Electronic Supplementary Information

for

Functionalized Geminal-diborylalkanes from Various Electron-Deficient Alkynes and B_2pin_2

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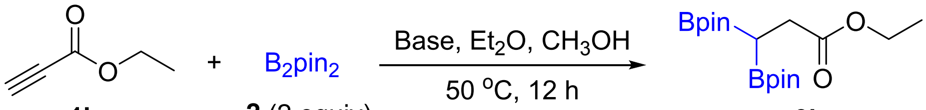
1. General information

All reactions were accomplished in Schlenk tubes under an atmosphere of N_2. Column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 500 M spectrometer and chemical shifts (in ppm) were referred to $CDCl_3$ (δ=7.26 ppm), d_6-DMSO (δ=2.5 ppm) (as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometer and were calibrated with $CDCl_3$ (δ=77.0ppm), d_6-DMSO(δ=40.0ppm). ^{19}F NMR spectrometers were operated on the same NMR spectrometer with $CDCl_3$ or d_6-DMSO. The following abbreviations were used to illuminate the diversities: δ= chemical shifts, J = coupling constant, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. HRMS (ESI) were measured with a quadrupole and TOF mass spectrometers. The X-ray single-crystal determination was performed on a Bruker APEX II X-ray single crystal diffractometer. All reagents and solvents were obtained from commercial suppliers, and used without further purification. Reactions were monitored by thin-layer chromatography (TLC). The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent.

2. Screening of conditions

Table S1. Base effect on the reaction.[a]

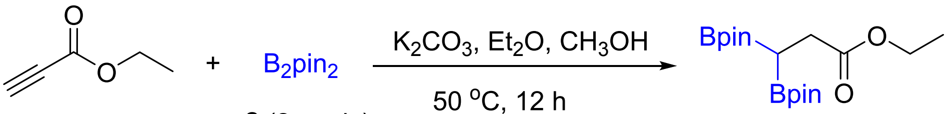


1b **2** (2 equiv) **3b**

Entry	Base (0.1 equiv)	Yield (%)[a]
1	Na_2CO_3	23
2	$NaHCO_3$	11
3	K_3PO_4	trace
4	K_2HPO4	trace
5	**K_2CO_3**	**56**
6	NaO-tBu	none
7	LiO-tBu	trace
8	KO-tBu	none
9	CsF	none
10	Cs_2CO_3	19
11	LiOMe	none
12	NaOMe	trace
13	NaOH	none
14	KOH	none

Conditions[a] : alkyne (0.2 mmol), CH_3OH (10 equiv.), Et_2O (1 mL), 12 h, N_2, GC yield.

Table S2. The amount of base effect on the reaction.[a]

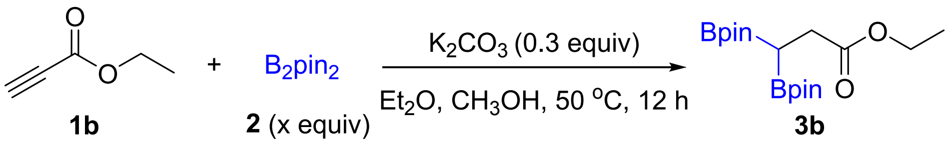


1b **2** (2 equiv) **3b**

Entry	K_2CO_3 (X equiv)	Yield (%)[a]
1	0.1	56
2	0.2	77
3	**0.3**	**92 (88)[b]**
4	0.4	88
5	0.5	66
6	0.8	53
7	1.0	35

Conditions[a] : alkyne (0.2 mmol), CH_3OH (10 equiv), Et_2O (1 mL) , 12 h, N_2, GC yield. [b] Isolated yield.

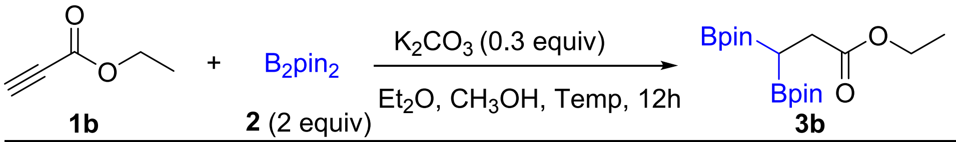
Table S3. The amount of B_2pin_2 effect on the reaction.[a]



Entry	B_2pin_2 (x equiv)	Yield (%)[a]
1	1.1	44
2	1.2	47
3	1.3	55
4	1.4	64
5	1.5	70
6	1.8	85
7	**2.0**	**92**
8	2.1	92

Conditions[a] : alkyne (0.2 mmol), CH_3OH (10 equiv), Et_2O (1 mL), 12 h, N_2, GC yield.

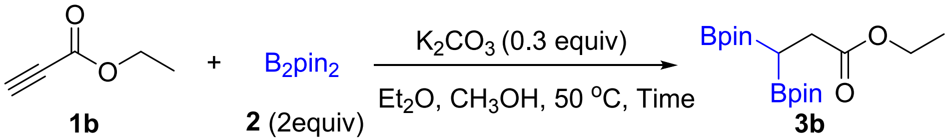
Table S4. Temperature effect on the reaction.[a]



Entry	Temp (°C)	Yield (%)[a]
1	r.t	44
2	40	79
3	**50**	**92**
4	60	77
5	70	72

Conditions[a] : alkyne (0.2 mmol), CH_3OH (10 equiv), Et_2O (1mL), 12h, N_2, GC yield.

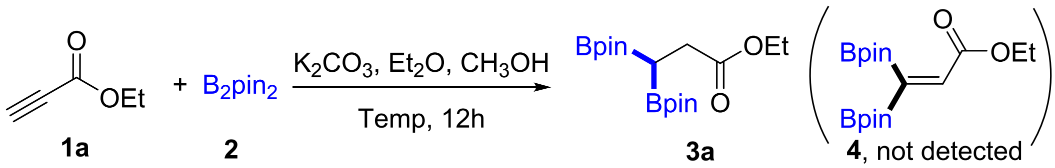
Table S5. Time effect on the reaction.[a]



Entry	Time (h)	Yield (%)[a]
1	3	34
2	4	48
3	6	55
4	**12**	**92**
5	16	89

Conditions[a] : alkyne (0.2 mmol), CH_3OH (10 equiv), Et_2O (1mL), N_2, GC yield.

Table S6. Summarizing of the reaction[a]

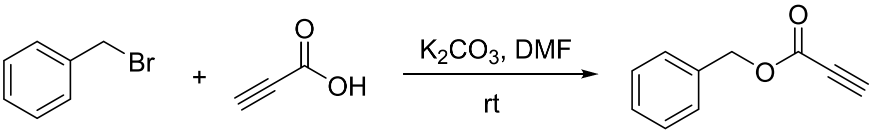


entry	B_2pin_2 (equiv)	K_2CO_3 (equiv)	Temp (°C)	Yield (%)[a]
1	1.1	0.3	50	44
2	1.5	0.3	50	70
3	**2**	**0.3**	**50**	**92 (88)[b]**
4	2	0.1	50	56
5	2	1	50	35
6	2	0.3	r.t	44
7	2	0.3	60	77
8[c]	2	0.3	50	55
9[d]	2	0.3	50	89
10[e]	2	0.3	50	30

[a] Conditions: alkyne (0.2 mmol), CH_3OH (10 equiv), Et_2O (1 mL), 12 h, N_2, GC yield. [b] Isolated yield. [c] 6 h. [d] 16 h. [e] air.

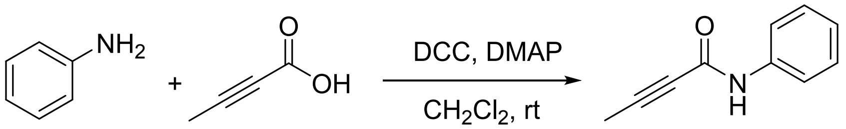
3. General procedure for starting materials

1). General procedure for the preparation of propiolates



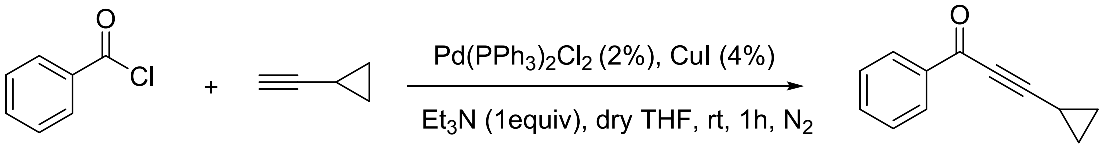
To a suspension of potassium carbonate (4.47 g, 32.3 mmol) in DMF (15 mL), propiolic acid (2.00 mL, 32.3 mmol) in DMF (8 mL) was added and stirred at 0 °C. After 10 min, benzyl bromide (3.20 mL, 26.9 mmol) was added and the reaction mixture was warmed to 25 °C. The resulting solution was stirred for 2 h and then water was added (45 mL). The mixture was extracted with EtOAc−hexanes 1:1 (3 × 30 mL). The combined organic layers were washed with brine and then dried (Na_2SO_4). After evaporation of the solvent under reduced pressure, the residue was purified through FCC (SiO_2; 30% EtOAc in hexanes) to yield a colorless oil (1.79 g, 90%).[1]

2). General procedure for the preparation of propiolamides



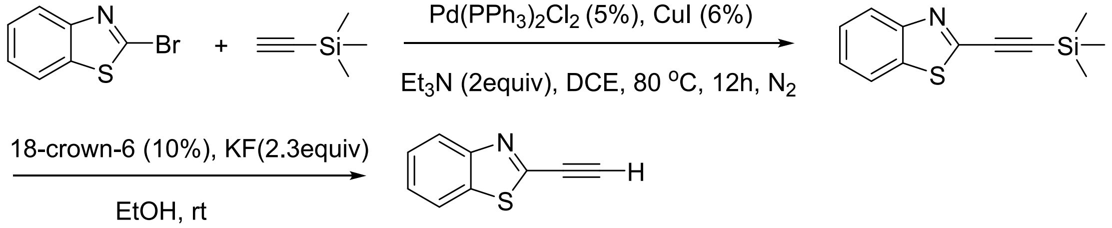
A solution of DMAP (15 mg, 0.13 mmol) and DCC (2.58 g, 13 mmol) in CH_2Cl_2 (15 mL) was added slowly over 1 h to a solution of propiolic acid (0.77 mL, 13 mmol) and aniline (1.4 mL, 14 mmol) in CH_2Cl_2 (15 mL) at 0°C. The suspension was then stirred for 5 h at room temperature, monitoring through by TLC (30% EtOAc in hexanes). Upon completion, the mixture was filtered through a layer of Celite and the filtrate concentrated in vacuo. The residue was purified through FCC (SiO_2; 30% EtOAc in hexanes) to yield a colorless oil (1.79 g, 90%). Spectral data matched those reported in the literature.[2]

3). General procedure for the preparation of ynones



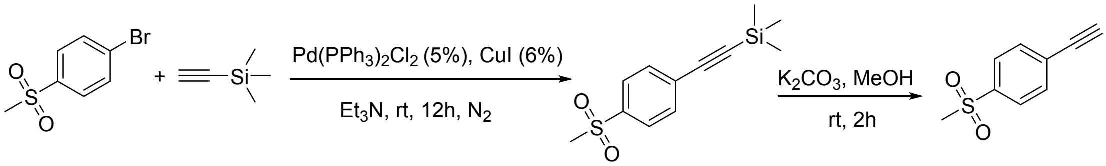
Ketones were prepared according to a literature procedure. Using standard Schlenk line, to a flame-dried round bottom flask equipped with stir bar under N_2 atmosphere was added acid chloride (10.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol, 2.0 mol%), CuI (76 mg,0.4 mmol,4.0 mol%), Et_3N(1.4 mL,10.0 mmol,1.0 equiv), and alkyne(1.0 equiv) in dry THF (50 mL) at 25°C. The resulting reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water (30 mL). The aqueous layer was extracted with EtOAc (3*30mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting crude solid was purified by silica gel flash column chromatography using an elution gradient from 100% hexanes to 10% EtOAc in hexanes. Product-containing fractions were combined and concentrated in vacuo to afford target product.[3]

4). General procedure for the preparation of 2-ethynylazoles



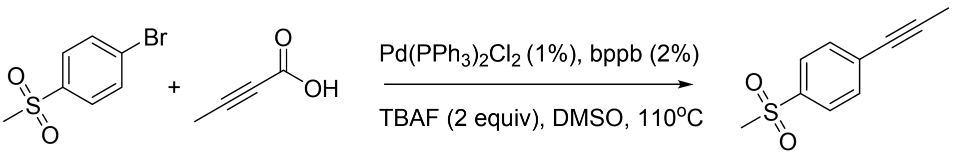
Under a nitrogen atmosphere, to a solution of 2-Bromobenzothiazole (346 mg, 2.1 mmol) in DCE (10 mL) and Et_3N (2 equiv) were added ethynyltrimethylsilane (0.4 mL, 251 mg, 2.6 mmol) and trans-dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.04 mmol). The reaction was stirred at rt for 15 min, and then CuI (4 mg, 0.023 mmol) was added. The reaction mixture was stirred at 80 ^{o}C for 12.0 h until no more starting product was detected by TLC analysis. The solvent was then evaporated under reduced pressure, and the crude material was purified by flash chromatography over a silica gel column using Hex/EtOAc (85:15) to afford the desired product as a pale yellow solid (489 mg, 91%). Then to a stirred solution of trimethyl(oxazole)silane (322 mg, 1.58 mmol) in EtOH (10mL) was added KF (123 mg, 2.3 equiv) and 18-crown-6 (10 mol%). The reaction was stirred at rt for 2.0 h. The residue was poured into H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 150 mL), washed with brine, and dried over Na_2SO_4. The solvent was removed at reduced pressure to give the desired product as an orange solid (145 mg, 44%).[4]

5). General procedure for the preparation of aryl alkynes



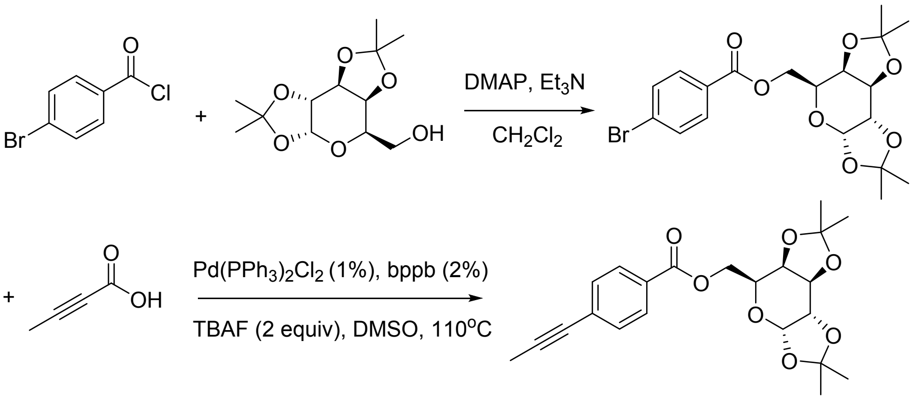
Under a nitrogen atmosphere, to a solution of 1-bromo-4- (methylsulfonyl)benzene (500 mg, 2.13 mmol) in Et_3N (10 mL) were added ethynyltrimethylsilane (0.35 mL, 251 mg, 2.56 mmol) and *trans*-dichlorobis(triphenylphosphine)palladium(II) (30 mg, 0.04 mmol). The reaction was stirred at rt for 15 min, and then CuI (4 mg, 0.023 mmol) was added. The reaction mixture was stirred at rt for 12.0 h until no more starting product was detected by TLC analysis. The solvent was then evaporated under reduced pressure, and the crude material was purified by flash chromatography over a silica gel column using Hex/EtOAc (85:15) to afford the desired trimethyl((4-(methylsulfonyl)phenyl)ethynyl)silane as a pale yellow solid (489 mg, 91%), Then to a stirred solution of trimethyl((4-(methylsulfonyl)phenyl)-ethynyl)silane (400 mg, 1.58 mmol) in MeOH (11 mL) was added K_2CO_3 (438 mg, 3.16 mmol). The reaction was stirred at rt for 2.0 h. The residue was poured into H_2O (100 mL) and extracted with CH_2Cl_2 (3 × 150 mL), washed with brine, and dried over Na_2SO_4. The solvent was removed at reduced pressure to give the desired product as an orange solid (279 mg, 98%).[5]

6). General procedure for the preparation of 1-aryl-1-propynes



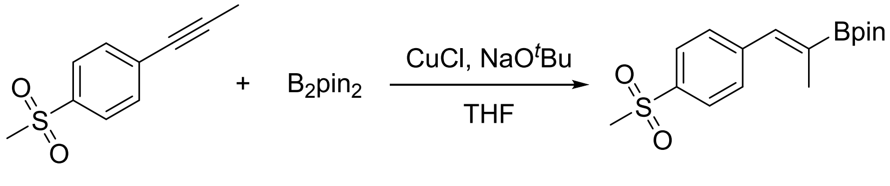
1-Aryl-1-propynes were prepared according to literature procedure. Reactions were performed in a schlenk tube equipped with a stirring bar and capped with a rubber septum. The followings were placed in the tube in order: 21.1 mg (1 mol%) of Pd, 25.6 mg of dppb (2 mol%), 6 ml of TBAF, 3.0 mmol (252.2 mg) of 2-butynoic acid and 3.0 mmol of arylbromobenzene. The mixture was stirred at 110°C for 3 h. The reaction mixture was extracted with aqueous NH_4Cl solution and diethyl ether. The ether extract was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressures. The reaction mixture was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate) to afford the product.[6]

7). General procedure for the preparation of medicinally relevant substrates



A round-bottom flask was charged with 4-bromobenzoyl chloride (720 mg, 1.1 equiv), 1,2:3,4-di-*O*-isopropylpylidene-α-D-galactopyranose (775 mg, 2.98 mmol), Et_3N (452 mg, 1.50 equiv), DMAP (36 mg, 0.03 equiv) and CH_2Cl_2 (20 mL). The reaction mixture was then filtered, and the filtrate was washed with 1M HCl. The organic layer was dried over anhydrous Na_2SO_4, and concentrated in vacuo, which was further purified by column chromatography to give a pure alkyl 4-bromobenzoate. The followings were placed in the tube in order: 21.1 mg (1 mol %) of Pd, 25.6 mg of dppb (2 mol %), 6 ml of TBAF, 3.0 mmol (252.2 mg) of 2-butynoic acid and 3.0 mmol of arylbromobenzene. The mixture was stirred at 110 °C for 3 h. The reaction mixture was extracted with aqueous NH_4Cl solution and diethyl ether. The ether extract was dried over anhydrous $MgSO_4$, filtered, and evaporated under reduced pressures. The reaction mixture was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate) to afford the product.[7]

8). General procedure for the preparation of vinyl(boronate)

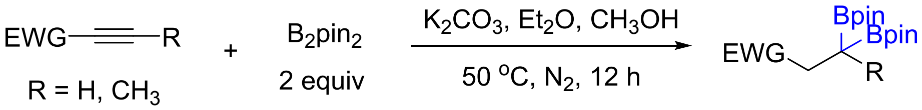


A-1 **B-1**

To an oven dried schlenk tube equipped with a stir bar were added $\mathbf{A_1}$ (0.25 mmol), B_2pin_2 (1.1 equiv), CuCl (2.5 mg, 0.025 mmol), NaOt-Bu (9.6 mg, 0.10 mmol), and

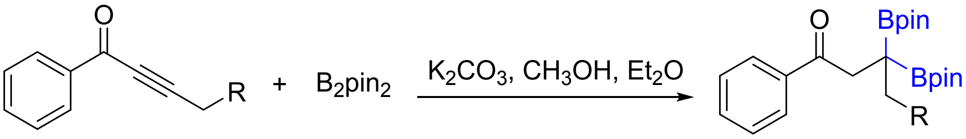
THF (2 mL) under nitrogen. After the mixture was stirred at room temperature for 4h, the reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.[13]

4. General procedure for the synthesis of diborylalkanes



General procedure A: the synthesis of Geminal-diborylalkanes from romatic acetylenes and B_2pin_2: In air, a 25 mL Schlenk tube was charged with B_2pin_2 (2.0 equiv) and K_2CO_3 (0.3 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et_2O (1 mL), alkynes (0.2 mmol) and CH_3OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 50 °C for 12 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

Or a 25 mL Young's tube was charged with B_2pin_2 (2.0 equiv) and K_2CO_3 (0.3 equiv), and filled with nitrogen. Then, Et_2O (0.1 mL), alkynes (0.2 mmol) and CH_3OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 50 °C for 12 hours. (**3a-3h, 3o-3q**)

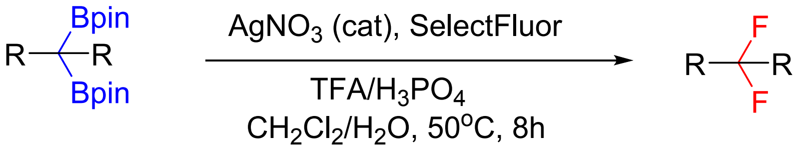


General procedure B: the synthesis of Geminal-diborylalkanes from carbonyl group-containing alkynes and B_2pin_2: In air, a 25 mL Schlenk tube was charged with B_2pin_2 (2.0 equiv) and K_2CO_3 (0.5 equiv). The flask was evacuated and filled with nitrogen for three cycles. Et_2O (1 mL), alkynes (0.2 mmol) and CH_3OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 60 °C for 16 hours. Upon completion, the reaction mixture was diluted with ethyl acetate, filtered through a silica gel plug, rinsed with ethyl acetate, and concentrated in vacuo. The crude reaction mixture was purified on silica gel to afford the desired product.

Or a 25 mL Young's tube was charged with B_2pin_2 (2.0 equiv) and K_2CO_3 (0.3 equiv), and filled with nitrogen. Then, Et_2O (0.1 mL), alkynes (0.2 mmol) and CH_3OH (80 uL, 10 equiv) were added. The reaction was allowed to stir at 60 °C for 12 hours. (**3i-3n**, **6a-6s**)

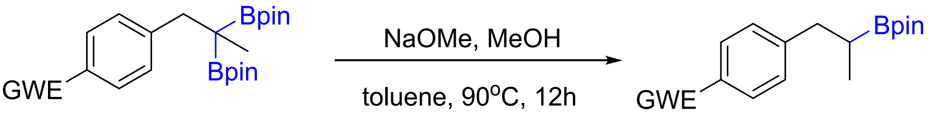
5. General procedure for the transformation of diborylalkanes

(1). Typical procedure for Silver-Catalyzed Fluorination of Secondary Alkylboronic Esters.



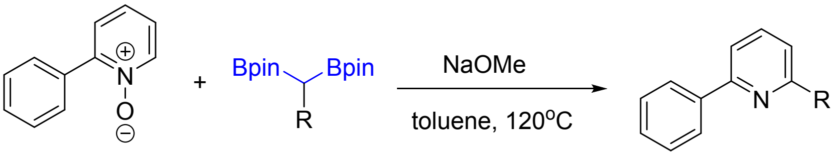
Geminal-diborylalkanes (0.2 mmol), $AgNO_3$ (14 mg, 0.08 mmol), Selectfluor (424 mg, 0.6 mmol) were placed in a Schlenk tube. The reaction vessel was evacuated and filled with nitrogen for three times. Then dichloromethane (1 mL), water (1 mL), and TFA (0.4 ml), H_3PO_4 (0.2 ml) were added successively at rt. The reaction mixture was stirred at 60 ºC for 8 h. The resulting mixture was extracted with CH_2Cl_2 (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate (50:1 - 40:1, v:v) as the eluent to give the pure product.[9]

(2). General procedure for the preparation of synthesis of alkyl mono(boronate)s



To a dried 10mL reaction tube was added geminal-diborylalkanes (0.26 mmol), NaOMe (14.2 mg, 0.26 mmol), MeOH (32.0 μL, 0.78 mmol) and toluene (2.0 mL). The mixture was stirred at 90 ºC for 12 h. The reaction was quenched by HCl aquerous (1%, 5 mL) and extracted with EtOAc (3 × 10 ml). The combined organic phase was washed with saturated brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash chromatography on silica gel using PE/EtOAc (40:1) as the eluent to give the pure product.[10]

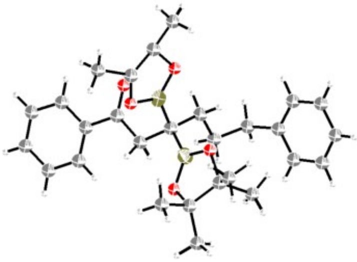
(3). General procedure for the preparation of synthesis of secondary alkylated N-heteroaromatic compounds

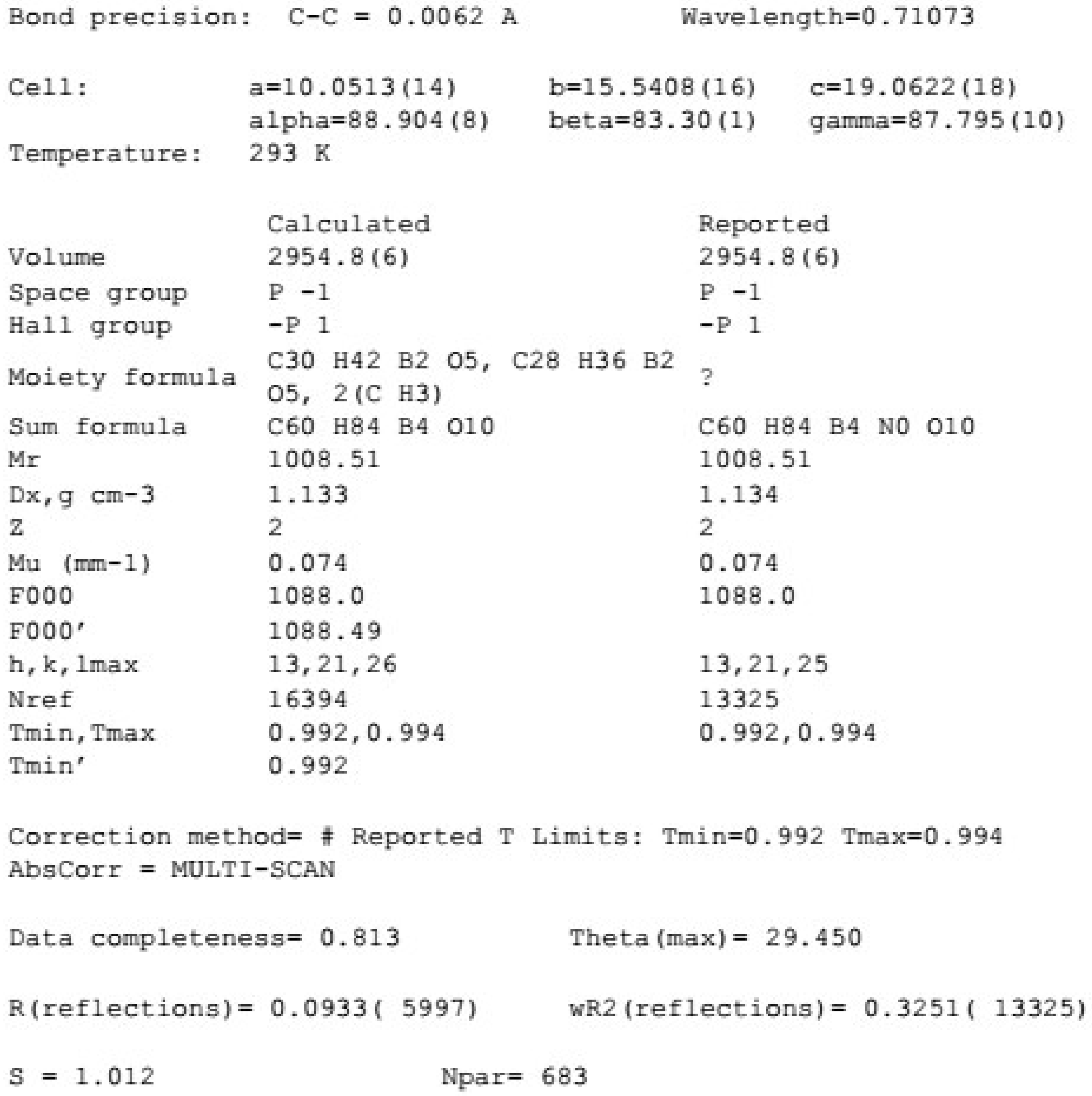


To an oven-dried 4-dram vial equipped with a Teflon coated magnetic stirring bar were added N-heteroaromatic N-oxide (0.20 mmol), NaOMe (3.0 equiv), geminal-diborylalkanes (2.0 equiv) and anhydrous toluene (2.0 mL). The vial was sealed with a PTFE/silicone-lined septum cap and the reaction mixture was stirred at the indicated temperature for 3 h. The reaction mixture was filtered through celite pad and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated under reduced pressure. To remove unreacted internal gem-bis[(pinacolato)boryl]alkane, $NaBO_3 \cdot 4H_2O$ (93 mg, 0.60 mmol) and THF/H_2O (3.0 mL, 1:1) were added to the above obtained crude mixture in a 20 mL vial and stirred for 3 h at room temperature. The reaction mixture was quenched with brine (5.0 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography to yield the desired product.[11]

6. Crystal data of 3n and 6a-*para*

Crystallographic data for compound **3n** (CCDC-1570208) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).





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Bond precision:   C-C = 0.0062 A          Wavelength=0.71073

Cell:            a=10.0513(14)      b=15.5408(16)     c=19.0622(18)
                 alpha=88.904(8)    beta=83.30(1)     gamma=87.795(10)
Temperature:     293 K

                 Calculated                       Reported
Volume           2954.8(6)                        2954.8(6)
Space group      P -1                             P -1
Hall group       -P 1                             -P 1
                 C30 H42 B2 O5, C28 H36 B2
Moiety formula                                    ?
                 O5, 2(C H3)
Sum formula      C60 H84 B4 O10                   C60 H84 B4 N0 O10
Mr               1008.51                          1008.51
Dx,g cm-3        1.133                            1.134
Z                2                                2
Mu (mm-1)        0.074                            0.074
F000             1088.0                           1088.0
F000'            1088.49
h,k,lmax         13,21,26                         13,21,25
Nref             16394                            13325
Tmin,Tmax        0.992,0.994                      0.992,0.994
Tmin'            0.992

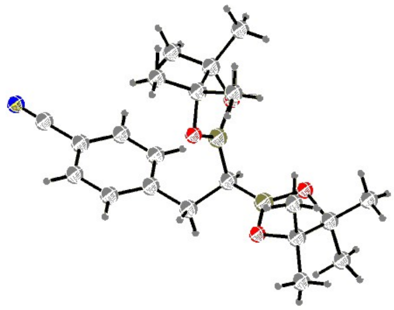
Correction method= # Reported T Limits: Tmin=0.992 Tmax=0.994
AbsCorr = MULTI-SCAN

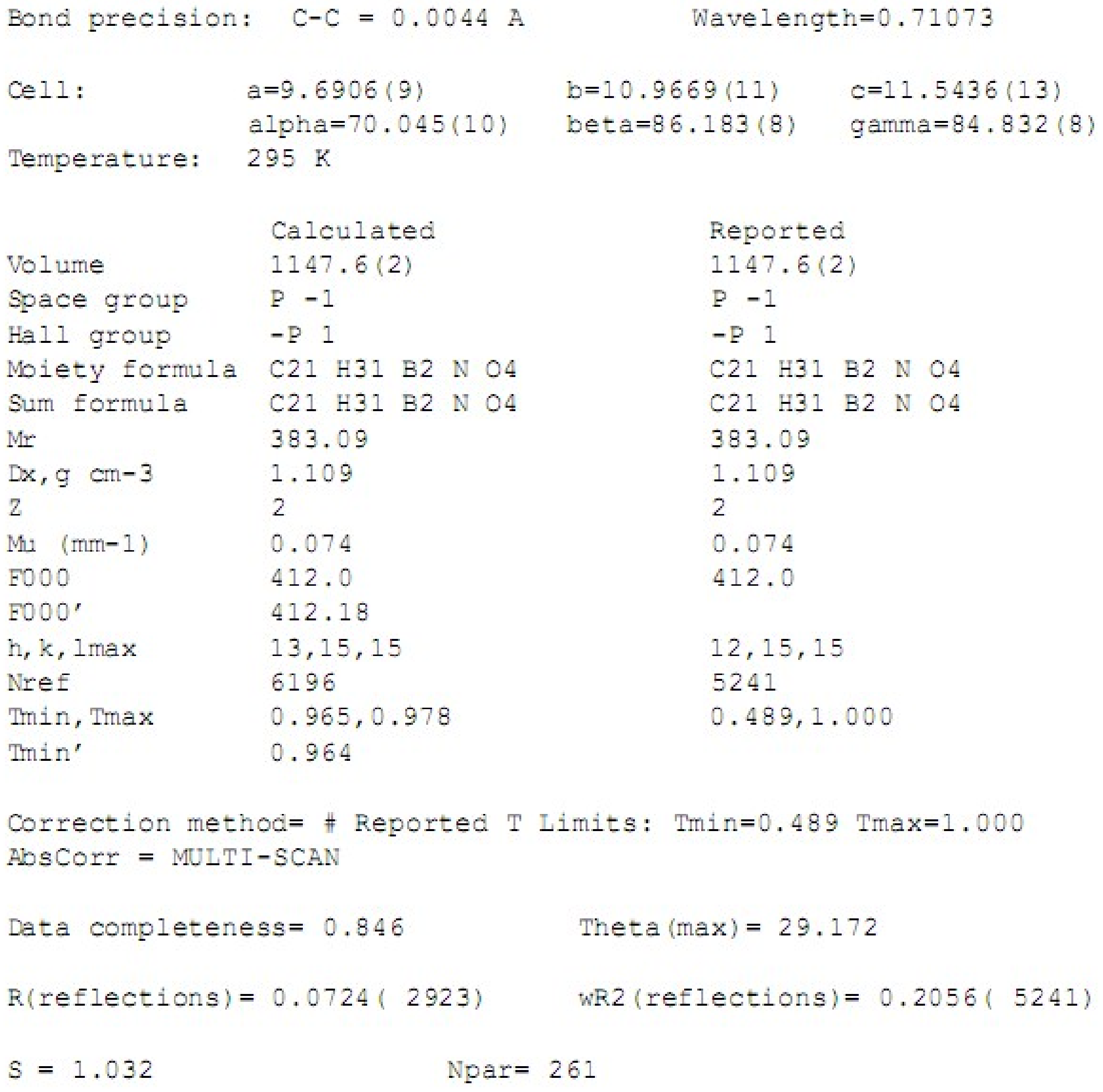
Data completeness= 0.813          Theta(max)= 29.450

R(reflections)= 0.0933( 5997)     wR2(reflections)= 0.3251( 13325)

