

Supporting Information

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1. Experimental supporting information

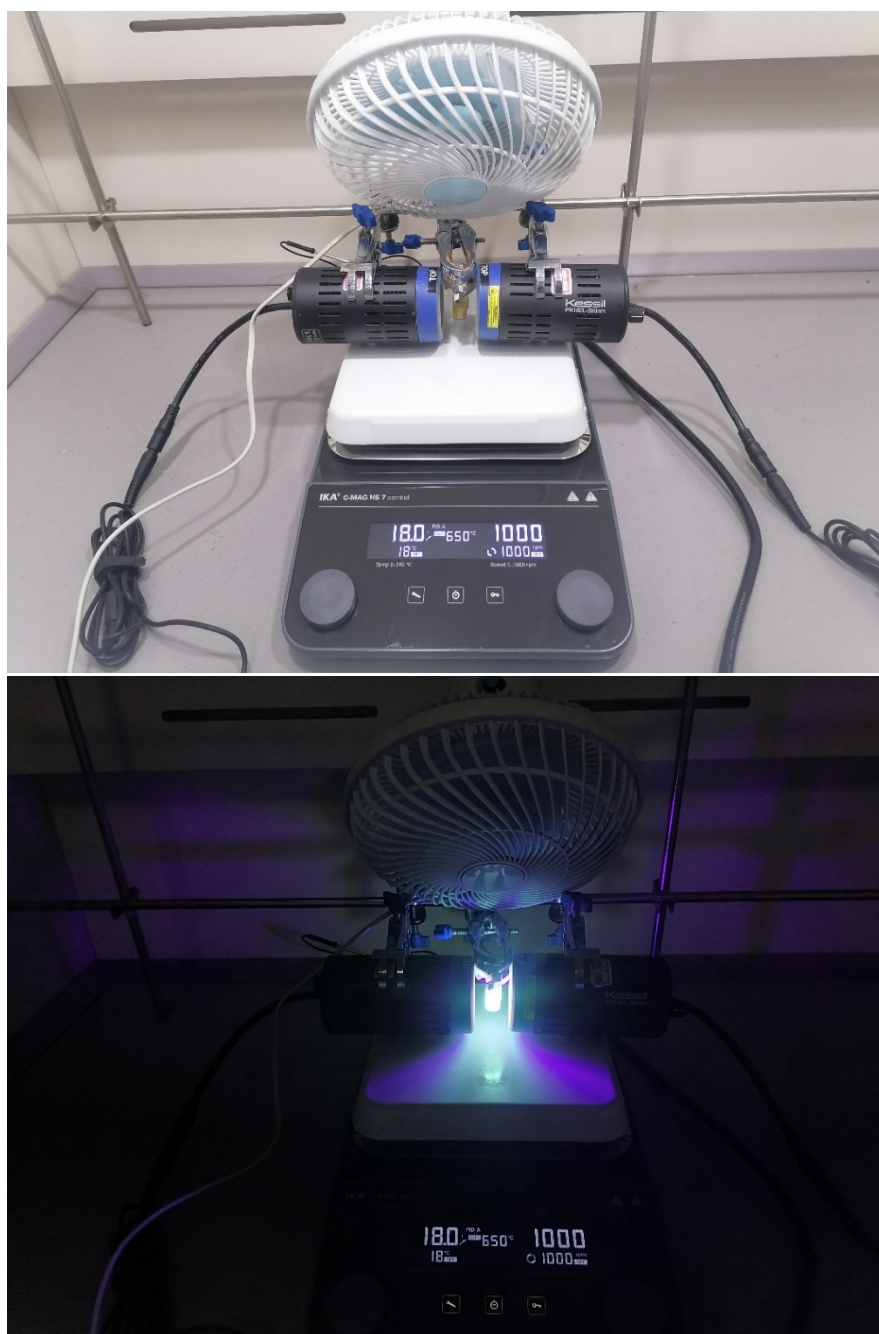
1.1 General Information

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 vial 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 and Heidolph. Fresh silica gel chromatography was performed using 300-400 mesh silica gel (Qingdao, China).

Proton and carbon magnetic resonance spectra (¹H NMR, ¹³C NMR, ¹¹B NMR and ¹⁹F NMR) were recorded on a Bruker AVANCE III (¹H NMR at 400 MHz or 600 MHz, ¹³C NMR at 101 MHz or 151 MHz, ¹¹B NMR at 128 MHz or 193MHz, ¹⁹F NMR at 377 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.16 ppm). NMR yield using pyrazine 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 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), tetrahydrofuran (THF) and dichloromethane (DCM) were purchased from Adamas-beta. Other common solvents such as petroleum ether (PE) and ethyl acetate (EtOAc) are rectification grade for fresh silica gel chromatography purchased from General-reagent.



Scheme S1 Photo reaction setup

1.2 Examination of Substituent Effects on Isoquinoline

General procedure (A):

An oven-dried 2 mL vial was charged with a magnetic stir bar, in the solvent of 4-bromo-dimethylaniline (0.2 mmol, 1.0 eq) in AcN (0.5 mL), B₂pin₂ (203.1 mg, 0.8 mmol, 4.0 eq), NEt₃ (139.0 μ L, 1.0 mmol, 5.0 eq) and suitable substituted isoquinoline (0.04 mmol, 20 mol%) were added. The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 24 h. Solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine as the internal standard.

Table S1 Examination of substituent effects on isoquinoline^a

Position	electron rich substituents					electron poor substituents				
	H	NH ₂	OMe	Me	OH	iPr	F	CN	COOMe	COOEt
3	40%	57%		56%	51%			27%	50%	56%
4		70%	57%		32%		48%	24%	48%	
5		60%	58%		50%			27%		
6		64%	63%	65%	62%	55%	37%	32%		
7		60%	64%		49%			53%	33%	
8		63%			57%			45%	31%	

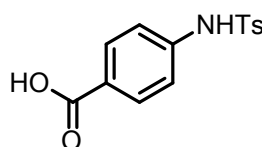
[a] NMR yields were using pyrazine as internal standard.

1.3 Preparation of N-Ts-Amine Derivatives

Substrates **3a-3b**^[1], **3c**^[2], **3e**^[3], **3f**^[4], **3g**^[5], **3h**^[1], **3i**^[6], **3j**^[7] were prepared according to general procedure (B), spectral data were in consistent with literature values.

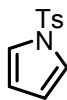
General procedure (B):

To a solution of the appropriate aniline (5.0 mmol, 1.0 eq) in pyridine (12 mL) was added p-toluenesulfonyl chloride (6.0 mmol, 1.2 eq) at 0 °C. Then the mixture was allowed to reach room temperature and stirred for 5-6 h. After the reaction was finished, pyridine was removed by rotary evaporator and the reaction mixture was poured into water. The resulting solution was extracted with CH₂Cl₂ (three times), then the combined organic phases were washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude material was purified by fresh silica gel chromatography (eluent: petroleum ether/EtOAc) to afford the desired product.

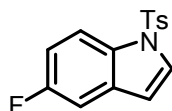


4-(4-methylphenyl)sulfonamido)benzoic acid (3d) was prepared according to Carretero's

procedure^[8], spectral data were in consistent with literature values.



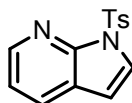
1-tosyl-1H-pyrrole (3k) was prepared according to Nicewicz's procedure^[9], spectral data were in consistent with literature values.^[10]



5-Fluoro-1-tosyl-1H-indole (3m) was prepared according to procedure (C), spectral data were in consistent with literature values.^[6]

Procedure (C):

To a solution of 5-Fluoro-1H-indole (5.0 mmol, 1.0 eq) in THF (12 mL) was added NaH (60% in mineral oil, 1.5 eq) at 0 °C. After the mixture was stirred for 10 min, p-toluenesulfonyl chloride (6.0 mmol, 1.2 eq) was added and the reaction was allowed to reach room temperature and stirred overnight. After the reaction was finished, a saturated aqueous solution of NH₄Cl was added to quench the reaction. The resulting solution was extracted with ethyl acetate, washed with brine, dried over anhydrous Na₂SO₄, and concentrated in vacuo. The crude material was purified by fresh silica gel chromatography (eluent: petroleum ether/EtOAc) to afford the desired product.



1-tosyl-1H-pyrrolo[2,3-*b*]pyridine (3l) was prepared according to procedure (C) using 7-Azaindole as starting material instead of 5-Fluoro-1H-indole, spectral data were in consistent with literature values.^[6]

1.4 General Procedure for Reductive Detosylation and Deoxygenation

General procedure (D):

To an oven-dried 2 mL vial charged with a magnetic stir bar was added N-Ts-Amine derivative substrate or fluorenyl substrate (0.2 mmol, 1.0 eq), B₂pin₂ (203.1 mg, 0.8 mmol, 4.0 eq), and 4-aminoisoquinoline (5.8 mg, 0.04 mmol, 20 mol%). The solid mixture was dissolved with 0.5 mL AcN, and then NEt₃ (139.0 μL, 1.0 mmol, 5.0 eq) was added. The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 36h. After completion, the solvent was removed by vacuum evaporation. NMR yield was determined by ¹H NMR using pyrazine as the internal standard. For deoxygenation reactions, the reaction mixture was further purified by fresh silica gel chromatography to afford the desired product.

1.5 Oxidant Screening of Aromatic C-H Bond Borylation

General procedure (E):

An oven-dried 2 mL vial was charged with a magnetic stir bar, in the solvent of *N*-methyl-*N*-phenylacetamide (29.8 mg, 0.2 mmol, 1.0 eq) in AcN (0.5 mL), different oxidants (1.1 eq), B₂pin₂ (203.1 mg, 0.8 mmol, 4.0 eq), NEt₃ (139.0 μL, 1.0 mmol, 5.0 eq), 4-aminoisoquinoline (5.8 mg, 0.04 mmol, 20 mol%) were added. 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 as the internal standard.

Table S2 Oxidant screening of aromatic C-H bond borylation



entry	oxidant (1.1 eq)	yield A (%) ^a	yield B (%) ^a
1	Oxone	0	<1
2	Selectfluoro	0	<1
3	(NH ₄) ₂ S ₂ O ₈	0	<1
4	CBr ₄	0	<1
5	Ph ₂ IOTf	0	<1
6	NCS	0	<2
7	NIS	0	<10
8	NBS	<1	28
9	NBS	<1 ^b	0 ^b

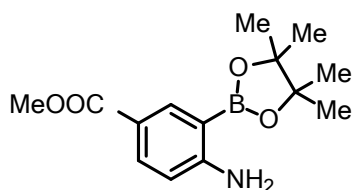
[a] Yields were determined by ¹H NMR using pyrazine as internal standard. [b] Without light.

1.6 Substrate Scope of Arenes and Characterization Data

General procedure (F):

An oven-dried 2 mL vial was charged with a magnetic stir bar, in the solvent of the according arenes (0.2 mmol, 1.0 eq) in AcN (0.5 mL), NBS (39.2 mg, 0.22 mmol, 1.1 eq), B₂pin₂ (203.1 mg, 0.8 mmol, 4.0 eq), NEt₃ (139.0 μL, 1.0 mmol, 5.0 eq) and 4-aminoisoquinoline (5.8 mg, 0.04 mmol, 20 mol%) were added. The vial was sealed with a plastic cap and then irradiated with 2*390 nm LEDs light for 36 h. After completion, the solvent was removed by vacuum evaporation. The reaction mixture was purified by fresh silica gel chromatography to afford the desired borylated product.

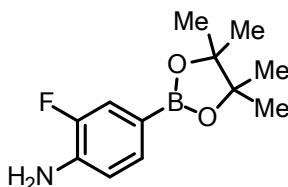
Methyl 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (2a)



Following general procedure (F), **2a** was obtained as white solid in 60% isolated yield from 4-(Methoxycarbonyl) aniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (d, $J = 2.2$ Hz, 1H), 7.87 (dd, $J = 8.6, 2.2$ Hz, 1H), 6.55 (d, $J = 8.6$ Hz, 1H), 3.84 (s, 3H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 167.40, 157.56, 139.64, 134.48, 118.12, 114.03, 83.92, 51.56, 24.97 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.94. The NMR data were in consistent with the reported data.^[11]

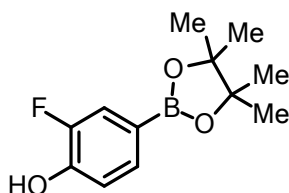
2-Fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**2b**)



Following general procedure (F), **2b** was obtained as pale-yellow solid in 74% isolated yield from 2-Fluoroaniline using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.44 – 7.34 (m, 2H), 6.76 (td, $J = 8.2, 1.8$ Hz, 1H), 1.32 (d, $J = 1.8$ Hz, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 151.25 (d, $J = 239.1$ Hz), 137.66 (d, $J = 12.6$ Hz), 131.64 (d, $J = 3.2$ Hz), 121.13 (d, $J = 16.5$ Hz), 116.09 (d, $J = 3.1$ Hz), 83.73, 24.97 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.18. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -137.19 (t, $J = 10.2$ Hz). The NMR data were in consistent with the reported data.^[12]

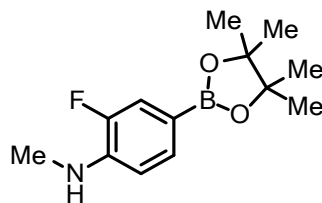
2-fluoro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenol (**2c**)



Following general procedure (F), **2c** was obtained as white solid in 34% isolated yield from 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). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 151.72, 150.14, 146.57 (d, $J = 14.2$ Hz), 131.94 (d, $J = 3.5$ Hz), 121.55 (d, $J = 16.1$ Hz), 117.04, 84.06, 24.92. $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.00. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -141.94 (dd, $J = 11.0, 8.4$ Hz). The NMR data were in consistent with the reported data.^[13]

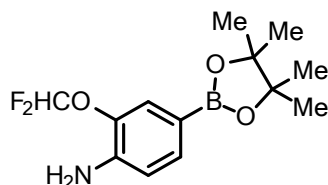
2-Fluoro-*N*-methyl-4-(tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**2d**)



Following general procedure (F), **2d** was obtained as colourless solid in 68% isolated yield from 2-Fluoro-*N*-methylaniline using 40:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.48 (dd, J = 7.8, 1.3 Hz, 1H), 7.37 (dd, J = 12.2, 1.3 Hz, 1H), 6.66 (t, J = 8.2 Hz, 1H), 2.90 (s, 3H), 1.32 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 151.20 (d, J = 239.1 Hz), 140.40, 132.13 (d, J = 3.0 Hz), 119.78 (d, J = 16.2 Hz), 110.79, 83.63, 30.11, 24.97 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (193 MHz, CDCl₃) δ 30.84. ¹⁹F NMR (377 MHz, CDCl₃) δ -139.06. The NMR data were in consistent with the reported data.^[14]

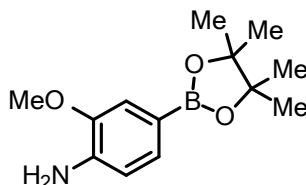
2-(difluoromethoxy)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- aniline (2e)



Following general procedure (F), **2e** was obtained as colourless crystal in 66% isolated yield from 2-(Difluoromethoxy) aniline using 20:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, J = 7.9, 1.3 Hz, 1H), 7.42 (d, J = 1.3 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 6.50 (t, J = 74.5 Hz, 1H), 1.32 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 141.69, 138.34, 133.54, 125.84, 117.14 (t, J = 258.9 Hz), 115.70, 83.78, 24.97 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (128 MHz, CDCl₃) δ 35.04. ¹⁹F NMR (377 MHz, CDCl₃) δ -79.18 (d, J = 74.7 Hz). The NMR data were in consistent with the reported data.^[15]

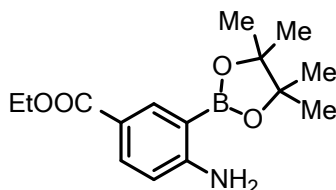
2-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (2f)



Following general procedure (F), **2f** was obtained as white solid in 50% isolated yield from 2-Aminomethoxybenzene using 10:1 petroleum ether/EtOAc as eluent.

¹H NMR (600 MHz, CDCl₃) δ 7.29 (d, J = 7.7 Hz, 1H), 7.20 (s, 1H), 6.70 (d, J = 7.7 Hz, 1H), 3.89 (s, 3H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 146.59, 139.56, 128.97, 115.96, 114.17, 83.48, 55.66, 24.98 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (193 MHz, CDCl₃) δ 31.16. The NMR data were in consistent with the reported data.^[16]

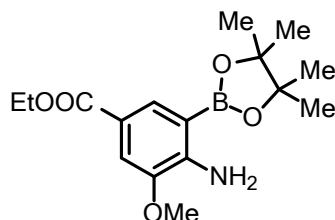
Ethyl 4-amino-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (2g)



Following general procedure (F), **2g** was obtained as colourless oil in 75% isolated yield from 4-(Ethoxycarbonyl) aniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.31 (d, $J = 2.2$ Hz, 1H), 7.88 (dd, $J = 8.6, 2.2$ Hz, 1H), 6.55 (d, $J = 8.6$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.37 (d, $J = 7.1$ Hz, 3H), 1.34 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.93, 157.46, 139.62, 134.53, 118.77, 114.04, 83.98, 60.32, 25.06, 14.65 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 32.31. **HRMS** calculated for $\text{C}_{15}\text{H}_{22}\text{BNO}_4$ ($M + \text{H}^+$): 292.1715, found: 292.1735.

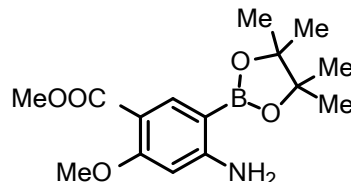
ethyl 4-amino-3-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (2h)



Following general procedure (F), **2h** was obtained as white solid in 55% isolated yield from ethyl 4-amino-3-methoxybenzoate using 8:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.98 (d, $J = 1.8$ Hz, 1H), 7.46 (d, $J = 1.9$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.89 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 167.22, 148.34, 145.69, 131.47, 117.97, 112.97, 83.93, 60.44, 55.77, 25.05, 14.70 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 31.05. **HRMS** calculated for $\text{C}_{16}\text{H}_{24}\text{BNO}_5$ ($M + \text{H}^+$): 322.1820, found: 322.1837.

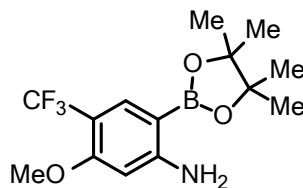
methyl 4-amino-2-methoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzoate (2i)



Following general procedure (F), **2i** was obtained as white solid in 62% isolated yield from 4-amino-2-methoxyphenyl acetate using 8:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.19 (s, 1H), 6.06 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 1.32 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 166.16, 164.09, 158.87, 142.81, 134.35, 96.70, 83.74, 55.77, 51.44, 25.02 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 31.02. **HRMS** calculated for $\text{C}_{15}\text{H}_{22}\text{BNO}_5$ ($M + \text{H}^+$): 308.1664, found: 308.1679.

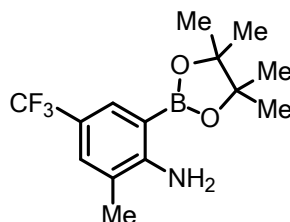
5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl) aniline (2j)



Following general procedure (F), **2j** was obtained as colourless crystal in 60% isolated yield from 3-methoxy-4-(trifluoromethyl) aniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.78 (s, 1H), 6.11 (s, 1H), 3.84 (s, 3H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 161.43, 158.37, 136.59 (d, $J = 5.1$ Hz), 124.55 (d, $J = 270.6$ Hz), 108.20 (d, $J = 31.2$ Hz), 97.14, 83.81, 55.65, 25.02 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 30.65. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -60.54. **HRMS** calculated for $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{NO}_3$ ($\text{M} + \text{H}^+$): 318.1483, found: 318.1498.

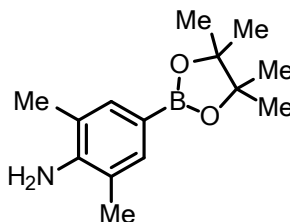
2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl) aniline (**2k**)



Following general procedure (F), **2k** was obtained as colourless crystal in 61% isolated yield from 2-methyl-4-(trifluoromethyl) aniline using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.76 (s, 1H), 7.33 (s, 1H), 2.16 (s, 3H), 1.35 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 154.49, 132.15 (d, $J = 3.9$ Hz), 130.20 (d, $J = 3.6$ Hz), 125.18 (d, $J = 270.5$ Hz), 121.25, 118.53 (d, $J = 32.3$ Hz), 84.12, 25.04, 17.61 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (128 MHz, CDCl_3) δ 31.47. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -60.99. **HRMS** calculated for $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{NO}_2$ ($\text{M} + \text{H}^+$): 302.1534, found: 302.1551.

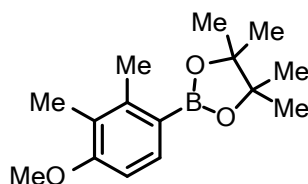
2,6-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) aniline (**2l**)



Following general procedure (F), **2l** was obtained as colourless crystal in 52% isolated yield from 2,6-dimethylaniline using 10:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.42 (s, 2H), 3.79 (s, 2H), 2.18 (s, 6H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 146.06, 135.27, 120.78, 83.37, 24.97, 17.40 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 32.63. The NMR data were in consistent with the reported data.^[17]

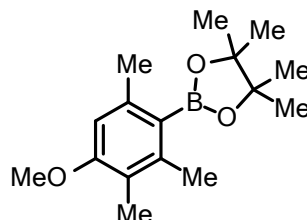
2-(4-methoxy-2,3-dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2m**)



Following general procedure (F), **2m** was obtained as colourless crystal in 82% isolated yield from ethyl 1-methoxy-2,3-dimethylbenzene using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.63 (d, $J = 8.3$ Hz, 1H), 6.71 (d, $J = 8.3$ Hz, 1H), 3.82 (s, 3H), 2.49 (s, 3H), 2.14 (s, 3H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 159.80, 144.95, 134.88, 125.12, 107.15, 83.28, 55.52, 25.00, 18.84, 11.67 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 32.24. **HRMS** calculated for $\text{C}_{15}\text{H}_{23}\text{BO}_3$ ($\text{M} + \text{H}^+$): 263.1813, found: 263.1831.

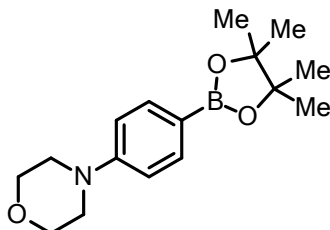
2-(4-methoxy-2,3,6-trimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)



Following general procedure (F), **2n** was obtained as colourless crystal in 36% isolated yield from 1-methoxy-2,3,5-trimethylbenzene using 80:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 6.51 (s, 1H), 3.78 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H), 1.38 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 158.36, 141.64, 140.21, 121.78, 109.57, 83.57, 55.50, 25.13, 22.55, 19.80, 11.32 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 32.35. **HRMS** calculated for $\text{C}_{16}\text{H}_{25}\text{BO}_3$ ($\text{M} + \text{H}^+$): 277.1970, found: 277.1979.

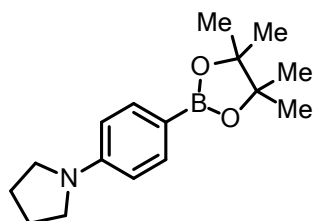
4-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl] morpholine (2o)



Following general procedure (F), **2o** was obtained as colourless crystal in 60% isolated yield from *N*-Phenylmorpholine using 40:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.72 (d, $J = 8.3$ Hz, 2H), 6.88 (d, $J = 8.3$ Hz, 2H), 3.87 – 3.83 (m, 4H), 3.24 – 3.20 (m, 4H), 1.33 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 153.48, 136.29, 114.23, 83.54, 66.90, 48.52, 24.97 (signal for the carbon that is attached to the boron atom was not observed). $^{11}\text{B NMR}$ (193 MHz, CDCl_3) δ 30.84. The NMR data were in consistent with the reported data.^[18]

1-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl] pyrrolidine (2p)

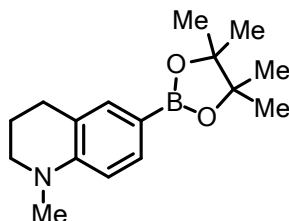


Following general procedure (F), **2p** was obtained as colourless crystal in 43% isolated yield from *N*-Phenylpyrrolidine using 60:1 petroleum ether/EtOAc as eluent.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.67 (d, $J = 8.6$ Hz, 2H), 6.55 (d, $J = 8.1$ Hz, 2H), 3.35 – 3.28 (m, 4H), 2.03 – 1.97 (m, 4H), 1.32 (s, 12H). $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 150.04, 136.37, 111.22, 83.23,

47.69, 25.56, 24.98(signal for the carbon that is attached to the boron atom was not observed). ^{11}B NMR (193 MHz, CDCl_3) δ 31.68. The NMR data were in consistent with the reported data.^[19]

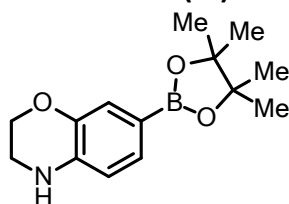
1-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,2,3,4-tetrahydroquinoline (2q)



Following general procedure (F), **2q** was obtained as white solid in 40% isolated yield from 1-methyl-1,2,3,4-tetrahydroquinoline using 60:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (dd, J = 8.2, 1.6 Hz, 1H), 7.40 (d, J = 1.6 Hz, 1H), 6.55 (d, J = 8.2 Hz, 1H), 3.30 – 3.23 (m, 2H), 2.91 (s, 3H), 2.76 (t, J = 6.4 Hz, 2H), 2.00 – 1.91 (m, 2H), 1.32 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 149.18, 135.43, 134.58, 121.75, 109.98, 83.23, 51.35, 38.90, 27.77, 24.97, 22.40(signal for the carbon that is attached to the boron atom was not observed). ^{11}B NMR (193 MHz, CDCl_3) δ 31.12. The NMR data were in consistent with the reported data.^[20]

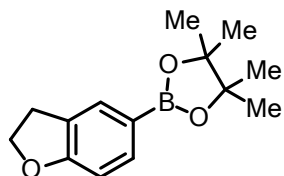
7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,4-dihydro-2H-benzo[b][1,4]oxazine (2r)



Following general procedure (F), **2r** was obtained as colourless solid in 41% isolated yield from 3,4-dihydro-2H-benzo[b][1,4]oxazine using 40:1 petroleum ether/EtOAc as eluent.

^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.19 (m, 2H), 6.56 (d, J = 8.1 Hz, 1H), 4.24 – 4.19 (m, 2H), 3.94 (s, 1H), 3.44 (dd, J = 5.3, 3.5 Hz, 2H), 1.31 (s, 12H). ^{13}C NMR (151 MHz, CDCl_3) δ 143.42, 136.86, 128.69, 123.08, 114.62, 83.45, 64.94, 41.11, 24.97(signal for the carbon that is attached to the boron atom was not observed). ^{11}B NMR (193 MHz, CDCl_3) δ 30.57. The NMR data were in consistent with the reported data.^[21]

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

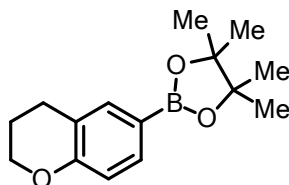


Following general procedure (F), **2s** was obtained as colourless liquid in 90% isolated yield from 2,3-dihydrobenzofuran using 60:1 petroleum ether/EtOAc as eluent.

^1H NMR (600 MHz, CDCl_3) δ 7.66 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 4.57 (t, J = 8.7 Hz, 2H), 3.19 (t, J = 8.7 Hz, 2H), 1.33 (s, 12H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.01, 135.71, 131.66, 126.65, 109.14, 83.64, 71.49, 29.35, 25.00(signal for the carbon that is attached to the boron atom was not observed). ^{11}B NMR (128 MHz, CDCl_3) δ 31.50. The NMR data were in consistent with

the reported data.^[22]

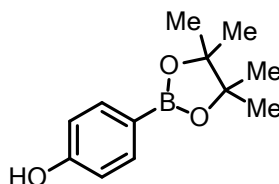
2-(chroman-6-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t)



Following general procedure (F), **2t** was obtained as colourless solid in 79% isolated yield from chromane using 40:1 petroleum ether/EtOAc as eluent.

¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, J = 8.6 Hz, 1H), 7.52 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 4.22 – 4.17 (m, 2H), 2.79 (t, J = 6.5 Hz, 2H), 2.02 – 1.97 (m, 2H), 1.33 (s, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 157.86, 137.02, 134.19, 121.77, 116.39, 83.63, 66.81, 24.98, 24.83, 22.46 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (193 MHz, CDCl₃) δ 33.26. HRMS calculated for C₁₅H₂₁BO₃ (M + H⁺): 261.1657, found: 261.1664.

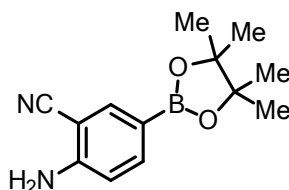
4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenol (2u)



Following general procedure (F), **2u** was obtained as white solid in 68% isolated yield from phenoxyacetone using 10:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.72 (s, 1H), 1.34 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 158.74, 136.89, 115.01, 83.81, 24.95 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (128 MHz, CDCl₃) δ 31.60. The NMR data were in consistent with the reported data.^[23]

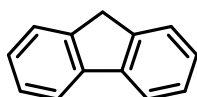
2-amino-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzonitrile (2v)



Following general procedure (F), **2v** was obtained as white solid in 65% isolated yield from N-tosyl-2-aminobenzonitrile using 20:1 petroleum ether/EtOAc as eluent.

¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, J = 1.5 Hz, 1H), 7.72 (dd, J = 8.3, 1.5 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 4.57 (s, 2H), 1.32 (s, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 151.65, 140.12 (d, J = 36.7 Hz), 117.54, 114.27, 95.93, 84.04, 24.98 (signal for the carbon that is attached to the boron atom was not observed). ¹¹B NMR (193 MHz, CDCl₃) δ 30.82. The NMR data were in consistent with the reported data.^[15]

9H-fluorene (4n)



Following general procedure (D), **4n** was obtained as white solid in either 75% isolated yield from 9-fluorenone, or 79% isolated yield from 9-fluorenone, using petroleum ether as eluent.

