Supporting Information

for

Efficient and Selective External Activator-Free Cobalt Catalyst for Hydroboration of Terminal Alkynes Enabled by BiPyPhos

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Content

1. General Information

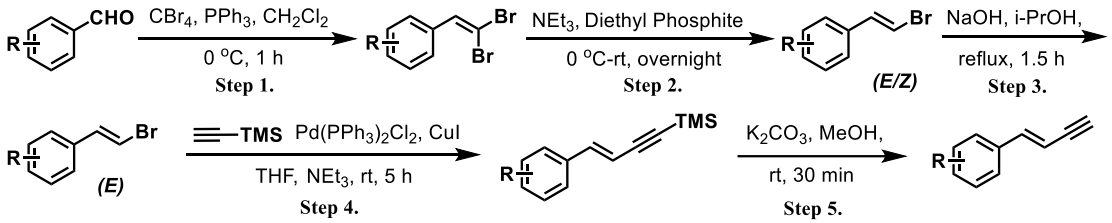
All reagents and starting materials were purchased from commercial sources and used as supplied, unless otherwise illustrated. It is specially noted that the ligand L1 is provided by CHENGDU XINHUAYUAN TECHNOLOGY CO, LTD. Column chromatography was performed with silica gel (Merck, 300-400 mesh). ^{1}H NMR spectra were recorded on Bruker Avance 400 MHz spectrometers. Chemical shifts were reported in ppm referenced to 7.26 ppm of chloroform-*d* (2.50 ppm of DMSO-d_6). The following abbreviations (or combination of thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, *J*, were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker Avance 101 MHz spectrometers, and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.16 ppm of chloroform-*d* (39.52 ppm of DMSO-d_6). HRMS was recorded on a commercial apparatus (ESI Source, TOF). For GC analyses, a PANNA A91 chromatograph (KB-1, 30 m × 0.25 mm × 0.50 μm, FID) was used. GC-MS analysis was recorded on GCMS-QP2020 of SHIMADZU (SH-Rtx-35MS, 30m × 0.25 mm × 0.25 μm). Continuous wave (CW) EPR spectra were recorded at 130K on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator and a Bruker PremiumX microwave bridge. The spectra were simulated using EasySpin for MATLAB®.

2. Experimental Procedures

2.1 Procedure for the synthesis of L6

A small amount of ligand L1 (27 mg, 0.05 mmol) and 2 mL of THF were added to Schlenk tube. The resulting solution stirred overnight in open air at room temperature. The mixture was purified by preparation of thin layer chromatography (silica gel, dichloromethane:ethanol = 50:1) to obtain a pure product. (18 mg, 61% yield)

2.2 General procedure A for the synthesis of the terminal conjugated enynes



The synthesis of terminal conjugated alkynes is performed by the previous work in our laboratory [1].

Step 1. 4-methoxybenzaldehyde (20 mmol, 2.96 g, 1.0 equiv.), CBr_4 (30 mmol, 9.95 g, 1.5 equiv.) and CH_2Cl_2 (80 mL) were added to a 250 mL round bottom flask equipped with a stir bar at 0 °C. Then a solution of PPh_3 (60 mmol, 15.7 g, 3.0 equiv.) in CH_2Cl_2 (70 mL) was added dropwise via dropping funnel over 30 min under N_2 atmosphere. The resulting mixture was stirred at 0 °C for 1 h, and then the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (eluent: pure PE) to give 1-(2,2-dibromovinyl)-4-methoxybenzene as colorless liquid.

Step 2. The dibromide from the first step (~ 20 mmol, 1.0 equiv.) and NEt_3 (60 mmol, 8.4 mL, 3.0 equiv.) were stirred in DMF (20 mL) in 250 mL round bottom flask equipped with a stir bar at 0 °C. Diethylphosphonate (60 mmol, 8.29 g, 3.0 equiv.) was added slowly via a syringe. The mixture was allowed to heat slowly to room temperature and stir overnight. Water (60 mL) was added into the reaction, and the mixture was extracted with n-hexane (2 × 50 mL). The combined organic phases were washed with an aqueous solution of HCl (1.0 M, 55 mL),

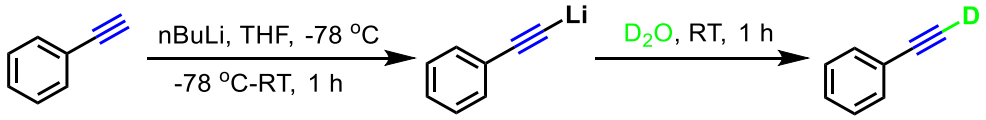
dried over Na_2SO_4, filtered and concentrated. The crude material was purified by flash chromatography (eluent: pure petroleum ether) to give (*Z/E*)-1-(2-bromovinyl)-4-methoxybenzene as colorless liquid.

Step 3. The crude product (~ 20 mmol, 1.0 equiv.) from step 2. was dissolved in *i*-PrOH (30 mL), then NaOH (17 mmol, 0.68 g, 0.85 equiv.) was added. The reaction mixture was heated to reflux for 30-90 min, and then cooled to room temperature. Water (2 × 100 mL) was added to the system, and extract with n-hexane (2 × 50 mL). The organic phase was collected and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (eluent: pure petroleum ether) to give (*E*)-1-(2-bromovinyl)-4-isopropylbenzene as colorless liquid.

Step 4. $Pd(PPh_3)_2Cl_2$ (224 mg, 1.6 mol%, 0.32 mmol) and CuI (121.8 mg, 3.2 mol%, 0.64 mmol) were added to dry THF (50 mL) in 100 mL round bottom flask equipped with a stir bar under N_2 atmosphere. Then *β*-bromostyrene obtained by the third step was added followed by TMS-acetylene (3.5 mL, 1.25 equiv., 25 mmol) and Et_3N (5.6 mL, 4.05 g, 2.0 equiv., 40 mmol). The resulting mixture was stirred at room temperature for 5 h [progress of the reaction was monitored by TLC (n-hexane)]. The reaction mixture was then diluted with EtOAc and filtered through a short pad of silica. Solvent was evaporated under vacuum and the residue was purified by flash column chromatography (eluent: pure petroleum ether) to give TMS protected (*E*)-1-(but-1-en-3-yn-1-yl)-4-methoxybenzene as colorless liquid.

Step 5. K_2CO_3 (2.8 g, 1.0 equiv., 20 mmol) was added to a stirred solution of the product from step 4. in MeOH (50 mL) at room temperature. After for 30 min, volatiles were evaporated under reduced pressure and the residue was purified by flash column chromatography (eluent: pure petroleum ether) to give (*E*)-1-(but-1-en-3-yn-1-yl)-4-methoxybenzene as colorless liquid (2.21 g, 16 mmol, 70% yield)

2.3 Procedure for the preparation of (ethynyl-*d*)benzene



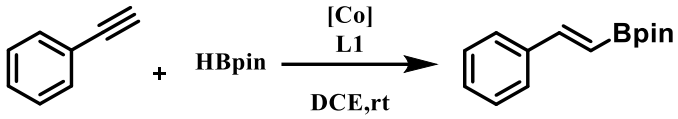
n-BuLi (1.6 M, 14 mL, 22.4 mmol, 1.2 equiv.) was added dropwise to a solution of phenylacetylene (2.0 mL, 18.2 mmol, 1.0 equiv.) in dry THF (10 mL) at -78 °C under N_2 atmosphere. The solution was allowed to heat slowly to room temperature, and stirred for 1 h. Then D_2O (4 mL) was added and stirred for a further 1 h at room temperature. The mixture was extracted with ether, and the extract was dried over anhydrous $NaSO_4$ and evaporated to dryness to give phenylacetylene-*d* (1.69 g, 90% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.35-7.29 (m, 3H) ppm. The **^{1}H NMR** analysis was consistent with the literature. [1]

2.4 General procedure B for hydroboration of terminal alkynes

An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with corresponding terminal alkynes (10 mmol, 1.0 equiv.), HBpin (15 mmol, 1.5 equiv.), L1 (0.011 mmol), $Co(acac)_2$ (0.01 mmol) and ethyl acetate (0.5 mL) in the air. The resulting solution was stirred at 25 °C via heating plate magnetic stirrer for 2 h. After cooling to ambient temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles were removed under vacuum and the residue was purified by preparative thin layer chromatography (silica gel, petroleum ether/ethyl acetate 100:1) to give pure product.

2.5 Optimization of reaction conditions

Table S1 Optimization of the reaction conditions[a]

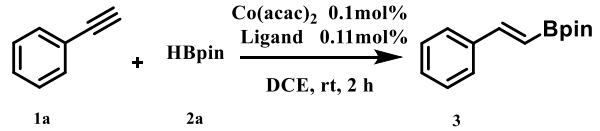


1a 2a 3

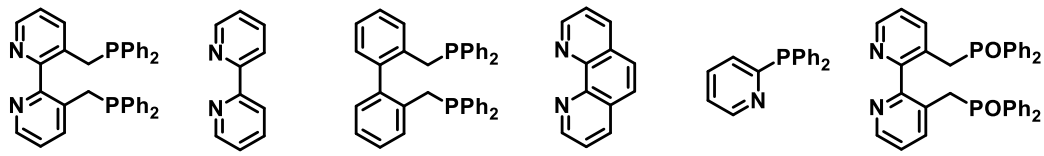
Entry	Co precursor	Temp./℃	P/Co	Yield of 3 /%[b]
1[a]	$Co(acac)_2$	60	4	81
2[a]	$Co(CO)_8$	60	4	40
3[a]	$CoCl_2$	60	4	13
4[a]	$Co(AcO)_2·4H_2O$	60	4	80
5[a]	/	60	4	/
6[a]	$Co(acac)_2$	60	/	/
7[b]	$Co(acac)_2$	25	2	91
8[b]	$Co(CO)_8$	25	2	1
9[b]	$CoCl_2$	25	2	11
10[b]	$Co(AcO)_2·4H_2O$	25	2	9
11[b]	$C_{32}H_{16}CoN_8$	25	2	1
12[b]	$Co(acac)_2$	25	/	/
13[b]	/	25	2	/

[a]Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), **2a** (1.0 mmol, 2.0 equiv.), L1 (0.11 mmol), [Co] (0.01 mmol) and DCE (1 mL), 2 h and yields of **3** were determined by GC. [b]conditions: L1 (0.02 mmol), [Co] (0.01 mmol).

Table S2 Optimization of the ligand[a]



1a 2a 3

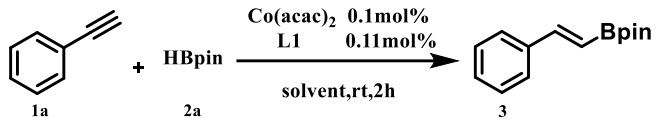


L1 L2 L3 L4 L5 L6

Entry	Ligand	Yield of 3 /%[d]
1[a]	L1	99
2[b]	L1	78.2
3[b]	L2	3.4
4[b]	L3	17
5[b]	L4	7.8
6[b, c]	L5	N.D.
7[b]	L6	2.4
8[b]	NEt_3 + L3	9.8
9[b]	L2 + L3	1.2

[a]Conditions: phenylacetylene (1.0 mmol, 1.0 equiv.), pinacolborane (1.5 mmol, 1.5 equiv.), ligand (1.1 mol%), $Co(acac)_2$ (1.0 mol%), and DCE (0.5 mL), rt, 2 min, and yield of **3** were determined by GC. [b]Conditions: phenylacetylene (10 mmol, 1.0 equiv.), pinacolborane (15 mmol, 1.5 equiv.), ligand (0.11 mol%), $Co(acac)_2$ (0.1 mol%), and DCE (0.5 mL), rt, 2 h, and yields of **3** were determined by GC. [c]N.D.: not detected.

Table S3 Optimization of the solvent[a]



Entry	Solvent	Yield of 3 /%[b]
1	DCM	28.5
2	EA	97.4
3	EtOH	29.4
4	Toluene	85
5	THF	91.9
6	MeCN	70.7
7	DCE	78.2
8	1,4-Dioxacyclohexane	55.9

[a] Reaction conditions: **1a** (10 mmol, 1.0 equiv.), **2a** (15 mmol, 1.5 equiv.), L1 (0.011 mmol), $Co(acac)_2$ (0.01 mmol) and solvent (0.5 mL), 2 h, and yields of **3** were determined by GC.

2.6 Evidence for stereospecificity of hydroboration

An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with corresponding terminal alkynes (10 mmol, 1.0 equiv.), HBpin (15 mmol, 1.5 equiv.), and ethyl acetate (0.5 mL) in the air. The resulting solution was stirred at 25 °C via heating plate with magnetic stirrer for 10 min. Addition of 5 mmol tetrachloroethane as internal standard, after oscillating, 0.1 mL reaction solution and deuterated chloroform were taken to detect the selectivity of product by ^{1}H NMR detection. As the Figure S1 shown, the peak at 6.01 (d, J = 18.4 Hz, 1H) ppm was corresponded to Hx of *E*-vinylboronate esters, and the yield of *E*-vinylboronate esters reached 92% within 10 min. Moreover, the peaks at δ 6.54 (dd, J = 17.8, 11.0 Hz, 1H) ppm, 5.57 (d, J = 17.5 Hz, 1H) ppm, 5.06 (d, J = 10.9 Hz, 1H) ppm belong to styrene with ca. 5% yield. Characteristic peaks of both *β-Z*-product [2] and *α*-product [3] were not identified in the system, demonstrating stereospecificity enabled by this Co system.

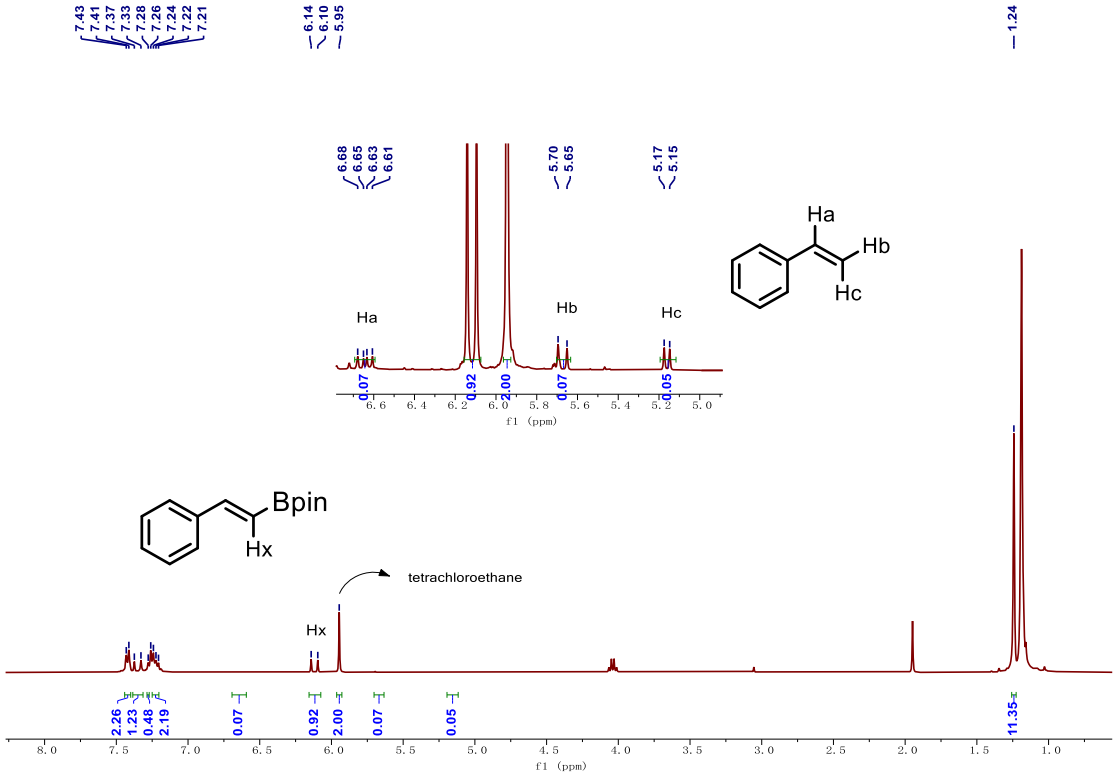


Figure S1 The crude ^{1}H NMR (tetrachloroethane as inter standard) of reaction mixture under the optimal condition (10 min)

3. Mechanistic studies

3.1 Radical-trapping experiments

General procedure: In an argon-filled glovebox, a 25 mL sealed tube was sequentially charged with 6.1 mg L1 (0.011 mmol), and 2.6 mg $Co(acac)_2$ (0.01mmol), 2.2 mL HBpin (15 mmol, 1.5 equiv.), 1.1 mL phenylacetylene (10 mmol, 1.0 equiv.), EA (0.5 mL) and radical scavenger (20 mmol, 2.0 equiv.). After stirring at room temperature for 3 h, the tube was removed from the glovebox and the reaction mixture was filtered through a short pad of silica gel (PE/EA = 100:1). ca. 20 μL filtrate was taken and analyzed by GC-MS. The remaining filtrate was concentrated by rotary evaporation and purified by flash column chromatography. The results are listed as follows.

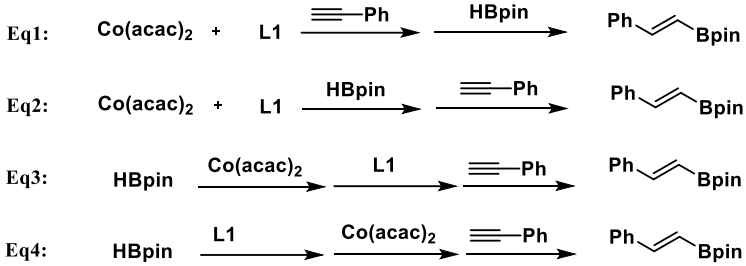
Table S4 Radical-trapping experiments[a]

Entry	Radical scavenger	Yield (%)	Recovery of radical scavenger (%)
1	TEMPO	91	96
2	BHT	89	96

[a]Isolate yields.

The above results showed that the addition of radical scavengers basically had no effect on the hydroboration reaction (both yield and regioselectivity), which ruled out a radical process to a large extent.

3.2 Effect of feeding sequence



Eq1: $Co(acac)_2$ (0.01 mmol), L1 (0.011 mmol), and phenylacetylene (10 mmol, 1.0 equiv.) were sequentially placed into a 25 mL Schlenk tube which was dried in an oven with a magnetic stir bar. After shaking for 30 s, HBpin (15 mmol, 1.5 equiv.) was added. The resulting solution was stirred (heated by a heating plate magnetic stirrer) at 25°C for 2 h. After cooling to ambient temperature, the yield of 45% was obtained by GC analysis.

Eq2: $Co(acac)_2$ (0.01mmol), L1 (0.011mmol), HBpin (15 mmol, 1.5 equiv.) were sequentially placed into a 25 mL Schlenk tube which was dried in an oven with a magnetic stirring bar. After shaking for 30 s, phenylacetylene (10 mmol,1.0 equiv.) was added. The resulting solution was stirred (heated by a heating plate magnetic stirrer) at 25°C for 2 h. After cooling to ambient temperature, the yield of 89% was obtained by GC analysis.

Eq3: The HBpin (15 mmol, 1.5 equiv.) was loaded into a 25 mL oven-dried Schlenk tube, equipment with a magnetic stir bar. Then $Co(acac)_2$ (0.01 mmol) was added and the solution was shaken for 30 s before L1 (0.011mmol) was added and the solution was shaken for another 30s before the phenylacetylene (10 mmol, 1.0 equiv.) was added. The resulting solution was stirred (heated by a heating plate magnetic stirrer) at 25°C for 2 h.

After cooling to ambient temperature, the yield of 86% was obtained by GC analysis.

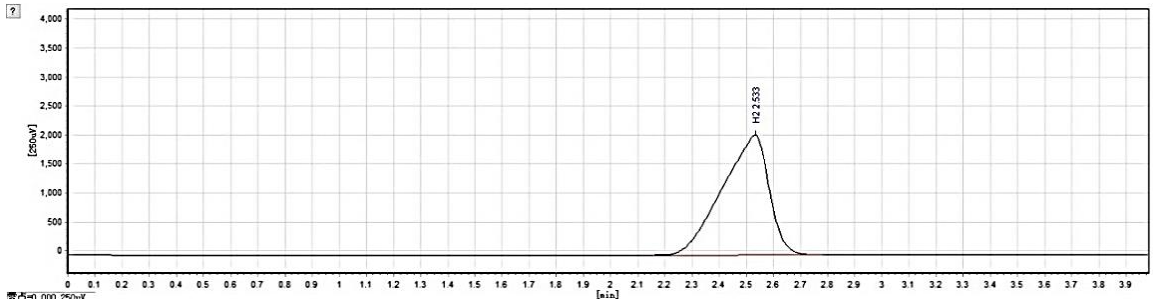
Eq4: The HBpin (15 mmol, 1.5 equiv.) was loaded into a 25 mL Schlenk tube, which was dried in an oven with a magnetic stir bar. Then L1 (0.011 mmol) was added and the solution was shaken for 30 s before $Co(acac)_2$(0.01 mmol) was added and the solution was shaken for another 30 s before the phenylacetylene (10 mmol, 1.0 equiv.) was added. The resulting solution was stirred (heated by a heating plate magnetic stirrer) at 25°C for 2 h. After cooling to ambient temperature, the yield of 96% was obtained by GC analysis.

3.3 Qualitative H_2 detection

$$\text{L1} + \text{Co(acac)}_2 + 2\text{HBpin} \xrightarrow[5\text{min}]{\text{EA, rt}} \underset{\text{A}}{\text{L1-Co-H}} + \text{H}_2\uparrow$$

In a nitrogen -filled glovebox, a 10 mL Schlenk tube was charged with $Co(acac)_2$ (0.05mmol), L1 (0.05mmol), and EA (1 mL). The mixture was stirred at room temperature for 1 min, then sealed with a rubber septum. The Schlenk tube was removed from the glovebox. To the sealed tube, HBpin (0.145mL, 0.1 mmol, 2 equiv) was added via microsyringe. After vigorously stirring for 5 min, 1 mL gas was taken from the headspace of Schlenk tube and analyzed by by PANNA GC-A60 gas chromatograph equipped with both TCD detector. [4]

[2]



$$\text{A} + \text{MeOH} \xrightarrow{\text{EA, rt, 5min}} \text{H}_2\uparrow$$

Figure S2 GC spectrum for qualitative detection of dihydrogen

In a nitrogen-filled glovebox, a 10 mL Schlenk tube was charged with A (30.0 mg) and EA (1 mL). The mixture was stirred at room temperature for 1 min, then sealed with a rubber septum and removed from the glovebox. To the sealed tube, MeOH (100 μL) was added via microsyringe. 5 min later, 1 mL gas was taken from the headspace of Schlenk tube via the precision analytical syringe and analyzed by gas chromatography equipped with TCD detector. The GC spectra were listed as follows. The results show that H_2 was indeed generated after mixing A with MeOH, which indicates that hydride may be present in A (Co-H).

3.4 Hydroboration of deuterium-labeled phenylacetylene

An oven-dried 25 mL Schlenk tube equipped with magnetic stirring bar was charged with deuterated phenylacetylene (1.0 mmol, 1.0 equiv.), HBpin (1.5 mmol, 1.5 equiv.), and ethyl acetate (0.5 mL) in the open air. The resulting solution was stirred at 25 °C via heating plate magnetic stirrer for 2 h. After cooling to ambient temperature, the mixture was diluted with dichloromethane and filtered through a short pad of celite, the volatiles

were removed under vacuum and the residue was purified by preparative thin layer chromatography (silica gel, petroleum ether/ethyl acetate 100:1) to give pure product. (0.222 g, 96%)

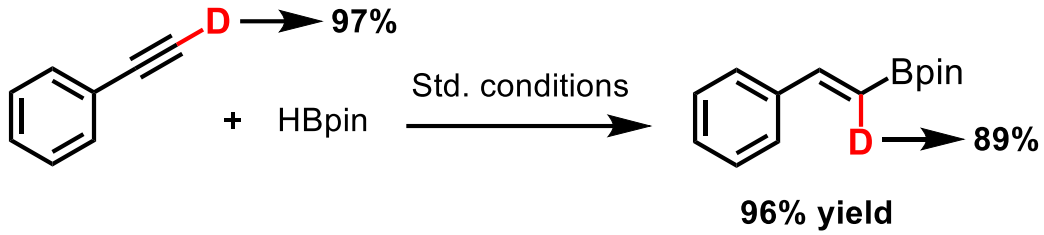


Figure S3 Hydroboration of deuterium-labeled phenylacetylene

3.5 X-ray photoelectron spectroscopy analysis of cobalt catalysts

To gain information about the oxidation state of the Co species in active catalyst A, analysis of Co 2p by X-ray photoelectron spectroscopy (XPS) was performed. All measurements were performed on a Krato Axis Ultra DLD spectrometer (UK) equipped with a monochromatic Al Kα X-ray source. The pressure throughout the analysis chamber was less than 10^{-7} mbar. Samples were finely ground in a glovebox and pressed into aluminum foil before being placed on a sample holder and transferred to the XPS instrument in a sealed container to avoid exposure to air during transport. All results were analyzed with use of the Avantage software package. Charge correction was calibrated with C 1s (284.6 eV) as reference. [4]

The spectra showed that the electron binding energies of Co $2p_{1/2}$ and $2p_{3/2}$ in the sample of HBPin/BiPyPhos/$Co(acac)_2$ were 796.7 eV and 781.4 eV respectively. The corresponding electron binding energies of Co $2p_{1/2}$ and $2p_{3/2}$ in $Co(acac)_2$ is 797.7 eV and 782.0 eV.

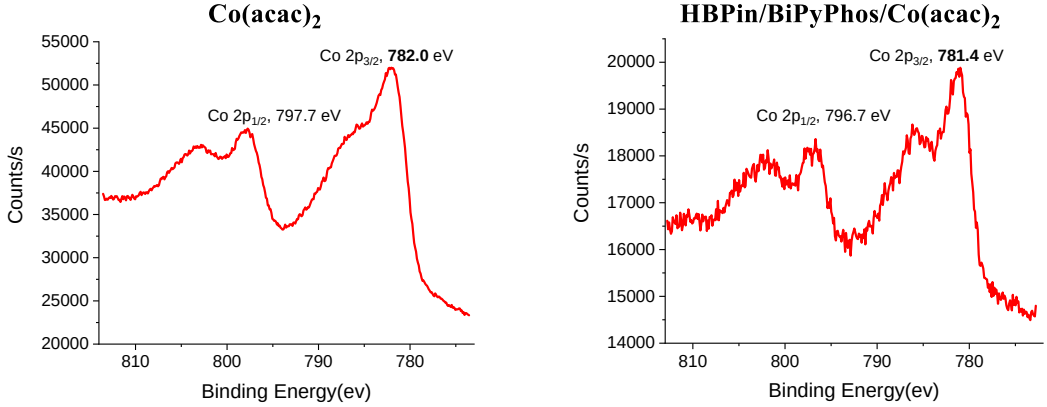


Figure S4: X-ray photoelectron spectroscopy of cobalt catalysts

3.6 X-band EPR spectrum

A 20 mL scintillation vial was charged with 0.130 g (0.5 mmol) $Co(acac)_2$, 0.276 g ligand (0.5 mmol), 3 mL (2 mmol) HBpin and 1 mL toluene. The resulting black solution was stirred at room temperature for 5 min, and 0.2 mL solution was taken and record EPR spectra at 130 K temperature. [5]

Table S5: Parameters used to fit the EPR spectrum of B-L-Co at 9.86 GHz and T = 130 K.

Parameter	B-L-Co
g_x	2.306
g_y	2.291

g_z	2.021

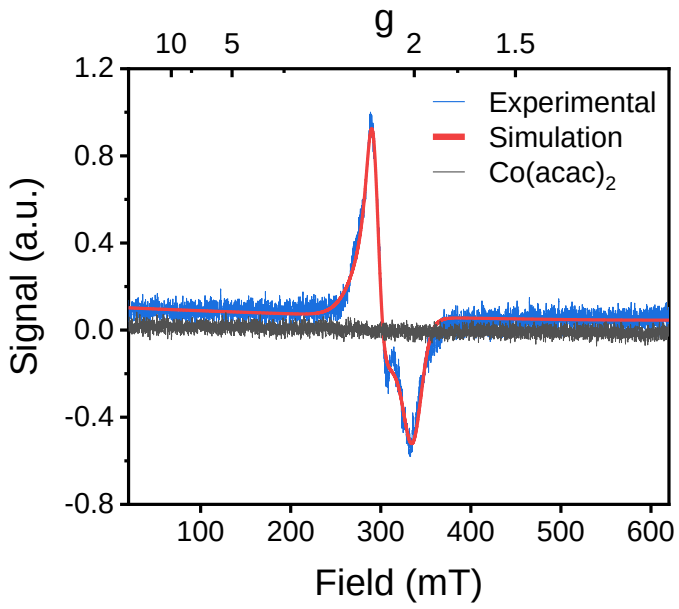
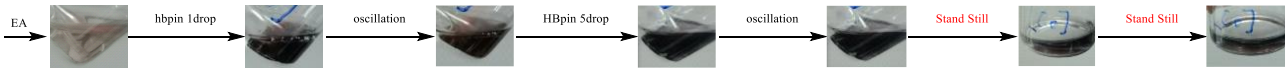


Figure S5: EPR spectra of B-L-Co (HBpin+L1+$Co(acac)_2$), $Co(acac)_2$

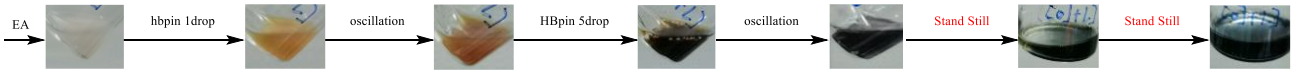
3.7 Color transition

a) $Co(acac)_2$ + EA



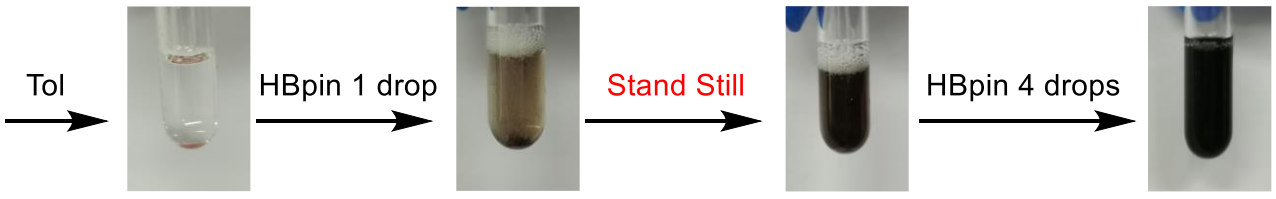
A 20 mL scintillation vial was charged with 2.6 mg (0.01 mmol) $Co(acac)_2$ and 0.5 mL EA. After shaking, it was an incompletely dissolved pink transparent solution, a drop of HBpin was added to it, the solution immediately turned dark brown, after shaking it became black-red, 5 drops of HBpin were added and no obvious change was observed after shaking, after standing for one minute it turned blue-black, subsequently after standing for two minutes it turned purple.

b) $Co(acac)_2$+ L+EA



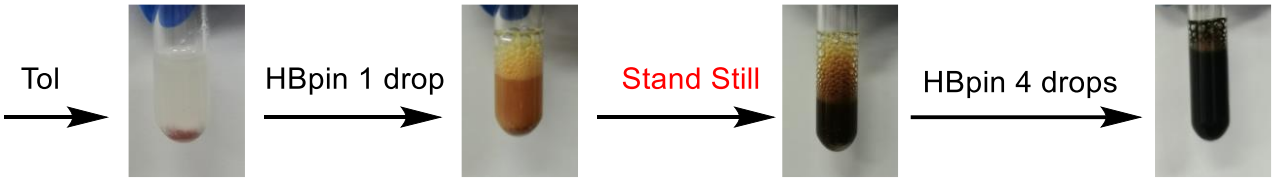
A 20 mL scintillation vial was charged with 2.6 mg (0.01 mmol) $Co(acac)_2$, 6.1 mg (0.011 mmol) L1 and 0.5 mL EA. After shaking, an incompletely dissolved white turbid solution was added to one drop of HBpin, the solution immediately turned orange-yellow, and it turned orange after shaking, 5 drops of HBpin were added, it turned black-brown, after standing for two minutes it turned dark green, subsequently after standing for another two minutes it turned blue-black.

c) $Co(acac)_2$



A 1 mL scintillation vial was charged with 2.6 mg (0.01mmol) $Co(acac)_2$. The solid did not dissolve when 0.1 mL toluene was added. After adding one drop of HBpin, the solution bubbled violently and gradually turned brownish-black, another four more drops of HBpin were added and the solution was black finally.

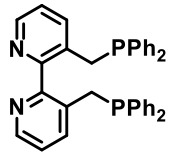
d) $Co(acac)_2$+ L



A 1 mL scintillation vial was charged with 2.6 mg (0.01mmol) $Co(acac)_2$, 6.08mg (0.011mmol) L1. After adding 0.1mL toluene, the liquid was a white suspension, and then one drop of HBpin was added, the solution bubbled violently and turned orange, and then quickly turned orange-black, subsequently four drops of HBpin were introduced and the solution turned black ultimately.

4. Spectral Data for Materials

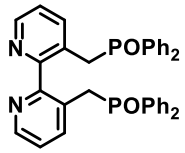
3,3'-bis((diphenylphosphaneyl)methyl)-2,2'-bipyridine (L1) [6]



L1

Ligand L1 (white solid) is supplied by CHENGDU XINHUAYUAN TECHNOLOGY CO, LTD., and the structure is determined by NMR. 1H NMR (400 MHz, CDCl3) δ 8.48 – 8.41 (m, 2H), 7.38 – 7.26 (m, 22H), 7.06 (dd, J = 7.8, 4.8 Hz, 2H), 3.44 (s, 4H) ppm. ^{31}P NMR (162 MHz, CDCl3) δ -13.41 ppm.

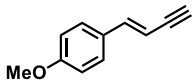
([2,2'-bipyridine]-3,3'-diylbis(methylene))bis(diphenylphosphine oxide) (L6)



L6

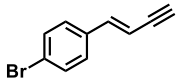
The compound was synthesized following the general procedure A. A white solid (18mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 4.7 Hz, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.59 (dd, J = 11.6, 7.6 Hz, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.35 (dt, J = 9.0, 4.5 Hz, 4H), 7.21 (dd, J = 8.0, 4.7 Hz, 1H), 6.98 (s, 1H), 3.61 (d, J = 13.5 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.0, 156.0, 146.6, 146.6, 140.1, 140.0, 133.1, 132.1, 131.8, 131.8, 130.9, 130.8, 128.6, 128.5, 128.4, 128.3, 123.1, 53.5, 32.8, 32.1 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.21 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd. for $C_{36}H_{30}N_2O_2P_2$: 585.1855; Found: 585.1852.

(*E*)-1-(but-1-en-3-yn-1-yl)-4-methoxybenzene (substrate for 31) [1]



According to the general procedure A after silica gel chromatography (pure petroleum ether) and the yield of (*E*)-1-(but-1-en-3-yn-1-yl)-4-methoxybenzene was 70% (2.21 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 2H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.91-6.83 (m, 2H), 5.99 (dd, *J* = 16.3, 2.3 Hz, 1H), 3.82 (s, 3H), 3.01 (d, *J* = 2.2 Hz, 1H) ppm.

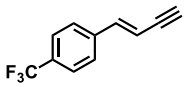
(*E*)-1-bromo-4-(but-1-en-3-yn-1-yl)benzene (substrate for 32) [1]



According to the general procedure A after silica gel chromatography (pure petroleum ether) and the yield of (*E*)-1-bromo-4-(but-1-en-3-yn-1-yl)benzene was 67% (2.77 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 2H), 7.24 (dd, *J* = 8.8, 2.0 Hz, 2H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.12 (dd, *J* = 16.3, 2.4 Hz,

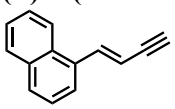
1H), 3.08 (d, *J* = 2.2 Hz, 1H) ppm.

(*E*)-1-(but-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (substrate for 33) [1]



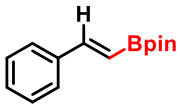
According to the general procedure A after silica gel chromatography (pure petroleum ether) and the yield of (*E*)-1-(but-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene was 53% (2.08 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 16.4 Hz, 1H), 6.22 (dd, *J* = 16.3, 2.3 Hz, 1H), 3.13 (d, *J* = 2.3 Hz, 1H) ppm.

(*E*)-1-(but-1-en-3-yn-1-yl)naphthalene (substrate for 34) [1]



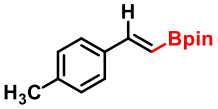
According to the general procedure A after silica gel chromatography (pure petroleum ether) and the yield of (*E*)-1-(but-1-en-3-yn-1-yl)naphthalene was 55% (1.96 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.86 (dd, *J* = 17.0, 5.3 Hz, 3H), 7.64 (d, *J* = 7.2 Hz, 1H), 7.57-7.50 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 1H), 6.21 (ddd, *J* = 3.5, 2.5, 1.5 Hz, 1H), 3.27-3.00 (m, 1H) ppm.

(*E*)-2-Phenylvinylboronic Acid Pinacol Ester (1) [7]



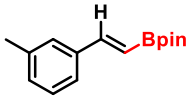
The compound was synthesized following the general procedure. A greyish yellow solid (2.23 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.39 – 7.27 (m, 4H), 6.18 (d, *J* = 18.5 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8 ppm.

(*E*)-4,4,5,5-Tetramethyl-2-(4-Methylstyryl)-1,3,2-Dioxaborolane (2) [7]



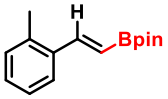
The compound was synthesized following the general procedure. A greyish yellow solid (2.35 g, 96%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.39 (m, 3H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.16 (d, *J* = 18.5 Hz, 1H), 2.37 (s, 3H), 1.34 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5, 138.9, 134.8, 129.3, 127.1, 83.2, 24.8, 21.3 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(3-methylphenyl)ethenyl]-1,3,2-dioxaborolane (3) [7]



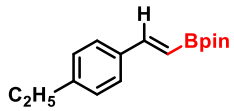
The compound was synthesized following the general procedure. A greyish yellow solid (1.88 g, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.30 (d, *J* = 5.8 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 138.1, 137.5, 129.8, 128.5, 127.8, 124.3, 83.3, 24.8, 21.4 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-methylphenyl)ethenyl]-1,3,2-dioxaborolane (4) [8]



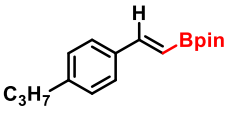
The compound was synthesized following the general procedure. A greyish yellow solid (1.44 g, 58%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 18.3 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.21 – 7.18 (m, 2H), 7.15 (dt, *J* = 5.4, 2.7 Hz, 1H), 6.09 (d, *J* = 18.3 Hz, 1H), 2.43 (s, 3H), 1.32 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 136.7, 136.3, 130.4, 128.6, 126.1, 125.8, 83.3, 24.8, 19.8 ppm.

