

Photoinduced Metal-Free Borylation of Aryl Halides Catalysed by *in situ* Formed Donor-Acceptor Complex

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1.) General Information

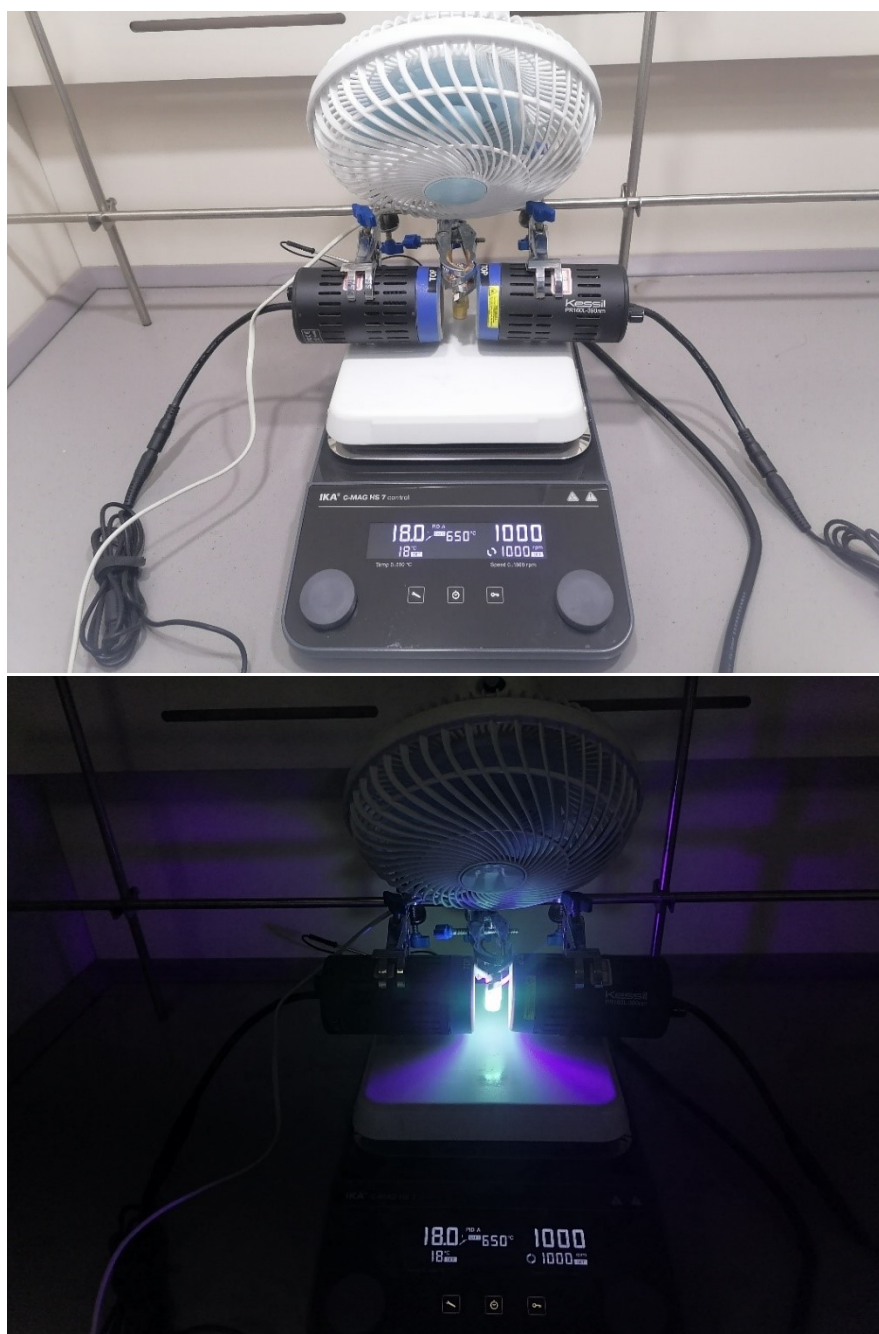
Methods and Materials: Irradiation of photochemical reaction was carried out using Kessil PR160L-390 nm ultraviolet lamps from both side at 1–2 cm with an average intensity of 159mW/cm² (measured

from 6 cm distance). Reactions were cooled using 20W clamp fan placed on the top of the reactor. Stirring was achieved by placing the assembled reactor on IKA C-MAG HS 7 control magnetic stir bars. All reactions were performed in 2mL vials and were run under air (see the picture below for reaction setup).

Analytical TLC was performed on silica gel GF254 plates. The TLC plates were visualized by ultraviolet light ($\lambda = 254$ nm). Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump purchased from EYELA. Fresh silica gel chromatography was performed using 300-400 mesh silica gel (Qingdao, China).

Proton and carbon magnetic resonance spectra (^1H NMR, ^{13}C NMR and ^{11}B NMR) were recorded on a Bruker AVANCE III (^1H NMR at 400 MHz, ^{13}C NMR at 125 MHz, ^{11}B NMR at 128 MHz) spectrometer with solvent resonance as the internal standard (^1H NMR: CDCl_3 at 7.26 ppm; ^{13}C NMR: CDCl_3 at 77.0 ppm). NMR yield using pyrazine or hexamethyldisiloxane (HMDSO) as internal standard. ^1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublets of doublets, dddd = doublet of doublets of doublets of doublets, dt = doublet of triplets, ddt = doublet of doublets of triplets, td = triplet of doublets, tt = triplet of triplets, m = multiplet, q = quartet), coupling constants (Hz), and integration.

Commercially available reagents were purchased from Sigma-Aldrich, Adamas-beta, TCI, Bidepharm and were used as received unless otherwise noted. Super Dry solvents such as acetonitrile (AcN), dimethylformamide (DMF), toluene (PhMe), 1,2-dichloroethane (DCE) and dimethyl sulfoxide (DMSO) were purchased from Adamas-beta. Other common solvents such as petroleum ether and ethyl acetate (EtOAc) are rectification grade for fresh silica gel chromatography purchased from General-reagent.



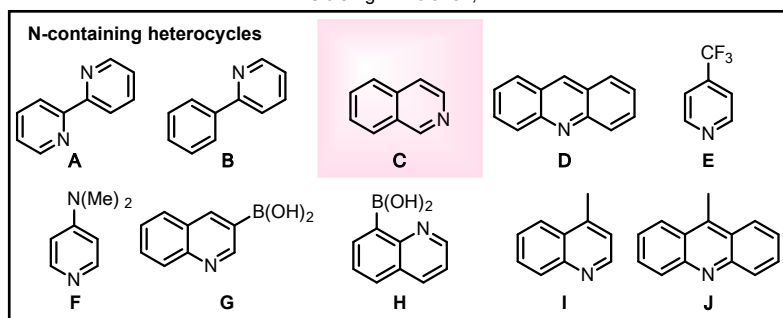
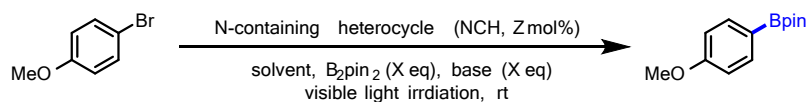
Scheme S1 Photo reaction setup

2.) Optimization of the Reaction Conditions

General procedure (A):

An oven-dried 2 mL vial was charged with a magnetic stir bar, substrate, B_2pin_2 , base, NCH, and solvent. The vial was sealed with a plastic cap and then irradiated with 2*390nm LEDs light for the indicated period of time. Solvent was removed by vacuum evaporation. Yield was determined by 1H NMR using pyrazine or hexamethyldisiloxane (HMDSO) as the internal standard. The reaction mixture was purified by fresh silica gel chromatography to afford the desired borylation product.

2.1 Optimization of Reaction Conditions for the Borylation of Aryl Bromides

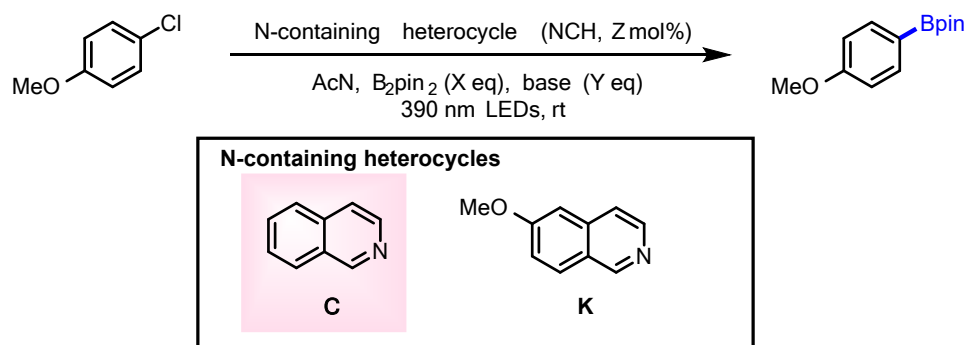


entry	solvent	B ₂ pin ₂ (X eq)	base (Y eq)	NCH (Z mol%)	visible light	reaction time	yield (%) ^a
1	AcN(1.0mL)	X = 2	NEt ₃ (3.0 eq)	A(50mol%)	440nm	12h	trace
2	AcN(1.0mL)	X = 2	NEt ₃ (3.0 eq)	B(50mol%)	456nm	12h	trace
3	AcN(1.0mL)	X = 2	NEt ₃ (3.0 eq)	C(50mol%)	456nm	12h	trace
4	AcN(1.0mL)	X = 2	NEt ₃ (3.0 eq)	C(50mol%)	390nm	12h	49
5	AcN(1.0mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	44
6	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	41
7	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	/	390nm	12h	trace
8	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	F(20mol%)	390nm	12h	trace
9	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	A(20mol%)	390nm	12h	27
10	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	B(20mol%)	390nm	12h	trace
11	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	E(20mol%)	390nm	12h	trace
12	DMSO(0.5mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	trace
13	DMF(0.5mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	NR
14	DCE(0.5mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	16
15	toluene(0.5mL)	X = 2	NEt ₃ (3.0 eq)	C(20mol%)	390nm	12h	47
16	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	C(20mol%)	390nm	36h	87(81) ^b
17	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	C(20mol%)	390nm	48h	88
18	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	G(20mol%)	390nm	12h	13
19	AcN(0.5mL)	X = 2	NEt ₃ (3.0 eq)	H(20mol%)	390nm	12h	9
20	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	I(20mol%)	390nm	36h	74
21	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	D(20mol%)	390nm	36h	19
22	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	J(20mol%)	390nm	36h	60
23	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	/	390nm	36h	14
24	AcN(0.5mL)	X = 4	NHEt ₂ (5.0 eq)	C(20mol%)	390nm	36h	53
25	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	C(20mol%)	390nm	24h	73
26	AcN(0.5mL)	X = 4	NEt ₃ (5.0 eq)	C(20mol%)	/	36h	NR

[a] NMR yield. [b] Isolated yield.

Table S1 Optimization of reaction conditions for aryl bromides

2.2 Optimization of Reaction Conditions for the Borylation of Aryl Chlorides



entry	B ₂ Pin ₂ (X eq)	base (Y eq)	NCH (Z mol%)	time	yield (%) ^a
1	X = 4	NEt ₃ (5.0 eq)	C (0.2 eq)	36 h	68
2	X = 4	NEt ₃ (5.0 eq)	K (0.2 eq)	36 h	60
3	X = 4	NEt ₃ (5.0 eq)	C (0.4 eq)	24 h	37
4	X = 4	NEt ₃ (5.0 eq)	C (1.0 eq)	36 h	70
5	X = 1.2	NEt ₃ (3.0 eq)	C (1.0 eq)	36 h	14
6	X = 4	Triisopentylamine (5.0 eq)	C (1.0 eq)	36 h	69
7	X = 4	Trihexylamine (5.0 eq)	C (1.0 eq)	36 h	69
8	X = 4	NEt ₃ (5.0 eq)	C (2.0 eq)	36 h	66
9	X = 2	NEt ₃ (3.0 eq)	C (2.0 eq)	36 h	23
10	X = 4	NEt ₃ (5.0 eq)	C (1.0 eq)	72 h	82(75) ^b

[a] NMR yield. [b] Isolated yield.

Table S2 Optimization of reaction conditions for aryl chlorides

In summary, the optimized reaction condition for borylation of aryl bromides: substrates (0.2 mmol, 1.0 eq), B₂pin₂ (203 mg, 0.8 mmol, 4.0 eq), isoquinoline (5.2 mg, 0.04 mmol, 20 mol%), NEt₃ (139 μL, 1.0 mmol, 5.0 eq), AcN (0.5 mL), under 2*390 nm LEDs for 36 h. The optimized reaction condition for borylation of arylchlorides: substrates (0.2 mmol, 1.0 eq), B₂pin₂ (203 mg, 0.8 mmol, 4.0 eq), isoquinoline (26 mg, 0.2 mmol, 1.0 eq), NEt₃(139 μL, 1.0 mmol, 5.0 eq), AcN (0.5 mL), under 2*390 nm LEDs for 72 h.

3.) Substrate Scope and Characterization Data

General procedure (B):

An oven-dried 2 mL vial was charged with a magnetic stir bar, aryl bromide (0.2 mmol, 1.0 eq), B₂pin₂ (203 mg, 0.8 mmol, 4.0 eq), isoquinoline (5.2 mg, 0.04 mmol, 20 mol%), NEt₃ (139 μL, 1.0 mmol, 5.0 eq), AcN (0.5 mL). The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 36 h. Solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine or HMDSO as the internal standard. The reaction mixture was purified by fresh silica gel chromatography to afford the desired borylation product.

General procedure (C):

An oven-dried 2 mL vial was charged with a magnetic stir bar, aryl chloride (0.2 mmol, 1.0 eq), B₂pin₂ (203 mg, 0.8 mmol, 4.0 eq), isoquinoline (26 mg, 0.2 mmol, 1.0 eq), NEt₃ (139 μL, 1.0 mmol, 5.0 eq), AcN (0.5 mL). The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 72 h. Solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine or HMDSO as the internal standard. The reaction mixture was purified by fresh silica gel chromatography to afford the desired borylation product.

General procedure (D):

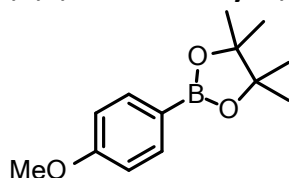
An oven-dried 2 mL vial was charged with a magnetic stir bar, 4-bromoanisole (37 mg, 0.2 mmol, 1.0 eq), diboron (0.8 mmol, 4.0 eq), isoquinoline (5.2 mg, 0.04 mmol, 20 mol%), NEt₃ (139 μL, 1.0 mmol, 5.0 eq), AcN (0.5 mL). The vial was sealed with a plastic cap and then irradiated with 2*390nm LED light for 36 h. Solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine as the internal standard. The reaction mixture was purified by fresh silica gel column chromatography to afford the desired borylation product.

General procedure (E):

An oven-dried 2 mL vial was charged with a magnetic stir bar, simple arenes (0.2 mmol), AcN (0.5 ml), N-Bromosuccinimide (NBS, 37.4mg, 0.21 mmol, 1.05 eq). The mixture was allowed to stir for 12 h, then B₂pin₂ (0.8 mmol, 4.0 eq), isoquinoline (5.2 mg, 0.04 mmol, 20 mol%), NEt₃ (139 μL, 1.0 mmol, 5.0 eq) were added without further purification. The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 36 h. Solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine or HMDSO as the internal standard. The reaction mixture was purified by fresh silica gel chromatography to afford the desired borylation product.

3.1 Substrate Scope and Characterization Data

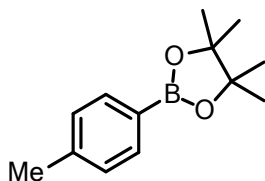
2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3a**)



Following general procedure (B), **3a** was obtained as colourless liquid in 87% NMR yield and 81% isolated yield from 4-bromoanisole using 40:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11a** was obtained in 83% NMR yield and 75% isolated yield from 4-chloroanisole using 40:1 petroleum ether/EtOAc as eluent. Following general procedure (E), **13a** was obtained in 76% NMR yield and 73% isolated yield from anisole using 40:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 162.28, 136.64, 113.44, 83.67, 55.21, 24.99. ¹¹B NMR (128 MHz, CDCl₃) δ 31.08. The NMR data were in consistent with the reported data.^[1]

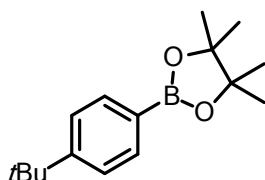
2-(4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3b**)



Following general procedure (B), **3b** was obtained as colourless liquid in 90% NMR yield and 51% isolated yield from 4-bromotoluene using 60:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11c** was obtained in 82% NMR yield and 76% isolated yield from 4-chlorotoluene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.5$ Hz, 2H), 7.20 (d, $J = 7.5$ Hz, 2H), 2.38 (s, 3H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 141.53, 134.95, 128.66, 83.76, 25.00, 21.86. $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 30.97. The NMR data were in consistent with the reported data.^[1]

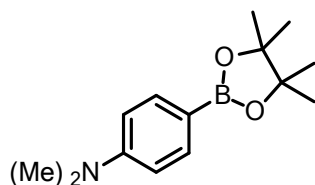
2-(4-(*tert*-butyl) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)



Following general procedure (B), **3c** was obtained as colourless solid in 74% isolated yield from 1-*tert*-butyl-4-bromobenzene using 60:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11d** was obtained in 66% isolated yield from 1-*tert*-butyl-4-chlorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 1.35 (s, 12H), 1.34 (s, 9H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 154.60, 134.80, 124.81, 83.72, 35.00, 31.31, 24.95. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.89. The NMR data were in consistent with the reported data.^[1]

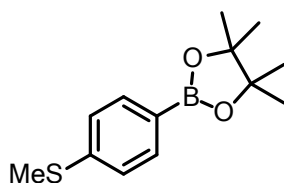
N, N-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (3d)



Following general procedure (B), **3d** was obtained as white solid in 79% NMR yield and 50% isolated yield from N, N-dimethyl-*p*-bromoaniline using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.2$ Hz, 2H), 6.70 (d, $J = 8.2$ Hz, 2H), 2.99 (s, 6H), 1.32 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.66, 136.27, 111.38, 83.28, 40.24, 24.97. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 31.39. The NMR data were in consistent with the reported data.^[2]

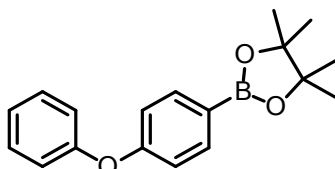
4,4,5,5-tetramethyl-2-(4-(methylthio) phenyl)-1,3,2-dioxaborolane (3e)



Following general procedure (B), **3e** was obtained as colourless solid in 62% NMR yield and 64% isolated yield from 4-bromothioanisole using 60:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11g** was obtained in 69% NMR yield and 64% isolated yield from 4-chlorothioanisole using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.71 (d, $J = 6.9$ Hz, 2H), 7.23 (d, $J = 7.5$ Hz, 2H), 2.49 (s, 3H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 142.69, 135.19, 125.11, 83.84, 24.97, 15.16. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.81. The NMR data were in consistent with the reported data.^[1]

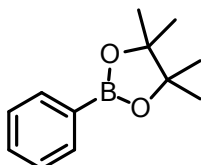
4,4,5,5-tetramethyl-2-(4-phenoxyphenyl)-1,3,2-dioxaborolane (3f)



Following general procedure (B), **3f** was obtained as white solid in 59% isolated yield from 4-bromodiphenyl ether using 40:1 petroleum ether/EtOAc as eluent. Following general procedure (E), **13b** was obtained in 52% NMR yield and 38% isolated yield from diphenyl ether using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.5$ Hz, 2H), 7.35 (t, $J = 7.9$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 7.04 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 8.5$ Hz, 2H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 160.33, 156.68, 136.77, 129.94, 123.80, 119.61, 117.81, 83.87, 25.00 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 32.20. The NMR data were in consistent with the reported data.^[3]

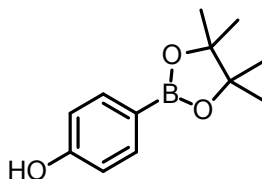
4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (3g)



Following general procedure (B), **3g** was obtained as colourless oil in 94% NMR yield and 58% isolated yield from bromobenzene using 60:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11b** was obtained in 59% NMR yield and 54% isolated yield from chlorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.3$ Hz, 2H), 7.47 (t, $J = 7.3$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 2H), 1.36 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 134.86, 131.38, 127.83, 83.89, 24.99. $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 31.03. The NMR data were in consistent with the reported data.^[1]

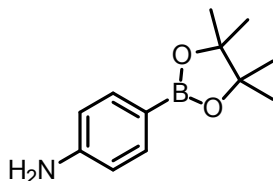
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol (3h)



Following general procedure (B), **3h** was obtained as white solid in 65% NMR yield and 61% isolated yield from 4-bromophenol using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11e** was obtained in 45% NMR yield and 44% isolated yield from 4-chlorophenol using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (E), **13e** was obtained in 36% NMR yield and 33% isolated yield from phenol using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.5$ Hz, 12H), 5.72 (s, 1H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.74, 136.89, 115.01, 83.81, 24.95. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.80. The NMR data were in consistent with the reported data.^[2]

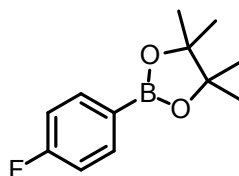
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**3i**)



Following general procedure (B), **3i** was obtained as colourless solid in 86% NMR yield and 77% isolated yield from 4-bromoaniline using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11f** was obtained in 44% NMR yield and 42% isolated yield from 4-chloroaniline using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (E), **13f** was obtained in 58% NMR yield and 39% isolated yield from aniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.9$ Hz, 2H), 6.66 (d, $J = 7.9$ Hz, 2H), 3.73 (brs, 2H), 1.32 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 149.41, 136.53, 114.21, 83.42, 24.97. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.86. The NMR data were in consistent with the reported data.^[1]

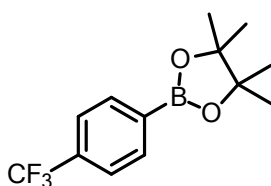
2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



Following general procedure (B), **3j** was obtained as colourless oil in 80% NMR yield and 69% isolated yield from 4-bromofluorobenzene using 40:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11h** was obtained in 75% NMR yield and 70% isolated yield from 4-chlorofluorobenzene using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.80 (dd, $J = 8.4, 6.3$ Hz, 2H), 7.05 (t, $J = 8.8$ Hz, 2H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 165.24 (d, $J = 250.5$ Hz), 137.12 (d, $J = 8.2$ Hz), 114.98 (d, $J = 20.2$ Hz), 84.04, 24.99. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.66. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -108.38 (tt, $J = 9.0, 6.0$ Hz). The NMR data were in consistent with the reported data.^[1]

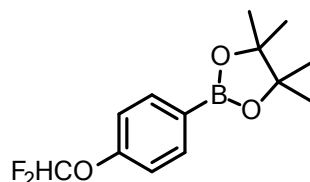
4,4,5,5-tetramethyl-2-(4-(trifluoromethyl) phenyl)-1,3,2-dioxaborolane (**3k**)



Following general procedure (B), **3k** was obtained as colourless solid in 59% NMR yield and 52% isolated yield from 4-bromobenzotrifluoride using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.91 (d, $J = 7.8$ Hz, 2H), 7.61 (d, $J = 7.7$ Hz, 2H), 1.36 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 135.15, 133.09, 124.48, 124.46, 84.42, 25.01. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.61. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -63.00. The NMR data were in consistent with the reported data.^[1]

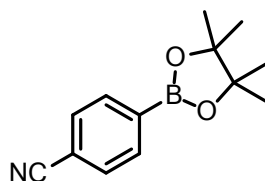
2-(4-(difluoromethoxy) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



Following general procedure (B), **3l** was obtained as colourless oil in 46% isolated yield from 1-bromo-4-(difluoromethyl) benzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.4$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 6.54 (t, $J = 73.9$ Hz, 1H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 153.91, 136.78, 118.34, 115.89 (t, $J = 259.4$ Hz), 84.10, 24.98. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.91. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -80.91 (d, $J = 74.2$ Hz). The NMR data were in consistent with the reported data.^[1]

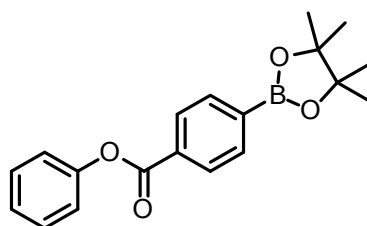
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile (3m)



Following general procedure (B), **3m** was obtained as colourless solid in 49% NMR yield and 34% isolated yield from 4-bromobenzonitrile using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.2$ Hz, 2H), 1.35 (s, 12H). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 30.49. The NMR data were in consistent with the reported data.^[1]

phenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (3n)

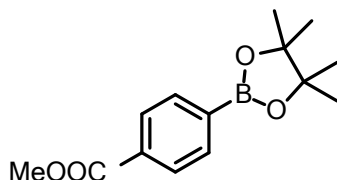


4-bromophenyl benzoate was synthesized according to the literature precedent:^[4] Benzoic acid (2.00 g, 16.38 mmol, 1.0 eq) was dissolved in dry CH_2Cl_2 (100 mL) under N_2 atmosphere and phenol (1.54 g, 16.38 mmol, 1.0 eq), DCC (5.07 g, 24.55 mmol, 1.5 eq), DMAP (0.40 g, 8.19 mmol, 0.5 eq) were slowly added and stirred for 8 h at rt. The reaction was quenched by adding water and extracted with CH_2Cl_2 (3*80 ml). The organic layer was washed with water and brine, dried over MgSO_4 , removed by filtration. The filtrate was concentrated in vacuo and chromatographed on silica gel to give a white solid. Analytical data matched that reported in the literature.^[4] $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.06 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 8.2$ Hz, 2H), 7.43 (t, $J = 7.7$ Hz, 2H), 7.32 – 7.25 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 2H).

Following general procedure (B), **3n** was obtained as white solid in 76% isolated yield from 4-bromophenyl benzoate using 50:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.0$ Hz, 2H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.28 (t, $J = 7.0$ Hz, 1H), 7.23 (d, $J = 7.7$ Hz, 2H), 1.38 (s, 12H). The NMR data were in consistent with the reported data.^[5]

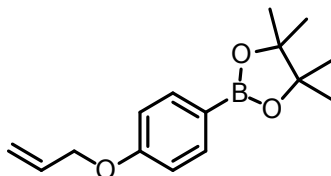
methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (**3o**)



Following general procedure (B), **3o** was obtained as colourless liquid in 58% NMR yield and 55% isolated yield from methyl 4-bromobenzoate using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.9$ Hz, 2H), 7.87 (d, $J = 7.6$ Hz, 2H), 3.92 (s, 3H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.29, 134.80, 132.43, 128.73, 84.32, 52.29, 25.01. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.94. The NMR data were in consistent with the reported data.^[1]

2-(4-(allyloxy) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3p**)

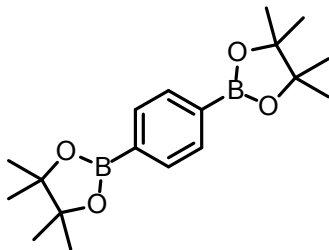


1-(allyloxy)-4-bromobenzene was synthesized according to the literature precedent:^[6] To a solution of 4-bromophenol (0.8 g, 4.62 mmol, 1.0 eq) in DMF (25 mL) were added potassium carbonate (1.28 g, 9.24 mmol, 2.0 eq) and allyl bromide at room temperature. The mixture was stirred for 24 h, poured into water, and then extracted with Et_2O . The extract was washed with brine, dried over MgSO_4 , and concentrated using a rotary evaporator. The yellow oil thus obtained and was distilled under reduced pressure to give as colourless oil. Analytical data matched that reported in the literature.^[6] $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (d, $J = 8.9$ Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 6.03 (ddd, $J = 22.6, 10.5, 5.3$ Hz, 1H), 5.40 (dq, $J = 17.2, 1.6$ Hz, 1H), 5.30 (dq, $J = 10.5, 1.4$ Hz, 1H), 4.51 (dt, $J = 5.3, 1.6$ Hz, 2H).

Following general procedure (B), **3p** was obtained as colourless liquid in 57% NMR yield and 52% isolated yield from 1-(allyloxy)-4-bromobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.75 (d, $J = 8.6$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 6.05 (ddt, $J = 17.3, 10.5, 5.2$ Hz, 1H), 5.41 (dd, $J = 17.3, 1.7$ Hz, 1H), 5.28 (dd, $J = 10.5, 1.5$ Hz, 1H), 4.56 (d, $J = 5.3$ Hz, 2H), 1.33 (s, 12H). The NMR data were in consistent with the reported data.^[7]

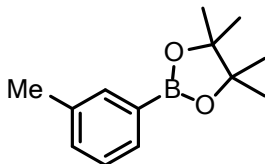
1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzene(**3q**)



Following general procedure (B), **3q** was obtained as colourless oil in 54% isolated yield from 1-bromo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (s, 4H), 1.35 (s, 24H). The NMR data were in consistent with the reported data.^[1]

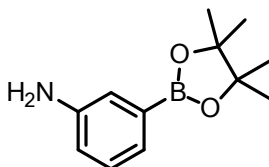
2-(3-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



Following general procedure (B), **3r** was obtained as colourless liquid in 80% NMR yield and 57% isolated yield from 3-methyl-1-bromobenzene using 60:1 petroleum ether/EtOAc as eluent. Following procedure (C), **11i** was obtained in 60% NMR yield and 49% isolated yield from 3-methyl-1-chlorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.62 – 7.60 (m, 1H), 7.28 – 7.26 (m, 2H), 2.35 (s, 3H), 1.35 (s, 12H). The NMR data were in consistent with the reported data.^[1]

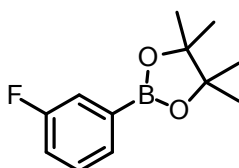
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (3s)



Following general procedure (B), **3s** was obtained as colourless solid in 74% NMR yield and 82% isolated yield from 3-bromoaniline using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11j** was obtained in 71% NMR yield and 73% isolated yield from 3-chloroaniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.21 (d, $J = 7.0$ Hz, 1H), 7.18 (d, $J = 7.5$ Hz, 1H), 7.14 (s, 1H), 6.79 (d, $J = 7.1$ Hz, 1H), 3.51 (brs, 2H), 1.34 (s, 12H). The NMR data were in consistent with the reported data.^[1]

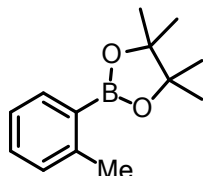
2-(3-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3t)



Following general procedure (B), **3t** was obtained as colourless oil in 89% NMR yield and 44% isolated yield from 3-bromofluorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.48 (d, $J = 9.5$ Hz, 2H), 7.38 – 7.30 (m, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 162.63 (d, $J = 246.4$ Hz), 130.41 (d, $J = 3.1$ Hz), 129.60 (d, $J = 7.1$ Hz), 121.09 (d, $J = 19.3$ Hz), 118.31 (d, $J = 21.1$ Hz), 84.22, 24.98. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.56. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -114.17 (td, $J = 9.0, 5.5$ Hz). The NMR data were in consistent with the reported data.^[1]

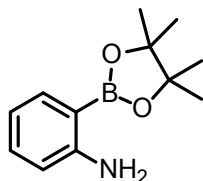
2-(2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3u**)



Following general procedure (B), **3u** was obtained as colourless liquid in 85% NMR yield and 59% isolated yield from 2-methyl-1-bromobenzene using 60:1 petroleum ether/EtOAc as eluent. Following procedure (C), **11k** was obtained in 69% NMR yield and 46% isolated yield from 2-methyl-1-chlorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (d, $J = 8.4$ Hz, 1H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.18 (s, 2H), 2.57 (d, $J = 9.5$ Hz, 3H), 1.36 (d, $J = 9.7$ Hz, 12H). The NMR data were in consistent with the reported data.^[1]

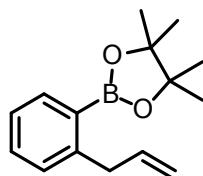
2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**3v**)



Following general procedure (B), **3v** was obtained as colourless solid in 90% NMR yield and 82% isolated yield from 2-bromoaniline using 15:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11l** was obtained in 72% NMR yield and 76% isolated yield from 2-chloroaniline using 15:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.61 (d, $J = 7.4$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 6.68 (t, $J = 7.3$ Hz, 1H), 6.60 (d, $J = 8.1$ Hz, 1H), 4.23 (brs, 2H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 153.73, 136.92, 132.87, 117.04, 114.91, 83.64, 25.05. $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 31.12. The NMR data were in consistent with the reported data.^[2]

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

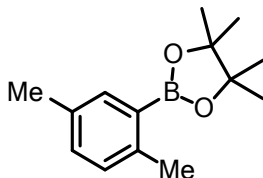


Following general procedure (B), **3w** was obtained as colourless liquid in 75% NMR yield and 63% isolated yield from 2-bromo-1-allylbenzene using 85:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.81 – 7.77 (m, 1H), 7.37 (td, $J = 7.5, 1.6$ Hz, 1H), 7.20 (dt, $J = 7.4, 3.3$ Hz, 2H), 6.00 (ddt, $J = 16.8, 10.0, 6.6$ Hz, 1H), 5.05 – 4.96 (m, 2H), 3.70 (d, $J = 6.6$ Hz, 2H), 1.34 (s,

12H). ^{13}C NMR (151 MHz, CDCl_3) δ 146.92, 139.34, 136.21, 131.17, 129.32, 125.45, 114.86, 83.62, 39.94, 25.02. ^{11}B NMR (193 MHz, CDCl_3) δ 31.35. The NMR data were in consistent with the reported data.^[8]

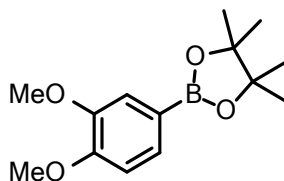
2-(2,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3x**)



Following general procedure (**B**), **3x** was obtained as colourless liquid in 77% NMR yield and 67% isolated yield from 2,5-dimethylbromobenzene using 60:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 7.07 (d, $J = 7.8$ Hz, 1H), 2.50 (s, 3H), 2.31 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 141.84, 136.49, 134.03, 131.69, 129.92, 83.47, 25.01, 21.83, 20.92. ^{11}B NMR (128 MHz, CDCl_3) δ 31.40. The NMR data were in consistent with the reported data.^[9]

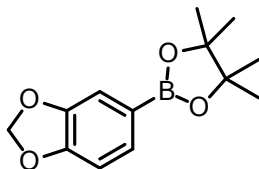
2-(3,4-dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3y**)



Following general procedure (**B**), **3y** was obtained as colourless solid in 72% isolated yield from 3,4-dimethoxy-1-bromobenzene using 30:1 petroleum ether/EtOAc as eluent. Following general procedure (**C**), **11m** was obtained in 87% NMR yield and 81% isolated yield from 3,4-dimethoxy-1-chlorobenzene using 30:1 petroleum ether/EtOAc as eluent. Following general procedure (**E**), **13g** was obtained in 76% NMR yield and 64% isolated yield from 1,2-dimethoxybenzene using 30:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 8.0$ Hz, 1H), 7.28 (s, 1H), 6.87 (d, $J = 8.0$ Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 1.33 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 151.76, 148.46, 128.68, 116.70, 110.61, 83.77, 55.96, 55.85, 25.04 (d, $J = 25.5$ Hz). ^{11}B NMR (128 MHz, CDCl_3) δ 30.69. The NMR data were in consistent with the reported data.^[1]

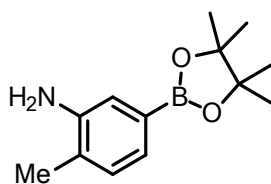
2-(benzo[d][1,3] dioxol-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3z**)



Following general procedure (**B**), **3z** was obtained as colourless liquid in 82% NMR yield and 57% isolated yield from 4-bromo-1,2-(methylenedioxy) benzene using 60:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.7$ Hz, 1H), 7.24 (s, 1H), 6.83 (d, $J = 7.6$ Hz, 1H), 5.95 (s, 2H), 1.33 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 150.29, 147.32, 129.84, 114.06, 108.40, 100.84, 83.82, 24.95. ^{11}B NMR (193 MHz, CDCl_3) δ 30.66. The NMR data were in consistent with the reported data.^[1]

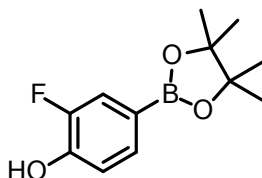
2-methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**3aa**)



Following general procedure (**B**), **3aa** was obtained as white solid in 81% NMR yield and 69% isolated yield from 2-methyl-5-bromoaniline using 10:1 petroleum ether/EtOAc as eluent. Following general procedure (**C**), **11n** was obtained in 68% NMR yield and 63% isolated yield from 2-methyl-5-chloroaniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.17 (d, $J = 7.3$ Hz, 1H), 7.12 (s, 1H), 7.07 (d, $J = 7.3$ Hz, 1H), 3.57 (brs, 2H), 2.19 (s, 3H), 1.33 (s, 12H). The NMR data were in consistent with the reported data.^[1]

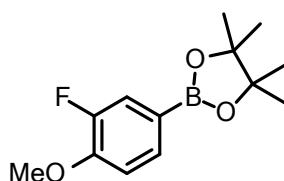
2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenol (**3ab**)



Following general procedure (**B**), **3ab** was obtained as white solid in 46% NMR yield and 45% isolated yield from 4-bromo-2-fluorophenol using 6:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 (dd, $J = 9.5, 5.4$ Hz, 2H), 6.98 (t, $J = 8.3$ Hz, 1H), 5.37 (s, 1H), 1.33 (s, 12H). $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -141.94 (dd, $J = 11.0, 8.4$ Hz). The NMR data were in consistent with the reported data.^[10]

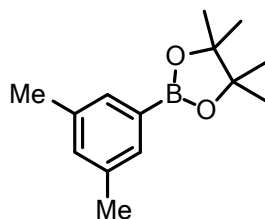
2-(3-fluoro-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ac**)



Following general procedure (**B**), **3ac** was obtained as white solid in 80% NMR yield and 64% isolated yield from 4-bromo-2-fluoroanisole using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.2$ Hz, 1H), 7.49 (d, $J = 11.7$ Hz, 1H), 6.95 (t, $J = 8.0$ Hz, 1H), 3.91 (s, 3H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 152.92, 151.29, 150.34 (d, $J = 10.6$ Hz), 131.59 (d, $J = 3.7$ Hz), 121.79 (d, $J = 16.1$ Hz), 112.60, 83.99, 56.11, 24.96. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.69. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -137.15 (dd, $J = 11.8, 8.2$ Hz). The NMR data were in consistent with the reported data.^[1]

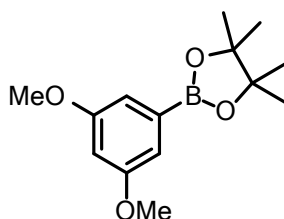
2-(3,5-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ad**)



Following general procedure (B), **3ad** was obtained as white solid in 68% isolated yield from 3,5-dimethylbromobenzene using 60:1 petroleum ether/EtOAc as eluent. Following general procedure (C), **11p** was obtained in 60% NMR yield and 55% isolated yield from 3,5-dimethylchlorobenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.45 (s, 2H), 7.11 (s, 1H), 2.33 (s, 6H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 137.29, 133.12, 132.53, 83.81, 24.98, 21.26. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 31.52. The NMR data were in consistent with the reported data.^[1]

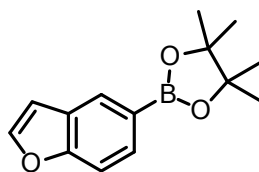
2-(3,5-dimethoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ae)



Following general procedure (B), **3ae** was obtained as white solid in 74% NMR yield and 73% isolated yield from 3,5-dimethoxy-1-bromobenzene using 30:1 petroleum ether/EtOAc as eluent. Following procedure (C), **11o** was obtained in 61% NMR yield and 44% isolated yield from 3,5-dimethoxy-1-chlorobenzene using 30:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.95 (t, $J = 1.8$ Hz, 2H), 6.57 (d, $J = 2.2$ Hz, 1H), 3.81 (s, 6H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 160.52, 111.73, 104.64, 83.81 (d, $J = 56.5$ Hz), 55.53, 25.06 (d, $J = 26.9$ Hz). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.82. The NMR data were in consistent with the reported data.^[1]

