



Supporting Information

for

Transition-metal-free synthesis of arylboronates via thermal generation of aryl radicals from triarylbismuthines in air

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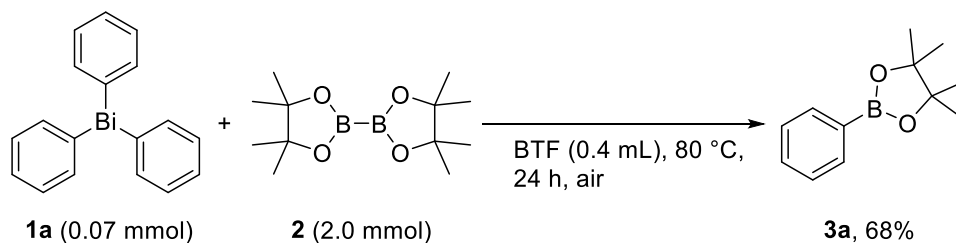
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Investigation of the boron residue in the crude mixture by ^{11}B NMR measurement, characterization data of the compounds, and copies of ^1H NMR and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra

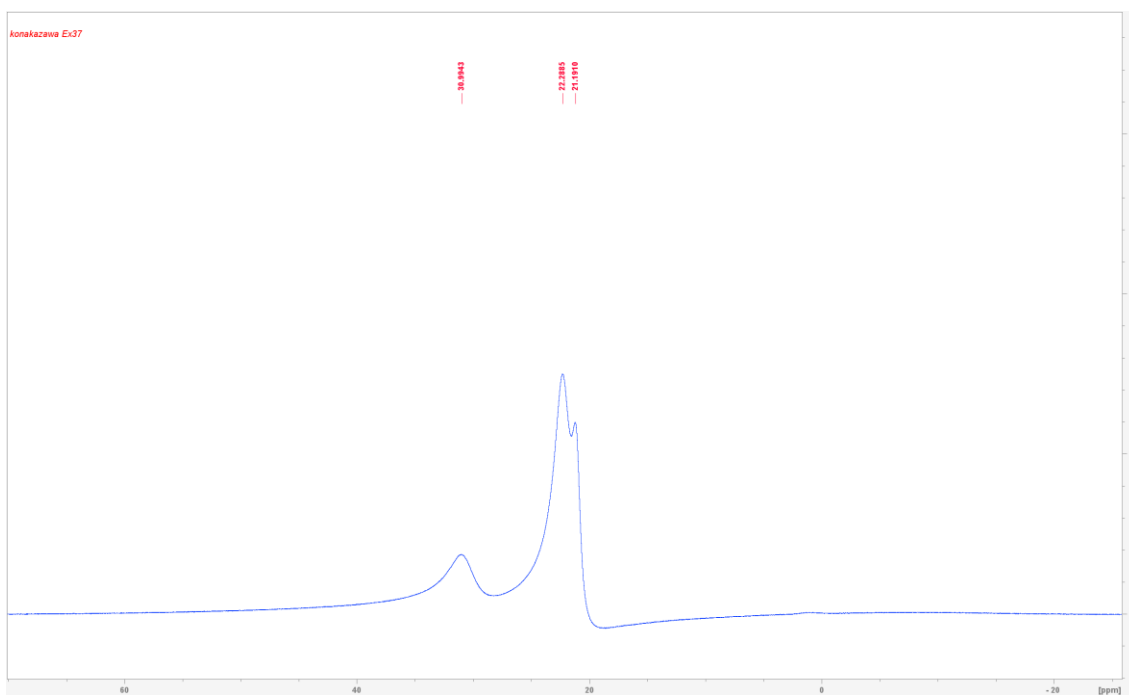
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Investigation of the boron residue in the crude mixture by ^{11}B NMR measurement



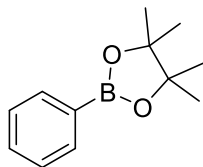
The reaction was carried out under the optimal condition (entry 2 in Scheme 2). The reaction mixture was then analyzed by ^{11}B NMR measurement in CDCl_3 using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the internal standard ($\delta = 0.0$ ppm).



The peaks of bispinacolatodiboron **2** ($\delta_{\text{B}} = 30.5$ ppm)^[1] and the product **3a** ($\delta_{\text{B}} = 30.9$ ppm)^[2] were overlapped in the ^{11}B NMR spectra. In addition, two other peaks were observed that could be attributed as pinB–O–Bpin ($\delta_{\text{B}} = 21.2$ ppm)^[1] and pinB–OH ($\delta_{\text{B}} = 22.3$ ppm)^[3], respectively. Therefore, we estimated that some of **2** might be decomposed under the reaction conditions.

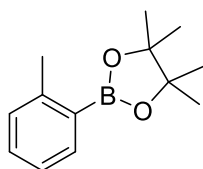
Characterization data of the arylboronates 3

4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (3a)^[2]



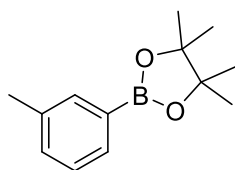
Light yellow solid, 22.6 mg, 53% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.46–7.44 (m, 1H), 7.38–7.35 (m, 2H), 1.35 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 134.8, 131.3, 127.8, 83.8, 24.9. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

4,4,5,5-Tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (3b)^[4]



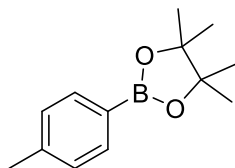
Colorless solid, 28.2 mg, 62% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.77–7.75 (m, 1H), 7.33–7.30 (m, 1H), 7.17–7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H) ¹³C NMR (126 MHz, CDCl₃): δ 144.9, 135.9, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

4,4,5,5-tetramethyl-2-(m-tolyl)-1,3,2-dioxaborolane (3c)^[4]



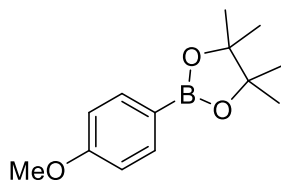
Colorless oil, 10.8 mg, 24% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.64 (s, 1H), 7.62–7.60 (m, 1H), 7.28–7.26 (m, 2H), 2.35 (s, 3H), 1.35 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 137.2, 135.4, 132.1, 131.8, 127.7, 83.7, 24.9, 21.3. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

