Supplementary Information

for

Highly Selective Copper-Catalyzed Trifunctionalization of Alkynyl Carboxylic Acids: An Efficient Route to Bis-Deuterated β-Borylated α, β-Styrene

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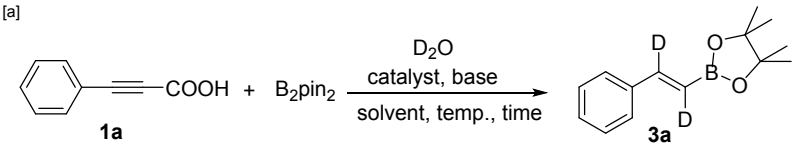
Condition screening

Table 1[a]

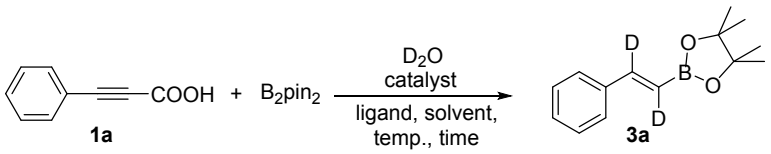


1a 3a

Entry	catalyst [10 mol%]	base [1.2 equiv.]	solvent	temp (^{o}C)	time (h)	yield (%)
1	$Cu(OTf)_2$	Na_2CO_3	benzene	100	21	65
2	$Cu(OAc)_2$	Na_2CO_3	benzene	100	21	45
3	$CuSO_4$	Na_2CO_3	benzene	100	21	27
4	$CuBr_2$	Na_2CO_3	benzene	100	21	24
5	CuCl	Na_2CO_3	benzene	100	21	20
6	$Cu(TFA)_2$	Na_2CO_3	benzene	100	21	73
7	$FeCl_2$	Na_2CO_3	benzene	100	21	7
8	$PdCl_2$	Na_2CO_3	benzene	100	21	0
9	$Cu(OAc)_2$	KOH	benzene	100	18	48
10	$Cu(OAc)_2$	K_2CO_3	benzene	100	18	9
11	$Cu(OAc)_2$	$NaHCO_3$	benzene	100	18	50
12	$Cu(OAc)_2$	KOtBu	benzene	100	18	7
13	$Cu(OAc)_2$	K_3PO_4	benzene	100	18	5
14	$Cu(OTf)_2$	Na_2CO_3	benzene	rt	18	0
15	$Cu(OTf)_2$	Na_2CO_3	benzene	50	18	trace
16	$Cu(OTf)_2$	Na_2CO_3	benzene	80	18	55
17	$Cu(OTf)_2$	Na_2CO_3	benzene	90	18	46
18	$Cu(OTf)_2$	Na_2CO_3	DMSO	80	18	26
19	$Cu(OTf)_2$	Na_2CO_3	DMF	80	18	0
20	$Cu(OTf)_2$	Na_2CO_3	CH_3CN	80	18	63
21	$Cu(OTf)_2$	Na_2CO_3	DMA	80	18	8
22	$Cu(OTf)_2$	Na_2CO_3	1,4-dioxane	80	18	65
23	$Cu(TFA)_2$	Na_2CO_3	1,4-dioxane	80	18	75
24	$Cu(TFA)_2$	–	1,4-dioxane	80	18	37

[a] Reaction conditions: phenylpropiolic acids (1a) (0.5 mmol), bis(pinacolato)diboron (1.2 equiv., 0.6 mmol), catalyst, base,s olvent (1 mL) in a sealed tube under the N_2 atmosphere, GC yield.

Table 2[a]

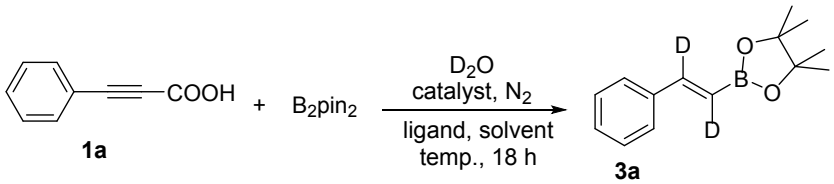


1a 3a

Entry	catalyst [10 mol%]	ligand	solvent	temp (^{o}C)	time (h)	yield (%)
1	$Cu(TFA)_2$	–	1,4-dioxane	80	18	37
2	$Cu(OAc)_2$	–	1,4-dioxane	80	18	42
3	$CuSO_4$	–	1,4-dioxane	80	18	19
4	$CuBr_2$	–	1,4-dioxane	80	18	0
5	Cu_2O	–	1,4-dioxane	80	18	76
6	CuI	–	1,4-dioxane	80	18	0
7	CuCl	–	1,4-dioxane	80	18	2
8	$Cu(OTf)_2$	–	1,4-dioxane	80	18	trace
9	CuOTf	–	1,4-dioxane	80	18	6
10	CuOAc	–	1,4-dioxane	80	18	62
11	$FeCl_2$	–	1,4-dioxane	80	18	0
12	$Pd(PPh_3)_4$	–	1,4-dioxane	80	18	trace
13	CuO	–	1,4-dioxane	80	18	61
14	Cu_2O	–	DMSO	80	18	19
15	Cu_2O	–	DMF	80	18	26
16	Cu_2O	–	CH_3CN	80	18	32
17	Cu_2O	–	toluene	80	18	25
18	Cu_2O	–	THF	80	18	49
19	Cu_2O	–	1,4-dioxane	60	18	17
20	Cu_2O	1,10-Phen	1,4-dioxane	80	18	0
21	Cu_2O	Dppf	1,4-dioxane	80	18	24
22	Cu_2O	Dpephos	1,4-dioxane	80	18	25
23	Cu_2O	Xantphos	1,4-dioxane	80	18	29
24	Cu_2O	PPh_3	1,4-dioxane	80	18	31
25[b]	Cu_2O	–	1,4-dioxane	80	18	35
26[c]	Cu_2O	–	1,4-dioxane	80	18	0
27	Cu_2O	PPh_3	1,4-dioxane	rt	18	96

[a] Reaction conditions: phenylpropiolic acids (1a) (0.5 mmol), bis(pinacolato)diboron (1.2 equiv.,0.6 mmol), catalyst, ligand,solvent (1 mL) in a sealed tube under the N_2 atmosphere, GC yield.
[b] Air atmosphere.
[c] O_2 atmosphere.

Table 3[a]



1a 3a

entry	catalyst [10 mol%]	ligand [10 mol%]	base [2.2 equiv.]	solvent	temp [°C]	yield [%][b]
1	Cu_2O	PPh_3	–	1,4-dioxane	rt	96
2	Cu_2O	Xantphos	–	1,4-dioxane	rt	99 (90)[c]
3	Cu_2O	–	–	1,4-dioxane	rt	0
4	Cu_2O	Dpephos	–	1,4-dioxane	rt	28
5	Cu_2O	PCy_3	–	1,4-dioxane	rt	87
6	Cu_2O	DPPE	–	1,4-dioxane	rt	88
7	Cu_2O	1,10-Phen	–	1,4-dioxane	rt	4
8	Cu_2O	DPPB	–	1,4-dioxane	rt	95
9	Cu_2O	P(*n*-Bu)$_3$	–	1,4-dioxane	rt	29
10	Cu_2O	NHC	–	1,4-dioxane	rt	trace
11	CuCl	Xantphos	–	1,4-dioxane	rt	0
12	$Cu(OAc)_2$	Xantphos	–	1,4-dioxane	rt	85
13	CuI	Xantphos	–	1,4-dioxane	rt	0
14	CuO	Xantphos	–	1,4-dioxane	rt	0

[a] Reaction conditions: phenylpropiolic acids (1a) (0.5 mmol), bis(pinacolato)diboron (1.2 equiv., 0.6 mmol), catalyst, ligand, base,solvent (1 mL) in a sealed tube under the corresponding atmosphere.

[b] GC yields.

[c] Isolated yields

General information

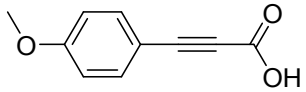
All experiments were conducted with a Schlenk tube. Flash column chromatography was performed over silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a Bruker AVIII-400M or AVIII-500M Bruker spectrometers, Chemical shifts (in ppm) were referenced to $CDCl_3$ (δ = 7.26 ppm) or DMSO-d_6 (δ = 2.50 ppm) as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ = 39.6 ppm). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aromatic alkynyl carboxylic acids were prepared according to the literature procedure. Solvents were dried by refluxing over sodium and freshly distilled prior to use.

General procedure for the synthesis of aryl alkynyl carboxylic acids from aryl iodides or aryl bromides

The method for the synthesis of aryl alkyne carboxylic acids from aryl iodides[1] or aryl bromides[2] was little modified from the method reported previously. A small round bottomed flask was charged with aryl iodide or aryl bromides (5.0 mmol), DBU (2.4 equiv., 12 mmol), $Pd(PPh_3)_4$ (2.5 mol%) and DMSO 6 mL. The solution of propiolic acid (1.2 equiv., 6.0 mmol) in DMSO (6 mL) was poured to the flask. The mixture was stirred at ambient temperature for 12 h. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (20 mL), then filtered through a pad of Celite and concentrated, and poured into EtOAc (50.0 mL), and extracted with $NaHCO_3$ (sat. aq). The aqueous layer was separated, acidified to pH 2.0 by adding cold HCl (1 N), and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, and the solvent was removed under reduced pressure. The resulting crude product was purified by flash chromatography (silica gel, ethyl acetate: petroleum ether = 4:1).

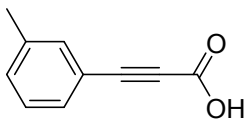
Characterization data of aryl alkynyl carboxylic acids

3-(4-methoxyphenyl)propiolic acid (1b)



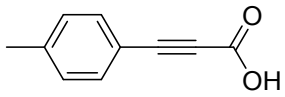
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.57 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 3.80 (s, 3H).^{13}C-NMR (100 MHz, DMSO-d_6) δ = 161.7, 155.0, 135.2, 115.2, 111.1, 85.8, 81.6, 56.0.

3-(m-tolyl)propiolic acid (1c)



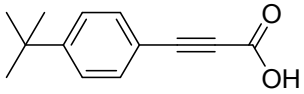
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.43–7.40 (m, 2H), 7.35-7.34 (m, 2H), 2.31(s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.8, 139.0, 133.4, 132.2, 130.2, 129.4, 119.3, 85.1, 82.0, 21.1.

3-(p-tolyl)propiolic acid (1d)



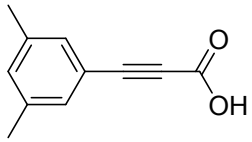
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.51 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ = 154.9, 141.7, 133.1, 130.2, 116.4, 85.4, 81.9, 21.7.

3-(4-(tert-butyl)phenyl)propiolic acid (1e)



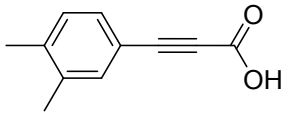
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.58 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 1.30 (s, 9H).^{13}C-NMR (100 MHz, DMSO-d_6) δ = 154.6, 154.0, 132.6, 126.0, 116.2, 84.9, 81.6, 34.9, 30.9.

3-(3, 5-dimethylphenyl)propiolic acid (1f)



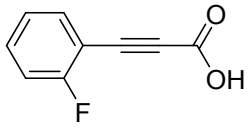
^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.26 (s, 2H), 7.20 (s, 1H), 2.31 (s, 6H).^{13}C-NMR (125 MHz, DMSO-d_6) δ = 155.5, 139.5, 133.6, 131.1, 119.7, 85.9, 82.3, 21.6.

3-(3,4-dimethylphenyl)propiolic acid (1g)



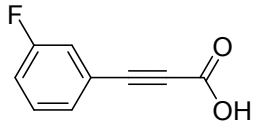
^{1}H NMR (500 MHz, DMSO) δ = 7.38 (s, 1H), 7.33 (dd, J = 7.8, 1.4 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 2.23 (d, J = 13.6 Hz, 6H). ^{13}C NMR (125 MHz, DMSO) δ = 155.0, 140.7, 137.9, 133.7, 130.6 (2C), 116.5, 85.7, 81.7, 19.9, 19.4.

3-(2-fluorophenyl)propiolic acid (1h)



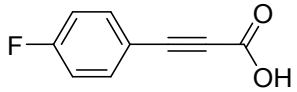
^{1}H NMR (500 MHz, DMSO-d_6): δ 7.71 (td, *J* = 7.5, 1.7 Hz, 1H), 7.61 (dddd, *J* = 8.4, 7.4, 5.6, 1.8 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.31 (td, *J* = 7.6, 1.0 Hz, 1H), 2.55 (s, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 163.3 (d, *J* = 250.8 Hz), 154.5, 135.0, 133.9 (d, *J* = 8.4Hz), 125.6 (d, *J* = 3.5Hz), 116.5 (d, *J* = 20.1 Hz), 108.0 (d, *J* = 15.0 Hz), 86.8 (d, *J* = 2.9 Hz), 78.1.

3-(3-fluorophenyl)propiolic acid (1i)



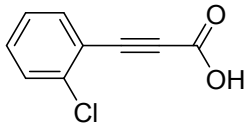
^{1}H-NMR (400 MHz, DMSO-d_6) *δ* = 7.53-7.45 (m, 3H), 7.41-7.37 (m, 1H).^{13}C-NMR (100 MHz, DMSO) *δ* = 162.3 (d, *J* = 245.0 Hz), 154.6, 131.8 (d, *J* = 8.0 Hz), 129.5 (d, *J* = 3.0 Hz), 121.4 (d, *J* = 10.0 Hz), 119.6 (d, *J* = 23.0 Hz), 118.8 (d, *J* = 21.0 Hz), 83.2 (d, *J* = 3.0 Hz), 82.1.

3-(4-fluorophenyl)propiolic acid (1j)



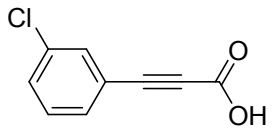
^{1}H-NMR (400 MHz, DMSO-d_6) *δ* = 7.71-7.67 (m, 2H), 7.32-7.27 (m 2H).^{13}C-NMR (100 MHz, DMSO-d_6) *δ* = 163.8 (d, *J* = 250.0 Hz), 154.8, 135.9 (d, *J* = 9.0Hz), 117.0 (d, *J* = 22.0 Hz), 116.0 (d, *J* = 2.0 Hz), 84.0, 82.1.

3-(2-chlorophenyl)propiolic acid (1k)



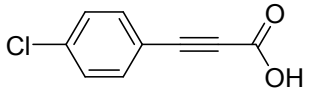
^{1}H NMR (500 MHz, DMSO-d_6) *δ* = 7.73 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.62 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.55 (td, *J* = 7.8, 1.6 Hz, 1H), 7.43 (td, *J* = 7.6, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO-d_6) $^{\delta}$ = 154.2, 135.8, 134.9, 132.6, 129.8, 127.8, 119.1, 86.2, 80.6.

3-(3-chlorophenyl)propiolic acid (1l)



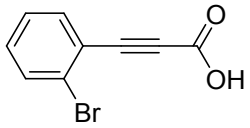
^{1}H-NMR (500 MHz, DMSO-d_6) δ = 7.71-7.61 (m, 1H), 7.60-7.58 (m, 2H), 7.48 (t, J = 8.0 Hz, 1H).^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.6 134.1, 132.4, 131.8, 131.5, 131.4, 121.5, 83.0, 83.0.

3-(4-chlorophenyl)propiolic acid (1m)



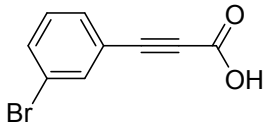
^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.68 – 7.62 (m, 2H), 7.56 – 7.51 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 154.3, 136.0, 134.5, 129.4, 118.0, 83.2, 82.7.

3-(2-bromophenyl)propiolic acid (1n)



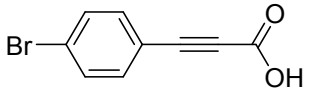
^{1}H NMR (500 MHz, DMSO-d_6) δ = 7.80 – 7.75 (m, 1H), 7.75 – 7.69 (m, 1H), 7.50 – 7.42 (m, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ = 154.2, 135.0, 132.9, 132.6, 128.2, 125.5, 121.4, 85.4, 82.3.

3-(3-bromophenyl)propiolic acid (1o)



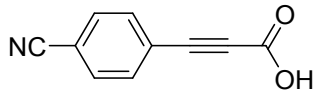
^{1}H NMR (400 MHz, DMSO-d^{6}) δ = 7.83 (t, J = 1.7 Hz, 1H), 7.74 (ddd, J = 8.1, 2.0, 1.0 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.42 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d^{6}) δ = 154.2, 134.75, 134.0, 131.7, 131.2, 121.97 (s), 121.4, 82.8, 82.6.

3-(4-bromophenyl)propiolic acid (1p)



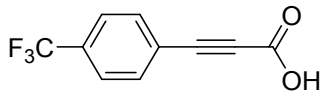
^{1}H NMR (400 MHz, DMSO-d^{6}) δ = 7.70 – 7.66 (m, 2H), 7.59 – 7.54 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d^{6}) δ = 154.3, 134.6, 132.3, 124.8, 118.3, 83.3, 82.7.

3-(4-cyanophenyl)propiolic acid (1q)



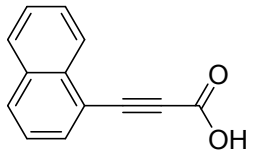
^{1}H NMR (400 MHz, DMSO-d^{6}) δ = 7.90 – 7.85 (m, 2H), 7.78 – 7.72 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d^{6}) δ = 154.1, 133.4, 132.9, 124.0, 118.2, 113.2, 84.7, 82.3.

3-(4-(trifluoromethyl)phenyl)propiolic acid (1r)



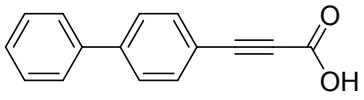
^{1}H-NMR (400 MHz, DMSO-d$_6$) δ = 7.86-7.80 (m, 4H) ^{13}C-NMR (100 MHz, DMSO-d$_6$) δ = 154.5, 133.8, 131.0 (d, J = 32.0Hz), 126.3 (q, J = 4.0 Hz), 124.2 (d, J = 270.0Hz), 123.8, 83.9, 82.8.

3-(naphthalen-1-yl)propiolic acid (1s)



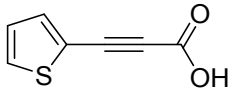
^{1}H-NMR (400 MHz, DMSO-d$_6$) δ = 8.22 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.94-7.92 (m, 1H), 7.75-7.70 (m, 1H), 7.66-7.62(m, 1H), 7.60-7.57(m, 1H).^{13}C-NMR (100 MHz, DMSO-d6) δ = 154.8, 133.4, 133.3, 132.2, 132.0, 129.3, 128.6, 127.7, 126.1 , 125.3, 116.8, 86.9, 82.9

3-([1, 1'-biphenyl]-4-yl)propiolic acid (1t)



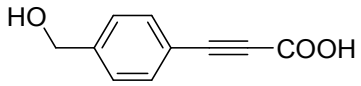
^{1}H-NMR (400 MHz, DMSO-d$_6$) δ = 7.77-7.75 (m, 2H), 7.72-7.69 (m, 4H), 7.50-7.46 (m 2H), 7.42-7.39 (m, 1H).^{13}C-NMR (100 MHz, DMSO-d$_6$) δ = 155.9, 142,8 139.2, 133.8, 129.6, 128.3, 127.7, 127.4, 118.4, 84.9, 82.9.

3-(thiophen-2-yl)propiolic acid (1u)



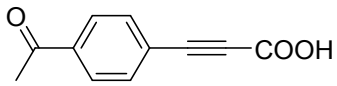
^{1}H-NMR (400 MHz, DMSO-d_6) δ = 7.87 (dd, J = 5.0, 1.2 Hz, 1H), 7.66 (dd, J = 5.0, 1.2 Hz, 1H), 7.20-7.18 (m, 1H).^{13}C-NMR (100 MHz, DMSO-d_6) δ = 154.6, 137.5, 133.2, 128.8, 118.7, 86.3, 79.0.

3-(4-(hydroxymethyl)phenyl)propiolic acid (1v)



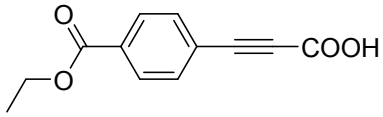
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.58 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 4.54 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.5, 146.0, 132.6, 126.8, 117.1, 84.9, 81.5, 62.5.

3-(4-acetylphenyl)propiolic acid (1w)



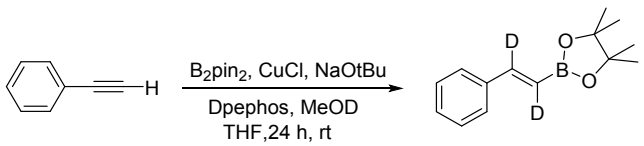
^{1}H NMR (500 MHz, DMSO-d_6) δ 8.00 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 2.60 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 197.4, 154.2, 137.8, 132.8), 128.6, 123.6, 84.2, 82.9, 27.0.

3-(4-(ethoxycarbonyl)phenyl)propiolic acid (1x)



^{1}H NMR (500 MHz, DMSO-d_6) δ 8.05 – 7.93 (m, 2H), 7.80 – 7.71 (m, 2H), 4.32 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.9, 154.1, 132.9, 131.5, 129.5, 123.6, 83.8, 83.0, 61.3, 14.2.

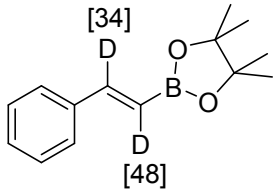
Control experiments



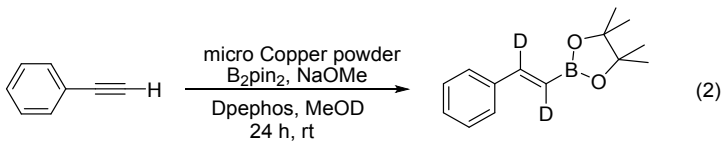
(1)

General procedure [3]**:** In an N_2 filled glovebox, CuCl (0.015 mmol, 1.6 mg), NaO*t*-Bu (0.030 mmol, 3.1 mg) and Dpephos ligand (0.015 mmol, 8 mg) were placed in an oven-dried Schlenk tube and anhydrous THF

(0.45mL) were added. The reaction mixture was stirred for 30 min at ambient temperature and then, bis(pinacolato)diboron (0.55 mmol, 141 mg) and anhydrous THF (0.50 mL) were added. The reaction mixture was stirred for 10 min and phenylacetylene (51 mg, 0.50 mmol) was added, followed by MeOD (2.0 mmol, 80 μL). The reaction tube was sealed, and stirred for 24 h [(Eq. (1)]. The reaction mixture was filtered through a pad of Celite and concentrated. The residue was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the product in 87% yield.



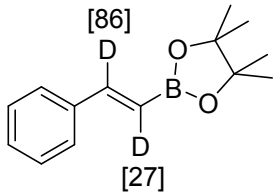
1H NMR (500 MHz, $CDCl_3$) δ = 7.49 (d, J = 7.3 Hz, 2H), 7.45 – 7.37 (m, 0.66H), 7.36 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 6.23 – 6.12 (m, 0.52H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.4 (d, J = 7.0 Hz), 137.4 (d, J = 9.1 Hz), 128.8 (d, J = 0.8 Hz), 128.5, 127.0 (d, J = 1.6 Hz), 83.3, 24.8.



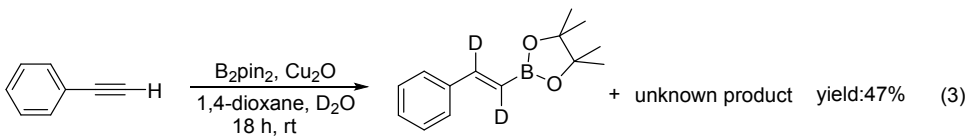
(2)

General procedure [4]**:** In an N_2 filled glovebox, B_2Pin_2 (0.75 mmol, 190.0 mg), micro copper powder (0.05 mmol, 3.4 mg) and MeONa (0.1 mmol, 5.5 mg) were added to a Schlenk tube equipped with a magnetic stirrer. Phenylacetylene (51 mg, 0.5 mmol) and MeOD (2 mL) were added and the tube was sealed and stirred at ambient temperature for 24 h [(Eq. (2)]. After the reaction finished, the resulting solution was dropped into water

(20 mL).The aqueous solution was extracted with CH_2Cl_2 (10 mL x 2). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated, and the residue was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the product in 84% yield.



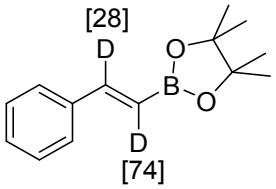
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.53 – 7.47 (m, 2H), 7.45 – 7.37 (m, 0.14H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 6.22 – 6.13 (m, 0.73H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.4 (d, J = 19.8 Hz), 149.1, 148.9, 137.4, 128.9, 128.5, 127.0, 83.3, 24.8.



General procedure: A Schlenk tube (25 ml) with a magnetic stirring bar was charged with Cu_2O (7 mg, 10 mol%) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then phenylacetylene (51 mg, 0.5 mmol), bis(pinacolato)diboro (153 mg, 1.2 equiv., 0.6 mmol), D_2O (6 equiv., 3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred at ambient temperature for 18 h (monitored by TLC and GC) [(Eq. (3)]. Upon completion of the reaction, the reaction mixture was diluted with

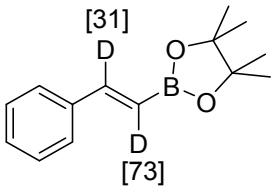
ethyl acetate (20 mL), transferred to a round bottom flask (100 mL). The solvents were removed via rotary evaporator and the residue was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the product. As shown on the ^{1}H NMR and ^{13}C (A and B), little discrepancy was detected on the degree of deuterium incorporation of (*E*)-bis-deuterated β-borylated α, β-styrene **3a** with unknown product as by-product in 47% yield.

A:



^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.38 (m, 0.72H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.32 – 7.27 (m, 1H), 7.26 – 7.15 (m, 2H), 6.95 (t, *J* = 7.6 Hz, 0.23H), 6.55 (dd, *J* = 7.5, 1.6 Hz, 0.20H), 6.22 – 6.15 (m, 0.26H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.5, 149.4 (d, *J* = 7.0 Hz), 137.3 (d, *J* = 7.8 Hz), 133.8 (t, *J* = 2 Hz), 134.0, 129.8, 128.8, 128.5, 128.1 (dd, *J* = 7.1, 3.7 Hz), 127.0 (d, *J* = 1.7 Hz), 126.2, 125.8 (d, *J* = 19.7 Hz), 123.3, 83.2, 34.4, 31.7, 24.7.

B: The repeated experiment:

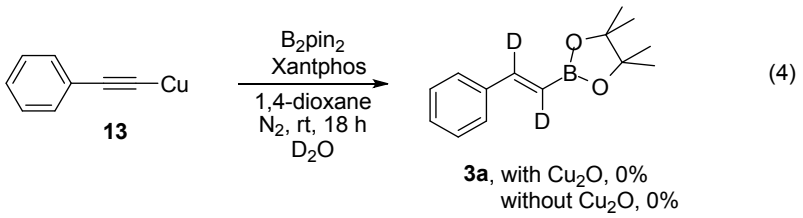


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.54 – 7.48 (m, 2H), 7.45 – 7.38 (m, 0.69H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H), 7.21 (dtd, *J* = 7.9, 6.7, 2.8 Hz, 2H), 6.96 (t, *J* = 7.6

Hz, 0.28H), 6.55 (ddd, *J* = 7.5, 3.5, 1.6 Hz, 0.24H), 6.22 – 6.15 (m, 0.27H), 1.33 (s, 12H).

General procedure for synthesis of (phenylethynyl)copper [5]:

To a solution of copper iodide (3.8 g, 20.0 mmol) in a mixture of ammonium hydroxide (28% NH_3 solution, 50 mL) and ethanol (30 mL) was added the alkyne (10.0 mmol) dropwise. The mixture was stirred overnight at room temperature under N_2 and the yellow precipitate was collected by filtration and successively washed with ammonium hydroxide (10% NH_3 solution, 3 x 50 mL), water (3 x 50 mL), ethanol (3 x 50 mL), and diethyl ether (3 x 50 mL). The bright yellow solid was then dried under high vacuum overnight to afford the desired polymeric alkynylcopper reagent which was used without further purification.

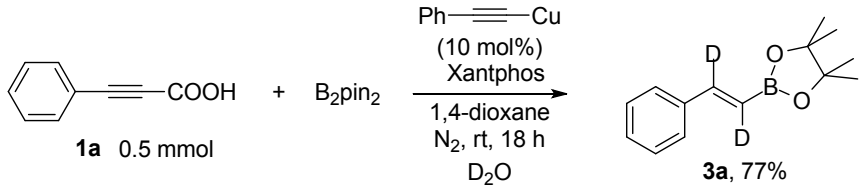


(4)

General procedure for the synthesis of (*E*)-bis-deuterated β-borylated α,β-styrene derivatives from (phenylethynyl)copper:

A Schlenk tube (25 ml) with a magnetic stirring bar was charged with Cu_2O (7 mg, 10 mol%) (without Cu_2O) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then (phenylethynyl)copper (82 mg, 0.5 mmol), bis(pinacolato)diboro (153 mg, 1.2 equiv., 0.6 mmol), D_2O (6

equiv., 3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2 [(Eq. (4)]. The reaction mixture was stirred at ambient temperature for 18 h (monitored by TLC and GC). No desired product (*E*)-bis-deuterated β-borylated α, β-styrene **3a** was detected with most starting material remaining.

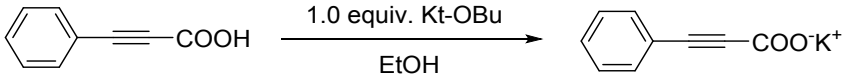


(5)

General procedure for the synthesis of (*E*)-bis-deuterated β-borylated α,β-styrene derivatives from phenylpropiolic acids and (phenylethynyl)copper (10 mol%) as catalyst:

A Schlenk tube (25 ml) with a magnetic stirring bar was charged with (phenylethynyl)copper (8.2 mg, 10 mol%) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then phenylpropiolic acids (73 mg, 0.5 mmol), bis(pinacolato)diboro (167 mg, 1.2 equiv., 0.66 mmol), D_2O (3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2 [(Eq. (5)]. The reaction mixture was stirred at ambient temperature for 18 h (monitored by TLC and GC). Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (20 mL), transferred to a round bottom flask (100 mL). The solvents were removed via rotary evaporator and the residue was purified

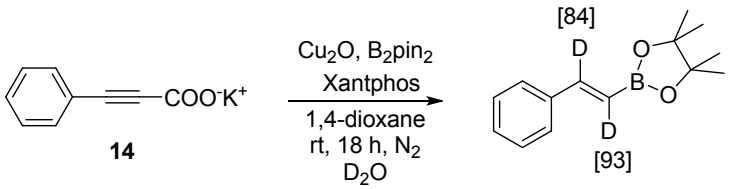
by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the desired product in 77% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 (dt, J = 8.3, 1.8 Hz, 2H), 7.40 (s, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.26 (m, 1H), 6.17 (dd, J = 4.8, 2.3 Hz, 1H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.4, 137.3 (d, J = 9.1 Hz), 128.8, 128.5, 127.0 (d, J = 1.7 Hz), 83.3, 24.7.



(6)

General procedure for synthesis of potassium 3-phenylpropiolate [6]:

A 100 mL round-bottomed flask was charged with the nitrophenyl phenylpropiolic acid (5.0 mmol) and ethanol (6 mL). To this, a solution of potassium tert-butoxide (5.0 mmol) in ethanol (6 mL) was added dropwise over 10 min. After completion of addition, the reaction mixture was stirred for another 1 h at ambient temperature [(Eq. (6)]. After removing the ethanol solvent by slow evaporation on rotary evaporator, 15 mL diethyl ether was added. The resulting solid was collected by filtration, washed sequentially with ethanol (1 mL x 2) and diethyl ether (10 mL x 2), transferred to a round-bottomed flask and dried under vacuum at 30 °C for 2 h to provide the 3-phenylpropiolate.

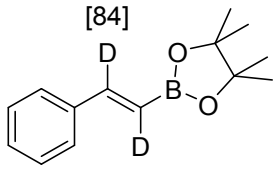


51% (7)

General procedure: A Schlenk tube (25 ml) with a magnetic stirring bar

was charged with Cu_2O (7 mg, 10 mol%) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then 3-phenylpropiolate (92 mg, 0.5 mmol), bis(pinacolato)diboro (153 mg, 1.2 equiv., 0.6 mmol), D_2O (6 equiv., 3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred at ambient temperature for 18 h (monitored by TLC and GC) [(Eq. (7)]. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (20 mL), transferred to a round bottom flask (100 mL). The solvents were removed via rotary evaporator and the residue was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the product in 51% yield.

[84]



[93]

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.49 (dt, J = 8.2, 1.8 Hz, 2H), 7.40 (s, 0.16H), 7.37 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 6.17 (s, 0.07H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.41 (s), 137.37 (d, *J* = 9.1 Hz), 128.84 (s), 128.52 (s), 127.00 (d, *J* = 1.6 Hz), 83.29 (s), 24.78 (s).

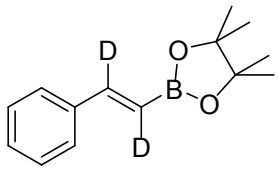
General procedure for the synthesis of (*E*)-bis-deuterated β-borylated α,β-styrene derivatives from alkynyl acids with bis(pinacolato)diboron:

A Schlenk tube (25 ml) with a magnetic stirring bar was charged with

Cu_2O (7 mg, 10 mol%) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then alkynyl acids **1** (0.5 mmol), bis(pinacolato)diboro **2** (153 mg, 1.2 equiv., 0.6 mmol), D_2O (6 equiv., 3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred at ambient temperature for 18 h (monitored by TLC and GC). Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate (20 mL), transferred to a round bottom flask (100 mL). The solvents were removed via rotary evaporator and the residue was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50:1) to give the desired products.

Characterization data of (*E*)-bis-deuterated β-borylated α, β-styrene derivatives

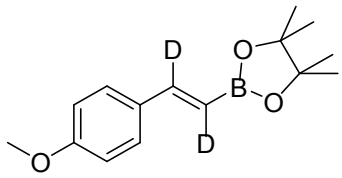
(*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1,2-d_2)-1,3,2-dioxaborolane (3a)



The title compound was prepared on a 0.5 mmol scale and obtained as a colorless oil (104 mg, 90% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.52 (dd, J = 8.2, 1.2 Hz, 2H), 7.43 (s, 0.16H), 7.39 – 7.34 (m, 2H), 7.34 – 7.29 (m, 1H), 6.20 (s, 0.08H), 1.34 (s, 12H). ^{13}C NMR (125

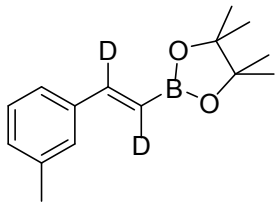
MHz, $CDCl_3$) δ = 149.4, 137.4 (d, J = 9.1 Hz), 128.8, 128.5, 127.0 (d, J = 1.6 Hz), 83.3, 24.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{14}H_{18}D_2BO_2^+$ 233.1676, found 233.1676.

(*E*)-2-(2-(4-methoxyphenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (113 mg, 87% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 – 7.38 (m, 2H), 7.34 (s, 0.10H), 6.94 – 6.75 (m, 2H), 3.81 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.2, 149.0, 130.3, 128.4, 113.9, 83.2, 55.2, 24.8. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{20}D_2BO_3^+$ 263.1782, found 263.1783.

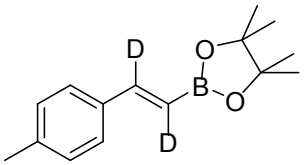
(*E*)-4,4,5,5-tetramethyl-2-(2-(m-tolyl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3c)



The title compound was prepared on a 0.5 mmol scale and obtained as a colorless oil (108 mg, 88% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.37 (s, 0.15H), 7.32 – 7.28 (m, 2H), 7.23 (t, J = 7.8 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 6.15 (s, 0.07H), 2.35 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 138.9, 134.7 (d, J = 9.0 Hz), 129.3, 127.0 (d, J = 1.5 Hz), 83.2, 24.8, 21.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{20}D_2BO_2^+$ 247.1833, found 247.1833.

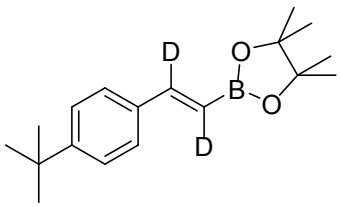
(*E*)-4,4,5,5-tetramethyl-2-(2-(p-tolyl)vinyl-1,2-d_2)-1,3,2-dioxaborolane

(3d)



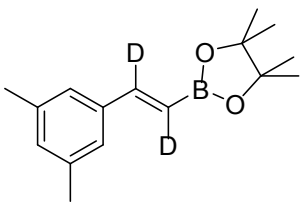
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (107 mg, 87% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.39 (d, J = 8.1 Hz, 2H), 7.37 (s, 0.11H), 7.14 (d, J = 7.9 Hz, 2H), 6.11 (s, 0.07H), 2.35 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.4, 138.9, 134.7 (d, J = 9.0 Hz), 129.3, 127.0 (d, J = 1.5 Hz), 83.2, 24.8, 21.3. HRMS (ESI) m/z $[M + H]^+$ calcd for $C_{15}H_{20}D_2BO_2^+$ 247.1833, found 247.1833.

(*E*)-2-(2-(4-(tert-butyl)phenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)



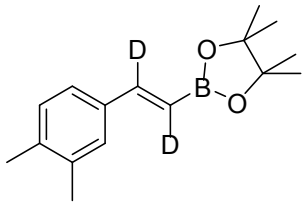
The title compound was prepared on a 0.5 mmol scale and obtained as a colorless crystal (115 mg, 80% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 (d, J = 8.5 Hz, 2H), 7.38 – 7.35 (m, 2H), 6.12 (s, 0.07H), 1.32 (s, 21H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 152.1, 149.3, 134.7 (d, J = 8.9 Hz), 126.8 (d, J = 1.7 Hz), 125.5), 83.2, 34.7, 31.2, 24.8. HRMS (EI+) m/z $[M\text{-}H^+]$ calcd for $C_{18}H_{25}D_2BO_2$ 287.2249, found 287.2259.

(*E*)-2-(2-(3,5-dimethylphenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)



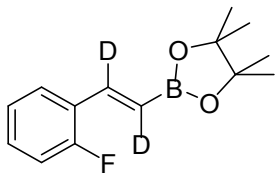
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (117 mg, 90% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 (s, 0.10H), 7.11 (s, 2H), 6.94 (s, 1H), 6.13 (s, 0.06H), 2.31 (s, 6H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 149.7, 137.9, 137.4 (d, J = 9.3 Hz), 130.6, 124.9, 83.2, 24.8, 21.2. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{16}H_{21}D_2BO_2$ 259.1944, found 259.1949.

(*E*)-2-(2-(3,4-dimethylphenyl)vinyl-1,2-d$_2$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (107 mg, 82% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.36 (s, 0.09H), 7.27 (s, 1H), 7.24 (dd, J = 7.8, 1.5 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 6.10 (s, 0.05H), 2.26 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 137.6, 136.6, 135.1 (d, J = 8.9 Hz), 129.8, 128.3, 124.55 (s), 83.2, 24.8, 19.8, 19.6. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{16}H_{21}D_2BO_2$ 259.1944, found 259.1954.

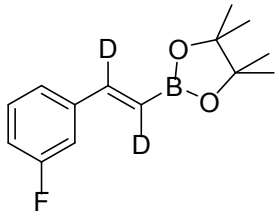
(*E*)-2-(2-(2-fluorophenyl)vinyl-1,2-d$_2$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (79 mg, 63% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58 (td, J = 7.6, 1.7 Hz, 1H), 7.27 (dddd, J = 8.1, 7.2, 5.6, 1.7 Hz, 1H), 7.13 (td, J = 7.6, 1.1 Hz, 1H), 7.05 (ddd, J = 10.6, 8.2, 1.0 Hz,

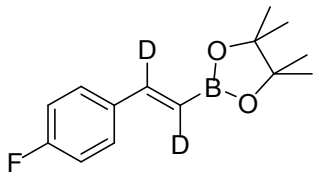
1H), 6.25 (s, 0.07H), 1.33 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 160.7 (d, J = 250 Hz), 141.2 (d, J = 4.1 Hz), 130.1 (d, J = 8.5 Hz), 127.4 (t, J = 3.0 Hz), 125.2 (d, J = 11.3 Hz), 124.1 (d, J = 3.6 Hz), 115.8 (d, J = 22.5 Hz), 83.4, 24.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{14}H_{16}D_2BFO_2$ 249.1542, found 249.1548.

(*E*)-2-(2-(3-fluorophenyl)vinyl-1,2-d$_2$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (89 mg, 75% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.33 (s, 0.14H), 7.29 (td, J = 7.9, 5.8 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.01 – 6.96 (m, 1H), 6.16 (s, 0.05H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.6 (d, J = 243.7 Hz), 148.0, 139.8, 130.0 (d, J = 8.3 Hz), 123.0, 115.7, 115.6 (d, J = 21.2 Hz), 113.3 (d, J = 21.2 Hz), 83.5, 24.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{14}H_{16}D_2BFO_2$ 249.1542, found 249.1543.

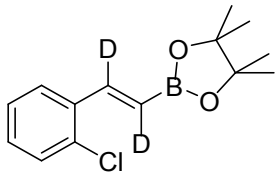
(*E*)-2-(2-(4-fluorophenyl)vinyl-1,2-d$_2$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (91 mg, 73% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.50 – 7.42 (m, 2H), 7.34 (s, 0.14H), 7.07 – 6.97 (m, 2H), 6.06 (s, 0.07H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 163.1 (d, J =

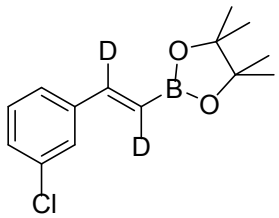
247.5 Hz), 148.1, 133.6, 128.7 (d, J = 8.2 Hz), 115.5 (d, J = 21.2 Hz), 83.4, 24.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BFO_2$ 250.1509, found 250.1505.

