

# Supporting Information

## Ligand-Controlled Regiodivergent Copper-Catalyzed Alkylboration of Unactivated Terminal Alkynes

Wei Su, Tian-Jun Gong, Qi Zhang, Qing Zhang, Bin Xiao,\* Yao Fu\*

Hefei National Laboratory for Physical Sciences at the Microscale, iChEM, CAS Key Laboratory of Urban Pollutant Conversion, Anhui Province Key Laboratory of Biomass Clean Energy, University of Science and Technology of China, Hefei 230026, China.

Email: [binxiao@ustc.edu.cn](mailto:binxiao@ustc.edu.cn); [fuyao@ustc.edu.cn](mailto:fuyao@ustc.edu.cn)

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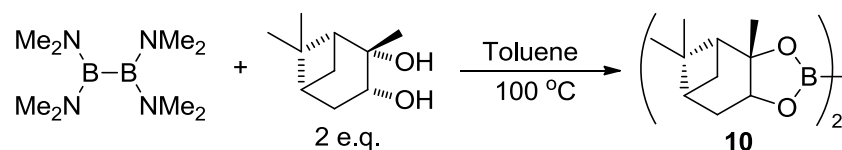
#### I. General Remark:

All solvents were obtained from commercial suppliers and used without further purification. The following Chemicals were purchased and used as received: LiO'Bu (99%, Acros), dppbz (98%, TCI), DMAP (99%, Adamas), DMA (99.5%, Extra Dry over Molecular Sieve, AcroSeal, Acros). CuCl (97%, Sinopharm Chemical Reagent) was purified with concentrated HCl. Alkynes and alkyl

halides were obtained from commercial suppliers or prepared according to standard procedures. Analytical TLC was done on pre-coated silica gel plates. Column chromatography was conducted with 300-400 mesh silica gel.  $^1\text{H}$  NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts of  $^1\text{H}$  NMR spectra were reported in parts per million relative to tetramethylsilane ( $\delta = 0$ ). The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. Coupling constants,  $J$ , were reported in hertz unit (Hz).  $^{13}\text{C}$  NMR spectra were recorded on 101 MHz spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane ( $\delta = 0$ ).  $^1\text{B}$  NMR signals are quoted relative to  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ . High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

## II. General Procedure for the Preparation of Starting Materials

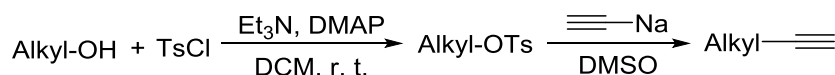
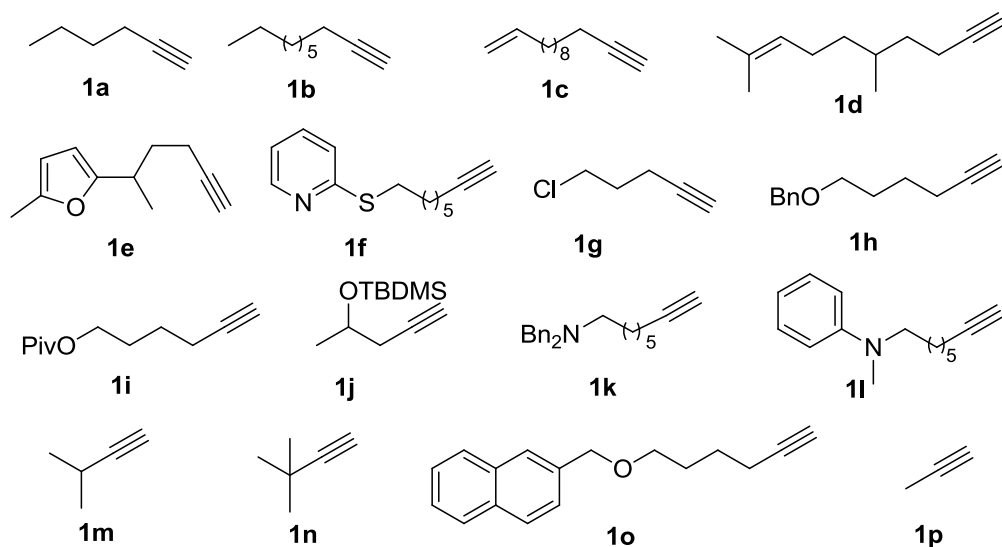
### A. Synthesis of 10.



(+)-Pinanediol (5.00 g, 29.37 mmol) in toluene (20 mL) was heated to 50°C and treated with tetrakis(dimethylamino)diboron (2.90 g, 14.65 mmol) within two minutes. This mixture was then slowly heated to 100°C and after an induction period of about 5 minutes evolution of  $\text{Me}_2\text{NH}$  gas commenced. The mixture was maintained at 100°C for 30 minutes. A slow stream of nitrogen was used to disperse  $\text{Me}_2\text{NH}$ . The toluene was removed (rotary evaporation) to give in quantitative yield a white solid bis((+)-pinanediolato)diboron. The solid was recrystallised from toluene: petroleum (80°C - 100°C) (1:9) (20 mL) and after standing at room temperature for 18 hours bis((+)-pinanediolato)diboron 4.51 g, 86.6%.

### B. The general procedures for preparation of alkyne substrates.

The Unactivated Terminal Alkyne Substrates:



### **C. Preparation of 1c, 1d, 1e, 1f, 1k, 1l**

To a solution of alcohol (5 mmol) in DCM (15 mL) was added Et<sub>3</sub>N (2 equiv), DMAP (0.5 mmol) and p-Toluenesulfonyl chloride (5 mmol), the reaction mixture was stirred at r.t. for 2 h. The mixture was sequentially washed with 1 M HCl, NaHCO<sub>3</sub> saturated aqueous solution and water. The organic extract was dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated in vacuo, and the residue purified by column chromatography.

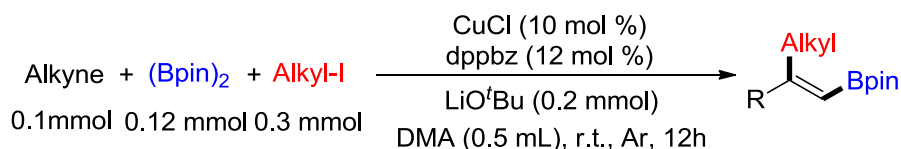
The alkyl tosylate (4 mmol) obtained from last step was added to DMSO (10 mL) and cooled to 0 °C, then added 2 mL Sodium acetylide (18 wt. % slurry in xylene). The reaction mixture was allowed to warm to r.t. The resulting red solution was stirred for 30 minutes and then quenched with 1 mL water. The layers were separated and the aqueous phase was extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic extracts were dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated in vacuo to give crude product. Purification of the crude product by column chromatography to obtain the alkyl substituted terminal alkynes.

### **D. Purification of CuCl.**

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with CuCl (10 mmol, 0.99g), then HCl aq. (18M, 10 mL) was added to the flask. After stirring for 10 min in room temperature, H<sub>2</sub>O (50 mL) was added to the flask, and white powder was dissolved out from the solution. After the filtration, the white powder was sequentially washed with EtOH and EtOAc. The white powder was collected and dried in vacuum.

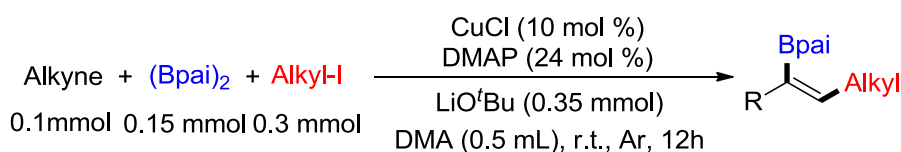
## **III. General Procedure for Copper-Catalyzed Alkylboration of Alkynes**

### **A. General Procedure for Copper-Catalyzed *anti*-Markovnikov Alkylboration**



A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1.0 mg, 10 mol %), dppbz (5.4 mg, 12 mol %), LiO<sup>t</sup>Bu (16.0 mg, 0.2 mmol) and (Bpin)<sub>2</sub> (30.5 mg, 0.12 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added. After stirring for 10 min, the alkyne (0.1 mmol) and alkyl iodide (0.3 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (2 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

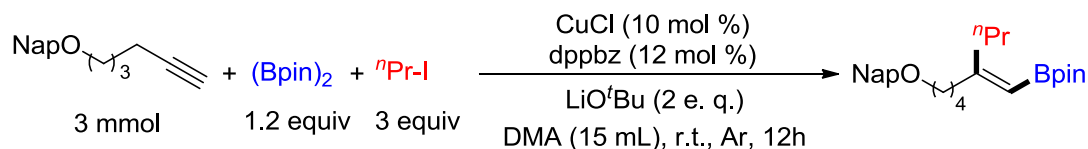
### **B. General Procedure for Copper-Catalyzed Markovnikov Alkylboration**



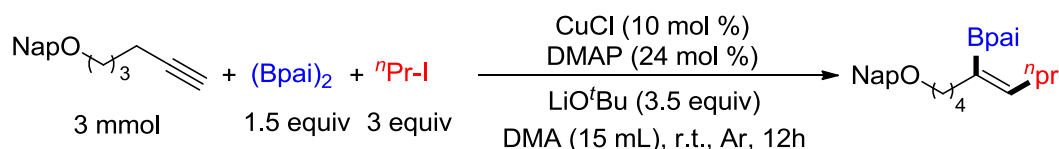
A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1.0 mg, 10 mol %), DMAP (2.9 mg, 24 mol %), LiO<sup>t</sup>Bu (28.0 mg, 0.35 mmol) and (Bpai)<sub>2</sub> (53.7 mg, 0.15 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added.

After stirring for 10 min, the alkyne (0.1 mmol) and alkyl iodide (0.3 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (2 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

### C. Procedure for Scaled-Up Alkylboration of **1o** with <sup>n</sup>PrI

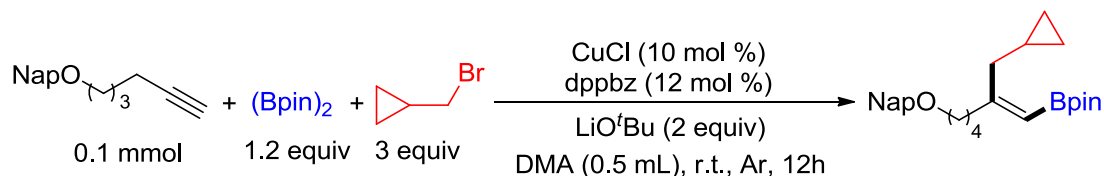


A 50 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (30 mg, 10 mol %), dppbz (162 mg, 12 mol %), LiO'Bu (480 mg, 6 mmol) and (Bpin)<sub>2</sub> (915 mg, 3.6 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (15 mL) was added. After stirring for 10 min, the alkyne **1o** (3 mmol) and <sup>n</sup>PrI (9 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.



A 50 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (30 mg, 10 mol %), DMAP (87 mg, 24 mol %), LiO'Bu (840 mg, 10.5 mmol) and (Bpai)<sub>2</sub> (1.6 g, 4.5 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (15 mL) was added. After stirring for 10 min, the alkyne **1o** (3 mmol) and <sup>n</sup>PrI (9 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

### D. Procedure for *anti*-Markovnikov Alkylboration of **1o** with (bromomethyl)cyclopropane

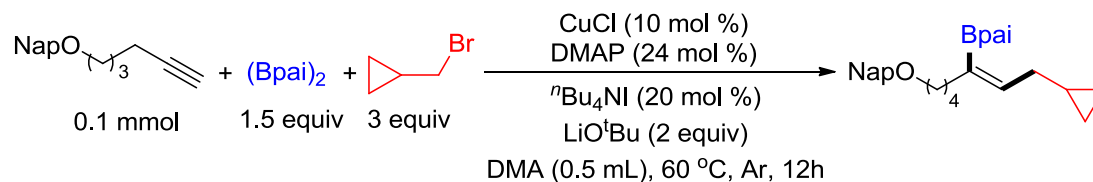


A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1 mg, 10 mol %), dppbz (5.4 mg, 12 mol %), LiO'Bu (16 mg, 0.2 mmol) and (Bpin)<sub>2</sub> (30.5 mg, 0.12 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added. After stirring for 10 min, the alkyne **1o** (0.1 mmol) and (bromomethyl)cyclopropane (0.3 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by



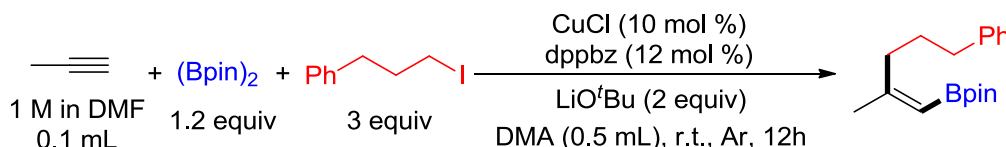
flash column chromatography on silica gel to give the target product.

### **E. Procedure for Markovnikov Alkylboration of **1o** with (bromomethyl)cyclopropane**



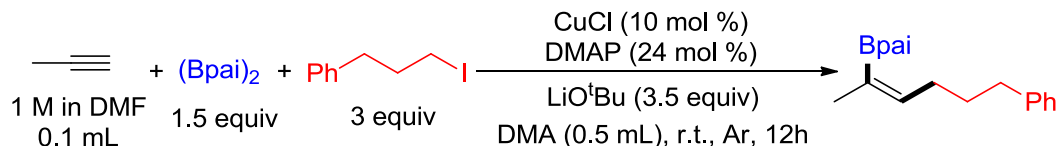
A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1 mg, 10 mol %), DMAP (2.9 mg, 24 mol %), LiOtBu (28 mg, 0.35 mmol), (Bpai)<sub>2</sub> (53.7 mg, 0.15 mmol) and  $n\text{Bu}_4\text{NI}$  (7.4 mg, 20 mmol%). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added. After stirring for 10 min, the alkyne **1o** (0.1 mmol) and (bromomethyl)cyclopropane (0.3 mmol) was added by syringe under Ar. The reaction mixture was heated and stirred at 60°C for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

### **F. Procedure for anti-Markovnikov Alkylboration of Propyne**



A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1 mg, 10 mol %), dppbz (5.4 mg, 12 mol %), LiOtBu (16 mg, 0.2 mmol) and (Bpin)<sub>2</sub> (30.5 mg, 0.12 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added. After stirring for 10 min, the alkyne Propyne (0.1 mL, 1M in DMF) and Phenylpropyl iodide (0.3 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

### **G. Procedure for Markovnikov Alkylboration of Propyne**



A 10 mL Schlenk tube equipped with a magnetic stirrer was charged with CuCl (1 mg, 10 mol %), DMAP (2.9 mg, 24 mol%), LiOtBu (28 mg, 0.35 mmol) and (Bpai)<sub>2</sub> (53.7 mg, 0.15 mmol). The tube was evacuated and backfilled with argon for three times, and then DMA (0.5 mL) was added. After stirring for 10 min, the alkyne Propyne (0.1 mL, 1M in DMF) and Phenylpropyl iodide (0.3 mmol) was added by syringe under Ar. The reaction mixture was stirred at r. t. for 12h. Et<sub>2</sub>O and water were added and the layers were separated. The aqueous phase was extracted with Et<sub>2</sub>O (20 mL x 3) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by flash column chromatography on silica gel to give the target product.

## IV. Procedures of Transformations of Alkylboration Products

### A. Procedure for Arylation<sup>1</sup>

To a 10-mL Schlenk flask were added **3p** or **4p** (0.1 mmol), Pd(OAc)<sub>2</sub> (1.1mg, 5.0 mol %) and SPhos (4.1mg, 10 mol %). The flask was evacuated and backfilled with argon three times. Then, THF (200  $\mu$ L), 4-bromotoluene (18  $\mu$ L, 1.5 equiv) and 2.5 M NaOH aq. (120  $\mu$ L, 3.0 equiv) were added in this order, and the resulting mixture was stirred at 60 °C for 16 h. After the reaction, the mixture was filtrated through a pad of Celite and all volatiles were removed in vacuo. The residue were purified by flash column chromatography on silica gel to give the target product.

### B. Procedure for Vinylation<sup>1</sup>

To a 10-mL Schlenk flask were added **3p** or **4p** (0.12 mmol, 1.2 equiv), Pd(OAc)<sub>2</sub> (1.1mg, 5.0 mol %) and SPhos (4.1mg, 10 mol %). The flask was evacuated and backfilled with argon three times. Then, THF (200  $\mu$ L), 1-bromo-2-methyl-1-propene (10  $\mu$ L, 0.10 mmol) and 2.5 M NaOH aq. (120  $\mu$ L, 3.0 equiv) were added in this order, and the resulting mixture was stirred at 60 °C for 16 h. After the reaction, the mixture was filtrated through a pad of Celite and all volatiles were removed in vacuo. The residue were purified by flash column chromatography on silica gel to give the target product.

### C. Procedure for Iodinolysis of Bpin<sup>2</sup>

To a stirred solution of boronate **3p** (0.1 mmol) in THF (0.2 mL) was added a solution of NaOH (0.1 mL, 1.5 mmol, 3 M in water). The resultant mixture was stirred for 10 min at 23°C, followed by dropwise addition of a solution of I<sub>2</sub> (50mg, 0.2 mmol) in THF (1 mL). After 1 h at 23°C, the reaction mixture was quenched with aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, extracted with ether, washed successively with saturated NaHCO<sub>3</sub> and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue were purified by flash column chromatography on silica gel to give the target product.

### D. Procedure for Bromination of Bpai<sup>3</sup>

To a 10-mL Schlenk flask were added **3p** or **4p** (0.1 mmol), CuBr<sub>2</sub> (0.2 mmol) and MeOH (1 mL). The resultant mixture was stirred for 12 h at 80°C, then cooled to room temperature. H<sub>2</sub>O (5 mL) was added into the reaction mixture, and extracted with Et<sub>2</sub>O (5 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

### E. Procedure for Oxidation<sup>4</sup>

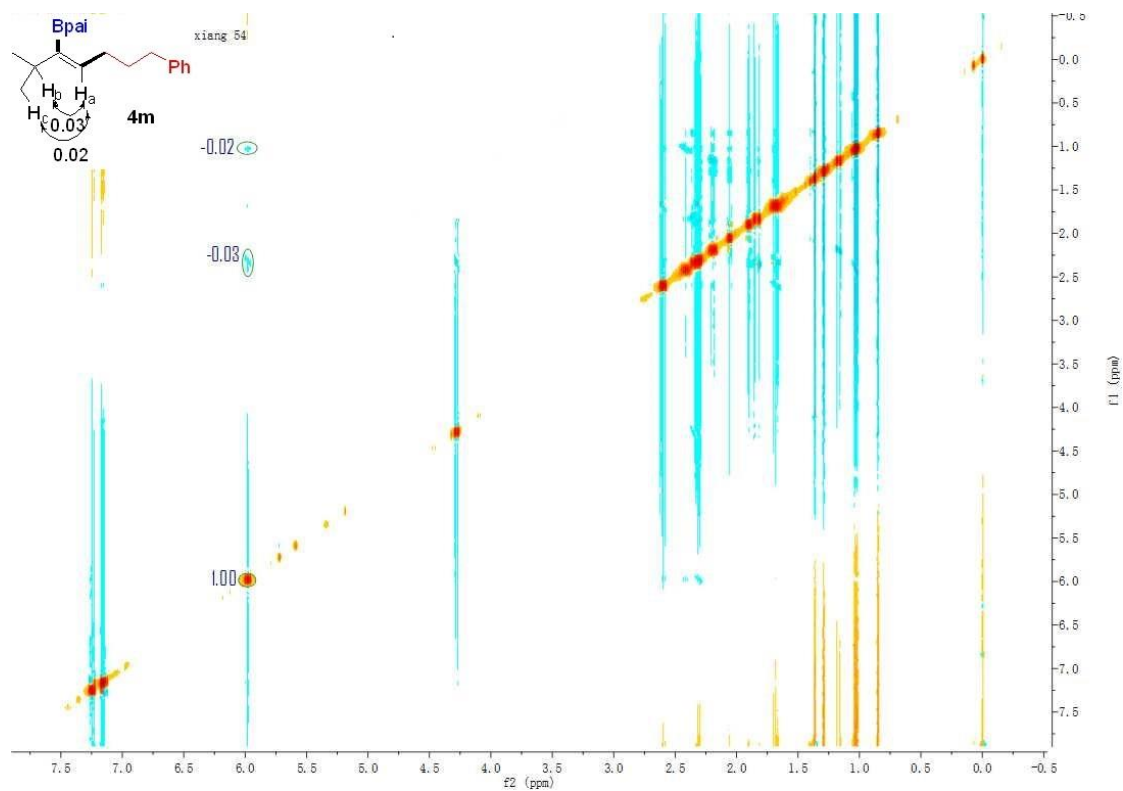
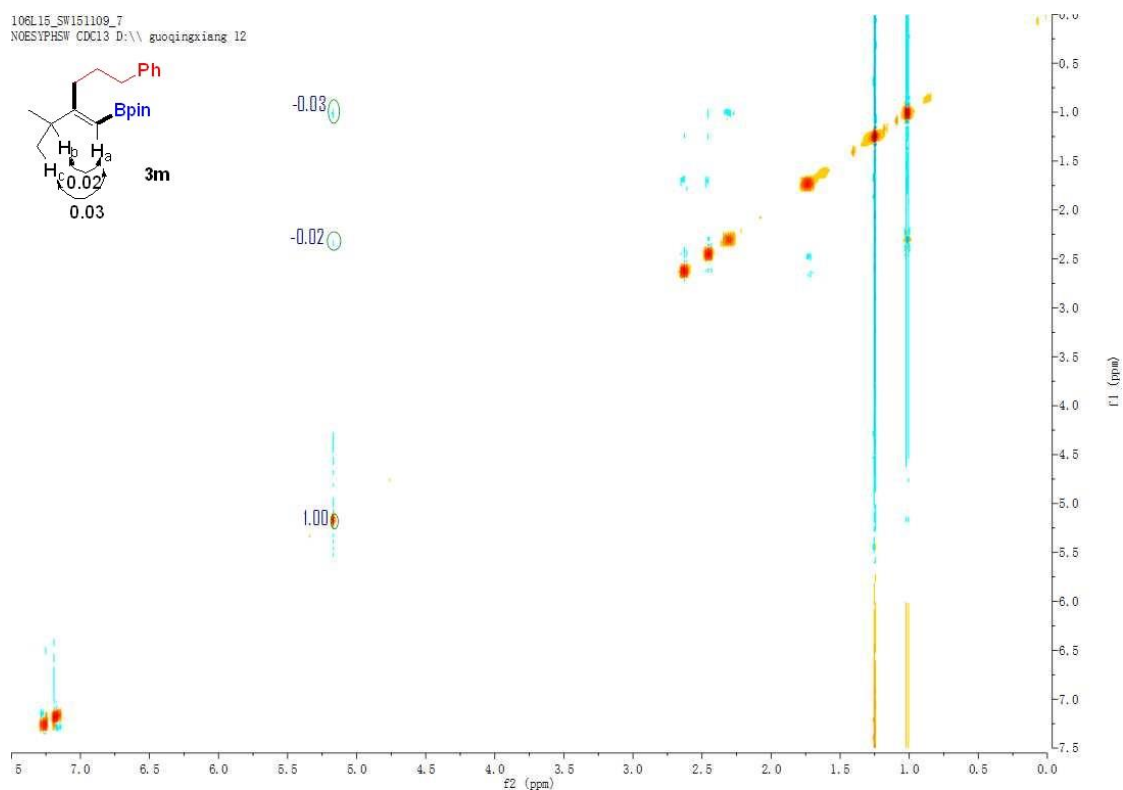
To a 25-mL round-bottom flask were added **3p** or **4p** (0.1 mmol) and NaBO<sub>3</sub>·4H<sub>2</sub>O (31 mg, 0.2 mmol), THF (1 mL), and H<sub>2</sub>O (1 mL). The solvent was stirred at room temperature for 4 h. H<sub>2</sub>O (10 mL) was added into the reaction mixture, and extracted with Et<sub>2</sub>O (10 mL x 3). The combined organic layers were washed with brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the target product.

### F. Procedure for Hydrogenation Reduction<sup>5</sup>

To a 10-mL Schlenk flask were added **3p** or **4p** (0.1 mmol), Pd/C (10 mol %, 0.01 mmol) and MeOH (1mL) under H<sub>2</sub> (1 atm). The solution was stirred for 16 h at 25 °C, then filtered and concentrated under reduced pressure. The residue was added Et<sub>3</sub>N (0.2 mmol), DMAP (0.01 mmol) and p-Toluenesulfonyl chloride (0.12 mmol), the reaction mixture was stir at r.t for 2 h. The mixtures was sequencely washed with 1 M HCl, NaHCO<sub>3</sub> saturated aqueous solution and water. The organic

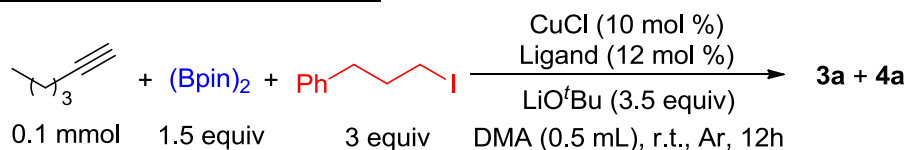
extract was dried ( $\text{Na}_2\text{SO}_4$ ), concentrated in vacuo, and the residue purified by column chromatography.

## V. H1-Noesy of 3m and 4m



## VI. Investigation of the Reaction Parameters

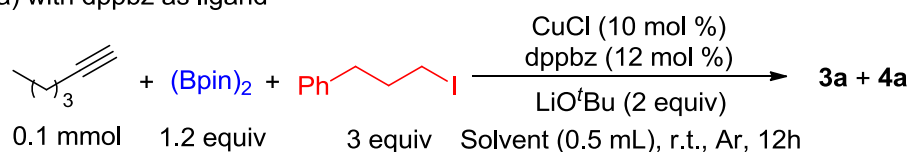
**Table S1. The effect of NHC ligand**



Entry	Ligand	yield of <b>3a+4a</b> (%)	r.r of <b>3a/4a</b>
1	IPr·HCl	82	2.2:1
2	IMes·HCl	52	9.0:1
3	ICy·BF <sub>4</sub>	41	7.4:1

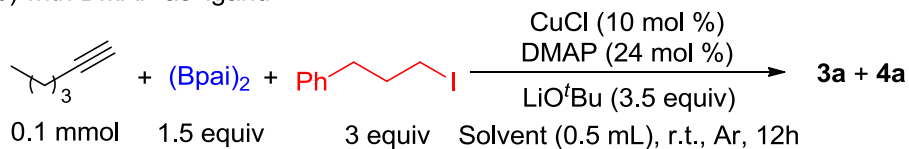
**Table S2. The effect of solvent**

a) with dppbz as ligand



Entry	Solvent	yield of <b>3a+4a</b> (%)	r.r of <b>3a/4a</b>
1	THF	0	--
2	1,4-dioxane	0	--
3	DMF	46	9.2:1
4	n-hexane	0	--

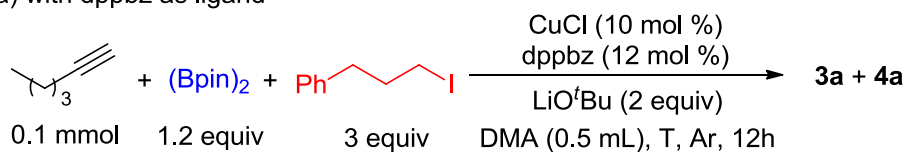
b) with DMAP as ligand



Entry	Solvent	yield of <b>3a+4a</b> (%)	r.r of <b>3a/4a</b>
1	THF	0	--
2	1,4-dioxane	23	1:15
3	DMF	73	1:4.3
4	n-hexane	14	1:14

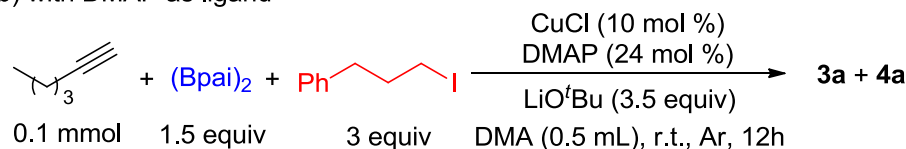
**Table S3. The effect of Temperature**

a) with dppbz as ligand



Entry	T (°C)	yield of <b>3a+4a</b> (%)	r.r of <b>3a/4a</b>
1	40	83	16:1
2	60	64	13:1

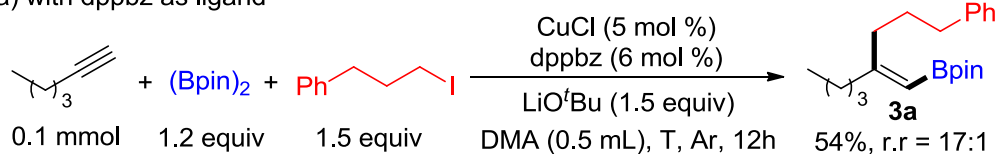
b) with DMAP as ligand



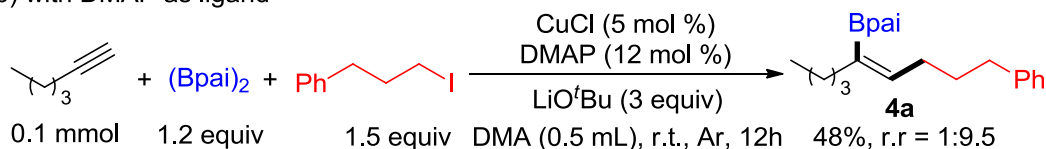
Entry	T (°C)	yield of <b>3a+4a</b> (%)	r.r of <b>3a/4a</b>
1	40	78	1:9.6
2	60	44	1:9.2

**Table S4. The effect with reduced copper, ligand, base and electrophile.**

a) with dppbz as ligand

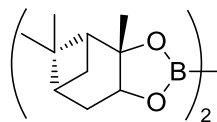


b) with DMAP as ligand



## VII. NMR Spectra

### Bis((+)-pinanediolato)diboron, **10**

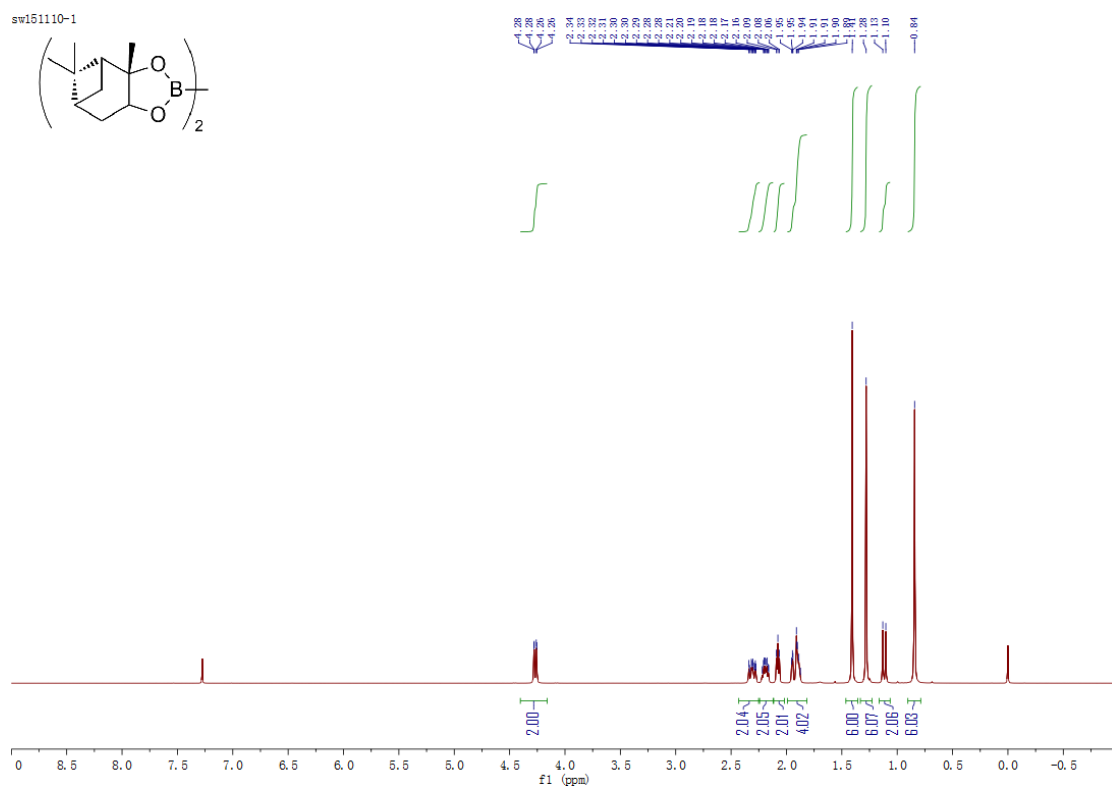
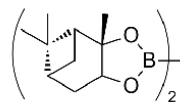


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.27 (dd,  $J = 8.7, 1.4$  Hz, 2H), 2.43 – 2.24 (m, 2H), 2.19 (ddd,  $J = 8.1, 6.2, 3.2$  Hz, 2H), 2.08 (t,  $J = 5.5$  Hz, 2H), 1.99 – 1.82 (m, 4H), 1.41 (s, 6H), 1.28 (s, 6H), 1.12 (d,  $J = 10.9$  Hz, 2H), 0.84 (s, 6H).

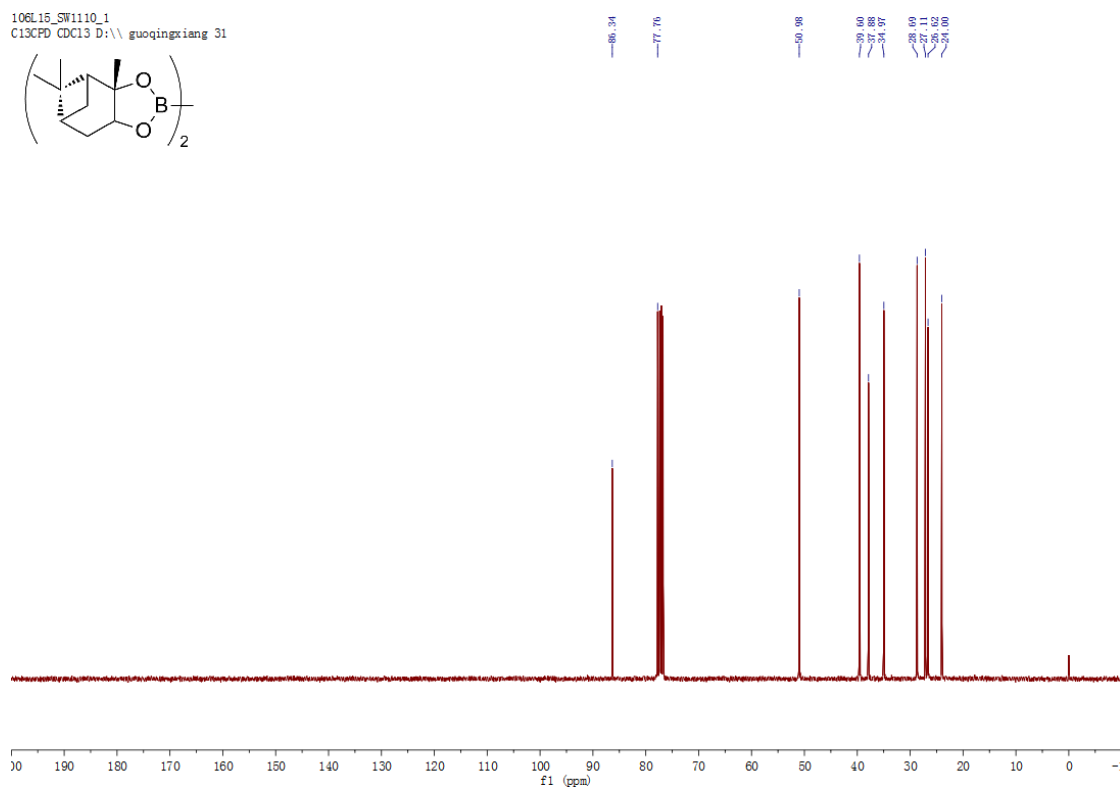
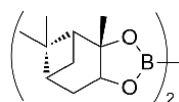
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  86.34 (s), 77.76 (s), 50.98 (s), 39.60 (s), 37.88 (s), 34.97 (s), 28.69 (s), 27.11 (s), 26.62 (s), 24.00 (s).

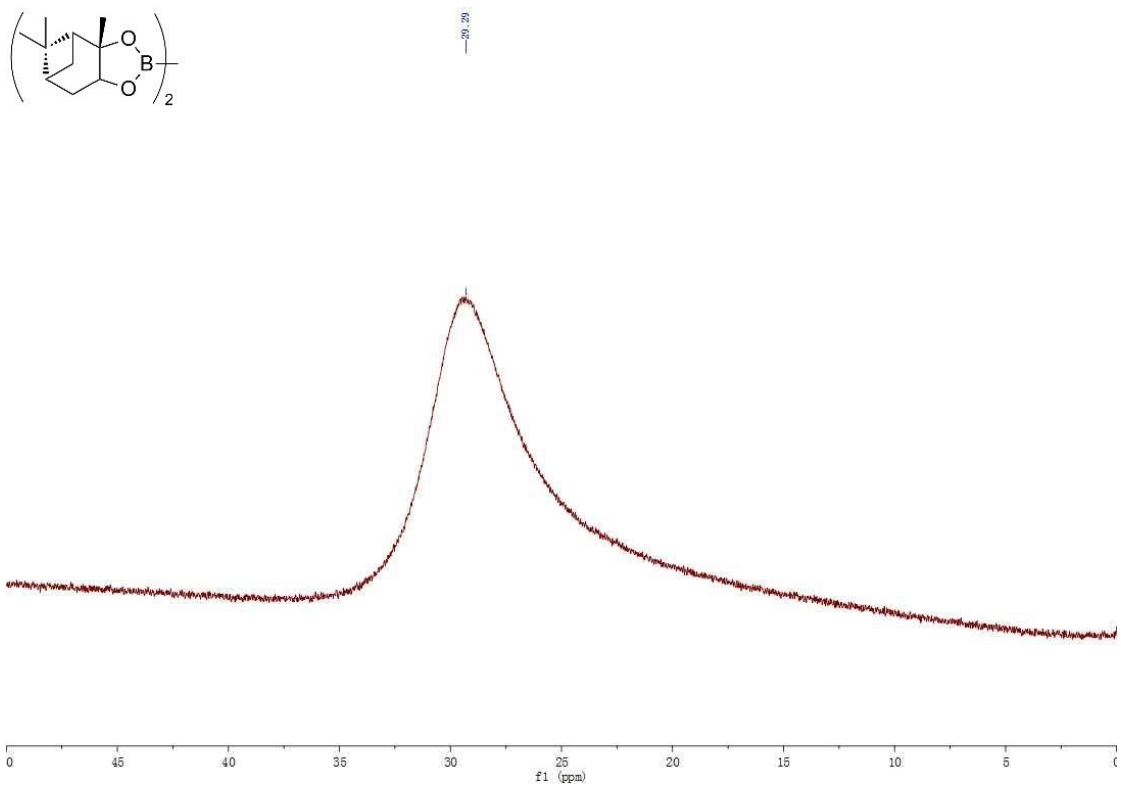
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.29.

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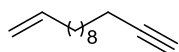


106L15\_SW1110\_1  
C13CPD CDCl3 D:\guoqingxiang 31





**tridec-1-en-12-yne, 1c**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.81 (m, 1H), 5.05 – 4.85 (m, 2H), 2.20 – 2.14 (m, 2H), 2.10 – 1.98 (m, 2H), 1.94 (m, 1H), 1.53 (m, 2H), 1.39 (m, 4H), 1.27 (s, 8H).

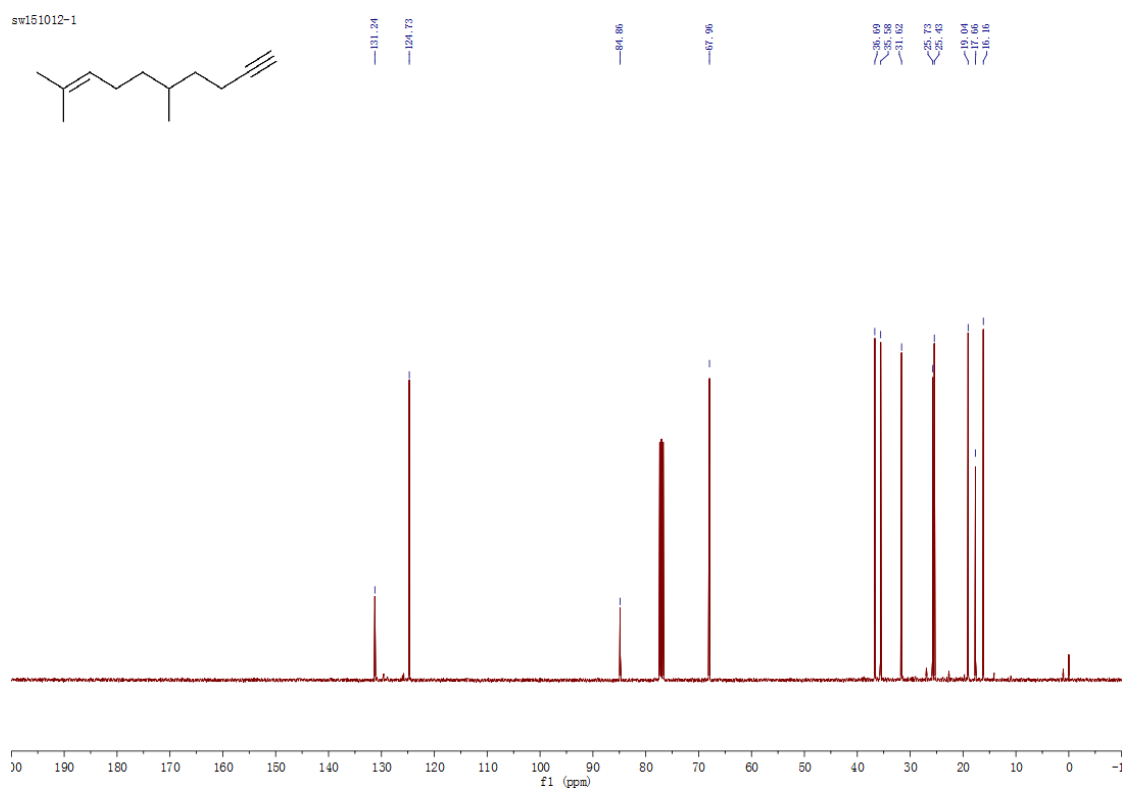
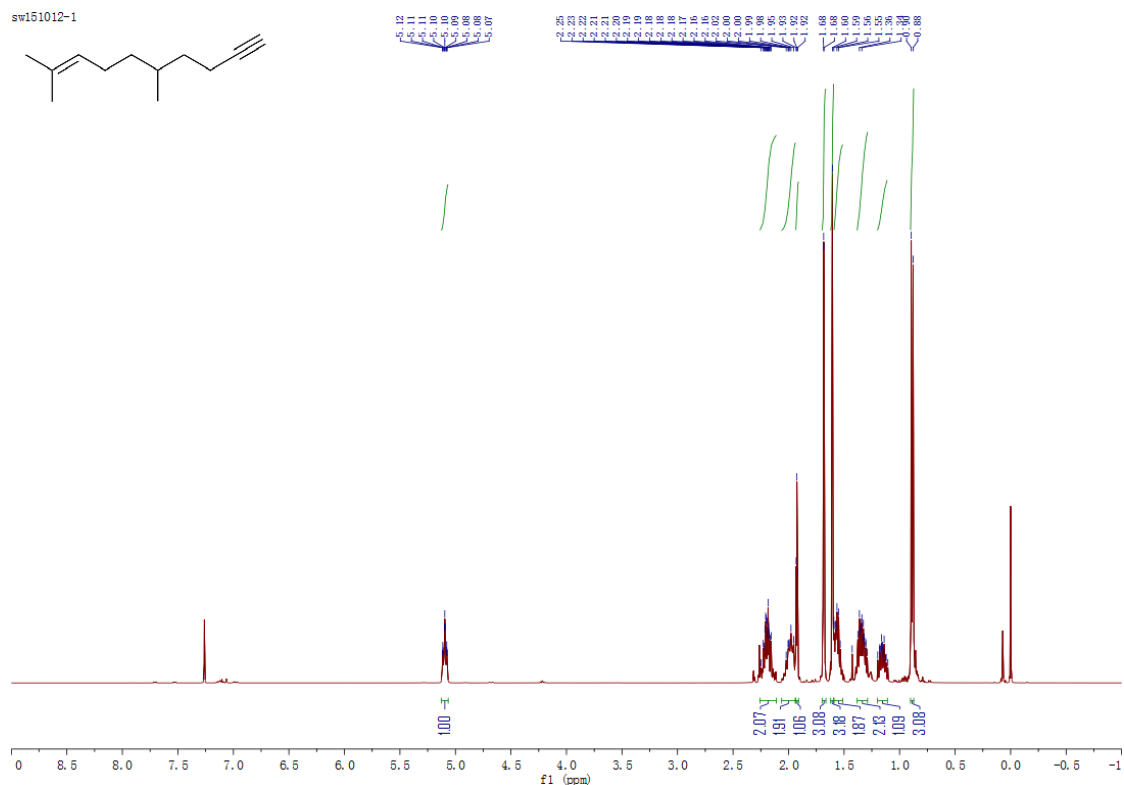
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.24 (s), 114.12 (s), 84.80 (s), 68.04 (s), 33.82 (s), 29.45 (s), 29.44 (s), 29.12 (s), 29.10 (s), 28.94 (s), 28.76 (s), 28.50 (s), 18.41 (s).



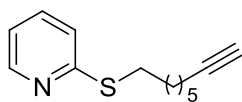


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.25 – 4.67 (m, 1H), 2.26 – 2.10 (m, 2H), 2.06 – 1.94 (m, 2H), 1.92 (m, 1H), 1.68 (m, 3H), 1.60 (s, 3H), 1.59 – 1.51 (m, 2H), 1.39 – 1.28 (m, 2H), 1.15 (m, 1H), 0.89 (d,  $J$  = 6.6 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  131.24 (s), 124.73 (s), 84.86 (s), 67.96 (s), 36.69 (s), 35.58 (s), 31.62 (s), 25.73 (s), 25.43 (s), 19.04 (s), 17.66 (s), 16.16 (s).

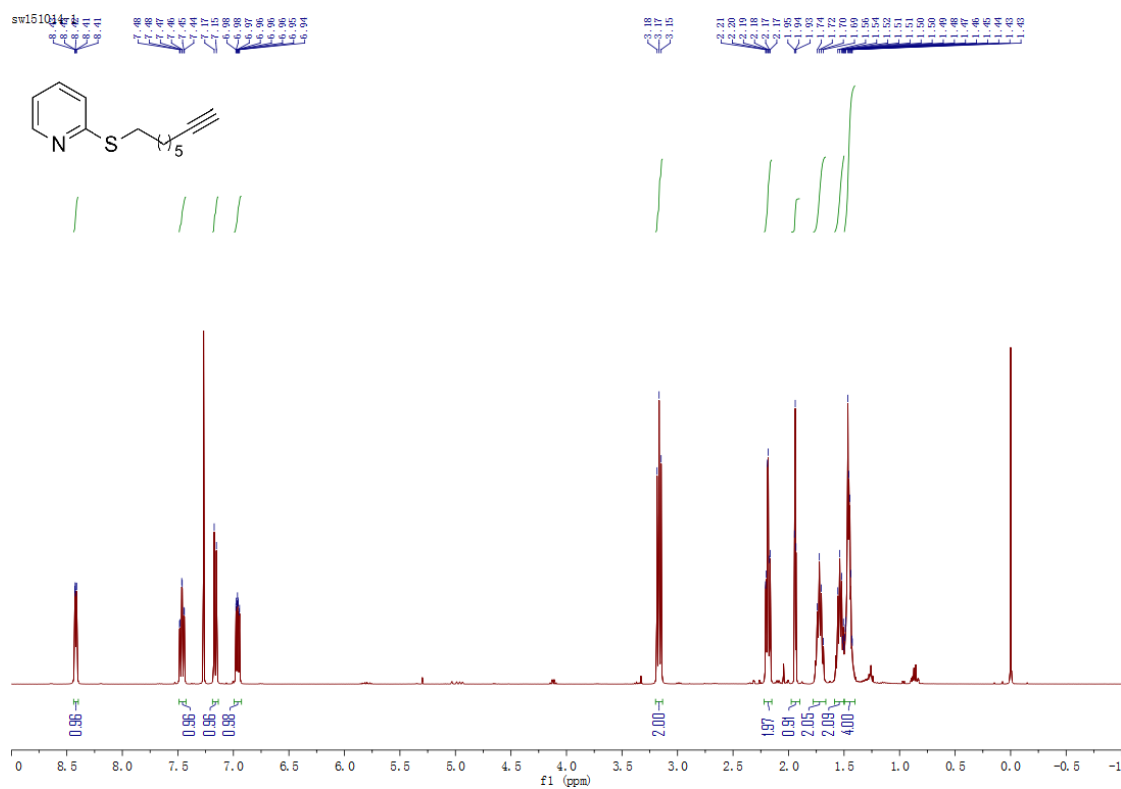


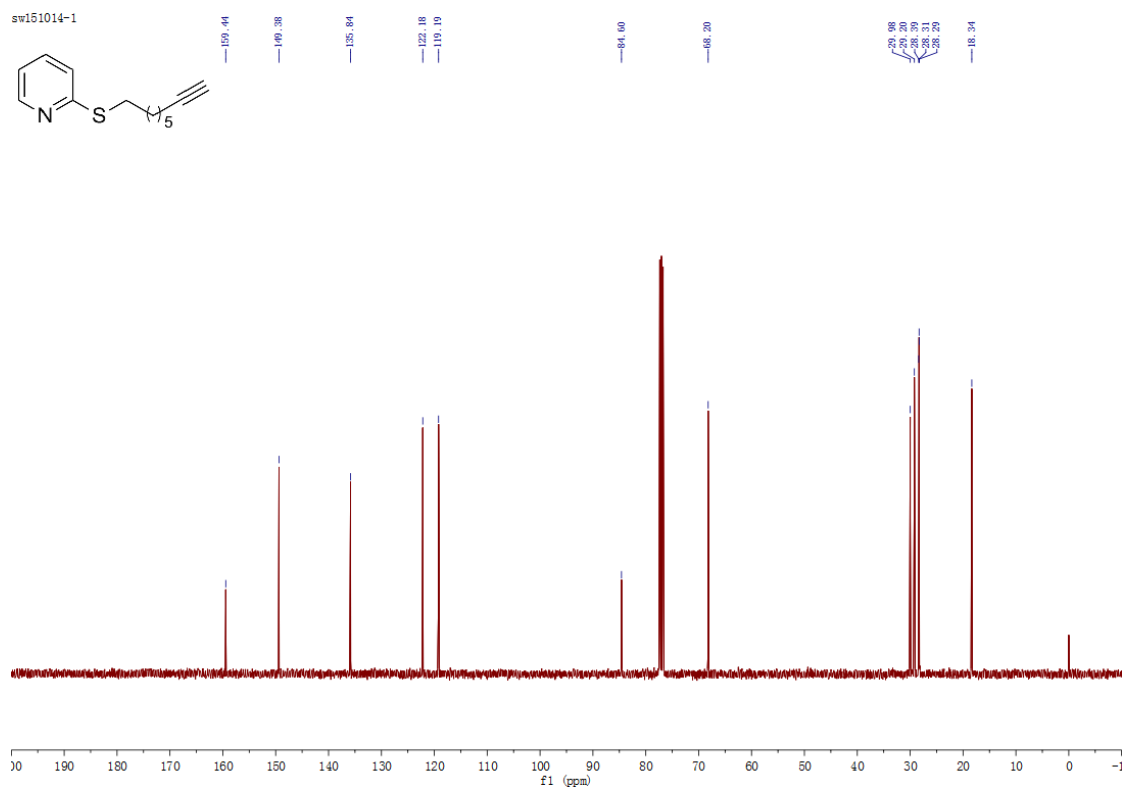
**2-(oct-7-yn-1-ylthio)pyridine, 1f**



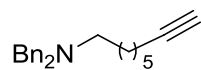
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.44 – 8.35 (m, 1H), 7.46 (m, 1H), 7.16 (d,  $J$  = 8.1 Hz, 1H), 6.96 (m, 1H), 3.19 – 3.14 (m, 2H), 2.19 (td,  $J$  = 6.9, 2.6 Hz, 2H), 1.94 (t,  $J$  = 2.6 Hz, 1H), 1.75 – 1.67 (m, 2H), 1.59 – 1.50 (m, 2H), 1.49 – 1.39 (m, 4H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.44 (s), 149.38 (s), 135.84 (s), 122.18 (s), 119.19 (s), 84.60 (s), 68.20 (s), 29.98 (s), 29.20 (s), 28.39 (s), 28.31 (s), 28.29 (s), 18.34 (s).



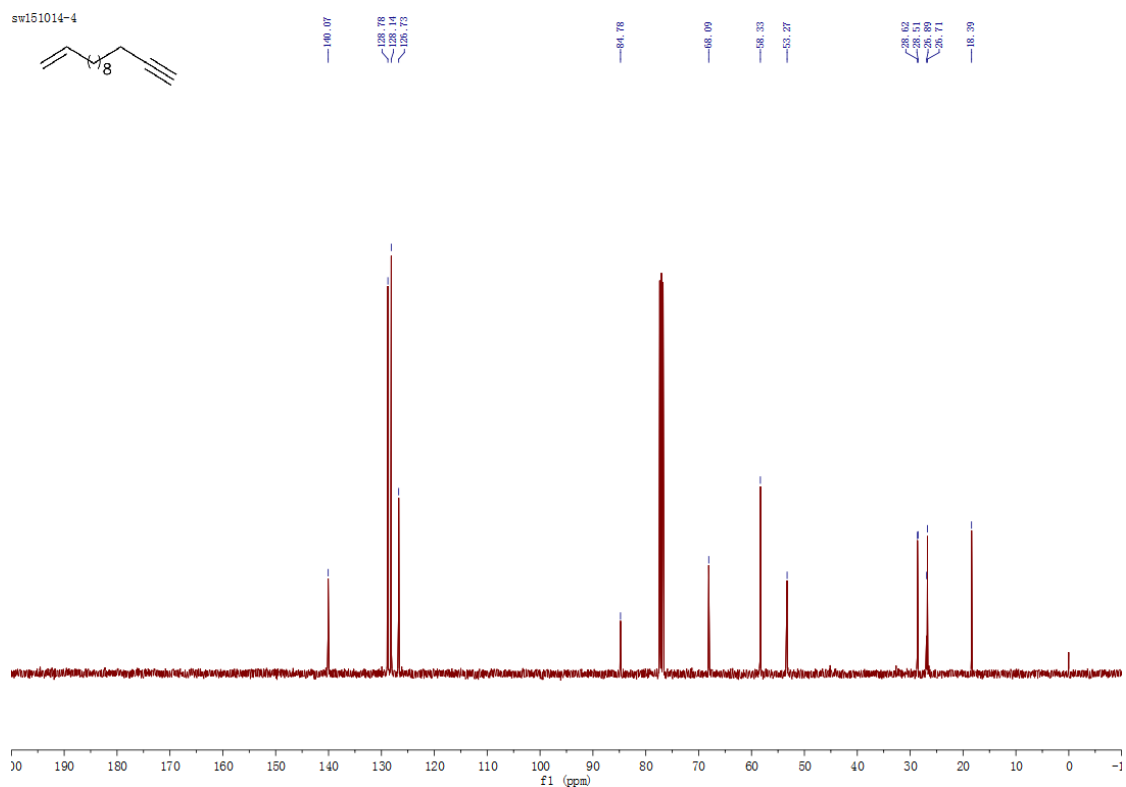
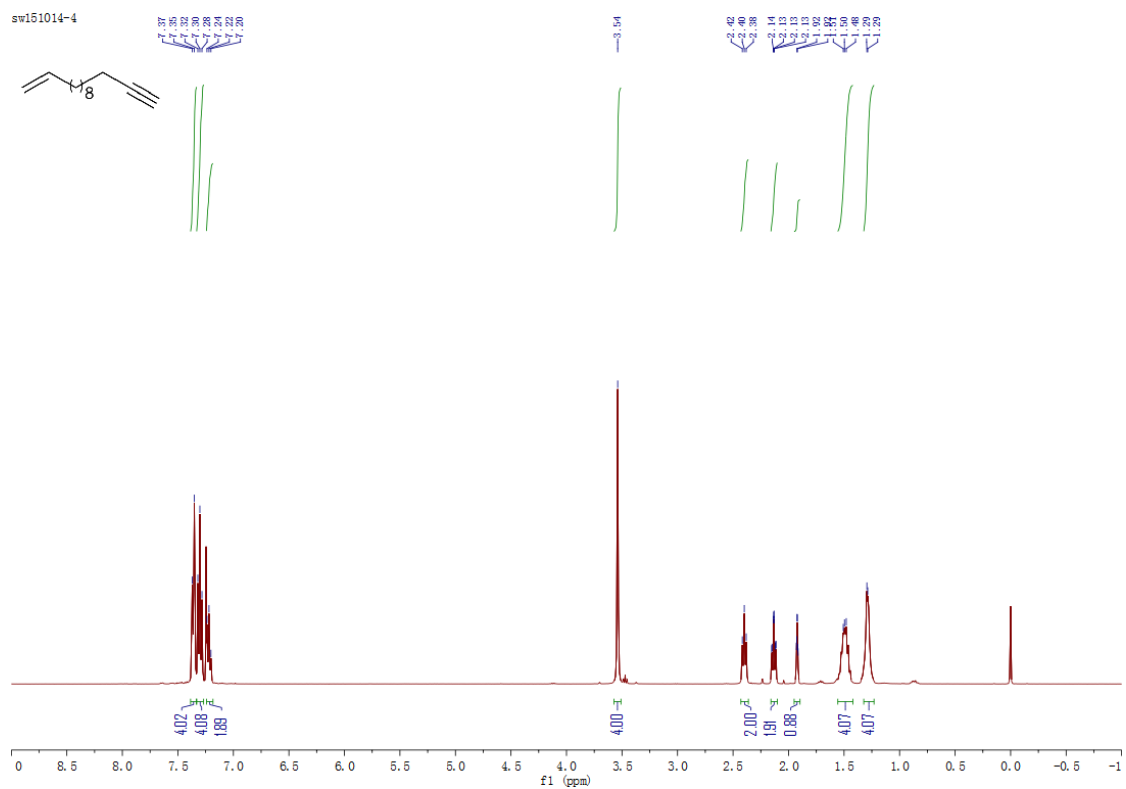


**N,N-dibenzyl-oct-7-yn-1-amine, 1k**

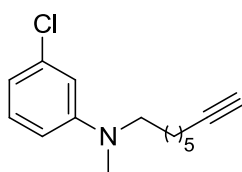


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (m, 4H), 7.30 (m, 4H), 7.22 (m, 2H), 3.54 (s, 4H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.10 (m, 2H), 1.92 (m, 1H), 1.56 – 1.44 (m, 4H), 1.29 (m, 4H).

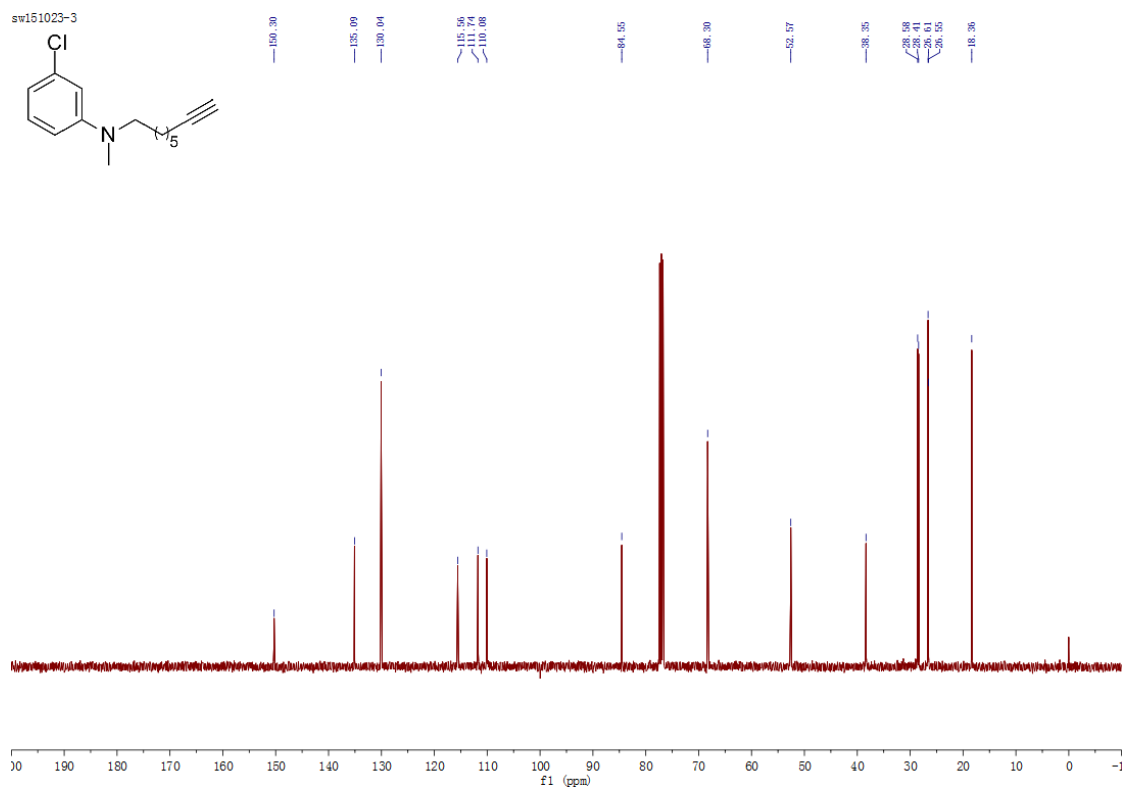
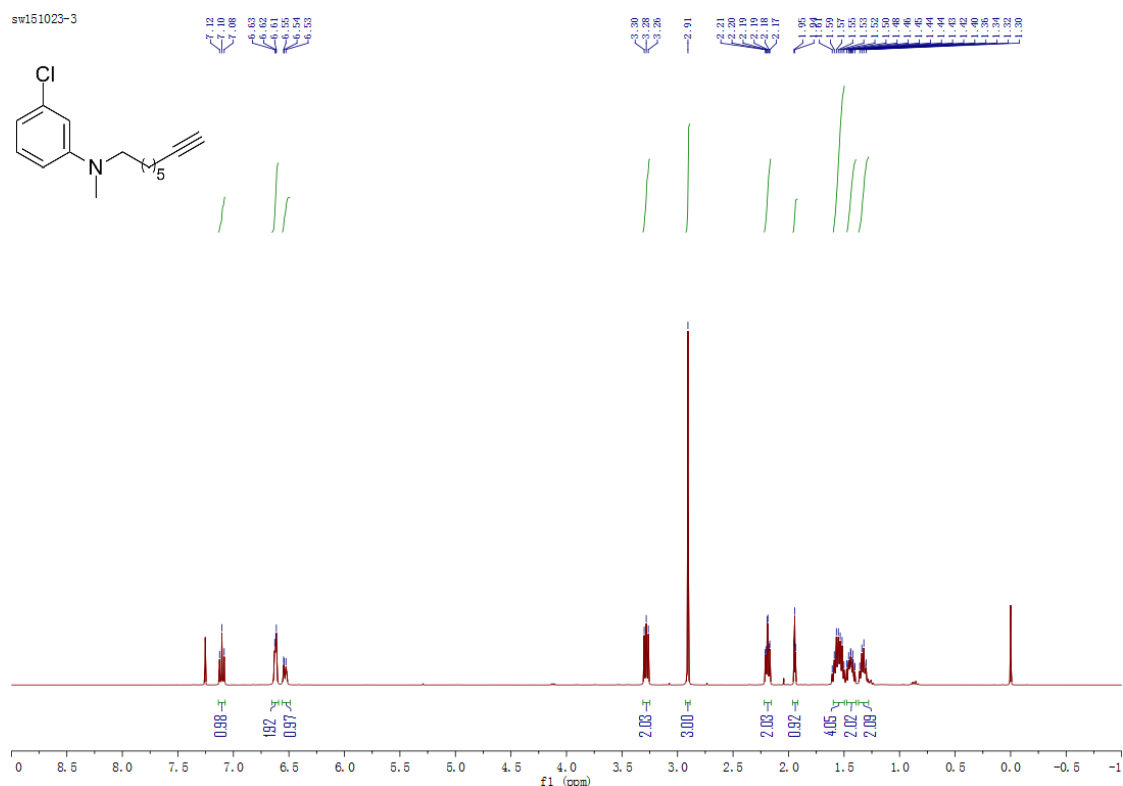
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.07 (s), 128.78 (s), 128.14 (s), 126.73 (s), 84.78 (s), 68.09 (s), 58.33 (s), 53.27 (s), 28.62 (s), 28.51 (s), 26.89 (s), 26.71 (s), 18.39 (s).



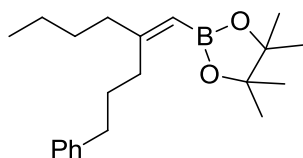
**3-chloro-N-methyl-N-(oct-7-yn-1-yl)aniline, 11**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (m, 1H), 6.65 – 6.60 (m, 2H), 6.56 – 6.51 (m, 1H), 3.31 – 3.25 (m, 2H), 2.91 (s, 3H), 2.19 (m, 2H), 1.94 (m, 1H), 1.63 – 1.49 (m, 4H), 1.44 (m, 2H), 1.33 (m, 2H).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.30 (s), 135.09 (s), 130.04 (s), 115.56 (s), 111.74 (s), 110.08 (s), 84.55 (s), 68.30 (s), 52.57 (s), 38.35 (s), 28.58 (s), 28.41 (s), 26.61 (s), 26.55 (s), 18.36 (s).



**(Z)-4,4,5,5-tetramethyl-2-(2-(3-phenylpropyl)hex-1-en-1-yl)-1,3,2-dioxaborolane, 3a**

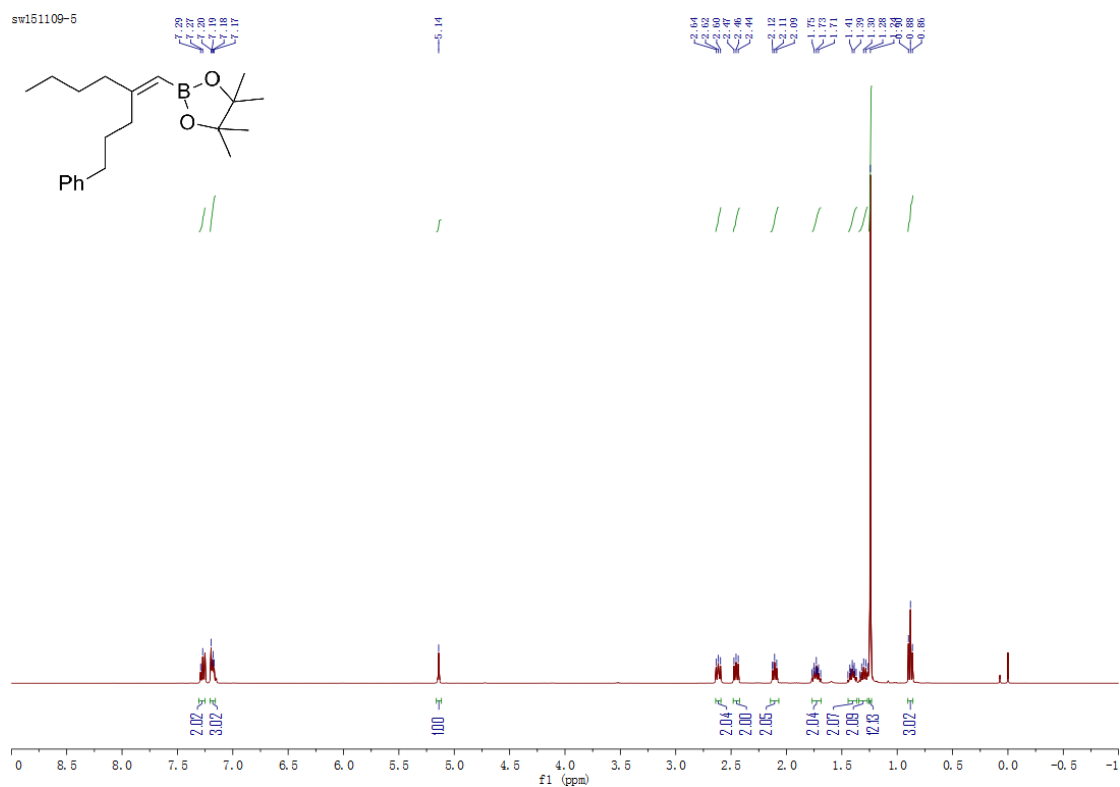


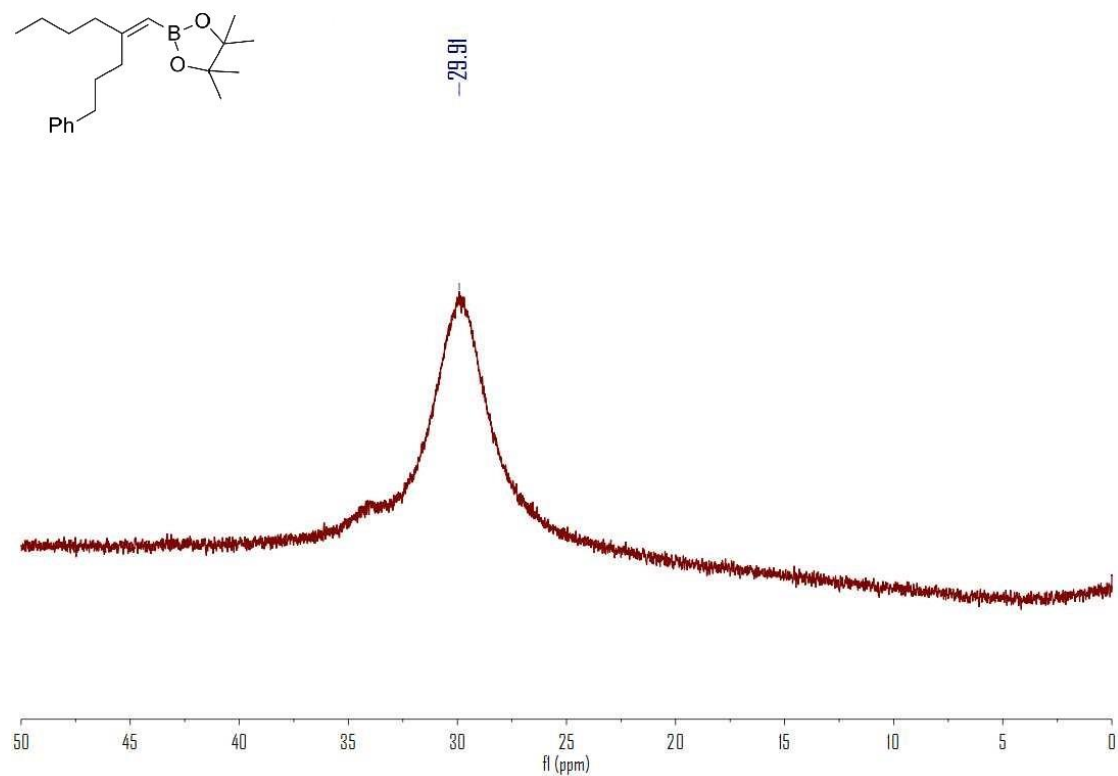
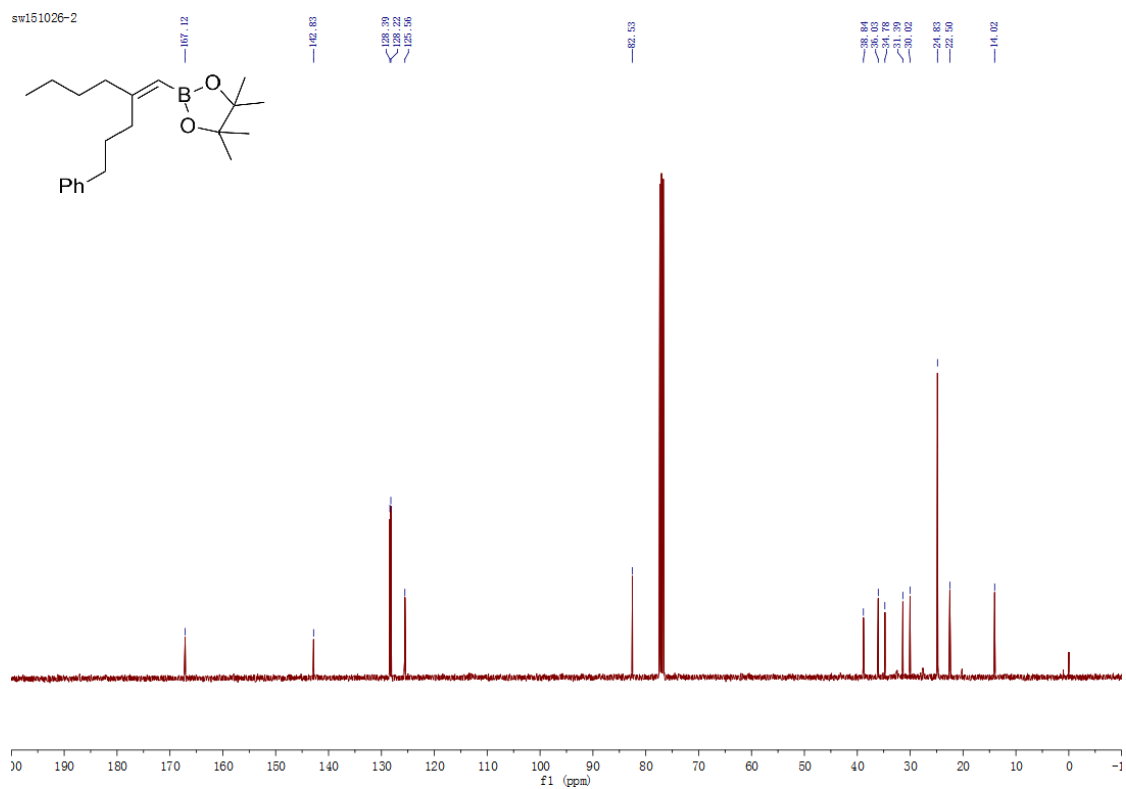
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 2H), 7.18 (m, 3H), 5.14 (s, 1H), 2.66 – 2.57 (m, 2H), 2.49 – 2.41 (m, 2H), 2.11 (m, 2H), 1.73 (tt,  $J = 9.7, 6.9$  Hz, 2H), 1.41 (tt,  $J = 7.3, 5.8$  Hz, 2H), 1.35 – 1.26 (m, 2H), 1.24 (s, 12H), 0.88 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.12 (s), 142.83 (s), 128.39 (s), 128.22 (s), 125.56 (s), 82.53 (s), 38.84 (s), 36.03 (s), 34.78 (s), 31.39 (s), 30.02 (s), 24.83 (s), 22.50 (s), 14.02 (s).