4,4,5,5-Tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane (3d)^[5]



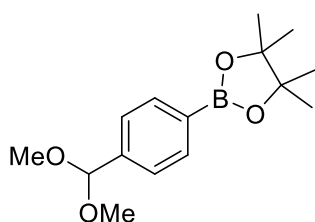
Light brown oil, 22.6 mg, 49% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.70 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 141.4, 134.8, 128.5, 83.6, 24.9, 21.8. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e)^[4]



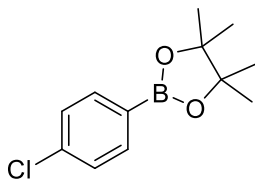
Colorless oil, 25.6 mg, 52% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.75 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 162.1, 136.5, 113.3, 83.6, 55.1, 24.9. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

2-(4-(Dimethoxymethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)^[5]



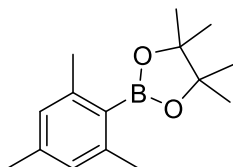
Colorless oil, 20.6 mg, 35% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 5.42 (s, 1H), 3.31 (s, 6H), 1.35 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 140.9, 134.7, 126.1, 102.9, 83.8, 52.6, 24.9. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)^[4]



Colorless oil, 22.5 mg, 45% yield; ¹H NMR (500 MHz, CDCl₃): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 1.34 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 137.5, 136.1, 128.1, 84.0, 24.9. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

2-Mesityl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)^[2]



Colorless oil, 31.7 mg, 61% yield; ¹H NMR (500 MHz, CDCl₃): δ 6.77 (s, 2H), 2.36 (s, 6H), 2.24 (s, 3H), 1.37 (s, 12H); ¹³C NMR (126 MHz, CDCl₃): δ 142.1, 138.9, 127.5, 83.5, 25.0, 22.2, 21.3. The ¹³C signal bound to boron could not be observed due to quadrupolar relaxation.

The isolation of arylboronates **3c**, **3i**, and **3j** with sufficient isolated yields was somewhat difficult due to strong adsorption or decomposition on silica gel. The characterization of the arylboronates was determined from previously reported spectra.^[2, 4, 6]

References

- [1] De Smet, G.; Bai, X.; Mensch, C.; Sergeev, S.; Evano, G.; Maes, B. U. W. *Angew. Chem. Int. Ed.* **2022**, *61*, e202201751.
- [2] Tan, X.; Wang, X.; Hua Li, Z.; Wang, H. *J. Am. Chem. Soc.* **2022**, *144*, 23286–23291.
- [3] Ji, P.; Sawano, T.; Lin, Z.; Urban, A.; Boures, D.; Lin, W. *J. Am. Chem. Soc.* **2016**, *138*, 14860–14863.
- [4] Zhang, J.; Wei, R.; Ren, C.; Liu, L. L.; Wu, L. *J. Am. Chem. Soc.* **2023**, *145*, 15619–15629.
- [5] Clary, J. W.; J. Rettenmaier, T. J.; Snelling, R.; Bryks, W.; Banwell, J.; Wipke, W. T.; Singaram, B. *J. Org. Chem.* **2011**, *76*, 9602–9610.
- [6] Li, D.; Wei, L.; Xiong, W.; Jiang, H.; Qi, C. *J. Org. Chem.* **2023**, *88*, 5231–5237.