2-[(*1E*)-2-(4-Ethylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5) [9]



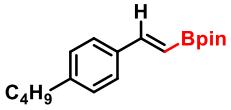
The compound was synthesized following the general procedure. A greyish yellow solid (2.41 g, 93%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.20 – 7.15 (m, 2H), 6.13 (d, *J* = 18.4 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 1.32 (s, 12H), 1.24 (t, *J* = 7.6 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 144.3, 133.9, 127.1, 126.1, 82.2, 27.7, 23.8, 14.4 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-propylphenyl)ethenyl]-1,3,2-dioxaborolane (6) [10]



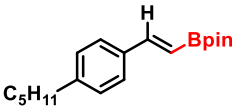
The compound was synthesized following the general procedure. A greyish yellow solid (2.21 g, 81%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 3H), 7.15 (d, *J* = 8.3 Hz, 2H), 6.13 (d, *J* = 18.4 Hz, 1H), 2.61 – 2.55 (m, 2H), 1.69 – 1.59 (m, 3H), 1.32 (s, 12H), 0.94 (t, *J* = 7.4 Hz, 4H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 142.7, 134.0, 127.7, 126.0, 82.2, 36.8, 23.8, 23.4, 12.8 ppm.

2-[(*1E*)-2-(4-Butylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7) [7]



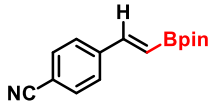
The compound was synthesized following the general procedure. A greyish yellow solid (2.58 g, 90%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 3H), 7.20 – 7.12 (m, 2H), 6.12 (d, *J* = 18.4 Hz, 1H), 2.64 – 2.57 (m, 2H), 1.60 (d, *J* = 7.7 Hz, 2H), 1.35 (d, *J* = 7.5 Hz, 2H), 1.31 (s, 12H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 142.9, 133.9, 127.6, 125.9, 82.2, 34.4, 32.4, 23.8, 21.3, 12.9 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-pentylphenyl)ethenyl]-1,3,2-dioxaborolane (8) [11]



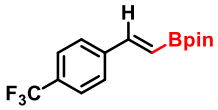
The compound was synthesized following the general procedure. A greyish yellow solid (2.61 g, 87%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.1 Hz, 1H), 7.40 (s, 1H), 7.37 (s, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.13 (d, *J* = 18.4 Hz, 1H), 2.63 – 2.56 (m, 2H), 1.68 – 1.57 (m, 2H), 1.34 (d, *J* = 3.3 Hz, 2H), 1.32 (s, 12H), 1.26 (d, *J* = 10.0 Hz, 2H), 0.92 – 0.87 (m, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 148.5, 143.0, 133.9, 127.6, 126.0, 82.2, 34.7, 30.4, 29.9, 23.7, 21.5, 12.9 ppm.

4-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzonitrile (9) [12]



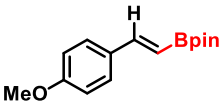
The compound was synthesized following the general procedure. A greyish yellow solid (2.33 g, 91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.53 (m, 4H), 7.36 (d, *J* = 18.4 Hz, 1H), 6.28 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.1, 141.7, 132.5, 127.4, 118.8, 112.0, 83.8, 24.8 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-[4-(trifluoromethyl)phenyl]ethenyl]-1,3,2-dioxaborolane (10) [13]



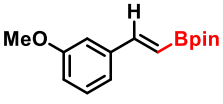
The compound was synthesized following the general procedure. A greyish yellow solid (2.31 g,77 %).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.40 (d, *J* = 18.4 Hz, 1H), 6.26 (d, *J* = 18.5 Hz, 1H), 1.32 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 140.8, 130.5 (d, *J* = 32.4 Hz), 127.2, 125.6 (q, *J* = 3.9 Hz), 124.1 (d, *J* = 271.9 Hz), 83.6, 24.9 ppm.

2-[(*1E*)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11) [7]



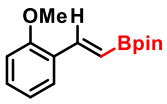
The compound was synthesized following the general procedure. A greyish yellow solid (2.34 g, 89%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 6.87 – 6.81 (m, 2H), 6.01 (d, *J* = 18.5 Hz, 1H), 3.79 (s, 3H), 1.30 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.1, 129.3, 127.4, 112.9, 82.2, 54.2, 23.7 ppm.

2-[(*1E*)-2-(3-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12) [8]



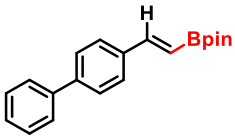
The compound was synthesized following the general procedure. A greyish yellow solid (1.95 g, 74%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 18.4 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.83 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.16 (d, *J* = 18.4 Hz, 1H), 3.77 (s, 3H), 1.30 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 148.3, 137.8, 128.4, 118.7, 113.6, 110.9, 82.2, 54.0, 23.7 ppm.

2-[(*1E*)-2-(2-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13) [12]



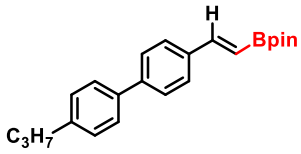
The compound was synthesized following the general procedure. A greyish yellow solid (1.37 g, 52%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 18.7 Hz, 1H), 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 – 7.24 (m, 1H), 6.93 (td, *J* = 7.5, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.19 (d, *J* = 18.6 Hz, 1H), 3.84 (s, 3H), 1.31 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.3, 144.1, 130.0, 127.0, 126.5, 120.5, 110.8, 83.2, 55.3, 24.8 ppm.

2-[(*1E*)-2-[1,1′-Biphenyl]-4-ylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14) [14]



The compound was synthesized following the general procedure. A greyish yellow solid (2.76 g, 90%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.5 Hz, 1H), 7.60 – 7.59 (m, 1H), 7.57 (d, *J* = 2.1 Hz, 3H), 7.47 – 7.41 (m, 4H), 7.36 (d, *J* = 7.3 Hz, 1H), 6.21 (d, *J* = 18.5 Hz, 1H), 1.33 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.0, 141.6, 140.5, 136.5, 128.81, 127.5, 127.4, 127.2, 127.0, 83.4, 24.8 ppm.

(*E*)-4,4,5,5-tetramethyl-2-(2-(4'-propyl-[1,1'-biphenyl]-4-yl)vinyl)-1,3,2-dioxaborolane (15)

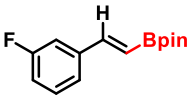


The compound was synthesized following the general procedure. A greyish yellow solid (3.00 g, 86%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.8 Hz, 3H), 7.53 (d, *J* = 8.2 Hz, 3H), 7.45 (d, *J* = 17.8 Hz, 1H), 7.26 (s, 1H), 7.24 (s, 1H), 6.21 (d, *J* = 18.4 Hz, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.69 (q, *J* = 7.4 Hz, 2H), 1.33 (s, 12H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 141.1, 140.6, 136.9, 135.2, 127.9, 126.5, 126.0, 125.8, 82.3, 36.7, 23.8,23.5, 12.6 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{29}BO_2$ 349.2334; Found: 349.2336.

2-[(*1E*)-2-(4-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16) [7]

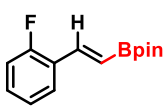
The compound was synthesized following the general procedure. A greyish yellow solid (2.32 g, 93%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.35 (d, *J* = 18.4 Hz, 1H), 7.04 – 6.97 (m, 2H), 6.07 (d, *J* = 18.4 Hz, 1H), 1.30 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 161.9, 148.2, 133.7 (d, *J* = 3.3 Hz), 128.7 (d, *J* = 8.3 Hz), 115.6 (d, *J* = 21.6 Hz), 83.4, 24.8 ppm.

2-[(*1E*)-2-(3-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17) [7]



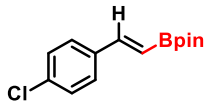
The compound was synthesized following the general procedure. A greyish yellow solid (2.07 g, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 18.4 Hz, 1H), 7.27 – 7.16 (m, 2H), 7.13 (dt, *J* = 10.0, 2.1 Hz, 1H), 6.92 (ddd, *J* = 9.8, 8.2, 2.4 Hz, 1H), 6.12 (d, *J* = 18.4 Hz, 1H), 1.26 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (d, *J* = 245.7 Hz), 148.1 (d, *J* = 2.6 Hz), 139.9 (d, *J* = 7.4 Hz), 130.0 (d, *J* = 8.2 Hz), 123.0 (d, *J* = 2.7 Hz), 115.7 (d, *J* = 21.5 Hz), 113.3 (d, *J* = 21.6 Hz), 83.5, 24.8 ppm.

2-[(*1E*)-2-(2-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18) [7]



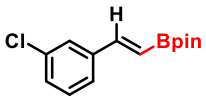
The compound was synthesized following the general procedure. A greyish yellow solid (1.99 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.27 (dddd, *J* = 8.3, 7.0, 5.1, 1.8 Hz, 1H), 7.13 (td, *J* = 7.6, 1.2 Hz, 1H), 7.05 (ddd, *J* = 10.7, 8.2, 1.2 Hz, 1H), 6.27 (d, *J* = 18.6 Hz, 1H), 1.34 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7 (d, *J* = 251.5 Hz), 141.3 (d, *J* = 4.0 Hz), 130.2 (d, *J* = 8.6 Hz), 127.4 (d, *J* = 3.4 Hz), 125.4 (d, *J* = 11.6 Hz), 124.1 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.1 Hz), 83.5, 24.8 ppm.

2-[(*1E*)-2-(4-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19) [7]



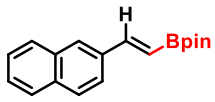
The compound was synthesized following the general procedure. A greyish yellow solid (2.33 g, 88%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 (s, 1H), 7.32 – 7.27 (m, 3H), 6.13 (d, *J* = 18.4 Hz, 1H), 1.31 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 135.9, 134.6, 128.8, 128.2, 83.4, 24.8, 24.6 ppm.

2-[(*1E*)-2-(3-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20) [8]



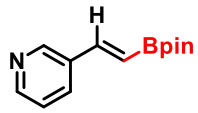
The compound was synthesized following the general procedure. A greyish yellow solid (1.80 g, 68%).1H NMR (400 MHz, $CDCl_3$) δ 7.42 (q, J = 1.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 6.13 (d, J = 18.4 Hz, 1H), 1.28 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 139.3, 134.5, 129.8, 128.7, 126.9, 125.2, 83.5, 24.8 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-naphthalenyl)ethenyl]-1,3,2-dioxaborolane (21) [12]



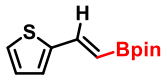
The compound was synthesized following the general procedure. A greyish yellow solid (2.31 g, 82%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.87 – 7.83 (m, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 7.74 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.64 (d, *J* = 18.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 6.36 (d, *J* = 18.4 Hz, 1H), 1.37 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.6, 135.0, 133.7, 133.4, 128.4, 128.3, 128.0, 127.7, 126.4, 126.3, 123.4, 83.4, 24.8 ppm.

3-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]pyridine (22) [7]



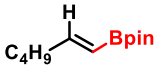
The compound was synthesized following the general procedure. A greyish yellow solid (2.13 g, 92%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 2.3 Hz, 1H), 8.41 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.74 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.29 (d, *J* = 18.5 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.17 (d, *J* = 18.5 Hz, 1H), 1.23 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.4, 144.4, 132.6, 82.6, 81.5, 74.0, 23.7 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-thienyl)ethenyl]-1,3,2-dioxaborolane (24) [10]



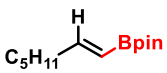
The compound was synthesized following the general procedure. A greyish yellow solid (2.22 g, 94%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 18.1 Hz, 1H), 7.22 (dt, *J* = 5.1, 1.0 Hz, 1H), 7.08 – 7.06 (m, 1H), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.92 (d, *J* = 18.1 Hz, 1H), 1.29 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 140.7, 126.6, 126.5, 125.2, 82.3, 23.7 ppm.

(*E*)-Hex-1-enylboronic acid pinacol ester (26) [10]



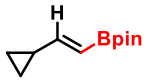
The compound was synthesized following the general procedure. A greyish yellow solid (1.77 g, 84%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dt, *J* = 18.0, 6.5 Hz, 1H), 5.40 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.13 (dtd, *J* = 7.9, 6.6, 1.6 Hz, 2H), 1.40 – 1.35 (m, 2H), 1.33 – 1.28 (m, 2H), 1.24 (s, 12H), 0.87 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 81.9, 36.9, 23.8, 23.7, 20.4, 12.8 ppm.

(*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27) [15]



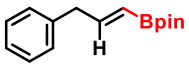
The compound was synthesized following the general procedure. A greyish yellow solid (1.71 g, 76%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dt, *J* = 18.0, 6.5 Hz, 1H), 5.40 (dt, *J* = 18.0, 1.6 Hz, 1H), 2.14 – 2.07 (m, 2H), 1.42 (q, *J* = 7.4 Hz, 2H), 1.24 (s, 12H), 0.88 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 82.9, 35.5, 31.6, 30.3, 24.7, 22.2, 13.9 ppm.

((*E*)-2-Cyclopropylethenyl) boronic acid pinacol ester (28) [7]



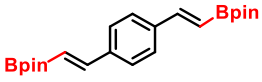
The compound was synthesized following the general procedure. A greyish yellow solid (1.77 g, 91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 6.03 (dd, *J* = 17.8, 9.3 Hz, 1H), 5.44 (dd, *J* = 17.7, 1.5 Hz, 1H), 1.46 (dqd, *J* = 12.7, 4.6, 3.2 Hz, 1H), 1.21 (d, *J* = 1.7 Hz, 12H), 0.79 – 0.72 (m, 2H), 0.49 (qd, *J* = 4.4, 2.2 Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 82.7, 24.6, 16.9, 7.7.^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 82.6, 24.6, 16.8, 7.7 ppm.

4,4,5,5-Tetramethyl-2-[(*1E*)-3-phenyl-1-propen-1-yl]-1,3,2-dioxaborolane (29) [15]



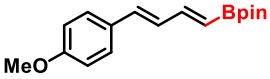
The compound was synthesized following the general procedure. A greyish yellow solid (2.08 g, 31%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.4 Hz, 2H), 7.22 (ddd, *J* = 8.8, 7.1, 1.8 Hz, 3H), 6.85 (dt, *J* = 17.8, 6.3 Hz, 1H), 5.54 (dt, *J* = 17.8, 1.8 Hz, 1H), 3.51 (dd, *J* = 6.4, 1.7 Hz, 2H), 1.29 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.5, 139.0, 128.9, 128.4, 126.2, 83.1, 42.3, 24.8 ppm.

2,2'-[1,4-phenylenedi-(1*E*)-2,1-ethenediyl]bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30) [16]



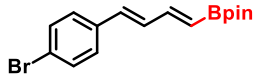
The compound was synthesized following the general procedure. A greyish yellow solid (1.08 g, 73%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 4H), 7.31 (s, 2H), 7.17 (s, 2H), 6.08 (d, *J* = 18.4 Hz, 2H), 1.22 (s, 24H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 136.9, 126.3, 82.4, 81.9, 23.7 ppm.

2-((*1E*,*3E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31)



The compound was synthesized following the general procedure. A greyish yellow solid (2.12 g, 74%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.8 Hz, 2H), 7.16 (dd, *J* = 17.6, 9.9 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.71 (dd, *J* = 9.9, 0.8 Hz, 1H), 6.67 (s, 1H), 5.61 (d, *J* = 17.6 Hz, 1H), 3.81 (s, 3H), 1.29 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 133.6, 130.7, 130.2, 127.2, 82.3, 23.7 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}BO_3$: 287.1814; Found: 287.1819.

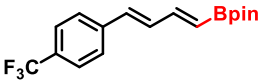
2-((*1E*,*3E*)-4-(4-bromophenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32)



The compound was synthesized following the general procedure. A greyish yellow solid (2.58 g, 77%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.18 – 7.10 (m, 1H), 6.82 (ddd, *J* = 15.6, 10.4, 0.9 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 5.72 – 5.66 (m, 1H), 1.29 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 149.1, 134.7, 128.5, 127.6, 127.1, 113.0, 82.1, 54.3, 23.8, 23.7, 23.5 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}BBrO_2$ 335.0812; Found: 335.0819.

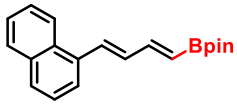
4,4,5,5-tetramethyl-2-((*1E*,*3E*)-4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (33)

The compound was synthesized following the general procedure. A greyish yellow solid (2.37 g, 73%).^{1}H NMR



(400 MHz, $CDCl_3$) δ 7.58 – 7.49 (m, 4H), 7.17 (dd, *J* = 17.5, 10.4 Hz, 1H), 6.91 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.70 (d, *J* = 15.6 Hz, 1H), 5.75 (d, *J* = 17.6 Hz, 1H), 1.30 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 139.2, 133.1, 131.8, 125.8, 124.5, 124.5, 82.4, 82.1, 23.7, 23.5 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{20}BF_3O_2$ 325.1582; Found: 325.1589.

4,4,5,5-tetramethyl-2-((*1E*,*3E*)-4-(naphthalen-1-yl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (34)



The compound was synthesized following the general procedure. A greyish yellow solid (2.425 g, 79%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.10 (m, 1H), 7.86 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.72 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.56 – 7.53 (m, 1H), 7.52 – 7.50 (m, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.38 – 7.32 (m, 1H), 6.95 (ddd, *J* = 15.4, 10.5, 0.9 Hz, 1H), 5.80 – 5.73 (m, 1H), 1.33 (s, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 134.0, 133.7, 133.2, 132.9, 131.2, 128.6, 128.5,

126.2, 125.8, 125.5, 123.7, 123.4, 83.3, 83.1, 24.8, 24.5 ppm. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}BO_2$ 307.1864; Found: 307.1867.

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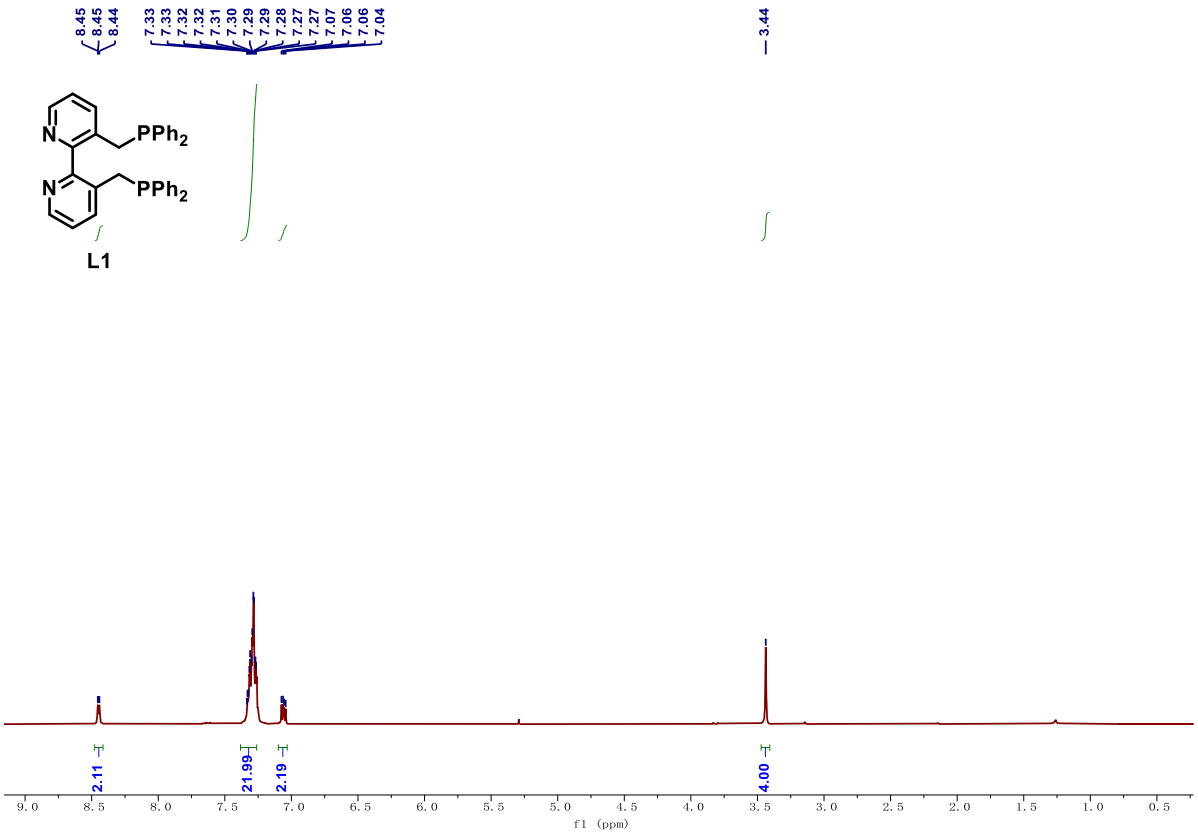
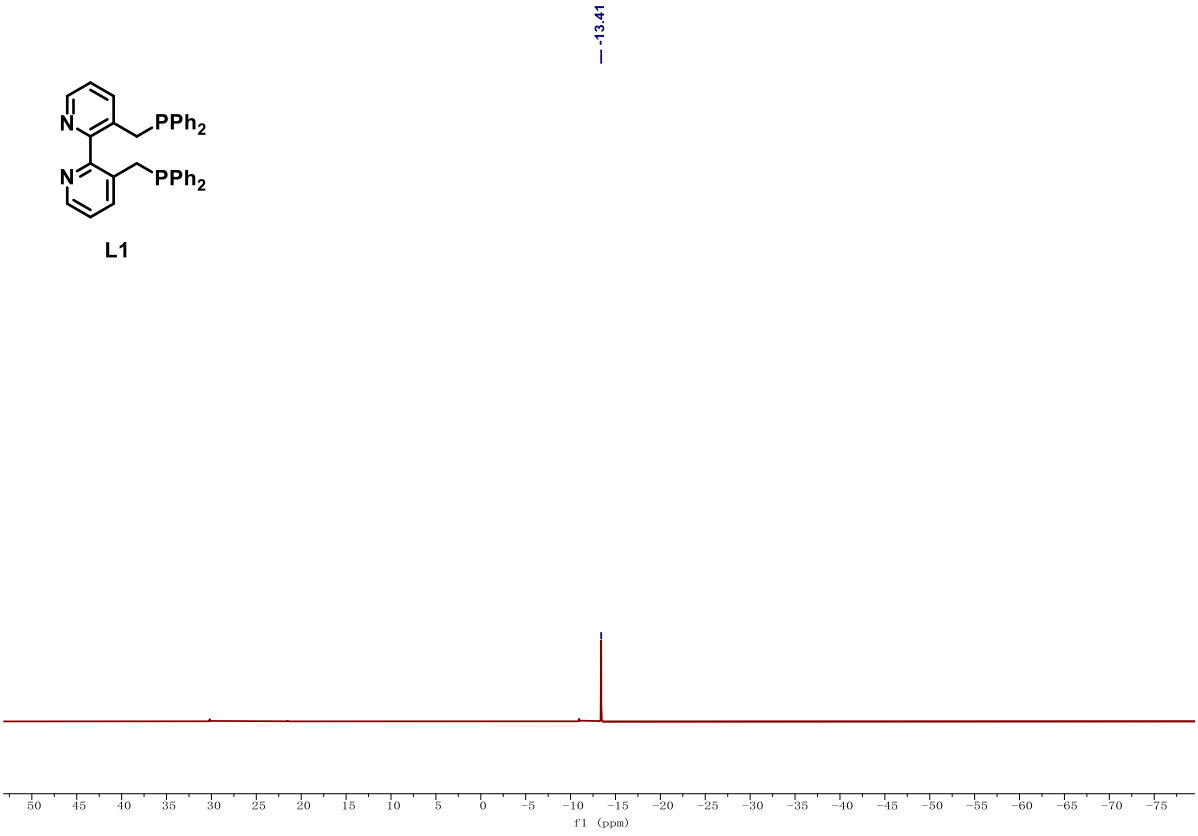
6. NMR spectra for ligands, conjugated enynes and *β*-*E*-vinylboronates

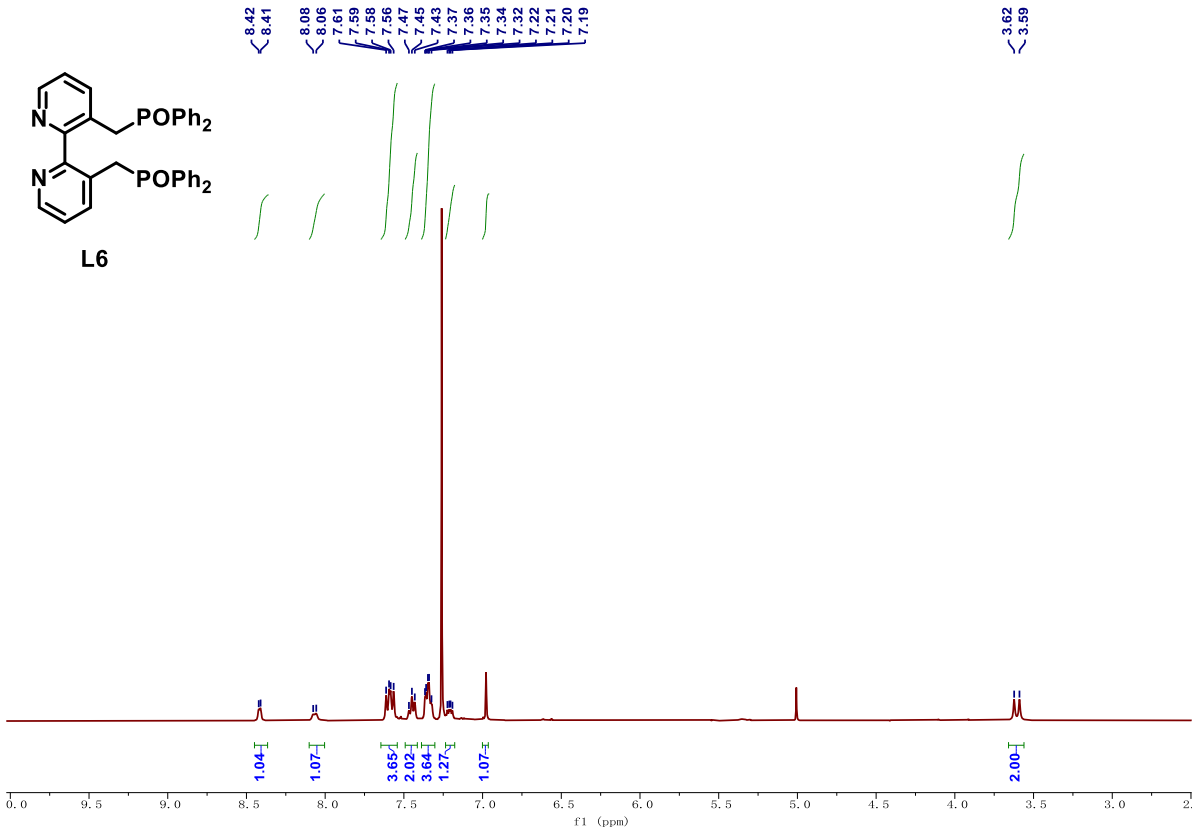
3,3'-bis((diphenylphosphaneyl)methyl)-2,2'-bipyridine (L1): ^{1}H NMR (400 MHz, $CDCl_3$):



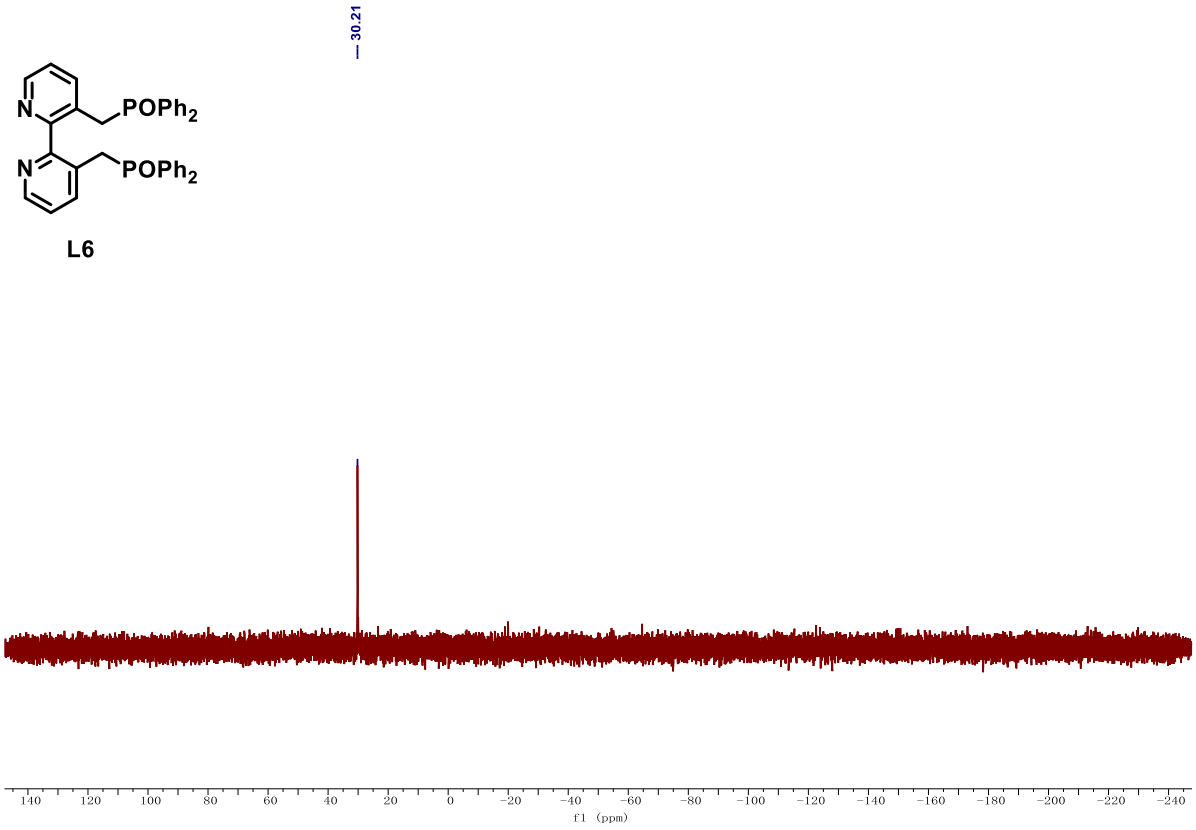
3,3'-bis((diphenylphosphaneyl)methyl)-2,2'-bipyridine (L1): ^{31}P NMR (162 MHz, $CDCl_3$):



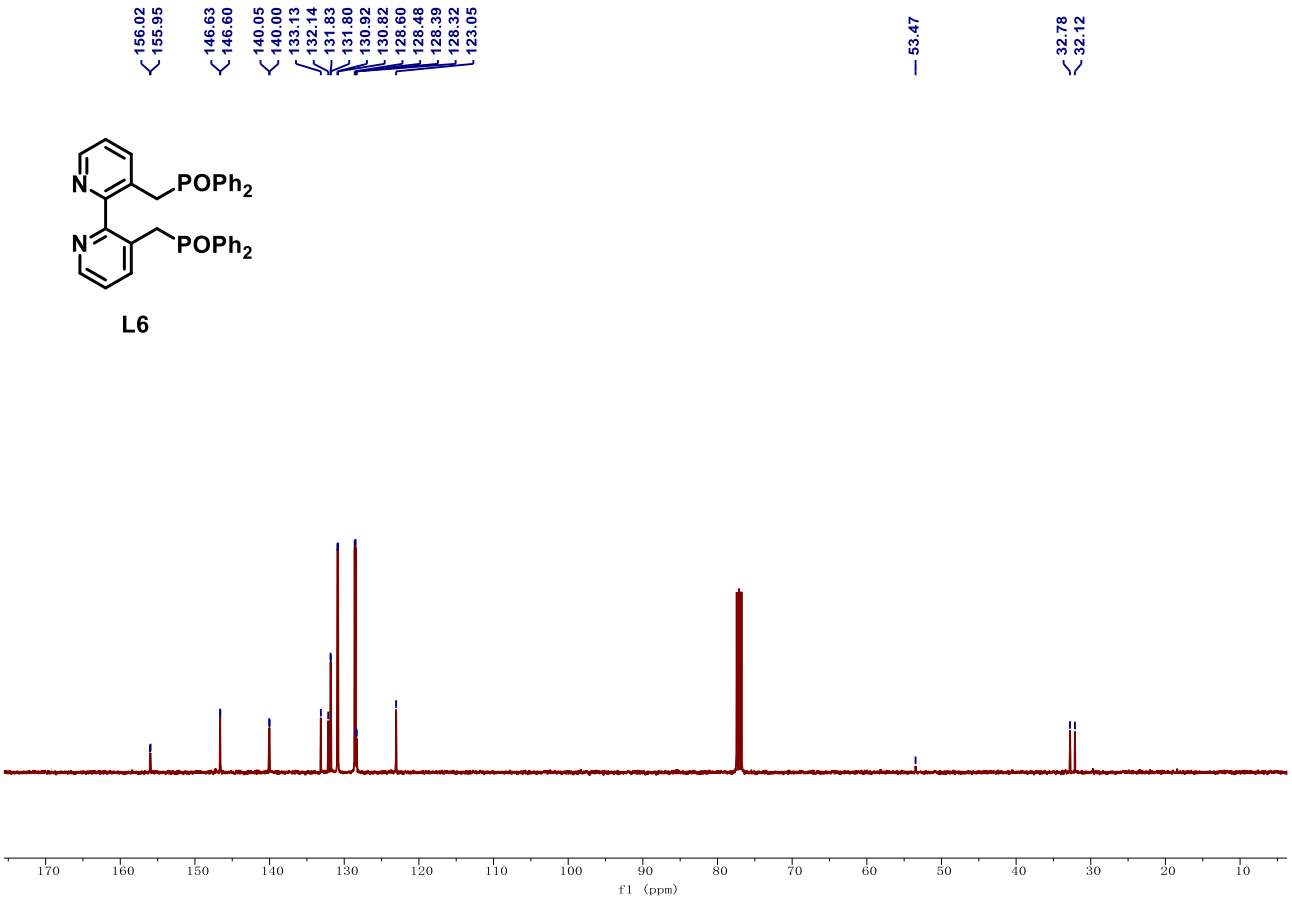
([2,2'-bipyridine]-3,3'-diylbis(methylene))bis(diphenylphosphine oxide) (L6): ^{1}H NMR (400 MHz, $CDCl_3$):



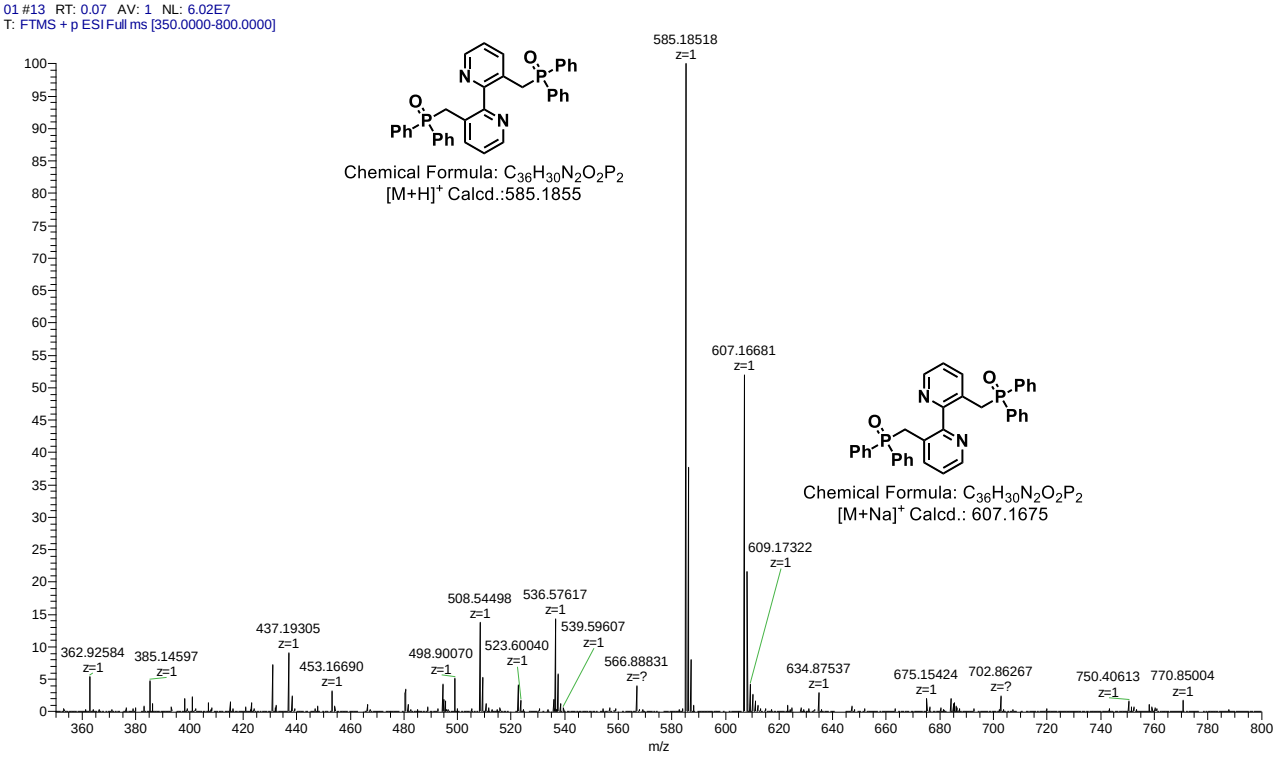
([2,2'-bipyridine]-3,3'-diylbis(methylene))bis(diphenylphosphine oxide) (L6): ^{31}P NMR (162 MHz, $CDCl_3$):



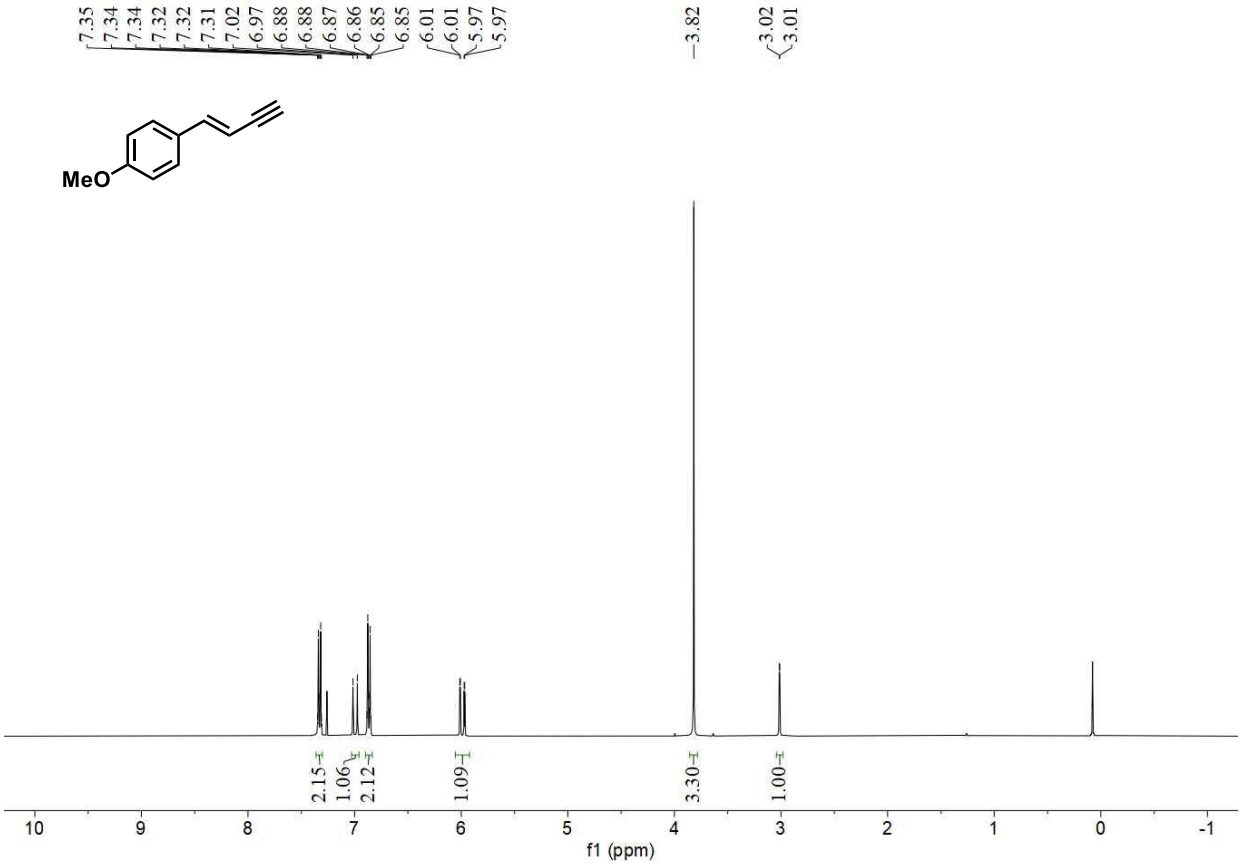
([2,2'-bipyridine]-3,3'-diylbis(methylene))bis(diphenylphosphine oxide) (L6): ^{13}C NMR (101 MHz, $CDCl_3$):



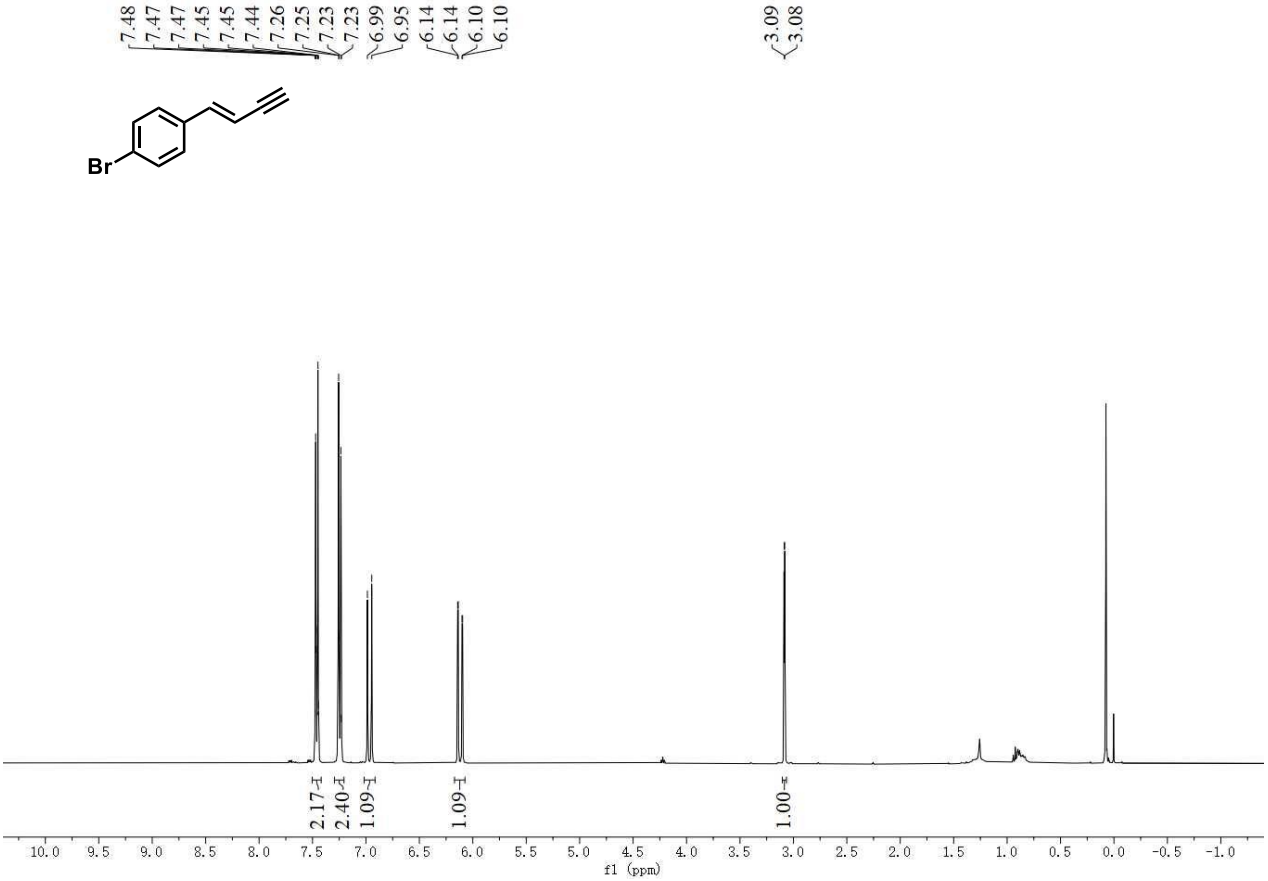
([2,2'-bipyridine]-3,3'-diylbis(methylene))bis(diphenylphosphine oxide) (L6): HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd.: 585.1855; Found: 585.1852. $[M+Na]^+$ Calcd.: 607.1675; Found: 607.1668.



