Supporting Information for

A drastic effect of cobalt and chromium catalyst in the borylation of arylzinc regents

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General Information

All reactions were performed using oven- or flame-dried glassware under argon. Flash column chromatography was performed with silica gel 60 (Kanto Chemical Co., Inc., 40-50 nm). Preparative recycling gel permeation chromatography (GPC) was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L column (chloroform as an eluent). TLC monitoring was carried out with silica gel aluminum sheets (Merck, type 60 F_{254}). Gas chromatography (GC) monitoring was performed on a Shimadzu GC-2014. Nuclear magnetic resonance (NMR) spectra were measured on Varian-400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 101 MHz) spectrometer or Varian-500 (^{1}H NMR: 500 MHz; ^{13}C NMR: 126 MHz) spectrometers, calibrated from residual deuterated chloroform as an internal standard at 7.26 ppm for ^{1}H NMR spectra and at 77.0 ppm for ^{13}C NMR spectra, respectively. Melting points were determined using melting point system Mettler Toledo MP90 and were unrecorded. Low-resolution mass spectrum (LRMS) was recorded on Shimadzu GCMS-QP2010SE (EI, 70 eV). High-resolution mass spectrum (HRMS) was performed by the Natural Science Center for Basic Research and Development (N-BARD) of Hiroshima University using LTQ Orbitrap XL from Thermo Fisher Scientific.

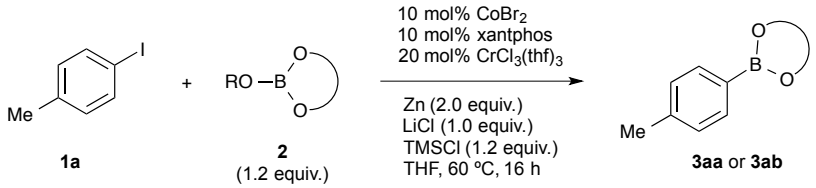
Materials

Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon prior to use. Acetonitrile (MeCN) was dried over P_2O_5 at reflux temperature for several hours, distilled and stored with activated molecular sieves 4Å under argon. $CoBr_2$, $CrCl_3(thf)_3$ and Zn powder as well as all ligands were purchased and used as received. Trimethylsilyl chloride (TMSCl) was previously distilled and stored under argon before use. Alkynylaryl iodides **4** were prepared by the iodation of phenol derivatives[1] and followed by substitution reactions under the Mitsunobu[2] or S_N2 reaction conditions.[3] Unless otherwise noted, other commercially available reagents were used as received without further purification.

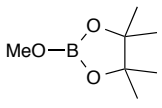
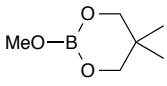
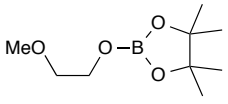
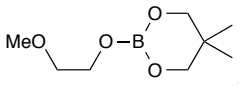
Effect of leaving group of boryl electrophiles 2 in the borylation

Boryl electrophiles **2b**, **2c** and **2d** were prepared by the following procedure. **2b**: A mixture of trimethyl borate (14.5 g, 140 mmol) and neopentyl glycol (7.3 g, 70 mmol) was refluxed for overnight. The title compound **2b** was obtained in 8.5 g (85% yield) by a distillation under the reduced pressure (120 ºC, 30 torr). **2c**: A mixture of $B(OCH_2CH_2OMe)_3$ (11.6 g, 49 mmol) and pinacol (5.79 g, 49 mmol) was heated at 150 ºC for overnight. The title compound **2c** was obtained in 9.0 g (91% yield) by a distillation under the reduced pressure (80 ºC, 13 torr). **2d**: A mixture of $B(OCH_2CH_2OMe)_3$ (12.5 g, 53 mmol) and neopentyl glycol (5.5 g, 53 mmol) was heated at 150 ºC for overnight. The title compound **2d** was obtained in 6.7 g (67% yield) by a distillation under the reduced pressure (115 ºC, 13 torr).

Table S1 Screening of boryl electrophiles (**2**) in the Co/Cr-catalysed borylation of 4-iodotoluene

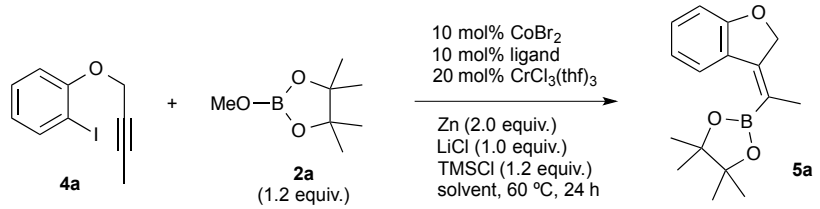


1a | **2** (1.2 equiv.) | **3aa** or **3ab**

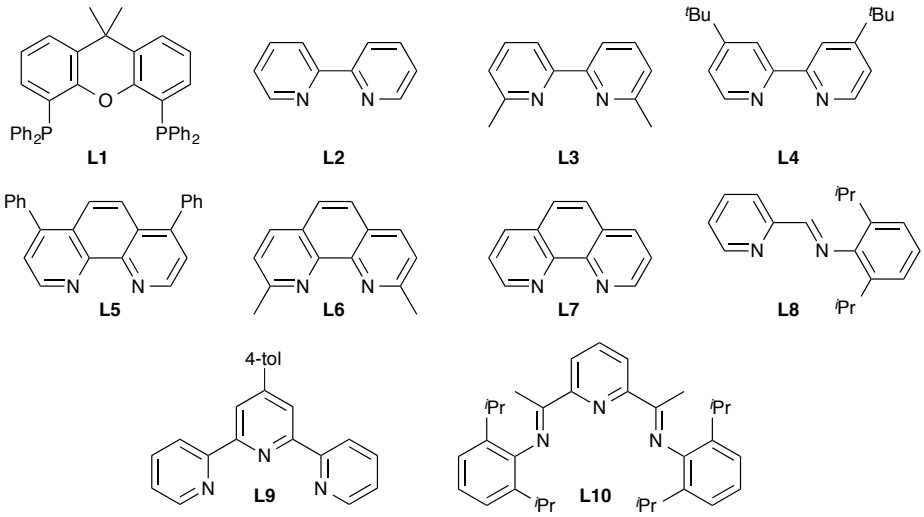
Entry	Boryl electrophile	NMR Yield /%
1	 **2a**	73
2	 **2b**	85
3	 **2c**	51
4	 **2d**	64

Optimisation of conditions in the Co/Cr-catalysed cyclisation/borylation

Table S2 Optimization of reaction conditions in the Co-Cr-catalysed cyclisation/borylation of **4a** with **2a**



Entry	Ligand	Solvent	GC Yield (Isolated yield)/%
1	**L1**	THF	30
2	**L1**	MeCN	trace
3	PPh_3 (20 mol%)	MeCN	trace
4	**L2**	MeCN	7
5	**L3**	MeCN	21
6	**L4**	MeCN	4
7	**L5**	MeCN	7
8	**L6**	MeCN	23
9	**L7**	MeCN	50
10	**L7** in the absence of LiCl	MeCN	trace
11	**L8**	MeCN	65 (50)
12	**L8**	EtCN	15
13	**L8**	DMF	trace
14	**L9**	MeCN	trace
15	**L10**	MeCN	9



Representative procedure for the Co/Cr-catalysed borylation of 4-MeC_6H_4ZnI·LiCl with MeOBpin (2a) (entry 4, Table 1)

To a flame -dried Schlenk tube, Zn powder (32.5 mg, 0.5 mmol) and $CoBr_2$ (5.5 mg, 0.025 mmol) were added and heated at 400 ºC for 15 min under vacuum. After cooling, the Schlenk tube was purged with argon and was added xantphos (14.5 mg, 0.025 mmol), $CrCl_3(thf)_3$ (18.7 mg, 0.05 mmol), dry THF (1 mL), and TMSCl (38 μL, 0.3 mmol), followed by stirring for about 5 minutes. 1.0 M THF solution of 4-MeC_6H_4ZnI·LiCl (0.25 mL, 0.25 mmol)[4] and MeOBpin (49 μL, 0.3 mmol) were successively added to the mixture. The reaction mixture was stirred at 60 ºC for 16 h. After the reaction, the mixture was cooled to room temperature, then diluted with ethyl acetate and quenched with water. The reaction mixture was added dimethyl terephthalate as an internal standard to determine the product yield by ^1H NMR. The aqueous phase was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude product was obtained. The yield was determined by ^1H NMR using the crude product.

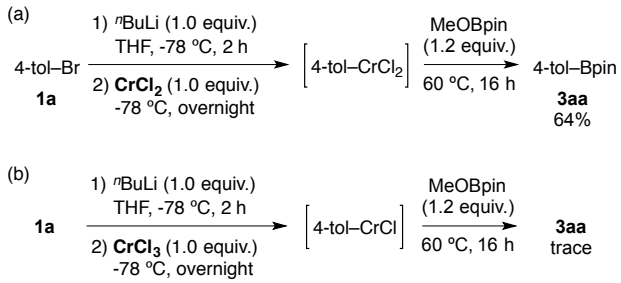
Representative procedure for the Co/Cr-catalysed borylation of aryl halide 1 with boryl electrophiles 2 (entry 1, Table 3)

Zn powder (32.5 mg, 0.5 mmol), LiCl (10.5 mg, 0.25 mmol) and $CoBr_2$ (5.5 mg, 0.025 mmol) were added into an oven-dried Schlenk tube, and were heated at 400 ºC for 15 min under vacuum. After cooling, the Schlenk tube was filled with argon and then was charged with xantphos (14.5 mg, 0.025 mmol), $CrCl_3(thf)_3$ (18.7 mg, 0.05 mmol), dry THF (1 mL) and TMSCl (38 μL, 0.3 mmol), followed by stirring for about 5 minutes. 4-Phenylphenyl iodide (**1b**, 54.5 mg, 0.25 mmol) and MeOBpin (49 μL, 0.3 mmol) were successively added to the mixture. The reaction mixture was stirred at 60 ºC for 16 h. After the reaction, the mixture was cooled to room temperature, then diluted with ethyl acetate and quenched with water. The aqueous phase was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, purification of the residue by flash chromatography on deactivated silica gel (5% w/w with Et_3N)[5] provided 4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl) benzene (**3ba**) as white solid in 71% yield. Note: If the borylated products were unstable to withstand the column chromatography purification, the purification was carried out by GPC with chloroform as an eluent.

Representative procedure for the Co/Cr-catalysed cyclisation/borylation of alkynylaryl iodide 4 with MeOBpin (2a) (synthesis of 5a in Table 2)

Zn powder (32.5 mg, 0.5 mmol), LiCl (10.5 mg, 0.25 mmol) and $CoBr_2$ (5.5 mg, 0.025 mmol) were added into an oven-dried Schlenk tube, and were heated at 400 ºC for 15 min under vacuum. After cooling, the

Schlenk tube was filled with argon and then was charged with the iminopyridine ligand (6.7 mg, 0.025 mmol), $CrCl_3(thf)_3$ (18.7 mg, 0.05 mmol), dry MeCN (1 mL) and TMSCl (38 μL, 0.3 mmol), followed by stirring for about 5 minutes. 1-(2-Butyn-1-yloxy)-2-iodobenzene (**4a**, 68 mg, 0.25 mmol) and MeOBpin (49 μL, 0.3 mmol) were successively added to the mixture. The reaction mixture was stirred at 60 ºC for 24 h. After the reaction, the mixture was cooled to room temperature, then diluted with ethyl acetate and quenched with water. The aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the residue was purified by flash chromatography on deactivated silica gel (5% w/w with Et_3N)[5] or GPC with chloroform as an eluent to afford (*Z*)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)ethylidene]-2,3-dihydrobenzofuran (**5a**) as brown oil in 50% yield.



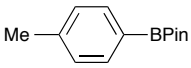
Scheme S1 Borylation of 4-tolCrCl$_2$ (a) and 4-tolCrCl$_2$ (b) with MeOBpin.

Representative procedure for the ArCr-mediated borylation with MeOBpin (2a) (Scheme S1)

To a flame-dried Schlenk tube, 4-bromotoluene (171 mg, 1.0 mmol) and dry THF (1 mL) were added and cooled to -78 ºC. The Schlenk tube was slowly poured 1.6 M hexane solution of *n*-butyl lithium (0.63 mL, 1.0 mmol) and was stirred for 2 h at same temperature. The generated tolyl lithium solution was added into a THF solution of $CrCl_2$ (122.9 mg, 1.0 mmol) in THF (1.0 mL) using cannula technique at -78 ºC. The mixture was stirred at -78 ºC for overnight. The resulting mixture was wormed to room temperature, MeOBpin (196 μL, 1.2 mmol) were added, followed by stirring for 24 h at 60 ºC. After the reaction, the obtained mixture was cooled to room temperature, then diluted with ethyl acetate and quenched with water. The reaction mixture was added dimethyl terephthalate to estimate the NMR yield. The aqueous phase was extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of solvent, the crude product was obtained.

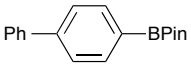
Spectra date for products

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl) toluene (3aa)[6]



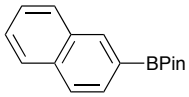
Isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 134.7, 128.4, 83.4, 24.7, 21.6. LRMS (70 eV) *m/z*: 218 (M^+, 26), 203 (32), 132 (66), 118 (51), 119 (100).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-phenyl benzene (3ba)[7]



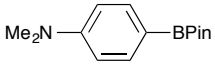
Isolated as white solid (Mp.: 108–109 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.63–7.36 (m, 7H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.9, 141.0, 135.2, 128.7, 127.5, 127.2, 126.4, 83.8, 24.9. LRMS (70 eV) *m/z*: 280 (M^+, 100), 265 (34), 194 (80), 181 (74), 180 (94).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl) naphthalene (3ca)[5]



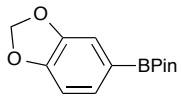
Isolated as white solid (Mp.: 64–65 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.90–7.82 (m, 4H), 7.53–7.46 (m, 2H), 1.39 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 127.0, 126.9, 125.8, 83.9, 24.9. LRMS (70 eV) *m/z*: 254 (M^+, 73), 168 (89), 155 (61), 154 (100), 153 (32).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-(*N*,*N*-dimethylamino)benzene (3da)[5]



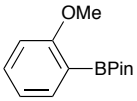
Isolated as white solid (Mp.: 115–116 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 2H), 6.68 (d, *J* = 8.8 Hz, 2H), 2.98 (s, 6H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.5, 136.1, 111.2, 83.1, 40.1, 24.8. LRMS (70 eV) *m/z*: 247 (M^+, 100), 246 (30), 148 (38), 147 (25), 146 (26).

3,4-Methylenedioxy-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl) benzene (3ea)[8]



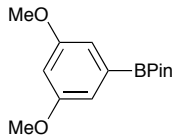
Isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.24 (s, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 5.95 (s, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 147.2, 129.7, 114.0, 108.2, 100.7, 83.7, 24.8. LRMS (70 eV) *m/z*: 248 (M^+, 90), 162 (61), 149 (75), 148 (100), 147 (51).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl) anisole (3fa)[6]



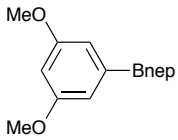
Isolated as white solid (Mp.: 82–83 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.3 Hz, 1.8 Hz, 1H), 7.40 (ddd, *J* = 8.5 Hz, *J* = 7.3 Hz, *J* = 1.8 Hz, 1H), 6.94 (m, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.1, 136.6, 132.4, 120.1, 110.3, 83.3, 55.7, 24.7. LRMS (70 eV) *m/z*: 234 (M^+, 64), 134 (100), 133 (66), 105 (42), 91 (66).

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-5-methoxyanisole (3ga)[9]



Isolated as white solid (Mp.: 90–91 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 2.4 Hz, 2H), 6.57 (t, *J* = 2.4 Hz, 1H), 3.81 (s, 6H), 1.34 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 111.5, 104.5, 83.8, 55.3, 24.8. LRMS (70 eV) *m/z*: 264 (M^+, 100), 179 (26), 178 (47), 165 (46), 164 (70).

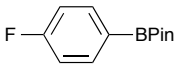
3-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-5-methoxyanisole (3gb)[10]



Isolated as white solid (Mp.: 113–114 ºC).

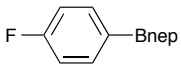
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 2.4 Hz, 2H), 6.54 (t, *J* = 2.4 Hz, 1H), 3.81 (s, 6H), 3.77 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 110.7, 103.9, 72.3, 55.3, 31.8, 21.8. LRMS (70 eV) *m/z*: 250 (M^+, 100), 249 (29), 164 (21), 134 (16), 121 (10).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-fluorobenzene (3ha)[11]



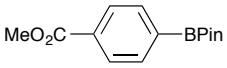
Isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.77 (m, 2H), 7.06–7.02 (m, 2H), 1.33 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0 (d, *J* = 252.0 Hz), 136.9 (d, *J* = 8.2 Hz), 114.8 (d, *J* = 20.2 Hz), 83.9, 4.8. LRMS (70 eV) *m/z*: 222 (M^+, 19), 207 (61), 136 (45), 123 (100), 122 (30).

4-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-fluorobenzene (3hb)[10]



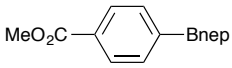
Isolated as white solid (Mp.: 66–67 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.77 (m, 2H), 7.05–7.00 (m, 2H), 3.76 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7 (d, *J* = 248.7 Hz), 135.9 (d, *J* = 8.0 Hz), 114.5 (d, *J* = 20.2 Hz), 72.3, 31.8, 21.8. LRMS (70 eV) *m/z*: 208 (M^+, 45), 165 (15), 123 (15), 56 (100), 41 (14).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-methoxycarbonyl benzene (3ia)[6]



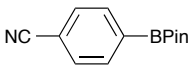
Isolated as white solid (Mp.: 66–67 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 3.92 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 134.4, 132.2, 128.6, 84.1, 52.1, 24.8. LRMS (70 eV) *m/z*: 262 (M^+, 27), 247 (77), 176 (100), 163 (97), 43 (28).

4-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-methoxycarbonyl benzene (3ib)[10]



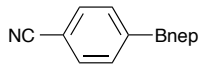
Isolated as white solid (Mp.: 111–112 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 3.90 (s, 3H), 3.77 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.2, 133.7, 131.7, 128.4, 72.3, 52.0, 31.8, 21.8. LRMS (70 eV) *m/z*: 248 (M^+, 42), 217 (100), 216 (22), 56 (71), 41 (20).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-cycanobenzene (3ja)[6]



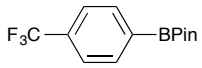
Isolated as white solid (Mp.: 94–95 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.1, 131.1, 118.9, 114.5, 84.5, 24.8. LRMS (70 eV) *m/z*: 214 (M^+-Me, 100), 143 (91), 130 (58), 43 (30), 42 (31).

4-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-cycanobenzene (3jb)[6]



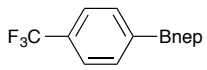
Isolated as white solid (Mp.: 115–120 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 3.78 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.2, 131.0, 119.1, 113.9, 72.4, 31.2, 21.8. LRMS (70 eV) *m/z*: 215 (M^+, 38), 172 (20), 171 (13), 56 (100), 41 (15).

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-trifluoromethyl benzene (3ka)[6]



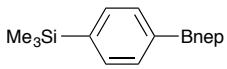
Isolated as white solid (Mp.: 73–74 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.0, 132.9 (q, *J* = 32.0 Hz), 124.3 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.0 Hz), 84.2, 24.8. LRMS (70 eV) *m/z*: 257 (M^+-Me, 100), 186 (90), 173 (78), 43 (56), 42 (54).

4-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-trifluoromethyl benzene (3kb)[12]



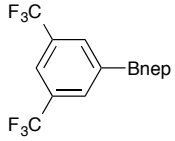
Isolated as white solid (Mp.: 112–113 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 3.79 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.0, 132.4 (q, *J* = 32.0 Hz), 124.2 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.0 Hz), 72.3, 31.9, 21.8. LRMS (70 eV) *m/z*: 258 (M^+, 27), 215 (14), 214 (9), 56 (100), 41 (18).

4-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-trimethylsilyl benzene (3lb)[13]



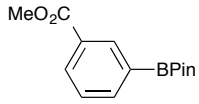
Isolated as white solid (Mp.: 74–75 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 3.78 (s, 4H), 1.03 (s, 6H), 0.28 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 132.9, 132.5, 72.3, 31.9, 21.9, 1.22. LRMS (70 eV) *m/z*: 262 (M^+, 10), 248 (20), 247 (100), 246 (22), 161 (9).

1-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-3,5-ditrifluoromethyl benzene (3mb)



Isolated as white solid (Mp.: 95–96 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 2H), 7.91 (s, 1H), 3.80 (s, 4H), 1.04 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.7 (m), 130.4 (q, *J* = 33.0 Hz), 132.4 (h, *J* = 3.8 Hz), 123.5 (q, *J* = 272.0 Hz), 72.3, 31.8, 21.6. LRMS (70 eV) *m/z*: 326 (M^+, 22), 283 (15), 282 (14), 56 (100), 41 (22). HRMS (ESI) *m/z*: calcd for $C_{13}H_{13}BF_6O_2$ [M^+]: 327.0931, found: 327.0936.

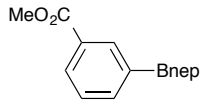
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-1-methoxycarbonyl benzene (3na)[8]



Isolated as white solid (Mp.: 94–95 ºC).

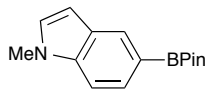
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.11 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.97 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 1.35 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 139.1, 135.8, 132.2, 129.5, 127.8, 84.0, 52.0, 24.8. LRMS (70 eV) *m/z*: 262 (M^+, 17), 247 (27), 219 (100), 163 (80), 131 (31).

3-(5,5-Dimethyl-1,3,2-dioxaborinanyl)-1-methoxycarbonyl benzene (3nb)[10]



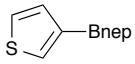
Isolated as white solid (Mp.: 67–68 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.09 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.97 (dt, *J* = 7.4, 1.3 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 3.91 (s, 3H), 3.78 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 138.3, 135.0, 131.7, 129.3, 127.6, 72.3, 51.9, 31.9, 21.8. LRMS (70 eV) *m/z*: 248 (M^+, 41), 217 (100), 216 (30), 56 (88), 41 (26).

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolanyl)-*N*-methylindole (3oa)[11]



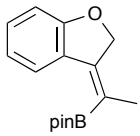
Isolated as white solid (Mp.: 92–93 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.67 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.51 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.78 (s, 3H), 1.38 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 128.9, 128.8, 128.1, 127.5, 108.5, 101.6, 83.3, 32.7, 24.8. LRMS (70 eV) *m/z*: 257 (M^+, 100), 171 (40), 158 (61), 157 (84), 156 (40).

3-(5,5-Dimethyl-1,3,2-dioxaborinanyl) thiophene (3pb)[12]



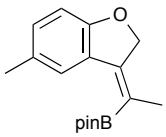
Isolated as white solid (Mp.: 98–99 ºC). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 2.7, 1.1 Hz, 1H), 7.38 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.31 (dd, *J* = 4.9, 2.7 Hz, 1H), 3.75 (s, 4H), 1.02 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.8, 131.6, 125.0, 72.2, 31.9, 21.9. LRMS (70 eV) *m/z*: 196 (M^+, 72), 195 (20), 153 (18), 111 (23), 56 (100).

(*Z*)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)ethylidene]-2,3-dihydrobenzofuran (5a)



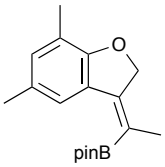
Isolated as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 7.20- 7.16 (m, 1H), 6.90- 6.83 (m, 1H), 5.06 (q, *J* = 2.0 Hz, 2H), 1.78 (t, *J* = 2.0 Hz, 3H), 1.36 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 149.0, 130.1, 125.3, 125.0, 120.4, 110.3, 83.5, 75.4, 24.9, 18.6. LRMS (70 eV) *m/z*: 272 (M^+, 79), 215 (66), 145 (96), 101 (100), 83 (45). HRMS (ESI) *m/z*: calcd for $C_{16}H_{22}BO_3$ [M+H^+]: 273.1656, found: 273.1657.

(*Z*)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)ethylidene]-5-methyl-2,3-dihydrobenzofuran (5b)



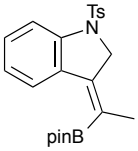
Isolated as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.2 Hz, 1H), 6.99 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 5.04 (q, *J* = 2.0 Hz, 2H), 2.30 (s, 3H), 1.77 (t, *J* = 2.0 Hz, 3H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.6, 149.0, 130.8, 129.5, 125.2, 112.0, 109.8, 83.5, 75.6, 24.9, 21.0, 18.5. LRMS (70 eV) *m/z*: 286 (M^+, 100), 229 (52), 186 (32), 159 (66), 101 (47). HRMS (ESI) *m/z*: calcd for $C_{17}H_{23}BO_3$ [M+H^+]: 287.1822, found: 287.1813.