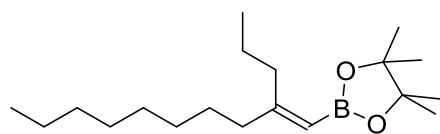
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.91.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{21}\text{H}_{33}\text{BO}_2[\text{H}]^+$ : 329.2652, Found: 329.2648.





**(E)-4,4,5,5-tetramethyl-2-(2-propyldec-1-en-1-yl)-1,3,2-dioxaborolane, 3b**

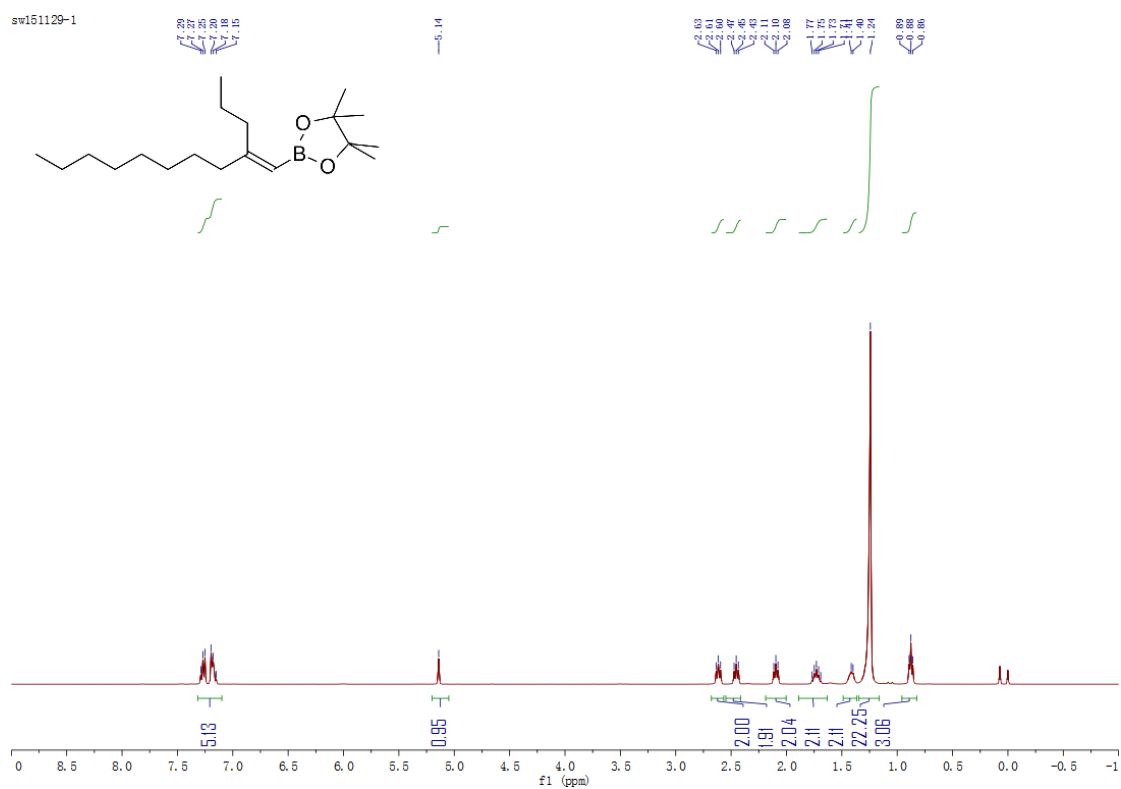


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.04 (m, 5H), 5.14 (s, 1H), 2.75 – 2.55 (m, 2H), 2.55 – 2.37 (m, 2H), 2.10 (t,  $J = 7.6$  Hz, 2H), 1.83 – 1.59 (m, 2H), 1.41 (m, 2H), 1.24 (m, 22H), 0.88 (t,  $J = 6.6$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.16 (s), 142.78 (s), 128.36 (s), 128.18 (s), 125.52 (s), 82.49 (s), 39.13 (s), 35.99 (s), 34.76 (s), 31.86 (s), 31.35 (s), 29.49 (s), 29.42 (s), 29.21 (s), 27.81 (s), 24.79 (s), 22.64 (s), 14.09 (s).

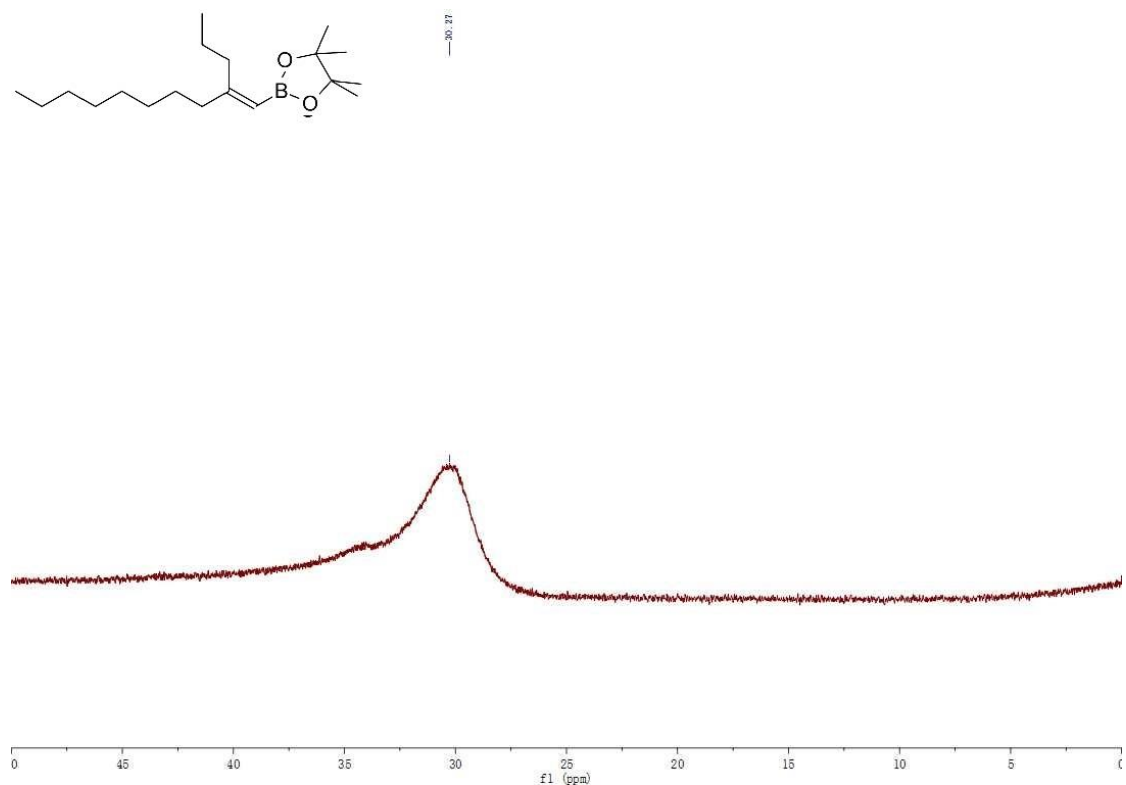
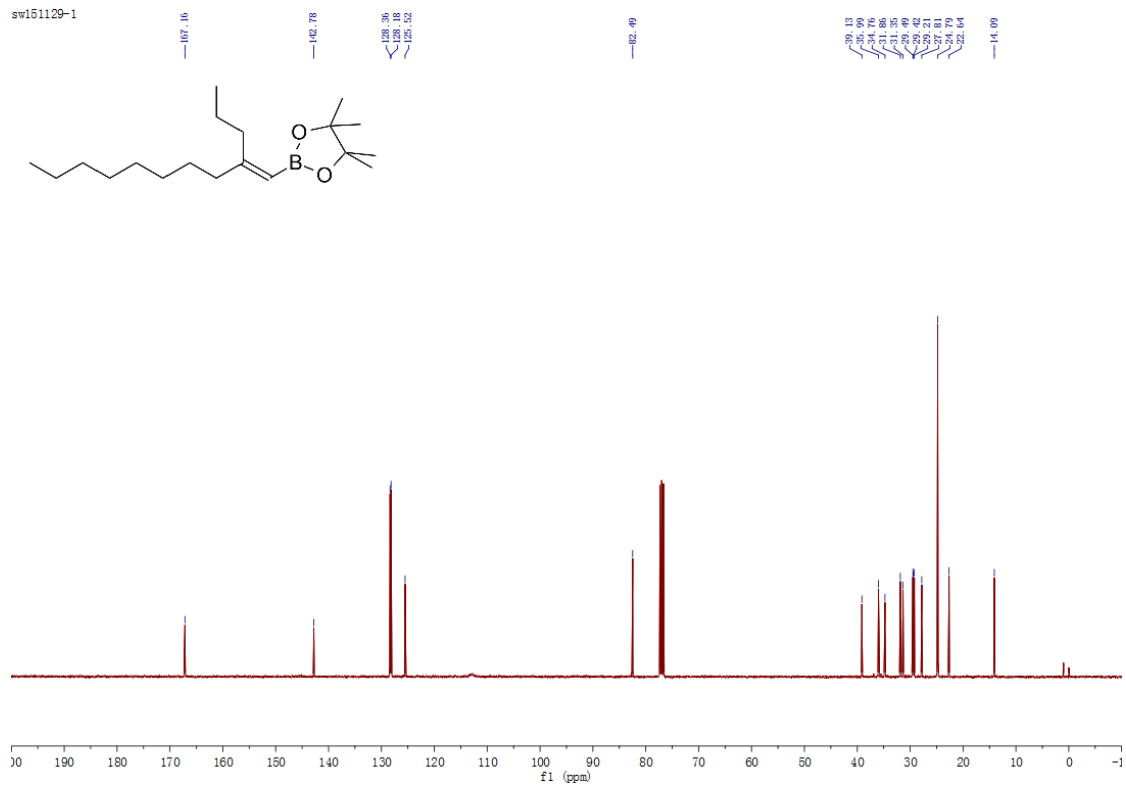
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.27.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{19}\text{H}_{37}\text{BO}_2$   $[\text{H}]^+$ : 309.2965, Found: 309.2961.

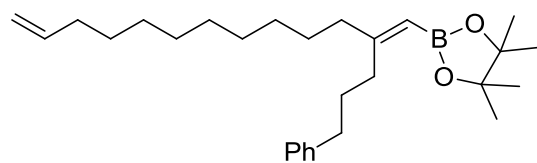




sw151129-1



**(Z)-4,4,5,5-tetramethyl-2-(2-(3-phenylpropyl)trideca-1,12-dien-1-yl)-1,3,2-dioxaborolane, 3c**

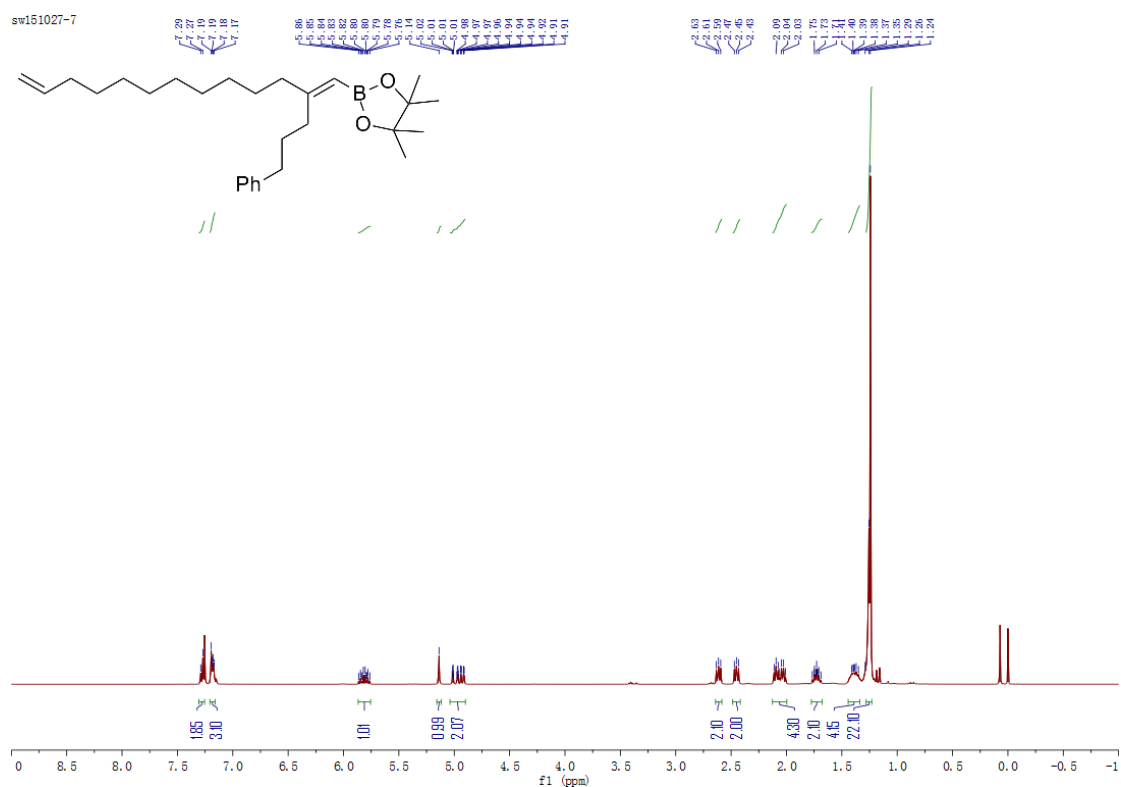


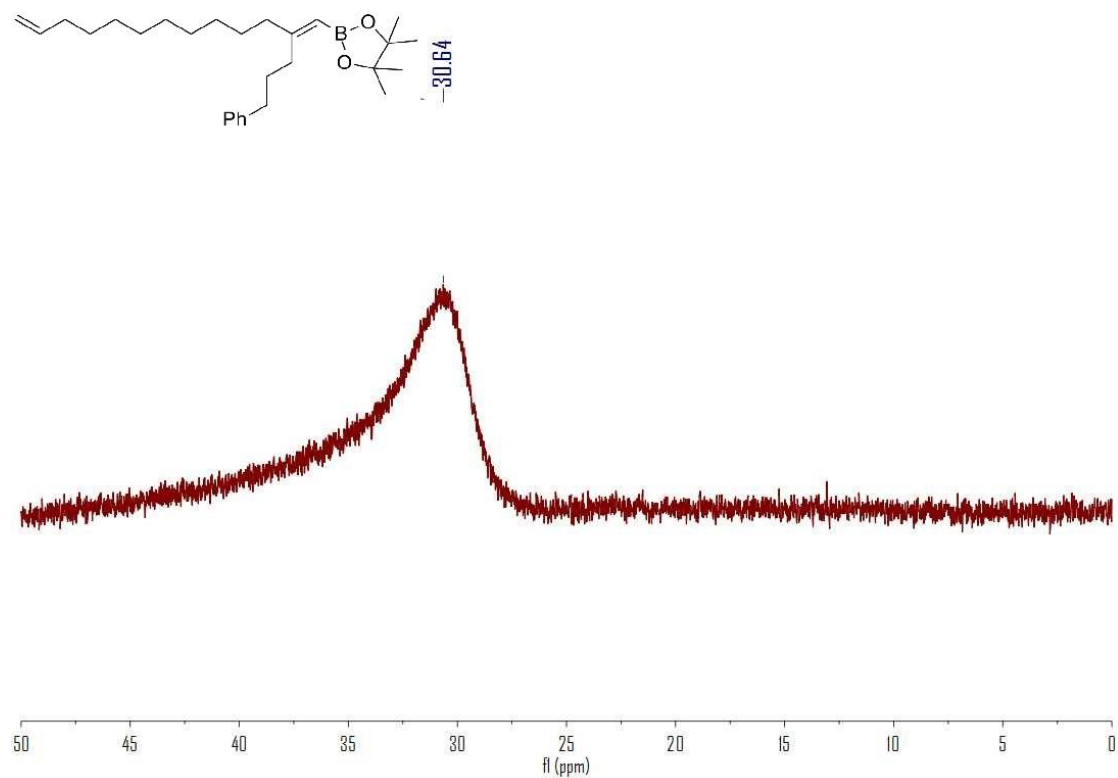
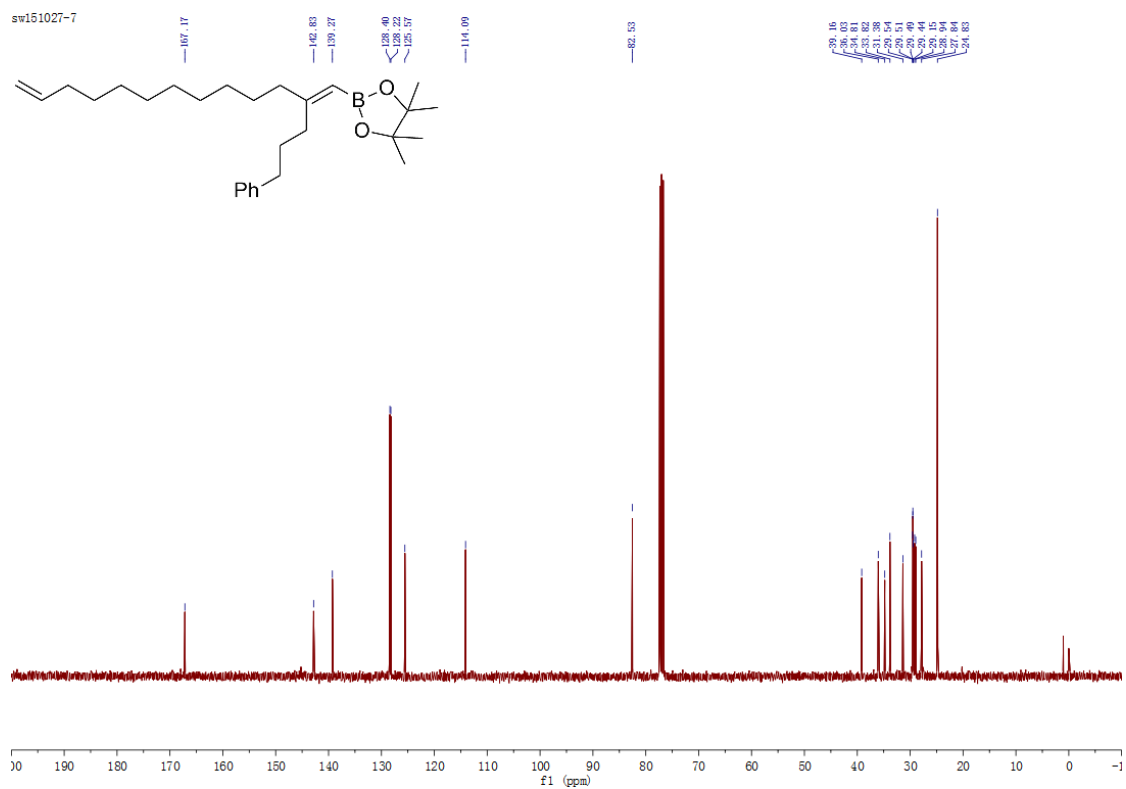
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.81 (ddt,  $J$  = 16.9, 10.2, 6.7 Hz, 1H), 5.14 (s, 1H), 5.04 – 4.90 (m, 2H), 2.64 – 2.58 (t,  $J$  = 8.0 Hz, 2H), 2.48 – 2.42 (t,  $J$  = 8.0 Hz, 2H), 2.14 – 1.99 (m, 4H), 1.73 (tt,  $J$  = 9.7, 6.9 Hz, 2H), 1.47 – 1.32 (m, 4H), 1.31 – 1.20 (m, 22H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.17 (s), 142.83 (s), 139.27 (s), 128.40 (s), 128.22 (s), 125.57 (s), 114.09 (s), 82.53 (s), 39.16 (s), 36.03 (s), 34.81 (s), 33.82 (s), 31.38 (s), 29.54 (s), 29.51 (s), 29.49 (s), 29.44 (s), 29.15 (s), 28.94 (s), 27.84 (s), 24.83 (s).

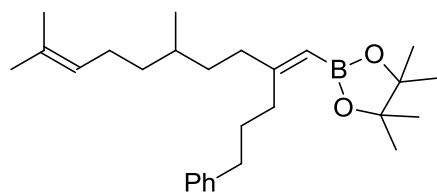
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.64.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{28}\text{H}_{45}\text{BO}_2[\text{H}]^+$ : 425.3391, Found: 425.3582.





**(E)-2-(5,9-dimethyl-2-(3-phenylpropyl)deca-1,8-dien-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3d**

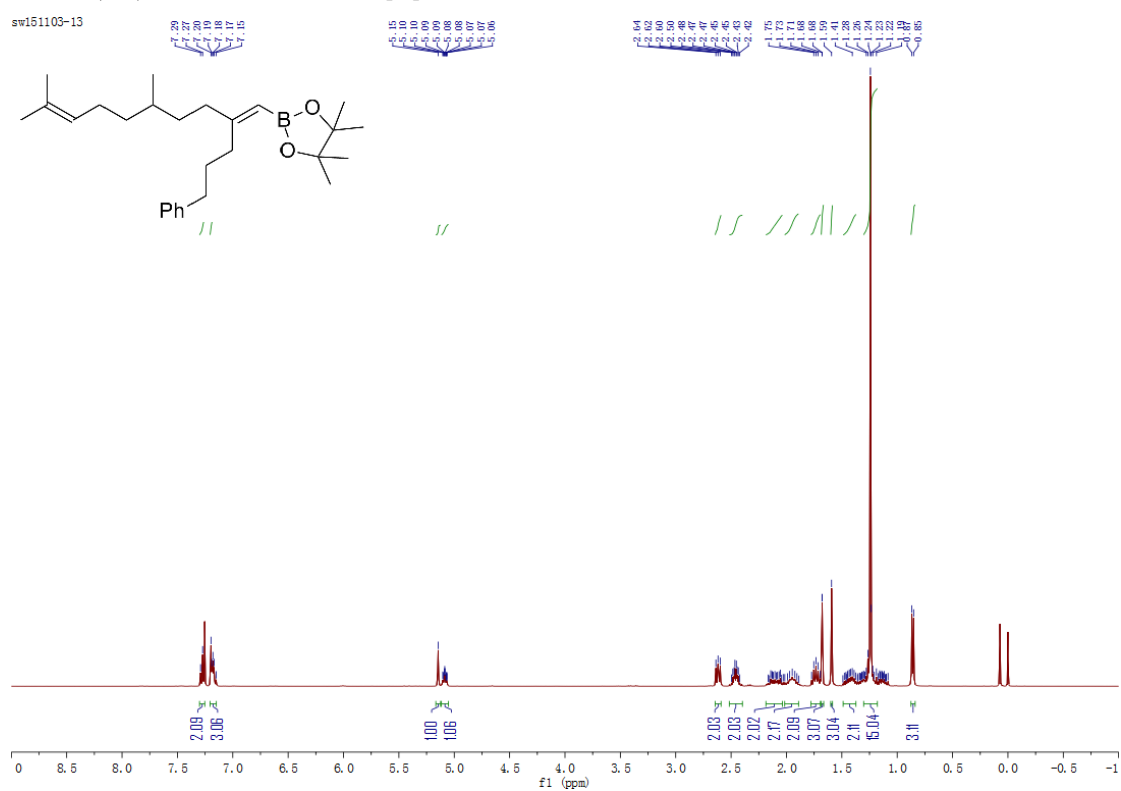


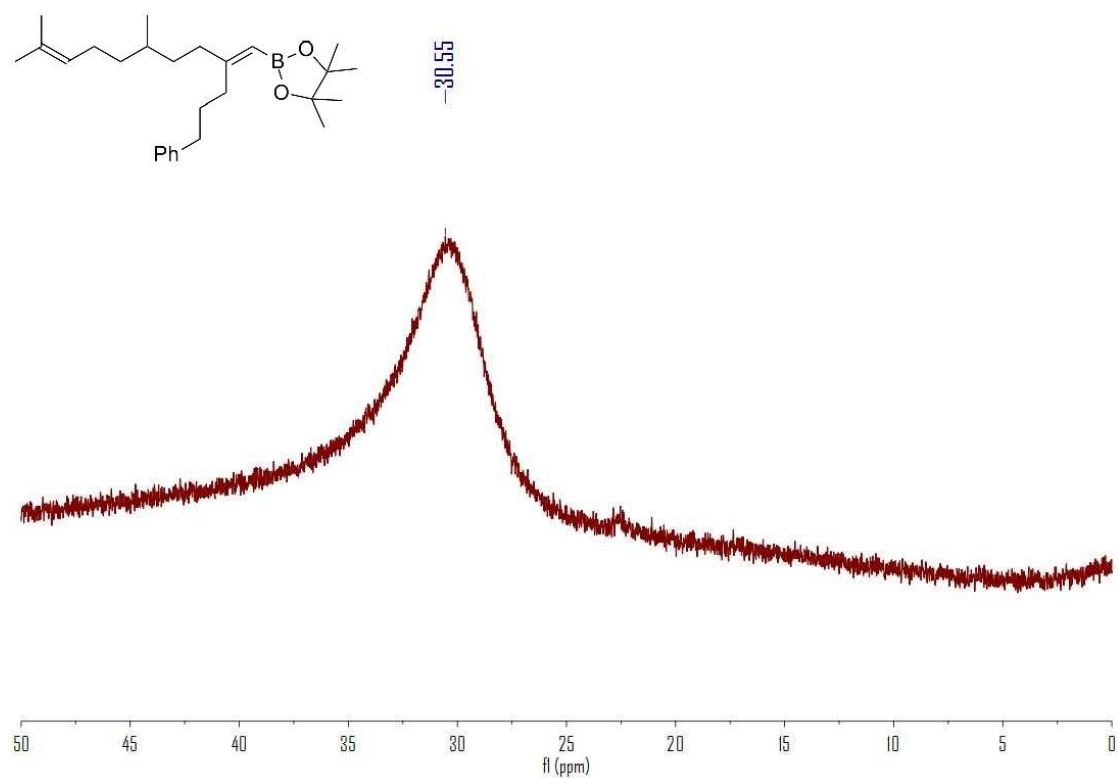
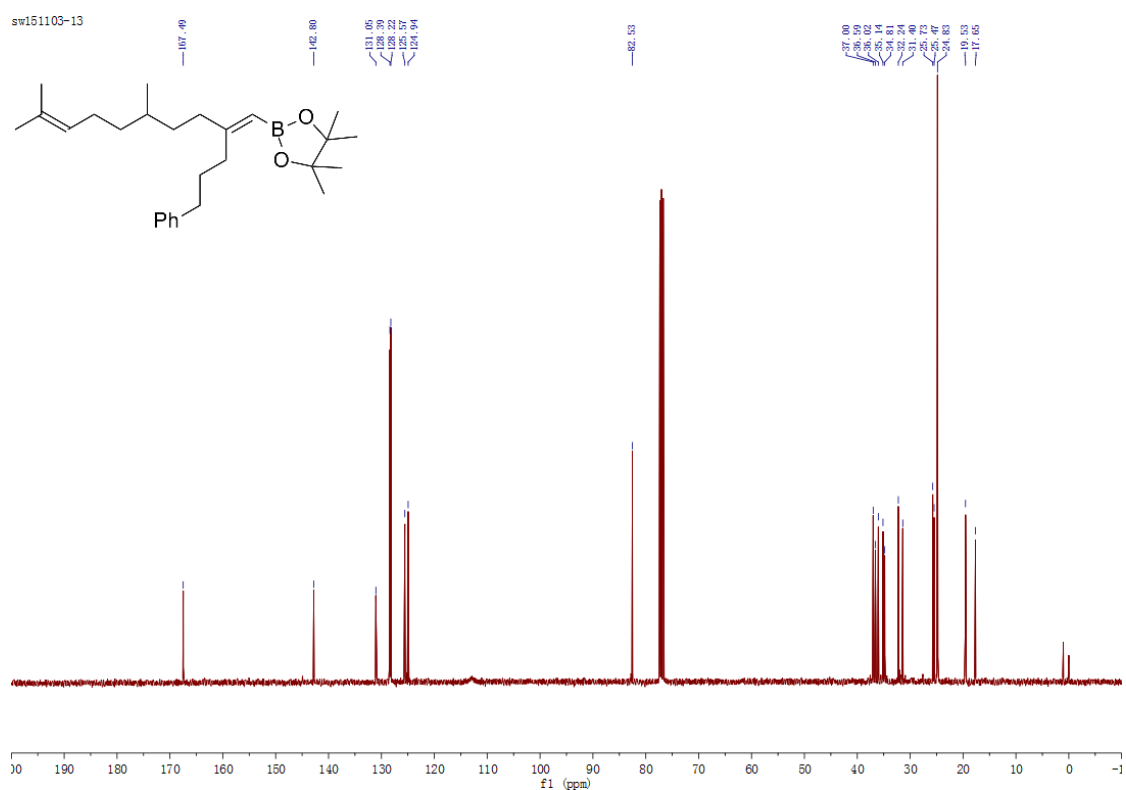
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 2H), 7.21 – 7.14 (m, 3H), 5.15 (s, 1H), 5.11 – 5.06 (m, 1H), 2.65 – 2.58 (m, 2H), 2.50 – 2.41 (m, 2H), 2.11 (m, 2H), 2.02 – 1.89 (m, 2H), 1.73 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H), 1.49 – 1.37 (m, 2H), 1.35 – 1.07 (m, 15H), 0.86 (d,  $J = 6.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.49 (s), 142.80 (s), 131.05 (s), 128.39 (s), 128.22 (s), 125.57 (s), 124.94 (s), 82.53 (s), 37.00 (s), 36.59 (s), 36.02 (s), 35.14 (s), 34.81 (s), 32.24 (s), 31.40 (s), 25.73 (s), 25.47 (s), 24.83 (s), 19.53 (s), 17.65 (s).

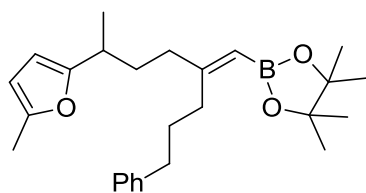
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.55.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{27}\text{H}_{43}\text{BO}_2[\text{H}]^+$ : 411.3434, Found: 411.3435.





**(E)-4,4,5,5-tetramethyl-2-(5-(5-methylfuran-2-yl)-2-(3-phenylpropyl)hex-1-en-1-yl)-1,3,2-dioxaborolane, **3e****

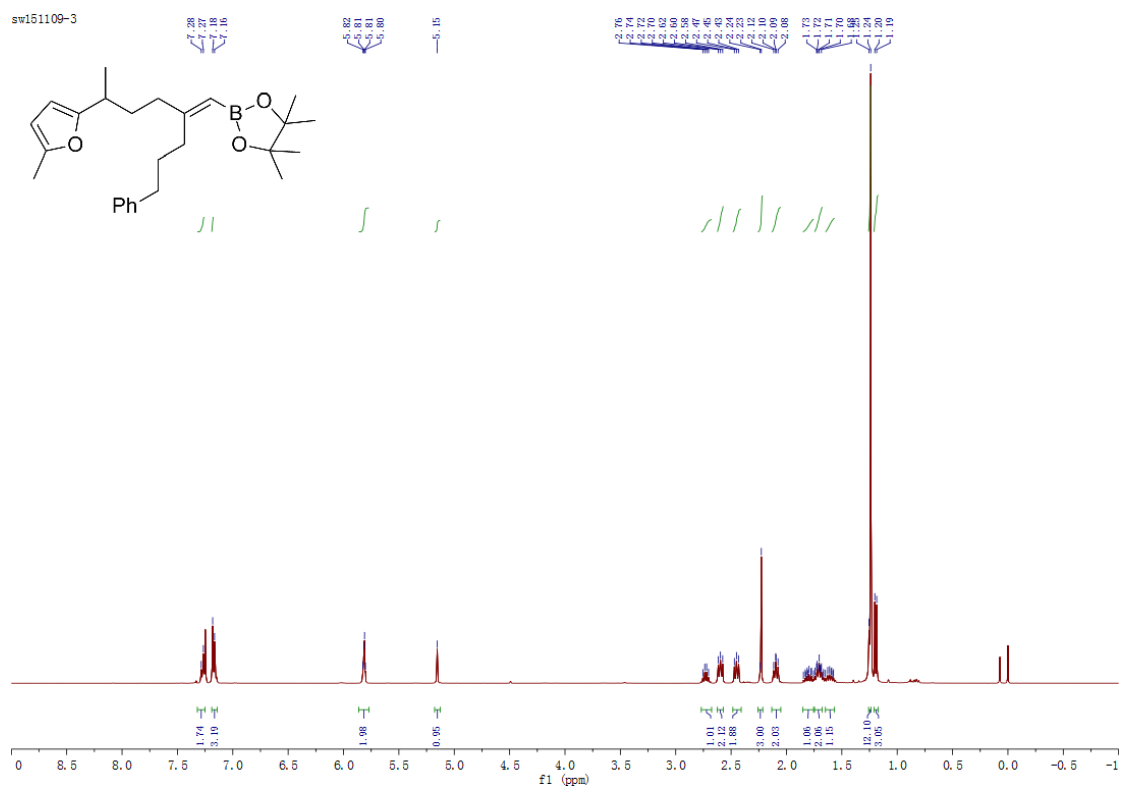


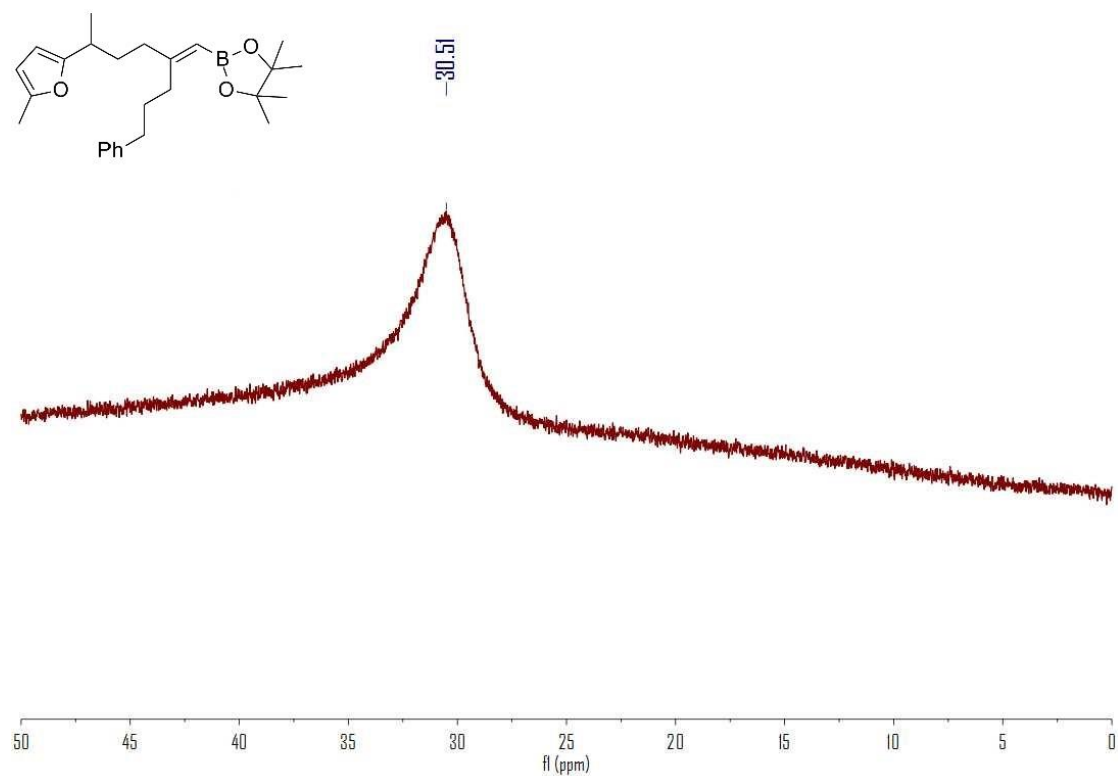
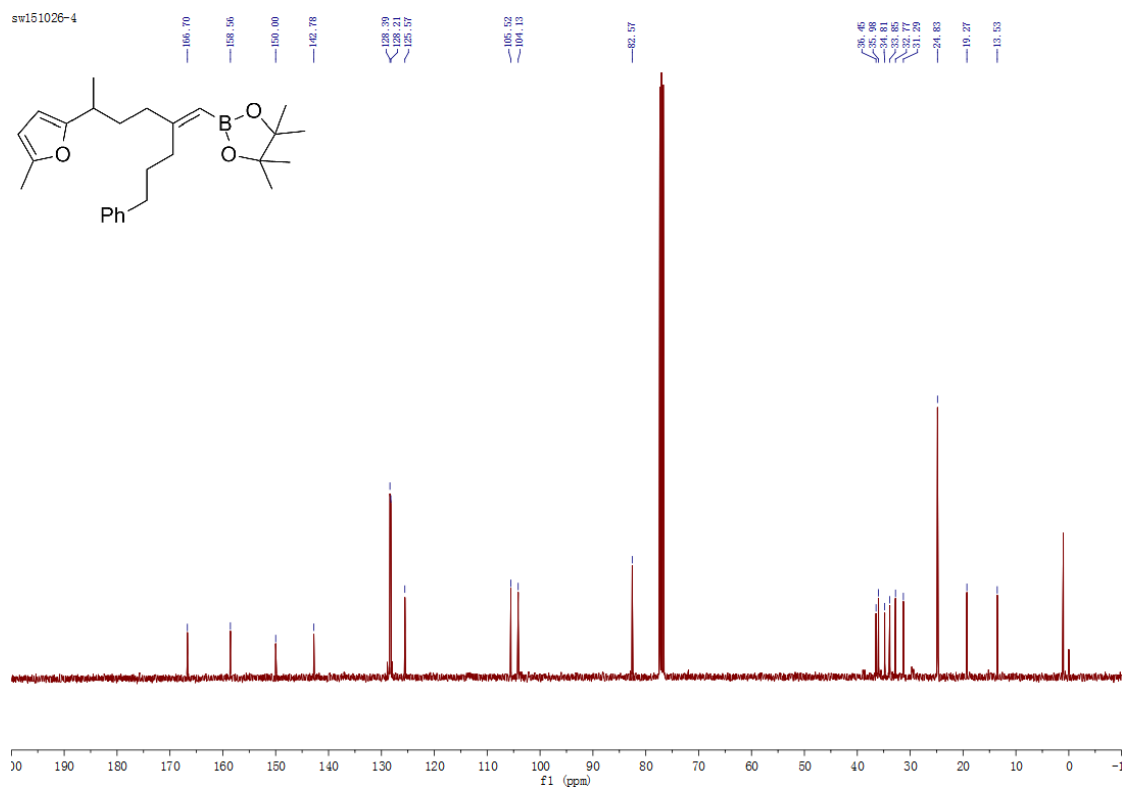
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 (m, 2H), 7.17 (m, 3H), 5.81 (m, 2H), 5.15 (s, 1H), 2.73 (m, 1H), 2.65 – 2.56 (t,  $J = 8.0$  Hz, 2H), 2.48 – 2.41 ( $J = 8.0$  Hz, 2H), 2.23 (m, 3H), 2.10 (m, 3H), 1.81 (m, 1H), 1.70 (m, 2H), 1.65 – 1.55 (m, 1H), 1.25 (m, 12H), 1.19 (d,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.70 (s), 158.56 (s), 150.00 (s), 142.78 (s), 128.39 (s), 128.21 (s), 125.57 (s), 105.52 (s), 104.13 (s), 82.57 (s), 36.45 (s), 35.98 (s), 34.81 (s), 33.85 (s), 32.77 (s), 31.29 (s), 24.83 (s), 19.27 (s), 13.53 (s).

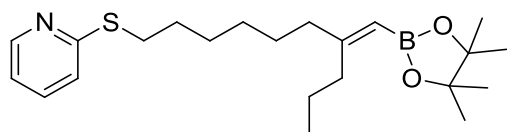
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.51.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{37}\text{BO}_3[\text{H}]^+$ : 409.2914, Found: 409.2908.





**(E)-2-((7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)decyl)thio)pyridine, 3f**

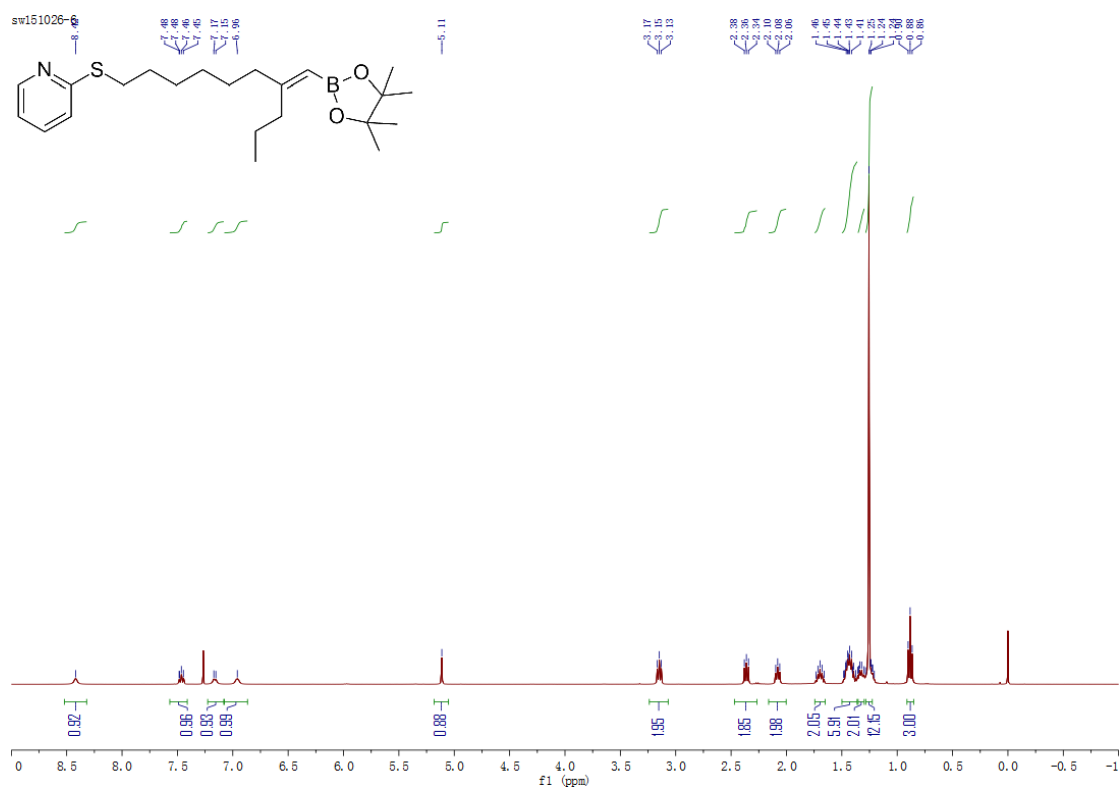


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 1H), 7.47 (m, 1H), 7.16 (d,  $J = 7.3$  Hz, 1H), 6.96 (m, 1H), 5.11 (s, 1H), 3.15 (t,  $J = 7.3$  Hz, 2H), 2.40 – 2.33 (t,  $J = 8.0$  Hz, 2H), 2.12 – 2.04 (t,  $J = 8.0$  Hz, 2H), 1.70 (dt,  $J = 14.9, 7.4$  Hz, 2H), 1.50 – 1.36 (m, 6H), 1.36 – 1.28 (m, 2H), 1.28 – 1.21 (m, 12H), 0.88 (t,  $J = 7.3$  Hz, 3H).

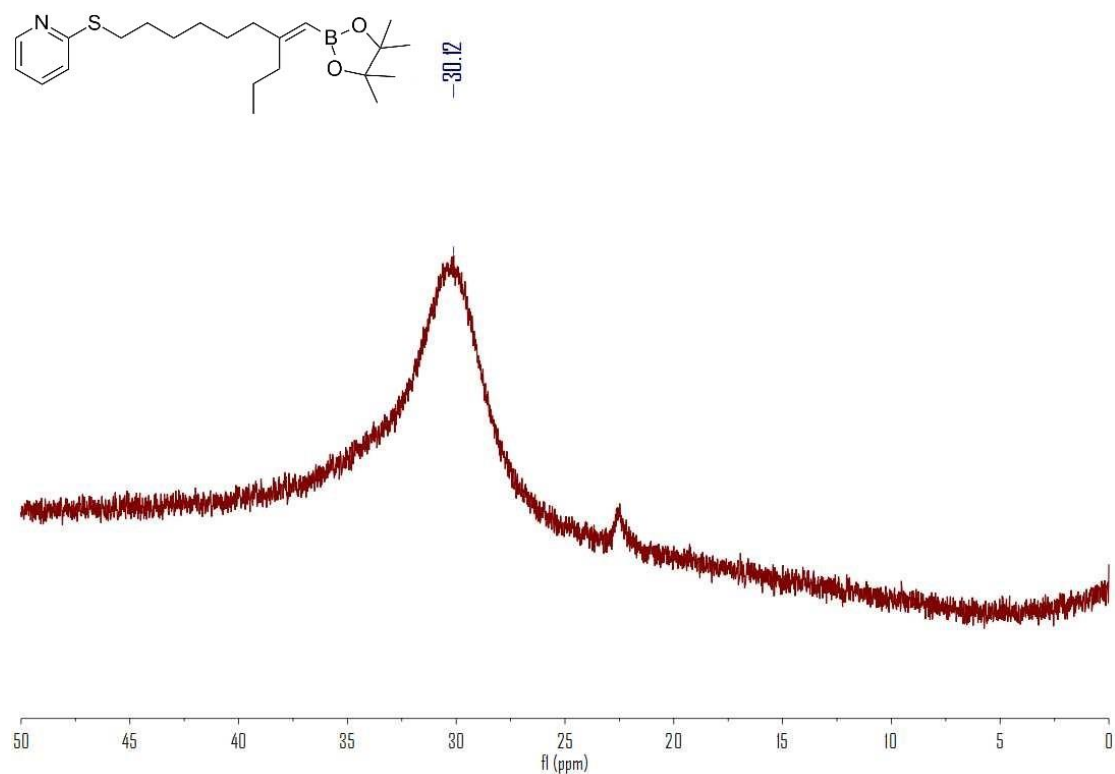
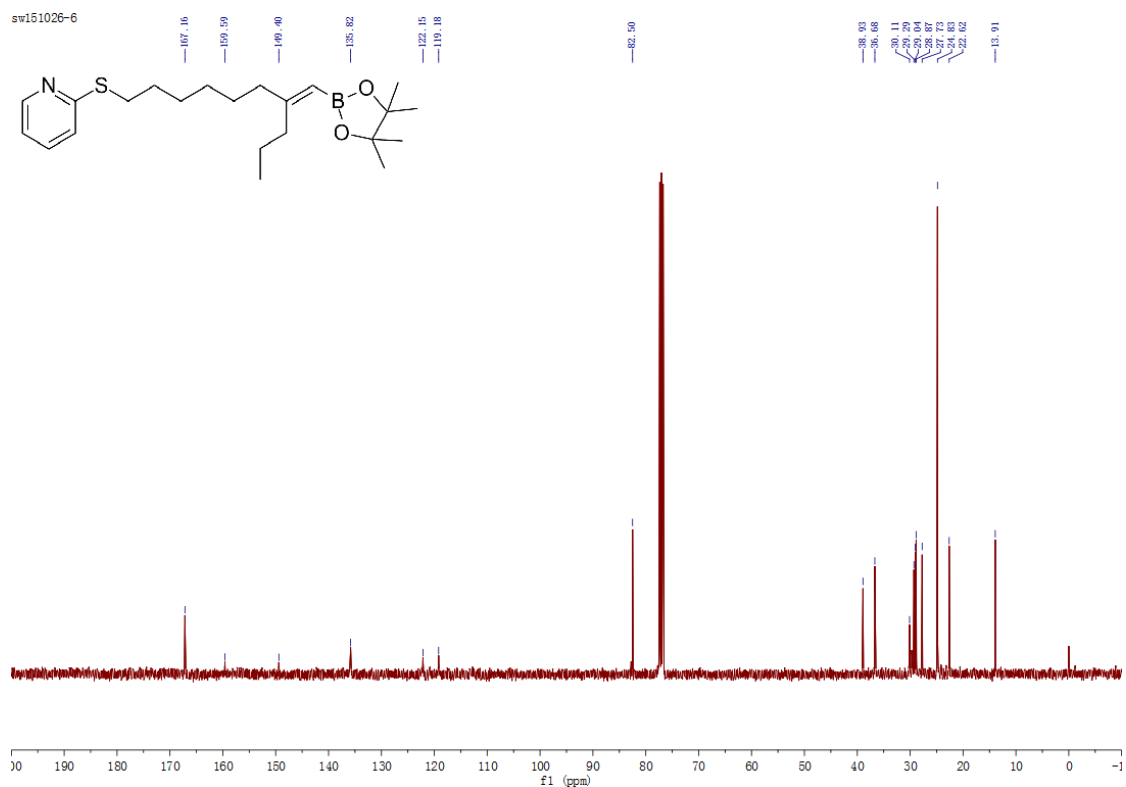
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.16 (s), 159.59 (s), 149.40 (s), 135.82 (s), 122.15 (s), 119.18 (s), 82.50 (s), 38.93 (s), 36.68 (s), 30.11 (s), 29.29 (s), 29.04 (s), 28.87 (s), 27.73 (s), 24.83 (s), 22.62 (s), 13.91 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.12.

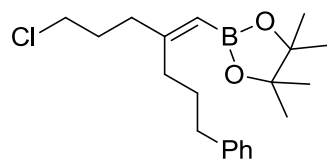
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{22}\text{H}_{36}\text{BNO}_2\text{S}[\text{H}]^+$ : 390.2638, Found: 390.2629.







**(E)-2-(5-chloro-2-(3-phenylpropyl)pent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3g**

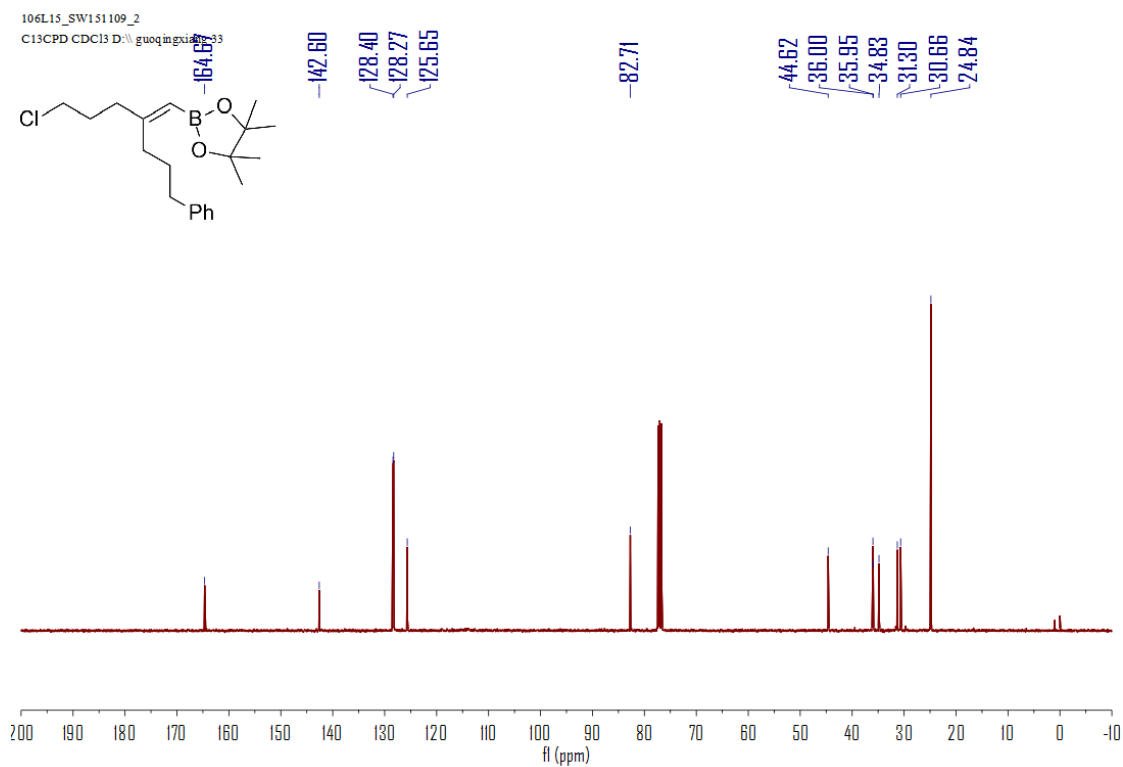
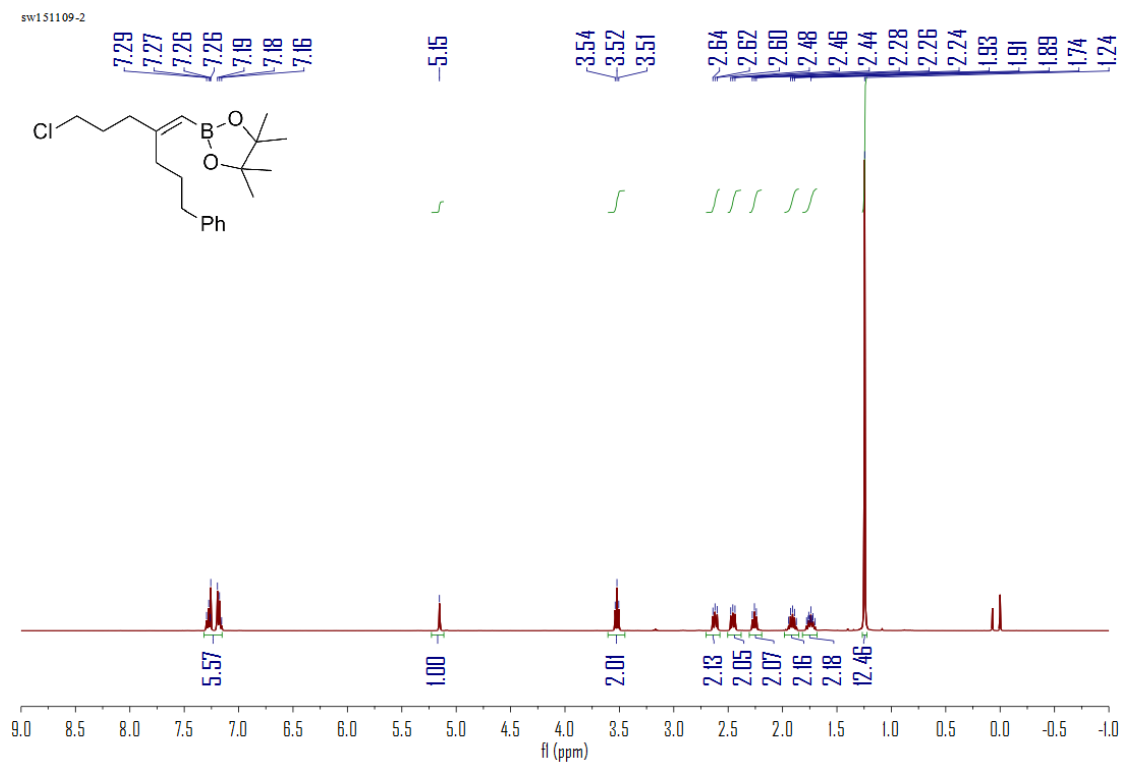


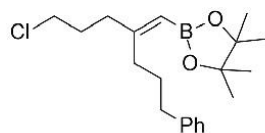
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.15 (m, 5H), 5.15 (s, 1H), 3.52 (t,  $J$  = 6.6 Hz, 2H), 2.70 – 2.58 (m, 2H), 2.50 – 2.38 (m, 2H), 2.26 (t,  $J$  = 7.4 Hz, 2H), 1.91 (m, 2H), 1.74 (m, 2H), 1.24 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.67 (s), 142.60 (s), 128.40 (s), 128.27 (s), 125.65 (s), 82.71 (s), 44.62 (s), 36.00 (s), 35.95 (s), 34.83 (s), 31.30 (s), 30.66 (s), 24.84 (s).

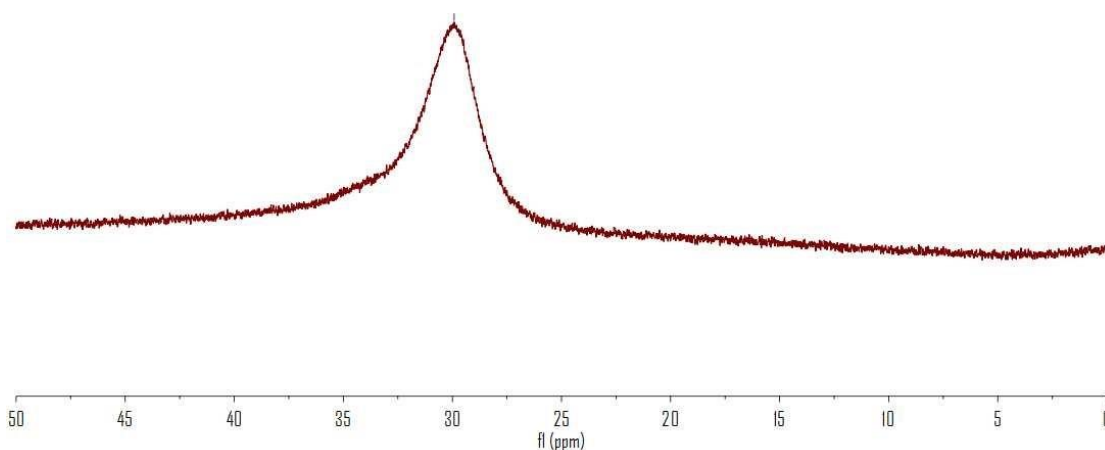
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.92.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{20}\text{H}_{30}\text{BClO}_2[\text{H}]^+$ : 349.2106, Found: 349.2104.

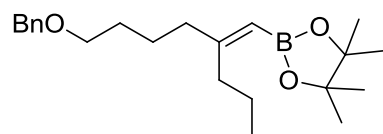




-29.92



**(E)-2-(6-(benzyloxy)-2-propylhex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3h**

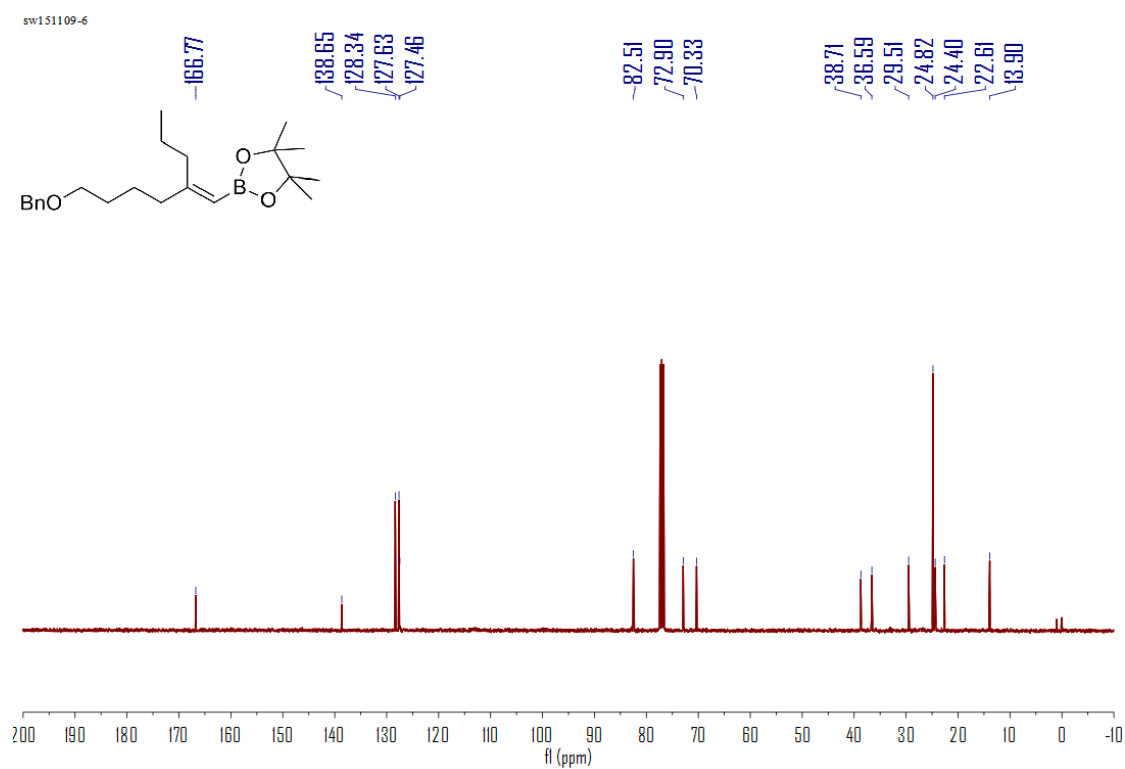
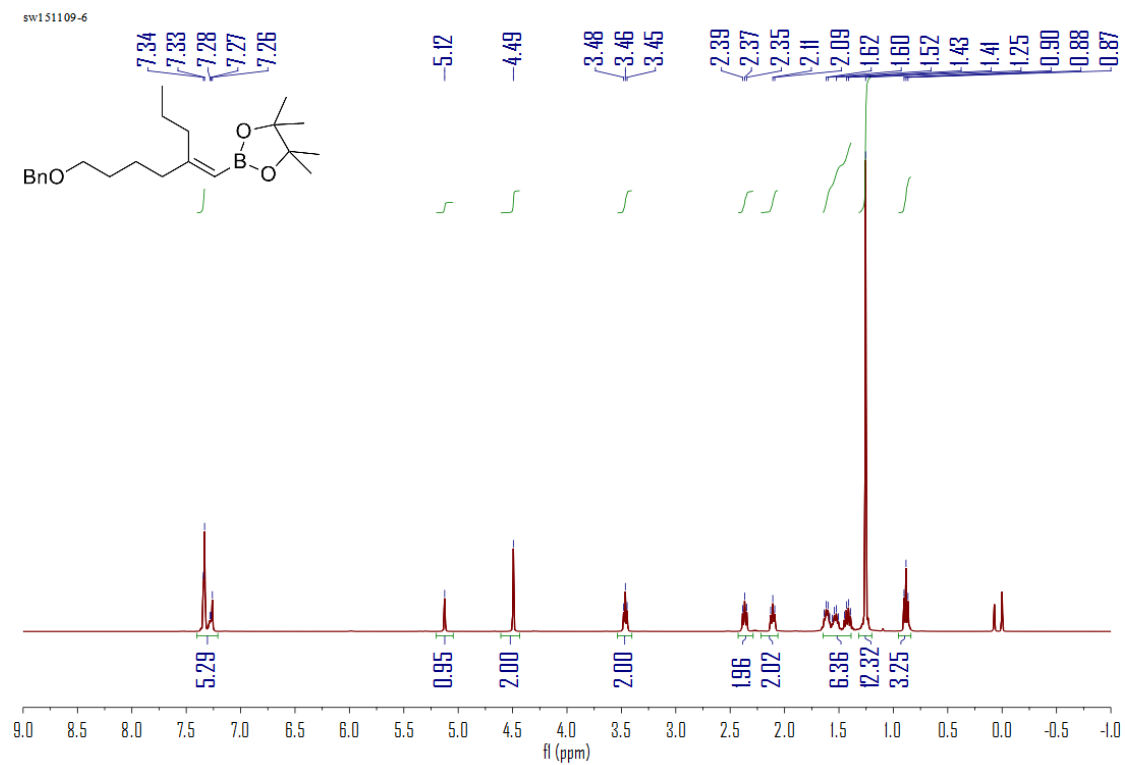


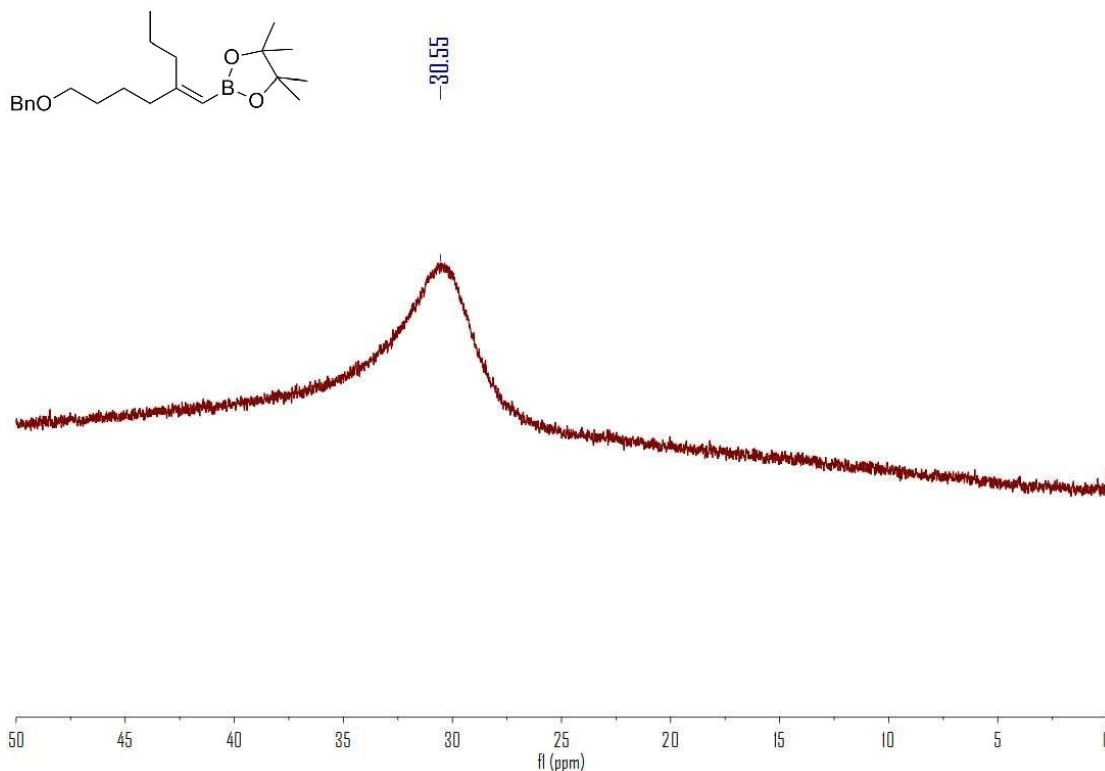
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.21 (m, 5H), 5.12 (s, 1H), 4.49 (s, 2H), 3.46 (t,  $J$  = 6.3 Hz, 2H), 2.37 (t,  $J$  = 7.6 Hz, 2H), 2.11 (t,  $J$  = 7.4 Hz, 2H), 1.64 – 1.39 (m, 6H), 1.25 (s, 12H), 0.88 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.77 (s), 138.65 (s), 128.34 (s), 127.63 (s), 127.46 (s), 82.51 (s), 72.90 (s), 70.33 (s), 38.71 (s), 36.59 (s), 29.51 (s), 24.82 (s), 24.40 (s), 22.61 (s), 13.90 (s).

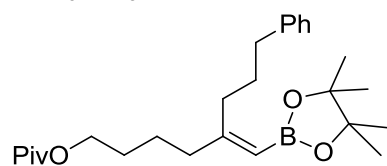
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.55.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{22}\text{H}_{35}\text{BO}_3[\text{H}]^+$ : 359.2758, Found: 359.2754.