S = 1.012                  Npar= 683
```

Crystallographic data for compound **6a-** ***para*** (CCDC-1523638) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).





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Bond precision:   C-C = 0.0044 A          Wavelength=0.71073

Cell:           a=9.6906(9)        b=10.9669(11)    c=11.5436(13)
                alpha=70.045(10)   beta=86.183(8)   gamma=84.832(8)
Temperature:    295 K

                 Calculated                  Reported
Volume           1147.6(2)                   1147.6(2)
Space group      P -1                        P -1
Hall group       -P 1                        -P 1
Moiety formula   C21 H31 B2 N O4             C21 H31 B2 N O4
Sum formula      C21 H31 B2 N O4             C21 H31 B2 N O4
Mr               383.09                      383.09
Dx,g cm-3        1.109                       1.109
Z                2                           2
Mu (mm-1)        0.074                       0.074
F000             412.0                       412.0
F000'            412.18
h,k,lmax         13,15,15                    12,15,15
Nref             6196                        5241
Tmin,Tmax        0.965,0.978                 0.489,1.000
Tmin'            0.964

Correction method= # Reported T Limits: Tmin=0.489 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 0.846          Theta(max)= 29.172

R(reflections)= 0.0724( 2923)     wR2(reflections)= 0.2056( 5241)

S = 1.032                   Npar= 261
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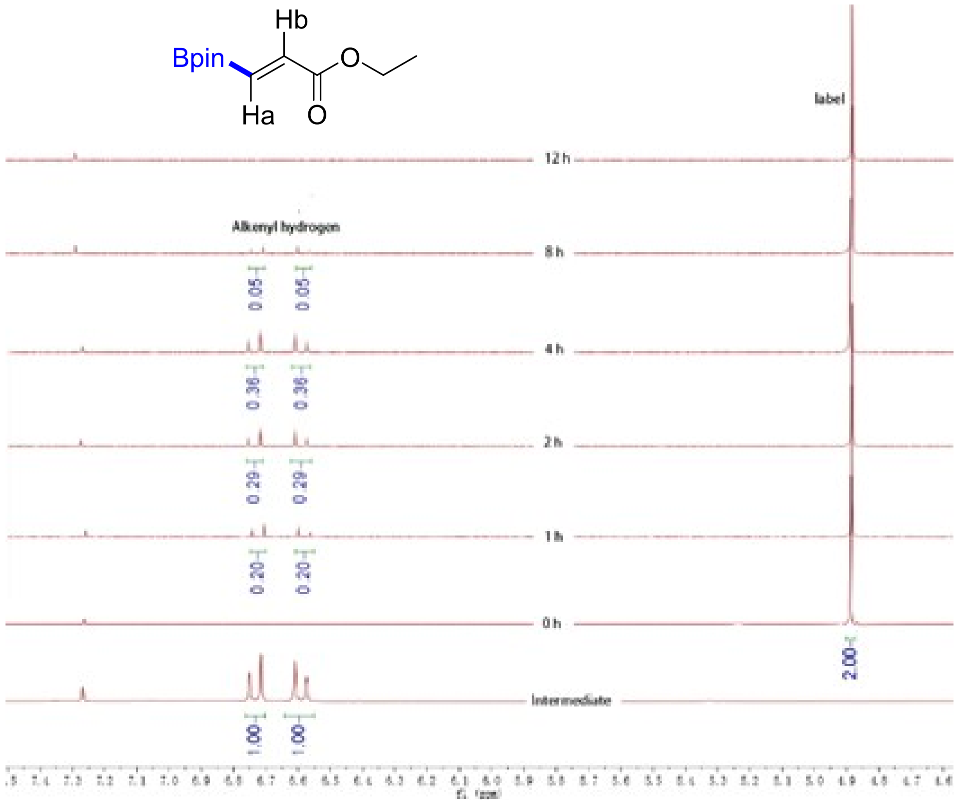
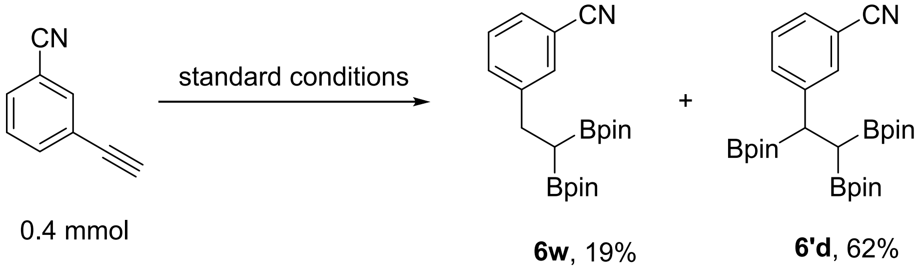
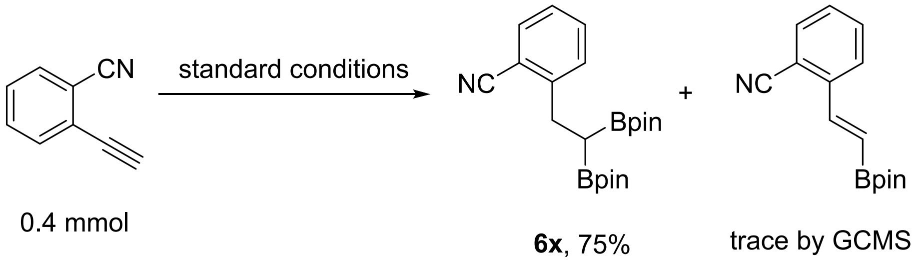
7. The in situ ^{1}H NMR of compound 3a from alkyne 1a



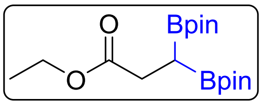
8. Extra contents for reviews comments





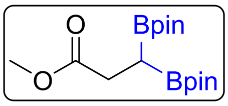
9. Characterization data for products

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3a) (CAS: No. 1302132-95-1)[4]



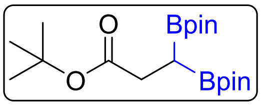
The reaction was performed following the general procedure A. Colorless oil, 88% yield (62.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (q, J = 7.1 Hz, 2H), 2.54 (d, J = 8.3 Hz, 2H), 1.24 – 1.20 (m, 15H), 1.20 (s, 12H), 1.09 – 1.03 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.9, 83.2, 60.2, 30.6, 24.8, 24.4, 14.3.

Methyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3b) (CAS: No. 1800103-38-1)[12]



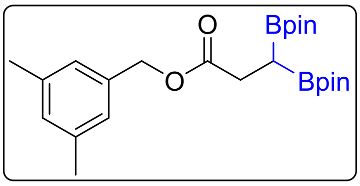
The reaction was performed following the general procedure A. Colorless oil, 80% yield (54.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (s, 3H), 2.55 (d, J = 8.3 Hz, 2H), 1.22 (s, 12H), 1.20 (s, 12H), 1.06 (dd, J = 10.7, 5.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.3, 83.2, 51.5, 30.3, 24.8, 24.4.

Tert-butyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3c)(CAS: No. 1812184-92-1)[12]



The reaction was performed following the general procedure A. Colorless oil, 78% yield (59.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.48 (d, J = 8.5 Hz, 2H), 1.40 (s, 9H), 1.22 (s, 12H), 1.19 (s, 12H), 1.03 (t, J = 8.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.2, 83.1, 79.6, 31.7, 28.1, 25.0, 24.8, 24.4.

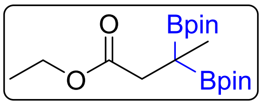
3,5-Dimethylbenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3d)



The reaction was performed following the general procedure A. Colorless oil, 50% yield (44.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.92 (s, 1H), 5.02 (s, 2H), 2.63 (d, J = 8.3 Hz, 2H), 2.30 (s, 6H), 1.22 (s, 12H), 1.19 (s, 12H), 1.11 (t, J = 8.3 Hz,

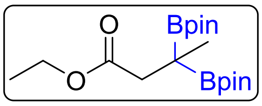
1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.7, 137.9, 136.1, 129.5, 125.8, 124.8, 83.2, 66.1, 30.6, 24.8, 24.4, 21.2.
HRMS (ESI, m/z) calcd for $^{12}C_{24}{}^{1}H_{38}{}^{10}B_{2}{}^{16}O_{6}[M+H]^{+}$: 443.3000; found: 443.3002.

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3e)(CAS: No. 1009307-15-6)[13]



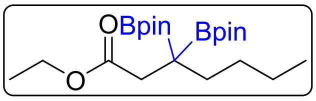
The reaction was performed following the general procedure A. Colorless oil, 84% yield (61.3 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.09 (q, J = 7.1 Hz, 2H), 2.56 (s, 2H), 1.28 – 1.25 (m, 3H), 1.23 (s, 12H), 1.21 (s, 12H), 1.09 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.1, 83.2, 60.0, 39.1, 24.6, 24.8, 16.7, 14.3.

Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3e)(CAS: No. 1009307-15-6)[13]



The reaction was performed following the general procedure A. Colorless oil, 84% yield (61.3 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.09 (q, J = 7.1 Hz, 2H), 2.56 (s, 2H), 1.28 – 1.25 (m, 3H), 1.23 (s, 12H), 1.21 (s, 12H), 1.09 (s, 3H). ^{13}C NMR (126 MHz, CDCl$_3$) δ 174.1, 83.2, 60.0, 39.1, 24.6, 24.8, 16.7, 14.3.

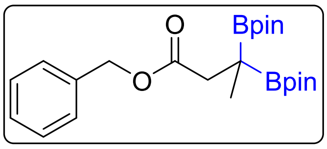
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3f)



The reaction was performed following the general procedure A. Colorless oil, 64% yield (52.5 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.08 (t, J = 7.1 Hz, 2H), 2.64 (s, 2H), 1.63 (dd, J = 10.2, 6.6 Hz, 2H), 1.25 (d, J = 2.3 Hz, 5H), 1.22 (s, 12H), 1.21 (s, 12H), 1.18 – 1.13 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 174.2, 83.1, 59.9, 34.9, 29.6, 29.8, 24.9, 24.7, 24.5, 23.3, 14.3, 14.1.

HRMS (ESI, m/z) calcd for $^{12}C_{21}{}^{1}H_{40}{}^{10}B_{2}{}^{16}O_{6}[M+H]^{+}$: 409.3156; found: 409.3157.

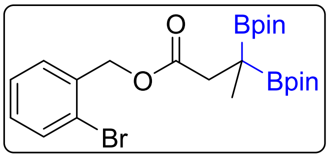
Benzyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3g)



The reaction was performed following the general procedure A. Colorless oil, 78% yield (67.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.32 (d, J = 4.5 Hz, 4H), 7.30 – 7.27 (m, 1H), 5.09 (s, 2H), 2.64 (s, 2H), 1.21 (s, 12H), 1.19 (s, 12H), 1.11 (s, 3H). ^{13}C

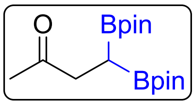
NMR (125 MHz, CDCl$_3$) δ 173.9, 136.3, 128.4, 128.0, 127.9, 83.2, 65.9, 39.0, 24.9, 24.6, 16.6.
HRMS (ESI, m/z) calcd for $^{12}C_{23}{}^{1}H_{36}{}^{10}B_2{}^{16}O_6[M+H]^+$: 429.2843; found: 429.2845.

2-Bromobenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3h)



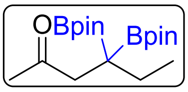
