Supporting Information for

Iridium-bipyridine periodic mesoporous organosilica catalyzed direct C-H borylation using a pinacolborane

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Table of Contents

1. Chemicals:

All chemicals, including dry solvents, were purchased from commercial suppliers (Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries Ltd.) and used without further purification. BPy-PMO was prepared according to the literature.[1] Ir-BPy-PMO was prepared according to the literature with slightly modified procedure. [1]

Synthesis of Ir-BPy-PMO. A 50 mL Schlenk tube was charged with a stir bar and end-capped BPy-PMO (77.5 mg, 0.226 mmol). Dry hexane (10 mL) was added. Then, a solution of $[Ir(OMe)(cod)]_2$ (5.0 mg, 0.015 mmol Ir) in dry hexane (20 mL) was added at room temperature. The reaction mixture was stirred at room temperature for 3-6 h. The resulting suspension was filtered and then washed with dry hexane. The material was dried over under reduced pressure to give Ir-BPy-PMO as a light-gray powder (80 mg, Ir content: 0.15-0.16 mmol Ir/g).

2. Characterization :

^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using a Jeol ECX-400 spectrometer operating at 400 MHz, 100 Hz, and 376 MHz, respectively. Chemical shifts are reported in δ parts per million referenced to tetramethylsilane (TMS) or residual protonated solvent as an internal standard.

Mass spectra were recorded on a Micromass GCT Premier mass spectrometer (FI: field ionization) and Micromass Q-TOF mass spectrometer (ESI: electrospray ionization).

GC mass analyses were performed on an Agilent 7890A GC instrument equipped with a capillary column (HP-5MS, 0.25 mm × 30 m) and a flame ionization detector.

IR spectra were collected on a Thermo Fisher Scientific Nicolet Avatar-360 FT-IR spectrometer using an attenuated total reflection (ATR) attachment.

XRD profiles were recorded on a Rigaku RINT-TTR diffractometer using Cu-Kα radiation (50 kV, 300 mV).

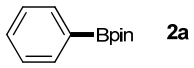
Nitrogen adsorption and desorption isotherms were measured using a Quantachrome Nova3000e sorptometer. BET surface areas were calculated from the linear sections of BET plots (P/P_0 = 0.1−0.2).

Pore-size distributions were calculated using the DFT method (DFT kernel: N2 at 77 K on silica, cylindrical pores, nonlinear density functional theory (NLDFT) equilibrium model). Pore volumes were estimated by the *t*-plot method.

3. General procedure for direct C-H borylation of arenes and heteroarenes:

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and arenes or heteroarenes (1.33 mmol) then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with diethyl ether (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was purified by flash silica gel column chromatography (eluent: hexane/EtOAc = 100/0 to 70/30) provided analytically pure samples. The recovered catalyst was used for next reaction in the presence of pinacolborane and dry benzene under same reaction condition.

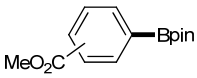
(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2a).



2a

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.35 (s, 12H), 7.37 (t, J = 7.4 Hz, 2H), 7.46 (t, J = 7.3 Hz, 1H), 7.81 (d, J = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.87, 83.75, 127.69, 131.23, 134.72.; IR (neat): υ_{max} 2983, 1604, 1437, 1350, 1137, 1092, 857, 705, 657 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{21}BNO_2$ ($M+NH_4^+$): 222.1662; found: 222.1664.

Methyl (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzoate (2b).

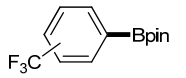


2b

Yield: 86% (*p*-isomer:*m*-isomer = 53:47). ^{1}H NMR (400 MHz, $CDCl_3$): δ (*m*-isomer) 1.36 (s, 12H), 3.91 (s, 3H), 7.44 (t, J = 8.0 Hz, 1H), 7.98 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.46 (s, 1H); (*p*-isomer) 1.36 (s, 12H), 3.92 (s, 3H), 7.86 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (*p*-isomer) 24.83, 52.10, 84.15, 128.52, 132.23, 134.59, 167.10, (*m*-isomer) 24.83, 52.00, 84.06, 127.74, 129.47, 135.76, 139.09, 167.07.; IR (neat): υ_{max} 2952, 1726, 1461, 1362, 906 cm^{-1};

ESI-HRMS *m*/*z* calcd. for $C_{14}H_{23}BNO_4$ ($M+NH_4^+$): 280.1717; found: 280.1719.

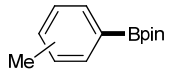
(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)(trifluoromethyl)benzene (2c).



2c

Yield: 91% (*p*-isomer:*m*-isomer = 31:69). ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ (*m*-isomer) 1.36 (s, 12H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 8.06 (s, 1H), (*p*-isomer) 1.36 (s, 12H), 7.61 (d, *J* =8.1 Hz, 2H), 7.91 (d, *J* = 7.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ (*m*-isomer) 24.85, 84.26, 124.29, 127.60, 127.99, 131.32, 137.96, (*p*-isomer) 24.53, 84.26, 124.15, 124. 29, 132.30, 134.96; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* (*m*-isomer)-62.93, (*p*-isomer) -62.51.; IR (solution): υ_{max} 2976, 1584, 1552, 1334, 1144, 966 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{13}H_{20}BF_3NO_2$ ($M+NH_4^+$): 250.1539; found: 250.1539.

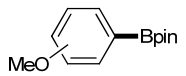
(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)toluene (2d).



2d

Yield: 92% (*p*-isomer:*m*-isomer = 40:60). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (*m*-isomer) 1.34 (s, 12H), 2.35 (s, 3H), 7.25-7.27 (m, 2H), 7.60 (t, *J* = 4.4 Hz, 1H), 7.63 (s, 1 H), (*p*-isomer) 1.34 (s, 12H), 2.36 (s, 3H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (*m*-isomer) 21.27, 24.85, 83.71, 127.66, 131.73, 132.01, 135.29, 137.10, (*p*-isomer) 21.73, 24.85, 83.60, 128.49, 134.76, 141.37.; IR (solution): υ_{max} 2960, 1611, 1461, 1358, 1089 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{13}H_{23}BNO_2$ ($M+NH_4^+$): 236.1819; found: 236.1819.

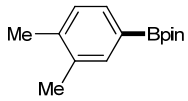
(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)anisole (2e).



2e

Yield: 87% (*p*-isomer:*m*-isomer = 49:51). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* (*m*-isomer) 1.34 (s, 12H), 3.83 (s, 3H), 7.00 (dd, *J* = 2.8, 8.4 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 2.8 Hz, 1H), 7.40 (d, *J* = 7.2 Hz, 1H), (*p*-isomer) 1.33 (s, 12H), 3.83 (s, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* (*m*-isomer) 24.85, 55.23, 83.80, 117.90, 118.61, 127.14, 128.91, 158.97, (*p*-isomer) 24.85, 55.08, 83.53, 113.27, 136.47, 162.08.; IR (solution): υ_{max} 2952, 1603, 1461, 1382, 1354, 1093 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{13}H_{23}BNO_3$ ($M+NH_4^+$): 252.1768; found: 252.1768.

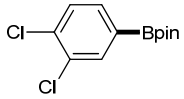
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-*o*-xylene (2f).



2f

Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H), 2.27 (s, 3H), 2.28 (s, 3H), 7.14 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 1H), 7.58 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.47, 20.00, 24.83, 83.56, 129.13, 132.36, 135.88, 140.12.; IR (solution): υ_{max} 2952, 1611, 1465, 1374, 1350, 1093 cm^{-1}; ESI-HRMS m/z calcd. for $C_{14}H_{25}BNO_2$ ($M+NH_4^+$): 250.1975; found: 250.1975.

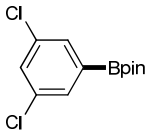
1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2g).



2g

Yield: 95%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.33 (s, 12H), 7.43 (d, J = 8.0 Hz, 1H), 7.59 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 7.86 (d, J = 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.15, 84.64, 130.29, 132.53, 134.04, 135.77, 136.83.; IR (solution): υ_{max} 2976, 1588, 1477, 1382, 1342, 1144, 1085, 1040, 960 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{19}BNCl_2O_2$ ($M+NH_4^+$): 290.0883; found: 290.0882.

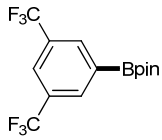
1,3-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2h).



2h

Yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 12H), 7.42 (t, J = 2.0 Hz, 1H), 7.64 (d, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.83, 84.48, 129.34, 131.04, 132.66, 134.68.; IR (solution): υ_{max} 2976, 1584, 1552, 1440, 1334, 144, 966 cm^{-1}; ESI-HRMS m/z calcd. for $C_{12}H_{19}BNCl_2O_2$ ($M+NH_4^+$): 290.0883; found: 290.0884.

1,3-Bis(trifluoromethyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (2i).

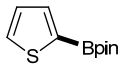


2i

Yield: 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 12H), 7.94 (s, 1 H), 8.23 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.86, 84.83, 122.09, 124.66, 124.69, 130.68, 131.02, 134.61.; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76.; IR (neat): υ_{max} 2983, 1618, 1279, 1123, 849, 677 cm^{-1}; ESI-HRMS m/z calcd. for

$C_{14}H_{19}BNF_6O_2$ ($M+NH_4^+$): 358.1410; found: 358.1408.

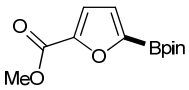
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (2j).



2j

Yield: 92%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 12H), 7.19 (dd, *J* = 3.6 Hz, 4.4 Hz, 1H), 7.63 (d, *J* = 4.8 Hz, 1H), 7.64 (d, *J* = 3.6 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 24.76, 84.07, 128.20, 132.34, 137.13.; IR (neat): υ_{max} 2966, 1519, 1423, 1358, 1132, 846 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{10}H_{19}BNO_2S$ ($M+NH_4^+$): 228.1224; found: 228.1224.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-furancarboxylic acid methyl ester (2k).

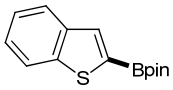


2k

Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ (2-isomer) 1.35 (s, 12H), 3.89 (s, 3H), 7.07 (d, *J* = 3.6 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), (3-isomer) 1.32 (s, 12H), 3.89 (s, 3H), 7.37 (s, 1H), 7.87 (s, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ (2-isomer) 24.70, 51.93, 84.70, 117.86, 124.00, 148.29, 159.03; (3-isomer) 24.75, 51,95, 83.91, 121.80, 123.9, 154.01, 159.07. 2:3 = 86/14.; IR (neat): υ_{max} 3112, 2977, 1714, 1575, 1527, 1437, 1358, 1324, 1284, 1103 , 780 cm^{-1};

ESI-HRMS *m*/*z* calcd. for $C_{12}H_{21}BNO_5$ ($M+NH_4^+$): 270.1507; found: 270.1508.

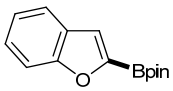
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*b*]thiophene (2l).



2l

Yield: 90%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.38 (s, 12H), 7.32-7.39 (m, 2H), 7.83-7.86 (m, 1H), 7.88 (s, 1H), 7.89-7.91 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 24.81, 84.42, 122.49, 124.07, 124.34, 125.27, 134.46, 140.39, 143.66.; IR (neat): υ_{max} 2977, 1595, 1553, 1522, 135, 1120, 849, 753, 662 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{14}H_{21}BNO_2S$ ($M+NH_4^+$): 278.1381; found: 278.1382.

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzofuran (2m).

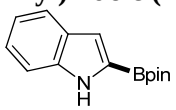


2m

Yield: 92%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ (2-isomer) 1.39 (s, 12H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.33 (dt, *J* = 1.2 Hz, 7.2 Hz, 1H), 7.40 (s, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H),

(3-isomer) 1.37 (s, 12H), 7.26-7.29 (m, 2H), 7.91-7.93 (m, 2H), 7.95 (s, 1H) ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ (2-isomer) 24.77, 84.66, 111.93, 119.51, 121.85, 122.70, 125.90, 127.44, 157.46; (3-isomer) 24.87, 83.48, 111.0, 122,84, 122.92, 124.19, 153.5. 2:3 = 80:20.; IR (neat): υ_{max} 2971, 1612, 1561, 1471, 1321, 1132, 1069, 750 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{14}H_{21}BNO_3$ ($M+NH_4^+$): 262.1609; found: 272.1612.

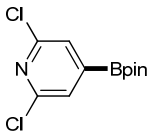
2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole (2n).



2n

Yield: 93%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.37 (s, 12H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.11 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 8.55 (br s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 24.83, 84.13, 111.24, 113.82, 119.76, 121.58, 123.60, 128.24, 138.17.; IR (neat): υ_{max} 3333, 2977, 1615, 1581, 1539, 1372, 1313, 1137, 968, 852, 696 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{14}H_{19}BNO_2$ ($M+H^+$): 244.1503; found: 244.1507.

2,6-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (2o).



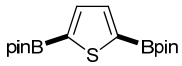
2o

Yield: 92%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 12H), 7.58 (s, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$, TMS): δ 24.82, 85.19, 127.75, 150.37.; IR (neat): υ_{max} 3007, 2983, 1516, 1369, 1341, 1163, 1137, 965, 807 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{11}H_{15}BCl_2NO_2$ ($M+H^+$): 274.0567; found: 274.0569.

4. General procedure for multiple-direct C-H borylation of thiophene derivatives:

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and thiophene derivatives **3** (0.22 mmol) and then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with chloroform (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was washed with cold hexane (1 mL) to afford analytically pure samples.

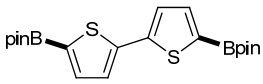
2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene (4a).



4a

Yield: 99%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (s, 24H), 7.66 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.76, 84.11, 137.64.; IR (neat): υ_{max} 2971, 1522, 1318, 1260, 1134, 1038, 855, 671 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{16}H_{27}B_2O_4S$ (M^+): 337.1811; found: 337.1718.

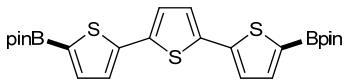
5,5'-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithiophene (4b).



4b

Yield: 99%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 24H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.76, 84.21, 125.60, 137.95, 143.83.; IR (neat): υ_{max} 2983, 1513, 1434, 1327, 1253, 1134, 1069, 852, 654 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{20}H_{29}B_2O_4S_2$ (M^+): 419.1688; found: 419.1698.

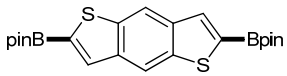
5,5''- Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':5',2''-terthiophene (4c).



4c

Yield: 99%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.35 (s, 24H), 7.14 (s, 2H), 7.23 (d, *J* = 3.6 Hz, 2H), 7.52 (d, *J* = 3.6 Hz, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.77, 84.22, 124.97, 125.11, 136.63, 137.95, 143.61.; IR (neat): υ_{max} 3056, 2977, 1510, 1448, 1349, 1321, 1137, 1067, 849, 660 cm^{-1}; FI-HRMS *m*/*z* calcd. for $C_{24}H_{31}B_2O_4S_3$ (M^+): 501.1565; found: 501.1577.

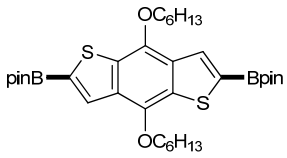
2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene (4d).



4d

Yield: 99%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.39 (s, 24H), 7.90 (s, 2H); 8.36 (s, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.83, 84.54, 117.52, 133.59, 139.31, 140.56.; IR (neat): υ_{max}2983, 1539, 1443, 1395, 1298, 1137, 852, 660 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{22}H_{29}B_2O_4S_2$ (M^+): 443.1688; found: 443.1696.

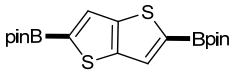
2,6-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,8-dihexyloxybenzo[1,2-*b*:4,5-*b*']dithiophene (4e).



4e

Yield: 92%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 0.93 (t, *J* = 6.8 Hz, 6H), 1.36-1.38 (m, 12H), 1.38 (s, 24H), 1.50-1.55 (m, 4H), 1.84-1.91 (m, 4H), 4.30 (t, *J* = 6.8 Hz, 4H), 8.01 (s, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 14.10, 22.65, 24.71, 24.81, 25.66, 30.53, 31.70, 73.94, 84.55, 130.82, 132.98, 133.77, 144.82.; IR (neat): υ_{max} 2981, 2926, 2853, 1553, 1448, 1348, 1307, 1129, 846, 665 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{34}H_{53}B_2O_6S_2$ (M^+): 643.3464; found: 643.3472.

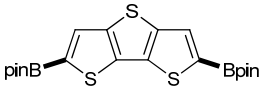
2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thieno[3,2-*b*]thiophene (4f).



4f

Yield: 99%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 24H), 7.75 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.79, 84.35, 128.87, 146.61.; IR (neat): υ_{max} 2983, 1485, 1338, 1259, 1134, 1030, 950, 849, 665 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{18}H_{27}B_2O_4S_2$ (M^+): 393.1531; found: 393.1539.

2,6- Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dithieno[3,2-*b*:2',3'-*d*]thiophene (4g).

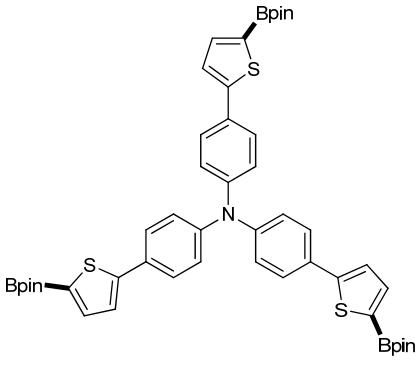


4g

Yield: 89%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 24H), 7.76 (s, 2H), ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.78, 84.40, 130.27, 144.74.; IR (neat): υ_{max} 2977, 1499, 1383, 1250, 1132, 1020, 950, 849, 660 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{20}H_{27}B_2O_4S_3$ (M^+): 449.1252; found: 449.1259.

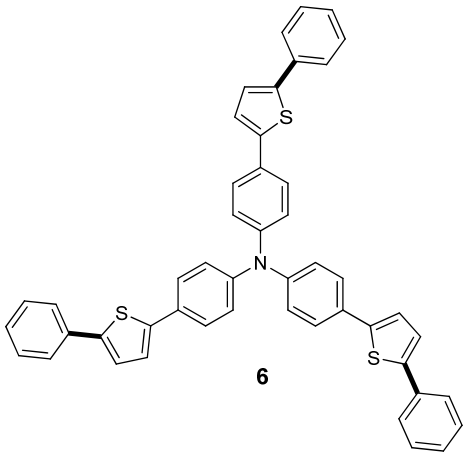
5. Synthesis of triarylamine derivative 6:

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (32.0 mg, 0.005 mmol Ir) and tris(4-(2-thienyl)phenyl)amine **5** (72 mg, 0.15 mmol) and then flushed with argon. Dry cyclohexane (2.0 mL) and pinacolborane (95 μL, 0.66 mmol) was added, and the mixture was stirred at 80 ºC for 12 h. The mixture was diluted with



chloroform (5 mL) and filtered through a membrane filter (0.20 μm). Solvent was removed under reduced pressure. The crude product was washed with cold hexane (1 mL) to afford analytically pure tribolylated amine **5'**. Yield: 98%. ^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ 1.36 (s, 36H), 7.13 (d, *J* = 8.8 Hz, 6H), 7.32 (d, *J* = 3.6 Hz, 3H), 7.55 (d, *J* = 8.8 Hz, 6H), 7.58 (d, *J* = 3.6 Hz, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, TMS) : δ 24.79, 84.11, 123.85, 124.42, 127.10, 129.13, 138.23, 146.73, 150.92.; IR (neat): υ_{max} 2977 1601, 1530, 1451, 1318, 1140, 1070, 950, 850, 804, 665 cm^{-1}; ESI-HRMS *m*/*z* calcd. for $C_{48}H_{55}B_3NO_6S_3$ (M^+): 870.3465; found: 870.3484.

A 50 mL two-neck flask connected to a condenser was charged with a stir bar, tribolylated amine **5'** (100 mg, 0.11 mmol), K_3PO_4 (146 mg, 0.69 mmol), and $Pd(PPh_3)_4$ (12 mg, 10.3 μmol). Dry 1,4-dioxane (7.5 mL), degassed distilled water (0.75 mL), and bromobenzene (108 mg, 0.69 mmol) were added. The reaction mixture was stirred at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and then the solvent was completely evaporated. The residue was purified by silica gel column chromatography (eluent: hexane/CH_2Cl_2 = 10:1) to give **6** (77 mg, 92%) as a yellow powder. IR (neat): υ_{max} 3016, 2909, 1595, 1482, 1315, 1265, 798, 750, 690 cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8) δ 7.15 (d, *J* = 8.8 Hz, 6H), 7.23 (t, *J* = 8.0 Hz, 3H), 7.32 (d, *J* = 3.6 Hz, 3H), 7.36 (d, *J* = 8.0 Hz, 6H), 7.37 (d, *J* = 3.6 Hz, 3H), 7.68 (d, *J* = 8.8 Hz, 6H), 7.64 (d, *J* = 8.4 Hz, 6H). ^{13}C NMR (100 MHz, THF-d_8) δ 124.44, 125.00, 125.31, 126.05, 127.22, 128.12, 129.67, 130.27, 135.28, 143.67, 143.96, 147.51.; ESI-HRMS *m*/*z* calcd. for $C_{48}H_{34}NS_3$ ($M+H^+$): 720.1848; found: 720.1842.



