Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Samarium(III) catalyzed synthesis of alkenylboron compounds via Hydroboration of alkynes

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SUPPORTING INFORMATION

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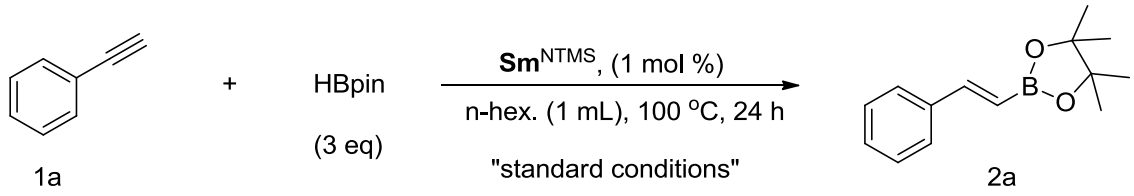
1. General information

All reactions were carried out under a moisture- and oxygen-free nitrogen atmosphere. Toluene, hexane and tetrahydrofuran (THF) were taken from a solvent purification system (PS-400-5, Unilab Mbraun, Inc.). Glassware was pre-dried in an oven at 120 °C for several hours and cooled prior to use. HBpin and part of alkynes were obtained commercially from Energy Chemical, J&K, Acros, Alfa Aesar or TCI without further purification. All liquid alkynes are stirred overnight with CaH_2 and then distilled under reduced pressure. $Ln[N(TMS)_2]_3$ was synthesized according to the corresponding literatures.[1] Deuterated solvents were obtained from Cambridge Isotope. ^1H NMR, ^{13}C NMR and ^{11}B NMR spectra were recorded on a JEOL ECA-500 NMR spectrometer (FT, 500 MHz for ^1H; 125 MHz for ^{13}C) at room temperature. All chemical shift values are quoted in ppm referenced to an internal tetramethylsilane at 0.00 ppm for ^1H NMR and relative to residual $CHCl_3$ at 77.16 ppm for ^{13}C unless otherwise noted. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constant (*J*) was reported in Hz unit. GC-MS analyses were measured on a Focus GC-ISQ MS instrument.

2. General procedure for the samarium(III) catalyzed hydroboration of alkynes

2.1 General procedure for the samarium(III) catalyzed synthesis of 2a

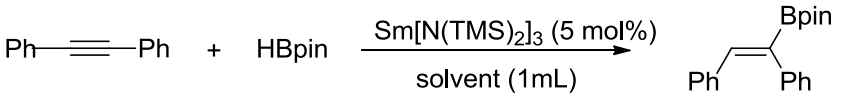


In a nitrogen-filled glovebox, to a 10 mL Schlenk reaction tube equipped with a magnetic stirrer, $Sm[N(TMS)_2]_3$ (2.5 mg, 0.004 mmol), hexane (1 mL), HBpin (168 μL 1.2 mmol) and the corresponding alkene (0.4 mmol) were added in sequence. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the reaction was quenched by exposing the solution to air and diluted with CH_2Cl_2 (30 mL). The mixture was filtered through silica gel to remove the metal salt, the crude mixture was monitored by ^1H NMR analysis using hexamethylbenzene or 1,3,5-trimethoxybenzene as internal standard. The crude mixture was purified by flash column chromatography using PE/EtOAc as the eluent to give the corresponding products.

2.2 General procedure for the samarium(III) catalyzed synthesis of 2zc

In a nitrogen-filled glovebox, to a 10 mL Schlenk reaction tube equipped with a magnetic stirrer, $Sm[N(TMS)_2]_3$ (2.5 mg, 0.004 mmol), hexane (1 mL), HBpin (168 μL 1.2 mmol) and **1zc** (0.4 mmol) were added in sequence. The reaction mixture was then heated at 100 °C (oil bath) with vigorous stirring for 24 hours. After the reaction equilibrium, the solution was quenched with 1 M NaOH/MeOH (2 mL) and then stirred at room temperature for 2 hours. Next, the reaction mixture was transferred to a separation funnel. The solvent was evaporated under reduced pressure. Then, the crude mixture was purified by flash column chromatography with SiO_2 using PE/EA (5:1) as eluents.

3. Reaction conditions screening for hydroboration of inner alkyne 2zf[a]



entry	solvent	*T* (°C)	yield (%)
1	hexane	100	26
2	toluene	100	41
3	DCE	100	27
4	THF	100	36
5	1,4-dioxane	100	34
6[b]	toluene	100	56
7	toluene	120	48

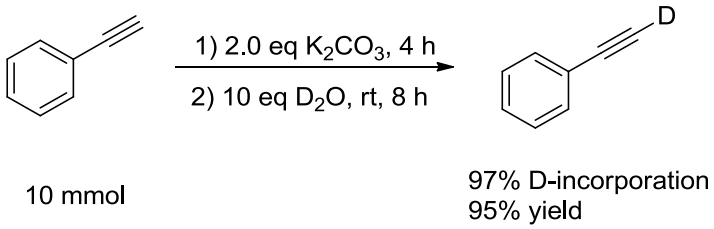
[a] All the experiments were carried out with internal alkynes (0.4 mmol), HBpin (1.2 mmol), $Sm[N(TMS)_2]_3$ (5 mol%), solvent (1 mL), N_2, 24 h, isolated yields. [b] 0.5 mL solvent was used.

Table S1: Reaction conditions screening for hydroboration of **2zf**

The the optimal reaction conditions can be summarized as follows: 0.4 mmol 1,2-diphenylethyne and 1.2 mmol HBpin in toluene (0.5 mL) with 0.02 mmol $Sm[N(SiMe_3)_2]_3$ at 100 °C for 24 h.

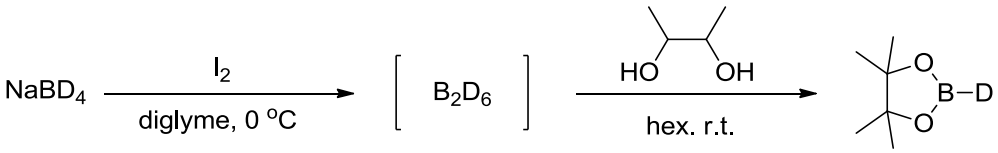
4. General method for the synthesis of deuterium phenylacetylene and DBpin

4.1 The synthesis of deuterium phenylacetylene[2]



A flame dried 10 mL 2-neck round-bottom flask was charged with phenylacetylene (1.02g, 10.0 mmol), potassium carbonate (2.76 g, 2.0 equiv.) and dry MeCN (10 mL). The reaction mixture was stirred under N_2 atmosphere for 4 h. To this mixture, D_2O (2.0 mL, 10.0 equiv.) was added and left to stir for additional 8 h. The resulting crude reaction mixture was diluted with CH_2Cl_2 (10.0 mL) and transferred to an oven dried separating funnel. The organic layer was separated and dried over $MgSO_4$, filtered and solvent removed under reduced pressure. The crude product was separated through column chromatography using distilled hexane to afford 969.0 mg (95%) deuterated phenylacetylene as colorless liquid. Spectral data are in accordance with the reported data.[3]

4.2 The synthesis of deuterium DBpin[4]



A Schlenk was charged with $NaBD_4$ (0.5 g, 12.2 mmol) and was suspended in diglyme (25 mL). To a second Schlenk pinacol (0.48 g, 4.08 mmol) was dissolved in hexane (25 mL). A canula was fitted between the two Schlenks with the canula submursed in the hexane solution. An exit needle was fitted to this flask. Iodine (1.55 g, 6.11 mmol) was dissolved in diglyme (25 mL) and this was added dropwise over 1h to the $NaBD_4$ suspension. On completion of the addition, a gentle stream of nitrogen was passed through the hexane for 1 hour to remove unreacted B_2D_6, the hexane solution of DBpin (b.p. = 110 °C) was distilled to give pure DBpin. The product was then analyzed by NMR. Spectral data are in accordance with the reported data.[5a]

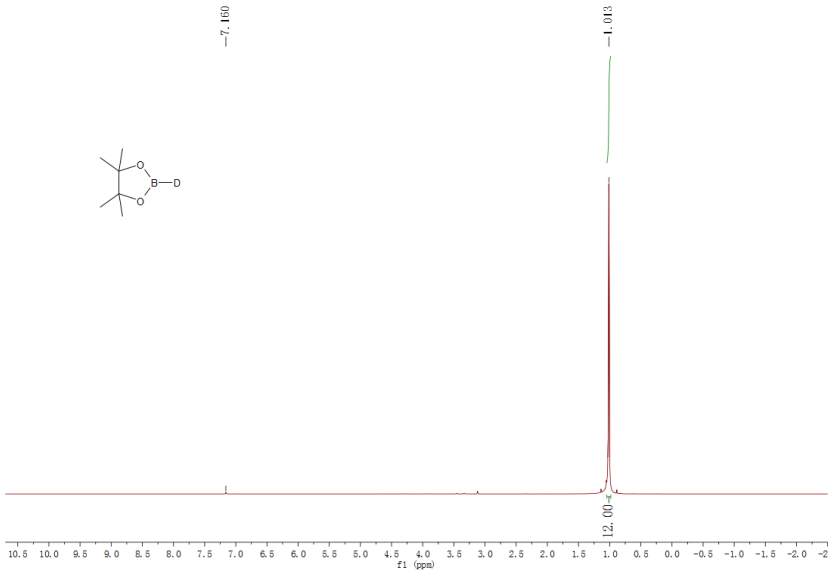
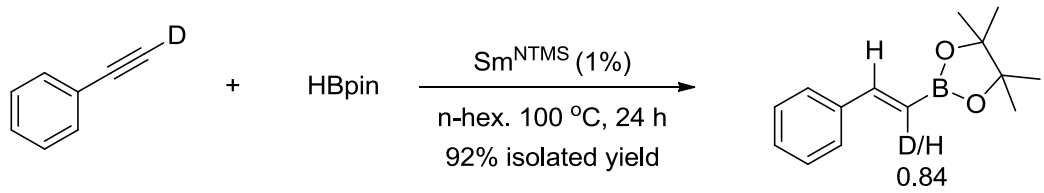


Figure S1: ^{1}H NMR (C_6D_6, 500 MHz) spectra of DBpin

5. Mechanistic Investigation

5.1. Deuterium labelling Experiments

A sealed Schlenk tube equipped with a magnetic stirring bar was charged with $Sm[N(TMS)_2]_3$ (1 mol %, 0.004 mmol), pinacol borane (3 equiv, 1.2 mmol), phenyl acetylene-*d*$_1$ (1 equiv, 0.4 mmol) and 1 mL of hexane. The reaction mixture was heated at 100 ^{o}C for 24 hours. ^{1}H NMR of vinyl borate shows that the hydrogen has been deuterated, which indicates a *cis* orientation of deuterium and phenyl group in **2a-D.**



1a-D **2a-D**

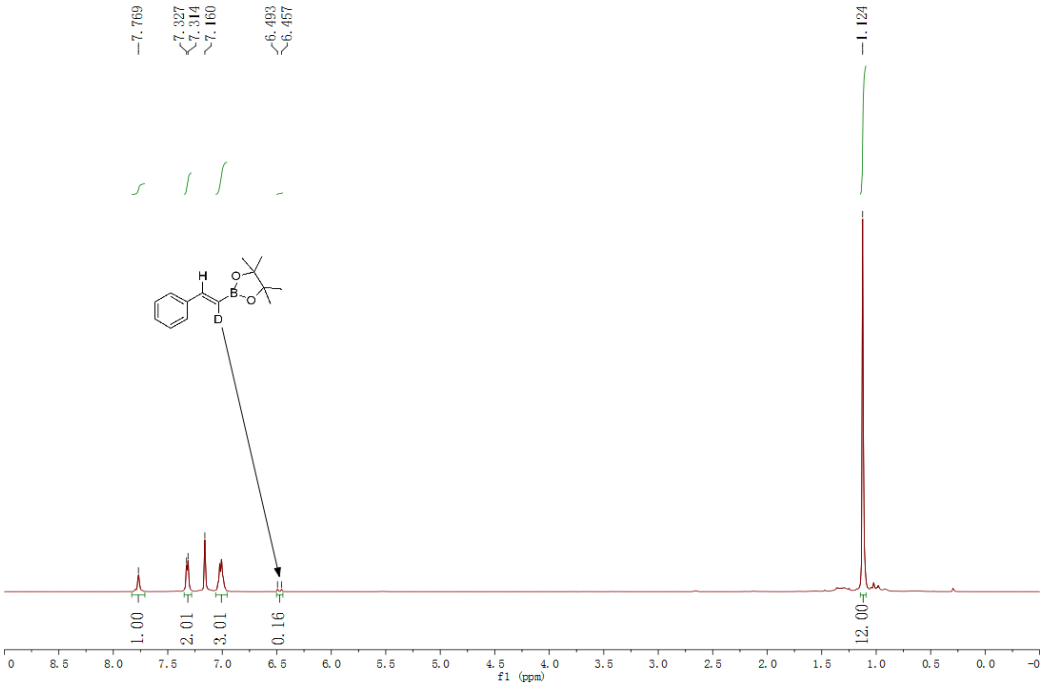
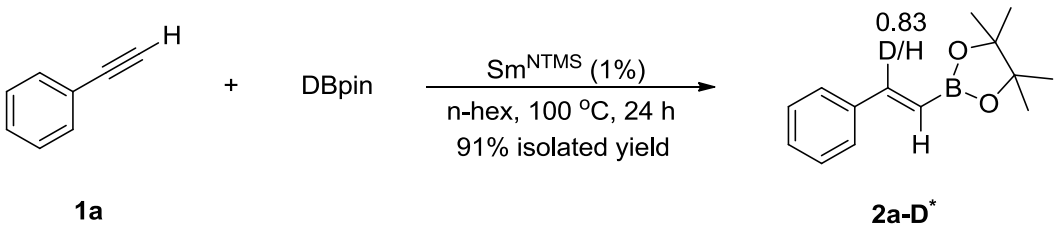


Figure S2: ^{1}H NMR (C_6D_6, 500 MHz) spectra of **2a-D**.

A sealed Schlenk tube equipped with a magnetic stirring bar was charged with Sm[N(TMS)$_2$]$_3$ (1 mol %, 0.004 mmol), pinacol borane-d_1 (3 equiv, 1.2 mmol), **1a** (1 equiv, 0.4 mmol) and 1 mL of hexane. The reaction mixture was heated at 100 °C for 24 h. ^{1}H NMR of vinyl borate shows that the hydrogen has been deuterated, which indicates a *cis* orientation of deuterium and Bpin unit in **2a-D*.**



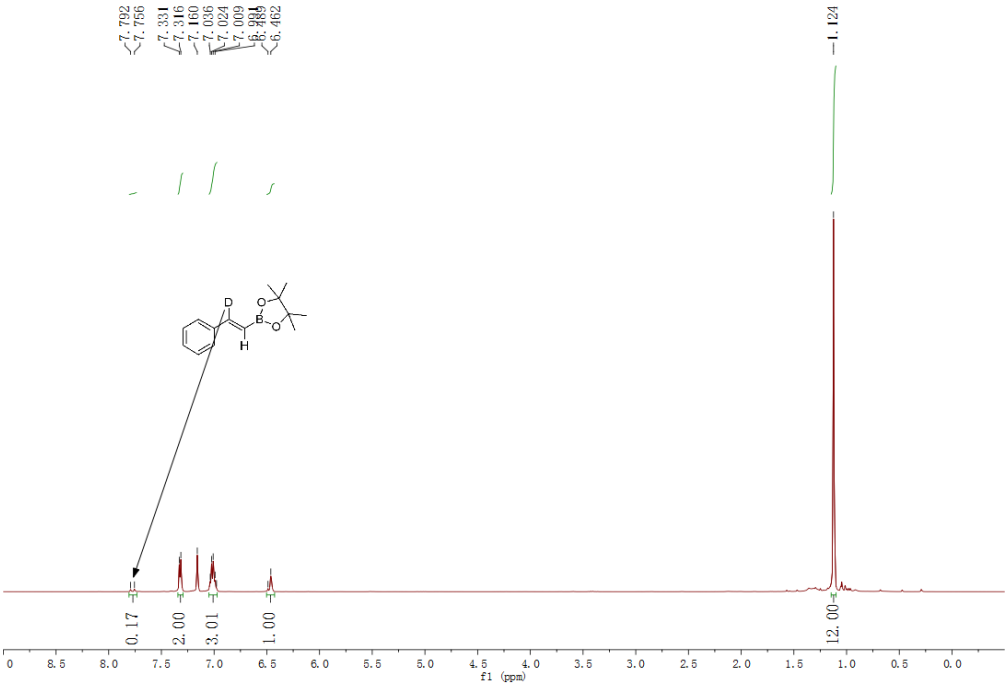


Figure S3: ^{1}H NMR (C_6D_6, 500 MHz) spectra of **2a-D***.

5.2 Intermediate capture

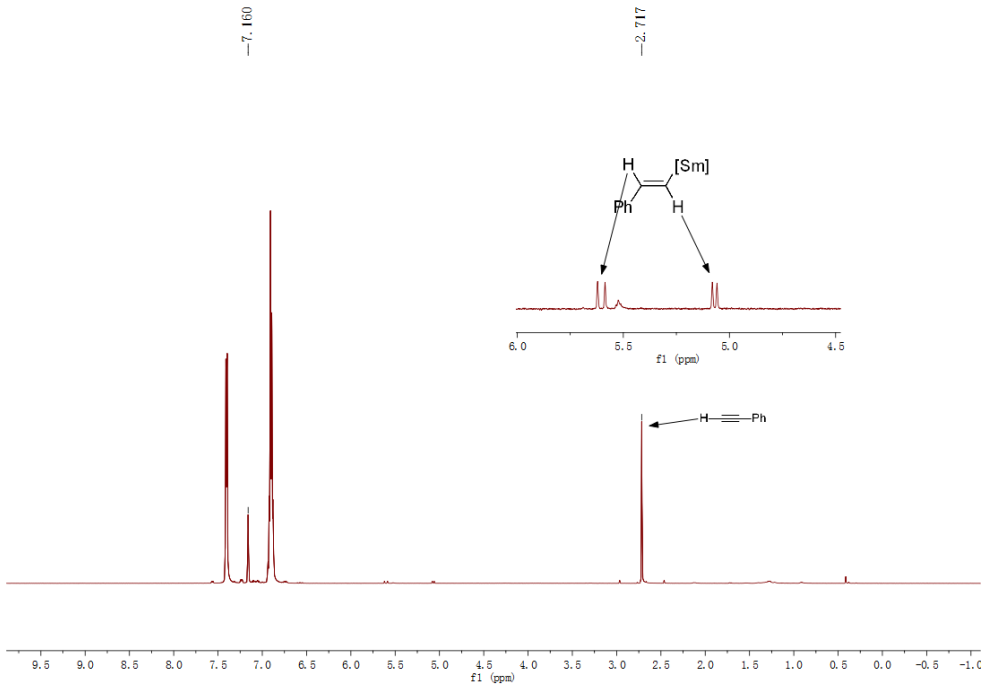
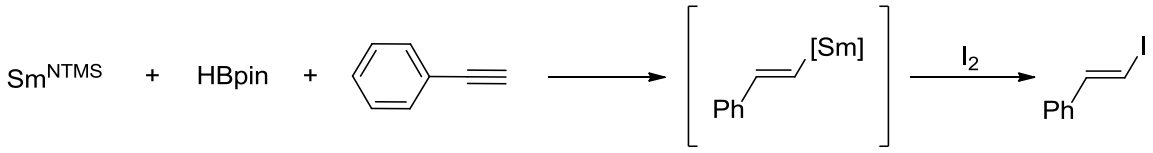


Figure S4: ^{1}H NMR (C_6D_6, 500 MHz) spectra of Sm^{NTMS}+ HBpin + phenyl acetylene (1:1:1)

Subsequent addition of phenyl acetylene (**1a**, 0.02 mmol) to the above reaction mixture showed an upfield shift for acetylenic proton of **1a** from 2.99[6] ppm to 2.72 ppm, which implies the side on coordination of **1a** with samarium centre. After careful observation of ^{1}H NMR spectrum of "Sm^{NTMS} + HBpin+ phenyl acetylene" reveals two set of distinct doublets at δ = 5.60 and 5.07 ppm,

which is growing in intensity upon increasing the time. The transient doublets can be assigned to Sm-alkenyl σ complex which may formed because of hydride migration from Samarium centre to alkyne.

I_2 quenching experiment[6]:



In order to confirm the existence of Sm-alkenyl intermediate, I_2 quenching experiment was carried out. In a NMR tube I_2 solution in C_6D_6 was added to the reaction mixture of Sm^{NTMS}(0.1 mmol) + HBpin(0.1 mmol) + **1a**(0.1 mmol). GC-MS analysis of the reaction mixture further confirmed the formation of (2-iodovinyl)benzene, m/z = 230 .

5.3 ^{1}H NMR-monitoring the model reaction

In a glovebox, $Sm[N(SiMe_3)_2]_3$ (1μL, 1 mmol/mL $Sm[N(TMS)_2]_3$ in toluene-d_8) and pinacolborane (0.0384 mg, 0.30 mmol) were weighed into a NMR tube equipped with a Teflon valve (J-Young). Then, to which a mixture of **1a** (10.2 mg, 0.1 mmol) in toluene-d_8 (0.5 mL) was added via syringe. The ensuing catalytic reaction was monitored by ^{1}H NMR spectroscopy. After 24 h at 100 ^{o}C in an oil bath, the catalytic reaction reaches > 99% completion.

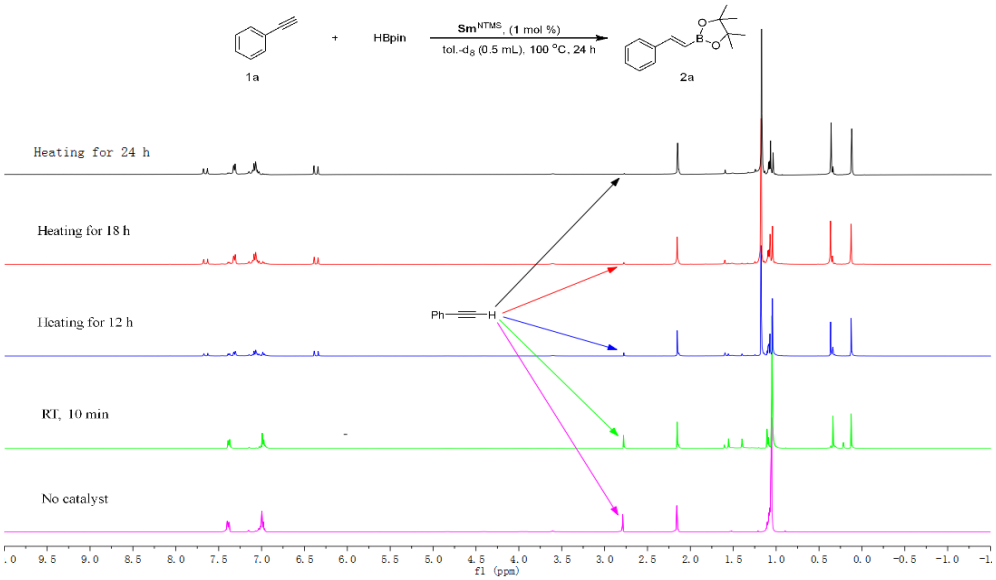


Figure S5: ^{1}H NMR spectra for the progress of the reaction of **1a** using $Sm[N(SiMe_3)_2]_3$ as catalyst in toluene-d_8 at 100 ^{o}C.

5.4 Kinetic Studies[5]

a. General procedure for typical reaction kinetics

For the reaction 1a of (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane:

In a glovebox, $Sm[N(SiMe_3)_2]_3$ (3.2 mg, 0.005 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, pinacolborane (153.6mg, 225µL, 1.5 mmol), 1a (51.0 mg, 56 µL, 0.5 mmol) with 2 mL hexane was added in sequence. The sealed tube was taken out from the glovebox, and was stirred at 100 ^oC taken out at 5, 10, 15, 20, 30, 60, 90, 120, 240, 360, 480, 600, 720, 1080, 14400, 21600, 28800, 36000, 43200, 64800, 86400 minutes. The sample was analyzed by ^1H NMR. The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in Table S2. The molar concentrations of the product **2a** were plotted against the reaction time to obtain a typical reaction kinetic profile.

Table S2: The molar concentraion of product 2 at different time interval.

Time (s)	Yield of 2a (M)
0	0
300	0
600	0
900	0
1800	0.006571
3600	0.010960
7200	0.035072
14400	0.083297
21600	0.118369
28800	0.149057
36000	0.166594

43200	0.192898
64800	0.206050
86400	0.217010

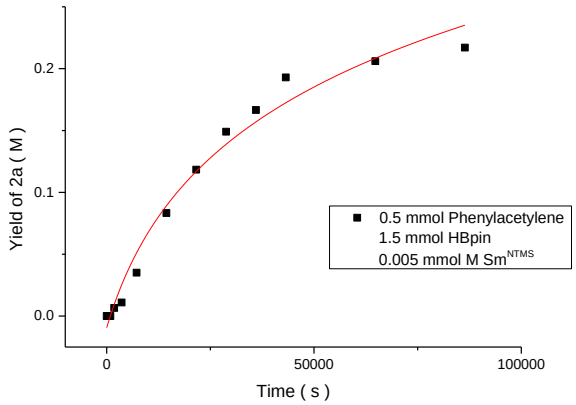


Figure S6: Plot of the rise of product **2a** from the reaction of **1a** (0.50 mmol), pinacolborane (1.50 mmol) and $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane. The reaction in different time interval at 100 ^oC.

b. General procedure to determine the dependence of reaction rate on the concentration of pinacolborane

For the reaction of 1a (0.50 mmol), pinacolborane (0.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane:

In a glovebox, $Sm[N(SiMe_3)_2]_3$ (3.2 mg 0.005 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, pinacolborane (153.6mg, 225µL, 1.5 mmol), 1a (51.0 mg, 56 µL, 0.5 mmol) with 2 mL hexane was added in sequence. The sealed tube was taken out from the glovebox, and was stirred at 100 ^oC taken out at 5, 10, 15, 20, 30, 60, 90, 120, 240 minutes. The sample was analyzed by ^1H NMR.

For the reaction of 1a (0.50 mmol), pinacolborane (1.00 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of pinacolborane (0.50 mmol), pinacolborane (1.00 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of pinacolborane (0.50 mmol), pinacolborane (1.50 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (2.00 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of pinacolborane (0.50 mmol), pinacolborane (2.00 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (2.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of pinacolborane (0.50 mmol), pinacolborane (2.50 mmol) were added in the reaction.

The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **2a** (only the data corresponding to the linear portion of the graph, typically < 40% yield was used) was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The table showing molar concentration of product **2a** in different concentration of pinacolborane, graph showing the rate at different concentration of pinacolborane, table with k_{in} in value and the graph showing k_{in} in versus [HBpin] are shown below.

Table S3: The molar concentration of product **2a** in different concentration of HBpin at different time interval

Time(s)	Yield of 2a (M)				
	0.2346 M	0.4533 M	0.6576 M	0.8489 M	1.0284 M
1800	0.000000	0.002267	0.005633	0.005900	0.005348
3600	0.006258	0.006346	0.010960	0.011800	0.015631
5400	0.012513	0.012897	0.018698	0.017678	0.026121
7200	0.018771	0.019334	0.028496	0.029499	0.036405

9000	0.025035	0.032185	0.033976	0.042445	0.055327
10800	0.031276	0.038758	0.050855	0.059000	0.070136
12600	0.037541	0.045104	0.056554	0.064941	0.080412
14400	0.050047	0.051678	0.068391	0.082556	

Table S4: The k_{in} value of product **2a** in different concentration of HBpin

HBpin (M)	k_{in}
0.2346	3.76519E-6
0.4533	4.16733E-6
0.6576	5.08748E-6
0.8489	6.2117E-6
1.0284	7.21048E-6

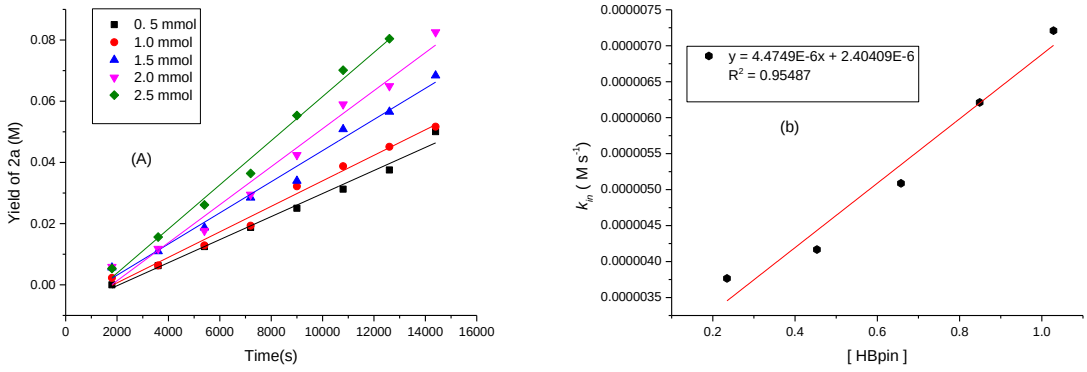


Figure S7: (A) Plot of the rise of product **2** from the reaction of **1a** (0.5 mmol) with 0.5 mmol, 1.0 mmol, 1.5 mmol, 2.0 mmol and 2.5 mmol of HBpin in different time interval at 100 ^{o}C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (0.5 mmol: a = 3.76519 × 10^{-6} , b = -0.782 × 10^{-2} , R^2 = 0.98638; 1.0 mmol : a = 4.16733 × 10^{-6} , b = -0.768 ×10^{-2}, R^2= 0.98648; 1.5 mmol : a = 5.08748 × 10^{-6}, b = -0.701× 10^{-2} , R^2 = 0.98276; 2.0 mmol : a = 6.2117 × 10^{-6} , b = -1.109 × 10^{-2}, R^2= 0.97581, 2.5 mmol: a = 7.21048 × 10^{-6} , b = -1.058 × 10^{-2}, R^2 = 0.98811. (a) Plot of *k*in versus [HBpin] from the reaction of **1a** (0.5 mmol) with 0.5 mmol, 1.0 mmol, 1.5 mmol, 2.0 mmol and 2.5 mmol of HBpin. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 4.4749 × 10^{-8}, b = 2.40409 × 10^{-6}, R^2 = 0.95478).

c. General procedure to determine the dependence of reaction rate on the concentration of

$Sm[N(TMS)_2]_3$ catalyst

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane:

In a glovebox, $Sm[N(SiMe_3)_2]_3$ (3.2 mg 0.005 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, pinacolborane (153.6mg, 225μL, 1.5 mmol), 1a (51.0 mg, 56 μL, 0.5 mmol) with 2 mL hexane was added in sequence. The sealed tube was taken out from the glovebox, and was stirred at 100 ^oC taken out at 5, 10, 15, 20, 30, 60, 90, 120, 240 minutes. The sample was analyzed by ^1H NMR.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.01 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of $Sm[N(TMS)_2]_3$ (0.005 mmol), $Sm[N(TMS)_2]_3$ (0.01 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.015 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of $Sm[N(TMS)_2]_3$ (0.05 mmol), $Sm[N(TMS)_2]_3$ (0.015 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.02 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of $Sm[N(TMS)_2]_3$ (0.05 mmol), $Sm[N(TMS)_2]_3$ (0.02 mmol) were added in the reaction.

The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **2a** (only the data corresponding to the linear portion of the graph, typically < 40% yield, was used) was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The table showing molar concentration of product **2a** in different concentration of $Sm[N(TMS)_2]_3$, graph showing the rate at different concentration of $Sm[N(TMS)_2]_3$, table with k_{in} in value and the graph showing k_{in} in versus $Sm[N(TMS)_2]_3$ are shown below.

Table S5: The molar concentration of product 2a in different concentration of catalyst at different time interval

Time(s)	Yield of 2a (M)			
	2.129E-3 M	4.384E-3 M	6.576E-3 M	8.768E-3 M
1800	0.005699	0.005918	0.011837	0.019728
3600	0.016221	0.017098	0.032661	0.035072
5400	0.029220	0.034416	0.052609	0.067953
7200	0.035072	0.040991	0.065761	0.080447
9000	0.040925	0.059184		
10800	0.051447			

Table S6: The k_{in} value of product 2a in different concentration of catalyst

Sm^{NTMS} (M)	k_{in}
2.129E-3	4.90006E-6
4.384E-3	7.24583E-6
6.576E-3	1.00956E-5
8.768E-3	1.19466E-5

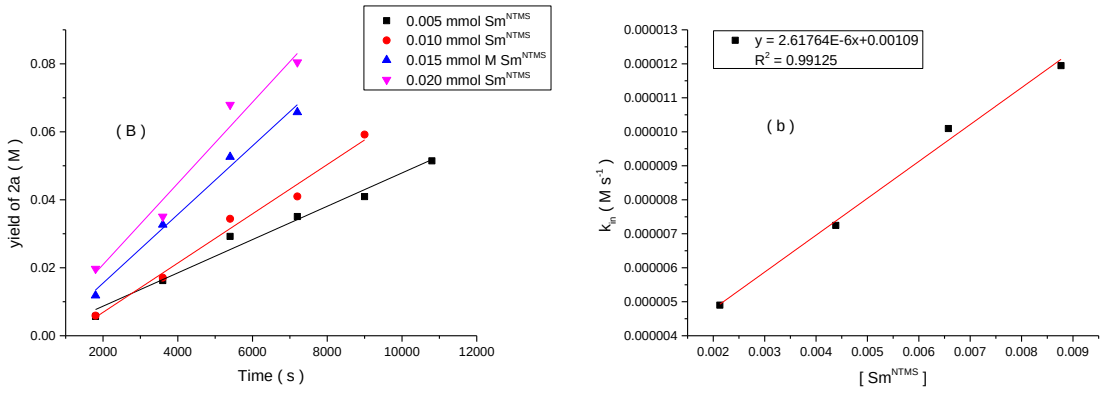


Figure S8: (B) Plot of the rise of product **2a** from the reaction of **1a** (0.5 mmol), HBpin (1.5 mmol) with 0.005mmol, 0.01mmol, 0.015mmol and 0.020mmol of [Sm^{NTMS}] respectively in different time interval. The curve depicts the results of an unweighted least-square fit to y = a*x + b (0.005 mmol: a = 4.90006×10^{-6} , b = - 0.111×10^{-2} , R^2= 0.97806; 0.010 mmol: a = 7.24583×10^{-6}, b = - 0.761 ×

10^{-2}, R^2 = 0.9801; 0.015 mmol: a = 1.00956 × 10^{-5} , b = - 0.471 × 10^{-2} , R^2 = 0.98519); 0.020 mmol: a = 1.19466 × 10^{-5} , b = - 0.296 × 10^{-2} , R^2 = 0.95352. (b) Plot of k_{in} versus [Sm^{NTMS}] from the reaction of 1a (0.5 mmol), pinacolborane (1.50 mmol) with 0.005 mmol, 0.010 mmol, 0.015 mmol and 0.020mmol of Sm^{NTMS}. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 2.61764 × 10^{-6}, b = 0.109 × 10^{-2}, R^2 = 0.99125).

d. General procedure to determine the dependence of reaction rate on the concentration of 1a

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane:

In a glovebox, $Sm[N(SiMe_3)_2]_3$ (3.2 mg, 0.005 mmol) was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, pinacolborane (153.6mg, 225μL, 1.5 mmol), 1a (51.0 mg, 56 μL, 0.5 mmol) with 2 mL hexane was added in sequence. The sealed tube was taken out from the glovebox, and was stirred at 100 ºC taken out at 5, 10, 15, 20, 30, 60, 90, 120, 240, 360, 480, 600, 720, 1080, 14400 minutes. The sample was analyzed by ^{1}H NMR.

For the reaction of 1a (1.00 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of 1a (0.50 mmol), 1a (1.00 mmol) were added in the reaction.

For the reaction of 1a (1.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of 1a (1.50 mmol), 1a (1.50 mmol) were added in the reaction.

For the reaction of 1a (2.00 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of 1a (0.50 mmol), 1a (2.00 mmol) were added in the reaction.

For the reaction of 1a (2.50 mmol), pinacolborane (1.50 mmol) with $Sm[N(TMS)_2]_3$ (0.005 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of 1a (0.50 mmol), 1a (2.50 mmol) were added in the reaction.

The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run

under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **2a** (only the data corresponding to the linear portion of the graph, typically < 40% yield, was used) was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The table showing molar concentration of product **2a** in different concentration of 1a, graph showing the rate at different concentration of 1a, table with k_{in} in value and the graph showing k_{in} in versus [1a] are shown below.