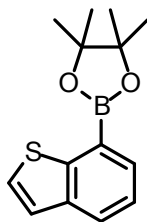
2-(benzofuran-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3af)



Following general procedure (B), **3af** was obtained as white solid in 29% NMR yield and 23% isolated yield from 5-bromo-1-benzofuran using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.11 (s, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.61 (d, $J = 2.2$ Hz, 1H), 7.50 (d, $J = 8.2$ Hz, 1H), 6.78 – 6.74 (m, 1H), 1.37 (s, 12H). The NMR data were in consistent with the reported data.^[1]

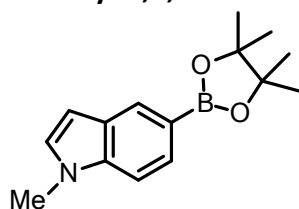
2-(benzo[b]thiophen-7-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ag)



Following general procedure **(B)** and extend the reaction time to 48h, **3ag** was obtained as white solid in 88% NMR yield and 54% isolated yield from 7-bromo-1-benzothiophene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.92 (d, $J = 8.0$ Hz, 1H), 7.84 (d, $J = 7.0$ Hz, 1H), 7.48 (d, $J = 5.5$ Hz, 1H), 7.38 (t, $J = 7.3$ Hz, 1H), 7.34 (d, $J = 5.5$ Hz, 1H), 1.41 (s, 12H). The NMR data were in consistent with the reported data.^[7]

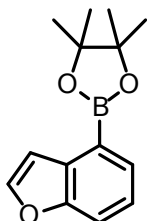
1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) indole (**3ah**)



Following general procedure **(B)**, **3ah** was obtained as colourless solid in 77% NMR yield and 61% isolated yield from 4-bromo-1-methyl-1H-indole using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.17 (s, 1H), 7.68 (d, $J = 8.2$ Hz, 1H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.04 (t, $J = 2.4$ Hz, 1H), 6.51 (t, $J = 2.3$ Hz, 1H), 3.79 (d, $J = 1.7$ Hz, 3H), 1.38 (s, 12H). The NMR data were in consistent with the reported data.^[12]

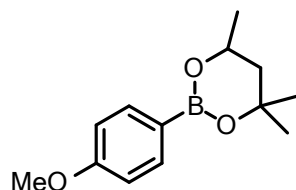
2-(benzofuran-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3ai**)



Following general procedure **(B)**, **3ai** was obtained as colourless liquid in 36% NMR yield and 21% isolated yield from 4-bromo-1-benzofuran using 50:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.2$ Hz, 1H), 7.65 (s, 1H), 7.59 (d, $J = 8.2$ Hz, 1H), 7.30 (t, $J = 7.7$ Hz, 1H), 7.23 (s, 1H), 1.39 (s, 12H). The NMR data were in consistent with the reported data.^[13]

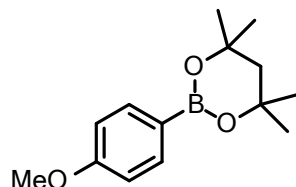
2-(4-methoxyphenyl)-4,4,6-trimethyl-1,3,2-dioxaborinane (**4a**)



Following general procedure **(D)**, **4a** was obtained as colourless liquid in 69% isolated yield using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.76 (d, $J = 8.4$ Hz, 2H), 6.87 (d, $J = 8.3$ Hz, 2H), 4.33 (dq, $J = 12.2, 6.2, 2.9$ Hz, 1H), 3.82 (s, 3H), 1.85 (dd, $J = 13.8, 3.0$ Hz, 1H), 1.57 (t, $J = 12.7$ Hz, 1H), 1.37 (s, 3H), 1.36 (s, 3H), 1.34 (d, $J = 6.2$ Hz, 3H). The NMR data were in consistent with the reported data.^[7]

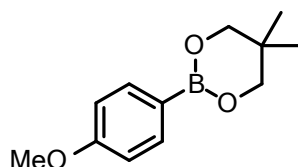
2-(4-methoxyphenyl)-4,4,6,6-tetramethyl-1,3,2-dioxaborinane (5a)



Following general procedure (D), **5a** was obtained as colourless liquid in 61% isolated yield using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.79 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 3.82 (s, 3H), 1.90 (s, 2H), 1.42 (s, 12H). The NMR data were in consistent with the reported data.^[14]

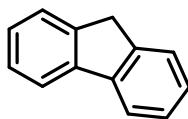
2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (6a)



Following general procedure (D), **6a** was obtained as white solid in 82% NMR yield and 49% isolated yield using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.74 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 3H), 3.75 (s, 4H), 1.02 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 161.88, 135.65, 113.27, 72.38, 55.17, 32.01, 22.04. $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 26.79. (signal for the carbon that is attached to the boron atom was not observed). The NMR data were in consistent with the reported data.^[7]

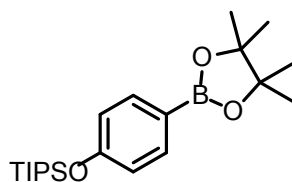
fluorene(9a)



Following general procedure (B), **9a** was obtained as white solid in 65% isolated yield using petroleum ether as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.5$ Hz, 2H), 7.57 (d, $J = 7.4$ Hz, 2H), 7.41 (t, $J = 7.4$ Hz, 2H), 7.33 (td, $J = 7.4, 1.3$ Hz, 2H), 3.93 (s, 2H). The NMR data were in consistent with the reported data.^[15]

2-(4-(triisopropylsilyloxy) phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(13c)

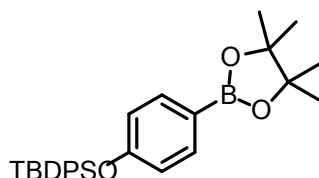


(triisopropylsilyloxy)benzene was synthesized according to the literature precedent:^[16] Phenol (2 g, 21.25 mmol) and imidazole (3.62 g, 53.13 mmol) were dissolved in 130 mL of DCM. Triisopropylsilyl chloride (5.45 mL, 25.5 mmol) was added to the mixture and the mixture stirred at room temperature until no starting material remained by TLC. The reaction mixture was extracted using distilled H₂O (1 x 70 mL) and the organic layer was washed with 1 N NaOH (1 x 70 mL) and brine (1 x 70 mL), dried over using Na₂SO₄ and concentrated to afford pure product as a faint-brown oil. Analytical data matched that reported in the literature.^[16] ¹H NMR (600 MHz, CDCl₃) δ 7.22 (dt, J = 7.0, 4.4 Hz, 2H), 6.93 (dt, J = 7.6, 4.6 Hz, 1H), 6.89 (dd, J = 8.3, 2.7 Hz, 2H), 1.30 – 1.23 (m, 3H), 1.11 (dd, J = 7.9, 3.0 Hz, 18H).

Following general procedure (E), **13c** was obtained as colourless liquid in 74% NMR yield and 37% isolated yield from (triisopropylsilyloxy)benzene using 90:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.72 – 7.65 (m, 2H), 6.90 – 6.83 (m, 2H), 1.33 (s, 12H), 1.31 – 1.20 (m, 3H), 1.09 (d, J = 7.3 Hz, 18H). ¹³C NMR (151 MHz, CDCl₃) δ 159.10, 136.57, 119.52, 83.65, 25.02, 18.05, 12.85 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (128 MHz, CDCl₃) δ 32.12. The NMR data were in consistent with the reported data.^[17]

2-[4-[[1,1-dimethylethyl] diphenylsilyl] oxy] phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(**13d**)

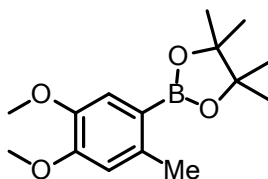


tert-Butyl(phenoxy)diphenylsilane was synthesized according to literature precedent:^[16] phenol (2 g, 21 mmol) and imidazole (2.6 g, 38.5 mmol) were dissolved in 20 mL of MeCN. *tert*Butyldiphenylsilyl chloride (4.6 mL, 17.5 mmol) was added to the mixture and the reaction was allowed to stir overnight. The reaction was diluted with 40 mL Et₂O and poured into 50 mL of water. The organic layer was extracted with Et₂O (2 x 40 mL), washed with brine (1 x 50 mL) and dried using Na₂SO₄. The crude product was purified by column chromatography to afford the pure product as a colourless oil. Analytical data matched that reported in the literature.^[18] ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.70 (m, 4H), 7.47 – 7.35 (m, 6H), 7.15 – 7.07 (m, 2H), 6.91 – 6.85 (m, 1H), 6.82 – 6.75 (m, 2H), 1.12 (s, 9H).

Following general procedure (E), **13d** was obtained as white solid in 43% NMR yield and 26% isolated yield from *tert*-Butyl(phenoxy)diphenylsilane using 60:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.73 (dd, J = 8.0, 1.5 Hz, 4H), 7.58 (d, J = 8.5 Hz, 2H), 7.46 – 7.34 (m, 6H), 6.81 – 6.74 (m, 2H), 1.31 (s, 12H), 1.11 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 136.37, 135.59, 132.87, 130.03, 127.91, 119.37, 83.61, 26.62, 25.17, 24.98, 19.60. (Signal for the carbon that is attached to the boron atom was not observed.). ¹¹B NMR (128 MHz, CDCl₃) δ 32.76. The NMR data were in consistent with the reported data.^[19]

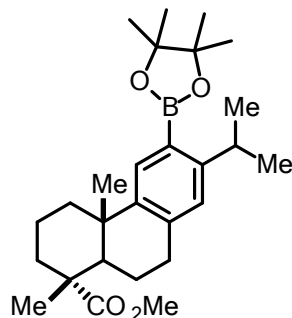
2-(4,5-dimethoxy-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(**13h**)



Following general procedure (E), **13h** was obtained as white solid in 76% NMR yield and 55% isolated yield from 1,2-dimethoxy-4-methylbenzene using 20:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 (s, 1H), 6.62 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 2.44 (s, 3H), 1.27 (s, 12H).

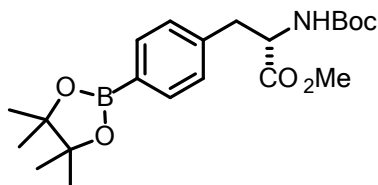
Methyl dehydroabietate derivative (**14**)



Following general procedure (E), **14** was obtained as white solid in 55% NMR yield and 51% isolated yield from methyl dehydroabietate using 75:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.62 (s, 1H), 6.95 (s, 1H), 3.66 (s, 3H), 3.61 (p, $J = 6.9$ Hz, 1H), 2.91 – 2.86 (m, 2H), 2.42 (dt, $J = 13.4, 3.0$ Hz, 1H), 2.22 (dd, $J = 12.6, 2.2$ Hz, 1H), 1.86 – 1.71 (m, 4H), 1.66 – 1.62 (m, 1H), 1.52 (dt, $J = 12.6, 6.2$ Hz, 1H), 1.41 (ddq, $J = 12.1, 5.7, 3.3, 2.5$ Hz, 1H), 1.33 (s, 12H), 1.28 (s, 3H), 1.22 (s, 3H), 1.21 (d, $J = 7.0$ Hz, 3H), 1.19 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 179.33, 152.45, 145.96, 138.08, 132.02, 125.17, 83.22, 52.02, 47.83, 45.08, 38.00, 36.98, 36.85, 31.02, 30.34, 25.12, 24.95 (d, $J = 4.2$ Hz), 24.77, 24.39, 21.76, 18.68 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 32.56. **HRMS** calculated for $\text{C}_{27}\text{H}_{41}\text{B}_1\text{O}_4$ ($M + \text{Na}^+$): 463.29901, found: 463.29868.

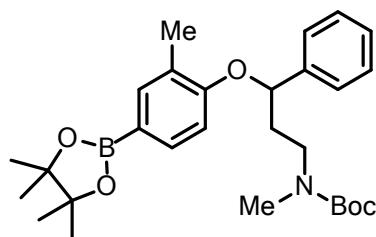
Phenylalanine derivative (**15**)



Following general procedure (B), **15** was obtained as colourless liquid in 66% NMR yield and 63% isolated yield from N-Boc-4-bromo-L-phenylalanine methyl ester using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.73 (d, $J = 7.6$ Hz, 2H), 7.12 (d, $J = 7.5$ Hz, 2H), 4.95 (d, $J = 8.3$ Hz, 1H), 4.58 (q, $J = 6.7$ Hz, 1H), 3.70 (s, 3H), 3.10 (qd, $J = 13.8, 5.7$ Hz, 2H), 1.42 (s, 9H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 172.35, 155.19, 139.35, 135.14, 128.83, 83.91, 80.07, 54.48, 52.32, 38.55, 28.43, 25.00 (d, $J = 2.6$ Hz) (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 31.41. **HRMS** calculated for $\text{C}_{21}\text{H}_{32}\text{B}_1\text{N}_1\text{O}_6$ ($M + \text{Na}^+$): 428.22149, found: 428.22122.

Atomoxetine derivative (**16**)

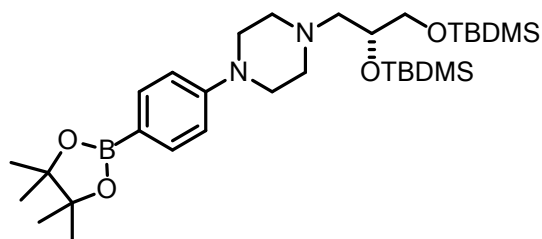


Following general procedure (E), **16** was obtained as colourless oil in 81% isolated yield from Atomoxetine derivative using 15:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.58 (s, 1H), 7.43 (d, $J = 6.6$ Hz, 1H), 7.30 (d, $J = 5.0$ Hz, 4H), 7.22 (dt, $J = 9.1, 4.6$ Hz, 1H), 6.57 (d, $J = 8.2$ Hz, 1H), 5.21 (d, $J = 8.5$ Hz, 1H), 3.41 (s, 2H), 2.83 (s, 3H), 2.33 (s, 3H), 2.24 – 2.05 (m, 2H), 1.43 – 1.34 (m, 9H), 1.29 (d, $J = 3.6$ Hz, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.55, 155.89, 141.60, 137.32, 134.08, 128.80, 127.69, 126.36, 125.74, 112.11, 83.56, 79.51, 46.10, 37.39, 34.61, 28.52, 24.95 (d, $J = 9.8$ Hz), 16.41 (signal for the carbon that is attached to the boron atom was not observed).

$^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 34.09. **HRMS** calculated for $\text{C}_{28}\text{H}_{40}\text{B}_1\text{N}_1\text{O}_5$ ($\text{M} + \text{Na}^+$): 504.28917, found: 504.28864.

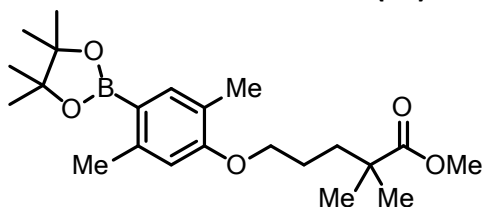
Levodropropizine derivative (17)



Following general procedure (E), **17** was obtained as colourless oil in 72% NMR yield and 66% isolated yield from Levodropropizine derivative using 25:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.70 (d, $J = 8.2$ Hz, 2H), 6.88 (d, $J = 8.2$ Hz, 2H), 3.84 – 3.76 (m, 1H), 3.60 (dd, $J = 10.1, 5.8$ Hz, 1H), 3.53 (dd, $J = 10.2, 5.5$ Hz, 1H), 3.24 (t, $J = 5.0$ Hz, 3H), 2.66 (dt, $J = 10.6, 5.0$ Hz, 2H), 2.62 – 2.54 (m, 2H), 2.49 (dd, $J = 13.1, 4.7$ Hz, 1H), 2.37 (dd, $J = 13.1, 6.0$ Hz, 1H), 2.04 (t, $J = 12.2$ Hz, 1H), 1.32 (s, 12H), 0.89 (d, $J = 5.2$ Hz, 18H), 0.09 – 0.07 (m, 6H), 0.06 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 153.66, 136.25, 114.34, 83.48, 72.00, 66.28, 62.12, 54.24, 48.29, 26.10 (d, $J = 12.0$ Hz), 25.00, -4.74 (dd, $J = 127.4, 9.3$ Hz) (signal for the carbon that is attached to the boron atom was not observed). **HRMS** calculated for $\text{C}_{31}\text{H}_{59}\text{B}_1\text{N}_2\text{O}_4\text{Si}_2$ ($\text{M} + \text{Na}^+$): 613.39986, found: 613.39868.

Gemfibrozil derivative (18)



Following general procedure (E), **18** was obtained as colourless liquid in 82% NMR yield and 76% isolated yield from Gemfibrozil derivative using 70:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.54 (s, 1H), 6.59 (s, 1H), 3.94 (t, $J = 5.4$ Hz, 2H), 3.67 (s, 3H), 2.51 (s, 3H), 2.17 (s, 3H), 1.72 (dd, $J = 4.6, 3.0$ Hz, 4H), 1.33 (s, 12H), 1.22 (s, 6H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 178.41, 159.30, 144.79, 138.43, 122.95, 112.63, 83.15, 67.80, 51.85, 42.21, 37.15, 25.30,

25.24, 24.99, 22.34, 15.55 (signal for the carbon that is attached to the boron atom was not observed). ^{11}B NMR (128 MHz, CDCl_3) δ 32.03. HRMS calculated for $\text{C}_{22}\text{H}_{35}\text{B}_1\text{O}_5$ ($\text{M} + \text{Na}^+$): 413.24698, found: 413.24646.

3.2 Reactivity of Dihaloarenes

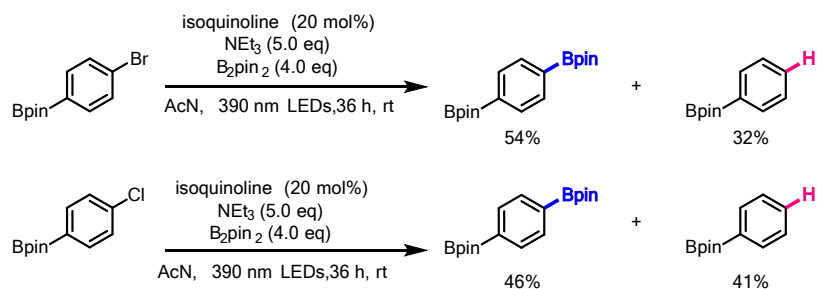
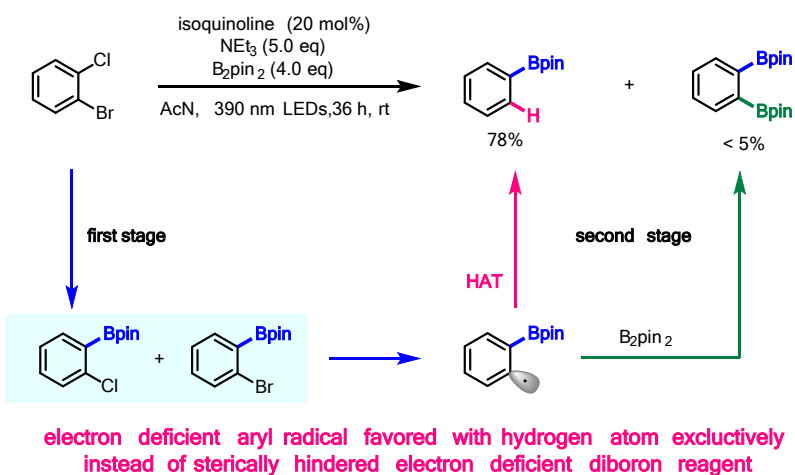
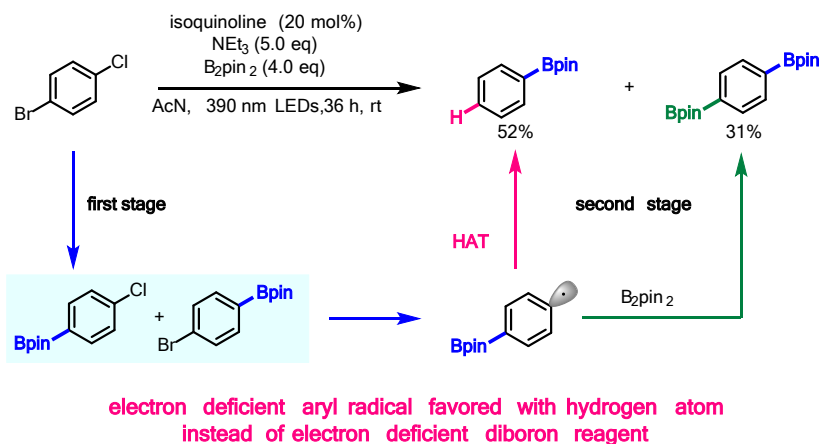


Table S3 Reactivity of dihaloarenes

3.3 Reactivities Screen of Aromatic Compounds with Different Leaving Groups

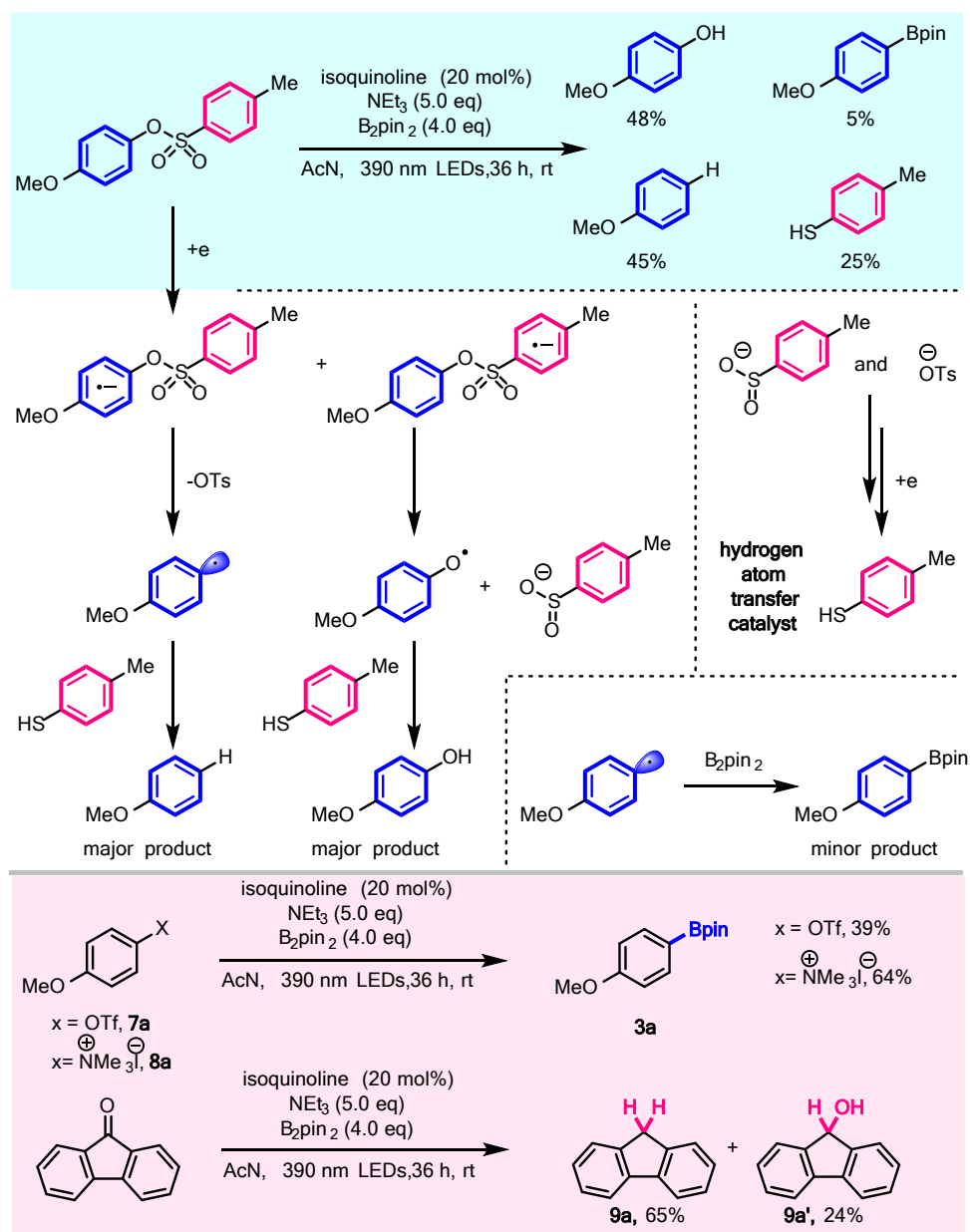
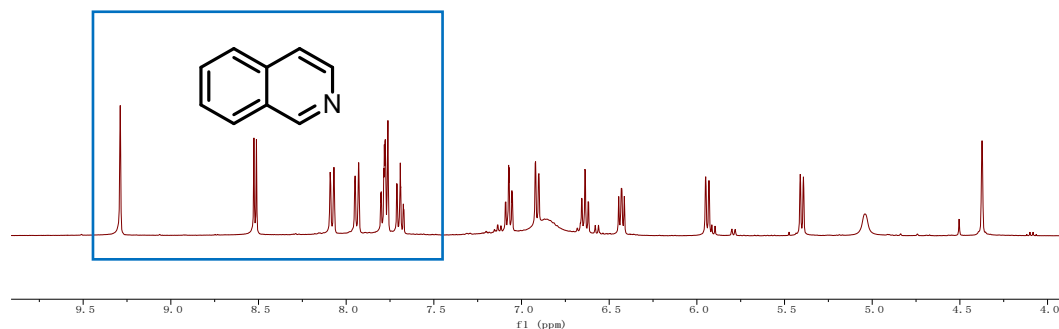


Table S4 Reactivities screen of aromatic compounds with different leaving groups

4.) Preliminary Mechanistic Studies

4.1 NMR Study of the B₂pin₂/NEt₃/ Isoquinoline System

An oven-dried 2 mL vial was charged with a magnetic stir bar, B₂pin₂ (51 mg, 0.2 mmol, 1.0 eq), NEt₃ (28 μL, 0.2 mmol, 1.0 eq), isoquinoline (26 mg, 0.2 mmol, 1.0 eq) and AcN (0.5 mL). The tube was sealed with a plastic cap and the reaction mixture was allowed to react at room temperature for 6 h.

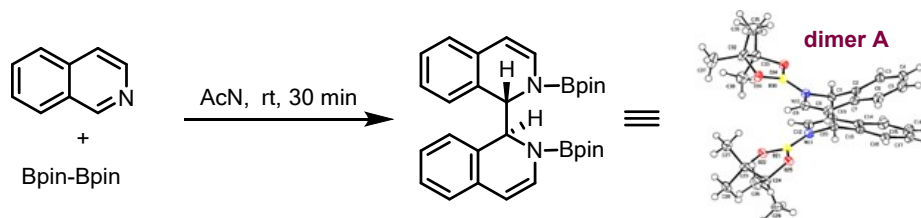


Schme S2 The aromatic region of ^1H NMR spectrum of $\text{B}_2\text{Pin}_2/\text{NEt}_3/\text{isoquinoline}$ system

The ^1H NMR spectrum of the $\text{B}_2\text{pin}_2/\text{NEt}_3/\text{isoquinoline}$ reaction mixture was quite clear, and the aromatic region showed that isoquinoline was partly transformed to an intermediate specie. The peaks all shifted to upfield area and which around 4.5 ppm implied the formation of a dearomatized isoquinoline ring, where two new chemical bonds were probably connected to the N atom and 1-positions.

4.2 Synthesis and Characterization of Dimer A

In order to determine the structure of intermediate specie. We found another kind of method to synthesize the intermediate in better efficiency. An oven-dried 2 mL vial was charged with a magnetic stir bar, B_2pin_2 (254 mg, 1.0 mmol, 1.0 eq), isoquinoline (258 mg, 2.0 mmol, 2.0 eq) and AcN (0.5 mL). The tube was sealed with a plastic cap and the reaction mixture was allowed to react at room temperature for 30 min. During this time, some kind of white solid insoluble in AcN appeared. After filtration and washed with hexane, the intermediate specie was obtained in almost 99% yield as white solid. And the structure was determined by X-ray diffraction analysis as a *trans* dimer.



Schme S3 Synthesis of dimer A and X-ray confirmation

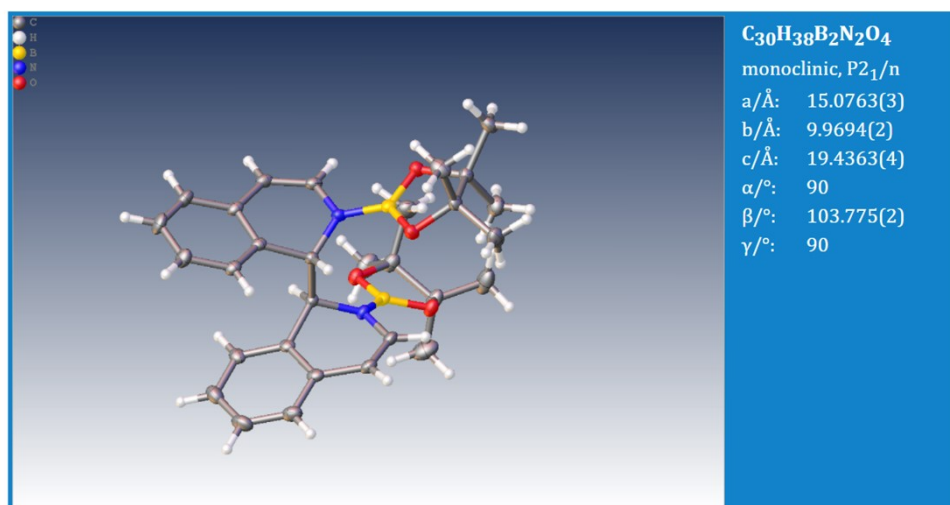
^1H NMR (400 MHz, CDCl_3) δ 7.10 (t, $J = 7.6$ Hz, 2H), 7.00 (d, $J = 7.6$ Hz, 2H), 6.67 (t, $J = 7.5$ Hz, 2H), 6.58 (d, $J = 7.3$ Hz, 2H), 5.87 (t, $J = 6.9$ Hz, 4H), 4.57 (s, 2H), 1.27 (s, 24H). ^{13}C NMR (101 MHz, CDCl_3) δ 132.41, 131.16, 129.00, 128.78, 127.25, 124.17, 122.92, 106.02, 83.35, 54.24, 25.52, 24.70. The NMR data were in consistent with the reported data.^[20]

4.3 X-ray Crystallographic Data of Dimer A

Single crystals of $\text{C}_{30}\text{H}_{38}\text{B}_2\text{N}_2\text{O}_4$ [dimer A] were obtained by recrystallization from AcN / DCM at room temperature. A suitable crystal was selected and put on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2^[21], the structure was solved with the SHELXT^[22] structure solution program using Intrinsic Phasing and refined with the SHELXL^[23] refinement package using Least Squares minimisation.

Crystal Data for $\text{C}_{30}\text{H}_{38}\text{B}_2\text{N}_2\text{O}_4$ ($M = 512.24$ g/mol): monoclinic, space group $P2_1/n$ (no. 14), $a = 15.0763(3)$ Å, $b = 9.9694(2)$ Å, $c = 19.4363(4)$ Å, $\beta = 103.775(2)^\circ$, $V = 2837.29(10)$ Å³, $Z = 4$, $T = 100.00(10)$ K, $\mu(\text{Cu K}\alpha) = 0.616$ mm⁻¹, $D_{\text{calc}} = 1.199$ g/cm³, 18990 reflections measured ($6.702^\circ \leq$

$2\theta \leq 150.928^\circ$), 5671 unique ($R_{\text{int}} = 0.0786$, $R_{\text{sigma}} = 0.0694$) which were used in all calculations. The final R_1 was 0.0512 ($I > 2\sigma(I)$) and wR_2 was 0.1438 (all data).



Diffractometer	XtaLAB Synergy R, DW system, HyPix
Radiation Source	Cu K α ($\lambda = 1.54184\text{\AA}$)
Data Collection	CrysAlisPro 1.171.41.112a (Rigaku OD, 2021)

Empirical formula	C ₃₀ H ₃₈ B ₂ N ₂ O ₄
Formula weight	512.24
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	15.0763(3)
b/Å	9.9694(2)
c/Å	19.4363(4)
$\alpha/^\circ$	90
$\beta/^\circ$	103.775(2)
$\gamma/^\circ$	90
Volume/Å ³	2837.29(10)
Z	4
$\rho_{\text{calc}}/\text{mm}^3$	1.199
μ/mm^{-1}	0.616
F(000)	1096
Crystal size/mm ³	0.15 × 0.1 × 0.1
2 θ range for data collection	6.702 to 150.928°
Index ranges	-17 ≤ h ≤ 18, -10 ≤ k ≤ 12, -24 ≤ l ≤ 24
Reflections collected	18990
Independent reflections	5671 [R(int) = 0.0786]

Data/restraints/parameters	5671/0/351
Goodness-of-fit on F ²	1.055
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0512, wR ₂ = 0.1356
Final R indexes [all data]	R ₁ = 0.0616, wR ₂ = 0.1438
Largest diff. peak/hole / e Å ⁻³	0.52/-0.31

Table S3 Crystal data and structure refinement for dimer A

Atom	x	y	z	U(eq)
O22	5742.0(7)	3059.7(11)	5580.9(6)	19.9(2)
O34	7402.4(7)	5578.4(11)	4421.8(6)	20.1(2)
O25	6704.3(7)	1299.6(11)	5490.2(6)	20.0(2)
O31	8377.5(7)	4975.2(11)	5480.0(6)	21.6(3)
N10	7926.6(8)	3236.4(13)	4577.2(7)	17.5(3)
N11	6038.1(8)	2588.2(13)	4413.6(7)	18.0(3)
C1	7380.8(10)	2798.6(15)	3884.6(8)	16.3(3)
C2	7970.6(10)	2031.3(15)	3493.4(8)	18.3(3)
C20	6573.1(10)	1879.7(14)	3986.6(8)	16.3(3)
C9	8500.4(10)	2264.0(16)	4972.9(8)	19.7(3)
C7	8613.3(10)	1134.1(16)	3895.9(9)	20.8(3)
C12	5384.4(10)	3505.9(15)	4061.9(9)	19.5(3)
C18	6173.2(10)	335.5(15)	2919.4(9)	20.1(3)
C19	5986.4(10)	1473.6(15)	3274.8(8)	17.3(3)
C13	5030.8(10)	3436.0(16)	3362.2(9)	20.5(3)
C24	6453.4(11)	1142.1(16)	6167.1(8)	20.4(3)
C8	8789.9(10)	1201.2(16)	4665.7(9)	20.8(3)
C14	5264.5(10)	2326.2(15)	2952.6(8)	19.2(3)
C3	7846.8(11)	2106.3(17)	2762.1(9)	22.6(3)
C15	4769.2(11)	2034.8(17)	2261.2(9)	24.4(3)
C23	6122.2(10)	2577.2(16)	6300.5(8)	19.9(3)
C32	8338.9(12)	6437.7(16)	5472.1(9)	25.6(4)
C6	9089.7(11)	284.5(18)	3538.9(10)	27.5(4)
C17	5672.3(11)	52.5(17)	2236.6(9)	25.5(3)
C4	8337.8(12)	1253.4(18)	2417.9(10)	29.2(4)
C28	5376.1(12)	2619.8(18)	6706.3(9)	27.2(4)
C33	7445.2(11)	6714.5(16)	4901.7(9)	25.0(3)
C16	4973.4(12)	920.4(18)	1905.2(9)	29.3(4)

C5	8947.1(12)	340.0(19)	2808.4(11)	31.7(4)
C27	6903.6(13)	3518.9(18)	6634.8(10)	29.6(4)
C29	5693.7(13)	108.8(17)	6057.1(10)	30.0(4)
C26	7283.3(13)	654(2)	6713.9(10)	32.4(4)
B21	6168.1(11)	2330.6(17)	5150.5(9)	17.7(3)
B30	7895.7(11)	4573.7(17)	4821.1(9)	17.8(3)
C38	6600.2(13)	6614.9(19)	5203.1(11)	32.5(4)
C35	7428.4(14)	8003.1(18)	4493.2(12)	36.5(4)
C37	8367.3(15)	6943(2)	6204.7(11)	40.8(5)
C36	9195.4(13)	6898(2)	5239.3(14)	41.2(5)

Table S4 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for dimer A. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O22	20.1(5)	22.8(5)	17.6(5)	2.2(4)	5.8(4)	3.4(4)
O34	20.1(5)	19.4(5)	18.9(5)	-0.1(4)	0.8(4)	-0.6(4)
O25	19.2(5)	23.8(5)	18.0(5)	2.4(4)	6.4(4)	3.6(4)
O31	20.9(5)	20.7(5)	19.9(6)	-3.0(4)	-1.7(4)	2.4(4)
N10	14.2(6)	20.5(6)	16.0(6)	-0.2(5)	0.1(5)	0.2(5)
N11	13.8(6)	21.9(6)	18.7(6)	1.7(5)	5.0(5)	2.3(5)
C1	14.8(6)	18.6(7)	14.8(7)	0.0(5)	2.1(5)	-0.6(5)
C2	13.3(6)	19.9(7)	22.2(8)	-2.2(6)	5.6(5)	-5.1(6)
C20	13.4(6)	18.9(7)	16.7(7)	-0.4(5)	3.9(5)	0.5(5)
C9	13.6(6)	24.0(7)	19.2(7)	1.0(6)	-0.5(5)	-0.7(6)
C7	13.6(6)	22.2(7)	26.9(8)	-3.0(6)	5.2(6)	-3.2(6)
C12	14.8(7)	21.1(7)	23.6(8)	3.4(6)	6.4(6)	1.9(6)
C18	15.8(7)	20.8(7)	22.7(8)	0.5(6)	2.7(6)	-2.4(6)
C19	13.1(6)	19.0(7)	19.7(7)	3.0(6)	3.5(5)	-2.2(5)
C13	14.5(7)	21.9(7)	24.6(8)	4.8(6)	4.0(6)	2.2(6)
C24	22.4(7)	23.2(8)	16.4(7)	3.1(6)	6.4(6)	0.9(6)
C8	13.8(7)	22.0(7)	24.5(8)	0.4(6)	0.7(6)	1.0(6)
C14	14.6(7)	20.0(7)	21.7(8)	3.2(6)	1.8(6)	-2.8(6)
C3	20.1(7)	26.2(8)	23.3(8)	-2.8(6)	8.6(6)	-7.7(6)
C15	18.1(7)	25.8(8)	25.0(8)	3.1(6)	-3.8(6)	0.1(6)
C23	20.2(7)	22.3(7)	17.4(7)	1.8(6)	4.8(6)	0.2(6)
C32	26.3(8)	17.1(7)	27.9(9)	-3.6(6)	-4.5(7)	-1.1(6)

C6	19.8(7)	27.1(8)	36.0(9)	-6.4(7)	7.4(7)	0.8(6)
C17	25.0(8)	22.9(8)	25.2(8)	-4.1(6)	-1.0(6)	-2.6(6)
C4	31.8(9)	34.4(9)	25.0(8)	-7.0(7)	14.0(7)	-8.6(7)
C28	29.7(8)	32.3(9)	23.3(8)	0.1(7)	13.7(7)	2.7(7)
C33	24.8(8)	20.3(8)	26.4(8)	-2.7(6)	-0.7(6)	1.9(6)
C16	28.2(8)	30.8(9)	22.8(8)	-3.6(7)	-6.0(7)	-3.1(7)
C5	28.4(8)	33.4(9)	38.2(10)	-11.7(8)	17.5(8)	-1.9(7)
C27	31.2(9)	29.2(9)	26.8(9)	-4.7(7)	4.0(7)	-5.4(7)
C29	35.5(9)	23.5(8)	35.0(10)	-0.4(7)	16.1(8)	-5.7(7)
C26	34.5(9)	38.0(10)	23.6(8)	6.2(7)	4.5(7)	11.5(8)
B21	13.8(7)	20.8(8)	18.5(8)	1.6(6)	3.7(6)	-1.7(6)
B30	13.2(7)	21.6(8)	18.2(8)	-0.6(6)	3.0(6)	-1.5(6)
C38	28.3(9)	31.2(9)	38.0(10)	-1.7(8)	7.9(8)	6.5(7)
C35	39.0(10)	22.7(9)	41.6(11)	5.5(8)	-2.7(8)	-0.5(7)
C37	45.4(11)	33.6(10)	34.6(11)	-12.9(8)	-7.8(9)	8.9(9)
C36	26.3(9)	33.9(10)	59.4(14)	-1.3(9)	2.5(9)	-7.2(8)

Table S5 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dimer A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	Atom	Length/ \AA	Atom	Atom	Length/ \AA
O22	C23	1.4610(19)	C12	C13	1.339(2)
O22	B21	1.377(2)	C18	C19	1.392(2)
O34	C33	1.459(2)	C18	C17	1.391(2)
O34	B30	1.373(2)	C19	C14	1.405(2)
O25	C24	1.4614(18)	C13	C14	1.455(2)
O25	B21	1.375(2)	C24	C23	1.557(2)
O31	C32	1.4591(19)	C24	C29	1.517(2)
O31	B30	1.373(2)	C24	C26	1.516(2)
N10	C1	1.4670(19)	C14	C15	1.404(2)
N10	C9	1.401(2)	C3	C4	1.398(2)
N10	B30	1.419(2)	C15	C16	1.382(3)
N11	C20	1.4687(18)	C23	C28	1.521(2)
N11	C12	1.398(2)	C23	C27	1.525(2)
N11	B21	1.422(2)	C32	C33	1.552(2)
C1	C2	1.509(2)	C32	C37	1.501(3)
C1	C20	1.5736(19)	C32	C36	1.537(3)

C2	C7	1.411(2)	C6	C5	1.386(3)
C2	C3	1.391(2)	C17	C16	1.397(3)
C20	C19	1.509(2)	C4	C5	1.385(3)
C9	C8	1.339(2)	C33	C38	1.527(2)
C7	C8	1.457(2)	C33	C35	1.507(2)
C7	C6	1.397(2)	□	□	□

Table S6 Bond lengths for dimer A.