(*Z*)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)ethylidene]-5,7-dimethyl-2,3-dihydrobenzofuran (5c)

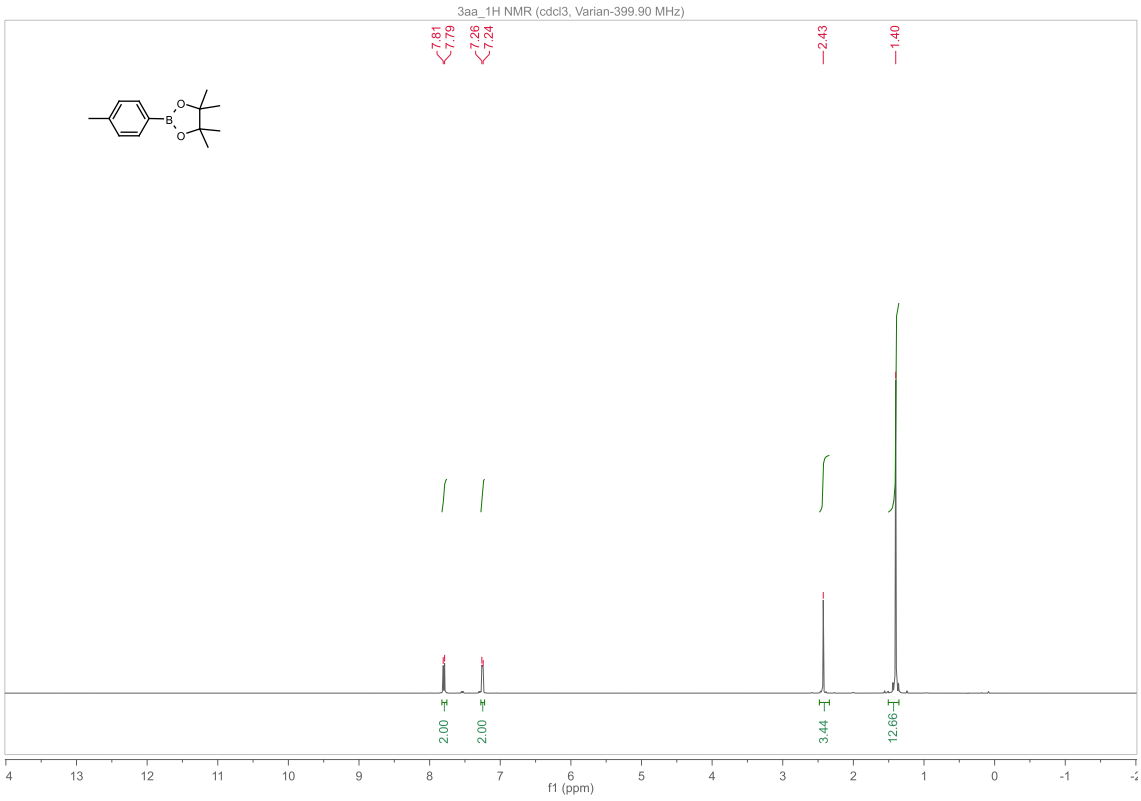


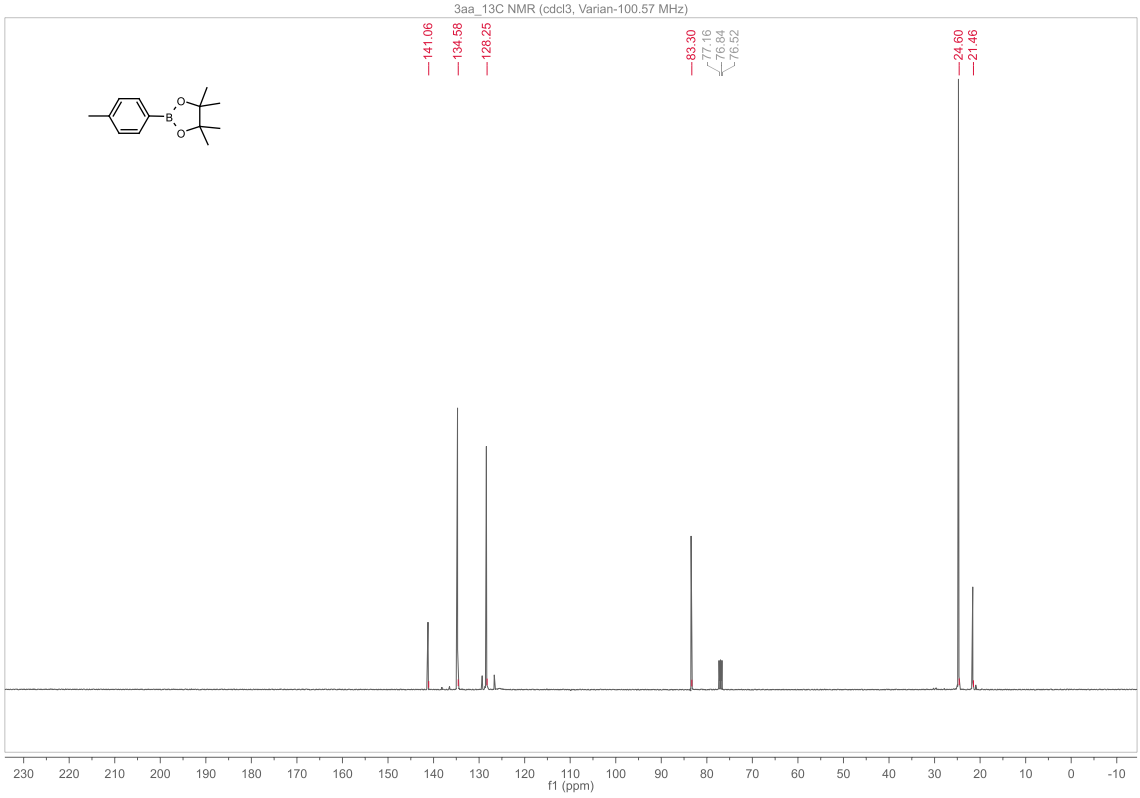
Isolated as brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ δ 8.01 (d, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 2.1 Hz, 1H), 5.04 (q, *J* = 2.0 Hz, 2H), 2.27 (s, 3H), 2.19 (s, 3H), 1.77 (t, *J* = 2.0 Hz, 3H), 1.37 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1, 149.7, 131.9, 129.3, 124.5, 122.5, 119.7, 83.4, 75.4, 25.0, 21.0, 18.5, 14.9. LRMS (70 eV) *m/z*: 300 (M^+, 100), 299 (31), 285 (44), 242 (40), 173 (46). HRMS (ESI) *m/z*: calcd for $C_{18}H_{25}BO_3$ [M^+]: 300.1967, found: 300.1965.

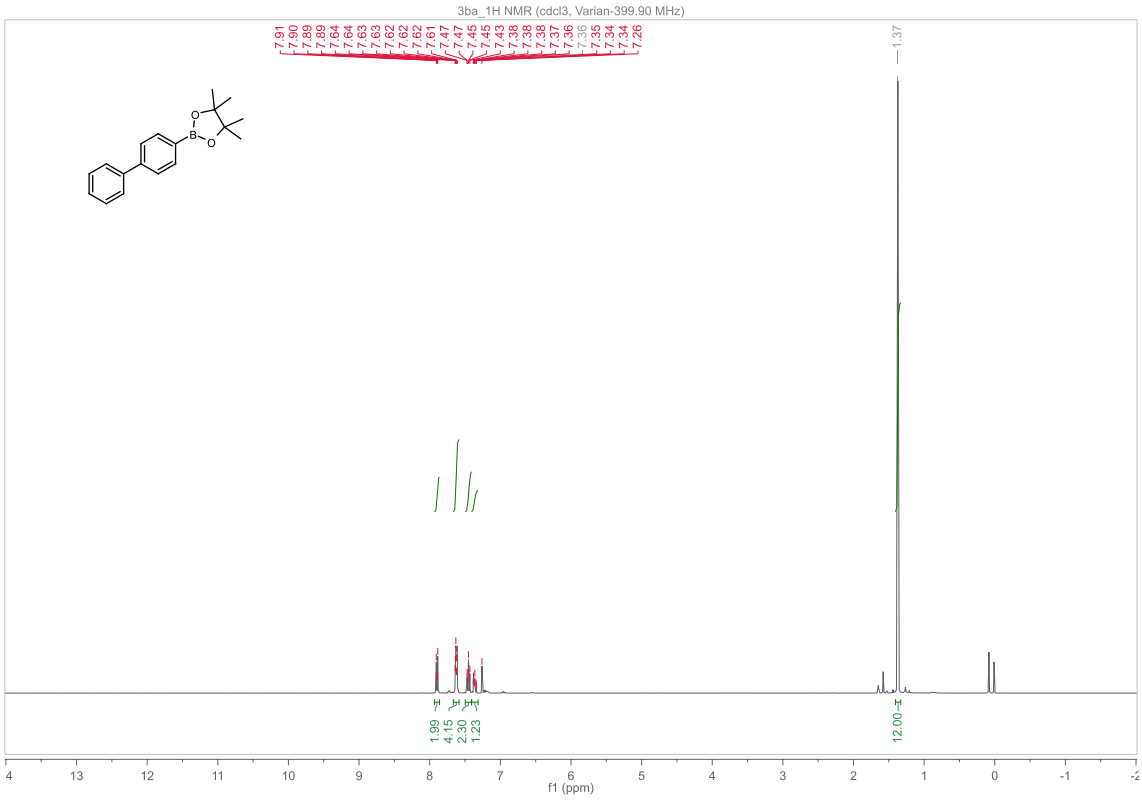
(*Z*)-3-[1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl)ethylidene]-*N*-tosyl indole (5d)

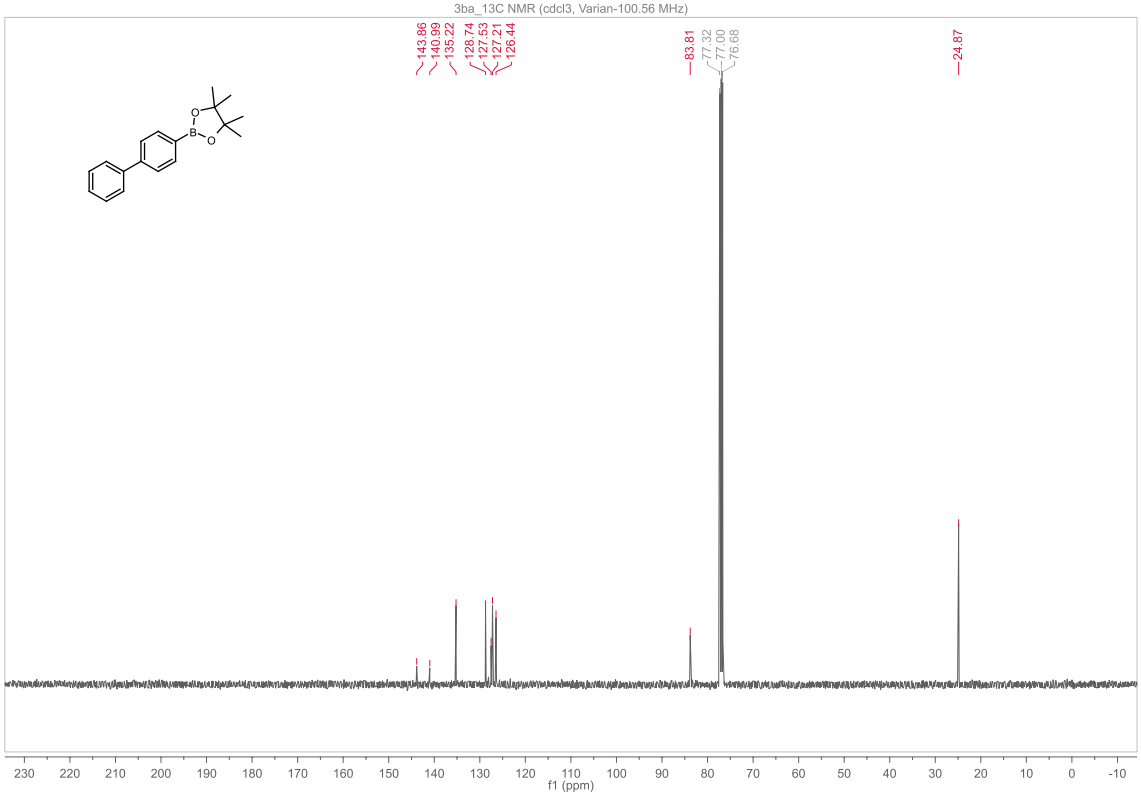


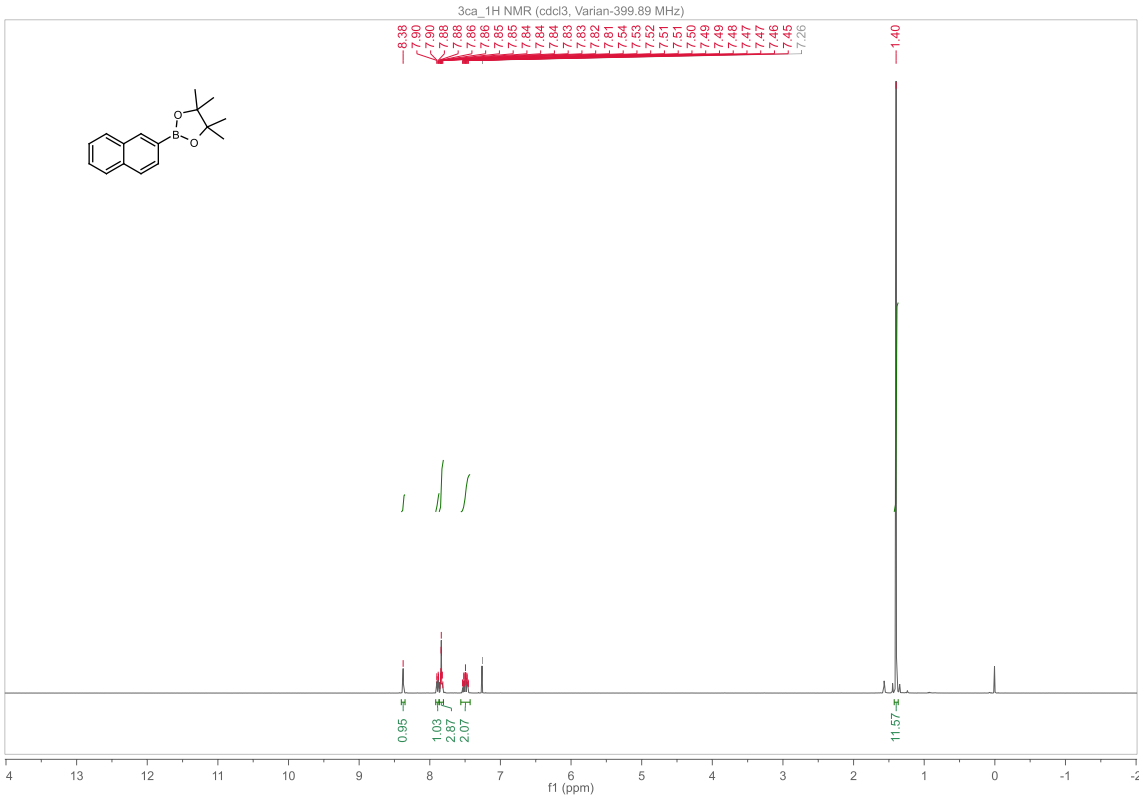
Isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.19–7.24 (m, 3H), 6.94–6.98 (m, 1H), 4.45 (q, *J* = 1.9 Hz, 2H), 2.35 (s, 3H), 1.77 (t, *J* = 1.9 Hz, 3H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.5, 144.2, 143.6, 133.9, 129.7, 129.5, 129.4, 127.1, 124.2, 123.1, 114.3, 83.7, 55.1, 24.8, 21.5, 19.1. LRMS (70 eV) *m/z*: 425 (M^+, 24), 270 (33), 206 (31), 188 (37), 144 (51), 143 (100), 90 (28). HRMS (ESI) *m/z*: calcd for $C_{23}H_{28}O_4NBNaS$ [M^++Na^+]: 448.17243, found: 448.17225.

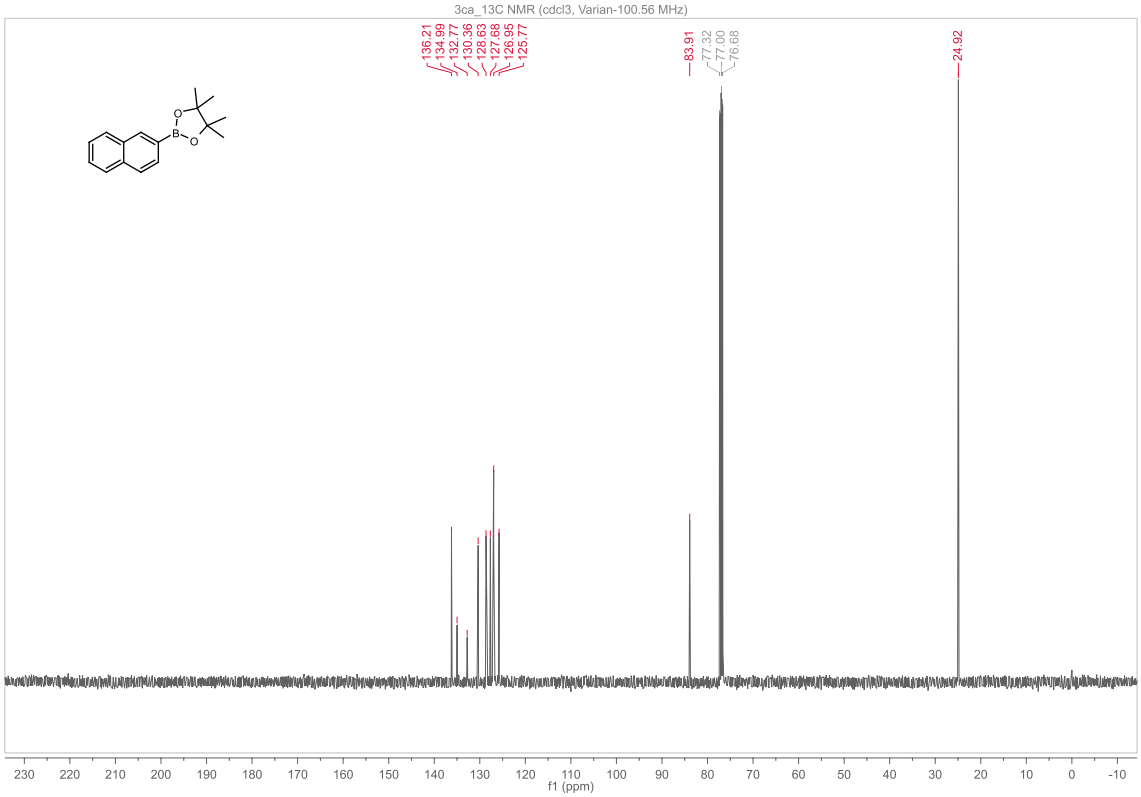

3aa_1H NMR (cdcl3, Varian-399.90 MHz)
7.81
7.79
7.26
7.24
2.43
1.40
2.00
2.00
3.44
12.66
f1 (ppm)

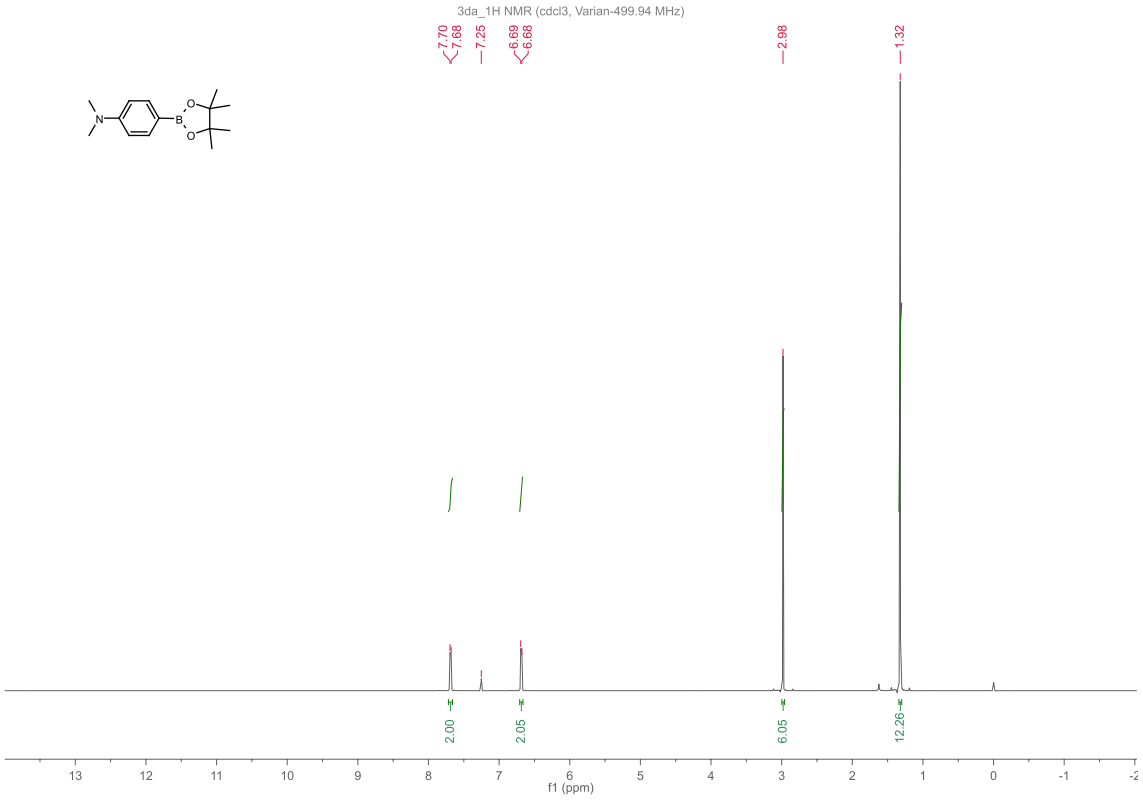

3aa_13C NMR (cdcl3, Varian-100.57 MHz)
141.06
134.58
128.25
83.30
77.16
76.84
76.52
24.60
21.46
f1 (ppm)

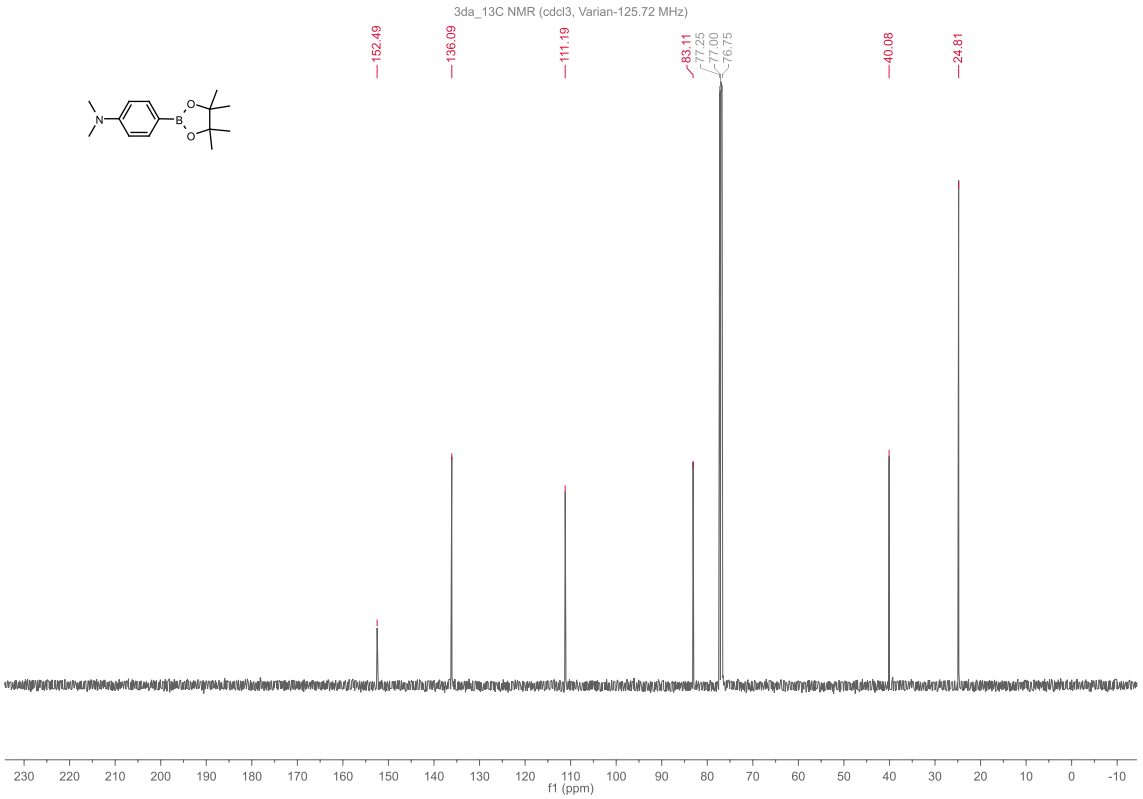

3ba_1H NMR (cdcl3, Varian-399.90 MHz)
7.91
7.90
7.89
7.89
7.64
7.64
7.63
7.63
7.62
7.62
7.62
7.61
7.47
7.47
7.45
7.45
7.43
7.38
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.26
1.37
1.99
4.15
2.30
1.23
12.00
f1 (ppm)