Table S7: The molar concentration of product 2a in different concentration of 1a at different time interval

Time(s)	Yield of **2a** (M)				
	0.2192 M	0.4279 M	0.6221 M	0.8130 M	0.9980 M
1800	0.006234	0.006134	0.005761	0.005736	0.005367
3600	0.012470	0.012266	0.011522	0.017209	0.016102
5400	0.031171	0.030659	0.028803	0.034411	0.026826
7200	0.037418	0.036800	0.034571	0.040163	0.037565
9000	0.049890	0.049059	0.051846	0.045894	0.048303
10800	0.056116	0.055199	0.057611	0.057358	0.059042
12600	0.068583	0.067458	0.069121	0.068841	0.069780
14400	0.074814	0.073599	0.074886	0.080304	0.075130

Table S8: The k_{in} value of product **2a** in different concentration of **1a**

1a (M)	k_{in}
0.2192	5.60802E-6
0.4279	5.51649E-6
0.6221	5.7908E-6
0.8130	5.65283E-6
0.9980	5.71506E-6

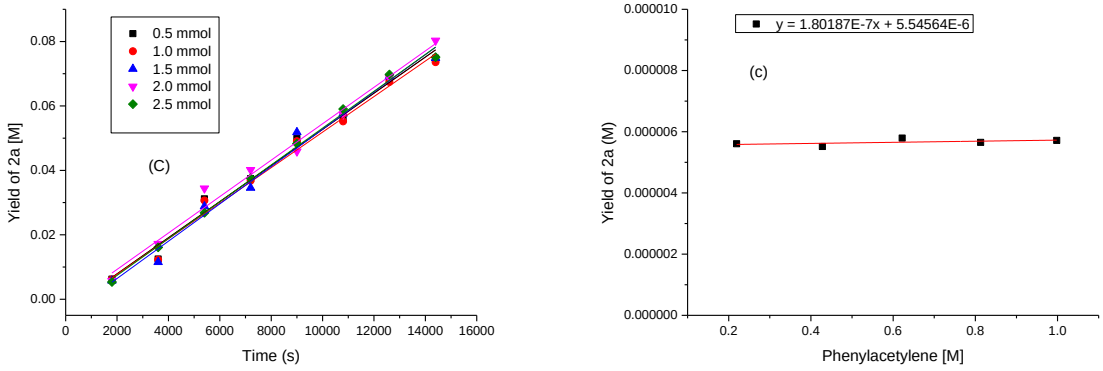


Figure S9: (C) Plot of the rise of product **2a** from the reaction of **1a** (0.5 mmol) with 0.5 mmol, 1.0 mmol, 1.5 mmol, 2.0 mmol and 2.5mmol of **1a** in different time interval at 100 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (0.5 mmol : a = 5.60802 × 10^{-6} , b = -0.334 ×10^{-2} , R^2 = 0.98529; 1.0 mmol : a = 5.51649 ×10^{-6} , b = -0.329 ×10^{-2} , R^2 = 0.98533; 1.5 mmol : a = 5.7908 ×10^{-6} , b = -0.514 ×10^{-2}, R^2 = 0.98348); 2.0 mmol : a = 5.65283 ×10^{-6} , b = -0.205 ×10^{-2} , R^2 = 0.98497; 2.5 mmol : a = 5.71506 ×10^{-6} , b = -0.403 ×10^{-2} , R^2 = 0.99558. (c) Plot of *k*in versus [**1a**] from the reaction of HBpin (1.5 mmol) with 0.5 mmol,1.0 mmol, 1.5 mmol, 2.0 mmol and 2.5 mmol of **1a**. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 1.80187 × 10^{-7} , b = 5.54564 × 10^{-6} , R^2 = 0.04303).

e. General procedure to determine the dependence of reaction rate on the concentration of BH_3·THF

In a glovebox, pinacolborane (153.6mg, 225 µL, 1.5 mmol), **1a** (51.0 mg, 56 µL, 0.5 mmol) with 2 mL hexane was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon cap. Then, BH_3·THF (1 mol/L in THF, 50 µL) was added. The sealed tube was taken out from the glovebox, and was stirred at 100 °C taken out at 1 2, 4, 6, 8, 10, 15, 20 minutes. The sample was analyzed by ^{1}H NMR.

The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The yields in molar concentrations are presented in Table S9. The molar concentrations of the product **2a** were

plotted against the reaction time to obtain a typical reaction kinetic profile.

Table S9: The molar concentraion of product **2** at different time interval.

Time (s)	Yield of 2a (M)
0	0
60	0.025712
120	0.042964
240	0.067032
360	0.090683
480	0.102302
600	0.114423
900	0.129329
1200	0.146865

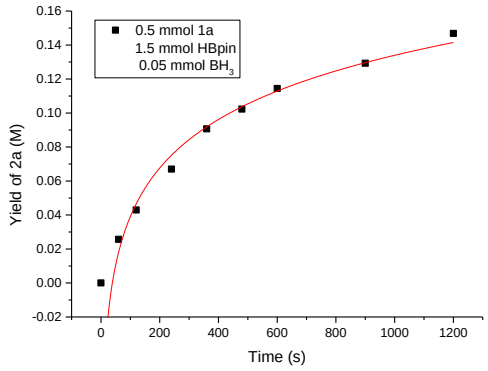


Figure S10: Plot of the rise of product **2a** from the reaction of **1a** (0.50 mmol), pinacolborane (1.50 mmol) and BH_3·THF (0.05 mmol) in 2 mL hexane. The reaction in different time interval at 100 ºC.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with BH_3·THF (0.05 mmol) in 2 mL hexane:

In a glovebox, pinacolborane (153.6mg, 225 µL, 1.5 mmol), **1a** (51.0 mg, 56 µL, 0.5 mmol) with 2 mL hexane was added to a Schlenk tube equipped with a magnetic stirring bar and a Teflon

cap. Then, BH_3·THF (1 mol/L in THF, 50 μL) was added. The sealed tube was taken out from the glovebox, and was stirred at 100 °C taken out at 2, 4, 6, 8, 10 minutes. The sample was analyzed by ^{1}H NMR.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with BH_3 (0.04 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of BH_3·THF (0.05 mmol), **BH_3** (0.04 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with BH_3 (0.03 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of BH_3·THF (0.05 mmol), **BH_3** (0.03 mmol) were added in the reaction.

For the reaction of 1a (0.50 mmol), pinacolborane (1.50 mmol) with BH_3 (0.02 mmol) in 2 mL hexane: The procedure for this reaction was the same as above but instead of BH_3·THF (0.05 mmol), BH_3·THF (0.02 mmol) were added in the reaction.

The percentage yields of the product **2a** were calculated by hexamethylbenzene as an internal standard, which were then converted to molar concentrations. A duplicate reaction was also run under otherwise identical conditions and an average value was taken for each time point. The molar concentration of product **2a** (Only the first 10 minutes of data were taken) was plotted against the reaction time and the slope of linear portion of the curve was used to determine the initial rates of the reaction. The table showing molar concentration of product **2a** in different concentration of BH_3·THF, graph showing the rate at different concentration of BH_3, table with k_{in} in value and the graph showing k_{in} in versus BH_3·THF are shown below.

Table S10: The molar concentration of product **2a** in different concentration of BH_3·THF at different time interval

Time (s)	Yield of **2a** (M)			
	0.0214500 M	0.017234 M	0.019814 M	0.00869187 M
120	0.042960	0.029132	0.021043	0.019268

240	0.067032	0.041210	0.038580	0.036037
360	0.090683	0.074813	0.057387	0.051293
480	0.102302	0.087681	0.070342	0.064796
600		0.100548	0.089632	0.077751

Table S11: The k_{in} value of product **2a** in different concentration of BH_3.

BH_3 (M)	k_{in}
0.869187 E-2	1.21438E-4
1.29814 E-2	1.40783E-4
1.72340E-2	1.57753E-4
2.14500E-2	1.68064E-4

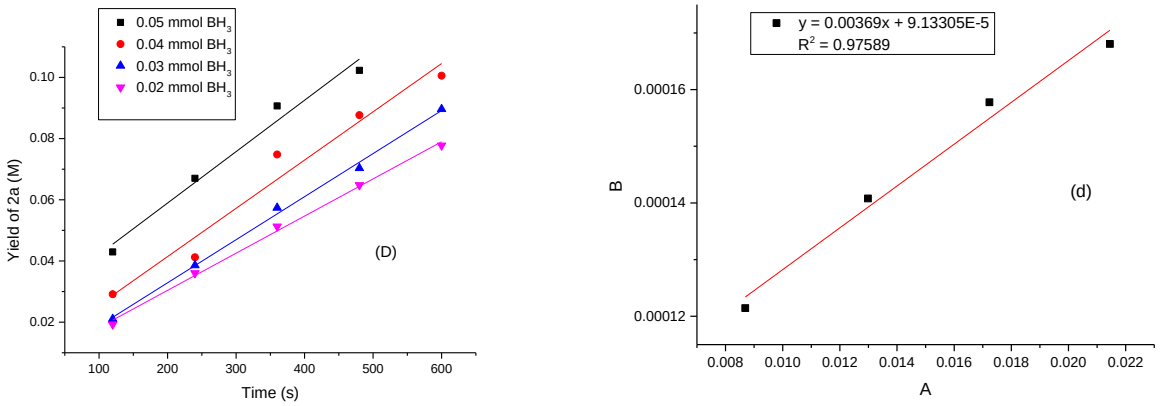


Figure S11: (D) Plot of the rise of product **2a** from the reaction of **1a** (0.5 mmol), HBpin (1.5 mmol) with 0.05 mmol, 0.04 mmol, 0.03 mmol and 0.02 mmol of [BH_3] respectively in different time interval. The curve depicts the results of an unweighted least-square fit to y = a*x + b (0.05 mmol: a = 1.68064E-4, b = 0.02532, R^2= 0.96717; 0.04 mmol: a = 1.57753E-4, b = 0.00989, R^2 = 0.95359; 0.03 mmol: a = 1.40783E-4, b = 0.00471, R^2 = 0.99614); 0.02 mmol: a = 1.21438E-4, b = 0.00611, R^2 = 0.99599. (d) Plot of k_{in} versus [BH_3] from the reaction of 1a (0.5 mmol), pinacolborane (1.50 mmol) with 0.05 mmol, 0.04 mmol, 0.03 mmol and 0.02mmol of BH_3. The curve depicts the results of an unweighted least-square fit to y = a*x + b(a = 0.00369, b = 9.12748E-4, R^2 = 0.97589).

6. Product Transformations

Procedure for the synthesis of 2-phenylacetaldehyde (3-1) from 2a[7]

The vinyl boronate ester **2a** (0.23 g, 1 mmol) was dissolved in acetone (10 mL) and cooled to 0 ℃, Oxone solution (0.3 g, 1.5 mmol in 15 mL H_2O) was then added dropwisely and further stirred for 1 h. Upon completion the reaction was quenched with 1M HCl (5 mL) and extracted with DCM, the combined organics were washed with water, brine and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and the crude product was isolated on silica gel using flash chromatography (PE: EA = 10:1).

Procedure for the synthesis of *trans*-potassium trifluoroborate (3-2) from 2a[7]

The vinyl boronate ester **2a** (0.23 g, 1 mmol) was dissolved in 5 mL MeOH and cooled to 0 ℃ then a solution of KHF_2 (0.392 g, 5 mmol) in H_2O (5 mL) was added dropwisely whereupon the mixture was stirred at rt for 2 h. The volatiles were removed under reduced pressure, water was added and the mixture was lyophilized. The crude product was dissolved in minimal amounts of dry acetone, filtered and evaporated to yield **3-2** as white powder.

Procedure for the synthesis of (*1E,3E*)-1,4-diphenylbuta-1,3-diene (3-3) from 2a[7]

The vinylboronate ester **2a** (0.23 g, 1 mmol), $Cu(OAc)_2$ (0.181 g, 1 mmol), DMF 2 mL and 0.5 mL EtOH were added in a 10 mL reaction tube and stirred under ambient condition at 60 ℃ for 8 h before quenching with 1 M HCl (3 mL). Then the solution was extracted with Et_2O (10 mL x 3). The combined ether layer was washed with aq. $NaHCO_3$ and brine and dried over $MgSO_4$. Then the solvent was removed and the product **3-3** was obtained after column chromatography (PE as eluent).

Procedure for the synthesis of (*E*)-(2-iodovinyl)benzene (3-4) from 2a[7]

The vinyl boronate ester **2a** (0.23 g, 1 mmol) was dissolved in 5 mL Et_2O in 25 mL round bottom flask, then 5 mL aqueous solution of NaOH (3 M) was added dropwisely at 0 ℃. Subsequently, a solution of 0.381 g I_2 (1.5 mmol) in 10 mL Et_2O was added slowly and stirred for 30 mins before quenching with a saturated solution of sodium thiosulfate. The organic solution was separated, and the aqueous solution was washed with Et_2O. The combined organic layers were dried

with $MgSO_4$, the solvent was evaporated and the crude product was isolated on silica gel using flash chromatography (PE as eluent).

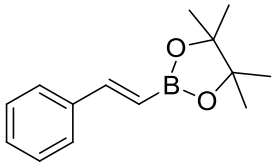
Procedure for the synthesis of (3-5) from 2a[7]

A 25 mL of Schlenk tube equipped with a magnetic stir bar was charged with $Pd(PPh_3)_4$ (5 mol%) and Cs_2CO_3 (3.0 equiv). Then toluene (2.0 mL), H_2O (7.0 equiv), **2a** (1mmol, 1.0 equiv) and 3-iodopyridine (2 mmol, 2.0 equiv) were added under nitrogen, respectively. The Schlenk tube was screw capped and heated to 80 ^oC (oil bath). After stirring for 24 h, the reaction mixture was cooled to room temperature. Then the reaction mixture was diluted with EtOAc and filtered with a pad of cellite. The filtrate was concentrated, and the residue was purified with silica gel chromatography to give product (PE: EA = 10:1).

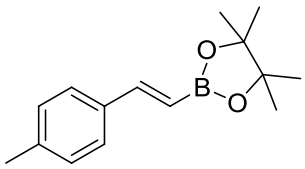
Procedure for the synthesis of vinyl ether(3-6) from 2a[7]

The vinylboronate ester **2a** (0.23 g, 1 mmol), $Cu(OAc)_2$ (0.362 g, 2 mmol), Et_3N (404 mg, 4 mmol, 4 equiv) and EtOH 2 mL were added in a round bottom flask and stirred under ambient condition for 16 h, then the solvent was removed and the product **3-6** was obtained after column chromatography (PE as eluent).

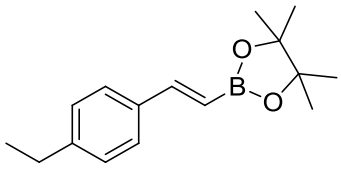
7. Characterization of products



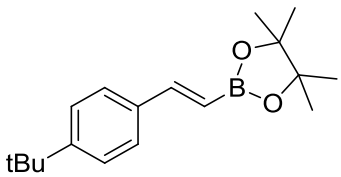
(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (2a) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (85.6 mg, 93% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.49 (d, *J* = 7 Hz, 2H), 7.40 (d, *J* = 18 Hz, 1H), 7.35 - 7.28 (m, 3H), 6.17 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.6, 137.5, 128.9, 128.6, 127.0, 83.3, 24.8. **^{11}B NMR** (160 MHz, Chloroform-*d*, ppm) δ 30.29. Spectroscopic data are in agreement with those previously reported.[7]



(*E*)-4,4,5,5-tetramethyl-2-(4-methylstyryl)-1,3,2-dioxaborolane (2b) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (92.7 mg, 95% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.40 - 7.36 (m, 3H), 7.12 - 7.10 (m, 2H), 6.11 (d, *J* = 18 Hz, 1H), 2.31 (s, 3H), 1.29 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.5, 138.9, 134.8, 129.3, 127.0, 83.2, 24.8, 21.3. Spectroscopic data are in agreement with those previously reported.[7]

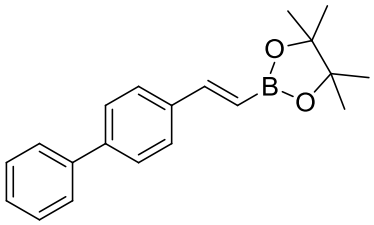


(*E*)-2-(4-ethylstyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (94.9 mg, 92% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.41 - 7.37 (m, 3H), 7.15 (d, *J* = 8 Hz, 2H), 6.12 (d, *J* = 18 Hz, 1H) 2.62 (q, *J* = 8 Hz, 2H), 1.32 (s, 12H), 1.21 (t, *J* = 8 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.6, 145.3, 135.1, 128.1, 127.2, 115.4 (br, C-B), 83.3, 28.8, 24.9, 15.5. Spectroscopic data are in agreement with those previously reported.[8]

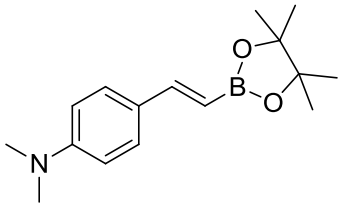


(*E*)-2-(4-(tert-butyl)styryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d) Eluent: petroleum ether/ethyl acetate (100:1). White solid (104.1 mg, 91% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.45 - 7.35 (m, 5H), 6.12 (d, *J* = 18 Hz, 1H), 1.31 (s, 21H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 152.2, 149.5, 134.9, 126.9, 125.6, 83.4, 34.8, 31.4, 24.9. ^{11}**B NMR** (160 MHz, Chloroform-*d*, ppm) δ 30.19.

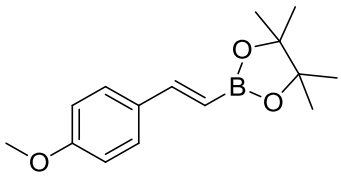
Spectroscopic data are in agreement with those previously reported.[7]



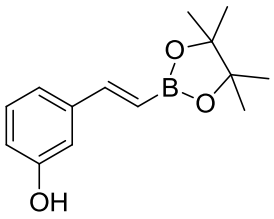
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e) Eluent: petroleum ether/ethyl acetate (100:1). Pale yellow solid (101.6 mg, 83% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.60 - 7.55 (m, 6H), 7.46 - 7.41 (m, 3H), 7.35 - 7.32 (m, 1H), 6.21 (d, *J* = 18, 1H), 1.32 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.1, 141.7, 140.6, 136.6, 128.9, 127.6, 127.5, 127.3, 127.0, 83.4, 24.9. Spectroscopic data are in agreement with those previously reported.[7]



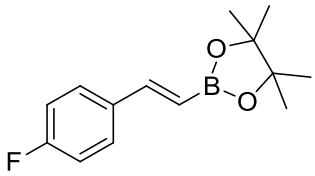
(*E*)-N,N-dimethyl-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)aniline (2f) Eluent: petroleum ether/ethyl acetate (100:1). White solid (87.4 mg, 80% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 9 Hz, 2H), 7.33 (d, *J* = 18 Hz, 1H), 6.66 (d, *J* = 9 Hz, 2H), 5.92 (d, *J* = 18 Hz, 1H), 2.98 (s, 6H), 1.30 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 151.1, 149.9, 128.5, 126.1, 112.1, 83.1, 40.4, 24.9. Spectroscopic data are in agreement with those previously reported.[7]



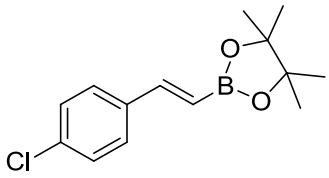
(*E*)-2-(4-methoxystyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2g). Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (82.2 mg, 79% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.43 (d, *J* = 9 Hz, 2H), 7.36 (d, *J* = 18 Hz, 1H), 6.86 (d, *J* = 9 Hz, 2H), 6.02 (d, *J* = 18 Hz, 1H), 3.81 (s, 3H), 1.31 (s, 12H); **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 160.3, 149.1, 130.4, 128.4, 114.0, 83.1, 55.1, 24.8. Spectroscopic data are in agreement with those previously reported.[9]



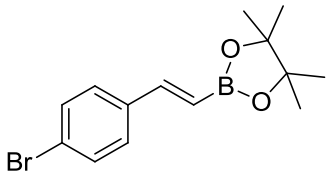
(*E*)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenol (2h) Eluent: petroleum ether/ethyl acetate (5:1). Colorless oil (44.3 mg, 45% yield), **^{1}H NMR** (500 MHz, C_6D_6, ppm) δ 7.72 (d, J = 18 Hz, 1H), 6.92 (d, J = 5 Hz, 2H), 6.75 (s, 1H), 6.58 (dt, J = 6, 2 Hz, 1H), 6.43 (d, J = 18 Hz, 1H), 4.69 (d, J = 15 Hz, 1H), 1.11 (s, 12H). **^{13}C NMR** (125 MHz, C_6D_6, ppm) δ.157.0, 150.4, 139.6, 130.1, 127.9, 120.2, 116.7, 113.8,83.5, 24.9.



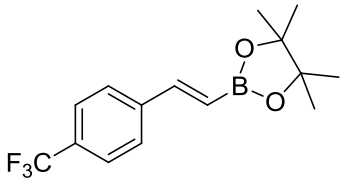
(*E*)-2-(4-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2j) Eluent: petroleum ether/ethyl acetate (100:1). White solid (87.3 mg, 88% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.46 - 7.44 (m, 2H), 7.35 (d, *J* = 18 Hz, 1H), 7.02 (m, 2H), 6.07 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 163.3 (d, ^{1}J = 246 Hz), 148.3, 133.9 (d, $^{4}J_{C\text{-}F}$= 4 Hz), 128.8 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 115.7 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 83.3, 24.7. **^{11}B NMR** (160 MHz, Chloroform-*d*, ppm) δ 30.21. **^{19}F NMR** (470M, Chloroform-*d*, ppm) δ 112.4 Hz. Spectroscopic data are in agreement with those previously reported.[7]



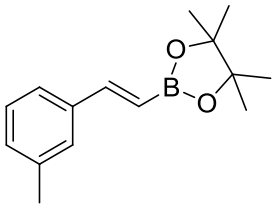
(*E*)-2-(4-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k) Eluent: petroleum ether/ethyl acetate (100:1). White solid (88.7 mg, 84% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.41 (d, *J* = 8 Hz, 2H), 7.36-7.29 (m, 3H), 6.13 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 148.2, 136.1, 134.7, 128.9, 128.4, 83.6, 24.9. Spectroscopic data are in agreement with those previously reported.[7]



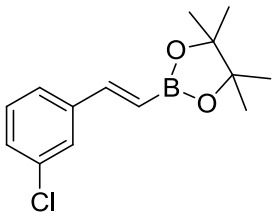
(*E*)-2-(4-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l) Eluent: petroleum ether/ethyl acetate (100:1). White solid (102.3 mg, 83 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.46 - 7.50 (d, *J* = 8 Hz, 2H), 7.35 - 7.30(m, 3H), 6.14 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 148.0, 136.4, 131.7, 128.5, 122.8, 83.3, 24.8. Spectroscopic data are in agreement with those previously reported.[10]



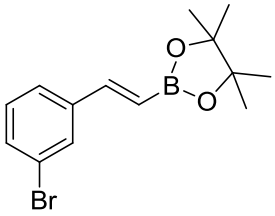
(*E*)-4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)styryl)-1,3,2-dioxaborolane (2m) Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (98.9 mg, 83% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.60-7.58 (m, 4H), 7.40 (d, *J* = 18 Hz, 1H), 6.26 (d, *J* = 18 Hz, 1H), 1.32 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 147.7, 141.0, 130.7 (q, $^{2}J_{C\text{-}F}$= 33 Hz), 127.3, 126.4 (q, $^{1}J_{C\text{-}F}$ = 270 Hz), 125.7 (q, $^{4}J_{C\text{-}F}$ = 4 Hz), 123.2, 83.8, 25.0. ^{19}F NMR (470M, Chloroform-*d*, ppm) δ 62.7 Hz. Spectroscopic data are in agreement with those previously reported.[7]



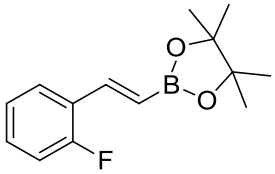
(*E*)-4,4,5,5-Tetramethyl-2-(3-methylphenyl-1-enyl)-1,3,2-dioxaborolane (**2n**) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (86.9 mg, 89% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm): δ 7.38 (d, *J* = 18 Hz, 1H), 7.29 (m, 2H), 7.21(m, 1H), 7.09 (d, *J* = 8 Hz, 1H), 6.15 (d, *J*= 18 Hz, 1H), 2.33 (s, 3H), 1.29 (s, 12H). **^{13}C NMR** (125 MHz; Chloroform-*d*, ppm): 149.8, 138.1, 137.6, 129.8, 128.5, 127.8, 124.3, 83.3, 24.9, 21.4. Spectroscopic data are in agreement with those previously reported.[9]



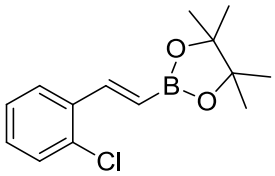
(*E*)-2-(3-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (95.0 mg, 90% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.61 (s, 1H), 7.50 - 7.46 (m, 2H), 7.40 - 7.39 (m, 2H), 6.33 (d, *J* = 18 Hz, 1H), 1.46 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 147.8, 139.5, 134.6, 129.8, 128.7, 127.0, 125.2, 83.5, 24.8. Spectroscopic data are in agreement with those previously reported.[7]



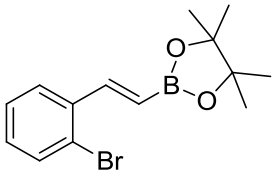
(*E*)-2-(3-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p) Eluent: petroleum ether/ethyl acetate (100:1). Pale yellow oil (102.3 mg, 83% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm): δ 7.61 (s, 1H), 7.39 (t, *J* = 8 Hz, 2H), 7.30 (d, *J* = 18 Hz, 1H), 7.18 (t, *J* = 8 Hz, 1H), 6.16 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H) **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 147.6, 139.6, 131.5, 130.0, 129.8, 125.5, 22.7, 83.3, 24.7. Spectroscopic data are in agreement with those previously reported.[10]



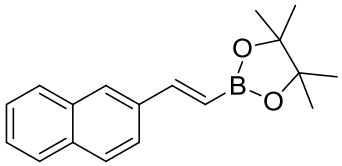
(*E*)-2-(2-fluorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (82.3 mg, 83% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.62 - 7.54 (m, 2H), 7.26 - 7.22 (m, 1H), 7.10 (t, *J* = 7 Hz, 1H), 7.04 - 7.00 (m, 1H), 6.24 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 160.8 (d, $^{1}J_{C\text{-}F}$ = 250 Hz), 141.4 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 130.3 (d, $^{3}J_{C\text{-}F}$ =8 Hz), 127.5 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 125.4 (d, $^{3}J_{C\text{-}F}$ = 11 Hz), 124.2 (d, $^{3}J_{C\text{-}F}$ = 4 Hz), 115.8 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 83.5, 24.8. **^{19}F NMR** (470M, Chloroform-*d*, ppm) δ 117.7 Hz. Spectroscopic data are in agreement with those previously reported.[7]



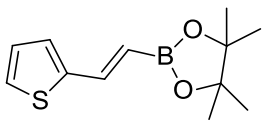
(*E*)-2-(2-chlorostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (85.5 mg, 81% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.79 (d, *J* = 18 Hz, 1H), 7.62 (m, 1H), 7.33 - 7.21 (m, 3H), 6.17 (d, *J* = 18 Hz, 1H), 1.31 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 145.0, 135.7, 133.9, 129.9, 129.8, 127.1, 126.9, 83.5, 24.9. Spectroscopic data are in agreement with those previously reported.[7]



(*E*)-2-(2-bromostyryl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (99.8 mg, 81 % yield). ^{1}**H NMR** (500 MHz, Chloroform-*d*, ppm): δ 7.73 (d, *J* = 18 Hz, 1H), 7.60 - 7.52 (m, 2H), 7.26 - 7.11 (m, 2H,), 6.13 (d, *J* = 18 Hz, 1H,), 1.30 (s, 12H,). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 147.5, 137.4, 133.1, 129.9, 127.5, 127.3, 124.3, 83.5, 24.9. Spectroscopic data are in agreement with those previously reported.[10]

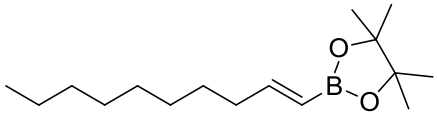


(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)vinyl)-1,3,2-dioxaborolane (2t) Eluent: petroleum ether/ethyl acetate (100:1). Yellow solid (98.6 mg, 88% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.83 - 7.78 (m, 4H), 7.70 - 7.68 (m, 1H), 7.57 (d, *J* = 18 Hz, 1H), 7.47 - 7.43 (m, 2H), 6.29 (d, *J* = 18 Hz, 1H), 1.32 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.6, 135.1, 133.9, 133.6, 128.5, 128.4, 128.1, 127.8, 126.5, 126.4, 123.5, 83.5, 25.0. Spectroscopic data are in agreement with those previously reported.[7]

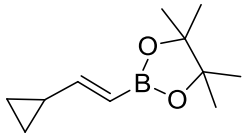


3-(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl)-1,3,2-dioxaborolane (2u) Eluent: petroleum ether/ethyl acetate (100:1). Yellow oil (60.4 mg, 64% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*,

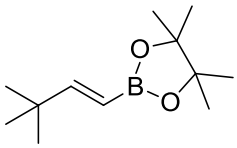
ppm) 7.47 (d, *J* = 18 Hz, 1H), 7.22 (m, 1H), 7.06 (m, 1H), 6.96 (m, 1H), 5.91 (d, *J* = 18 Hz, 1H), 1.28 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 144.0, 141.9, 127.7, 127.8, 126.3, 83.4, 24.8. Spectroscopic data are in agreement with those previously reported.[7]



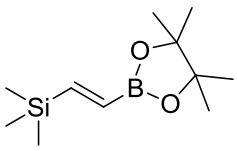
(*E*)-2-(dec-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2v) Eluent: petroleum ether/ethyl acetate (100:1), colourless oil (89.4 mg, 84% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 6.62 (dt, *J* = 18 Hz, 1H), 5.41 (d, *J* = 18 Hz, 1H), 2.13(dd, *J* = 14 Hz, 2H), 1.41-1.38 (m, 2H), 1.25 (m, 22H), 0.87 (t, *J* = 6 Hz, 3H). Spectroscopic data are in agreement with those previously reported.[11]



(*E*)-2-(2-cyclopropylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2w) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (56.6 mg, 73% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 6.05 (dd, *J* = 18 Hz, 1H), 5.46 (d, *J* = 18 Hz, 1H), 1.54 (m, 1H), 0.80 - 0.76 (m, 2H), 0.53 - 0.49 (m, 2H), 1.23 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 158.6, 115.3 (br, C-B), 83.0, 24.9, 17.1, 8.0. Spectroscopic data are in agreement with those previously reported.[6]

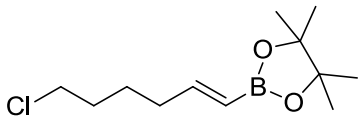


(*E*)-2-(3,3-dimethylbut-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2x) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (60.5 mg, 72% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 6.64 (d, *J* = 18 Hz, 1H), 5.35 (d, *J* = 18 Hz, 1H), 1.28 (s, 12H), 1.02 (s, 9H). **^{13}C NMR** (125Mz, Chloroform-*d*, ppm) δ 164.5, 112.6, 83.1, 35.1, 28.9, 24.9. Spectroscopic data are in agreement with those previously reported.[8]

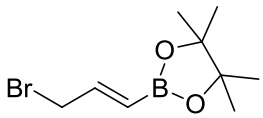


(*E*)-trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)silane (2y) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (66.9 mg, 74% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*,

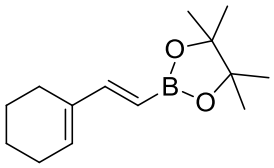
ppm) δ 7.12 (d, *J* = 21 Hz, 1H), 6.24 (d, *J* = 21 Hz, 1H,), 1.28 (s, 12H,), 0.07 (s, 9H). **^{13}C NMR** (125Mz, Chloroform-*d*, ppm) δ 158.1, 83.5, 25.0, -1.7. Spectroscopic data are in agreement with those previously reported.[12]



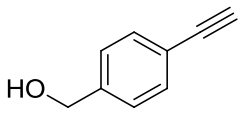
(*E*)-2-(6-Chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2z) Eluent: petroleum ether/ethyl acetate (100:1). Colorless oil (87.8 mg, 90% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 6.60 (dt, *J* = 18 Hz, 1H), 5.45 (dt, *J* = 18 Hz, 1H), 3.53 (t, *J* = 7 Hz, 2H), 2.19 (m, 2H), 1.79 (m, 2H), 1.16-1.55 (m, 2H), 1.27 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 152.6, 83.2, 45.0, 35.0, 32.1, 25.5. 24.9. Spectroscopic data are in agreement with those previously reported.[13]



(*E*)-2-(3-bromoprop-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2za) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (77.7 mg, 79% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) 6.67 (dt, *J* = 18 Hz, 1H), 5.66 (d, *J* = 18 Hz, 1H), 3.96 (d, *J* = 7 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 146.8, 83.7, 33.7, 24.9. Spectroscopic data are in agreement with those previously reported.[6]

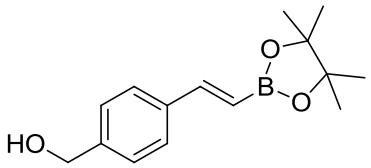


(*E*)-2-(2-(cyclohex-1-en-1-yl)vinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2zb) Eluent: petroleum ether/ethyl acetate (100:1). Colourless oil (71.1 mg, 76 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.02 (d, *J* = 18 Hz, 1H), 5.96 (m, 1H), 5.43 (d, *J* = 18 Hz, 1H), 2.16 - 2.15 (m, 4H), 1.70 - 1.56 (m, 4H), 1.28 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 153.3, 137.3, 134.3, 112.0 (br, *C-B*), 83.1, 26.3, 24.9, 23.9, 22.5, 22.5. Spectroscopic data are in agreement with those previously reported.[6]

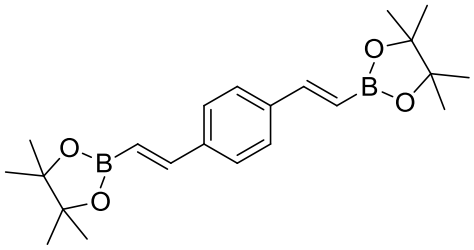


(4-ethynylphenyl)methanol (2zc-1) Eluent: petroleum ether/ethyl acetate (5:1). Colourless oil (18

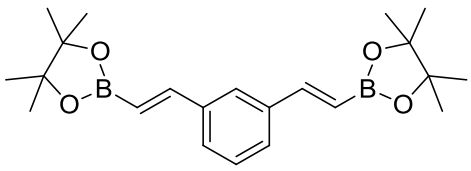
mg, 34% yield). ^{1}**H NMR** (500 MHz, Benzene-*d*, ppm) δ 7.40 (d, *J* = 8 Hz, 2H), 6.93 (d, *J* = 8 Hz, 2H), 4.14 (s, 2H), 2.76 (s, 1H). **^{13}C NMR** (125 MHz, Benzene-*d*, ppm) 142.5, 132.4, 126.8, 121.6, 83.4, 77.6, 64.4.



(*E*)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)methanol (2zc-2) Eluent: petroleum ether/ethyl acetate (5:1). Colourless oil (80 mg, 77% yield). ^{1}**H NMR** (500 MHz, Chloroform-*d,* ppm) δ 7.44 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 18 Hz, 1H), 7.30 (d, *J* = 8 Hz, 2H), 6.11 (d, *J* = 18 Hz, 1H), 4.63 (s, 2H), 2.61 (brs, 1H), 1.30 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.3, 141.9, 136.9, 127.3, 12.2, 83.5, 64.9,24.9. Spectroscopic data are in agreement with those previously reported.[18]

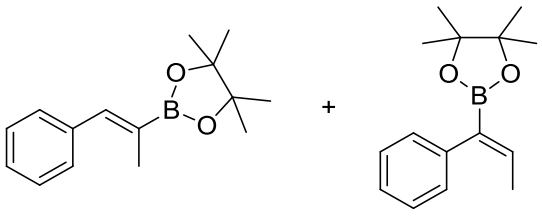


1,4-Bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (2zd) Eluent: petroleum ether/ethyl acetate (100:1). White solid (103.9 mg, 68% yield). ^{1}**H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.46 (s, 4H), 7.38 (d, *J* = 18 Hz, 2H), 6.18 (d, *J* = 18 Hz, 2H), 1.31 (s, 24H); **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) 148.9, 138.1, 127.4, 83.4, 24.9. Spectroscopic data are in agreement with those previously reported.[14]



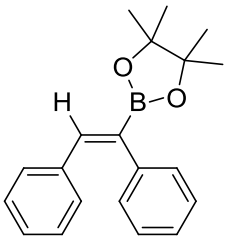
1,3-bis((*E*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)benzene (2ze) Eluent: petroleum ether/ethyl acetate (100:1). White solid (96 mg, 63 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.58 (s, 1H), 7.44 - 7.41 (m, 3H), 7.37 (s, 1H), 7.37 - 3.39 (m, 1H), 6.18 (d, J = 15 Hz, 2H), 1.31 (s, 24H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 149.2, 137.9, 128.9, 127.4, 126.1, 83.4,

24.9. Spectroscopic data are in agreement with those previously reported.[15]

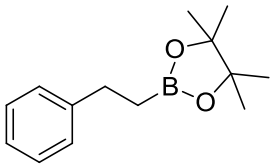


2zg-1 2zg-2

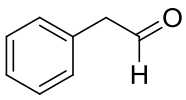
(*Z*)-4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (2zg-1) The NMR is consistent with literature data.[6] ^{1}H NMR data for major isomer is given below. Eluent: petroleum ether/ethyl acetate (50:1). Colourless oil (52.7 mg, 54 % in mixture of two isomers). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.38 (d, *J* = 7, 2H), 7.34 (m, 2H), 7.25 - 7.22 (m, 2H), 2.00 (d, *J* = 7 Hz, 3H), 1.31 (s, 12 H).