Atom	Atom	Atom	Angle/°
B21	O22	C23	105.91(11)
B30	O34	C33	105.64(12)
B21	O25	C24	105.30(11)
B30	O31	C32	105.70(12)
C9	N10	C1	115.85(12)
C9	N10	B30	122.11(13)
B30	N10	C1	122.01(13)
C12	N11	C20	117.16(12)
C12	N11	B21	121.52(13)
B21	N11	C20	121.31(13)
N10	C1	C2	110.13(12)
N10	C1	C20	109.84(12)
C2	C1	C20	109.57(12)
C7	C2	C1	116.83(14)
C3	C2	C1	122.41(14)
C3	C2	C7	120.54(14)
N11	C20	C1	109.68(12)
N11	C20	C19	111.47(12)
C19	C20	C1	110.06(12)
C8	C9	N10	121.79(14)
C2	C7	C8	118.27(14)
C6	C7	C2	118.38(15)
C6	C7	C8	123.22(15)
C13	C12	N11	121.76(14)
C17	C18	C19	120.74(15)
C18	C19	C20	122.01(13)
C18	C19	C14	119.91(14)

C14	C19	C20	117.98(13)
C12	C13	C14	120.37(14)
O25	C24	C23	102.31(11)
O25	C24	C29	107.14(13)
O25	C24	C26	108.55(12)
C29	C24	C23	112.71(13)
C26	C24	C23	114.95(14)
C26	C24	C29	110.51(15)
C9	C8	C7	119.65(14)
C19	C14	C13	118.62(14)
C15	C14	C19	118.73(15)
C15	C14	C13	122.58(14)
C2	C3	C4	119.92(16)
C16	C15	C14	120.97(15)
O22	C23	C24	102.21(12)
O22	C23	C28	108.50(13)
O22	C23	C27	106.99(13)
C28	C23	C24	114.72(13)
C28	C23	C27	110.71(14)
C27	C23	C24	112.99(13)
O31	C32	C33	102.17(12)
O31	C32	C37	109.45(15)
O31	C32	C36	105.52(14)
C37	C32	C33	116.21(15)
C37	C32	C36	110.06(17)
C36	C32	C33	112.58(16)
C5	C6	C7	120.80(17)
C18	C17	C16	119.53(16)
C5	C4	C3	119.70(16)
O34	C33	C32	102.55(12)
O34	C33	C38	106.31(13)
O34	C33	C35	109.41(15)
C38	C33	C32	112.09(15)
C35	C33	C32	115.50(15)
C35	C33	C38	110.28(15)
C15	C16	C17	120.06(16)

C4	C5	C6	120.58(15)
O22	B21	N11	122.96(14)
O25	B21	O22	114.13(14)
O25	B21	N11	122.87(14)
O34	B30	O31	114.19(14)
O34	B30	N10	123.58(14)
O31	B30	N10	122.22(14)

Table S7 Bond angles for dimer A.

A	B	C	D	Angle^o
O25	C24	C23	O22	31.34(14)
O25	C24	C23	C28	148.53(13)
O25	C24	C23	C27	-83.28(15)
O31	C32	C33	O34	-30.84(16)
O31	C32	C33	C38	82.80(16)
O31	C32	C33	C35	-149.75(15)
N10	C1	C2	C7	40.54(17)
N10	C1	C2	C3	-144.68(14)
N10	C1	C20	N11	54.66(15)
N10	C1	C20	C19	177.64(11)
N10	C9	C8	C7	8.6(2)
N11	C20	C19	C18	-149.79(13)
N11	C20	C19	C14	33.91(18)
N11	C12	C13	C14	5.1(2)
C1	N10	C9	C8	23.2(2)
C1	N10	B30	O34	-3.9(2)
C1	N10	B30	O31	177.38(13)
C1	C2	C7	C8	-11.89(19)
C1	C2	C7	C6	172.04(14)
C1	C2	C3	C4	-172.26(14)
C1	C20	C19	C18	88.29(16)
C1	C20	C19	C14	-88.01(15)
C2	C1	C20	N11	175.76(12)
C2	C1	C20	C19	-61.25(15)
C2	C7	C8	C9	-14.1(2)
C2	C7	C6	C5	1.2(2)

C2	C3	C4	C5	-0.2(2)
C20	N11	C12	C13	22.4(2)
C20	N11	B21	O22	173.82(13)
C20	N11	B21	O25	-8.6(2)
C20	C1	C2	C7	-80.40(16)
C20	C1	C2	C3	94.39(16)
C20	C19	C14	C13	-9.4(2)
C20	C19	C14	C15	173.74(13)
C9	N10	C1	C2	-46.17(16)
C9	N10	C1	C20	74.60(15)
C9	N10	B30	O34	174.15(13)
C9	N10	B30	O31	-4.6(2)
C7	C2	C3	C4	2.3(2)
C7	C6	C5	C4	0.9(3)
C12	N11	C20	C1	81.78(15)
C12	N11	C20	C19	-40.37(17)
C12	N11	B21	O22	-7.4(2)
C12	N11	B21	O25	170.09(14)
C12	C13	C14	C19	-11.5(2)
C12	C13	C14	C15	165.31(15)
C18	C19	C14	C13	174.26(13)
C18	C19	C14	C15	-2.6(2)
C18	C17	C16	C15	-1.5(3)
C19	C18	C17	C16	-0.1(2)
C19	C14	C15	C16	1.1(2)
C13	C14	C15	C16	-175.69(15)
C24	O25	B21	O22	13.46(17)
C24	O25	B21	N11	-164.27(14)
C8	C7	C6	C5	-174.63(15)
C14	C15	C16	C17	1.0(3)
C3	C2	C7	C8	173.22(14)
C3	C2	C7	C6	-2.8(2)
C3	C4	C5	C6	-1.5(3)
C23	O22	B21	O25	7.82(17)
C23	O22	B21	N11	-174.45(14)
C32	O31	B30	O34	-11.37(17)

C32	O31	B30	N10	167.50(14)
C6	C7	C8	C9	161.79(15)
C17	C18	C19	C20	-174.06(14)
C17	C18	C19	C14	2.2(2)
C33	O34	B30	O31	-9.56(17)
C33	O34	B30	N10	171.58(14)
C29	C24	C23	O22	-83.39(15)
C29	C24	C23	C28	33.81(19)
C29	C24	C23	C27	161.99(14)
C26	C24	C23	O22	148.77(13)
C26	C24	C23	C28	-94.04(17)
C26	C24	C23	C27	34.15(19)
B21	O22	C23	C24	-24.04(14)
B21	O22	C23	C28	-145.61(13)
B21	O22	C23	C27	94.91(14)
B21	O25	C24	C23	-27.22(15)
B21	O25	C24	C29	91.51(15)
B21	O25	C24	C26	-149.14(14)
B21	N11	C20	C1	-99.43(15)
B21	N11	C20	C19	138.43(14)
B21	N11	C12	C13	-156.44(15)
B30	O34	C33	C32	24.76(15)
B30	O34	C33	C38	-93.05(15)
B30	O34	C33	C35	147.87(14)
B30	O31	C32	C33	25.71(16)
B30	O31	C32	C37	149.44(15)
B30	O31	C32	C36	-92.17(16)
B30	N10	C1	C2	131.95(14)
B30	N10	C1	C20	-107.28(15)
B30	N10	C9	C8	-154.90(15)
C37	C32	C33	O34	-149.90(15)
C37	C32	C33	C38	-36.3(2)
C37	C32	C33	C35	91.2(2)
C36	C32	C33	O34	81.88(16)
C36	C32	C33	C38	-164.49(15)
C36	C32	C33	C35	-37.0(2)

Table S8 Torsion angles for dimer A.

Atom	x	y	z	U(eq)
H1	7123.11	3604.8	3600.34	20
H20	6837.1	1051.3	4246.6	20
H9	8689.22	2361.18	5472.71	24
H12	5185.85	4197.49	4326.3	23
H18	6648.16	-254.62	3145.7	24
H13	4624.95	4115.13	3132.03	25
H8	9108.61	494.74	4948.06	25
H3	7429.08	2736.39	2496.82	27
H15	4286.46	2612.32	2034.56	29
H6	9516.57	-338.81	3800.12	33
H17	5804.65	-725.83	1997.18	31
H4	8253.78	1300.27	1918.35	35
H28A	5172.25	3547.74	6732.63	41
H28B	5615.71	2272.06	7186.26	41
H28C	4859.33	2066.94	6461.61	41
H16	4638.15	744.45	1434.72	35
H5	9270.24	-253.91	2573.37	38
H27A	7380.28	3468.72	6369.8	44
H27B	7158.89	3252.69	7127.56	44
H27C	6673.72	4440.31	6621.7	44
H29A	5155.94	451.88	5714.62	45
H29B	5535.26	-68.81	6509.22	45
H29C	5899.15	-724.1	5876.56	45
H26A	7435.58	-259.04	6594.99	49
H26B	7149.58	656.62	7183.21	49
H26C	7801.34	1249.93	6716.86	49
H38A	6050.18	6630.32	4814.34	49
H38B	6587.91	7375.47	5520.08	49
H38C	6620.25	5774.89	5468.24	49
H35A	7912.72	7985.14	4234.77	55
H35B	7527.2	8762.6	4822.78	55
H35C	6834.43	8099.4	4156.46	55
H37A	7862.92	6546.52	6373.45	61
H37B	8307.82	7921.66	6194.67	61

H37C	8949.51	6689.01	6524.11	61
H36A	9740.6	6535.1	5565.4	62
H36B	9224.39	7880.44	5245.29	62
H36C	9167.43	6573.33	4758.75	62

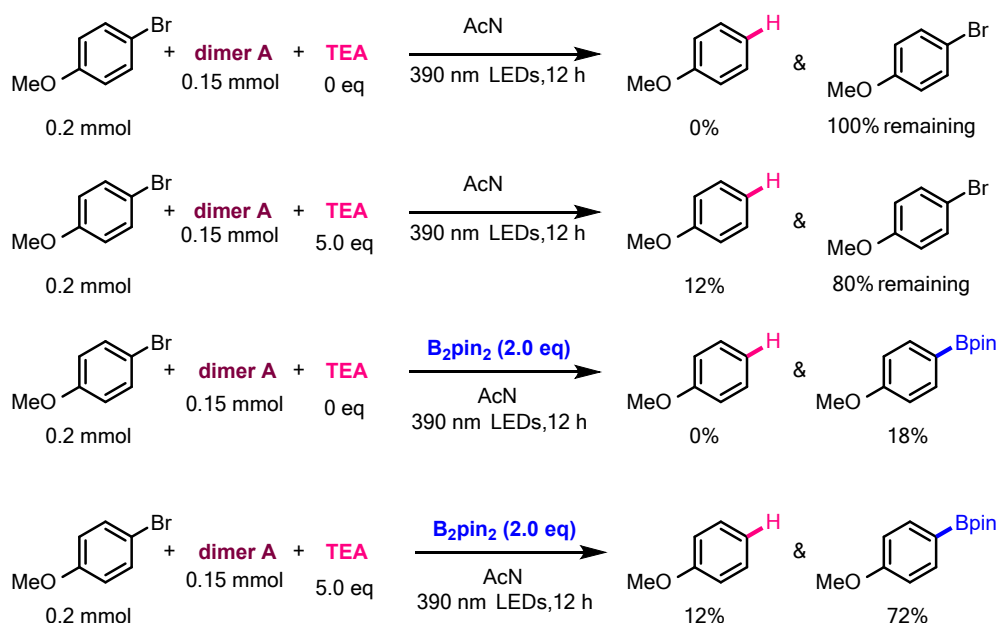
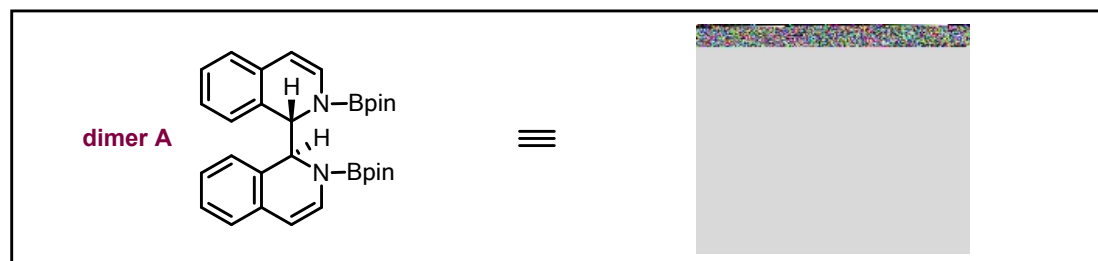
Table S9 Hydrogen atom coordinates ($\text{\AA} \times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dimer A.

4.4 The Involvement of Dimer A in the Borylation Reaction

In order to figure out the action of dimer A in borylation reaction, the synthesized dimer was utilized as reactant in the borylation reaction.

General procedure (F):

An oven-dried 2 mL vial was charged with a magnetic stir bar, 4-bromoanisole (0.2 mmol), B_2pin_2 (0 or 2.0 eq), dimer A (0.15 mmol, 0.75 eq), NEt_3 (0 or 5.0 eq), AcN (0.5 mL). The vial was sealed with a plastic cap and then irradiated with 2*390nm LEDs for 12 h. Solvent was removed by vacuum evaporation. Yield was determined by ^1H NMR using pyrazine or HDMSO as the internal standard.



Scheme S4 Mechanistic experiments

4.5 UV-Vis Spectroscopic Study

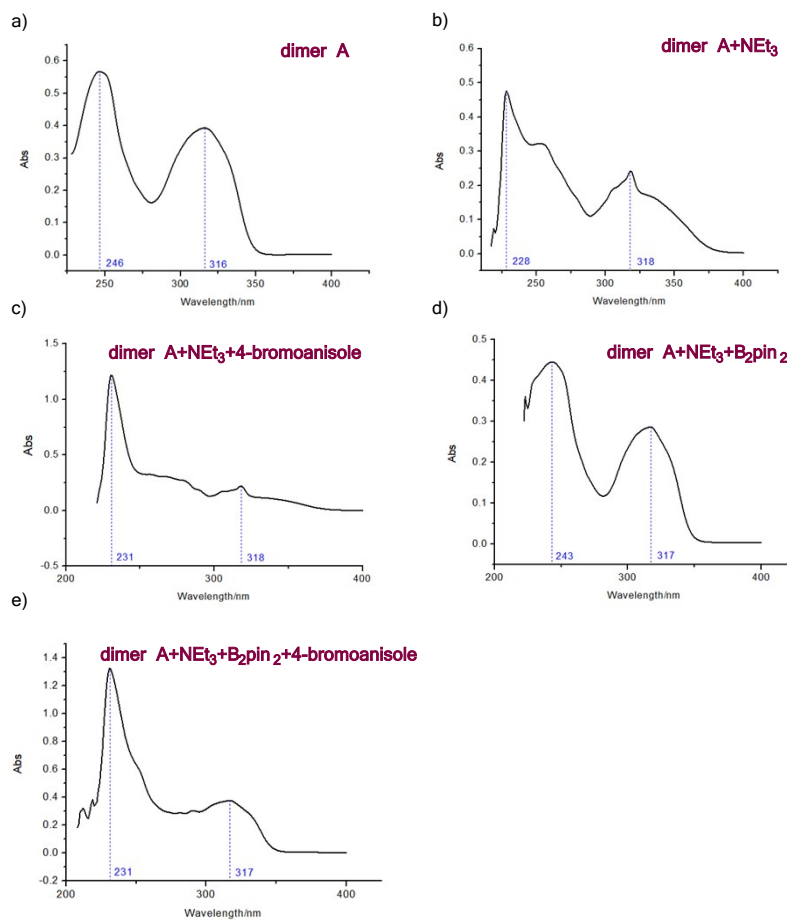


Figure S1 Experimental UV-Vis Spectra: a) UV-Vis of dimer A; b) UV-Vis of dimer A+ NEt₃; c) UV-Vis of dimer A+ NEt₃+bromoanisole; d) UV-Vis of dimer A+ NEt₃+ B₂Pin₂; e) UV-Vis of dimer A+ NEt₃+ B₂Pin₂+bromoanisole;

Experimental procedure: An oven-dried 4 mL vial was charged with a magnetic stir bar and the corresponding samples: dimer A (10 μmol/mL, 1.0 eq), NEt₃ (50 μmol/mL 5.0 eq), 4-bromoanisole (10 μmol/mL, 1.0eq), B₂pin₂ (20 μmol/mL, 2.0 eq), DCM (1.0 mL). After dissolving, transferring 8 μL of solution in 3mL of DCM to the cuvette for detection.

4.6 Fluorescence quenching experiment

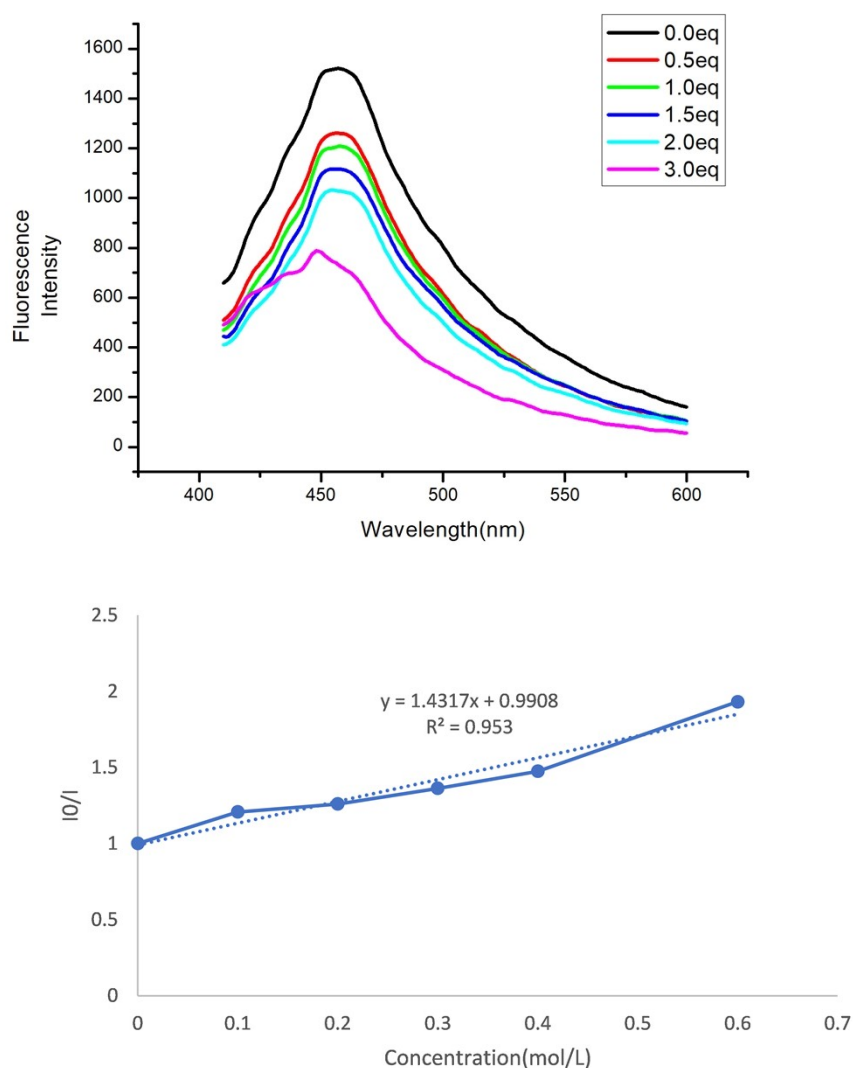


Figure S1 Fluorescence quenching experiment

Experimental procedure: Fluorescence quenching experiments were carried out with the following samples: isoquinoline(25.83 mg, 0.2 mmol, 1.0 eq), B₂pin₂ (50.79 mg, 0.2 mmol, 1.0 eq), NEt₃(27.80 μL, 0.2 mmol, 1.0 eq), 4-bromoanisole with different concentration gradient (0.0 eq, 0.5 eq, 1.0 eq, 1.5 eq, 2.0 eq) in AcN (3.0 ml) for detection. The solutions were irradiated at 399 nm and emission was monitored from 410-650 nm.

5.) Computational data

All DFT calculations were performed using Gaussian 16 software.^[24] Geometry optimization and frequency calculation of ground state were carried out with the M062X^[25]- def2SVP^[26] level of theory in PCM^[27]-AcN solvent. The geometry optimization and single point energy of excited state was performed under time dependent density functional theory (TD-DFT) calculations^[28-30] using M062X-def2SVP level of theory in PCM-AcN solvent. The relative free energies with zero-point energy (ZPE) and thermal energy corrections at 298.15K are shown in kcal/mol.

Standard reduction potential reference to the Saturated Calomel Electrode, E^0 (V vs. SCE) was calculated as indicated in Eq. (1), -100.5 kcal/mol was assumed for the reduction free energy of the standard hydrogen electrode.^[31] $\Delta G_{\text{OX}} = G(\mathbf{B}^*) - G(\mathbf{B}^+)$.

$$E^0 \text{ (V vs. SCE)} = (-100.5 - \Delta G_{\text{OX}}) / 23.06 - 0.24 \quad (1)$$

The excited-state reduction potential of \mathbf{B}^* compared to the Saturated Calomel Electrode were estimated to be -3.12 V by TD-DFT calculations. The binding energy for \mathbf{B} is 11.6 kcal/mol.

The UV-VIS spectrums calculated by TD-DFT are in the following figures.

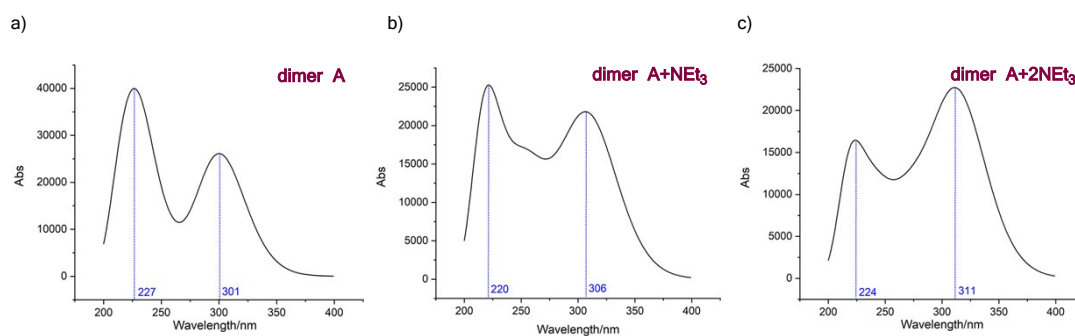


Figure S2 Computational UV-Vis Spectra: a) UV-Vis of dimer A; b) UV-Vis of dimer A+ NEt_3 ; c) UV-Vis of dimer A+ 2NEt_3 ;

\square	H	G
\mathbf{B}^*	-1915.644431	-1915.760427
B cation	-1915.589781	-1915.706134
Initial reactant	-1915.783309	-1915.90804
complex B	-1915.774421	-1915.889618

Table S10 Energies for key geometries.

Cartesian coordinates**B***

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C -4.64427000 -1.17965300 -0.13772900
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C 0.34321200 -3.51912700 -0.10795500
B -2.70028300 -0.06209100 0.16279600
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H	5.78706300	-2.44645800	-0.55040500	O	-2.89218100	0.29353300	-1.73439300
Initial reactant				C	3.12884400	3.58514900	-0.24082100
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				C	-2.41061300	1.10436500	1.86785900

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H -1.21637500 1.96122200 -1.11136500
N 5.88741600 -1.42641900 -0.50774800
C 5.57861400 -0.98830200 -1.85260500
H 6.23375500 -1.52736400 -2.56184400
H 5.86564800 0.07429300 -1.92415200
C 4.12992800 -1.15247800 -2.32106900
H 3.42509600 -0.63125800 -1.65845500
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H 3.84527800 -2.21534800 -2.35716500
C 5.59495900 -2.80283900 -0.17020100
H 5.68304300 -3.39437500 -1.09602800
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C 4.24066800 -3.08383100 0.49062400
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H 4.10942100 -4.16413700 0.65549300
H 4.18096400 -2.59052800 1.47214700
C 5.78869000 -0.44347200 0.55067500
H 6.56857400 0.32492000 0.39429800
H 6.05150400 -0.94969600 1.49439200
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H 3.61479800 -0.41916000 0.87849800
H 4.48772200 0.97916800 1.55812200
H 4.20743300 0.87360900 -0.18718200

complex B

C -4.27772100 -0.19262900 -1.48774500
C -4.74893200 -0.86639600 -0.14335500
C 0.27399900 -3.07794300 1.42588100
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B 1.29901900 -1.53076900 -0.00850700

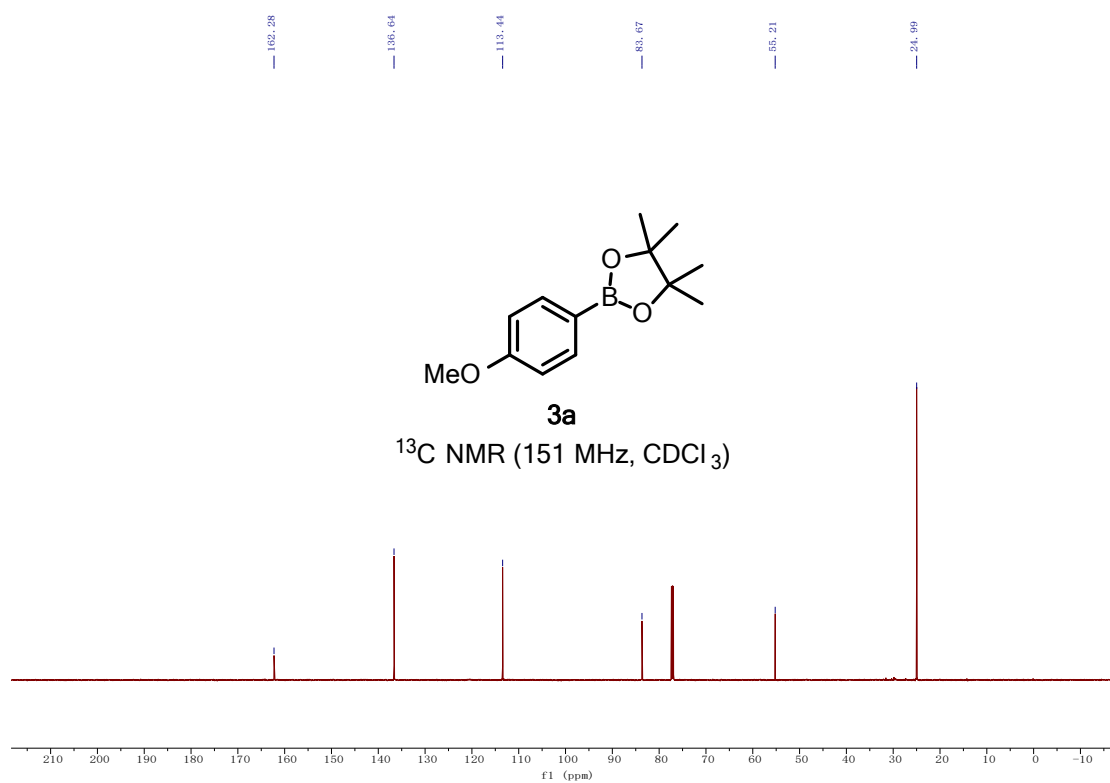
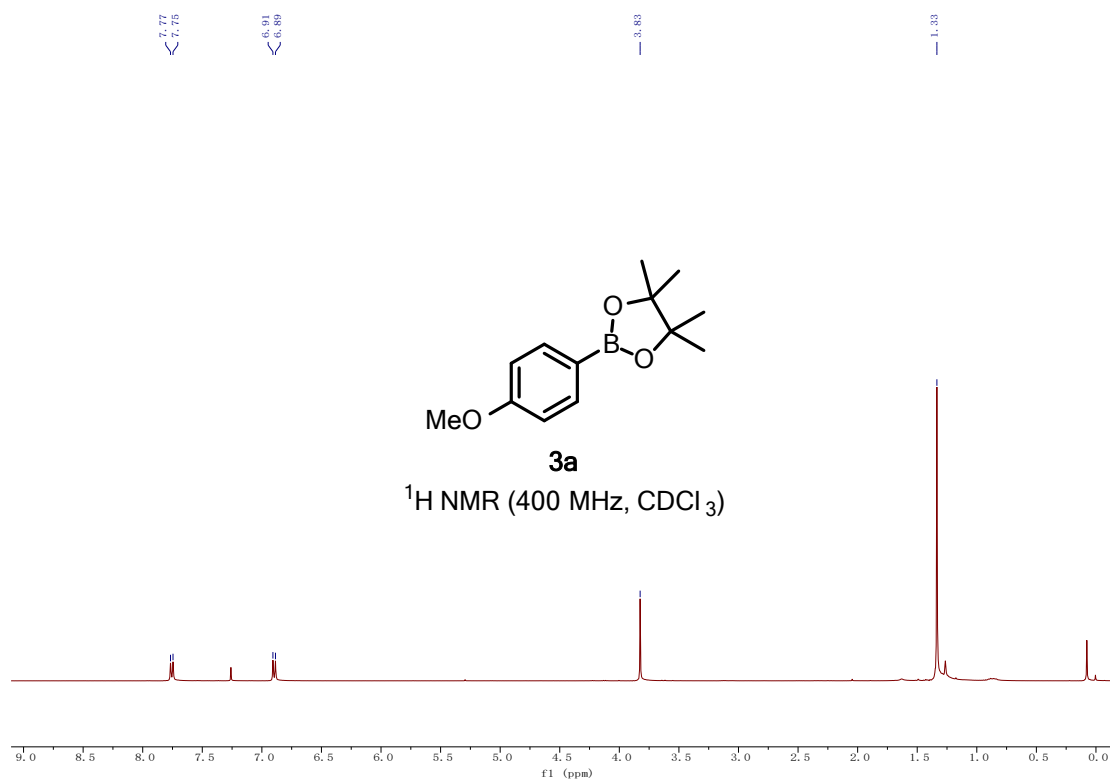
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O 0.92431700 -1.80900200 1.34357100
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O -3.17269000 0.62584900 -1.05662000
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C 2.34182300 2.99175100 -0.34755000
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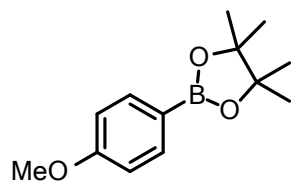
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C 0.32147800	-0.26000200	-1.94964300			
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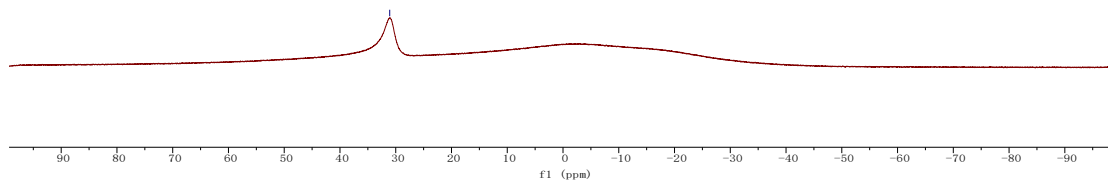
7.) NMR Spectroscopic Data





3a

^{11}B NMR (128 MHz, CDCl_3)

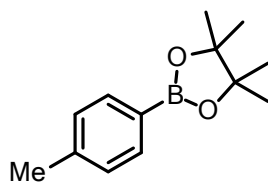


7.73
7.71

7.01
7.19

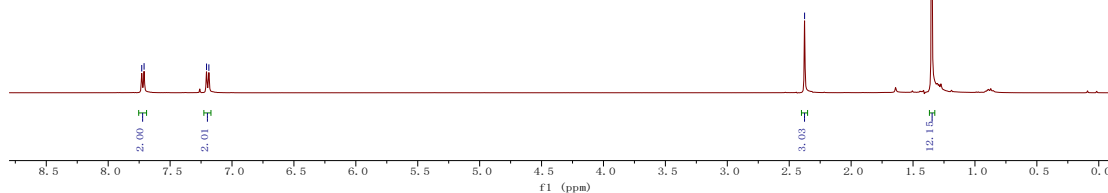
2.38

1.35



3b

^1H NMR (400 MHz, CDCl_3)



141.53

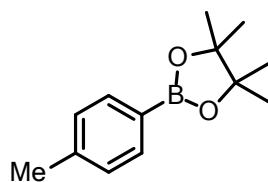
134.95

128.06

83.76

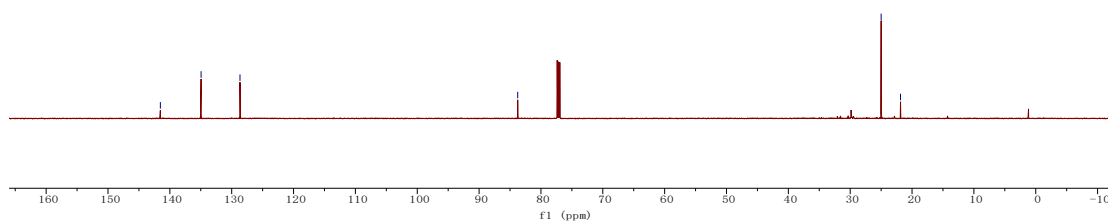
25.00

21.86

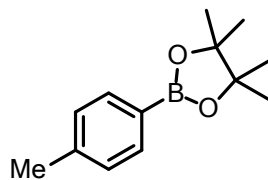


3b

¹³C NMR (151 MHz, CDCl₃)

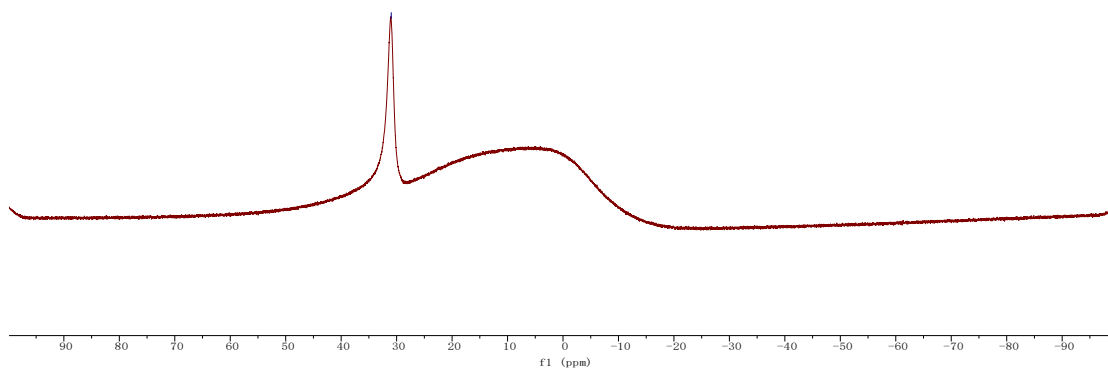


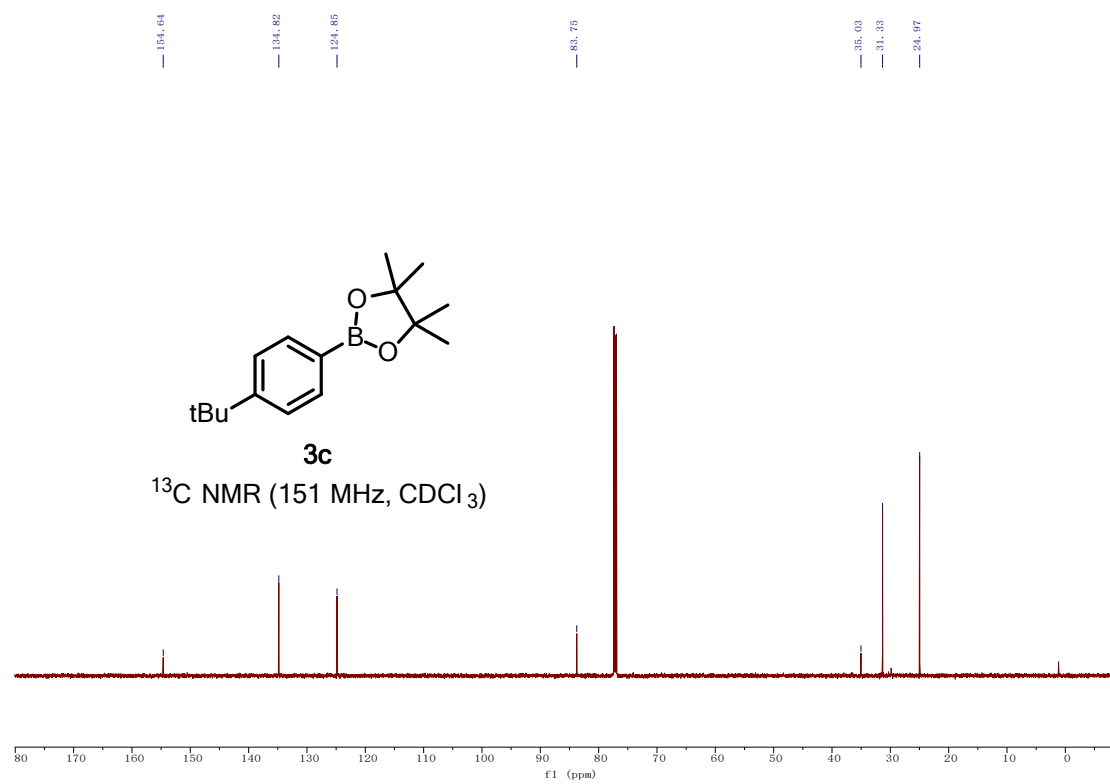
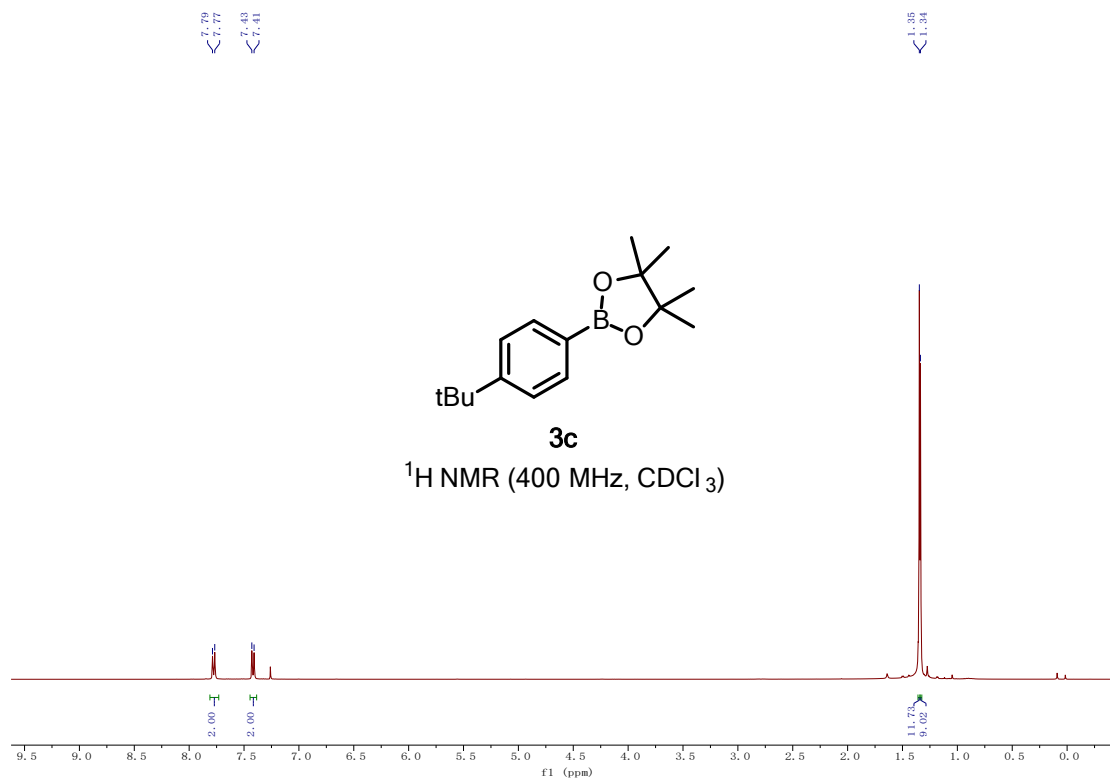
30.97



