Borylation of phenols by sulfuryl fluoride activation

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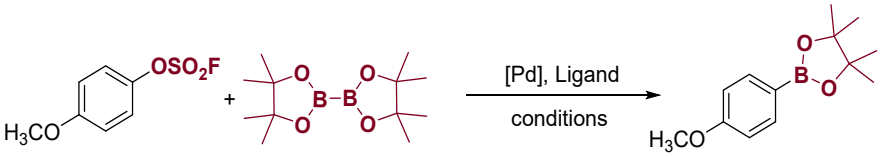
1. Optimization of reaction conditions for the synthesis of aryl boronic esters

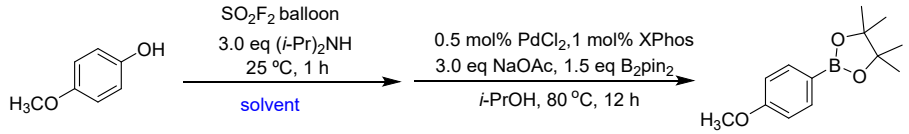
Table S1. Optimization of borylation conditions[a]



Entry	Catalyst	Ligands	Solvent	Bases	T (°C)	Yield (%)
1	5 mol% $PdCl_2$	none	PEG 400	NaOAc	80	21
2	5 mol% $Pd(OAc)_2$	none	PEG 400	NaOAc	80	8
3	5 mol% $Pd(dba)_2$	none	PEG 400	NaOAc	80	17
4	5 mol% Pd/C	none	PEG 400	NaOAc	80	7
5	5 mol% $Pd(acac)_2$	none	PEG 400	NaOAc	80	11
6	5 mol% $PdCl_2$	10 mol% PPh_3	PEG 400	NaOAc	80	69
7	5 mol% $PdCl_2$	10 mol% SPhos	PEG 400	NaOAc	80	75
8	5 mol% $PdCl_2$	10 mol% XPhos	PEG 400	NaOAc	80	89
9	5 mol% $PdCl_2$	10 mol% dppf	PEG 400	NaOAc	80	50
10	5 mol% $PdCl_2$	10 mol% XPhos	EtOH	NaOAc	80	90
11	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	NaOAc	80	95
12	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	NaOAc	25	81
13	5 mol% $PdCl_2$	10 mol% XPhos	MeOH	NaOAc	80	87
14	5 mol% $PdCl_2$	10 mol% XPhos	CH_3CN	NaOAc	80	24
15	5 mol% $PdCl_2$	10 mol% XPhos	THF	NaOAc	80	88
16	5 mol% $PdCl_2$	10 mol% XPhos	H_2O	NaOAc	100	trace
17	5 mol% $PdCl_2$	10 mol% XPhos	DMSO	NaOAc	100	20
18	5 mol% $PdCl_2$	10 mol% XPhos	DMF	NaOAc	100	25
20	5 mol% $Pd(OAc)_2$	10 mol% XPhos	*i*-PrOH	NaOAc	80	88
21	5 mol% $Pd(dba)_2$	10 mol% XPhos	*i*-PrOH	NaOAc	80	85
22	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	Na_2CO_3	80	52
23	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	K_2CO_3	80	87
24	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	K_3PO_4	80	90
25	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	$NaHCO_3$	80	36
26	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	Cs_2CO_3	80	24
27	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	NaOH	80	51
28	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	$(i\text{-Pr})_2NH$	80	91
29	5 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	Et_3N	80	65
30	1 mol% $PdCl_2$	10 mol% XPhos	*i*-PrOH	NaOAc	80	95
31	0.5 mol% $PdCl_2$	1 mol% XPhos	*i*-PrOH	NaOAc	80	94
32	0.2 mol% $PdCl_2$	1 mol% XPhos	*i*-PrOH	NaOAc	80	89
33	0.5 mol% $PdCl_2$	1 mol% XPhos	*i*-PrOH	NaOAc	80	94[b]
34	0.5 mol% $PdCl_2$	1 mol% XPhos	*i*-PrOH	NaOAc	80	10[c]
35	0.5 mol% $PdCl_2$	0.5 mol% XPhos	*i*-PrOH	NaOAc	80	50[b]

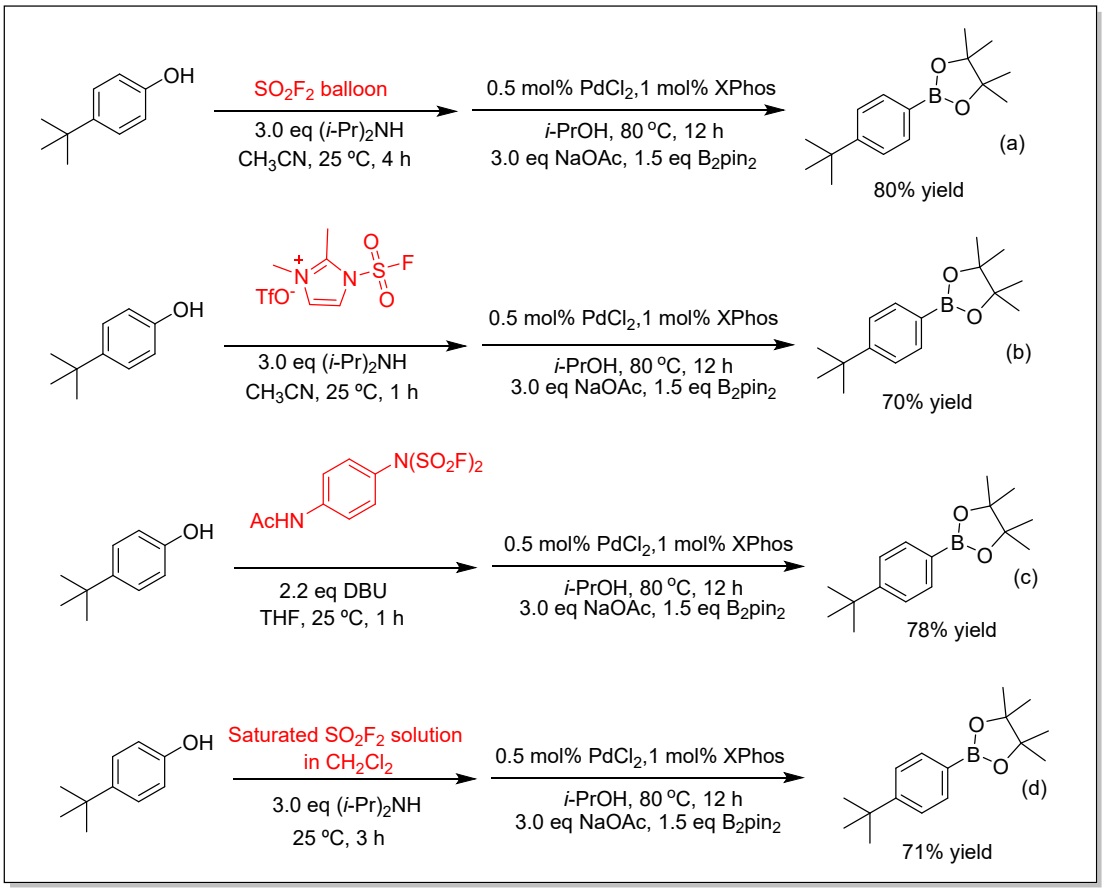
[a]Reaction conditions: Under the nitrogen atmosphere, 4-methoxyphenyl fluorosulfonate (0.5 mmol), B_2pin_2 (0.75 mmol), base (2 mmol), Pd catalyst, ligand, *i*-PrOH (4 mL), 7 h. Yield was determined by ^1H NMR spectroscopy by using 1, 3, 5-trimethylbenzene as an internal standard. [b]1.5 mmol NaOAc. [c]1.0 mmol NaOAc.

Table S2. One-pot borylation using different solvent[a]

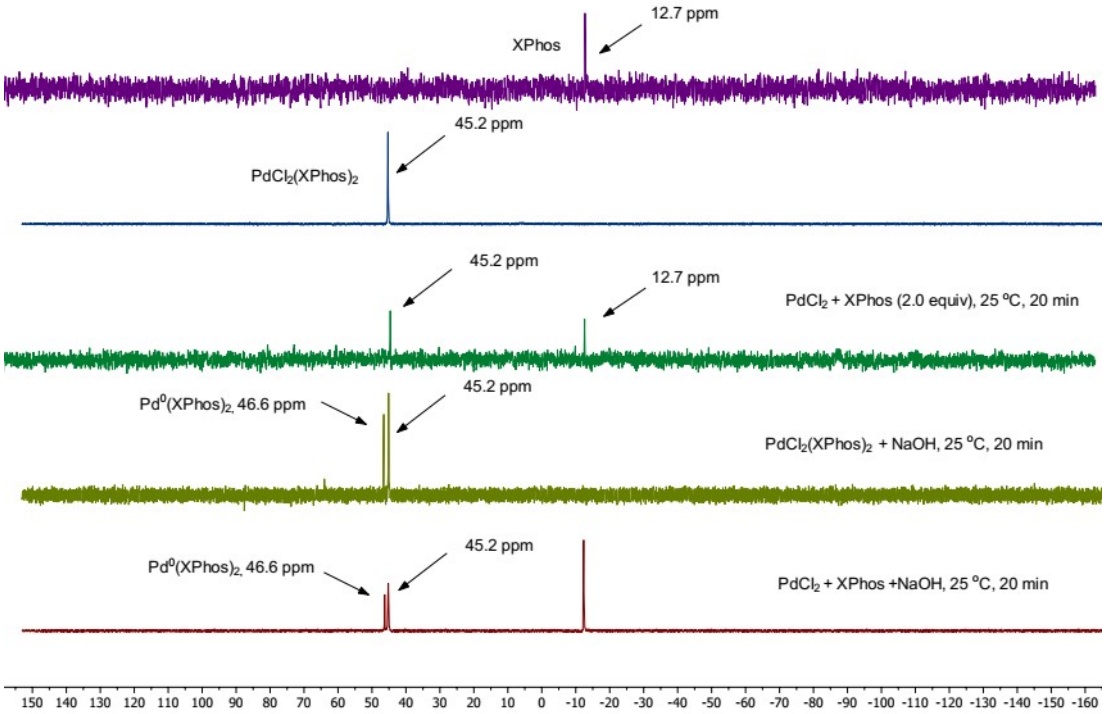


Entry	Solvent	Yield (%)
1	CH_2Cl_2	94
2	MeOH	16
3	EtOH	48
4	*i*-PrOH	49
5	*n*-BuOH	51
6	EtOH/H_2O	76
7	*i*-PrOH/H_2O	85
8	H_2O	trace

[a]Reaction conditions: 4-methoxyphenol (0.5 mmol), $(i\text{-Pr})_2NH$ (1.5 mmol), solvent (10 mL), SO_2F_2 balloon, 25 °C, 1 h; then the removal of solvent and addition of $PdCl_2$ (0.5 mol%), XPhos (1 mol%), B_2pin_2 (0.75 mmol), NaOAc (1.5 mmol), *i*-PrOH (4 mL), under nitrogen atmosphere, 12 h, yield was determined by ^{1}H-NMR spectroscopy by using 1, 3, 5-trimethylbenzene as an internal standard.

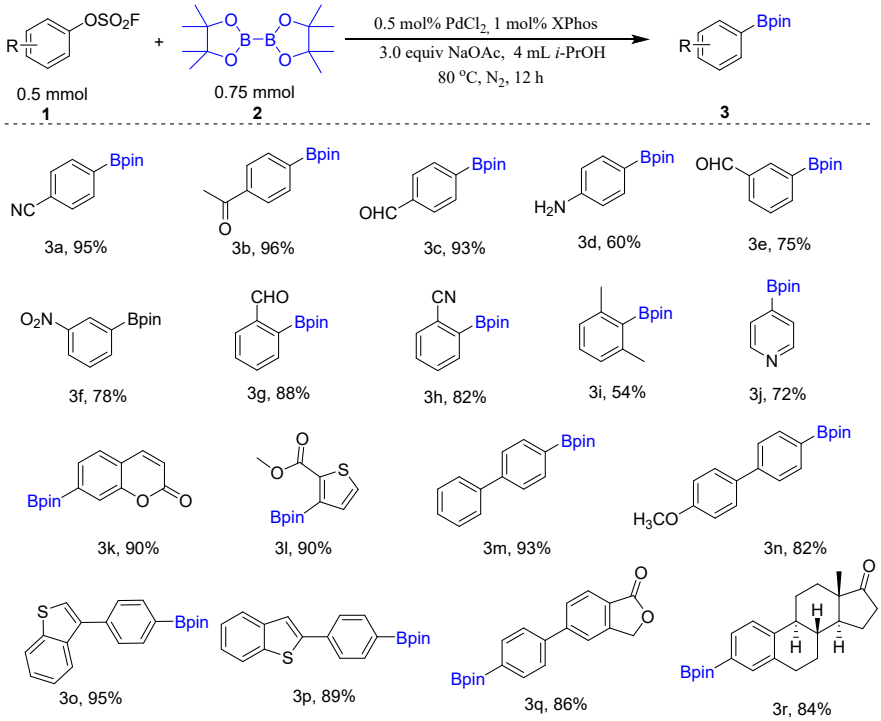


Scheme S1. One-pot borylation reaction using different sulfuryl fluoride reagents.



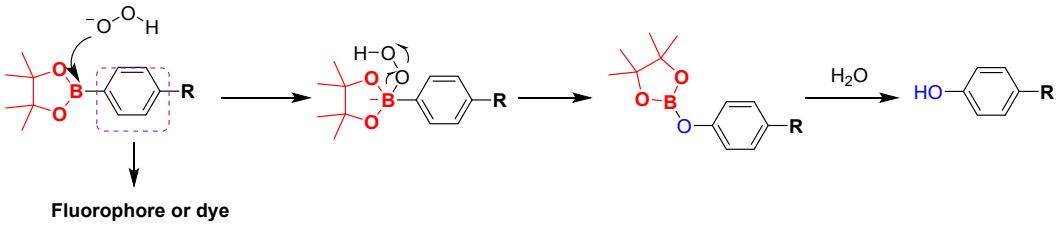
Scheme S2. ^{31}P NMR monitoring of the Pd species in the reaction

2. The synthesis of aryl/heteroayl boronic esters from aryl fluorosulfonates



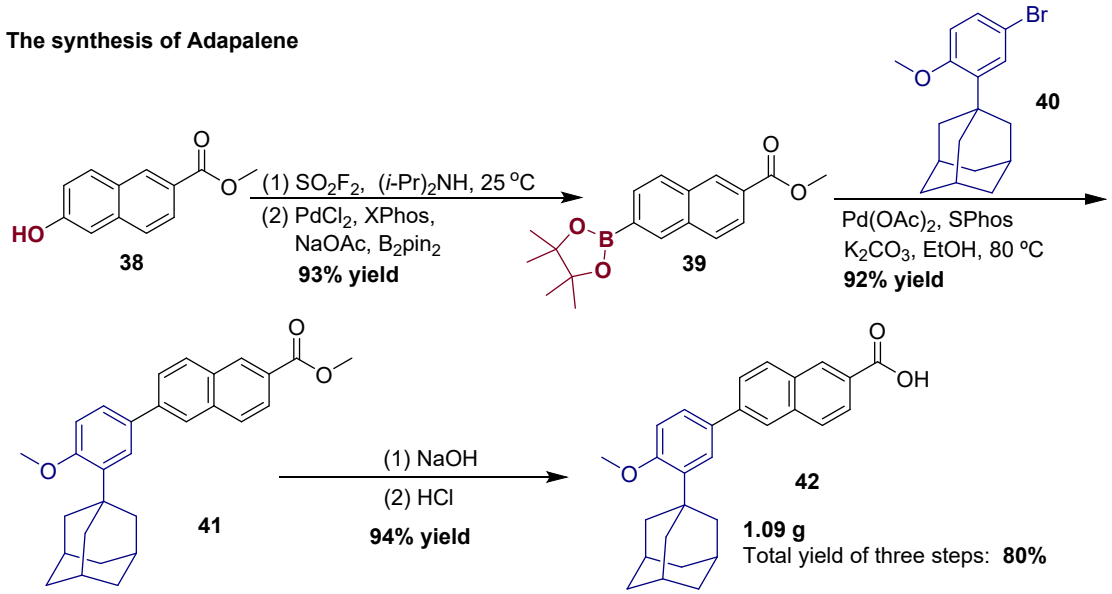
Scheme S3. Palladium catalyzed borylation of aryl fluorosulfonate. Reaction conditions: Under the nitrogen atmosphere, aryl fluorosulfates (0.5 mmol), B_2pin_2 (0.75 mmol), NaOAc (1.5 mmol), $PdCl_2$ (0.5 mol%), XPhos (1 mol%), *i*-PrOH (4 mL). 80 °C, 12 h, isolated yields.

3. The mechanism of hydrogen peroxide response to arylboronic esters



Scheme S4 The mechanism of hydrogen peroxide response to arylboronic esters

4. Application to the synthesis of drug molecules and the borylation of natural products



Scheme S5. The synthesis of differin using one-pot borylation reaction

The synthesis of methyl 2-naph-6-boronic acid pinacol ester (39):

A mixture of methyl 6-hydroxy-2-naphthoate **38** (4 mmol), (*i*-Pr)$_2$NH (12 mmol) CH_2Cl_2 (25 mL) was added to a reaction flask (100 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (6 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (12 mmol), *i*-PrOH (20 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were concentrated in vacuo and the product was isolated by column chromatography. White solid, 1.19 g, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.40 (s, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.94 (s, 1H), 7.93 (s, 1H), 7.90 (d, J = 8.6 Hz, 1H), 3.98 (s, 3H), 1.39 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.19, 135.82, 134.75, 133.98, 131.15, 130.79, 128.83, 128.32, 128.23, 125.16, 84.13, 52.26, 24.90. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.68.

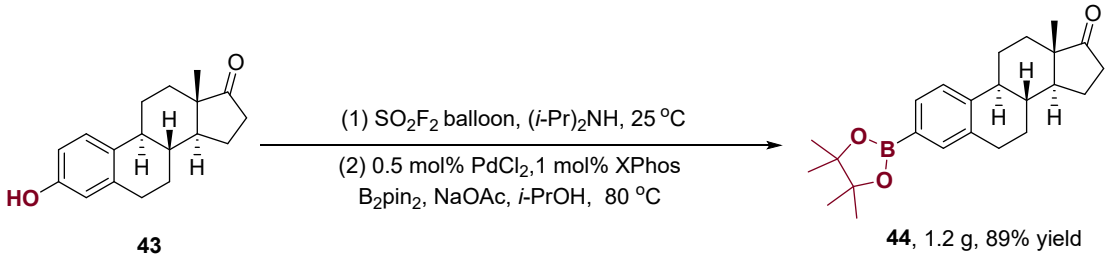
The synthesis of methyl 6-[3-(1-adamantyl)-4-methoxyphenyl]-2-naphthoate (41)

A mixture of **40** (3.8 mmol), **39** (3 mmol), $Pd(OAc)_2$ (3 mol%), SPhos (6 mol%), K_2CO_3 (6 mmol), EtOH (20 mL) was added to a reaction flask (100 mL) and stirred at 80 °C under nitrogen atmosphere for 5 h. Subsequently, the mixture was added to brine (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were concentrated in vacuo and the product was isolated by column chromatography. White solid, 1.18 g, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.07 (d, J = 8.6 Hz, 1H), 8.01 (s, 1H), 7.98 (s, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.60 (d, J = 2.0 Hz, 1H), 7.55 (dd, J = 8.3, 2.1 Hz, 1H), 7.00 (d, J = 8.4 Hz, 1H), 3.99 (s, 3H), 3.91 (s, 3H), 2.18 (s, 6H), 1.80 (s, 6H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 158.9, 141.4, 138.9, 135.9, 132.5, 131.2, 130.8, 129.7, 128.2, 126.5, 126.0, 125.7, 125.5, 124.7, 112.0, 55.1, 52.2, 40.6, 37.2, 37.1, 29.1.

The synthesis of Adapalene (42):

A mixture of **41** (2.8 mmol), 2 mol/L sodium hydroxide aqueous solution (60 mL) and methanol (50 mL) was added to a reaction flask (200 mL) and stirred at 80 °C for 8 h. The methanol was removed under reduced pressure. Subsequently, acidified with 6 mol/L HCl to pH = 1, then filtered and washed with 3×10 mL water, and dried in empty space. white solid, 1.09 g, 94% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.06 (s, 1H), 8.60 (s, 1H), 8.22 (s, 1H), 8.15 (d, J = 8.7 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.3 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 1.9 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 3.86 (s, 3H), 2.13 (s, 6H), 2.06 (s, 3H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.9, 159.0, 140.6, 138.4, 135.9, 131.9, 131.3, 130.7, 130.3, 128.8, 128.0, 126.4, 126.2, 125.9, 125.5, 124.5, 113.1, 55.8, 40.5, 37.0, 28.8.

The synthesis of 44:

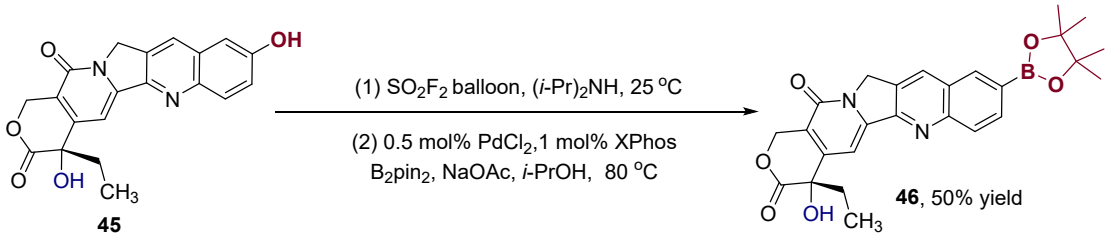


Scheme S6. One-pot borylation reaction of estrone

A mixture of estrone **43** (5.5 mmol), $(i\text{-Pr})_2$NH (16.5 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (100 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (8.25 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (16.5 mmol), i-PrOH (20 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (50 mL) and extracted with ethyl acetate (3 × 50 mL). The combined organic layers were concentrated in vacuo and the product was isolated by column chromatography. White solid, 1.20 g, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.9 Hz, 1H), 7.57 (s, 1H), 7.32 (d, J = 7.8 Hz, 1H), 2.93 (m 2H), 2.52 (m, 1H), 2.32 (m, 1H), 2.17 (t, J = 8.9 Hz, 1H), 2.11 (m, 1H), 2.01 (m, 4H), 1.62 (m, 2H), 1.52 (m, 3H), 1.34 (s, 12H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 220.9,

143.1, 135.8, 135.6, 132.1, 124.8, 83.7, 50.5, 48.0, 44.7, 38.0, 35.8, 31.6, 29.1, 26.4, 25.6, 24.8, 21.6, 13.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.67.

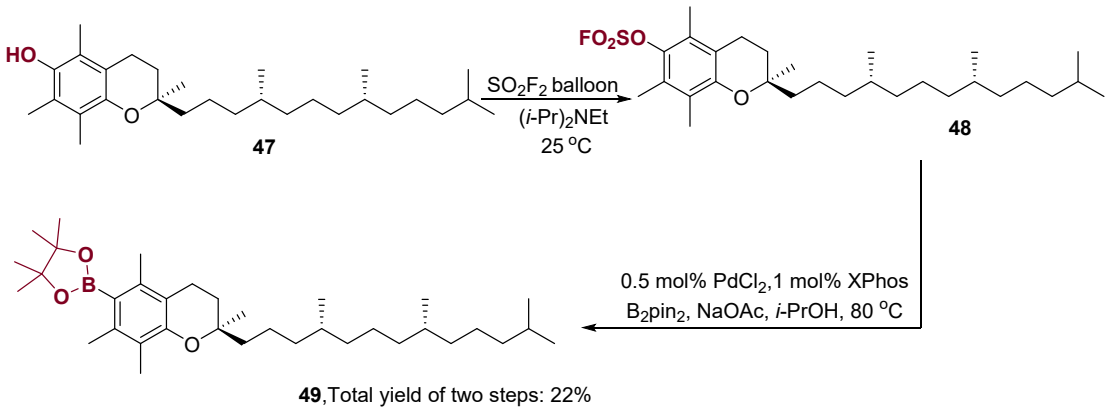
The synthesis of 46:



Scheme S7. One-pot borylation reaction for the preparation of **46**

A mixture of 10-hydroxycamptothecin (0.5 mmol), (i-Pr)$_2$NH (1.5 mmol) CH_2Cl_2 (10 mL) was added to a reaction flask (25 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), i-PrOH (10 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.47 (s, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.99 (m, 1H), 7.35 (d, J = 2.3 Hz, 1H), 6.57 (s, 1H), 5.42 (s, 2H), 5.25 (s, 1H), 3.97 (s, 2H), 1.86 (t, J = 7.3 Hz, 2H), 1.36 (s, 12H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 172.9, 157.2, 153.9, 150.4, 149.7, 145.7, 136.8, 134.8, 132.6, 130.4, 128.8, 127.8, 119.7, 97.5, 84.6, 74.0, 72.8, 65.7, 50.6, 30.7, 25.2, 8.2. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, DMSO-d_6) δ 30.76. HR-MS: m/z calcd for $C_{26}H_{27}BN_2NaO_6^+$ $[M+Na]^+$ 497.1860, found, 497.1853;

The synthesis of 49

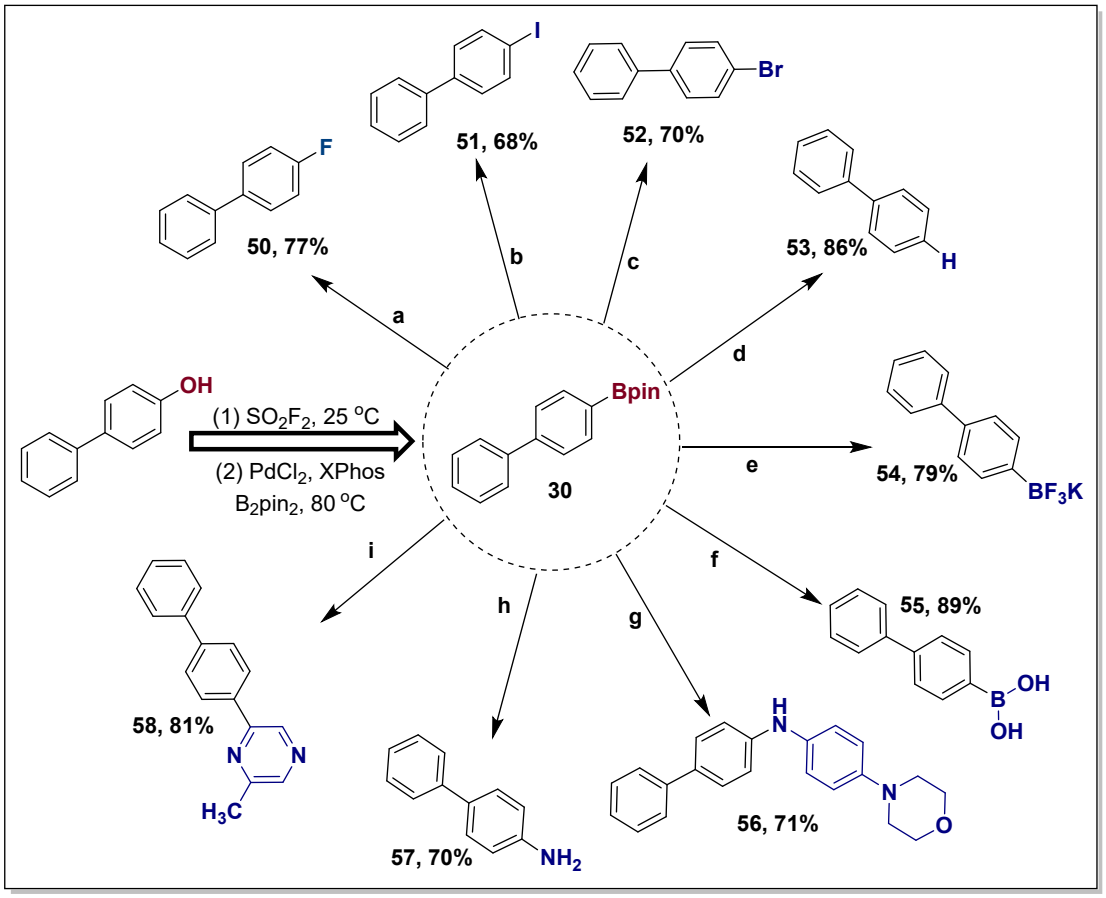


Scheme S8. The synthesis of **43**

A mixture of vitamin E **47** (0.5 mmol), (i-Pr)$_2$NH (1.5 mmol) was added to a reaction flask (50 mL), before SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, and the mixtures was stirred in CH_3CN (5 mL) at 25 °C for 4 hours. The mixtures were concentrated in vacuo and the product was isolated by column chromatography to give a colourless liquid **48**.

Subsequently, the intermediate **48**, B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.19 (s, 3H), 2.09 (s, 3H), 1.80 (m, 2H), 1.53 (m, 3H), 1.39 (m, 4H), 1.25 (m,24H), 1.10 (m, 7H), 0.85 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 141.8, 127.5, 126.0, 124.3, 118.4, 83.3, 39.9, 39.4, 37.4, 32.8, 32.6, 30.8, 30.7, 28.0, 24.9, 24.8, 24.6, 24.4, 23.8, 22.7, 22.6, 21.0, 20.6, 19.7, 19.6, 19.5, 13.5, 12.7, 11.9. The ipso-carbon to boron was not observed in NMR. HR-MS: m/z calcd for $C_{35}H_{62}BO_3^+$ $[M+H]^+$ 541.4792, found, 541.4740; ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.50.

5. Application of one-pot three-step process for the functionalization of phenols



Scheme S9. One-pot three-step process for the functionalization of phenolic compounds

The Synthesis of 50[1]

A mixture of 4-phenylphenol (1 mmol), $(i\text{-Pr})_2NH$ (3 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (50 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (1.5 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid, selectfluor (1.1 mmol),

KHF_2 (2.0 mmol), NaF (1.0 mmol), Pd complex 1 (0.02 mmol), and 2,2′:6′,2″-terpyridine (0.04 mmol) MeCN (4 mL), was added to a reaction flask and the reaction mixture was heated at 40 °C with vigorous stirring. After 15 hours, the reaction mixture was cooled to room temperature. Then the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel. White solid, 132 mg, 77% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 2H), 7.55 (m, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.37 (t, J = 7.3 Hz, 1H), 7.15 (t, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 161.2, 140.2, 137.3, 128.8, 127.3, 127.0, 115.7.

The Synthesis of 51[2]

A mixture of 4-phenylphenol (1 mmol), (i-Pr)$_2$NH (3 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (50 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (1.5 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), i-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid was dissolved in MeOH/H_2O (4 mL/1 mL), and Cu_2O (5.0 mol%), 1,10-phenanthroline (20 mol%), KI (1.0 mmol) was added to the flask, and the mixture was stirred at 50 °C for 1 h. Then the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel. White solid 189 mg, 68% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (m, 2H), 7.56 (d, J = 6.1 Hz, 2H), 7.45 (t, J = 5.8 Hz, 2H), 7.38 (m, 1H), 7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.0, 137.8, 129.0, 128.9, 127.7, 126.9, 93.1.

The Synthesis of 52[3]

A mixture of 4-phenylphenol (1 mmol), (i-Pr)$_2$NH (3 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (50 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (1.5 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), i-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid was added to a flask and dissolved in MeOH (10 mL). Copper (II) bromide (3.0 mmol) in water (10 mL) was added to the flask, and the mixture was stirred in reflux for 6 h. Then the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel. White solid, 161 mg 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 4.4 Hz, 2H), 7.60 (d, J = 3.2 Hz, 2H), 7.52 (d, J = 2.3 Hz, 2H), 7.49 (m, 2H), 7.43 (t, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 140.0, 131.9, 129.0, 128.8, 127.7, 127.0, 121.6.

The Synthesis of 53[4]

A mixture of 4-phenylphenol (1 mmol), (i-Pr)$_2$NH (3 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (50 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture

was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (1.5 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid, $AgNO_3$ (30 mol%), Et_3N (1 mmol) and EtOH/H_2O (2.0 mL/2.0 mL) were added to a flask and stirred at 80 °C under air for 2 h. Then the solvent was removed in vacuo, and the crude product was purified by column chromatography on silica gel. White solid, 132 mg, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 4H), 7.47 (t, J = 7.6 Hz, 4H), 7.38 (t, J = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 128.8, 127.2, 127.1.

The Synthesis of 54[5]

A mixture of 4-phenylphenol (1 mmol), (*i*-Pr)$_2$NH (3 mmol) CH_2Cl_2 (20 mL) was added to a reaction flask (50 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (1.5 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid was dissolved in methanol (10 mL) and followed adding KHF_2 (1.0 mL of 4.5 M saturated aqueous solution, 4.5 mmol) by dropwise at ambient temperature and the reaction mixture was stirred for 30 min. Afterward the solvent was removed under vacuum and the crude product was recrystallized from acetone. White solid, 205 mg, 79% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.58 (m, 2H), 7.41 (s, 2H), 7.39 (s, 2H), 7.38 (d, J = 2.8 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 141.9, 137.3, 132.4, 132.3, 129.2, 127.0, 126.8, 125.1.

The Synthesis of 55[6]

A mixture of 4-phenylphenol (0.5 mmol), (*i*-Pr)$_2$NH (1.5 mmol) CH_2Cl_2 (10 mL) was added to a reaction flask (25 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid was stirred at reflux with 20% (w/v) HCl (10 mL). A white precipitate formed, then the reaction was allowed to continue until the starting material was completely consumed as monitored by TLC (ca. 12 h). The mixture was cooled to room temperature, and the precipitate was then collected by filtration, washed with H_2O, and dried to afford the desired product. White solid, 196 mg, 89% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 (s, 2H), 7.91 (d, J = 7.7 Hz, 2H), 7.70 (m, 2H), 7.65 (d, J = 7.7 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 142.0, 140.5, 135.2, 129.4, 128.0, 127.1, 126.3, 126.1.

The Synthesis of 56[7]

A mixture of 4-phenylphenol (0.5 mmol), (*i*-Pr)$_2$NH (1.5 mmol) CH_2Cl_2 (10 mL) was added to a reaction flask (25 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid and 4-(4-bromophenyl)morpholine (1.5 mmol) were added to a flask and dissolved in 5 mL toluene. Then $Pd(OAc)_2$ (2 mol%), SPhos (4 mol%) and Cs_2CO_3 (2.0 mmol) were added to the flask, and the mixture was stirred at 100 °C for 8 h. Afterward the solvent was removed in vacuo the crude product was purified by column chromatography on silica gel. White solid, 234 mg, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.4 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 7.43 (t, J = 7.3 Hz, 2H), 7.31 (t, J = 6.8 Hz, 1H), 7.13 (d, J = 6.9 Hz, 2H), 7.01 (d, J = 7.6 Hz, 2H), 6.92 (d, J = 7.9 Hz, 2H), 3.90 (s, 4H), 3.14 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 141.0, 135.3, 132.3, 132.0, 128.7, 127.9, 126.4, 121.7, 117.2, 115.9,114.5, 67.0, 50.2.

The synthesis of 57[8]

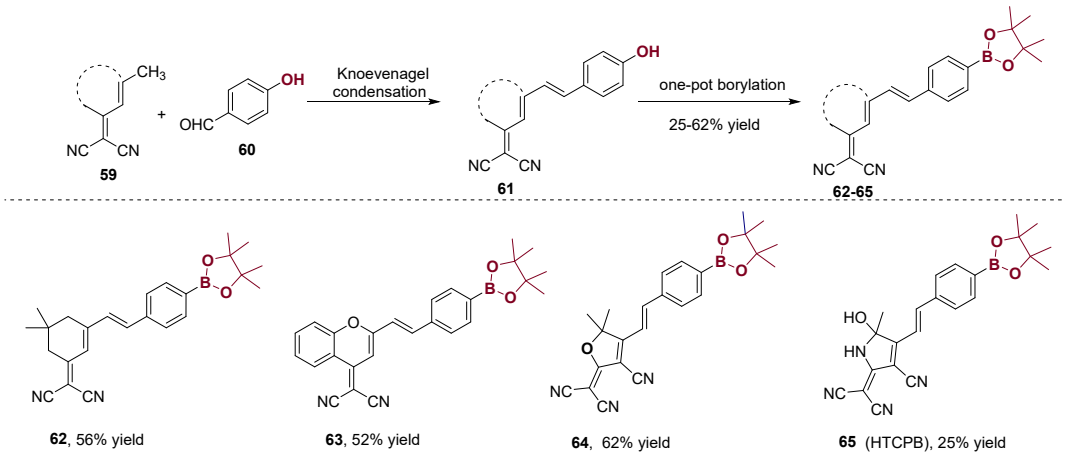
A mixture of 4-phenylphenol (0.5 mmol), (*i*-Pr)$_2$NH (1.5 mmol) CH_2Cl_2 (10 mL) was added to a reaction flask (25 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid and MeCN (5.0 mL) were added to a 25 mL flask, followed adding HAS (1.5 mmol) and aq 1 M NaOH (5.0 mmol). The mixture was capped and set to stir for 16 h. Subsequently, the reaction mixture was diluted with H_2O (30 mL) and extracted with EtOAc (2×30 mL). The combined organic extracts were dried by anhydrous Na_2SO_4 and concentrated in vacuo and the product was isolated by column chromatography. Brown Solid, 118 mg, 70% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (m, 2H), 7.37 (m, 4H), 7.20 (s, 1H), 6.69 (d, J = 6.9 Hz, 2H), 5.26 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.8, 141.1, 129.1, 127.8, 127.6, 126.1, 125.8, 114.7.

The Synthesis of 58[9]

A mixture of 4-phenylphenol (0.5 mmol), (*i*-Pr)$_2$NH (1.5 mmol) CH_2Cl_2 (10 mL) was added to a reaction flask (25 mL), and SO_2F_2 was introduced into the mixture by slowly bubbling from a balloon, then the mixture was allowed to stir at room temperature for 4 h. After that, the mixture was concentrated in a vacuum to fast remove CH_2Cl_2. And then B_2pin_2 (0.75 mmol), 0.5 mol% $PdCl_2$, 1 mol% XPhos, NaOAc (1.5 mmol), *i*-PrOH (4 mL) were add to the flask and stirred at 80 °C under nitrogen atmosphere for another 12 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were filtered and concentrated in vacuo and white solid was obtained. Next, the white solid, 2-bromo-6-methylpyrazine (1.5 mmol), $Pd(OAc)_2$ (4 mol%), K_2CO_3 (0.6 mmol) and H_2O (5 mL) were added

in a flask and the mixture was stirred at 100 °C for 6 h. Then, the solvent was removed in vacuo the crude product was purified by column chromatography on silica gel. White solid, 199 mg, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 7.66 (m, 2H), 7.57 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 7.5 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 156.5, 141.4, 140.7, 138.6, 136.9, 128.8, 127.4, 127.3 127.1, 121.6, 117.5, 24.8.

6. The synthesis of fluorescent probes and their application in cell imaging



Scheme S10. The synthesis of fluorescent probes

General protocol of the synthesis of fluorescent probes

According to the literature, the dicyanide phenolic compound intermediate was prepared by the Knoevenagel condensation.[10] After that the dicyanide compounds (3 mmol) was dissolved in 10 mL anhydrous ethanol and added in to a 50 mL flask, and 4-hydroxybenzaldehyde (549 mg, 4.5 mmol), dried ammonium acetate (346 mg, 4.5 mmol) were added to the above solution. The mixture solution was stirred at 80 °C until the reaction was completed. The solvent was removed at a reduced pressure, intermediate was obtained by column chromatography for the product. The probe was next prepared by general procedure for one-pot synthesis of aryl boronic esters from phenols.

62[11] Yellow solid, 112 mg, 56% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.69 (s, 2H), 7.68 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 16.2 Hz, 1H), 7.28 (d, J = 16.2 Hz, 1H), 6.94 (s, 1H), 2.62 (s, 2H), 2.55 (s, 2H), 1.30 (s, 12H), 1.01 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.8, 155.9, 139.2, 137.4, 135.3, 131.2, 127.6, 123.9, 114.2, 113.4, 84.2, 77.3, 42.7, 38.5, 32.1, 27.9, 25.1. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, DMSO-d_6) δ 30.78.

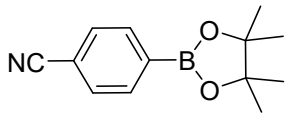
63[12] Yellow solid, 109 mg, 52% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.73 (d, J = 8.3 Hz, 1H), 7.94 (t, J = 8.4 Hz, 1H), 7.82 (s, 1H), 7.79 (d, J = 6.0 Hz, 1H), 7.75 (m, 4H), 7.62 (m, 2H), 7.09 (s, 1H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.2, 153.4, 152.5, 150.0, 138.4, 138.1, 136.0, 135.4, 127.9, 126.7, 125.1, 121.4, 119.6, 117.5, 116.1, 107.8, 84.3, 58.5, 25.1. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, DMSO-d_6) δ 28.43.

64[13] Yellow solid, 128 mg, 62% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (s, 1H), 7.91 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 16.6 Hz, 1H), 1.80 (s, 6H), 1.31 (s, 12H). ^{13}C

NMR (101 MHz, DMSO-d_6) δ 177.5, 175.3, 147.0, 137.3, 135.5, 129.0, 116.8, 113.0, 112.2, 111.2, 100.7, 100.0, 84.5, 55.2, 25.4, 25.1. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, DMSO-d_6) δ 30.59.

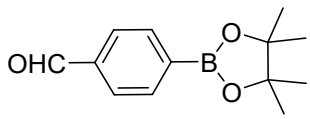
65 Yellow solid, 51 mg, 25% yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.64 (s, 1H), 7.82 (s, 1H), 7.81 (d, J = 3.8 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.23 (s, 1H), 7.20 (d, J = 5.1 Hz, 1H), 1.71 (s, 3H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 170.5, 160.5, 145.3, 137.6, 135.6, 128.5, 117.6, 115.6, 114.3, 112.0, 101.6, 94.2, 84.4, 73.9, 45.1, 25.8, 25.4. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, DMSO-d_6) δ 29.78. HR-MS: m/z calcd for $C_{23}H_{24}BN_4O_3^+$ $[M+H]^+$ 415.1941, found 415.1936; calcd for $C_{23}H_{27}BN_5O_3$ $[M+NH_4]^+$ 432.2207, found 432.2217.

7. Characterization data and spectrum of products



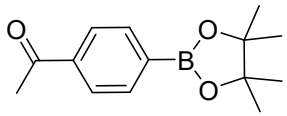
4-Cyanobenzeneboronic acid pinacol ester (1)[14]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 131.0, 118.8, 114.4, 84.4, 83.4, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.40.



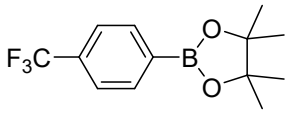
4-Formylphenylboronic acid pinacol ester (2)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 88% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.96 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.2 Hz, 2H), 1.36 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 138.0, 135.1, 128.6, 84.3, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.55.



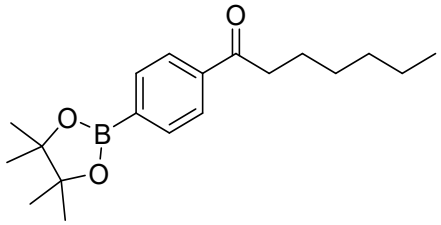
4-Acetylphenylboronic acid pinacol ester (3)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.84 (d, J = 8.3 Hz, 2H), 2.56 (s, 3H), 1.30 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 138.8, 134.8, 127.2, 84.1, 83.4, 26.7, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.63.



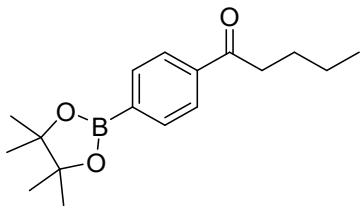
4-Trifluoromethylphenylboronic acid,pinacol ester (4)[14]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 50% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H), 1.36 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 132.7 (q, J = 31.3 Hz), 124.0 (q, J = 272.7 Hz), 124.2 (q, J = 3.8 Hz), 84.2, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.53.



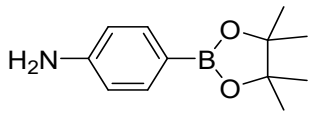
4-Heptanonephenyl boronic acid pinacol ester (5)[16]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 1.71 (m, 2H), 1.35 (m, 18H), 0.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 138.9, 134.9, 128.7, 127.0, 84.2, 38.8, 31.7, 29.7, 29.0, 24.9, 22.5, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.41.



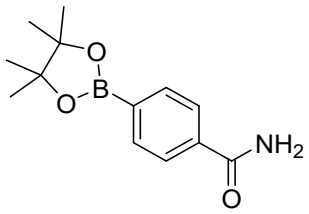
4-Amylphenylboronic acid pinacol ester (6)[16]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 65% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.86 (d, J = 8.3 Hz, 2H), 2.94 (t, J = 7.4 Hz, 2H), 1.68 (m, 2H), 1.36 (m, 2H), 1.32 (s, 12H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 138.9, 134.9, 127.0, 84.1, 38.5, 29.7, 26.4, 24.8, 22.4, 14.0. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.47.



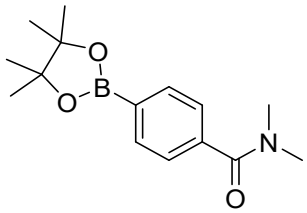
4-Aminophenylboronic acid pinacol ester (7)[17]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 56% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 9.0 Hz, 2H), 6.67 (d, J = 9.0 Hz, 2H), 1.26 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 142.0, 121.7, 115.4, 83.5, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.63.



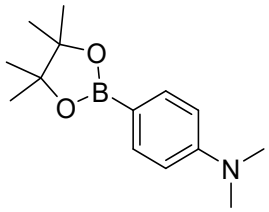
4-Aminocarbonylphenylboronic acid pinacol ester (8)[17]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) to give the product as white solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 135.6, 134.9, 126.5, 84.2, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.71.



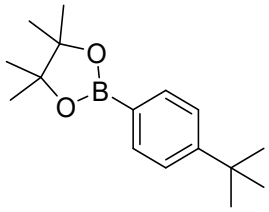
4-(N, N-Dimethylaminocarbonyl)phenylboronic acid, pinacol ester (9)[18]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) to give the product as white solid in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 3.09 (s, 3H), 2.93 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 138.8, 134.7, 126.2, 84.0, 39.4, 35.2, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.67.



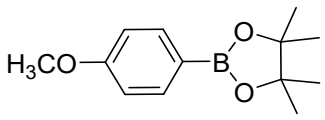
N, N-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (10)[19]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v) to give the product as white solid in 70% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 3.00 (s, 6H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 136.2, 111.2, 83.2, 40.1, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.98.



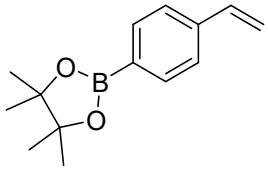
4-t-Butylphenylboronic acid, pinacol ester (11)[20]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.42 (d, J = 8.3 Hz, 2H), 1.35 (s, 12H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.88.



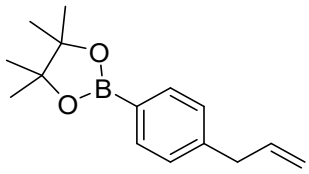
4-Methoxyphenylboronic acid pinacol ester (12)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with ether/ethyl acetate (100:1, v/v) to give the product as white solid in 94% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.14, 136.50, 113.29, 83.51, 55.01, 24.83. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.78.



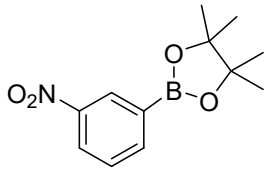
4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (13)[21]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 2H), 7.42 (d, J = 7.7 Hz, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.82 (d, J = 17.6 Hz, 1H), 5.30 (d, J = 11.0 Hz, 1H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 136.9, 135.0, 127.3, 125.5, 114.9, 87.8, 29.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.82.



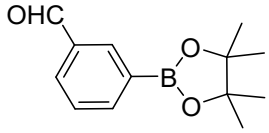
4,4,5,5-Tetramethyl-2-(4-prop-2-enylphenyl)-1,3,2-dioxaborolane (14)[22]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.19 (m, 1H), 6.34 (m, 2H), 1.85 (d, J = 4.9 Hz, 2H), 1.31 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 135.0, 131.1, 128.1, 127.0, 125.1, 83.7, 40.4, 24.9. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.86.



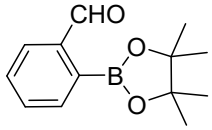
3-Nitrophenylboronic acid pinacol ester (15)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 2.1 Hz, 1H), 8.10 – 8.06 (m, 1H), 7.75 – 7.70 (m, 1H), 7.55 – 7.49 (m, 1H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.7, 140.6, 131.4, 129.3, 128.7, 125.8, 84.6, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.38.



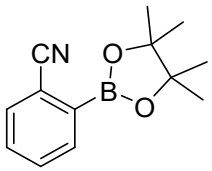
3-Formylphenylboronic acid pinacol ester (16)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.28 (s, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 7.8 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 140.6, 137.1, 135.6, 131.2, 128.3, 84.2, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.53.



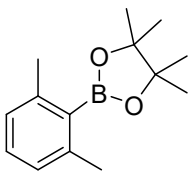
2-Formylphenylboronic acid pinacol ester (17)[23]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 8.28 (s, 1H), 8.03 (d, J = 7.3 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 1.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 140.6, 137.1, 135.6, 131.3, 128.3, 84.2, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.11.



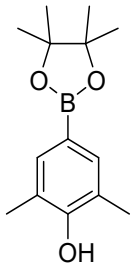
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile (18)[15]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) 7.87 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.56 (m, 1H), 7.51 (m, 1H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 133.4, 131.6, 131.1, 119.0, 117.2, 84.8, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.20.



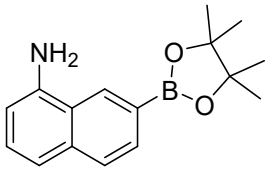
2-(2,6-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19)[19]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 54% yield.. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (t, J = 7.6 Hz, 1H), 6.93 (d, J = 7.6 Hz, 2H), 2.39 (s, 6H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 129.1, 126.4, 83.6, 24.9, 22.2. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.73.



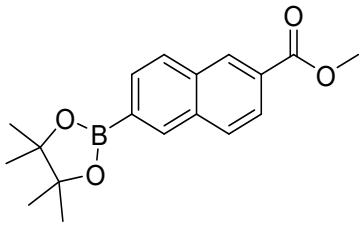
2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (20)[24]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 2.24 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 135.6, 122.4, 83.5, 24.8, 15.6. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.79.



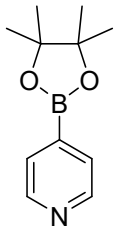
1-Amino-7- naphthalen boronic acid pinacol ester (21)[25]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.82 (d, J = 8.2 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.29 (d, J = 5.5 Hz, 1H), 6.78 – 6.73 (m, 1H), 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 136.0, 130.4, 129.0, 127.7, 127.6, 122.8, 118.5, 109.4, 83.9, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.10.



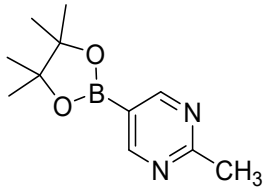
Methyl 6-(4,4,5,5-tetraMethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (22)[25]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.40 (s, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.92 (q, J = 8.2 Hz, 3H), 3.98 (s, 3H), 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 135.8, 134.7, 134.0, 131.1, 130.8, 128.8, 128.3, 128.2, 125.2, 84.1, 52.3, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.68.



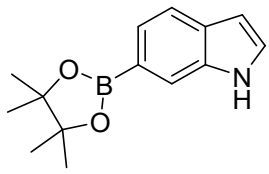
4-Pyridineboronic acid pinacol ester (23)[26]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with dichloromethane/methanol (50:1, v/v) to give the product as white solid in 75% yield. ^{1}H NMR (400 MHz, CD_3OD) δ 8.46 (dd, J = 6.3, 5.1 Hz, 2H), 7.74 (dd, J = 8.2, 6.4 Hz, 2H), 1.19 (d, J = 14.1 Hz, 12H). ^{13}C NMR (100 MHz, CD_3OD) δ 142.9, 129.0, 128.5, 82.2, 24.4. ^{11}B NMR (128 MHz, CD_3OD) δ 30.26.



2-Methylpyrimidine-5-boronic acid pinacol ester (24)[27]

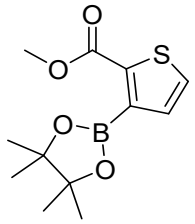
Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 2H), 2.69 (s, 3H), 1.29 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 162.7, 84.5, 26.3, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.34.



Indole-6-boronic acid pinacol ester (25)[28]

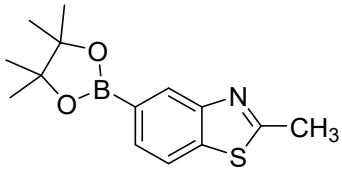
Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 83% yield. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.47 (d, J = 3.8 Hz, 1H), 6.81 – 6.79 (m, 1H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.5, 132.7, 130.7, 127.0, 121.2, 119.5, 110.9, 84.1, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.79.



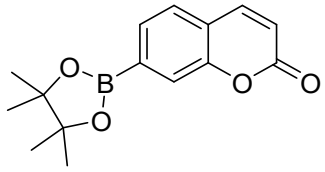
4-(Methoxycarbonyl)thiophene-2-boronic acid pinacol ester (26)[29]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 4.9 Hz, 1H), 7.16 (d, J = 4.9 Hz, 1H), 3.87 (s, 3H), 1.40 (d, J = 1.3 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 138.0, 132.0, 131.8, 84.4, 52.2, 24.8. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.58.



2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d]thiazole (27)[30]

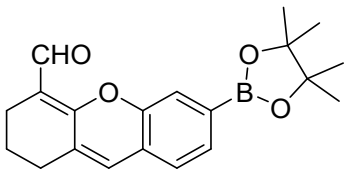
Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H), 2.78 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 153.1, 138.8, 130.4, 128.9, 120.7, 83.9, 24.8, 20.1. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.05.



Coumarin-7-pinacolboronate (28)[31]

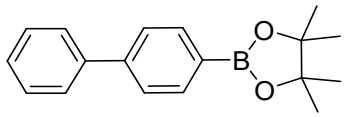
Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 2.5 Hz, 1H), 7.68 (d, J = 5.8 Hz, 1H), 7.65 (s, 1H), 7.46 (d, J = 7.6 Hz, 1H), 6.44 (d, J = 9.5 Hz, 1H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 153.4, 143.2, 130.2, 127.0, 122.8, 120.8, 117.7, 84.4, 25.0, 24.8. The ipso-carbon to boron was not

observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.43.



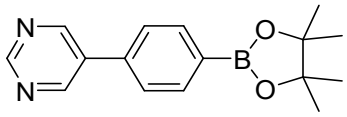
6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-xanthene-4-carbaldehyde (29)

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with dichloromethane/methanol (50:1, v/v) to give the product as yellow solid. in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.52 (s, 1H), 7.49 (d, J = 7.5 Hz, 1H), 7.16 (d, J = 7.5 Hz, 1H), 6.69 (s, 1H), 2.60 (m, 2H), 2.44 (t, J = 6.0 Hz, 2H), 1.71 (dd, J = 14.4, 8.3 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 160.3, 151.5, 131.0, 129.8, 126.7, 126.0, 123.5, 121.2, 113.3, 84.2, 30.2, 29.7, 24.9, 21.4, 20.2. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.49. HR-MS: m/z calcd for $C_{20}H_{24}BO_4^+$ $[M+H]^+$ 339.1768, found 339.1762; calcd for $C_{20}H_{23}NaBO_4^+$ $[M+Na]^+$ 361.1587, found, 361.1516.



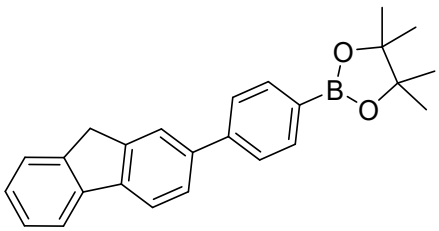
4-Biphenylboronic acid, pinacol ester (30)[32]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.4 Hz, 2H), 7.64 (d, J = 6.9 Hz, 4H), 7.46 (t, J = 7.1 Hz, 2H), 7.38 (d, J = 6.5 Hz, 1H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 140.9, 135.2, 128.8, 127.5, 127.2, 126.4, 83.8, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.73.



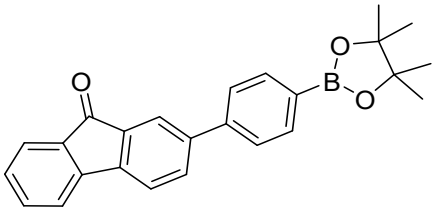
5-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]pyrimidine (31)[33]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v) to give the product as white solid in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.95 (s, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 154.9, 136.7, 135.7, 134.2, 126.2, 84.1, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.93.



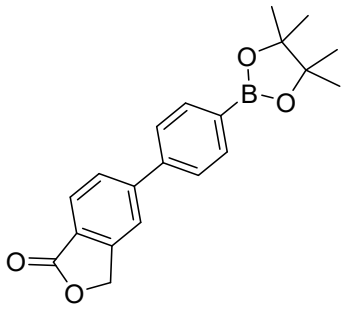
2-(4-(9H-fluoren-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32)

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 85% yield.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.86 (s, 1H), 7.84 (d, J = 3.7 Hz, 1H), 7.82 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 3.97 (s, 2H), 1.39 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 143.9, 143.5, 141.3, 141.2, 139.6, 135.3, 126.8, 126.7, 126.4, 126.1, 125.1, 123.8, 121.1, 120.1, 120.0, 83.8, 37.0, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.88. HR-MS: m/z calcd for $C_{25}H_{26}BO_2^+$ $[M+H]^+$ 369.2026, found 369.2020; calcd for $C_{25}H_{25}NaBO_4^+$ $[M+Na]^+$ 391.1845, found 391.1839.



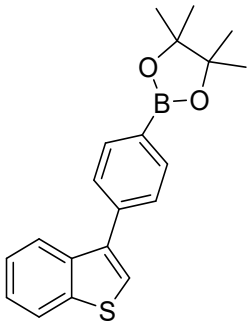
2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-fluoren-9-one (33)

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v) to give the product as white solid in 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.89 (s, 1H), 7.76 – 7.73 (m, 1H), 7.68 (d, J = 7.3 Hz, 1H), 7.64 (d, J = 8.1 Hz, 2H), 7.58 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.49 (d, J = 7.4 Hz, 1H), 7.30 (t, J = 7.3 Hz, 1H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 144.2, 143.5, 142.3, 142.0, 135.4, 134.8, 134.4, 133.3, 129.1, 126.5, 126.0, 124.4, 123.0, 120.7, 120.4, 83.9, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.85. HR-MS: m/z calcd for $C_{25}H_{25}BO_3^+$ $[M+H]^+$ 383.1819, found 383.1813; calcd for $C_{25}H_{24}NaBO_3^+$ $[M+Na]^+$ 405.1638, found 405.1632.



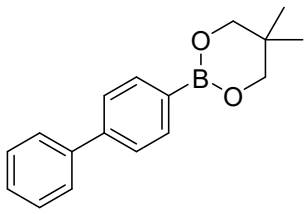
5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)isobenzofuran-1(3H)-one (34)

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.62 (d, J = 7.9 Hz, 2H), 5.37 (s, 2H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 147.3, 147.2, 142.2, 135.5, 128.5, 126.8, 126.1, 124.7, 120.7, 84.0, 69.6, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.78. HR-MS: m/z calcd for $C_{20}H_{22}BO_4^+$ $[M+H]^+$ 337.1611, found 337.1606; calcd for $C_{20}H_{21}BNaO_4Na^+$ $[M+Na]^+$ 359.1431, found 359.1425.



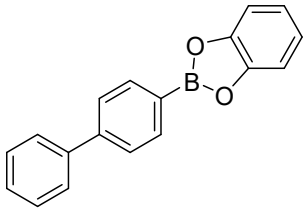
2-(4-(benzo[b]thiophen-3-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (35)

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 88% yield. 1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 2H), 8.00 – 7.97 (m, 1H), 7.97 – 7.94 (m, 1H), 7.67 (d, J = 7.9 Hz, 2H), 7.47 (s, 1H), 7.45 – 7.41 (m, 2H), 1.43 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.8, 138.0, 137.7, 135.3, 128.0, 124.5, 124.4, 123.9, 123.0, 122.9, 83.9, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.09. HR-MS: m/z calcd for $C_{20}H_{22}BO_2S^+$ $[M+H]^+$ 337.1434, found 337.1428. ^{11}B NMR (128 MHz, $CDCl_3$) δ 31.38.



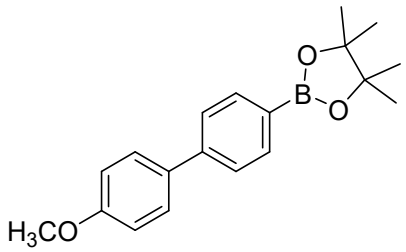
2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-1,3,2-dioxaborinane (36)[34]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (200:1, v/v) to give the product as white solid in 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.1 Hz, 2H), 7.65 (m, 4H), 7.47 (t, J = 7.5 Hz, 2H), 7.38 (t, J = 7.3 Hz, 1H), 3.82 (s, 4H), 1.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 141.2, 134.4, 128.7, 127.4, 127.2, 126.4, 72.3, 31.9, 21.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 26.79.



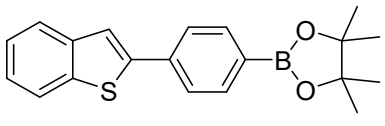
2-([1,1'-biphenyl]-4-yl)benzo[d][1,3,2]dioxaborole (37)[35]

Prepared according to general procedure of one-pot synthesis of aryl/heteroaryl boronic esters from phenols, the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 7.68 (d, 2H), 7.49 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.3, 6.4 Hz, 1H), 7.35 (m, 2H), 7.15 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 145.0, 143.5, 140.6, 135.5, 128.9, 127.9, 127.3, 127.0, 122.8, 112.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.41.



2-(4'-methoxy-[1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n)[36]

Prepared according to general procedure using 4-(4-methoxyphenyl) fluorides (0.5 mol), bis(pinacolato)diboron (0.75 mol), 0.2% mol $PdCl_2$, 0.4% mol X-Phos, NaOAc (1.5 mol), *i*-PrOH (4 mL) was stirred at 80 °C under nitrogen atmosphere for 7 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were concentrated in vacuo and the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (100:1, v/v) to give the product as white solid in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.59 (m, 4H), 6.99 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 1.37 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 143.5, 135.3, 133.4, 128.3, 126.0, 114.2, 83.8, 55.4, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.99.