**(E)-8-phenyl-5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)octyl pivalate, 3i**



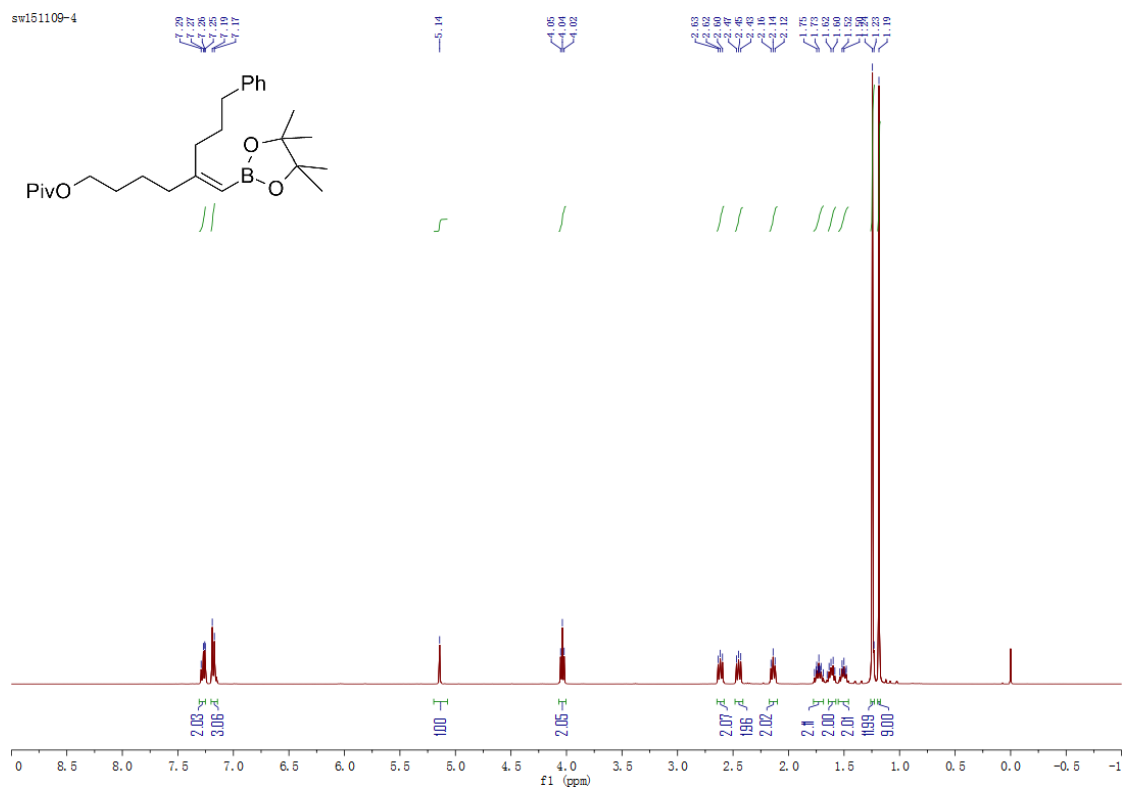
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.25 (m, 2H), 7.18 (m, 3H), 5.14 (s, 1H), 4.04 (t,  $J$  = 6.4 Hz, 2H), 2.65 – 2.58 (m, 2H), 2.47 – 2.42 (t,  $J$  = 8.0 Hz, 2H), 2.14 (t,  $J$  = 7.4 Hz, 2H), 1.73 (tt,  $J$  = 9.6, 6.9 Hz, 2H), 1.65 – 1.57 (m, 2H), 1.55 – 1.47 (m, 2H), 1.24 (d,  $J$  = 5.5 Hz, 12H), 1.19 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.66 (s), 166.13 (s), 142.70 (s), 128.40 (s), 128.25 (s), 125.63 (s), 82.63 (s), 64.26 (s), 38.75 (s), 38.61 (s), 36.04 (s), 34.73 (s), 31.40 (s), 28.38 (s), 27.23 (s), 24.84 (s), 24.11 (s).

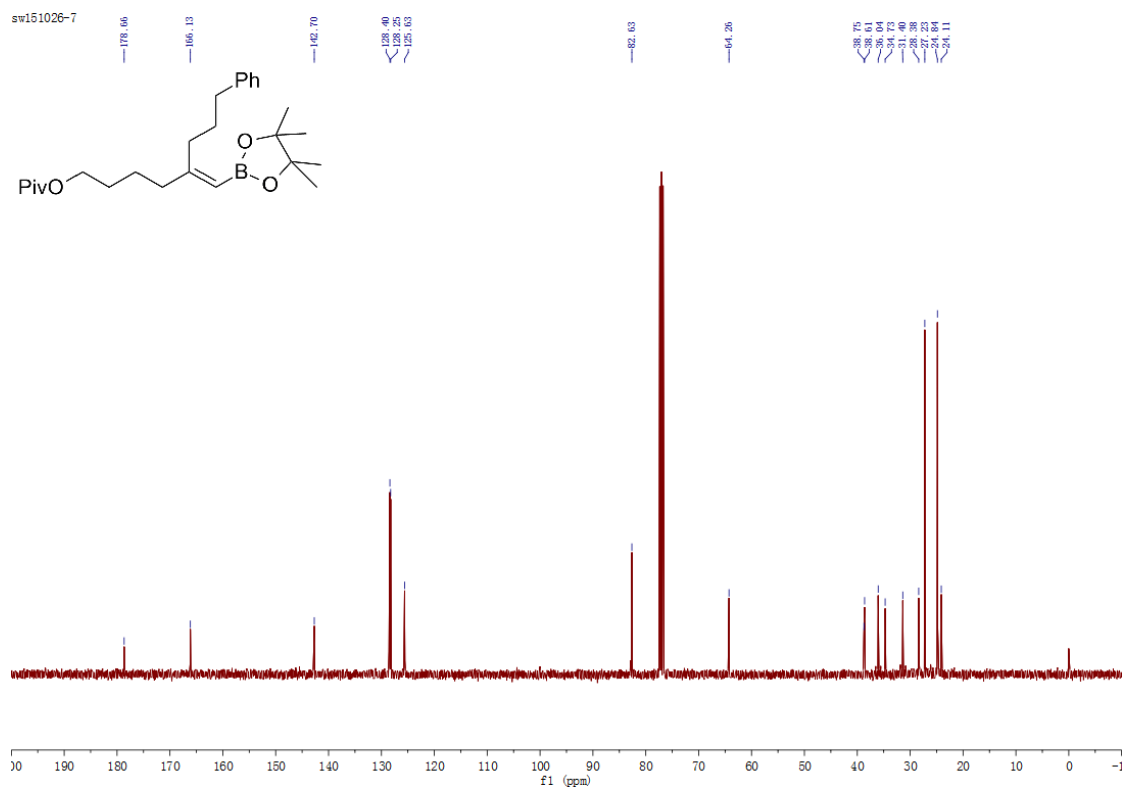
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.23.

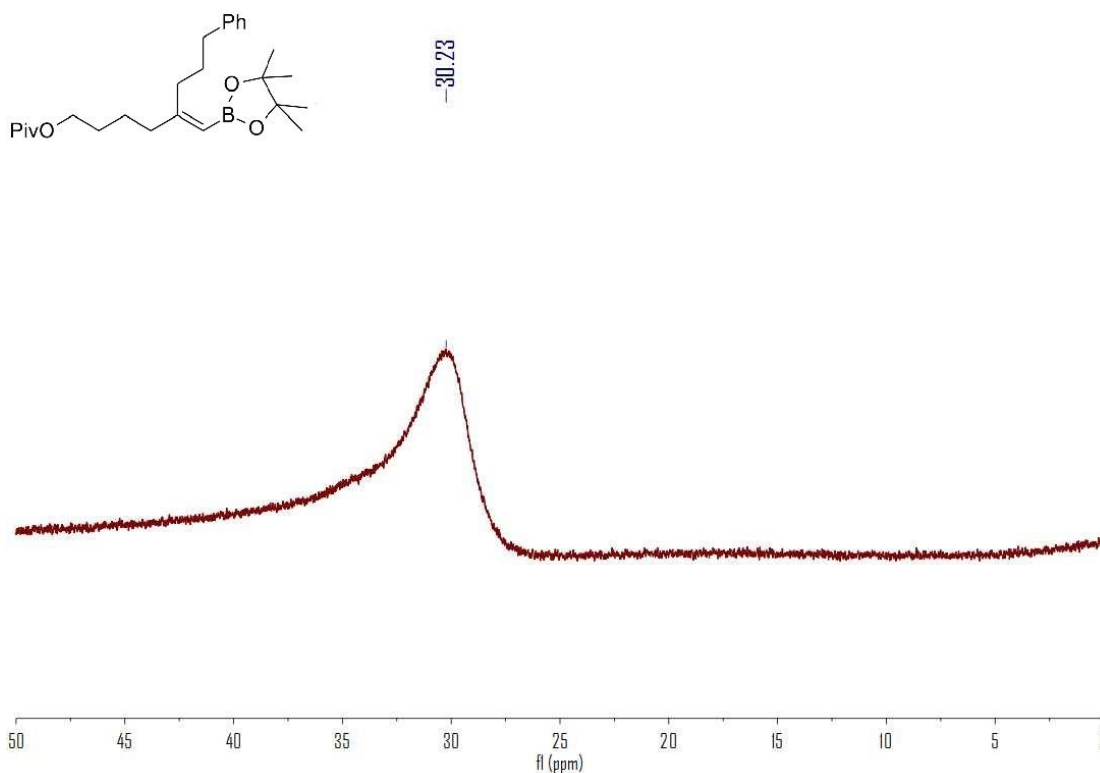
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{41}\text{BO}_4[\text{H}]^+$ : 429.3176, Found: 429.3171.

sw151109-4

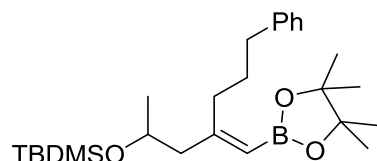


sw151026-7





**(E)-tert-butyl dimethyl((7-phenyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)heptan-2-yl)oxy)silane, 3j**



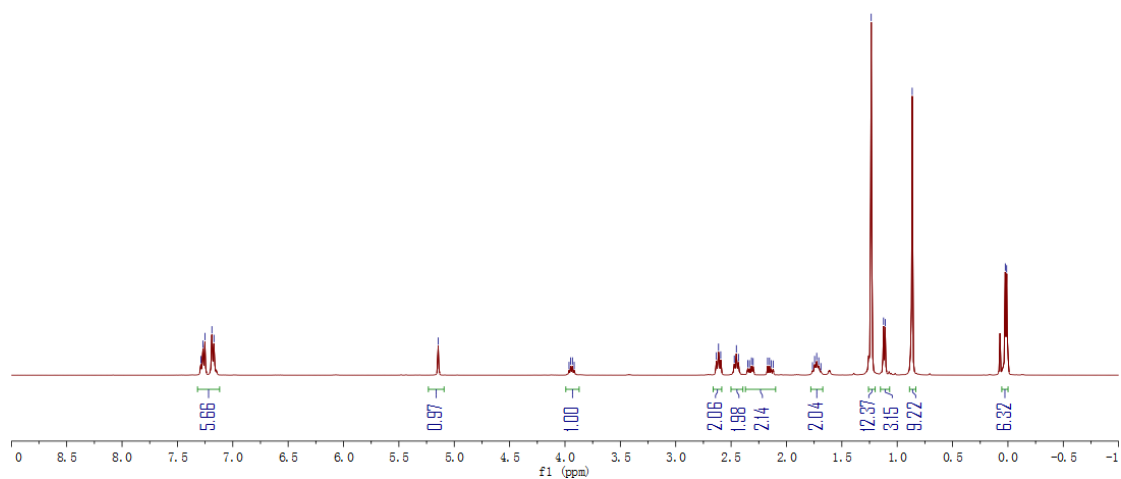
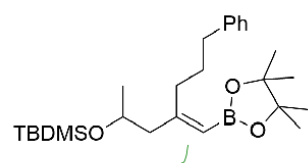
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.12 (m, 5H), 5.14 (s, 1H), 3.94 (dd,  $J$  = 12.4, 6.2 Hz, 1H), 2.61 (t,  $J$  = 7.8 Hz, 2H), 2.45 (t,  $J$  = 7.6 Hz, 2H), 2.23 (ddd,  $J$  = 20.3, 13.3, 6.5 Hz, 2H), 1.73 (dt,  $J$  = 15.1, 7.7 Hz, 2H), 1.23 (s, 12H), 1.12 (d,  $J$  = 6.0 Hz, 3H), 0.86 (s, 9H), 0.02 (d,  $J$  = 5.2 Hz, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.92 (s), 142.77 (s), 128.41 (s), 128.25 (s), 125.60 (s), 82.56 (s), 68.04 (s), 49.41 (s), 36.02 (s), 35.19 (s), 31.28 (s), 25.93 (s), 24.81 (s), 23.71 (s), 18.19 (s), -4.66 (d,  $J$  = 12.1 Hz).

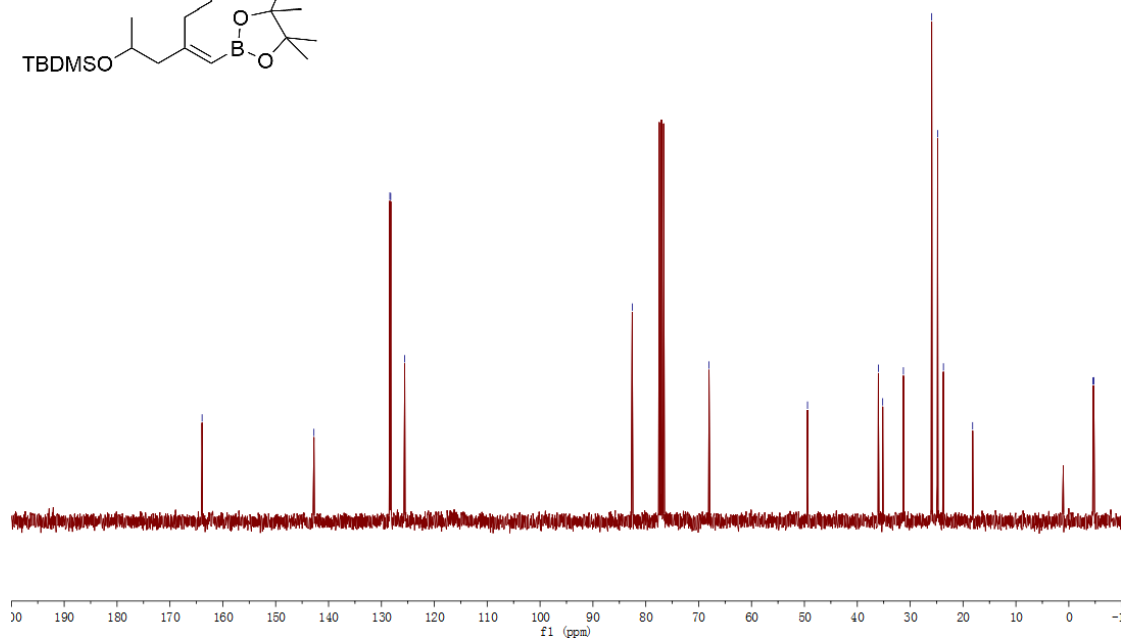
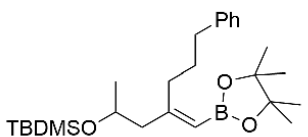
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.74.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{45}\text{BO}_3\text{Si}[\text{H}]^+$ : 445.3309, Found: 445.3303.

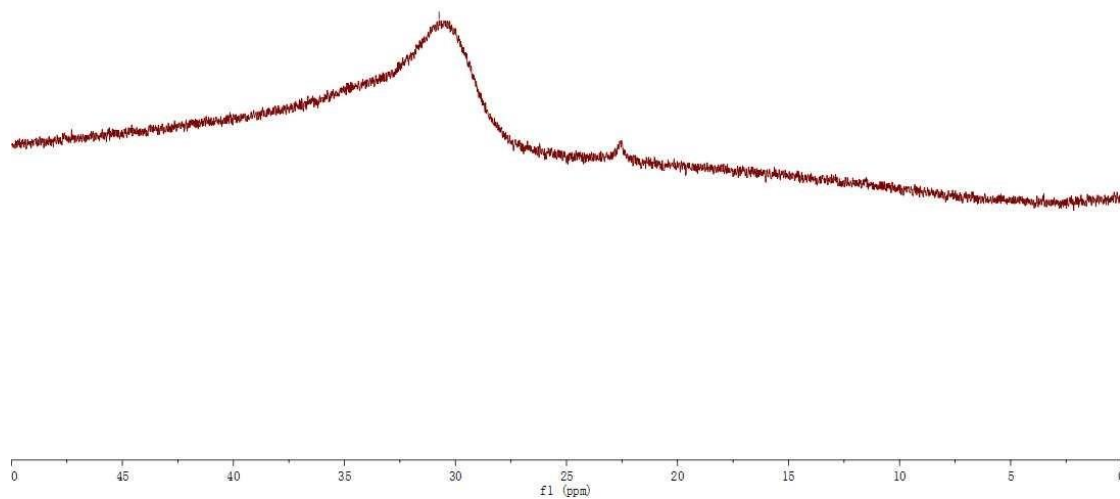
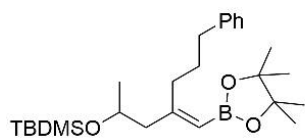
sw151130-4



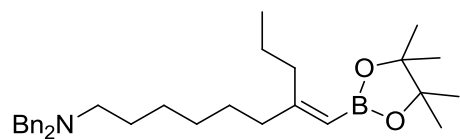
sw151130-4-33







**(E)-N,N-dibenzyl-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)decan-1-amine, 3k**

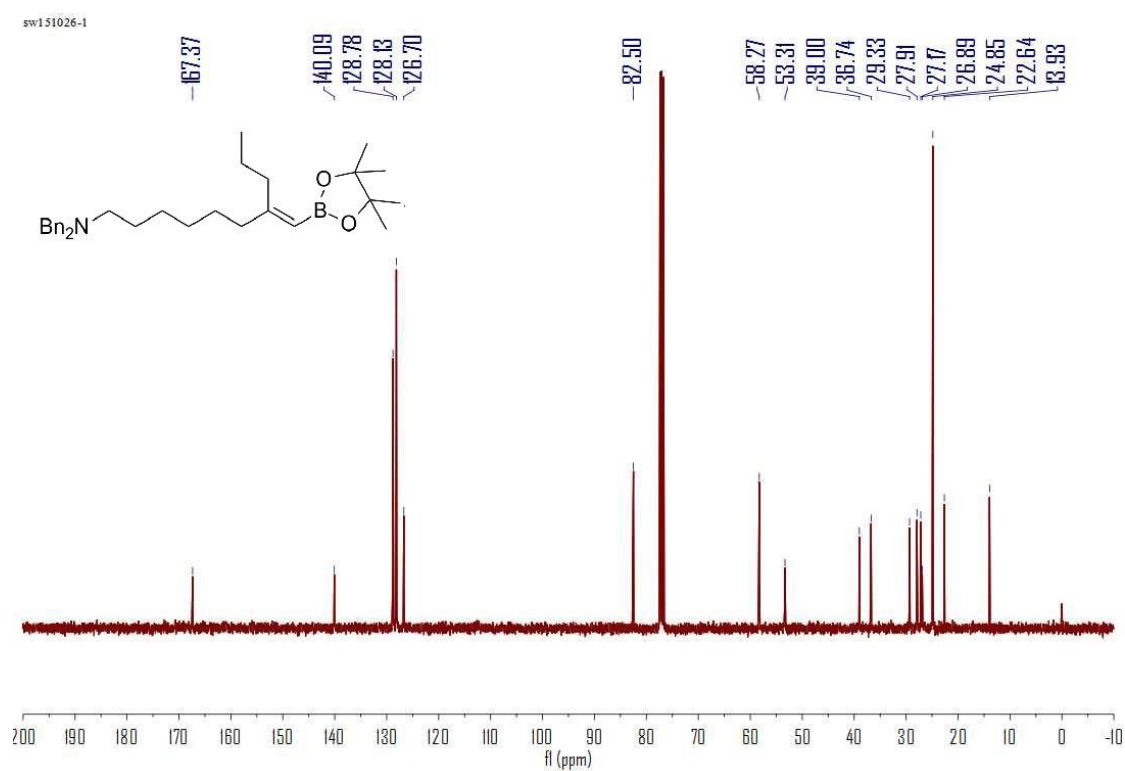
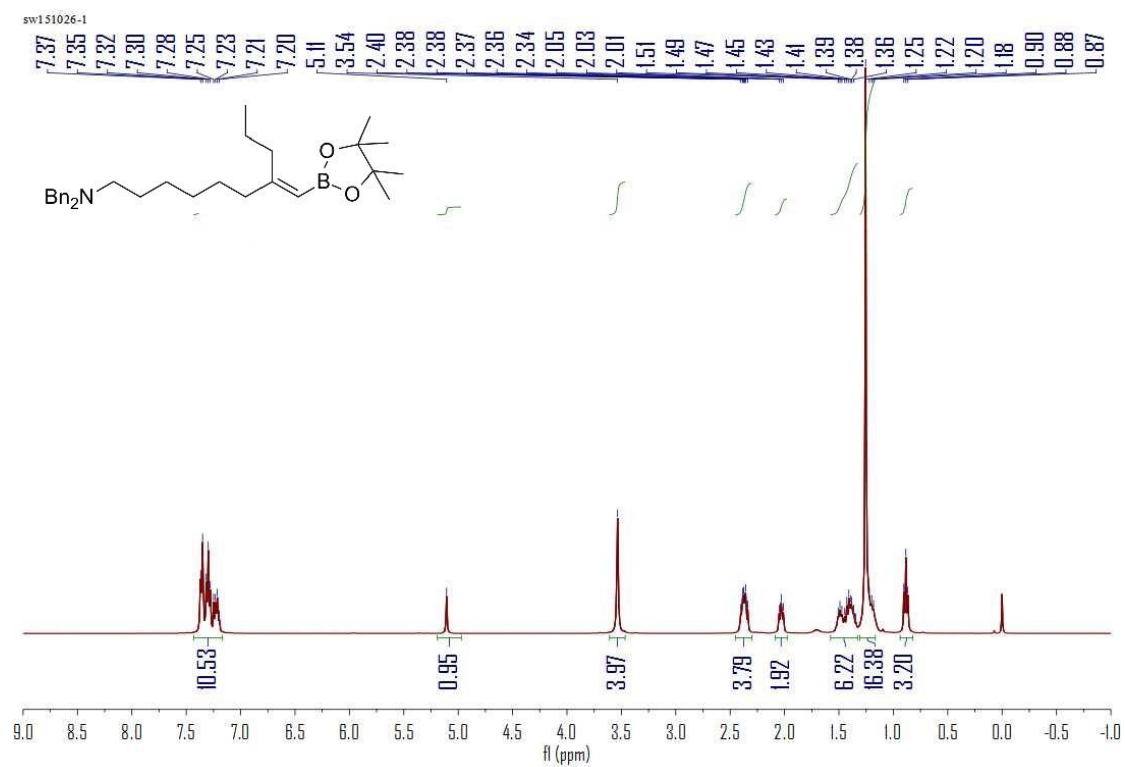


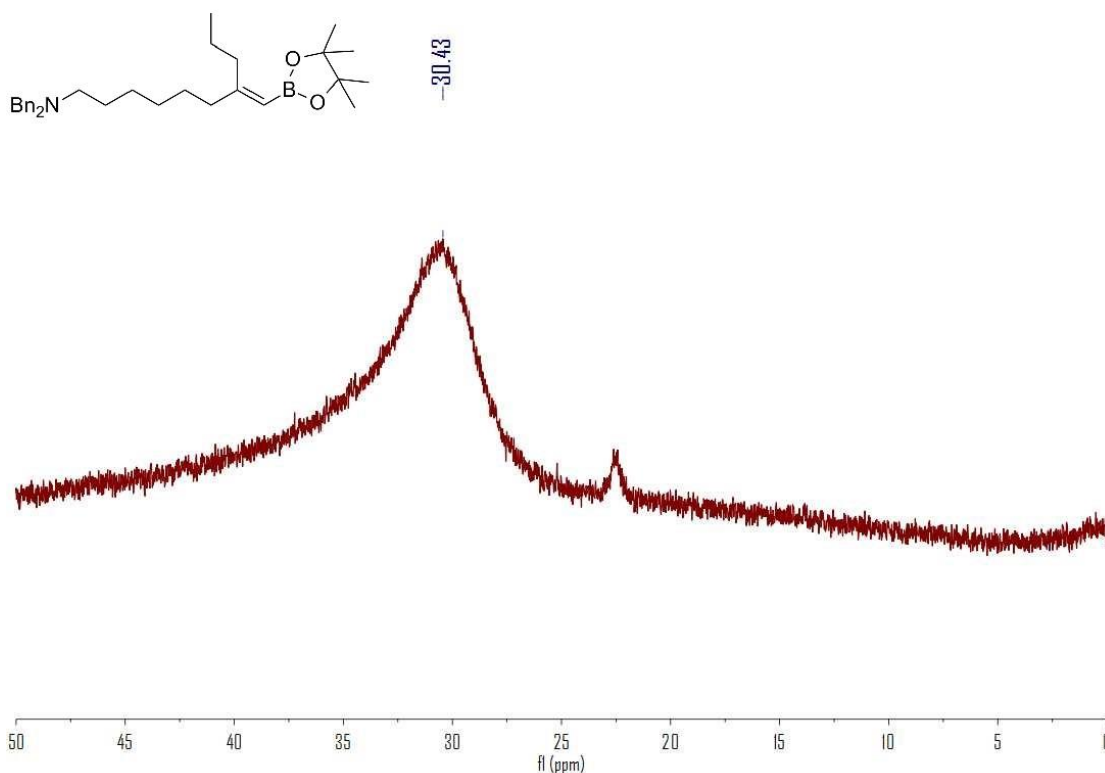
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 – 7.02 (m, 12H), 5.11 (s, 1H), 3.54 (s, 4H), 2.37 (m, 4H), 2.13 – 1.87 (t,  $J$  = 8.0Hz, 2H), 1.56 – 1.33 (m, 6H), 1.32 – 1.09 (m, 16H), 0.88 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.37 (s), 140.09 (s), 128.78 (s), 128.13 (s), 126.70 (s), 82.50 (s), 58.27 (s), 53.31 (s), 39.00 (s), 36.74 (s), 29.33 (s), 27.91 (s), 27.17 (s), 26.89 (s), 24.85 (s), 22.64 (s), 13.93 (s).

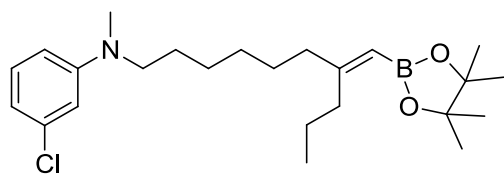
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.43.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{30}\text{H}_{39}\text{BO}_3[\text{H}]^+$ : 476.3700, Found: 476.3692.





**(E)-3-chloro-N-methyl-N-(7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)decyl)-aniline, 31**



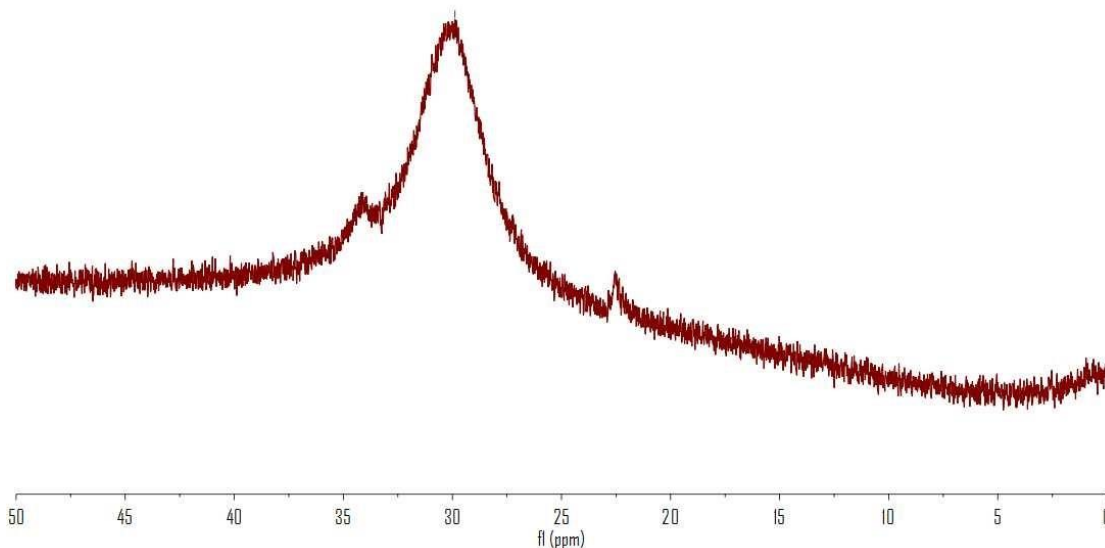
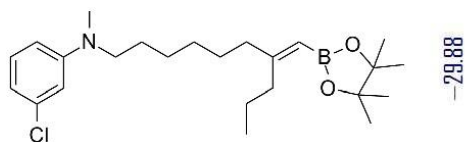
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (m, 1H), 6.66 – 6.59 (m, 2H), 6.53 (m, 1H), 5.12 (s, 1H), 3.31 – 3.21 (m, 2H), 2.90 (s, 3H), 2.36 (t,  $J$  = 8.0 Hz, 2H), 2.08 (t,  $J$  = 7.2 Hz, 2H), 1.54 (m, 2H), 1.42 (m, 4H), 1.33 – 1.28 (m, 3H), 1.25 (m, 12H), 0.89 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.08 (s), 150.30 (s), 135.07 (s), 130.01 (s), 115.46 (s), 111.70 (s), 110.05 (s), 82.53 (s), 52.65 (s), 38.89 (s), 38.34 (s), 36.70 (s), 29.30 (s), 27.80 (s), 27.05 (s), 26.56 (s), 24.84 (s), 22.63 (s), 13.92 (s).

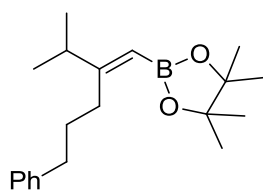
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.88.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{24}\text{H}_{38}\text{BClNO}_2[\text{H}]^+$ : 420.2841, Found: 420.2834.





**(E)-2-(2-isopropyl-5-phenylpent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3m**



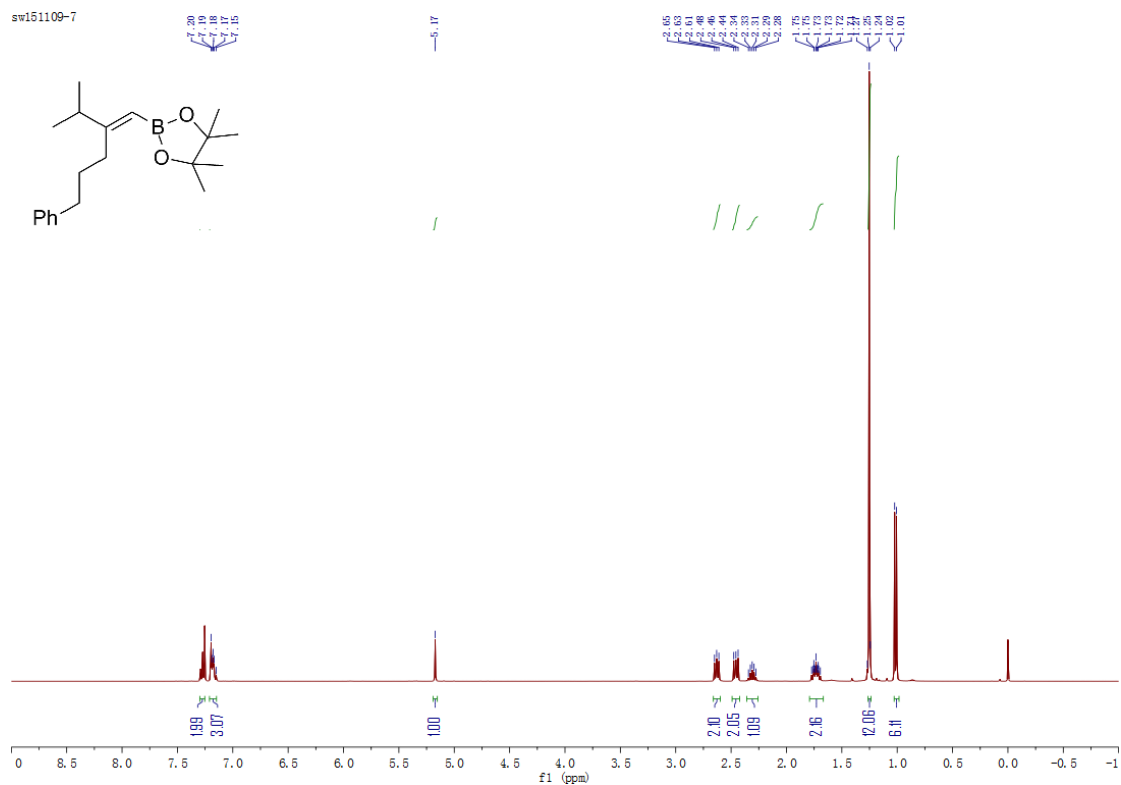
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.26 (m, 2H), 7.21 – 7.14 (m, 3H), 5.17 (s, 1H), 2.67 – 2.59 (m, 2H), 2.49 – 2.42 (m, 2H), 2.31 (dt,  $J$  = 13.6, 6.8 Hz, 1H), 1.79 – 1.68 (m, 2H), 1.29 – 1.21 (m, 12H), 1.01 (d,  $J$  = 6.8 Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.16 (s), 142.85 (s), 128.41 (s), 128.24 (s), 125.58 (s), 82.57 (s), 36.30 (s), 36.02 (s), 34.40 (s), 32.41 (s), 27.62 (s), 24.88 (s), 22.19 (s).

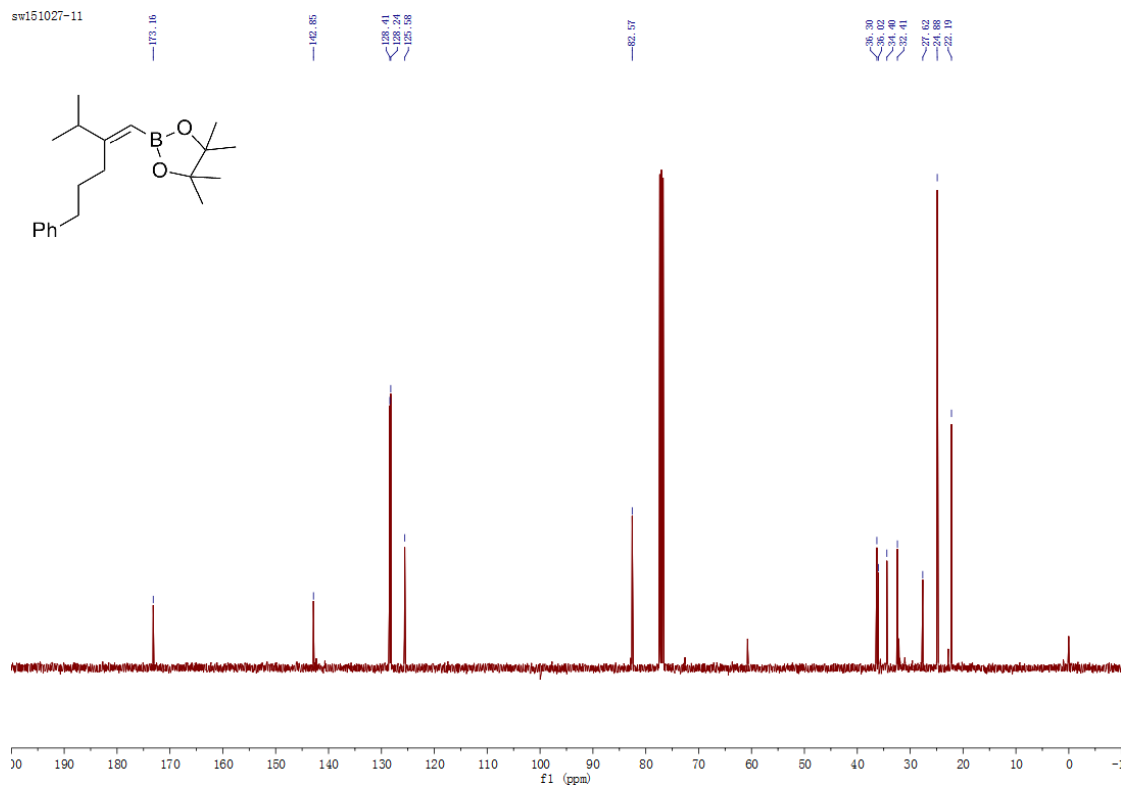
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.37.

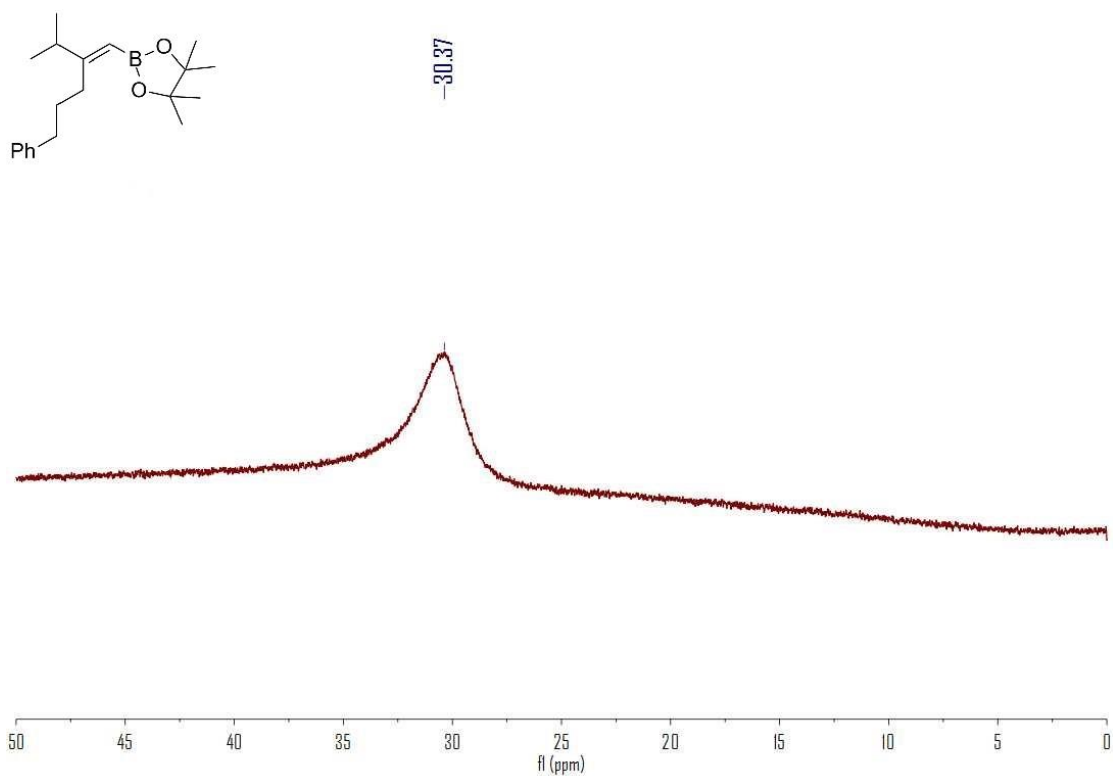
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{20}\text{H}_{31}\text{BO}_2[\text{H}]^+$ : 315.2495, Found: 315.2491.

sw151109-7

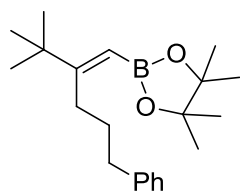


sw151027-11





**(E)-2-(2-(tert-butyl)-5-phenylpent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3n**



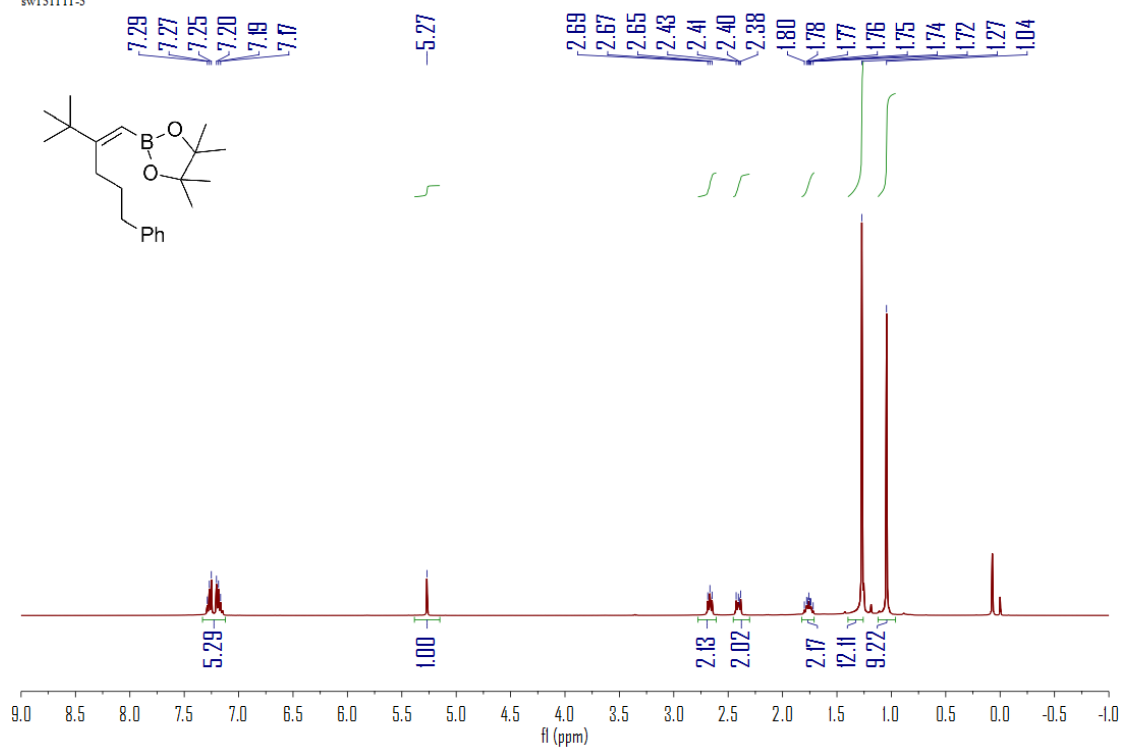
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (m, 5H), 5.27 (s, 1H), 2.78 – 2.61 (m, 2H), 2.40 (m, 2H), 1.82 – 1.71 (m, 2H), 1.27 (s, 12H), 1.04 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.96 (s), 142.88 (s), 128.45 (s), 128.25 (s), 125.60 (s), 82.62 (s), 38.73 (s), 36.99 (s), 35.29 (s), 31.96 (s), 29.40 (s), 24.97 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.49.

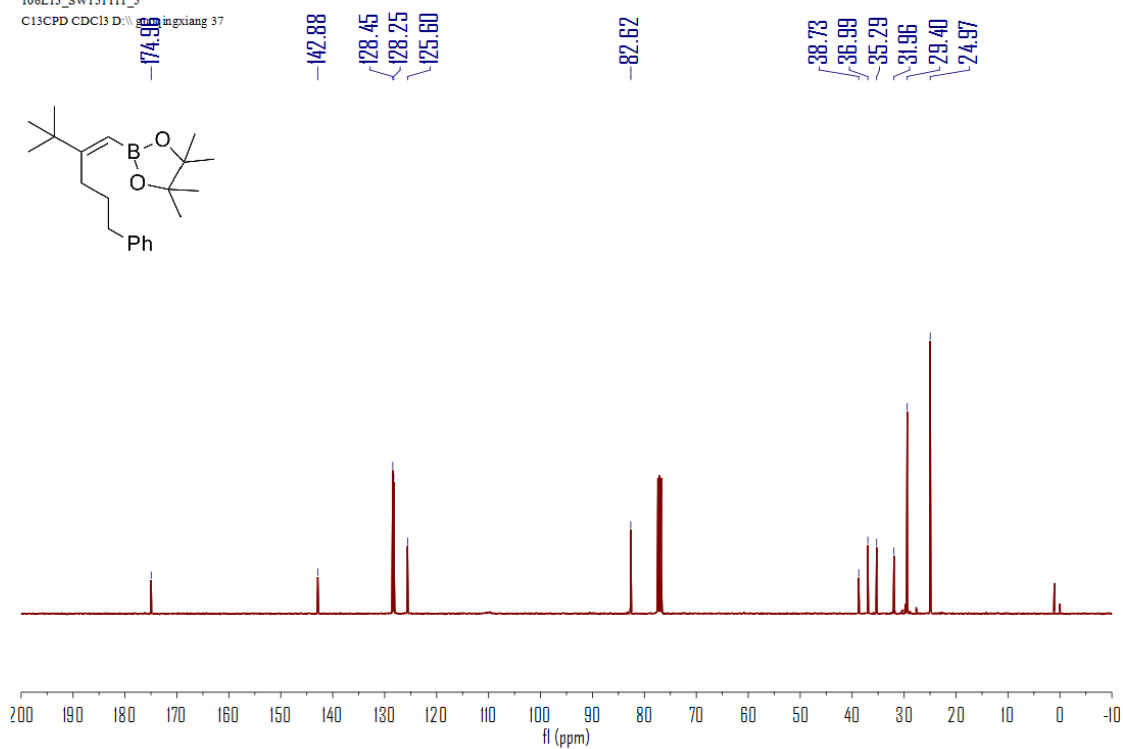
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{21}\text{H}_{33}\text{BO}_2[\text{H}]^+$ : 329.2652, Found: 329.2652.

sw151111-5

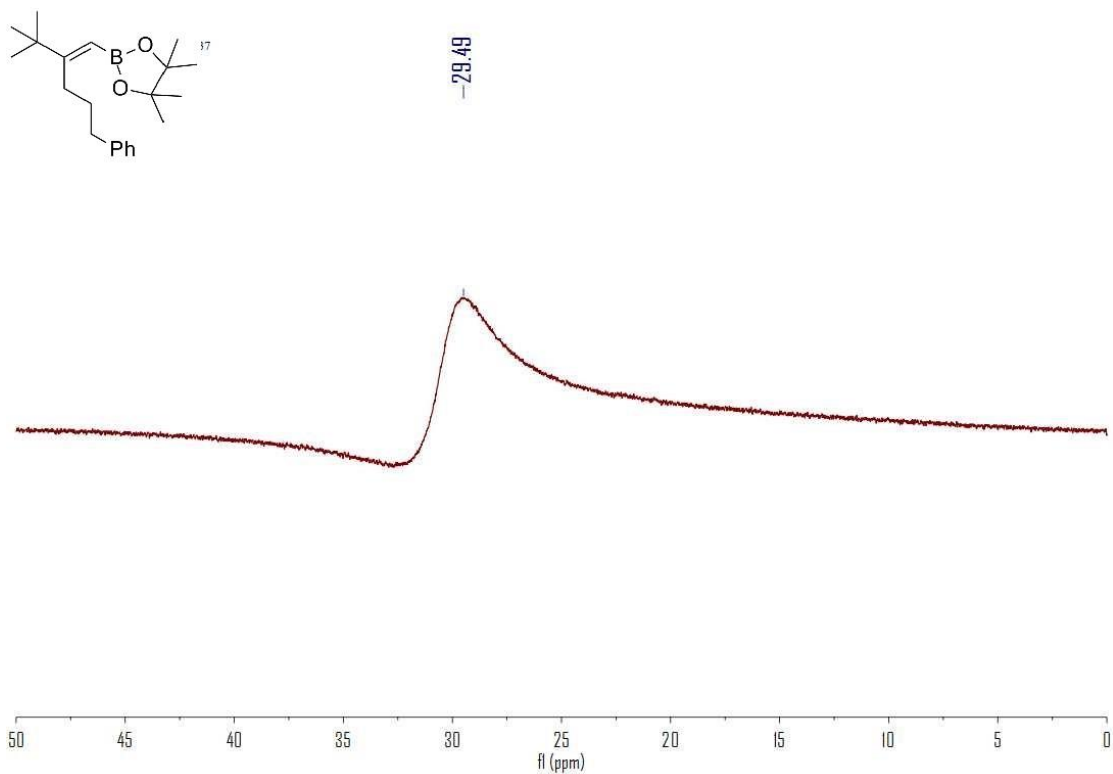


106L15\_SW151111\_5

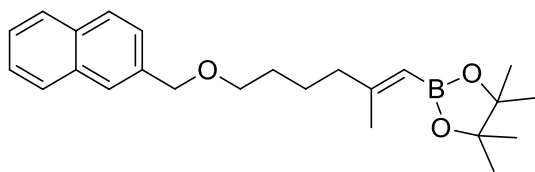
C13CPD CDC13 D:\\\dingxiang 37







**(E)-4,4,5,5-tetramethyl-2-(2-methyl-6-(naphthalen-2-ylmethoxy)hex-1-en-1-yl)-1,3,2-dioxaborolane, 3o**

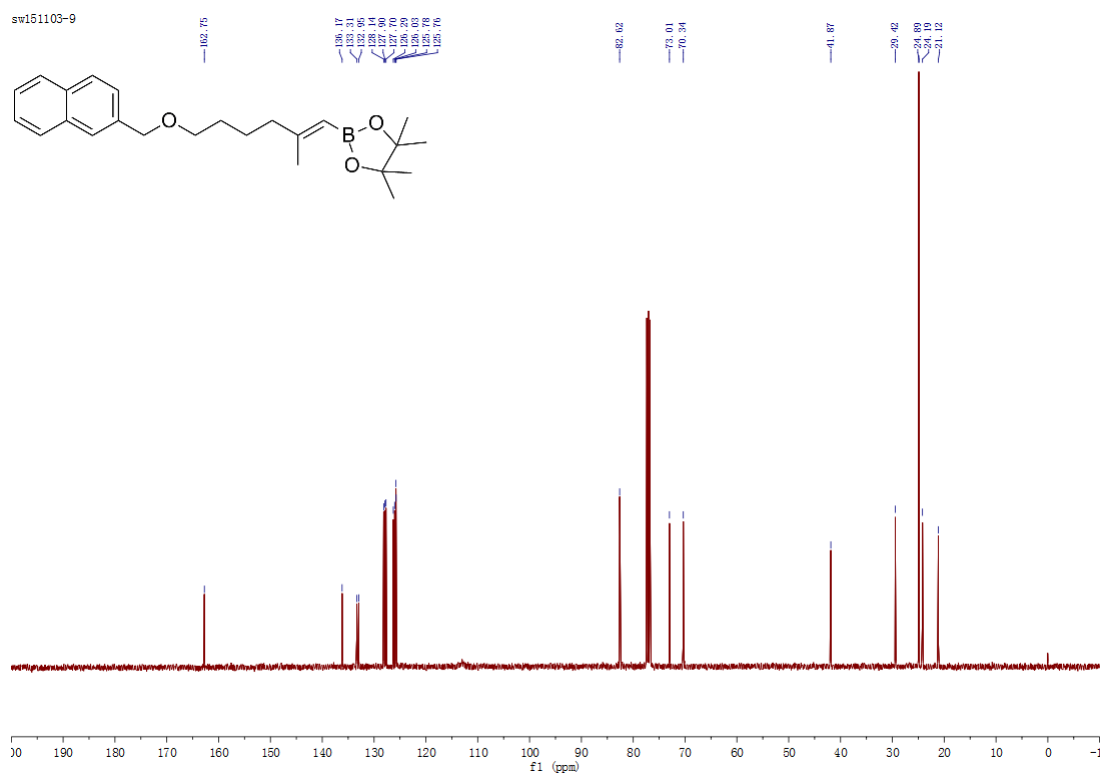
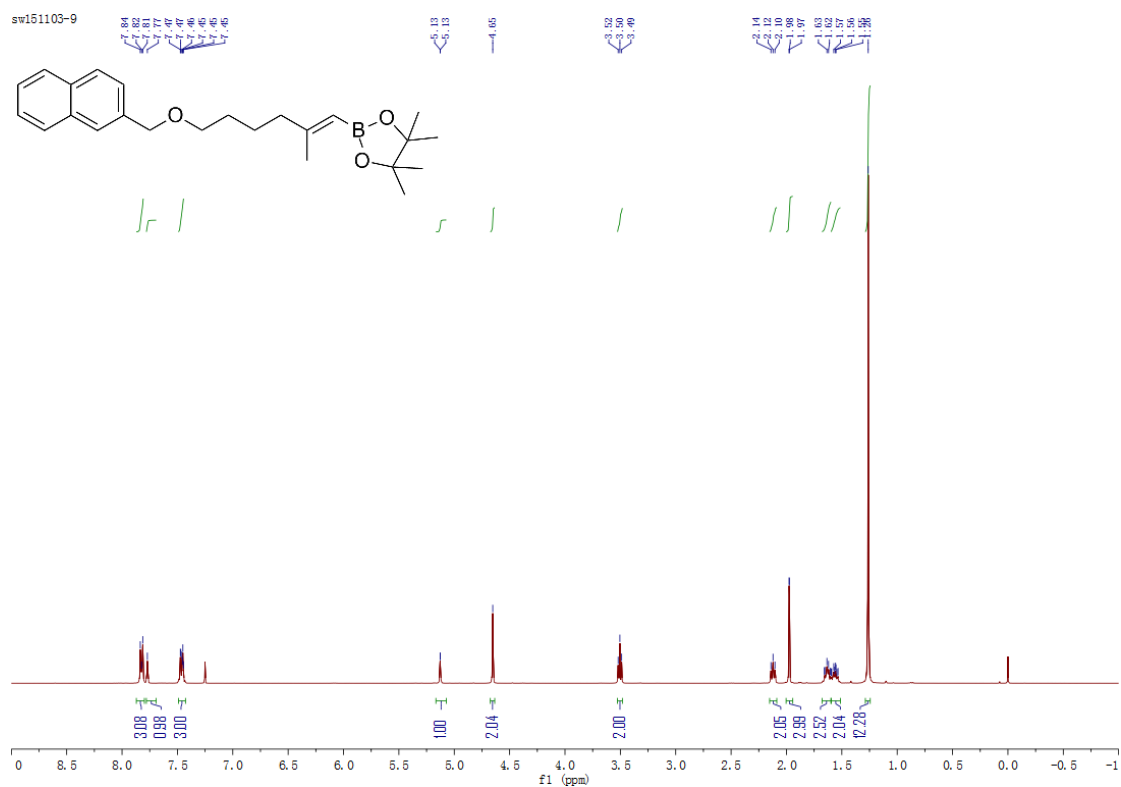


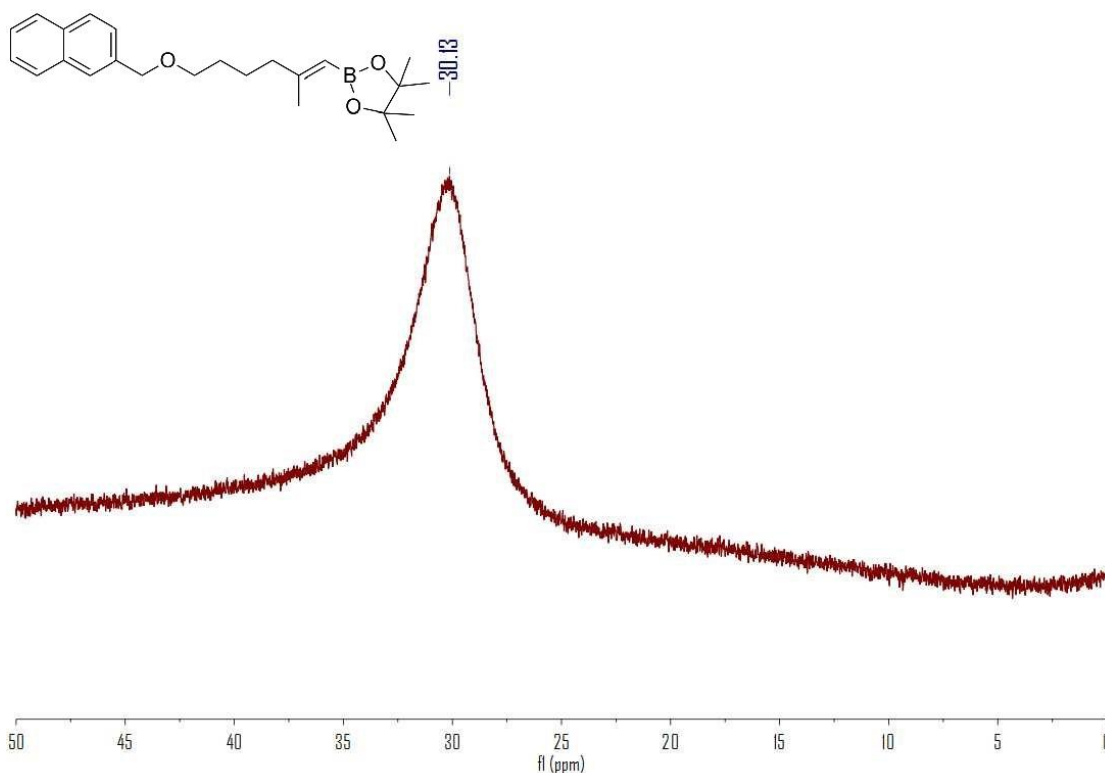
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.80 (m, 3H), 7.77 (s, 1H), 7.51 – 7.42 (m, 3H), 5.13 (s, 1H), 4.65 (s, 2H), 3.50 (t,  $J$  = 6.3 Hz, 2H), 2.12 (t,  $J$  = 7.3 Hz, 2H), 1.98 (s, 3H), 1.70 – 1.60 (m, 2H), 1.56 (m, 2H), 1.26 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.75 (s), 136.17 (s), 133.31 (s), 132.95 (s), 128.14 (s), 127.90 (s), 127.70 (s), 126.29 (s), 126.03 (s), 125.78 (s), 125.76 (s), 82.62 (s), 73.01 (s), 70.34 (s), 41.87 (s), 29.42 (s), 24.89 (s), 24.19 (s), 21.12 (s).

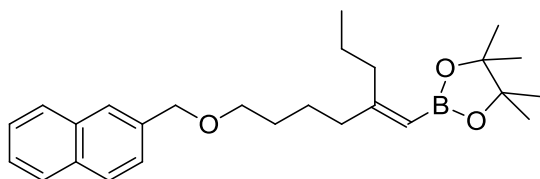
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.13.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{24}\text{H}_{33}\text{BO}_3[\text{H}]^+$ : 381.2601, Found: 381.2600.





**(E)-4,4,5,5-tetramethyl-2-(6-(naphthalen-2-ylmethoxy)-2-propylhex-1-en-1-yl)-1,3,2-dioxaborolane, 3p**

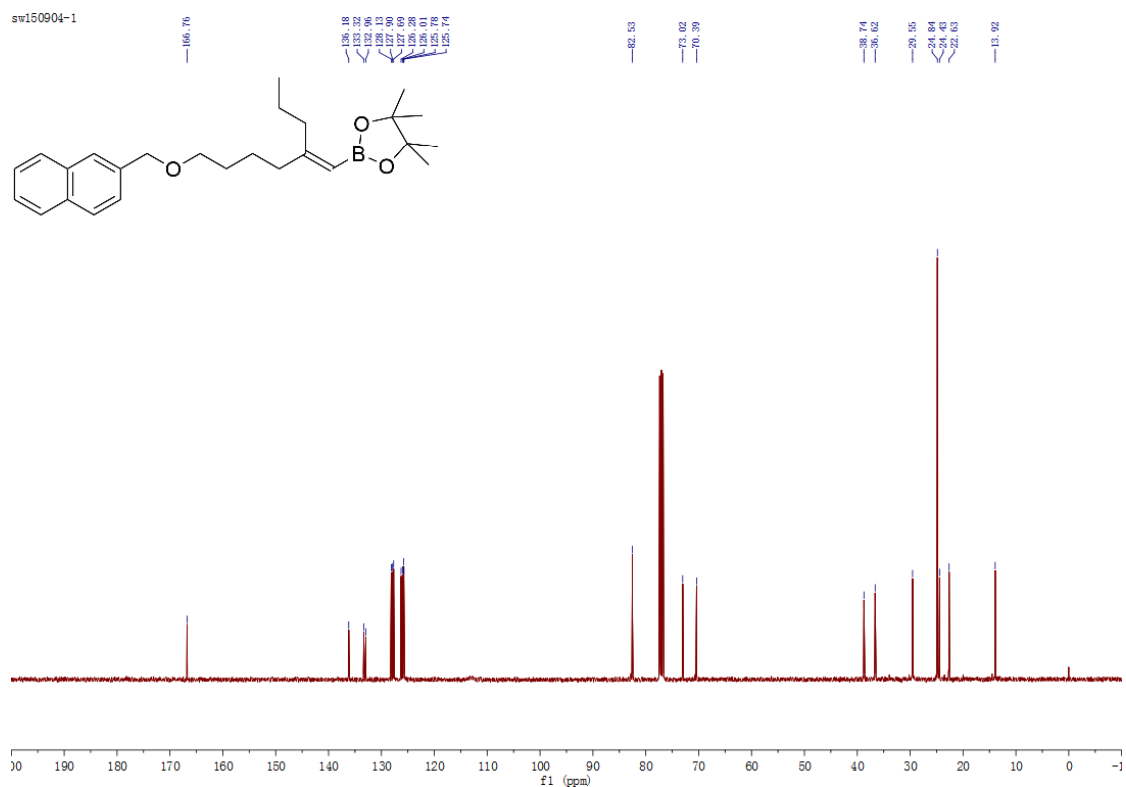
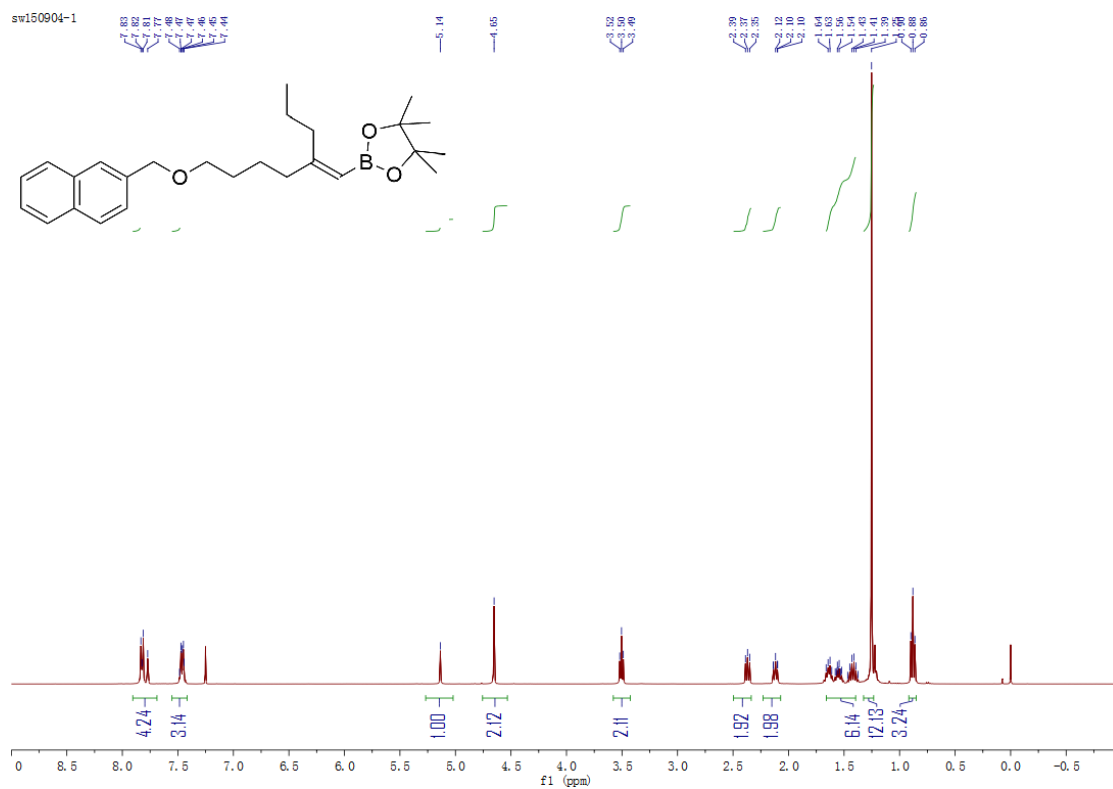


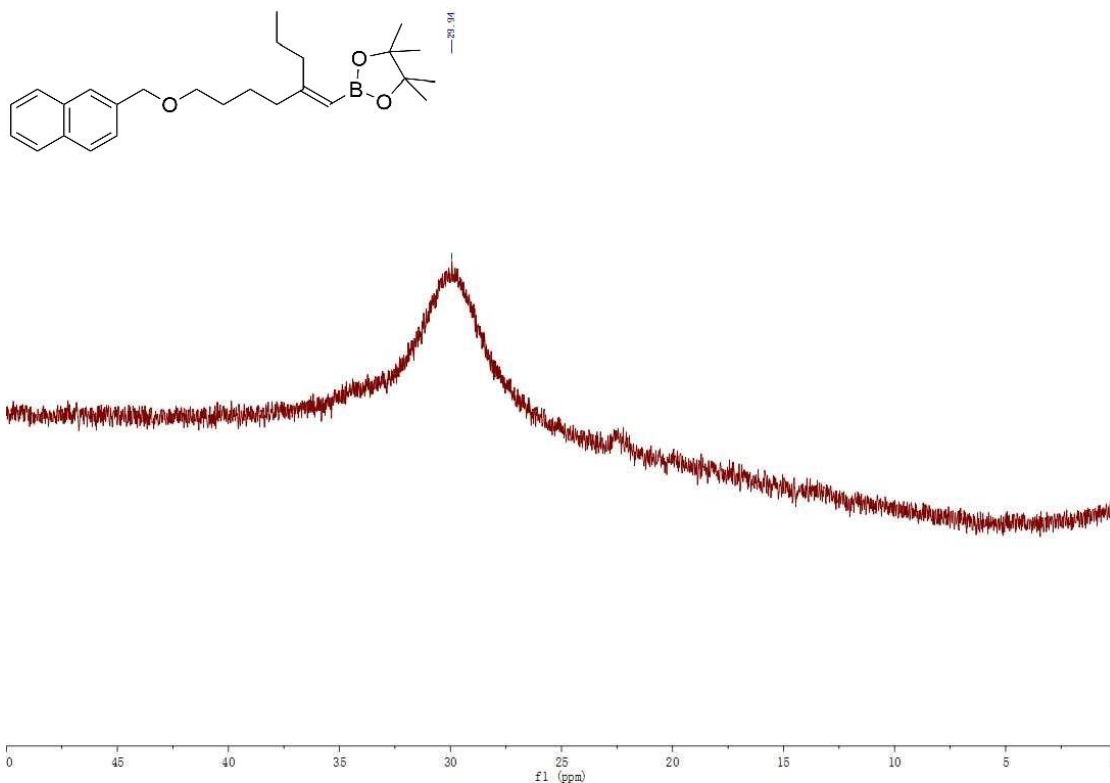
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.62 – 7.35 (m, 3H), 5.14 (s, 1H), 4.65 (s, 2H), 3.50 (t,  $J$  = 6.4 Hz, 2H), 2.43 – 2.25 (m, 2H), 2.25 – 1.98 (m, 2H), 1.83 – 1.32 (m, 6H), 1.25 (s, 12H), 0.88 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.76 (s), 136.18 (s), 133.32 (s), 132.96 (s), 128.13 (s), 127.90 (s), 127.69 (s), 126.28 (s), 126.01 (s), 125.78 (s), 125.74 (s), 82.53 (s), 73.02 (s), 70.39 (s), 38.74 (s), 36.62 (s), 29.55 (s), 24.84 (s), 24.43 (s), 22.63 (s), 13.92 (s).

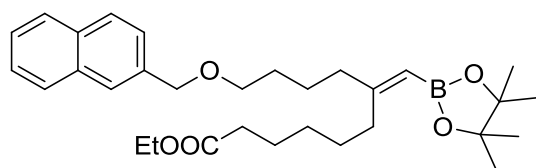
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.94.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{37}\text{BO}_3$   $[\text{H}]^+$ : 409.2914, Found: 409.2911.