Copies of ^1H NMR and ^{13}C NMR spectra of the arylboronates **3**

Figure S1. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3a**

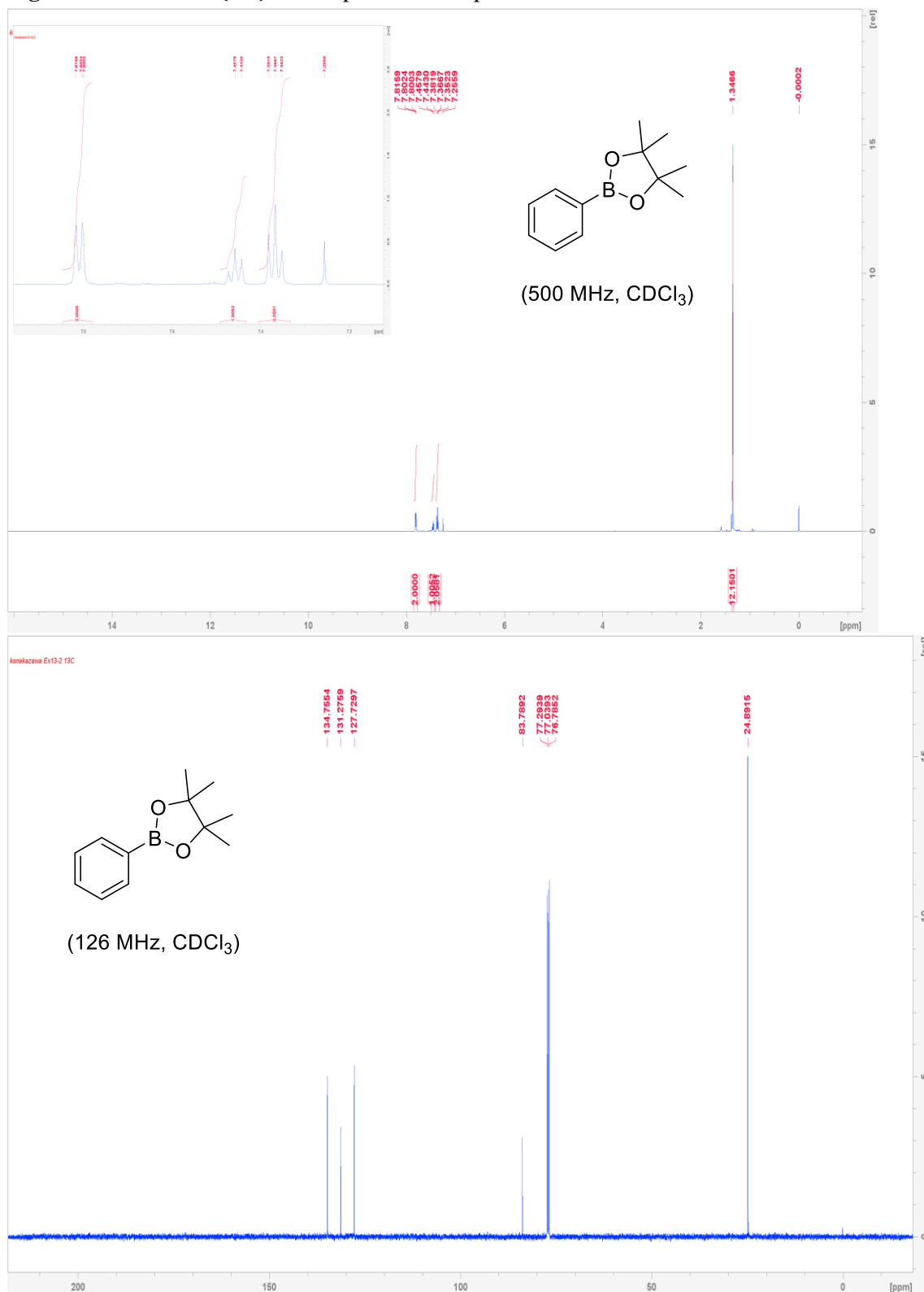


Figure S2. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3b**