(*E*)-2-(2-(2-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (79 mg, 63% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.77 (s, 0.14H), 7.65 – 7.61 (m, 1H), 7.37 – 7.34 (m, 1H), 7.26 – 7.19 (m, 2H), 6.16 (s, 0.07H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.9, 135.5, 133.8, 129.8, 129.6, 127.0, 126.8, 83.5, 24.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BClO_2$ 266.1214, found 266.1208.

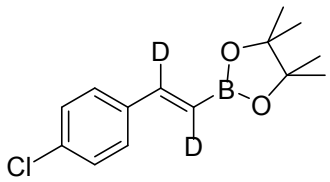
(*E*)-2-(2-(3-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (116 mg, 84% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (d, J = 0.9 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.30 (s, 0.19H), 7.26 – 7.22 (m, 2H), 6.15 (s, 0.07H), 1.30 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.7, 139.2 (d, J = 9.1 Hz), 134.5, 129.7, 128.7, 126.9 (d, J = 1.3 Hz), 125.1 (d, J = 1.9 Hz), 83.4 (s), 24.7 (s). HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BClO_2$ 266.1214, found 266.1219.

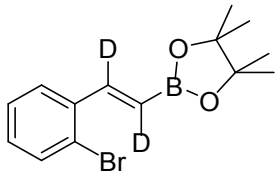
(*E*)-2-(2-(4-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (3m)



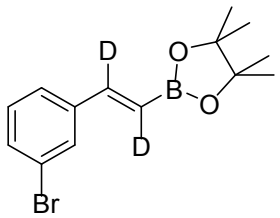
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (112 mg, 87% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.43 – 7.38 (m, 2H), 7.32 (s, 0.16H), 7.32 – 7.28 (m, 2H), 6.12 (s, 0.06H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.9, 135.9 (d, J = 9.1 Hz), 134.6, 128.8, 128.2 (d, J = 1.5 Hz), 83.4, 24.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BClO_2$ 266.1214, found 266.1210.

(*E*)-2-(2-(2-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)



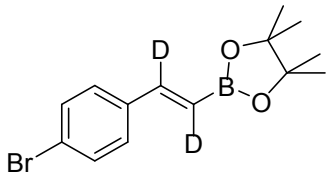
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (50 mg, 34% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.70 (s, 0.15H), 7.61 (dd, J = 7.8, 1.6 Hz, 1H), 7.55 (dd, J = 8.0, 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.13 (td, J = 7.8, 1.6 Hz, 1H), 6.12 (s, 0.05H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.4, 137.3 (d, J = 10.2 Hz), 133.0, 129.9, 127.5, 127.3, 124.2, 83.5, 24.8. HRMS (EI+) m/z $[M\text{-}H^+]$ calcd for $C_{14}H_{16}D_2BBrO_2$ 309.0736, found 309.0741.

(*E*)-2-(2-(3-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)



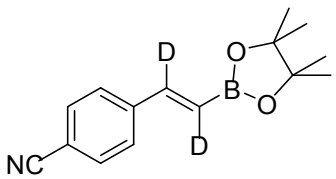
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (114 mg, 74% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.61 (t, J = 1.7 Hz, 1H), 7.39 (tdd, J = 8.2, 1.7, 1.0 Hz, 2H), 7.29 (s, 0.16H), 7.19 (t, J = 7.8 Hz, 1H), 6.15 (s, 0.08H), 1.30 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.6, 139.5, 131.6, 130.0, 129.9, 125.6 (d, J = 2.0 Hz), 122.7, 83.4, 24.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BBrO_2$ 310.0709, found 310.0706.

(*E*)-2-(2-(4-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)



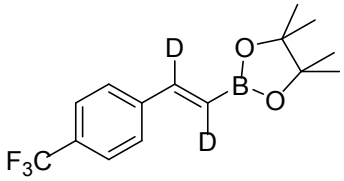
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (114 mg, 77% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 – 7.44 (m, 2H), 7.36 – 7.32 (m, 2H), 7.31 (s, 0.20H), 6.14 (s, 0.07H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.0, 136.3 (d, J = 9.2 Hz), 131.7, 128.5 (d, J = 1.6 Hz), 122.9, 83.4, 24.8. HRMS (EI+) m/z $[M]^+$ calcd for $C_{14}H_{16}D_2BBrO_2$ 310.0709, found 310.0710.

(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d_2)benzonitrile (3q)



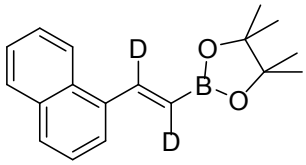
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (76 mg, 70% yield). Deuterium incorporation was determined by 1H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 – 7.58 (m, 2H), 7.54 (d, J = 8.6 Hz, 2H), 7.35 (s, 0.21H), 6.27 (s, 0.08H), 1.31 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.99 (s), 141.58 (d, J = 9.3 Hz), 132.4, 128.8, 127.4 (d, J = 1.8 Hz), 118.7, 111.9, 83.7, 24.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{15}H_{16}D_2BNO_2$ 256.1576, found 256.1588.

(*E*)-4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)vinyl-1,2-d$_2$)-1,3,2-dioxaborolane (3r)



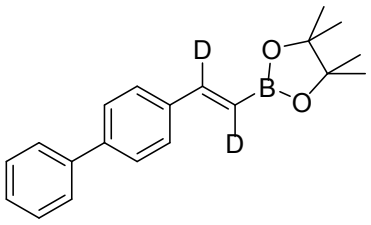
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (99 mg, 70% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.62 – 7.50 (m, 4H), 7.39 (s, 0.22H), 6.25 (s, 0.07H), 1.32 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.6, 140.7 (d, J = 8.7 Hz), 130.4 (q, J = 32.5), 127.1 (d, J = 1.7 Hz), 125.5 (q, J = 3.8 Hz), 125.1, 123.0, 83.6, 24.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{15}H_{16}D_2BF_3O_2$ 299.1518, found 299.1515.

(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl-1,2-d$_2$)-1,3,2-dioxaborolane (3s)



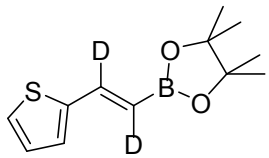
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (113 mg, 80% yield ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.29 (d, J = 8.2 Hz, 1H), 8.24 (s, 0.16H), 7.89 – 7.80 (m, 2H), 7.79 – 7.73 (m, 1H), 7.59 – 7.44 (m, 3H), 6.29 (s, 0.06H), 1.37 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 146.3, 135.2 (d, J = 14.1 Hz), 133.6, 131.0, 129.0, 128.4, 126.1, 125.7, 125.5, 124.0, 123.7, 83.4, 24.8. HRMS (ESI) m/z [M + H]$^+$ calcd for $C_{18}H_{20}D_2BO_2^+$ 283.1833, found 283.1836.

(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



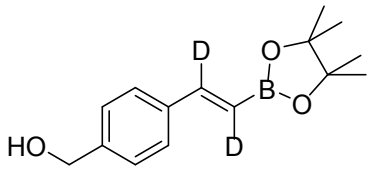
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (136 mg, 93% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.64 – 7.56 (m, 6H), 7.45 (dd, J = 10.5, 4.9 Hz, 2H), 7.38 – 7.33 (m, 1H), 6.22 (s, 0.06H), 1.34 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 148.9, 141.5, 140.5, 136.4 (d, J = 9.3 Hz), 128.8, 127.5 (d, J = 2.5 Hz), 127.4, 127.2, 126.9, 83.3, 24.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{20}H_{21}D_2BO_2$ 307.1968, found 307.1959.

(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3u)



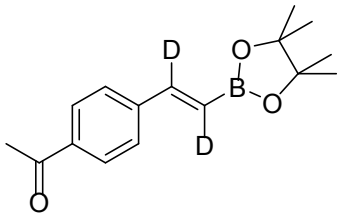
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (64 mg, 54% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.46 (s, 0.14H), 7.24 (dd, J = 5.0, 1.1 Hz, 1H), 7.08 (dd, J = 3.6, 1.1 Hz, 1H), 6.98 (dd, J = 5.0, 3.6 Hz, 1H), 5.90 (s, 0.06H), 1.30 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 143.8, 141.7, 127.6 (d, J = 3.7 Hz), 127.5, 126.2, 83.3, 24.8. HRMS (EI+) m/z [M]$^+$ calcd for $C_{12}H_{15}D_2BO_2S$ 238.1168, found 238.1163.

(*E*)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)phenyl)methanol (3v)



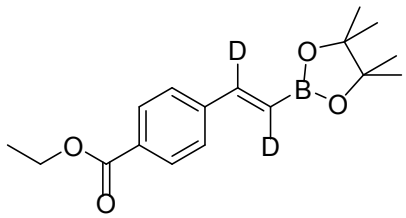
The title compound was prepared on a 0.45 mmol scale and obtained as a colorless oil (92 mg, 79% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 2.2 Hz, 0.27H), 7.31 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 0.13H), 4.66 (s, 2H), 1.30 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0 (d, J = 7.2 Hz), 141.6, 136.7 (d, J = 8.9 Hz), 132.2, 127.1, 83.3, 64.8, 24.7. HRMS (APCI+) m/z $[M+H]^+$ calcd for $C_{15}H_{20}D_2BO_3$ 263.1782, found 263.1783.

(*E*)-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)phenyl)ethan-1-one (3w)



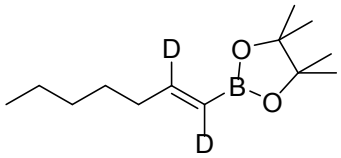
The title compound was prepared on a 0.5 mmol scale and obtained as a colorless oil (123 mg, 83% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.3 Hz, 0.14H), 7.54 (d, J = 8.3 Hz, 2H), 7.39 (s, 0.23H), 2.58 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.5, 147.9, 141.7 (d, J = 9.1 Hz), 136.9, 128.6, 127.0 (d, J = 1.8 Hz), 83.5, 26.6, 24.7. HRMS (APCI+) m/z $[M+H]^+$ calcd for $C_{16}H_{20}D_2BO_3$ 275.1782, found 275.1779.

Ethyl(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)benzoate (3x)



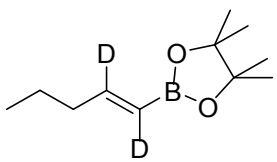
The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (95 mg, 71% yield). Deuterium incorporation was determined by ^{1}H NMR analysis.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.92 (d, J = 8.3 Hz, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.38 (s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.29 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 148.0, 141.4 (d, J = 9.2 Hz), 130.4, 129.8, 126.7, 83.4, 60.9, 24.7, 14.2. HRMS (APCI+) m/z $[M+H]^+$ calcd for $C_{17}H_{22}D_2BO_4$ 305.1888, found 305.1884.

(*E*)-2-(hept-1-en-1-yl-1,2-d$_2$)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3y)



The title compound was prepared on a 0.5 mmol scale and obtained as a colorless oil (46 mg, 41% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.13 (t, J = 7.2 Hz, 2H), 1.44 – 1.38 (m, 2H), 1.33 – 1.22 (m, 16H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.8, 83.0, 35.6, 31.4, 27.9, 24.8, 22.5, 14.0. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{13}H_{23}D_2BO_2$ 225.2109, found 225.2102.

(*E*)-4,4,5,5-tetramethyl-2-(pent-1-en-1-yl-1,2-d$_2$)-1,3,2-dioxaborolane (3z)



The title compound was prepared on a 0.5 mmol scale and obtained as a white solid (42 mg, 42% yield). Deuterium incorporation was determined by ^{1}H NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 2.12 (t, J = 7.3 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.26 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 154.5, 83.0, 37.7, 24.8, 21.4, 13.8. HRMS (EI+) m/z [M-H$^+$] calcd for $C_{11}H_{19}D_2BO_2$ 197.1788, found 197.1793.

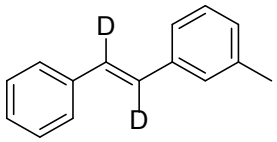
Synthetic utility of the (*E*)-bis-deuterated β-borylated α, β-styrene derivatives

General procedure for the synthesis of (*E*)-1-methyl-3-(2-phenylvinyl-1,2-d$_2$)benzene 4 through a two-step one-pot Suzuki-Miyaura cross-coupling reaction sequence with phenylpropiolic acid as the starting material [7]:

A Schlenk tube (50 ml) with a magnetic stirring bar was charged with Cu_2O (7 mg, 10 mol%) and Xantphos (28 mg, 10 mol%), and shook to make them mix well. Then phenylpropiolic acid **1a** (73 mg, 0.5 mmol), bis(pinacolato)diboron 2 (153 mg, 1.2 equiv., 0.6 mmol), D_2O (60 mg, 6 equiv., 3 mmol) and 1,4-dioxane (1 mL) were added into the tube. A rubber septum was replaced with a glass stopper, and the system was then evacuated twice and back filled with N_2. The reaction mixture was stirred at ambient temperature for 18 h. To a solution of crude mixture of **3** were added palladium(II) acetate(6 mg, 0.025 mmol, 5 mol%), Cs_2CO_3 (491m g, 1.5 mmol), tri-tert-butylphosphine (24 μL, 0.1 mmol) and

bromobenzene (79 μL, 0.75 mmol) and 1,4 dioxane (2.5mL). The vial was sealed and heated to 80 °C overnight. Then the suspension was diluted with ethyl acetate (20 mL) and filtered through a pad of Celite. After that, the solution was washed with brine (10 mL), dried (Na_2SO_4) and concentrated in vacuo. The crude was purified by flash chromatography (silica gel, petroleum ether: ethyl acetate = 30 : 1) to give the desired product **4** (75 mg) in 78% overall yield as a white solid.

(*E*)-1-methyl-3-(2-phenylvinyl-1,2-d_2)benzene (4)



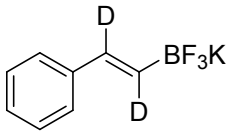
^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.59 – 7.52 (m, 2H), 7.42 – 7.32 (m, 4H), 7.28 (t, J = 7.7 Hz, 2H), 7.11 (d, J = 7.5 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.2, 137.3, 137.1, 128.6, 128.5, 128.4, 128.3, 127.5, 127.1, 126.4 (2 C), 123.7, 21.4. HRMS (EI+) m/z $[M]^+$ calcd for $C_{15}H_{12}D_2$ 196.1211, found 196.1218.

General Procedure for the Conversion of (*E*)-bis-deuterated β-borylated α, β-styrene to the (*E*)-bis-deuterated potassium alkenyltrifluoroborate 5 [8]:

After dissolving compound (*E*)-bis-deuterated β-borylated α, β-styrene **3a** (116mg, 0.5 mmol) in MeOH (1 mL) at ambient temperature, a saturated aqueous solution of potassium hydrogen fluoride (~ 4.5 M, 0.6 mL) was added dropwise and the reaction was allowed to stir at ambient temperature for 4 h. The solvent was then removed in vacuo to afford a

mixture of solids that was dried under high vacuum overnight. Extraction of the solid mixture with acetone (3 × 4 mL), followed by Buchner funnel filtration (3×) afforded a solution of the product in acetone. This solution was then reduced in vacuo to afford a concentrated acetone solution of the product (~ 1 mL). After addition of Et_2O (10 mL) and Buchner funnel filtration of the precipitate, the desired product **5** (89 mg) was obtained in 84% yield as a white crystalline solid.

(*E*)-trifluoro(2-phenylvinyl-1,2-d_2)-l4-borane, potassium salt (5)



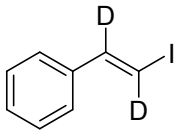
^{1}H NMR (500 MHz, DMSO-d^6) δ = 7.30 (d, J = 7.5 Hz, 2H), 7.24 (t, J = 7.7 Hz, 2H), 7.10 (t, J = 7.2 Hz, 1H), 6.47 (s, 0.21H), 6.15 (s, 0.1H). ^{13}C NMR (125 MHz, DMSO) δ = 140.5 (d, J = 8.1 Hz), 134.1 (d, J = 4.7 Hz), 128.9, 126.6, 125.9 (d, J = 2.7 Hz) ^{19}F NMR (471 MHz, DMSO) δ = −137.5. HRMS (EI+) m/z [M-F]$^+$ calcd for $C_8H_5D_2BF_2$ 153.0771, found 153.0775.

General Procedure for the Conversion of (*E*)-bis-deuterated β-borylated α, β-styrene to the (*E*)-(2-iodovinyl-1,2-d_2)benzene (6) [9]:

To a solution of (*E*)-bis-deuterated β-borylated α, β-styrene **3a** (116mg, 0.5 mmol) in THF (5 mL) were added a 3.0 M solution of NaOH (1.5 mmol, 3 equiv) followed 10 minute later by a 0.2 M solution of I_2 in THF (1.0 mmol, 2 equiv). The reaction is complete after 20 minutes. The organic solution was diluted in Et_2O and then the organic phase was washed with a saturated solution of $Na_2S_2O_3$ then with brine. The organic

phase was dried over Na_2SO_4 and concentrated under vacuum. The crude was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50 : 1) to give the desired product **8** (96 mg) in 84% yield as a faint yellow oil.

(*E*)-(2-iodovinyl-1,2-d_2)benzene (6)

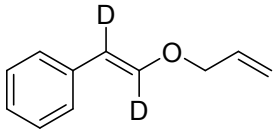


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.44 (dd, J = 8.5, 6.4 Hz, 0.35H), 7.38 – 7.27 (m, 5H), 6.84 (dd, J = 8.5, 6.3 Hz, 0.16H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 144.8, 137.6 (d, J = 10.8 Hz), 128.6, 128.3, 125.9 (d, J = 1.9 Hz). HRMS (EI+) m/z $[M]^+$ calcd for $C_8H_5D_2I$ 231.9718, found 231.9725.

General Procedure for the Conversion of (*E*)-bis-deuterated β-borylated α, β-styrene to the (*E*)-(2-(allyloxy)vinyl-1,2-d_2)benzene (7) [10]**:**

(*E*)-bis-deuterated β-borylated α, β-styrene **3a** (116mg, 0.5 mmol) was added to a round bottom flsk (10 mL), followed by ally alcohol (3 mL), triethylamine (202 mg, 4 equiv. 2 mmol) and $Cu(OAc)_2$ (181 mg, 2equiv., 1 mmol). The reaction was capped and stirred overnight. The reaction mixture was poured into ether (20 mL) and washed with water (2 x 30 mL) and brine (30 mL) and dried over anhydrous Na_2SO_4. The solvent were removed under reduced pressure. The crude was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50 : 1) to give the desired product **7** (72 mg) in a 89% yield as a colorless oil.

(*E*)-(2-(allyloxy)vinyl-1,2-d$_2$)benzene (7)

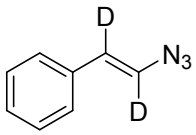


^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 – 7.22 (m, 4H), 7.16 (ddd, J = 8.6, 3.0, 1.5 Hz, 1H), 7.01 (dd, J = 4.5, 2.8 Hz, 0.1H), 6.03 (ddt, J = 17.2, 10.7, 5.4 Hz, 1H), 5.92 (s, 0.24H), 5.42 (dq, J = 17.2, 1.6 Hz, 1H), 5.31 (ddd, J = 10.5, 2.7, 1.3 Hz, 1H), 4.40 (dt, J = 5.4, 1.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 147.4 (d, J = 8.3 Hz), 136.2 (d, J = 7.1 Hz), 133.1, 128.5, 125.6, 125.0 (d, J = 4.6 Hz), 117.8, 106.4, 70.6. HRMS (EI+) m/z $[M]^+$ calcd for $C_{11}H_{10}D_2O$ 162.1014, found 102.1020.

General Procedure for the Conversion of (*E*)-bis-deuterated β-borylated α, β-styrene to the (*E*)-(2-azidovinyl-1,2-d$_2$)benzene (8) [11]:

In an oven dried round bottom flask were introduced sodium azide (0.75 mmol, 1.5 equiv) followed by anhydrous $CuSO_4$ (48 mg, 0.3 mmol, 0.6 equiv), (*E*)-bis-deuterated β-borylated α, β-styrene **3a** (116mg, 0.5 mmol) diluted in MeOH (2 mL) was added dropwise. After 4 h, all volatile solvents were removed under reduced pressure. The crude was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 50 : 1) to give the desired product **6** (62 mg) in 84% yield as a faint yellow oil.

(*E*)-(2-azidovinyl-1,2-d2)benzene (8)



^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.34 – 7.27 (m, 3H), 7.26 – 7.21 (m, 1H), 6.61 (dd, J = 3.8, 2.0 Hz, 0.08H), 6.31 – 6.25 (m, 0.22H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 134.9

(d, J = 7.9 Hz), 128.7, 127.3, 125.7, 119.6. HRMS (EI+) m/z $[M]^+$ calcd for $C_8H_5D_2N_3$ 147.0766, found 147.0773.

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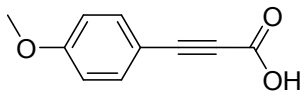
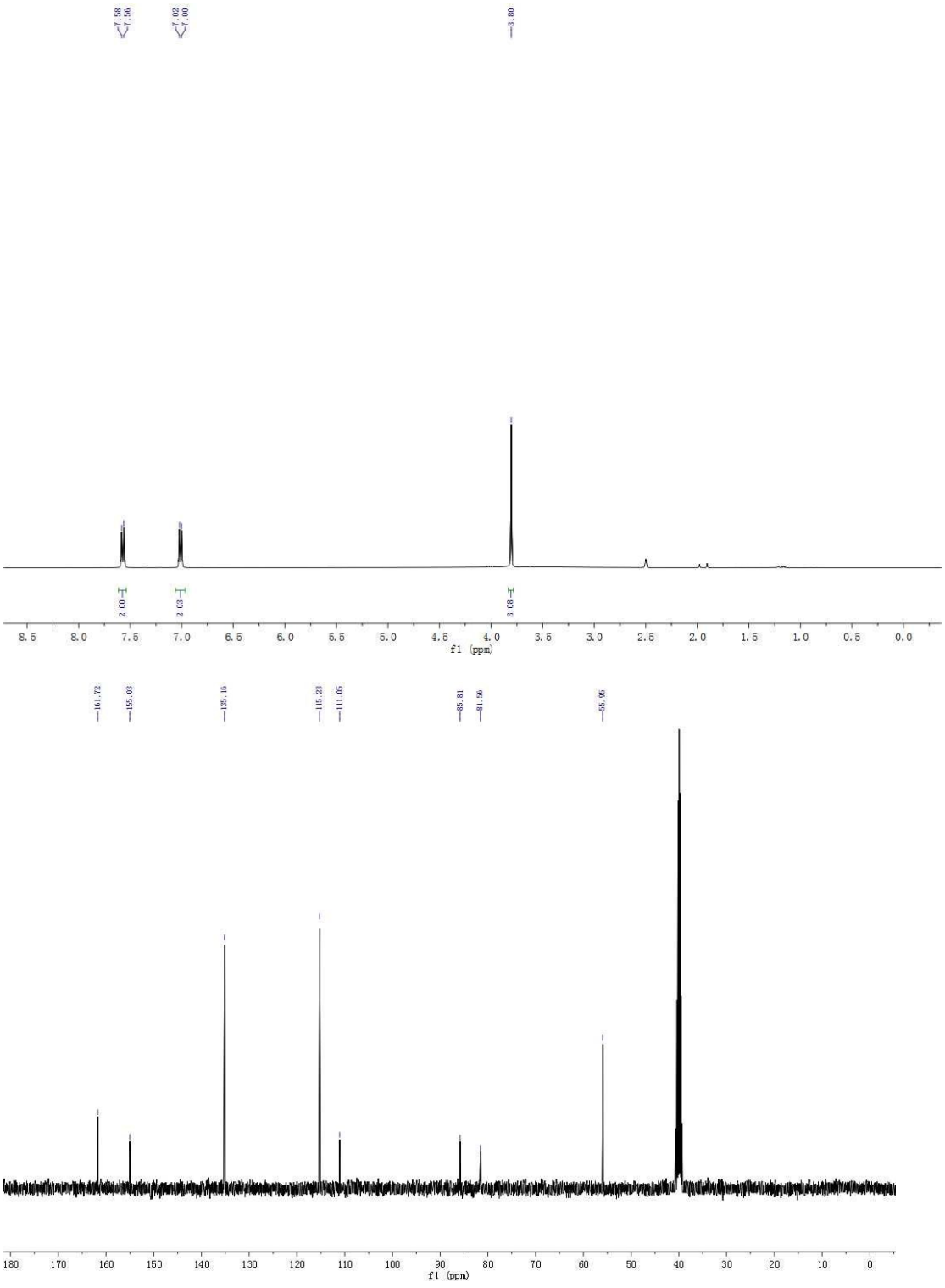
Spectroscopic data

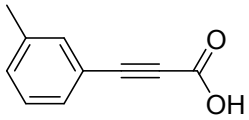
Spectroscopic data of aryl alkynyl carboxylic acids

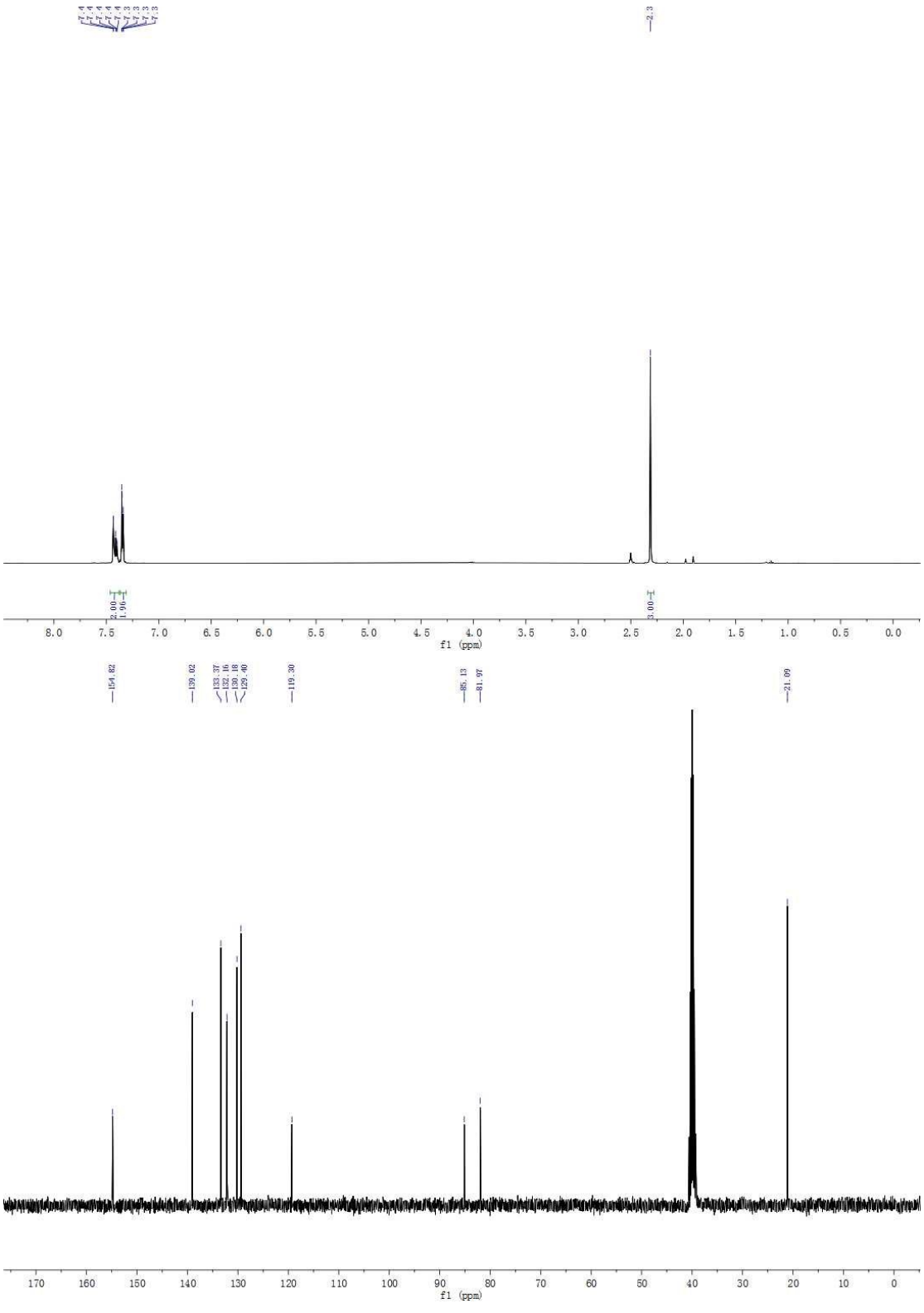
3-(4-methoxyphenyl)propiolic acid (1b)



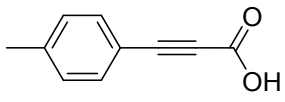


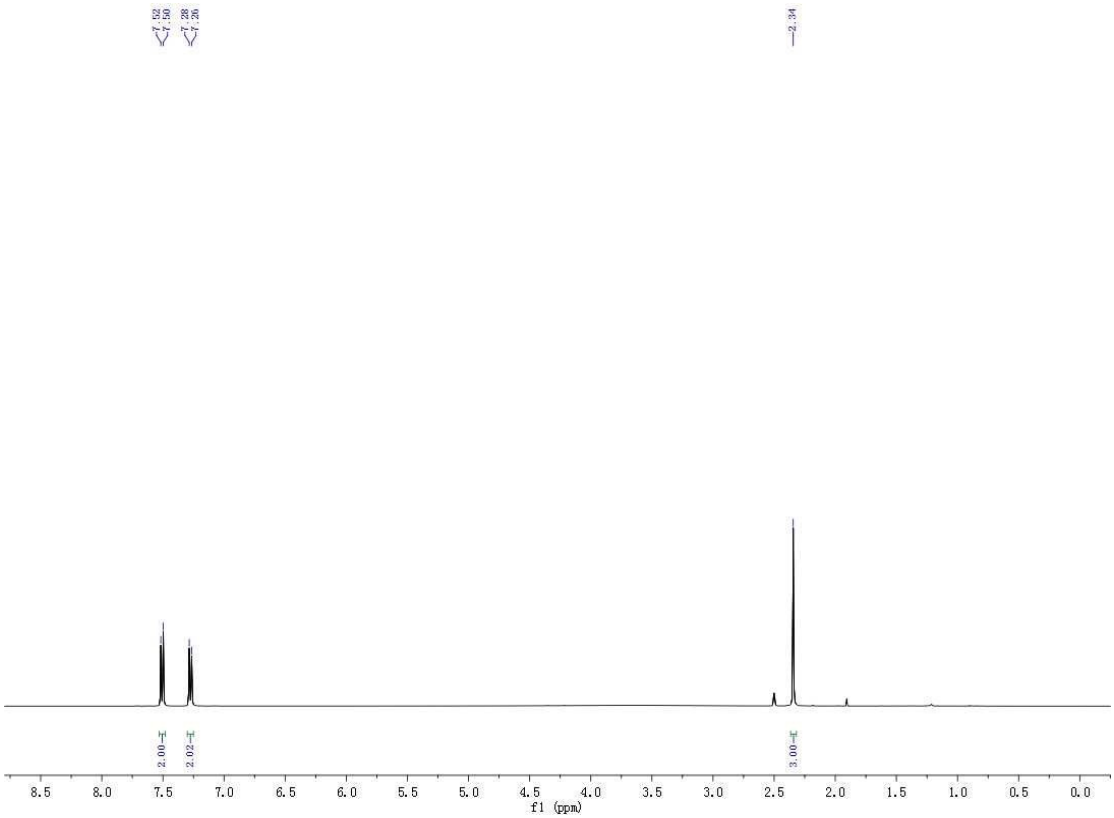
3-(m-tolyl)propiolic acid (1c)

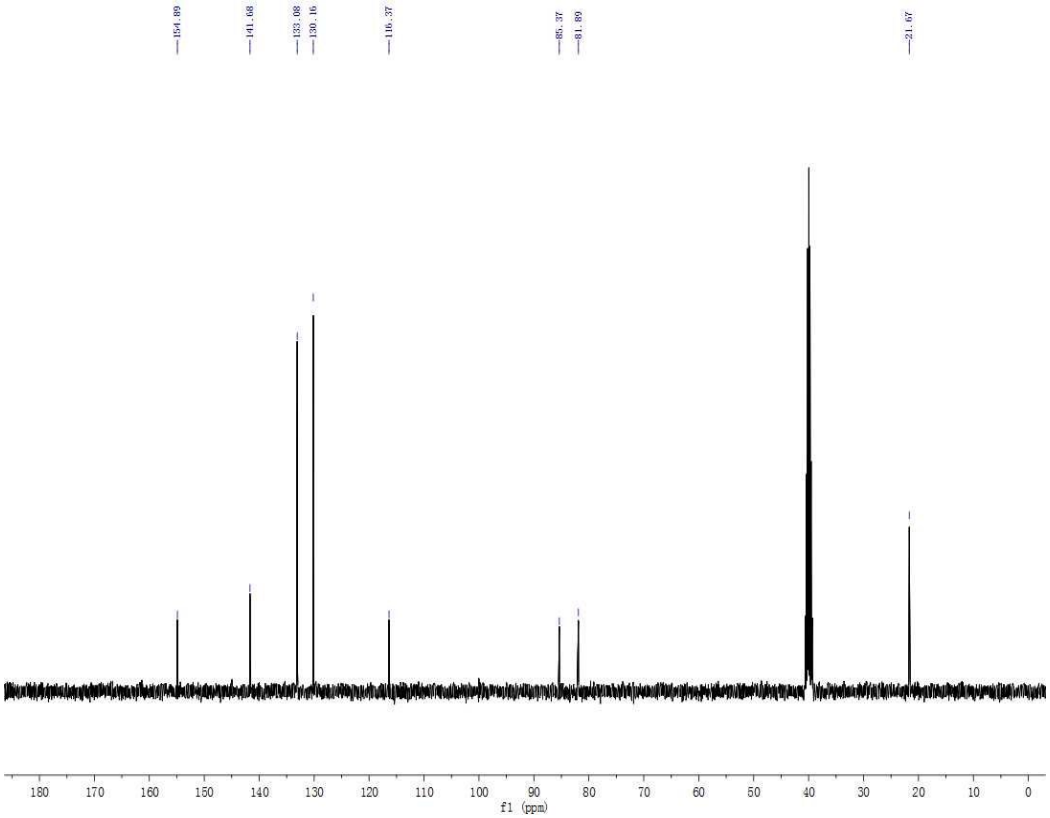




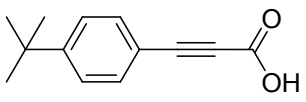
3-(p-tolyl)propiolic acid (1d)

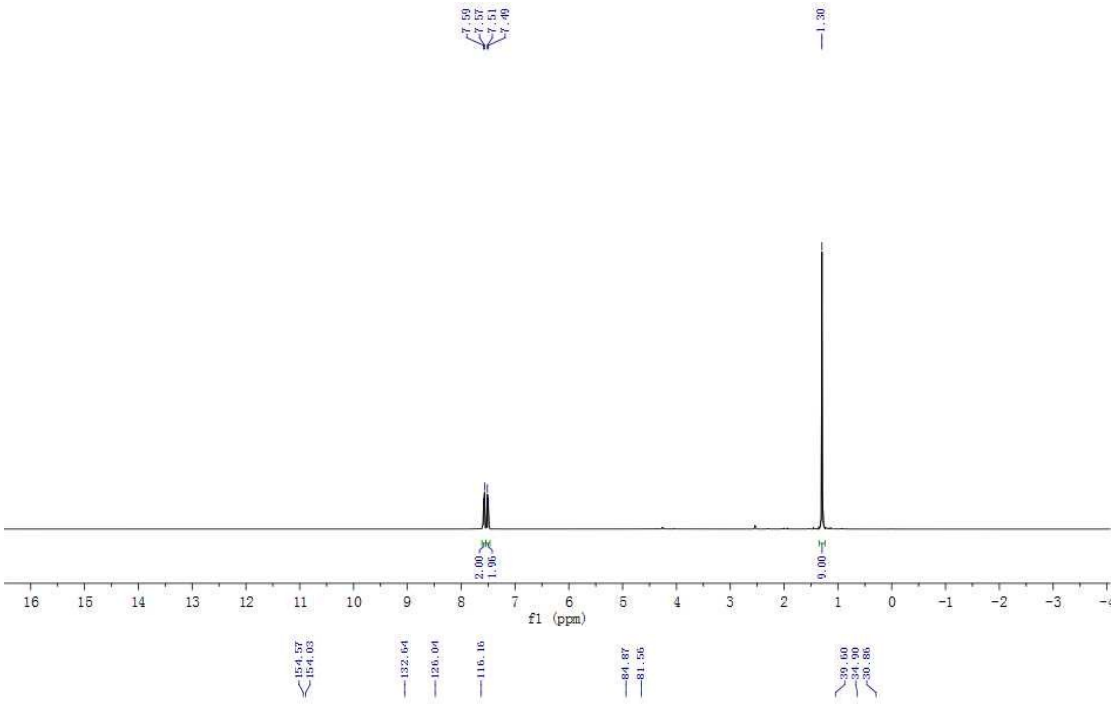


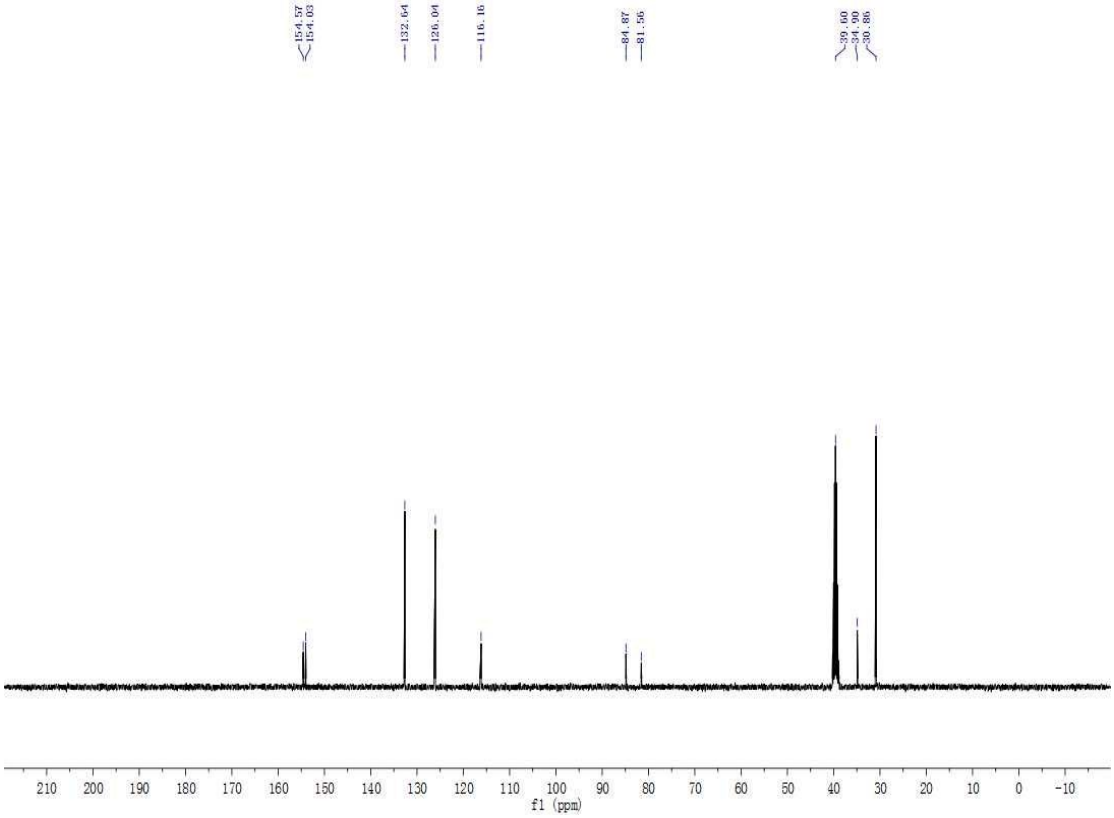




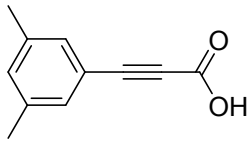
3-(4-(tert-butyl)phenyl)propiolic acid (1e)