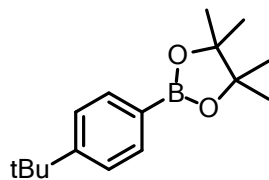
3b

¹¹B NMR (193 MHz, CDCl₃)



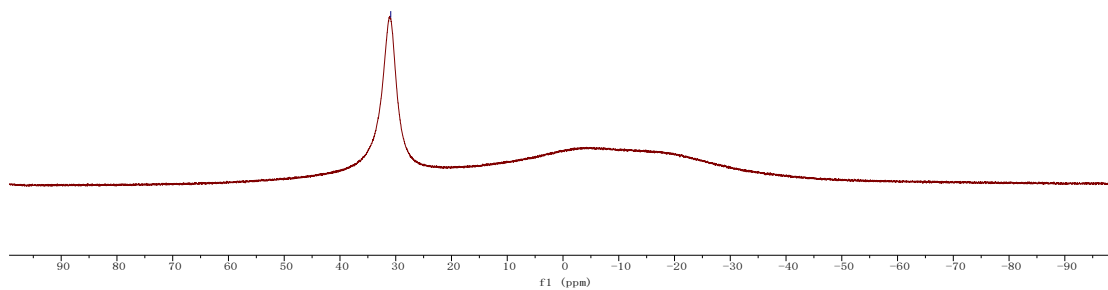


30.89



3c

^{11}B NMR (128 MHz, CDCl_3)

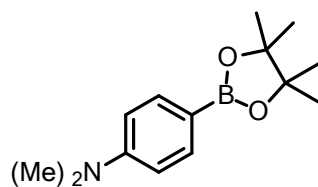


7.70
7.68

6.71
6.69

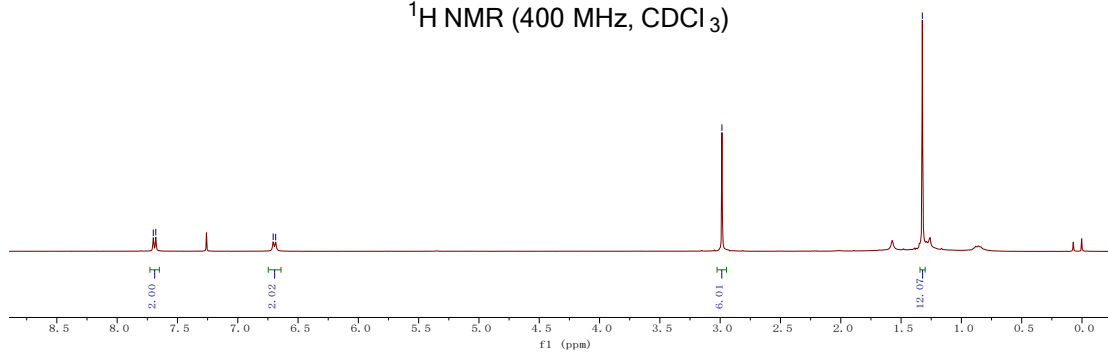
3.99

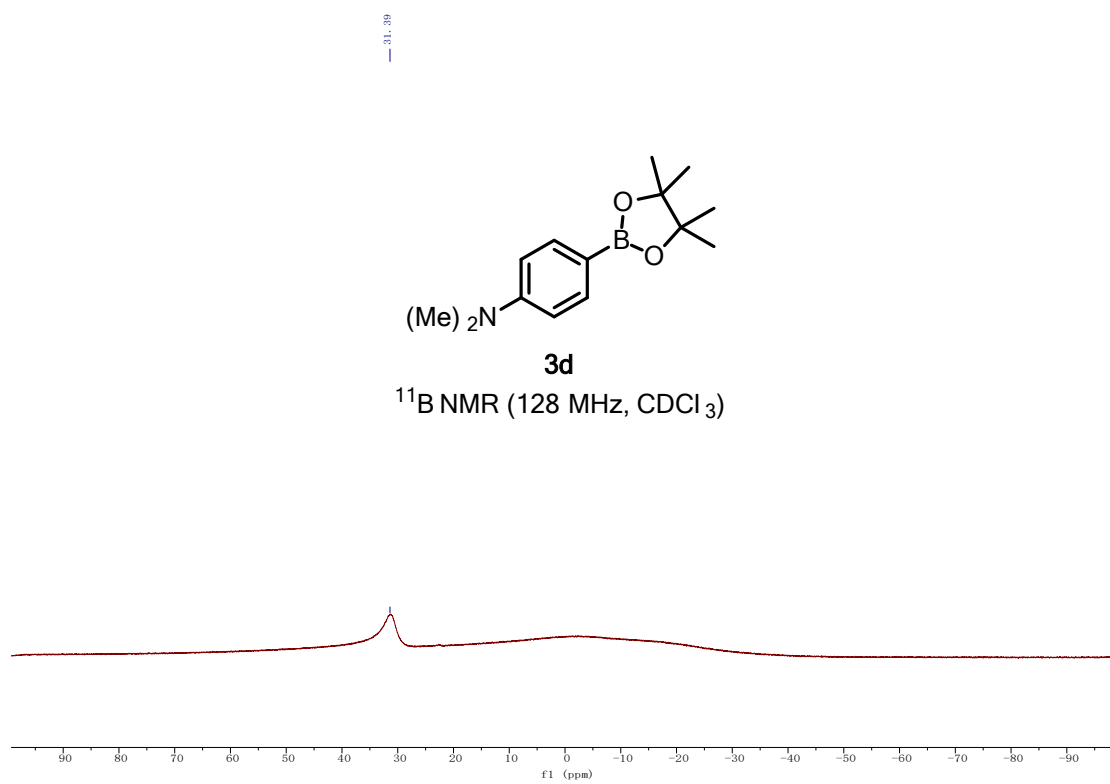
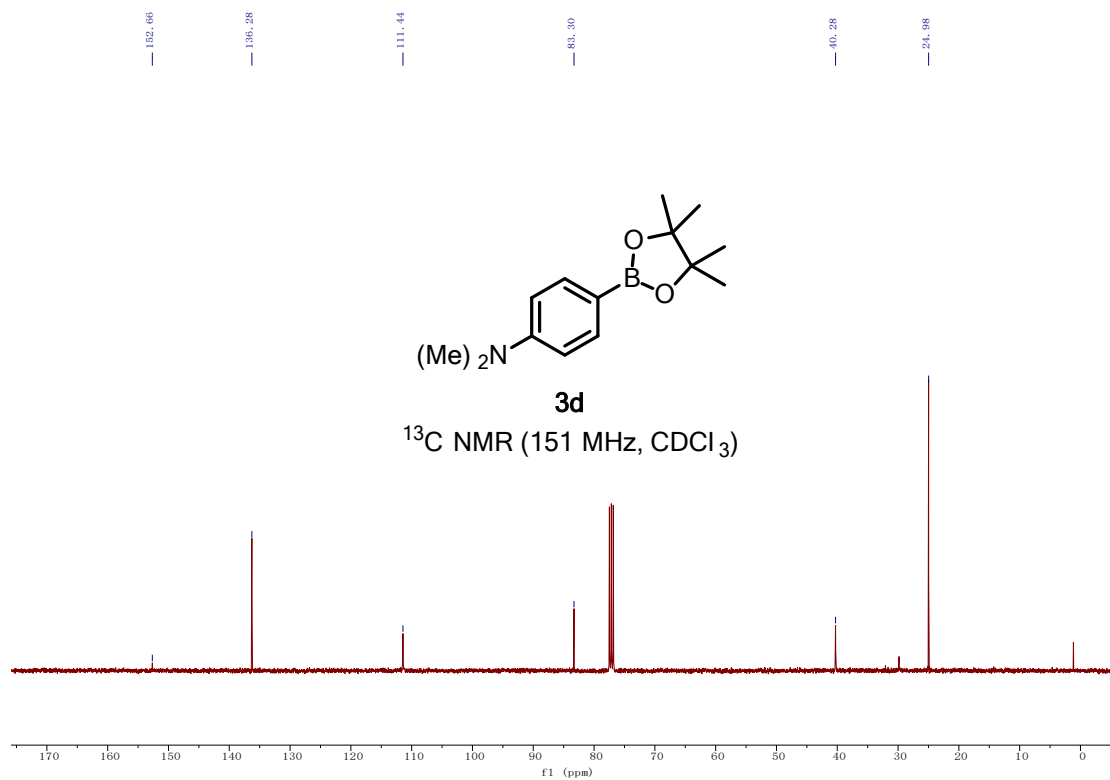
1.32



3d

^1H NMR (400 MHz, CDCl_3)



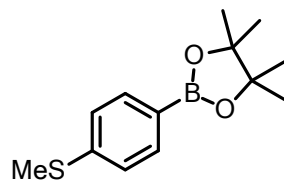


7.71
7.70

7.24
7.22

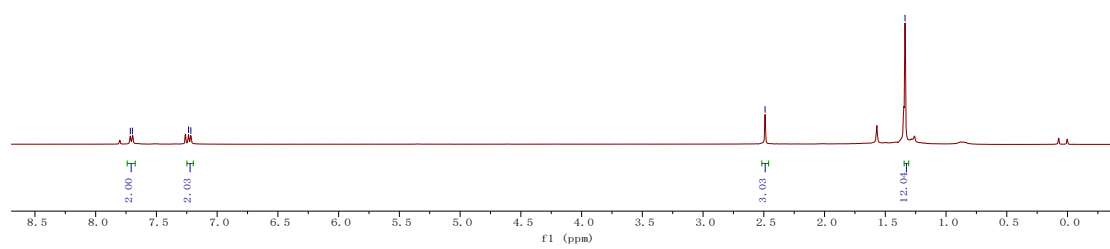
2.49

1.34



3e

¹H NMR (400 MHz, CDCl₃)



142.69

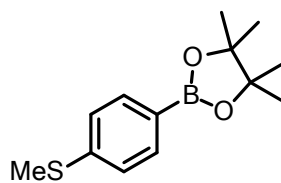
135.19

125.11

83.84

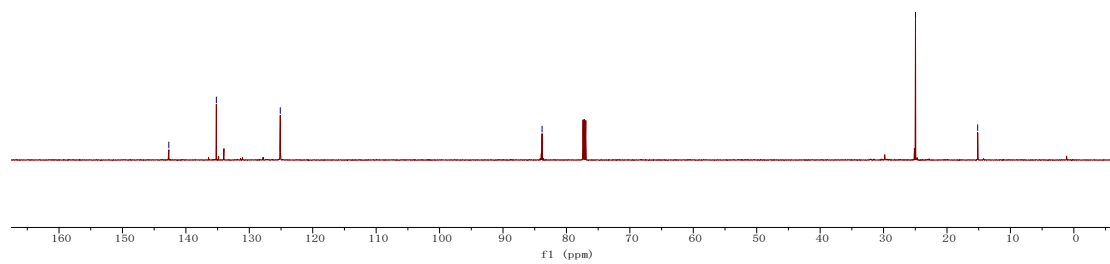
24.97

15.16

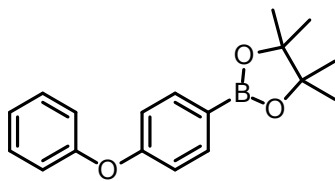


3e

¹³C NMR (151 MHz, CDCl₃)

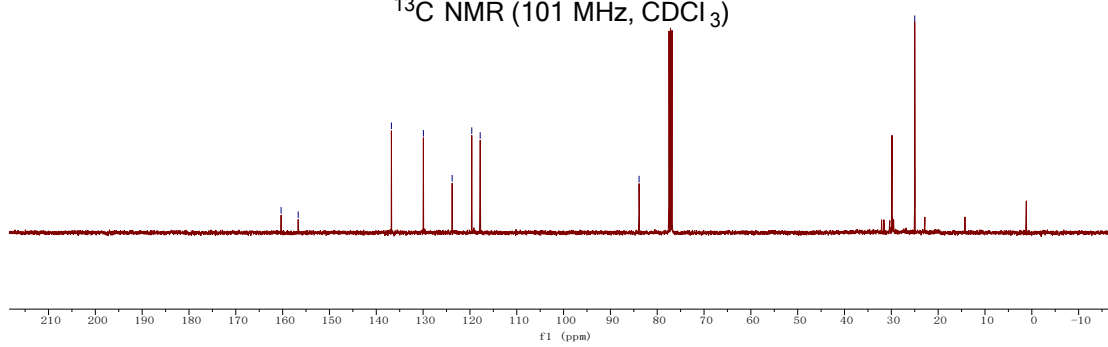


160.33
156.08
136.77
129.94
123.80
119.61
117.81
83.87
25.00



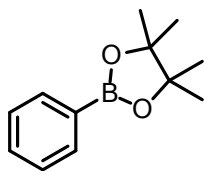
3f

¹³C NMR (101 MHz, CDCl₃)



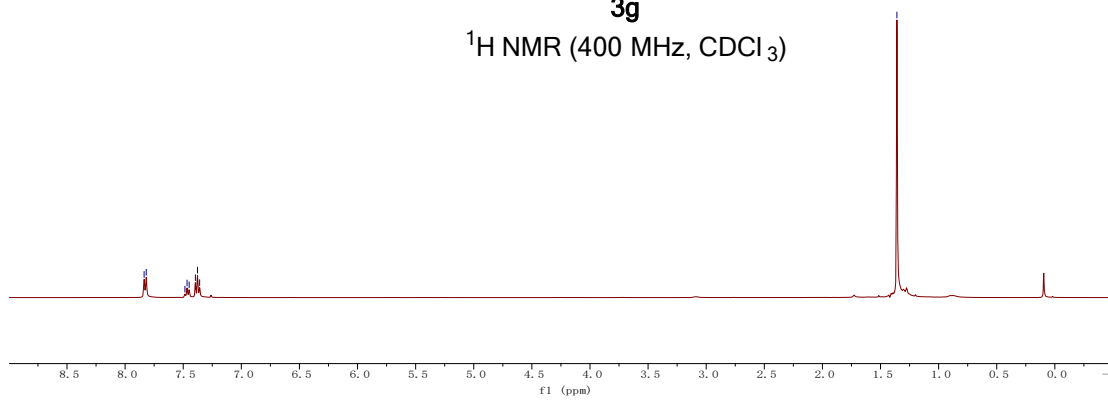
7.82
7.80
7.49
7.47
7.46
7.38
7.36

1.36



3g

¹H NMR (400 MHz, CDCl₃)

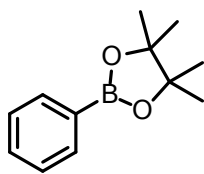


134.86
131.38
127.83

83.89

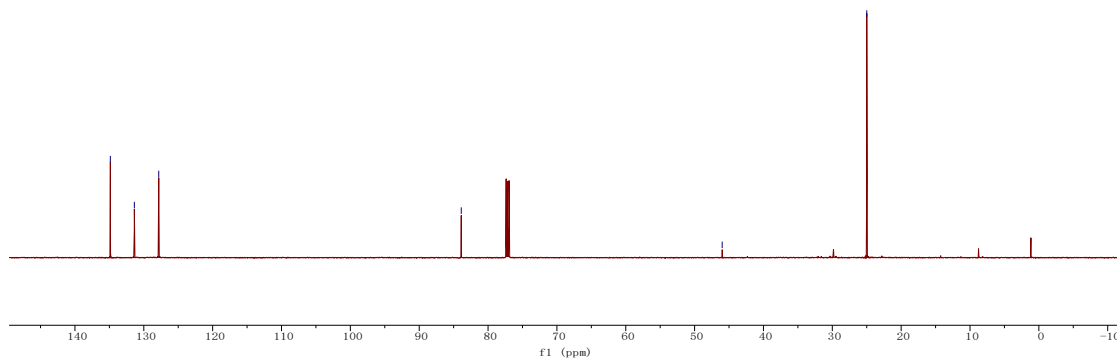
46.00

24.99

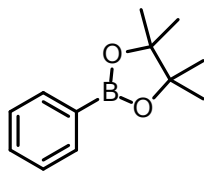


3g

^{13}C NMR (151 MHz, CDCl_3)

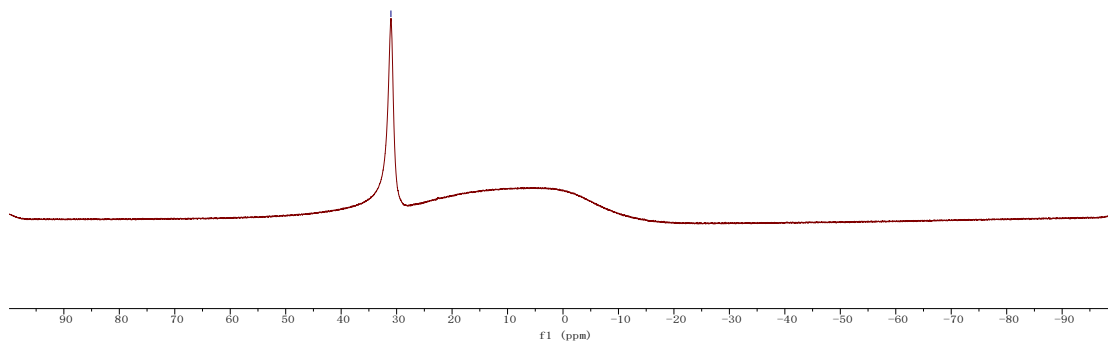


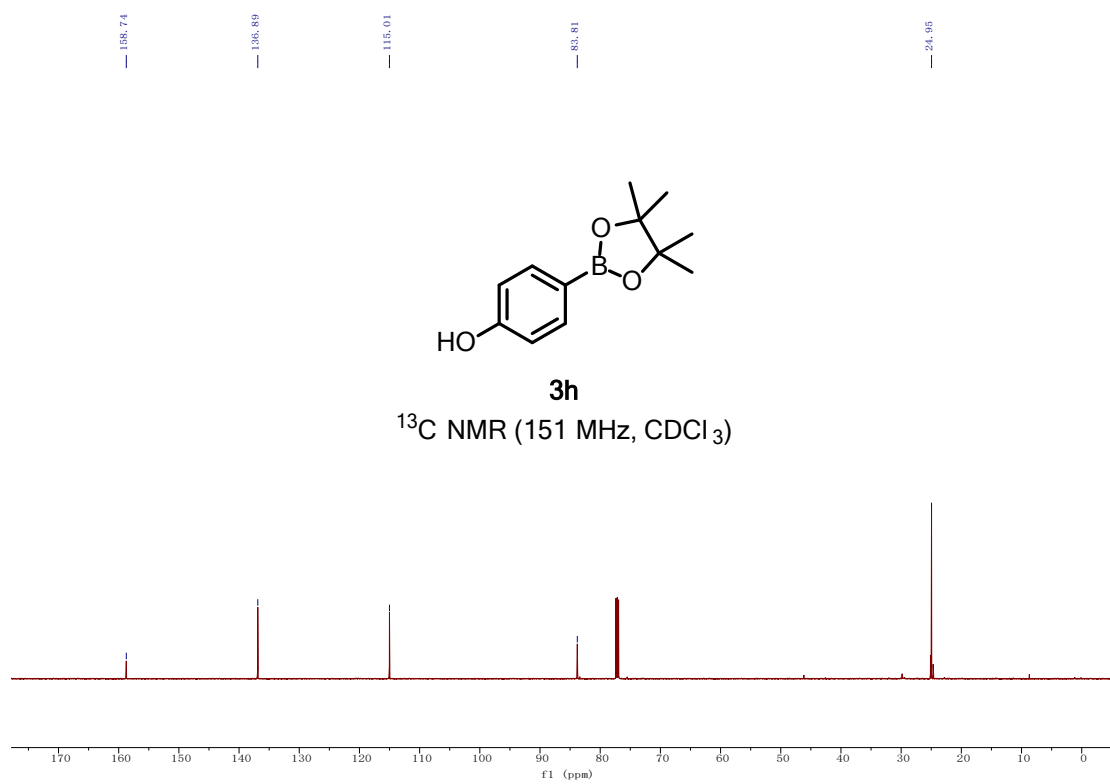
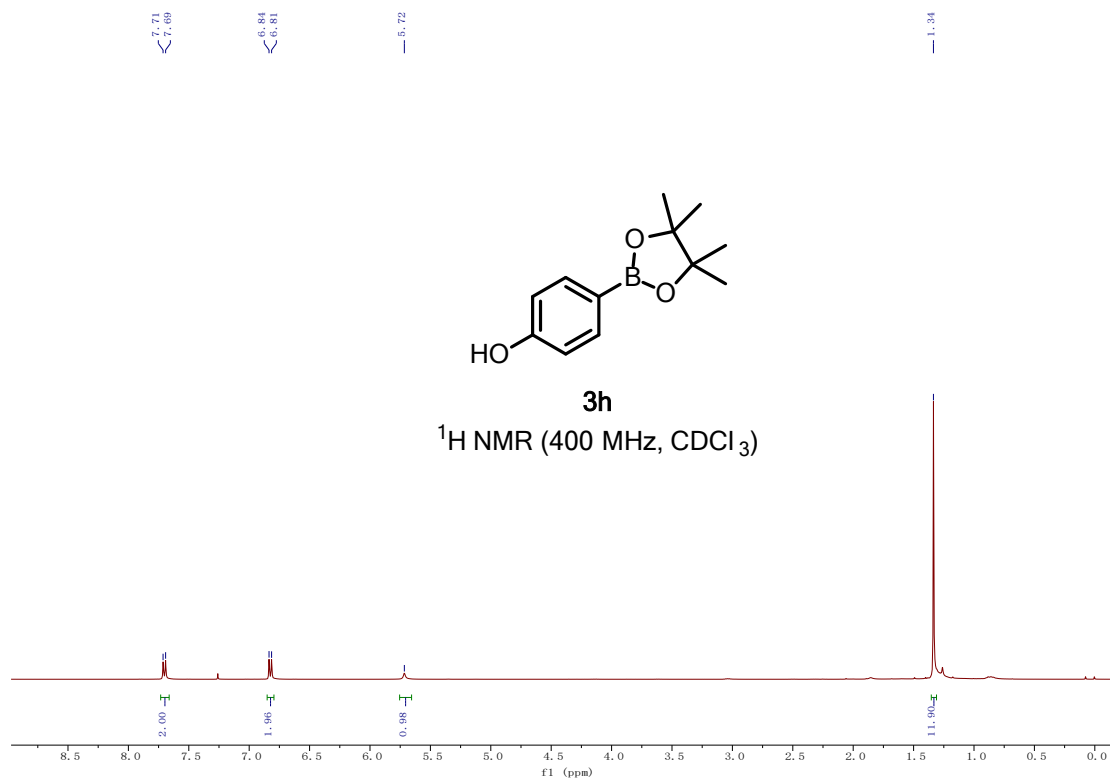
31.03



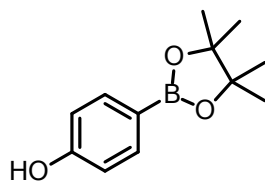
3g

^{11}B NMR (193 MHz, CDCl_3)



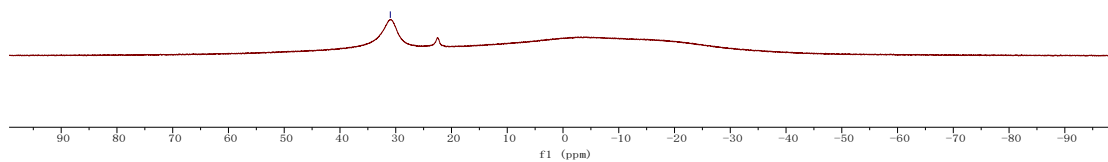


— 30.97



3h

^{11}B NMR (128 MHz, CDCl_3)

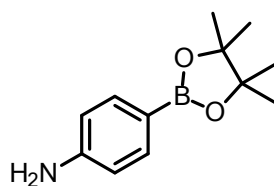


7.63
7.61

6.67
6.65

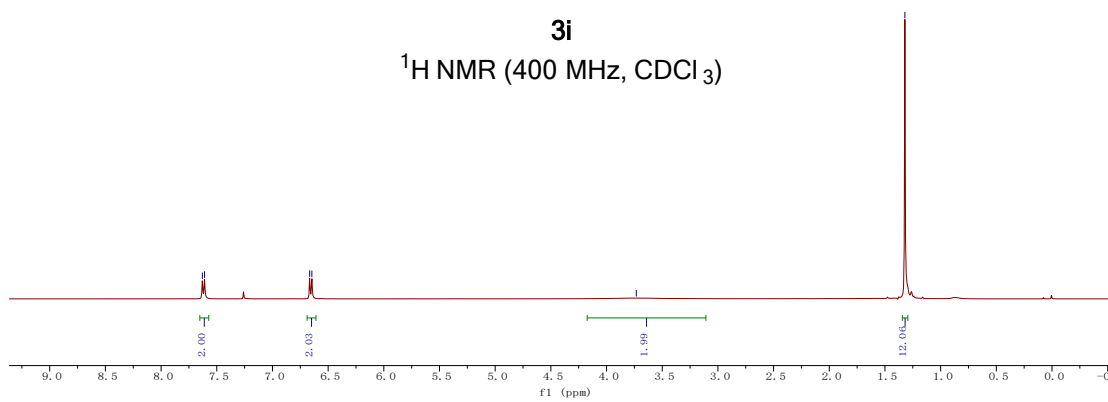
3.73

1.32

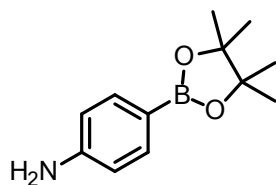


3i

^1H NMR (400 MHz, CDCl_3)

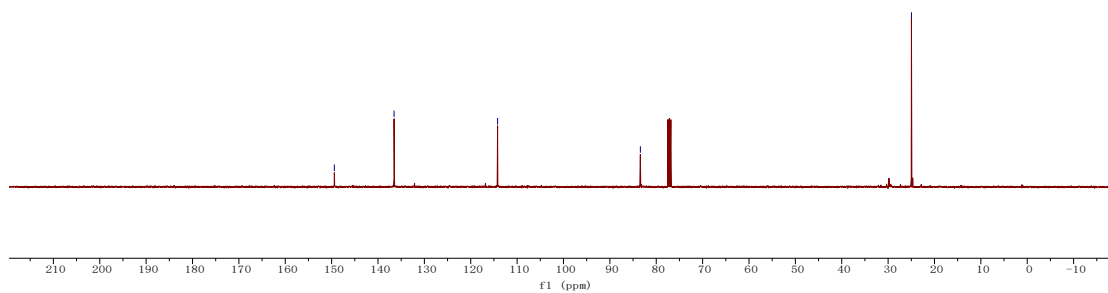


149.41
136.53
114.21
83.42
24.97

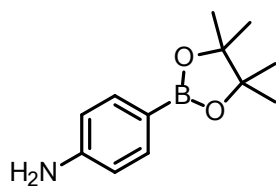


3i

^{13}C NMR (101 MHz, CDCl_3)

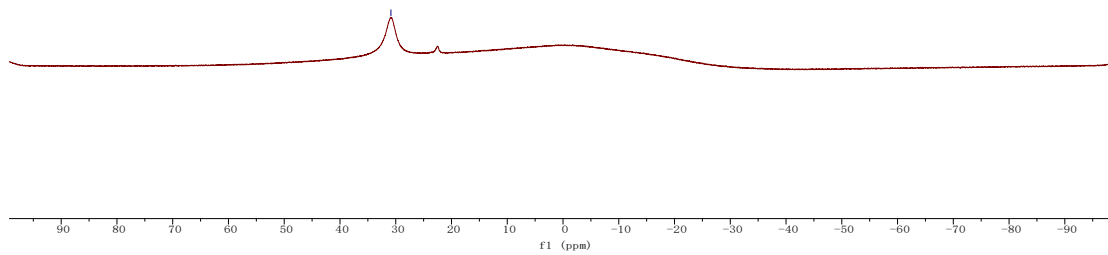


30.86



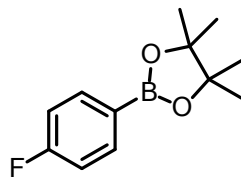
3i

^{11}B NMR (128 MHz, CDCl_3)



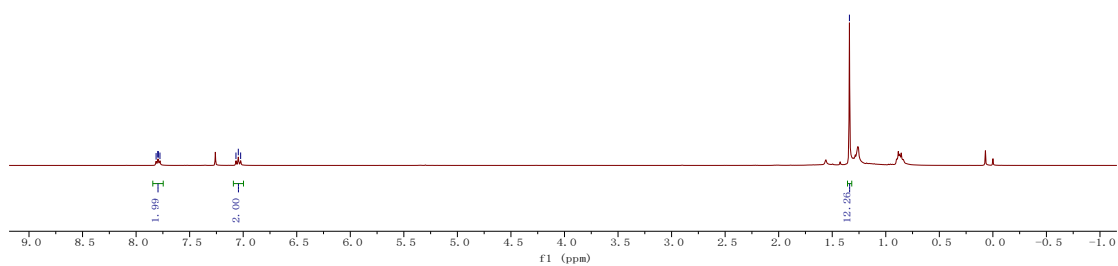
7.81
7.79
7.78
7.07
7.05
7.02

1.34



3j

¹H NMR (400 MHz, CDCl₃)



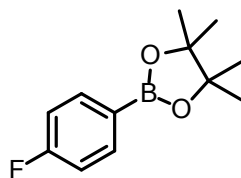
168.07
164.41

137.15
137.09

118.04
114.91

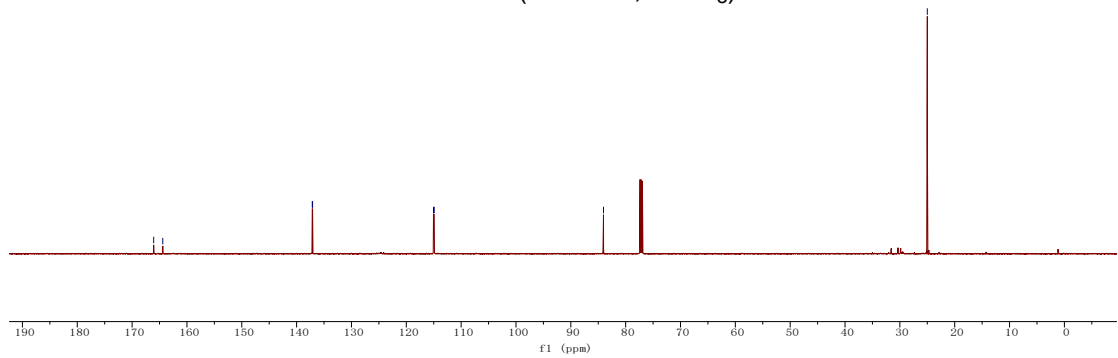
81.04

24.99

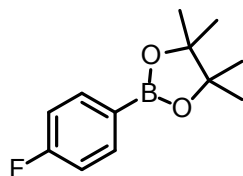


3j

¹³C NMR (151 MHz, CDCl₃)

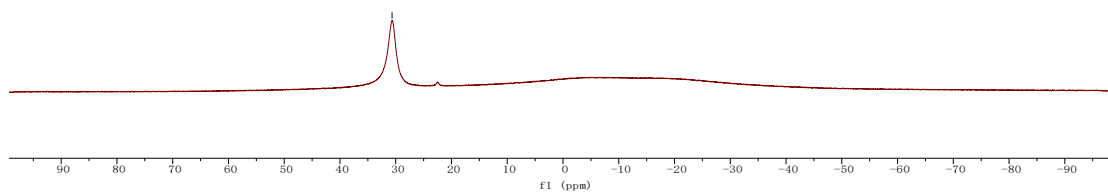


30.66

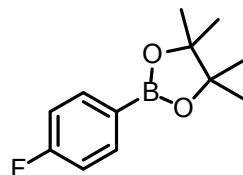


3j

^{11}B NMR (128 MHz, CDCl_3)

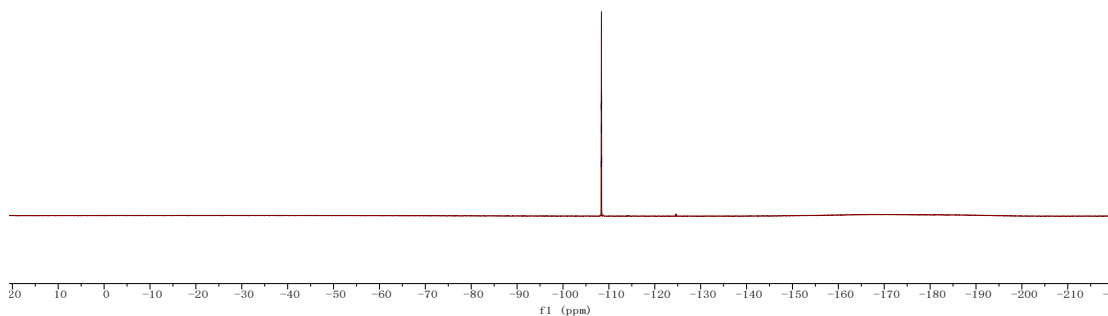


108.34
108.36
108.37
108.38
108.39
108.40
108.42



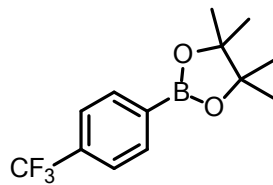
3j

^{19}F NMR (377 MHz, CDCl_3)



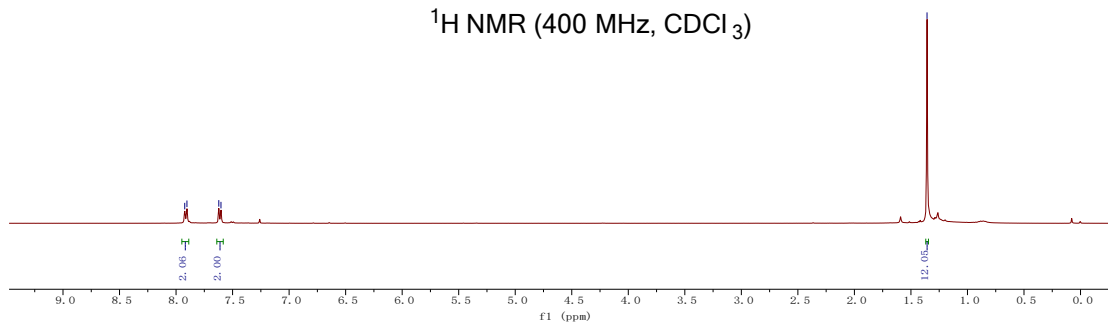
7.92
7.90
7.62
7.60

1.38



3k

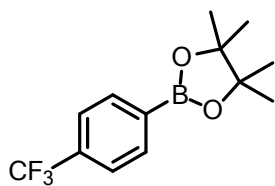
^1H NMR (400 MHz, CDCl_3)



135.15
131.09
128.96
124.48
124.46

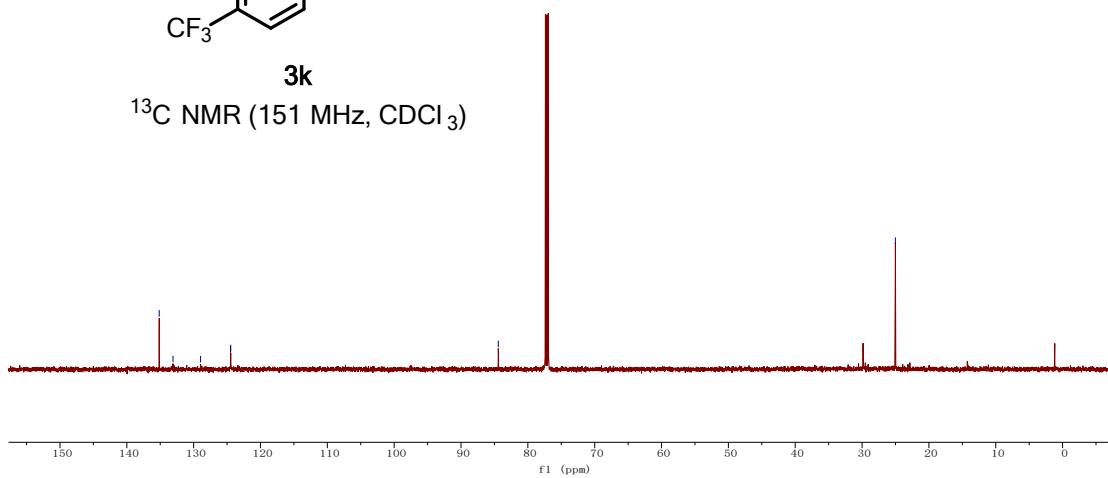
84.42

25.01

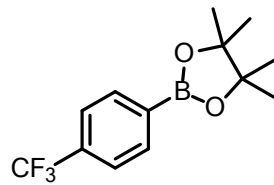


3k

^{13}C NMR (151 MHz, CDCl_3)

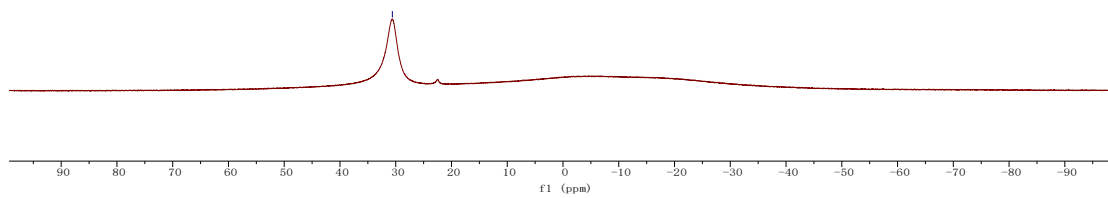


30.61

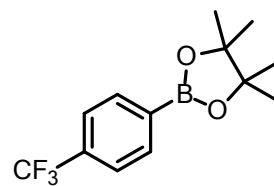


3k

^{11}B NMR (128 MHz, CDCl_3)