**(E)-ethyl 11-(naphthalen-2-ylmethoxy)-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)undecanoate, 3q**

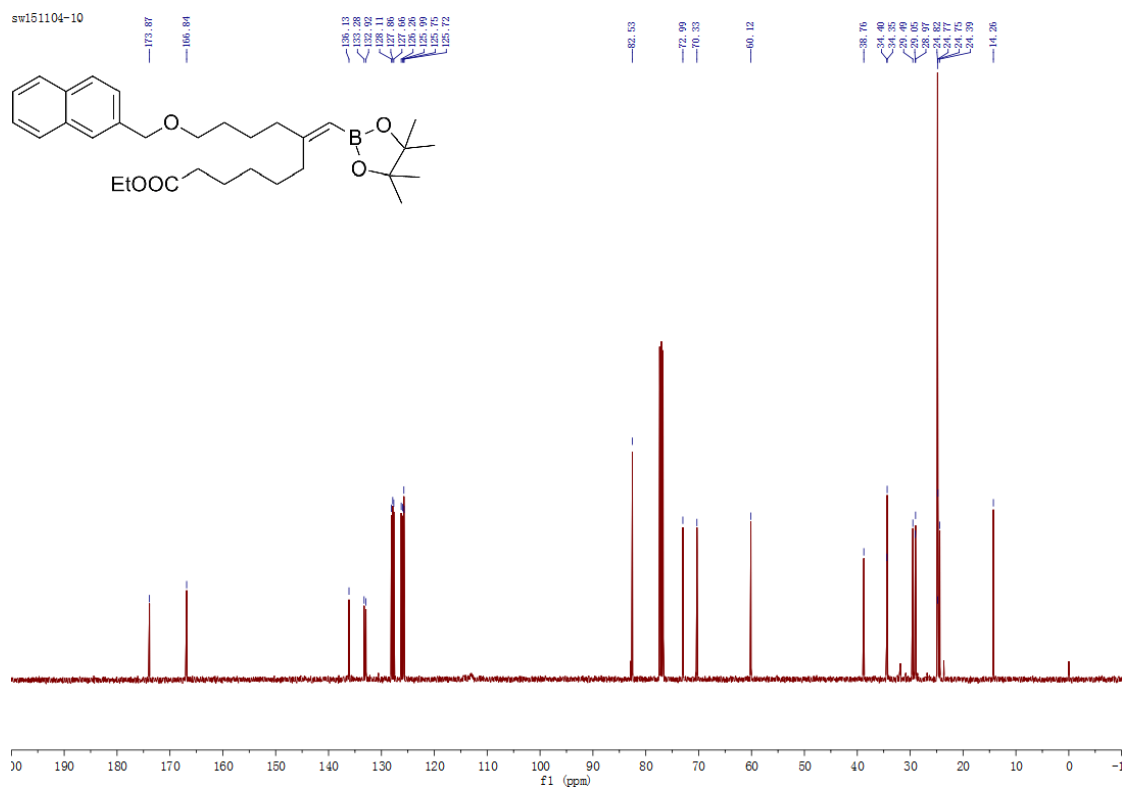
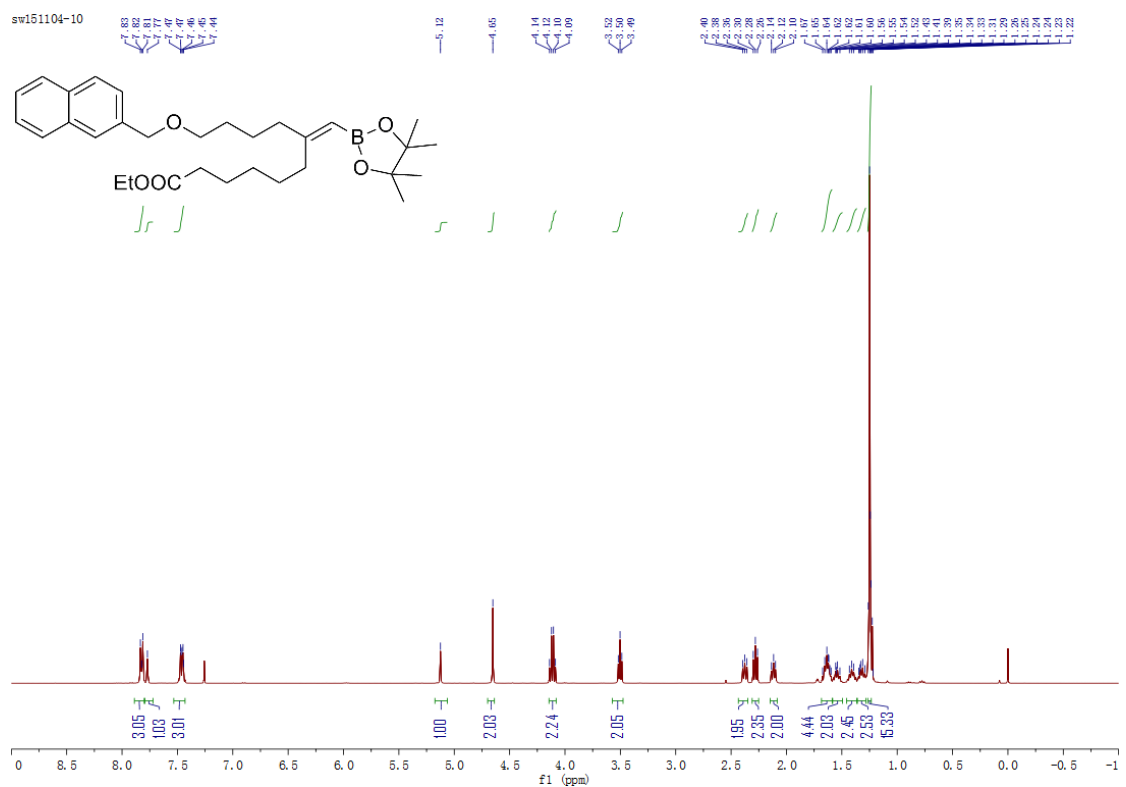


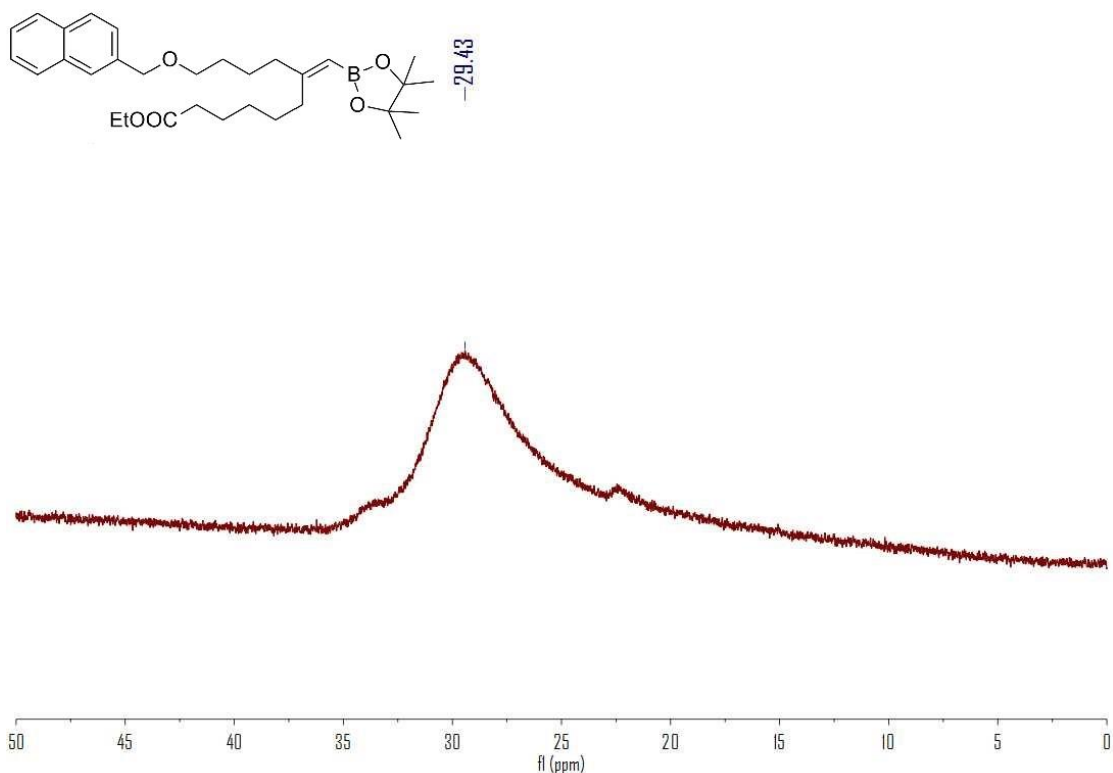
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.79 (m, 3H), 7.77 (s, 1H), 7.53 – 7.39 (m, 3H), 5.12 (s, 1H), 4.65 (s, 2H), 4.11 (q,  $J$  = 7.1 Hz, 2H), 3.50 (t,  $J$  = 6.4 Hz, 2H), 2.36 (t,  $J$  = 8.0 Hz, 2H), 2.28 (t,  $J$  = 7.6 Hz, 2H), 2.12 (t,  $J$  = 7.3 Hz, 2H), 1.69 – 1.59 (m, 4H), 1.54 (m, 2H), 1.46 – 1.37 (m, 2H), 1.35 – 1.28 (m, 2H), 1.27 – 1.20 (m, 15H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.87 (s), 166.84 (s), 136.13 (s), 133.28 (s), 132.92 (s), 128.11 (s), 127.86 (s), 127.66 (s), 126.26 (s), 125.99 (s), 125.75 (s), 125.72 (s), 82.53 (s), 72.99 (s), 70.33 (s), 60.12 (s), 38.76 (s), 34.40 (s), 34.33 (s), 29.49 (s), 29.05 (s), 28.97 (s), 24.82 (s), 24.75 (s), 24.39 (s), 14.26 (s).

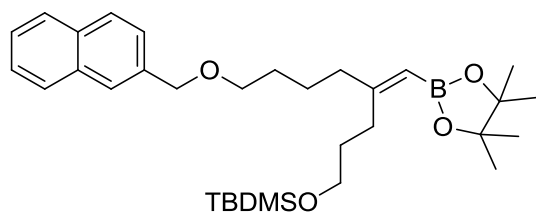
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.43.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{31}\text{H}_{45}\text{BO}_5[\text{H}]^+$ : 509.3438, Found: 509.3435.





**(Z)-tert-butyl dimethyl((8-(naphthalen-2-ylmethoxy)-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)octyl)oxy)silane, 3r**

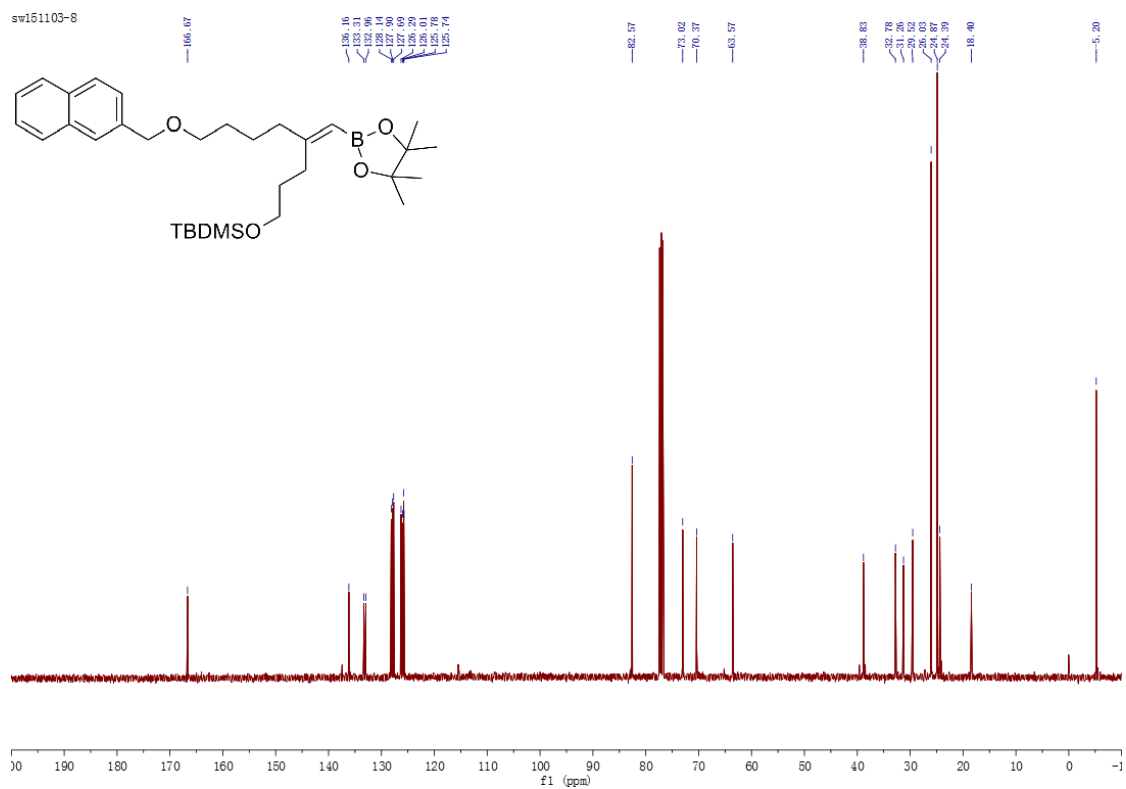
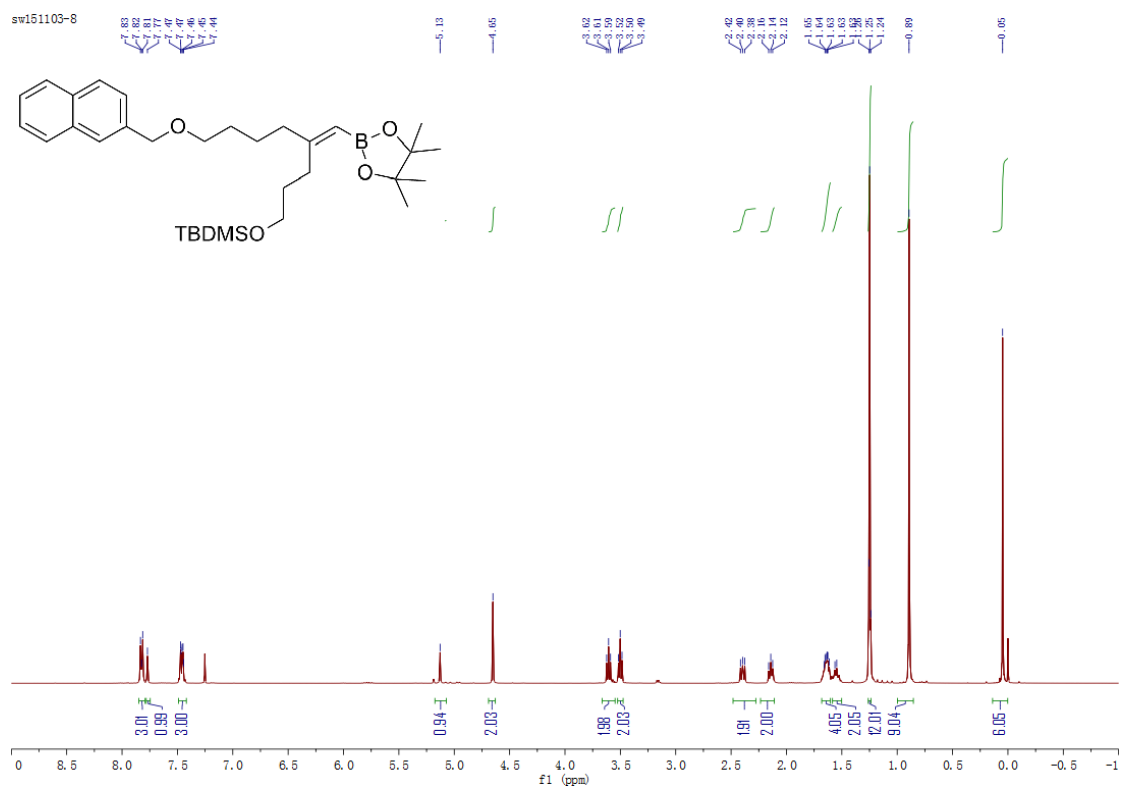


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.55 – 7.40 (m, 3H), 5.13 (s, 1H), 4.65 (s, 2H), 3.61 (t,  $J$  = 7.0 Hz, 2H), 3.50 (t,  $J$  = 6.4 Hz, 2H), 2.49 – 2.29 (t,  $J$  = 8.0 Hz, 2H), 2.14 (t,  $J$  = 7.3 Hz, 2H), 1.77 – 1.57 (m, 4H), 1.55 (m, 2H), 1.25 (s, 12H), 0.89 (s, 9H), 0.05 (s, 6H).

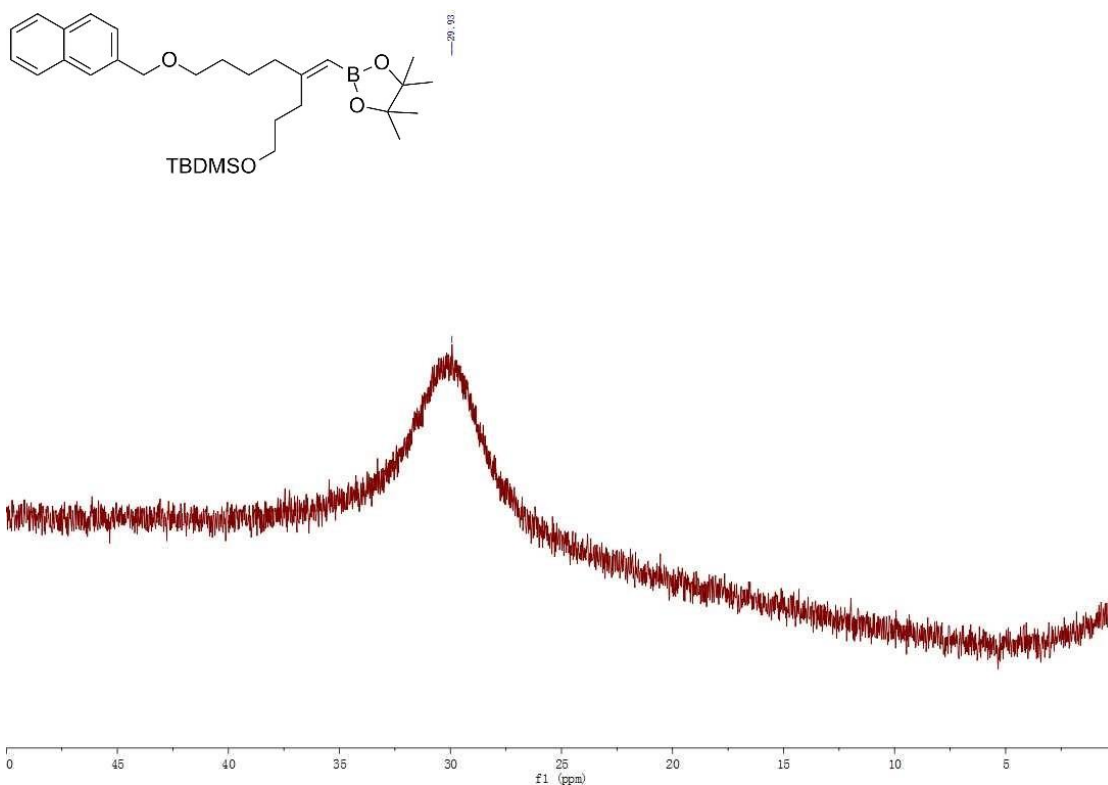
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.67 (s), 136.16 (s), 133.31 (s), 132.96 (s), 128.14 (s), 127.90 (s), 127.69 (s), 126.29 (s), 126.01 (s), 125.78 (s), 125.74 (s), 82.57 (s), 73.02 (s), 70.37 (s), 63.57 (s), 38.83 (s), 32.78 (s), 31.26 (s), 29.52 (s), 26.03 (s), 24.87 (s), 24.39 (s), 18.40 (s), -5.20 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.93.

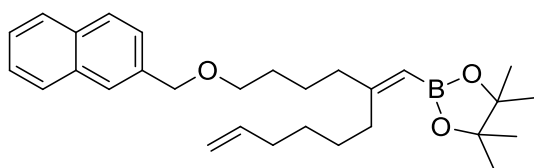
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{32}\text{H}_{51}\text{BO}_4\text{Si}[\text{H}]^+$ : 539.3728, Found: 539.3726.







**(E)-4,4,5,5-tetramethyl-2-(2-(4-(naphthalen-2-ylmethoxy)butyl)octa-1,7-dien-1-yl)-1,3,2-dioxaborolane, 3s**

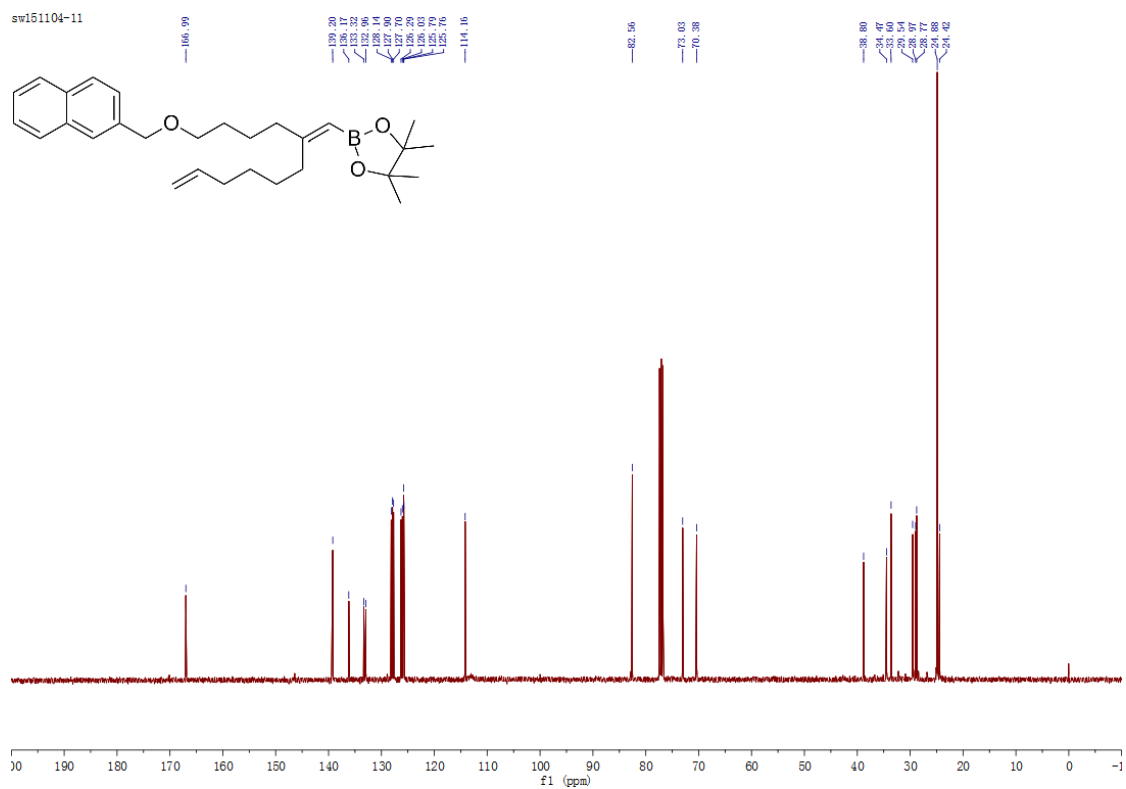
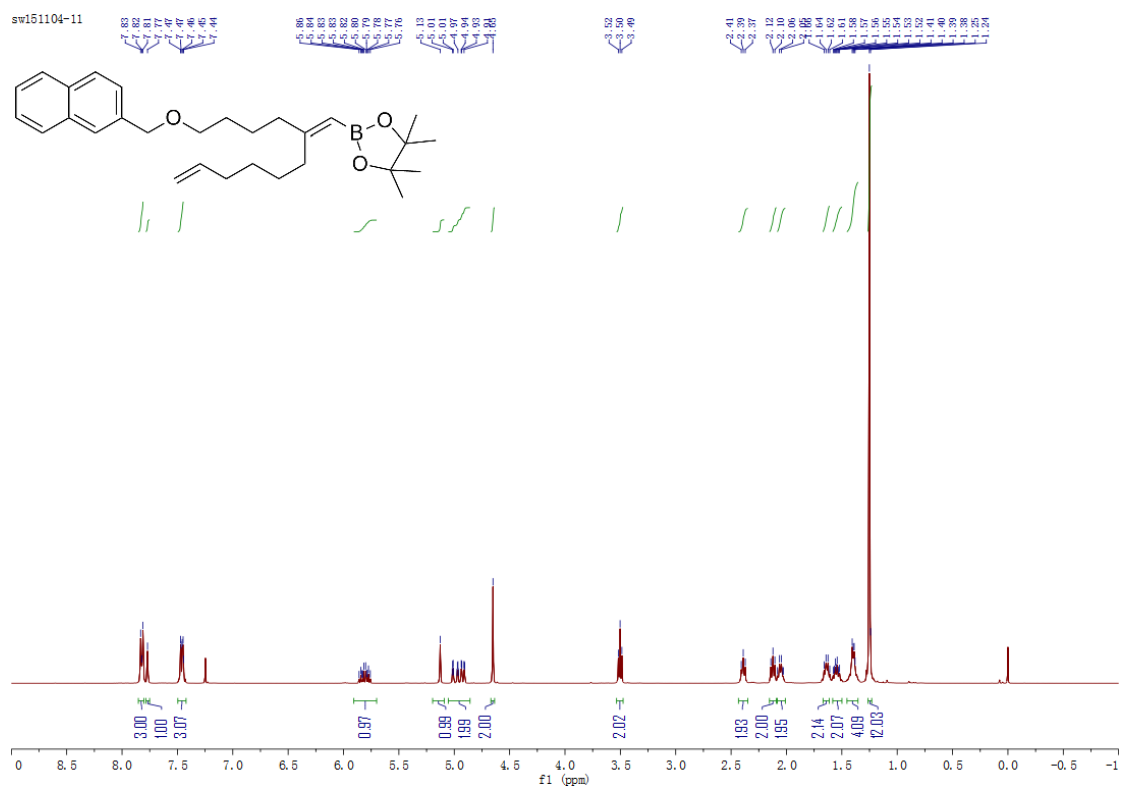


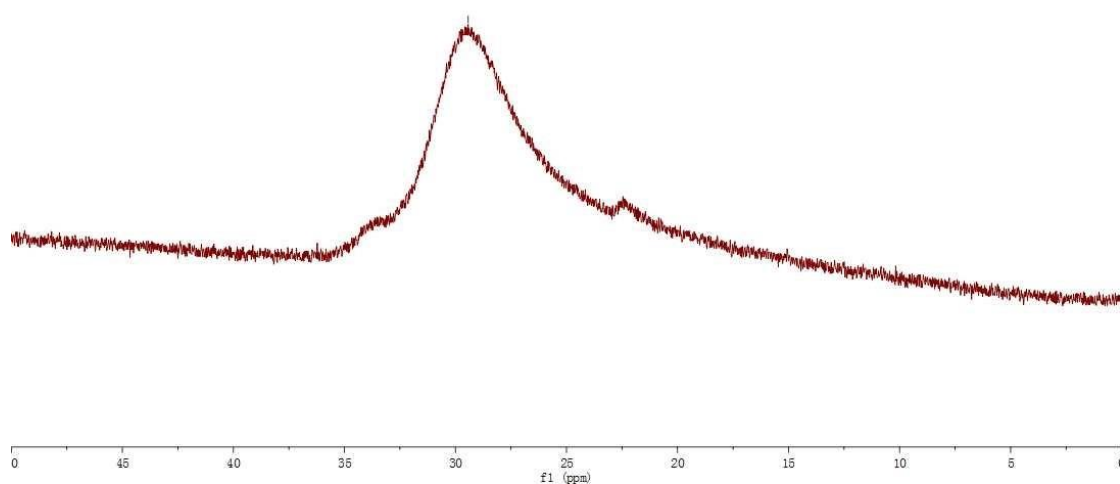
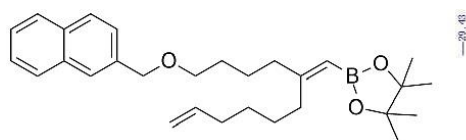
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 – 7.79 (m, 3H), 7.77 (s, 1H), 7.49 – 7.43 (m, 3H), 5.81 (m, 1H), 5.13 (s, 1H), 5.03 – 4.90 (m, 2H), 4.65 (s, 2H), 3.50 (t,  $J$  = 6.4 Hz, 2H), 2.39 (m, 2H), 2.12 (t,  $J$  = 7.3 Hz, 2H), 2.08 – 2.02 (m, 2H), 1.63 (m, 2H), 1.59 – 1.50 (m, 2H), 1.39 (m, 4H), 1.25 (m, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.99 (s), 139.20 (s), 136.17 (s), 133.32 (s), 132.96 (s), 128.14 (s), 127.90 (s), 127.70 (s), 126.29 (s), 126.03 (s), 125.79 (s), 125.76 (s), 114.16 (s), 82.56 (s), 73.03 (s), 70.38 (s), 38.80 (s), 34.47 (s), 33.60 (s), 29.54 (s), 28.97 (s), 28.77 (s), 24.88 (s), 24.42 (s).

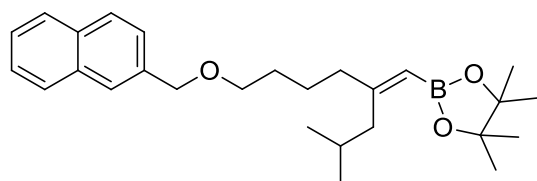
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.43.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{29}\text{H}_{41}\text{BO}_3[\text{H}]^+$ : 449.3227, Found: 449.3222.





**(Z)-2-(2-isobutyl-6-(naphthalen-2-ylmethoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3t**

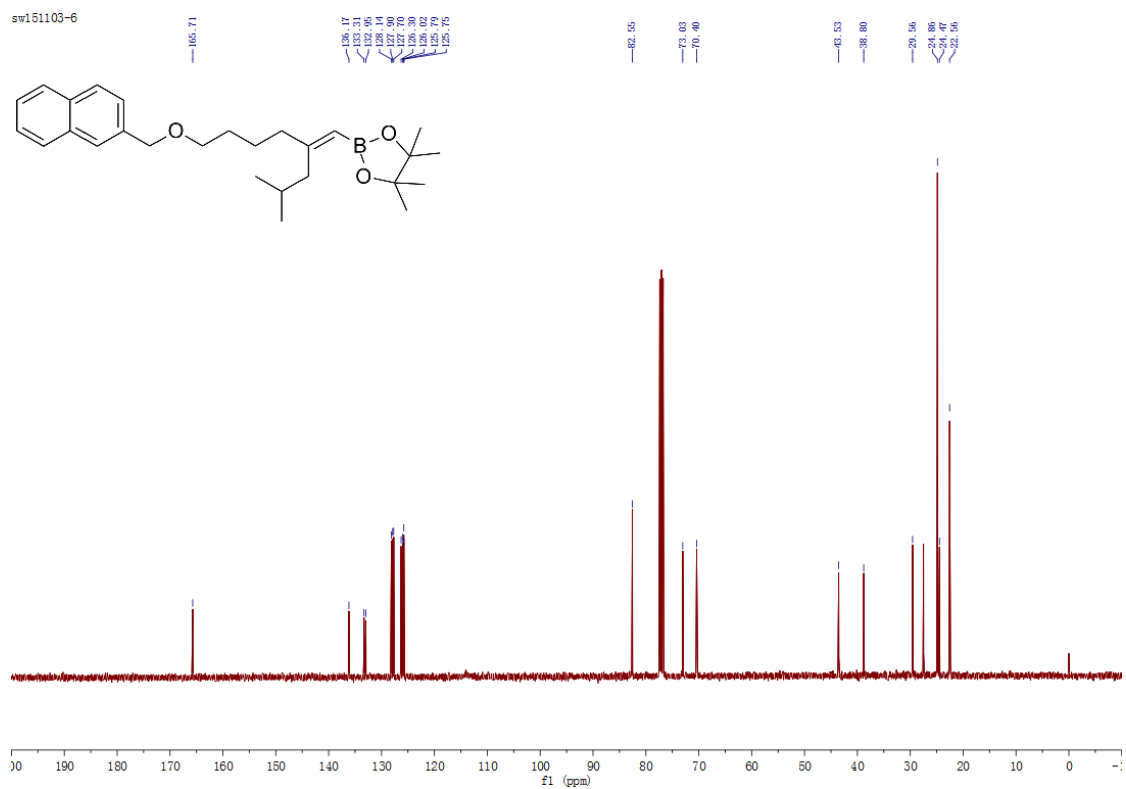
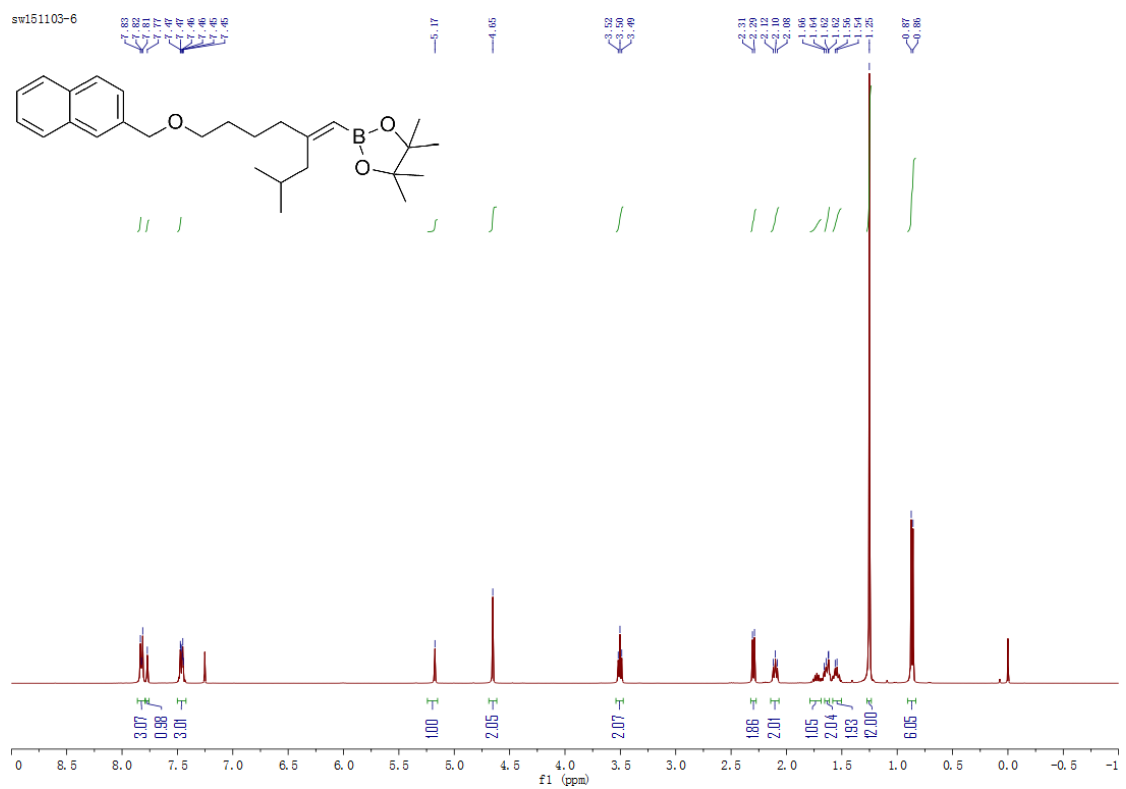


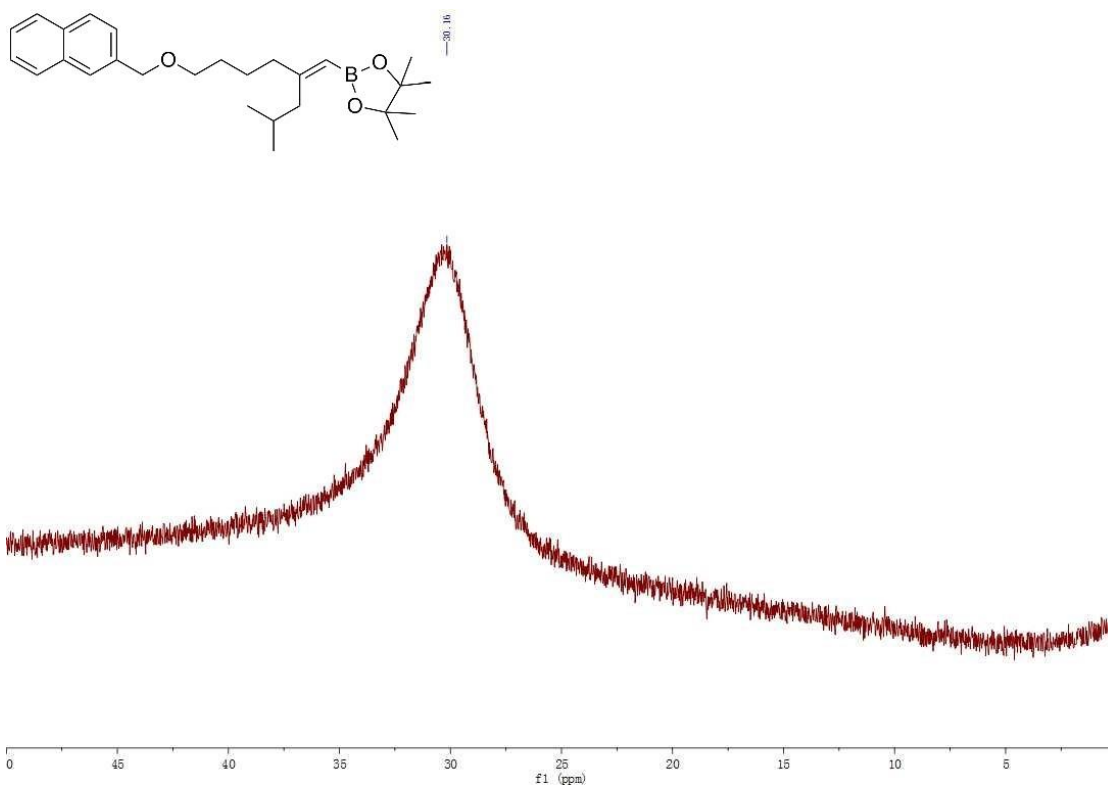
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.63 – 7.29 (m, 3H), 5.17 (s, 1H), 4.65 (s, 2H), 3.50 (t,  $J$  = 6.4 Hz, 2H), 2.30 (d,  $J$  = 7.3 Hz, 2H), 2.10 (t,  $J$  = 7.4 Hz, 2H), 1.73 (m, 1H), 1.64 (m, 2H), 1.55 (m, 2H), 1.25 (s, 12H), 0.87 (d,  $J$  = 4.0 Hz, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.71 (s), 136.17 (s), 133.31 (s), 132.95 (s), 128.14 (s), 127.90 (s), 127.70 (s), 126.30 (s), 126.02 (s), 125.79 (s), 125.75 (s), 82.55 (s), 73.03 (s), 70.40 (s), 43.53 (s), 38.80 (s), 29.56 (s), 27.49 (s), 24.86 (s), 24.47 (s), 22.56 (s).

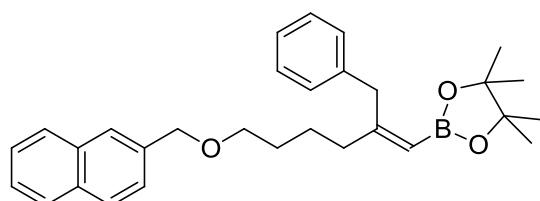
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.16.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{27}\text{H}_{40}\text{BO}_3[\text{H}]^+$ : 423.3071, Found: 423.3062.





**(Z)-2-(2-benzyl-6-(naphthalen-2-ylmethoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3u**

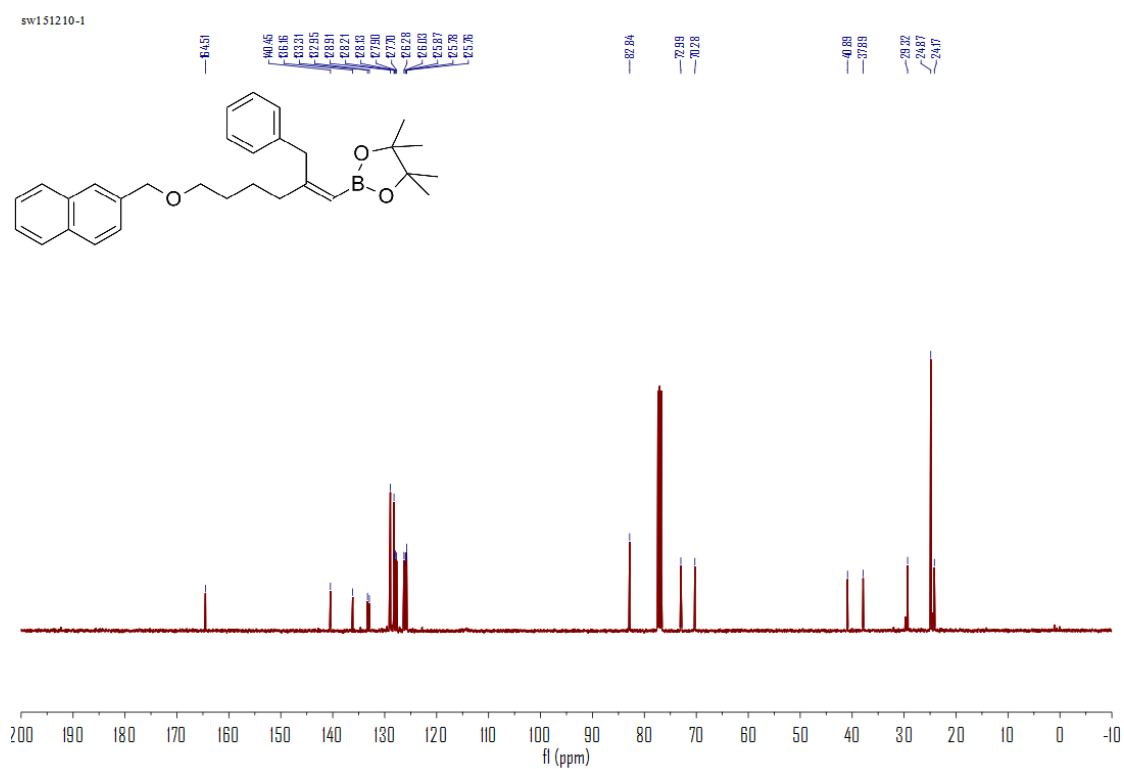
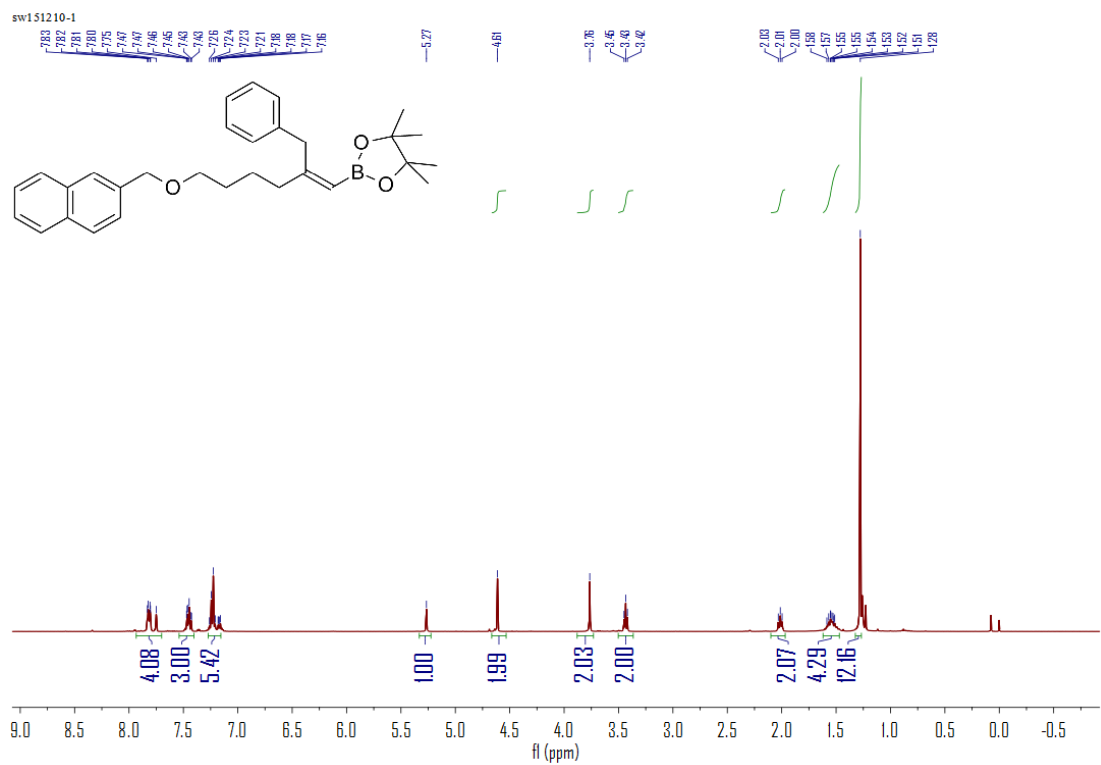


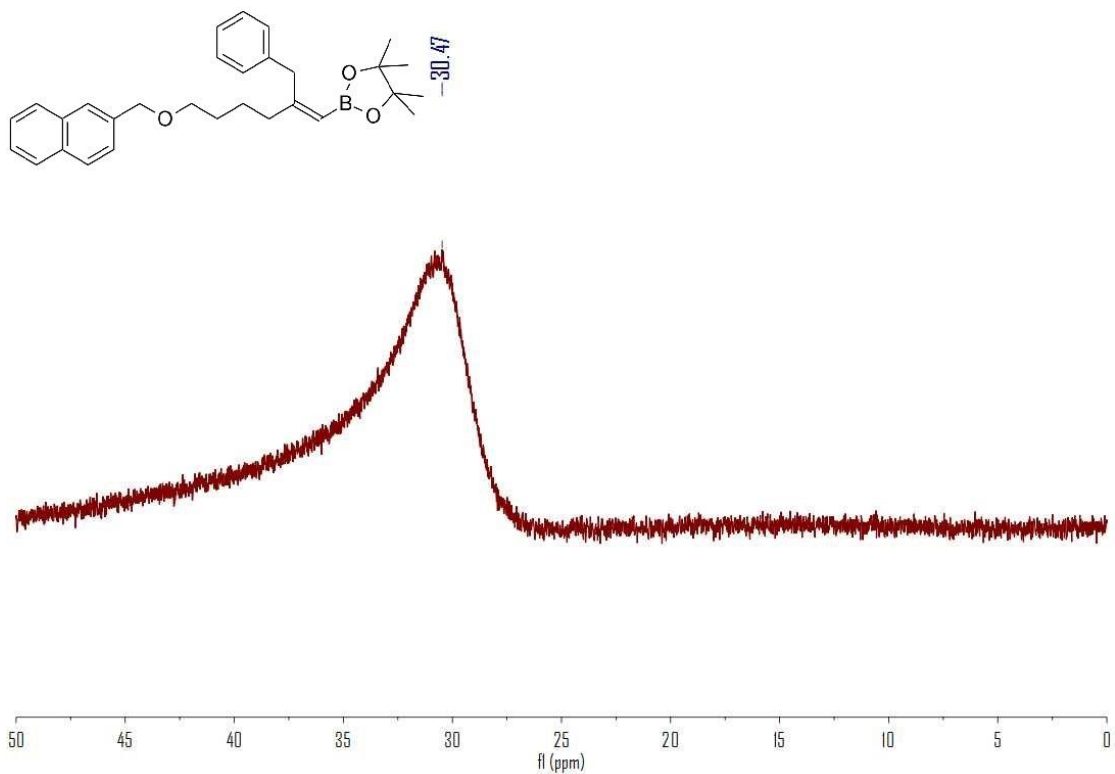
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 – 7.70 (m, 4H), 7.54 – 7.40 (m, 3H), 7.27 – 7.16 (m, 5H), 5.27 (s, 1H), 4.61 (s, 2H), 3.76 (s, 2H), 3.43 (t,  $J$  = 6.2 Hz, 2H), 2.01 (t,  $J$  = 7.0 Hz, 2H), 1.54 (ddd,  $J$  = 10.2, 9.5, 5.0 Hz, 4H), 1.28 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  164.51 (s), 140.45 (s), 136.16 (s), 133.31 (s), 132.95 (s), 128.91 (s), 128.21 (s), 128.13 (s), 127.90 (s), 127.70 (s), 126.28 (s), 126.03 (s), 125.87 (s), 125.78 (s), 125.76 (s), 82.84 (s), 72.99 (s), 70.28 (s), 40.89 (s), 37.89 (s), 29.32 (s), 24.87 (s), 24.17 (s).

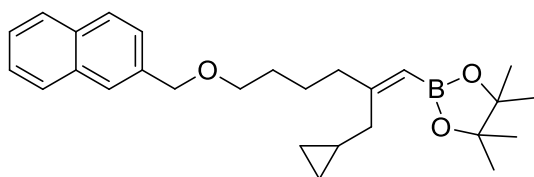
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.47.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{30}\text{H}_{37}\text{BO}_3$   $[\text{H}]^+$ : 457.2914, Found: 457.2913.





**(Z)-2-(2-(cyclopropylmethyl)-6-(naphthalen-2-ylmethoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, 3v**

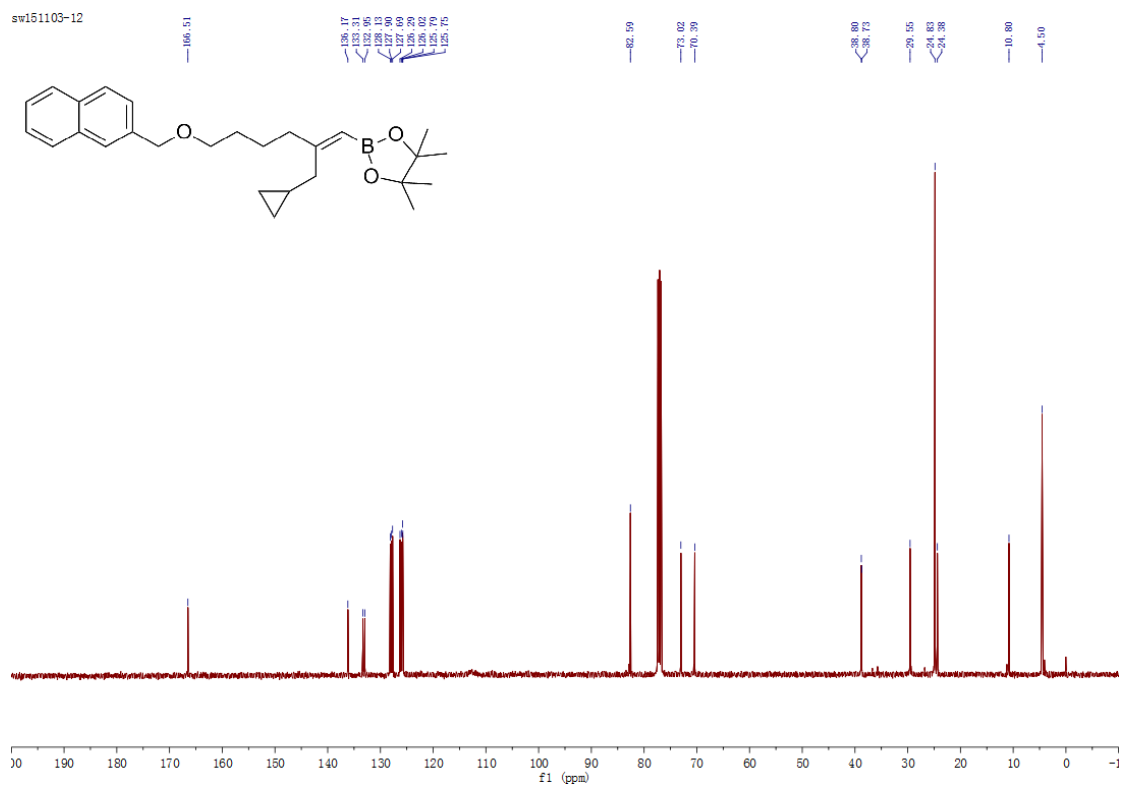
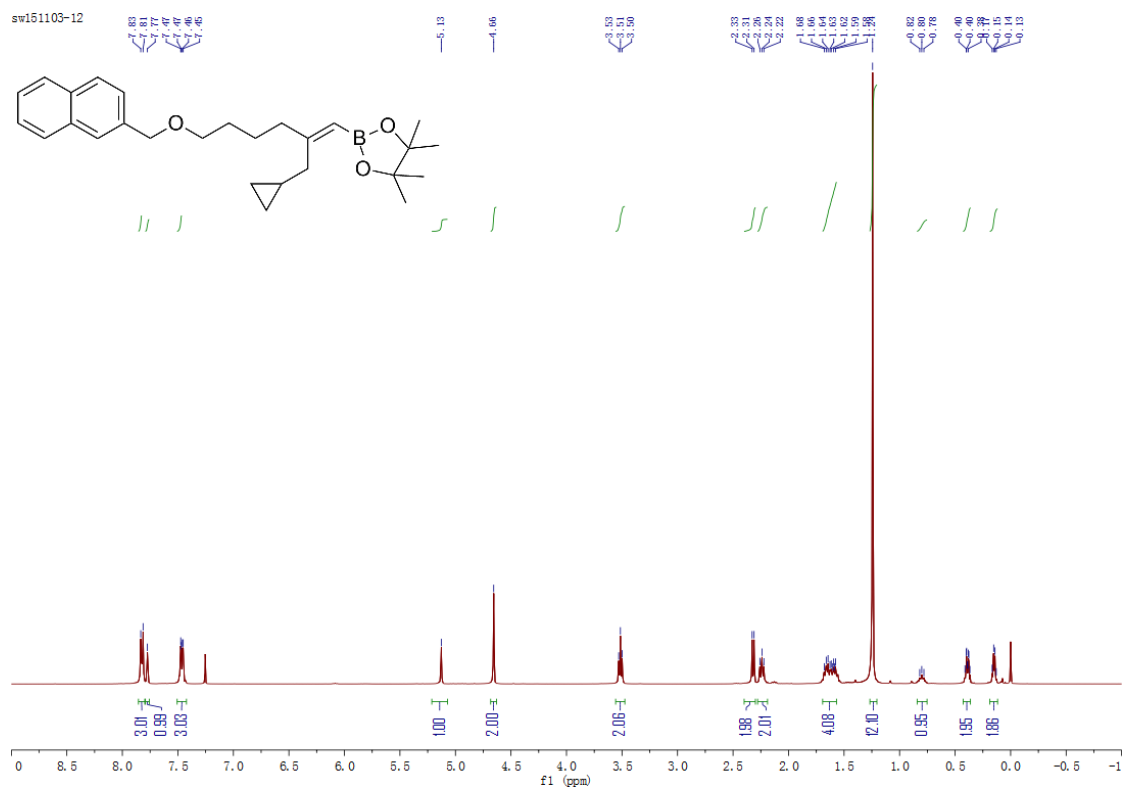


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (m, 3H), 7.77 (s, 1H), 7.46 (m, 3H), 5.13 (s, 1H), 4.66 (s, 2H), 3.51 (t,  $J = 6.3$  Hz, 2H), 2.32 (d,  $J = 7.0$  Hz, 2H), 2.24 (t,  $J = 7.2$  Hz, 2H), 1.69 – 1.55 (m, 4H), 1.24 (s, 12H), 0.85 – 0.76 (m, 1H), 0.43 – 0.36 (m, 2H), 0.15 (m, 2H).

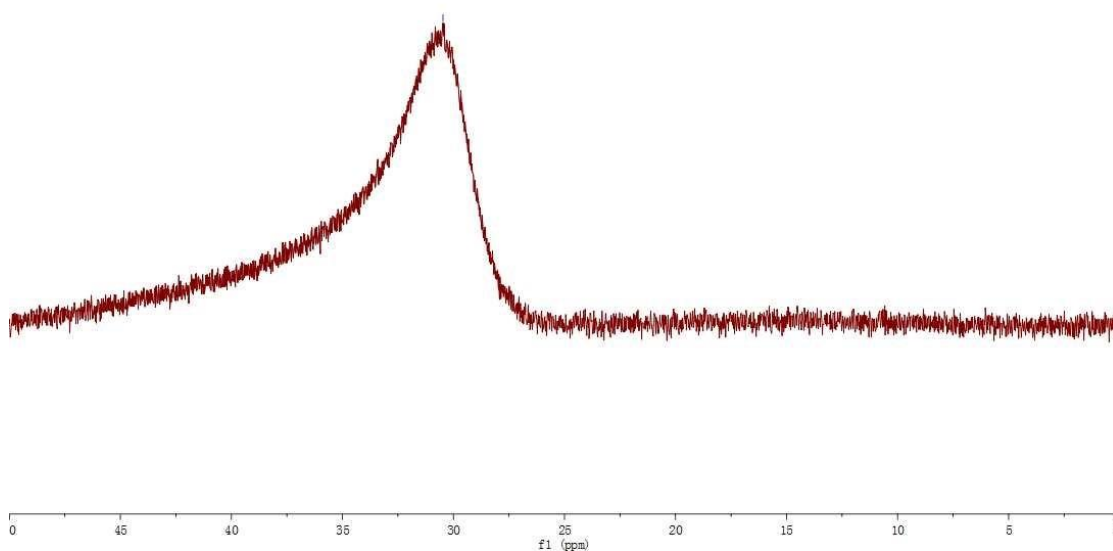
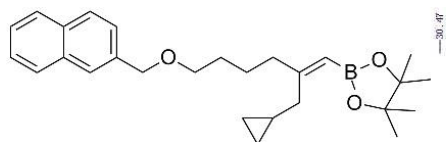
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.51 (s), 136.17 (s), 133.31 (s), 132.95 (s), 128.13 (s), 127.90 (s), 127.69 (s), 126.29 (s), 126.02 (s), 125.79 (s), 125.75 (s), 82.59 (s), 73.02 (s), 70.39 (s), 38.80 (s), 38.73 (s), 29.55 (s), 24.83 (s), 24.38 (s), 10.80 (s), 4.50 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.47.

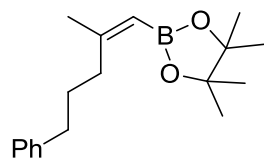
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{27}\text{H}_{37}\text{BO}_3[\text{H}]^+$ : 421.2914, Found: 421.2907.







**(Z)-4,4,5,5-tetramethyl-2-(2-methyl-5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane, 3w**



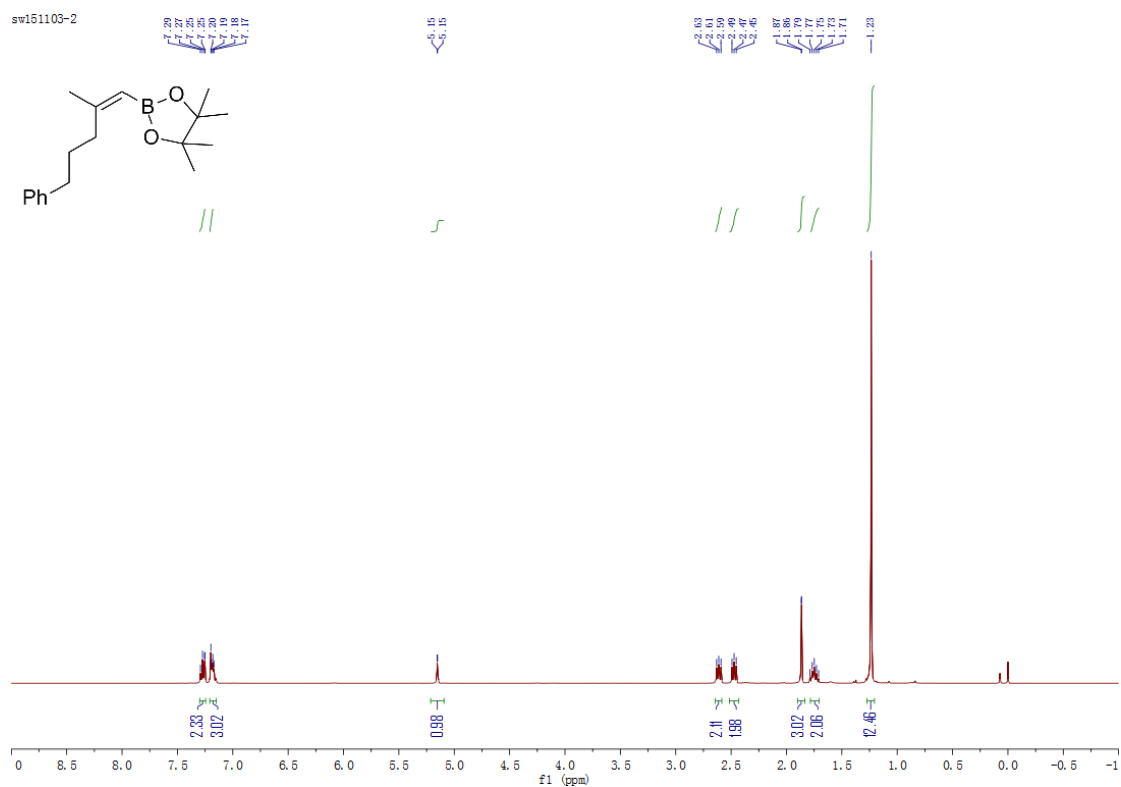
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.27 (m, 2H), 7.18 (m, 3H), 5.15 (s, 1H), 2.68 - 2.54 (t,  $J = 8.0\text{Hz}$ , 2H), 2.52 - 2.42 (t,  $J = 8.0\text{Hz}$ , 2H), 1.87 (s, 3H), 1.75 (m, 2H), 1.23 (s, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.04 (s), 142.78 (s), 128.40 (s), 128.23 (s), 125.58 (s), 82.53 (s), 35.96 (s), 35.82 (s), 30.75 (s), 26.45 (s), 24.80 (s).

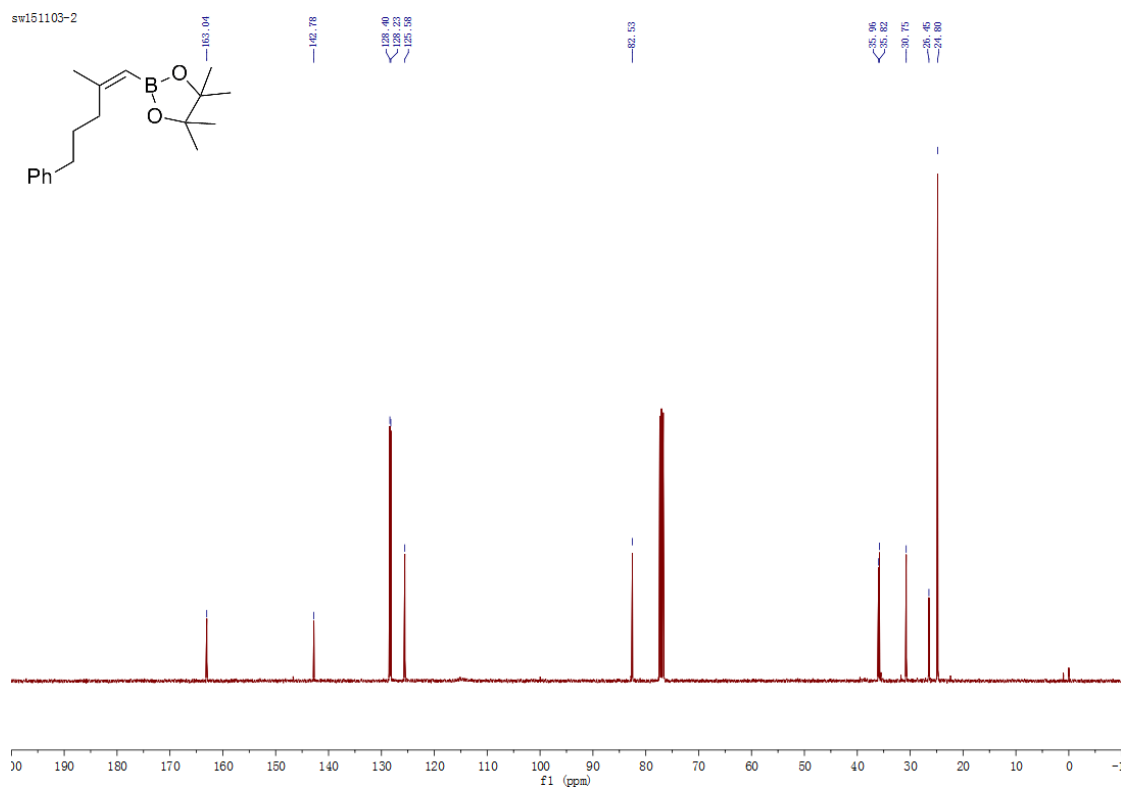
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.52.

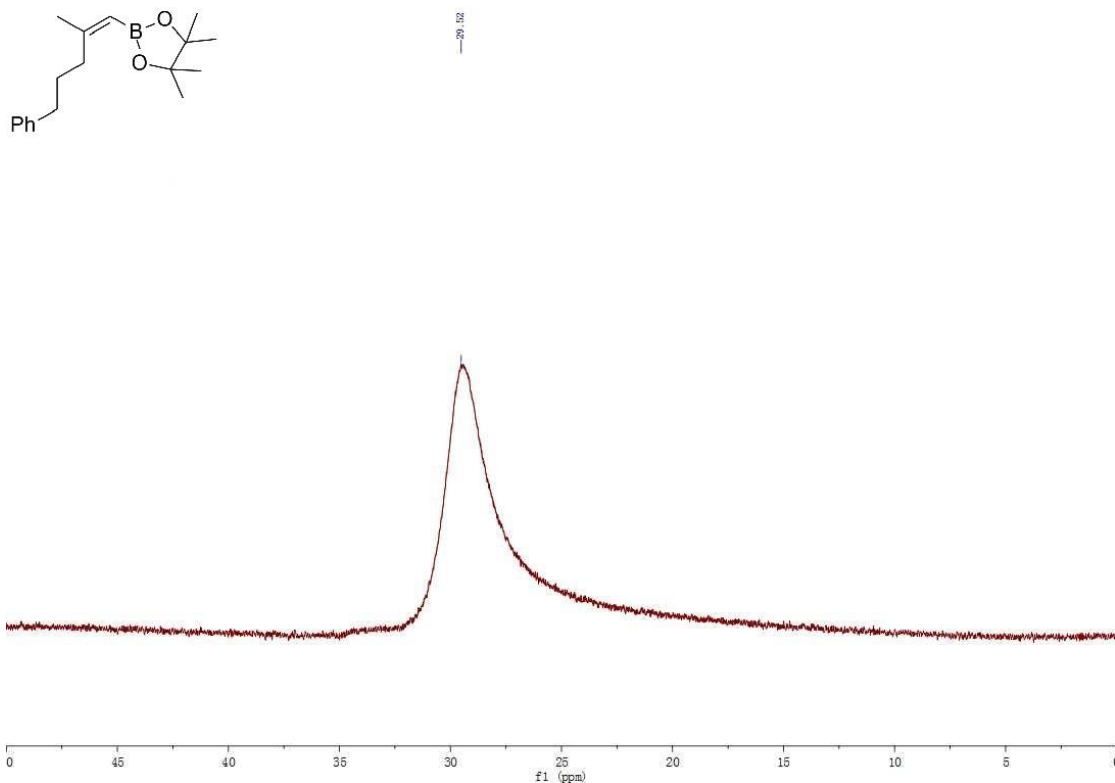
HRMS (EI $^+$ ): Calcd for  $\text{C}_{18}\text{H}_{27}\text{BO}_2[\text{H}]^+$ : 287.2182, Found: 287.2181.

sw151103-2

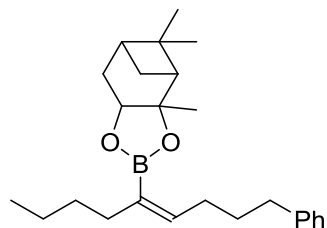


sw151103-2





**(E)-3a,5,5-trimethyl-2-(1-phenylnon-4-en-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4a**



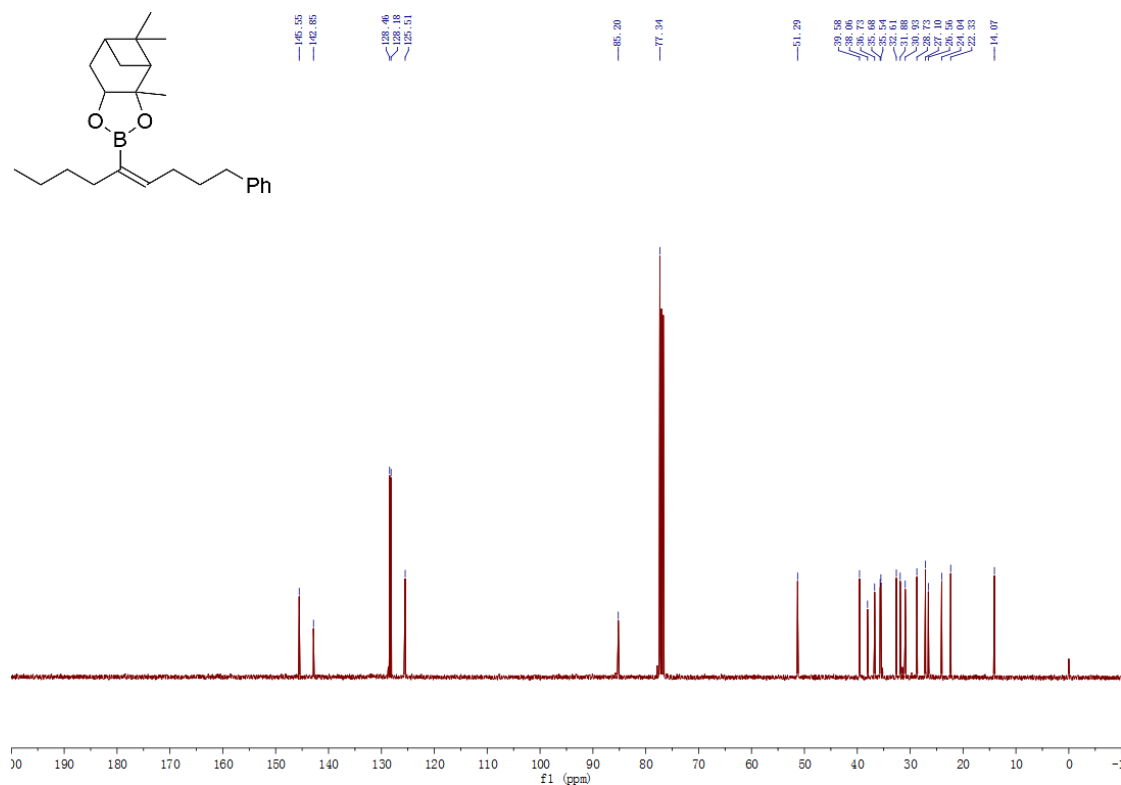
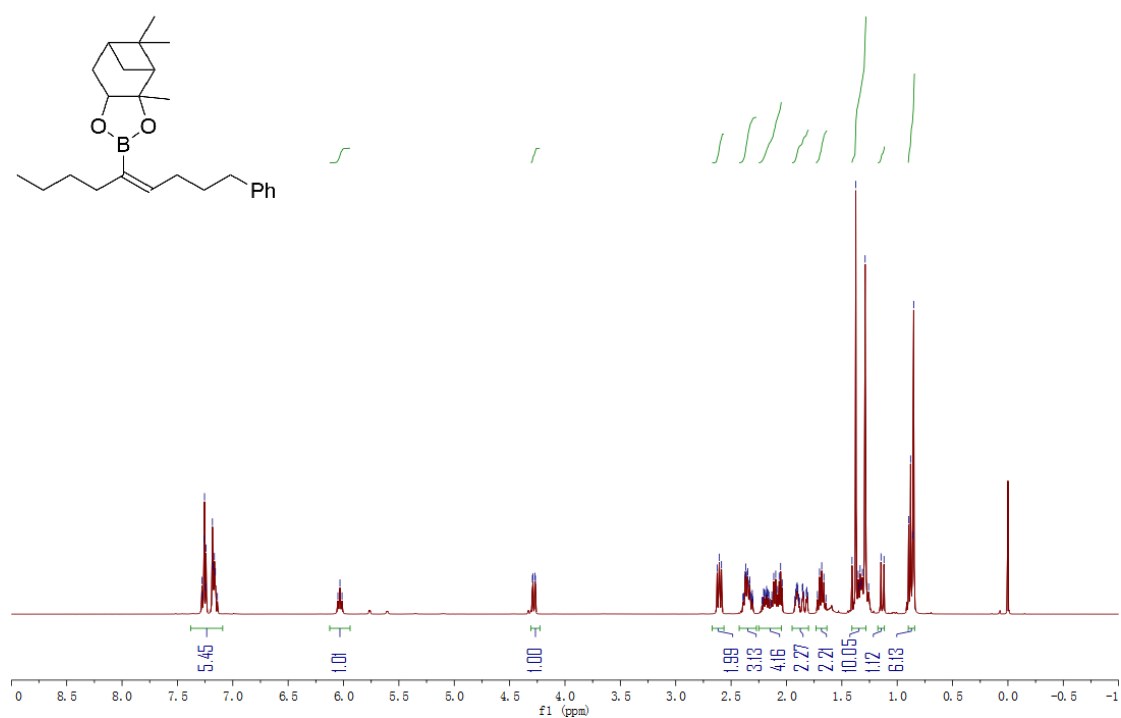
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.09 (m, 5H), 6.03 (t,  $J = 7.5$  Hz, 1H), 4.28 (dd,  $J = 8.8, 2.0$  Hz, 1H), 2.66 – 2.57 (m, 2H), 2.42 – 2.28 (m, 3H), 2.24 – 2.00 (m, 4H), 1.97 – 1.78 (m, 2H), 1.67 (m, 2H), 1.42 – 1.23 (m, 10H), 1.13 (d,  $J = 10.8$  Hz, 1H), 0.87 (m, 6H).

