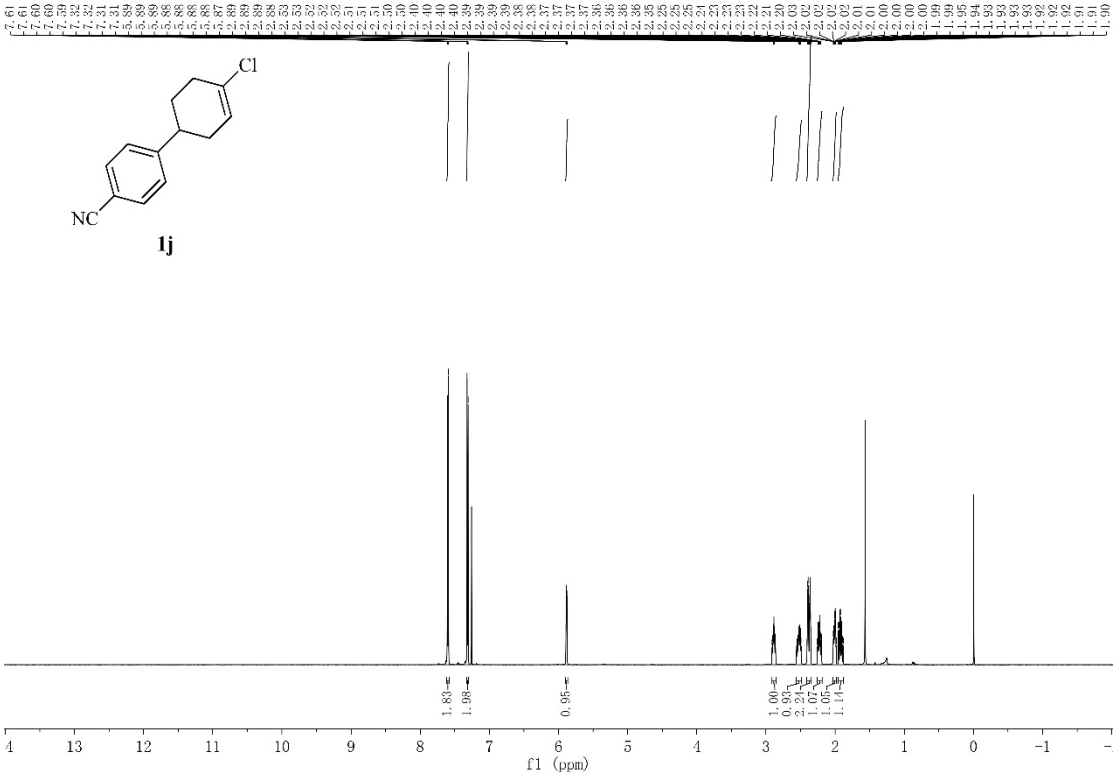
^{1}H NMR of **1i** (600 MHz, $CDCl_3$)



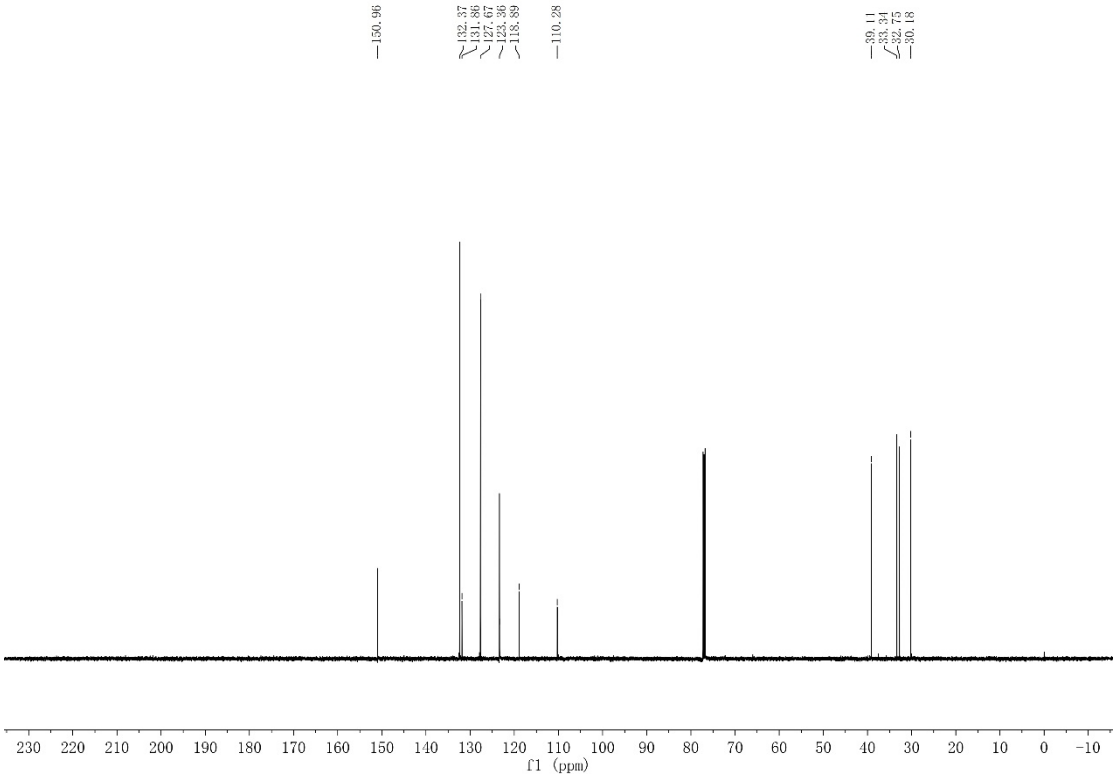
^{13}C NMR of **1i** (151 MHz, $CDCl_3$)



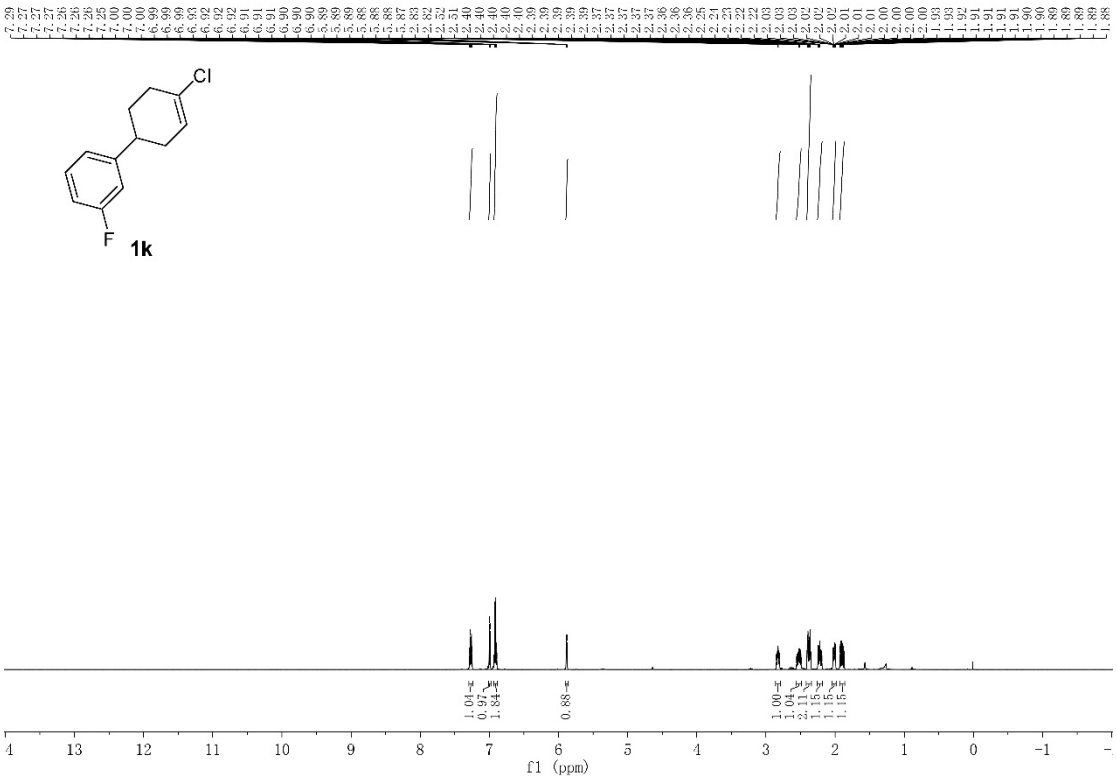
^{1}H NMR of **1j** (600 MHz, $CDCl_3$)



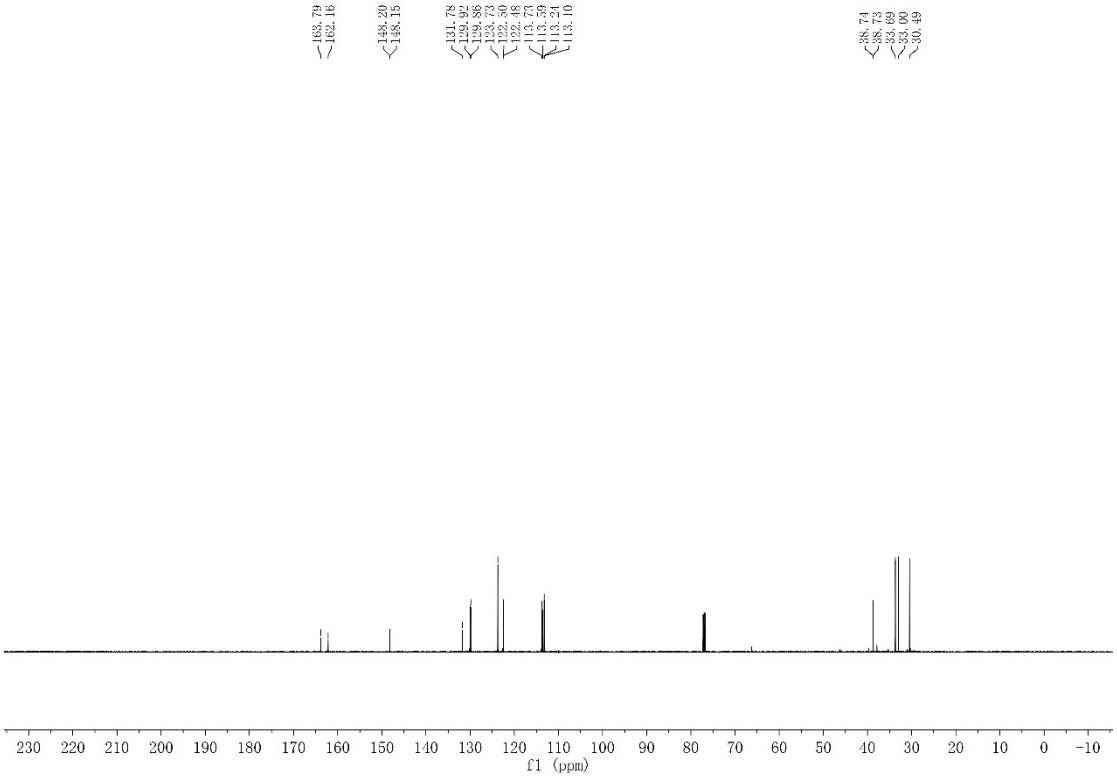
^{13}C NMR of **1j** (151 MHz, $CDCl_3$)



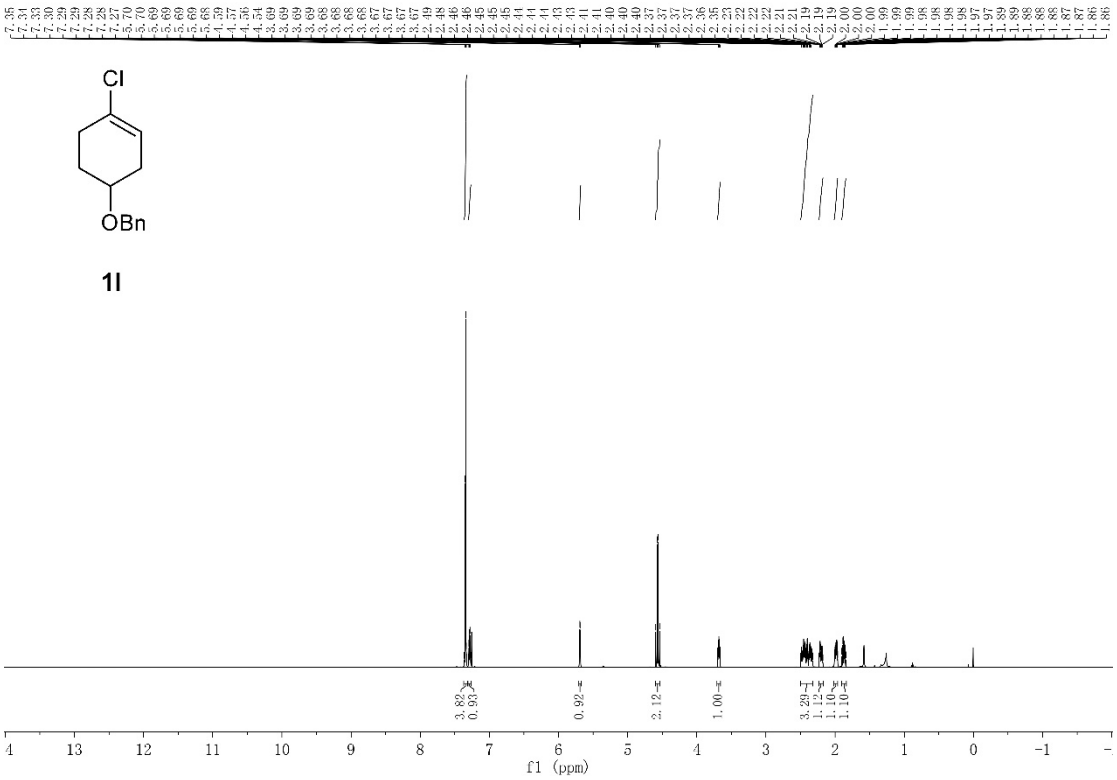
^{1}H NMR of **1k** (600 MHz, $CDCl_3$)



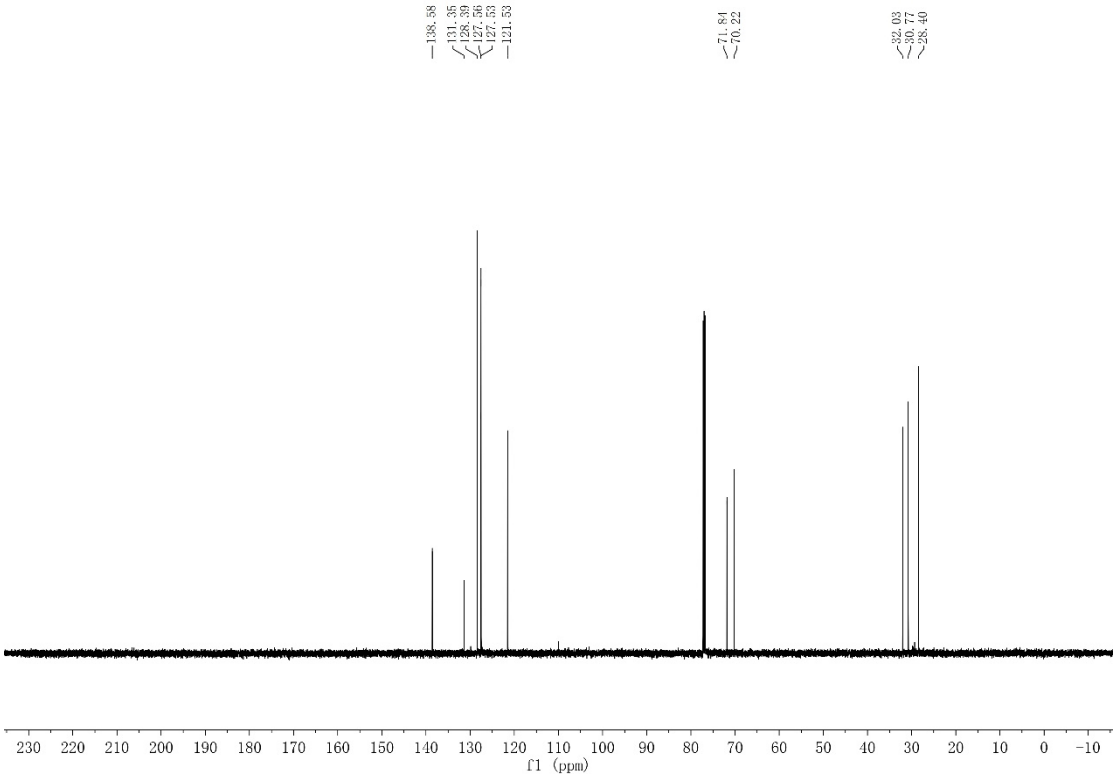
^{13}C NMR of **1k** (151 MHz, $CDCl_3$)



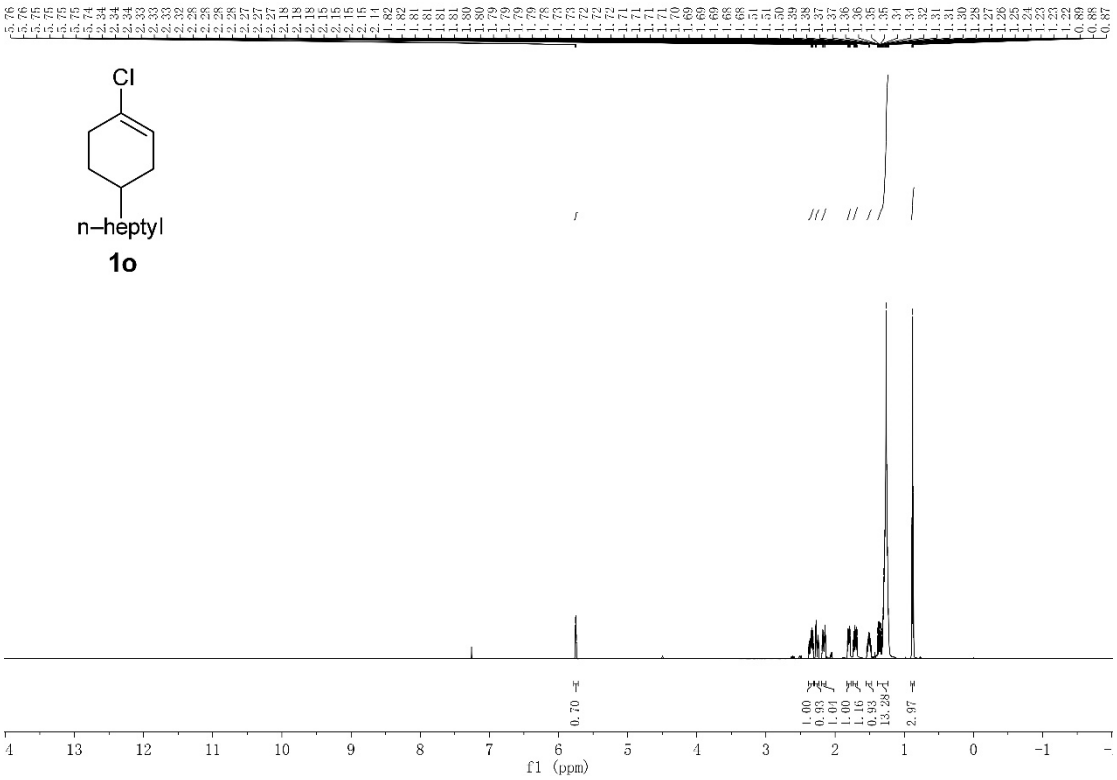
^{1}H NMR of **1l** (600 MHz, $CDCl_3$)



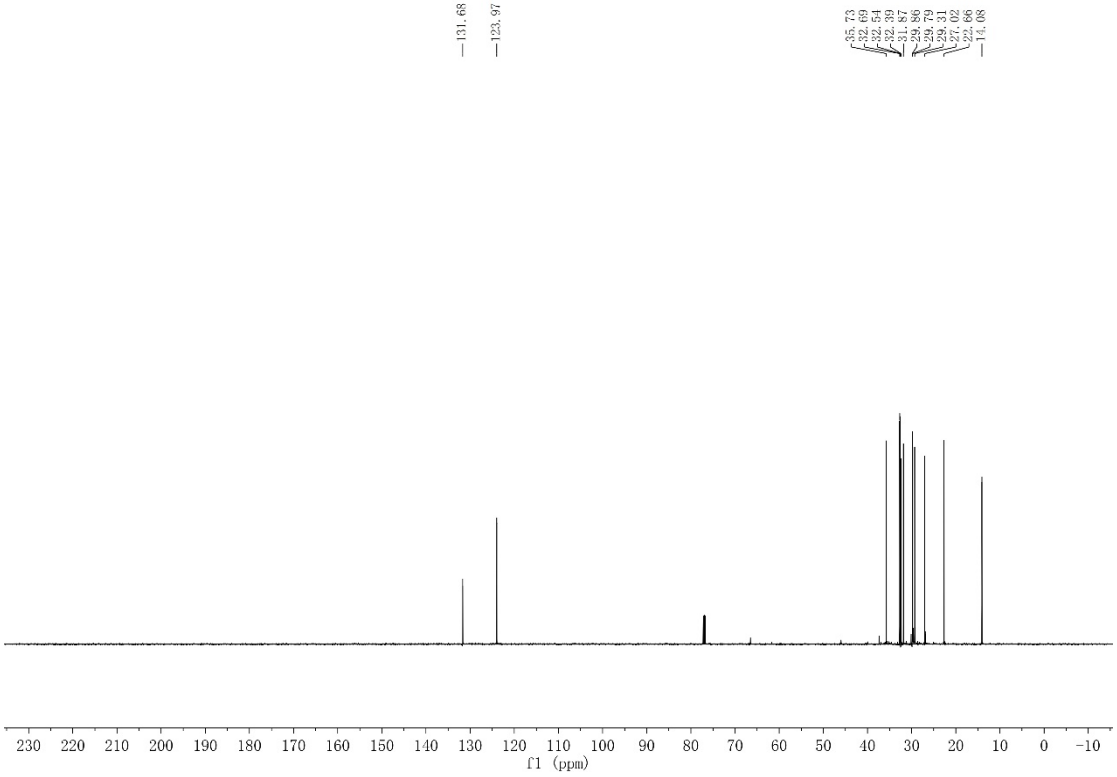
^{13}C NMR of **1l** (151 MHz, $CDCl_3$)



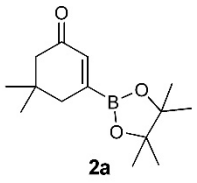
^{1}H NMR of **1o** (600 MHz, $CDCl_3$)



^{13}C NMR of **1o** (151 MHz, $CDCl_3$)

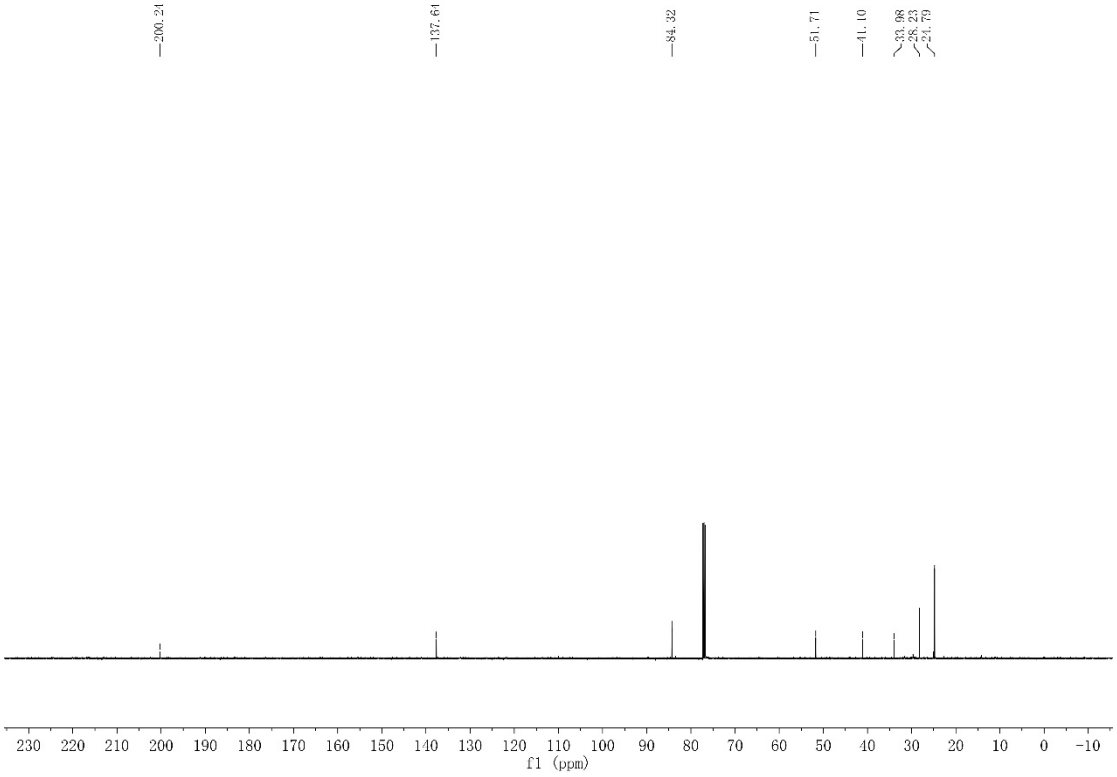


^{1}H NMR of **2a** (600 MHz, $CDCl_3$)