The reaction was performed following the general procedure A. Colorless oil, 68% yield (74.8 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 (d, *J* = 8.7 Hz, 1H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 8.5 Hz, 1H), 5.17 (s, 2H), 2.68 (s, 2H), 1.21 (s, 12H), 1.20 (s, 12H), 1.13 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.6, 135.7, 132.6, 129.4, 129.3, 127.3, 122.9, 83.5, 83.2, 65.4, 38.9, 24.9, 24.6, 24.5, 16.7.
HRMS (ESI, m/z) calcd for $^{12}C_{23}{}^{1}H_{35}{}^{10}B_2{}^{16}O_6{}^{80}Br[M+H]^+$: 507.1949; found: 507.1950.

4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (3i)(CAS: No. 1175712-38-5)[14]



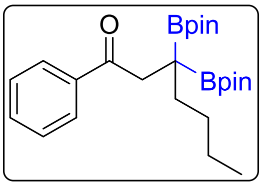
The reaction was performed following the general procedure A. Colorless oil, 73% yield (46.7 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.73 (d, *J* = 8.1 Hz, 2H), 2.10 (s, 3H), 1.23 (s, 12H), 1.20 (s, 12H), 0.96 (t, *J* = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 209.03, 83.1, 40.7, 29.1, 25.0, 24.7, 24.5.

4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3j)



The reaction was performed following the general procedure A. Colorless oil, 70% yield (49.3 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.83 (s, 2H), 2.09 (s, 3H), 1.64 (q, *J* = 7.5 Hz, 2H), 1.24 (s, 12H), 1.22 (s, 12H), 0.78 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 208.9, 83.09, 44.39, 29.6, 24.9, 24.8, 24.7, 22.8, 11.7.
HRMS (ESI, m/z) calcd for $^{12}C_{18}{}^{1}H_{34}{}^{10}B_2{}^{16}O_5[M+Na]^+$: 373.2506; found: 373.2506.

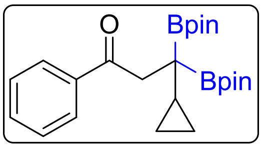
1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (3k)



The reaction was performed following the general procedure B. Colorless oil, 74% yield (65.4 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.99 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.52 (t,

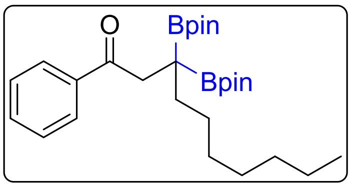
J = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 3.37 (s, 2H), 1.68 (dd, *J* = 10.1, 6.6 Hz, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.22 – 1.19 (m, 2H), 1.15 – 1.10 (m, 2H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.5, 137.1, 132.7, 128.4, 127.9, 82.9, 41.0, 31.3, 30.2, 24.7, 24.6, 22.9, 14.1.
HRMS (ESI, m/z) calcd for $^{12}C_{25}{}^{1}H_{40}{}^{10}B_2{}^{16}O_5[M+Na]^+$: 463.3027; found: 463.3027.

3-Cyclopropyl-1-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3l)



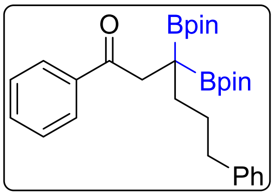
The reaction was performed following the general procedure B. Colorless oil, 67% yield (57.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 3.29 (s, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.11 – 1.06 (m, 1H), 0.35 (ddd, *J* = 8.4, 5.8, 4.4 Hz, 2H), 0.22 – 0.18 (m, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.3, 137.2, 132.6, 128.3, 128.1, 82.9, 42.5, 24.7, 24.6, 12.9, 3.5.
HRMS (ESI, m/z) calcd for $^{12}C_{24}{}^{1}H_{36}{}^{10}B_2{}^{16}O_5[M+H]^+$: 425.2894; found: 425.28

1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one (3m)



The reaction was performed following the general procedure B. Colorless oil, 78% yield (75.5 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.02 – 7.96 (m, 2H), 7.51 (t, *J* = 6.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 3.37 (s, 2H), 1.71 – 1.64 (m, 2H), 1.26 (s, 12H), 1.24 (s, 12H), 1.16 (dt, *J* = 19.0, 11.4 Hz, 10H), 0.81 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.2, 137.3, 132.5, 128.3, 128.1, 83.0, 40.1, 31.8, 30.0, 29.2, 27.7, 24.8, 24.7, 22.6, 14.1.
HRMS (ESI, m/z) calcd for $^{12}C_{28}{}^{1}H_{46}{}^{10}B_2{}^{16}O_5[M+Na]^+$: 505.3496; found: 505.3498.

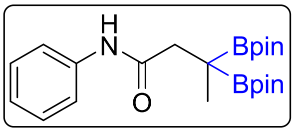
1,6-Diphenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3n)



The reaction was performed following the general procedure B. Colorless oil, 70% yield (75.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.98 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.4 Hz, 2H), 7.10 (dd, *J* = 12.0, 6.5 Hz, 3H), 3.38 (s, 2H), 2.56 – 2.50 (m, 2H), 1.84 – 1.80 (m, 2H), 1.54 – 1.45 (m, 2H), 1.28 (s, 12H), 1.25 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.0, 143.0, 137.1,

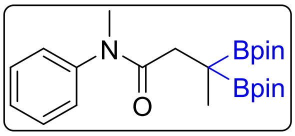
132.6, 128.2, 128.1, 125.4, 83.1, 77.3, 77.0, 76.8, 40.0, 36.7, 31.6, 30.2, 30.1, 24.8, 24.7, 22.6, 14.1.
HRMS (ESI, m/z) calcd for $^{12}C_{30}{}^{1}H_{42}{}^{10}B_{2}{}^{16}O_{5}[M+H]^{+}$: 503.3364; found: 503.3367.

N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3o)



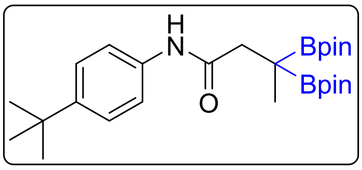
The reaction was performed following the general procedure A. Colorless oil, 66% yield (54.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.27 (dd, *J* = 10.5, 5.0 Hz, 2H), 7.04 (t, *J* = 7.3 Hz, 1H), 2.61 (s, 2H), 1.24 (s, 24H), 1.16 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.4, 138.3, 128.8, 123.56, 119.4, 83.4, 42.3, 24.7, 24.6, 16.6.
HRMS (ESI, m/z) calcd for $^{12}C_{22}{}^{1}H_{35}{}^{10}B_{2}{}^{16}O_{5}{}^{14}N[M+H]^{+}$: 414.2847; found: 414.2848.

N-methyl-N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3p)



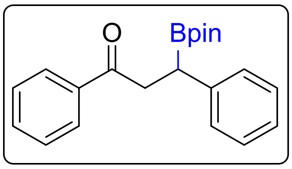
The reaction was performed following the general procedure A. Colorless oil, 78% yield (67.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 6.9 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 3.27 (s, 3H), 2.35 (s, 2H), 1.20 (d, *J* = 4.5 Hz, 24H), 0.98 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.5, 129.7, 129.1, 127.8, 127.2, 82.4, 41.1, 38.2, 29.7, 24.8, 18.0.
HRMS(ESI, m/z) calcd for $^{12}C_{23}{}^{1}H_{37}{}^{10}B_{2}{}^{16}O_{5}{}^{14}N[M+Na]^{+}$: 450.2823; found: 450.2825.

N-(4-(tert-butyl)phenyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3q)



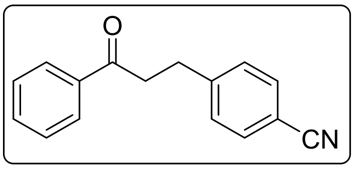
The reaction was performed following the general procedure A. Colorless oil, 66% yield (62.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 2.60 (s, 2H), 1.29 (s, 9H), 1.25 (s, 24H), 0.07 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 146.4, 135.7, 125.6, 119.2, 83.3, 42.2, 34.3, 31.3, 25.0, 24.7, 24.6, 16.5.
HRMS (ESI, m/z) calcd for $^{12}C_{26}{}^{1}H_{43}{}^{10}B_{2}{}^{16}O_{5}{}^{14}N[M+H]^{+}$: 470.3473; found: 470.3473.

1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3r)



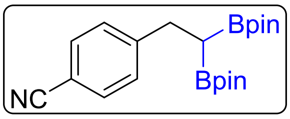