6

6. GC-MS analyses of side products after the reaction of Ir-BPy-PMO with boron reagent.

A 20 mL Schlenk-tube assembled a stir bar and a septum inlet was charged with Ir-BPy-PMO (173 mg,

27 μmol Ir) and then flushed with argon. Then, dry cyclohexane (3.0 mL) and HBpin (58 μL, 0.40 mmol) was added, and the mixture was stirred at 80 ºC for 3 h. In the case of B_2pin_2, B_2pin_2 (51 mg, 0.20 mmol) was directly charged with Ir-BPy-PMO in the Schlenk-tube. The mixture was filtered through a membrane filter (0.20 μm). The obtained reaction solution was analyzed by GC mass spectroscopy. The amount of side product was determined using the calibration curve obtained from known standard chemicals. In the case of HBpin system, cyclooctane (7.5 μmol), cyclooctene (0.03 μmol) and MeOBpin (1.8 μmol) were obtained. In the case of B_2pin_2 system, cyclooctane (0.94 μmol), cyclooctene (0.19 μmol), cyclooctadiene (0.008 μmol), and MeOBpin (1.35 μmol) were obtained.

7. Reaction kintetics of direct C-H borylation of benzene, 1,3-dichlorobenzene, thiophene, and 2,2':5',2''-terthiophene catalyzed by Ir-BPy-PMO with HBpin.

In order to investigate the relationships between the size of substrate and reaction behaviors, kinetic study was carried out for direct C-H borylation of benzene vs. 1,3-dichlorobenzene and double C-H borylation of thiophene vs. 2,2':5',2''-terthiophene.

The reaction of benzene and 1,3-dichlorobenzene between HBpin in cyclohexane finished within 8 h and 2 h, respectively. Although the molecular size of 1,3-dichlorobenzene is larger than that of benzene, the TOF at initial 60 min for 1,3-dichlorobenzene reached 121 h^{-1}, which is about 3.3 times higher than that for benzene (37 h^{-1}). This suggests that reaction kinetics mainly affected by electronic structure and density of substrates rather than the size of substrate.

In the cases of the thiophene derivatives, double C-H borylation proceeded efficiently within 1 h even large size of 2,2':5',2''-terthiophene. These results clearly indicate that high activity of α-positions of thiophene ring compared with aromatic ring such as benzene.

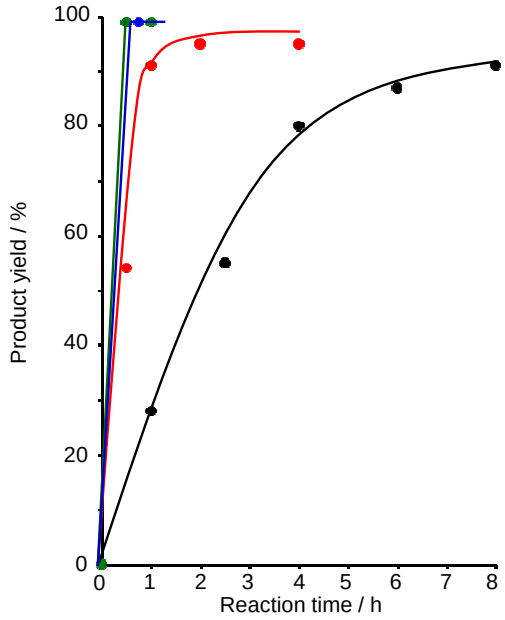


Figure S1. Reaction kinetic curves of direct C-H borylation of benzene (black lines), 1,3-dichlorobenzene (red lines), thiophene (blue lines) and 2,2':5',2''-terthiophene (green lines) catalyzed by Ir-BPy-PMO with HBpin under dilute condition in cyclohexane (Reaction conditions were shown in Tables 2 and 3 in main text.)

8. Structural properties of Ir-BPy-PMO before and after direct C-H borylation of benzene

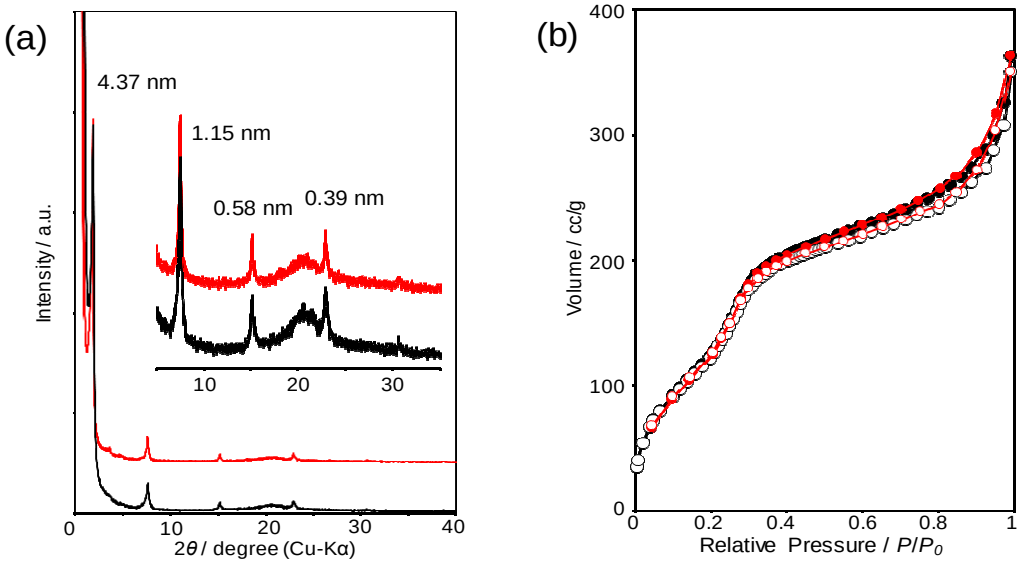
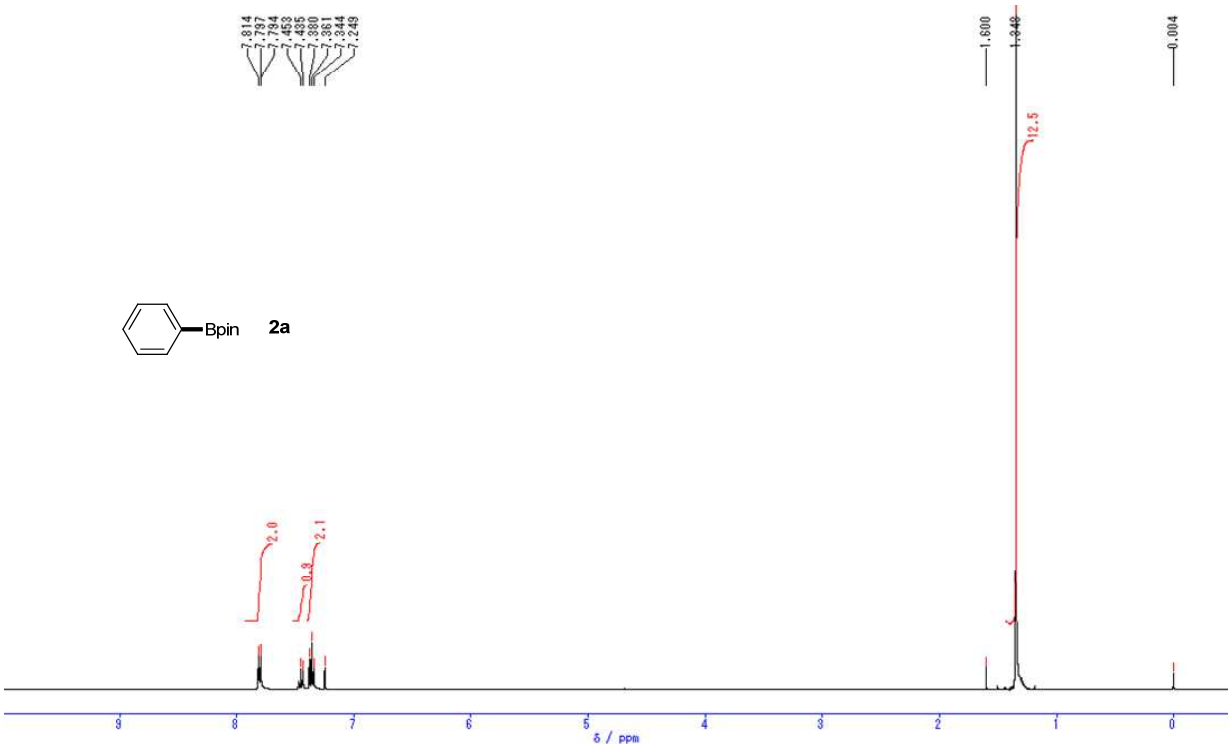
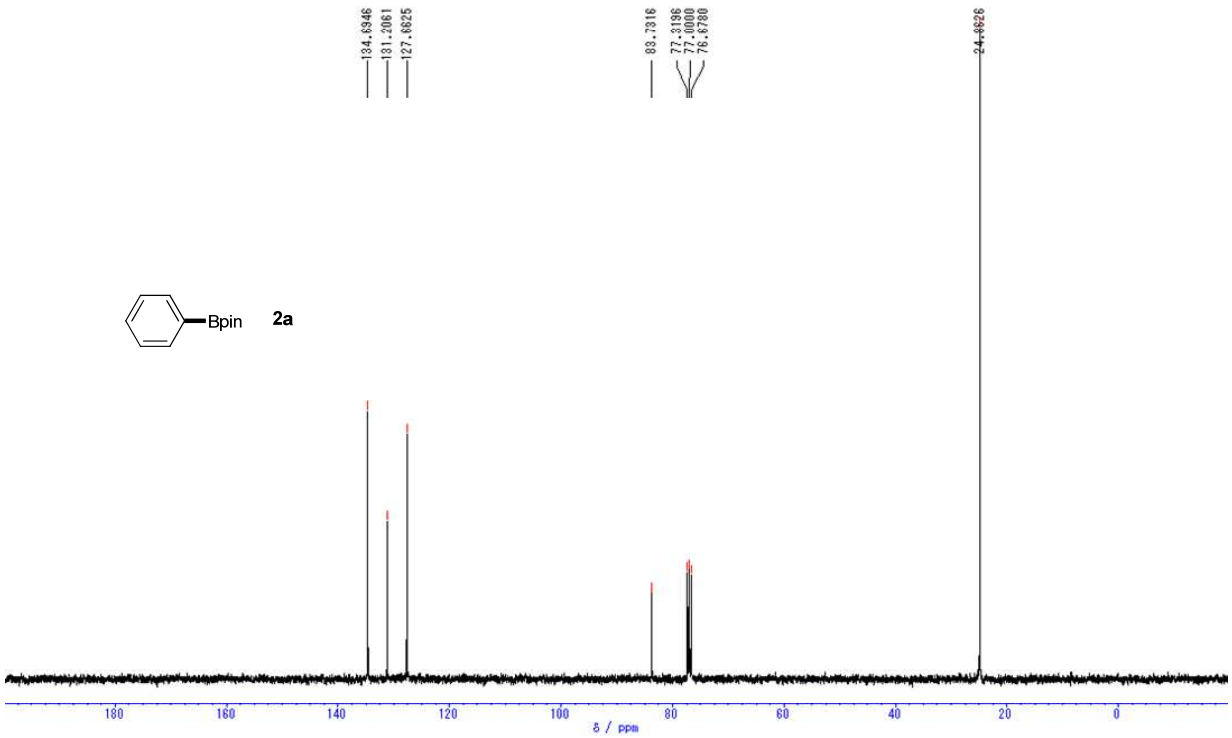
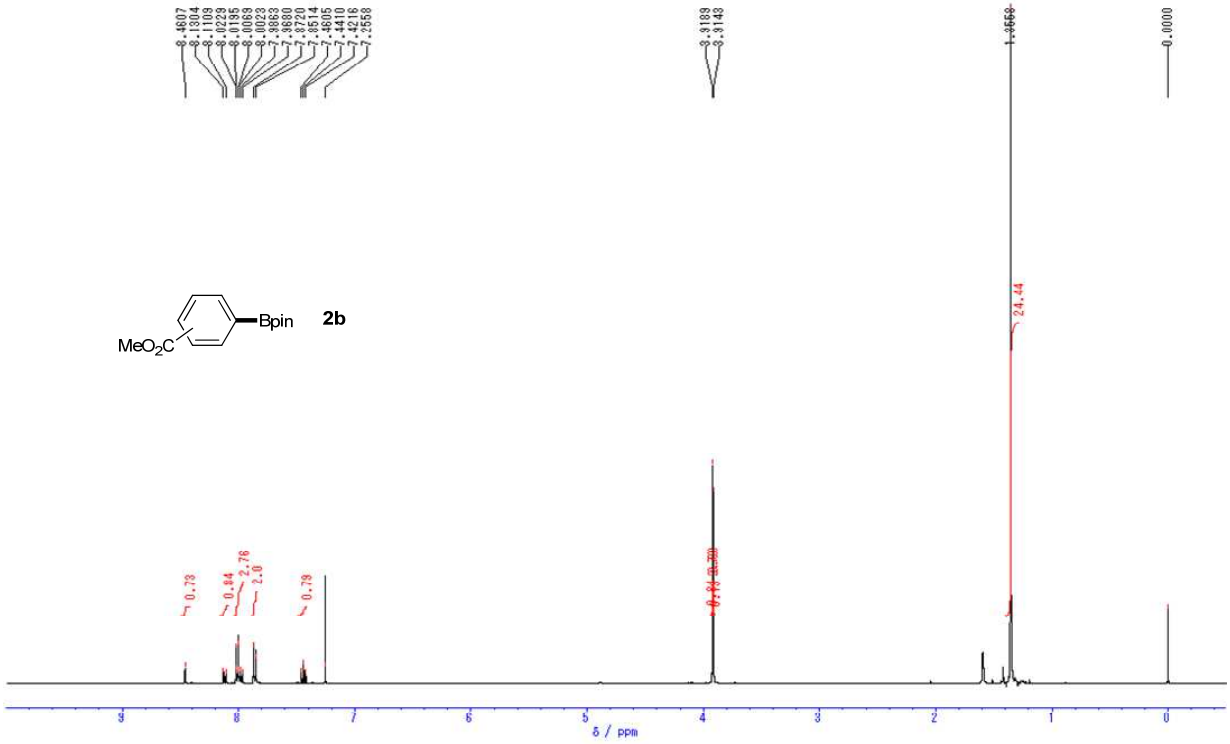


Figure S2. Structural properties of Ir-BPy-PMO before (black lines) and after 3rd reactions (red lines). (a) XRD profile, (b) nitrogen adsorption/desorption isotherms.

9. NMR spectra



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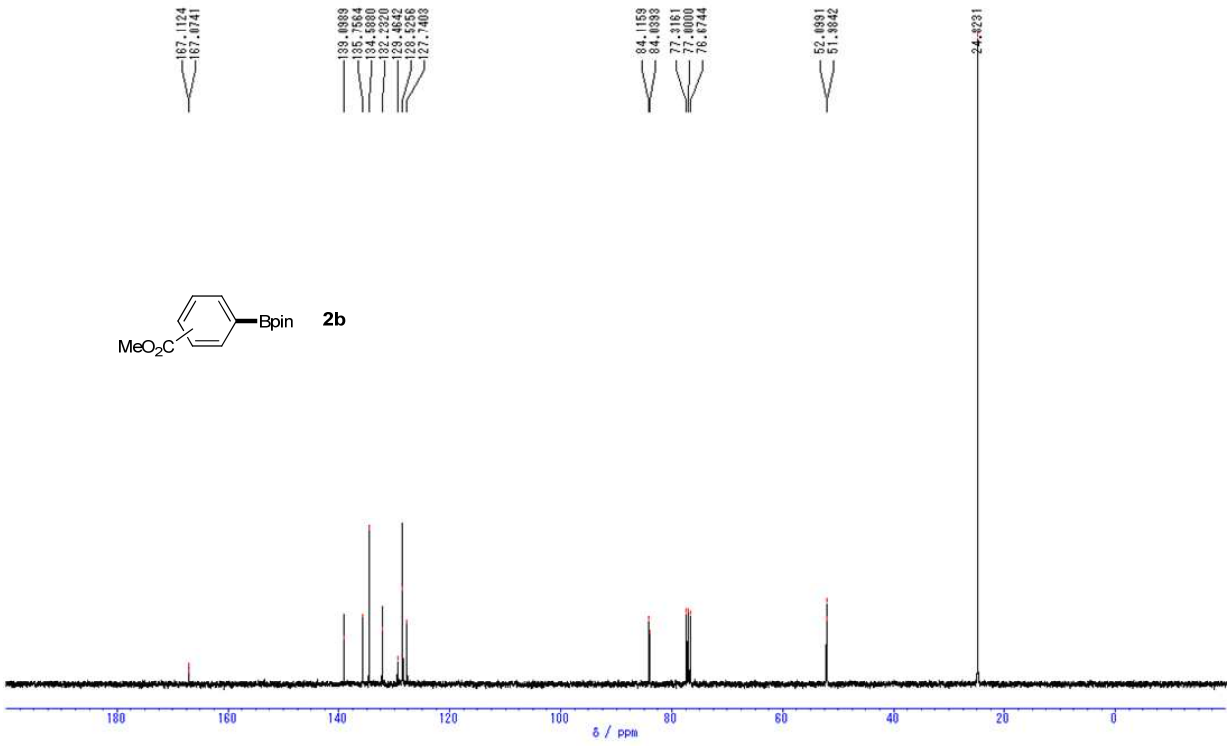
2b
δ / ppm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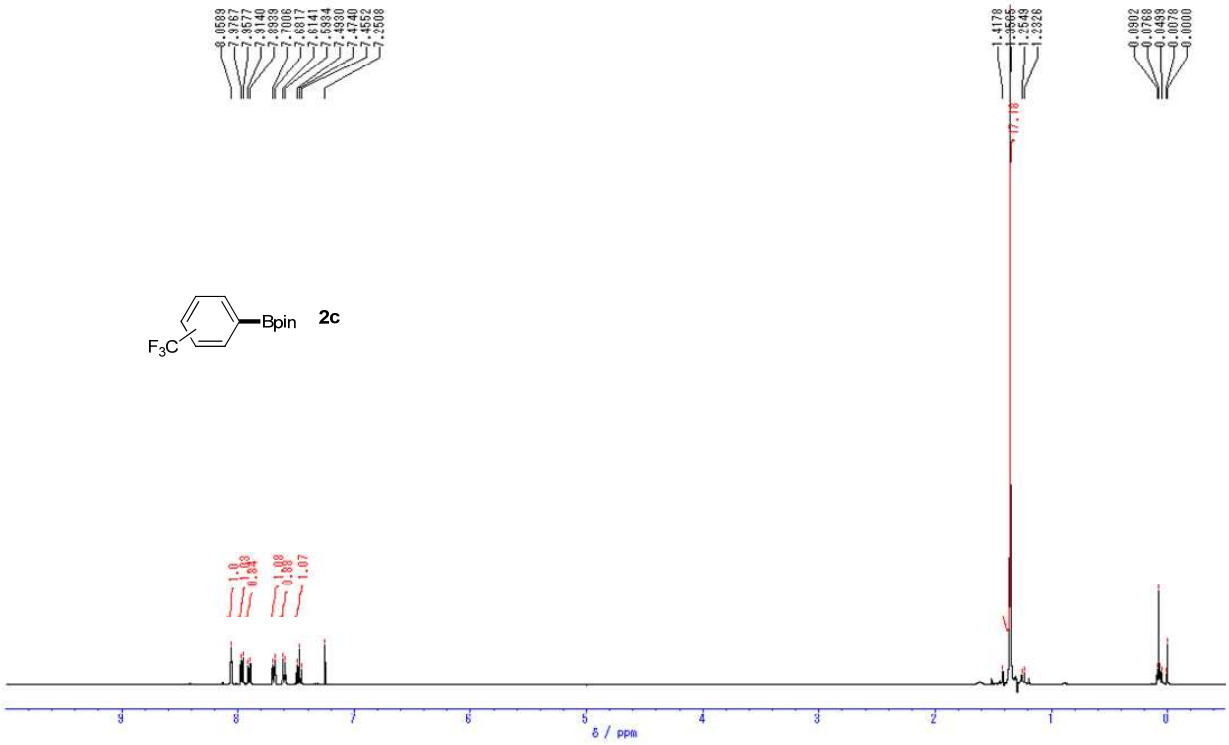
MeO2C
2b
δ / ppm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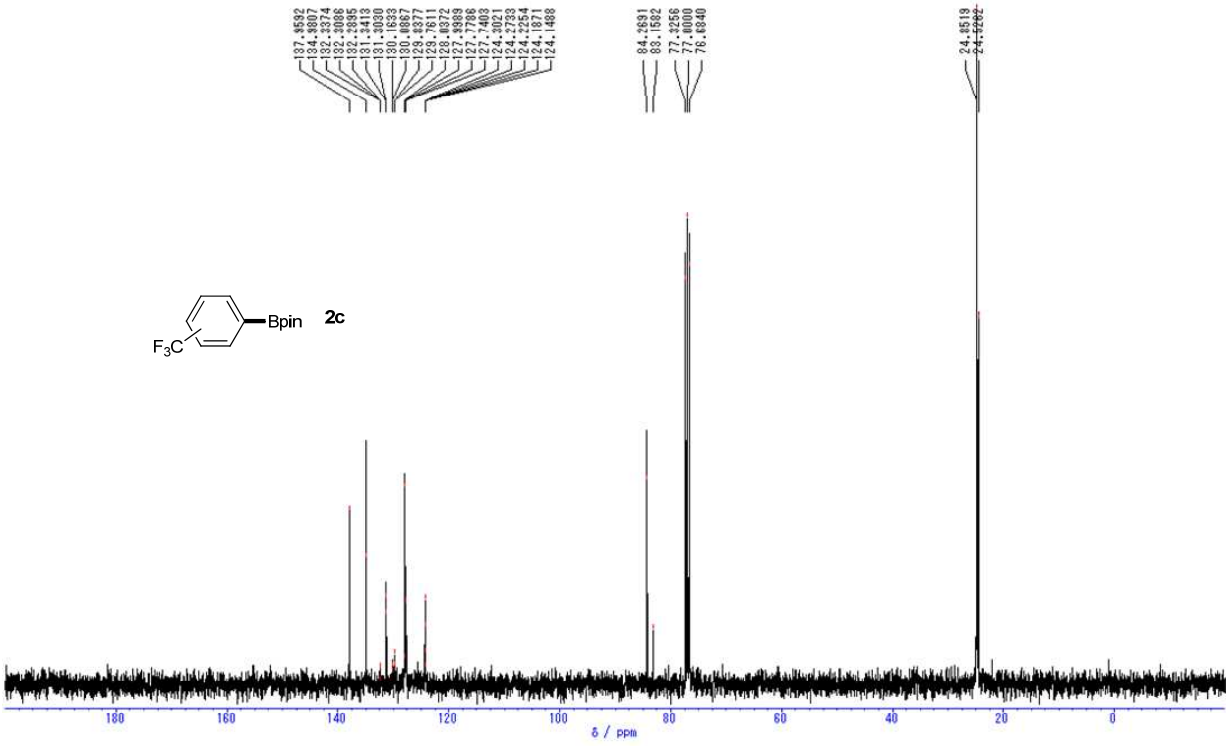
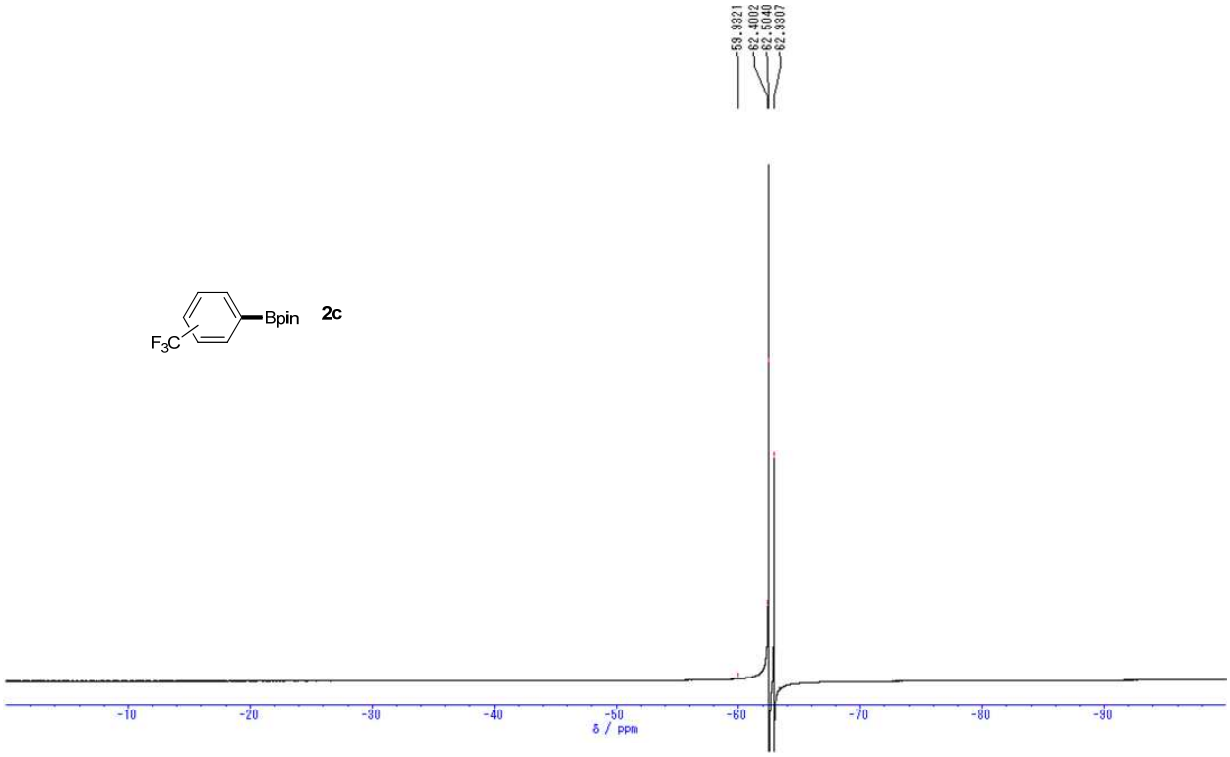
2c
F3C
δ / ppm