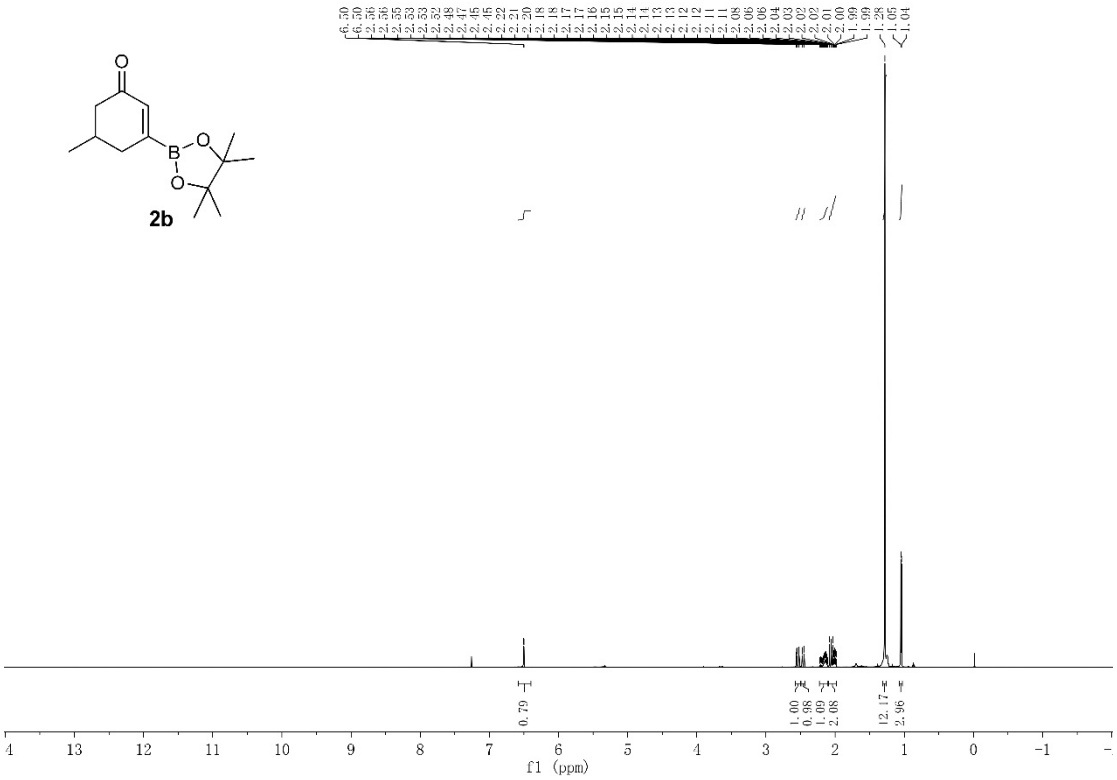


2a

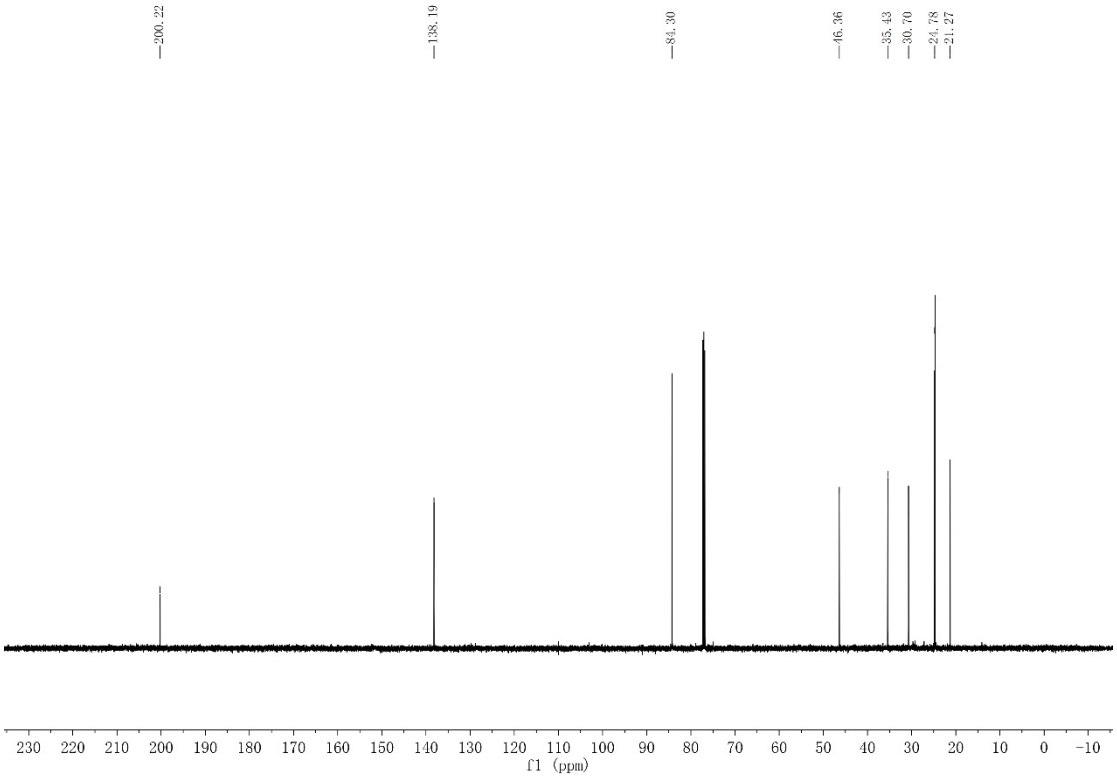
^{13}C NMR of **2a** (151 MHz, $CDCl_3$)



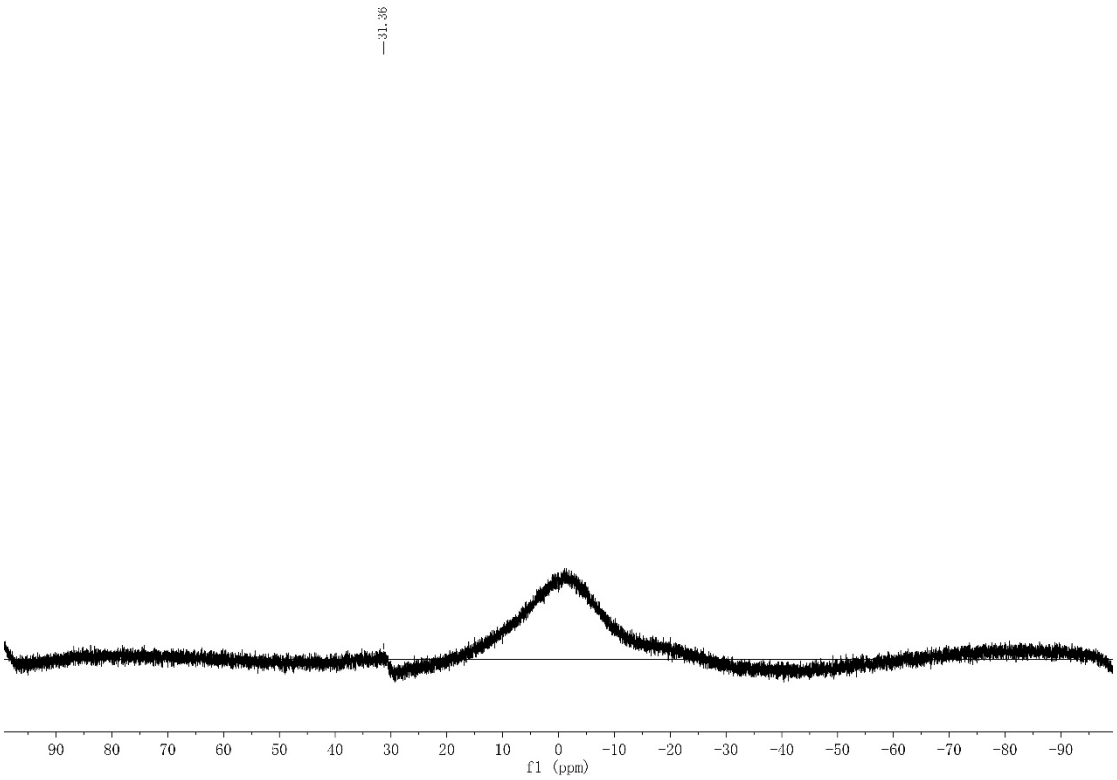
^{1}H NMR of 2b (600 MHz, $CDCl_3$)



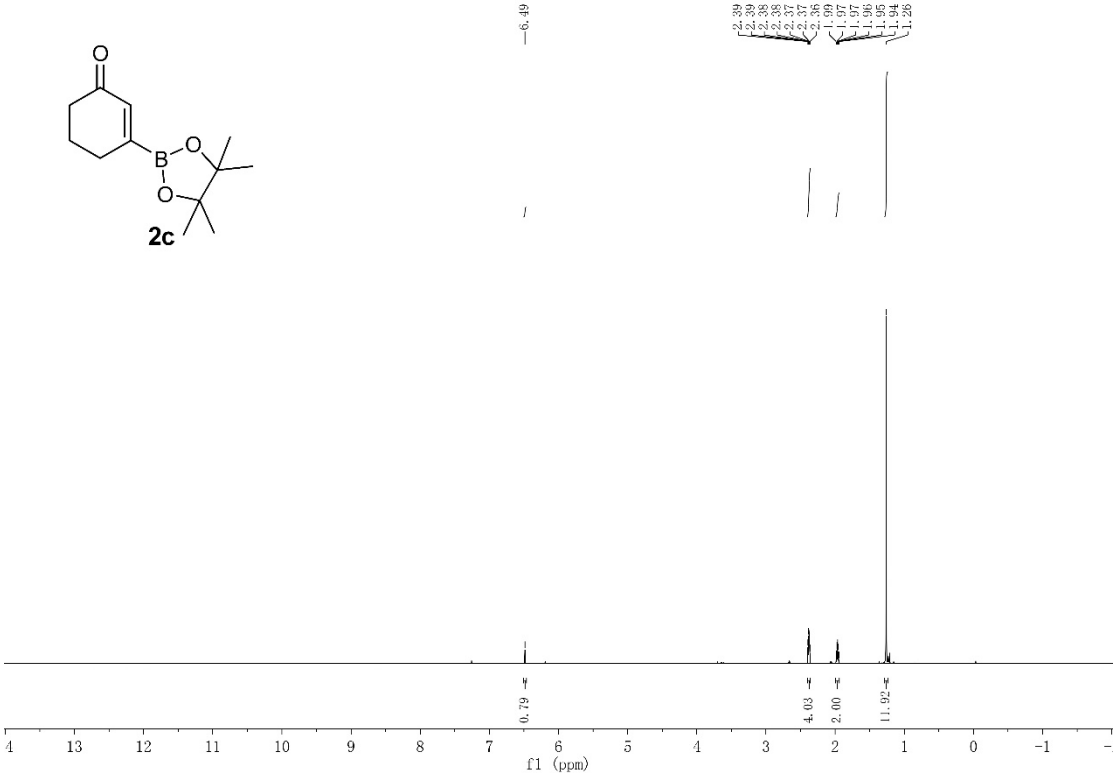
^{13}C NMR of 2b (151 MHz, $CDCl_3$)



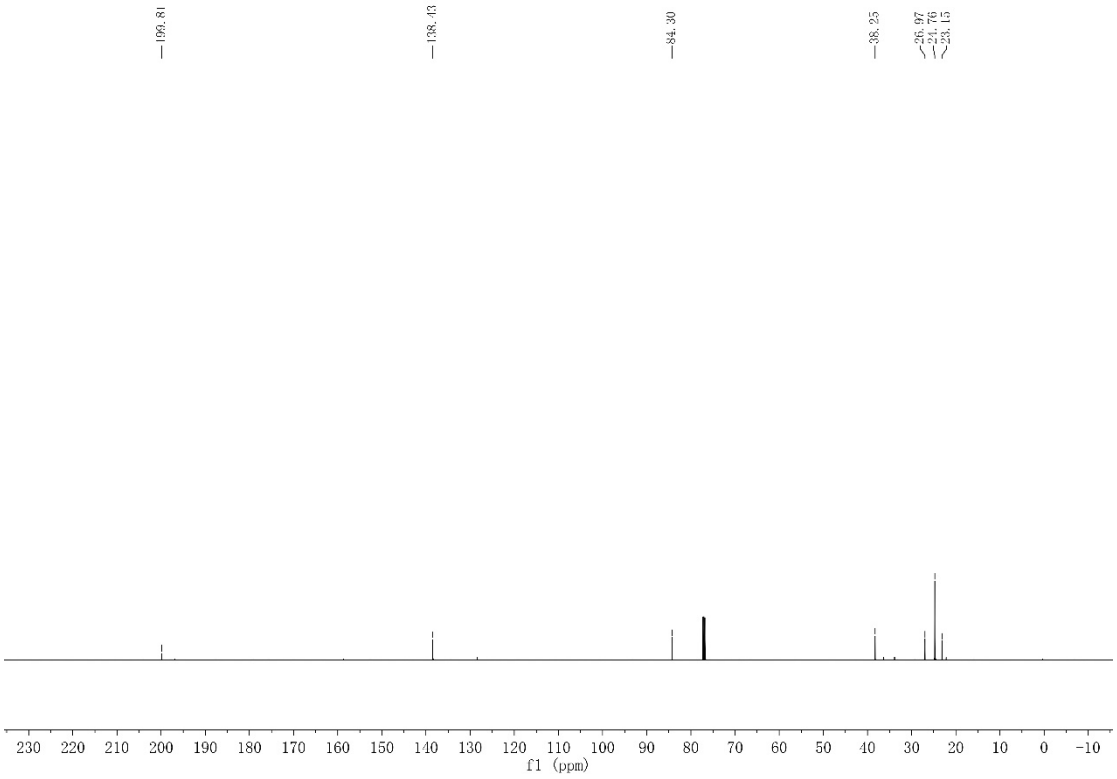
^{13}B NMR of 2b (128 MHz, $CDCl_3$)



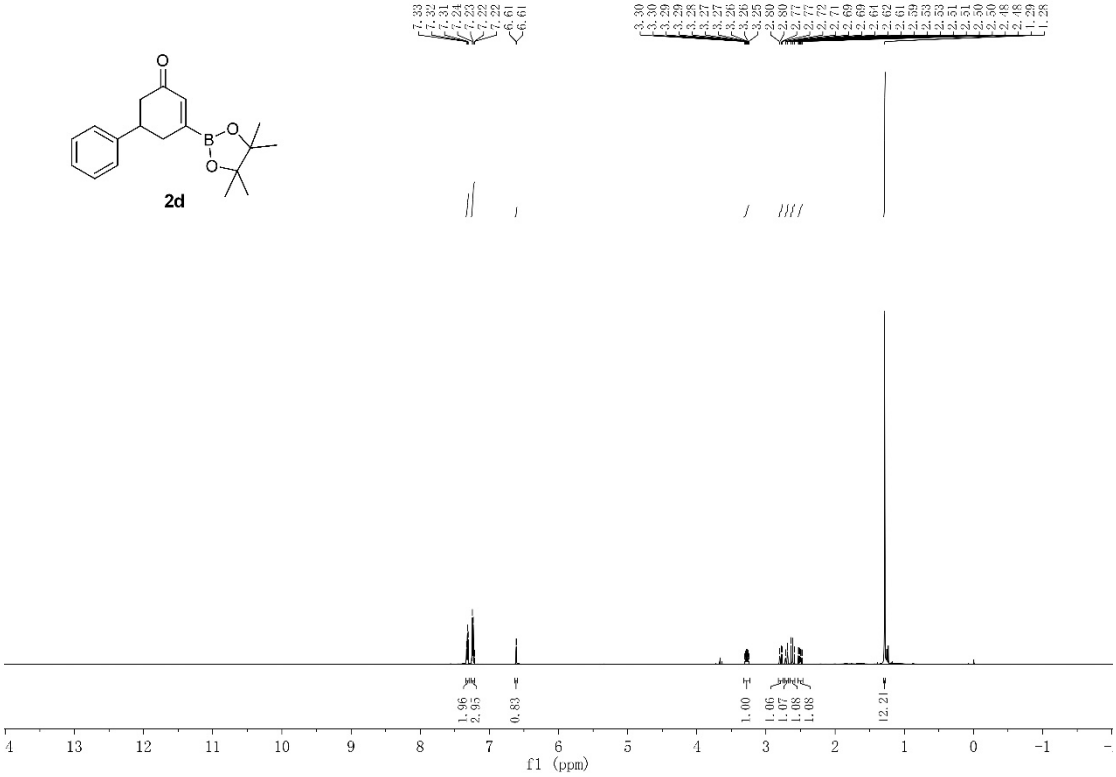
^{1}H NMR of **2c** (600 MHz, $CDCl_3$)



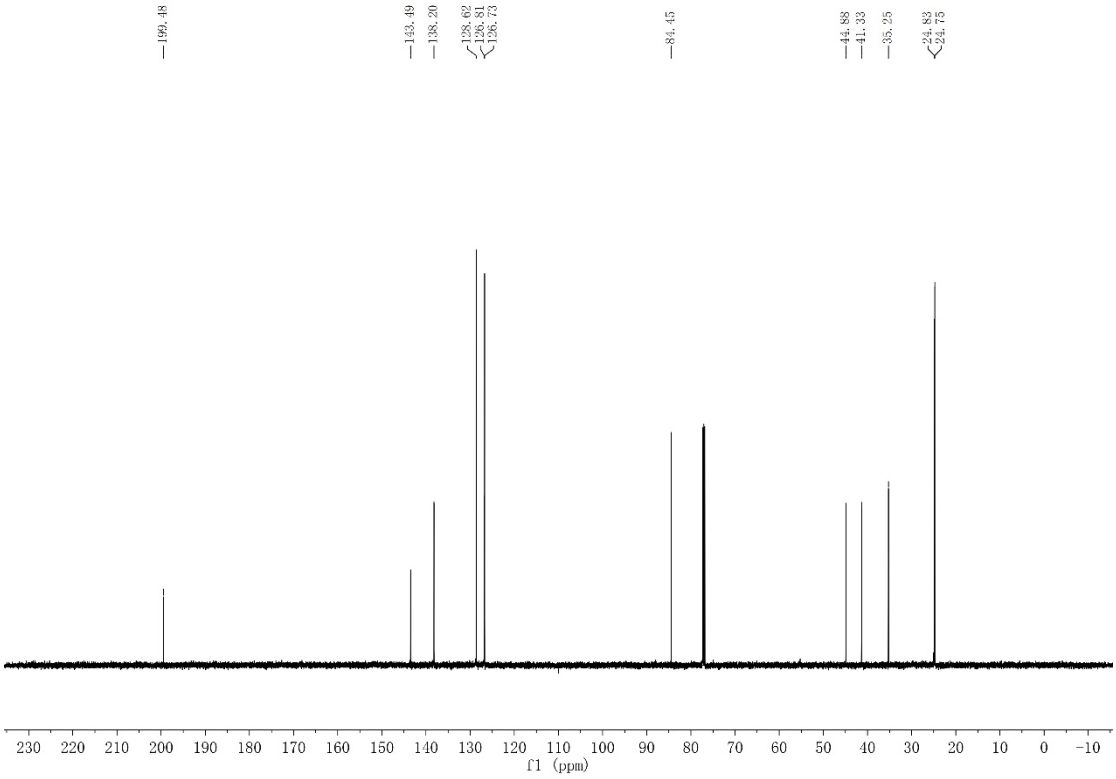
^{13}C NMR of **2c** (151 MHz, $CDCl_3$)



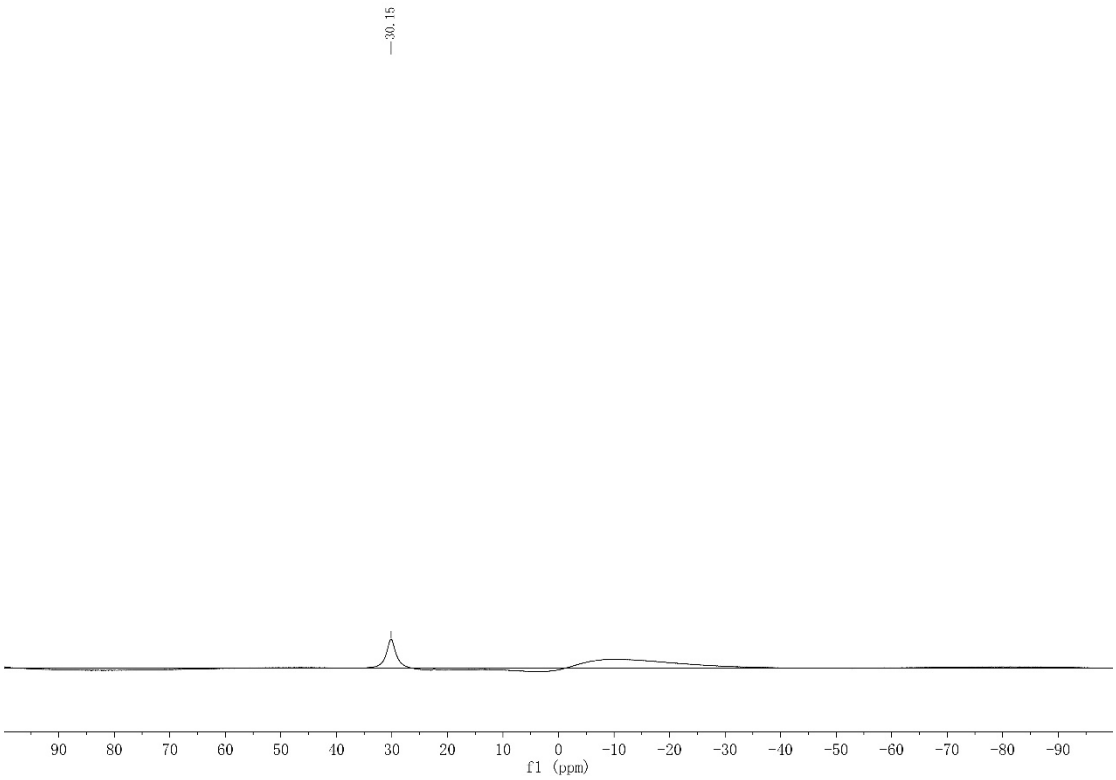
^{1}H NMR of **2d** (600 MHz, $CDCl_3$)



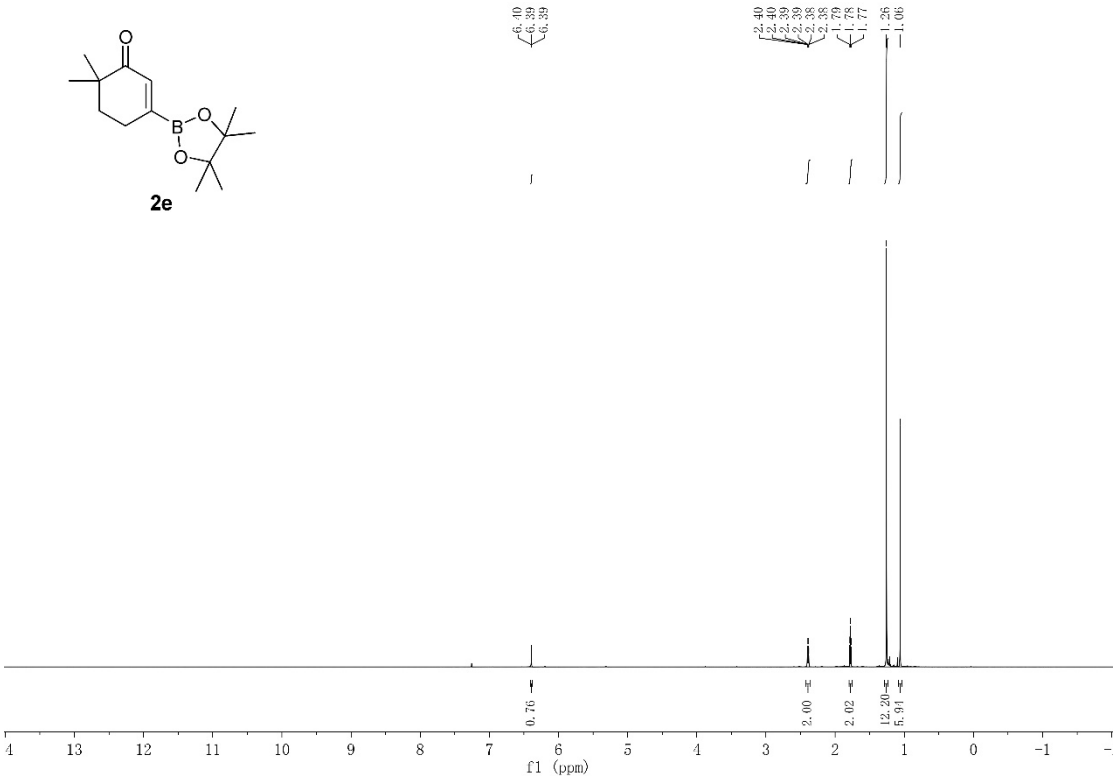
^{13}C NMR of **2d** (151 MHz, $CDCl_3$)