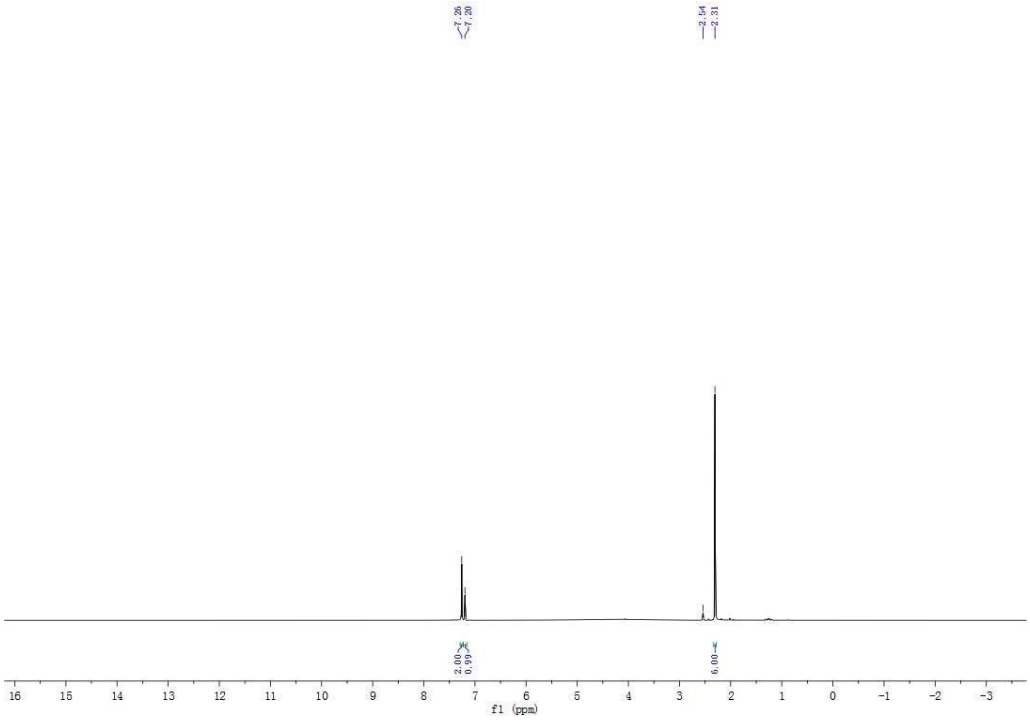


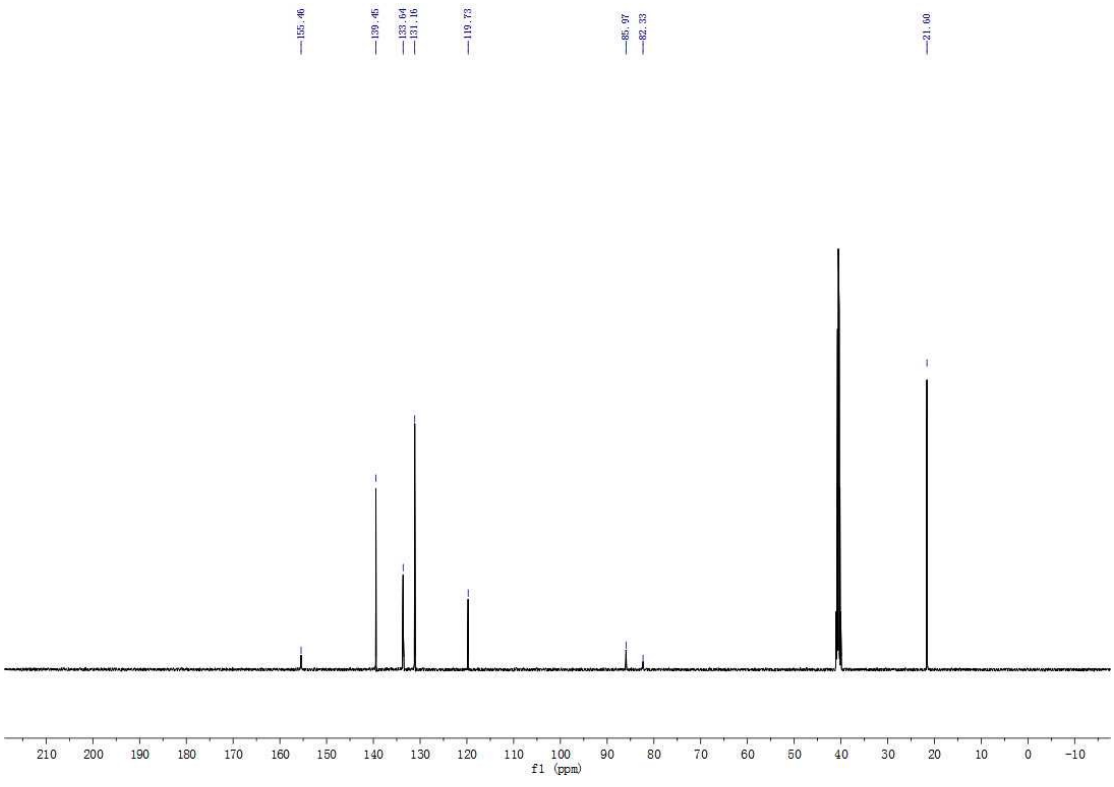




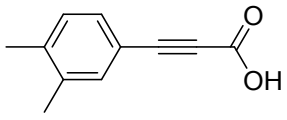
3-(3, 5-dimethylphenyl)propiolic acid (1f)

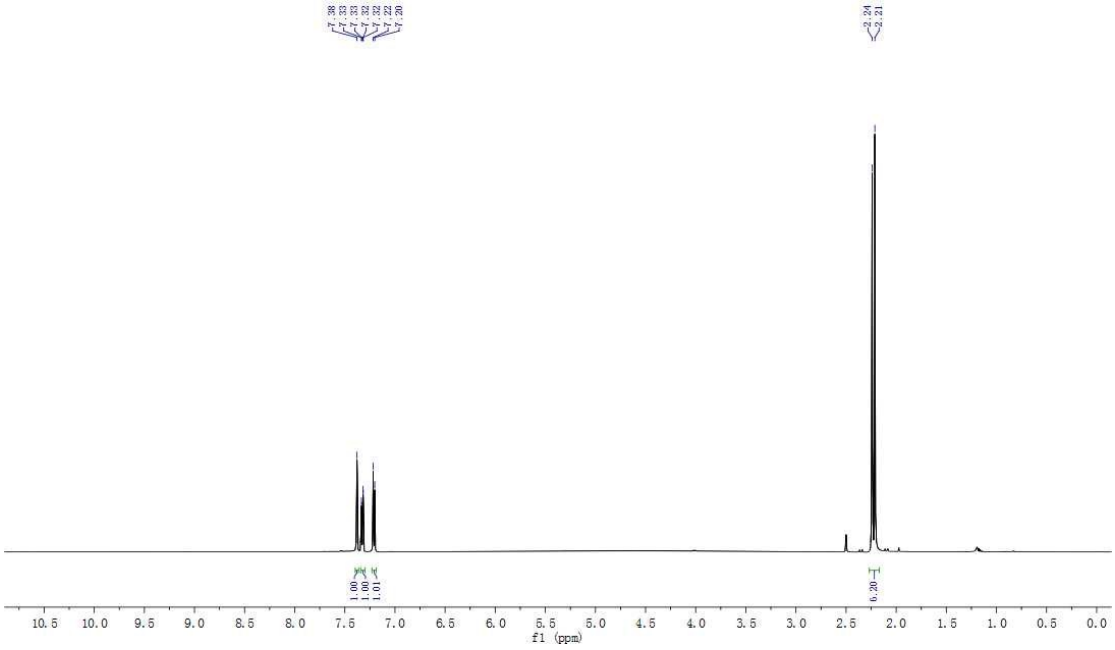


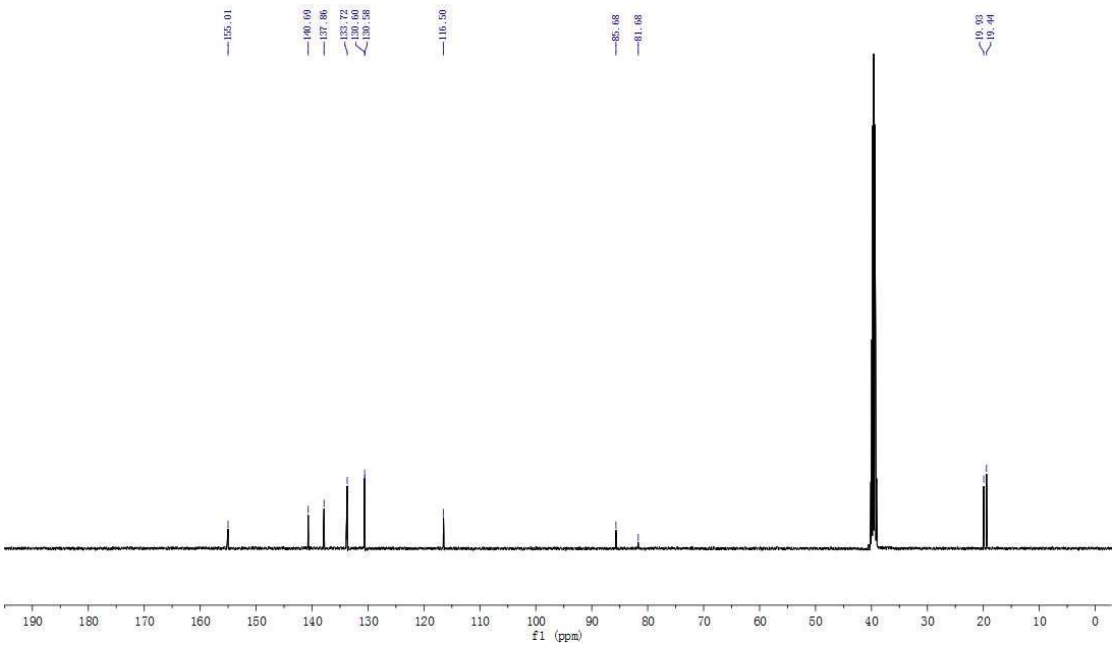




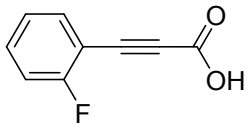
3-(3,4-dimethylphenyl)propiolic acid (1g)

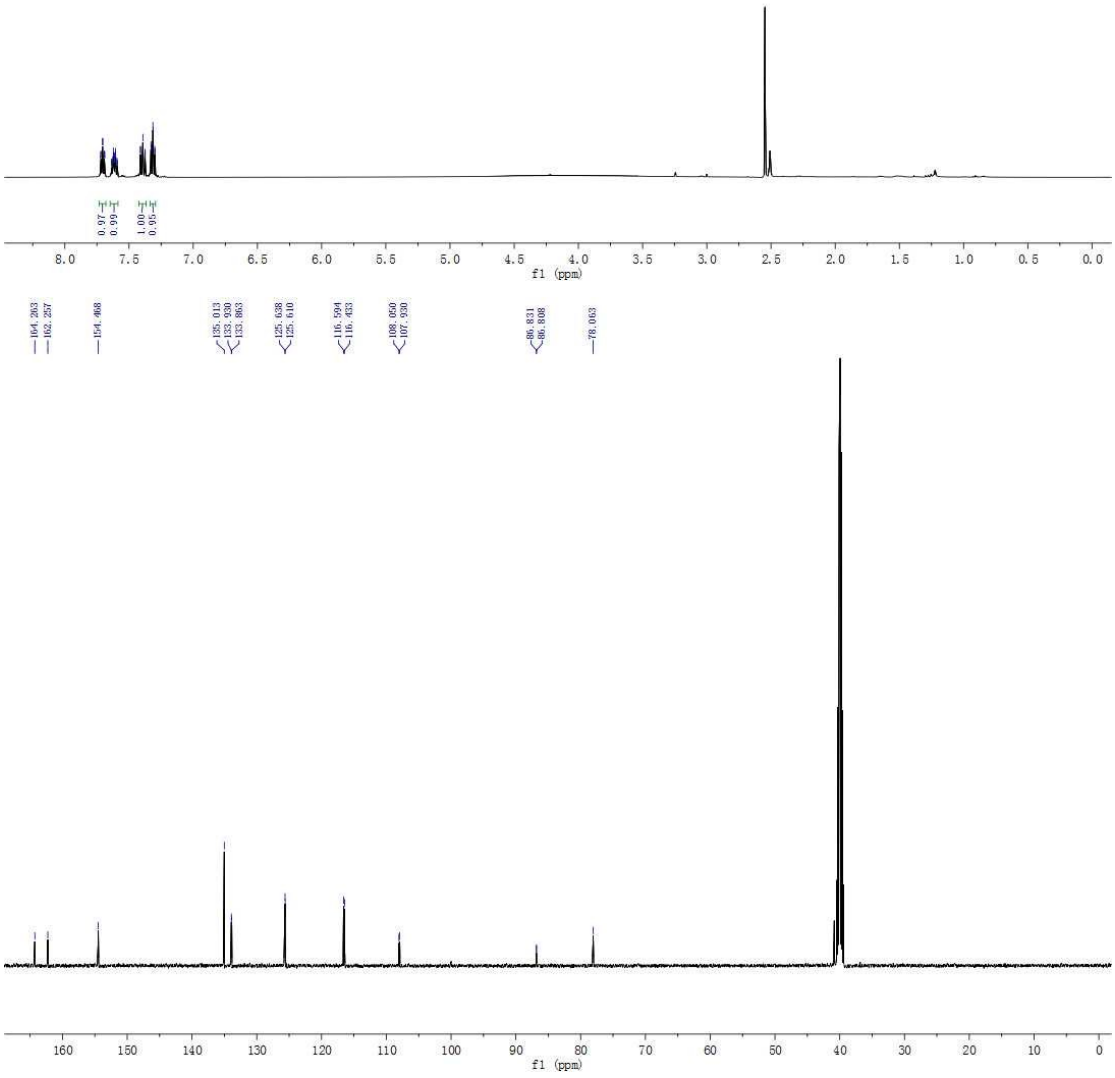




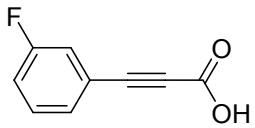


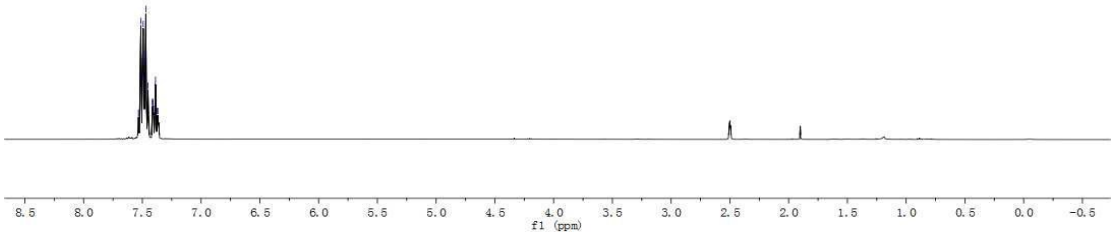
3-(2-fluorophenyl)propiolic acid (1h)

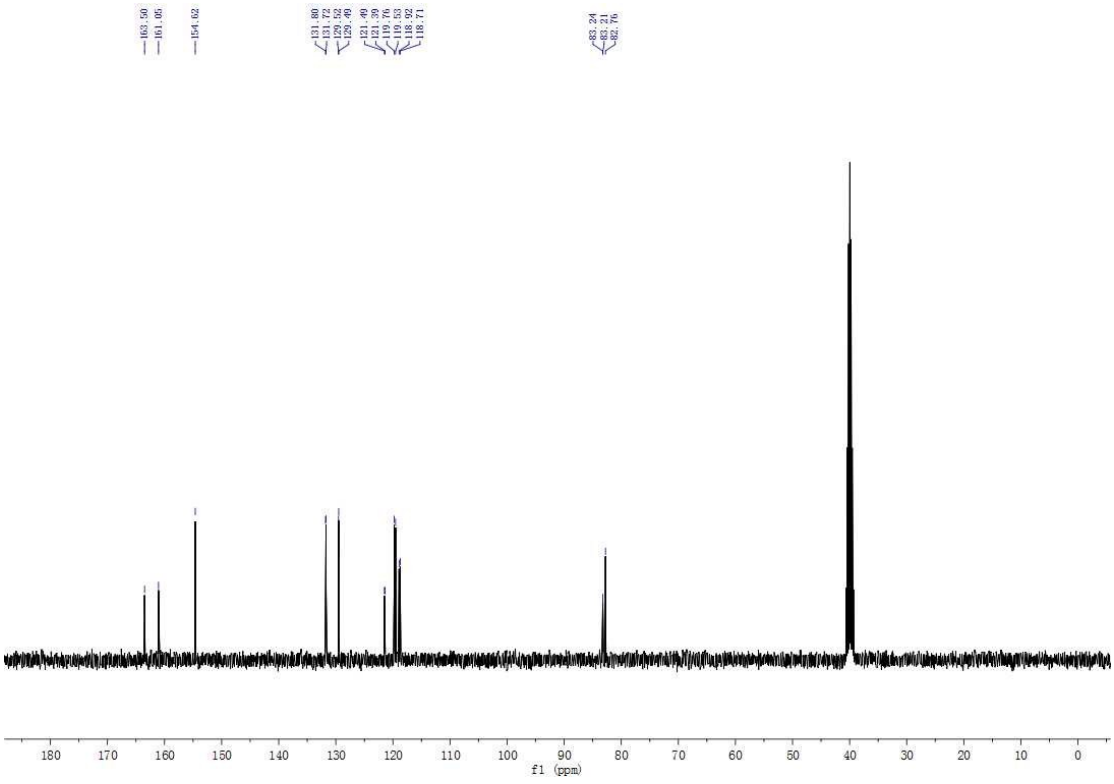




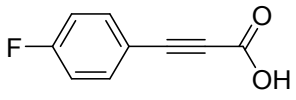
3-(3-fluorophenyl)propiolic acid (1i)

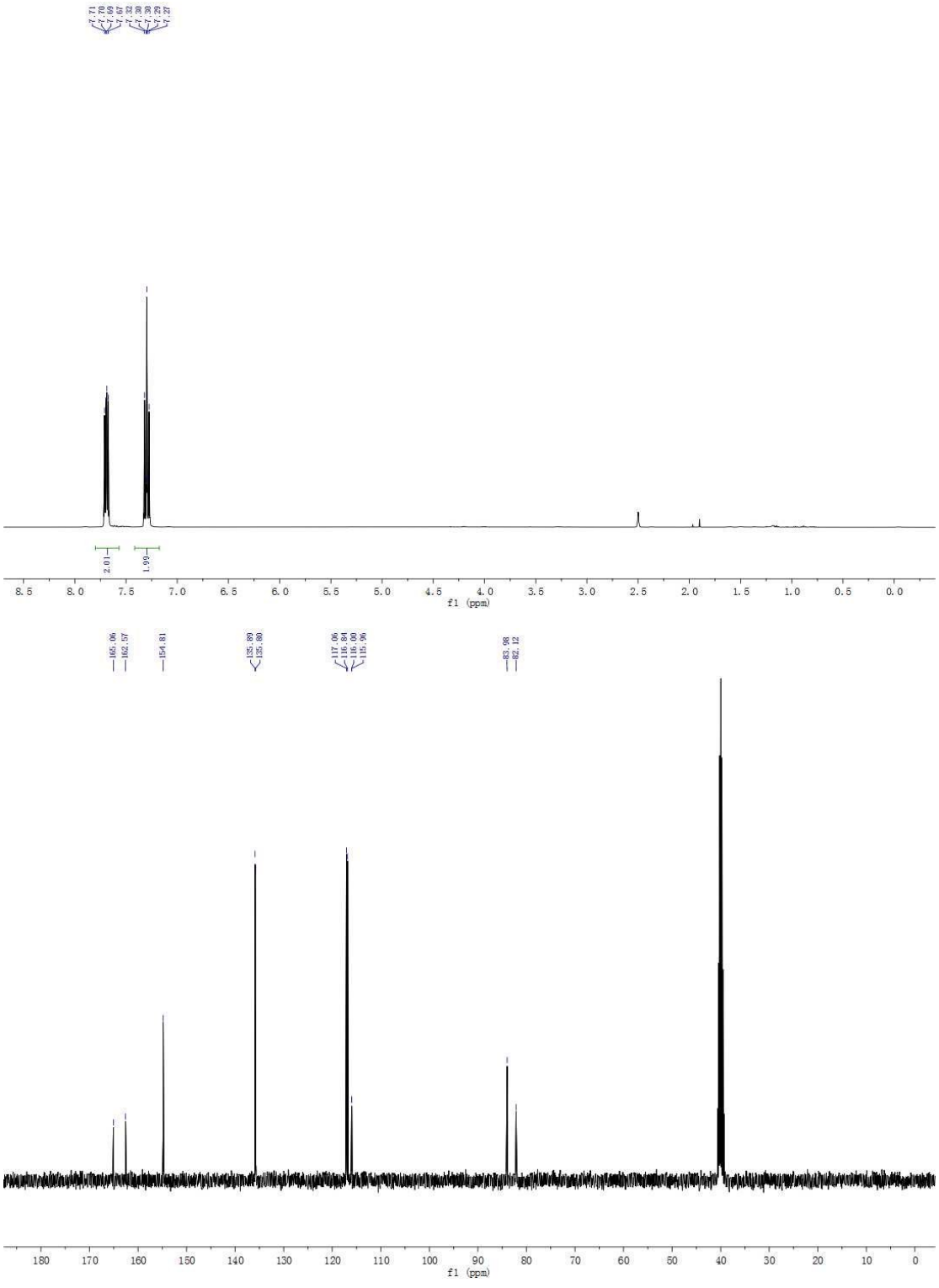




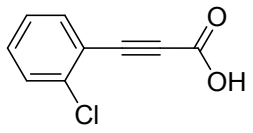


3-(4-fluorophenyl)propiolic acid (1j)





3-(2-chlorophenyl)propiolic acid (1k)


O
OH
Cl


7.74
7.74
7.73
7.72
7.63
7.61
7.61
7.56
7.56
7.55
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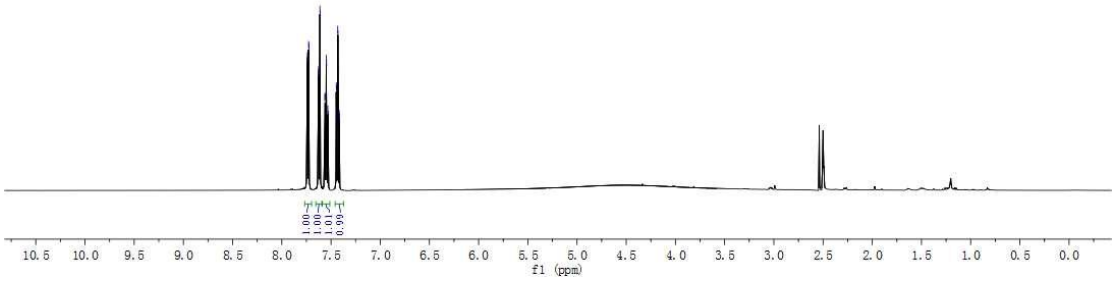
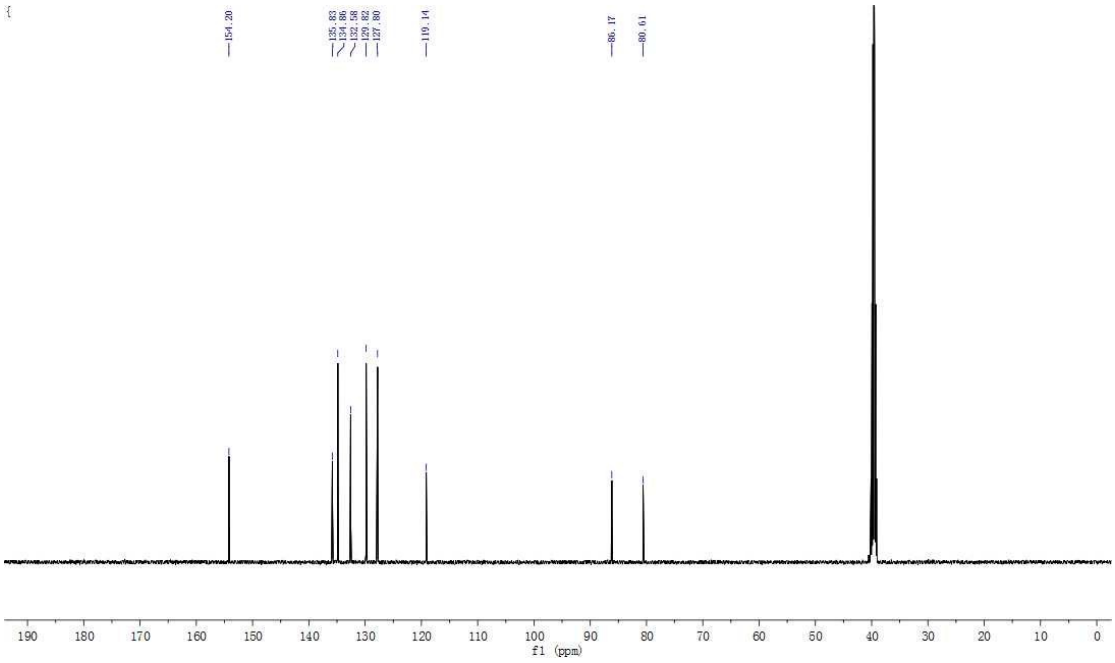
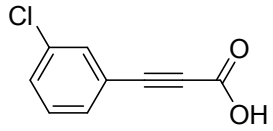
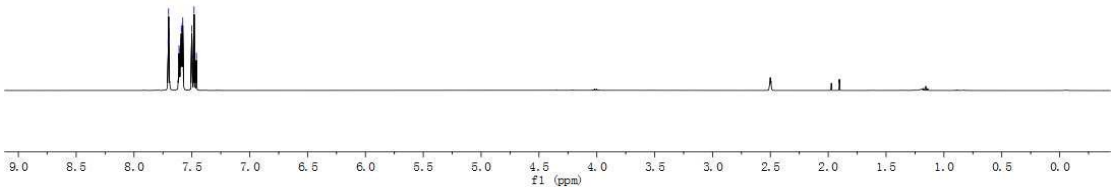
7.53
7.45
7.44
7.43
7.43
7.42
7.41

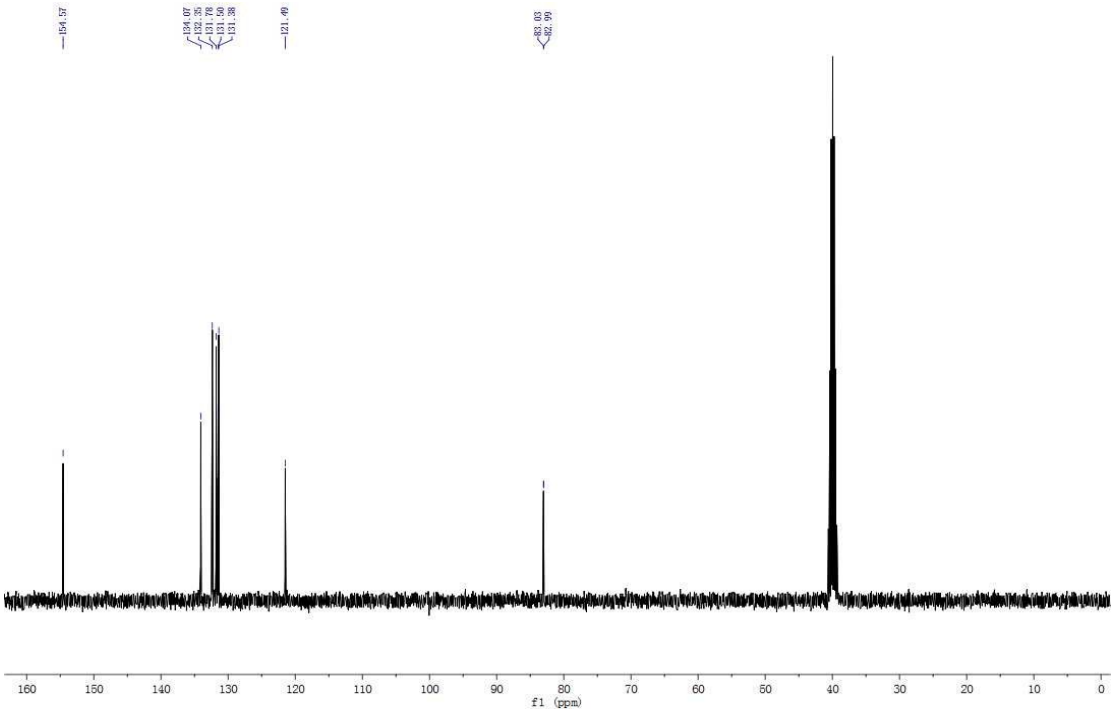

1.00
1.00
1.01
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.20
135.83
134.86
132.58
130.82
127.80
119.14
86.17
80.61
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

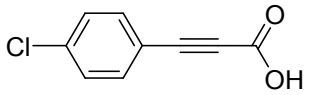
3-(3-chlorophenyl)propiolic acid (1l)

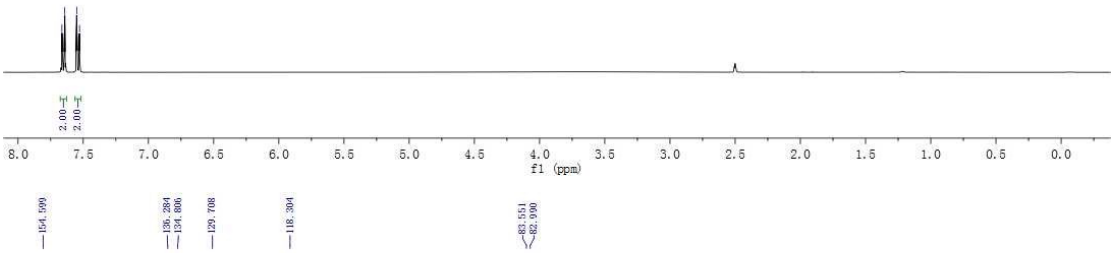


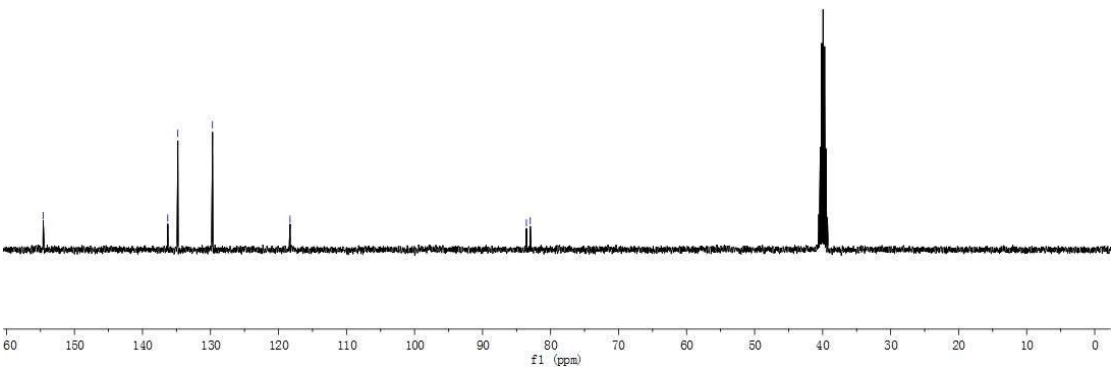




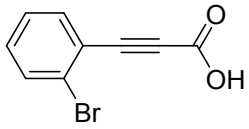
3-(4-chlorophenyl)propiolic acid (1m)

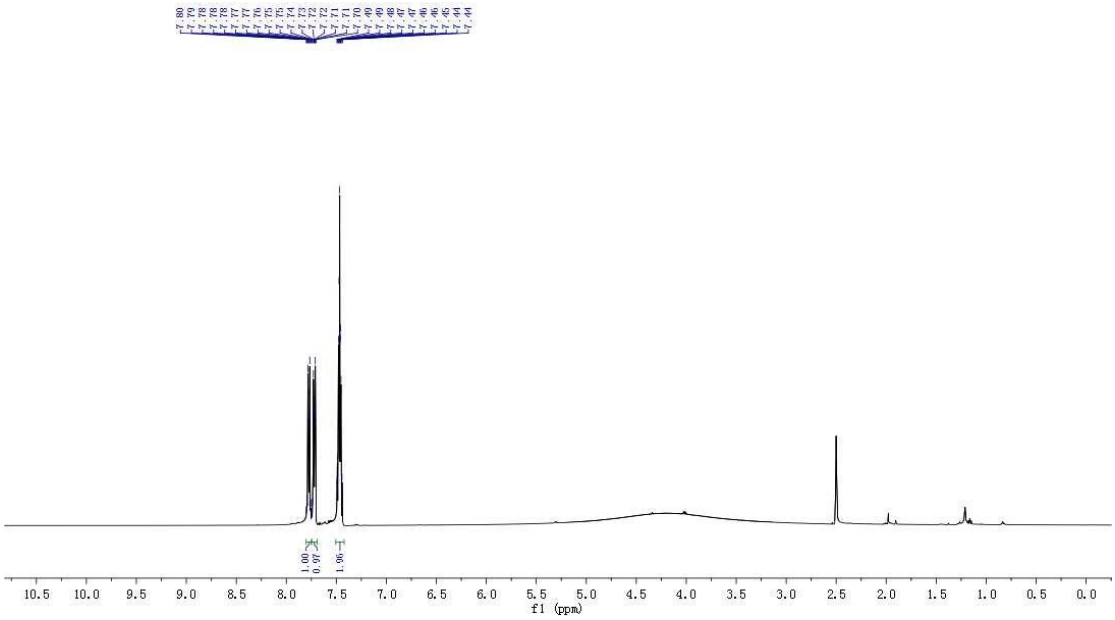


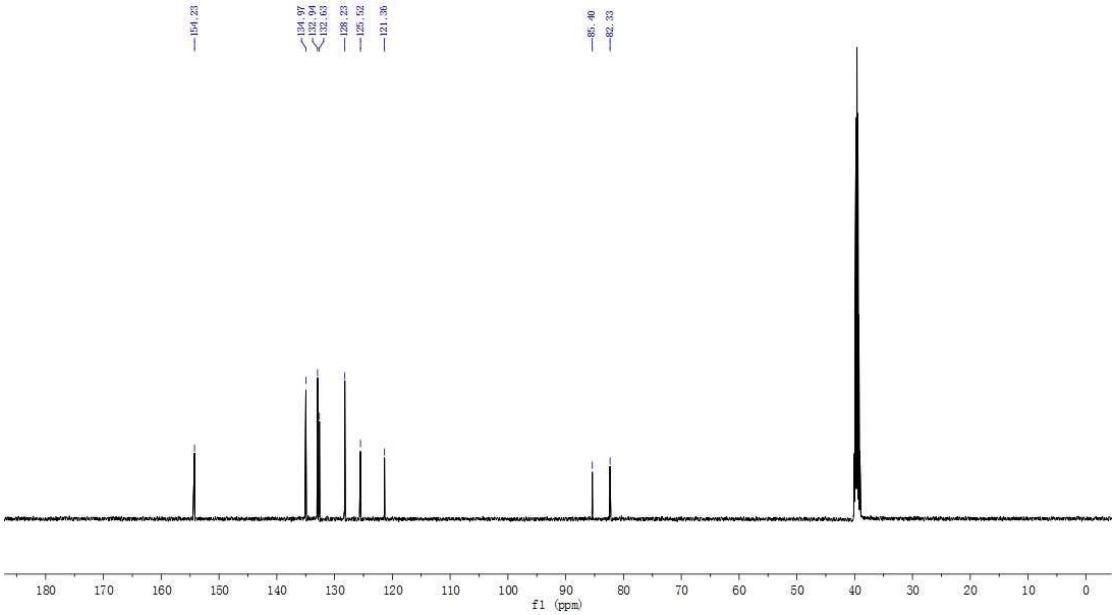




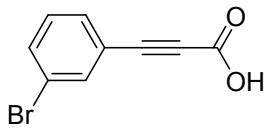
3-(2-bromophenyl)propiolic acid (1n)

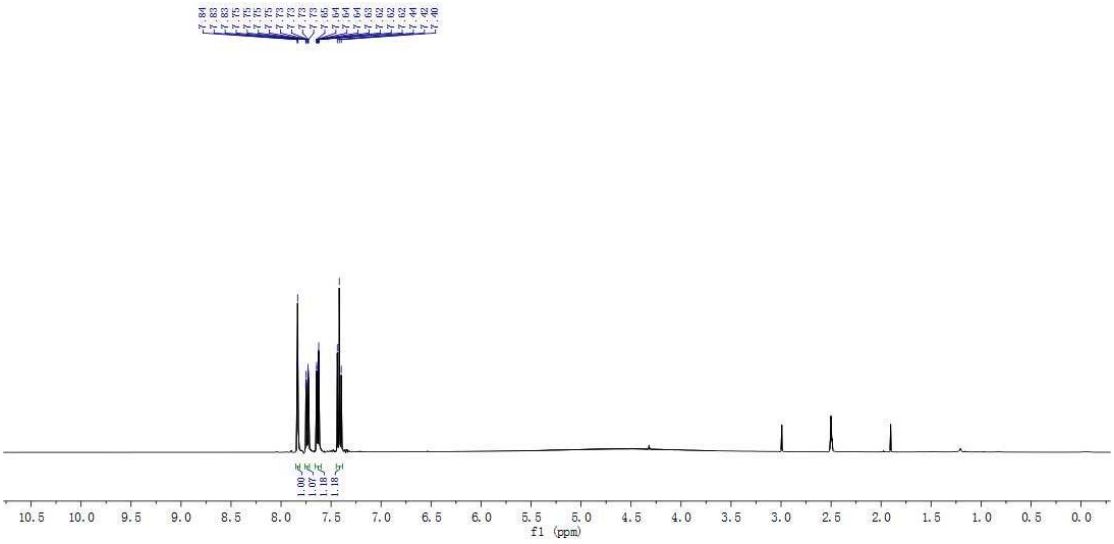


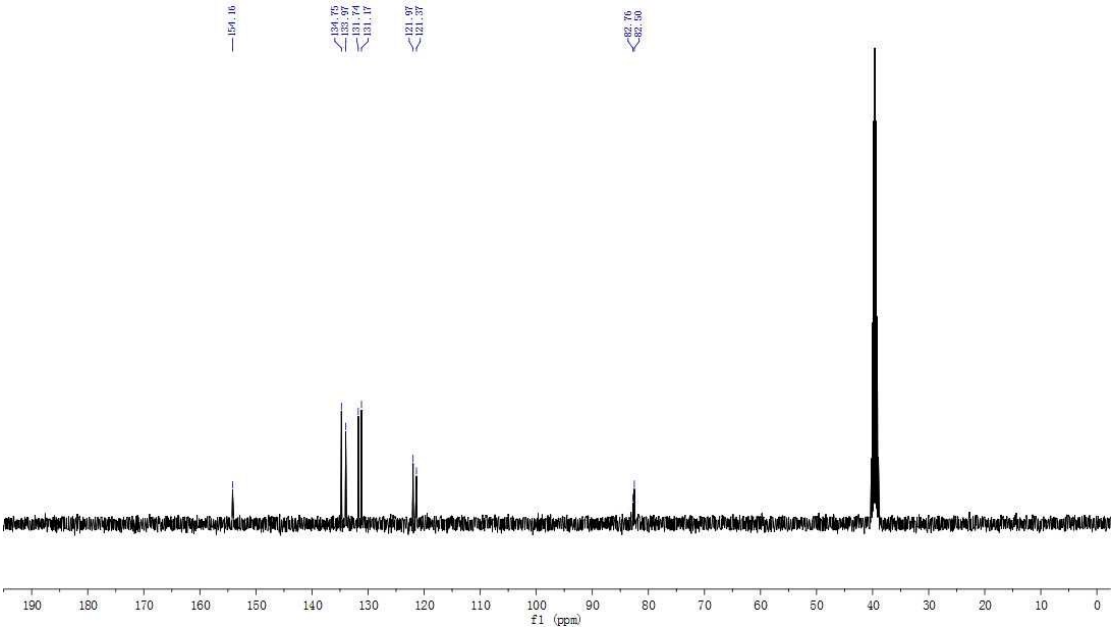




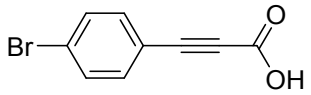
3-(3-bromophenyl)propiolic acid (1o)

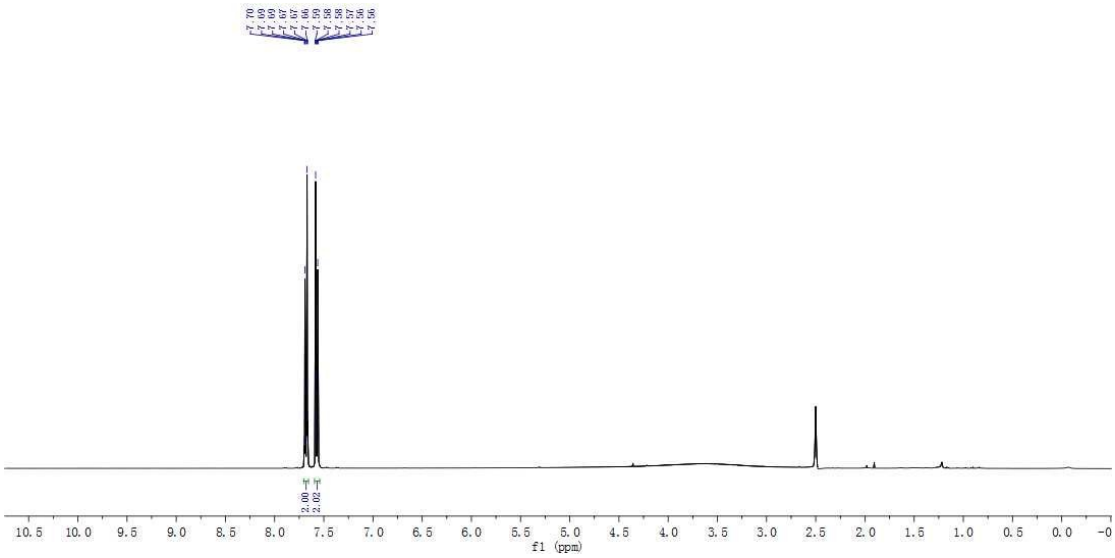


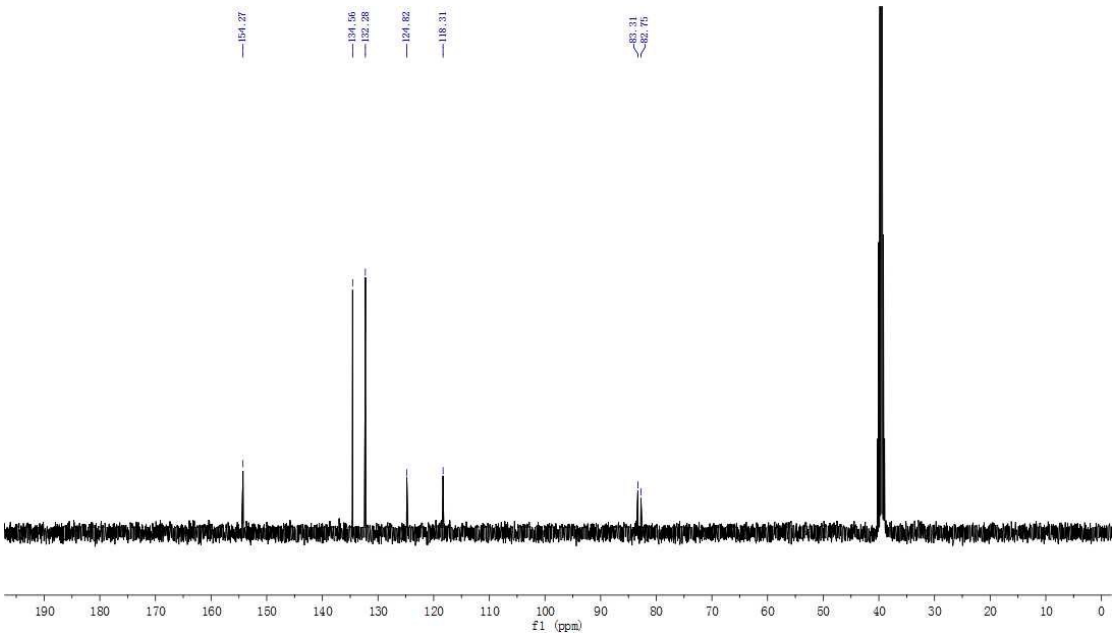




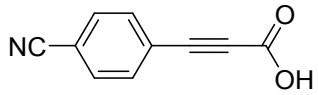
3-(4-bromophenyl)propiolic acid (1p)