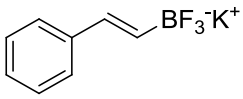
(*Z*)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2zf) Eluent: petroleum ether/ethyl acetate (100:1). White solid (31.8 mg, 26 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.37 (s, 1H), 7.27 - 7.25 (m, 2H), 7.21 - 7.20(m, 1H), 7.17 - 7.16 (m, 2H), 7.11 - 7.10 m, 3H), 7.06-7.05 (m, 2H), 130 (s, 12H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 143.3, 140.6, 137.2, 130.1, 129.0, 128.4, 128.0, 127.7, 126.4, 83.9, 24.9. Spectroscopic data are in agreement with those previously reported.[9]



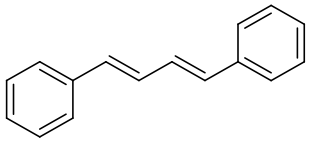
4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2zi) Eluent: petroleum ether. Colourless oil (42.7 mg, 46% yield). **^{1}H NMR** (500 MHz, Chloroform-*d,* ppm) δ 7.24 (d, *J* = 7 Hz, 2H), 7.21 (d, *J* = 7 Hz, 2H), 7.14 (t, *J* = 7 Hz, 1H), 2.76(t, *J* = 8 Hz, 2H), 1.22 (s, 12H), 1.14 (t, *J* = 8Hz, 2H). Spectroscopic data are in agreement with those previously reported.[19]



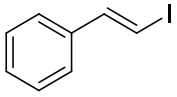
2-phenylacetaldehyde (3-1) Eluent: petroleum ether/ethyl acetate (10:1). Yellow oil in 81% yield (38.9 mg, 81% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 9.69 (t, *J* = 20 Hz, 1H), 7.34 (t, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8 MHz, 1H), 7.18 (d, *J* = 8 Hz, 2H), 3.64 (d, *J* = 2Hz, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 199.5, 131.9, 129.7, 129.0, 127.4, 50.5. Spectroscopic data are in agreement with those previously reported.[16]



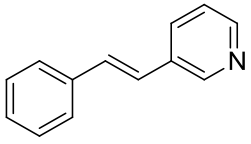
Potassium (*E*)-2-Phenylvinyltrifluoroborate (3-2) (63.8 mg, 76 % yield). ^{1}H NMR (500 MHz, Acetone-d_6, ppm) δ 7.37 - 7.32 (m, 2H), 7.25 - 7.19 (m, 2H), 7.10 - 7.05 (m, 1H), 6.64 (d, *J* = 18 Hz, 1H), 6.39 - 6.29 (m, 1H). **^{13}C NMR** (125 MHz, Acetone-d_6, ppm) δ 141.0, 133.7, 128.1, 125.6, 125.6. Spectroscopic data are in agreement with those previously reported.[7]



(1*E*,3*E*)-1,4-diphenylbuta-1,3-diene (3-3) Eluent: petroleum ether. White soild (45.3 mg, 55 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.42 (d, *J* = 8 Hz, 4H), 7.31 (d, *J* = 8 Hz, 4H), 7.21 (t, *J* = 8 Hz, 2H), 6.96 - 6.90 (m, 2H), 6.68 - 6.62 (m, 2H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 137.5, 133.0, 129.4, 128.8, 127.7, 126.5. Spectroscopic data are in agreement with those previously reported.[7]

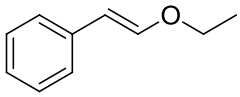


(*E*)-(2-iodovinyl)benzene (3-4) Eluent: petroleum ether. Yellow oil (91mg, 99% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.43 (d, *J* = 15 Hz, 1H), 7.34 - 7.28 (m, 5H), 6.82 (d, *J* = 15 Hz, 1H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 144.9, 137.7, 128.7, 128.4, 126.0, 77.0Spectroscopic data are in agreement with those previously reported.[7]



(*E*)-3-styrylpyridine (3-5) Eluent: petroleum ether/ethyl acetate (50:1). White solid (62.3 mg, 86% yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 8.76 (s, 1H), 8.52 (s, 1H), 7.83 (d, *J* = 8 Hz, 1H),

7.39 (d, *J* = 8 Hz, 2H), 7.38 (t, *J* = 7 Hz, 2H), 7.31 - 7.28 (m, 2H), 7.17 (d, *J* = 16 Hz, 1H), 7.07 (d, *J* = 16 Hz,1H). **^{13}C NMR** (125 MHz, Chloroform-d, ppm) δ 148.6, 136.9, 133.2, 132.8, 131.0, 128.9, 128.4, 126.8, 125.0, 123.7. Spectroscopic data are in agreement with those previously reported.[17]



(*E*)-(2-ethoxyvinyl)benzene (3-6) Eluent: petroleum ether. Yellow oil (43.2 mg, 73 % yield). **^{1}H NMR** (500 MHz, Chloroform-*d*, ppm) δ 7.24 - 7.20 (m, 4H), 7.13 - 7.09 (m, 1H), 6.97 (d, *J* = 13 Hz, 1H), 5.83 (d, *J* = 13 Hz, 1H), 3.84 (q, *J* = 7 Hz, 2H), 1.32 (t, *J* = 7 Hz, 3H). **^{13}C NMR** (125 MHz, Chloroform-*d*, ppm) δ 148.0, 136.7, 128.7, 125.7, 125.2, 106.1, 65.6, 14.9. Spectroscopic data are in agreement with those previously reported.[7]

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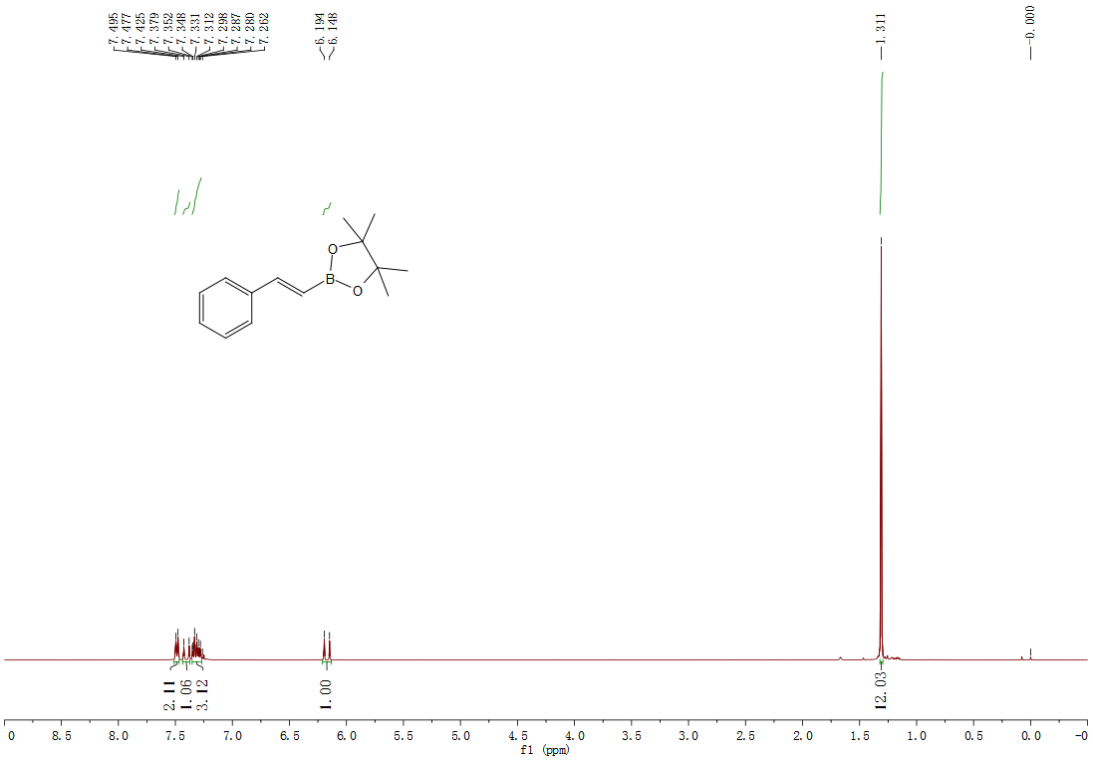
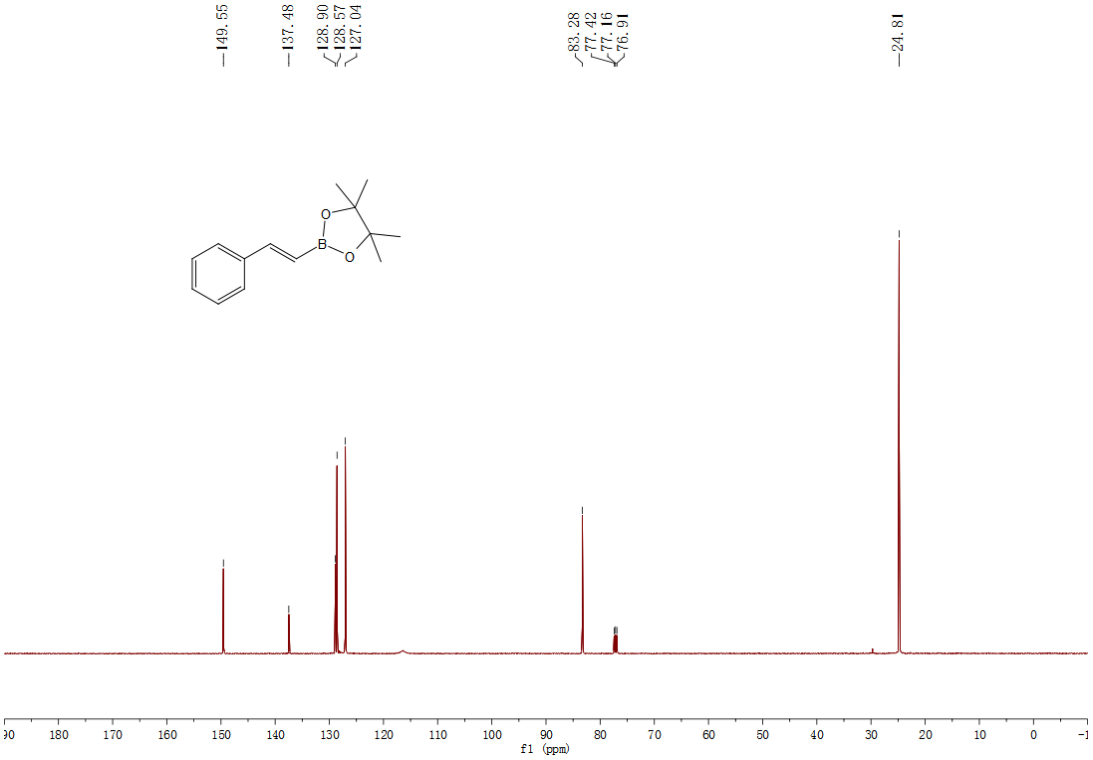
9. Copies of ^{1}H and ^{13}C NMR spectra



^{1}H NMR spectrum of **2a** (Chloroform-*d*)



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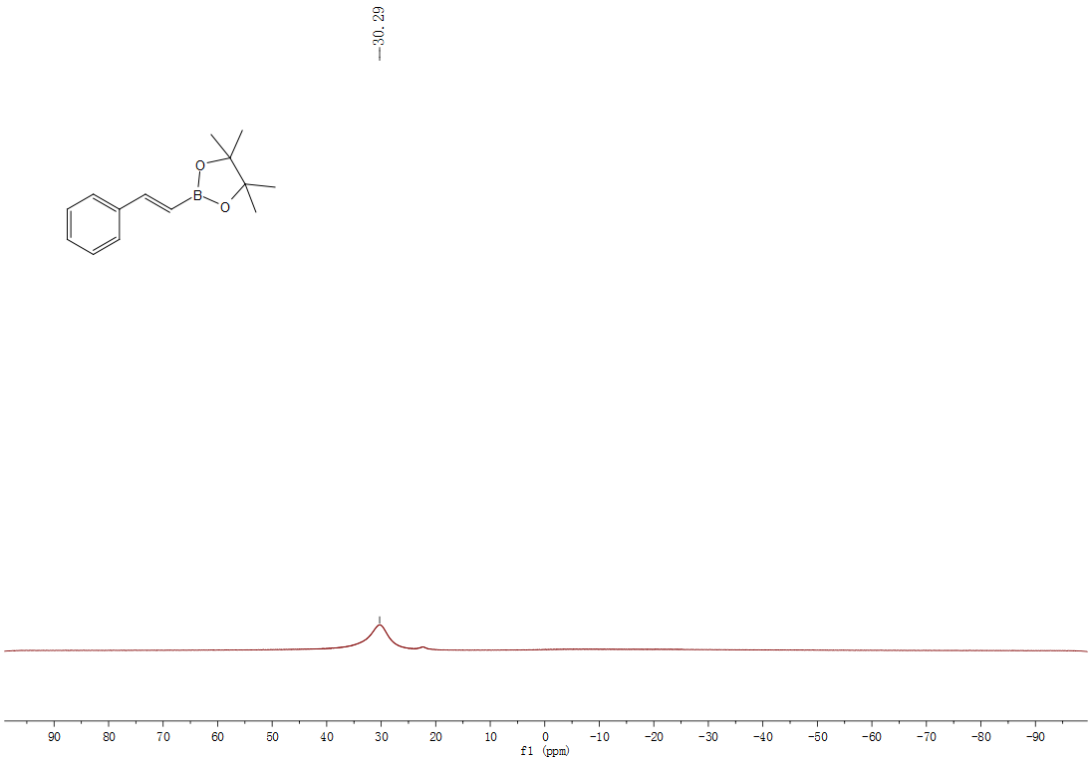
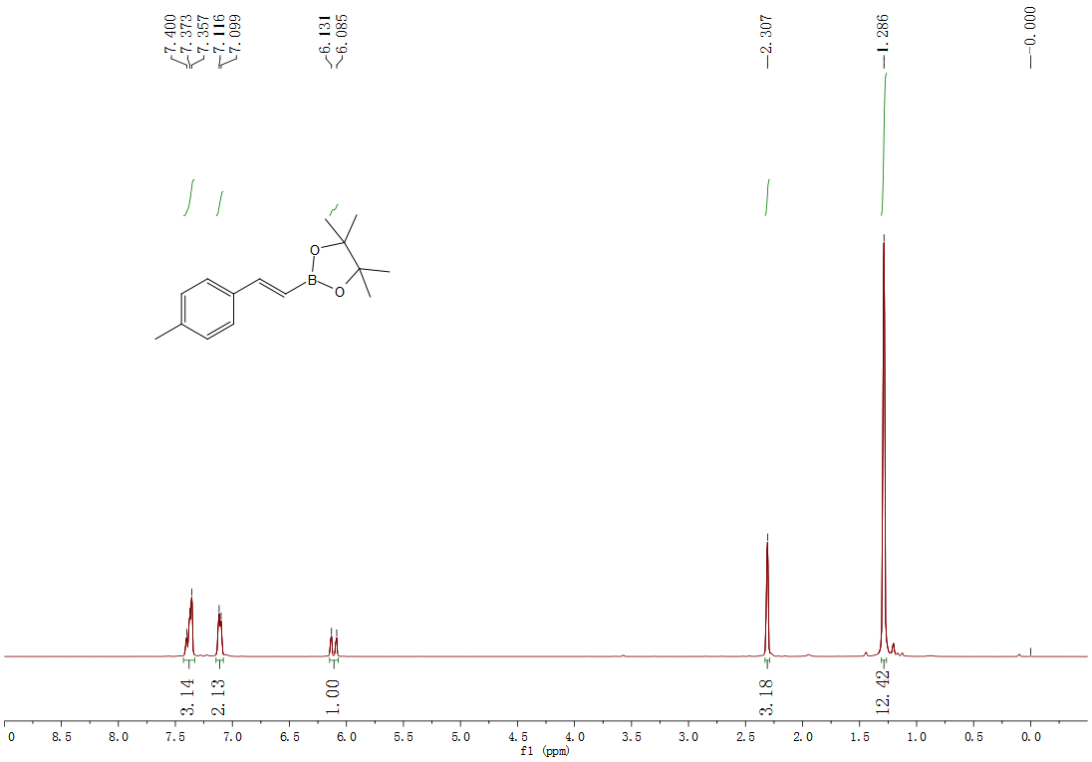
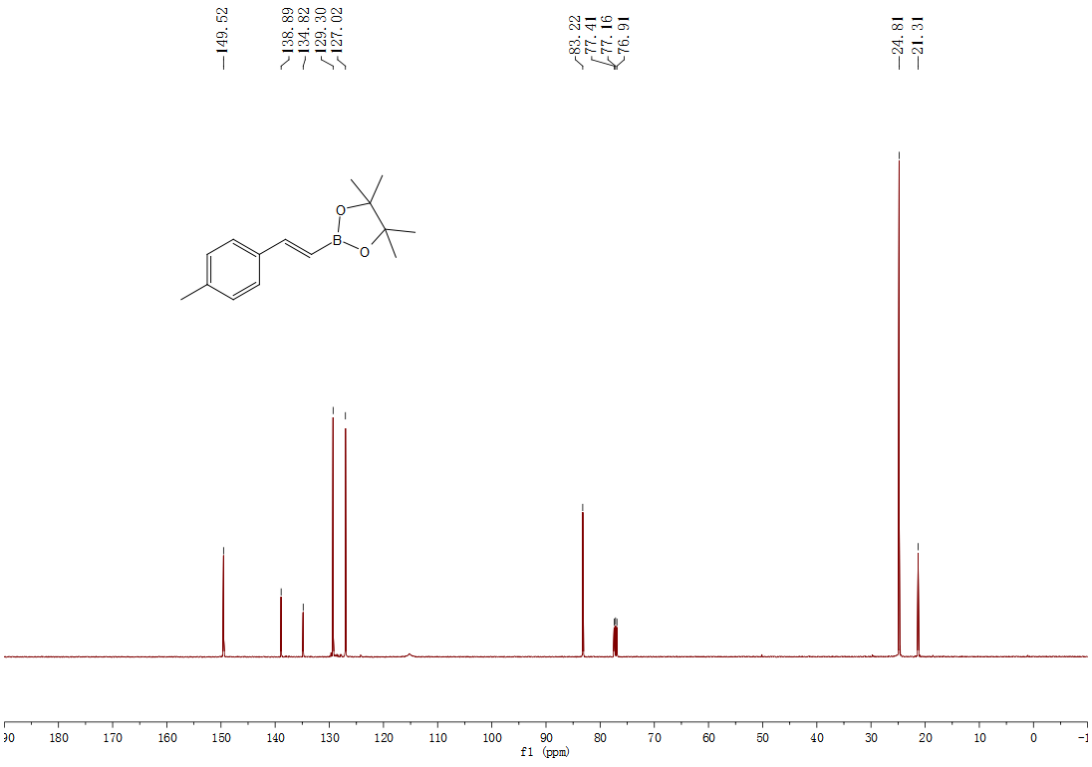


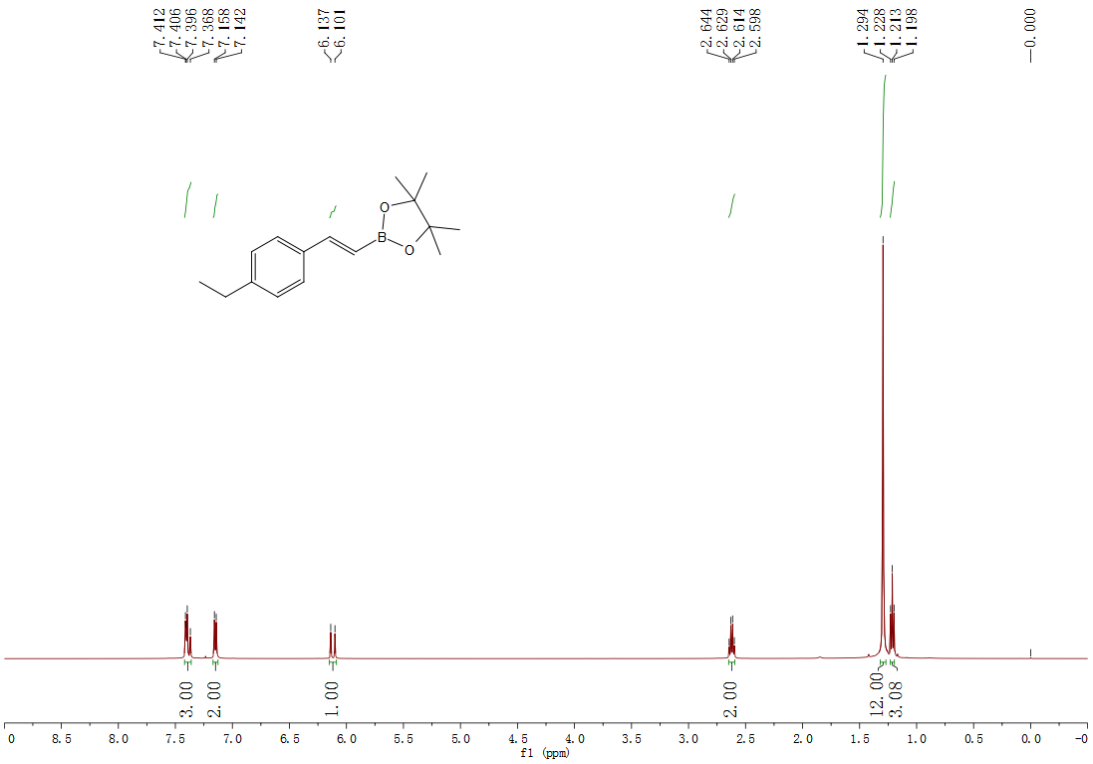
^{11}B NMR spectrum of **2a** (Chloroform-*d*)



^{1}H NMR spectrum of **2b** (Chloroform-*d*)



^{13}C NMR spectrum of **2b** (Chloroform-*d*)



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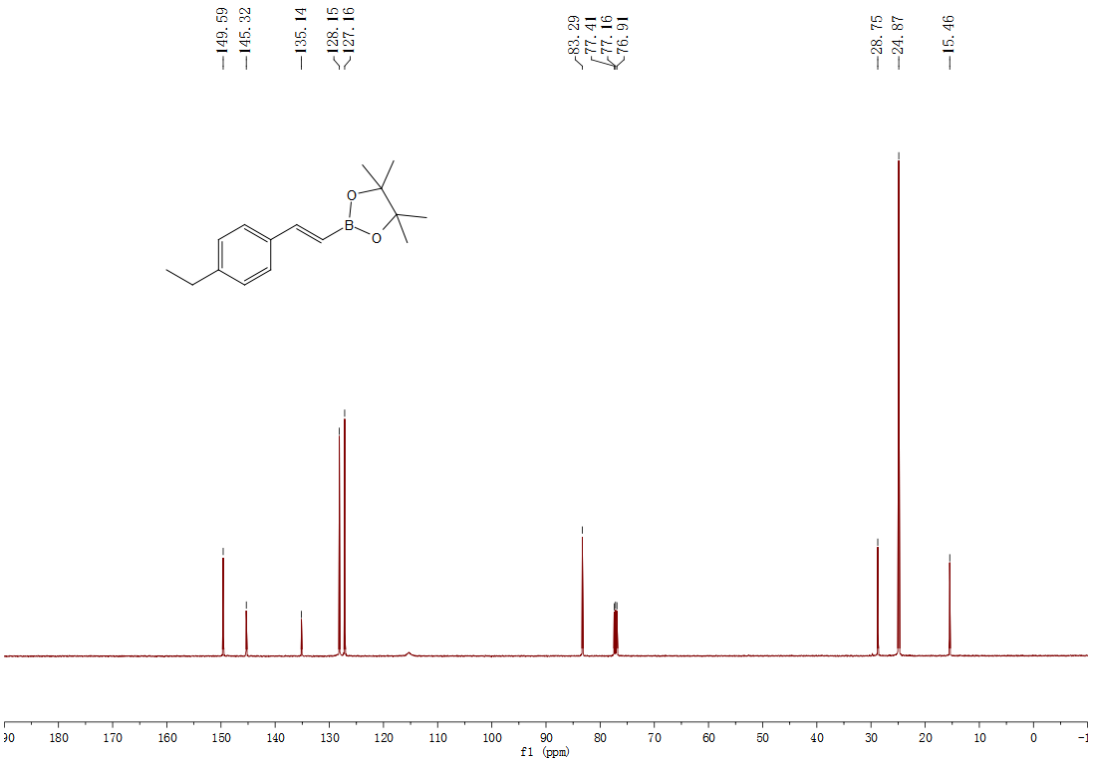
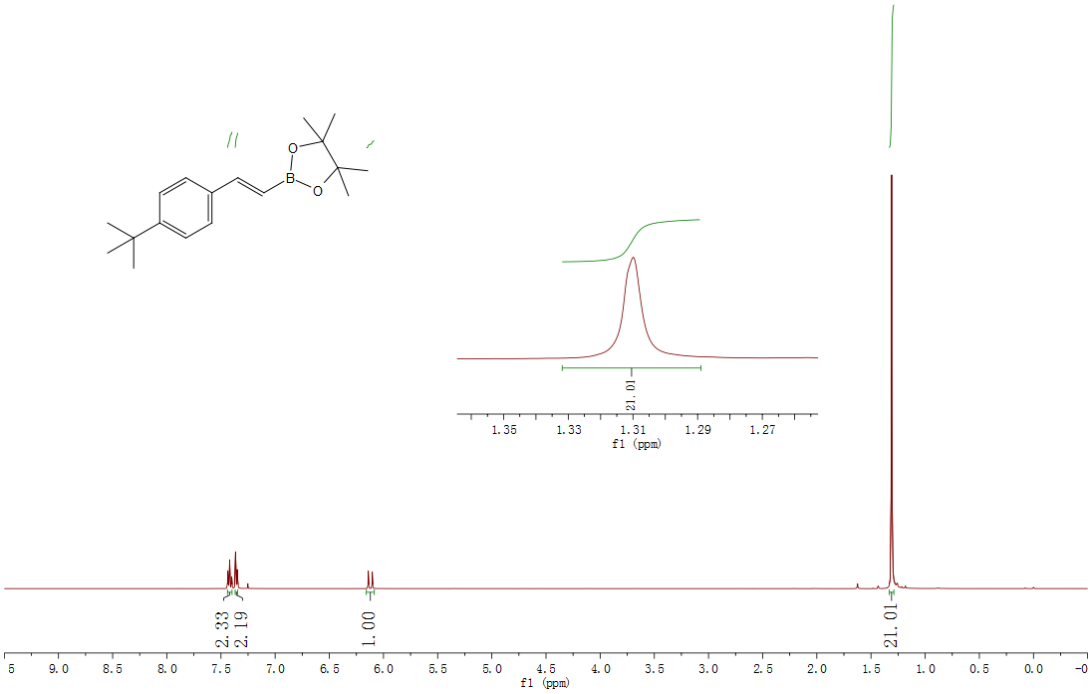
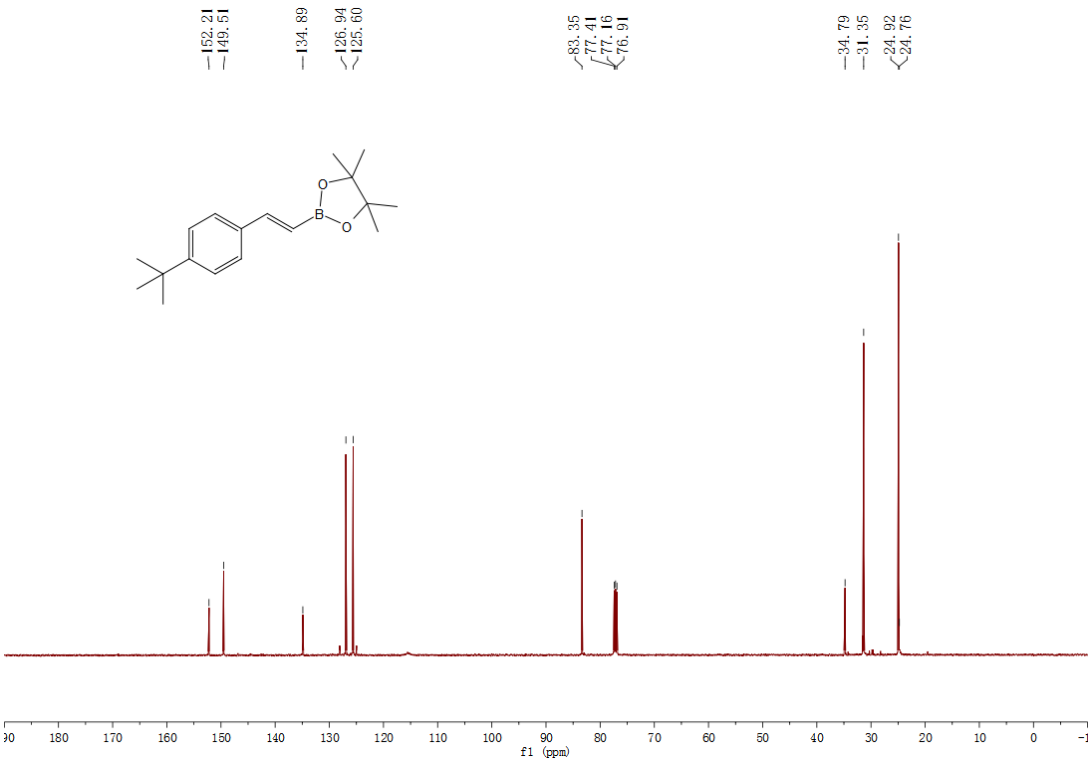


^{1}H NMR spectrum of **2c** (Chloroform-*d*)



^{1}H NMR spectrum of **2d** (Chloroform-*d*)



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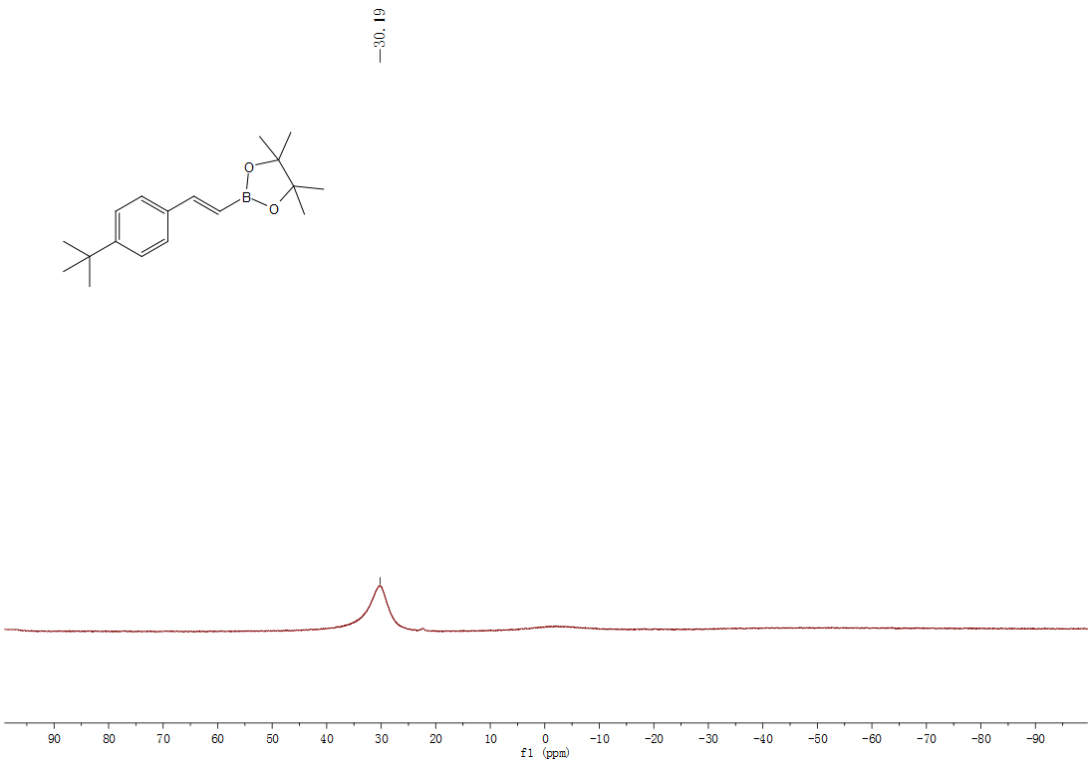

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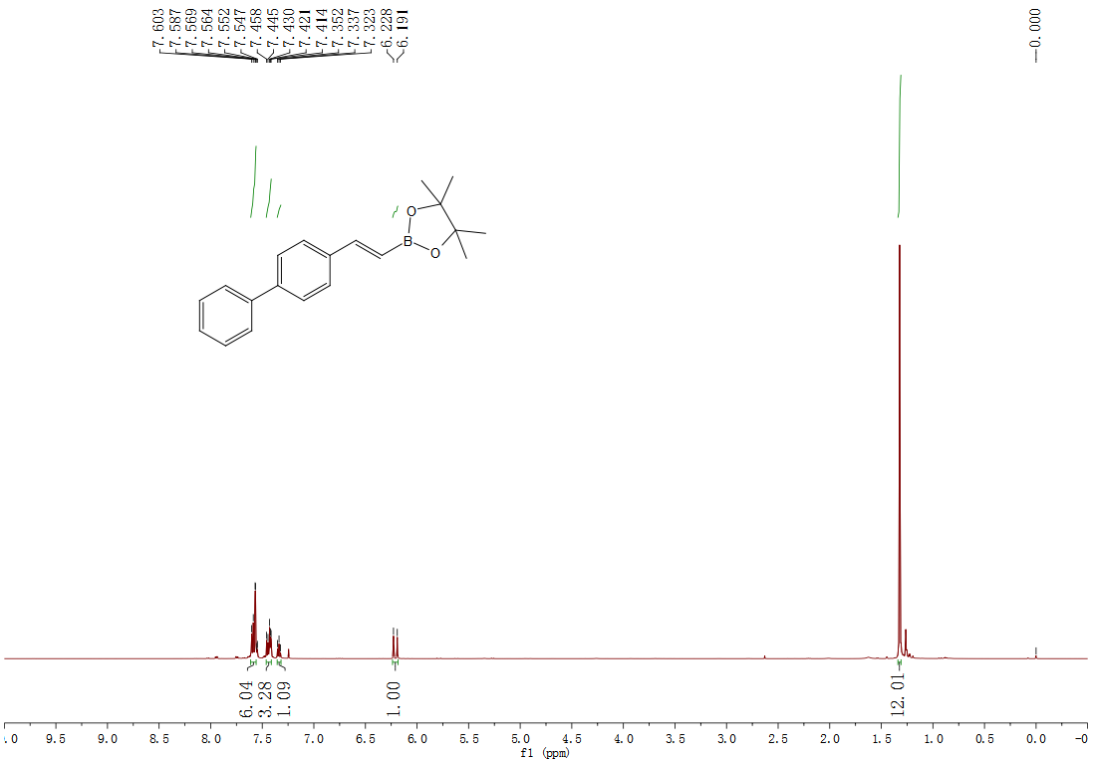
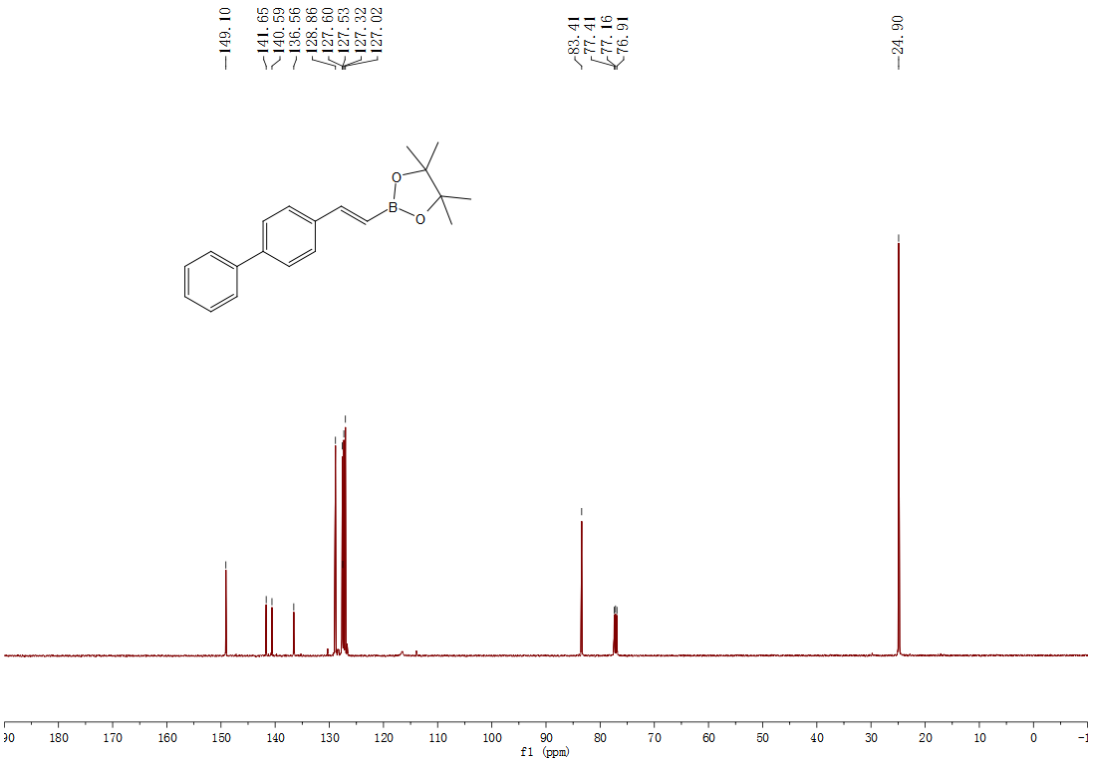


^{1}H NMR spectrum of **2e** (Chloroform-*d*)



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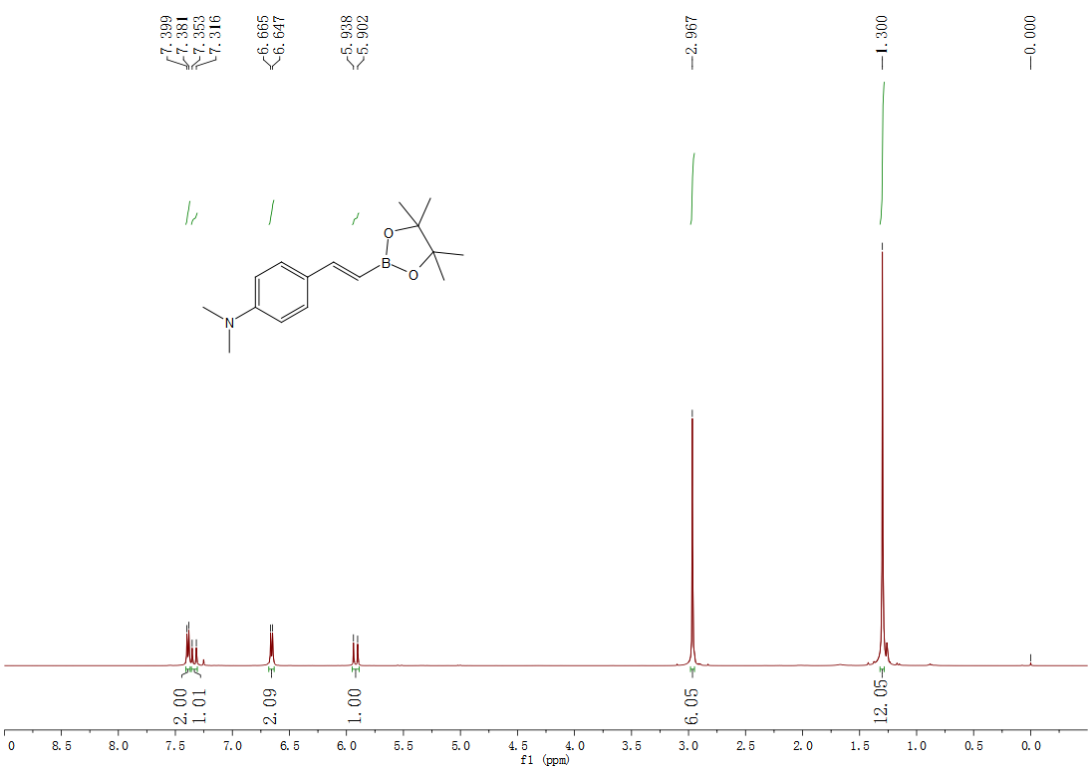