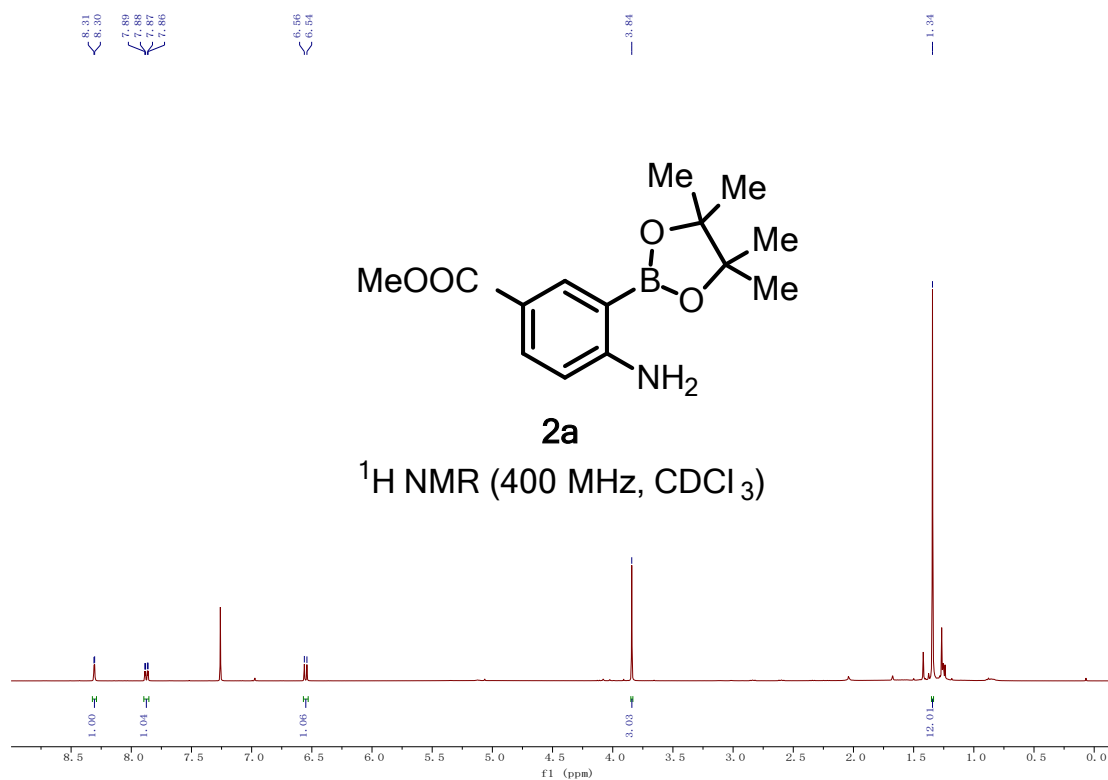
¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J = 7.5 Hz, 2H), 7.60 (d, J = 7.4 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.35 (td, J = 7.4, 1.3 Hz, 2H), 3.95 (s, 2H). The NMR data were in consistent with the reported data.^[24]

1.7 References

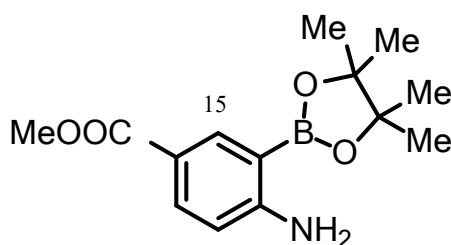
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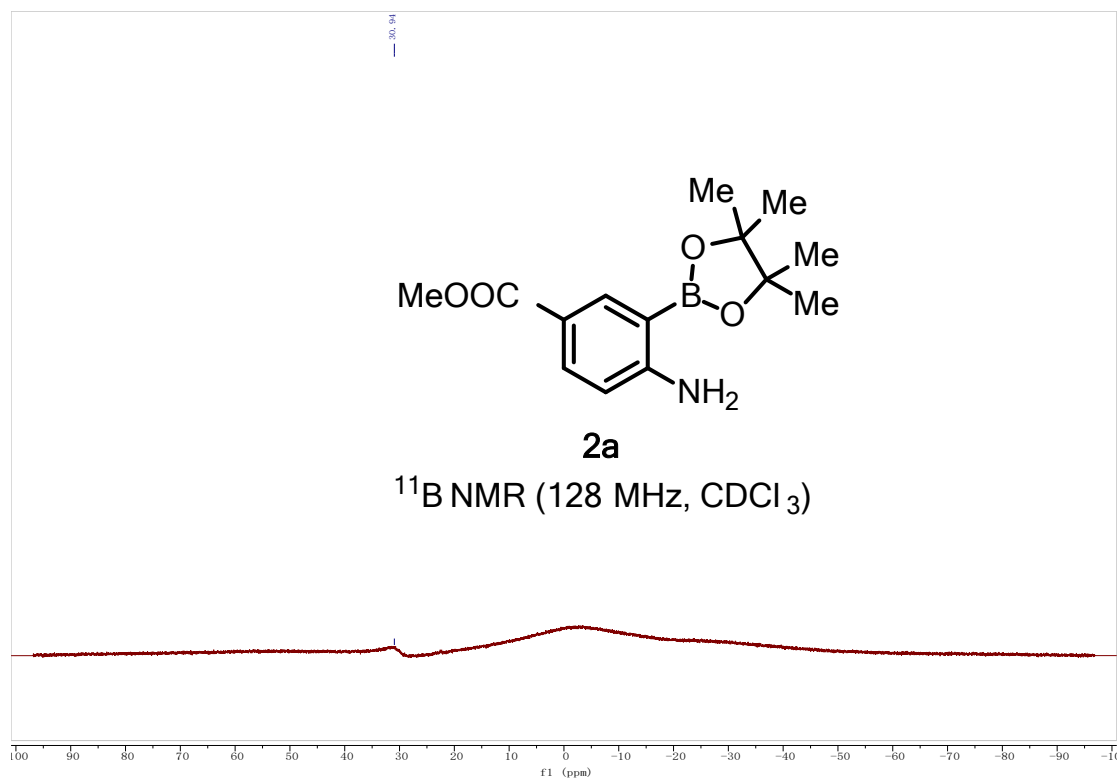
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1.8 NMR Spectroscopic Data



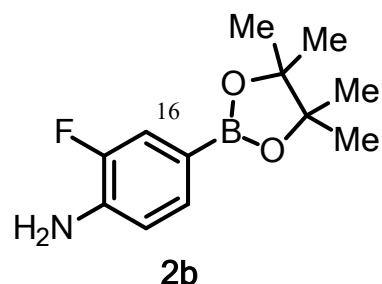
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23.50

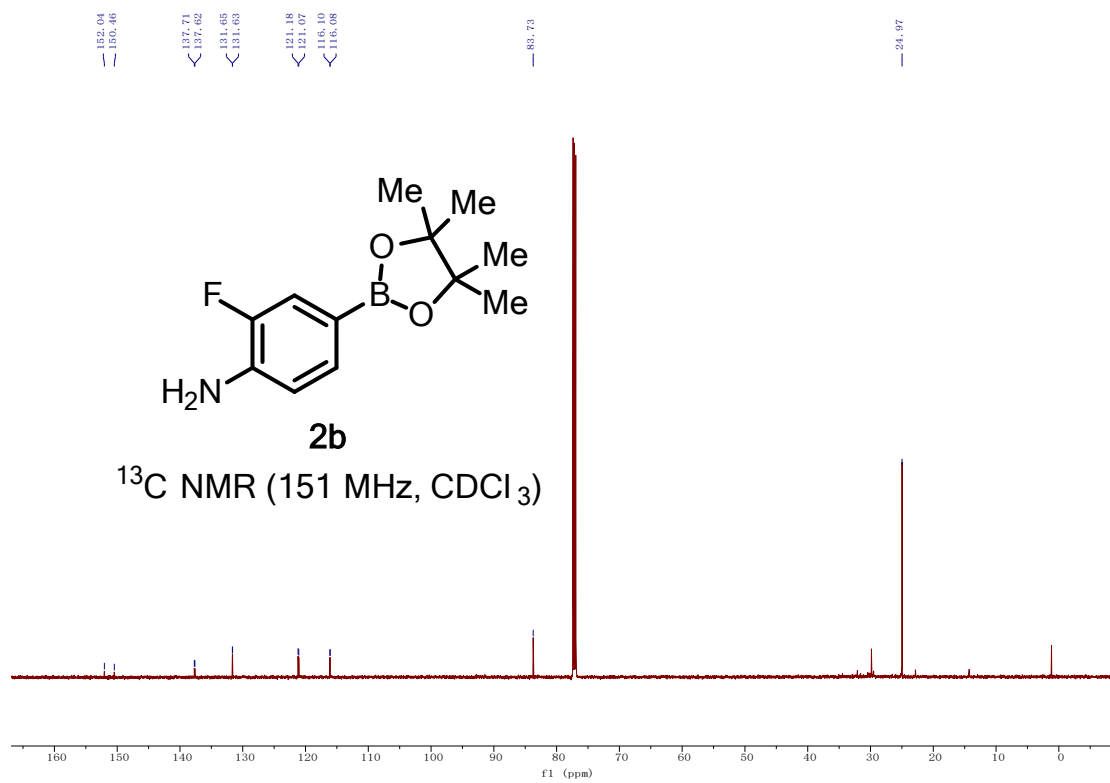


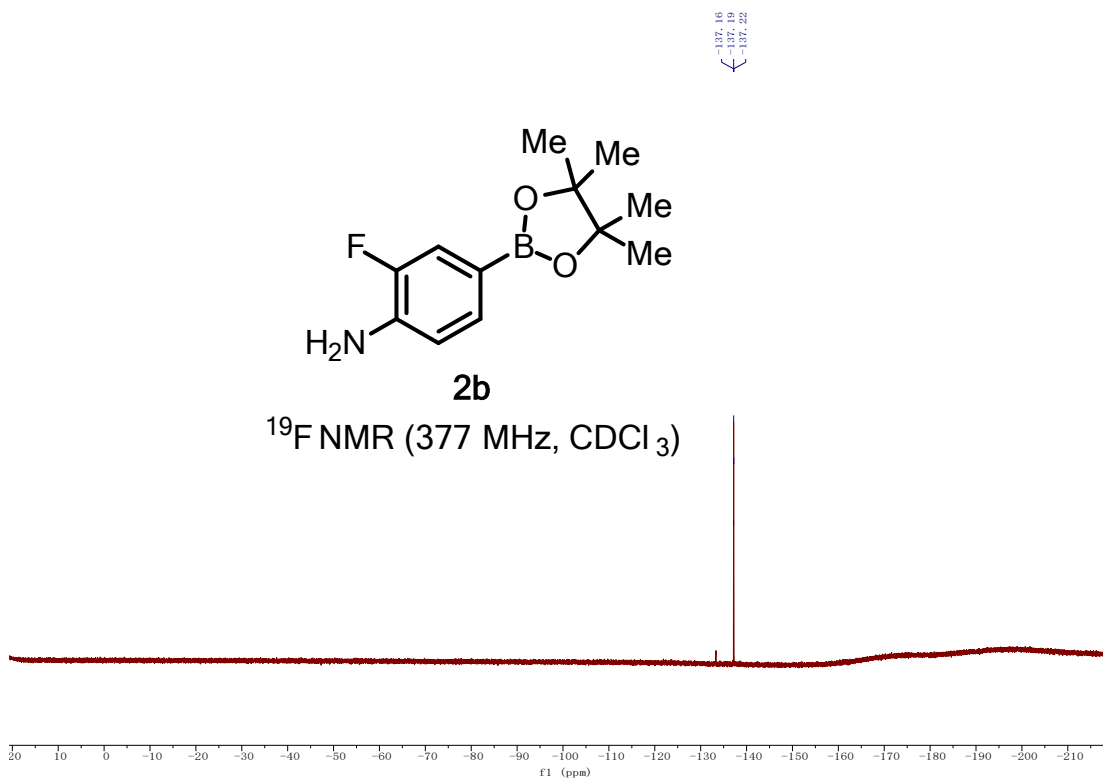
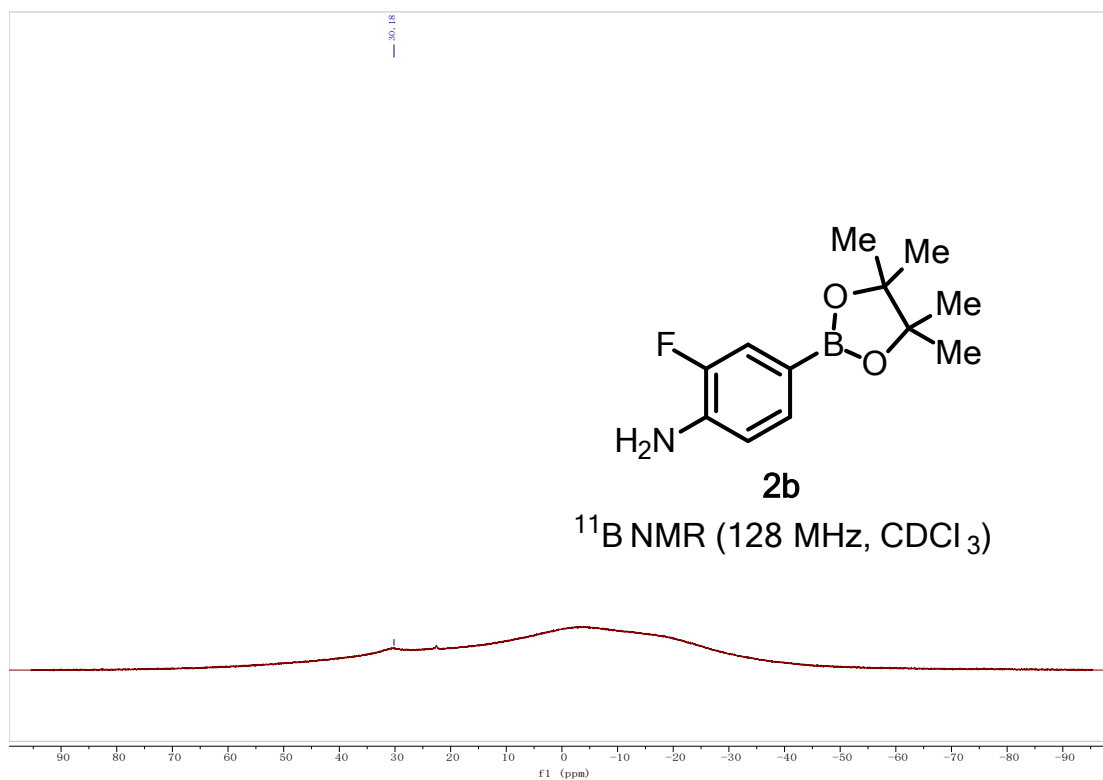


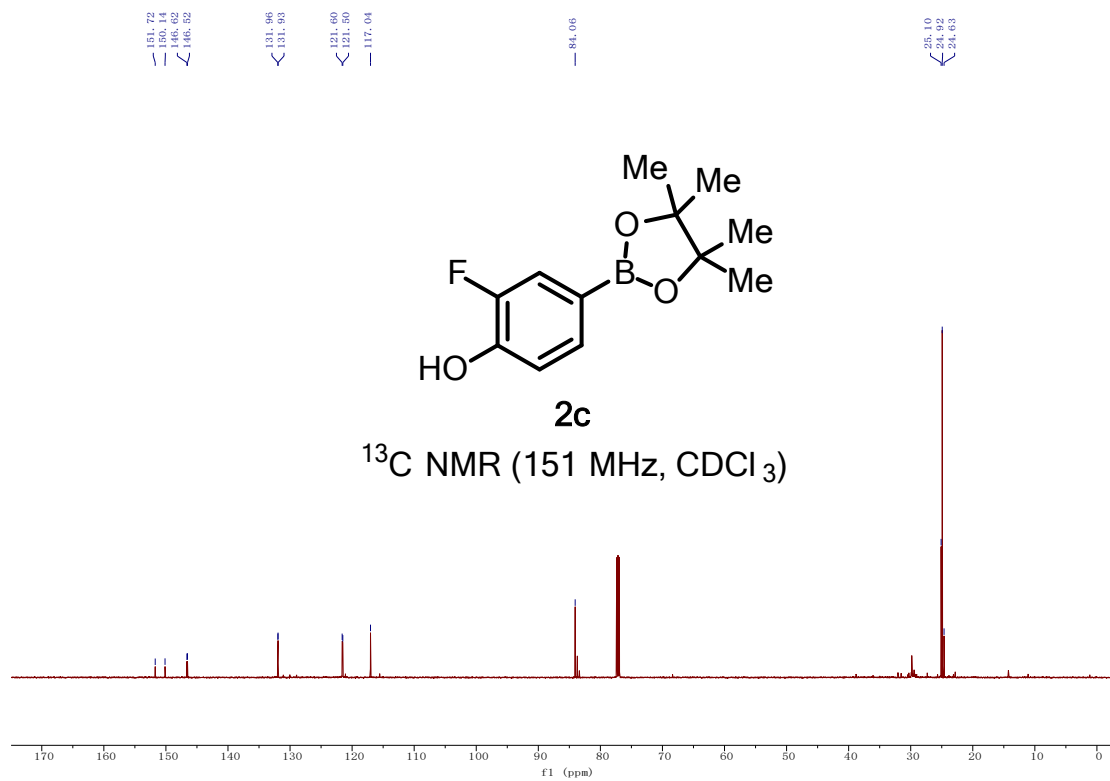
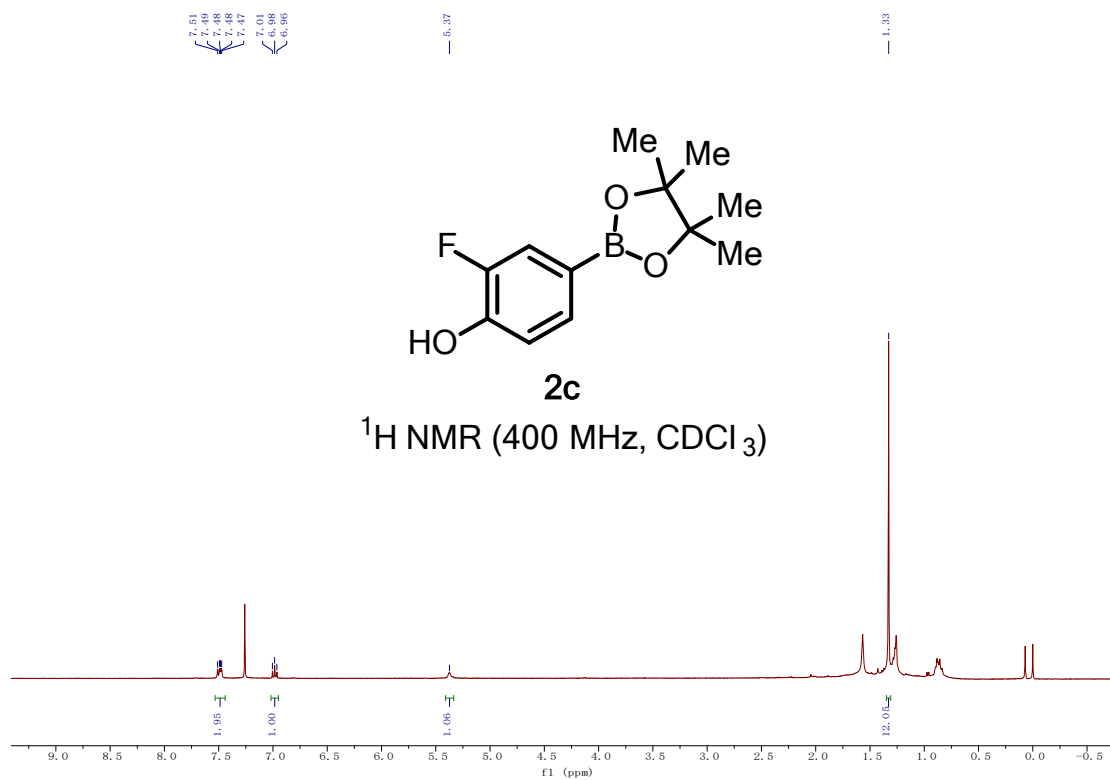
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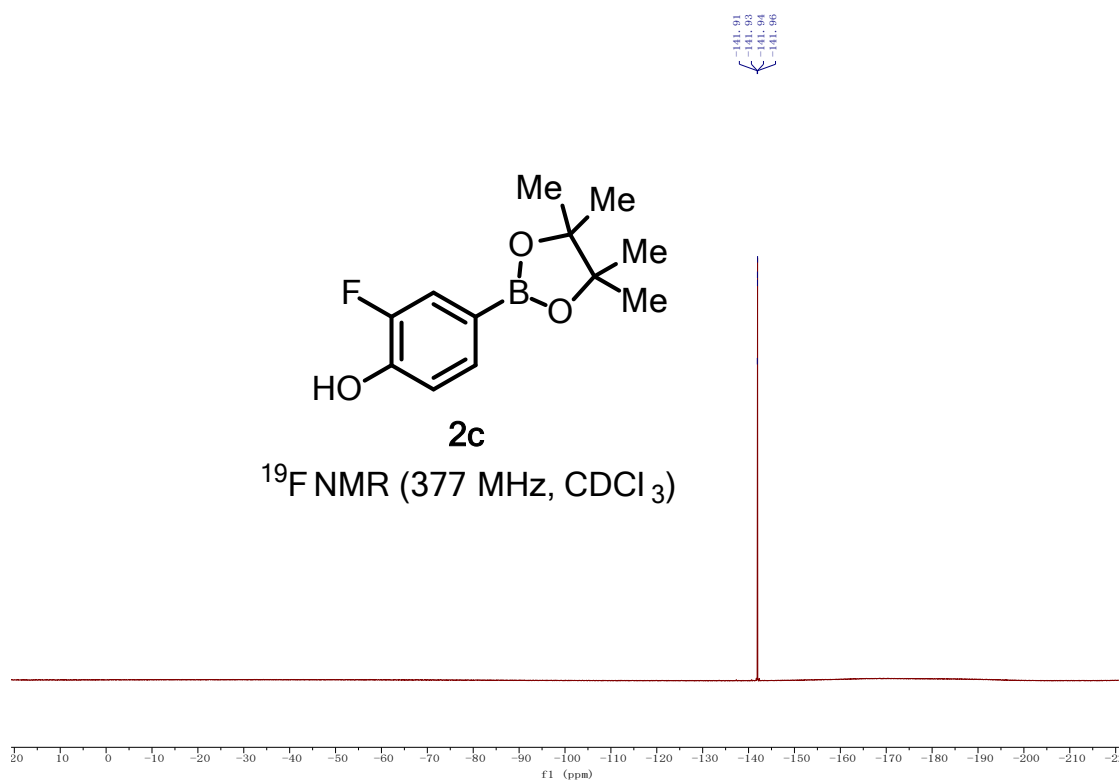
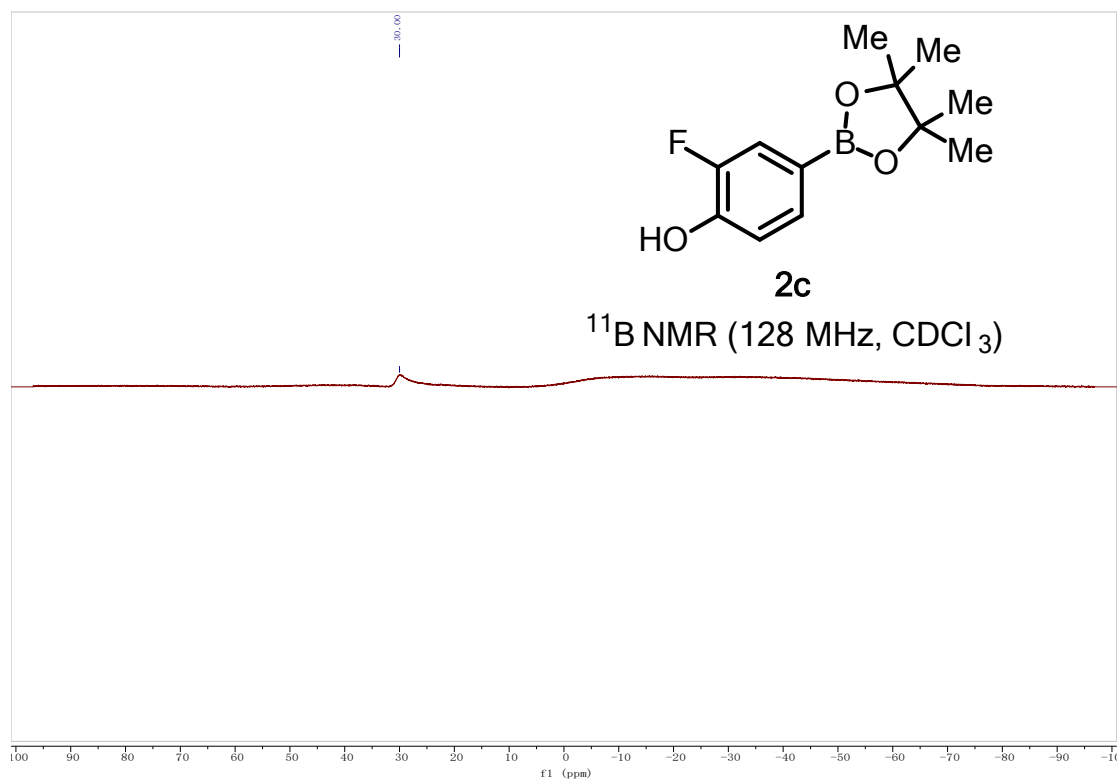
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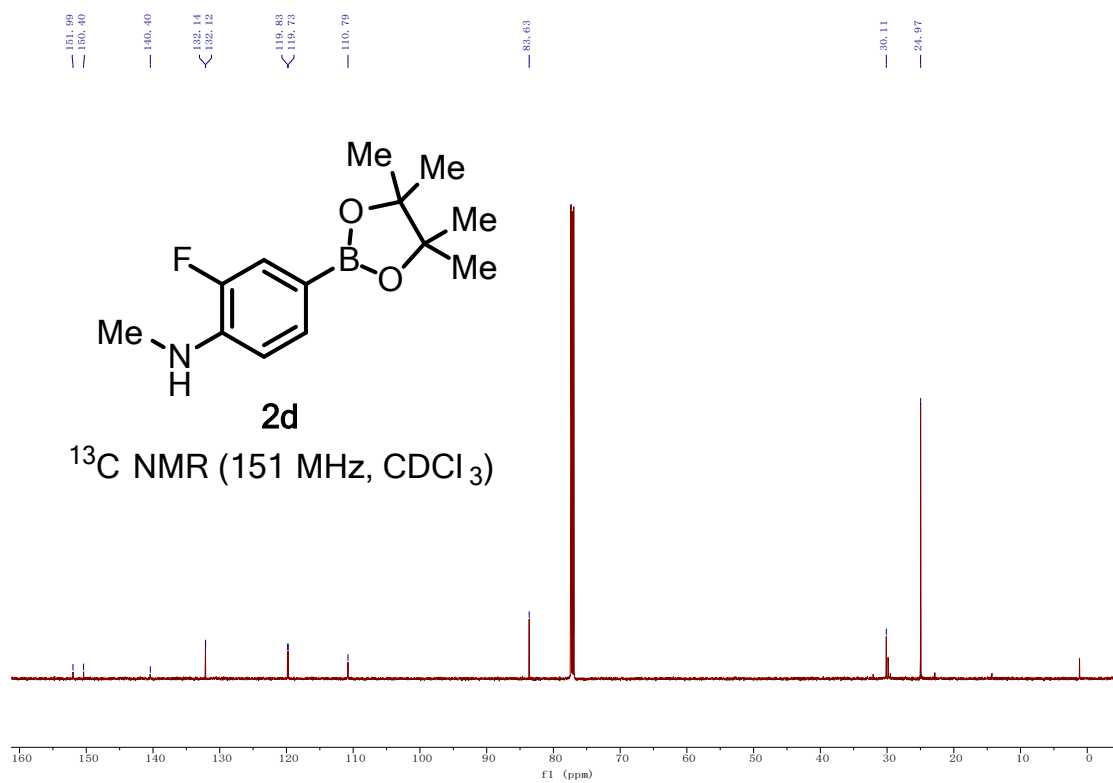
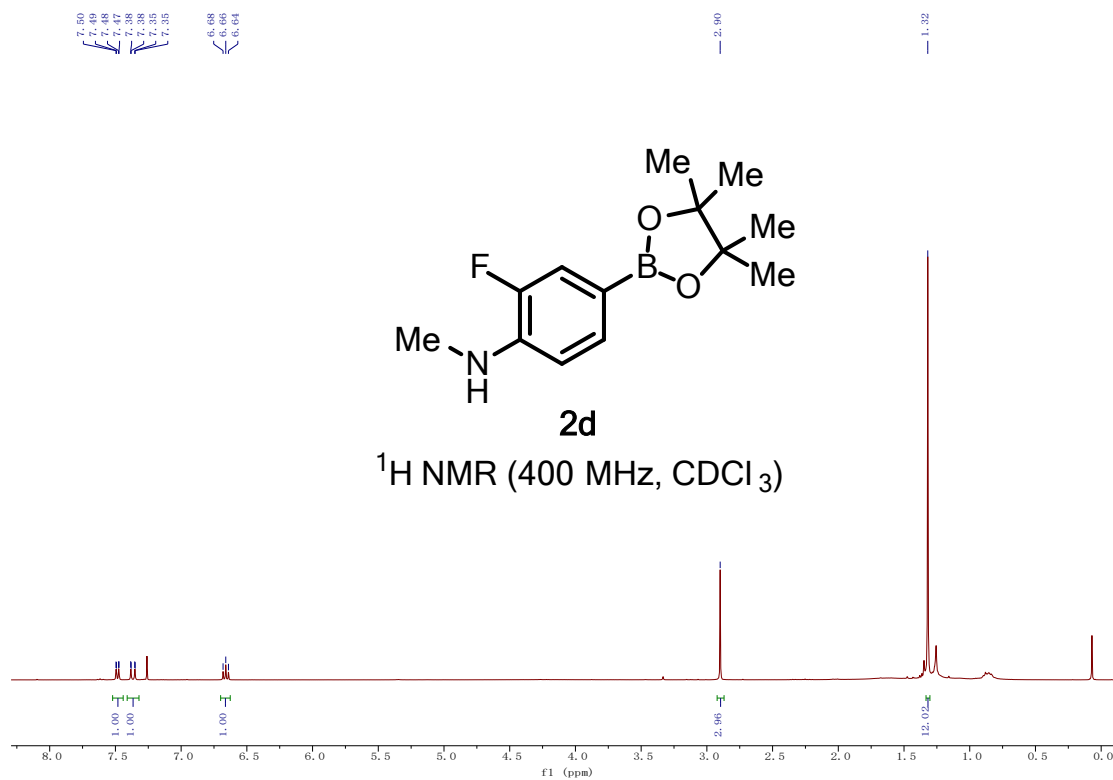




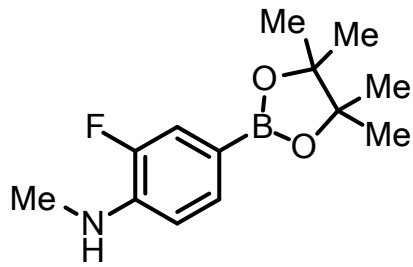






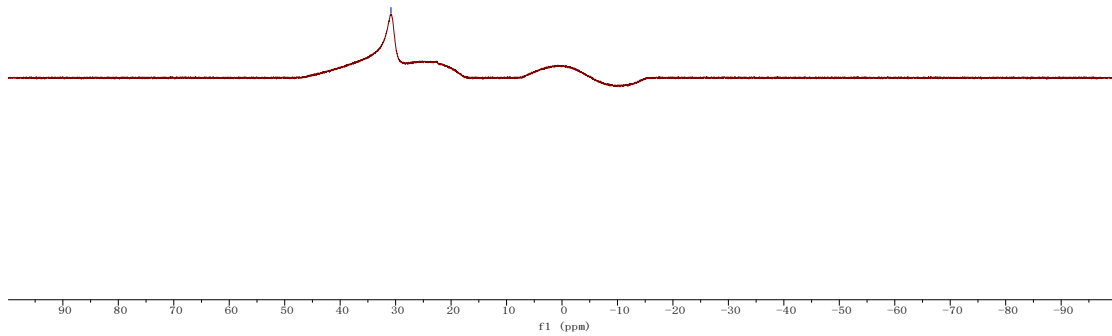


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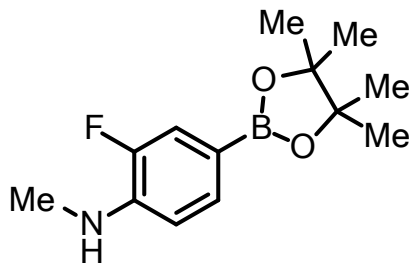