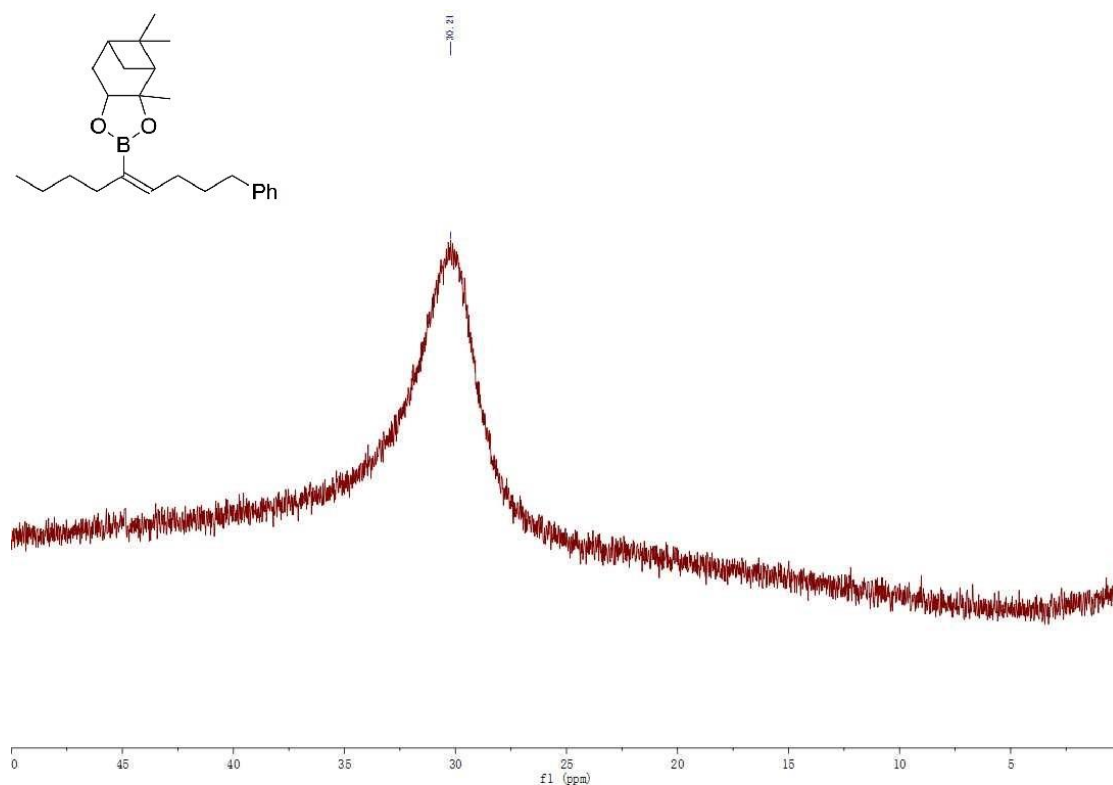
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.55 (s), 142.85 (s), 128.46 (s), 128.18 (s), 125.51 (s), 85.20 (s), 77.34 (s), 51.29 (s), 39.58 (s), 38.06 (s), 36.73 (s), 35.68 (s), 35.54 (s), 32.61 (s), 31.88 (s), 30.93 (s), 28.73 (s), 27.10 (s), 26.56 (s), 24.04 (s), 22.33 (s), 14.07 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.21.

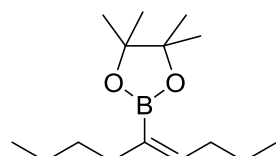
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{25}\text{H}_{37}\text{BO}_2$   $[\text{H}]^+$ : 381.2965, Found: 381.2962.

sw151106-2





**(E)-4,4,5,5-tetramethyl-2-(non-4-en-5-yl)-1,3,2-dioxaborolane, 4a-Bpin**



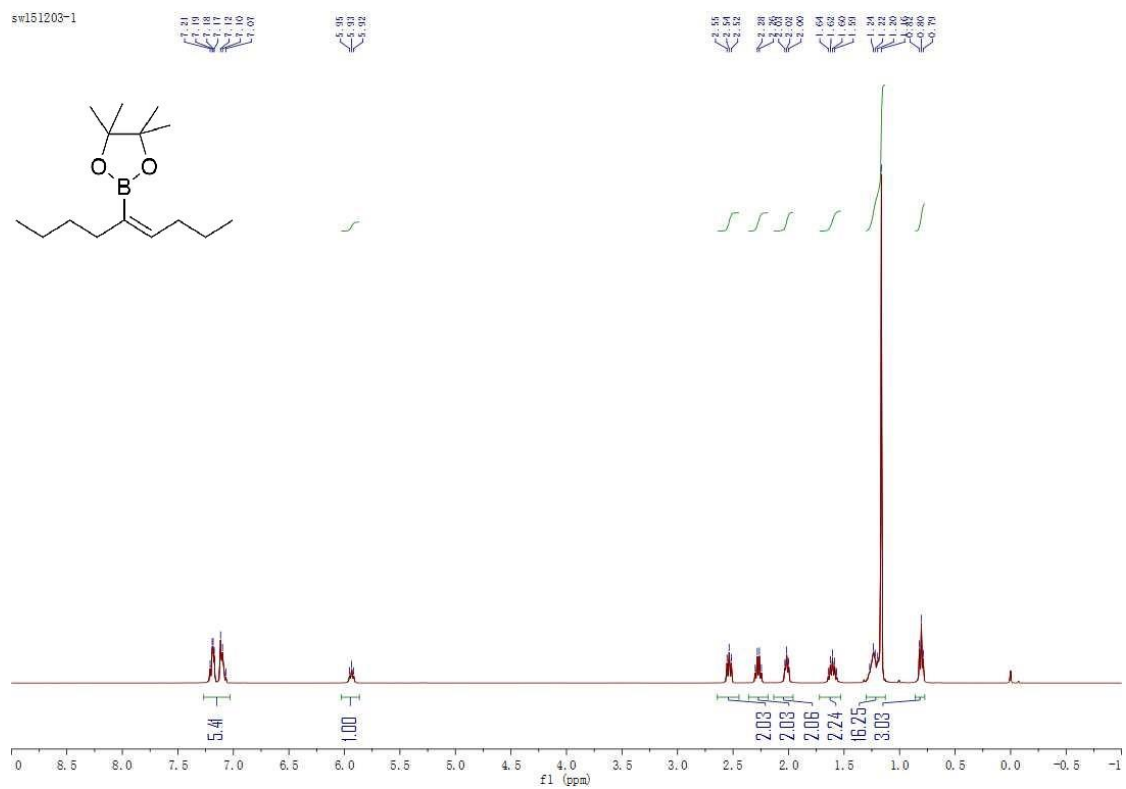
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 – 6.89 (m, 5H), 5.93 (t, *J* = 7.4 Hz, 1H), 2.53 (t, *J* = 7.8 Hz, 2H), 2.27 (m, 2H), 2.02 (m, 1H), 1.85 – 1.44 (m, 2H), 1.39 – 1.04 (m, 16H), 0.80 (t, *J* = 6.9 Hz, 3H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 145.21 (s), 142.86 (s), 128.48 (s), 128.20 (s), 125.53 (s), 82.79 (s), 36.58 (s), 35.58 (s), 32.57 (s), 31.90 (s), 30.92 (s), 24.77 (s), 22.33 (s), 14.07 (s).

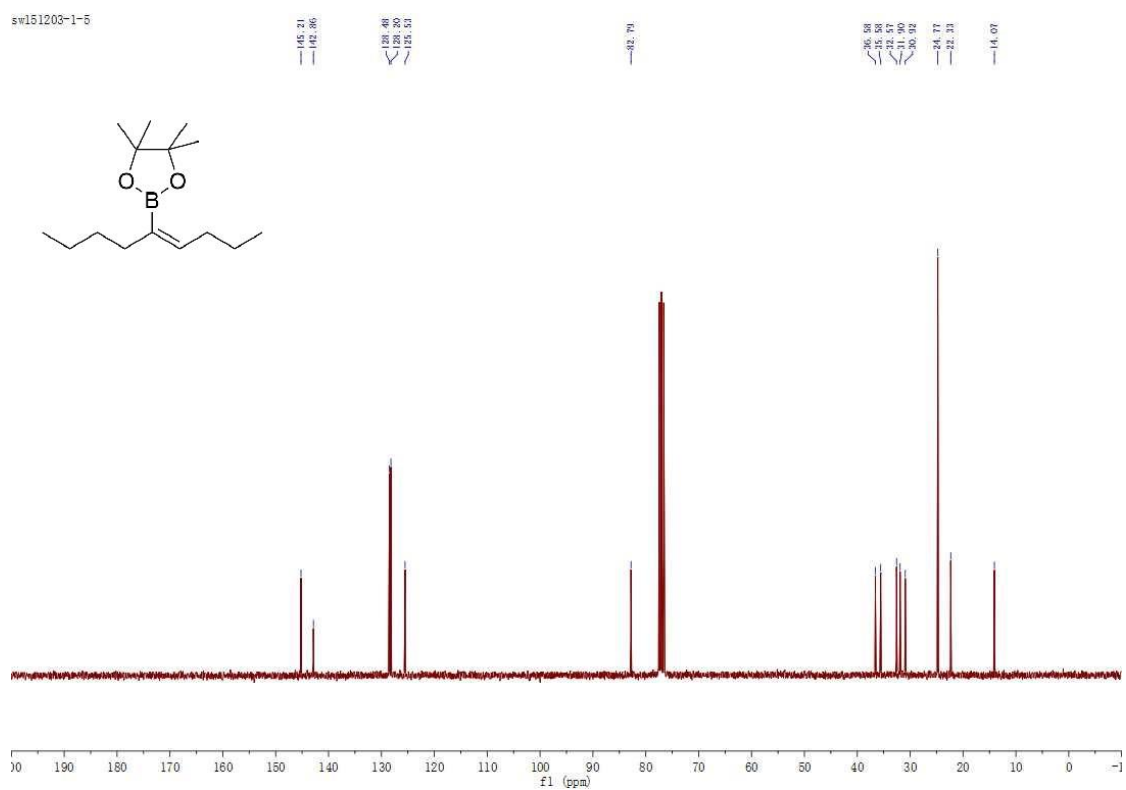
<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.93.

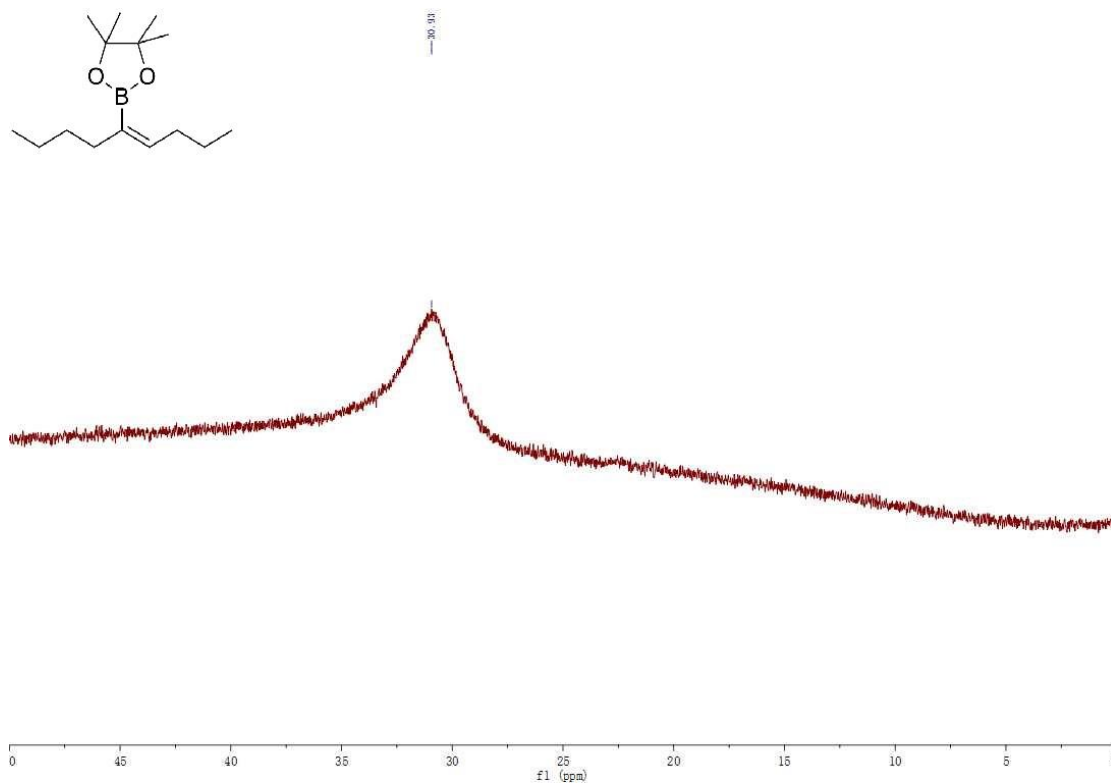
HRMS (EI<sup>+</sup>): Calcd for C<sub>15</sub>H<sub>29</sub>BO<sub>2</sub>[H]<sup>+</sup>: 253.2339, Found: 253.2334.

sw151203-1

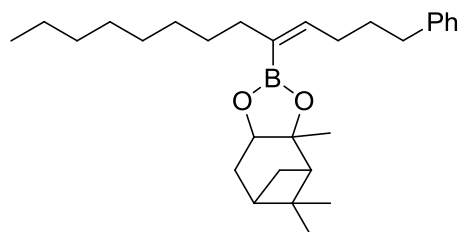


sw151203-1-5





**(E)-3a,5,5-trimethyl-2-(1-phenyltridec-4-en-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4b**

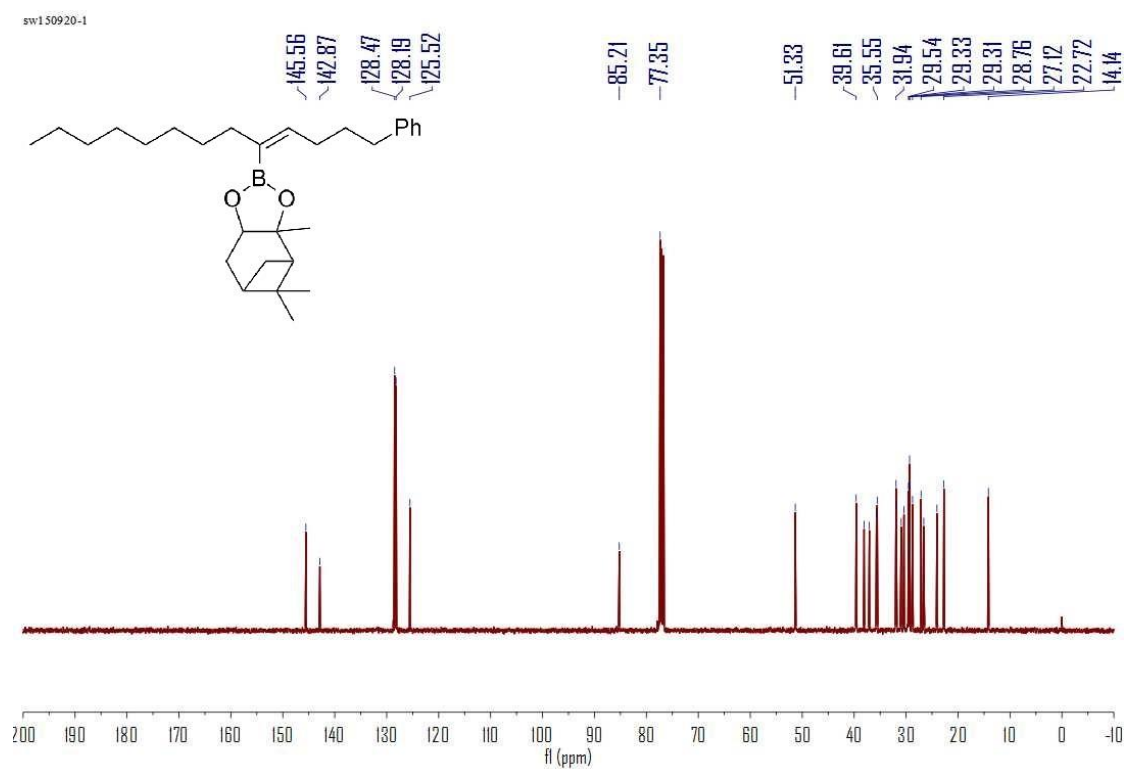
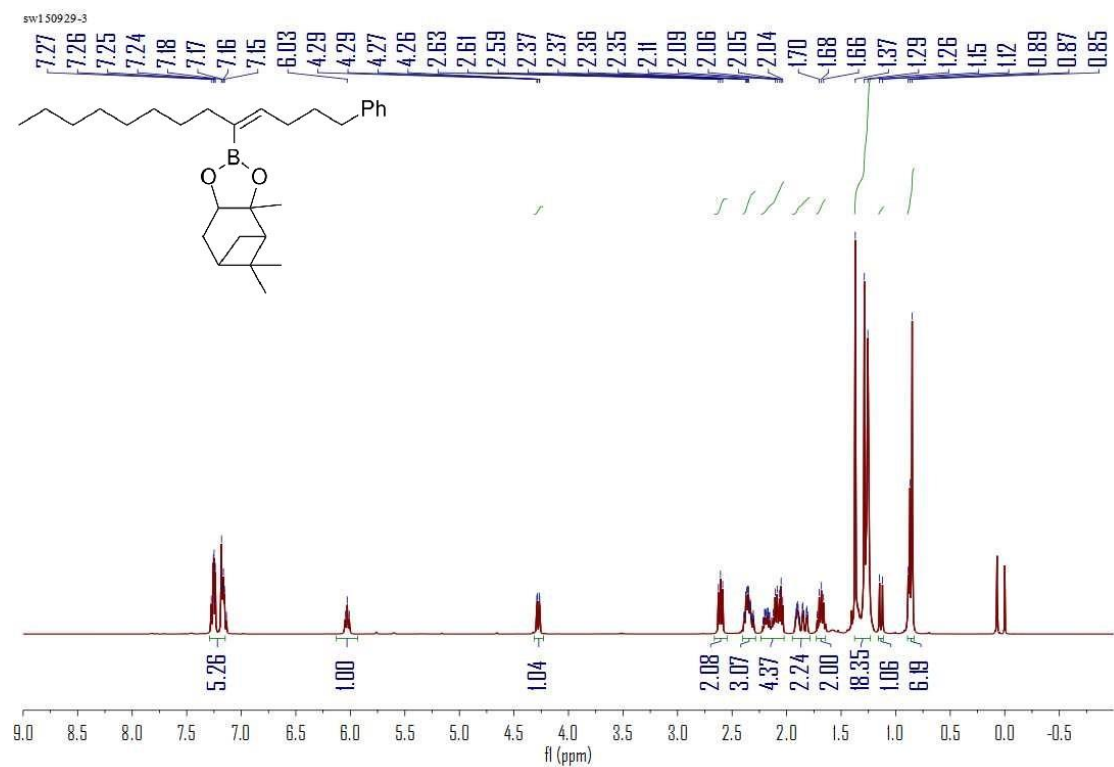


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.15 (m, 5H), 6.03 (t,  $J = 7.5$  Hz, 1H), 4.28 (dd,  $J = 8.8, 1.9$  Hz, 1H), 2.66 – 2.55 (m, 2H), 2.40 – 2.28 (m, 3H), 2.23 – 2.02 (m, 4H), 1.95 – 1.79 (m, 2H), 1.69 (dd,  $J = 15.5, 7.6$  Hz, 2H), 1.38 – 1.23 (m, 18H), 1.13 (d,  $J = 10.8$  Hz, 1H), 0.89 – 0.83 (m, 6H).

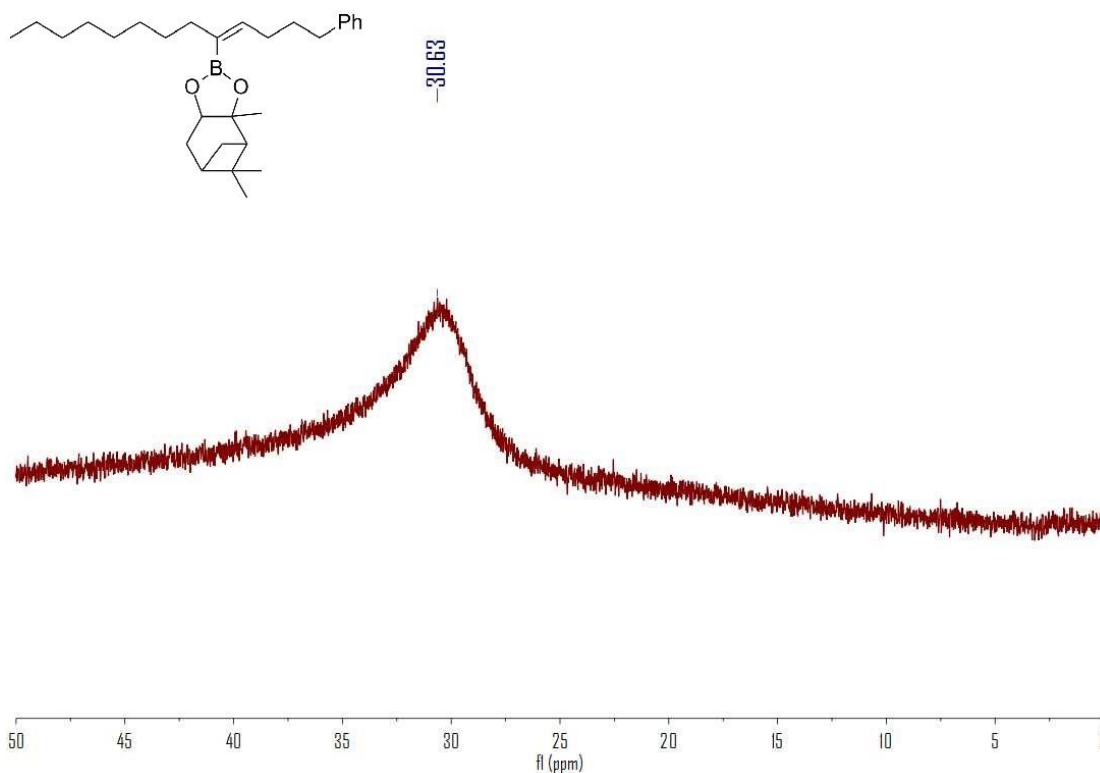
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.56 (s), 142.87 (s), 128.47 (s), 128.19 (s), 125.52 (s), 85.21 (s), 77.35 (s), 51.33 (s), 39.61 (s), 38.09 (s), 37.08 (s), 35.70 (s), 35.55 (s), 31.94 (s), 31.89 (s), 30.95 (s), 30.41 (s), 29.54 (s), 29.33 (s), 29.31 (s), 28.76 (s), 27.12 (s), 26.60 (s), 24.06 (s), 22.72 (s), 14.14 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.63.

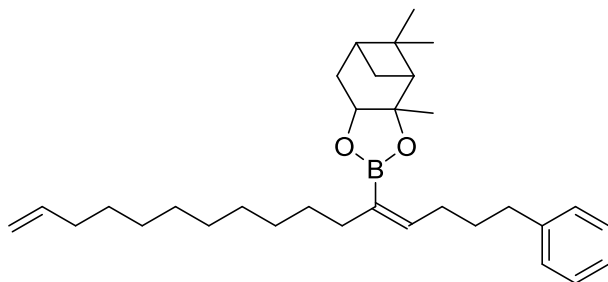
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{29}\text{H}_{45}\text{BO}_2[\text{H}]^+$ : 437.3591, Found: 437.3590.







**(E)-3a,5,5-trimethyl-2-(1-phenylhexadeca-4,15-dien-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4c**



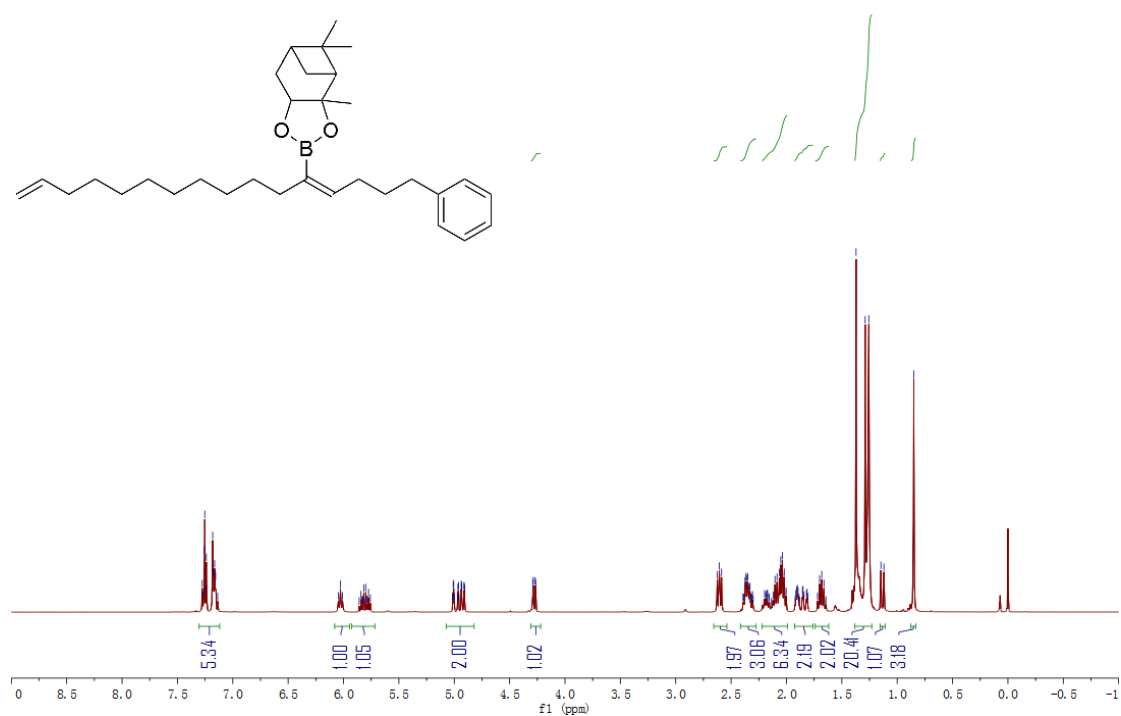
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.12 (m, 5H), 6.03 (t,  $J = 7.5$  Hz, 1H), 5.81 (ddt,  $J = 16.9, 10.2, 6.7$  Hz, 1H), 5.07 – 4.82 (m, 2H), 4.28 (dd,  $J = 8.8, 2.0$  Hz, 1H), 2.66 – 2.54 (m, 2H), 2.42 – 2.27 (m, 3H), 2.12 (dddd,  $J = 32.9, 19.4, 9.9, 5.5$  Hz, 6H), 1.93 – 1.76 (m, 2H), 1.74 – 1.62 (m, 2H), 1.38 – 1.23 (m, 20H), 1.13 (d,  $J = 10.8$  Hz, 1H), 0.85 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.57 (s), 142.86 (s), 139.31 (s), 128.47 (s), 128.19 (s), 125.52 (s), 114.08 (s), 85.22 (s), 77.35 (s), 51.33 (s), 39.61 (s), 38.09 (s), 37.07 (s), 35.70 (s), 35.55 (s), 33.86 (s), 31.89 (s), 30.95 (s), 30.40 (s), 29.59 (s), 29.55 (s), 29.53 (s), 29.29 (s), 29.20 (s), 28.97 (s), 28.76 (s), 27.12 (s), 26.60 (s), 24.06 (s).

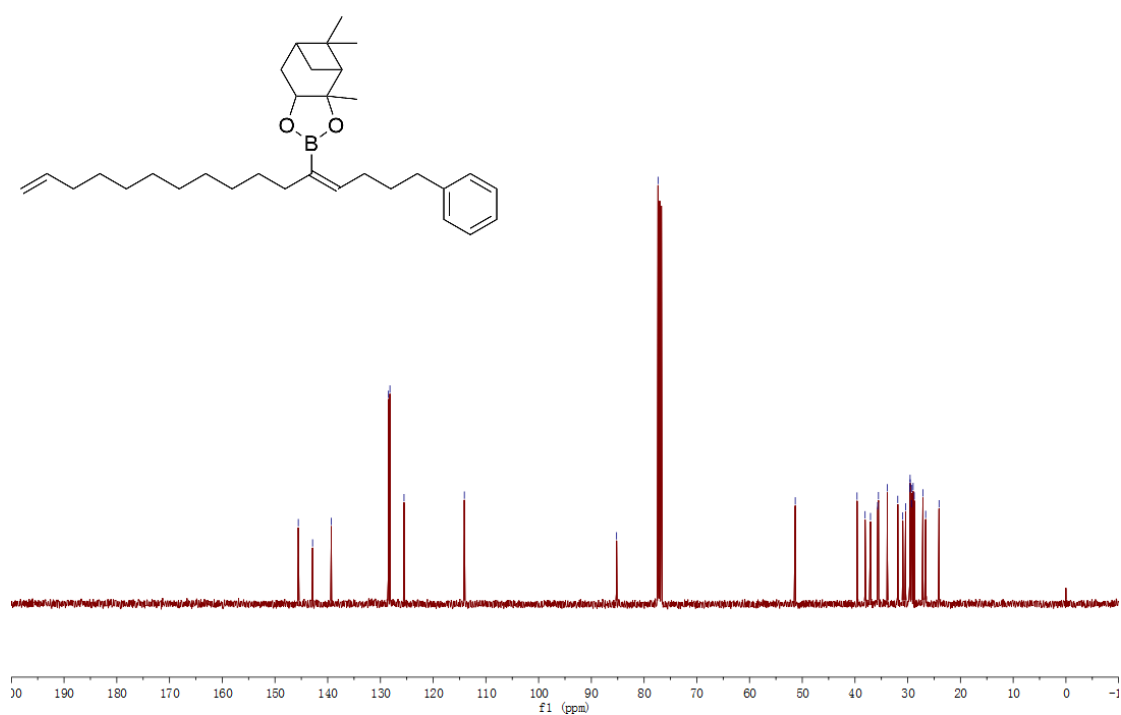
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.12.

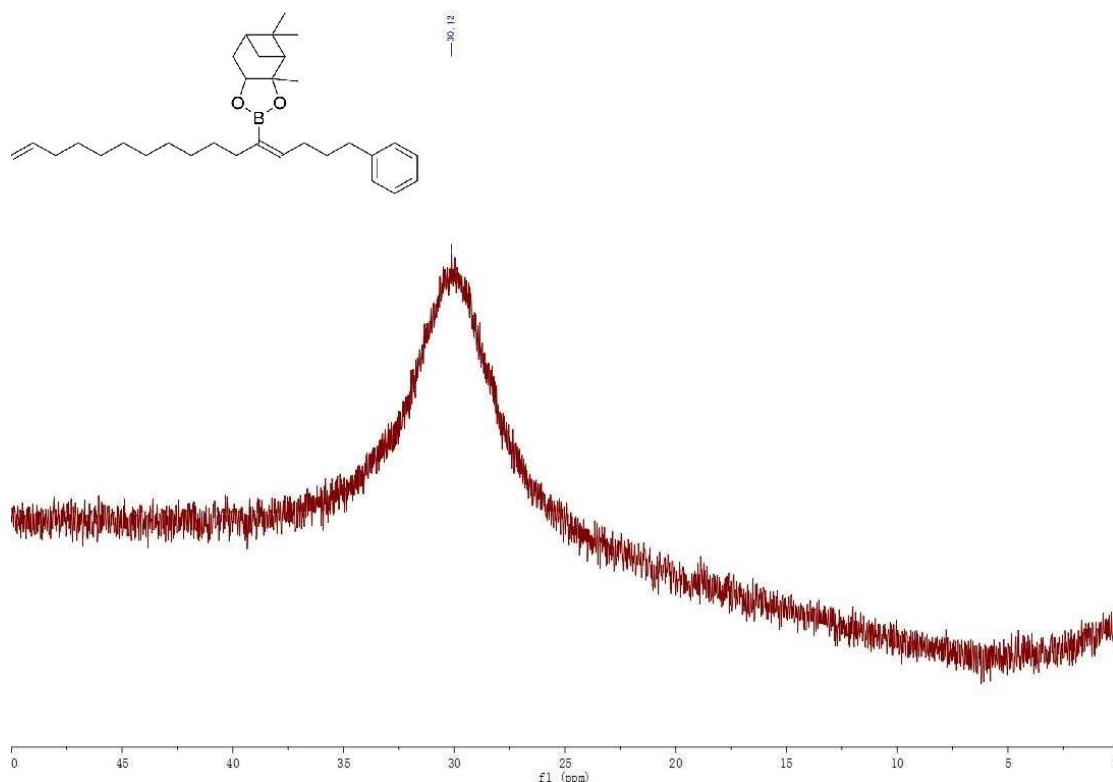
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{32}\text{H}_{50}\text{BO}_2$   $[\text{H}]^+$ : 477.3904, Found: 477.3895.

sw151027-4

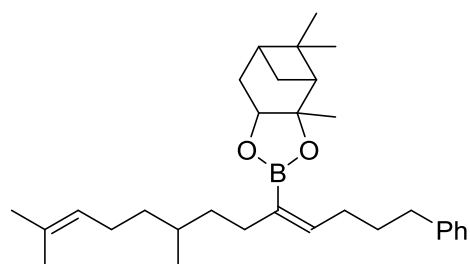


sw151027-4





**(E)-2-(8,12-dimethyl-1-phenyltrideca-4,11-dien-5-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4d**



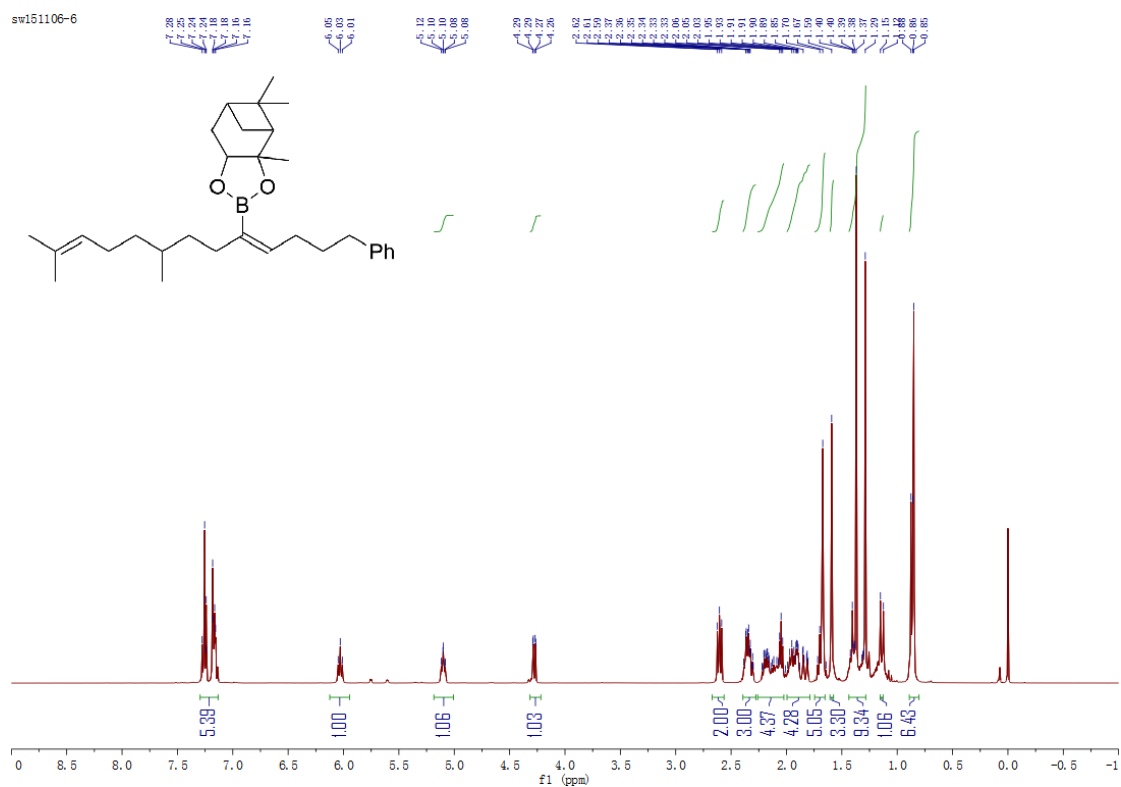
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.13 (m, 5H), 6.03 (t,  $J = 7.5$  Hz, 1H), 5.18 – 5.01 (m, 1H), 4.28 (dd,  $J = 8.7, 1.9$  Hz, 1H), 2.67 – 2.56 (m, 2H), 2.39 – 2.28 (m, 3H), 2.26 – 2.02 (m, 4H), 1.89 (m, 4H), 1.75 – 1.65 (m, 5H), 1.59 (s, 3H), 1.45 – 1.30 (m, 6H), 1.29 (s, 3H), 1.22 – 1.10 (m, 3H), 0.89 – 0.80 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.27 (s), 142.83 (s), 130.87 (s), 128.45 (s), 128.17 (s), 125.50 (s), 125.17 (s), 85.20 (s), 77.33 (s), 51.28 (s), 39.58 (s), 38.06 (s), 37.63 (d,  $J = 4.1$  Hz), 37.04 (d,  $J = 11.0$  Hz), 35.67 (s), 35.53 (s), 34.50 (s), 32.07 (d,  $J = 3.3$  Hz), 31.86 (s), 30.94 (s), 28.73 (s), 27.10 (s), 26.59 (s), 25.73 (s), 25.51 (s), 24.04 (s), 19.58 (d,  $J = 10.1$  Hz), 17.63 (s).

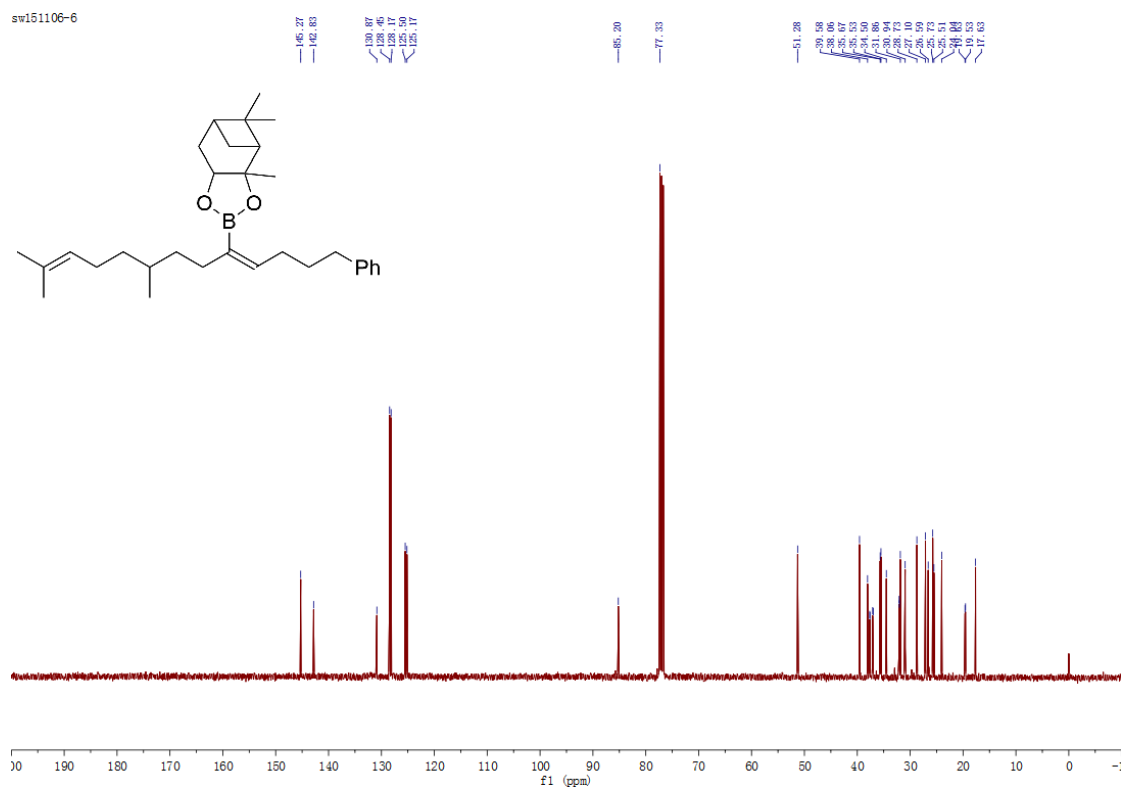
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.43.

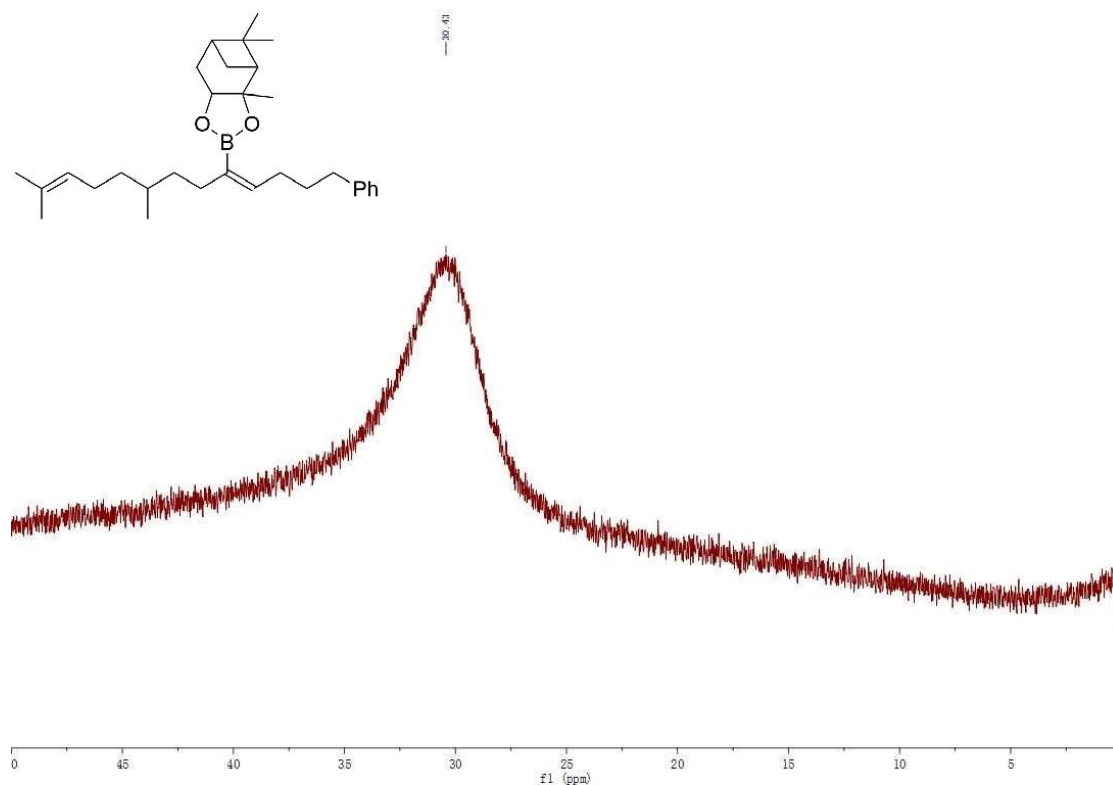
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{31}\text{H}_{47}\text{BO}_2$   $[\text{H}]^+$ : 463.3747, Found: 463.3743.

sw151106-6

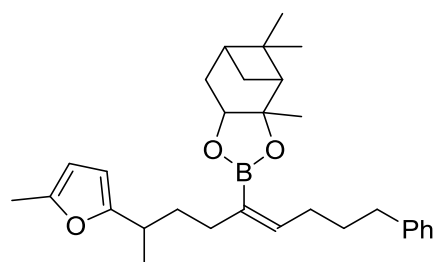


sw151106-6





**(E)-3a,5,5-trimethyl-2-(8-(5-methylfuran-2-yl)-1-phenylnon-4-en-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4e**



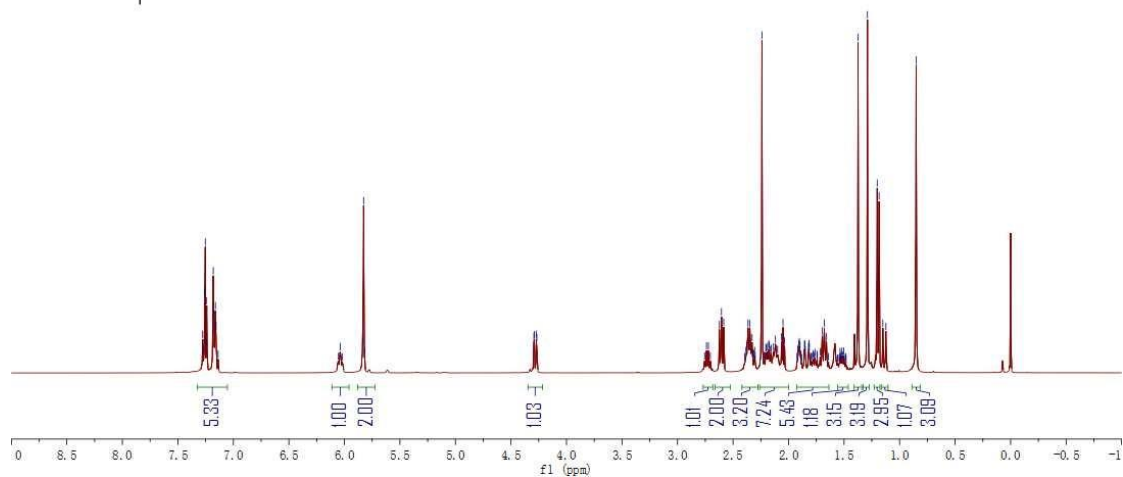
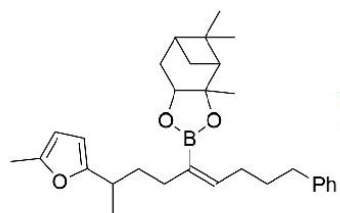
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 6.95 (m, 5H), 6.04 (t,  $J$  = 6.6 Hz, 1H), 5.96 – 5.68 (m, 2H), 4.28 (dd,  $J$  = 8.7, 1.9 Hz, 1H), 2.73 (m, 1H), 2.65 – 2.54 (m, 2H), 2.49 – 2.28 (m, 3H), 2.28 – 2.02 (m, 7H), 1.95 – 1.64 (m, 5H), 1.58 – 1.49 (m, 1H), 1.37 (s, 3H), 1.29 (s, 3H), 1.19 (d,  $J$  = 6.9 Hz, 3H), 1.14 (d,  $J$  = 10.9 Hz, 1H), 0.85 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.22 (d,  $J$  = 7.6 Hz), 149.82 (s), 146.03 (d,  $J$  = 7.7 Hz), 142.83 (s), 128.48 (s), 128.21 (s), 125.54 (s), 105.50 (s), 103.84 (d,  $J$  = 5.1 Hz), 85.27 (s), 77.39 (s), 51.31 (s), 39.61 (s), 38.08 (s), 36.24 (d,  $J$  = 7.6 Hz), 35.67 (s), 35.55 (s), 34.63 (s), 32.58 (d,  $J$  = 5.6 Hz), 31.85 (s), 30.97 (s), 28.75 (s), 27.13 (s), 26.62 (s), 24.07 (s), 19.21 (d,  $J$  = 16.8 Hz), 13.57 (s).

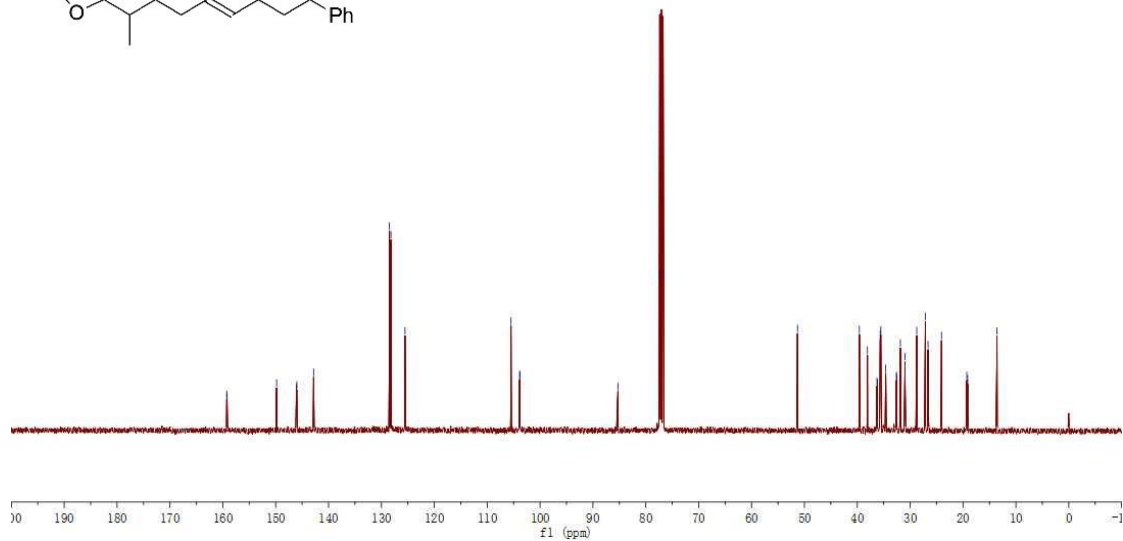
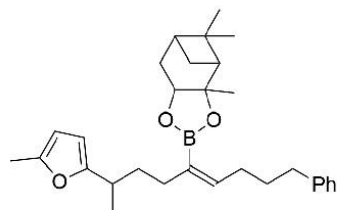
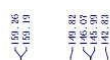
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.36.

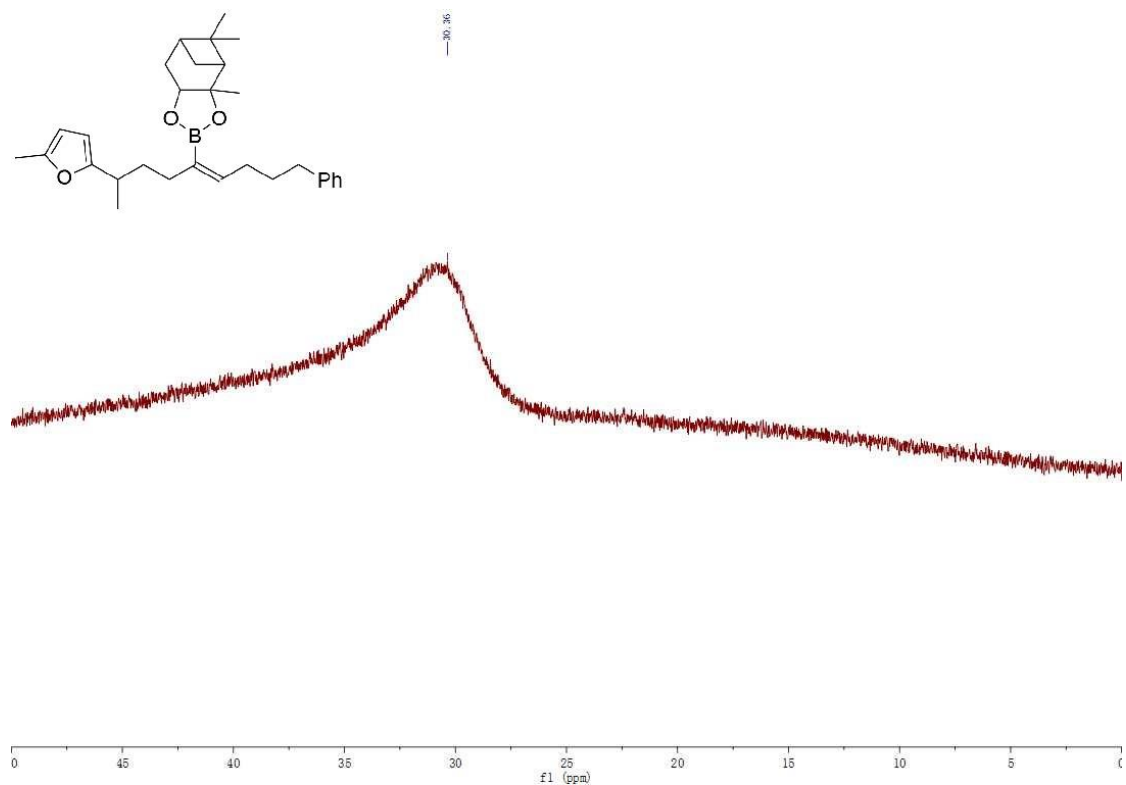
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{30}\text{H}_{41}\text{BO}_3$  [ $\text{H}$ ] $^+$ : 461.3227, Found: 461.3218.

sw151106-5

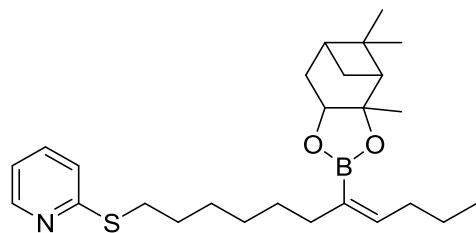


sw151106-5





**(E)-2-((7-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)undec-7-en-1-yl)thio)pyridine, 4f**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 1H), 7.47 (m, 1H), 7.16 (d,  $J = 7.8$  Hz, 1H), 7.06 – 6.85 (m, 1H), 6.00 (t,  $J = 7.5$  Hz, 1H), 4.30 (dd,  $J = 8.8, 1.9$  Hz, 1H), 3.15 (t,  $J = 7.4$  Hz, 2H), 2.41 – 2.02 (m, 7H), 1.96 – 1.78 (m, 2H), 1.69 (m, 2H), 1.52 – 1.21 (m, 14H), 1.16 (d,  $J = 10.8$  Hz, 1H), 0.87 (m, 6H).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.71, 149.31, 146.18, 135.90, 122.12, 119.15, 85.17, 77.36, 51.33, 39.60, 38.09, 36.99, 35.74, 33.17, 30.26, 30.23, 29.26, 28.86, 28.83, 28.77, 27.11, 26.60, 24.06, 23.17, 13.72.

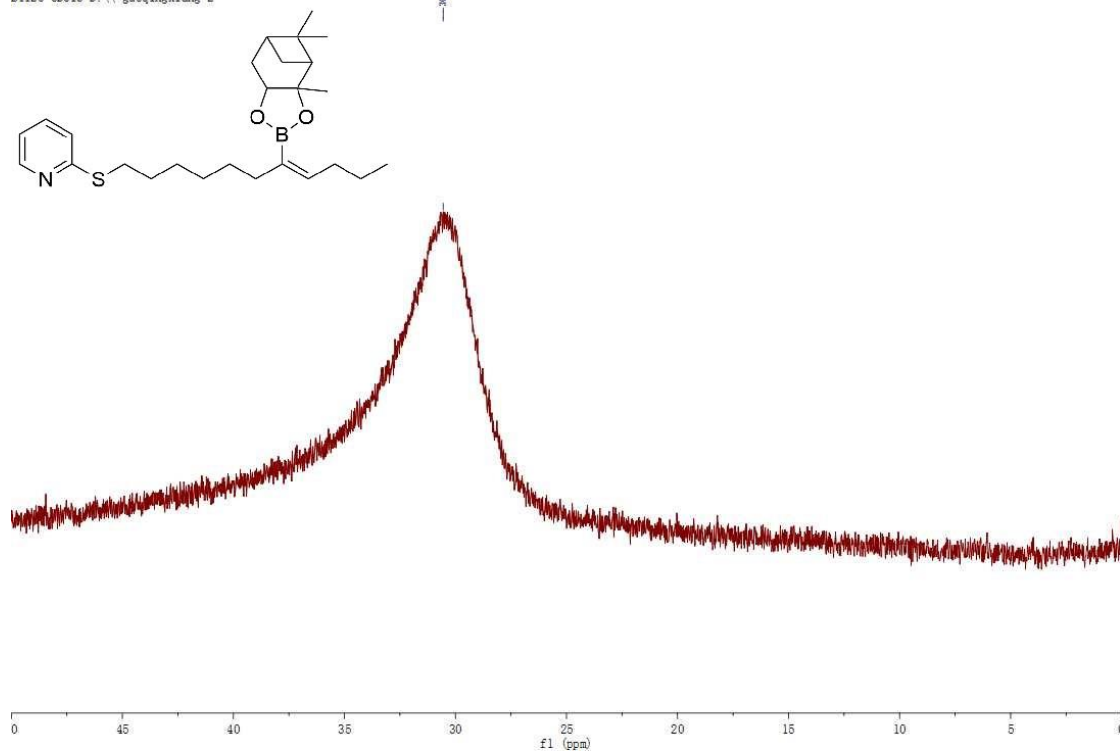
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.55.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{40}\text{BNO}_2\text{S}[\text{H}]^+$ : 442.2951, Found: 442.2942.

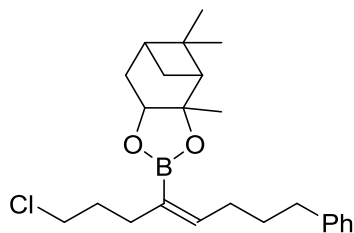




106L15\_SW151026\_5  
B11ZG CDC13 D:\ guoqingxiang 2



**(E)-2-(1-chloro-8-phenyloct-4-en-4-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4g**



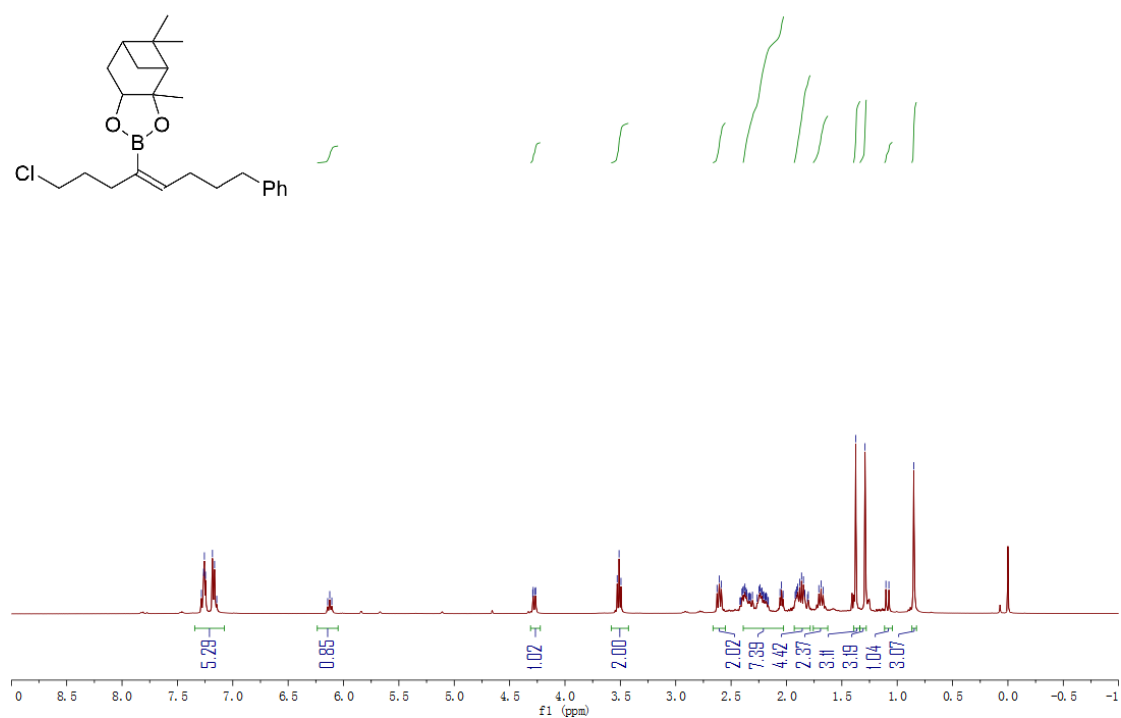
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (m, 5H), 6.12 (t,  $J = 7.5$  Hz, 1H), 4.28 (dd,  $J = 8.7, 1.7$  Hz, 1H), 3.51 (t,  $J = 6.8$  Hz, 2H), 2.65 – 2.58 (m, 2H), 2.45 – 1.95 (m, 7H), 1.92 – 1.78 (m, 4H), 1.74 – 1.64 (m, 2H), 1.37 (s, 3H), 1.29 (s, 3H), 1.09 (d,  $J = 10.8$  Hz, 1H), 0.85 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.81 (s), 142.71 (s), 128.46 (s), 128.22 (s), 125.58 (s), 85.35 (s), 77.47 (s), 51.35 (s), 44.68 (s), 39.62 (s), 38.09 (s), 35.65 (s), 35.55 (s), 34.11 (s), 33.03 (s), 31.77 (s), 30.89 (s), 28.74 (s), 27.11 (s), 26.59 (s), 24.02 (s).

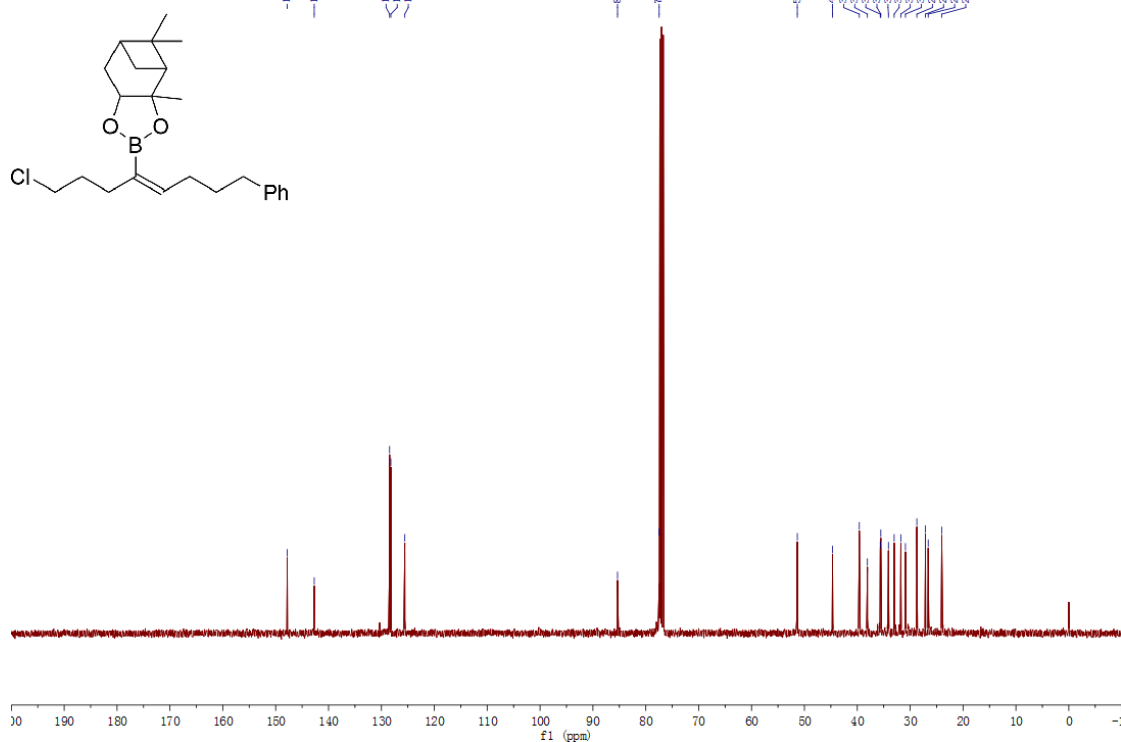
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.98.

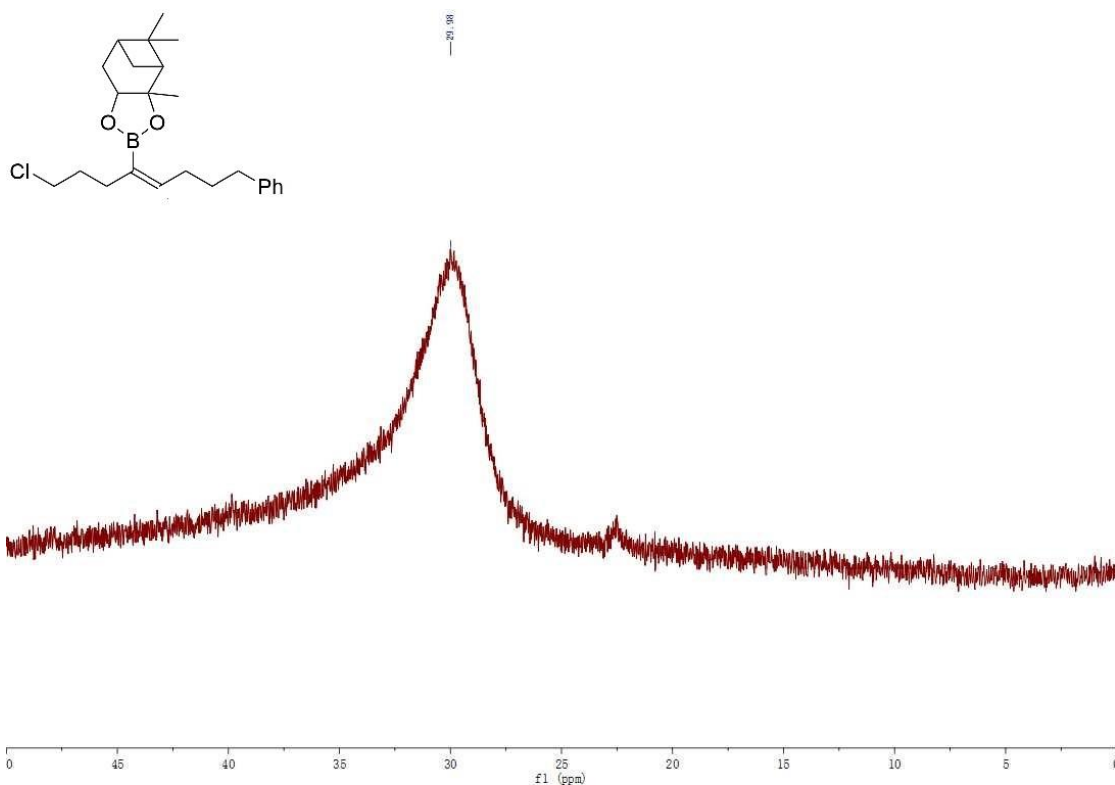
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{24}\text{H}_{34}\text{BO}_2\text{Cl}$   $[\text{H}]^+$ : 401.2419, Found: 401.2413.

sw151111-4

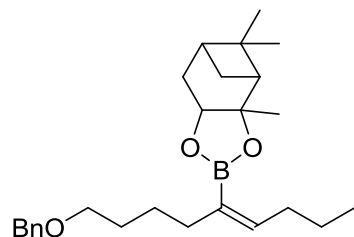


106L15\_SW151111\_4  
C13CPD CDCl3 D:\guoqingxiang 36





**(E)-2-(9-(benzyloxy)non-4-en-5-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4h**



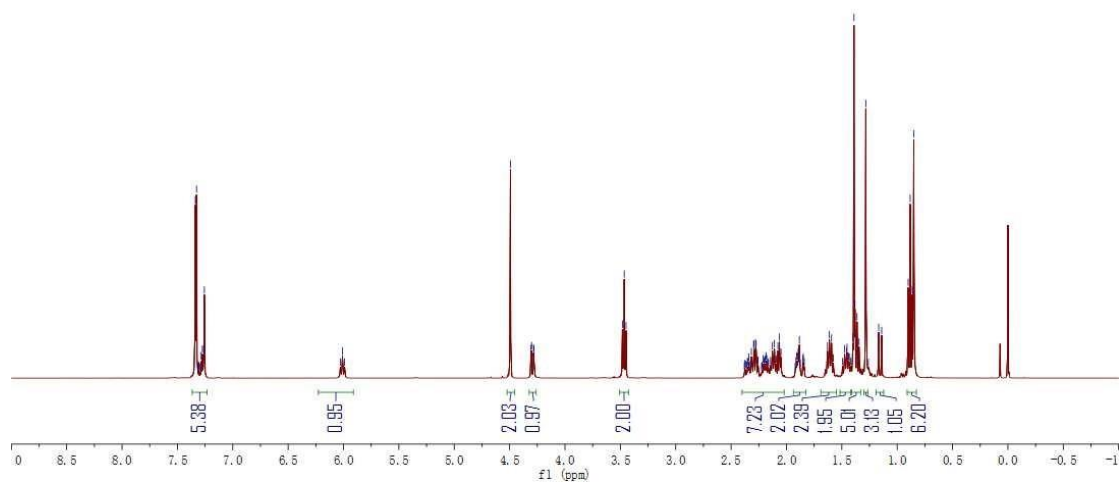
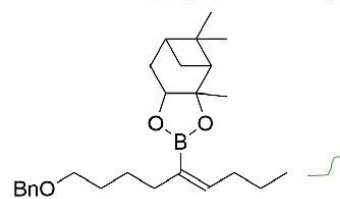
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 – 7.05 (m, 5H), 6.01 (t,  $J = 7.5$  Hz, 1H), 4.49 (s, 2H), 4.29 (dd,  $J = 8.8, 1.9$  Hz, 1H), 3.47 (t,  $J = 6.7$  Hz, 2H), 2.47 – 2.00 (m, 7H), 1.96 – 1.81 (m, 2H), 1.60 (m, 2H), 1.53 – 1.41 (m, 2H), 1.40 – 1.33 (m, 5H), 1.28 (s, 3H), 1.15 (d,  $J = 10.8$  Hz, 1H), 0.87 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.56 (s), 138.82 (s), 128.31 (s), 127.61 (s), 127.40 (s), 85.18 (s), 77.36 (s), 72.77 (s), 70.54 (s), 51.34 (s), 39.61 (s), 38.09 (s), 36.84 (s), 35.74 (s), 33.16 (s), 29.37 (s), 28.77 (s), 27.12 (s), 26.87 (s), 26.60 (s), 24.06 (s), 23.16 (s), 13.73 (s).

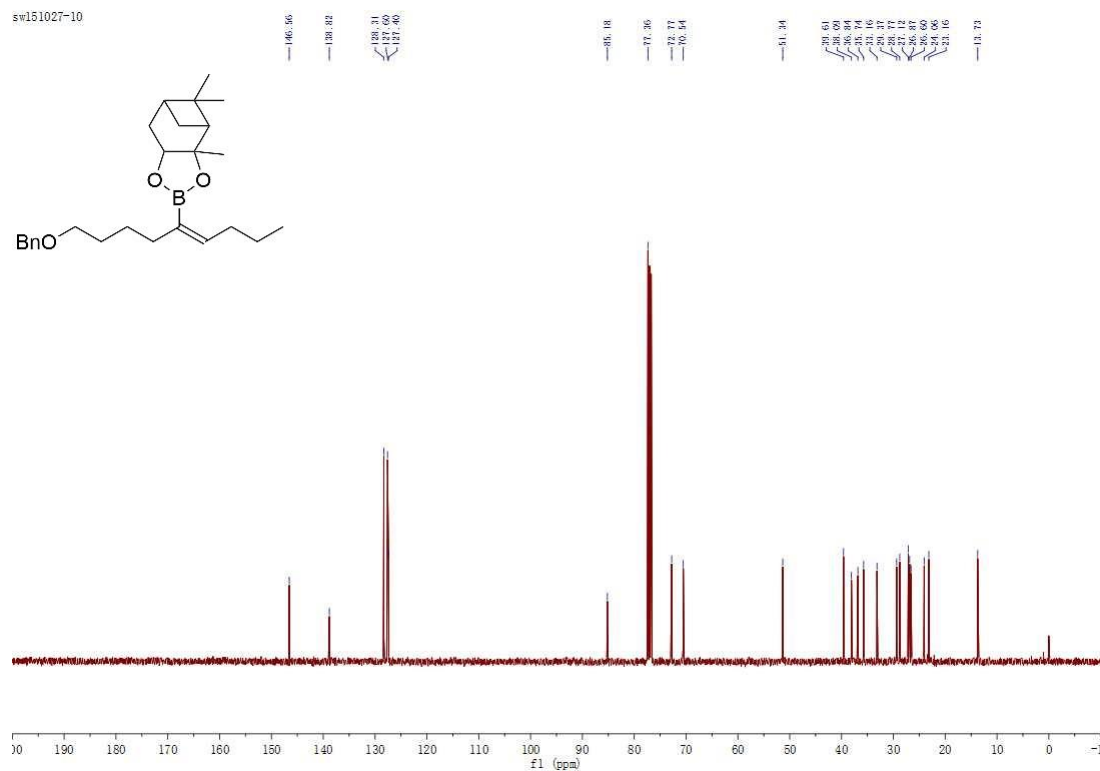
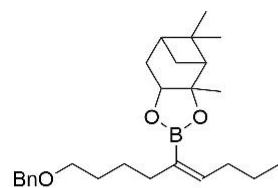
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.64.