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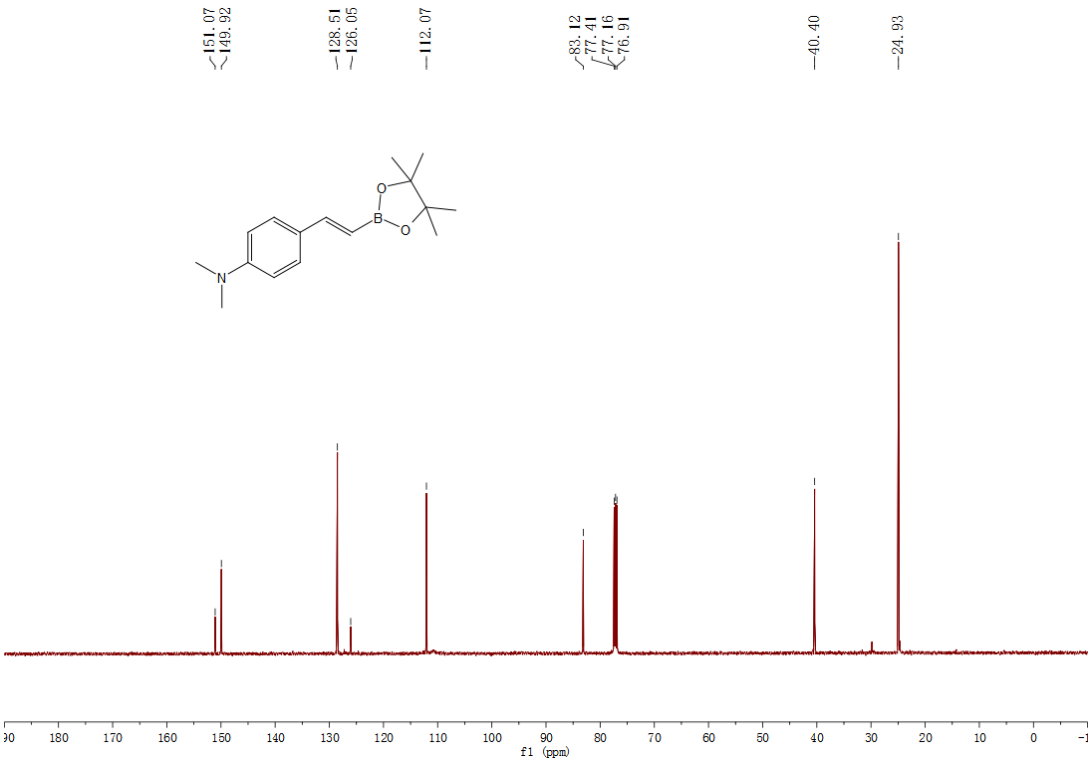
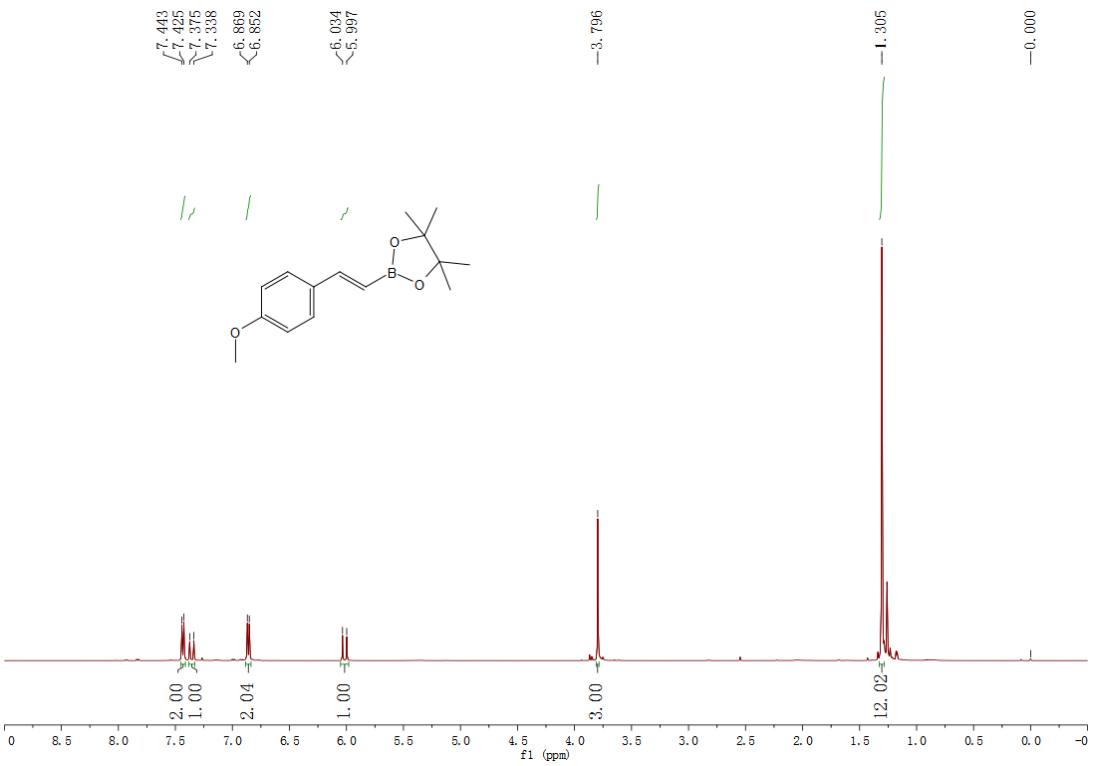


^{13}C NMR spectrum of **2f** (Chloroform-*d*)



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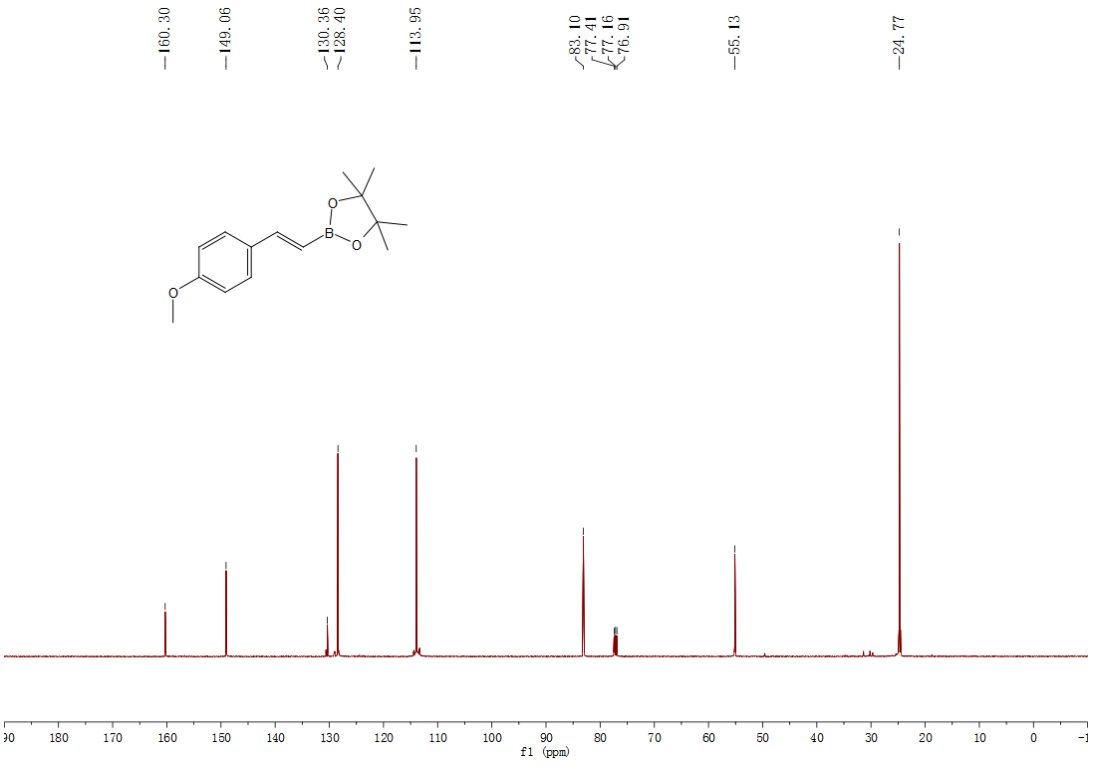
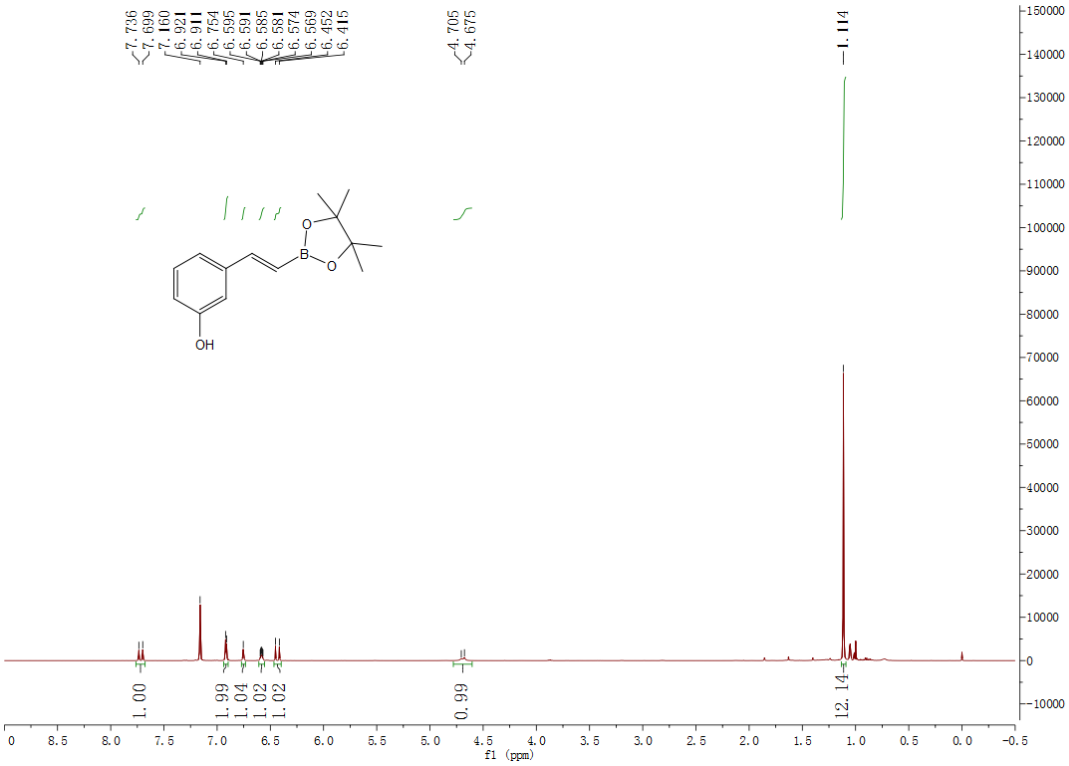


^{13}C NMR spectrum of **2g** (Chloroform-*d*)



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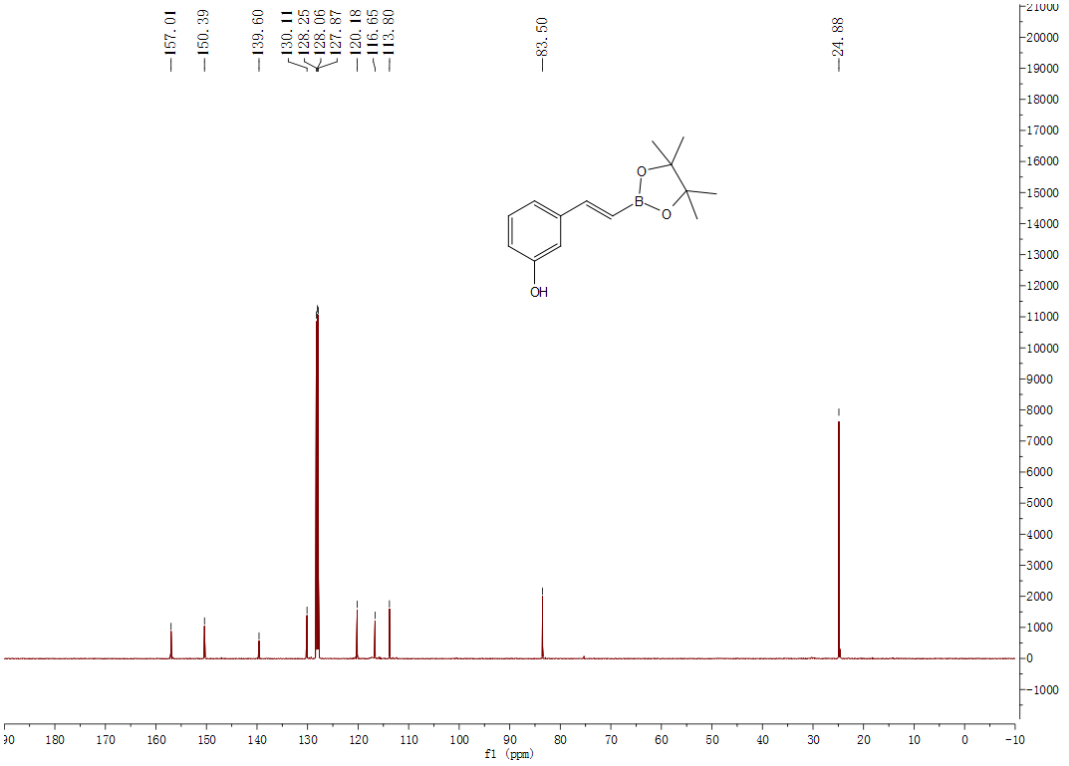
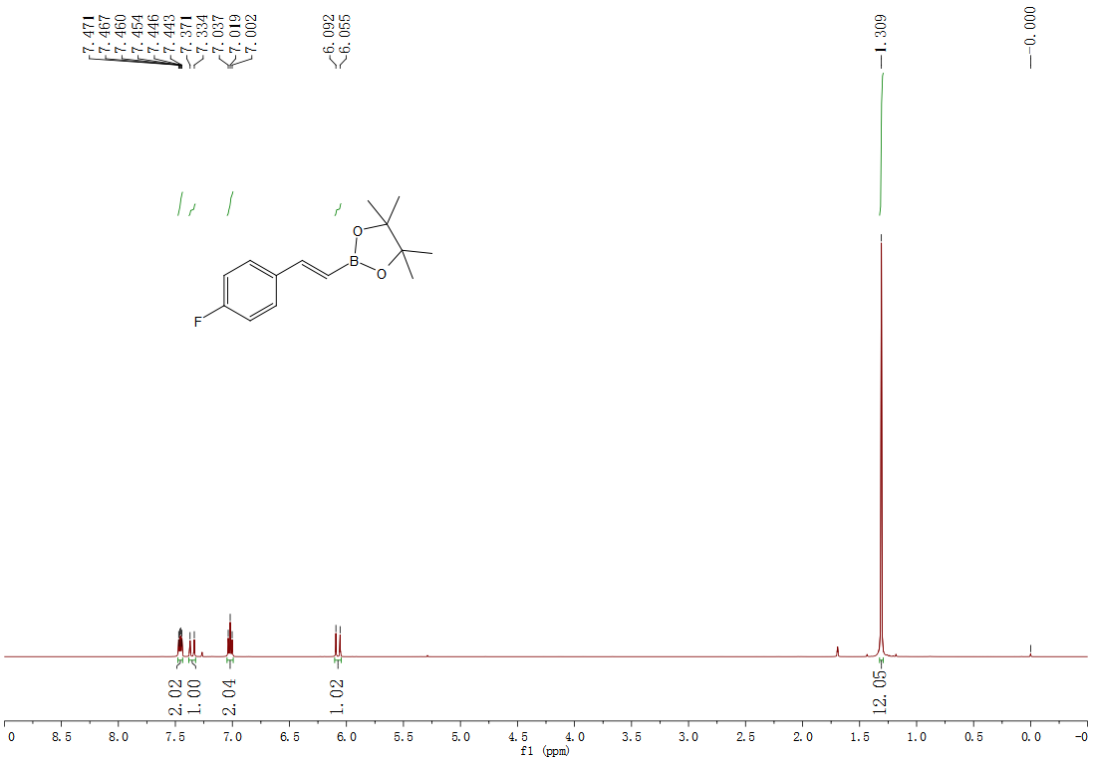


^{13}C NMR spectrum of **2h** (Benzene-*d*)



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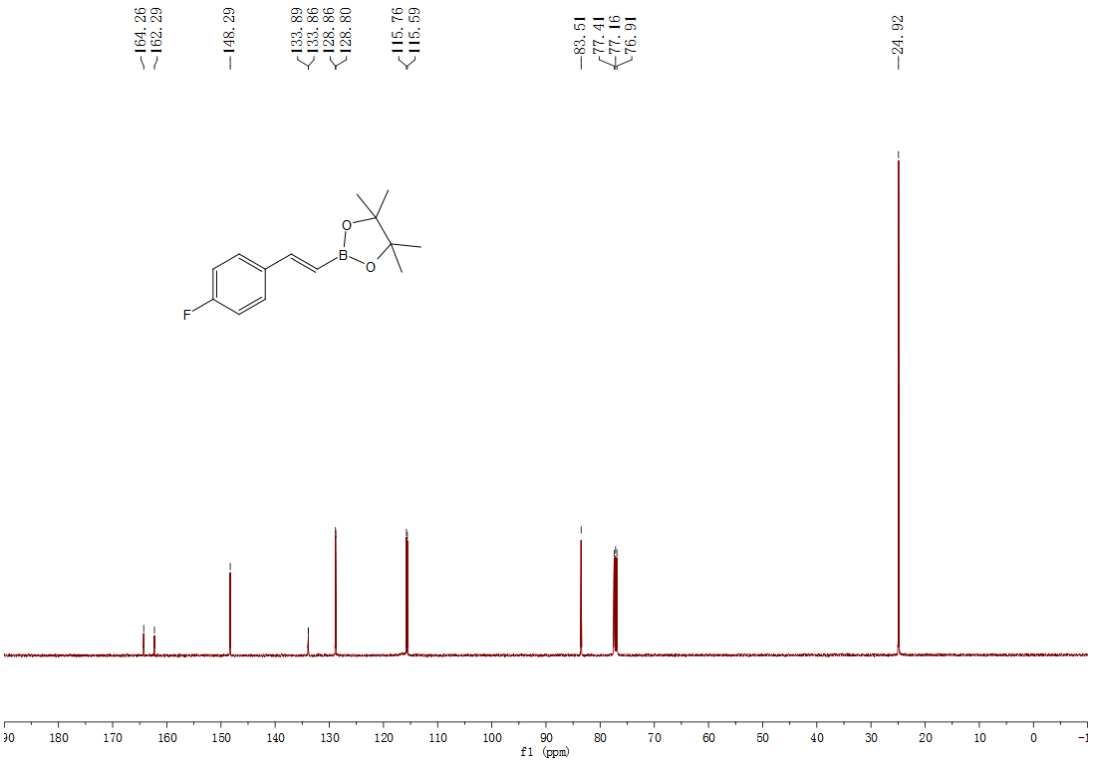

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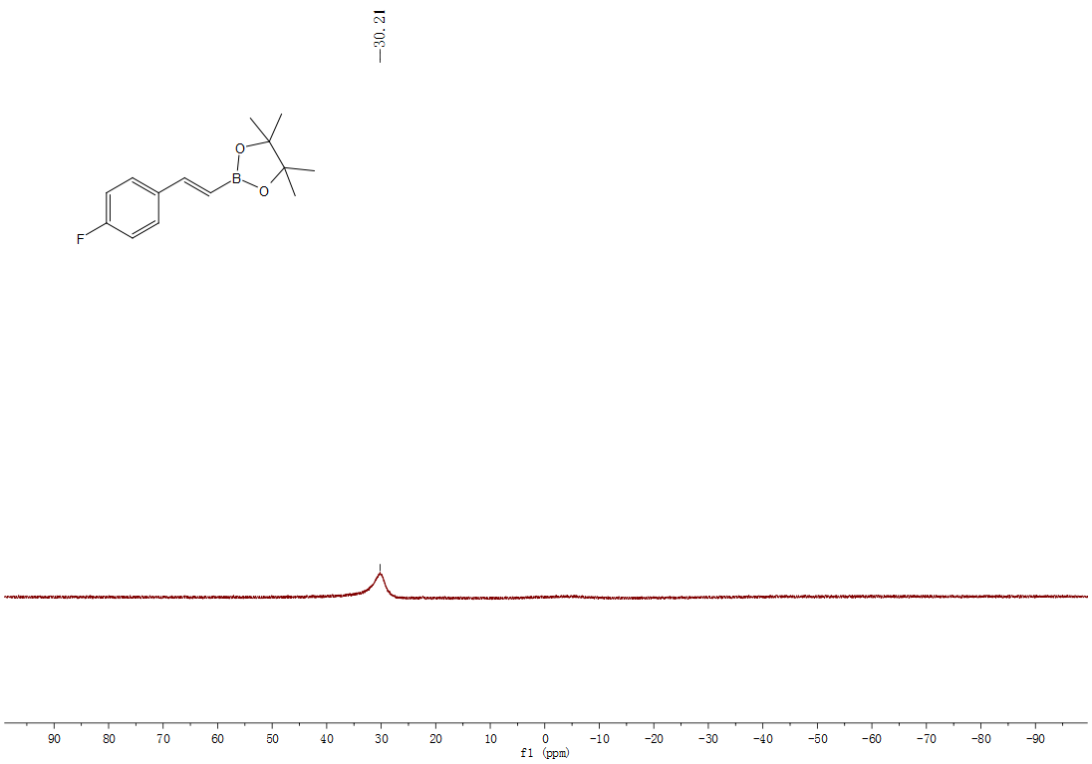
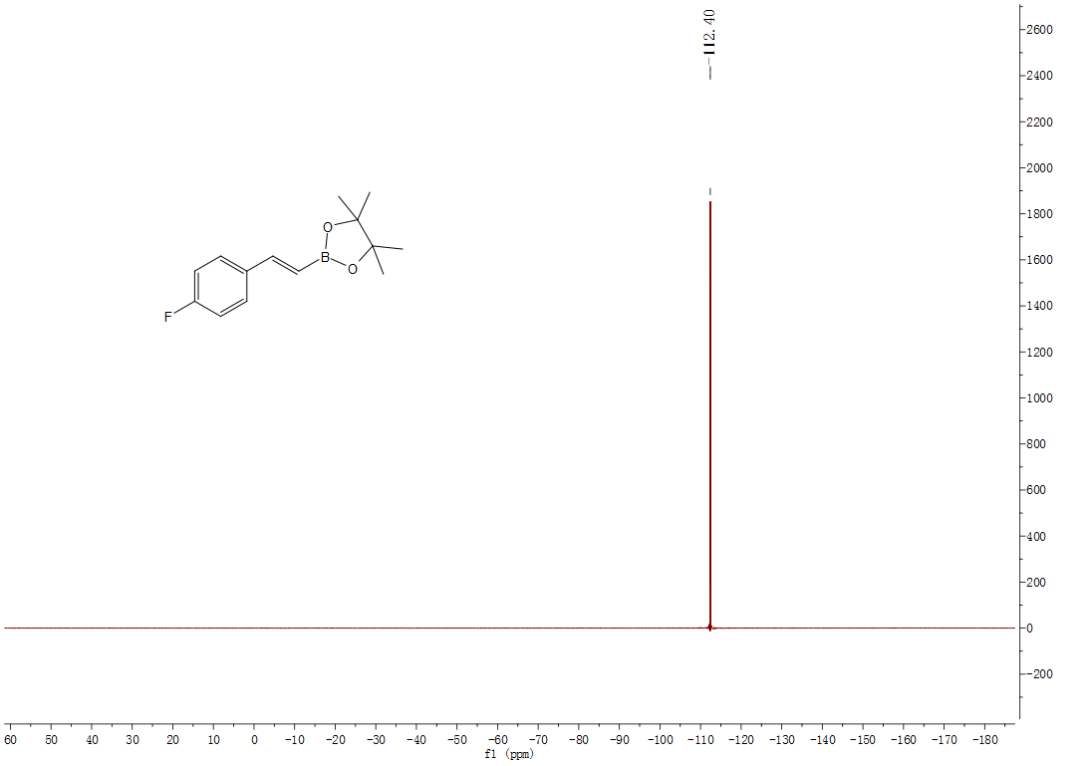
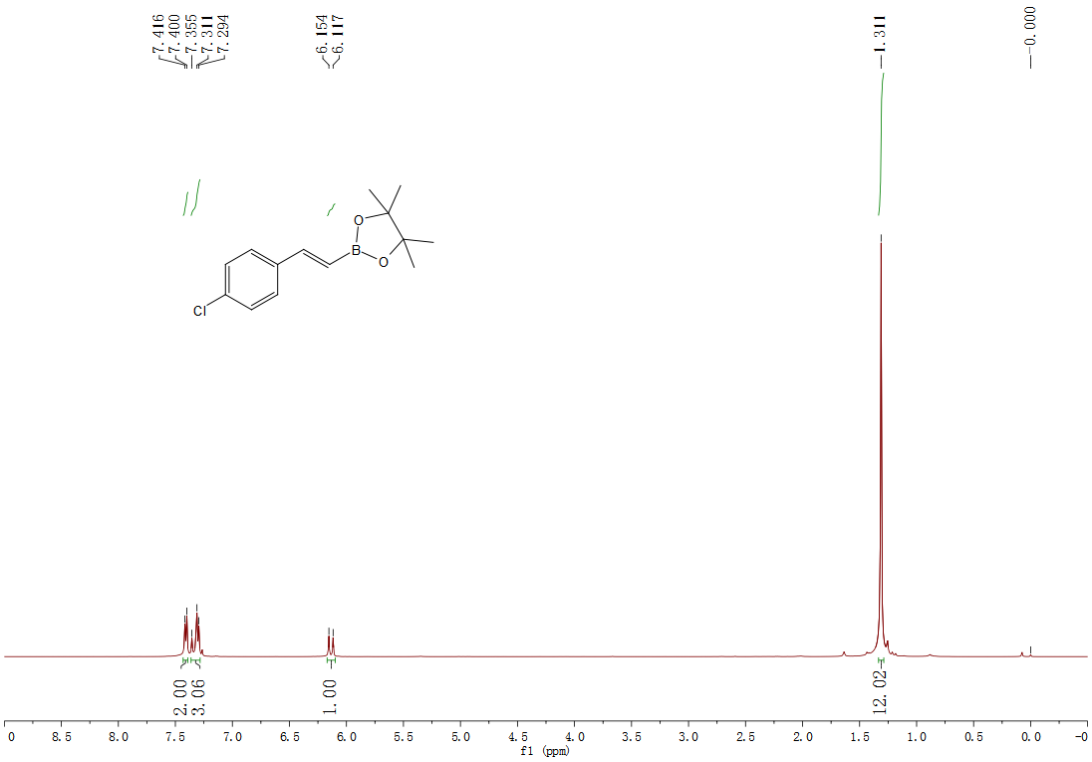


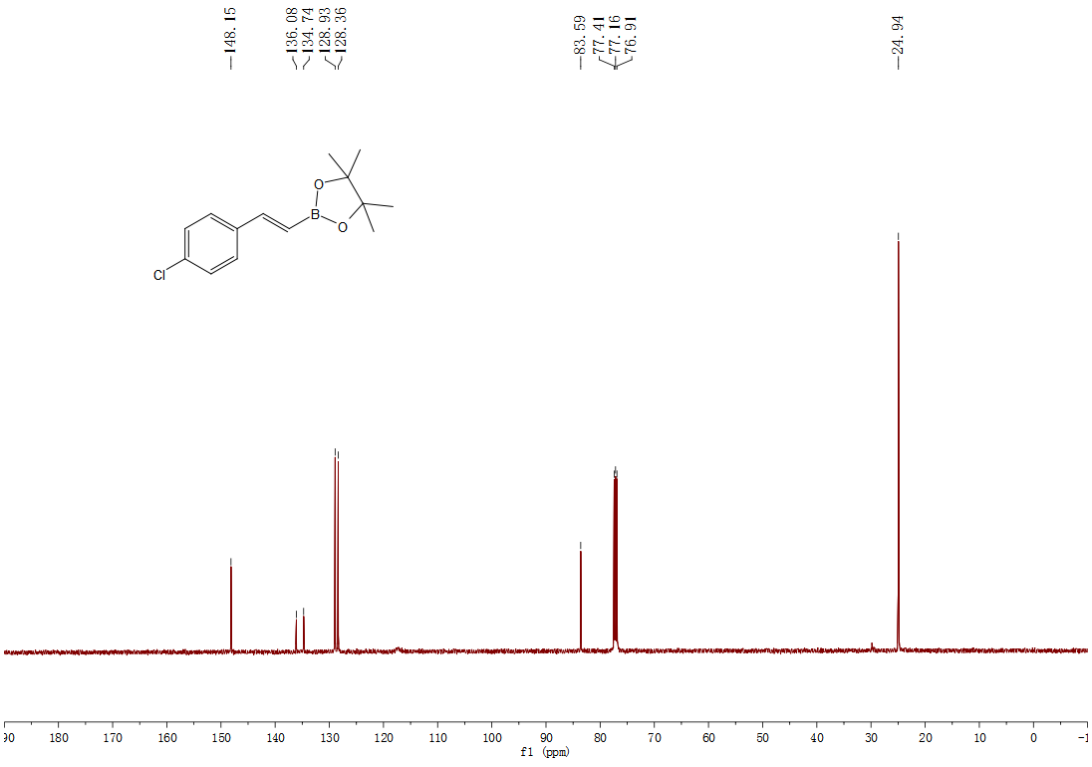
^{11}B NMR spectrum of **2j** (Chloroform-*d*)



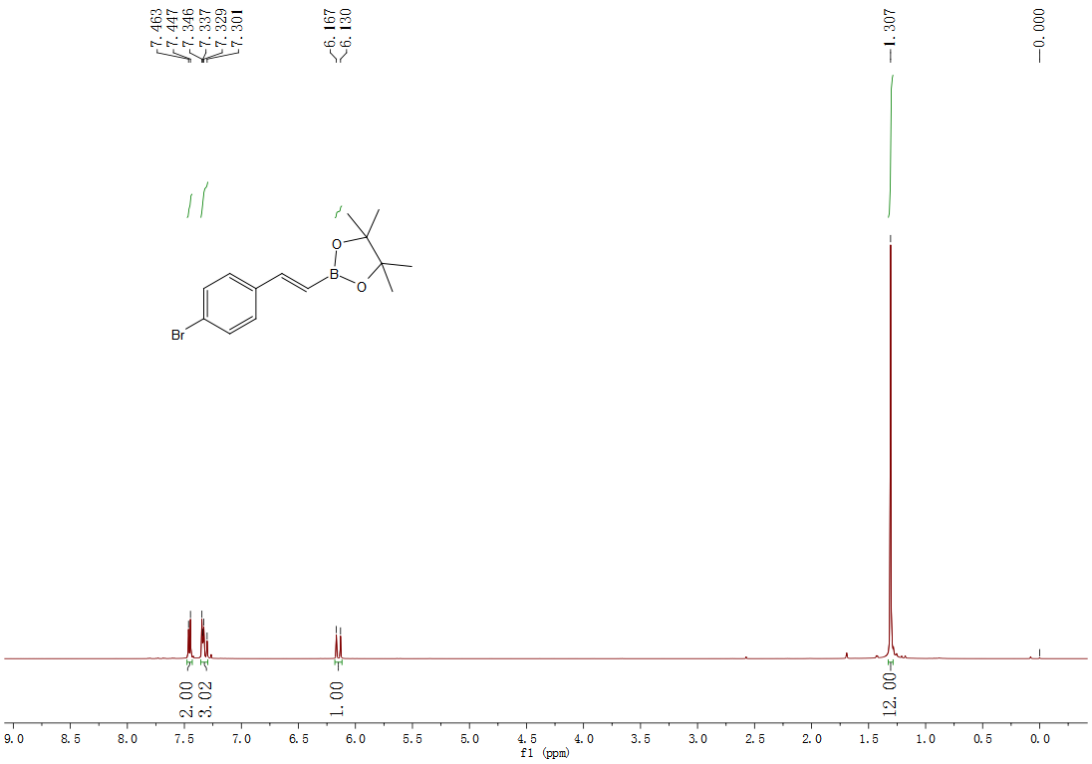
^{19}F NMR spectrum of **2j** (Chloroform-*d*)



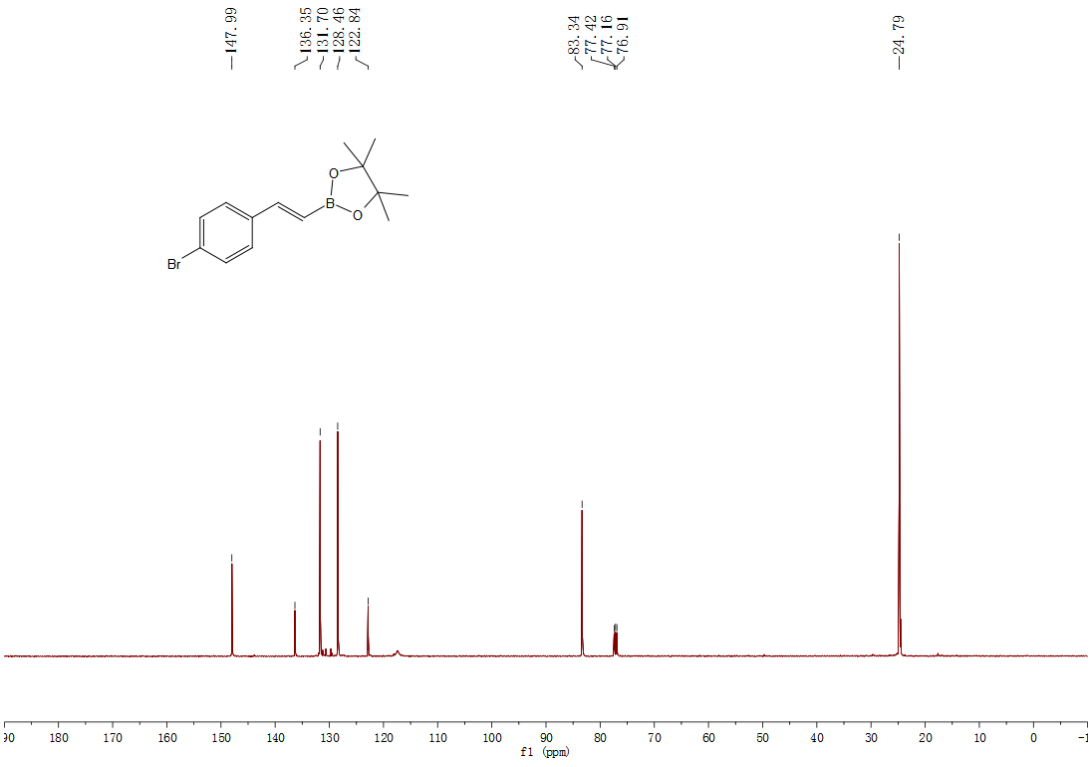
^{1}H NMR spectrum of **2k** (Chloroform-*d*)



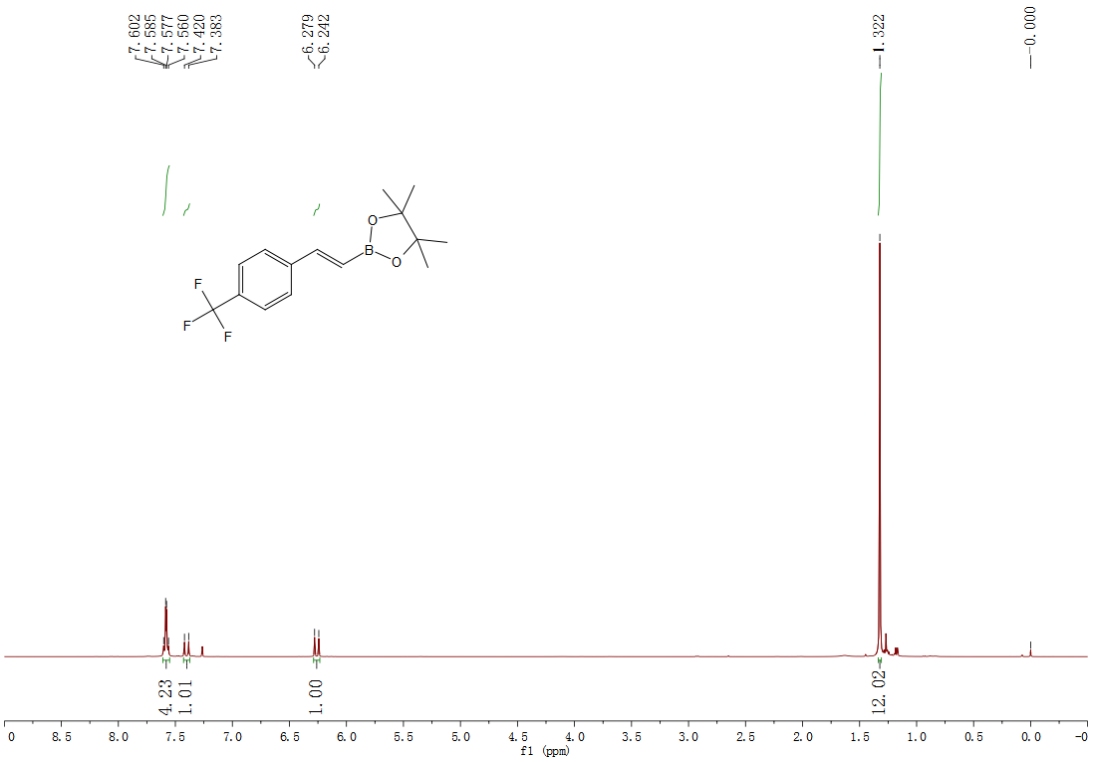
^{13}C NMR spectrum of **2k** (Chloroform-*d*)