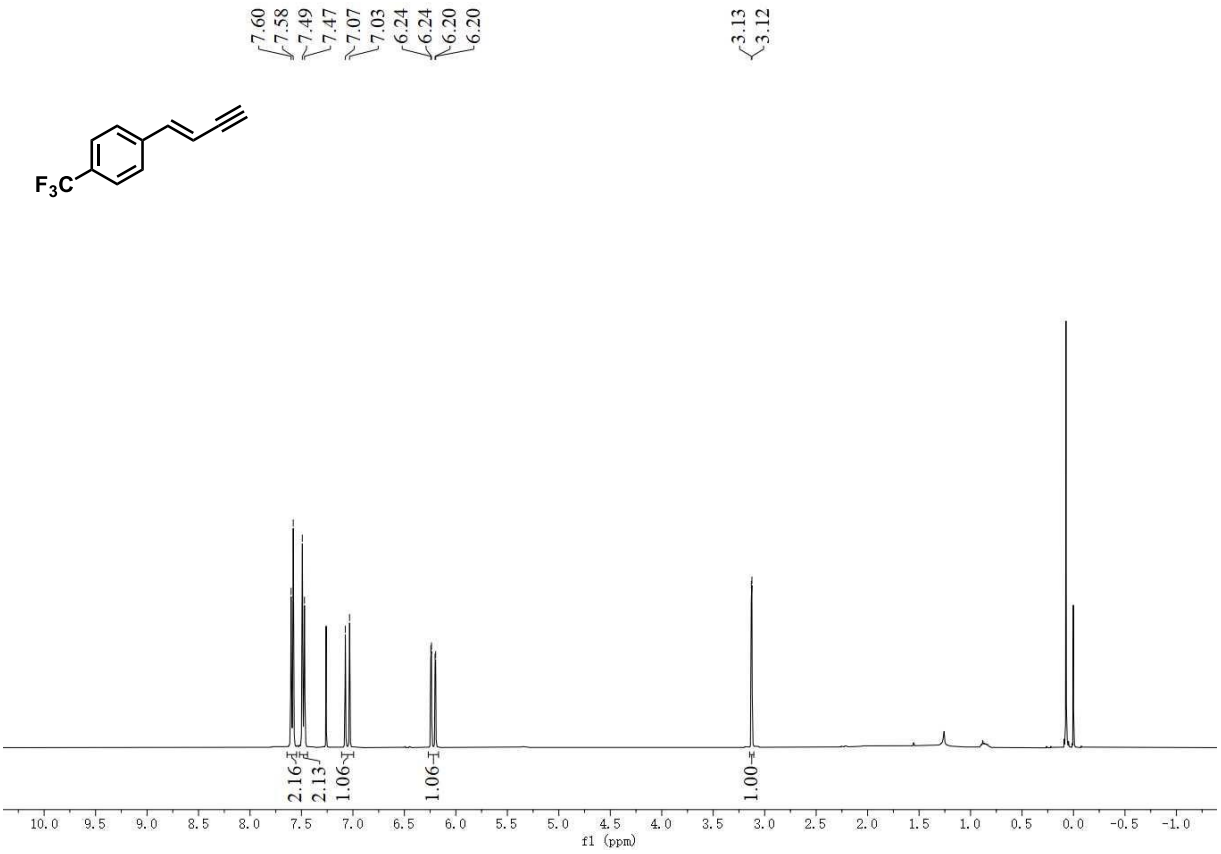
(*E*)-1-(but-1-en-3-yn-1-yl)-4-methoxybenzene (substrate for 31): **^{1}H NMR (400 MHz, $CDCl_3$)**



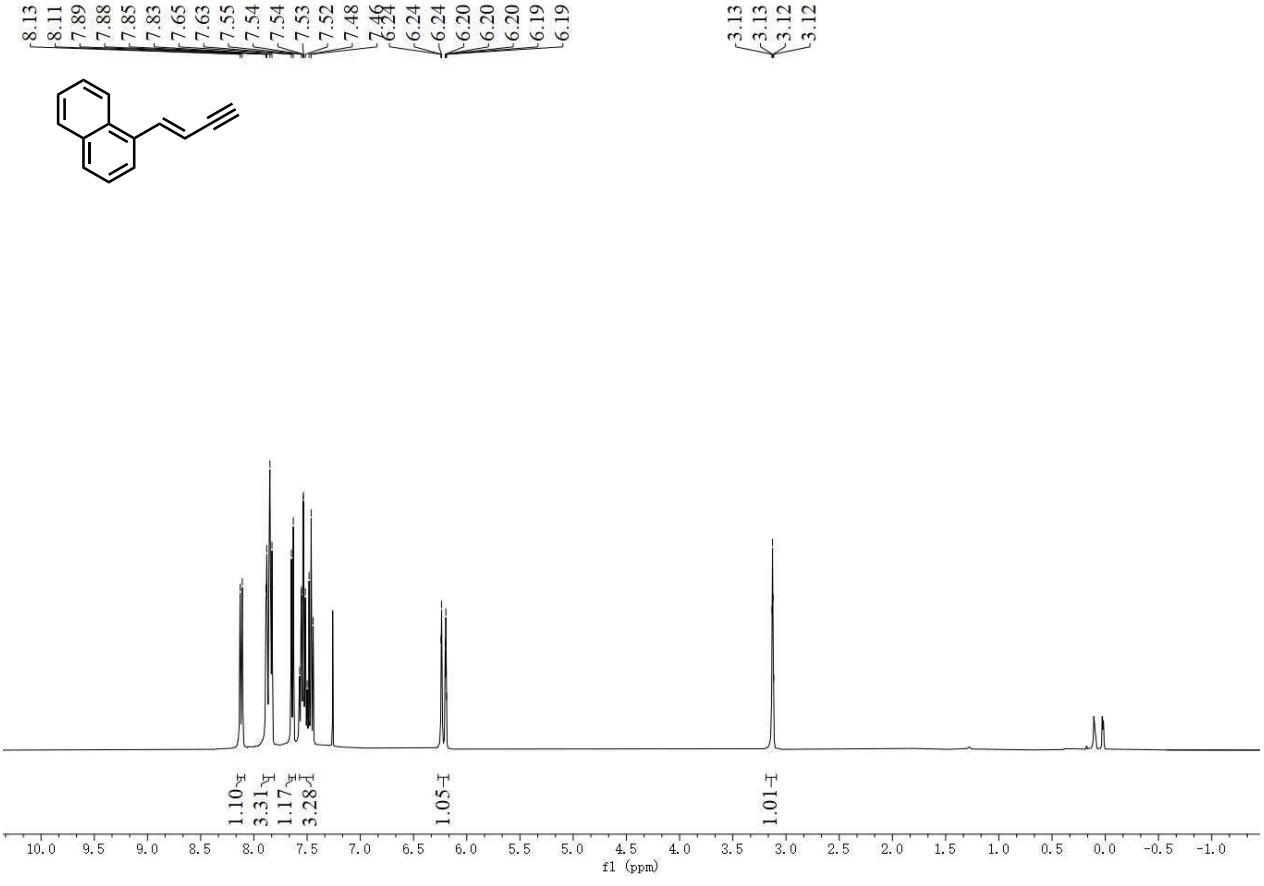
(*E*)-1-bromo-4-(but-1-en-3-yn-1-yl)benzene (substrate for 32): ^{1}H NMR (400 MHz, $CDCl_3$)



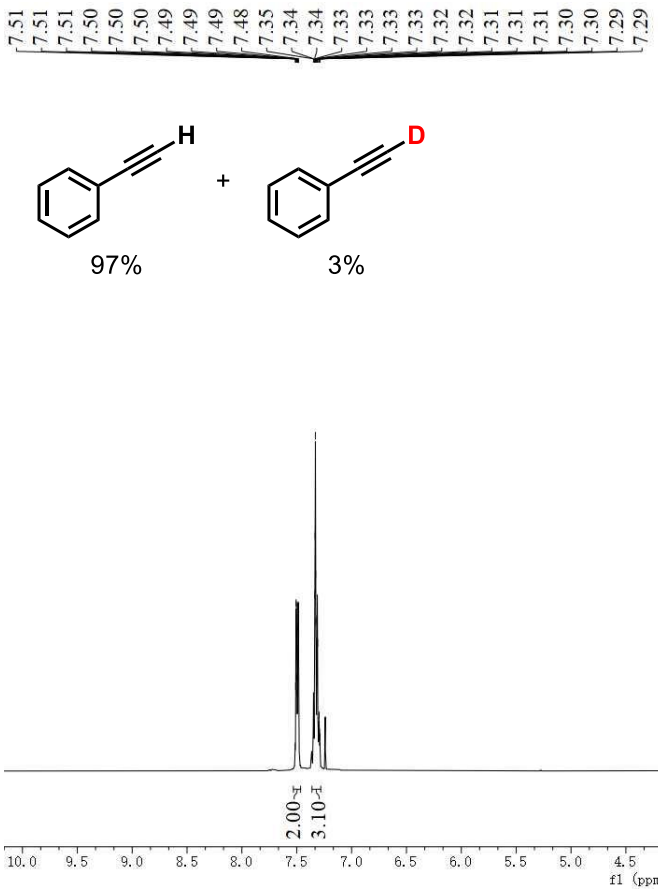
(*E*)-1-(but-1-en-3-yn-1-yl)-4-(trifluoromethyl)benzene (substrate for 33) : **^{1}H NMR (400 MHz, $CDCl_3$)**



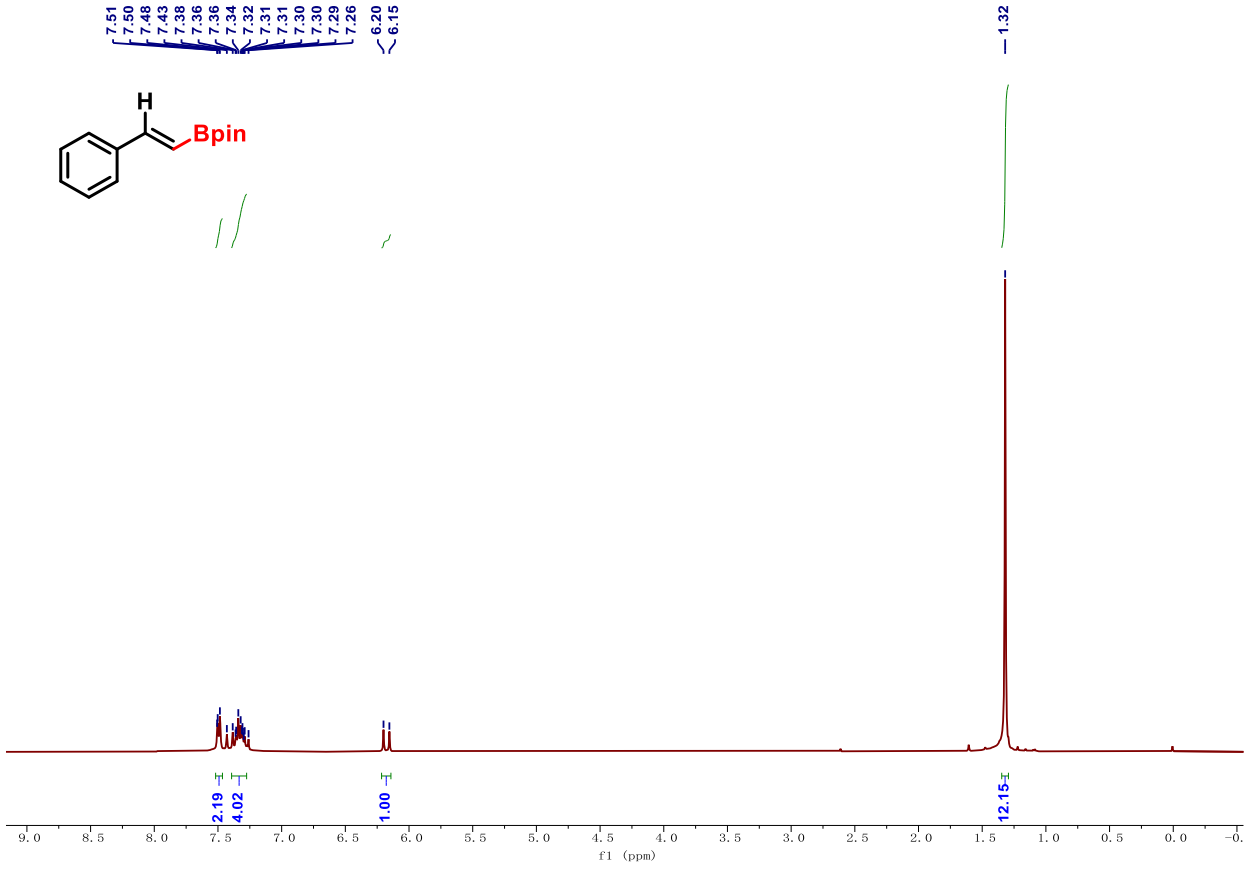
(*E*)-1-(but-1-en-3-yn-1-yl)naphthalene (substrate for 34) : **^{1}H NMR (400 MHz, $CDCl_3$)**



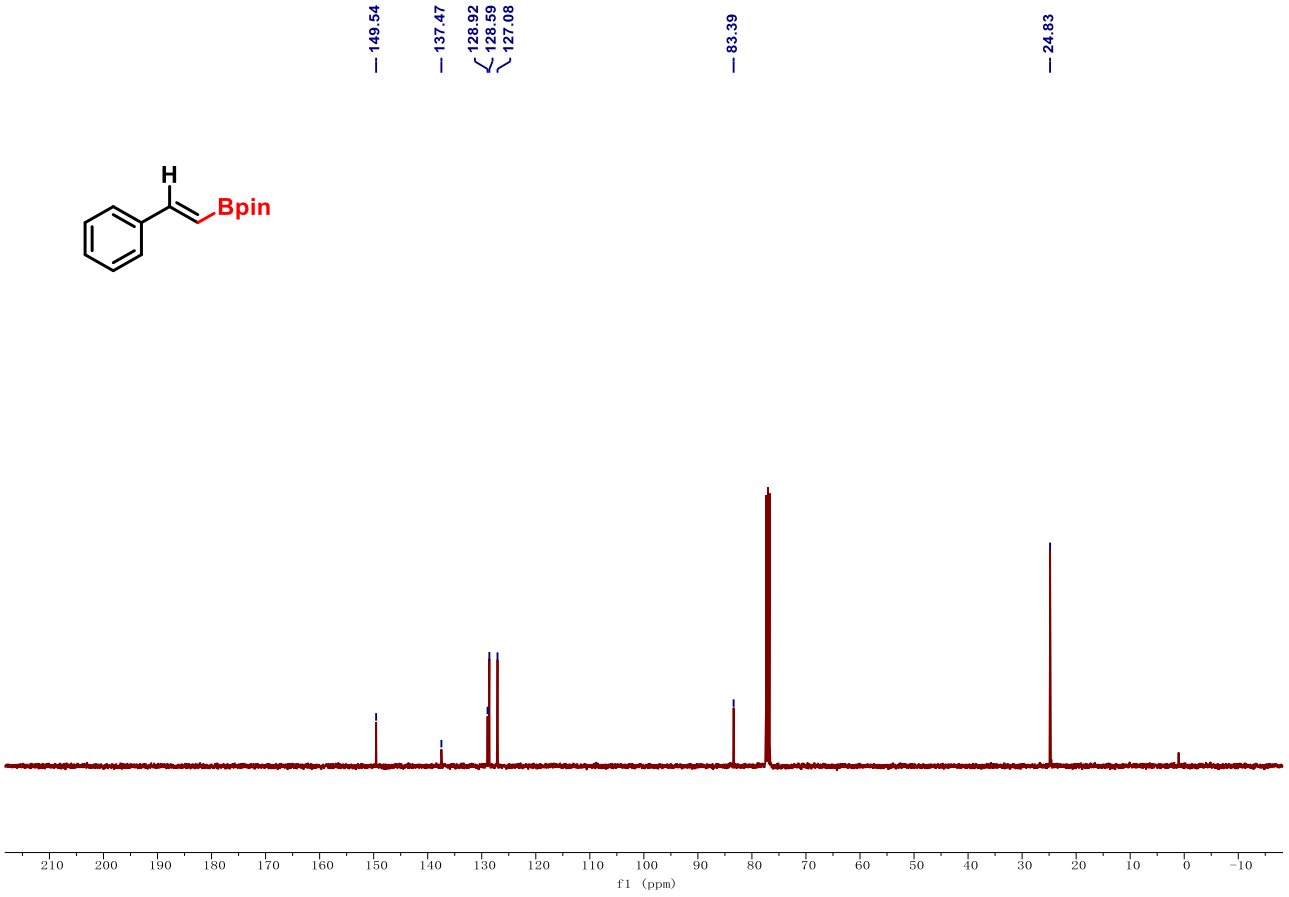
(ethynyl-*d*)benzene: ^{1}H NMR (400 MHz, $CDCl_3$)



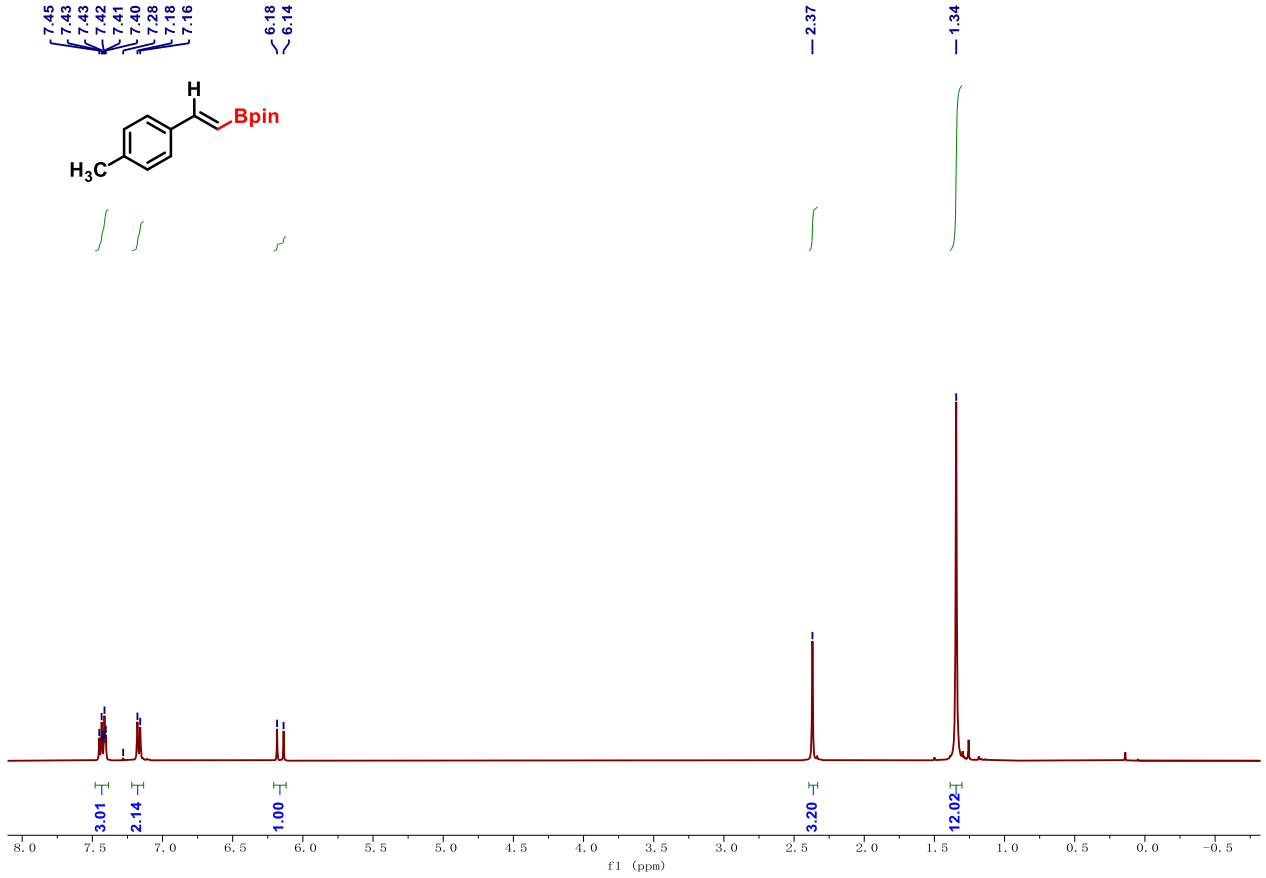
(*E*)-2-Phenylvinylboronic Acid Pinacol Ester (1): ^{1}H NMR (400 MHz, $CDCl_3$)



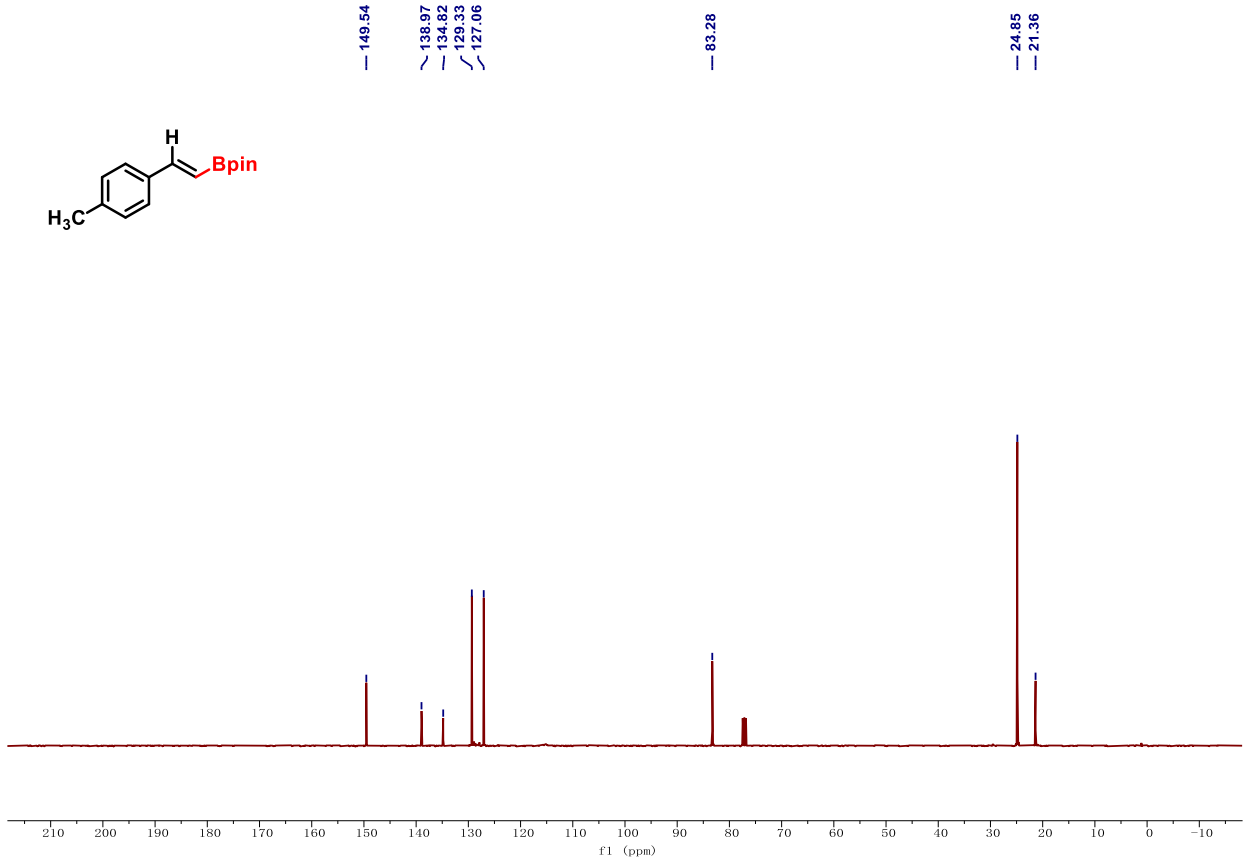
(*E*)-2-Phenylvinylboronic Acid Pinacol Ester (1): ^{13}C NMR (101MHz, $CDCl_3$)



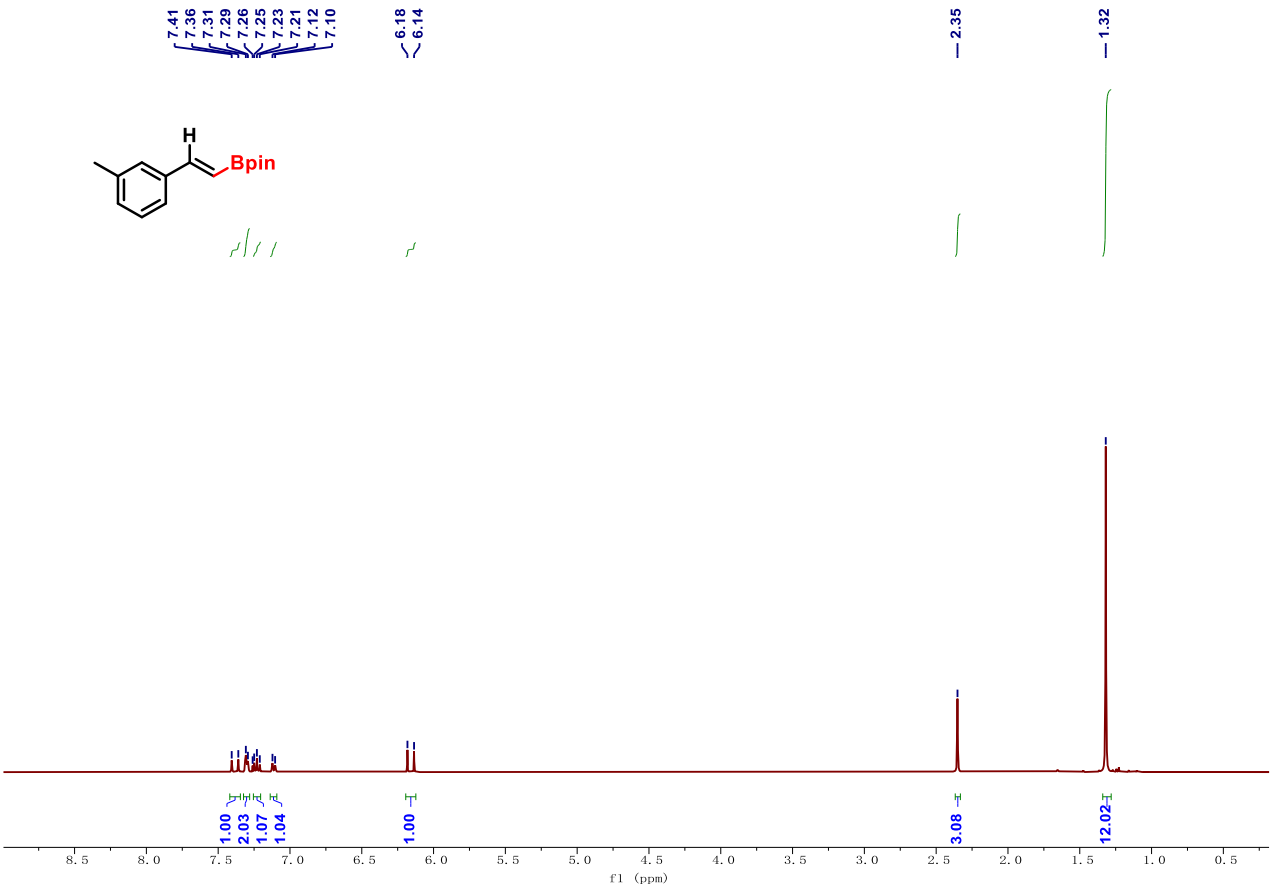
(*E*)-4,4,5,5-Tetramethyl-2-(4-Methylstyryl)-1,3,2-Dioxaborolane (2): ^{1}H NMR (400 MHz, $CDCl_3$)



(*E*)-4,4,5,5-Tetramethyl-2-(4-Methylstyryl)-1,3,2-Dioxaborolane (2): ^{13}C NMR (101 MHz, $CDCl_3$)

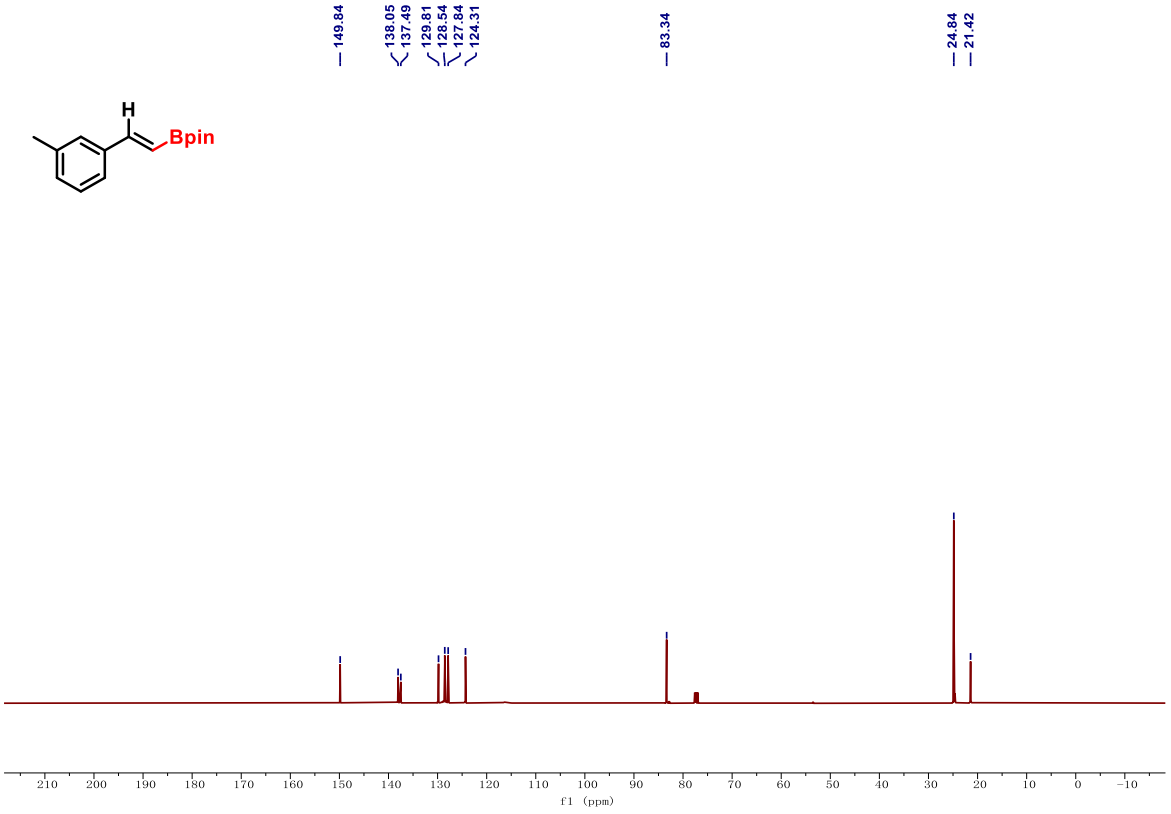


4,4,5,5-Tetramethyl-2-[(*1E*)-2-(3-methylphenyl)ethenyl]-1,3,2-dioxaborolane (3)：^{1}H NMR (400 MHz, $CDCl_3$)

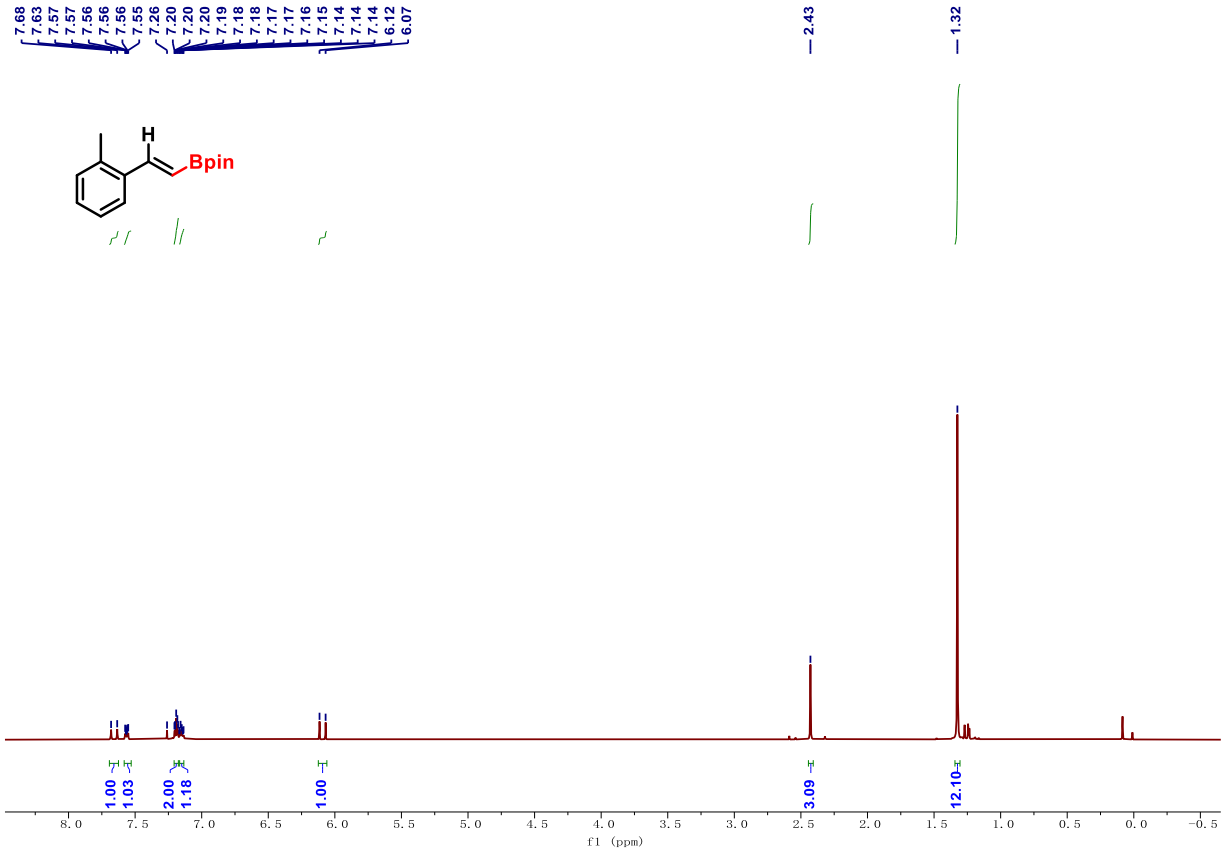


4,4,5,5-Tetramethyl-2-[(*1E*)-2-(3-methylphenyl)ethenyl]-1,3,2-dioxaborolane (3)：^{13}C NMR (400