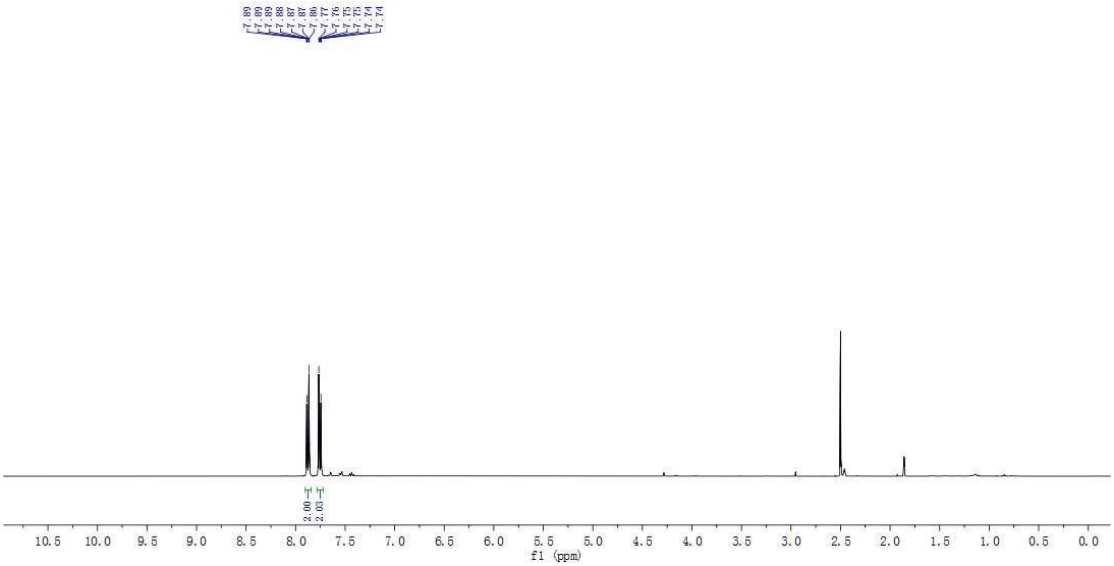


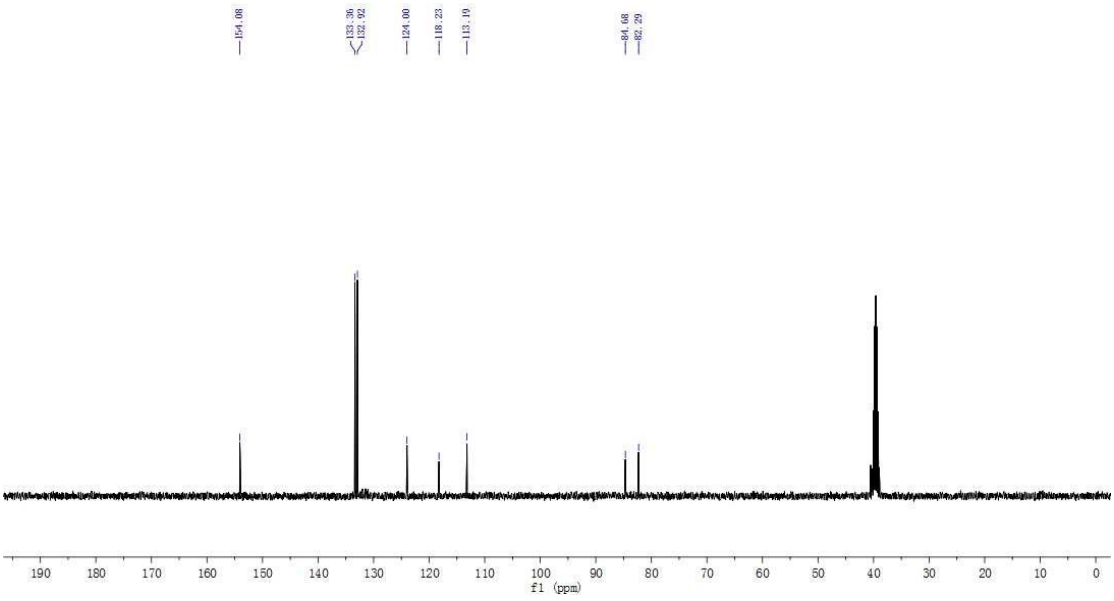




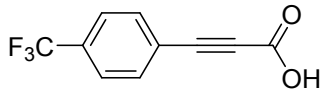
3-(4-cyanophenyl)propiolic acid (1q)

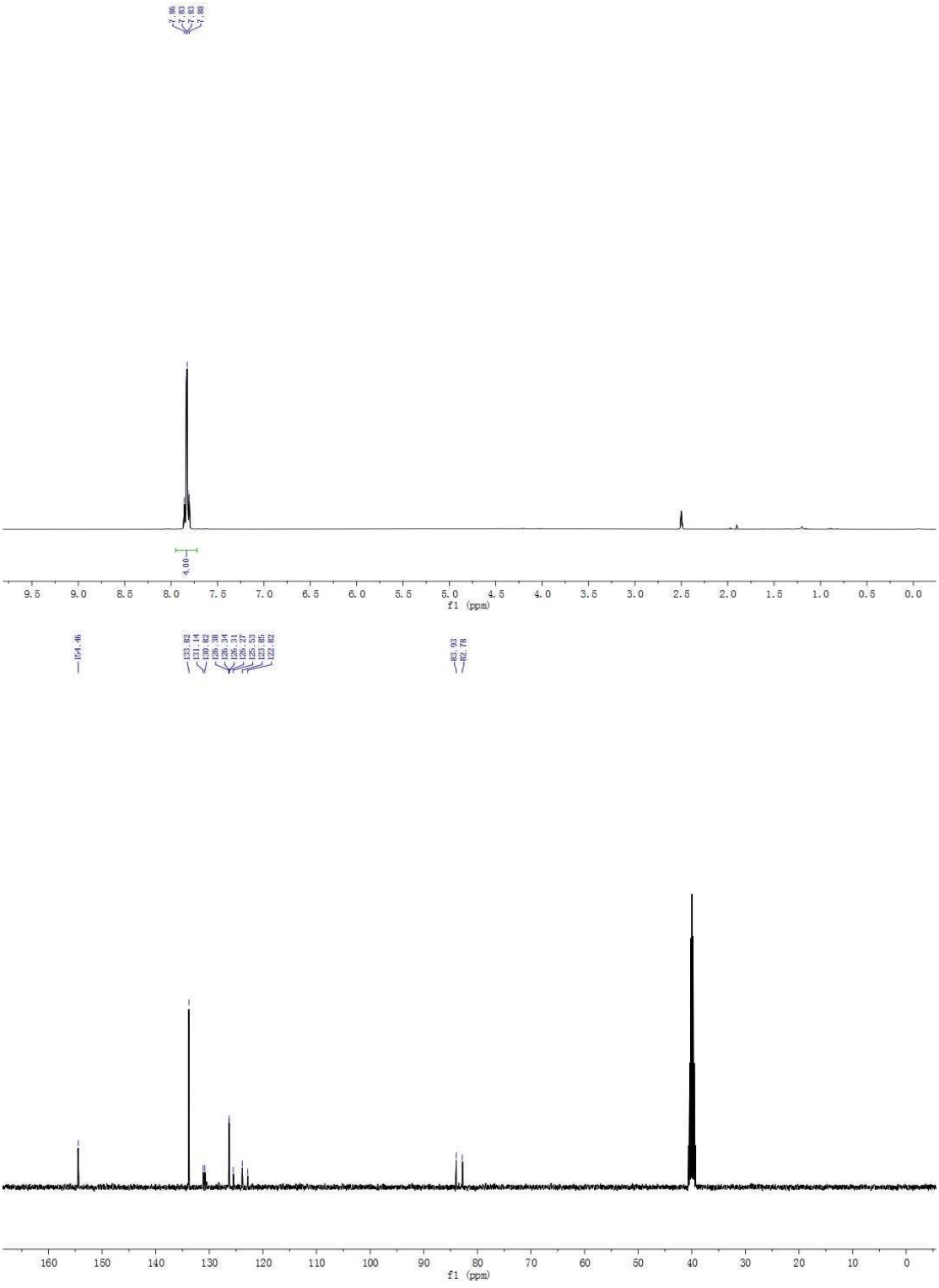




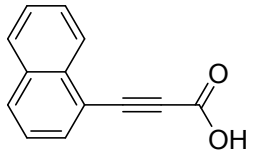


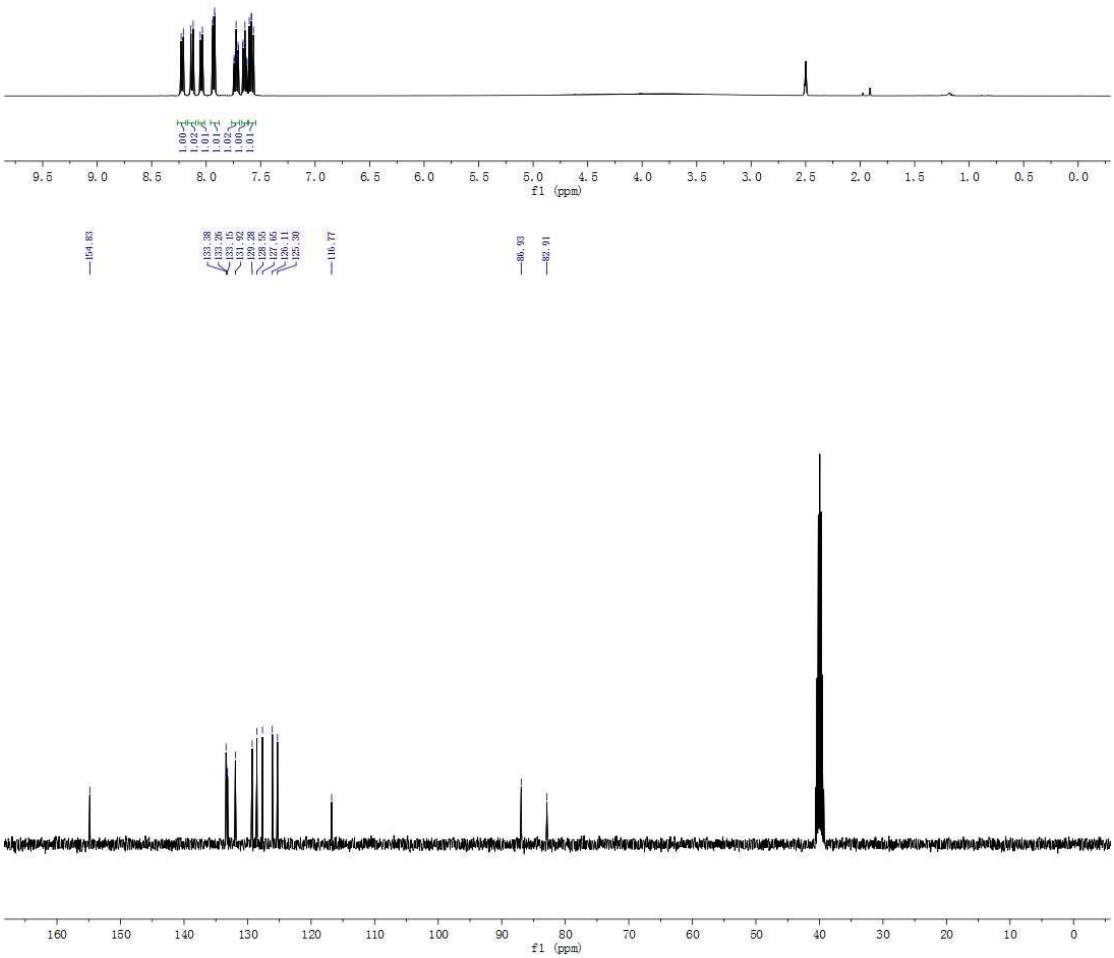
3-(4-(trifluoromethyl)phenyl)propiolic acid (1r)



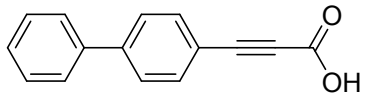


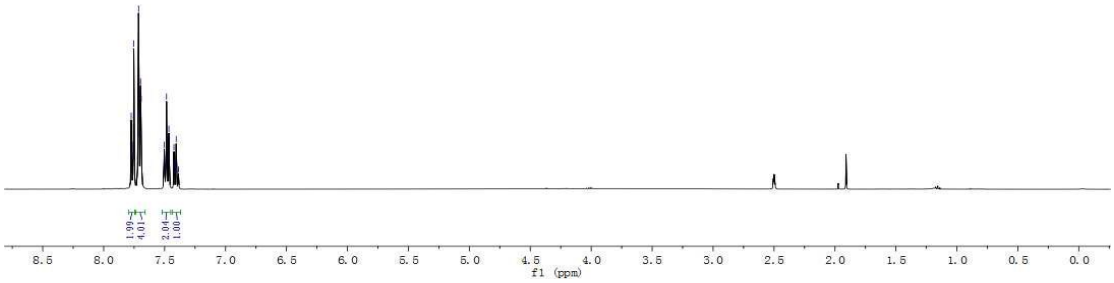
3-(naphthalen-1-yl)propiolic acid (1s)

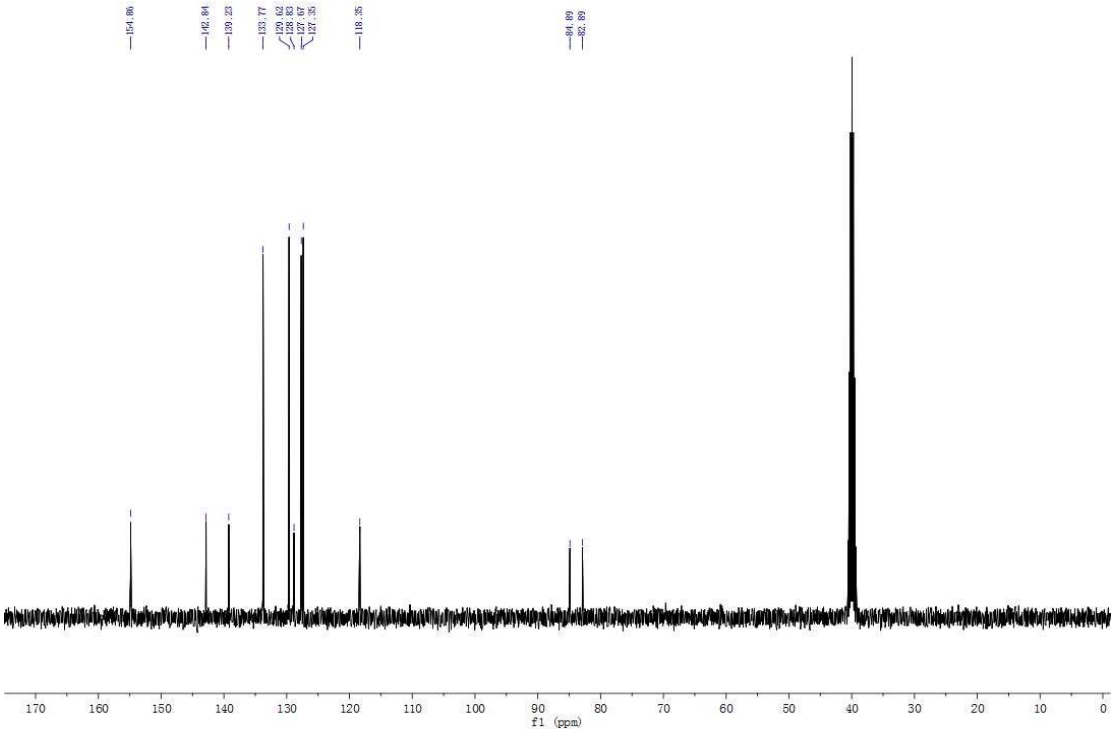




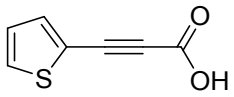
3-([1, 1'-biphenyl]-4-yl)propiolic acid (1t)

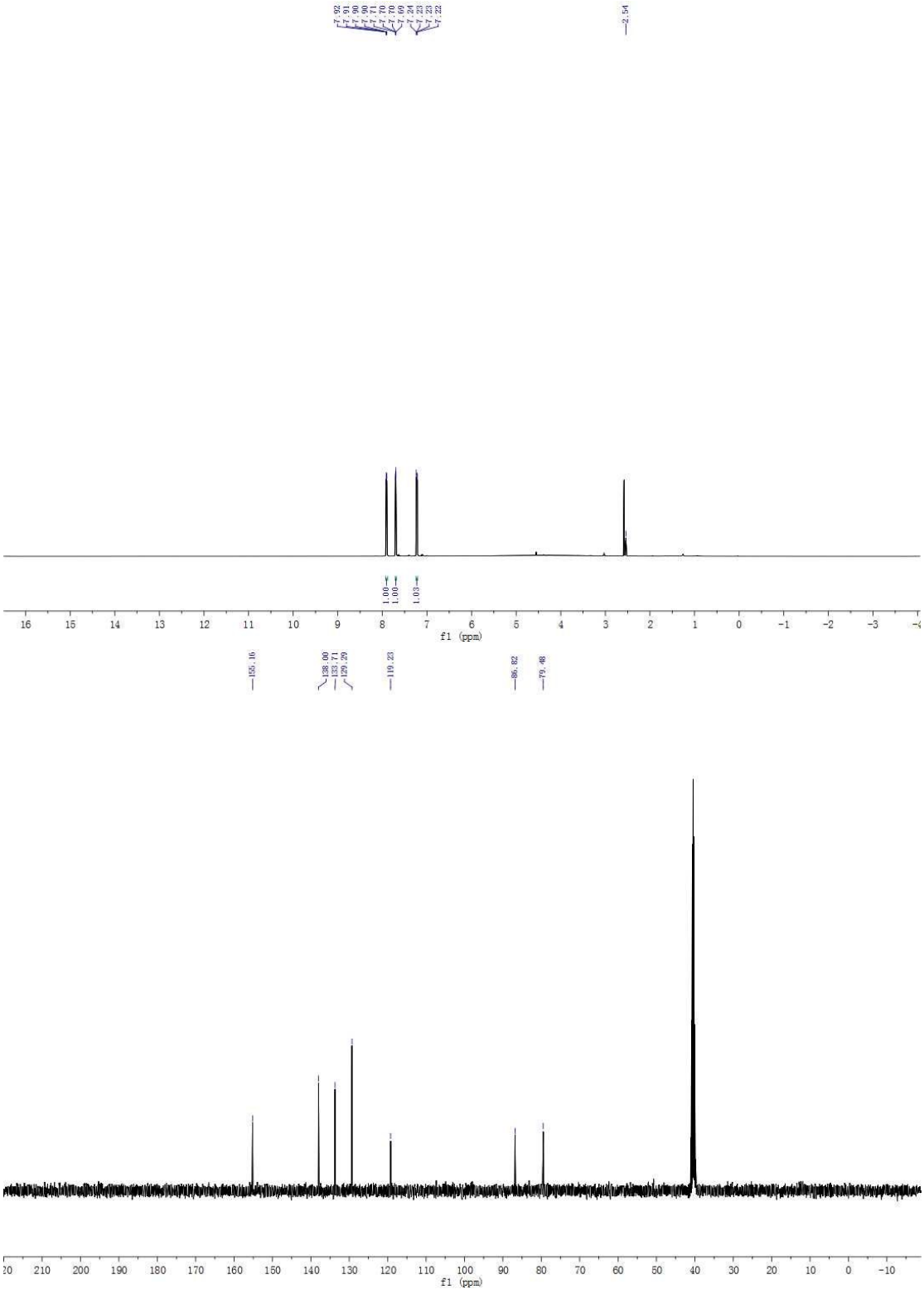




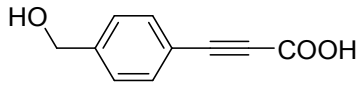


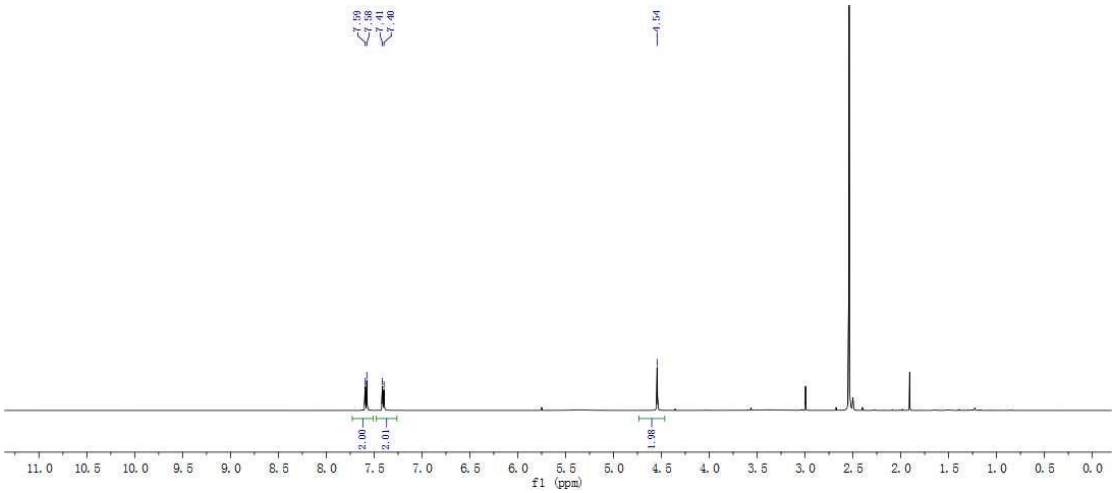
3-(thiophen-2-yl)propiolic acid (1u)

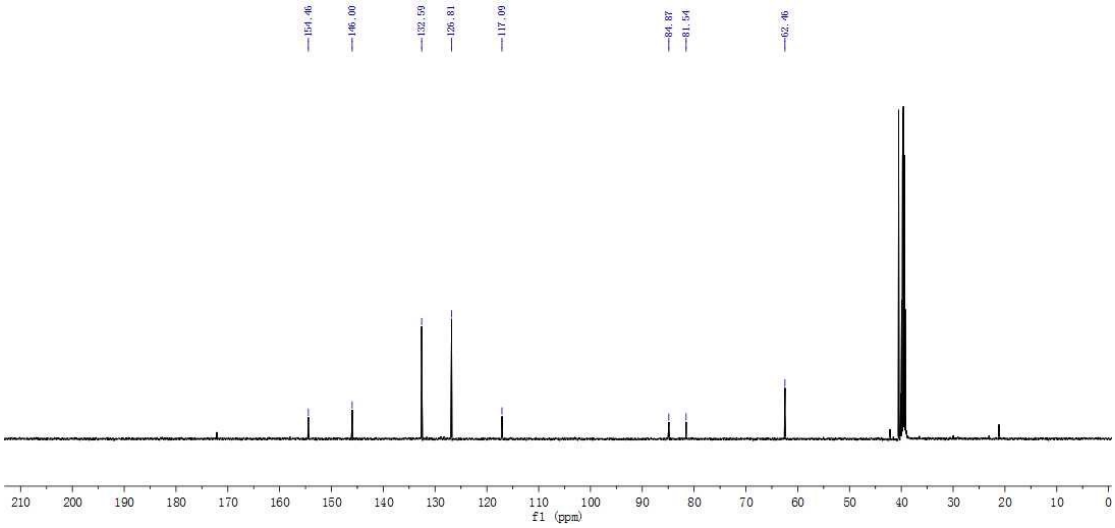




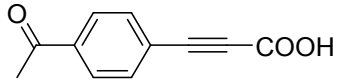
3-(4-(hydroxymethyl)phenyl)propiolic acid (1v)

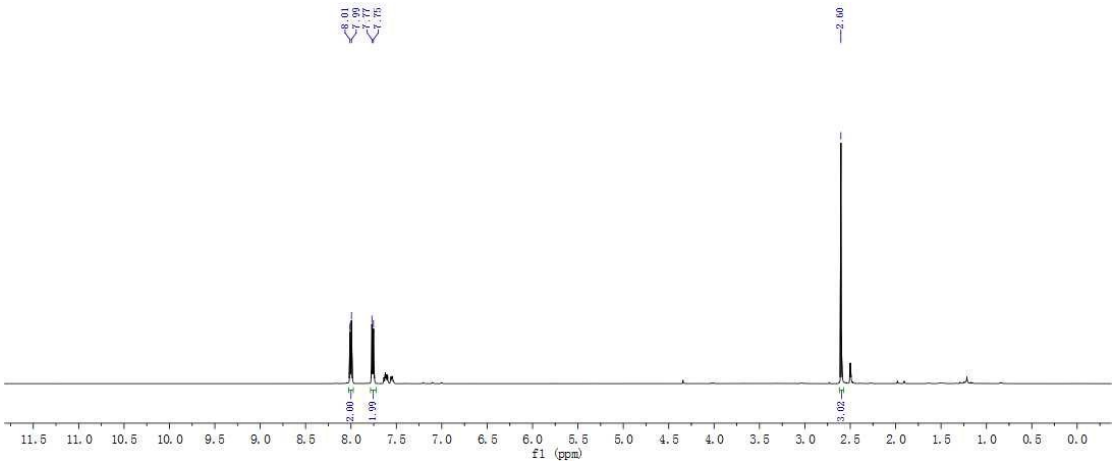


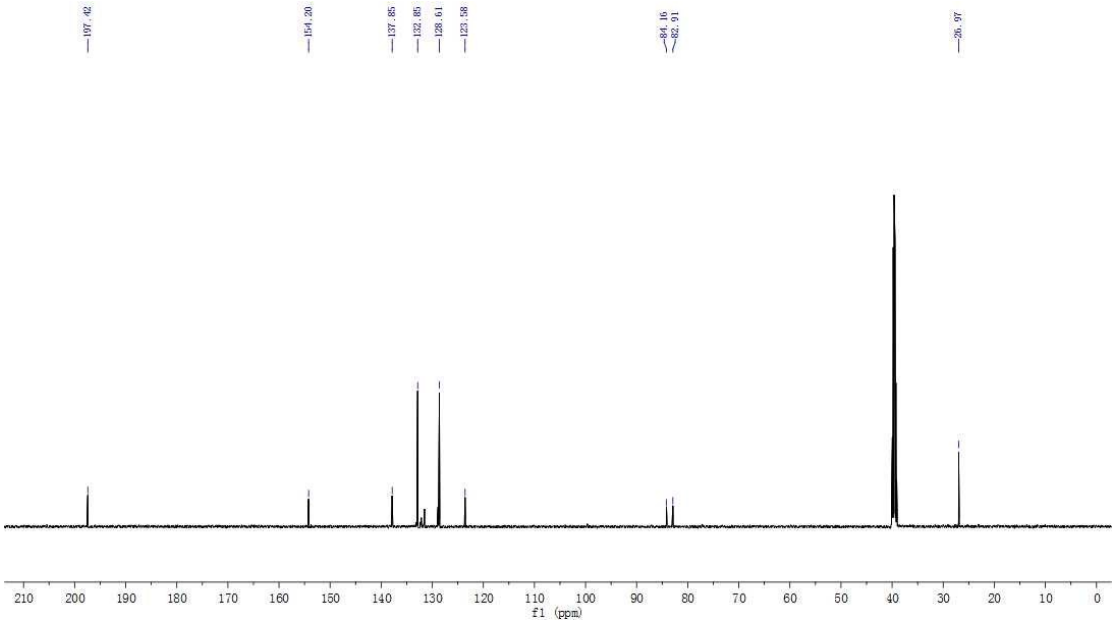




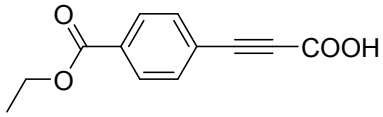
3-(4-acetylphenyl)propiolic acid (1w)

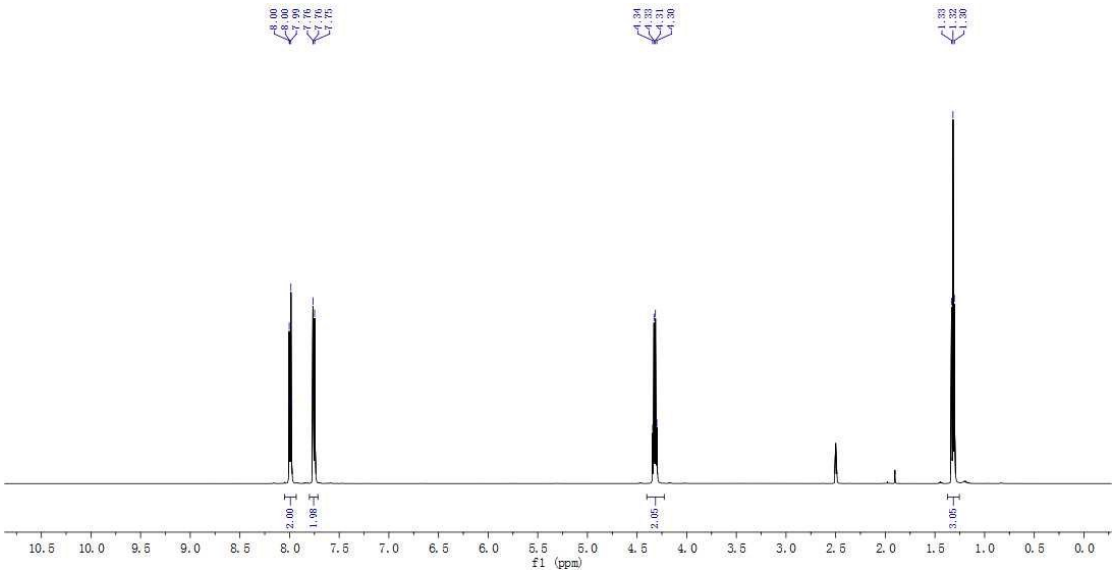


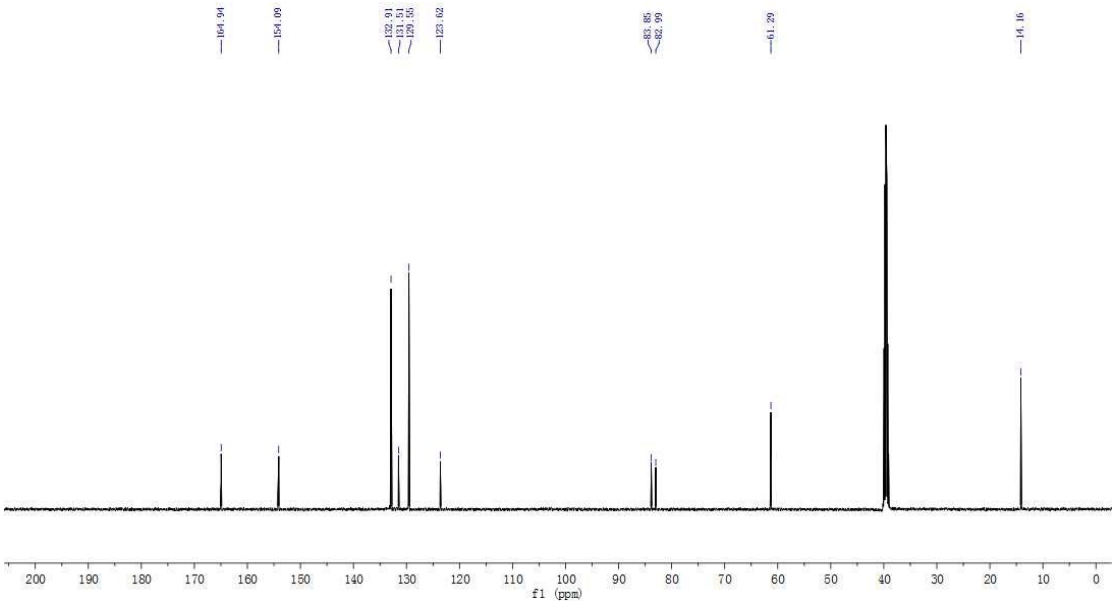




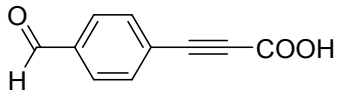
3-(4-(ethoxycarbonyl)phenyl)propiolic acid (1x)

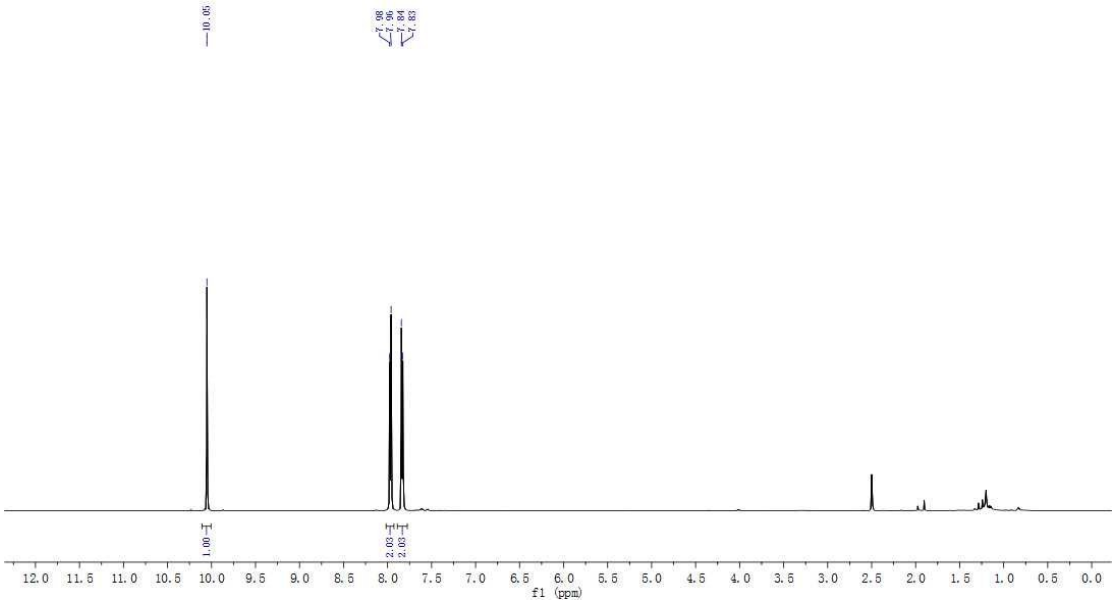


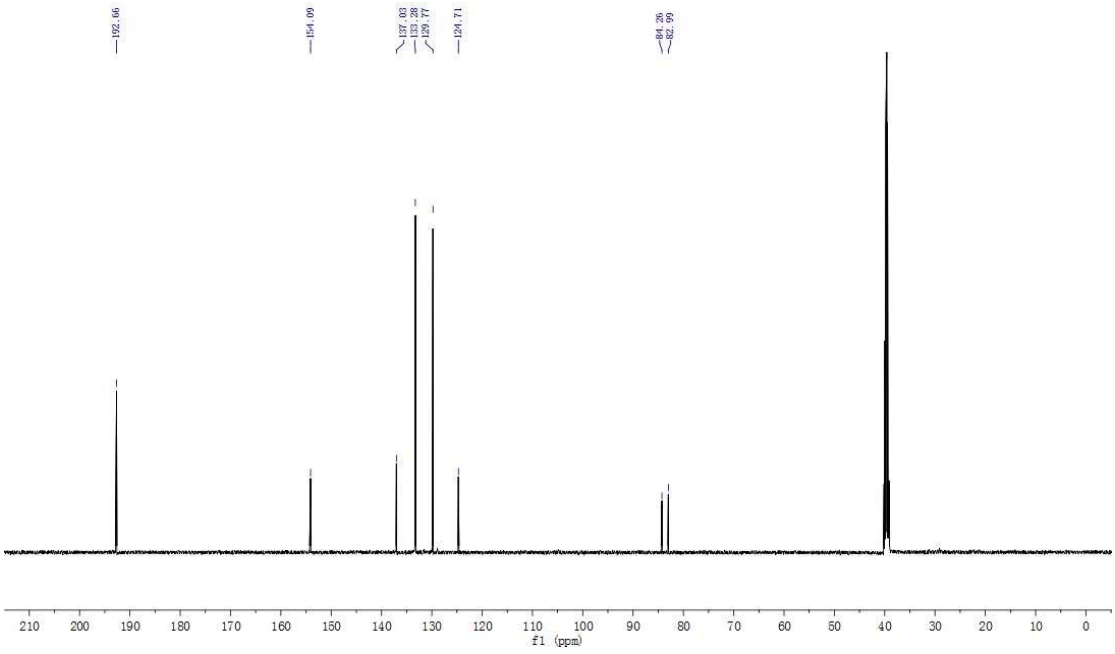




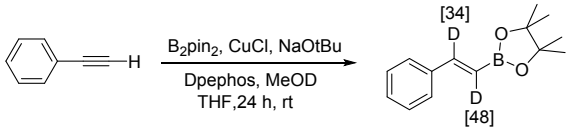
3-(4-formylphenyl)propiolic acid (1y)

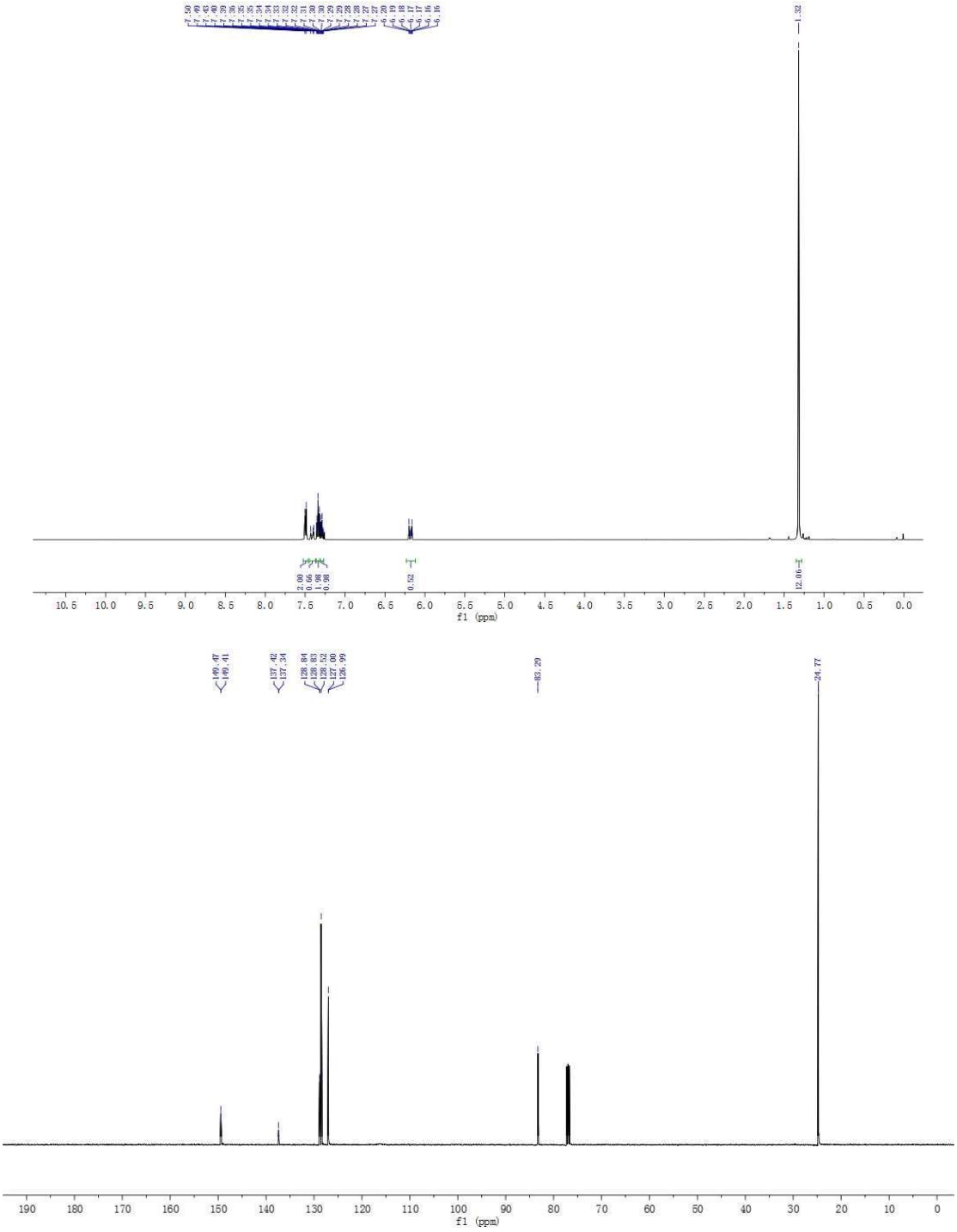


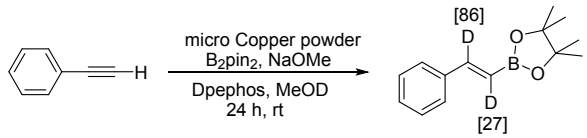




Spectroscopic data of (*E*)-bis-deuterated β-borylated α, β-styrene **3a** in control experiments