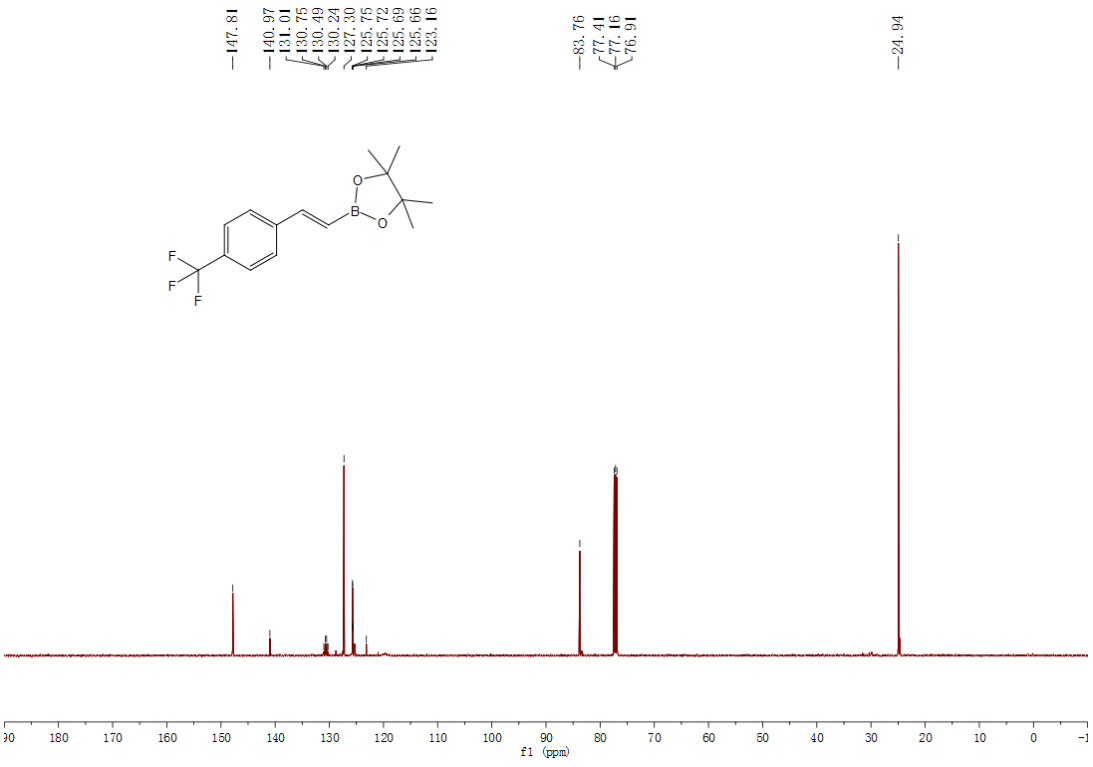
^{1}H NMR spectrum of **2l** (Chloroform-*d*)



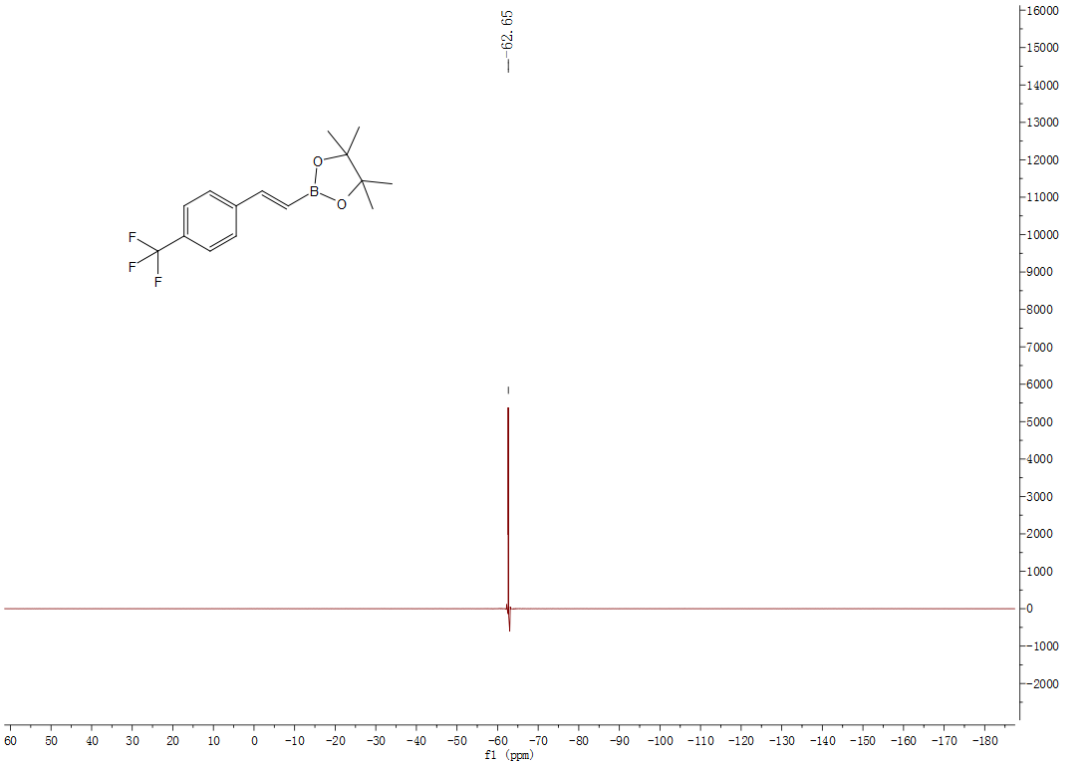
^{13}C NMR spectrum of **2l** (Chloroform-*d*)



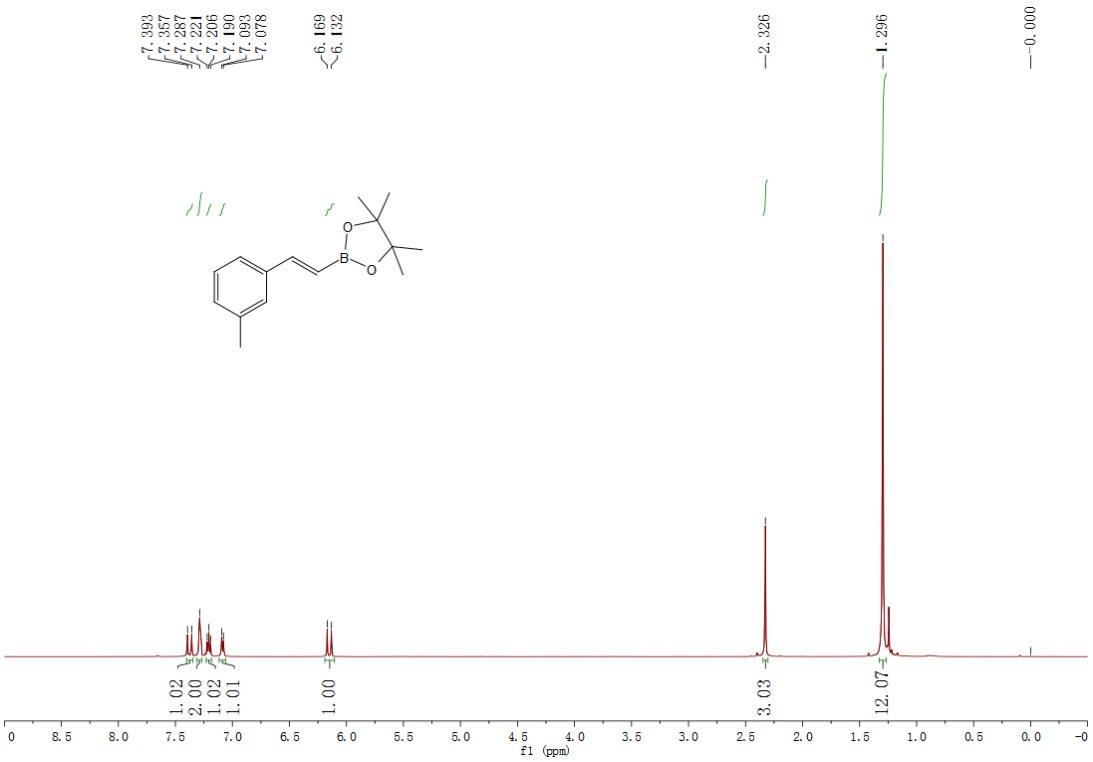
^{1}H NMR spectrum of **2m** (Chloroform-*d*)



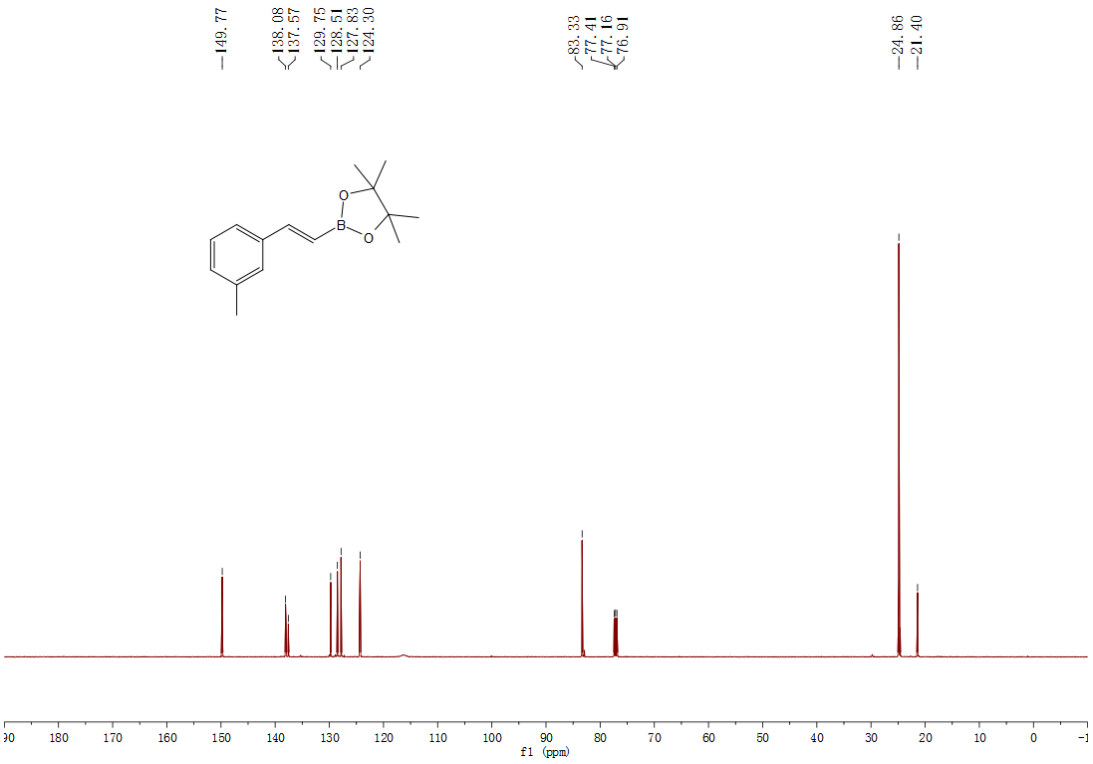
^{13}C NMR spectrum of **2m** (Chloroform-*d*)



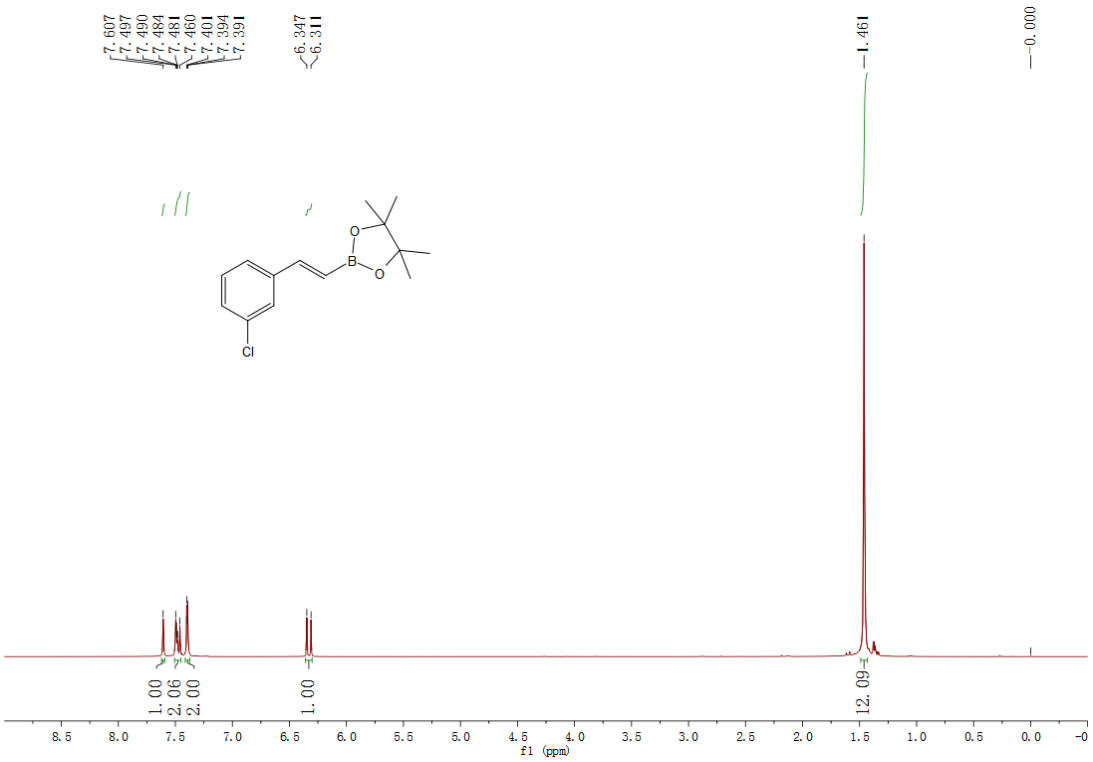
^{19}F NMR spectrum of **2m** (Chloroform-*d*)



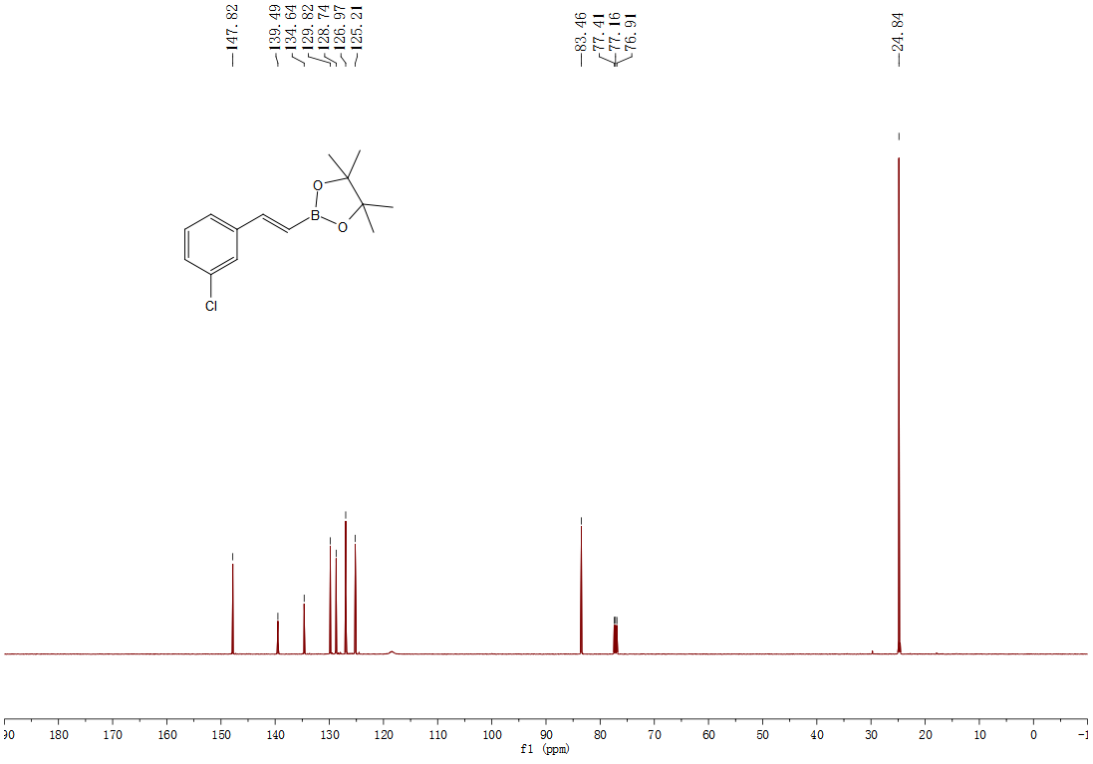
^{1}H NMR spectrum of **2n** (Chloroform-*d*)



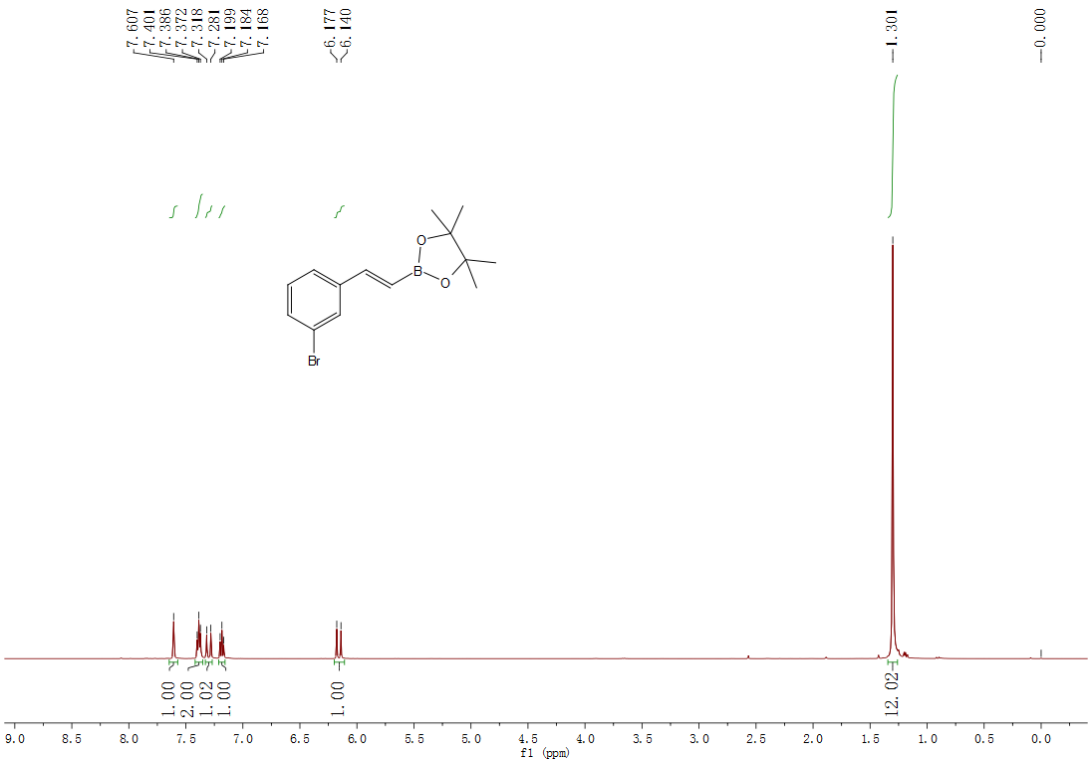
^{13}C NMR spectrum of **2n** (Chloroform-*d*)



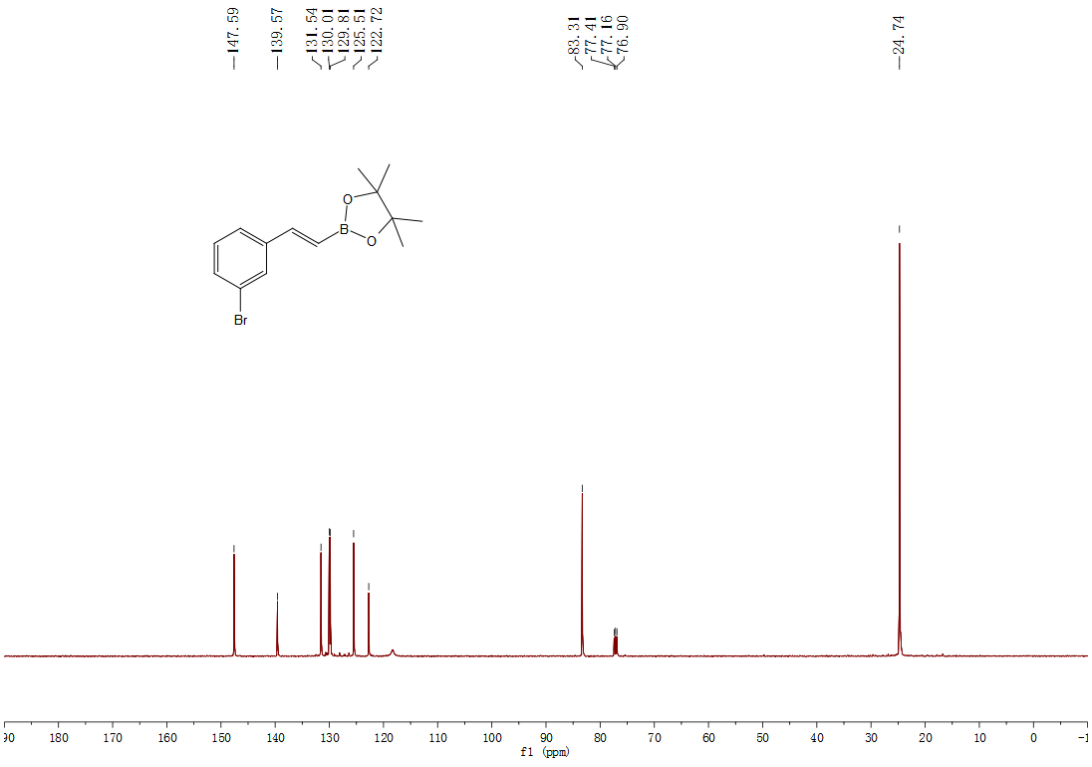
^{1}H NMR spectrum of **2o** (Chloroform-*d*)



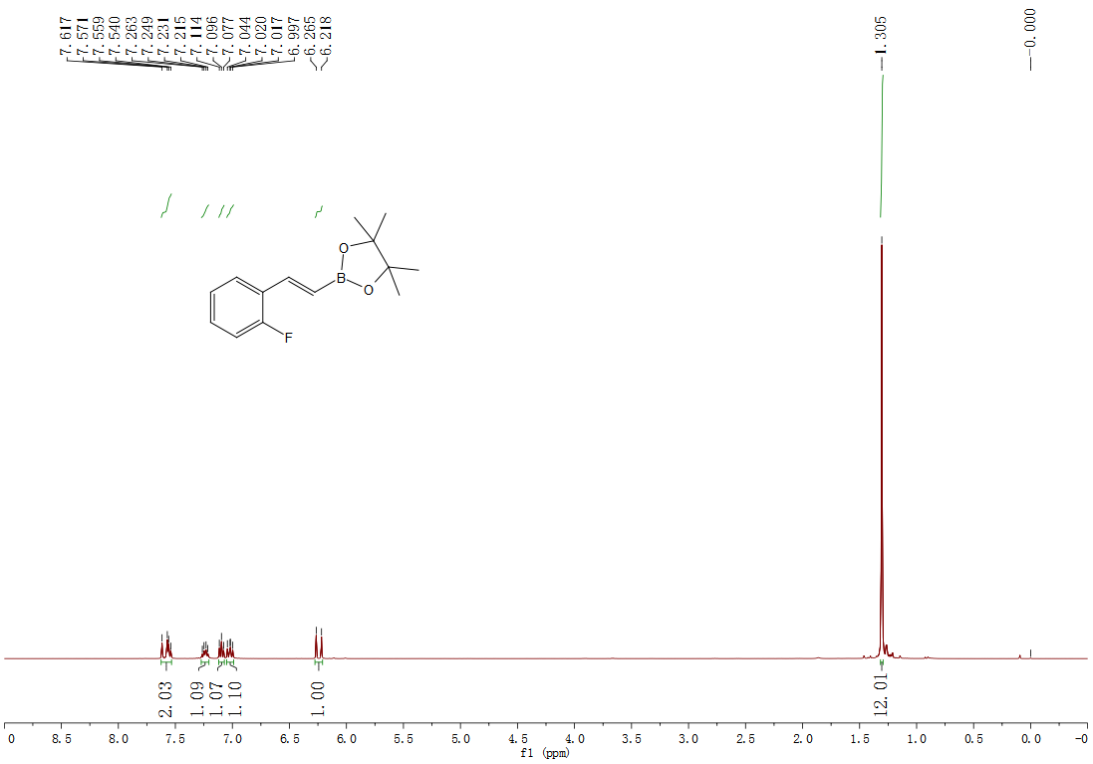
^{13}C NMR spectrum of **2o** (Chloroform-*d*)



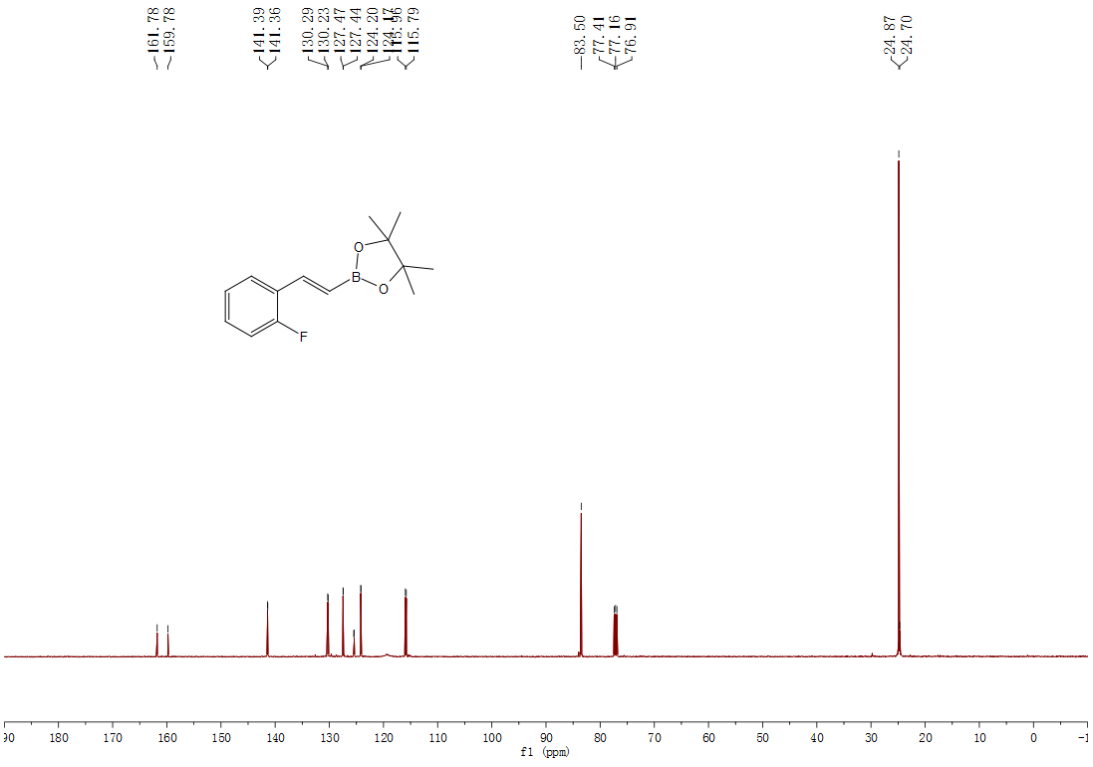
^{1}H NMR spectrum of **2p** (Chloroform-*d*)



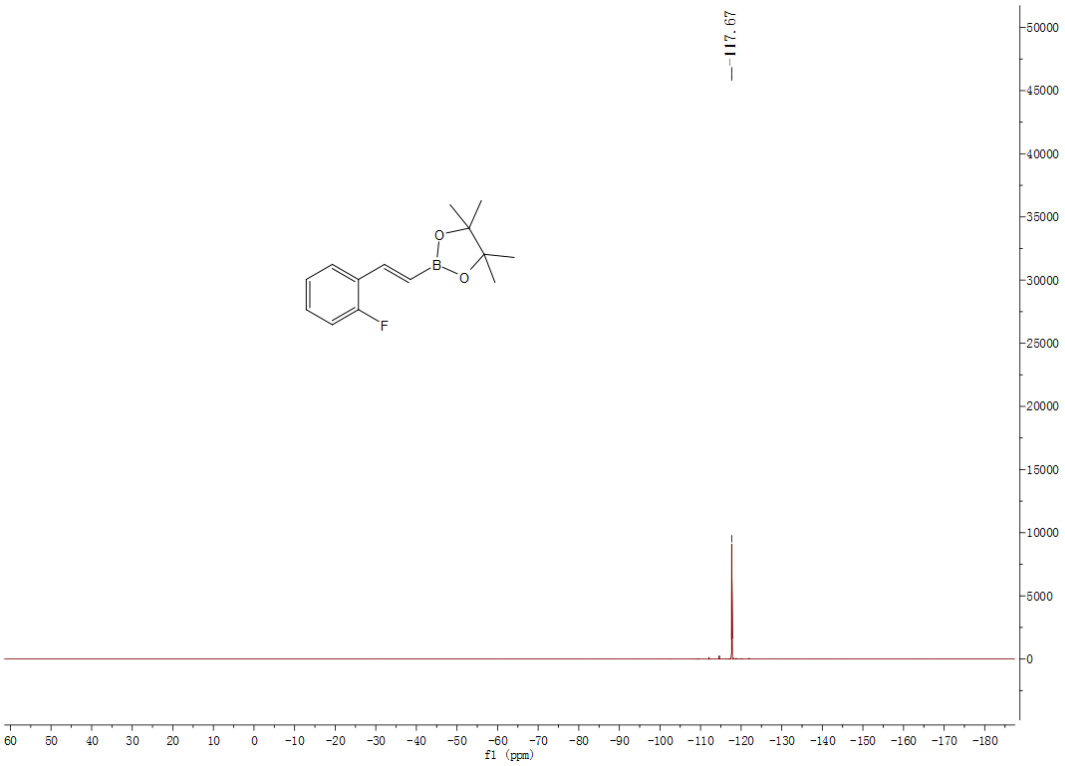
^{13}C NMR spectrum of **2p** (Chloroform-*d*)



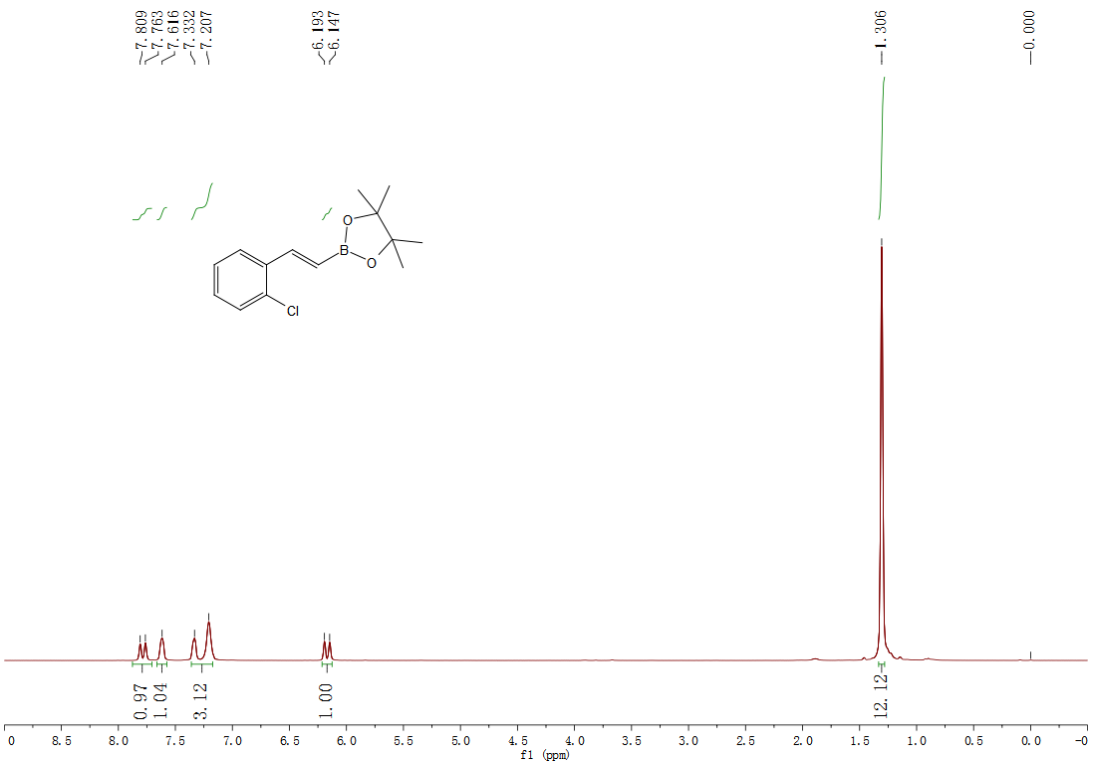
^{1}H NMR spectrum of **2q** (Chloroform-*d*)



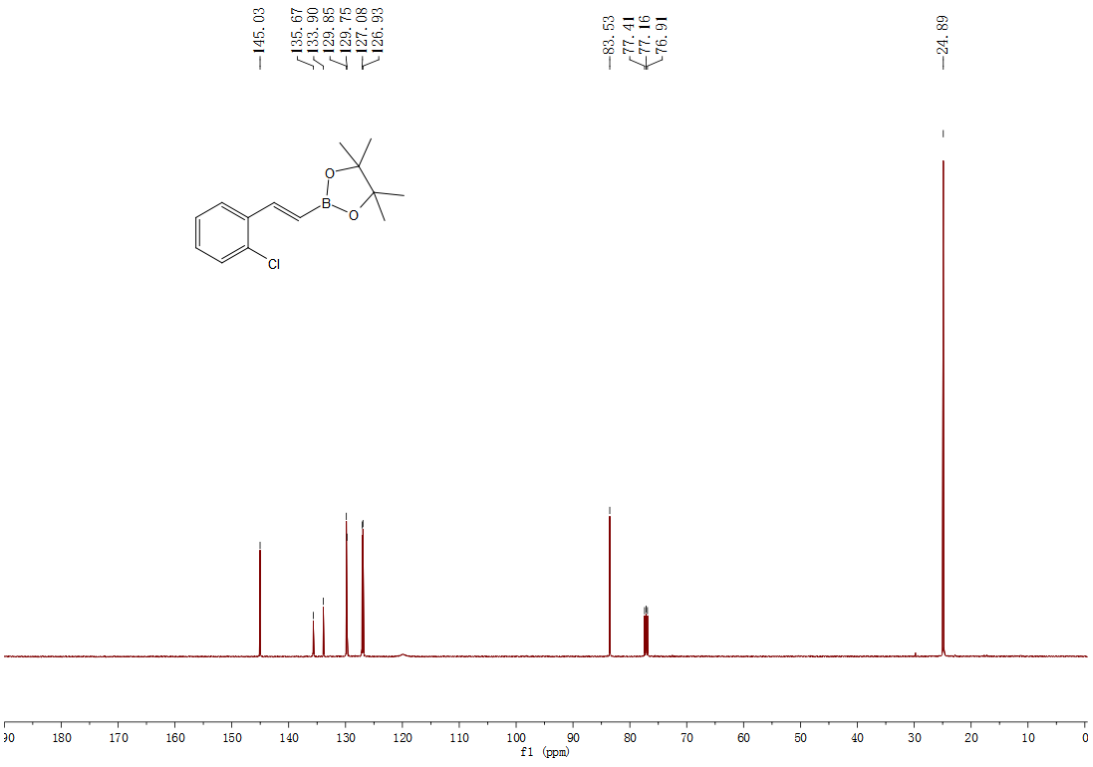
^{13}C NMR spectrum of **2q** (Chloroform-*d*)



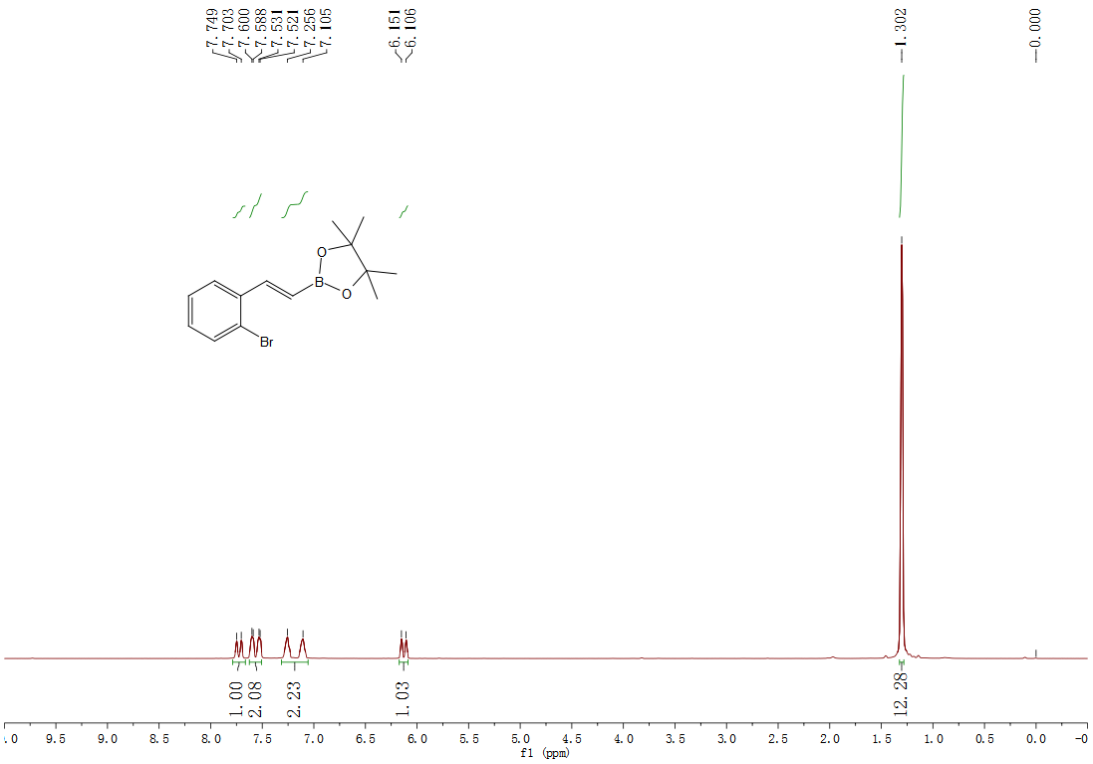
^{19}F NMR spectrum of **2q** (Chloroform-*d*)



