Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Rhenium-Catalyzed Dehydrogenative Borylation of Primary and Secondary C(sp^3)–H Bonds Adjacent to a Nitrogen Atom

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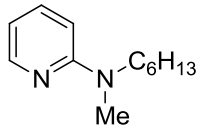
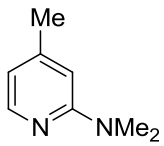
General Methods. All reactions were carried out in dry solvent under an argon atmosphere. Unless otherwise noted, other chemicals obtained from commercial suppliers were used without further purification. 1,2-Dichloroethane was purchased from Wako Pure Chemical Industries and was dried by the usual methods, distilled, and degassed with an argon gas for 20 min before use. $Re_2(CO)_{10}$ was purchased from Sigma-Aldrich. $[ReBr(CO)_3(thf)]_2$ was synthesized by the reported method.[1] 2-(*N*,*N*-Dimethylamino)pyridine **1a** was purchased from Tokyo Chemical Industry CO. LTD. fine chemicals. Column chromatography was performed with silica gel 60N (neutral, 40-50 μm) purchased from Kanto Chemical. 9-BBN (9-borabicyclo[3.3.1]nonane) was purchased from Sigma-Aldrich and kept under the argon in the dark. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{11}B (130 MHz) NMR spectra were recorded on a JEOL JNN-LA400 or Varian 400 MR or Varian 300 MR spectrometer. Proton chemical shifts are reported in ppm based on the solvent resonance resulting from incomplete deuteration ($CDCl_3$ at 7.26 ppm) as the internal standard. ^{13}C NMR was recorded with complete proton decoupling and the chemical shifts are reported relative to $CDCl_3$ at 77.00 ppm. Boron chemical shifts are reported relative to BF_3-OEt_2 at 0.0 ppm in $CDCl_3$ as the external standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, quint: quintet, m: multiplet. IR spectra were recorded on a SHIMADZU IRAFFINITY-1 100V J. High-resolution mass spectra (HRMS) was measured with JEOL JMS-700 MStation FAB-MS. Melting points were measured on a Yanaco micromelting point apparatus and are uncorrected.

Procedure for the Synthesis of 2-Aminopyridine.

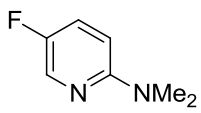


2-(*N*-Hexyl-*N*-methylamino)pyridine (1b). A solution of *N*-hexyl-*N*-methylamine (1.8 mL, 12 mmol) in THF (6.0 mL) was cooled to 0 ^{o}C, and 1.6 M hexane solution of ^{n}BuLi (6.9 mL, 11 mmol) was added dropwise over 10 min.

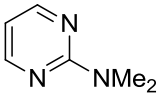
To a mixture of 2-fluoropyridine (0.86 mL, 10 mmol) in THF (6.0 mL) was added the above lithium amide solution at 0 ^{o}C. The resultant mixture was warmed to 25 ^{o}C gradually and stirred additionally for 12 h. The reaction mixture was quenched with H_2O (10 mL) and extracted with EtOAc for three times. The combined organic layer was dried over $MgSO_4$, and then the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane and ethyl acetate as eluents to afford 2-(*N*-hexyl-*N*-methylamino)pyridine **1b** (1.88 g, 9.8 mmol, 98% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ0.88 (t, *J* = 6.8 Hz, 3H), 1.27-1.34 (m, 6H), 1.57 (quint, *J* = 7.2 Hz, 2H), 3.03 (s, 3H), 3.47 (t, *J* = 7.2 Hz, 3H), 6.45 (d, *J* = 8.0 Hz, 1H), 6.47 (dd, *J* = 4.8, 6.8 Hz, 1H), 7.39 (dt, *J* = 2.0, 8.0 Hz, 1H), 8.14 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ14.0, 22.6, 26.7, 27.1, 31.7, 36.2. 50.2, 105.6, 111.0, 137.0, 147.9, 158.5. IR (neat / cm^{-1}): 3009, 2955, 2928, 2857, 1597, 1558, 1504, 1472, 1421, 1373, 1319, 1277, 1219, 1159, 1094, 982, 768, 731. HRMS (FAB^{+}): calcd for $C_{12}H_{20}N_2$ ($[M]^{+}$) 192.1626; found. 192.1603.