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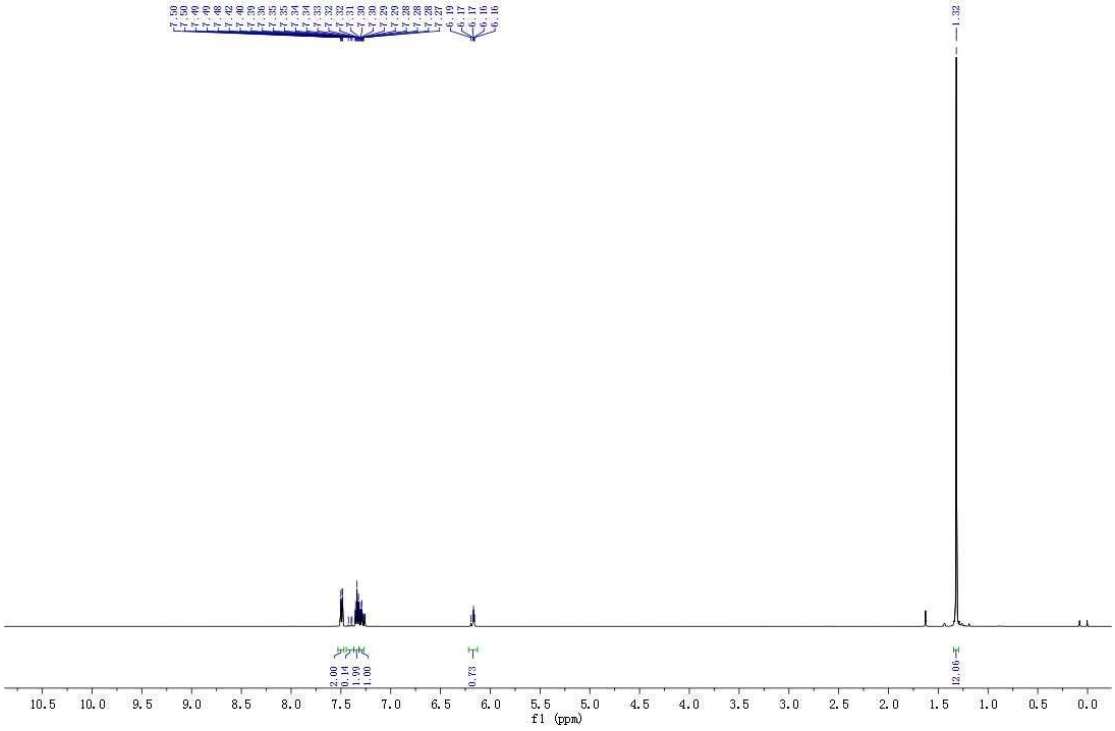
B2pin2, NaOMe
Dpephos, MeOD
24 h, rt
[86]
D
D
[27]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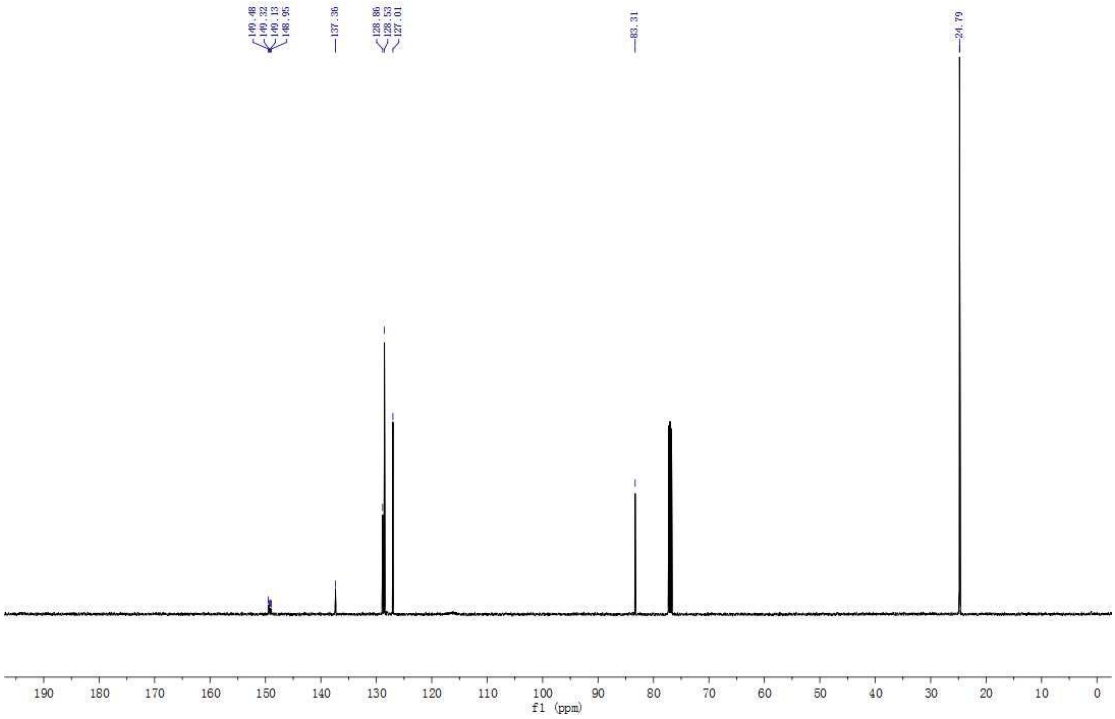
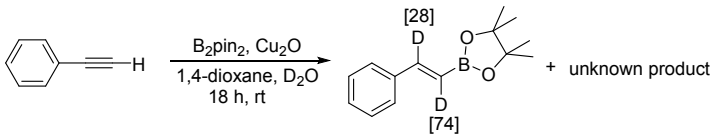
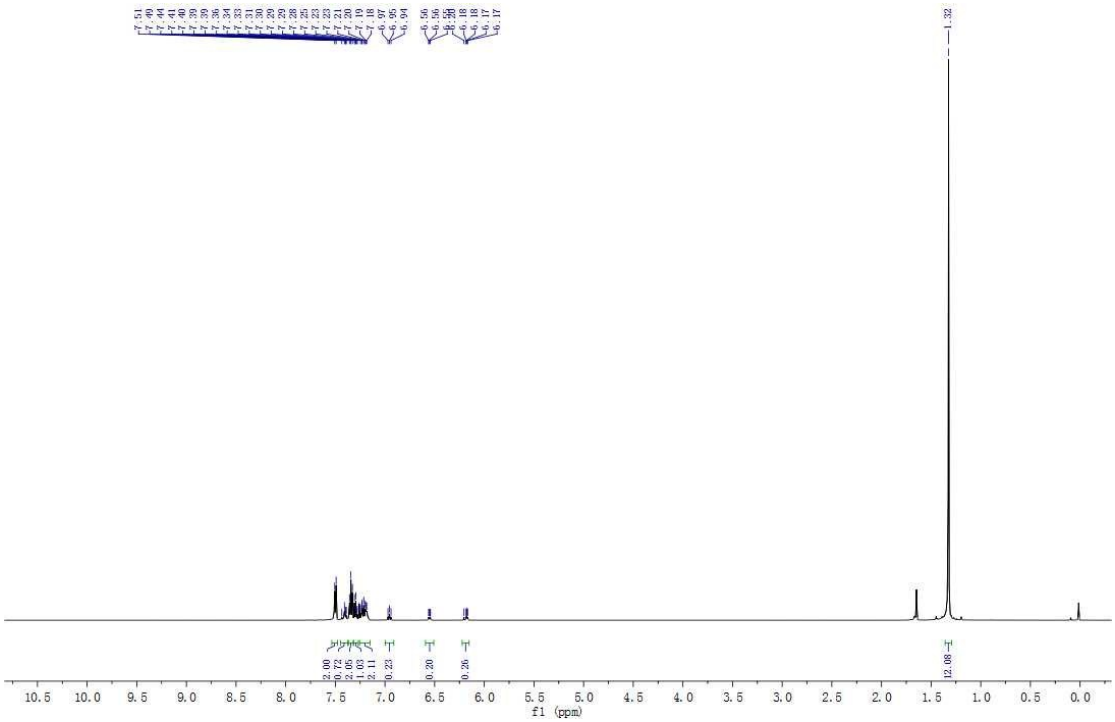
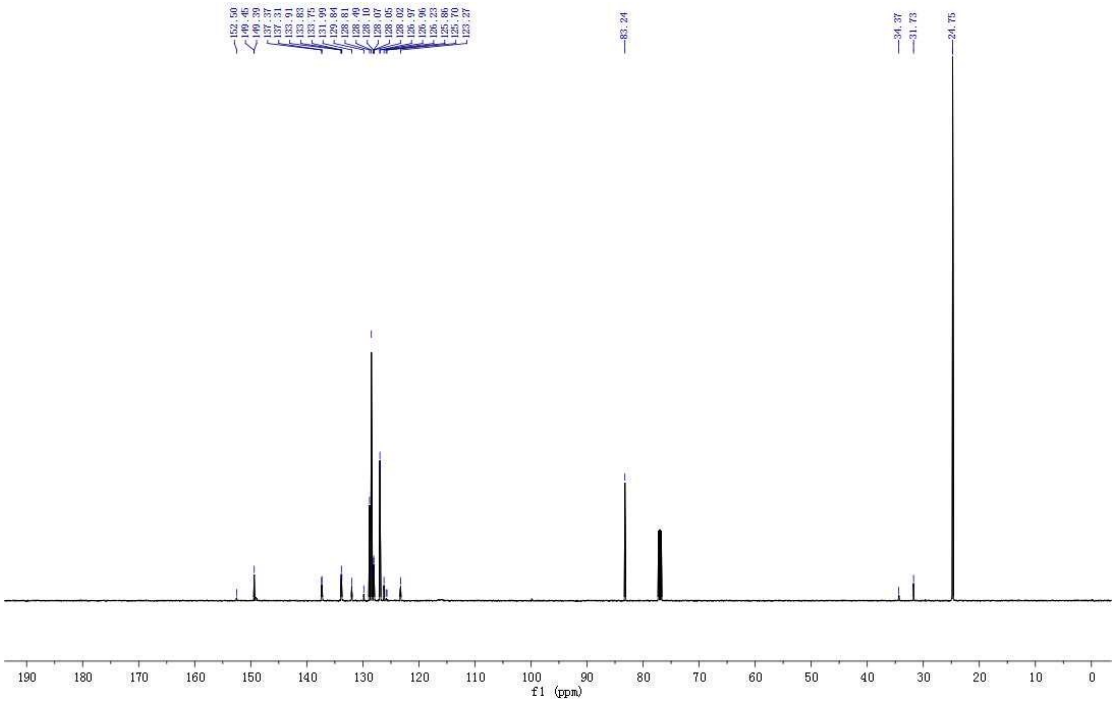
2.00
0.14
1.99
1.00
0.73
12.06
f1 (ppm)


149.48
149.32
149.13
148.95
137.36
128.86
128.53
127.01
83.31
24.79
f1 (ppm)

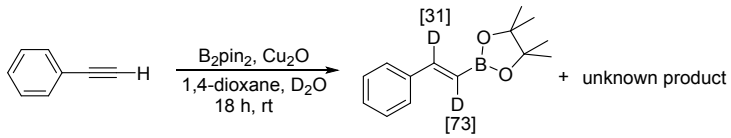
A:

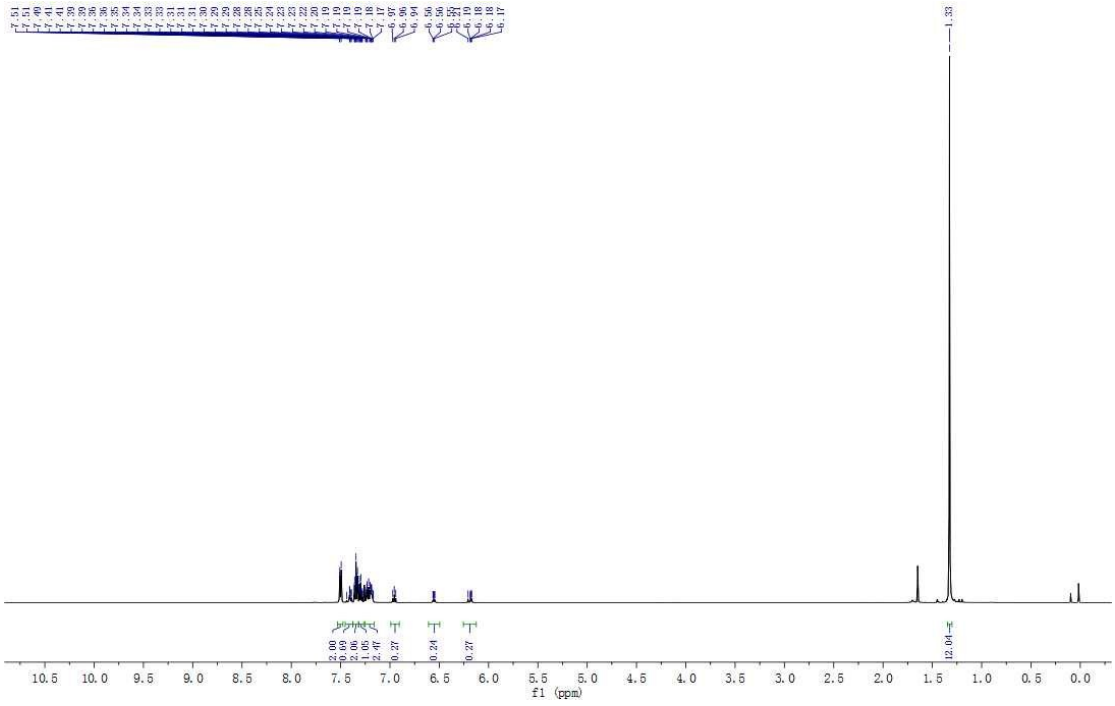

B2pin2, Cu2O
1,4-dioxane, D2O
18 h, rt
[28]
D
[74]
D
+ unknown product

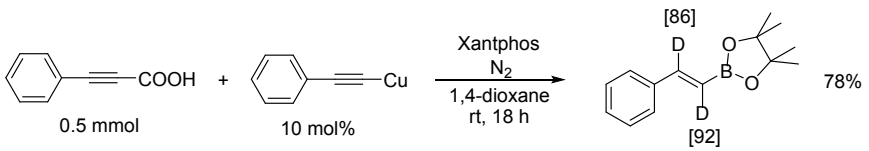

f1 (ppm)

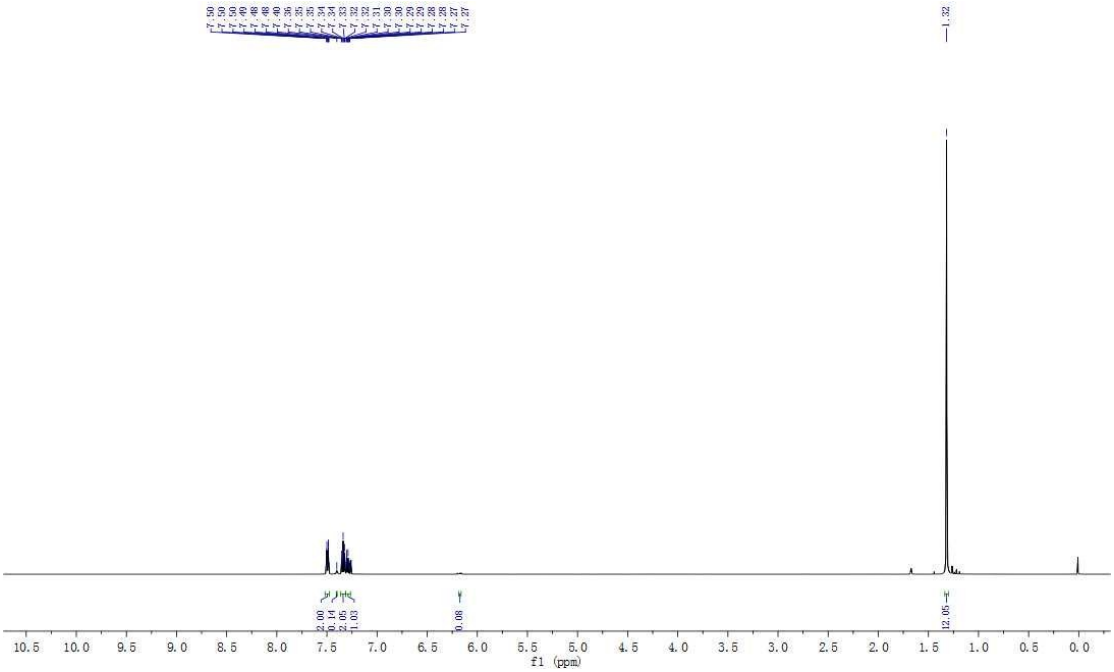

f1 (ppm)

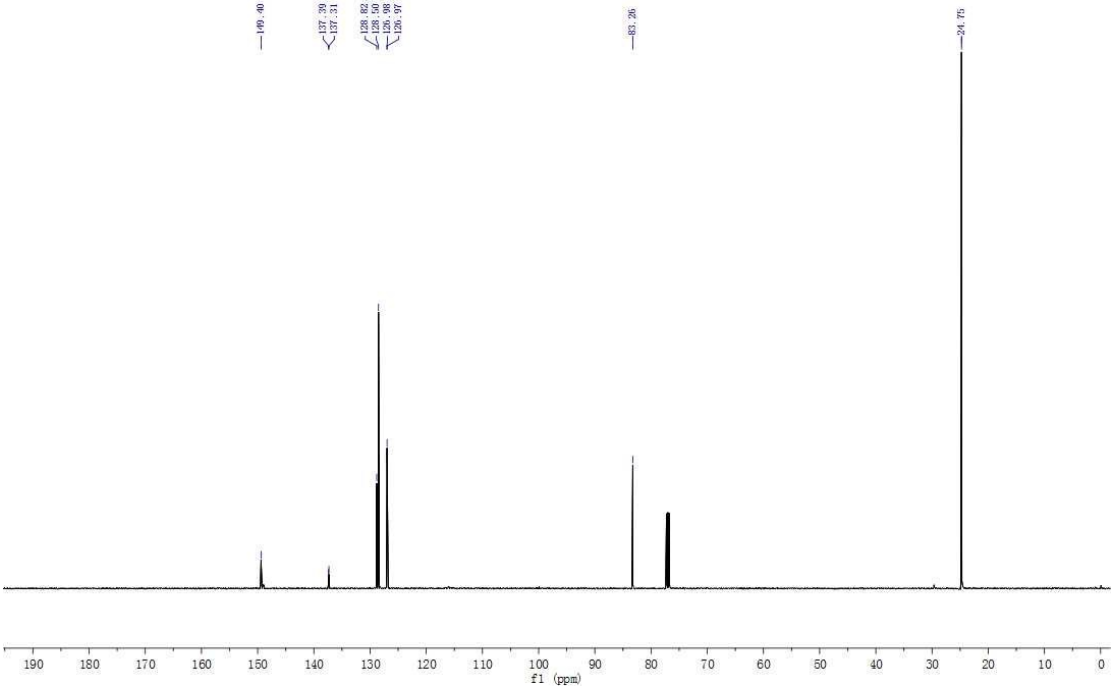
B:

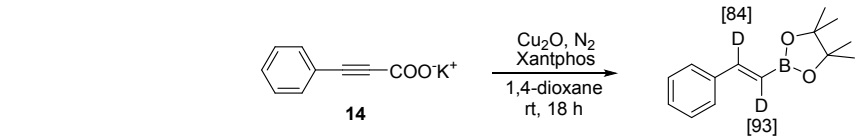

B2pin2, Cu2O
1,4-dioxane, D2O
18 h, rt
[31]
D
[73]
D
O
B
O
+ unknown product

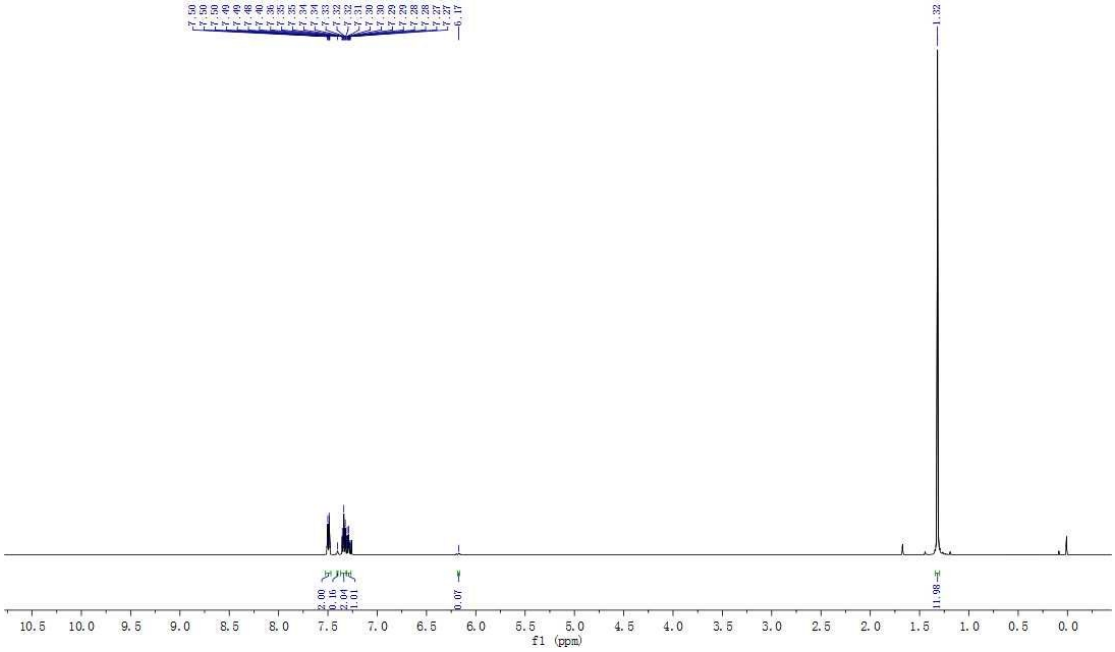

f1 (ppm)

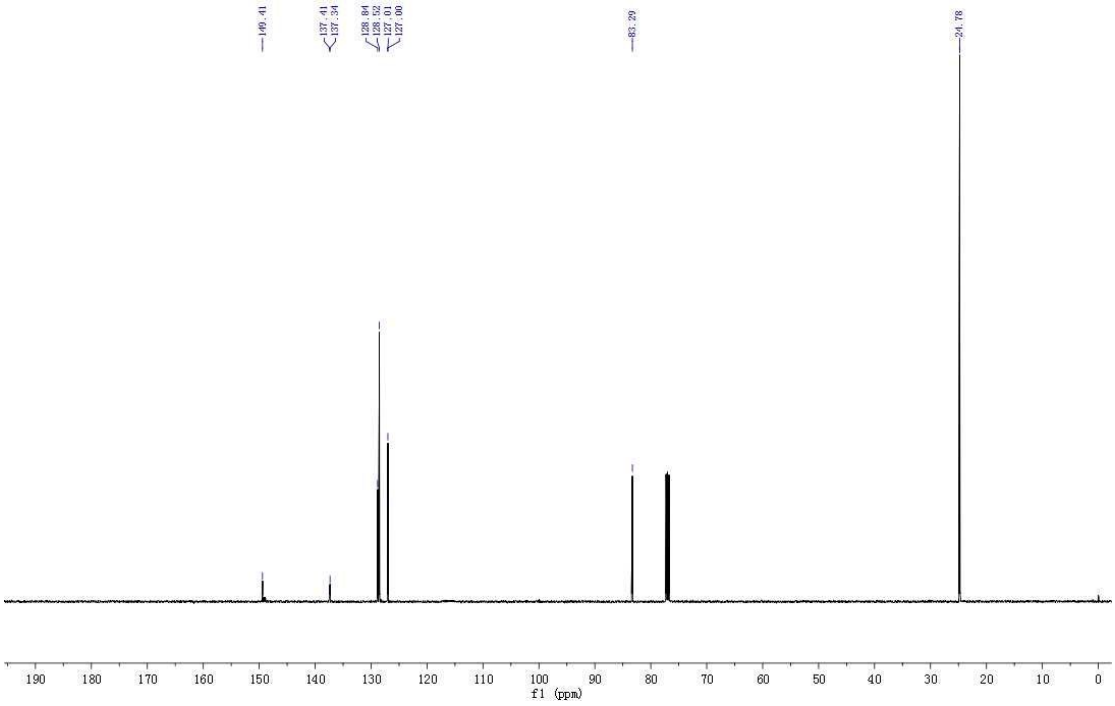

COOH
0.5 mmol
Cu
10 mol%
Xantphos
N2
1,4-dioxane
rt, 18 h
[86]
D
O
B
O
D
[92]
78%


f1 (ppm)


f1 (ppm)

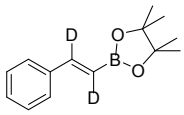

COO⁻K⁺
14
Cu2O, N2
Xantphos
1,4-dioxane
rt, 18 h
[84]
D
O
B
O
D
[93]

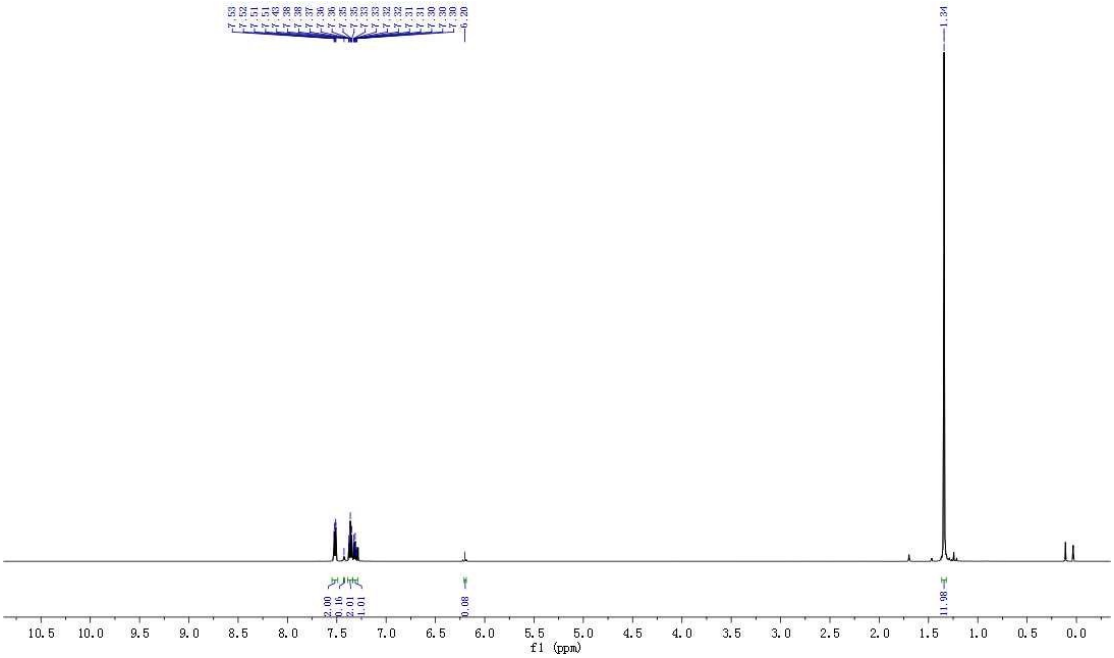

1.32
2.00
0.16
2.04
1.01
0.07
11.98
f1 (ppm)

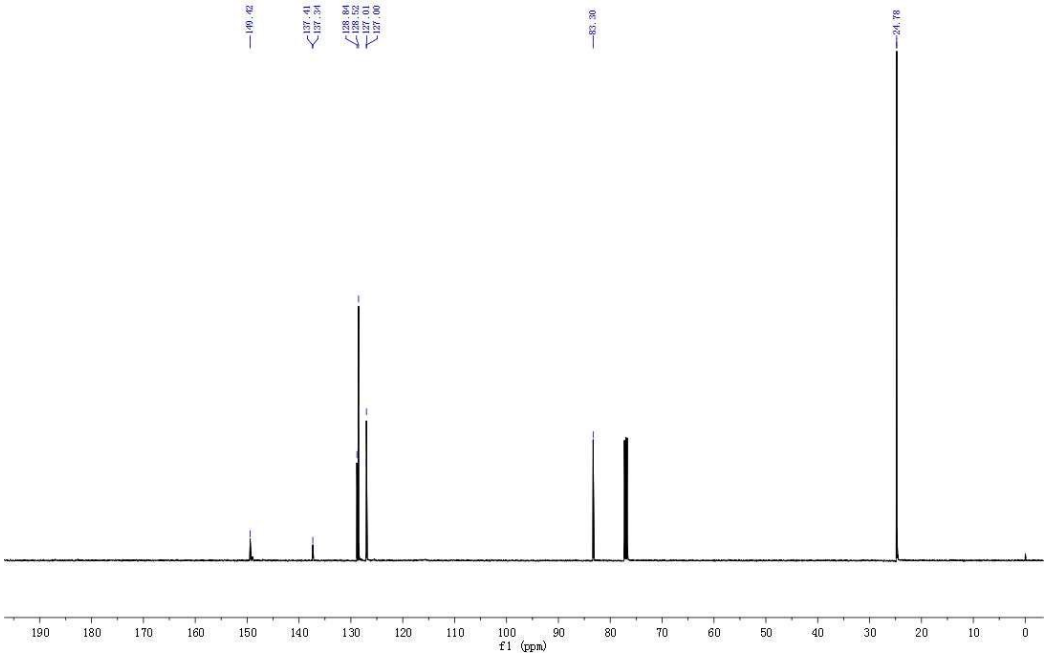

149.41
137.41
137.34
128.84
128.52
127.01
127.00
83.29
24.78
f1 (ppm)

Spectroscopic data of (E)-bis-deuterated β-borylated α, β-styrene derivatives

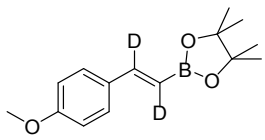
(*E*)-4,4,5,5-tetramethyl-2-(2-phenylvinyl-1,2-d_2)-1,3,2-dioxaborolane (3a)

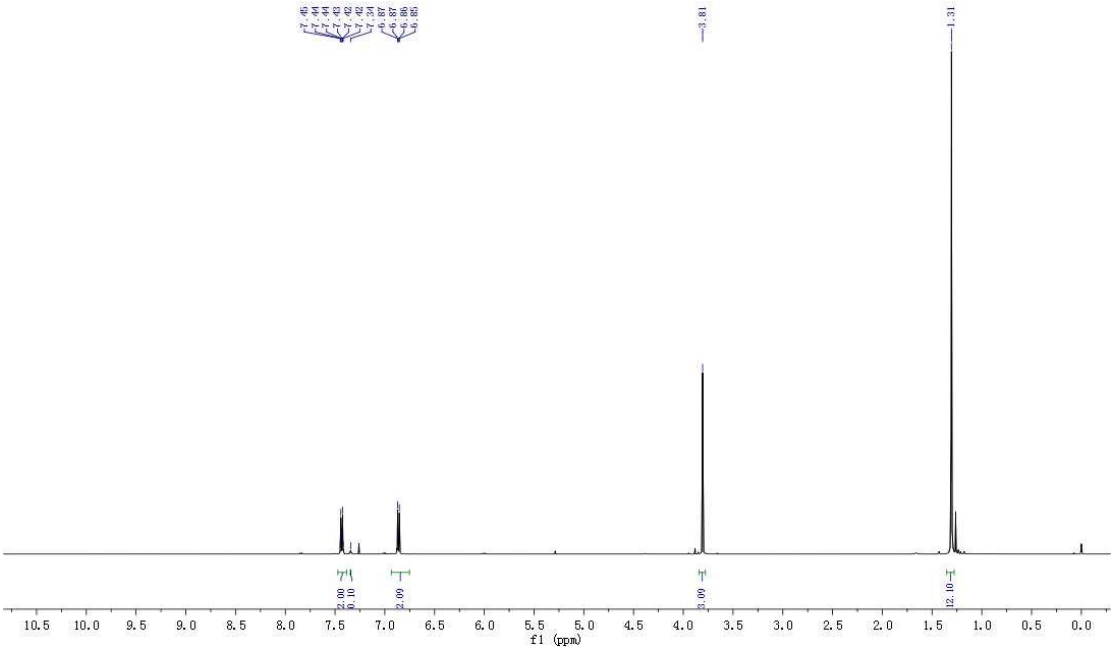


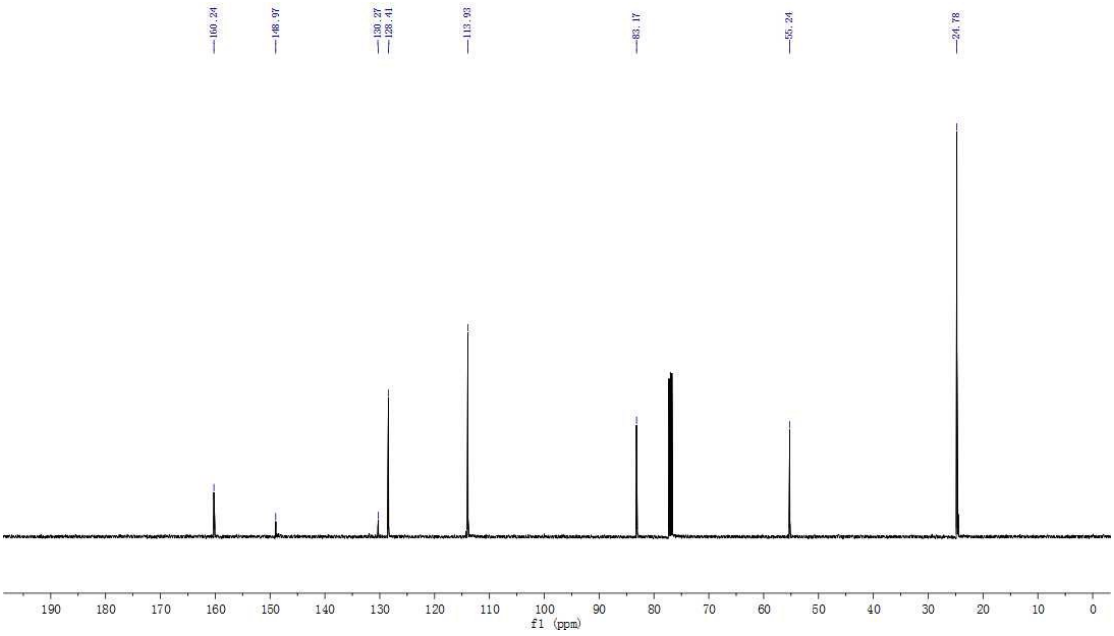




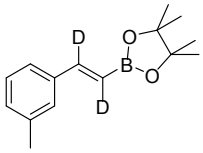
(*E*)-2-(2-(4-methoxyphenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)

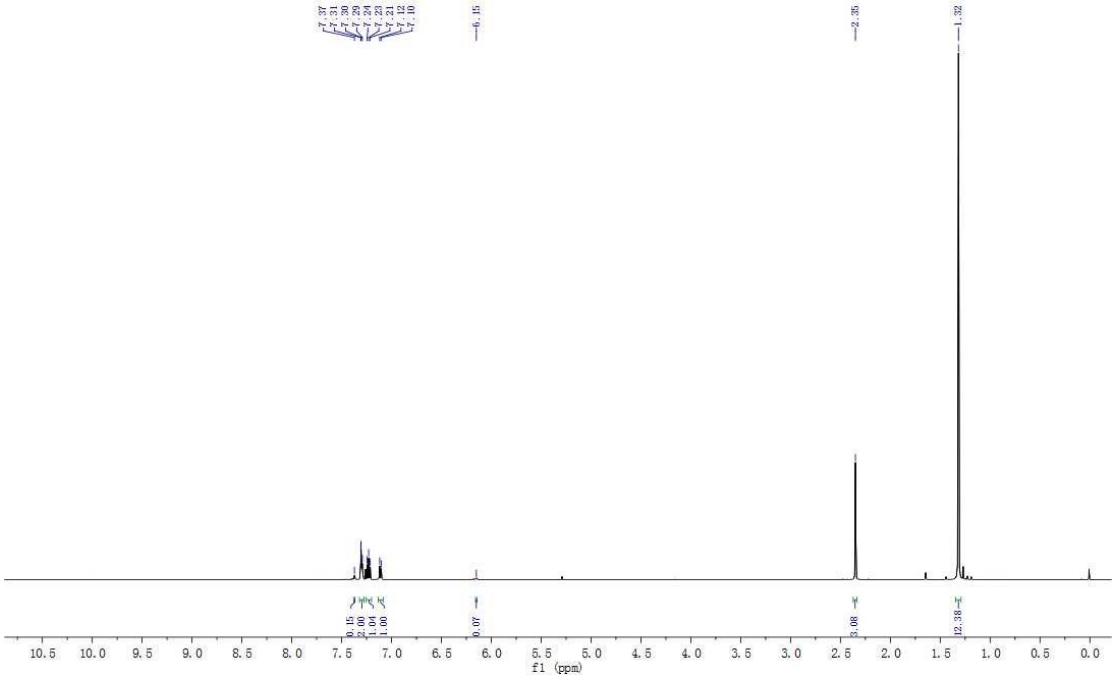


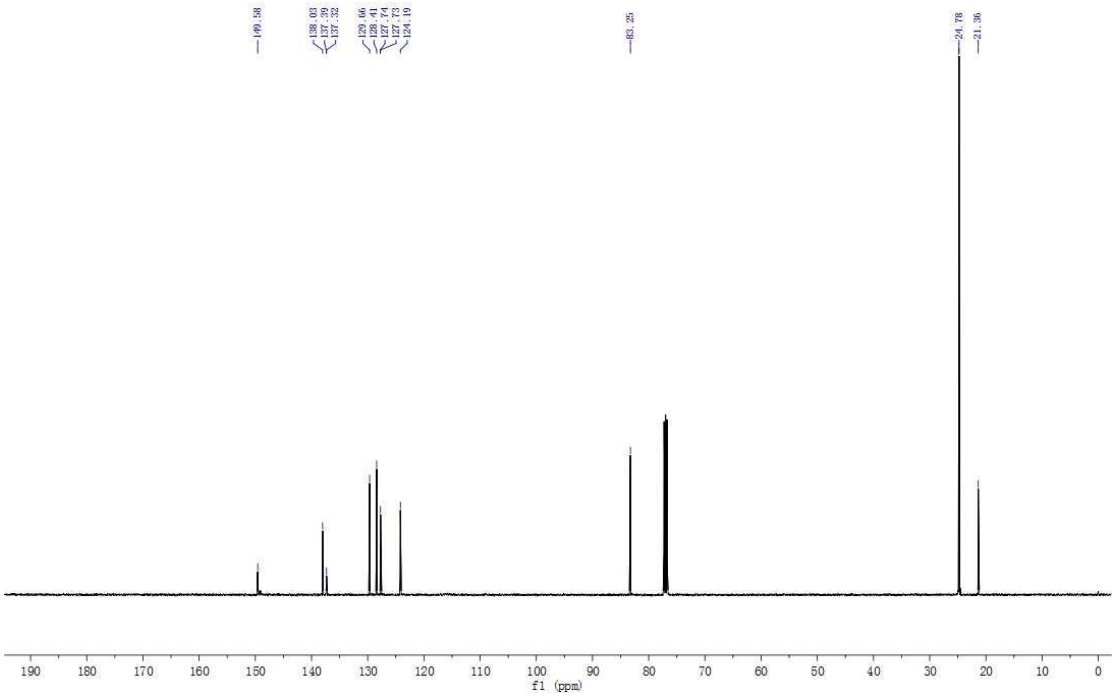




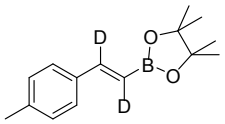
(*E*)-4,4,5,5-tetramethyl-2-(2-(m-tolyl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3c)