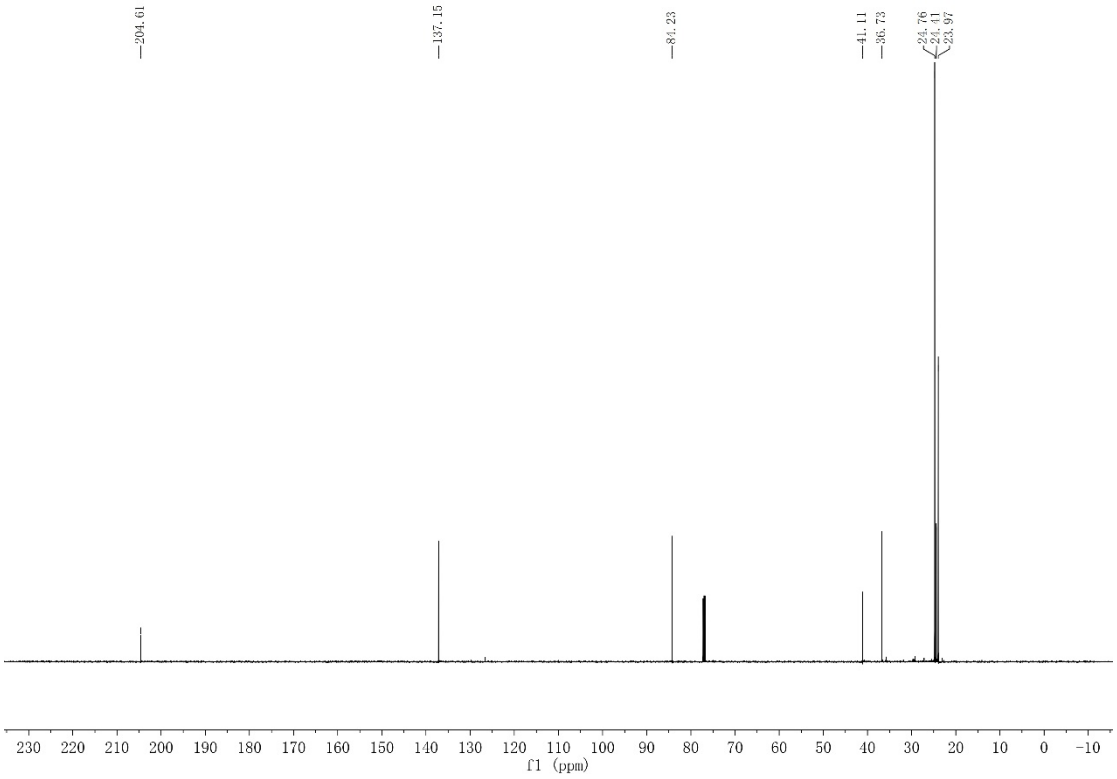
^{11}B NMR of **2d** (193 MHz, $CDCl_3$)



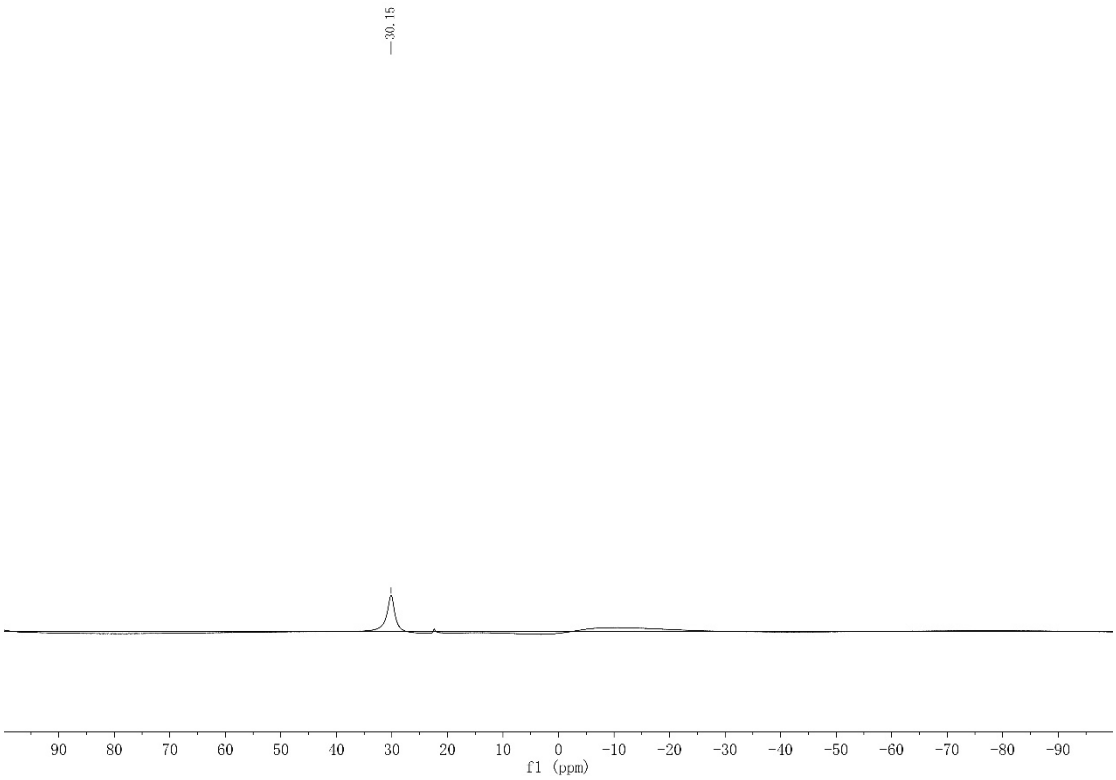
^{1}H NMR of **2e** (600 MHz, $CDCl_3$)



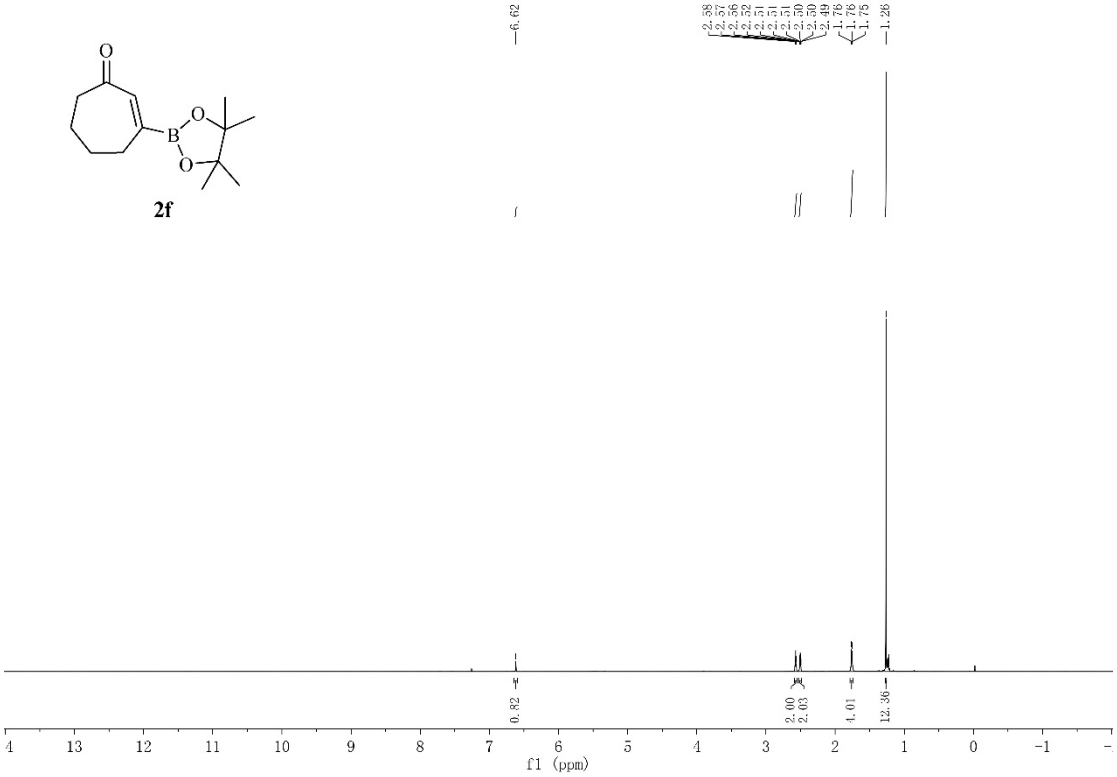
^{13}C NMR of **2e** (151 MHz, $CDCl_3$)



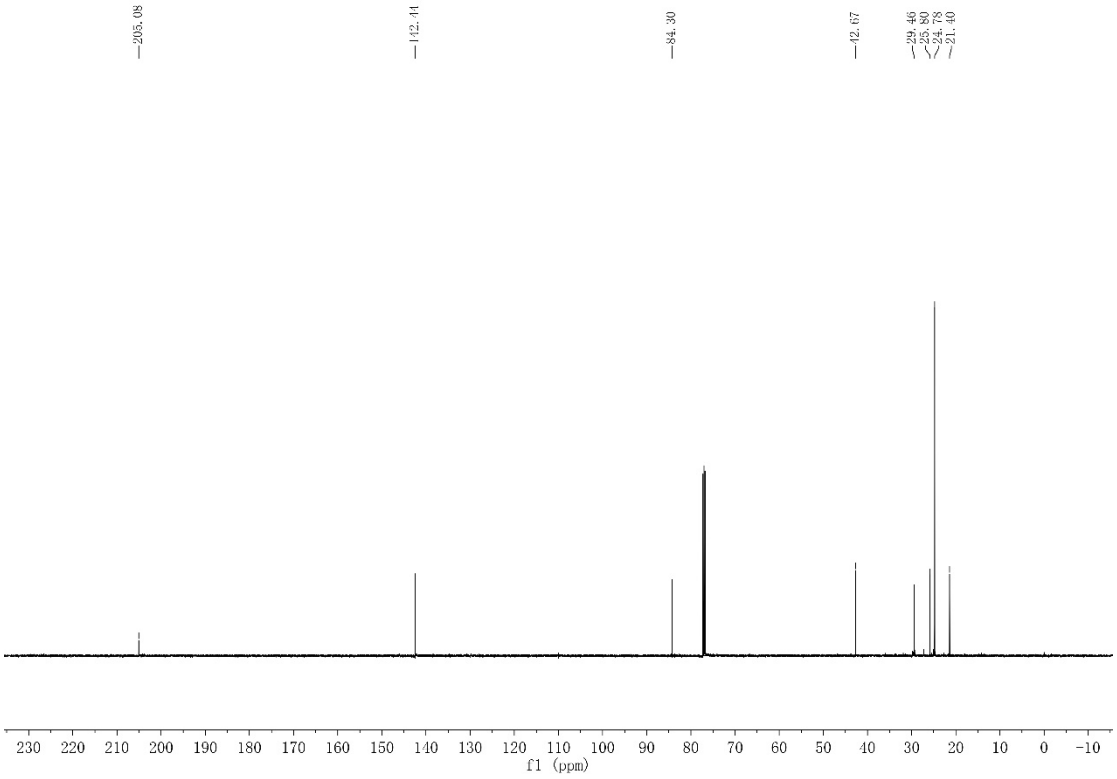
^{11}B NMR of **2e** (193 MHz, $CDCl_3$)



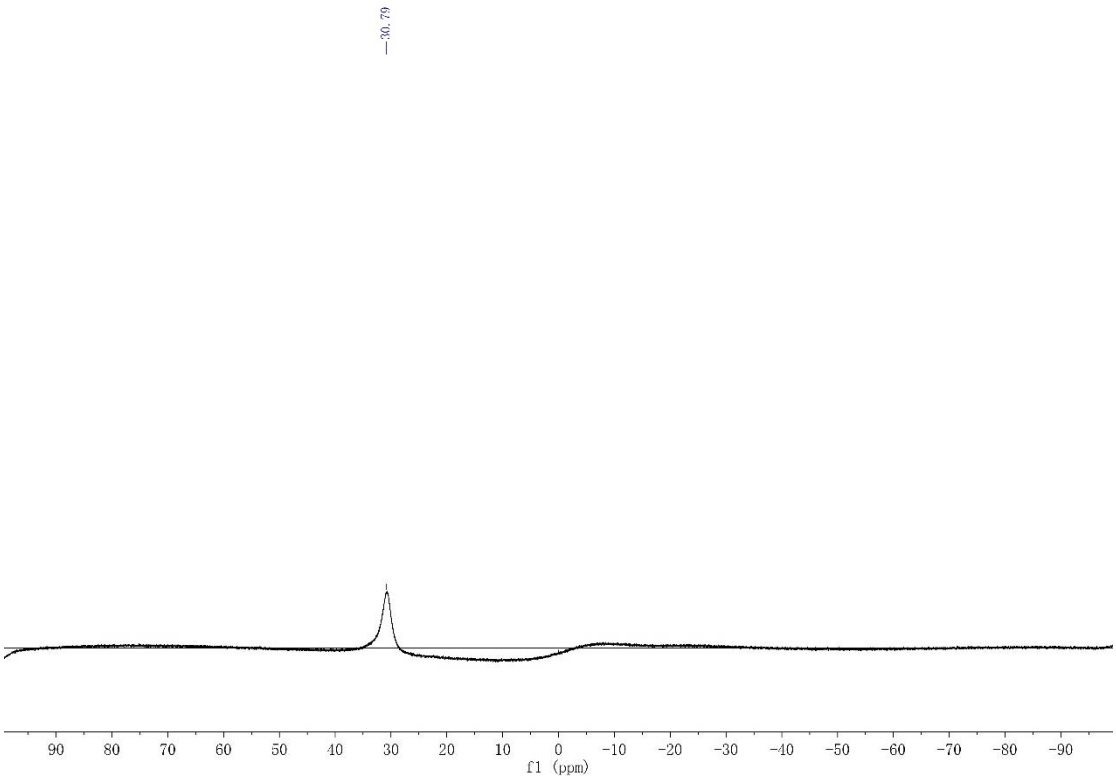
^{1}H NMR of **2f** (600 MHz, $CDCl_3$)



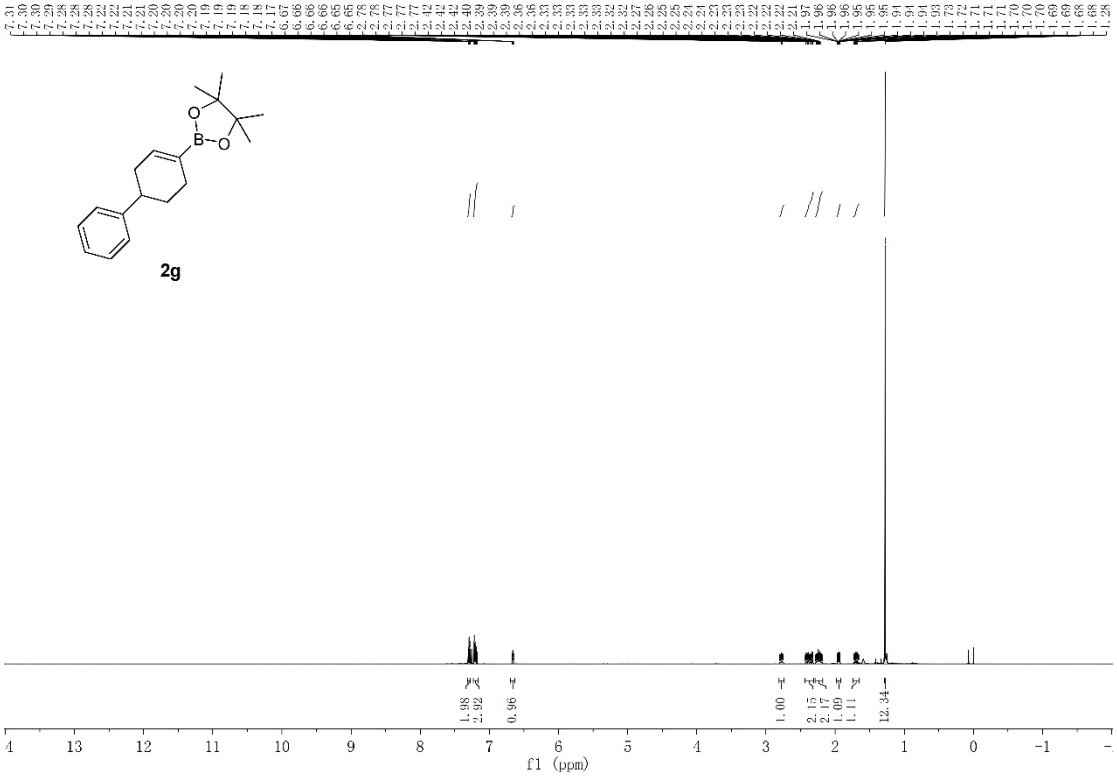
^{13}C NMR of **2f** (151 MHz, $CDCl_3$)



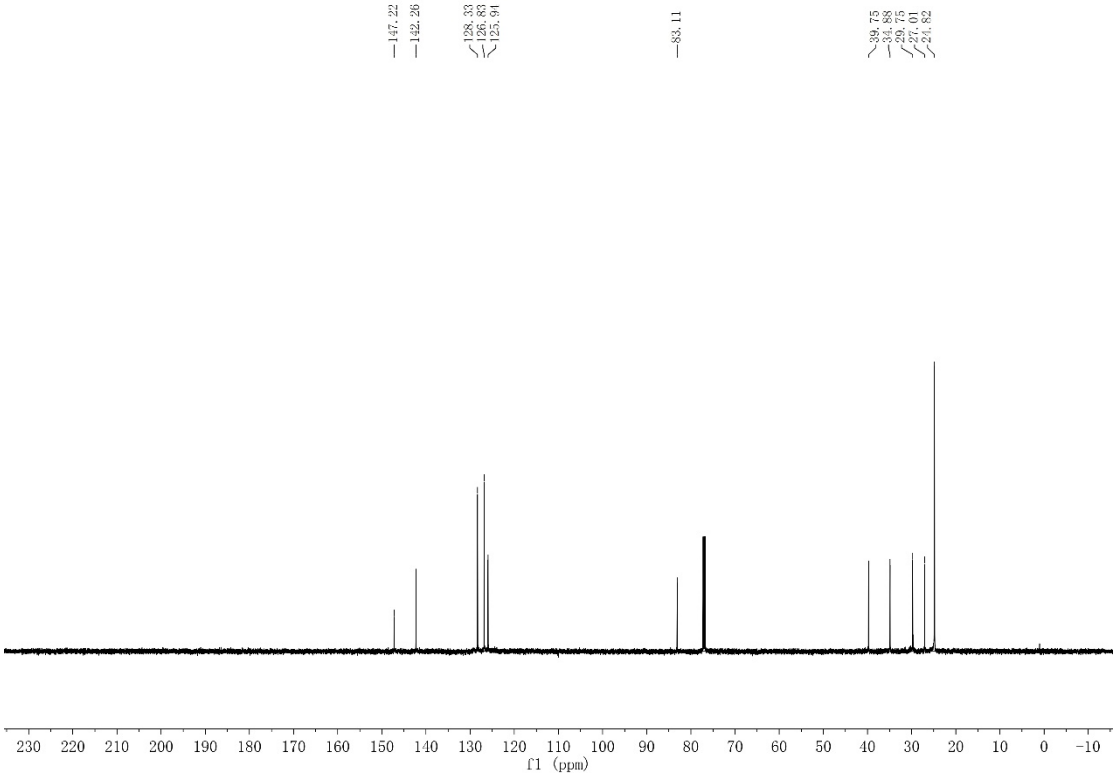
^{11}B NMR of **2f** (128 MHz, $CDCl_3$)



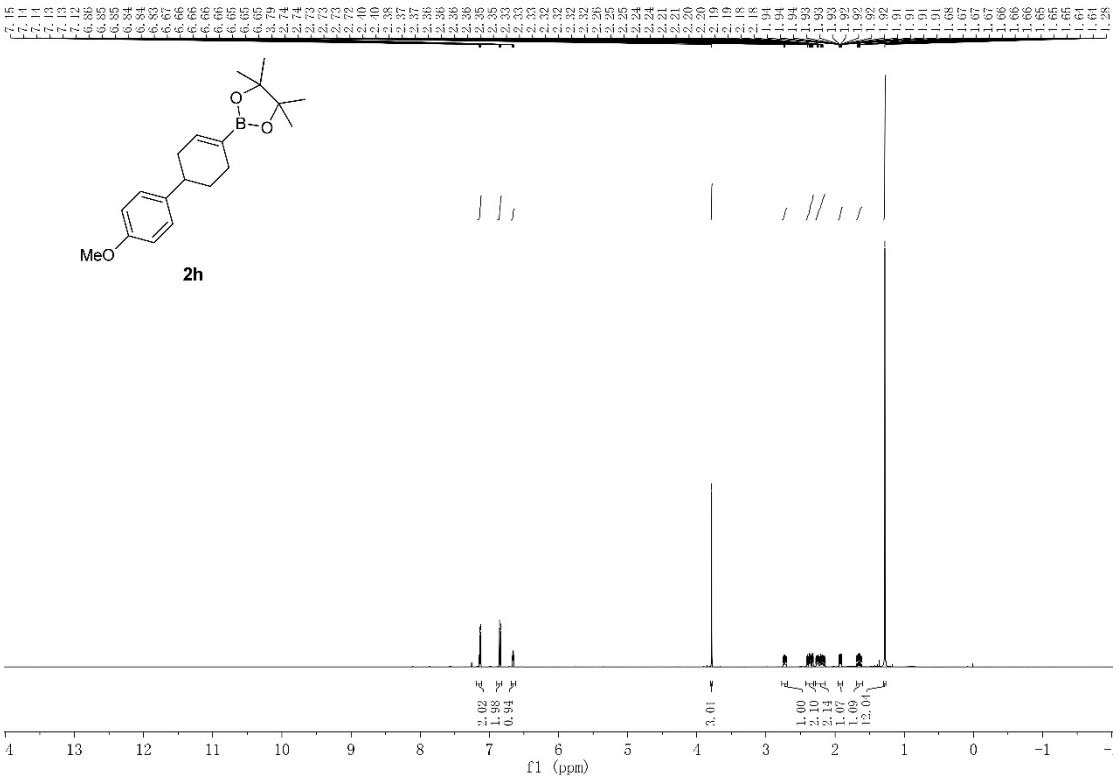
^{1}H NMR of **2g** (600 MHz, $CDCl_3$)



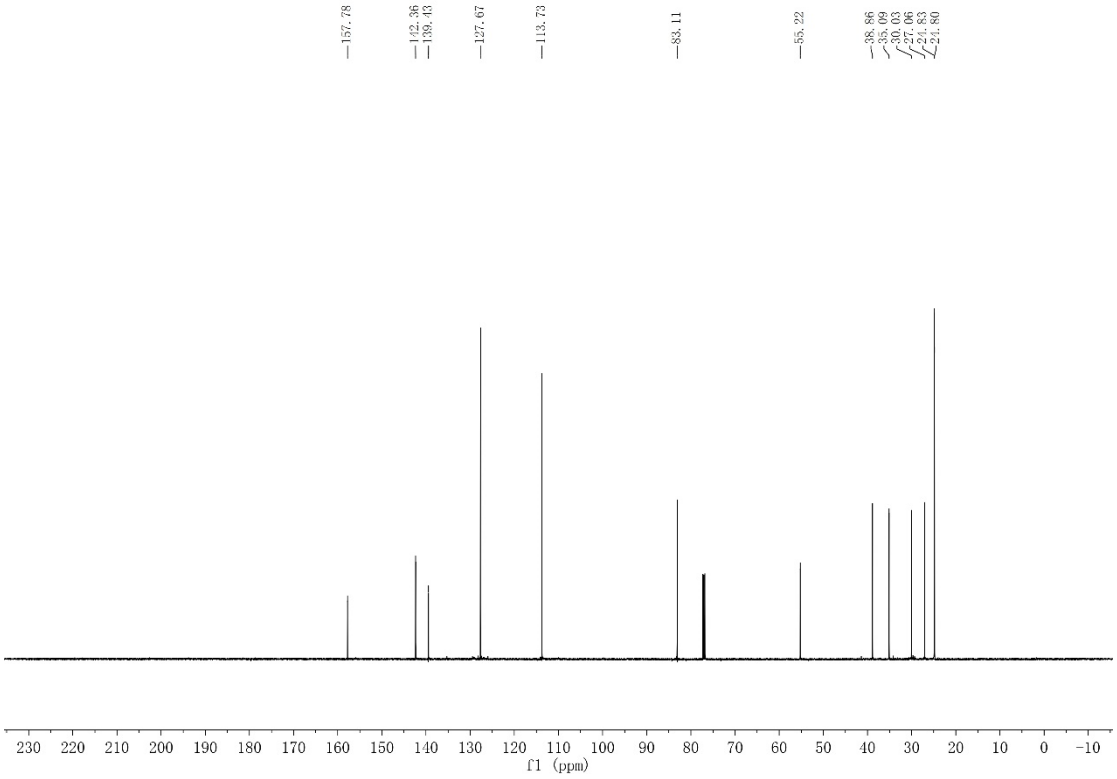
^{13}C NMR of **2g** (151 MHz, $CDCl_3$)