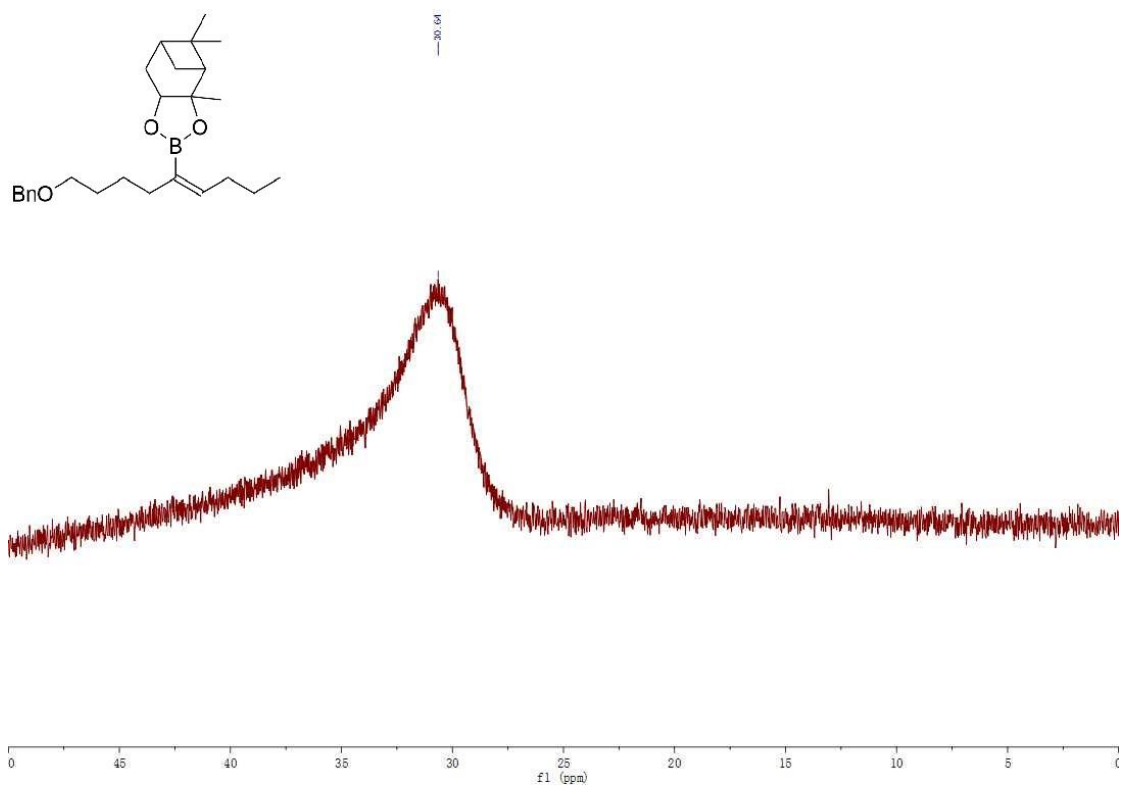
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{39}\text{BO}_3$   $[\text{H}]^+$ : 411.3071, Found: 411.3062.

sw151027-10

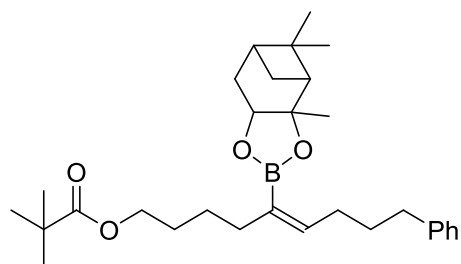


sw151027-10





**(E)-9-phenyl-5-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)non-5-en-1-yl pivalate, 4i**



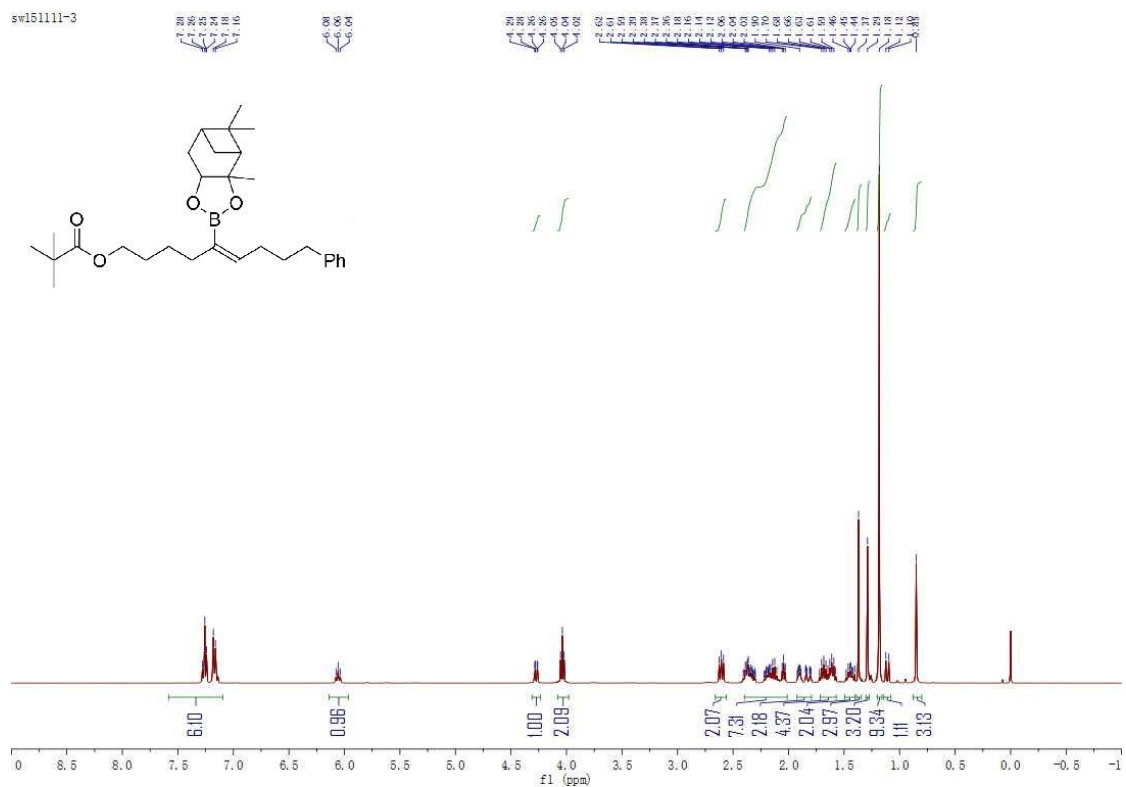
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.23 (m, 5H), 6.06 (t, *J* = 7.5 Hz, 1H), 4.27 (dd, *J* = 8.7, 1.9 Hz, 1H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.64 – 2.53 (m, 2H), 2.44 – 1.99 (m, 7H), 1.86 (m, 2H), 1.76 – 1.56 (m, 4H), 1.49 – 1.39 (m, 2H), 1.37 (s, 3H), 1.29 (s, 3H), 1.18 (s, 9H), 1.11 (d, *J* = 10.9 Hz, 1H), 0.85 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 178.65 (s), 146.48 (s), 142.77 (s), 128.45 (s), 128.19 (s), 125.54 (s), 85.26 (s), 77.41 (s), 64.50 (s), 51.35 (s), 39.62 (s), 38.72 (s), 38.08 (s), 36.66 (s), 35.67 (s), 35.55 (s), 31.82 (s), 30.89 (s), 28.75 (s), 28.29 (s), 27.22 (s), 27.11 (s), 26.72 (s), 26.59 (s), 24.03 (s).

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.75.

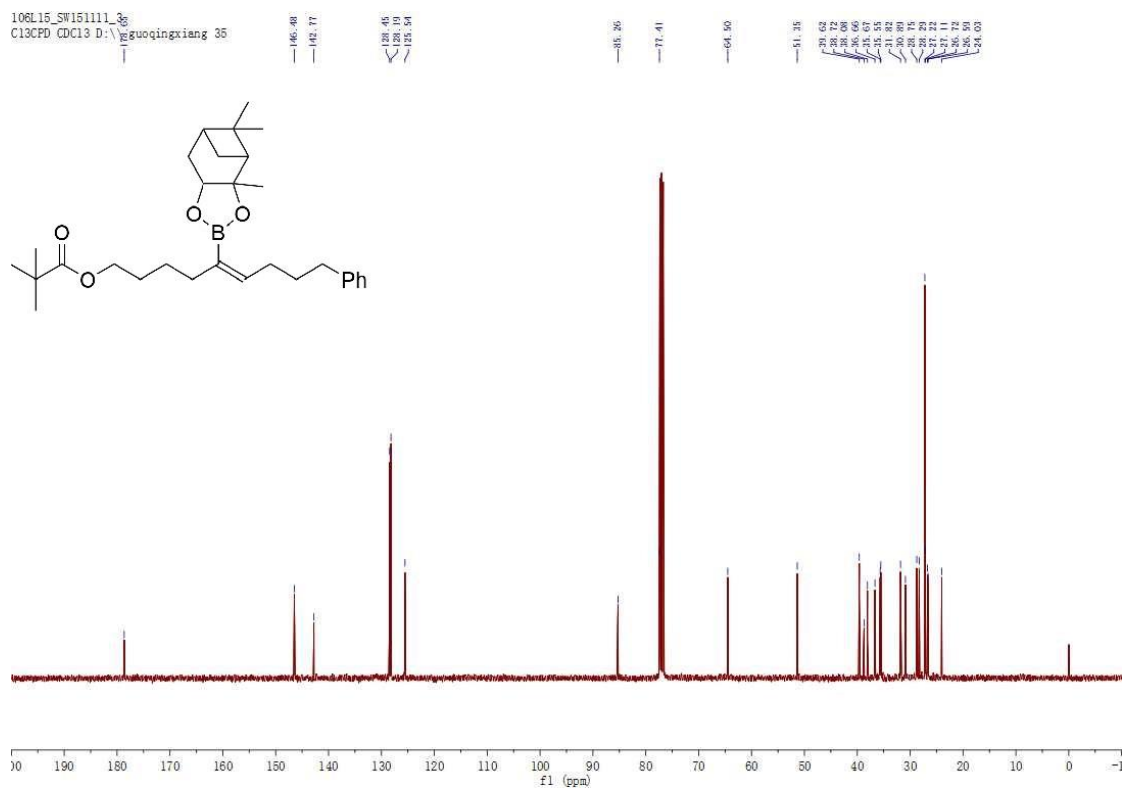
HRMS (EI<sup>+</sup>): Calcd for C<sub>30</sub>H<sub>45</sub>BO<sub>4</sub> [H]<sup>+</sup>: 481.3489, Found: 481.3181.

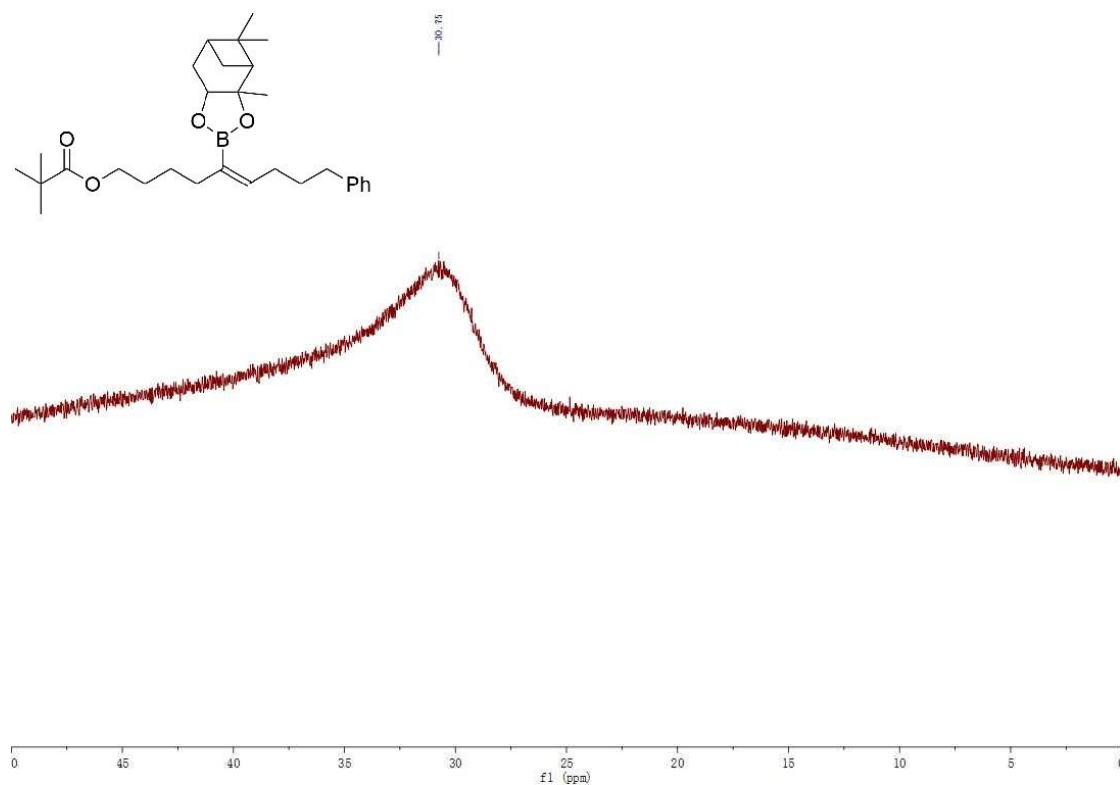
sw151111-3



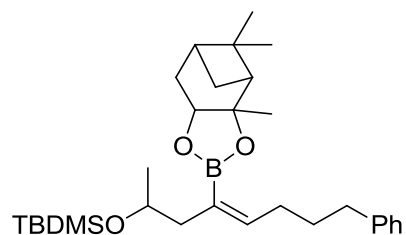
108L15\_SW151111\_3

C13CPD CDCl3 D:\gsguoqingxiang 35





**(E)-tert-butyl dimethyl((8-phenyl-4-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)oct-4-en-2-yl)oxy)silane, 4j**



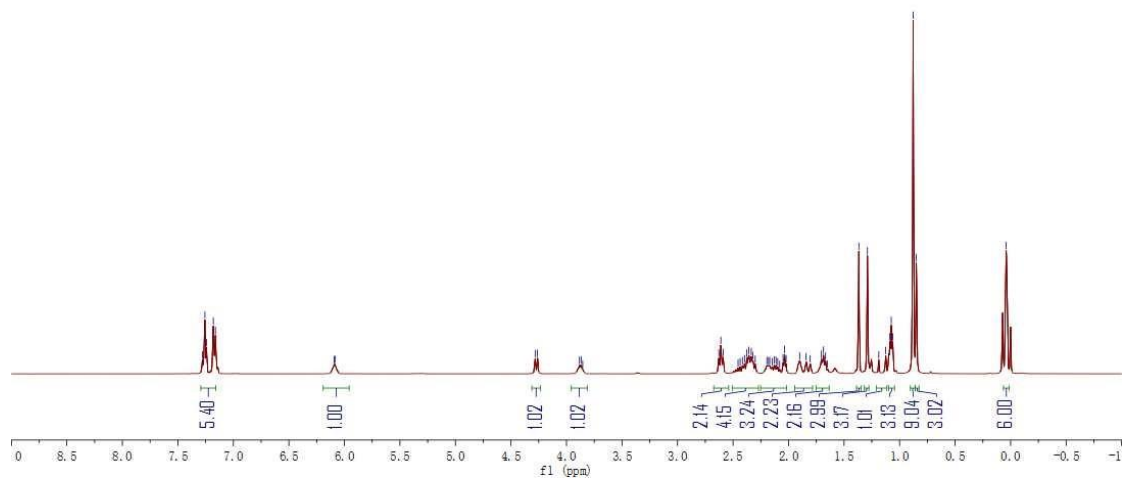
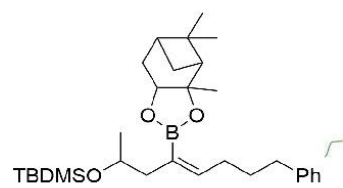
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 – 7.16 (m, 5H), 6.09 (d,  $J = 2.8$  Hz, 1H), 4.27 (d,  $J = 8.2$  Hz, 1H), 3.96 – 3.81 (m, 1H), 2.61 (t,  $J = 7.7$  Hz, 2H), 2.51 – 2.27 (m, 4H), 2.25 – 2.02 (m, 3H), 1.94 – 1.78 (m, 2H), 1.68 (m, 2H), 1.37 (s, 3H), 1.29 (s, 3H), 1.16 (d,  $J = 24.9$  Hz, 1H), 1.07 (m, 3H), 0.88 (s, 9H), 0.85 (s, 3H), 0.04 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  149.27 (d,  $J = 28.8$  Hz), 142.72 (s), 128.38 (s), 128.13 (s), 125.48 (s), 85.09 (d,  $J = 10.6$  Hz), 77.37 (d,  $J = 6.5$  Hz), 68.71 (d,  $J = 18.0$  Hz), 51.28 (s), 47.69 (s), 39.53 (s), 39.51 (s), 38.02 (s), 35.56 (s), 31.67 (s), 30.92 (d,  $J = 3.4$  Hz), 28.68 (s), 27.06 (s), 26.50 (s), 25.95 (s), 23.98 (s), 23.13 (d,  $J = 8.1$  Hz), 18.21 (s), -4.62 (dd,  $J = 7.7, 2.0$  Hz).

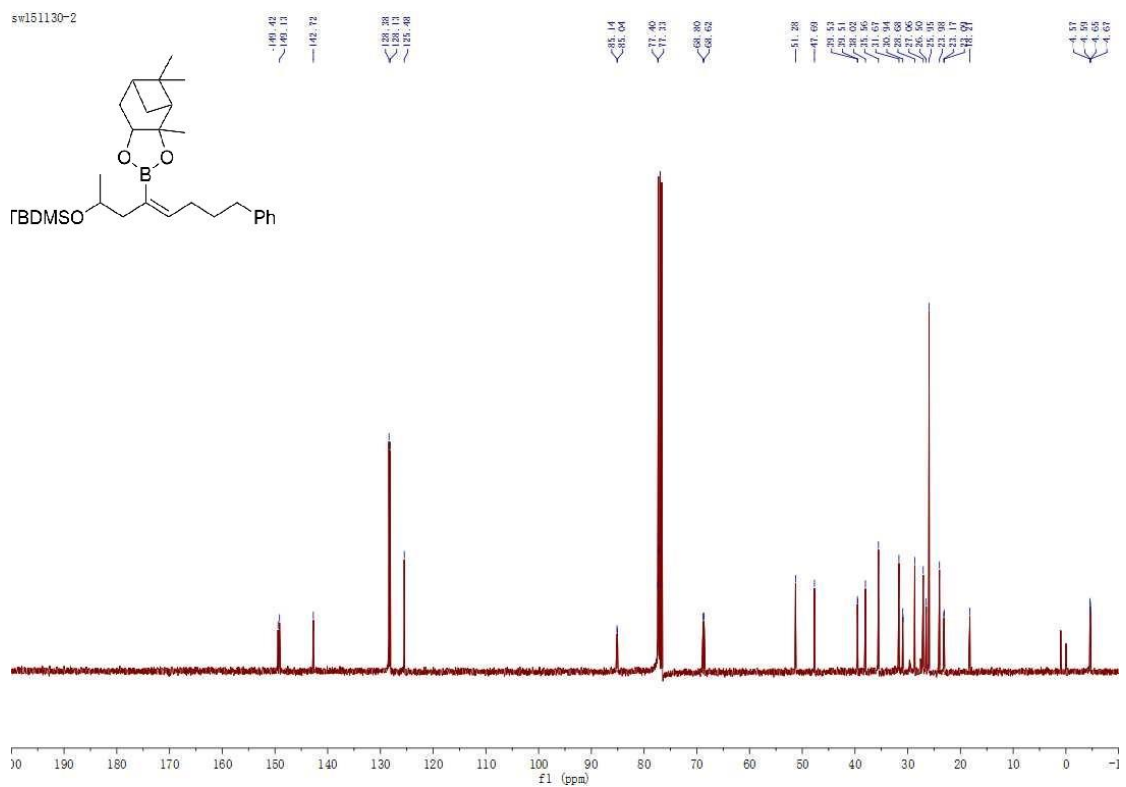
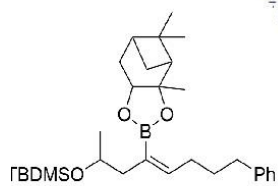
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.41.

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{30}\text{H}_{49}\text{BO}_3\text{Si}[\text{H}]^+$ : 497.3622, Found: 497.3614.

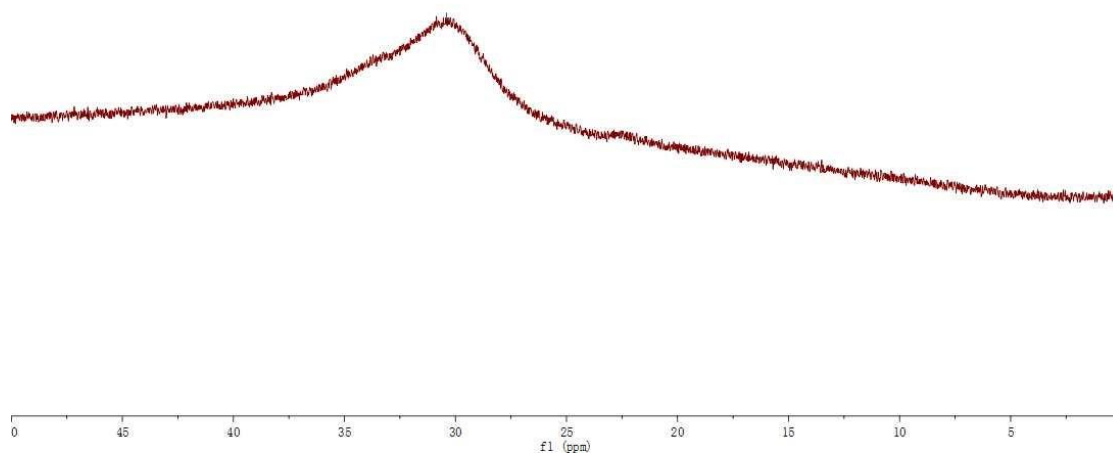
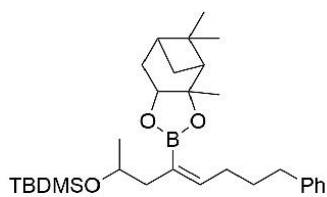
sw151130-2



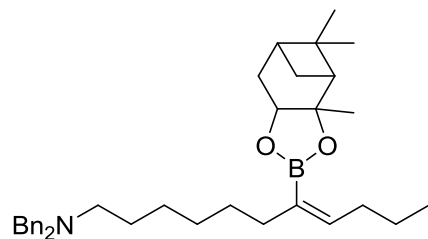
sw151130-2







**(E)-N,N-dibenzyl-7-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)undec-7-en-1-amine, 4k**



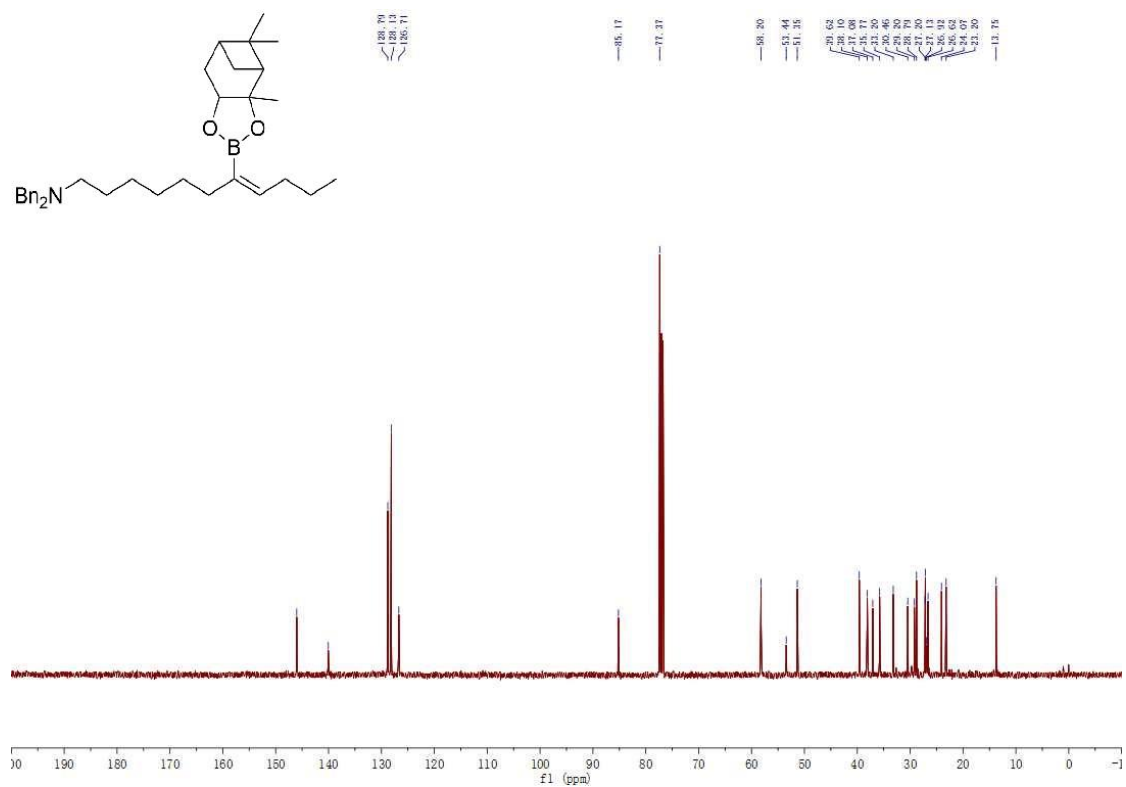
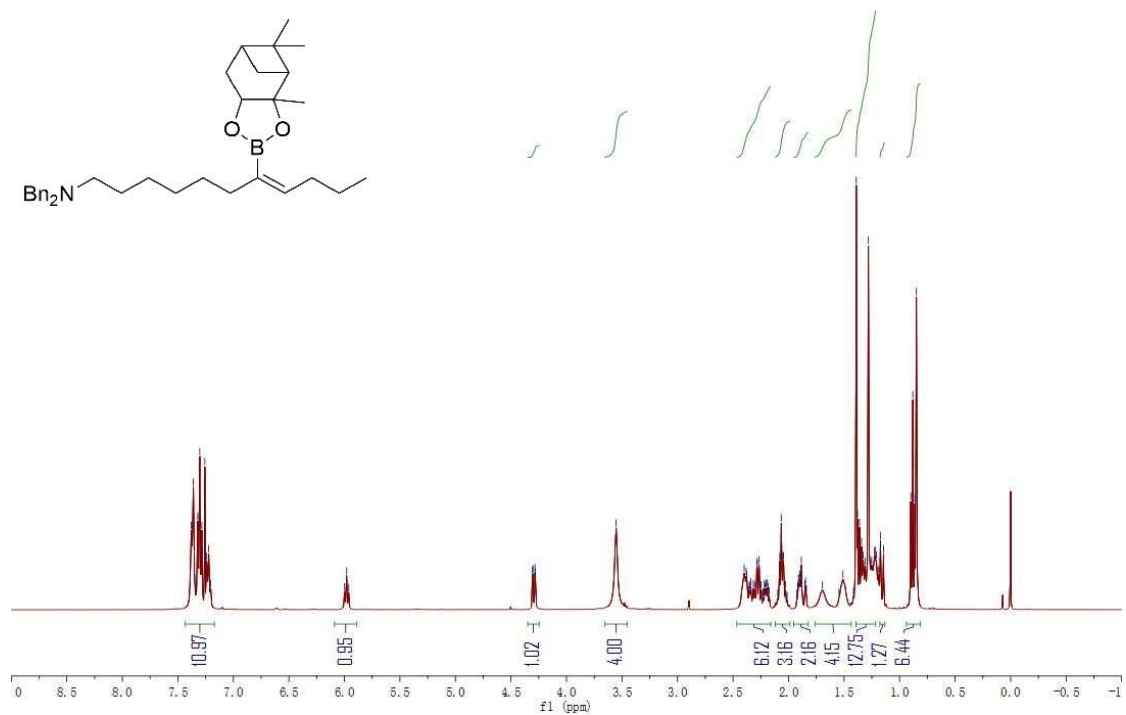
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.05 (m, 10H), 5.98 (t, *J* = 7.5 Hz, 1H), 4.29 (dd, *J* = 8.7, 1.7 Hz, 1H), 3.55 (s, 4H), 2.47 – 2.16 (m, 6H), 2.13 – 1.97 (m, 3H), 1.94 – 1.82 (m, 2H), 1.74 – 1.47 (m, 4H), 1.42 – 1.19 (m, 12H), 1.16 (d, *J* = 10.8 Hz, 1H), 0.87 (dd, *J* = 13.9, 6.5 Hz, 6H).

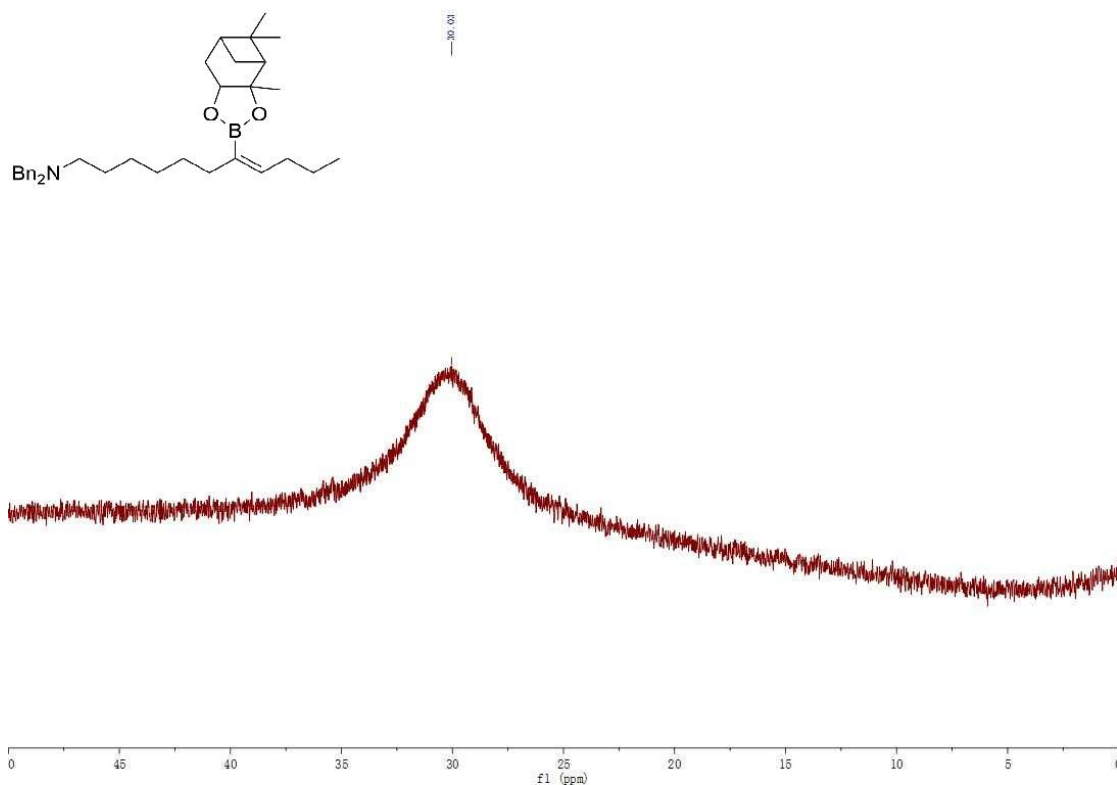
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.02 (s), 140.05 (s), 128.79 (s), 128.13 (s), 126.71 (s), 85.17 (s), 77.37 (s), 58.20 (s), 53.44 (s), 51.35 (s), 39.62 (s), 38.10 (s), 37.08 (s), 35.77 (s), 33.20 (s), 30.46 (s), 29.20 (s), 28.79 (s), 27.20 (s), 27.13 (s), 26.92 (s), 26.62 (s), 24.07 (s), 23.20 (s), 13.75 (s).

<sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) δ 30.03.

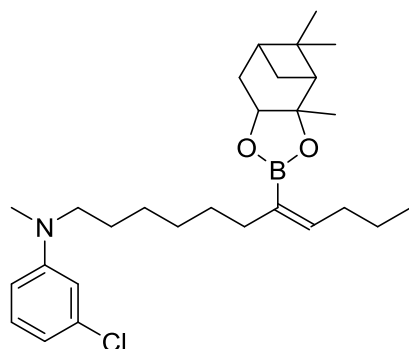
HRMS (EI<sup>+</sup>): Calcd for C<sub>35</sub>H<sub>50</sub>BNO<sub>2</sub> [H]<sup>+</sup>: 528.4013, Found: 528.4004.

sw151027-6





**(E)-3-chloro-N-methyl-N-(7-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)undec-7-en-1-yl)aniline, 4l**



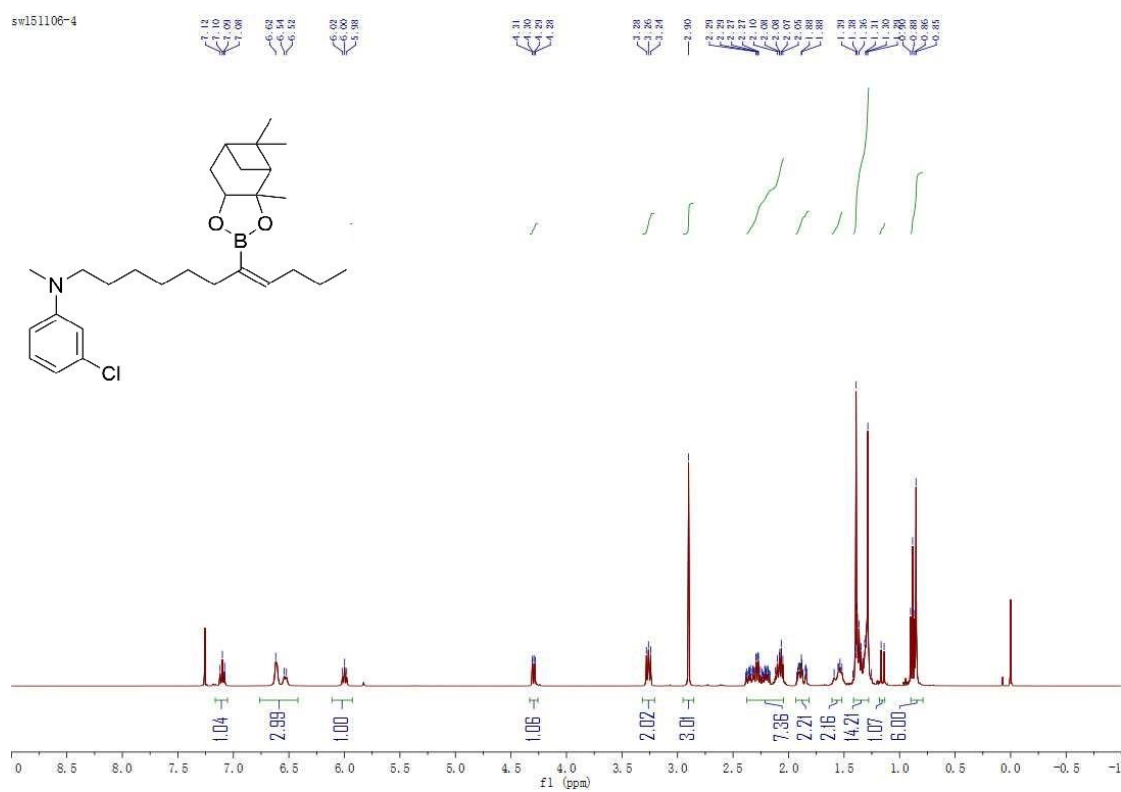
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (dd,  $J = 10.5, 6.2$  Hz, 1H), 6.80 – 6.47 (m, 3H), 6.00 (t,  $J = 7.5$  Hz, 1H), 4.30 (dd,  $J = 8.8, 1.9$  Hz, 1H), 3.48 – 3.23 (m, 2H), 2.90 (s, 3H), 2.50 – 2.00 (m, 7H), 1.88 (m, 2H), 1.65 – 1.49 (m, 2H), 1.44 – 1.26 (m, 14H), 1.15 (d,  $J = 10.8$  Hz, 1H), 0.88 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.28 (s), 146.23 (s), 135.04 (s), 129.98 (s), 115.41 (s), 111.67 (s), 110.03 (s), 85.17 (s), 77.34 (s), 52.68 (s), 51.30 (s), 39.57 (s), 38.31 (s), 38.07 (s), 36.96 (s), 35.73 (s), 33.15 (s), 30.33 (s), 29.07 (s), 28.76 (s), 27.09 (s), 26.95 (s), 26.58 (s), 26.53 (s), 24.04 (s), 23.16 (s), 13.71 (s).

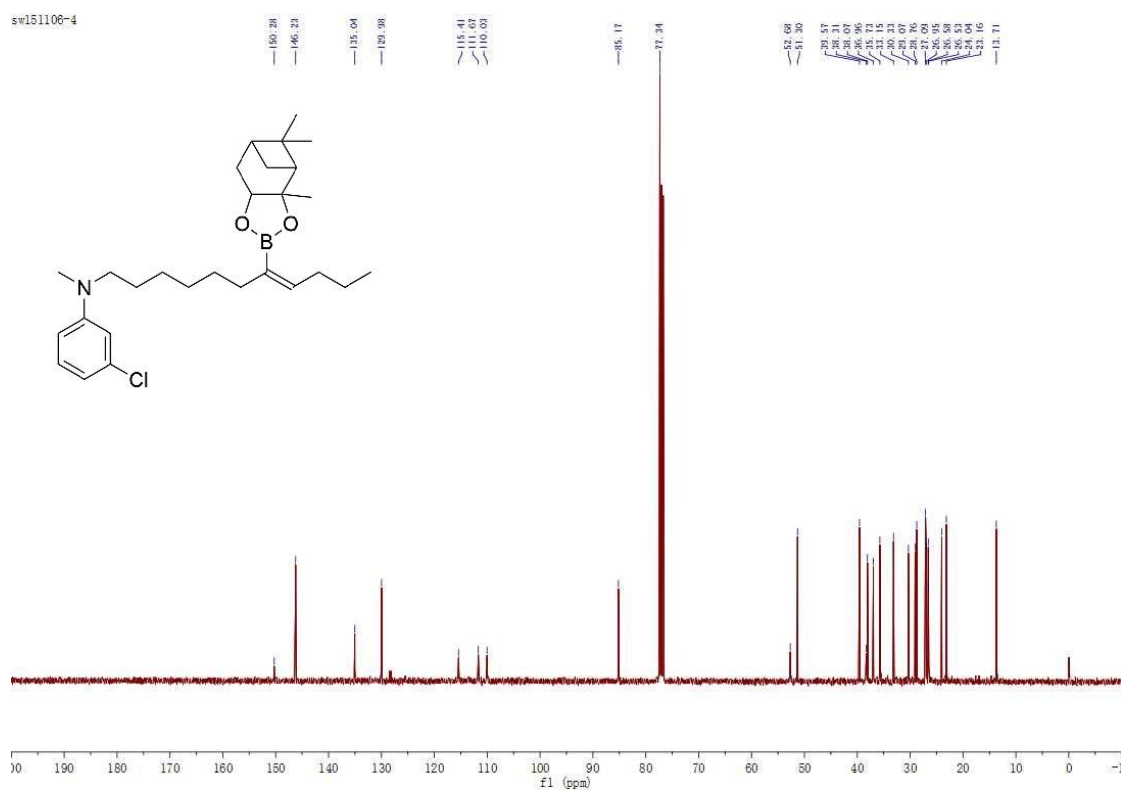
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.62.

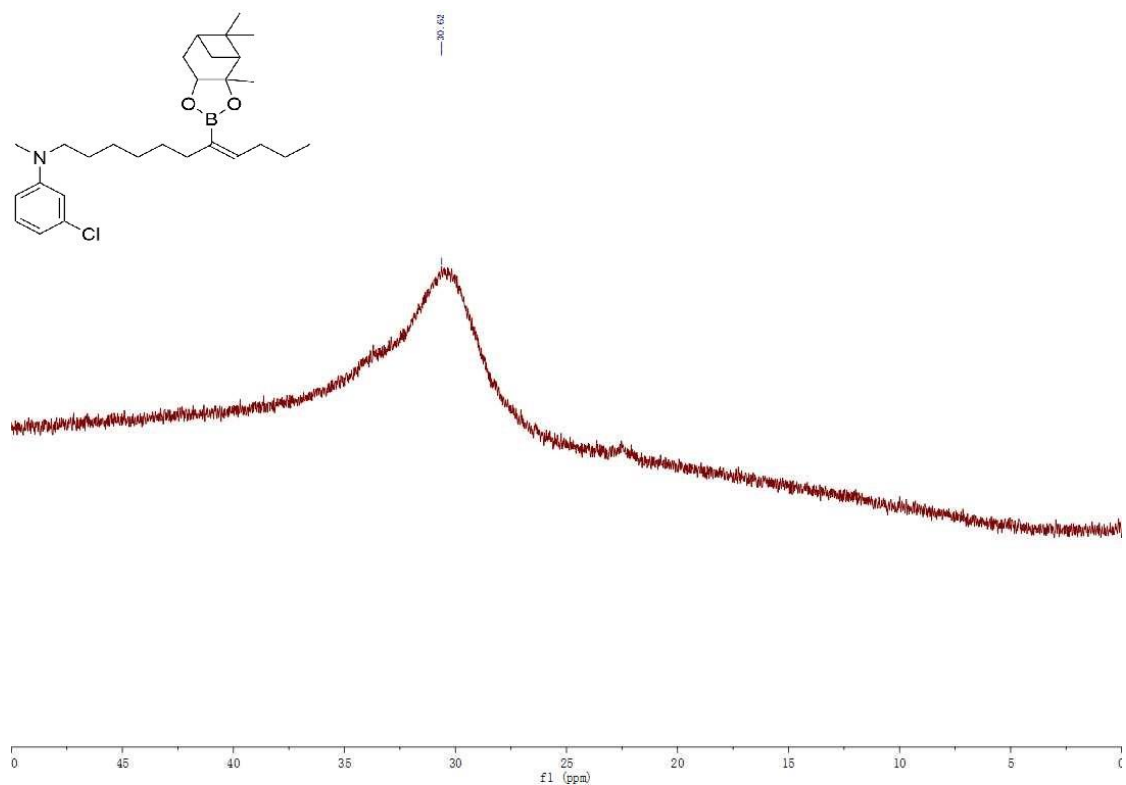
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{28}\text{H}_{43}\text{BNCIO}_2$   $[\text{H}]^+$ : 472.3154, Found: 472.3148.

sw151106-4

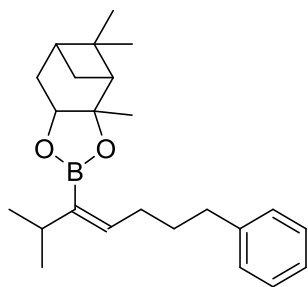


sw151106-4





**(E)-3a,5,5-trimethyl-2-(2-methyl-7-phenylhept-3-en-3-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4m**



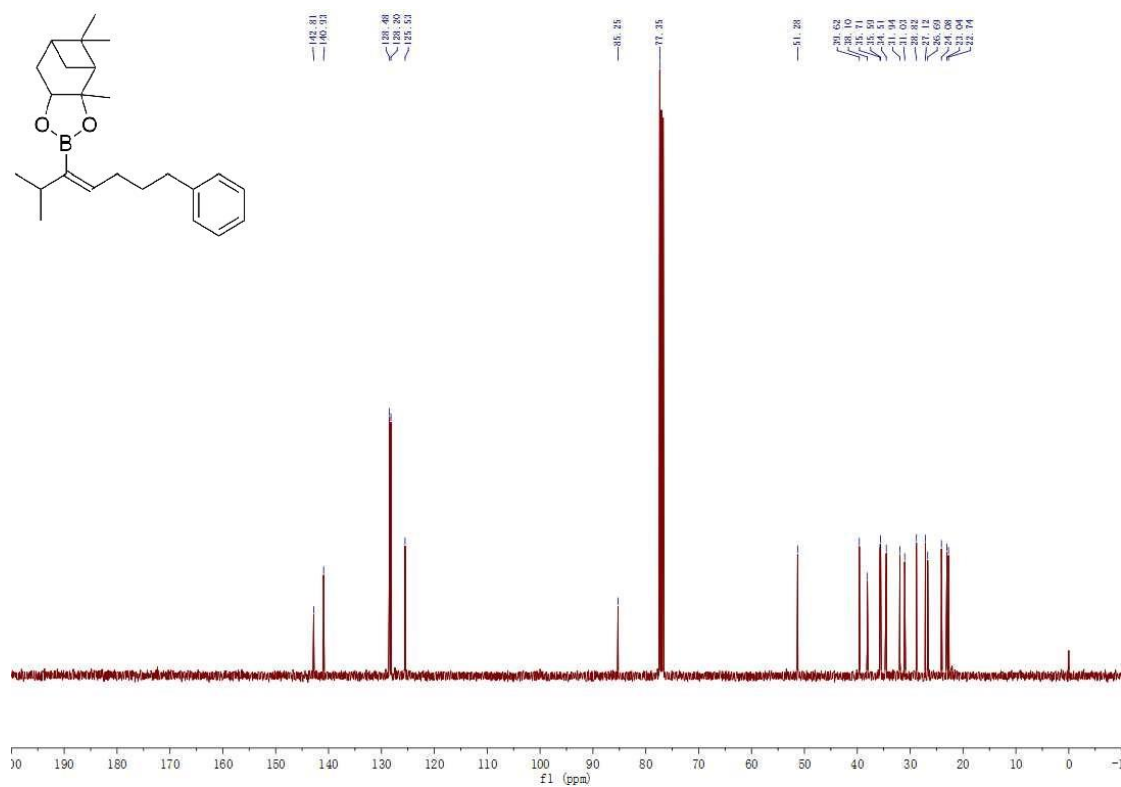
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 6.74 (m, 5H), 5.98 (t,  $J = 7.4$  Hz, 1H), 4.29 (dd,  $J = 8.8, 2.1$  Hz, 1H), 2.66 – 2.57 (m, 2H), 2.43 (m, 1H), 2.38 – 2.26 (m, 3H), 2.25 – 2.12 (m, 1H), 2.11 – 2.01 (m, 1H), 1.97 – 1.77 (m, 2H), 1.76 – 1.59 (m, 2H), 1.37 (s, 3H), 1.29 (s, 3H), 1.17 (d,  $J = 10.8$  Hz, 1H), 1.03 (dd,  $J = 6.8, 2.4$  Hz, 6H), 0.85 (s, 3H).

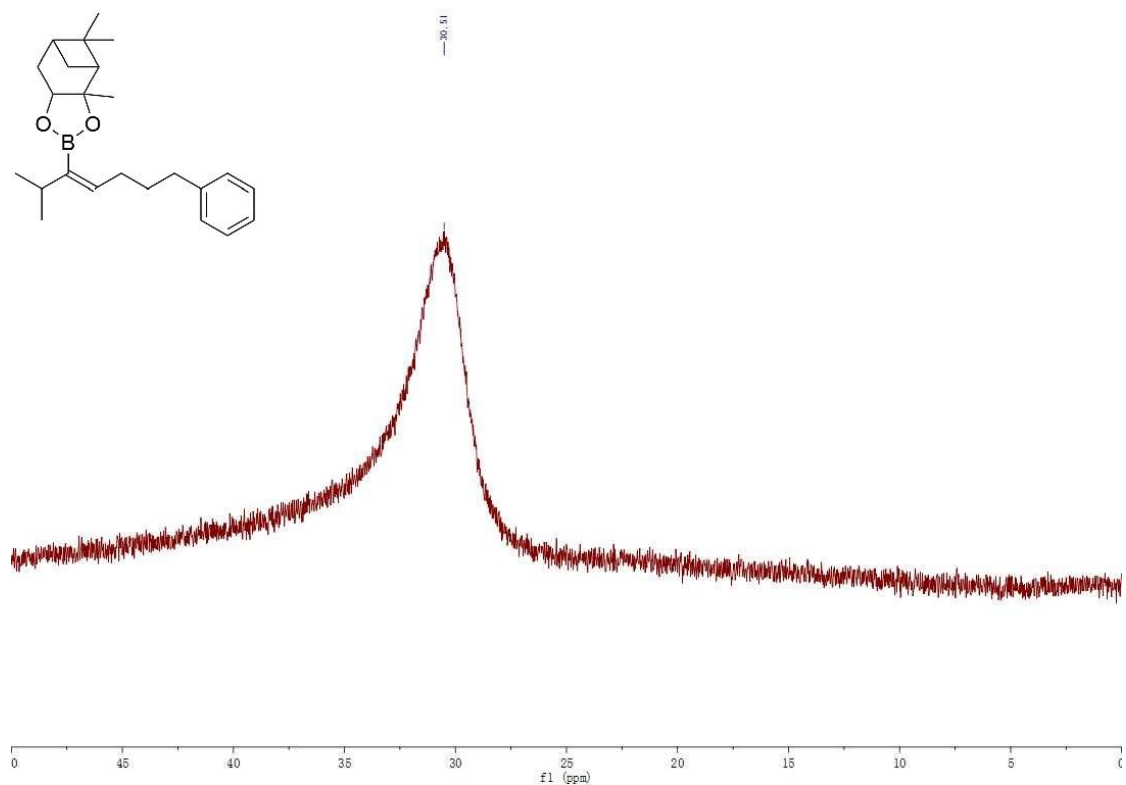
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.81 (s), 140.93 (s), 128.48 (s), 128.20 (s), 125.53 (s), 85.25 (s), 77.35 (s), 51.28 (s), 39.62 (s), 38.10 (s), 35.71 (s), 35.59 (s), 34.51 (s), 31.94 (s), 31.03 (s), 28.82 (s), 27.12 (s), 26.69 (s), 24.08 (s), 23.04 (s), 22.74 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.51.

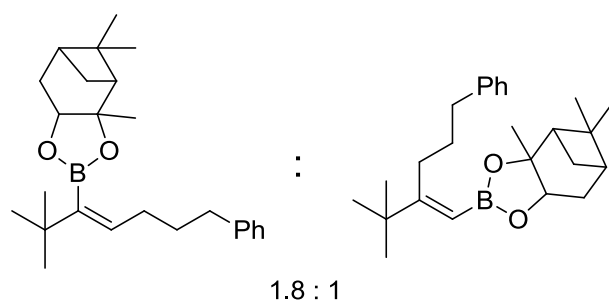
HRMS (EI $^+$ ): Calcd for  $\text{C}_{24}\text{H}_{35}\text{BO}_2$   $[\text{H}]^+$ : 367.2808, Found: 367.2801.

106L15\_S\151027\_1 PROTON CDC13 D:\ guoqingxiang





**(E)-2-(2,2-dimethyl-7-phenylhept-3-en-3-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4n**

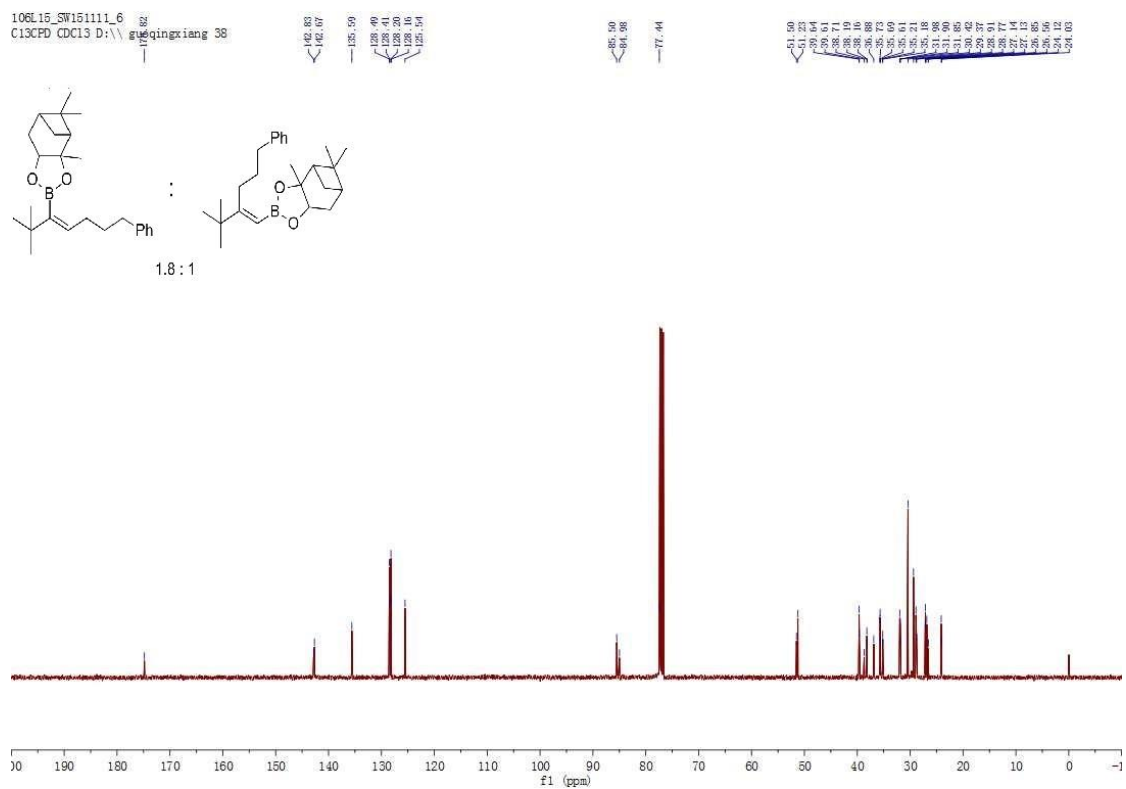
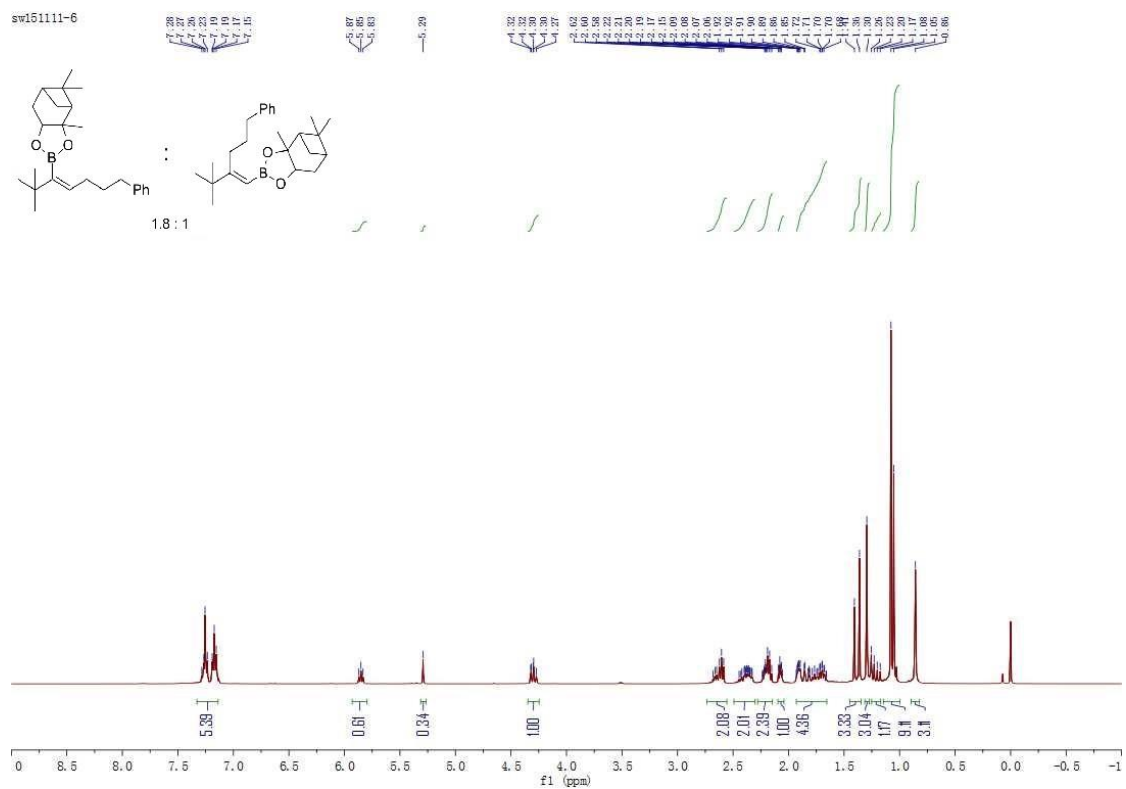


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (m, 5H), 5.85 (t,  $J = 7.4$  Hz, 0.61H), 5.29 (s, 0.34H), 4.35 – 4.25 (m, 1H), 2.63 (m, 2H), 2.49 – 2.30 (m, 2H), 2.28 – 2.15 (m, 2H), 2.10 – 2.04 (m, 1H), 1.93 – 1.66 (m, 4H), 1.38 (m, 3H), 1.30 (s, 3H), 1.25 – 1.17 (m, 1H), 1.06 (m, 9H), 0.86 (s, 3H).

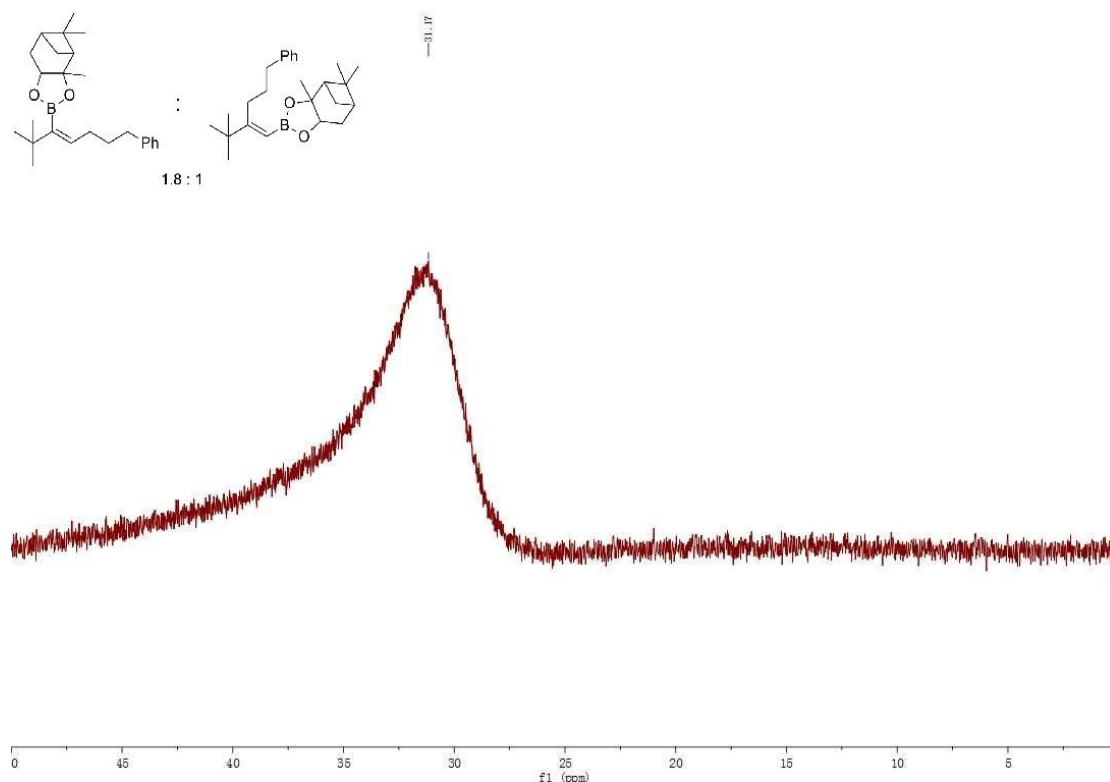
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.82 (s, 2C), 142.83 (s), 142.67 (s), 135.59 (s), 128.49 (s), 128.41 (s), 128.20 (s), 128.16 (s), 125.54 (s), 85.50 (s), 84.98 (s), 77.44 (s, 2C), 51.50 (s), 51.23 (s), 39.64 (s), 39.61 (s), 38.71 (s), 38.19 (s), 38.16 (s), 36.88 (s), 35.73 (s), 35.69 (s), 35.61 (s), 35.21 (s), 35.18 (s), 31.98 (s), 31.90 (s), 31.85 (s), 30.42 (s), 29.37 (s), 28.91 (s), 28.77 (s), 27.14 (s), 27.13 (s), 26.85 (s), 26.56 (s), 24.12 (s), 24.03 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  31.17.

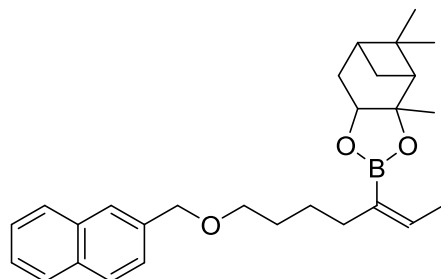
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{25}\text{H}_{37}\text{BO}_2$   $[\text{H}]^+$ : 381.2965, Found: 381.2956.







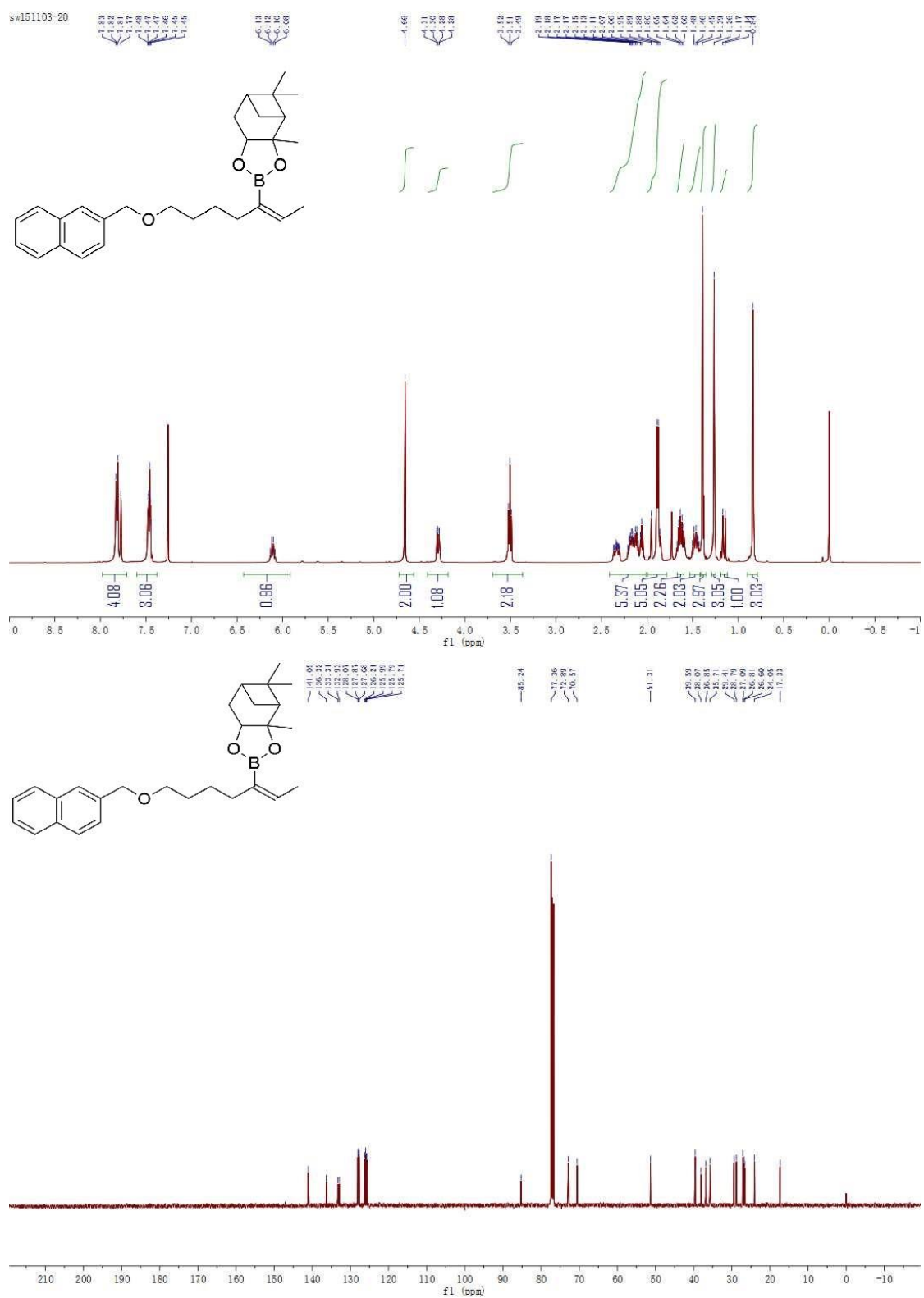
**433.29(E)-3a,5,5-trimethyl-2-(7-(naphthalen-2-ylmethoxy)hept-2-en-3-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4o**

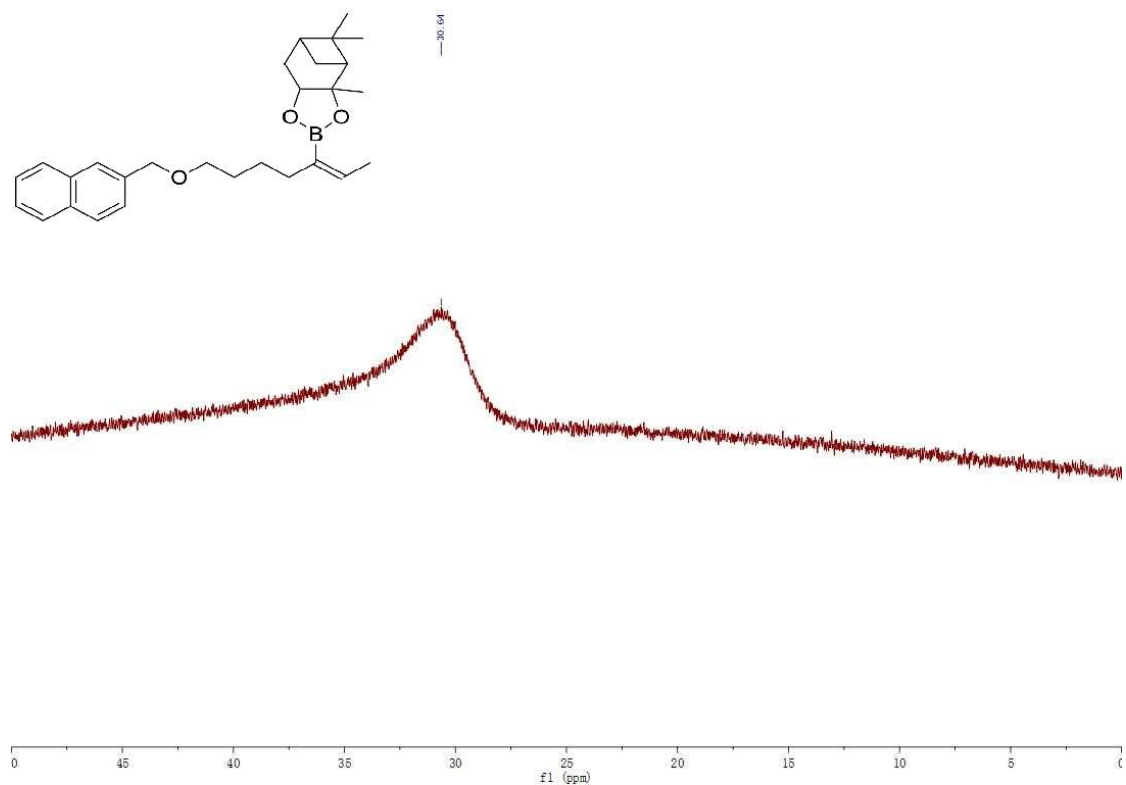


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.58 – 7.33 (m, 3H), 6.11 (q,  $J = 6.8$  Hz, 1H), 4.66 (s, 2H), 4.29 (dd,  $J = 8.7, 1.7$  Hz, 1H), 3.50 (t,  $J = 6.7$  Hz, 2H), 2.43 – 2.02 (m, 5H), 1.97 – 1.84 (m, 5H), 1.68 – 1.58 (m, 2H), 1.47 (m, 2H), 1.39 (s, 3H), 1.26 (s, 3H), 1.16 (d,  $J = 10.8$  Hz, 1H), 0.84 (s, 3H).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.05 (s), 136.32 (s), 133.31 (s), 132.93 (s), 128.07 (s), 127.87 (s), 127.68 (s), 126.21 (s), 125.99 (s), 125.79 (s), 125.71 (s), 85.24 (s), 77.36 (s), 72.89 (s), 70.57 (s), 51.31 (s), 39.59 (s), 38.07 (s), 36.85 (s), 35.71 (s), 29.41 (s), 28.79 (s), 27.09 (s), 26.81 (s), 26.60 (s), 24.05 (s), 17.33 (s).

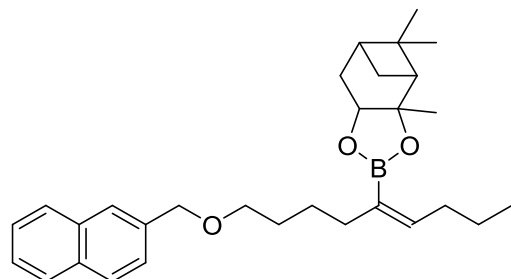
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.64 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{28}\text{H}_{37}\text{BO}_3$   $[\text{H}]^+$ : 433.2914, Found: 433.2906.