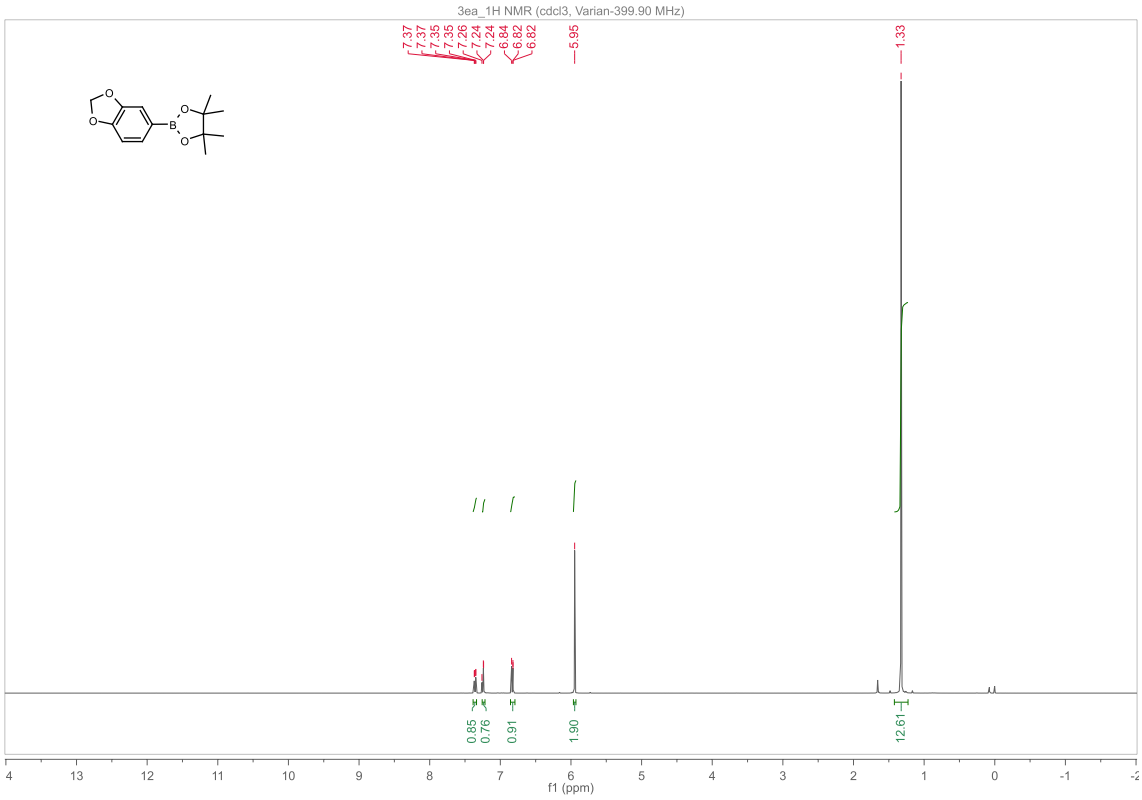

3ba_13C NMR (cdcl3, Varian-100.56 MHz)
143.86
140.99
135.22
128.74
127.53
127.21
126.44
83.81
77.32
77.00
76.68
24.87
f1 (ppm)

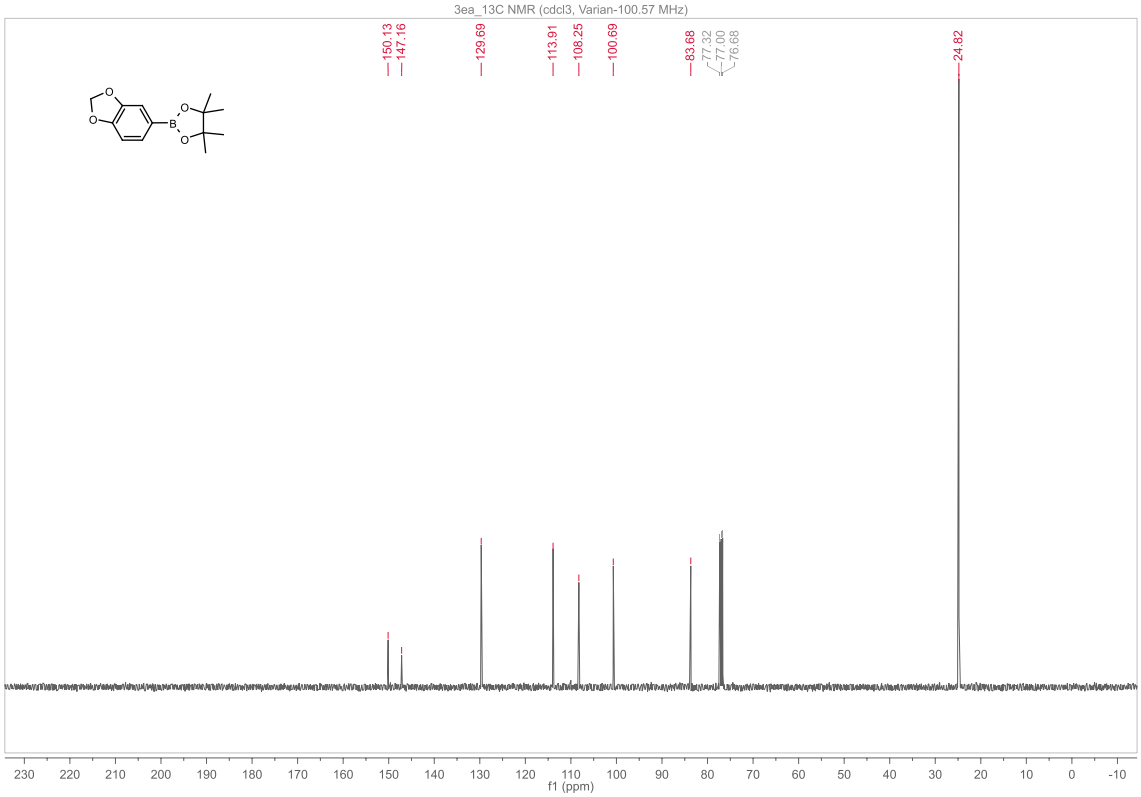

3ca_1H NMR (cdcl3, Varian-399.89 MHz)
8.38
7.90
7.90
7.88
7.88
7.86
7.86
7.85
7.85
7.84
7.84
7.84
7.83
7.83
7.82
7.81
7.54
7.53
7.52
7.51
7.51
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.45
7.26
1.40
0.95
1.03
2.87
2.07
11.57
f1 (ppm)

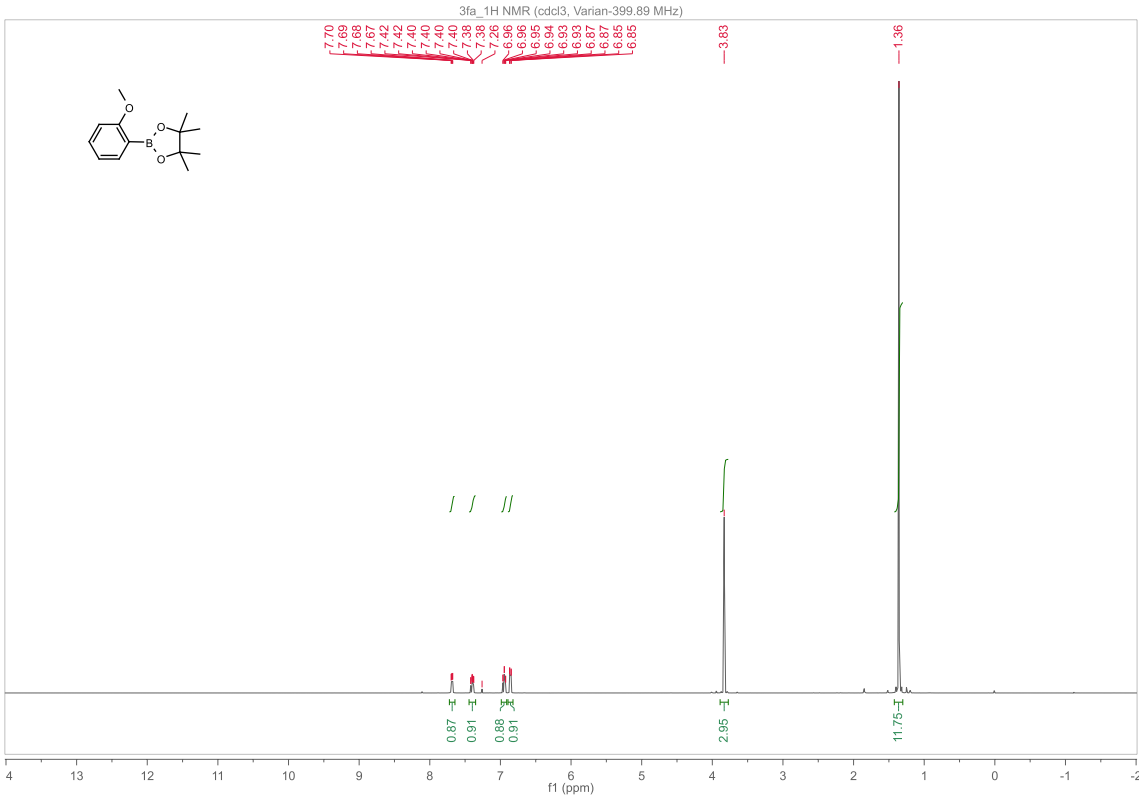

3ca_13C NMR (cdcl3, Varian-100.56 MHz)
136.21
134.99
132.77
130.36
128.63
127.68
126.95
125.77
83.91
77.32
77.00
76.68
24.92
f1 (ppm)

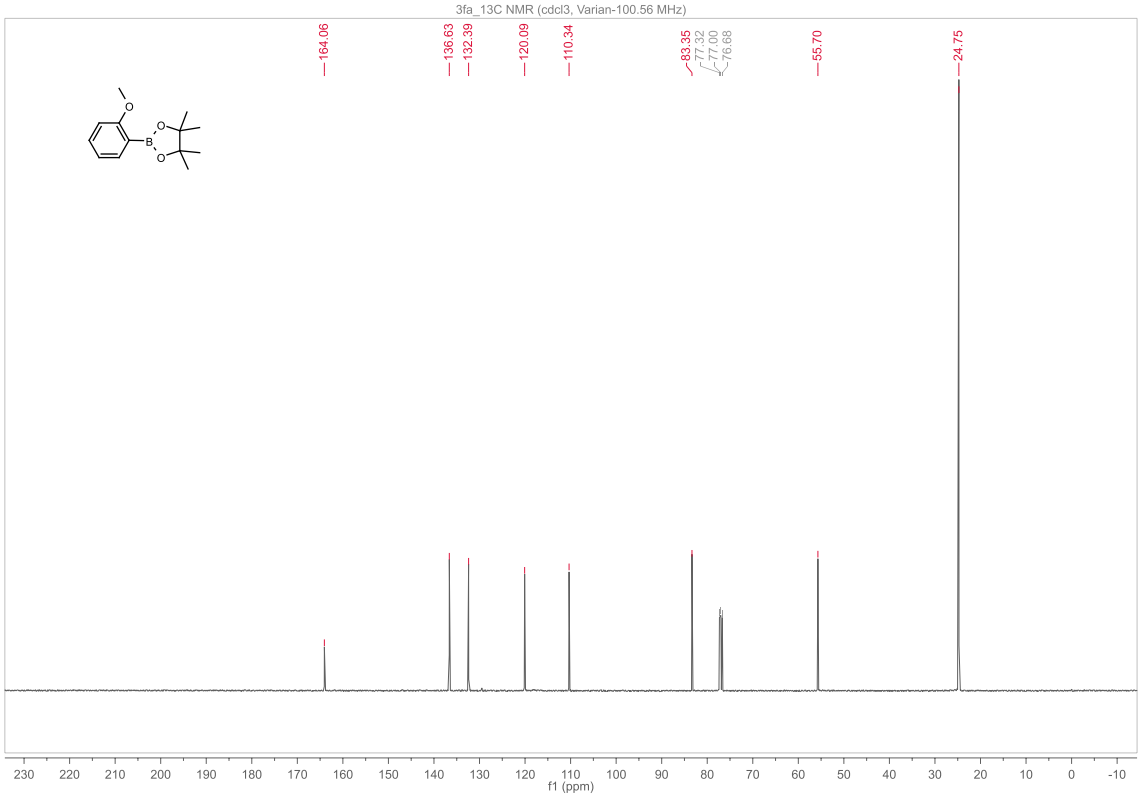

3da_1H NMR (cdcl3, Varian-499.94 MHz)
7.70
7.68
7.25
6.69
6.68
2.98
1.32
2.00
2.05
6.05
12.26
f1 (ppm)

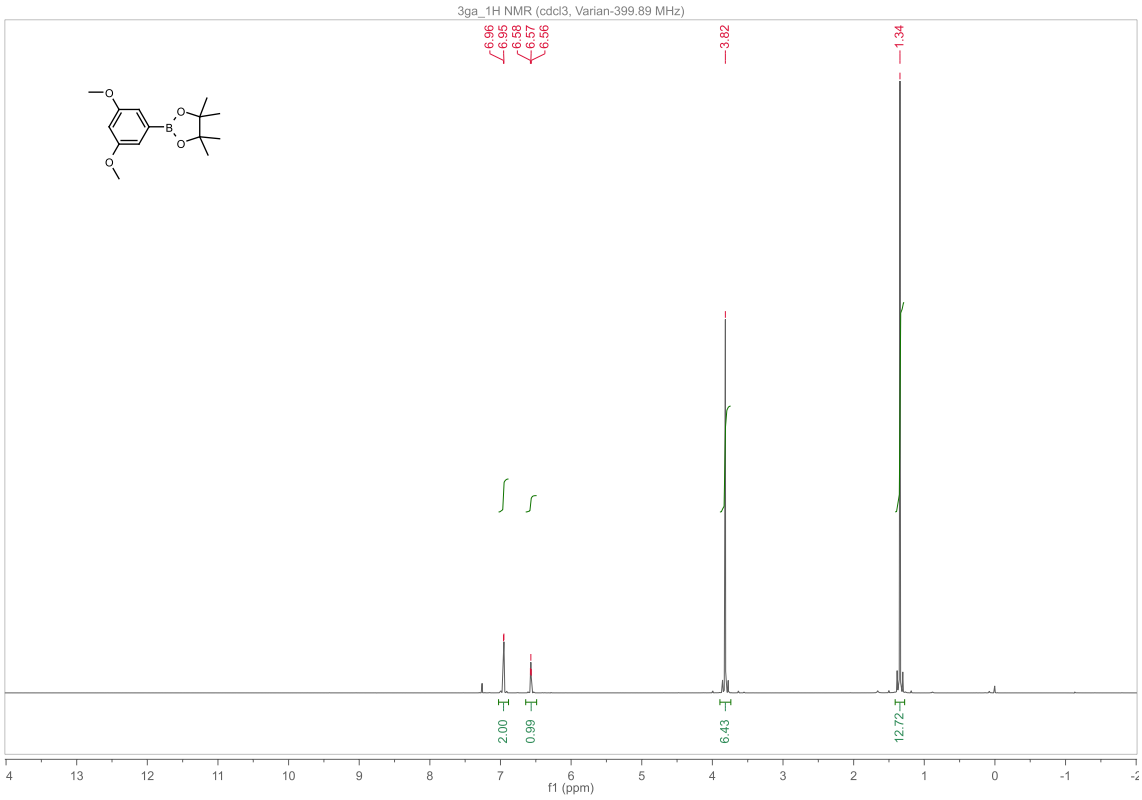

3da_13C NMR (cdcl3, Varian-125.72 MHz)
152.49
136.09
111.19
83.11
77.25
77.00
76.75
40.08
24.81
f1 (ppm)

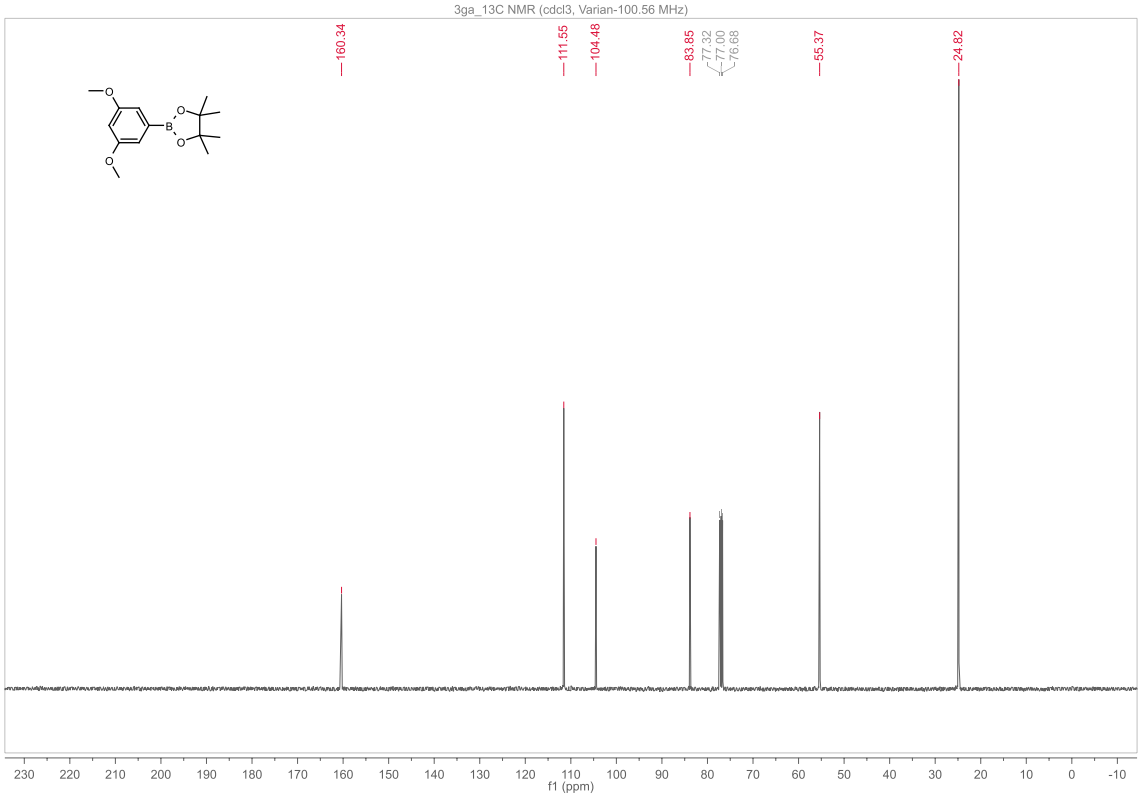

3ea_1H NMR (cdcl3, Varian-399.90 MHz)
7.37
7.37
7.35
7.35
7.26
7.24
7.24
6.84
6.82
6.82
5.95
1.33
0.85
0.76
0.91
1.90
12.61
f1 (ppm)

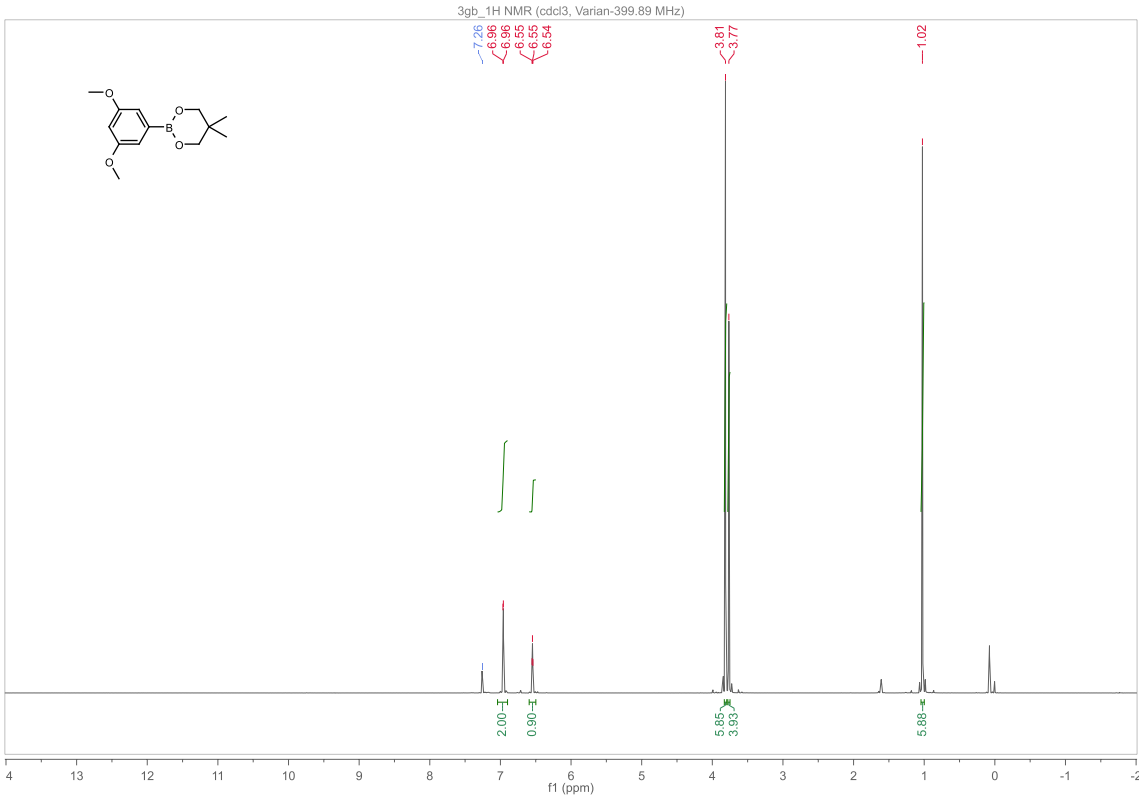

3ea_13C NMR (cdcl3, Varian-100.57 MHz)
150.13
147.16
129.69
113.91
108.25
100.69
83.68
77.32
77.00
76.68
24.82
f1 (ppm)

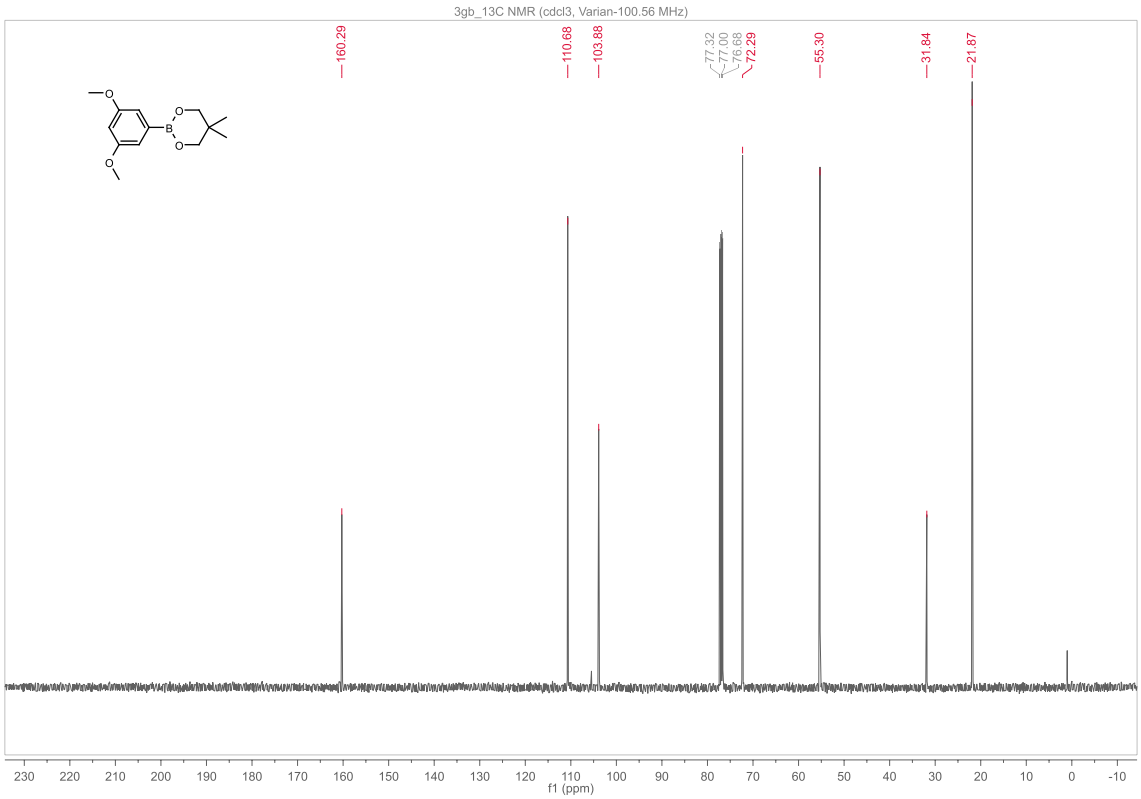

3fa_1H NMR (cdcl3, Varian-399.89 MHz)
7.70
7.69
7.68
7.67
7.42
7.42
7.40
7.40
7.40
7.40
7.38
7.38
7.26
6.96
6.96
6.95
6.94
6.93
6.93
6.87
6.87
6.85
6.85
3.83
1.36
0.87
0.91
0.88
0.91
2.95
11.75
f1 (ppm)