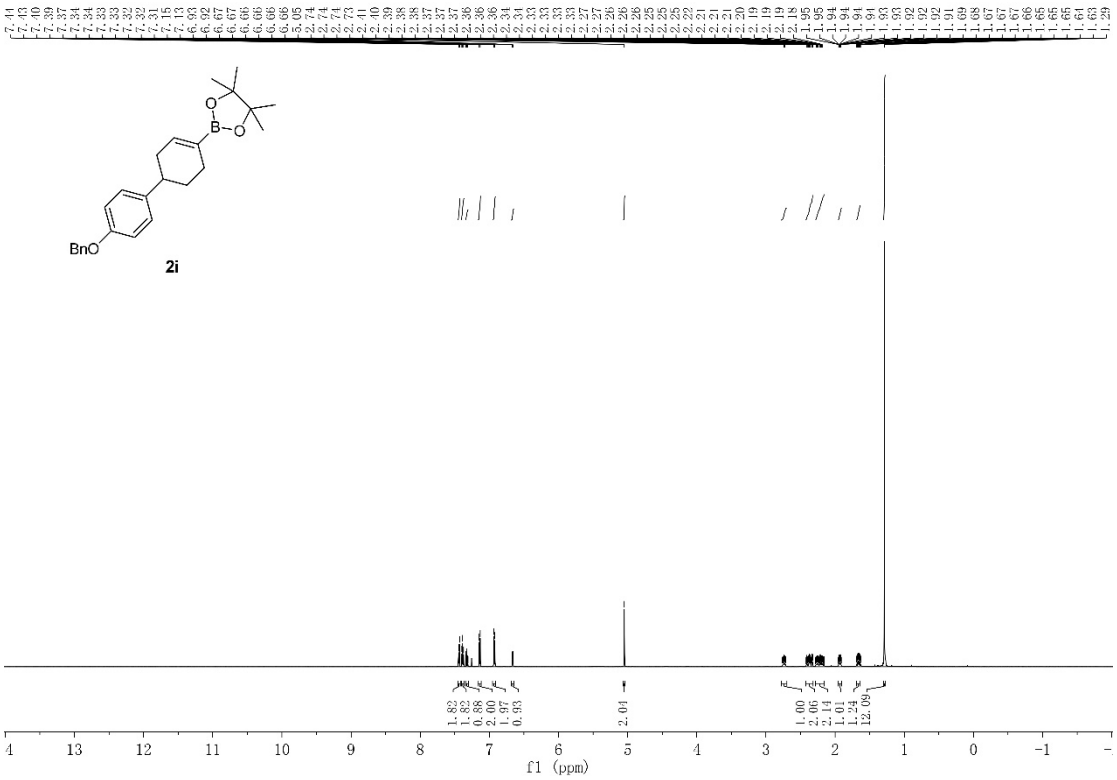
^{1}H NMR of **2h** (600 MHz, $CDCl_3$)



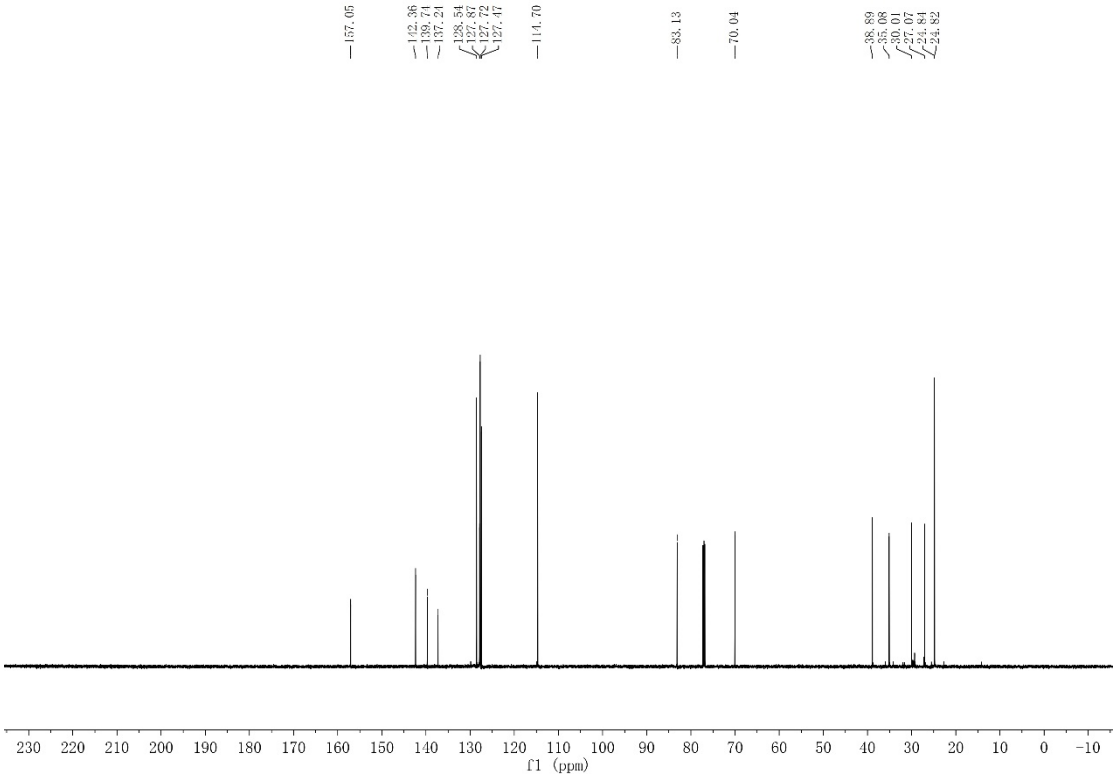
^{13}C NMR of **2h** (151 MHz, $CDCl_3$)



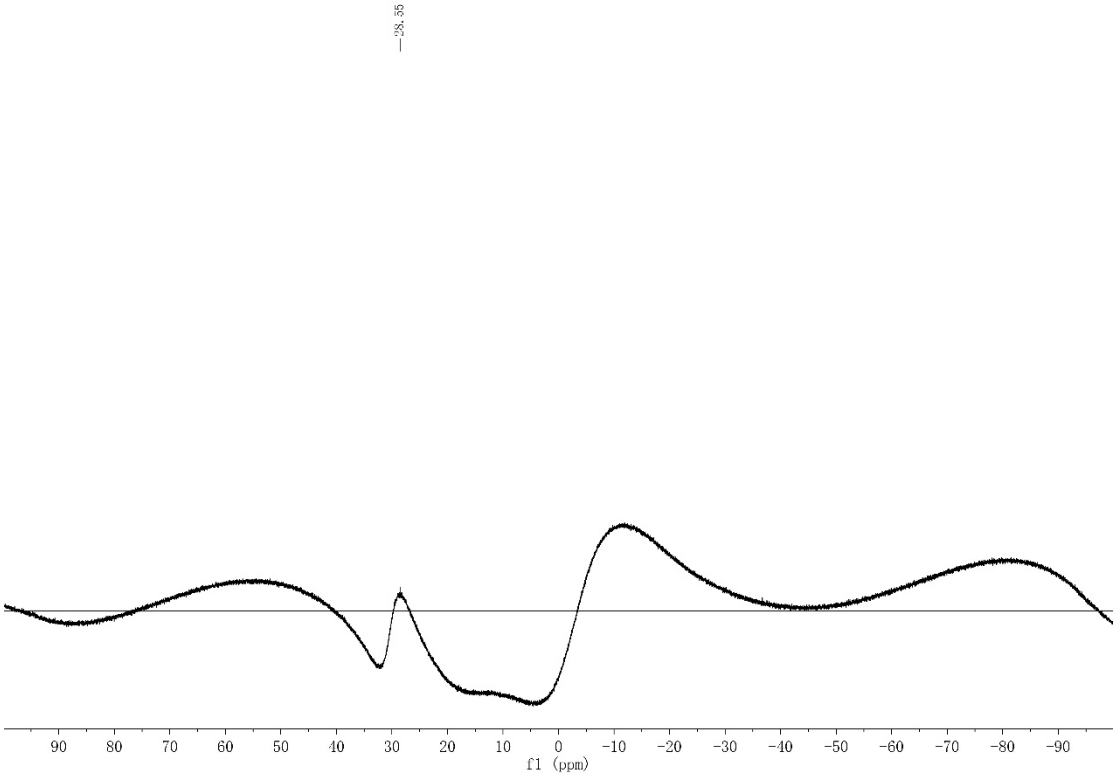
^{1}H NMR of **2i** (600 MHz, $CDCl_3$)



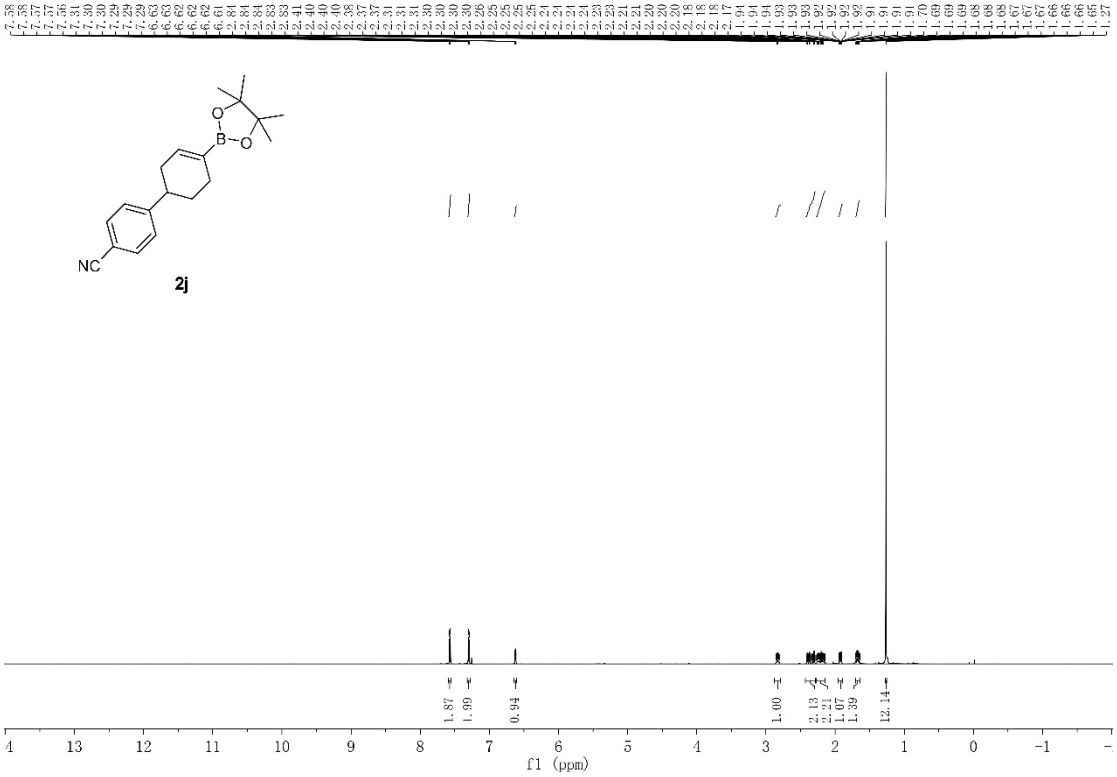
^{13}C NMR of **2i** (151 MHz, $CDCl_3$)



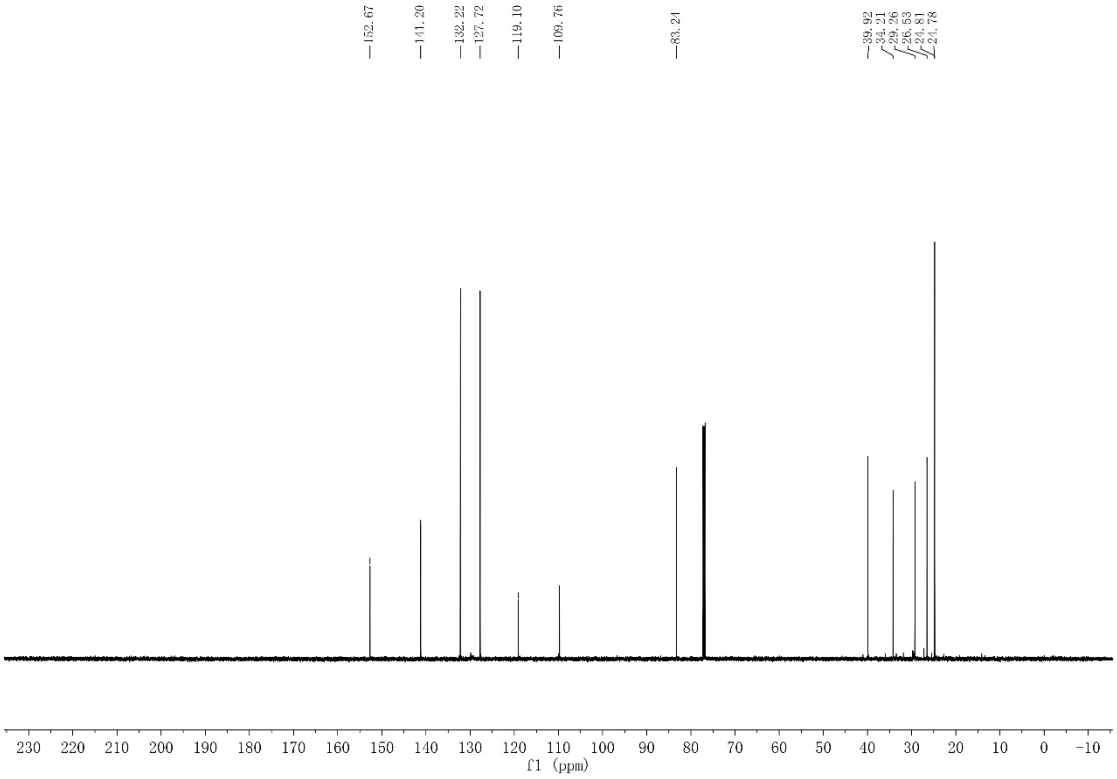
^{11}B NMR of **2i** (193 MHz, $CDCl_3$)



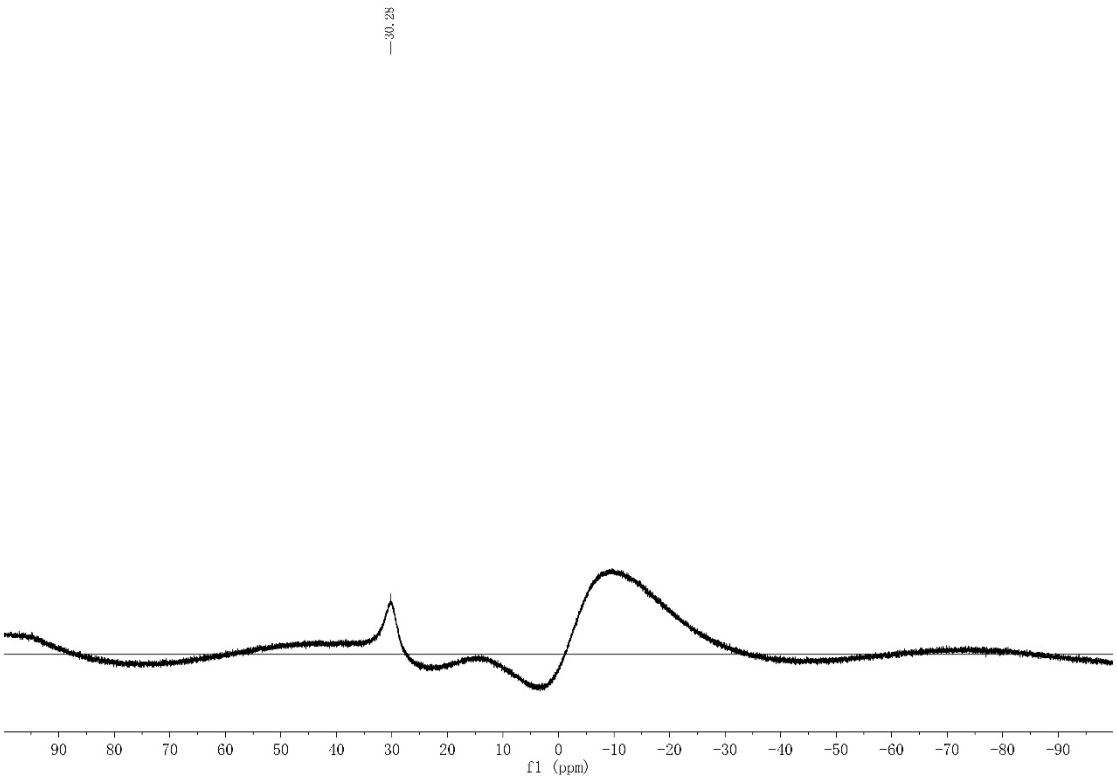
^{1}H NMR of **2j** (600 MHz, $CDCl_3$)



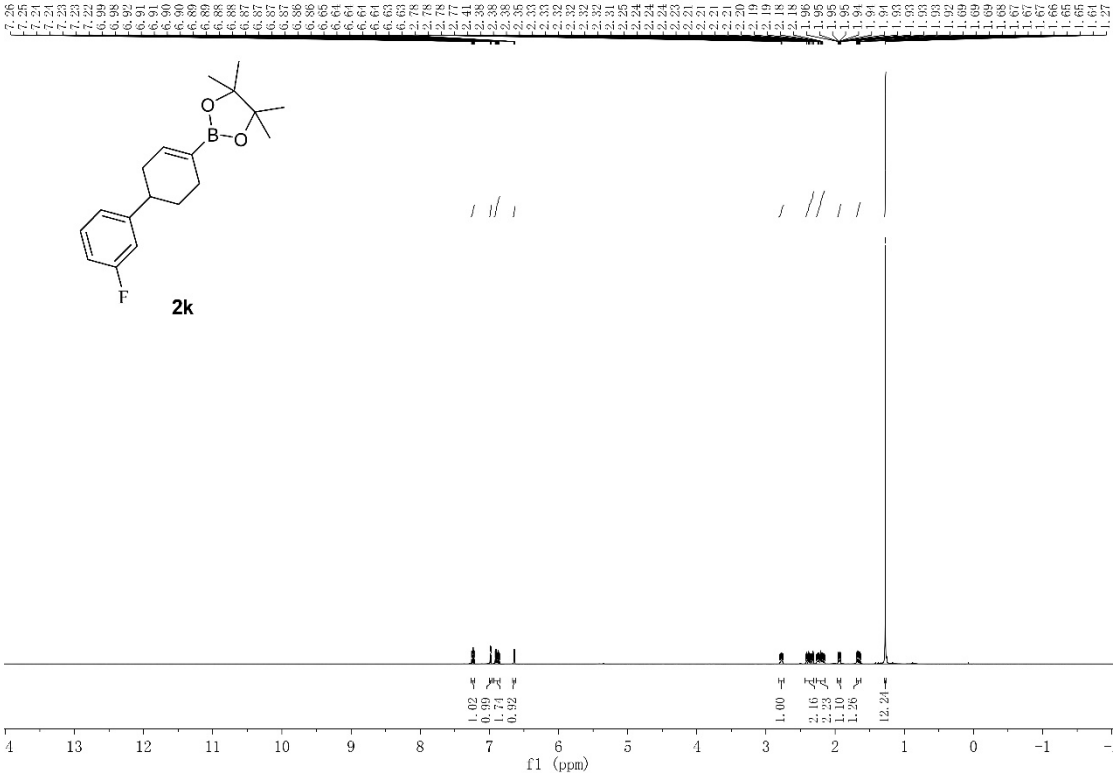
^{13}C NMR of **2j** (151 MHz, $CDCl_3$)



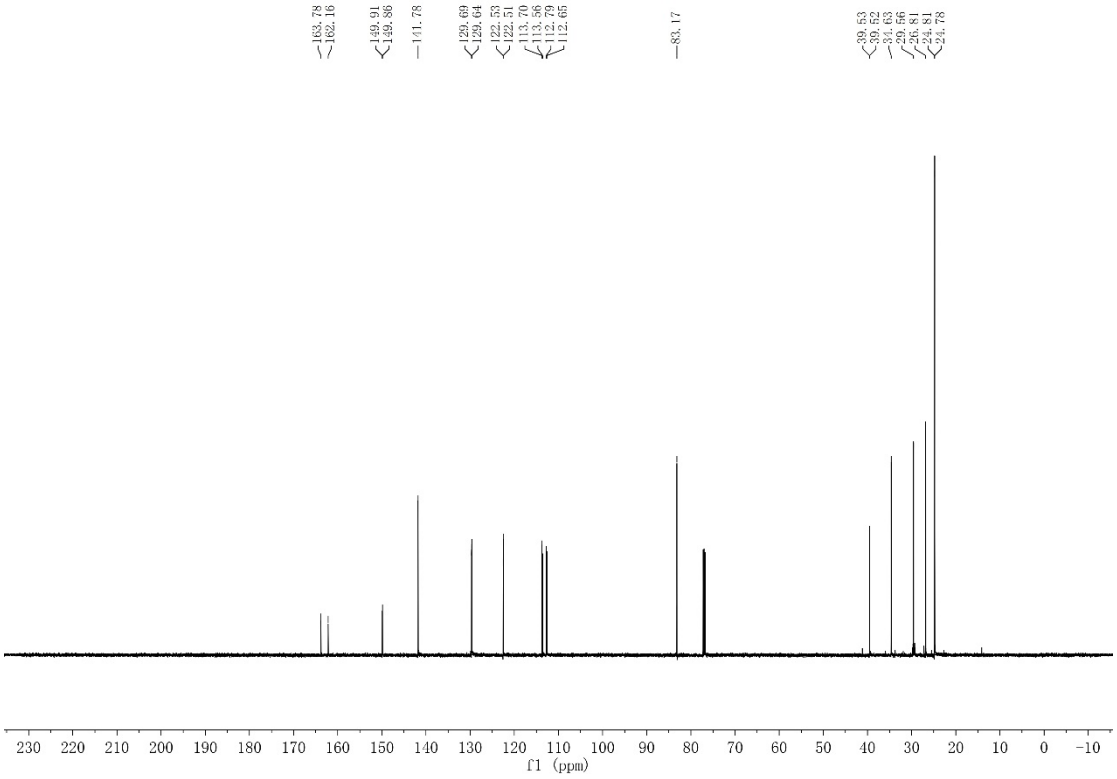
^{11}B NMR of **2j** (193 MHz, $CDCl_3$)



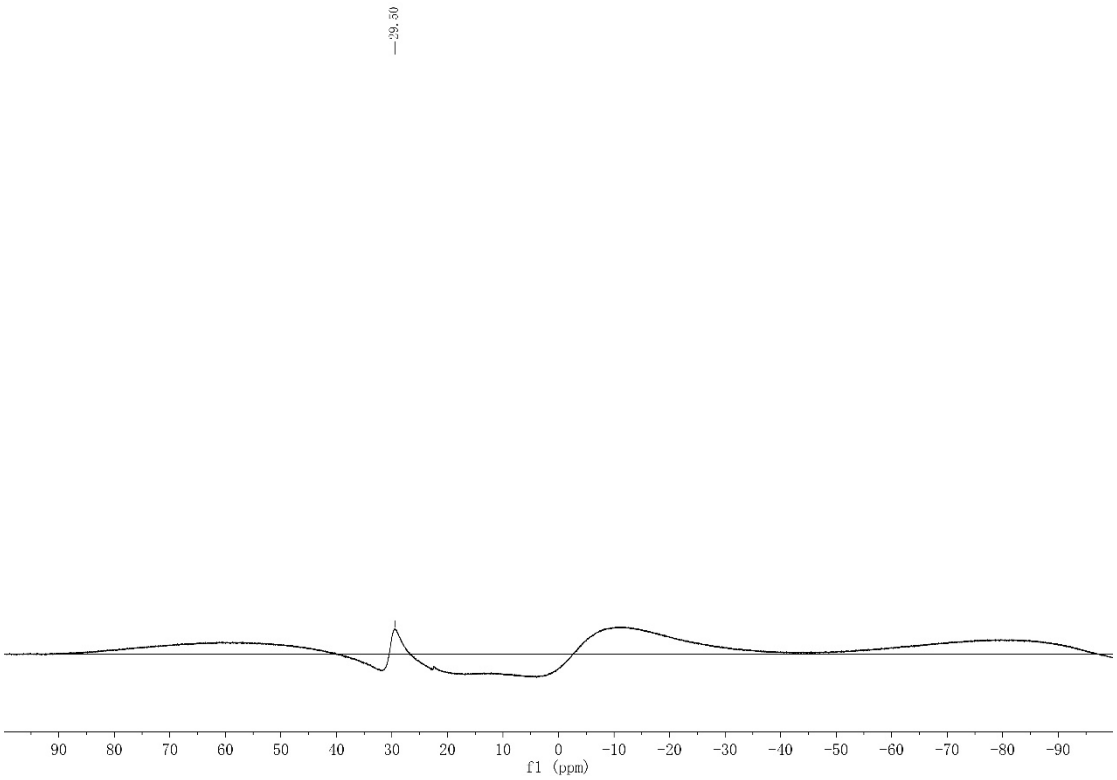
^{1}H NMR of **2k** (600 MHz, $CDCl_3$)