Bpin
2c
F3C
δ / ppm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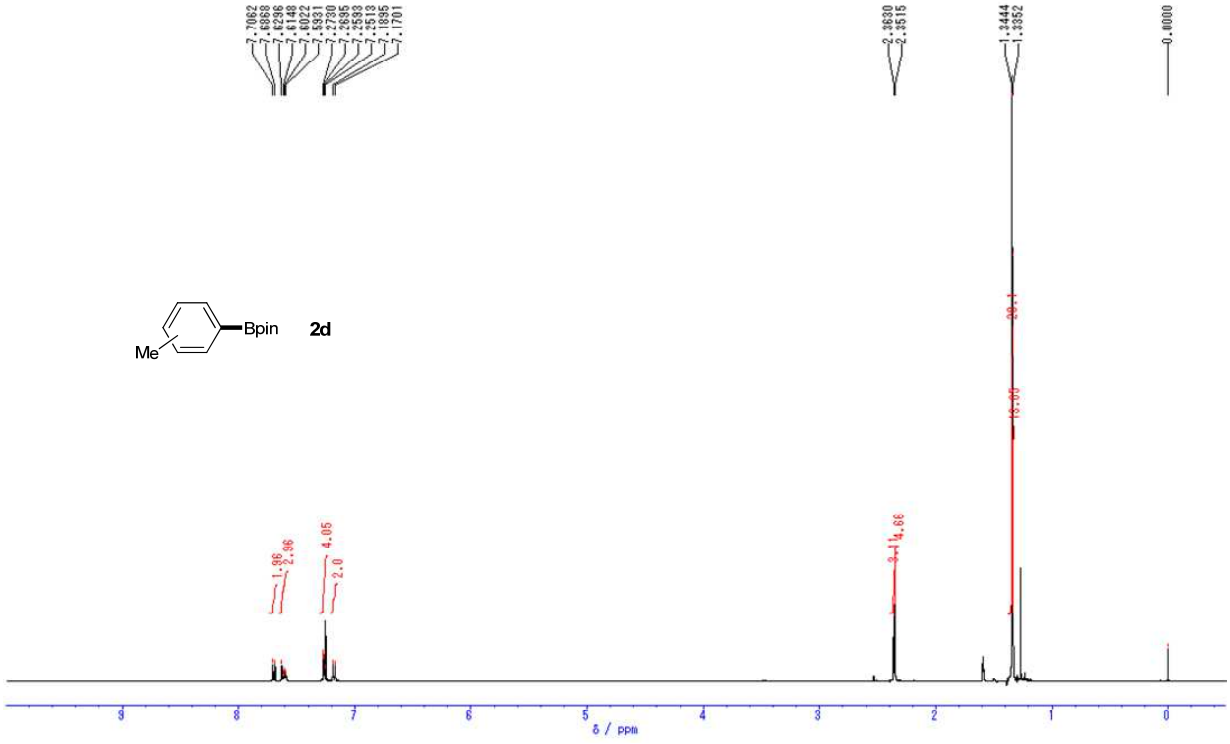
62.5040
62.9307
Bpin
F3C
2c
-10
-20
-30
-40
-50
-60
-70
-80
-90
δ / ppm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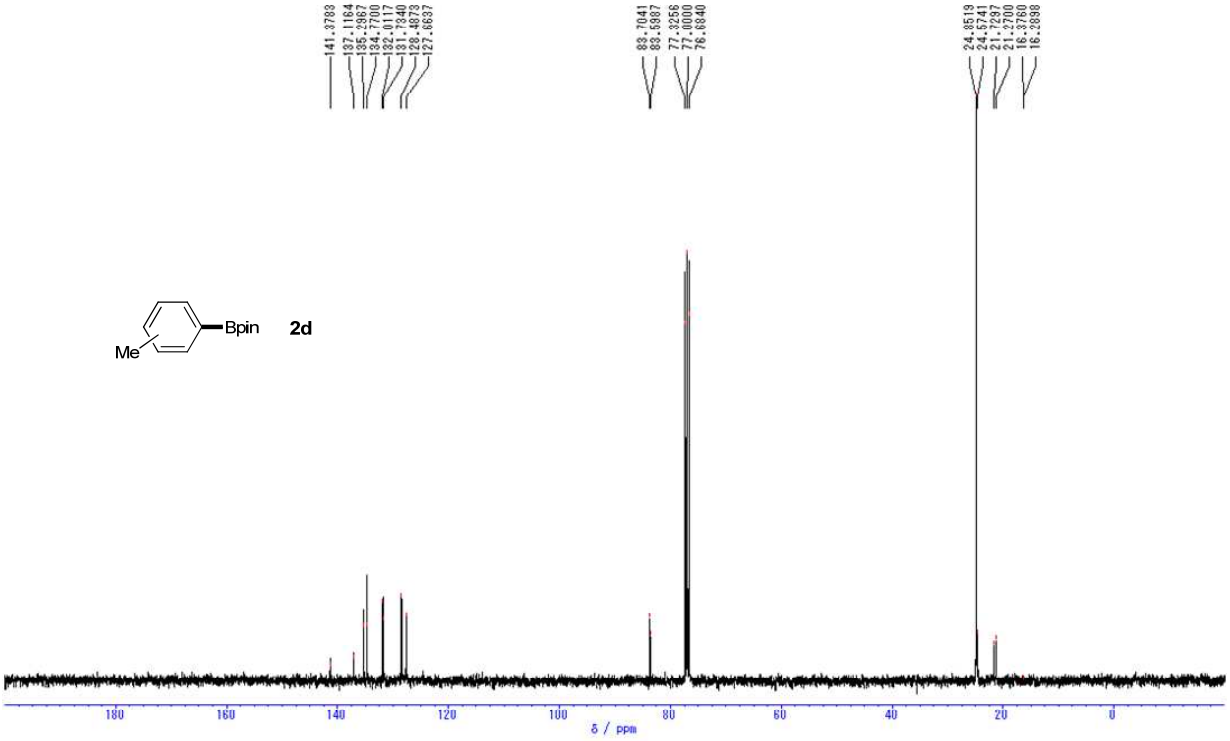
7.1701
2.3830
2.3515
1.2444
1.2352
0.0000
Bpin
Me
2d
1.98
2.96
4.05
2.0
3.14
4.66
20.1
18.00
9
8
7
6
5
4
3
2
1
0
δ / ppm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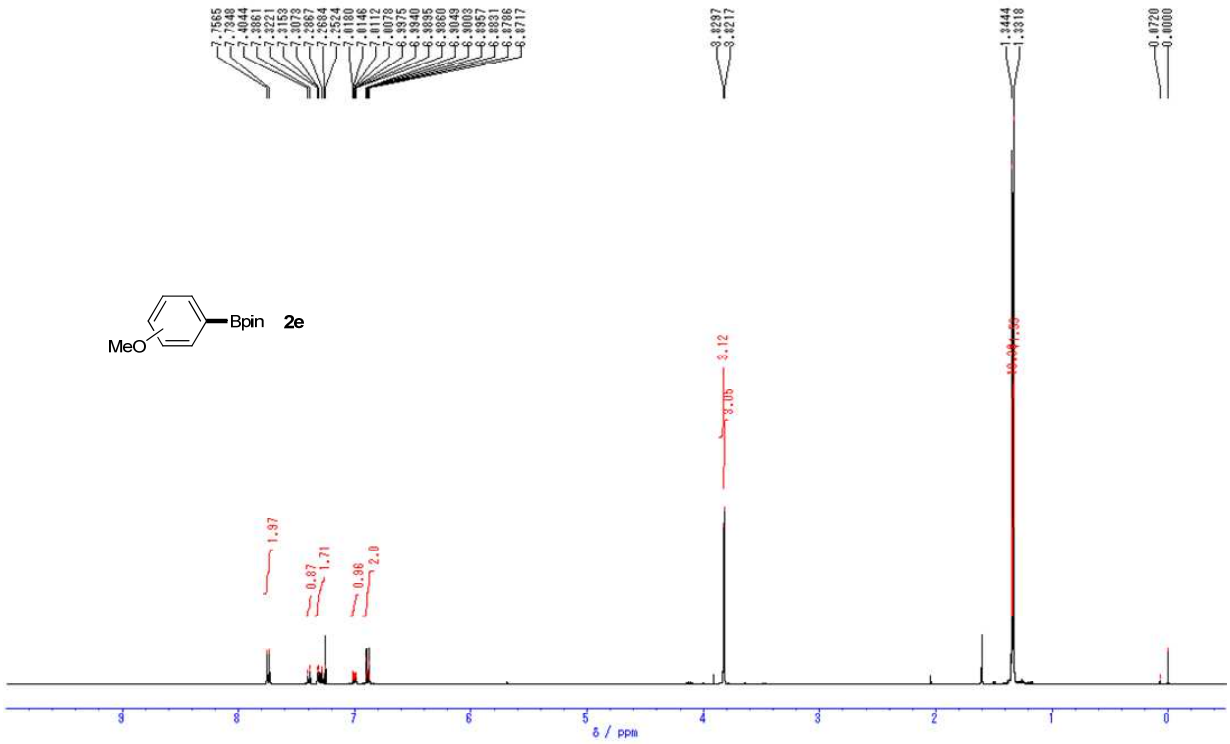
Me
2d
δ / ppm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6.8003
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0.87
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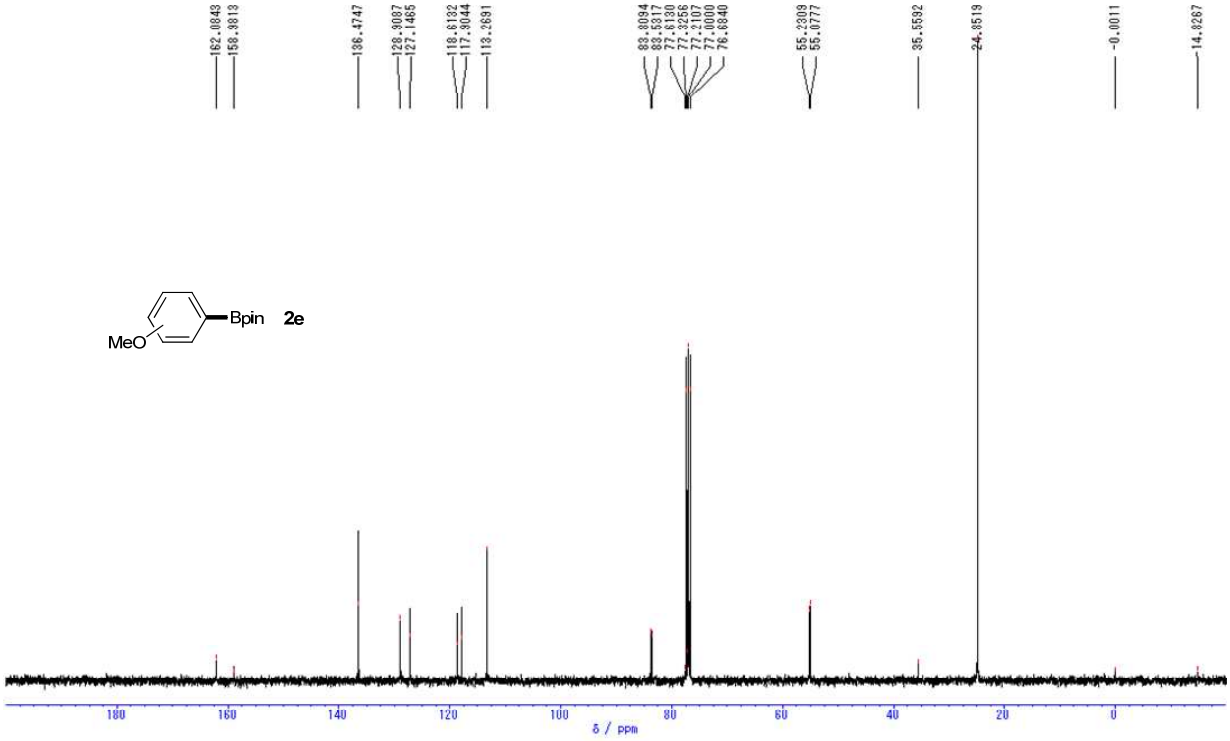
δ / ppm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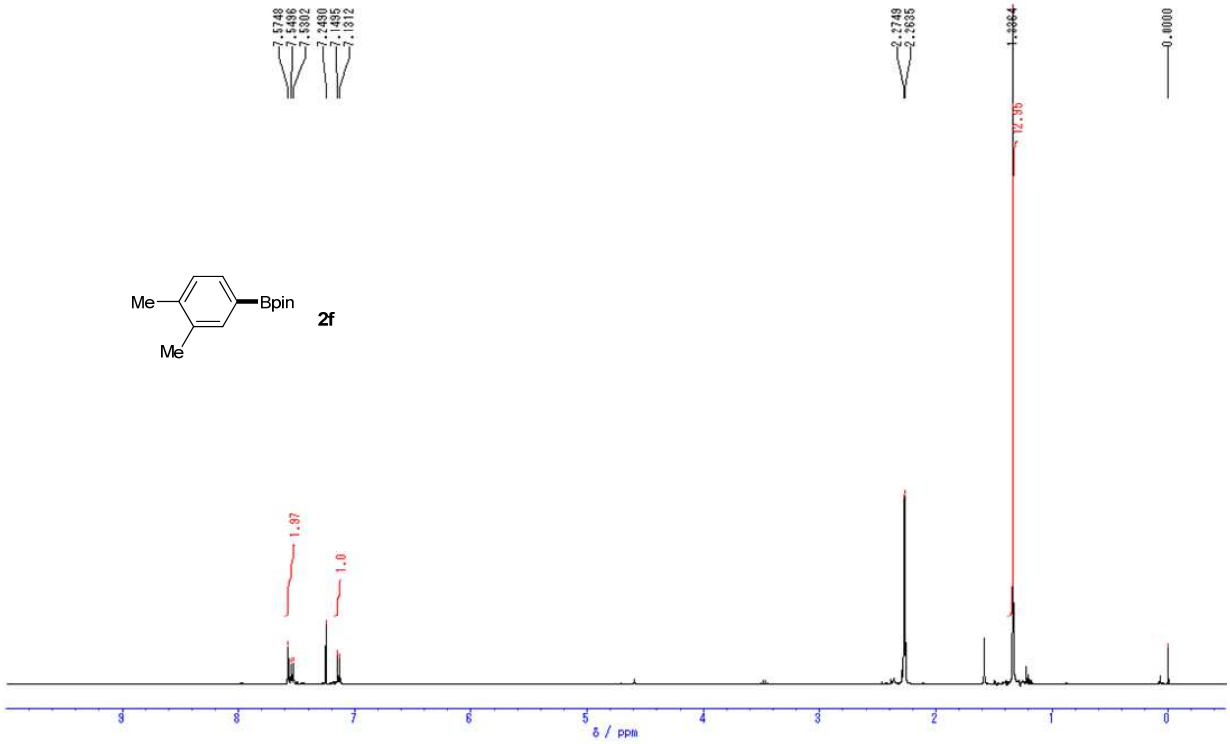
MeO
2e
δ / ppm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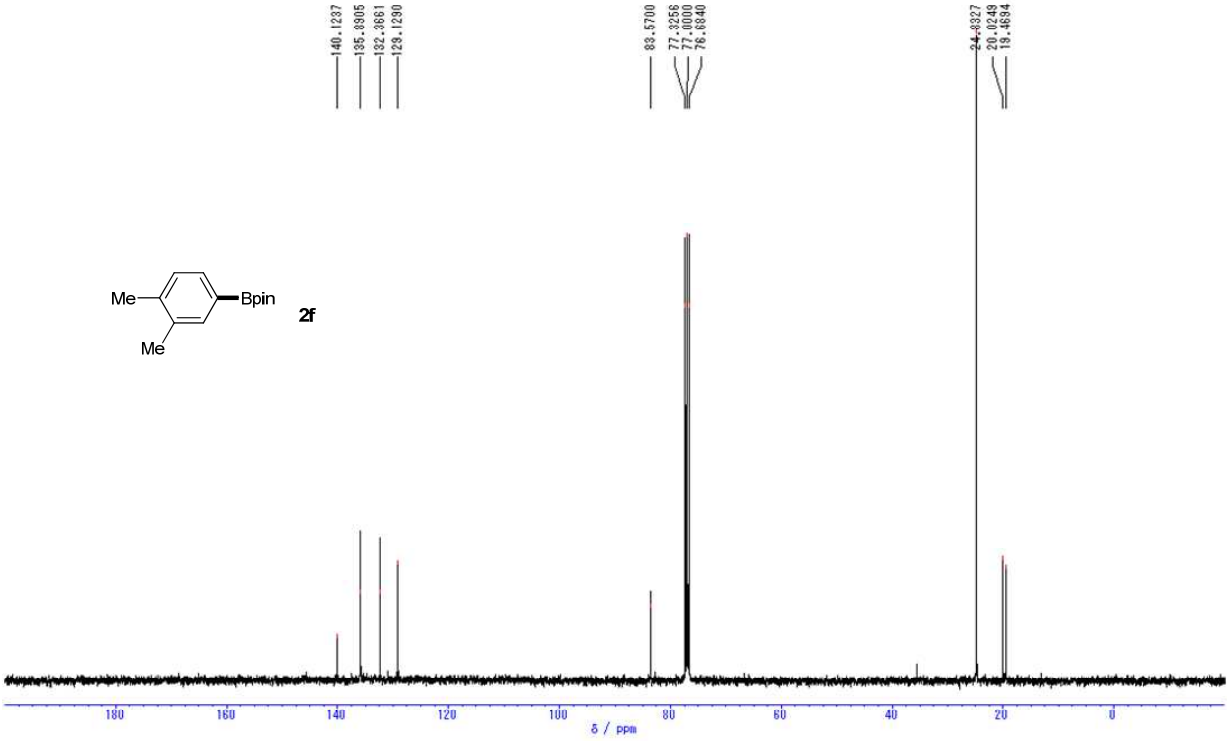
1.0
Me
Me
Bpin
2f
δ / ppm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Bpin
Me
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20
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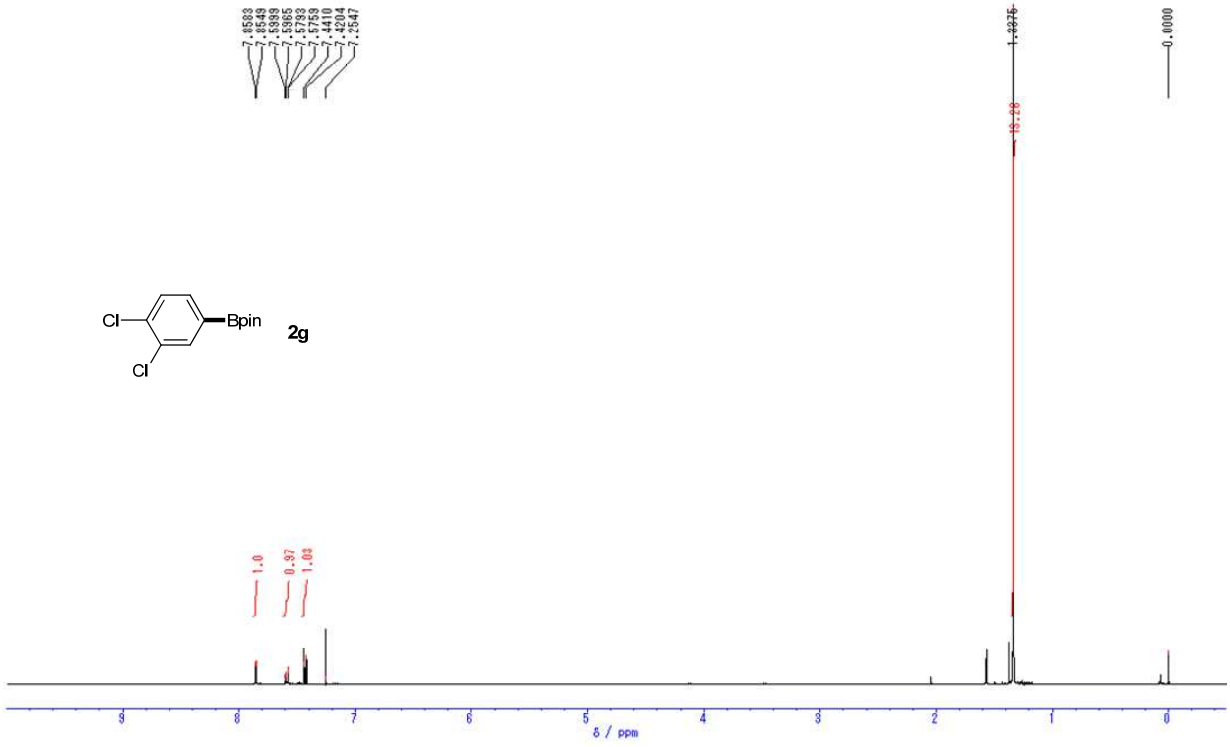
δ / ppm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0.0000
Cl
Bpin
Cl
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1.0
0.97
1.03
9
8
7
6
5
4
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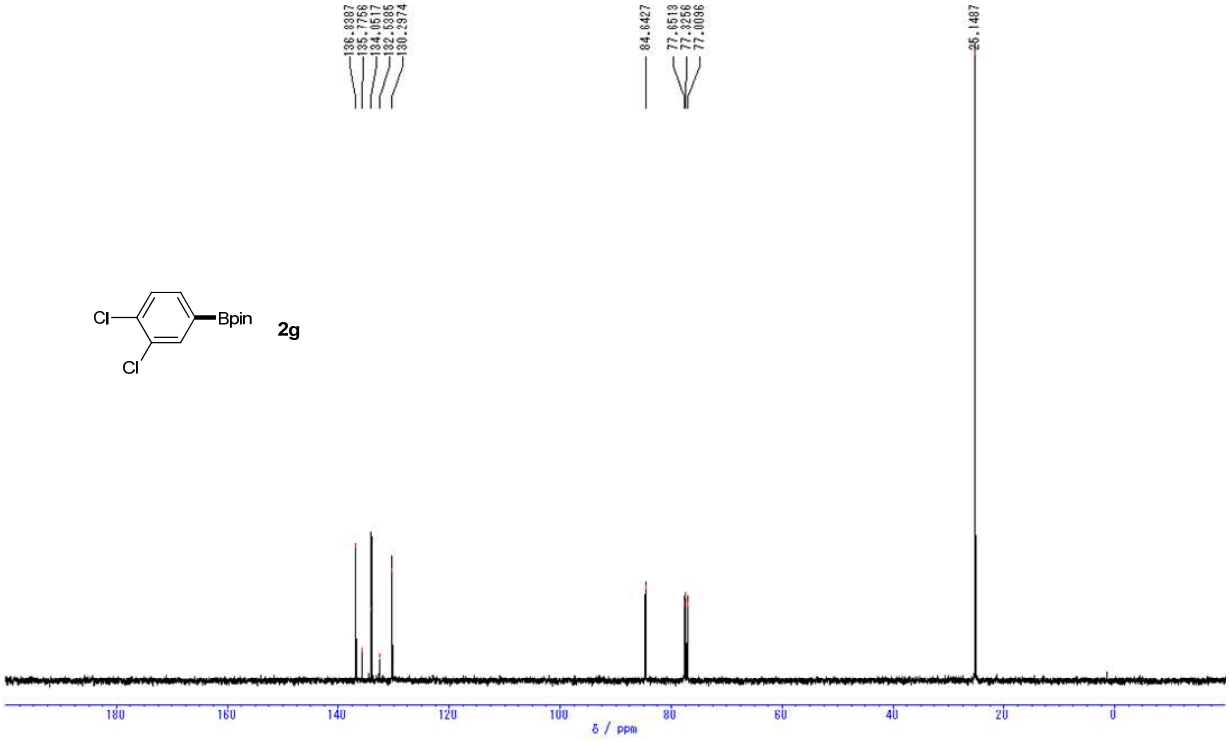
2
1
0
δ / ppm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2g
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160
140
120
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80