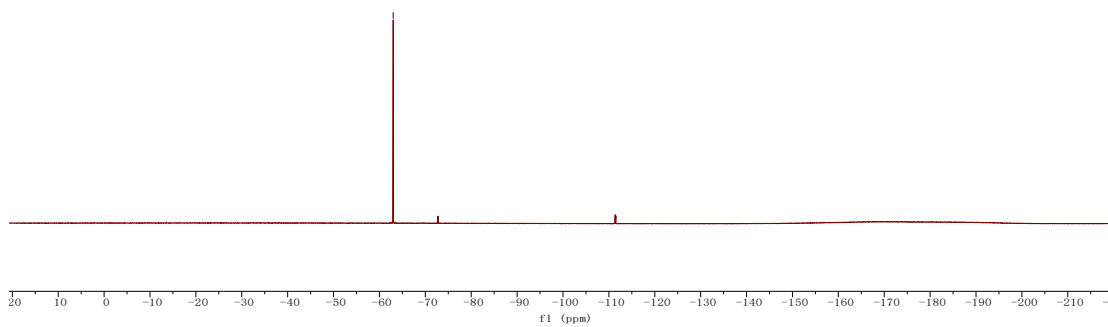


-63.00



3k

^{19}F NMR (377 MHz, CDCl_3)

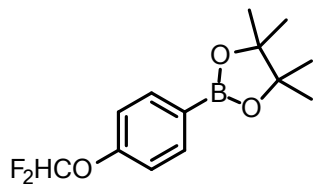


< 7.82
< 7.80

< 7.10
< 7.08

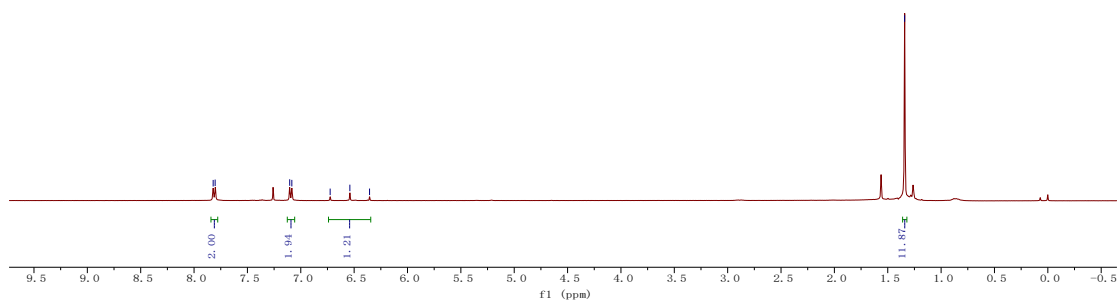
> 6.72
> 6.54
> 6.36

— 1.34

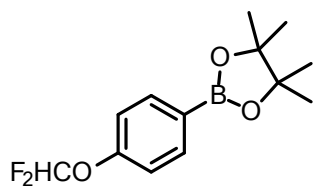


3l

^1H NMR (400 MHz, CDCl_3)

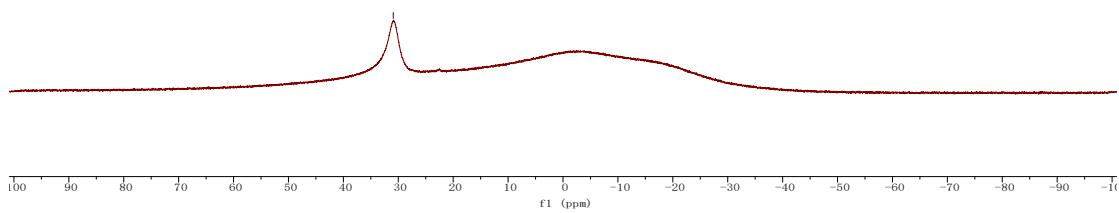


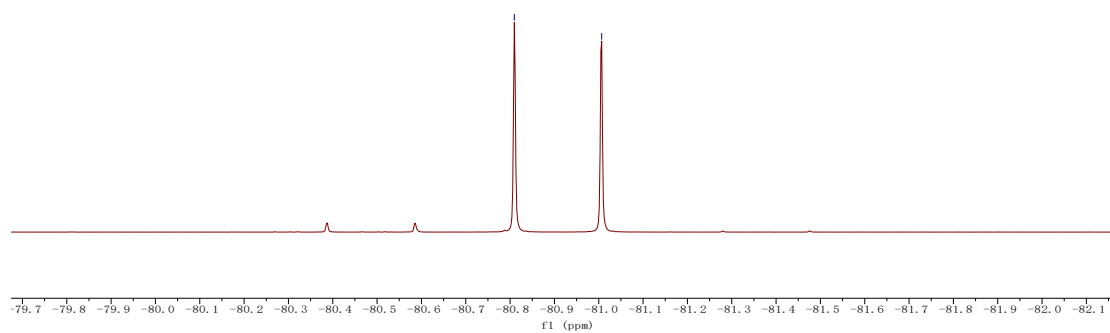
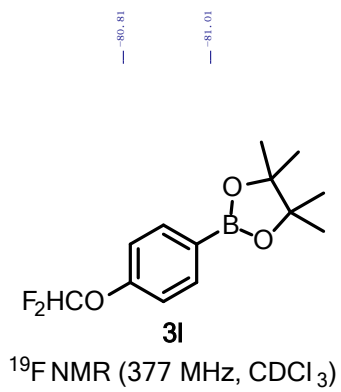
— 30.91



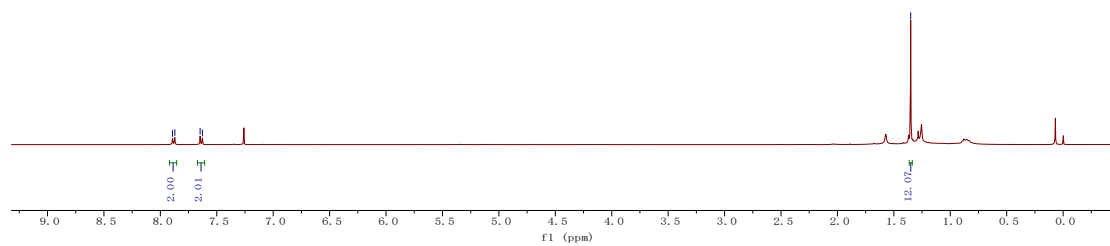
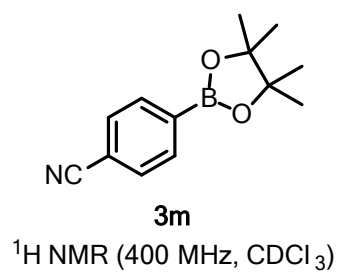
3l

^{11}B NMR (128 MHz, CDCl_3)

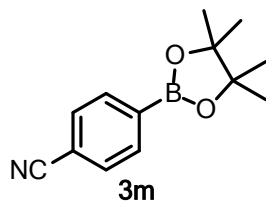




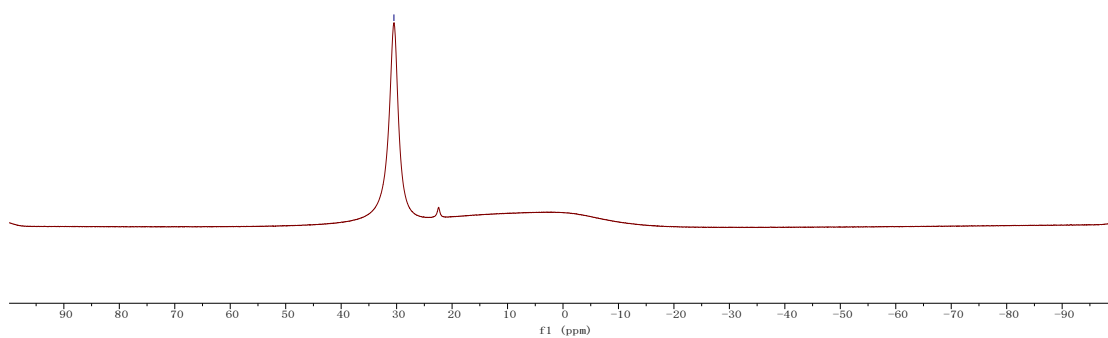
7.88
7.87
7.65
7.65



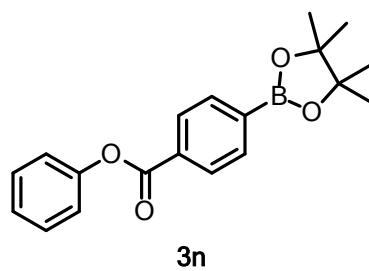
30.49



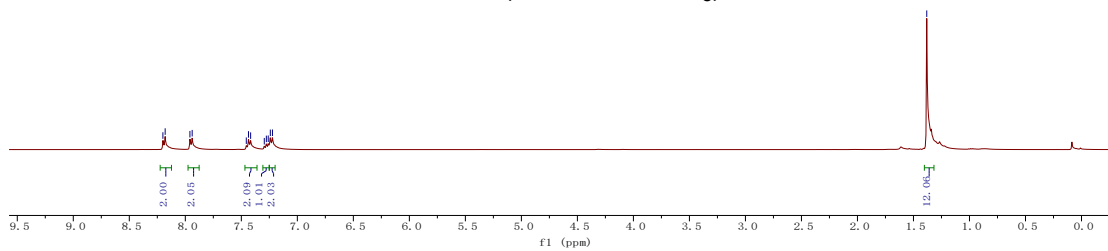
^{11}B NMR (193 MHz, CDCl_3)



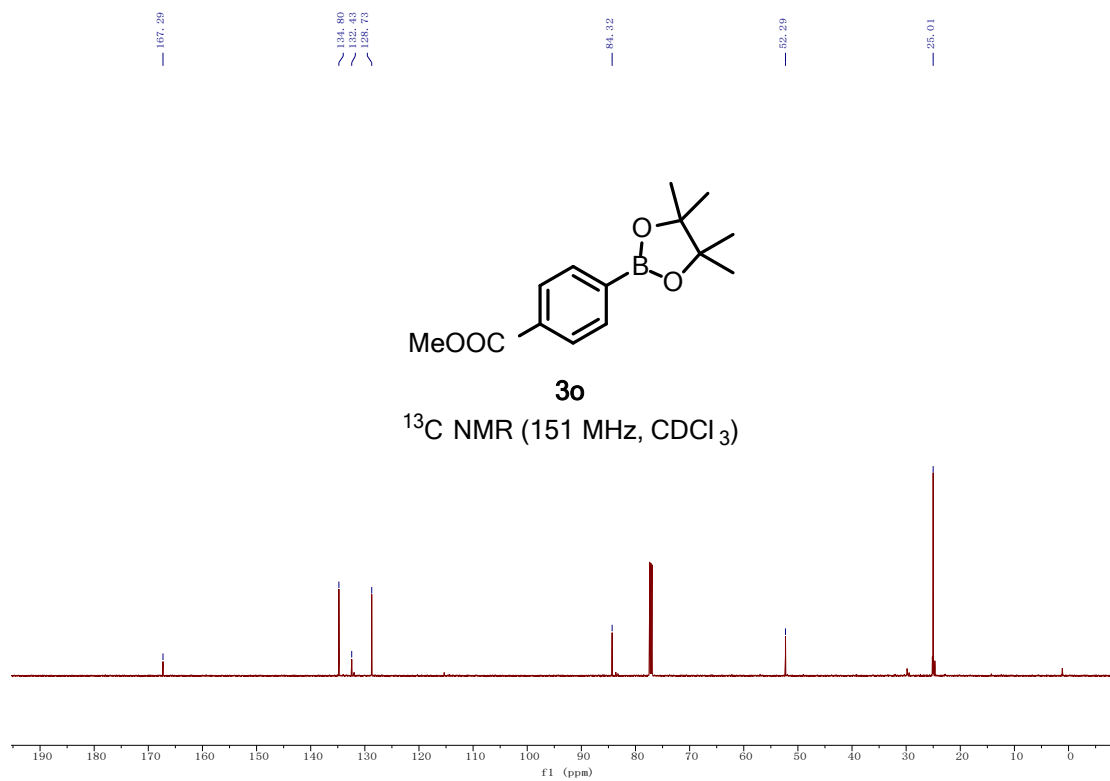
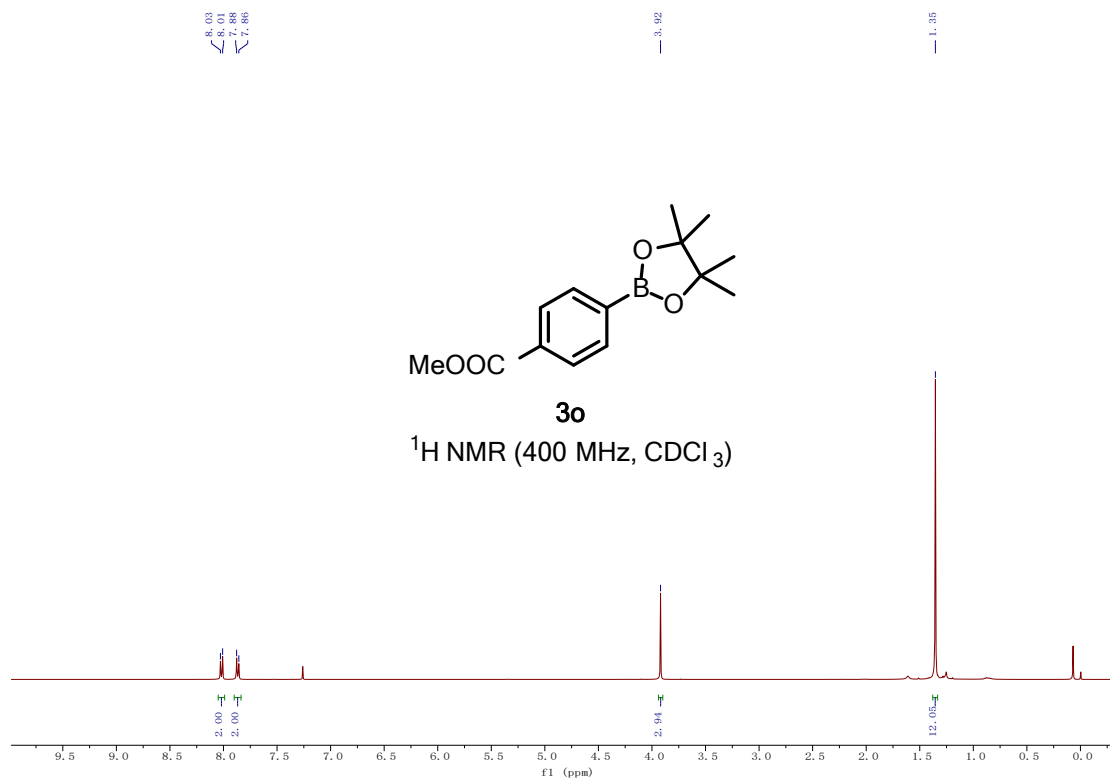
8.20
8.18
7.94
7.94
7.46
7.46
7.42
7.42
7.30
7.28
7.28
7.24
7.22

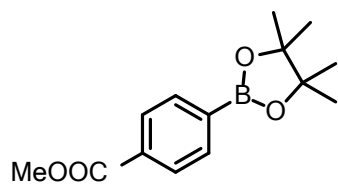


^1H NMR (400 MHz, CDCl_3)



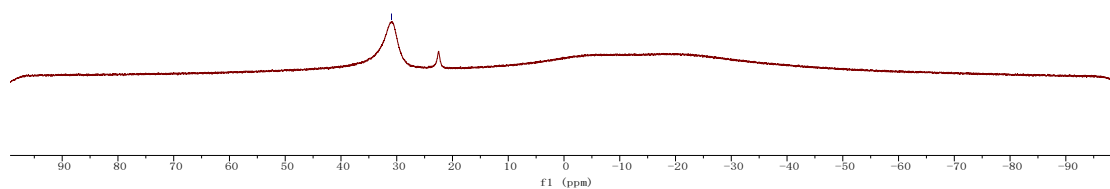
1.38



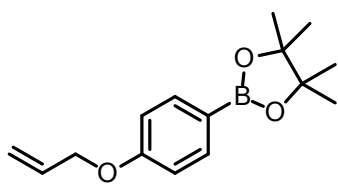


3o

^{11}B NMR (128 MHz, CDCl_3)

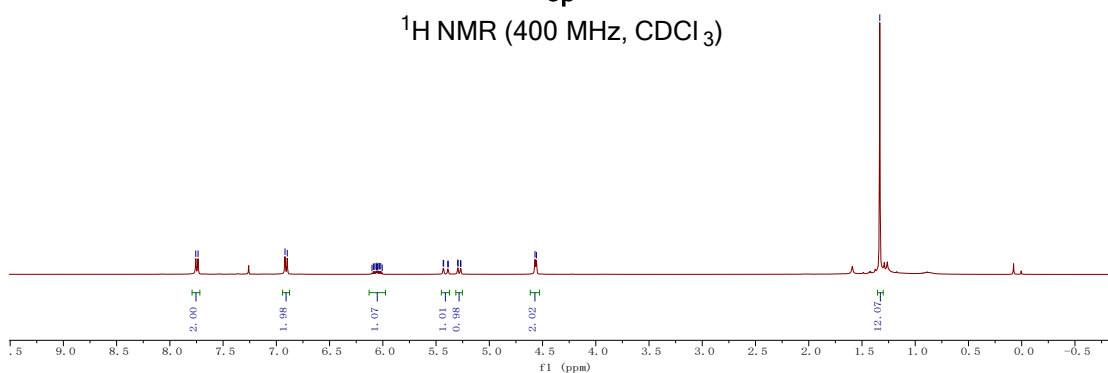


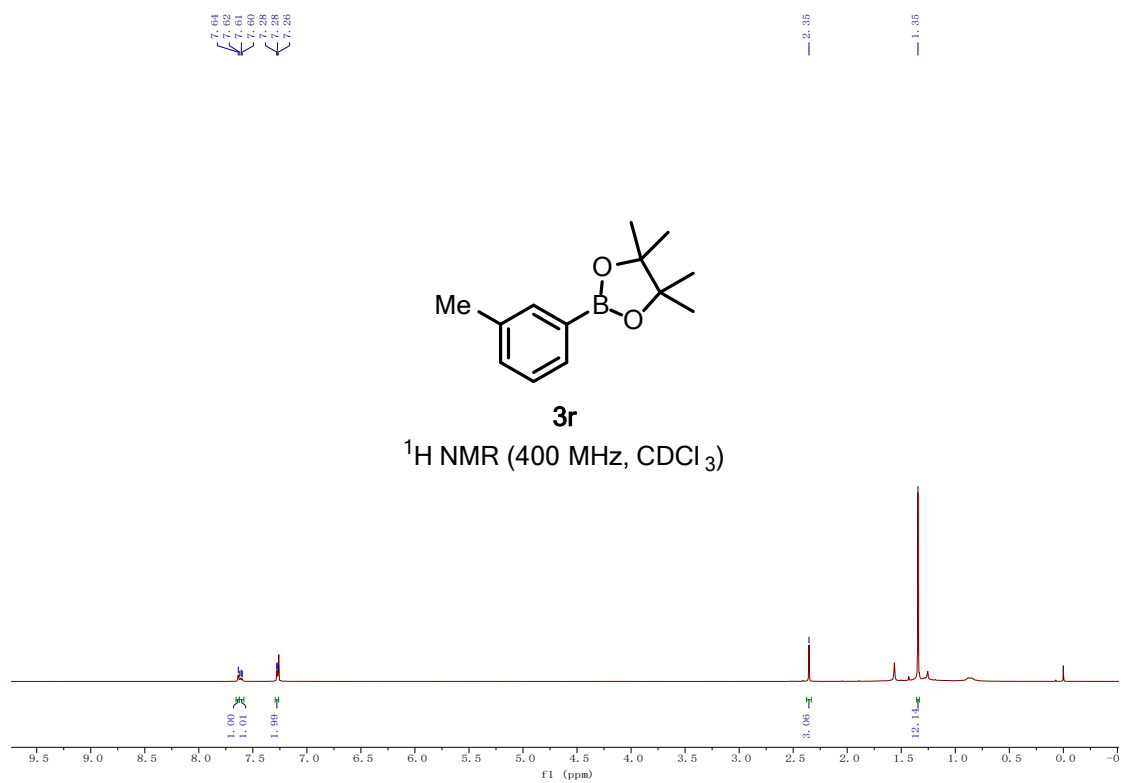
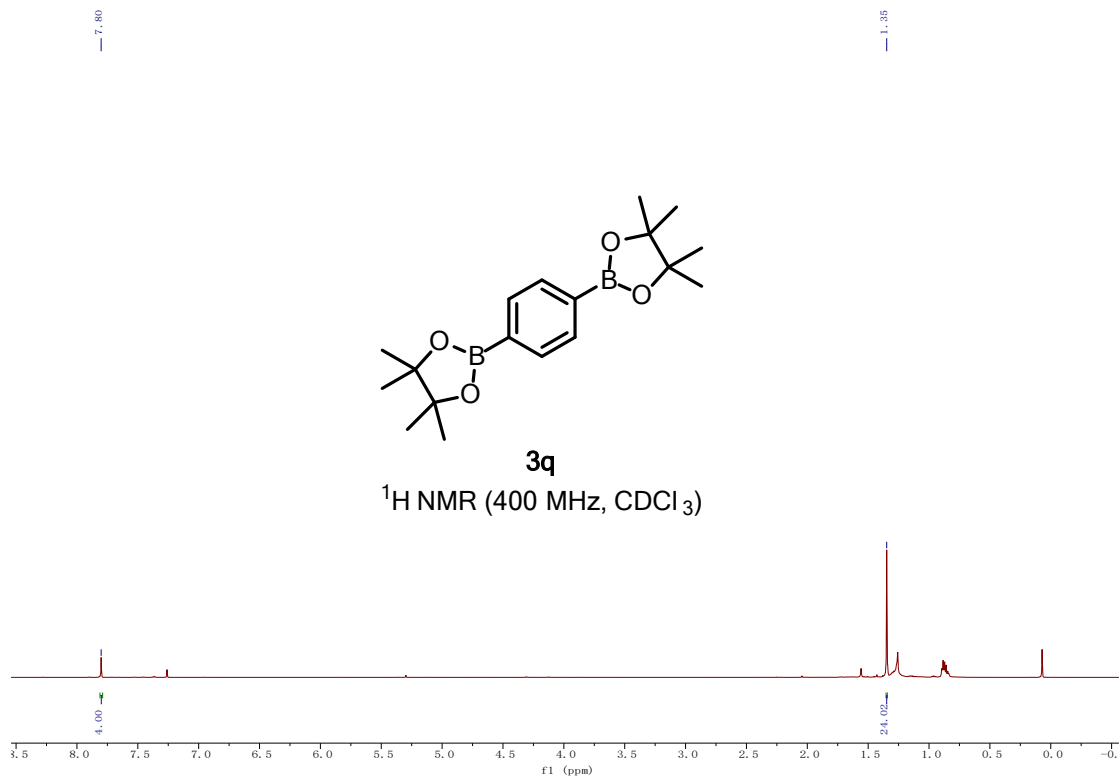
7.76
7.74
6.92
6.10
6.09
6.08
6.05
6.05
6.02
6.01
5.43
5.39
5.39
5.30
5.29
5.27
4.57
4.56
1.33



3p

^1H NMR (400 MHz, CDCl_3)

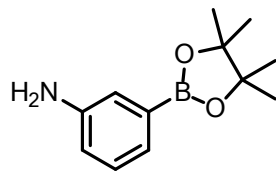




7.222
7.199
7.177
7.154
7.131
6.890
6.788

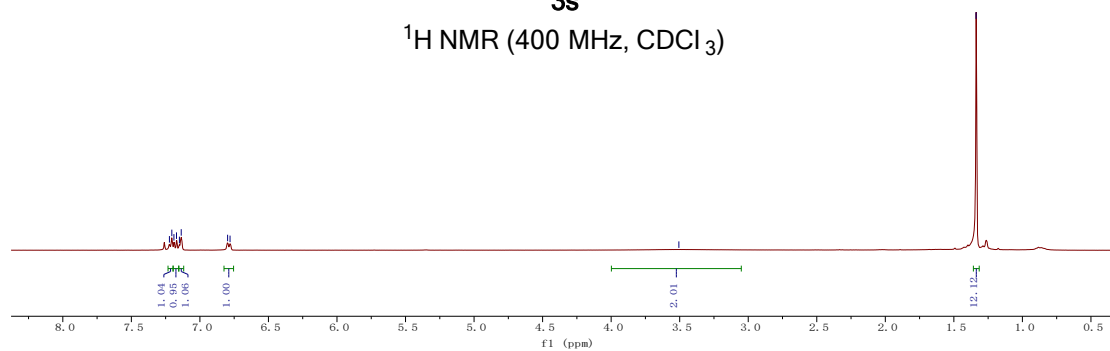
3.51

1.34



3s

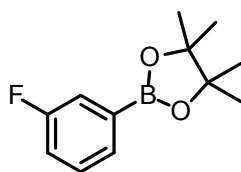
^1H NMR (400 MHz, CDCl_3)



f

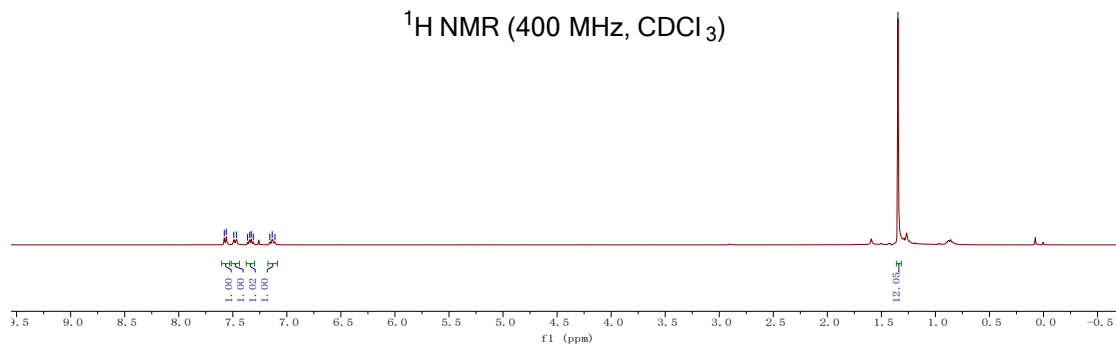
7.58
7.56
7.49
7.47
7.36
7.33
7.31
7.16
7.14
7.11

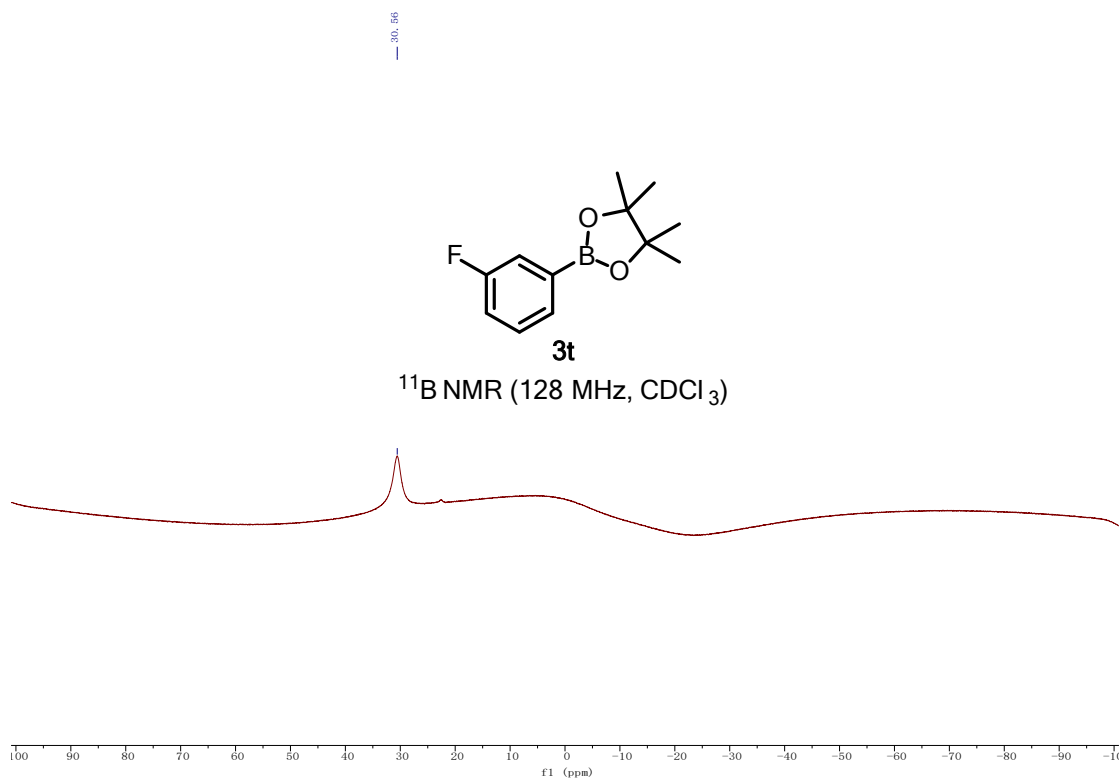
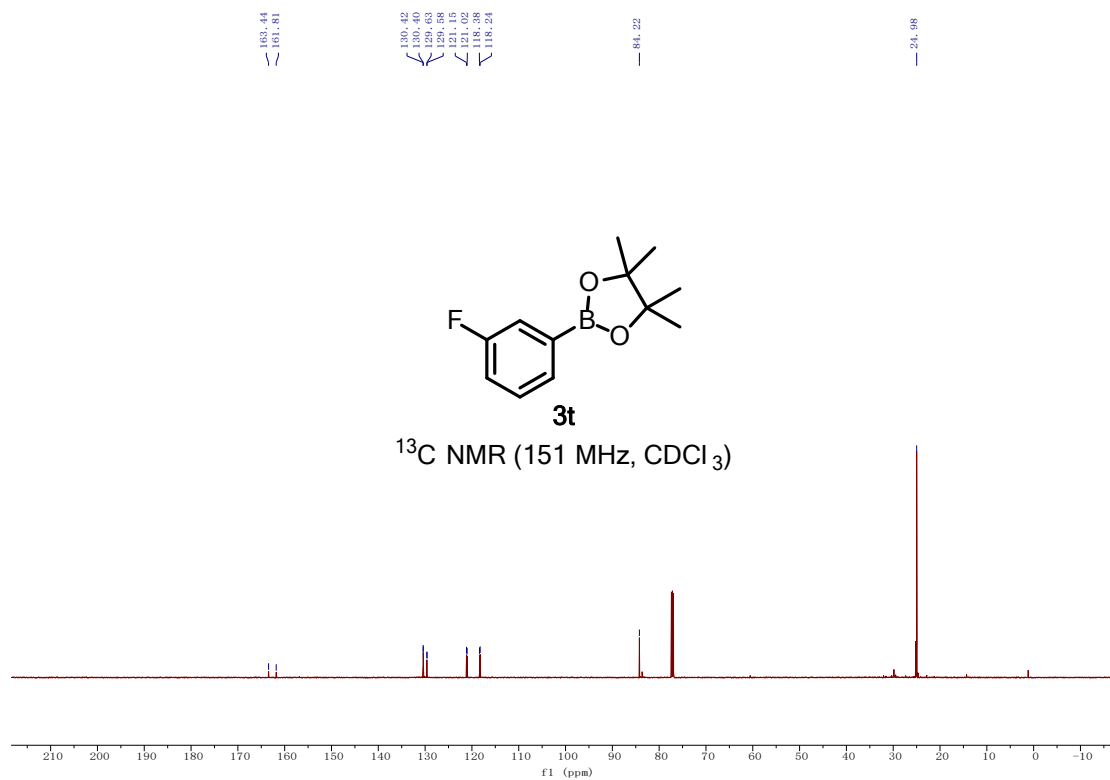
1.35



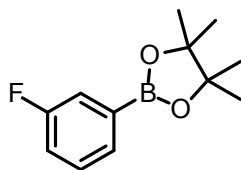
3t

^1H NMR (400 MHz, CDCl_3)



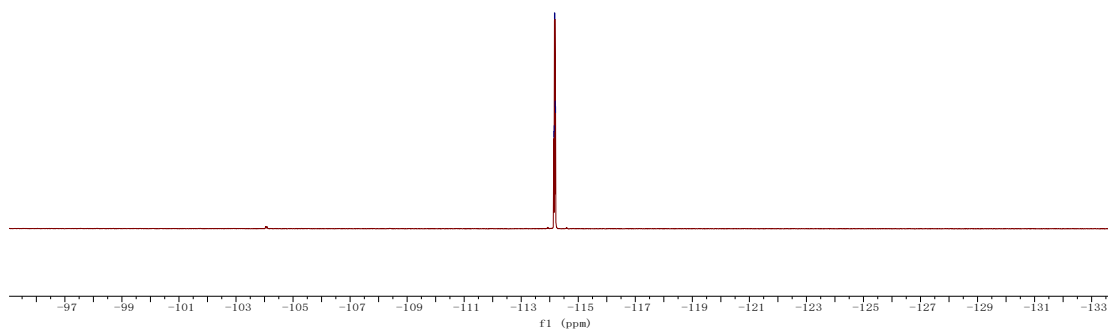


-114.14
-114.16
-114.17
-114.18
-114.19
-114.20



3t

^{19}F NMR (377 MHz, CDCl_3)

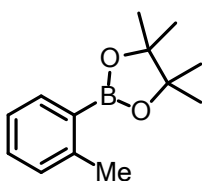


7.81
7.79
7.77

7.34
7.32
7.18

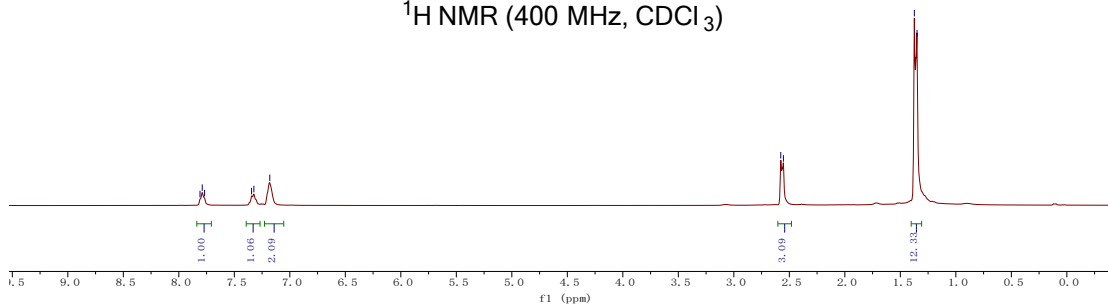
2.58
2.35

1.37
1.35



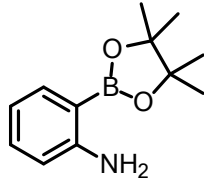
3u

^1H NMR (400 MHz, CDCl_3)



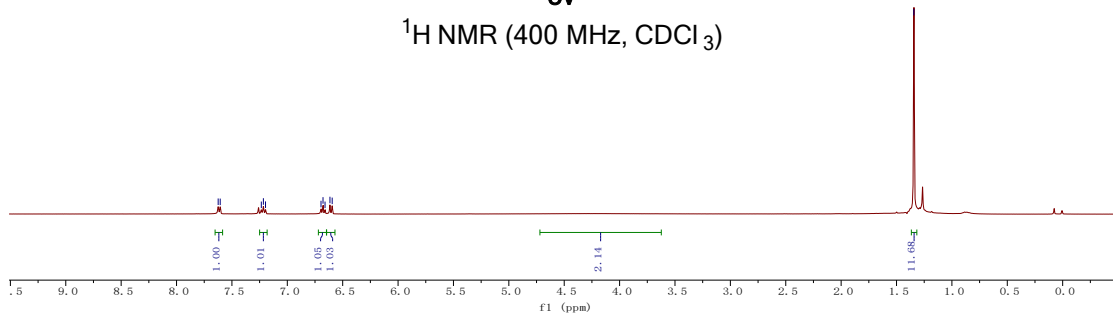
7.62
7.61
7.53
7.52
7.50
6.70
6.68
6.62
6.59

1.34



3v

¹H NMR (400 MHz, CDCl₃)



153.73

136.92

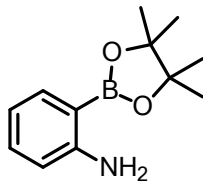
132.87

117.04

114.91

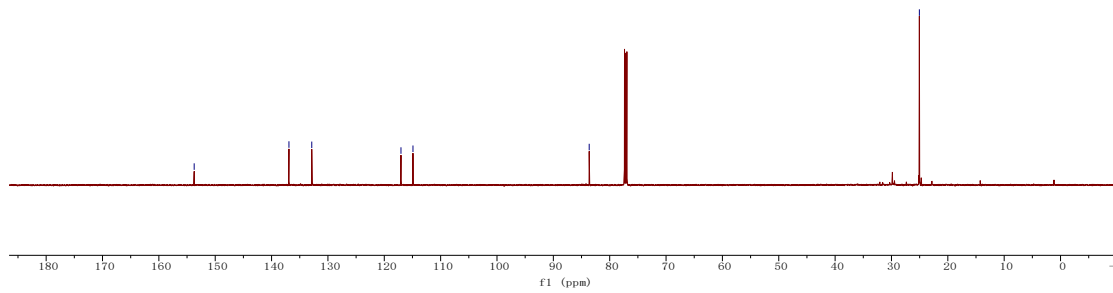
83.64

25.05

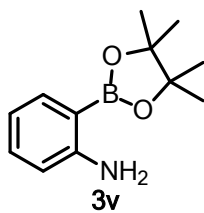


3v

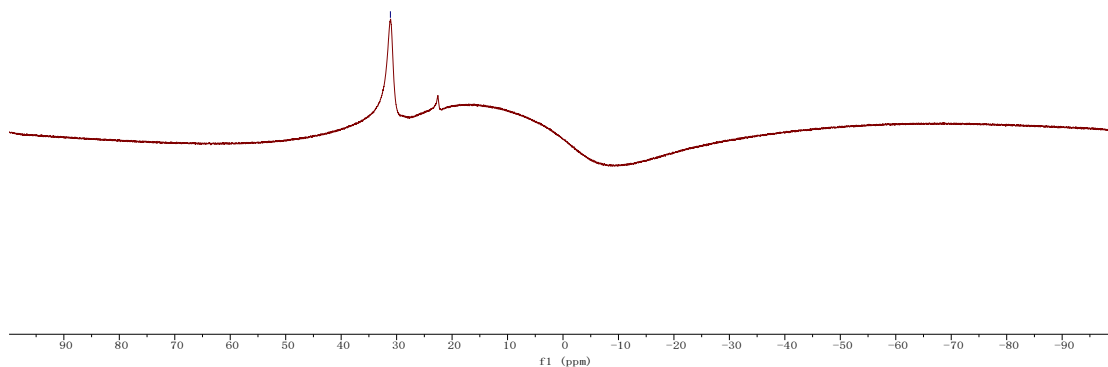
¹³C NMR (151 MHz, CDCl₃)



— 31.12

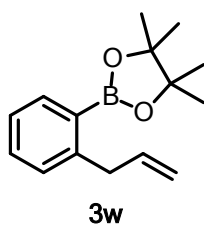


^{11}B NMR (193 MHz, CDCl_3)

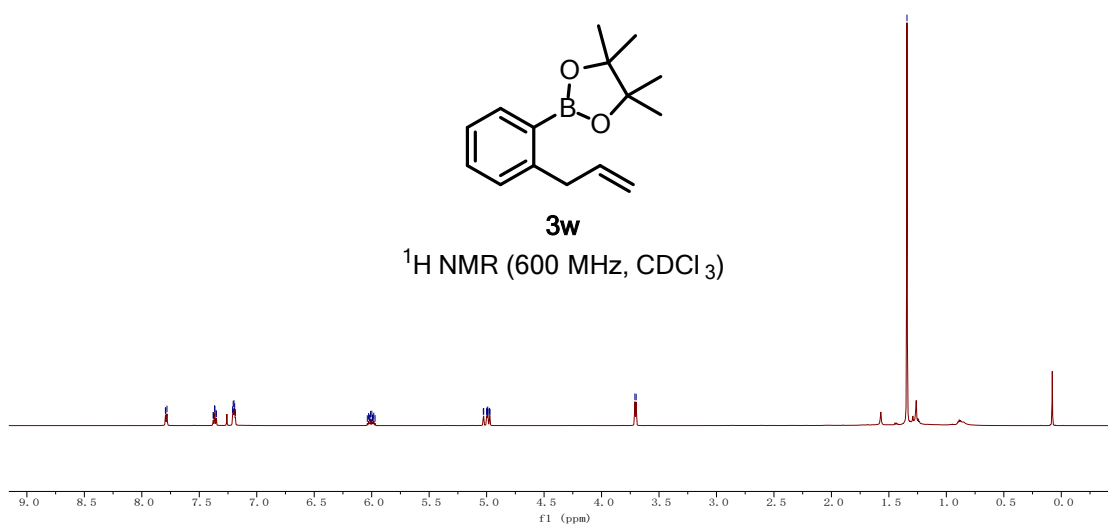


7.729
7.728
7.727
7.337
7.336
7.335
7.211
7.210
7.209
7.119
6.604
6.603
6.602
6.601
6.600
6.599
6.598
6.597
6.503
6.502
6.501
6.500
4.999
4.998
4.997
4.87
3.71
3.70