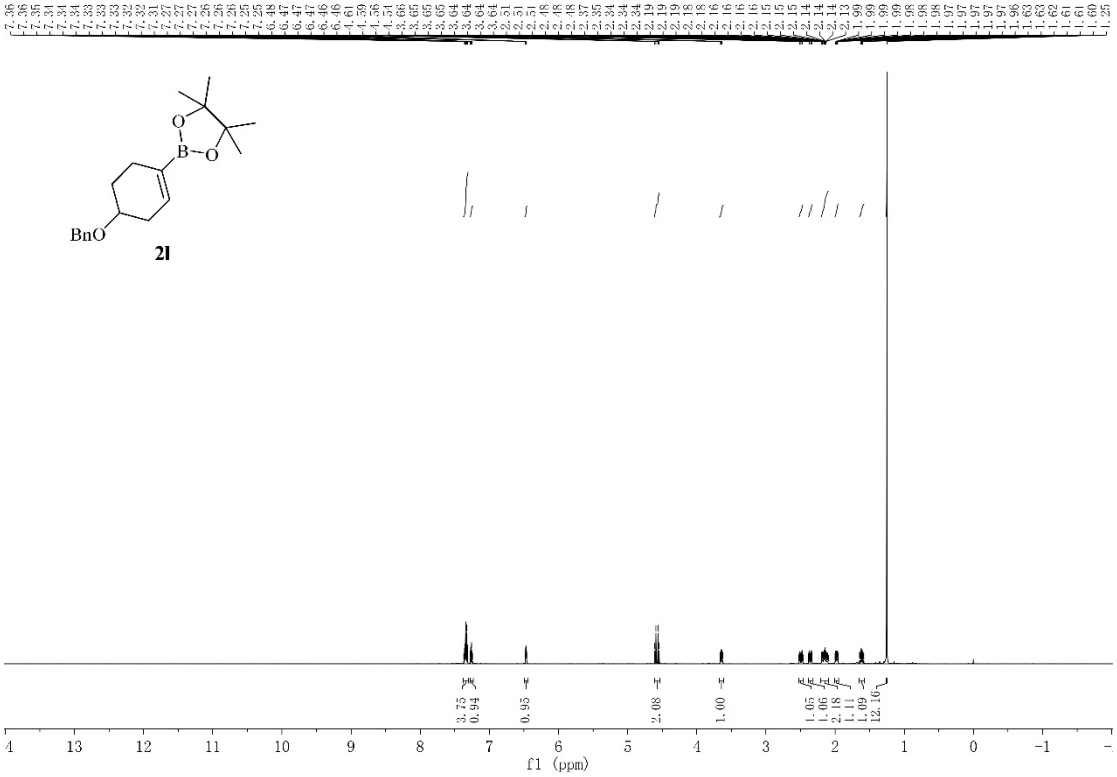
^{13}C NMR of **2k** (151 MHz, $CDCl_3$)



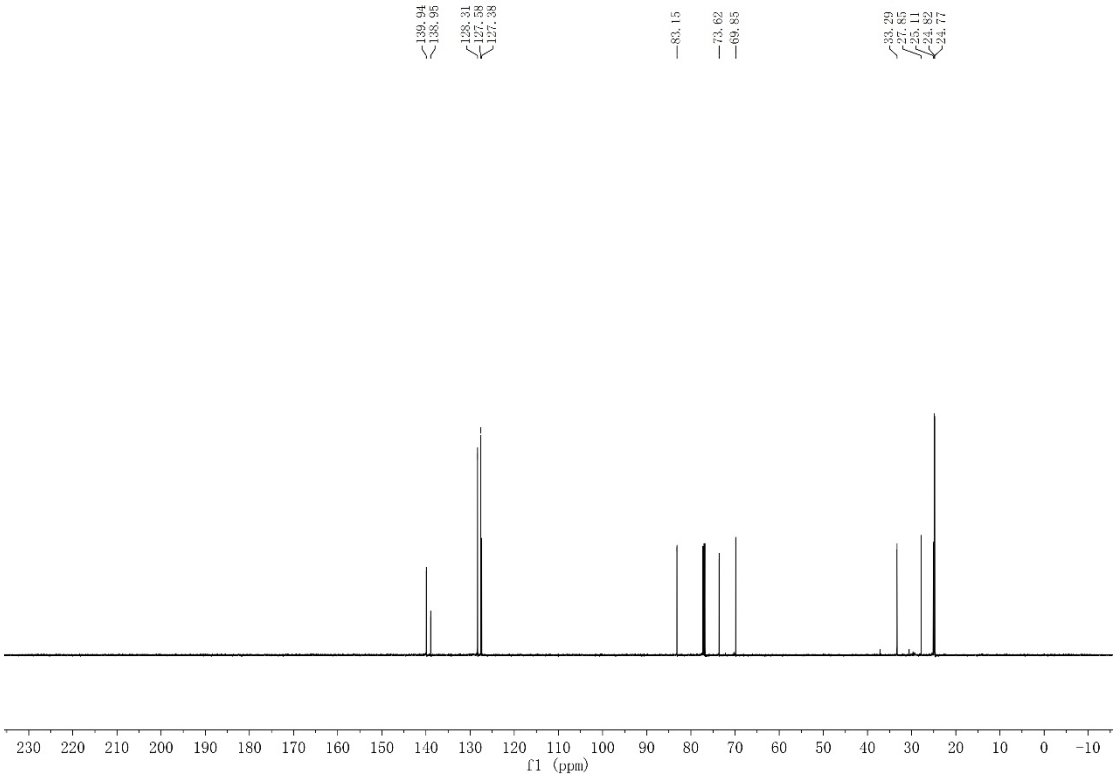
^{11}B NMR of **2k** (193 MHz, $CDCl_3$)



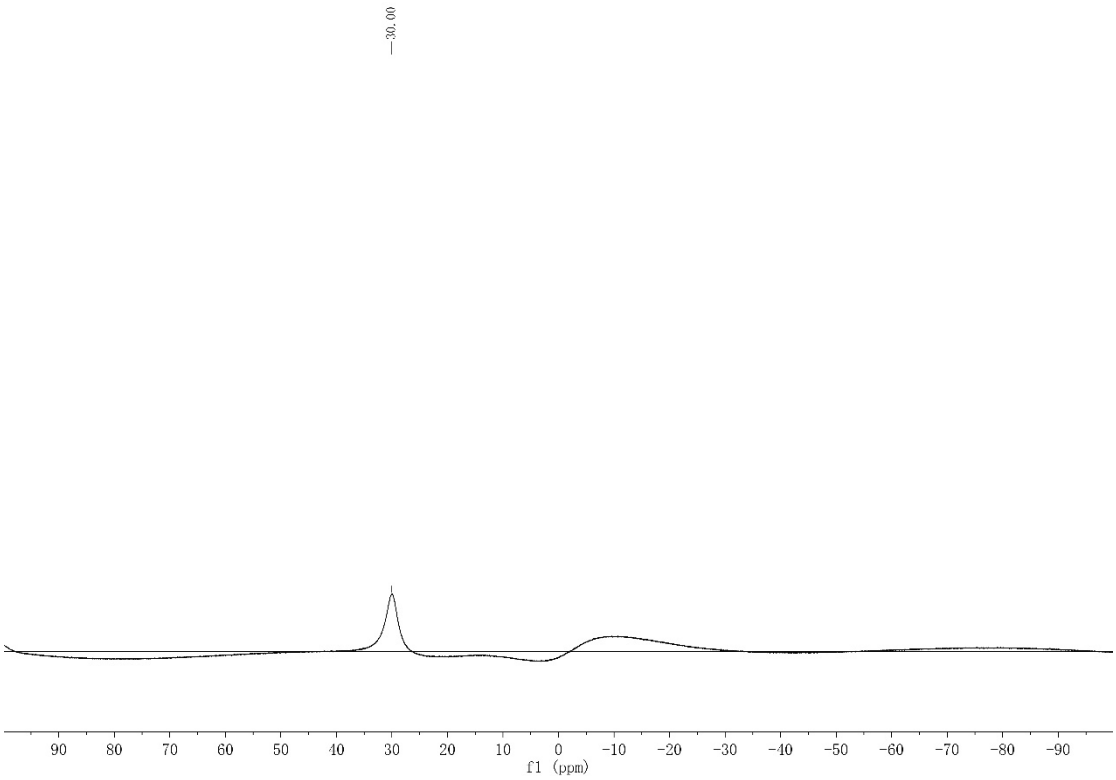
^{1}H NMR of **2l** (600 MHz, $CDCl_3$)



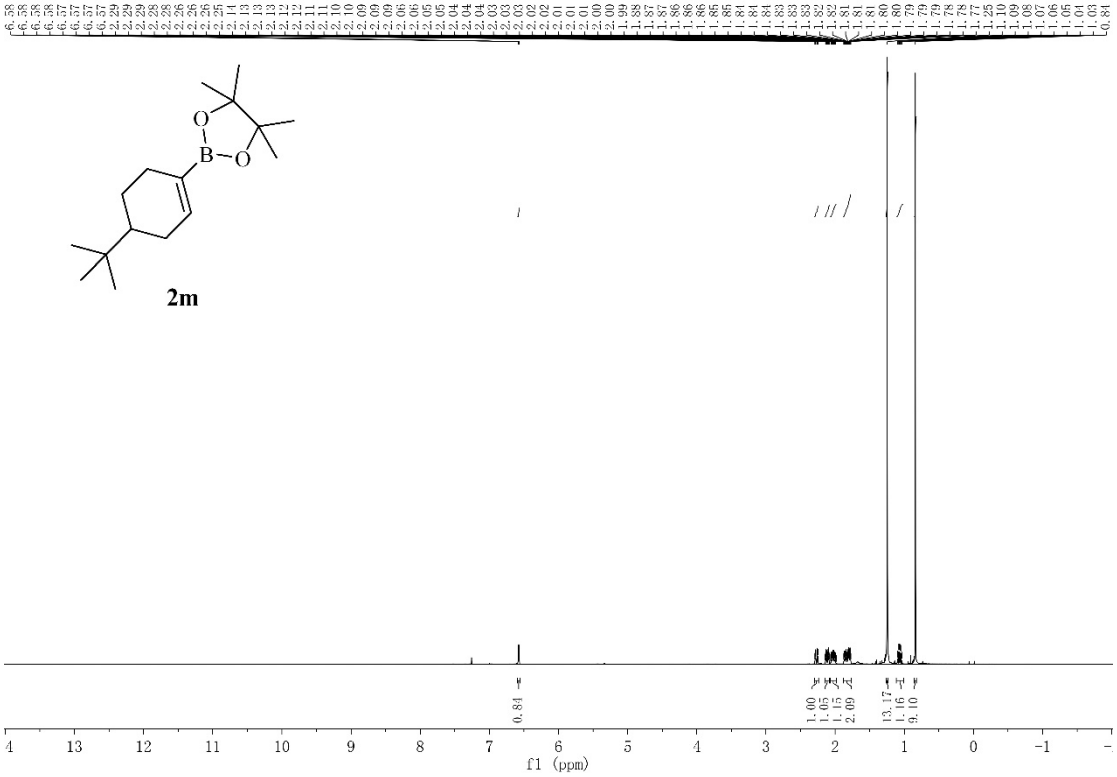
^{13}C NMR of **2l** (151 MHz, $CDCl_3$)



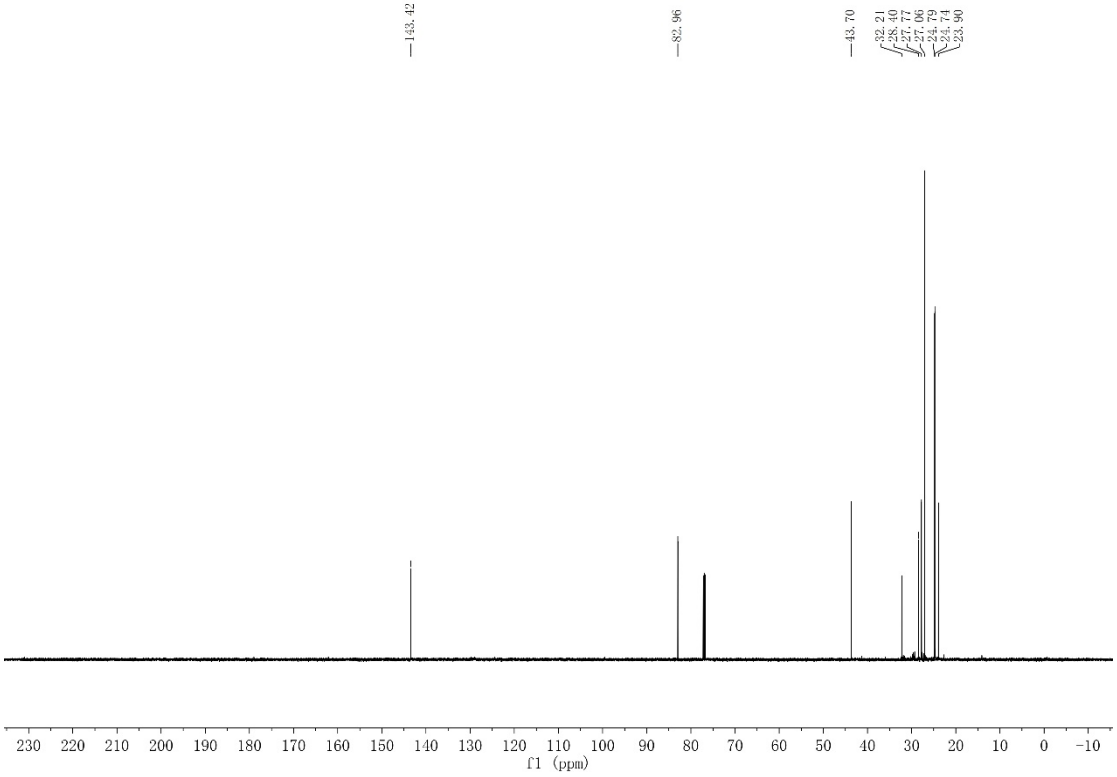
^{11}B NMR of **2l** (193 MHz, $CDCl_3$)



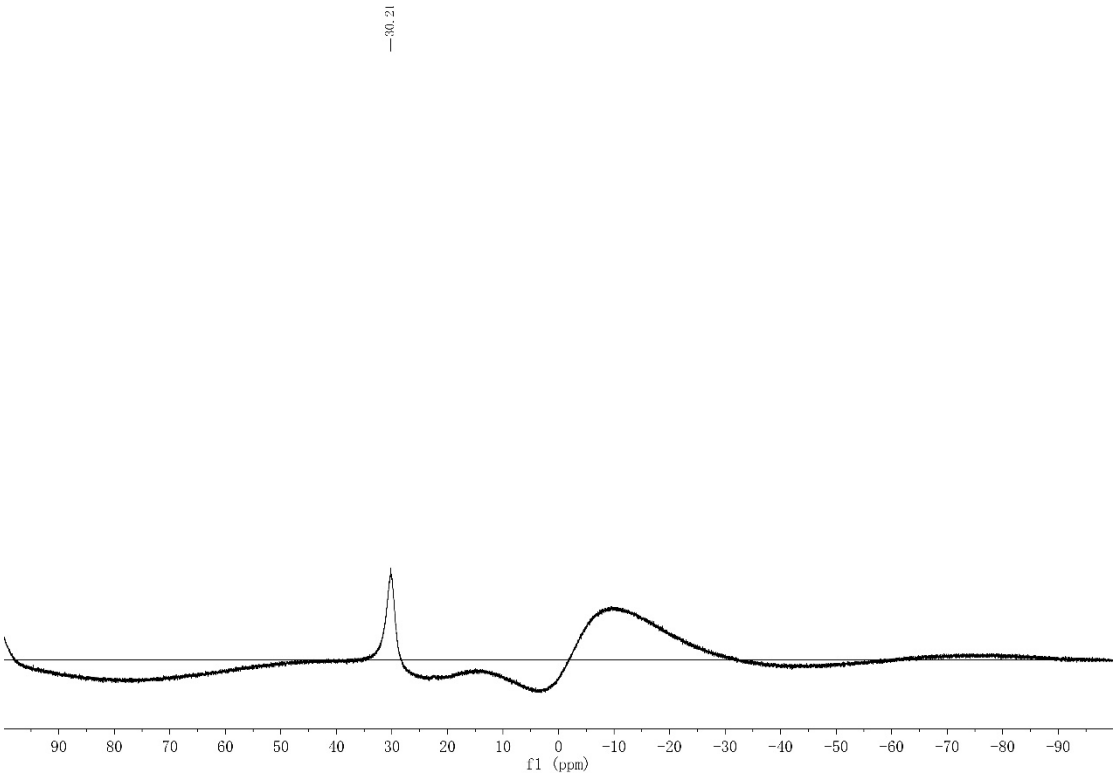
^{1}H NMR of **2m** (600 MHz, $CDCl_3$)



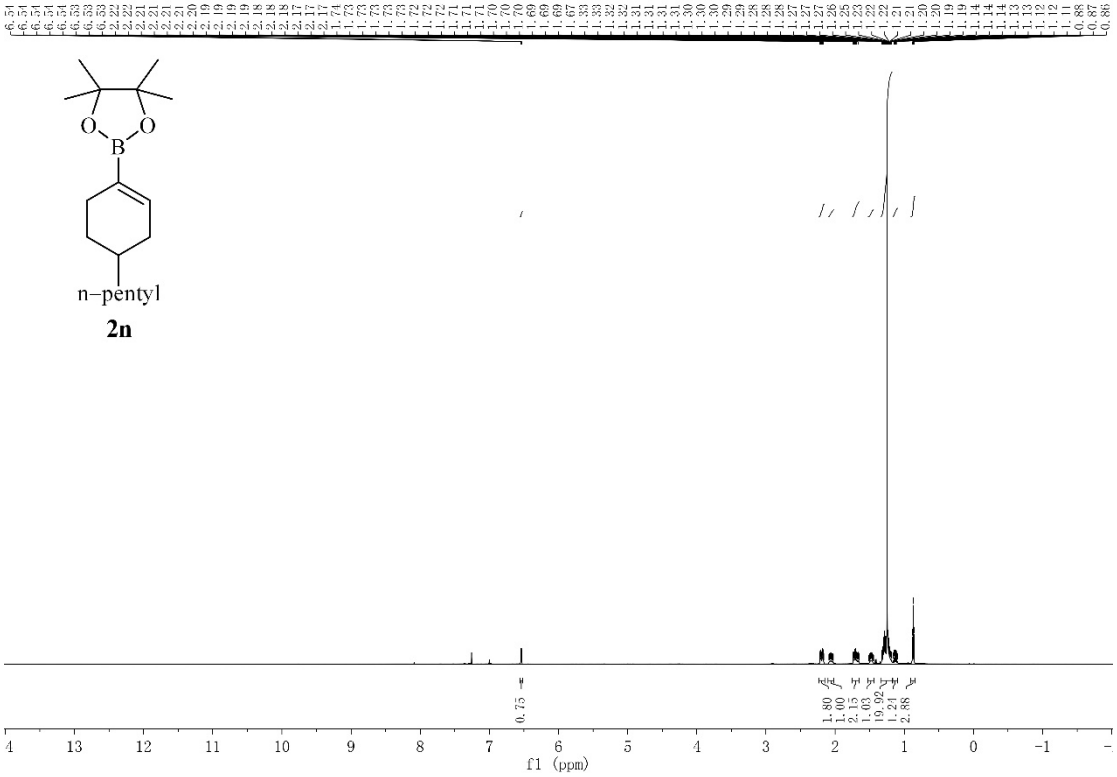
^{13}C NMR of **2m** (151 MHz, $CDCl_3$)



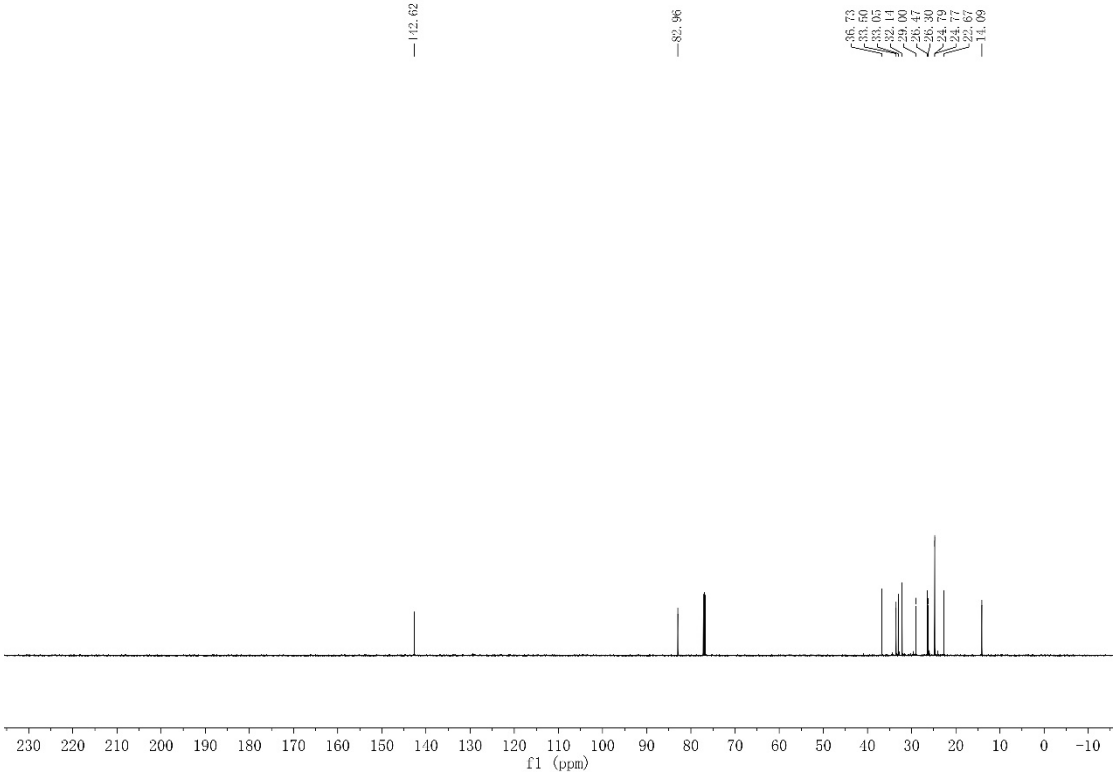
^{11}B NMR of **2m** (193 MHz, $CDCl_3$)