2-(4-(benzo[b]thiophen-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p)

Prepared according to general procedure using 4-indole fluorides (0.5 mol), bis(pinacolato)diboron (0.75 mol), 0.2% mol $PdCl_2$, 0.4% mol X-Phos, NaOAc (1.5 mol), *i*-PrOH (4 mL) was stirred at 80 °C under nitrogen atmosphere for 10 h. Subsequently, the mixture was added to brine (10 mL) and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were concentrated in vacuo and the crude product was purified via silica gel column chromatography with petroleum ether/ethyl acetate (50:1, v/v) to give the product as white solid in

89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 7.7 Hz, 1H), 7.78 (d, J = 7.5 Hz, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.63 (s, 1H), 7.37 (d, J = 6.3 Hz, 1H), 7.34 – 7.29 (m, 1H), 1.38 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0, 140.6, 139.6, 136.8, 135.4, 125.6, 124.5, 124.4, 123.7, 122.3, 120.0, 83.9, 24.9. The ipso-carbon to boron was not observed in NMR. ^{11}B NMR (128 MHz, $CDCl_3$) δ 30.89.

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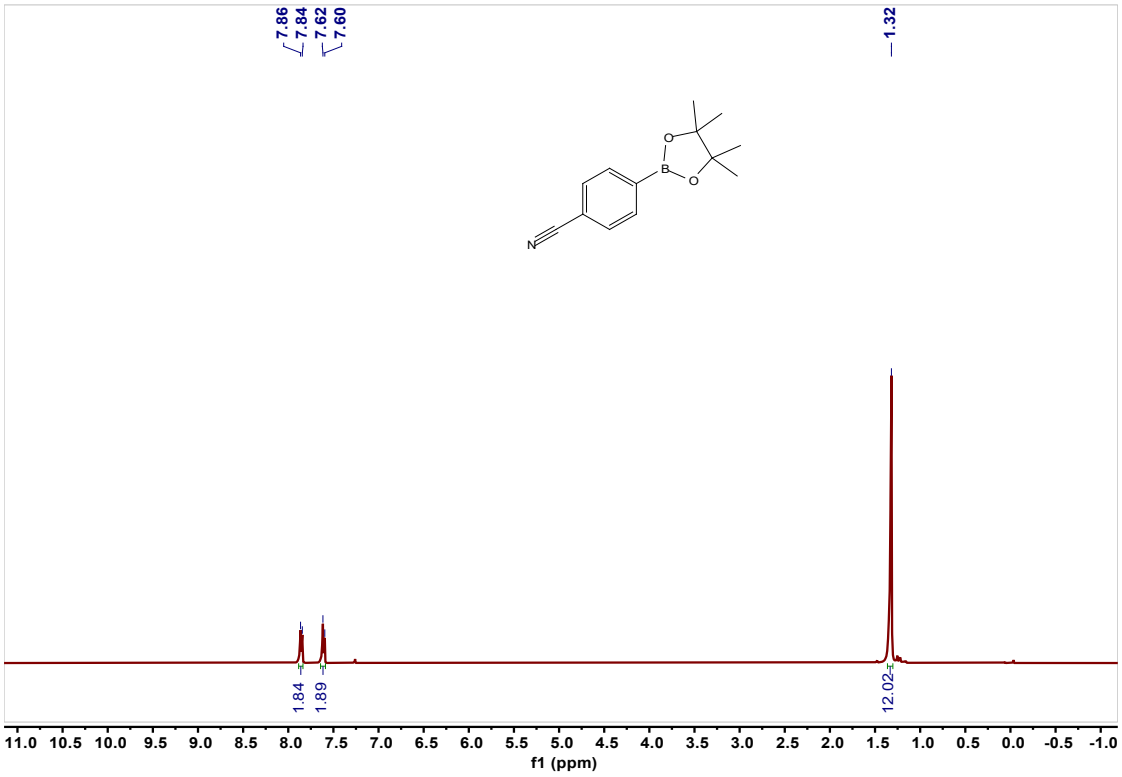
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7.60
1.32
1.84
1.89
12.02
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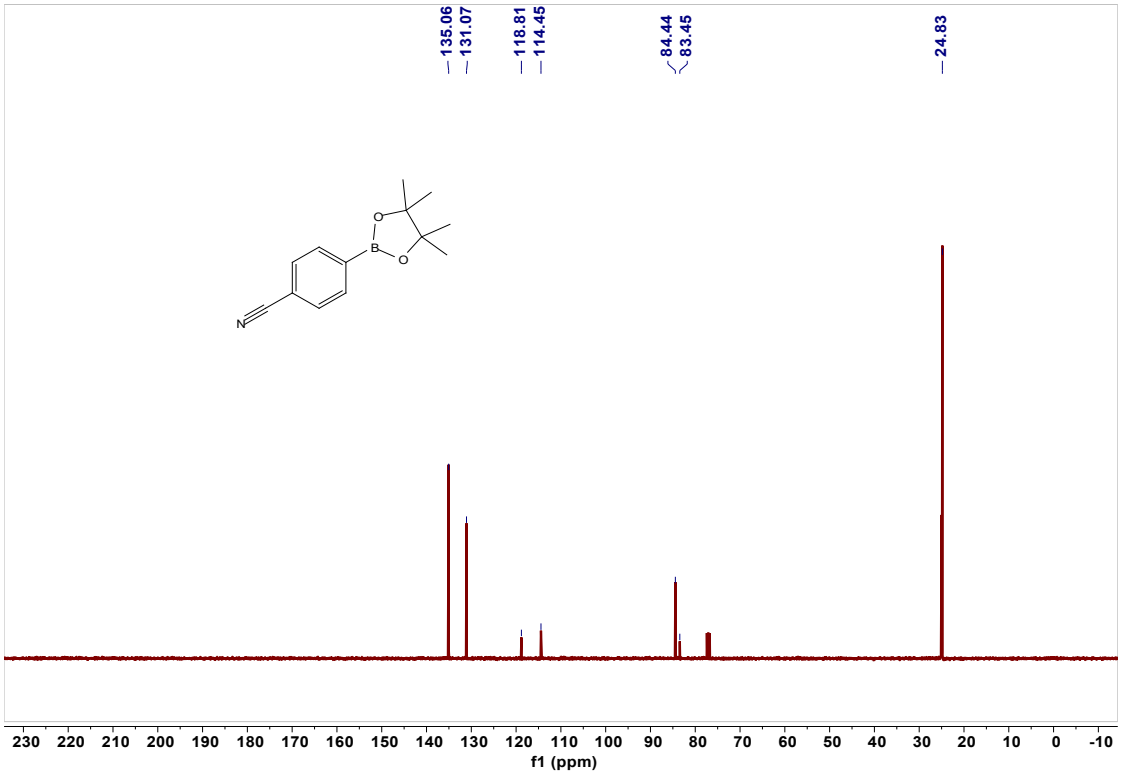
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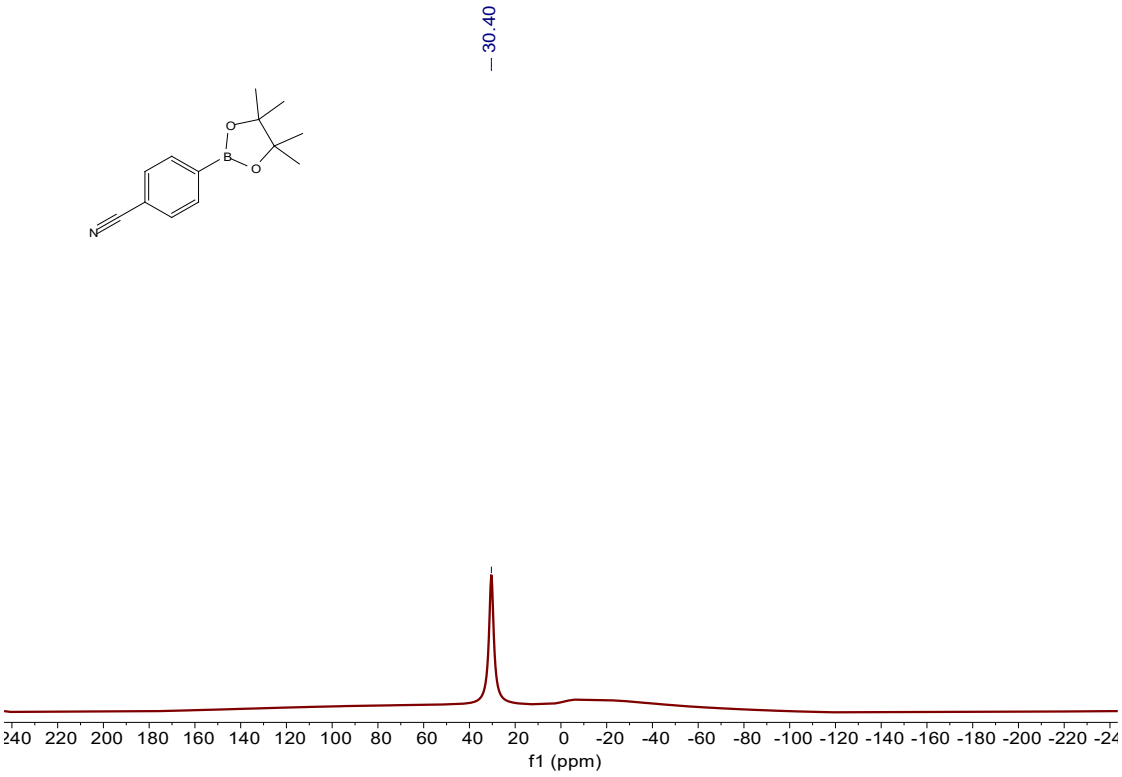
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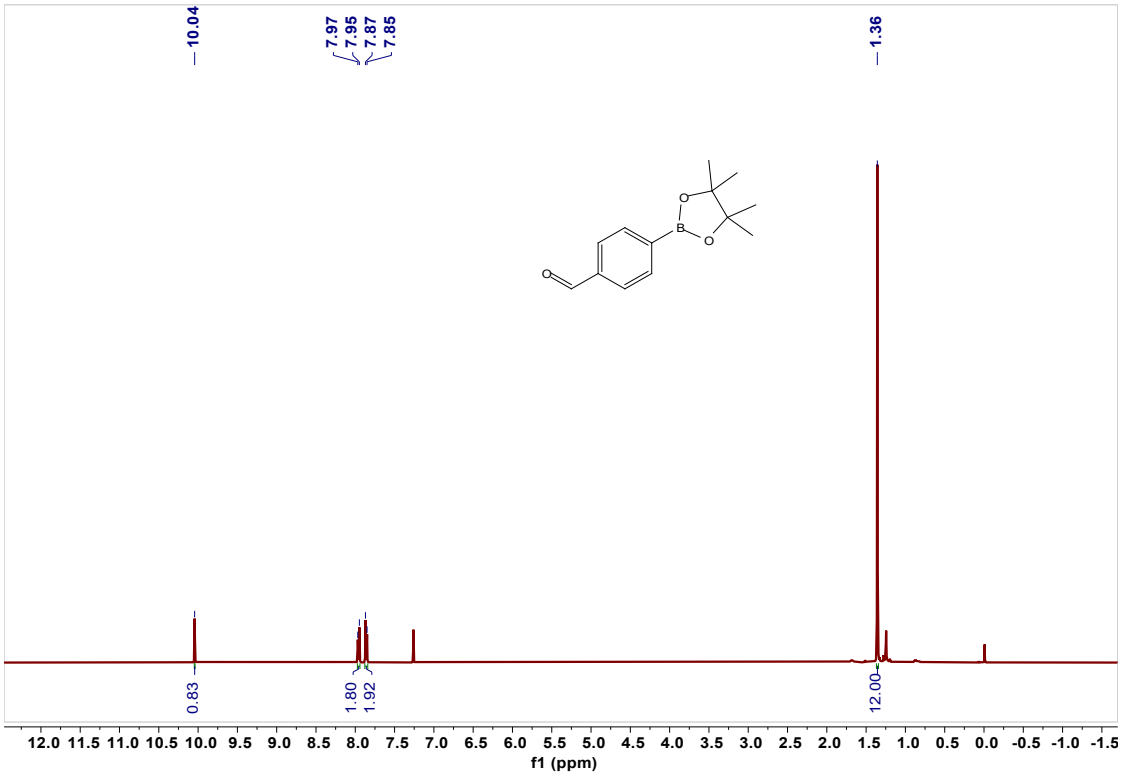
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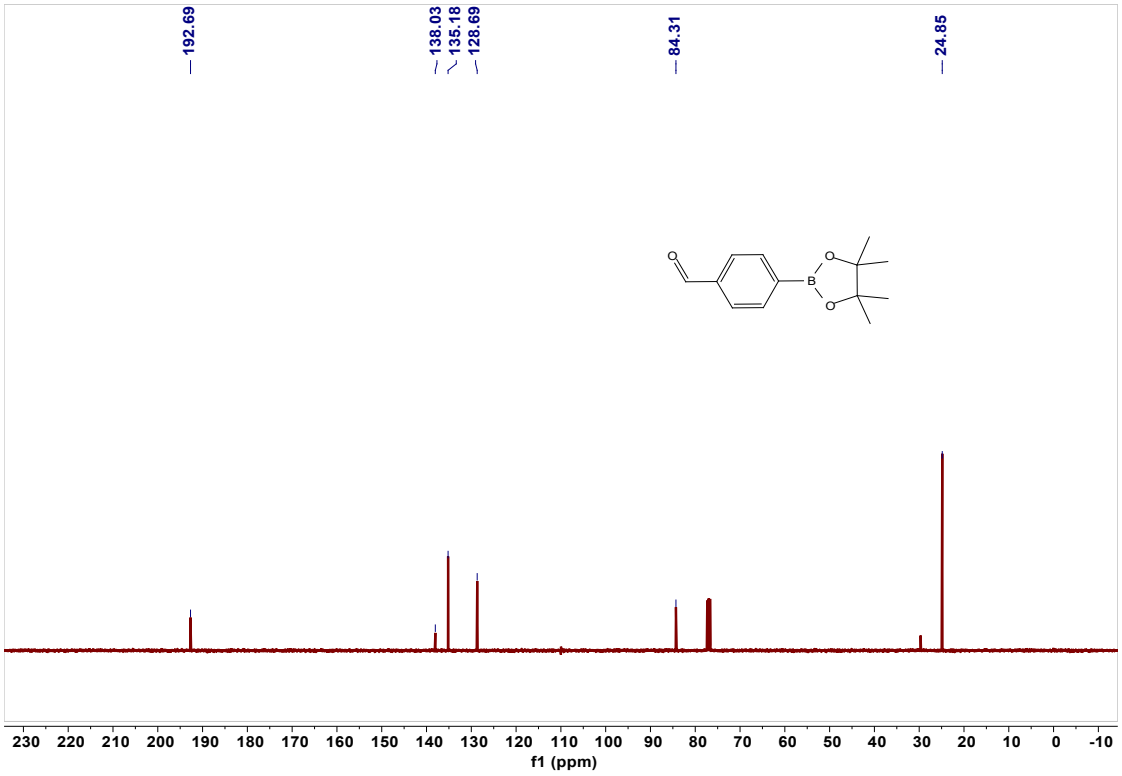
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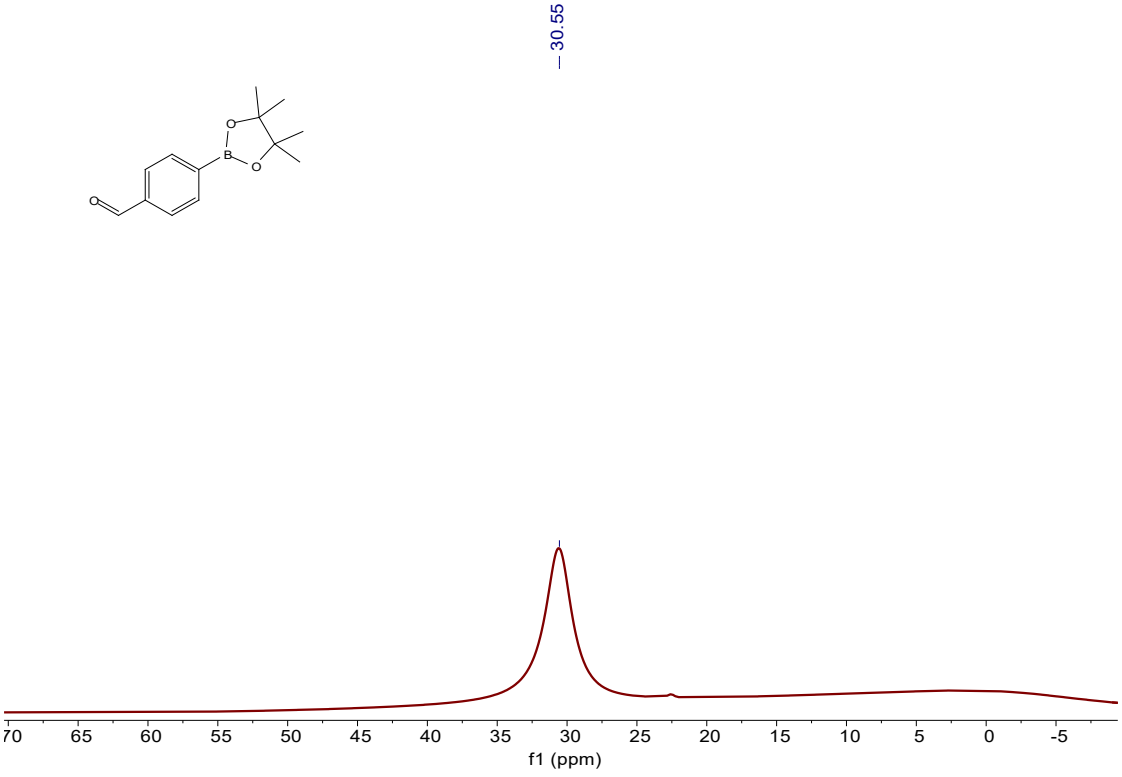
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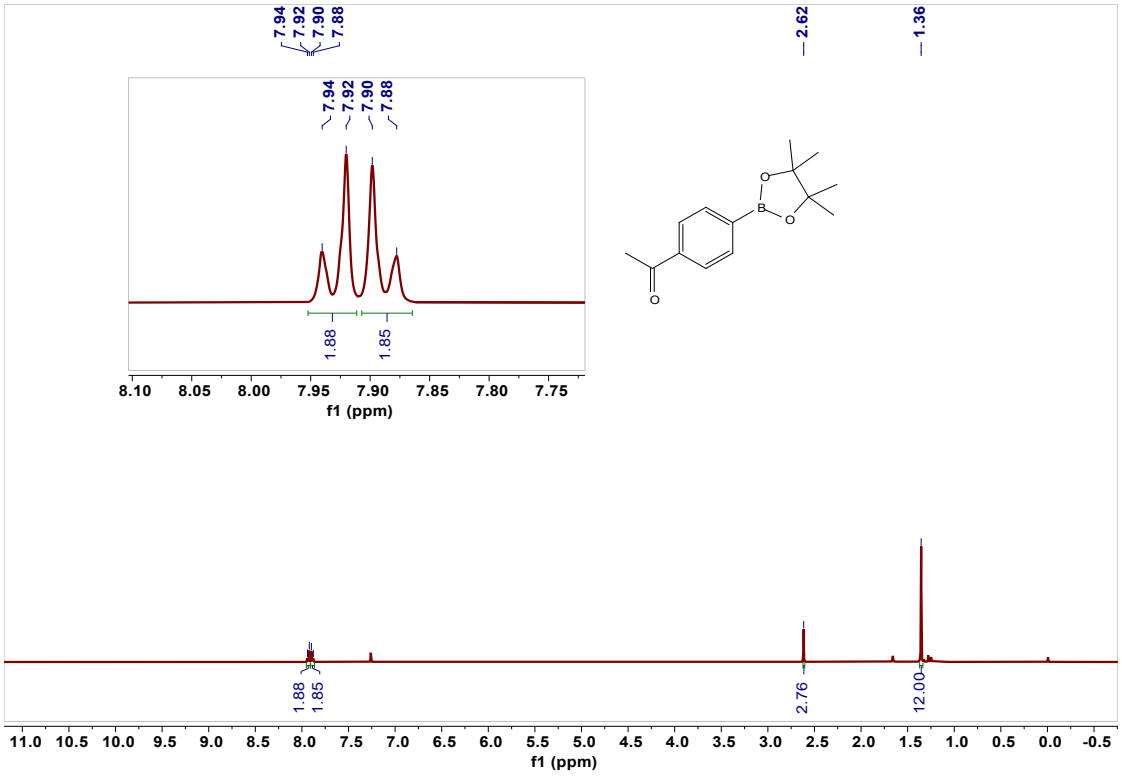
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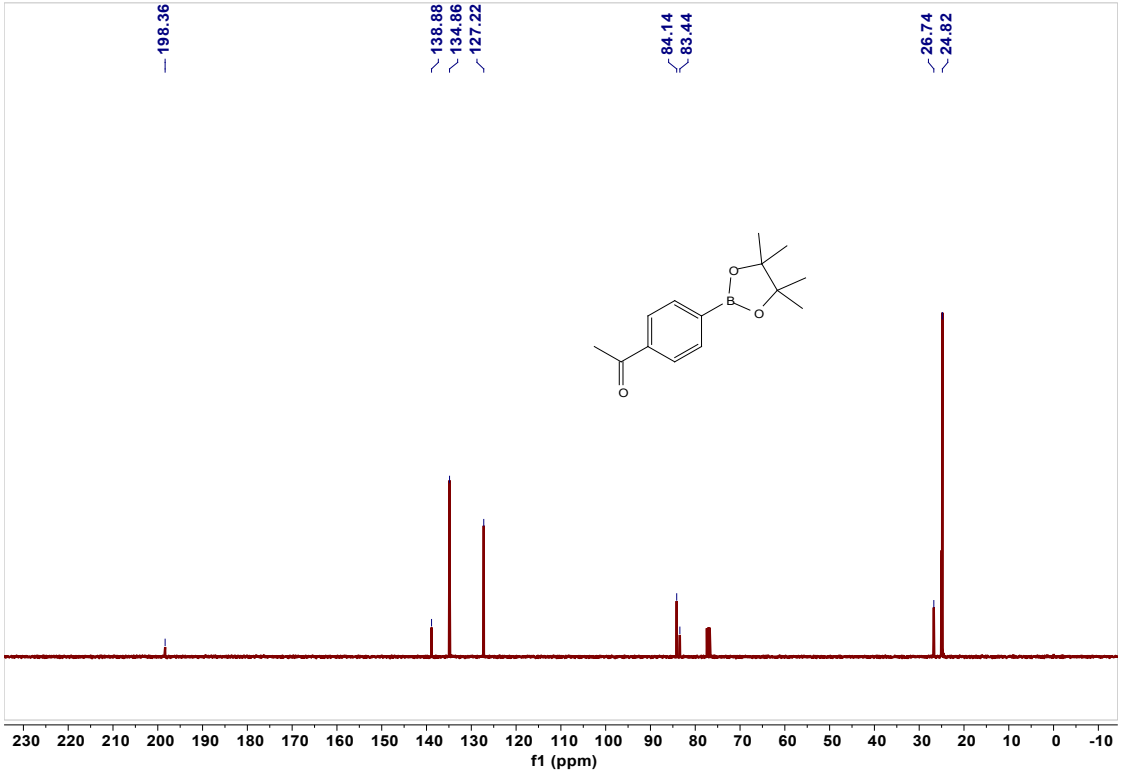
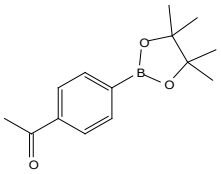
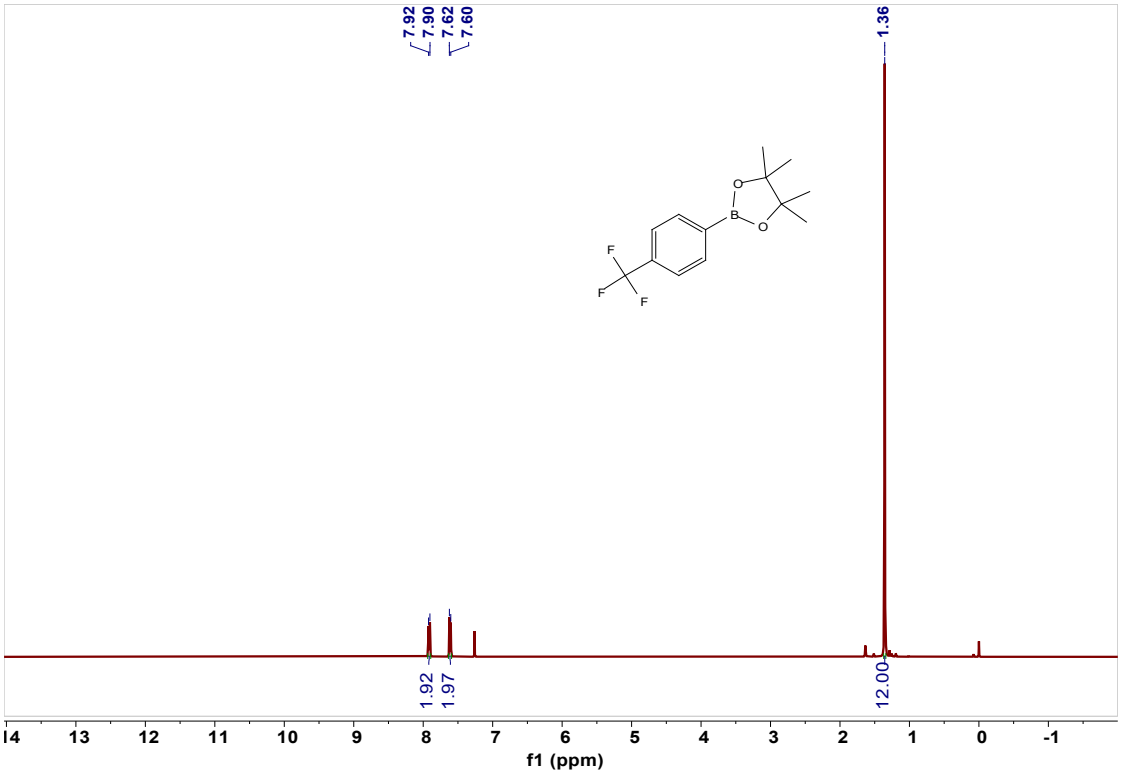
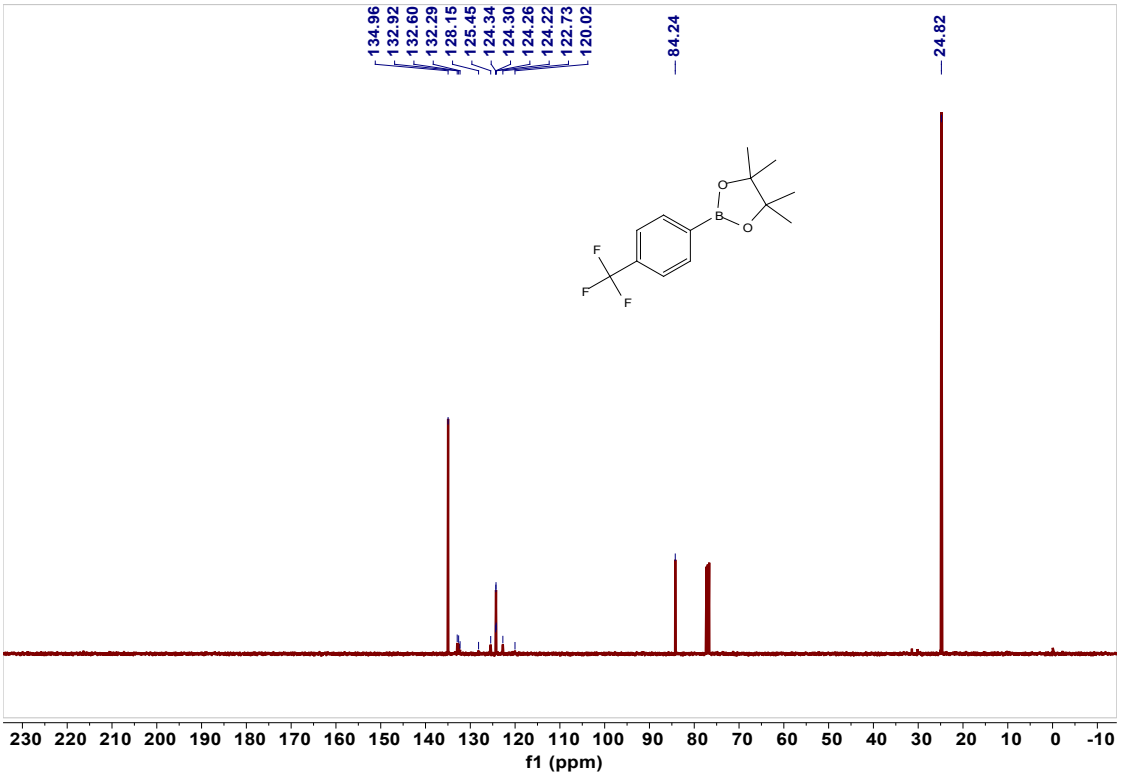
12.00
f1 (ppm)


198.36
138.88
134.86
127.22
84.14
83.44
26.74
24.82
f1 (ppm)


O
B
O
O

30.63
64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)


7.92
7.90
7.62
7.60
1.36
O
B
O
F
F
F
1.92
1.97
12.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


134.96
132.92
132.60
132.29
128.15
125.45
124.34
124.30
124.26
124.22
122.73
120.02
84.24
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B
O
F
F
F
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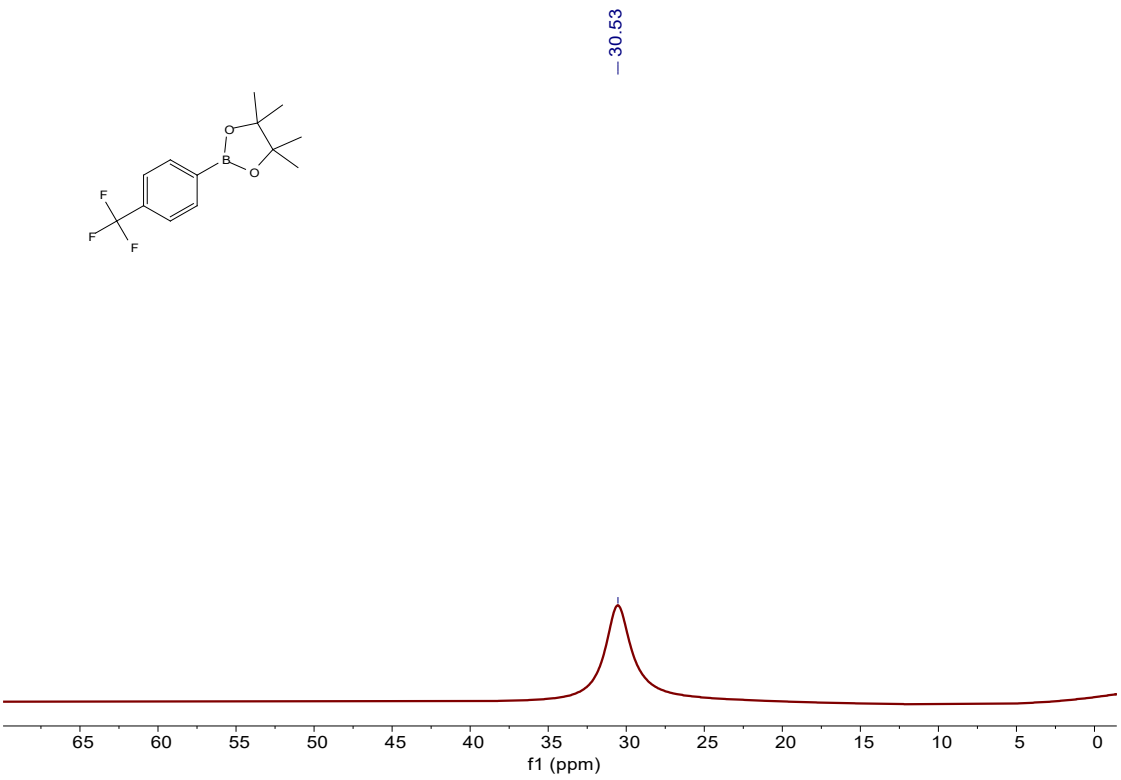
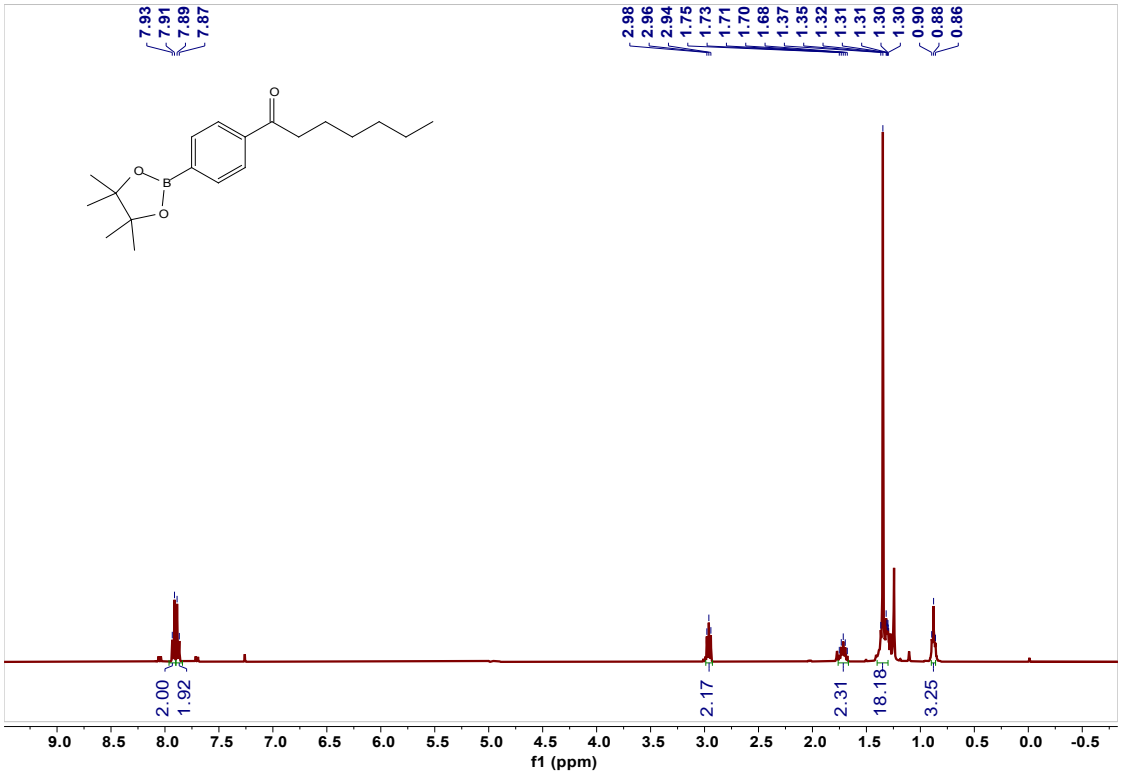
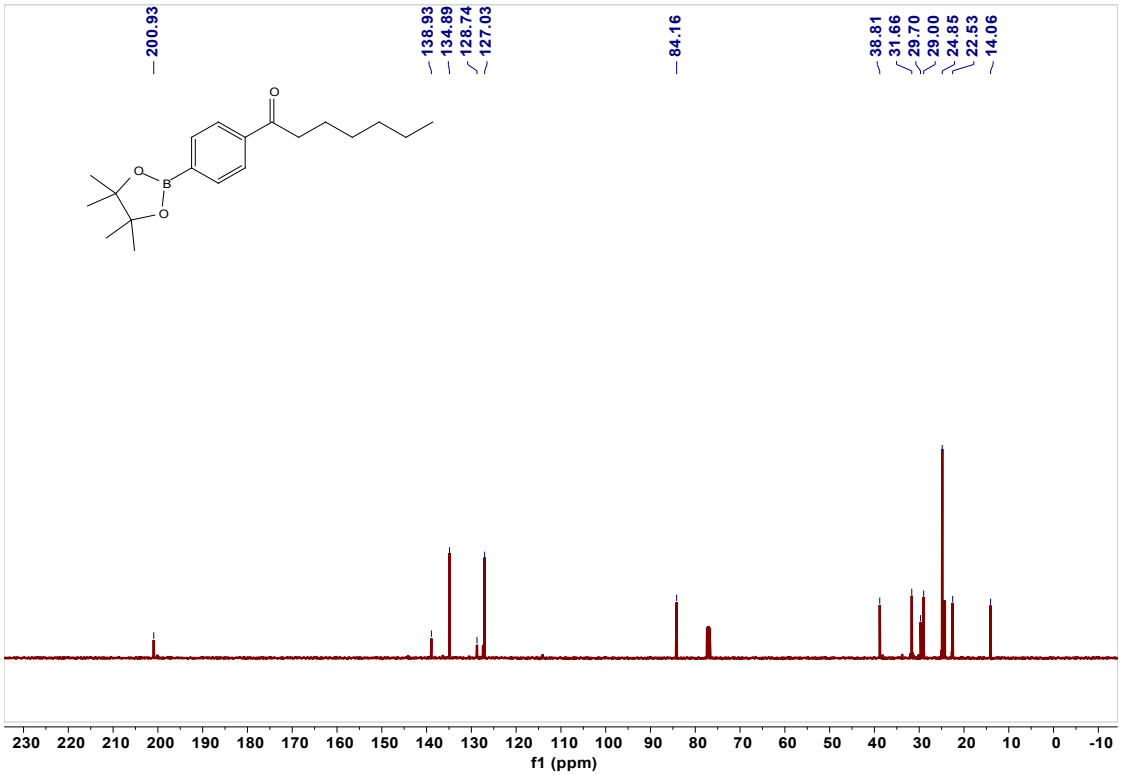
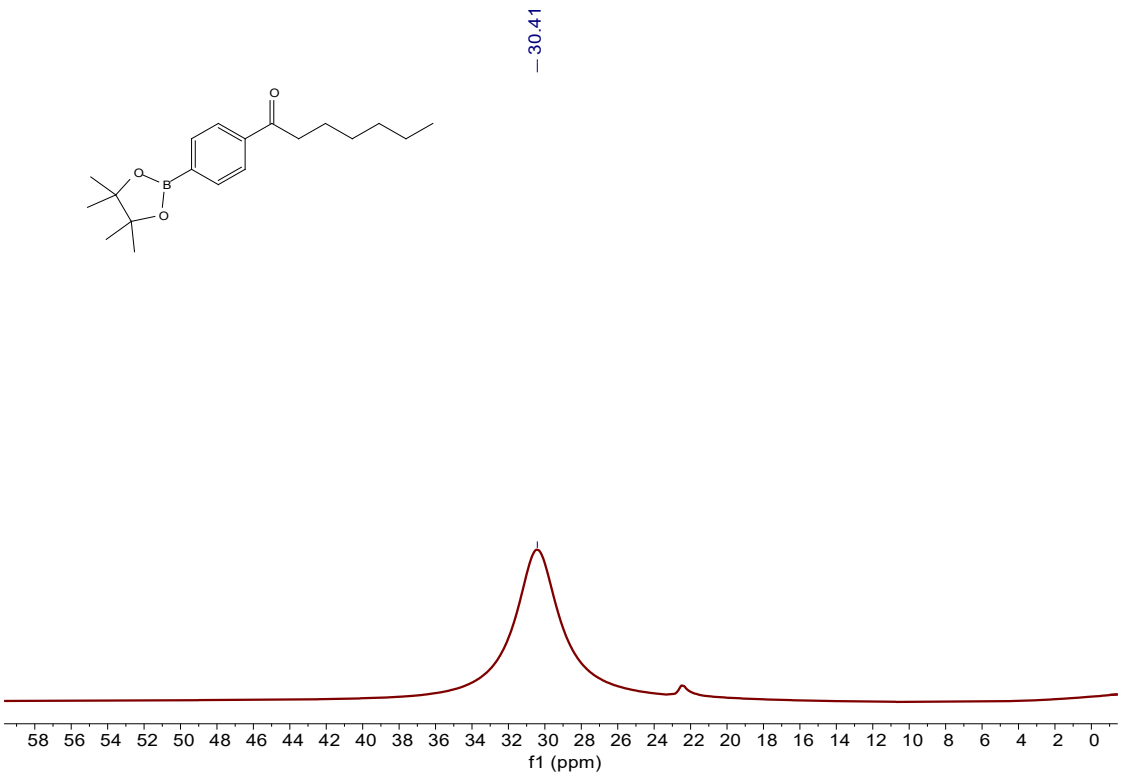
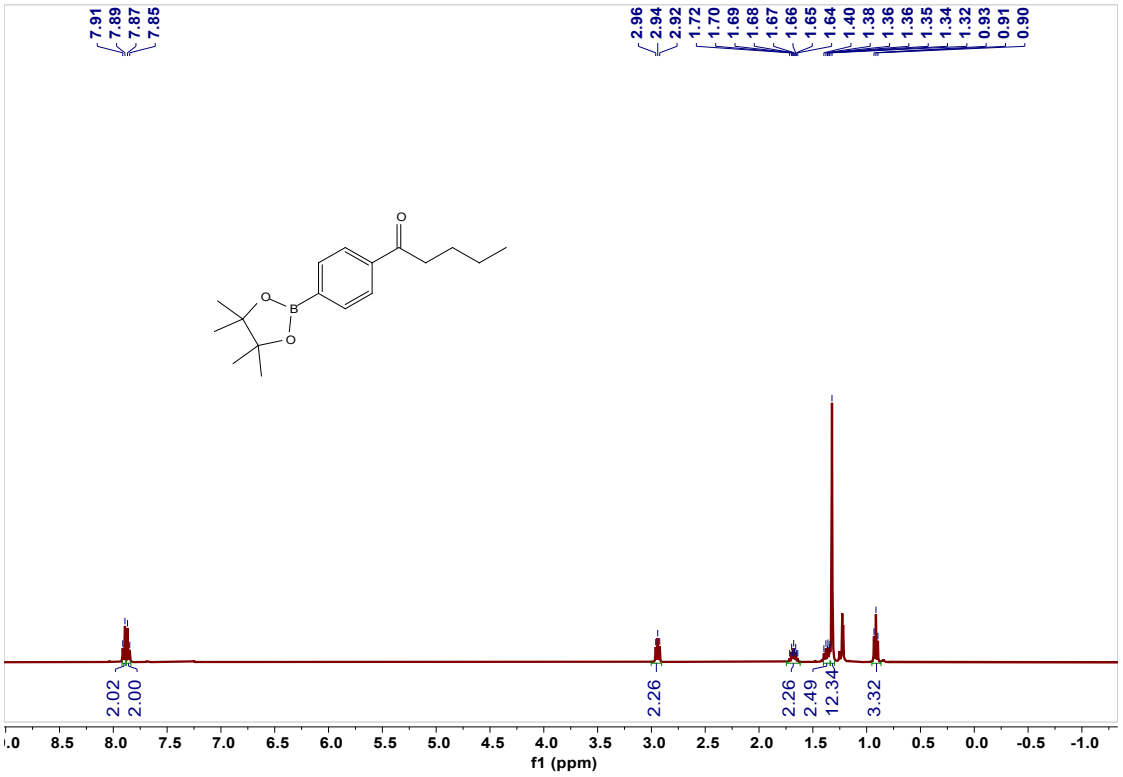
f1 (ppm)

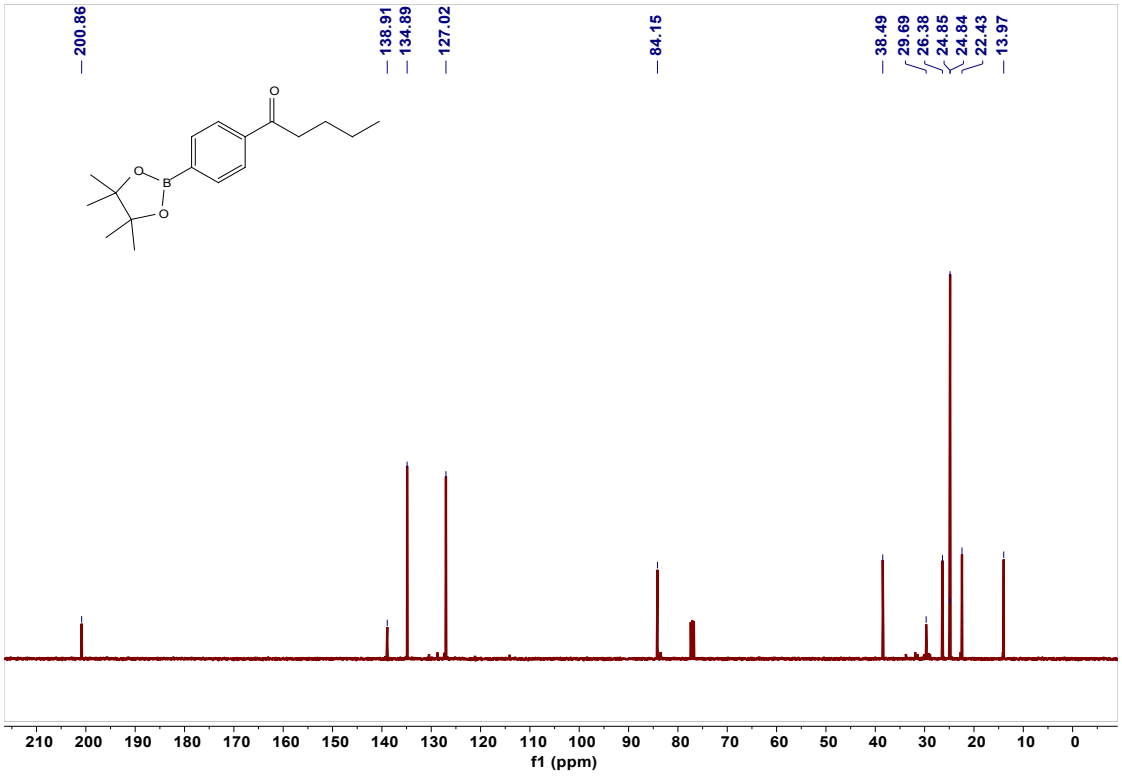

30.53
O
B
O
F
F
F
65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

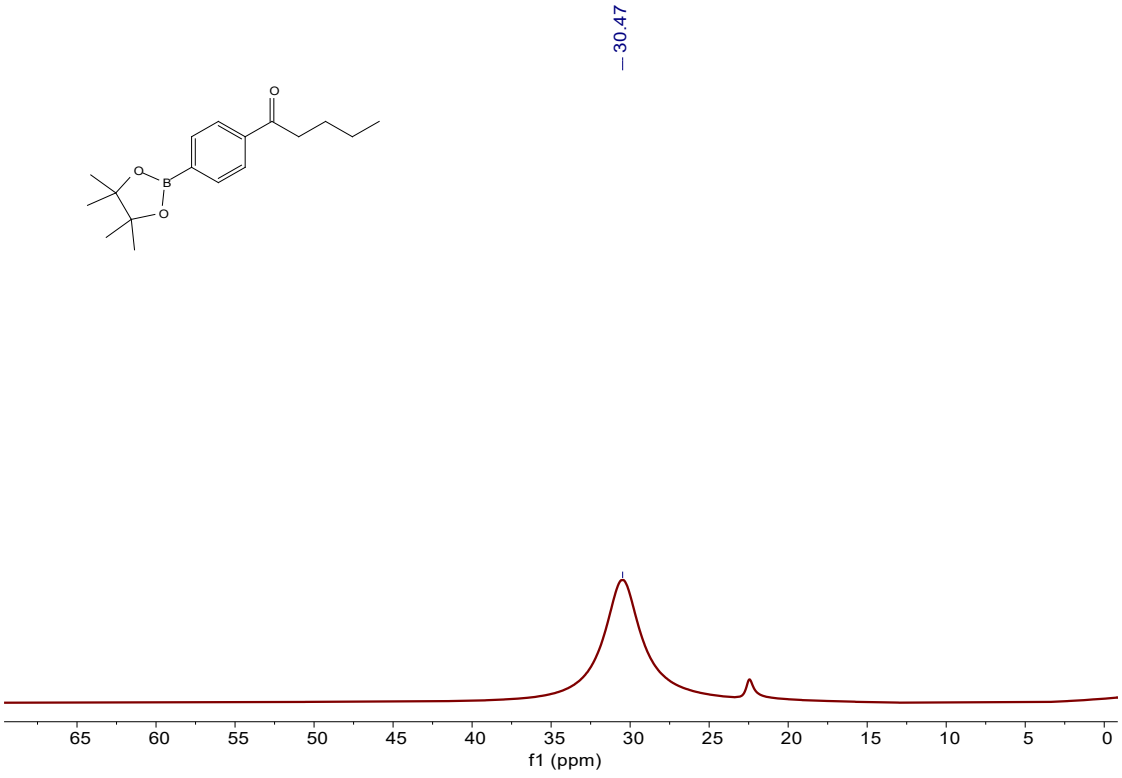

7.93
7.91
7.89
7.87
2.98
2.96
2.94
1.75
1.73
1.71
1.70
1.68
1.37
1.35
1.32
1.31
1.31
1.30
1.30
0.90
0.88
0.86
O
O
B
O
2.00
1.92
2.17
2.31
18.18
3.25
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

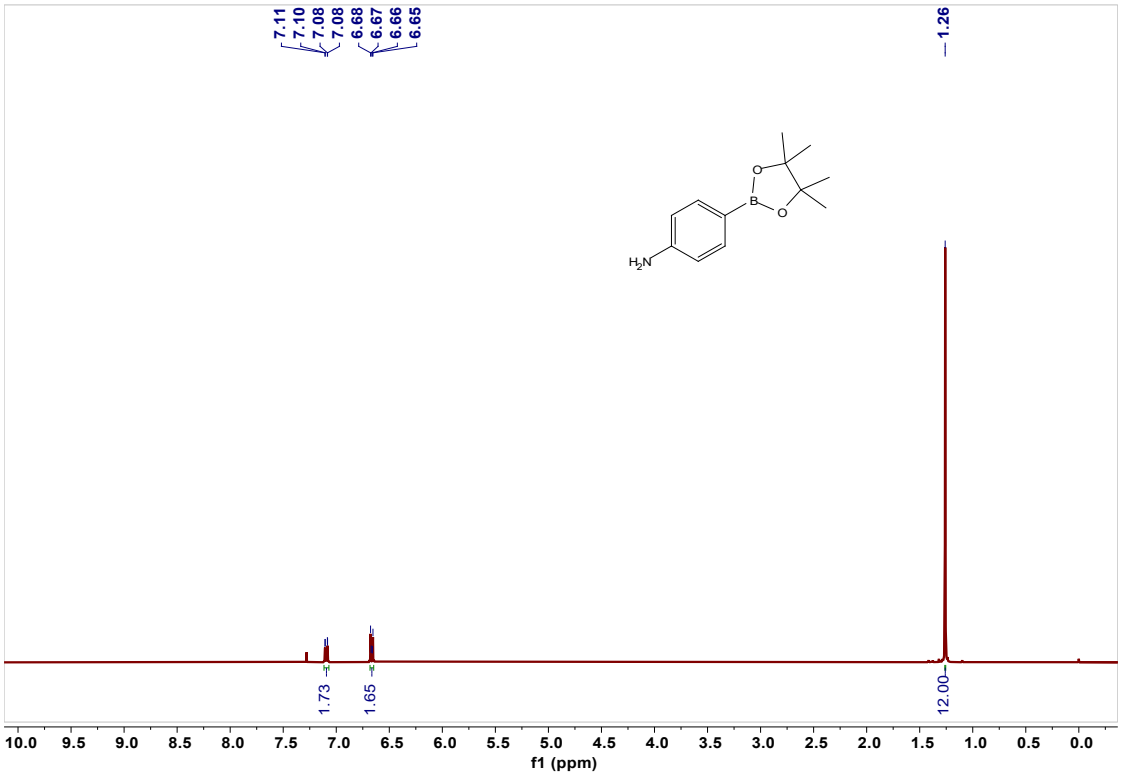

200.93
138.93
134.89
128.74
127.03
84.16
38.81
31.66
29.70
29.00
24.85
22.53
14.06
O
O
B
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

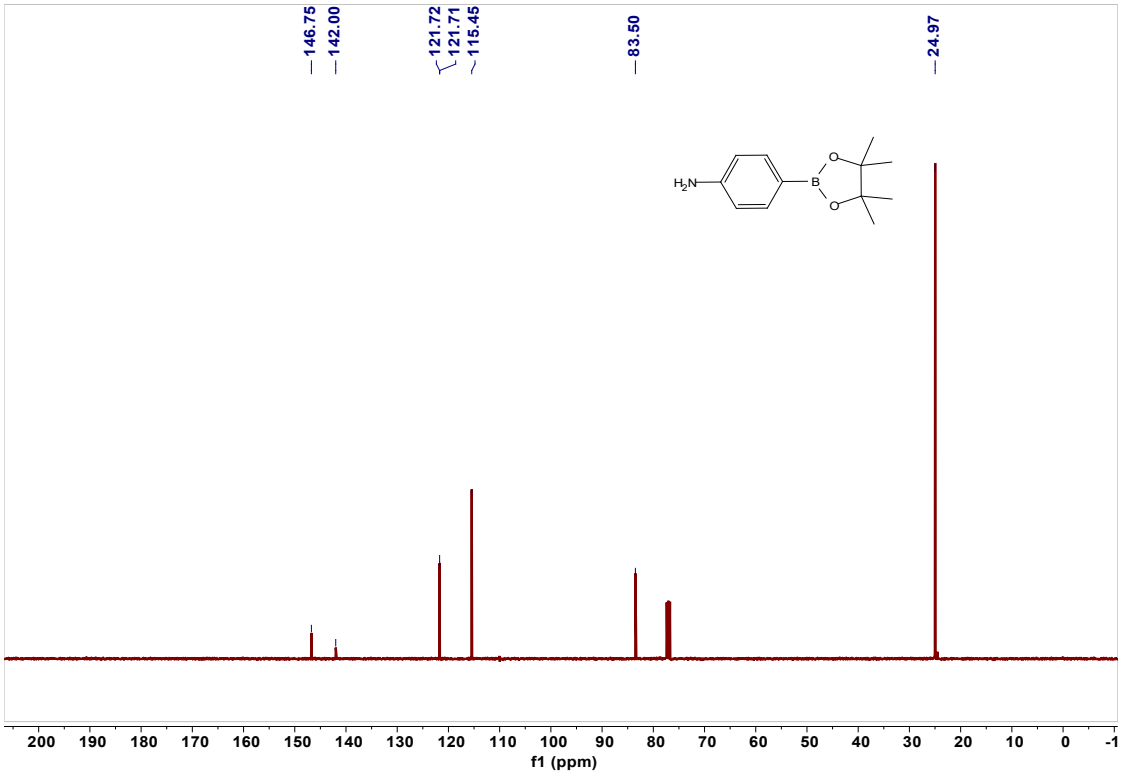

30.41
O
O
B
O
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)

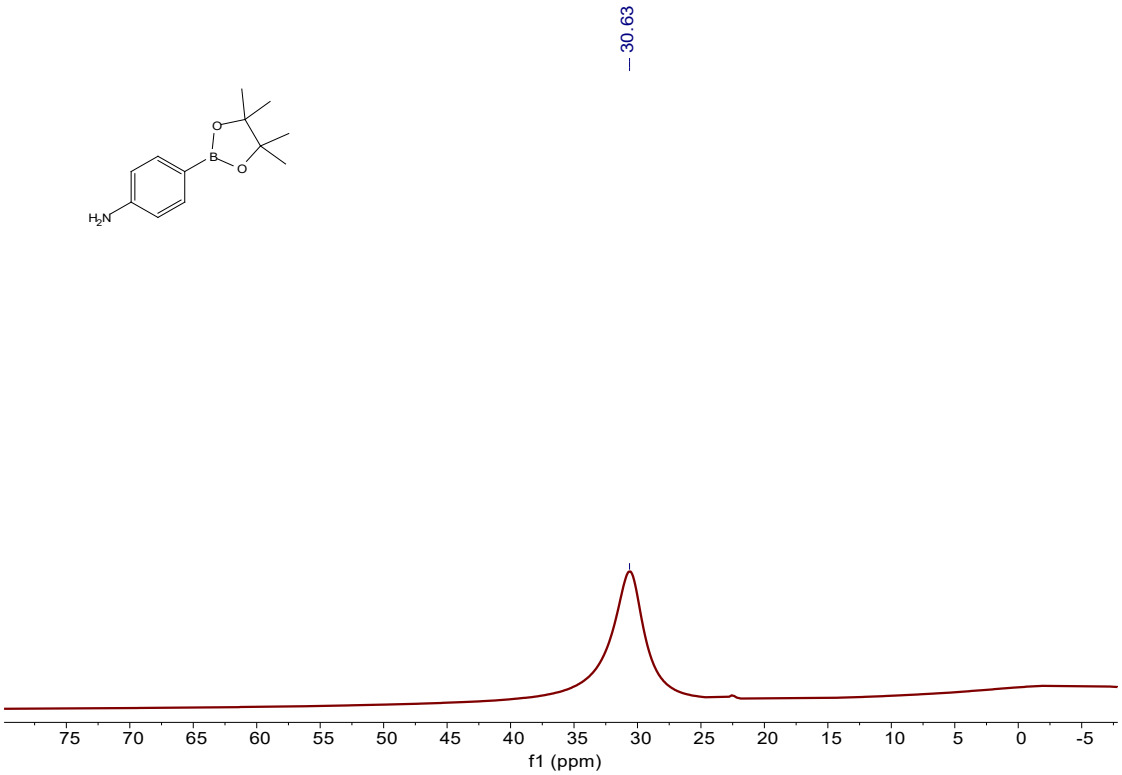

7.91
7.89
7.87
7.85
2.96
2.94
2.92
1.72
1.70
1.69
1.68
1.67
1.66
1.65
1.64
1.40
1.38
1.36
1.36
1.35
1.34
1.32
0.93
0.91
0.90
O
O
B
O
2.02
2.00
2.26
2.26
2.49
12.34
3.32
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

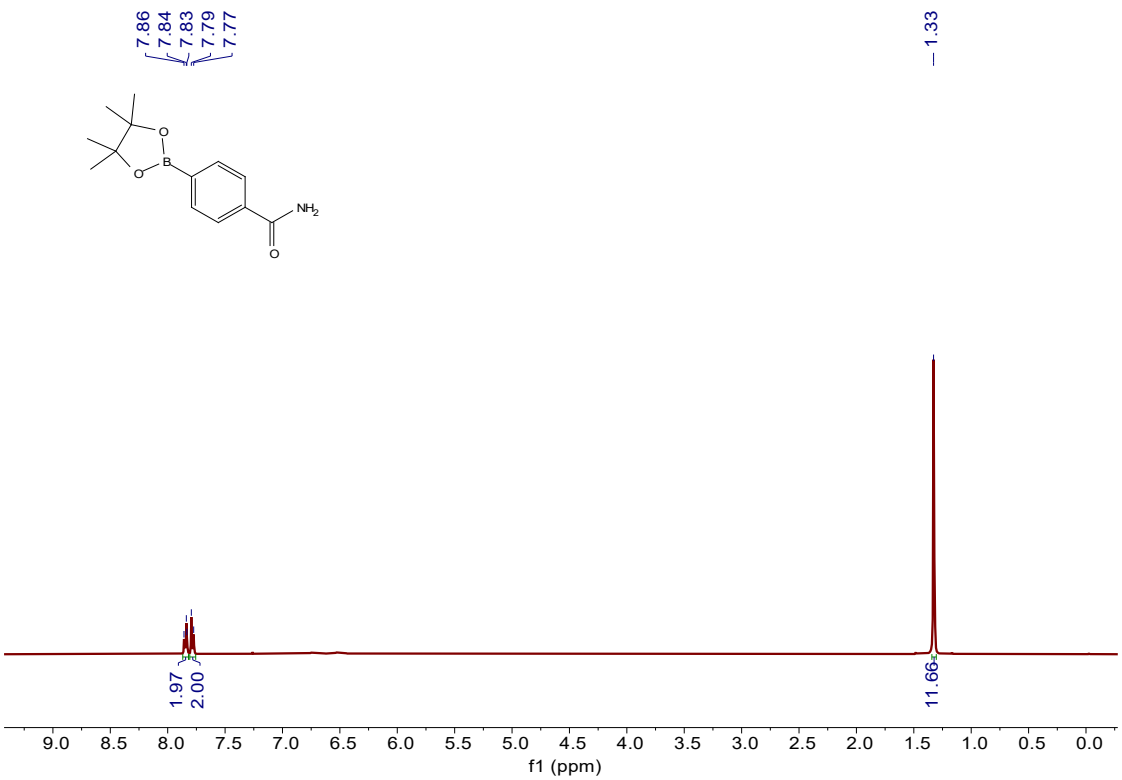

200.86
138.91
134.89
127.02
84.15
38.49
29.69
26.38
24.85
24.84
22.43
13.97
O
O
B
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