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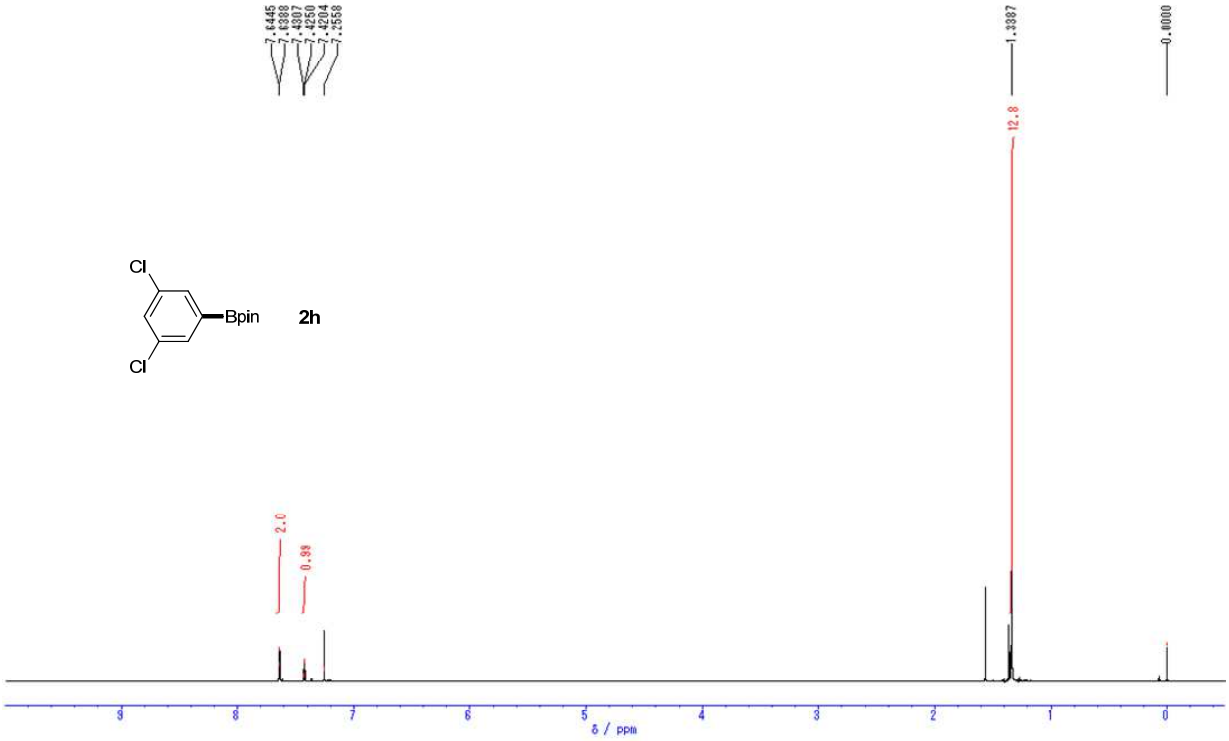
40
20
0
δ / ppm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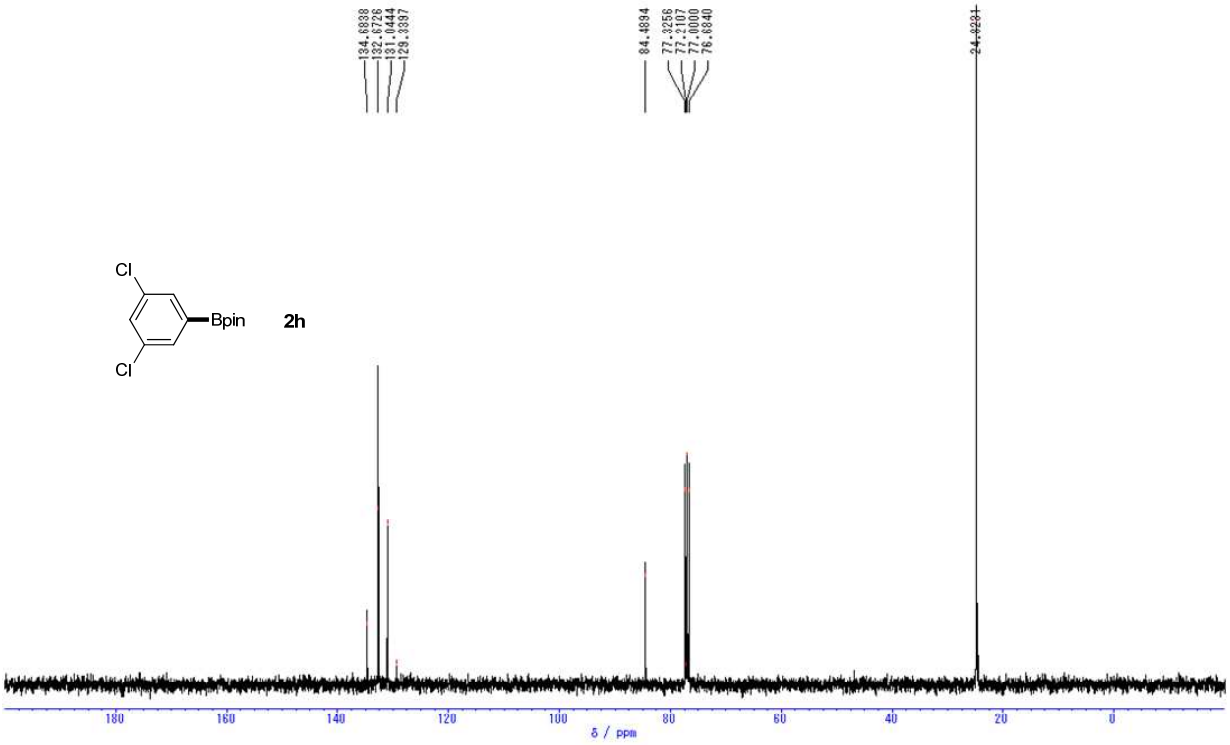
12.8
Cl
Bpin
Cl
2h
2.0
0.88
9
8
7
6
5
4
3
2
1
0
δ / ppm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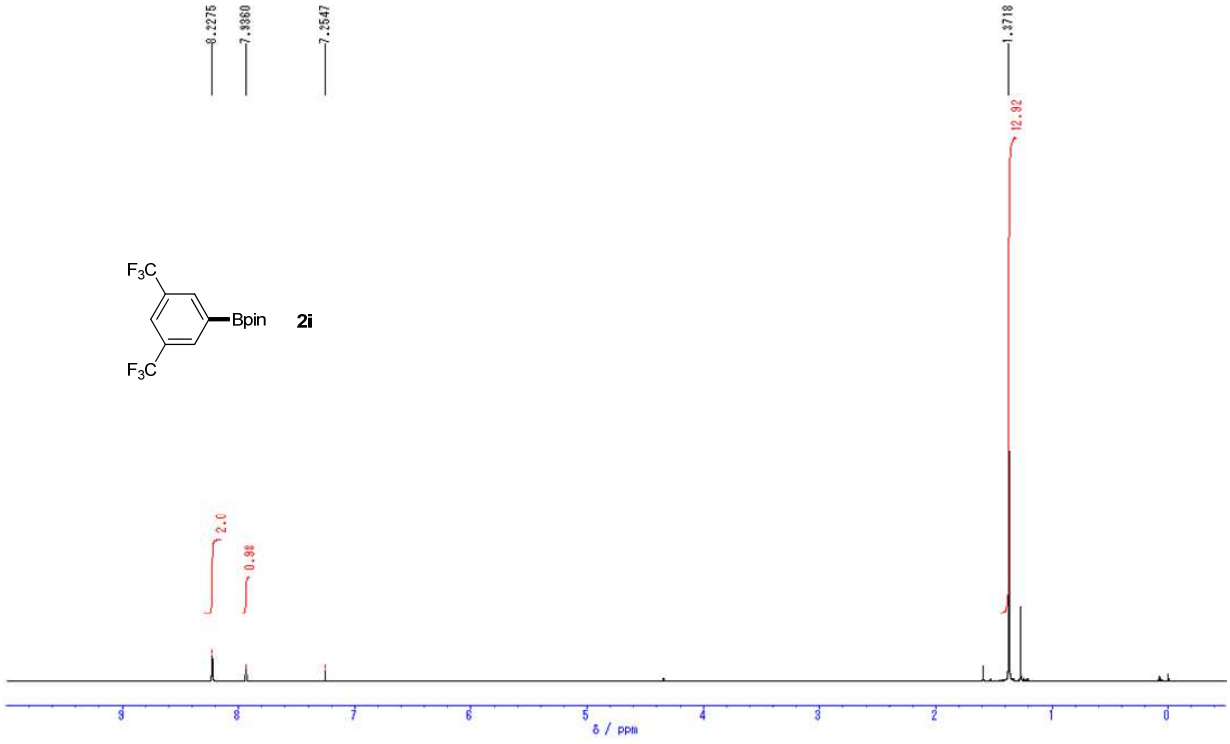
132.6726
131.0444
129.3397
84.4894
77.3256
77.2107
77.0000
76.6840
24.8231
Cl
Bpin
Cl
2h
180
160
140
120
100
80
60
40
20
0
δ / ppm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12.92
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Bpin
F3C
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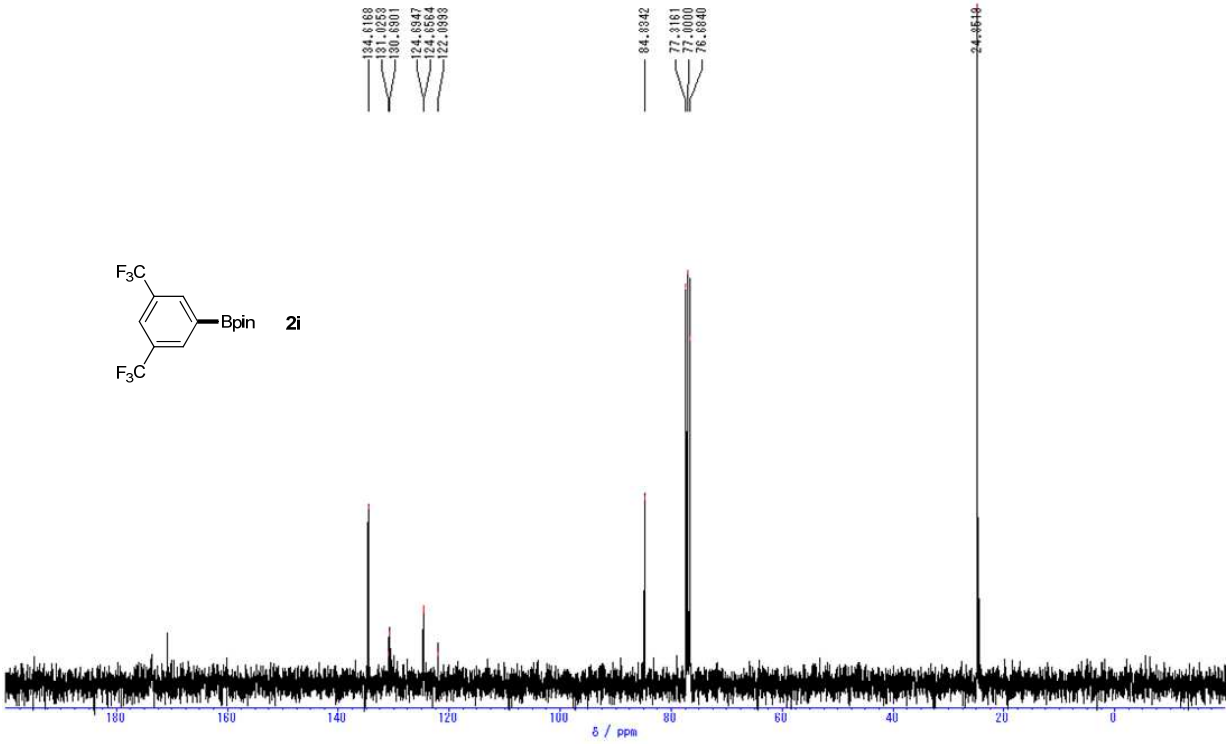
2.0
0.98
9
8
7
6
5
4
3
2
1
0
δ / ppm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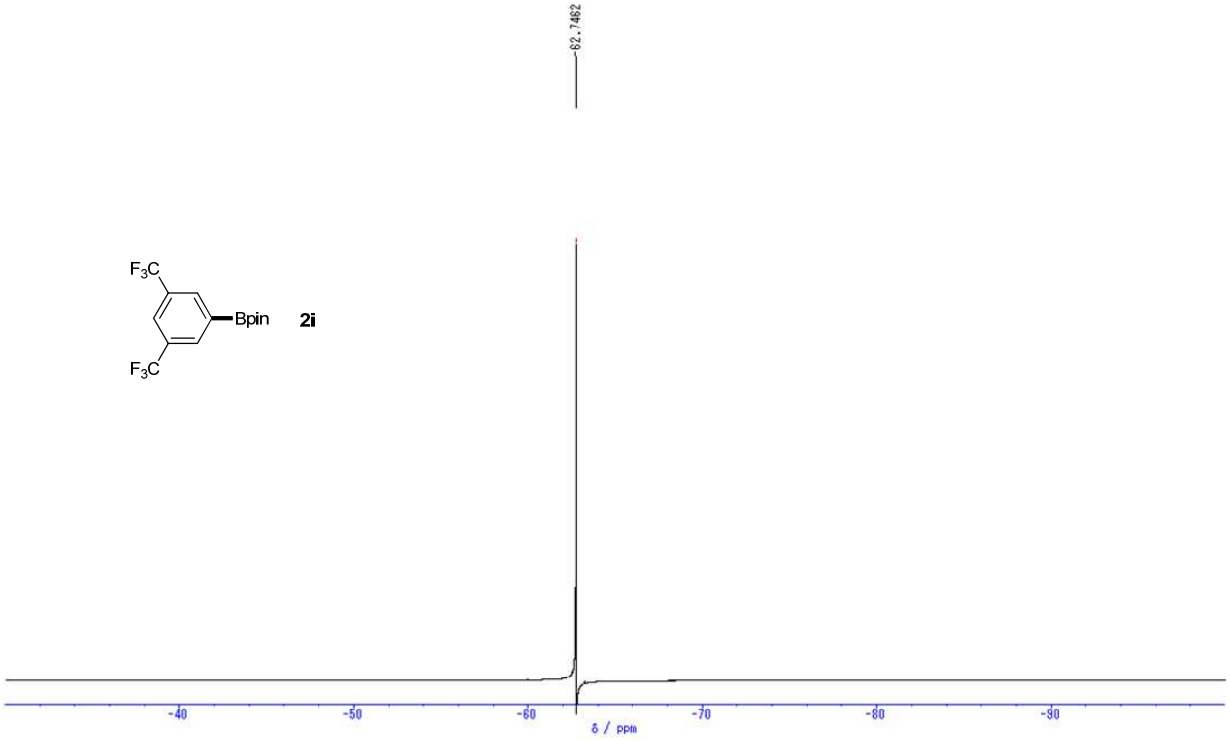
Bpin
2i
F3C
180
160
140
120
100
80
60
40
20
0
δ / ppm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Bpin
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F3C
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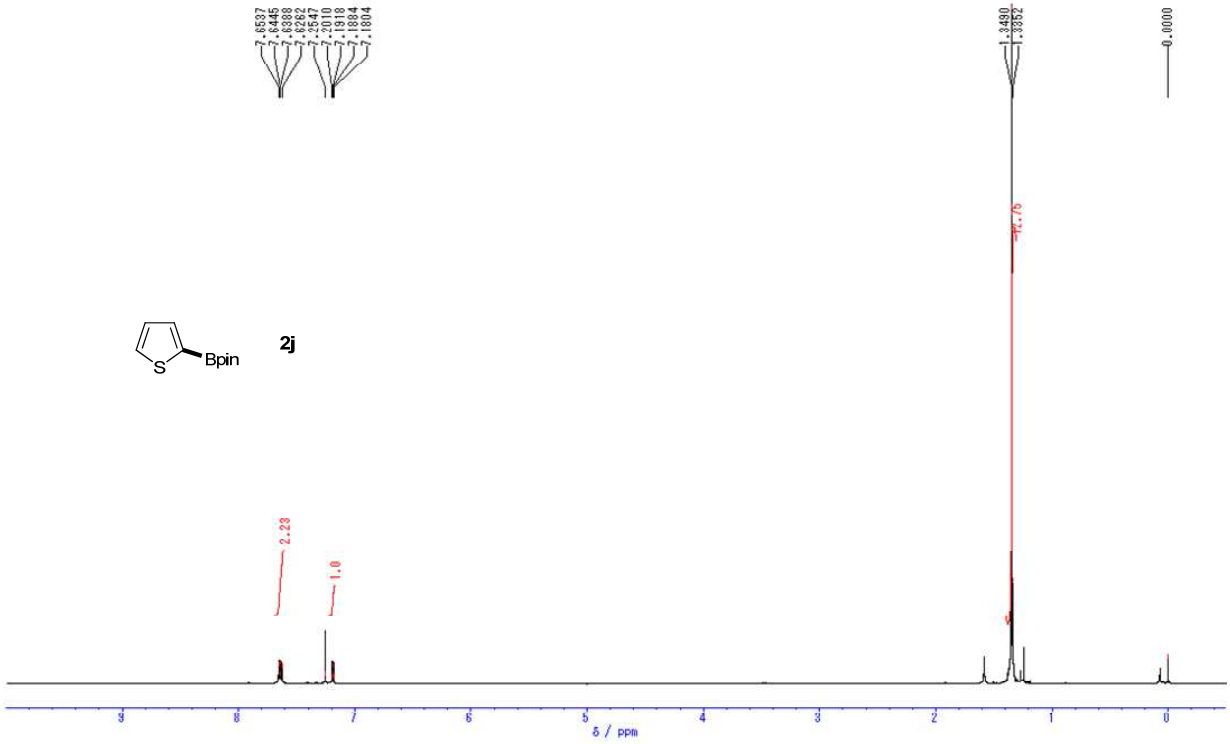
-50
-60
-70
-80
-90
δ / ppm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7.6388
7.6262
7.2547
7.2010
7.1918
7.1884
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1.3490
1.3352
0.0000
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2.23
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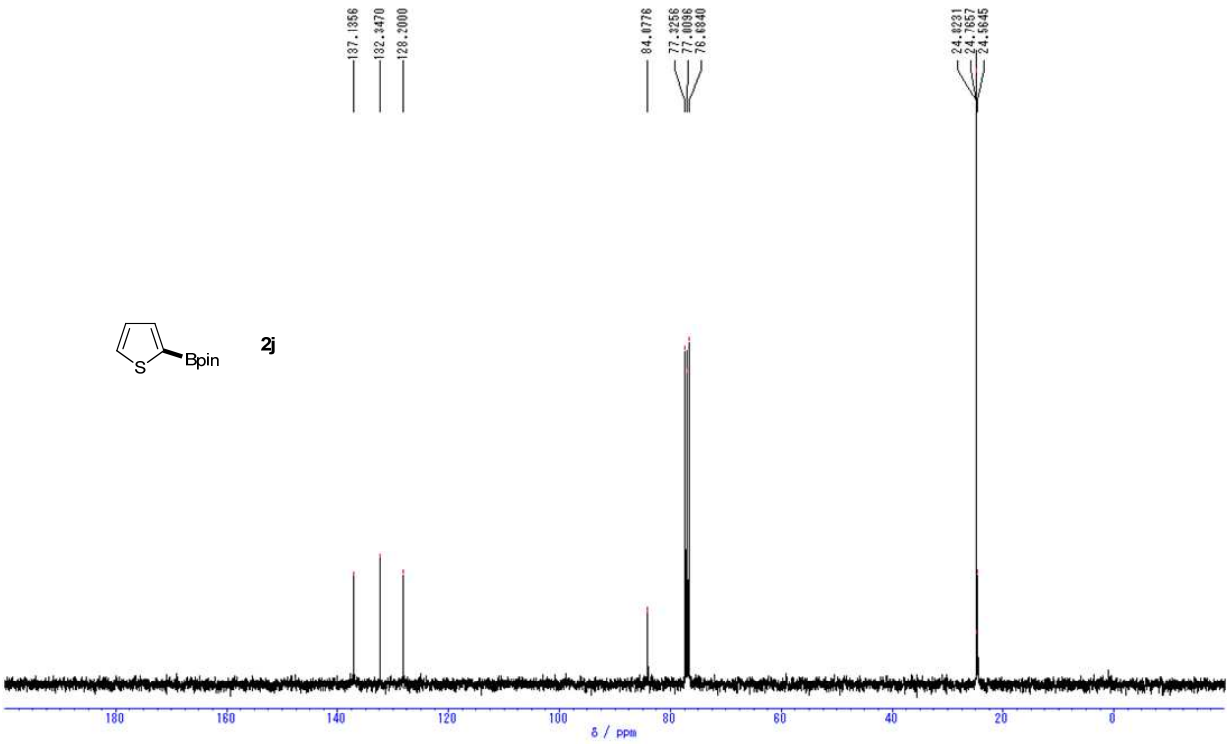
Bpin
2j
δ / ppm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128.2000
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77.0095
76.6840