2d

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

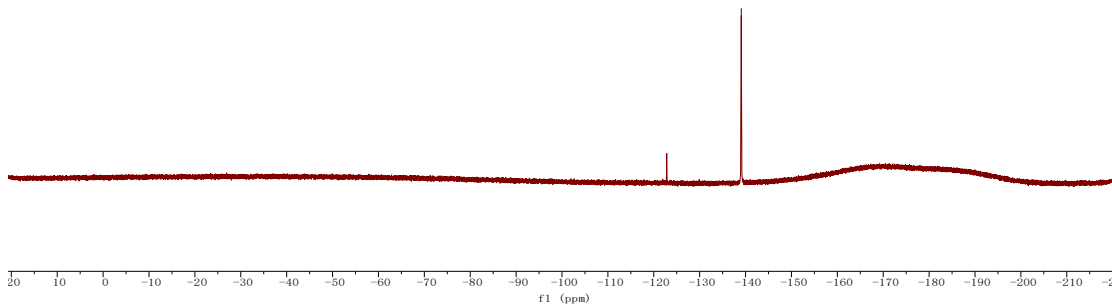


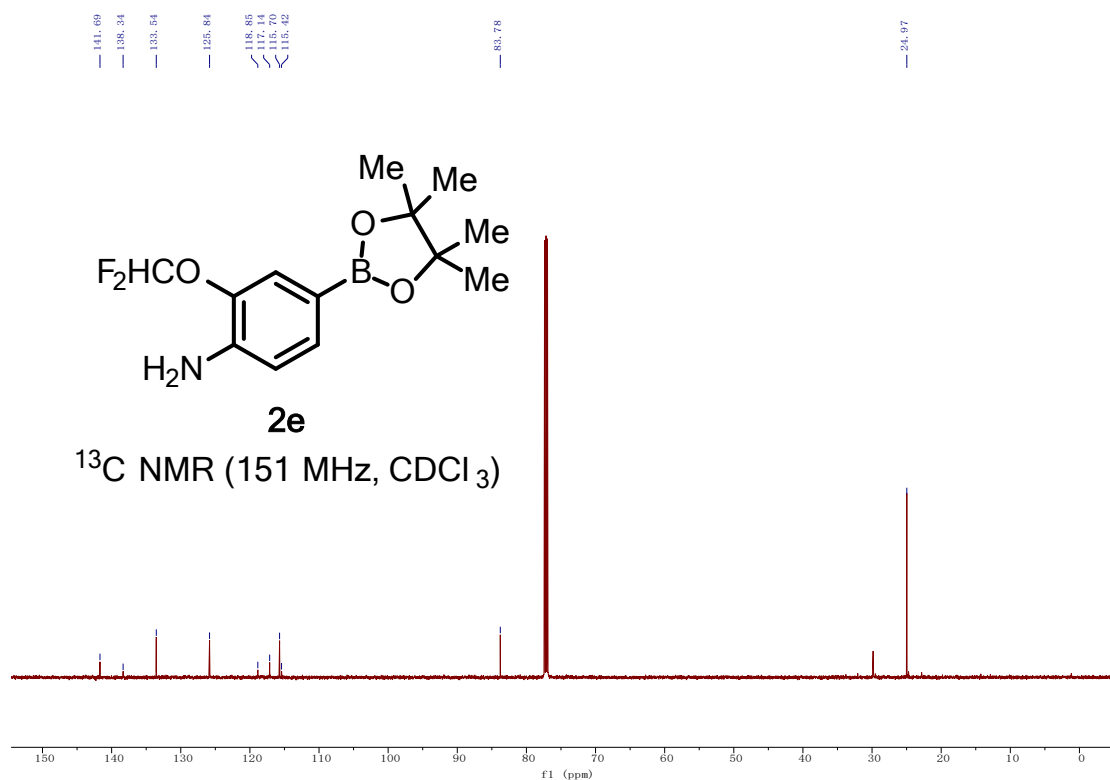
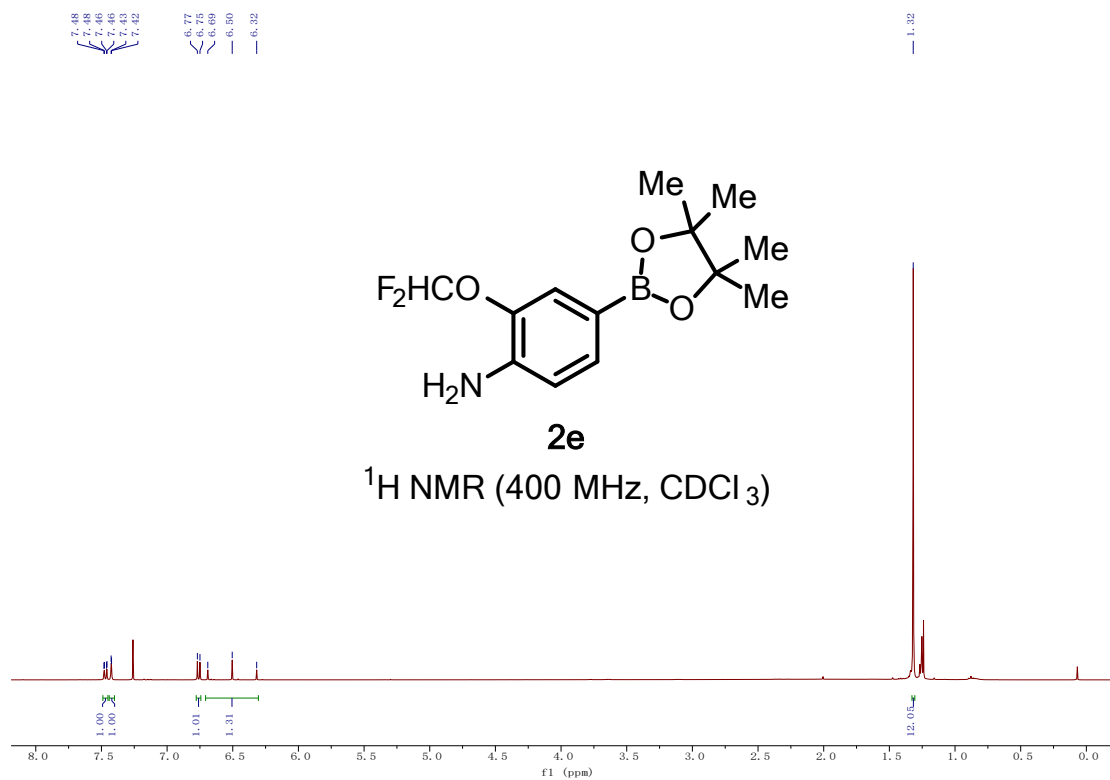
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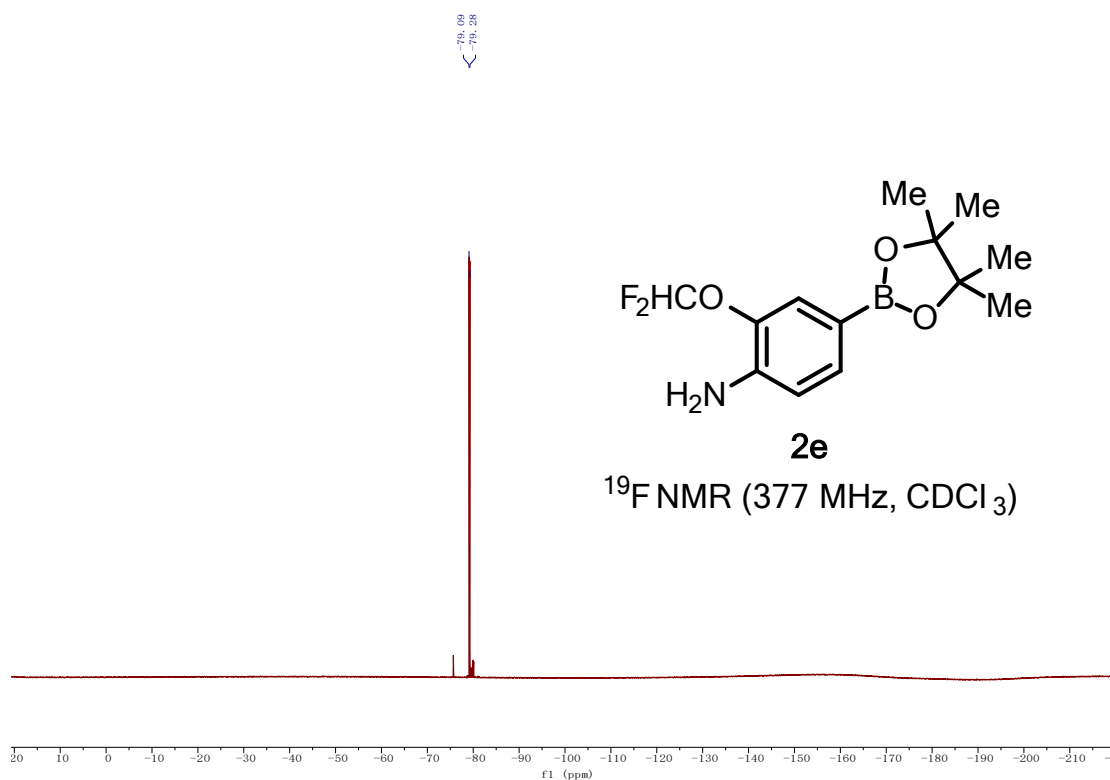
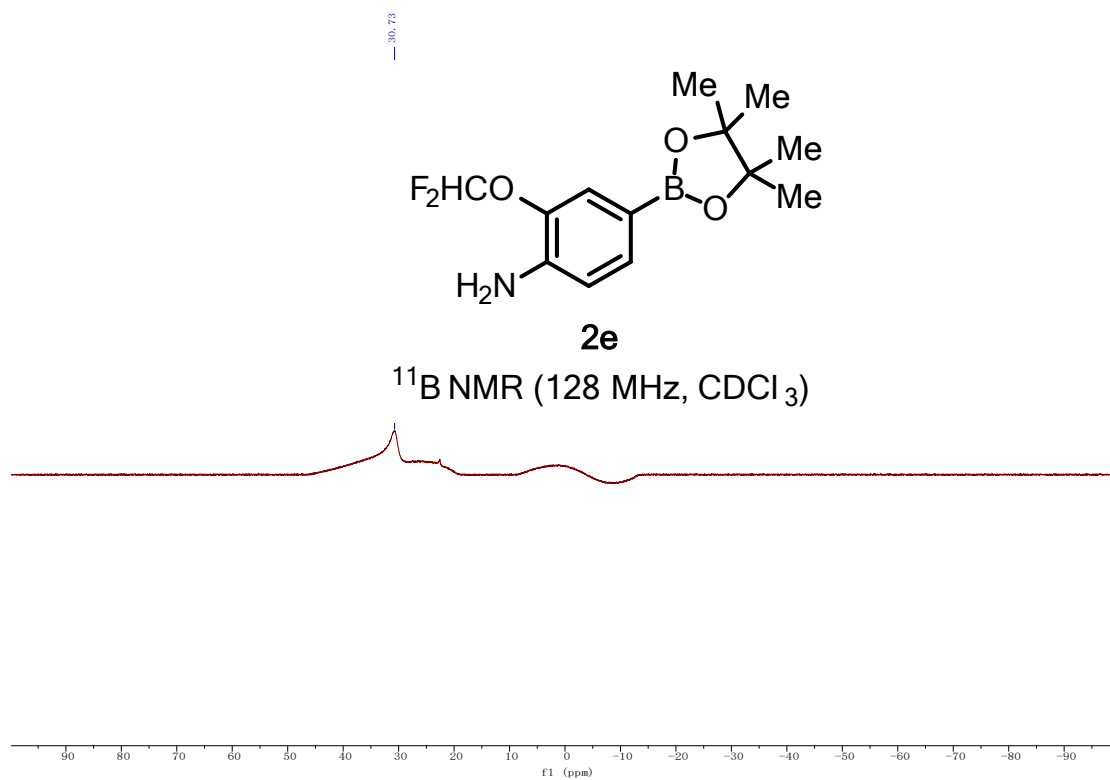


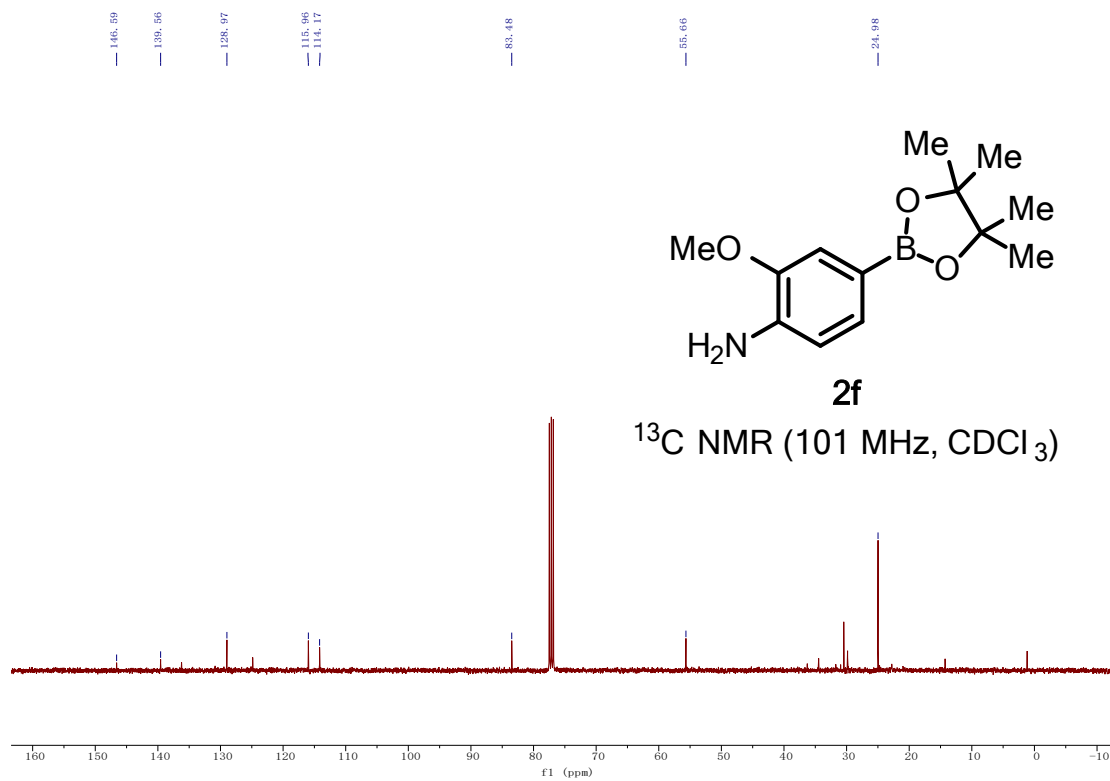
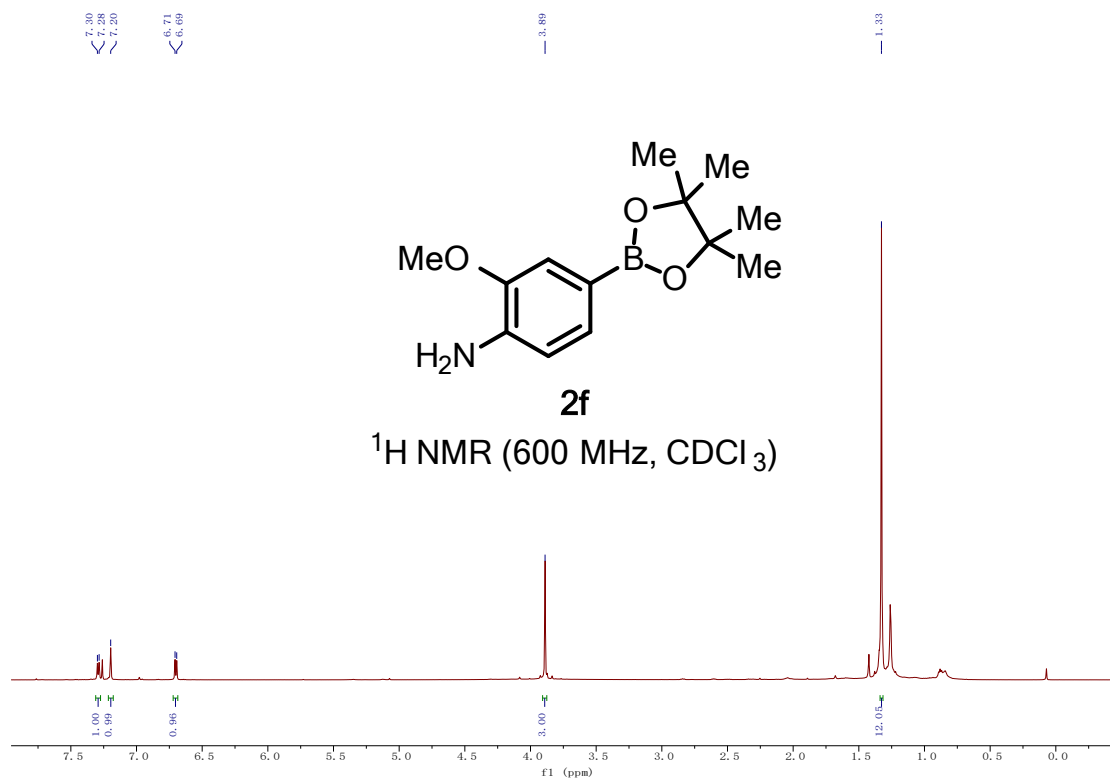
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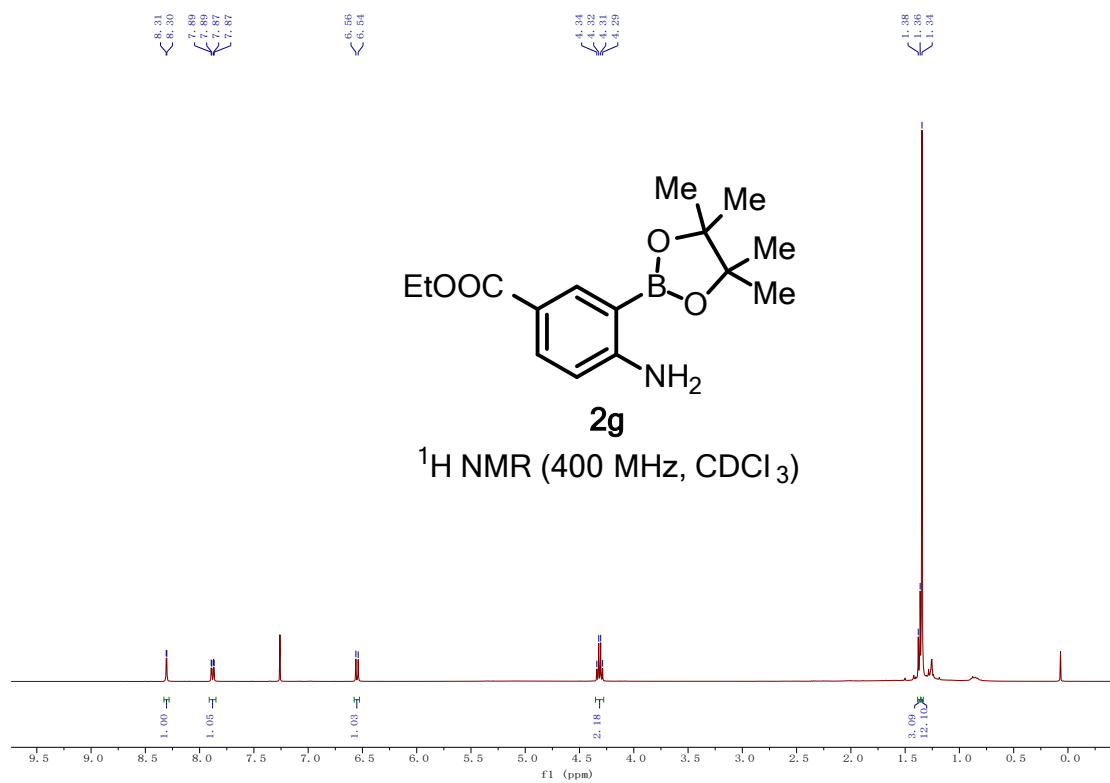
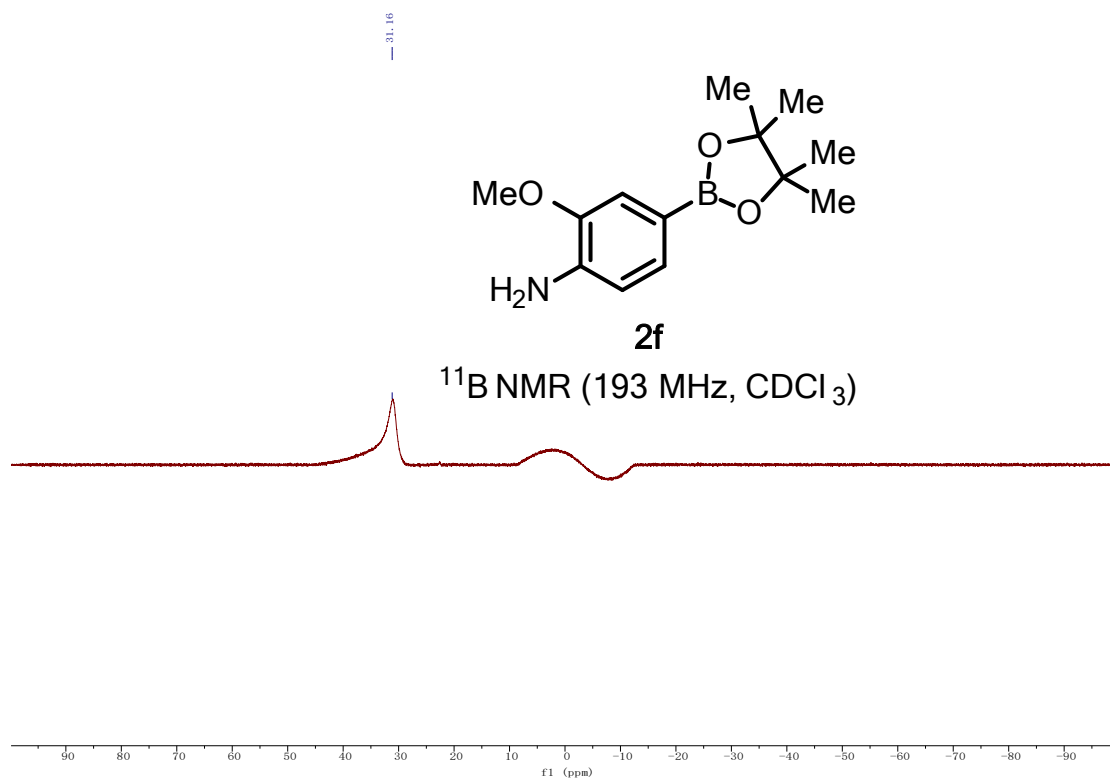
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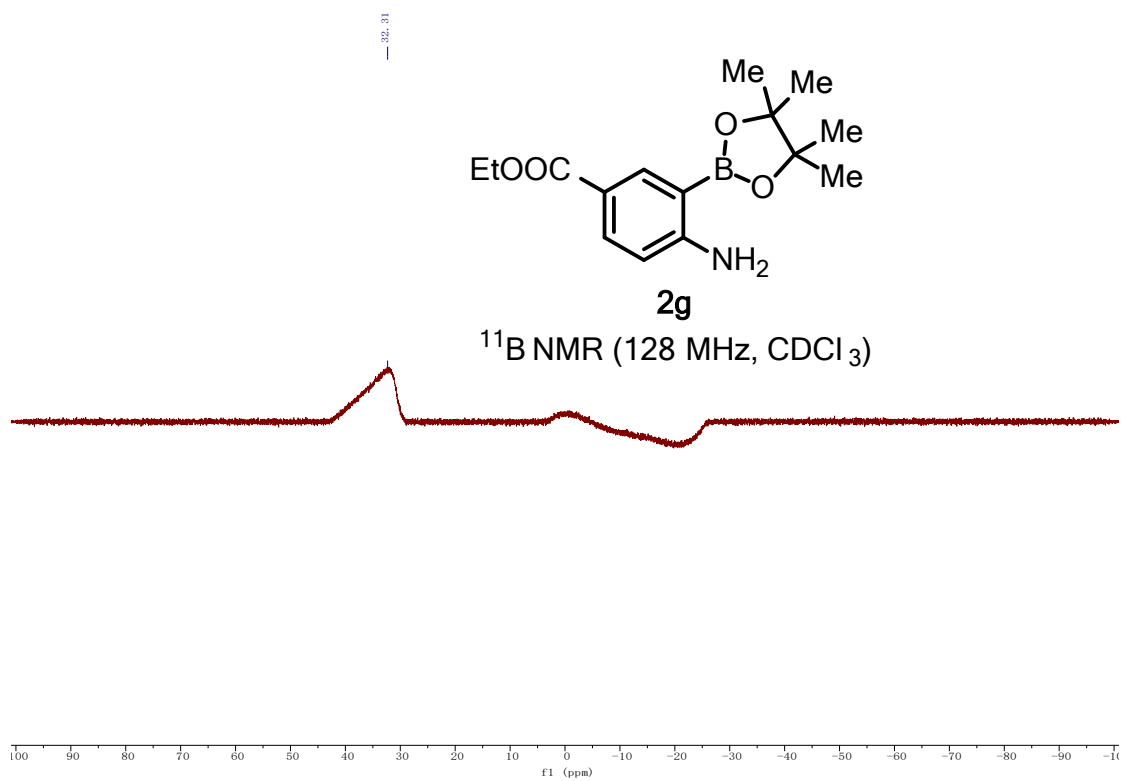
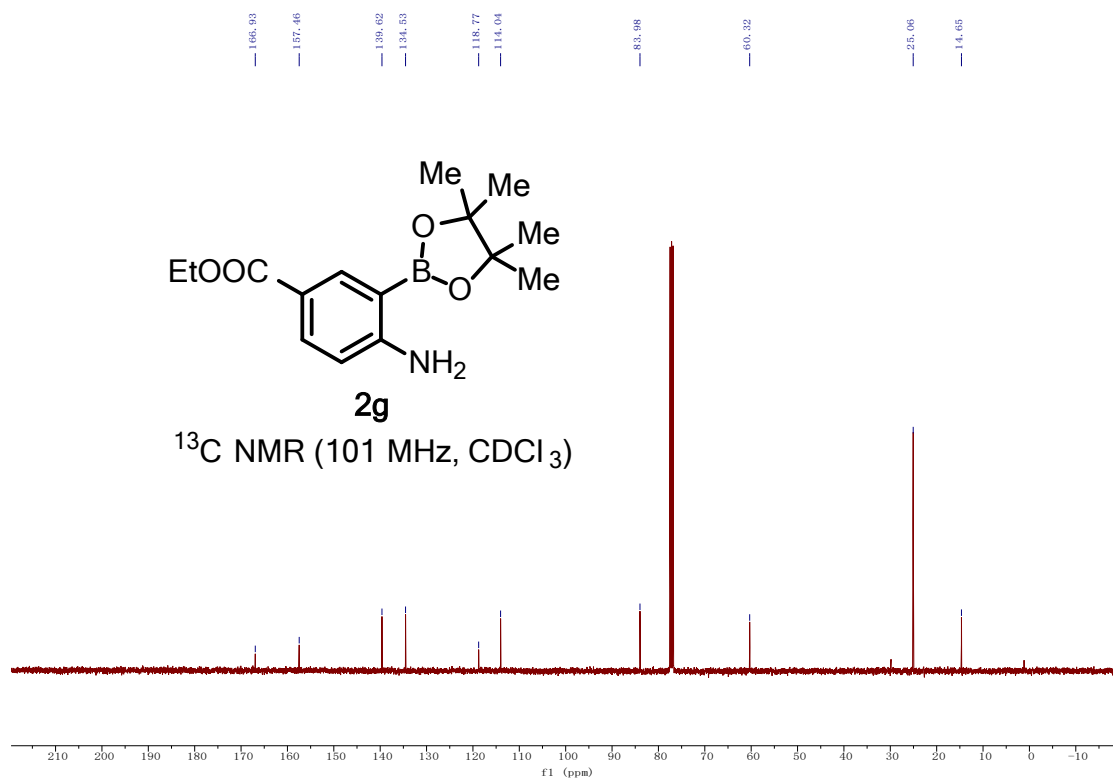


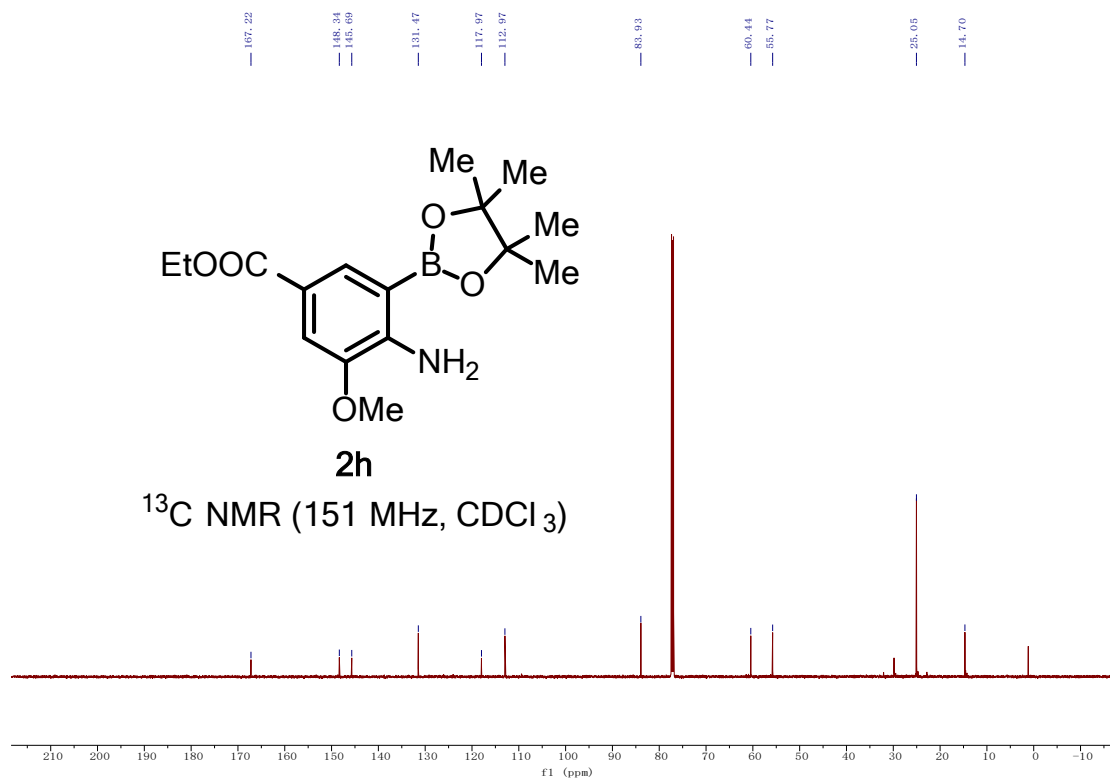
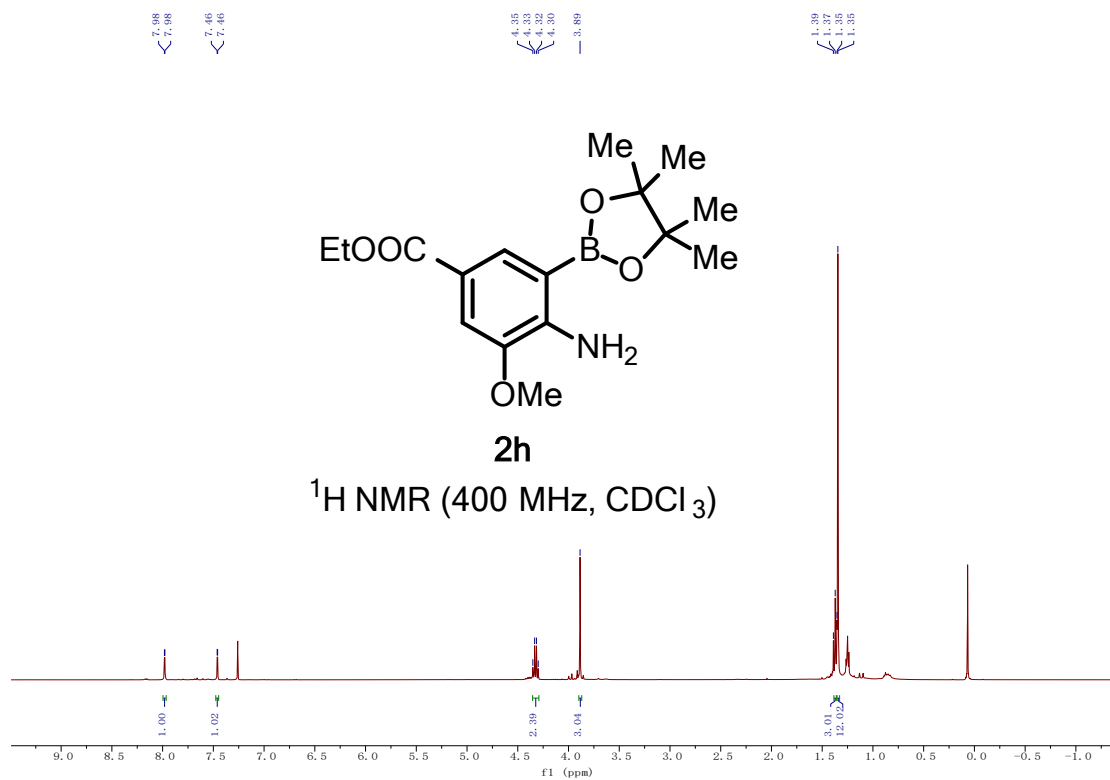