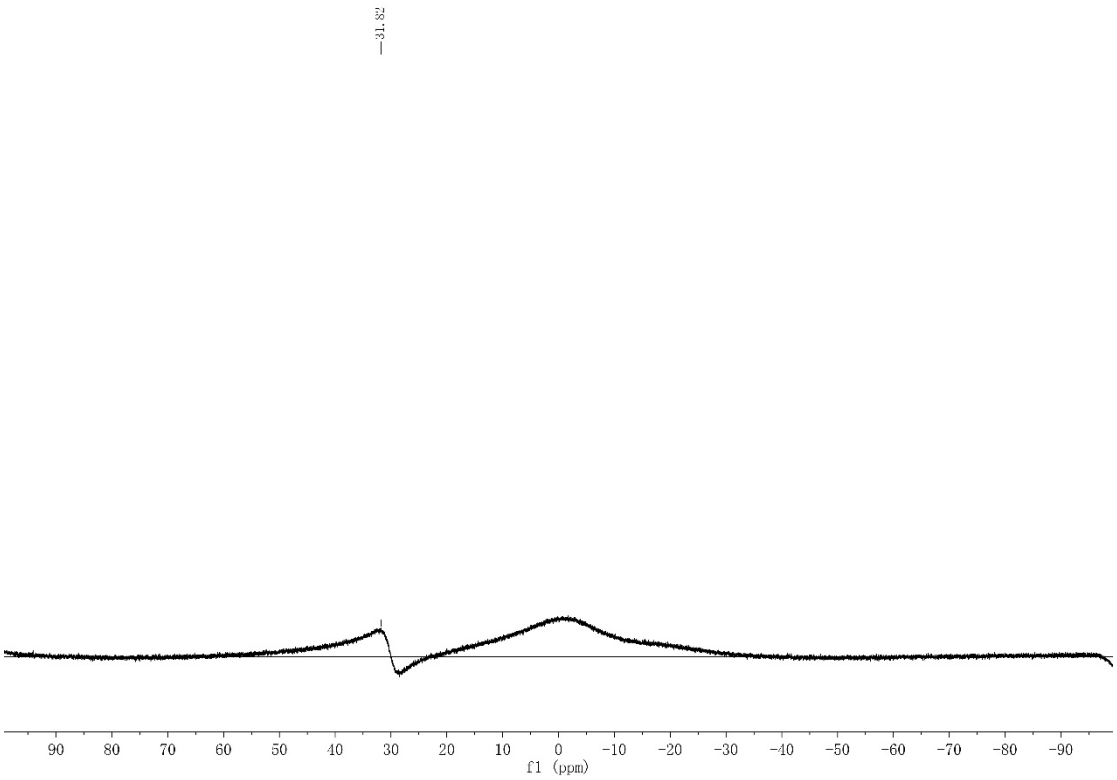
^{1}H NMR of **2n** (600 MHz, $CDCl_3$)



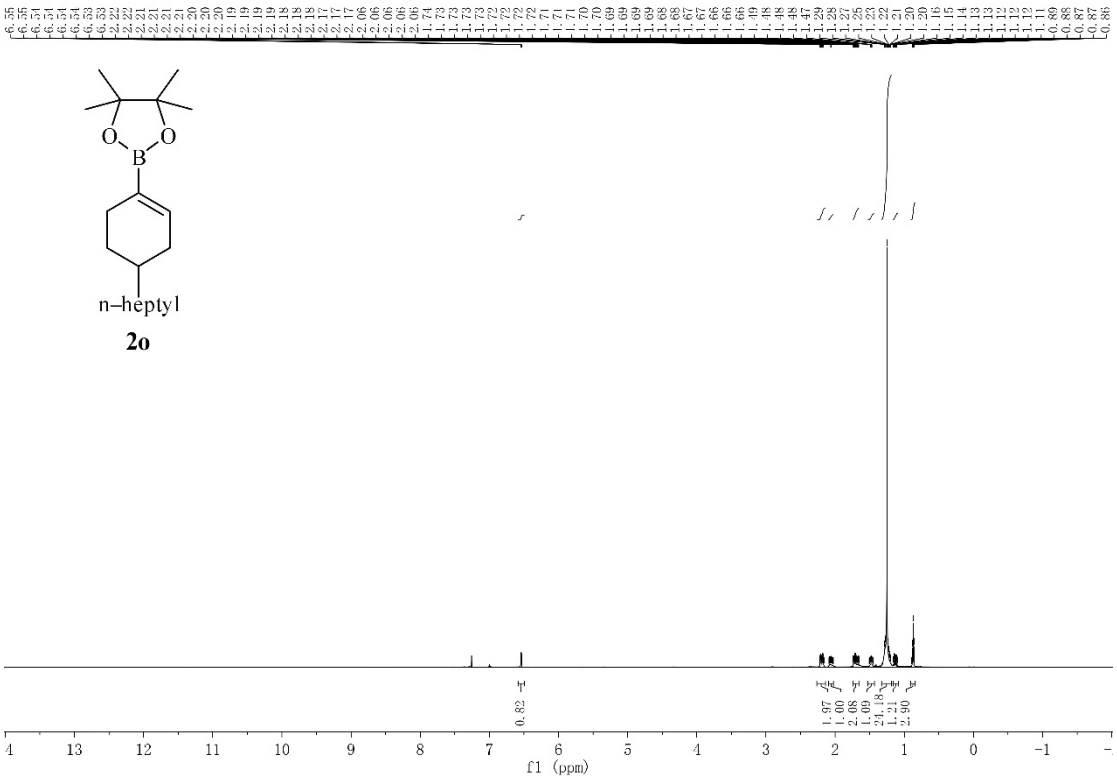
^{13}C NMR of **2n** (151 MHz, $CDCl_3$)



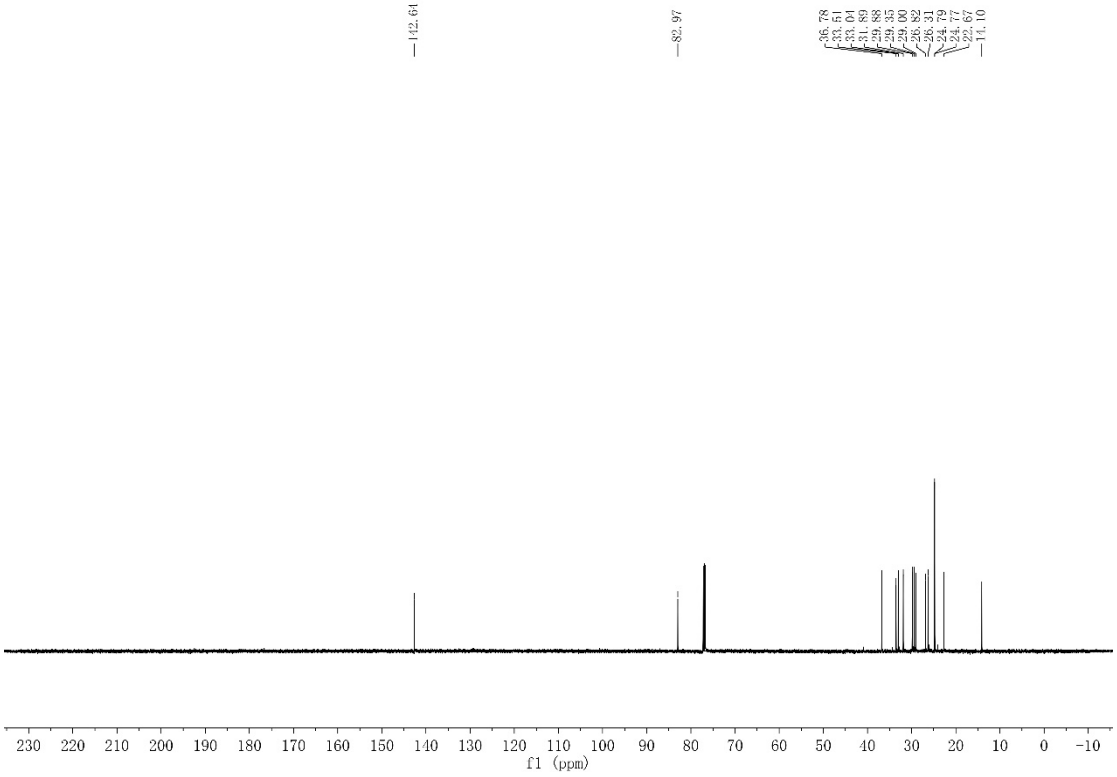
^{11}B NMR of **2n** (128 MHz, $CDCl_3$)



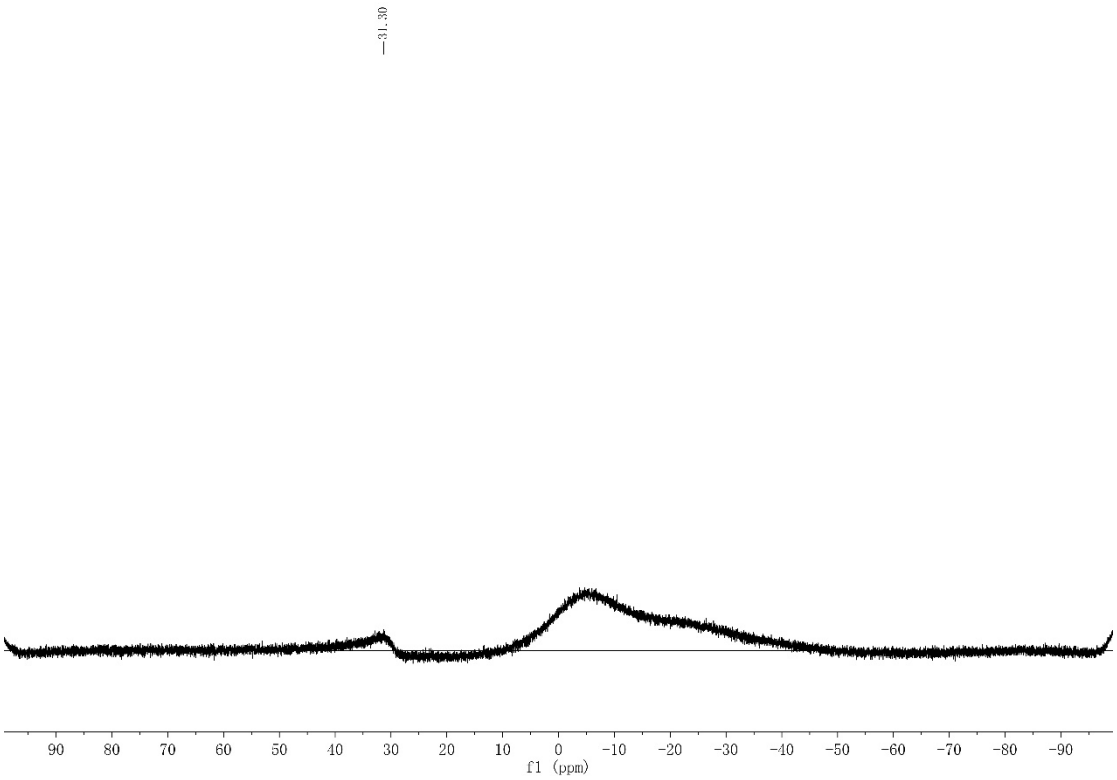
^{1}H NMR of **2o** (600 MHz, $CDCl_3$)



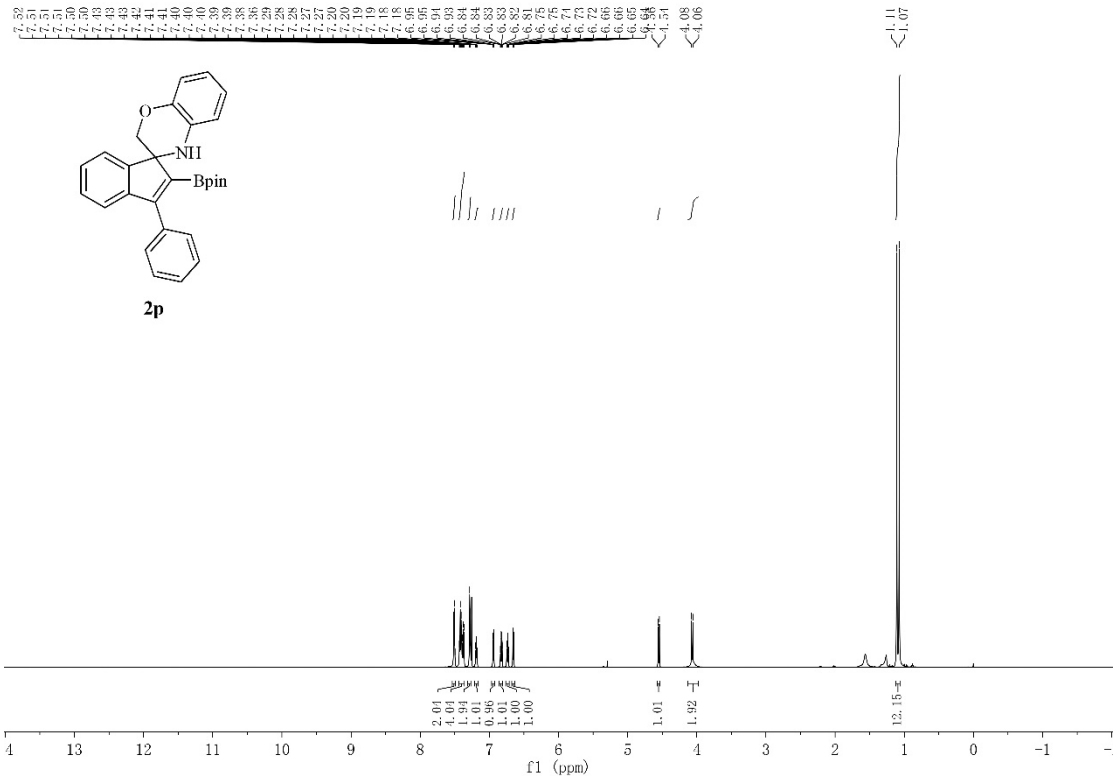
^{13}C NMR of **2o** (151 MHz, $CDCl_3$)



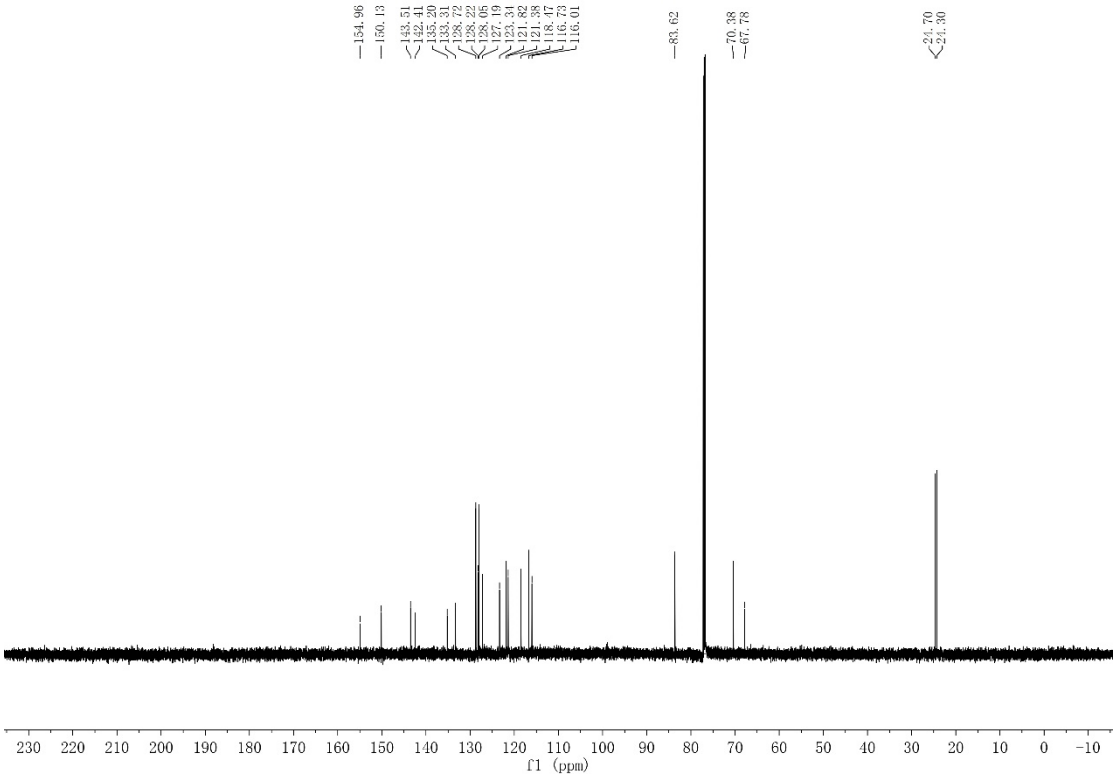
^{11}B NMR of **2o** (128 MHz, $CDCl_3$)



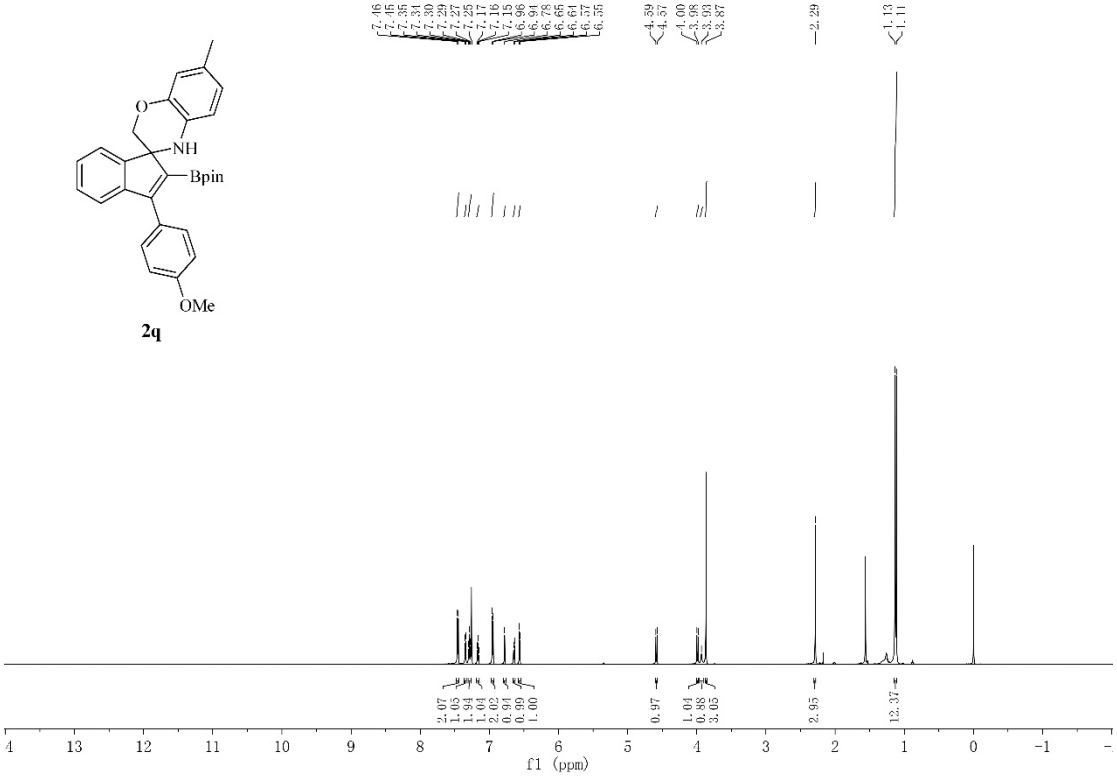
^{1}H NMR of **2p** (600 MHz, $CDCl_3$)



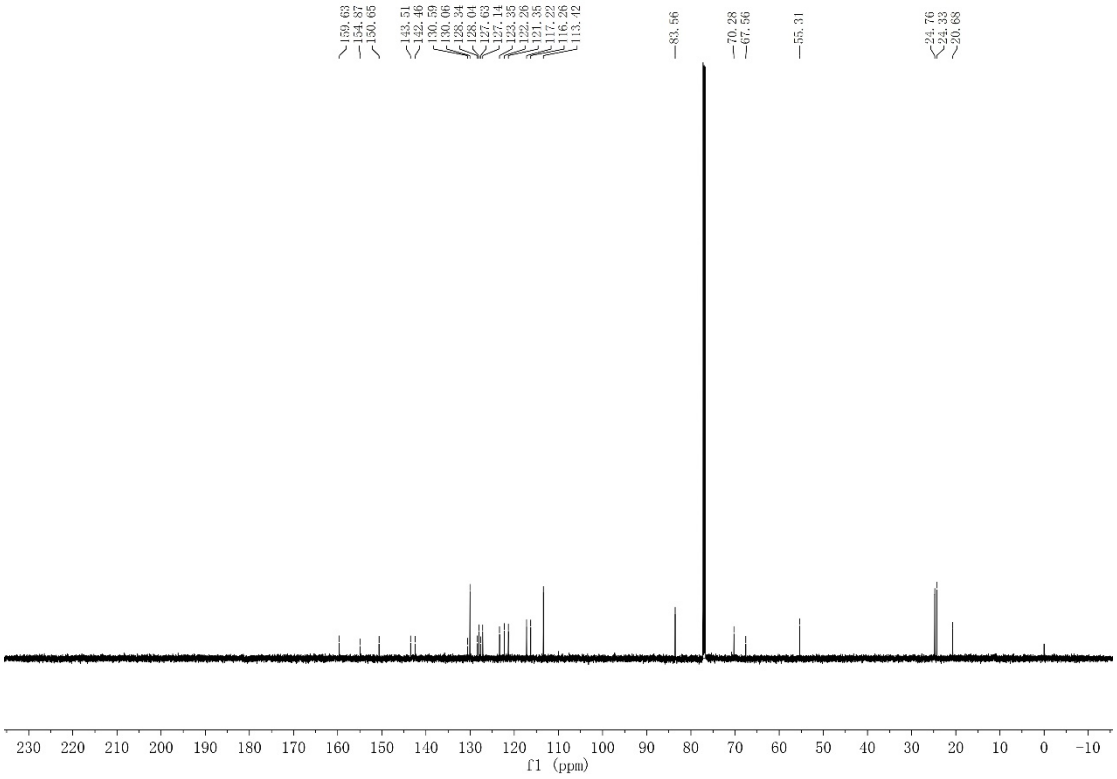
^{13}C NMR of **2p** (151 MHz, $CDCl_3$)



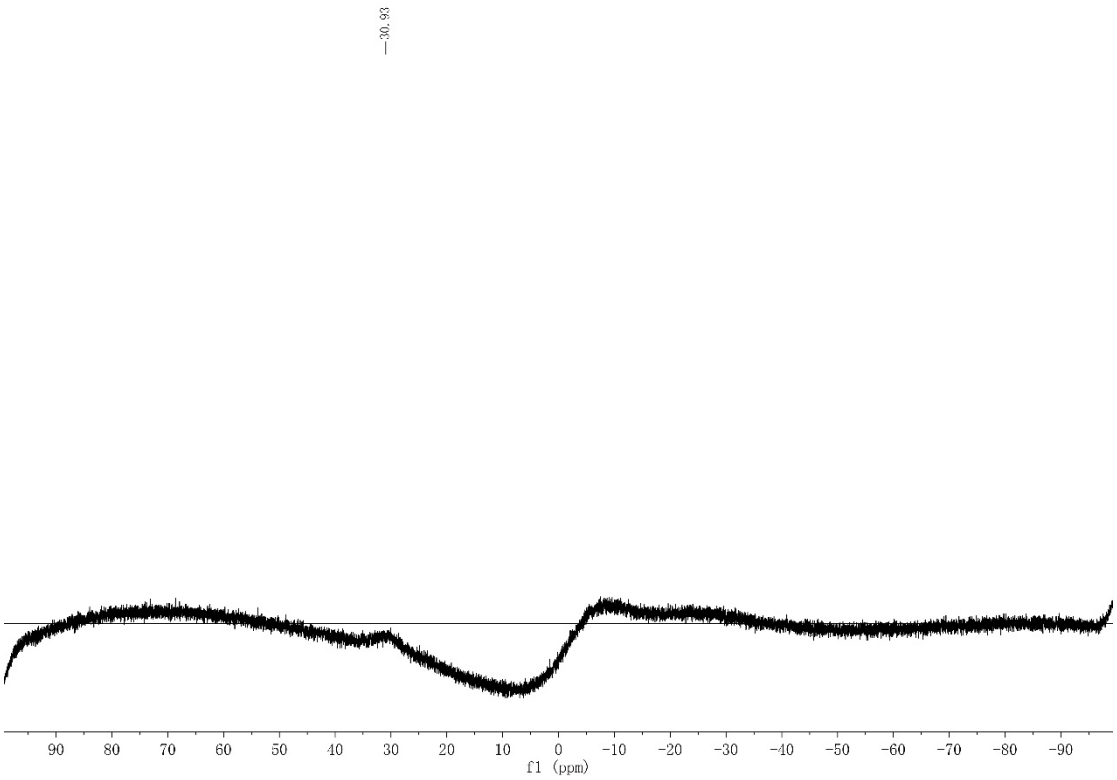
^{1}H NMR of **2q** (600 MHz, $CDCl_3$)