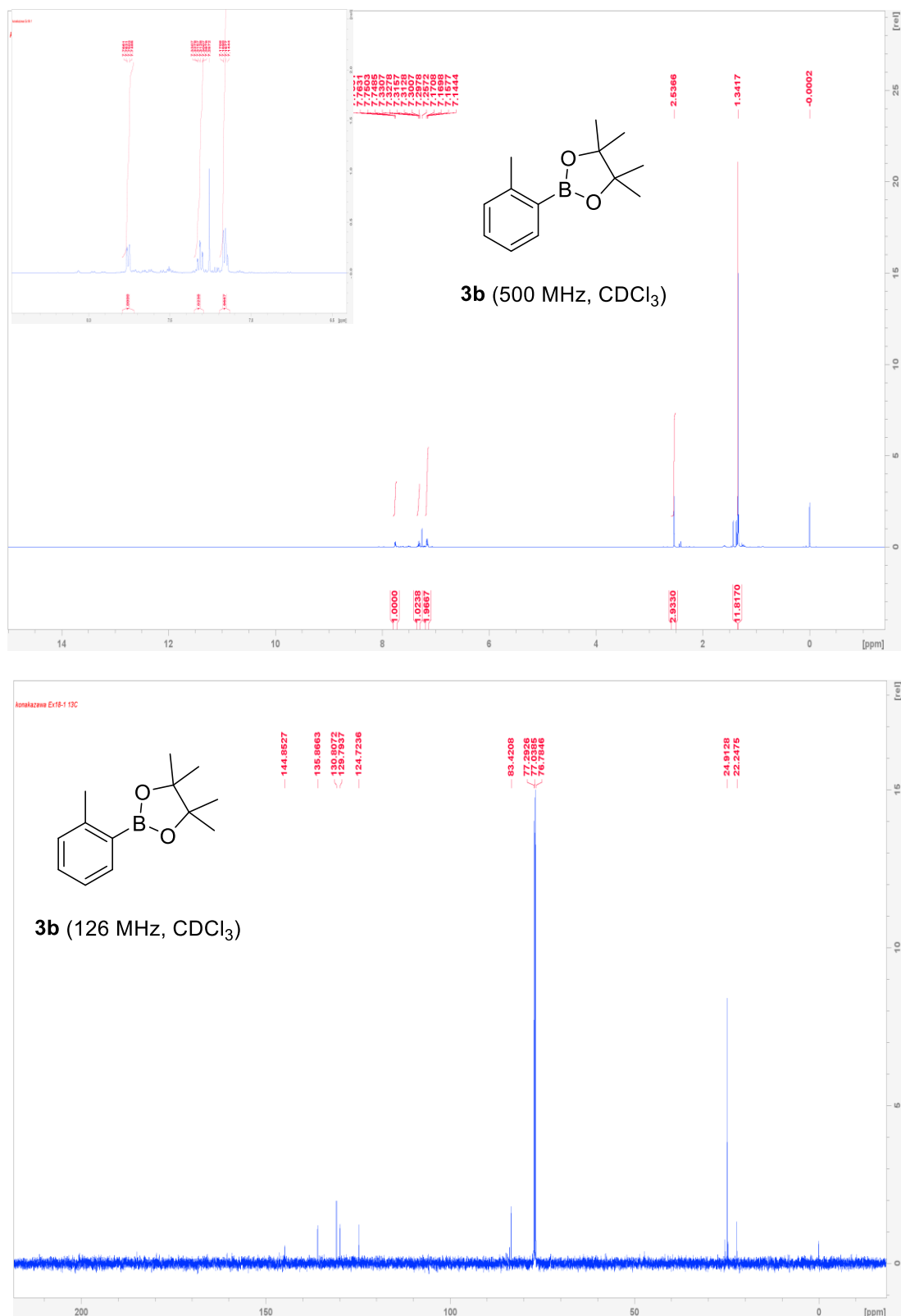


Figure S3. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3c**

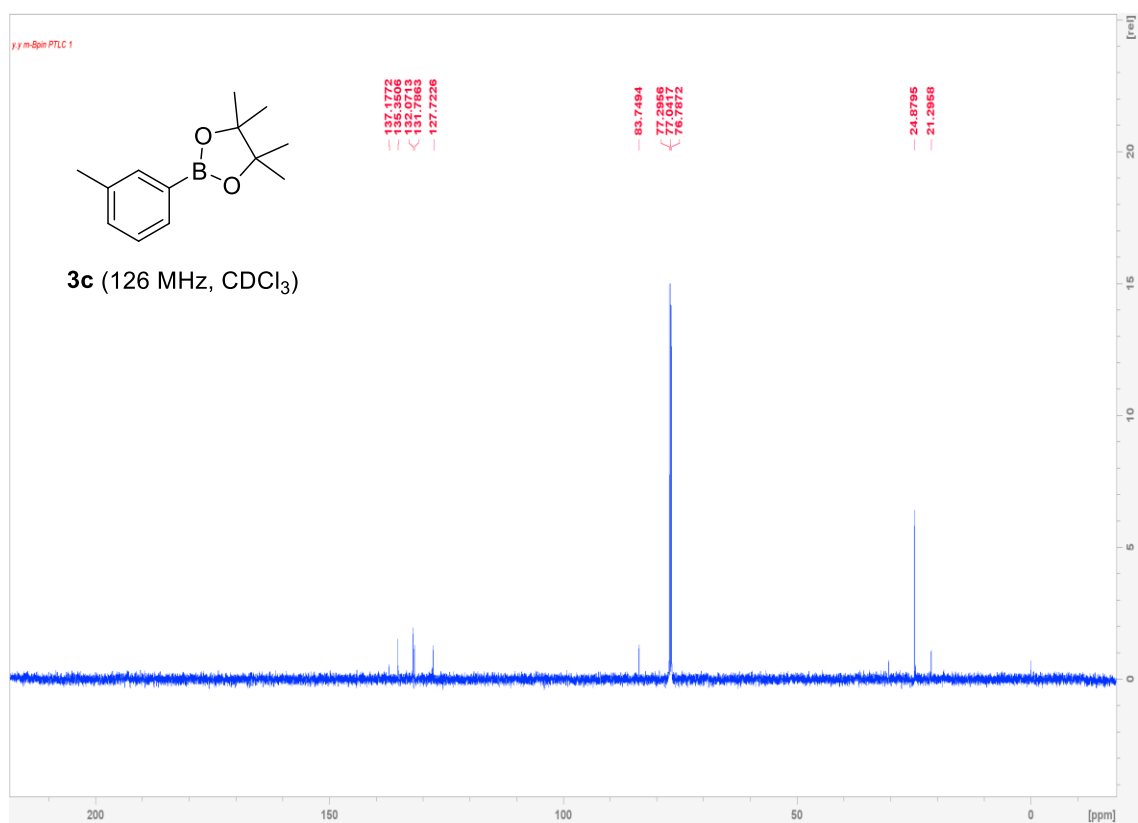
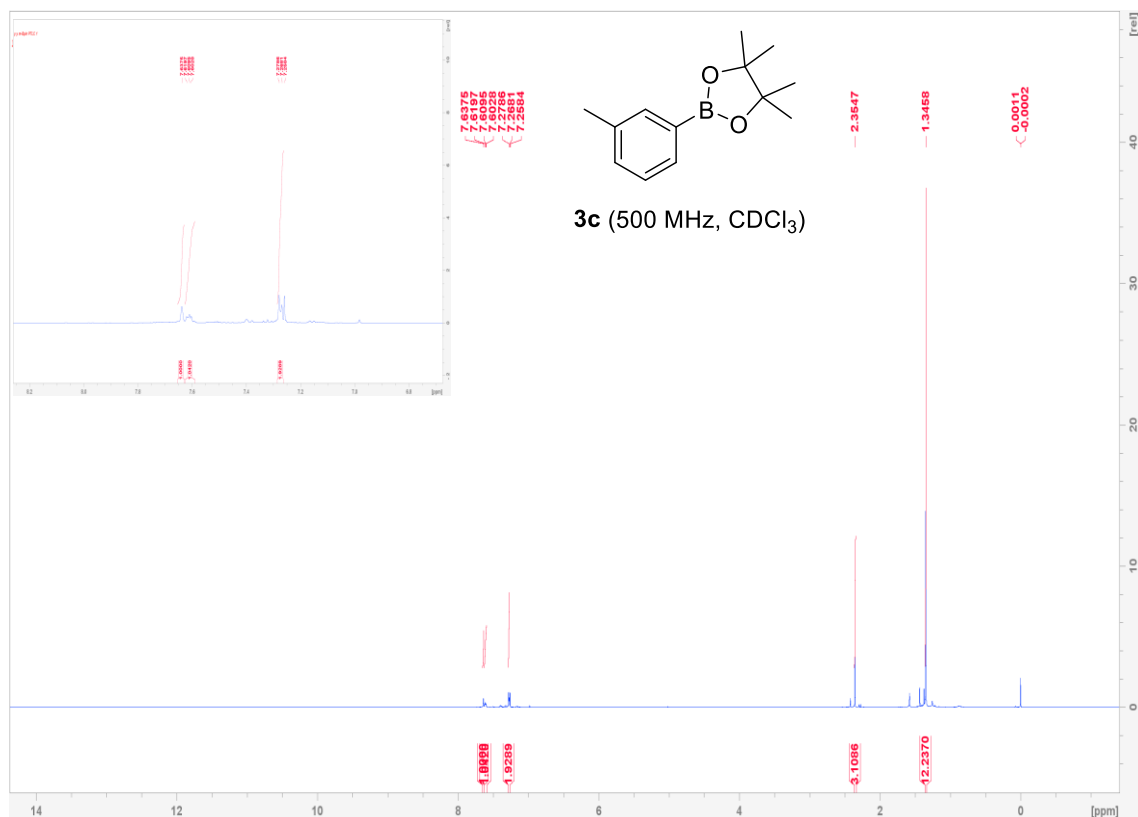