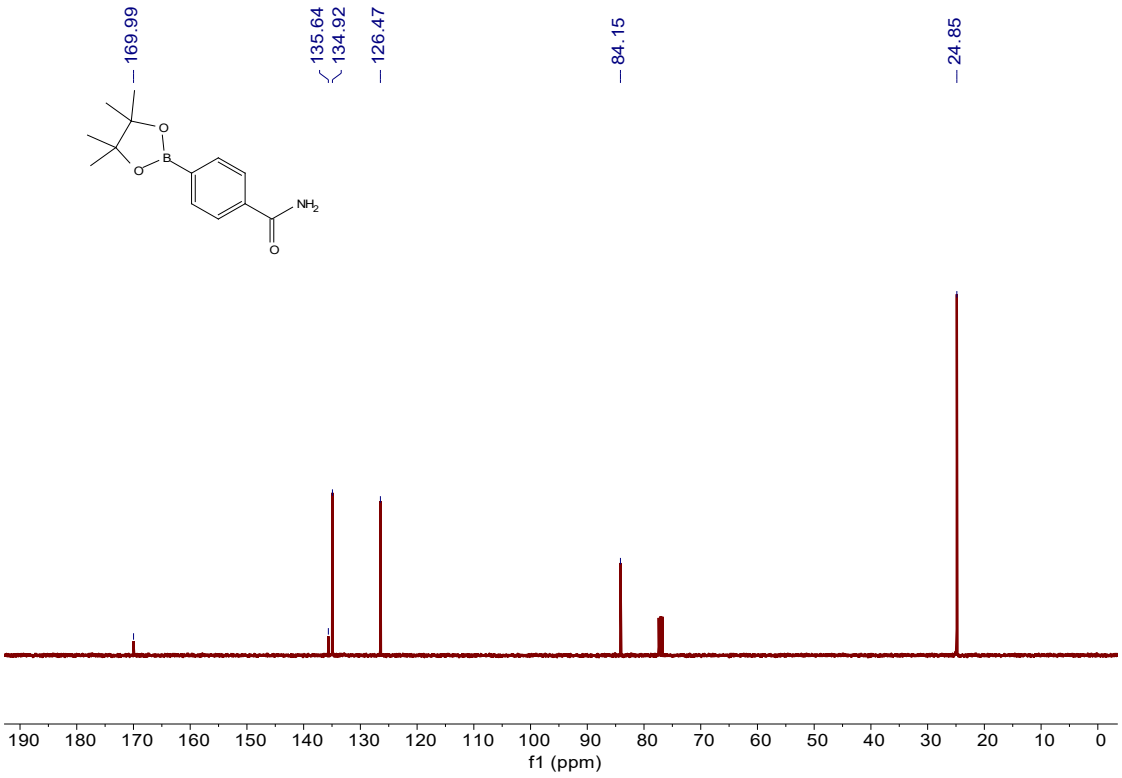

30.47
O
O
B
O
65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

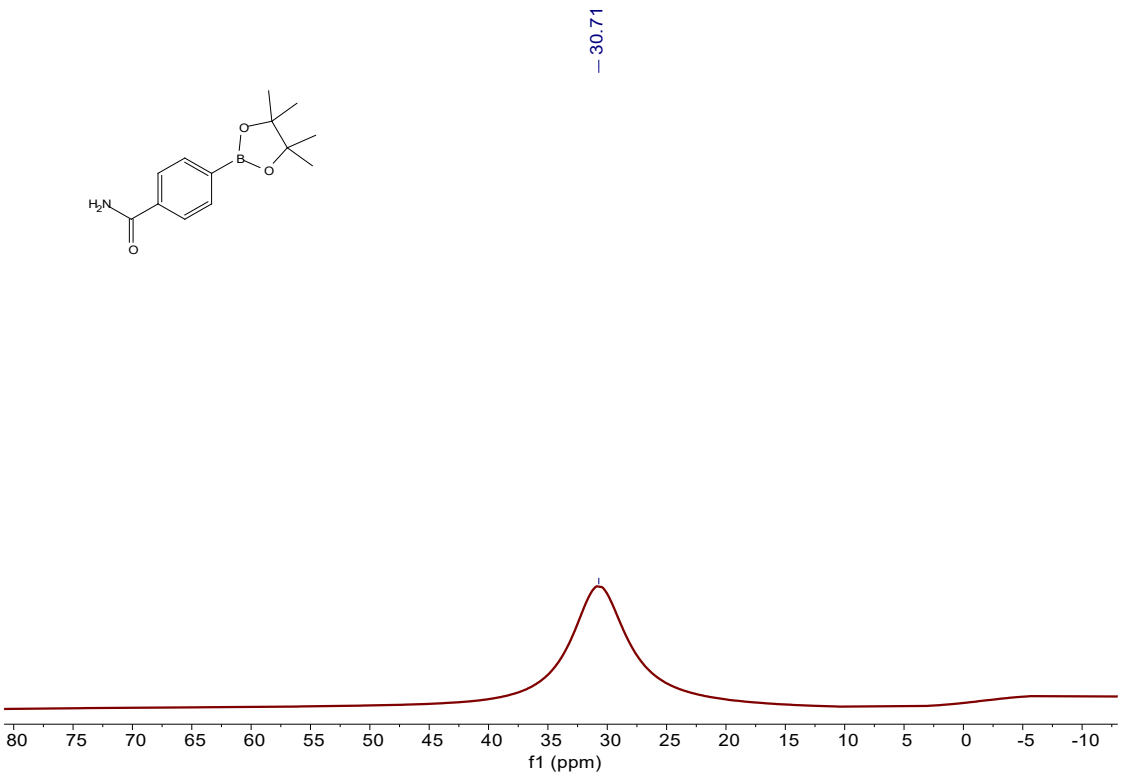

7.11
7.10
7.08
7.08
6.68
6.67
6.66
6.65
1.26
1.73
1.65
12.00
f1 (ppm)

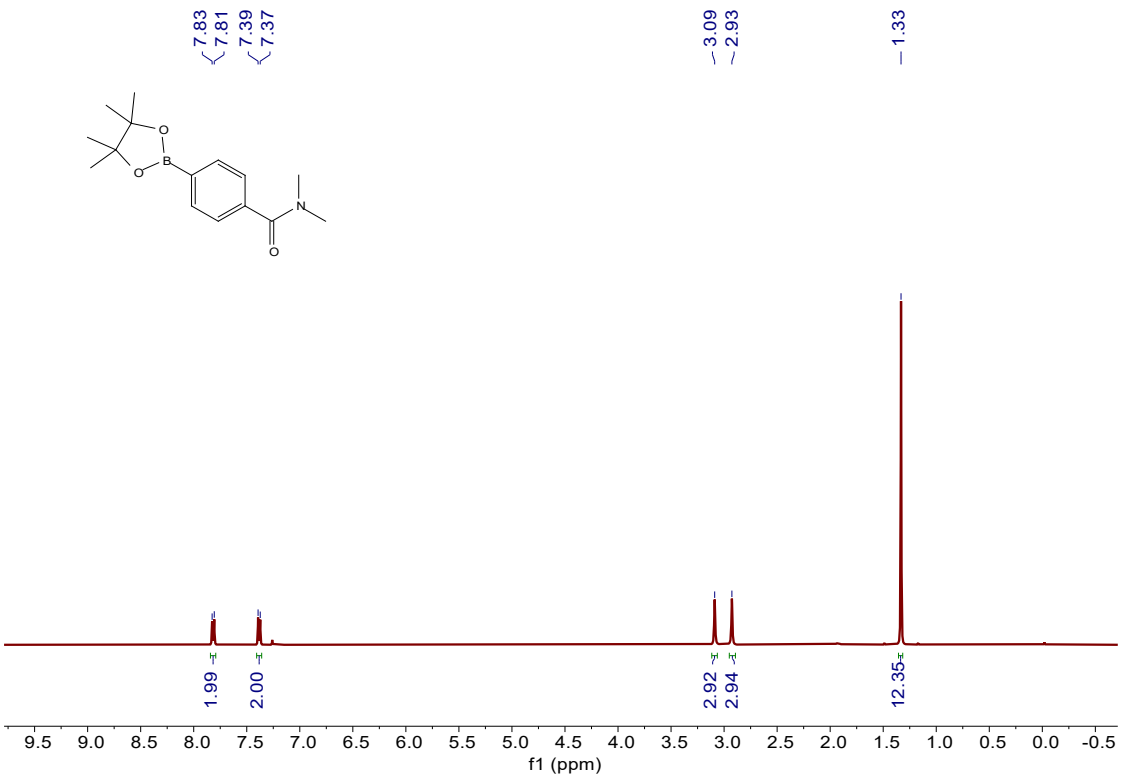

146.75
142.00
121.72
121.71
115.45
83.50
24.97
f1 (ppm)

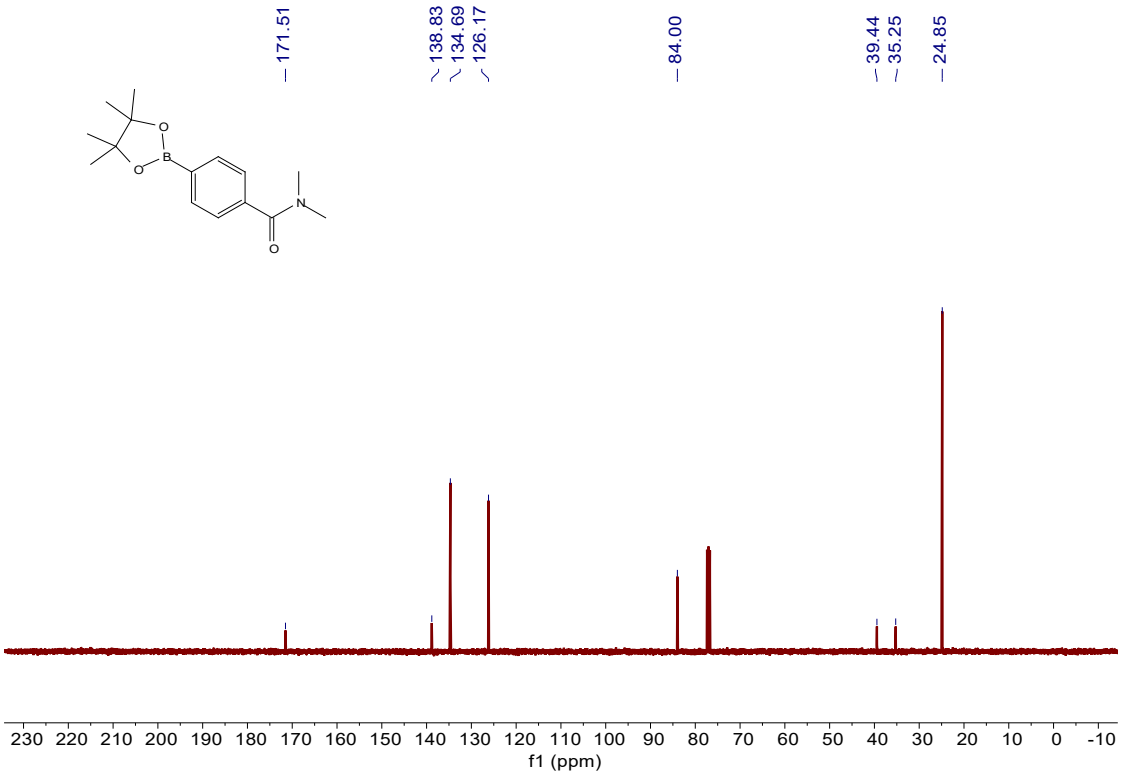

30.63
O
B
O
H2N
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

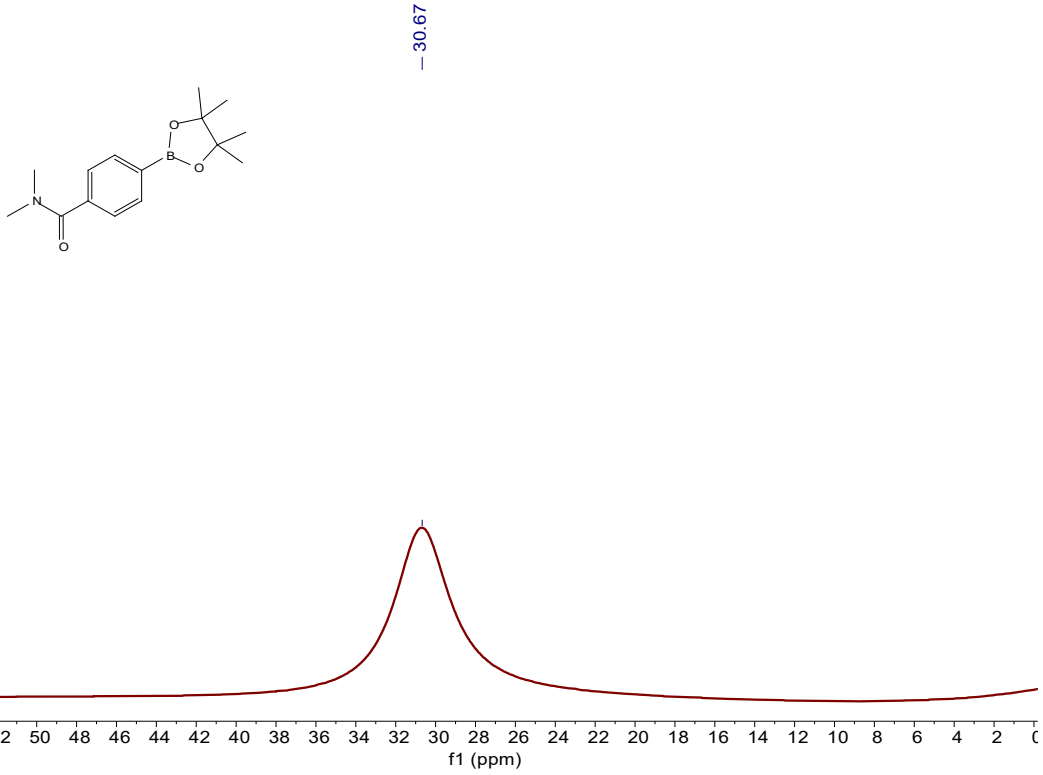

7.86
7.84
7.83
7.79
7.77
1.33
O
B
O
NH2
O
1.97
2.00
11.66
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

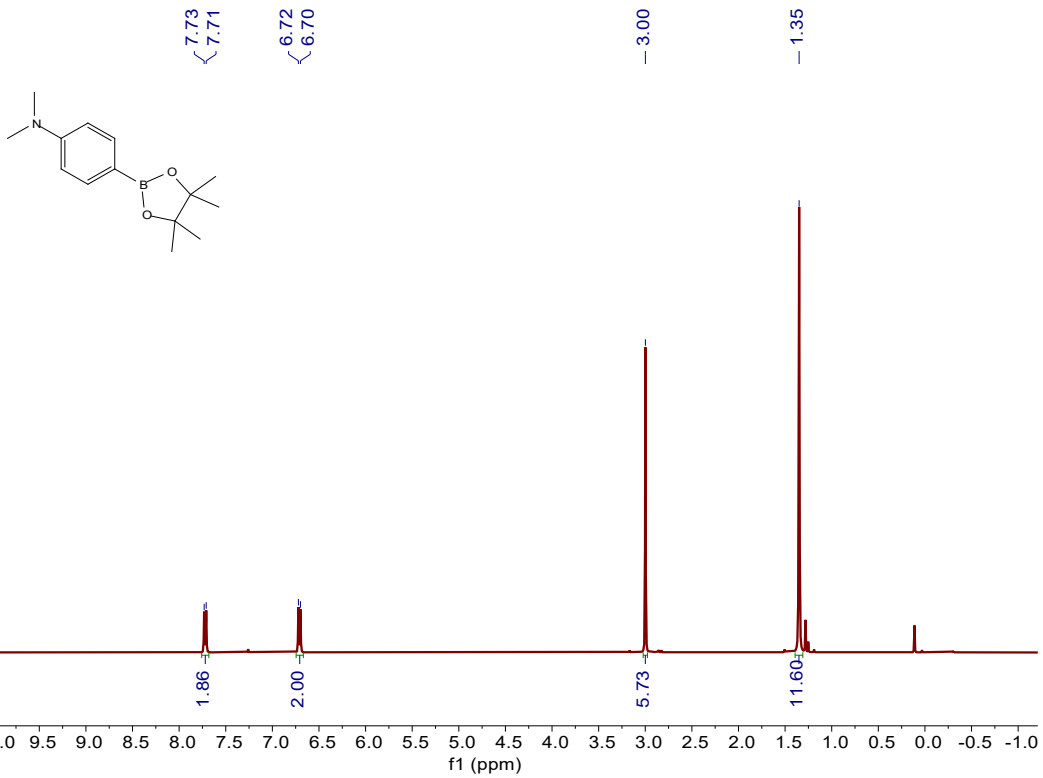

169.99
135.64
134.92
126.47
84.15
24.85
NH2
O
B
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

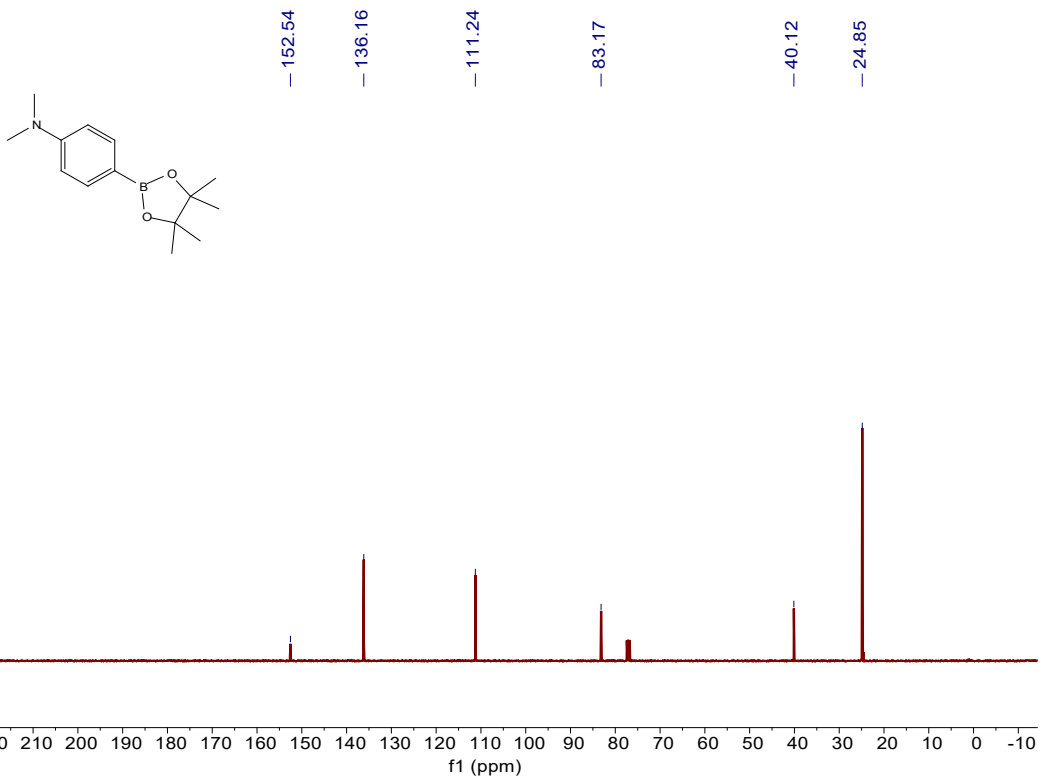

30.71
H2N
O
B
O
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

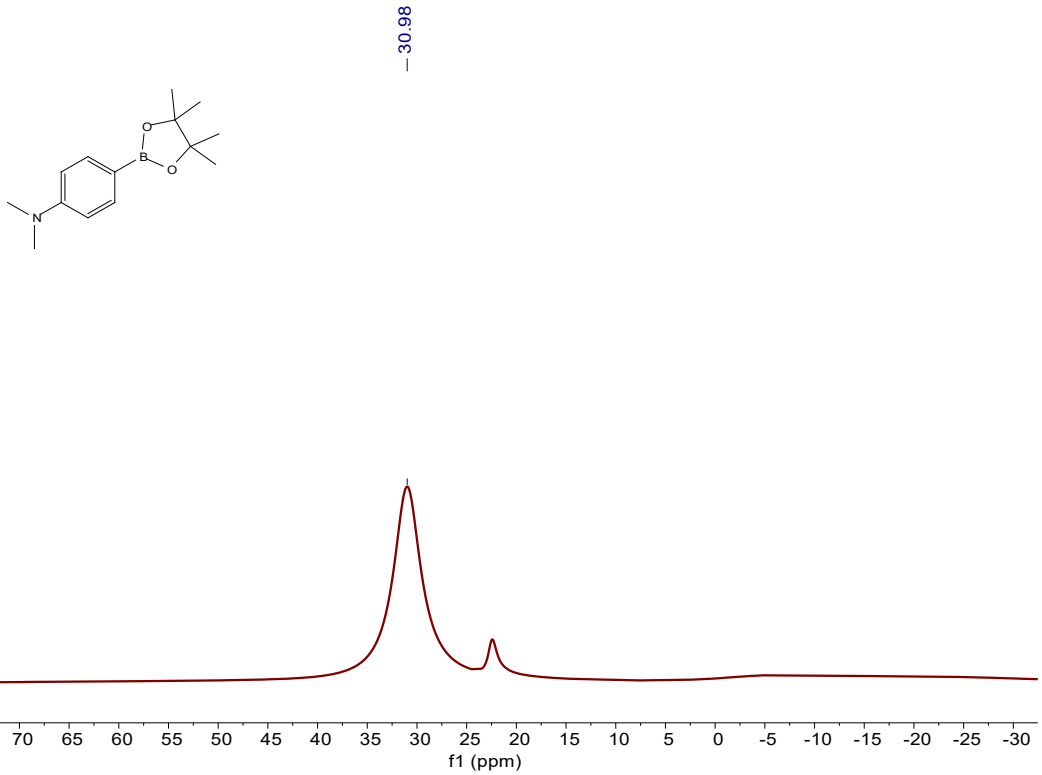

7.83
7.81
7.39
7.37
3.09
2.93
1.33
1.99
2.00
2.92
2.94
12.35
f1 (ppm)

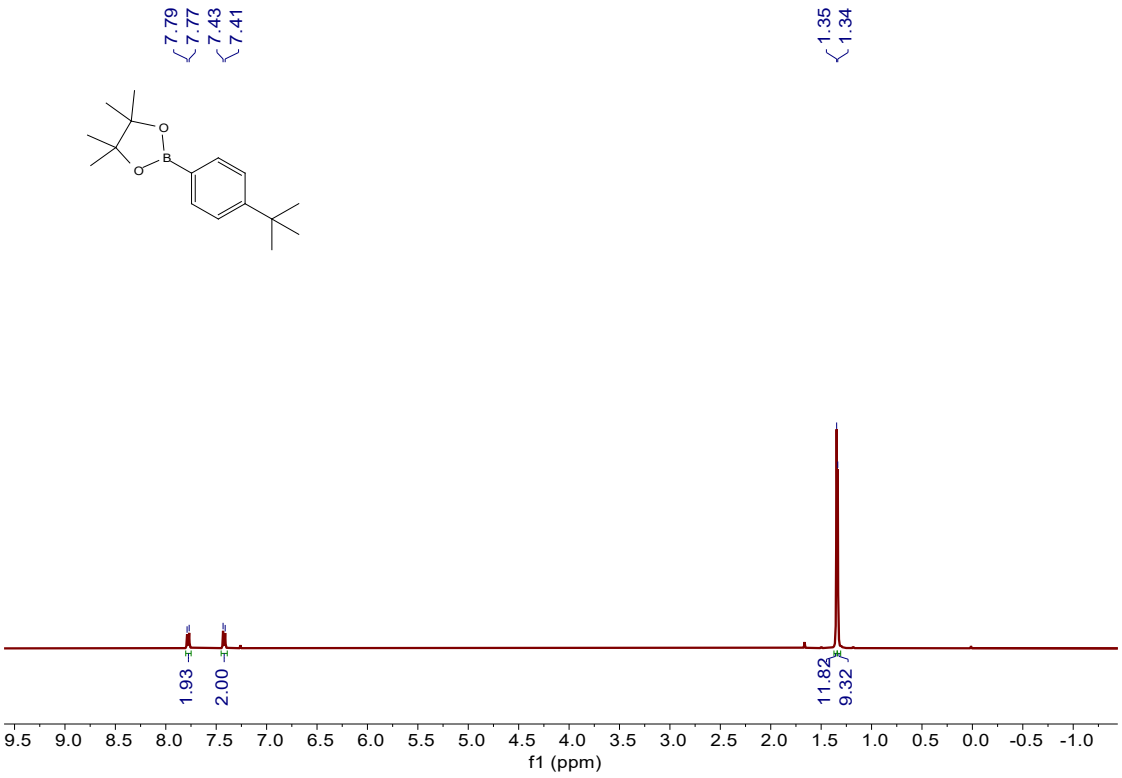

171.51
138.83
134.69
126.17
84.00
39.44
35.25
24.85
f1 (ppm)

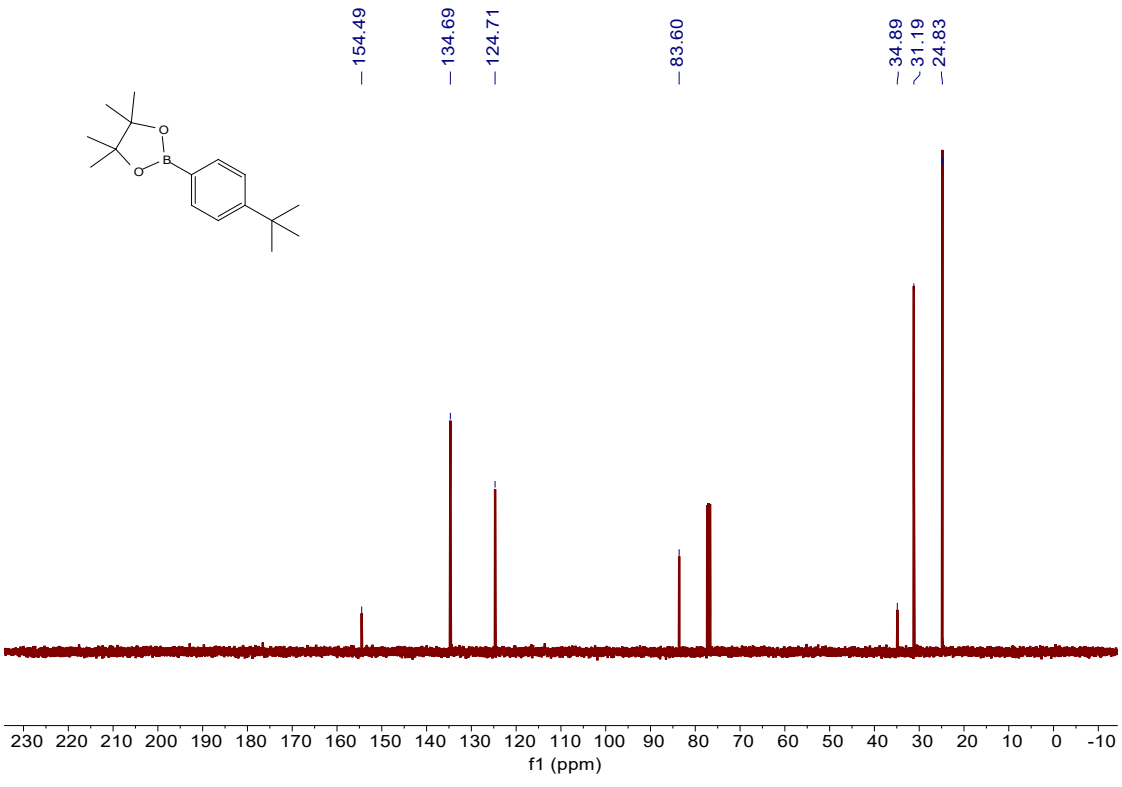

30.67
O
B
O
N
O
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

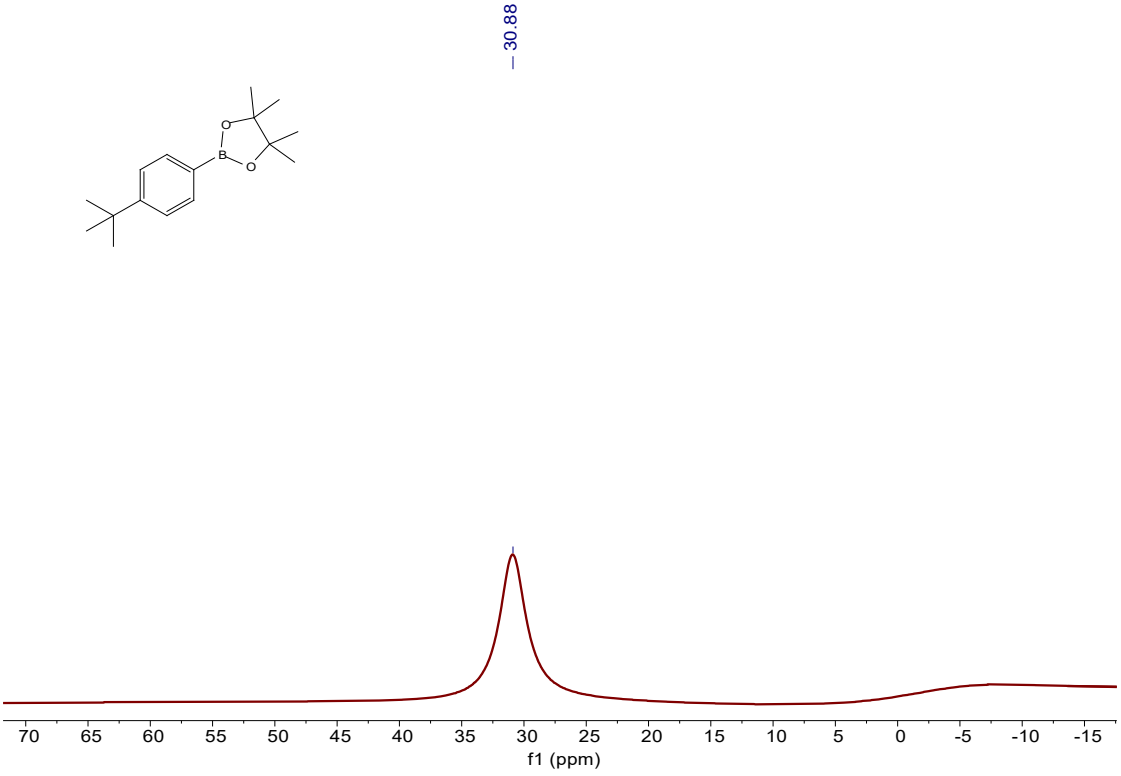

7.73
7.71
6.72
6.70
3.00
1.35
N
B
O
O
1.86
2.00
5.73
11.60
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

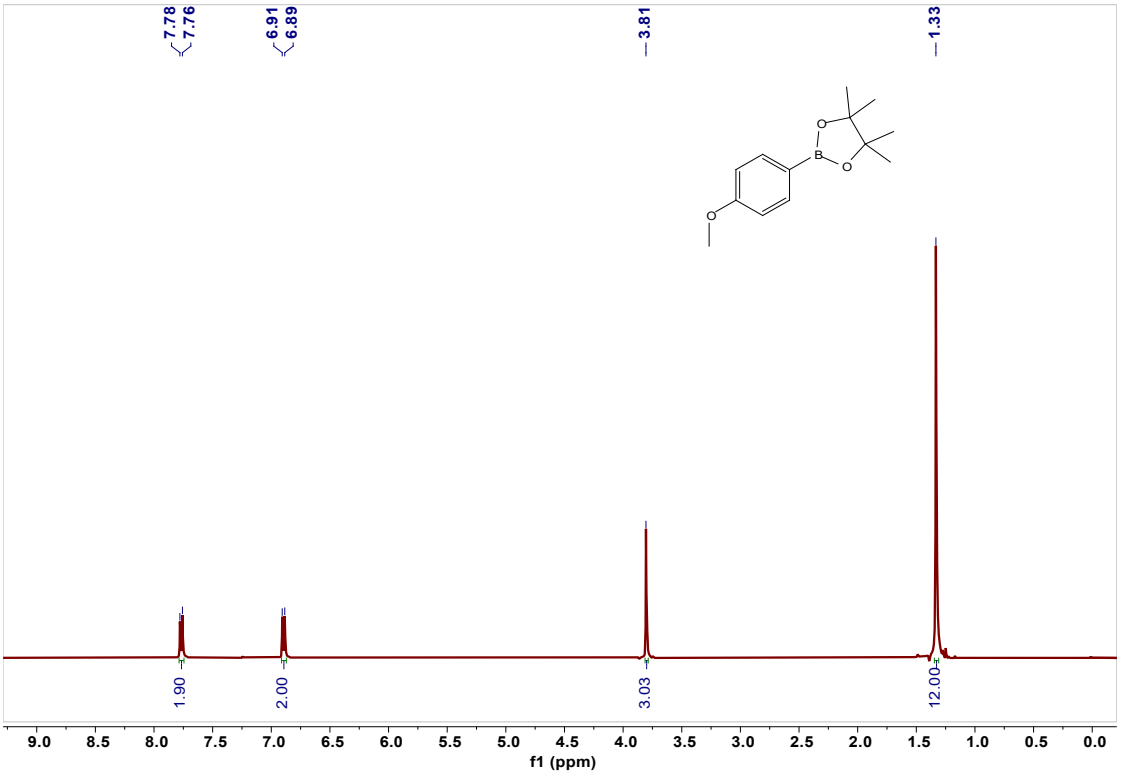

152.54
136.16
111.24
83.17
40.12
24.85
N
B
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

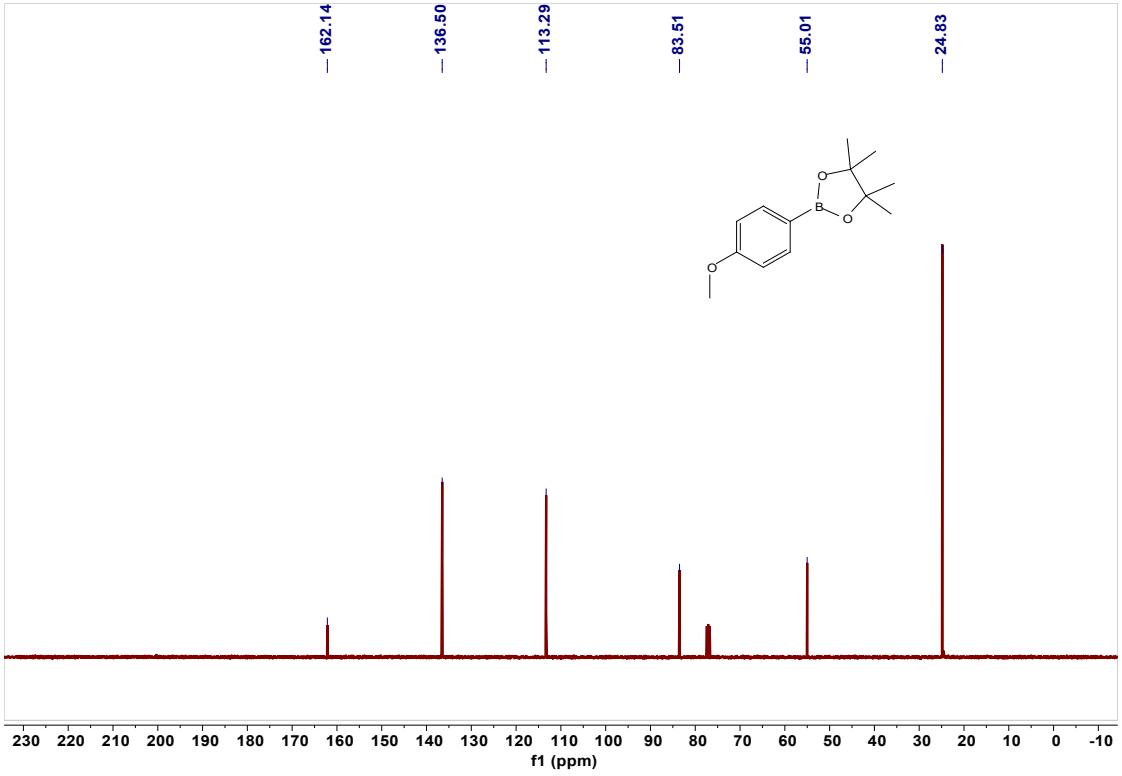

30.98
O
B
O
N
75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30
f1 (ppm)

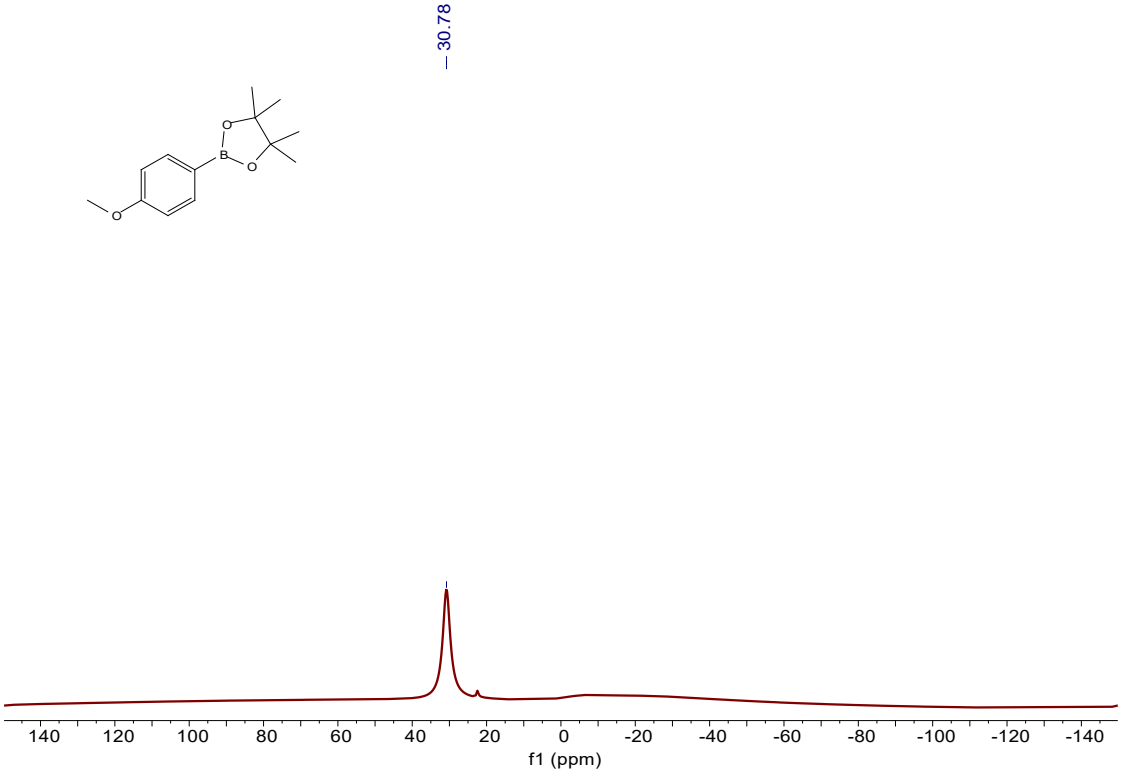

7.79
7.77
7.43
7.41
1.35
1.34
O
B
O
1.93
2.00
11.82
9.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

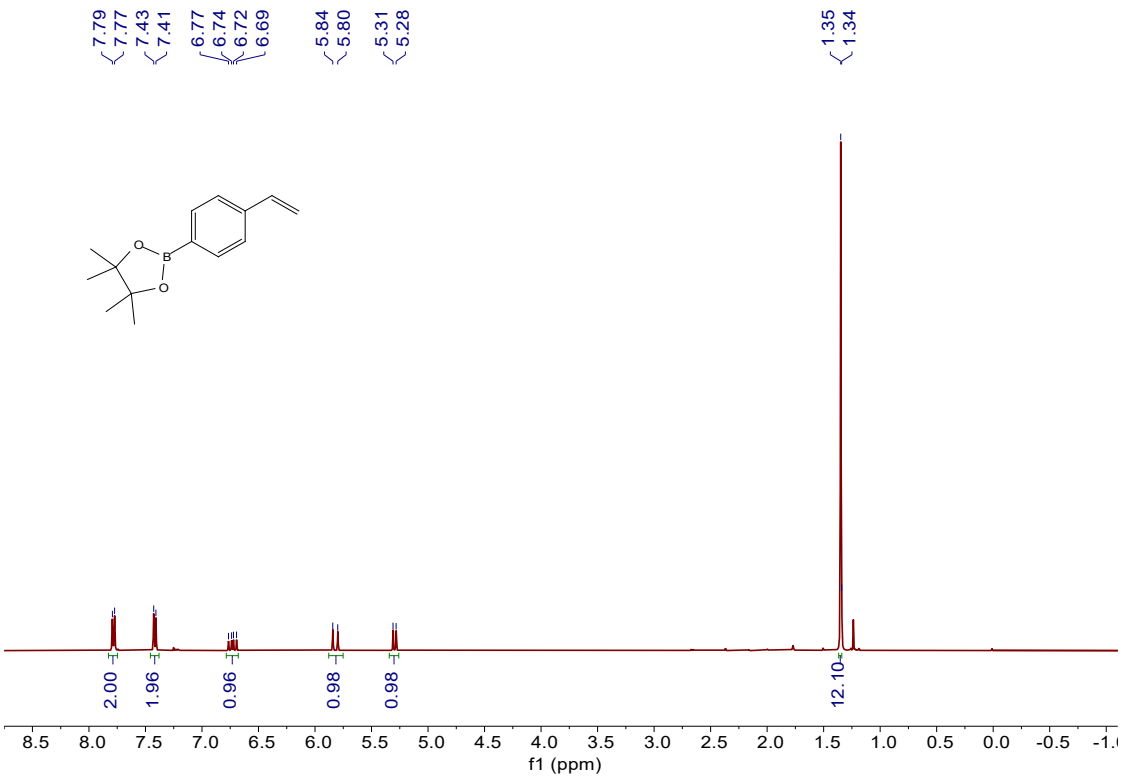

154.49
134.69
124.71
83.60
34.89
31.19
24.83
O
B
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

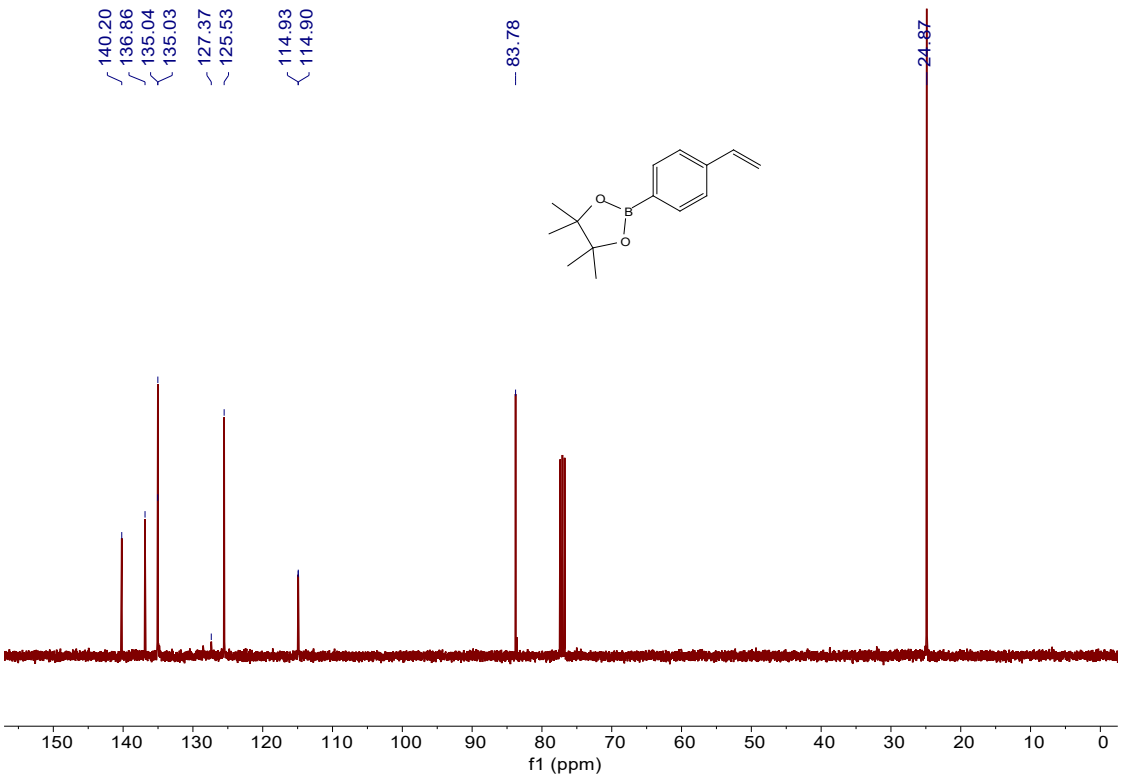

30.88
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

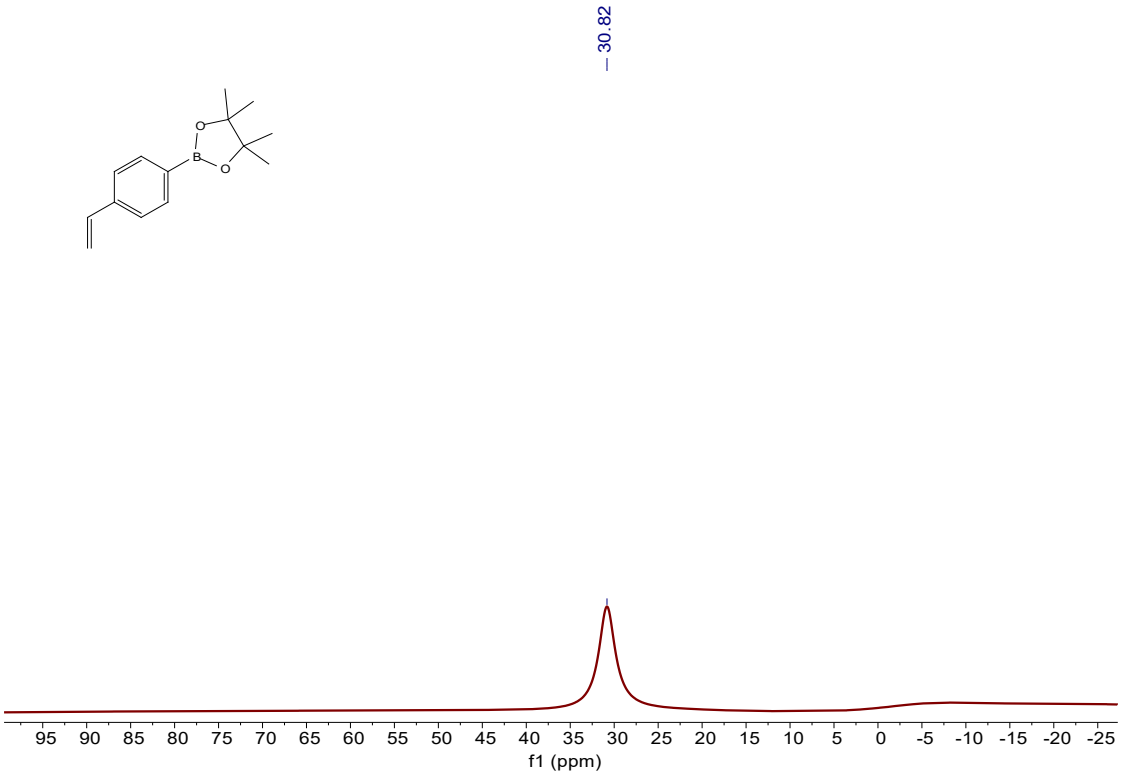

7.78
7.76
6.91
6.89
3.81
1.33
1.90
2.00
3.03
12.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

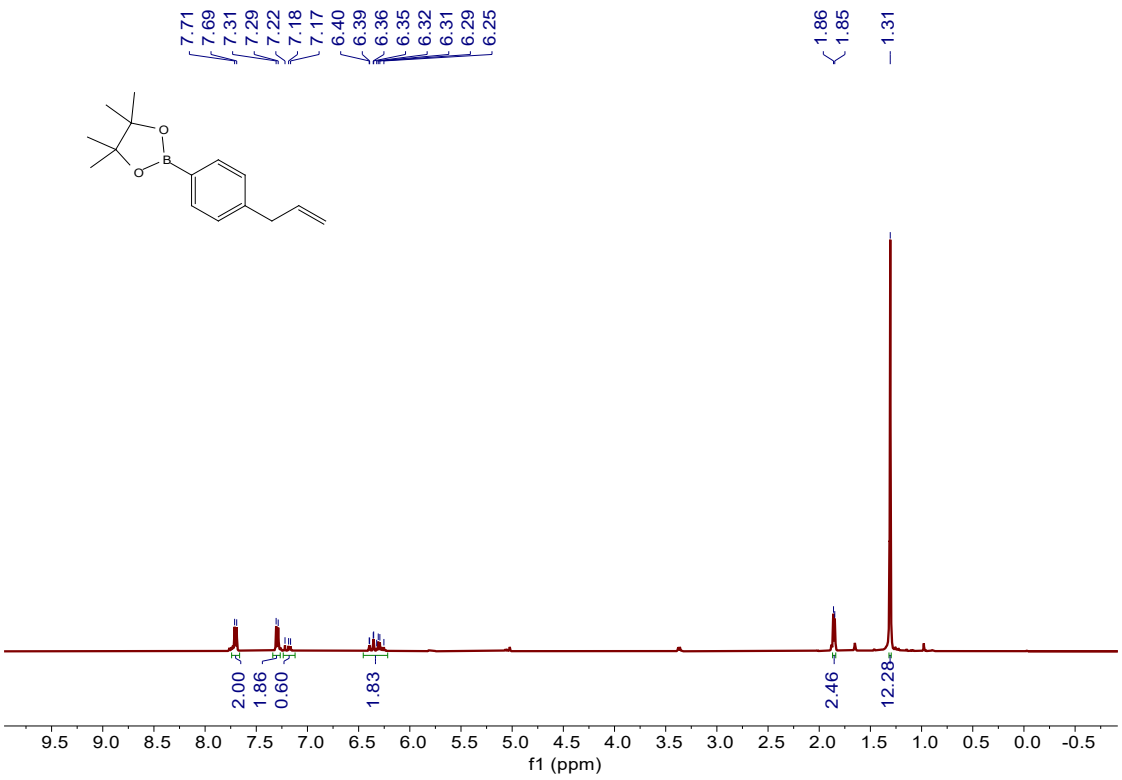

162.14
136.50
113.29
83.51
55.01
24.83
O
B
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

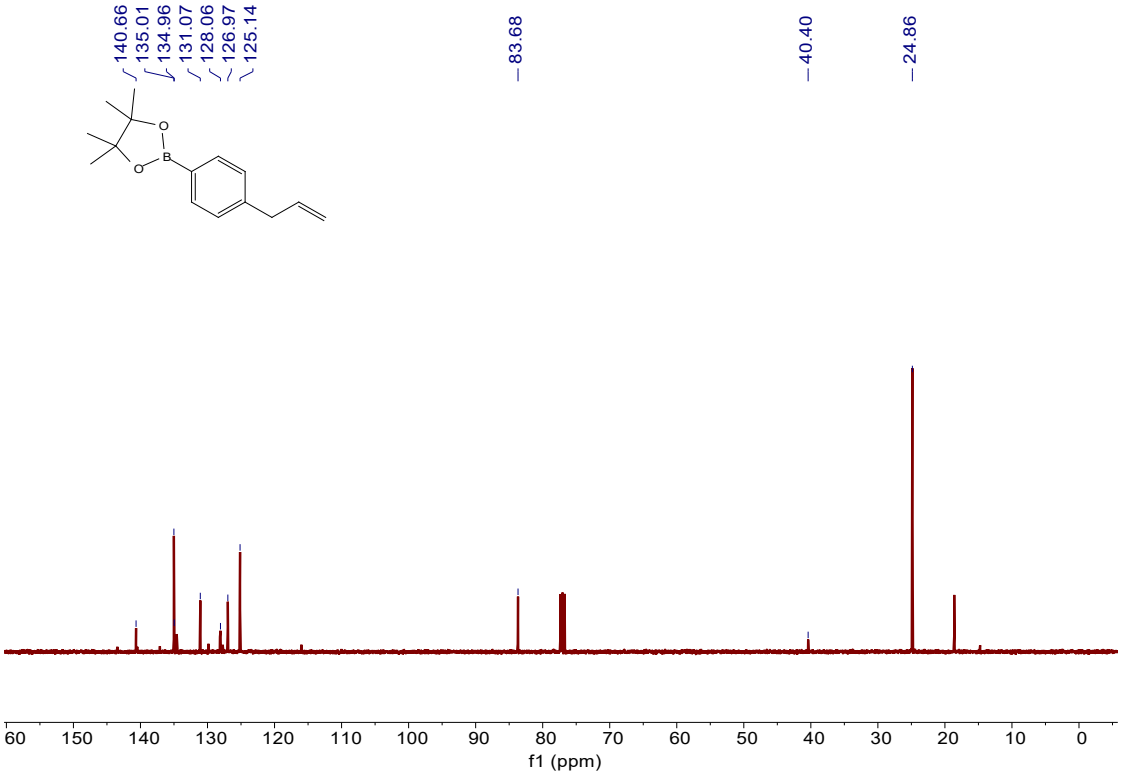

30.78
O
B
O
O
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140
f1 (ppm)

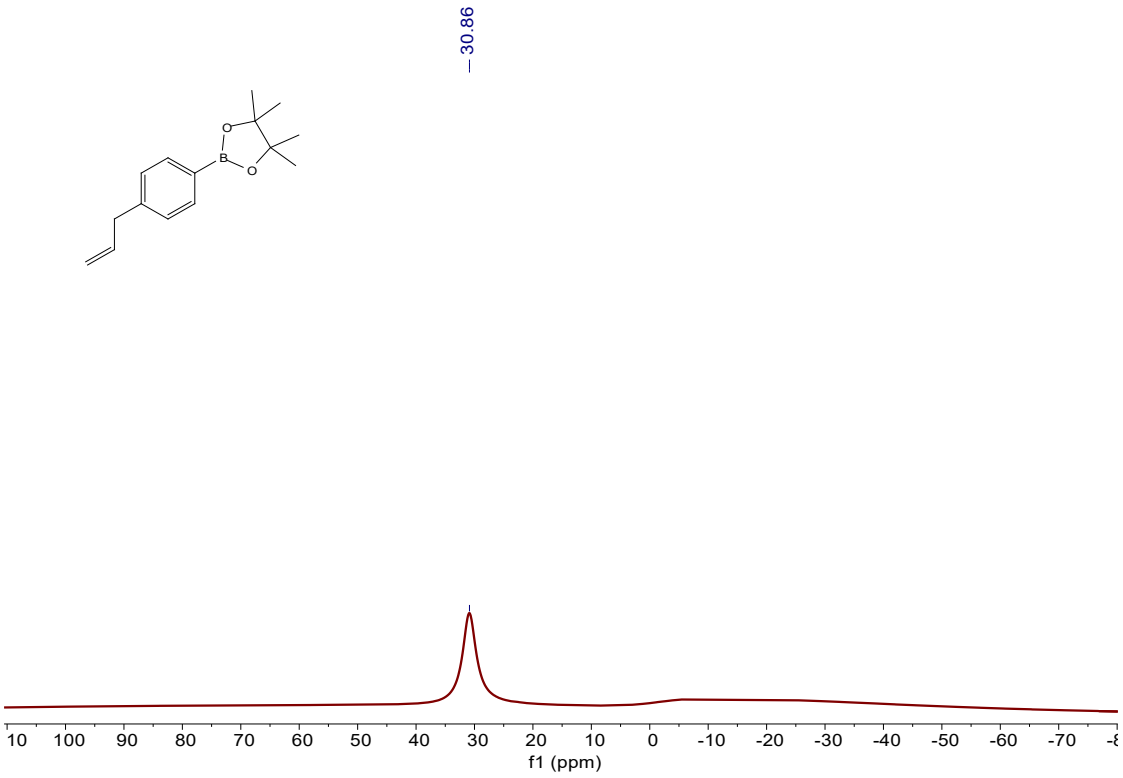

7.79
7.77
7.43
7.41
6.77
6.74
6.72
6.69
5.84
5.80
5.31
5.28
1.35
1.34
O
B
O
2.00
1.96
0.96
0.98
0.98
12.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

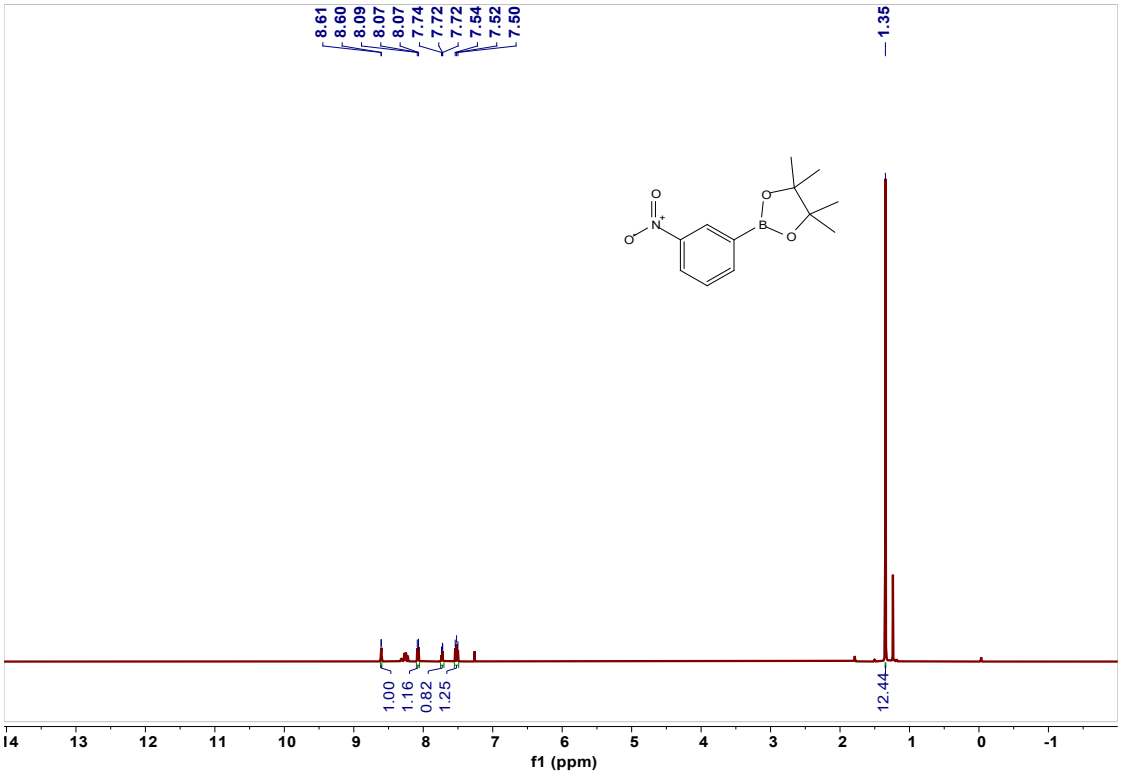

140.20
136.86
135.04
135.03
127.37
125.53
114.93
114.90
83.78
24.87
O
B
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

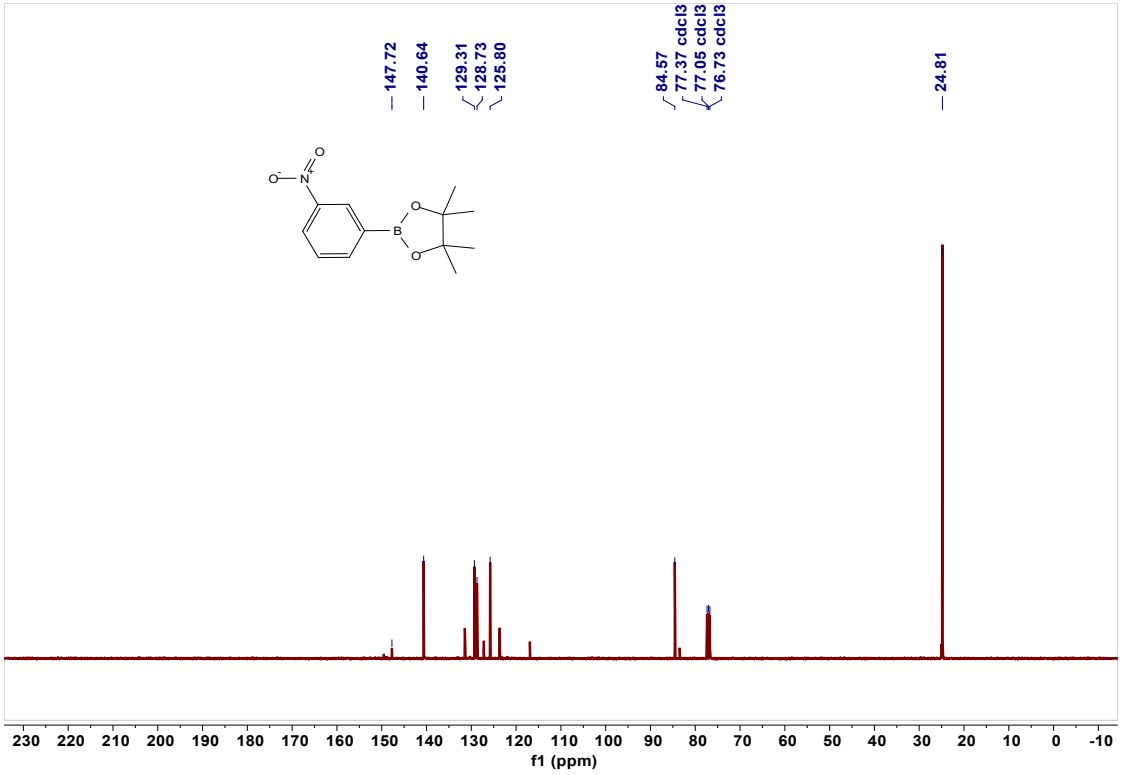

30.82
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25
f1 (ppm)

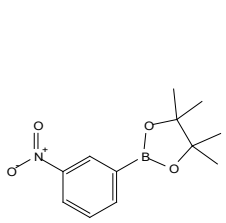

7.71
7.69
7.31
7.29
7.22
7.18
7.17
6.40
6.39
6.36
6.35
6.32
6.31
6.29
6.25
1.86
1.85
1.31
2.00
1.86
0.60
1.83
2.46
12.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


140.66
135.01
134.96
131.07
128.06
126.97
125.14
83.68
40.40
24.86
O
B
O
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