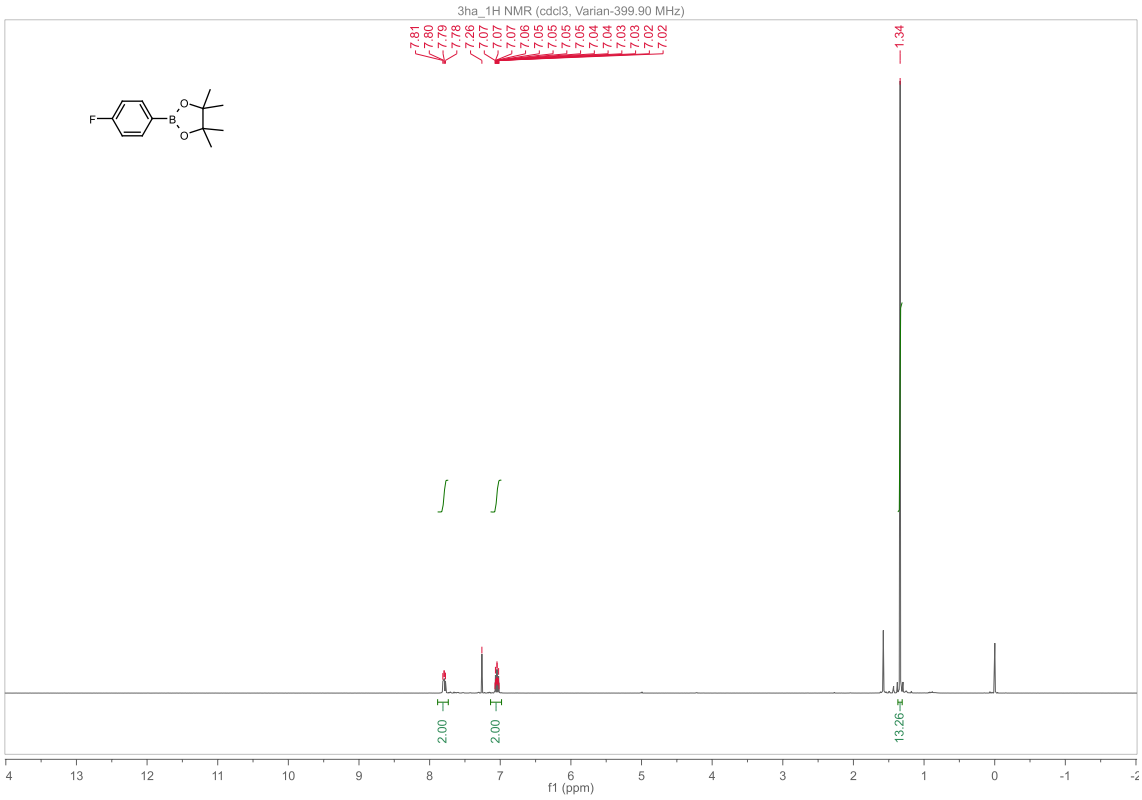

3fa_13C NMR (cdcl3, Varian-100.56 MHz)
164.06
136.63
132.39
120.09
110.34
83.35
77.32
77.00
76.68
55.70
24.75
f1 (ppm)

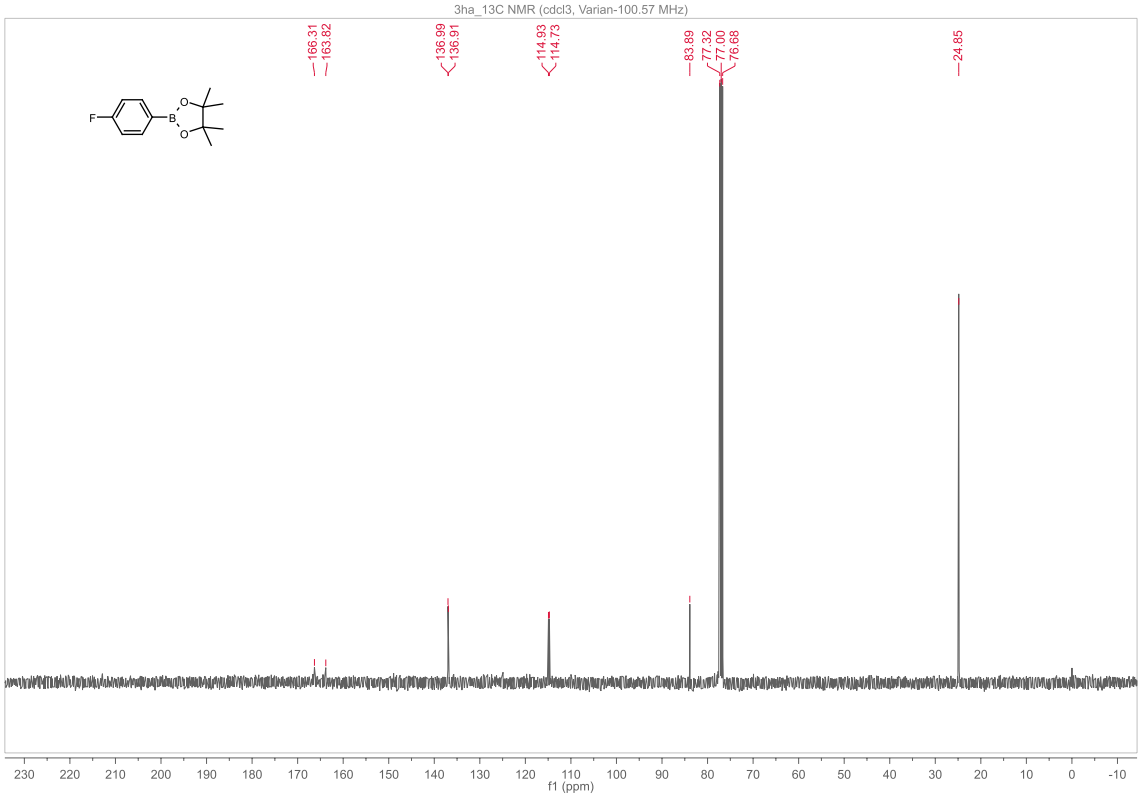

3ga_1H NMR (cdcl3, Varian-399.89 MHz)
6.96
6.95
6.58
6.57
6.56
3.82
1.34
2.00
0.99
6.43
12.72
f1 (ppm)

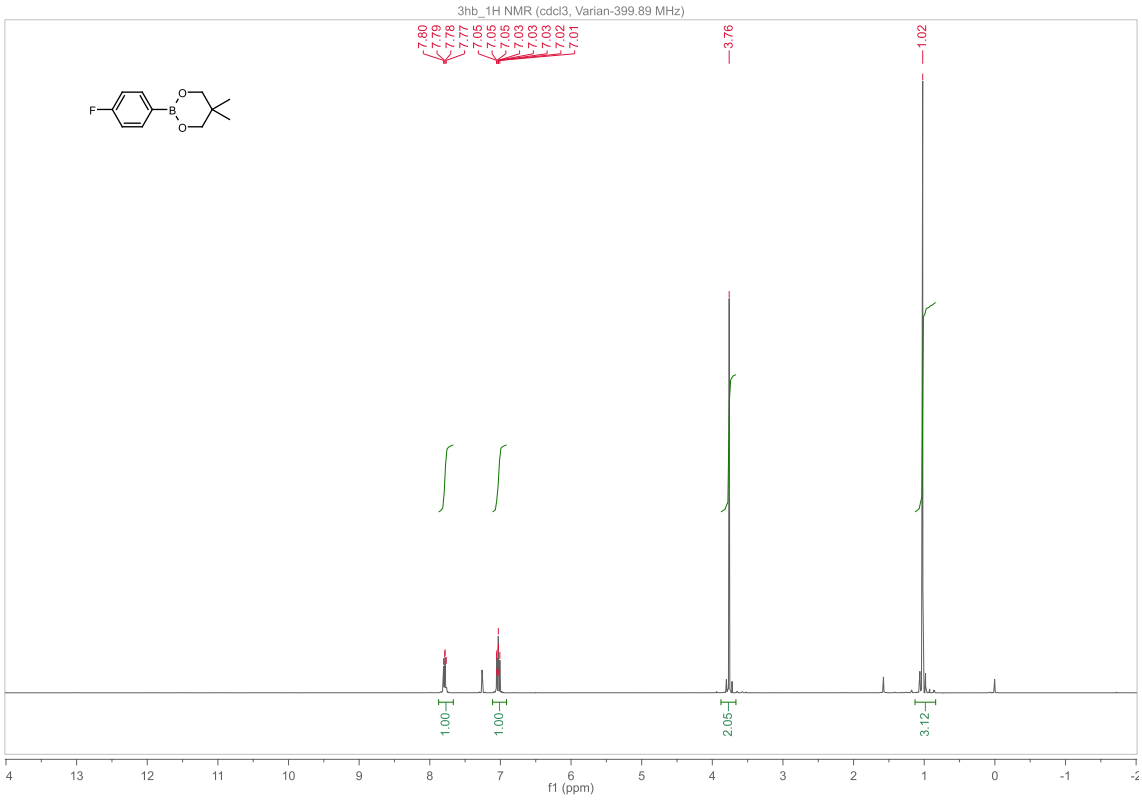

3ga_13C NMR (cdcl3, Varian-100.56 MHz)
160.34
111.55
104.48
83.85
77.32
77.00
76.68
55.37
24.82
f1 (ppm)

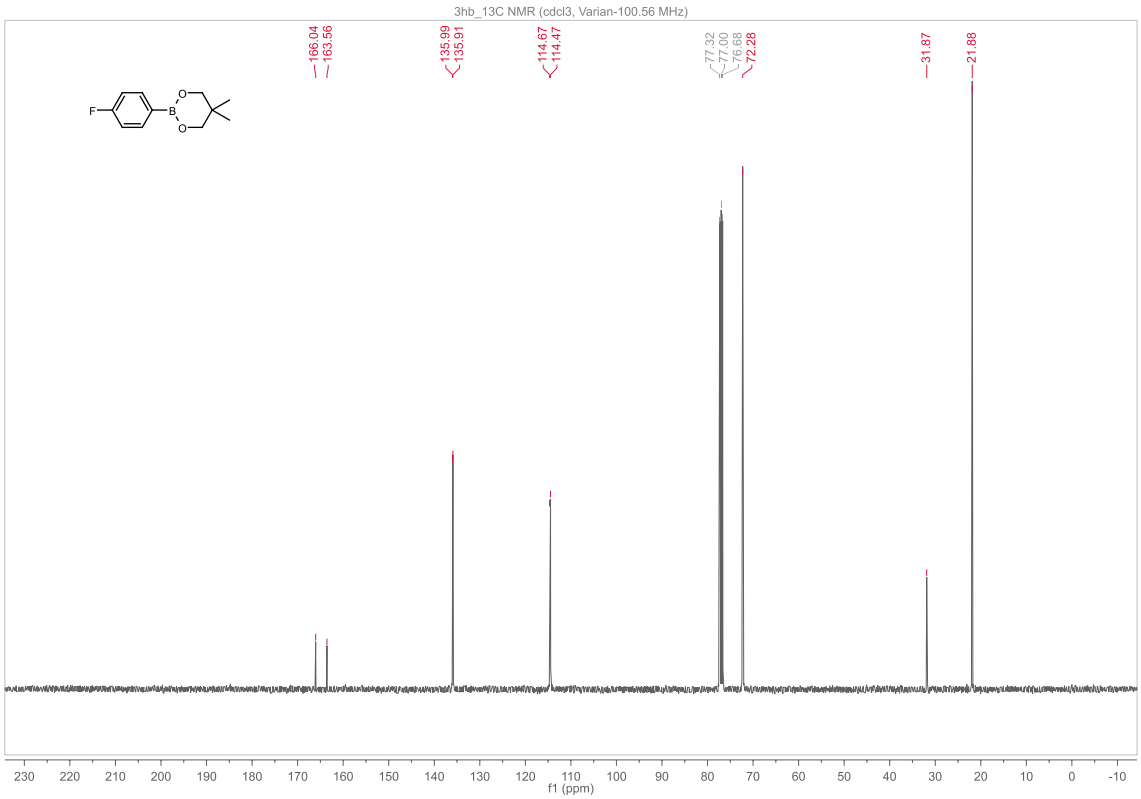

3gb_1H NMR (cdcl3, Varian-399.89 MHz)
7.26
6.96
6.96
6.55
6.55
6.54
3.81
3.77
1.02
2.00
0.90
5.65
3.93
5.88
f1 (ppm)

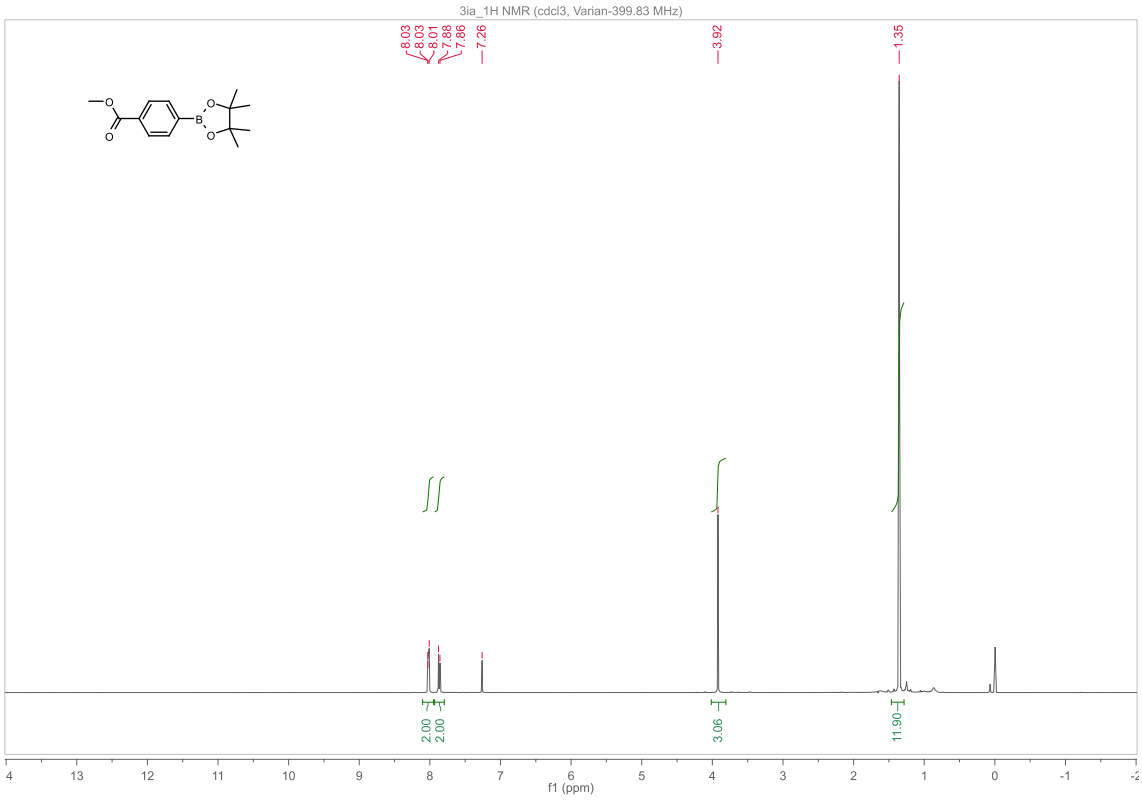

3gb_13C NMR (cdcl3, Varian-100.56 MHz)
160.29
110.68
103.88
77.32
77.00
76.68
72.29
55.30
31.84
21.87
f1 (ppm)

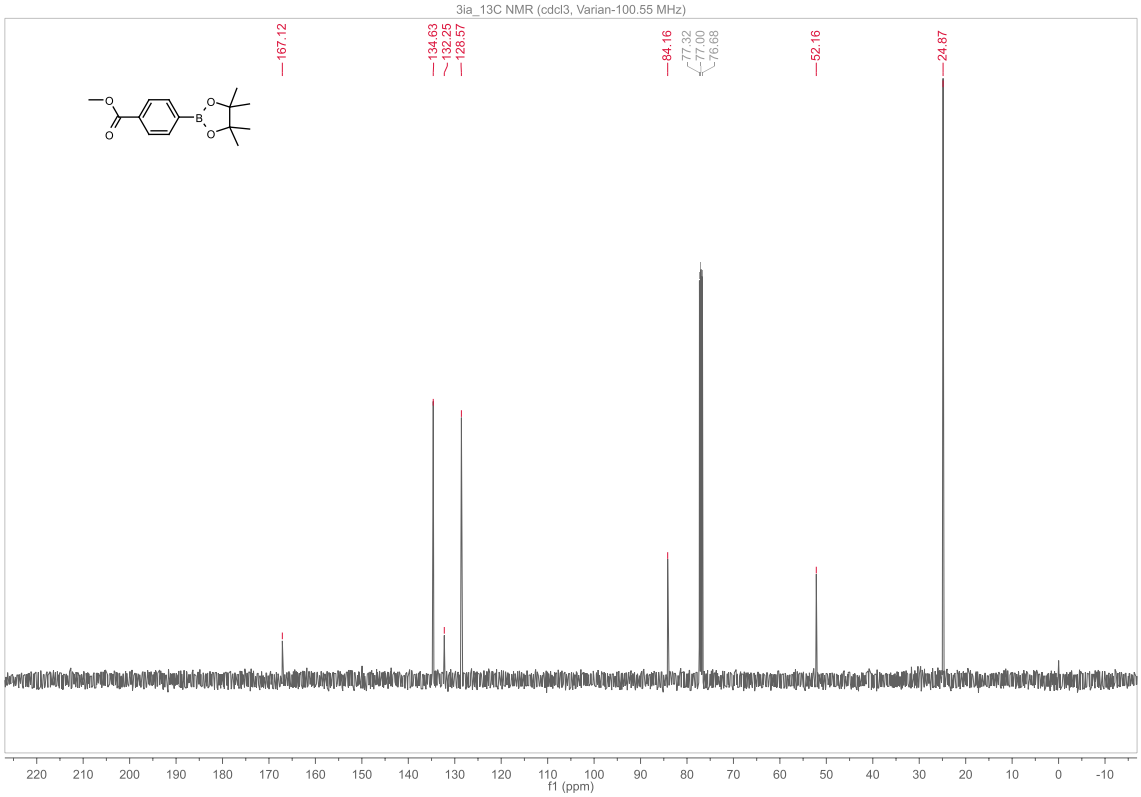

3ha_1H NMR (cdcl3, Varian-399.90 MHz)
7.81
7.80
7.79
7.78
7.26
7.07
7.07
7.06
7.05
7.05
7.05
7.05
7.04
7.04
7.03
7.03
7.02
7.02
1.34
F
B
O
O
2.00
2.00
13.26
f1 (ppm)

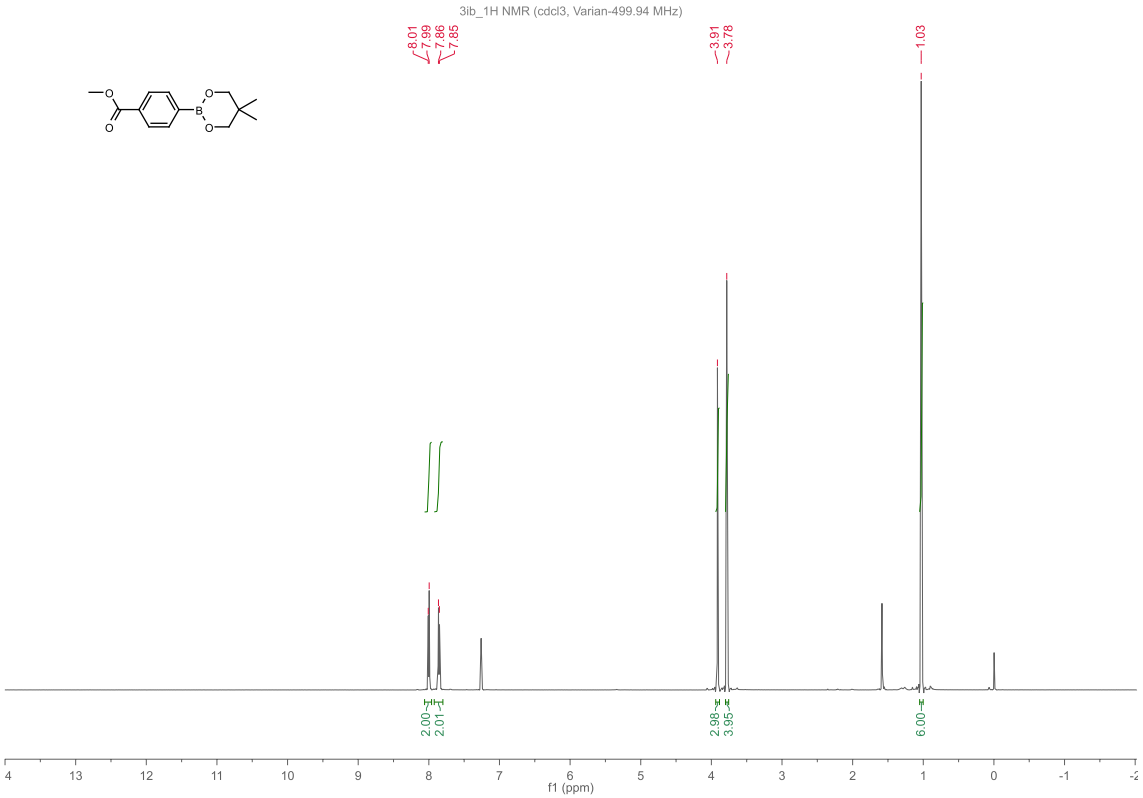

3ha_13C NMR (cdcl3, Varian-100.57 MHz)
166.31
163.82
136.99
136.91
114.93
114.73
83.89
77.32
77.00
76.68
24.85
F
B
O
O
f1 (ppm)

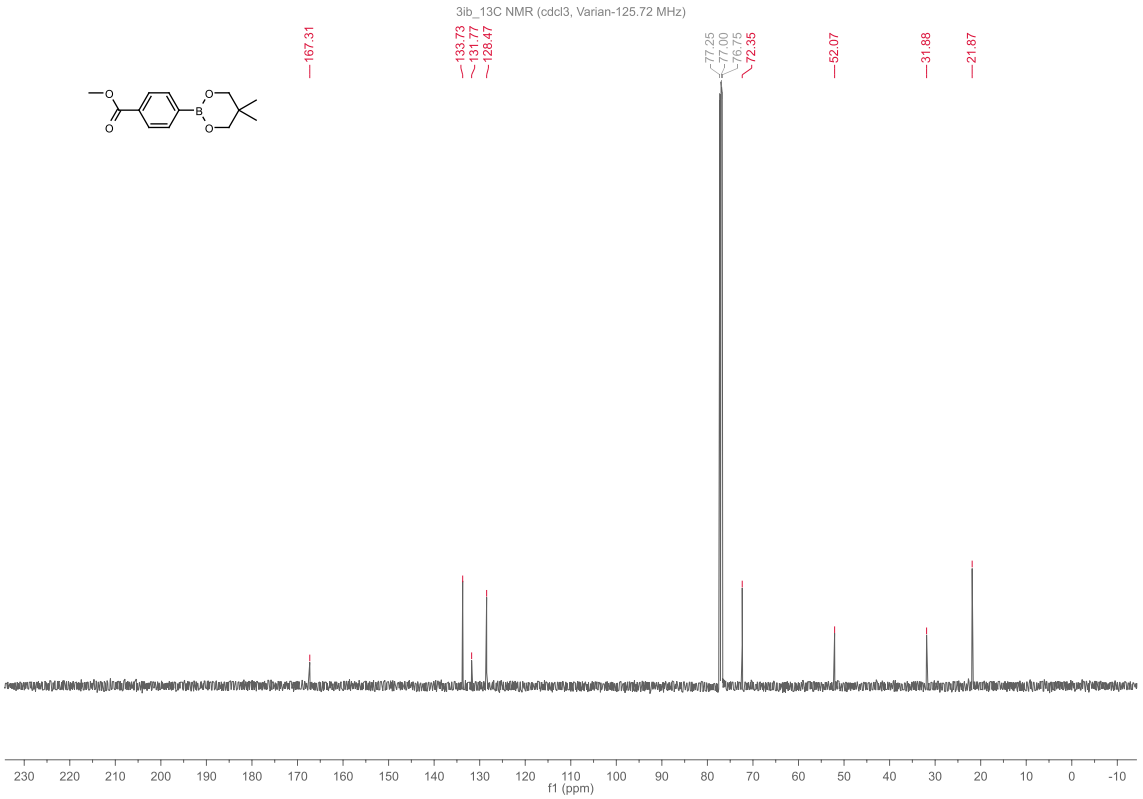

3hb_1H NMR (cdcl3, Varian-399.89 MHz)
7.80
7.79
7.78
7.77
7.05
7.05
7.05
7.03
7.03
7.03
7.02
7.01
3.76
1.02
F
O
B
O
1.00
1.00
2.05
3.12
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