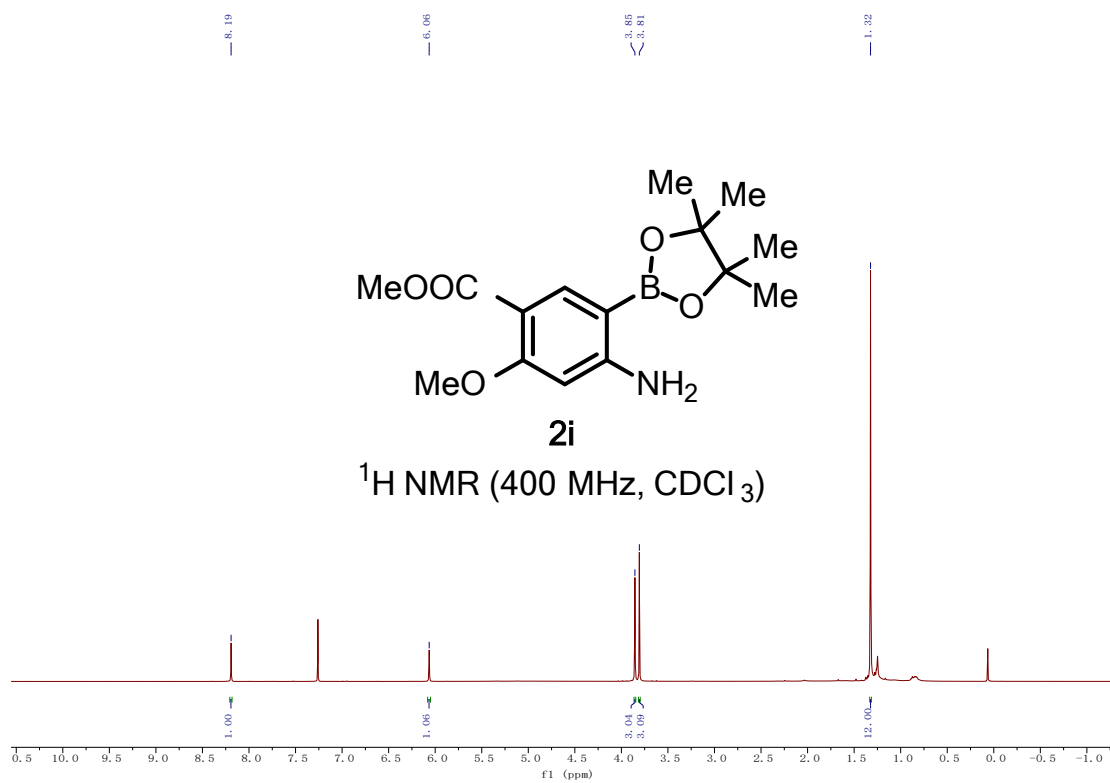
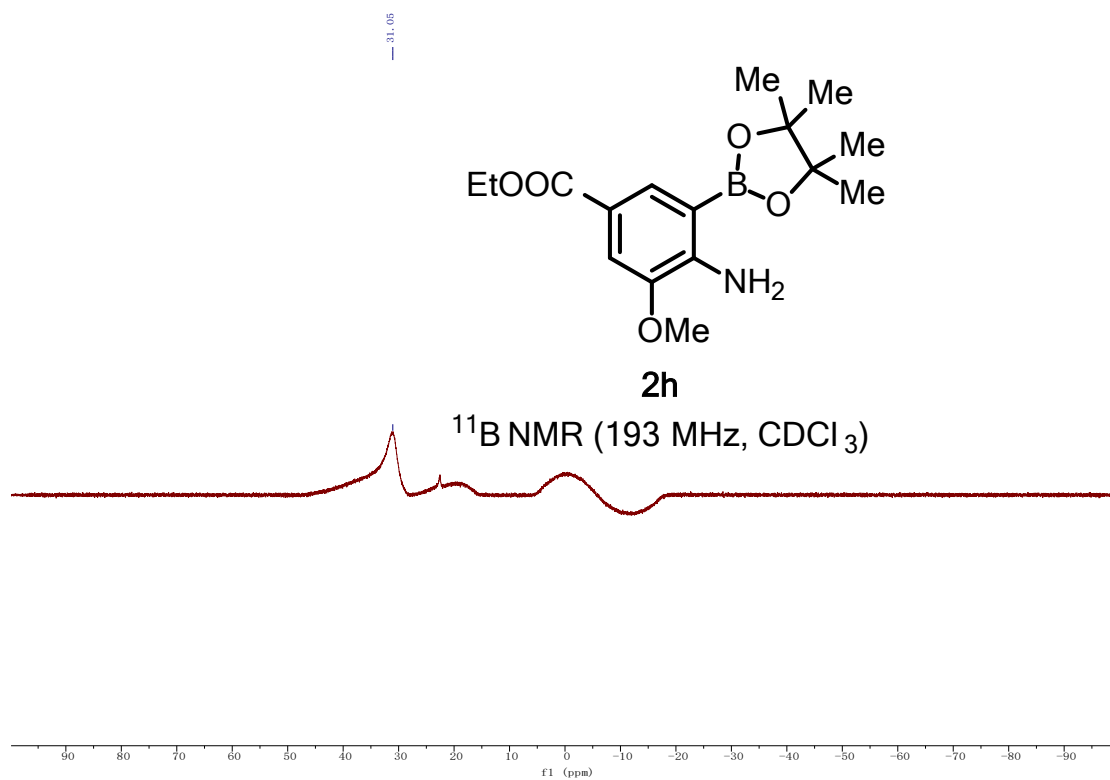


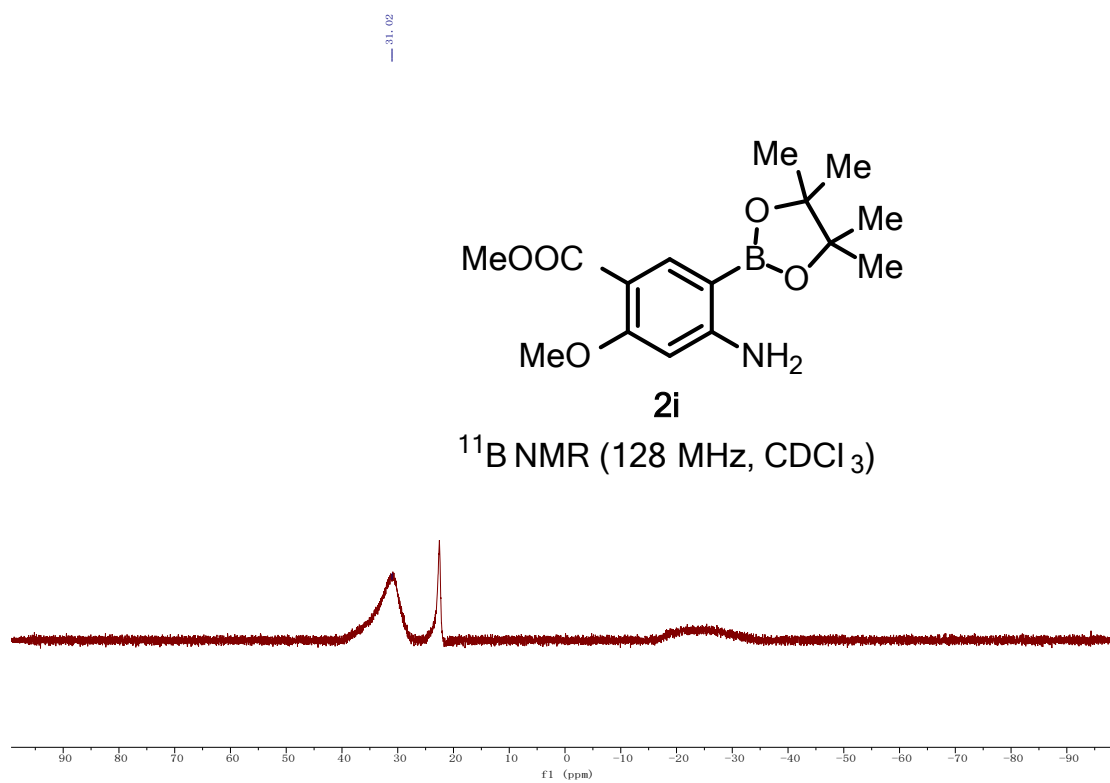
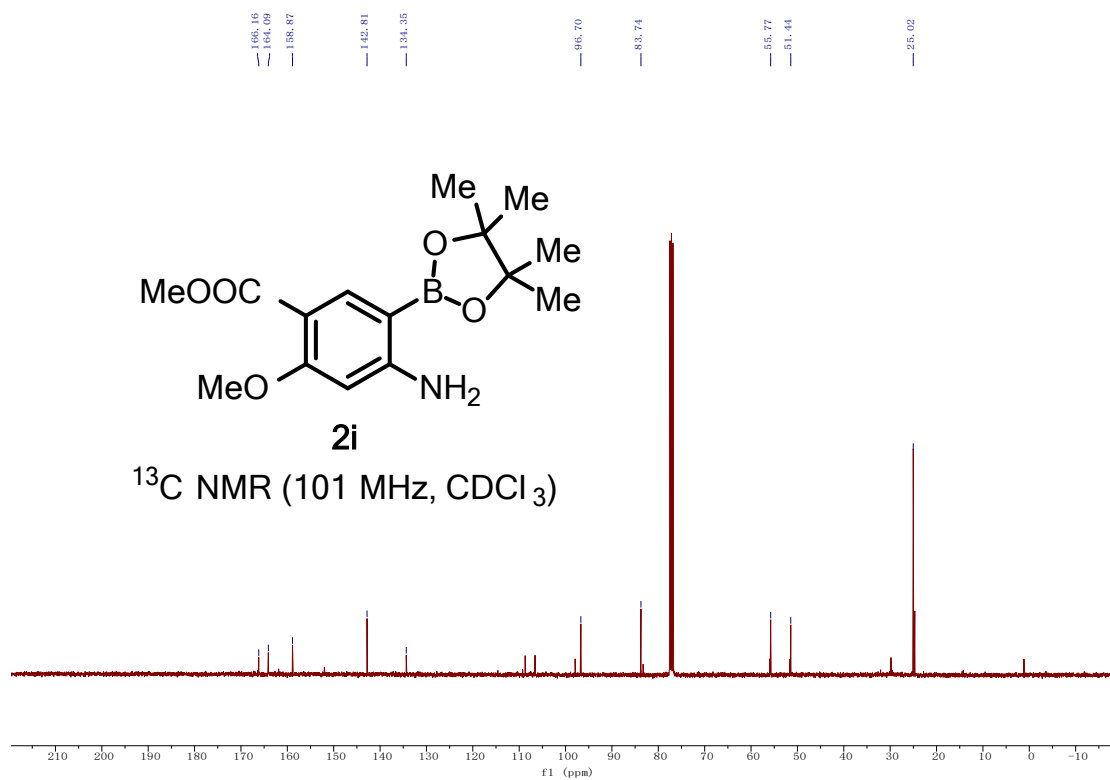


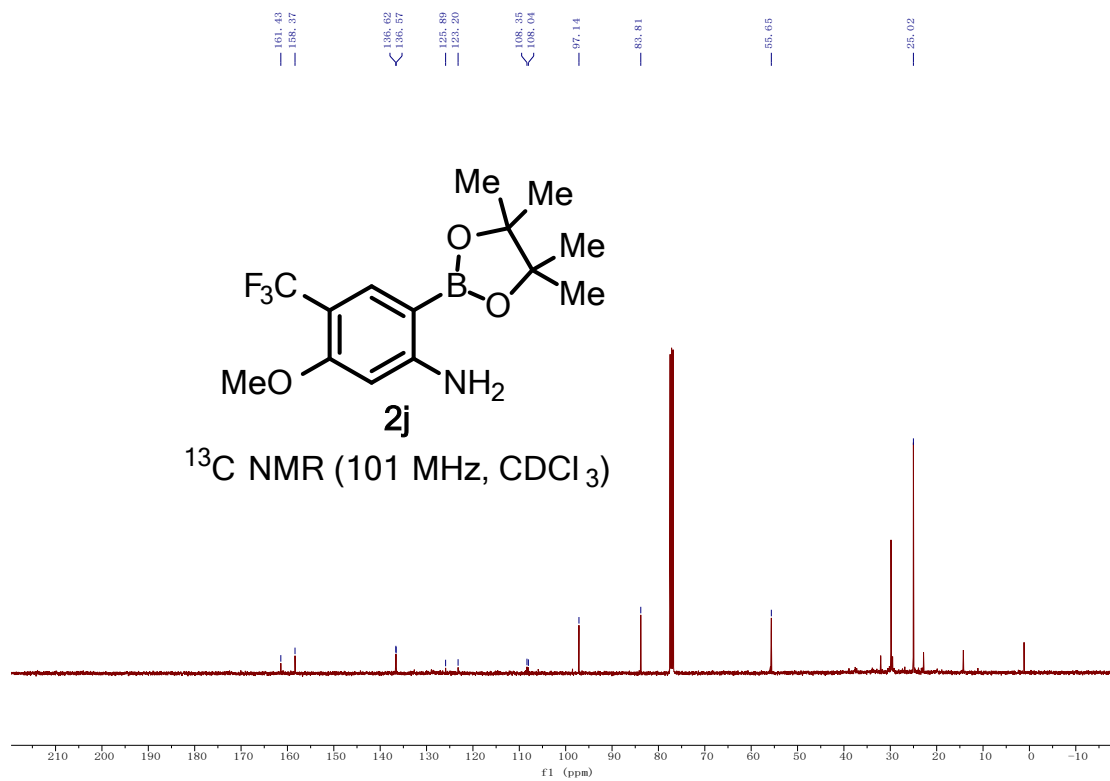
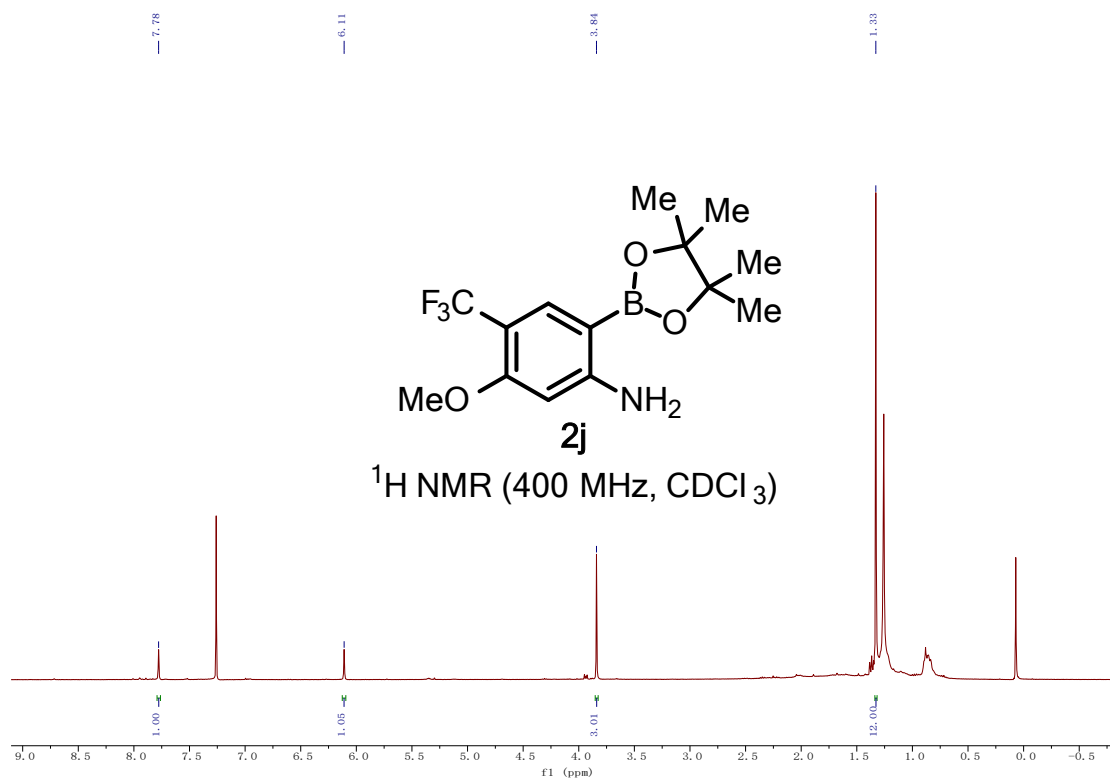




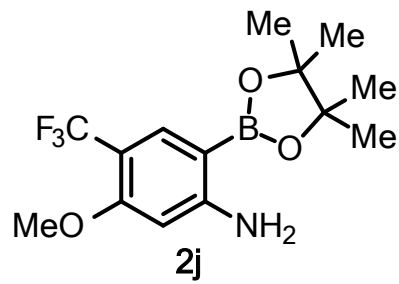




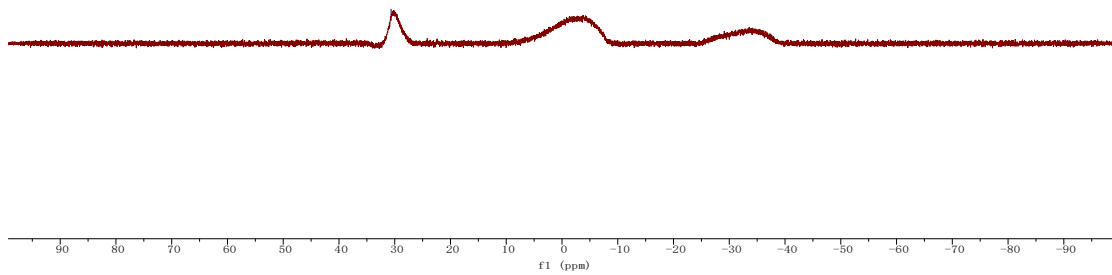




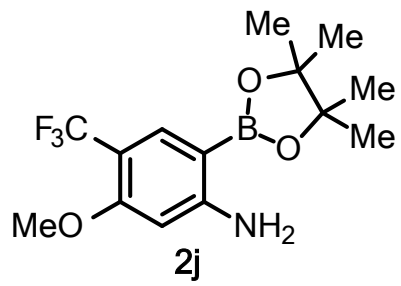
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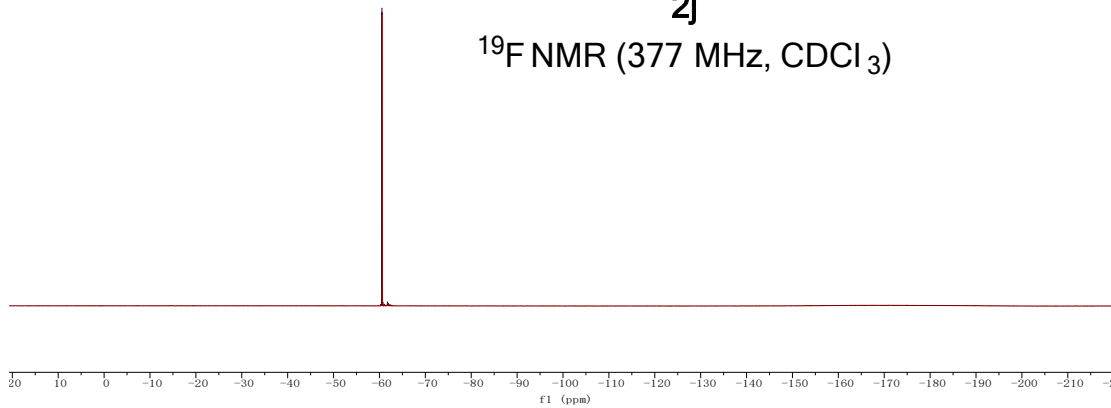
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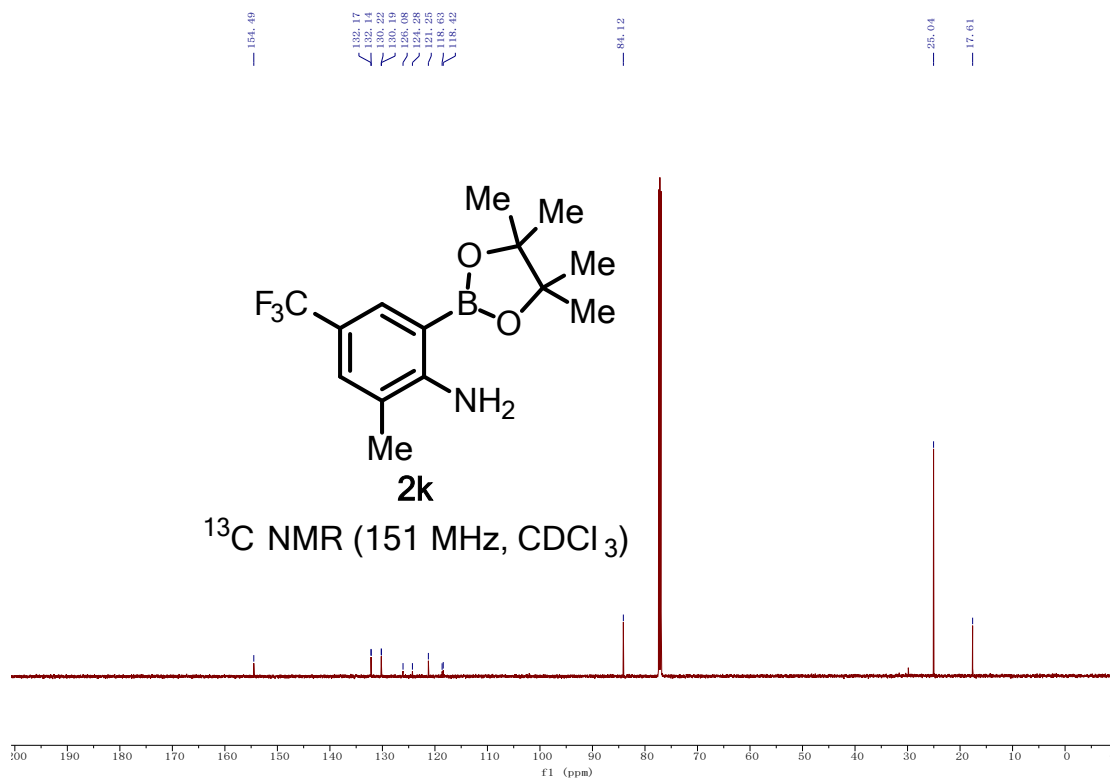
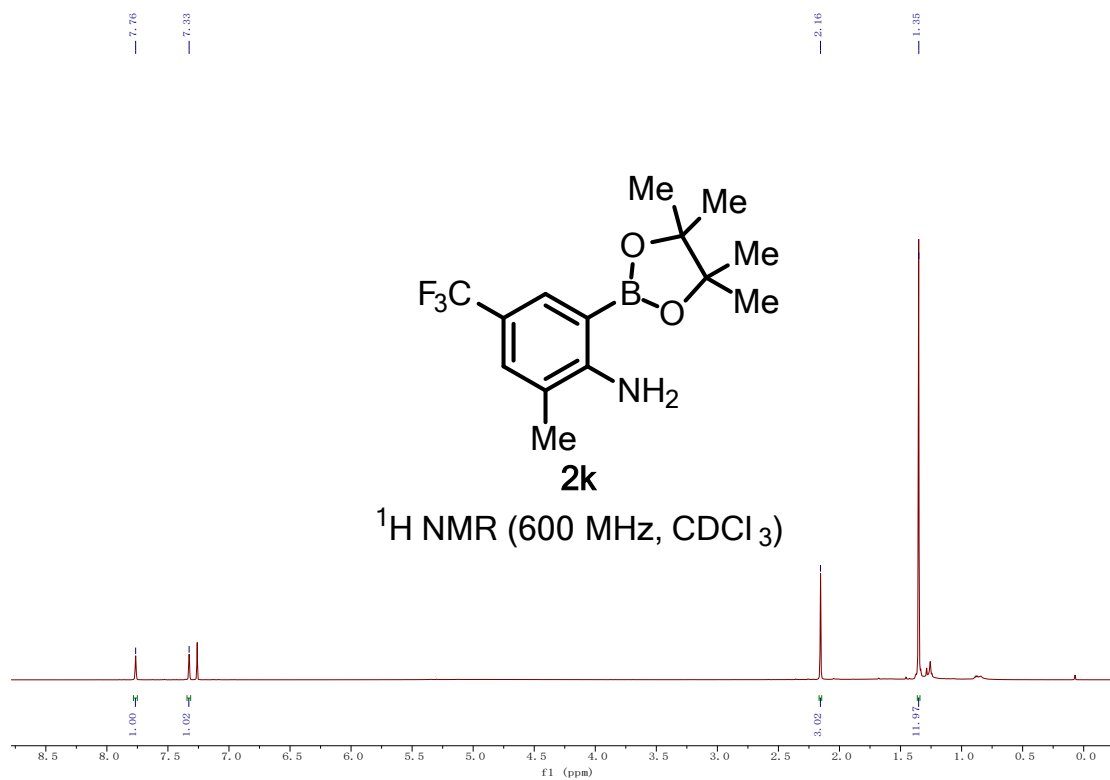


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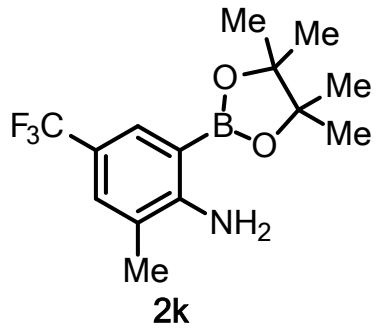


^{19}F NMR (377 MHz, CDCl_3)

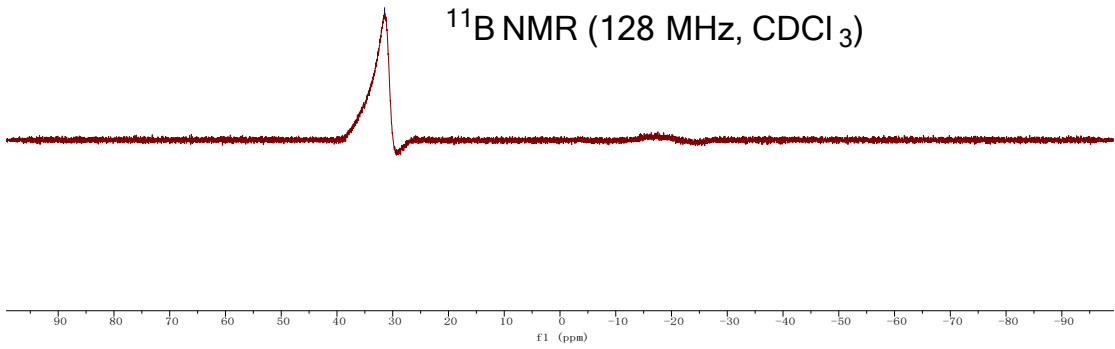




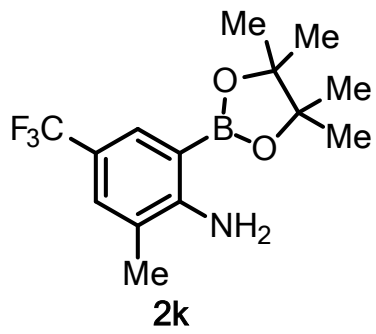
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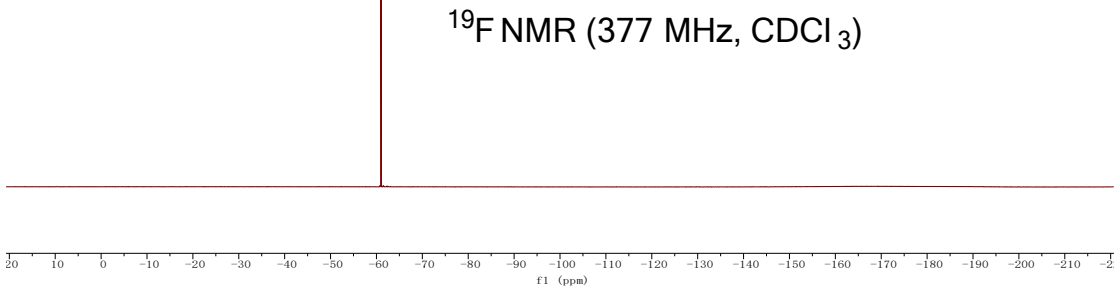
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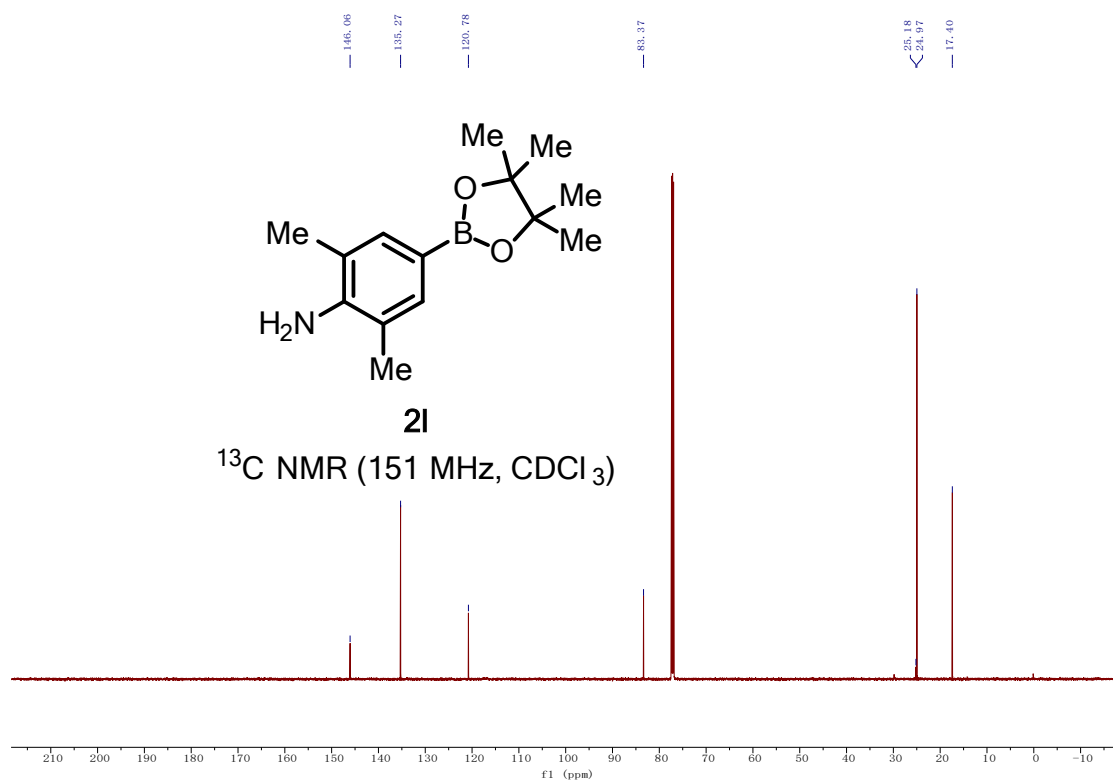
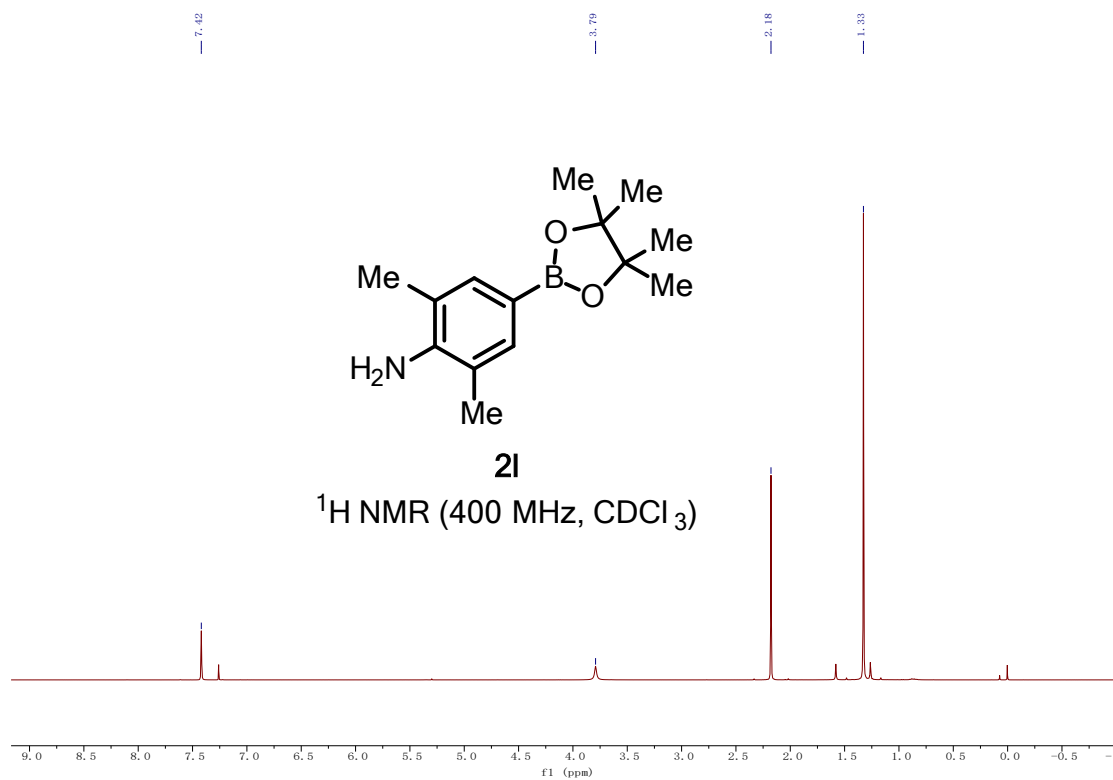