The reaction was performed following the general procedure A. Colorless oil, 60% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.30 (dt, *J* = 15.2, 7.4 Hz, 4H), 7.17 (t, *J* = 6.9 Hz, 1H), 3.56 (dd, *J* = 18.3, 10.9 Hz, 1H), 3.43 (dd, *J* = 18.3, 5.0 Hz, 1H), 2.80 (dd, *J* = 10.9, 5.0 Hz, 1H), 1.25 (s, 6H), 1.17 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 199.7, 141.9, 136.7, 132.9, 128.5, 128.4, 128.3, 128.0, 125.6, 83.4, 43.2, 24.53, 24.50.

4-(3-oxo-3-phenylpropyl)benzonitrile (3s)



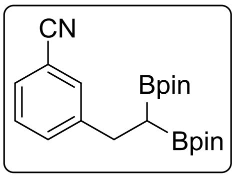
The reaction was performed following the general procedure A. Colorless oil, 78% yield.^{1}H NMR (500 MHz, CDCl$_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 3.33 (t, *J* = 7.4 Hz, 2H), 3.14 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 198.2, 147.0, 136.5, 133.3, 132.2, 129.3, 128.7, 127.9, 118.9, 110.0, 39.4, 29.9.

4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-*para*)



The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 °C), 88% yield (67.4 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.91 (d, *J* = 8.4 Hz, 2H), 1.16 (d, *J* = 10.5 Hz, 24H), 1.12 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 150.3, 131.8, 129.1, 119.3, 109.1, 83.3, 31.5, 24.8, 24.5.
HRMS-(DART) for: $^{12}C_{21}{}^{1}H_{31}{}^{10}B_{2}{}^{14}N^{16}O_{4}$[M+H]$^{+}$: calculated: 382.2585, found: 382.2585.

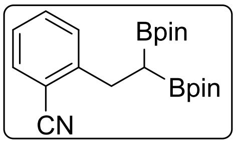
3-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-*meta*)



The reaction was performed following the general procedure A. Colorless oil, 19% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.55 (s, 1H), 7.47 – 7.40 (m, 2H), 7.31 (t, *J* = 7.7 Hz, 1H), 2.88 (d, *J* = 8.3 Hz, 2H), 1.25 (d, *J* = 3.0 Hz, 1H), 1.18 (s, 12H), 1.17 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.9, 133.0, 132.1, 129.3, 128.8, 119.2, 111.8, 83.4, 31.0, 25.0, 24.8, 24.6, 24.5.

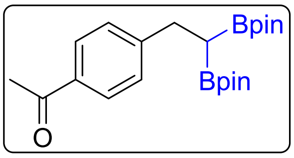
HRMS(ESI,m/z) calcd for $^{12}C_{21}{}^{1}H_{31}{}^{11}B_{2}{}^{14}N^{16}O_{4}{}^{23}Na[M+Na]^{+}$: 406.2331; found: 406.2329.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-*ortho*)



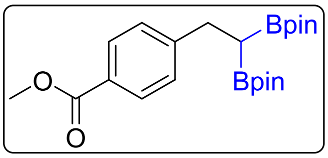
The reaction was performed following the general procedure A. Colorless oil, 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.21 (td, *J* = 7.5, 1.5 Hz, 1H), 3.08 (d, *J* = 8.2 Hz, 2H), 1.25 (t, *J* = 4.0 Hz, 1H), 1.17 (d, *J* = 8.1 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 132.6, 132.2, 129.2, 126.0, 118.1, 112.4, 83.3, 29.8, 25.0, 24.8, 24.4.
HRMS(ESI,m/z) calcd for $^{12}C_{21}{}^{1}H_{31}{}^{11}B_{2}{}^{14}N^{16}O_{4}{}^{23}Na[M+Na]^{+}$: 406.2331; found: 406.2332.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one (6b)



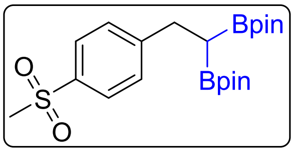
The reaction was performed following the general procedure A. White solid (mp: 174.2-175.3 °C), 78% yield (62.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H), 2.91 (d, *J* = 8.3 Hz, 2H), 1.30 (d, *J* = 1.9 Hz, 1H), 1.16 (d, *J* = 8.4 Hz, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 150.1, 129.4, 128.3, 127.3, 83.2, 51.9, 31.4, 24.8, 24.5.
HRMS-(DART) for:$^{12}C_{22}{}^{1}H_{34}{}^{10}B_{2}{}^{16}O_{5}[M+H]^{+}$: calculated: 398.2664, found: 398.2665.

Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6c)



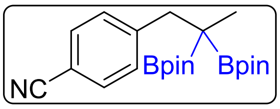
The reaction was performed following the general procedure A. White solid (mp: 183.2-184.8 °C), 80% yield (66.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 3H), 2.91 (d, *J* = 8.3 Hz, 2H), 1.39 – 1.21 (m, 1H), 1.17 (s, 12H), 1.15 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.3, 150.1, 129.4, 128.3, 127.3, 83.2, 51.9, 31.4, 24.8, 24.5.
HRMS (ESI, m/z) calcd for $^{12}C_{22}{}^{1}H_{34}{}^{10}B_{2}{}^{16}O_{6}[M+Na]^{+}$: 437.2506; found: 437.2509.

2,2'-(2-(4-(Methylsulfonyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6d)



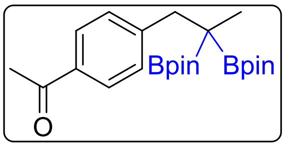
The reaction was performed following the general procedure A. White solid (mp: 177.2-178.3 °C), 80% yield (66.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 2.99 (s, 3H), 2.93 (d, *J* = 8.3 Hz, 2H), 1.16 (s, 12H), 1.15 (s, 12H), 1.12 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.3, 137.6, 129.3, 127.1, 83.3, 44.6, 31.3, 24.8, 24.5.
HRMS (ESI, m/z) calcd for $^{12}C_{21}{}^{1}H_{34}{}^{10}B_2{}^{16}O_6{}^{32}S[M+Na]^+$: 457.2227; found: 457.2227.

4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzonitrile (6e)



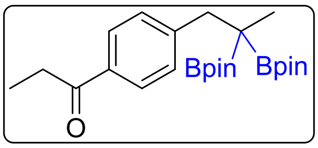
The reaction was performed following the general procedure A. White solid (mp: 177.2-178.3 °C), 84% yield (67.2 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 2.91 (s, 2H), 1.22 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.7, 131.4, 130.7, 119.3, 109.3, 83.4, 39.4, 24.8, 24.6, 15.8.
HRMS (ESI, m/z) calcd for $^{12}C_{22}{}^{1}H_{33}{}^{10}B_2{}^{16}O_4{}^{14}N[M+Na]^+$:418.2561; found: 418.2563.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)ethan-1-one (6f)



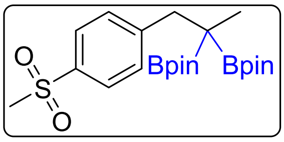
The reaction was performed following the general procedure A. White solid (mp: 177.0-178.6 °C), 90% yield (74.5 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 2.92 (s, 2H), 2.55 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 198.1, 147.9, 134.7, 130.0, 127.8, 83.3, 39.2, 26.5, 24.8, 24.6, 15.8.
HRMS (ESI, m/z) calcd for $^{12}C_{23}{}^{1}H_{36}{}^{10}B_2{}^{16}O_5[M+H]^+$: 413.2894; found: 413.2896.

1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)propan-1-one (6g)



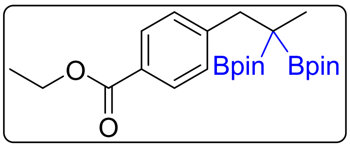
The reaction was performed following the general procedure A. White solid (mp: 169.2-171.3 ºC), 87% yield (74.8 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 2.96 (q, *J* = 7.2 Hz, 2H), 2.91 (s, 2H), 1.23 (s, 12H), 1.21 – 1.17 (m, 15H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 200.7, 147.6, 134.4, 130.0, 127.5, 83.3, 39.2, 31.6, 24.8, 24.6, 15.8, 8.3.
HRMS (ESI, m/z) calcd for $^{12}C_{24}{}^1H_{38}{}^{10}B_2{}^{16}O_5[M+H]^+$: 427.3051; found: 427.3051.

2,2'-(1-(4-(Methylsulfonyl)phenyl)propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6h)



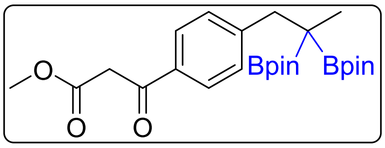
The reaction was performed following the general procedure A. White solid (mp: 188.2-190.3 ºC), 90% yield (81.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 – 7.76 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 3.02 (s, 3H), 2.95 (s, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 0.97 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 148.8, 137.6, 130.8, 126.7, 83.4, 44.6, 39.2, 24.8, 24.7, 15.8.