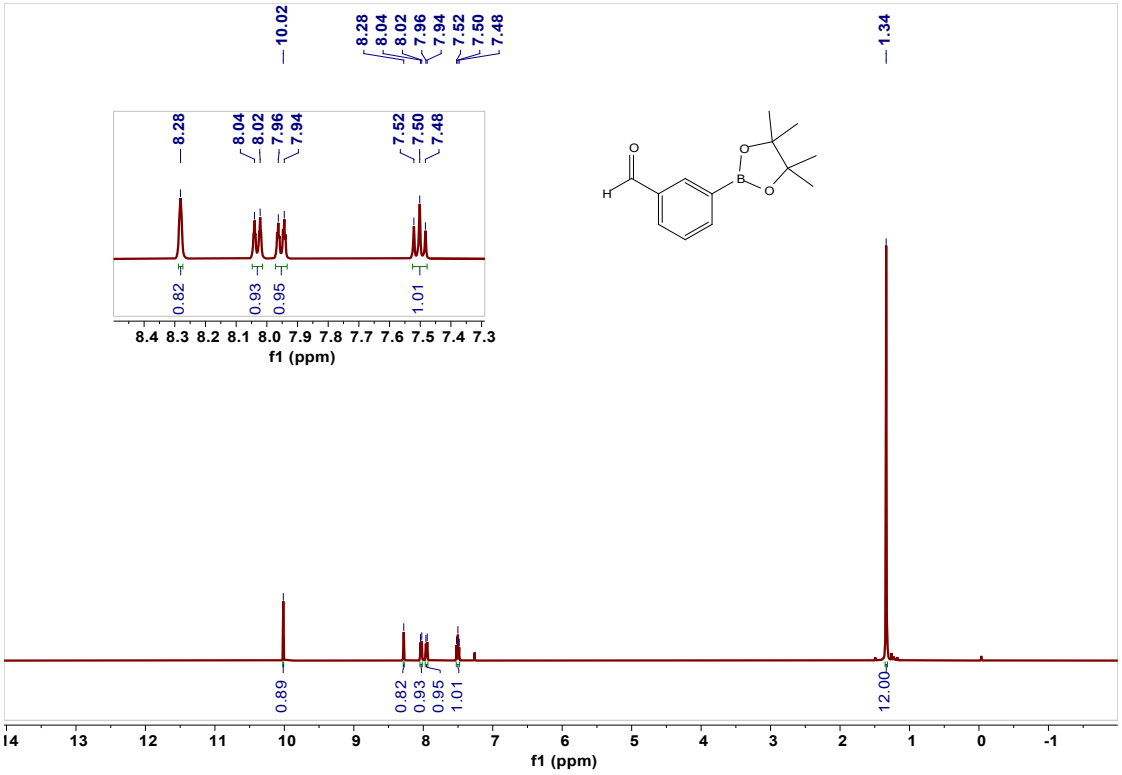

30.86
O
B
O
10 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

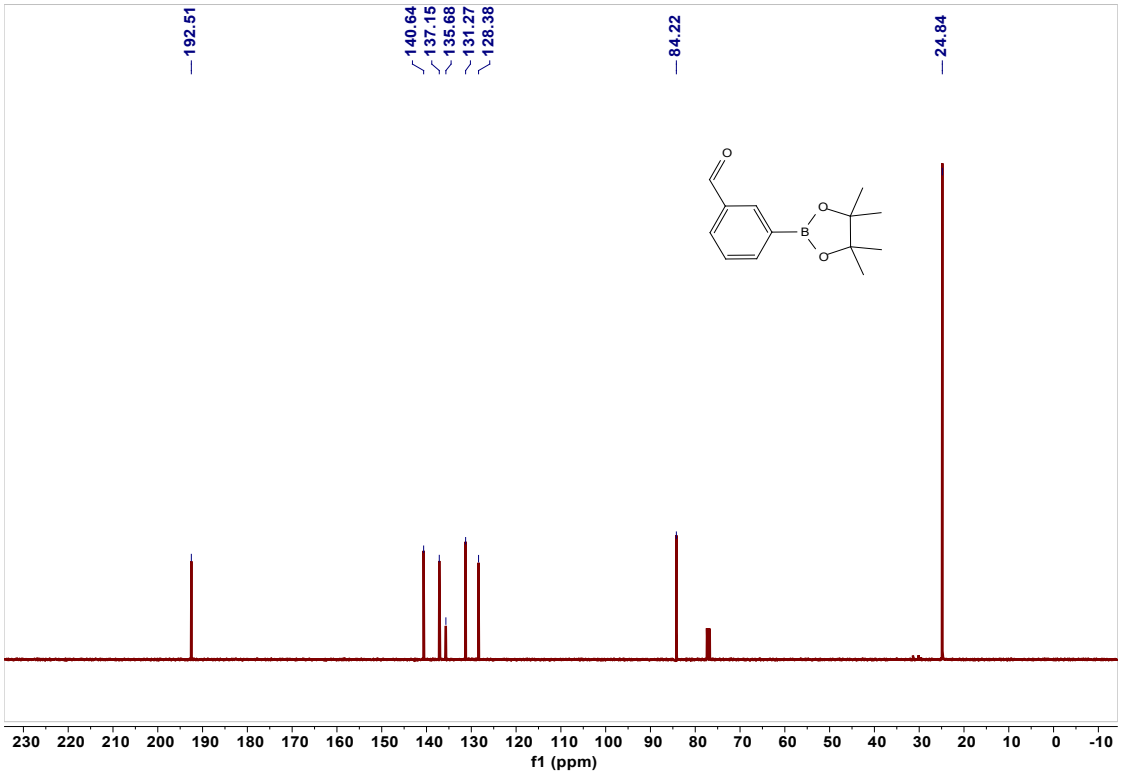

8.61
8.60
8.09
8.07
8.07
7.74
7.72
7.72
7.54
7.52
7.50
1.35
1.00
1.16
0.82
1.25
12.44
f1 (ppm)

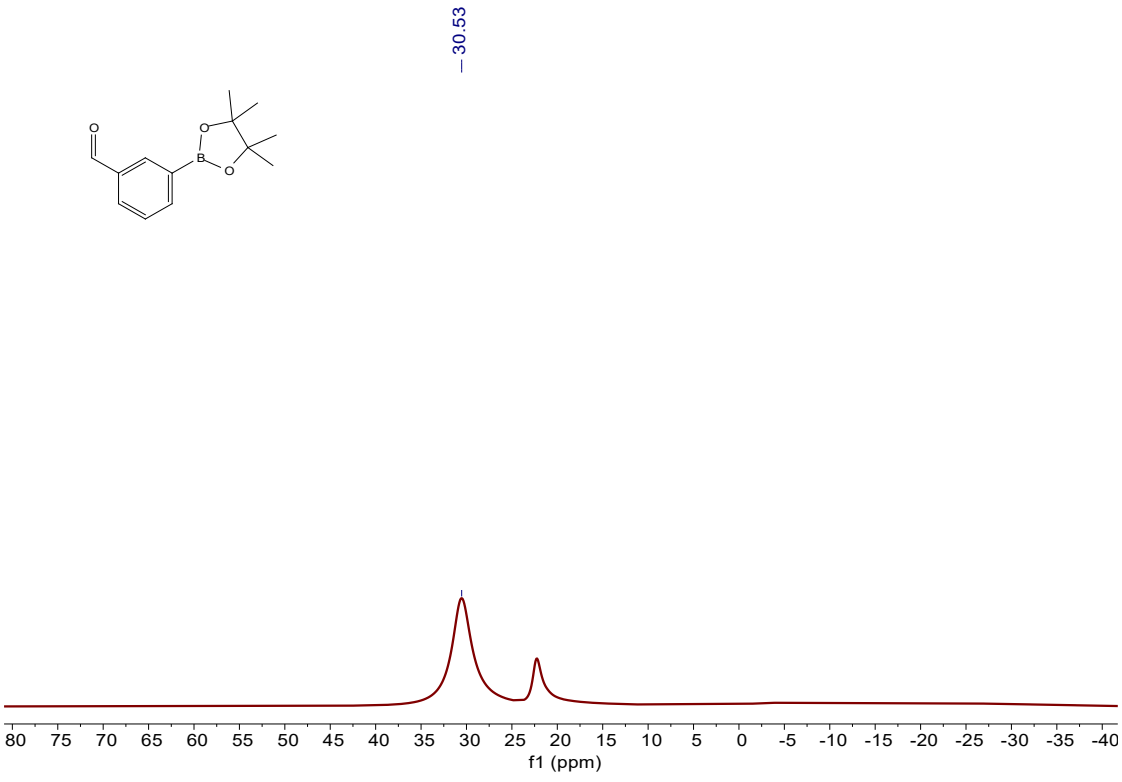

147.72
140.64
129.31
128.73
125.80
84.57
77.37 cdcl3
77.05 cdcl3
76.73 cdcl3
24.81
f1 (ppm)

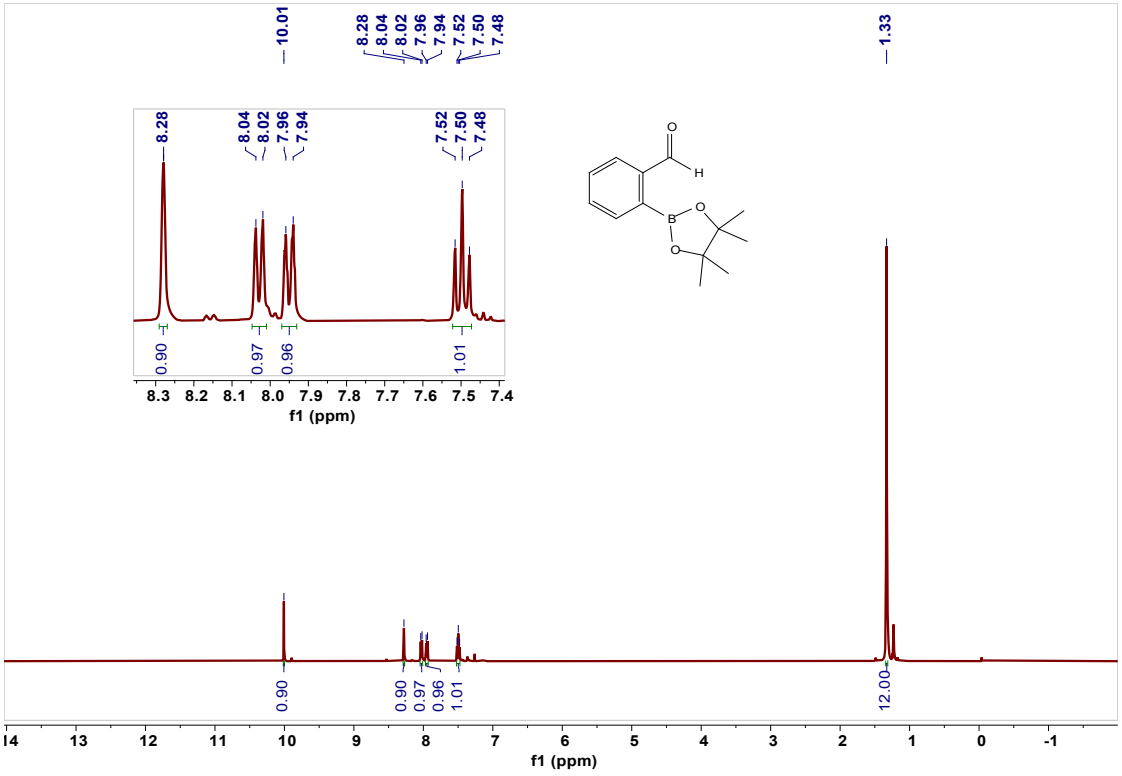


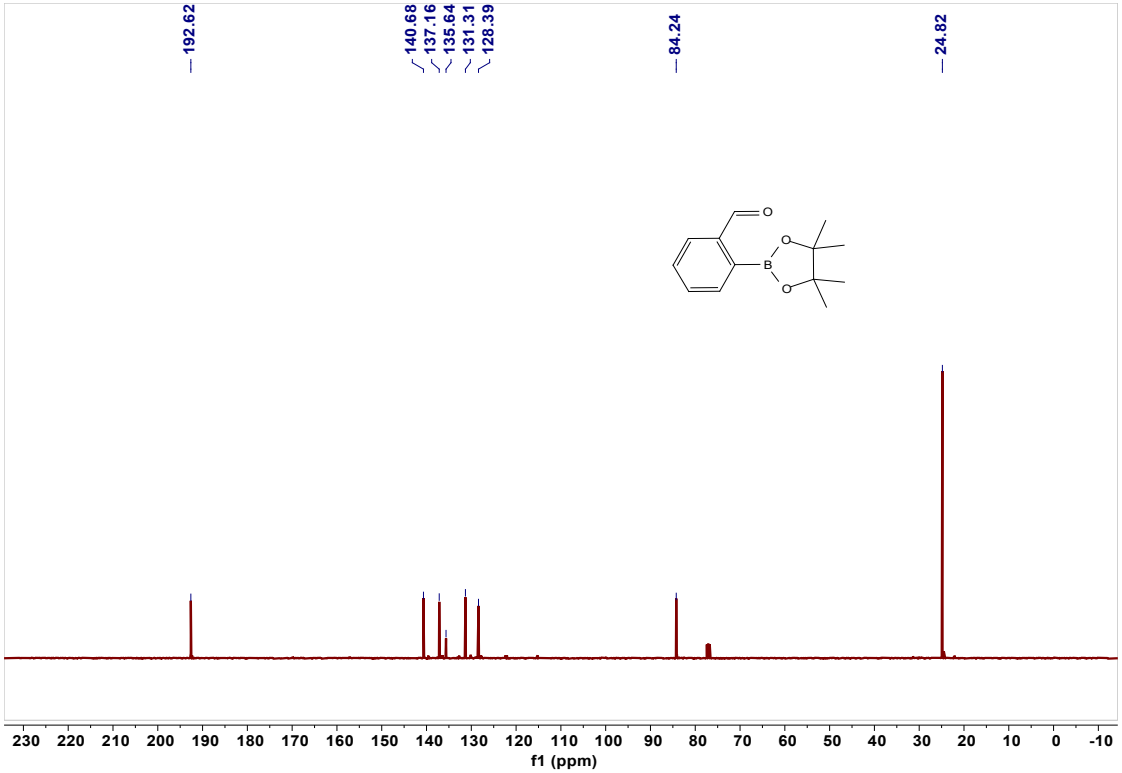
30.38
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10
f1 (ppm)

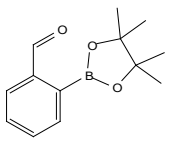

10.02
8.28
8.04
8.02
7.96
7.94
7.52
7.50
7.48
1.34
0.82
0.93
0.95
1.01
8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
f1 (ppm)
0.89
0.82
0.93
0.95
1.01
12.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


192.51
140.64
137.15
135.68
131.27
128.38
84.22
24.84
O
O
B
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

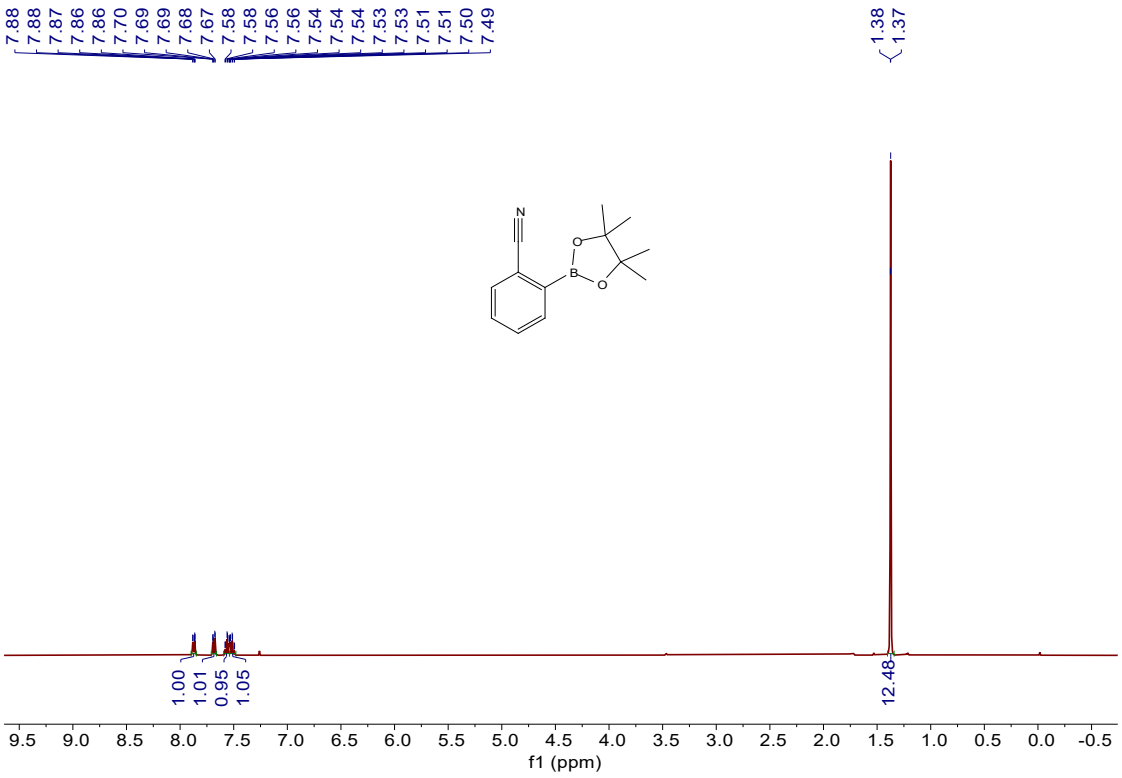

30.53
O
O
B
O
80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)

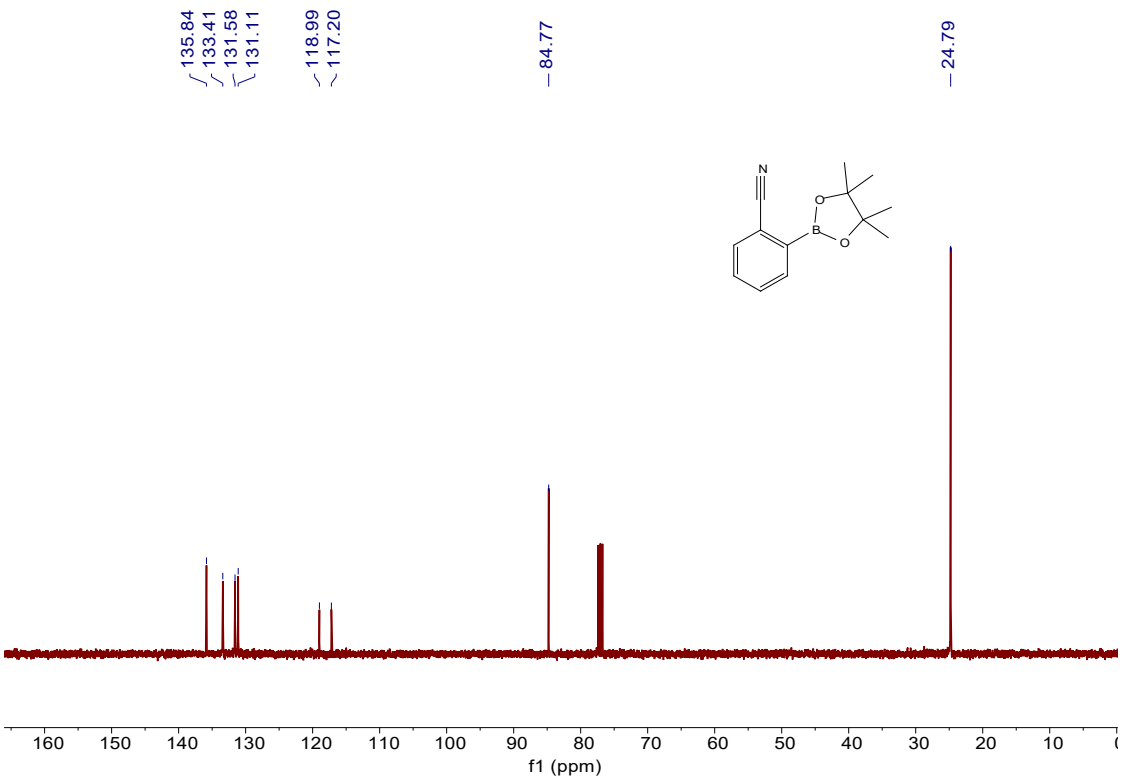

10.01
8.28
8.04
8.02
7.96
7.94
7.52
7.50
7.48
1.33
0.90
0.97
0.96
1.01
12.00
f1 (ppm)

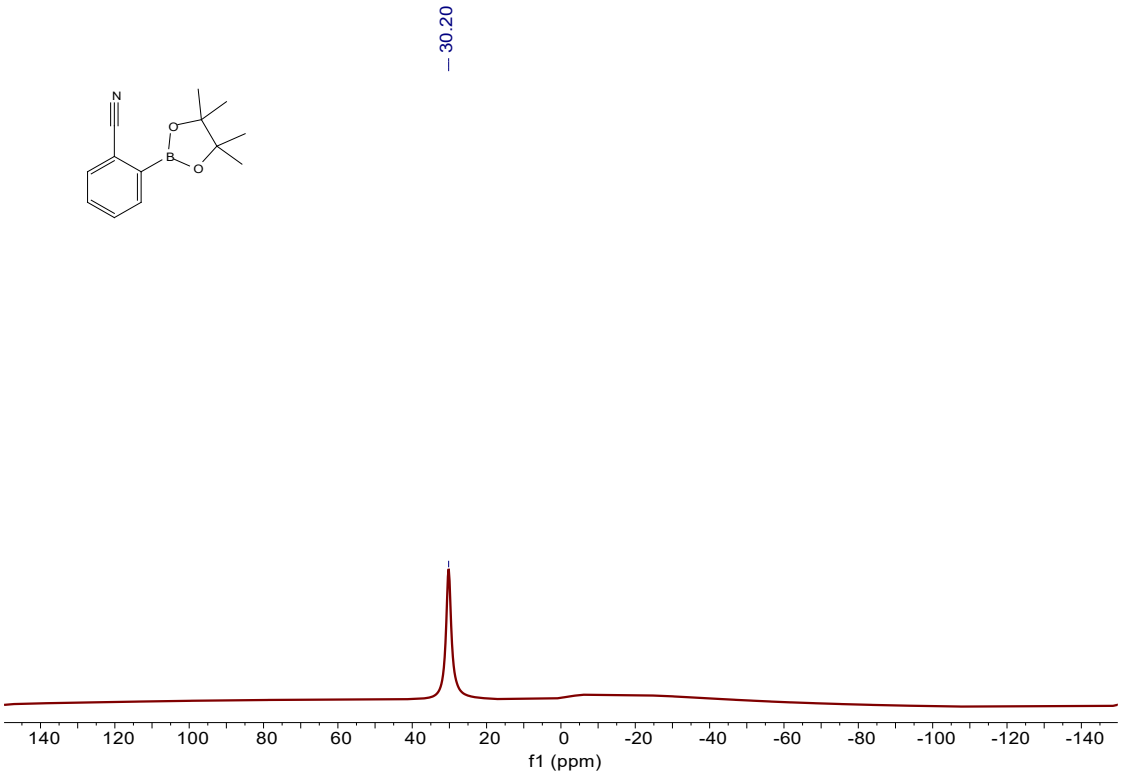

192.62
140.68
137.16
135.64
131.31
128.39
84.24
24.82
f1 (ppm)

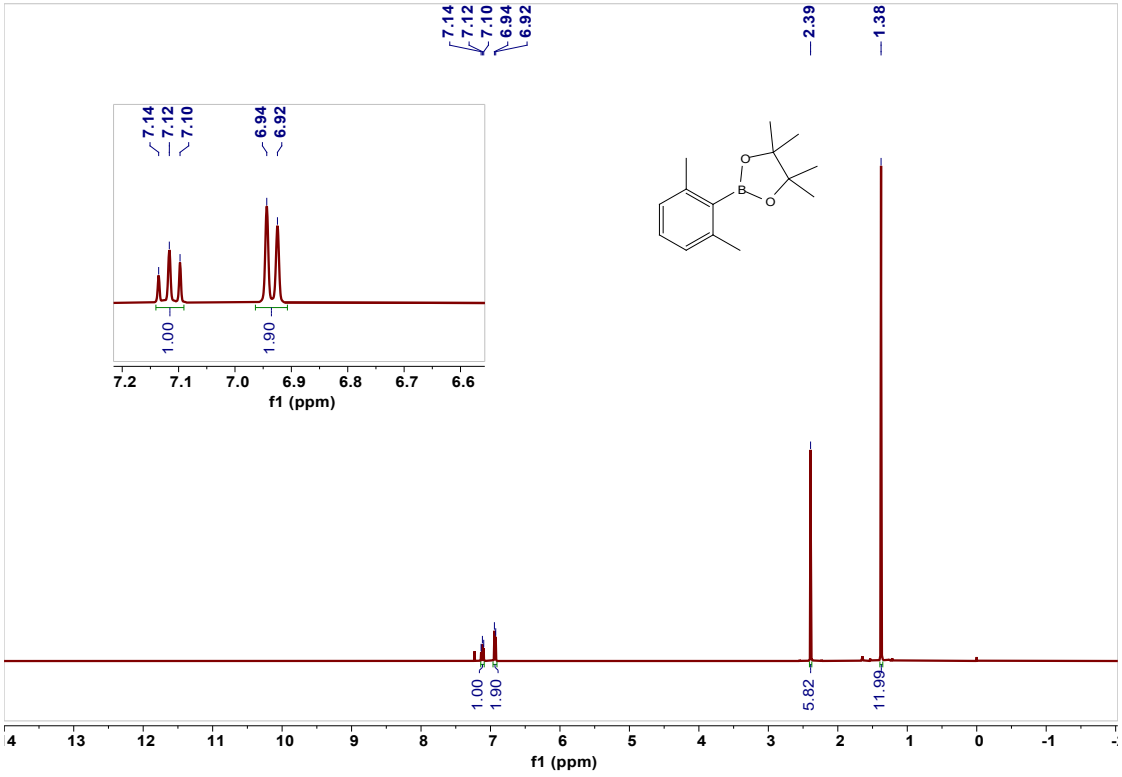

O
O
B
O

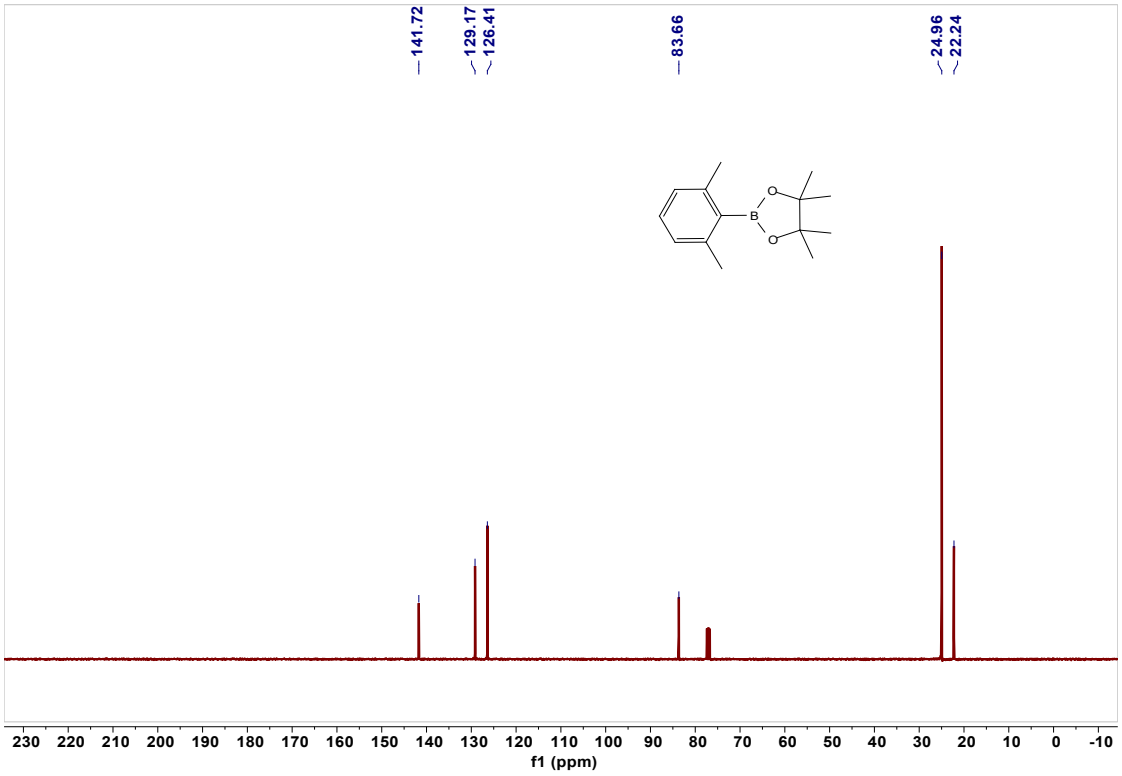
31.11
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
-10
f1 (ppm)

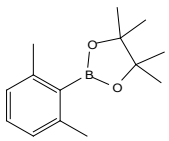

7.88
7.88
7.87
7.86
7.86
7.70
7.69
7.69
7.68
7.67
7.58
7.58
7.56
7.56
7.54
7.54
7.54
7.53
7.53
7.51
7.51
7.50
7.49
1.38
1.37
N
O
B
O
1.00
1.01
0.95
1.05
12.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


135.84
133.41
131.58
131.11
118.99
117.20
84.77
24.79
N
O
B
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

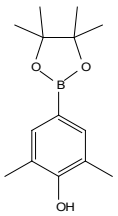

30.20
N
O
B
O
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)


7.14
7.12
7.10
6.94
6.92
2.39
1.38
1.00
1.90
5.82
11.99
f1 (ppm)

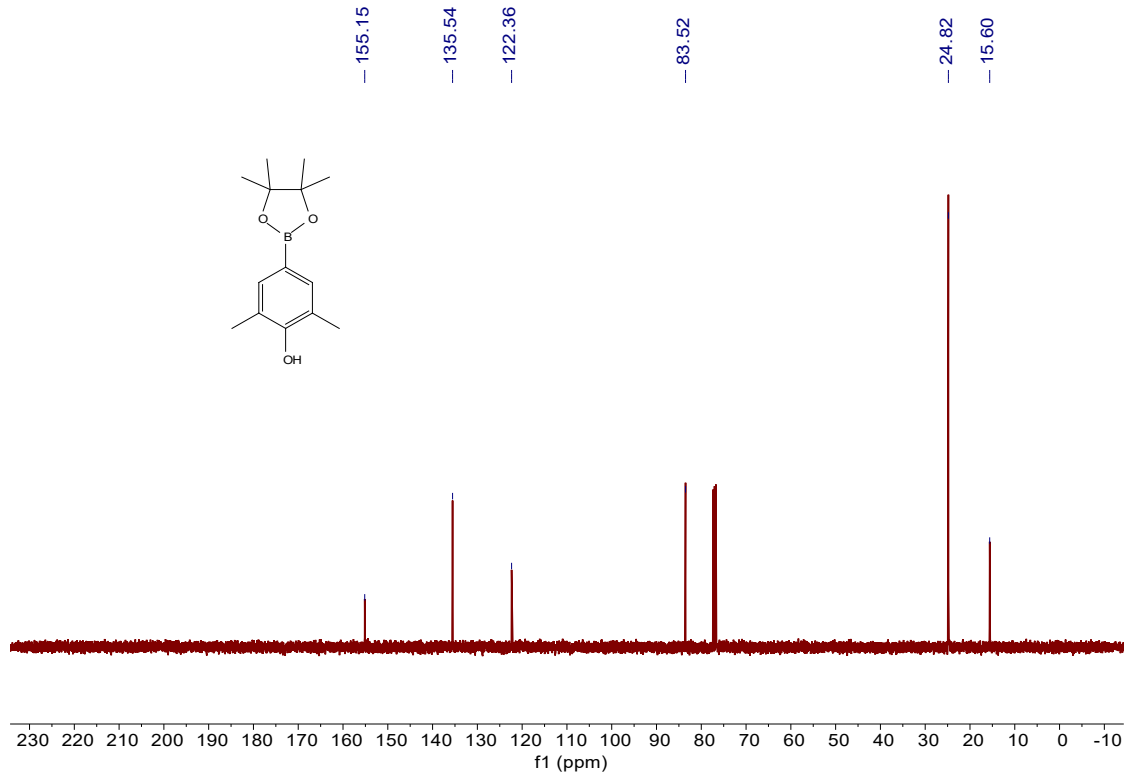

141.72
129.17
126.41
83.66
24.96
22.24
f1 (ppm)

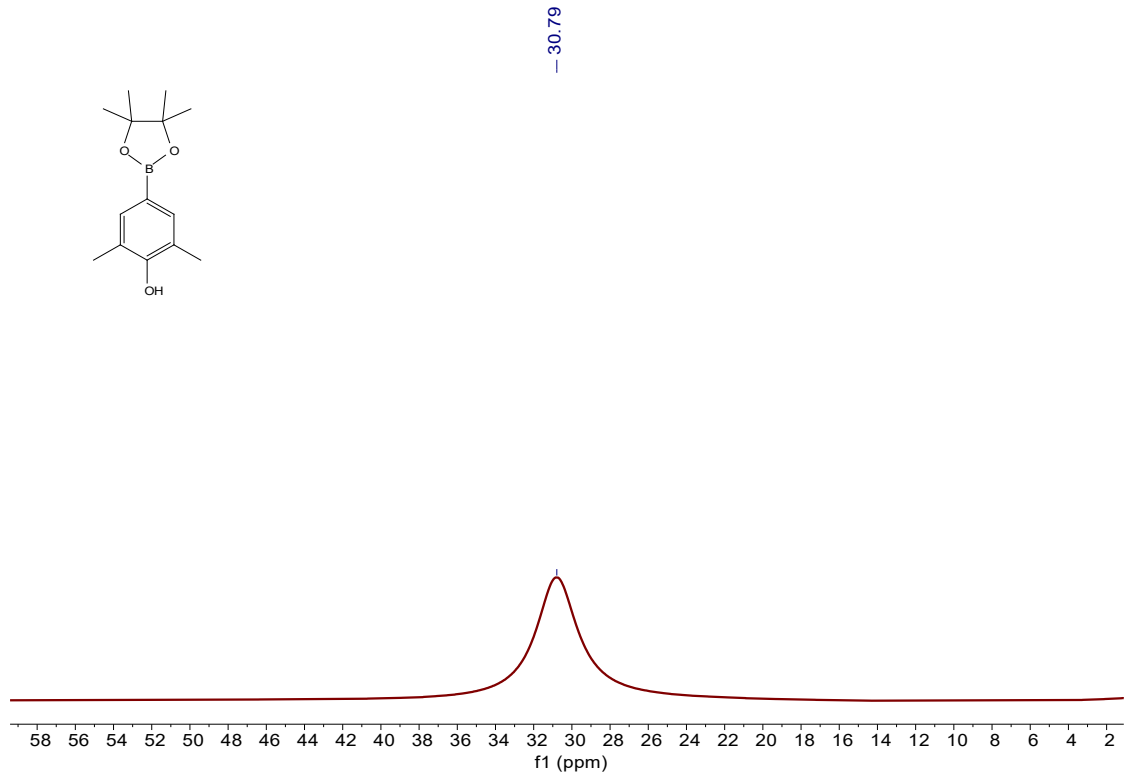

O
B
O

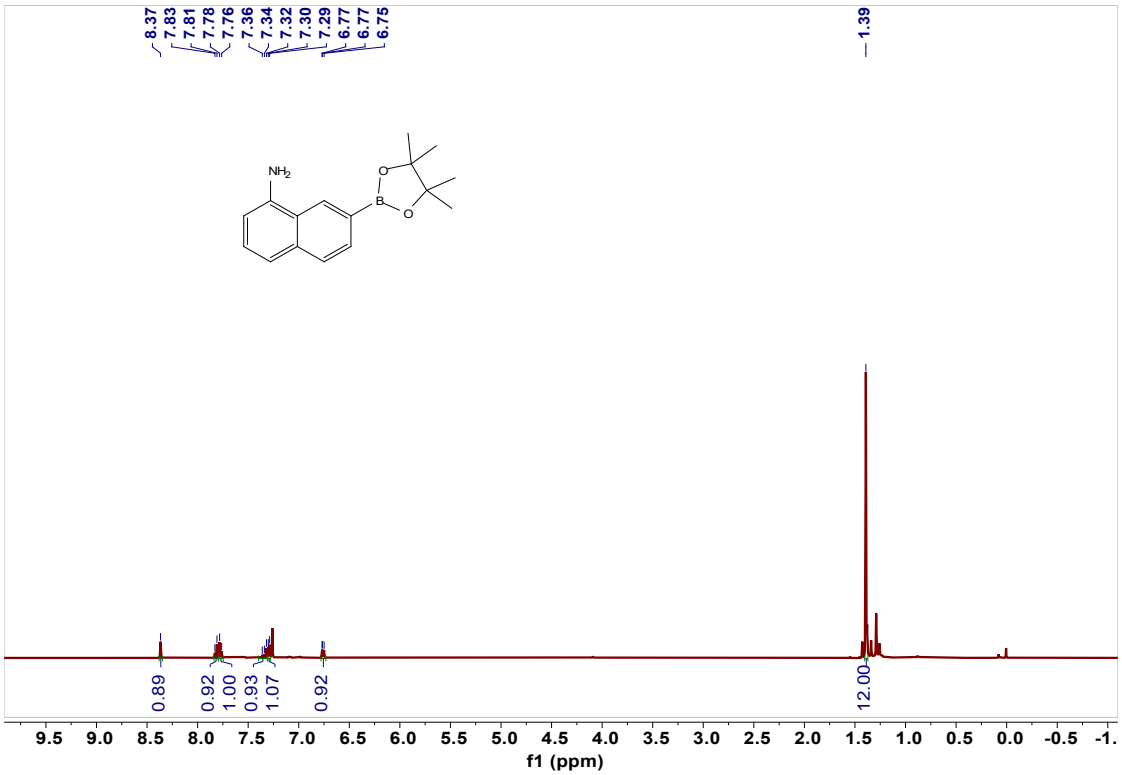
30.73
66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

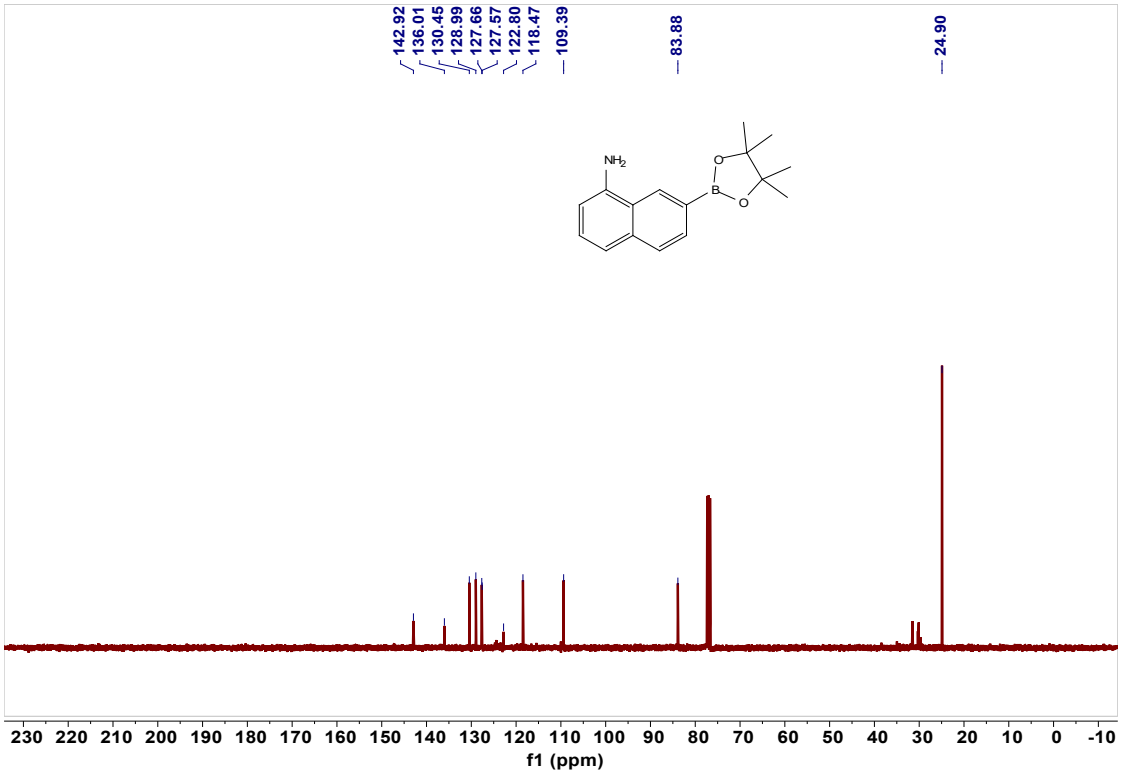

O
O
B
OH

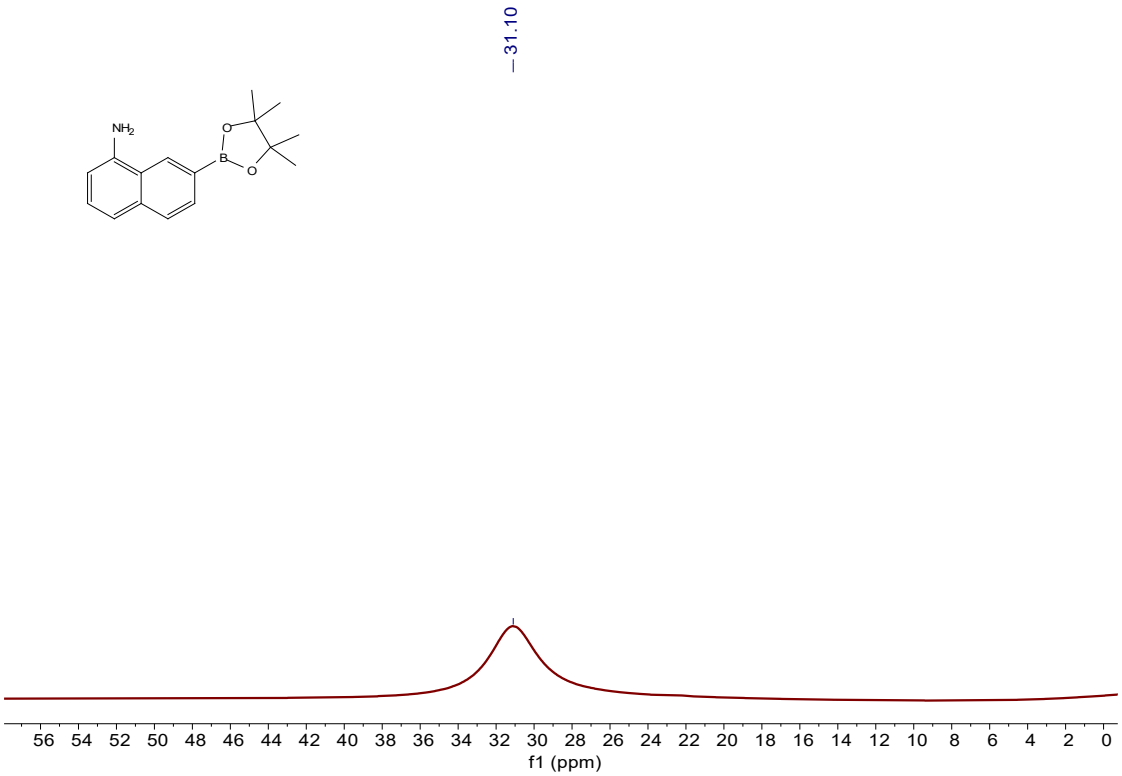
7.46
2.24
1.34
2.00
6.31
12.45
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

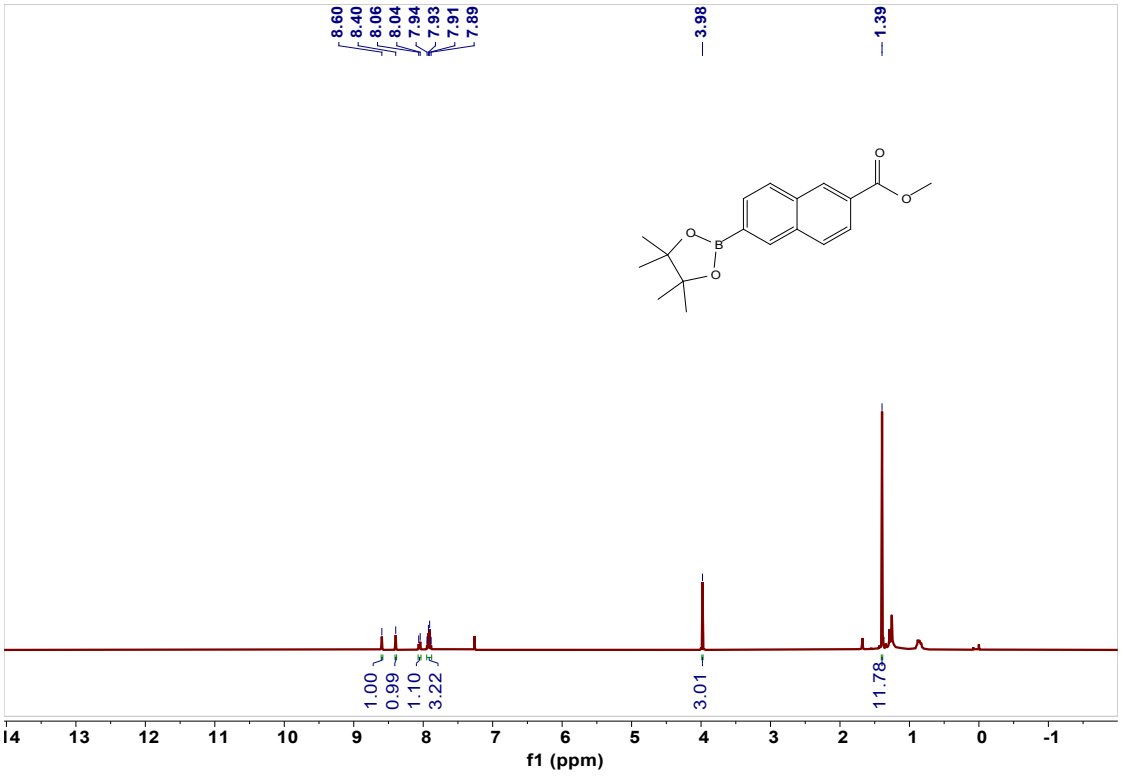

155.15
135.54
122.36
83.52
24.82
15.60
O
O
B
OH
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

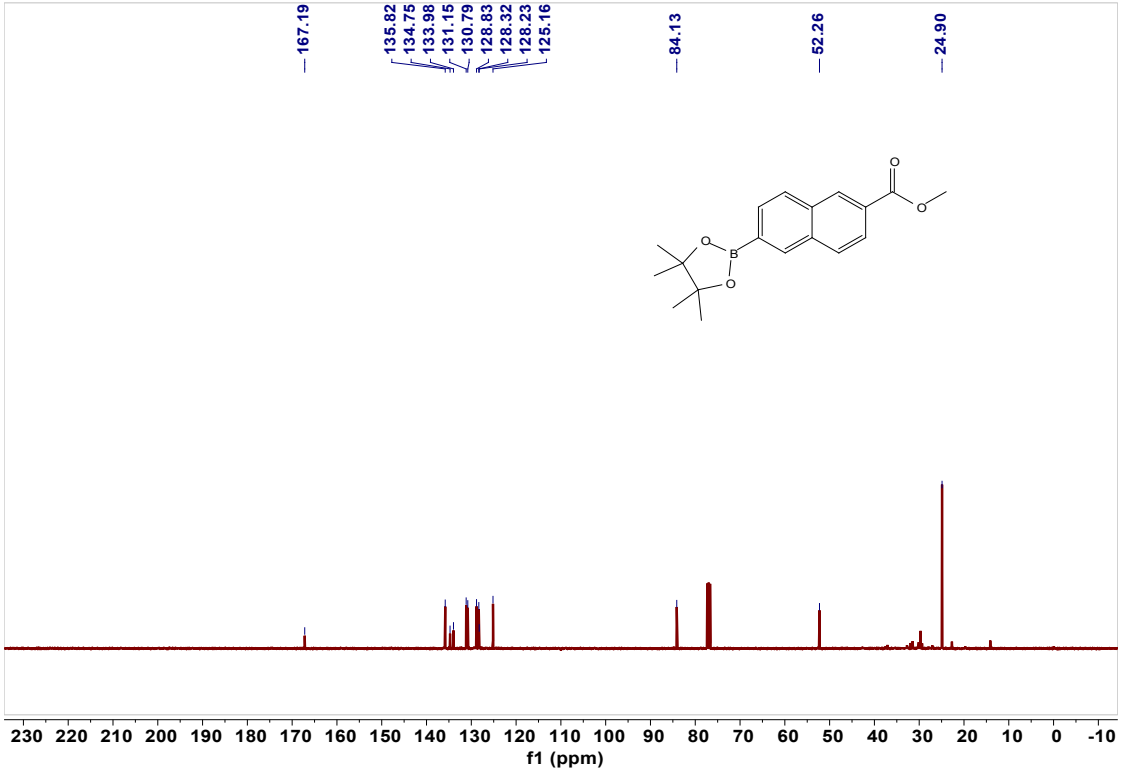

30.79
O
O
B
OH
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

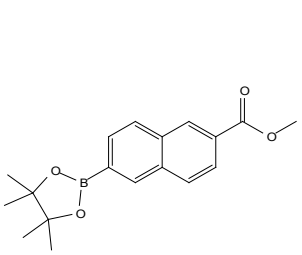

8.37
7.83
7.81
7.78
7.76
7.36
7.34
7.32
7.30
7.29
6.77
6.77
6.75
1.39
NH2
O
B
O
0.89
0.92
1.00
0.93
1.07
0.92
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


142.92
136.01
130.45
128.99
127.66
127.57
122.80
118.47
109.39
83.88
24.90
NH2
O
B
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

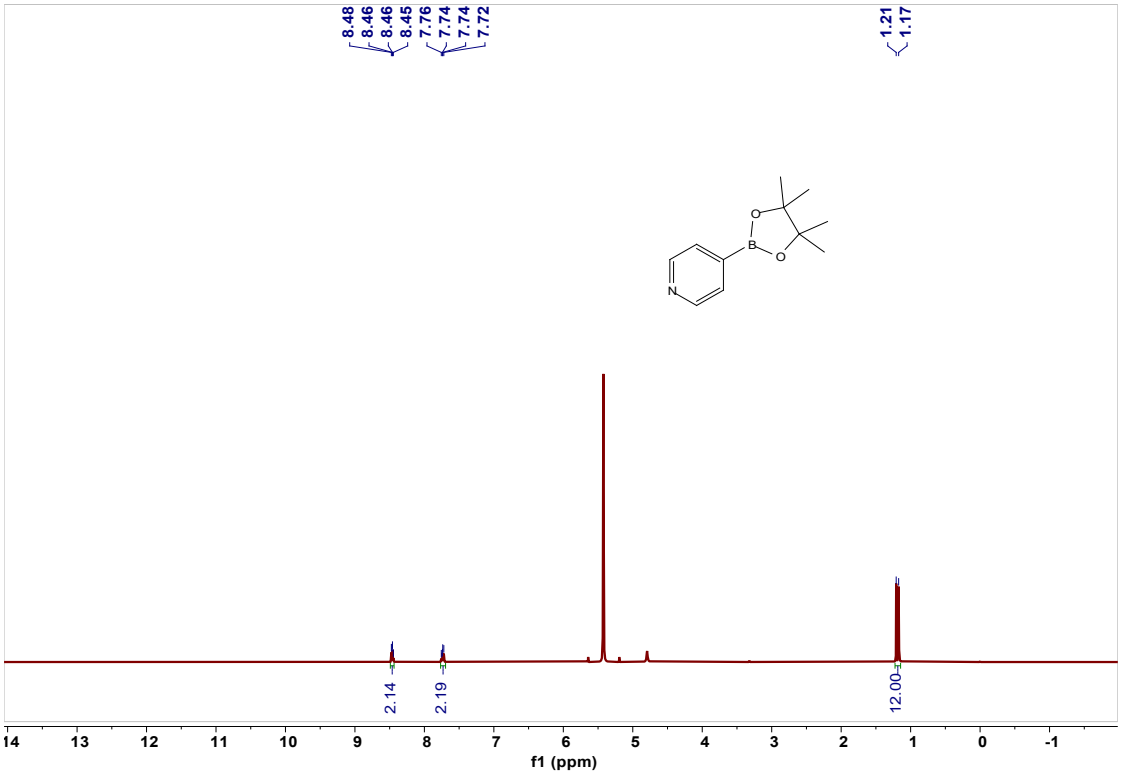

31.10
NH2
O
B
O
56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)

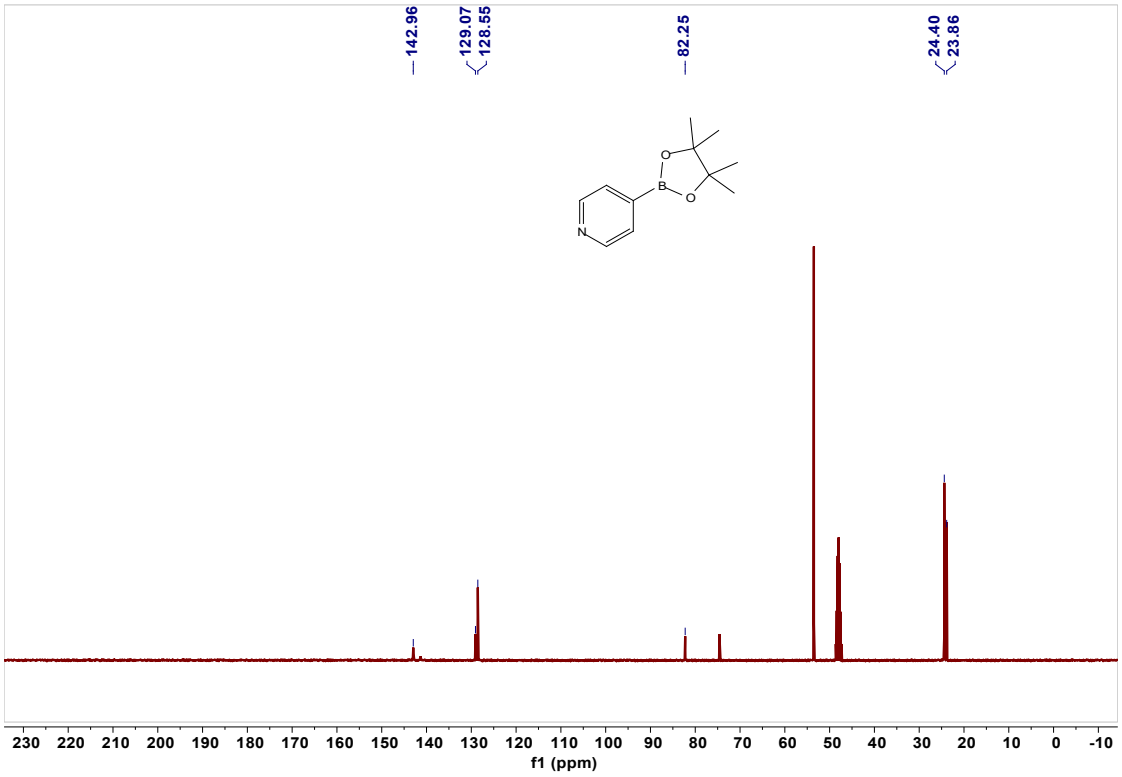

8.60
8.40
8.06
8.04
7.94
7.93
7.91
7.89
3.98
1.39
1.00
0.99
1.10
3.22
3.01
11.78
f1 (ppm)

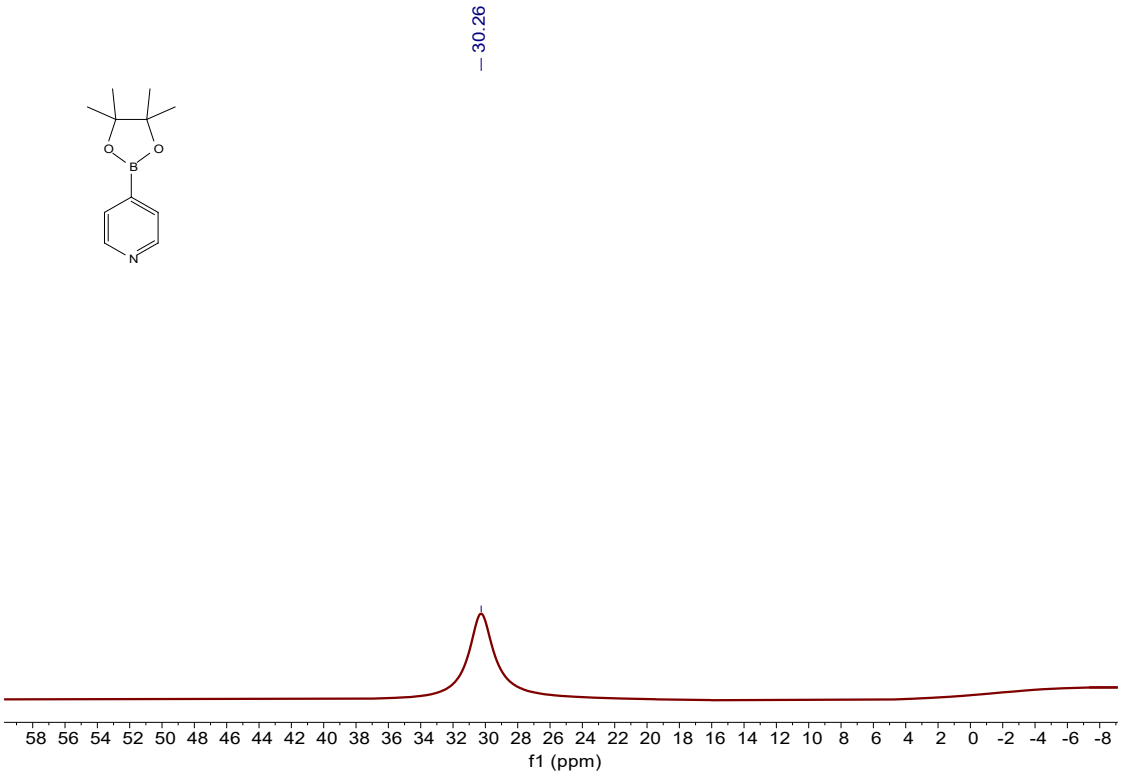

167.19
135.82
134.75
133.98
131.15
130.79
128.83
128.32
128.23
125.16
84.13
52.26
24.90
f1 (ppm)

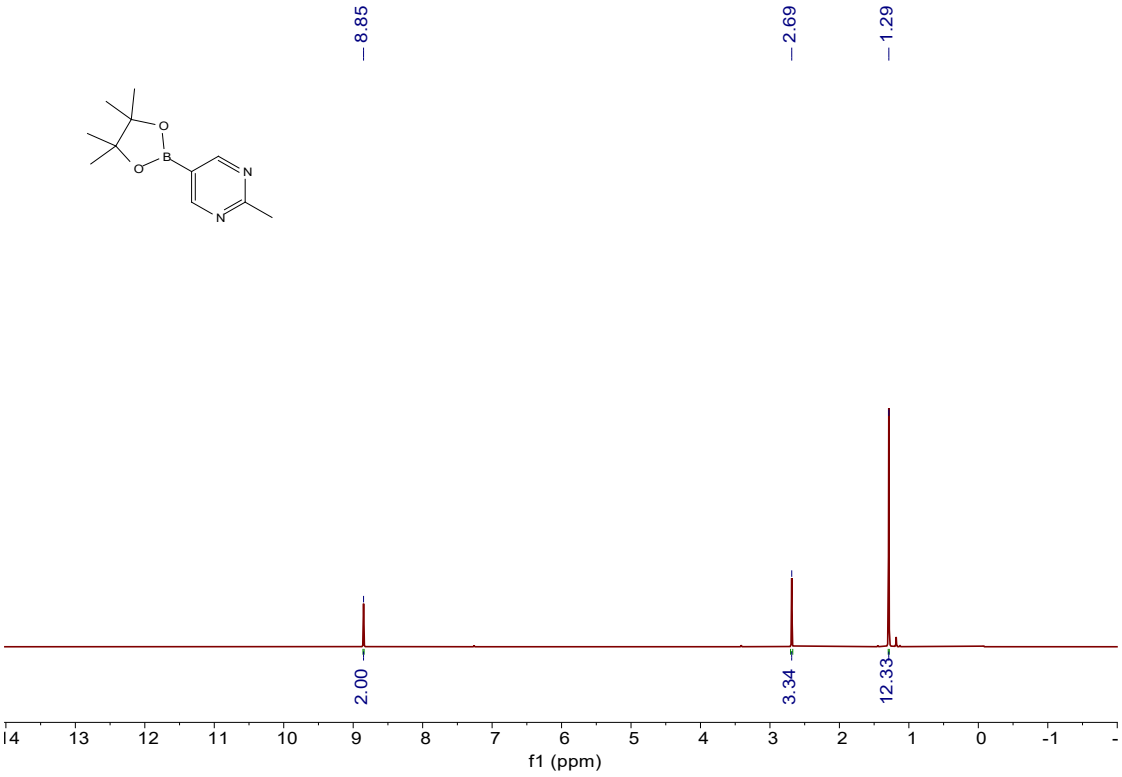

O
O
B
O
O

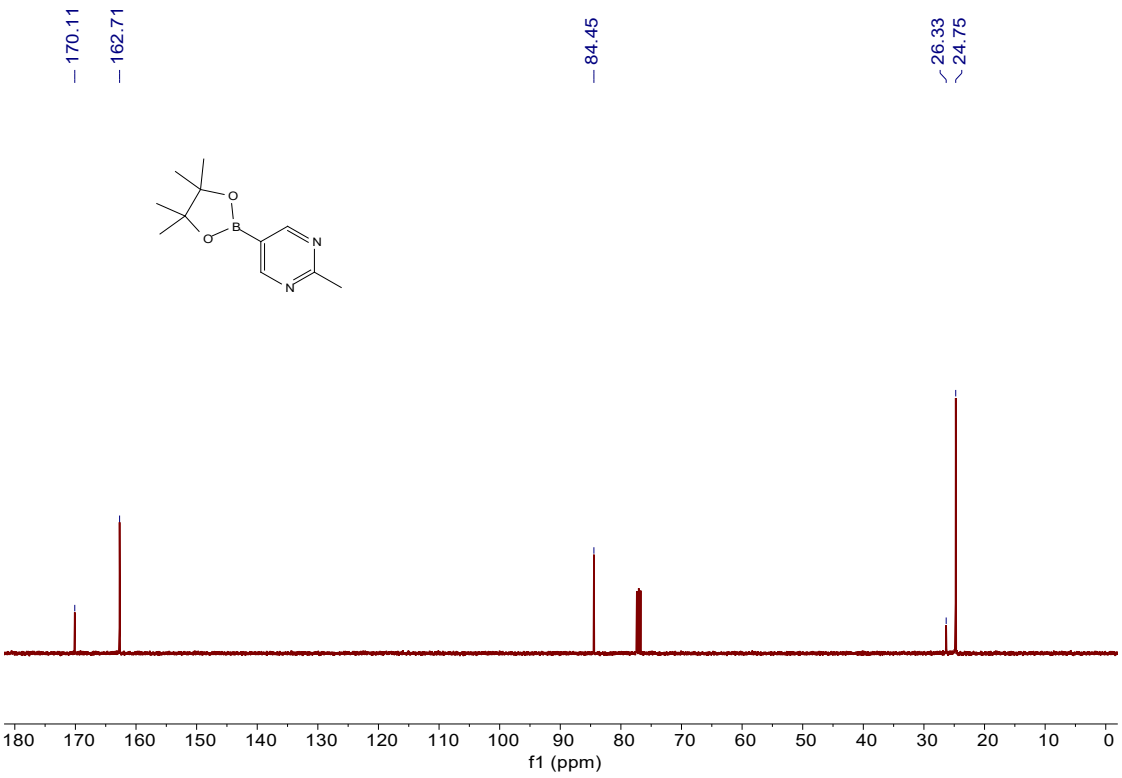
30.68
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