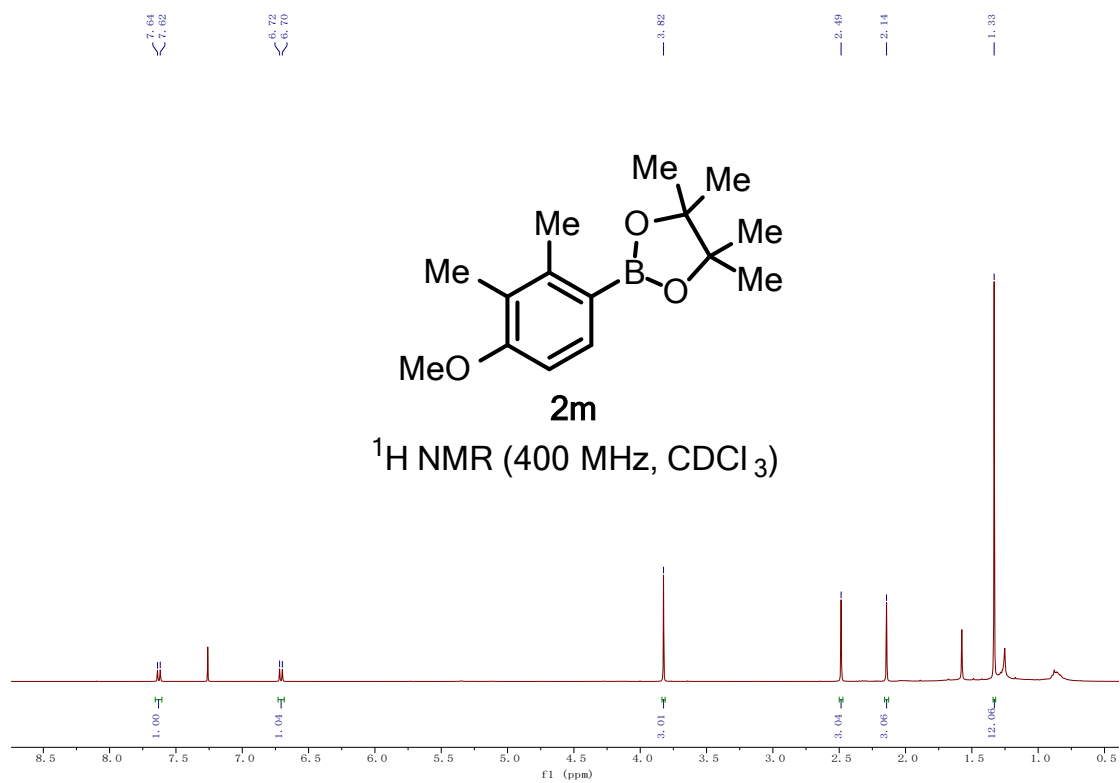
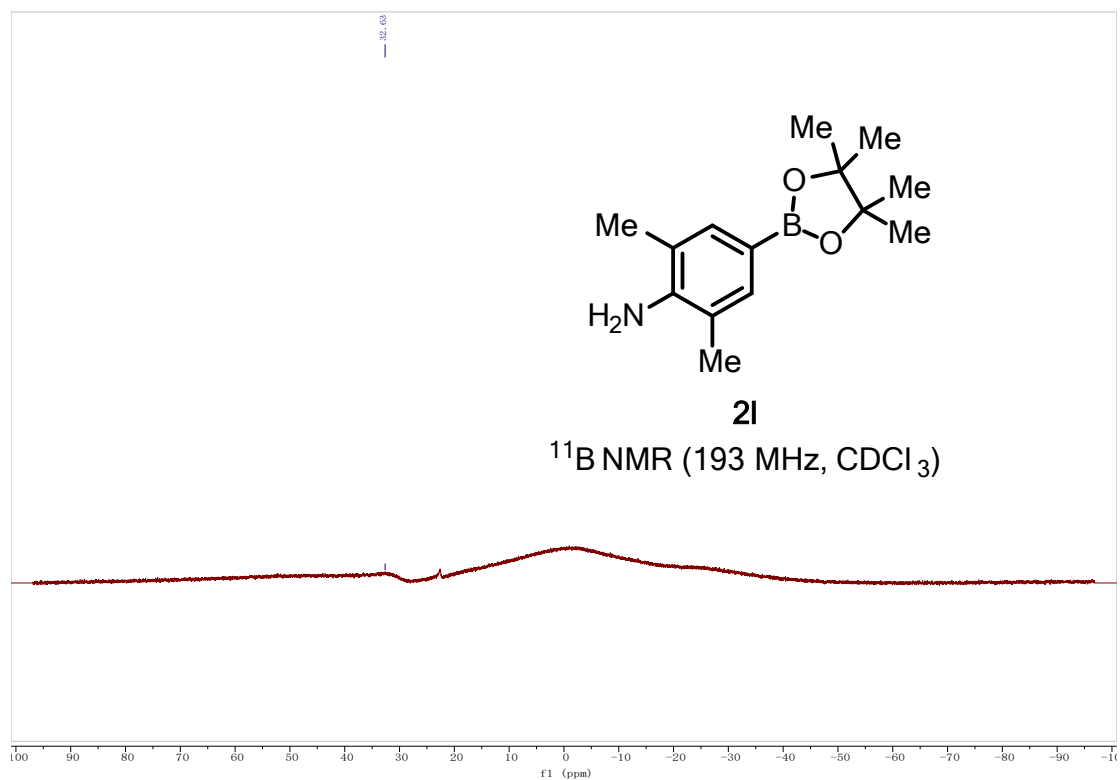
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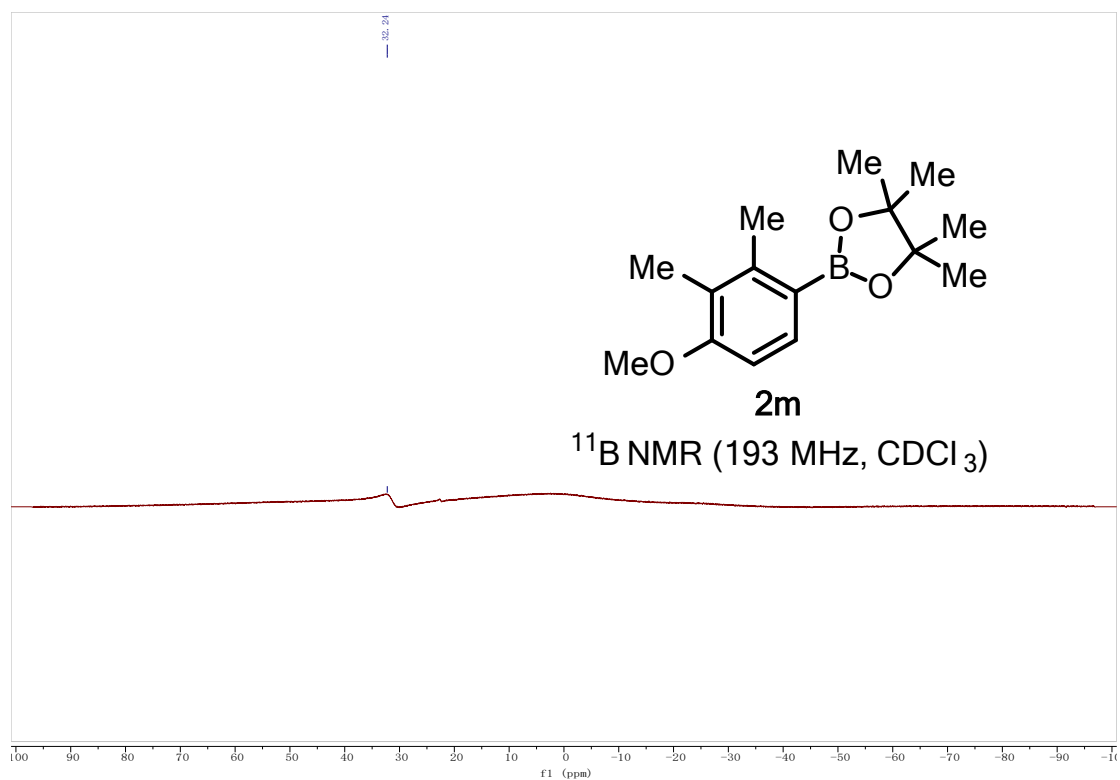
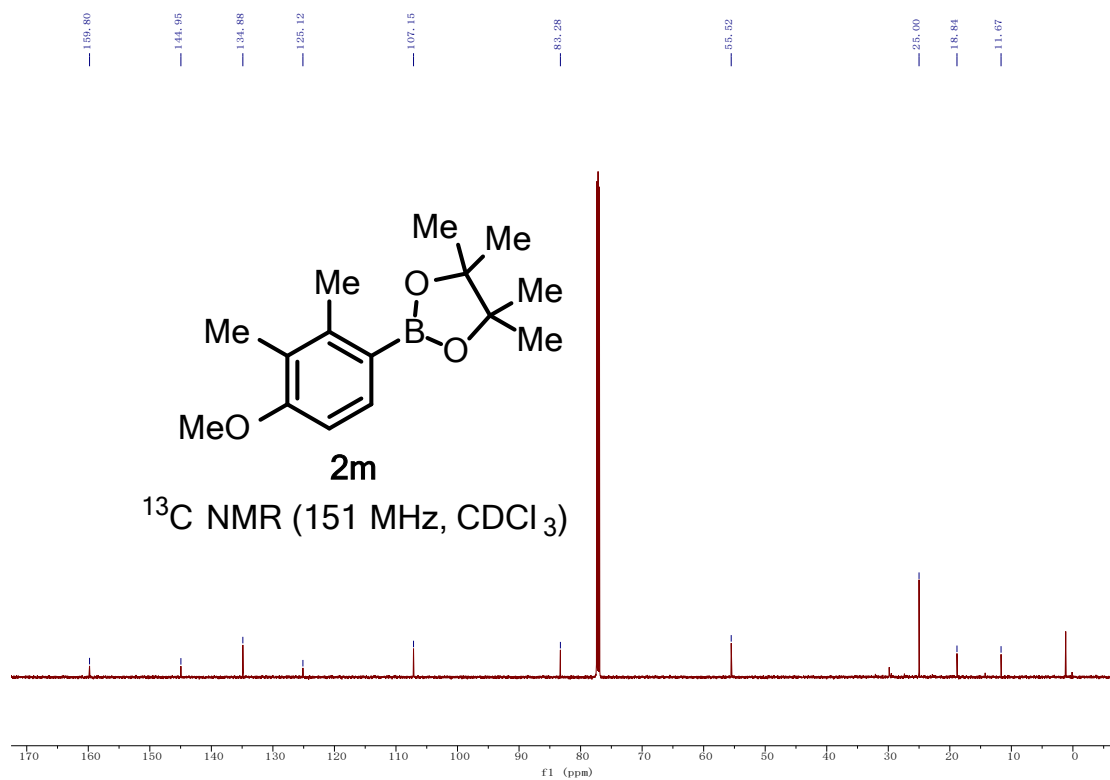


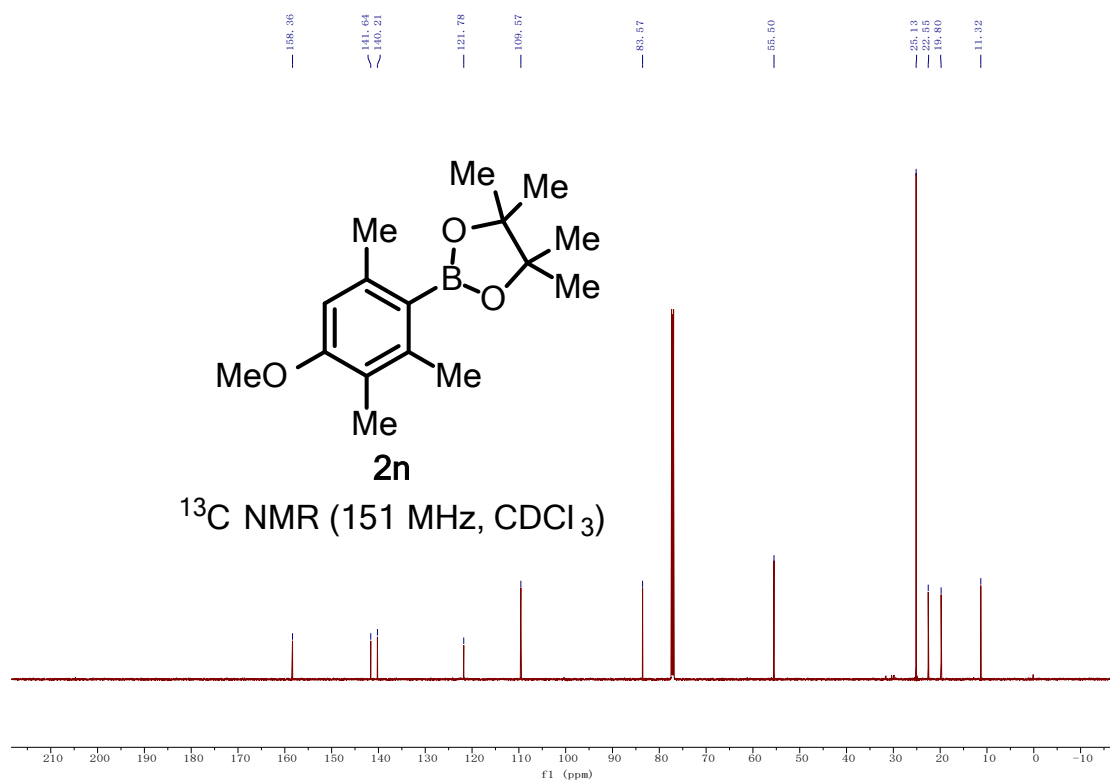
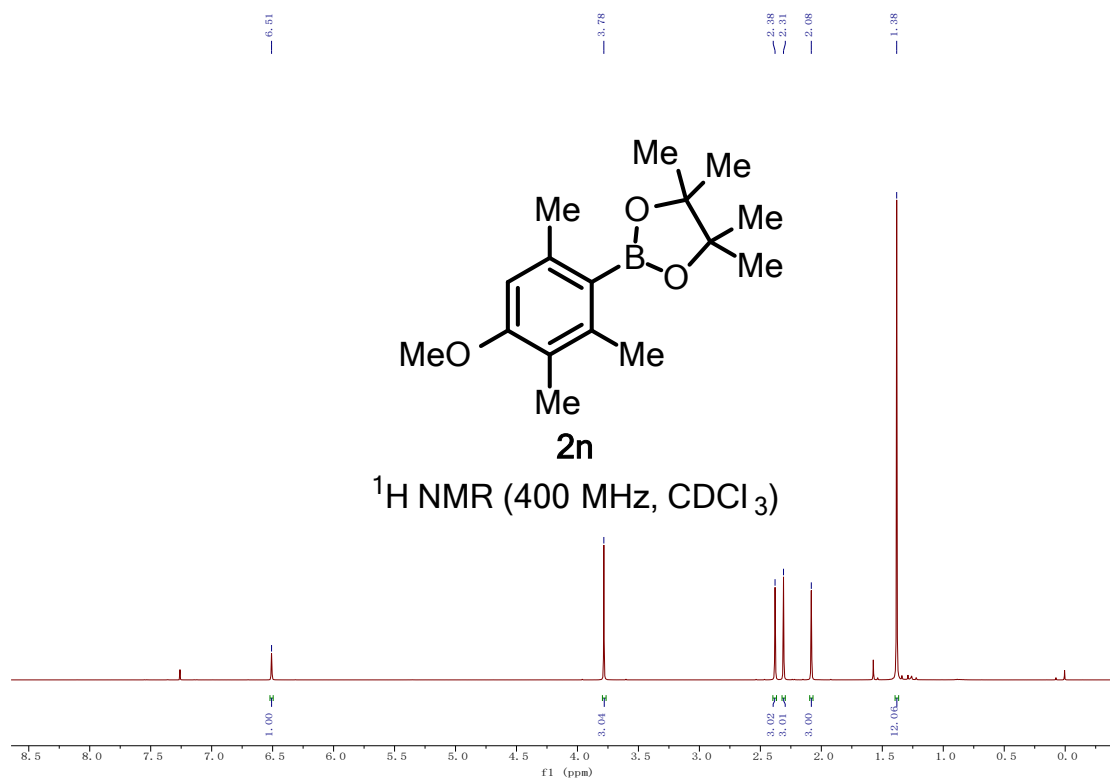
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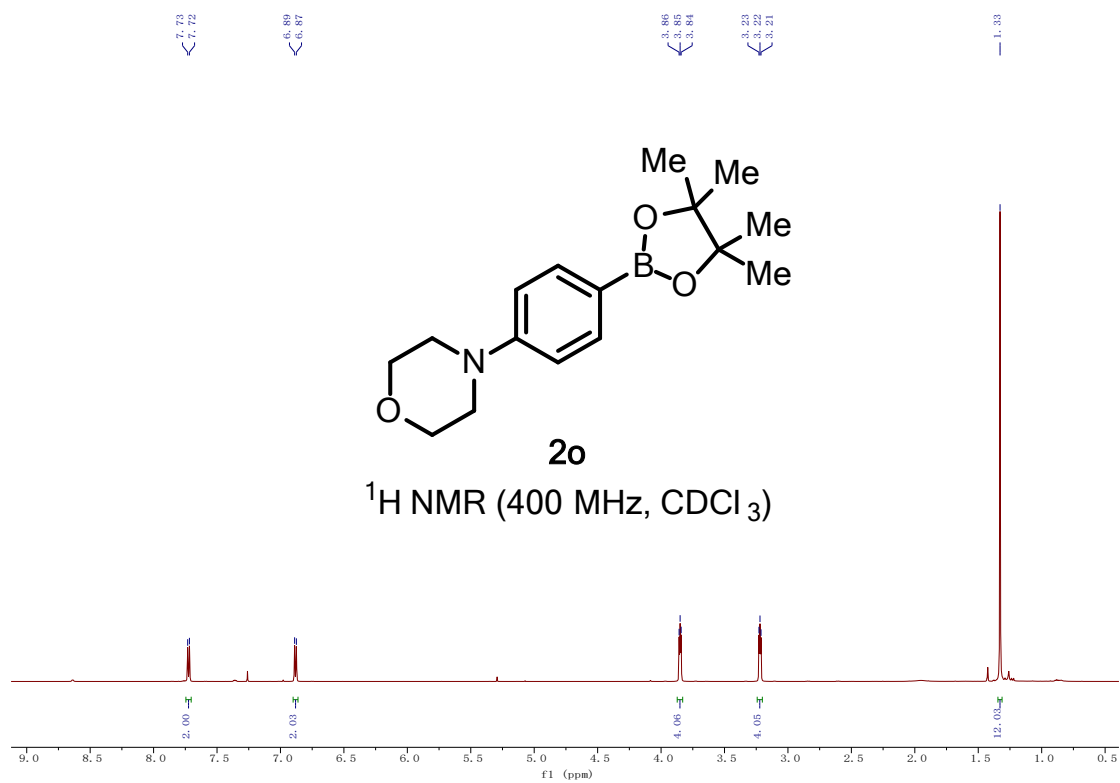
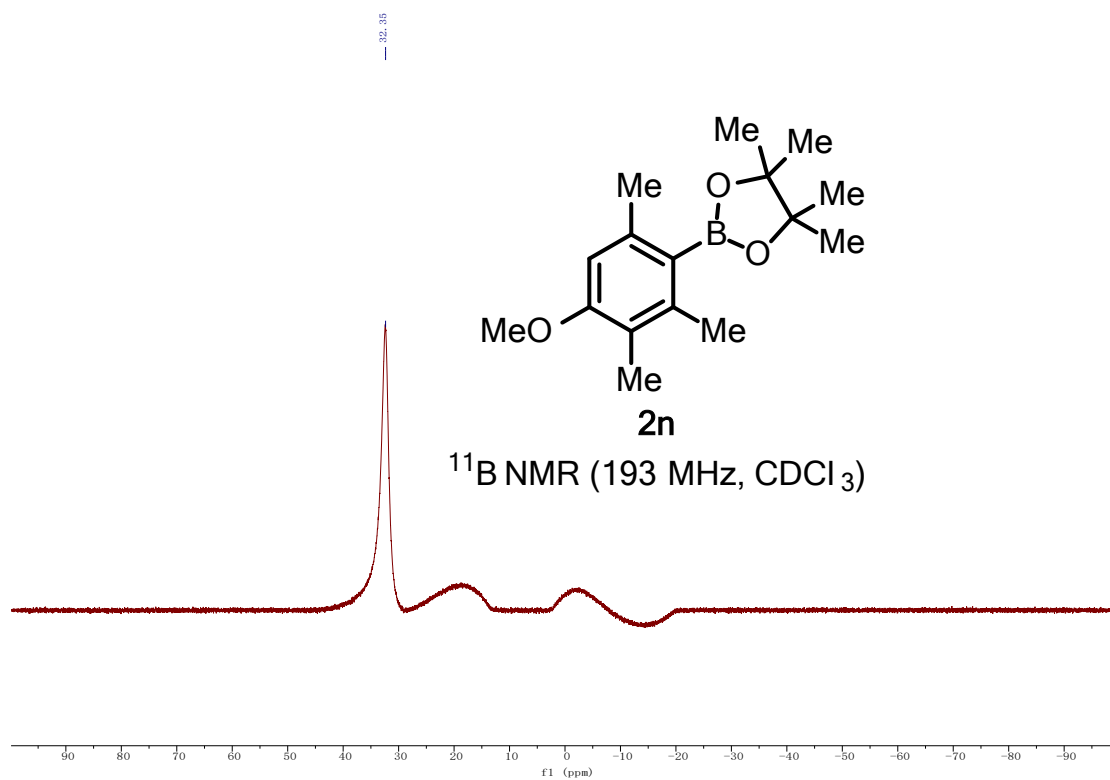


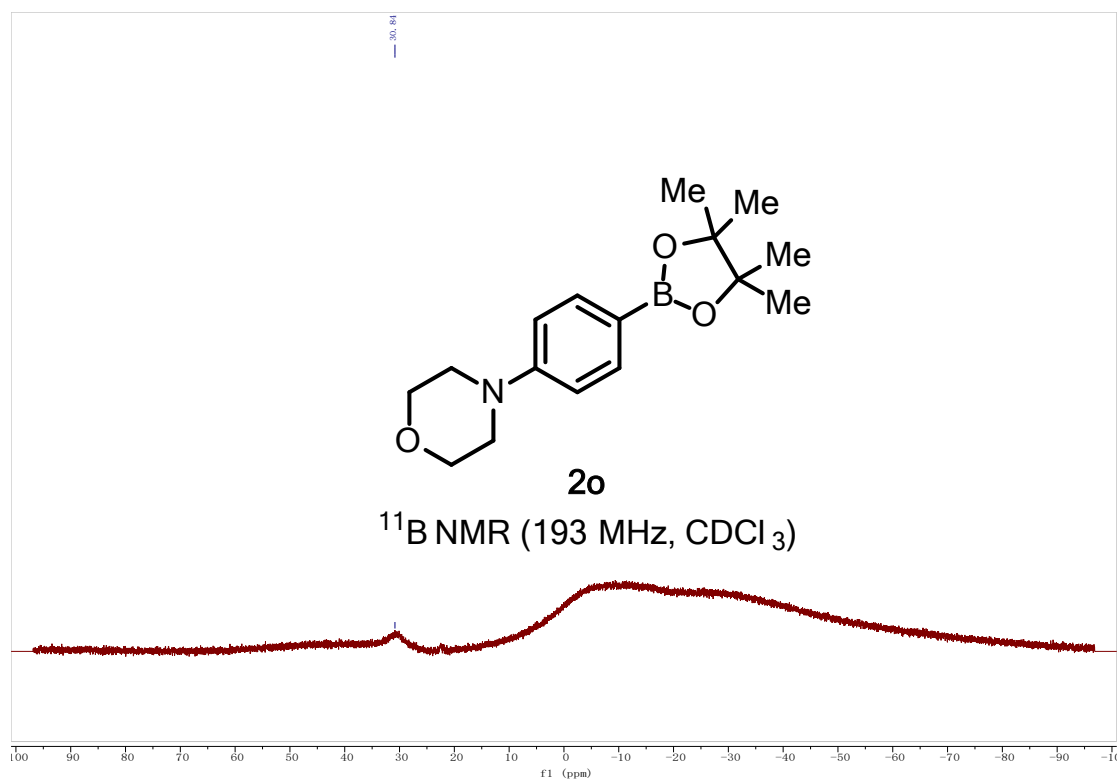
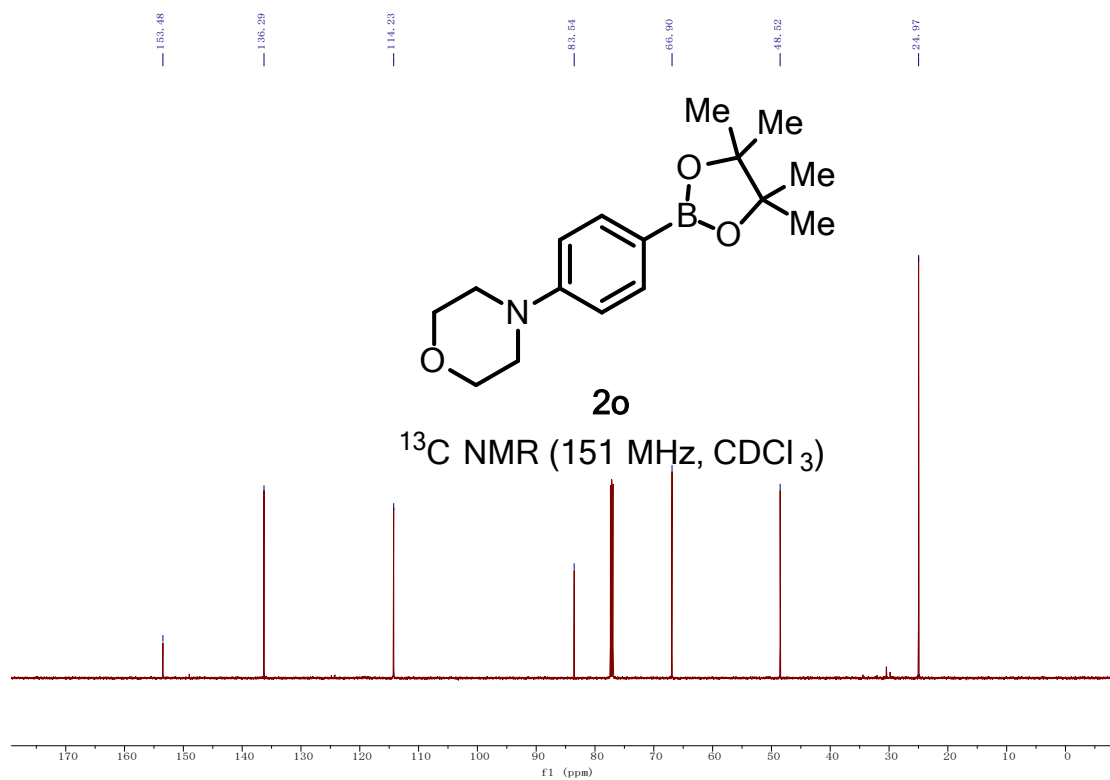


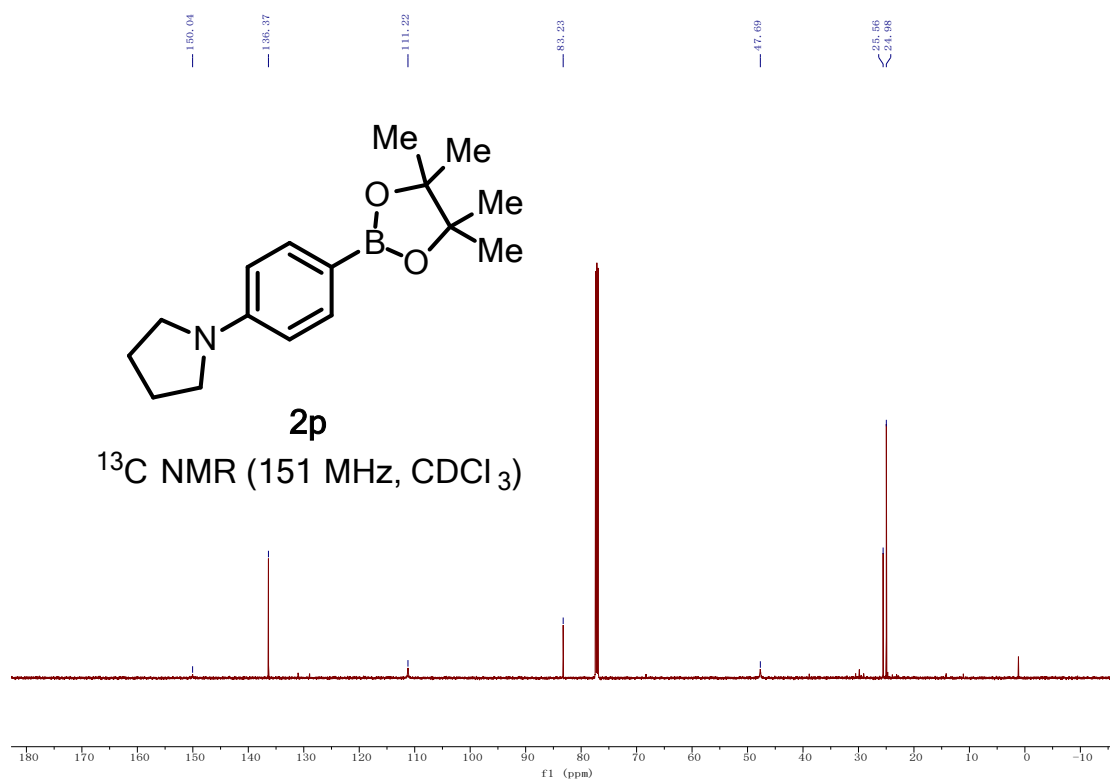
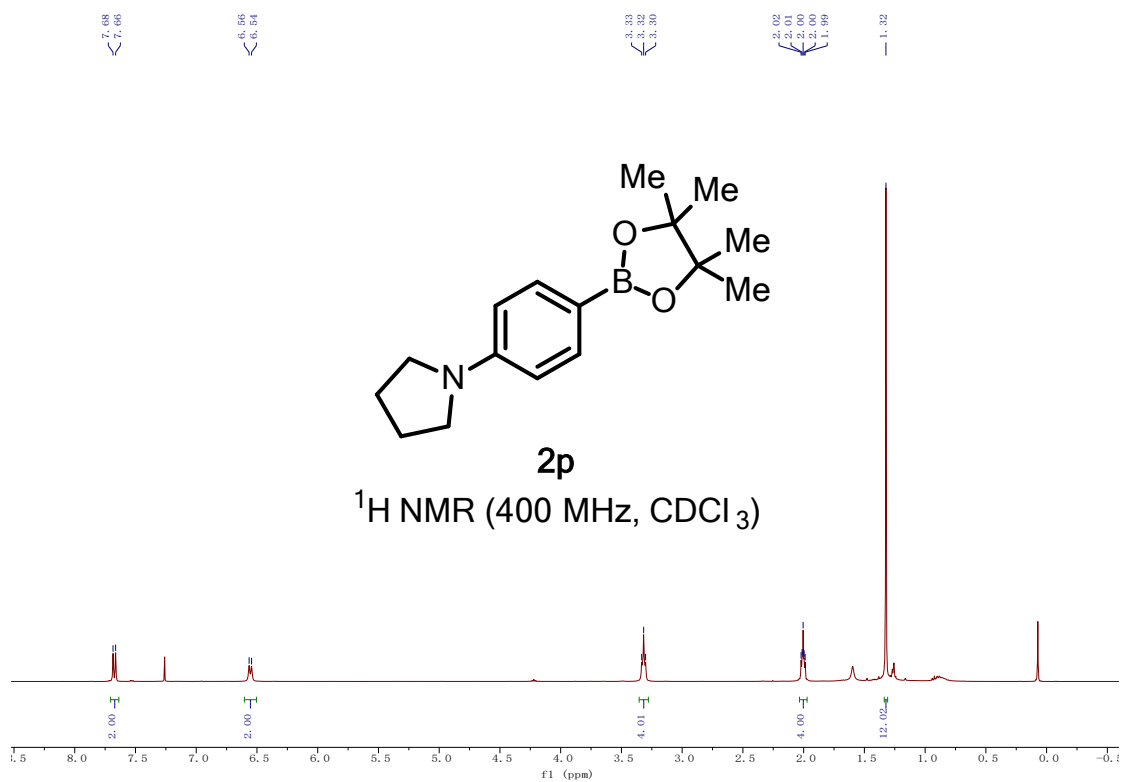