Figure S4. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3d**

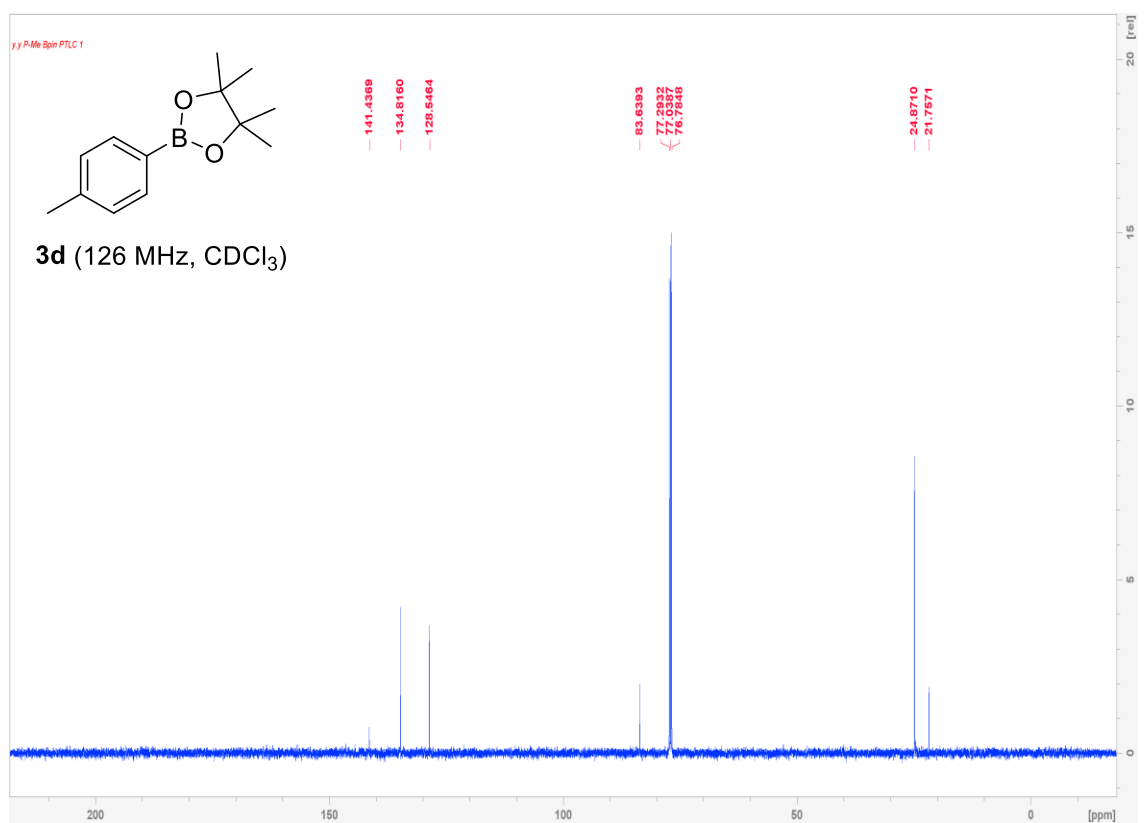
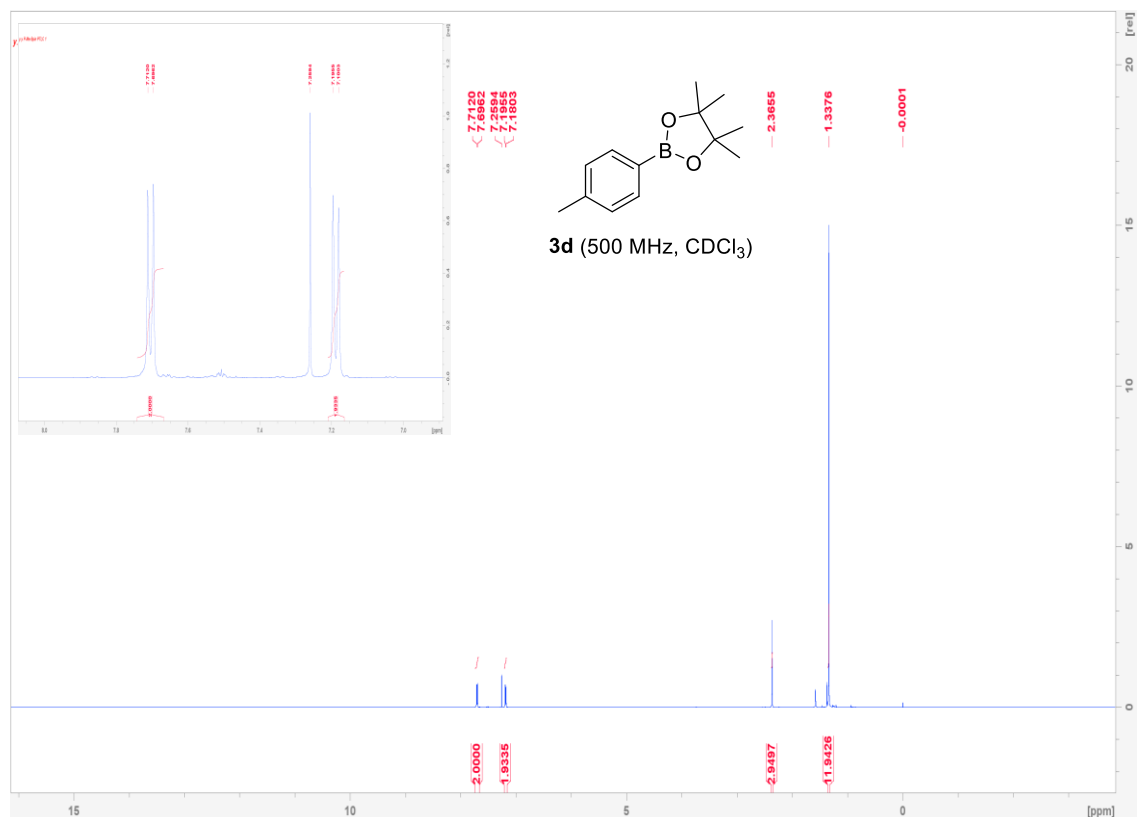