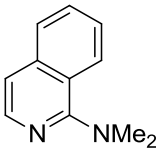
2-(*N*,*N*-Dimethylamino)-4-methylpyridine (**1c**)**:** This compound was prepared by the reported procedure.[2] A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ8.03 (d, *J* = 5.2 Hz, 1H), 6.39 (d, *J* = 4.8 Hz, 1H), 6.33 (s, 1H), 3.07 (s, 6H), 2.26 (s, 3H). The analytical data match those reported in the literature (*Chem. Commun.* **2008**, 5779).



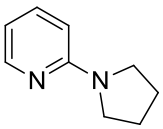
2-(*N*,*N*-Dimethylamino)-5-fluoropyridine (1d): This compound was prepared by the reported procedure.[2] A pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ3.02 (s, 6H), 6.42 (dd, *J* = 2.8, 8.0 Hz, 1H), 7.18 (dd, *J* = 2.8, 8.0 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H). The analytical data match those reported in the literature (*Chem. Asian J.* 2013, **8**, 2970).



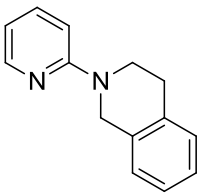
2-(*N*,*N*-Dimethylamino)pyrimidine (1e): This compound was prepared by the reported procedure.[2] A colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ3.08 (s, 6H), 6.34 (t, *J* = 4.8 Hz, 1H), 8.20 (d, *J* = 4.8 Hz, 2H). The analytical data match those reported in the literature (*Chem. Asian J.* 2013, **8**, 2970).



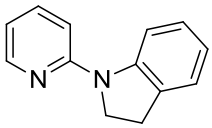
1-(*N*,*N*-Dimethylamino)isoquinoline (1f): This compound was prepared by the reported procedure.[2] A pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ3.10 (s, 6H), 7.16 (d, *J* = 6.8 Hz, 1H), 7.47 (t, *J* = 6.8 Hz, 1H), 7.58 (t, *J* = 6.8 Hz, 1H) 7.71 (d, *J* =8.0 Hz, 1H), 8.10 (d, *J* =8.0 Hz, 1H), 8.12 (d, *J* =8.0 Hz, 1H). The analytical data match those reported in the literature (*Chem. Asian J.* 2013, **8**, 2970).



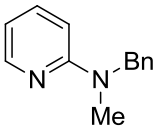
2-(Pyrrolidino)pyridine (1g): This compound was prepared by the reported procedure.[3] A pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ2.00-2.03 (m, 4H), 3.45-3.47 (m, 4H), 6.36 (d, *J* = 8.8 Hz, 1H), 6.51 (t, *J* = 6.8 Hz, 1H), 7.43 (dt, *J* = 2.0, 8.8 Hz, 1H), 8.16 (d, *J* = 4.8 Hz, 1H). The analytical data match those reported in the literature (*Org. Lett.* 2003, **5**, 3867).



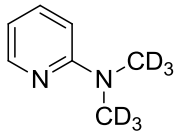
***N*-(2-Pyridinyl)-1,2,3,4-tetrahydroisoquinoline (1i):** This compound was prepared according to the similar procedure reported in the literature.[3] An orange oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ2.98 (t, J = 6.0 Hz, 2H), 3.85 (t, *J* = 6.0 Hz, 2H), 4.71 (s, 2H), 6.60 (dd, *J* = 5.2, 6.8 Hz, 1H), 6.68 (d, *J* = 8.8 Hz, 1H), 7.18-7.21 (m, 4H), 7.50 (dt, *J* = 2.0, 8.8 Hz, 1H), 8.23 (d, *J* = 4.8 Hz, 1H). The analytical data match those reported in the literature (*J. Am. Chem. Soc.* 2001, **123**, 10935.).