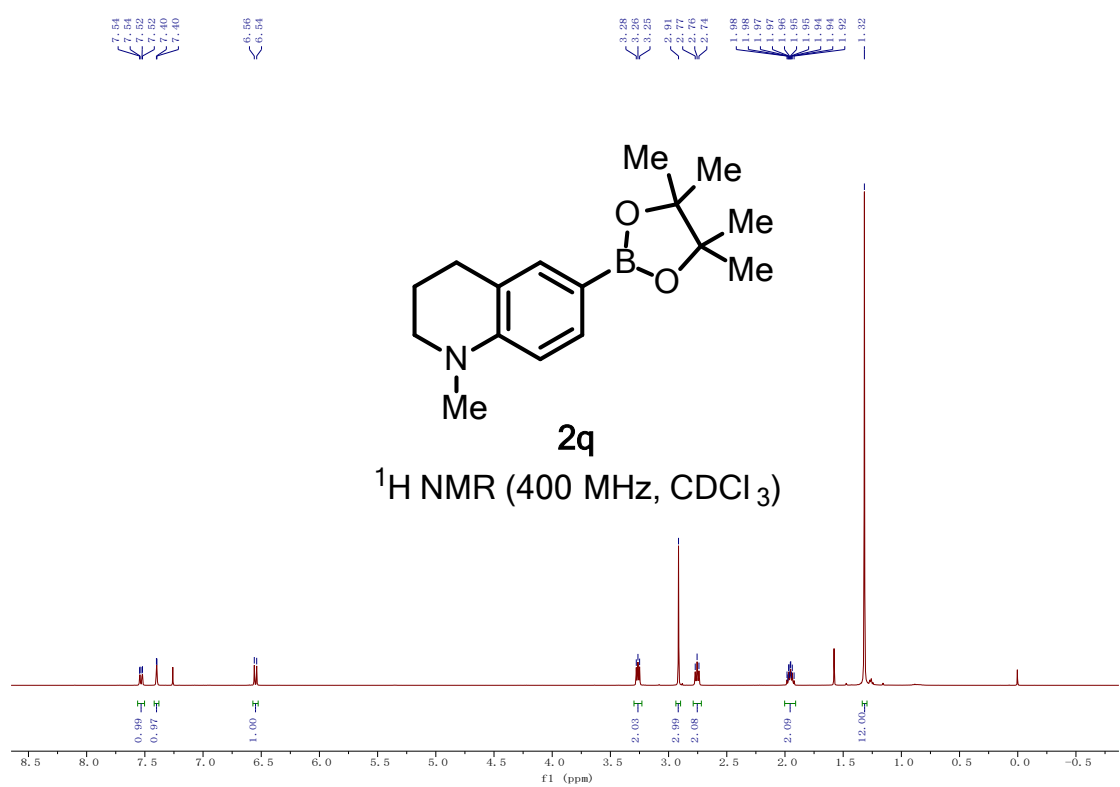
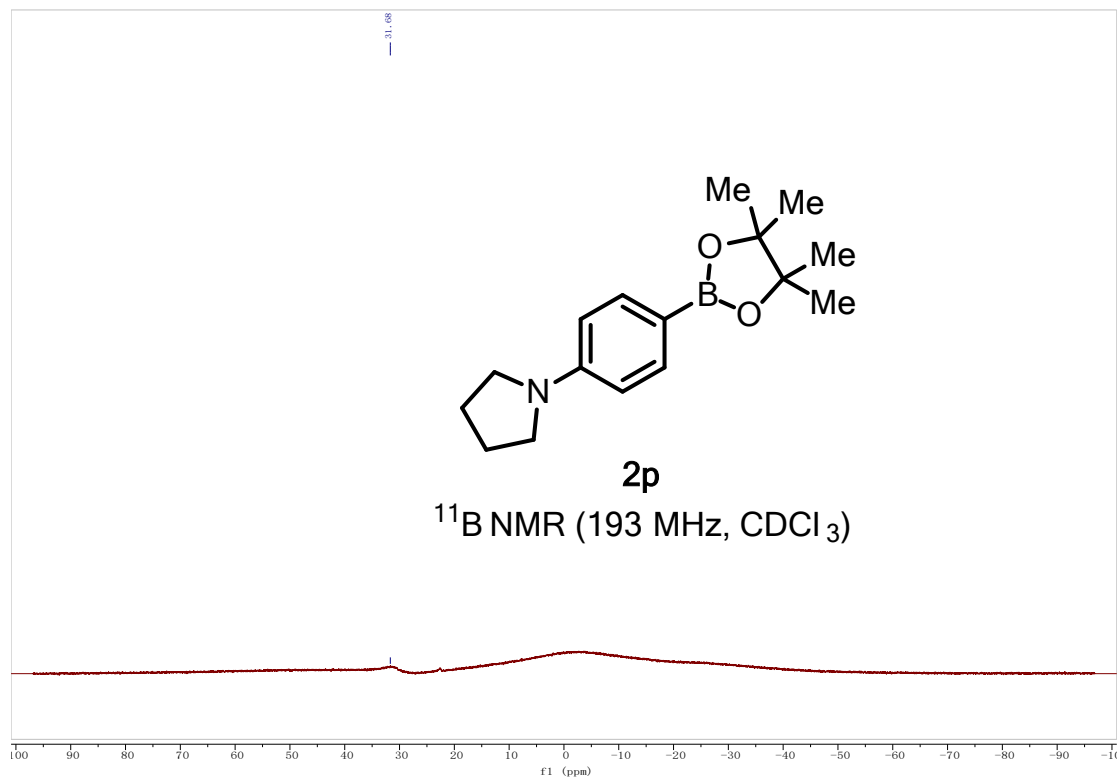


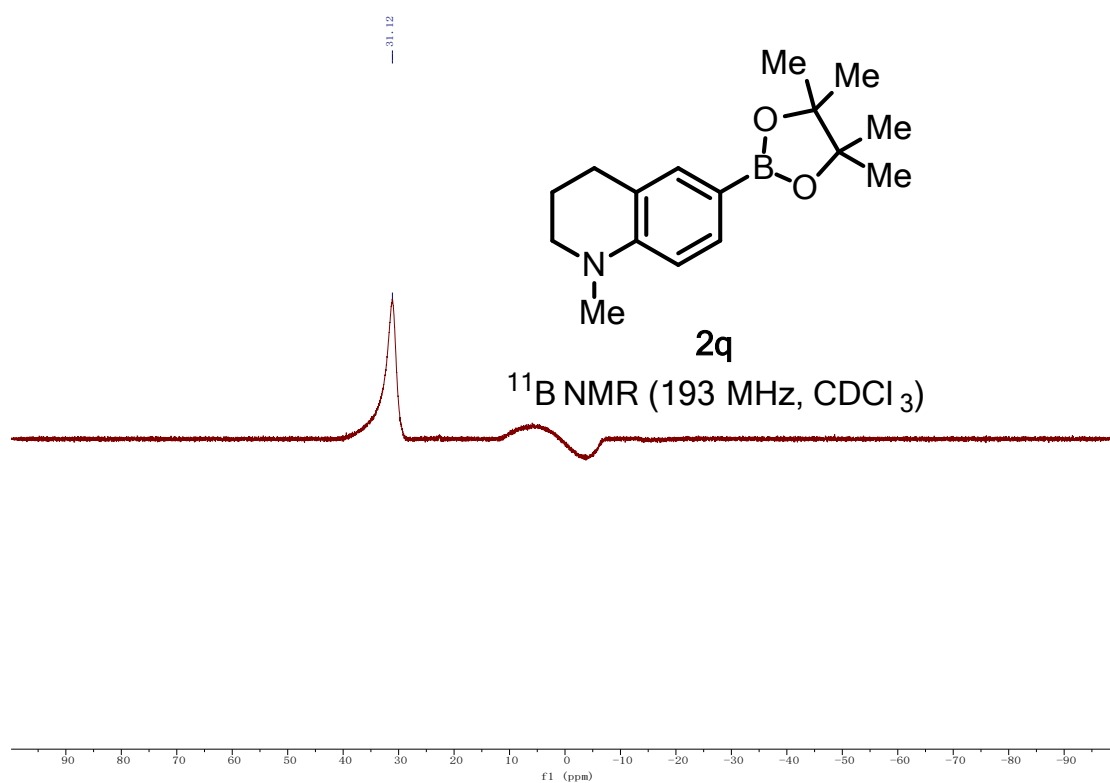
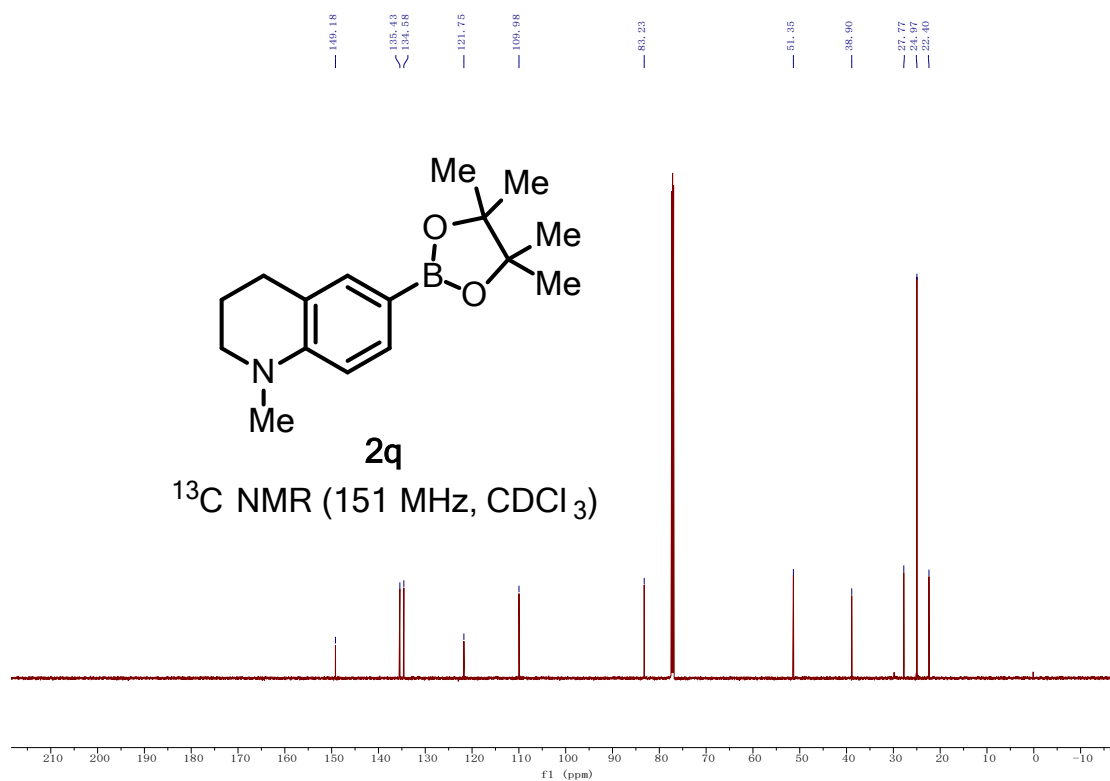


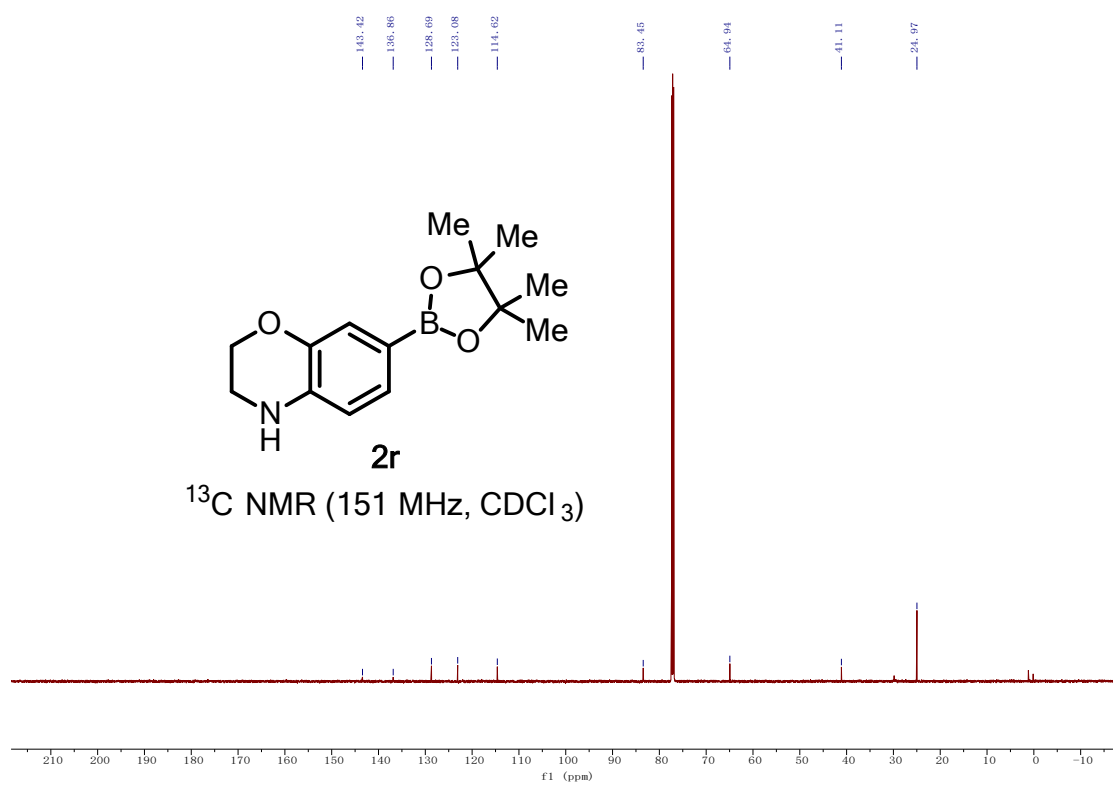
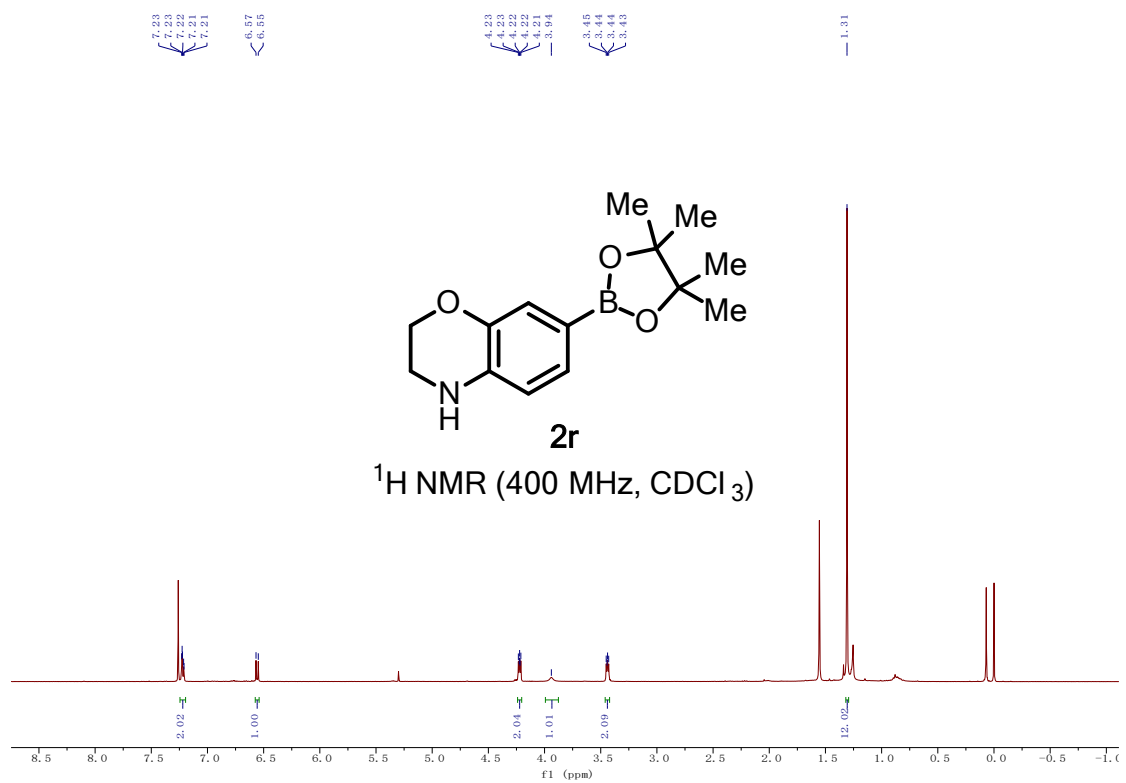




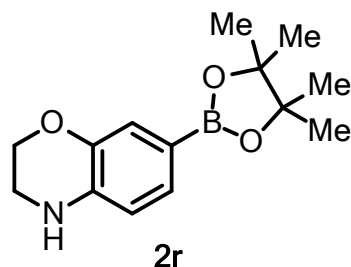




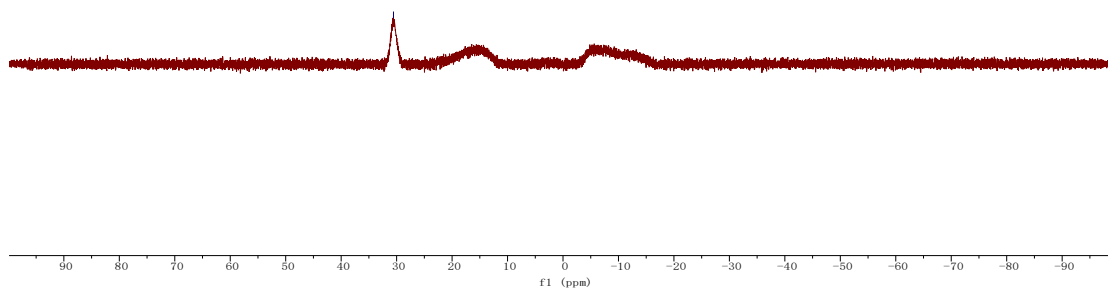




-30.57



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



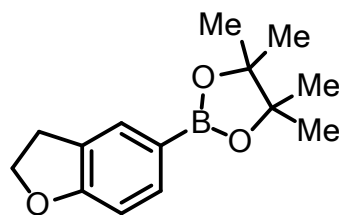
7.66
7.60

6.79
6.78

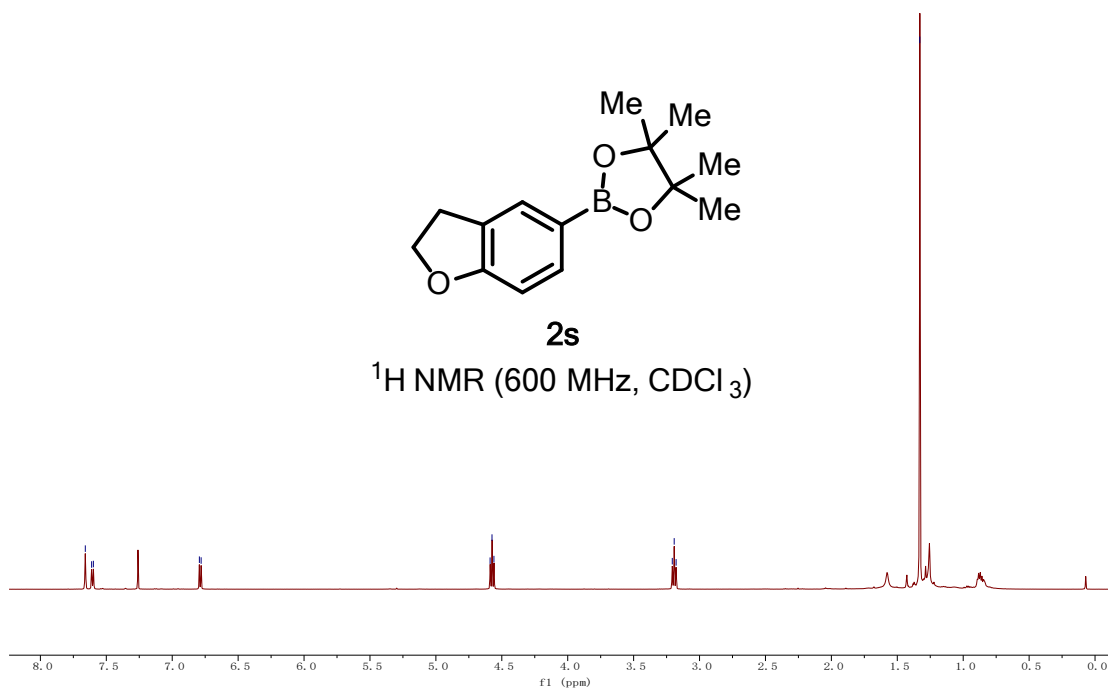
4.59
4.57
4.56

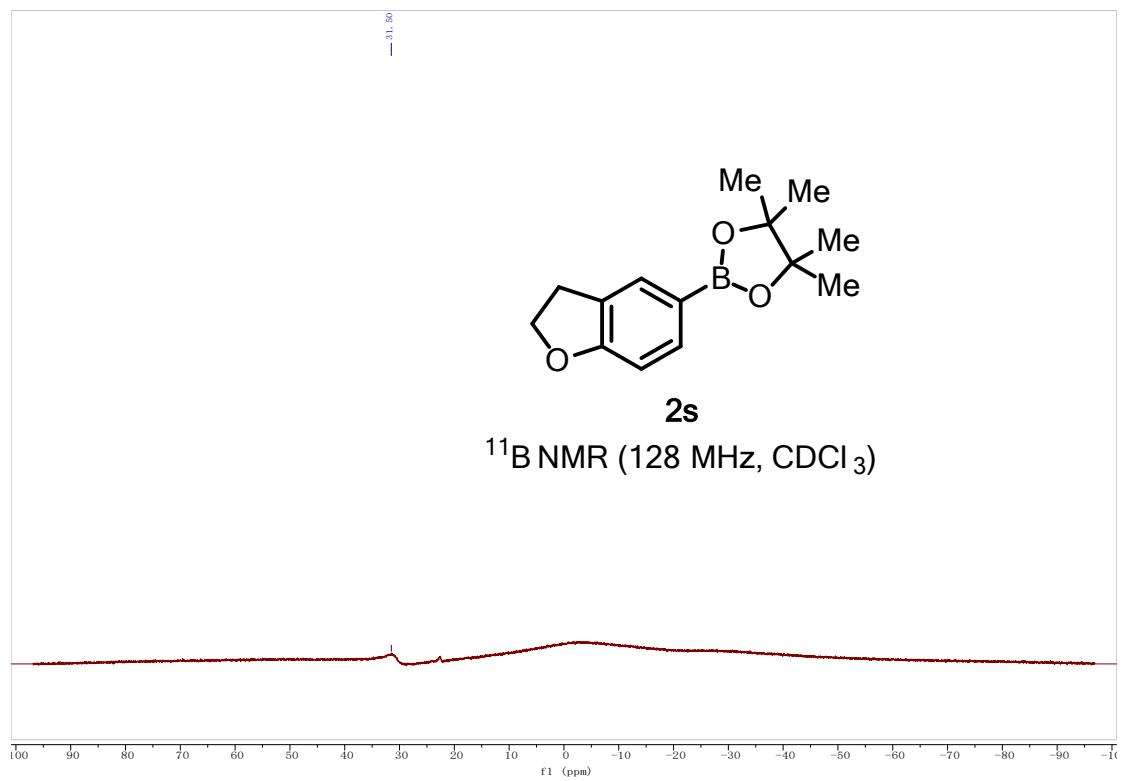
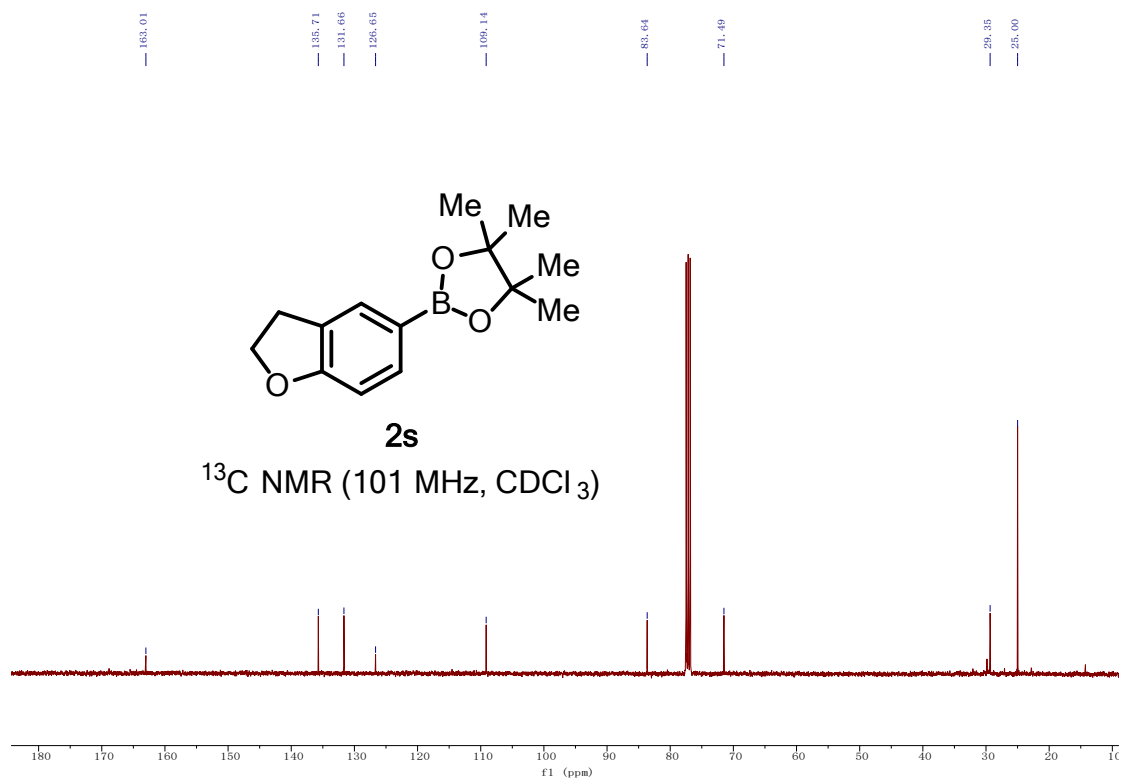
3.91
3.19
3.18

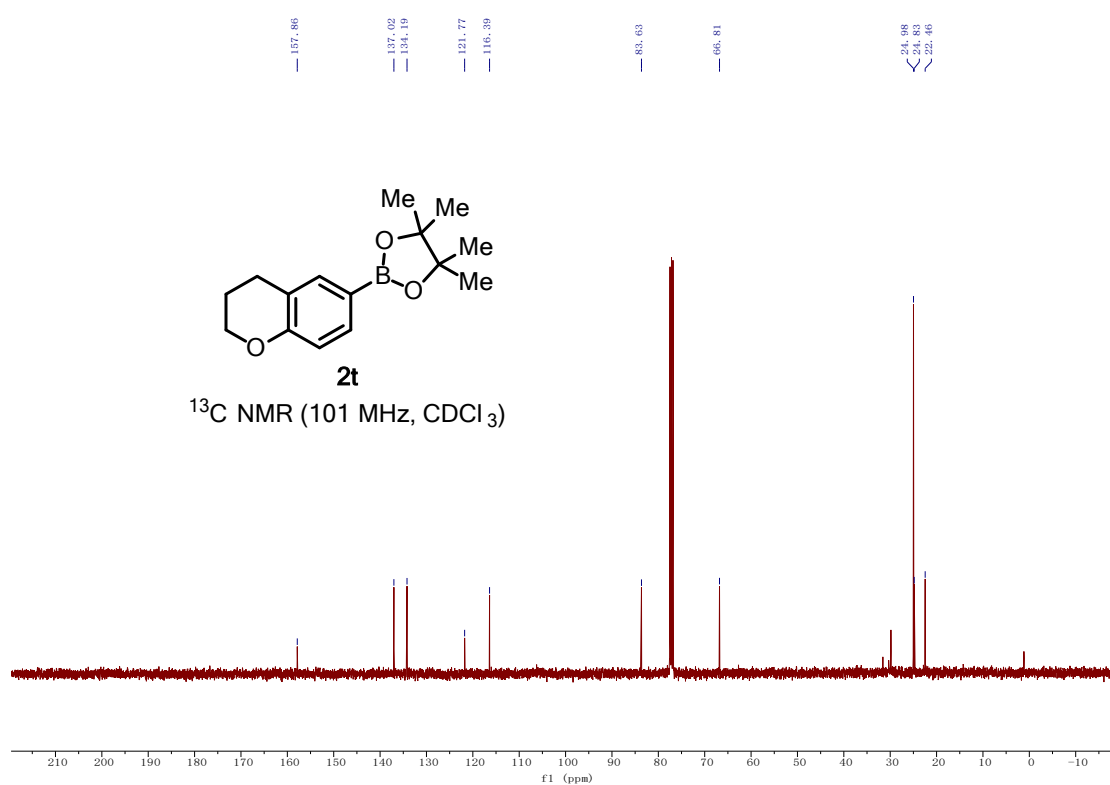
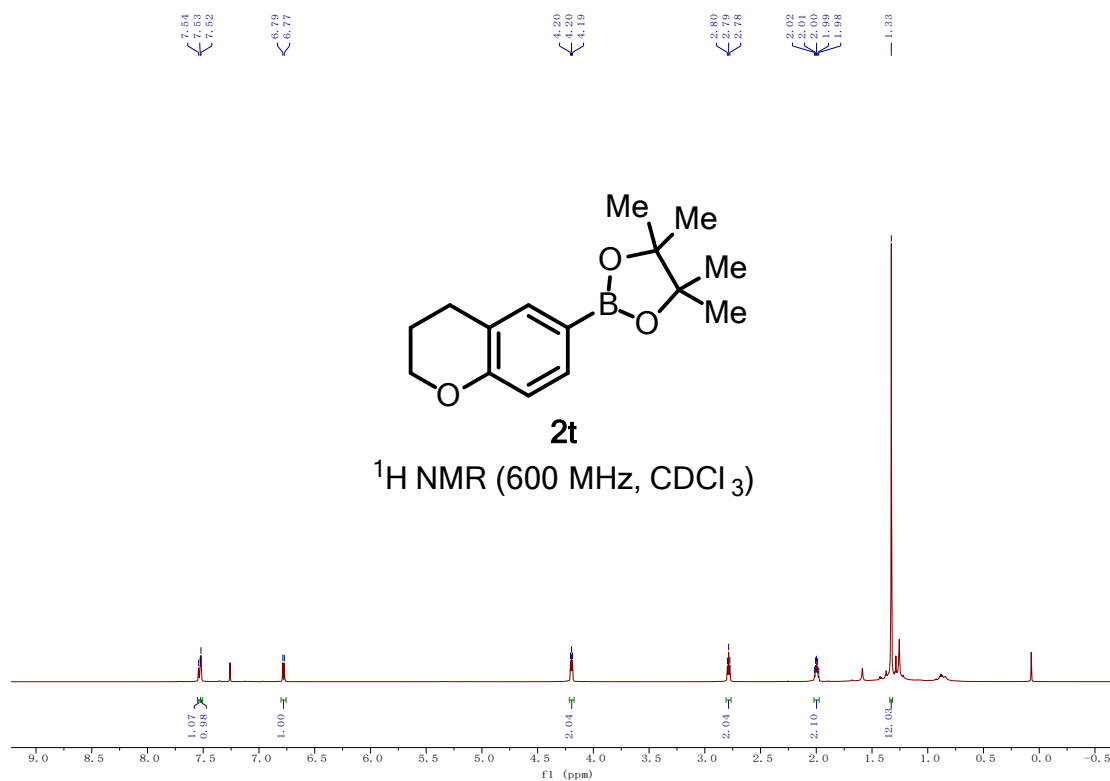
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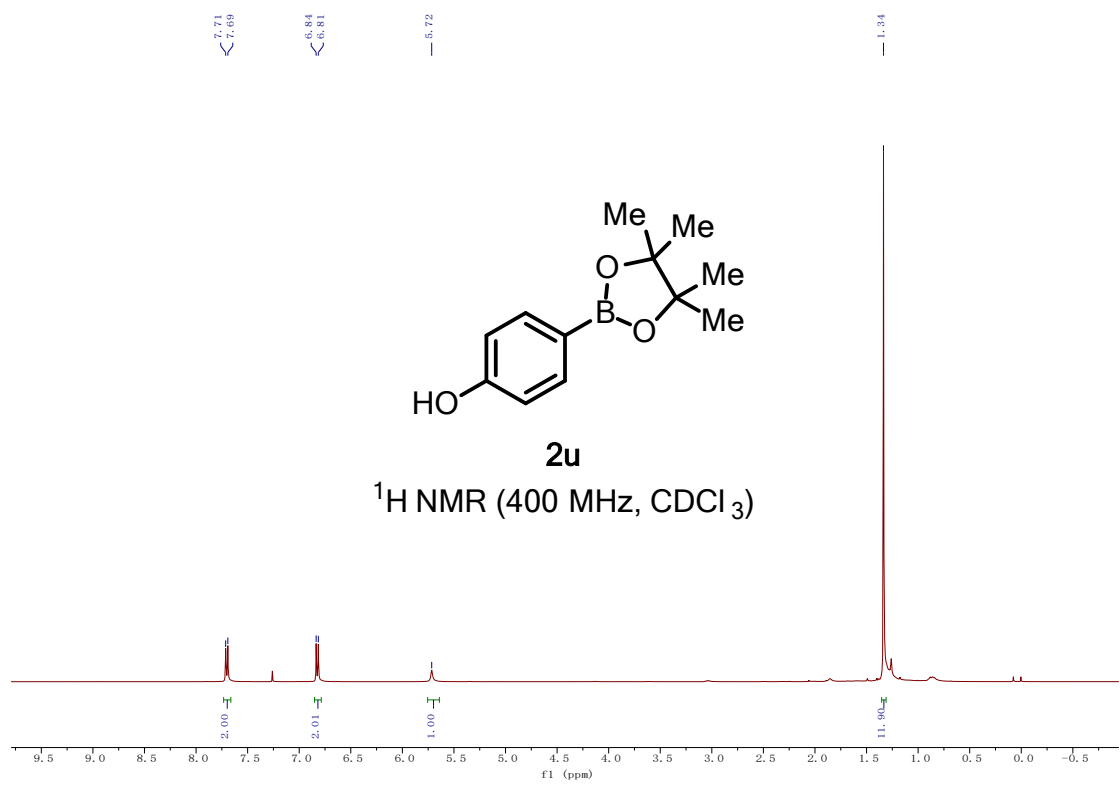
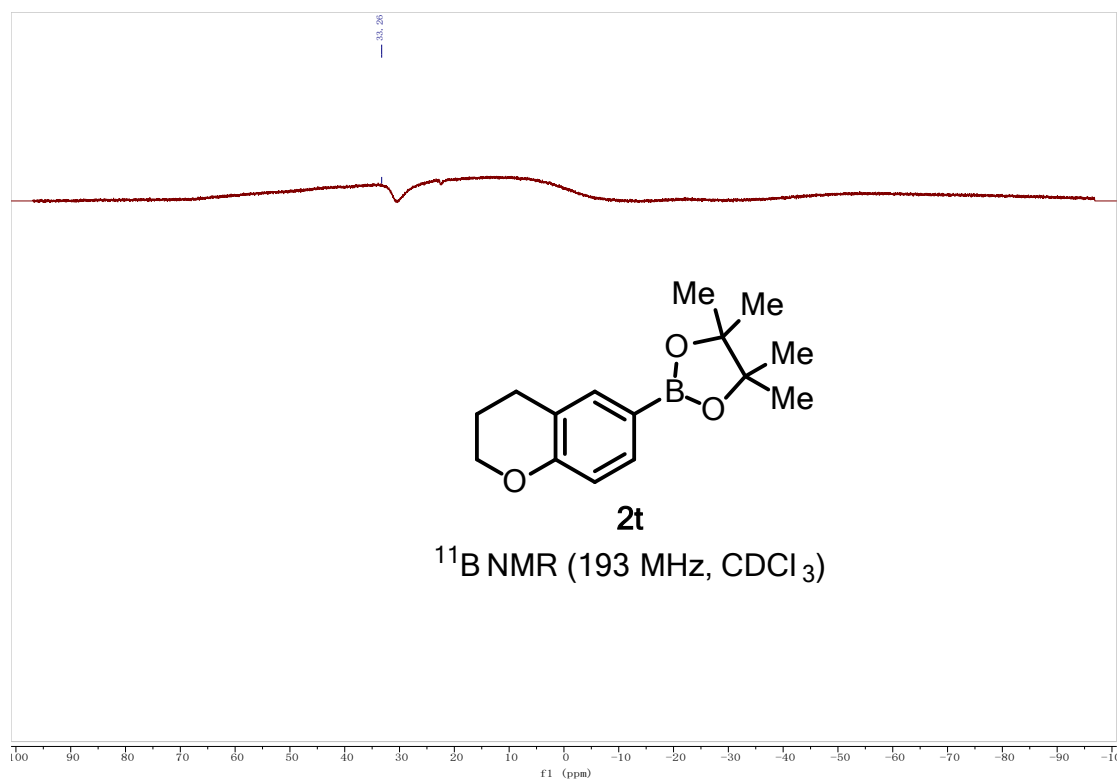