Figure S5. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3e**

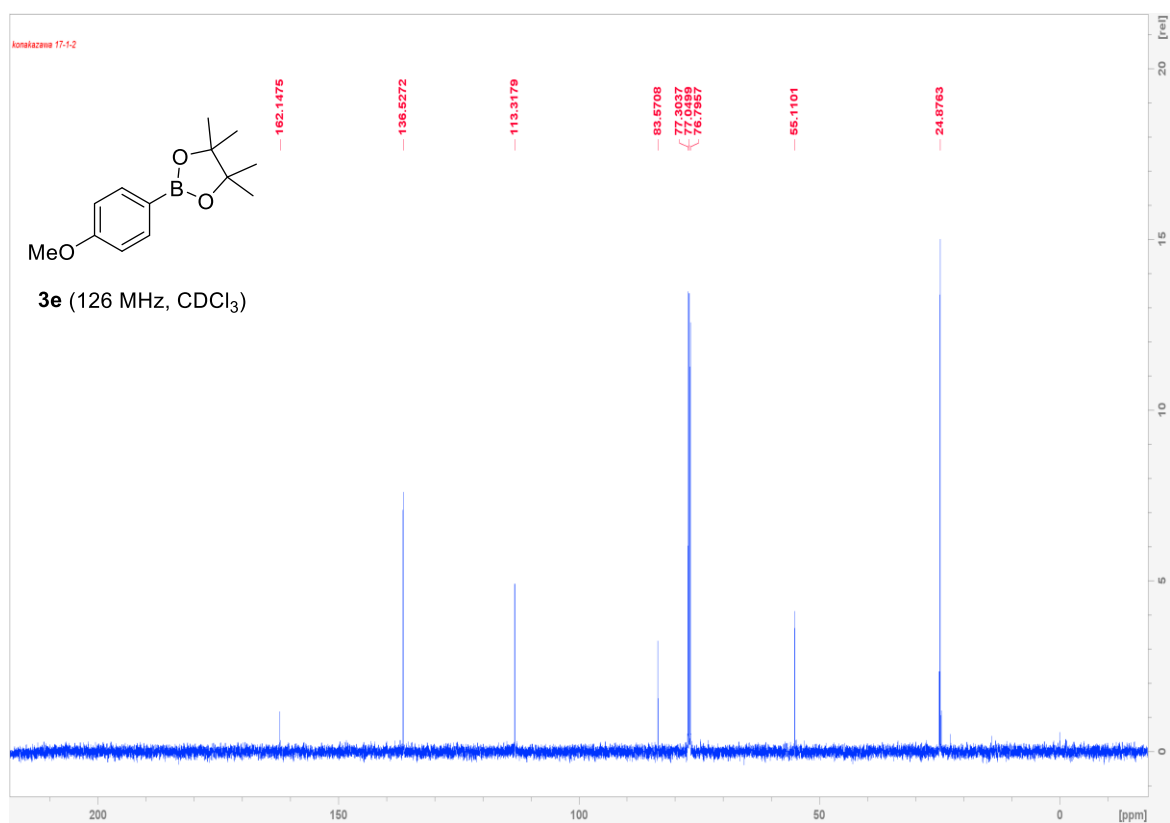
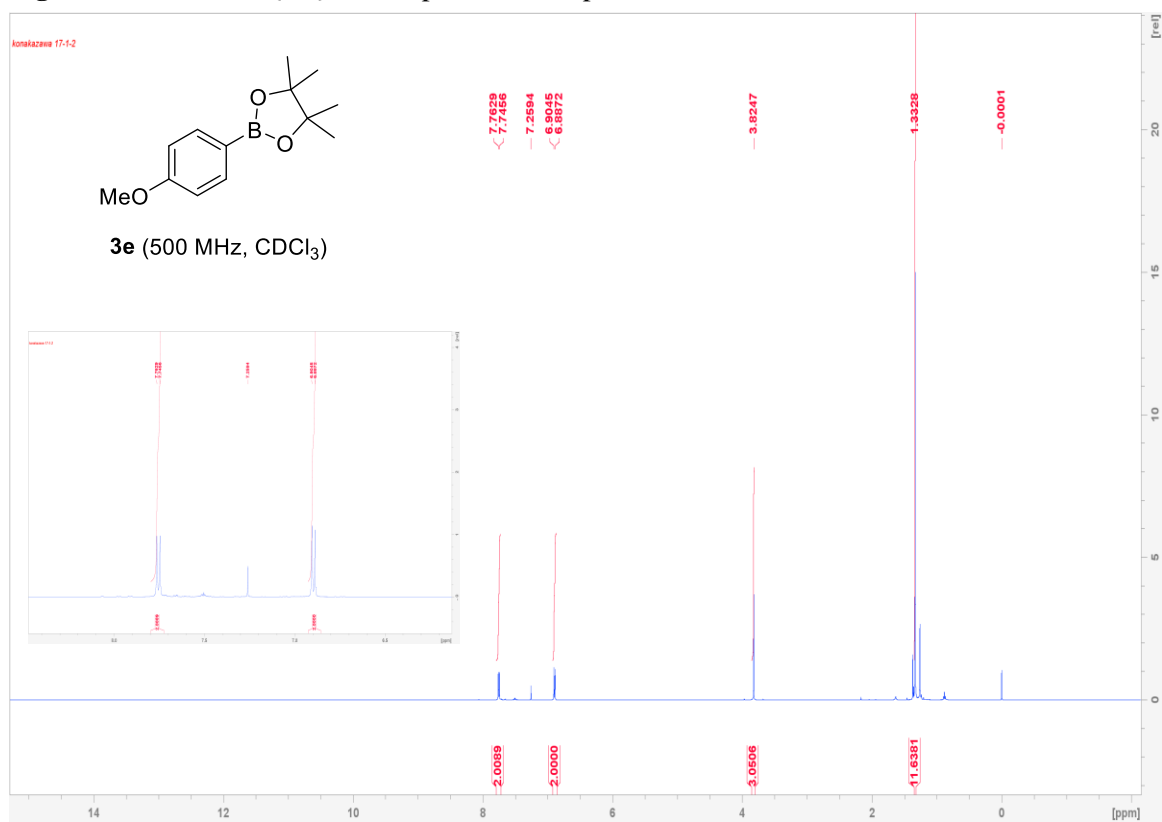