***N*-(1-Pyridinyl)-2,3-dihydro-1*H*-indole (3):** This compound was prepared according to the similar procedure reported in the literature.[3] A colorless solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.19 (t, J = 8.8 Hz, 2H), 4.02 (t, J = 8.8 Hz, 2H), 6.75 (d, J = 7.6 Hz, 1H), 6.76 (d, J = 8.8 Hz, 1H), 6.85 (t, J = 6.8 Hz, 1H), 7.15-7.18 (m, 2H), 7.56 (dt, J = 2.0, 6.8 Hz, 1H), 8.18 (d, J = 7.6 Hz, 1H), 8.34 (d, J = 4.0 Hz, 1H). The analytical data match those reported in the literature (*J. Am. Chem. Soc.* 2001, **123**, 10935).



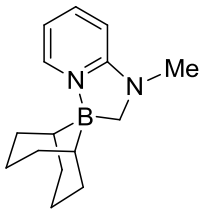
2-(*N*-Benzyl-*N*-methylamino)pyridine (5): This compound was prepared by the reported procedure.[2] A pare yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.09 (s, 3H), 4.81 (s, 2H), 6.52 (d, J = 8.8 Hz, 1H), 6.57 (dd, J = 4.8, 6.8 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 7.28-7.33 (m, 3H), 7.44 (dt, J = 2.0, 7.8 Hz, 1H), 8.19 (d, J = 4.0 Hz, 1H). The analytical data match those reported in the literature (*Eur. J. Org. Chem.* 2009, 4586).



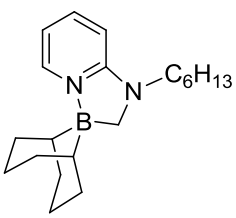
[D$_6$]2-(*N*,*N*-Dimethylamino)pyridine (1a-d_6): A solution of 2-amino-pyridine (565 mg, 6.0 mmol) in THF (10 mL) was cooled to 0 ^{o}C, and 1.6 M hexane solution of ^{n}BuLi (4.1 mL, 6.6 mmol) was added dropwise over 10 min. To a mixture of [D_3]methyl *p*-toluenesulphonate[4] (2.27 g, 12 mmol) in THF (2.0 mL) was added the above lithium amide solution at -78 ^{o}C. The resultant mixture was warmed to 25 ^{o}C gradually and stirred additionally for 12 h. The reaction mixture was quenched with H_2O (10 mL) and extracted with EtOAc for three times. The combined organic layer was dried over $MgSO_4$, and then the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel with hexane and ethyl acetate as eluents to afford [D_6]2-(*N*,*N*-dimethylamino)pyridine **1a**-d_6 (462 mg, 3.6 mmol, 60% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.49 (d, J = 8.4 Hz,

1H), 6.52 (t, J = 7.2 Hz, 1H), 7.43 (dt, J = 1.2, 7.2 Hz, 1H), 8.16 (d, J = 4.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ105.7, 111.3, 137.0, 147.8, 159.4. The analytical data match those reported in the literature (*Chem. Asian J.* 2013, **8**, 2970).

Rhenium-Catalyzed Dehydrogenative Borylation of C(sp^3)–H Bond. A flame dried sealed tube was charged with $[ReBr(CO)_3(thf)]_2$ (10.6 mg, 0.0125 mmol), 2-aminopyridine (0.25 mmol), 9-BBN (42.7 mg, 0.175 mmol), and toluene (2.5 mL), and the resulting mixture was stirred at 125 ^{o}C or 150 ^{o}C. After 24 h, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography on silica gel with hexane / benzene / Et_3N = 1 / 1 / 0.025 as eluents to afford the corresponding borylated compounds **2**, **5**, and **7**, respectively.