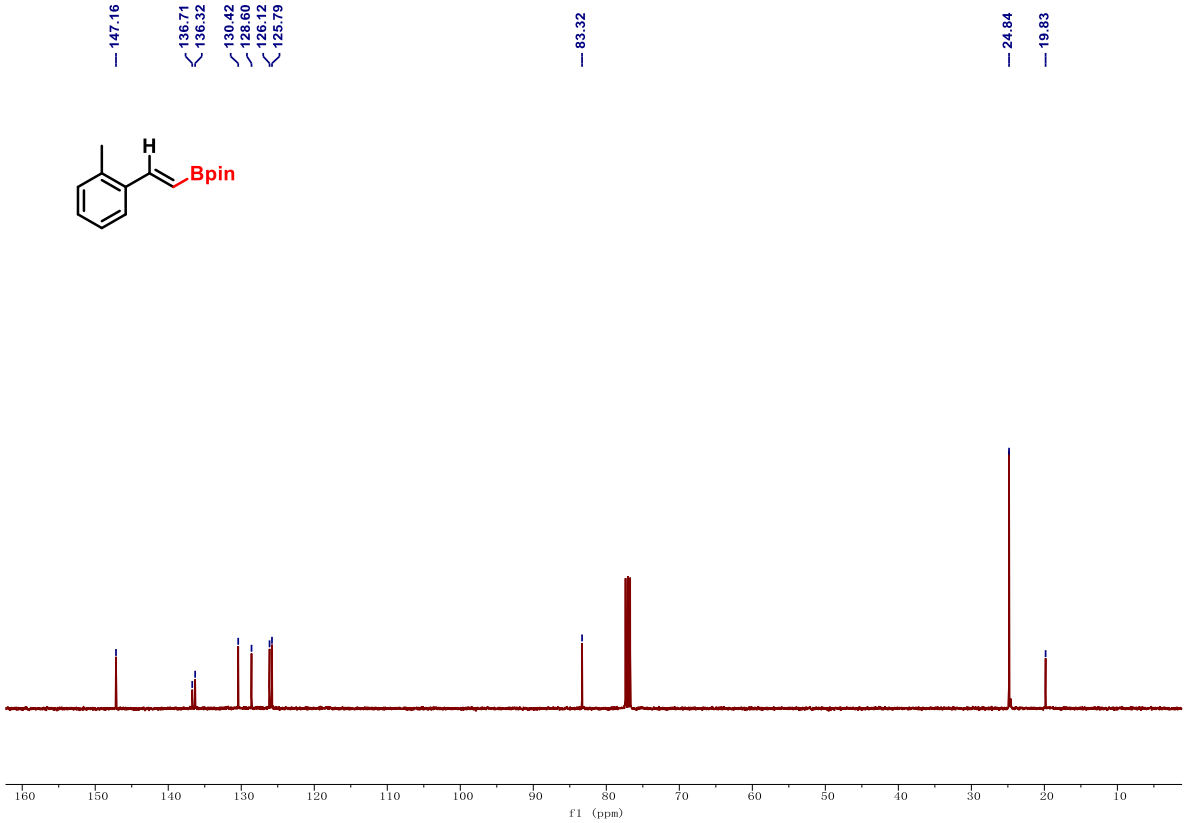
MHz, $CDCl_3$)



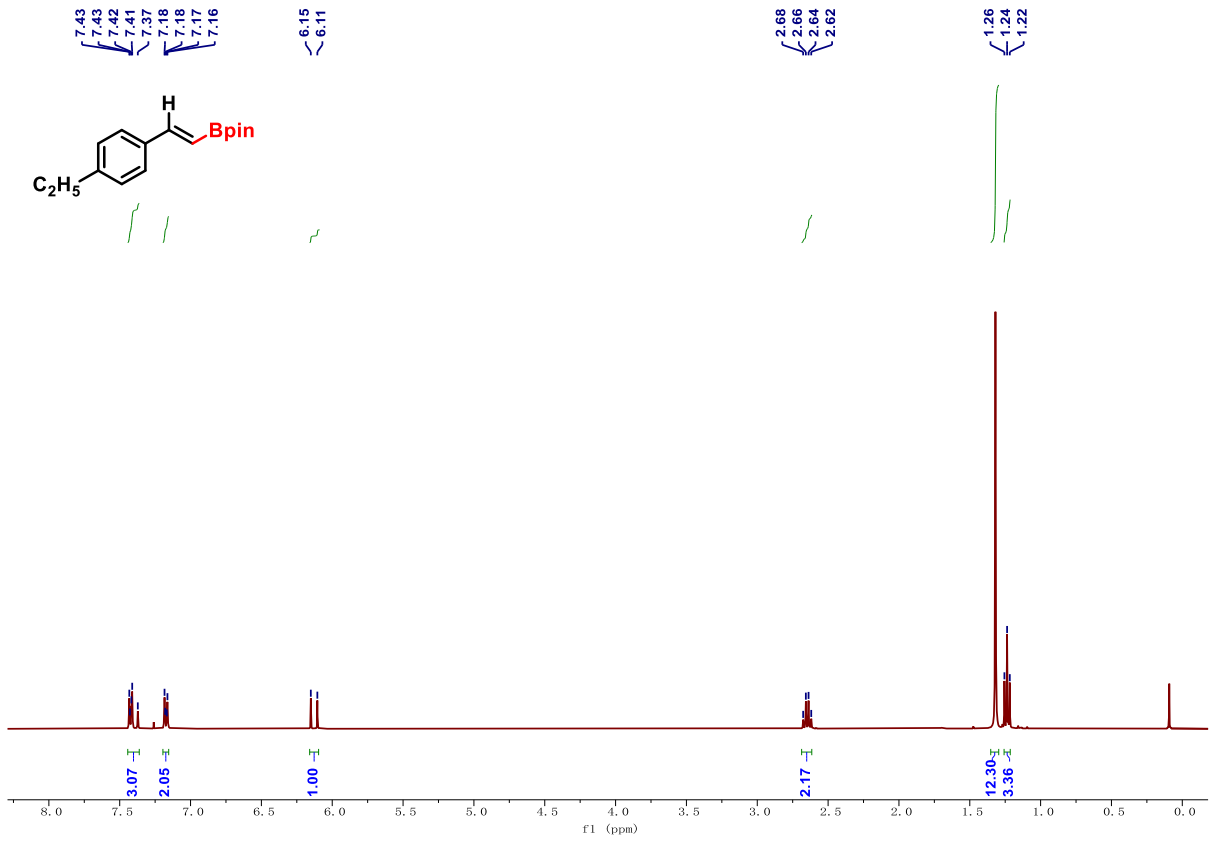
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-methylphenyl)ethenyl]-1,3,2-dioxaborolane (4)：^{1}H NMR (400 MHz, $CDCl_3$)



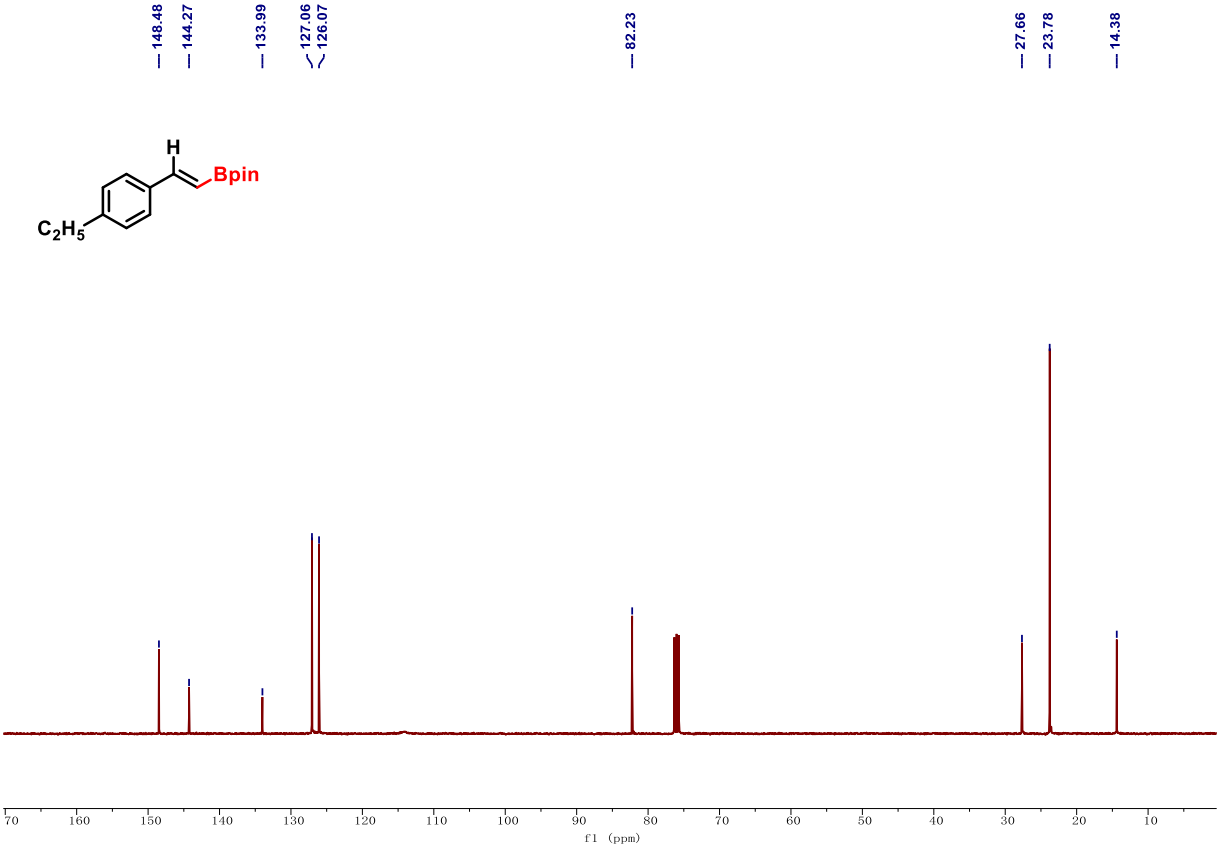
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-methylphenyl)ethenyl]-1,3,2-dioxaborolane (4)：^{13}C NMR (101 MHz, $CDCl_3$)



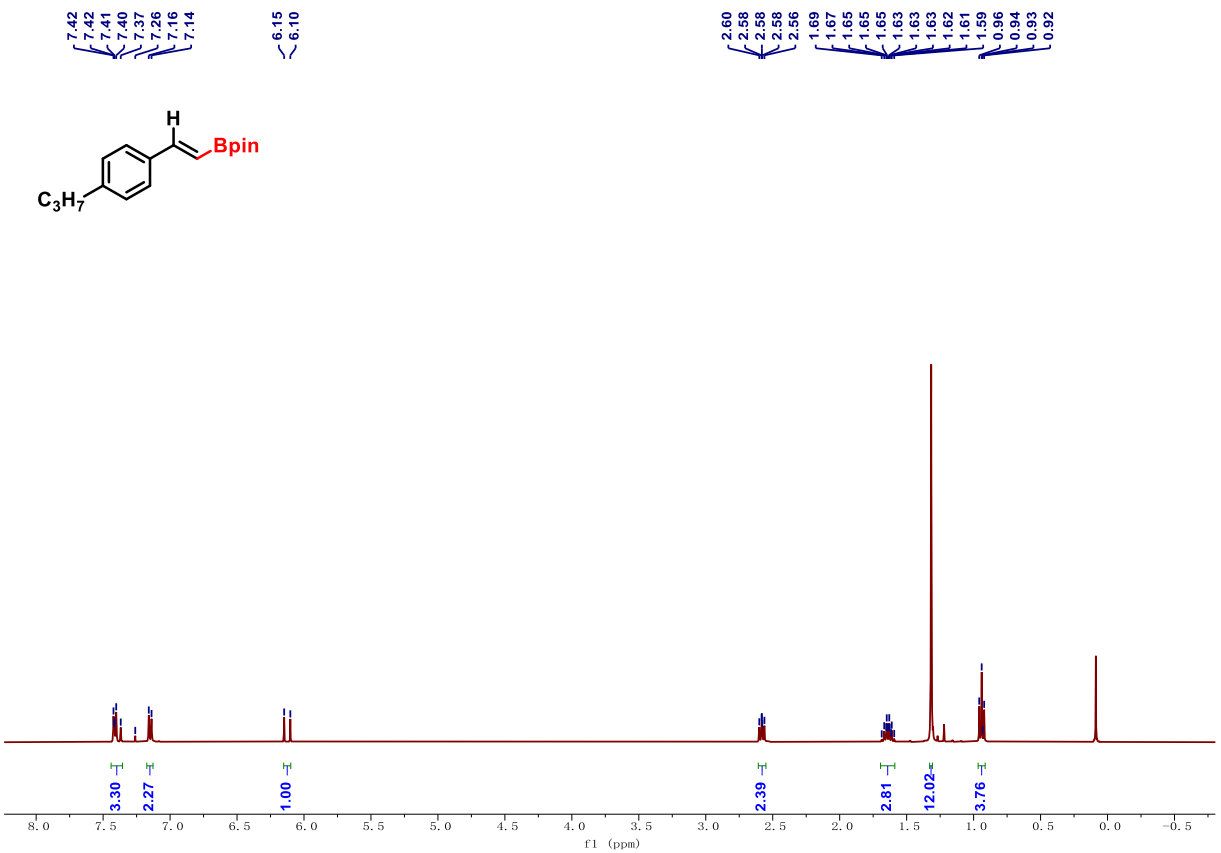
2-[(*1E*)-2-(4-Ethylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5): ^{1}H NMR (400 MHz, $CDCl_3$):



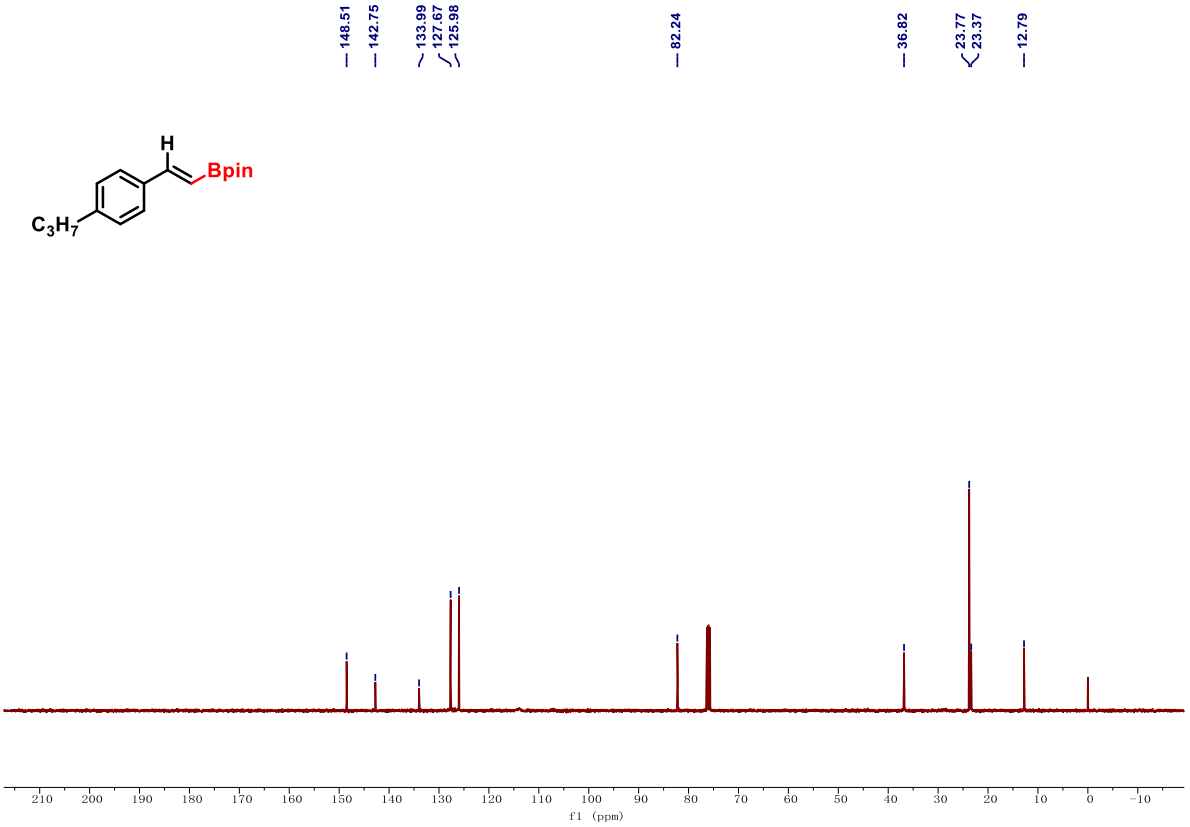
2-[(*1E*)-2-(4-Ethylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5): ^{13}C NMR (101 MHz, $CDCl_3$):



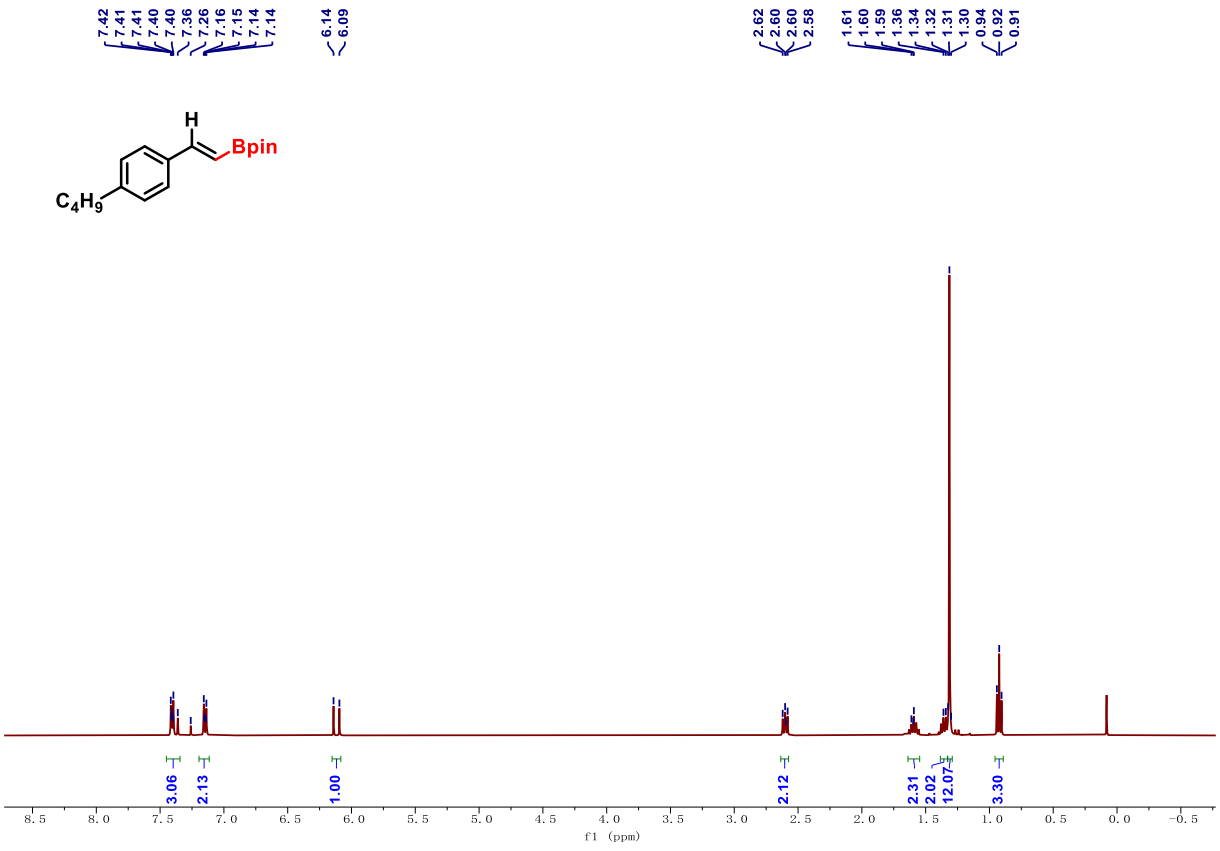
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-propylphenyl)ethenyl]-1,3,2-dioxaborolane (6): ^{1}H NMR (400 MHz, $CDCl_3$):



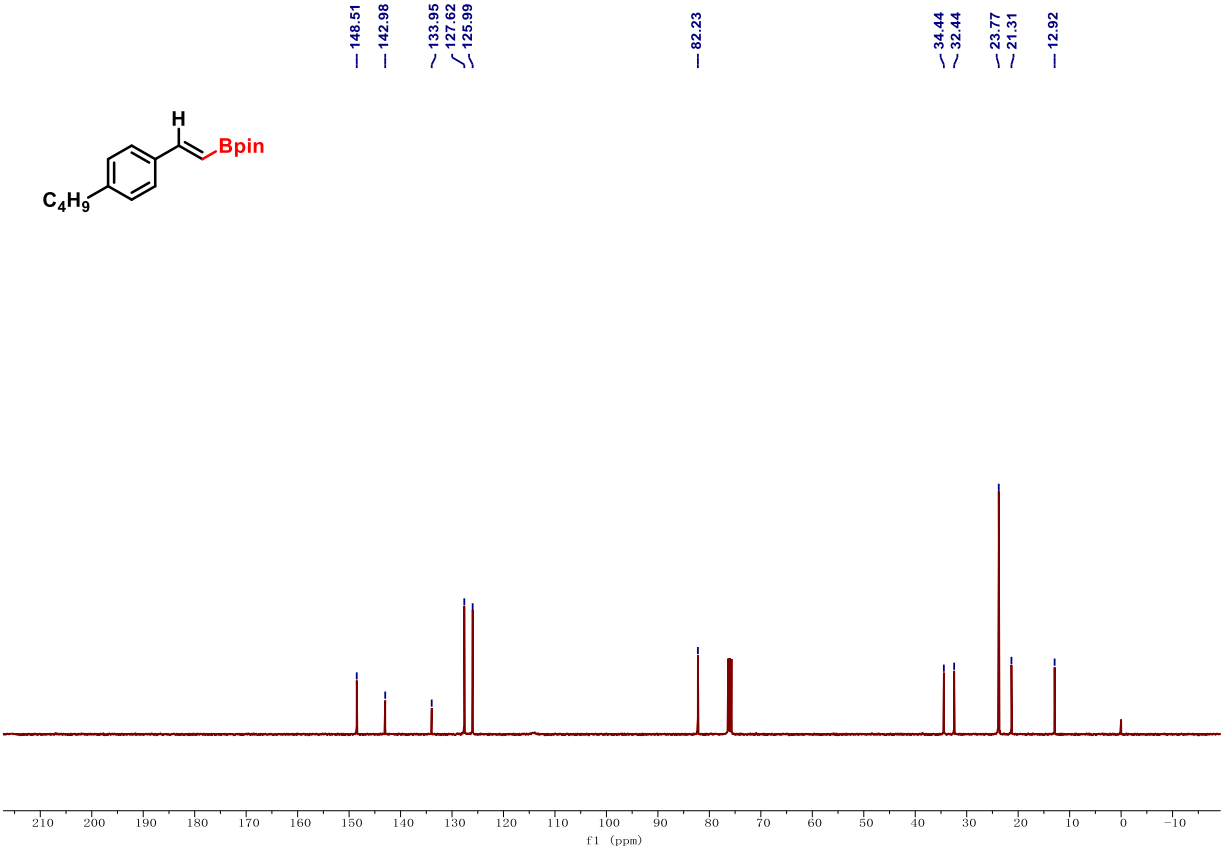
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-propylphenyl)ethenyl]-1,3,2-dioxaborolane (6): ^{13}C NMR (101 MHz, $CDCl_3$):



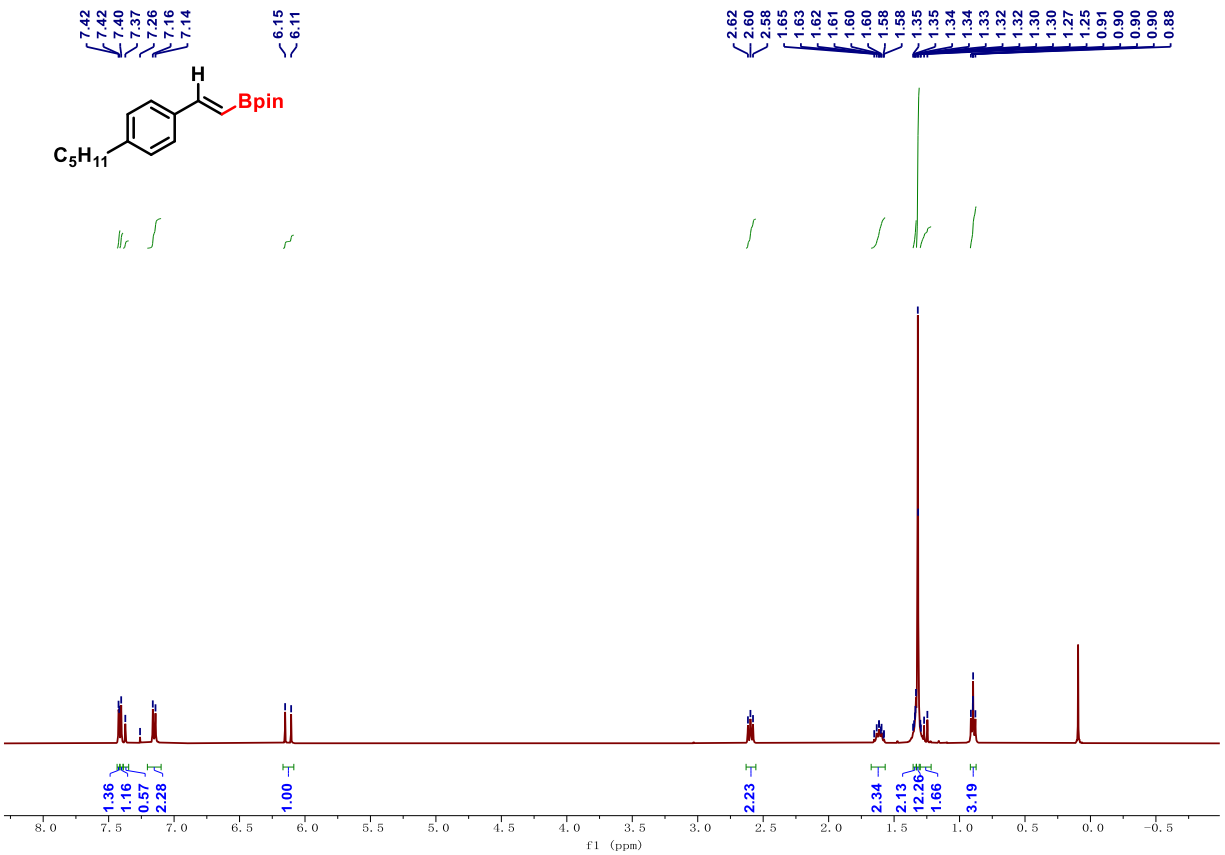
2-[(*1E*)-2-(4-Butylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): ^{1}H NMR (400 MHz, $CDCl_3$):



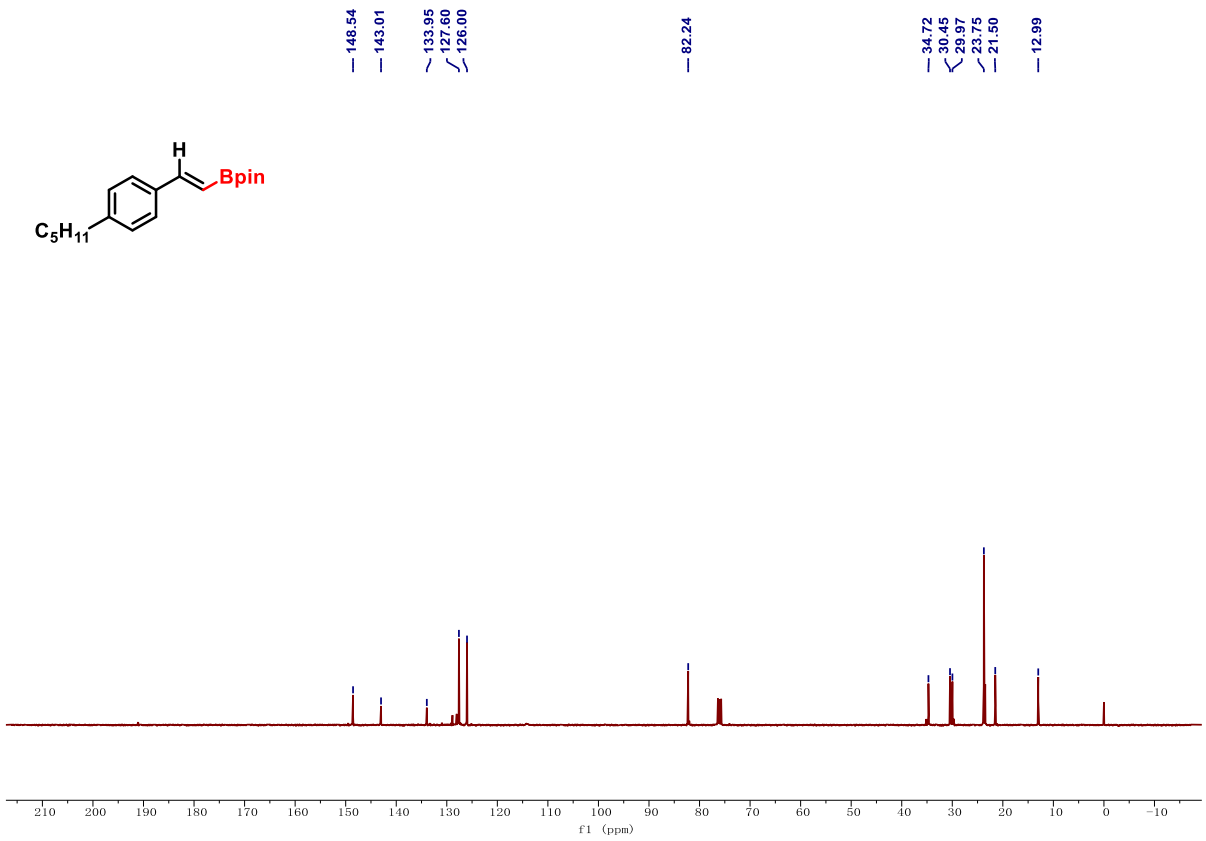
2-[(*1E*)-2-(4-Butylphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7): ^{13}C NMR (101 MHz, $CDCl_3$):



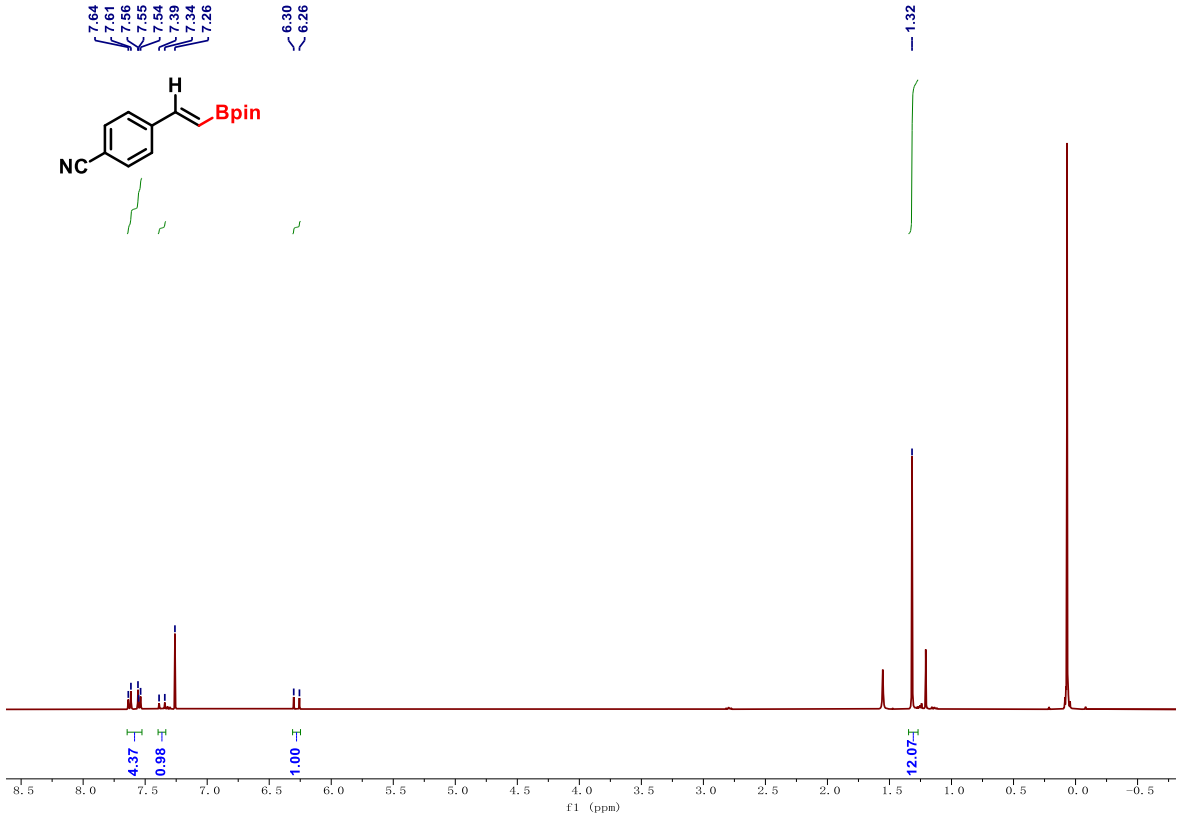
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-pentylphenyl)ethenyl]-1,3,2-dioxaborolane (8) : ^{1}H NMR (400 MHz, $CDCl_3$):



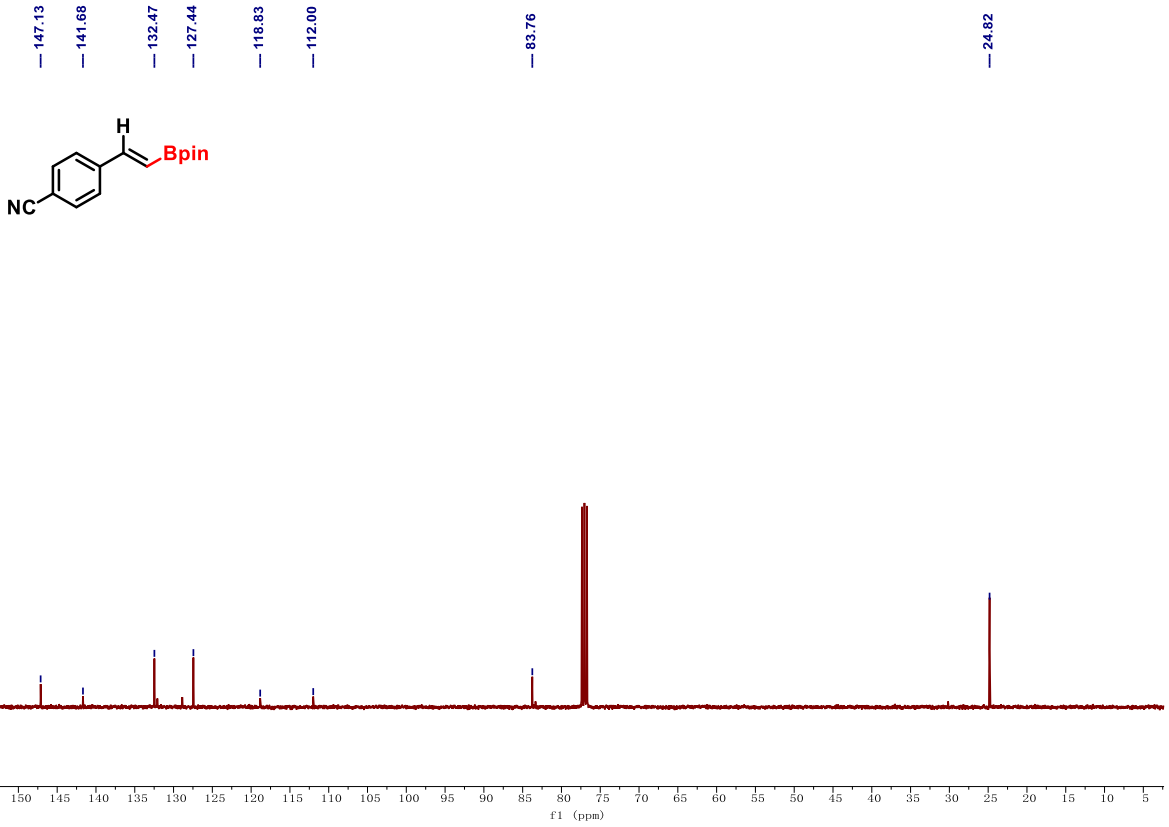
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(4-pentylphenyl)ethenyl]-1,3,2-dioxaborolane (8) : ^{13}C NMR (101 MHz, $CDCl_3$):