HRMS (ESI, m/z) calcd for $^{12}C_{22}{}^1H_{36}{}^{10}B_2{}^{16}O_6{}^{32}S[M+Na]^+$: 471.2384; found: 471.2386.

Ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6i)



The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 ºC), 88% yield (78.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.33 (q, *J* = 7.0 Hz, 2H), 2.91 (s, 2H), 1.36 (t, *J* = 7.0 Hz, 3H), 1.22 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.8, 147.4, 129.8, 128.9, 127.7, 83.2, 60.6, 39.2, 24.9, 24.8, 24.6, 15.8, 14.3.
HRMS (ESI, m/z) calcd for $^{12}C_{24}{}^1H_{38}{}^{10}B_2{}^{16}O_6[M+Na]^+$: 465.2819; found: 465.2824.

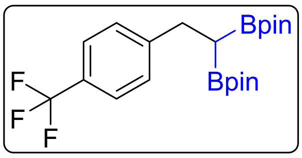
Ethyl 3-(4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)-3-oxopropanoate (6j)



The reaction was performed following the general procedure A. White solid (mp: 168.2-169.3 ºC), 85% yield (78.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.81 (d, *J* = 8.3

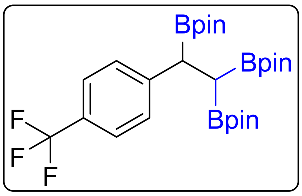
Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 2.93 (s, 2H), 2.56 (s, 3H), 1.25 (s, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 0.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 147.9, 134.8, 130.1, 127.8, 83.3, 39.2, 29.7, 26.5, 24.8, 24.7, 15.8.
HRMS (ESI, m/z) calcd for $^{12}C_{25}{}^{1}H_{38}{}^{10}B_{2}{}^{16}O_{7}[M+Na]^{+}$: 473.2874; found: 473.2876.

2,2'-(2-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6k)



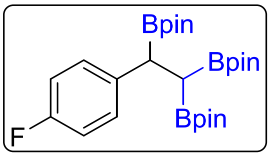
The reaction was performed following the general procedure A. Colorless oil, 24% yield (20.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.92 (d, *J* = 8.4 Hz, 2H), 1.28 (t, *J* = 2.9 Hz, 1H), 1.18 (s, 12H), 1.16 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6 (d, *J* = 1.2 Hz), 128.6, 127.1, 125.5, 124.9 (q, *J* = 3.8 Hz), 83.3, 31.2, 24.80, 24.77, 24.5.
HRMS (ESI, m/z) calcd for $^{12}C_{21}{}^{1}H_{31}{}^{11}B_{2}{}^{16}O_{4}{}^{18}F_{3}[M+H]^{+}$: 427.2442; found: 427.2433.

2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6’a)



The reaction was performed following the general procedure A. Colorless oil, 64% yield (62.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.74 (d, *J* = 12.6 Hz, 1H), 1.44 (d, *J* = 12.6 Hz, 1H), 1.23 (d, *J* = 5.5 Hz, 12H), 1.14 (d, *J* = 8.6 Hz, 12H), 0.92 (d, *J* = 20.6 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.92, 128.6, 127.1, 124.71 (q, *J* = 3.7 Hz), 83.2, 83.1, 82.8, 31.6, 25.0, 24.81, 24.80, 24.6, 24.4, 24.22, 24.20, 22.6.
HRMS(ESI, m/z) calcd for $^{12}C_{27}{}^{1}H_{42}{}^{11}B_{3}{}^{16}O_{6}{}^{18}F_{3}[M+Na]^{+}$: 575.3104; found: 575.3105.

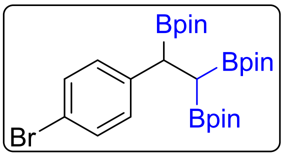
2,2',2''-(2-(4-fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6’b)



The reaction was performed following the general procedure A. Colorless oil, 80% yield (81.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.7, 5.6 Hz, 2H), 6.86 (t,

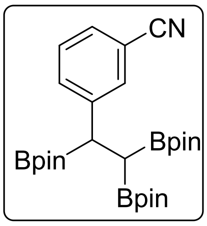
J = 8.8 Hz, 2H), 2.64 (d, *J* = 12.8 Hz, 1H), 1.42 – 1.37 (m, 1H), 1.23 (d, *J* = 6.0 Hz, 12H), 1.13 (d, *J* = 9.1 Hz, 12H), 0.95 (d, *J* = 12.4 Hz, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 161.7, 159.8, 140.9, 129.7, 114.5, 114.4, 83.1, 83.0, 82.7, 25.0 24.82, 24.80 24.6, 24.5, 24.4, 24.2.
HRMS-(DART) for: $^{12}C_{26}{}^{1}H_{42}{}^{10}B_{3}{}^{18}F^{16}O_{6}[M+H]^{+}$: calculated: 500.3426, found: 500.3425.

2,2',2''-(2-(4-bromophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'c)



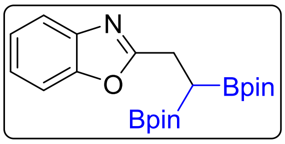
The reaction was performed following the general procedure A. Colorless oil, 84% yield (84.3 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.29 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 2.63 (d, *J* = 12.7 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 1H), 1.23 (d, *J* = 5.5 Hz, 12H), 1.14 (d, *J* = 7.5 Hz, 12H), 0.96 (d, *J* = 16.7 Hz, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.5, 130.8, 130.2, 118.3, 83.2, 83.1, 82.8, 25.0, 24.82, 24.80, 24.6, 24.5, 24.3, 24.2.
HRMS(ESI,m/z) calcd for $^{12}C_{26}{}^{1}H_{42}{}^{11}B_{3}{}^{16}O_{6}{}^{80}Br[M+Na]^{+}$: 563.2526; found: 563.2517.

3-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6'd)



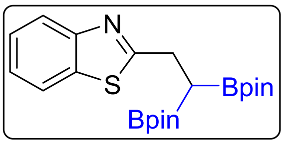
The reaction was performed following the general procedure A. Colorless oil, 62% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.52 (s, 1H), 7.46 – 7.42 (m, 1H), 7.35 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.27 (dd, *J* = 10.5, 4.9 Hz, 1H), 2.71 (d, *J* = 12.5 Hz, 1H), 1.41 – 1.35 (m, 1H), 1.23 (d, *J* = 4.4 Hz, 12H), 1.14 (d, *J* = 8.9 Hz, 12H), 0.97 (s, 6H), 0.93 (s, 6H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.2, 133.0, 132.2, 128.61, 128.55, 119.34, 111.6, 83.5, 83.3, 82.9, 24.8, 24.7, 24.6, 24.5, 24.3.
HRMS(ESI,m/z) calcd for $^{12}C_{27}{}^{1}H_{42}{}^{11}B_{3}{}^{14}N^{16}O_{6}{}^{23}Na[M+Na]^{+}$: 532.3184; found: 532.3191.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]oxazole (6l)[15]



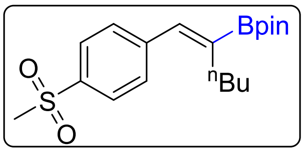
The reaction was performed following the general procedure A. Colorless oil, 87% yield (69.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 – 7.59 (m, 1H), 7.43 – 7.39 (m, 1H), 7.25 – 7.21 (m, 2H), 3.16 (d, J = 8.2 Hz, 2H), 1.40 (t, J = 8.1 Hz, 1H), 1.23 (s, 12H), 1.19 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 150.8, 141.4, 123.9, 123.7, 119.4, 110.1, 83.4, 24.8, 24.4.

2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (6m)[15]



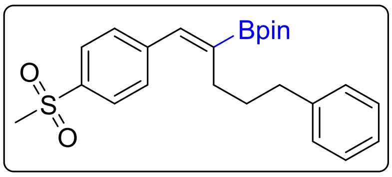
The reaction was performed following the general procedure A. Colorless oil, 72% yield (59.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.1 Hz, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 3.36 (d, J = 8.0 Hz, 2H), 1.43 (t, J = 7.9 Hz, 1H), 1.24 (s, 12H), 1.20 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.9, 153.1, 135.4, 125.5, 124.2, 122.4, 121.4, 83.4, 30.34, 24.8, 24.5.

4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)hex-1-en-2-yl)-1,3,2-dioxaborolane (6n)



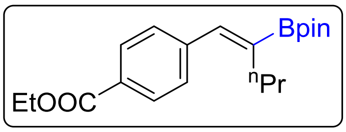