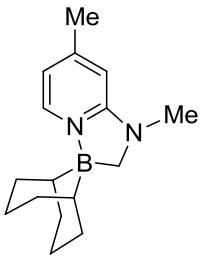


[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)-*N*-methyl]pyridin-2-ylamine (2a): A colorless crystal; mp 155.4-156.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (br, 2H), 1.36-1.43 (m, 1H), 1.66-1.73 (m, 7H), 1.78-1.86 (m, 1H), 1.93-2.06 (m, 3H), 2.65 (s, 2H), 2.96 (s, 3H), 6.31 (d, J = 8.8 Hz, 1H), 6.36 (t, J = 6.8 Hz, 1H), 7.43 (dt, J = 1.6, 8.0 Hz, 1H); 8.19 (d, J = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ24.0, 24.6, 29.7, 33.1, 35.9, 104.8, 108.4, 139.3, 143.0, 158.3. ^{11}B NMR (130 MHz, $CDCl_3$): δ -1.69. IR (KBr / cm^{-1}): 2916, 2835, 1638, 1545, 1458, 1420, 1290, 1240, 1196, 1157, 1141, 1105, 1031, 962, 907, 764, 735, 669, 582, 548, 527. HRMS (FAB$^+$): calcd for $C_{15}H_{23}BN_2$ ([M]$^+$) 242.1954; found. 242.1928.

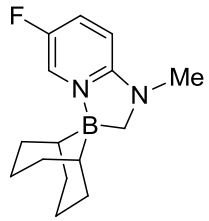


[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)-*N*-hexyl]pyridin-2-ylamine (2b): A colorless solid; mp 56.5-57.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ0.52 (br, 2H), 0.73-0.82 (m, 3H), 1.10-1.26 (m, 6H), 1.26-1.35 (m, 2H), 1.42-1.67 (m, 8H), 1.67-1.80 (m, 1H), 1.80-2.00 (m, 3H), 2.52 (s, 2H),

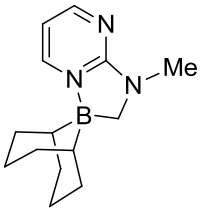
3.13 (t, J = 6.2 Hz, 2H), 6.21 (d, J = 7.2 Hz, 2H); 7.25-7.29 (m, 1H), 8.07 (d, J = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ14.0, 22.6, 24.1, 24.6, 26.4, 26.5, 29.7, 31.6, 33.2, 48.4, 104.9, 108.1, 139.1, 143.0, 157.8. ^{11}B NMR (130 MHz, $CDCl_3$): δ-1.64. IR (KBr / cm^{-1}): 3090, 2918, 2839, 2654, 1634, 1545, 1447, 1371, 1288, 1238, 1198, 1161, 1107, 1038, 968, 908, 827, 758, 677, 527. HRMS (FAB$^+$): calcd for $C_{20}H_{33}BN_2$ ([M]$^+$) 312.2737; found. 312.2739.



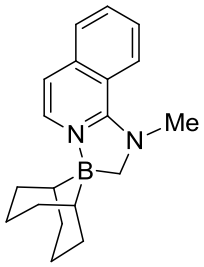
[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)-4-methylpyridin-2-yl]-*N*-methylamine (2c): A colorless crystal; mp 156.9-157.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.59 (br, 2H), 1.36-1.43 (m, 1H), 1.64-1.74 (m, 7H), 1.80-1.87 (m, 1H), 1.93-2.05 (m, 3H), 2.23 (s, 3H), 2.63 (s, 2H), 2.94 (s, 3H), 6.11 (s, 1H), 6.21 (dd, J = 1.6, 6.4 Hz, 1H), 8.05 (d, J = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ21.5, 24.1, 24.7, 29.8, 33.2, 35.9, 104.5, 110.4, 142.1, 151.0, 158.5. IR (KBr / cm^{-1}): 2912, 2838, 1633, 1545, 1448, 1241, 1194, 1160, 1108, 1031, 964, 908, 757, 672, 554, 527. HRMS (FAB$^+$): calcd for $C_{16}H_{25}BN_2$ ([M]$^+$) 256.2111; found. 256.2089.