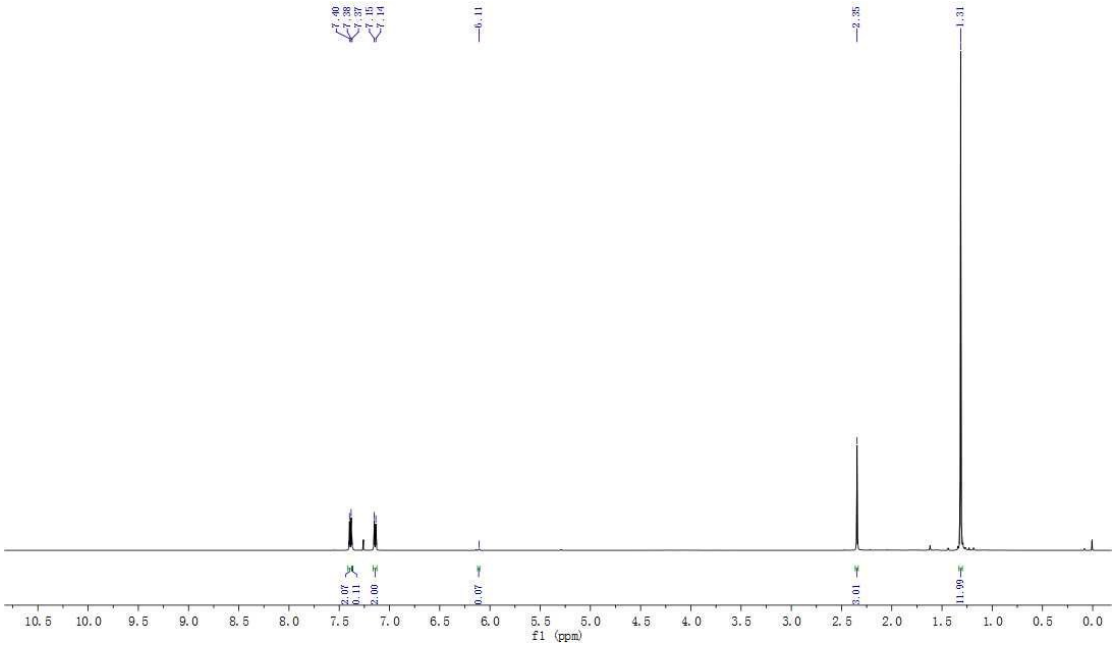


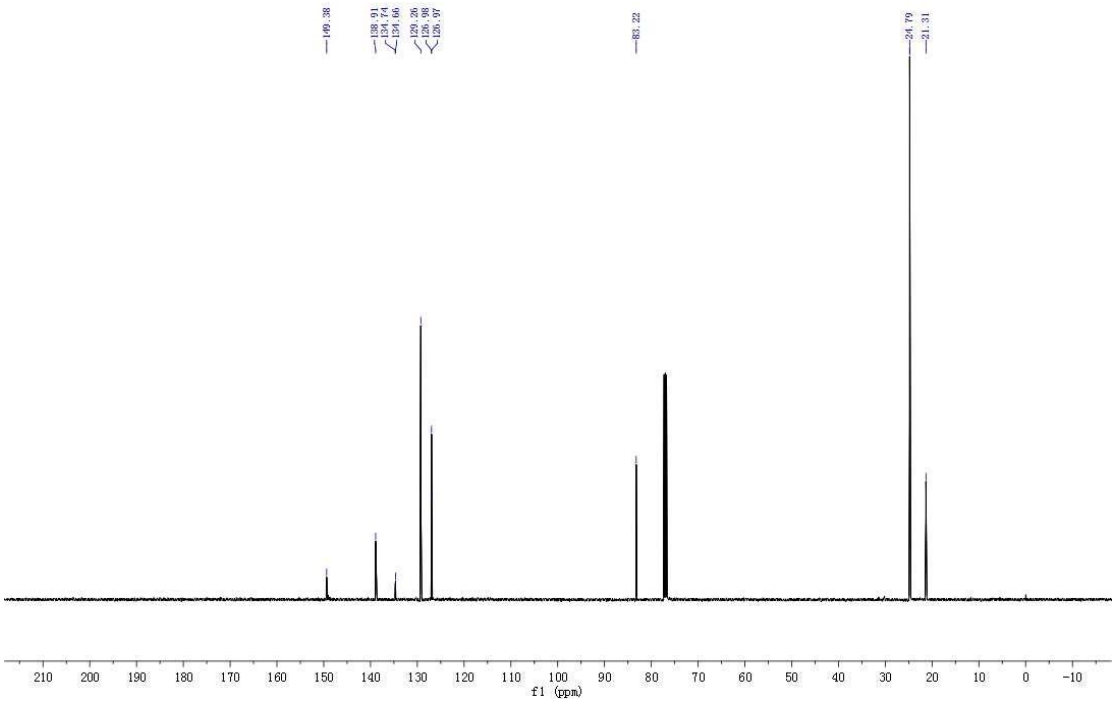




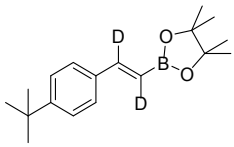
(*E*)-4,4,5,5-tetramethyl-2-(2-(p-tolyl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3d)

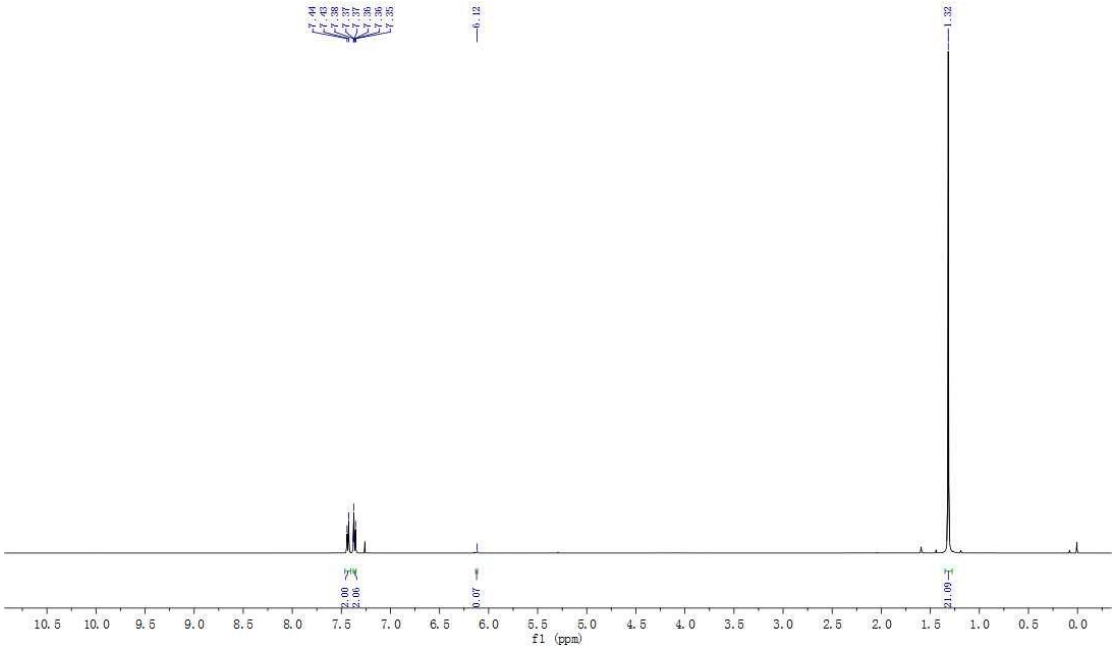


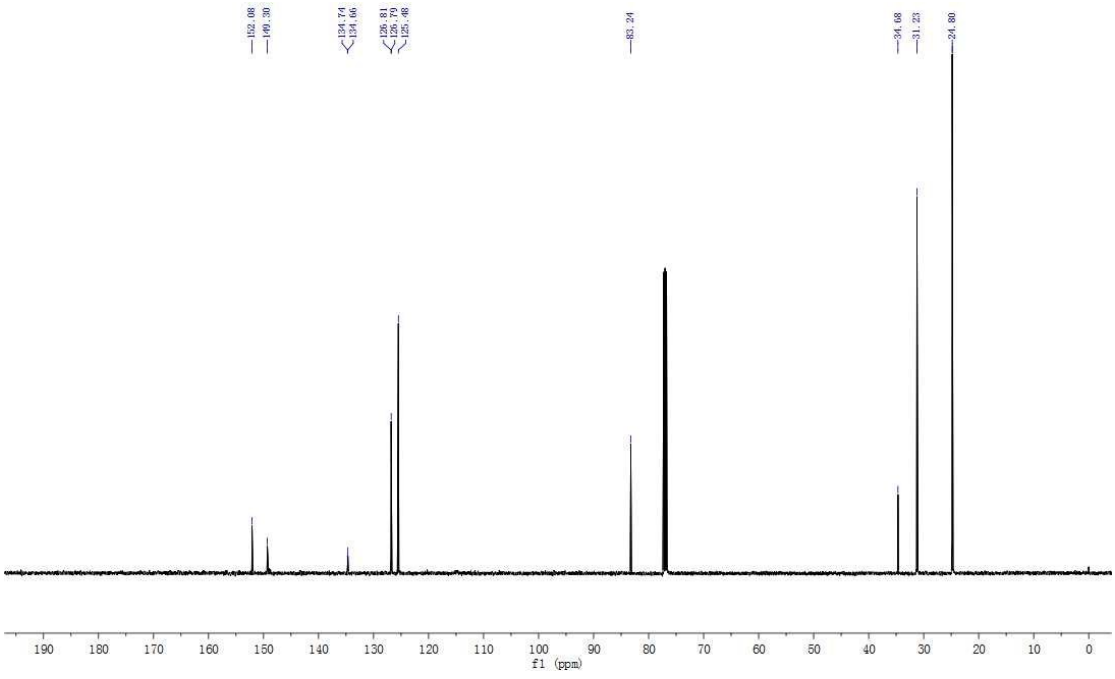




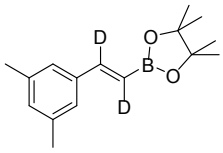
(*E*)-2-(2-(4-(tert-butyl)phenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)

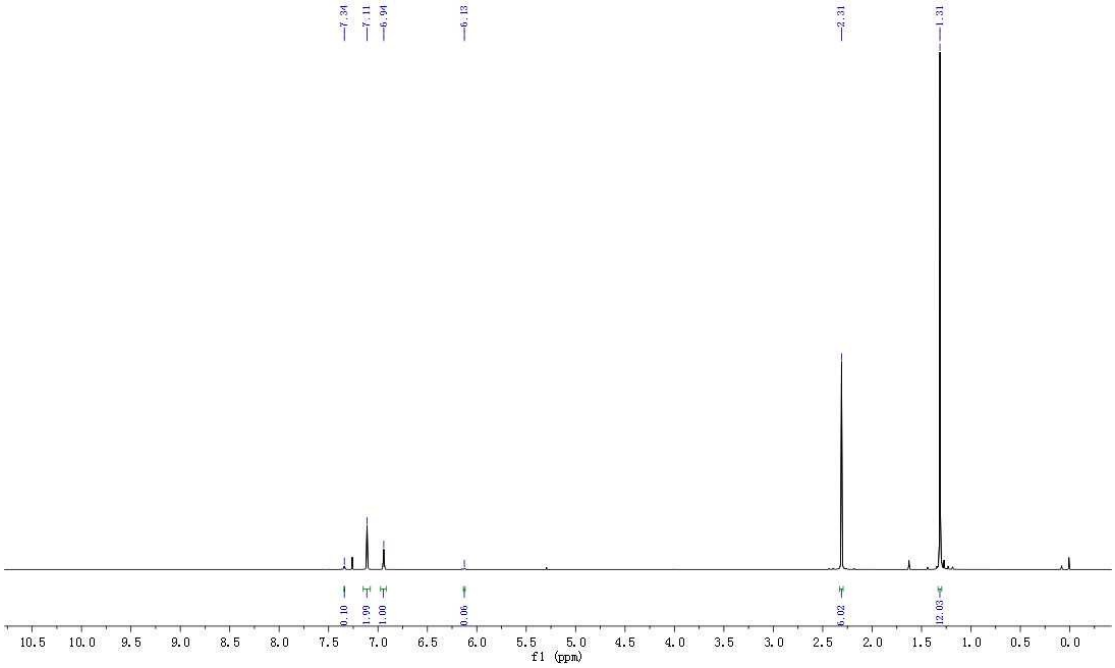


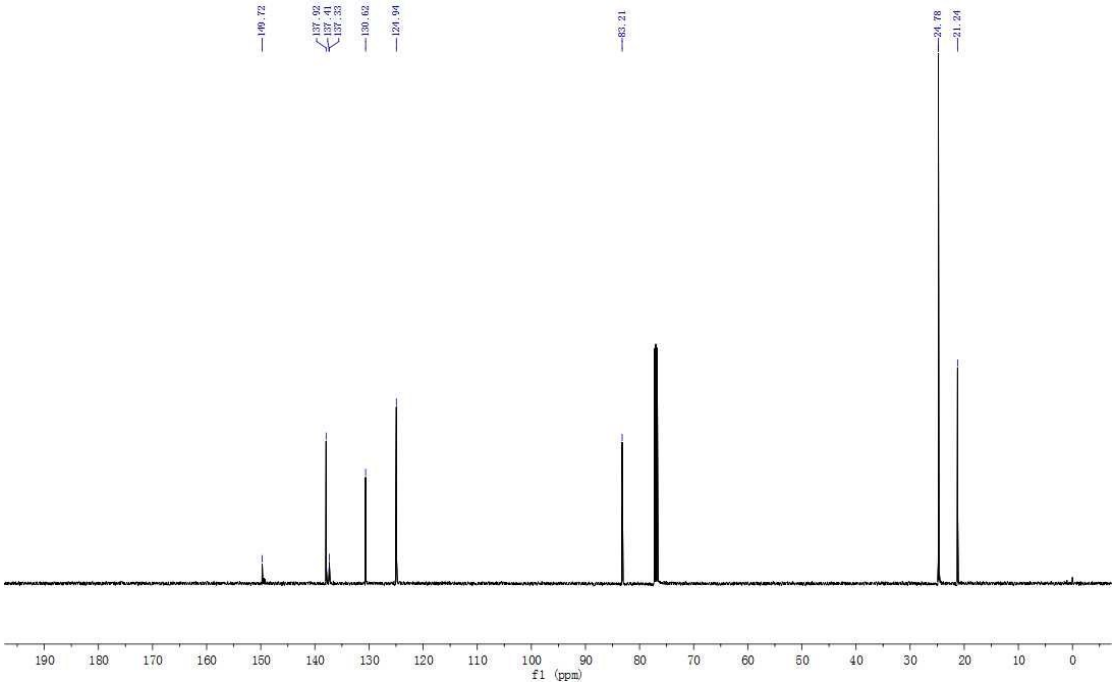




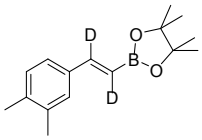
(*E*)-2-(2-(3,5-dimethylphenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)

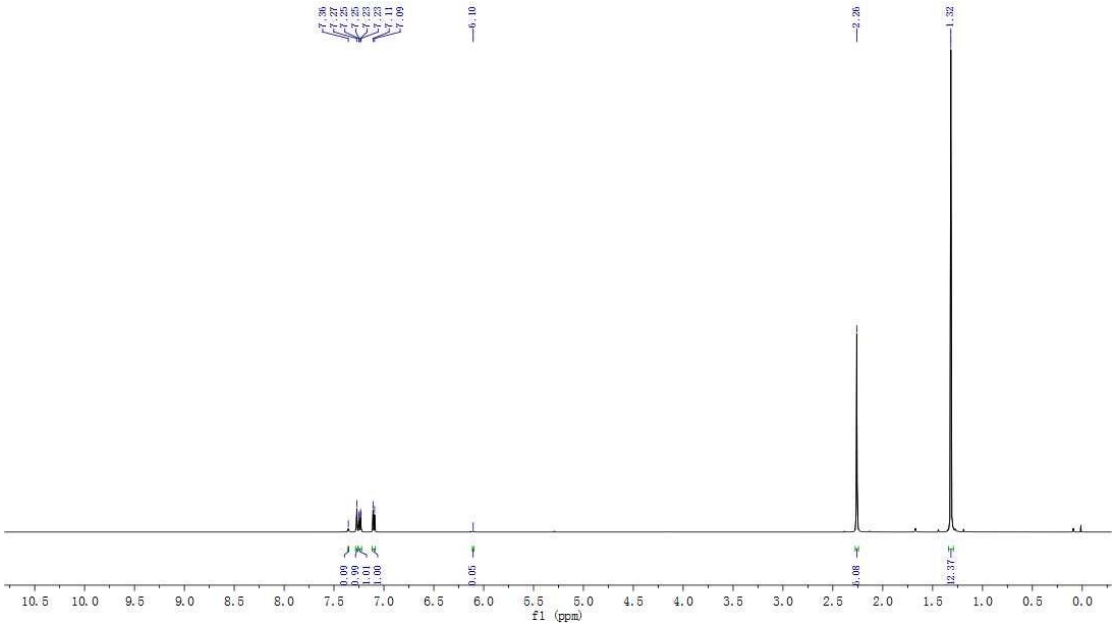


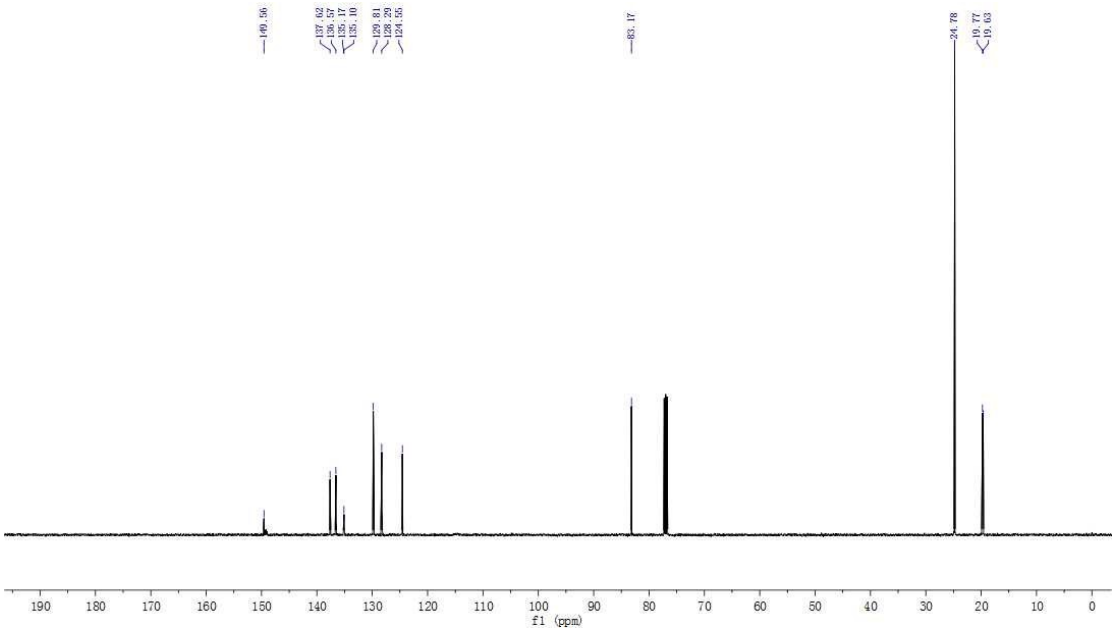




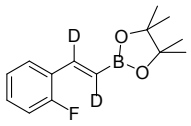
(*E*)-2-(2-(3,4-dimethylphenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)

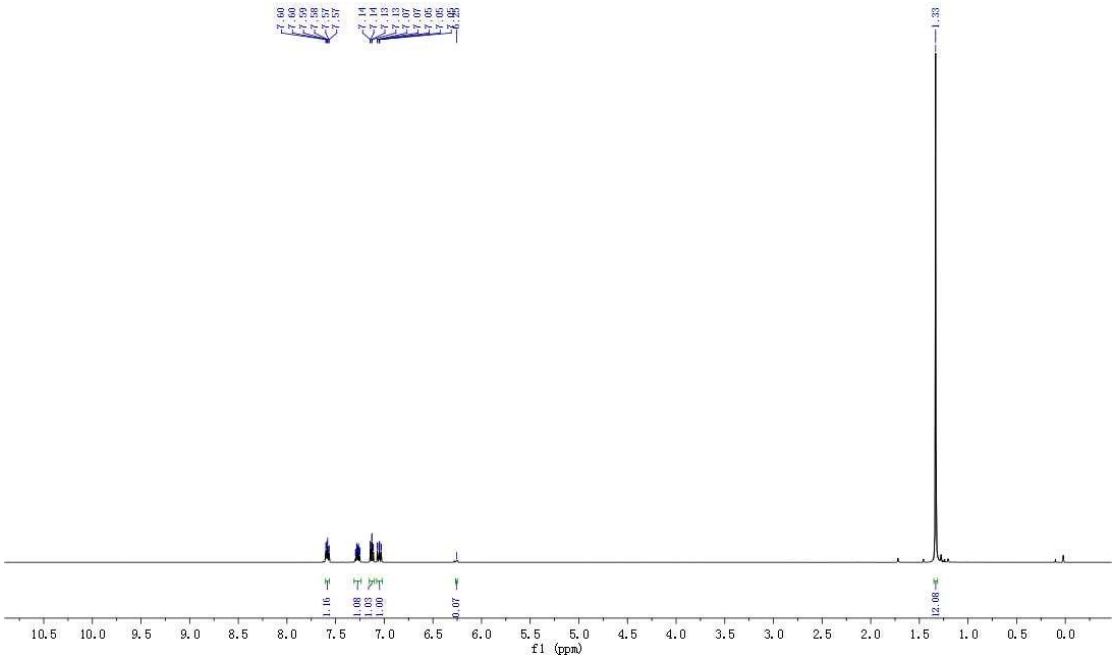


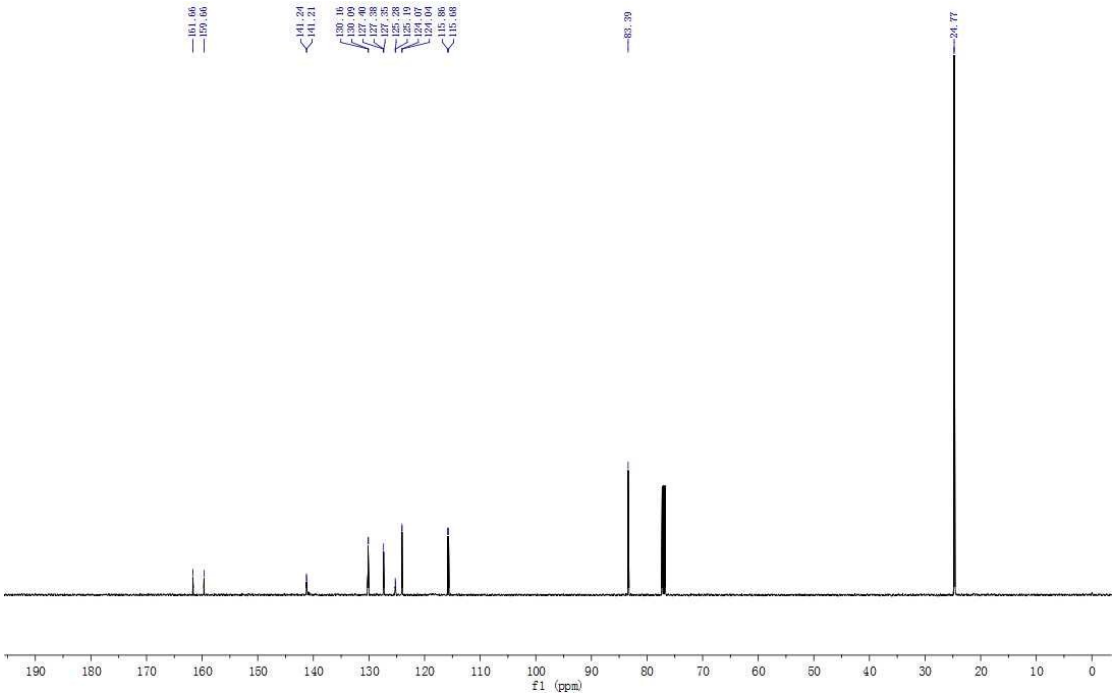




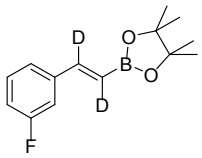
(*E*)-2-(2-(2-fluorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)

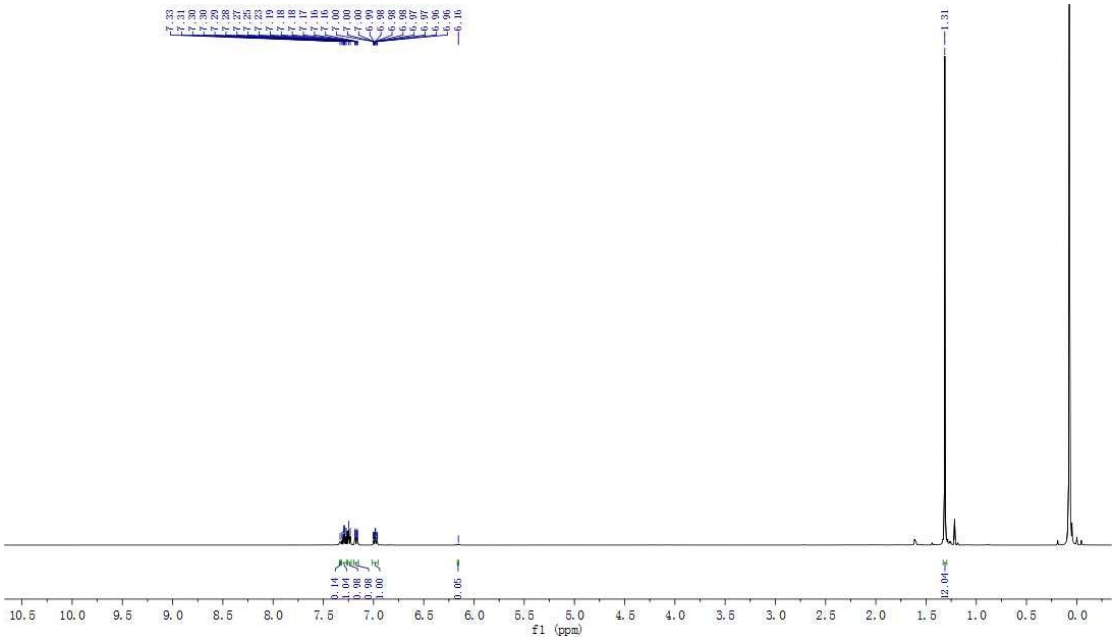


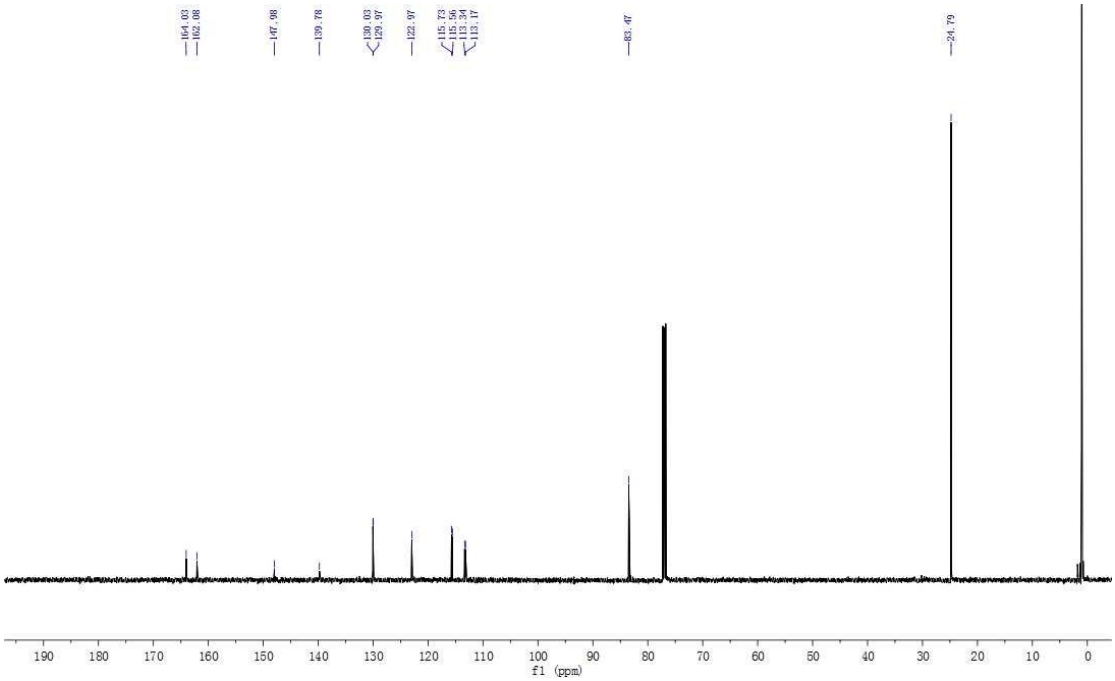




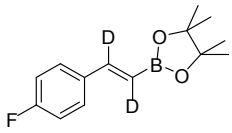
(*E*)-2-(2-(3-fluorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)

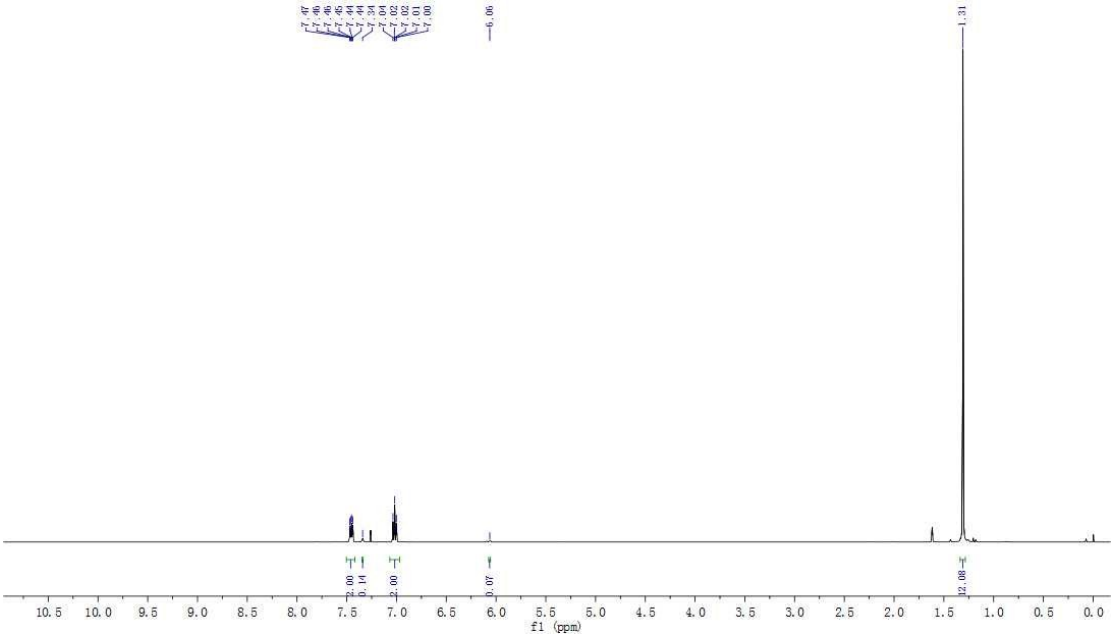


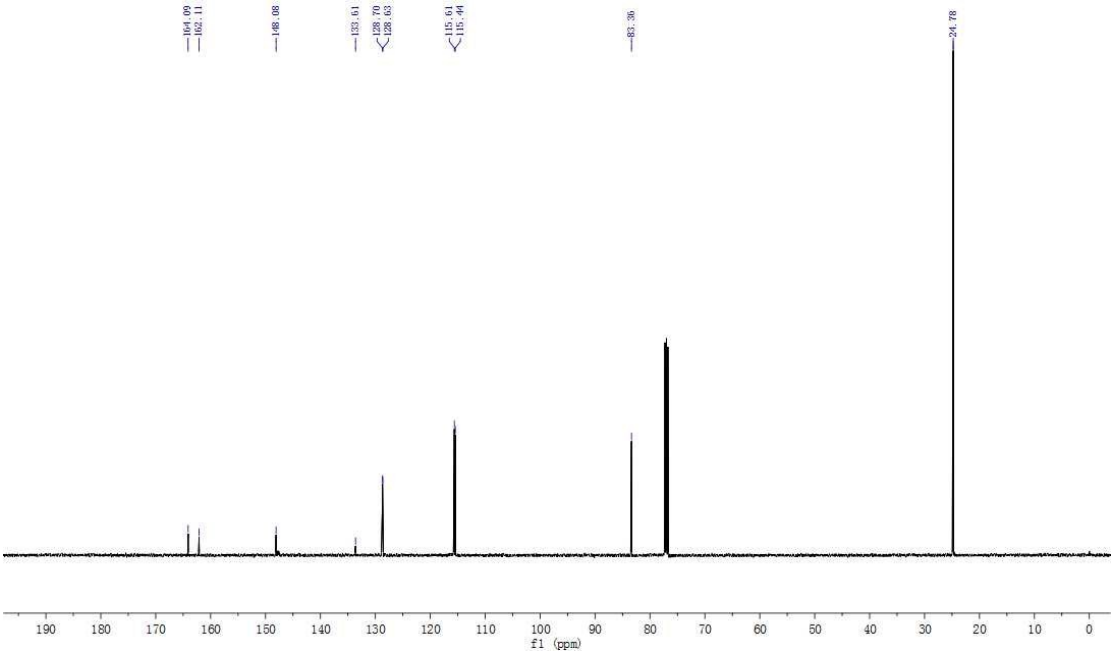




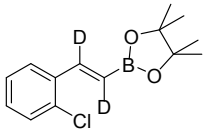
(*E*)-2-(2-(4-fluorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)

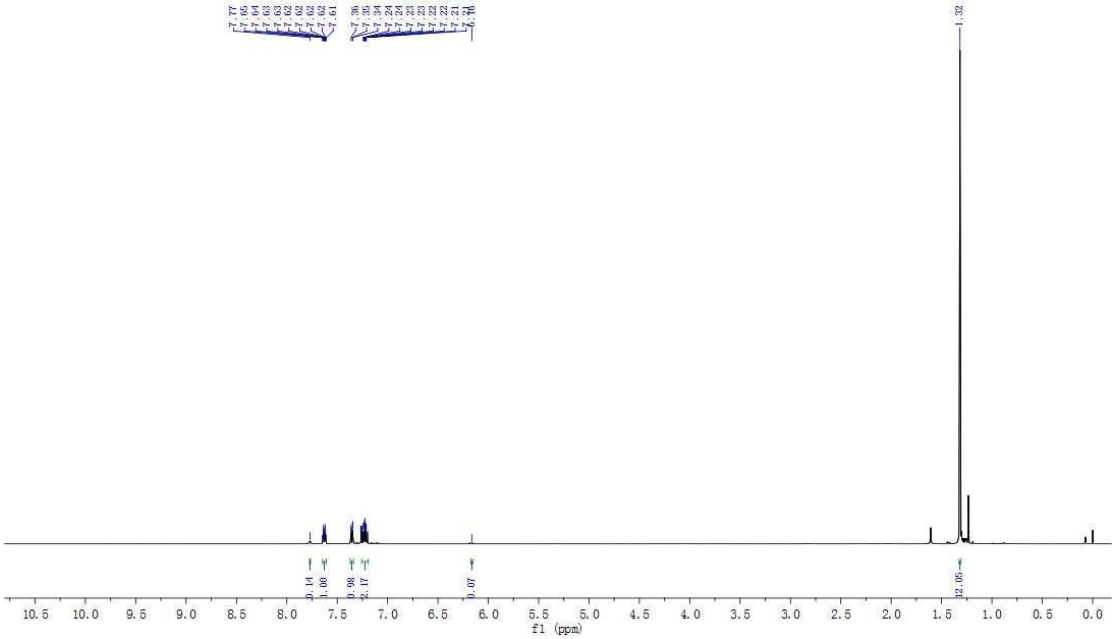


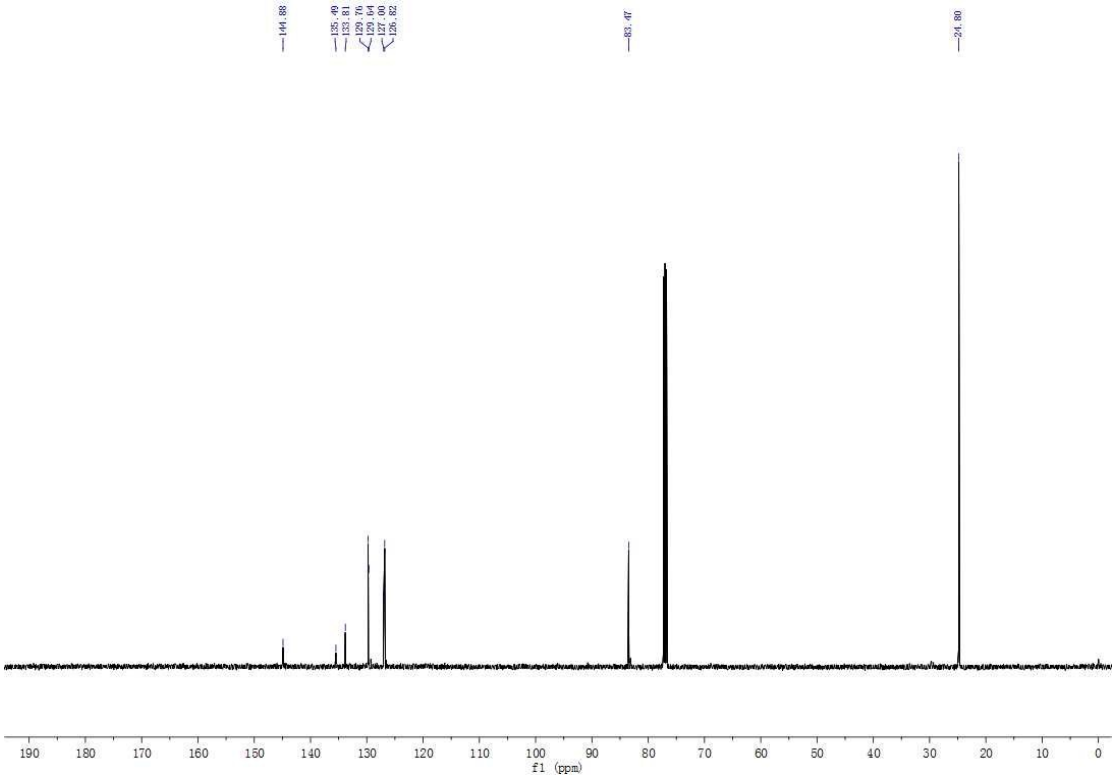




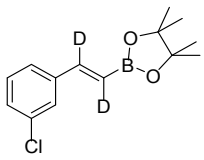
(*E*)-2-(2-(2-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)

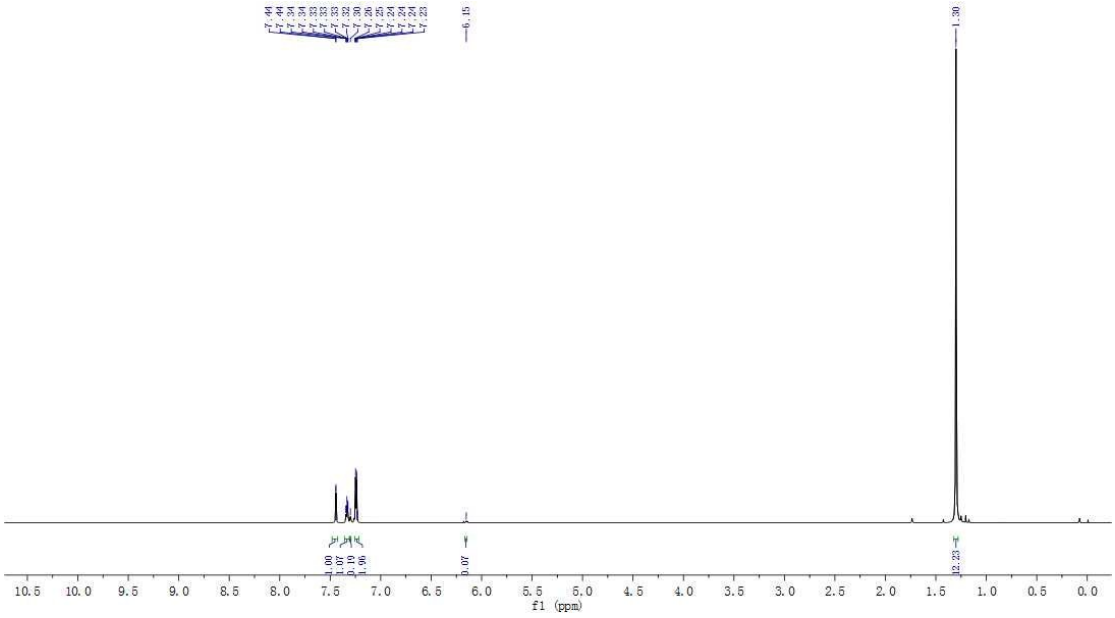


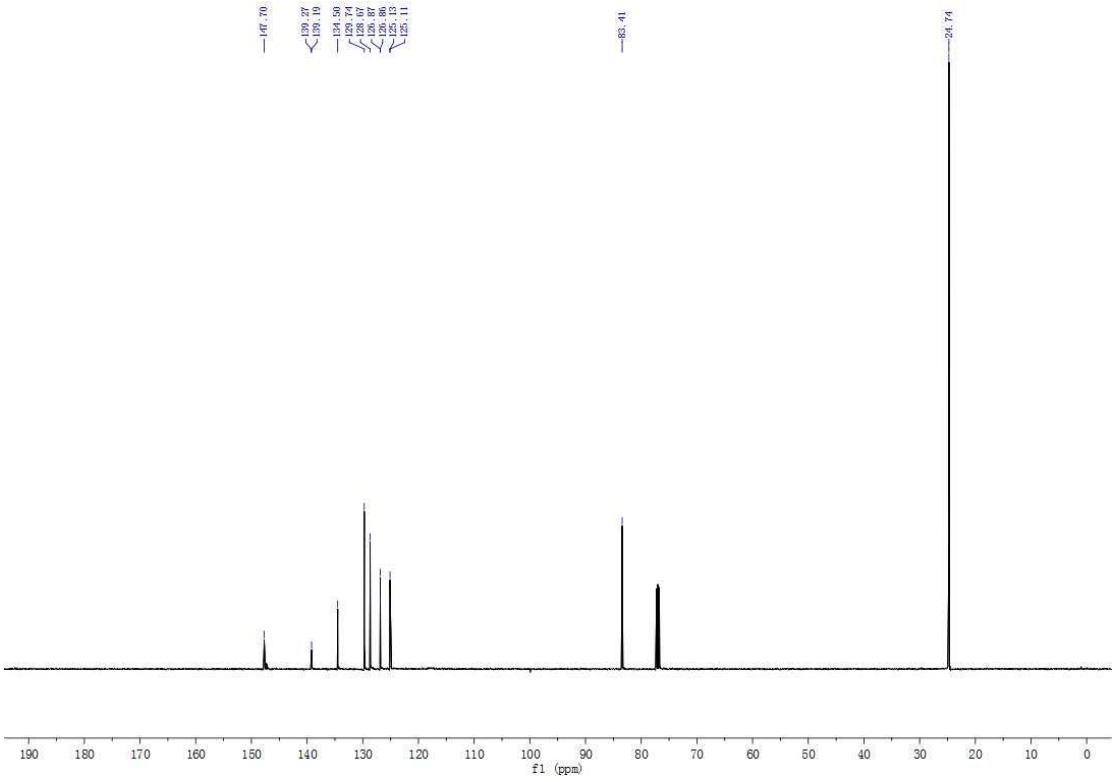




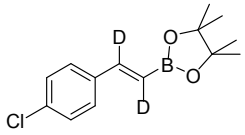
(*E*)-2-(2-(3-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)