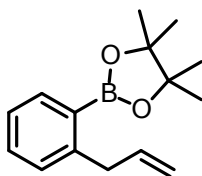
1.34



^1H NMR (600 MHz, CDCl_3)

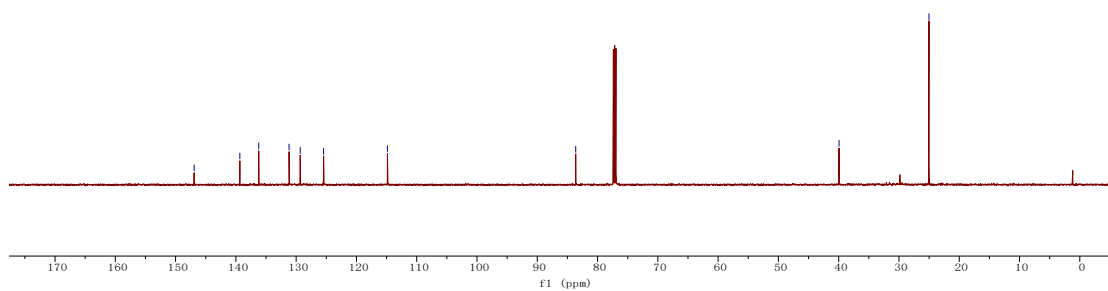


146.92
138.34
136.21
131.17
129.32
128.45
114.86
82.62
39.94
25.02

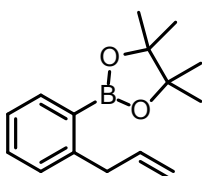


3w

^{13}C NMR (151 MHz, CDCl_3)

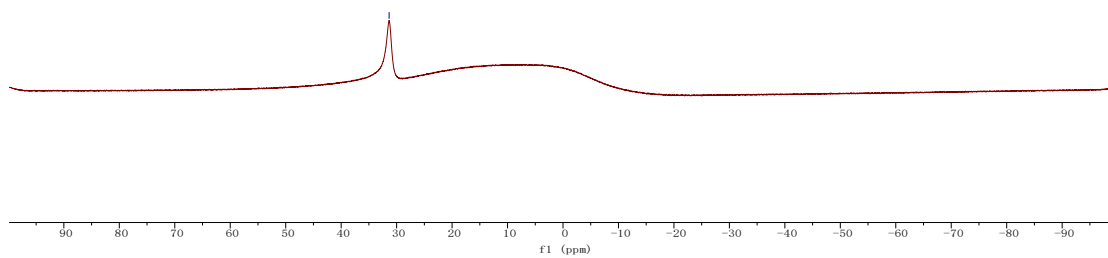


31.35



3w

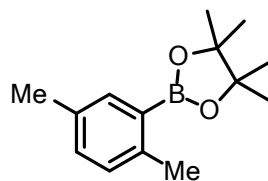
^{11}B NMR (193 MHz, CDCl_3)



7.60
7.16
7.14
7.07

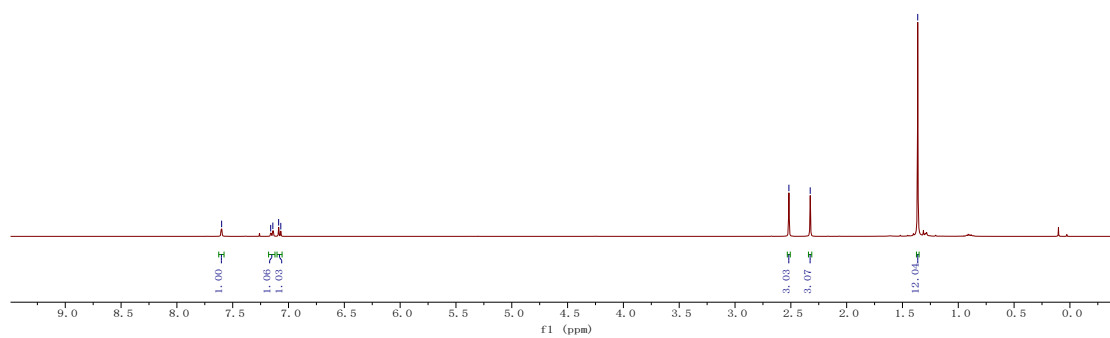
2.62
2.33

1.36



3x

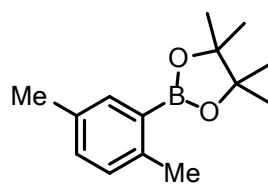
¹H NMR (400 MHz, CDCl₃)



141.84
135.69
134.05
131.69
129.92

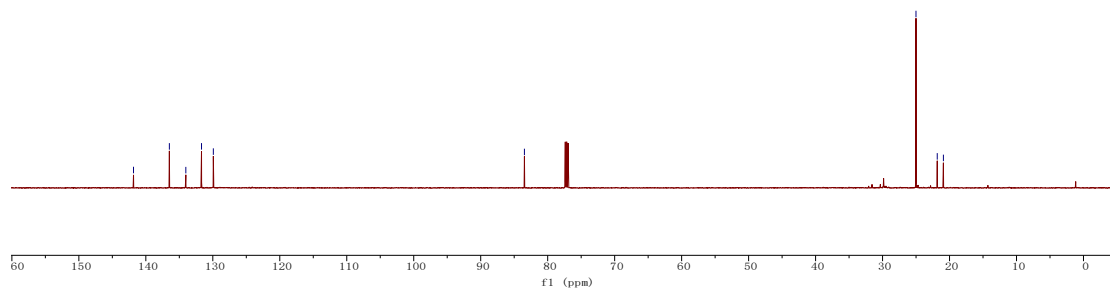
83.47

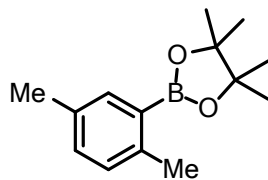
25.01
21.83
20.82



3x

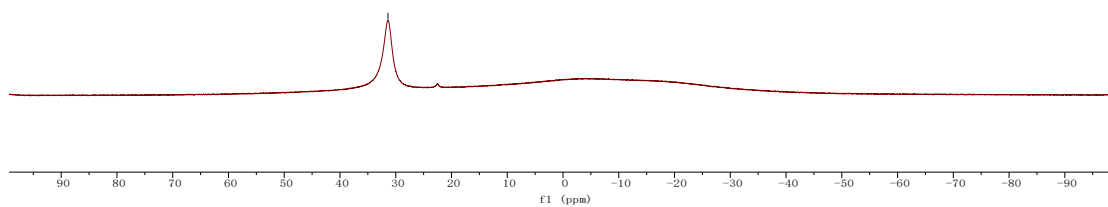
¹³C NMR (151 MHz, CDCl₃)





3x

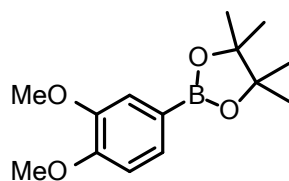
^{11}B NMR (128 MHz, CDCl_3)



7.43
7.43
7.41
7.41
7.29
7.29
6.89
6.89

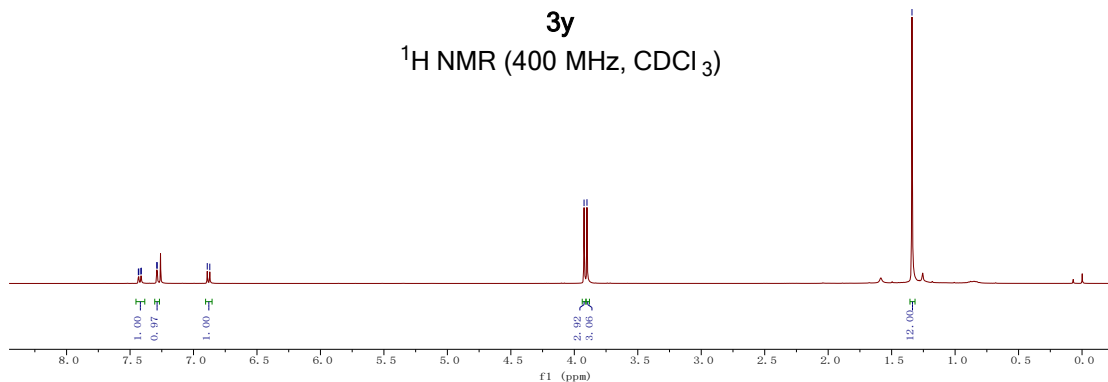
3.92
3.90

1.34



3y

^1H NMR (400 MHz, CDCl_3)



151.79
148.49

138.70

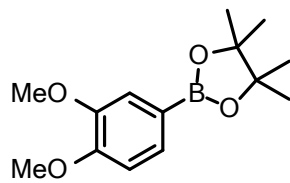
116.71

110.63

83.80

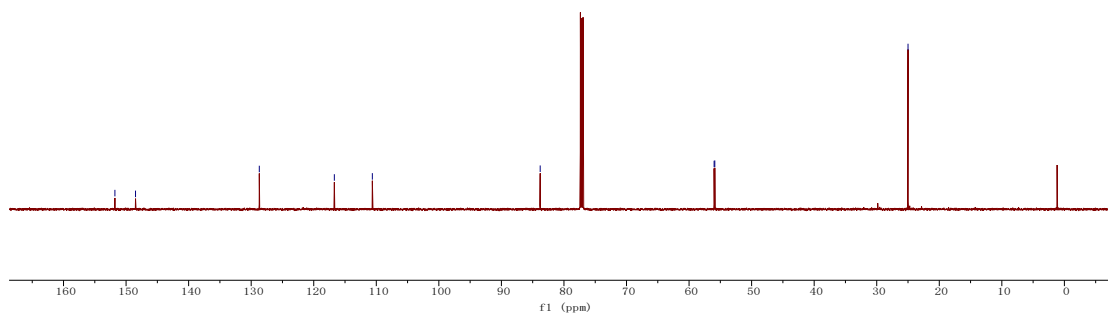
56.00
55.88

25.00

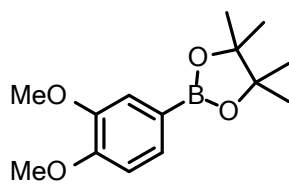


3y

¹³C NMR (151 MHz, CDCl₃)

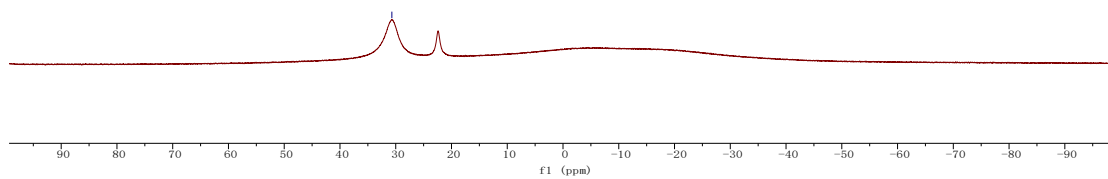


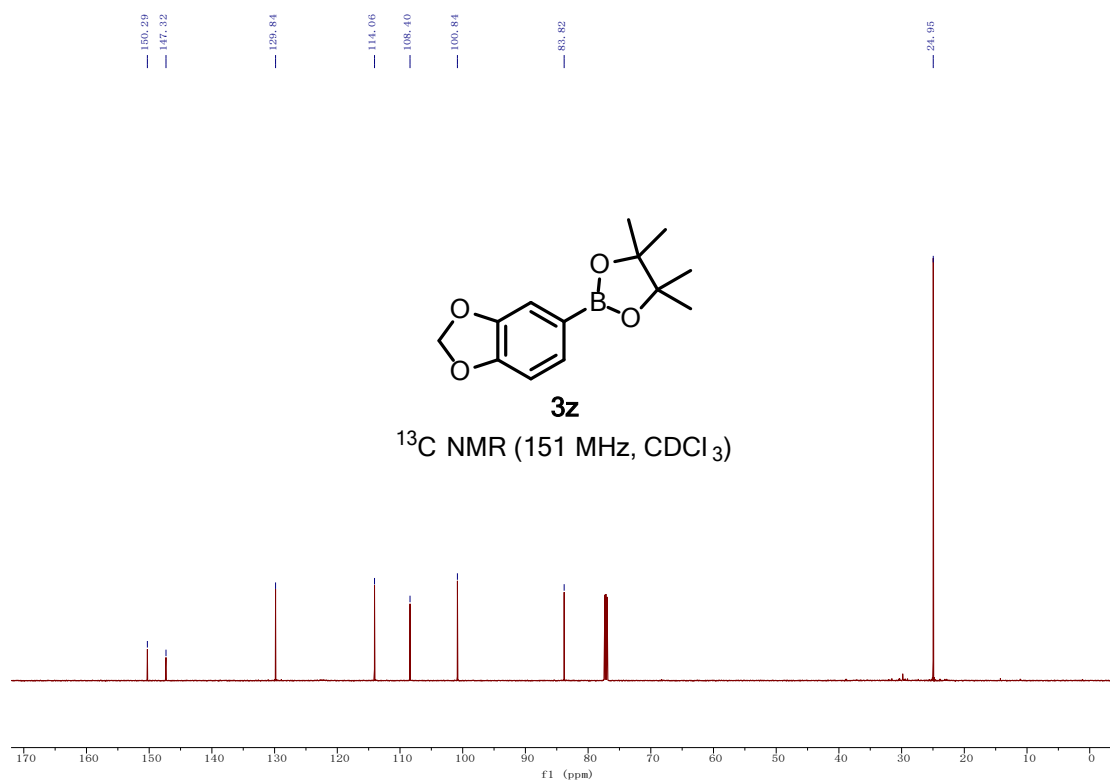
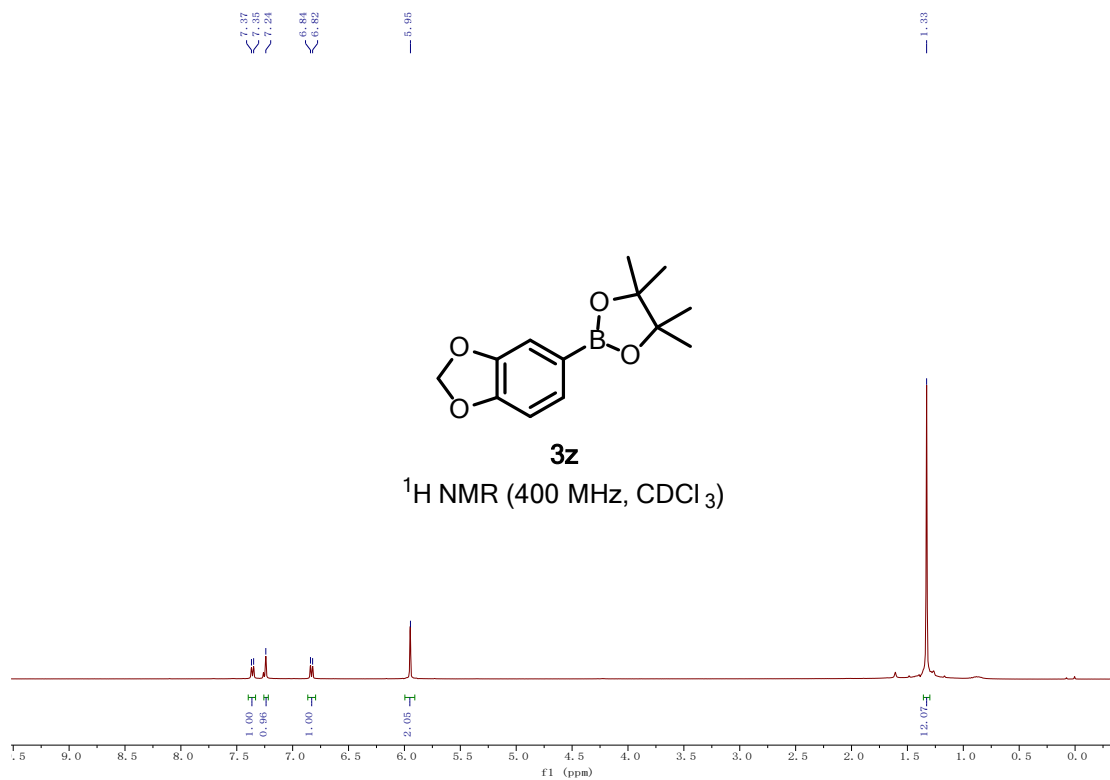
30.69



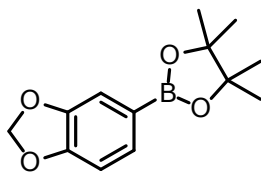
3y

¹¹B NMR (128 MHz, CDCl₃)



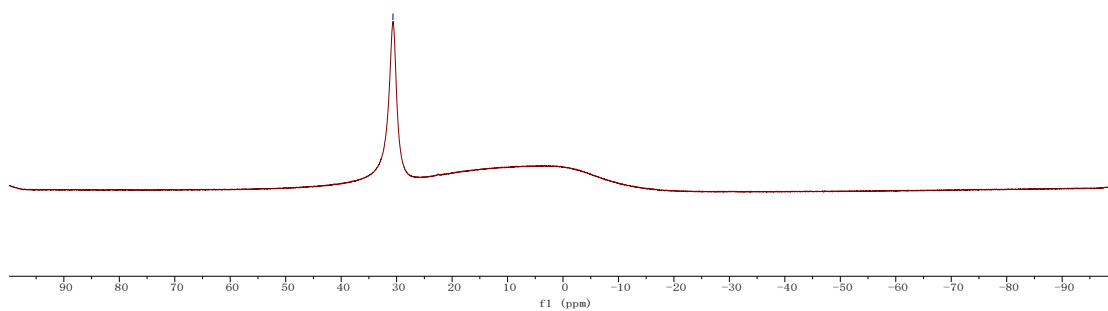


30.06



3z

^{11}B NMR (193 MHz, CDCl_3)

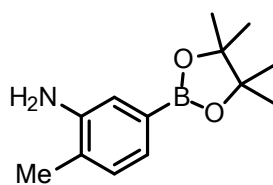


7.18
7.16
7.15
7.08
7.06

3.57

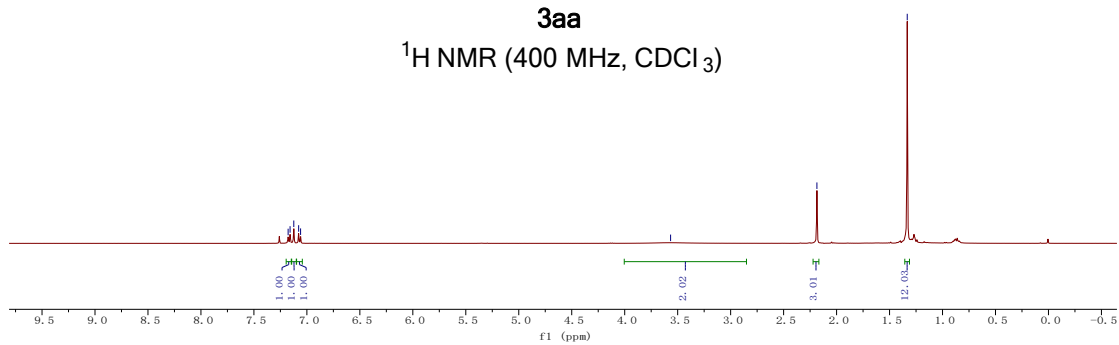
2.19

1.33



3aa

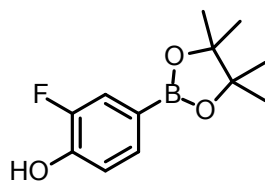
^1H NMR (400 MHz, CDCl_3)



7.51
7.49
7.48
7.47
7.01
6.98
6.96

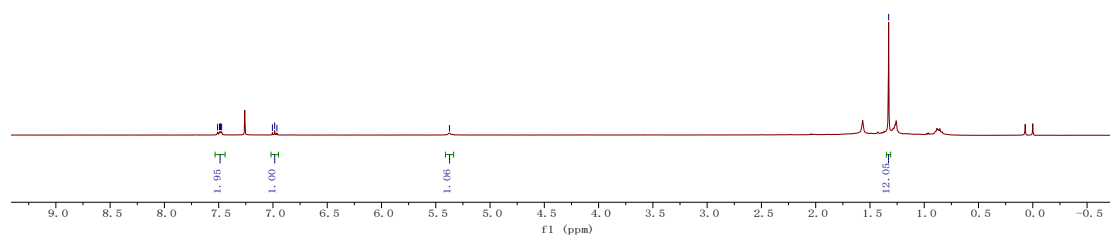
5.37

1.33

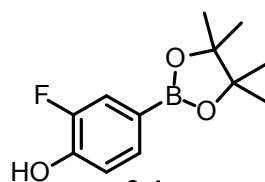


3ab

¹H NMR (400 MHz, CDCl₃)

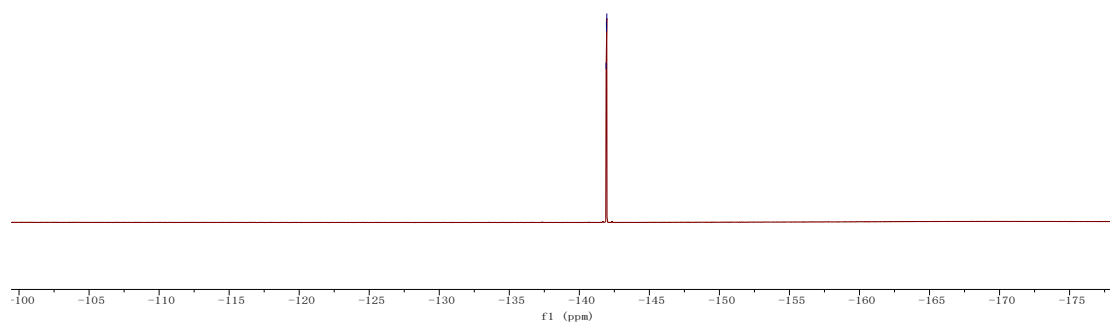


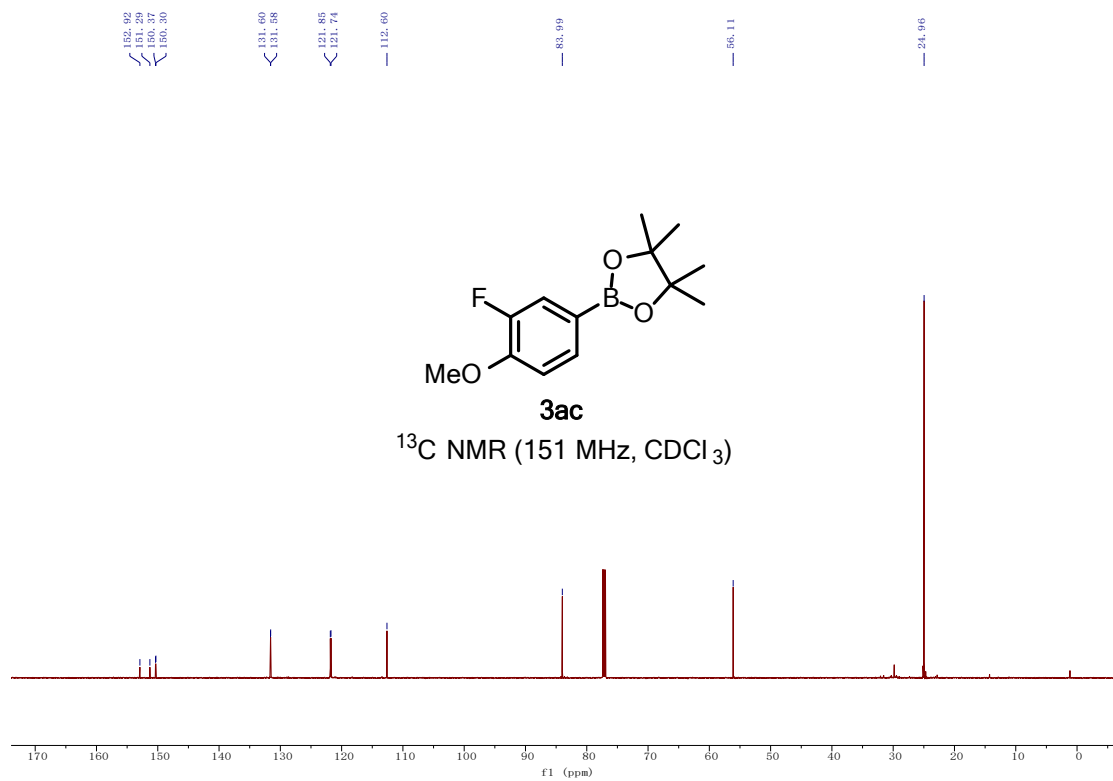
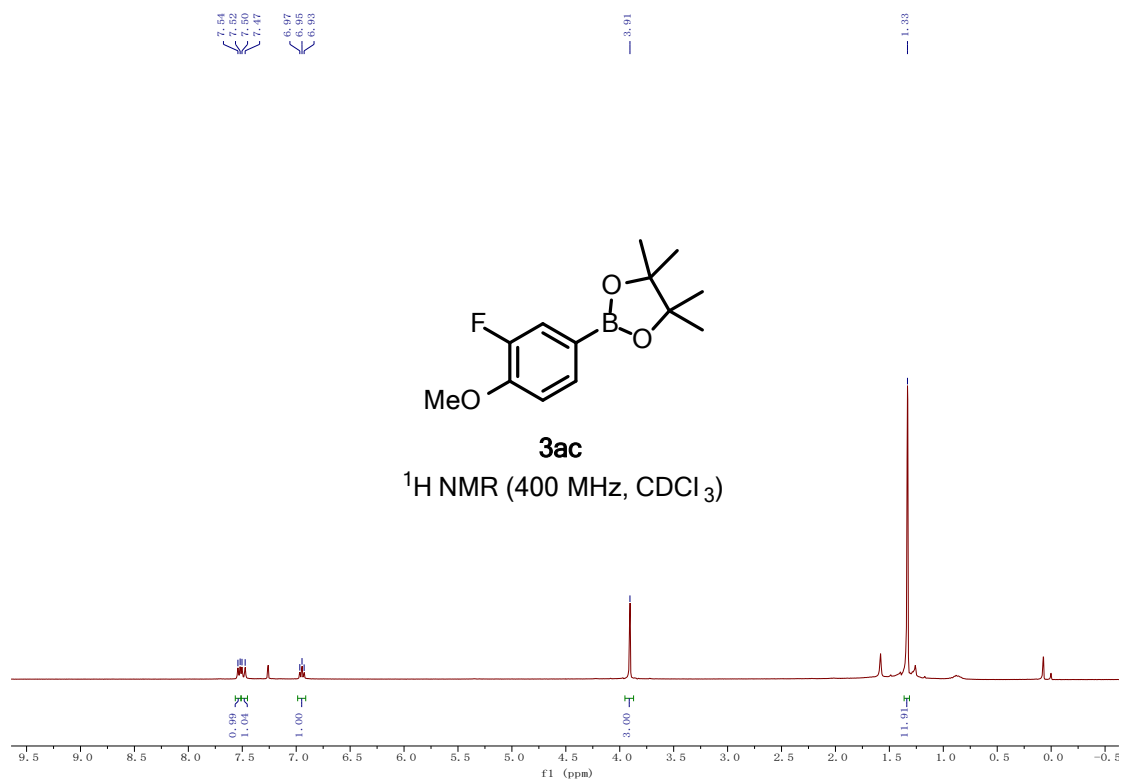
-141.91
-141.90
-141.89
-141.88



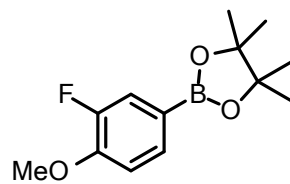
3ab

¹⁹F NMR (377 MHz, CDCl₃)



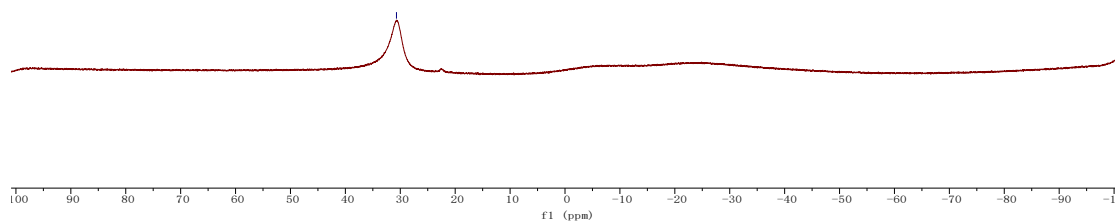


30.69

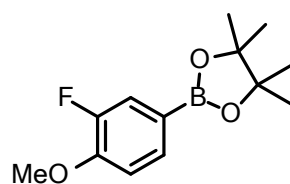


3ac

^{11}B NMR (128 MHz, CDCl_3)

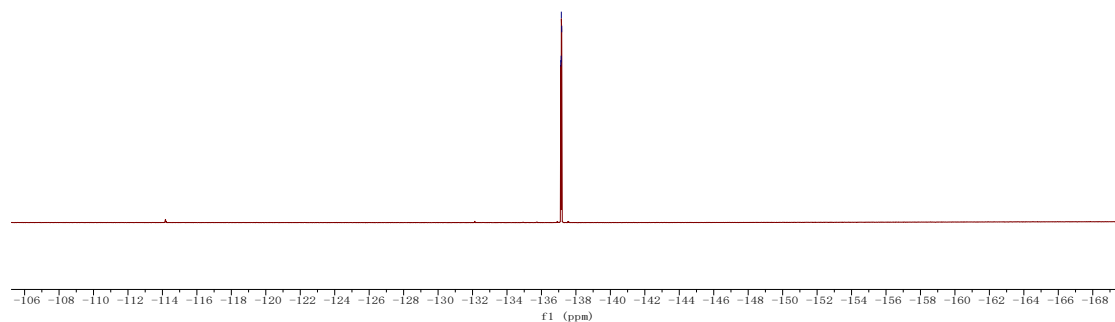


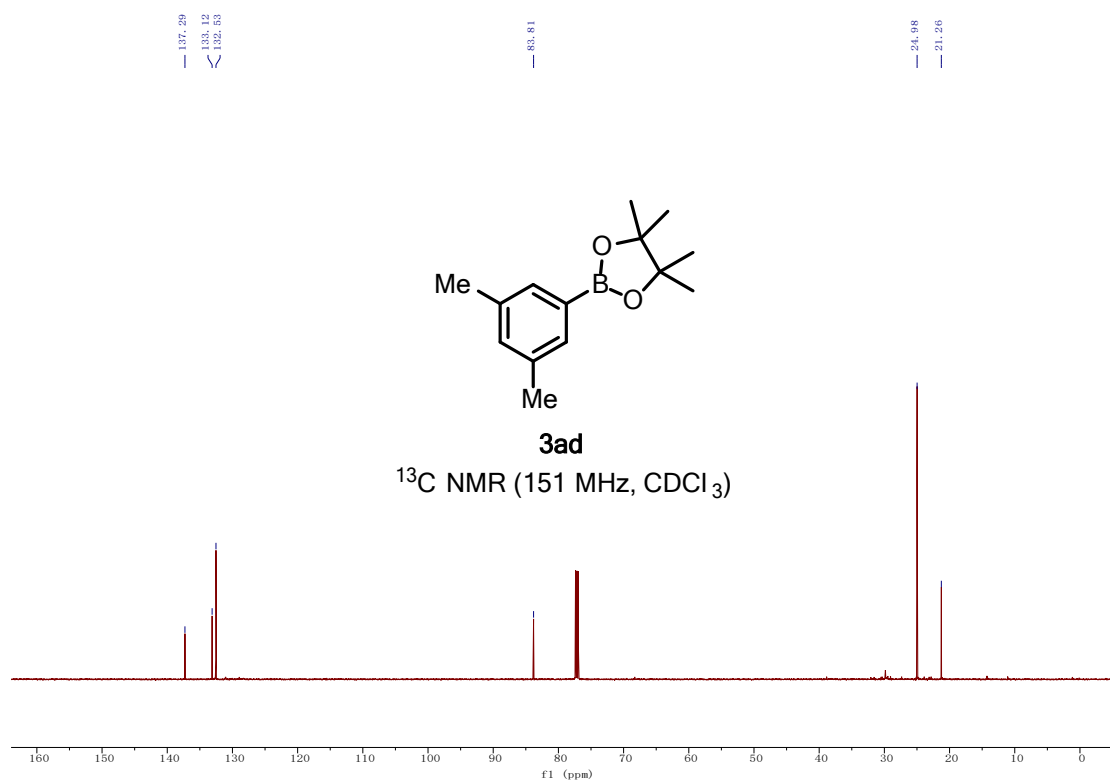
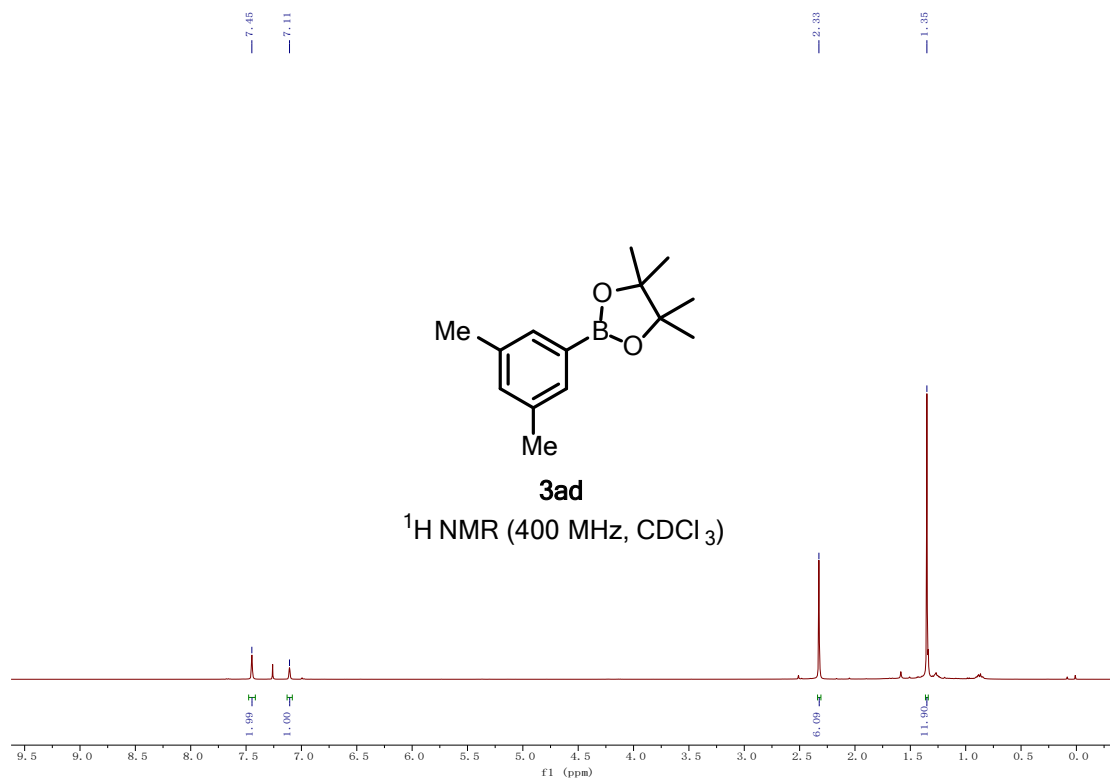
137.12
137.18
137.18

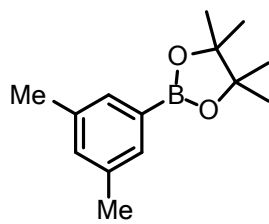


3ac

^{19}F NMR (377 MHz, CDCl_3)

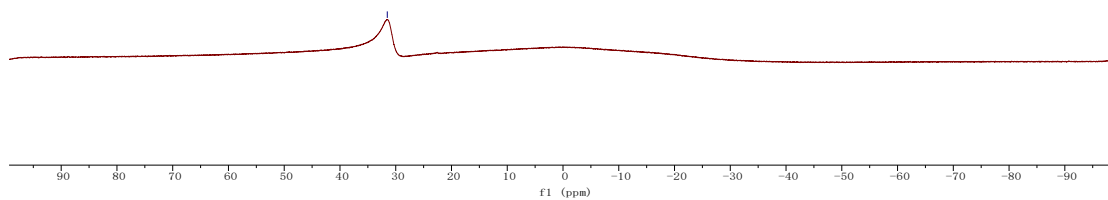






3ad

^{11}B NMR (128 MHz, CDCl_3)