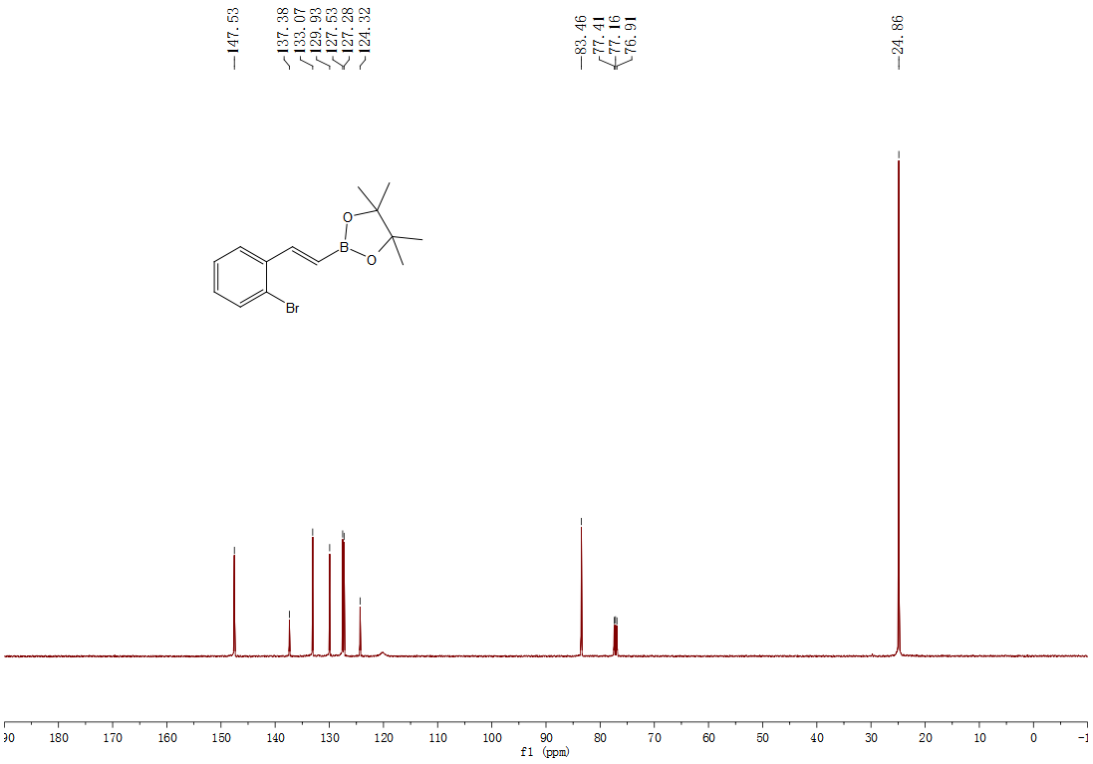
^{1}H NMR spectrum of **2r** (Chloroform-*d*)



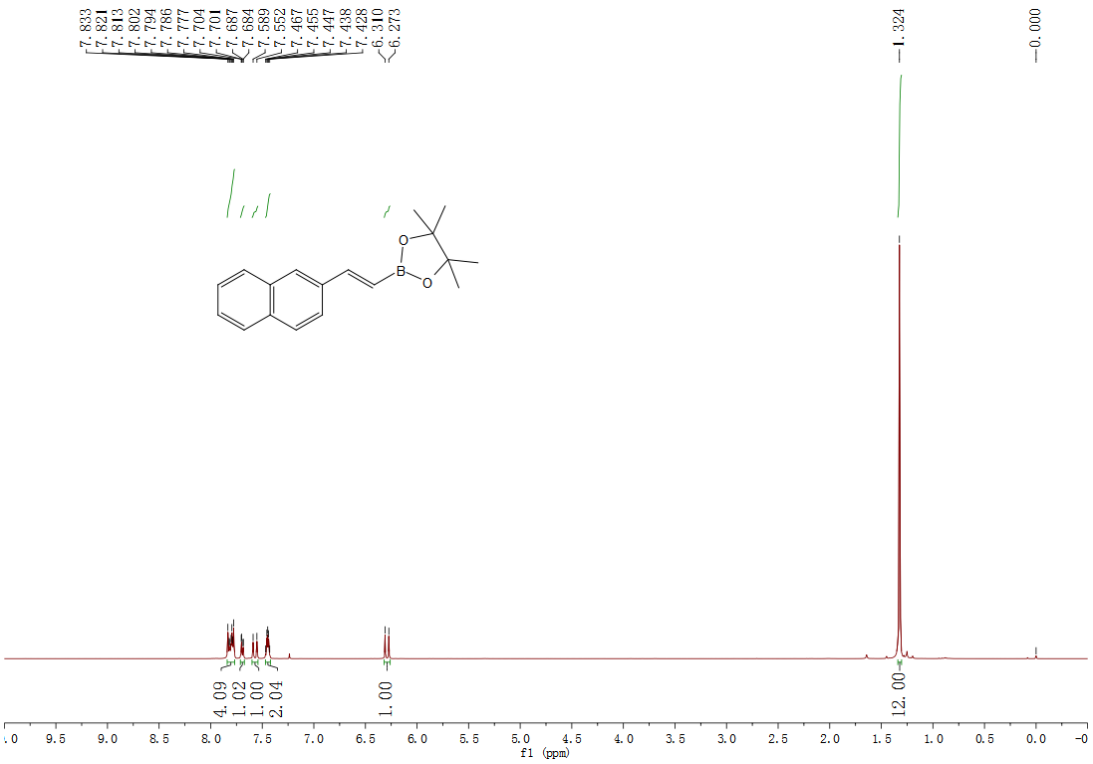
^{13}C NMR spectrum of **2r** (Chloroform-*d*)



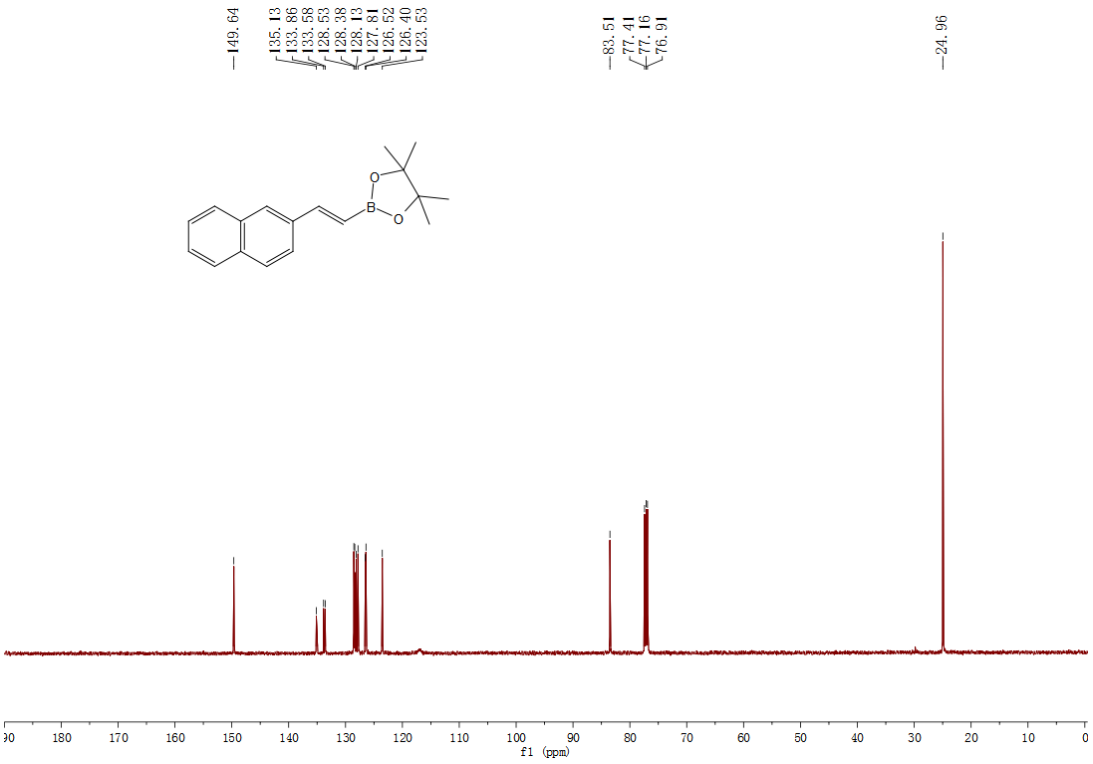
^{1}H NMR spectrum of **2s** (Chloroform-*d*)



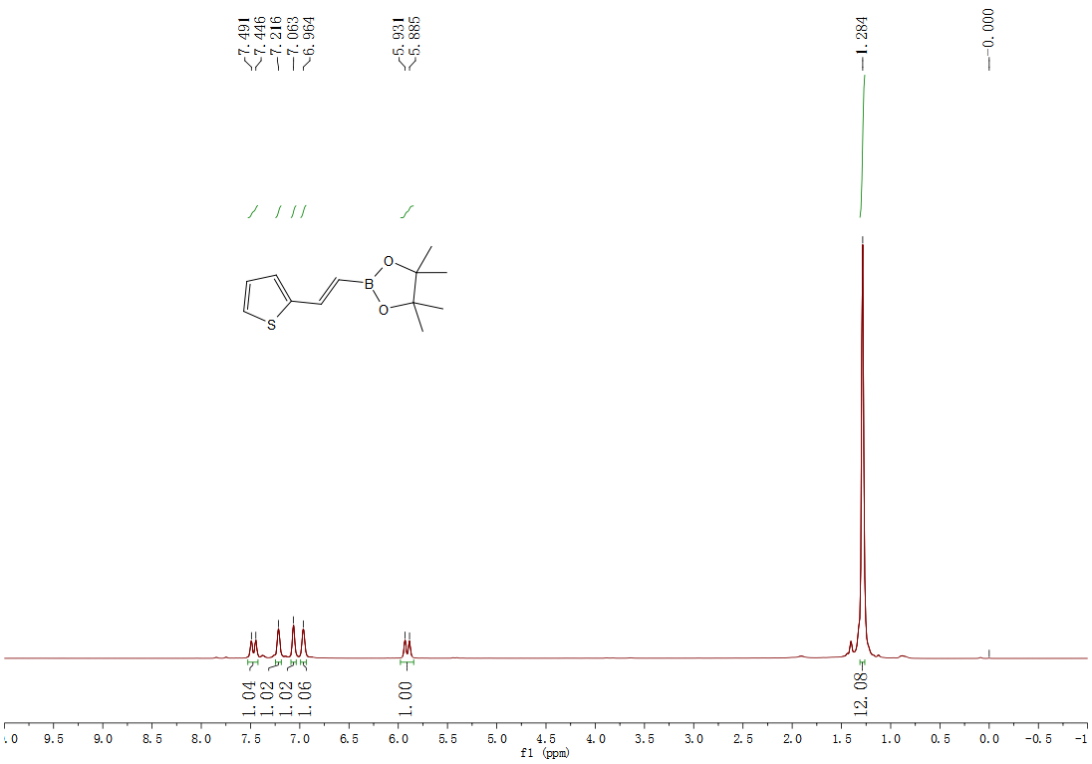
^{13}C NMR spectrum of **2s** (Chloroform-*d*)



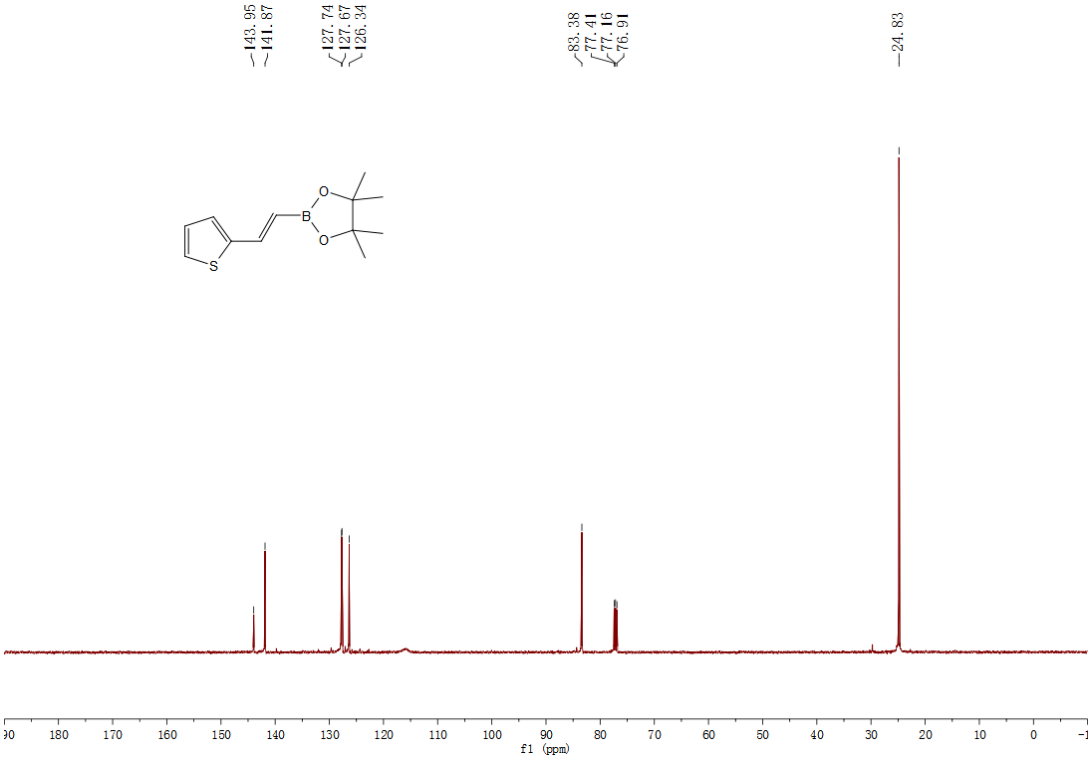
^{1}H NMR spectrum of **2t** (Chloroform-*d*)



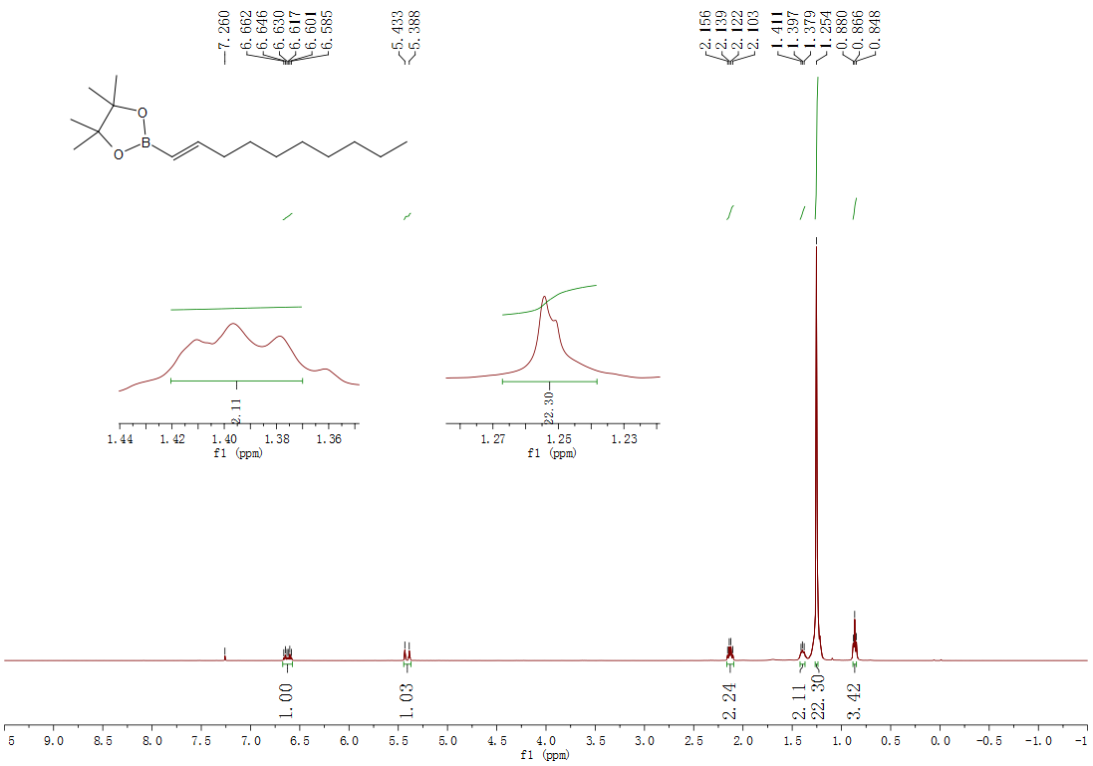
^{13}C NMR spectrum of **2t** (Chloroform-*d*)



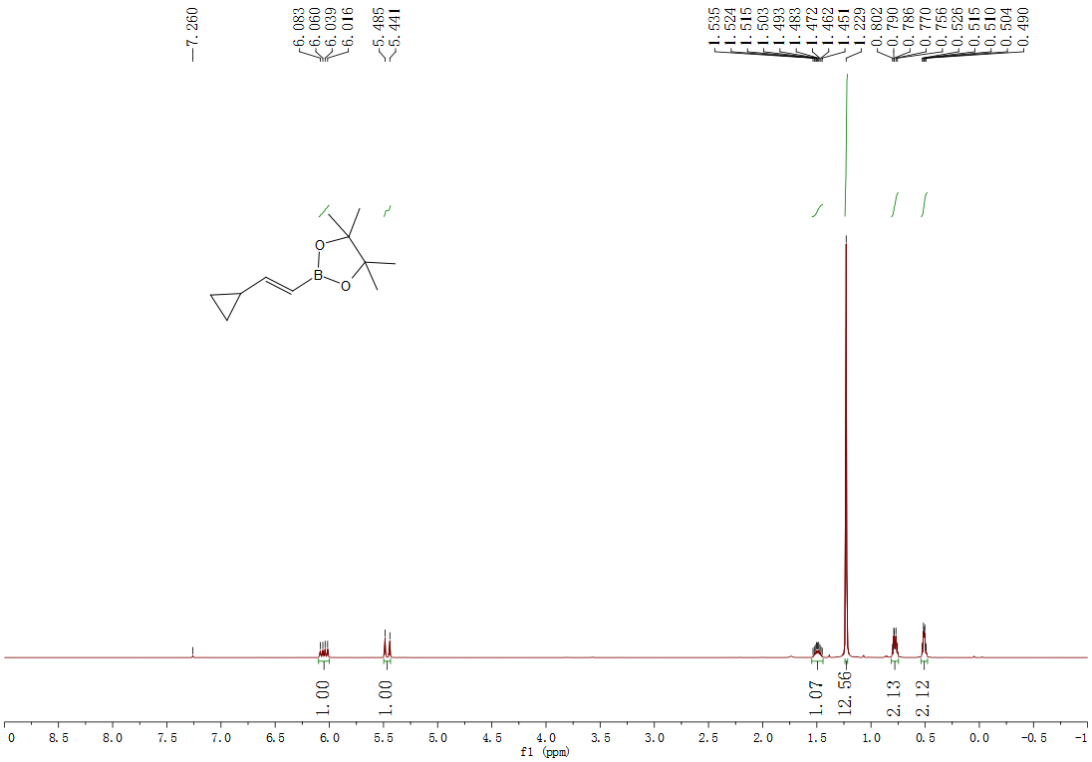
^{1}H NMR spectrum of **2u** (Chloroform-*d*)



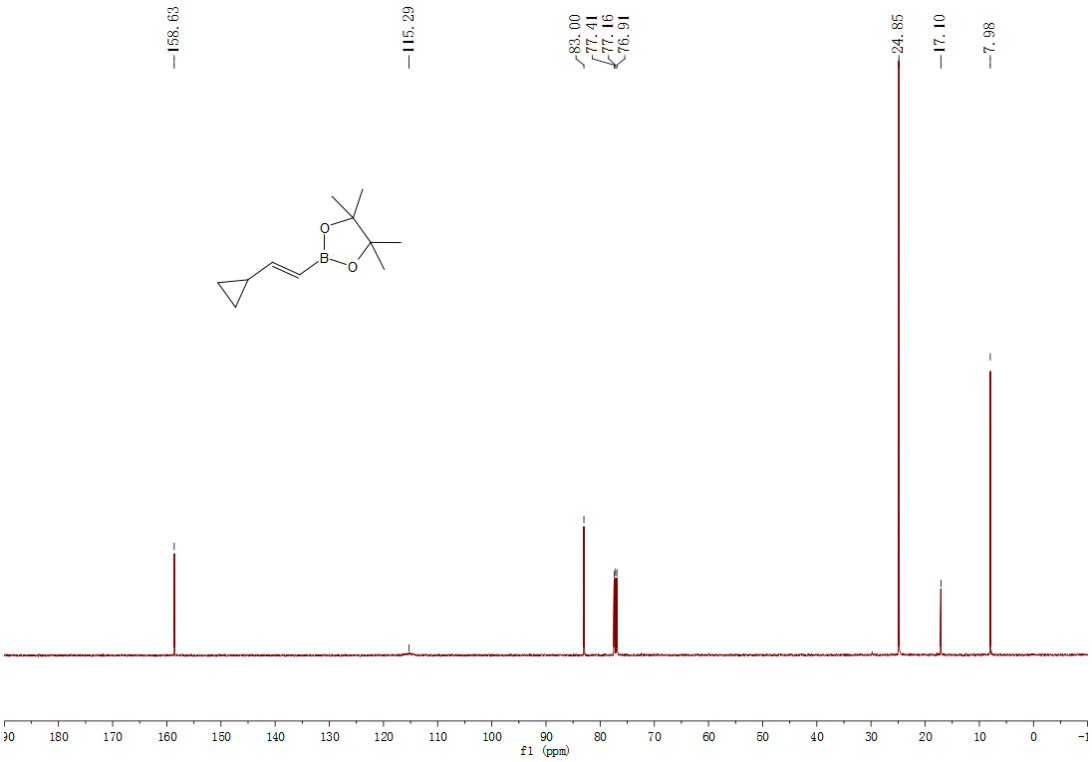
^{13}C NMR spectrum of **2u** (Chloroform-*d*)



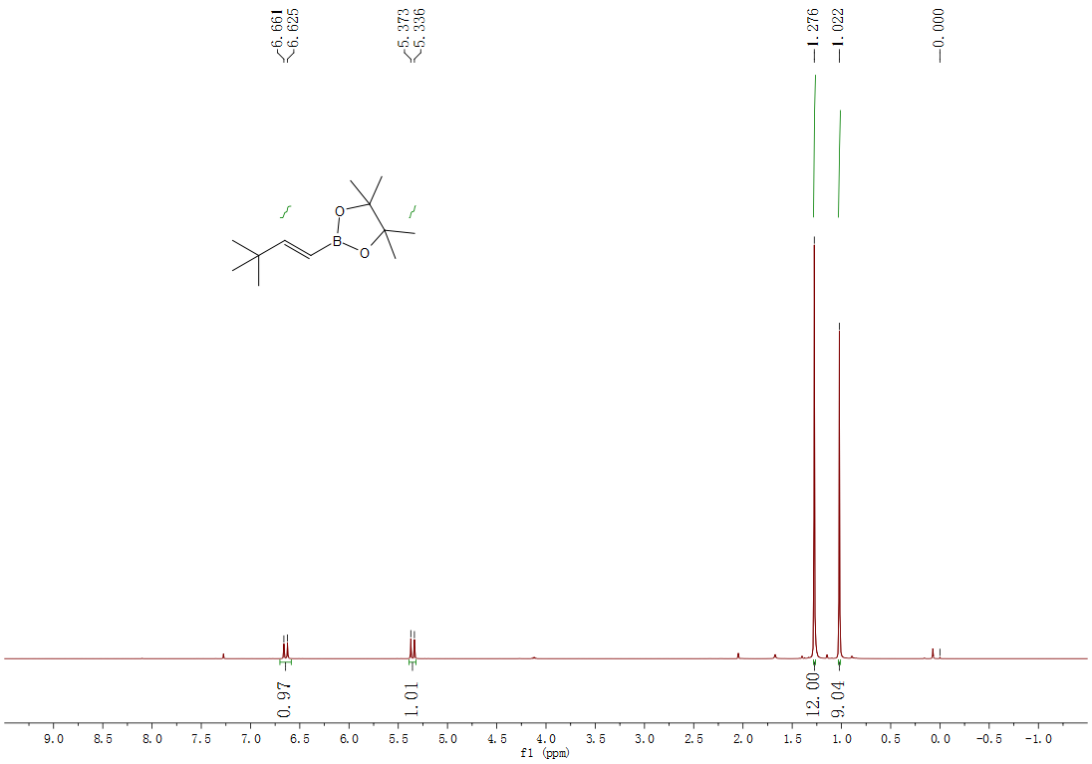
^{1}H NMR spectrum of **2v** (Chloroform-*d*)



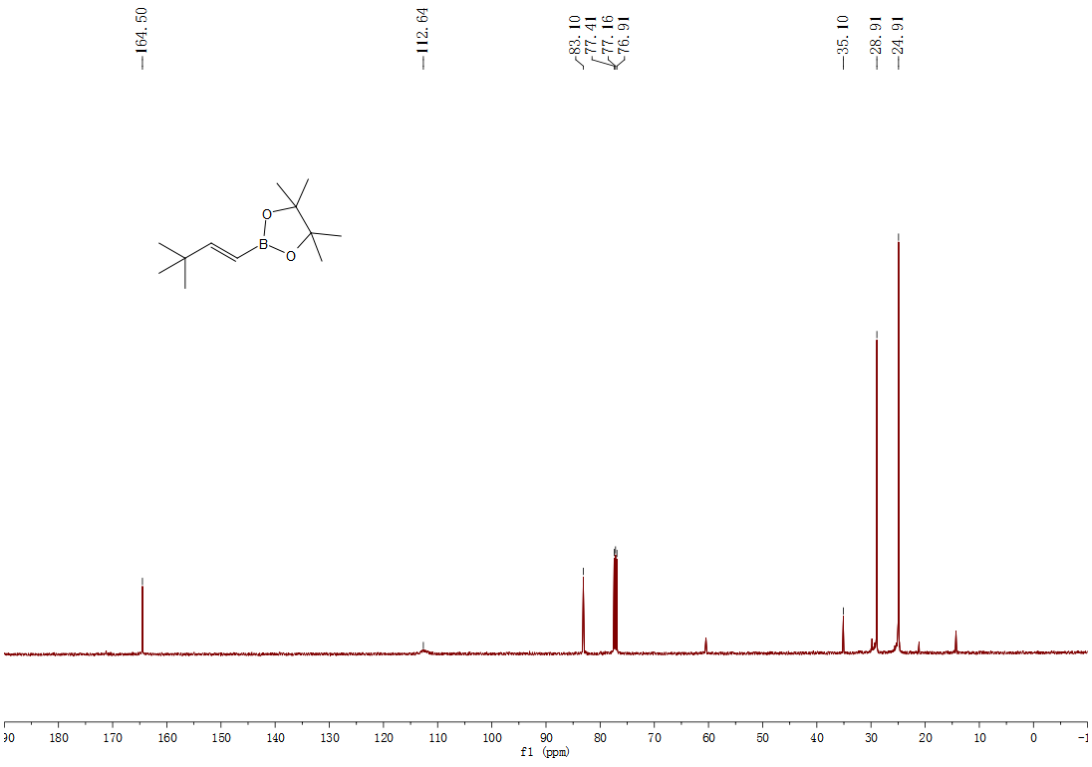
^{1}H NMR spectrum of **2w** (Chloroform-*d*)



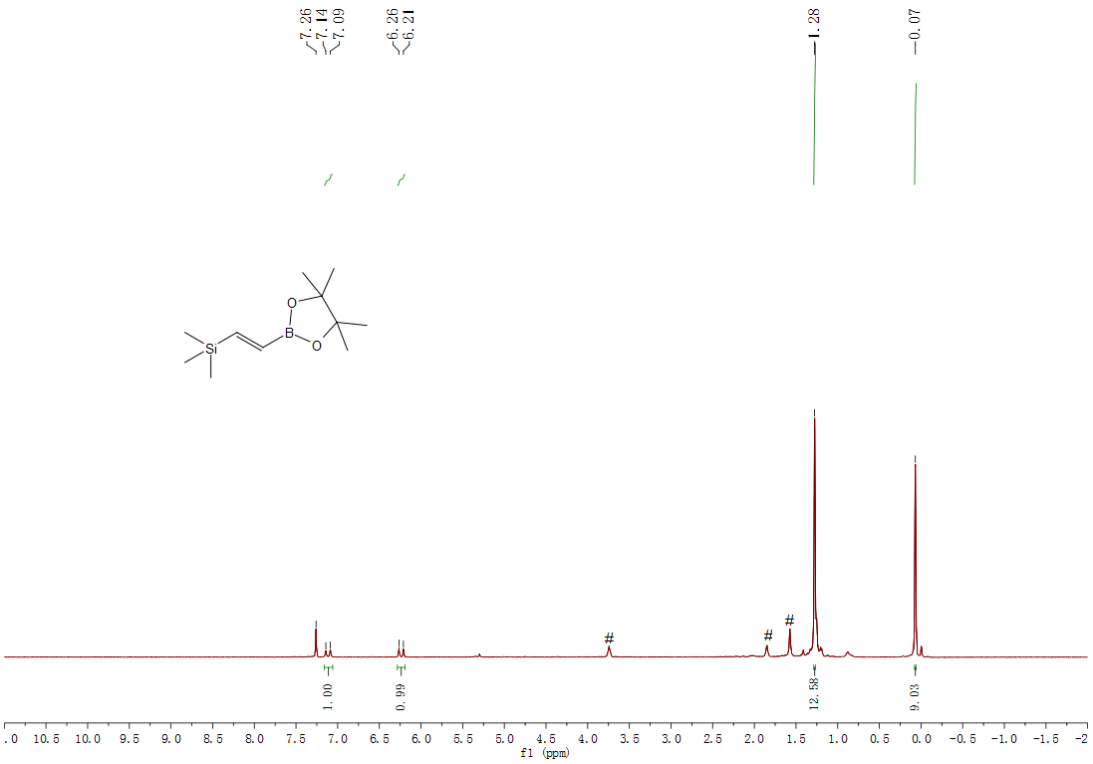
^{13}C NMR spectrum of **2w** (Chloroform-*d*)



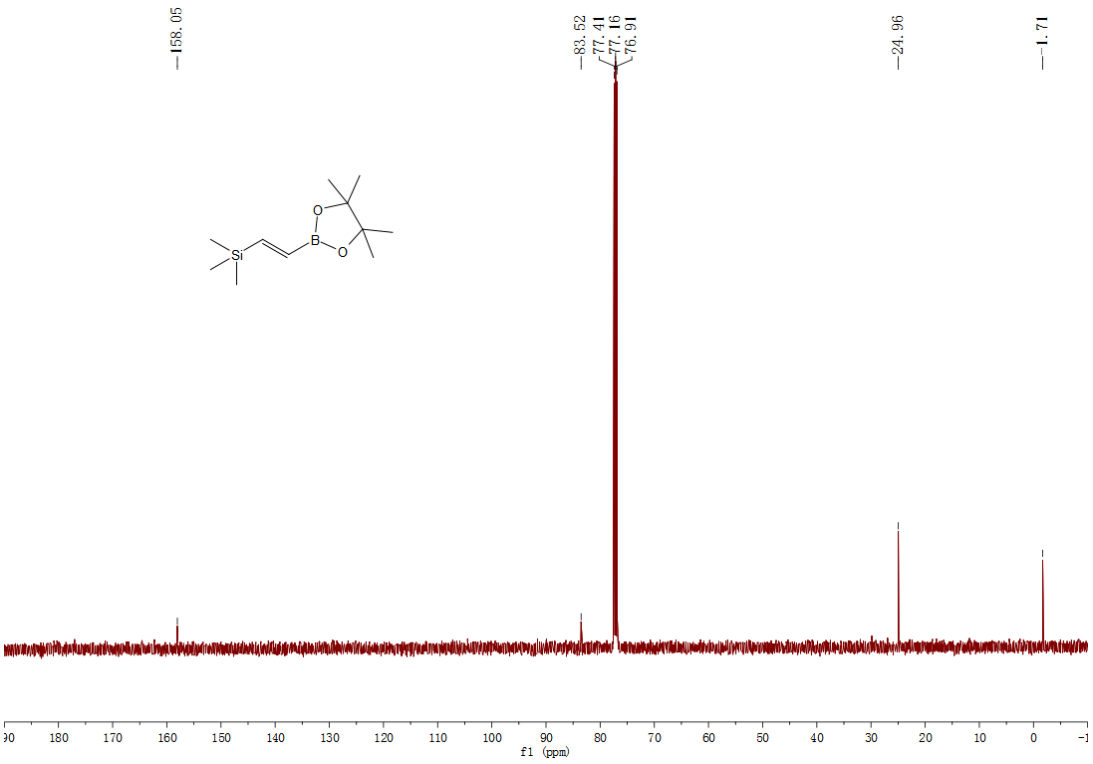
^{1}H NMR spectrum of **2x** (Chloroform-*d*)



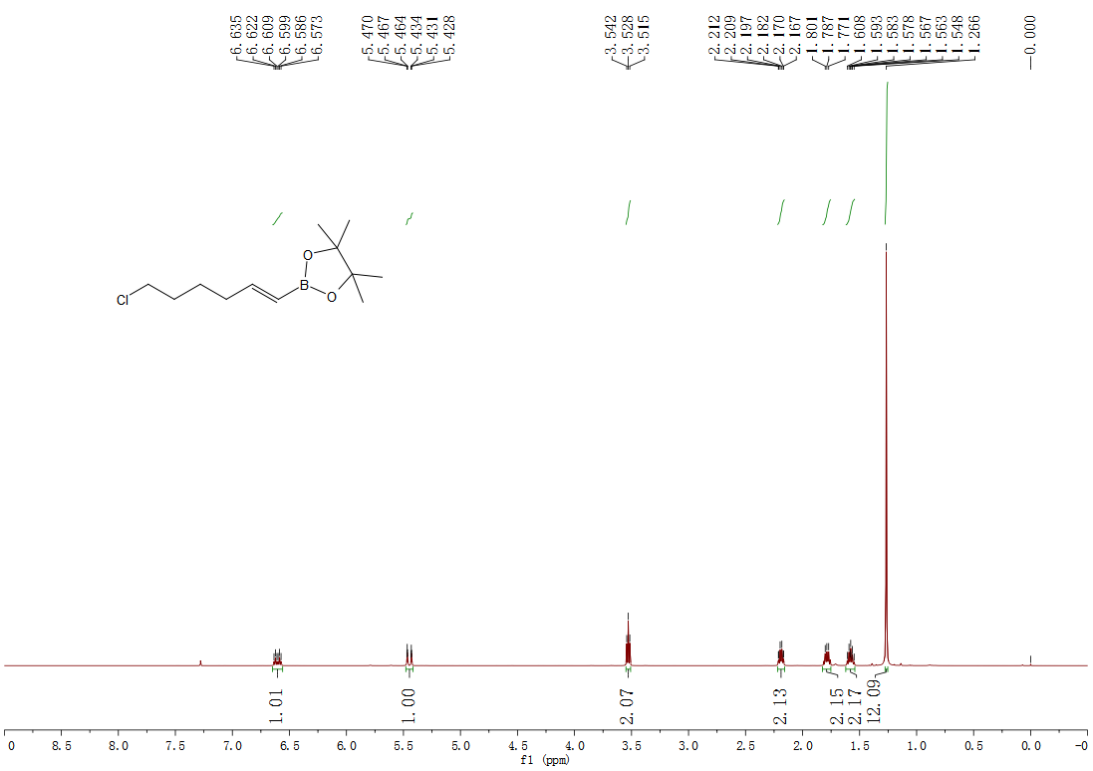
^{13}C NMR spectrum of **2x** (Chloroform-*d*)



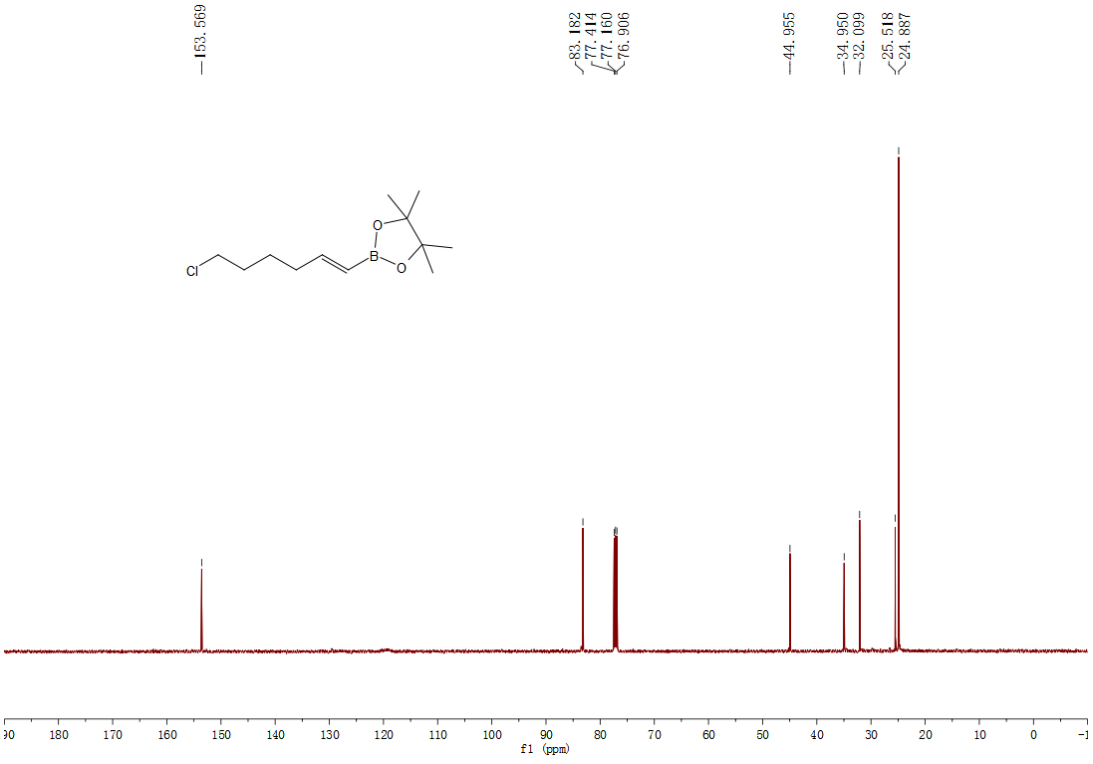
^{1}H NMR spectrum of **2y** (Chloroform-*d*)