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.18 (s, 1H), 3.05 (s, 3H), 2.34 – 2.29 (m, 2H), 1.48 – 1.39 (m, 3H), 1.29 (s, 12H), 1.26 (dd, J = 7.1, 3.7 Hz, 1H), 0.85 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 139.2, 138.4, 129.5, 127.1, 83.6, 44.5, 31.9, 29.2, 26.8, 24.9, 24.7, 22.7, 13.9.
HRMS(ESI,m/z) calcd for $^{12}C_{19}{}^1H_{30}{}^{11}B^{16}O_4{}^{32}S[M+H]^+$: 365.1952; found: 365.1951.

4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)-5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (6o)



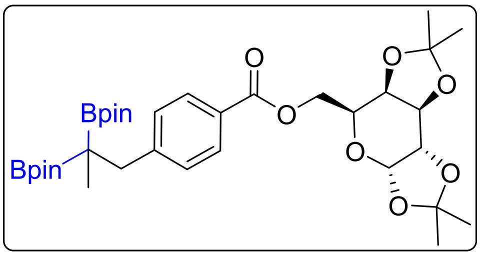
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.26 (t, J = 7.3 Hz, 2H), 7.19 (dd, J = 13.2, 5.8 Hz, 2H), 7.14 (d, J = 6.9 Hz, 2H), 3.05 (s, 3H), 2.62 (t, J = 7.5 Hz, 2H), 2.40 – 2.35 (m, 2H), 1.85 – 1.78 (m, 2H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 142.0, 139.6, 138.4, 129.3, 128.3, 128.1, 127.0, 125.6, 83.6, 44.2, 35.6, 31.1, 28.8, 24.6, 20.8.
HRMS(ESI,m/z) calcd for $^{12}C_{24}{}^1H_{31}{}^{11}BNa^{16}O_4{}^{32}S[M+Na]^+$: 449.1928; found: 449.1926.

ethyl -4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)benzoate (6p)



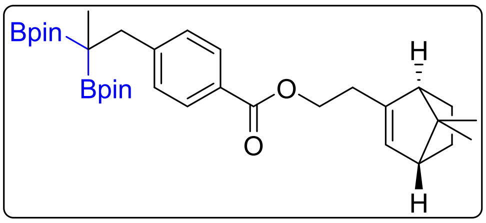
^{1}H NMR (500 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.23 (s, 1H), 4.38 – 4.34 (m, 2H), 2.35 – 2.31 (m, 2H), 1.49 (dd, *J* = 15.3, 7.6 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.30 (s, 12H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 166.5, 142.6, 140.7, 134.6, 129.3, 128.8, 83.5, 60.9, 31.7, 24.8, 23.2, 14.3, 14.2.
HRMS(ESI,m/z) calcd for $^{12}C_{20}{}^{1}H_{29}{}^{11}BNa^{16}O_4[M+Na]^+$: 367.2051; found: 367.2054.

((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6q)



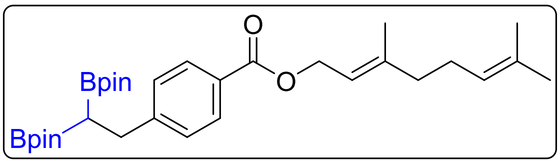
The reaction was performed following the general procedure A. Colorless oil, 84% yield (101.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.55 (d, *J* = 4.9 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.50 (dd, *J* = 11.4, 5.1 Hz, 1H), 4.38 (dd, *J* = 11.4, 7.4 Hz, 1H), 4.35 – 4.30 (m, 2H), 4.16 (ddd, *J* = 7.0, 5.1, 1.7 Hz, 1H), 2.91 (s, 2H), 1.50 (s, 3H), 1.46 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.96 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 170.9, 147.6, 129.8, 129.0, 109.5, 108.7, 96.2, 83.2, 71.0, 70.6, 66.1, 63.5, 60.3, 25.8, 24.8, 24.7, 24.5, 24.4, 20.9, 15.7, 14.1.
HRMS (ESI, m/z) calcd for $^{12}C_{34}{}^{1}H_{52}{}^{10}B_2{}^{16}O_{11}[M+H]^+$: 657.3841; found: 657,3841.

2-((1S,4R)-7,7-dimethylbicyclo[2.2.1]hept-2-en-2-yl)ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6r)



The reaction was performed following the general procedure A. Colorless oil, 80% yield (89.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.36 – 5.33 (m, 1H), 4.32 – 4.26 (m, 2H), 2.92 (s, 2H), 2.40 (dd, *J* = 11.8, 5.0 Hz, 2H), 2.38 – 2.34 (m, 1H), 2.21 (t, *J* = 17.2 Hz, 2H), 2.11 (t, *J* = 6.3 Hz, 1H), 2.09 – 2.06 (m, 1H), 1.33 (s, 1H), 1.26 (s, 3H), 1.23 (s, 12H), 1.19 (s, 12H), 0.98 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 129.5, 128.5, 118.4, 82.8, 62.6, 45.4, 40.4, 38.9, 35.7, 31.2, 30.9, 25.8, 24.4, 24.2, 20.7, 20.4, 15.5, 13.7.
HRMS (ESI, m/z) calcd for $^{12}C_{33}{}^{1}H_{50}{}^{10}B_2{}^{16}O_6[M+Na]^+$: 585.3758; found: 585.3757.

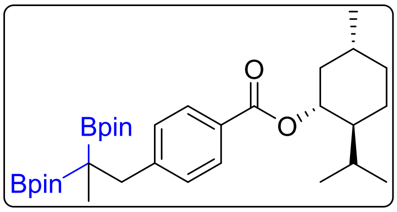
(E)-3,7-dimethylocta-2,6-dien-1-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6s)



The reaction was performed following the general procedure A. Colorless oil, 62% yield (66.9 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.43 (t, *J* = 7.2 Hz, 1H), 5.08 (t, *J* = 6.4 Hz, 1H), 4.08 (d, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 2.90 (d, *J* = 8.3 Hz, 2H), 2.09 – 2.04 (m, 4H), 1.73 (s, 3H), 1.59 (s, 3H), 1.37 – 1.31 (m, 1H), 1.16 (s, 12H), 1.15 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 167.3, 150.1, 139.9, 129.4, 128.3, 127.3, 124.4, 123.8, 83.5, 83.2, 58.9, 51.9, 31.9, 31.4, 26.5, 25.6, 24.9, 24.7, 24.5, 23.4, 17.6.

HRMS (ESI, m/z) calcd for $^{12}C_{31}{}^{1}H_{48}{}^{10}B_2{}^{16}O_6[M+Na]^+$: 561.3527; found: 561.3529.

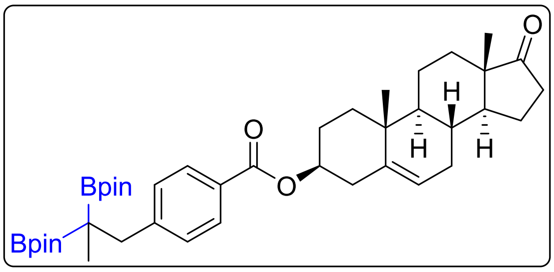
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6t)



The reaction was performed following the general procedure A. Colorless oil, 65% yield (76.7 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.90 (td, *J* = 10.9, 4.4 Hz, 1H), 2.95 – 2.89 (m, 2H), 2.10 (d, *J* = 11.7 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.73 – 1.69 (m, 2H), 1.53 (t, *J* = 11.7 Hz, 2H), 1.33 (s, 1H), 1.24 (s, 12H), 1.20 (s, 12H), 1.10 (dd, *J* = 21.8, 9.9 Hz, 2H), 0.97 (s, 3H), 0.90 (t, *J* = 6.4 Hz, 6H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.6, 146.9, 129.4, 128.5, 127.7, 82.7, 73.8, 46.9, 40.6, 38.7, 33.9, 30.9, 26.0, 24.3, 24.1, 23.2, 21.4, 15.9, 15.2.

HRMS (ESI, m/z) calcd for $^{12}C_{32}{}^{1}H_{52}{}^{10}B_2{}^{16}O_6[M+Na]^+$: 575.3915; found: 575.3914.

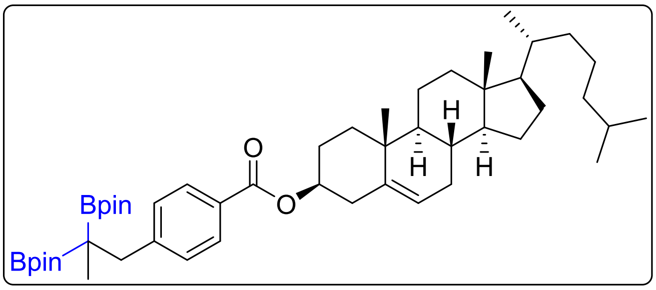
(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6u)



The reaction was performed following the general procedure A. Colorless oil, 74% yield (102.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.44 (d, *J* = 5.0 Hz, 1H), 4.83 (dq, *J* = 16.3, 5.3 Hz, 1H), 2.92 (s, 2H), 2.46 (dd, *J* = 18.9, 9.3 Hz, 3H), 2.14 – 2.05 (m, 2H), 1.95 (ddd, *J* = 17.2, 14.8, 7.0 Hz, 3H), 1.87 – 1.83 (m, 1H), 1.78 – 1.63 (m, 6H), 1.52 (ddd, *J* = 16.7, 12.8, 3.7 Hz, 2H), 1.23 (s, 12H), 1.20 (s, 12H), 1.08 (s, 3H), 0.96 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.1, 166.2, 147.4, 140.0, 129.8, 128.9, 128.0, 121.8, 83.2, 73.9,

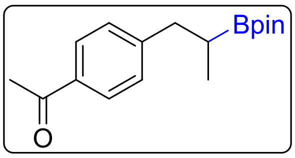
60.3, 51.7, 50.1, 47.5, 39.2, 38.2, 36.9, 36.8, 35.8, 31.4, 30.8, 27.8, 24.7, 24.6, 21.9, 20.9, 20.3, 19.4, 15.8, 14.2, 13.5.
HRMS (ESI, m/z) calcd for $^{12}C_{41}{}^{1}H_{60}{}^{10}B_{2}{}^{16}O_{7}[M+Na]^{+}$: 707.4490; found: 707.4491.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1Hcyclopenta[a]phenanthren-3-yl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6v)



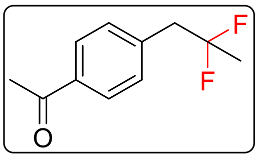