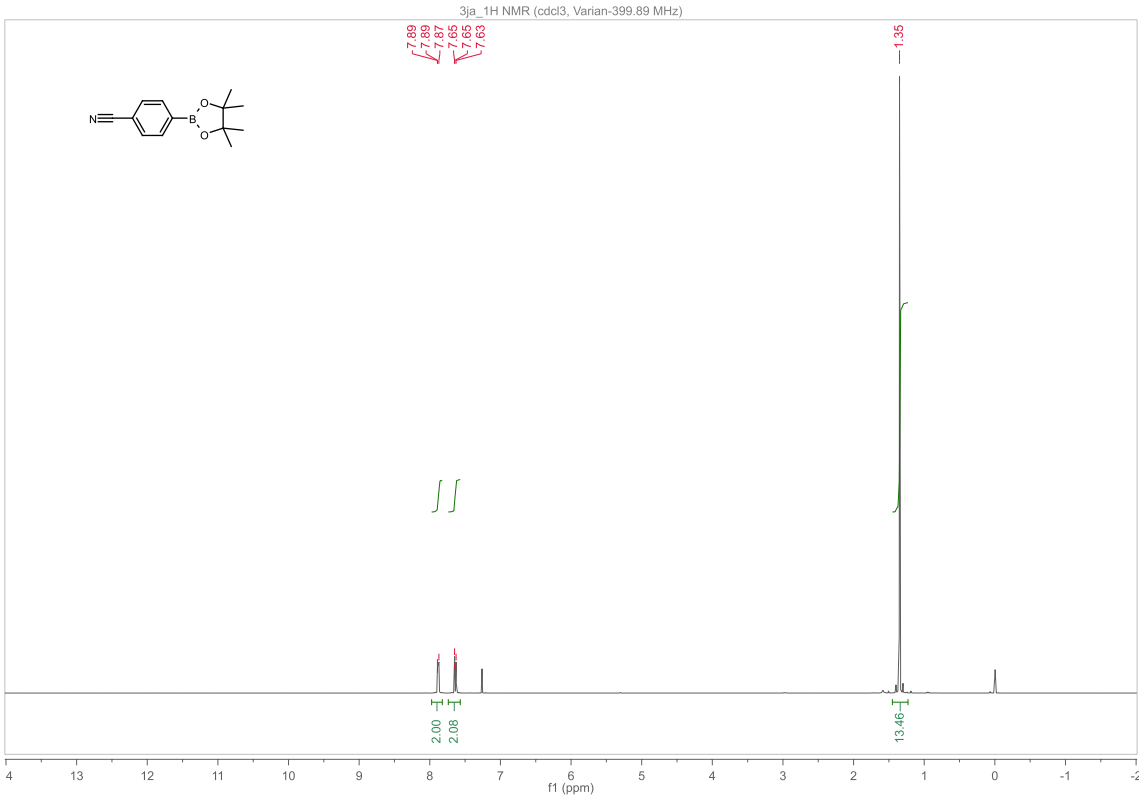

3hb_13C NMR (cdcl3, Varian-100.56 MHz)
166.04
163.56
135.99
135.91
114.67
114.47
77.32
77.00
76.68
72.28
31.87
21.88
F
O
B
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

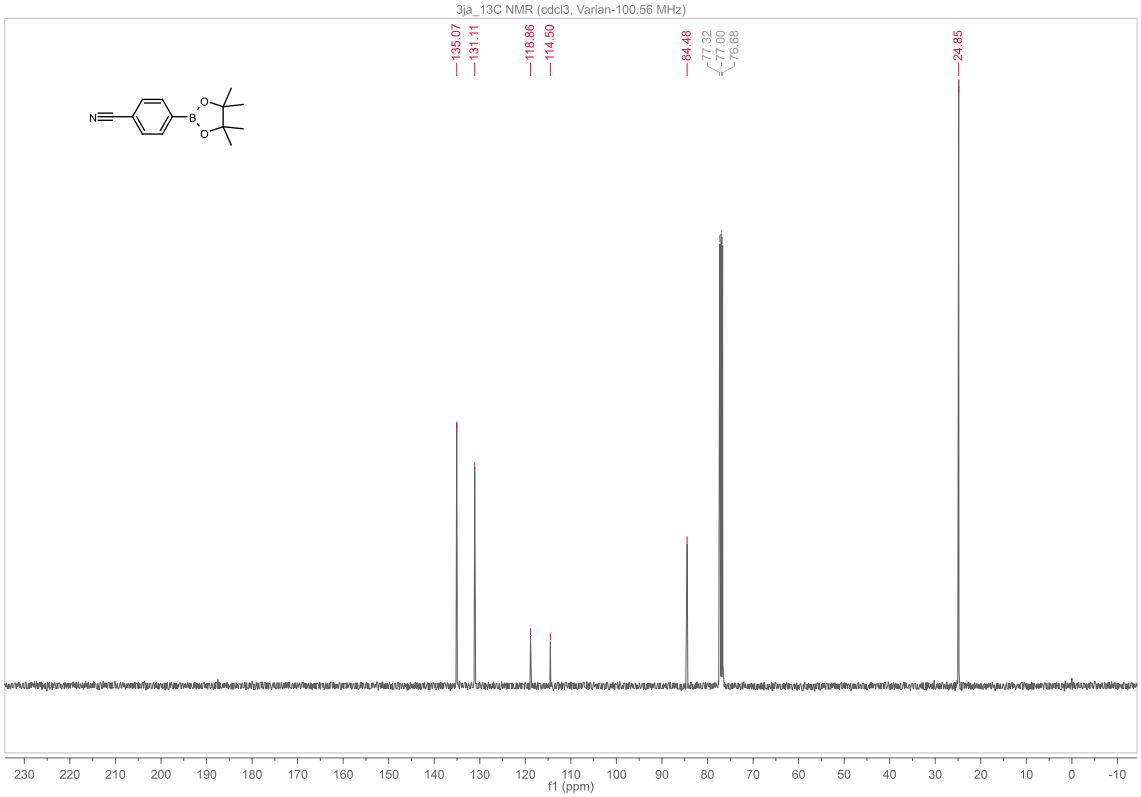

3ia_1H NMR (cdcl3, Varian-399.83 MHz)
8.03
8.03
8.01
7.88
7.86
7.26
3.92
1.35
2.00
2.00
3.06
11.90
f1 (ppm)

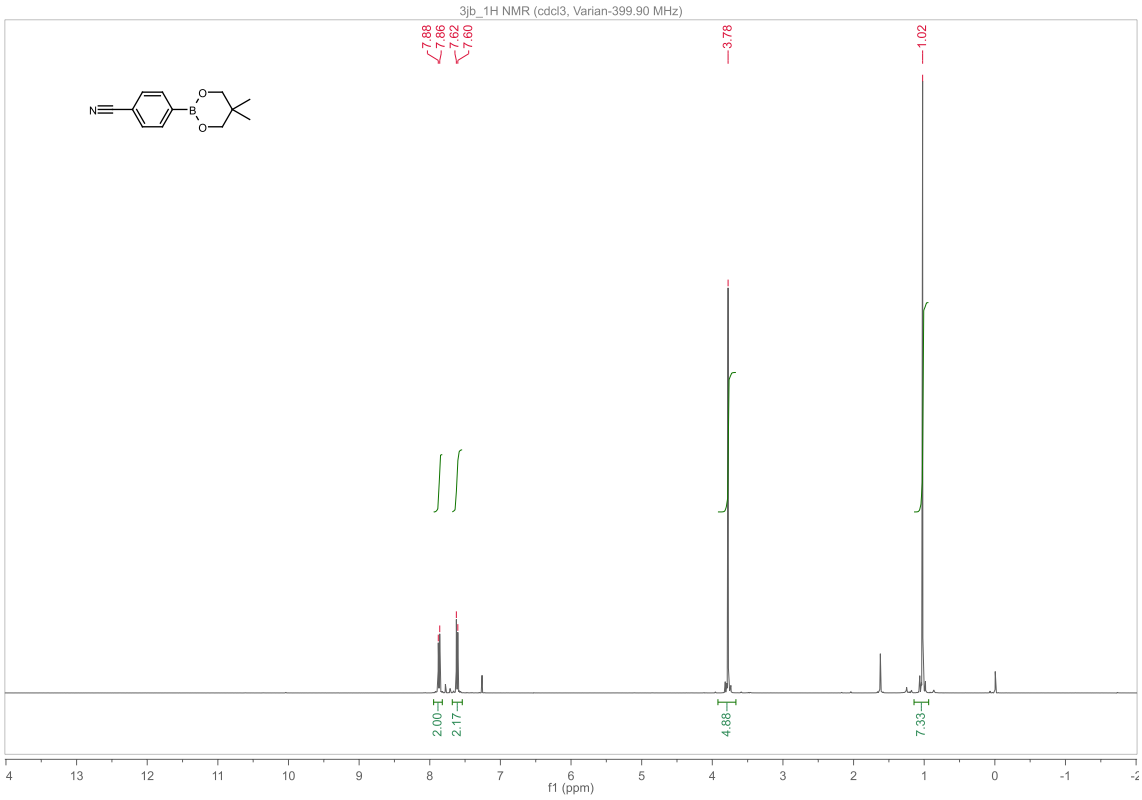

3ia_13C NMR (cdcl3, Varian-100.55 MHz)
167.12
134.63
132.25
128.57
84.16
77.32
77.00
76.68
52.16
24.87
f1 (ppm)

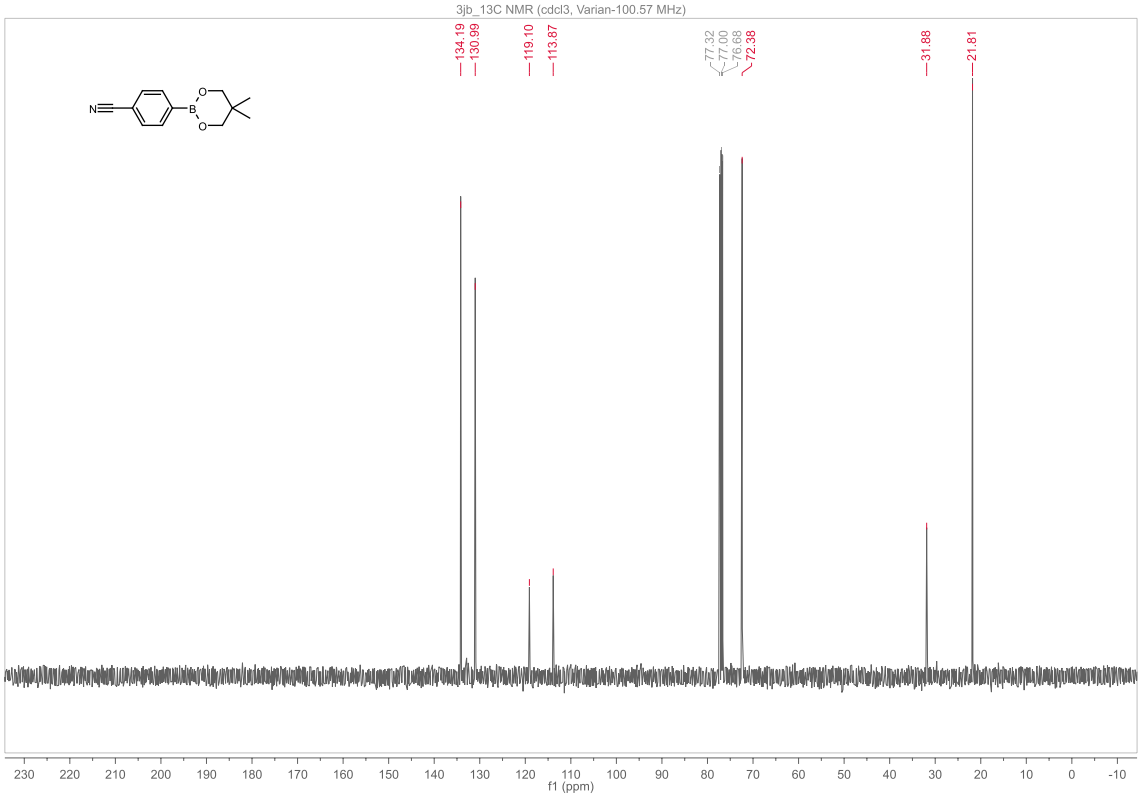

3ib_1H NMR (cdcl3, Varian-499.94 MHz)
8.01
7.99
7.86
7.85
3.91
3.78
1.03
2.00
2.01
2.98
3.95
6.00
f1 (ppm)

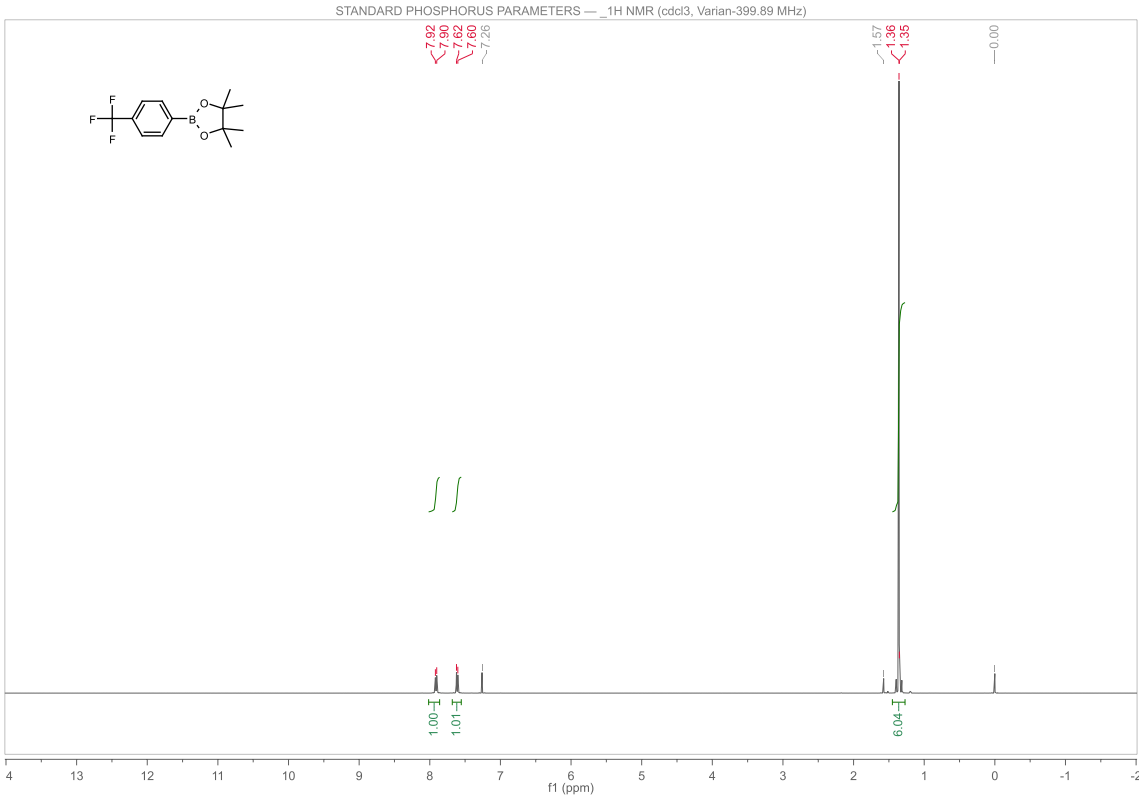

3ib_13C NMR (cdcl3, Varian-125.72 MHz)
167.31
133.73
131.77
128.47
77.25
77.00
76.75
72.35
52.07
31.88
21.87
f1 (ppm)

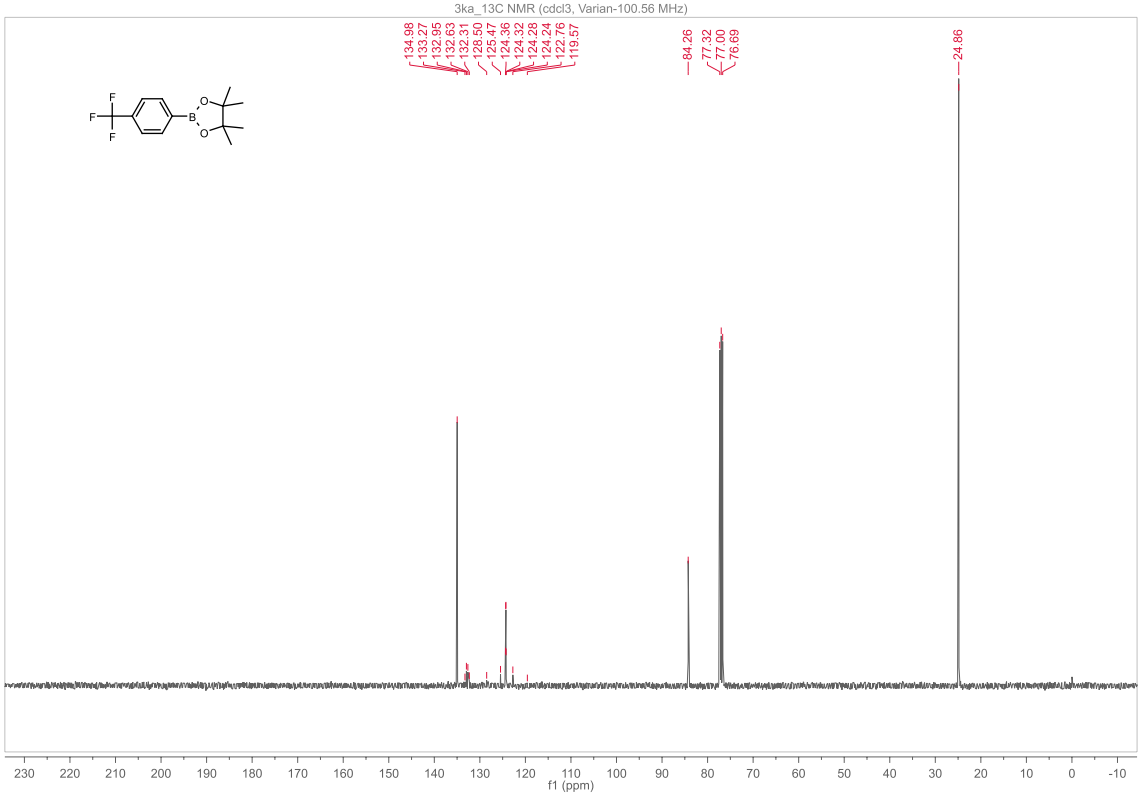

3ja_1H NMR (cdcl3, Varian-399.89 MHz)
7.89
7.89
7.87
7.65
7.65
7.63
1.35
2.00
2.08
13.46
f1 (ppm)

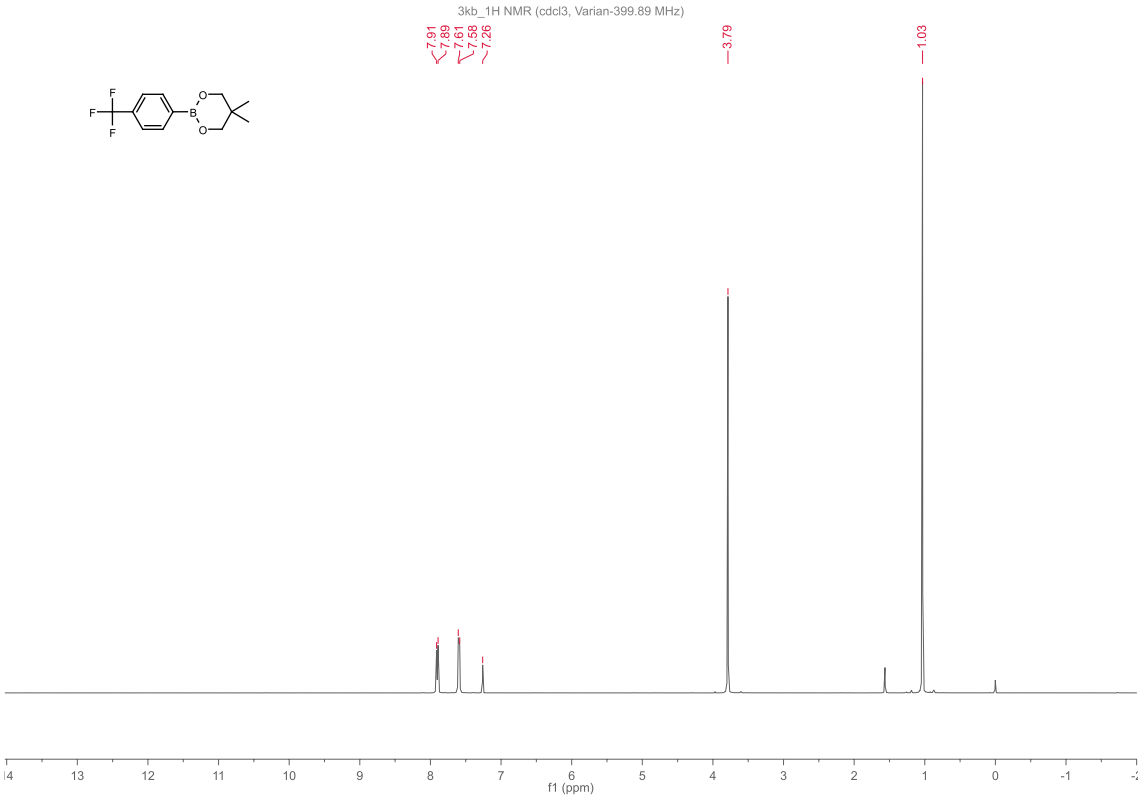

3ja_13C NMR (cdcl3, Varian-100.56 MHz)
135.07
131.11
118.86
114.50
84.48
77.32
77.00
76.68
24.85
f1 (ppm)

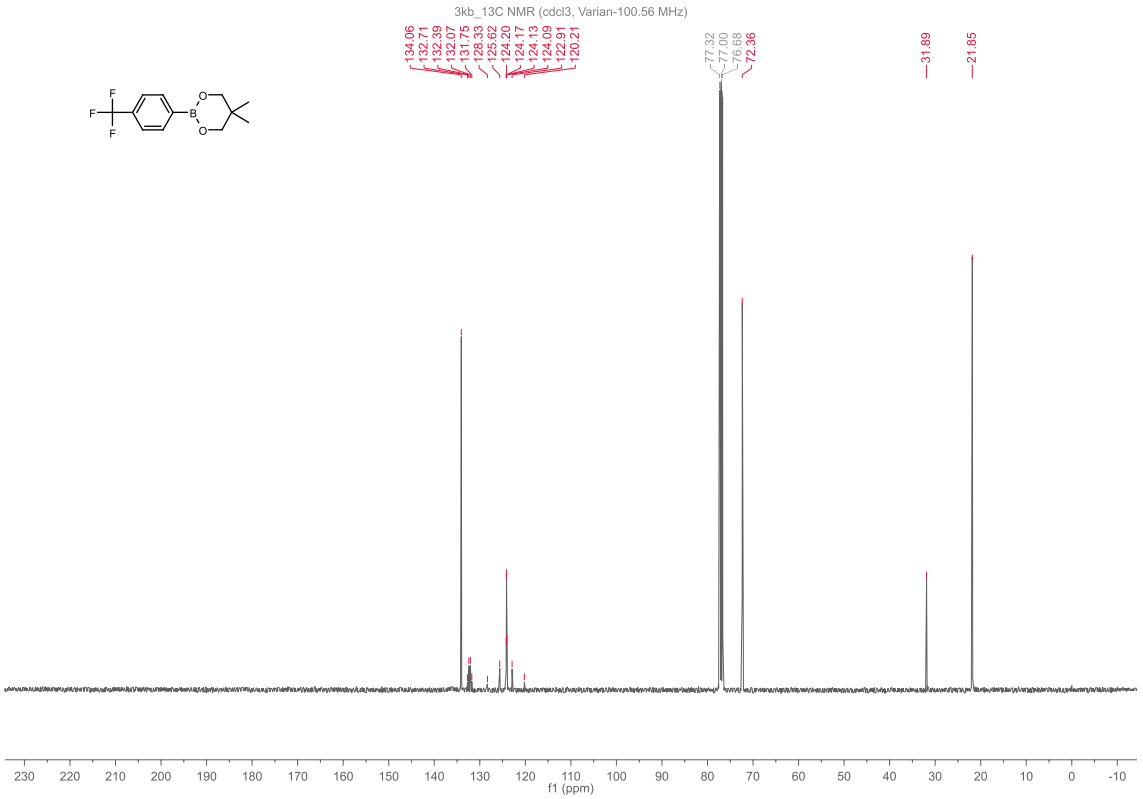

3jb_1H NMR (cdcl3, Varian-399.90 MHz)
7.88
7.86
7.62
7.60
3.78
1.02
2.00
2.17
4.88
7.33
f1 (ppm)