24.8231
24.7857
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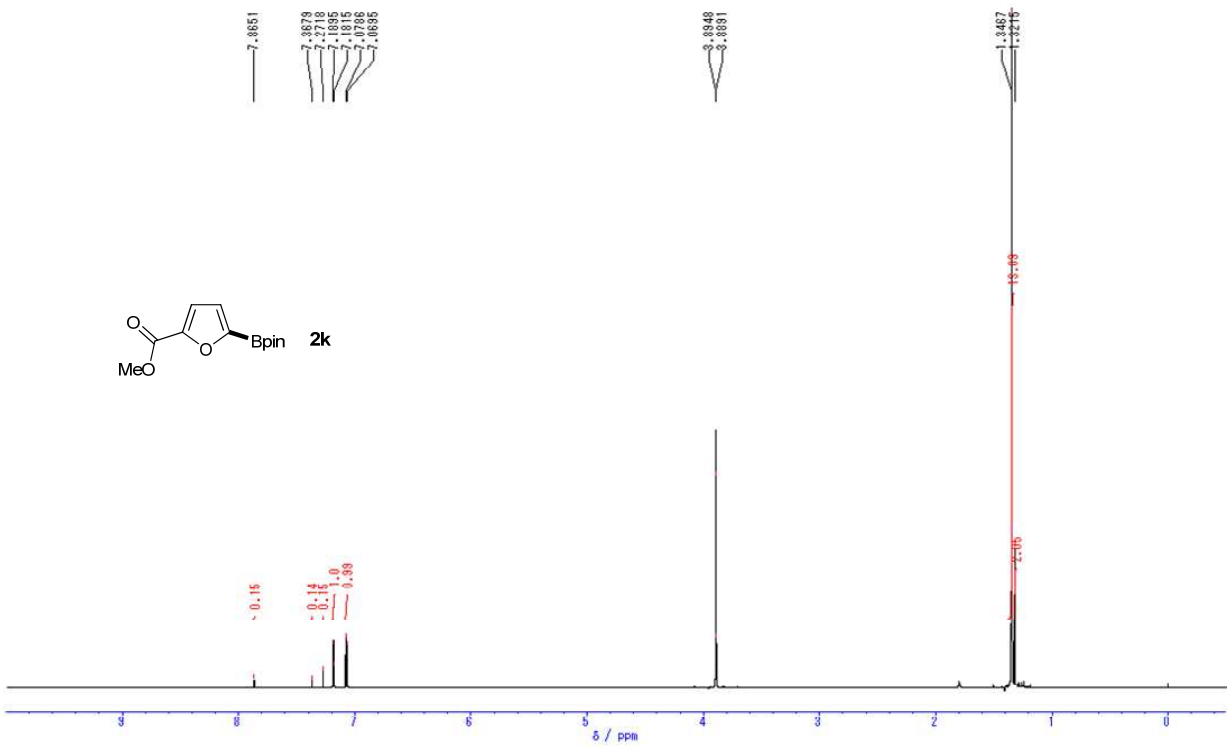
Bpin
2j
δ / ppm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7.1815
7.0788
7.0695
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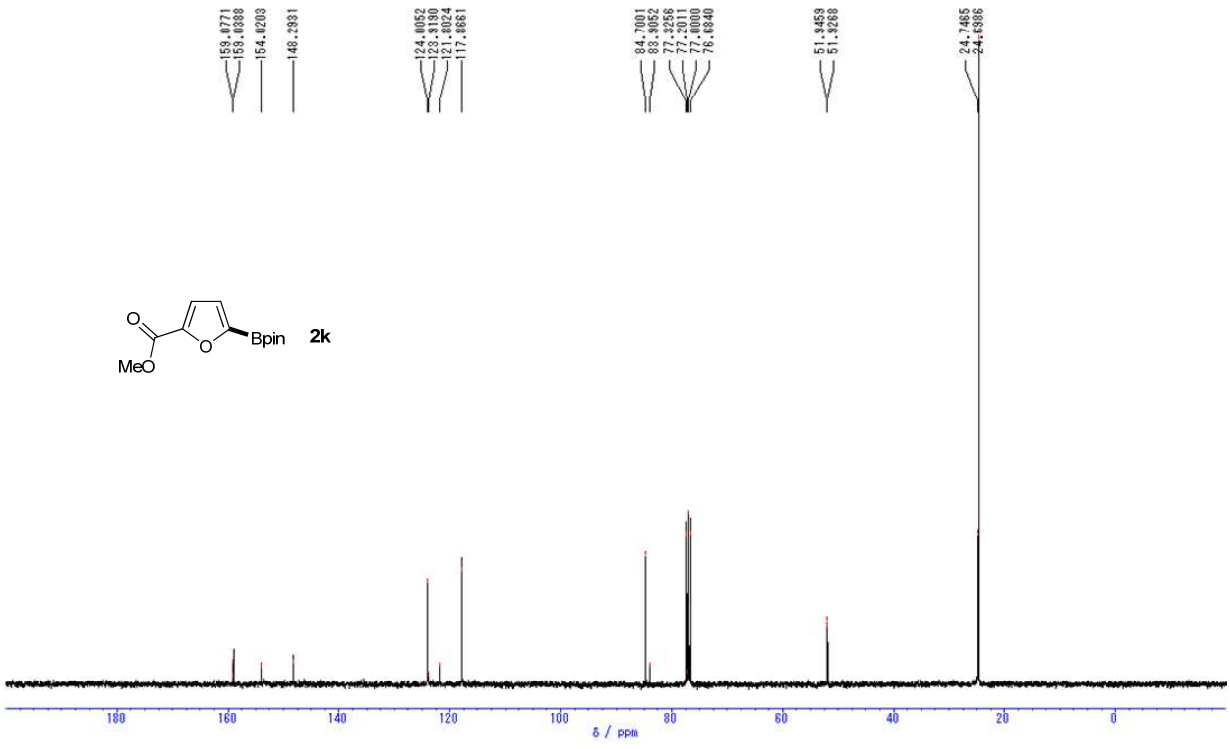
3.8891
1.3467
1.3215
15.00
2.05
0.15
0.14
0.15
1.0
0.99
O
MeO
O
Bpin
2k
δ / ppm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154.4203
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124.8052
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121.8024
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84.7001
83.3052
77.3258
77.2011
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51.9459
51.9268
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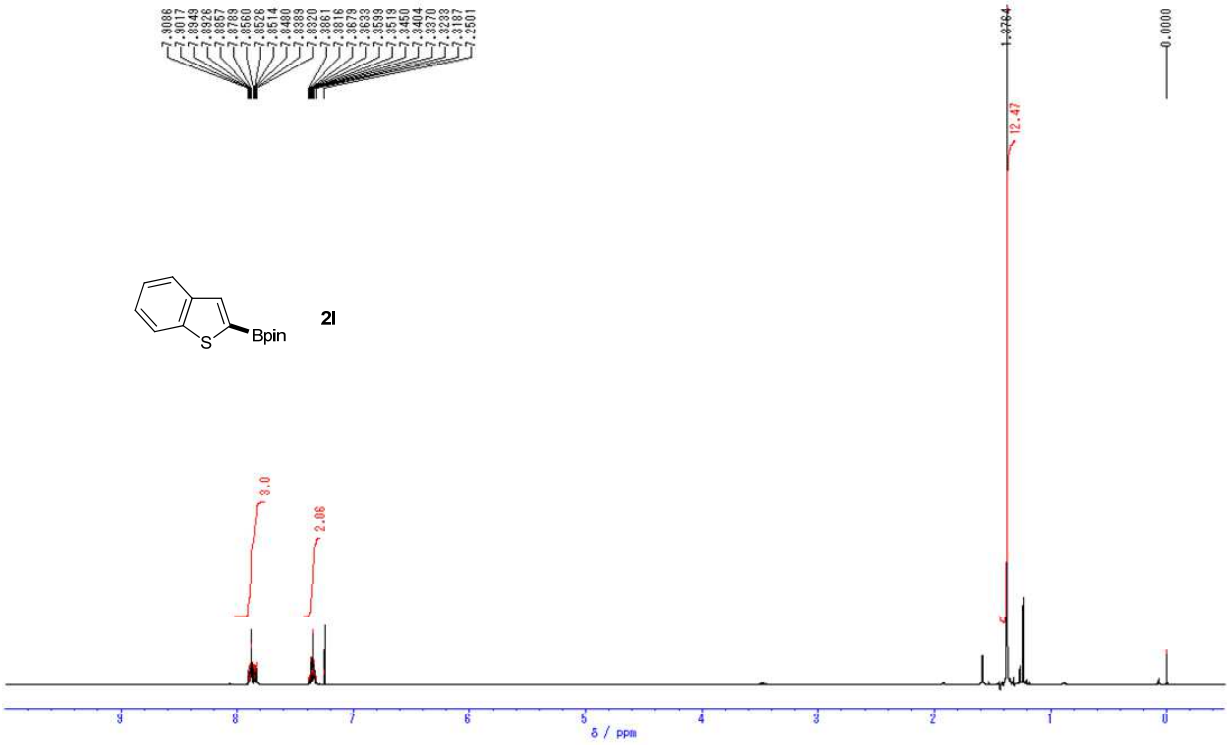
O
MeO
O
Bpin
2k
δ / ppm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7.3017
7.2949
7.2926
7.2857
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7.2560
7.2528
7.2514
7.2480
7.2389
7.2320
7.2261
7.2215
7.2179
7.2133
7.1959
7.1519
7.1450
7.1404
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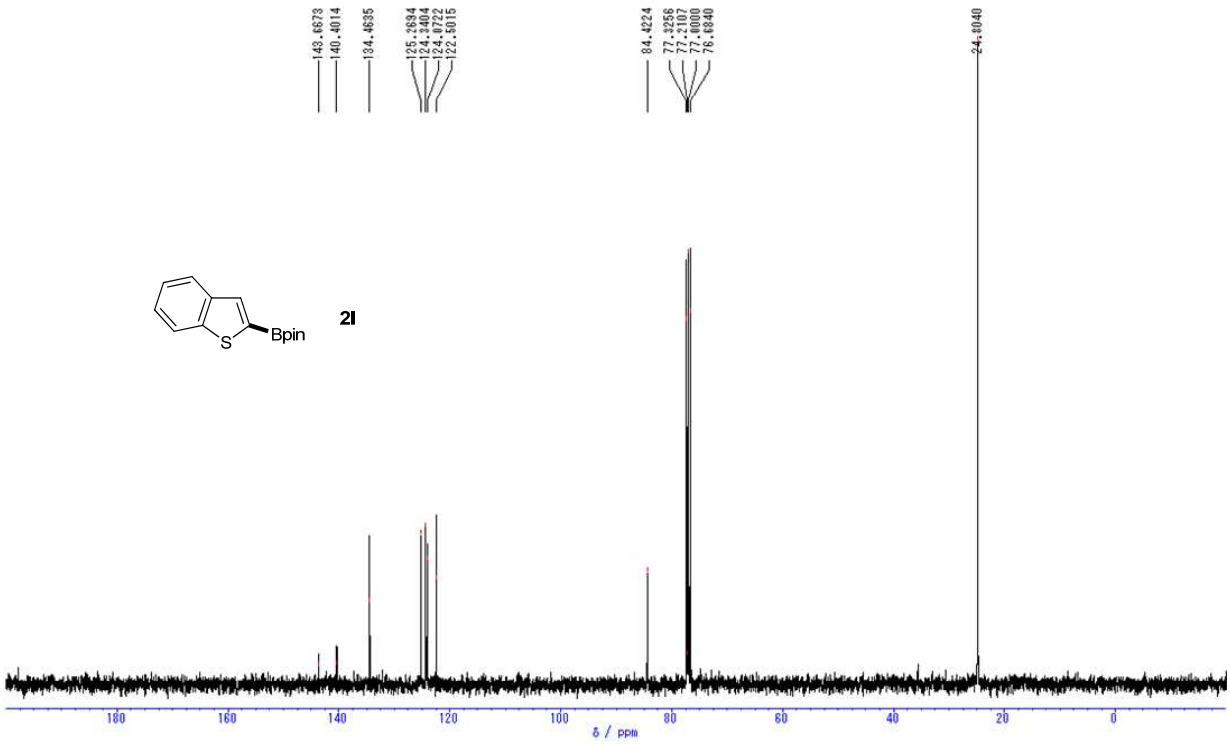
7.1233
7.1187
7.2501
1.3764
12.47
0.0000
Bpin
2l
3.0
2.06
δ / ppm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134.4635
125.2694
124.3404
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122.9015
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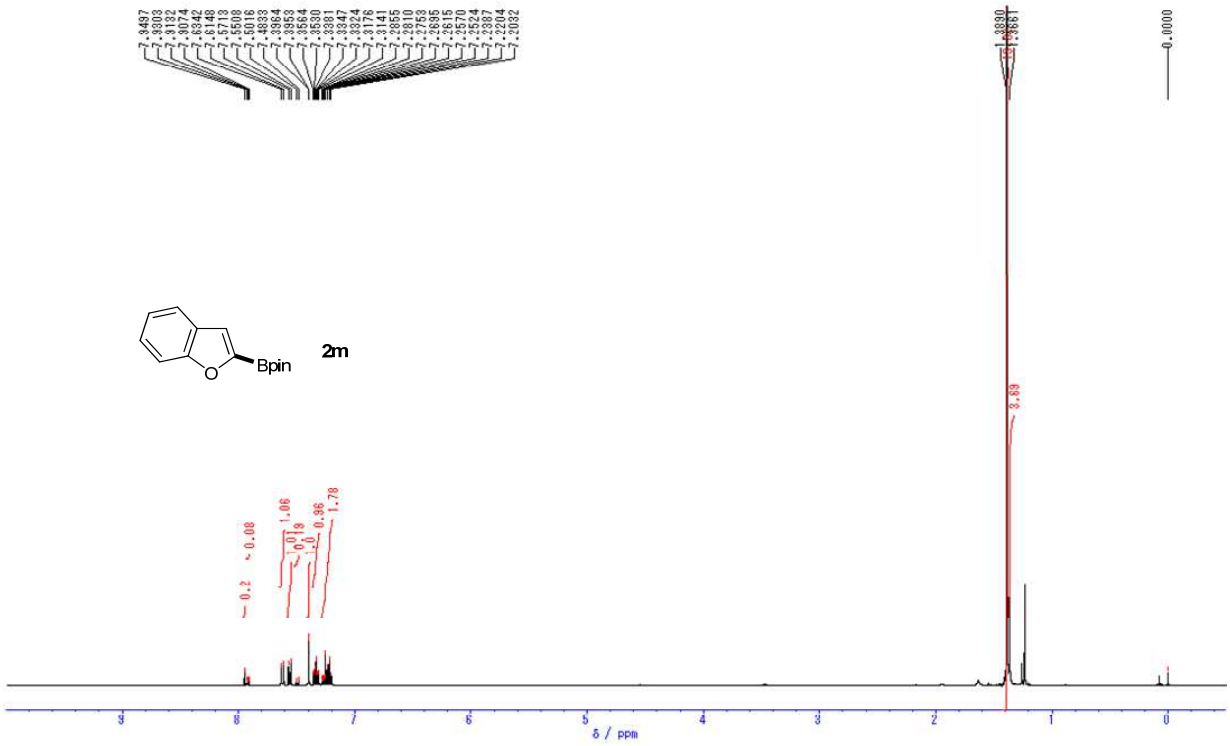
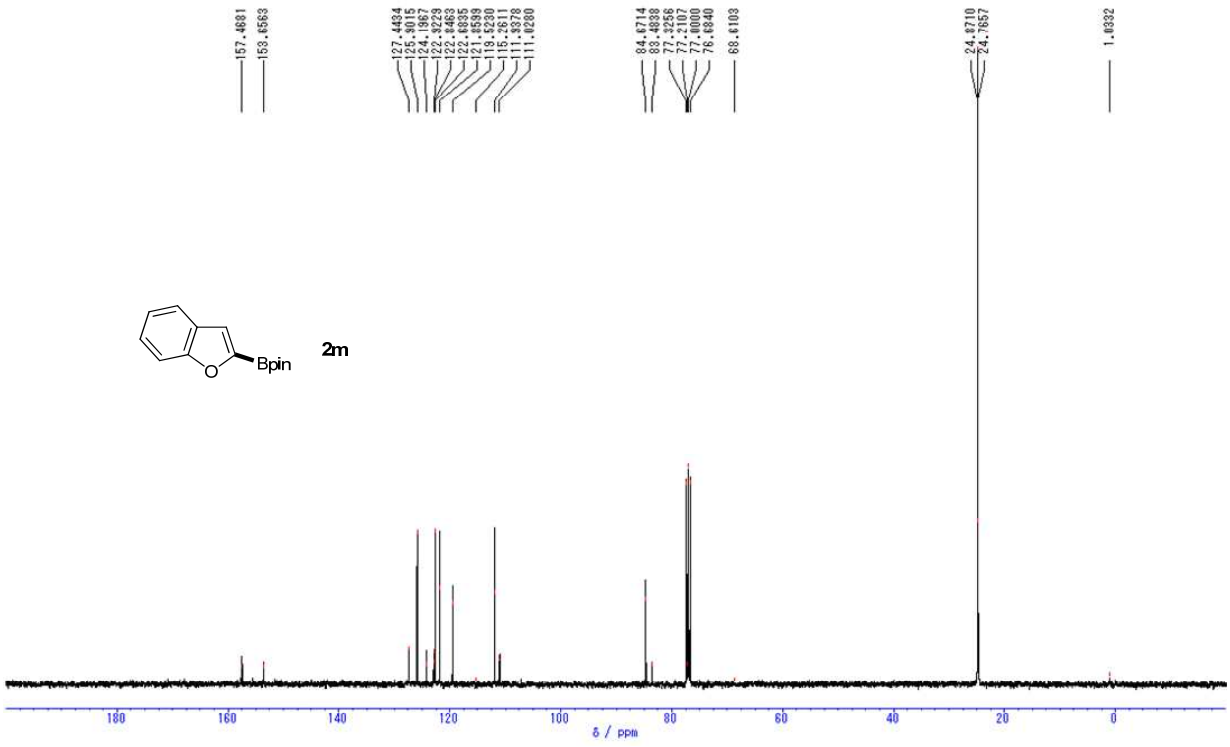
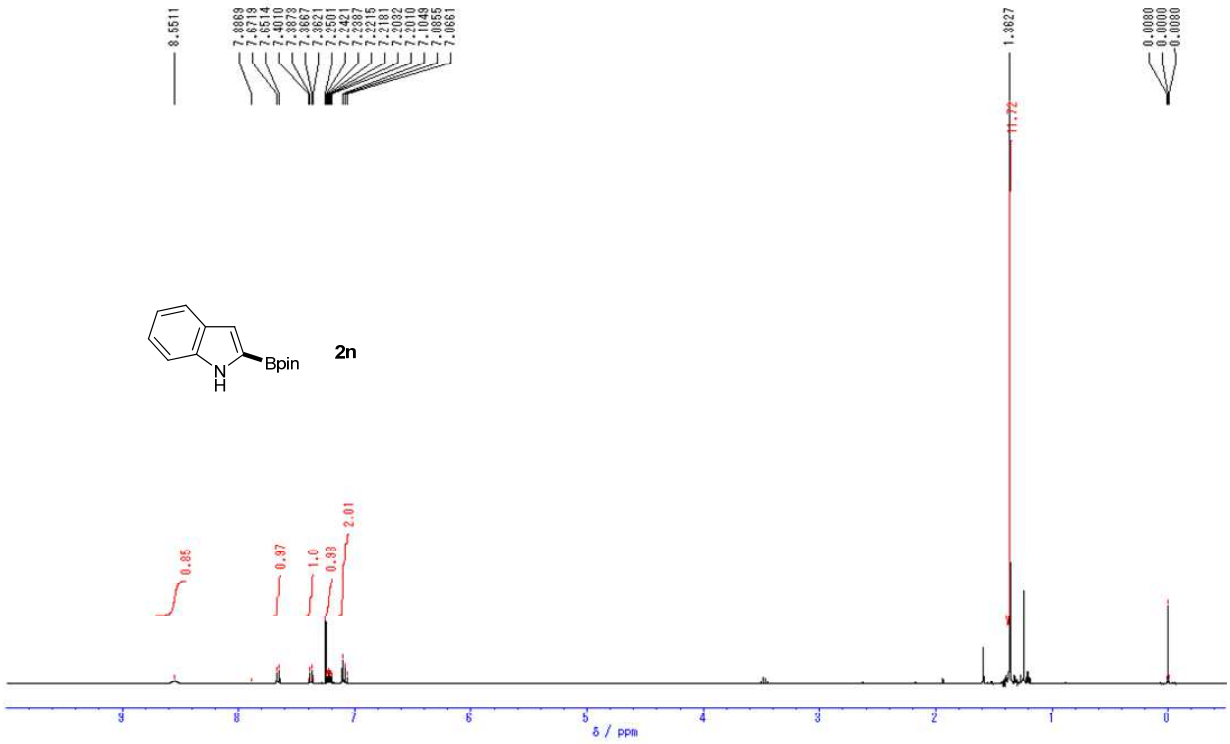
77.2107
77.0000
76.6840
24.8040
Bpin
2l
δ / ppm