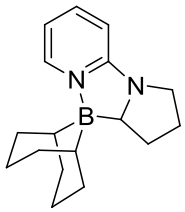
[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)-5-fluoropyridin-2-yl]-*N*-methylamine (2d): A pale yellow crystal; mp 110.1-111.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ0.63 (br, 2H), 1.35-1.43 (m, 1H), 1.61-2.15 (m, 11H), 2.67 (s, 2H), 2.96 (s, 3H), 6.25 (dd, J = 4.4, 9.6 Hz, 1H), 7.31 (dt, J = 2.4, 7.2 Hz, 1H), 8.11 (t, J = 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ23.8, 24.5, 29.5, 32.9, 36.3, 104.6 (d, J_{CF} = 5.3 Hz), 128.6 (d, J_{CF} = 21.6 Hz), 130.0 (d, J_{CF} = 32.7), 149.9 (d, J_{CF} = 232.1 Hz), 156.0. ^{11}B NMR (130 MHz, $CDCl_3$): δ-0.94. IR (KBr / cm^{-1}): 2913, 2857, 1653, 1560, 1449, 1410, 1389, 1275, 1240, 1107, 1036, 962, 893, 797, 735, 586, 557, 527. HRMS (FAB$^+$): calcd for $C_{15}H_{22}BFN_2$ ([M]$^+$) 260.1860; found. 260.1862.



[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)-*N*-methyl]pyrimidin-2-yl amine (2e): A yellow solid; mp 111.2-112.1 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62 (br, 2H), 1.36-1.43 (m, 1H), 1.60-1.70 (m, 6H), 1.70-1.90 (m, 4H), 1.93-2.10 (m, 1H), 2.64 (s, 2H), 3.12 (s, 3H), 6.34 (t, J = 6.0 Hz, 1H), 8.29 (dd, J = 2.2, 6.0 Hz, 1H), 8.39 (dd, J = 2.2, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 24.4, 29.4, 32.3, 34.7, 105.7, 152.0, 161.1. ^{11}B NMR (130 MHz, $CDCl_3$): δ -3.14. IR (KBr / cm^{-1}): 2918, 2868, 2839, 1626, 1549, 1443, 1408, 1381, 1294, 1248, 1227, 1200, 1105, 1028, 962, 907, 833, 777, 738, 675, 586, 529. HRMS (FAB^{+}): calcd for $C_{14}H_{22}BN_3$ ([M]$^{+}$) 243.1907; found. 243.1892.

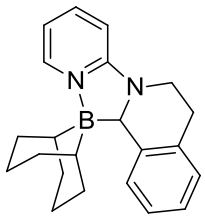


[*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)isoquinolin-1-yl]-*N*-methyl amine (2f): A colorless solid; mp 183.2-184.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.64 (br, 2H), 1.25 (br, 1H), 1.38-1.45 (m, 1H), 1.62-1.79 (m, 6H), 1.79-1.93 (m, 1H), 1.98-2.12 (m, 3H), 2.90 (s, 2H), 3.63 (s, 3H), 6.68 (d, J = 6.8 Hz, 1H), 7.39 (dt, J = 6.4 Hz, 1H), 7.57-7.62 (m, 2H), 8.02 (d, J = 6.4 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 24.6, 29.9, 33.4, 42.8, 108.0, 117.8, 125.2, 126.2, 126.8, 131.2, 135.8, 139.0. ^{11}B NMR (130 MHz, $CDCl_3$): δ -2.97. IR (KBr / cm^{-1}): 2913, 2843, 1740, 1628, 1560, 1450, 1435, 1408, 1356, 1339, 1248, 1196, 1144, 1101, 1034, 910, 887, 866, 787, 739, 679, 633, 569. HRMS (FAB^{+}): calcd for $C_{19}H_{25}BN_2$ ([M]$^{+}$) 292.2111; found. 292.2085.