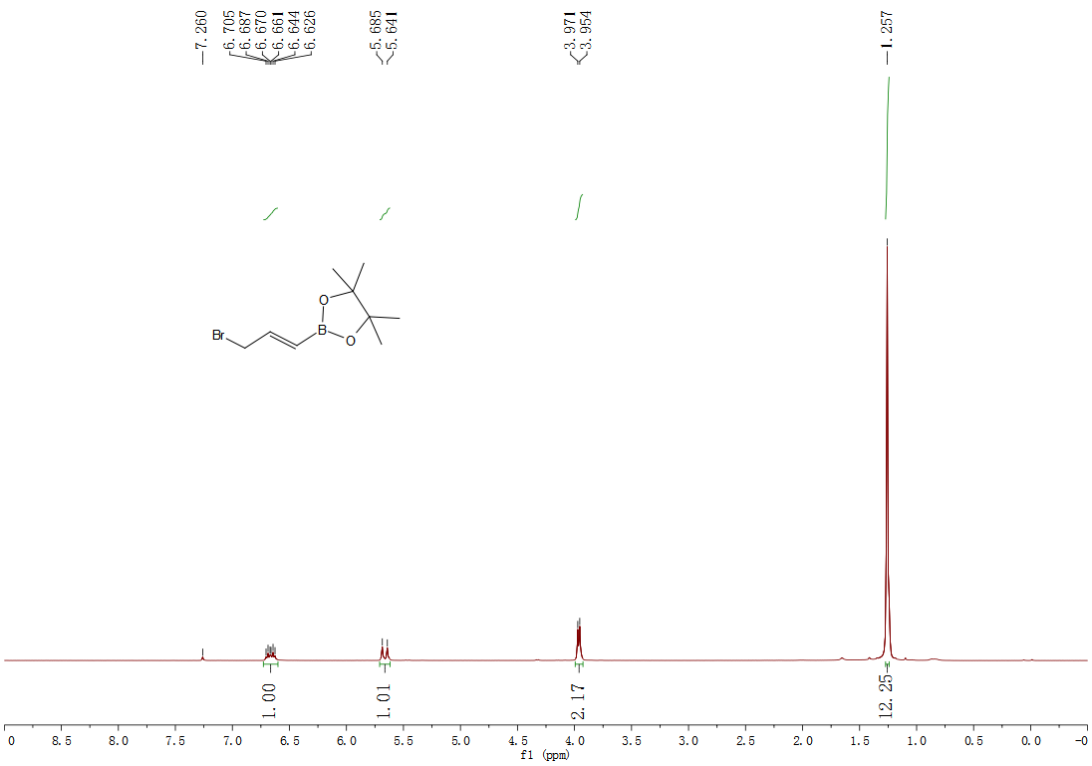
^{13}C NMR spectrum of **2y** (Chloroform-*d*)



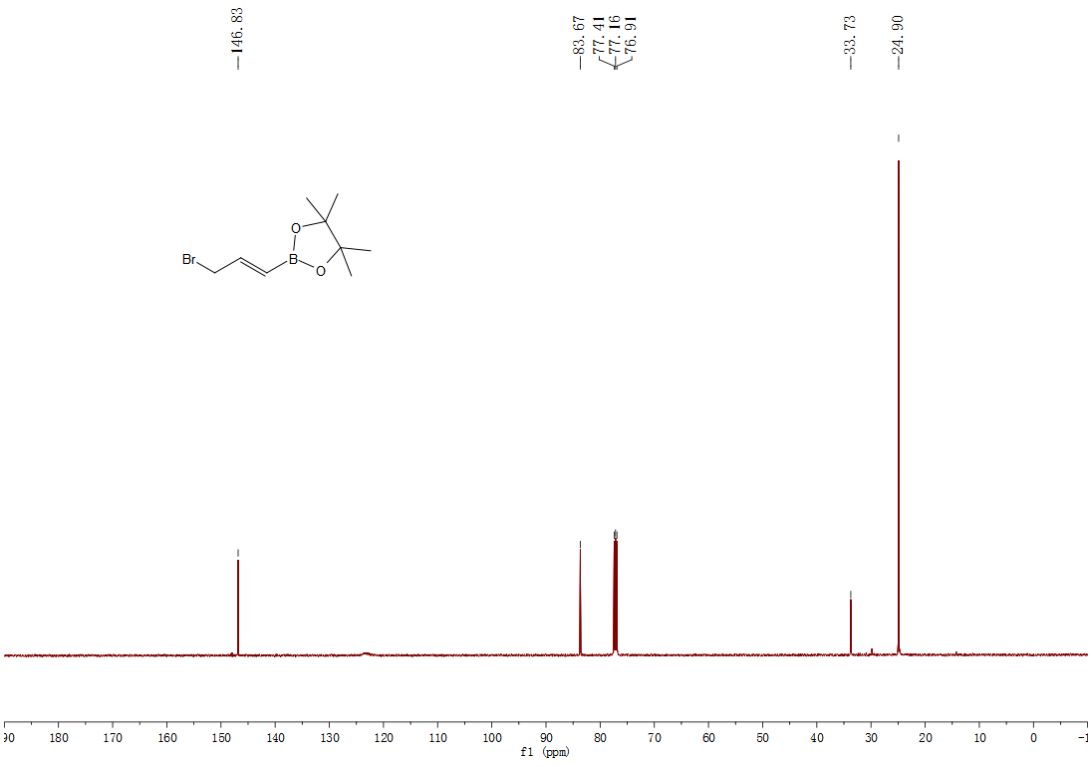
^{1}H NMR spectrum of **2z** (Chloroform-*d*)



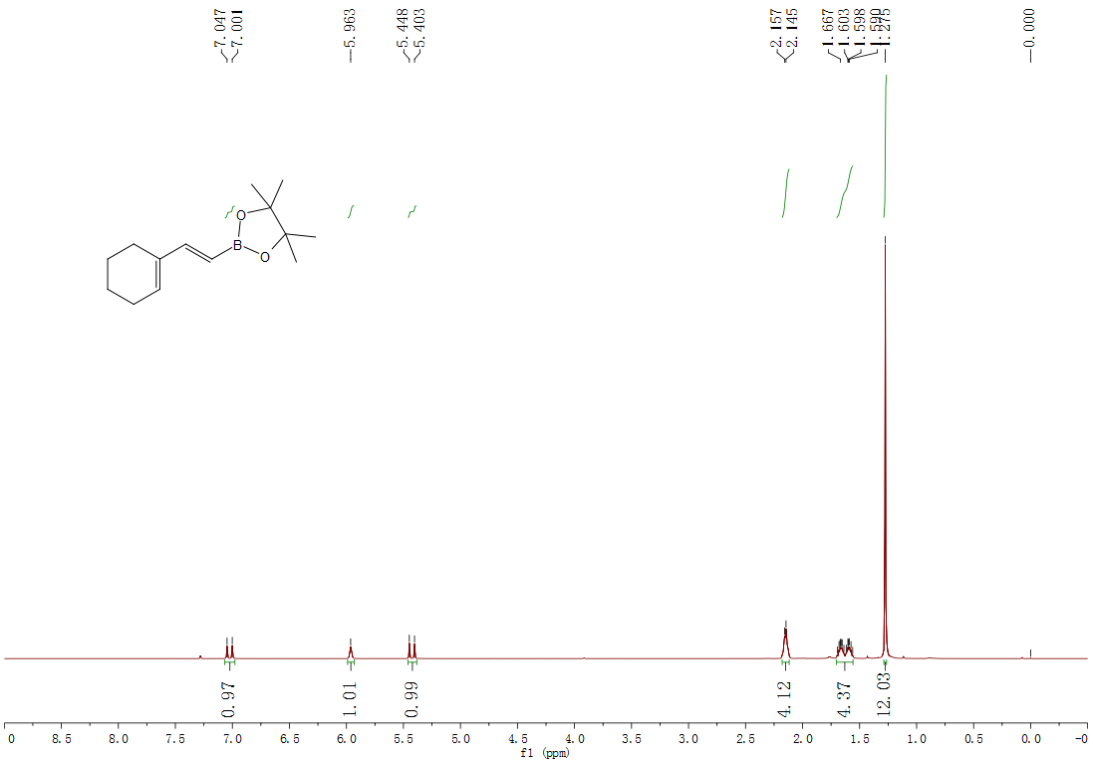
^{13}C NMR spectrum of **2z** (Chloroform-*d*)



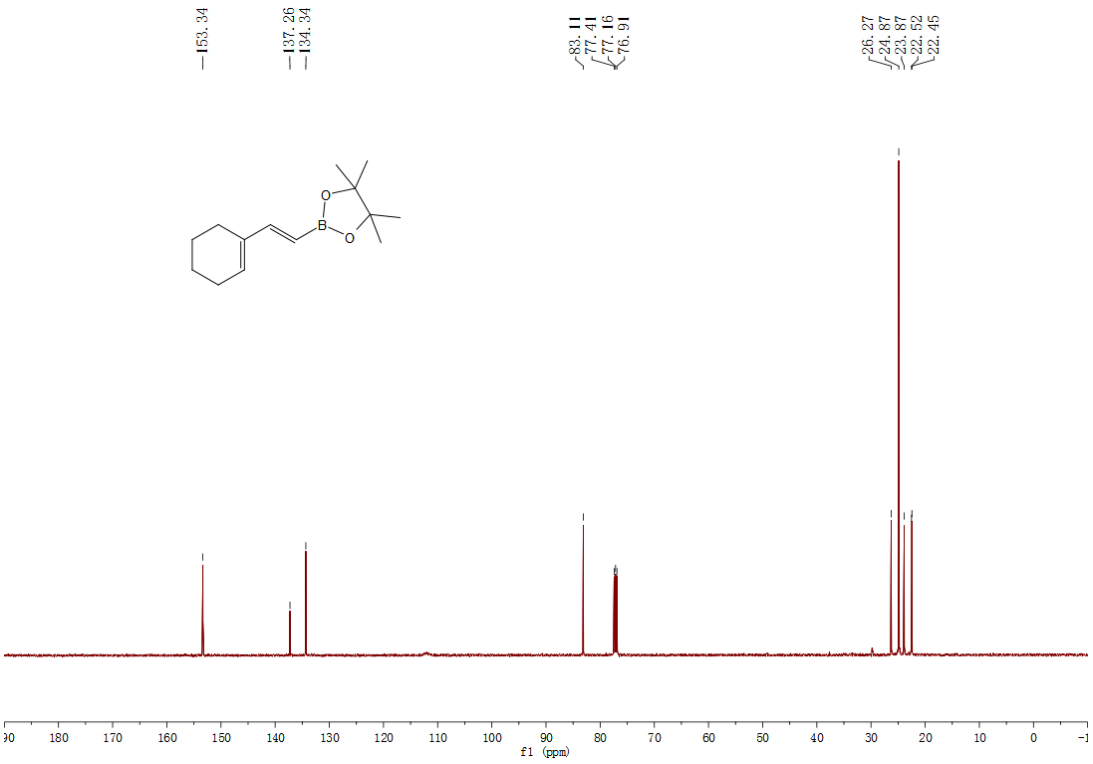
^{1}H NMR spectrum of **2za** (Chloroform-*d*)



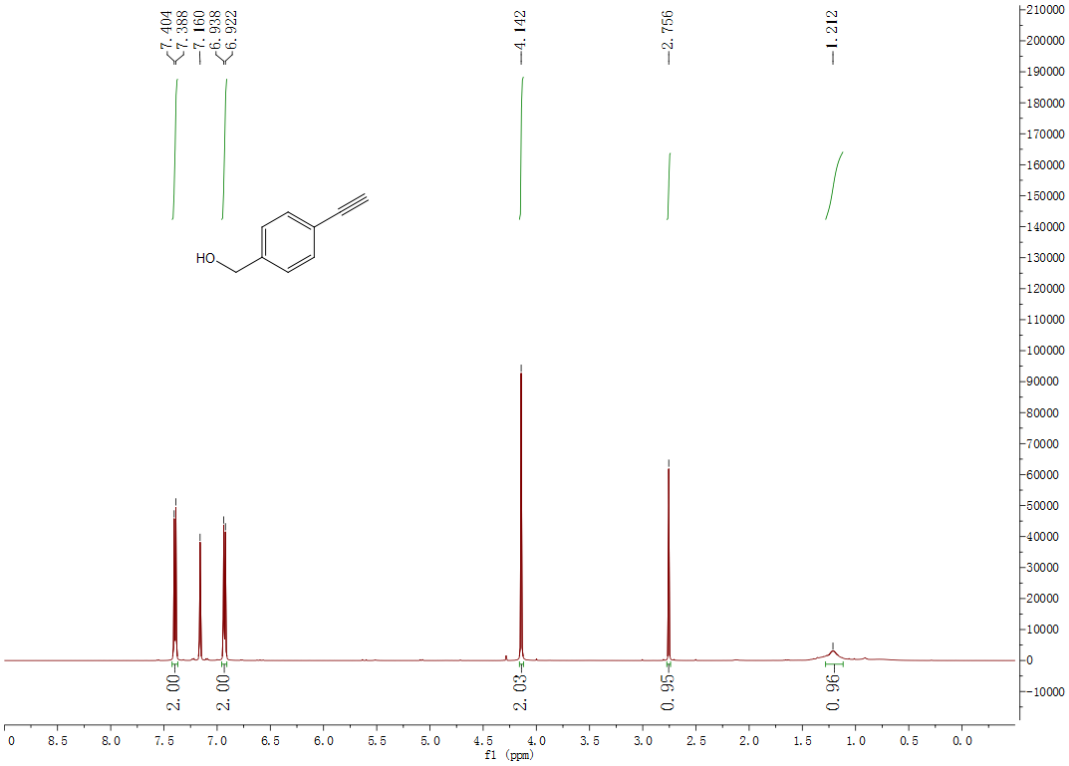
^{13}C NMR spectrum of **2za** (Chloroform-*d*)



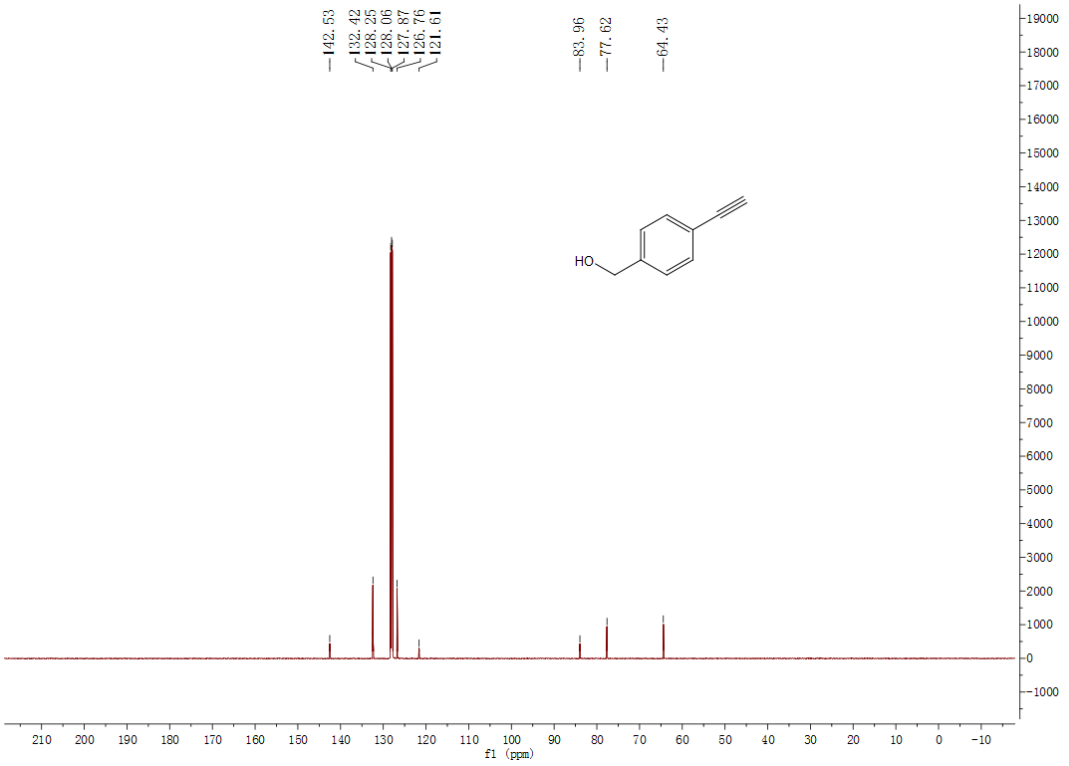
^{1}H NMR spectrum of **2zb** (Chloroform-*d*)



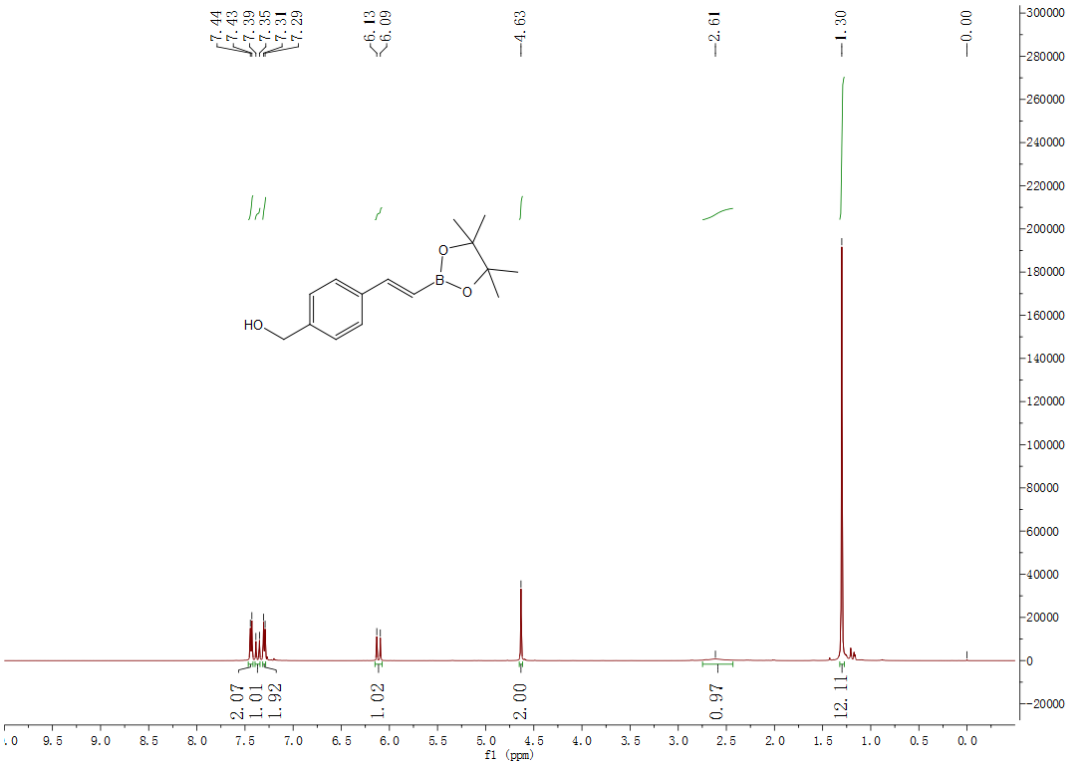
^{13}C NMR spectrum of **2zb** (Chloroform-*d*)



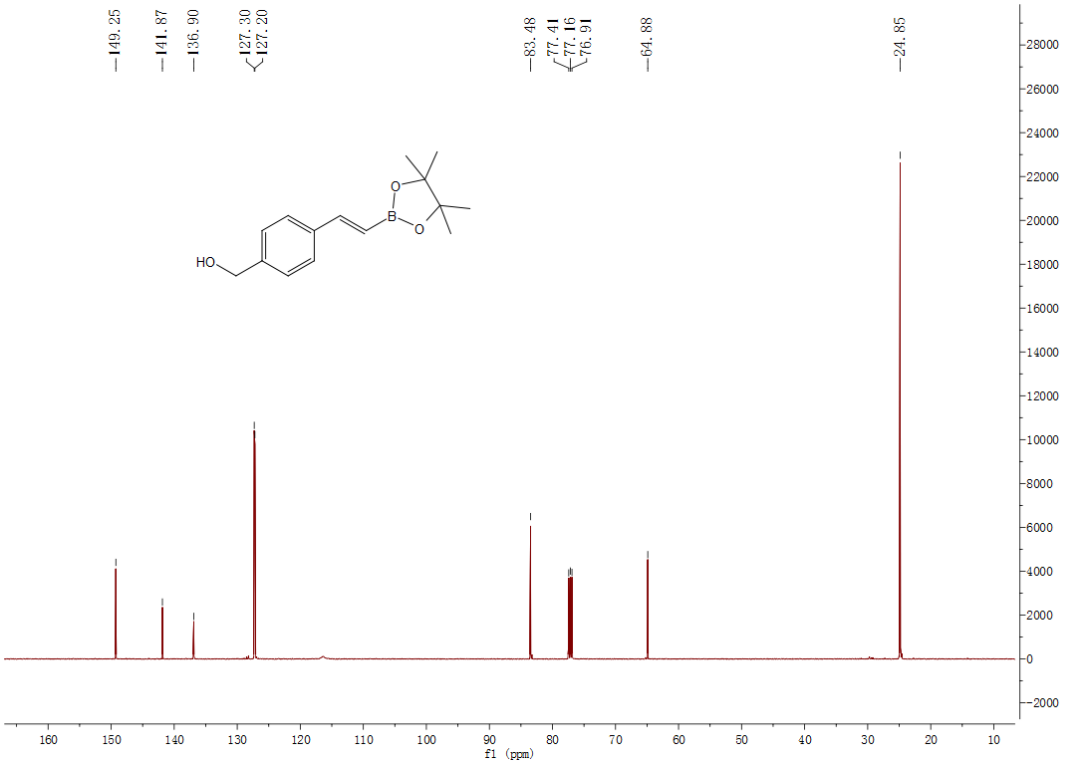
^{1}H NMR spectrum of **2zc-1 (**Benzene-*d*)



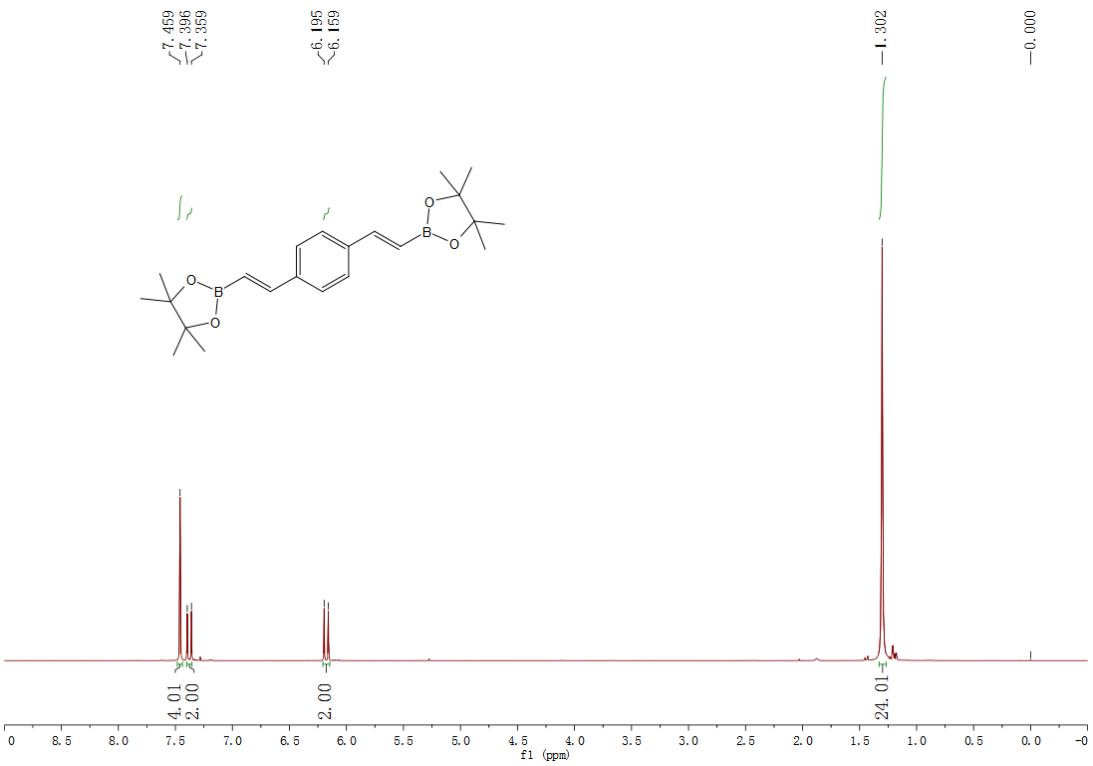
^{13}C NMR spectrum of **2zc-1 (**Benzene-*d*)



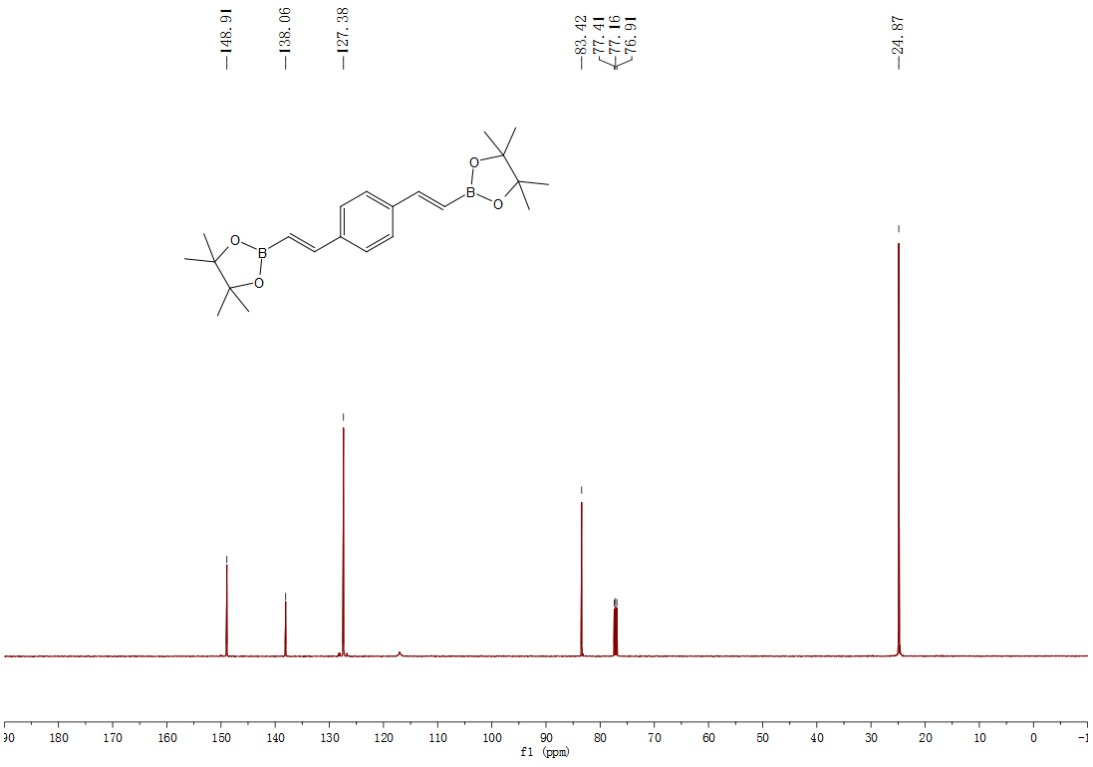
^{1}H NMR spectrum of **2zc-2** (Chloroform-*d*)



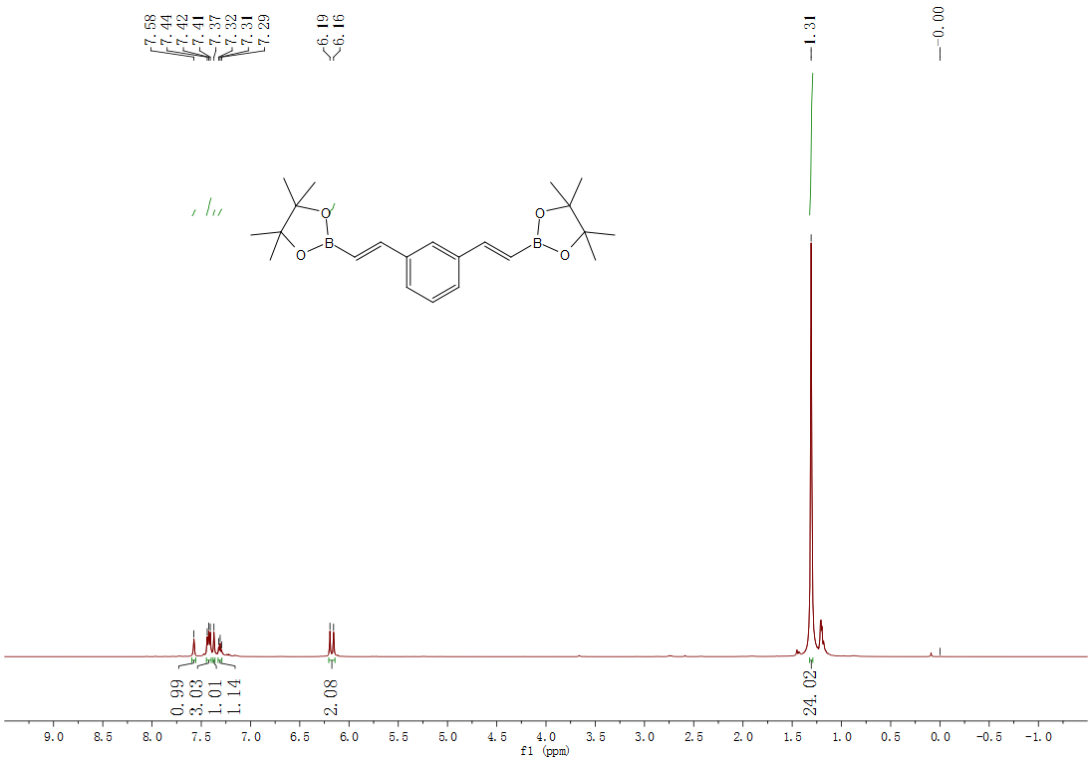
^{13}C NMR spectrum of **2zc-2** (Chloroform-*d*)



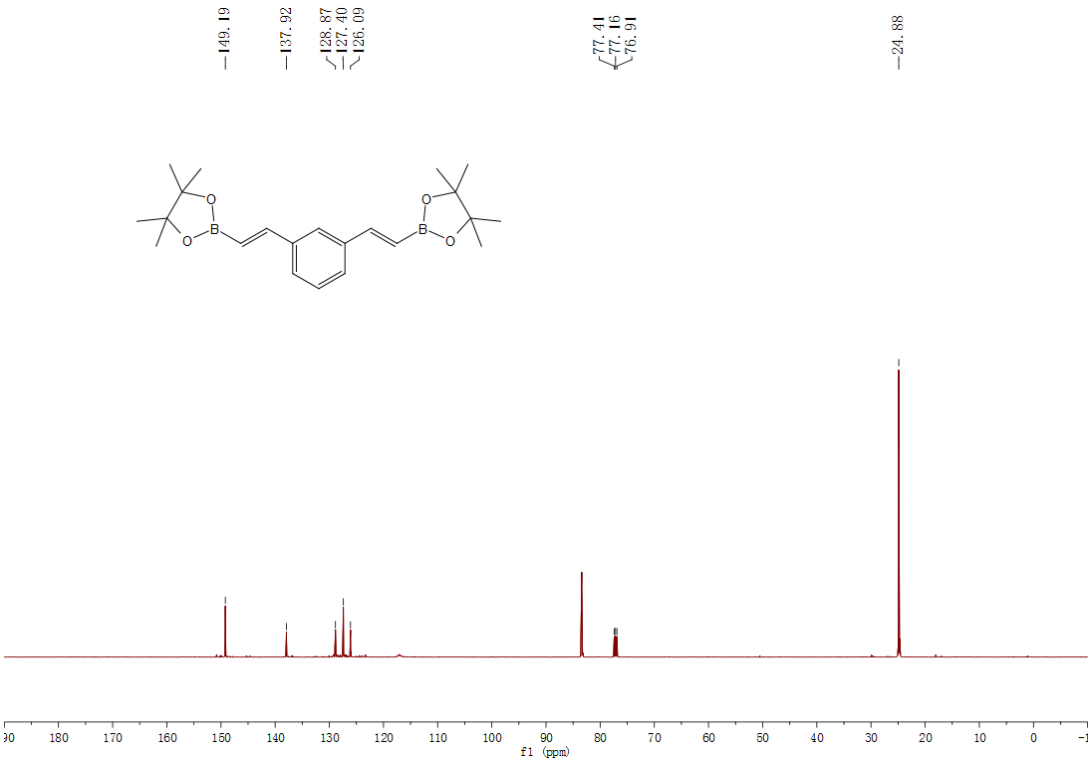
^{1}H NMR spectrum of **2zd** (Chloroform-*d*)



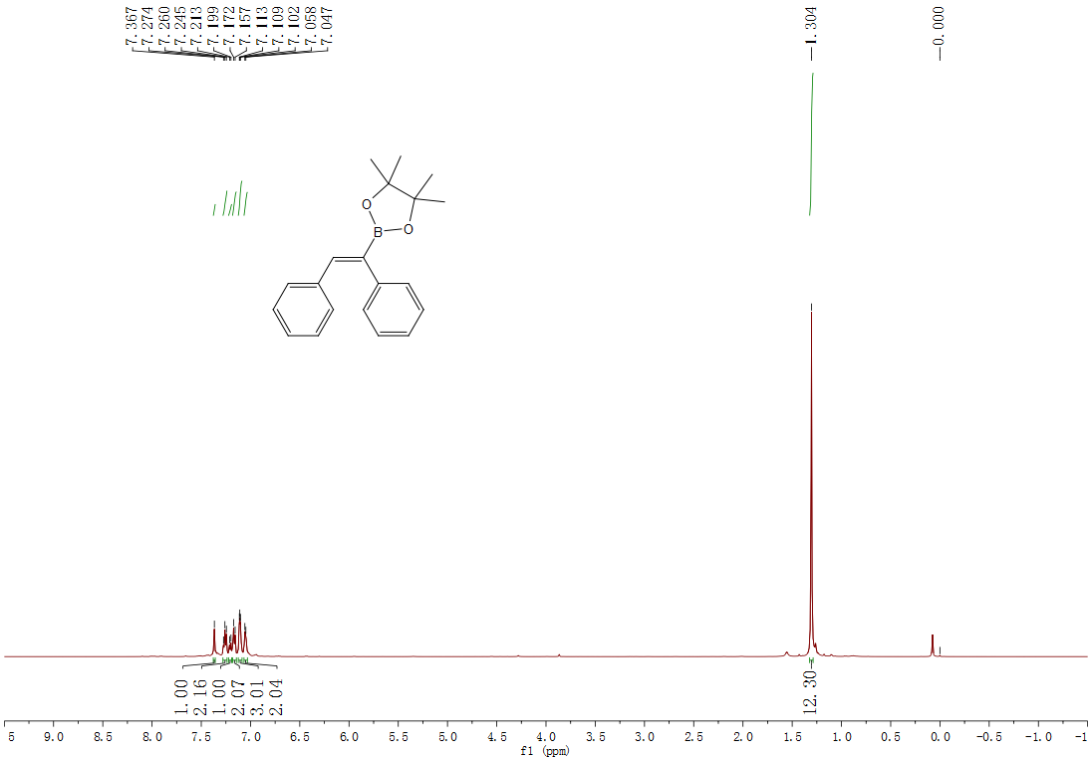
^{13}C NMR spectrum of **2zd** (Chloroform-*d*)



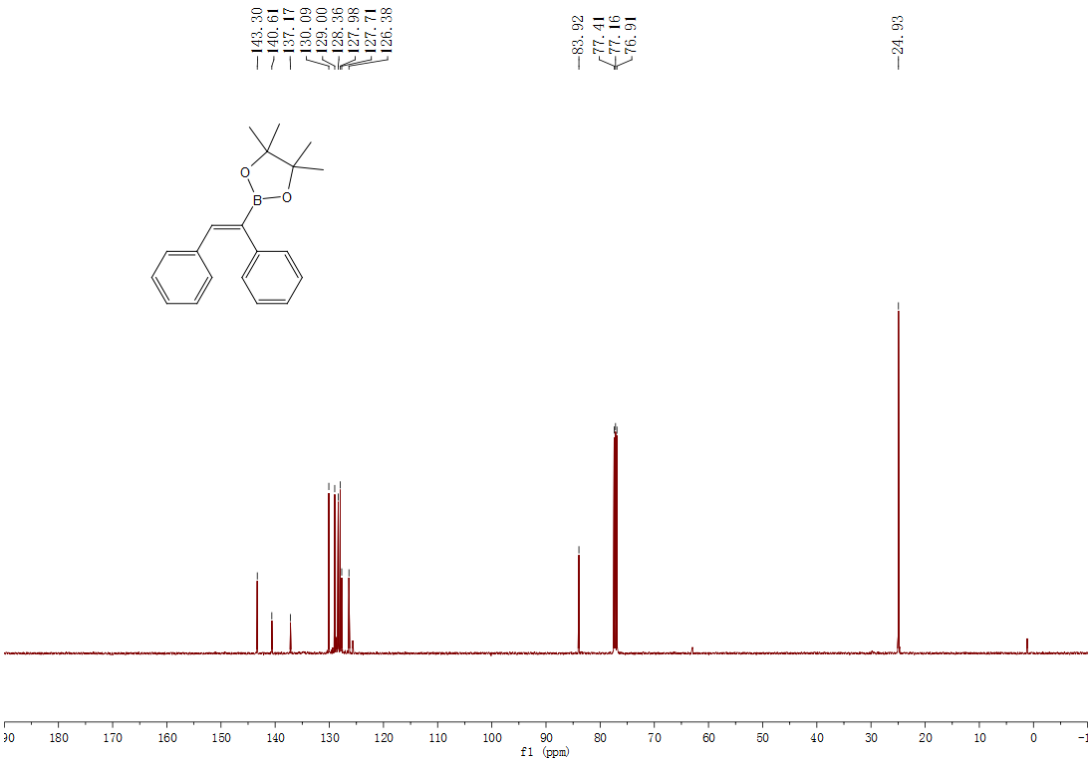
^{1}H NMR spectrum of **2ze** (Chloroform-*d*)