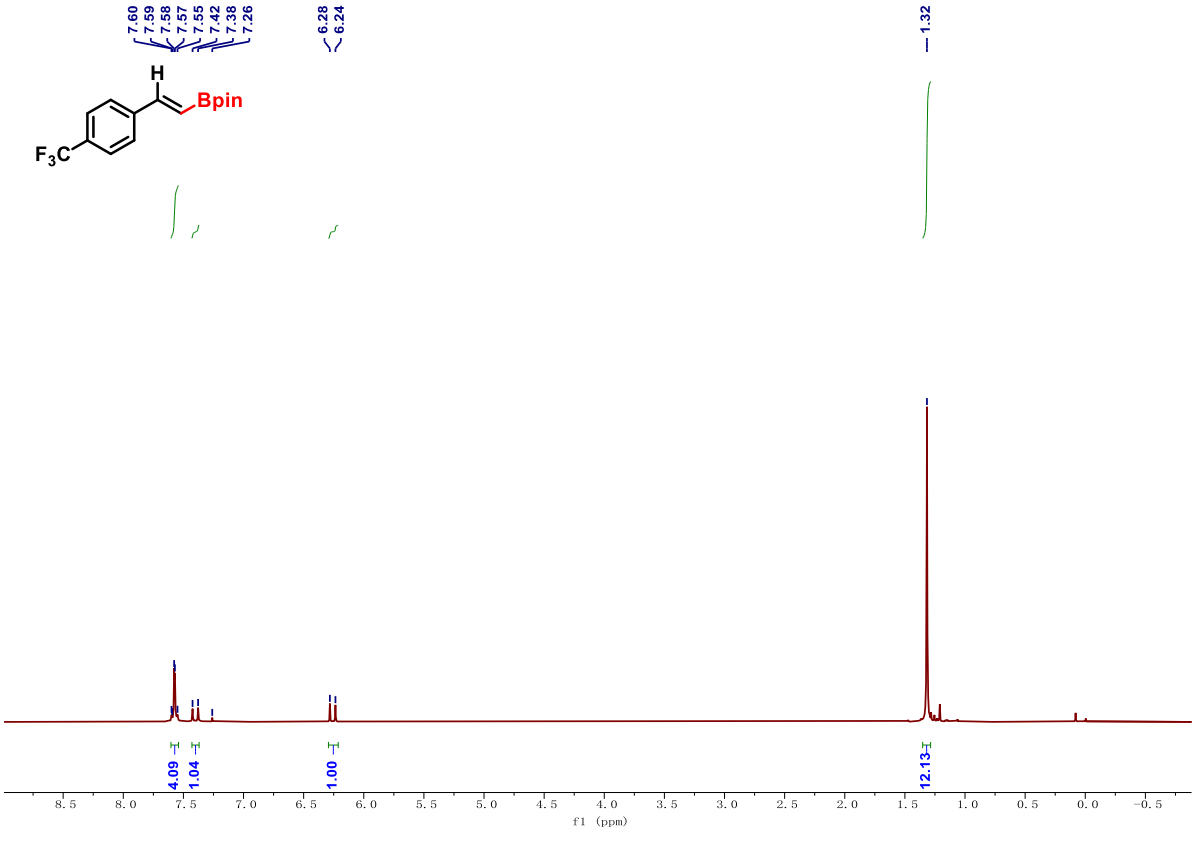
4-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzonitrile (9) : ^{1}H NMR (400 MHz, $CDCl_3$):



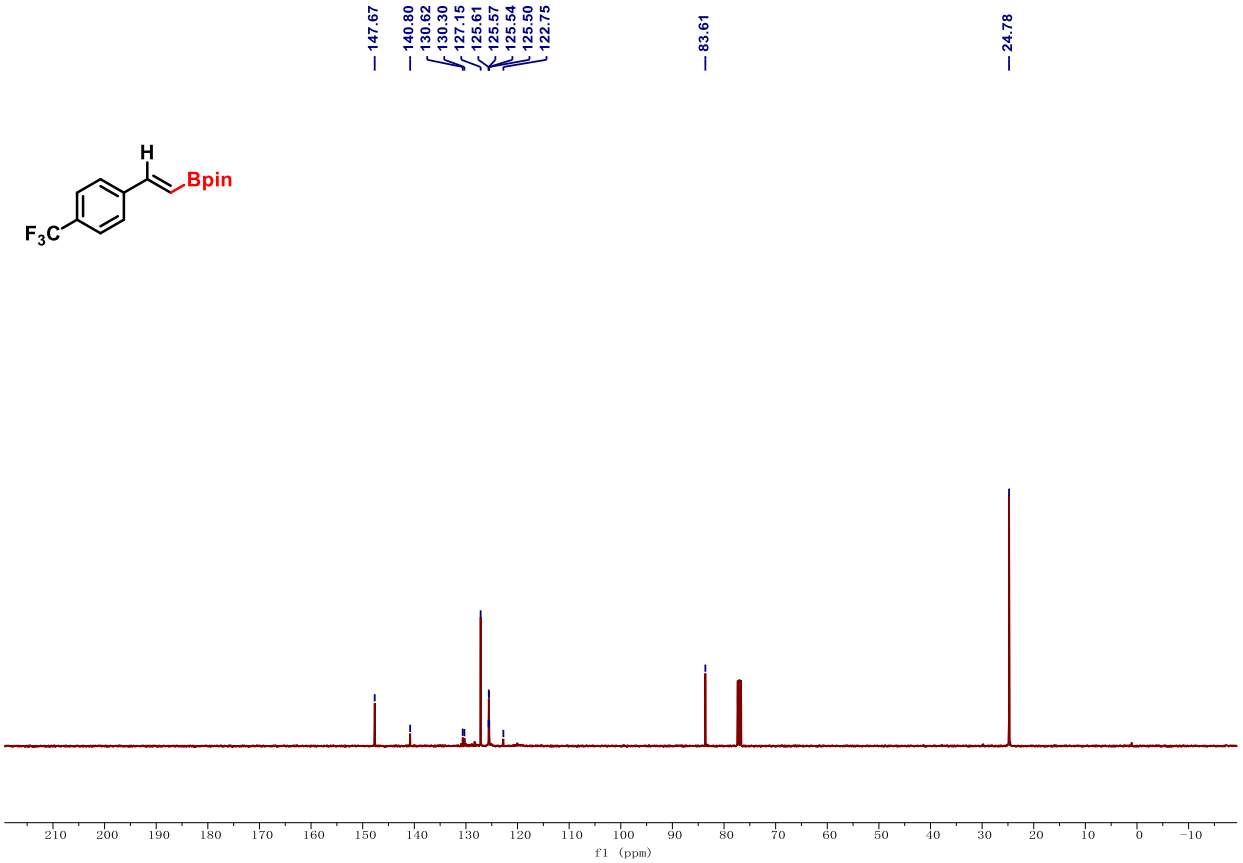
4-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]benzonitrile (9) : ^{13}C NMR (101 MHz, $CDCl_3$):



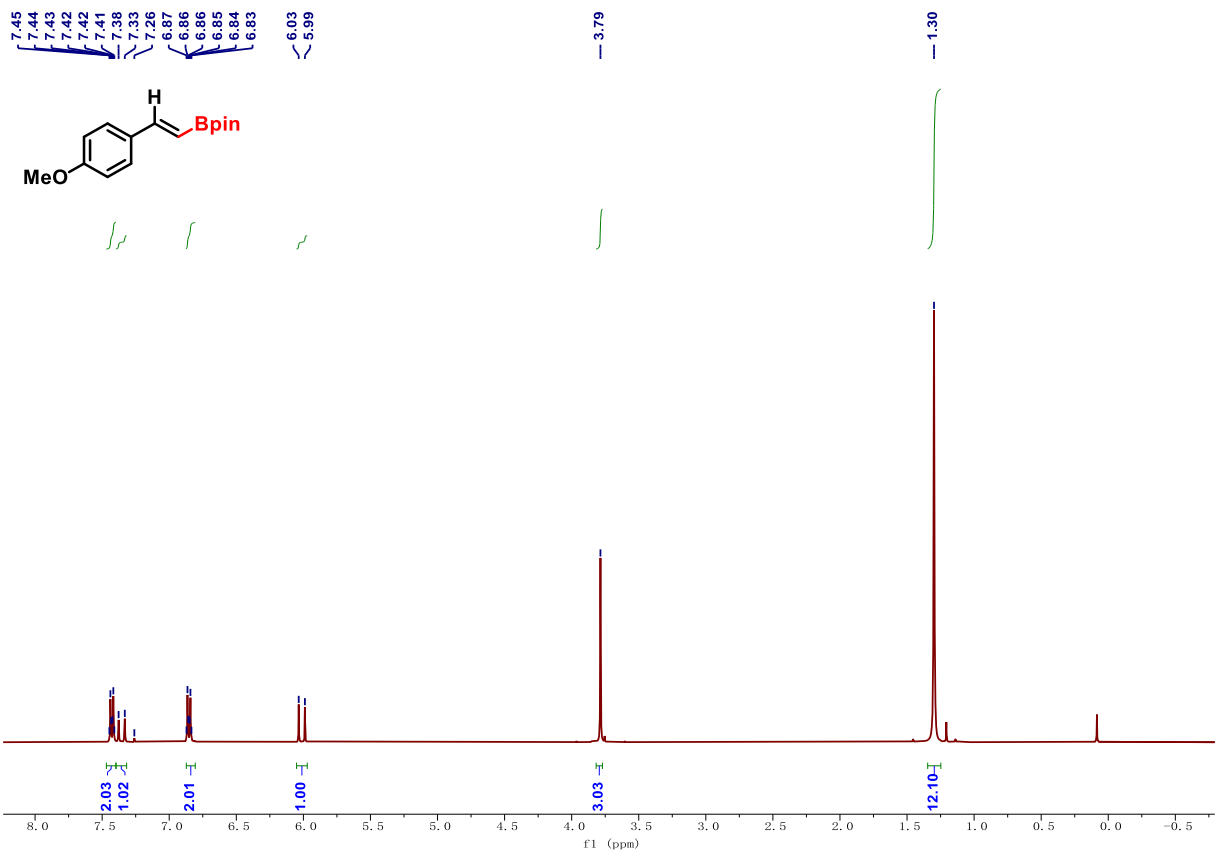
4,4,5,5-Tetramethyl-2-[(*1E*)-2-[4-(trifluoromethyl)phenyl]ethenyl]-1,3,2-dioxaborolane (10): ^{1}H NMR (400 MHz, $CDCl_3$)



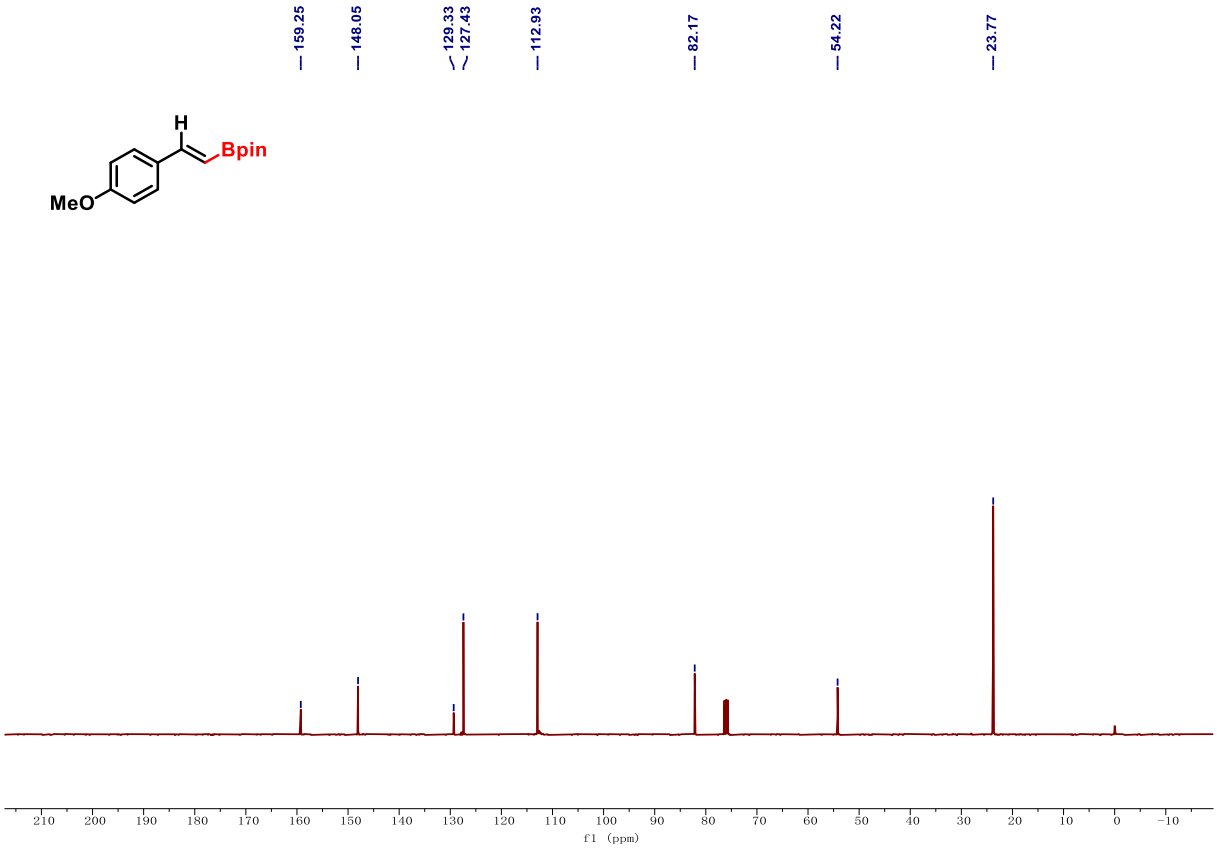
4,4,5,5-Tetramethyl-2-[(*1E*)-2-[4-(trifluoromethyl)phenyl]ethenyl]-1,3,2-dioxaborolane (10): ^{13}C NMR (101 MHz, $CDCl_3$)



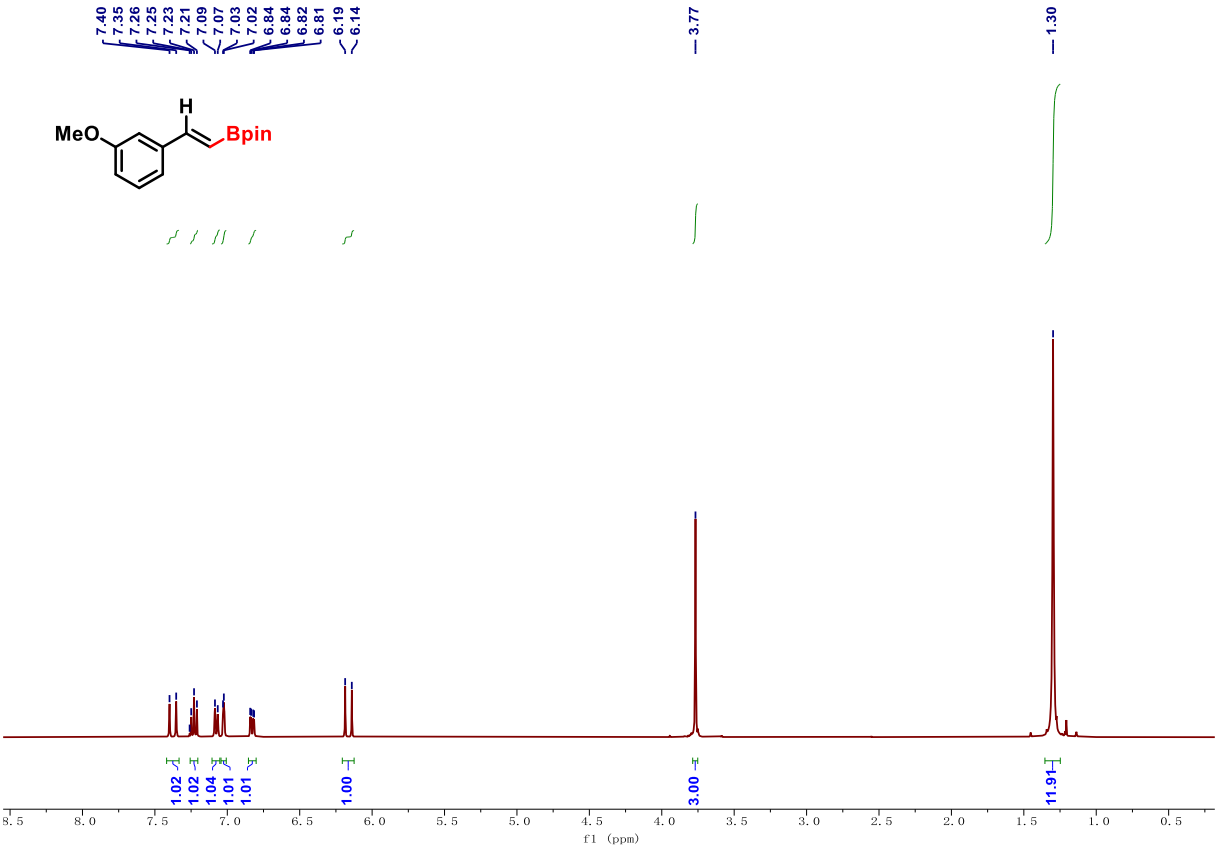
2-[(*1E*)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11): ^{1}H NMR (400 MHz, $CDCl_3$)



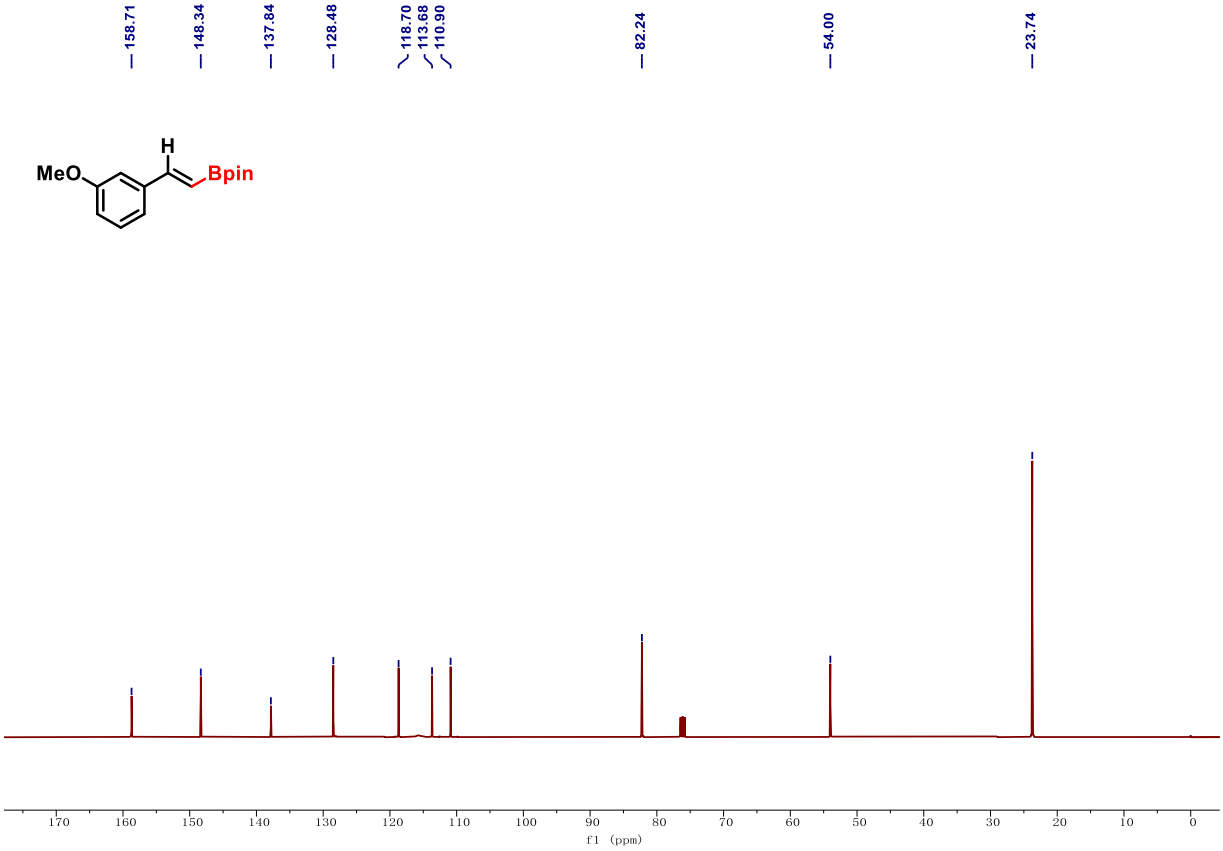
2-[(*1E*)-2-(4-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11): ^{13}C NMR (101 MHz, $CDCl_3$)



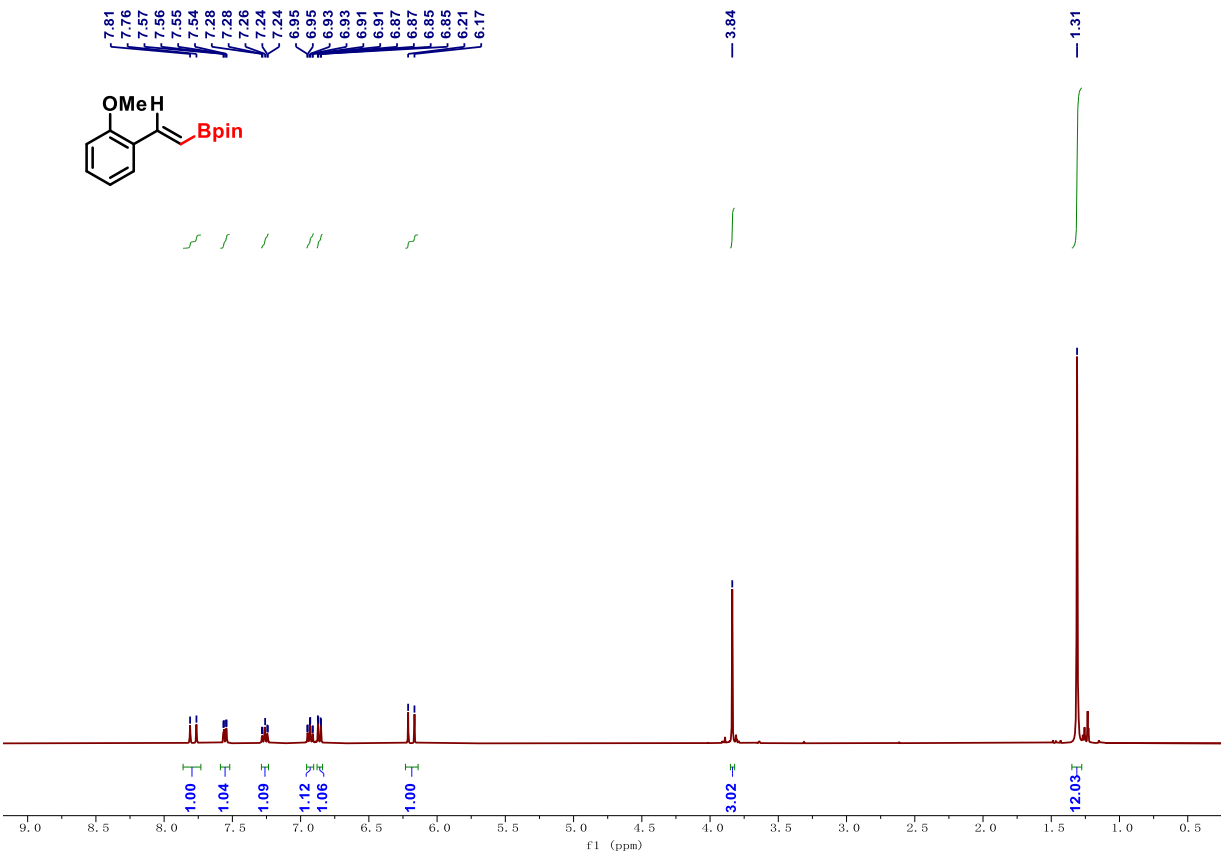
2-[(*1E*)-2-(3-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12) : ^{1}H NMR (400 MHz, $CDCl_3$):



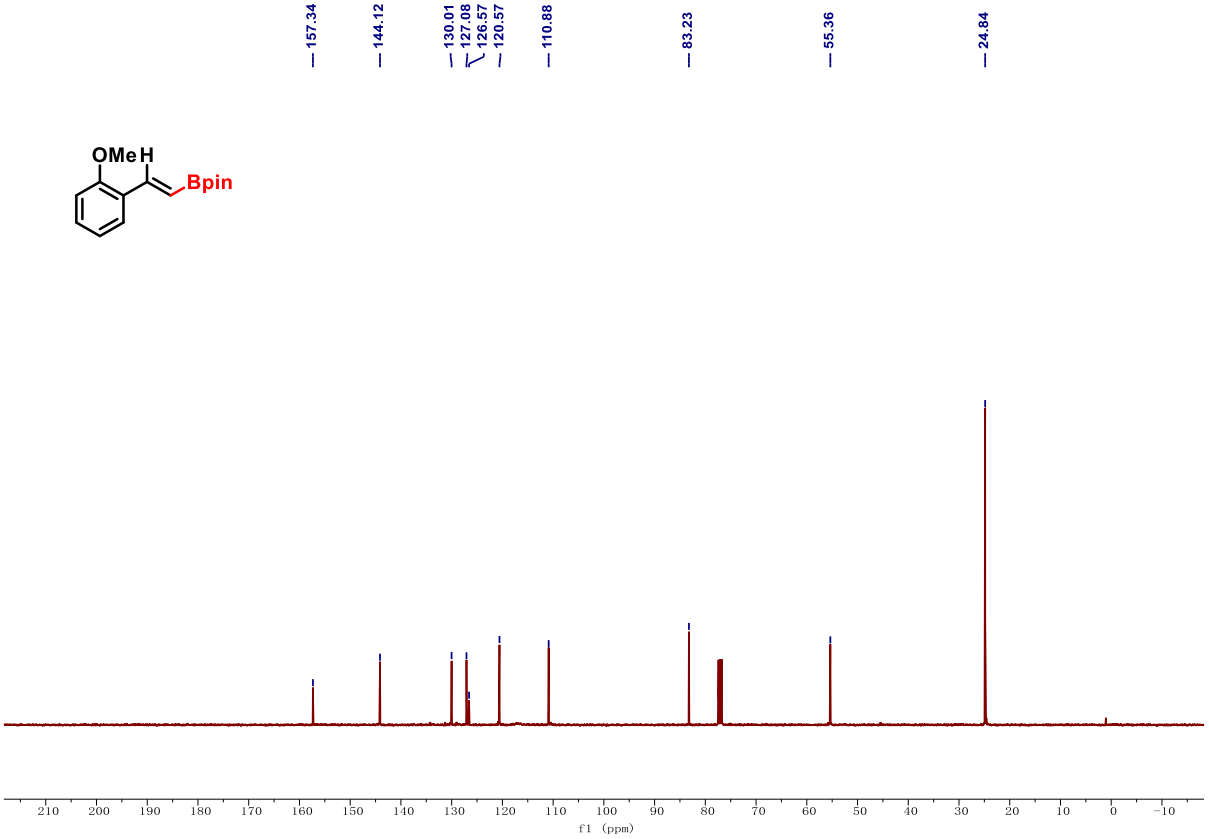
2-[(*1E*)-2-(3-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12) : ^{13}C NMR (101 MHz, $CDCl_3$):



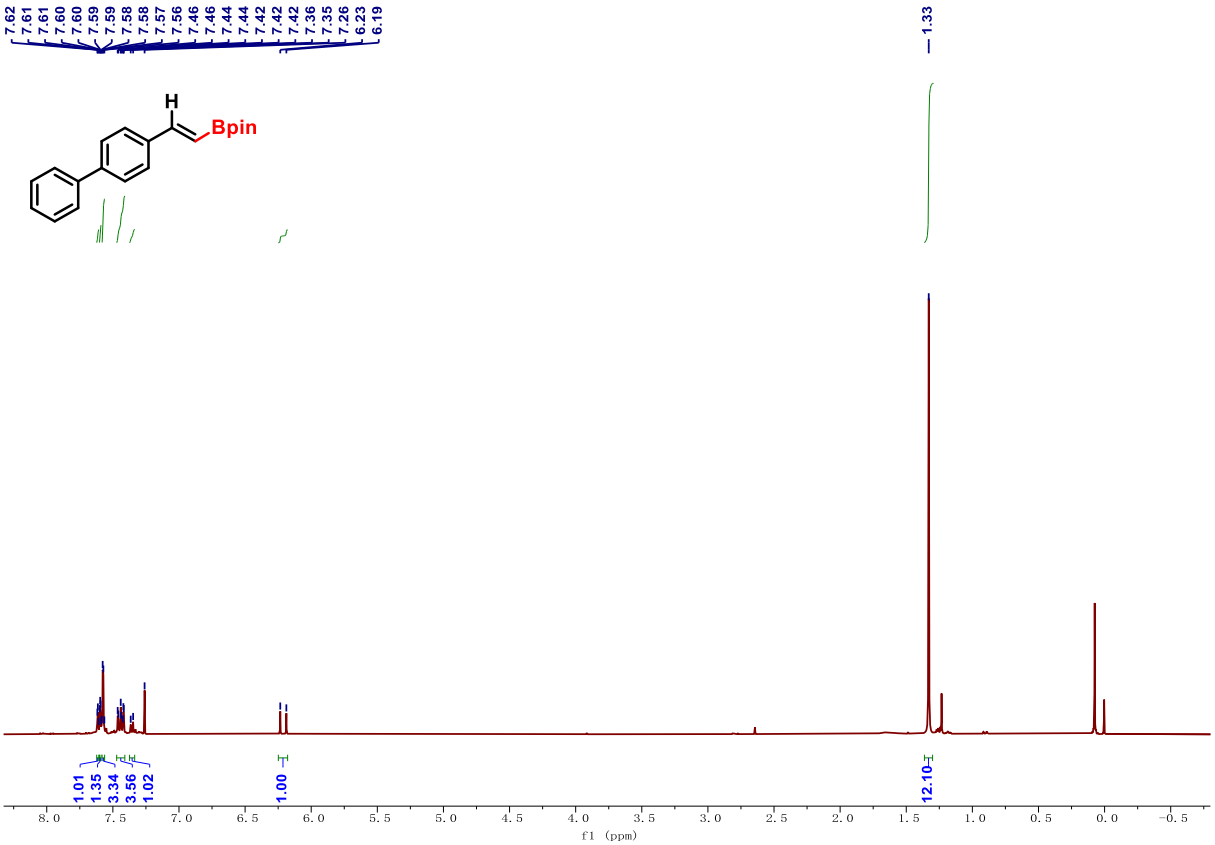
2-[(*1E*)-2-(2-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13): ^{1}H NMR (400 MHz, $CDCl_3$):



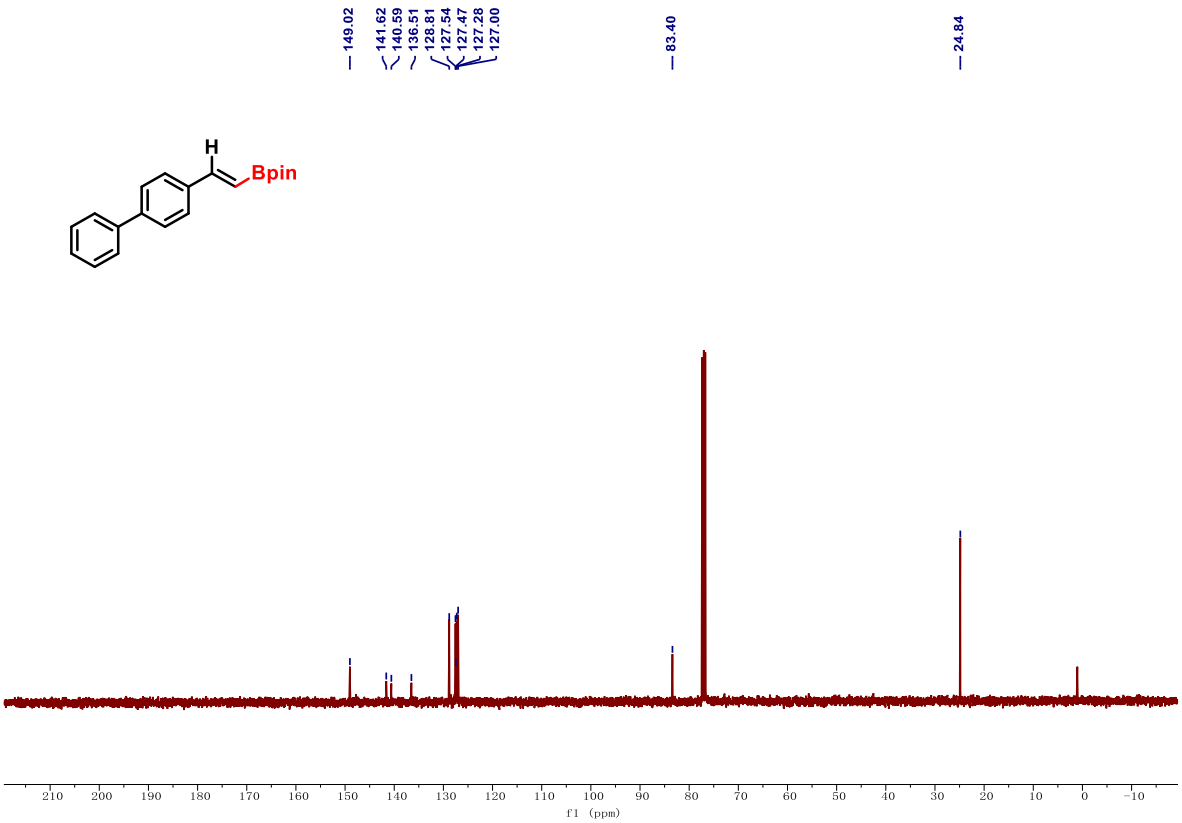
2-[(*1E*)-2-(2-Methoxyphenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (13): ^{13}C NMR (101 MHz, $CDCl_3$):



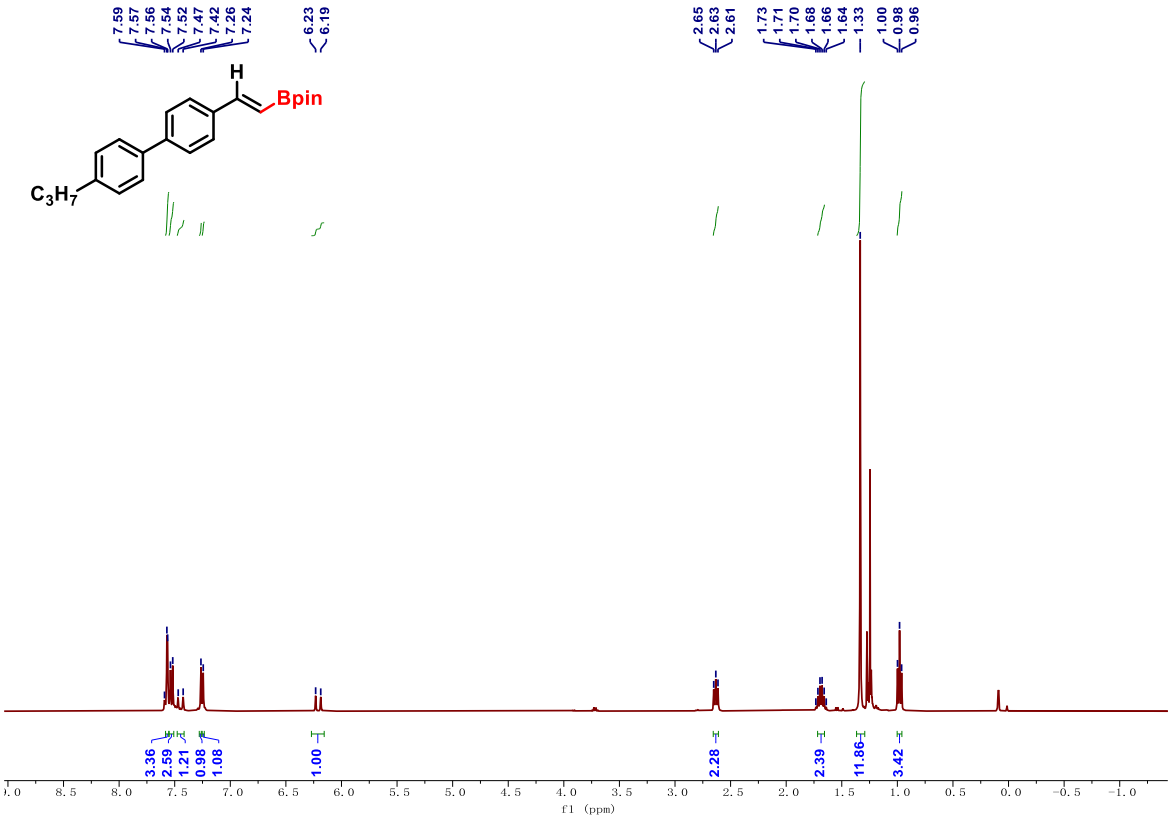
2-[(*1E*)-2-[1,1′-Biphenyl]-4-ylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14): ^{1}H NMR (400 MHz, $CDCl_3$):



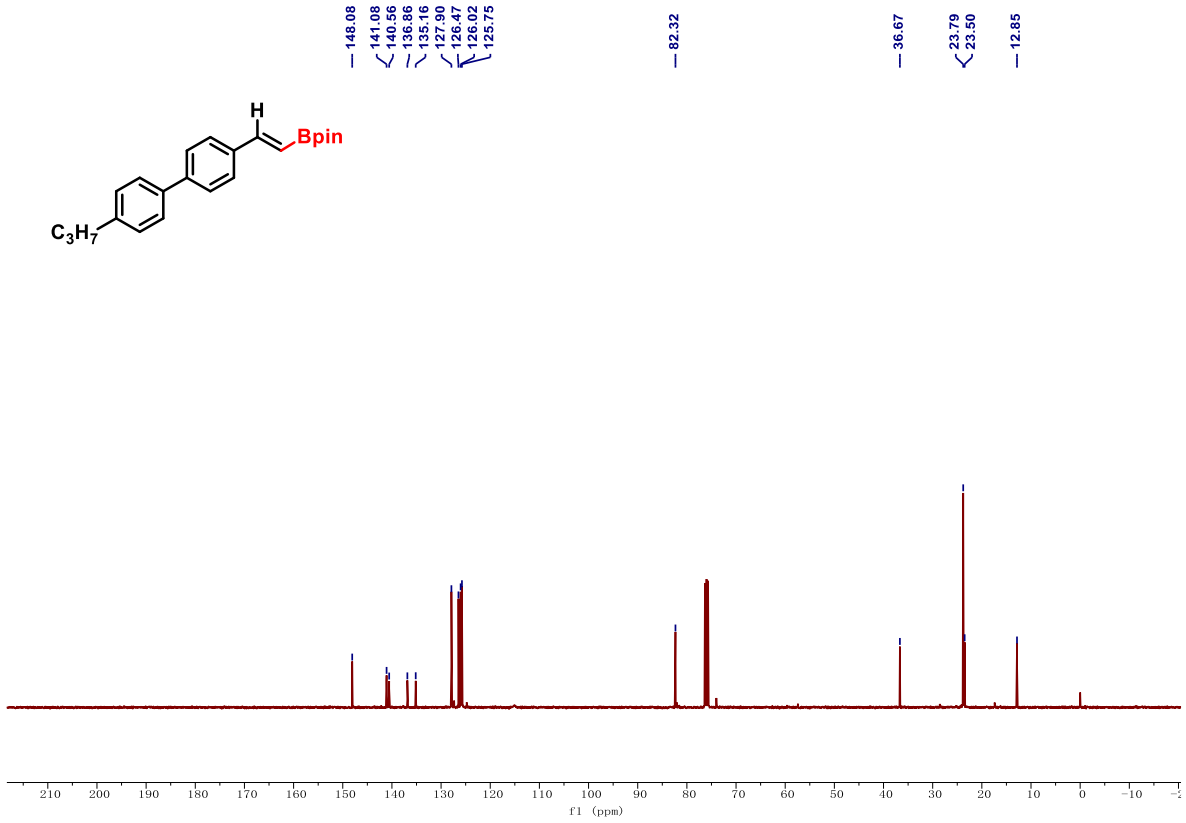
2-[(*1E*)-2-[1,1′-Biphenyl]-4-ylethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14): ^{13}C NMR (101 MHz, $CDCl_3$):