Figure S6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3f**

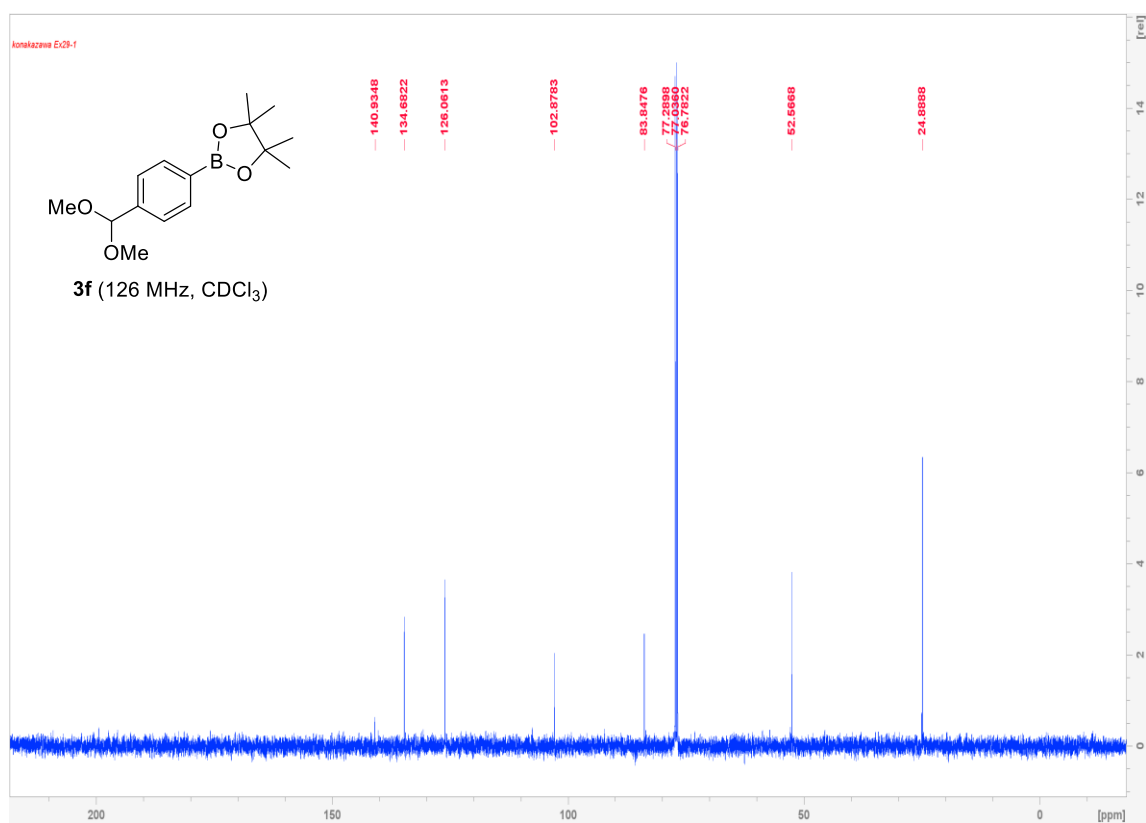
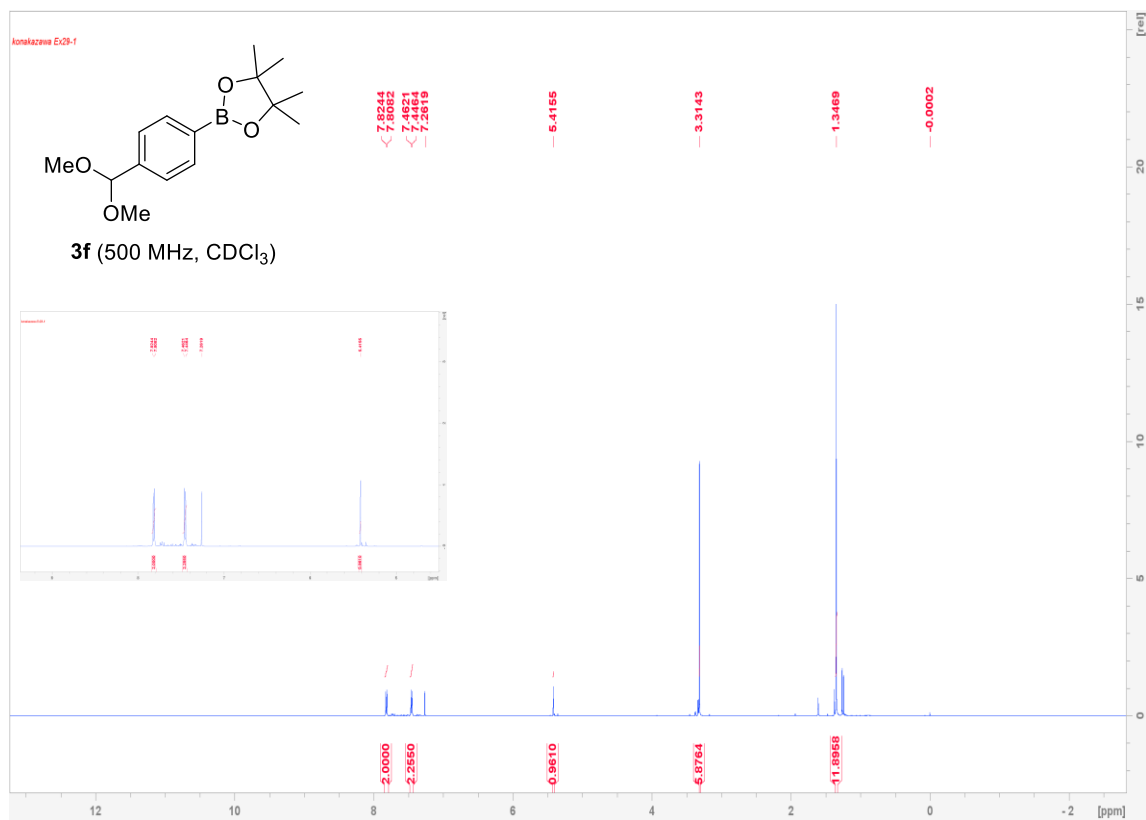