**(E)-3a,5,5-trimethyl-2-(9-(naphthalen-2-ylmethoxy)non-4-en-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4p**

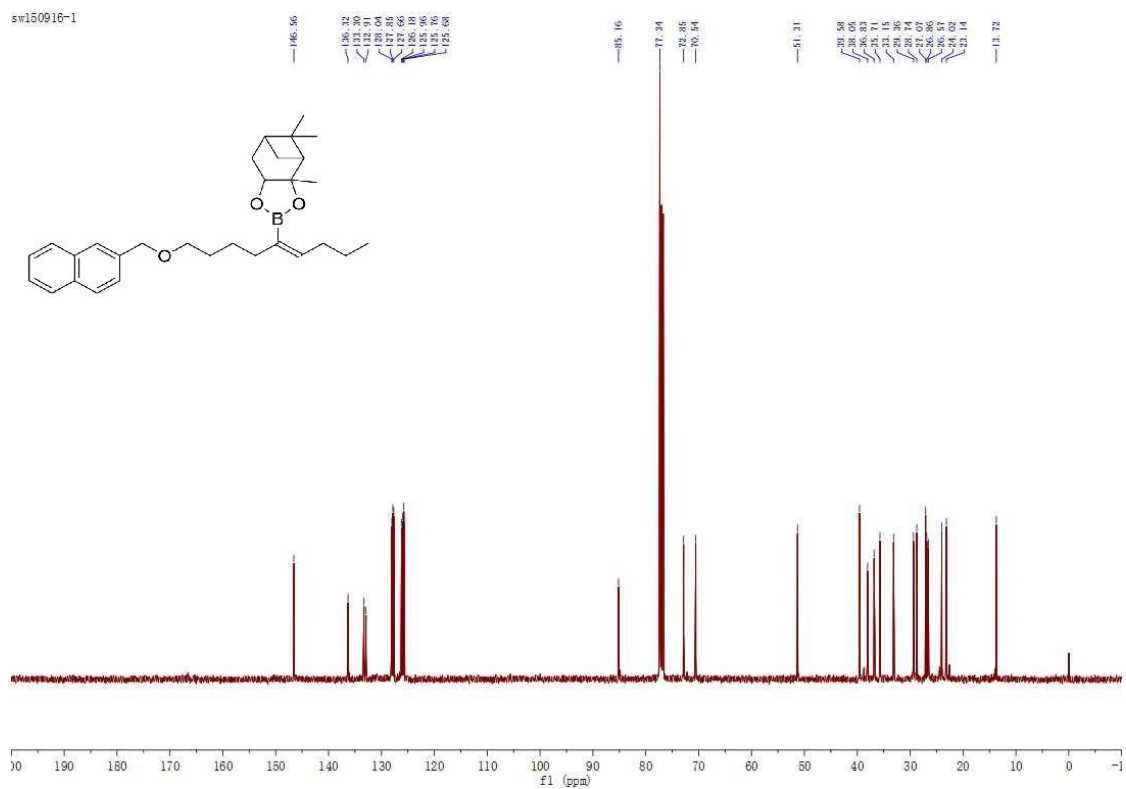
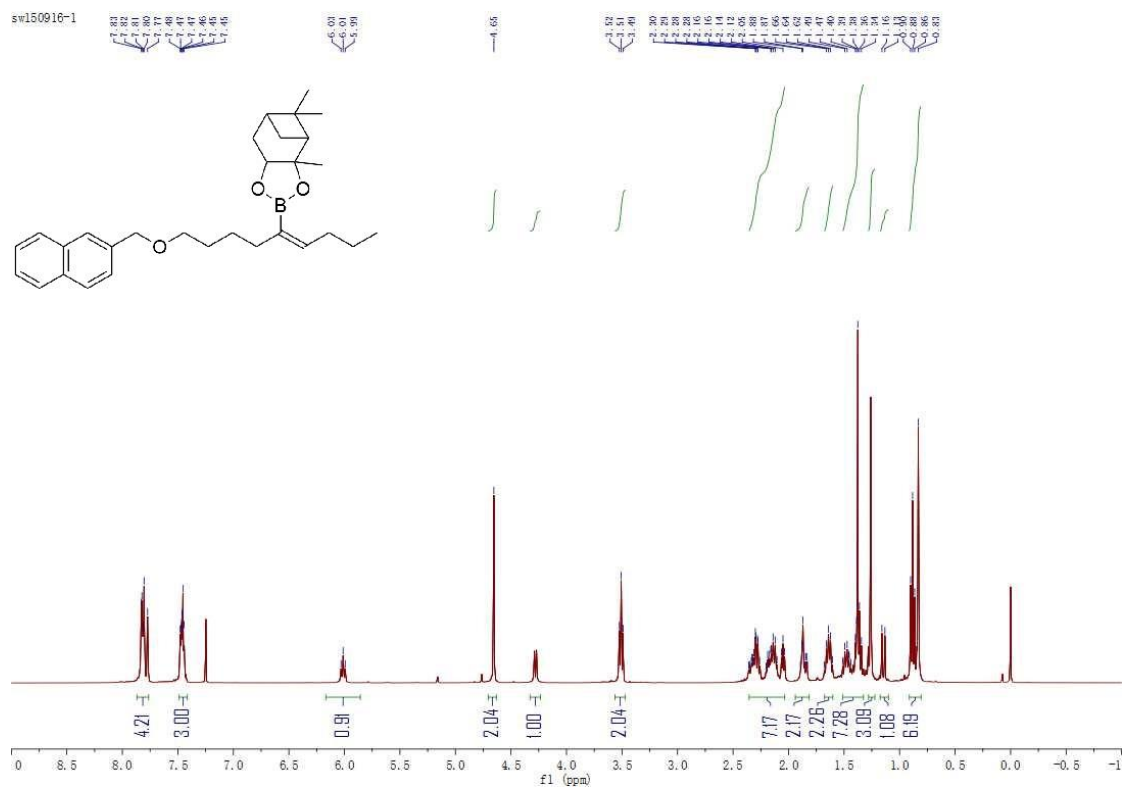


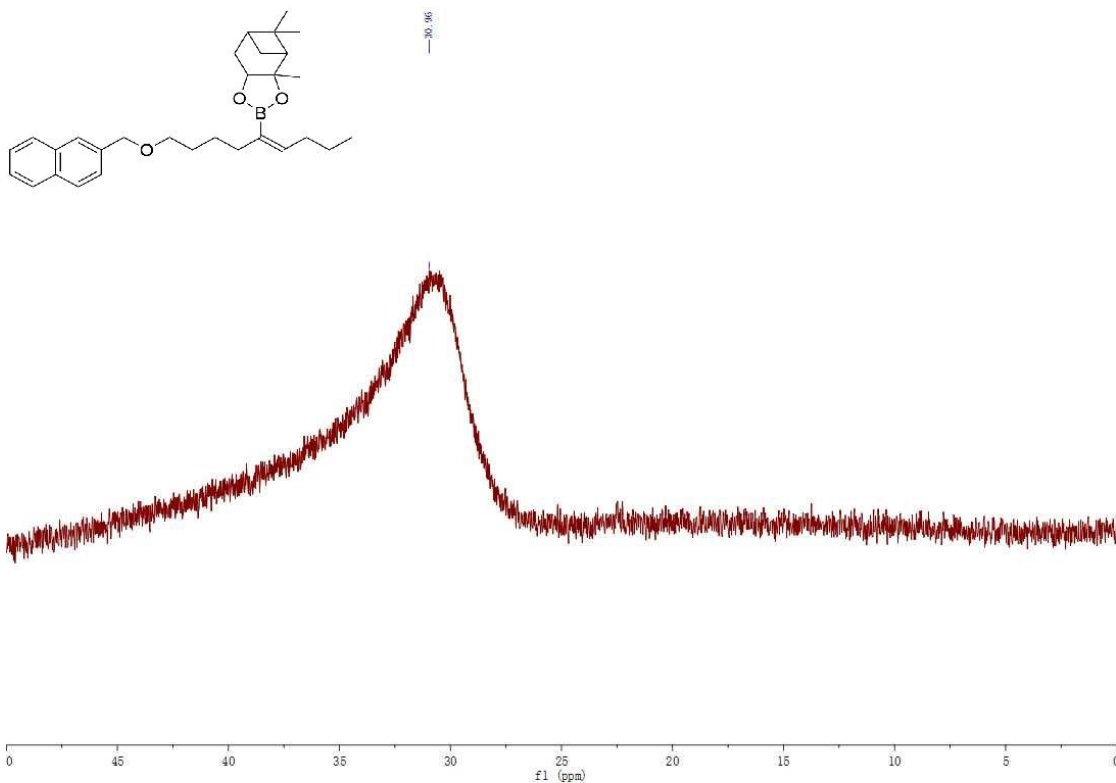
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 – 7.70 (m, 4H), 7.66 – 7.40 (m, 3H), 6.01 (t,  $J = 7.5$  Hz, 1H), 4.65 (s, 2H), 4.27 (dd,  $J = 17.6, 10.5$  Hz, 1H), 3.51 (t,  $J = 6.7$  Hz, 2H), 2.42 – 2.02 (m, 7H), 1.91 – 1.81 (m, 2H), 1.69 – 1.59 (m, 2H), 1.54 – 1.31 (m, 7H), 1.26 (s, 3H), 1.15 (d,  $J = 10.8$  Hz, 1H), 0.87 (m, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.56 (s), 136.32 (s), 133.30 (s), 132.91 (s), 128.04 (s), 127.85 (s), 127.66 (s), 126.18 (s), 125.96 (s), 125.76 (s), 125.68 (s), 85.16 (s), 77.34 (s), 72.85 (s), 70.54 (s), 51.31 (s), 39.58 (s), 38.05 (s), 36.83 (s), 35.71 (s), 33.15 (s), 29.36 (s), 28.74 (s), 27.07 (s), 26.86 (s), 26.57 (s), 24.02 (s), 23.14 (s), 13.72 (s).

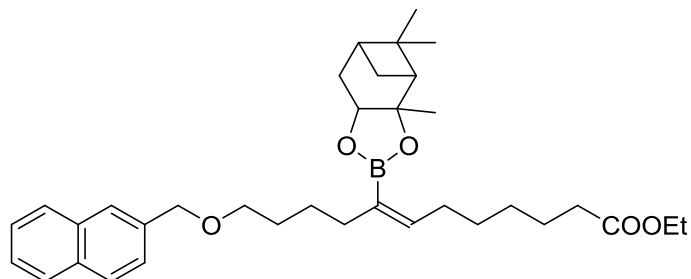
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.96 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{30}\text{H}_{41}\text{BO}_3$   $[\text{H}]^+$ : 461.3227, Found: 461.3220.





**Ethyl (E)-12-(naphthalen-2-ylmethoxy)-8-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)dodec-7-enoate, 4q**

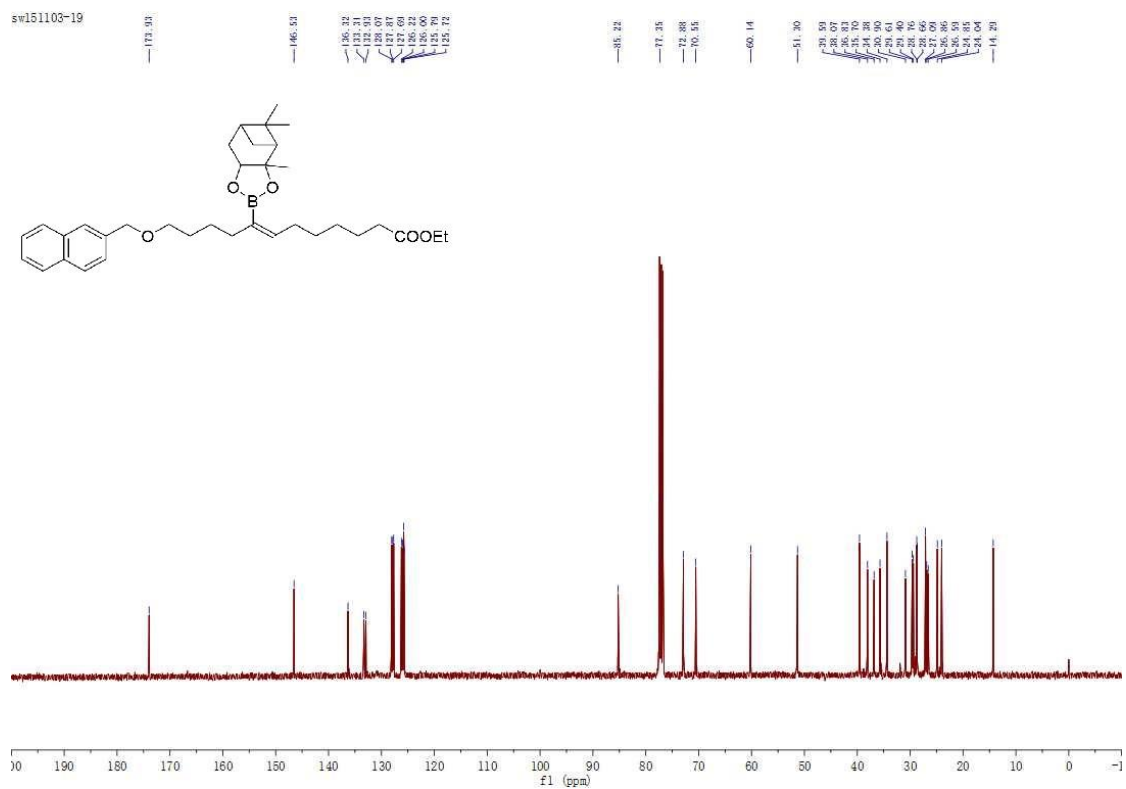
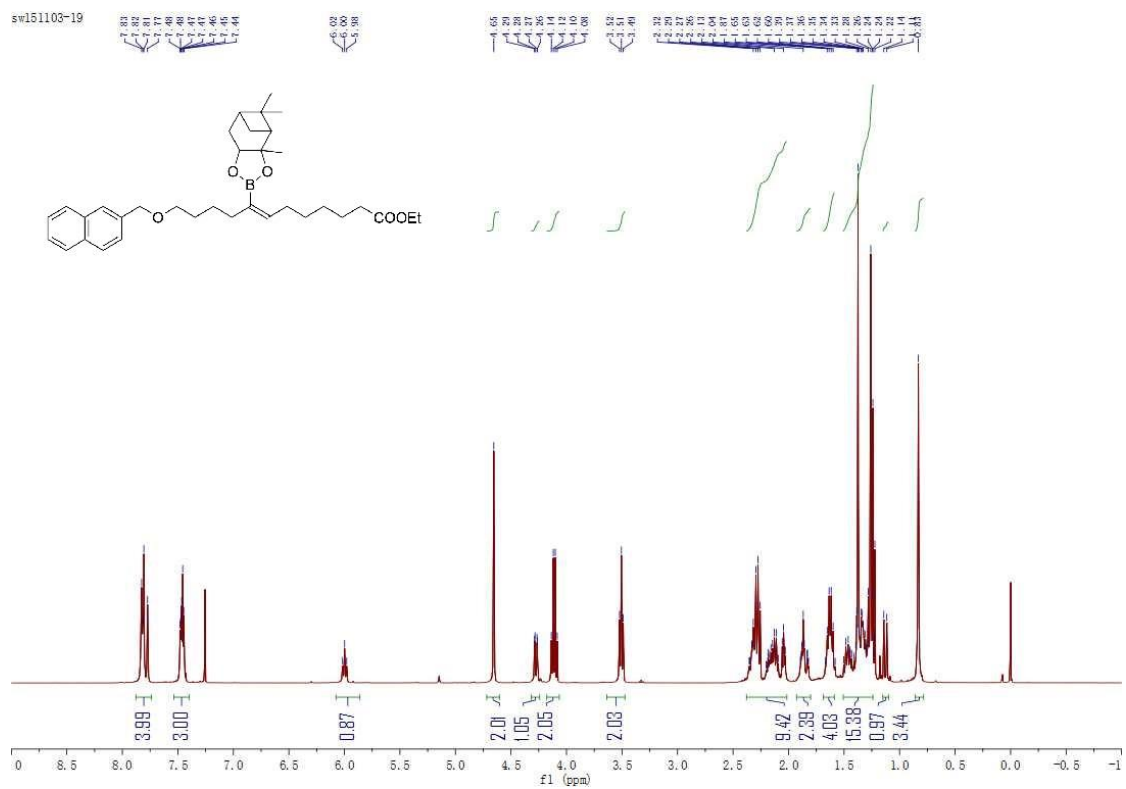


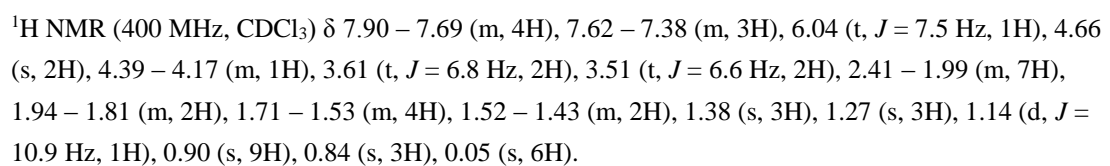
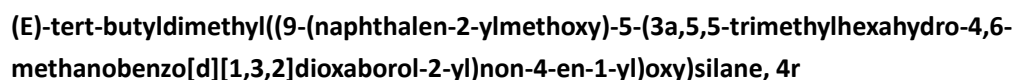
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.60 – 7.29 (m, 3H), 6.00 (t,  $J = 7.5$  Hz, 1H), 4.65 (s, 2H), 4.27 (dd,  $J = 8.7, 1.6$  Hz, 1H), 4.11 (q,  $J = 7.1$  Hz, 2H), 3.51 (t,  $J = 6.7$  Hz, 2H), 2.44 – 2.02 (m, 9H), 1.86 (m, 2H), 1.63 (m, 4H), 1.54 – 1.17 (m, 15H), 1.13 (d,  $J = 10.9$  Hz, 1H), 0.83 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.93 (s), 146.53 (s), 136.32 (s), 133.31 (s), 132.93 (s), 128.07 (s), 127.87 (s), 127.69 (s), 126.22 (s), 126.00 (s), 125.79 (s), 125.72 (s), 85.22 (s), 77.35 (s), 72.88 (s), 70.55 (s), 60.14 (s), 51.30 (s), 39.59 (s), 38.07 (s), 36.83 (s), 35.70 (s), 34.38 (s), 30.90 (s), 29.61 (s), 29.40 (s), 28.76 (s), 28.66 (s), 27.09 (s), 26.86 (s), 26.59 (s), 24.85 (s), 24.04 (s), 14.29 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.85 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{35}\text{H}_{49}\text{BO}_5$   $[\text{H}]^+$ : 561.3751, Found: 561.3742.

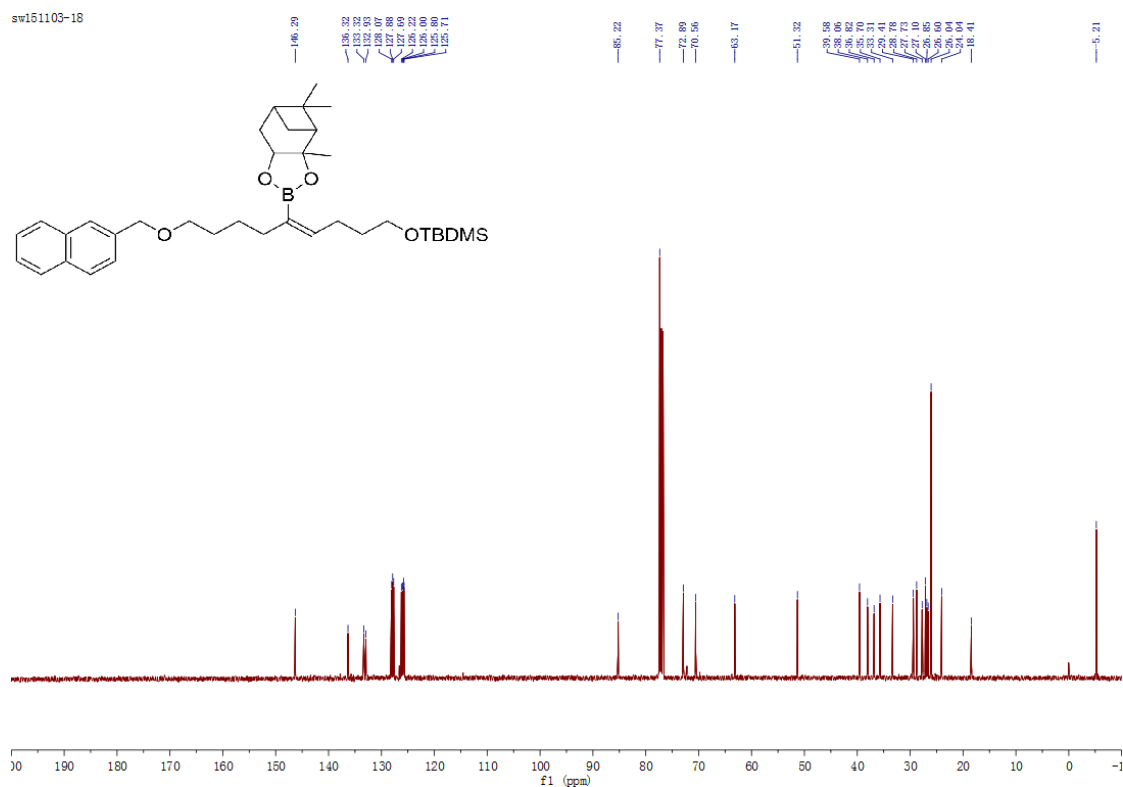
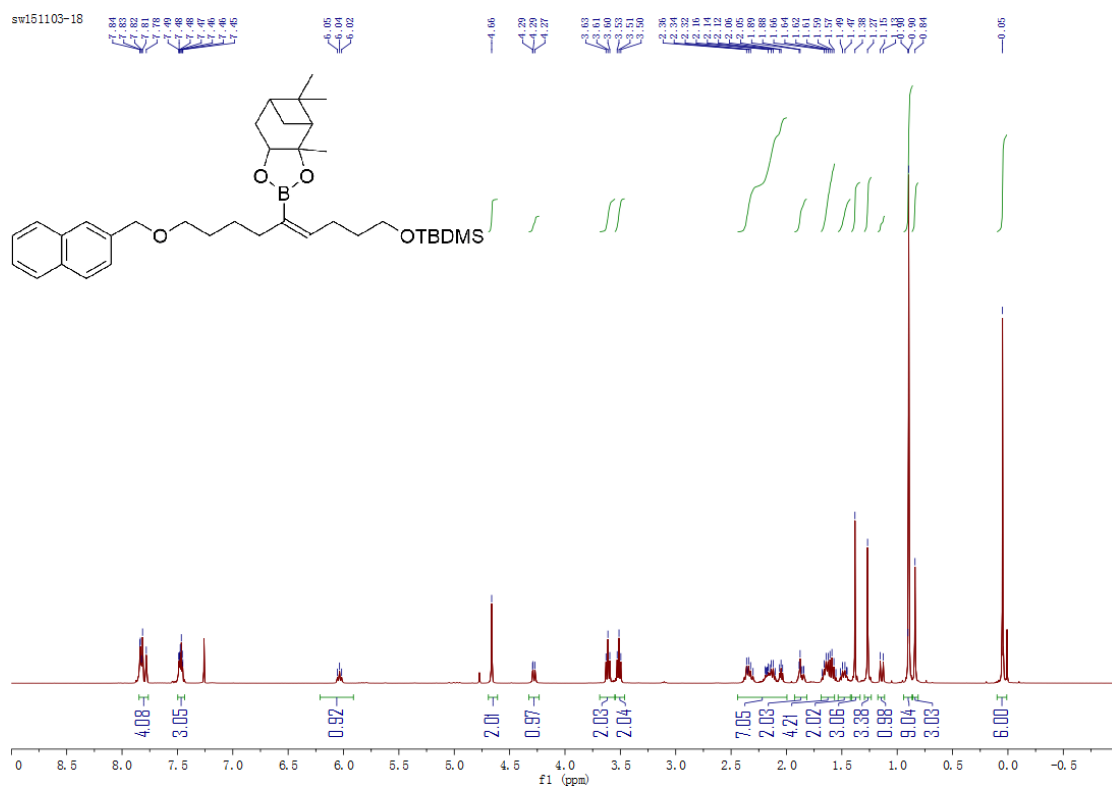




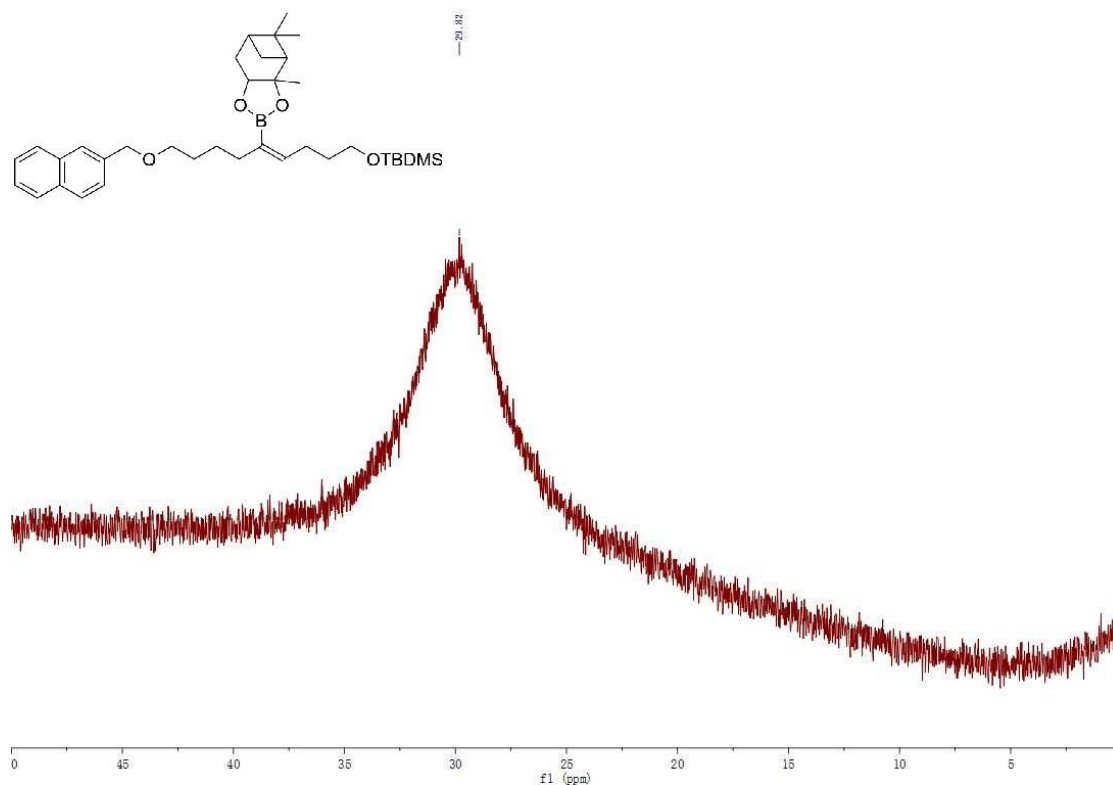
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.29 (s), 136.32 (s), 133.32 (s), 132.93 (s), 128.07 (s), 127.88 (s), 127.69 (s), 126.22 (s), 126.00 (s), 125.80 (s), 125.71 (s), 85.22 (s), 77.37 (s), 72.89 (s), 70.56 (s), 63.17 (s), 51.32 (s), 39.58 (s), 38.06 (s), 36.82 (s), 35.70 (s), 33.31 (s), 29.41 (s), 28.78 (s), 27.73 (s), 27.10 (s), 26.85 (s), 26.60 (s), 26.04 (s), 24.04 (s), 18.41 (s), -5.21 (s).

 $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.82 (s).

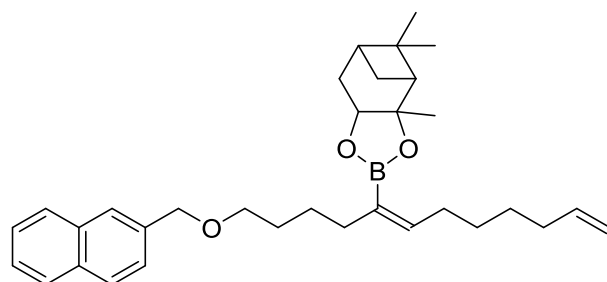
HRMS (EI<sup>+</sup>): Calcd for C<sub>36</sub>H<sub>55</sub>BO<sub>4</sub>Si [H]<sup>+</sup>: 591.4041, Found: 591.4033.







**(E)-3a,5,5-trimethyl-2-(1-(naphthalen-2-ylmethoxy)dodeca-5,11-dien-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4s**

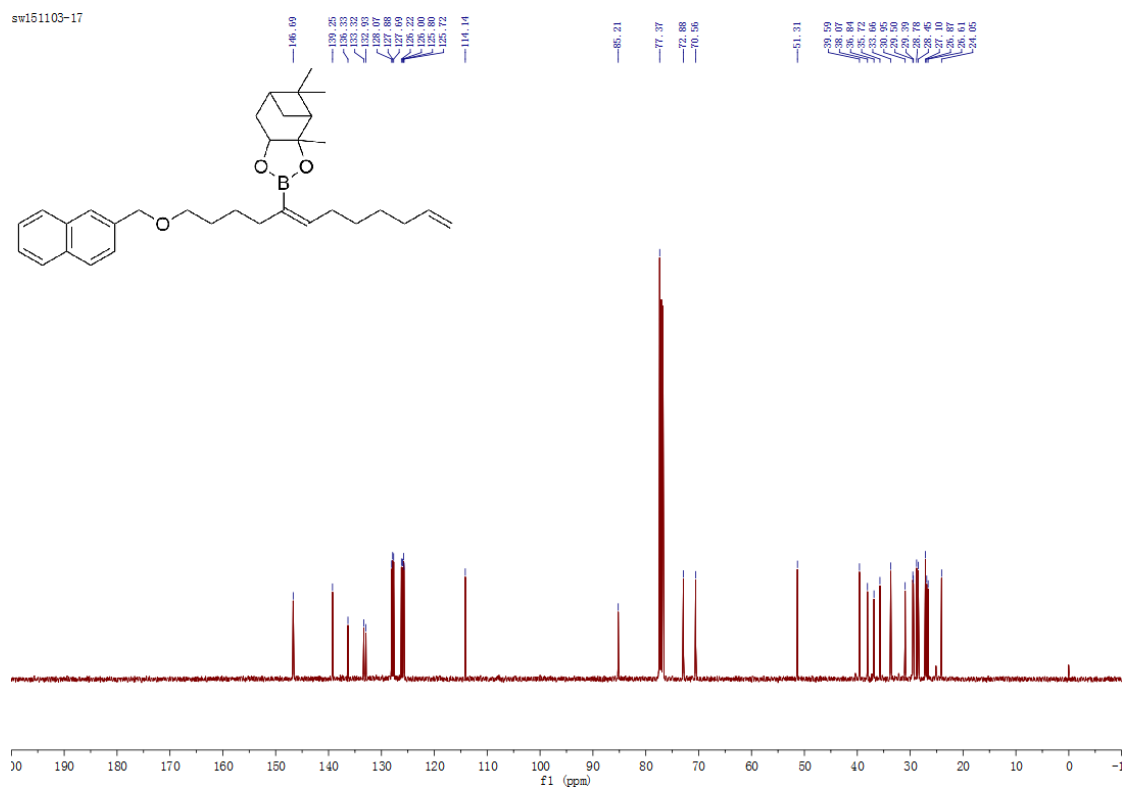
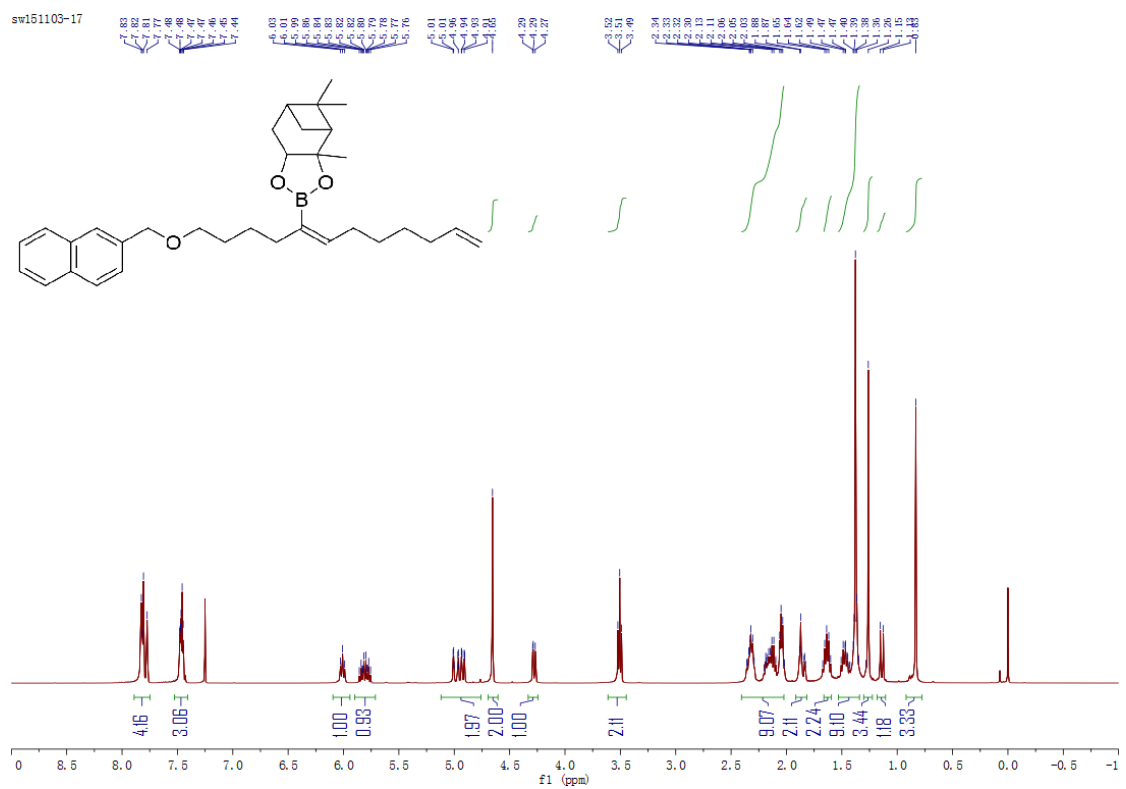


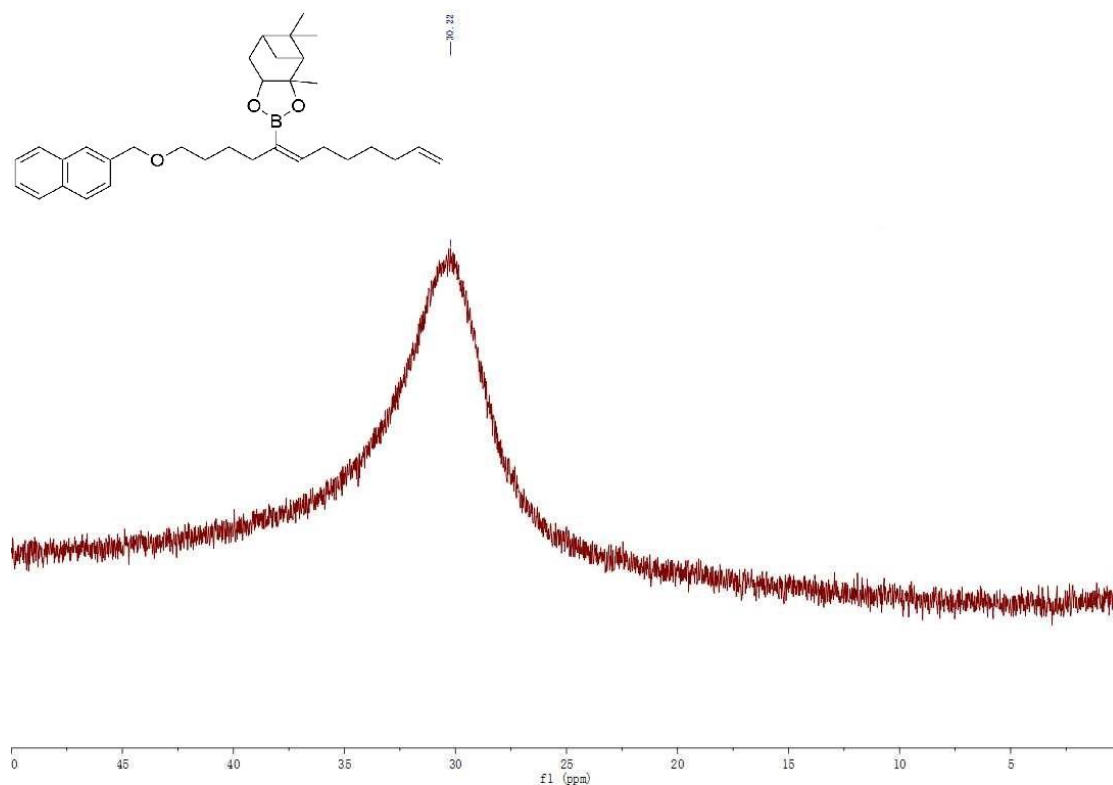
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.64 – 7.38 (m, 3H), 6.01 (t,  $J = 7.5$  Hz, 1H), 5.81 (ddt,  $J = 16.9, 10.2, 6.7$  Hz, 1H), 5.20 – 4.83 (m, 2H), 4.65 (s, 2H), 4.49 – 4.22 (m, 1H), 3.51 (t,  $J = 6.7$  Hz, 2H), 2.46 – 1.96 (m, 9H), 1.85 (m, 2H), 1.73 – 1.58 (m, 2H), 1.56 – 1.36 (m, 9H), 1.26 (s, 3H), 1.14 (d,  $J = 10.9$  Hz, 1H), 0.83 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.69 (s), 139.25 (s), 136.33 (s), 133.32 (s), 132.93 (s), 128.07 (s), 127.88 (s), 127.69 (s), 126.22 (s), 126.00 (s), 125.80 (s), 125.72 (s), 114.14 (s), 85.21 (s), 77.37 (s), 72.88 (s), 70.56 (s), 51.31 (s), 39.59 (s), 38.07 (s), 36.84 (s), 35.72 (s), 33.66 (s), 30.95 (s), 29.50 (s), 29.39 (s), 28.78 (s), 28.45 (s), 27.10 (s), 26.87 (s), 26.61 (s), 24.05 (s).

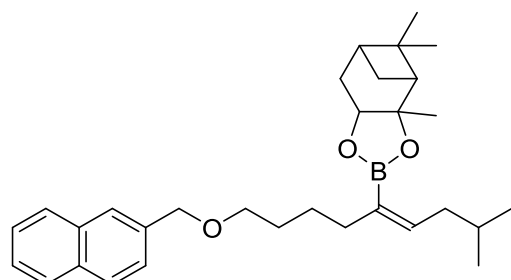
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.22 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{33}\text{H}_{45}\text{BO}_3$   $[\text{H}]^+$ : 501.3540, Found: 501.3532.





**(E)-3a,5,5-trimethyl-2-(2-methyl-9-(naphthalen-2-ylmethoxy)non-4-en-5-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4t**



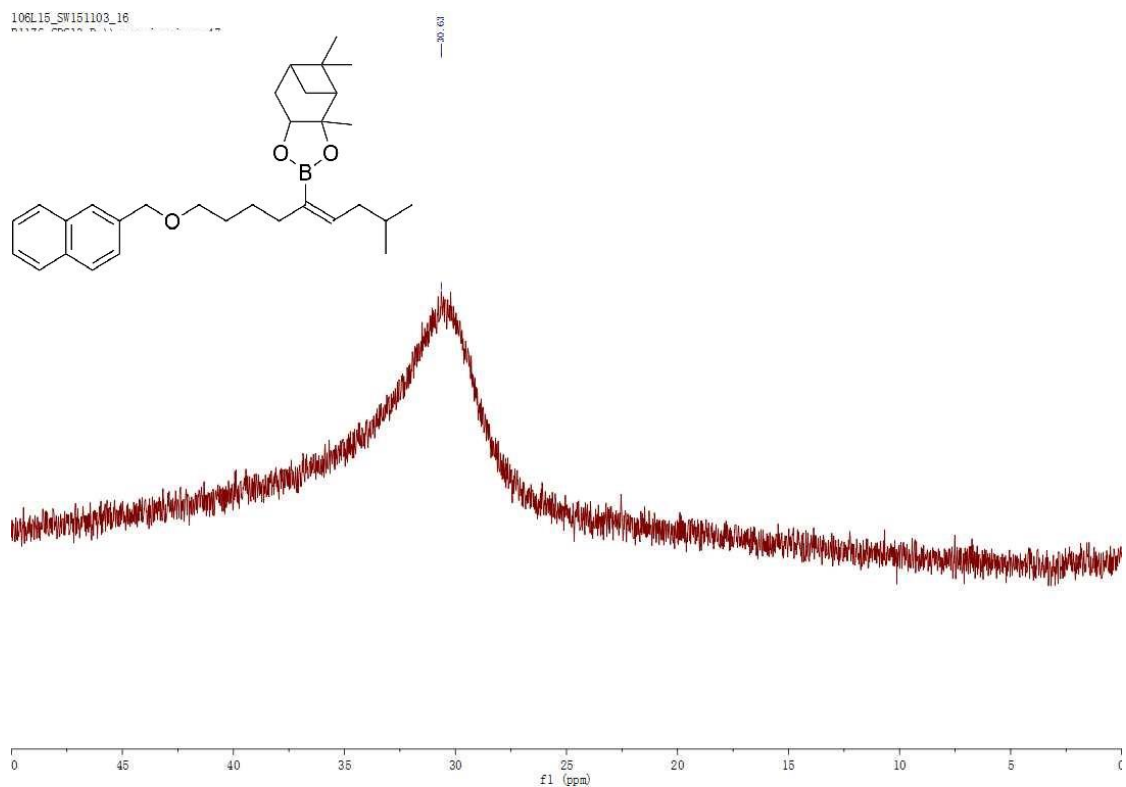
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.63 – 7.39 (m, 3H), 6.03 (t,  $J = 7.7$  Hz, 1H), 4.66 (s, 2H), 4.48 – 4.19 (m, 1H), 3.51 (t,  $J = 6.7$  Hz, 2H), 2.46 – 1.99 (m, 7H), 1.85 (m, 2H), 1.61 (m, 3H), 1.53 – 1.42 (m, 2H), 1.38 (s, 3H), 1.26 (s, 3H), 1.14 (d,  $J = 10.9$  Hz, 1H), 1.01 – 0.78 (m, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.53 (s), 136.33 (s), 133.31 (s), 132.92 (s), 128.06 (s), 127.87 (s), 127.68 (s), 126.21 (s), 125.99 (s), 125.79 (s), 125.71 (s), 85.18 (s), 77.36 (s), 72.86 (s), 70.55 (s), 51.31 (s), 40.13 (s), 39.59 (s), 38.07 (s), 36.93 (s), 35.73 (s), 29.39 (s), 29.00 (s), 28.76 (s), 27.10 (s), 26.92 (s), 26.60 (s), 24.05 (s), 22.45 (s), 22.38 (s).

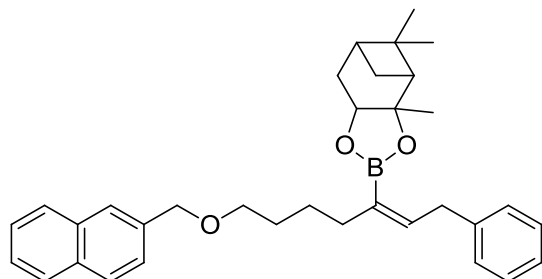
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.63 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{31}\text{H}_{43}\text{BO}_3$   $[\text{H}]^+$ : 475.3384, Found: 475.3376.





**(E)-3a,5,5-trimethyl-2-(7-(naphthalen-2-ylmethoxy)-1-phenylhept-2-en-3-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4u**

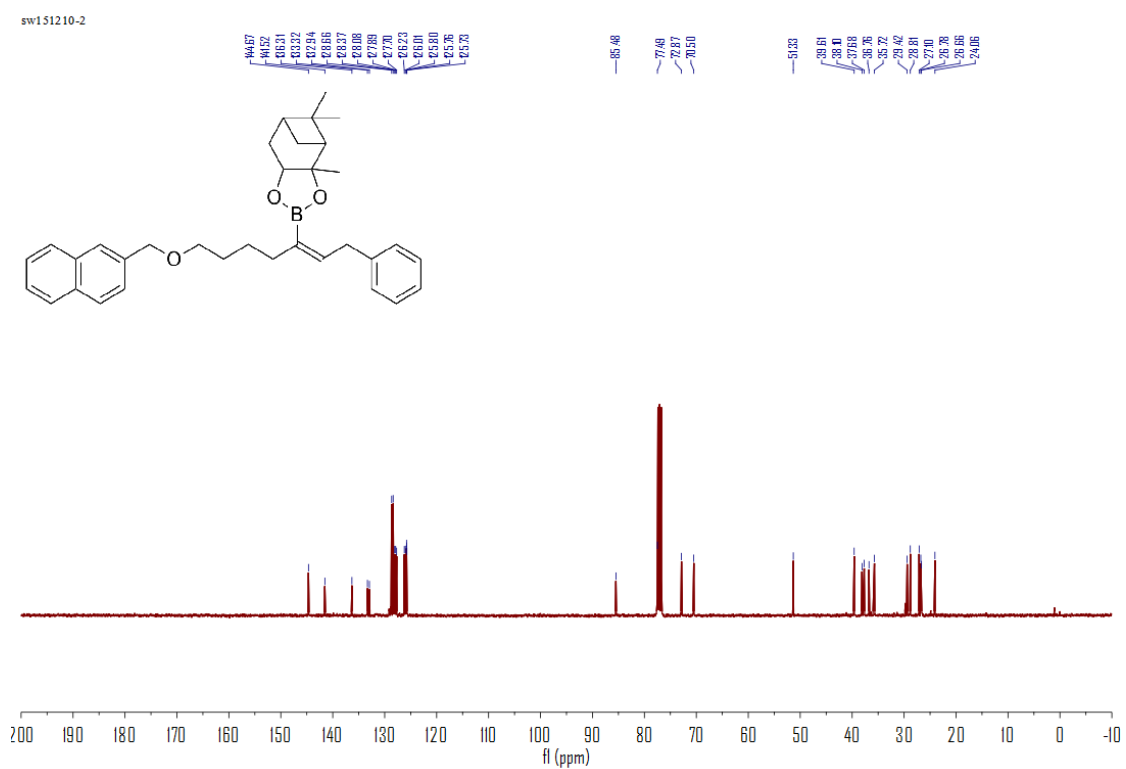
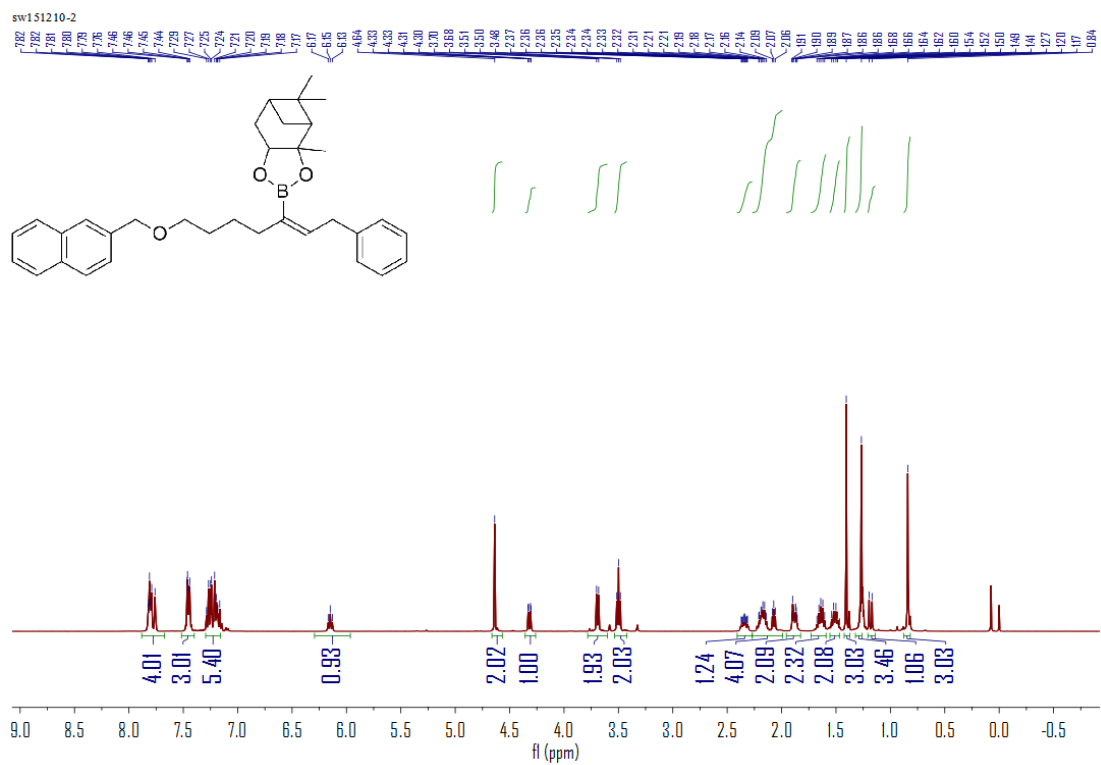


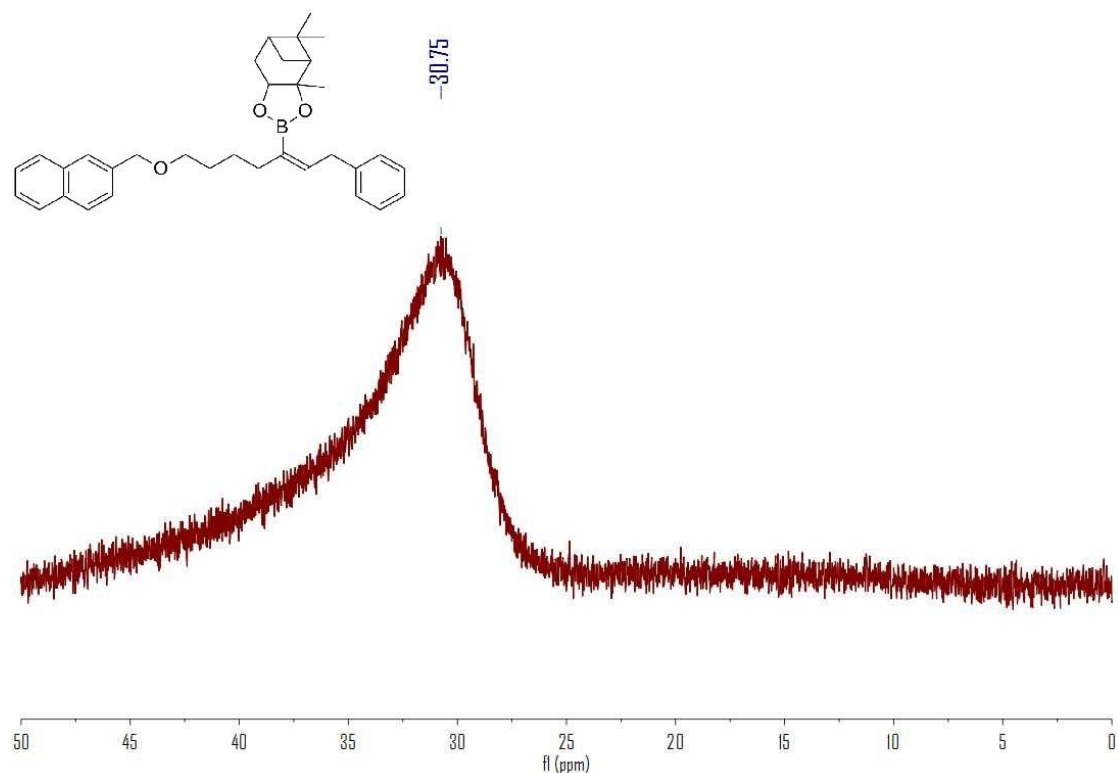
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.67 (m, 4H), 7.45 (m, 3H), 7.22 (m, 5H), 6.15 (t,  $J = 7.6$  Hz, 1H), 4.64 (s, 2H), 4.32 (dd,  $J = 8.7, 1.7$  Hz, 1H), 3.69 (d,  $J = 7.6$  Hz, 2H), 3.50 (t,  $J = 6.6$  Hz, 2H), 2.41 – 2.27 (m, 1H), 2.27 – 1.99 (m, 4H), 1.88 (m, 2H), 1.73 – 1.59 (m, 2H), 1.51 (m, 2H), 1.41 (s, 3H), 1.27 (s, 3H), 1.18 (d,  $J = 10.8$  Hz, 1H), 0.84 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.67 (s), 141.52 (s), 136.31 (s), 133.32 (s), 132.94 (s), 128.66 (s), 128.37 (s), 128.08 (s), 127.89 (s), 127.70 (s), 126.23 (s), 126.01 (s), 125.80 (s), 125.76 (s), 125.73 (s), 85.48 (s), 77.49 (s), 72.87 (s), 70.50 (s), 51.33 (s), 39.61 (s), 38.10 (s), 37.68 (s), 36.76 (s), 35.72 (s), 29.42 (s), 28.81 (s), 27.10 (s), 26.78 (s), 26.66 (s), 24.06 (s).

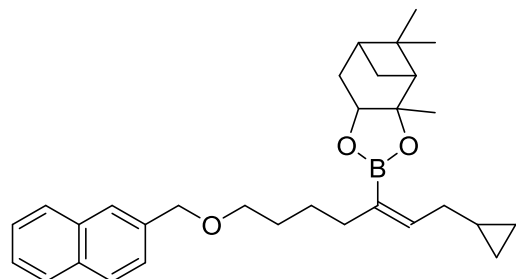
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  30.75 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{34}\text{H}_{41}\text{BO}_3$   $[\text{H}]^+$ : 509.3227, Found: 509.3214.





**(E)-2-(1-cyclopropyl-7-(naphthalen-2-ylmethoxy)hept-2-en-3-yl)-3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4v**

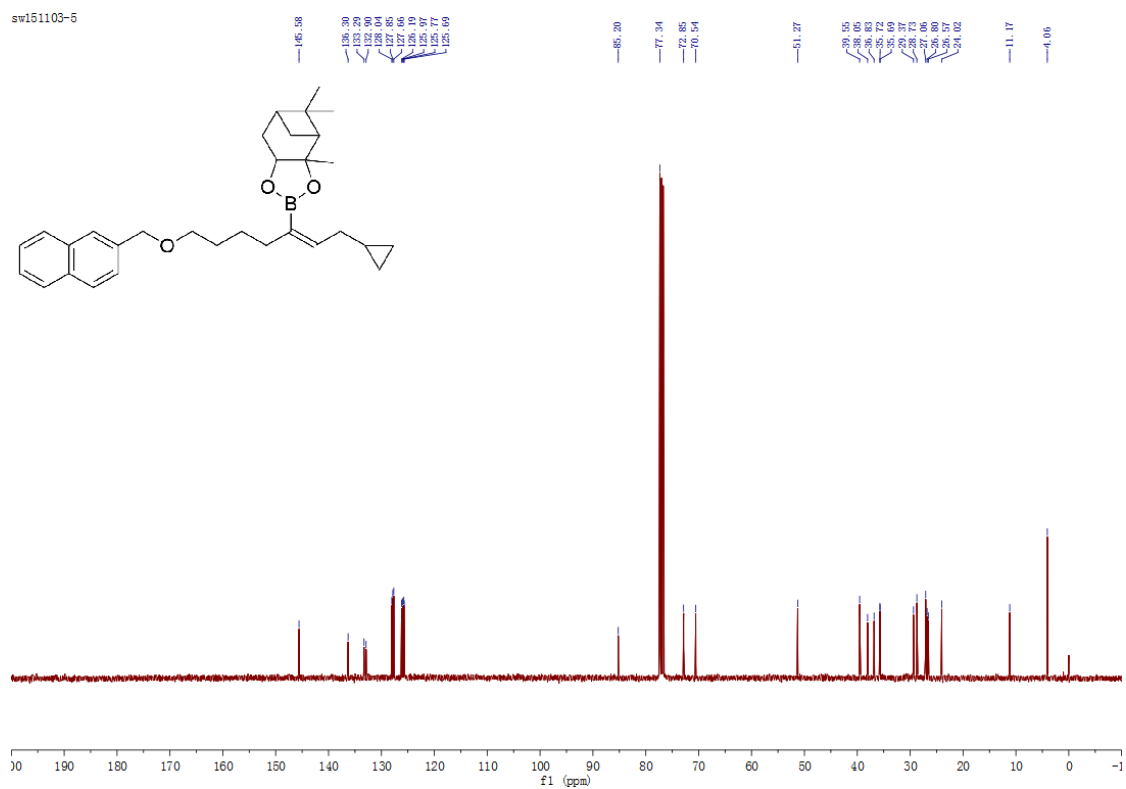
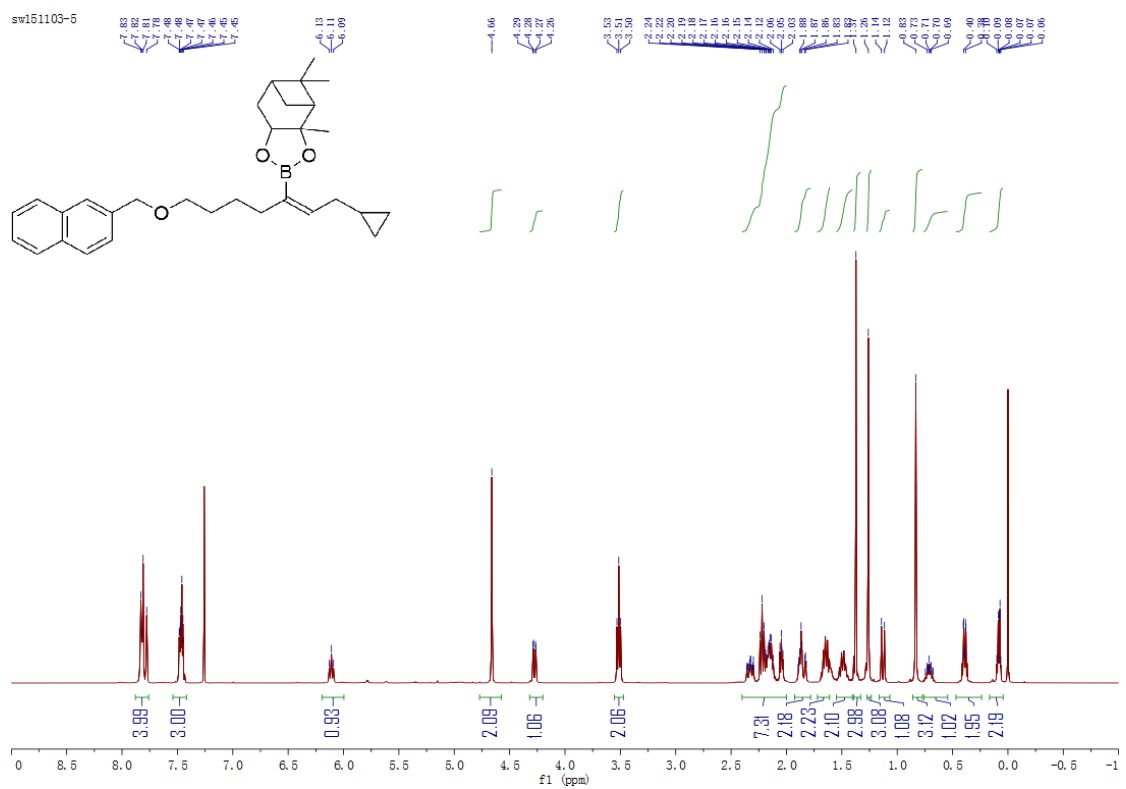


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (m, 4H), 7.69 – 7.33 (m, 1H), 6.11 (t,  $J = 7.4$  Hz, 1H), 4.66 (s, 2H), 4.27 (dd,  $J = 8.8, 1.8$  Hz, 1H), 3.51 (t,  $J = 6.7$  Hz, 2H), 2.40 – 1.96 (m, 7H), 1.86 (m, 2H), 1.68 – 1.56 (m, 2H), 1.55 – 1.44 (m, 2H), 1.37 (s, 3H), 1.26 (s, 3H), 1.13 (d,  $J = 10.9$  Hz, 1H), 0.83 (s, 3H), 0.77 – 0.64 (m, 1H), 0.57 – 0.31 (m, 2H), 0.19 – 0.03 (m, 2H).

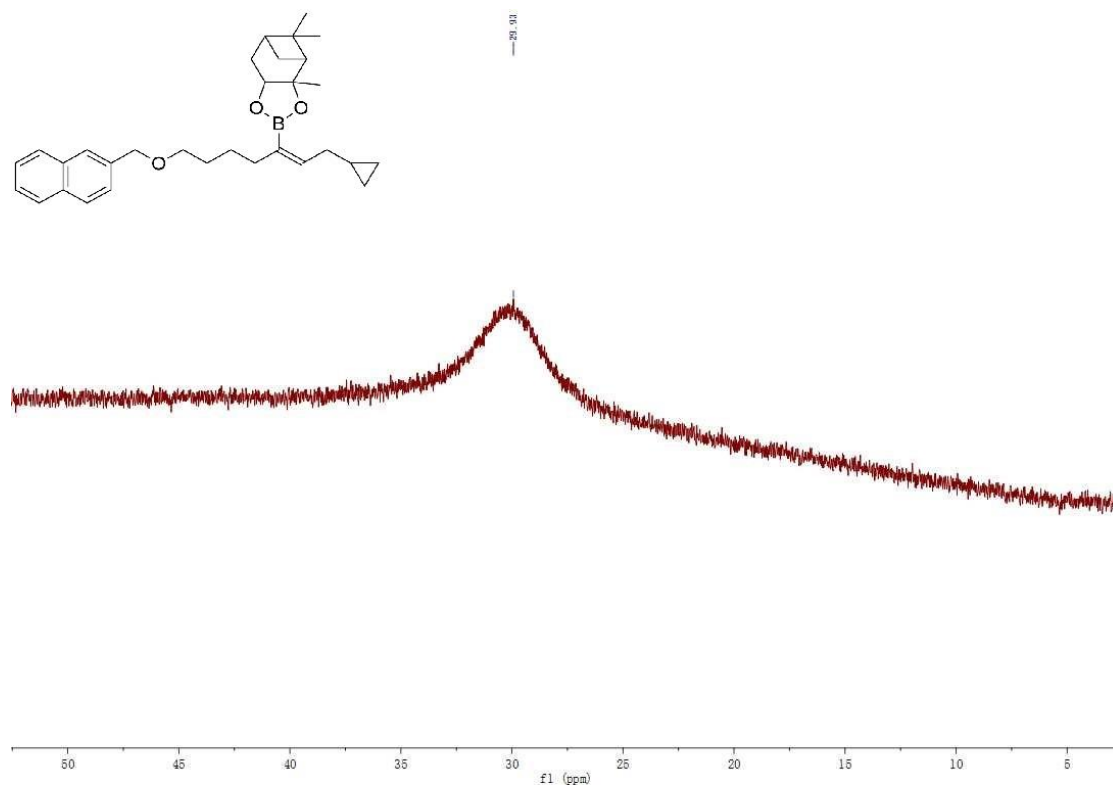
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.58 (s), 136.30 (s), 133.29 (s), 132.90 (s), 128.04 (s), 127.85 (s), 127.66 (s), 126.19 (s), 125.97 (s), 125.77 (s), 125.69 (s), 85.20 (s), 77.34 (s), 72.85 (s), 70.54 (s), 51.27 (s), 39.55 (s), 38.05 (s), 36.83 (s), 35.72 (s), 35.69 (s), 29.37 (s), 28.73 (s), 27.06 (s), 26.80 (s), 26.57 (s), 24.02 (s), 11.17 (s), 4.06 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.93 (s).

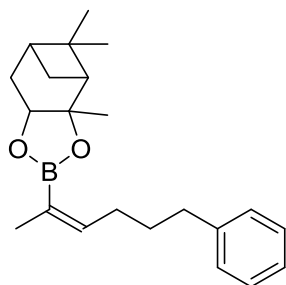
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{31}\text{H}_{41}\text{BO}_3$   $[\text{H}]^+$ : 473.3227, Found: 473.3221.







**(E)-3a,5,5-trimethyl-2-(6-phenylhex-2-en-2-yl)hexahydro-4,6-methanobenzo[d][1,3,2]dioxaborole, 4w**

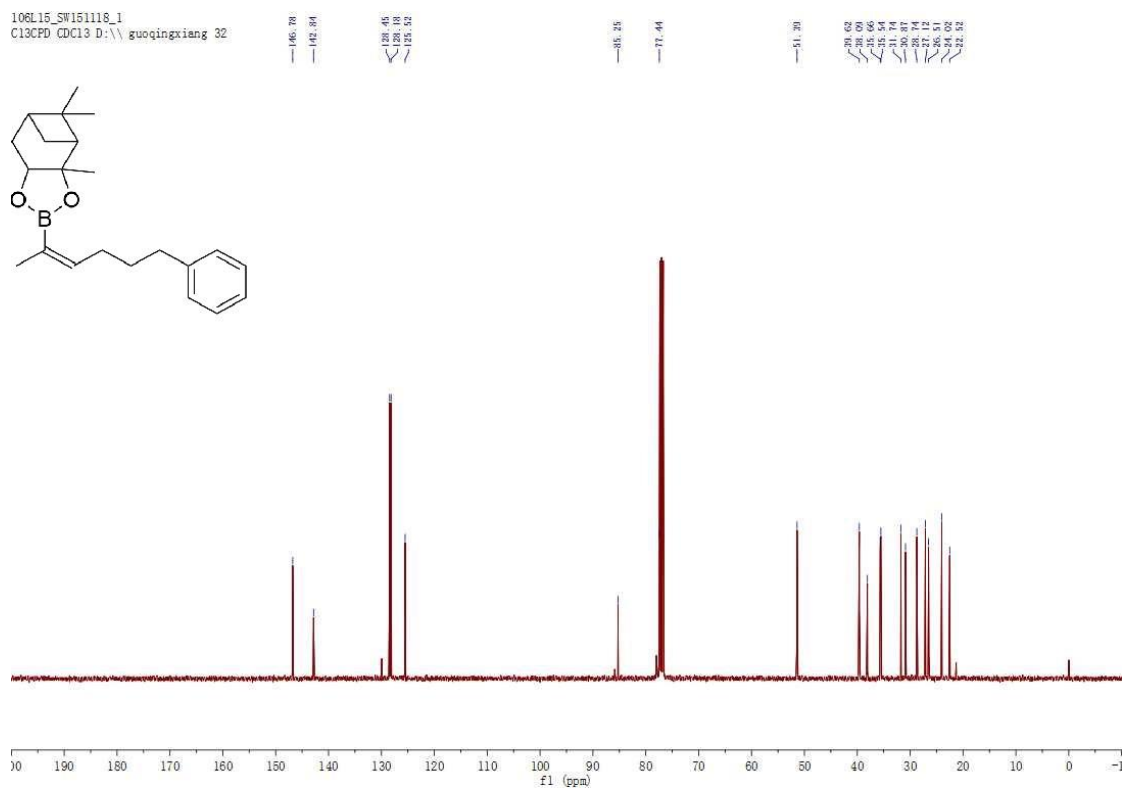
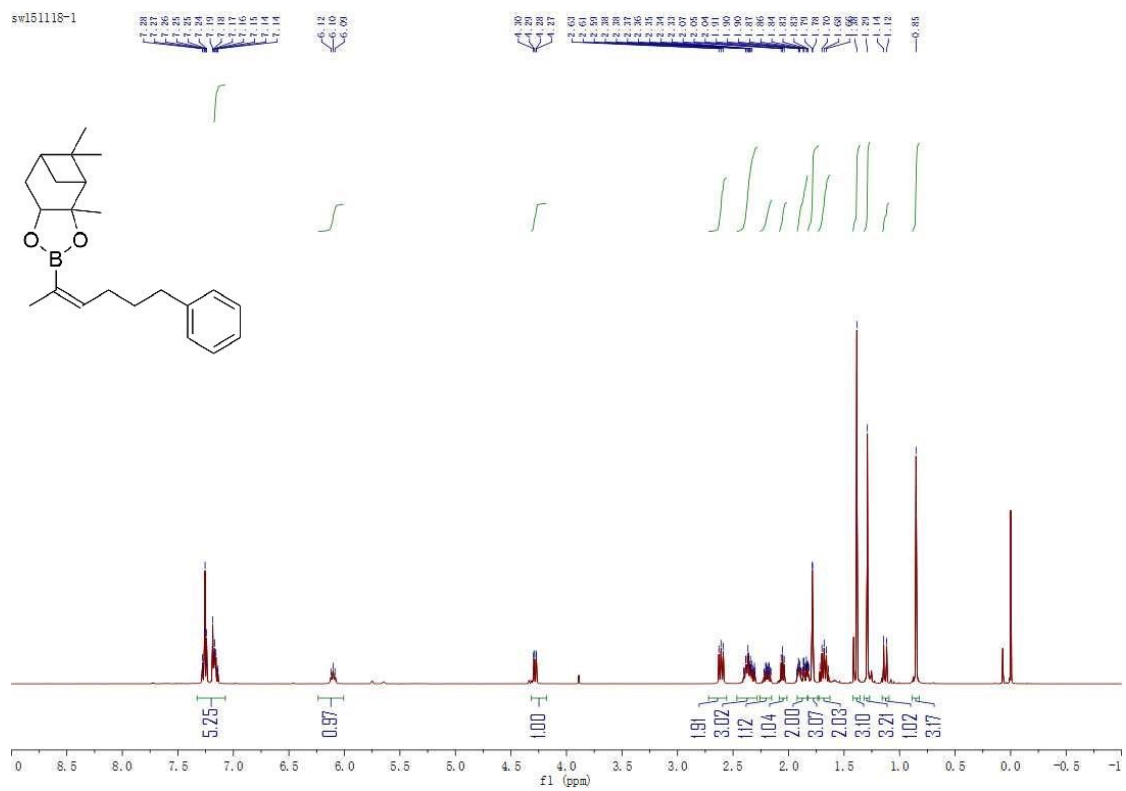


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.06 (m, 5H), 6.10 (t,  $J$  = 6.9 Hz, 1H), 4.28 (dd,  $J$  = 8.7, 2.0 Hz, 1H), 2.68 – 2.51 (m, 2H), 2.45 – 2.25 (m, 3H), 2.25 – 2.10 (m, 1H), 2.10 – 2.00 (m, 1H), 1.98 – 1.80 (m, 2H), 1.78 (d,  $J$  = 1.3 Hz, 3H), 1.68 (m, 2H), 1.38 (s, 3H), 1.29 (s, 3H), 1.13 (d,  $J$  = 10.9 Hz, 1H), 0.85 (s, 3H).

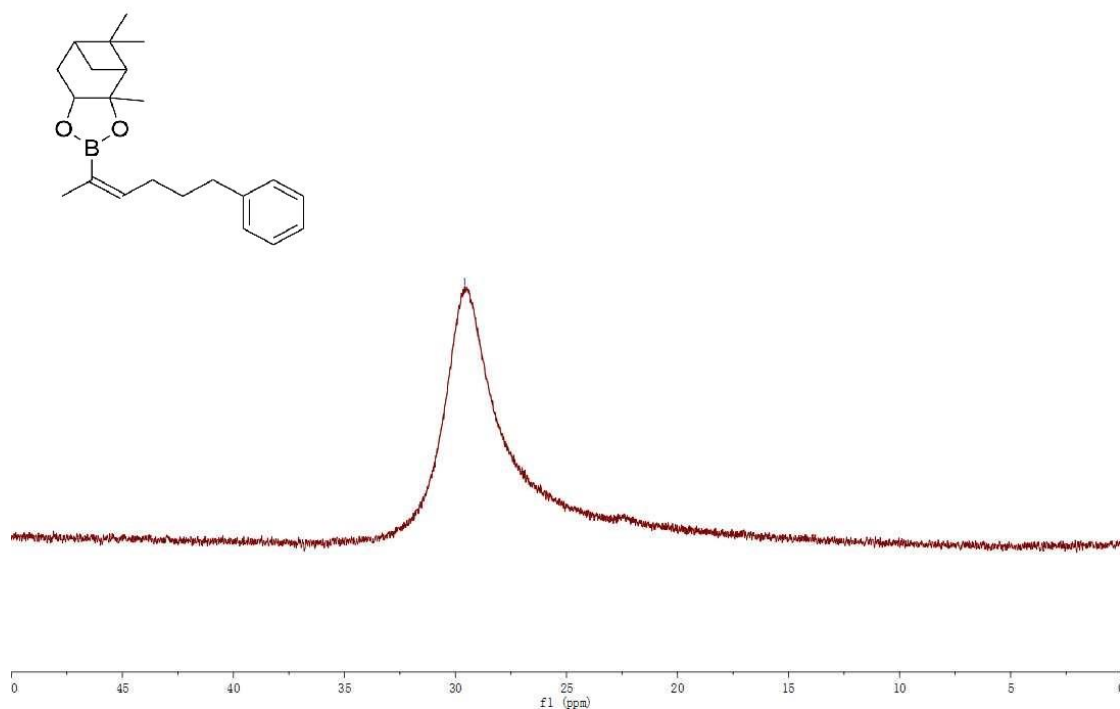
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.78 (s), 142.84 (s), 128.45 (s), 128.18 (s), 125.52 (s), 85.25 (s), 77.44 (s), 51.39 (s), 39.62 (s), 38.09 (s), 35.66 (s), 35.54 (s), 31.74 (s), 30.87 (s), 28.74 (s), 27.12 (s), 26.51 (s), 24.02 (s), 22.52 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  29.59 (s).