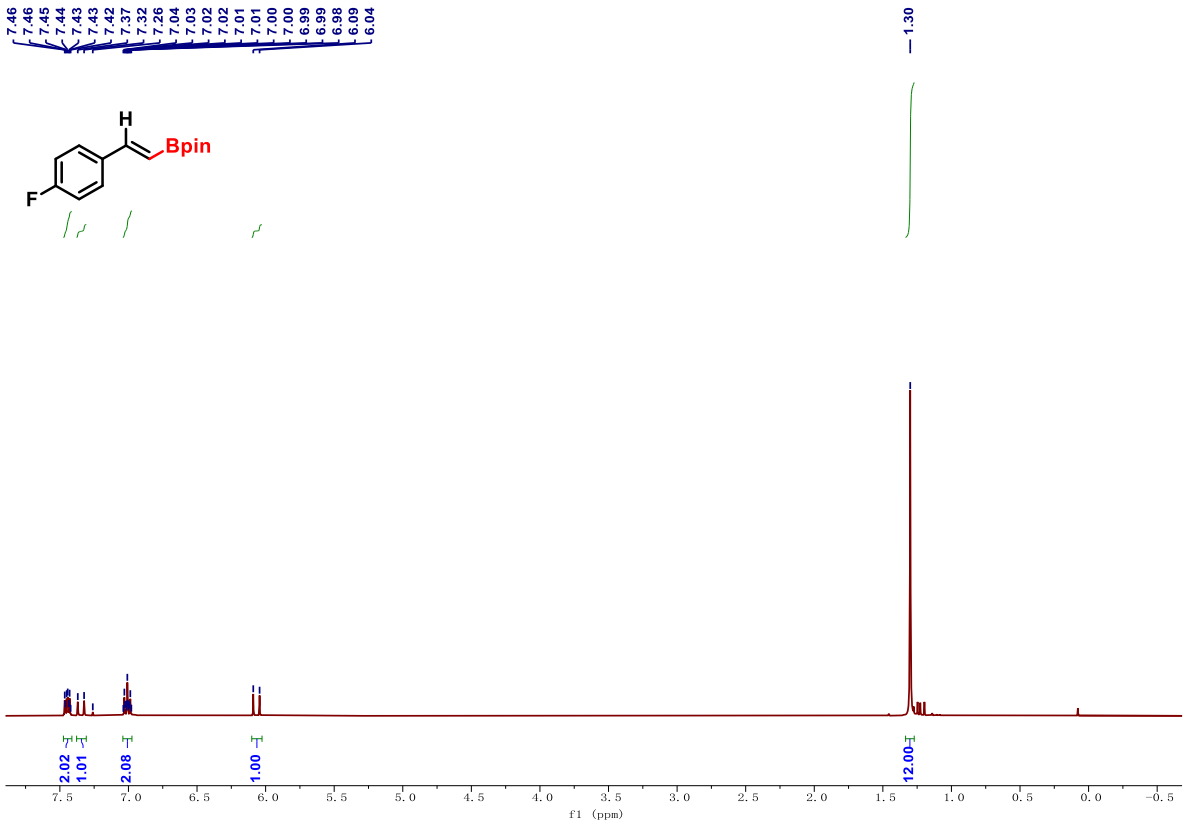
(*E*)-4,4,5,5-tetramethyl-2-(2-(4'-propyl-[1,1'-biphenyl]-4-yl)vinyl)-1,3,2-dioxaborolane (15): ^{1}H NMR (400 MHz, $CDCl_3$):



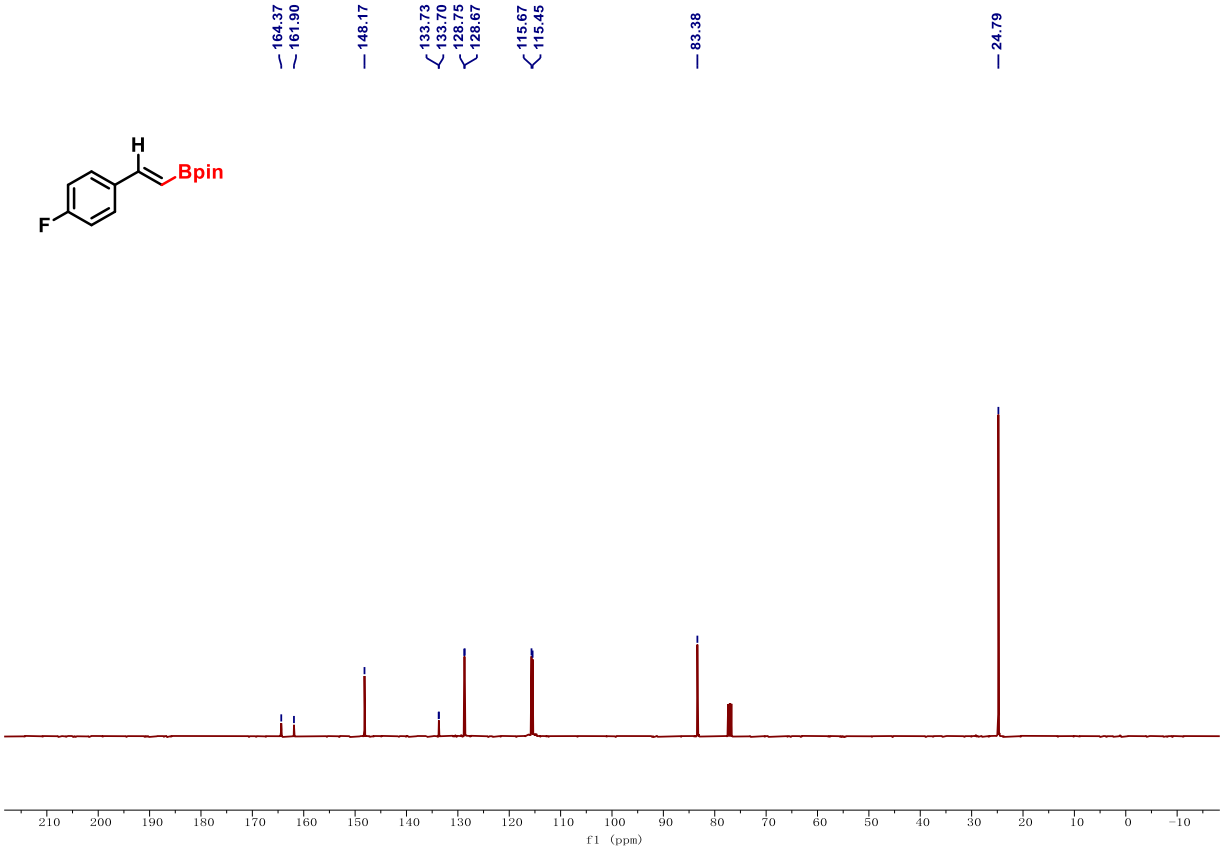
(*E*)-4,4,5,5-tetramethyl-2-(2-(4'-propyl-[1,1'-biphenyl]-4-yl)vinyl)-1,3,2-dioxaborolane (15): ^{13}C NMR (101 MHz, $CDCl_3$):



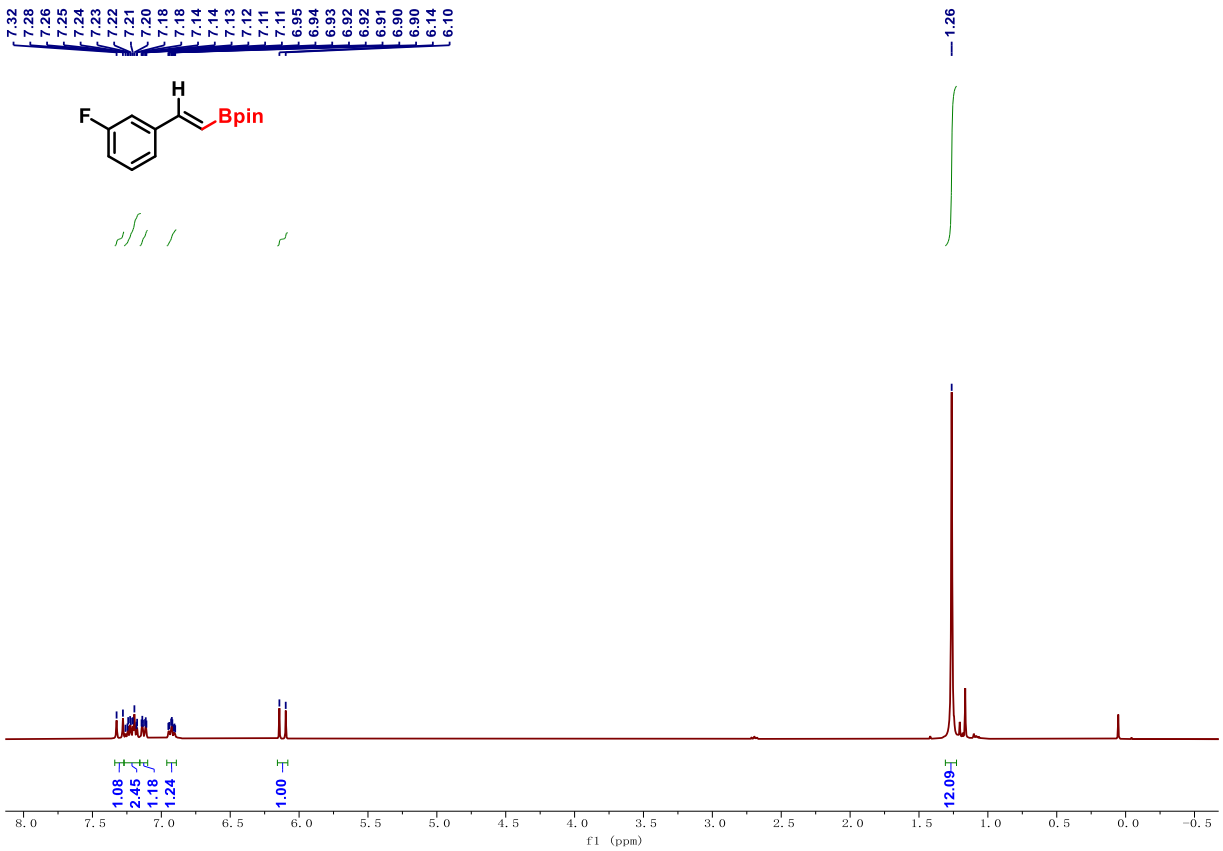
2-[(*1E*)-2-(4-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16): ^{1}H NMR (400 MHz, $CDCl_3$):



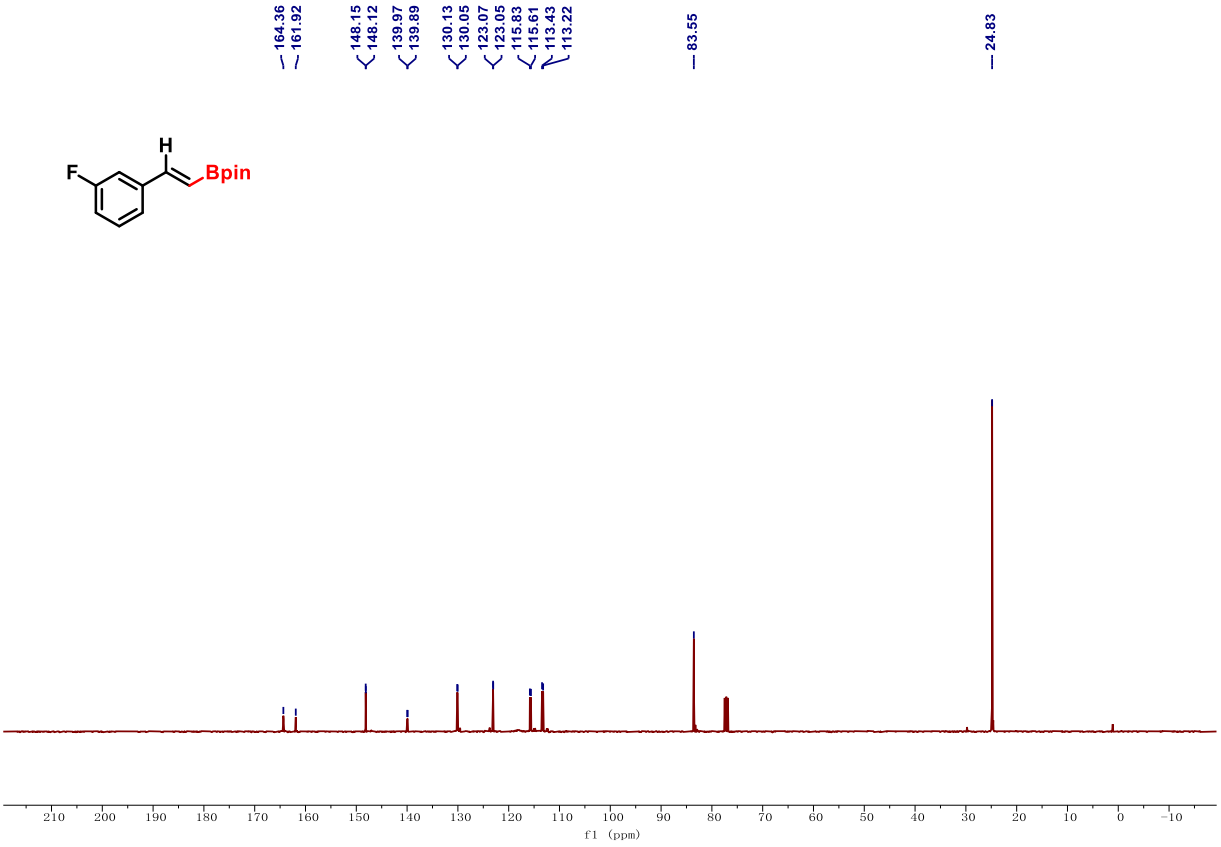
2-[(*1E*)-2-(4-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16): **^{13}C NMR (101 MHz, $CDCl_3$):**



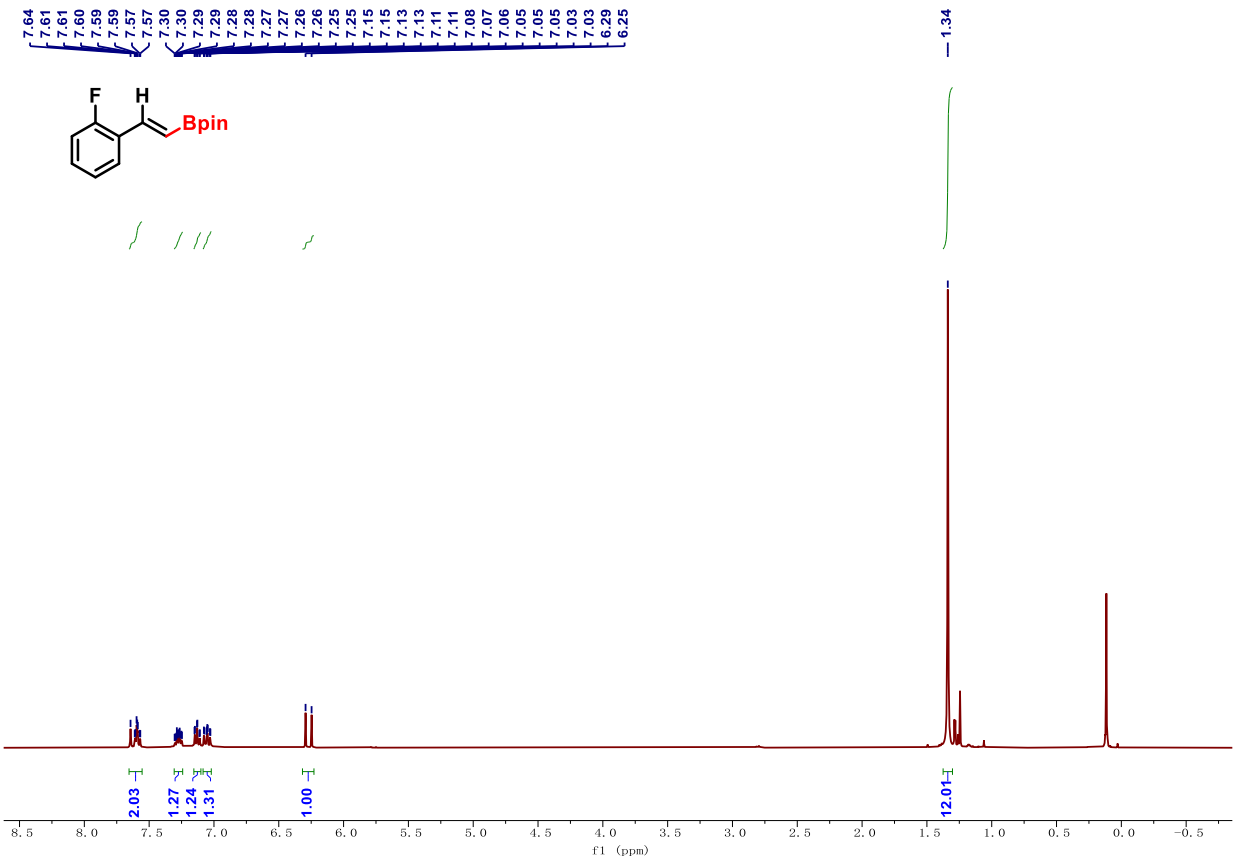
2-[(*1E*)-2-(3-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17): ^{1}H NMR (400 MHz, $CDCl_3$):



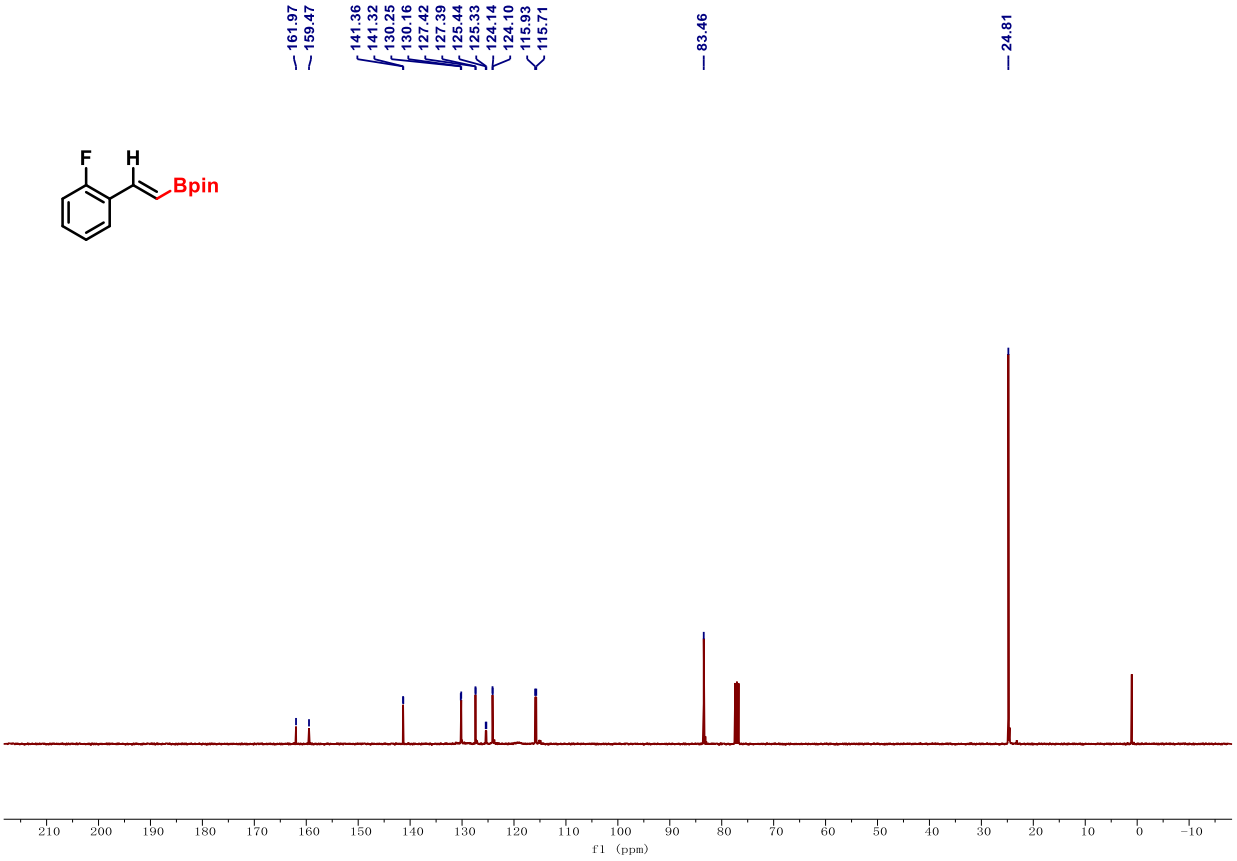
2-[(*1E*)-2-(3-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17): ^{13}C NMR (101 MHz, $CDCl_3$):



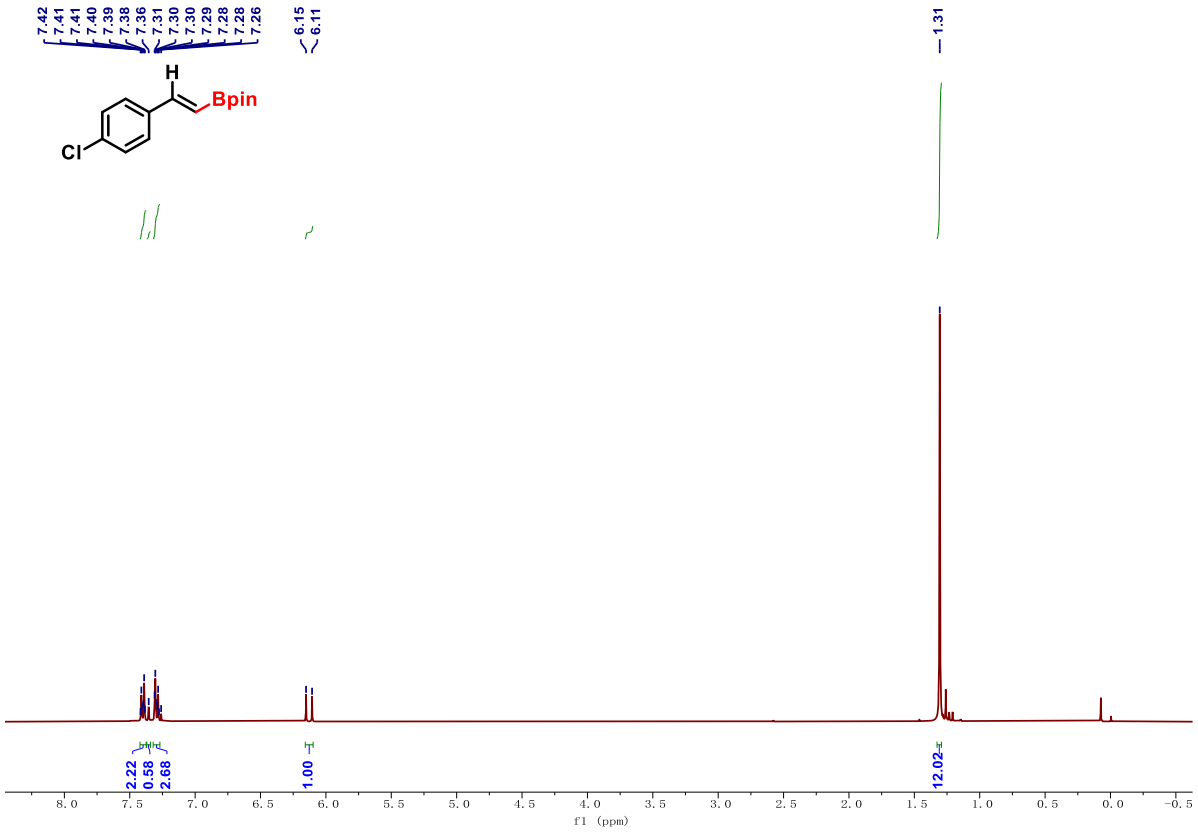
2-[(*1E*)-2-(2-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18): ^{1}H NMR (400 MHz, $CDCl_3$):



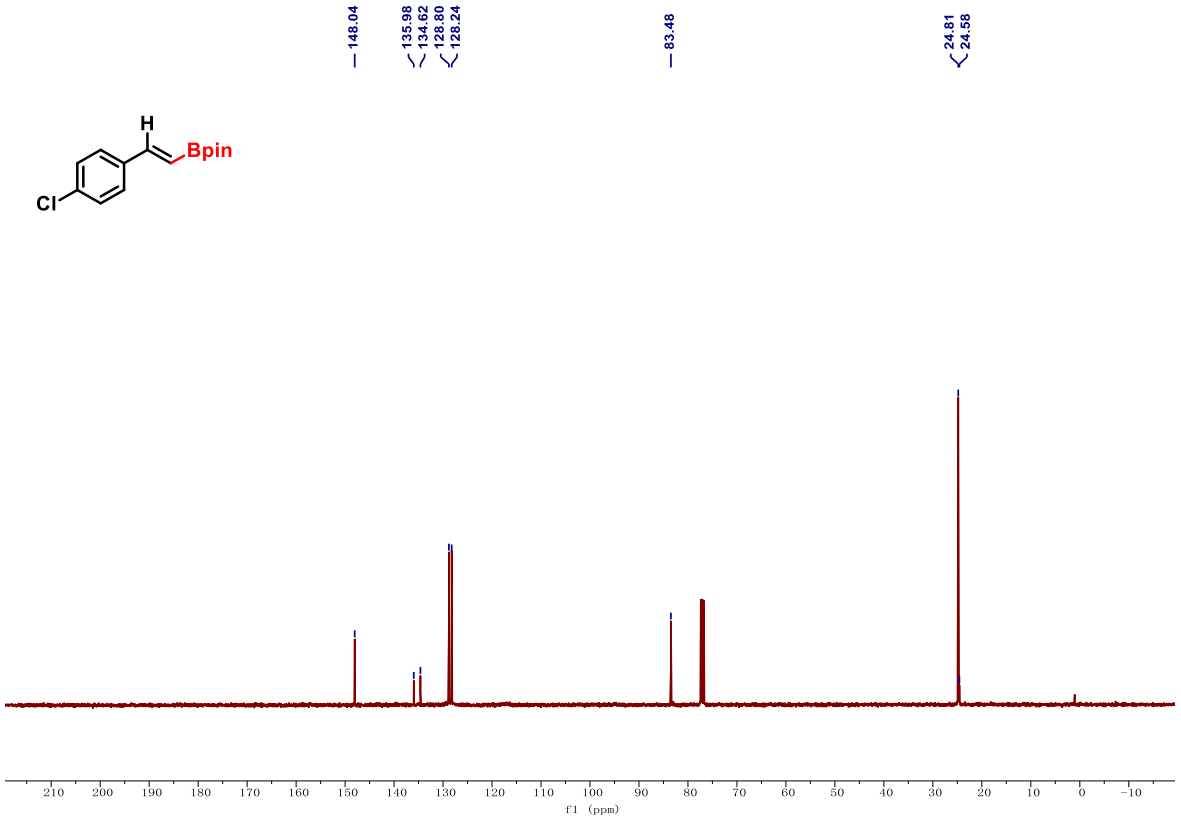
2-[(*1E*)-2-(2-Fluorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18): ^{13}C NMR (101 MHz, $CDCl_3$):



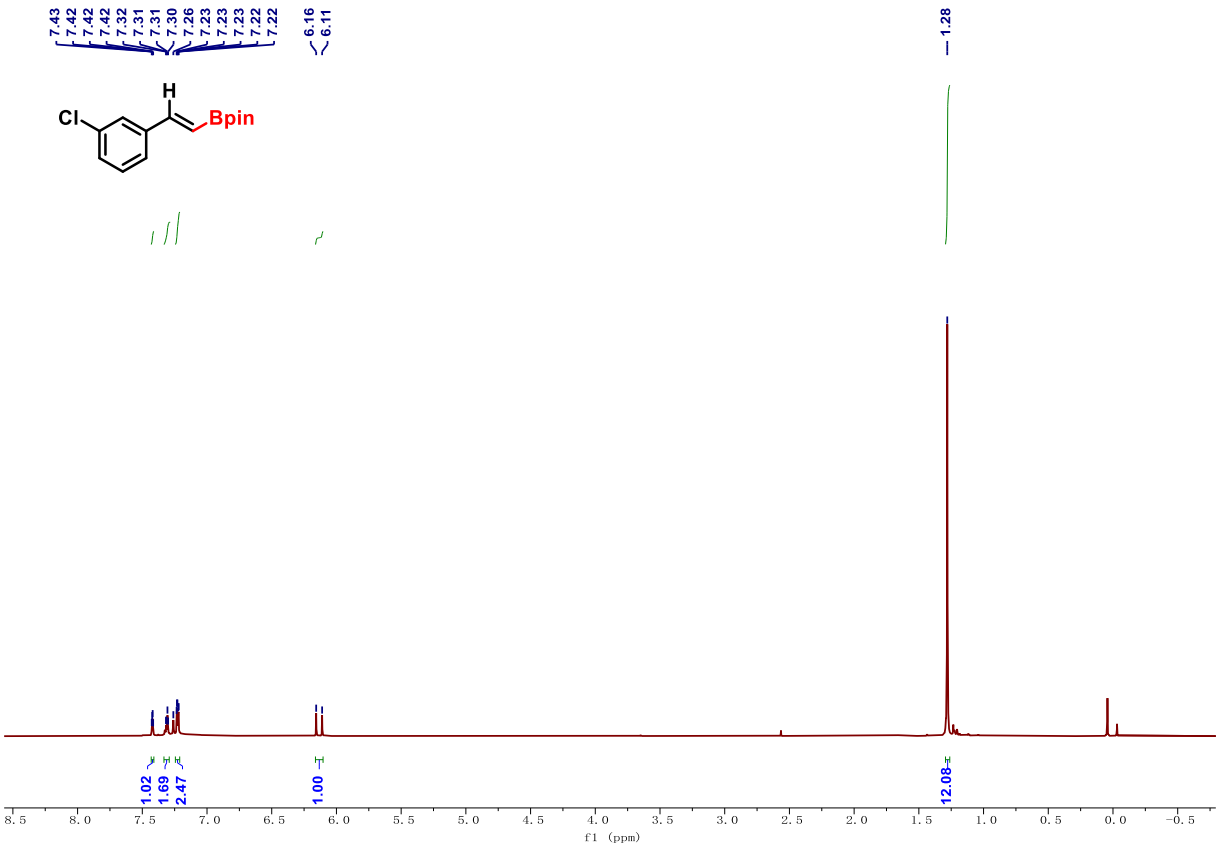
2-[(*1E*)-2-(4-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19): ^{1}H NMR (400 MHz, $CDCl_3$):



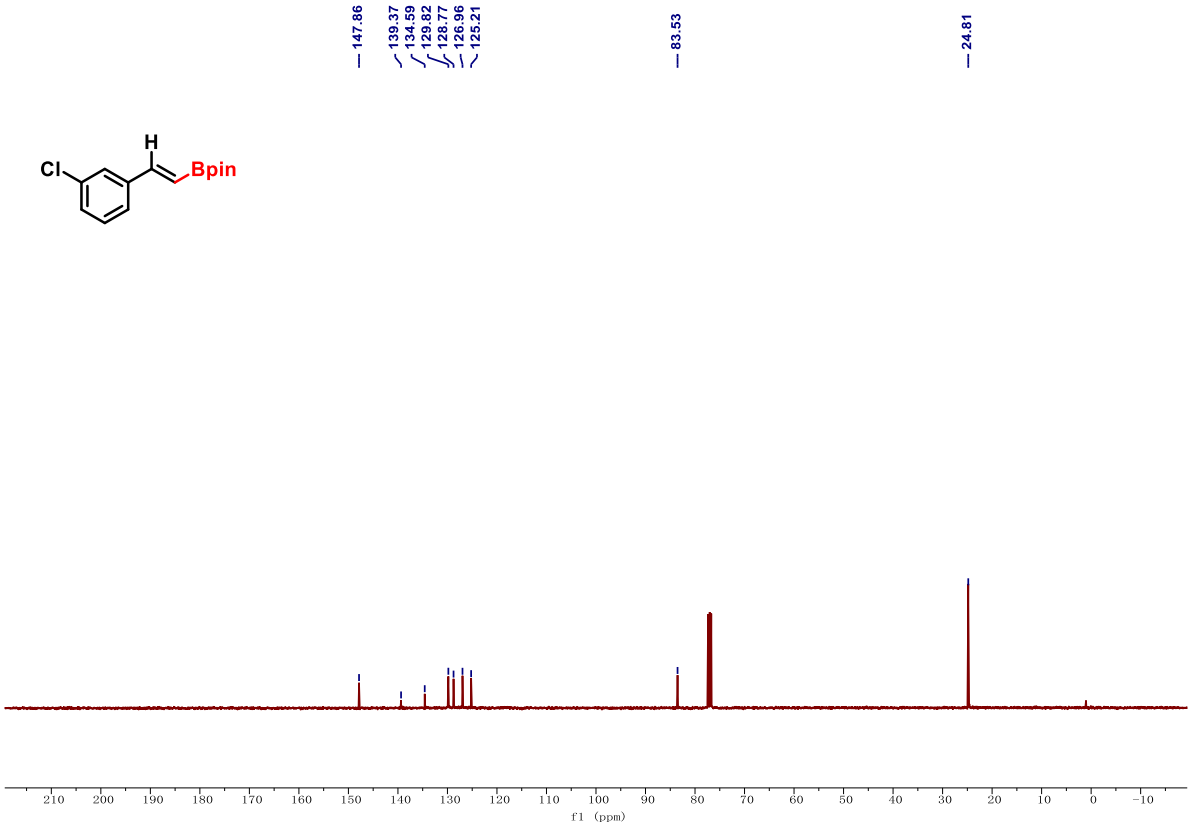
2-[(*1E*)-2-(4-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19): ^{13}C NMR (101 MHz, $CDCl_3$):



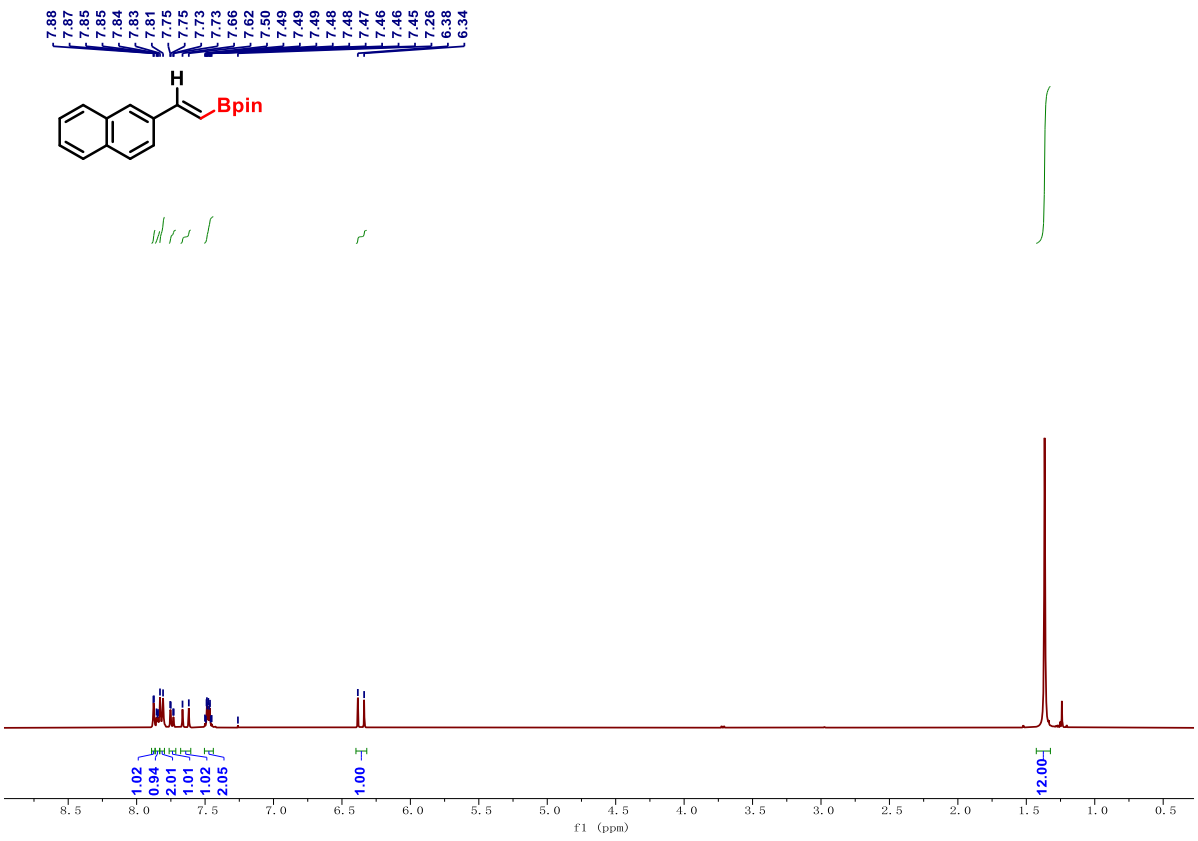
2-[(*1E*)-2-(3-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20): ^{1}H NMR (400 MHz, $CDCl_3$):