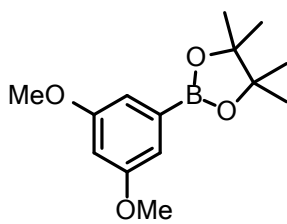


6.95

6.57

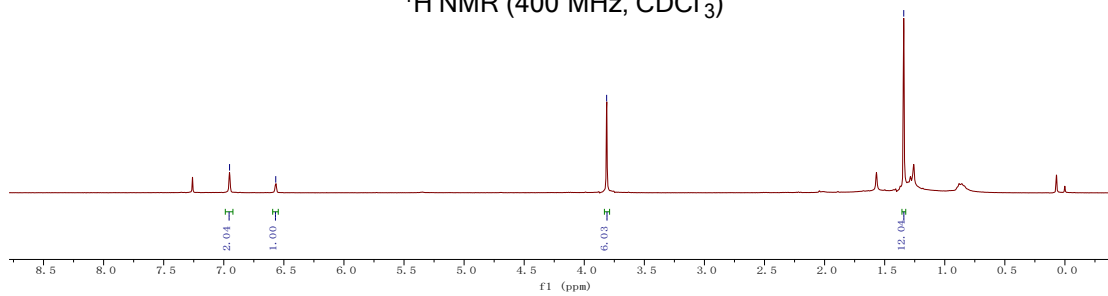
3.81

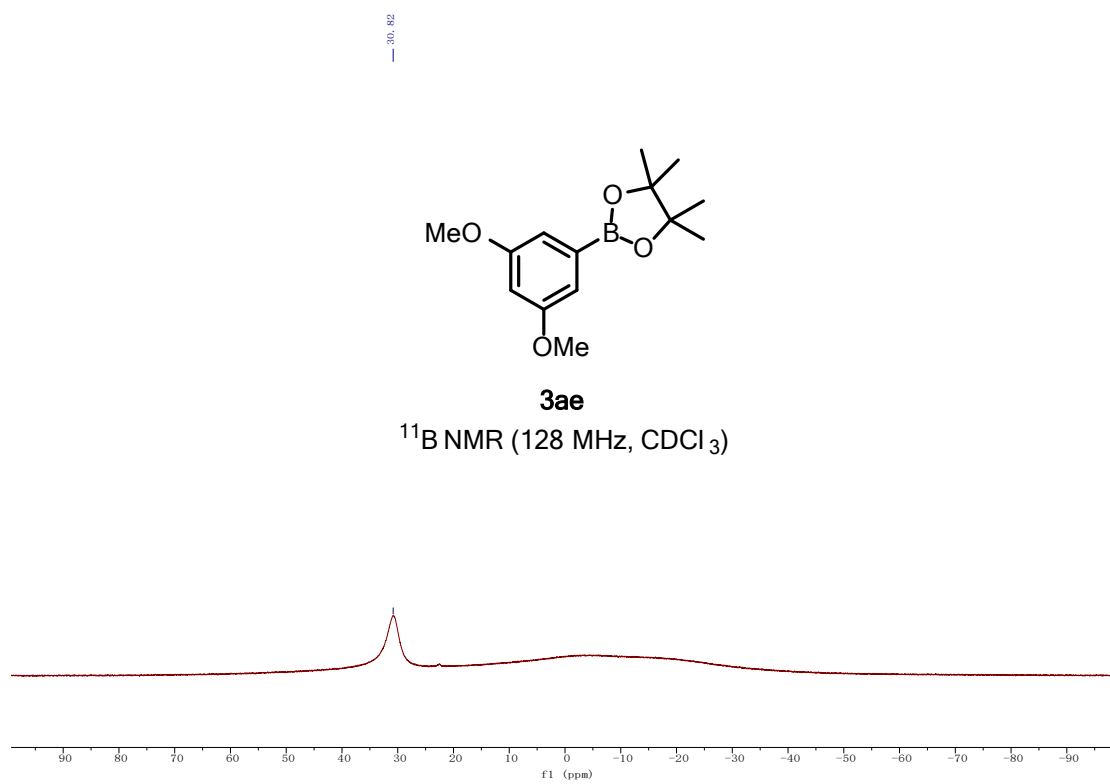
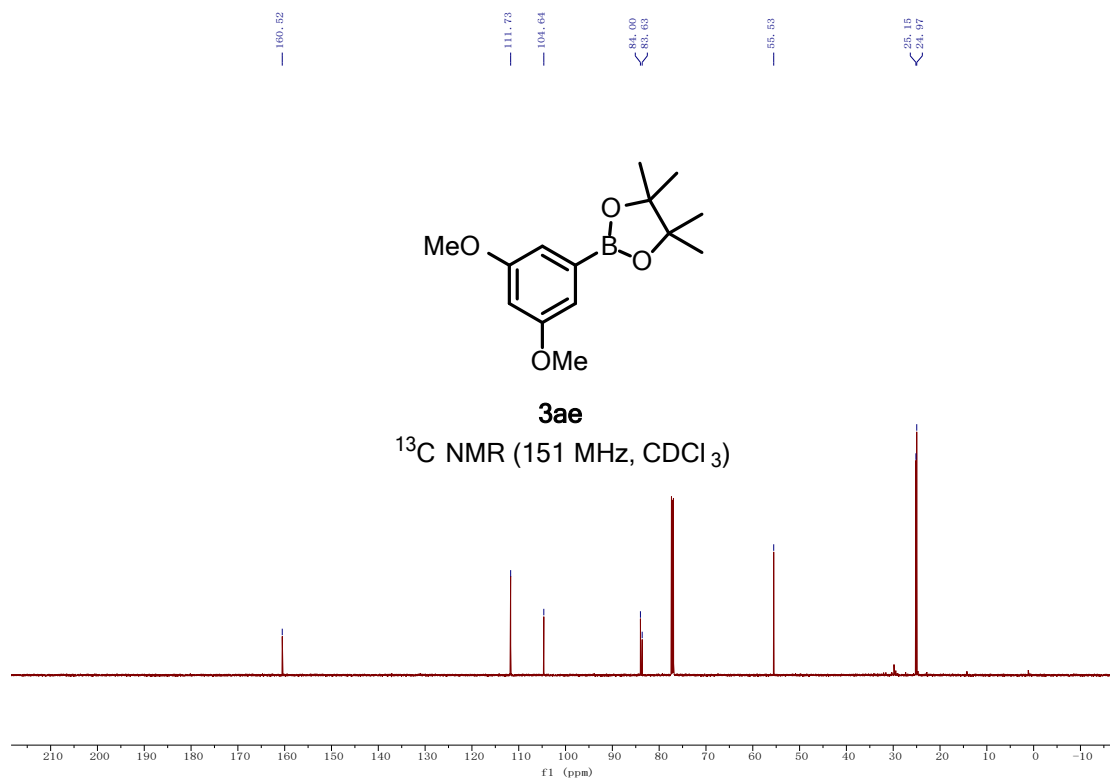
1.34

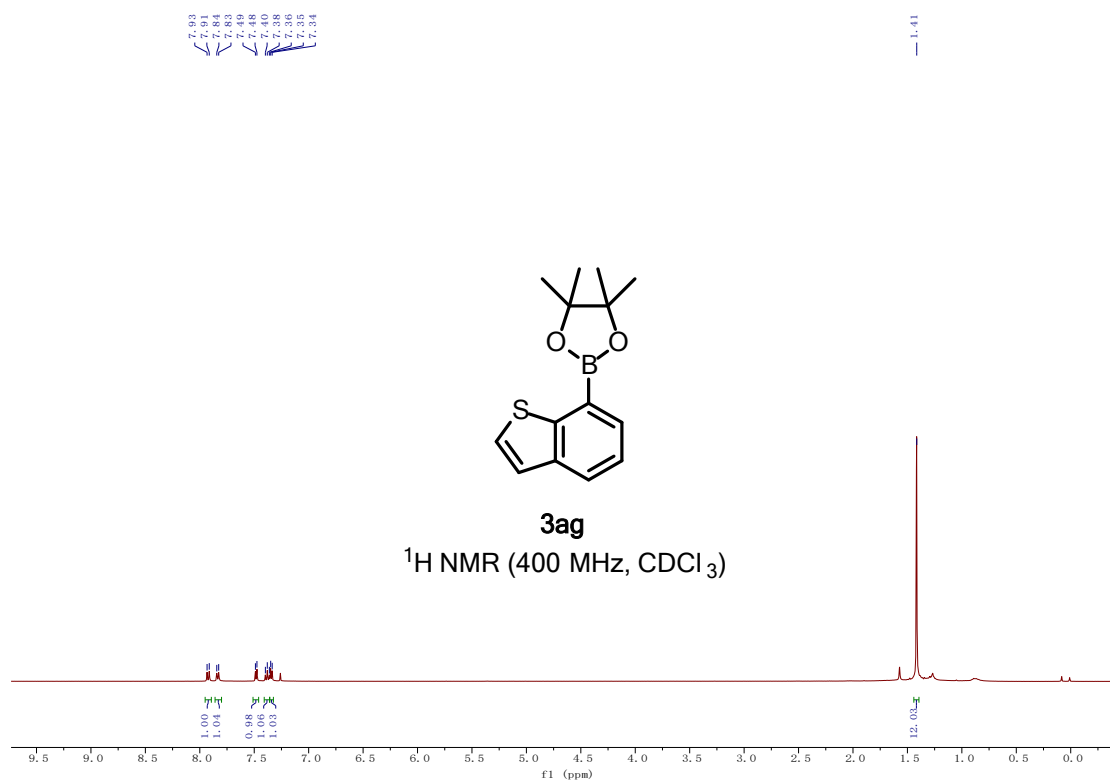
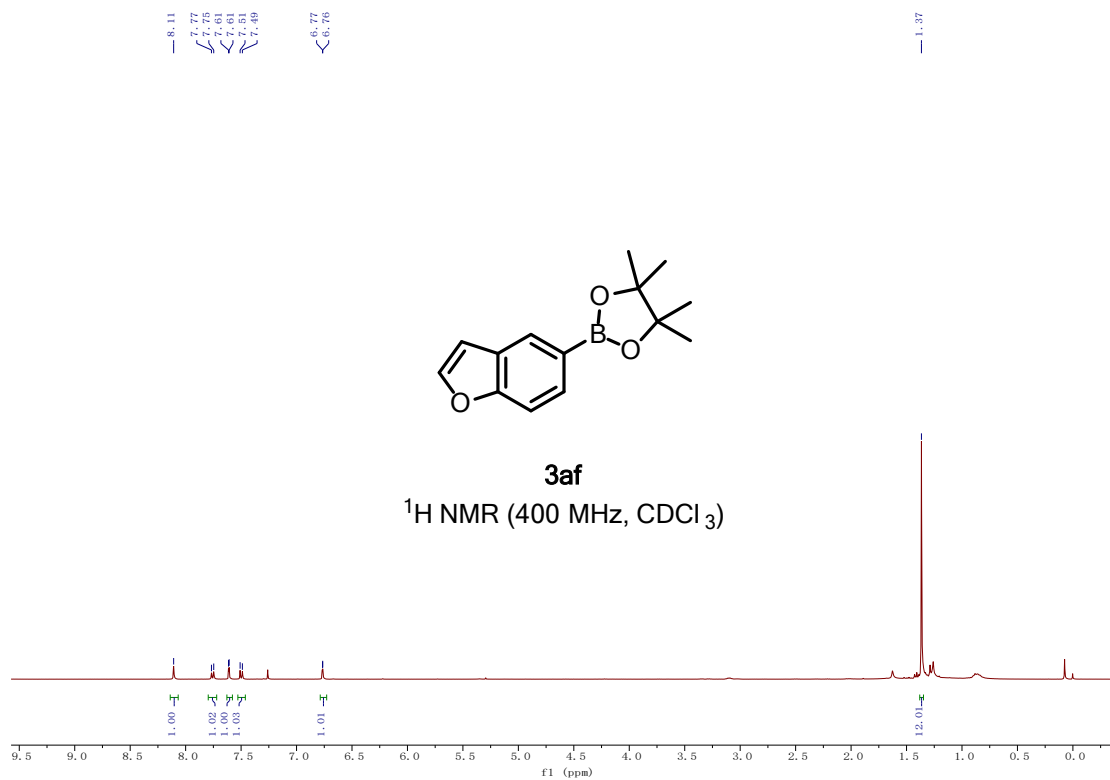


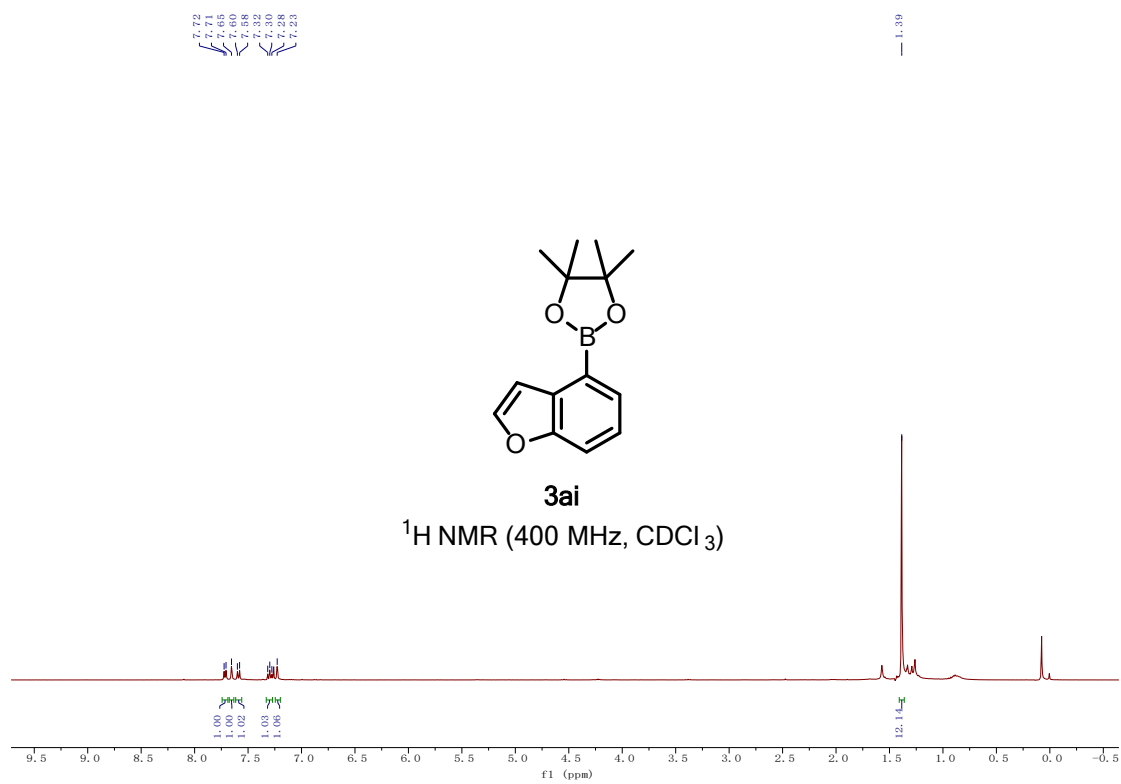
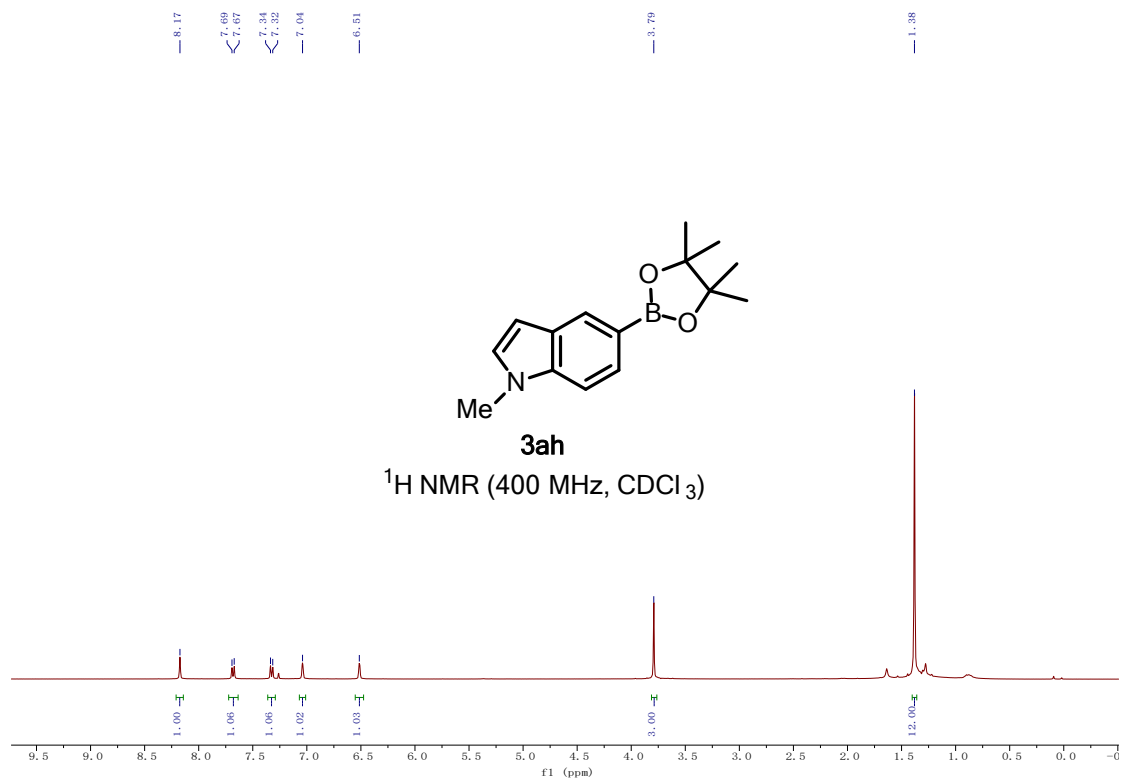
3ae

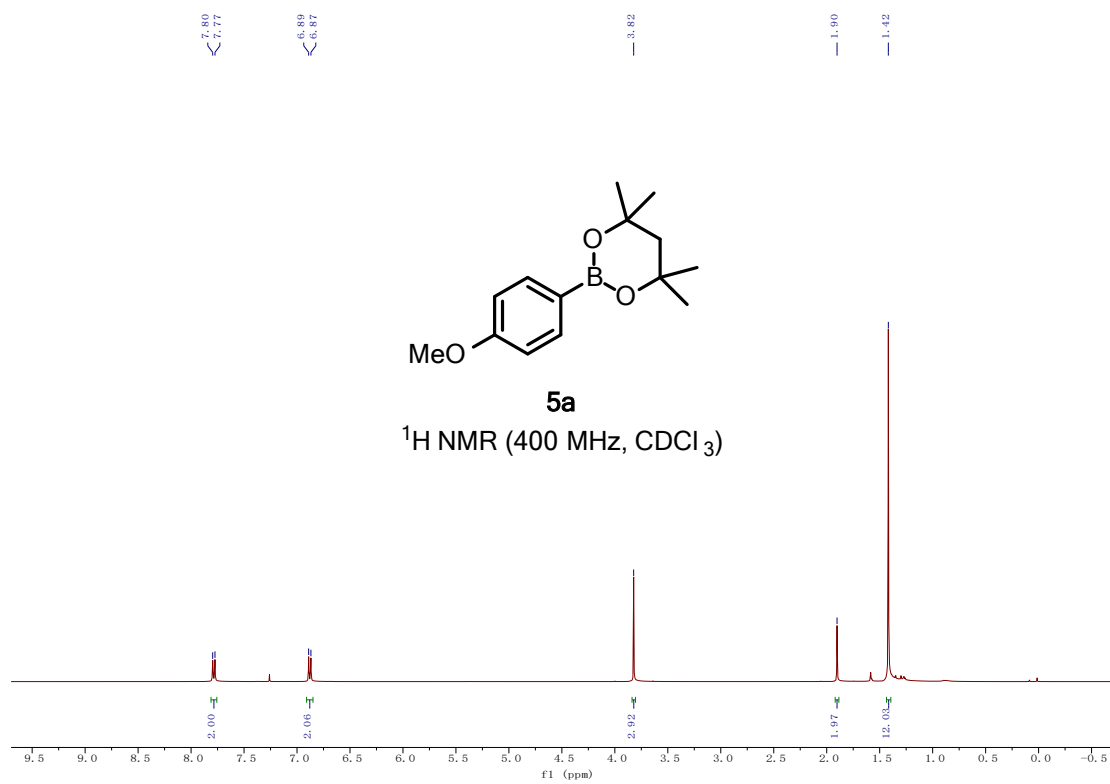
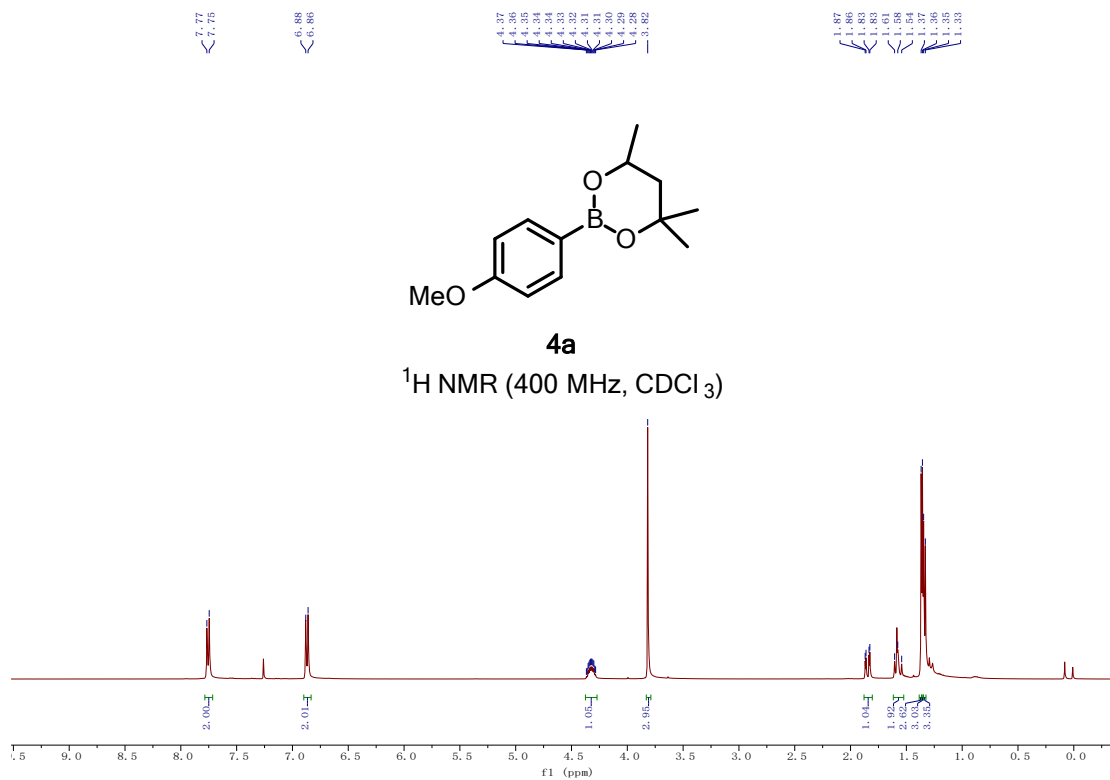
^1H NMR (400 MHz, CDCl_3)

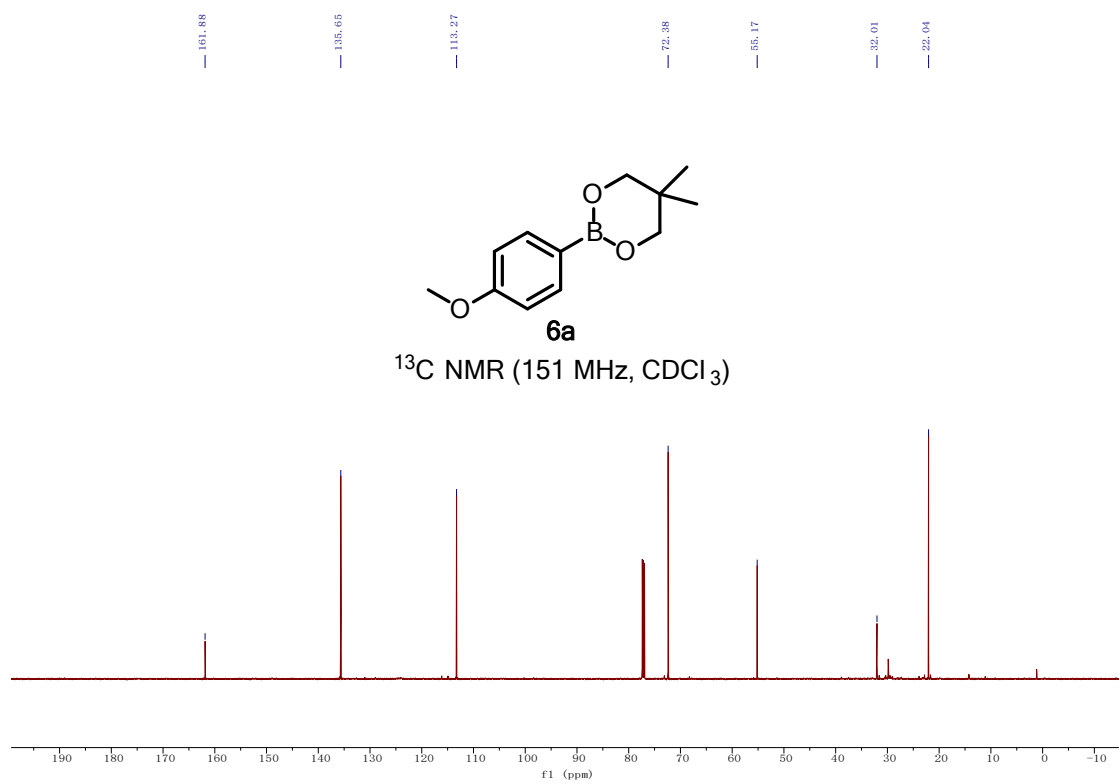
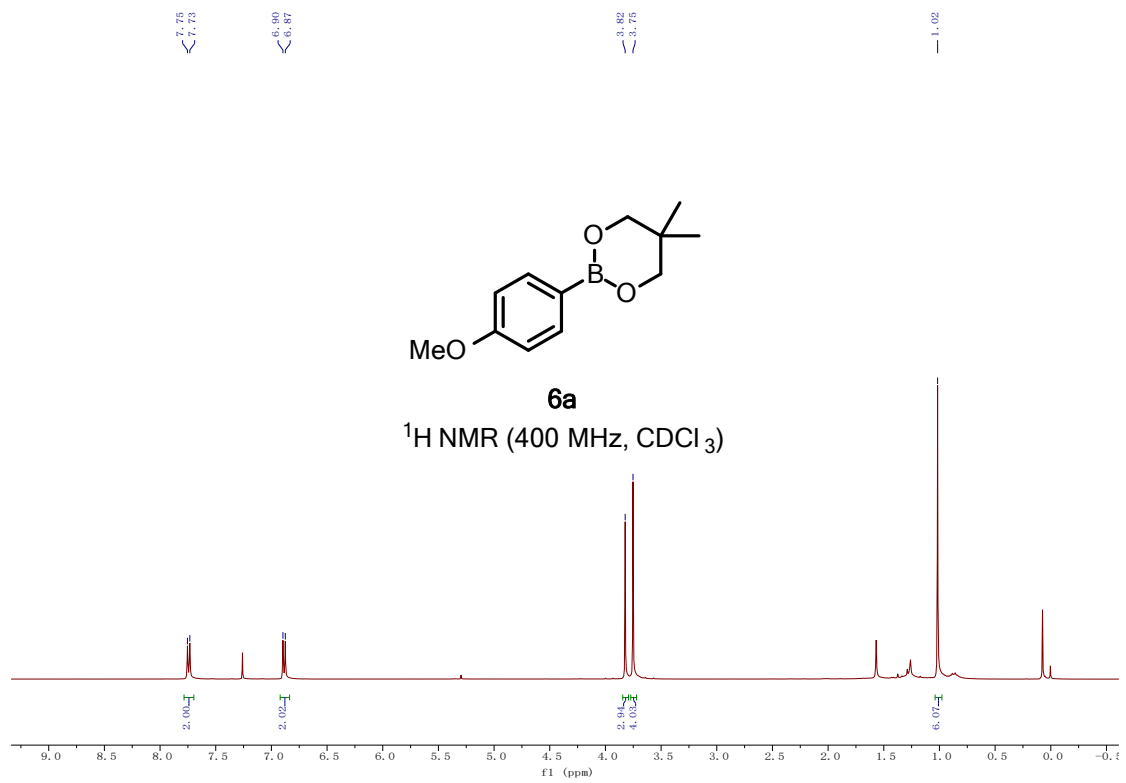




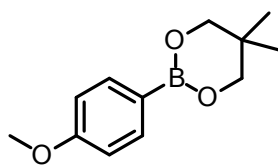






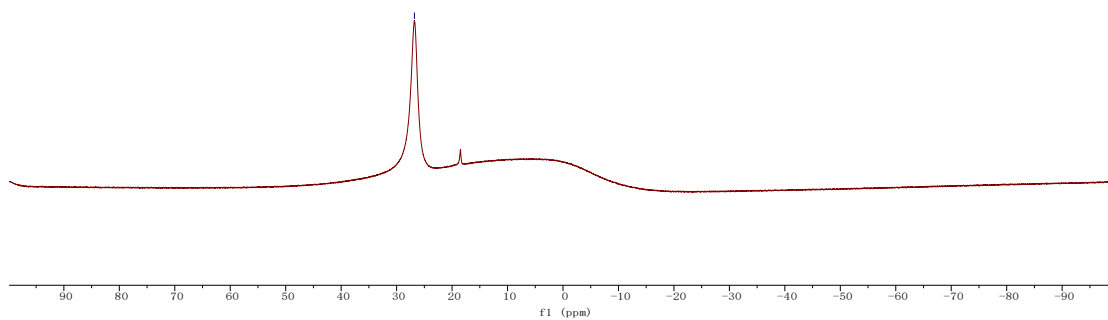


36.79



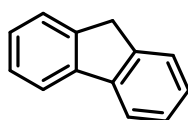
6a

^{11}B NMR (193 MHz, CDCl_3)



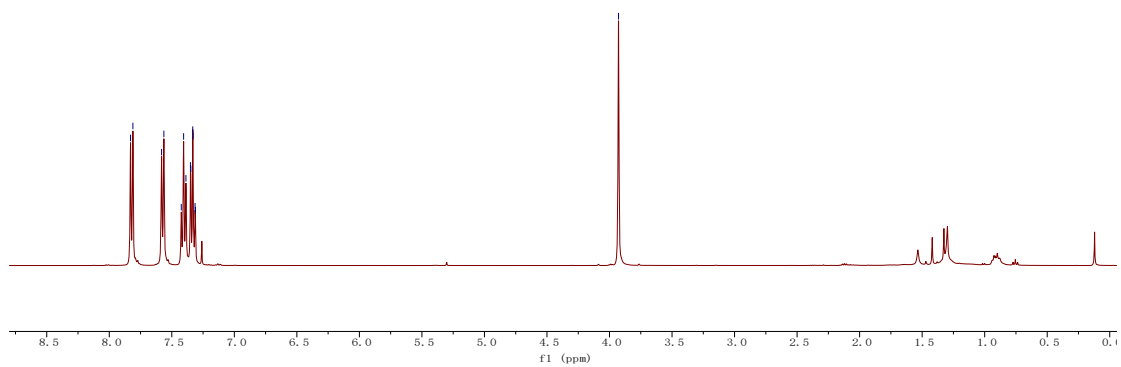
7.83
7.58
7.56
7.42
7.39
7.35
7.35
7.33
7.31
7.31

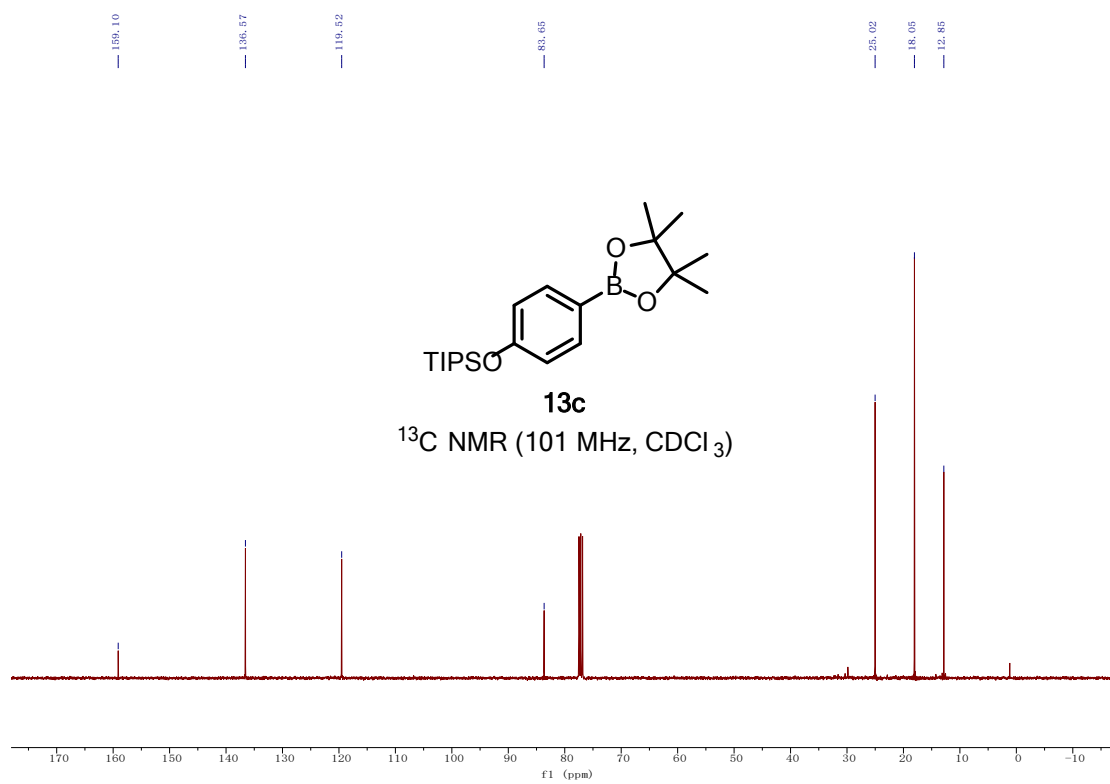
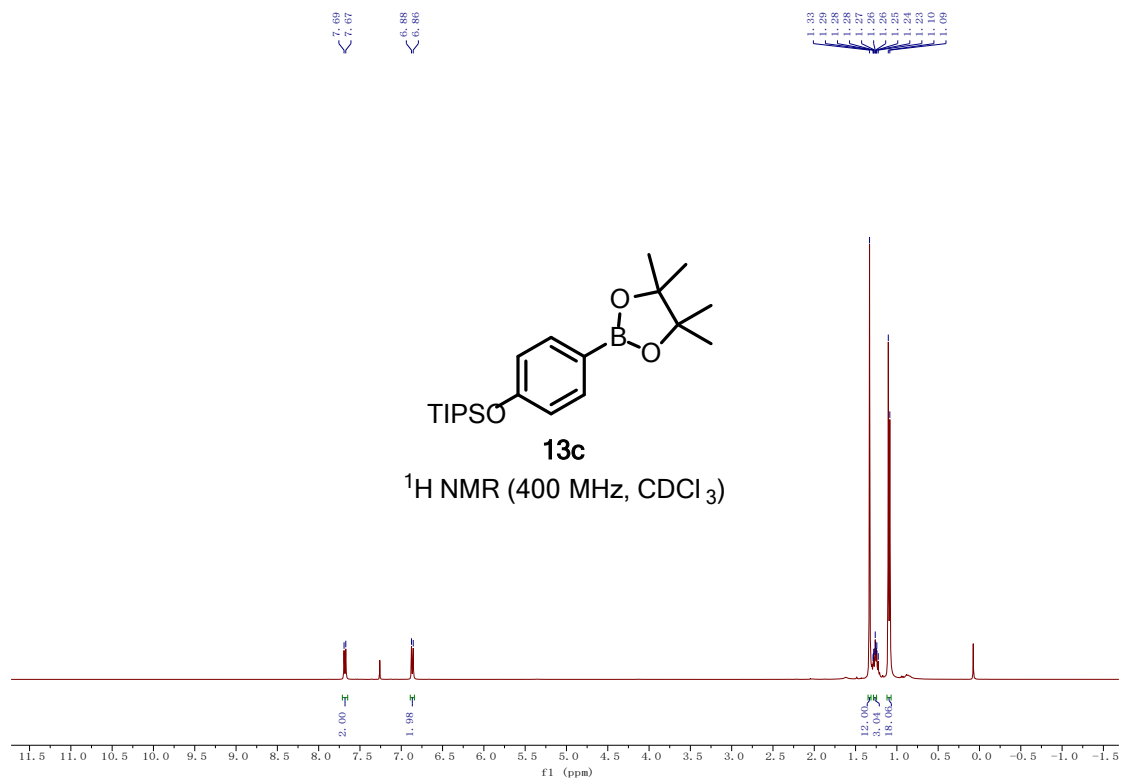
3.93

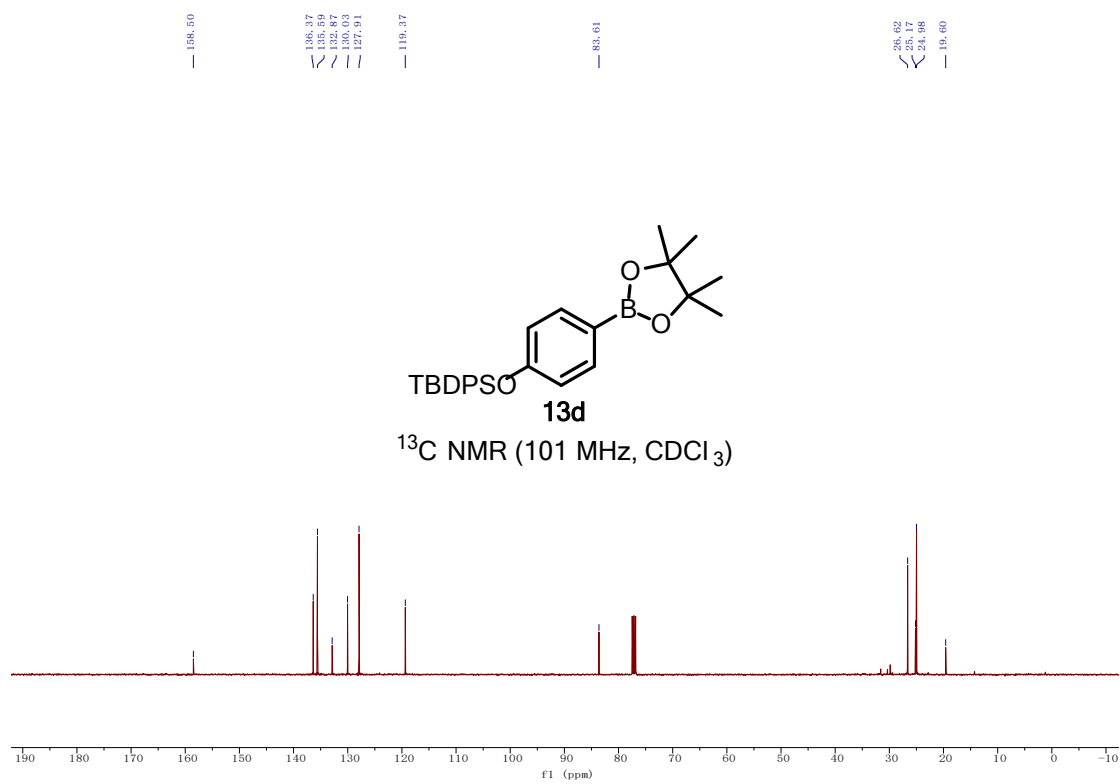
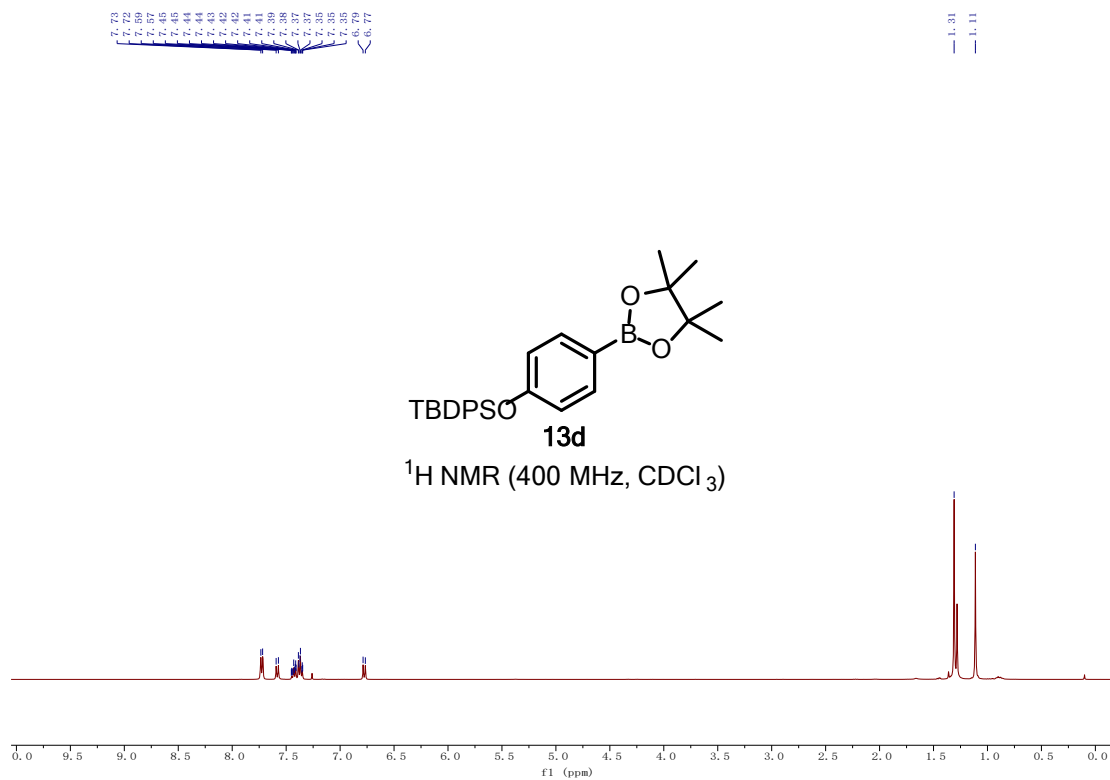