Bpin
2m
δ / ppm


Bpin
2m
δ / ppm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7.4010
7.3873
7.3867
7.3821
7.2501
7.2421
7.2387
7.2215
7.2181
7.2032
7.2010
7.1048
7.1035
7.0681
1.3627
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0.0080
0.0000
0.0080
Bpin
2n
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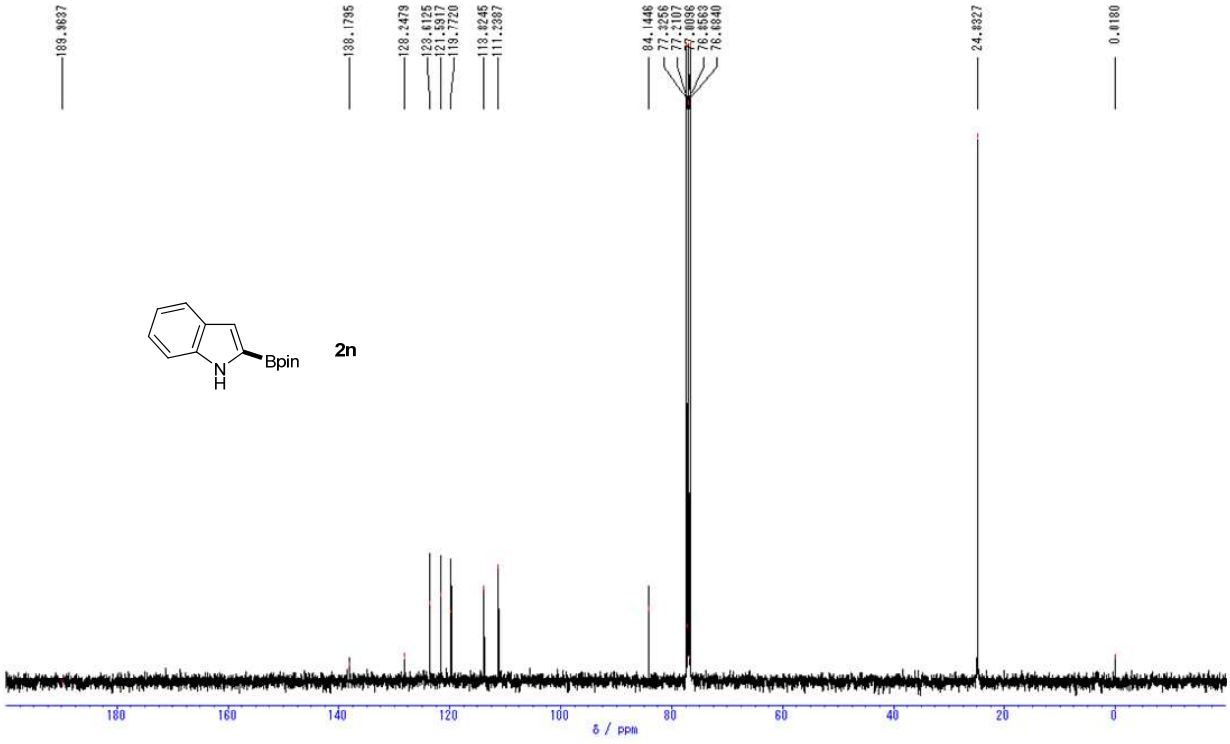
0.97
1.0
0.93
2.01
δ / ppm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113.8245
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77.2107
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76.6040
24.8327
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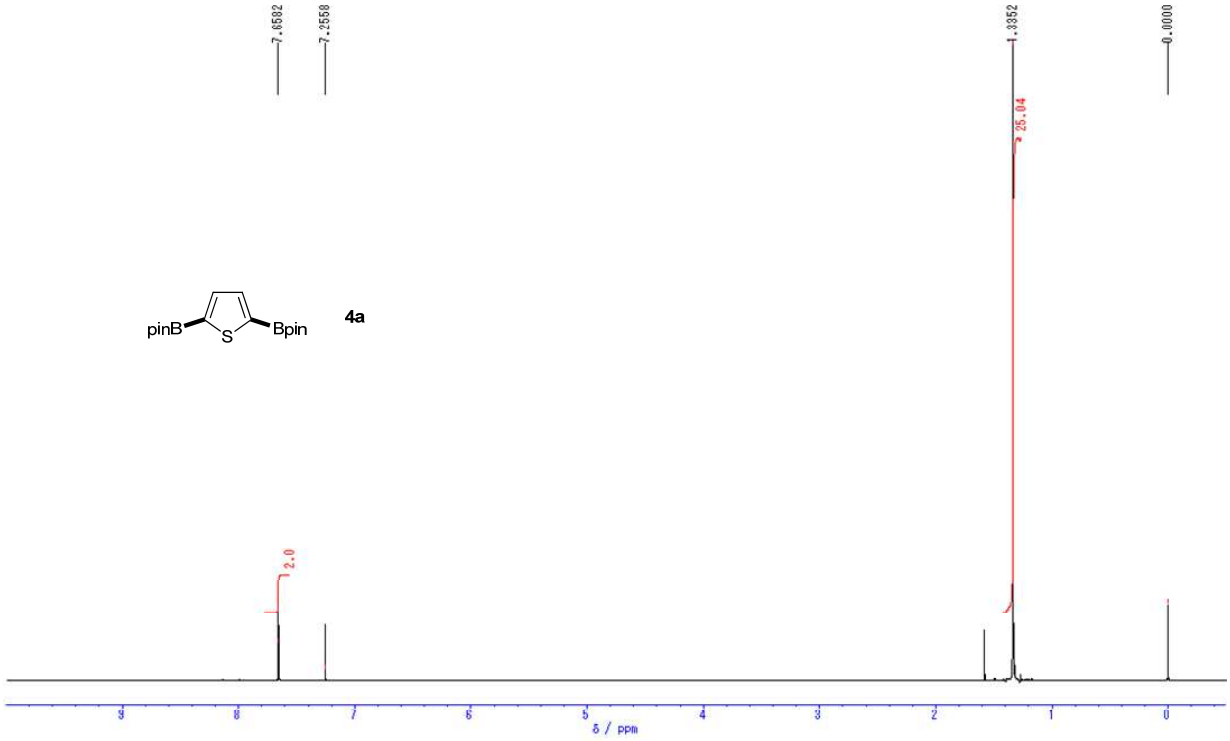
Bpin
2n
δ / ppm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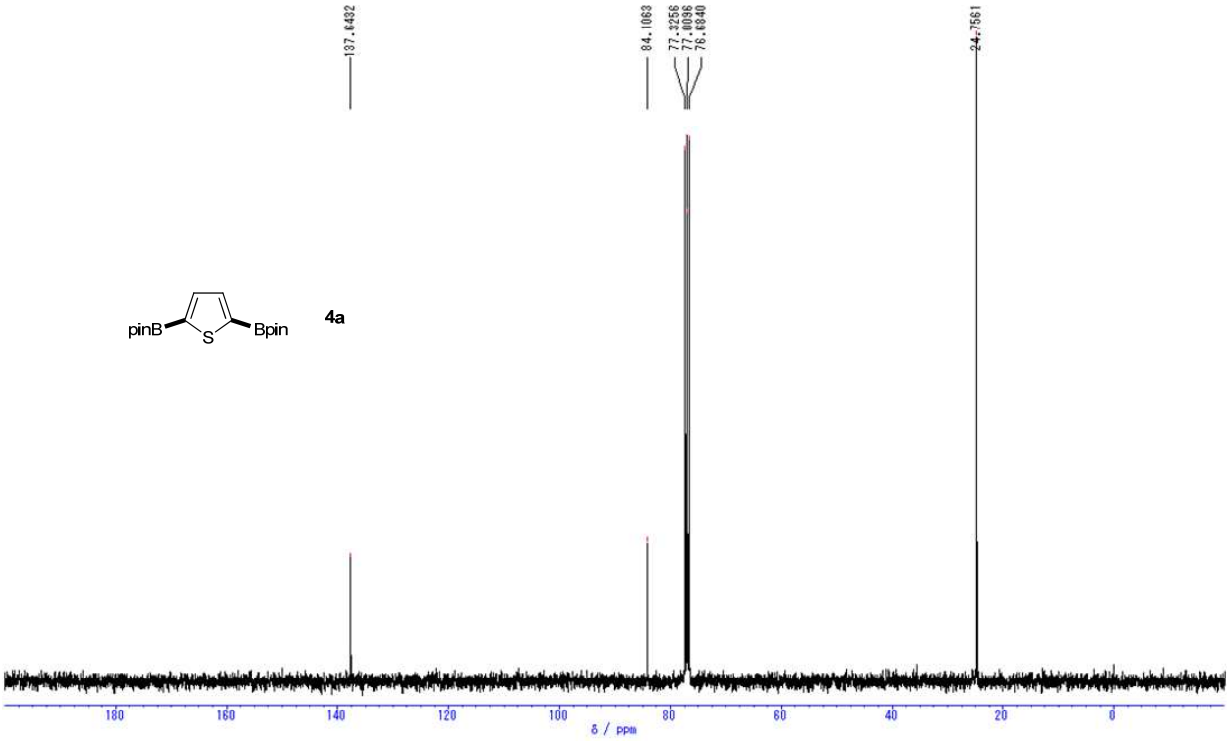
7.2558
1.3352
0.0000
25.04
2.0
pinB
S
Bpin
4a
δ / ppm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77.0095
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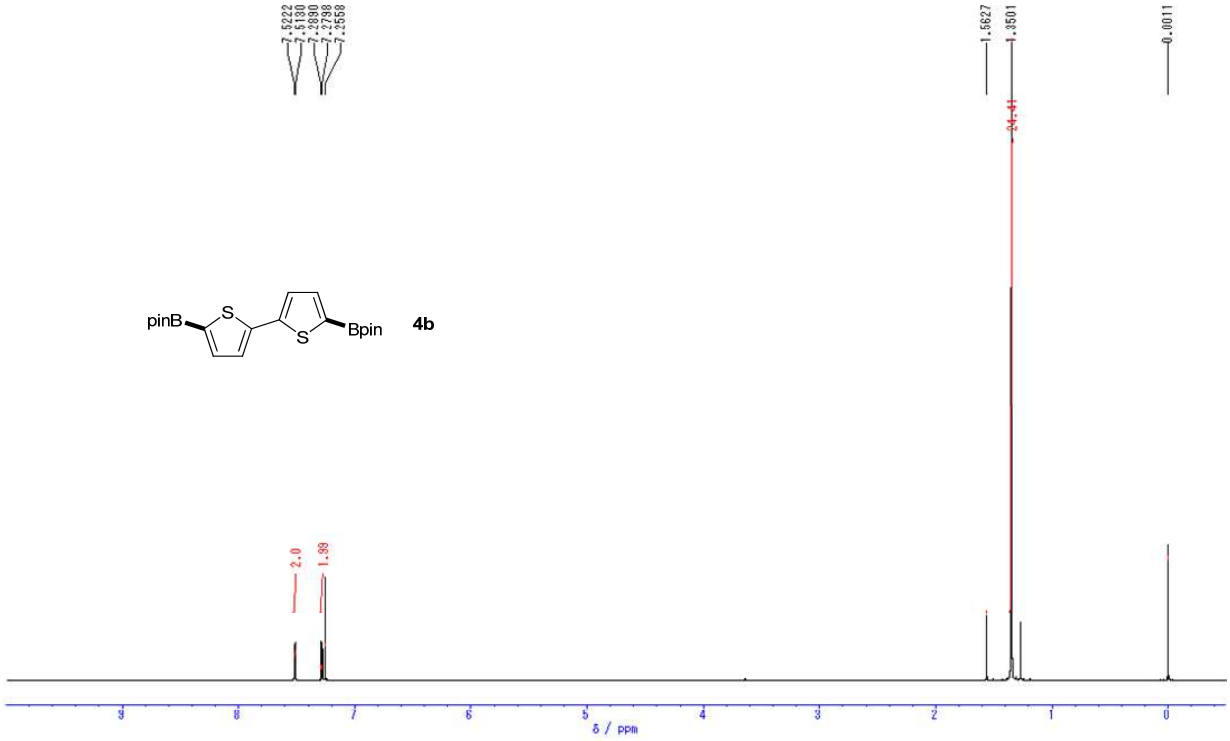
S
Bpin
4a
δ / ppm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7.6130
7.2890
7.2798
7.2558
1.5627
1.3501
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24.41
2.0
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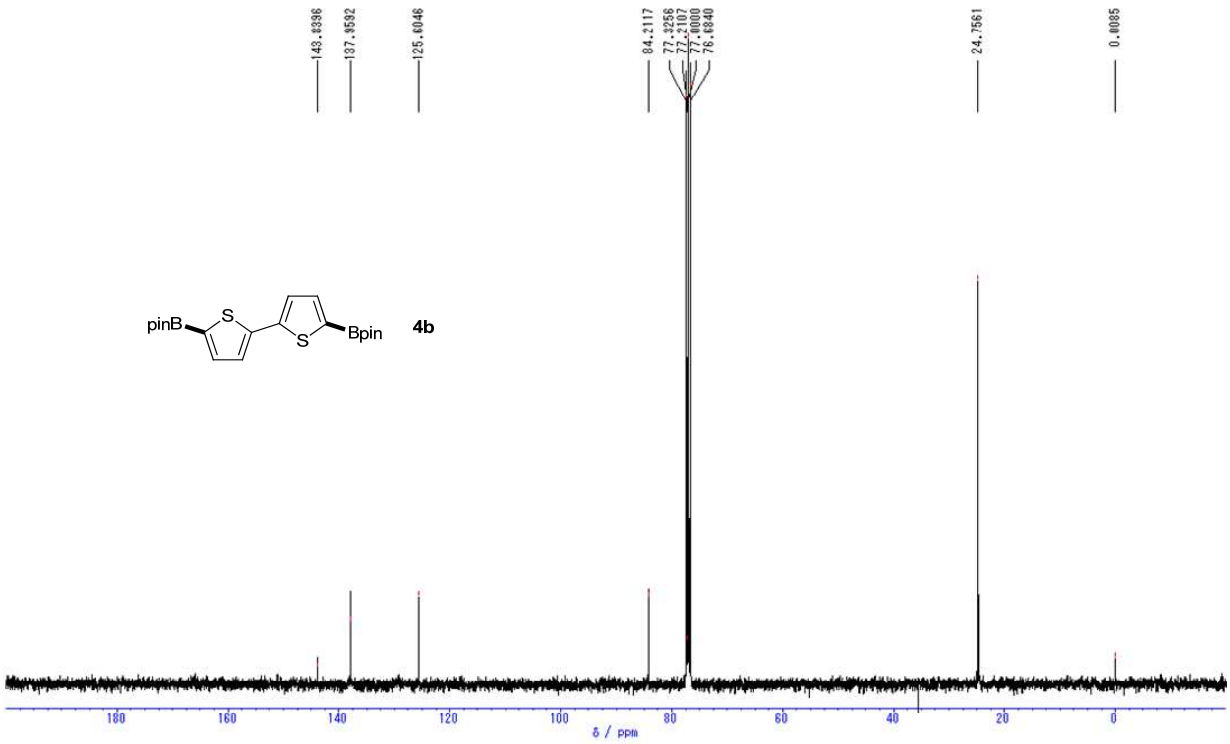
pinB
S
S
Bpin
4b
δ / ppm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137.9582
125.6046
84.2117
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77.0000
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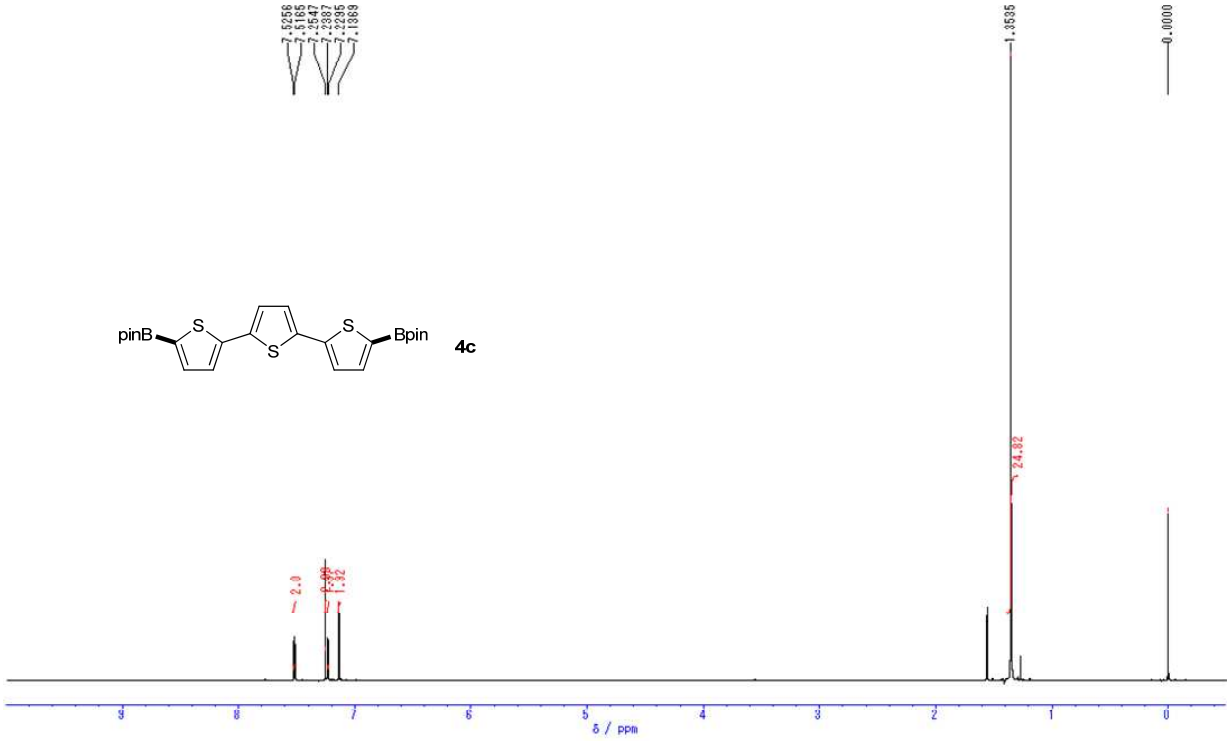
pinB
S
S
Bpin
4b
δ / ppm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7.2547
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pinB
Bpin
4c
24.82