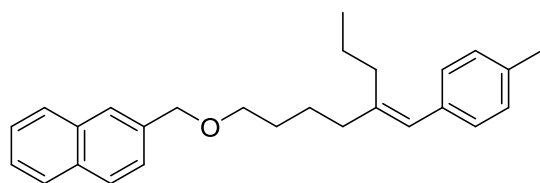
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{22}\text{H}_{31}\text{BO}_2$   $[\text{H}]^+$ : 339.2495, Found: 339.2487.



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B112G CDCl3 D:\ guoqingxiang 32



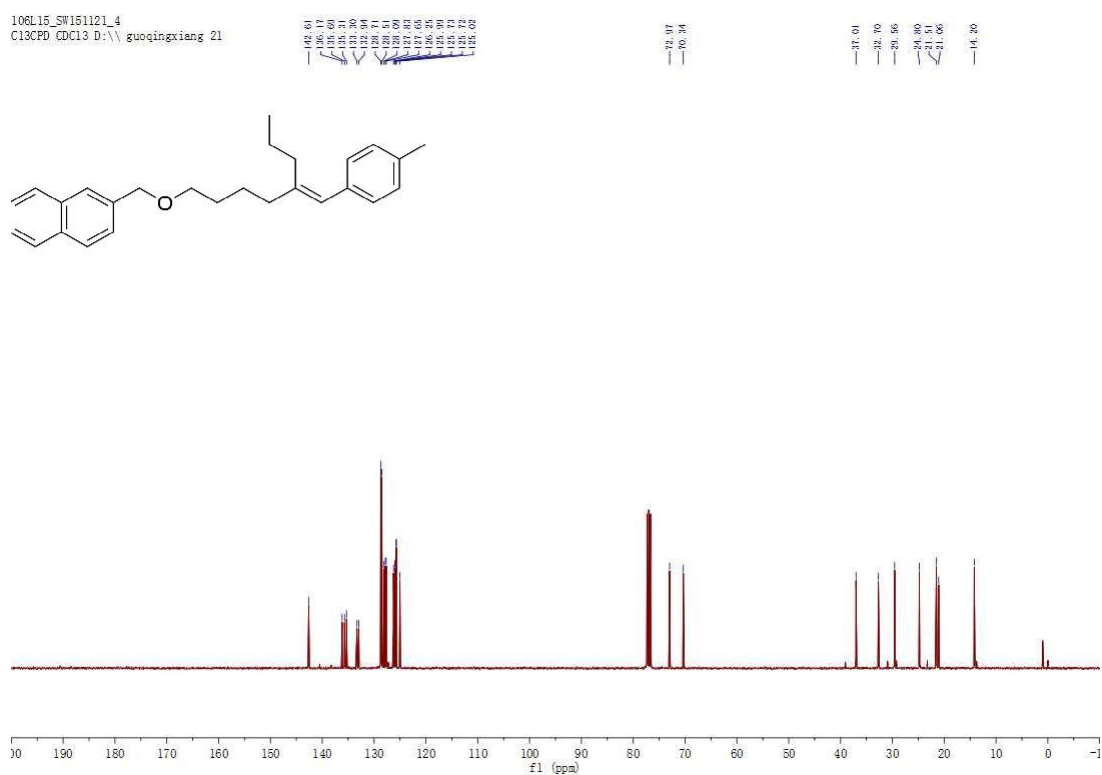
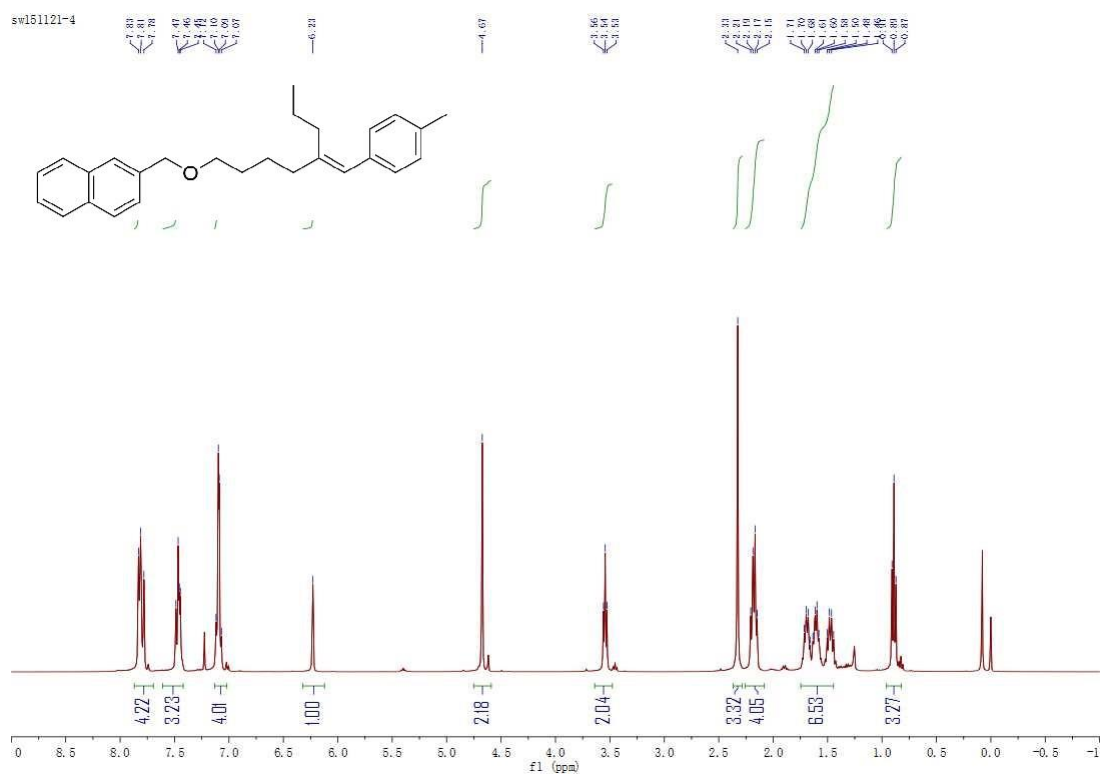
**(E)-2-(((5-(4-methylbenzylidene)octyl)oxy)methyl)naphthalene, 5a**



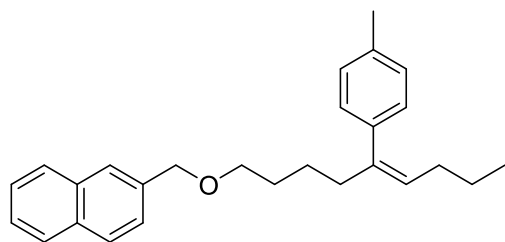
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 – 7.71 (m, 4H), 7.46 (m, 3H), 7.18 – 7.00 (m, 4H), 6.23 (s, 1H), 4.67 (s, 2H), 3.54 (t,  $J$  = 6.4 Hz, 2H), 2.33 (s, 3H), 2.18 (m, 4H), 1.98 – 1.31 (m, 6H), 0.89 (t,  $J$  = 7.3 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.61 (s), 136.17 (s), 135.69 (s), 135.31 (s), 133.30 (s), 132.94 (s), 128.71 (s), 128.51 (s), 128.09 (s), 127.83 (s), 127.65 (s), 126.25 (s), 125.99 (s), 125.73 (s), 125.72 (s), 125.02 (s), 72.97 (s), 70.34 (s), 37.01 (s), 32.70 (s), 29.56 (s), 24.80 (s), 21.51 (s), 21.06 (s), 14.20 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{27}\text{H}_{32}\text{O}[\text{H}]^+$ : 373.2531, Found: 373.2526.



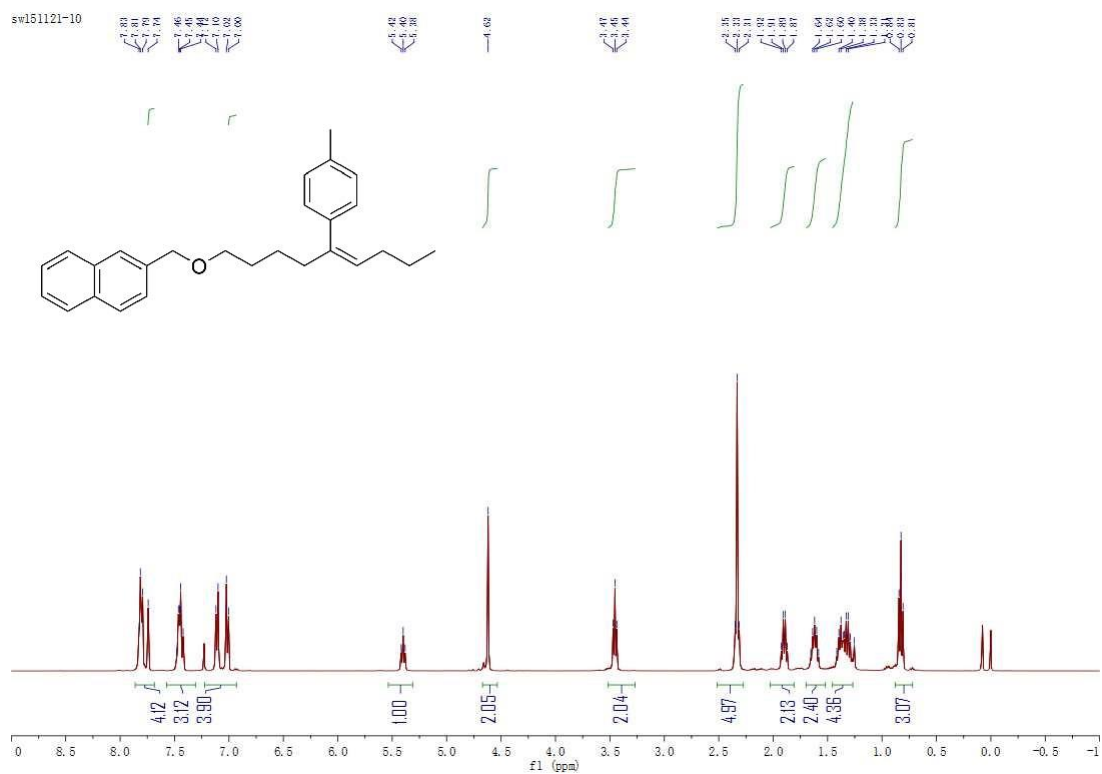
**(Z)-2-(((5-(p-tolyl)non-5-en-1-yl)oxy)methyl)naphthalene**



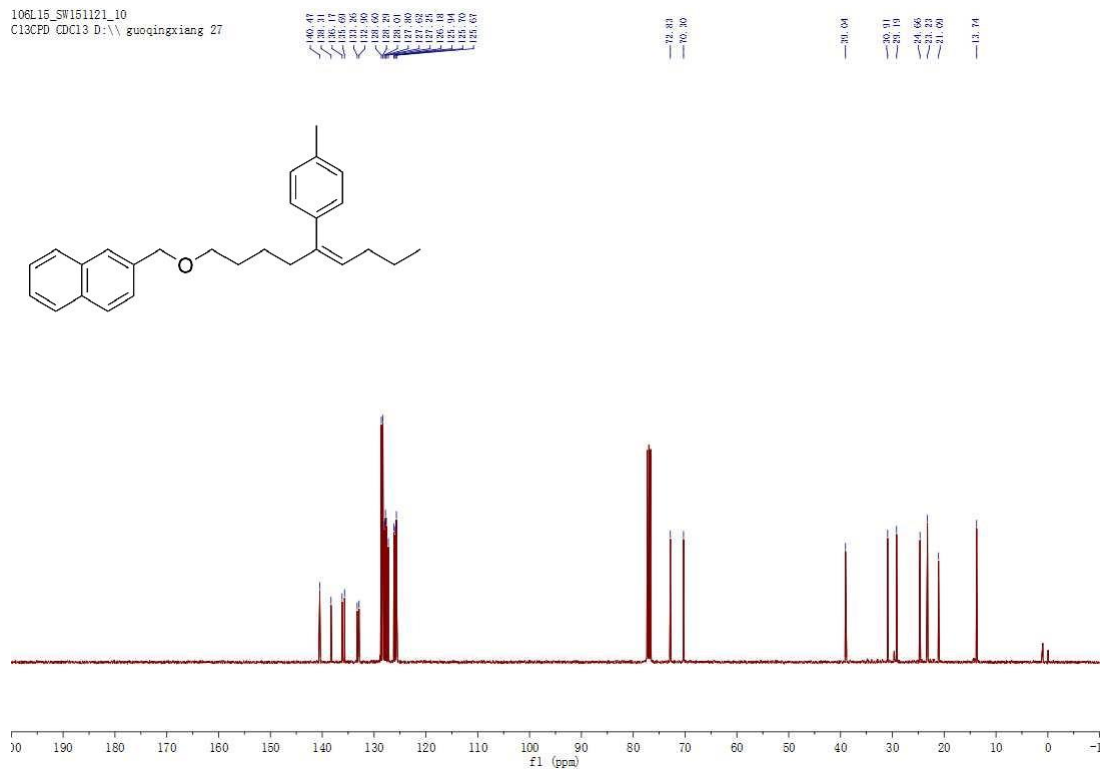
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (m, 4H), 7.63 – 7.32 (m, 3H), 7.06 (dd,  $J = 38.4, 7.7$  Hz, 4H), 5.40 (t,  $J = 7.2$  Hz, 1H), 4.62 (s, 2H), 3.45 (t,  $J = 6.7$  Hz, 2H), 2.39 – 2.14 (m, 5H), 1.90 (m, 2H), 1.74 – 1.52 (m, 2H), 1.50 – 1.23 (m, 4H), 0.83 (t,  $J = 7.4$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.47 (s), 138.31 (s), 136.17 (s), 135.69 (s), 133.26 (s), 132.90 (s), 128.60 (s), 128.29 (s), 128.01 (s), 127.80 (s), 127.62 (s), 127.25 (s), 126.18 (s), 125.94 (s), 125.70 (s), 125.67 (s), 72.83 (s), 70.30 (s), 39.04 (s), 30.91 (s), 29.19 (s), 24.66 (s), 23.23 (s), 21.09 (s), 13.74 (s).

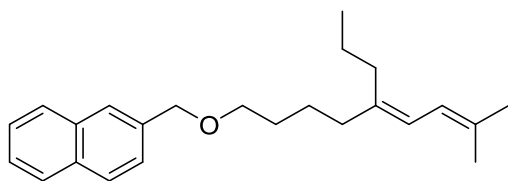
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{27}\text{H}_{32}\text{O}[\text{H}]^+$ : 373.2531, Found: 373.2526.



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C13CPD CDCl3 D:\ guoqingxiang 27



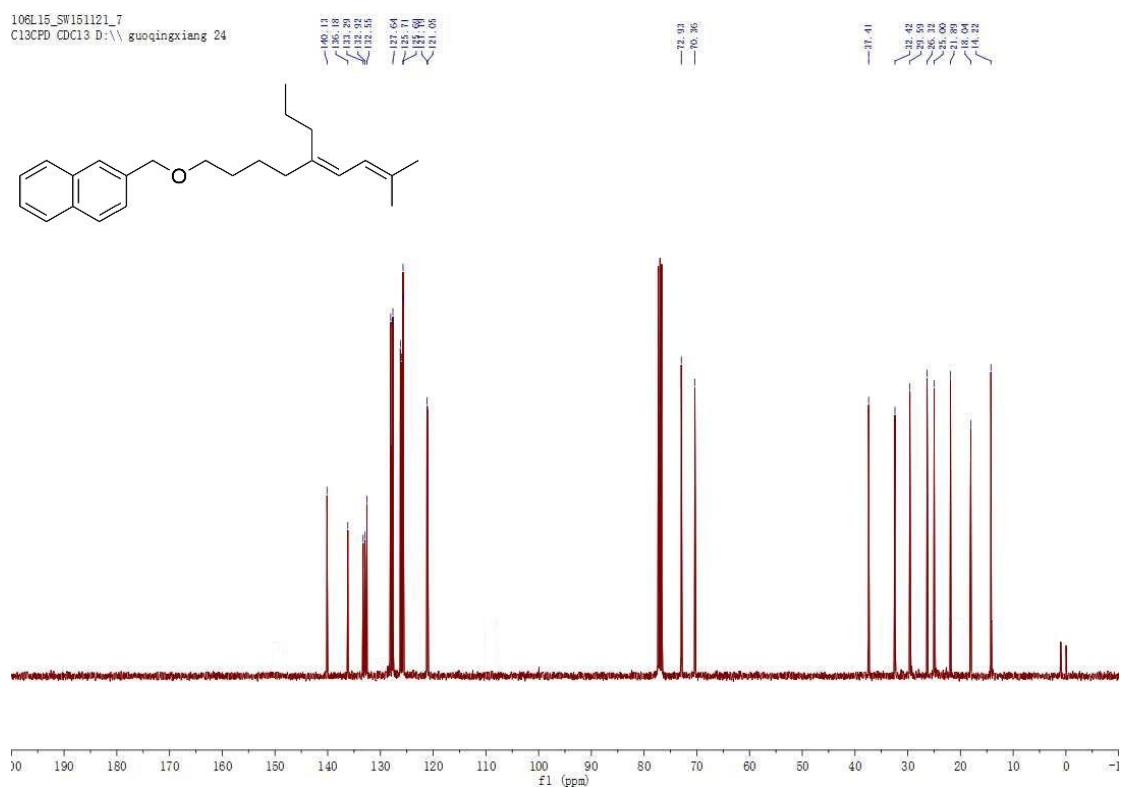
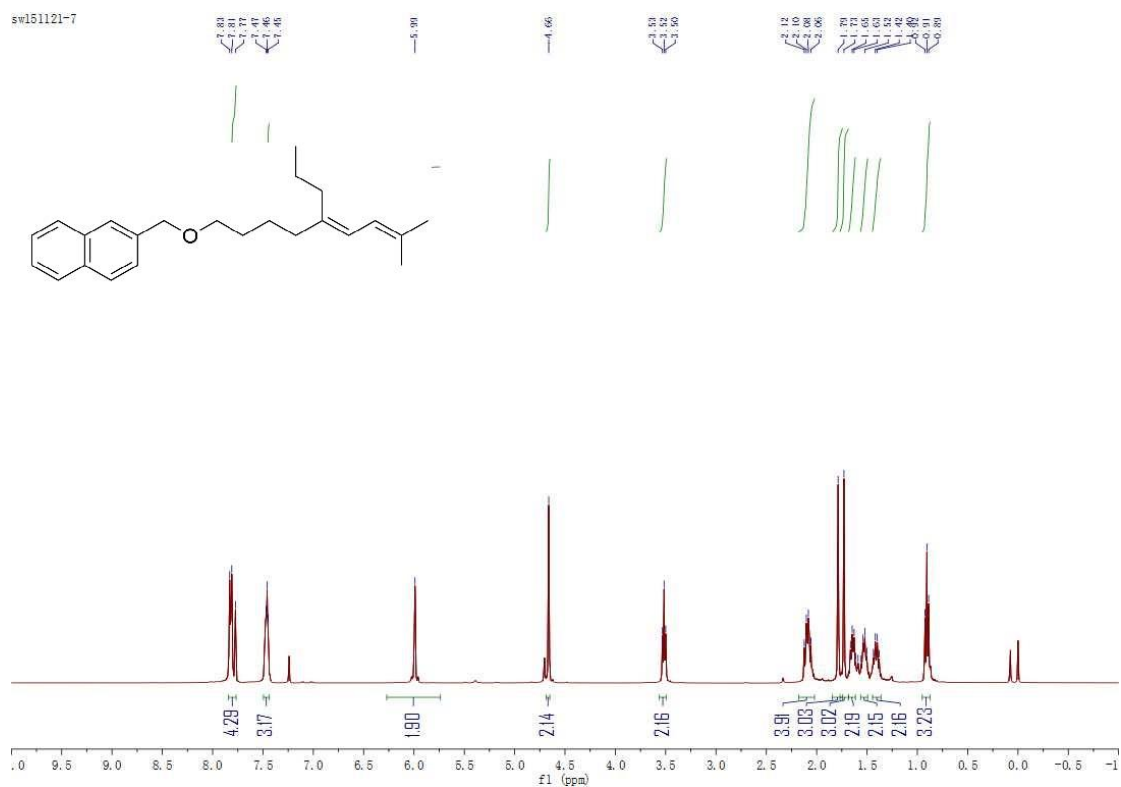
**(E)-2-(((8-methyl-5-propylnona-5,7-dien-1-yl)oxy)methyl)naphthalene, 6a**



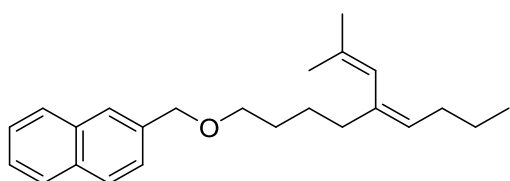
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 – 7.67 (m, 4H), 7.59 – 7.34 (m, 3H), 5.99 (s, 2H), 4.66 (s, 2H), 3.52 (t,  $J$  = 6.4 Hz, 2H), 2.09 (M, 4H), 1.79 (s, 3H), 1.73 (s, 3H), 1.64 (M, 2H), 1.53 (M, 2H), 1.41 (M, 2H), 0.91 (t,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.13 (s), 136.18 (s), 133.29 (s), 132.92 (s), 132.55 (s), 128.06 (s), 127.81 (s), 127.64 (s), 126.22 (s), 125.97 (s), 125.71 (s), 125.69 (s), 121.19 (s), 121.05 (s), 72.93 (s), 70.36 (s), 37.41 (s), 32.42 (s), 29.59 (s), 26.32 (s), 25.00 (s), 21.89 (s), 18.04 (s), 14.22 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{24}\text{H}_{32}\text{O}[\text{H}]^+$ : 337.2531, Found: 337.2526.



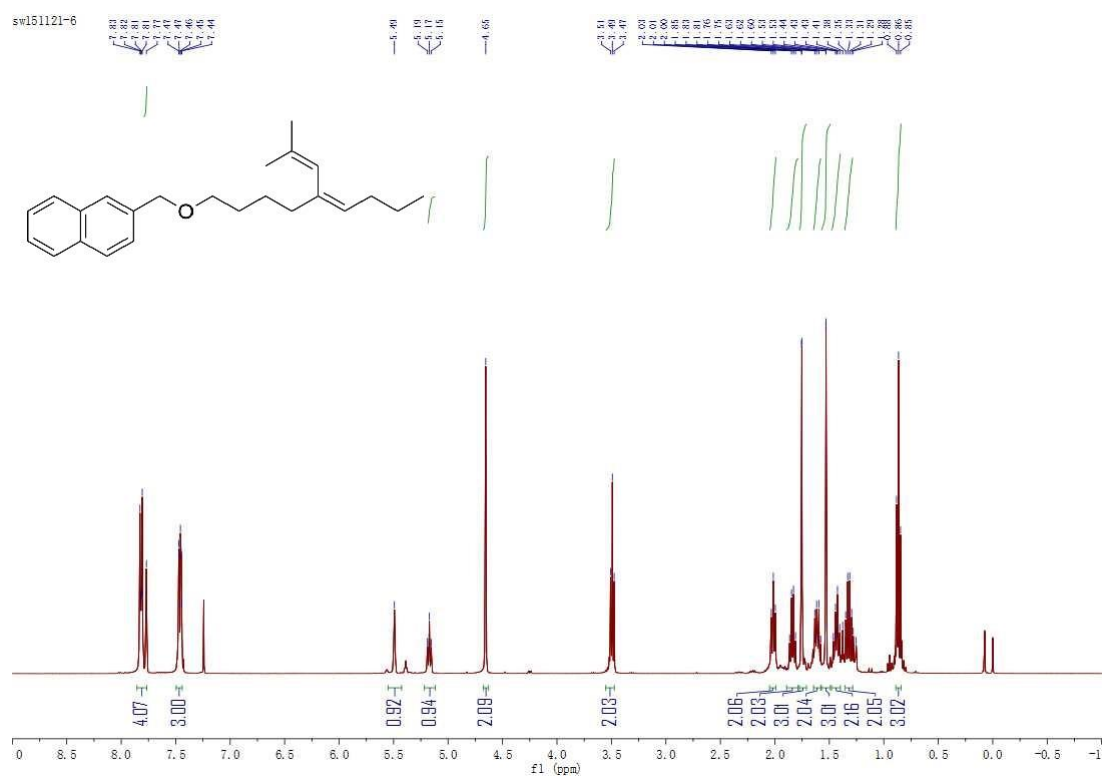
**(Z)-2-(((5-(2-methylprop-1-en-1-yl)non-5-en-1-yl)oxy)methyl)naphthalene, 6b**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 – 7.77 (m, 4H), 7.50 – 7.44 (m, 3H), 5.49 (s, 1H), 5.17 (t,  $J = 7.0$  Hz, 1H), 4.65 (s, 2H), 3.49 (t,  $J = 6.7$  Hz, 2H), 2.01 (t,  $J = 7.5$  Hz, 2H), 1.86 (m, 2H), 1.75 (d,  $J = 1.2$  Hz, 3H), 1.64 – 1.58 (m, 2H), 1.53 (d,  $J = 0.8$  Hz, 3H), 1.48 – 1.40 (m, 2H), 1.32 (m, 2H), 0.86 (t,  $J = 7.4$  Hz, 3H). The protonation product is hard to separated and mixed in it.

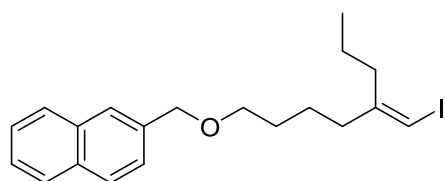
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.16 (s), 136.21 (s), 133.88 (s), 133.25 (s), 132.88 (s), 128.01 (s), 127.77 (s), 127.61 (s), 126.77 (s), 126.15 (s), 125.93 (s), 125.67 (s), 125.65 (s), 123.72 (s), 72.83 (s), 70.39 (s), 38.02 (s), 31.21 (s), 29.39 (s), 25.36 (s), 24.88 (s), 22.71 (s), 19.58 (s), 13.88 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{24}\text{H}_{32}\text{O}[\text{H}]^+$ : 337.2531, Found: 337.2526.





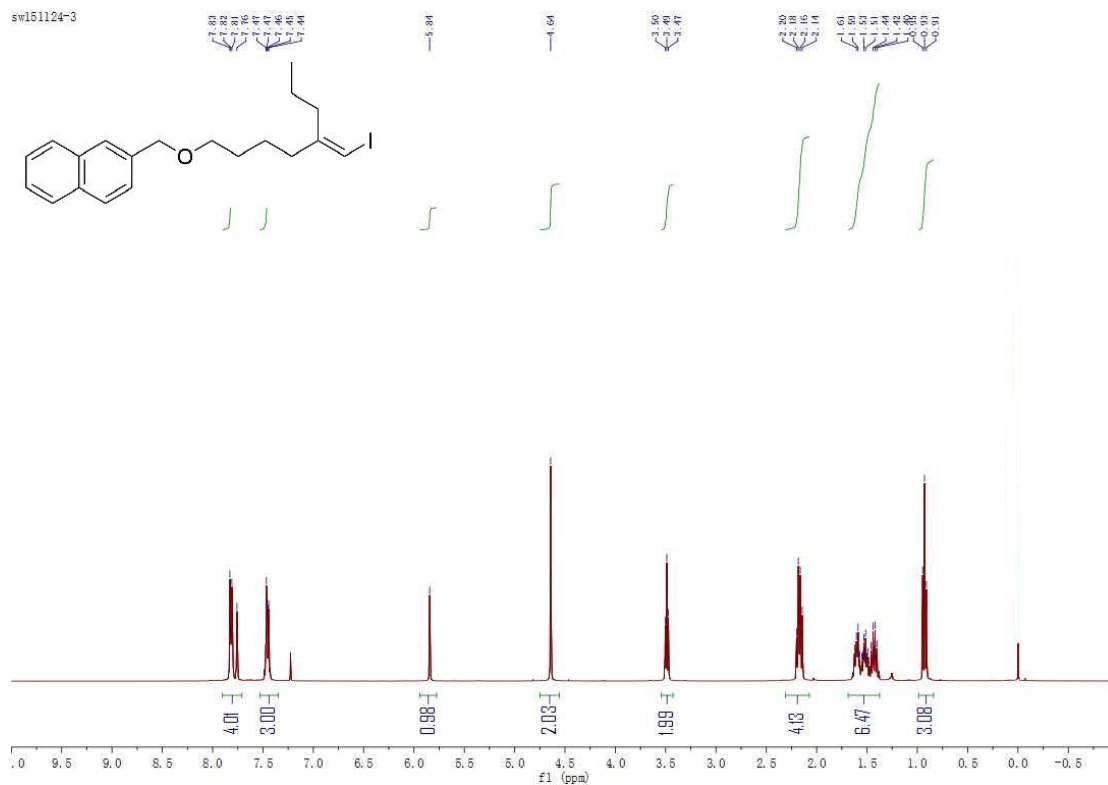
137.16  
136.21  
133.88  
133.25  
132.88  
128.01  
127.77  
127.61  
126.77  
126.15  
125.93  
125.67  
125.65  
123.72



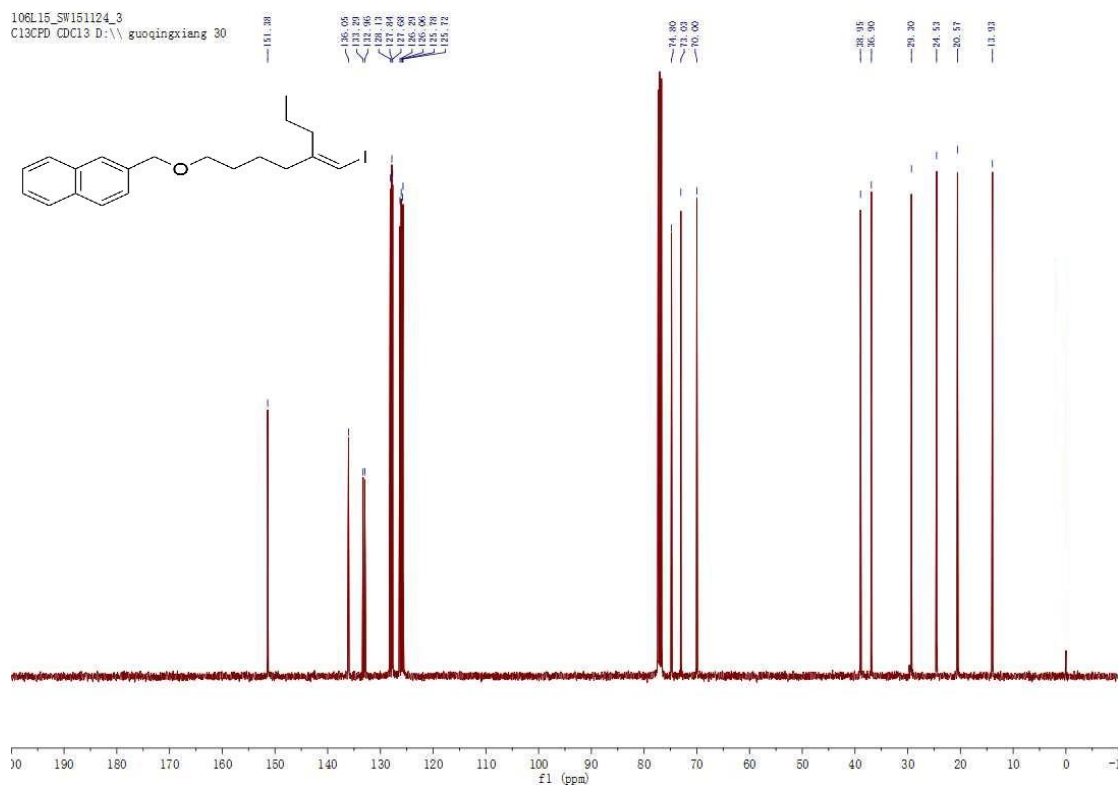
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.38 (s), 136.05 (s), 133.29 (s), 132.96 (s), 128.13 (s), 127.84 (s), 127.68 (s), 126.29 (s), 126.06 (s), 125.78 (s), 125.72 (s), 74.80 (s), 73.03 (s), 70.00 (s), 38.95 (s), 36.90 (s), 29.30 (s), 24.53 (s), 20.57 (s), 13.93 (s).

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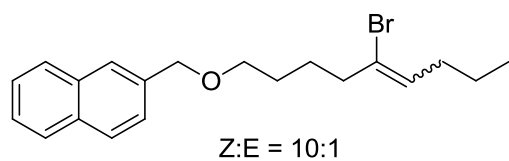
sw151124-3



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C13CPD CDCl3 D:\ guoqingxiang 30



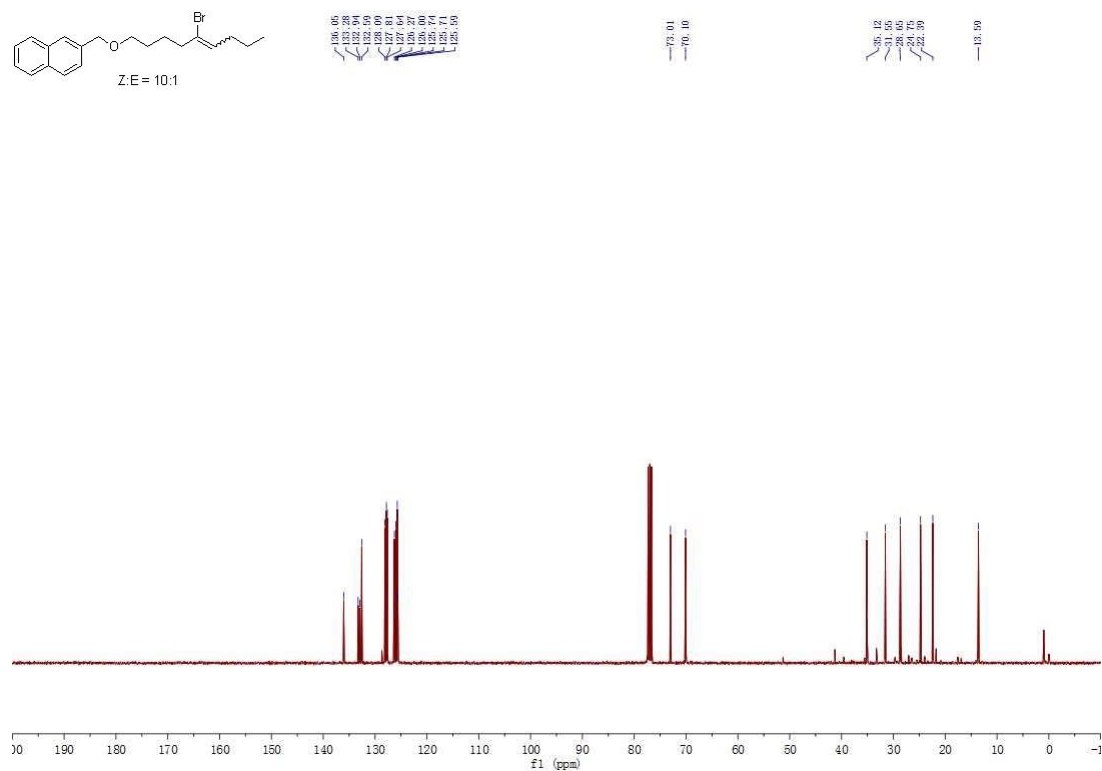
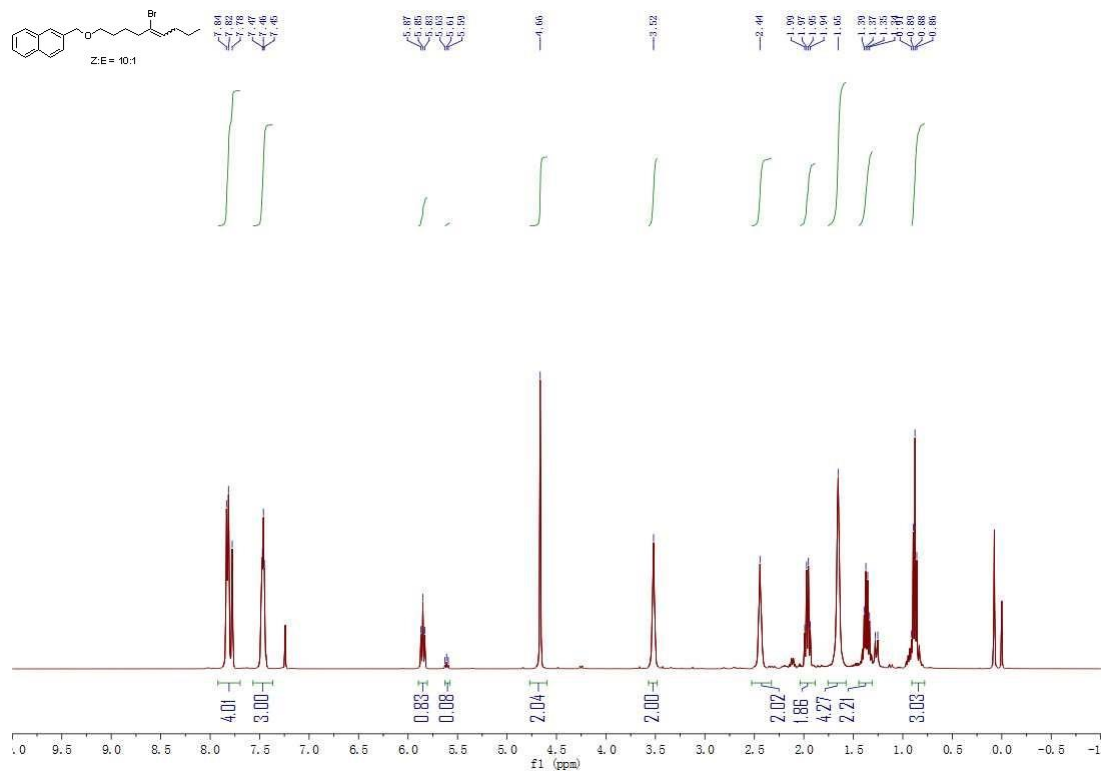
(Z)-2-(((5-bromonon-5-en-1-yl)oxy)methyl)naphthalene, 7b



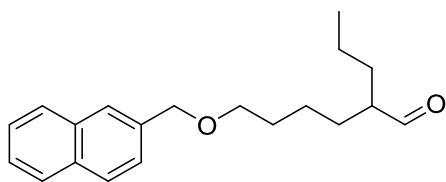
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 – 7.68 (m, 4H), 7.63 – 7.43 (m, 3H), 5.73 (m, 1H), 4.66 (s, 2H), 3.52 (m, 2H), 2.44 (m, 2H), 1.96 (m, 2H), 1.65 (m, 4H), 1.36 (m, 2H), 0.88 (t,  $J = 7.3$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.05 (s), 133.28 (s), 132.94 (s), 132.59 (s), 128.09 (s), 127.81 (s), 127.64 (s), 126.27 (s), 126.00 (s), 125.74 (s), 125.71 (s), 125.59 (s), 73.01 (s), 70.10 (s), 35.12 (s), 31.55 (s), 28.65 (s), 24.75 (s), 22.39 (s), 13.59 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{20}\text{H}_{25}\text{BrO}[\text{Na}]^+$ : 383.0986, Found: 383.0983.



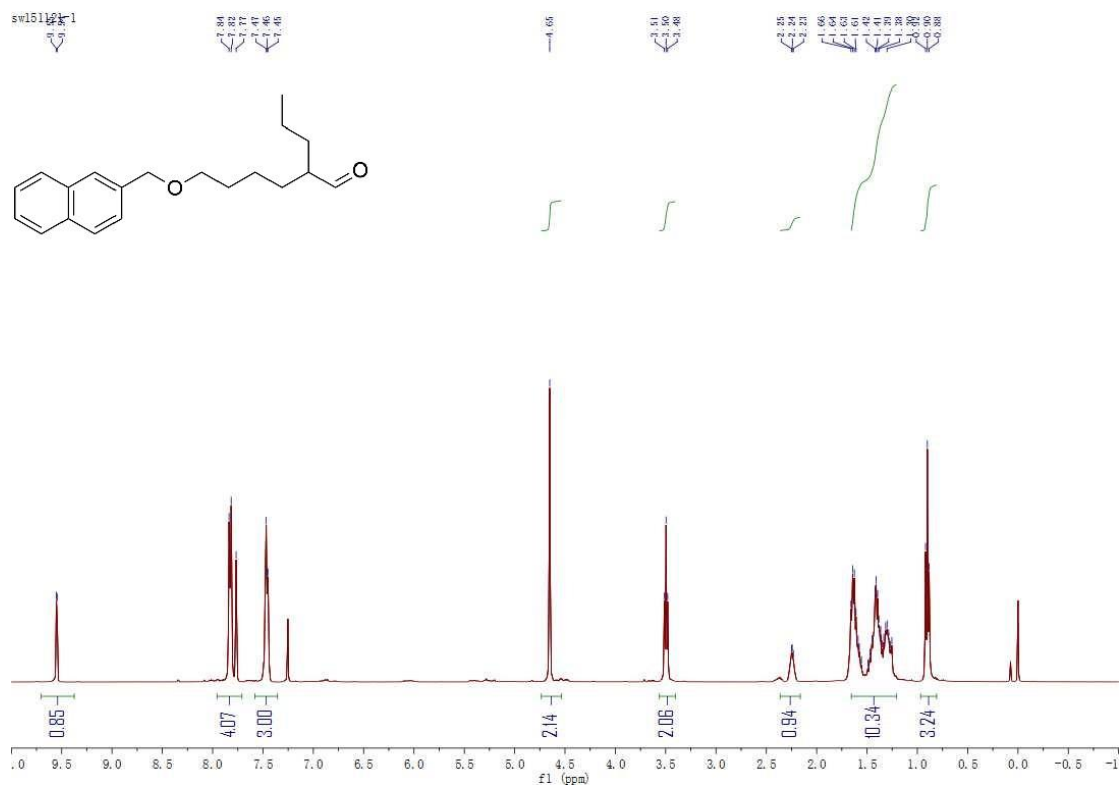
**6-(naphthalen-2-ylmethoxy)-2-propylhexanal, 8a**



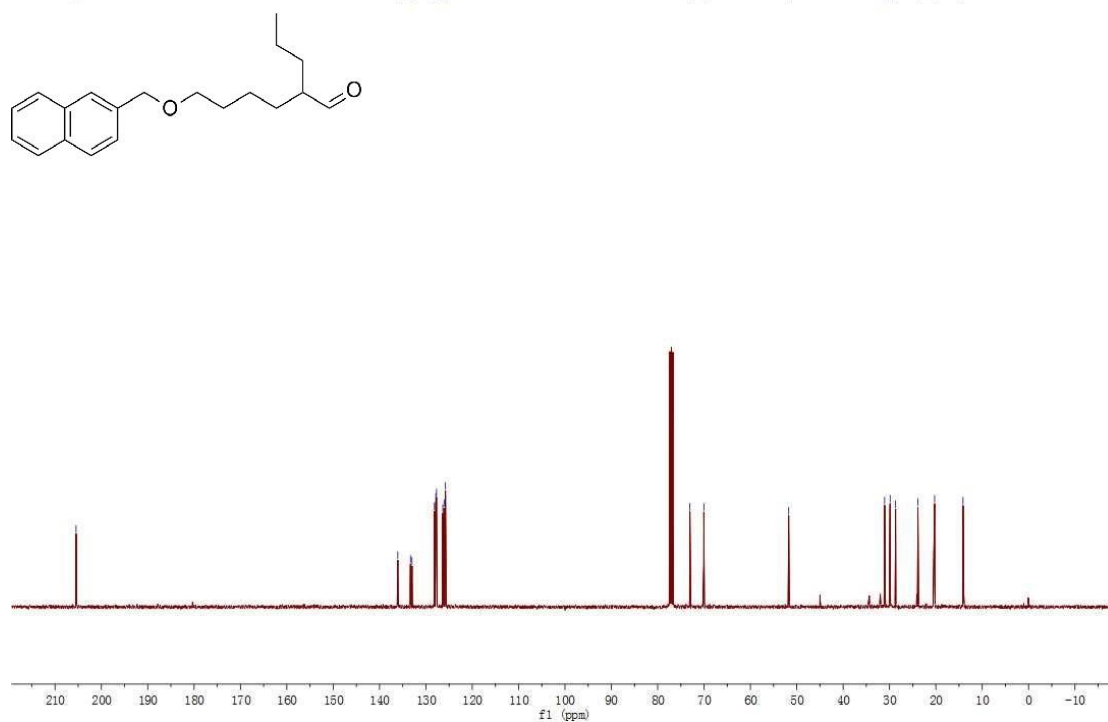
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.55 (d,  $J = 3.0$  Hz, 1H), 8.17 – 7.73 (m, 4H), 7.67 – 7.29 (m, 3H), 4.65 (s, 2H), 3.50 (t,  $J = 6.4$  Hz, 2H), 2.43 – 2.05 (m, 1H), 1.74 – 1.12 (m, 10H), 0.90 (t,  $J = 7.2$  Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  205.46 (s), 136.06 (s), 133.32 (s), 133.00 (s), 128.16 (s), 127.87 (s), 127.70 (s), 126.35 (s), 126.08 (s), 125.81 (s), 125.77 (s), 73.05 (s), 70.05 (s), 51.74 (s), 31.05 (s), 29.86 (s), 28.68 (s), 23.86 (s), 20.27 (s), 14.14 (s).

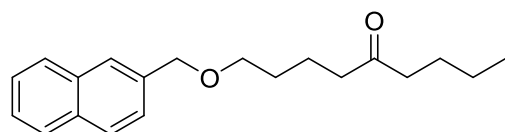
HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_2[\text{H}]^+$ : 299.2011, Found: 299.2005.



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# **1-(naphthalen-2-ylmethoxy)nonan-5-one, 8b**

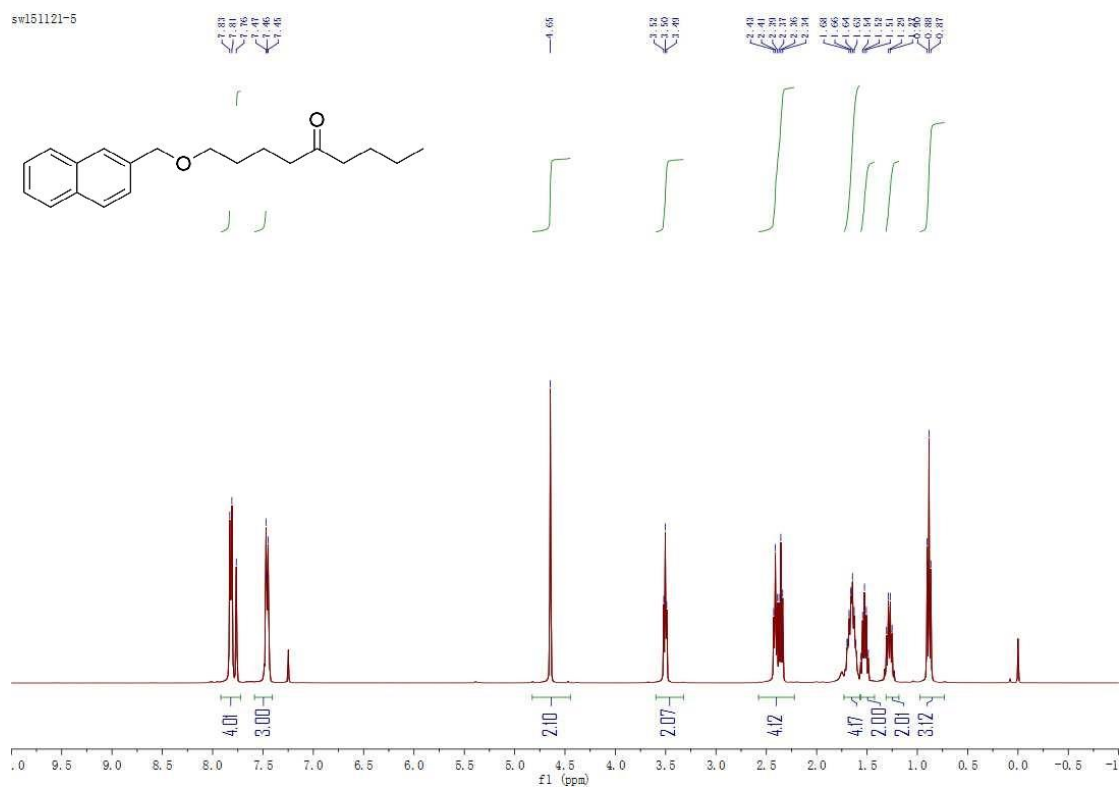


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 – 7.67 (m, 4H), 7.67 – 7.41 (m, 3H), 4.65 (s, 2H), 3.50 (t,  $J$  = 5.9 Hz, 2H), 2.38 (m, 4H), 1.83 – 1.58 (m, 4H), 1.58 – 1.45 (m, 2H), 1.28 (m, 2H), 0.88 (t,  $J$  = 7.3 Hz, 3H).

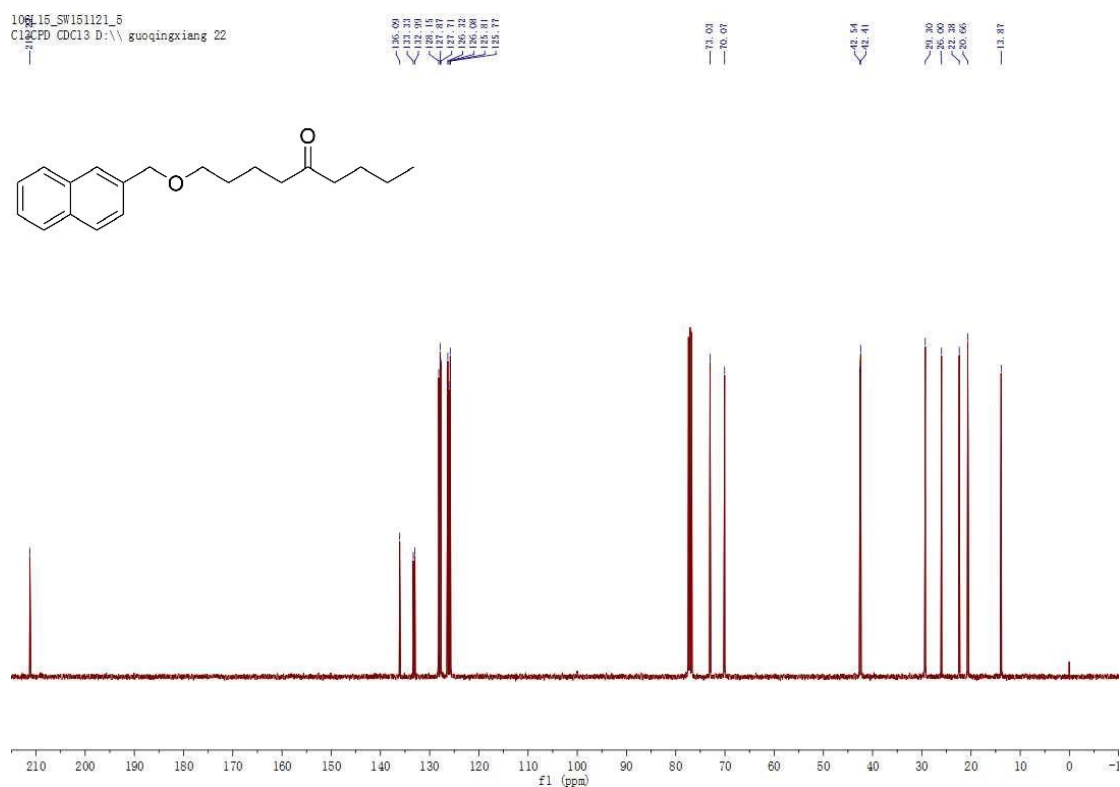
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  211.23 (s), 136.09 (s), 133.33 (s), 132.99 (s), 128.15 (s), 127.87 (s), 127.71 (s), 126.32 (s), 126.08 (s), 125.81 (s), 125.77 (s), 73.03 (s), 70.07 (s), 42.54 (s), 42.41 (s), 29.30 (s), 26.00 (s), 22.38 (s), 20.66 (s), 13.87 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{20}\text{H}_{26}\text{O}_2[\text{H}]^+$ : 299.2011, Found: 299.2006.

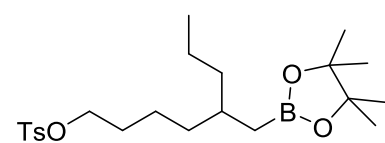
sw151121-5



106115 SW151121\_5  
Cl<sub>3</sub>PD CDCl<sub>3</sub> D:\ guoqingxiang 22



5-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)octyl 4-methylbenzenesulfonate, 9a

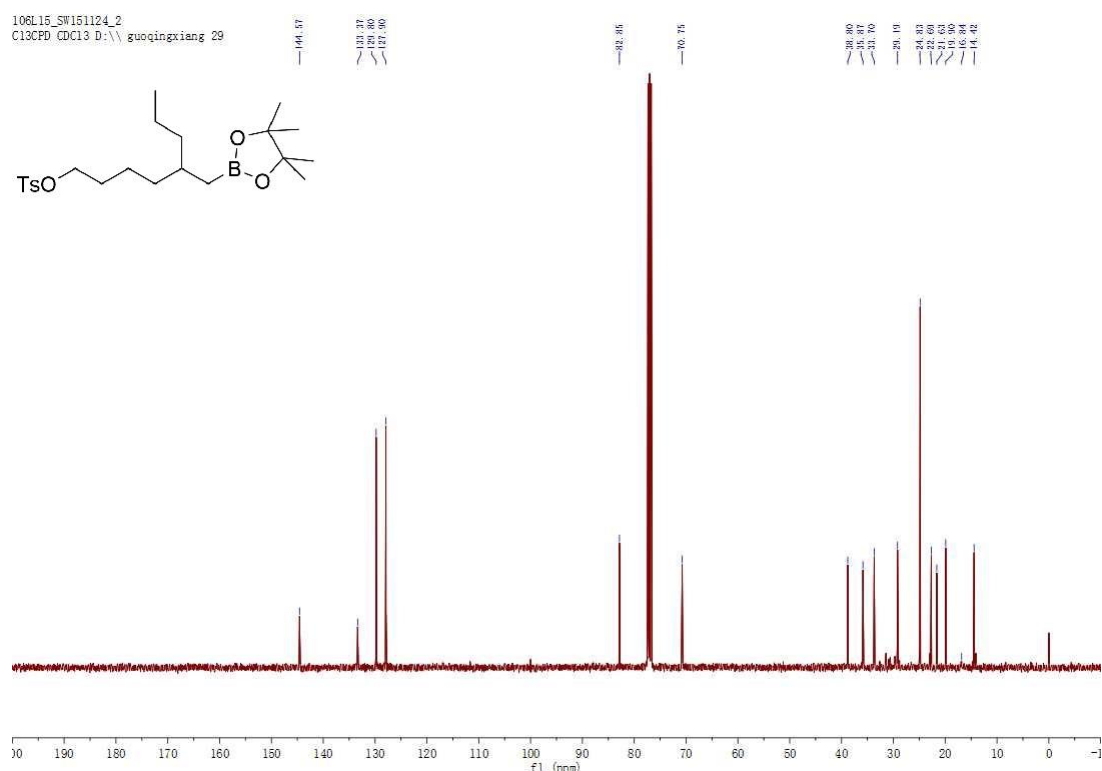
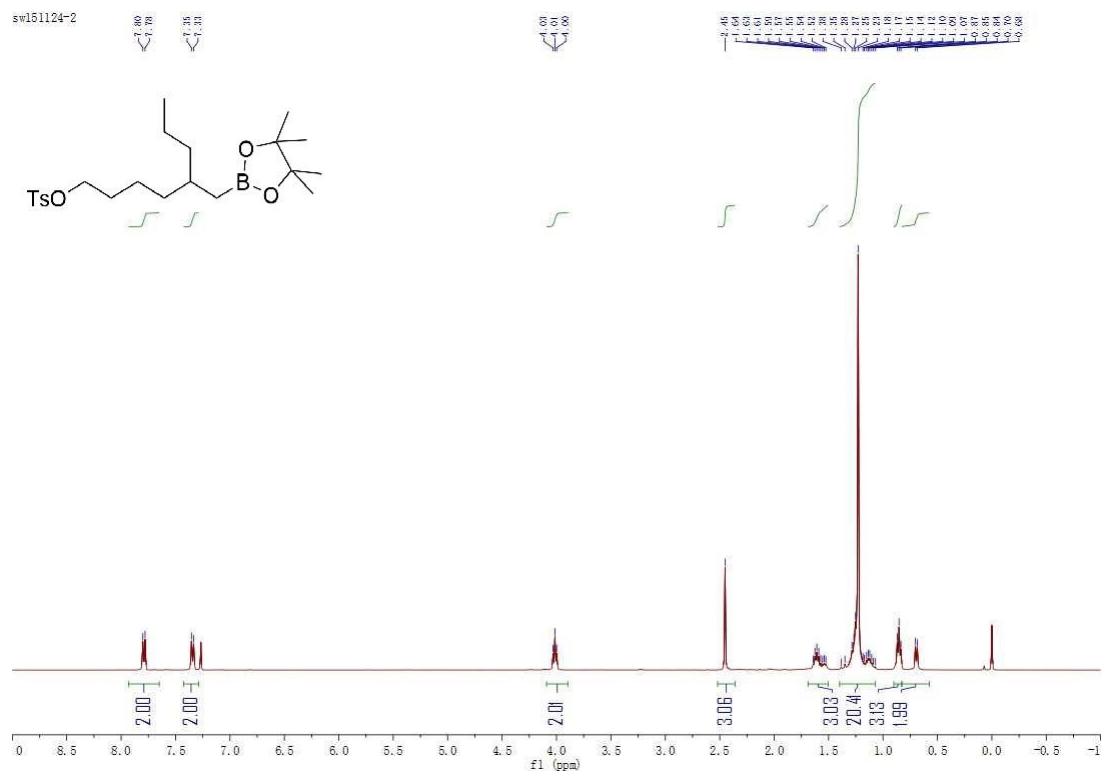


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 8.1 Hz, 2H), 7.34 (d,  $J$  = 8.0 Hz, 2H), 4.01 (t,  $J$  = 6.5 Hz, 2H), 2.45 (s, 3H), 1.58 (m, 3H), 1.40 – 1.05 (m, 20H), 0.85 (t,  $J$  = 6.7 Hz, 3H), 0.69 (d,  $J$  = 6.8 Hz, 2H).

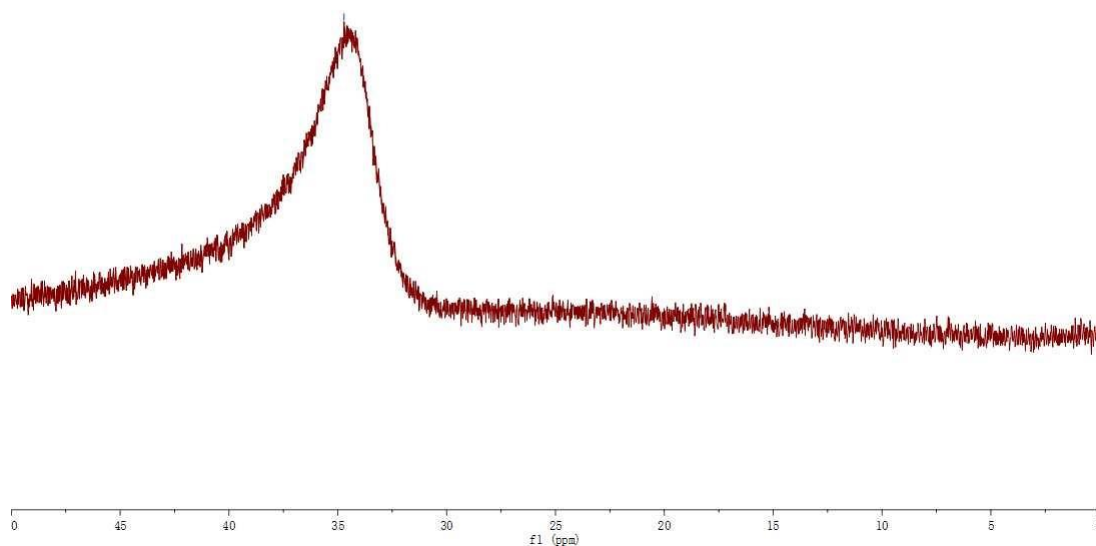
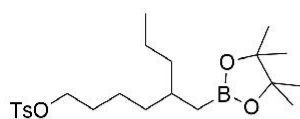
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.57 (s), 133.37 (s), 129.80 (s), 127.90 (s), 82.85 (s), 70.75 (s), 38.80 (s), 35.87 (s), 33.70 (s), 29.19 (s), 24.83 (s), 22.69 (s), 21.63 (s), 19.90 (s), 16.84 (s), 14.42 (s).

$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  34.71 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{22}\text{H}_{37}\text{BO}_5\text{S}[\text{H}]^+$ : 425.2533, Found: 425.2527.

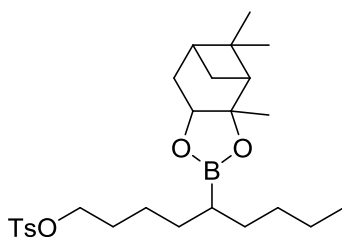


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**5-(3a,5,5-trimethylhexahydro-4,6-methanobenzo[d][1,3,2]dioxaborol-2-yl)nonyl methylbenzenesulfonate, 9b**

**4-**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J = 8.0$  Hz, 2H), 7.34 (d,  $J = 7.9$  Hz, 2H), 4.24 (d,  $J = 8.5$  Hz, 1H), 4.01 (t,  $J = 6.5$  Hz, 2H), 2.45 (s, 3H), 2.34 (dd,  $J = 13.0, 10.2$  Hz, 1H), 2.26 – 2.15 (m, 1H), 2.04 (t,  $J = 5.5$  Hz, 1H), 1.91 (s, 1H), 1.79 (d,  $J = 14.5$  Hz, 1H), 1.73 – 1.57 (m, 2H), 1.45 – 1.21 (m, 16H), 1.08 (d,  $J = 10.8$  Hz, 1H), 0.99 – 0.78 (m, 7H).

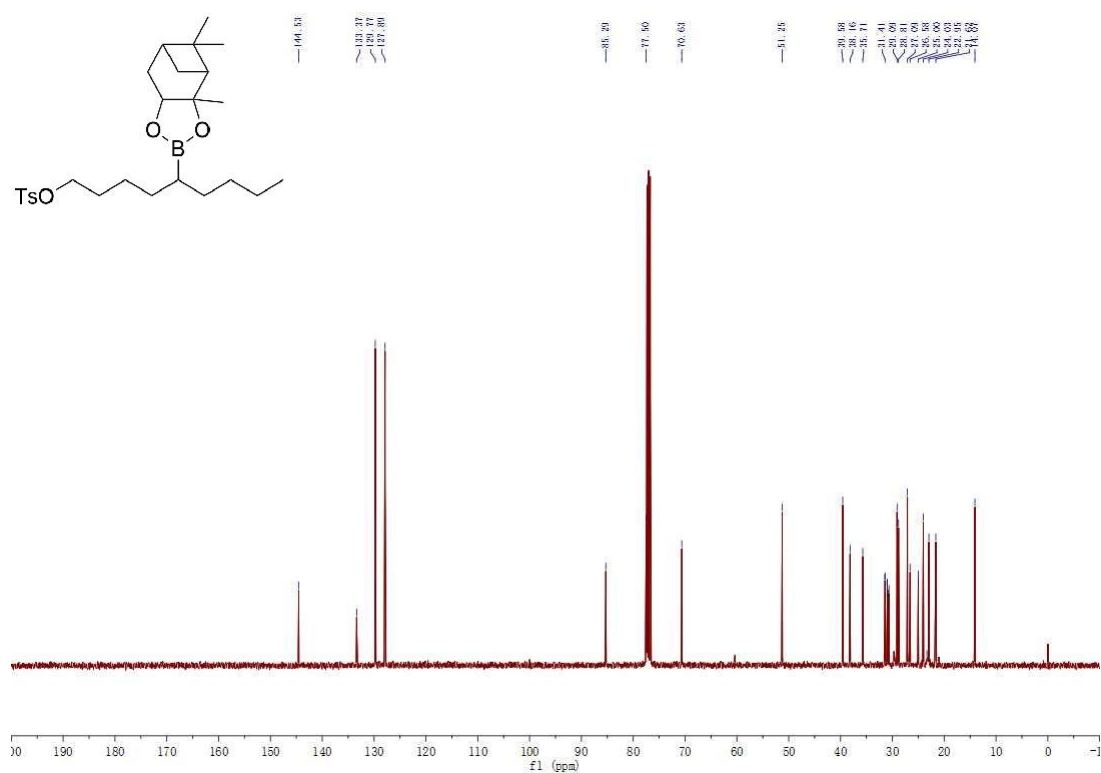
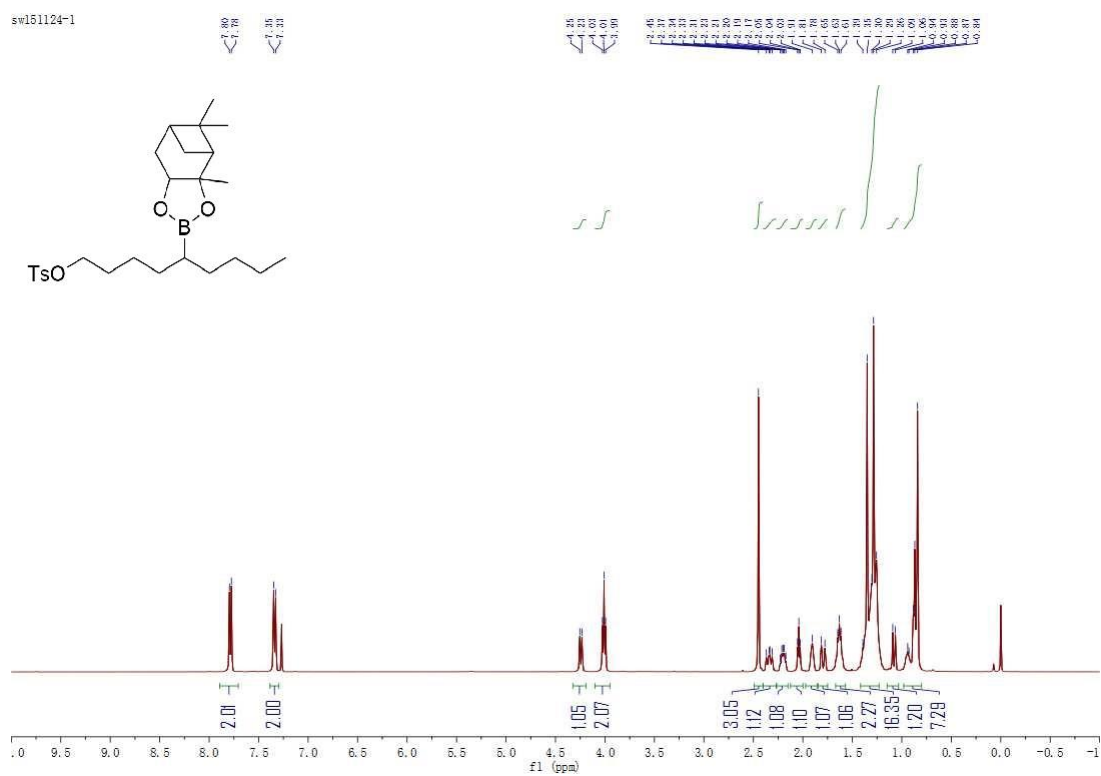
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.53 (s), 133.37 (s), 129.77 (s), 127.89 (s), 85.29 (s), 77.50 (s), 70.63 (s), 51.25 (s), 39.58 (s), 38.16 (s), 35.71 (s), 31.44 (d,  $J = 5.2$  Hz), 30.99 (d,  $J = 6.6$  Hz), 30.70 (d,  $J = 9.0$  Hz), 29.09 (s), 28.81 (s), 27.09 (s), 26.58 (s), 24.99 (d,  $J = 2.1$  Hz), 24.03 (s), 23.33 (s), 22.95 (s), 21.62 (s), 14.07 (s).

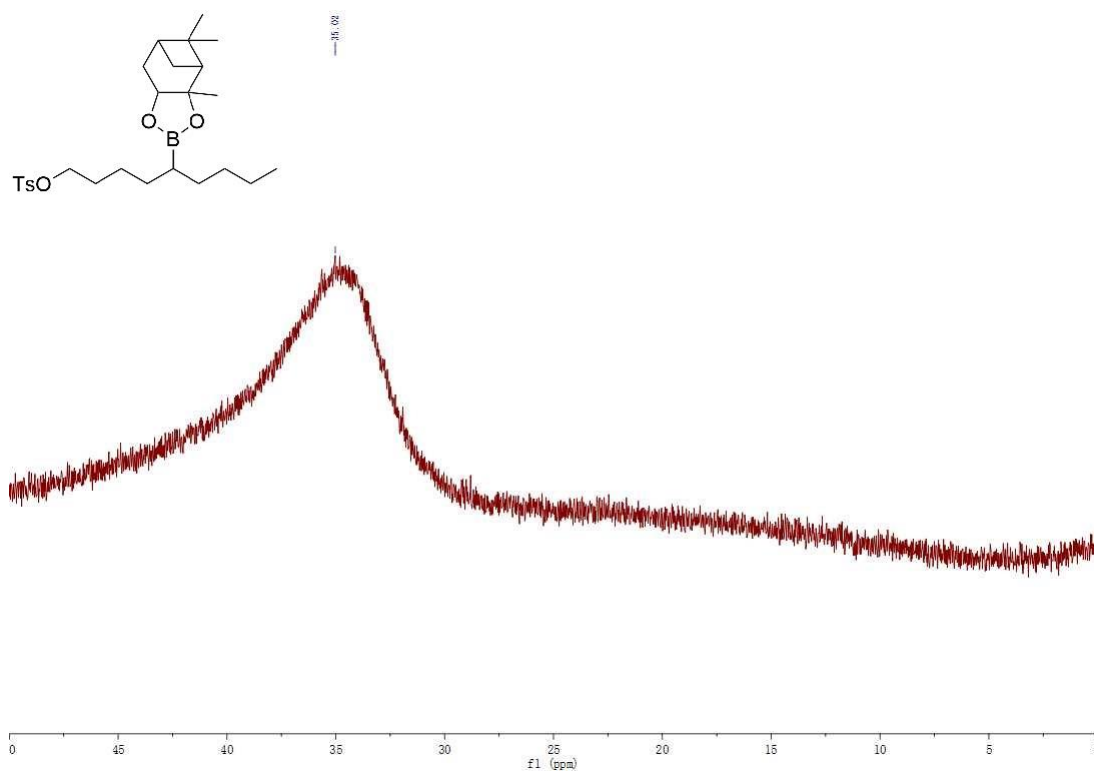
$^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ )  $\delta$  35.02 (s).

HRMS ( $\text{EI}^+$ ): Calcd for  $\text{C}_{26}\text{H}_{41}\text{BO}_5\text{S}[\text{H}]^+$ : 477.2846, Found: 477.2838.



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