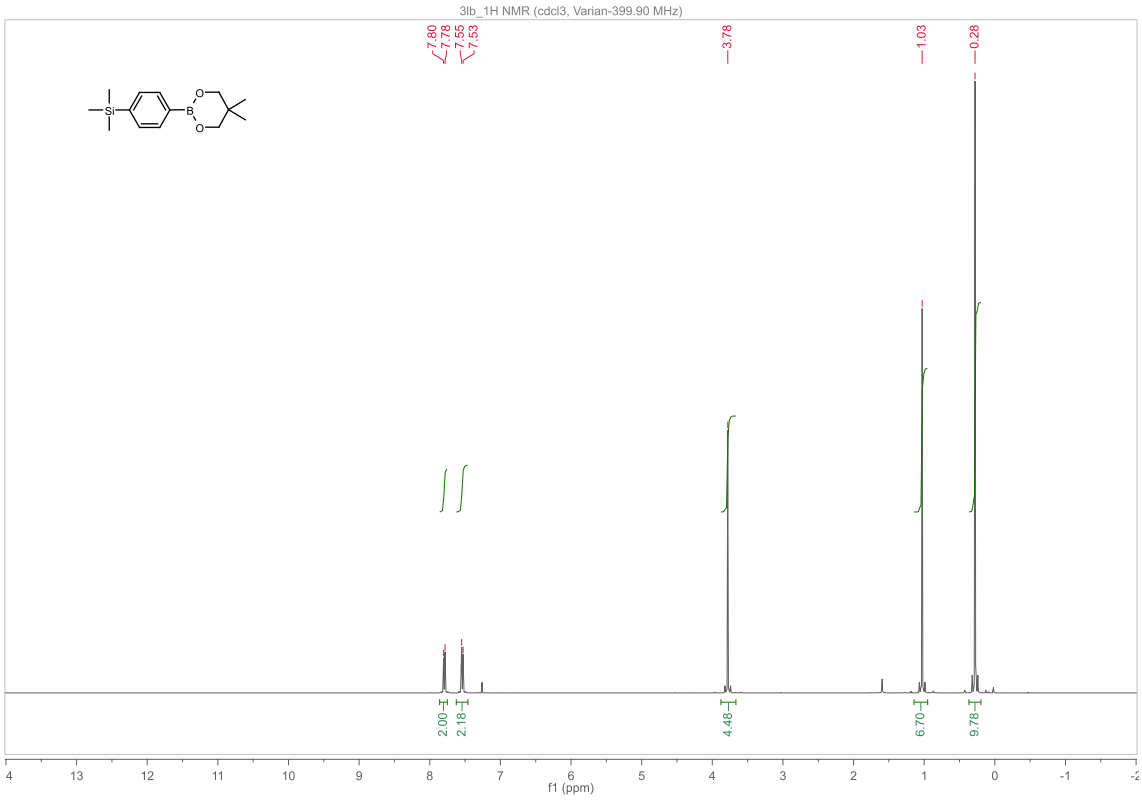

3jb_13C NMR (cdcl3, Varian-100.57 MHz)
134.19
130.99
119.10
113.87
77.32
77.00
76.68
72.38
31.88
21.81
f1 (ppm)

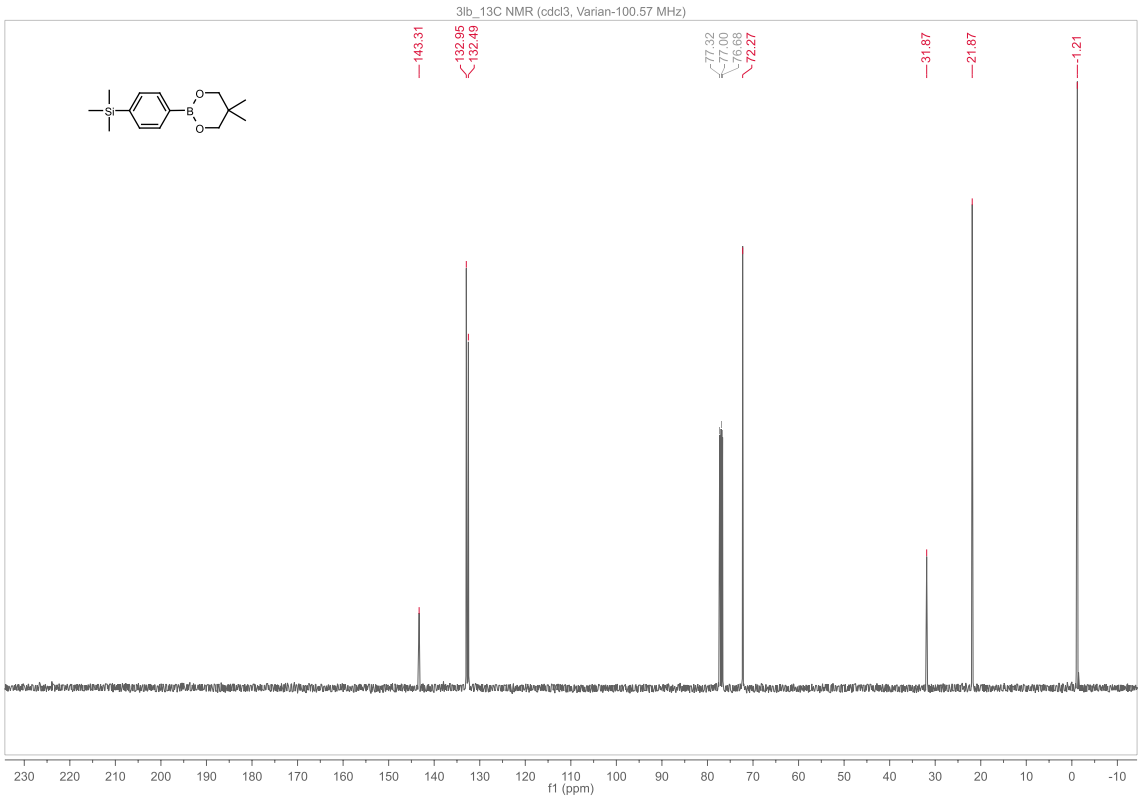

STANDARD PHOSPHORUS PARAMETERS — _1H NMR (cdcl3, Varian-399.89 MHz)
7.92
7.90
7.62
7.60
7.26
1.57
1.36
1.35
0.00
1.00
1.01
6.04
f1 (ppm)

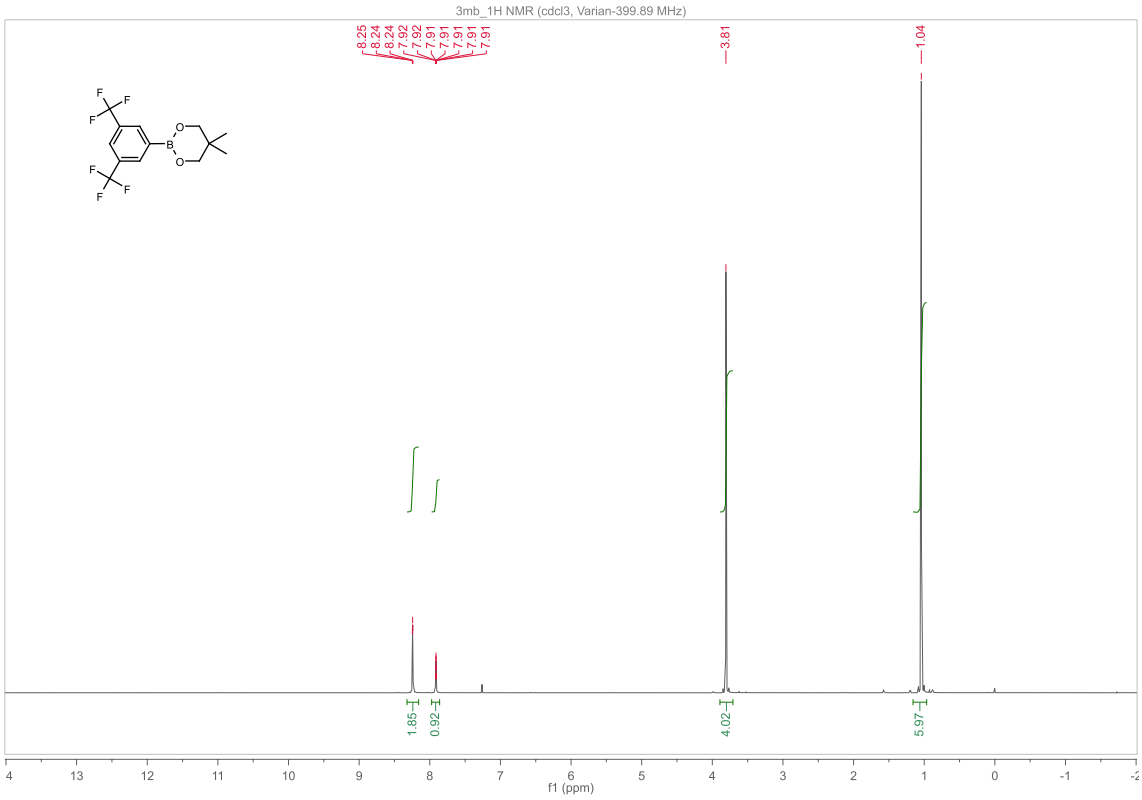

3ka_13C NMR (cdcl3, Varian-100.56 MHz)
134.98
133.27
132.95
132.63
132.31
128.50
125.47
124.36
124.32
124.28
124.24
122.76
119.57
84.26
77.32
77.00
76.69
24.86
f1 (ppm)

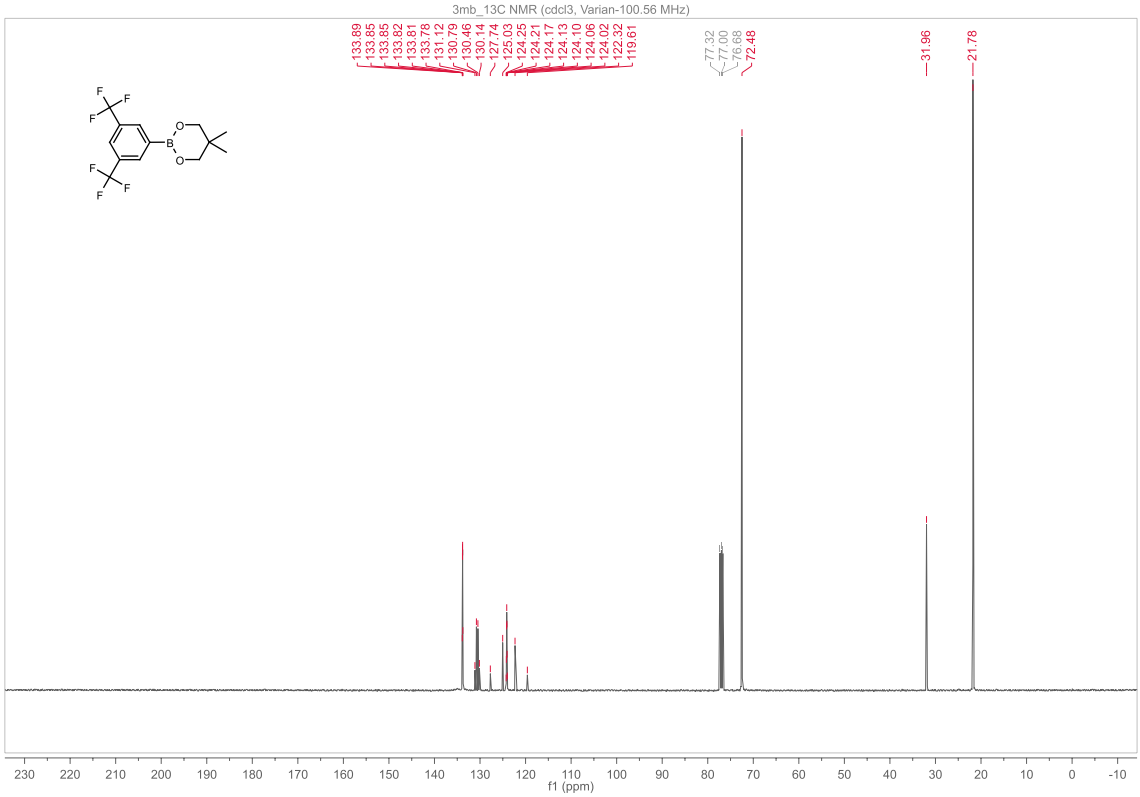

3kb_1H NMR (cdcl3, Varian-399.89 MHz)
7.91
7.89
7.61
7.58
7.26
3.79
1.03
F
F
F
O
B
O
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

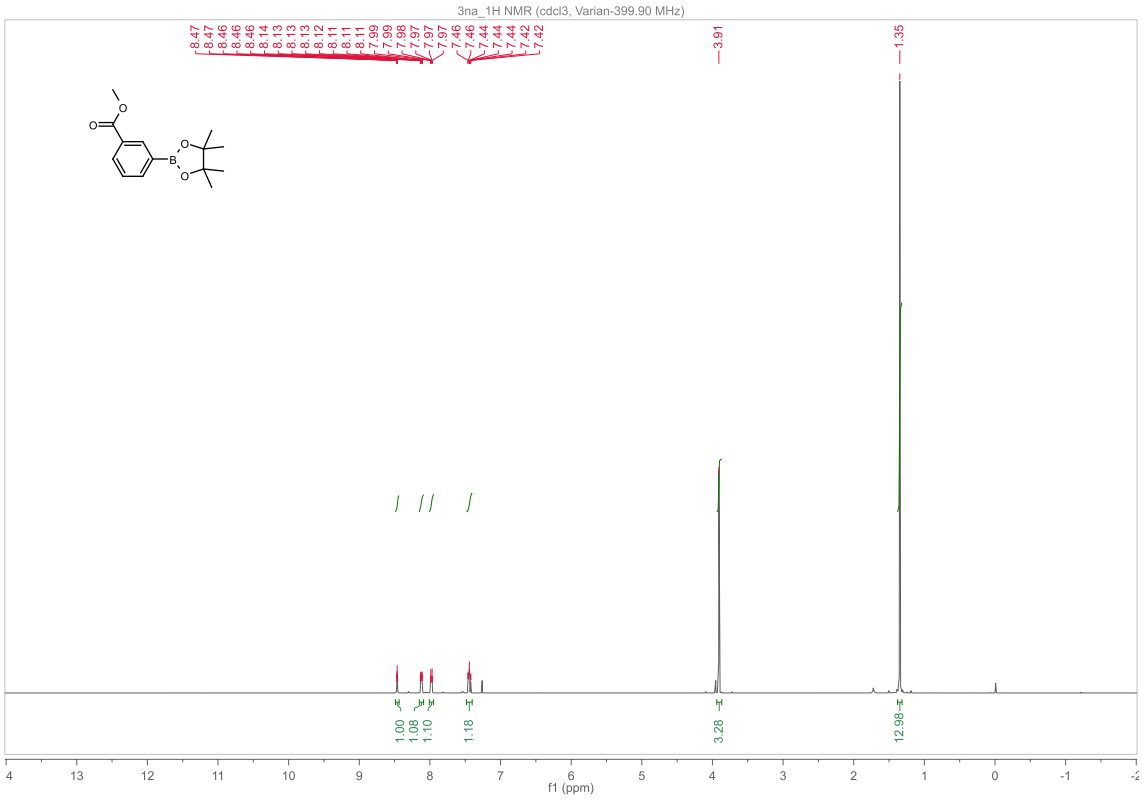

3kb_13C NMR (cdcl3, Varian-100.56 MHz)
134.06
132.71
132.39
132.07
131.75
128.33
125.62
124.20
124.17
124.13
124.09
122.91
120.21
77.32
77.00
76.68
72.36
31.89
21.85
F
F
F
O
B
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

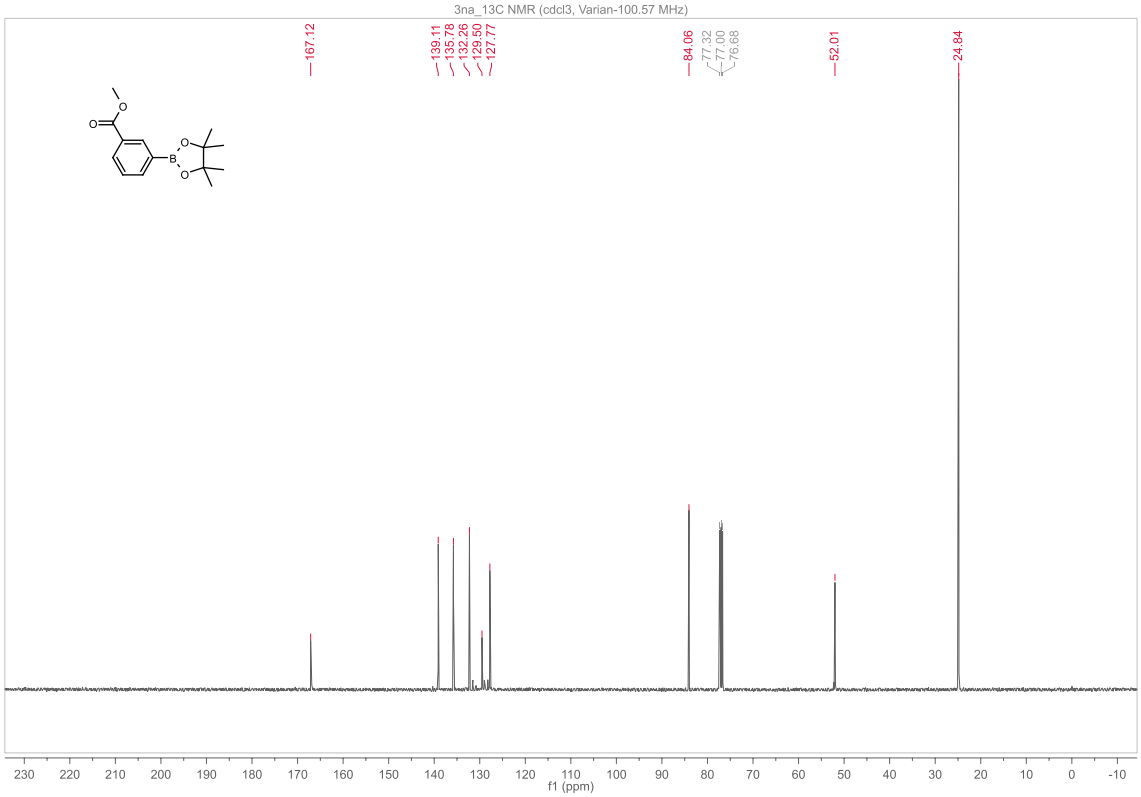

3lb_1H NMR (cdcl3, Varian-399.90 MHz)
7.80
7.78
7.55
7.53
3.78
1.03
0.28
2.00
2.18
4.48
6.70
9.78
f1 (ppm)

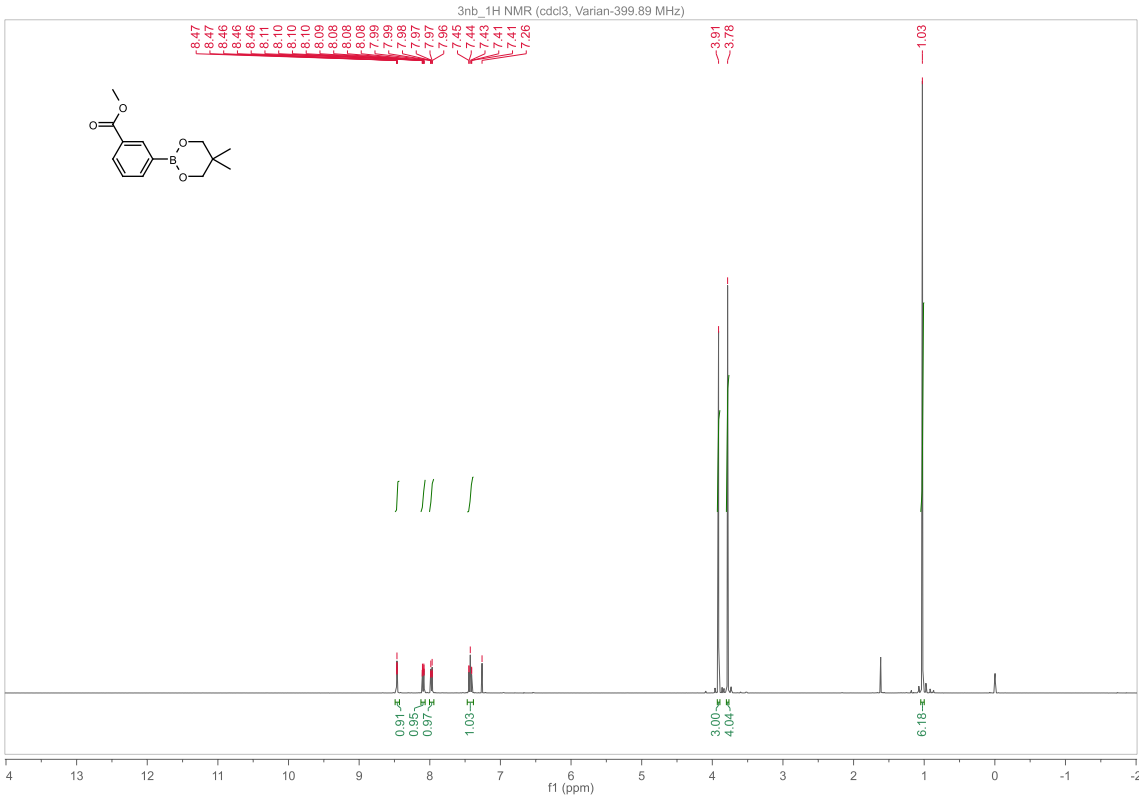

3lb_13C NMR (cdcl3, Varian-100.57 MHz)
143.31
132.95
132.49
77.32
77.00
76.68
72.27
31.87
21.87
-1.21
f1 (ppm)

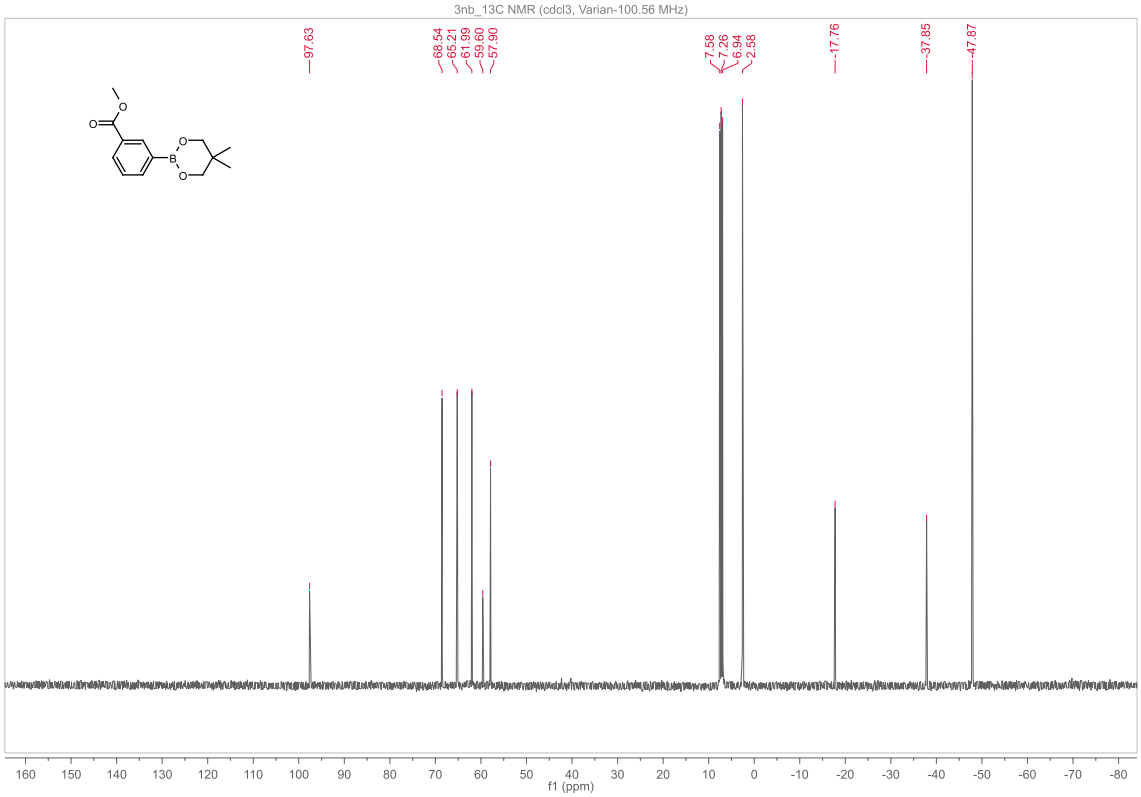

3mb_1H NMR (cdcl3, Varian-399.89 MHz)
8.25
8.24
8.24
7.92
7.92
7.91
7.91
7.91
7.91
7.91
3.81
1.04
1.85
0.92
4.02
5.97
f1 (ppm)