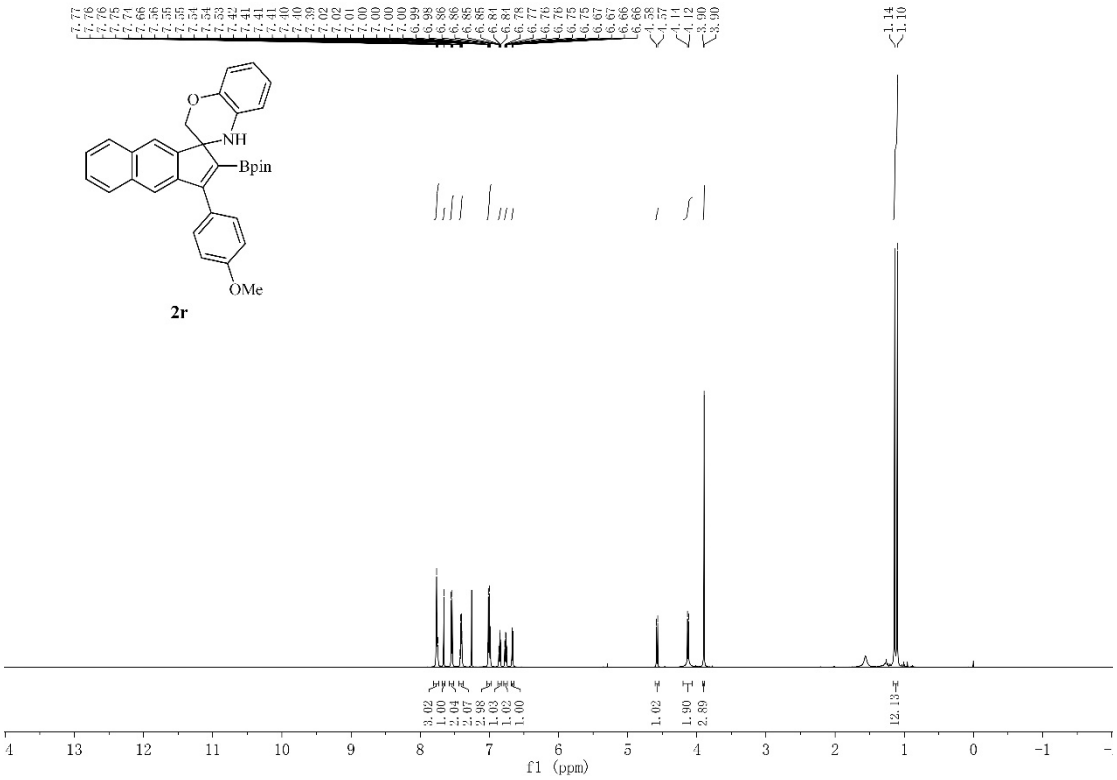
^{13}C NMR of **2q** (151 MHz, $CDCl_3$)



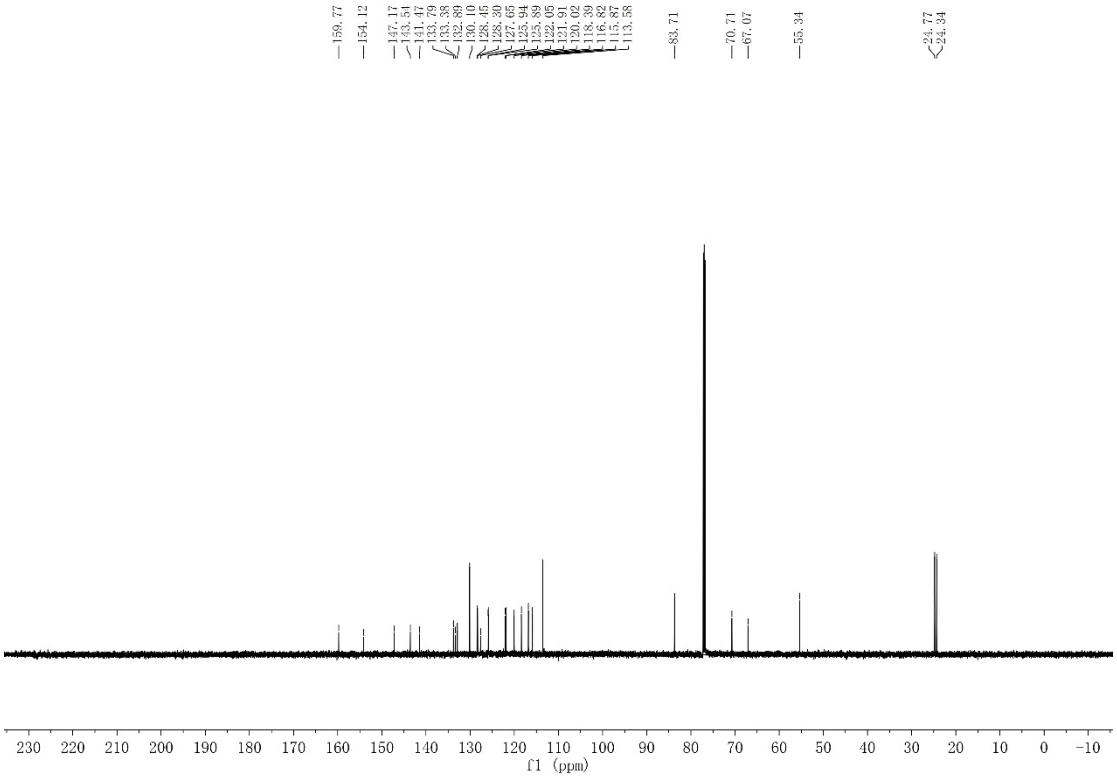
^{11}B NMR of **2q** (128 MHz, $CDCl_3$)



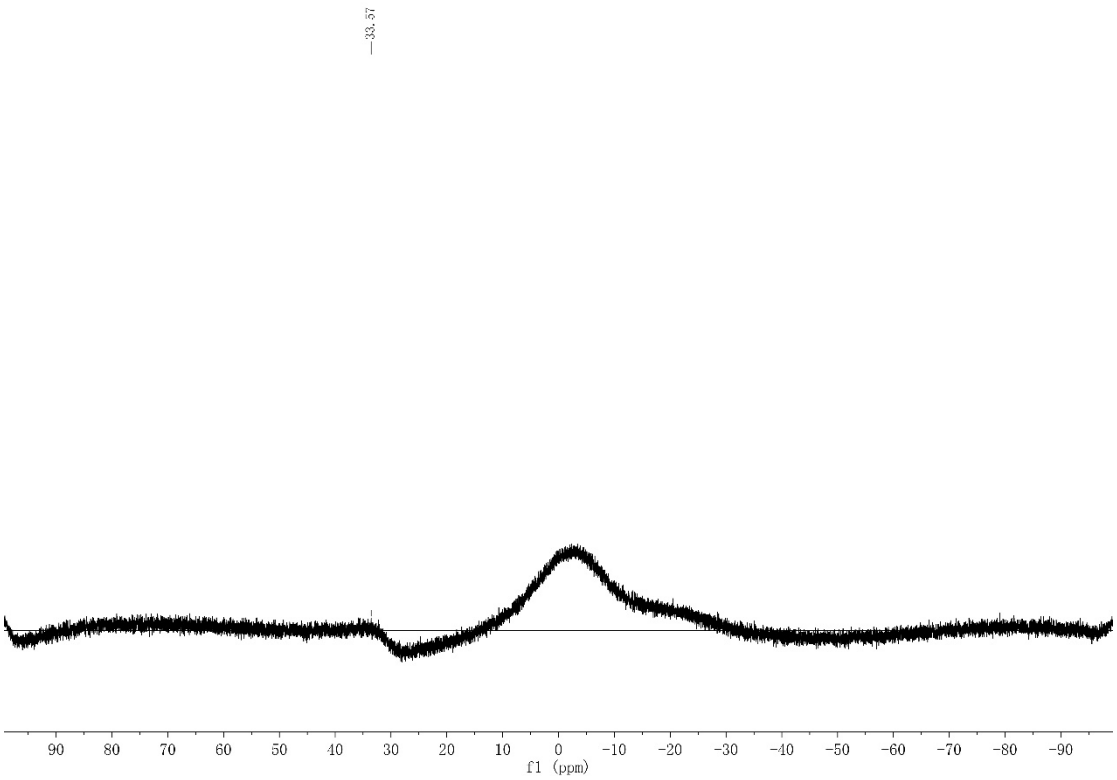
^{1}H NMR of **2r** (600 MHz, $CDCl_3$)



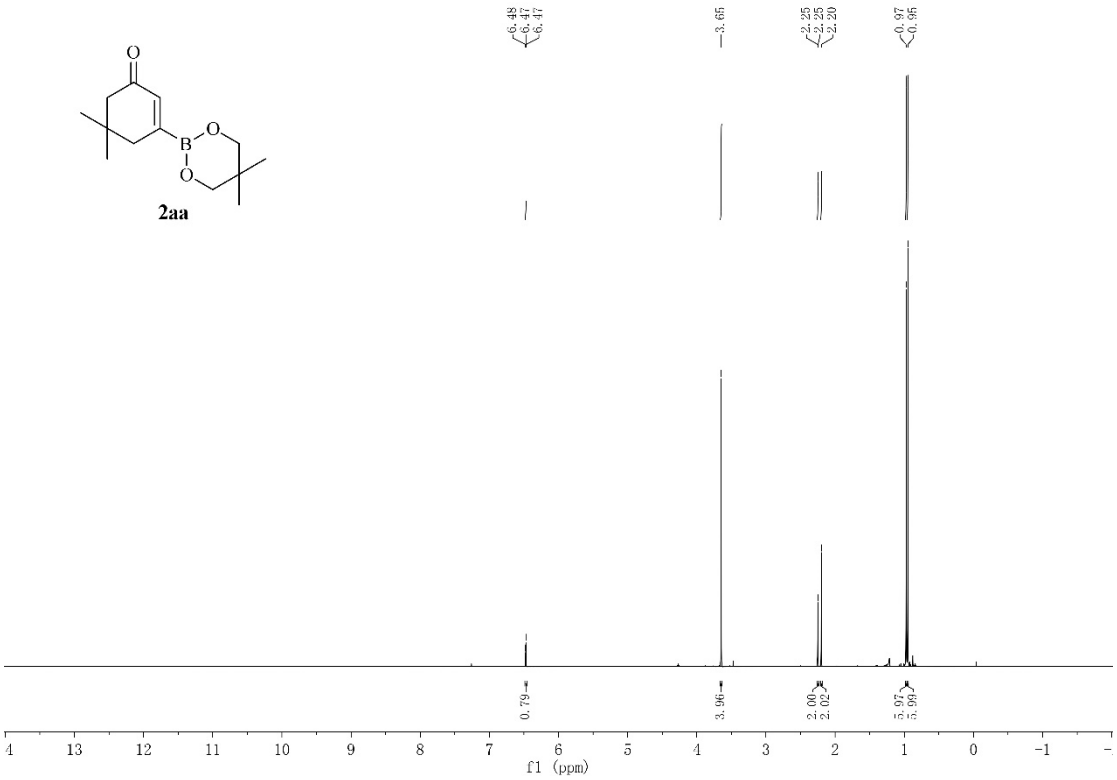
^{13}C NMR of **2r** (151 MHz, $CDCl_3$)



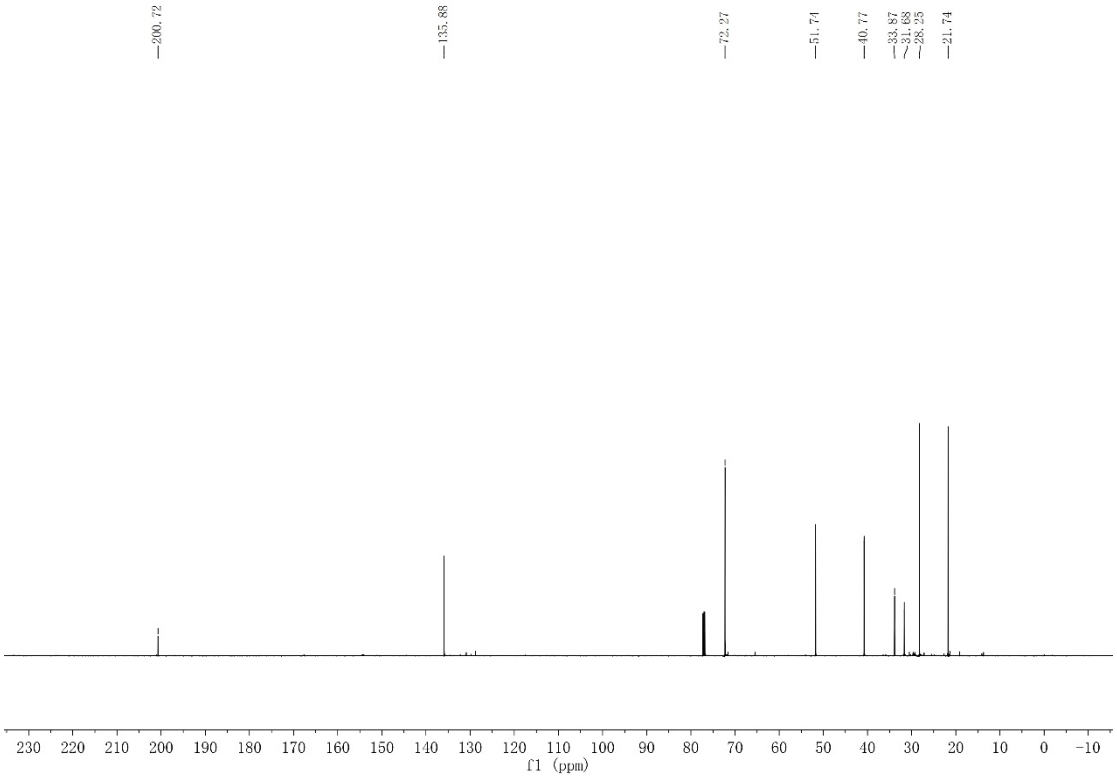
^{11}B NMR of **2r** (128 MHz, $CDCl_3$)



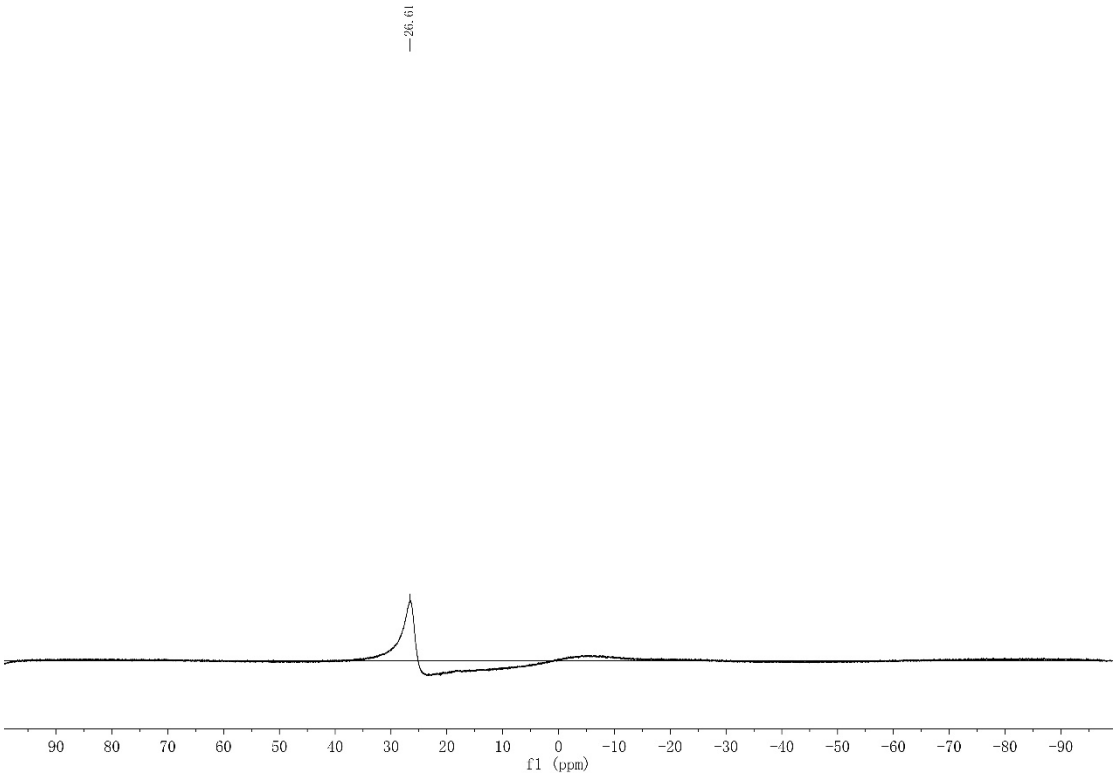
^{1}H NMR of **2aa** (600 MHz, $CDCl_3$)



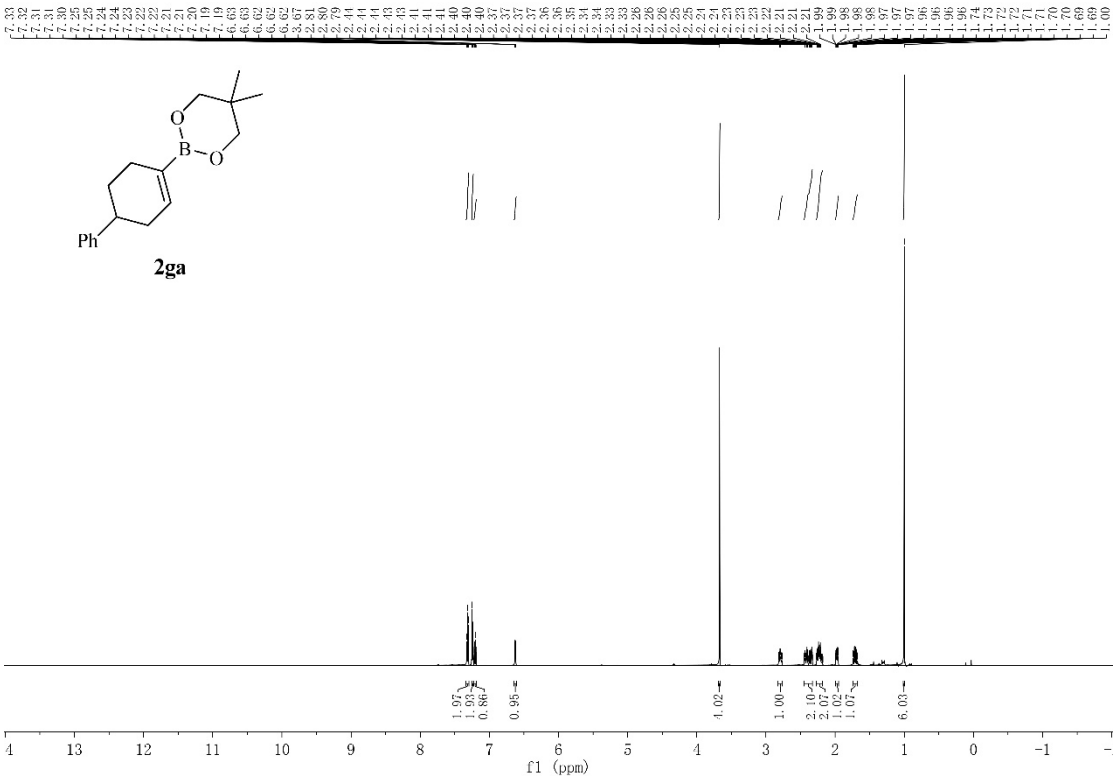
^{13}C NMR of **2aa** (151 MHz, $CDCl_3$)



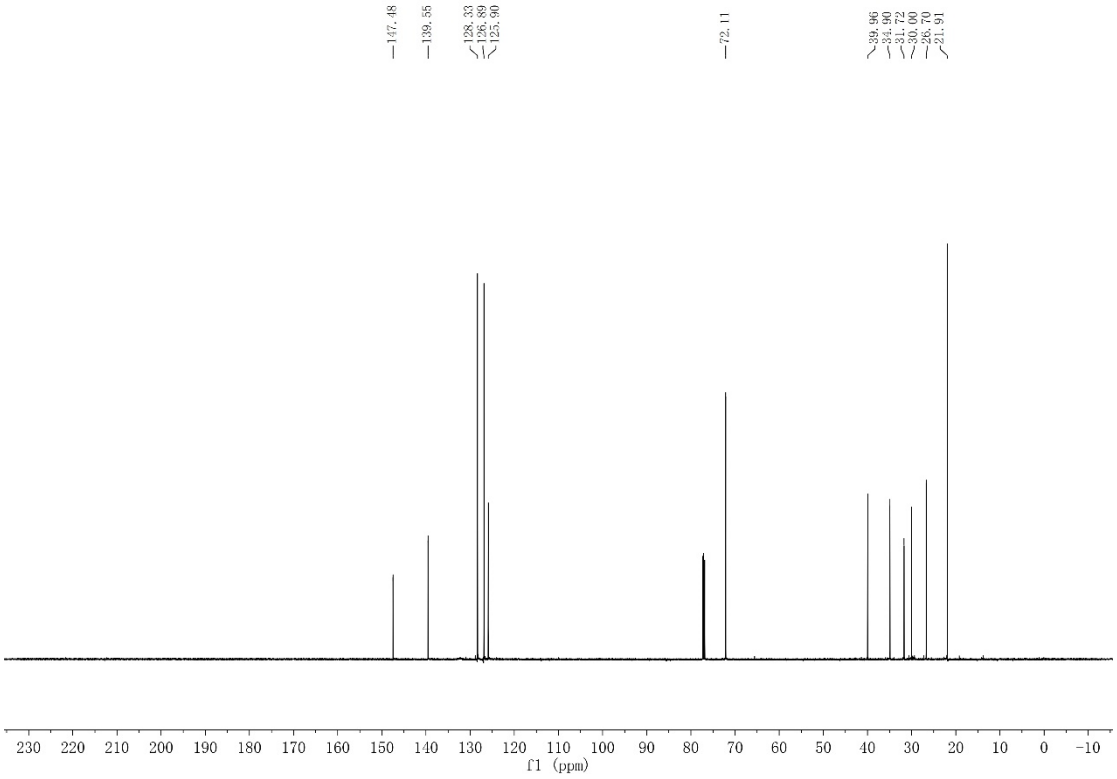
^{11}B NMR of **2aa** (128 MHz, $CDCl_3$)



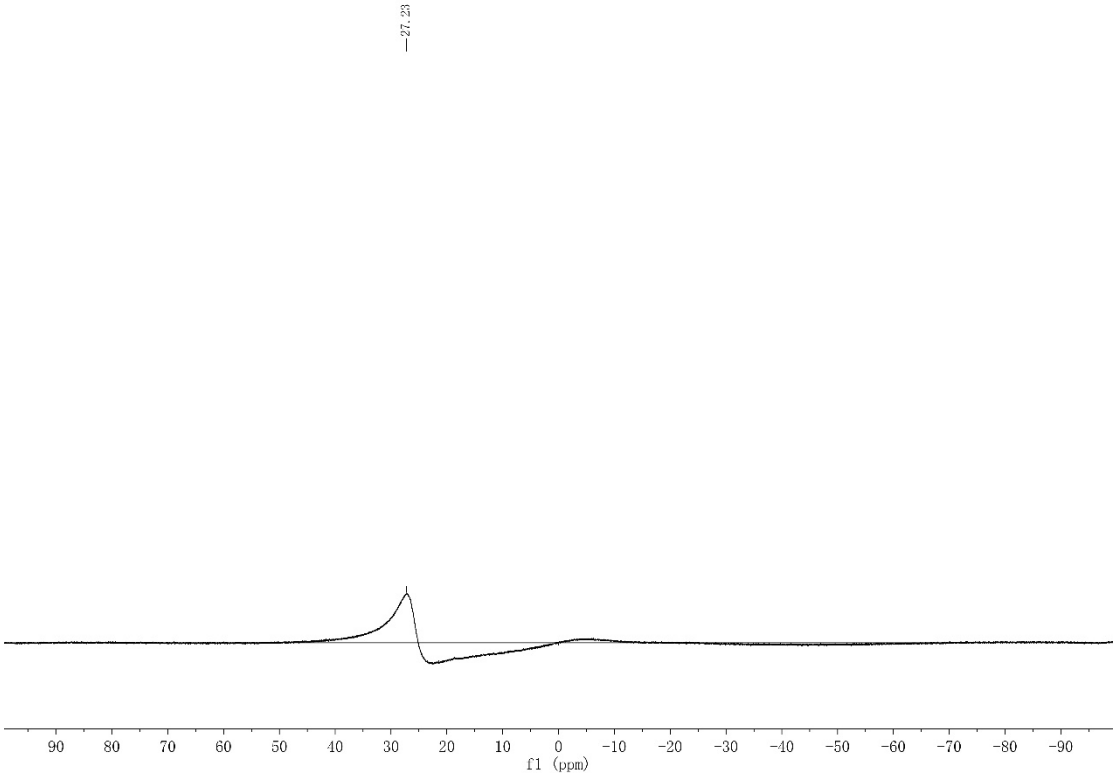
^{1}H NMR of **2ga** (600 MHz, $CDCl_3$)