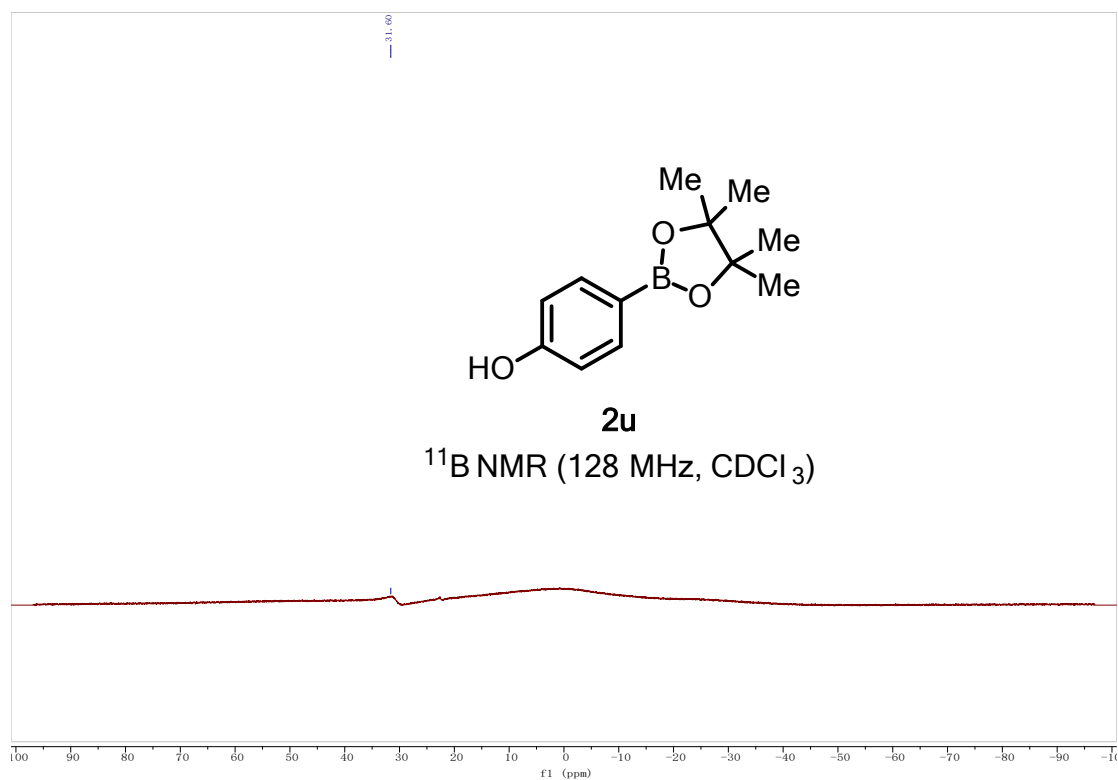
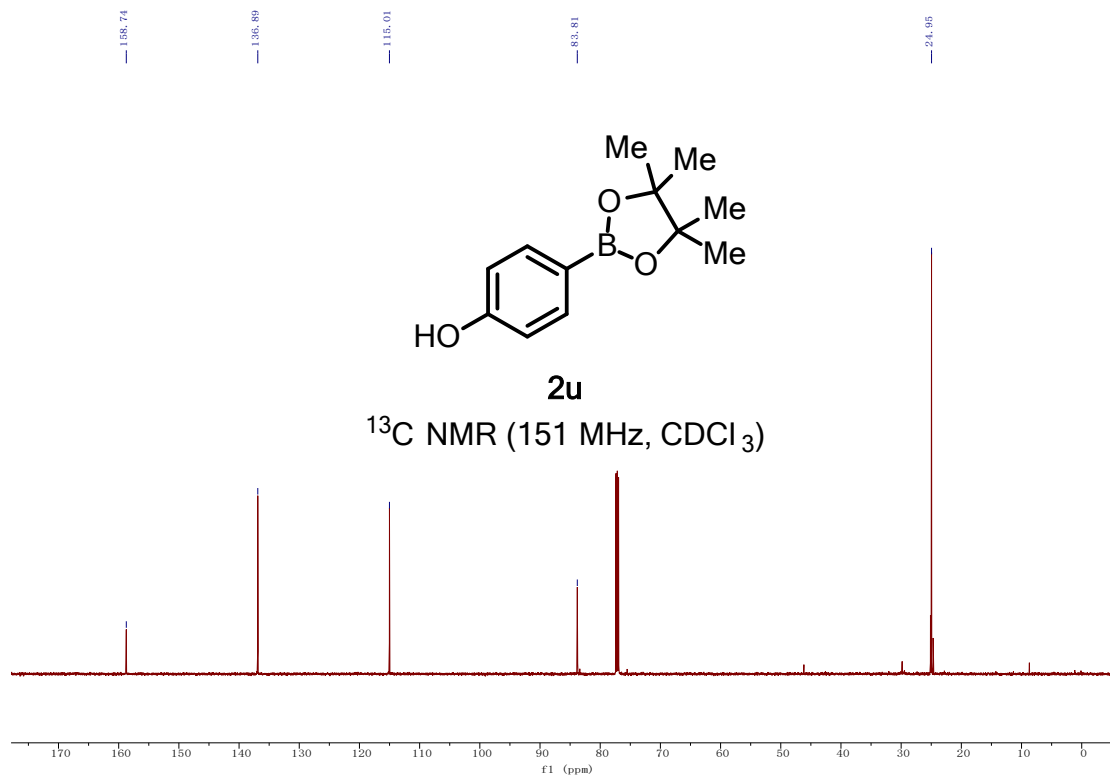
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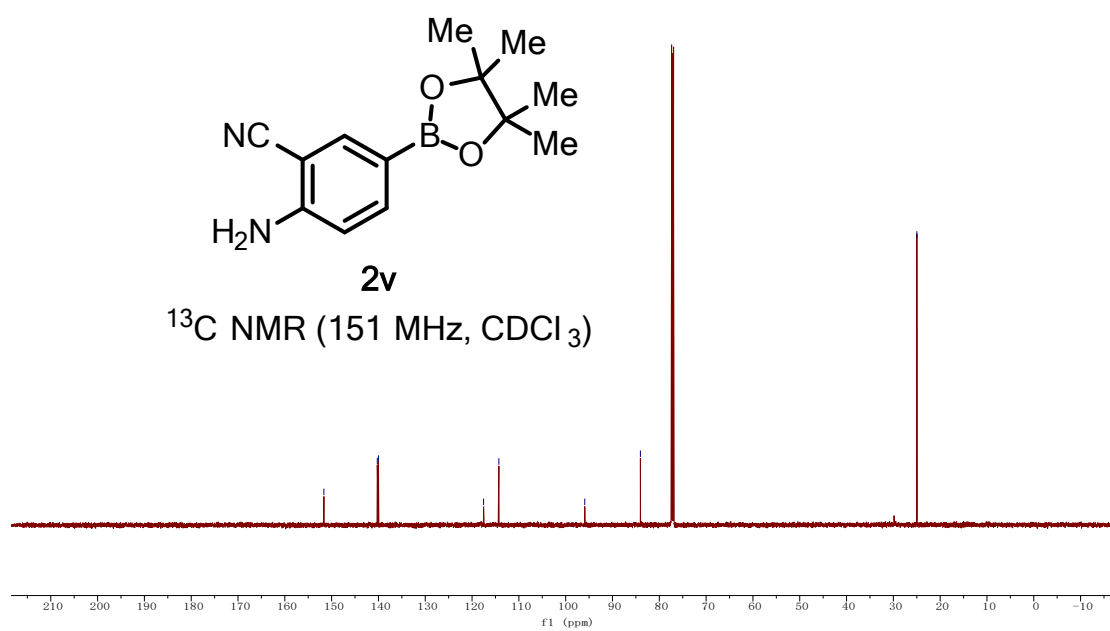
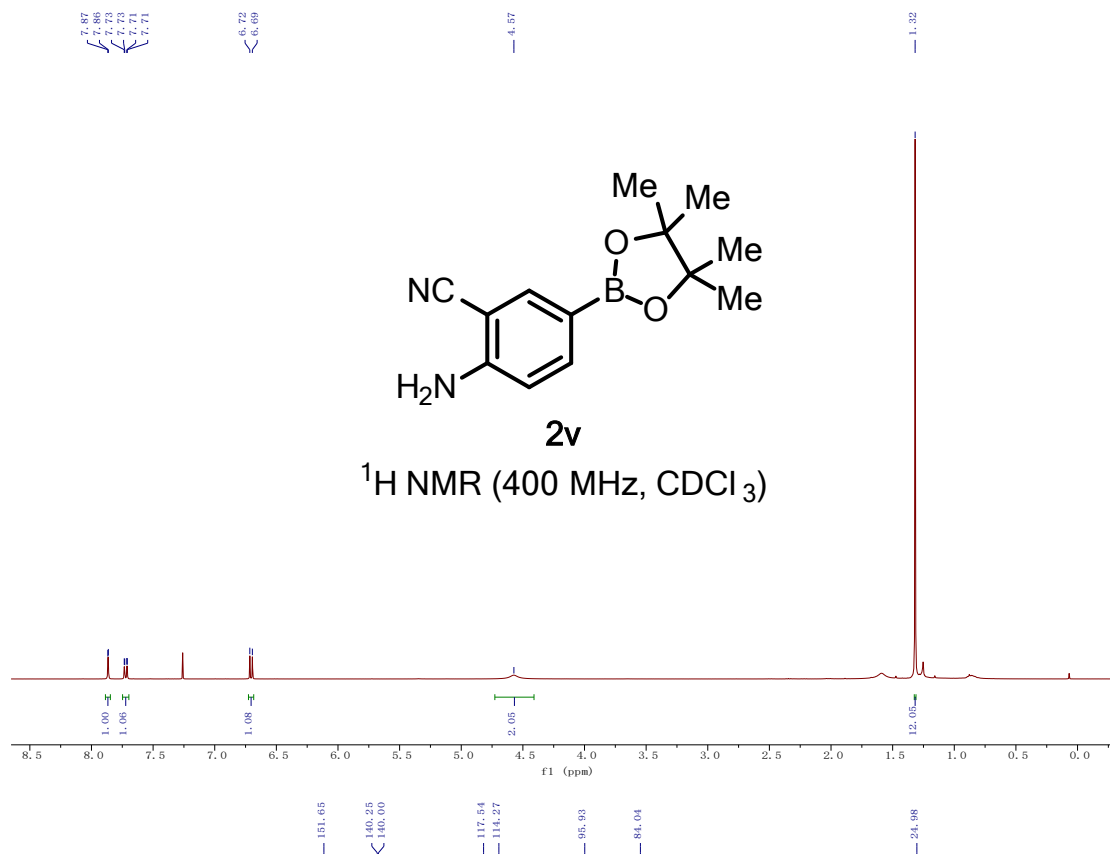


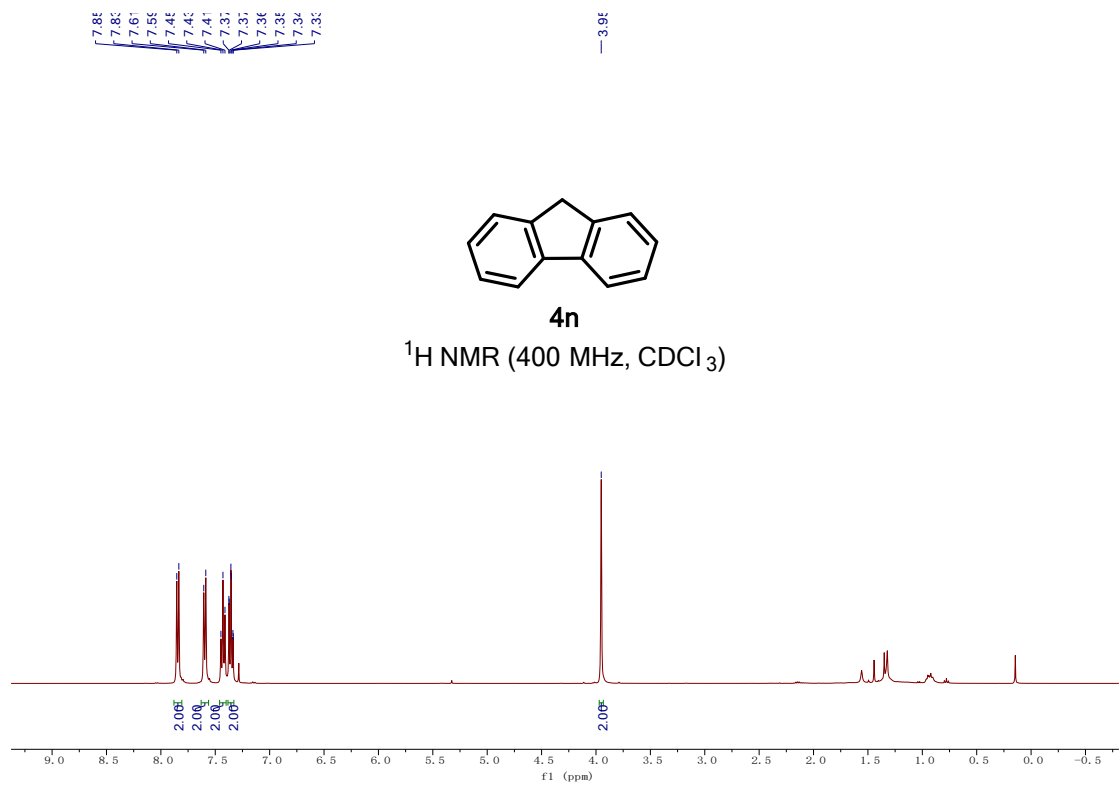
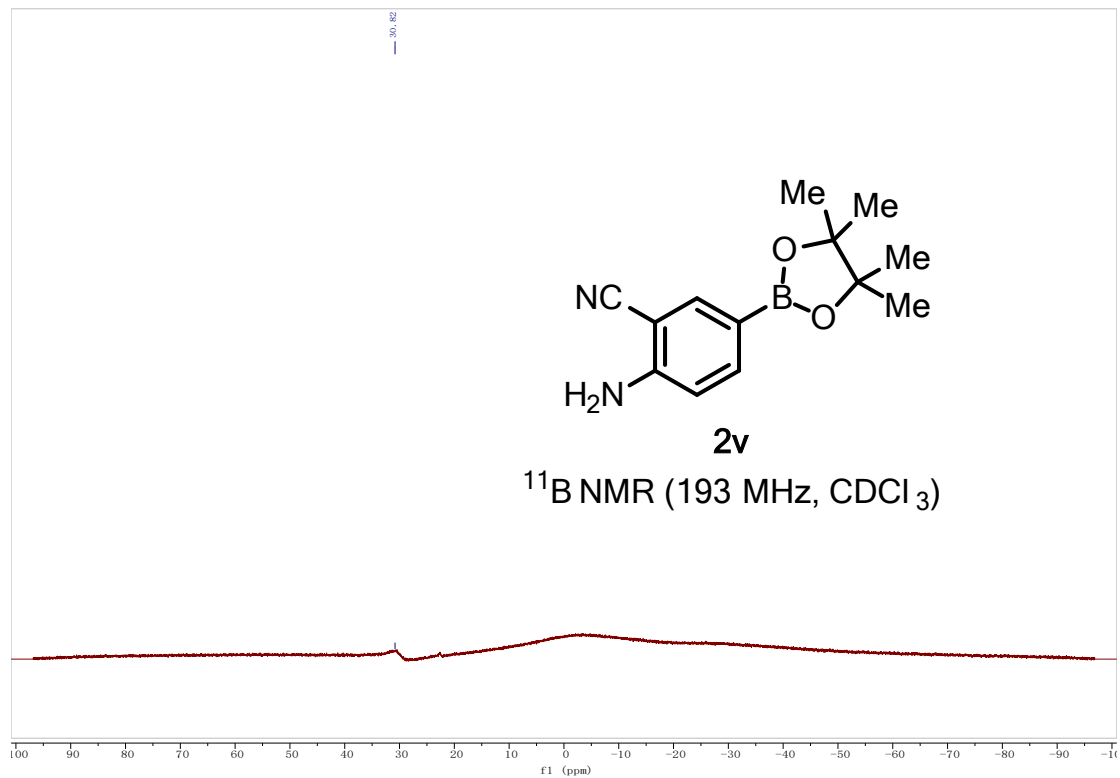




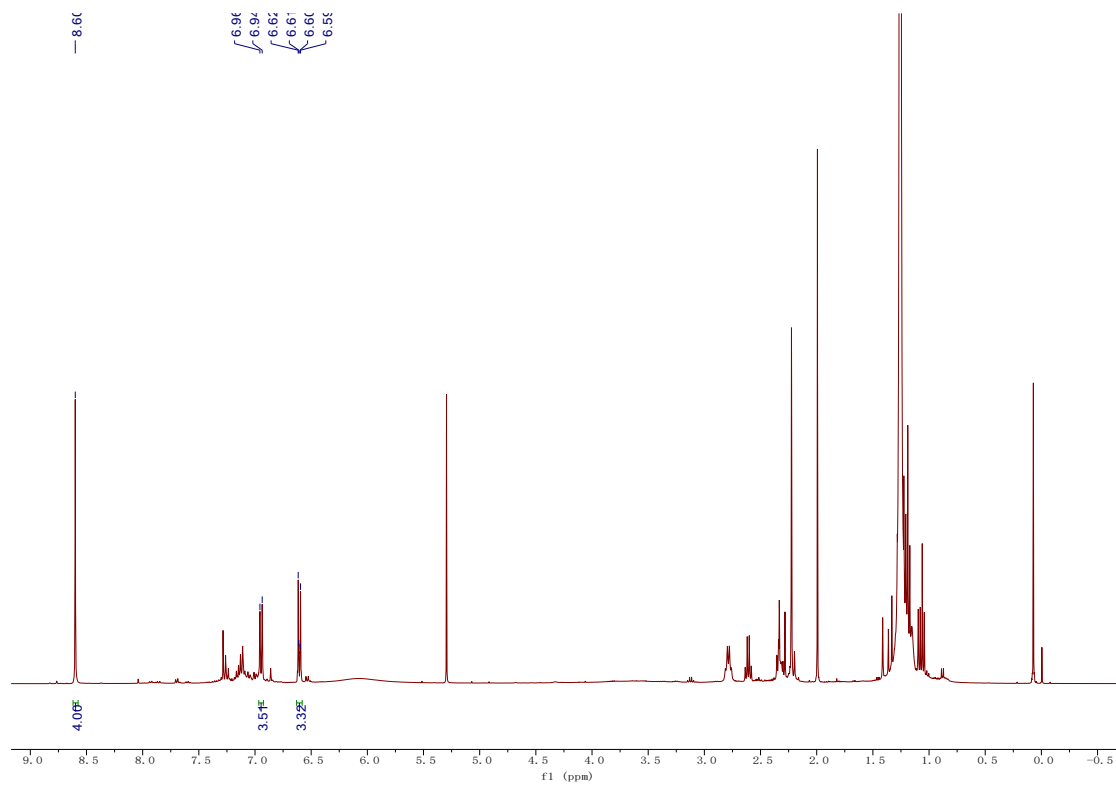
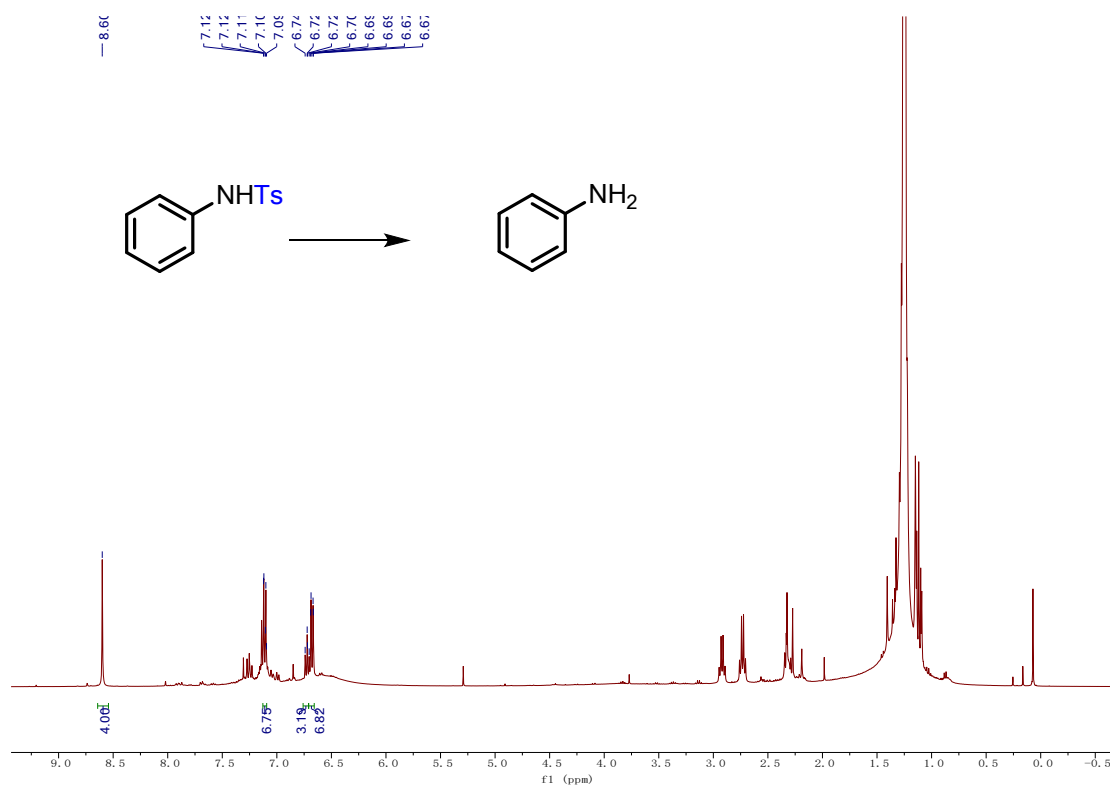


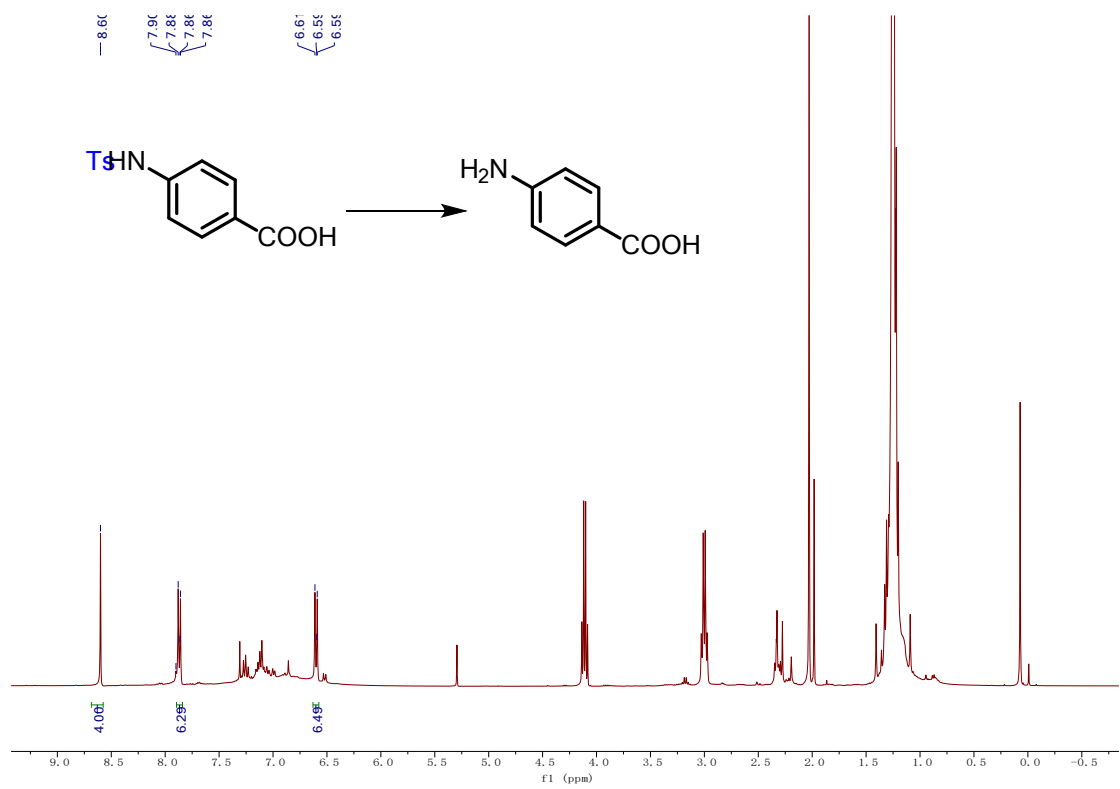
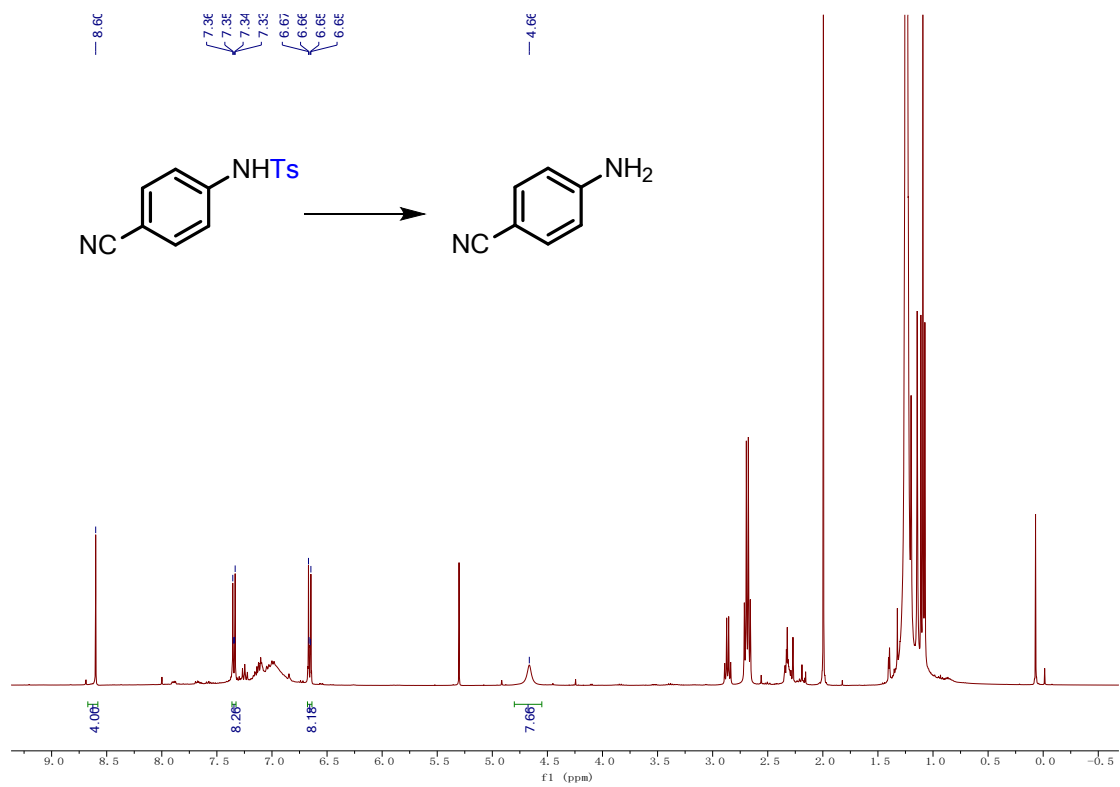