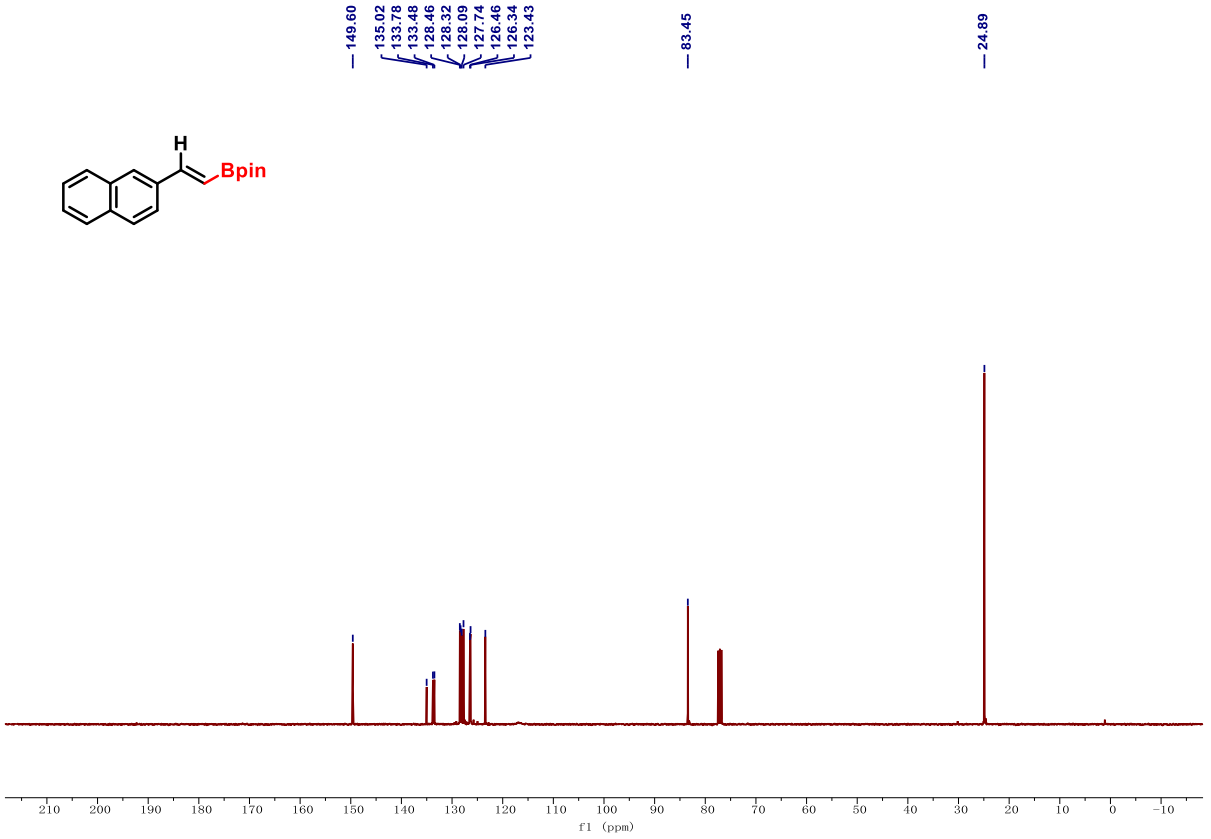
2-[(*1E*)-2-(3-Chlorophenyl)ethenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20): ^{13}C NMR (101 MHz, $CDCl_3$):



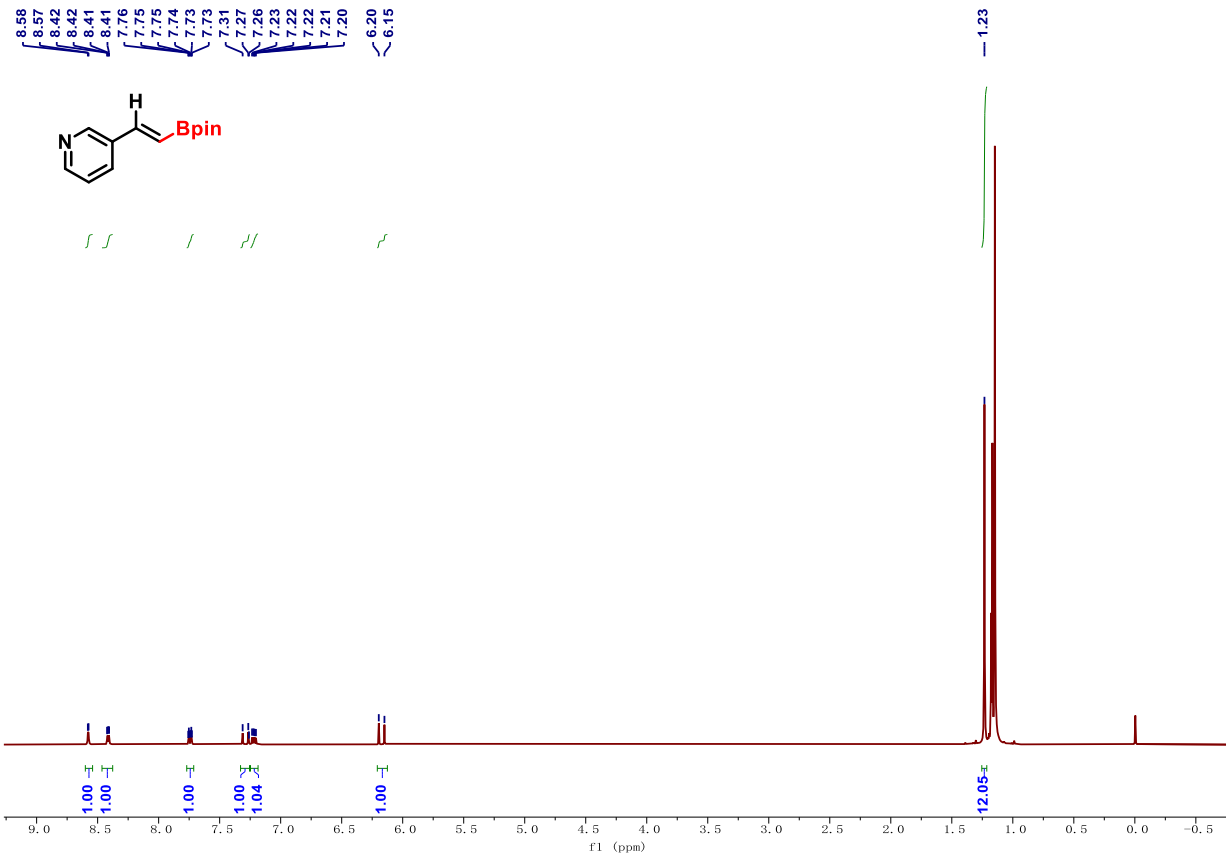
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-naphthalenyl)ethenyl]-1,3,2-dioxaborolane (21): ^{1}H NMR (400 MHz, $CDCl_3$):



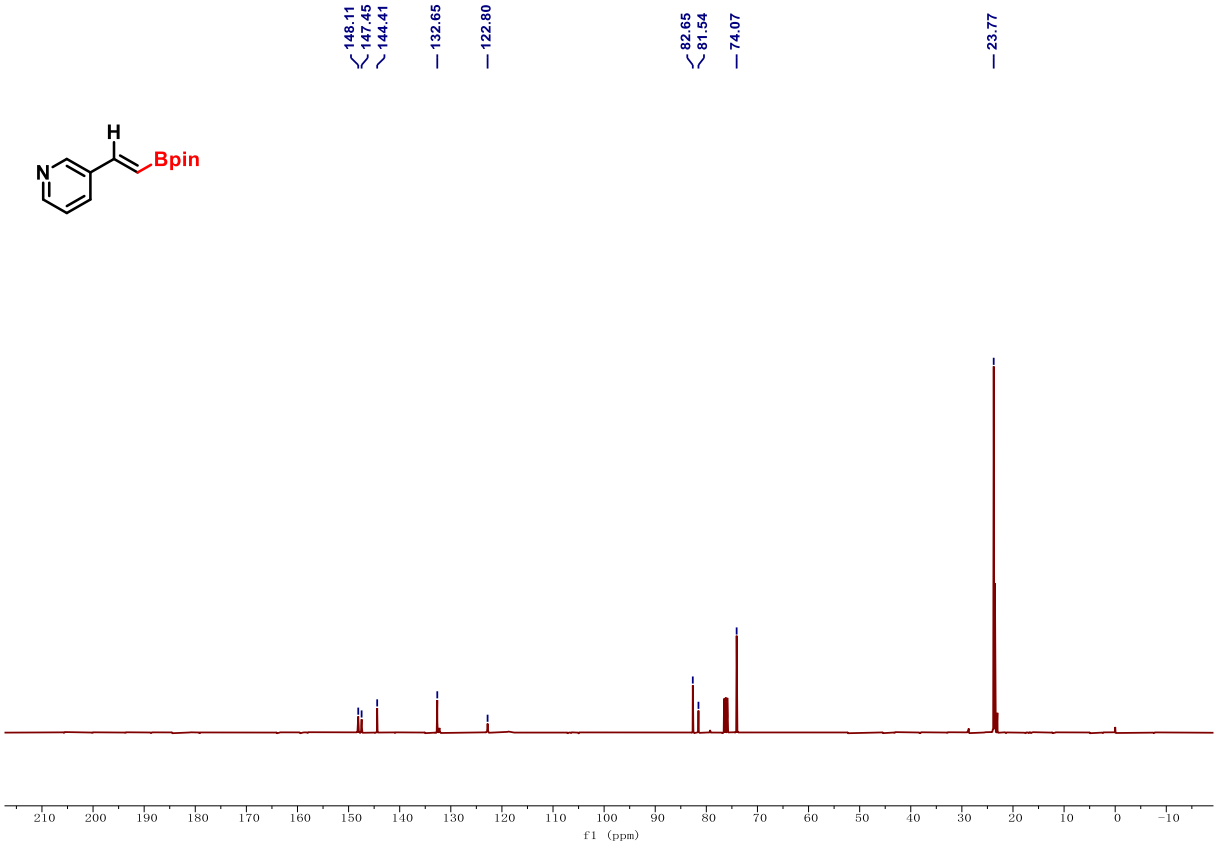
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-naphthalenyl)ethenyl]-1,3,2-dioxaborolane (21): ^{13}C NMR (101 MHz, $CDCl_3$):



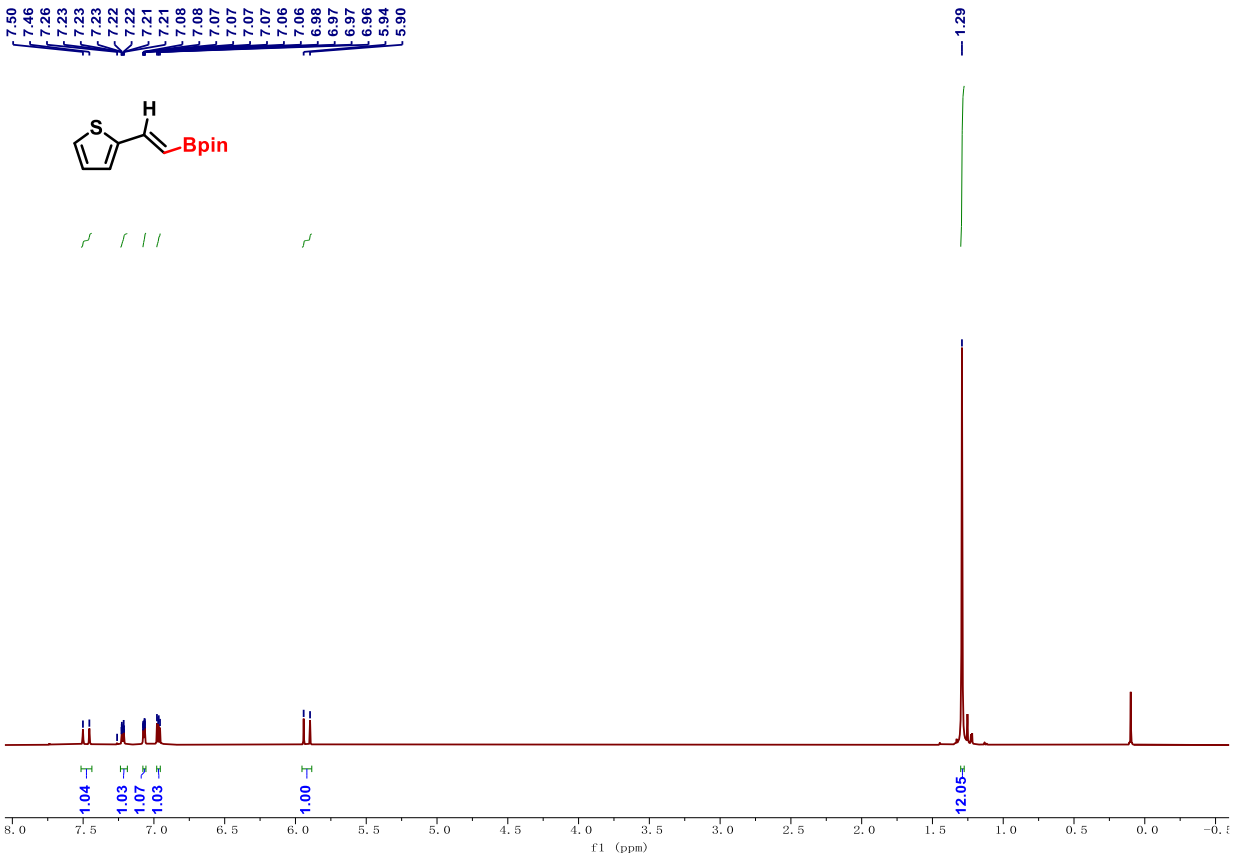
3-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]pyridine (22): ^{1}H NMR (400 MHz, $CDCl_3$):



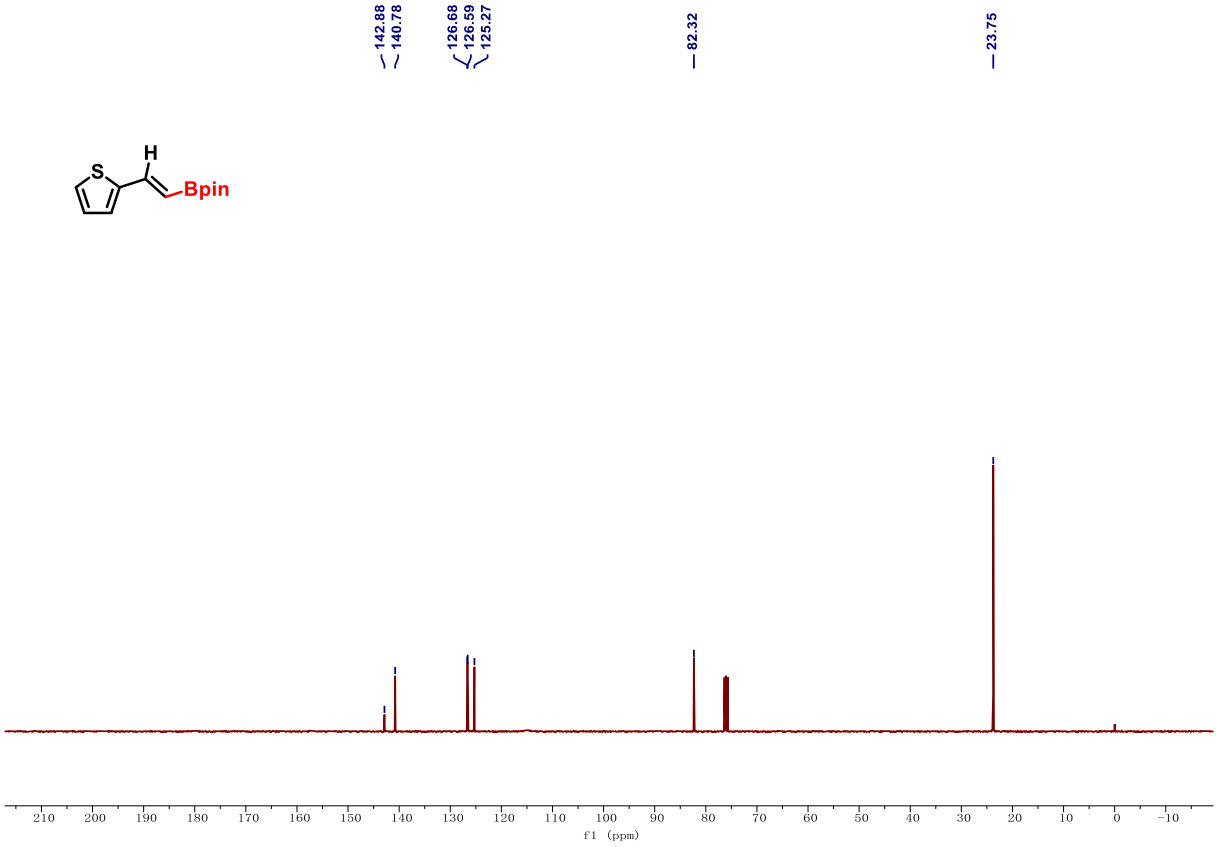
3-[(*1E*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethenyl]pyridine (22): ^{13}C NMR (101 MHz, $CDCl_3$):



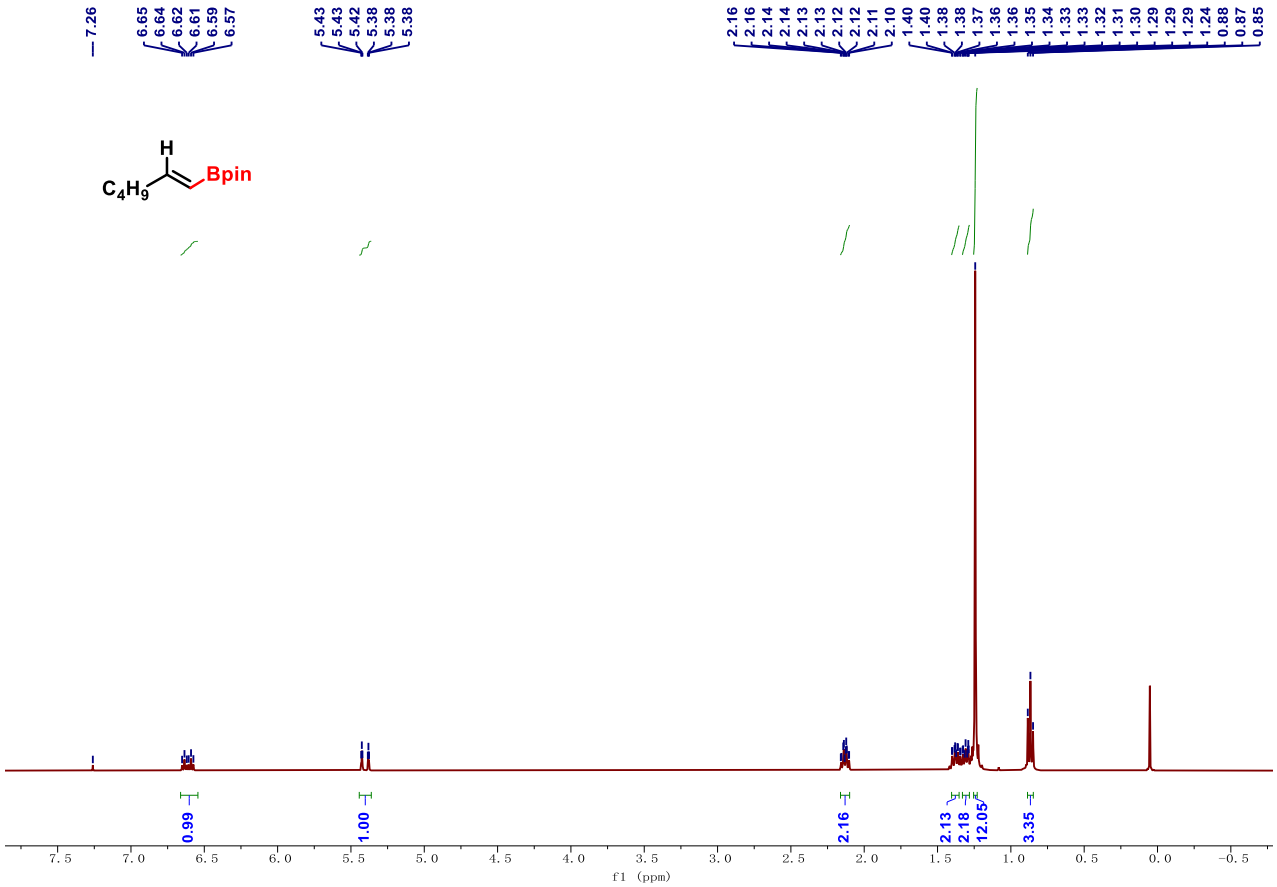
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-thienyl)ethenyl]-1,3,2-dioxaborolane (24): ^{1}H NMR (400 MHz, $CDCl_3$):



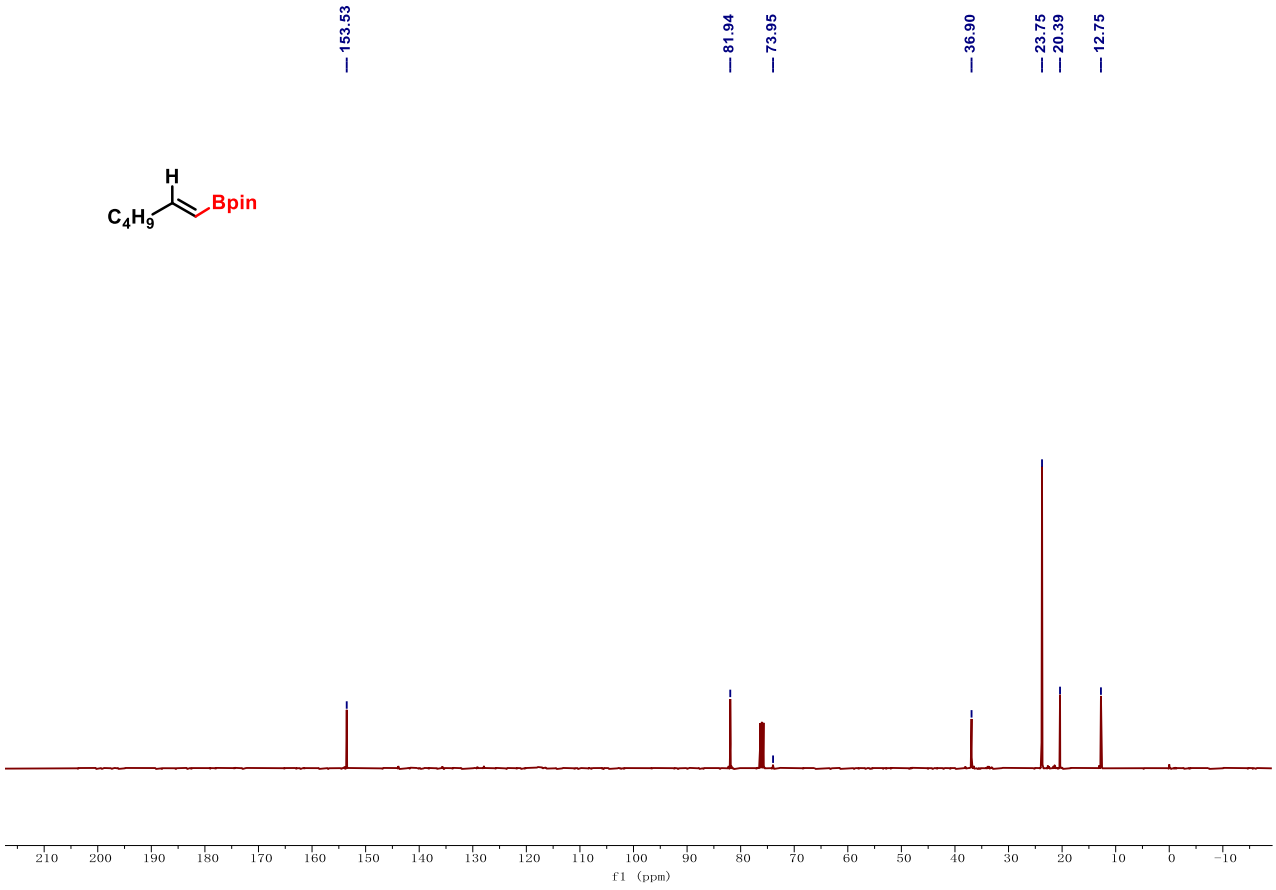
4,4,5,5-Tetramethyl-2-[(*1E*)-2-(2-thienyl)ethenyl]-1,3,2-dioxaborolane (24): ^{13}C NMR (101 MHz, $CDCl_3$):



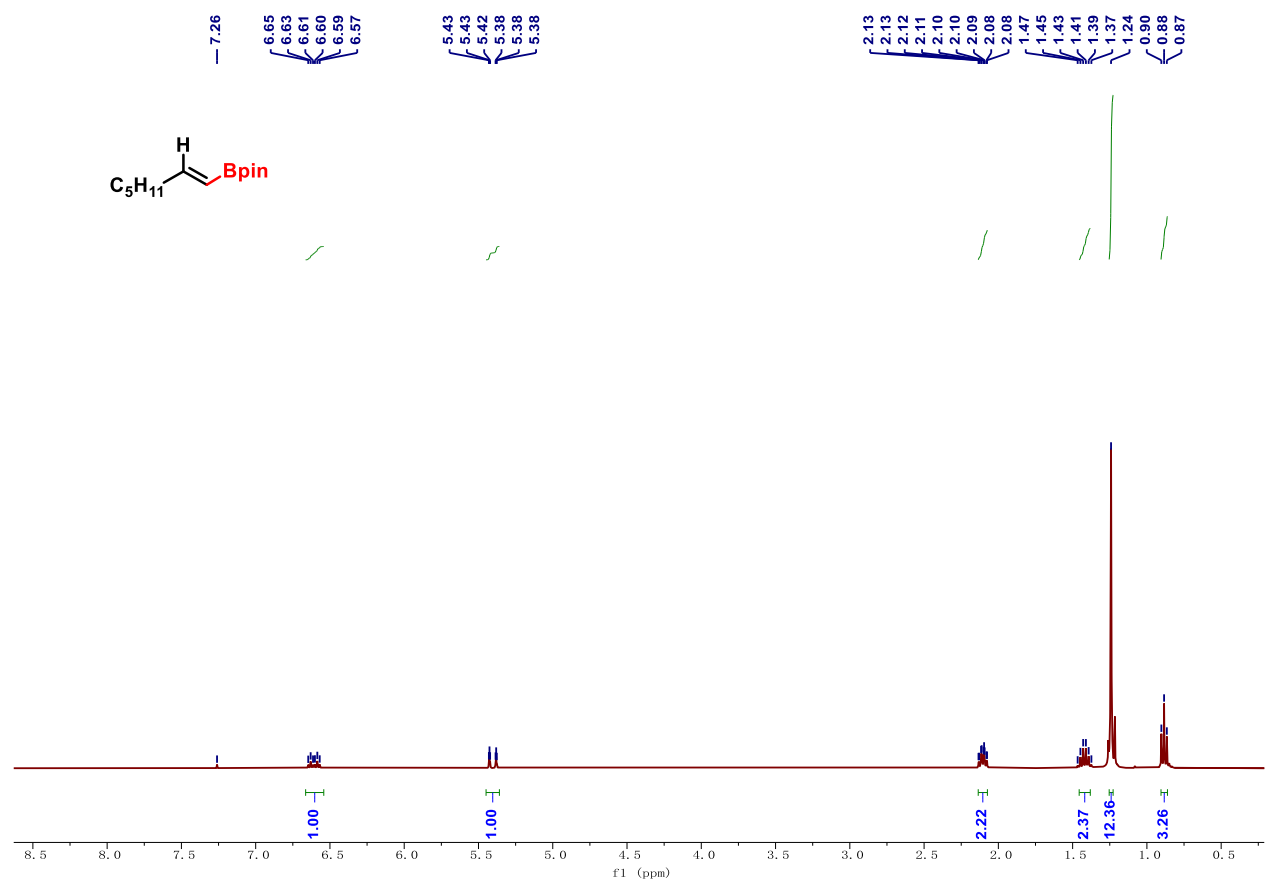
(*E*)-Hex-1-enylboronic acid pinacol ester (26): ^{1}H NMR (400 MHz, $CDCl_3$):



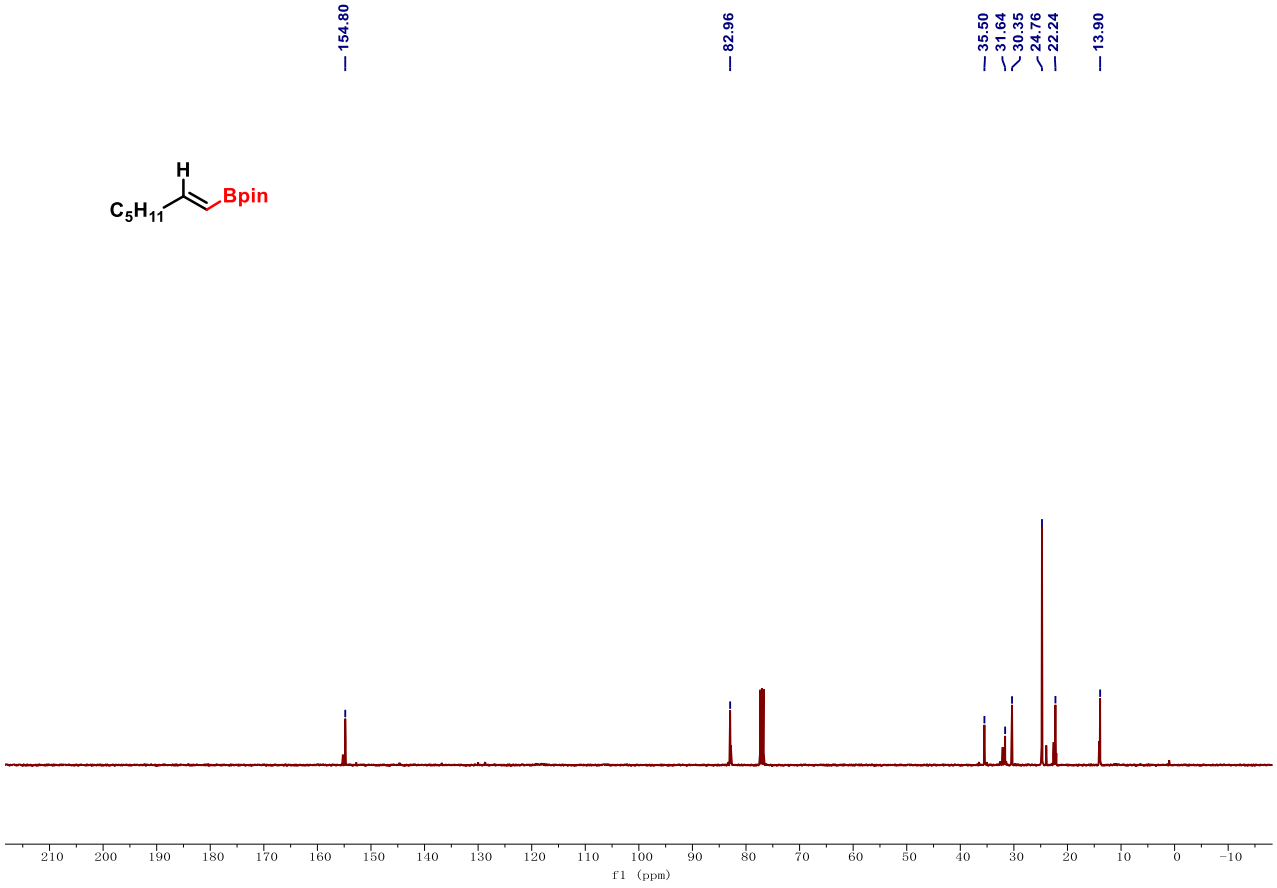
(*E*)-Hex-1-enylboronic acid pinacol ester (26): ^{13}C NMR (101 MHz, $CDCl_3$):



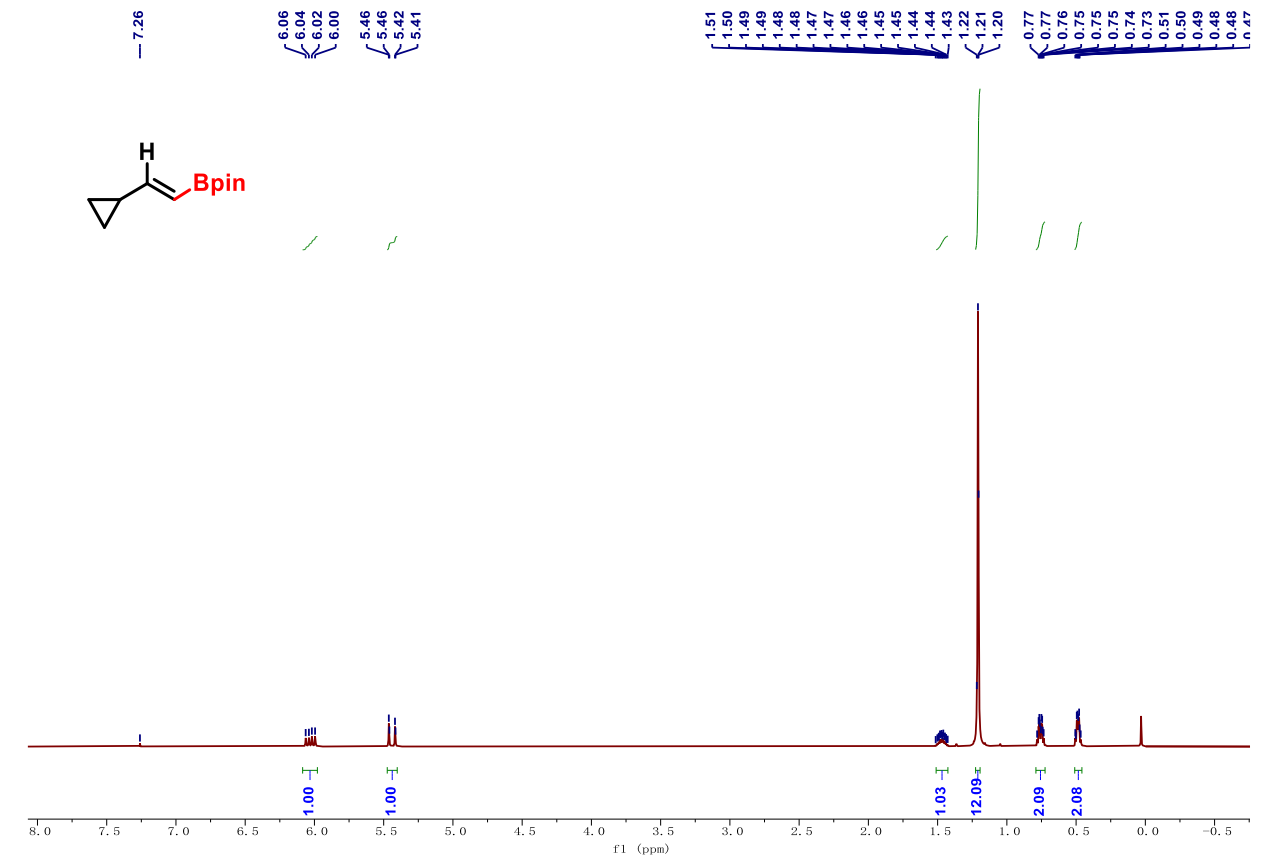
(*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27): ^{1}H NMR (400 MHz, $CDCl_3$):



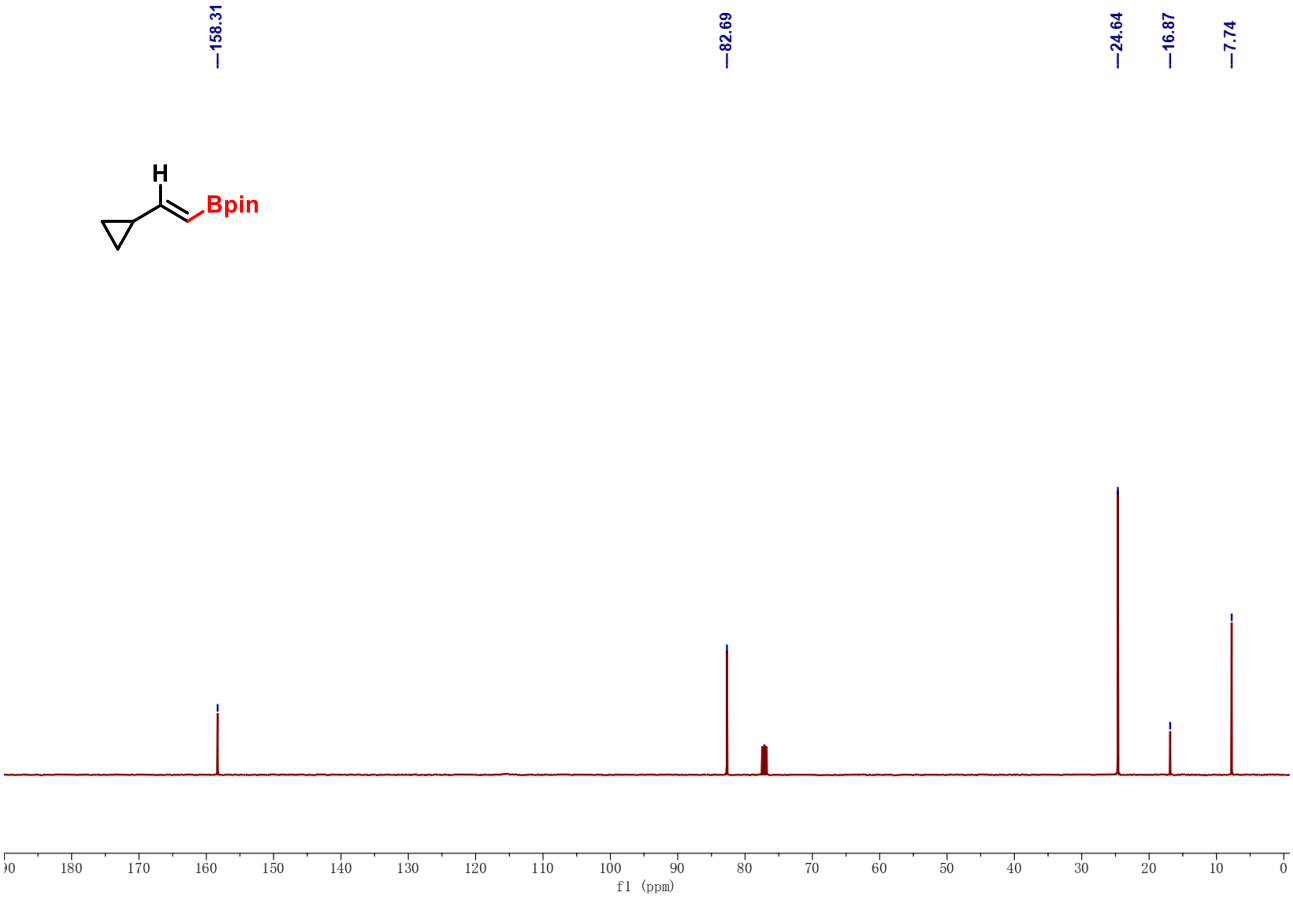
(*E*)-2-(hept-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (27): ^{13}C NMR (101 MHz, $CDCl_3$):