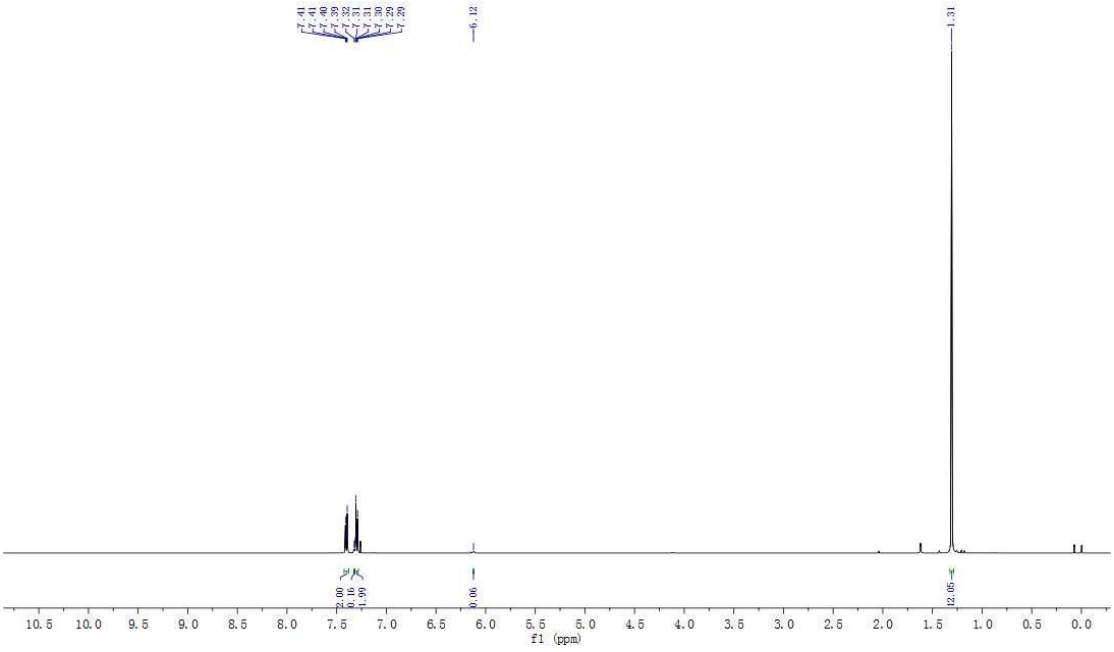


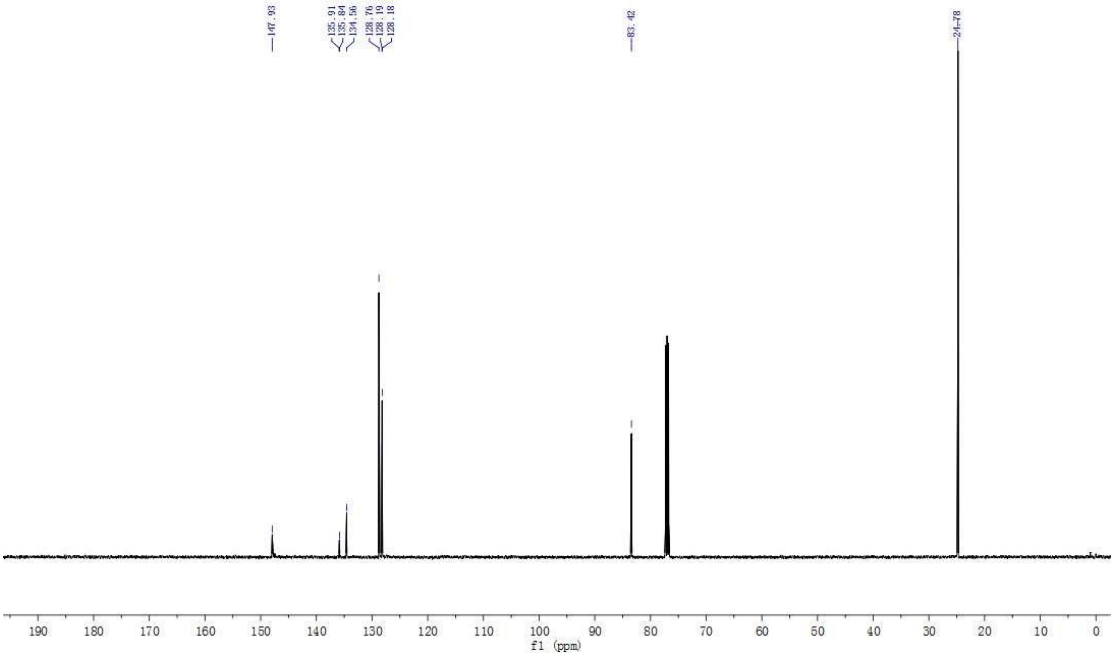




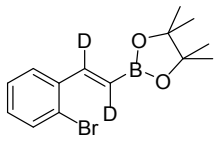
(*E*)-2-(2-(4-chlorophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m)

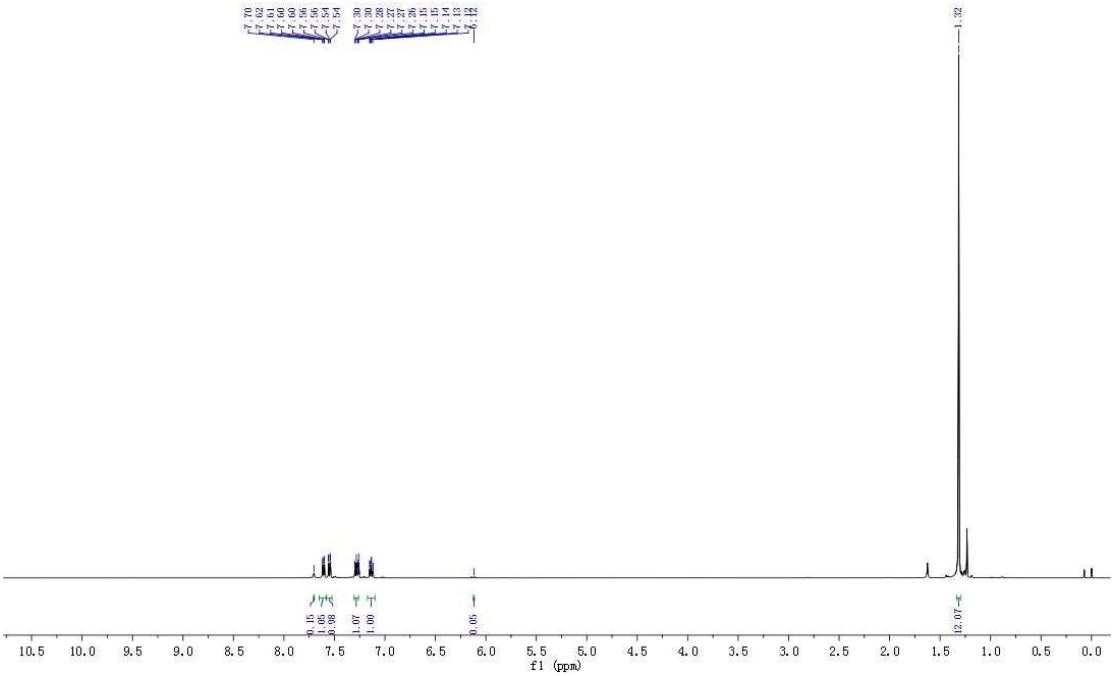


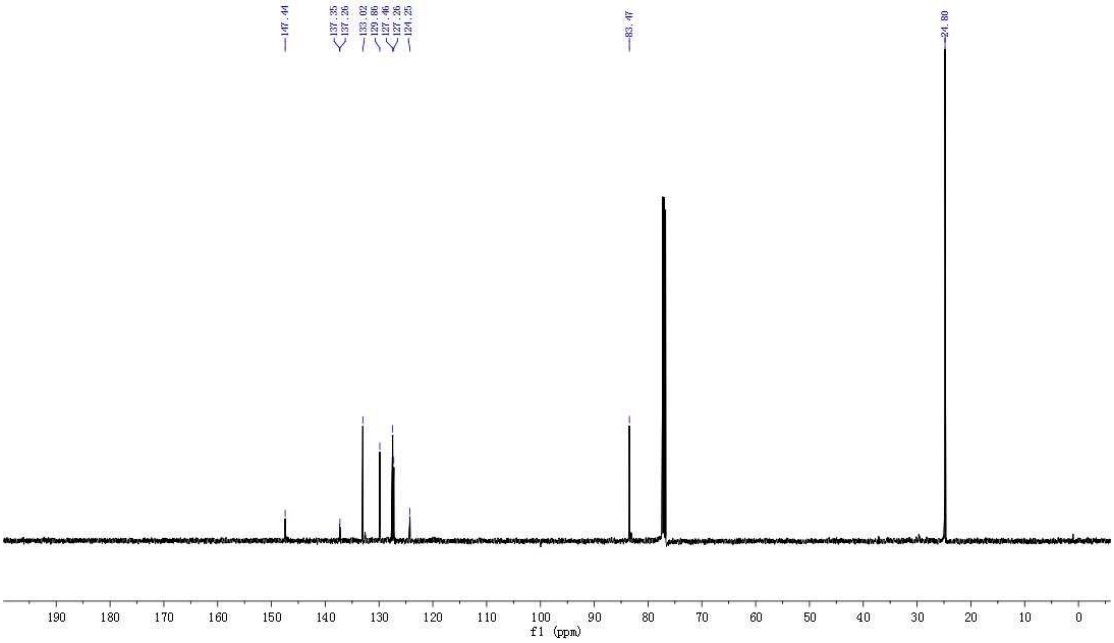




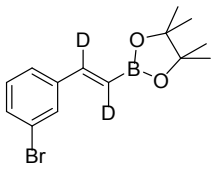
(*E*)-2-(2-(2-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)

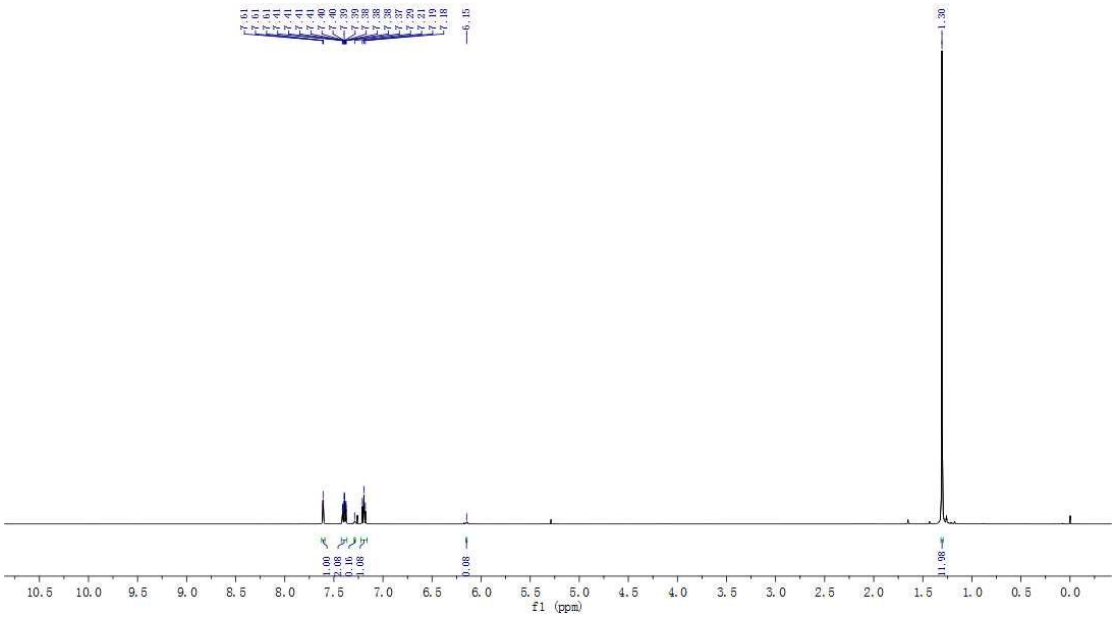


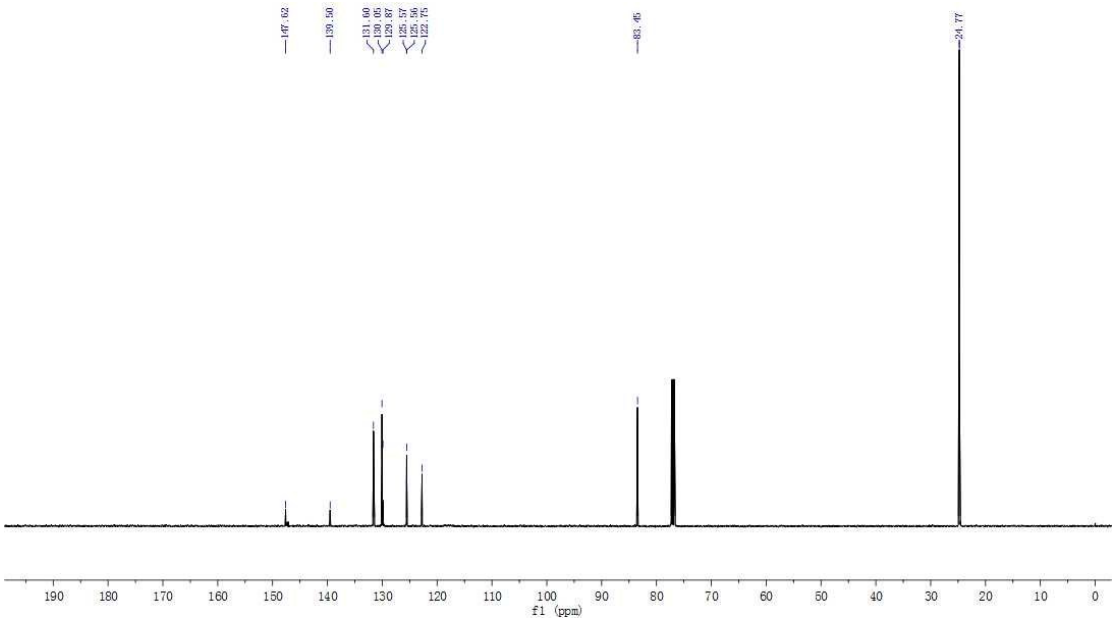




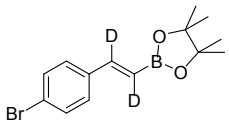
(*E*)-2-(2-(3-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o)

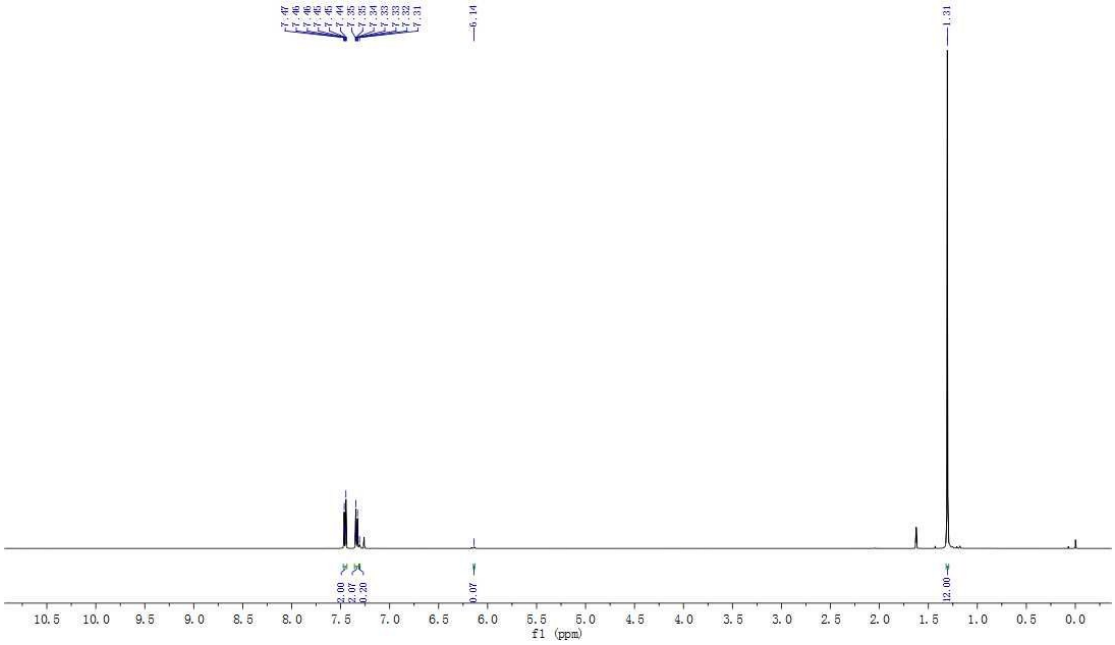


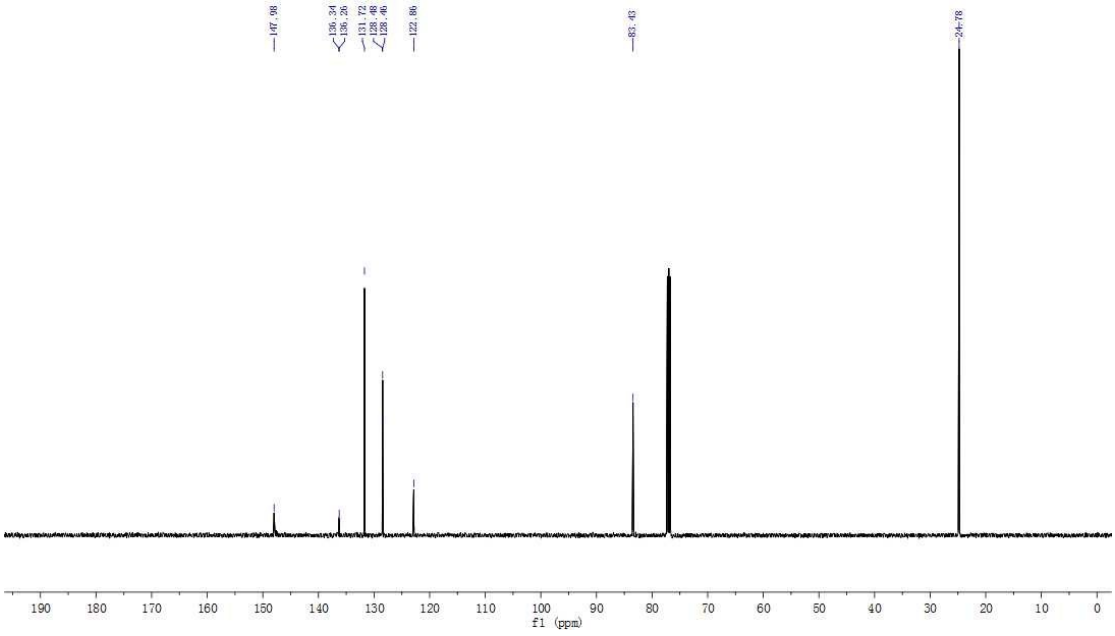




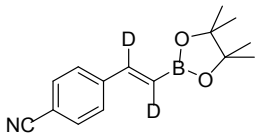
(*E*)-2-(2-(4-bromophenyl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)

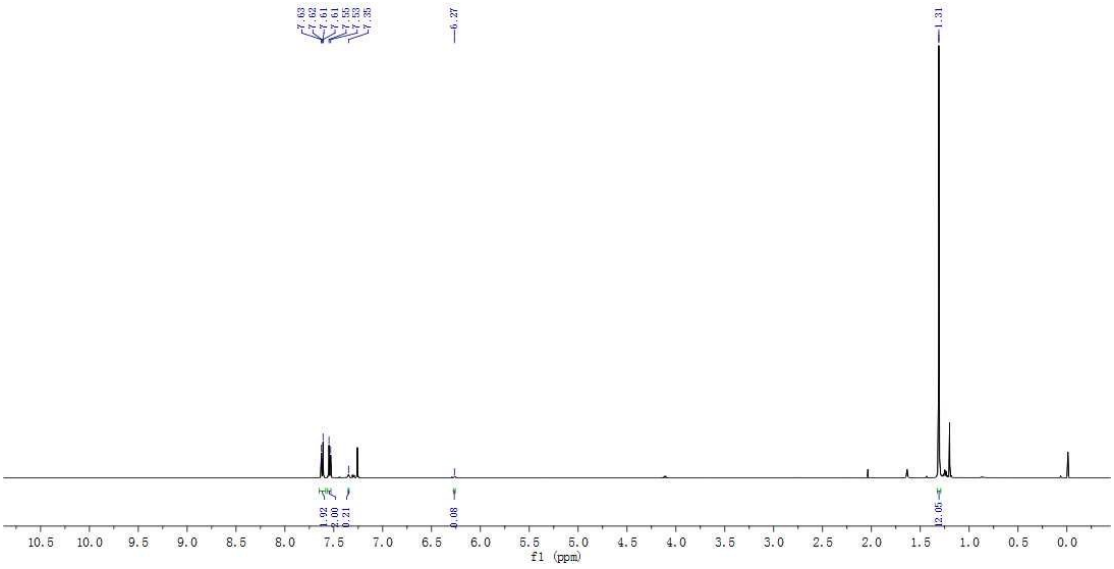


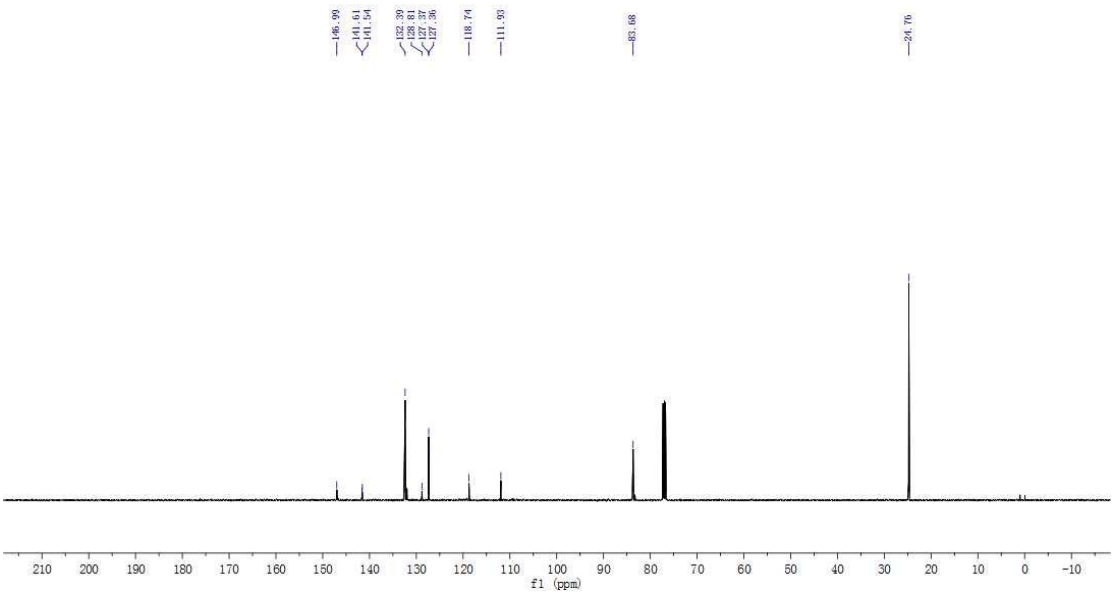




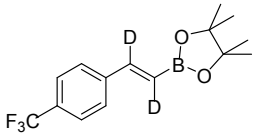
(*E*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d_2)benzonitrile (3q)

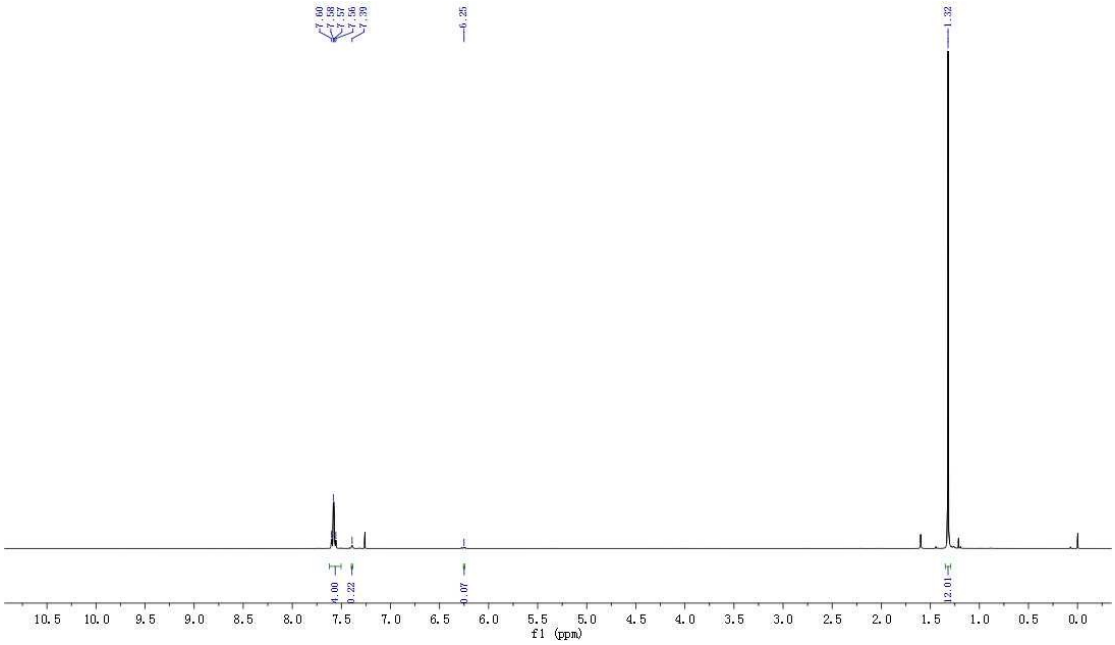


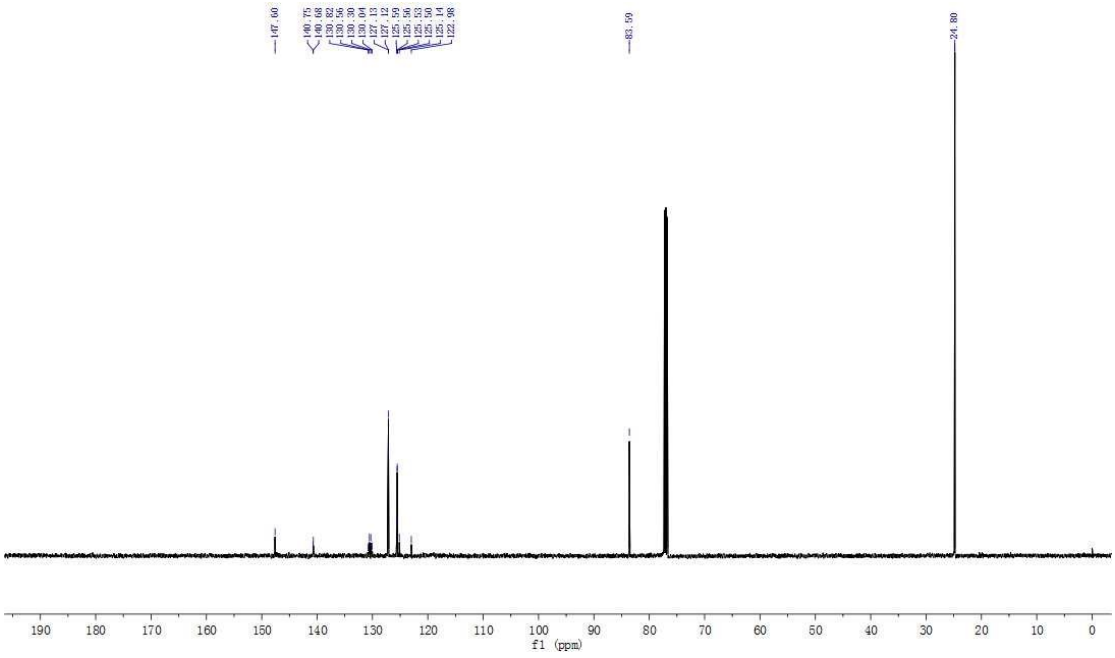




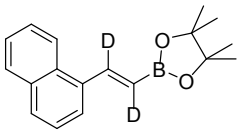
(*E*)-4,4,5,5-tetramethyl-2-(2-(4-(trifluoromethyl)phenyl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3r)

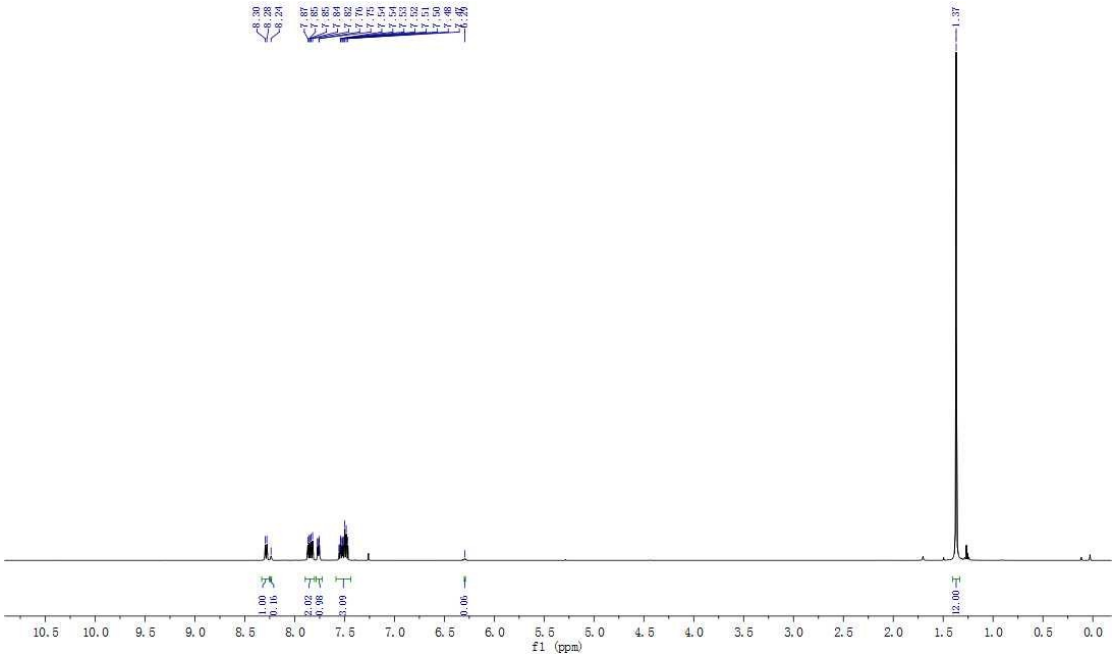


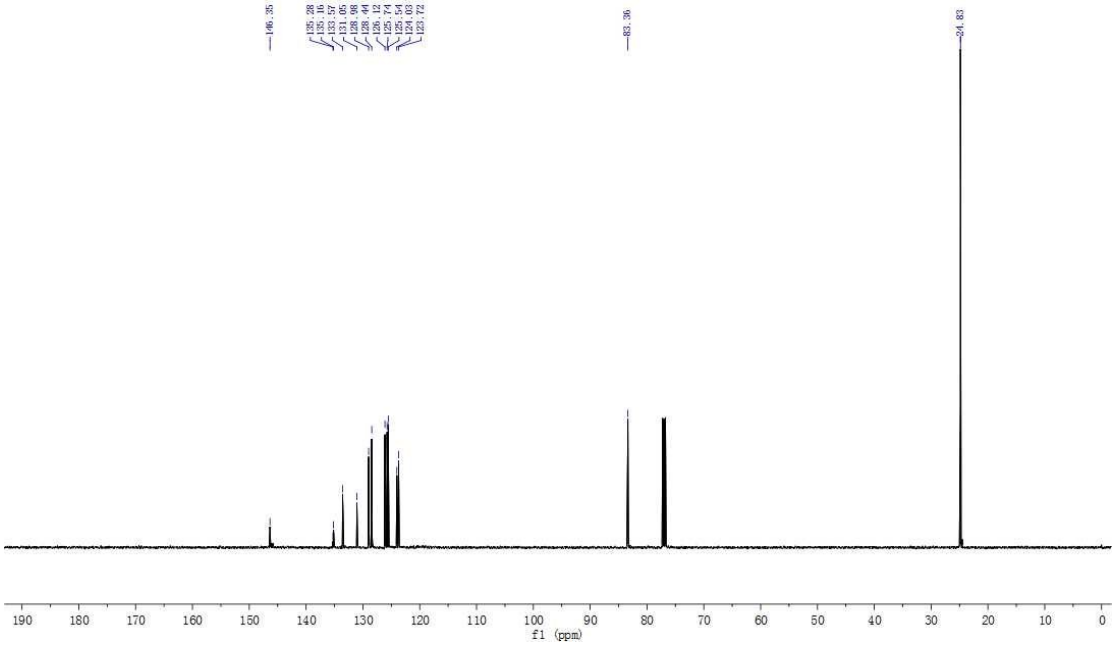




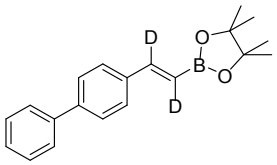
(*E*)-4,4,5,5-tetramethyl-2-(2-(naphthalen-1-yl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3s)

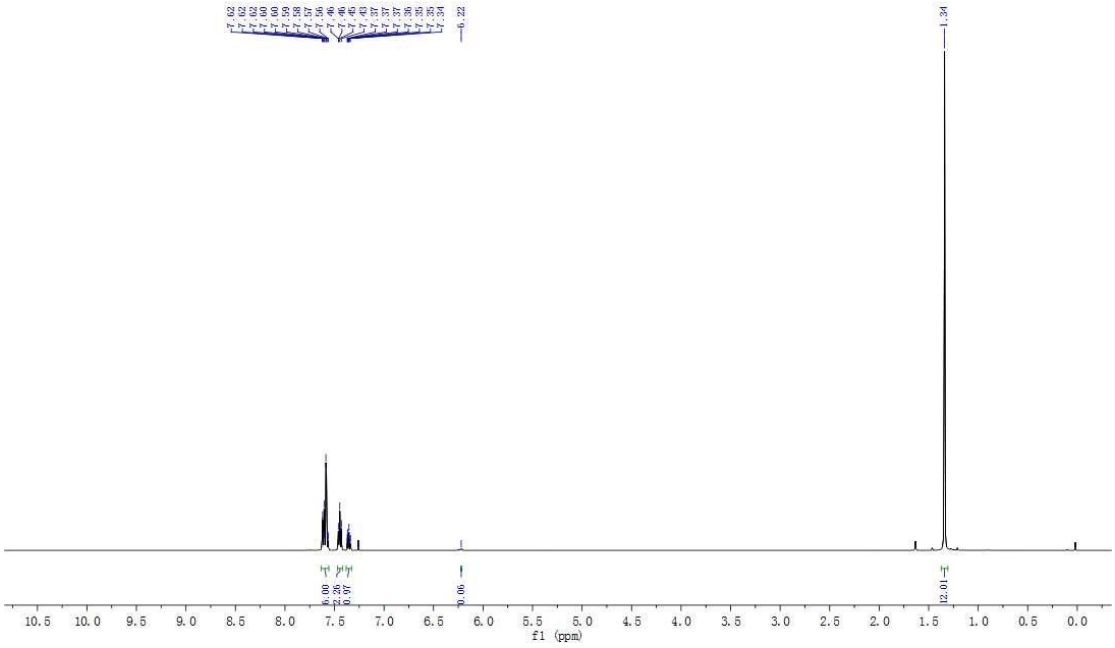


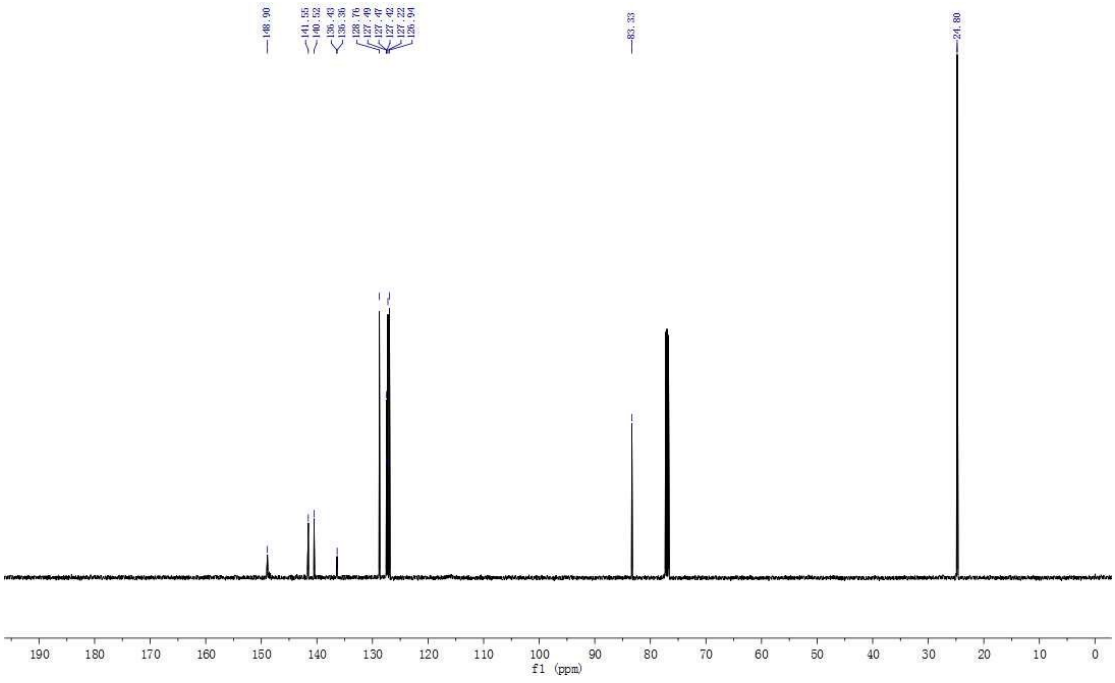




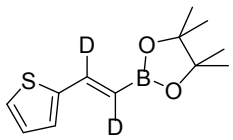
(*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)

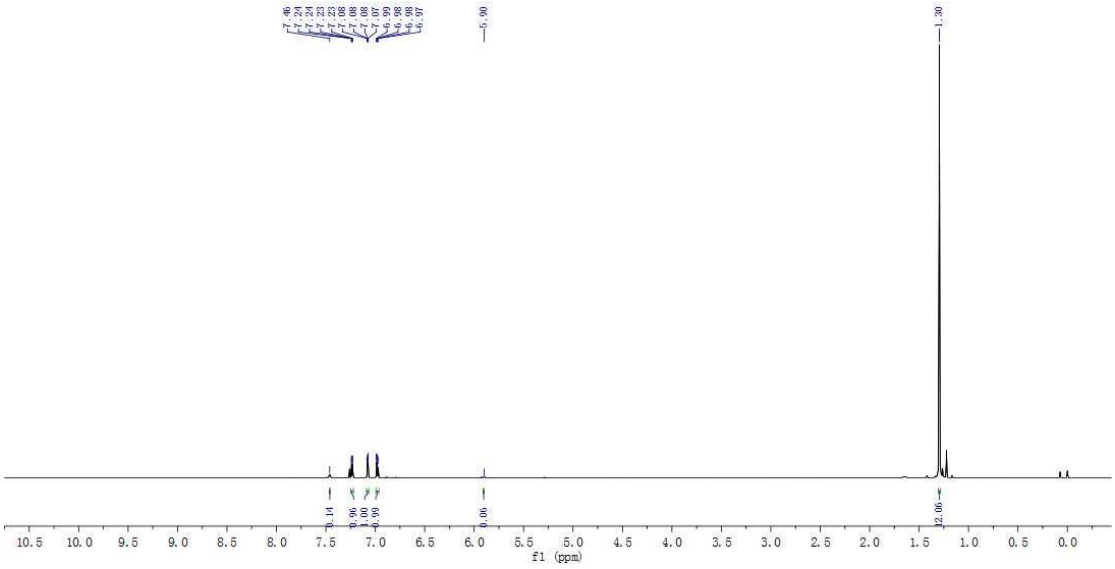


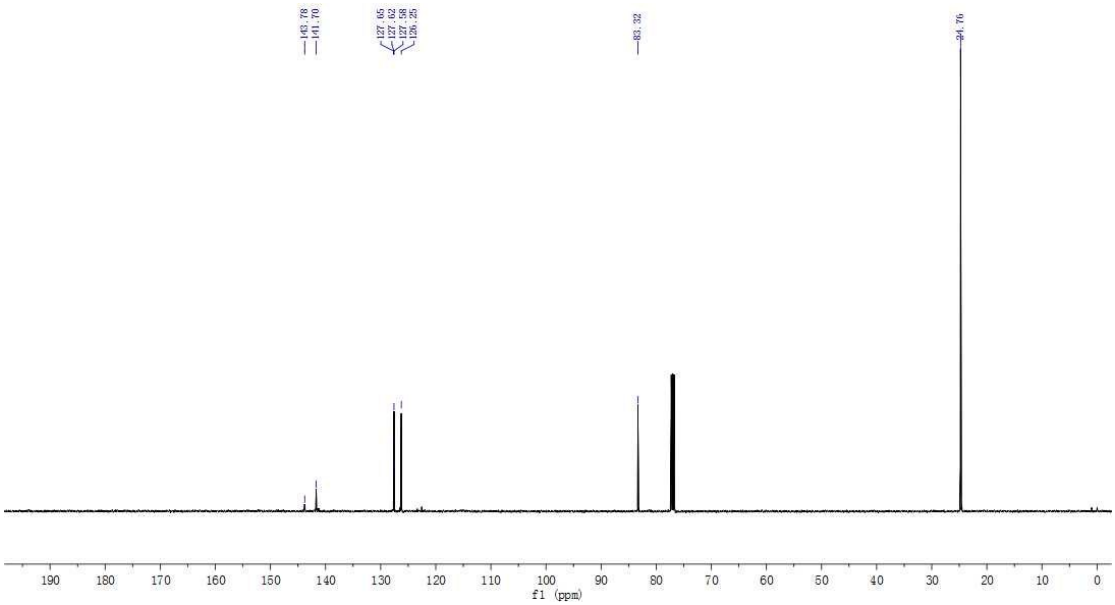




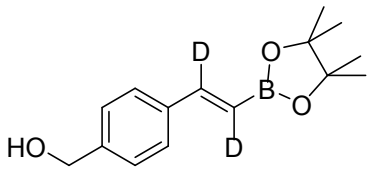
(*E*)-4,4,5,5-tetramethyl-2-(2-(thiophen-2-yl)vinyl-1,2-d_2)-1,3,2-dioxaborolane (3u)