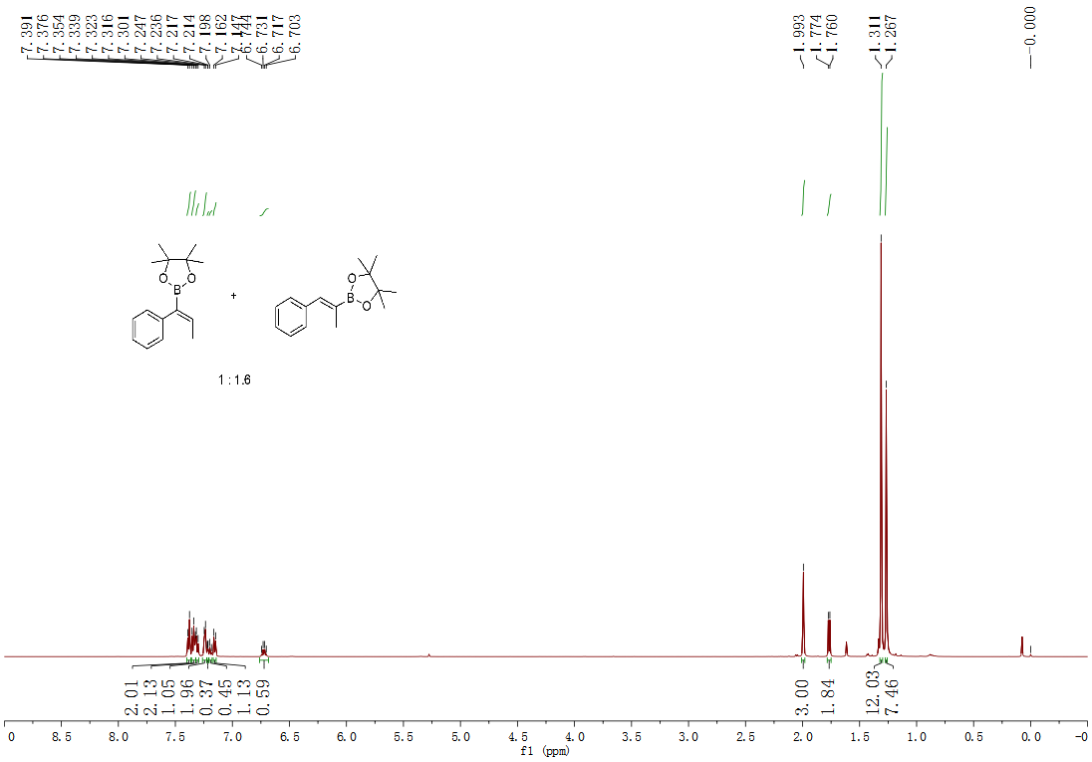
^{13}C NMR spectrum of **2ze** (Chloroform-*d*)



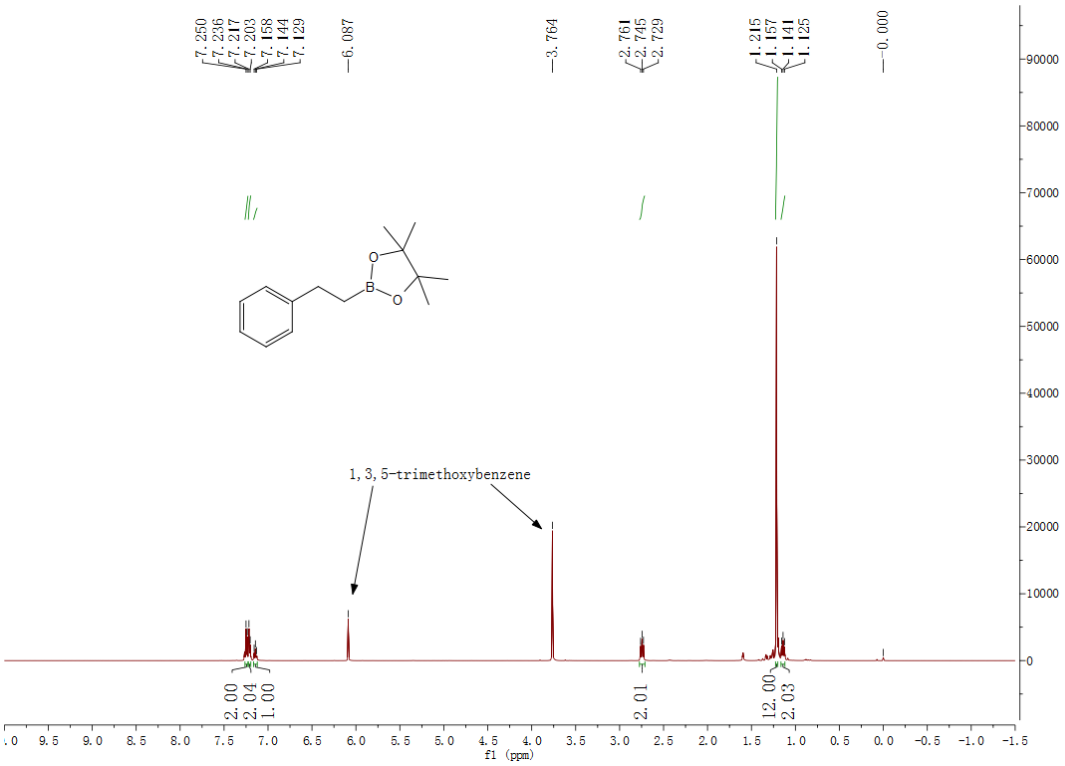
^{1}H NMR spectrum of **2zf** (Chloroform-*d*)



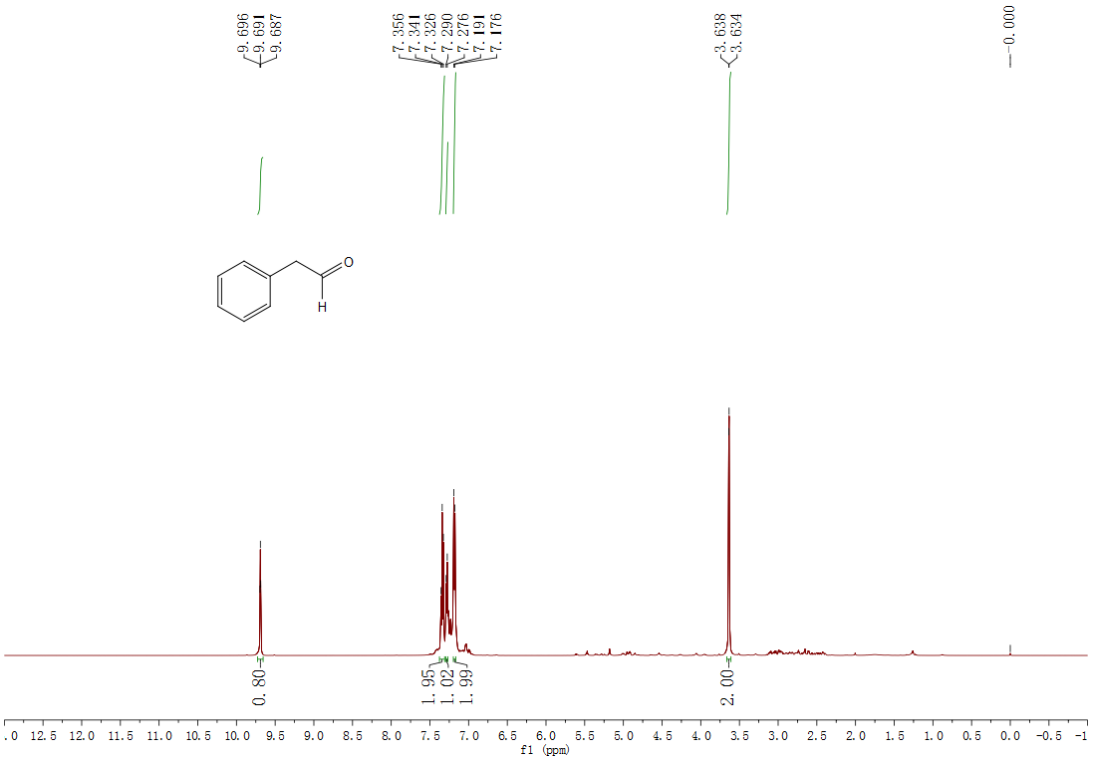
^{13}C NMR spectrum of **2zf** (Chloroform-*d*)



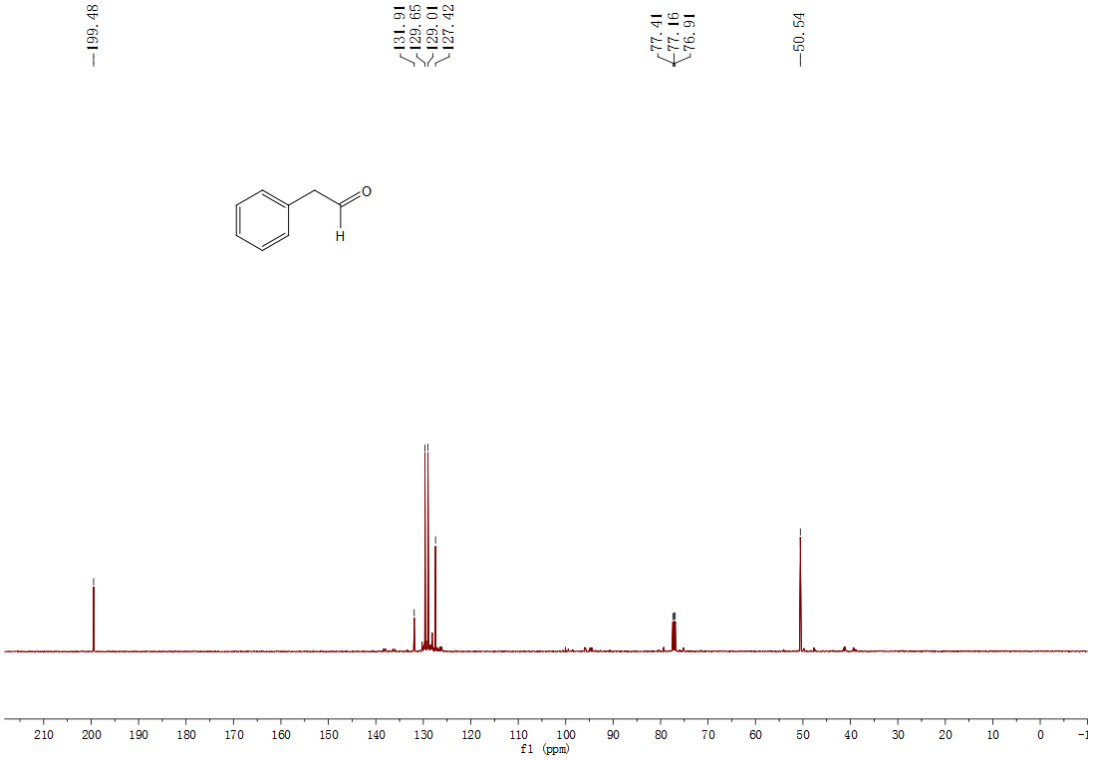
^{1}H NMR spectrum of **2zg** (Chloroform-*d*)



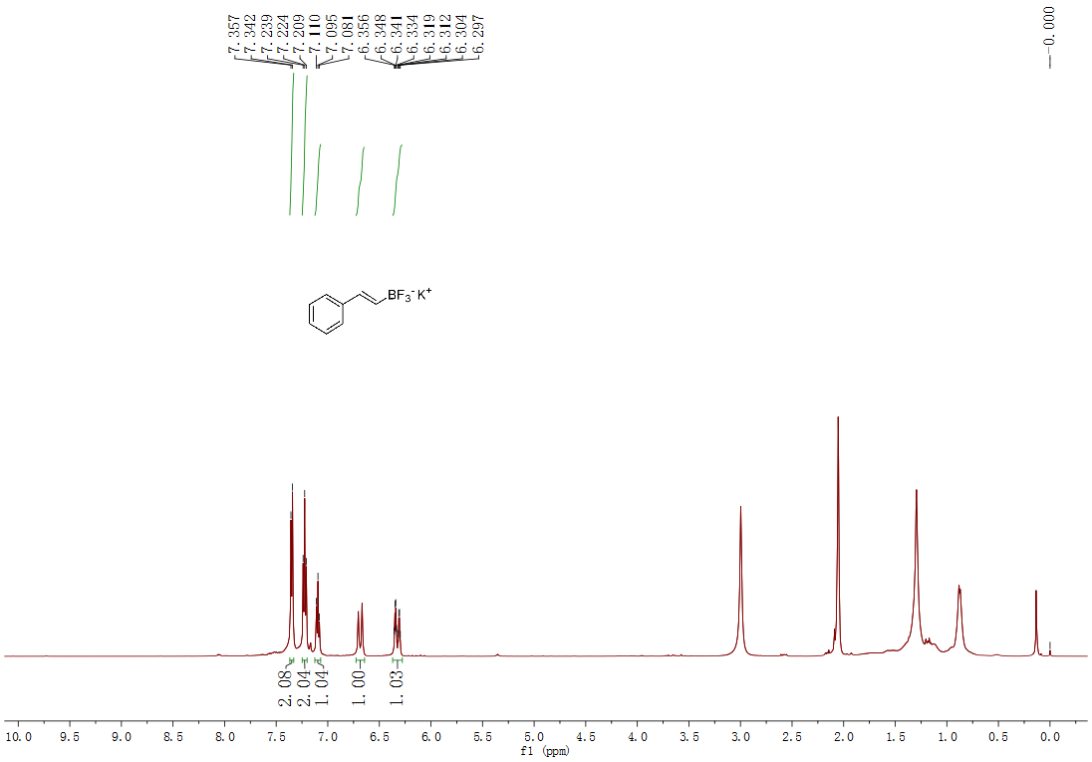
^{1}H NMR spectrum of **2zi** (Chloroform-*d*)



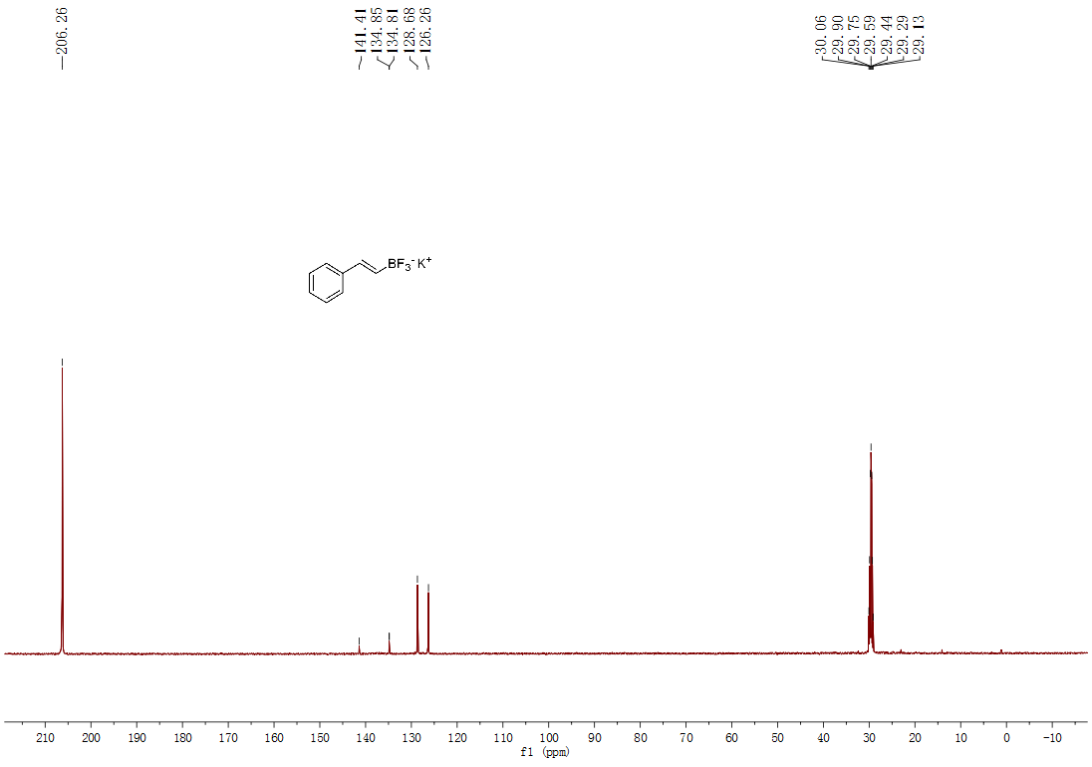
^{1}H NMR spectrum of **3-1** (Chloroform-*d*)



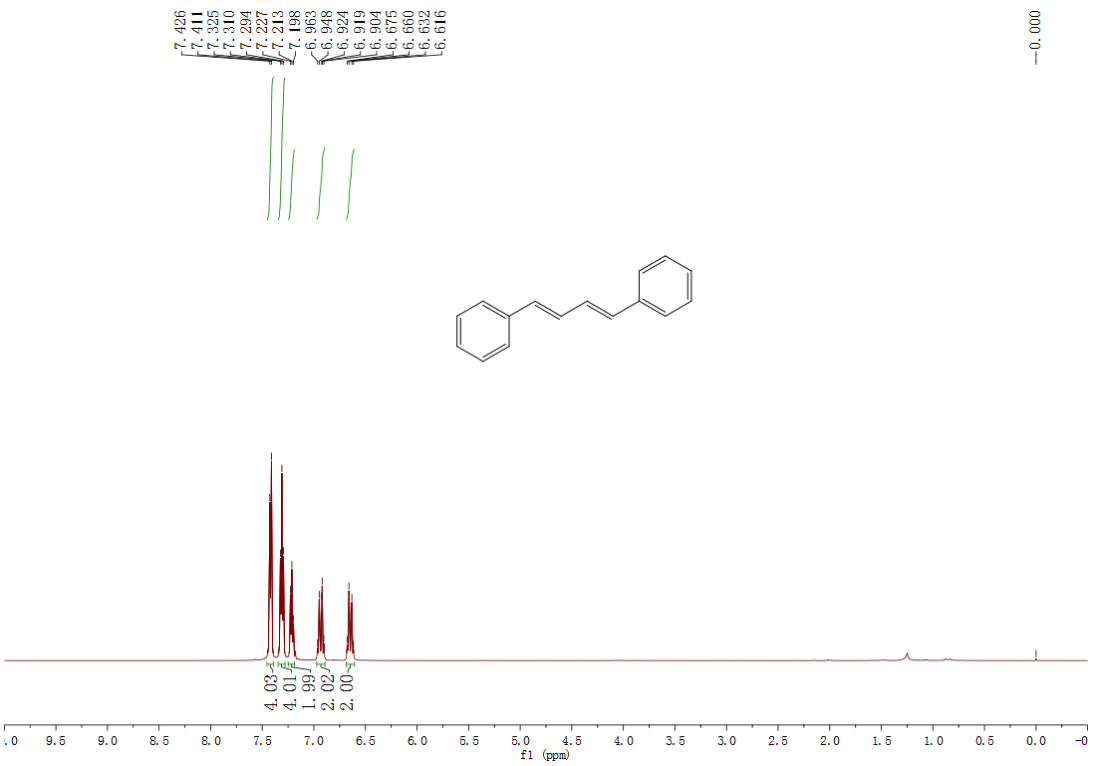
^{13}C NMR spectrum of **3-1** (Chloroform-*d*)



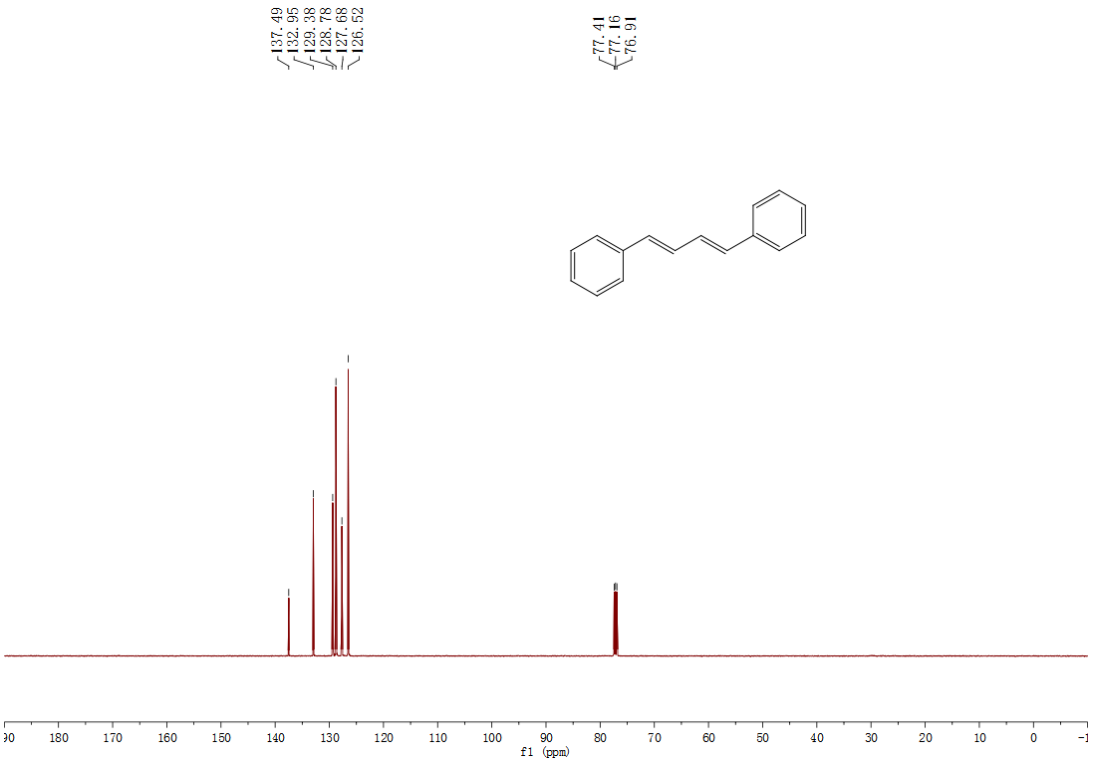
^{1}H NMR spectrum of **3-2** (Acetone-d_6)



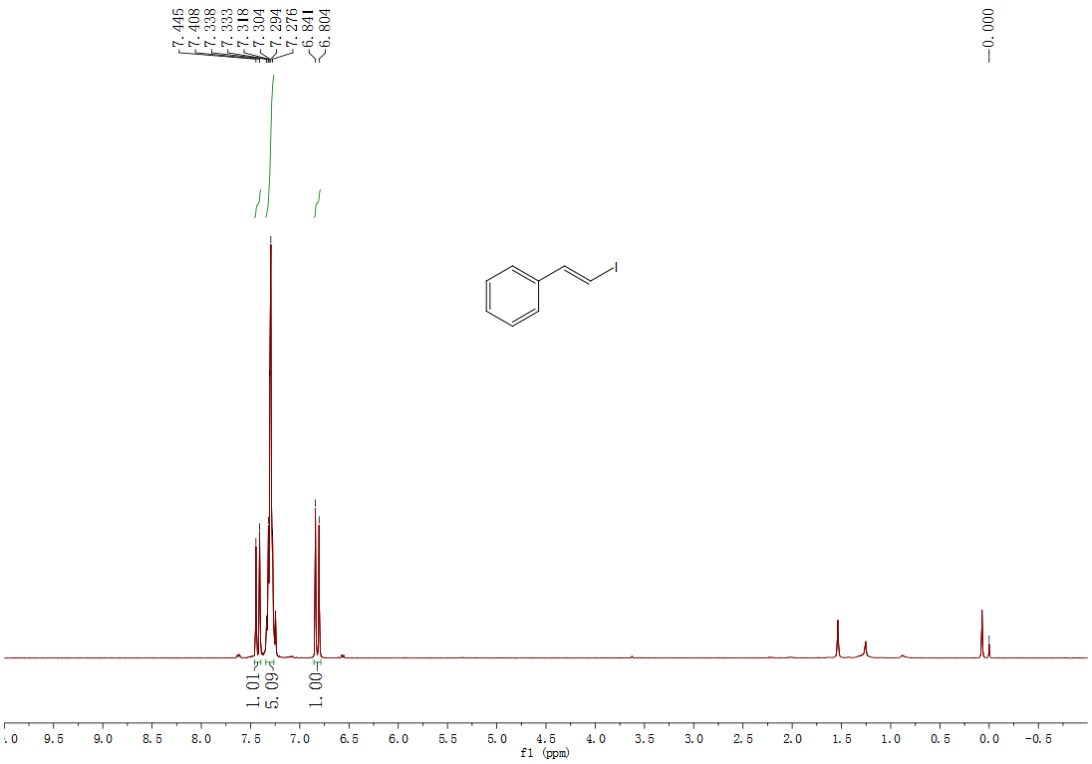
^{13}C NMR spectrum of **3-2** (Acetone-d_6)



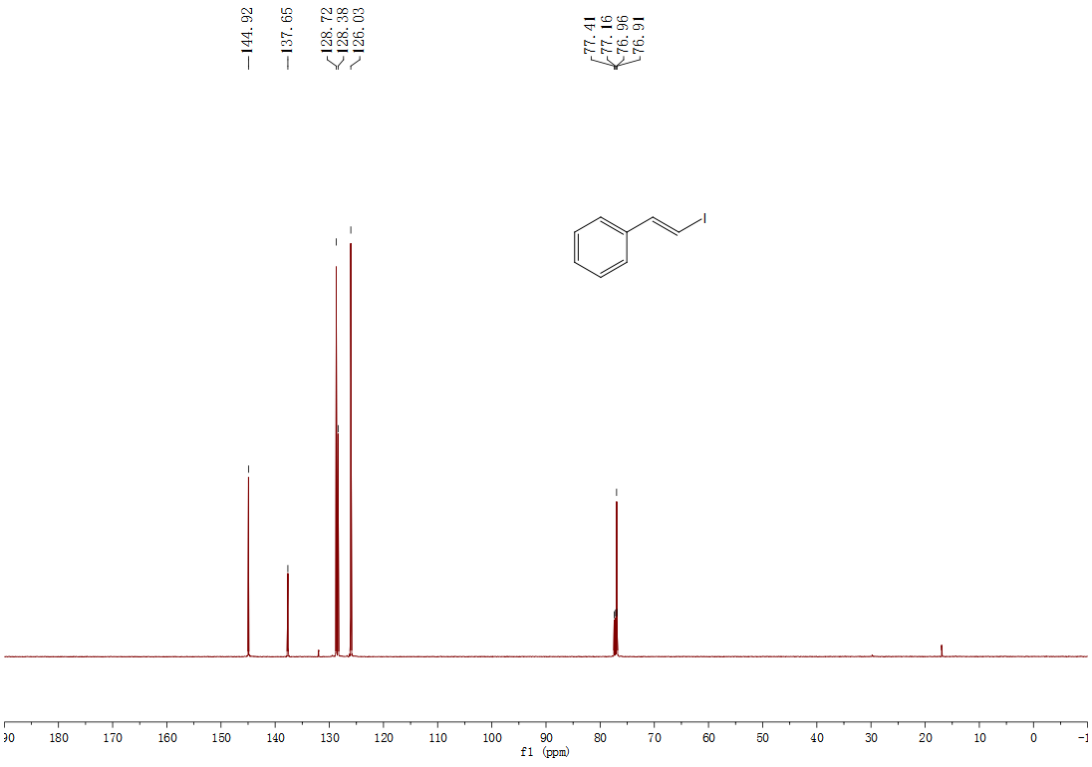
^{1}H NMR spectrum of **3-3** (Chloroform-*d*)



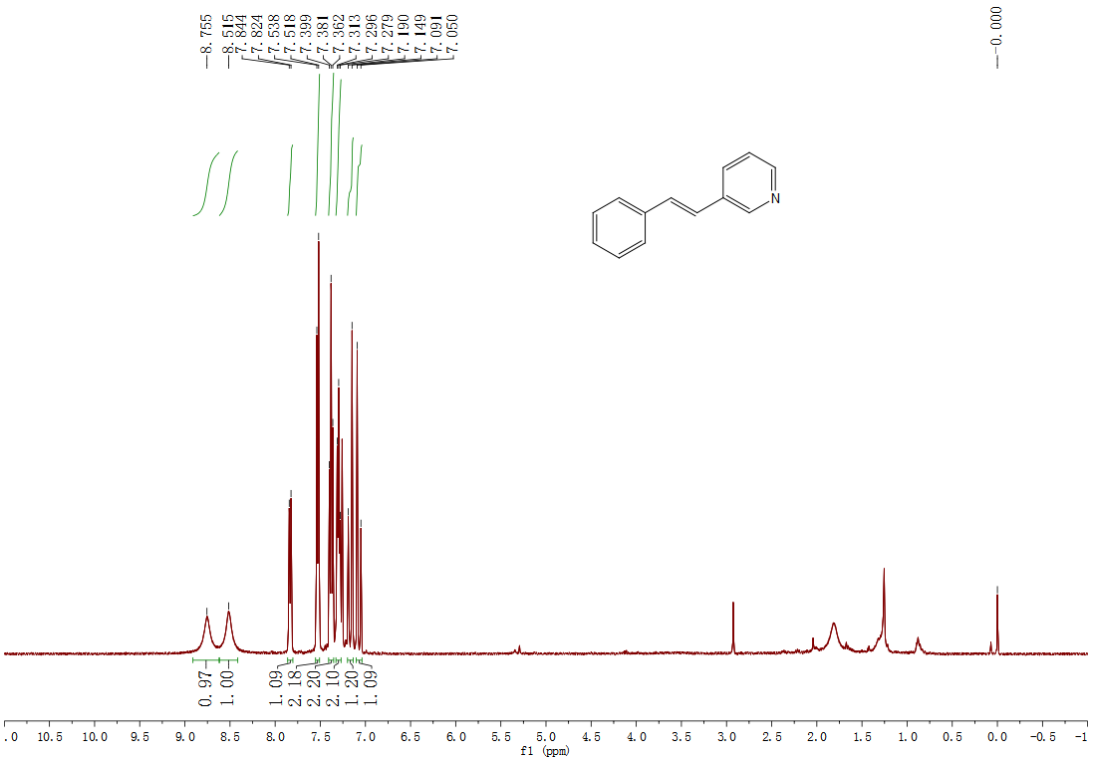
^{13}C NMR spectrum of **3-3** (Chloroform-*d*)



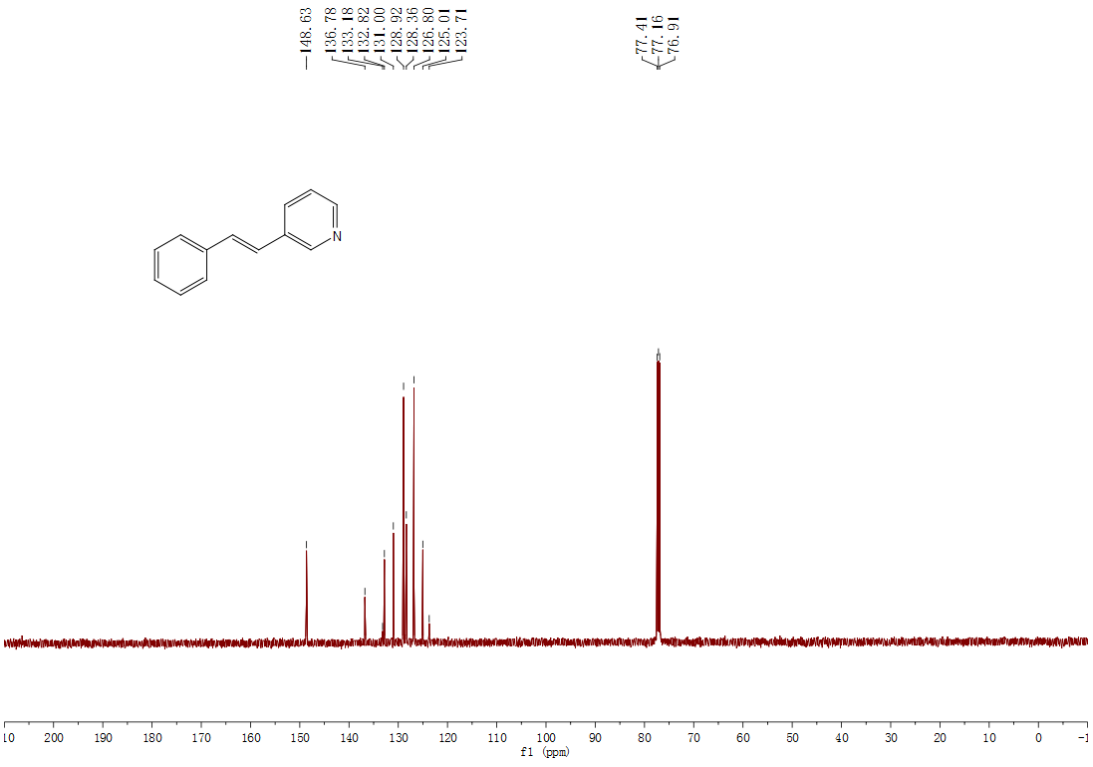
^{1}H NMR spectrum of **3-4** (Chloroform-*d*)



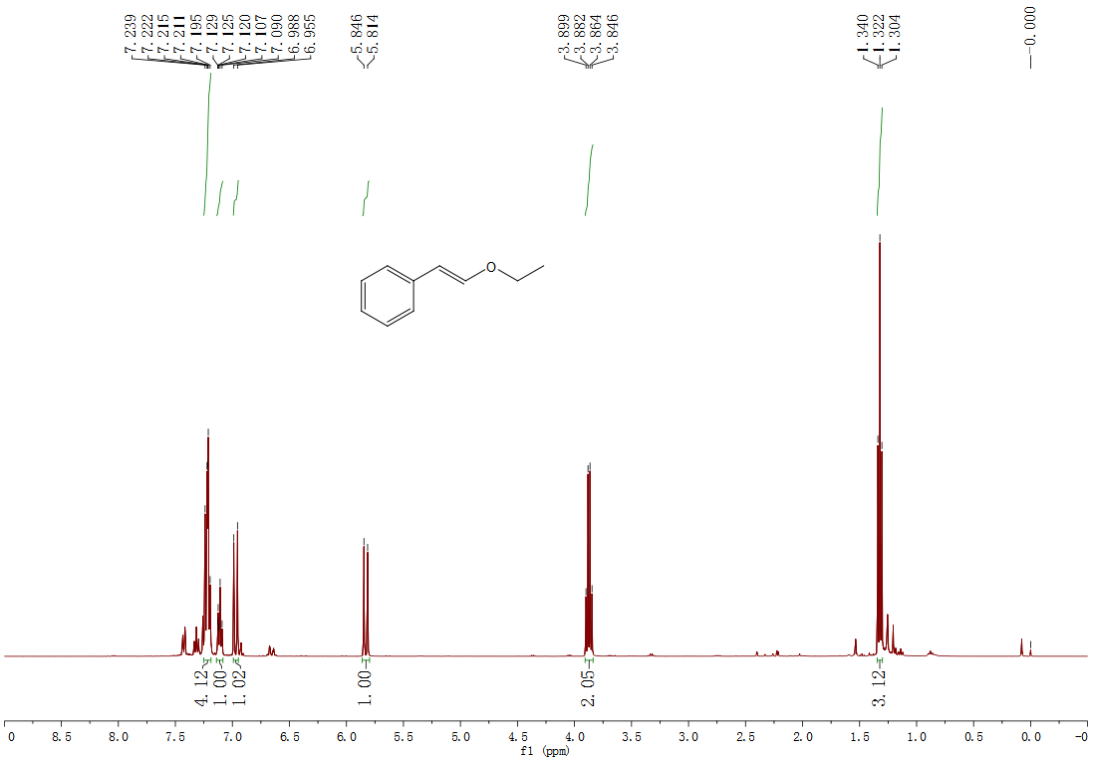
^{13}C NMR spectrum of **3-4** (Chloroform-*d*)



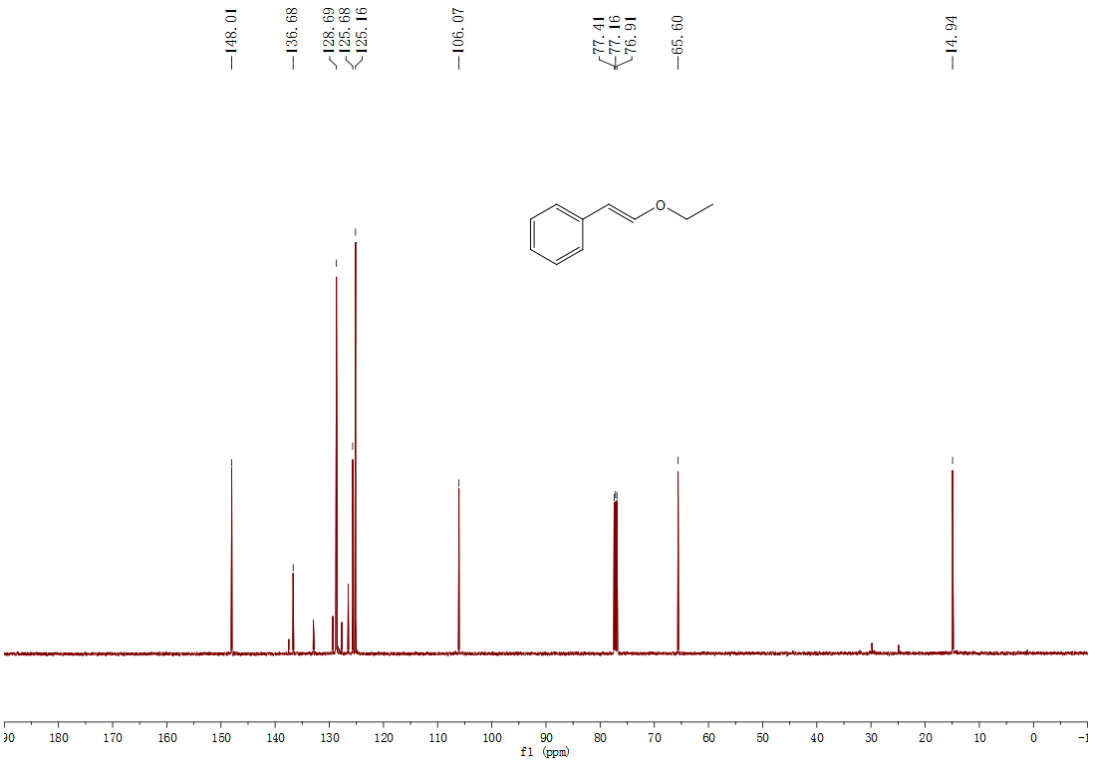
^{1}H NMR spectrum of **3-5** (Chloroform-*d*)



^{13}C NMR spectrum of **3-5** (Chloroform-*d*)



^{1}H NMR spectrum of 3-6 (Chloroform-*d*)



^{13}C NMR spectrum of **3-6** (Chloroform-*d*)