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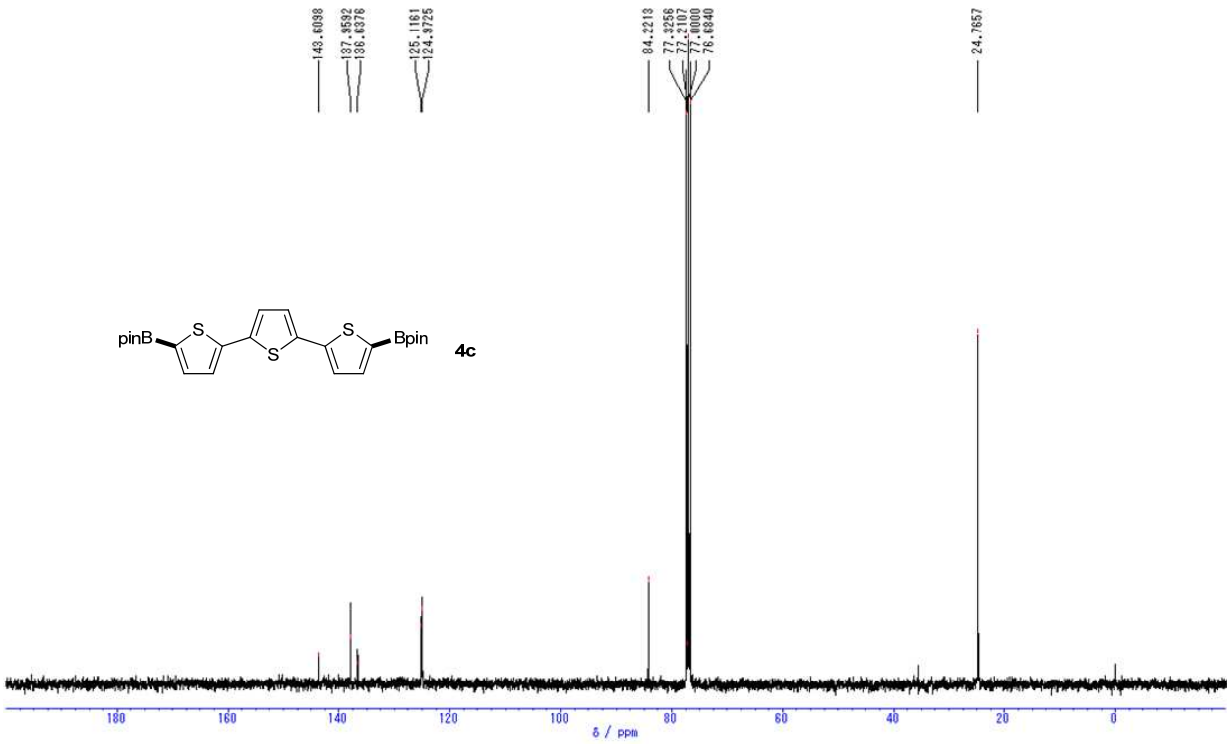
1.92
δ / ppm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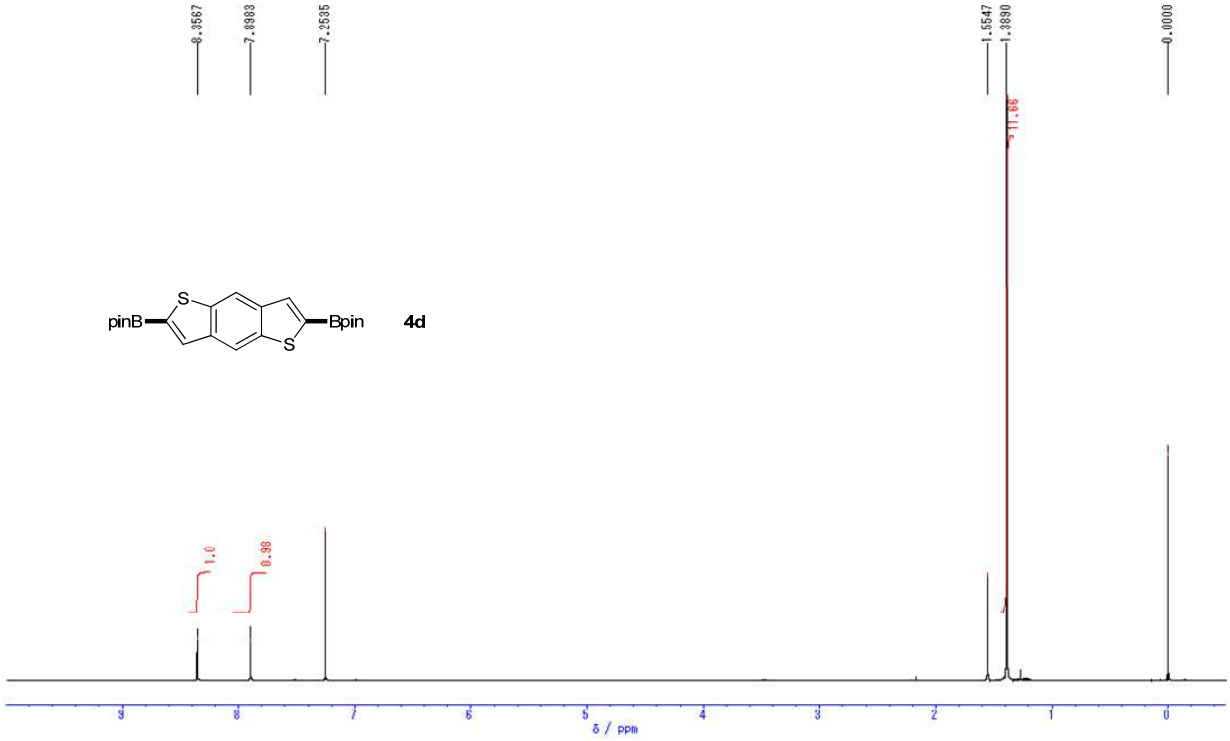
4c
δ / ppm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pinB
Bpin
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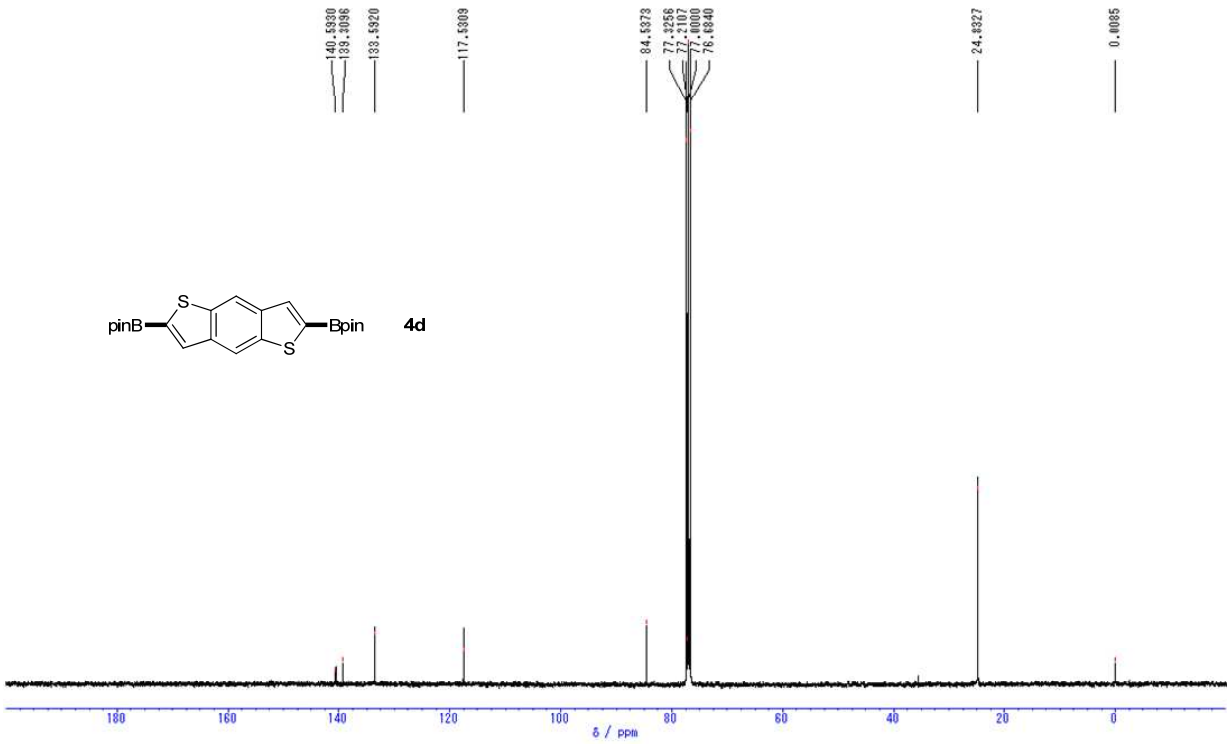
1.0
0.98
δ / ppm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117.5309
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77.2107
77.0000
76.6840
24.8327
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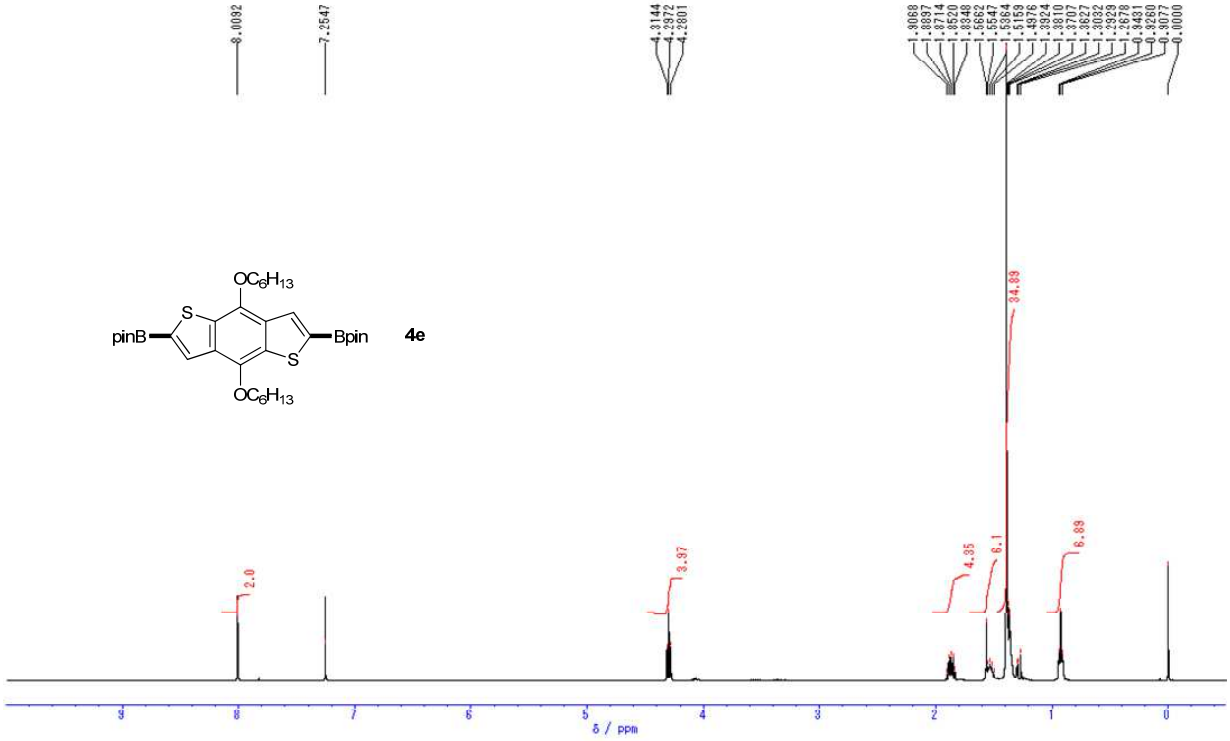
pinB
Bpin
4d
δ / ppm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1.8714
1.8520
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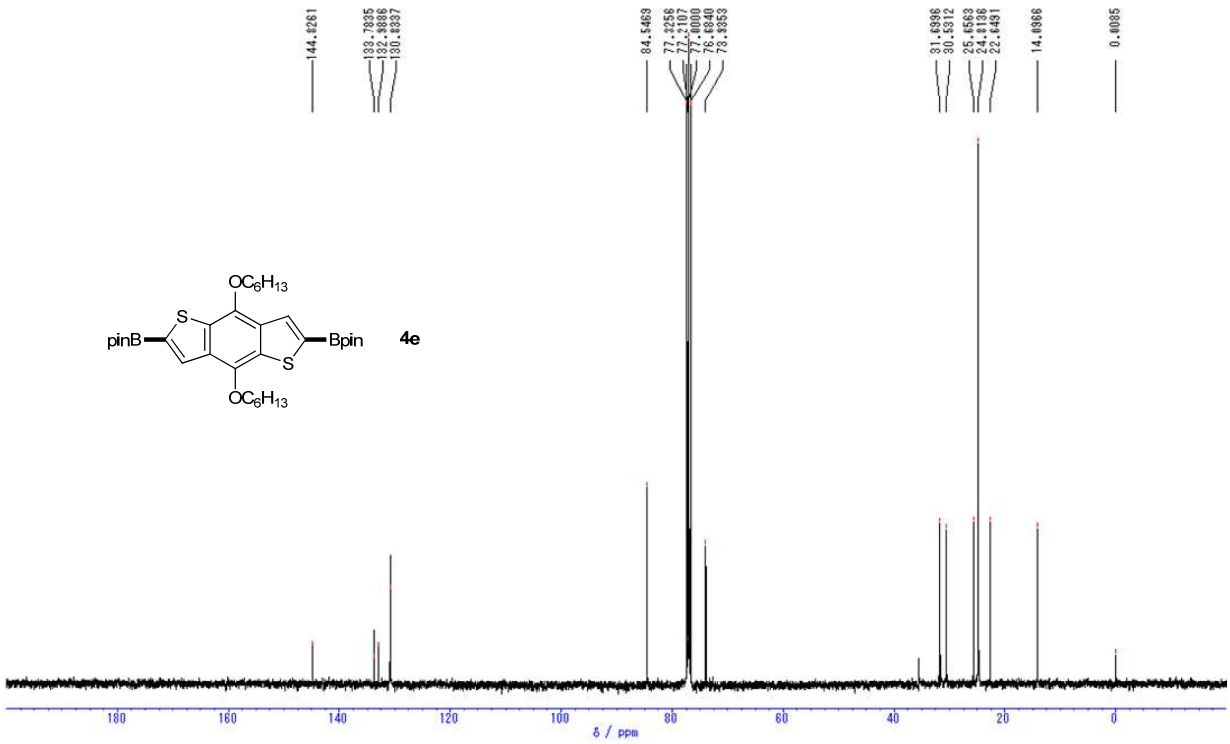
1.5662
1.5547
1.5364
1.5159
1.4976
1.3824
1.3810
1.3707
1.3627
1.3032
1.2929
1.2678
0.8481
0.8361
0.8077
0.0000
OC6H13
S
pinB
Bpin
S
OC6H13
4e
84.89
2.0
3.97
4.85
6.1
6.89
δ / ppm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77.2107
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76.6940
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31.6996
30.5312
25.4563
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OC6H13
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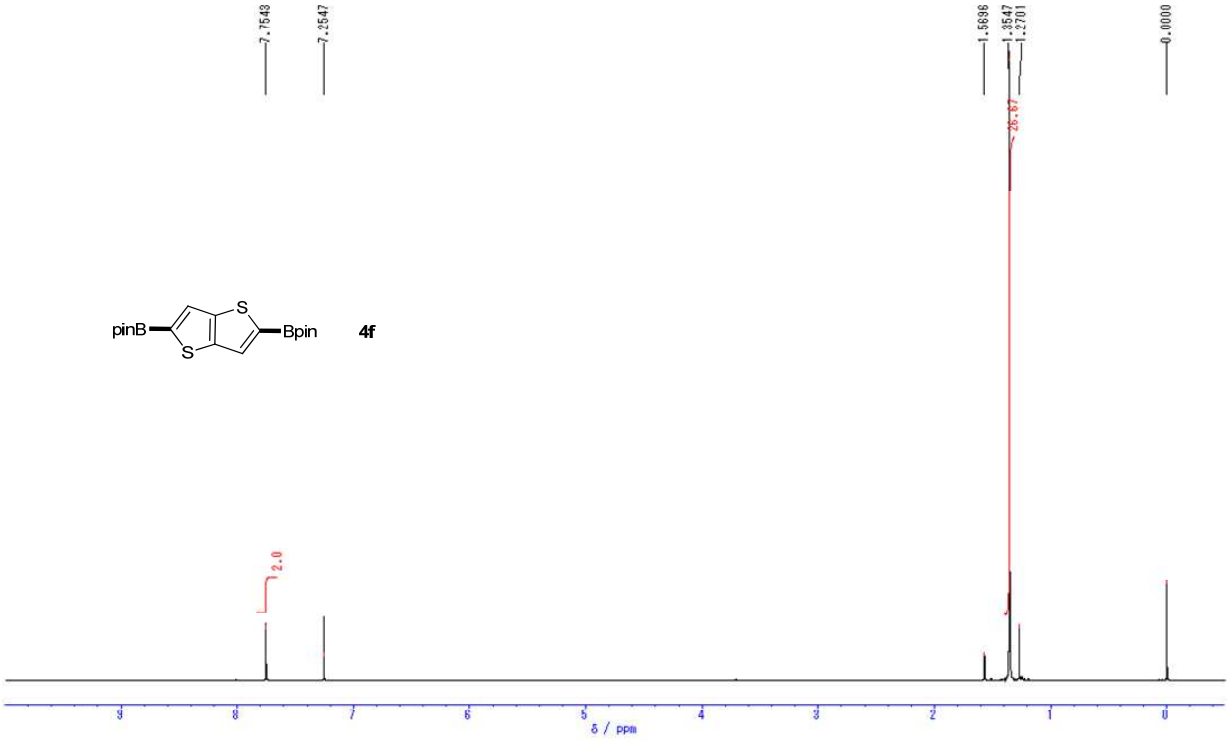
pinB
Bpin
S
OC6H13
4e
δ / ppm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0.0000
26.67
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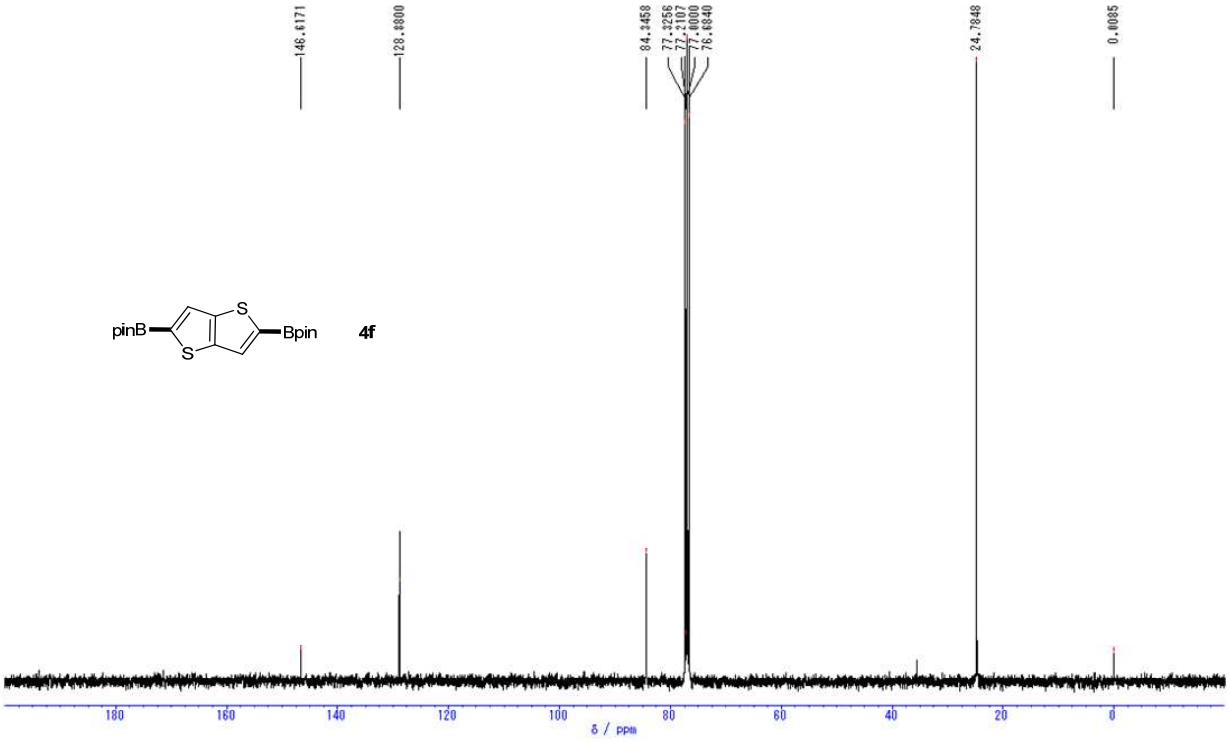
Bpin
4f
δ / ppm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76.6840
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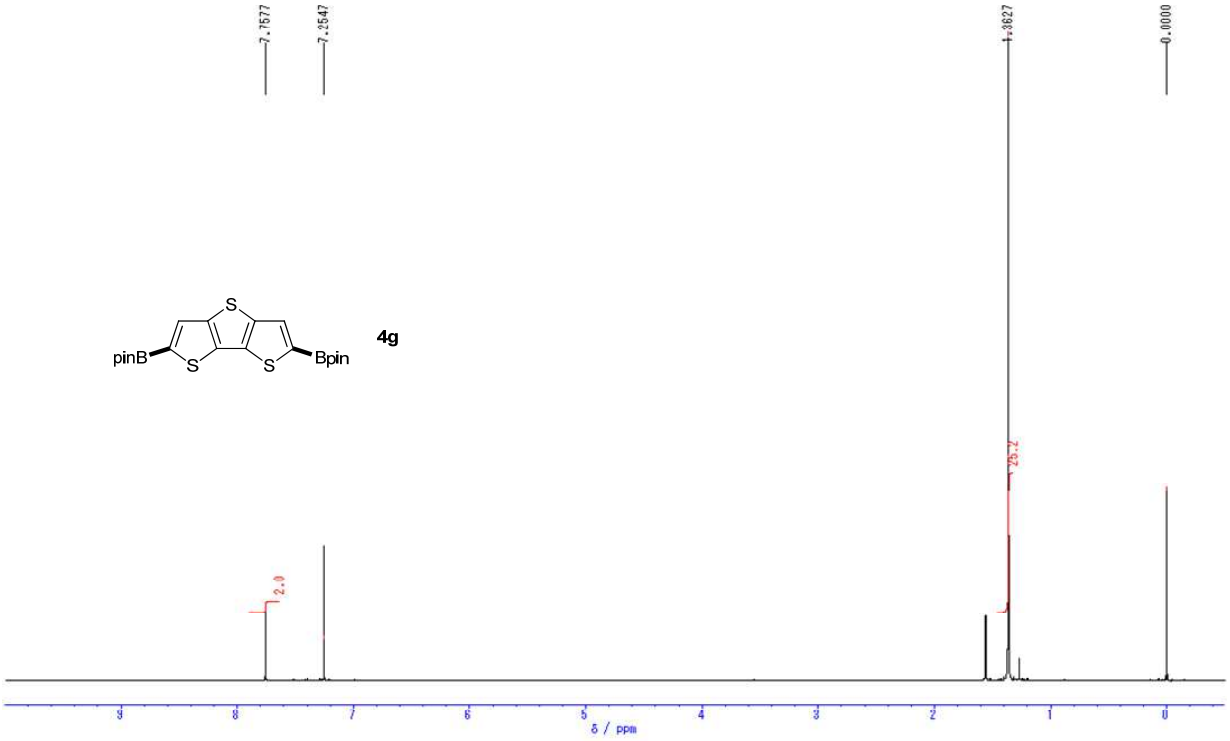
Bpin
4f