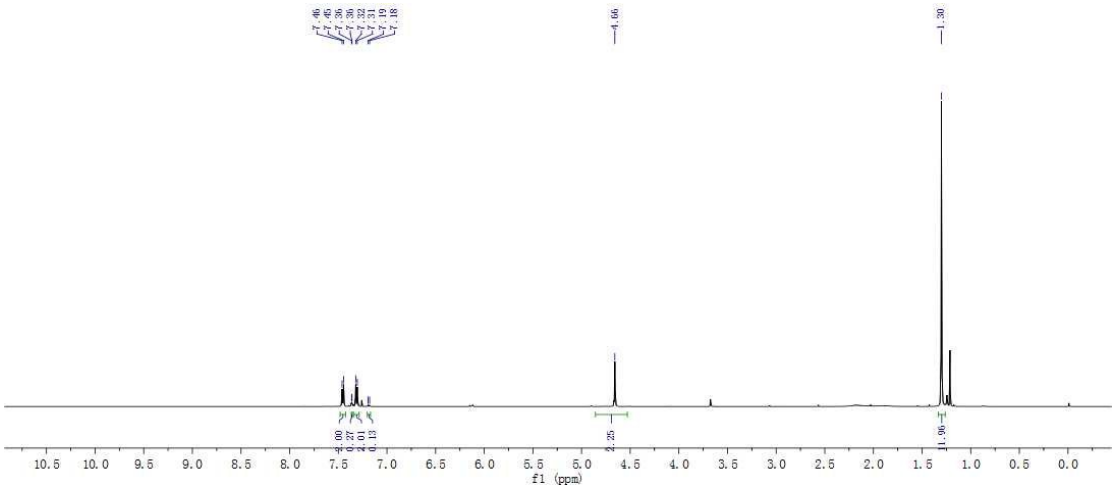


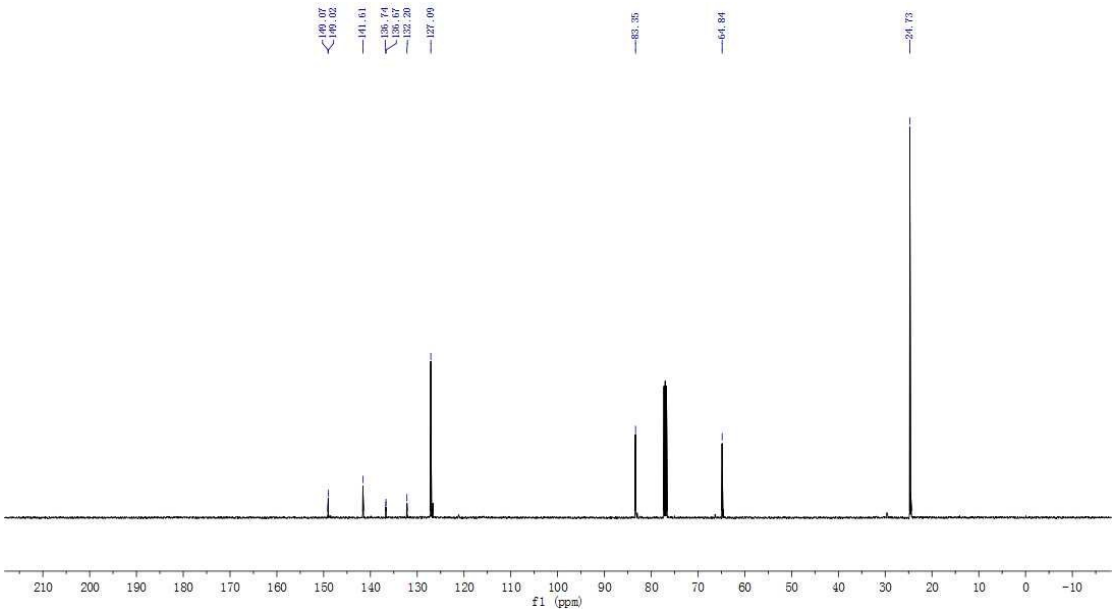




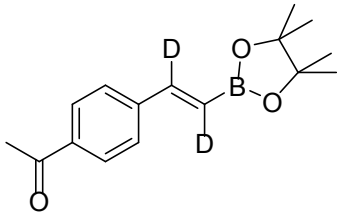
(*E*)-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)phenyl)methanol (3v)

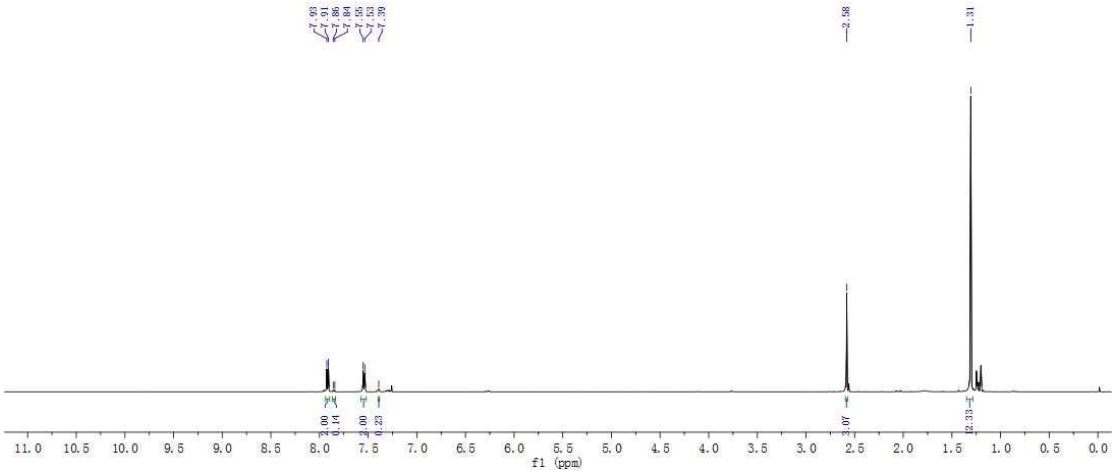


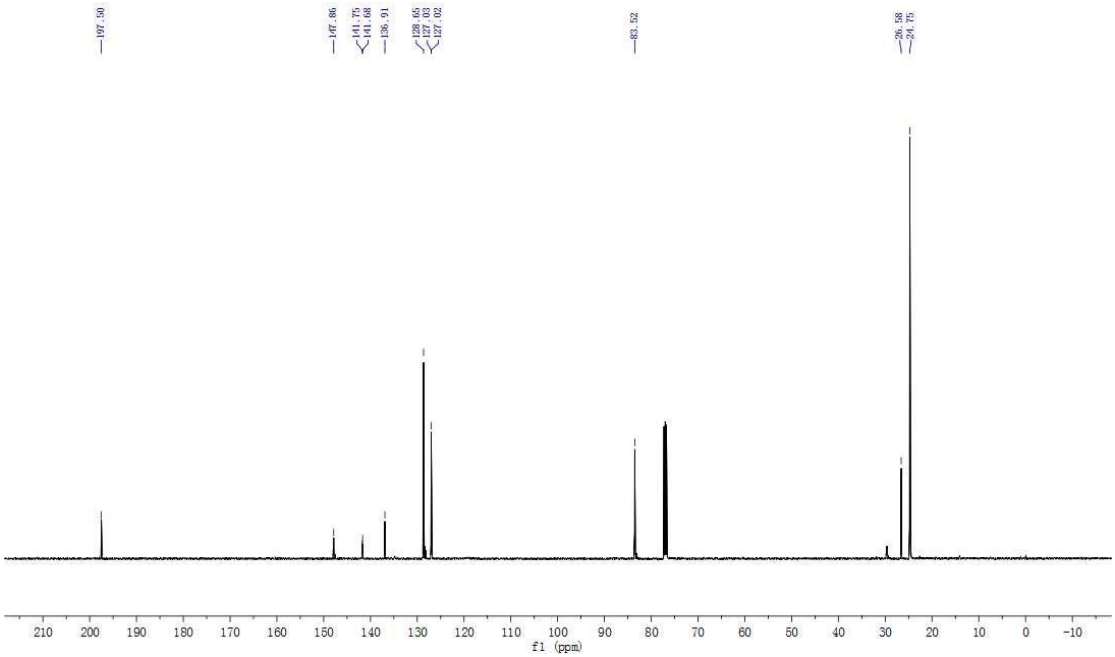




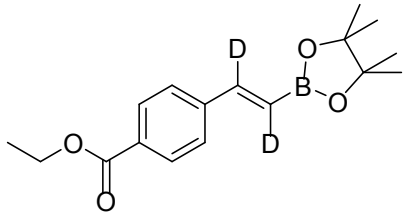
(*E*)-1-(4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)phenyl)ethan-1-one (3w)

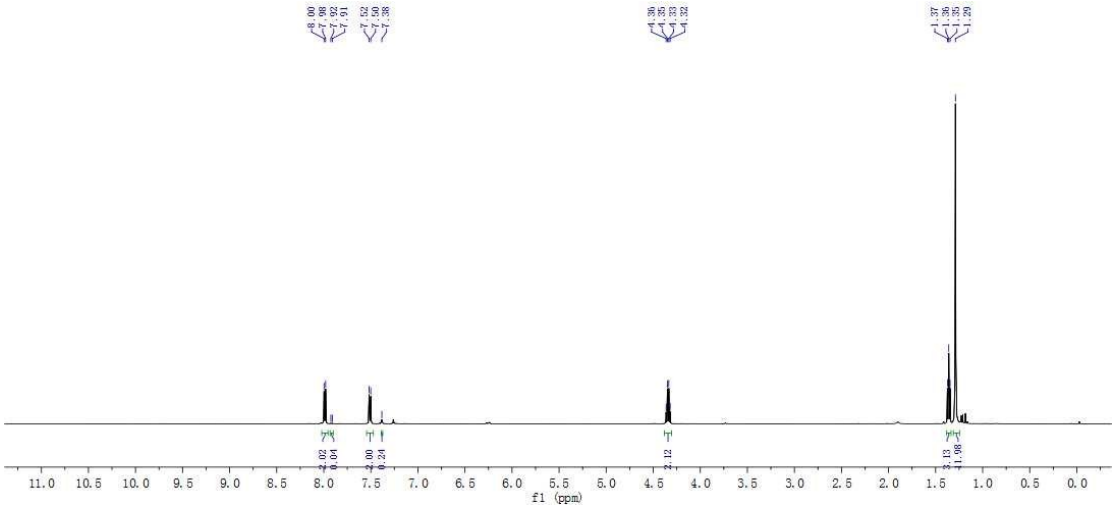


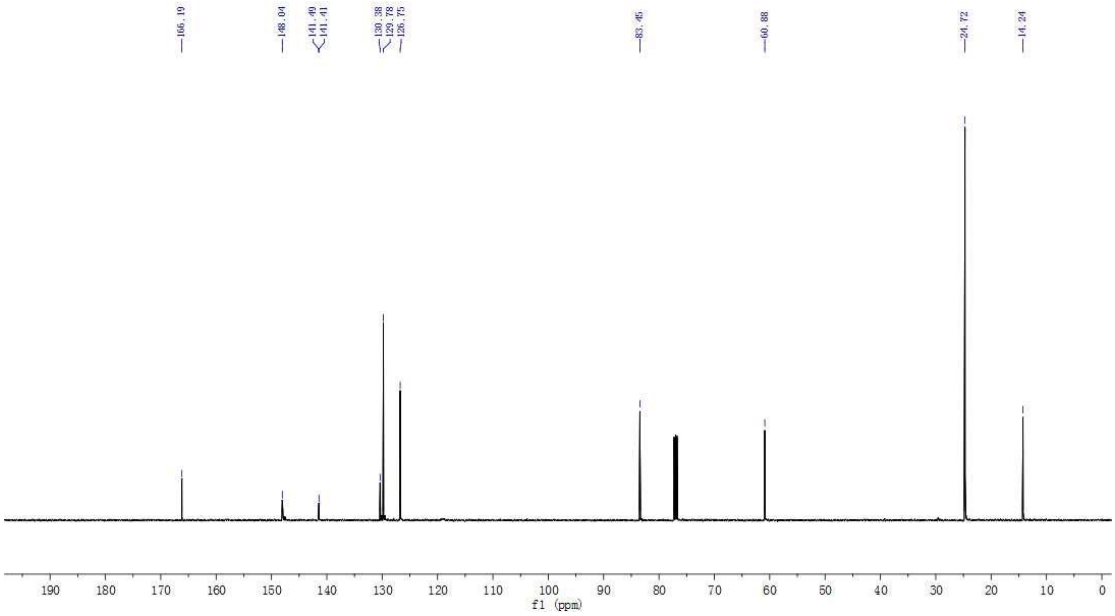




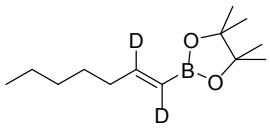
Ethyl(E)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl-1,2-d2)benzoate (3x)

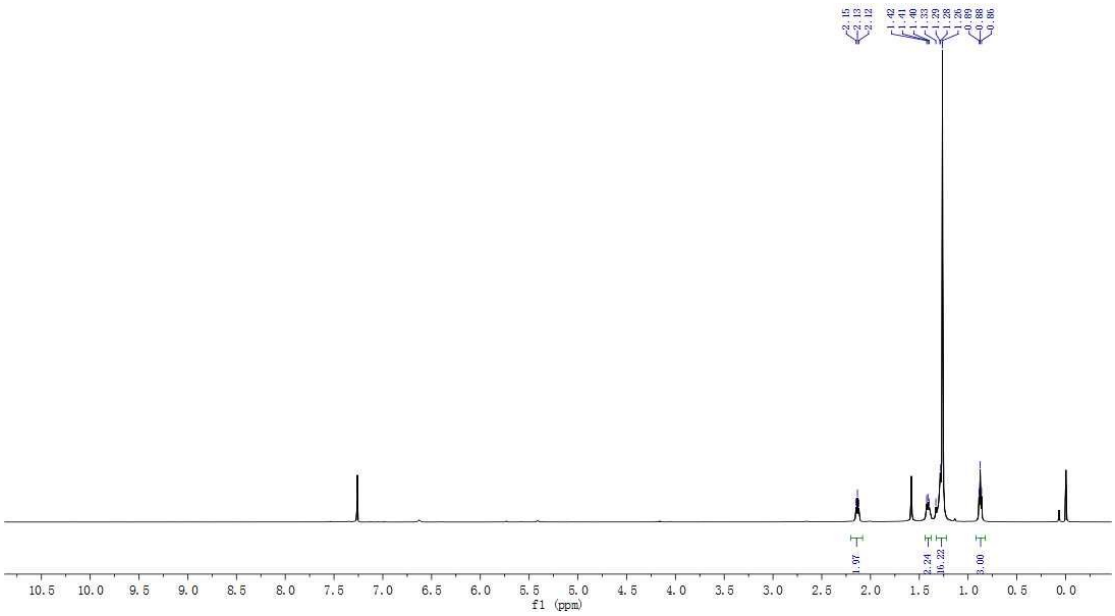


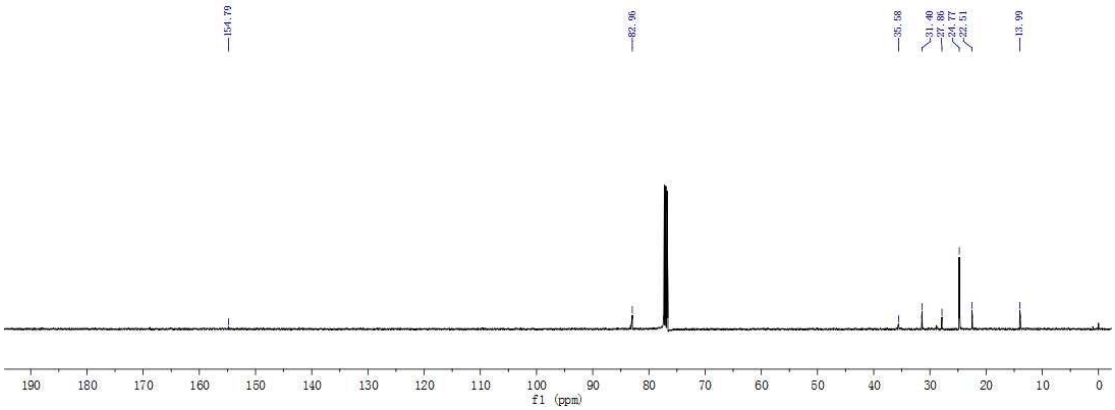




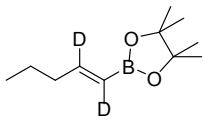
(*E*)-2-(hept-1-en-1-yl-1,2-d_2)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3y)

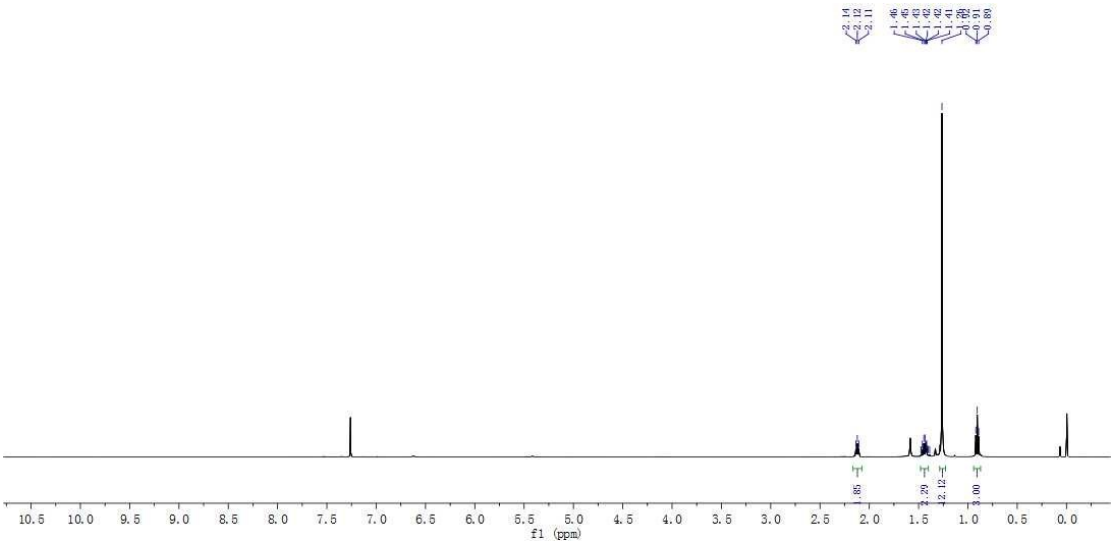


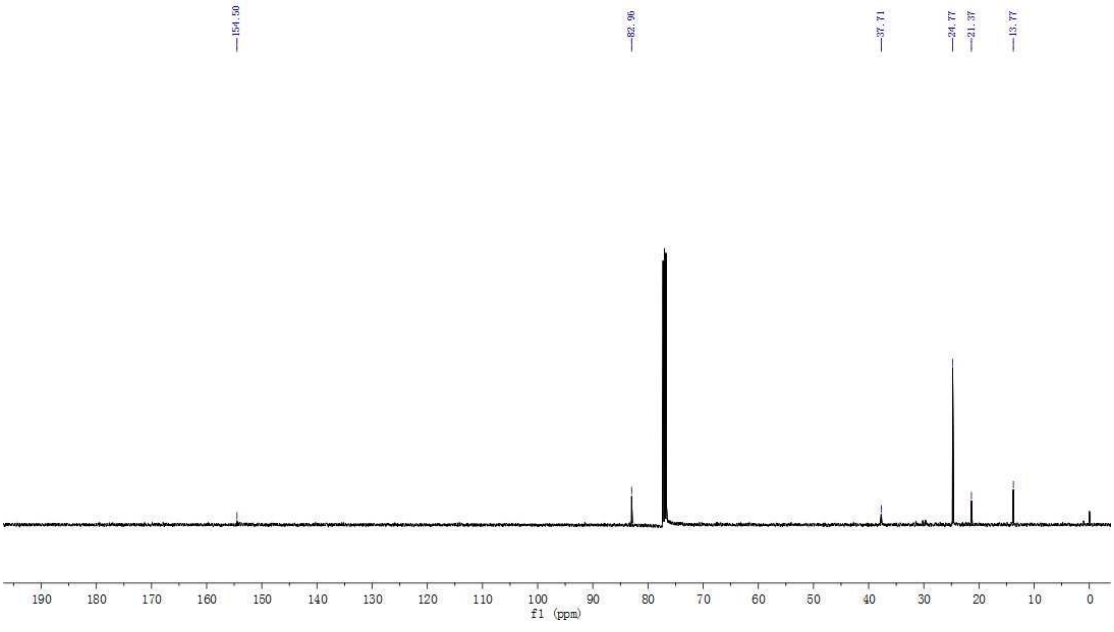




(*E*)-4,4,5,5-tetramethyl-2-(pent-1-en-1-yl-1,2-d$_2$)-1,3,2-dioxaborolane (3z)

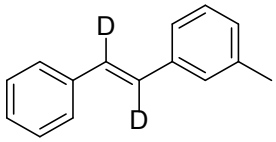


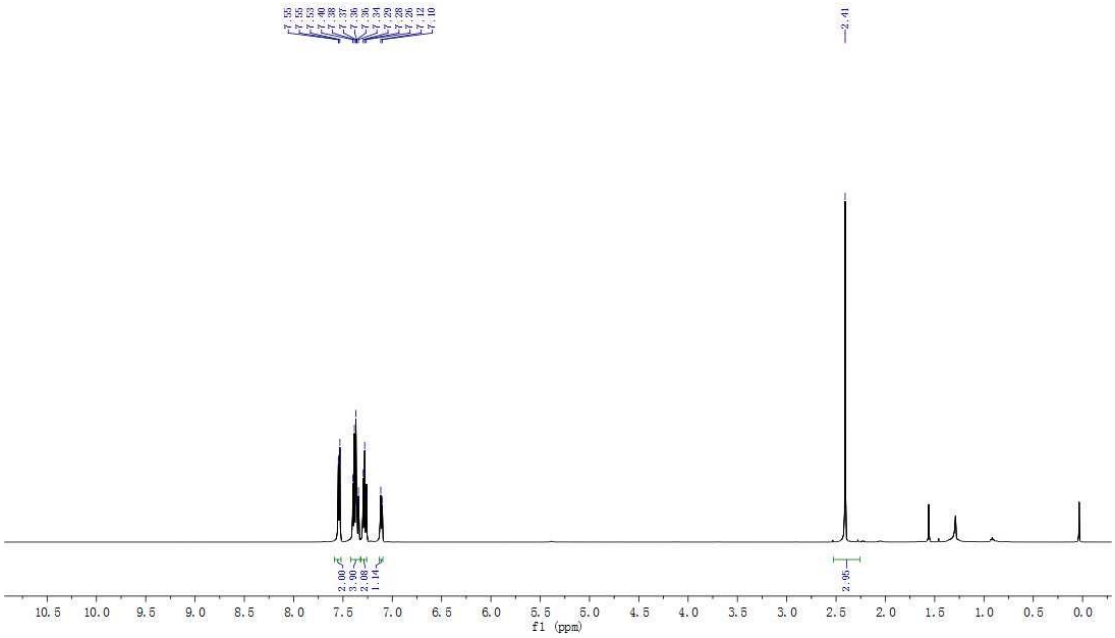


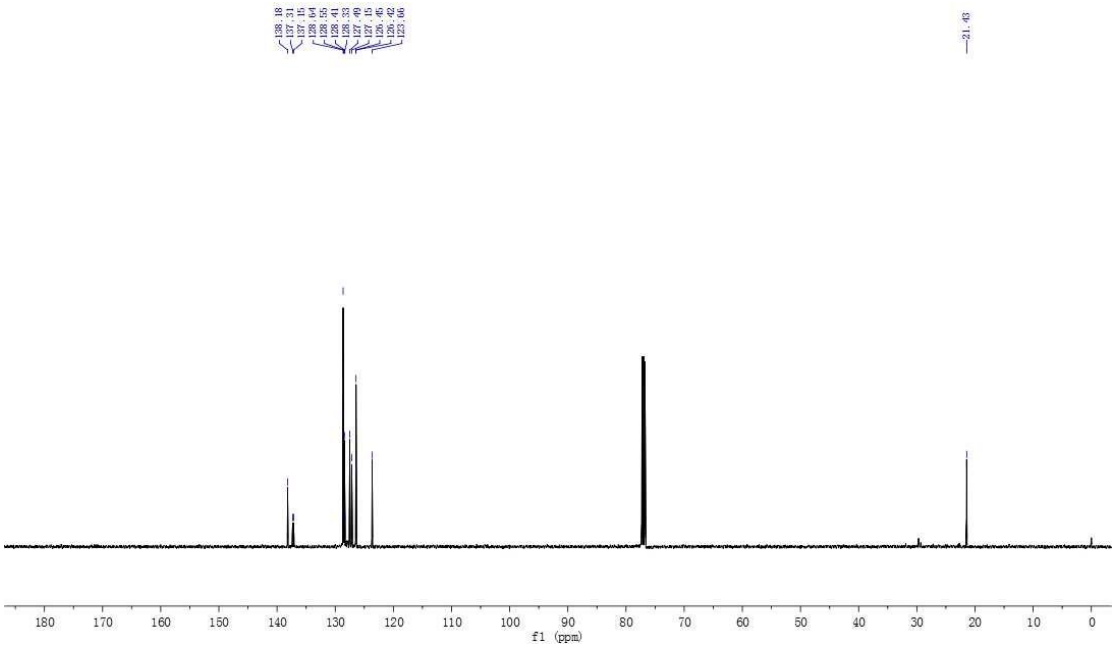


Spectroscopic data of bis-deuterated styrene derivatives

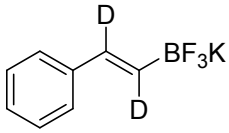
(*E*)-1-methyl-3-(2-phenylvinyl-1,2-d$_2$)benzene (4)

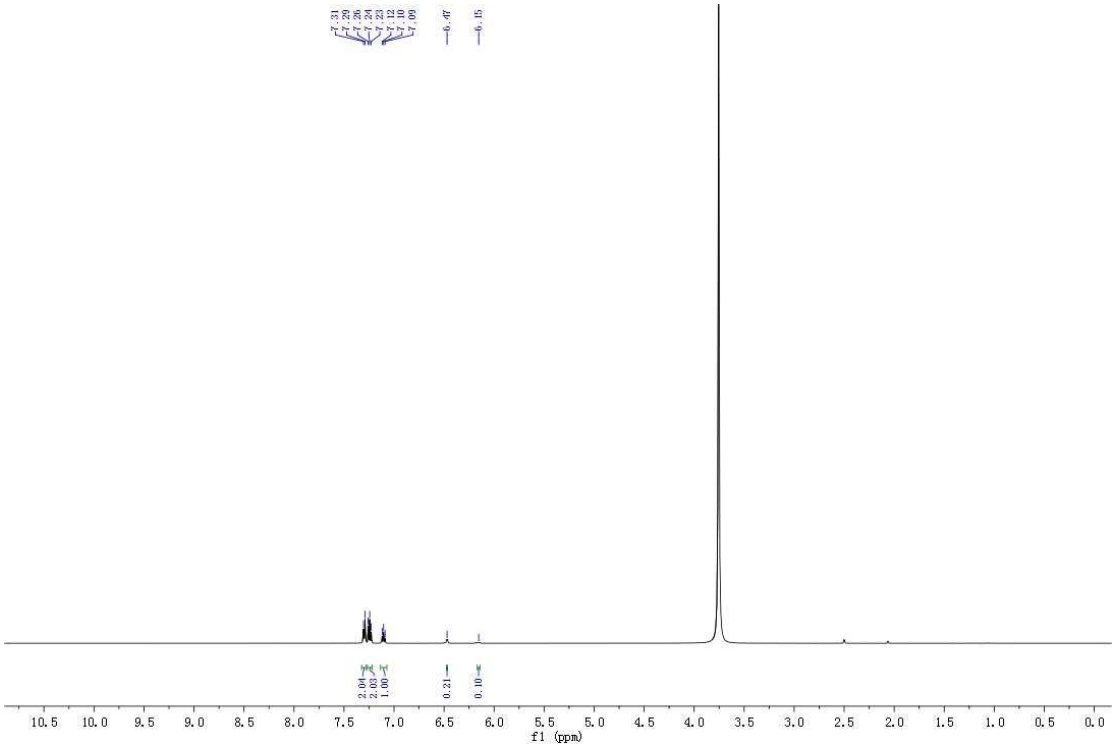


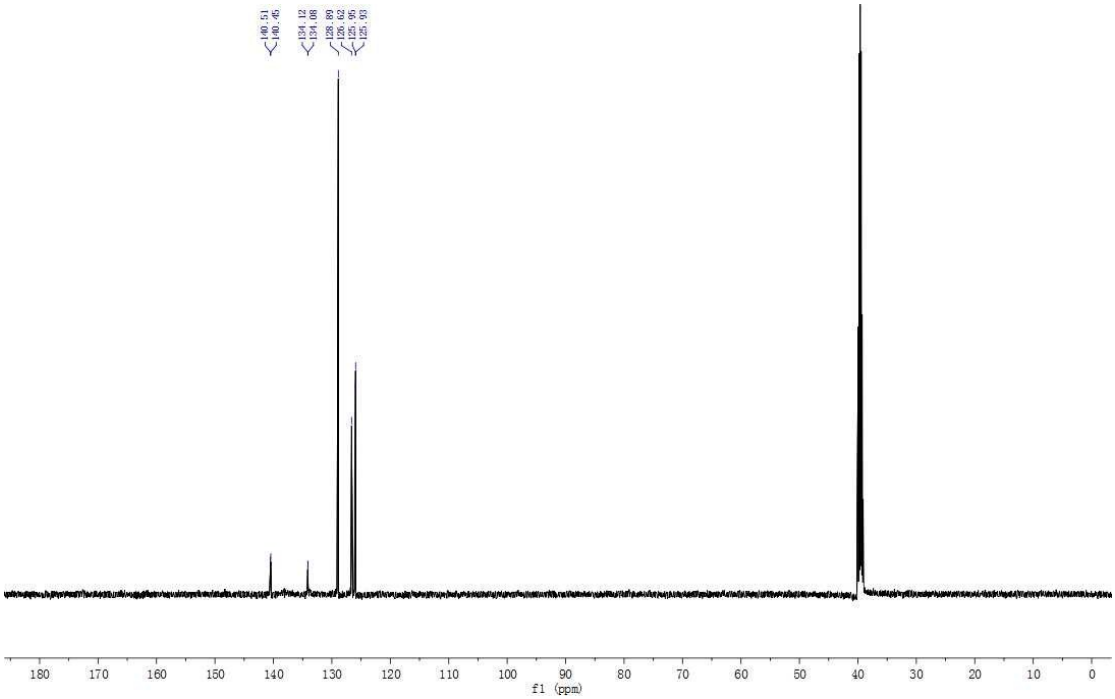


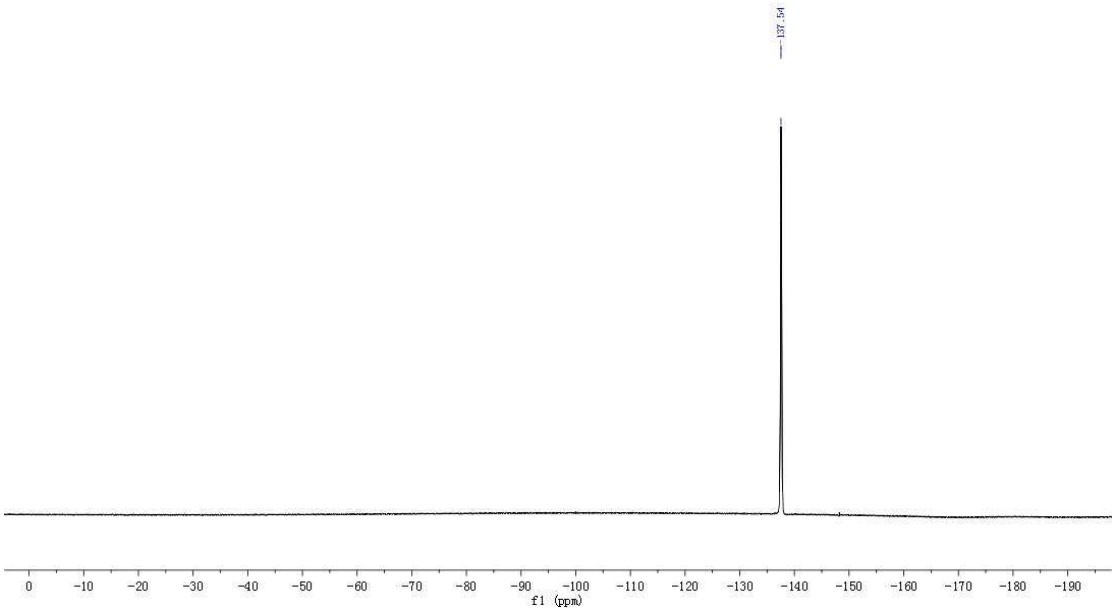


(*E*)-trifluoro(2-phenylvinyl-1,2-d_2)-l4-borane, potassium salt (5)

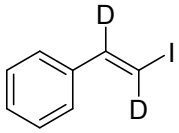


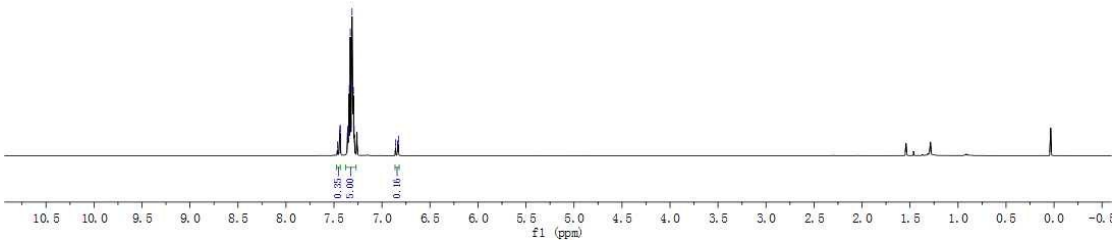


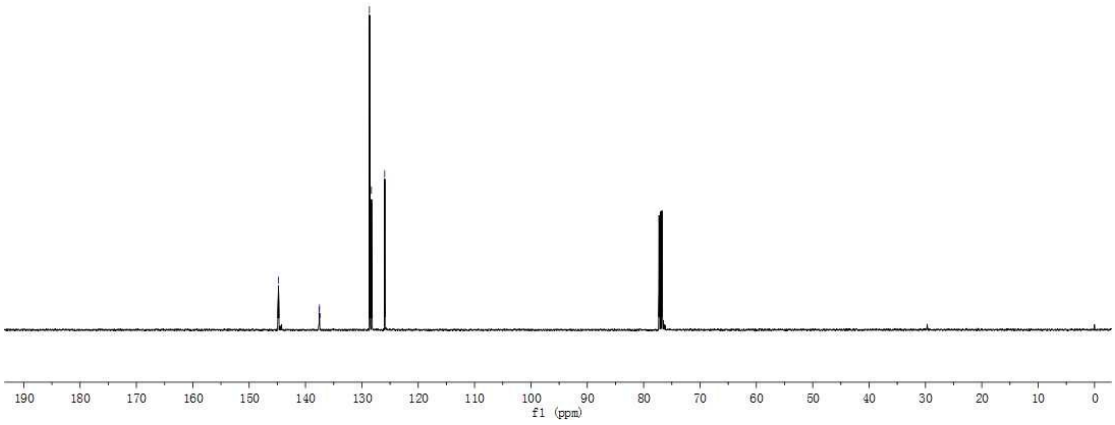



-137.54
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

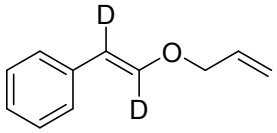
(*E*)-(2-iodovinyl-1,2-d$_2$)benzene (6)

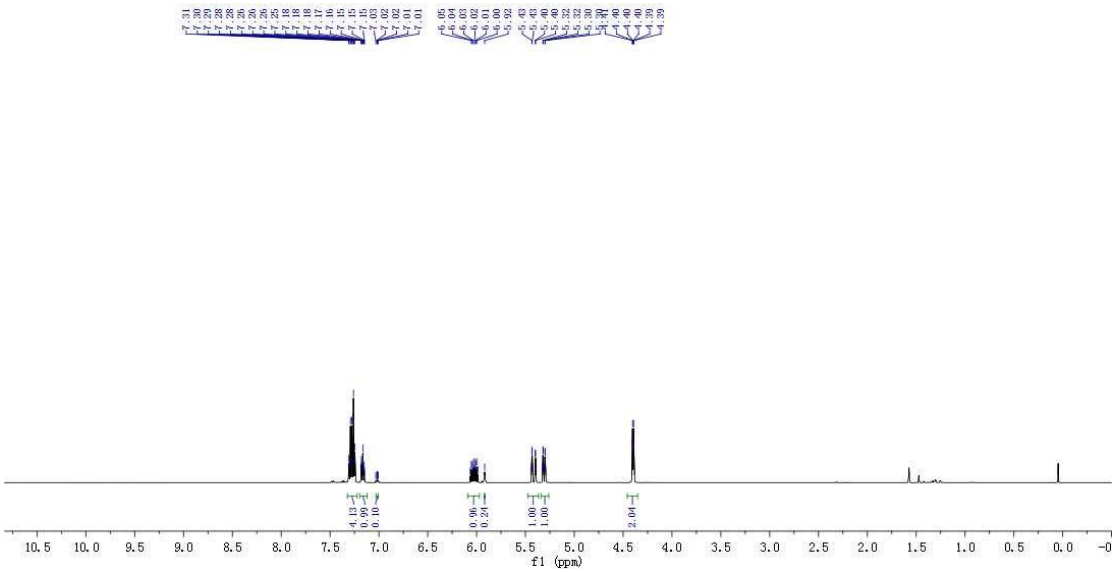


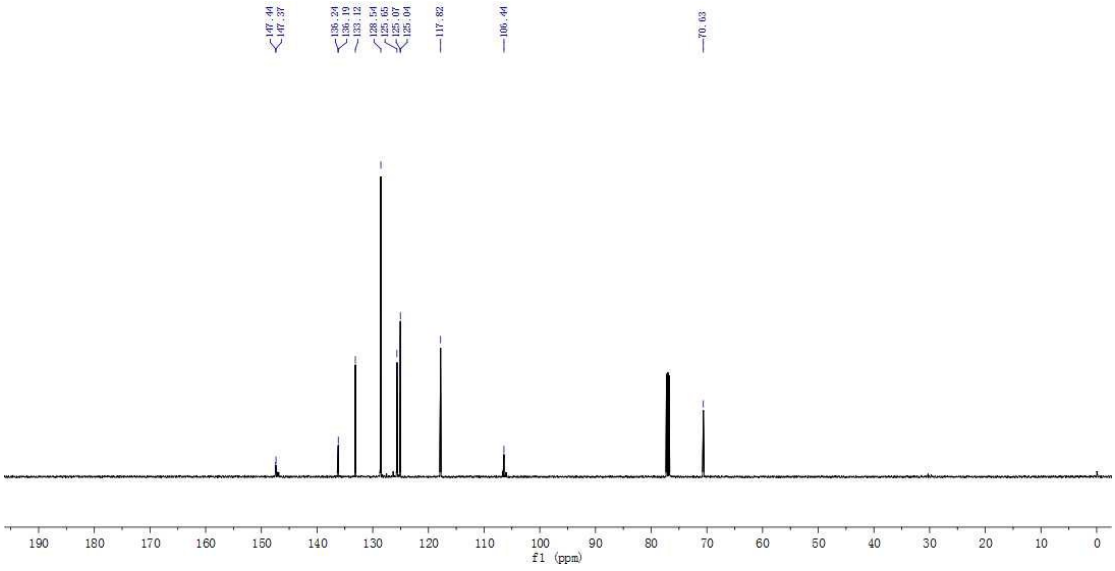




(*E*)-(2-(allyloxy)vinyl-1,2-d_2)benzene (7)







(*E*)-(2-azidovinyl-1,2-d2)benzene (8)