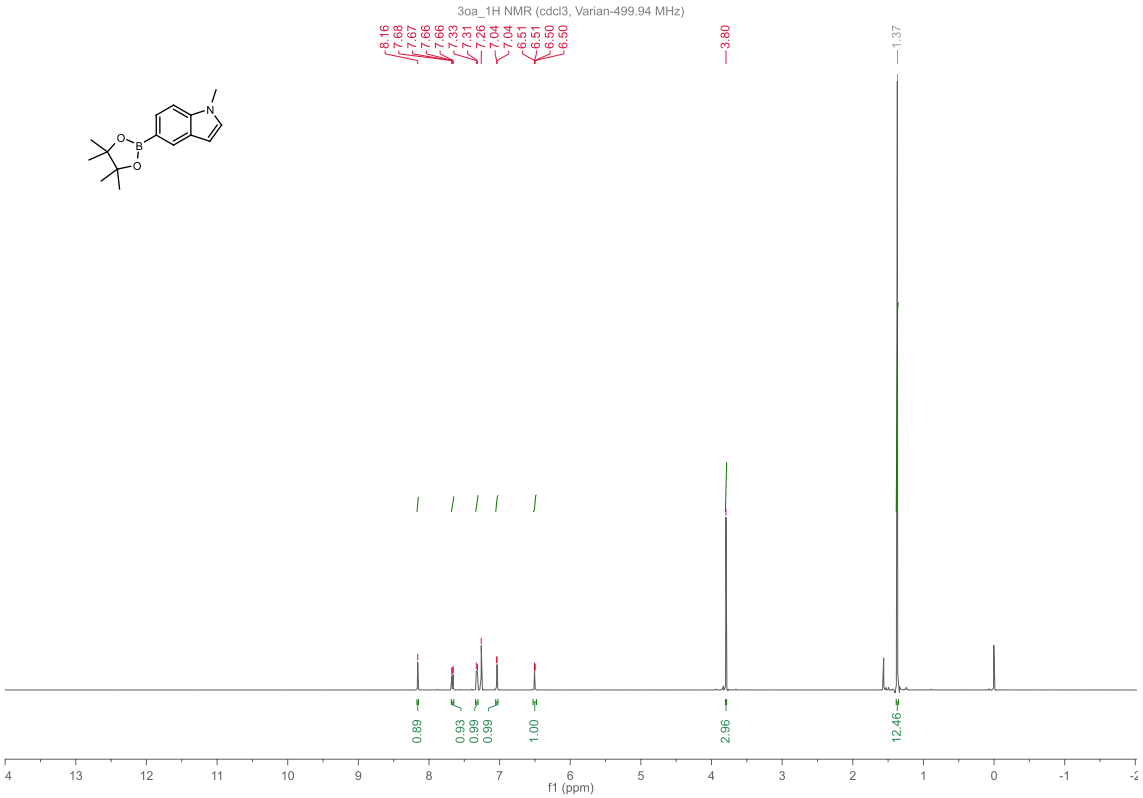

3mb_13C NMR (cdcl3, Varian-100.56 MHz)
133.89
133.85
133.85
133.82
133.81
133.78
131.12
130.79
130.46
130.14
127.74
125.03
124.25
124.21
124.17
124.13
124.10
124.06
124.02
122.32
119.61
77.32
77.00
76.68
72.48
31.96
21.78
f1 (ppm)

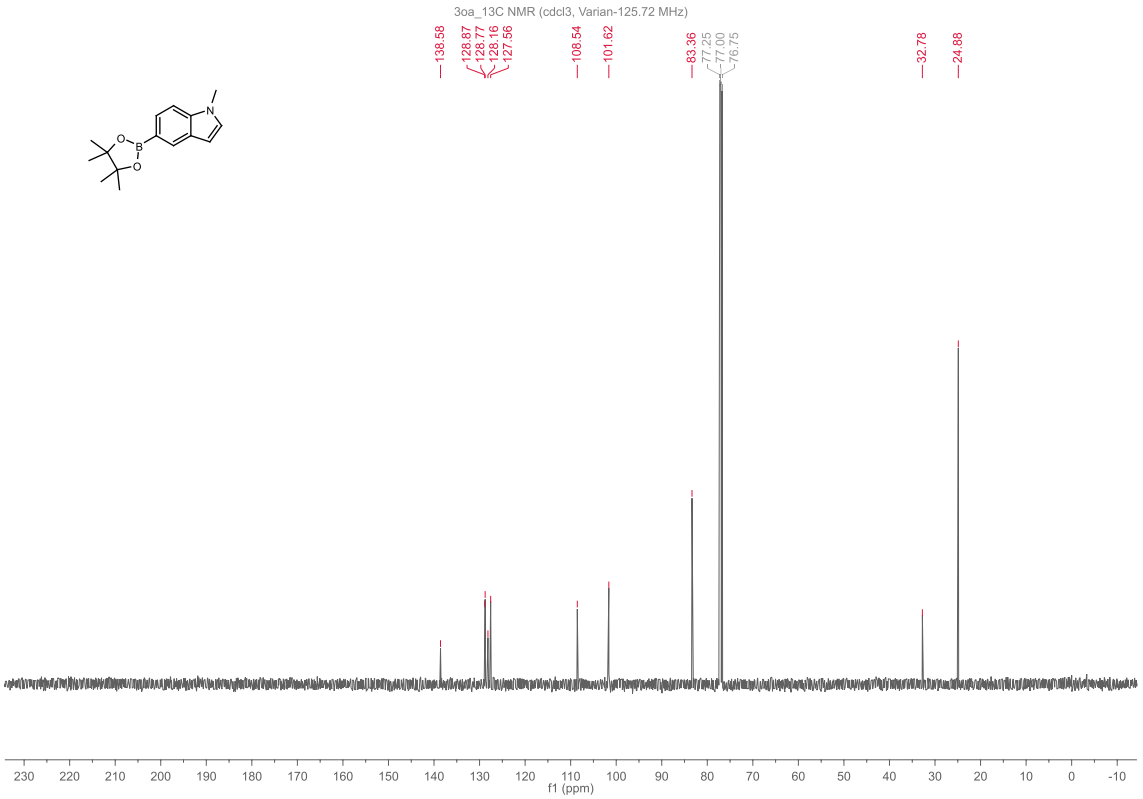

3na_1H NMR (cdcl3, Varian-399.90 MHz)
8.47
8.47
8.46
8.46
8.46
8.14
8.13
8.13
8.12
8.11
8.11
8.11
7.99
7.99
7.98
7.97
7.97
7.97
7.46
7.46
7.44
7.44
7.44
7.42
7.42
3.91
1.35
1.00
1.08
1.10
1.18
3.28
12.98
f1 (ppm)

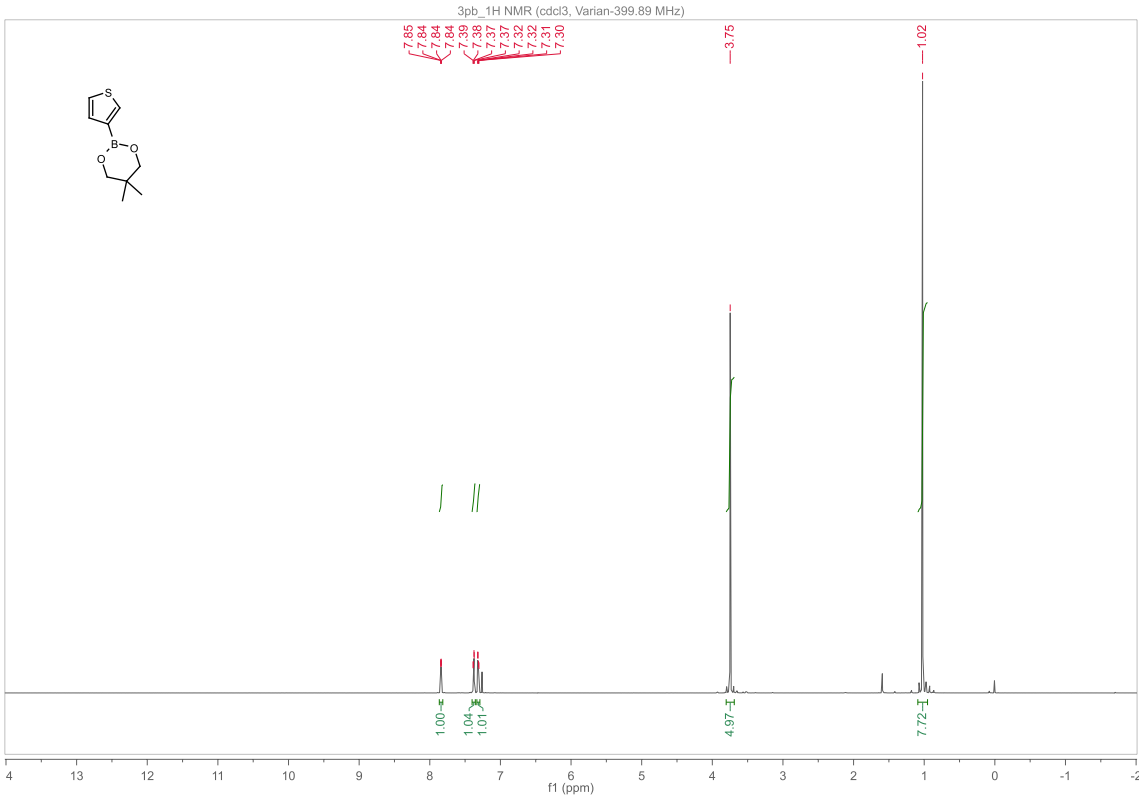

3na_13C NMR (cdcl3, Varian-100.57 MHz)
167.12
139.11
135.78
132.26
129.50
127.77
84.06
77.32
77.00
76.68
52.01
24.84
f1 (ppm)

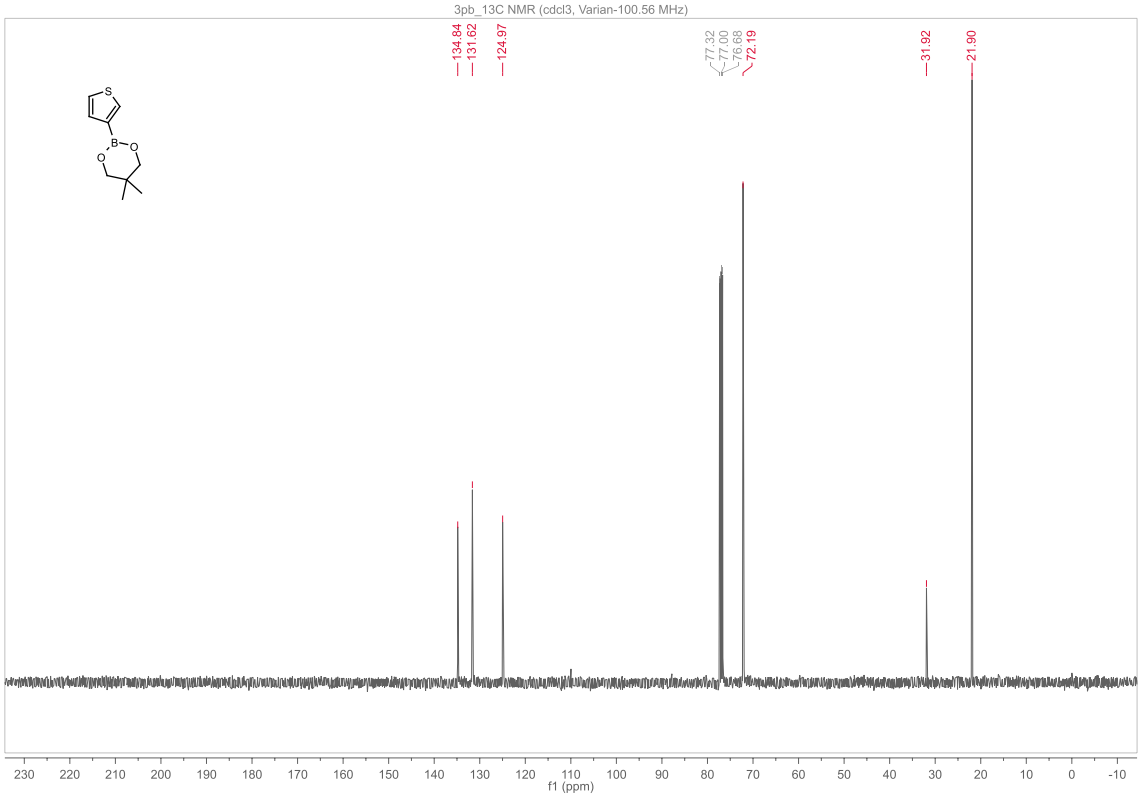

3nb_1H NMR (cdcl3, Varian-399.89 MHz)
8.47
8.47
8.46
8.46
8.46
8.11
8.10
8.10
8.09
8.08
8.08
8.08
7.99
7.99
7.98
7.97
7.97
7.96
7.45
7.44
7.43
7.41
7.41
7.26
3.91
3.78
1.03
0.91
0.95
0.97
1.03
3.00
4.04
6.18
f1 (ppm)

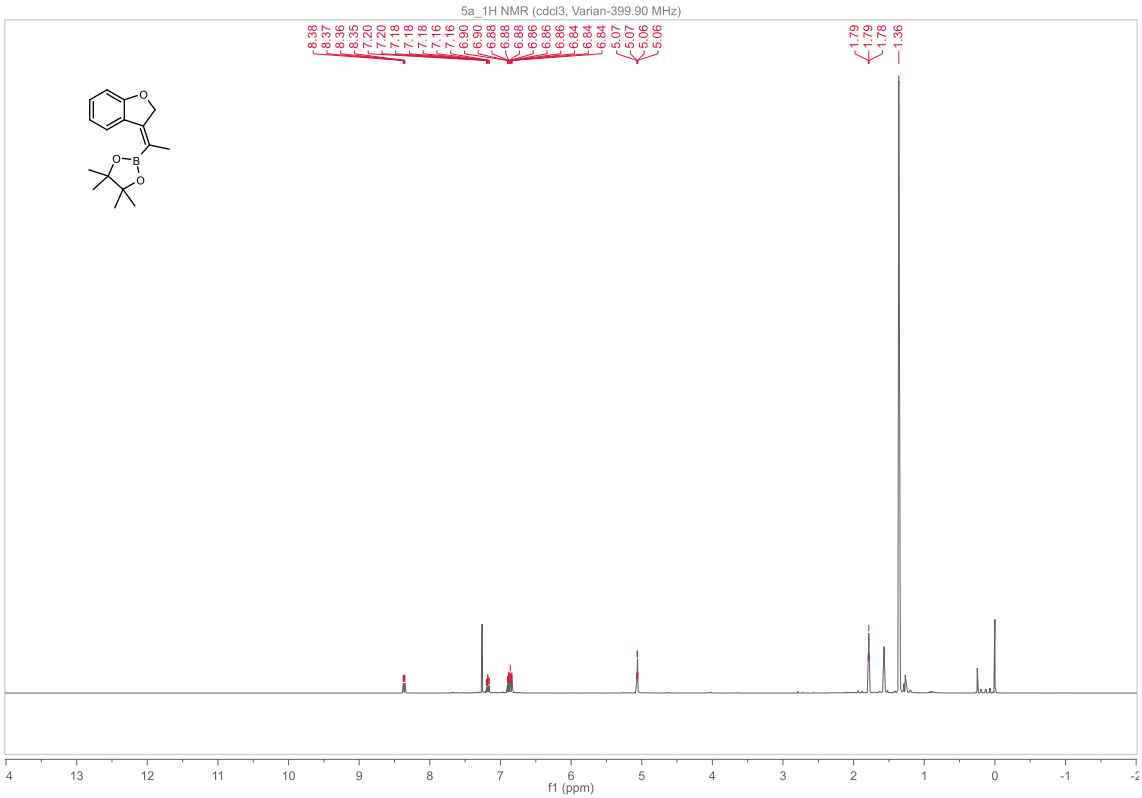

3nb_13C NMR (cdcl3, Varian-100.56 MHz)
97.63
68.54
65.21
61.99
59.60
57.90
7.58
7.26
6.94
2.58
17.76
37.85
47.87
f1 (ppm)

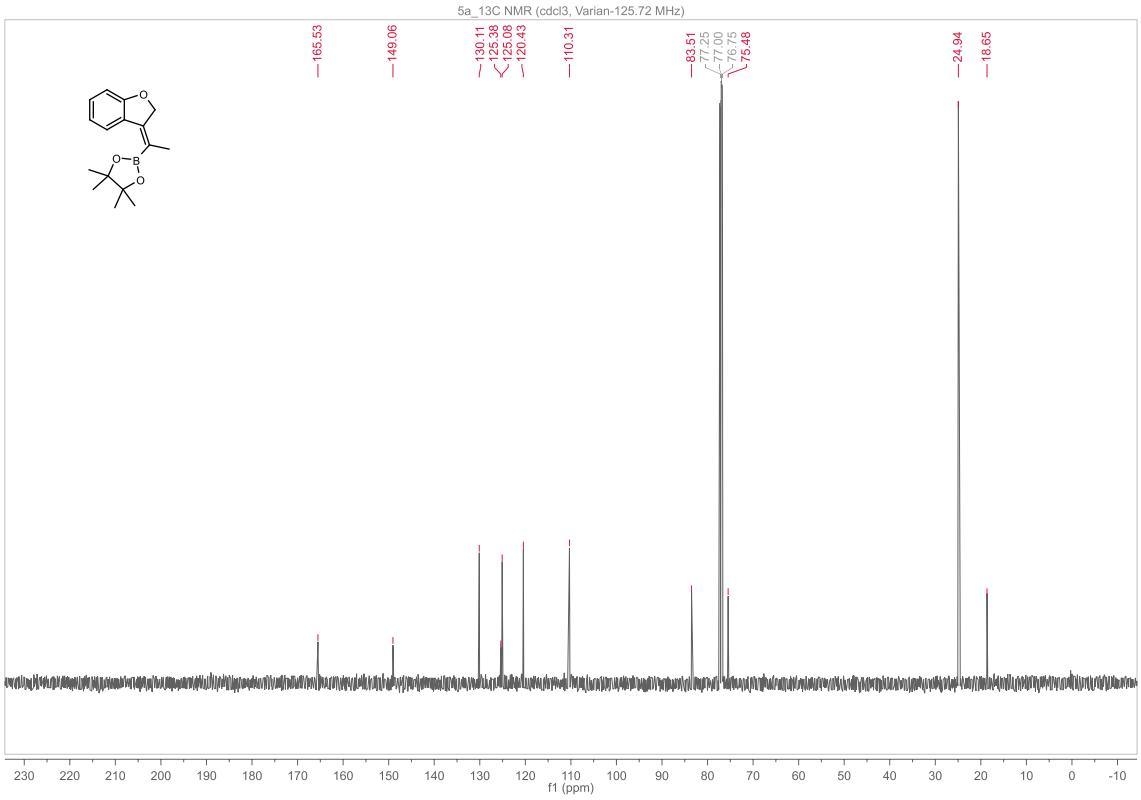

3oa_1H NMR (cdcl3, Varian-499.94 MHz)
8.16
7.68
7.67
7.66
7.66
7.33
7.31
7.26
7.04
7.04
6.51
6.51
6.50
6.50
3.80
1.37
0.89
0.93
0.99
0.99
1.00
2.96
12.46
f1 (ppm)

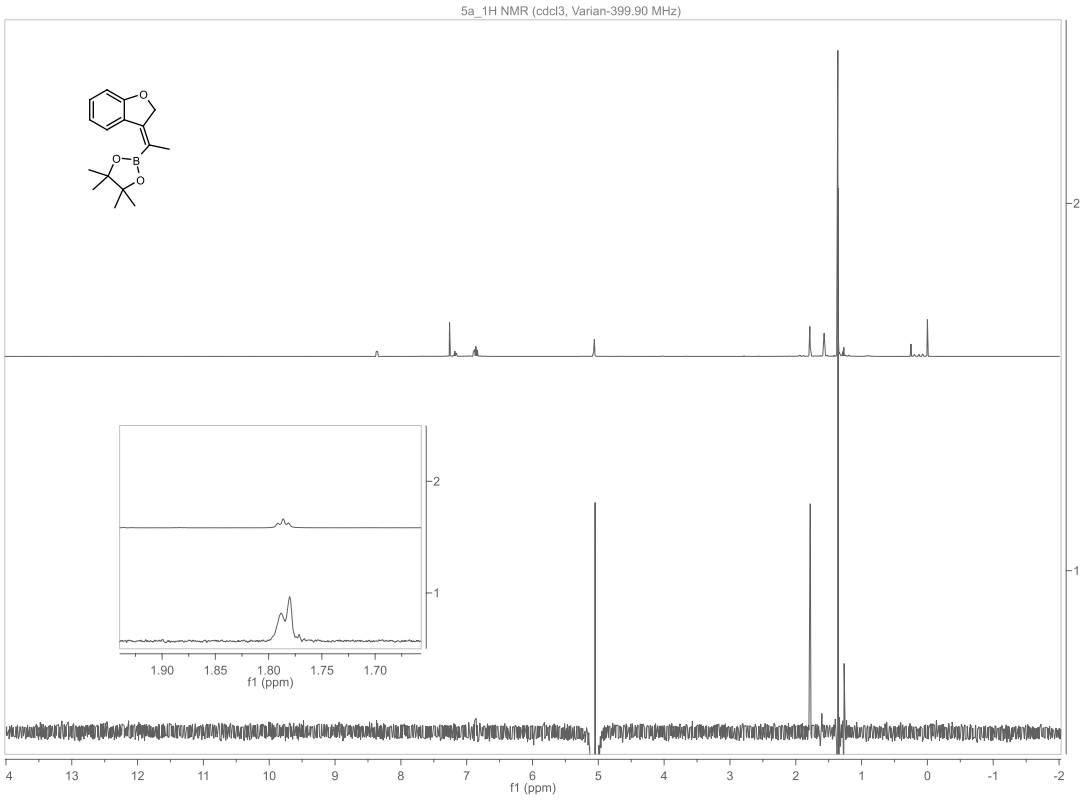

3oa_13C NMR (cdcl3, Varian-125.72 MHz)
138.58
128.87
128.77
128.16
127.56
108.54
101.62
83.36
77.25
77.00
76.75
32.78
24.88
f1 (ppm)

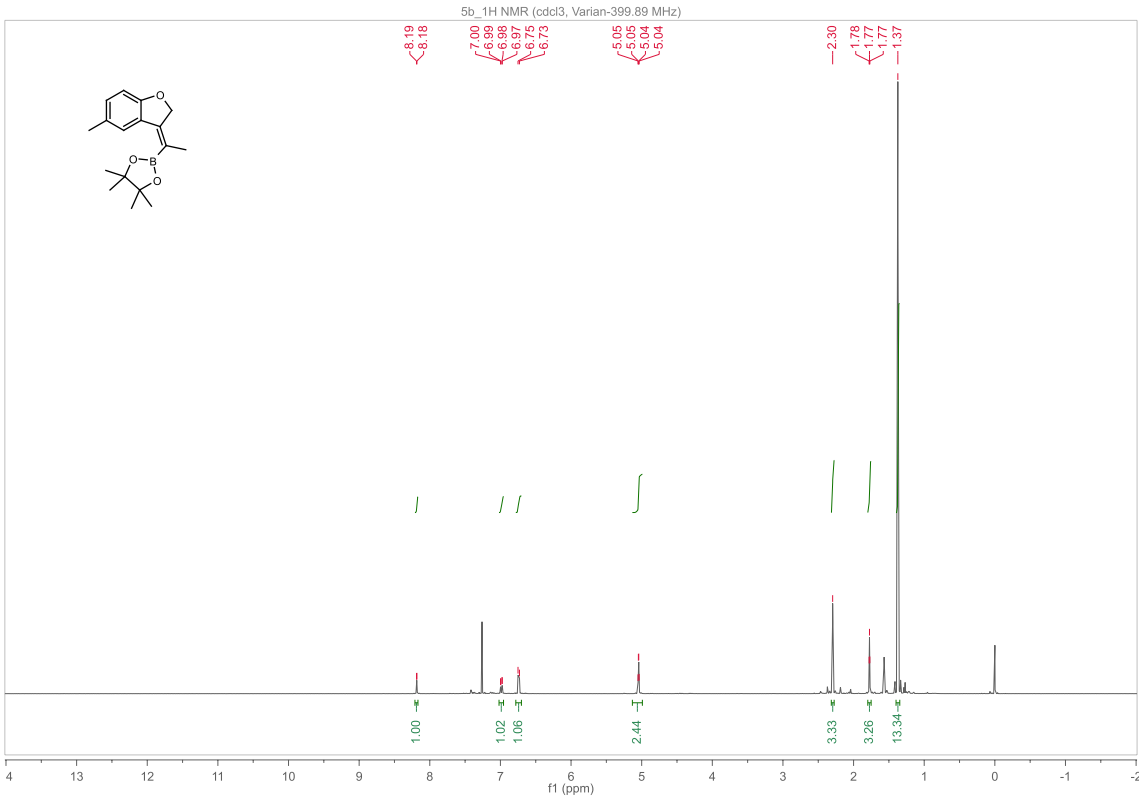

3pb_1H NMR (cdcl3, Varian-399.89 MHz)
7.85
7.84
7.84
7.84
7.39
7.38
7.37
7.37
7.32
7.32
7.31
7.30
3.75
1.02
1.00
1.04
1.01
4.97
7.72
f1 (ppm)