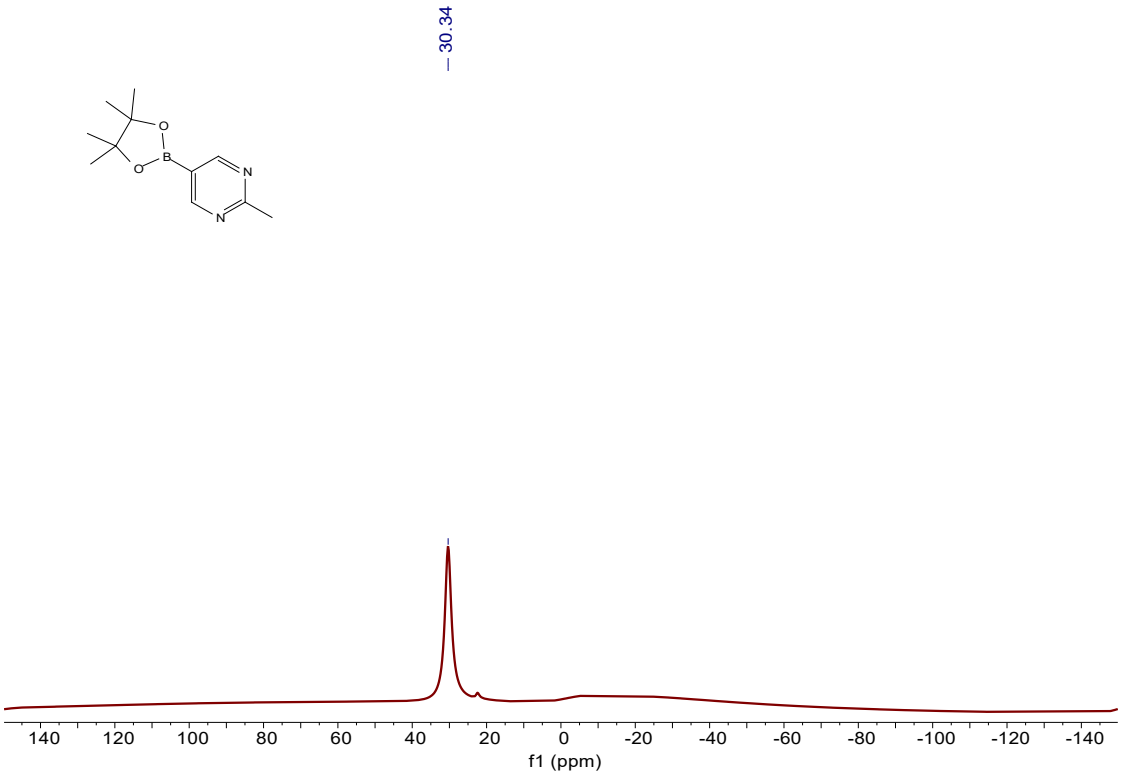

8.48
8.46
8.46
8.45
7.76
7.74
7.74
7.72
1.21
1.17
O
O
B
O
N
2.14
2.19
12.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

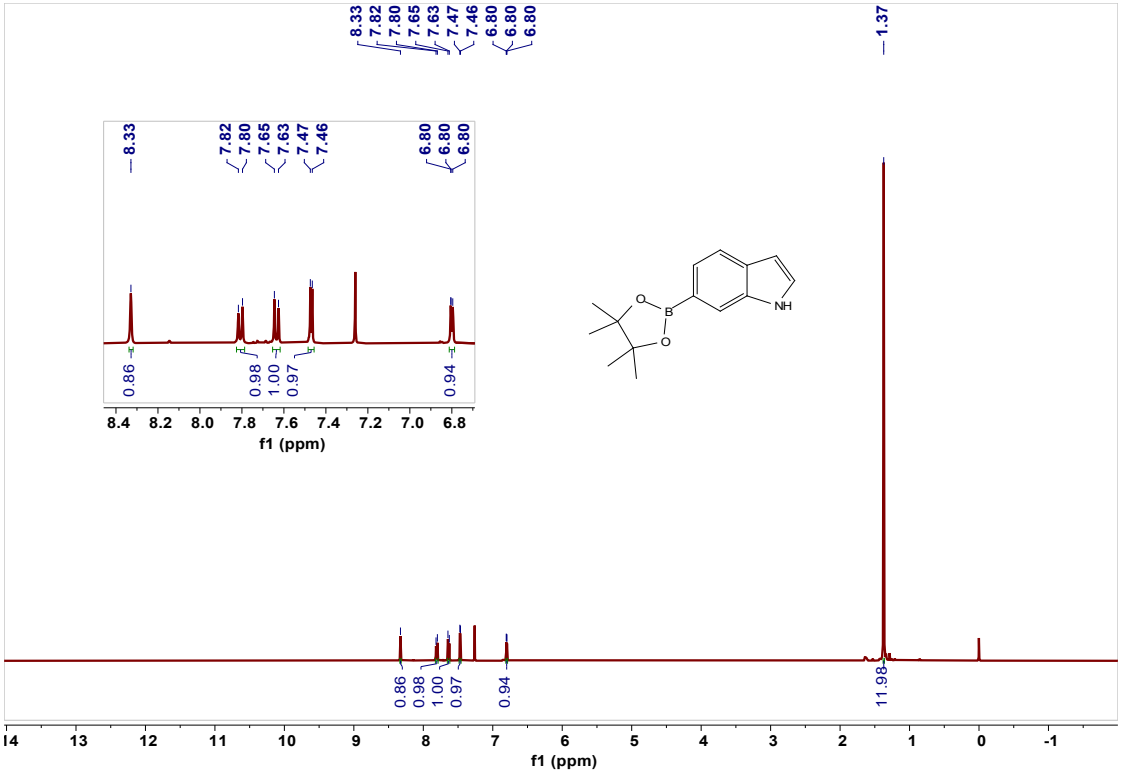

142.96
129.07
128.55
82.25
24.40
23.86
O
B
O
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

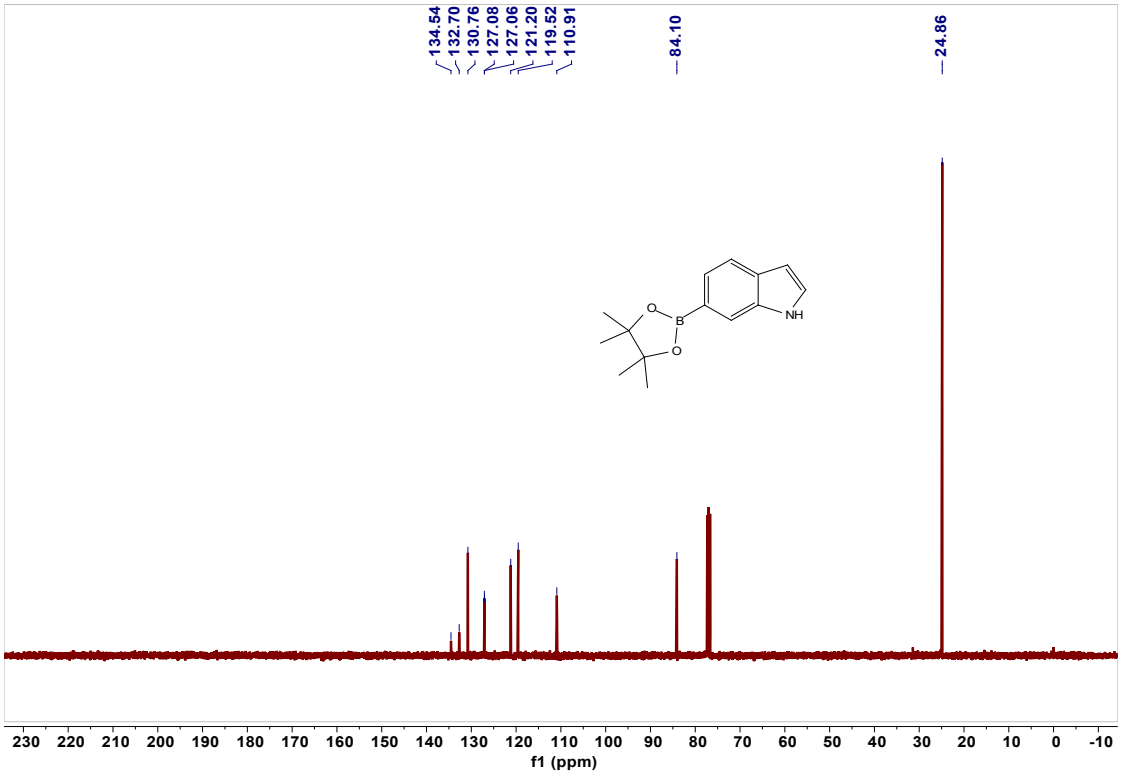

30.26
O
B
O
N
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4 -6 -8
f1 (ppm)

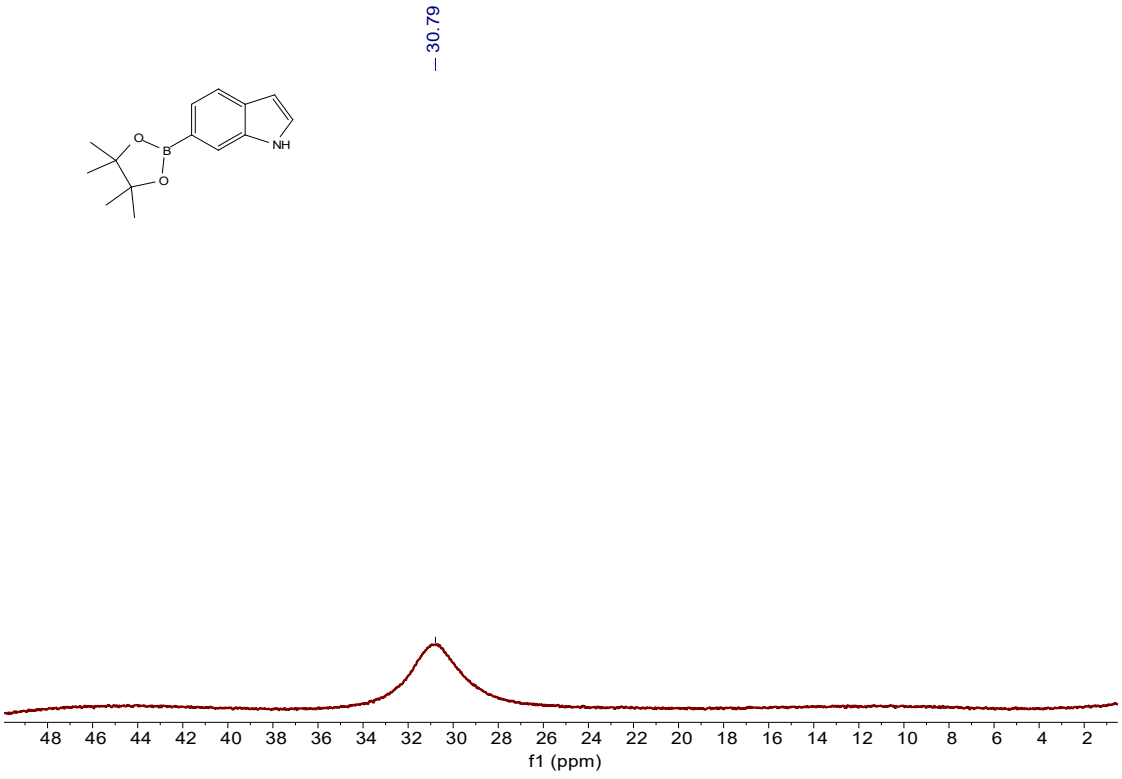

8.85
2.69
1.29
2.00
3.34
12.33
f1 (ppm)

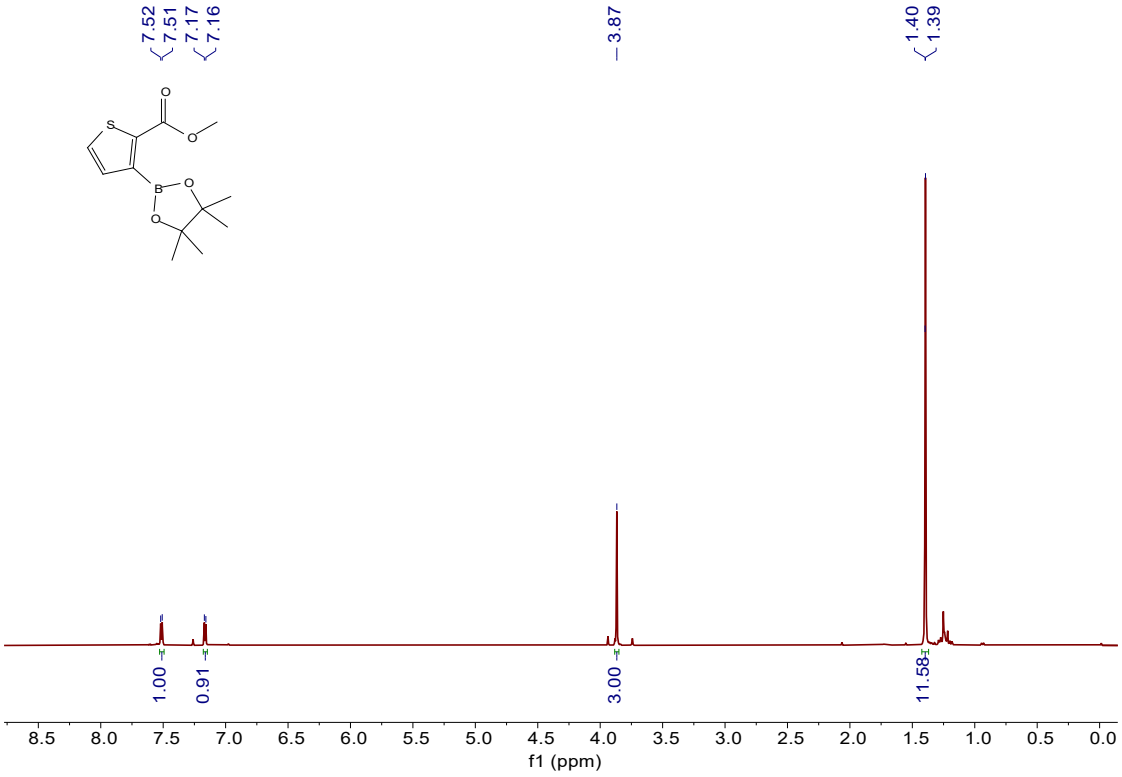

170.11
162.71
84.45
26.33
24.75
f1 (ppm)

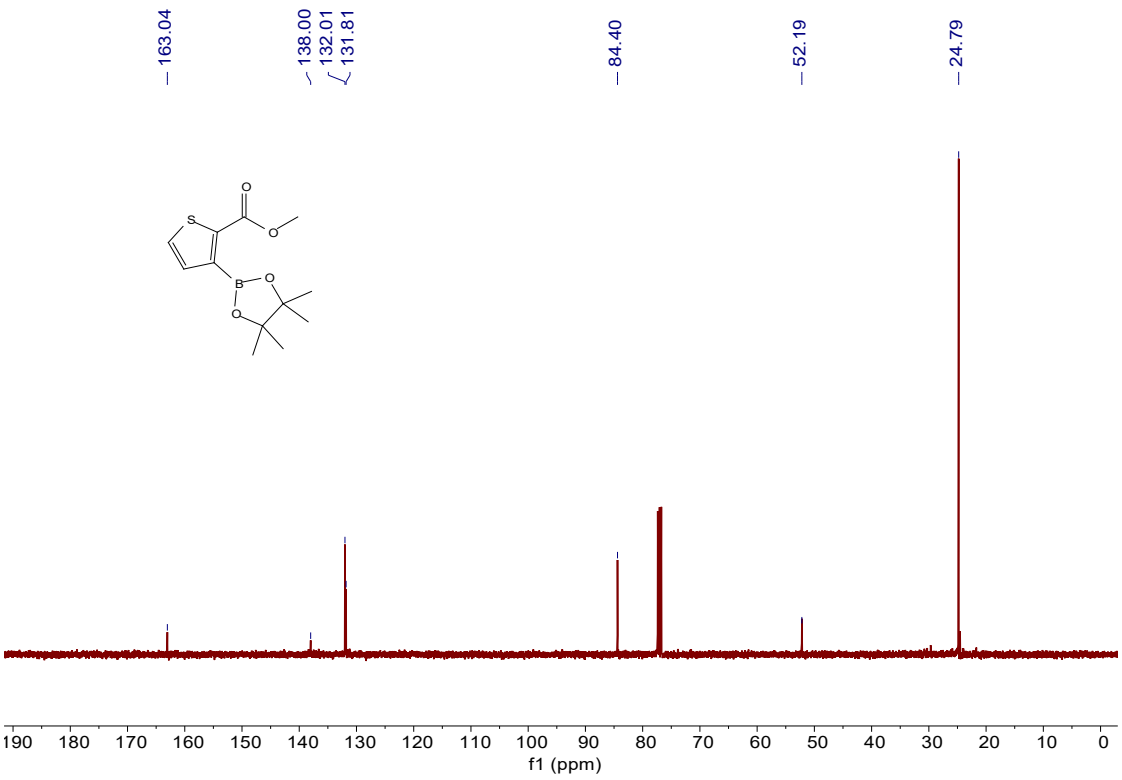

30.34
O
B
O
N
N
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)

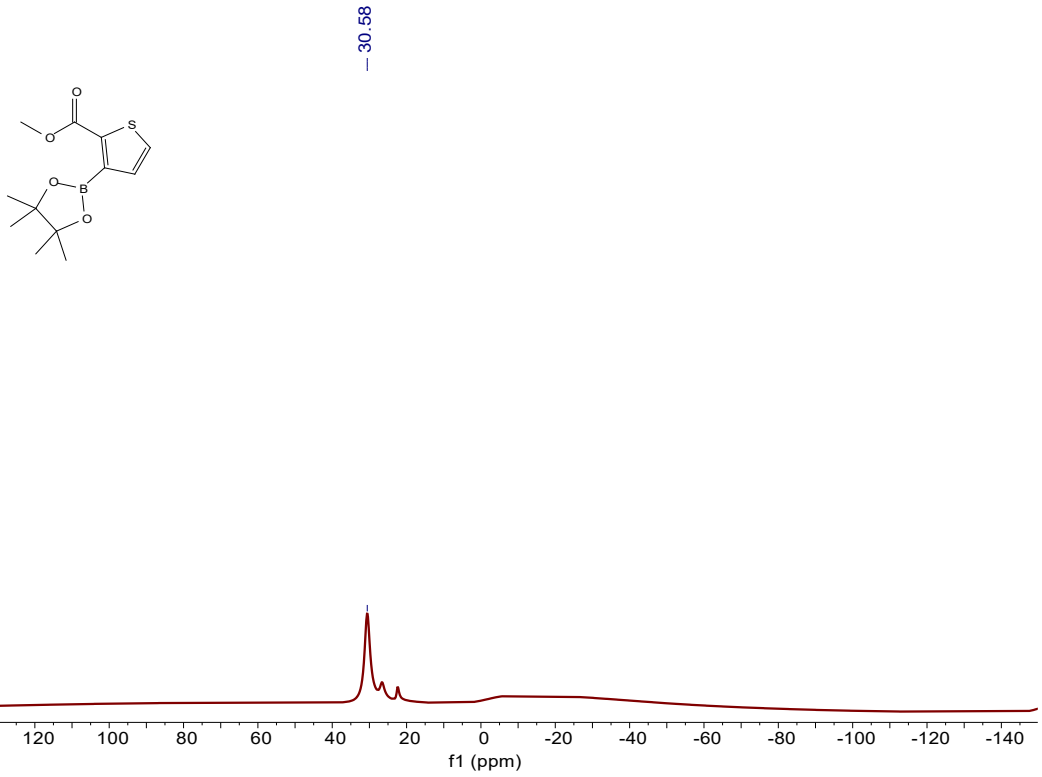

8.33
7.82
7.80
7.65
7.63
7.47
7.46
6.80
6.80
6.80
1.37
8.33
7.82
7.80
7.65
7.63
7.47
7.46
6.80
6.80
6.80
0.86
0.98
1.00
0.97
0.94
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
O
B
O
NH
0.86
0.98
1.00
0.97
0.94
11.98
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

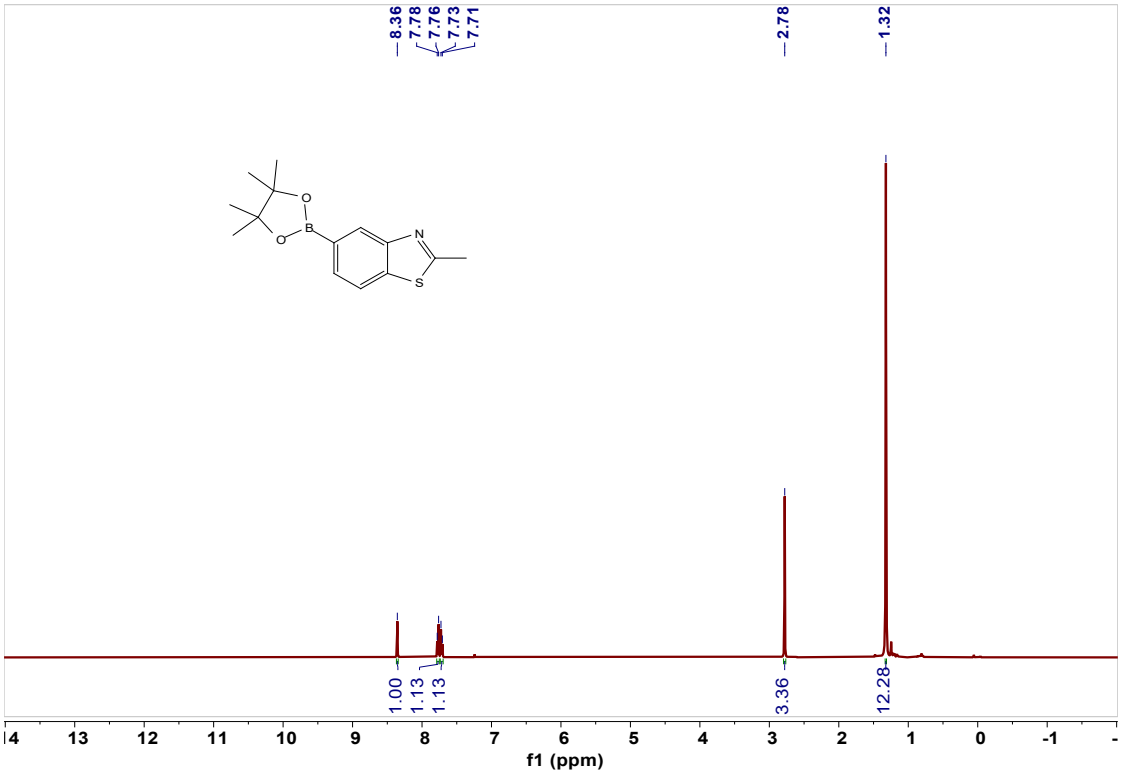

134.54
132.70
130.76
127.08
127.06
121.20
119.52
110.91
84.10
24.86
O
B
O
NH
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

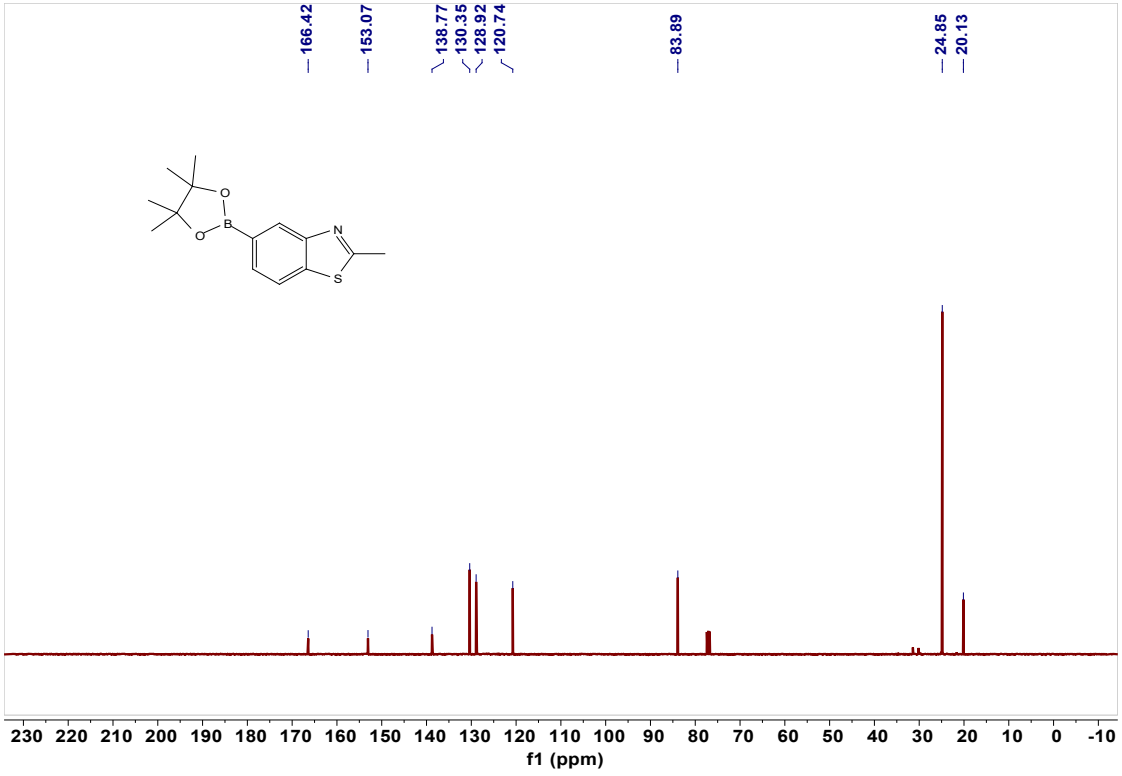

30.79
O
B
O
NH
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

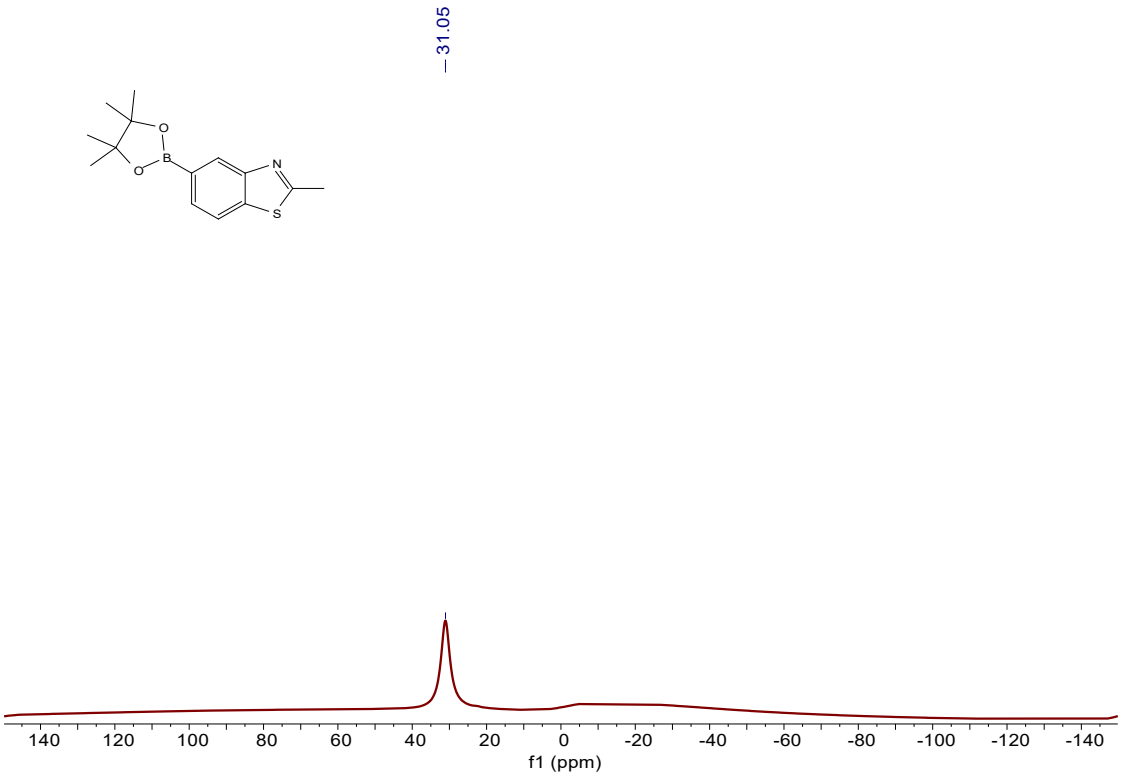

7.52
7.51
7.17
7.16
3.87
1.40
1.39
1.00
0.91
3.00
11.58
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

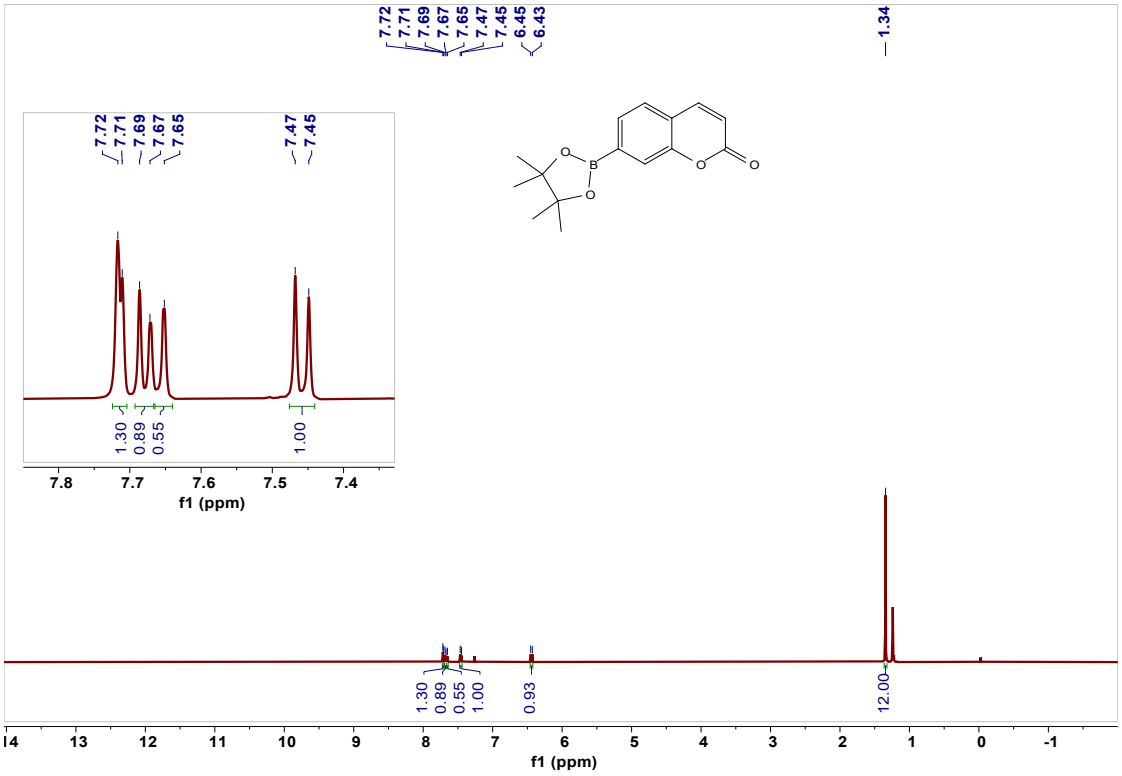

163.04
138.00
132.01
131.81
84.40
52.19
24.79
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

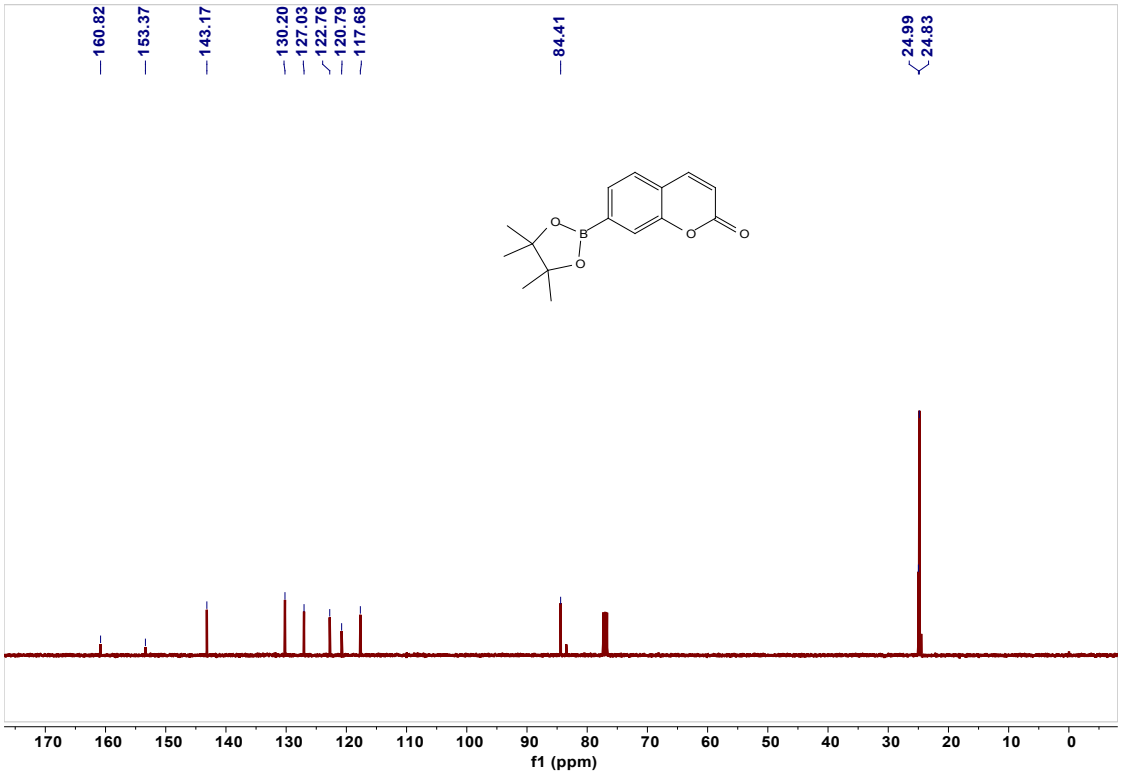

30.58
O
O
S
O
B
O
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)

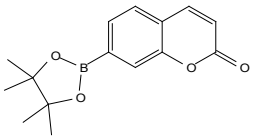

8.36
7.78
7.76
7.73
7.71
2.78
1.32
O
O
B
N
S
1.00
1.13
1.13
3.36
12.28
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)


166.42
153.07
138.77
130.35
128.92
120.74
83.89
24.85
20.13
O
B
O
N
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


31.05
O
B
O
N
S
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140
f1 (ppm)


7.72
7.71
7.69
7.67
7.65
7.47
7.45
6.45
6.43
1.34
1.30
0.89
0.55
1.00
0.93
12.00
f1 (ppm)

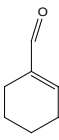

160.82
153.37
143.17
130.20
127.03
122.76
120.79
117.68
84.41
24.99
24.83
f1 (ppm)



30.43

60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0

f1 (ppm)



10.32

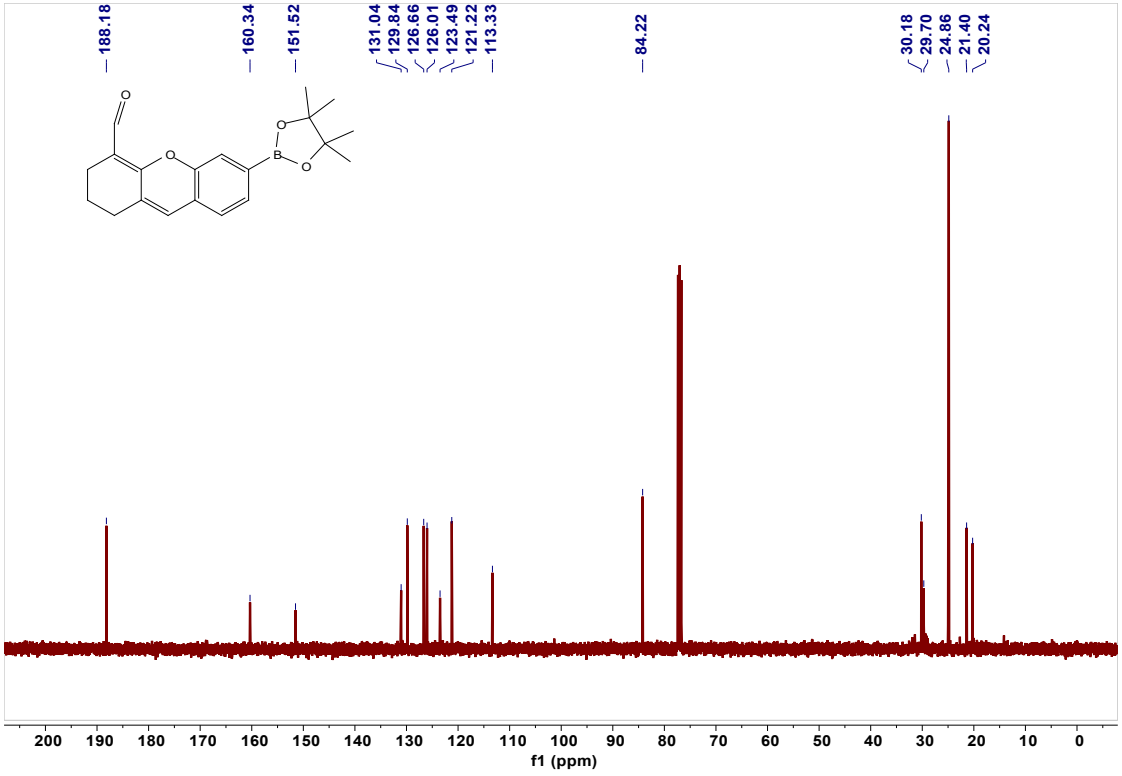
7.52 7.50 7.50 7.48 7.48 7.26 7.17 7.15 6.69

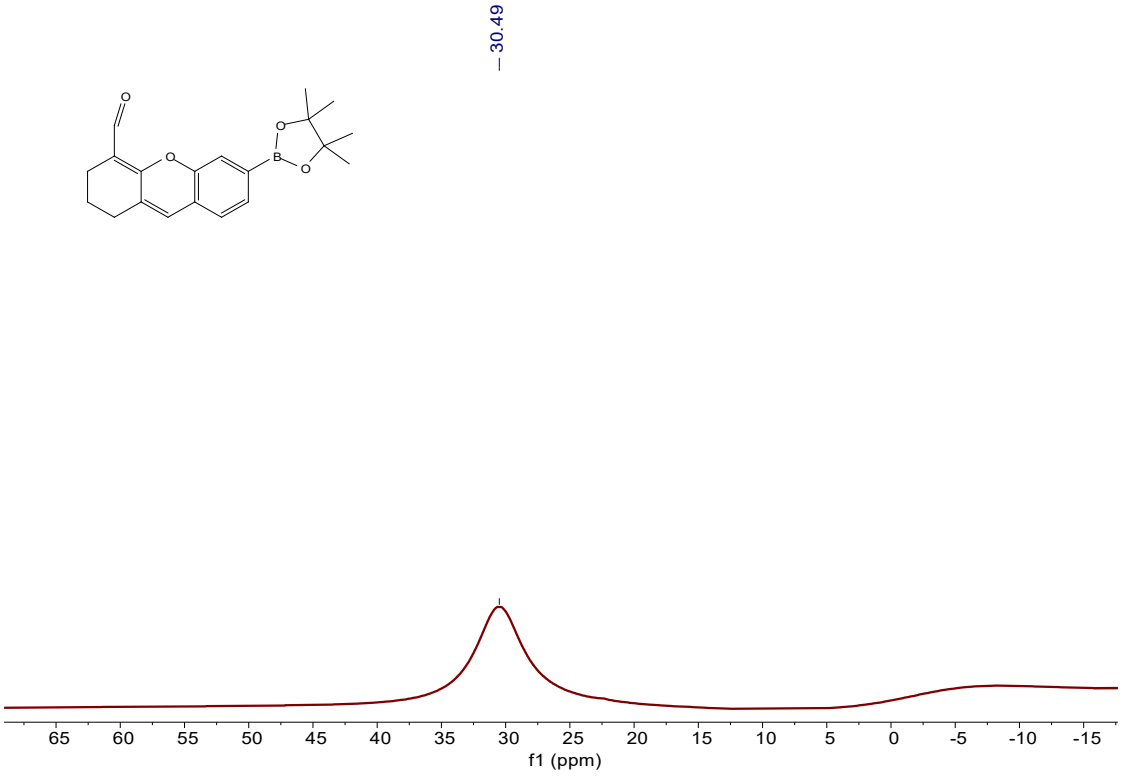
2.61 2.61 2.59 2.58 2.58 2.45 2.44 2.42 1.75 1.74 1.72 1.71 1.68 1.35

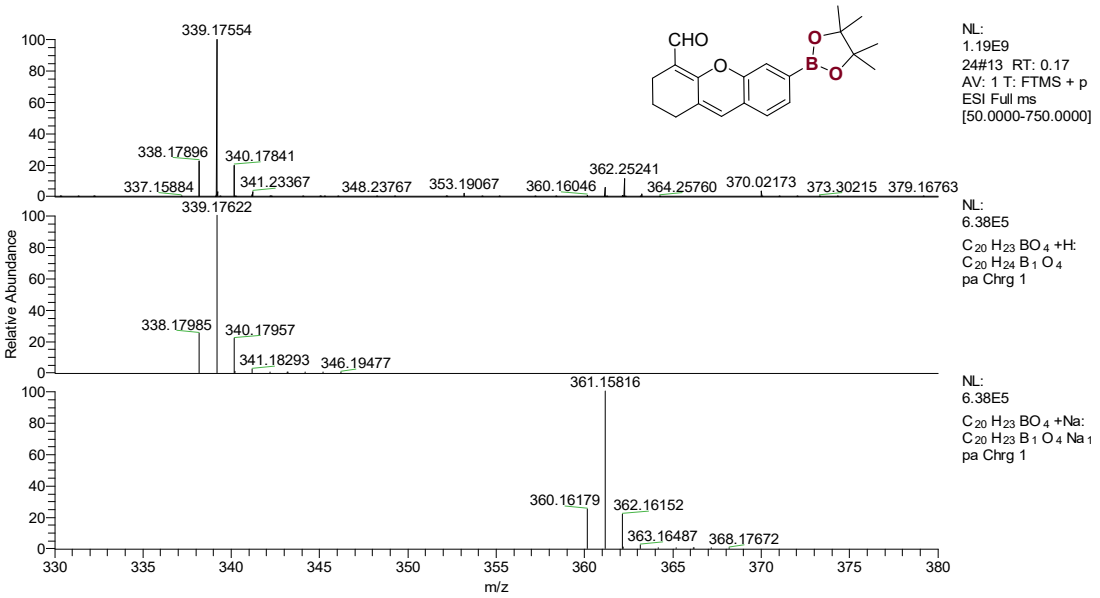
0.81 0.87 0.94 0.97 0.95 2.00 1.97 2.42 12.12

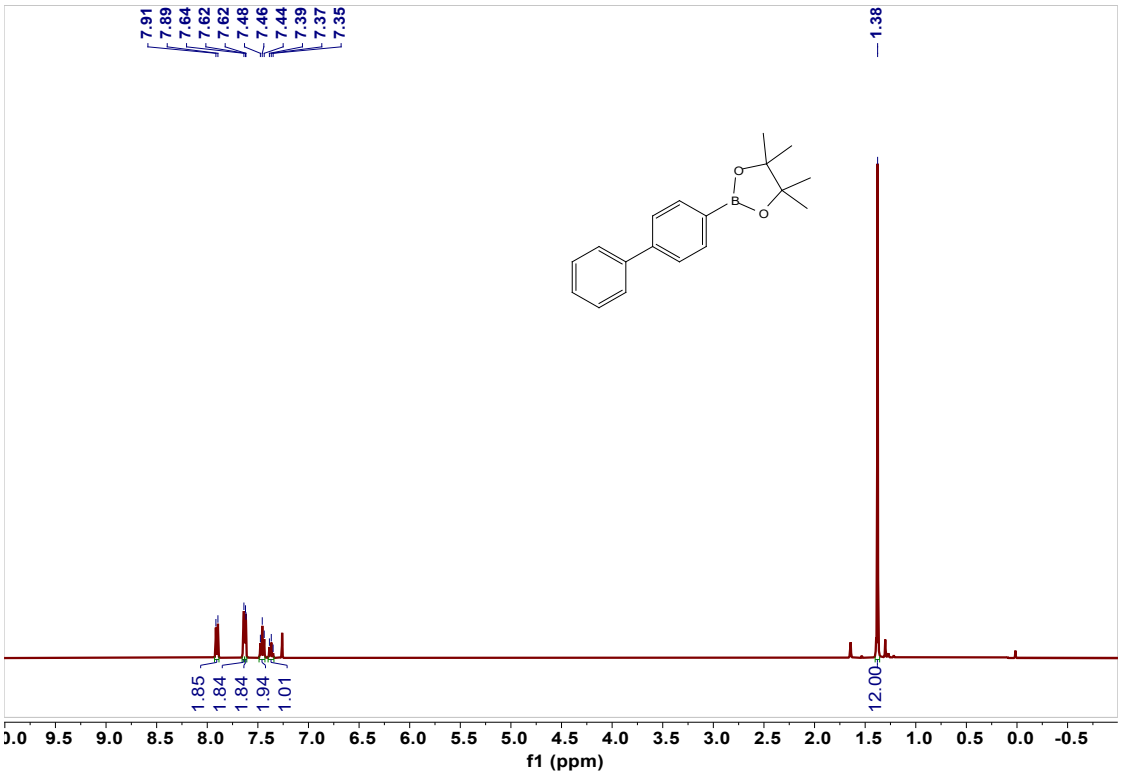
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

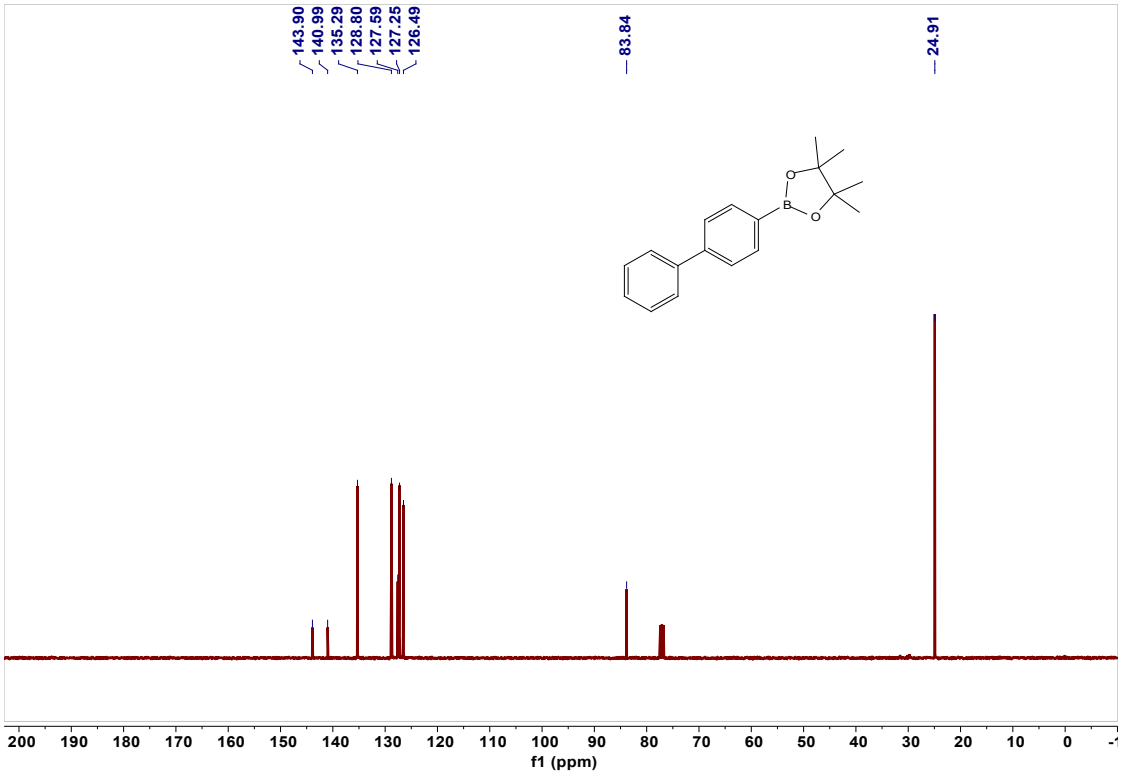
f1 (ppm)

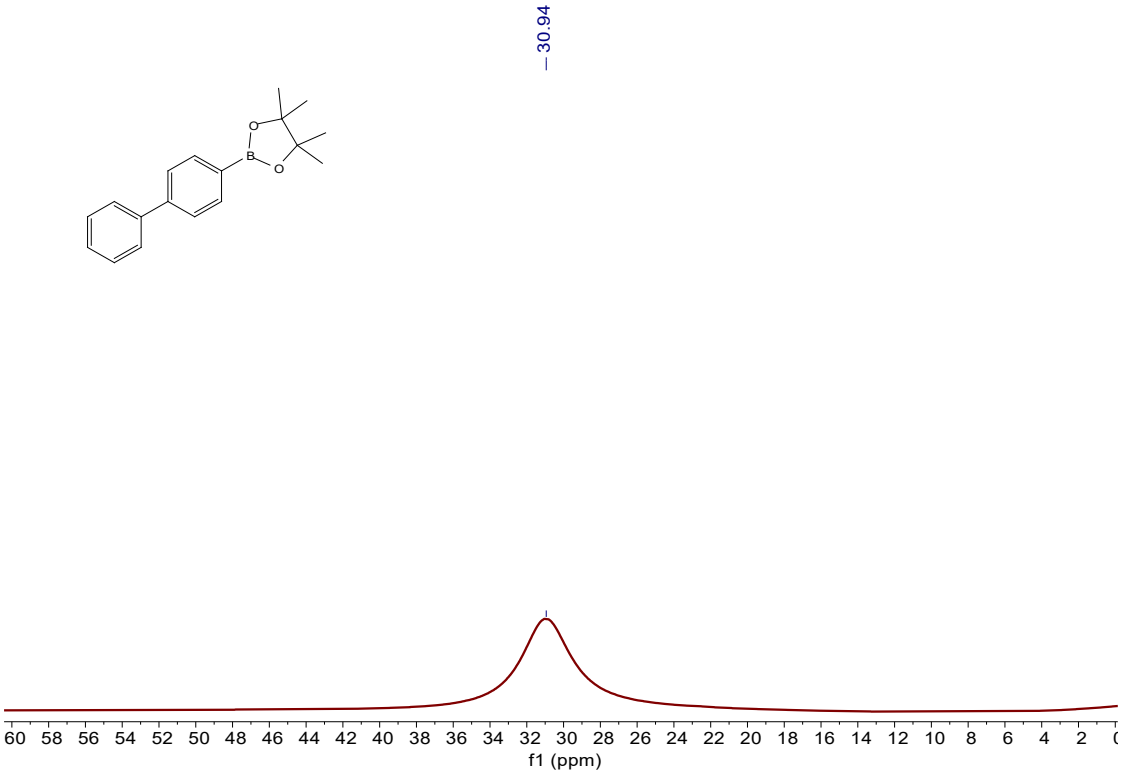

188.18
160.34
151.52
131.04
129.84
126.66
126.01
123.49
121.22
113.33
84.22
30.18
29.70
24.86
21.40
20.24
O
O
B
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

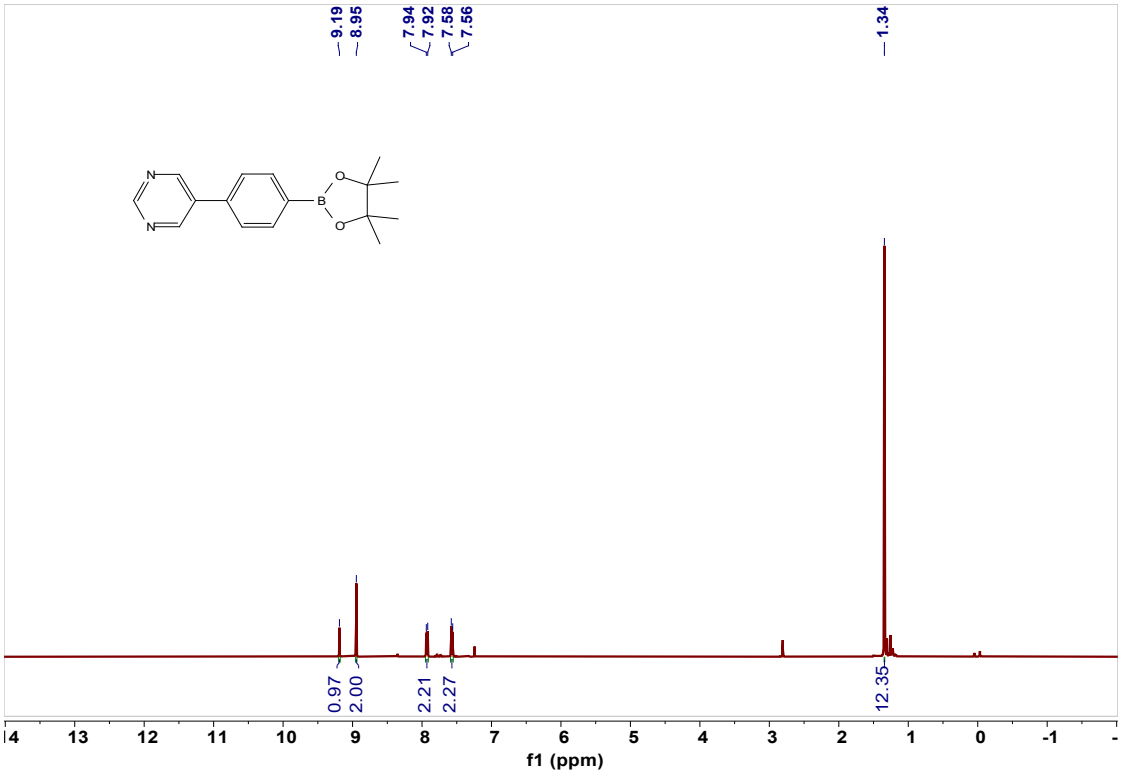

30.49
O
O
B
O
O
65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15
f1 (ppm)

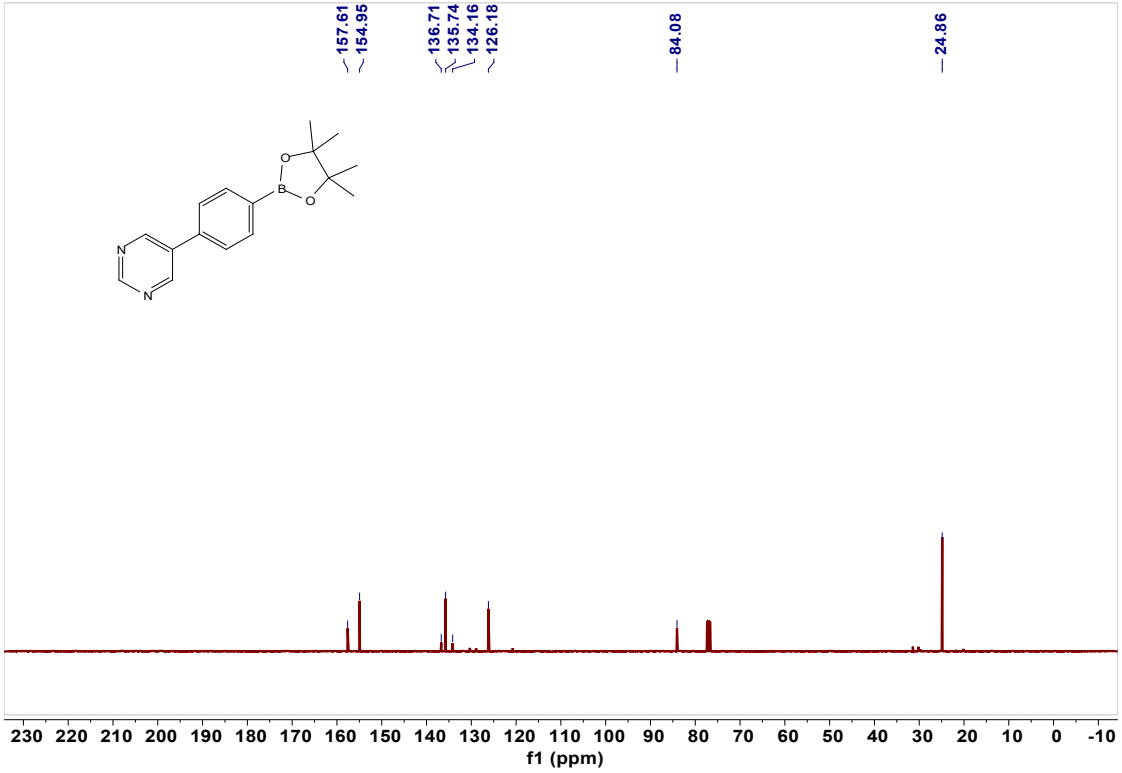

CHO
O
B
O
O
NL:
1.19E9
24#13 RT: 0.17
AV: 1 T: FTMS + p
ESI Full ms
[50.0000-750.0000]
339.17554
338.17896
340.17841
337.15884
341.23367
348.23767
353.19067
360.16046
362.25241
364.25760
370.02173
373.30215
379.16763
NL:
6.38E5
C20 H23 BO4 +H:
C20 H24 B1 O4
pa Chrg 1
339.17622
338.17985
340.17957
341.18293
346.19477
NL:
6.38E5
C20 H23 BO4 +Na:
C20 H23 B1 O4 Na1
pa Chrg 1
361.15816
360.16179
362.16152
363.16487
368.17672
Relative Abundance
m/z

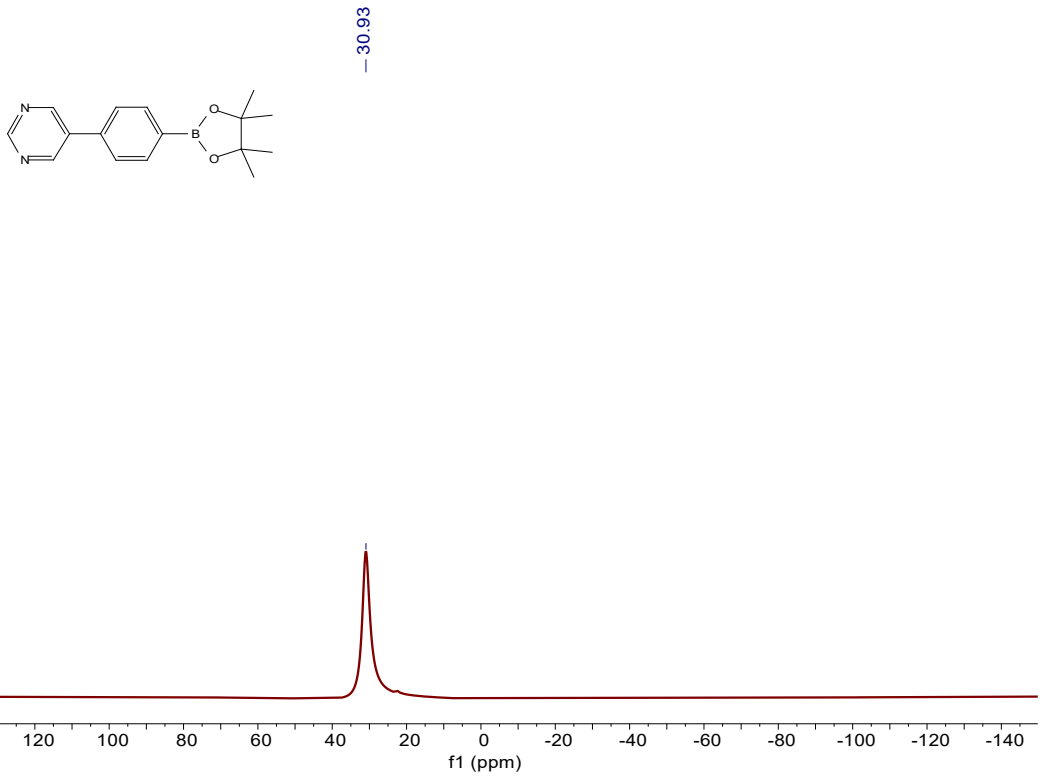

7.91
7.89
7.64
7.62
7.62
7.48
7.46
7.44
7.39
7.37
7.35
1.38
O
B
O
1.85
1.84
1.84
1.94
1.01
12.00
f1 (ppm)

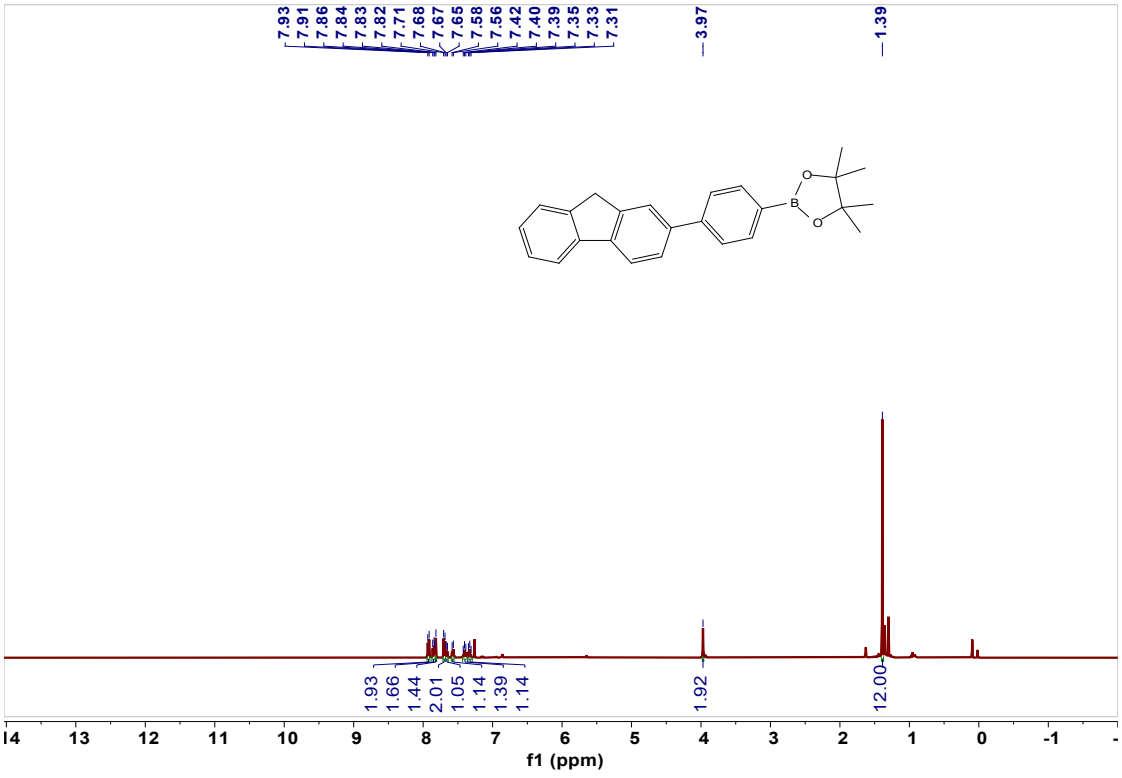

143.90
140.99
135.29
128.80
127.59
127.25
126.49
83.84
24.91
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