Figure S7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3g**

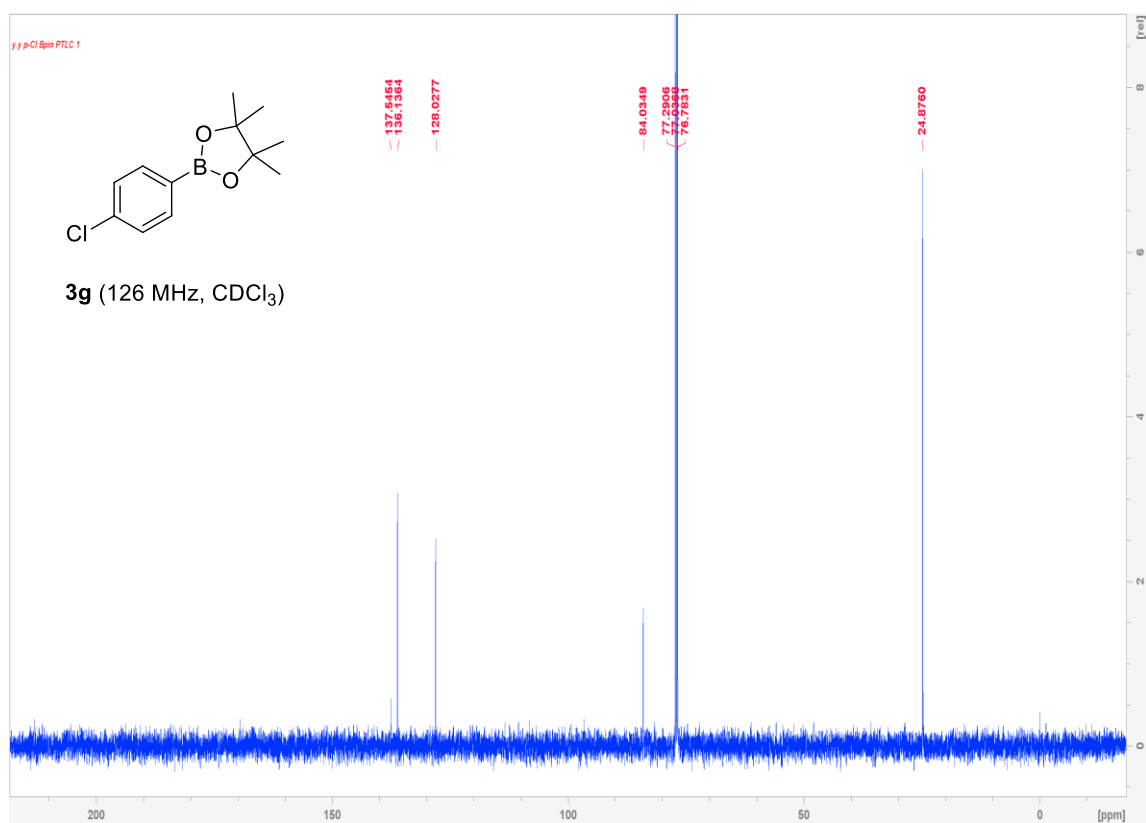
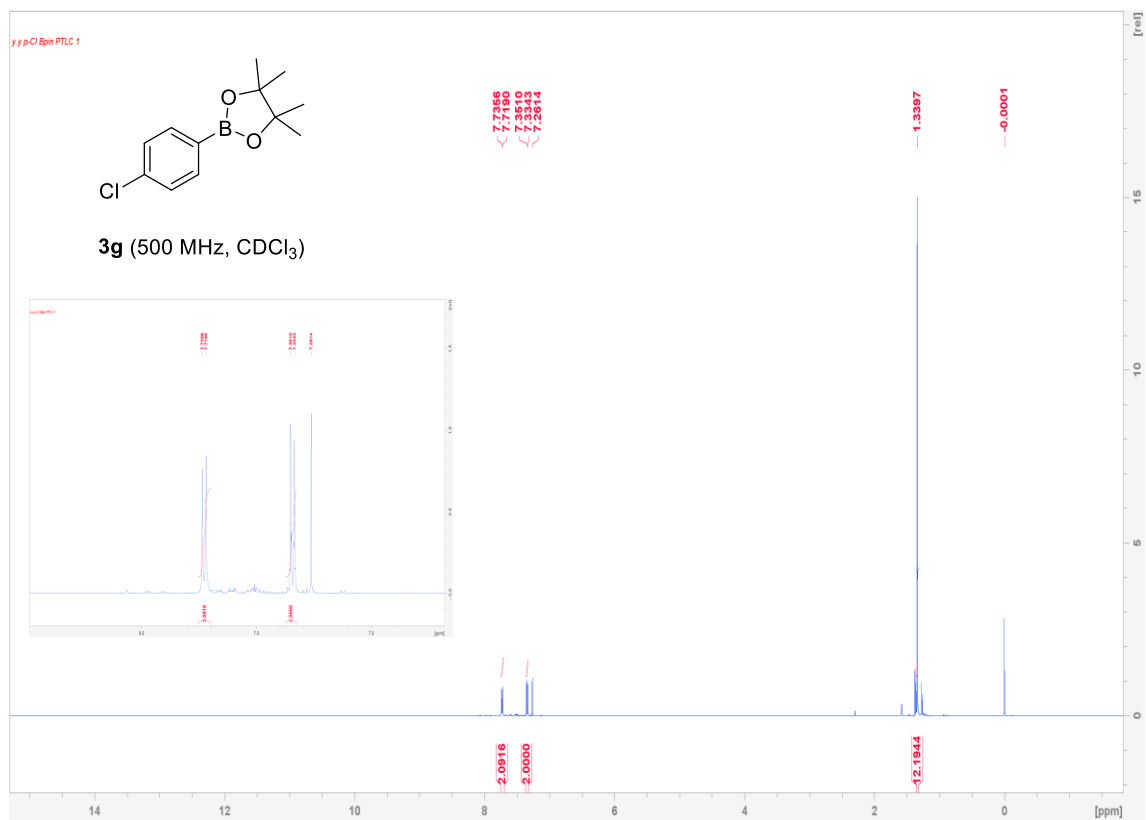


Figure S8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of compound **3I**