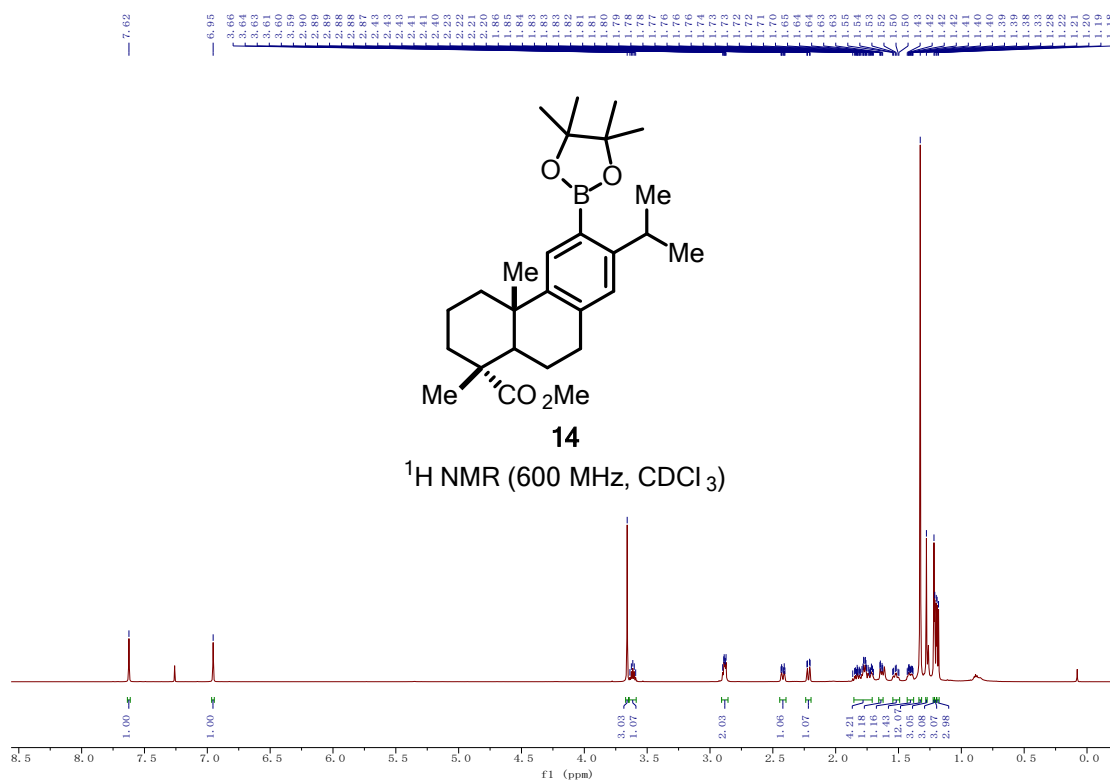
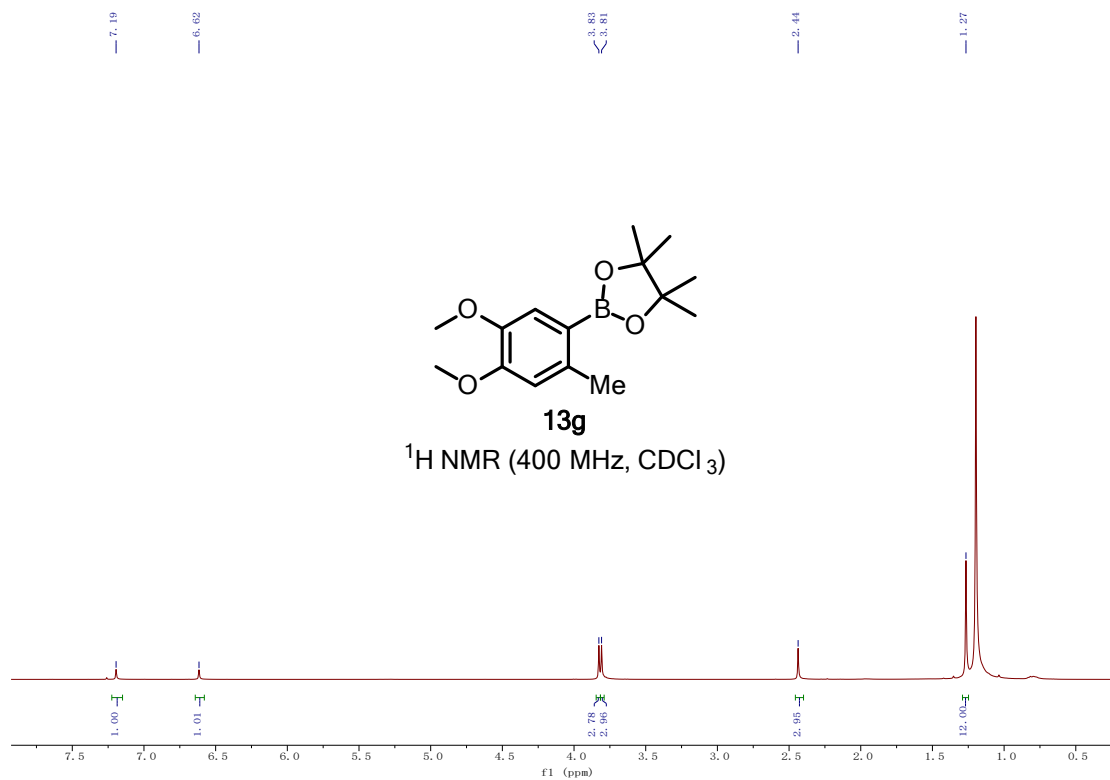
9a

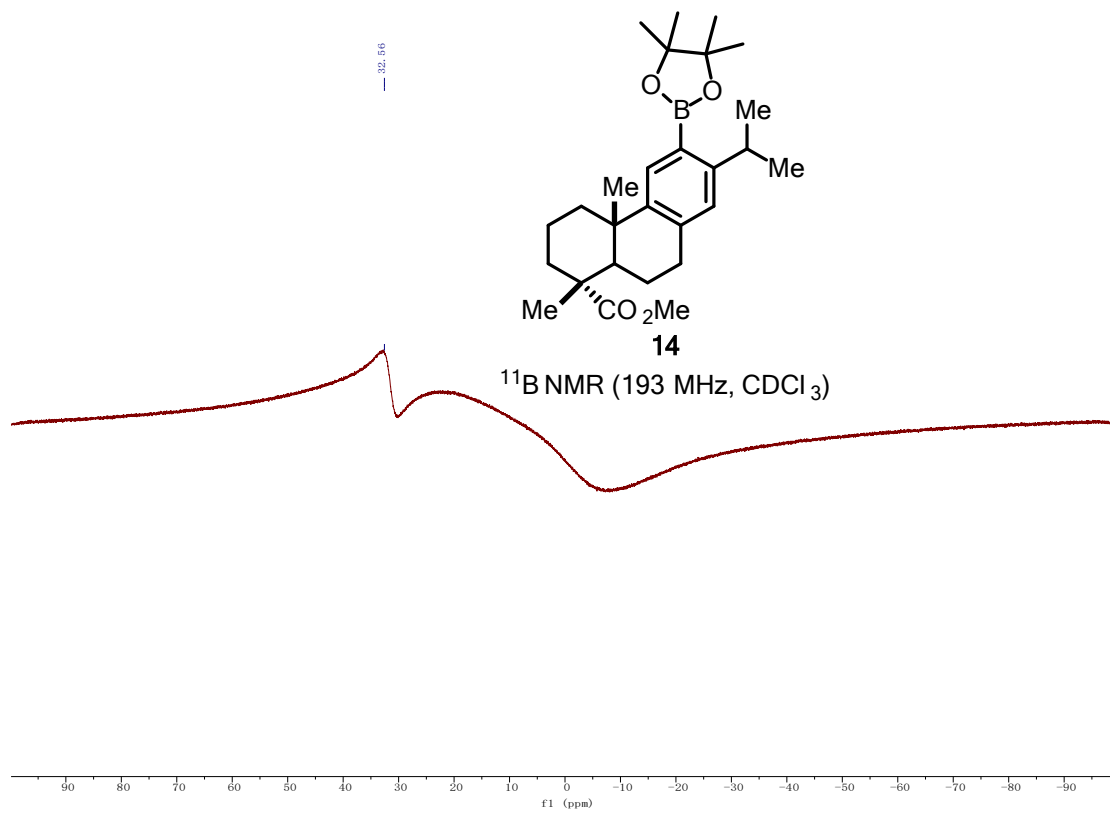
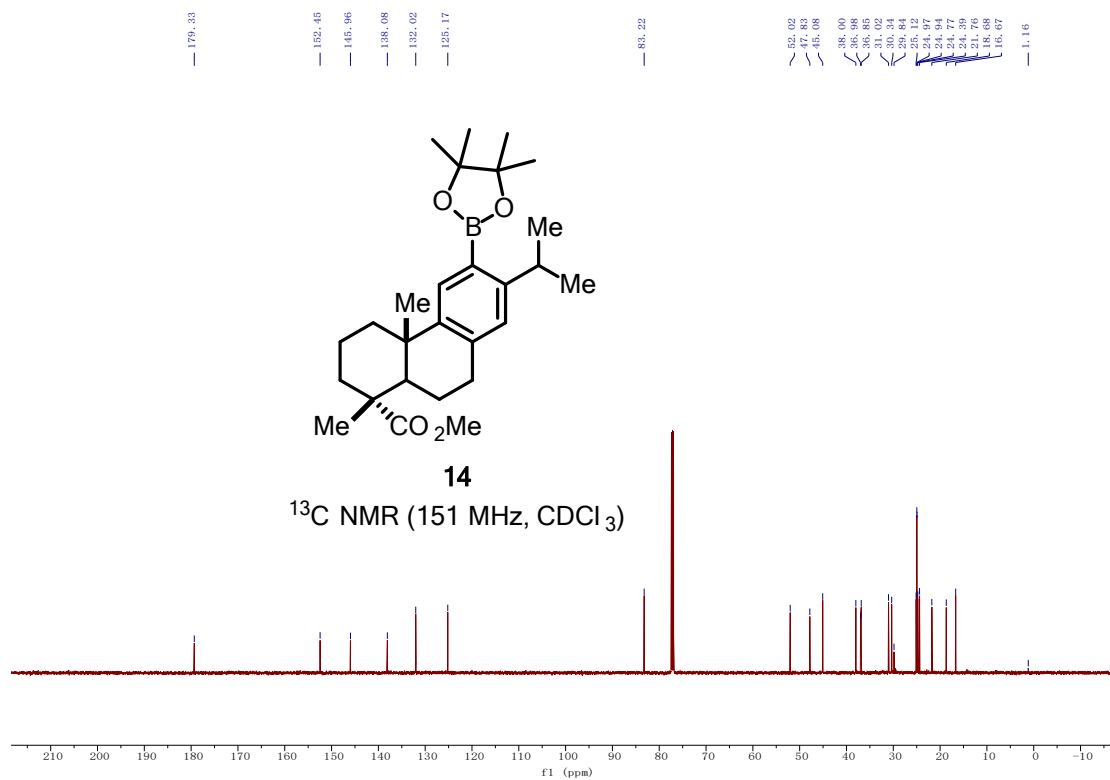
^1H NMR (400 MHz, CDCl_3)

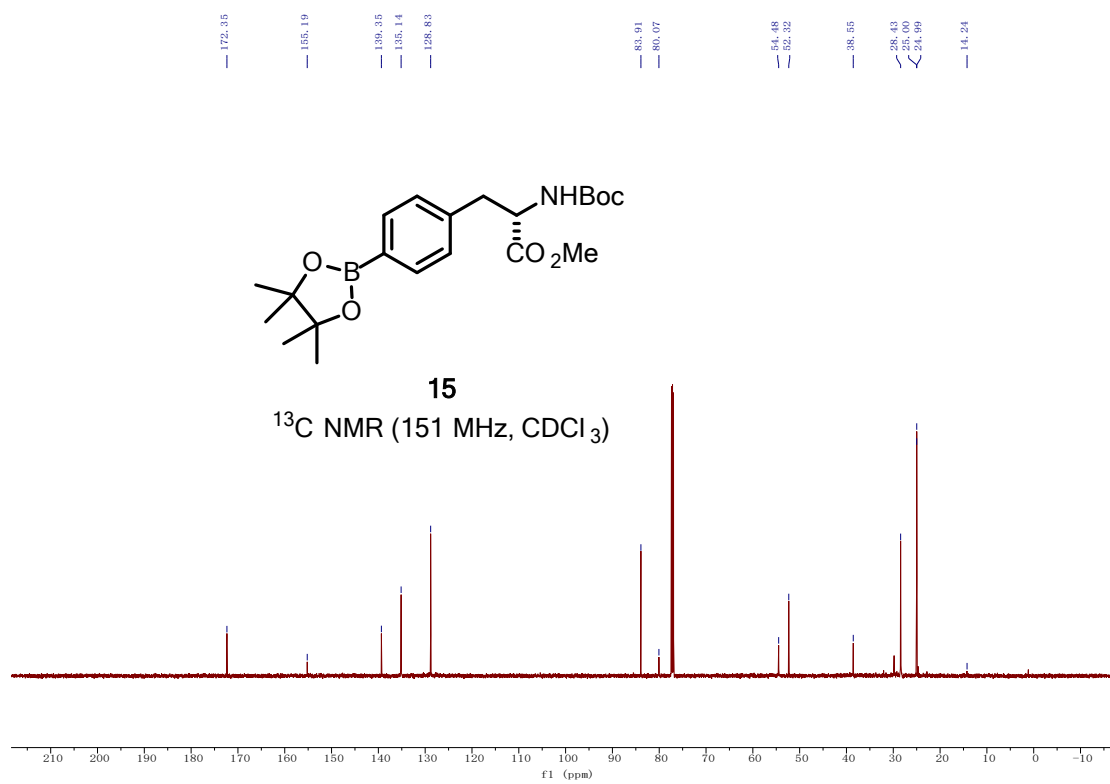
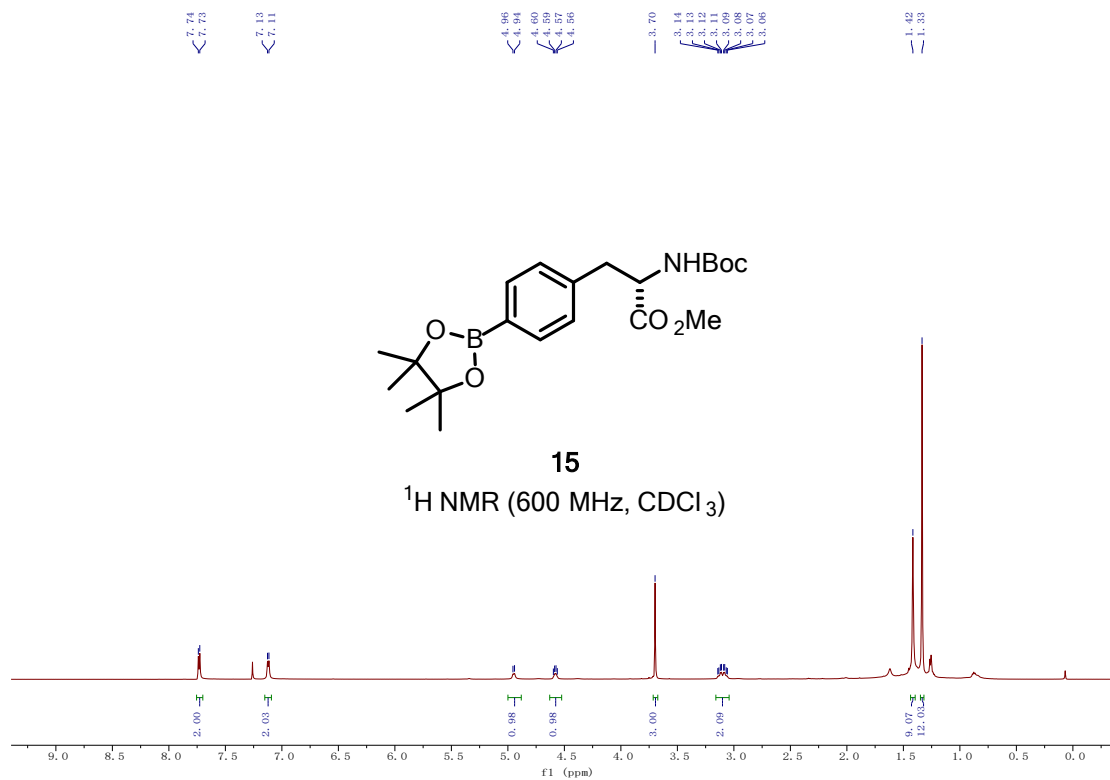


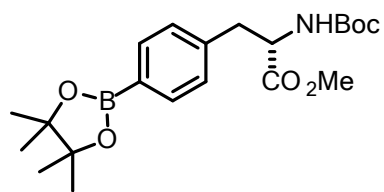






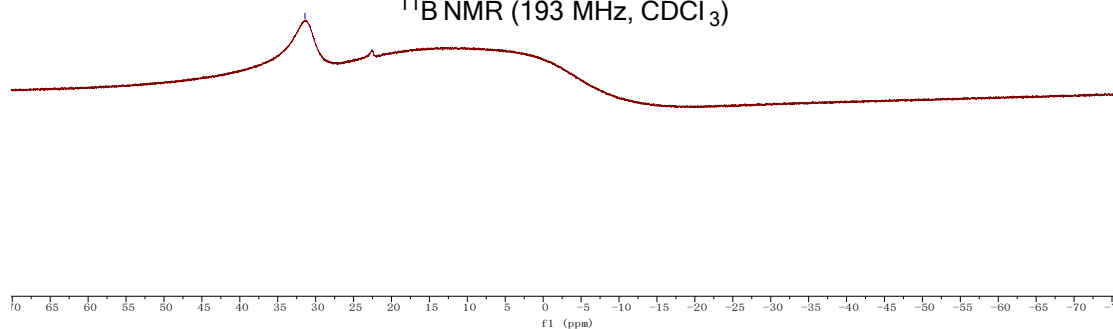






15

^{11}B NMR (193 MHz, CDCl_3)



7.58
7.48
7.42
7.30
7.29
7.28
7.23
7.22
7.22
7.22
7.20

6.58
6.57

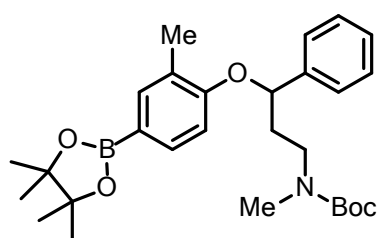
5.22
5.20

3.41

2.83

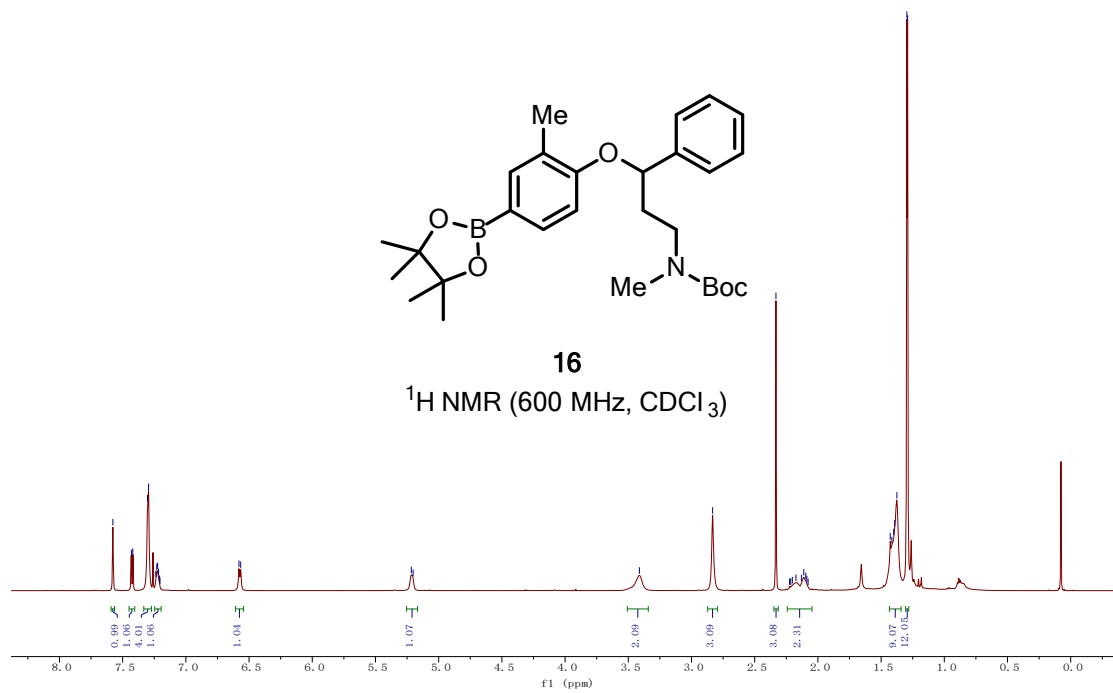
2.33
2.22
2.21
2.17
2.13
2.11
2.09
2.08

1.43
1.42
1.39
1.37
1.36
1.30
1.29



16

^1H NMR (600 MHz, CDCl_3)



0.99
1.06
1.01
1.06

1.04

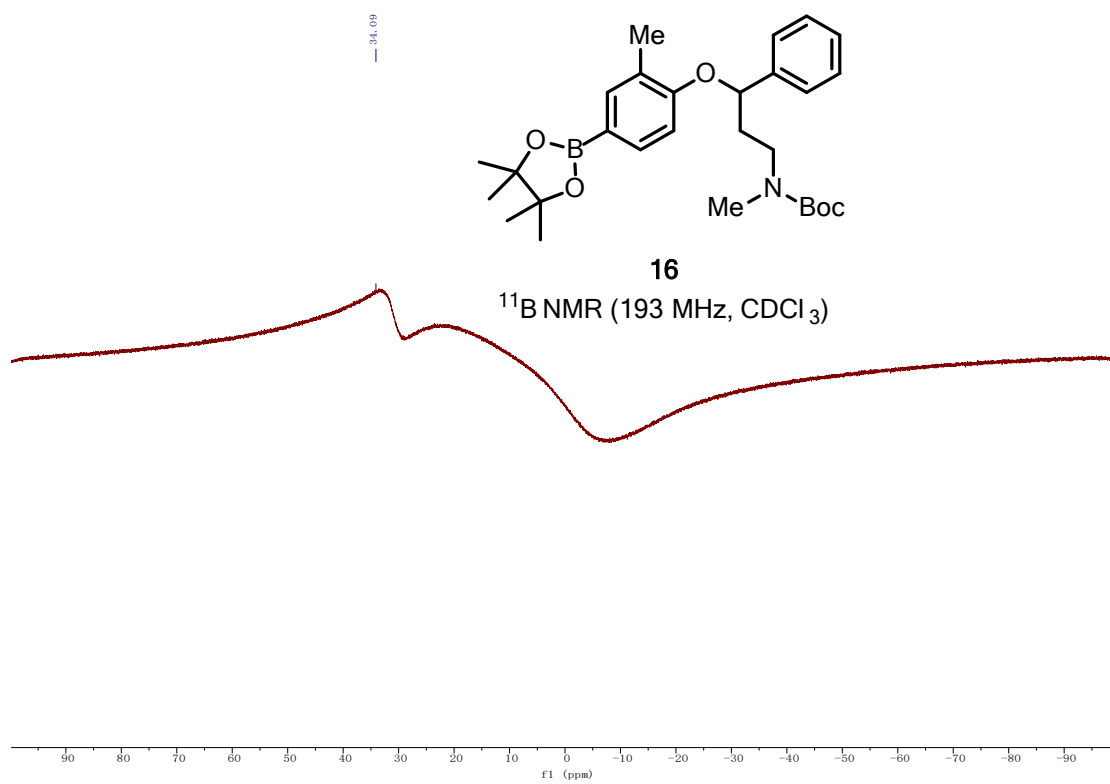
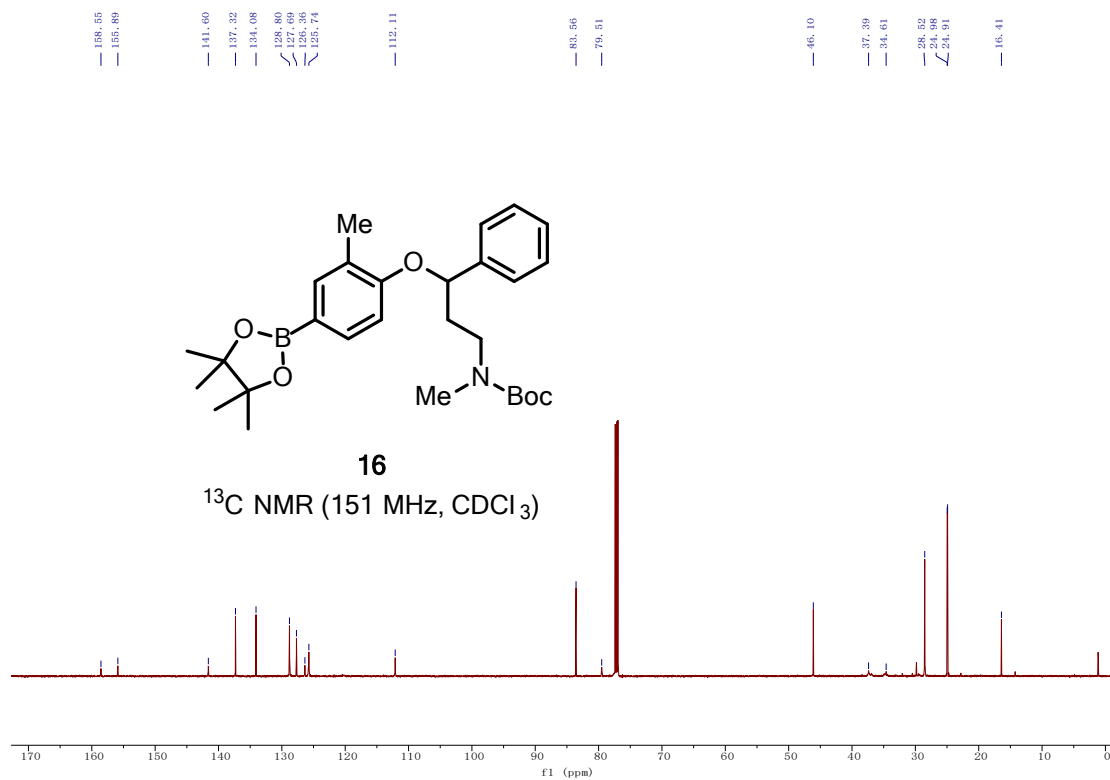
1.07

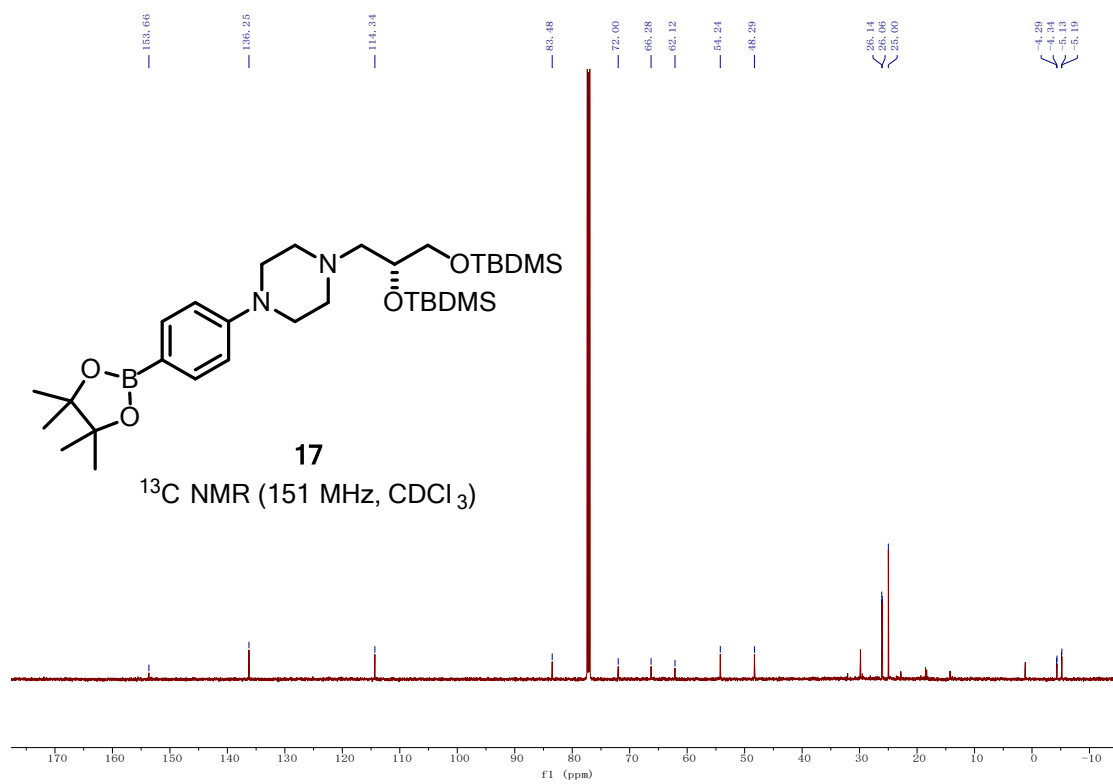
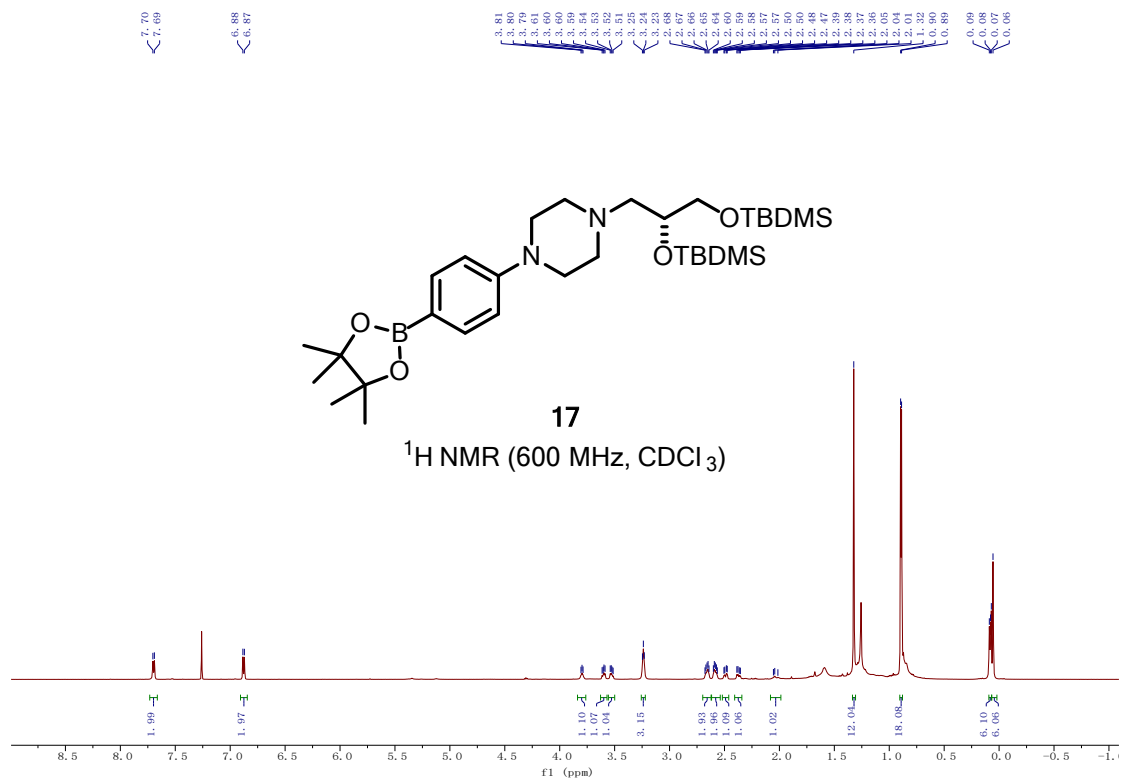
2.09

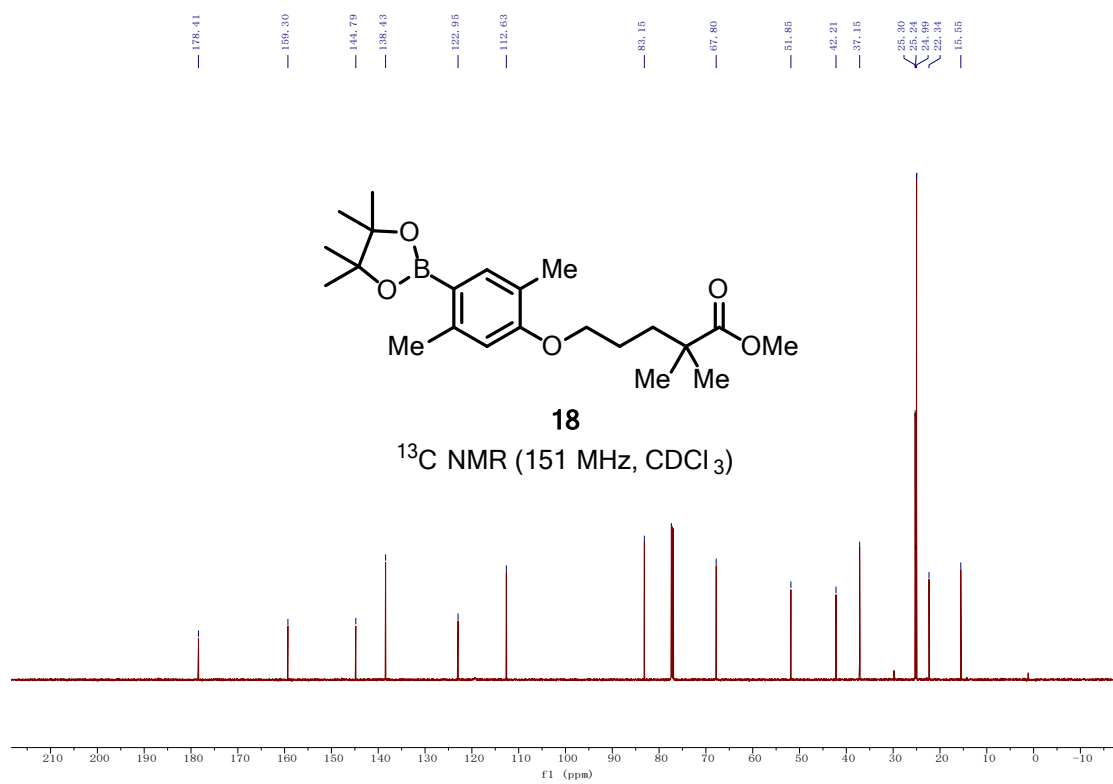
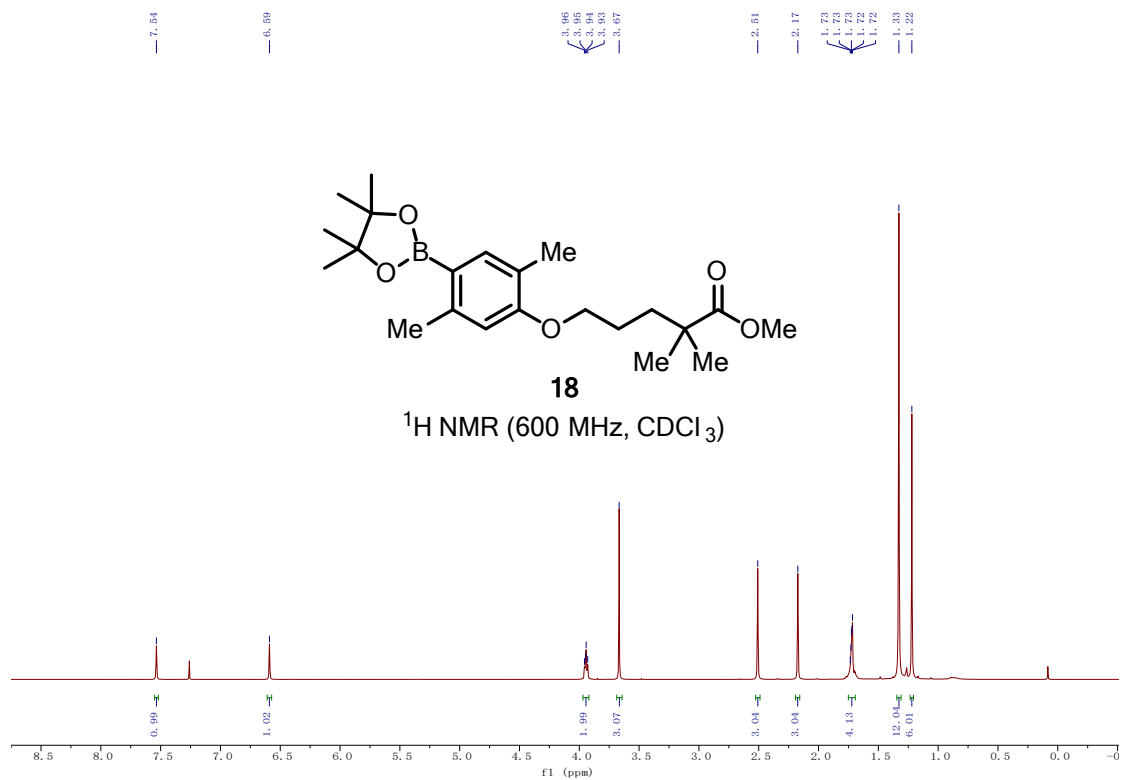
3.09

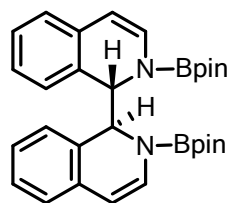
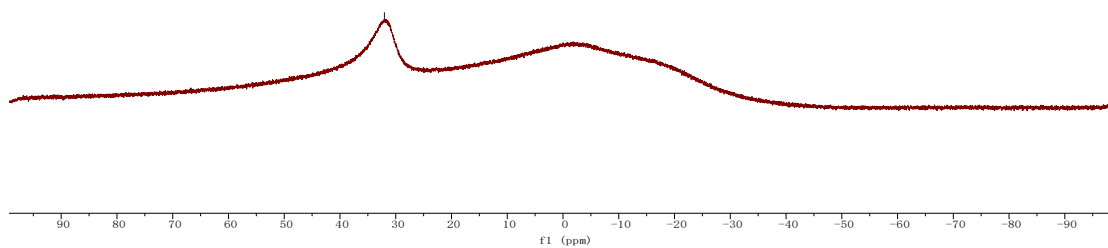
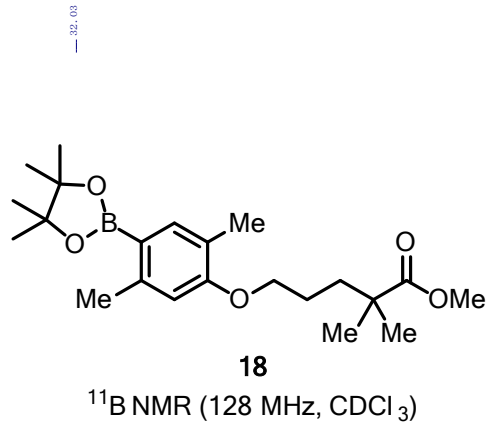
3.08
2.31

9.07
12.04

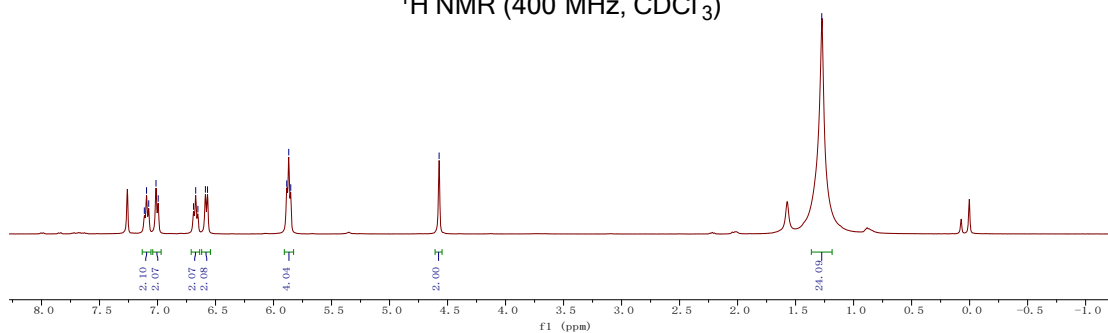








dimer A
¹H NMR (400 MHz, CDCl₃)



132.41
131.16
128.00
127.38
124.17
122.92

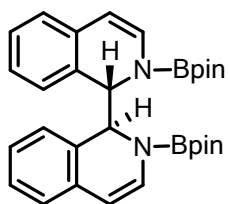
106.02

83.35

56.21

25.59
24.70

w



dimer A

^{13}C NMR (101 MHz, CDCl_3)