The reaction was performed following the general procedure A. Colorless oil, 74% yield (102.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 5.41 (d, *J* = 3.6 Hz, 1H), 4.87 – 4.79 (m, 1H), 2.92 (s, 2H), 2.44 (d, *J* = 7.7 Hz, 2H), 1.98 (d, *J* = 17.1 Hz, 3H), 1.93 – 1.69 (m, 4H), 1.57 – 1.43 (m, 6H), 1.36 – 1.31 (m, 4H), 1.24 (s, 12H), 1.20 (s, 12H), 1.17 – 1.08 (m, 6H), 1.06 (s, 3H), 1.01 (dd, *J* = 16.9, 6.4 Hz, 3H), 0.96 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 2.3 Hz, 6H), 0.68 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.1, 166.2, 147.3, 139.8, 129.8, 128.9, 122.6, 83.3, 74.2, 60.4, 56.7, 56.1, 50.0, 42.3, 39.5, 38.2, 37.1, 36.7, 36.2, 35.8, 31.9, 28.2, 28.0, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 15.8, 14.2, 11.9.
HRMS (ESI, m/z) calcd for $^{12}C_{49}{}^{1}H_{78}{}^{10}B_{2}{}^{16}O_{6}[M+Na]^{+}$: 807.5873; found: 807.5877.

1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolayl)propyl)phenyl)ethan-1-one (8)



The reaction was performed following the general procedure **(2)**. Colorless oil, 88% yield (50.7 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 2.85 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.63 – 2.58 (m, 1H), 2.57 (s, 3H), 1.38 (dd, *J* = 15.3, 7.6 Hz, 1H), 1.18 (d, *J* = 2.6 Hz, 12H), 0.96 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 197.9, 148.4, 134.9, 129.1, 128.2, 83.1, 38.9, 26.5, 24.7, 24.7, 15.2.
HRMS (ESI, m/z) calcd for $^{12}C_{17}{}^{1}H_{25}{}^{10}B^{16}O_{3}[M+H]^{+}$: 289.1974; found: 289.1970.

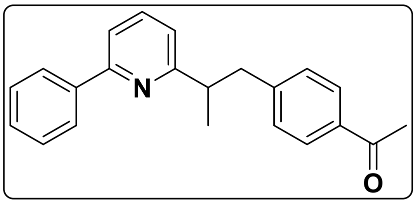
1-(4-(2,2-difluoropropyl)phenyl)ethan-1-one (7) (CAS: No. 1785555-40-9)



The reaction was performed following the general procedure **(1)**. Colorless oil, 45% yield (17.8 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.92 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* =

8.1 Hz, 2H), 3.20 (t, *J* = 15.5 Hz, 2H), 2.60 (s, 3H), 1.55 (t, *J* = 18.3 Hz, 3H).^{13}C NMR (125 MHz, CDCl$_3$) δ 197.8, 139.0, 136.2, 130.5, 128.4, 122.9 (t, *J* = 240.0 Hz), 44.3 (t, *J* = 26.5 Hz), 26.6, 23.0 (t, *J* = 27.4 Hz). ^{19}F NMR (471 MHz, CDCl$_3$) δ -89.07. HRMS (ESI, m/z) calcd for $^{12}C_{11}{}^{1}H_{13}{}^{19}F_2{}^{16}O[M+H]^+$: 199.0929; found: 199.0932.

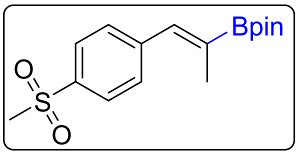
1-(4-(2-(6-phenylpyridin-2-yl)propyl)phenyl)ethan-1-one (9)



The reaction was performed following the general procedure **(3)**. Colorless oil, 74% yield (46.6 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 9.21 (d, *J* = 2.1 Hz, 1H), 8.41 (d, *J* = 2.1 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 8.06 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.79 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.72 (d, *J* = 8.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 2.67 (s, 3H), 2.65 (s, 1H), 1.33 (s, 1H), 1.28 (s, 1H), 1.25 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 197.5, 148.9, 142.1, 136.6, 134.4, 132.6, 130.3, 129.6, 128.9, 128.8, 128.2, 127.5, 127.4, 31.4, 30.2, 29.7, 26.7.

HRMS (ESI, m/z) calcd for $^{12}C_{22}{}^{1}H_{22}{}^{14}N^{16}O[M+H]^+$: 316.1696; found: 316.1695.

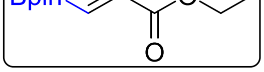
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (B-1)



The reaction was performed following the general procedure **(8)**. Colorless oil, 94% yield (60.5 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.21 (s, 1H), 3.05 (s, 3H), 1.96 (d, *J* = 1.6 Hz, 3H), 1.29 (s, 12H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.3, 139.9, 138.4, 132.6, 129.9, 127.1, 83.8, 44.4, 24.8, 15.9.

HRMS(ESI,m/z) calcd for $^{12}C_{16}{}^{1}H_{24}{}^{11}B^{16}O_4{}^{32}S[M+H]^+$: 323.1483; found: 323.1482.

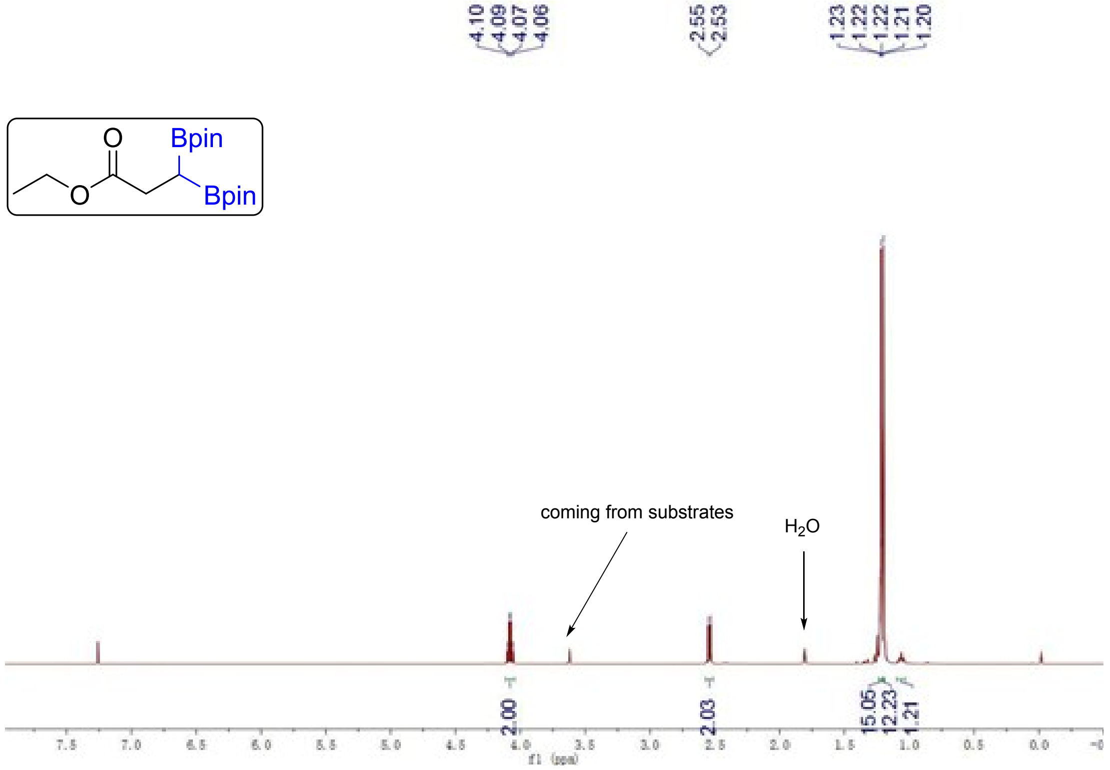
Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (B-2) (CAS: No. 1009307-13-4)[13]

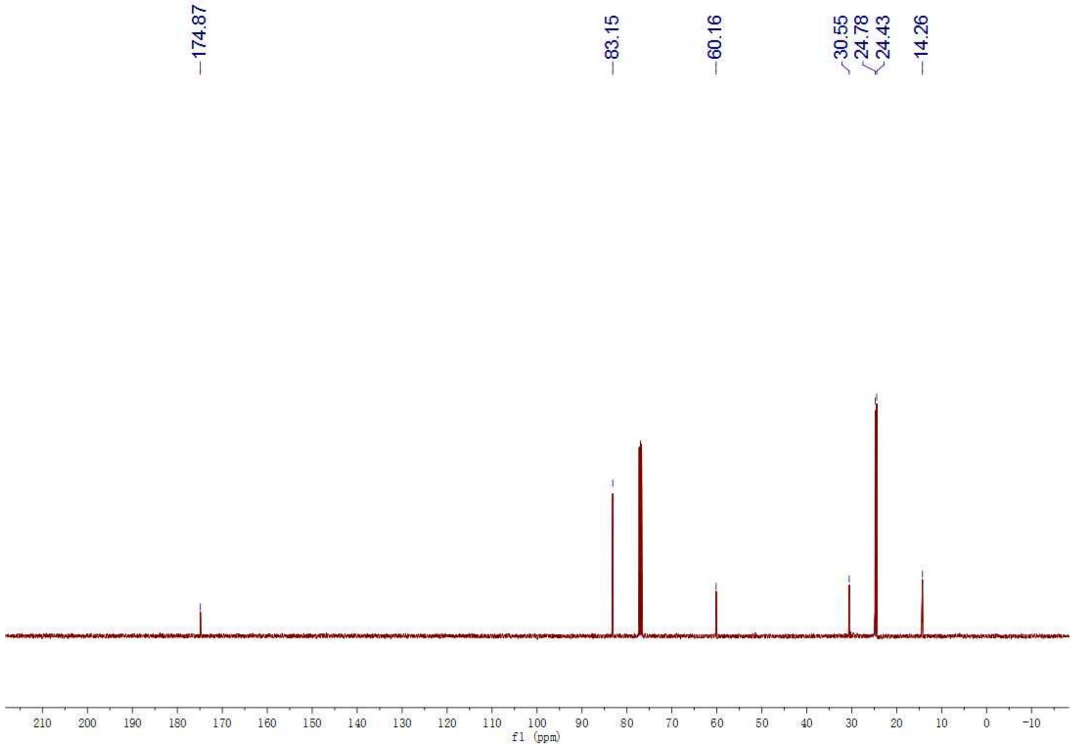


The reaction was performed following the general procedure **(8)**. Colorless oil, 89% yield (40.1 mg). ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.76 (d, *J* = 18.2 Hz, 1H), 6.61 (d, *J* = 18.2 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.27 (s, 12H), 1.25 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 165.9, 138.7, 83.9, 60.6, 24.9, 24.7, 14.1.

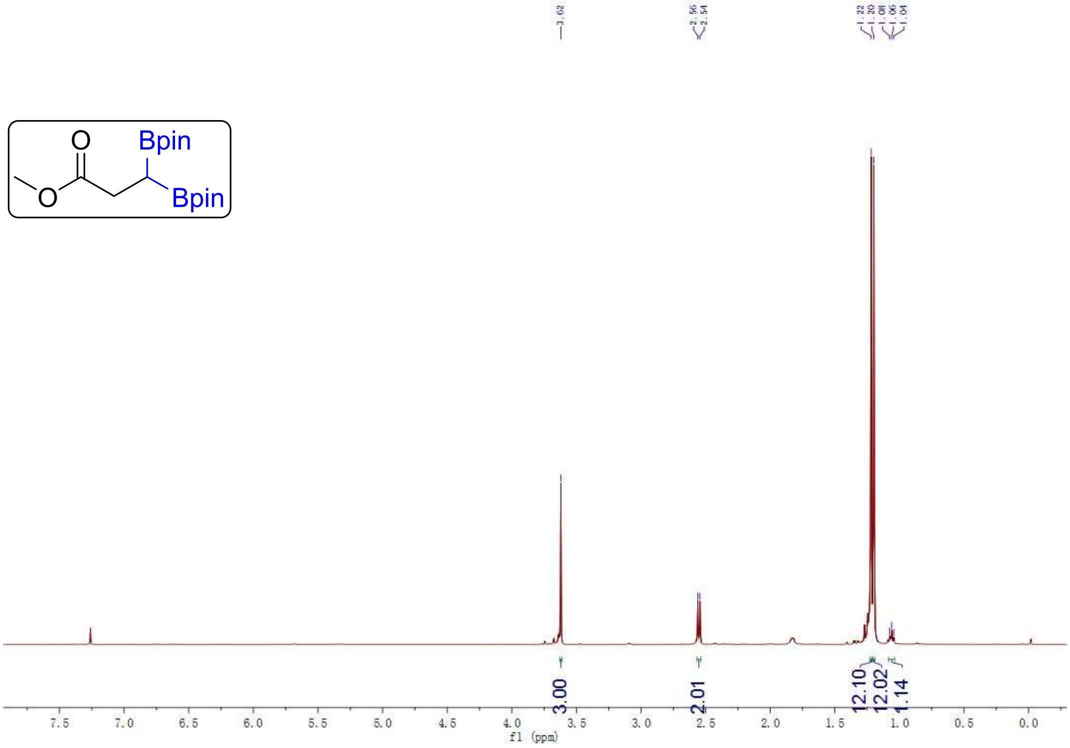
10. NMR spectrum

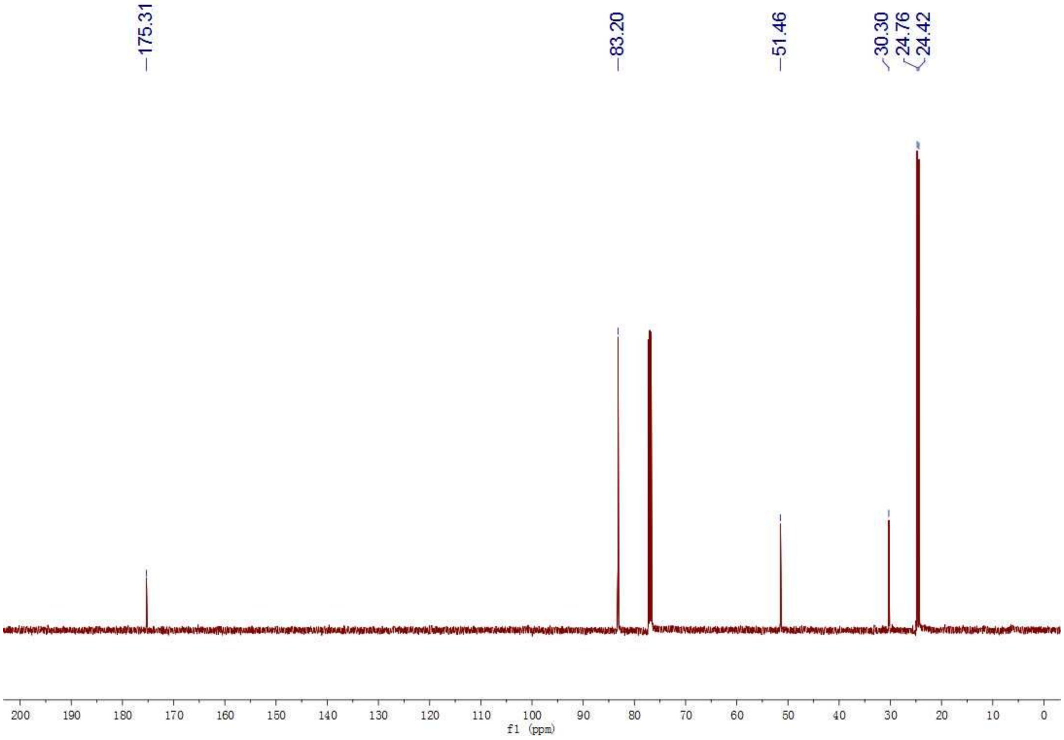
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3a)



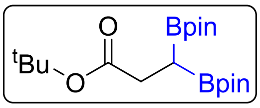


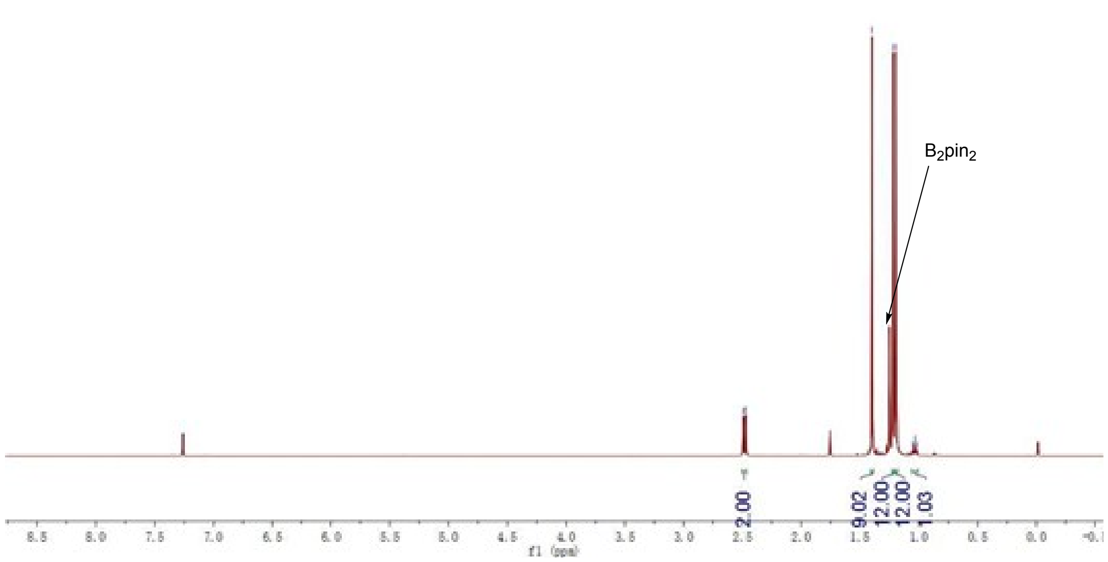
Methyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3b)

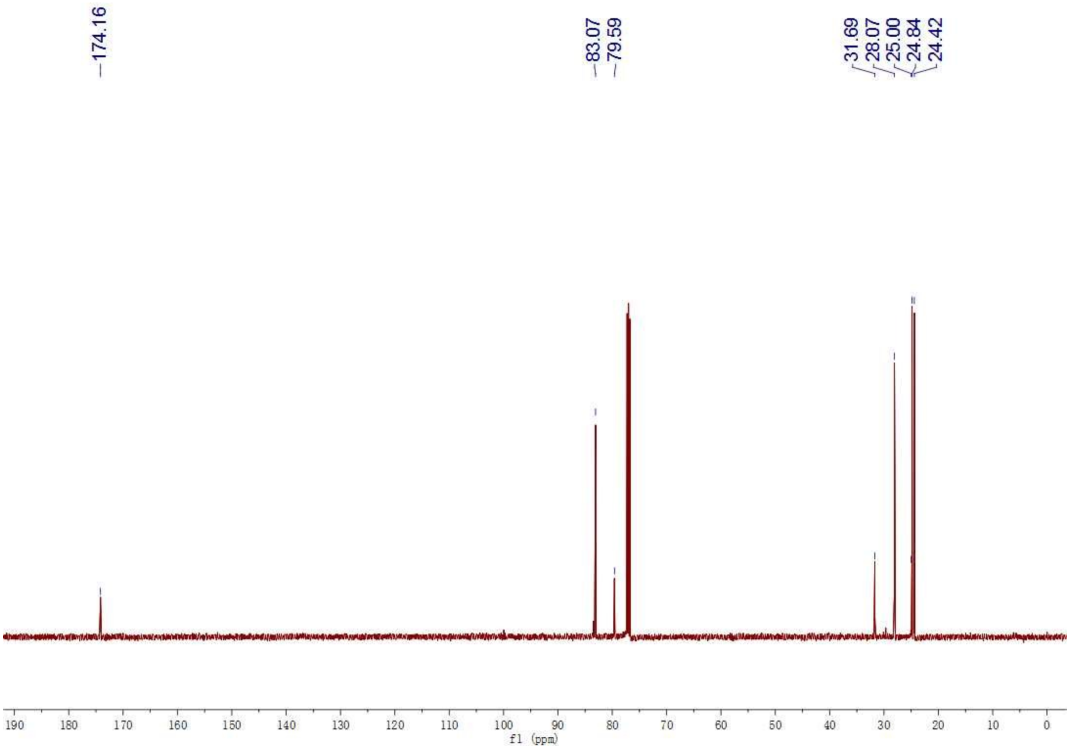




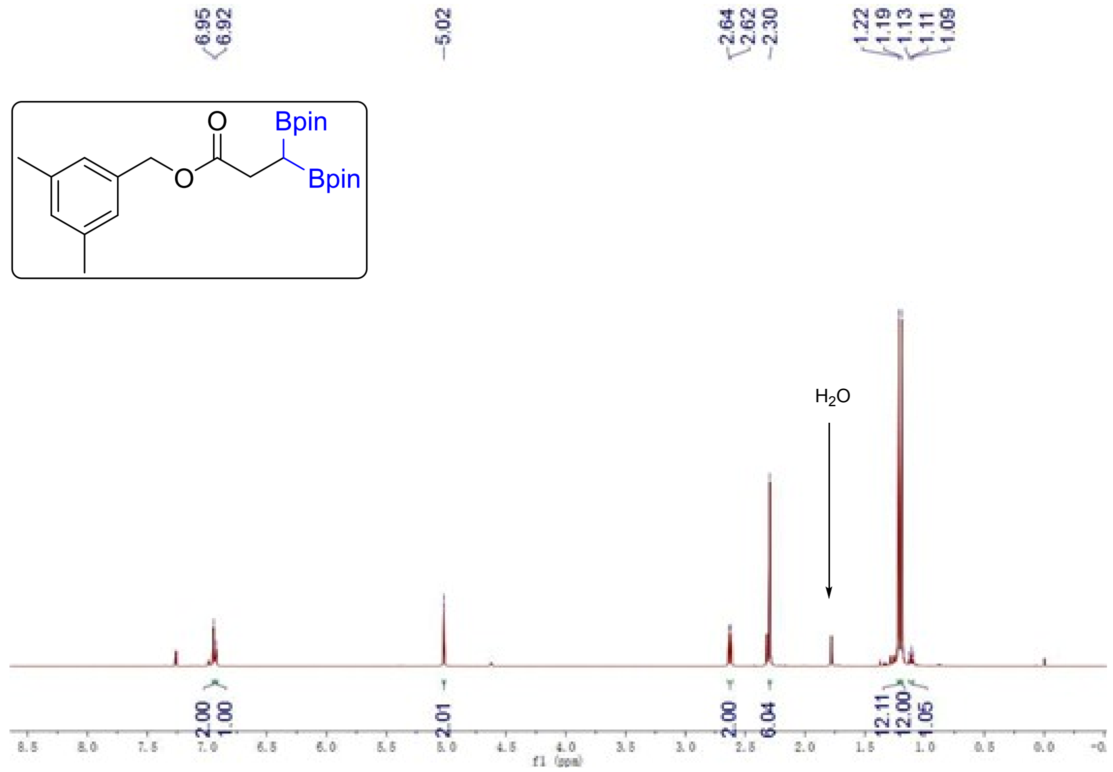
Tert-butyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (3c)

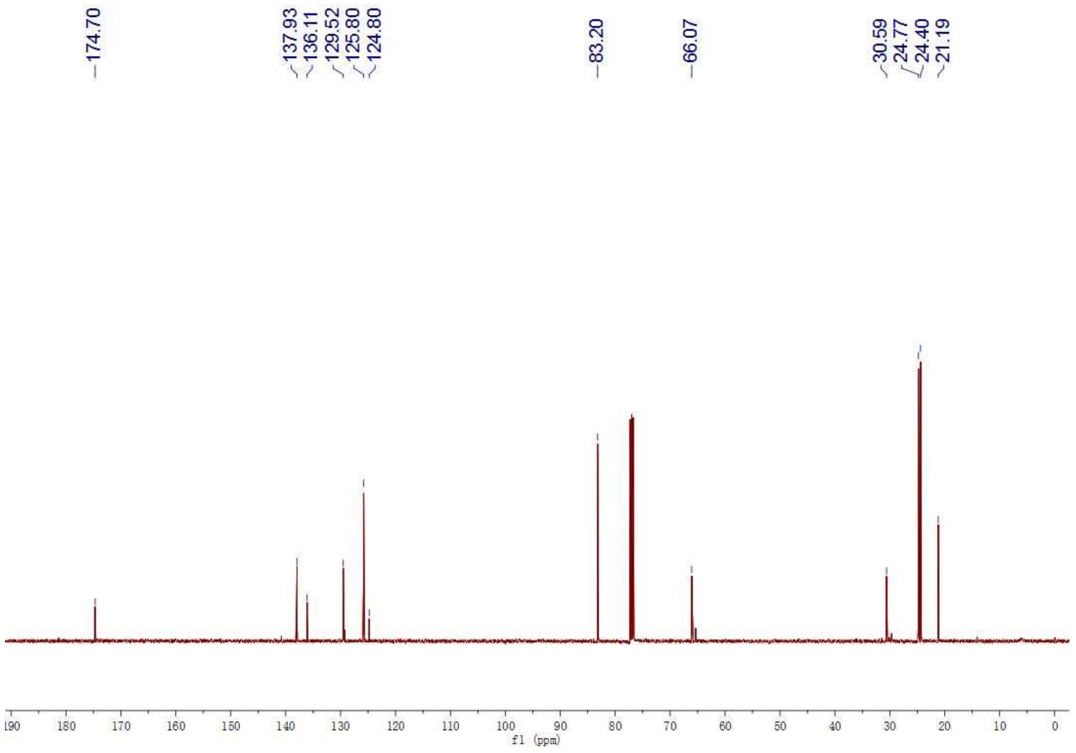




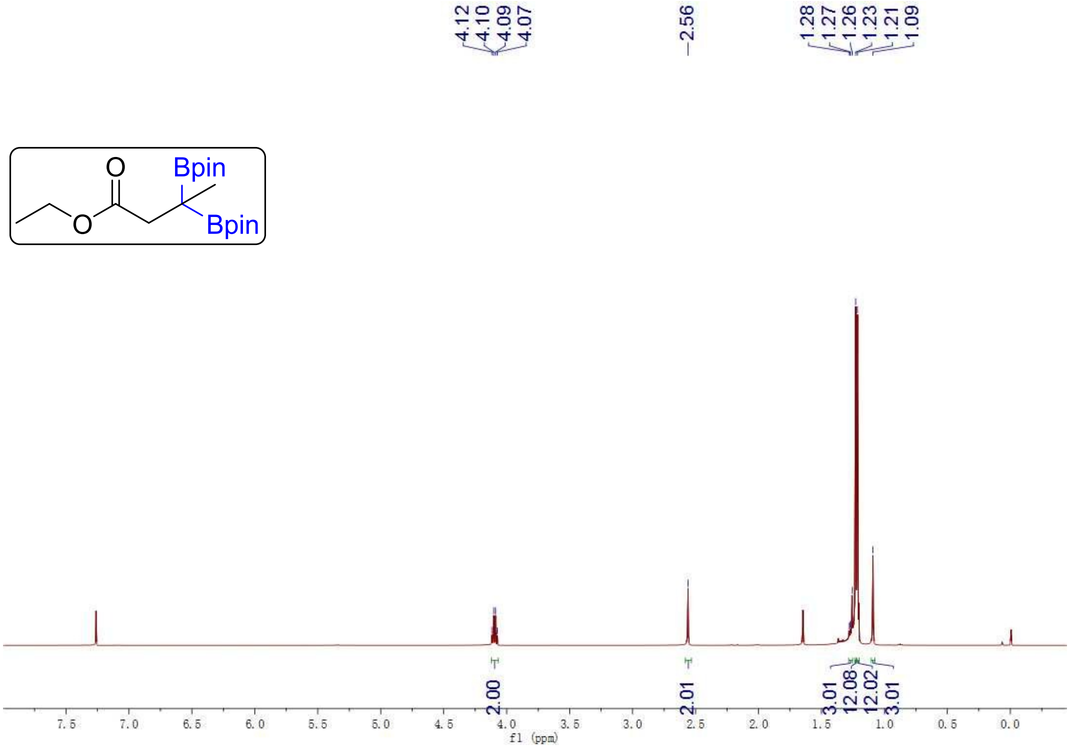


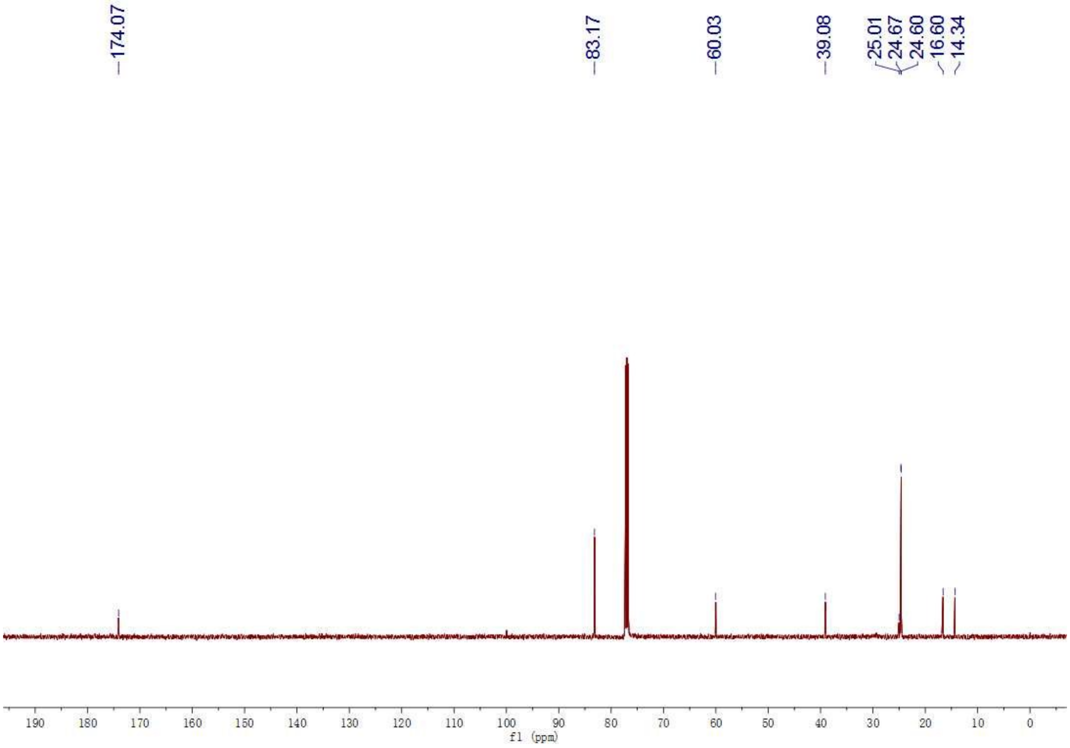
3,5-Dimethylbenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl)propanoate (3d)



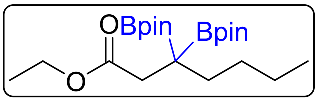


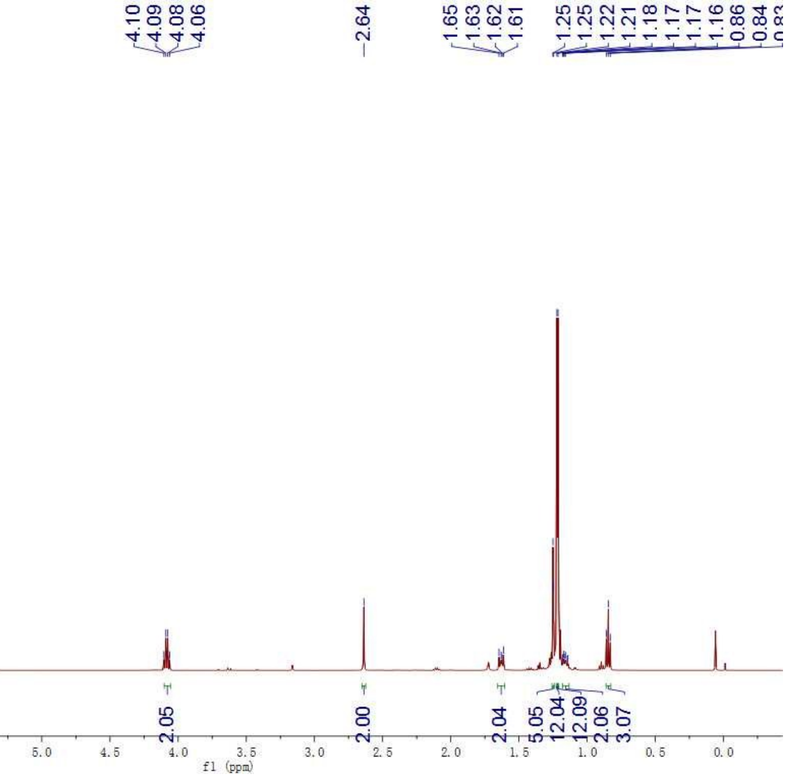
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3e)

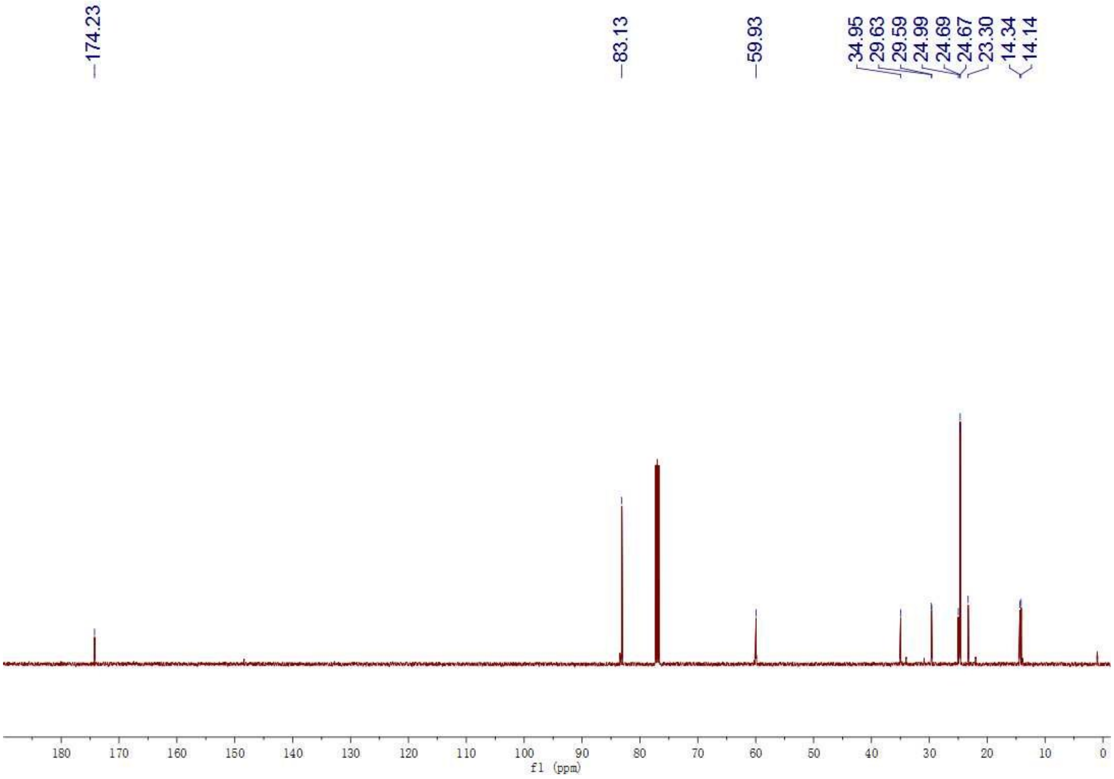




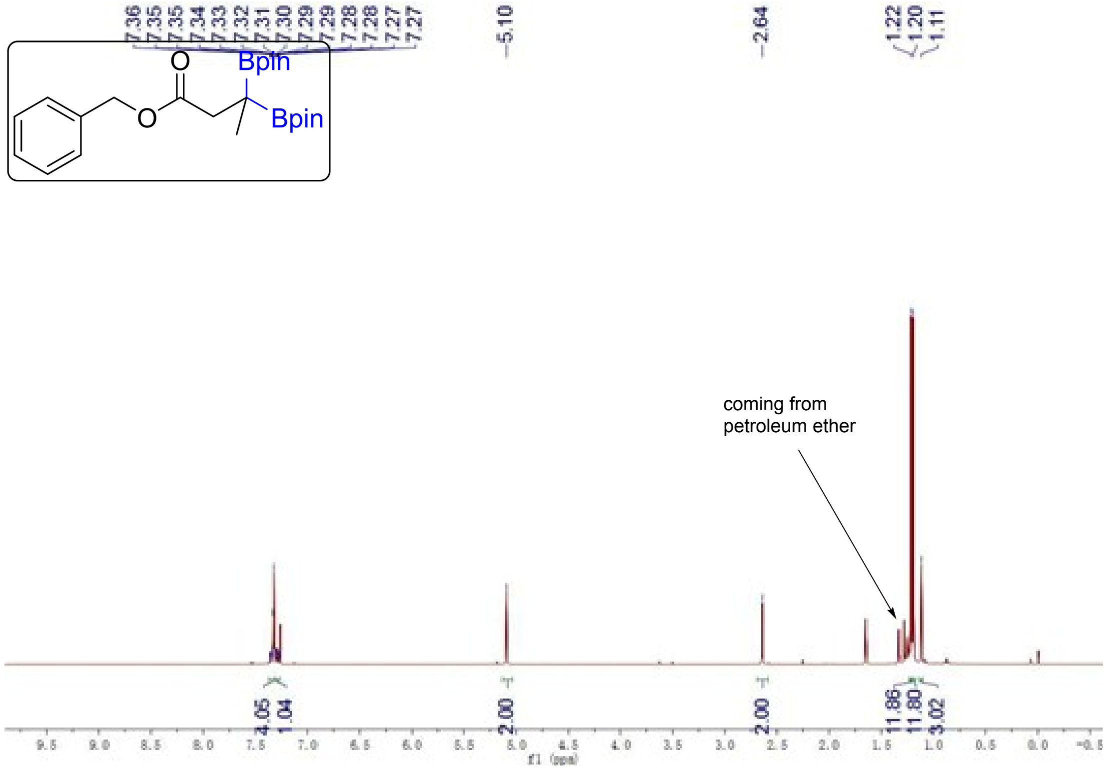
Ethyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3f)

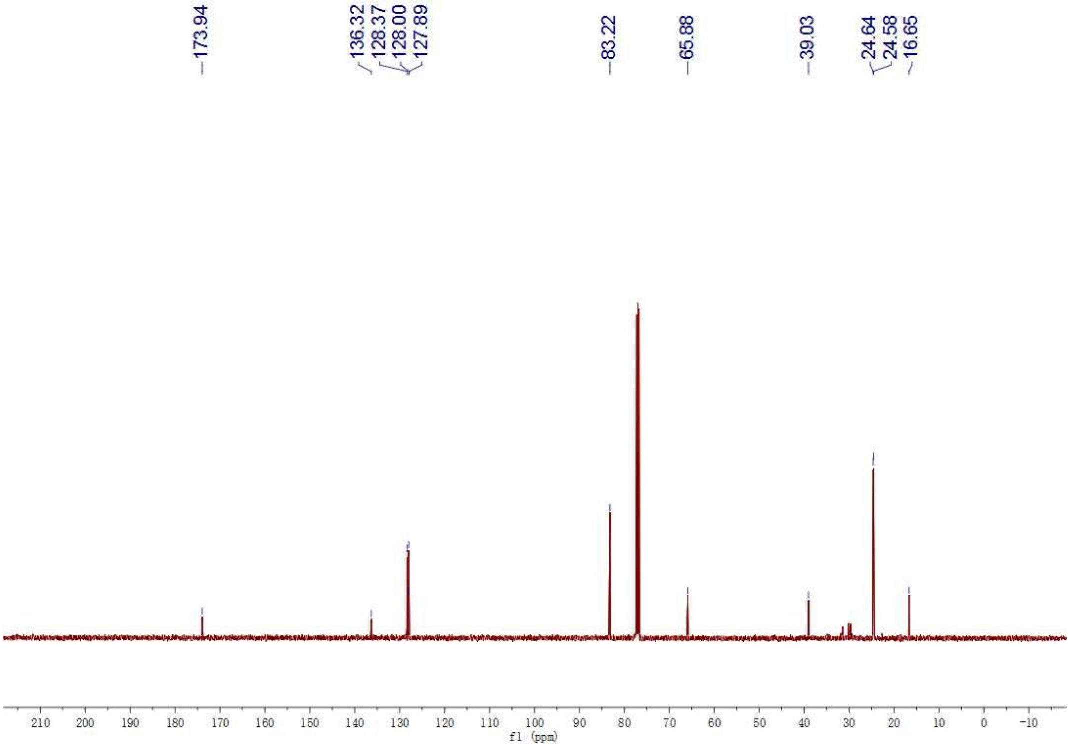




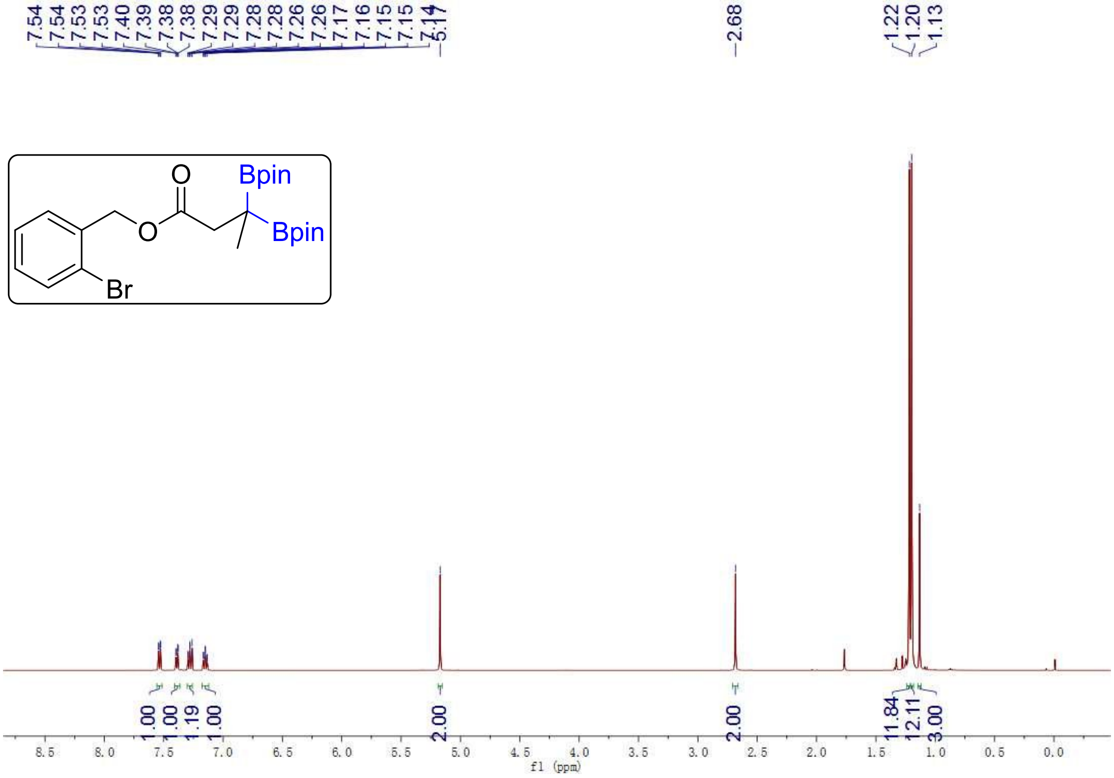


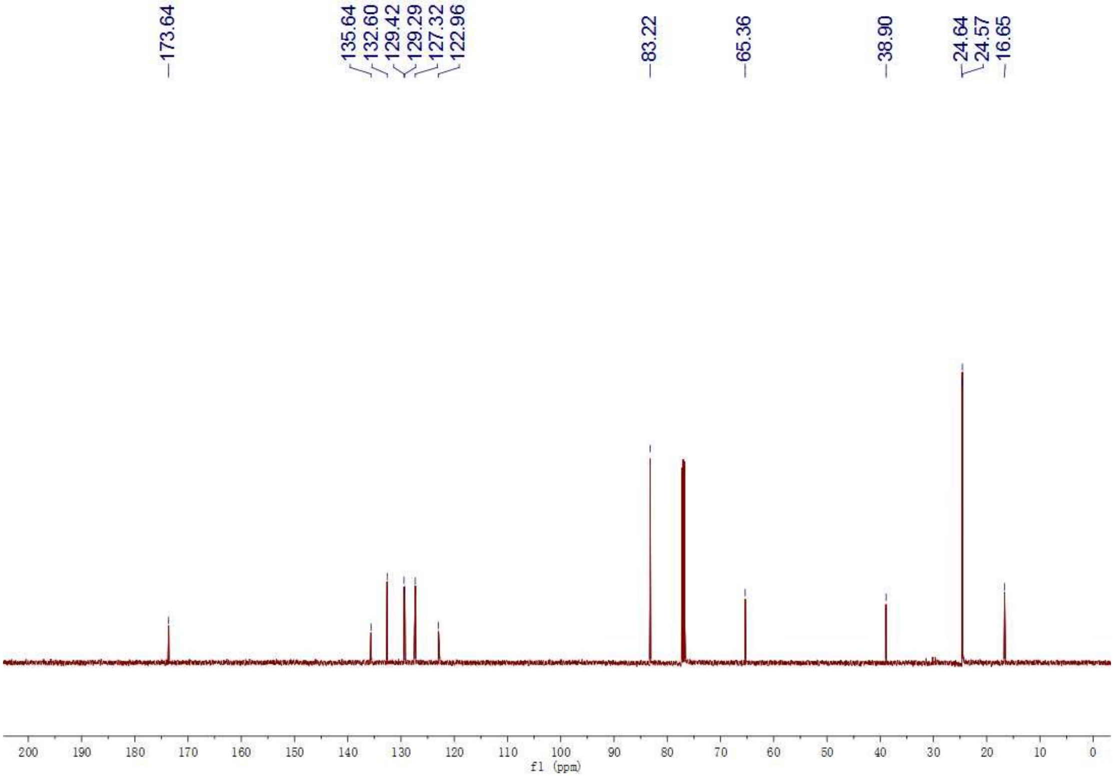
Benzyl 3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3g)



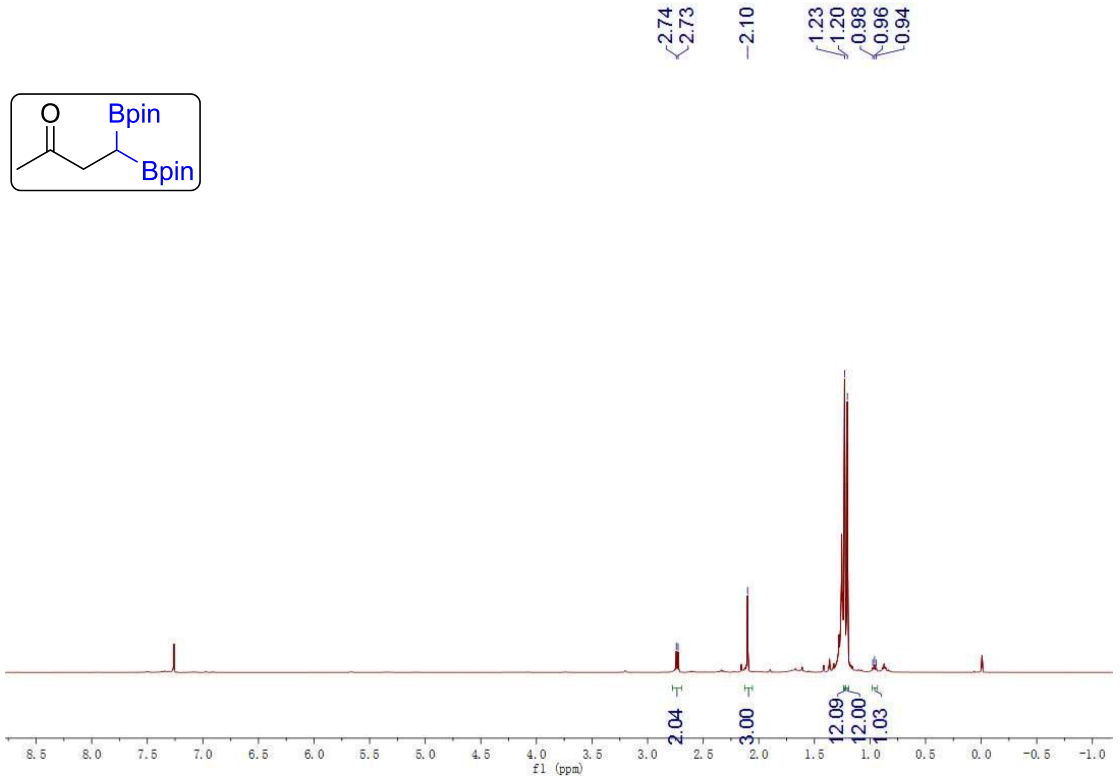


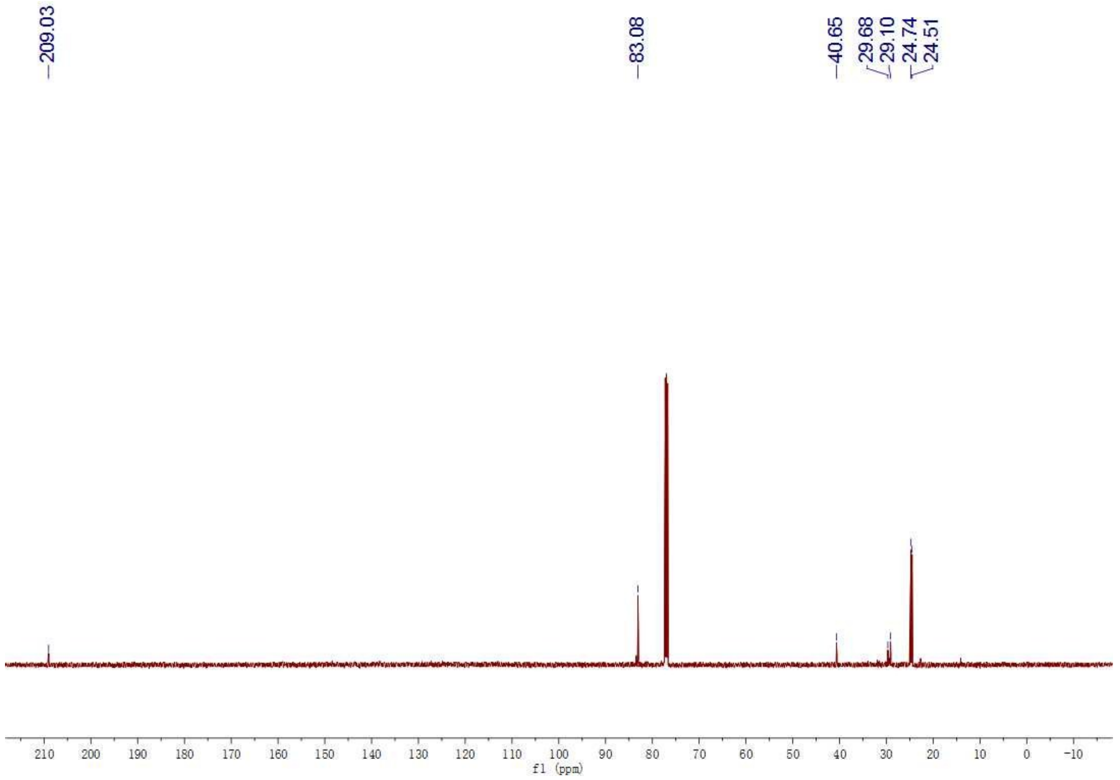
2-Bromobenzyl3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (3h)



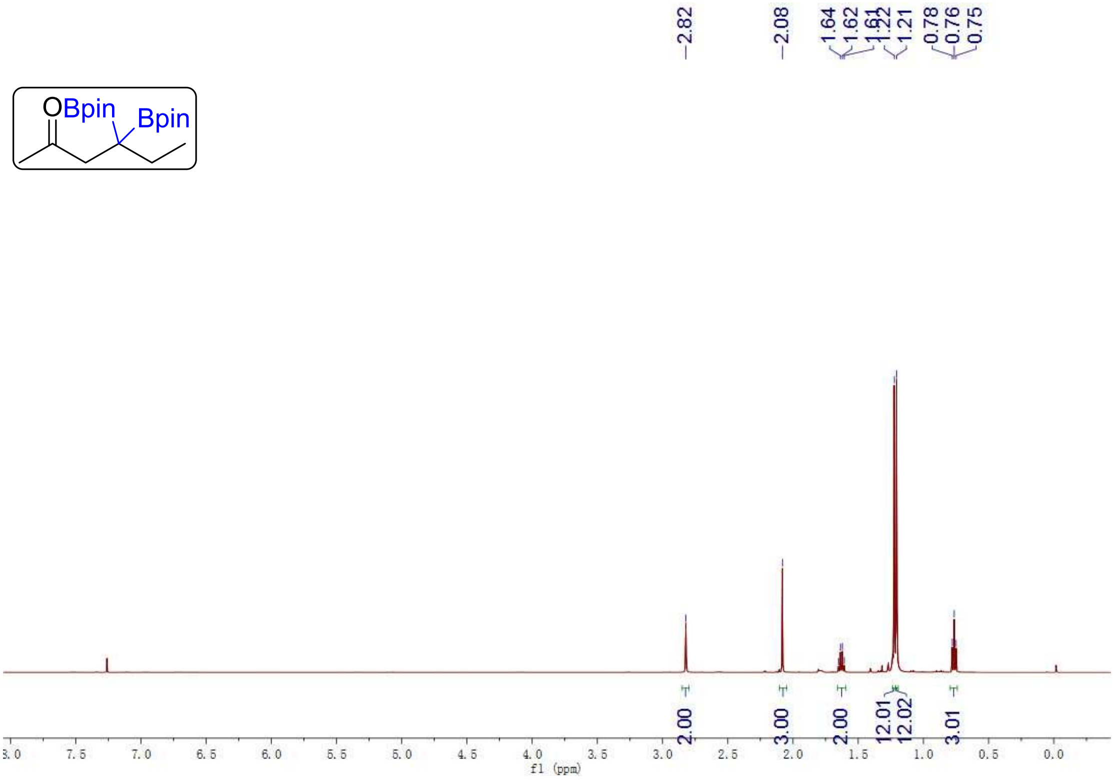


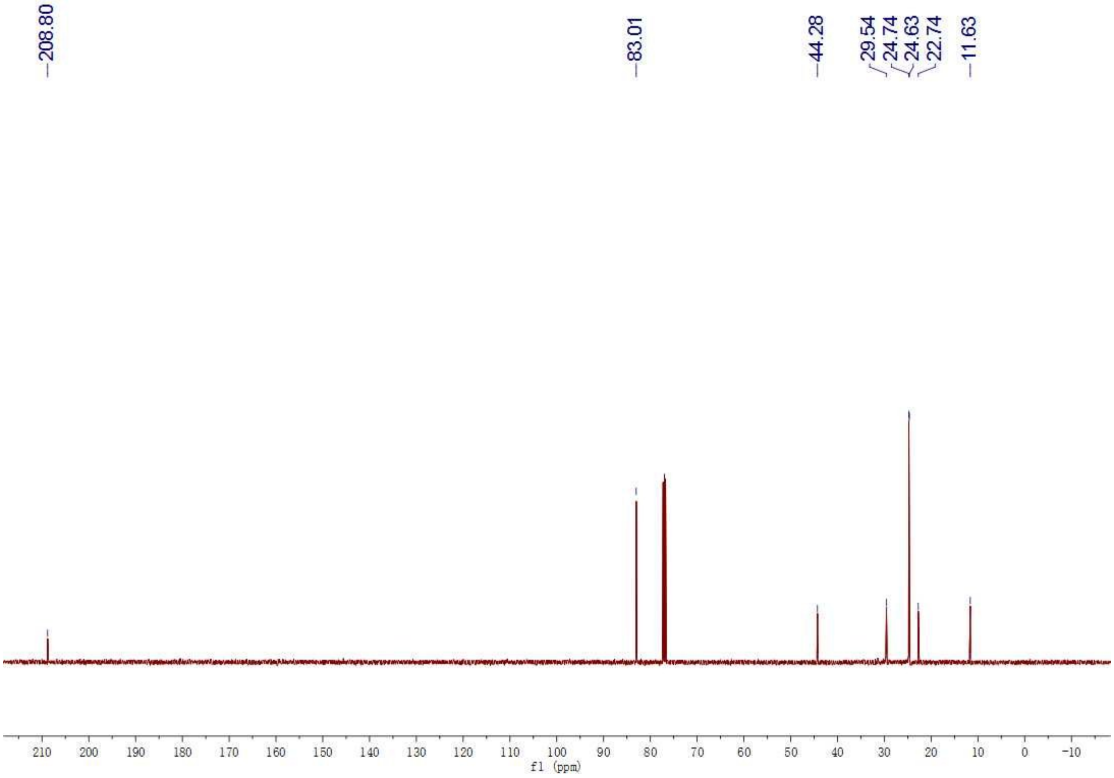
4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one (3i)



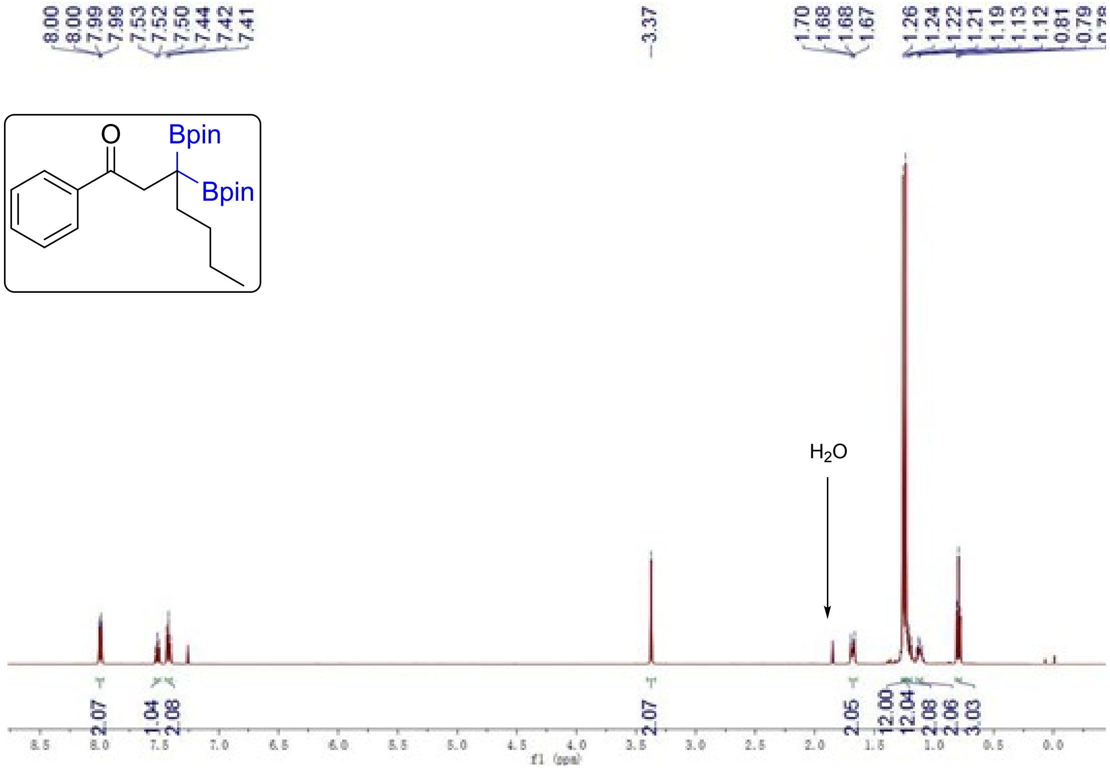


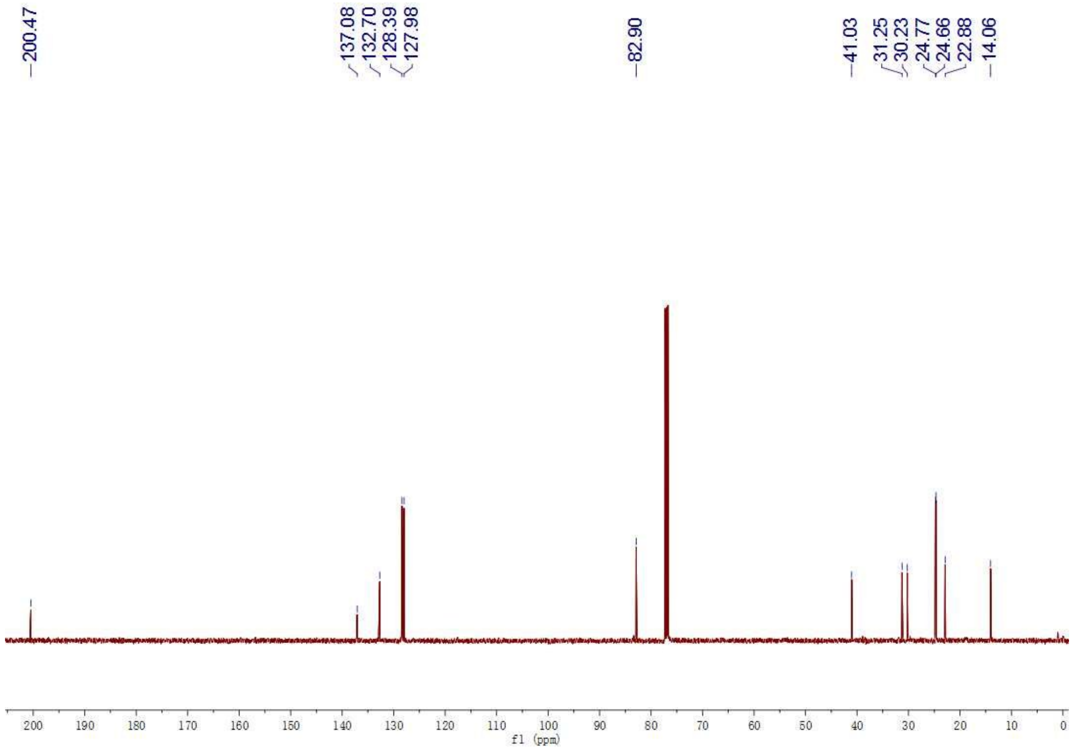
4,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-one (3j)



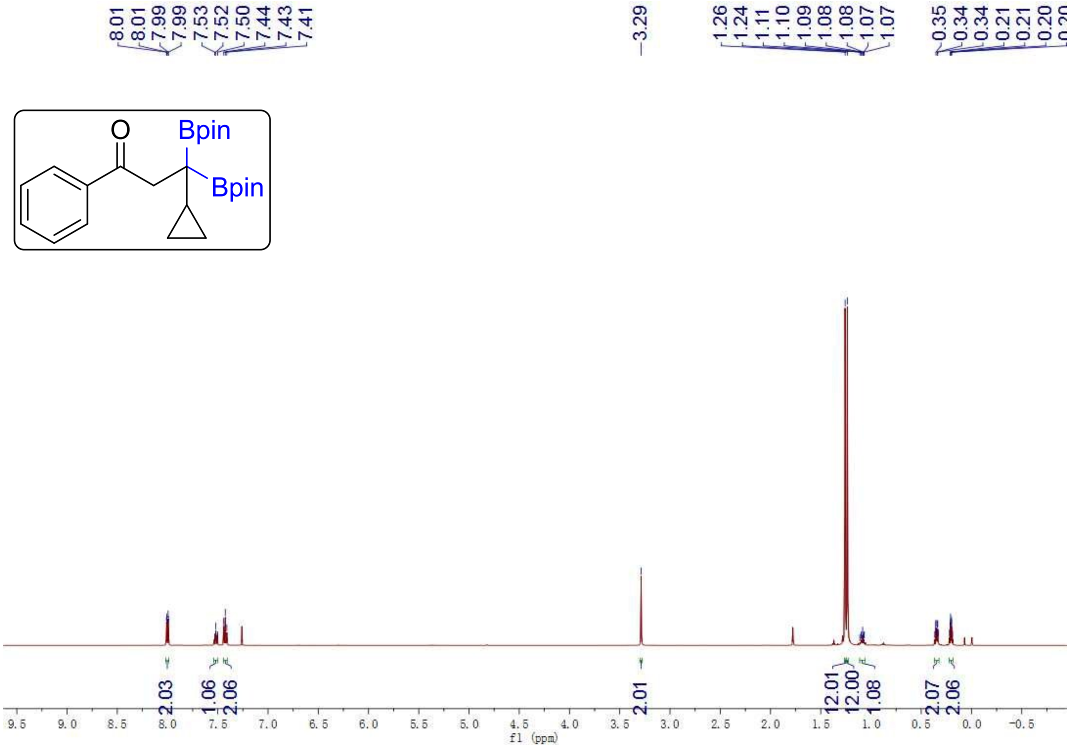


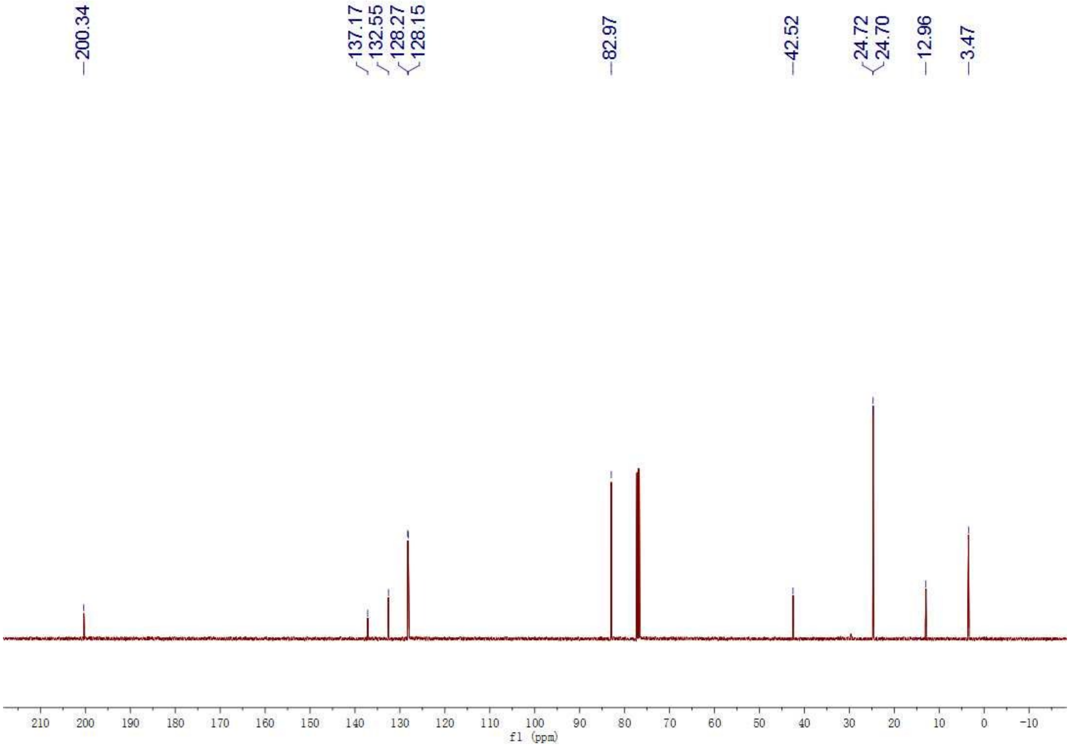
1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (3k)



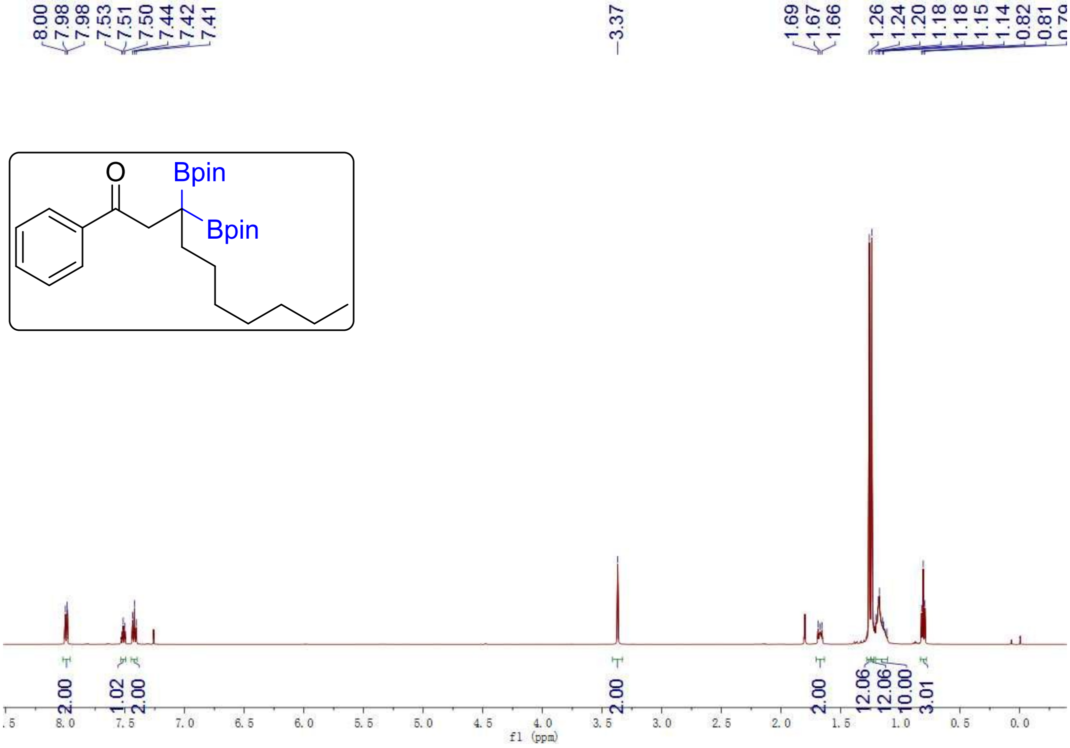


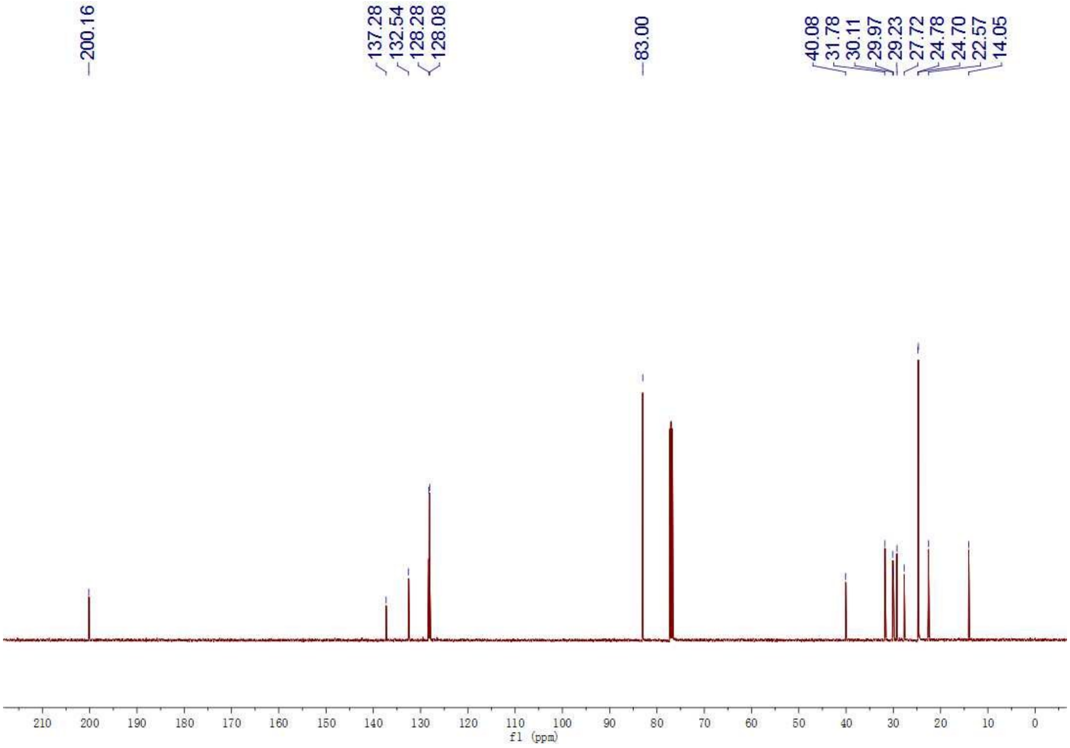
3-Cyclopropyl-1-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3l)



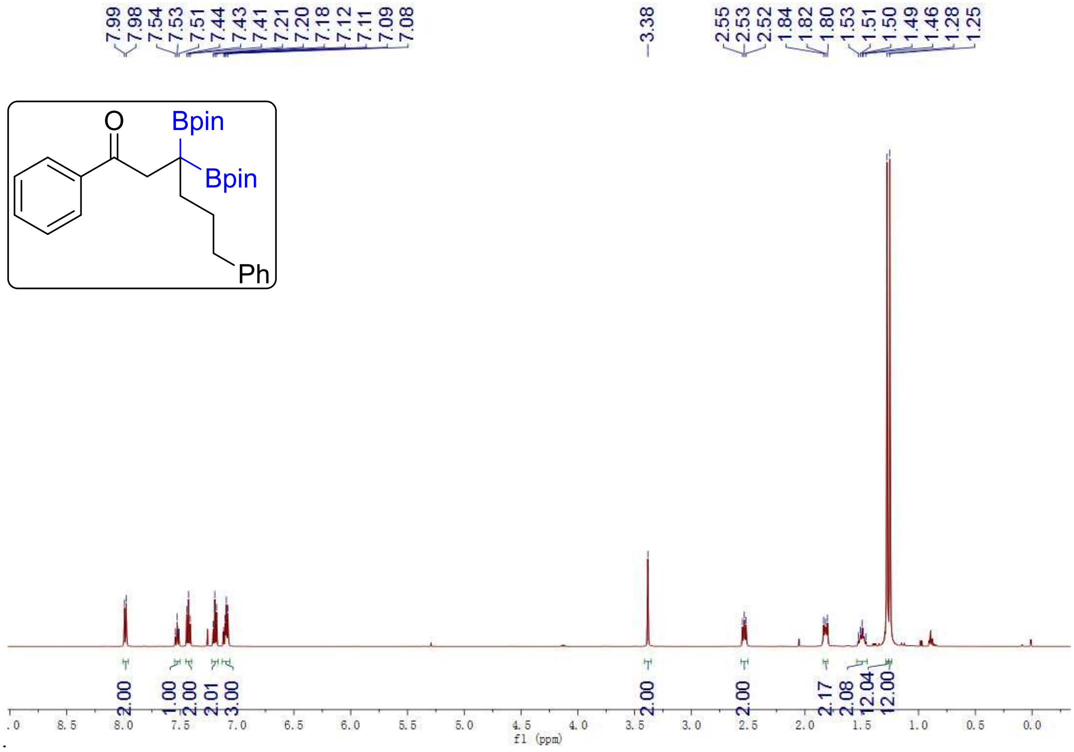


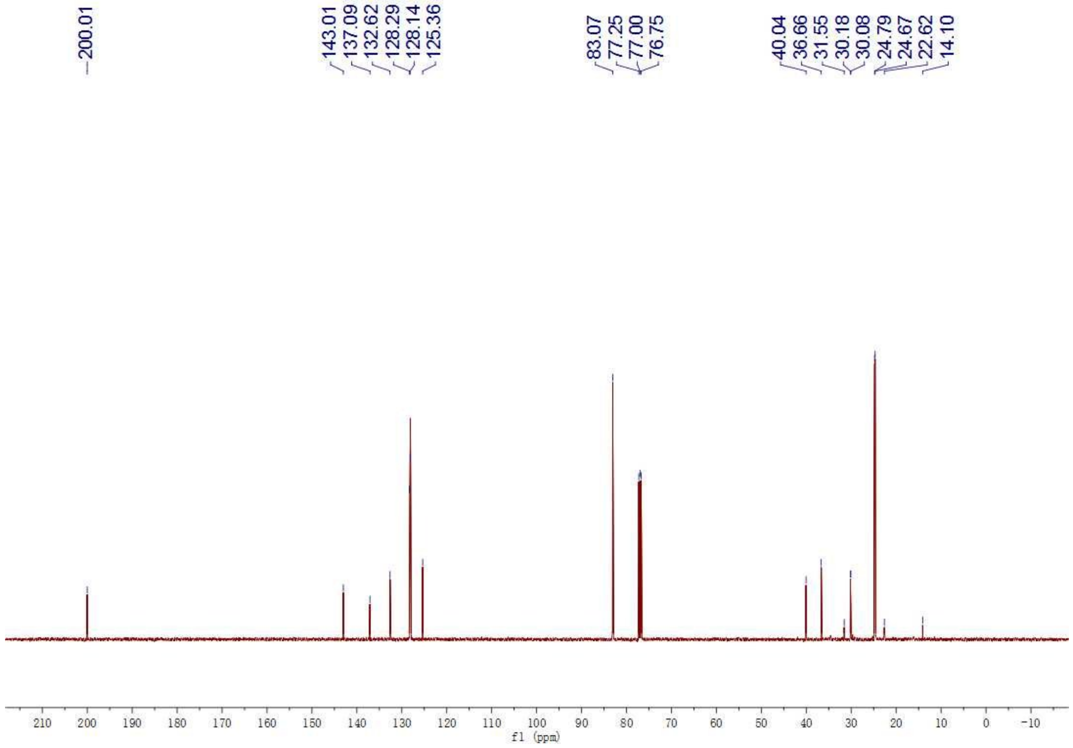
1-Phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one (3m)



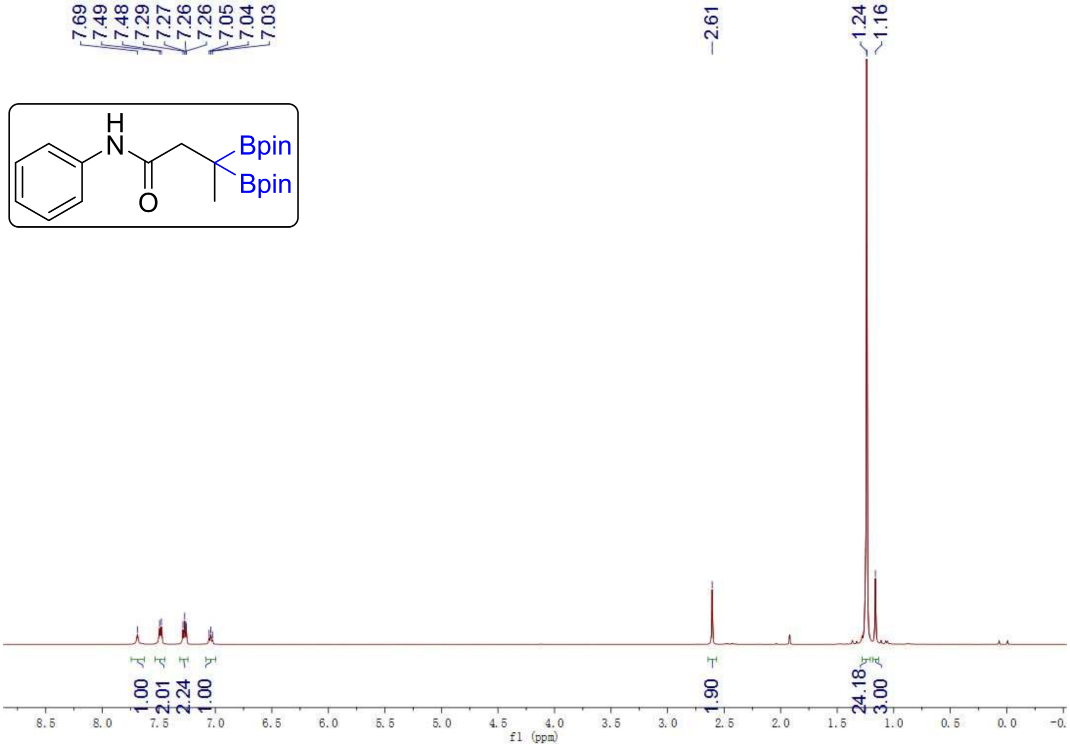


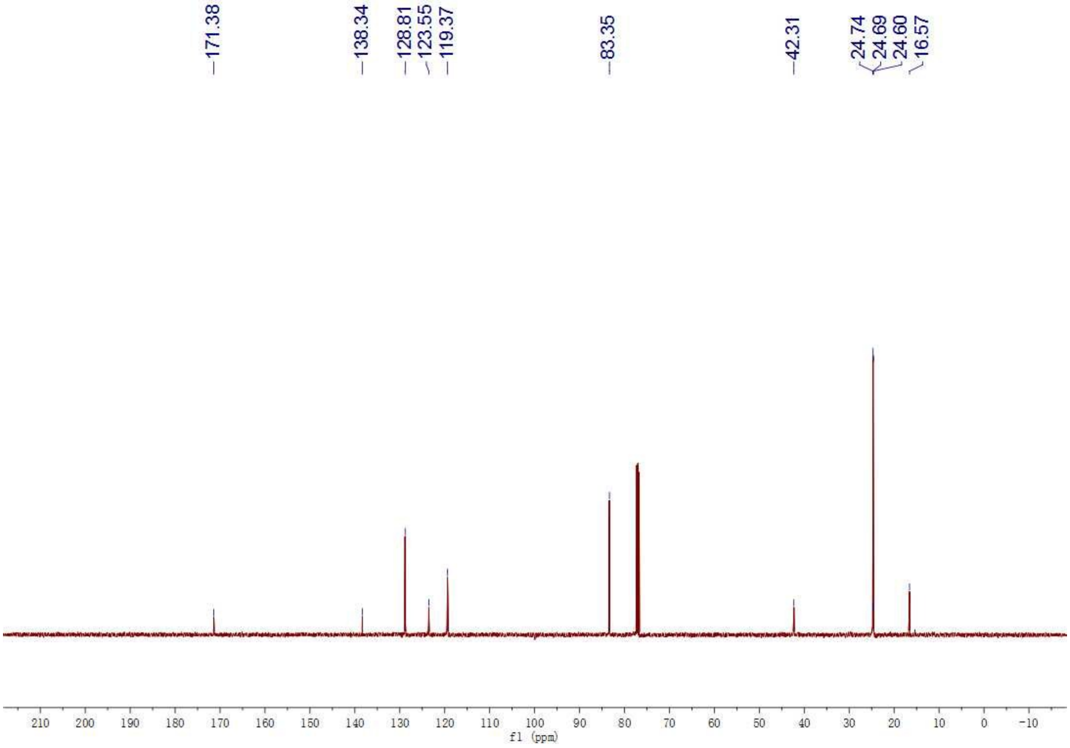
1,6-Diphenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3n)



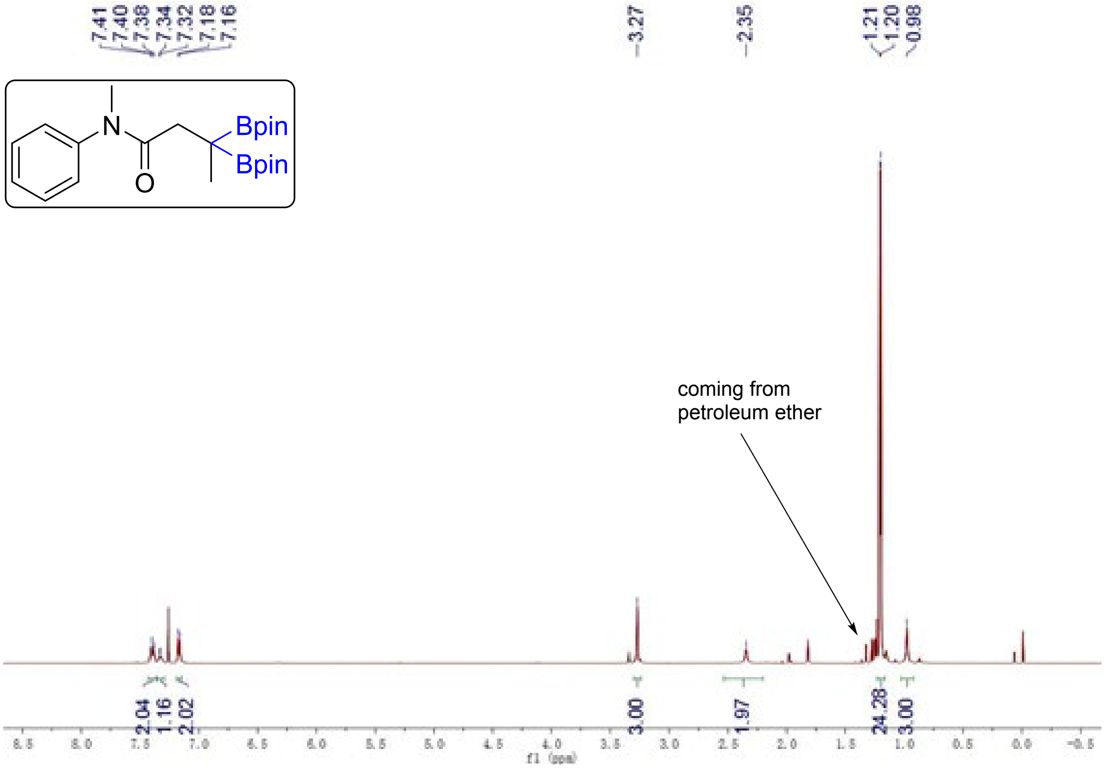


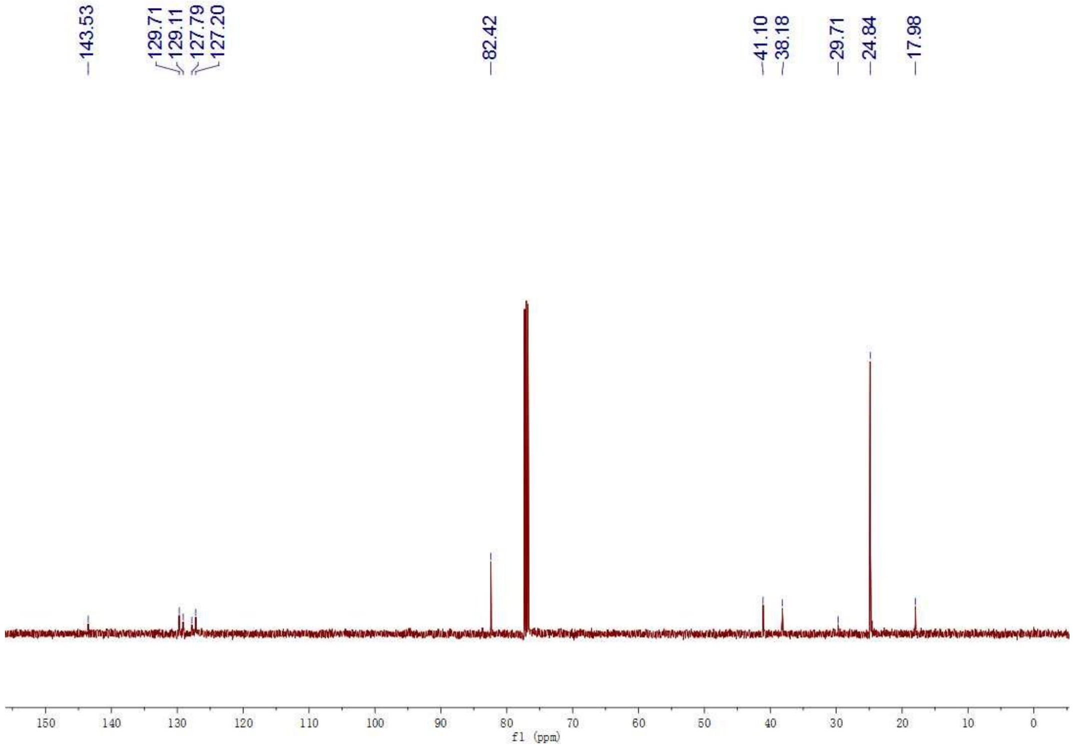
N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3o)