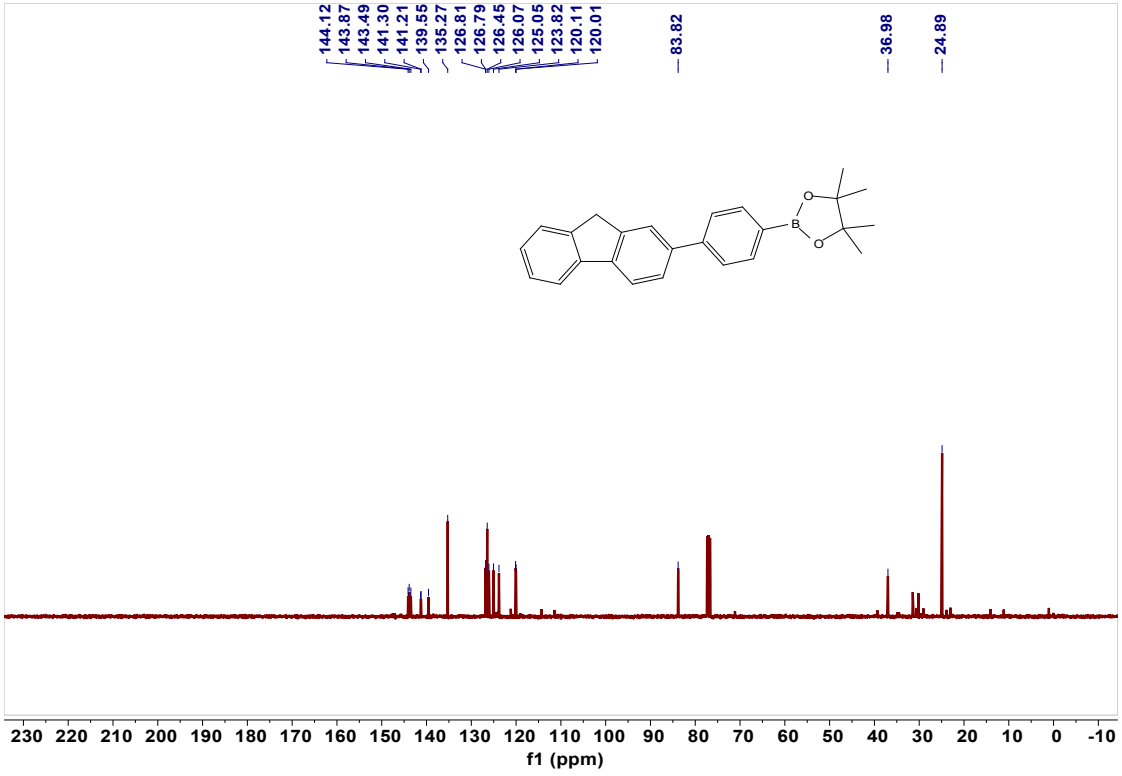

30.94
60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

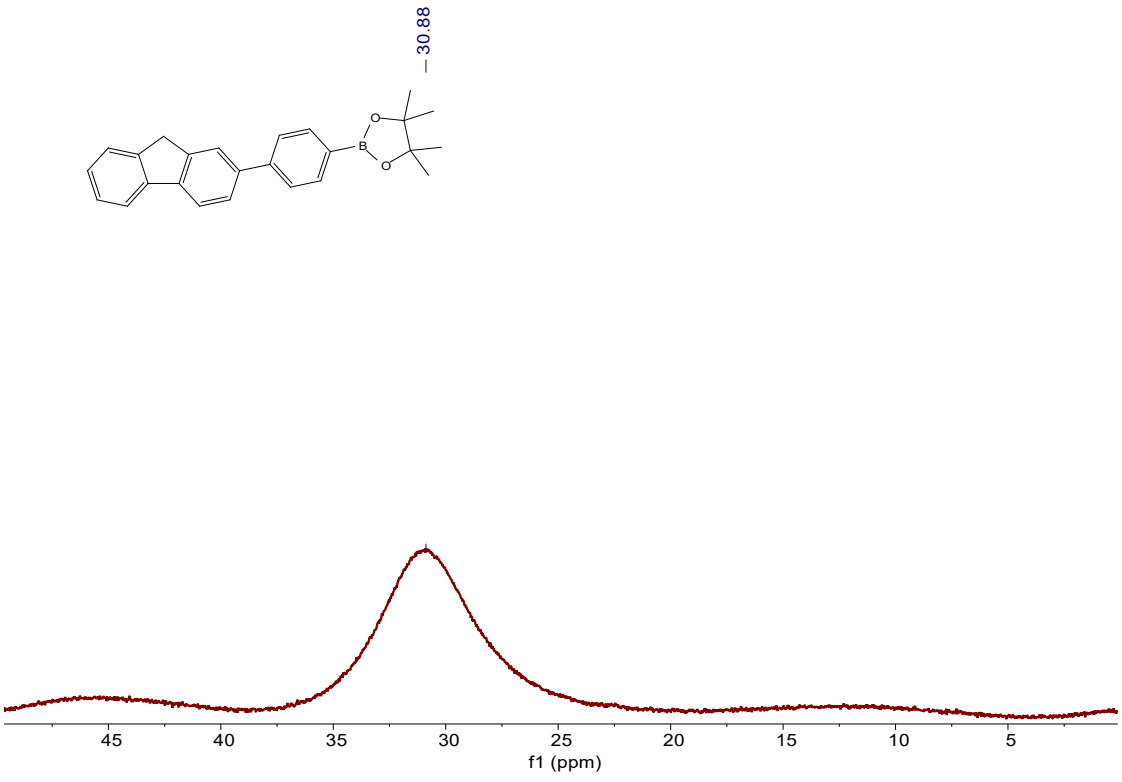

9.19
8.95
7.94
7.92
7.58
7.56
1.34
0.97
2.00
2.21
2.27
12.35
f1 (ppm)

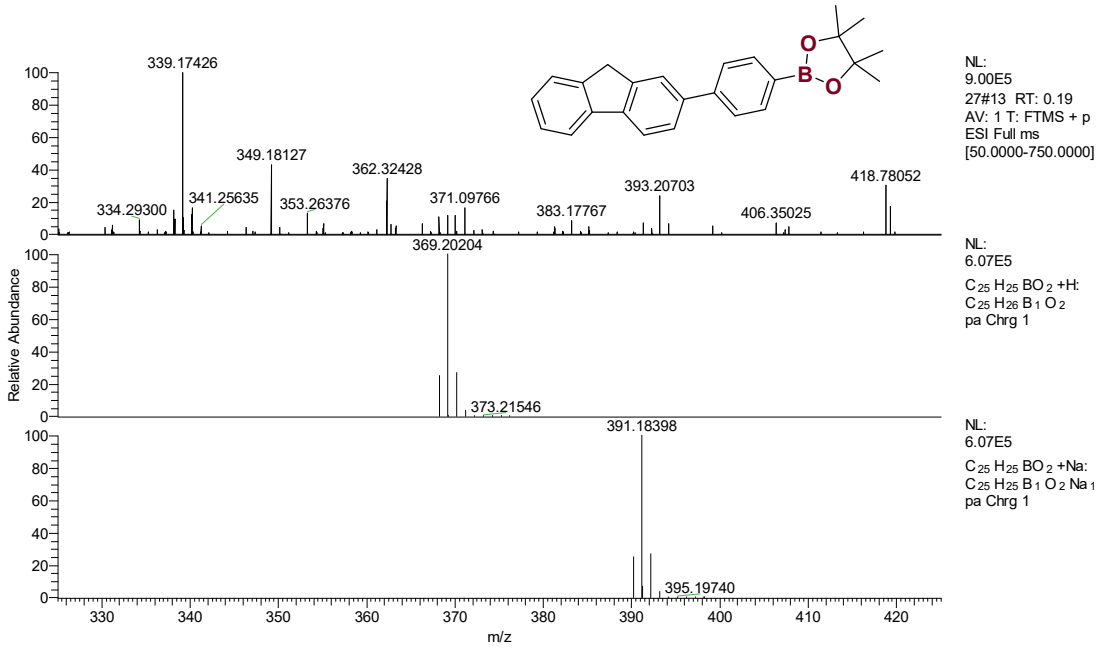

157.61
154.95
136.71
135.74
134.16
126.18
84.08
24.86
f1 (ppm)

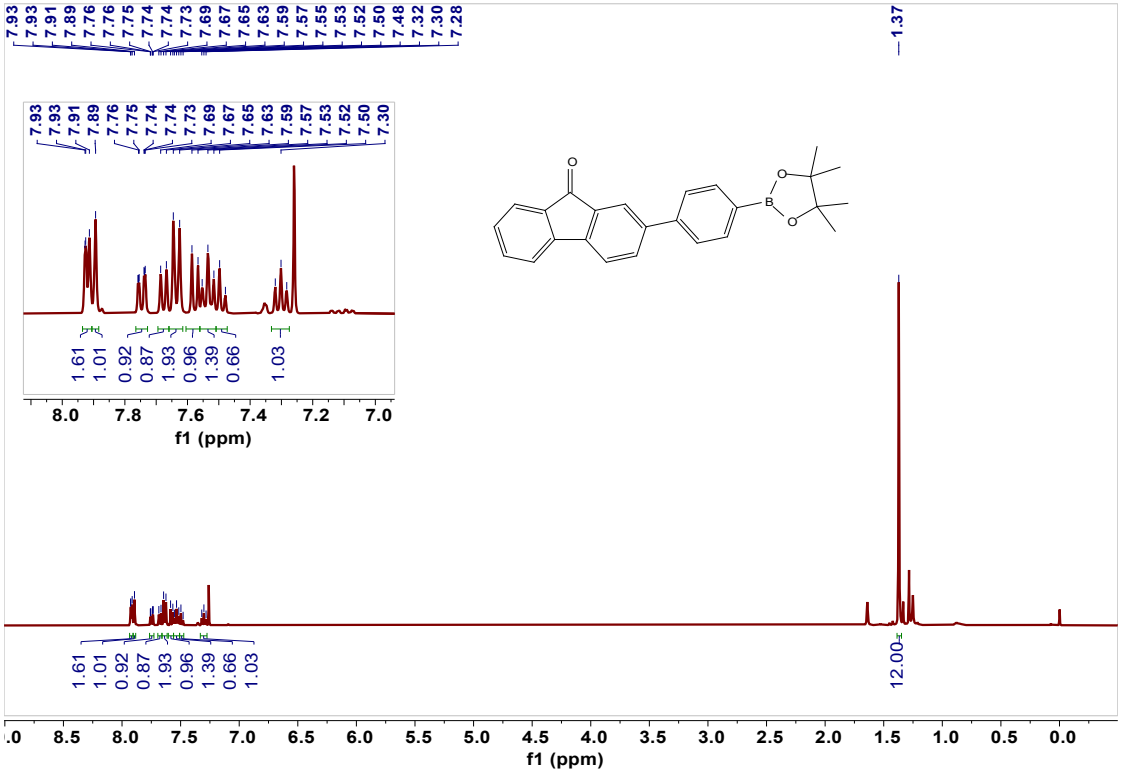

30.93
N
N
B
O
O
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
f1 (ppm)

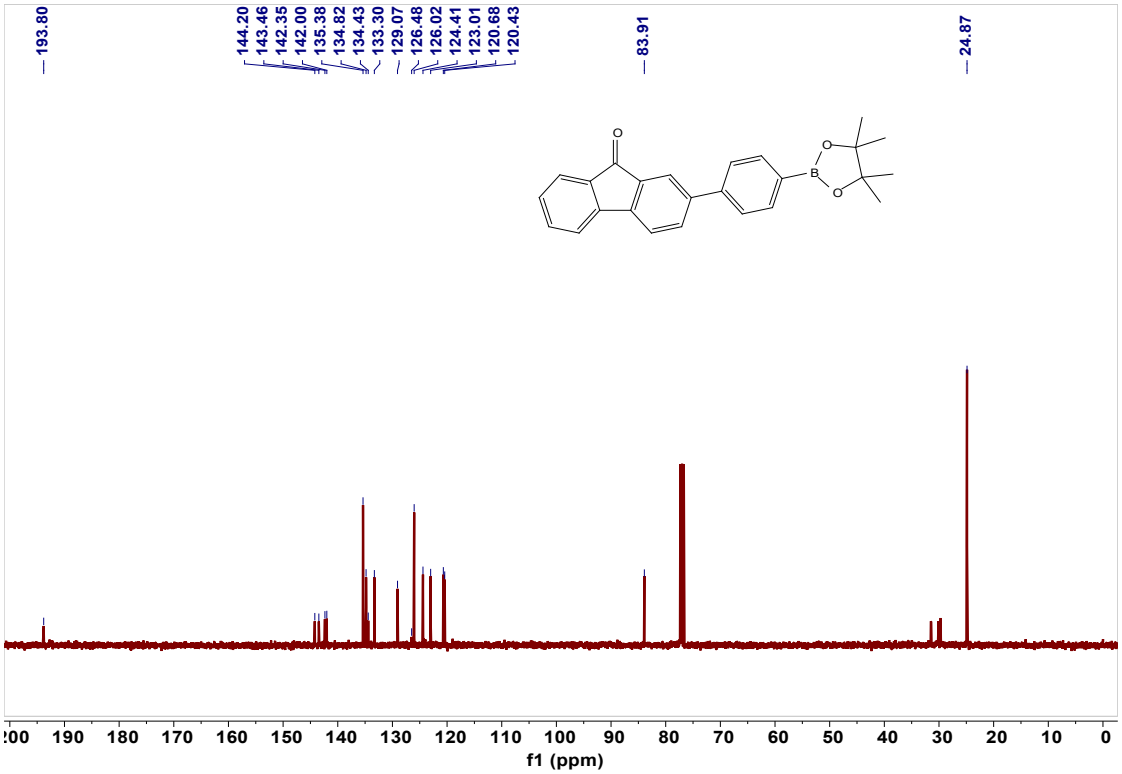

7.93
7.91
7.86
7.84
7.83
7.82
7.71
7.68
7.67
7.65
7.58
7.56
7.42
7.40
7.39
7.35
7.33
7.31
3.97
1.39
B
O
O
1.93
1.66
1.44
2.01
1.05
1.14
1.39
1.14
1.92
12.00
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

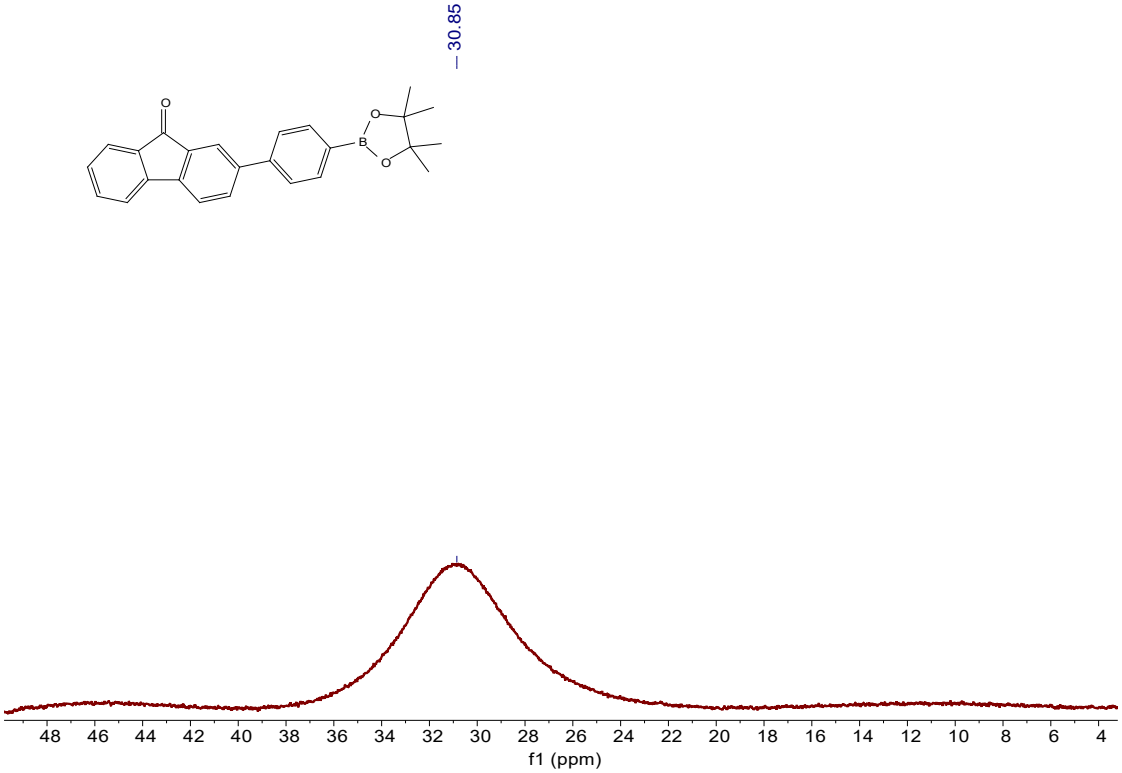

144.12
143.87
143.49
141.30
141.21
139.55
135.27
126.81
126.79
126.45
126.07
125.05
123.82
120.11
120.01
83.82
36.98
24.89
O
B
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

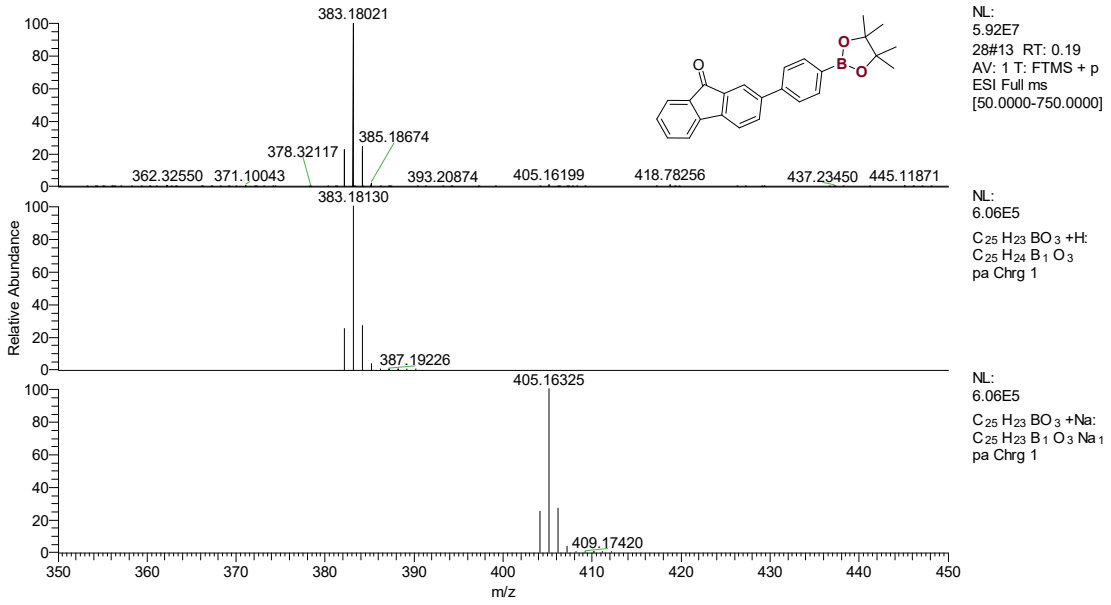

30.88
O
B
O
45 40 35 30 25 20 15 10 5
f1 (ppm)

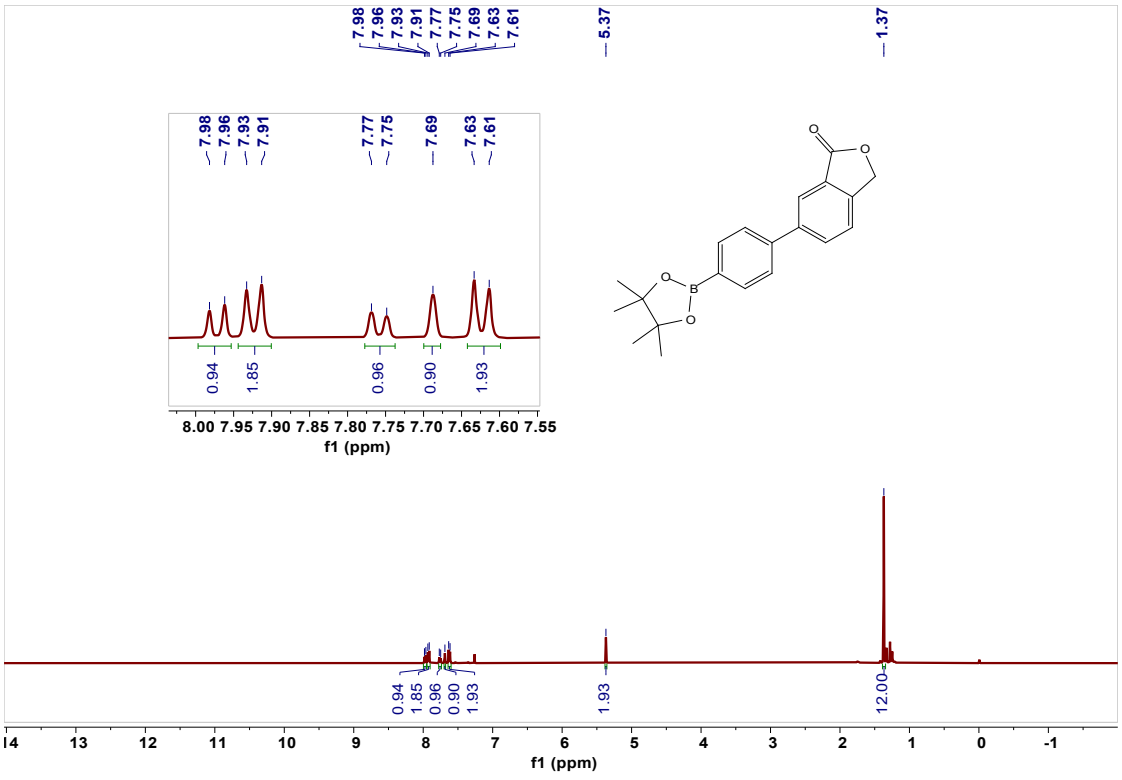

339.17426
349.18127
362.32428
334.29300
341.25635
353.26376
371.09766
383.17767
393.20703
406.35025
418.78052
NL:
9.00E5
27#13 RT: 0.19
AV: 1 T: FTMS + p
ESI Full ms
[50.0000-750.0000]
369.20204
373.21546
NL:
6.07E5
C25 H25 BO2 +H:
C25 H26 B1 O2
pa Chrg 1
391.18398
395.19740
NL:
6.07E5
C25 H25 BO2 +Na:
C25 H25 B1 O2 Na1
pa Chrg 1
Relative Abundance
m/z

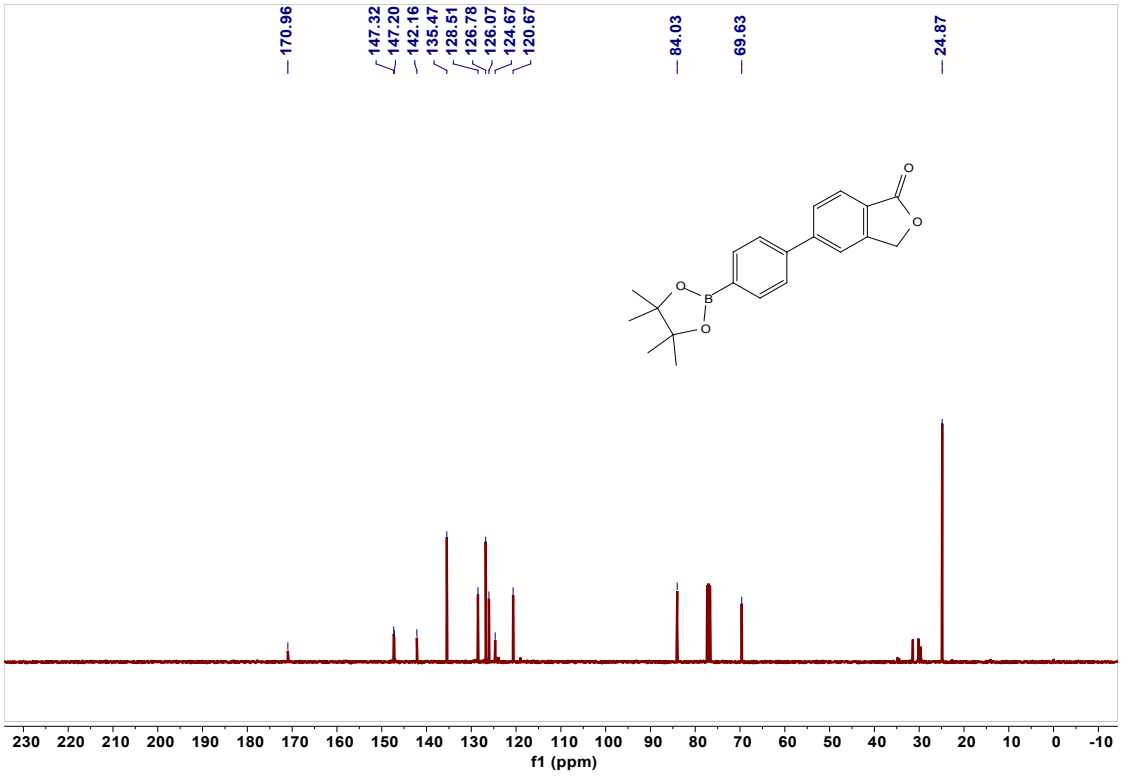

1.61
1.01
0.92
0.87
1.93
0.96
1.39
0.66
1.03
12.00
f1 (ppm)

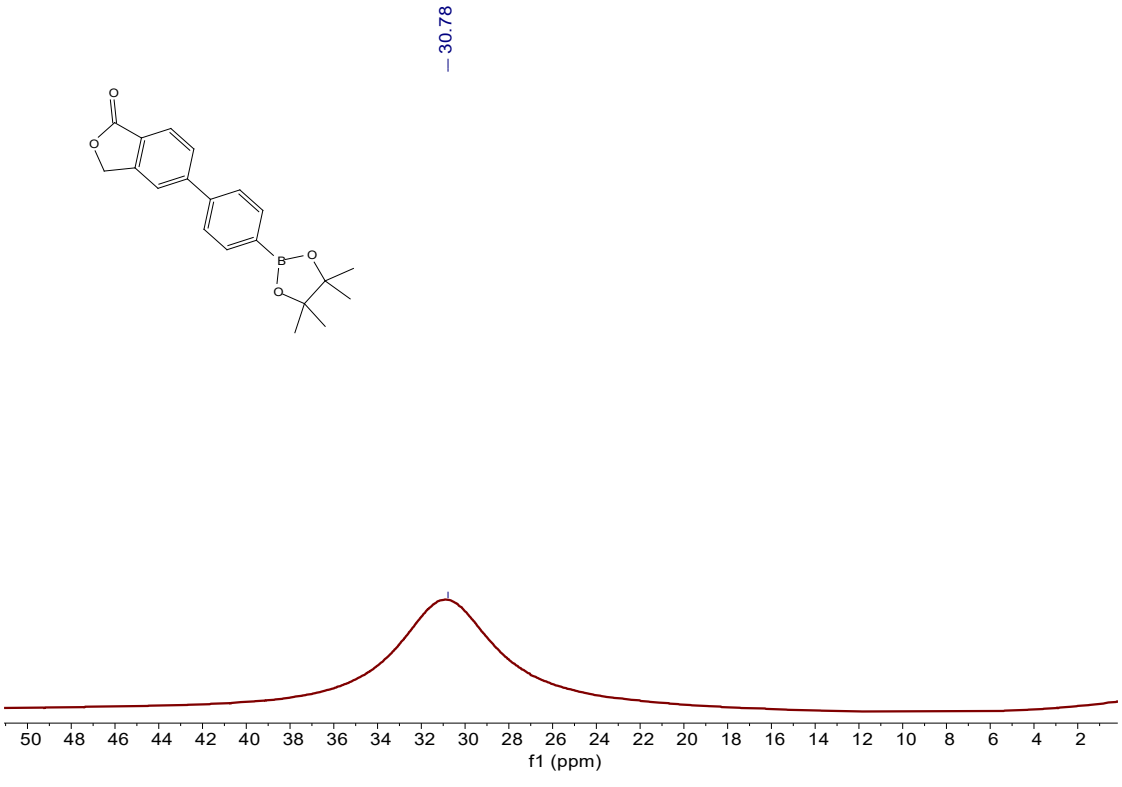

193.80
144.20
143.46
142.35
142.00
135.38
134.82
134.43
133.30
129.07
126.48
126.02
124.41
123.01
120.68
120.43
83.91
24.87
O
O
B
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

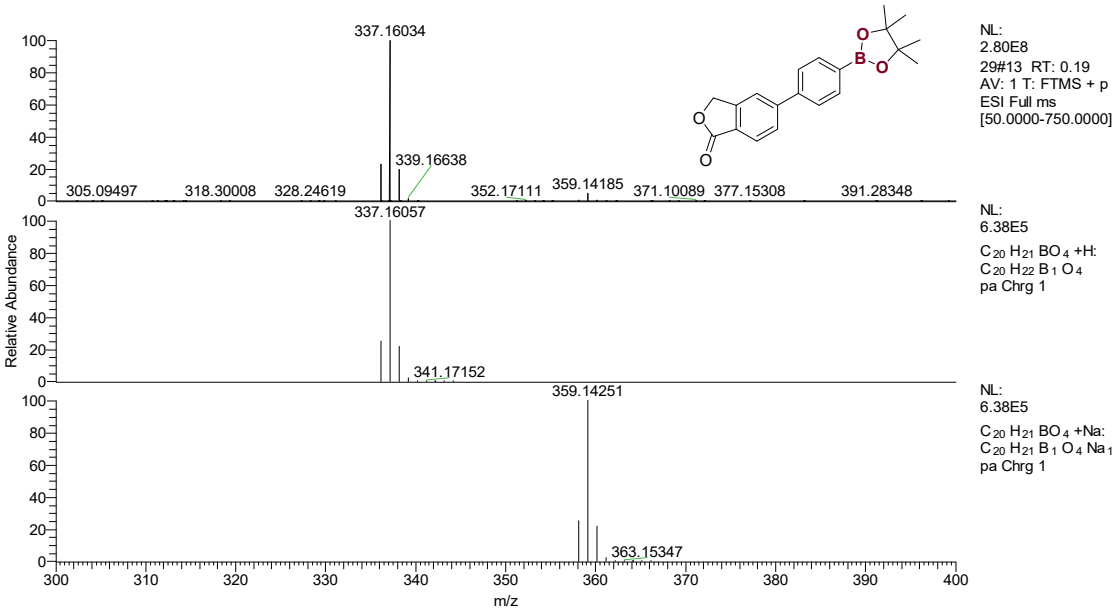

30.85
O
O
B
O
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4
f1 (ppm)

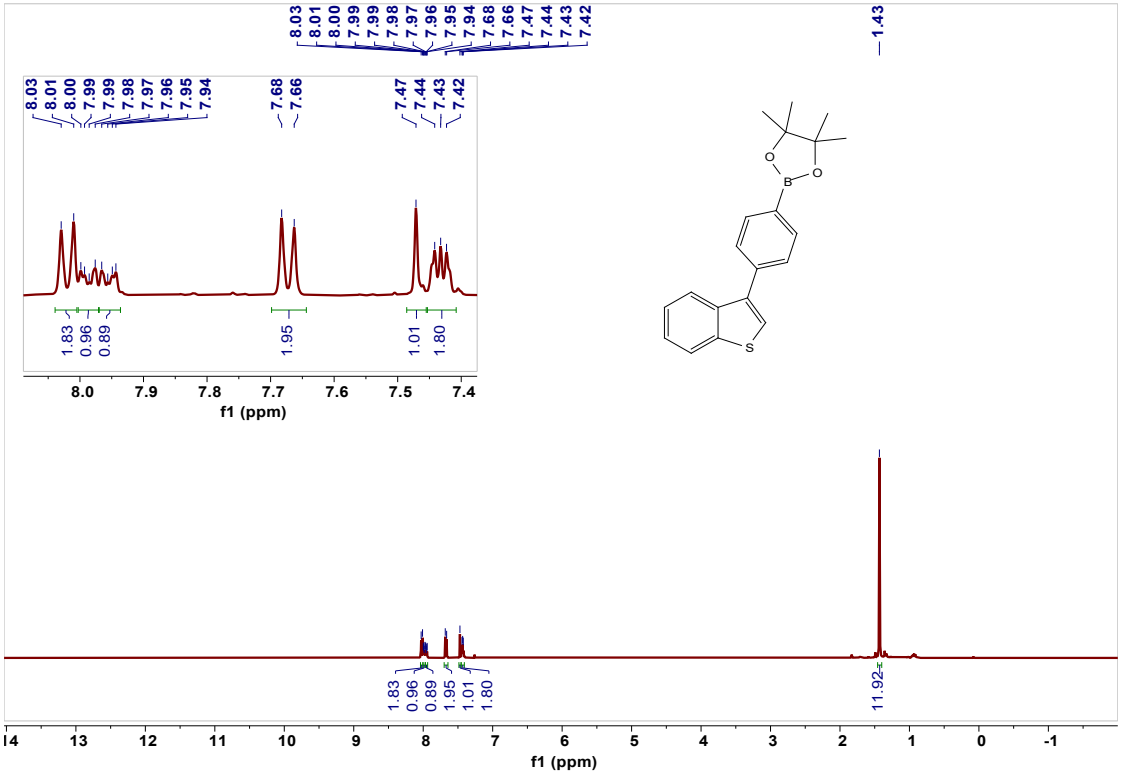

383.18021
385.18674
378.32117
362.32550
371.10043
393.20874
405.16199
418.78256
437.23450
445.11871
NL:
5.92E7
28#13 RT: 0.19
AV: 1 T: FTMS + p
ESI Full ms
[50.0000-750.0000]
383.18130
387.19226
NL:
6.06E5
C25 H23 BO3 +H:
C25 H24 B1 O3
pa Chrg 1
405.16325
409.17420
NL:
6.06E5
C25 H23 BO3 +Na:
C25 H23 B1 O3 Na1
pa Chrg 1
Relative Abundance
m/z

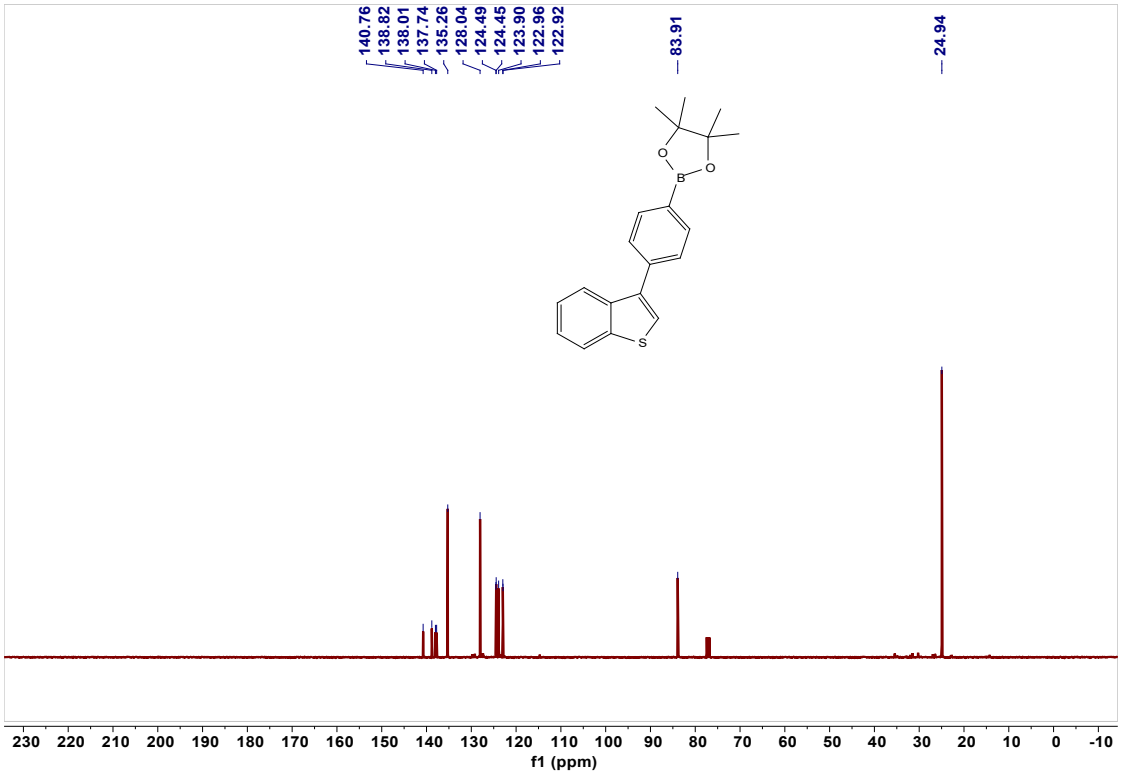

7.98
7.96
7.93
7.91
7.77
7.75
7.69
7.63
7.61
5.37
1.37
0.94
1.85
0.96
0.90
1.93
12.00
f1 (ppm)

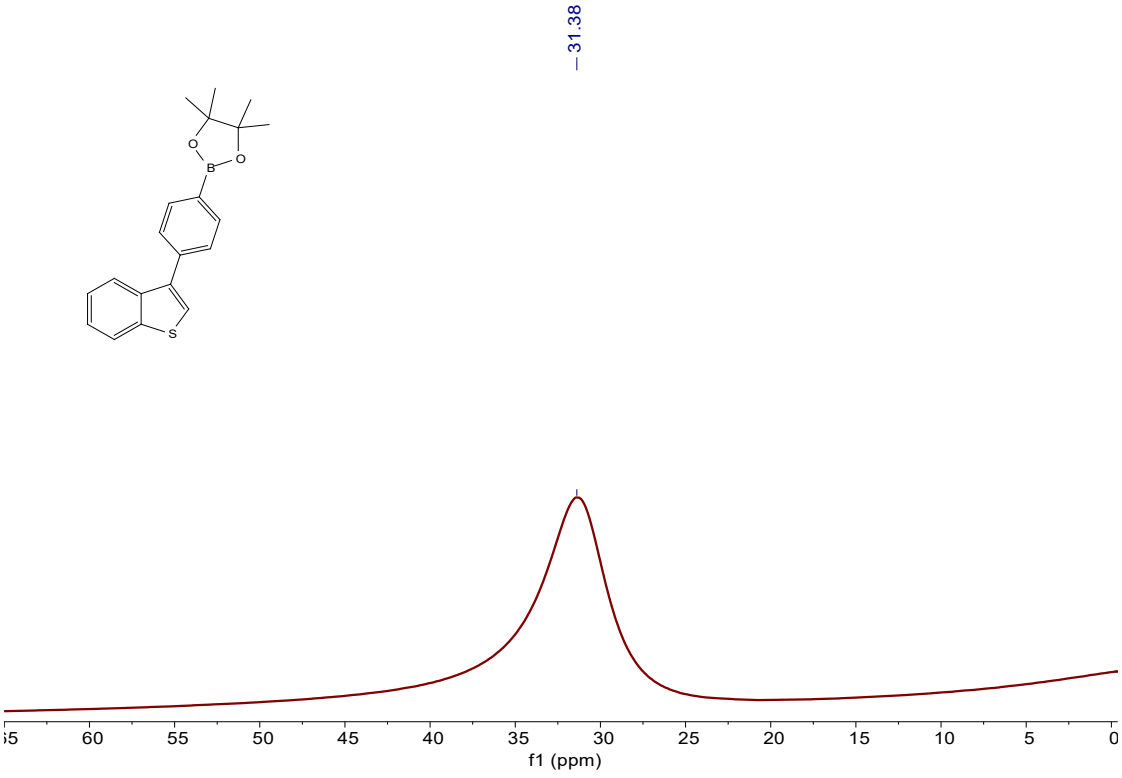

170.96
147.32
147.20
142.16
135.47
128.51
126.78
126.07
124.67
120.67
84.03
69.63
24.87
O
O
O
B
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

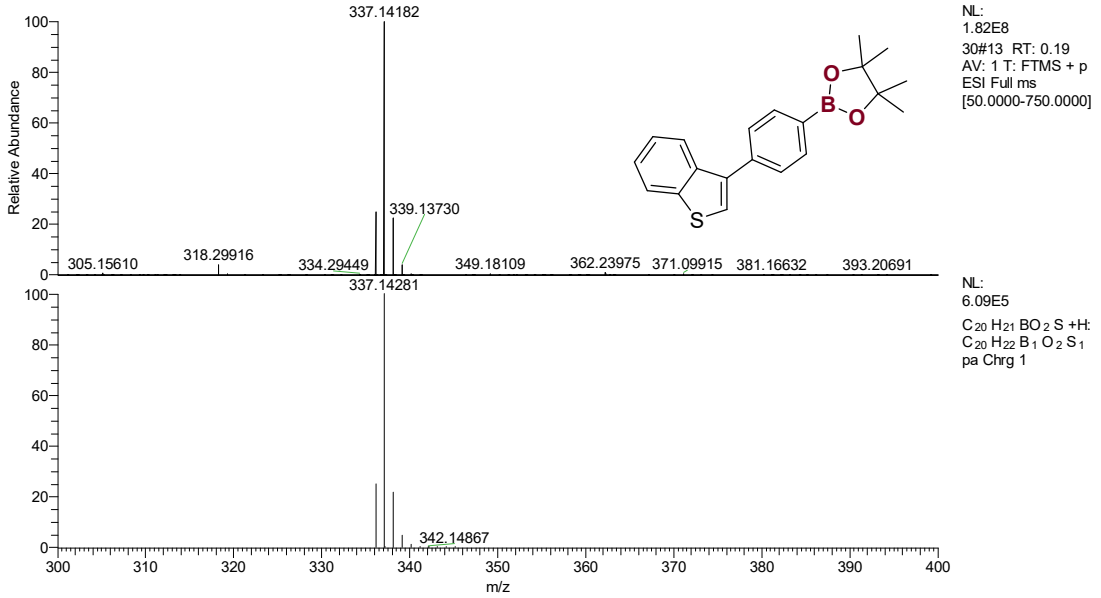

30.78
O
O
B
O
O
50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

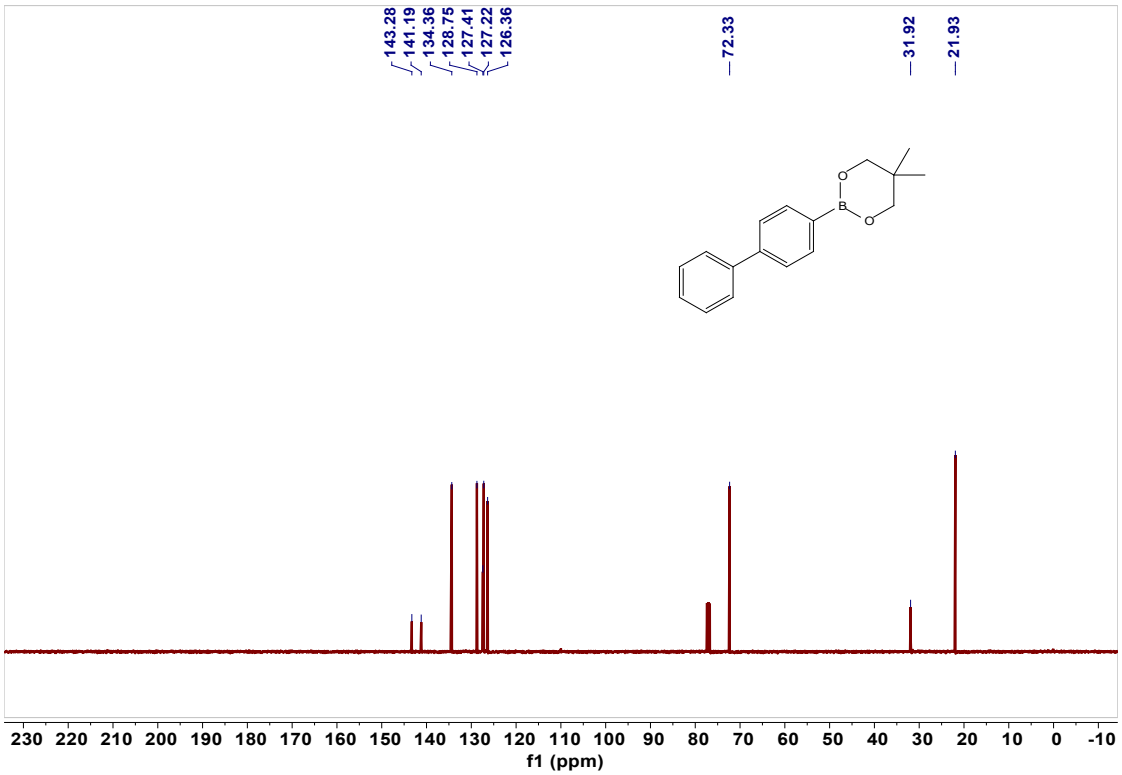

337.16034
339.16638
305.09497
318.30008
328.24619
352.17111
359.14185
371.10089
377.15308
391.28348
NL:
2.80E8
29#13 RT: 0.19
AV: 1 T: FTMS + p
ESI Full ms
[50.0000-750.0000]
337.16057
341.17152
NL:
6.38E5
C20 H21 BO4 +H:
C20 H22 B1 O4
pa Chrg 1
359.14251
363.15347
NL:
6.38E5
C20 H21 BO4 +Na:
C20 H21 B1 O4 Na1
pa Chrg 1
Relative Abundance
m/z

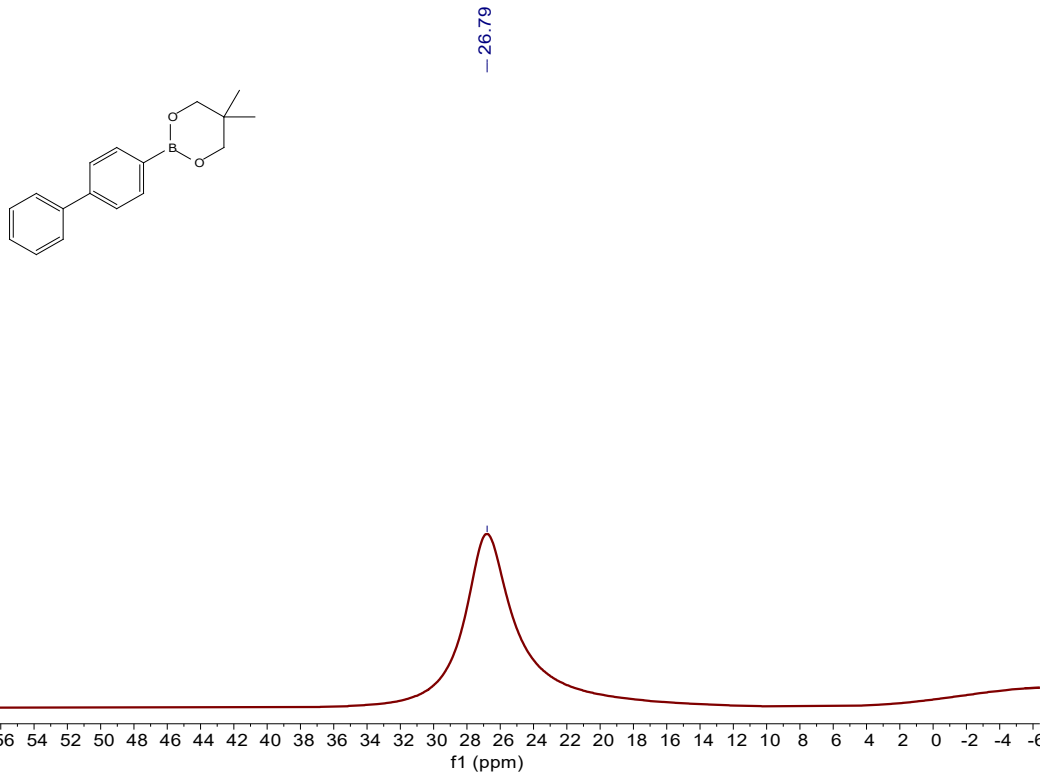

8.03
8.01
8.00
7.99
7.99
7.98
7.97
7.96
7.95
7.94
7.68
7.66
7.47
7.44
7.43
7.42
1.43
1.83
0.96
0.89
1.95
1.01
1.80
11.92
f1 (ppm)

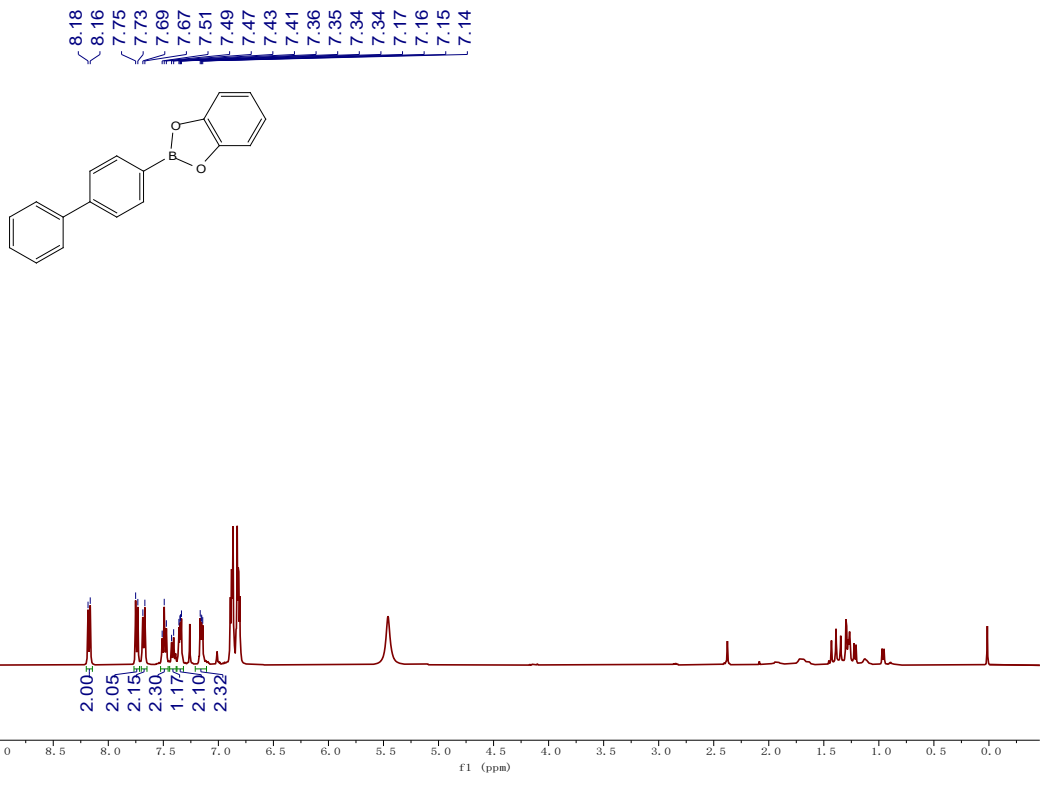

140.76
138.82
138.01
137.74
135.26
128.04
124.49
124.45
123.90
122.96
122.92
83.91
24.94
O
B
O
S
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

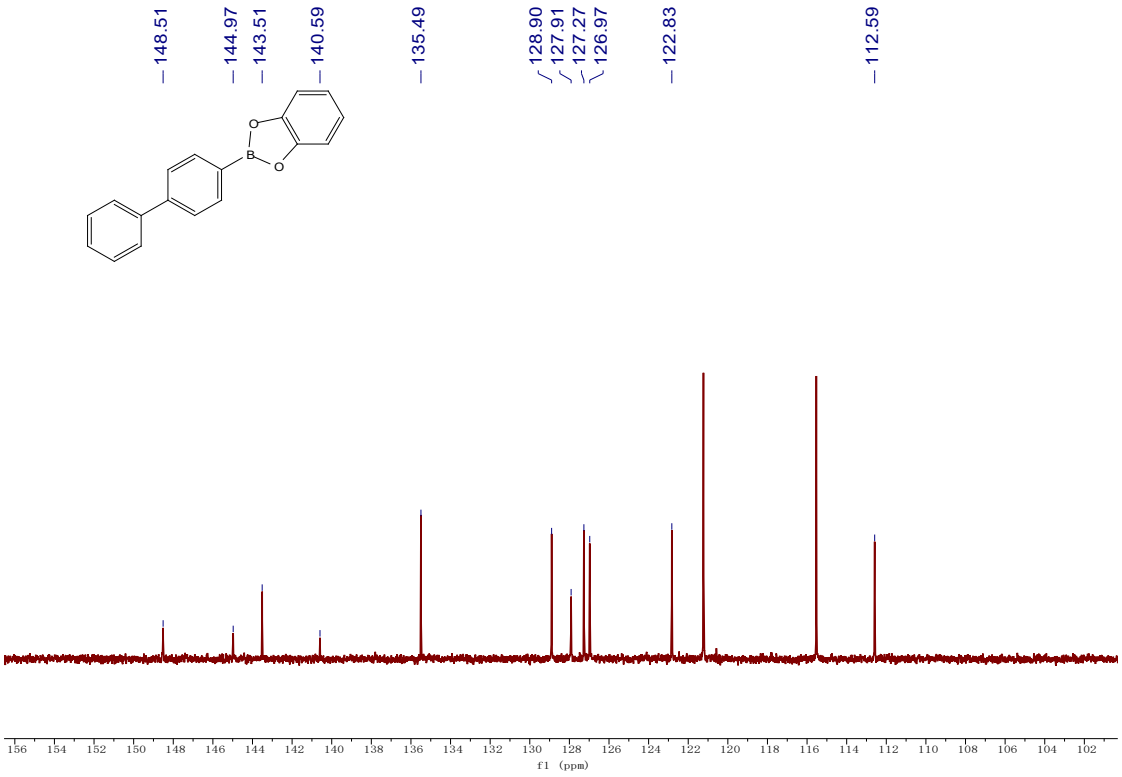

31.38
O
B
O
S
60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

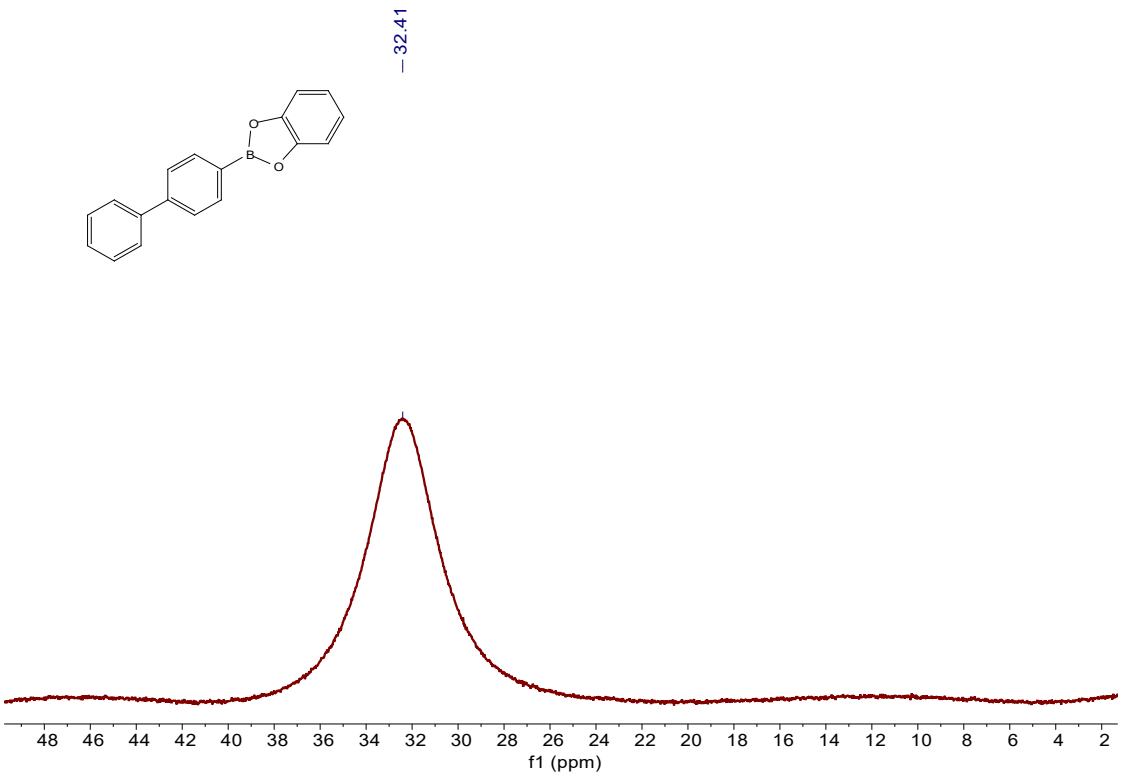

337.14182
339.13730
305.15610
318.29916
334.29449
349.18109
362.23975
371.09915
381.16632
393.20691
337.14281
342.14867
Relative Abundance
m/z
NL:
1.82E8
30#13 RT: 0.19
AV: 1 T: FTMS + p
ESI Full ms
[50.0000-750.0000]
NL:
6.09E5
C20 H21 BO2 S +H:
C20 H22 B1 O2 S1
pa Chrg 1

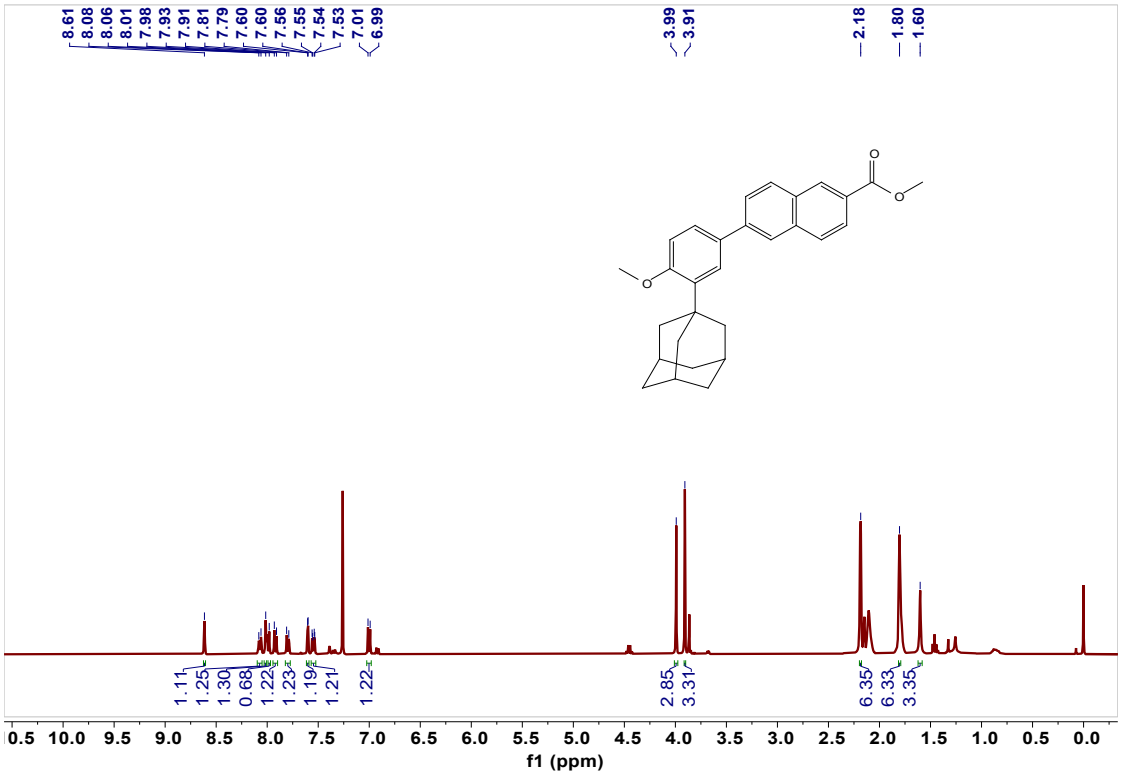

143.28
141.19
134.36
128.75
127.41
127.22
126.36
72.33
31.92
21.93
f1 (ppm)