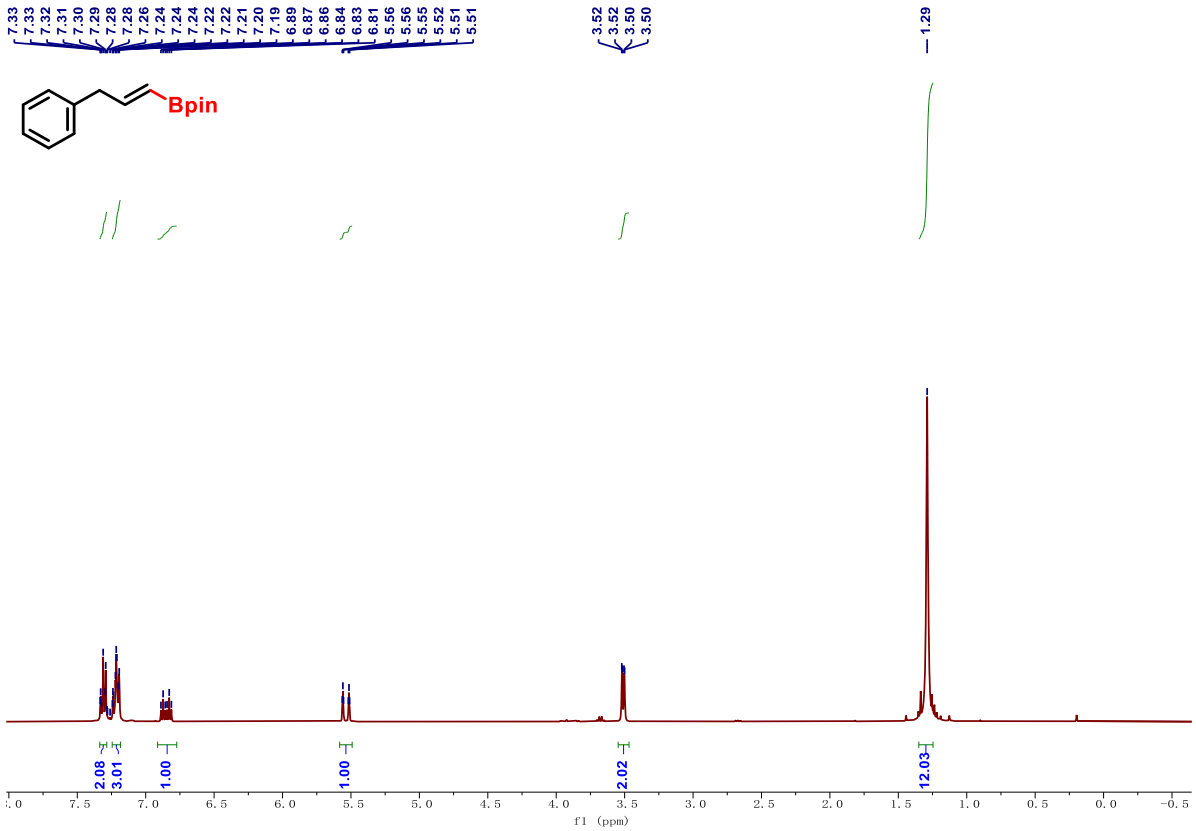
((*E*)-2-Cyclopropylethenyl)boronic acid pinacol ester (28): ^{1}H NMR (400 MHz, $CDCl_3$):



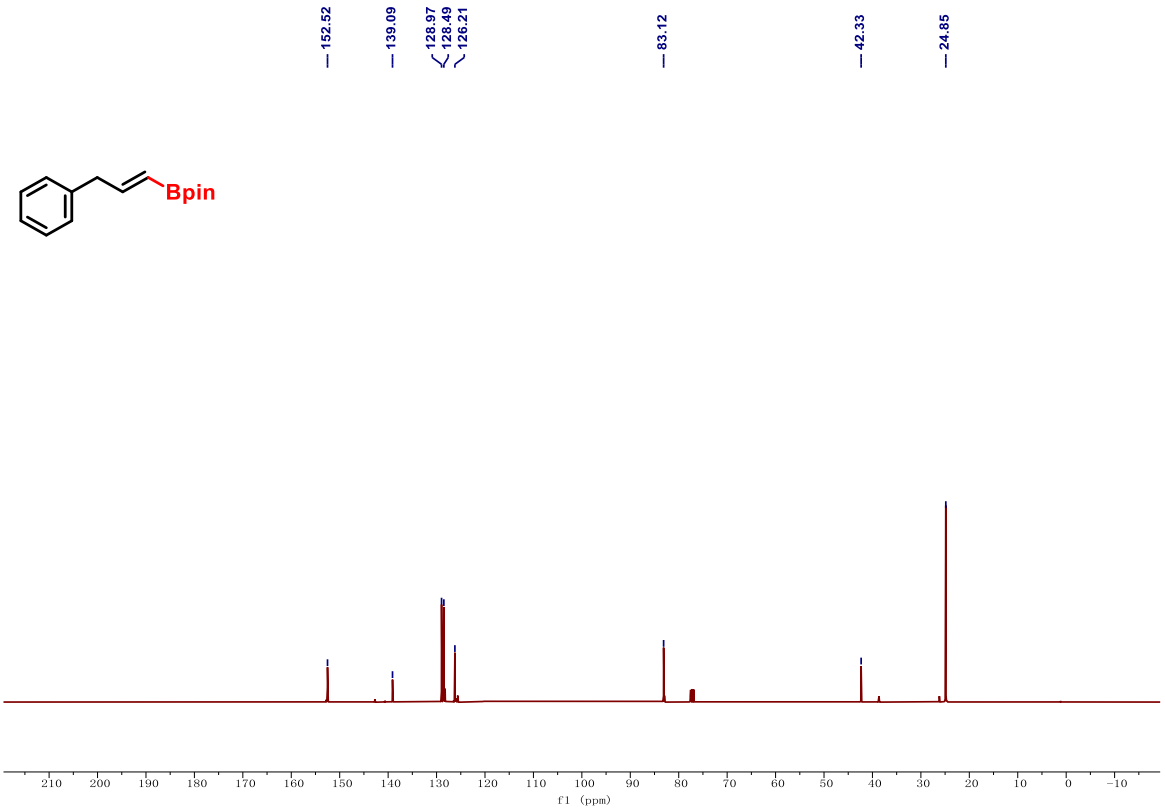
((*E*)-2-Cyclopropylethenyl)boronic acid pinacol ester (28): ^{13}C NMR (101 MHz, $CDCl_3$):



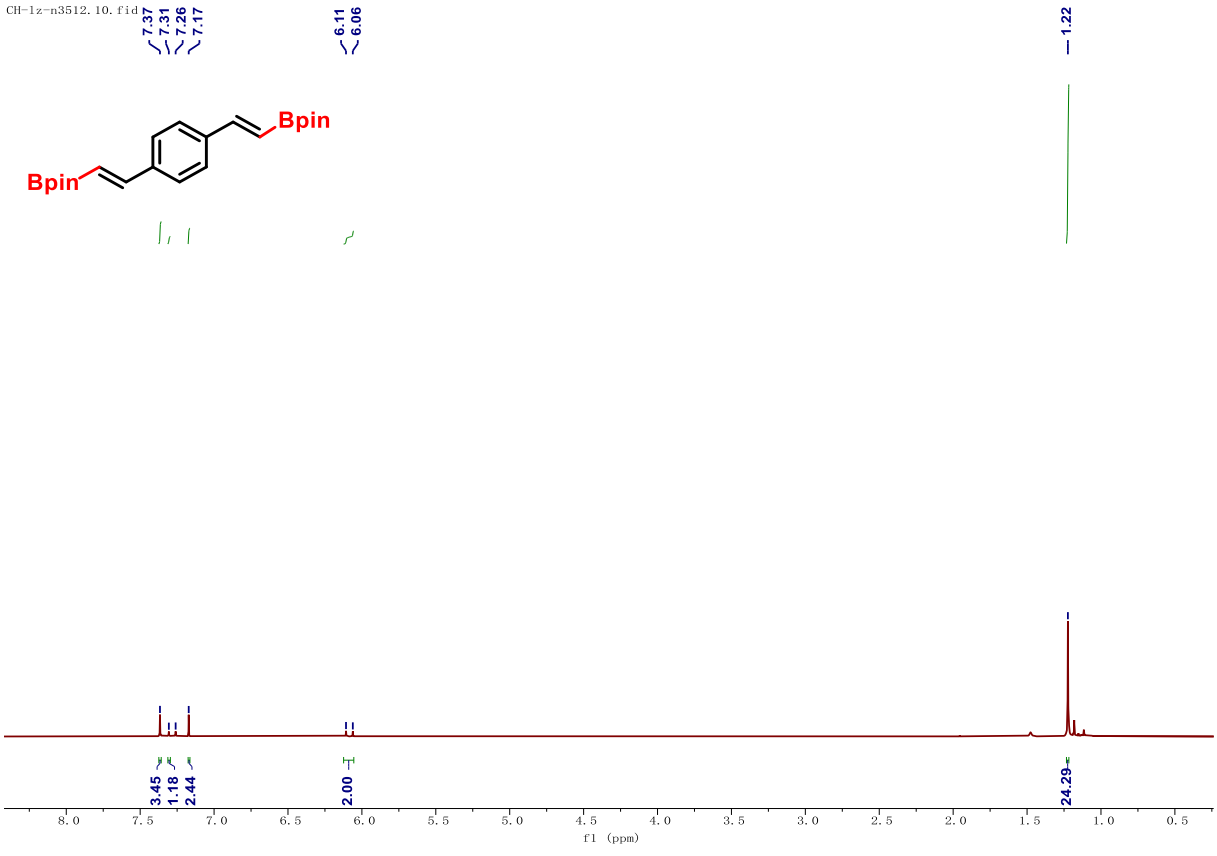
4,4,5,5-Tetramethyl-2-[(*1E*)-3-phenyl-1-propen-1-yl]-1,3,2-dioxaborolane (29): ^{1}H NMR (400 MHz, $CDCl_3$):



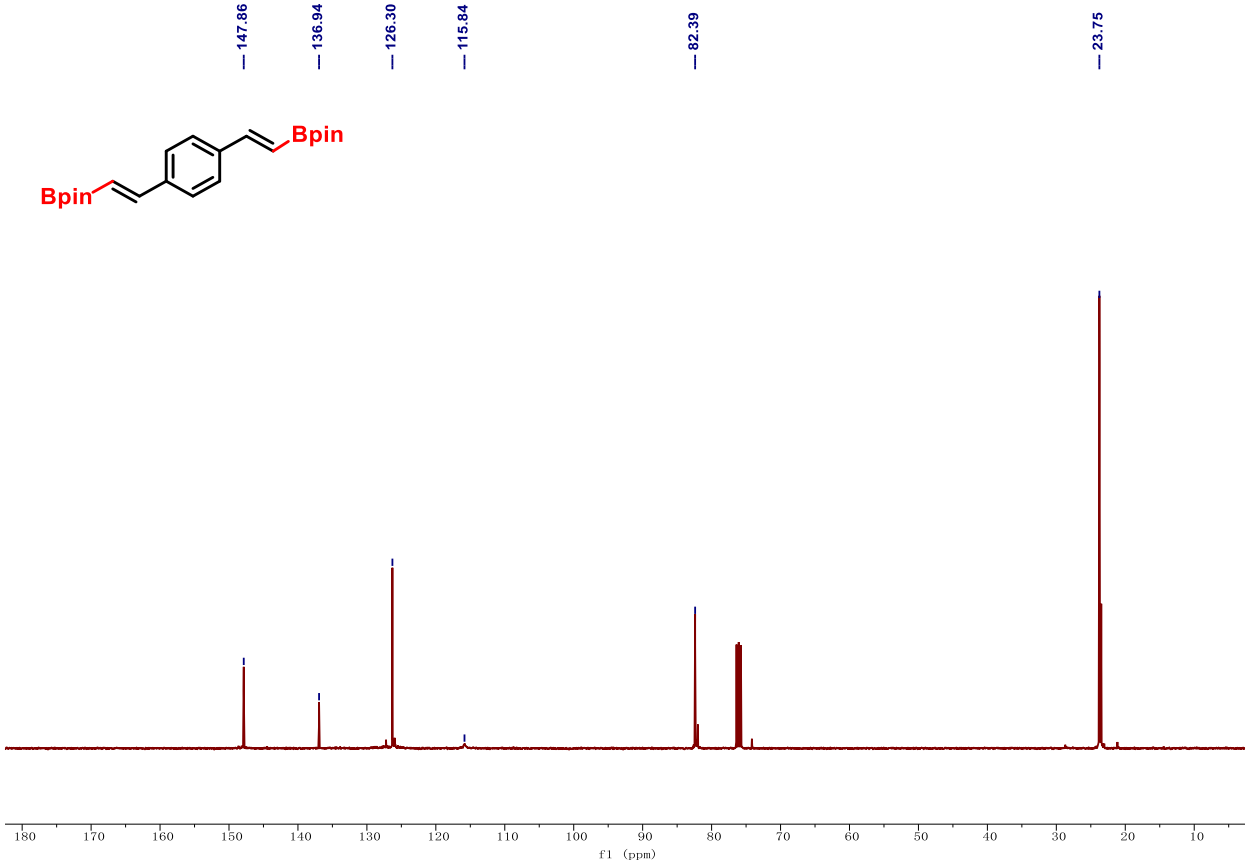
4,4,5,5-Tetramethyl-2-[(*1E*)-3-phenyl-1-propen-1-yl]-1,3,2-dioxaborolane (29): ^{13}C NMR (101 MHz, $CDCl_3$):



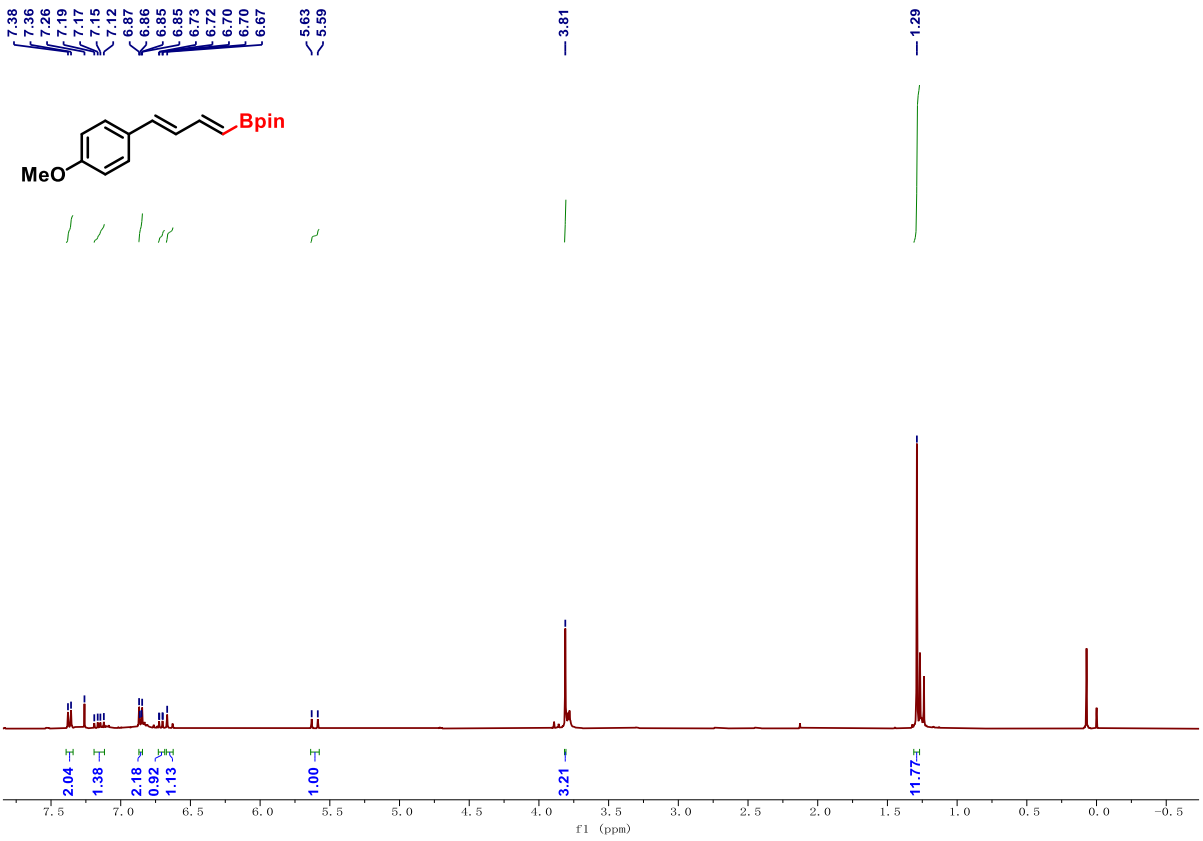
1,3,2-Dioxaborolane,2,2'-[1,4-phenylenedi-(*1E*)-2,1-ethenediyl]bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30): ^{1}H NMR (400 MHz, $CDCl_3$):



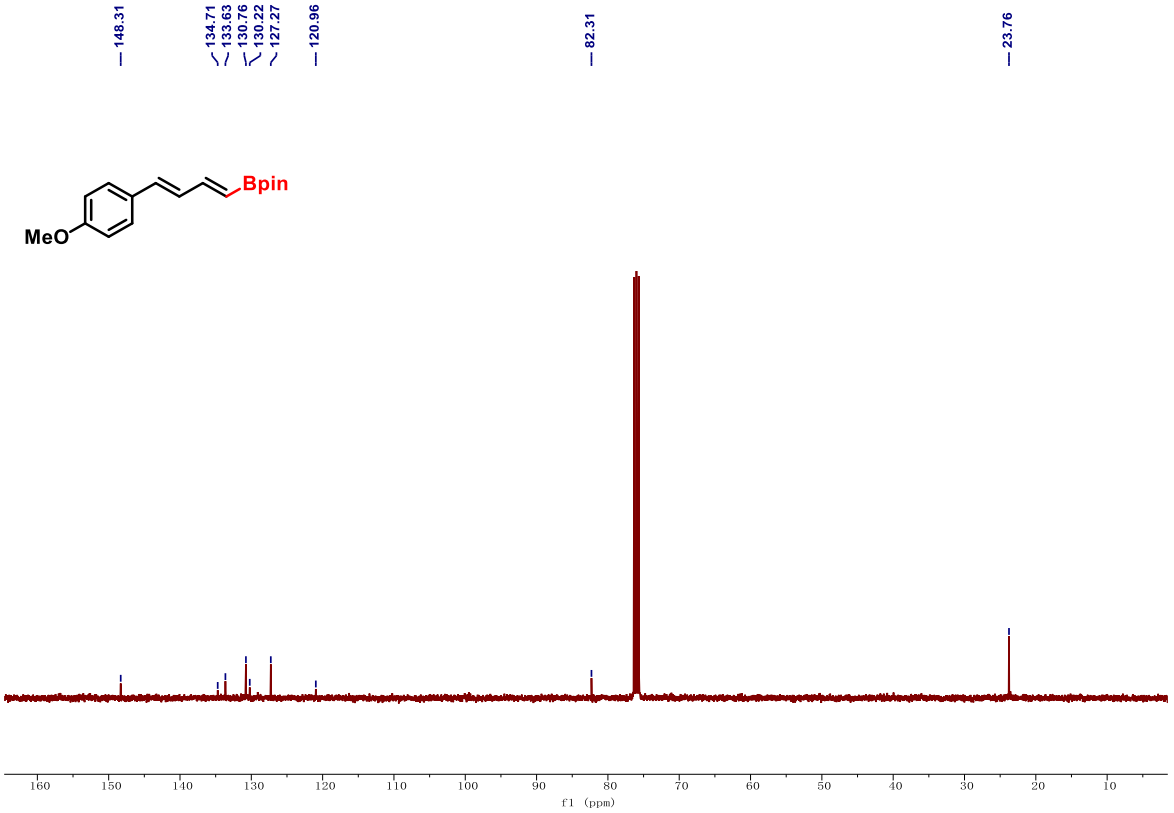
1,3,2-Dioxaborolane,2,2'-[1,4-phenylenedi-(*1E*)-2,1-ethenediyl]bis[4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30): ^{13}C NMR (101 MHz, $CDCl_3$):



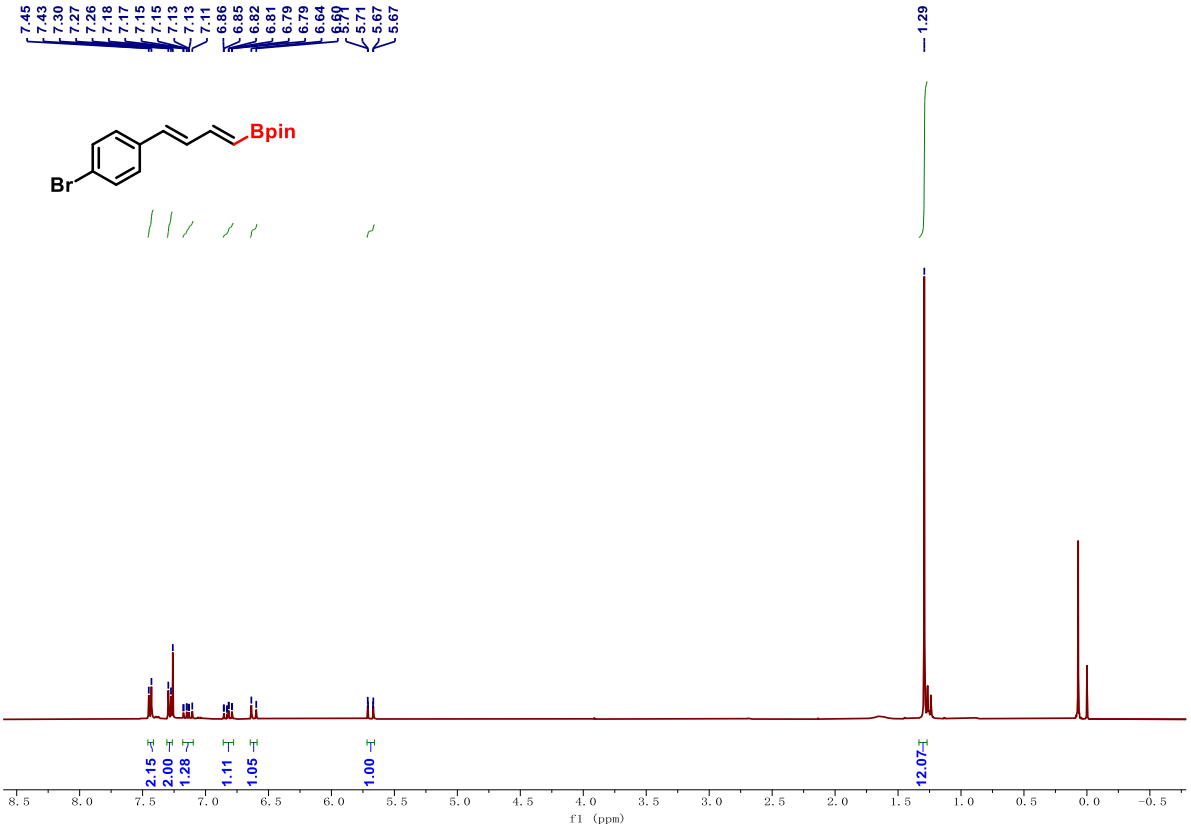
2-((*1E*,*3E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31): ^{1}H NMR (400 MHz, $CDCl_3$):



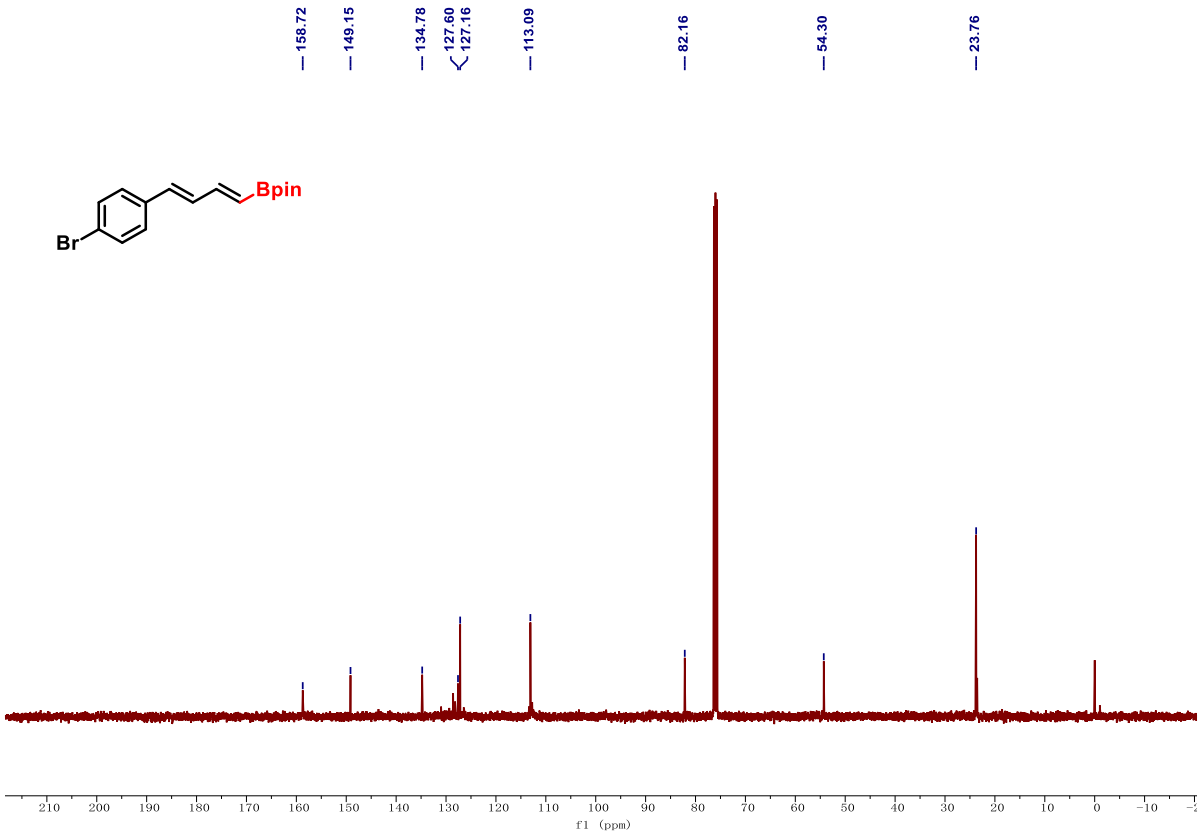
2-((*1E*,*3E*)-4-(4-methoxyphenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (31): ^{13}C NMR (101 MHz, $CDCl_3$):



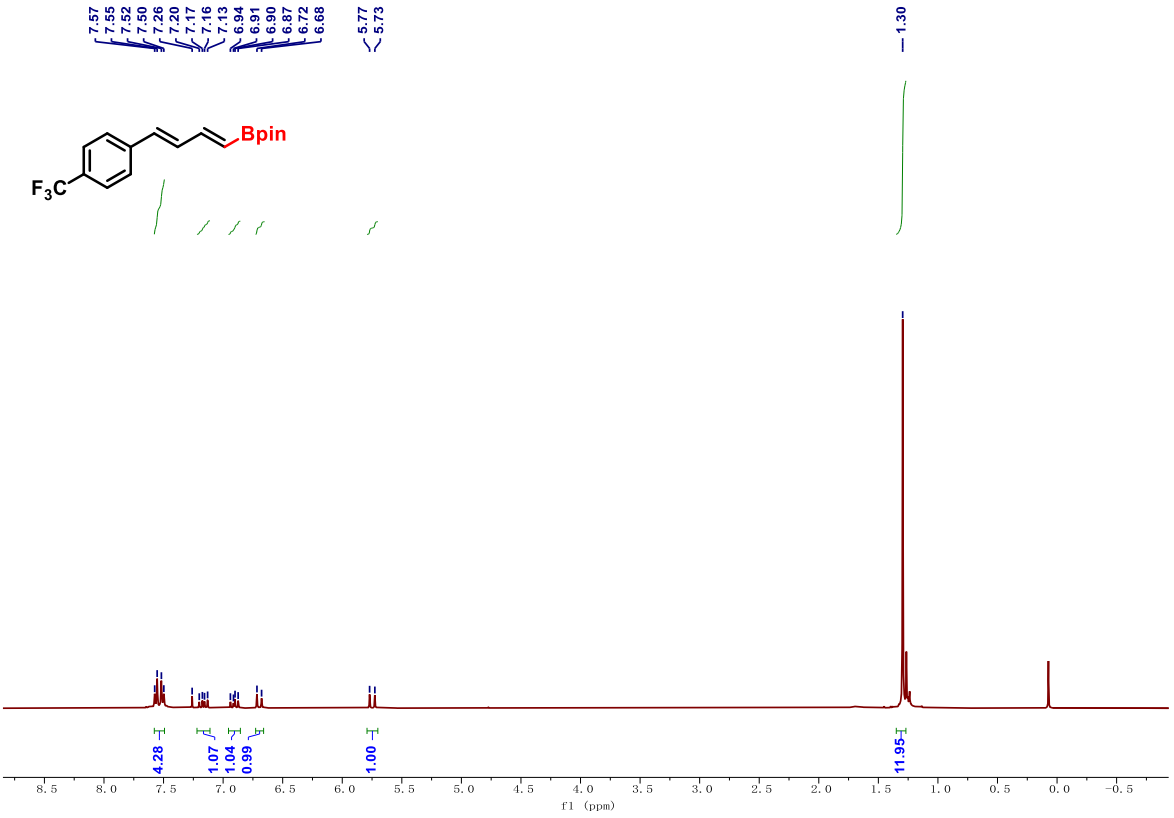
2-((*1E*,*3E*)-4-(4-bromophenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32): ^{1}H NMR (400 MHz, $CDCl_3$):



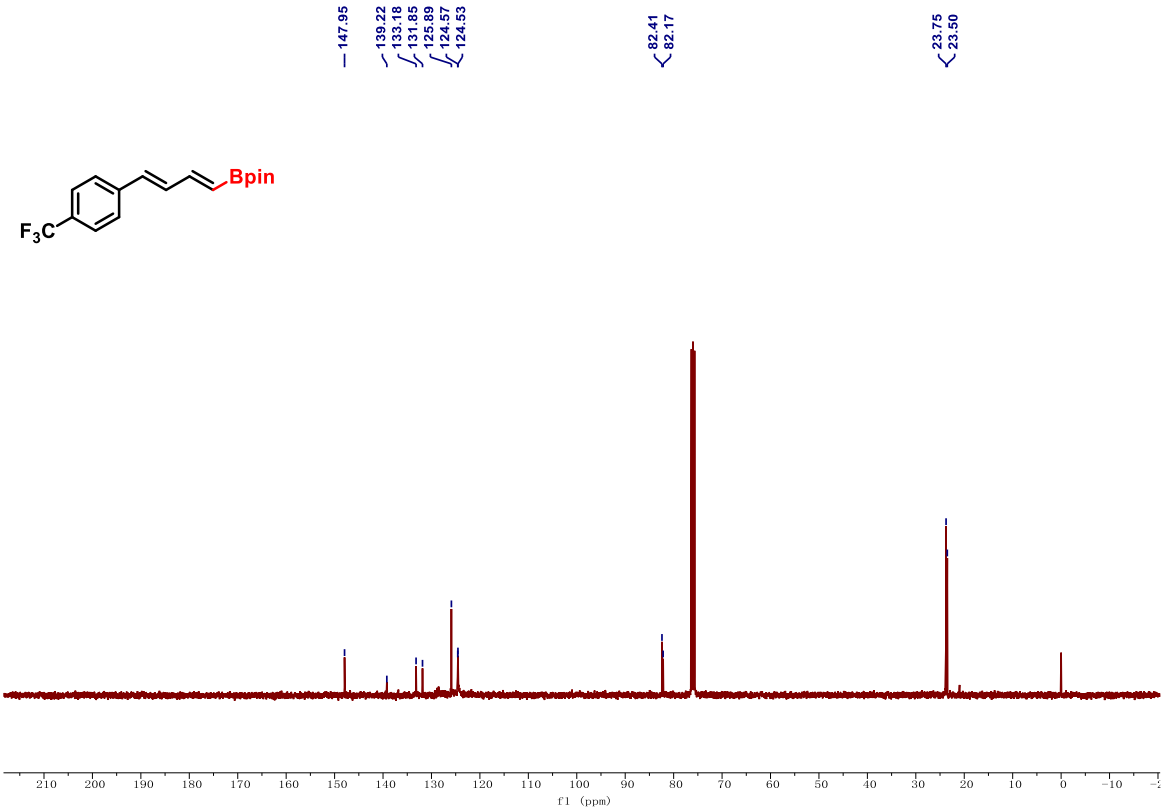
2-((*1E*,*3E*)-4-(4-bromophenyl)buta-1,3-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32): ^{13}C NMR (101 MHz, $CDCl_3$):



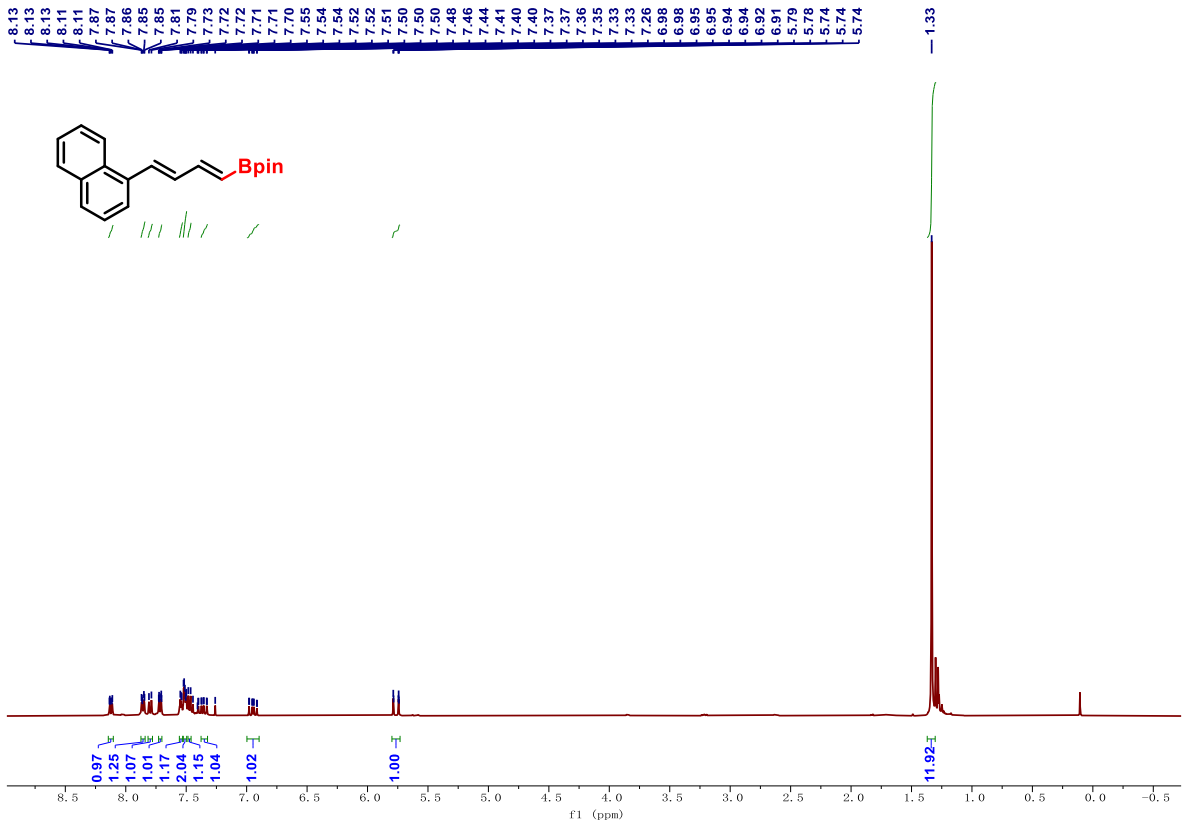
4,4,5,5-tetramethyl-2-((*1E*,*3E*)-4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (33): ^{1}H NMR (400 MHz, $CDCl_3$):



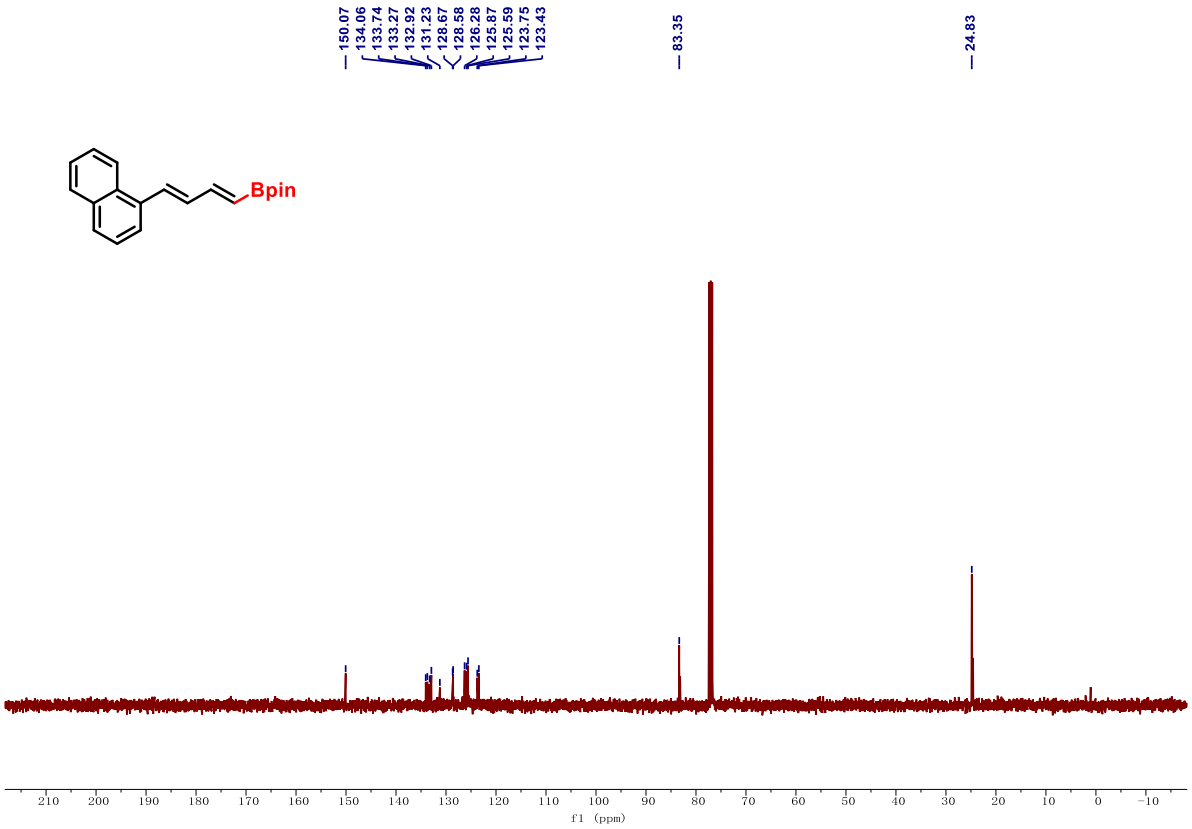
4,4,5,5-tetramethyl-2-((*1E*,*3E*)-4-(4-(trifluoromethyl)phenyl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (33): ^{13}C NMR (101 MHz, $CDCl_3$):



4,4,5,5-tetramethyl-2-((*1E*,*3E*)-4-(naphthalen-1-yl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (34): ^{1}H NMR (400 MHz, $CDCl_3$):



4,4,5,5-tetramethyl-2-((*1E,3E*)-4-(naphthalen-1-yl)buta-1,3-dien-1-yl)-1,3,2-dioxaborolane (34): ^{13}C NMR (101 MHz, $CDCl_3$):



(*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1-d)-1,3,2-dioxaborolane : ^{1}H NMR (400 MHz, $CDCl_3$):