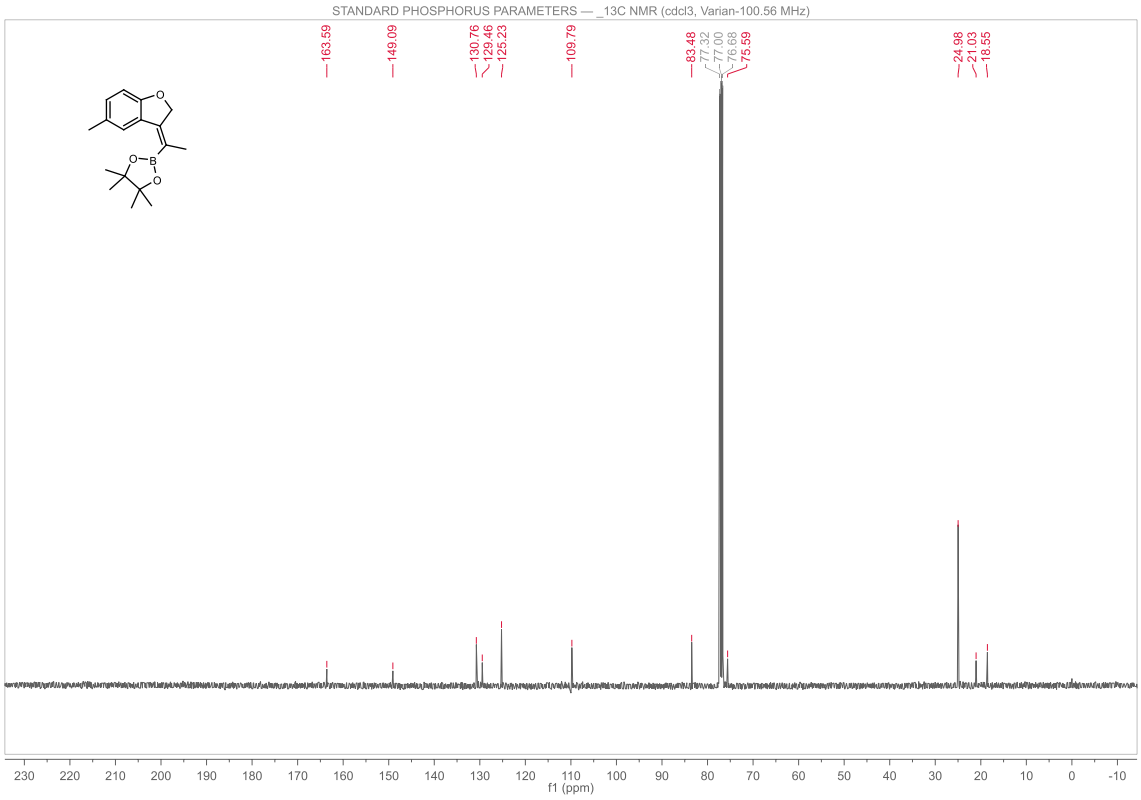

3pb_13C NMR (cdcl3, Varian-100.56 MHz)
134.84
131.62
124.97
77.32
77.00
76.68
72.19
31.92
21.90
f1 (ppm)

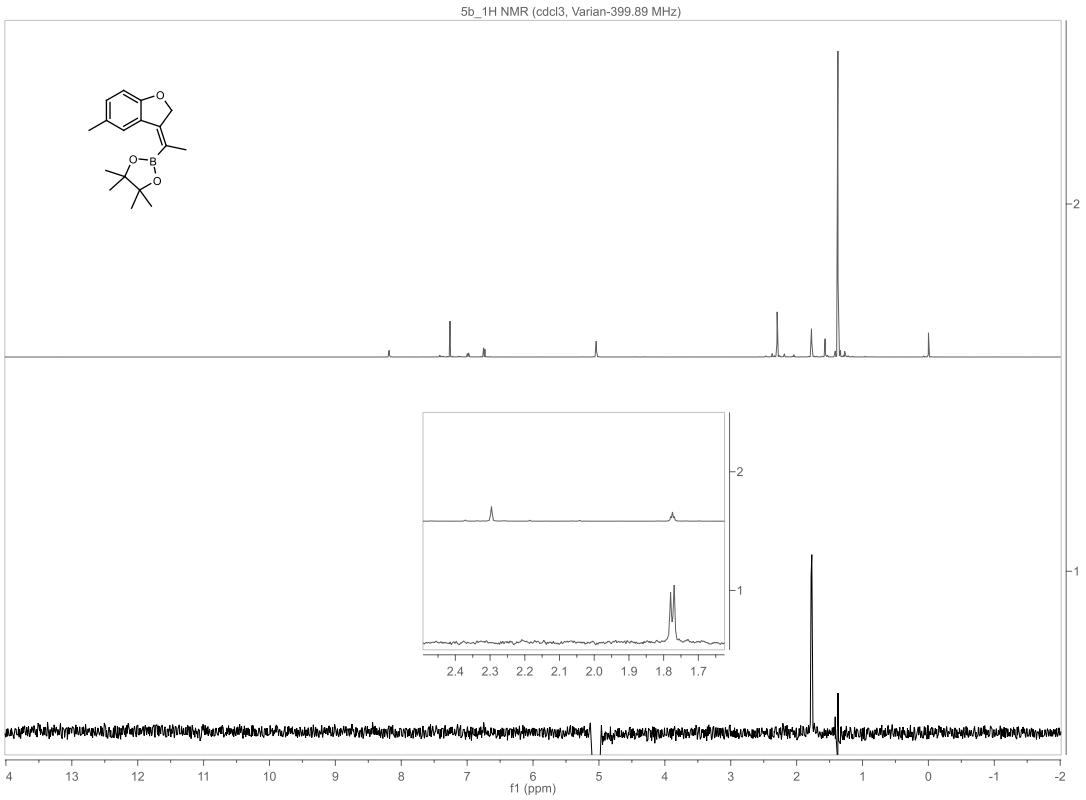

5a_1H NMR (cdcl3, Varian-399.90 MHz)
8.38
8.37
8.36
8.35
7.20
7.18
7.18
7.18
7.16
7.16
6.90
6.88
6.88
6.88
6.86
6.86
6.86
6.84
6.84
6.84
5.07
5.07
5.06
5.06
1.79
1.79
1.78
1.36
O
O
B
O
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

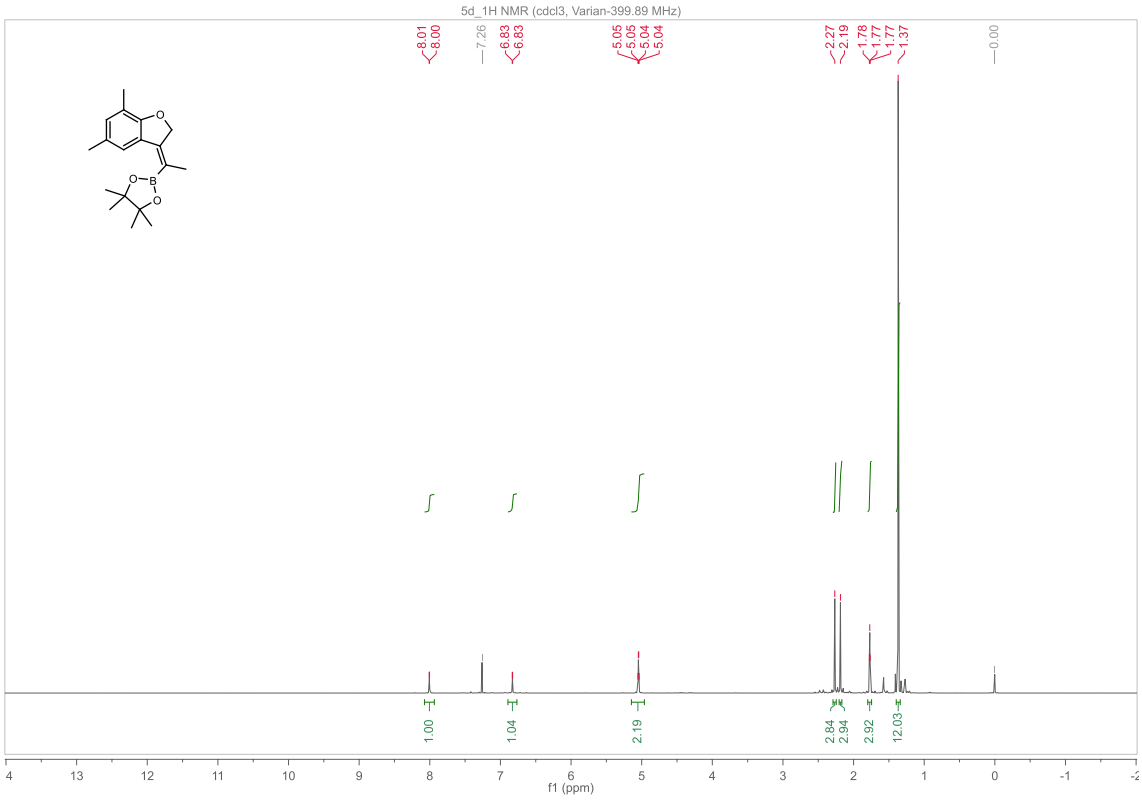

5a_13C NMR (cdcl3, Varian-125.72 MHz)
165.53
149.06
130.11
125.38
125.08
120.43
110.31
83.51
77.25
77.00
76.75
75.48
24.94
18.65
O
O
B
O
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

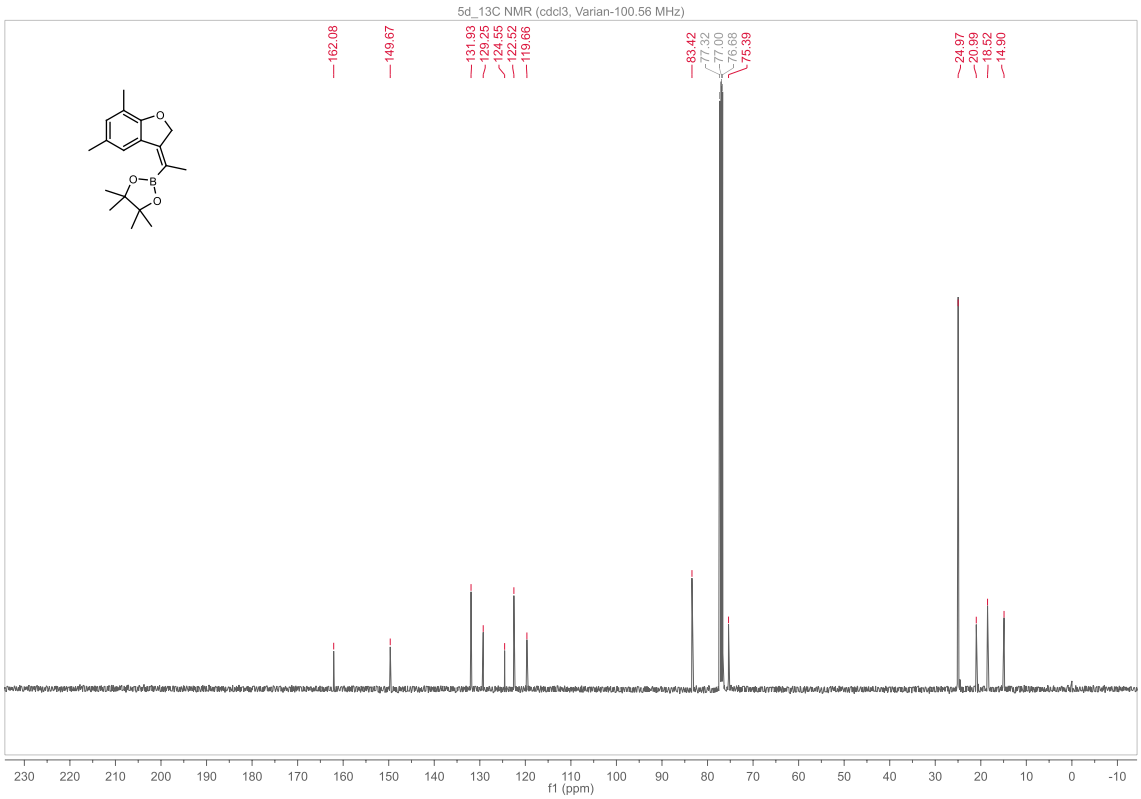

5a_1H NMR (cdcl3, Varian-399.90 MHz)
f1 (ppm)

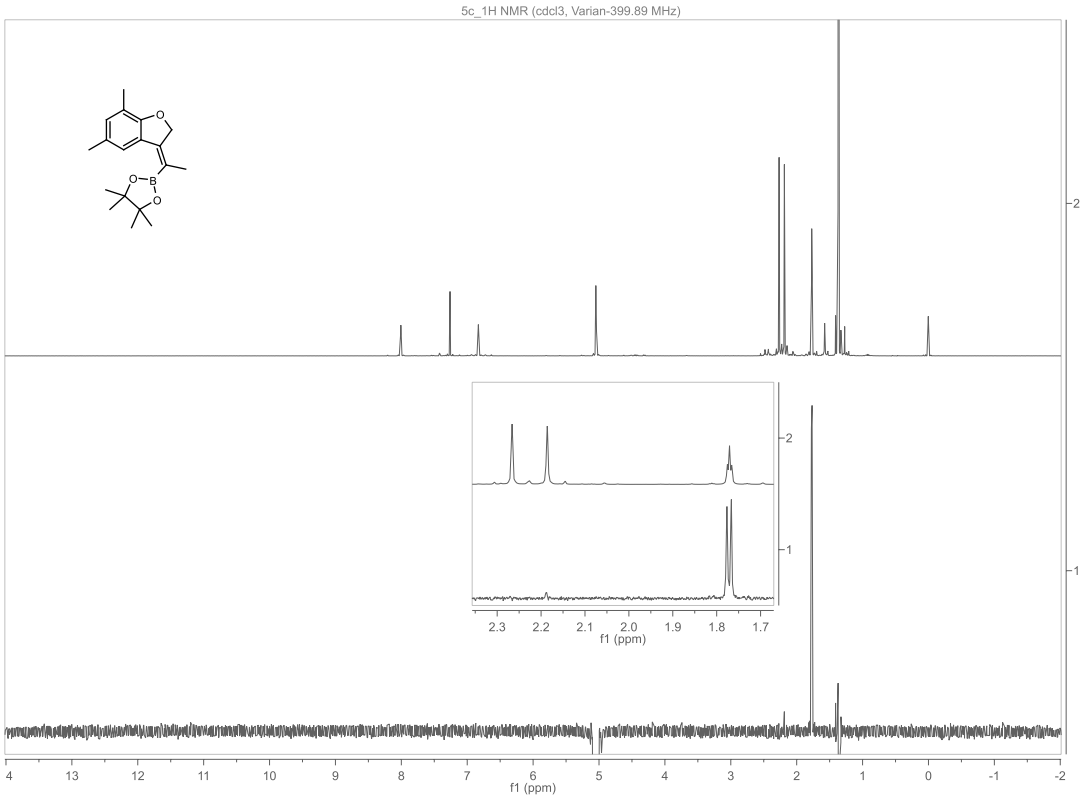

5b_1H NMR (cdcl3, Varian-399.89 MHz)
8.19
8.18
7.00
6.99
6.98
6.97
6.75
6.73
5.05
5.05
5.04
5.04
5.04
2.30
1.78
1.77
1.77
1.37
1.00
1.02
1.06
2.44
3.33
3.26
13.34
f1 (ppm)

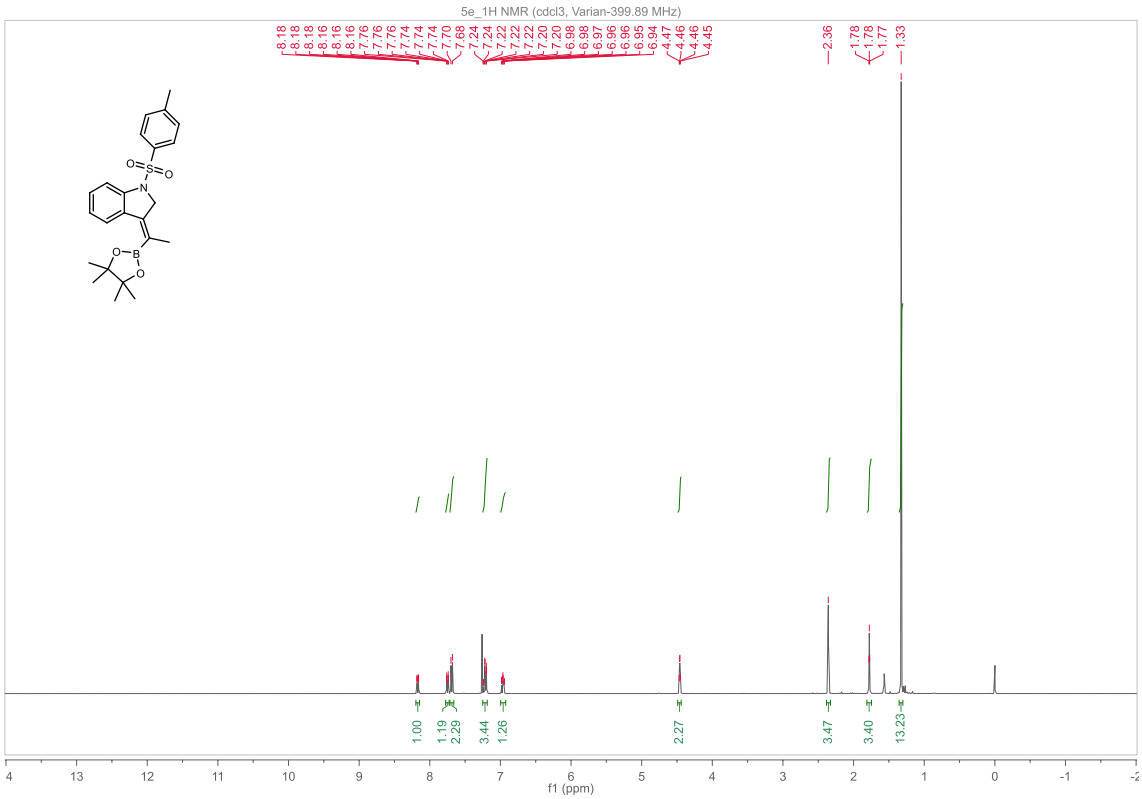

STANDARD PHOSPHORUS PARAMETERS — _13C NMR (cdcl3, Varian-100.56 MHz)
163.59
149.09
130.76
129.46
125.23
109.79
83.48
77.32
77.00
76.68
75.59
24.98
21.03
18.55
f1 (ppm)

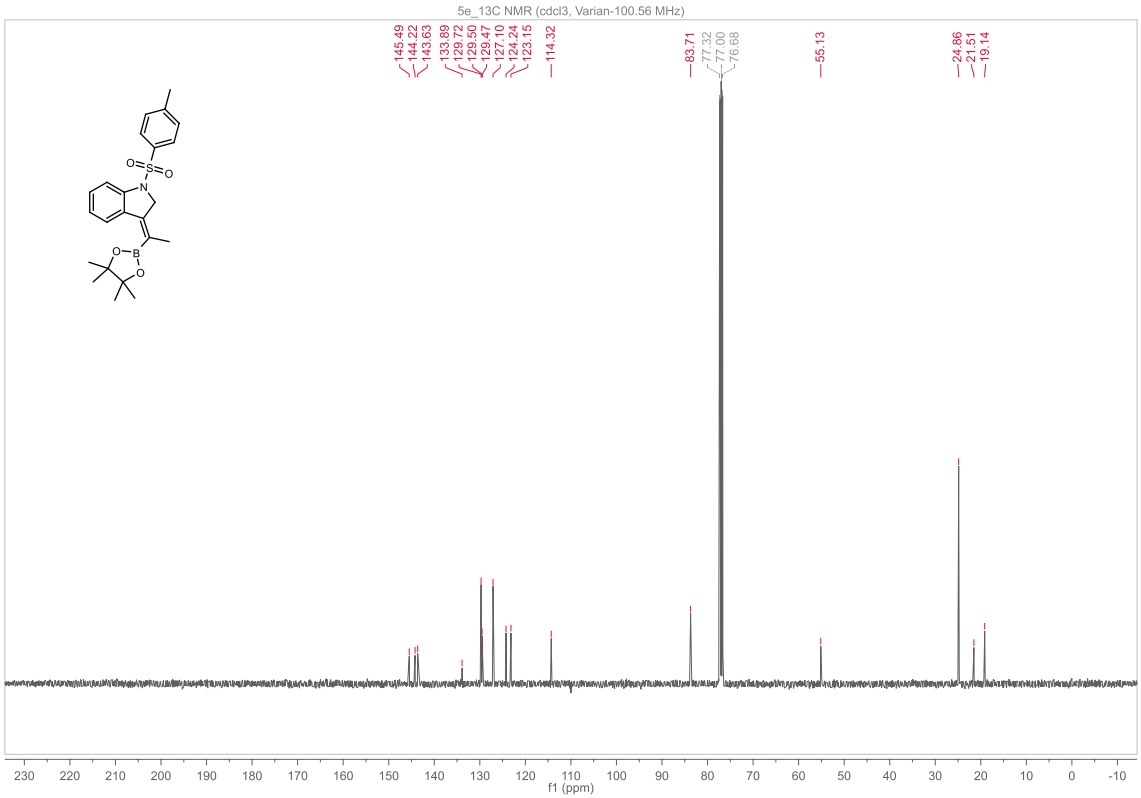

5b_1H NMR (cdcl3, Varian-399.89 MHz)
f1 (ppm)

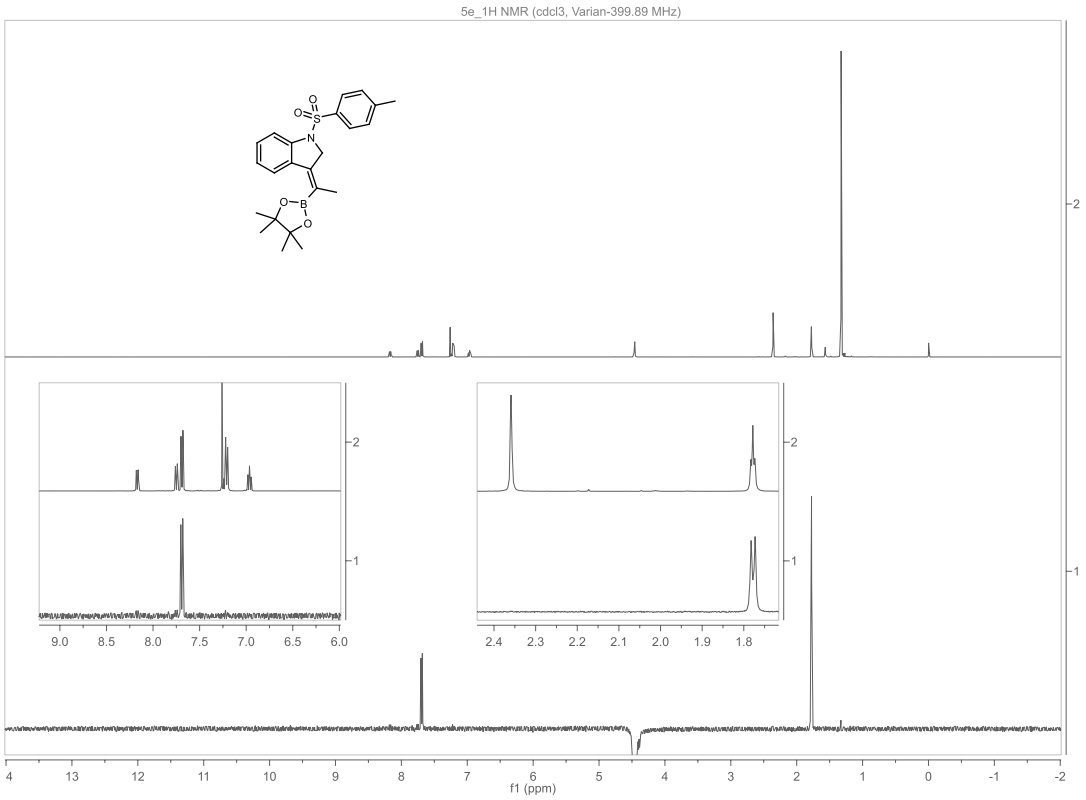

5d_1H NMR (cdcl3, Varian-399.89 MHz)
8.01
8.00
7.26
6.83
6.83
5.05
5.05
5.04
5.04
2.27
2.19
1.78
1.77
1.77
1.37
0.00
1.00
1.04
2.19
2.84
2.94
2.92
12.03
f1 (ppm)


5d_13C NMR (cdcl3, Varian-100.56 MHz)
162.08
149.67
131.93
129.25
124.55
122.52
119.66
83.42
77.32
77.00
76.68
75.39
24.97
20.99
18.52
14.90
f1 (ppm)


5c_1H NMR (cdcl3, Varian-399.89 MHz)
f1 (ppm)


5e_1H NMR (cdcl3, Varian-399.89 MHz)
f1 (ppm)


5e_13C NMR (cdcl3, Varian-100.56 MHz)
145.49
144.22
143.63
133.89
129.72
129.50
129.47
127.10
124.24
123.15
114.32
83.71
77.32
77.00
76.68
55.13
24.86
21.51
19.14
f1 (ppm)


5e_1H NMR (cdcl3, Varian-399.89 MHz)
f1 (ppm)

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