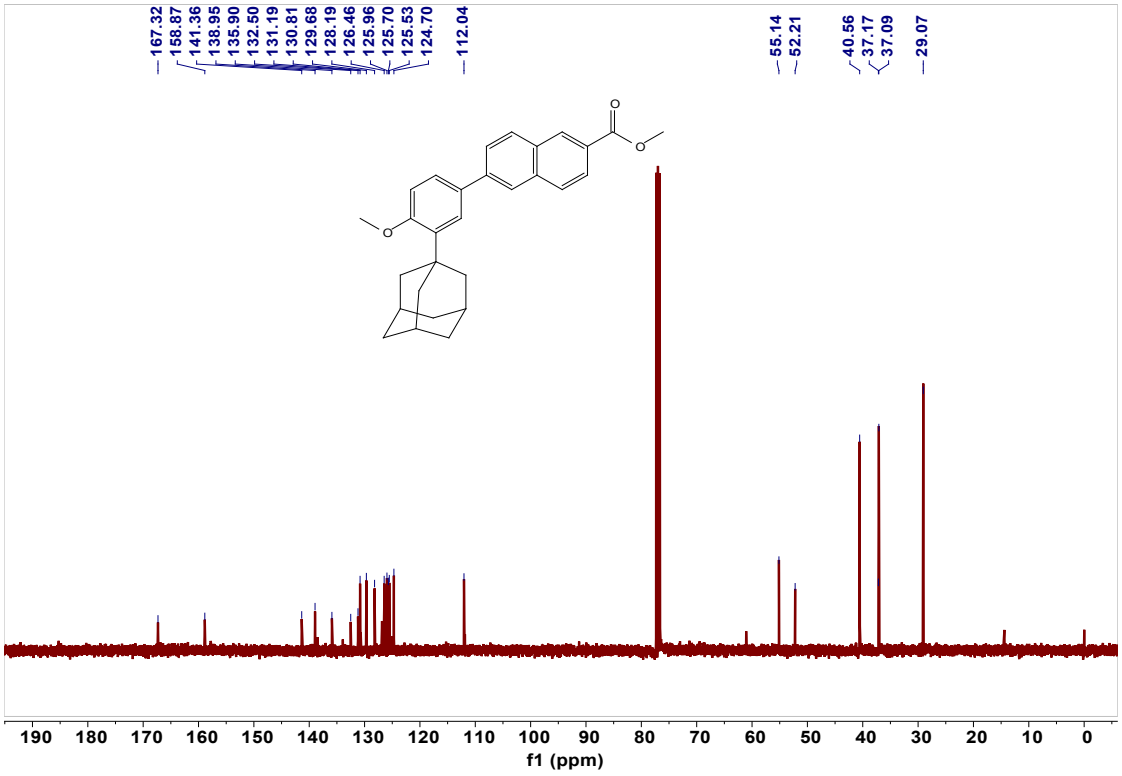

26.79
O
B
O
60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0 -2 -4
f1 (ppm)

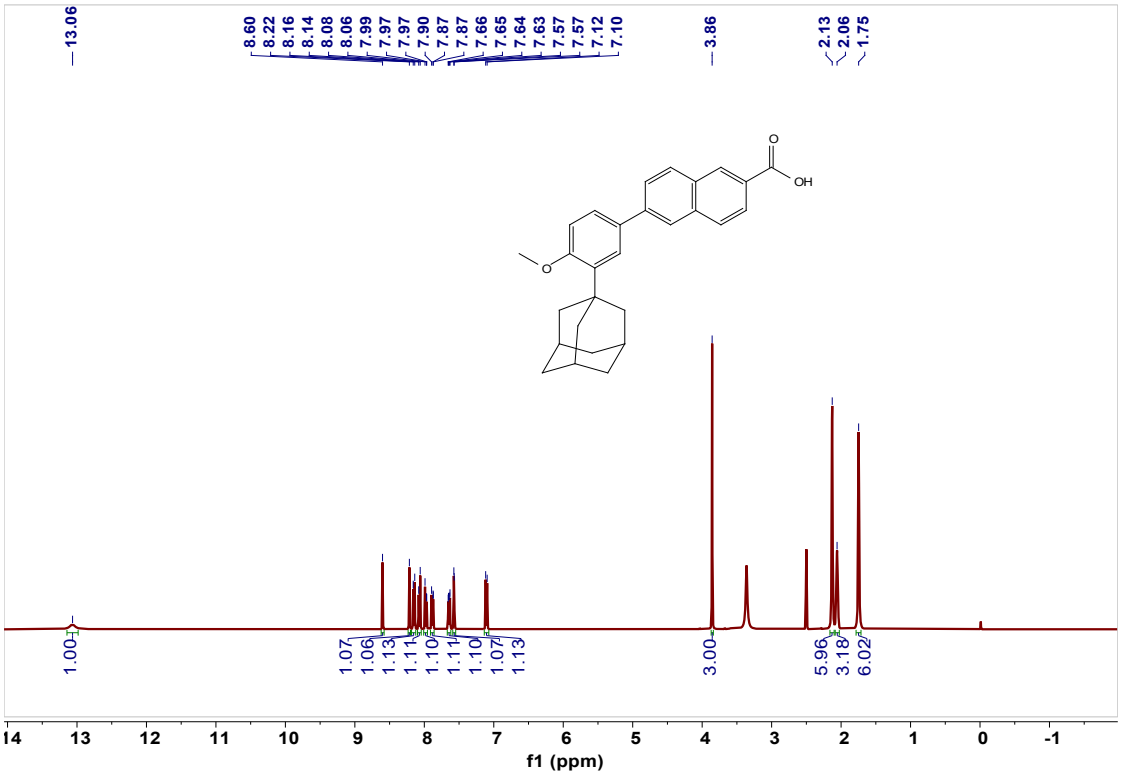

8.18
8.16
7.75
7.73
7.69
7.67
7.51
7.49
7.47
7.43
7.41
7.36
7.35
7.34
7.34
7.17
7.16
7.15
7.14
O
B
O
2.00
2.05
2.15
2.30
1.17
2.10
2.32
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

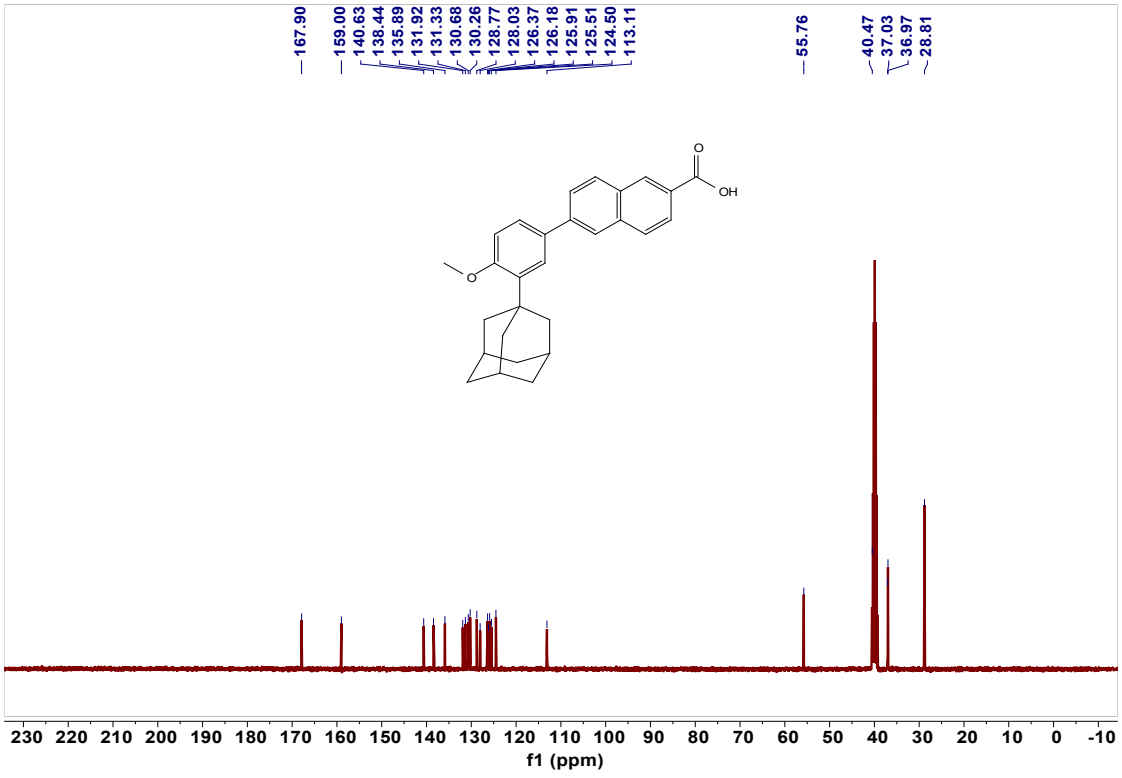

148.51
144.97
143.51
140.59
135.49
128.90
127.91
127.27
126.97
122.83
112.59
O
B
O
156 154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102
f1 (ppm)

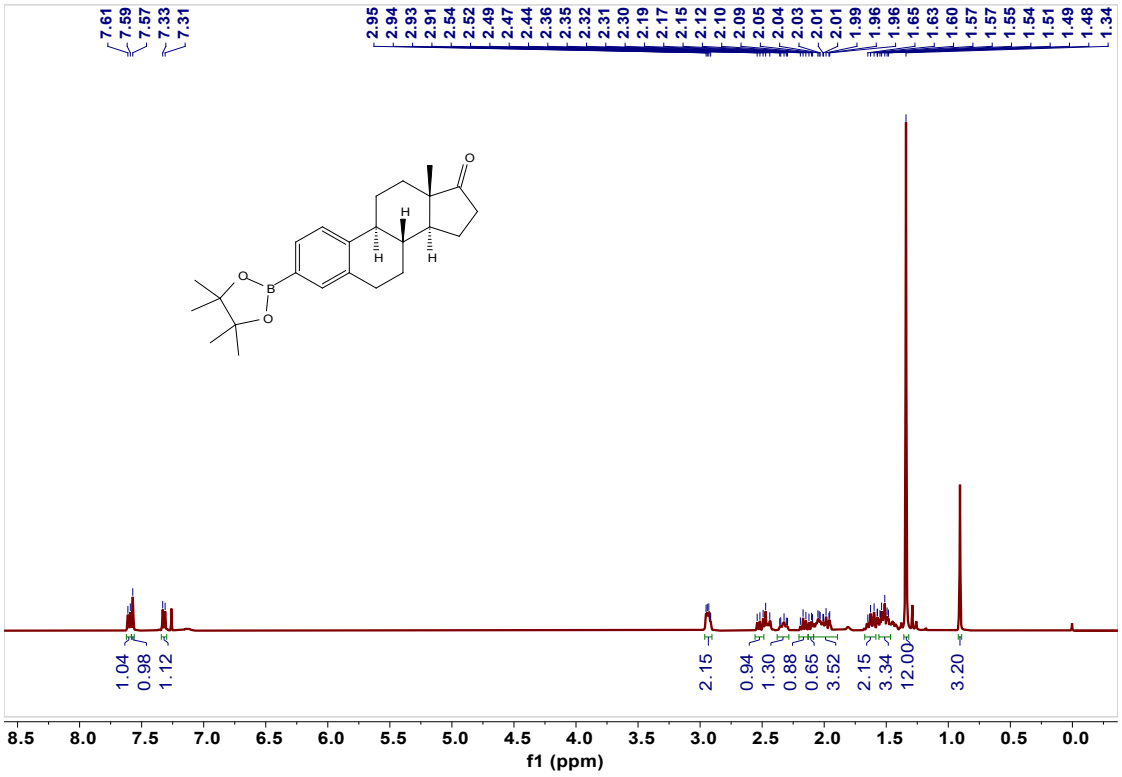

32.41
O
B
O
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

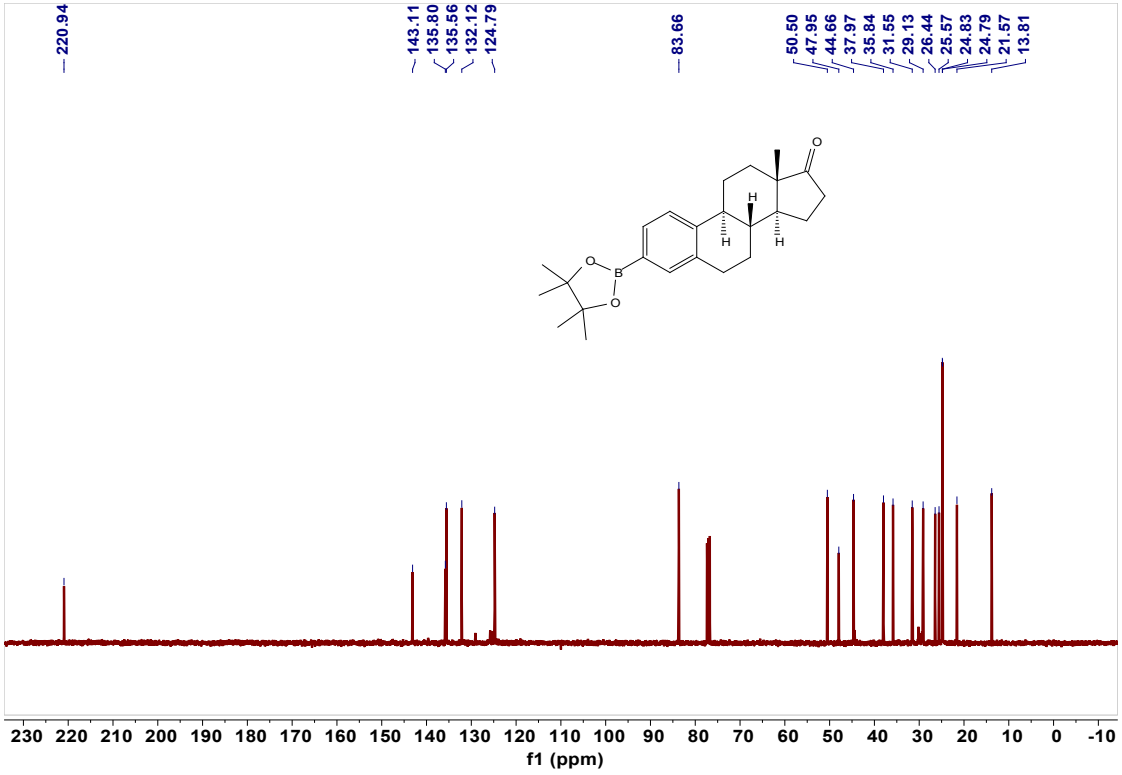

8.61
8.08
8.06
8.01
7.98
7.93
7.91
7.81
7.79
7.60
7.60
7.56
7.55
7.54
7.53
7.01
6.99
3.99
3.91
2.18
1.80
1.60
1.11
1.25
1.30
0.68
1.22
1.23
1.19
1.21
1.22
2.85
3.31
6.35
6.33
3.35
f1 (ppm)

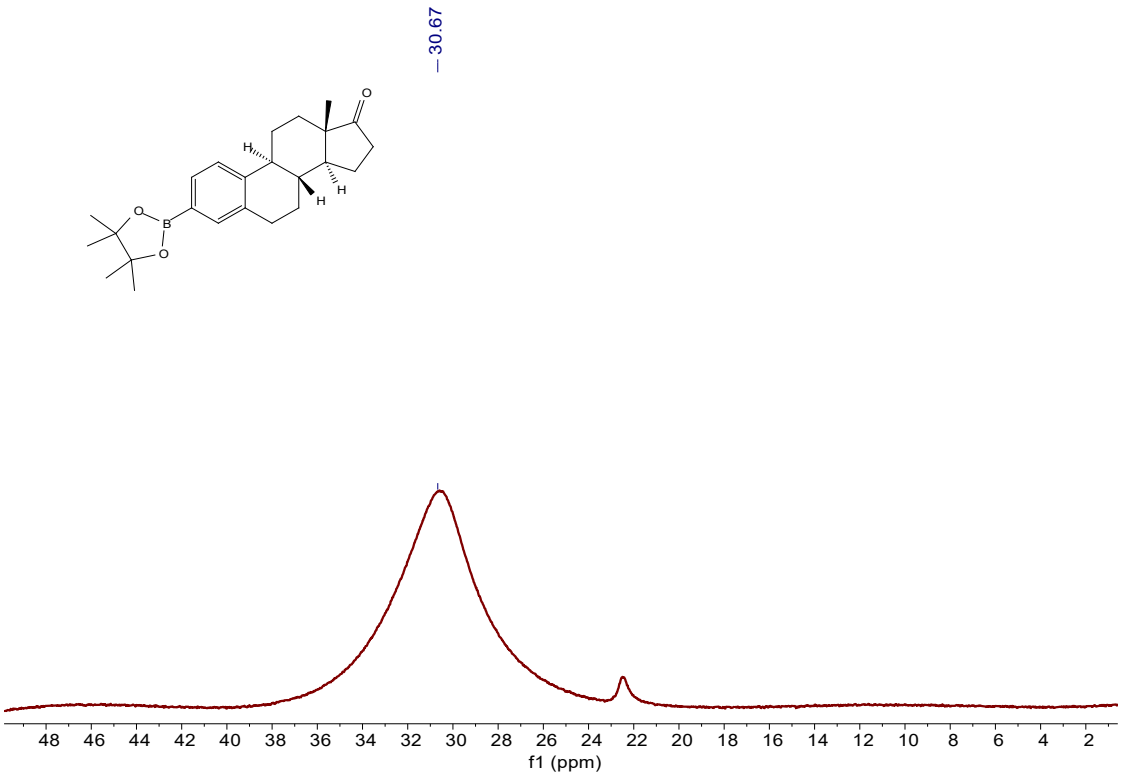

167.32
158.87
141.36
138.95
135.90
132.50
131.19
130.81
129.68
128.19
126.46
125.96
125.70
125.53
124.70
112.04
55.14
52.21
40.56
37.17
37.09
29.07
f1 (ppm)

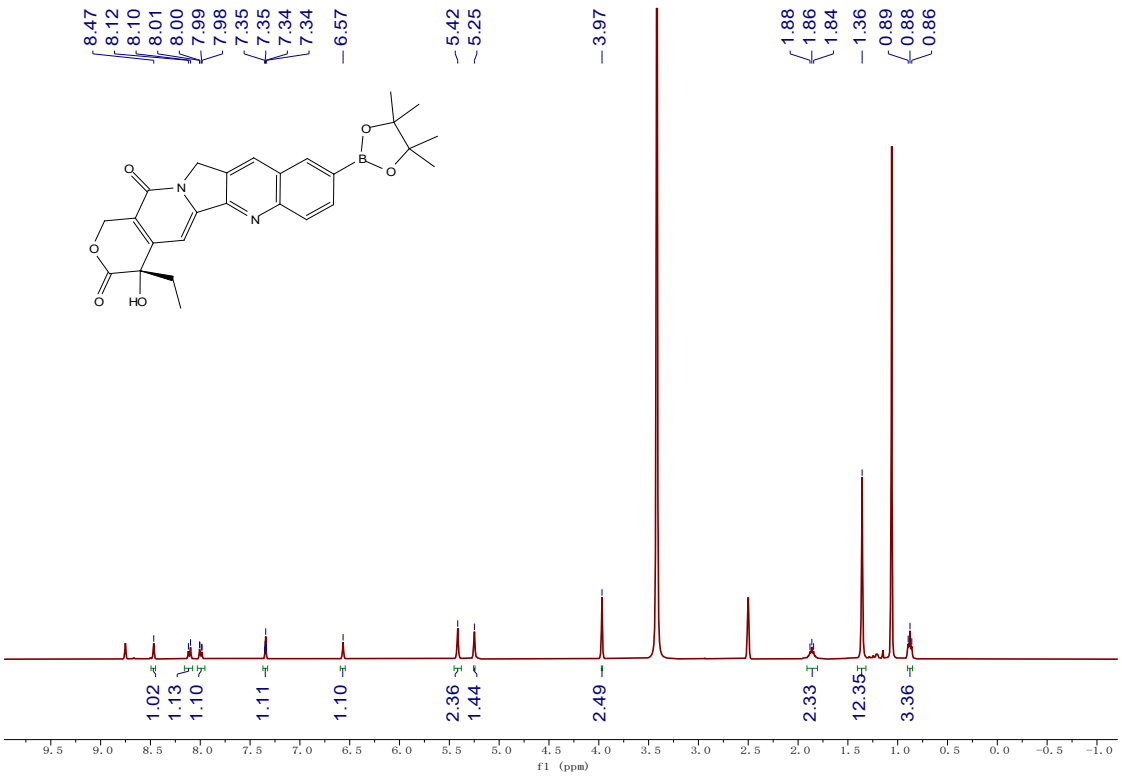

13.06
8.60
8.22
8.16
8.14
8.08
8.06
7.99
7.97
7.97
7.90
7.87
7.87
7.66
7.65
7.64
7.63
7.57
7.57
7.12
7.10
3.86
2.13
2.06
1.75
O
OH
O
1.00
1.07
1.06
1.13
1.14
1.10
1.14
1.10
1.07
1.13
3.00
5.96
3.18
6.02
f1 (ppm)

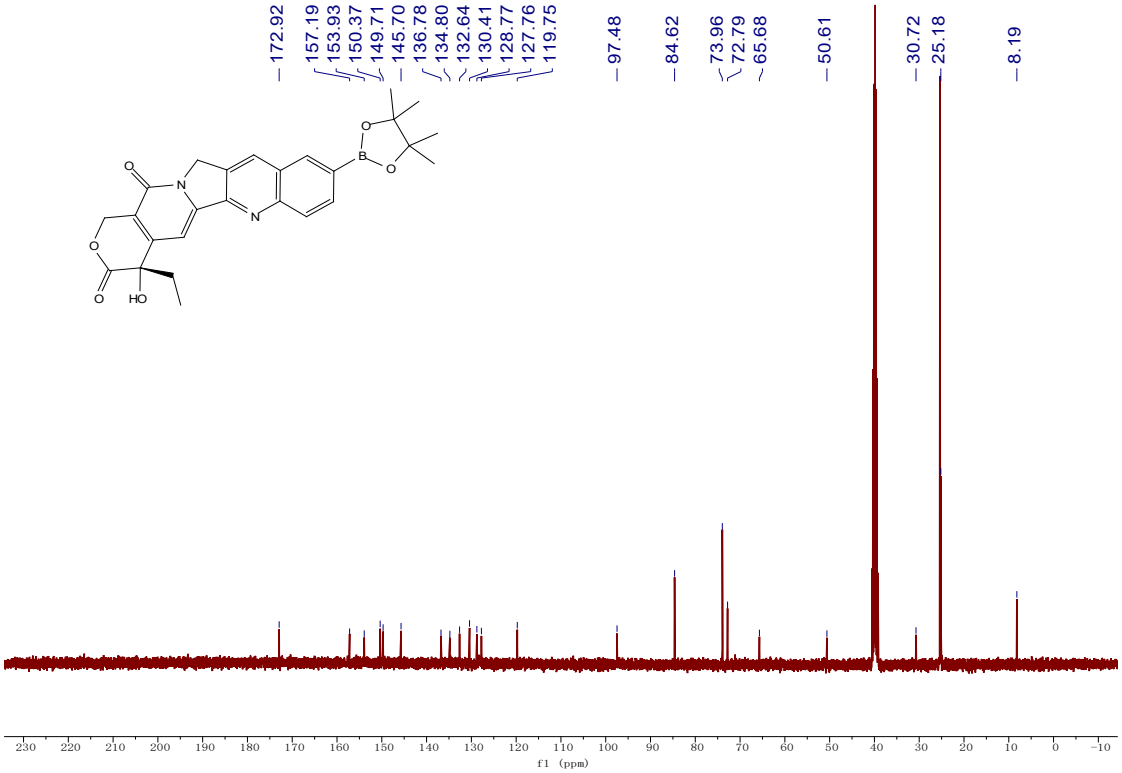

167.90
159.00
140.63
138.44
135.89
131.92
131.33
130.68
130.26
128.77
128.03
126.37
126.18
125.91
125.51
124.50
113.11
55.76
40.47
37.03
36.97
28.81
O
OH
O
f1 (ppm)

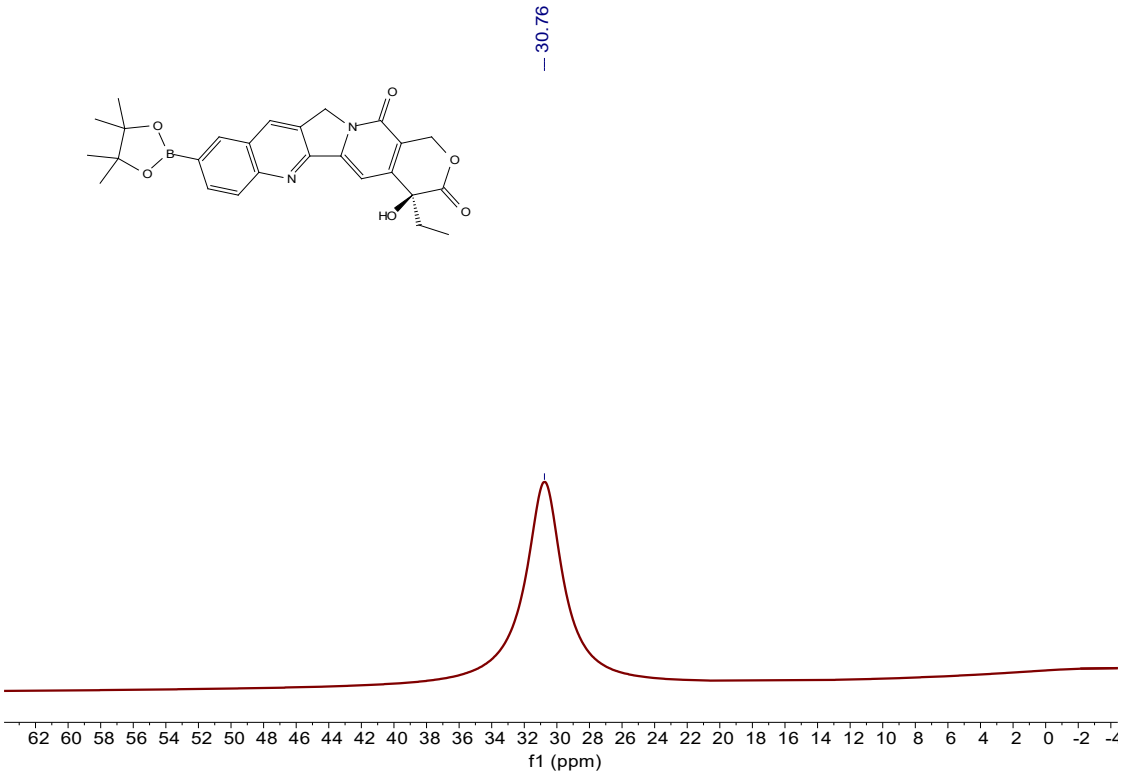

7.61
7.59
7.57
7.33
7.31
2.95
2.94
2.93
2.91
2.54
2.52
2.49
2.47
2.44
2.36
2.35
2.32
2.31
2.30
2.19
2.17
2.15
2.12
2.10
2.09
2.05
2.04
2.03
2.01
2.01
1.99
1.96
1.96
1.65
1.63
1.60
1.57
1.57
1.55
1.54
1.51
1.49
1.48
1.34
1.04
0.98
1.12
2.15
0.94
1.30
0.88
0.65
3.52
2.15
3.34
12.00
3.20
8.5 8.0 7.5 7.0 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)

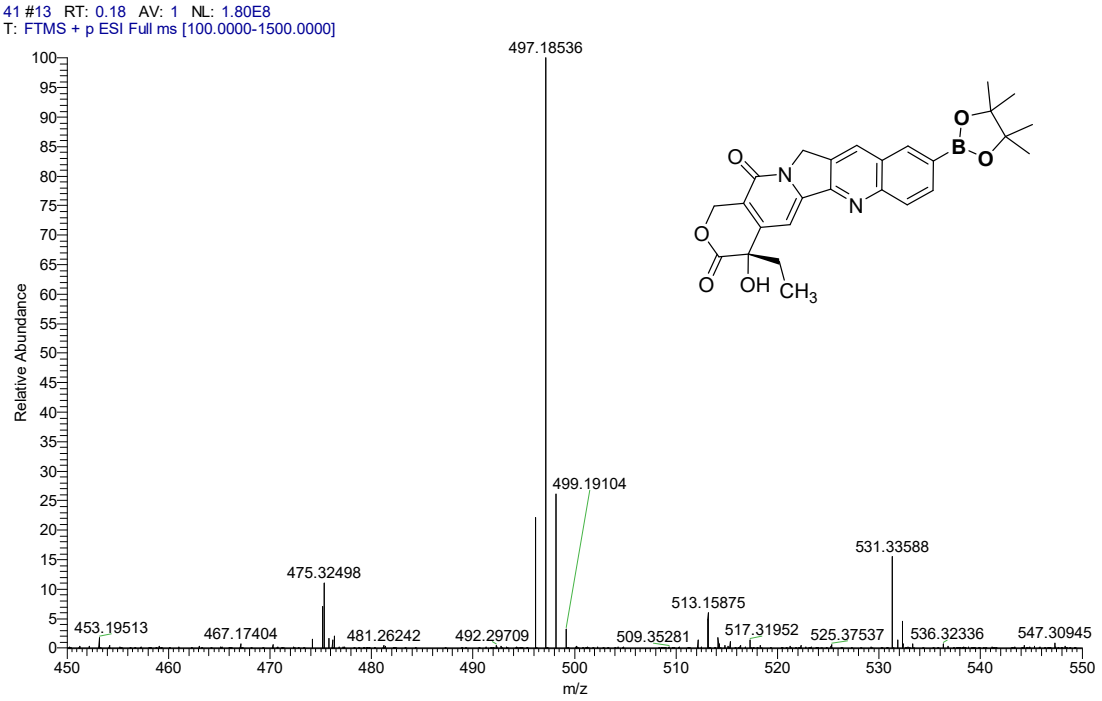

220.94
143.11
135.80
135.56
132.12
124.79
83.66
50.50
47.95
44.66
37.97
35.84
31.55
29.13
26.44
25.57
24.83
24.79
21.57
13.81
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

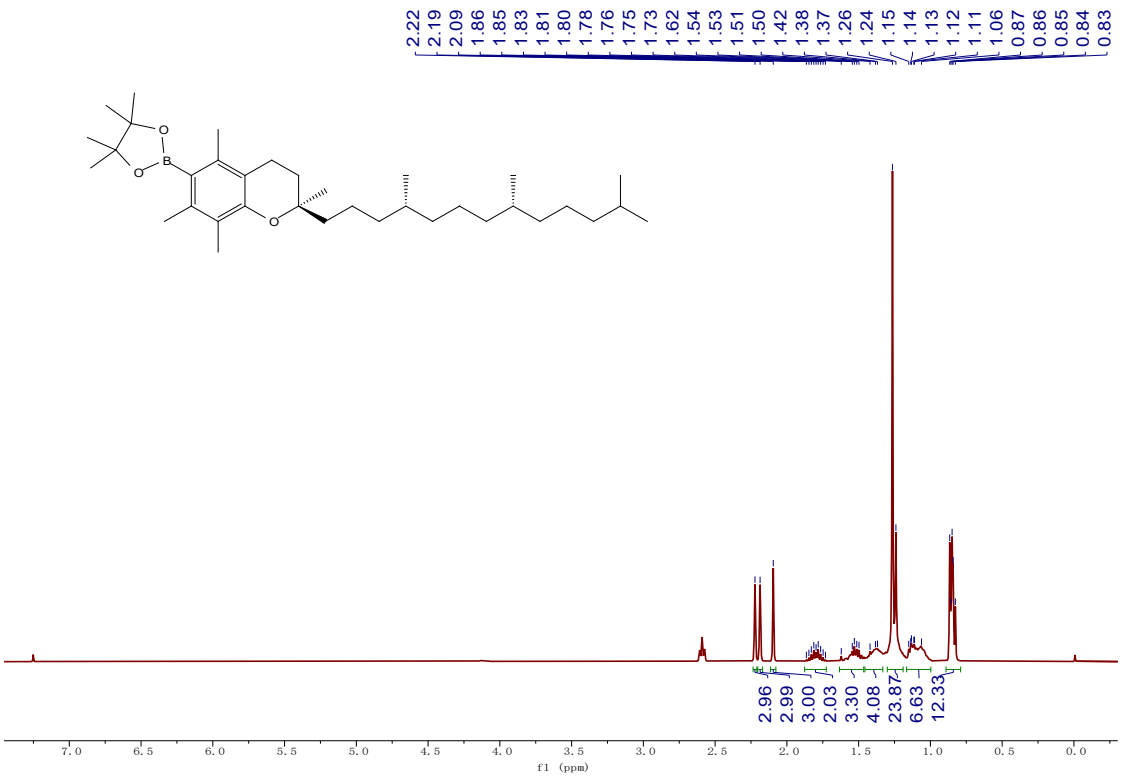

30.67
O
H
H
H
O
B
O
48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2
f1 (ppm)

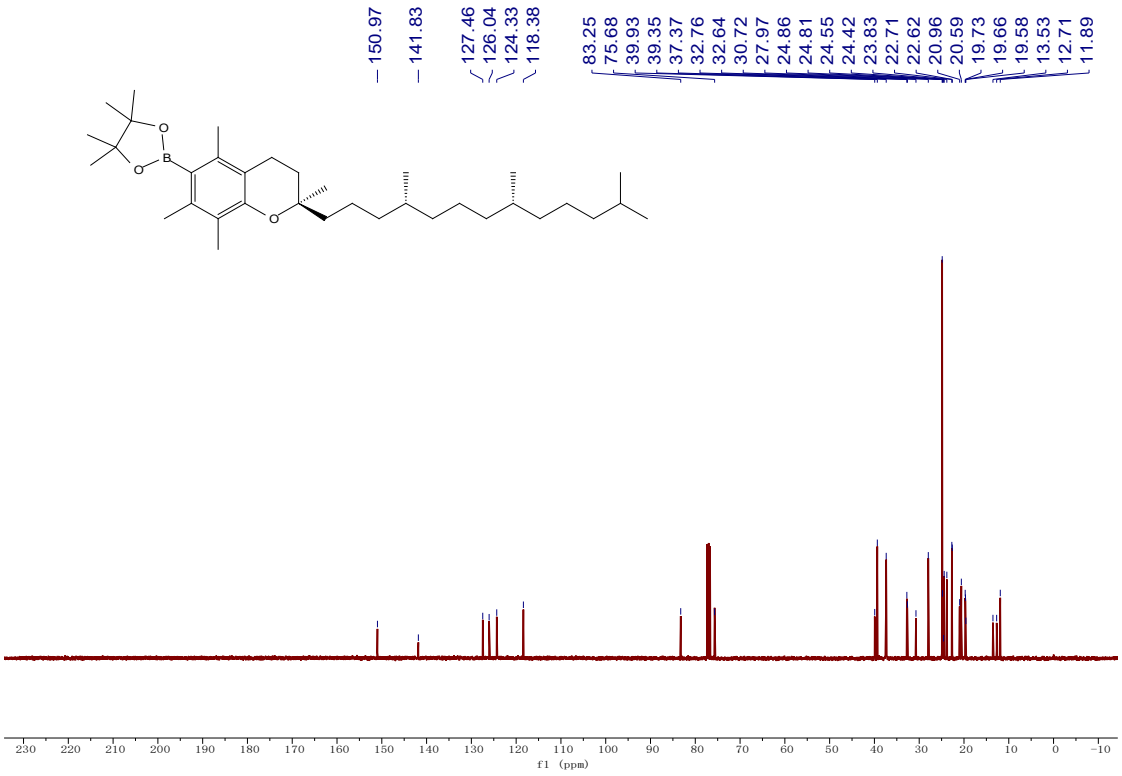

8.47
8.12
8.10
8.01
8.00
7.99
7.98
7.35
7.35
7.34
7.34
6.57
5.42
5.25
3.97
1.88
1.86
1.84
1.36
0.89
0.88
0.86
O
N
N
O
B
O
O
O
HO
1.02
1.13
1.10
1.11
1.10
2.36
1.44
2.49
2.33
12.35
3.36
f1 (ppm)

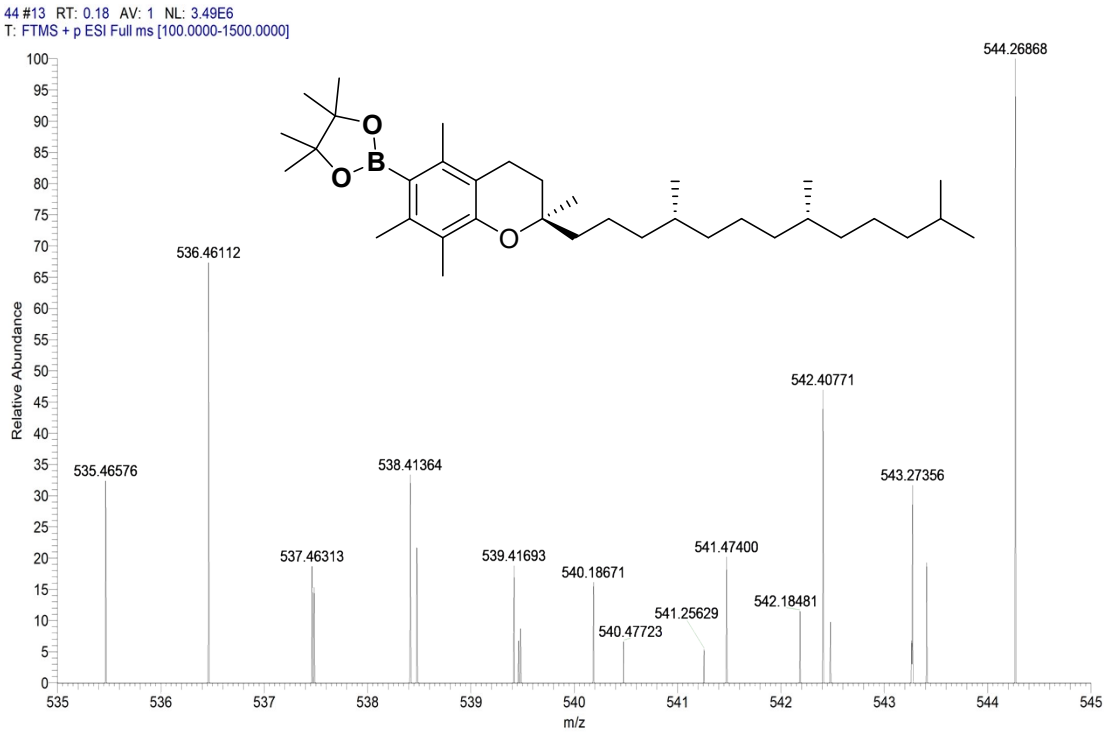

172.92
157.19
153.93
150.37
149.71
145.70
136.78
134.80
132.64
130.41
128.77
127.76
119.75
97.48
84.62
73.96
72.79
65.68
50.61
30.72
25.18
8.19
f1 (ppm)

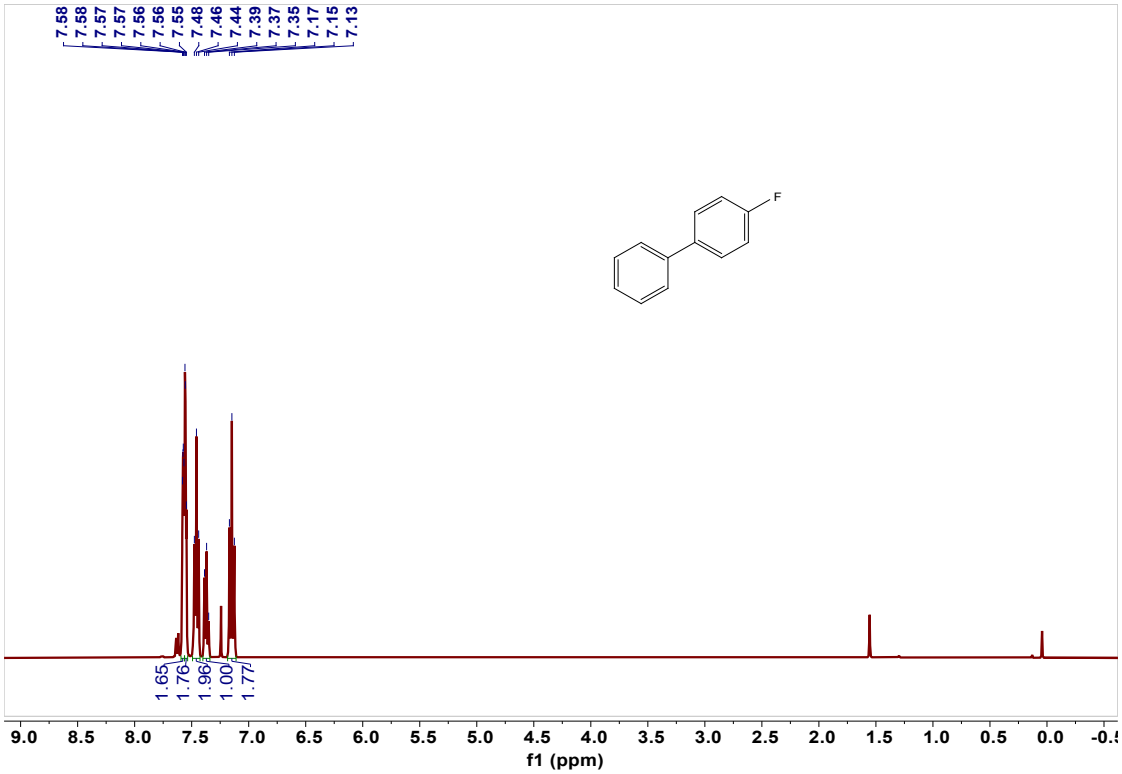

30.76
f1 (ppm)

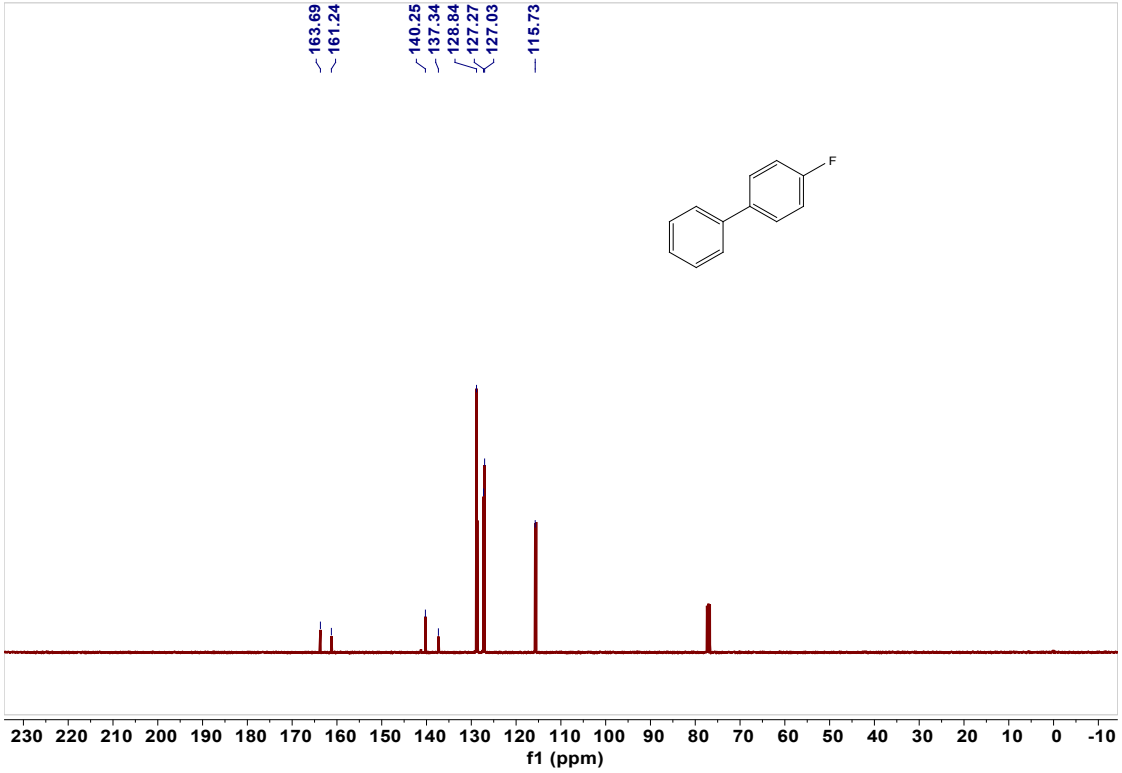

41 #13 RT: 0.18 AV: 1 NL: 1.80E8
T: FTMS + p ESI Full ms [100.0000-1500.0000]
497.18536
499.19104
475.32498
531.33588
513.15875
453.19513
467.17404
481.26242
492.29709
509.35281
517.31952
525.37537
536.32336
547.30945
Relative Abundance
m/z

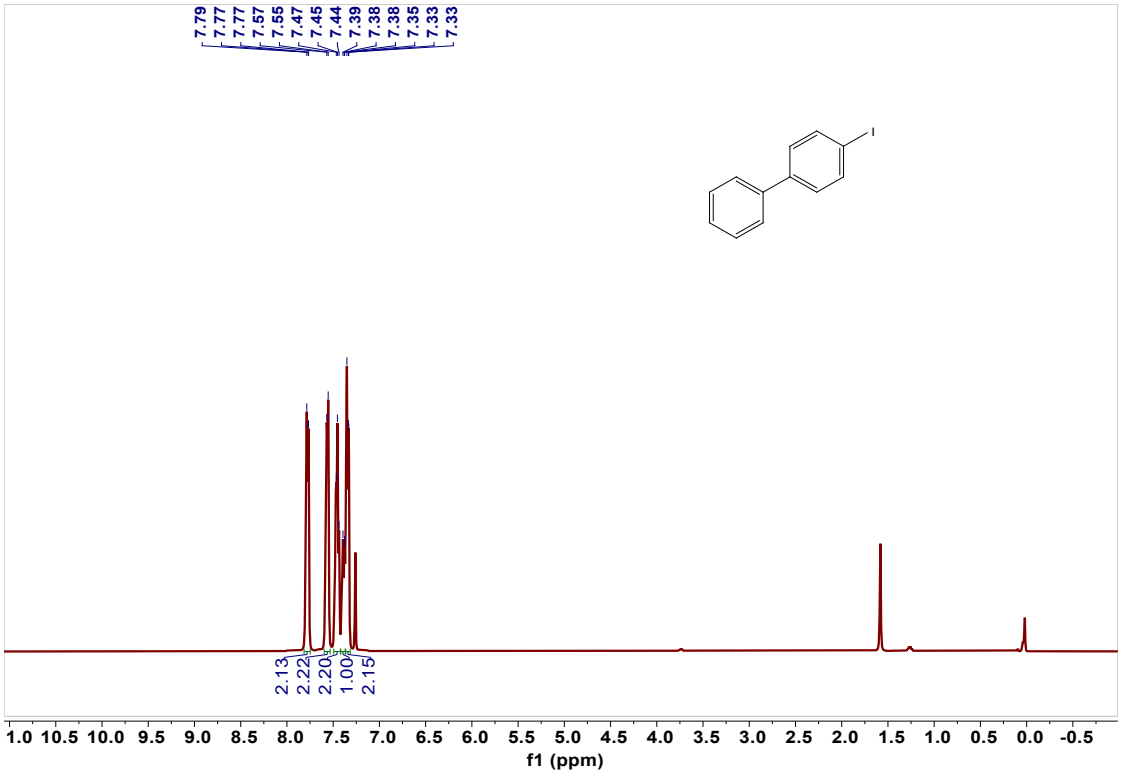

2.22
2.19
2.09
1.86
1.85
1.83
1.81
1.80
1.78
1.76
1.75
1.73
1.62
1.54
1.53
1.51
1.50
1.42
1.38
1.37
1.26
1.24
1.15
1.14
1.13
1.12
1.11
1.06
0.87
0.86
0.85
0.84
0.83
2.96
2.99
3.00
2.03
3.30
4.08
23.87
6.63
12.33
f1 (ppm)

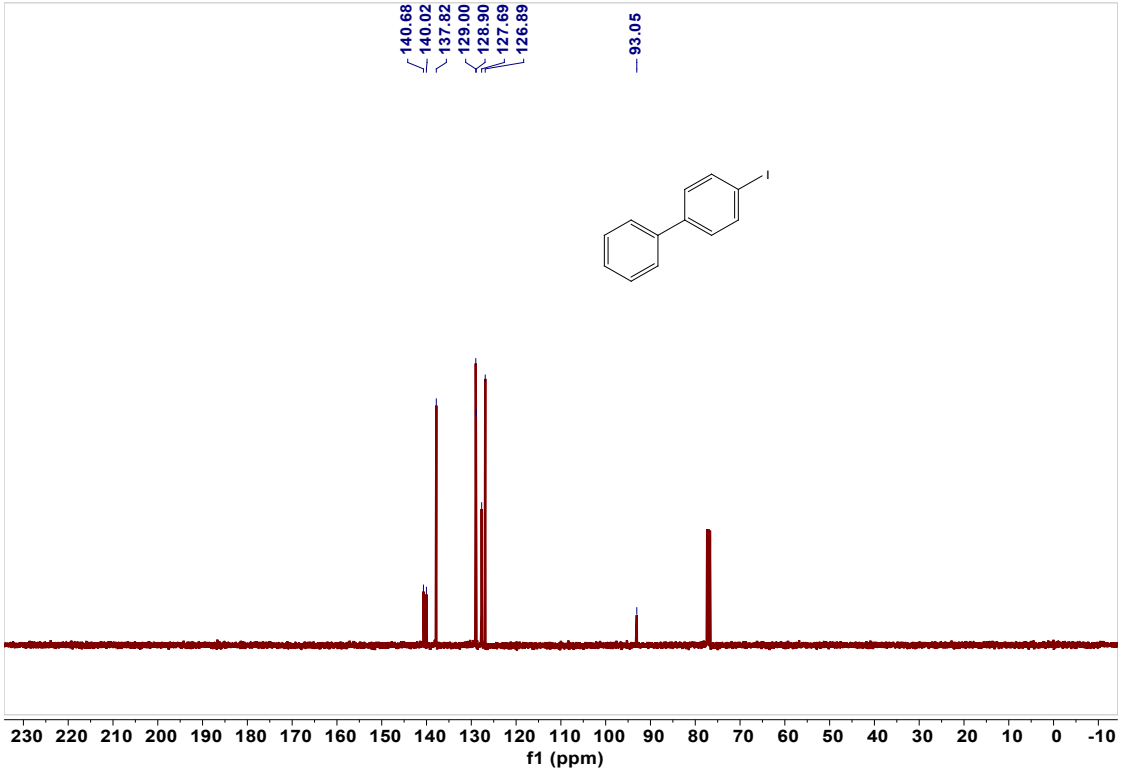

150.97
141.83
127.46
126.04
124.33
118.38
83.25
75.68
39.93
39.35
37.37
32.76
32.64
30.72
27.97
24.86
24.81
24.55
24.42
23.83
22.71
22.62
20.96
20.59
19.73
19.66
19.58
13.53
12.71
11.89
f1 (ppm)

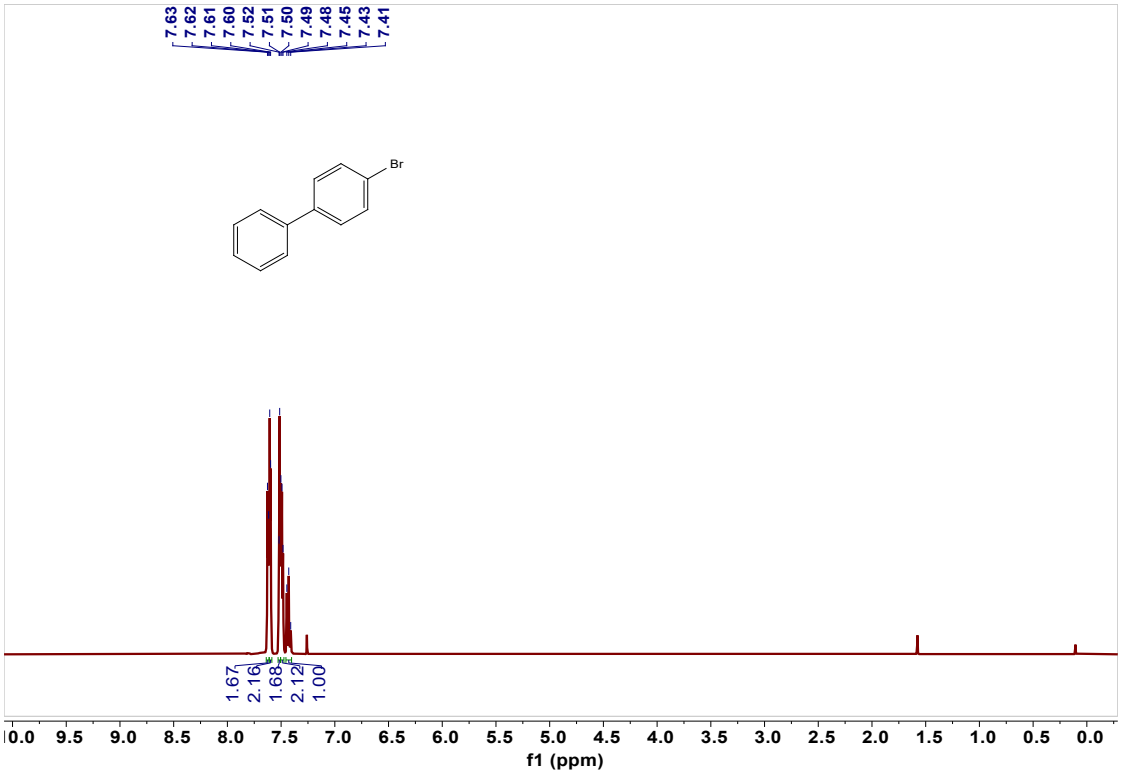

44 #13 RT: 0.18 AV: 1 NL: 3.49E6
T: FTMS + p ESI Full ms [100.0000-1500.0000]
544.26868
536.46112
542.40771
535.46576
538.41364
543.27356
537.46313
539.41693
541.47400
540.18671
542.18481
541.25629
540.47723
Relative Abundance
m/z

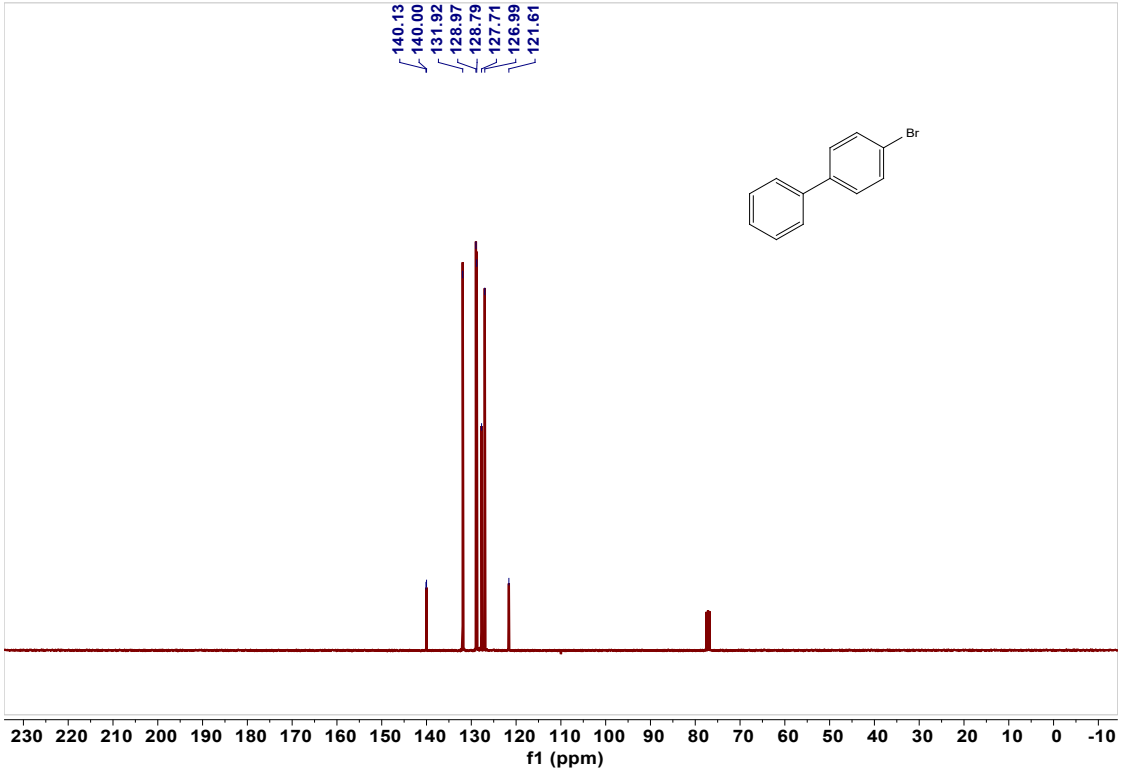

7.58
7.58
7.57
7.57
7.56
7.56
7.55
7.48
7.46
7.44
7.39
7.37
7.35
7.17
7.15
7.13
F
1.65
1.76
1.96
1.00
1.77
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

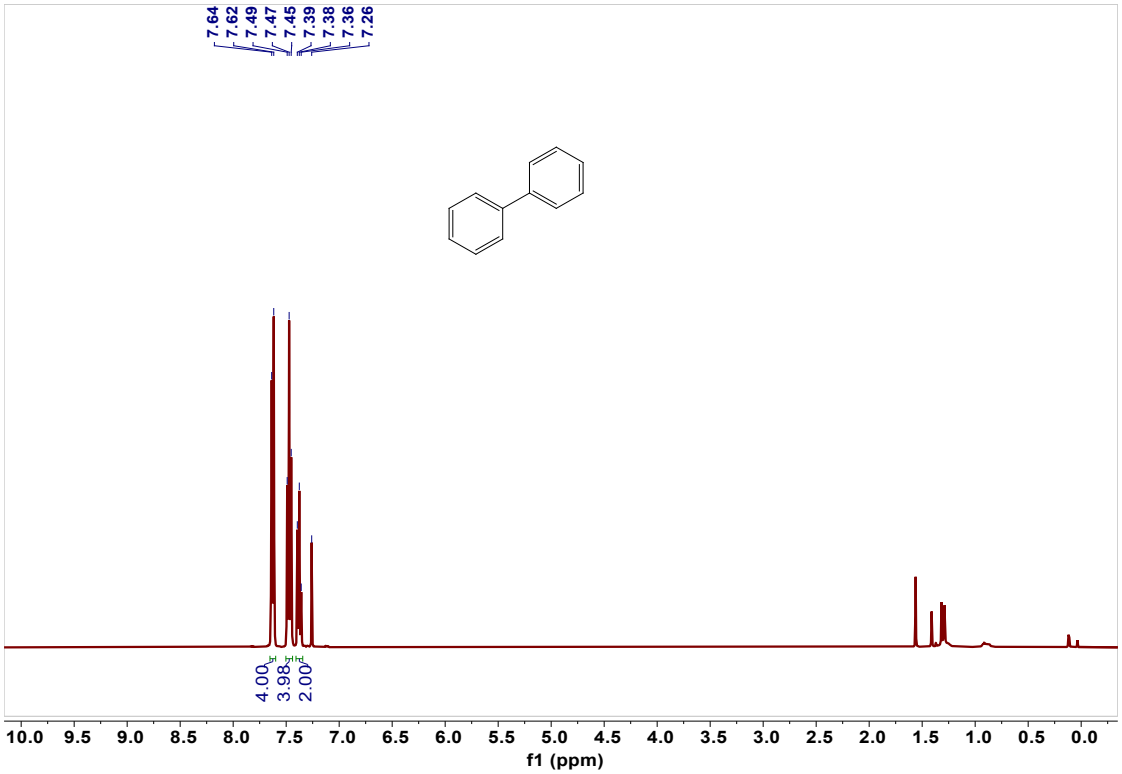

163.69
161.24
140.25
137.34
128.84
127.27
127.03
115.73
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

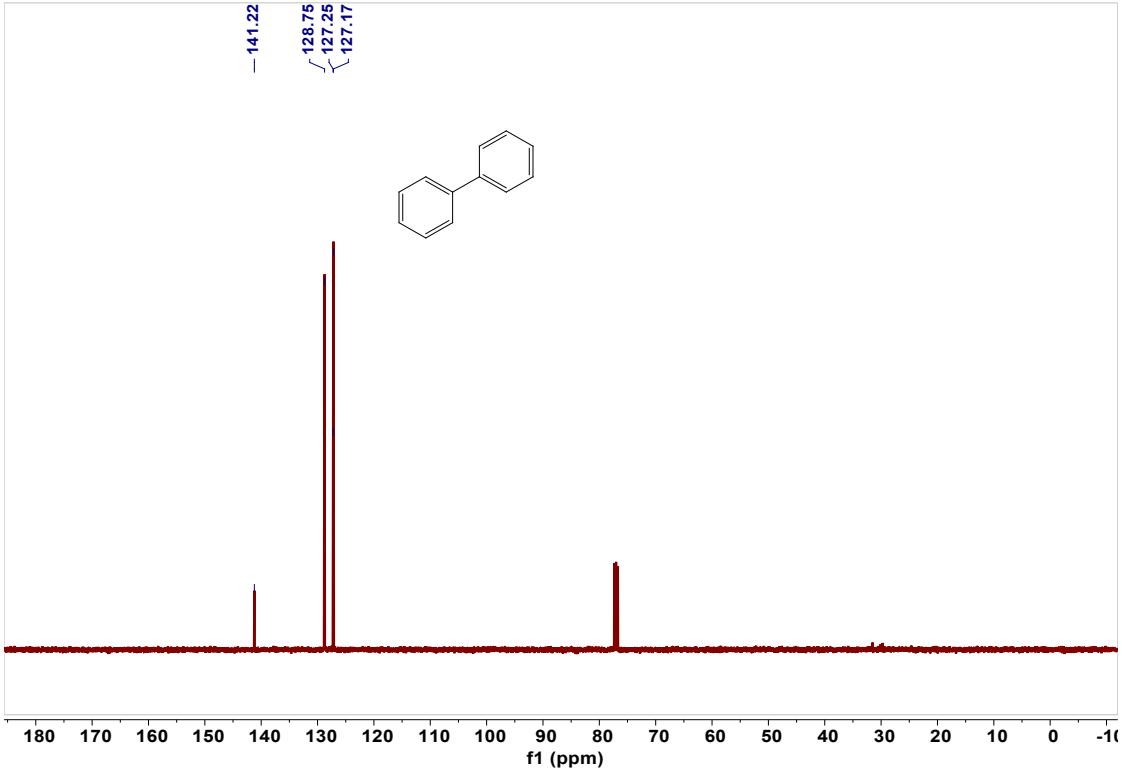

7.79
7.77
7.77
7.57
7.55
7.47
7.45
7.44
7.39
7.38
7.38
7.35
7.33
7.33
I
2.13
2.22
2.20
1.00
2.15
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

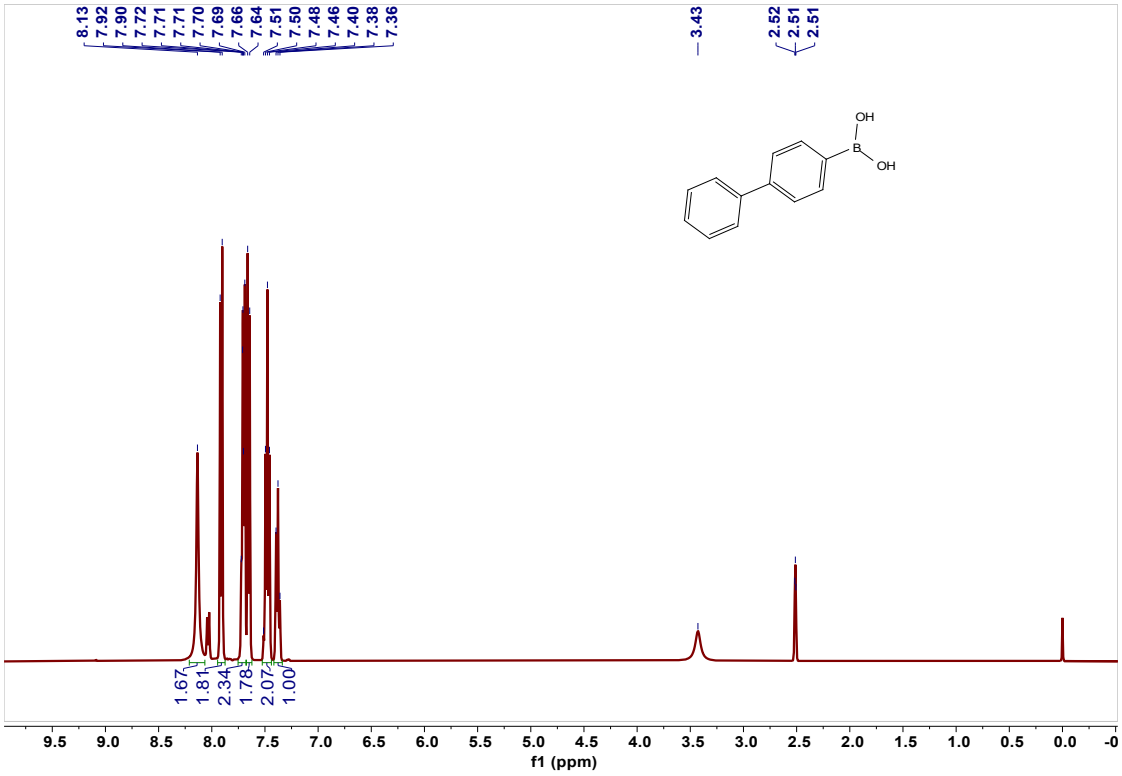

140.68
140.02
137.82
129.00
128.90
127.69
126.89
93.05
I
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