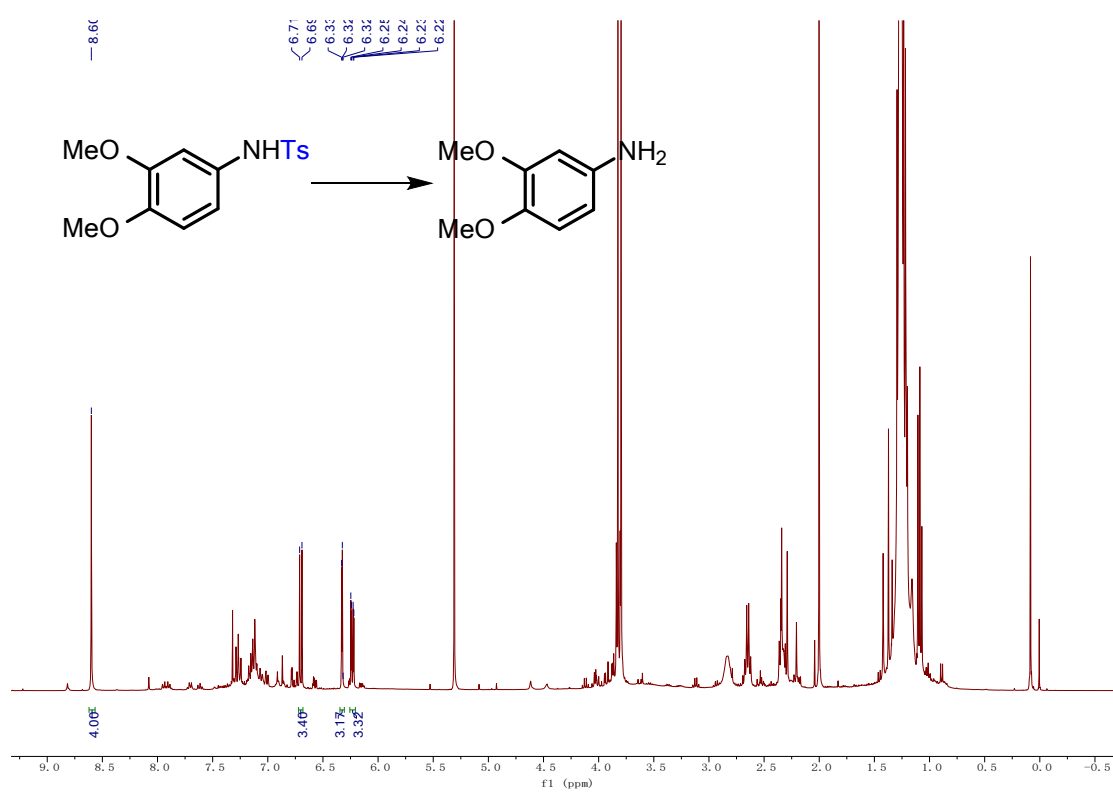
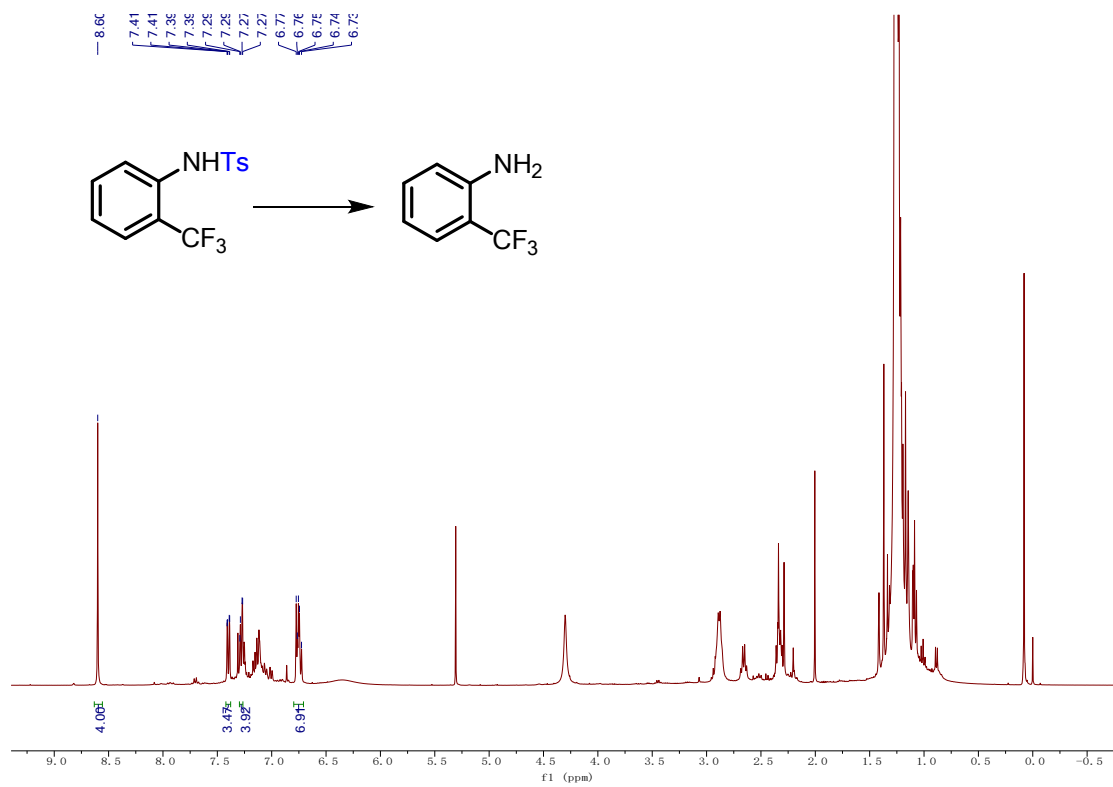


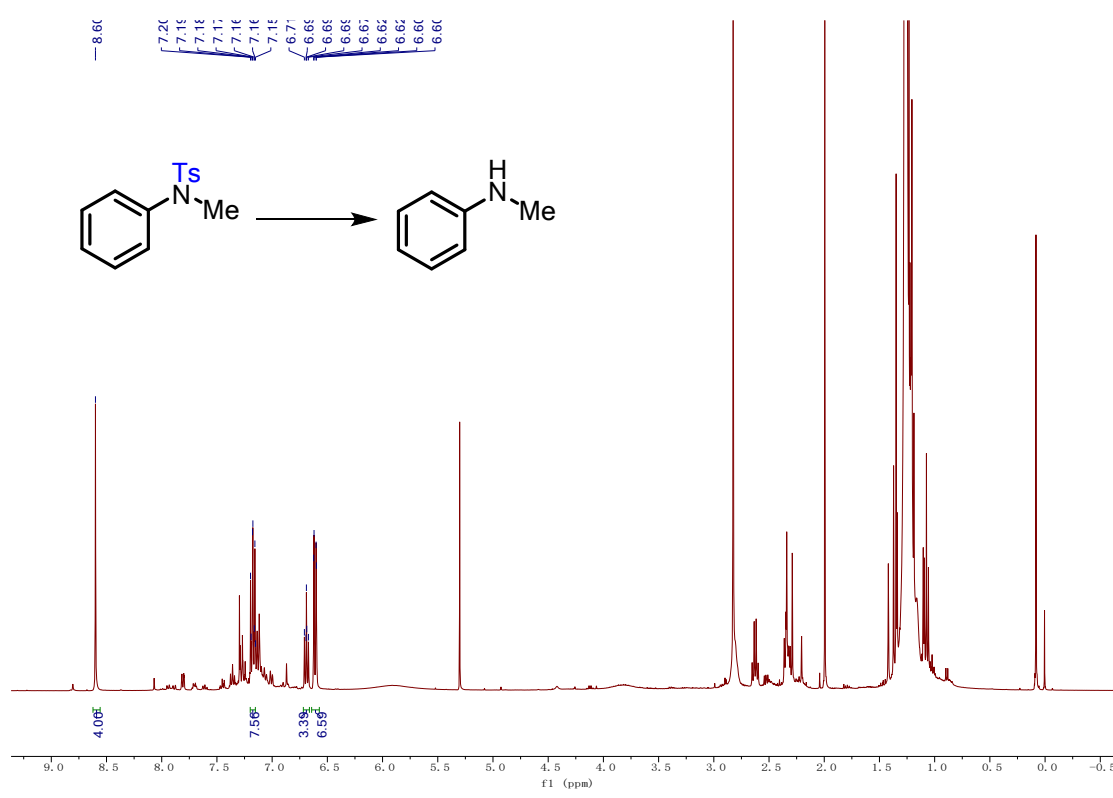
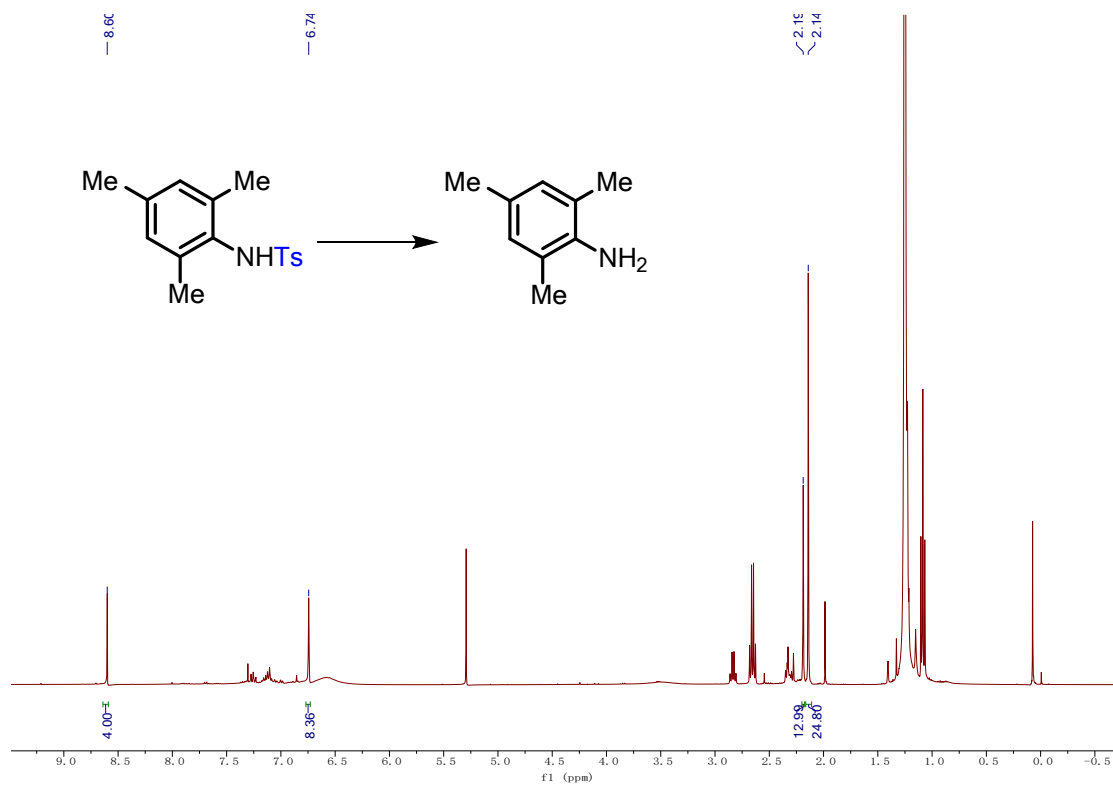


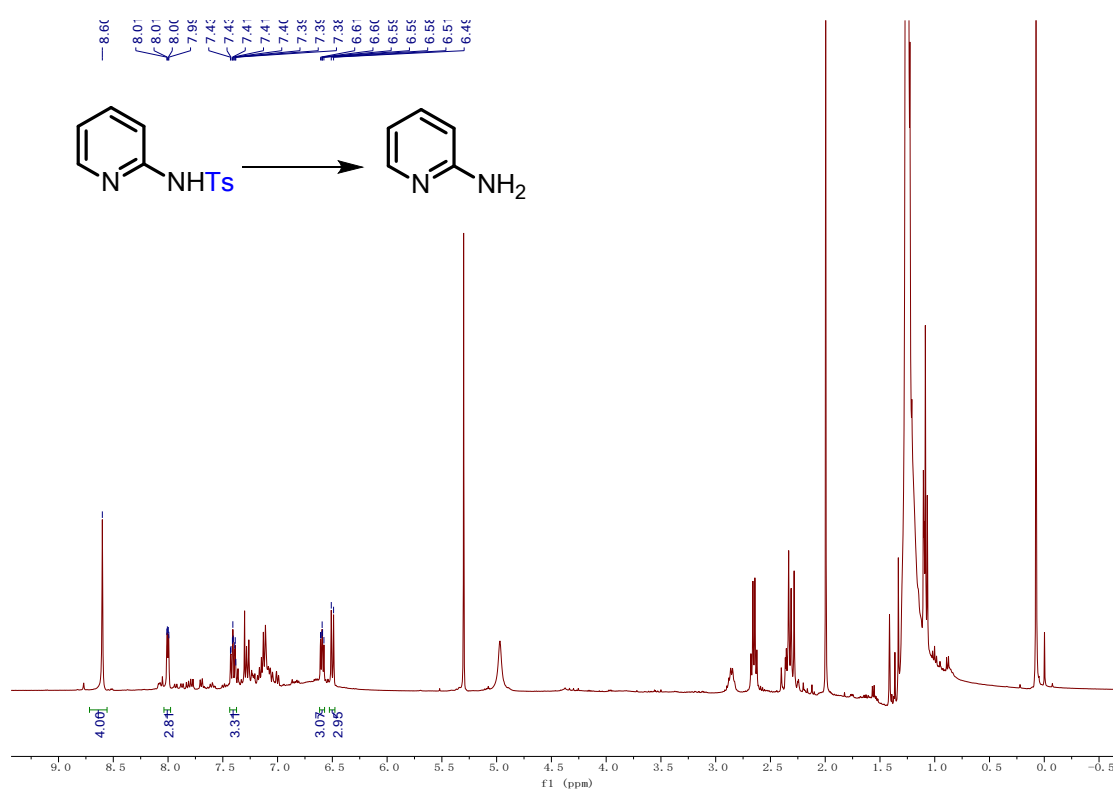
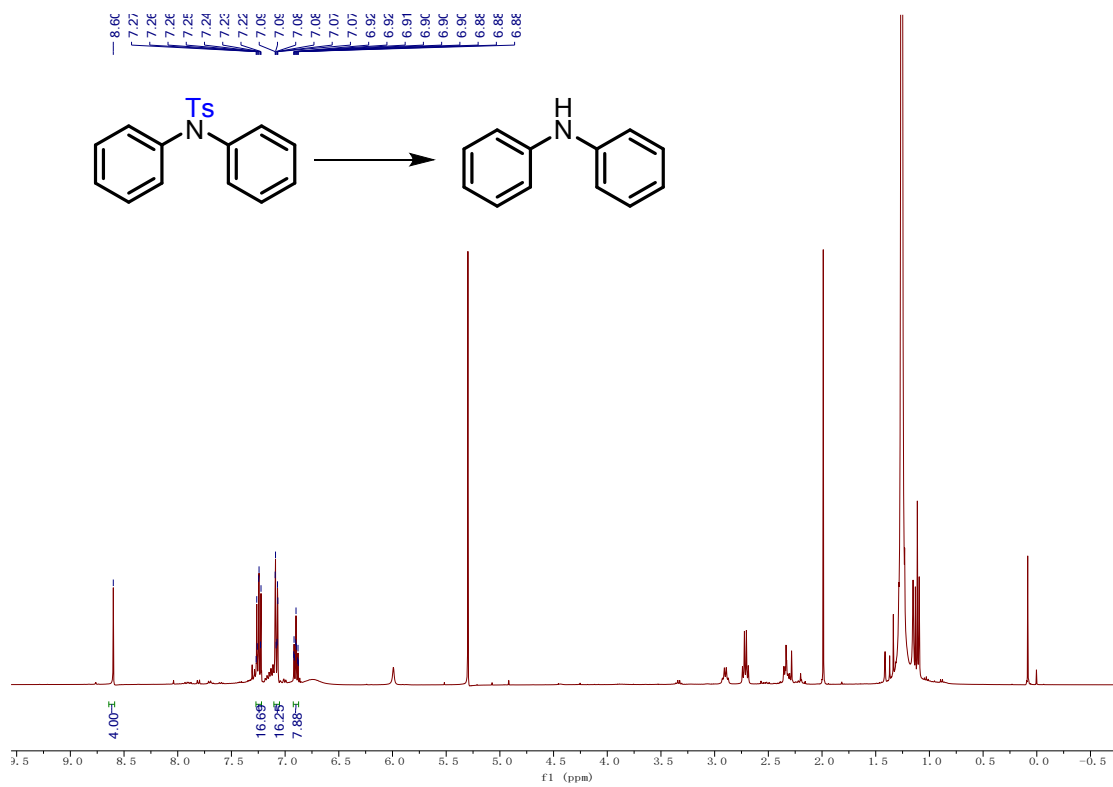
**¹H NMR Spectra of crude detosylation reactions
(pyrazine included for calculation of yield):**

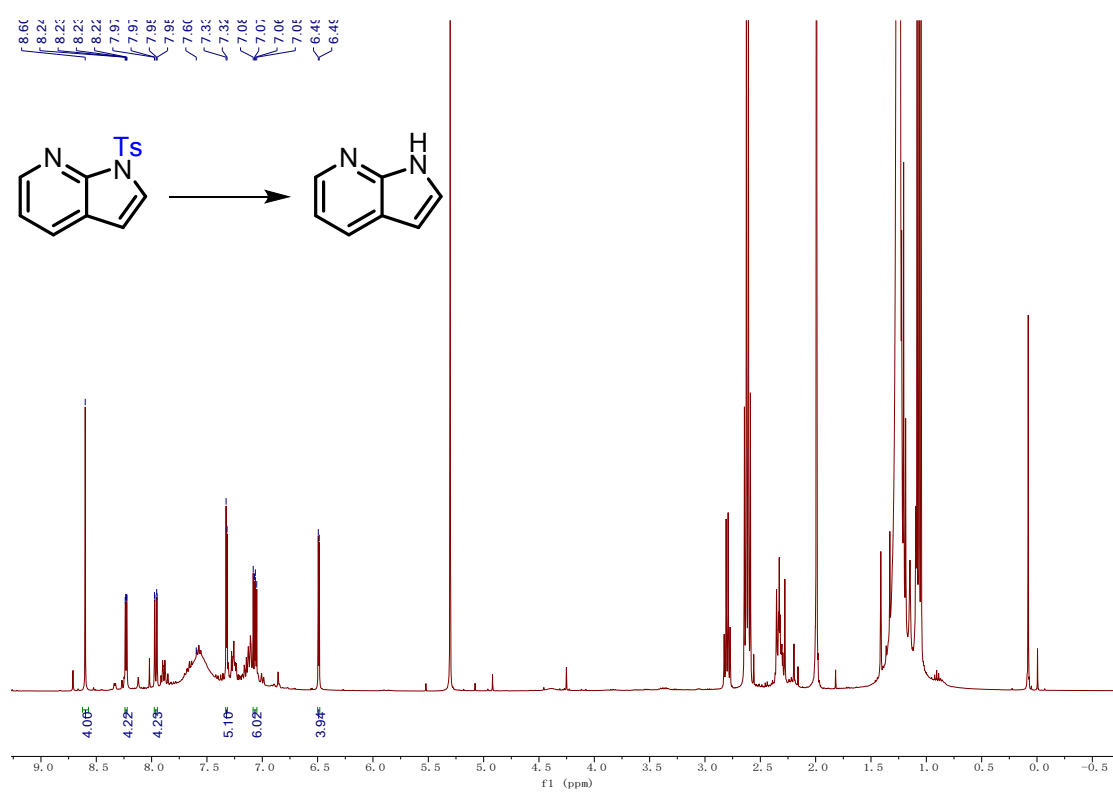
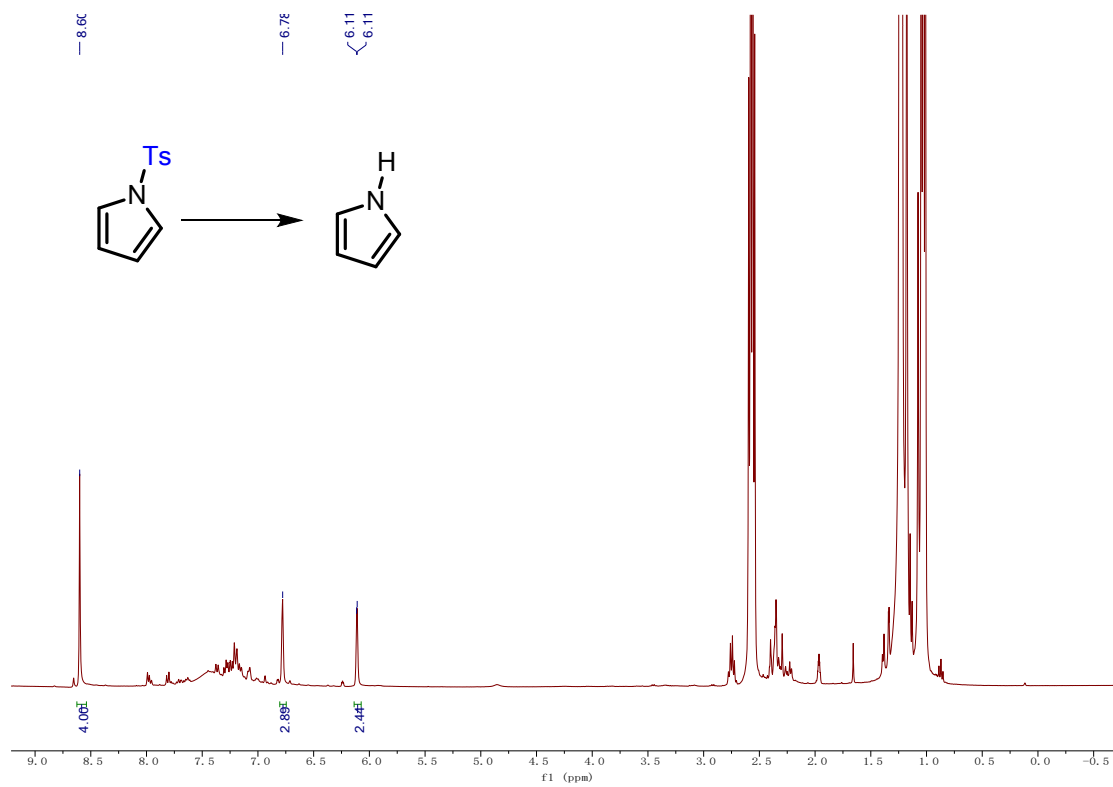


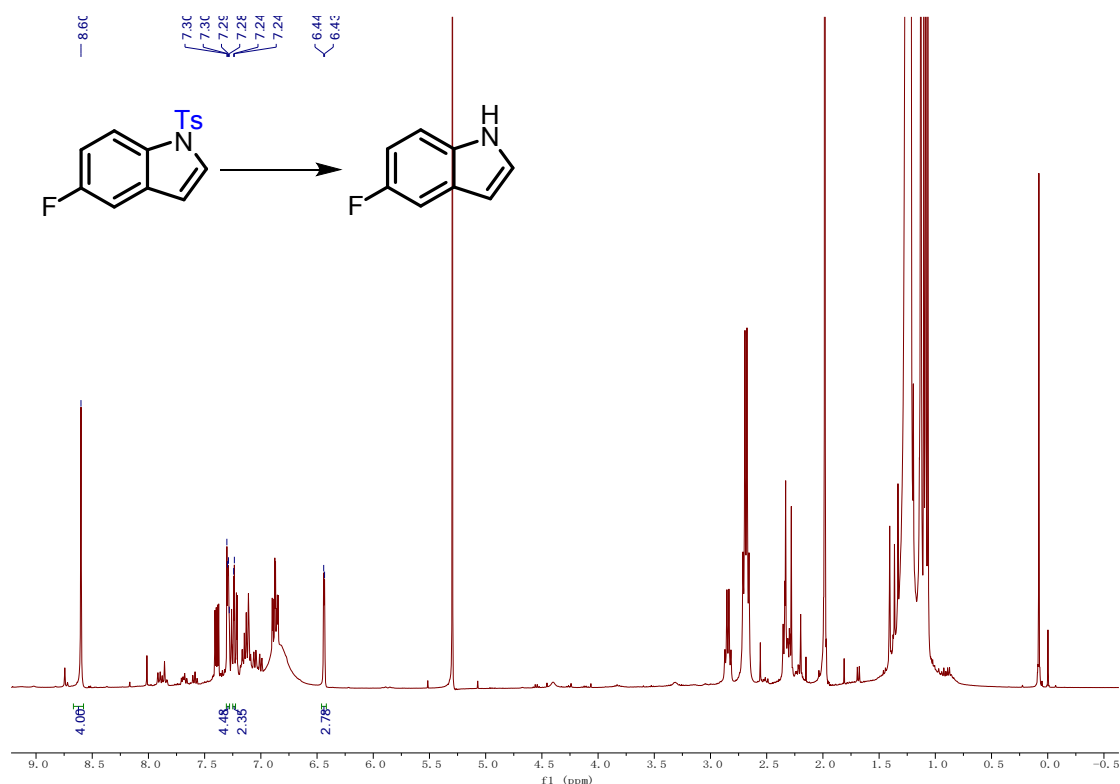












2. Computational supporting information

2.1 Computational details

All density functional theory (DFT) calculations were conducted with the Gaussian 16 program.¹ Geometry optimization and frequency calculation of ground state were carried out with the M062X² - def2SVP³ level of theory in PCM⁴-AcN solvent. The Gibbs free energies of excited state were performed under time dependent density functional theory⁵⁻⁷ (TD-DFT) calculations at M062X-def2TZVP level of theory in PCM-AcN solvent (single point energy) using geometries optimized at M062X- def2SVP level of theory in PCM-AcN solvent. The Gibbs free energies of cation radical were calculated at the unrestricted M062X- def2TZVP level of theory in PCM-AcN solvent (single point energy) using geometries optimized at unrestricted 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. $\Delta G_{OX}=G(\mathbf{B}^*)-G(\mathbf{B}^+)$.⁸⁻¹¹

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

Table S3. S₁ Excited state photoredox properties of D-A complex with different substituents calculated by DFT.

Substituent	E _{ex} (eV)	λ (nm)	f	E ⁰ _{S1,calc.} (² PC ⁺ / ¹ PC [*]) (V vs. SCE)	Electronic transition configuration	Coefficient
4-NH ₂	3.602	344	0.169	-3.453	174 → 175 (H → L)	0.537
					174 → 176 (H → L+1)	-0.420
					174 → 177 (H → L+2)	-0.131
6-CN	3.585	346	0.086	-2.512	178 → 179 (H → L)	0.595
					178 → 180 (H → L+1)	0.319
					178 → 182 (H → L+2)	0.101
6-H	3.953	314	0.225	-3.117	165 → 168 (H-1 → L+2)	0.106
					166 → 167 (H → L)	0.540
					166 → 168 (H → L+1)	-0.394
					166 → 169 (H → L+2)	-0.149
6-NH ₂	4.003	310	0.245	-3.257	173 → 176 (H-1 → L+2)	0.147
					174 → 175 (H → L)	0.494
					174 → 176 (H → L+1)	-0.452

a.λ is the transition wavelength and f is the oscillator strength. b.DFTcalculations performed at M06-2X/Def2TZVP//M06-2X/Def2SVP level of theory with CPCM-described solvation in aqueous solvent.

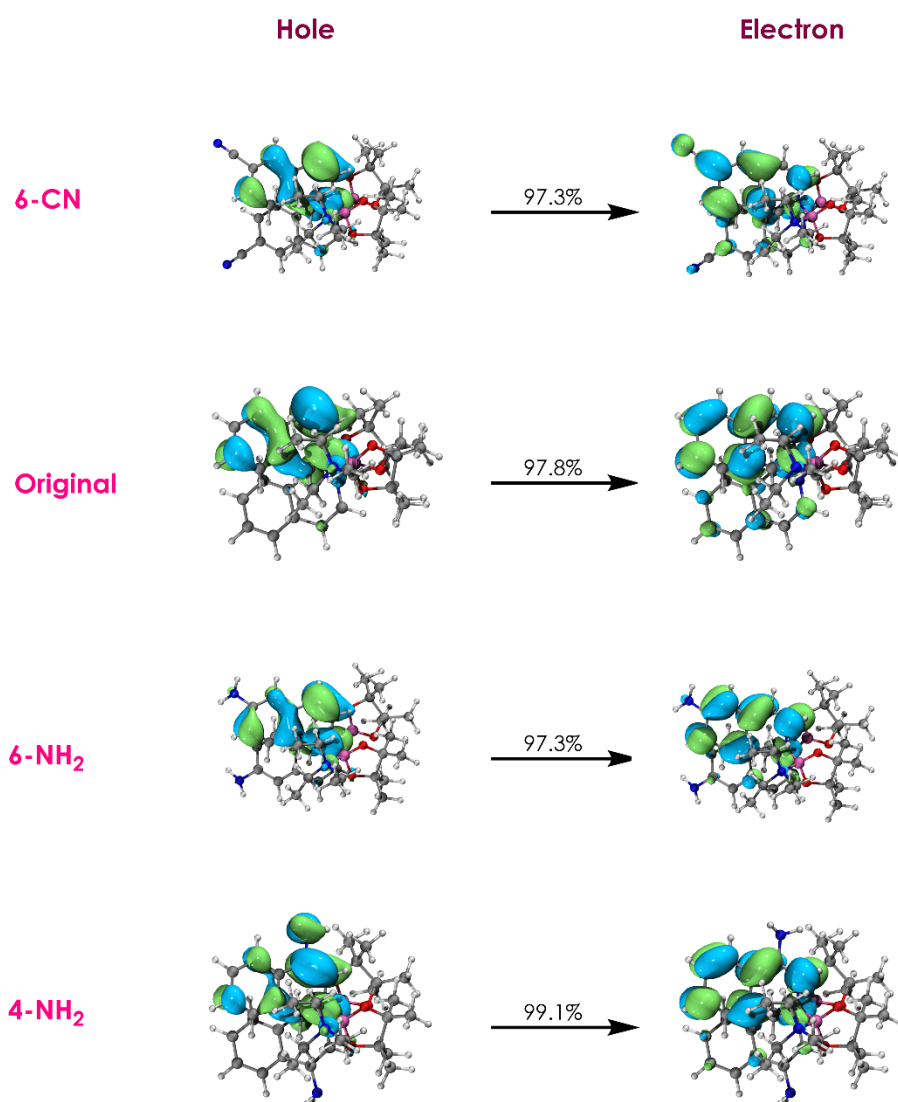


Figure S1. Natural transitions orbital (NTO) pair for S_1 excited state of original and substituted complexes (Top view).

2.2 Natural transitions orbital analysis

In addition to visualizing the hole and electron NTOs, the percentage contribution of each NTO pair to the overall transition density can provide a quantitative understanding of the transition. The higher the percentage, the more that specific hole-electron NTO pair contributes to the overall electron density shift during the excitation. The NTOs analysis reveal the S_1 transition involves excitation from the bonding orbitals of the benzene ring, olefin, and amine/triethylamine lone pairs into the anti-bonding orbitals of the benzene ring and olefin (Figure S1).

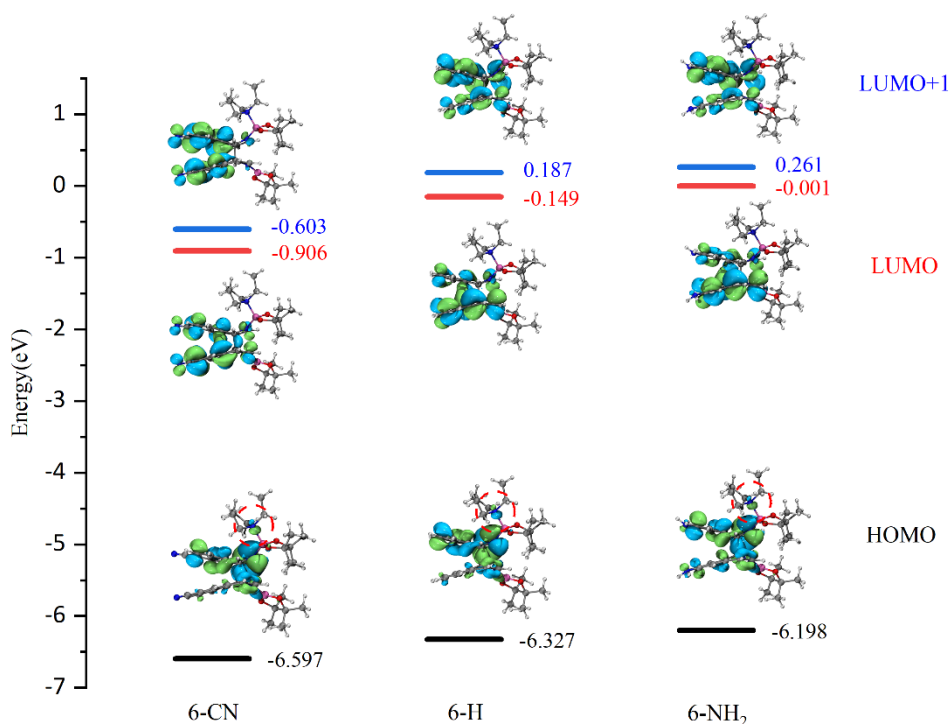


Figure S2. The orbital energies and contour plots of the HOMO, LUMO and LUMO+1 of the original and substituted complexes (Front view).

2.3 Frontier molecular orbital analysis

Analysis of the orbital transition coefficients showed that the primary description of the first singlet excited state involves the transition from HOMO to LUMO and HOMO to LUMO+1 transition across all three complexes. The orbital energies and contour plots of HOMO, LUMO and LUMO+1 orbitals of the original and substituted complexes are depicted in Figure S2. The proximity in energy levels of the LUMO and LUMO+1 orbitals across the three complexes align with the TDDFT results, indicating the S_1 state is a combination of HOMO- \rightarrow LUMO and HOMO- \rightarrow LUMO+1 transitions.

The HOMO orbitals are predominantly localized on the dimer core. But the molecular orbitals are delocalized over many atoms, making specific charge transfers difficult to visualize, a discernible electron density is distributed on the triethylamine group in HOMO orbitals (see red circle in Figure S2).

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