δ / ppm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28.2
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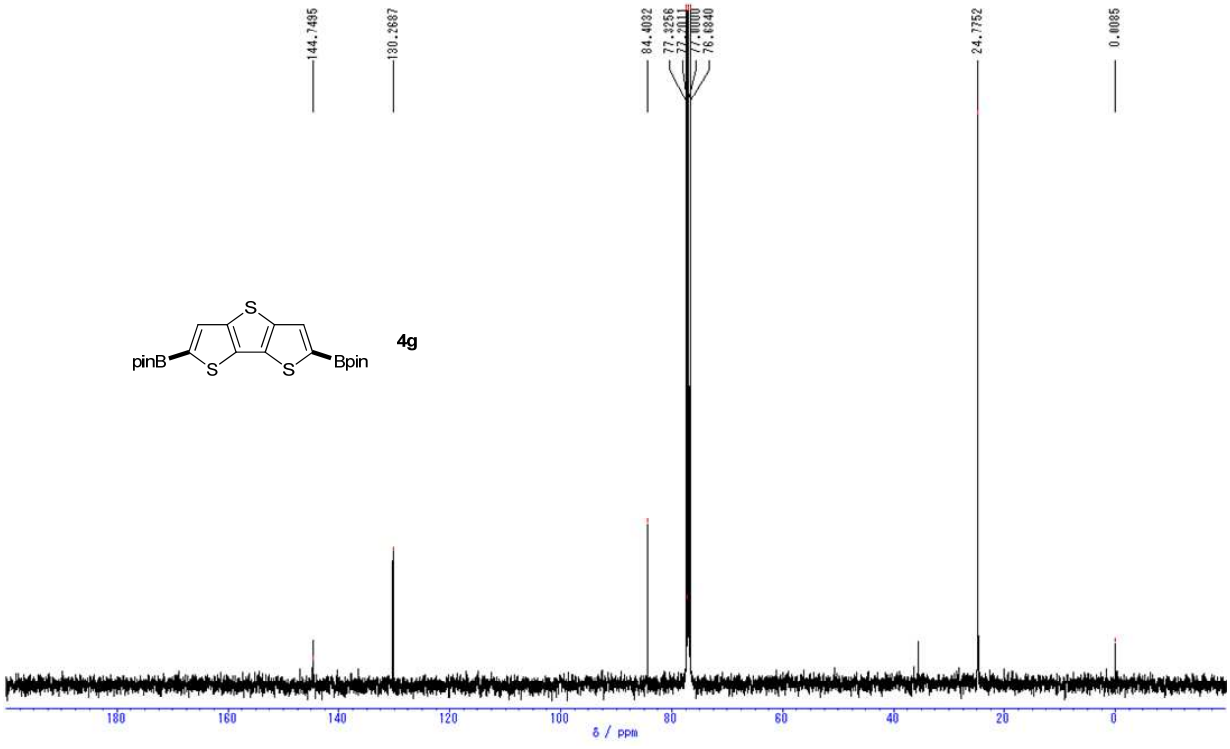
Bpin
S
S
S
4g
δ / ppm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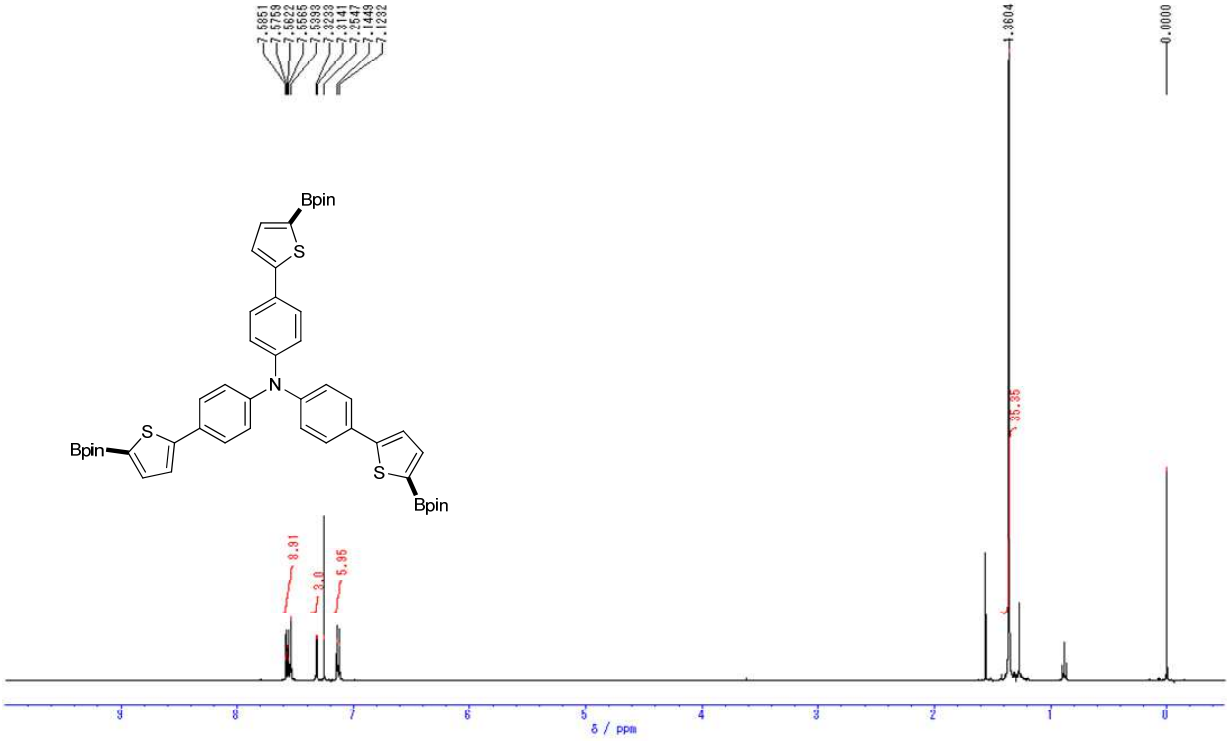
S
4g
δ / ppm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7.1448
7.1232
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8.31
3.0
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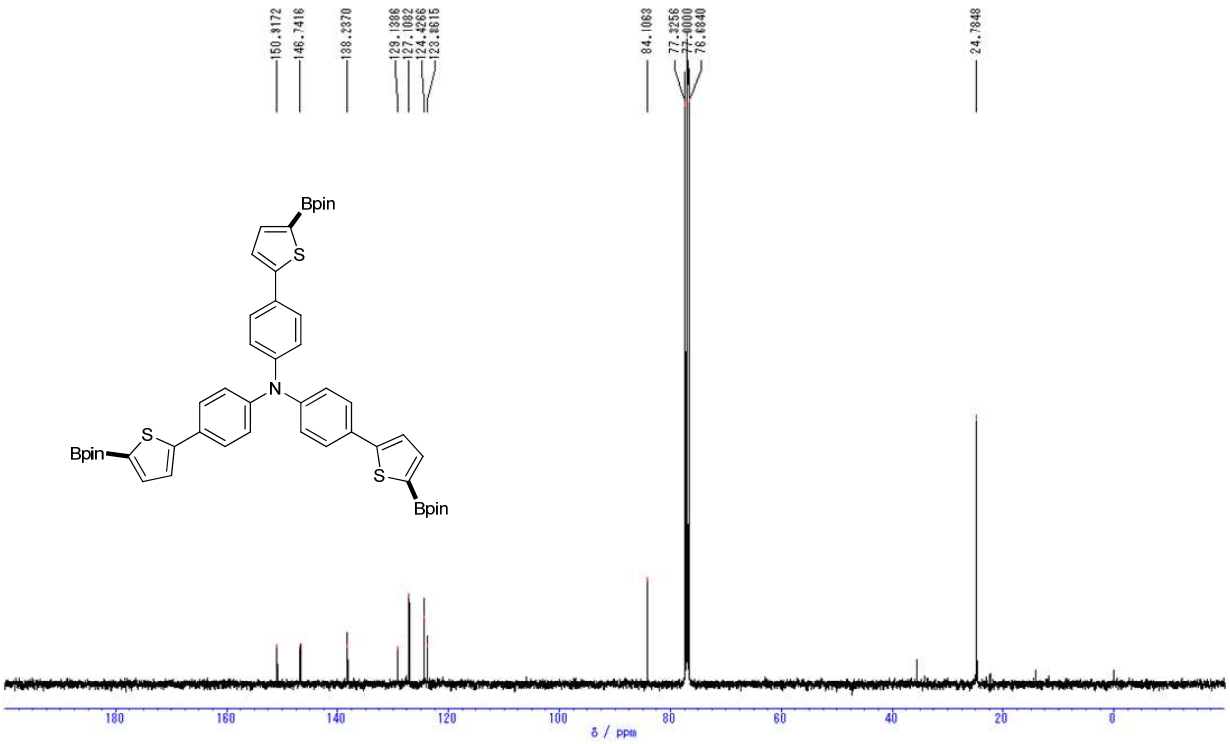
S
N
Bpin
S
S
Bpin
δ / ppm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123.8615
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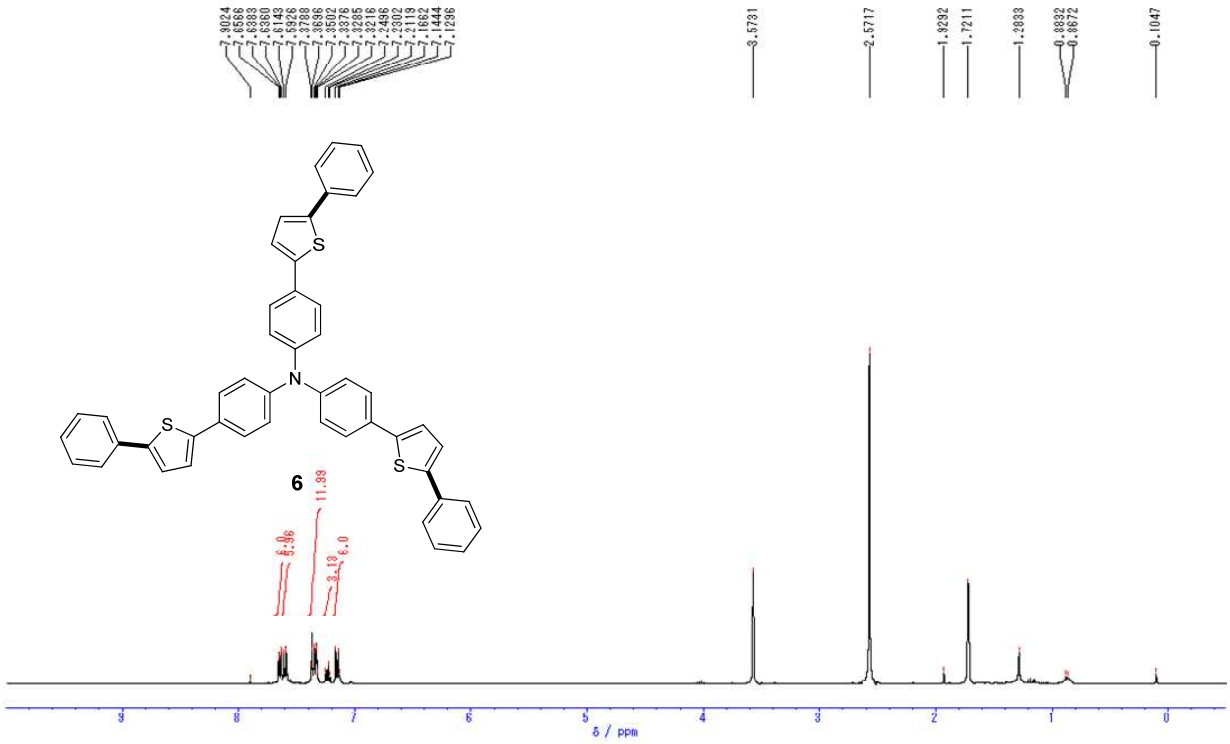
77.0000
76.6840
24.7848
Bpin
S
N
Bpin
S
S
Bpin
δ / ppm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7.8383
7.6360
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7.5926
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7.3502
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7.3285
7.3216
7.2486
7.2302
7.2119
7.1932
7.1744
7.1236
3.5731
2.5717
1.9232
1.7211
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0.8832
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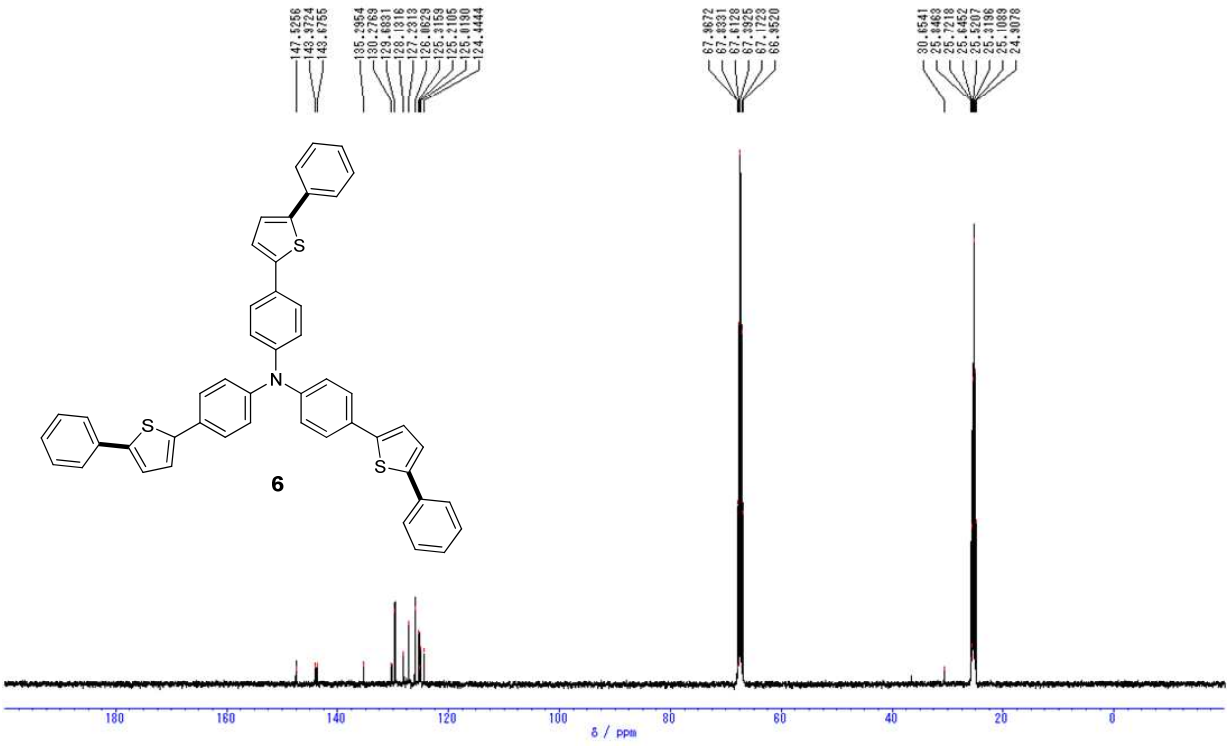
0.1047
6
11.39
5.96
6.0
3.13
δ / ppm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126.8629
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126.2105
125.8190
124.4444
67.4672
67.2831
67.0128
66.7925
66.7723
66.5920
30.6541
25.8463
25.7218
25.6452
25.5207
25.3196
25.1089
24.9078
6
δ / ppm

10. Reference

[1] M. Waki, Y. Maegawa, K. Hara, Y. Goto, S. Shirai, Y. Yamada, N. Mizoshita, T. Tani, W.-J. Chun, S. Muratsugu, M. Tada, A. Fukuoka and S. Inagaki, *J. Am. Chem. Soc.* **2014**, *136*, 4003-4011.