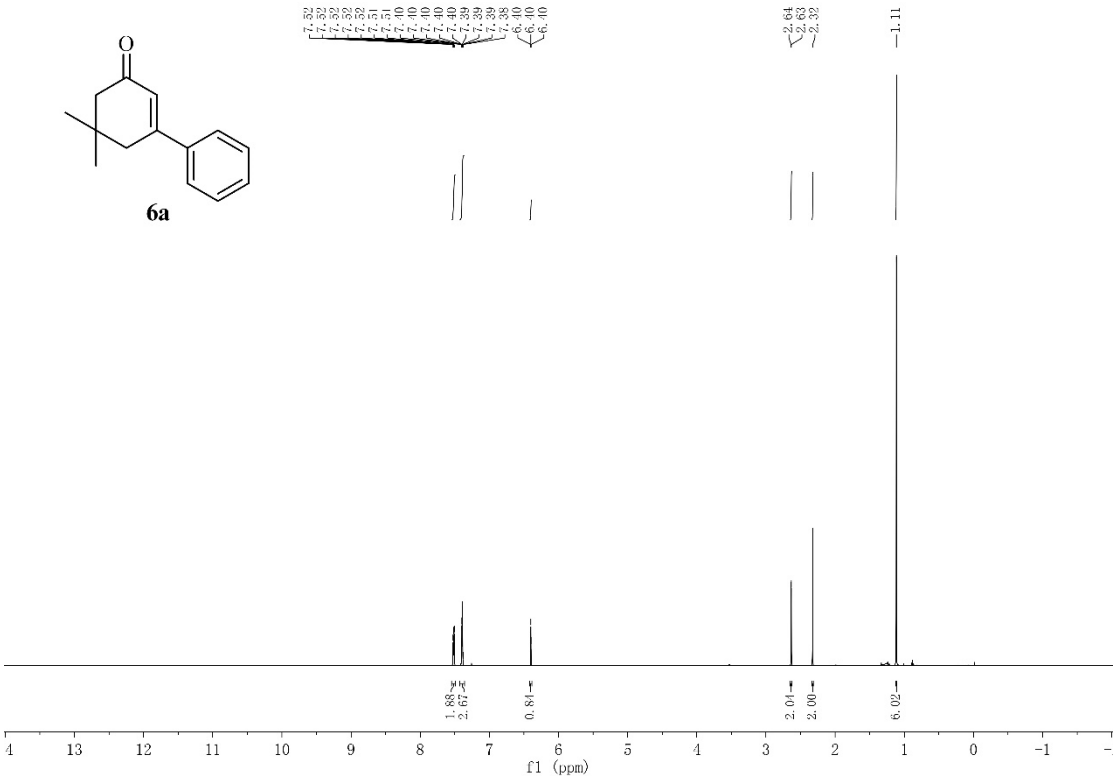
^{13}C NMR of **2ga** (151 MHz, $CDCl_3$)



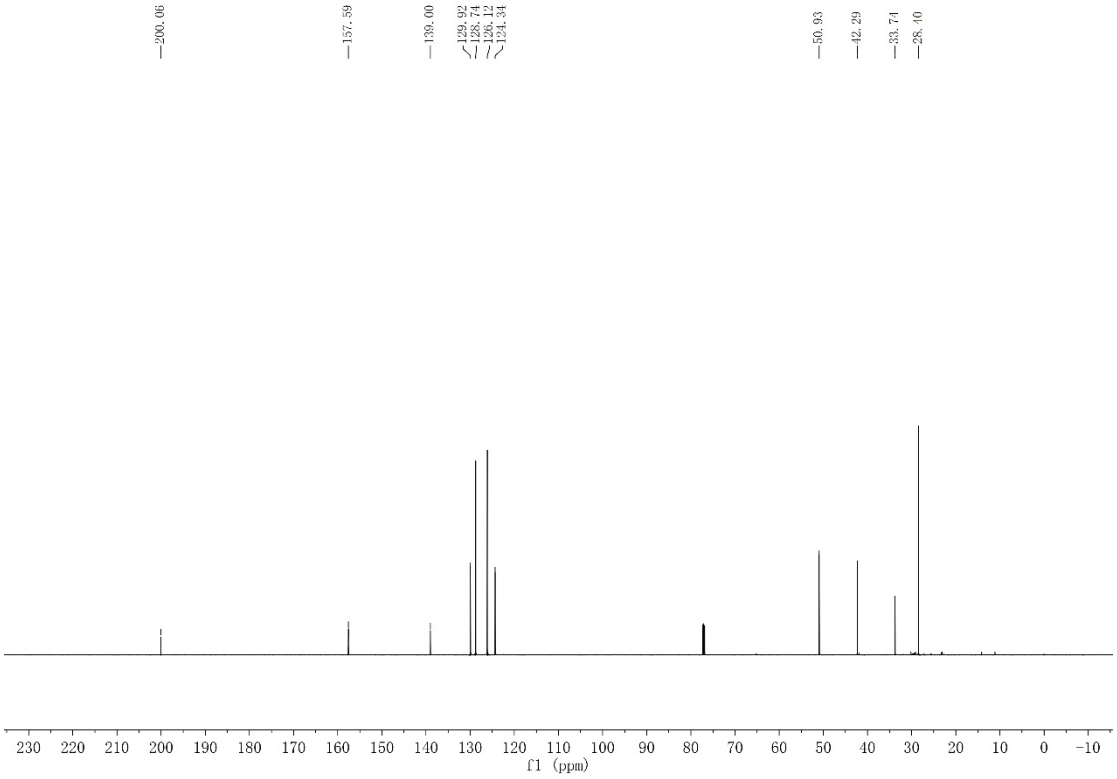
^{11}B NMR of **2ga** (128 MHz, $CDCl_3$)



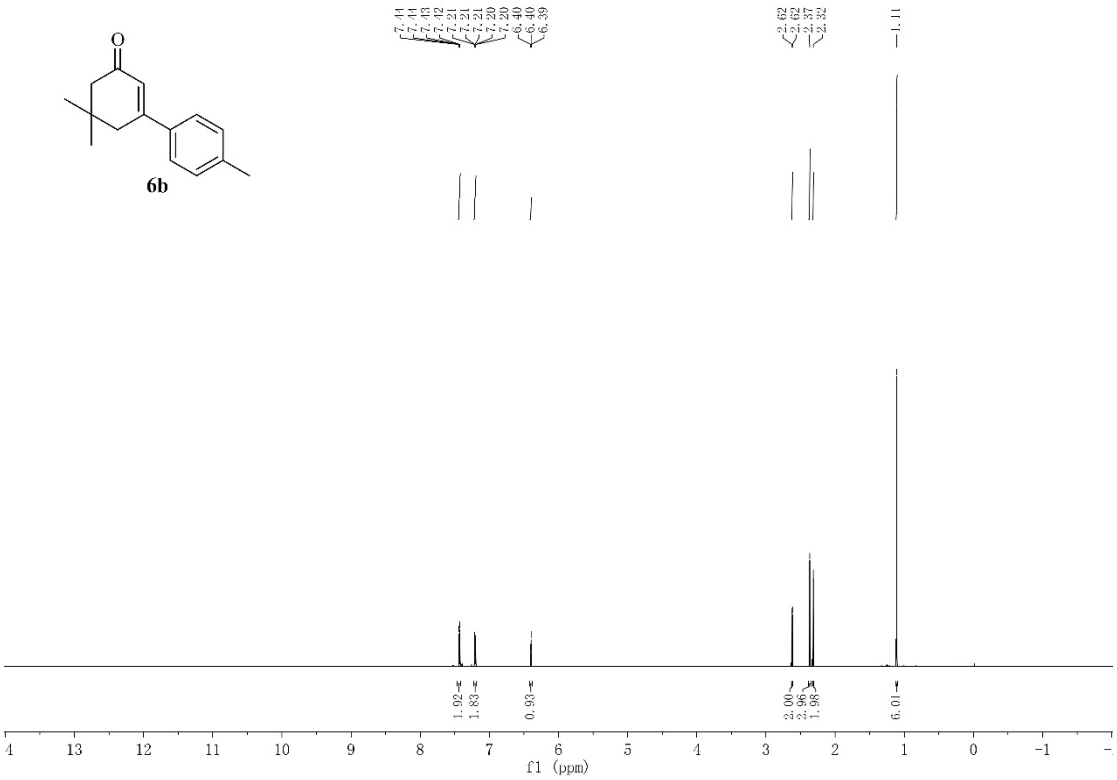
^{1}H NMR of **6a** (600 MHz, $CDCl_3$)



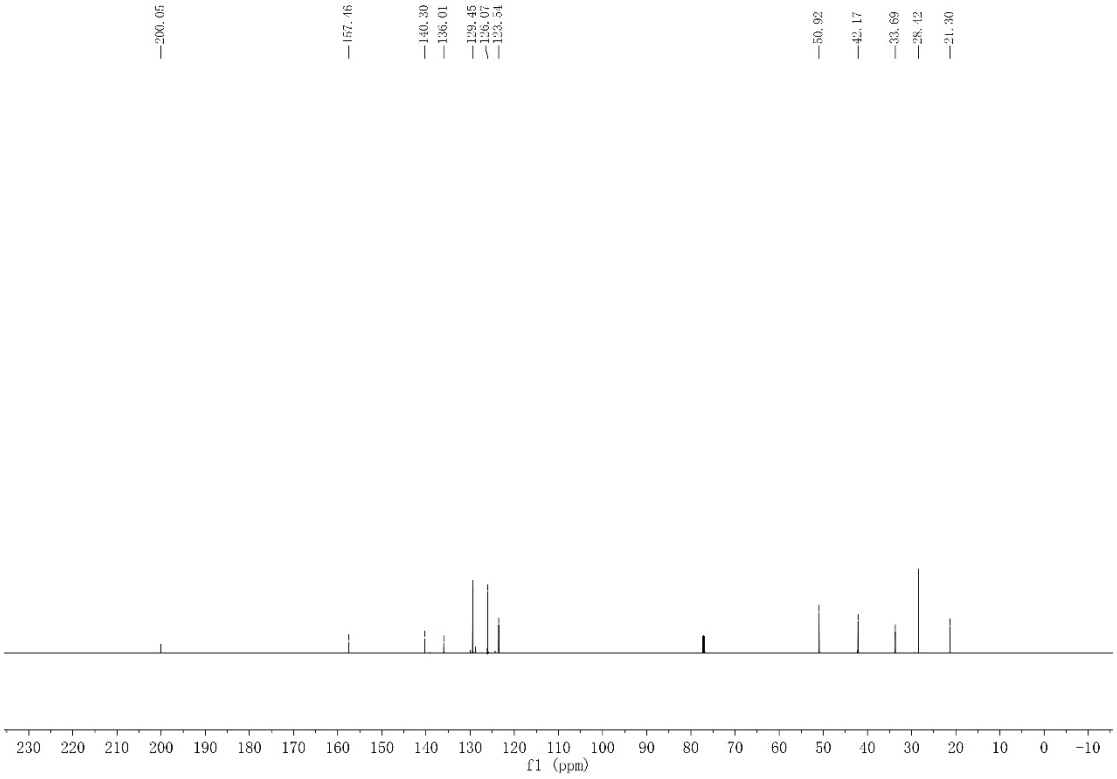
^{13}C NMR of **6a** (151 MHz, $CDCl_3$)



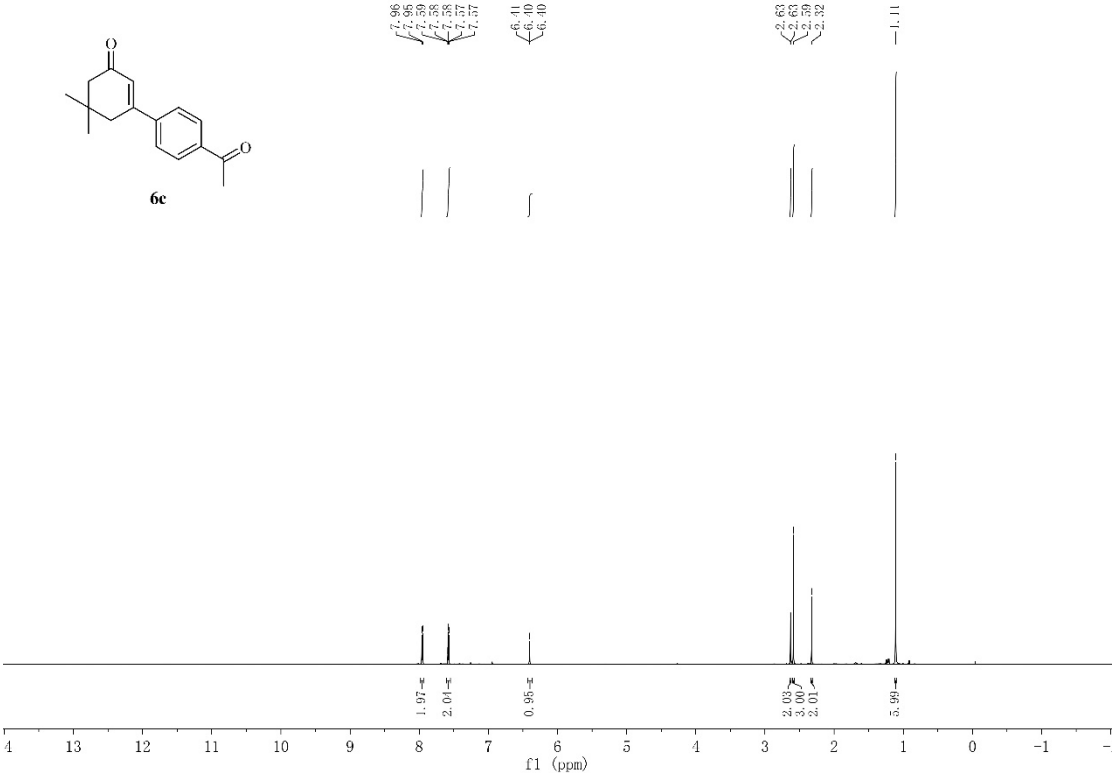
^{1}H NMR of **6b** (600 MHz, $CDCl_3$)



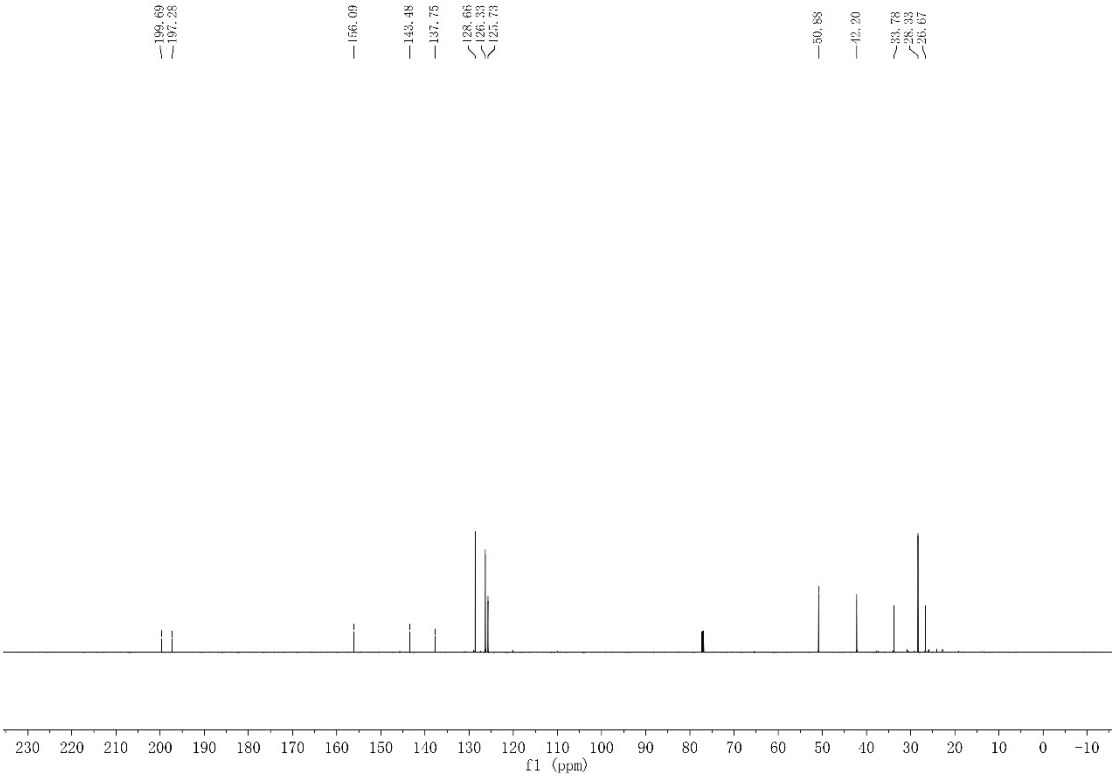
^{13}C NMR of **6b** (151 MHz, $CDCl_3$)



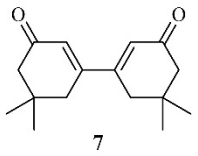
^{1}H NMR of **6c** (600 MHz, $CDCl_3$)



^{13}C NMR of **6c** (151 MHz, $CDCl_3$)

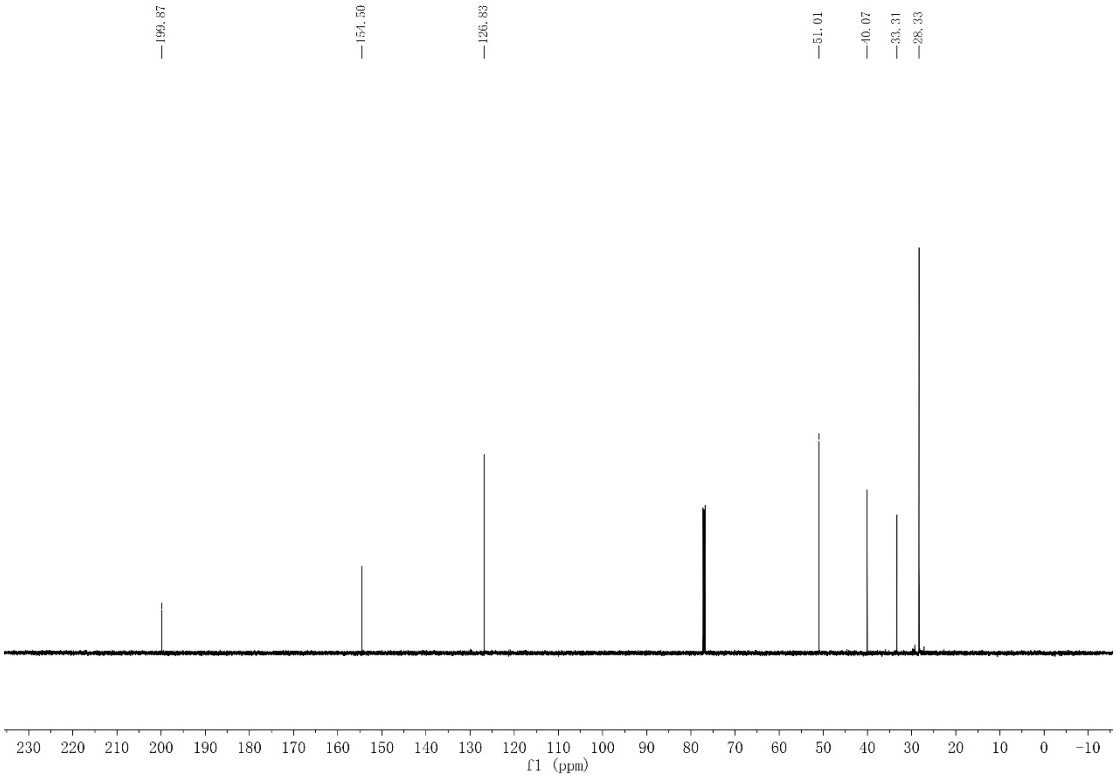


^{1}H NMR of **7** (600 MHz, $CDCl_3$)

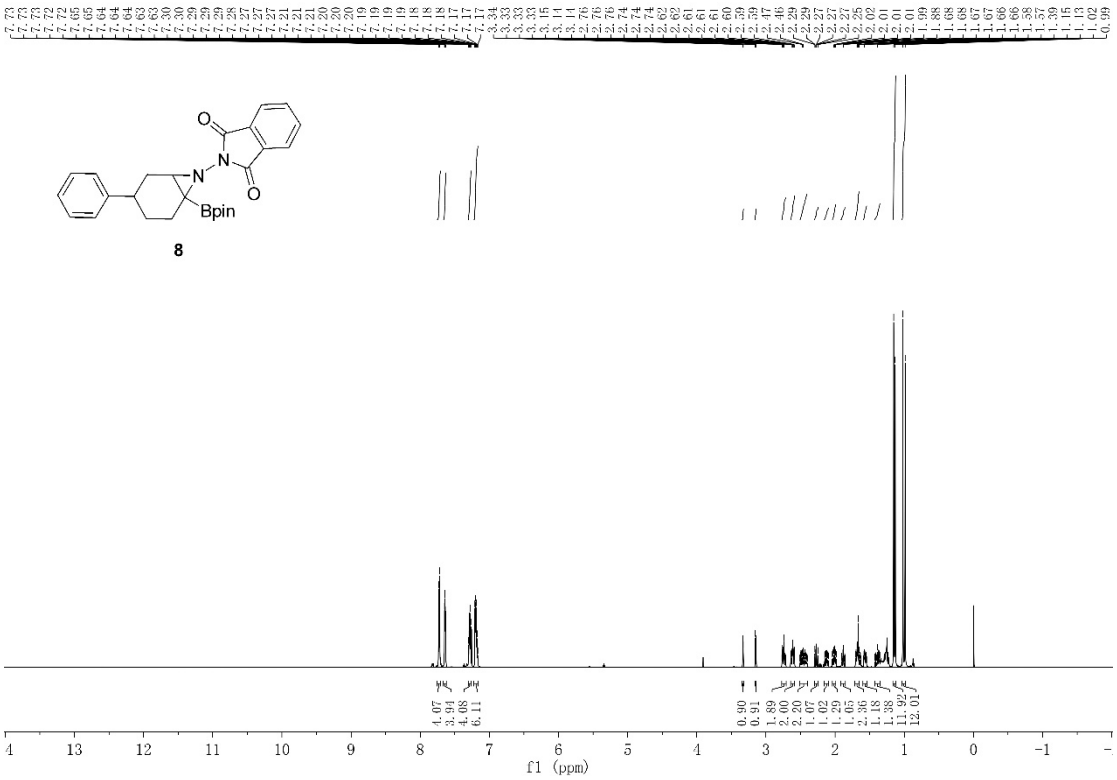


7

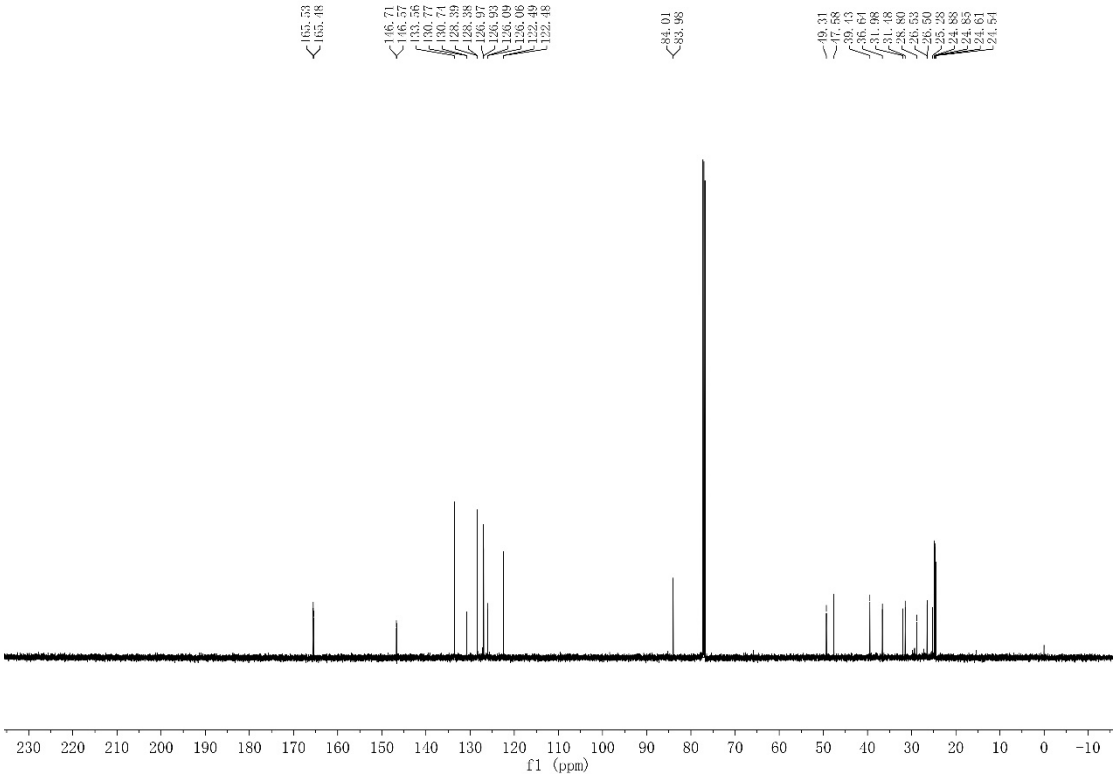
^{13}C NMR of **7** (151 MHz, $CDCl_3$)



^{1}H NMR of **8** (600 MHz, $CDCl_3$)



^{13}C NMR of **8** (151 MHz, $CDCl_3$)



^{11}B NMR of **8** (193 MHz, $CDCl_3$)