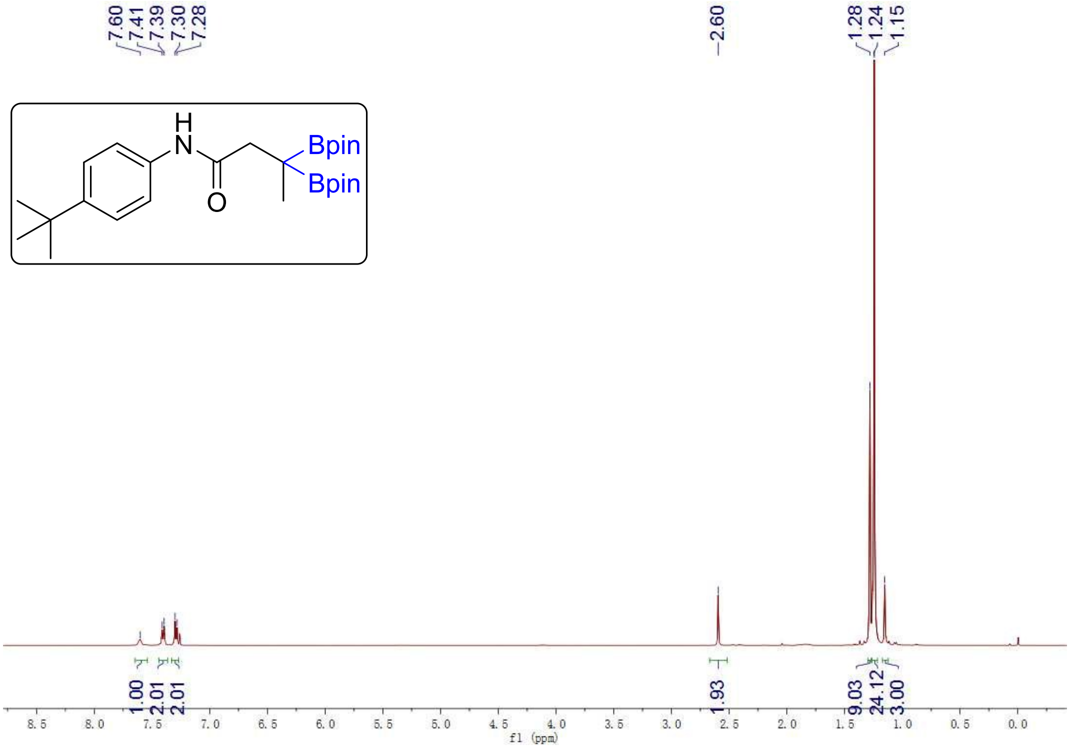


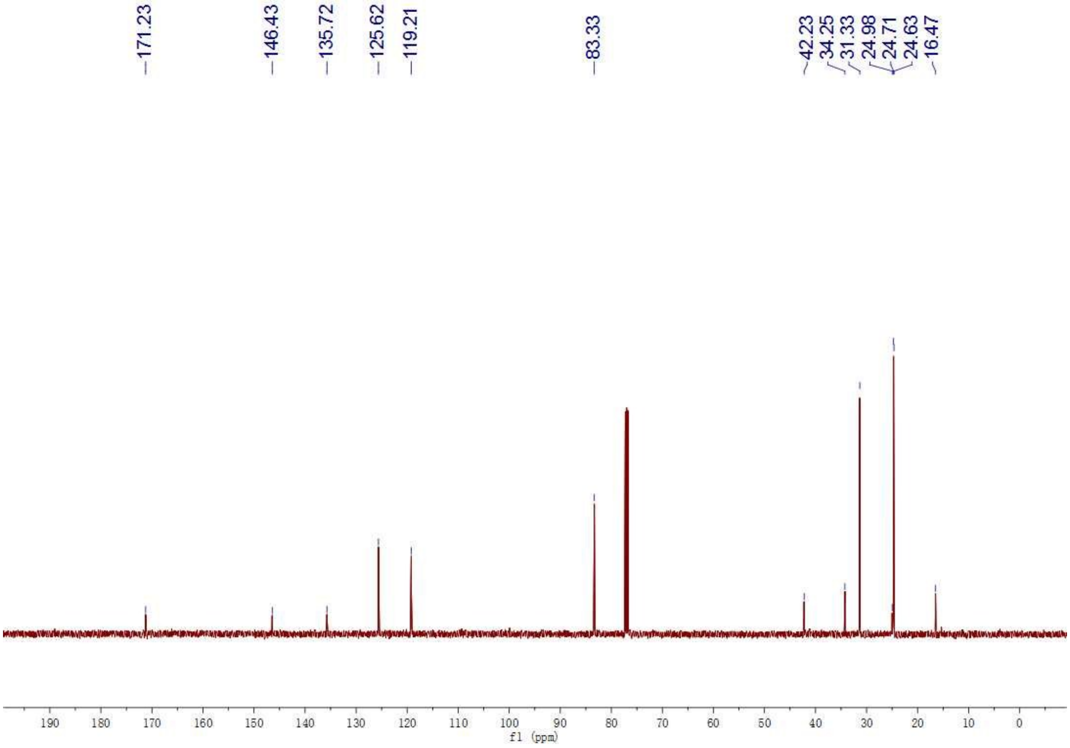
N-methyl-N-phenyl-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3p)



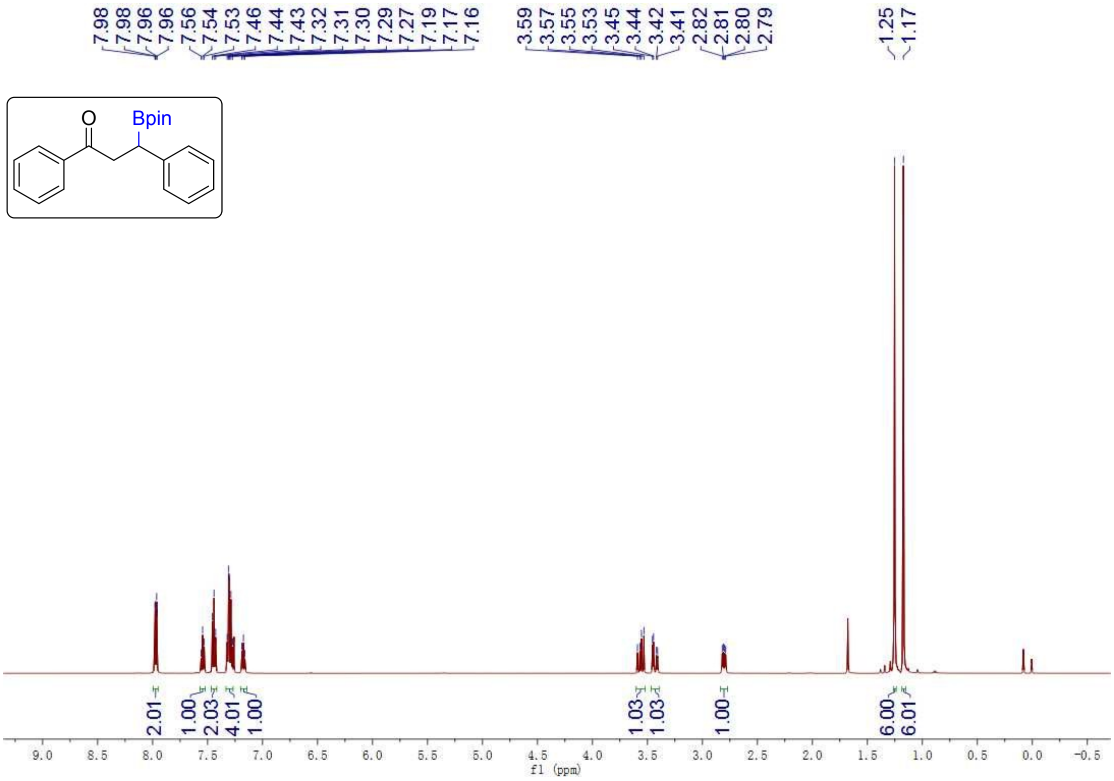


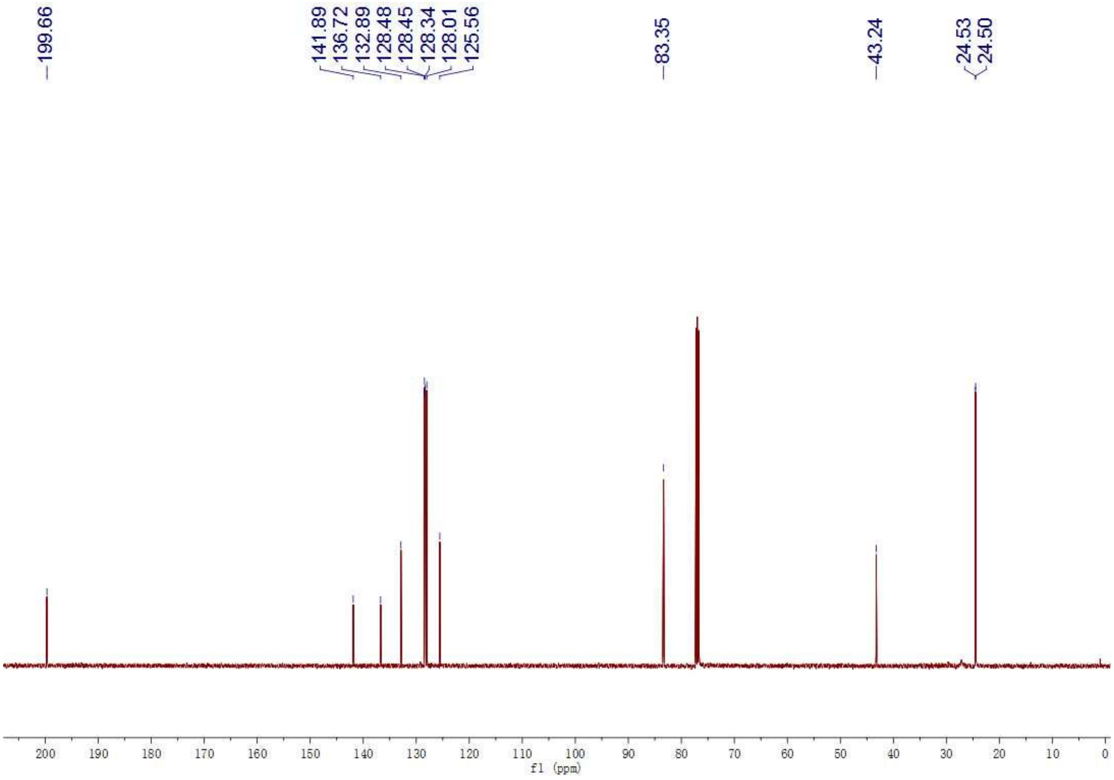
N-(4-(tert-butyl)phenyl)-3,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide (3q)



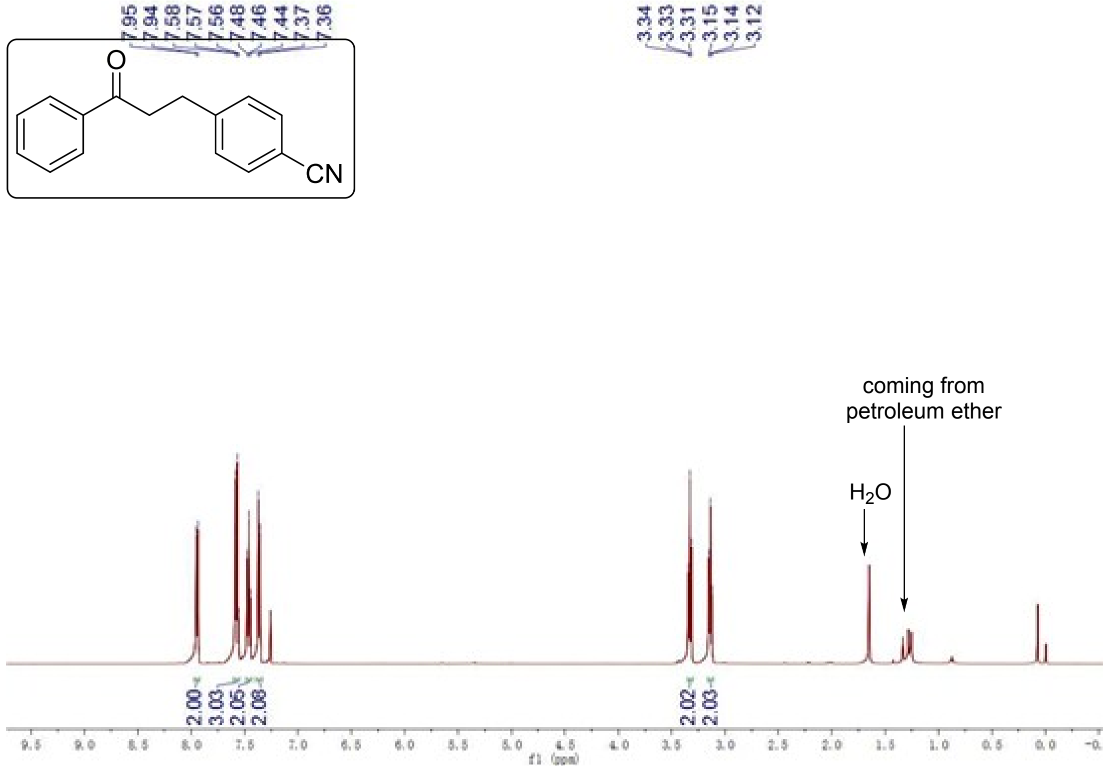


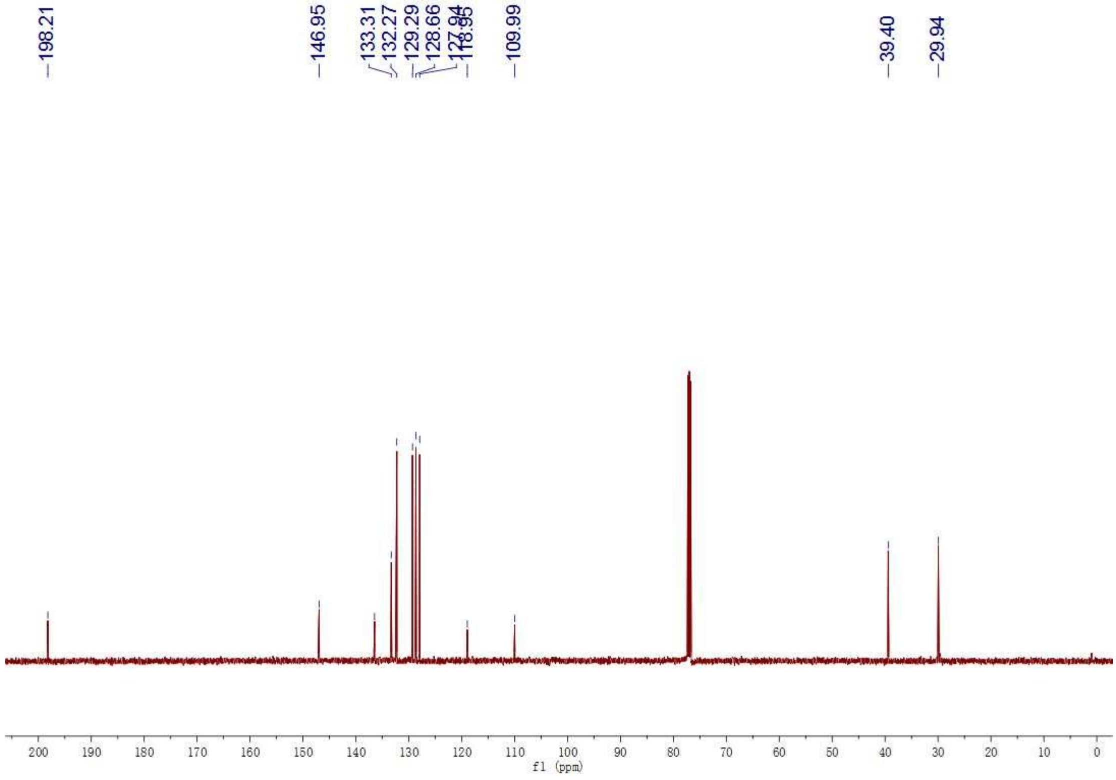
1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (3r)



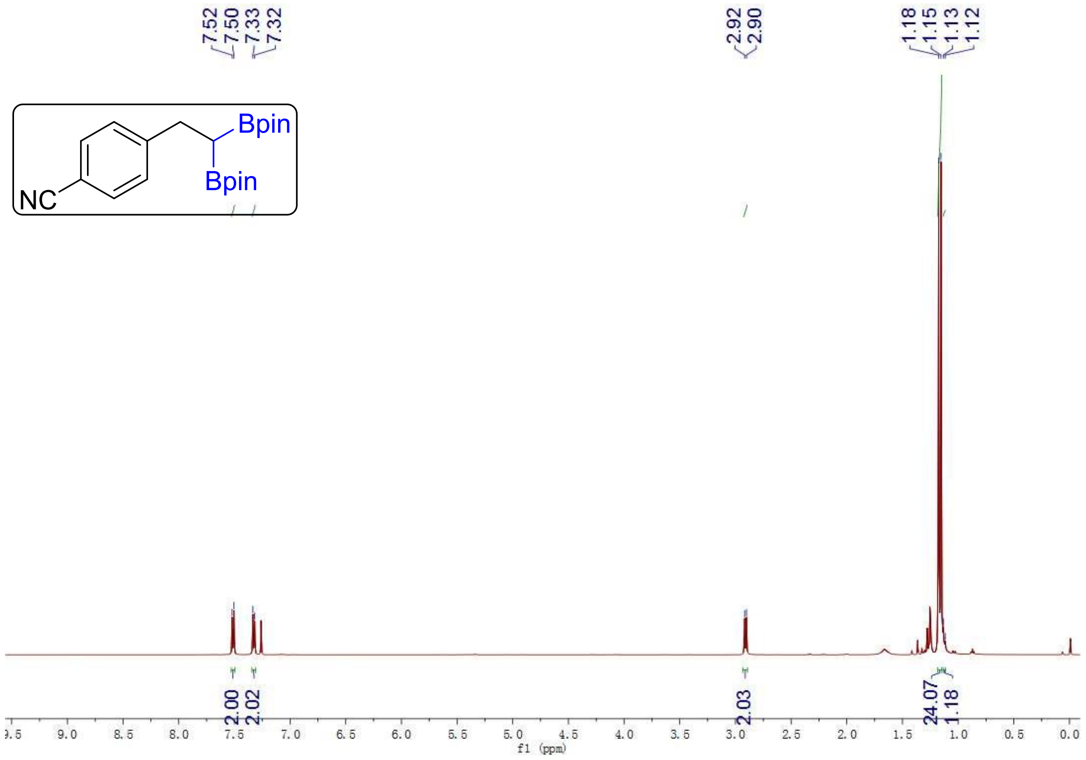


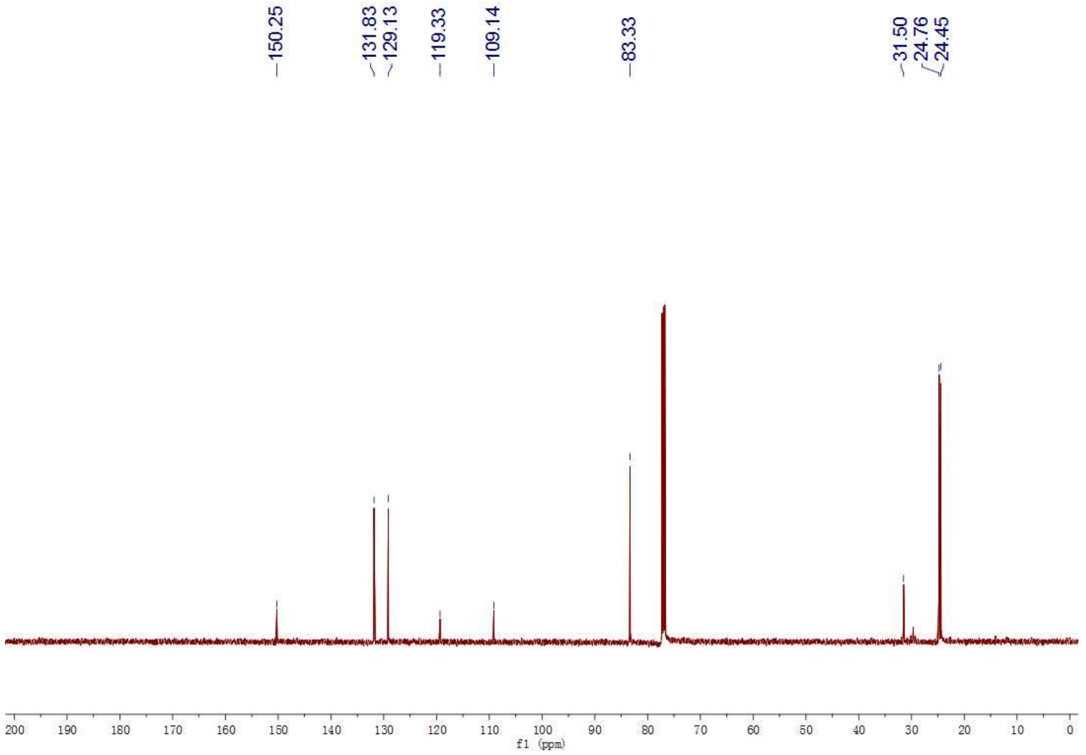
4-(3-oxo-3-phenylpropyl)benzonitrile (3s)



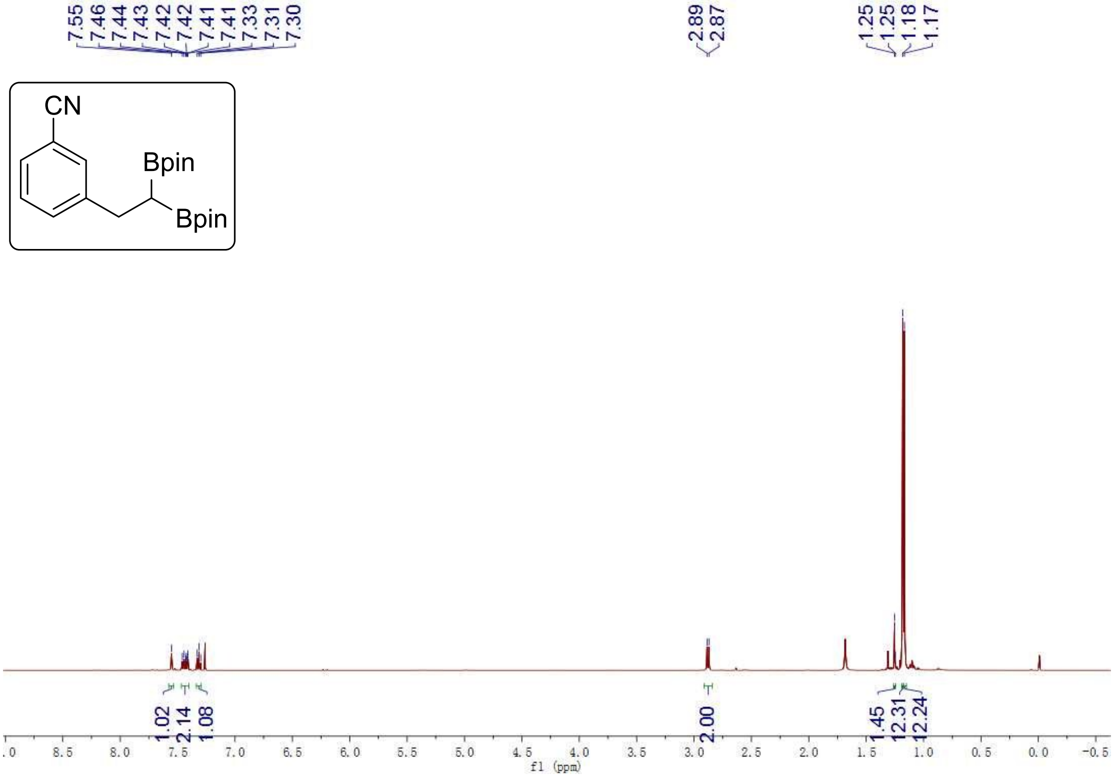


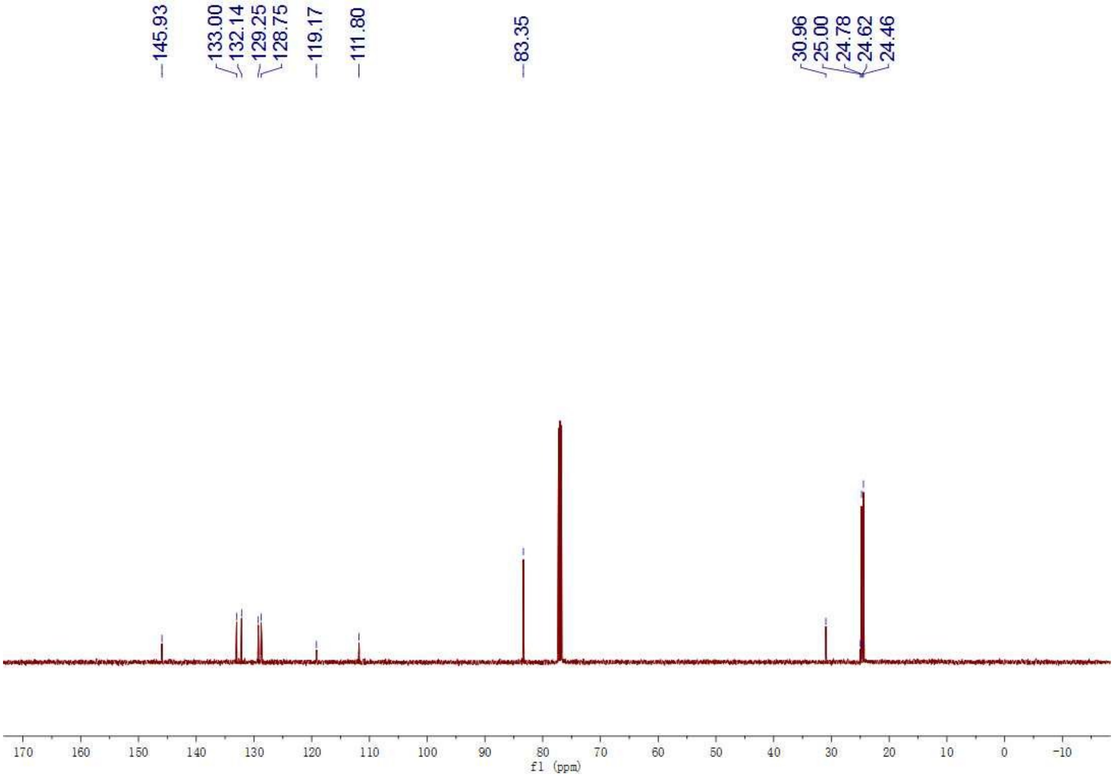
4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6a-*para*)



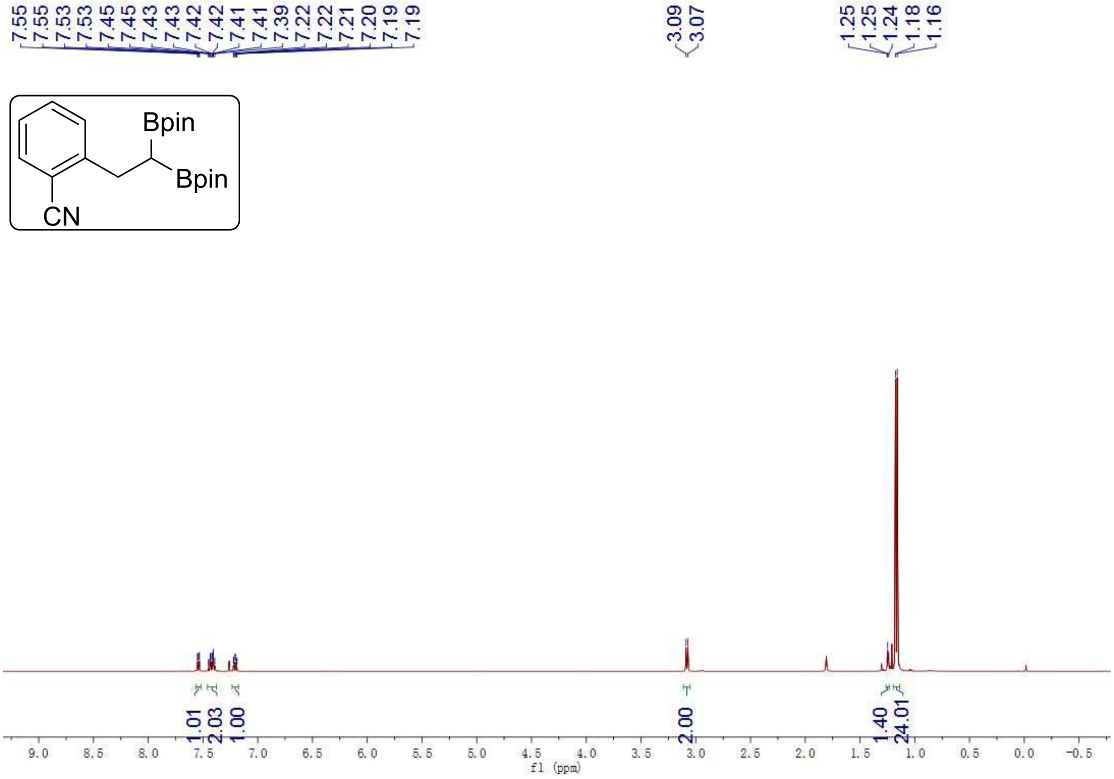


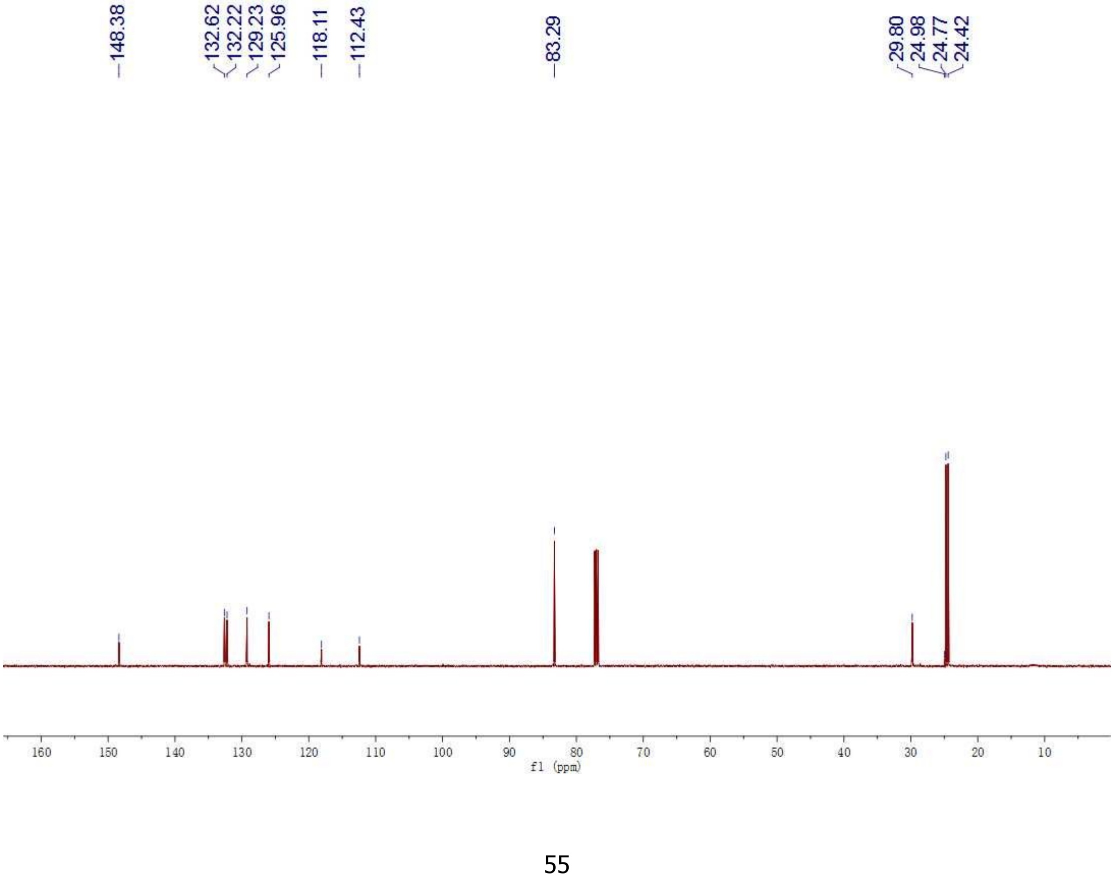
3-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6-*meta)*



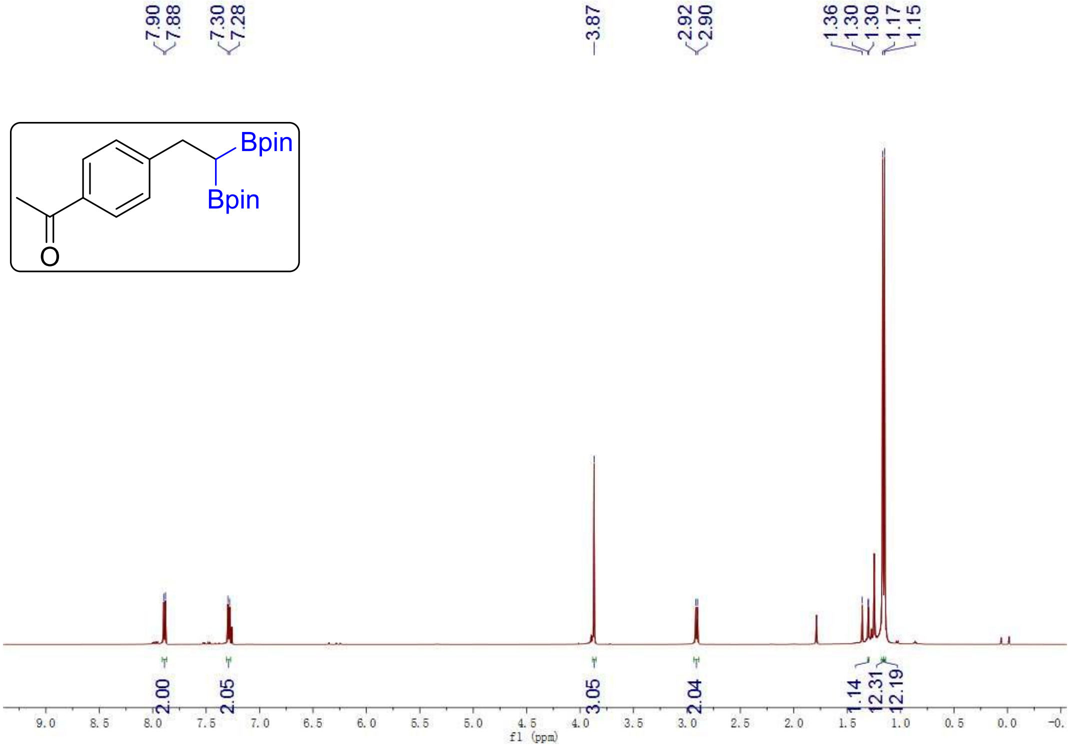


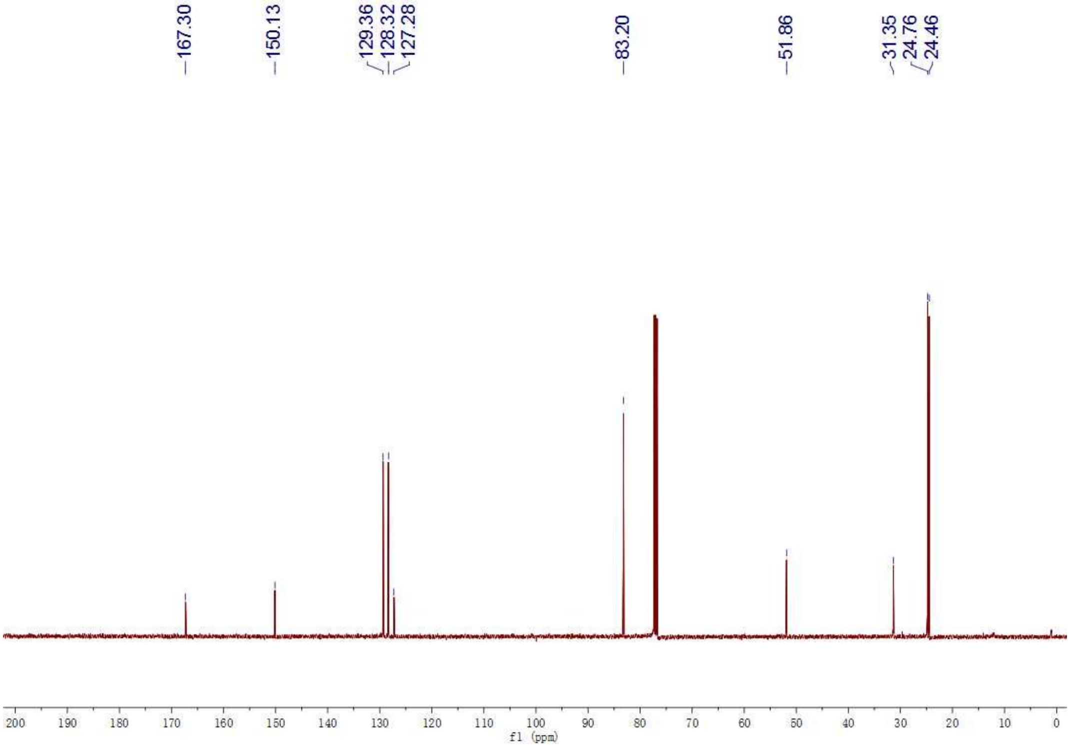
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6-*ortho*)



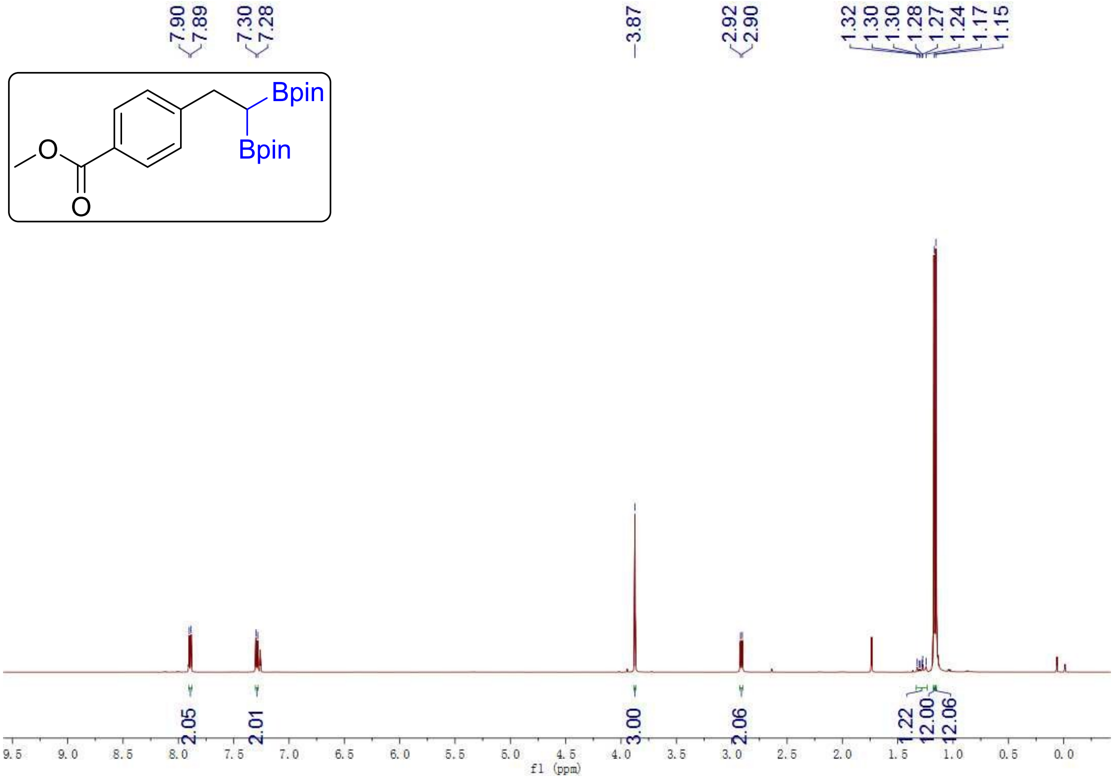


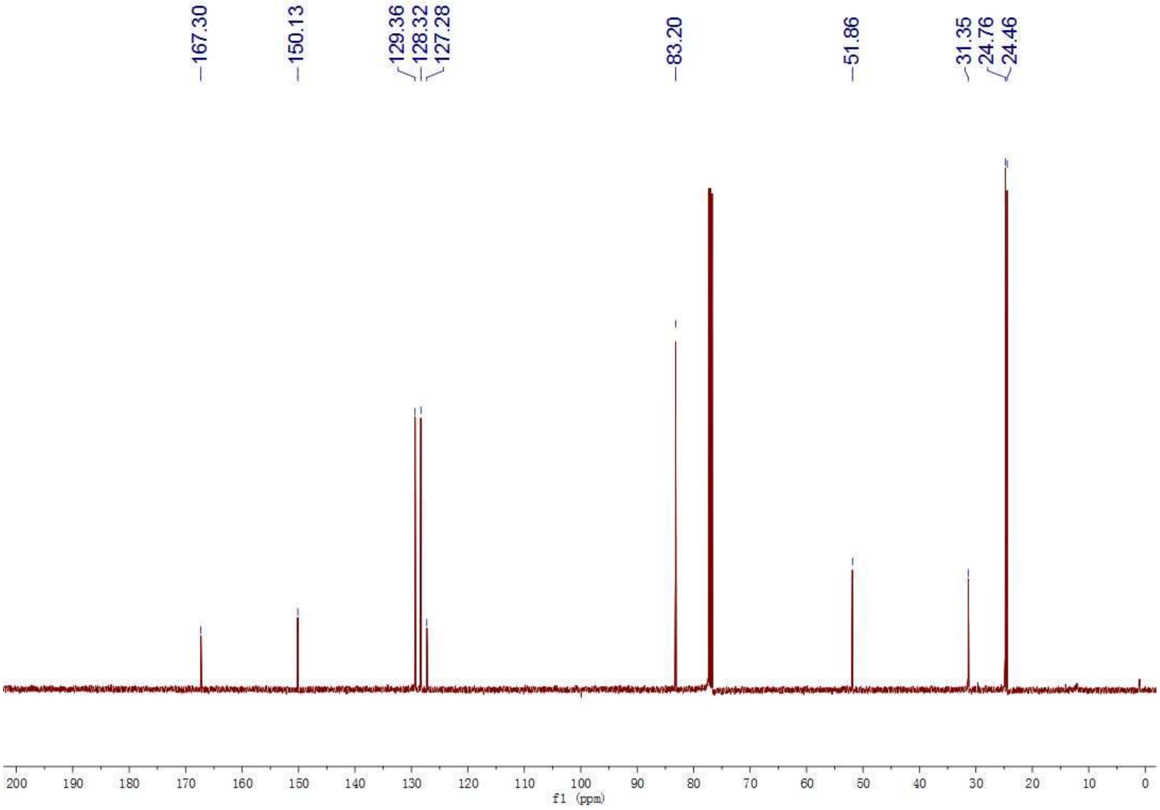
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)phenyl)ethan-1-one (6b)



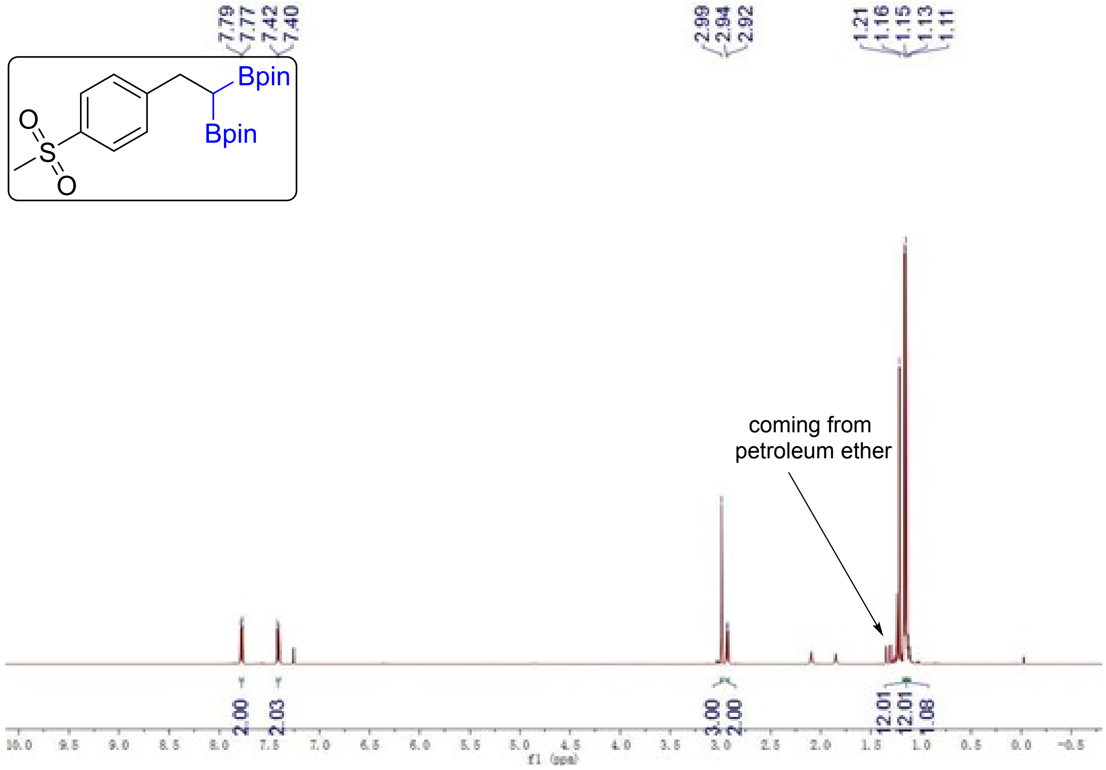


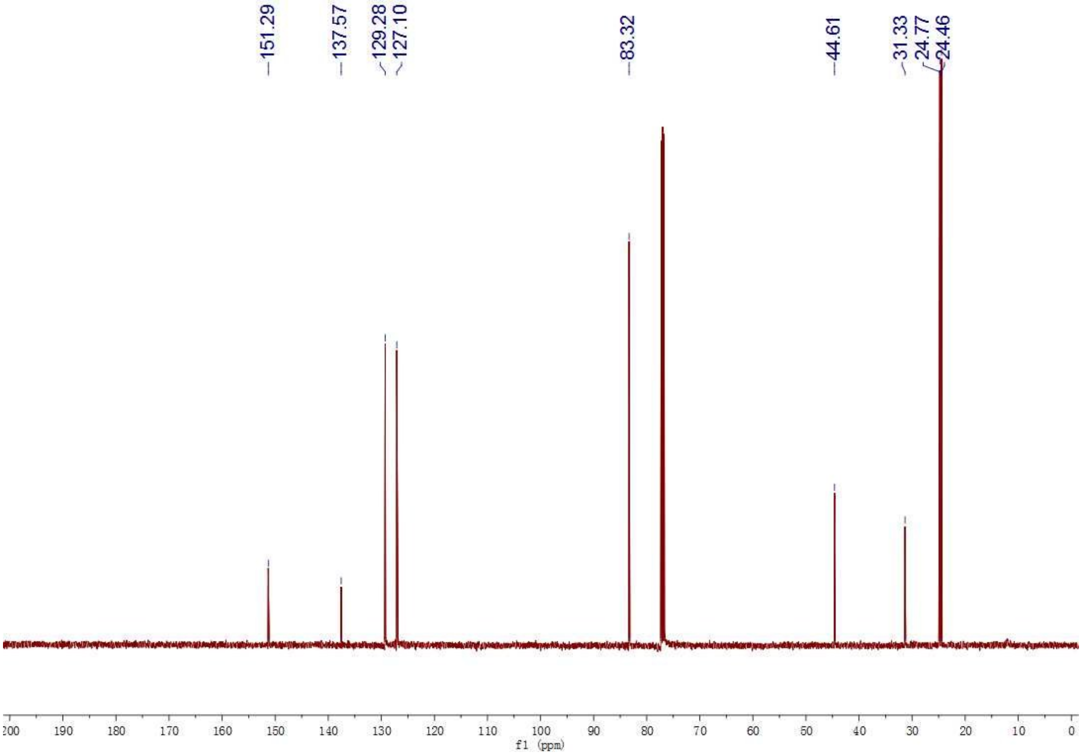
Methyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6c)



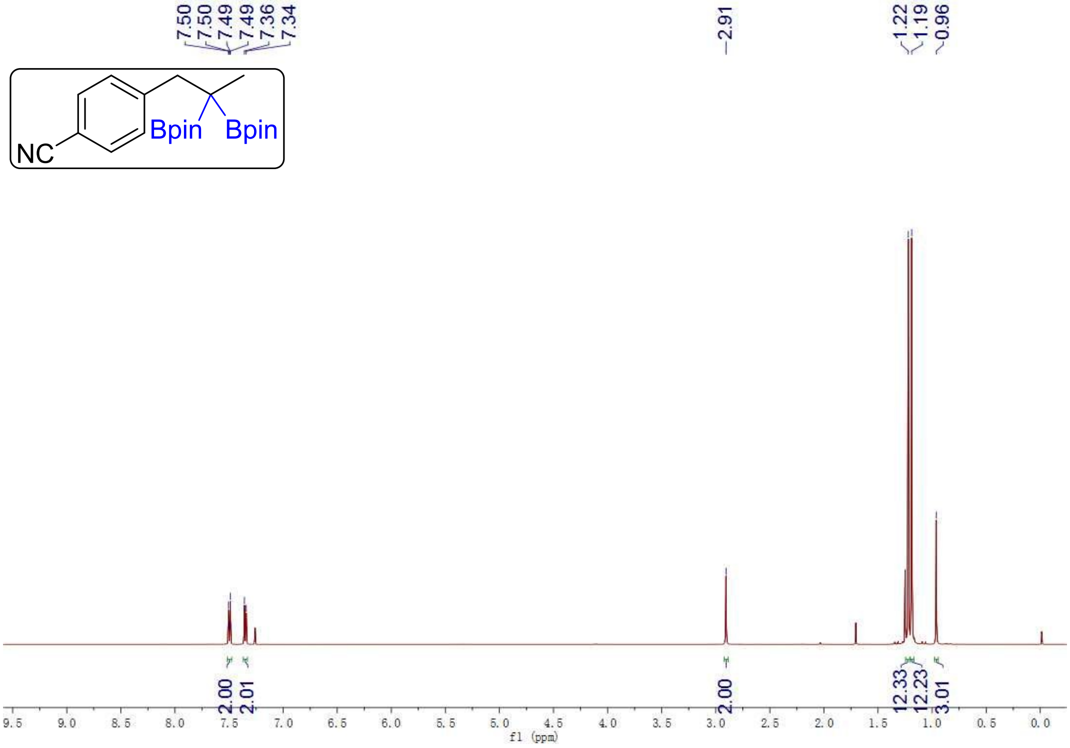


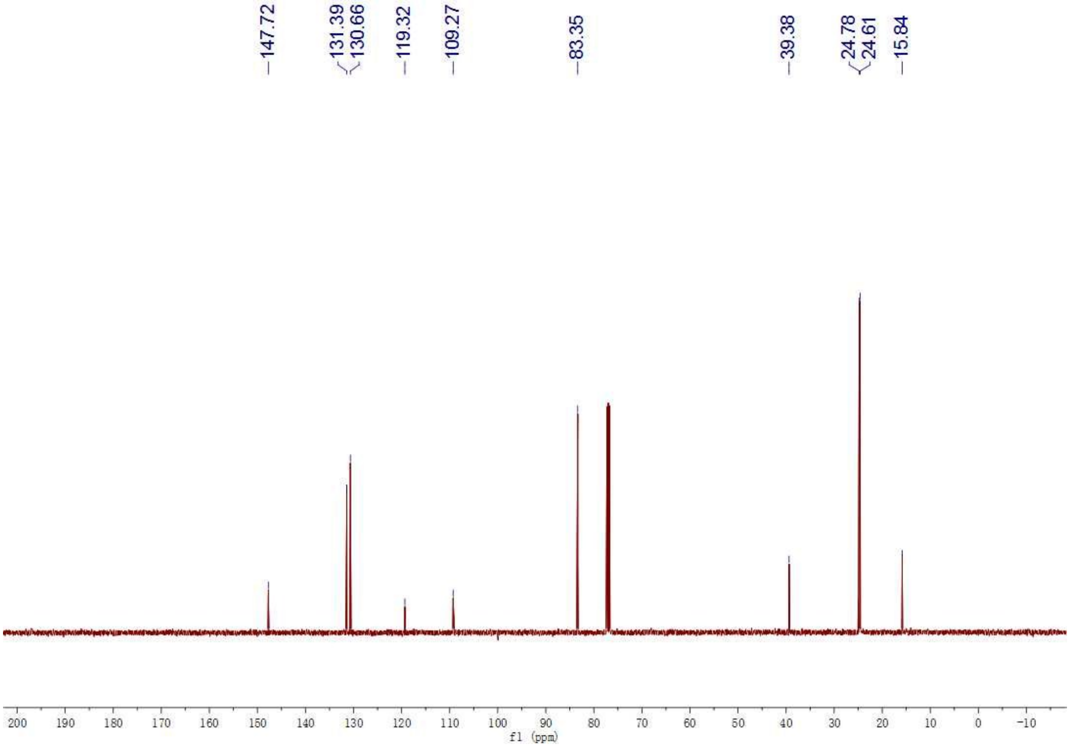
2,2'-(2-(4-(Methylsulfonyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6d)



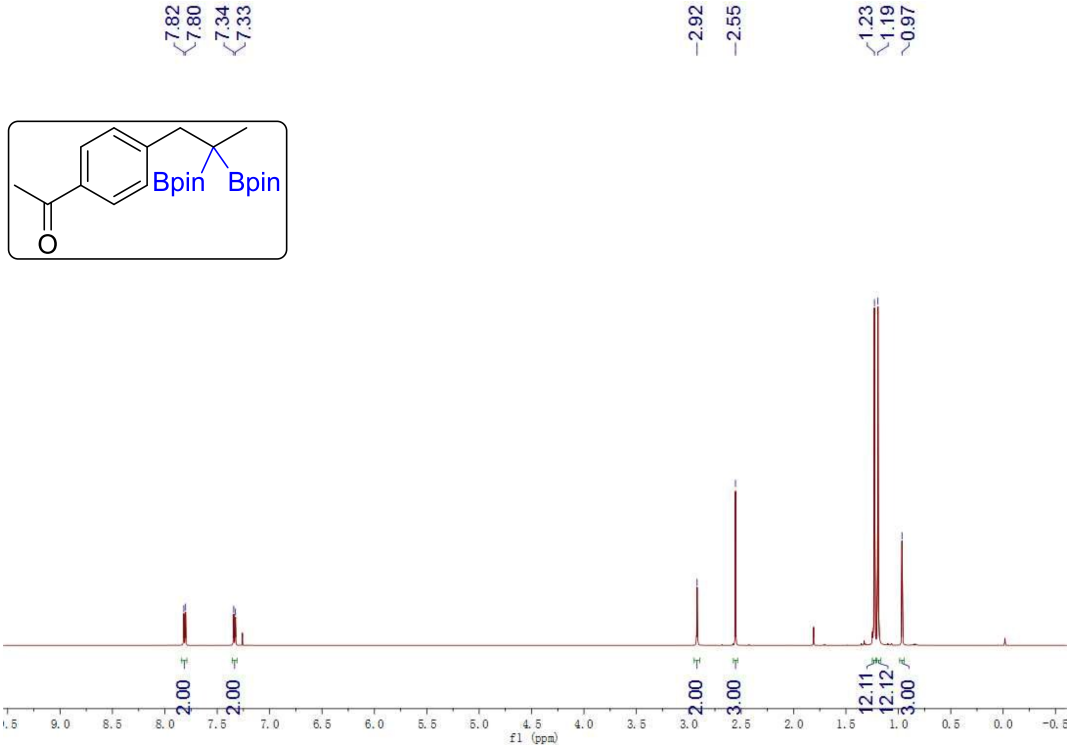


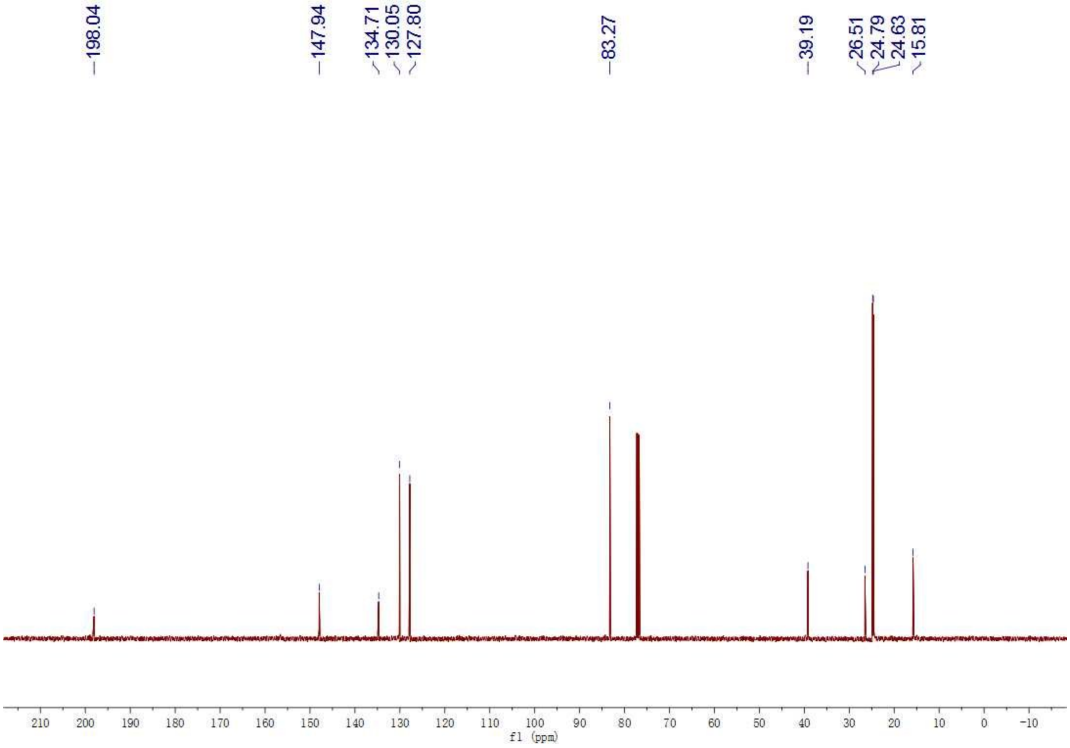
4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzonitrile (6e)



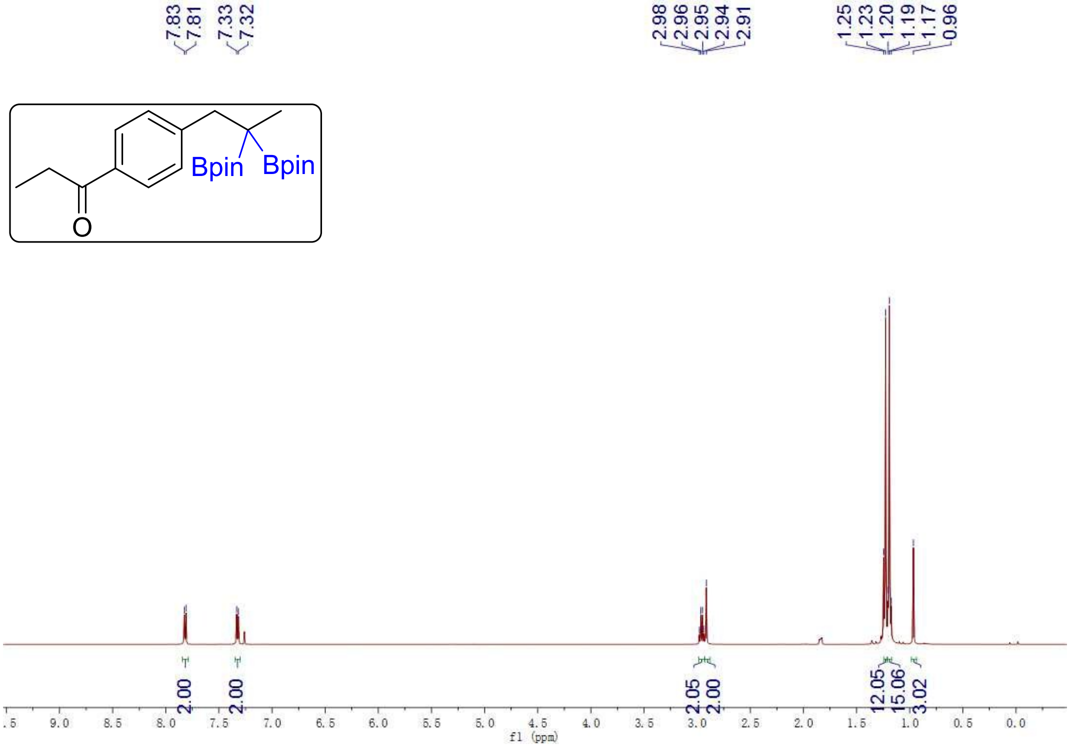


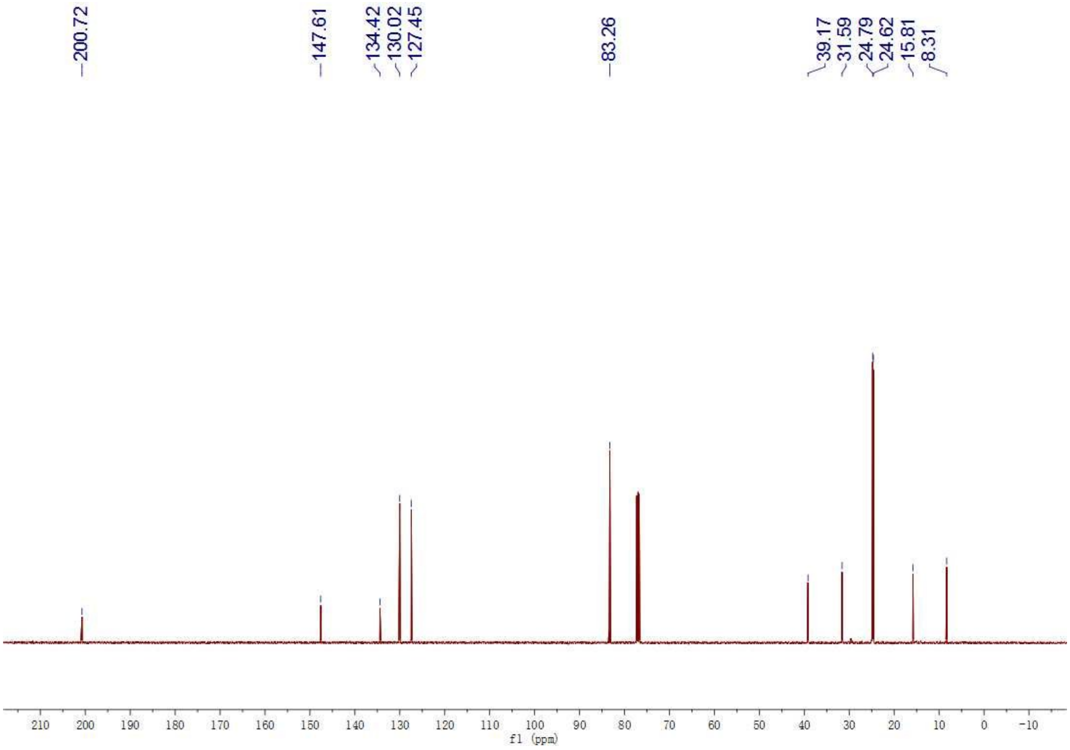
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)ethan-1-one (6f)



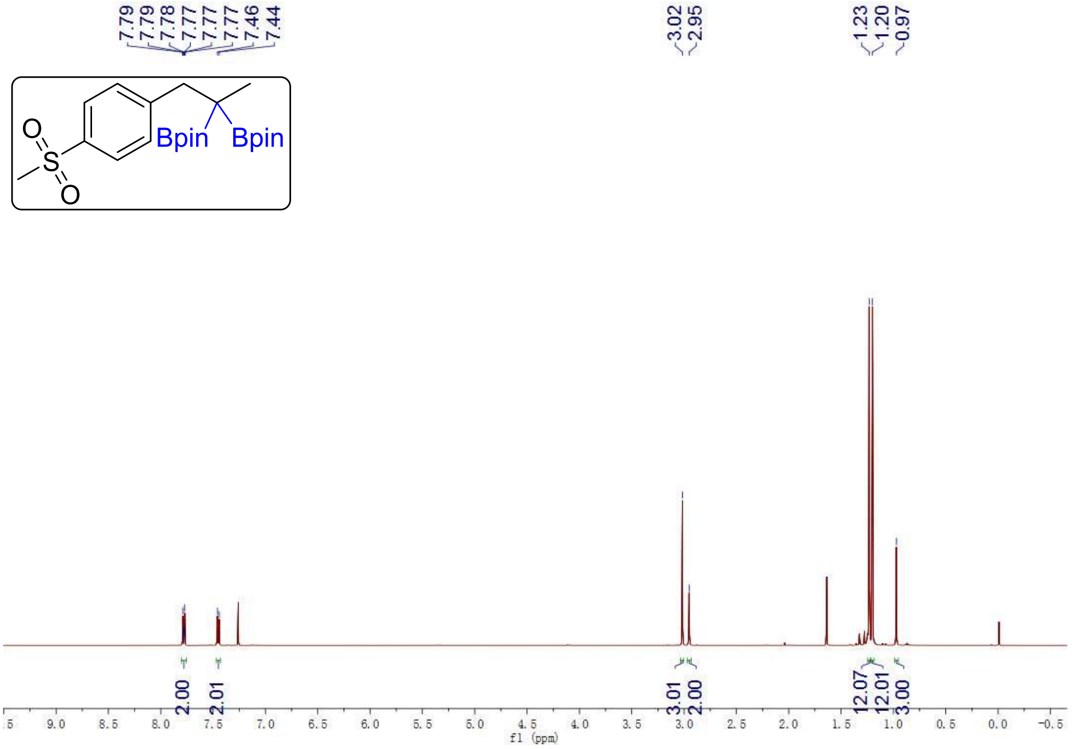


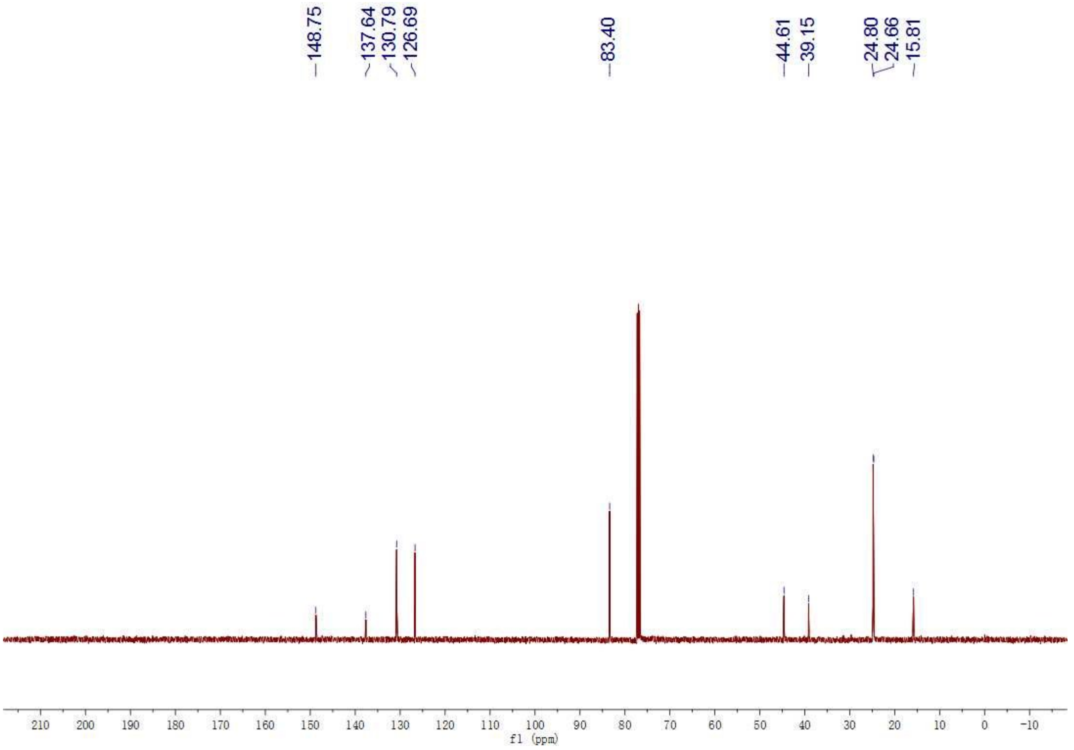
1-(4-(2,2-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)propan-1-one (6g)



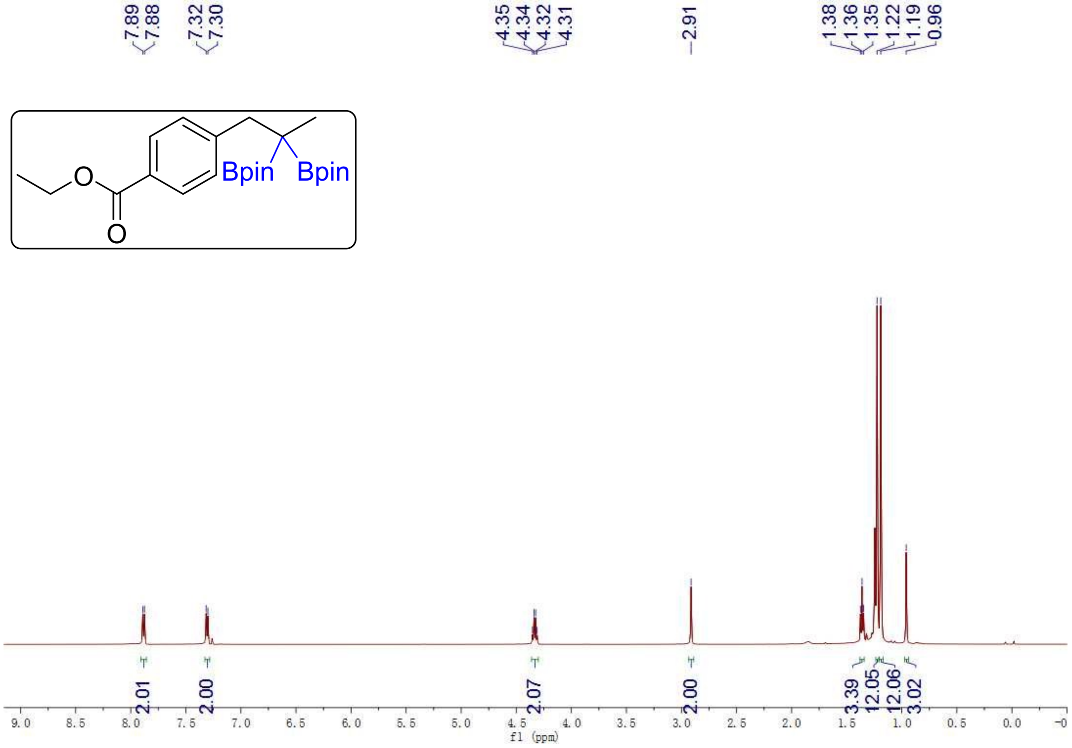


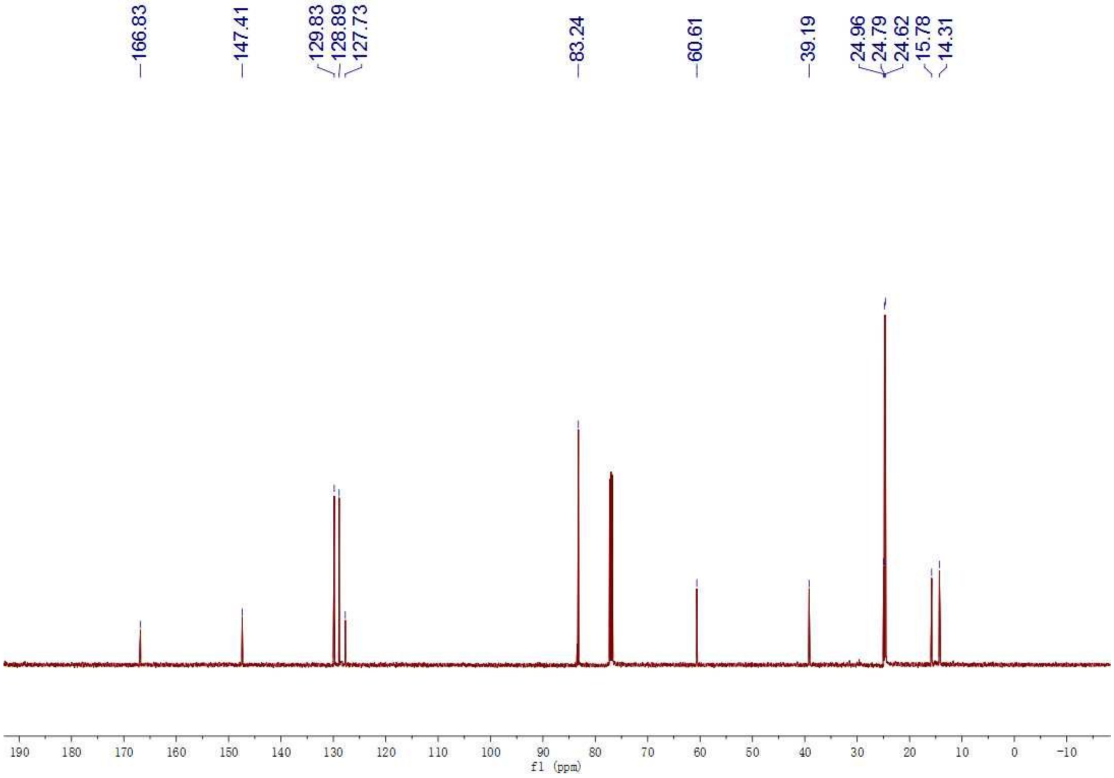
2,2'-(1-(4-(Methylsulfonyl)phenyl)propane-2,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (6h)



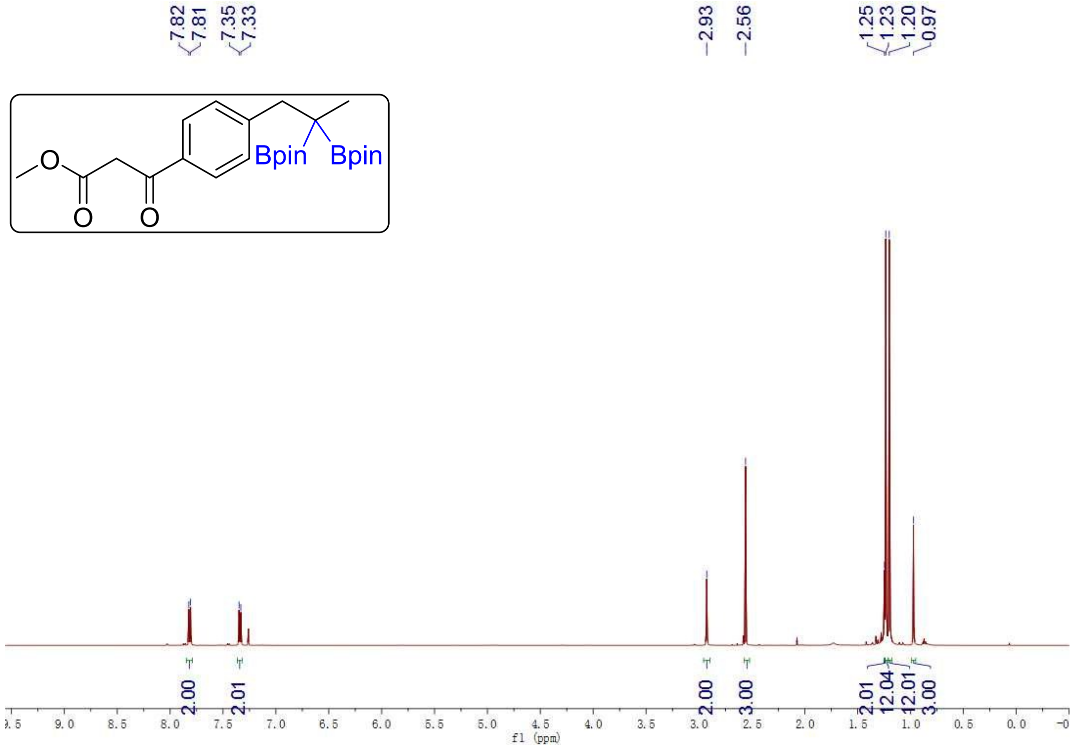


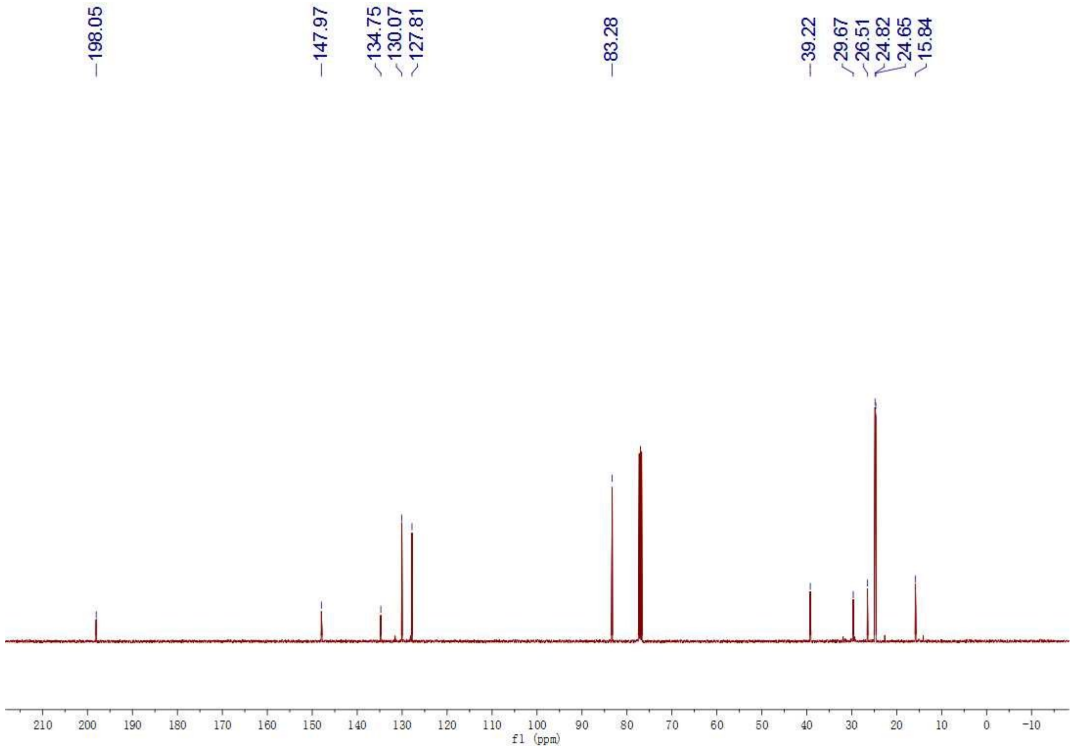
Ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6i)



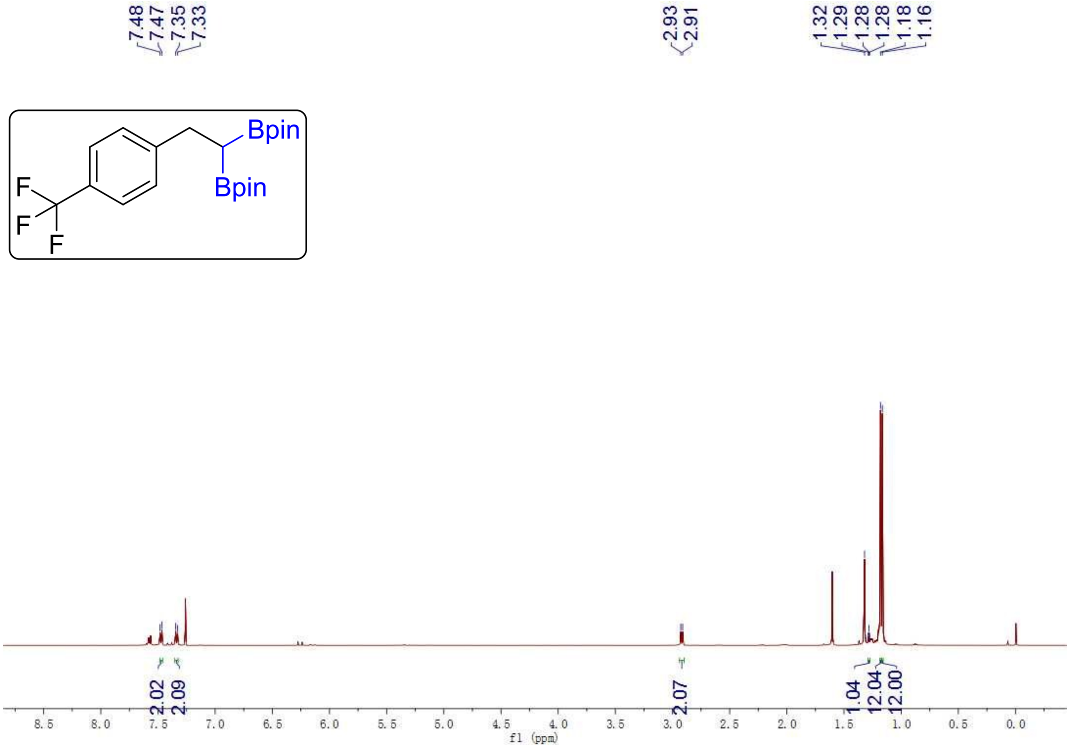


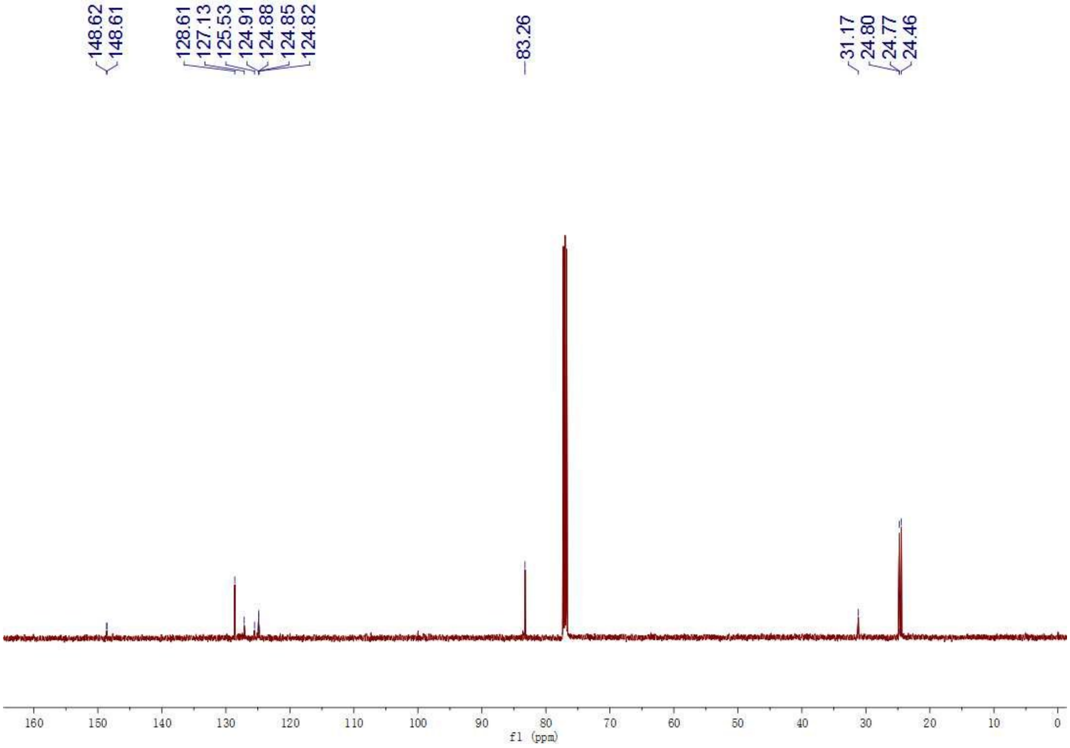
Ethyl 3-(4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)phenyl)-3-oxopropanoate (6j)



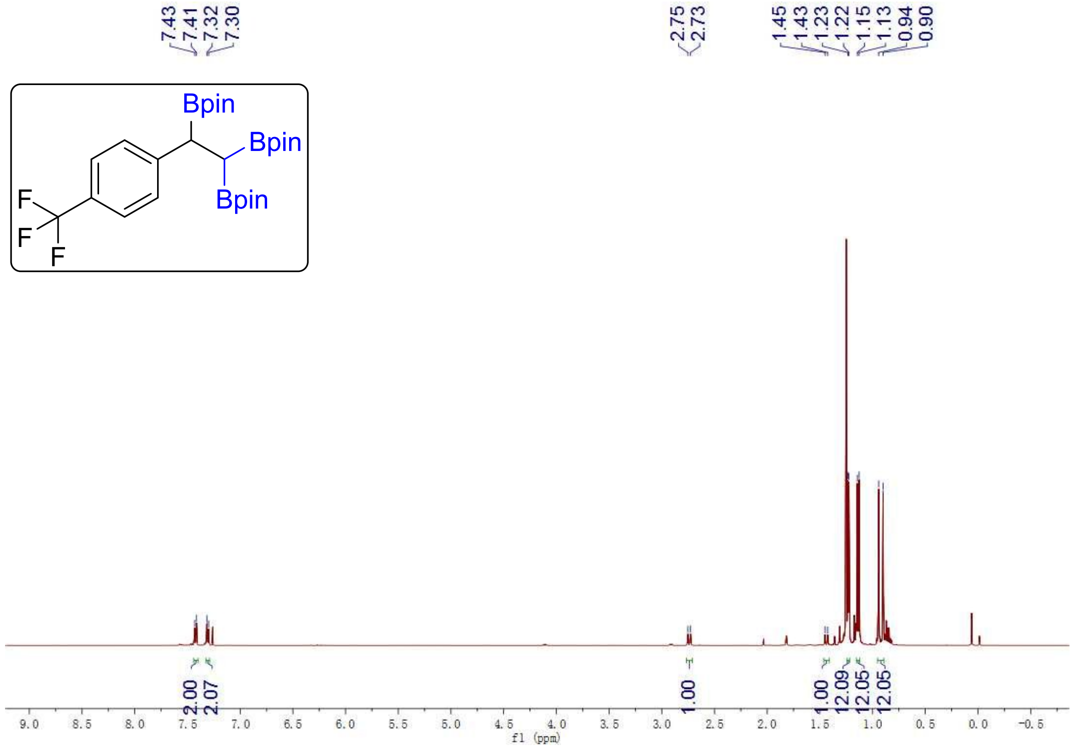


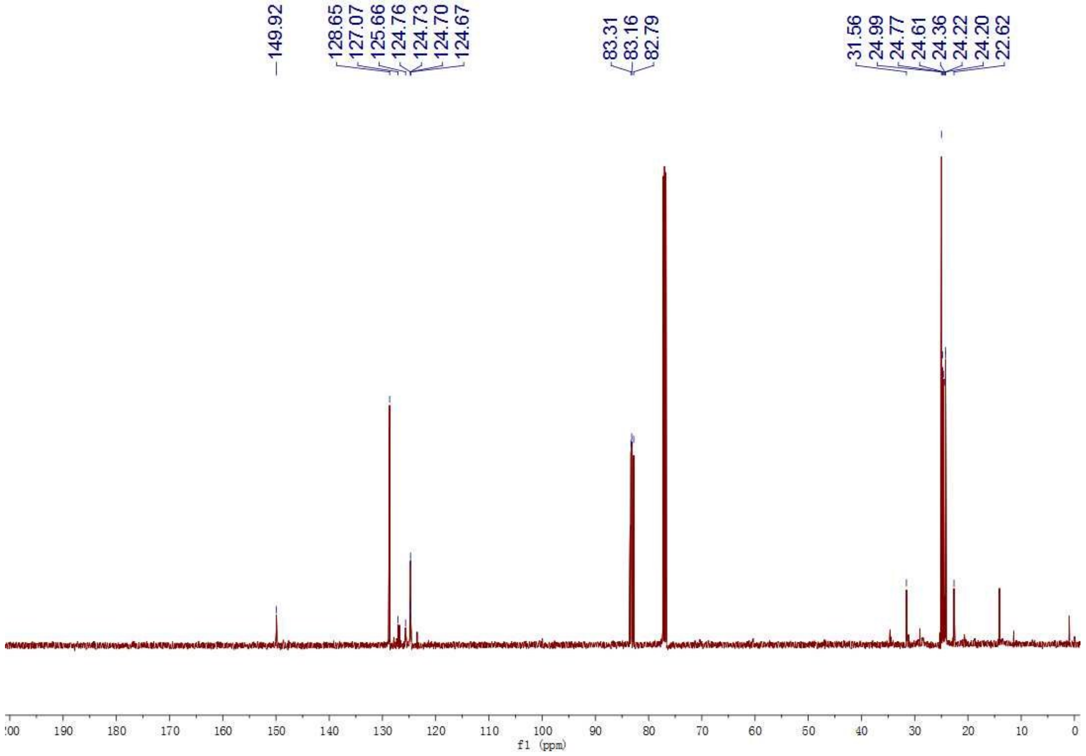
2,2'-(2-(4-(trifluoromethyl)phenyl)ethane-1,1-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6k)



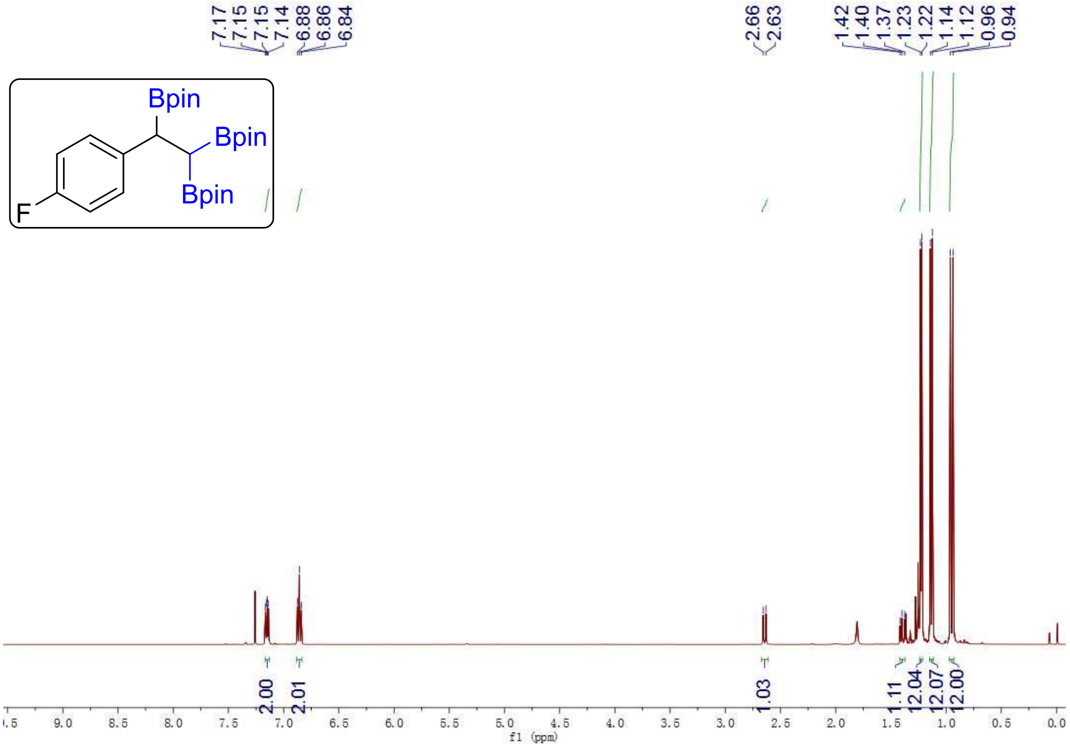


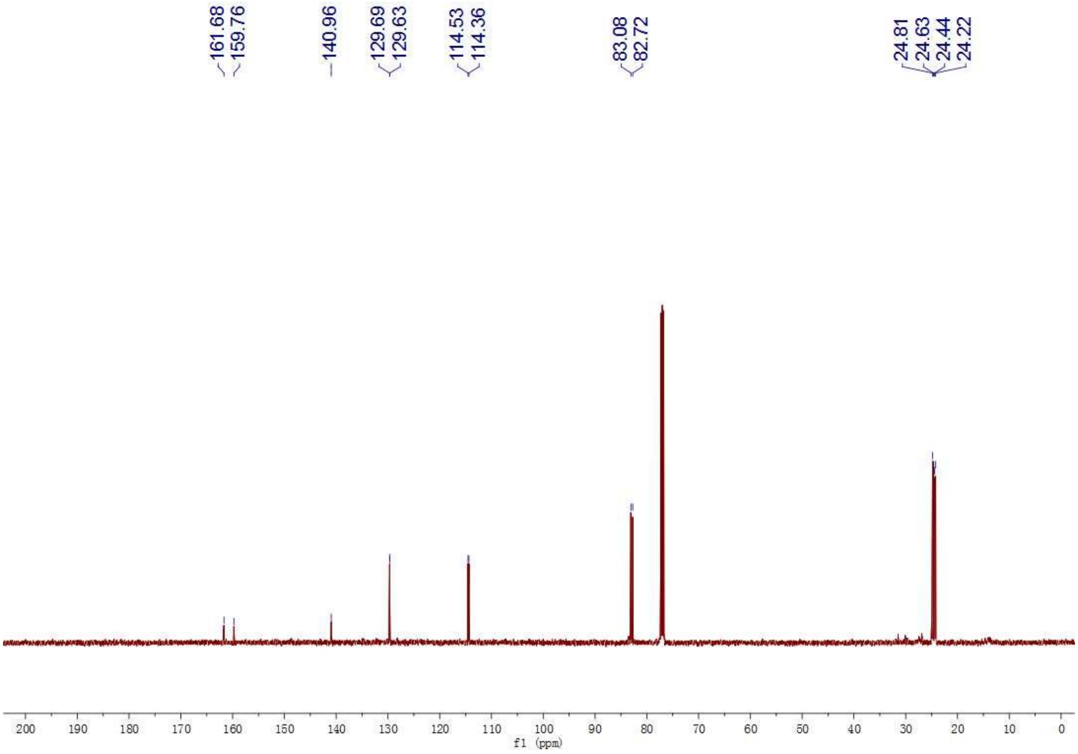
2,2',2''-(2-(4-(trifluoromethyl)phenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'a)



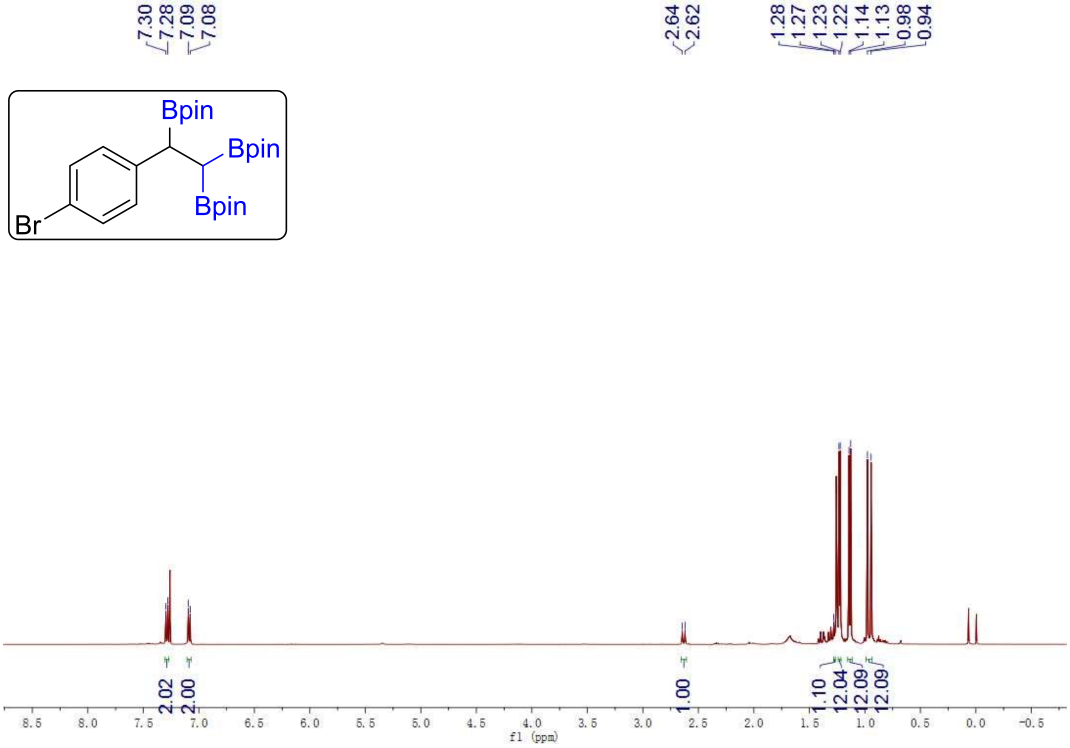


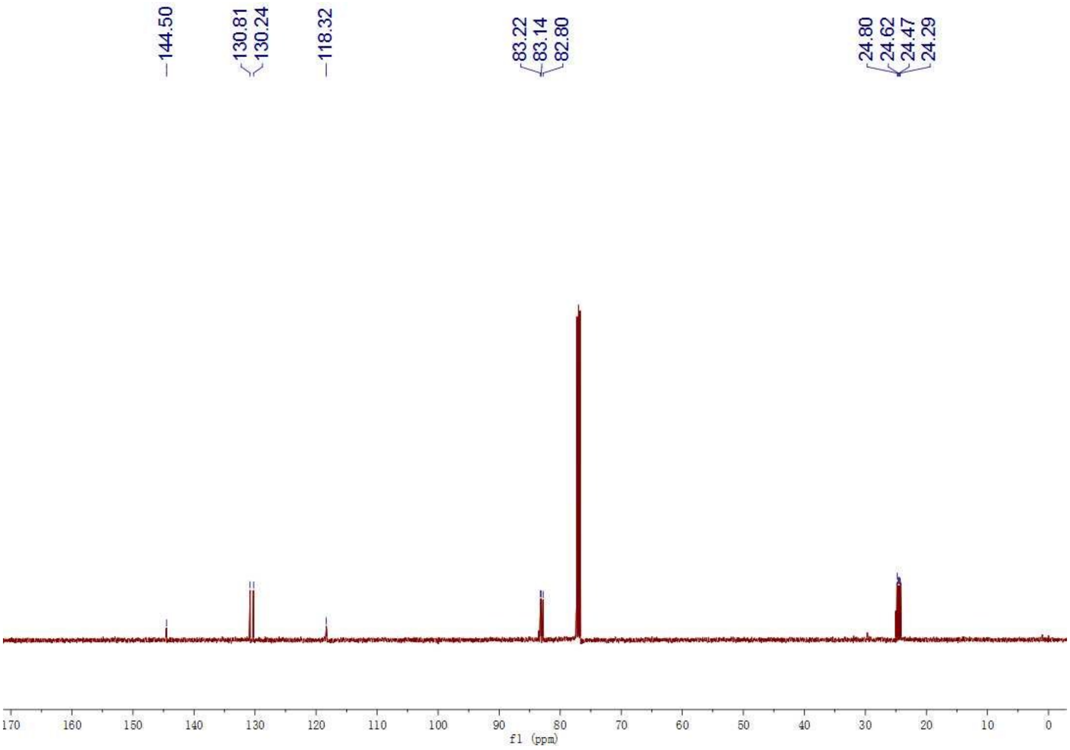
2,2',2''-(2-(4-fluorophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6’b)



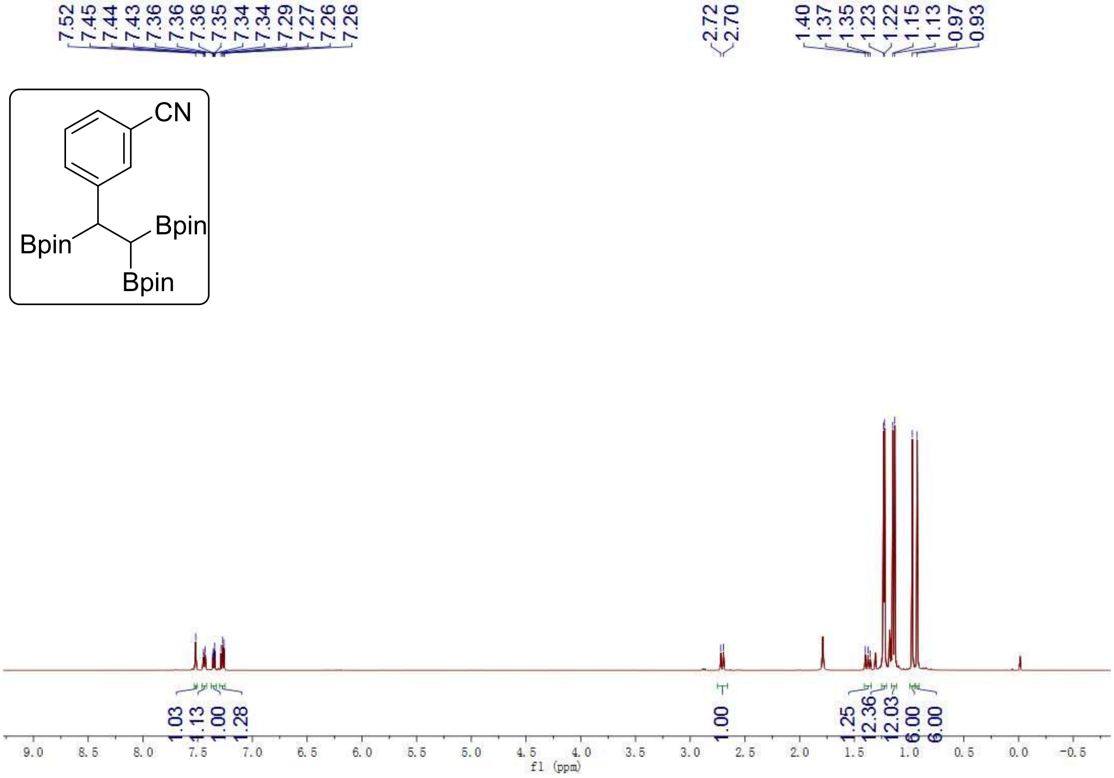


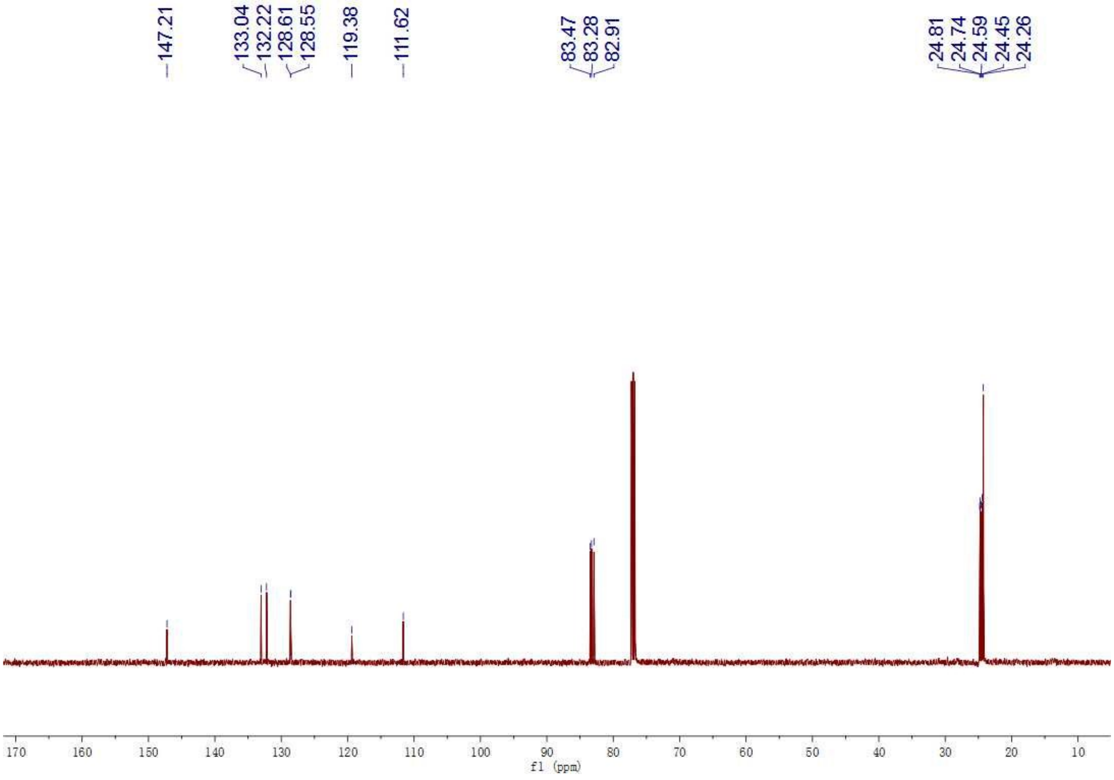
2,2',2''-(2-(4-bromophenyl)ethane-1,1,2-triyl)tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)(6'c)



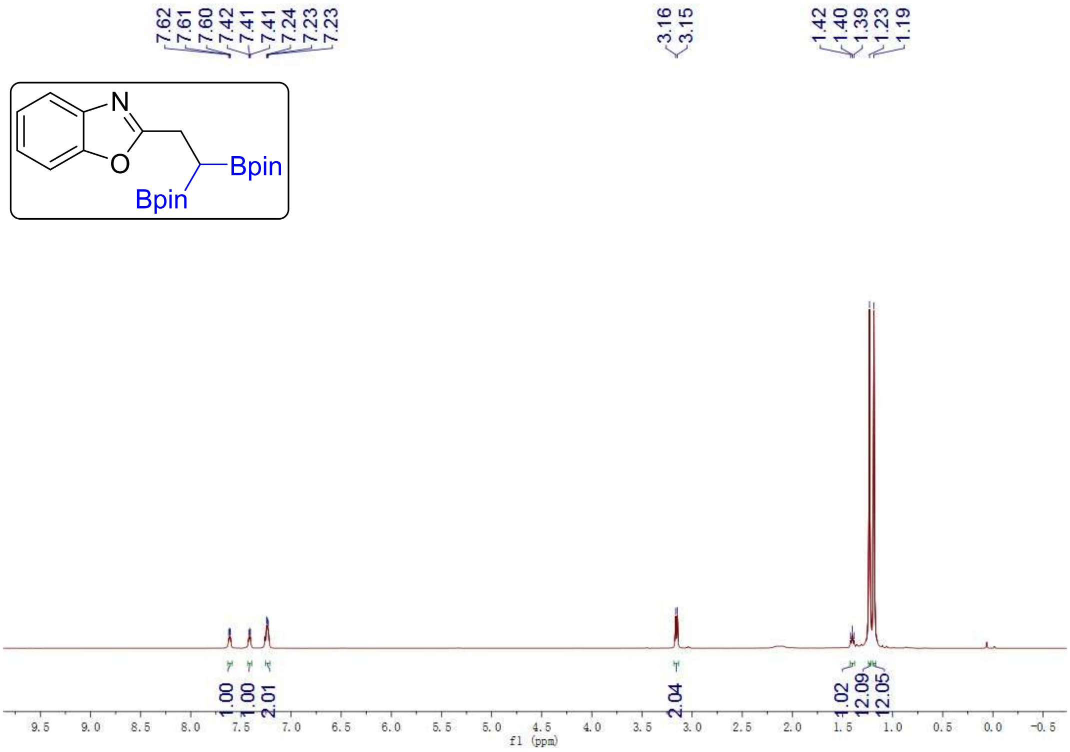


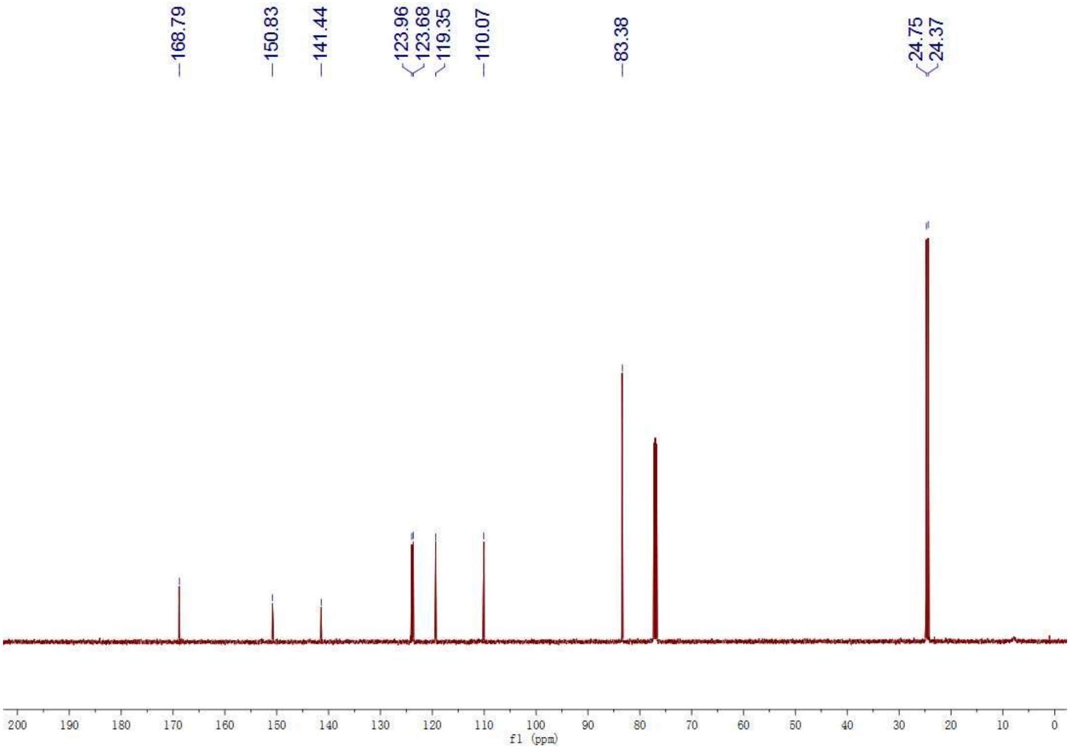
3-(1,2,2-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (6ʾd)



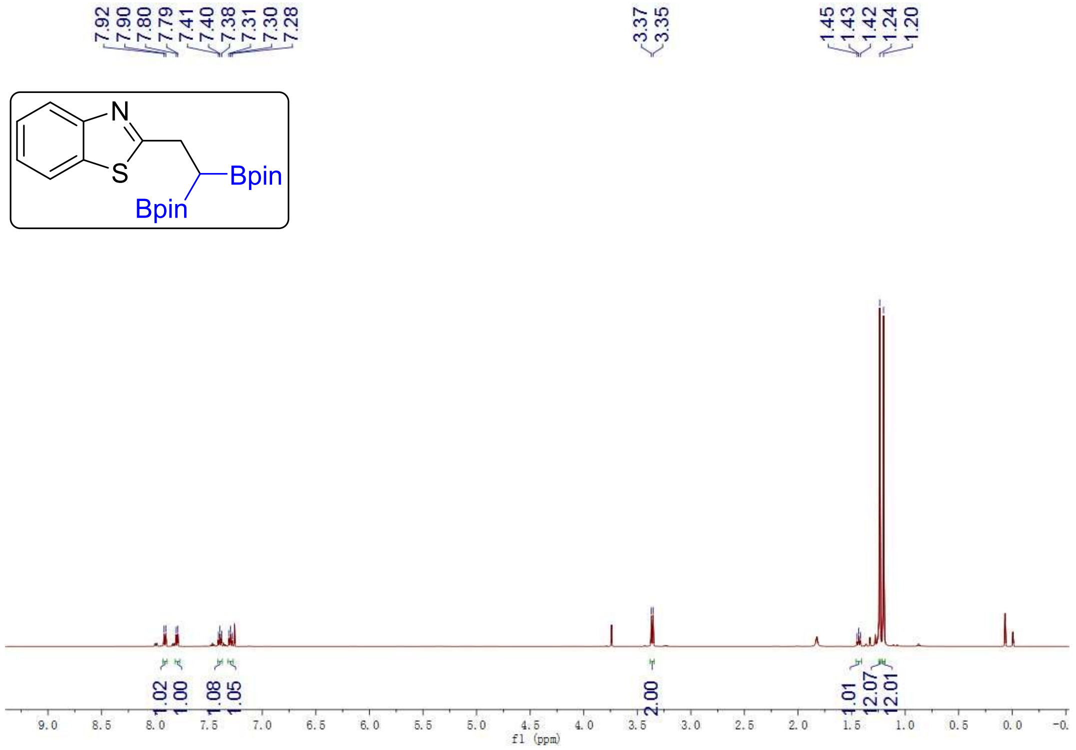


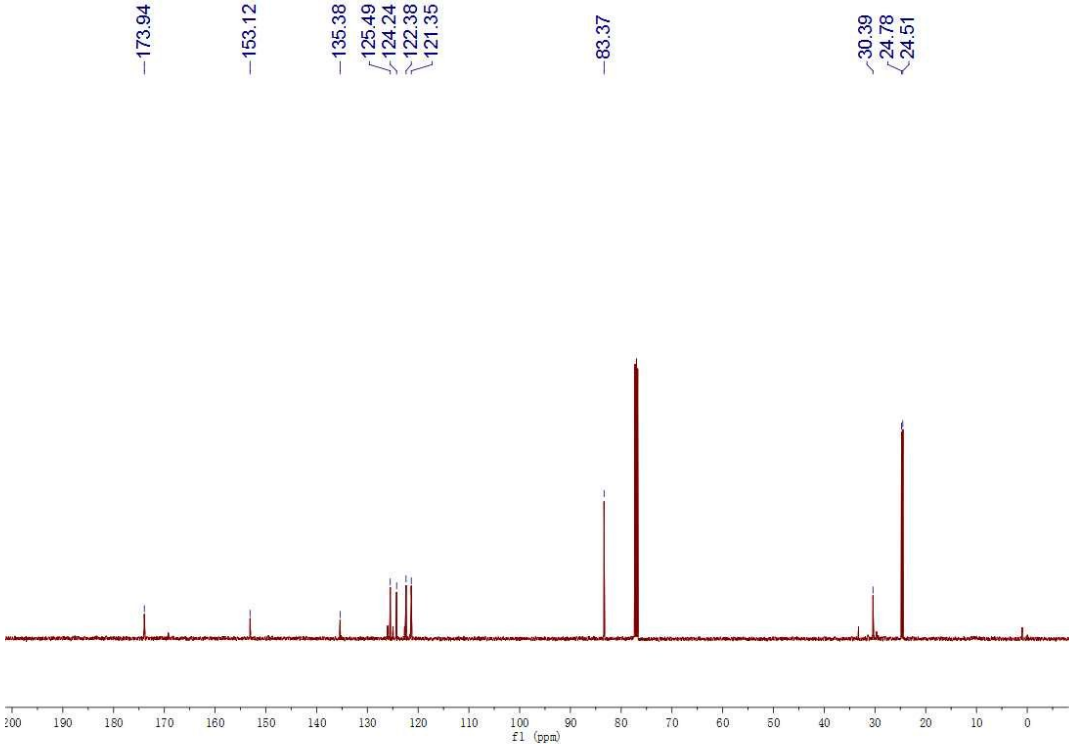
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]oxazole (6l)[15]



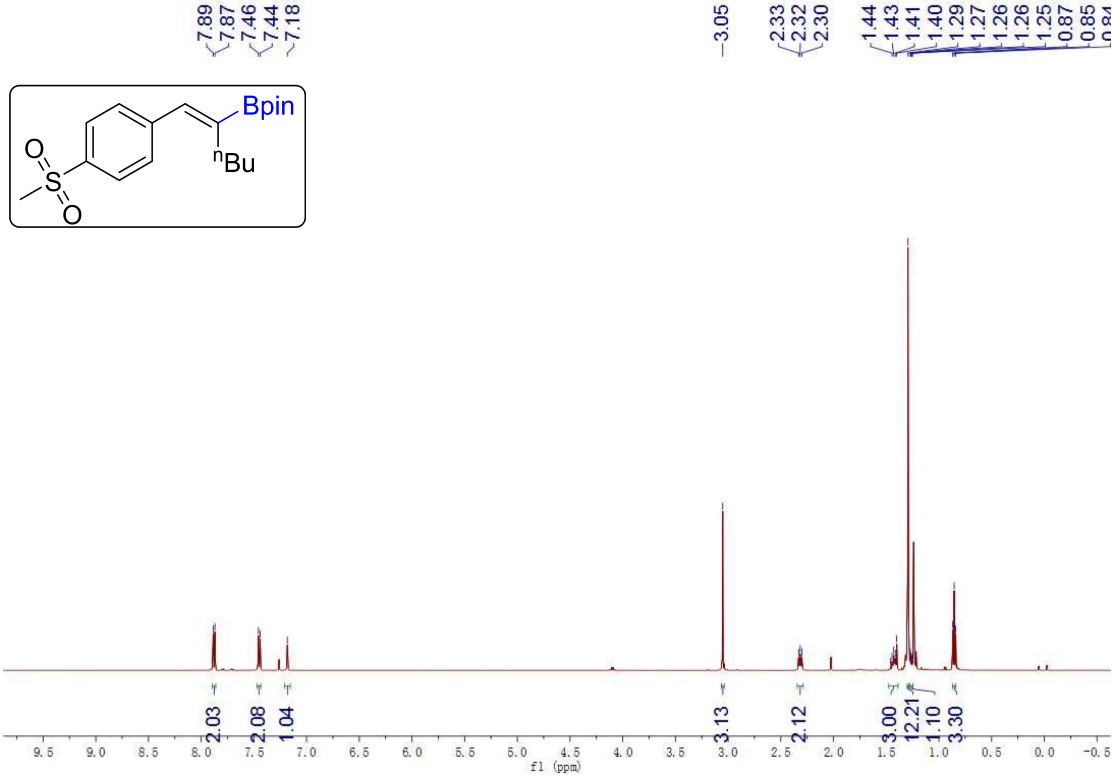


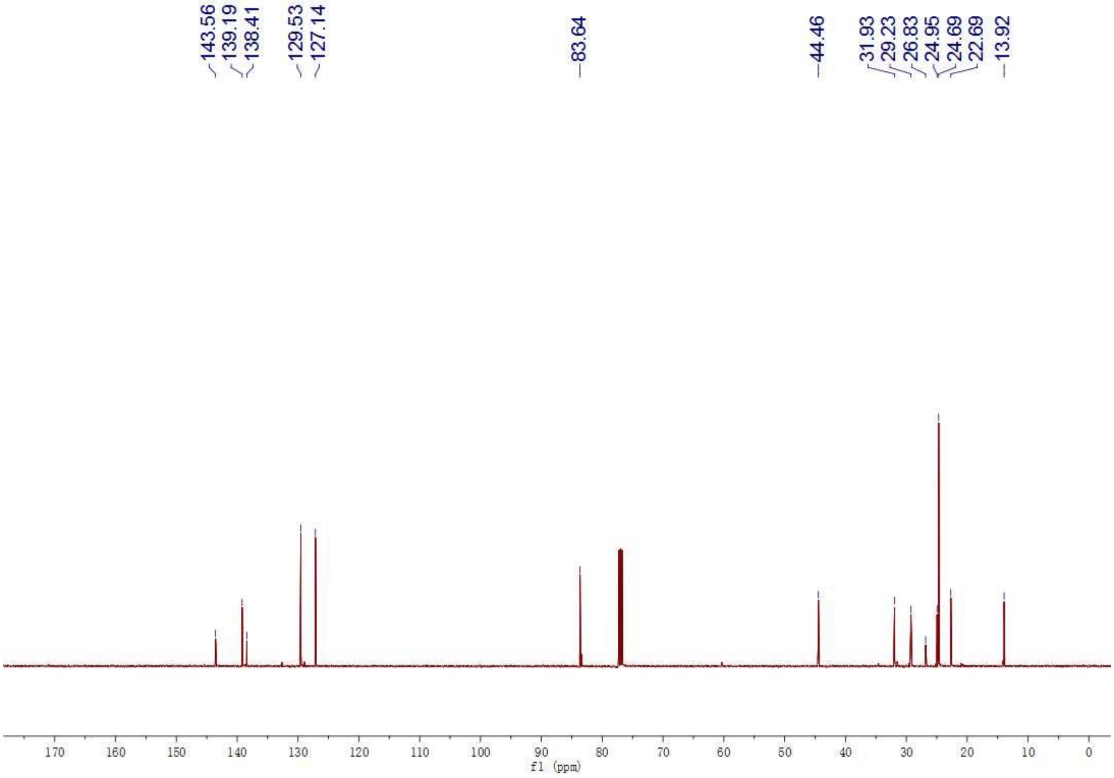
2-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzo[d]thiazole (6m)



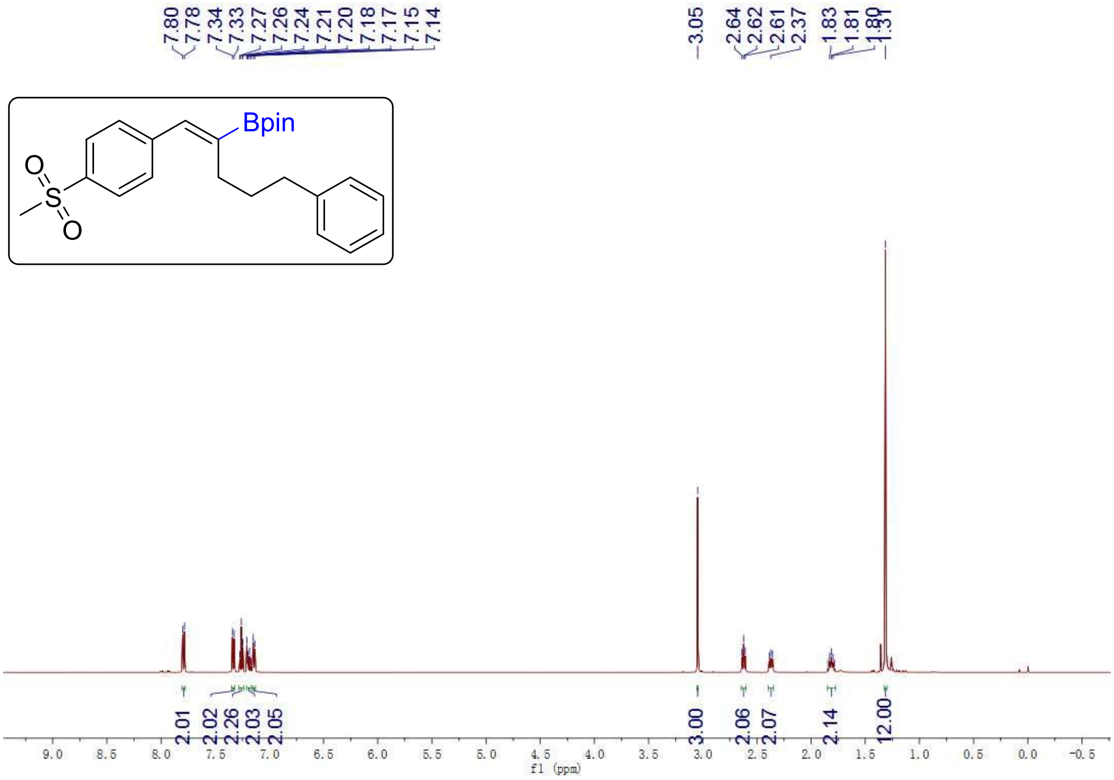


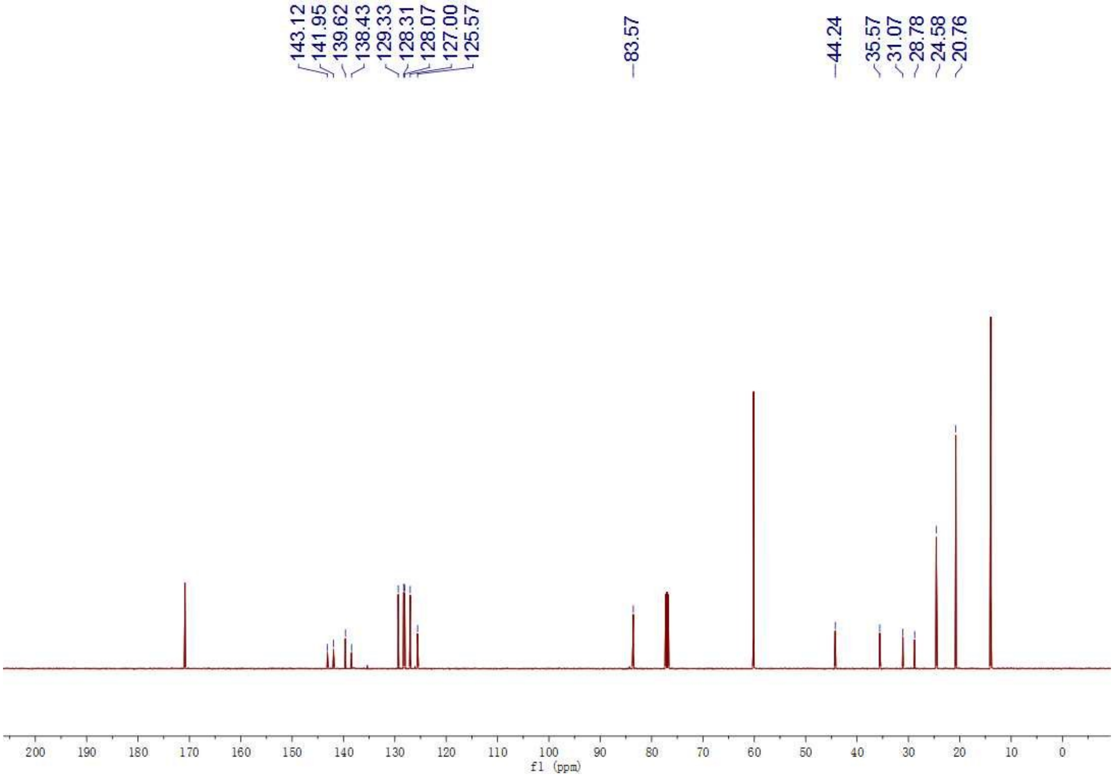
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)hex-1-en-2-yl)-1,3,2-dioxaborolane (6n)



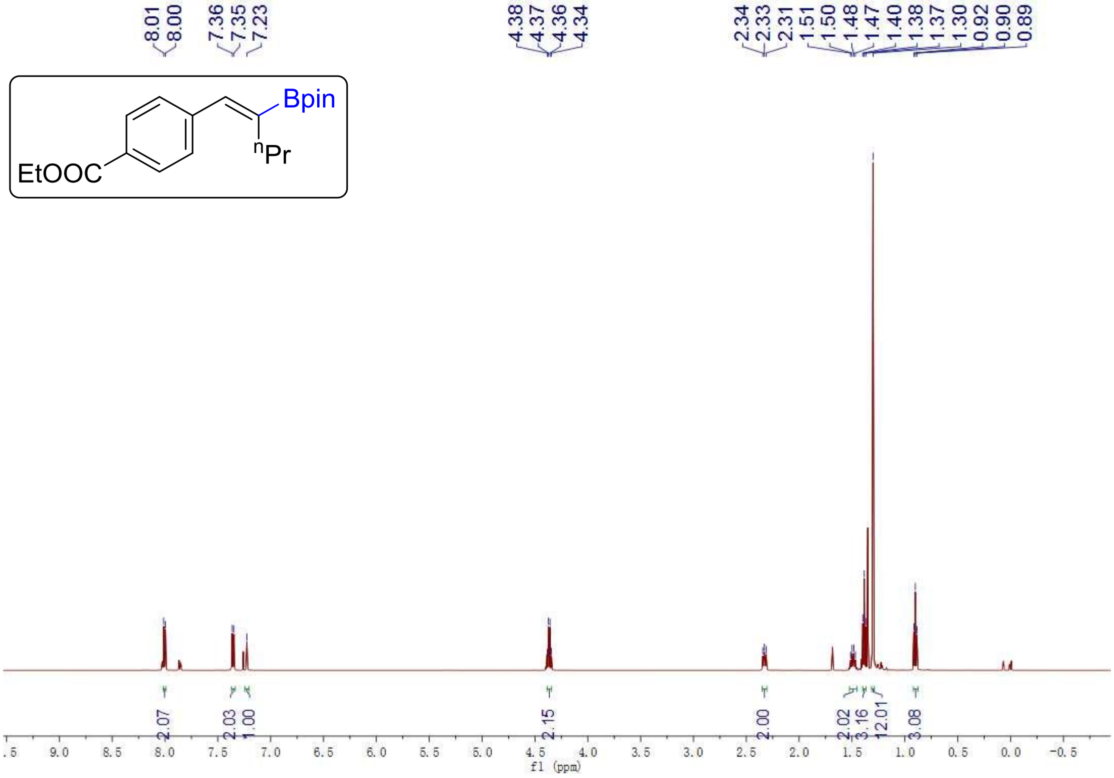


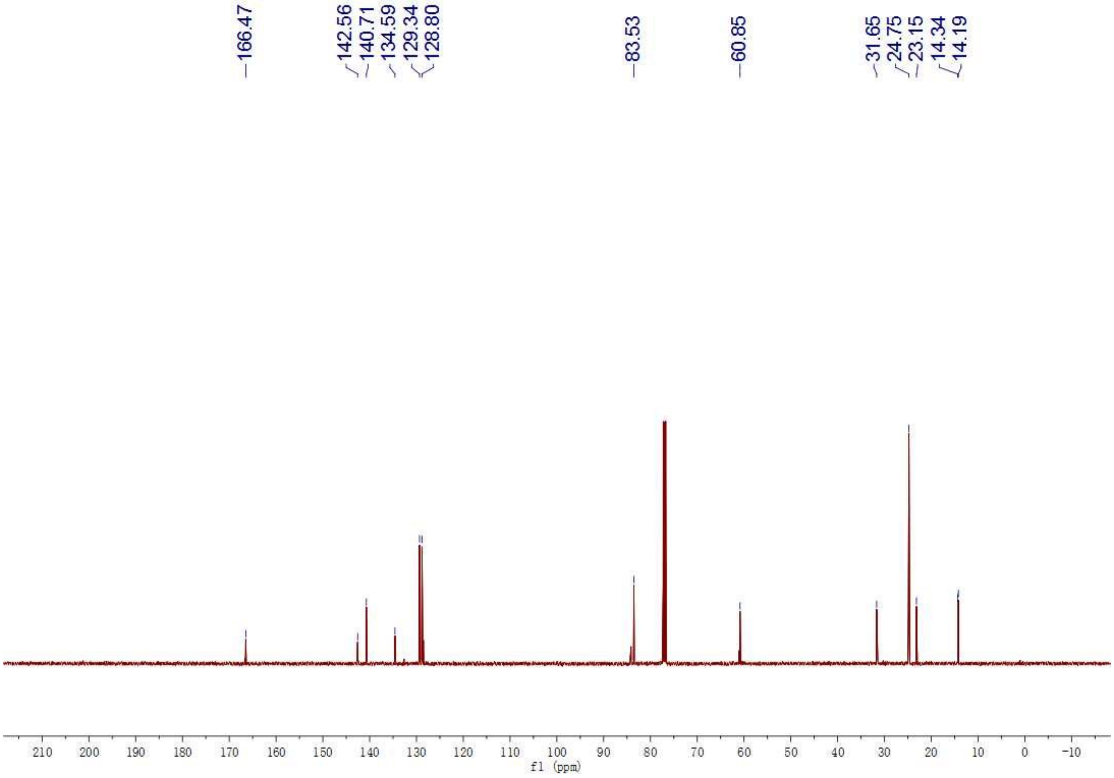
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)-5-phenylpent-1-en-2-yl)-1,3,2-dioxaborolane (6o)



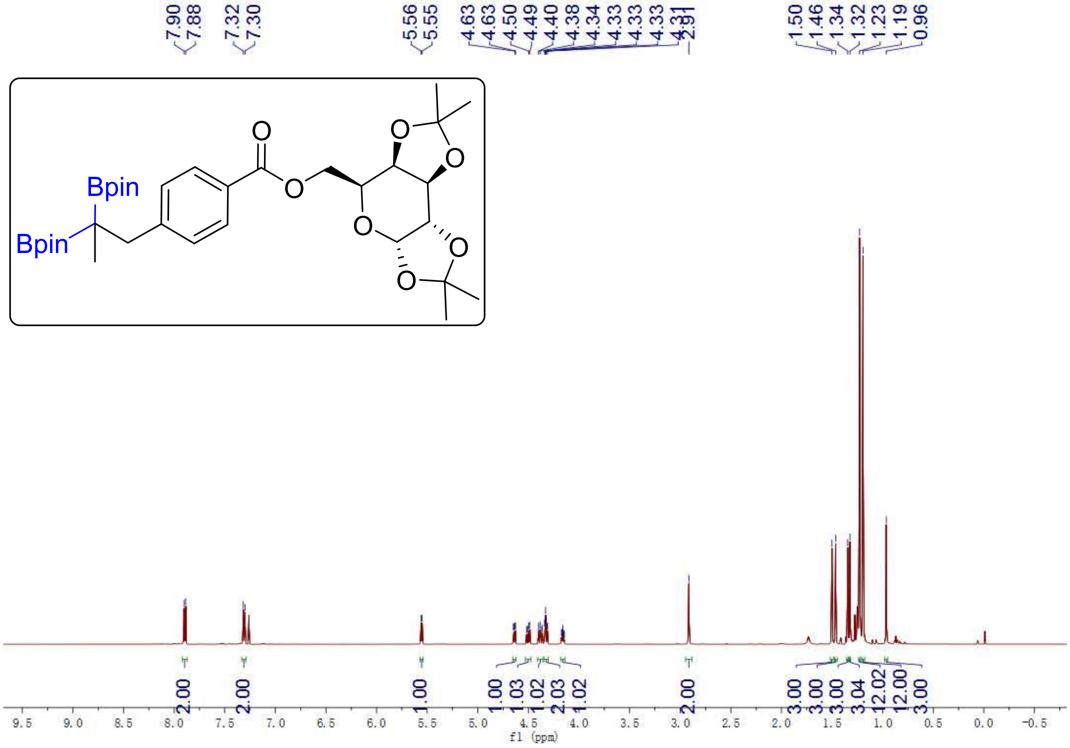


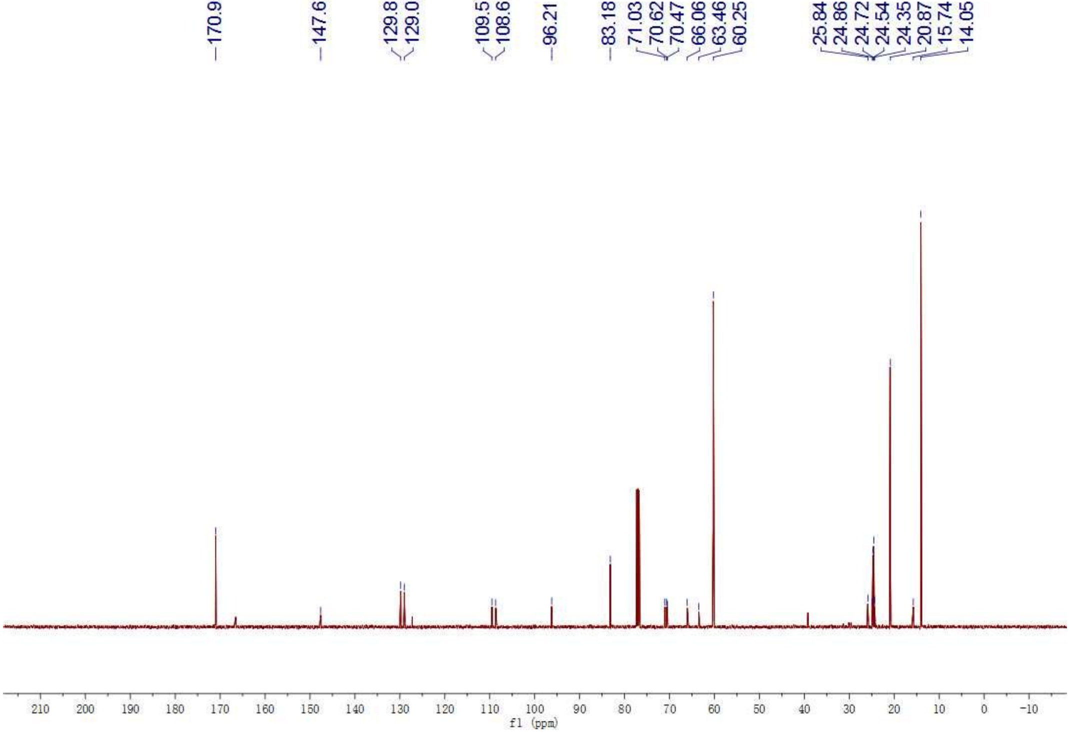
ethyl -4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)benzoate (6p)



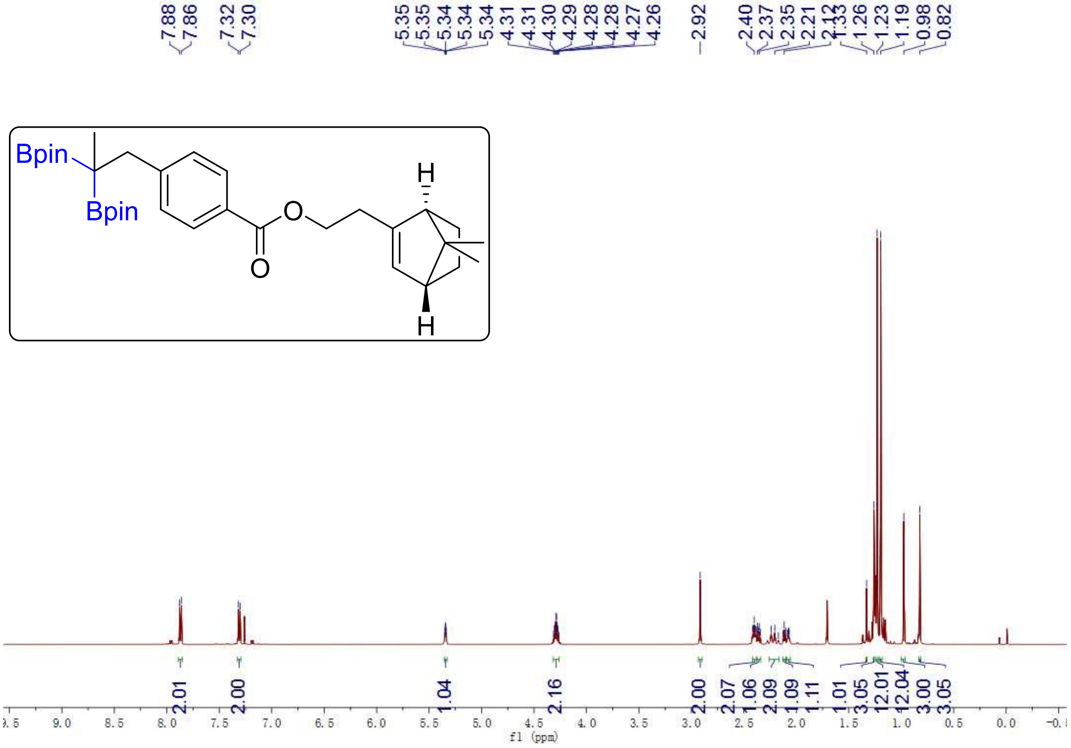


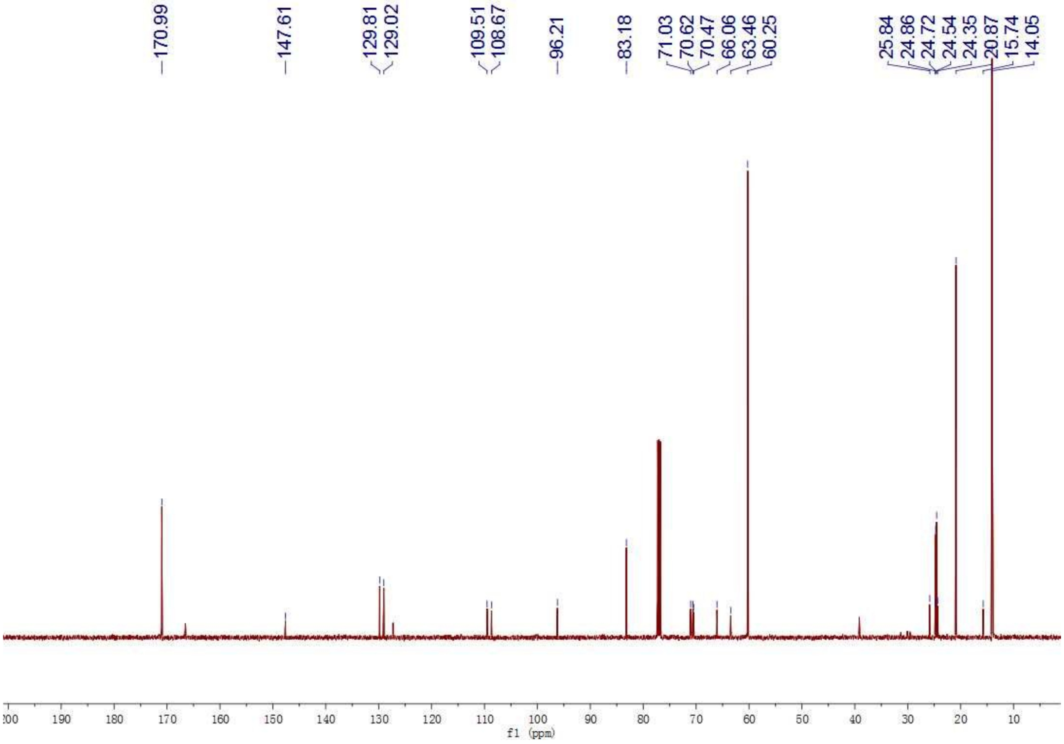
((3aS,5S,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6q)



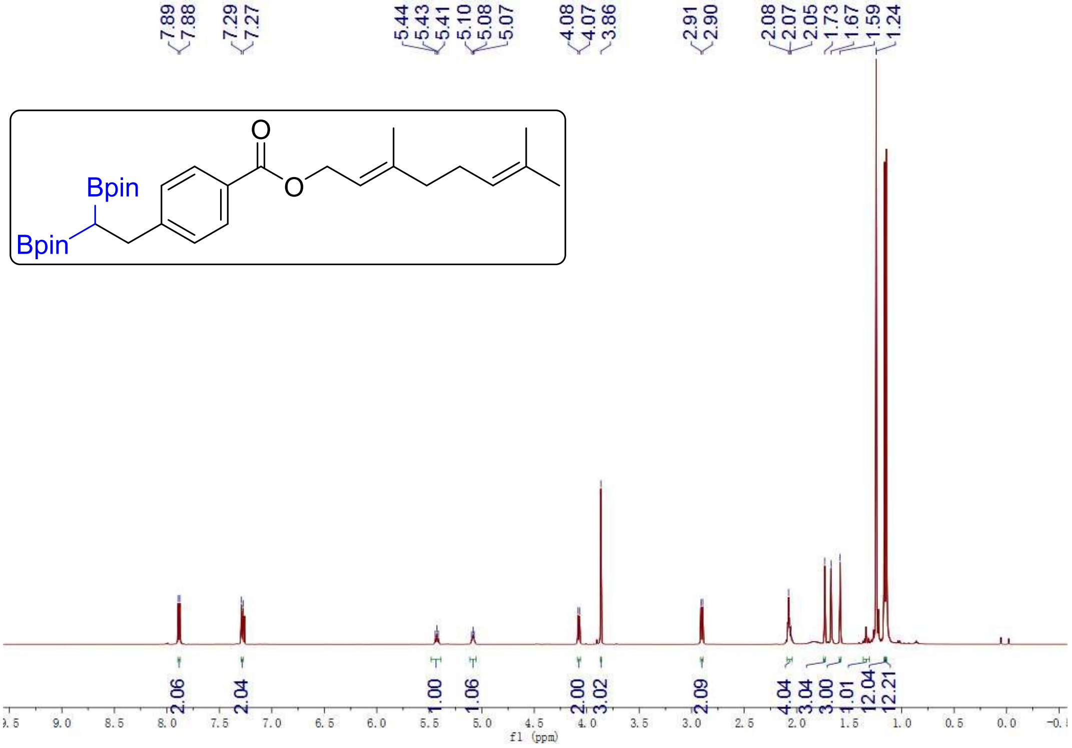


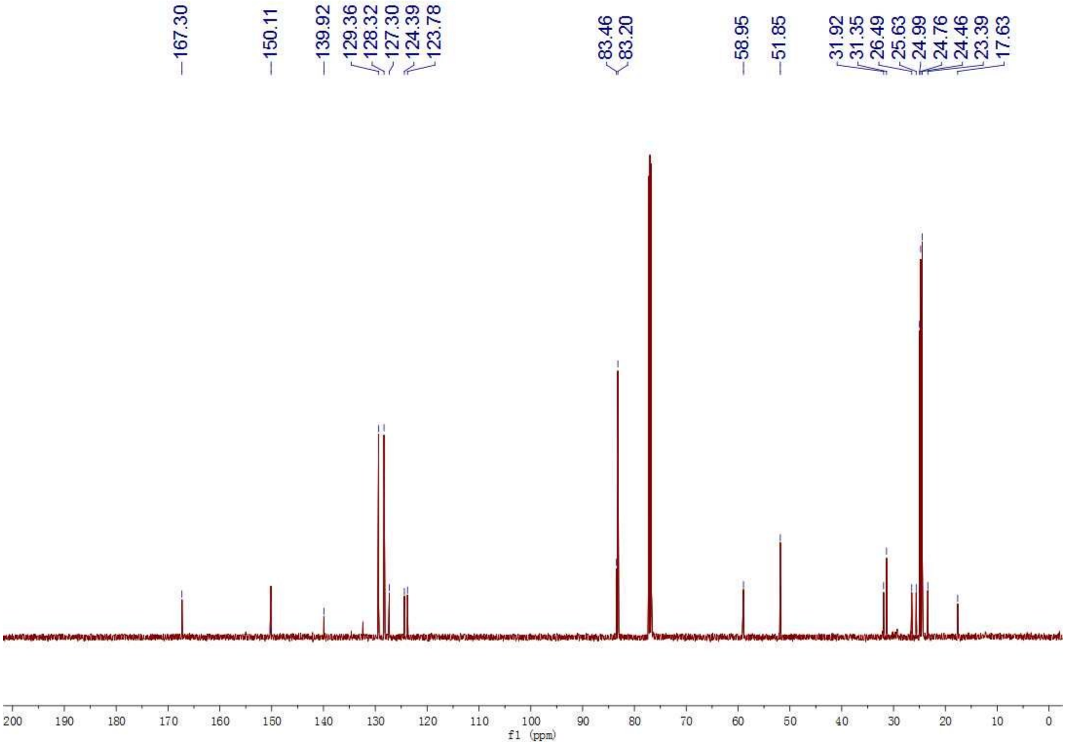
2-((1S,4R)-7,7-dimethylbicyclo[2.2.1]hept-2-en-2-yl)ethyl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6r)



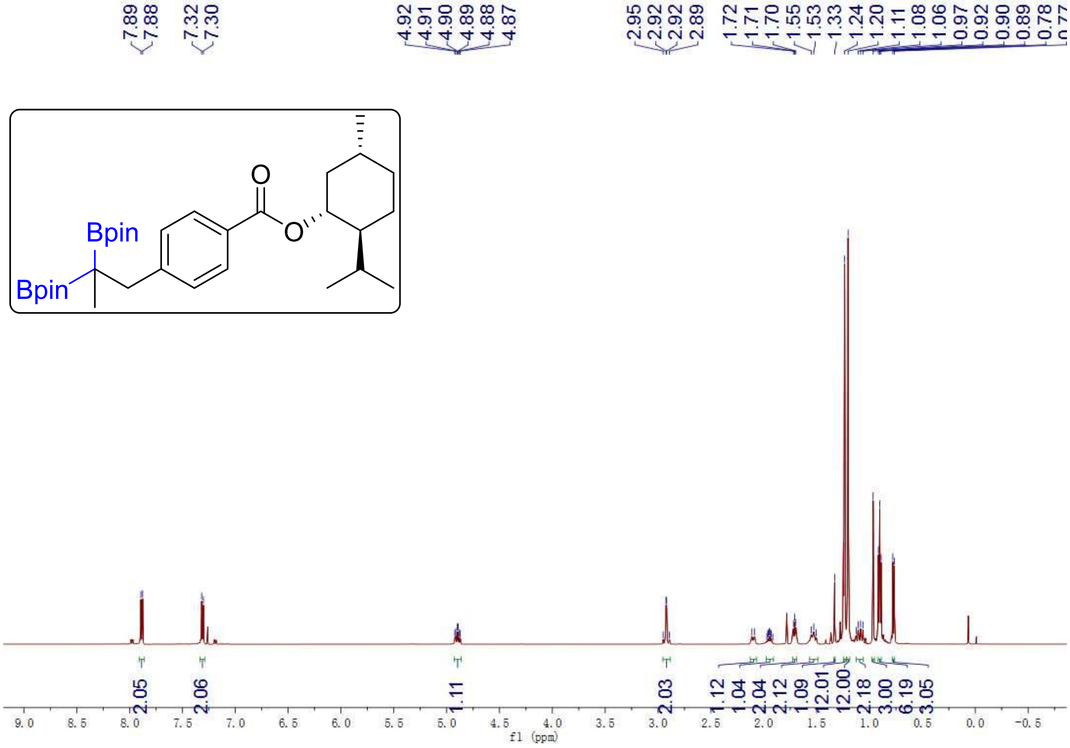


(E)-3,7-dimethylocta-2,6-dien-1-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzoate (6s)

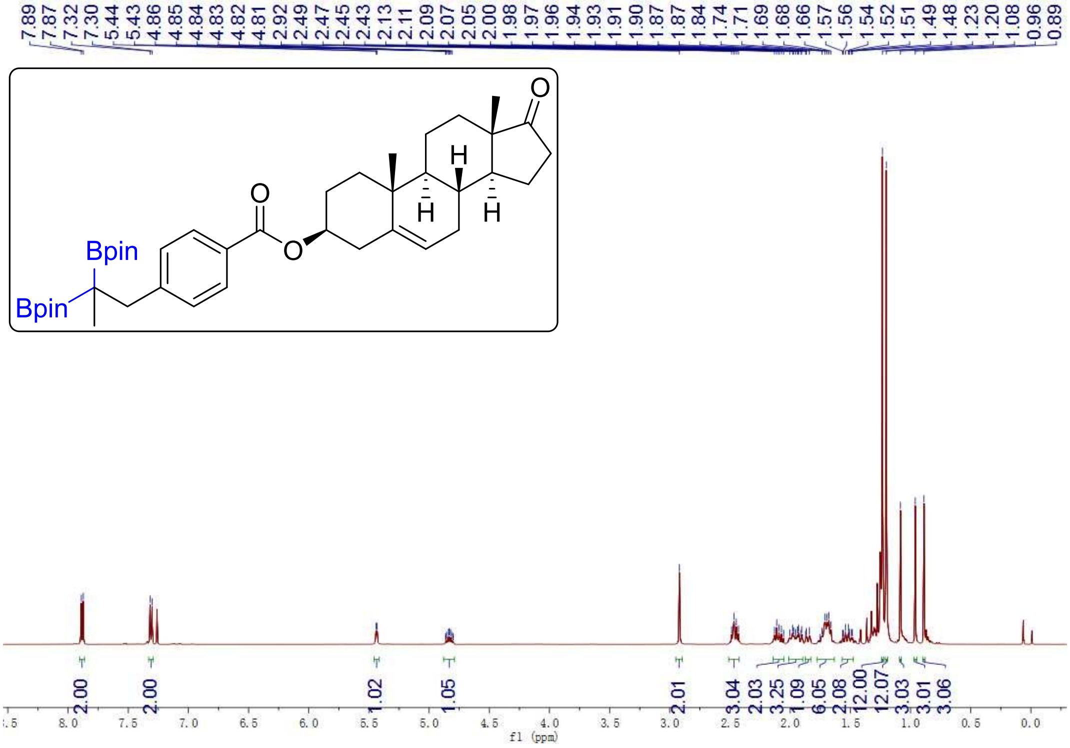


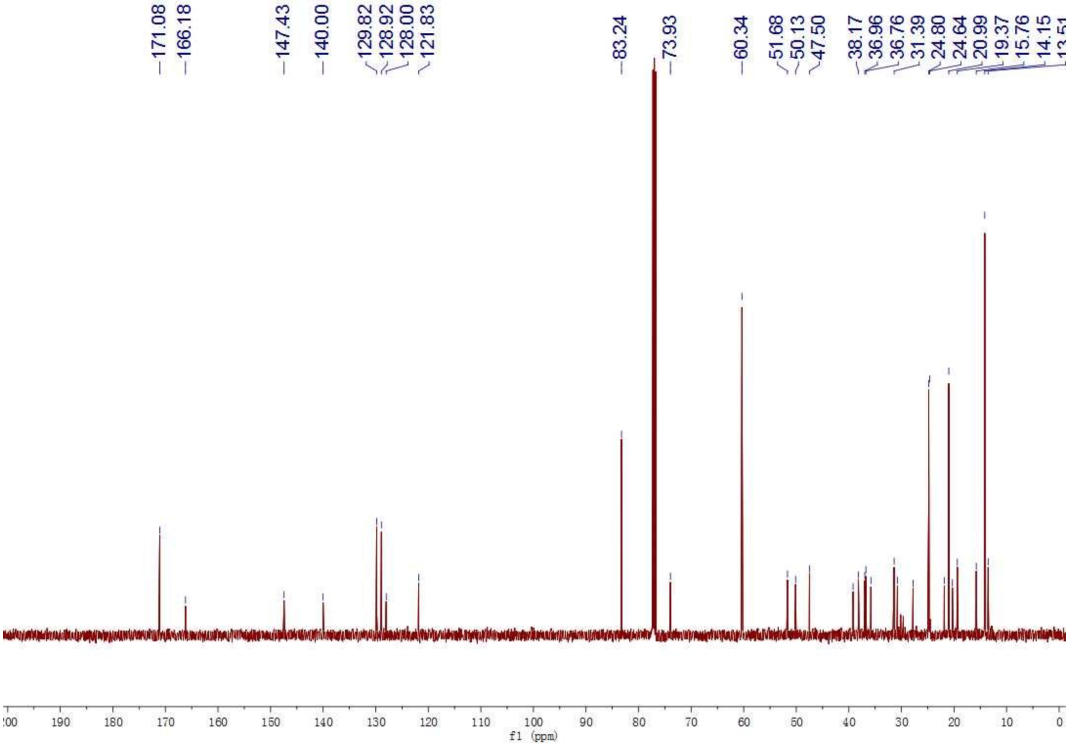


(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6t)

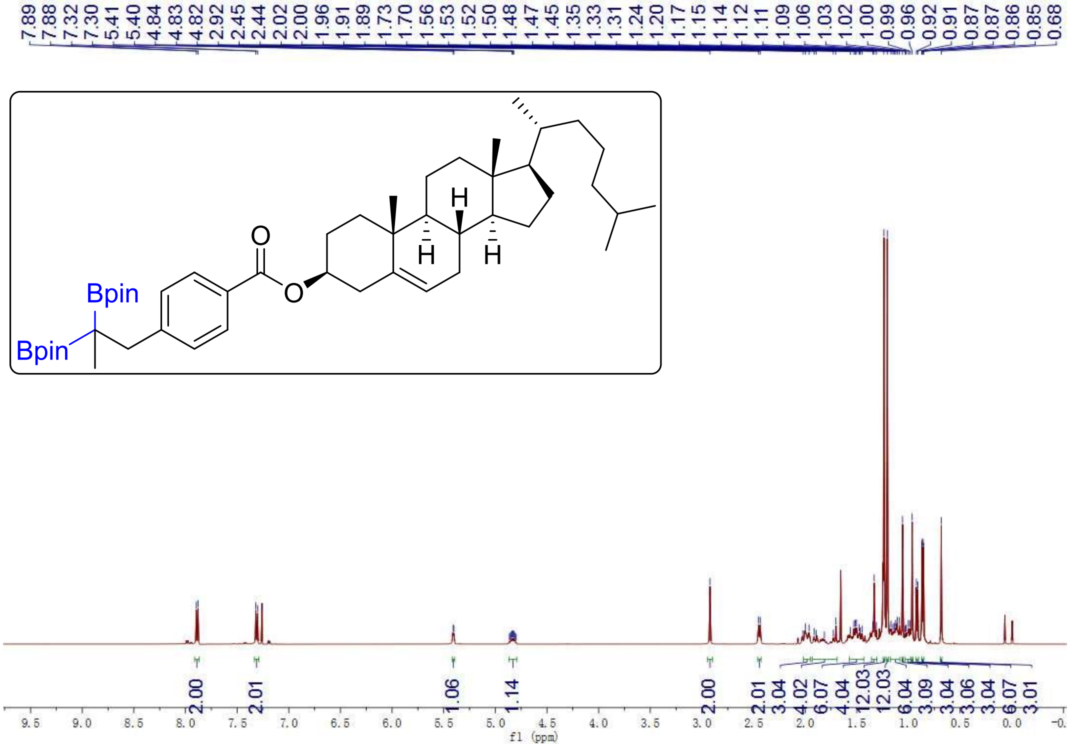


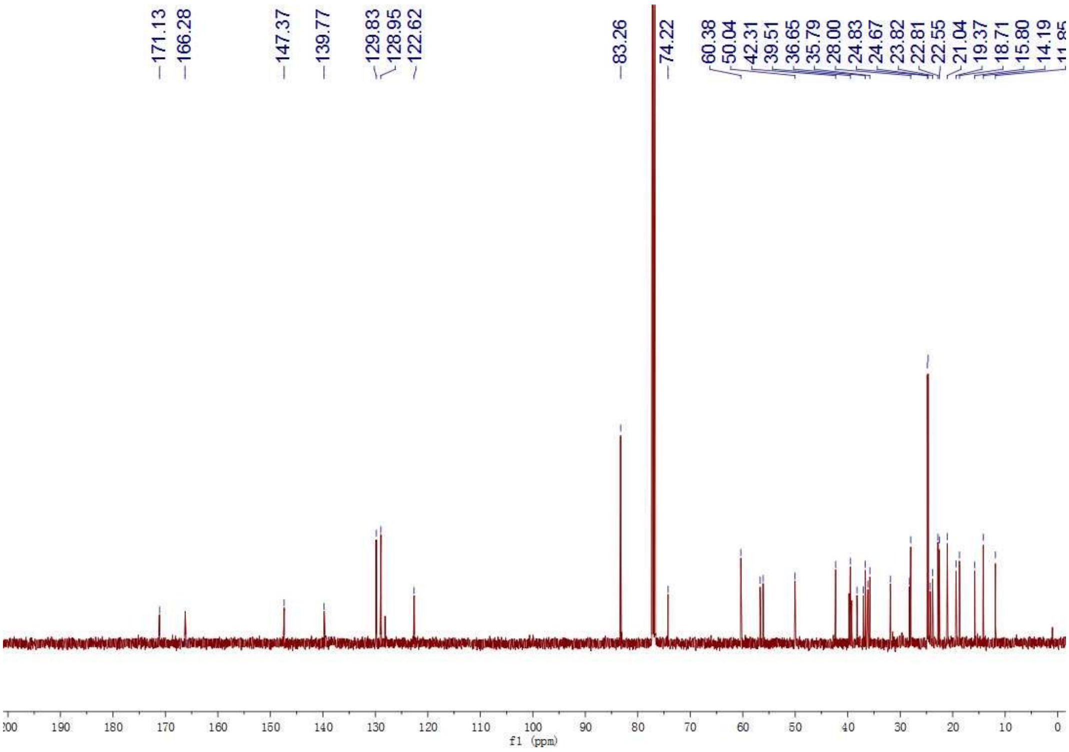
(3S,8R,9S,10R,13S,14S)-10,13-dimethyl-17-oxo2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6u)



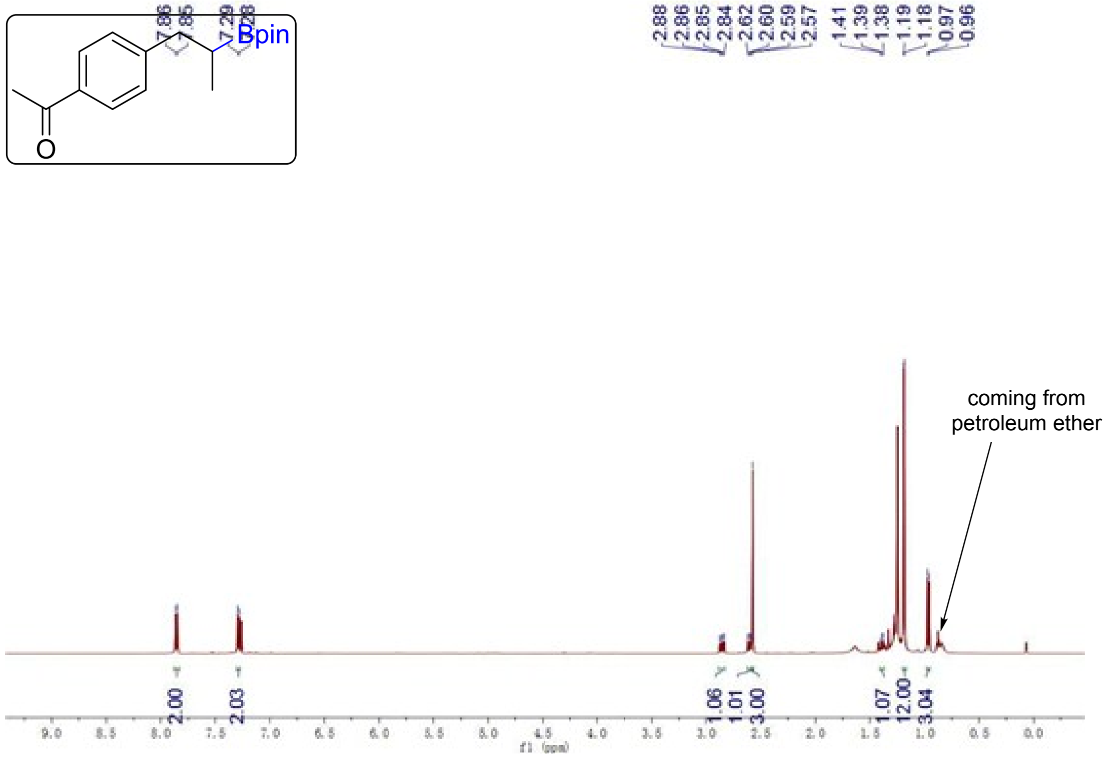


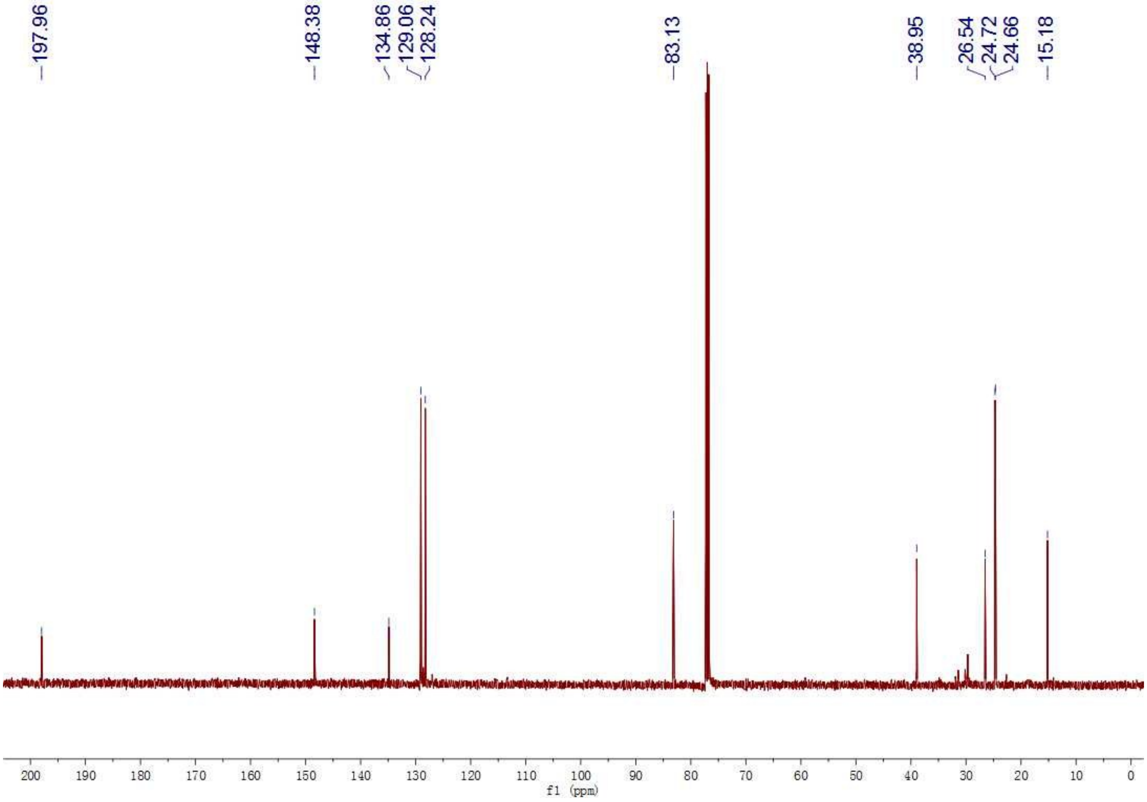
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1Hcyclopenta[a]phenanthren-3-yl 4-(2,2-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)benzoate (6v)



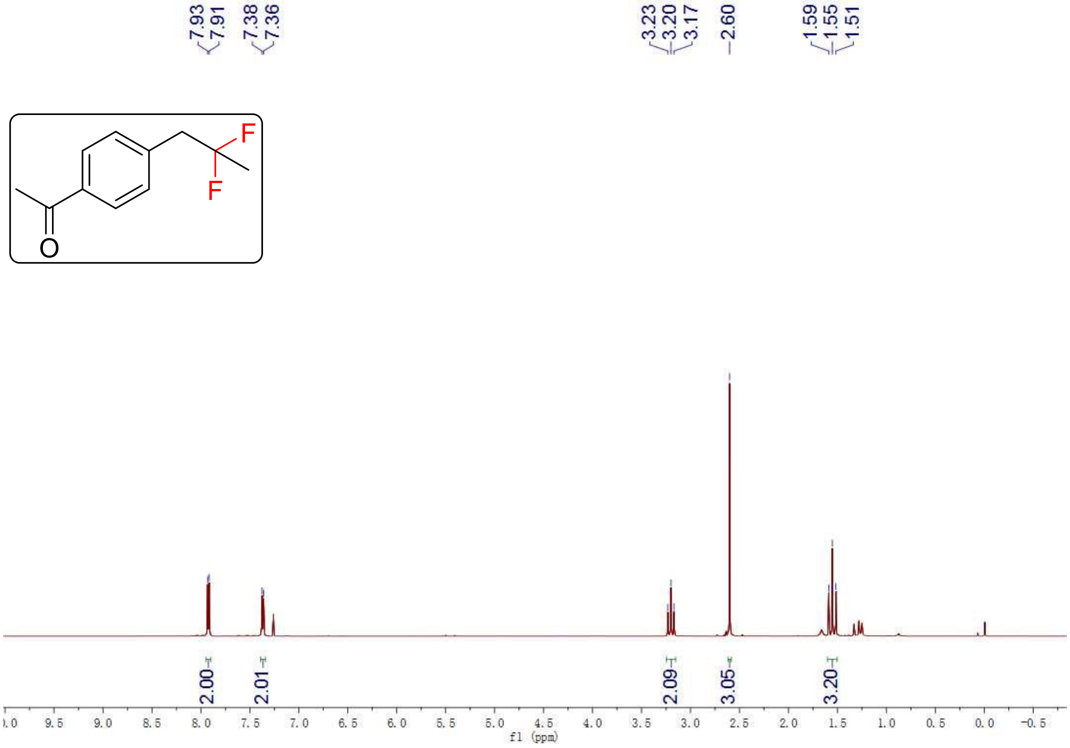


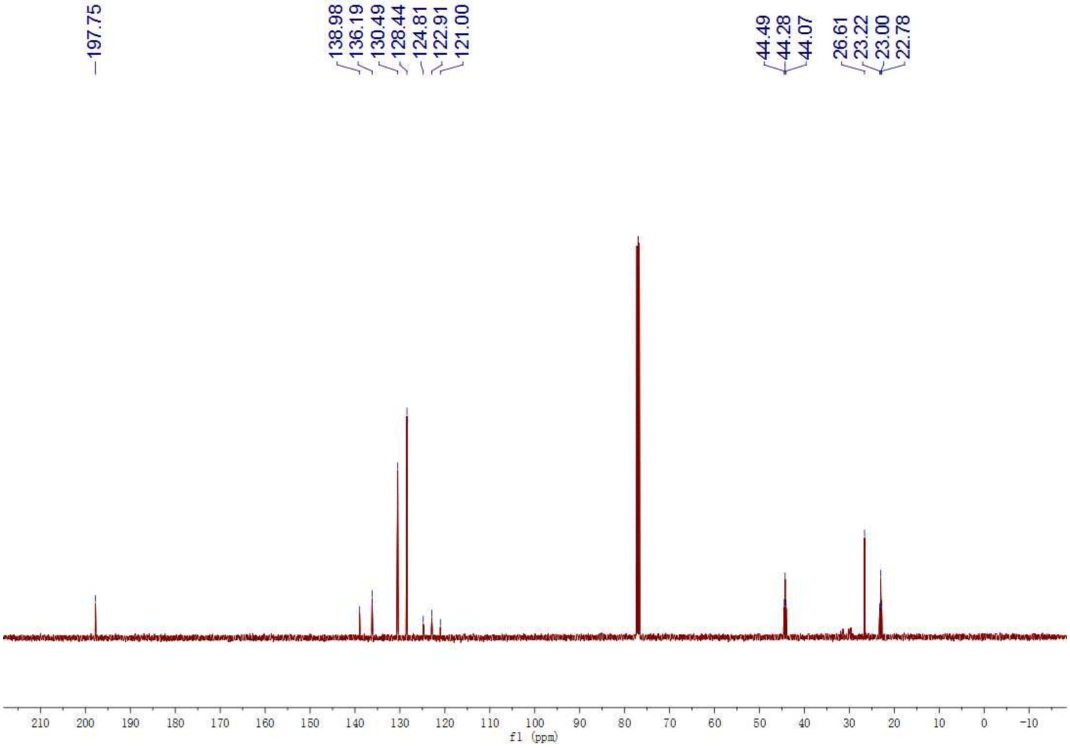
1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolayl)propyl)phenyl)ethan-1-one (8)

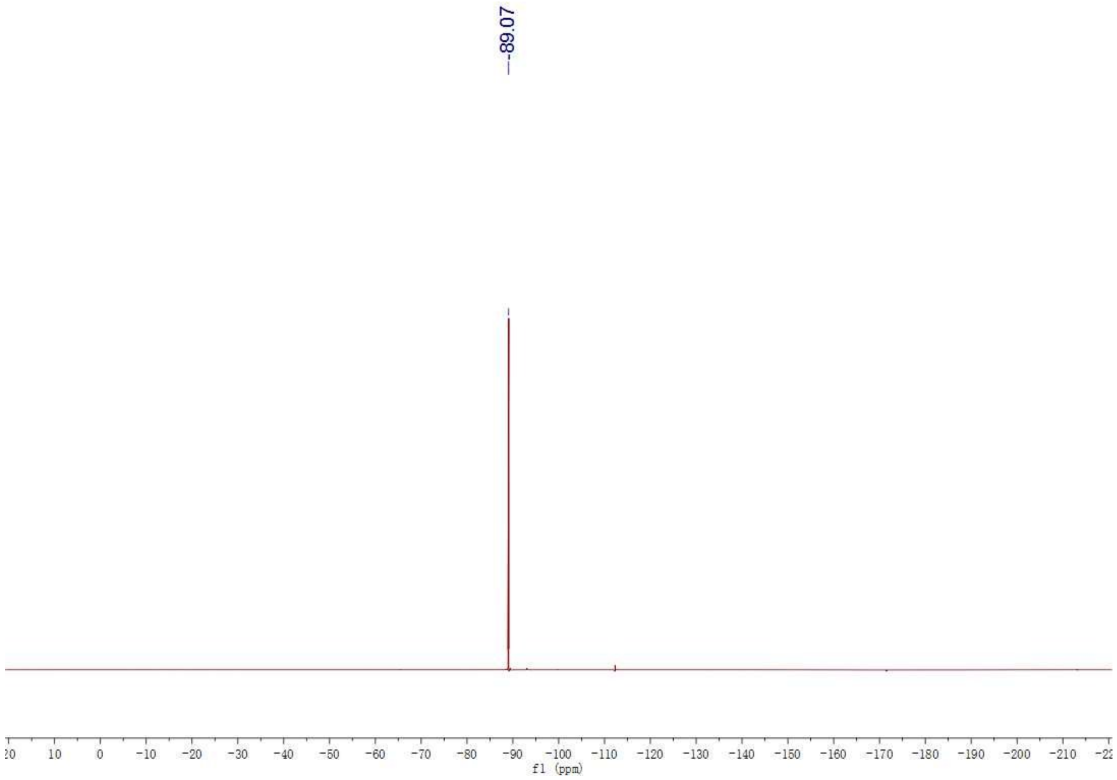




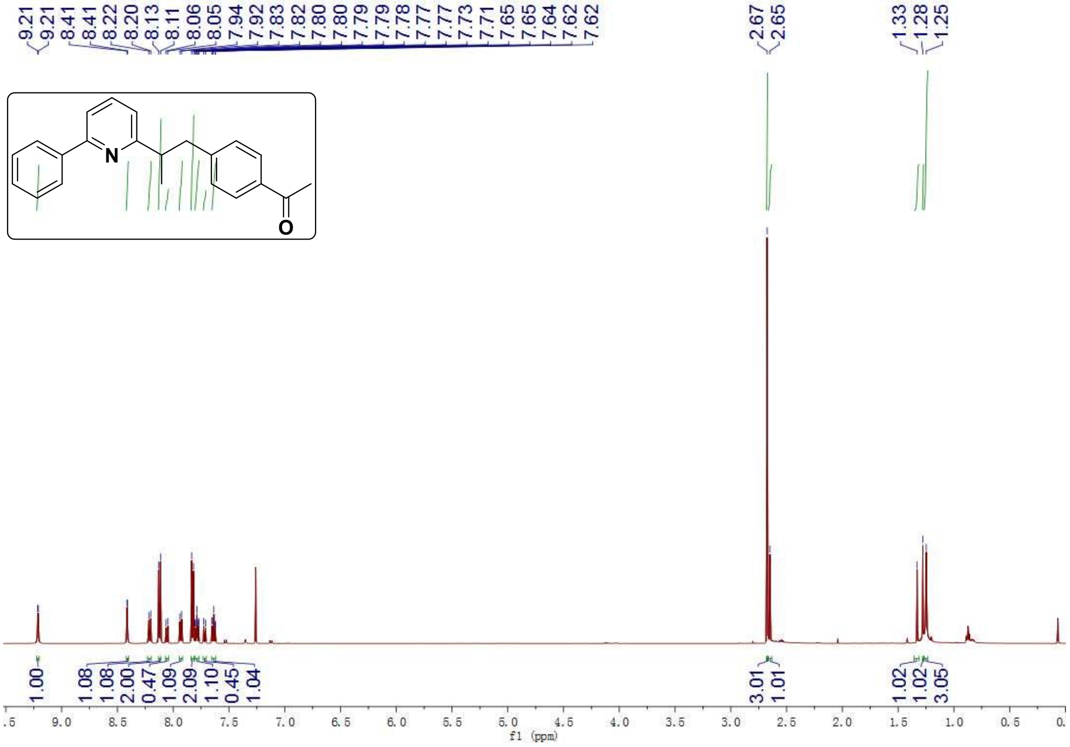
1-(4-(2,2-difluoropropyl)phenyl)ethan-1-one (7)

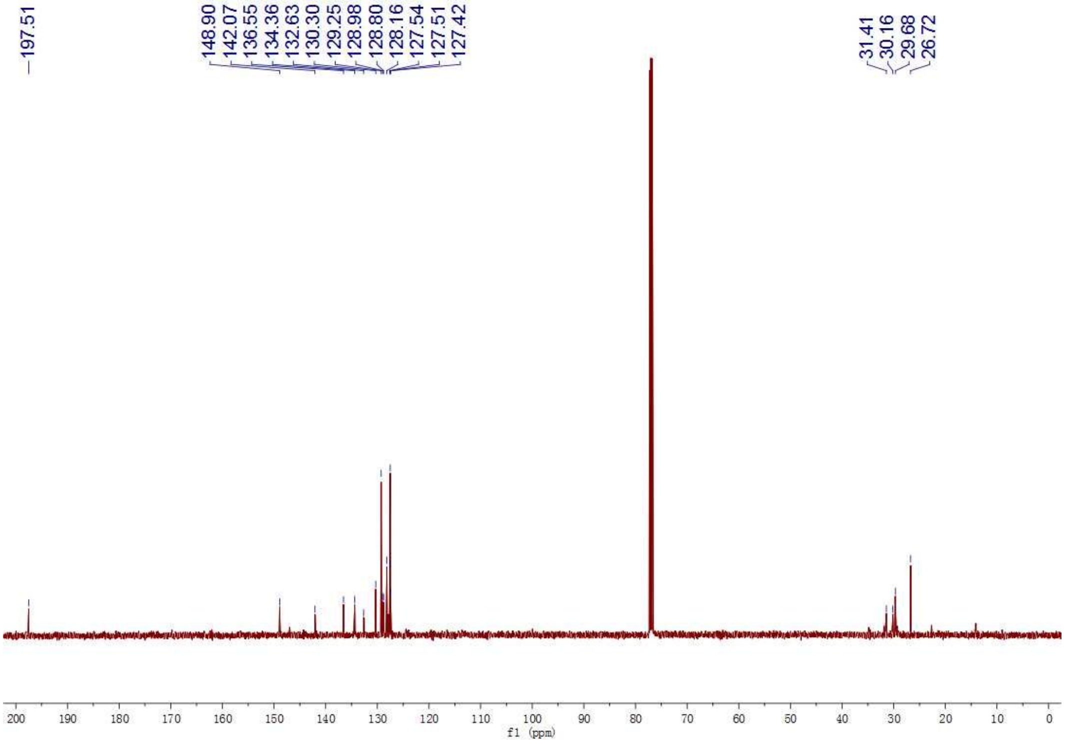




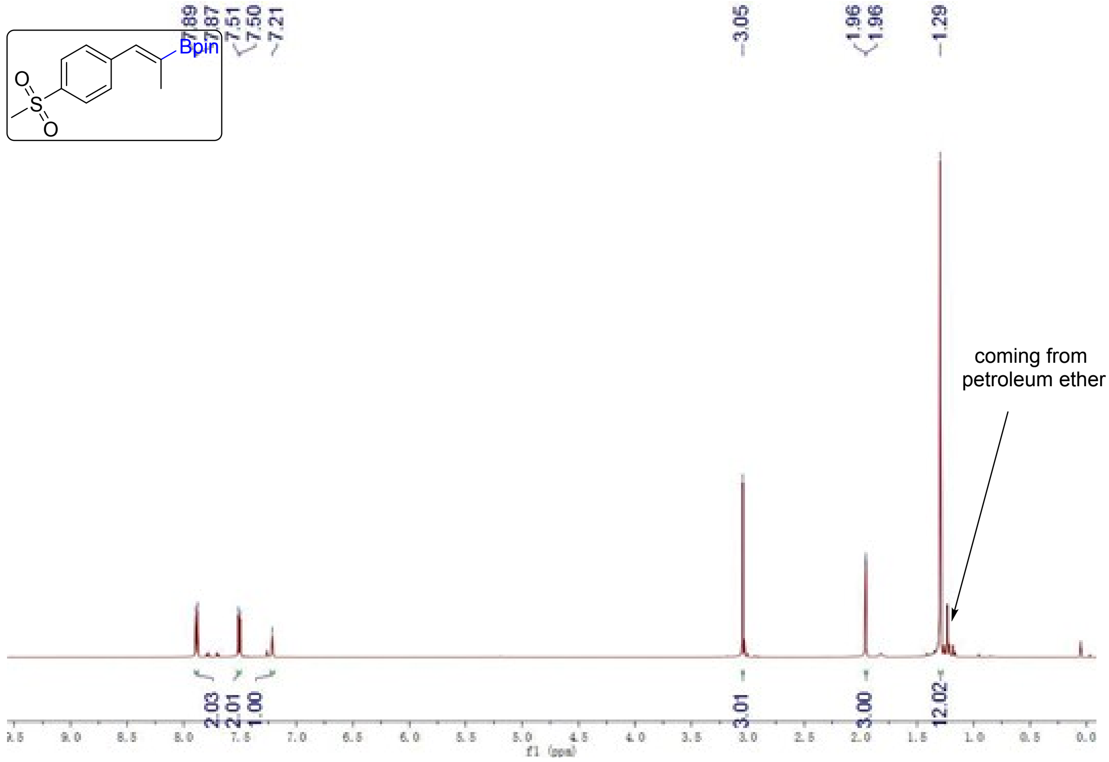

-89.07
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−22
f1 (ppm)

1-(4-(2-(6-phenylpyridin-2-yl)propyl)phenyl)ethan-1-one (9)

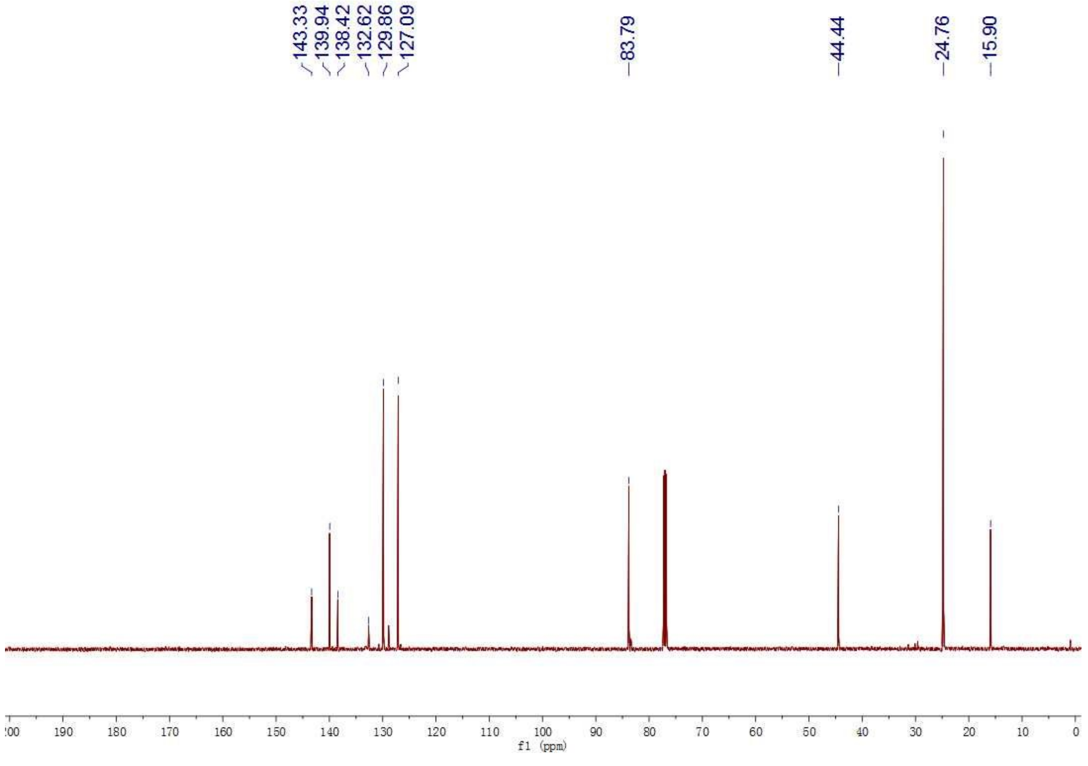




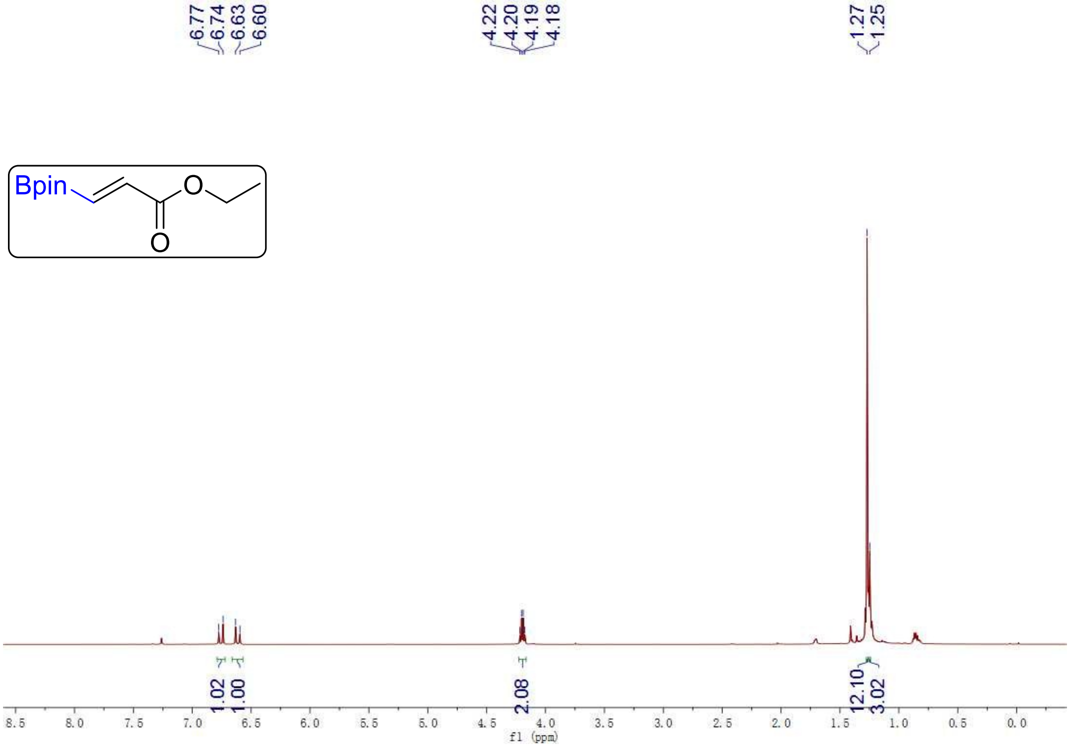
4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)prop-1-en-2-yl)-1,3,2-dioxaborolane (B-1)

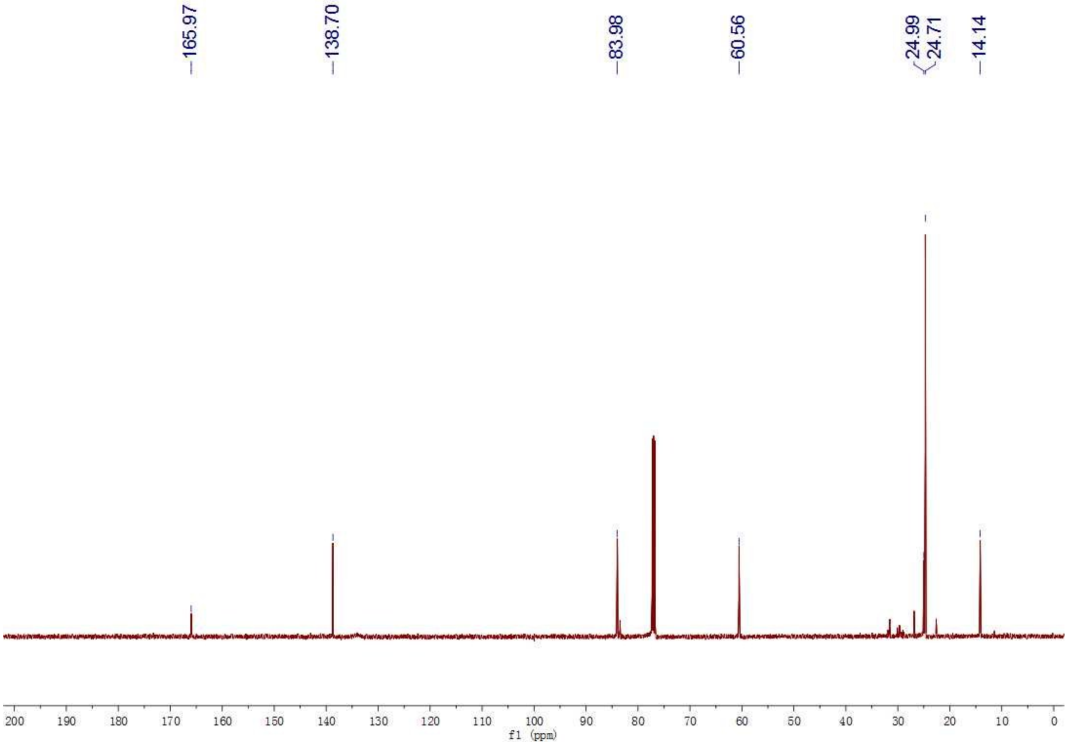


coming from petroleum ether



Ethyl (E)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)acrylate (B-2)





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