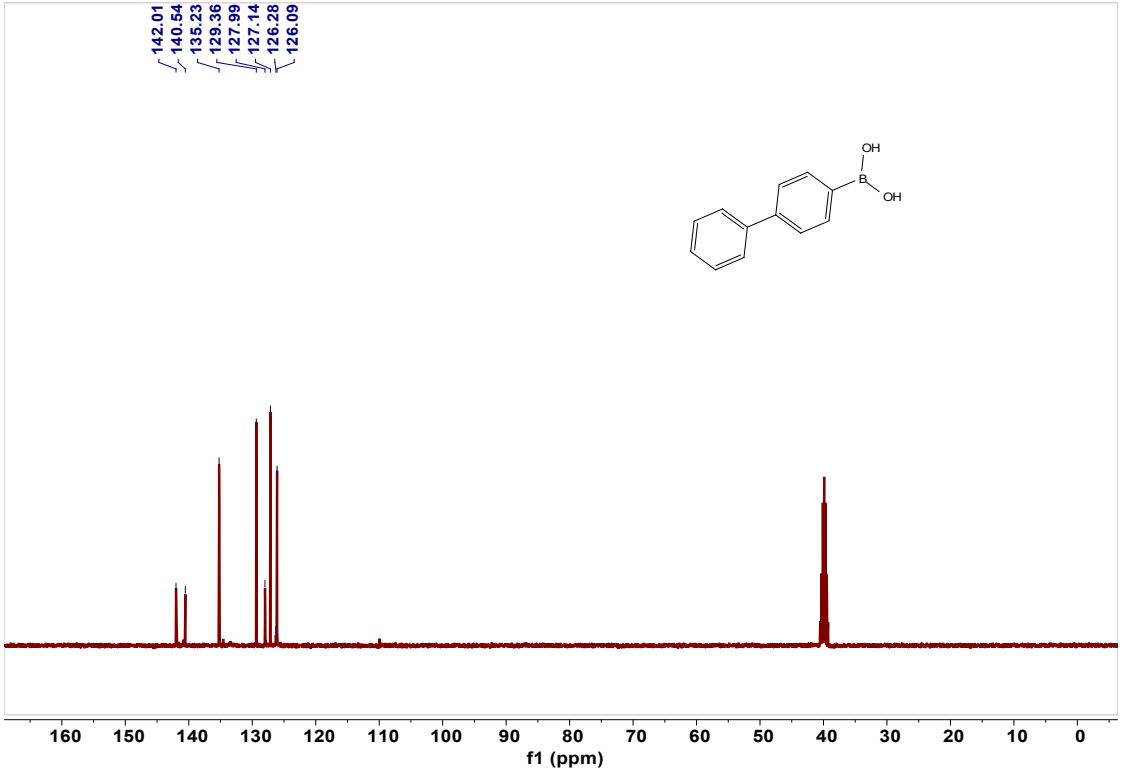

7.63
7.62
7.61
7.60
7.52
7.51
7.50
7.49
7.48
7.45
7.43
7.41
Br
1.67
2.16
1.68
2.12
1.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

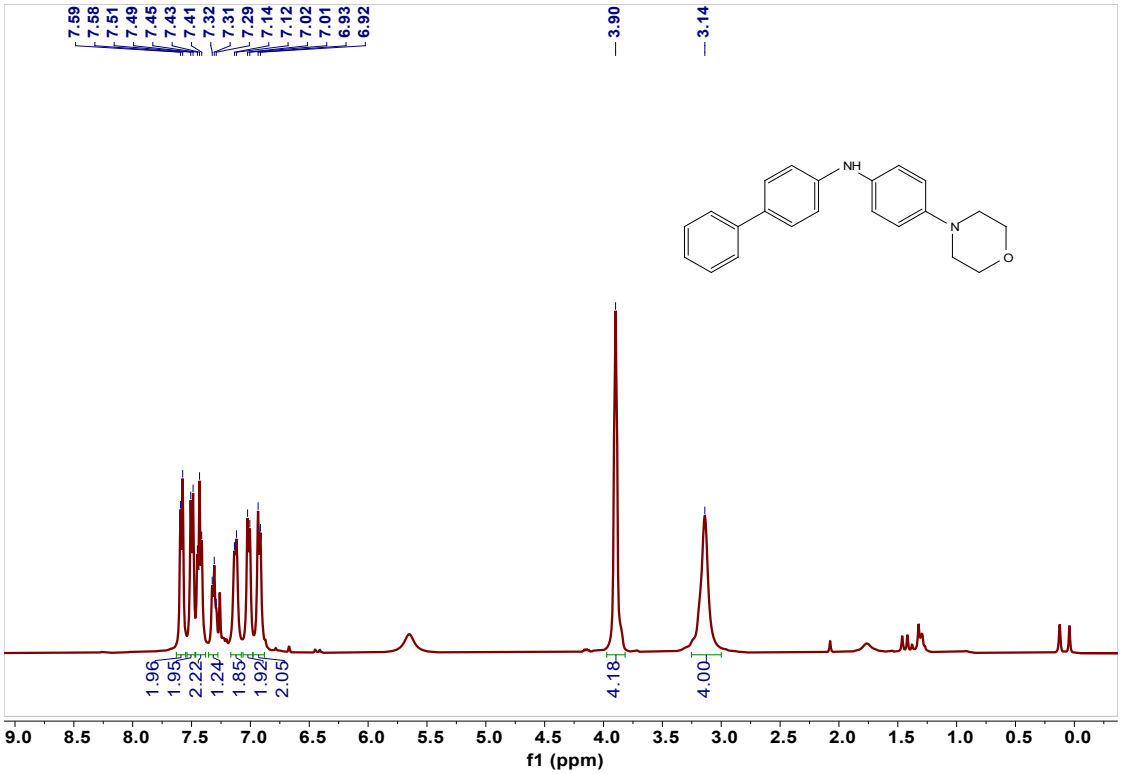

140.13
140.00
131.92
128.97
128.79
127.71
126.99
121.61
Br
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

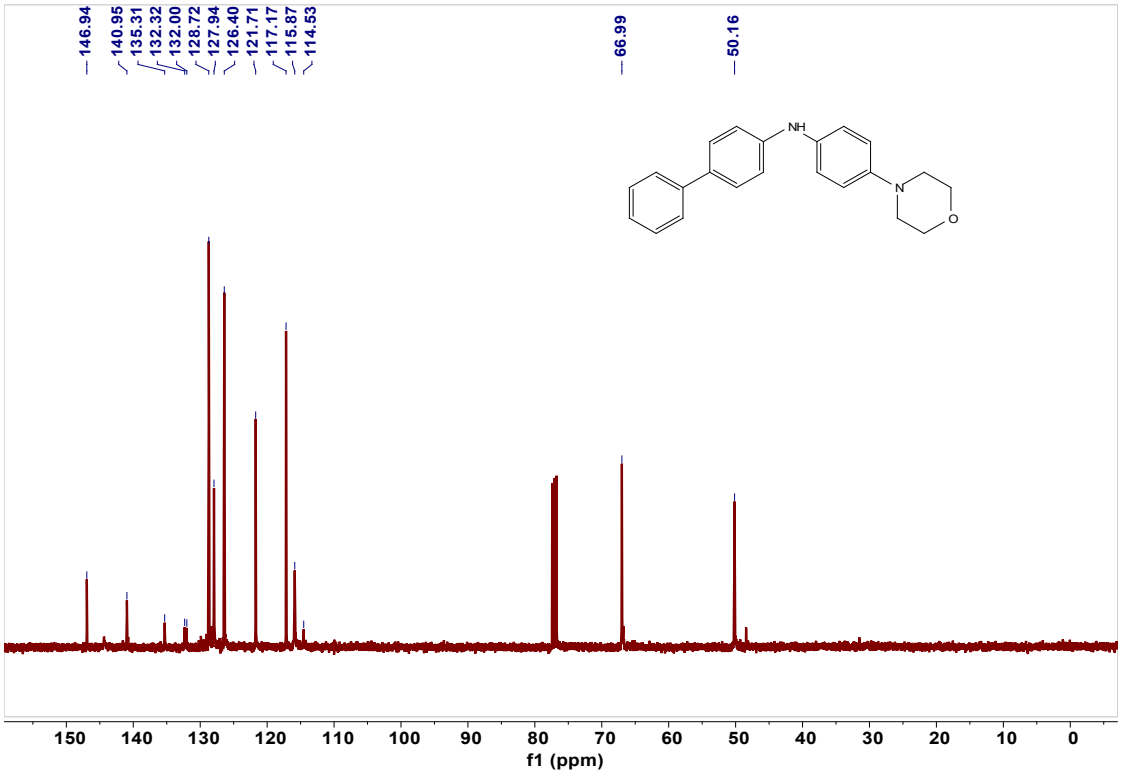

7.64
7.62
7.49
7.47
7.45
7.39
7.38
7.36
7.26
4.00
3.98
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

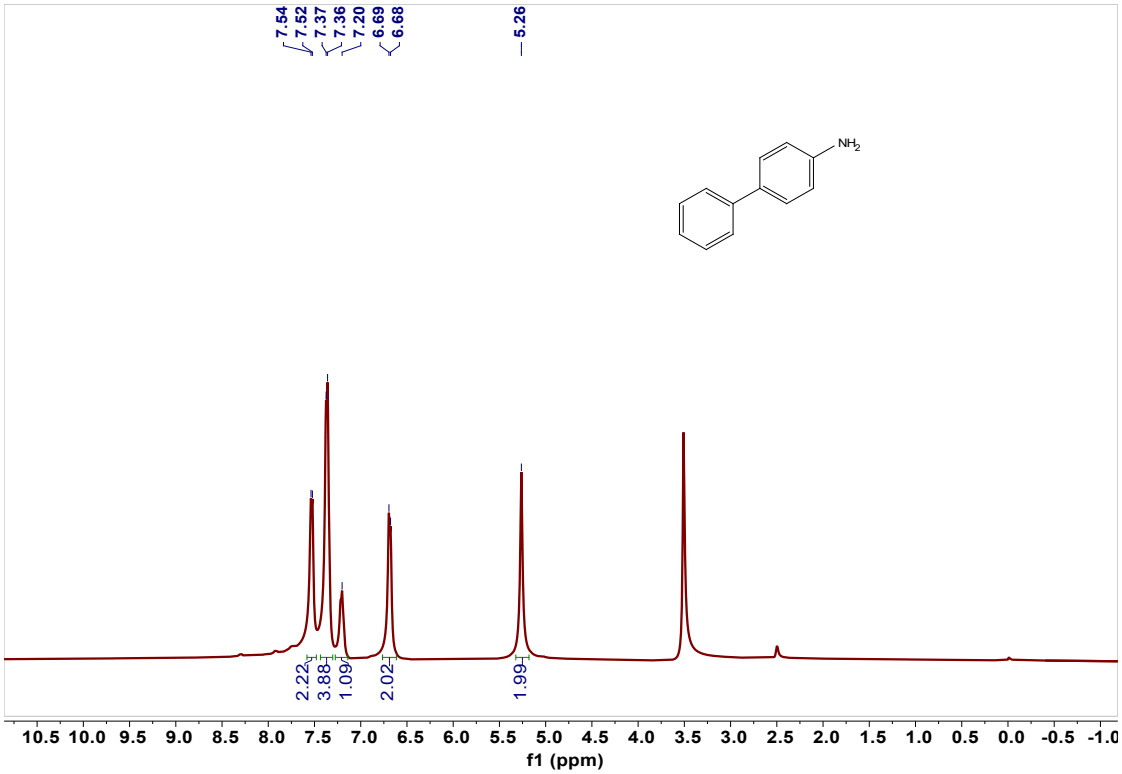

141.22
128.75
127.25
127.17
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

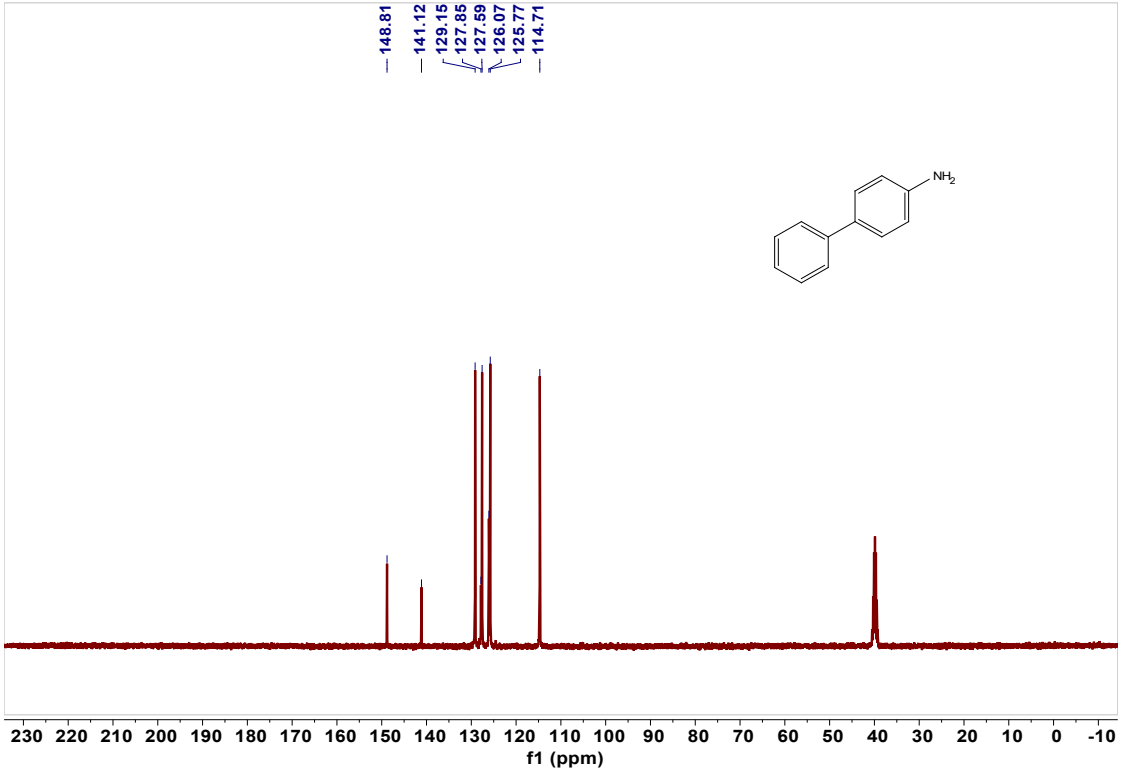

8.13
7.92
7.90
7.72
7.71
7.71
7.70
7.69
7.66
7.64
7.51
7.50
7.48
7.46
7.40
7.38
7.36
3.43
2.52
2.51
2.51
OH
B
OH
1.67
1.81
2.34
1.78
2.07
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

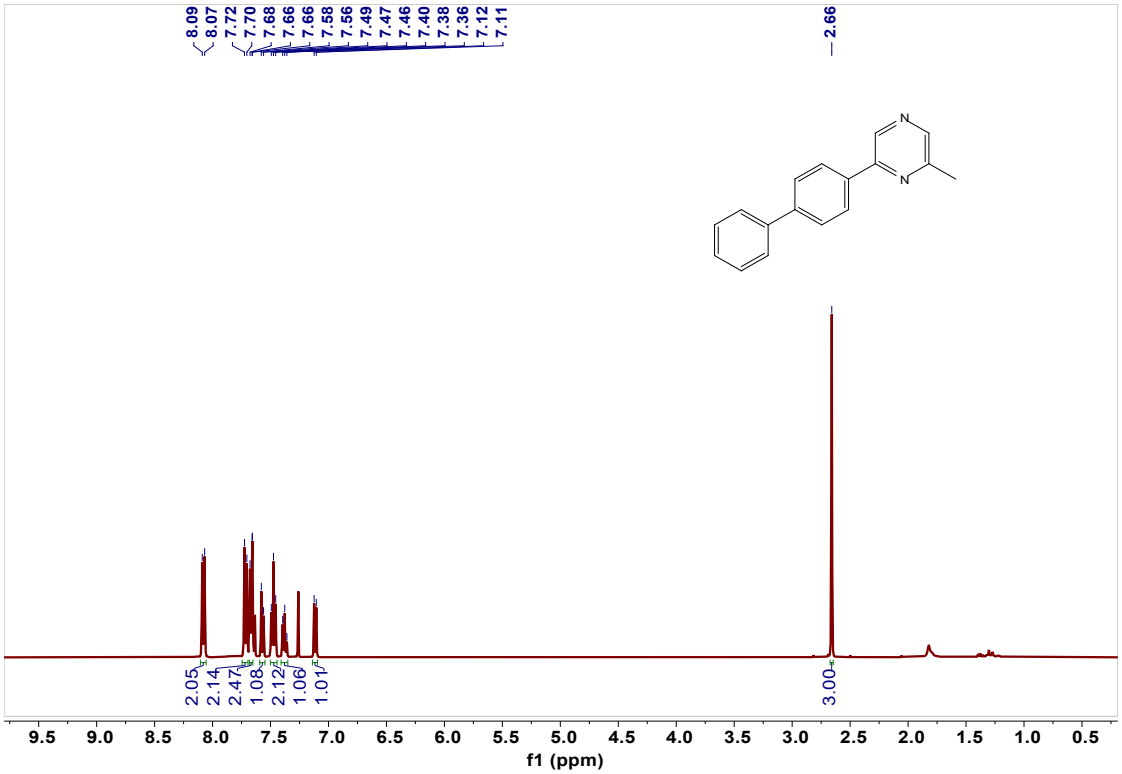

142.01
140.54
135.23
129.36
127.99
127.14
126.28
126.09
OH
B
OH
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

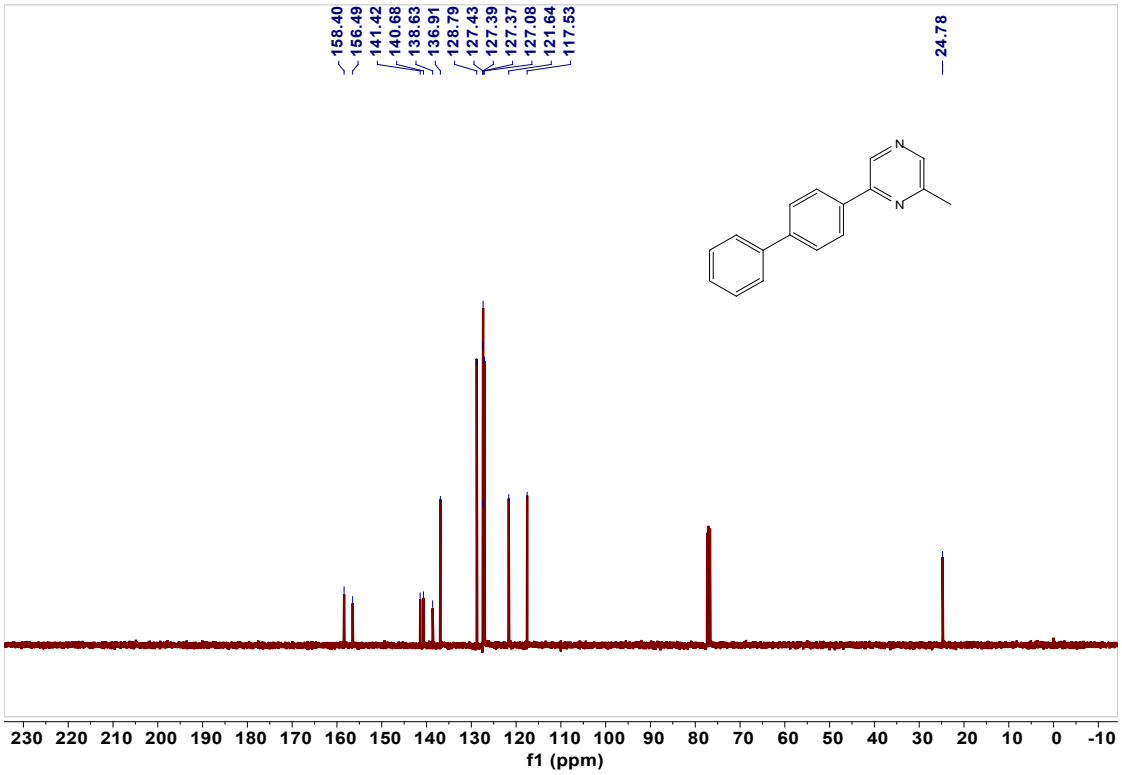

7.59
7.58
7.51
7.49
7.45
7.43
7.41
7.32
7.31
7.29
7.14
7.12
7.02
7.01
6.93
6.92
3.90
3.14
NH
N
O
1.96
1.95
2.22
1.24
1.85
1.92
2.05
4.18
4.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

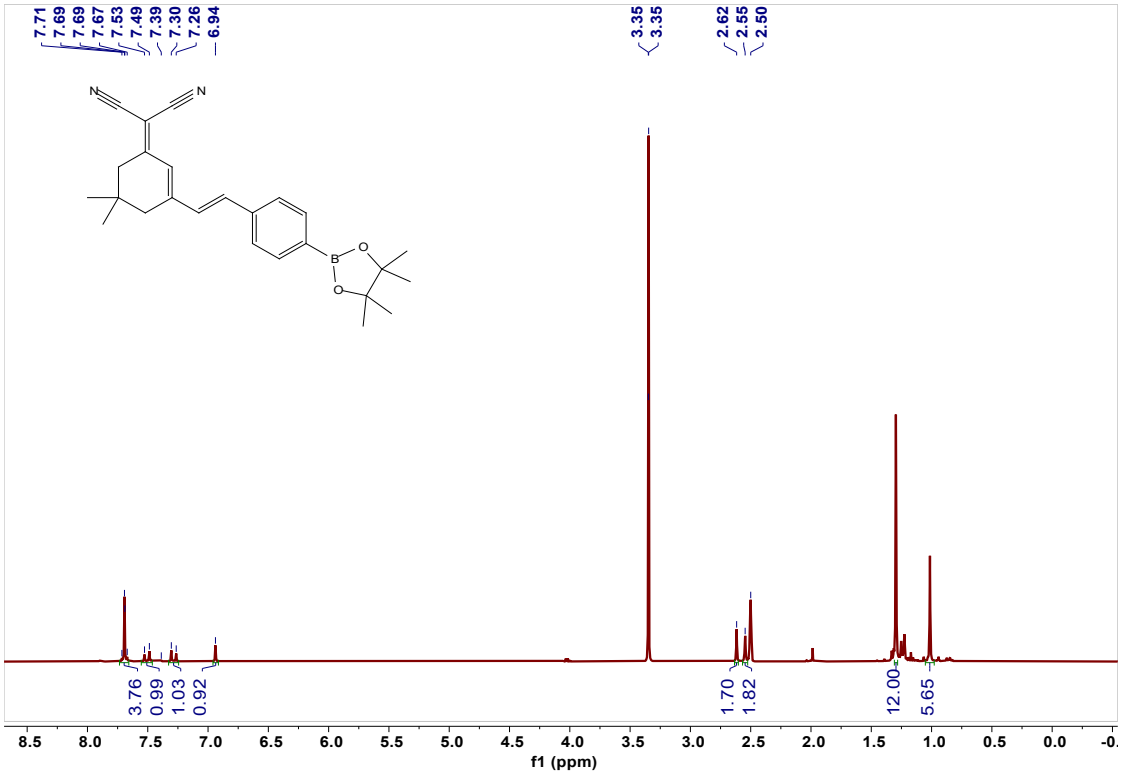

146.94
140.95
135.31
132.32
132.00
128.72
127.94
126.40
121.71
117.17
115.87
114.53
66.99
50.16
NH
N
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

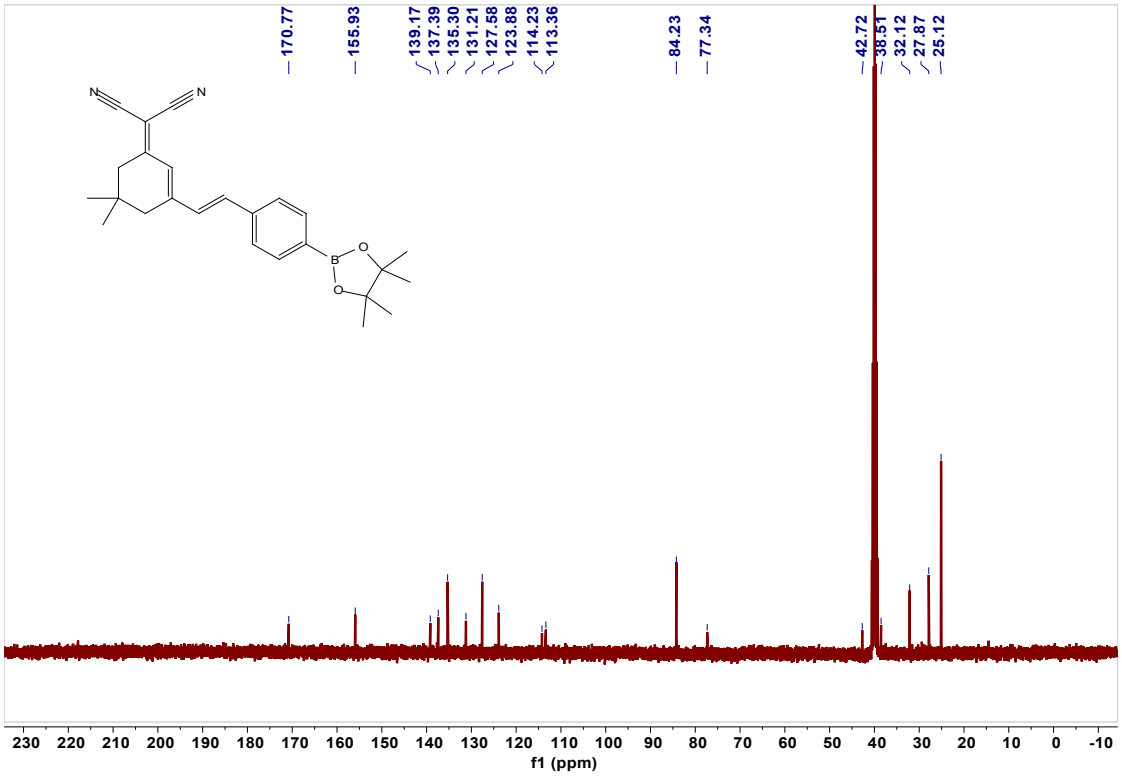

7.54
7.52
7.37
7.36
7.20
6.69
6.68
5.26
NH2
2.22
3.88
1.09
2.02
1.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

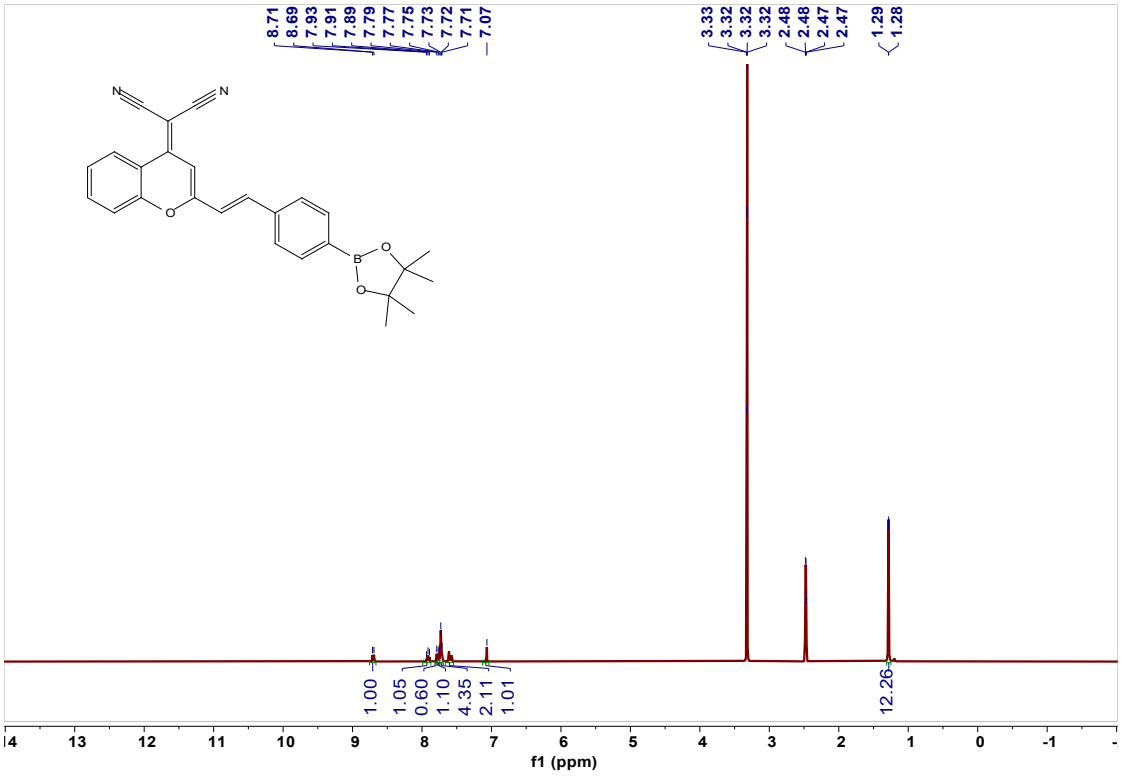

148.81
141.12
129.15
127.85
127.59
126.07
125.77
114.71
NH2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

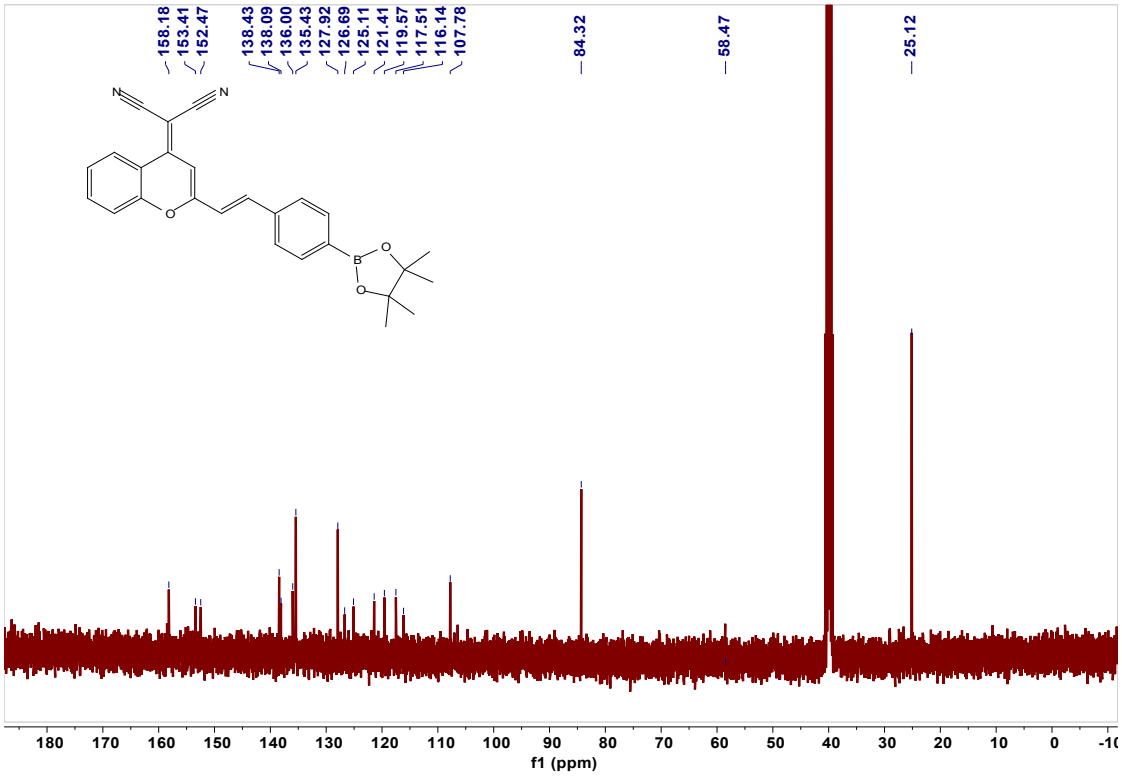

8.09
8.07
7.72
7.70
7.68
7.66
7.66
7.58
7.56
7.49
7.47
7.46
7.40
7.38
7.36
7.12
7.11
2.66
N
N
2.05
2.14
2.47
1.08
2.12
1.06
1.01
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

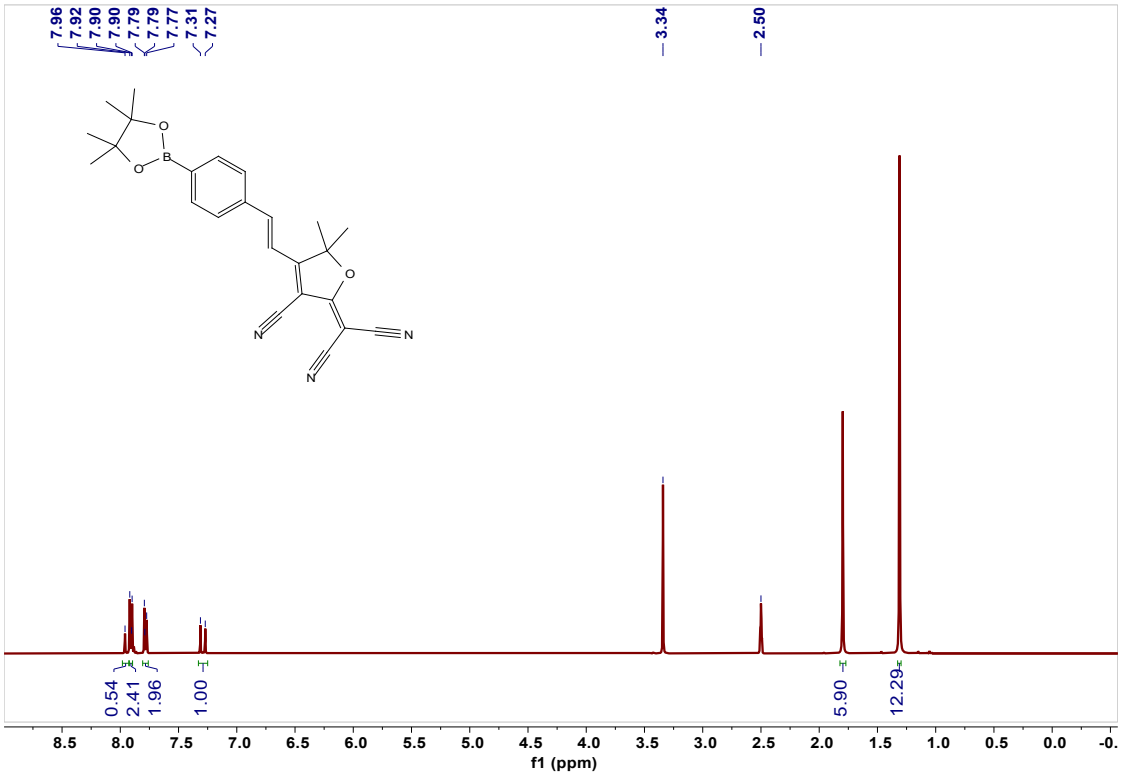

158.40
156.49
141.42
140.68
138.63
136.91
128.79
127.43
127.39
127.37
127.08
121.64
117.53
24.78
N
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

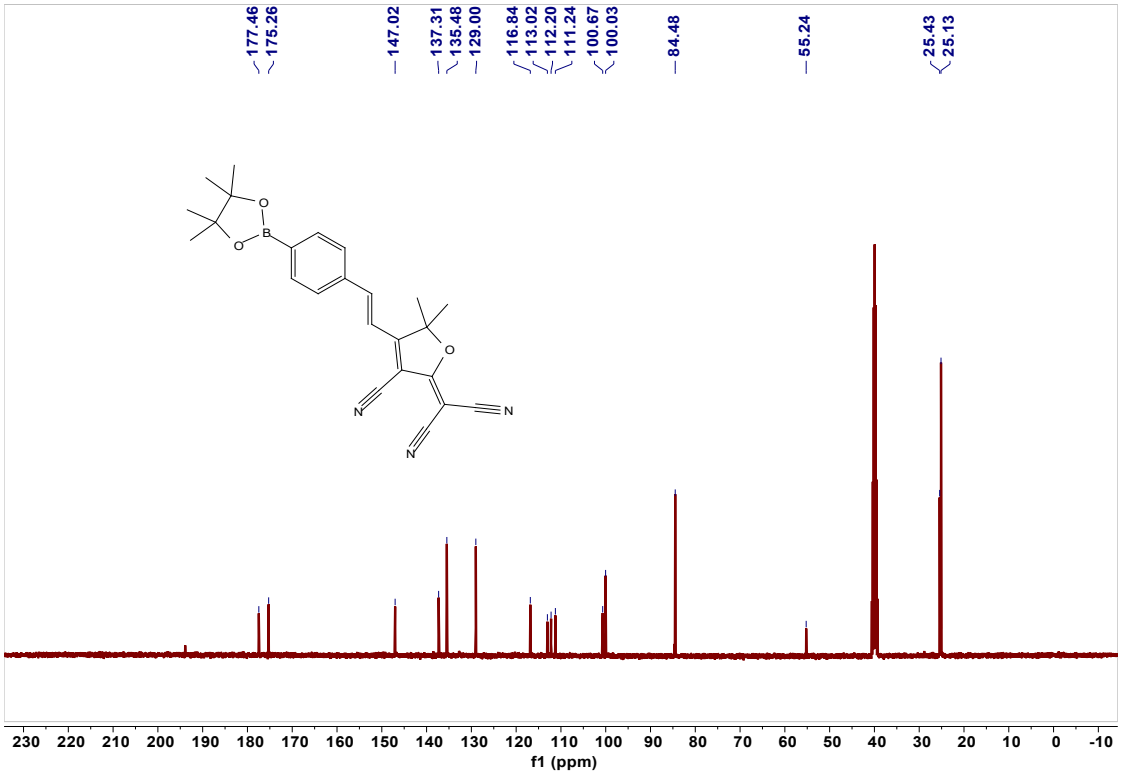

7.71
7.69
7.69
7.67
7.53
7.49
7.39
7.30
7.26
6.94
3.35
3.35
2.62
2.55
2.50
3.76
0.99
1.03
0.92
1.70
1.82
12.00
5.65
f1 (ppm)

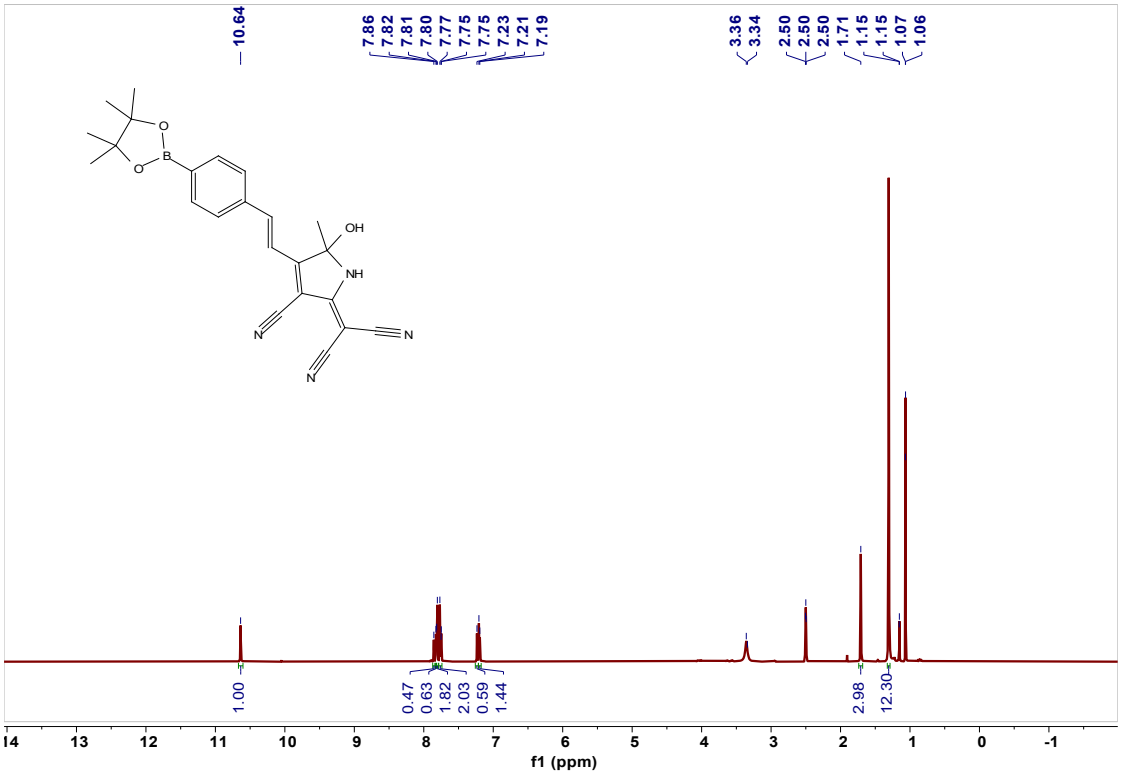

170.77
155.93
139.17
137.39
135.30
131.21
127.58
123.88
114.23
113.36
84.23
77.34
42.72
38.51
32.12
27.87
25.12
f1 (ppm)

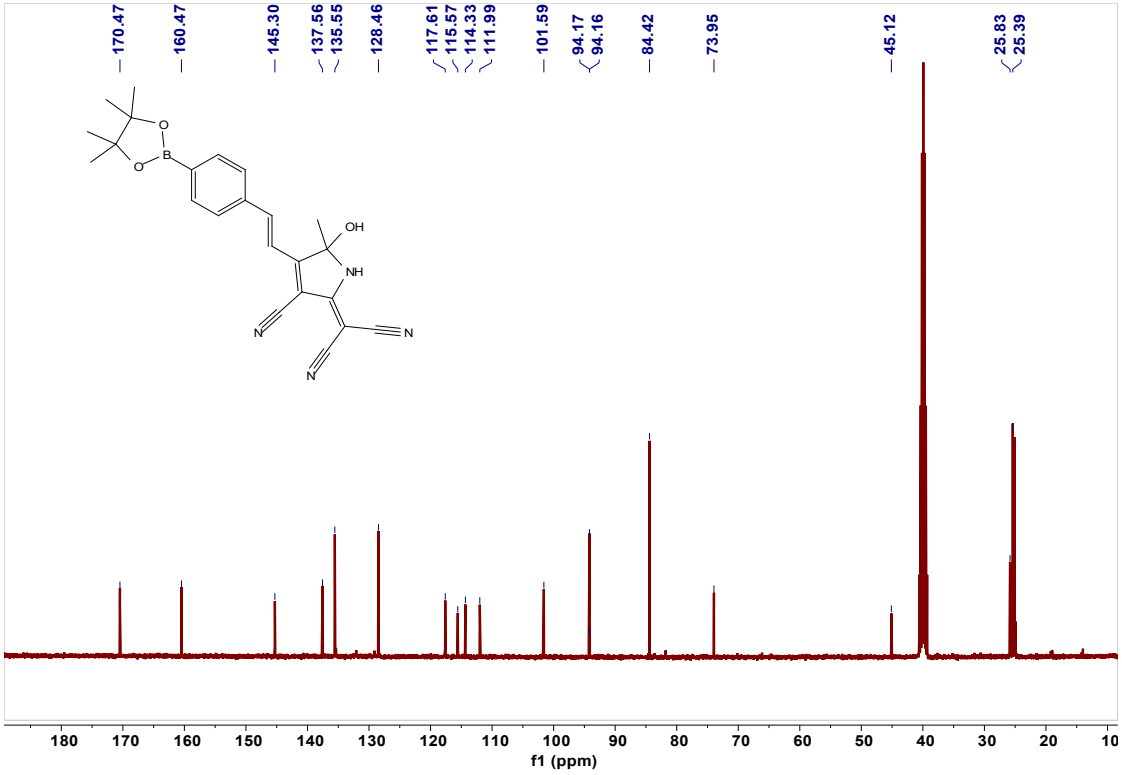

8.71
8.69
7.93
7.91
7.89
7.79
7.77
7.75
7.73
7.72
7.71
7.07
3.33
3.32
3.32
3.32
2.48
2.48
2.47
2.47
1.29
1.28
1.00
1.05
0.60
1.10
4.35
2.11
1.01
12.26
f1 (ppm)

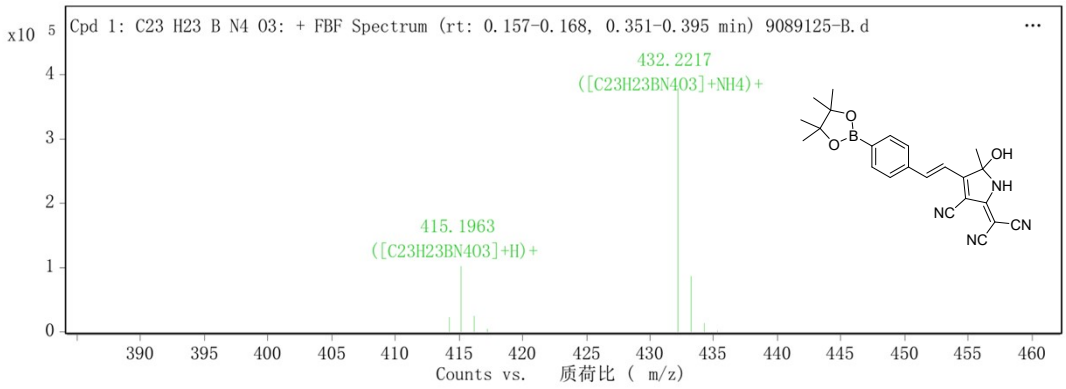

158.18
153.41
152.47
138.43
138.09
136.00
135.43
127.92
126.69
125.11
121.41
119.57
117.51
116.14
107.78
84.32
58.47
25.12
f1 (ppm)

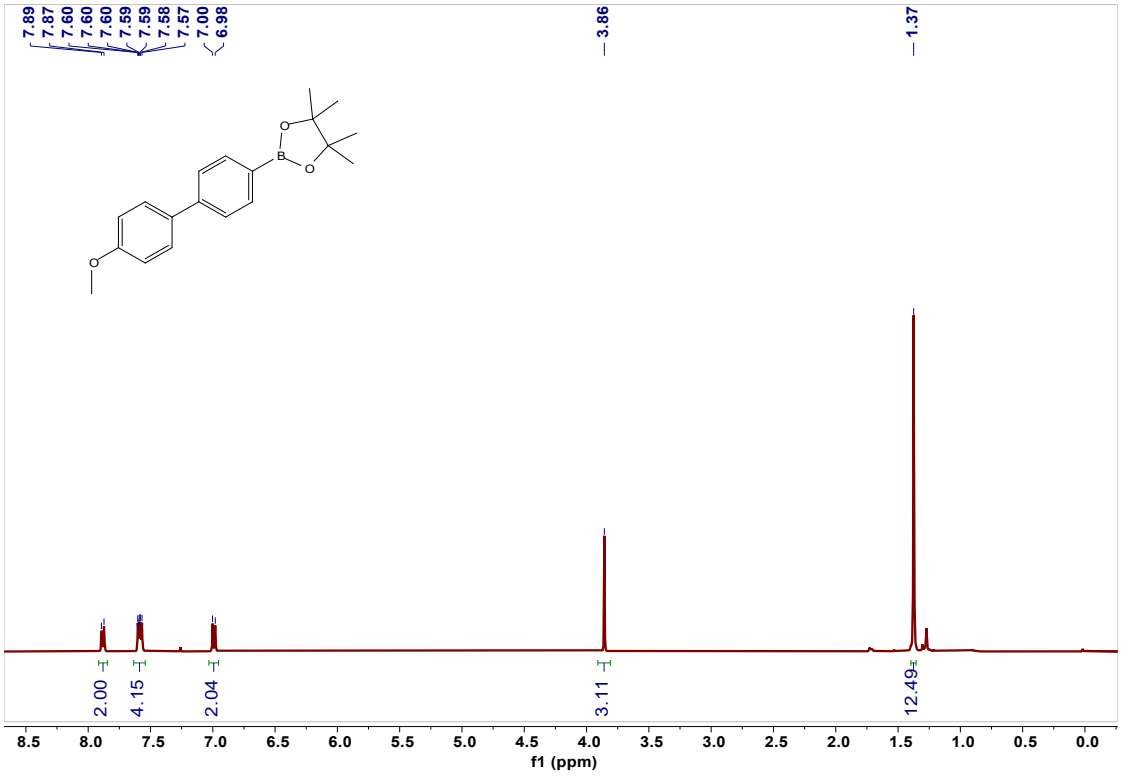

7.96
7.92
7.90
7.90
7.79
7.79
7.77
7.31
7.27
3.34
2.50
0.54
2.41
1.96
1.00
5.90
12.29
f1 (ppm)

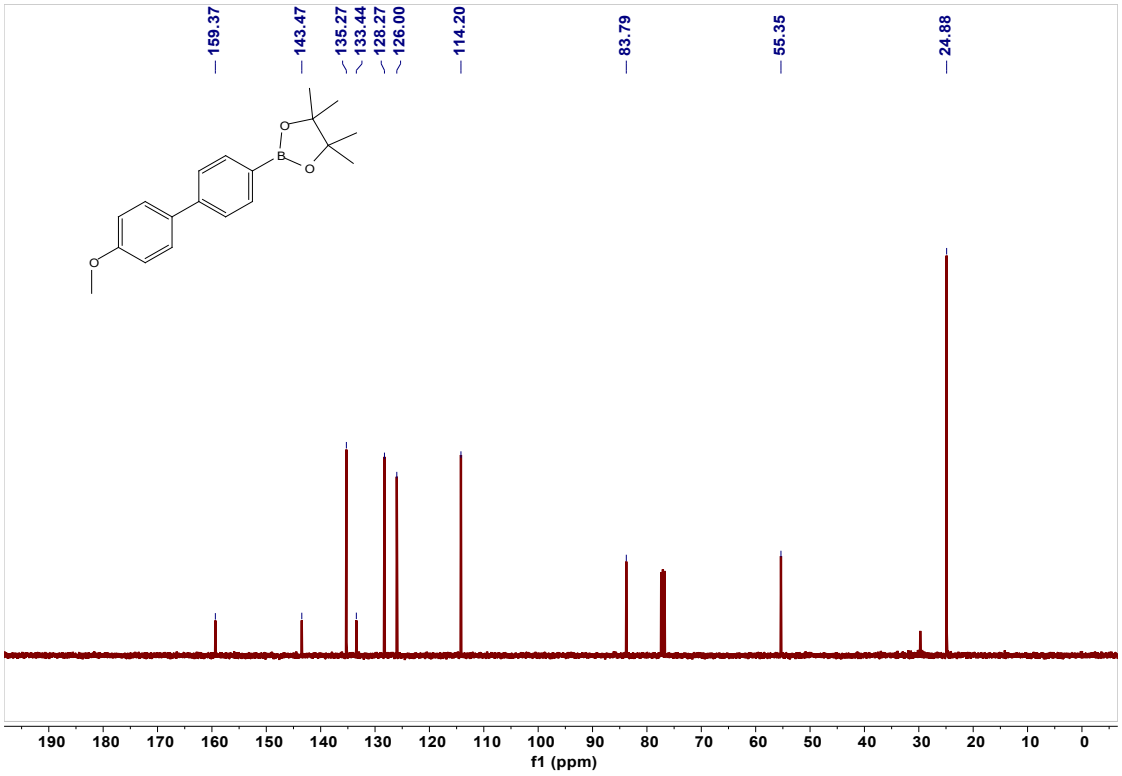

177.46
175.26
147.02
137.31
135.48
129.00
116.84
113.02
112.20
111.24
100.67
100.03
84.48
55.24
25.43
25.13
f1 (ppm)

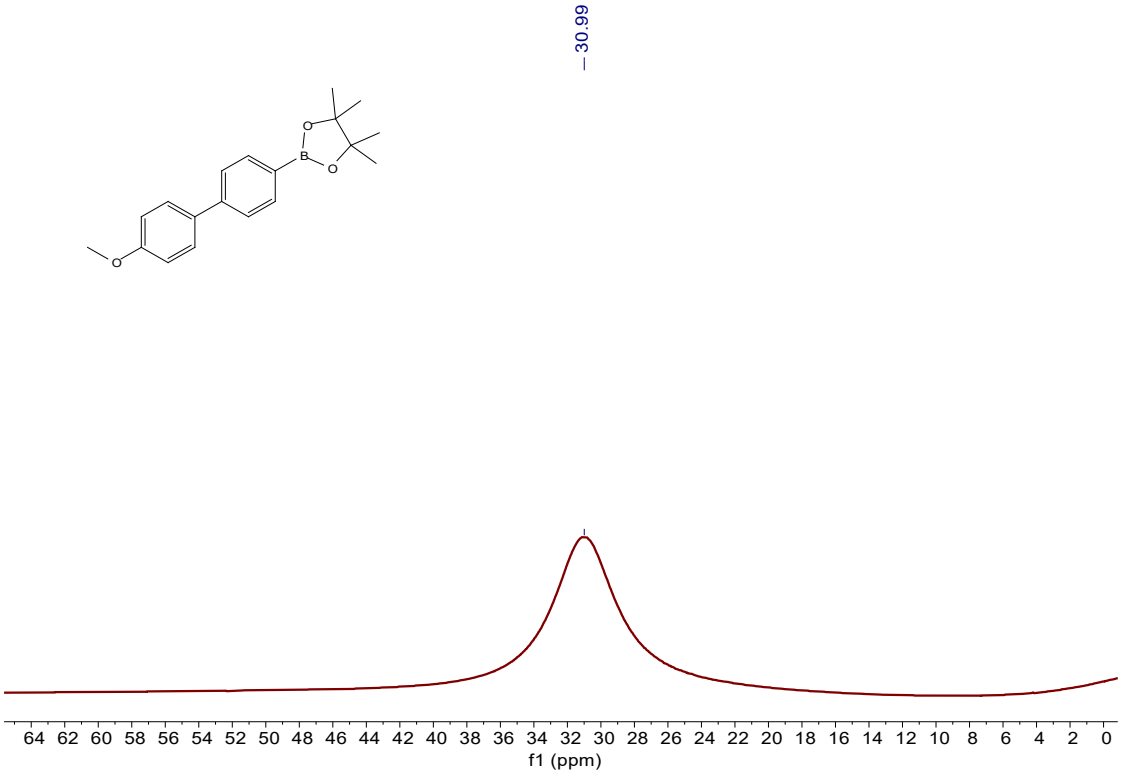

10.64
7.86
7.82
7.81
7.80
7.77
7.75
7.75
7.23
7.21
7.19
3.36
3.34
2.50
2.50
2.50
1.71
1.15
1.15
1.07
1.06
1.00
0.47
0.63
1.82
2.03
0.59
1.44
2.98
12.30
f1 (ppm)

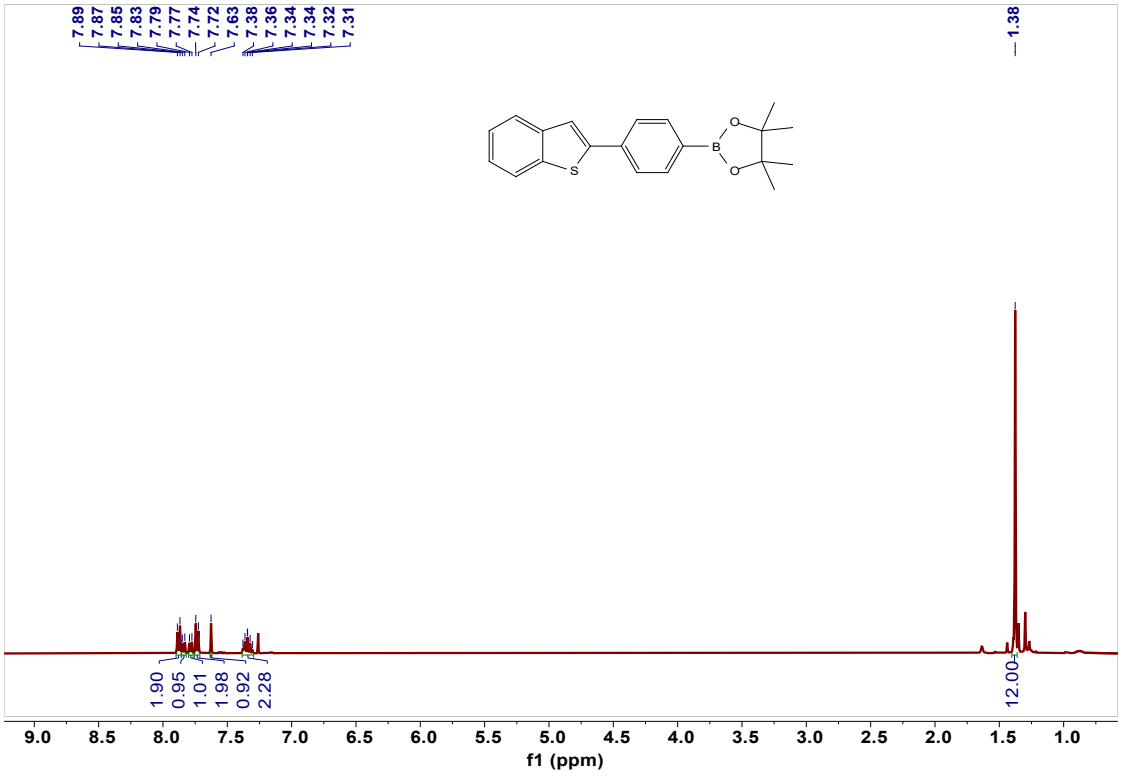

170.47
160.47
145.30
137.56
135.55
128.46
117.61
115.57
114.33
111.99
101.59
94.17
94.16
84.42
73.95
45.12
25.83
25.39
f1 (ppm)

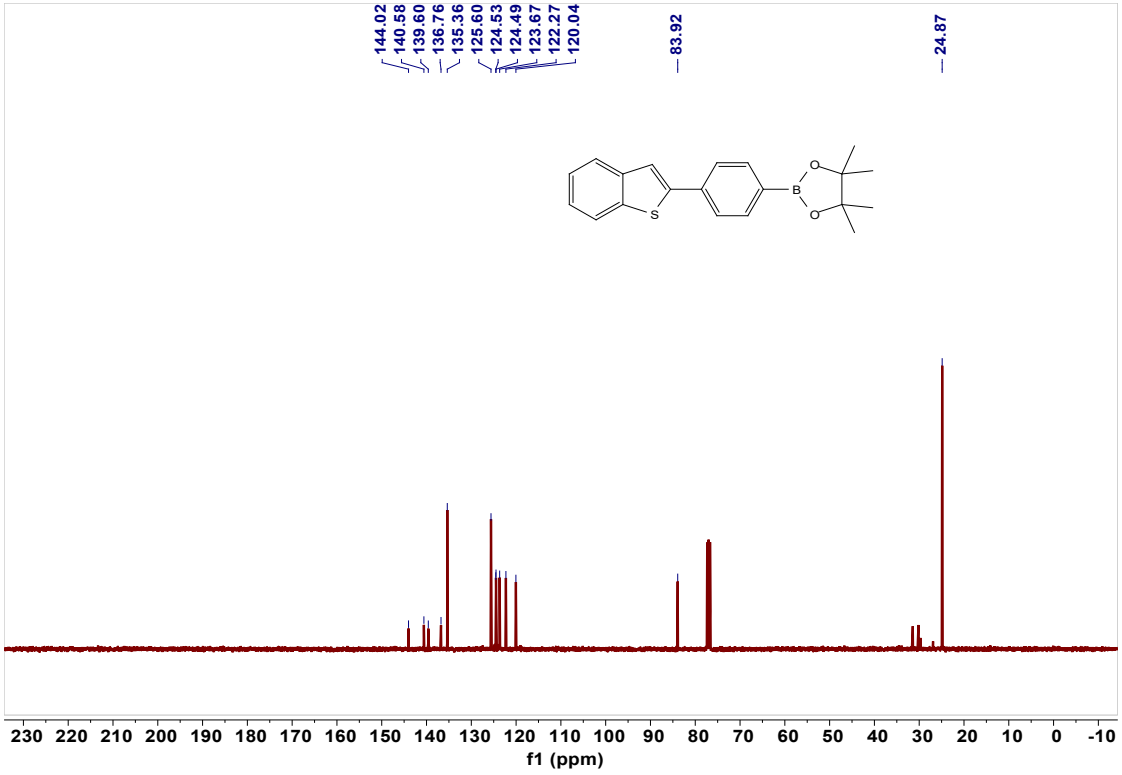

Cpd 1: C23 H23 B N4 O3: + FBF Spectrum (rt: 0.157-0.168, 0.351-0.395 min) 9089125-B.d
x10 5
4
3
2
1
0
432.2217
([C23H23BN4O3]+NH4)+
415.1963
([C23H23BN4O3]+H)+
OH
NH
NC
CN
NC
390 395 400 405 410 415 420 425 430 435 440 445 450 455 460
Counts vs. 质荷比 (m/z)

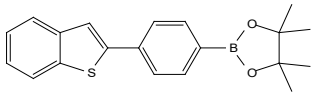

7.89
7.87
7.60
7.60
7.60
7.59
7.59
7.58
7.57
7.00
6.98
3.86
1.37
O
B
O
O
2.00
4.15
2.04
3.11
12.49
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


159.37
143.47
135.27
133.44
128.27
126.00
114.20
83.79
55.35
24.88
O
B
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


30.99
O
B
O
O
64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10 8 6 4 2 0
f1 (ppm)


7.89
7.87
7.85
7.83
7.79
7.77
7.74
7.72
7.63
7.38
7.36
7.34
7.34
7.32
7.31
1.38
1.90
0.95
1.01
1.98
0.92
2.28
12.00
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
f1 (ppm)


144.02
140.58
139.60
136.76
135.36
125.60
124.53
124.49
123.67
122.27
120.04
83.92
24.87
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


S
B
O
O

30.89
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)