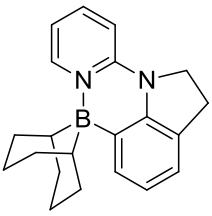


2-[2-(9-Borabicyclo[3.3.1]non-9-yl)pyrrolidin-1-yl]pyridine (2g): A colorless crystal; mp 117.5-118.2 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.55 (br, 1H), 0.83 (br, 1H), 1.25-1.40 (m, 1H), 1.40-1.57 (m, 1H), 1.57-1.68 (m, 1H), 1.68-1.81 (m, 5H), 1.81-1.99 (m, 5H), 1.99-2.08 (m, 1H), 2.08-2.19 (m, 2H), 2.96 (dd, J = 4.6 Hz, 1H), 3.14 (dq, J = 8.0 Hz, 1H), 3.42 (dt, J = 9.6 Hz, 1H), 6.45 (d,

J = 7.2 Hz, 1H), 6.49 (dt, *J* = 2.4, 7.2 Hz, 1H), 7.47 (dt, *J* = 2.4, 7.8 Hz, 1H), 8.21 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 24.7, 27.5, 28.4, 29.3, 30.3, 32.6, 34.6, 48.3, 107.6, 110.3, 139.3, 143.0, 159.8. ^{11}B NMR (130 MHz, $CDCl_3$): δ -0.35. IR (KBr / cm^{-1}): 2949, 1951, 1902, 1639, 1533, 1450, 1402, 1331, 1298, 1248, 1194, 1152, 1105, 1035, 943, 901, 883, 833, 797, 758, 739, 675, 646, 623, 569, 530. HRMS (FAB^+): calcd for $C_{17}H_{25}BN_2$ ($[M]^+$) 268.2111; found. 268.2096.

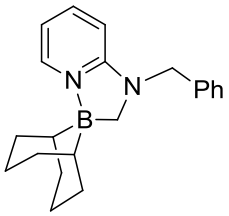


1-[(9-Borabicyclo[3.3.1]non-9-yl)-2-pyridin-2-yl]-1,2,3,4-tetrahydro isoquinoline (2i): A colorless solid; mp 158.2-159.0 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.56 (br, 1H), 1.39-1.50 (m, 1H), 1.50-1.62 (m, 2H), 1.62-1.80 (m, 3H), 1.80-2.17 (m, 6H), 2.21-2.32 (m, 1H), 3.01 (t, *J* = 6.4 Hz, 2H), 3.35 (dt, *J* = 7.2, 11.6 Hz, 1H), 3.70 (dt, *J* = 5.6, 11.6 Hz, 1H), 4.11 (s, 1H), 6.40 (d, *J* = 8.8 Hz, 1H), 6.46 (t, *J* = 6.6 Hz 1H), 7.08-7.19 (m, 3H), 7.45 (dt, *J* = 7.0 Hz, 1H), 7.68 (d, *J* = 7.2 Hz, 1H), 8.27 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.4, 24.7, 28.4, 29.7, 30.7, 31.9, 35.8, 43.8, 105.7, 109.6, 125.2, 125.9, 126.7, 127.5, 136.7, 139.3, 142.8, 143.7, 157.5. ^{11}B NMR (130 MHz, $CDCl_3$): δ 0.20. IR (KBr / cm^{-1}): 2918, 2880, 1633, 1558, 1519, 1471, 1365, 1288, 1269, 1213, 1159, 1103, 1067, 1034, 995, 970, 920, 899, 862, 833, 806, 758, 743, 679, 644, 623, 604, 557, 525. HRMS (FAB^+): calcd for $C_{22}H_{27}BN_2$ ($[M]^+$) 330.2267; found. 330.2257.



7-[(9-Borabicyclo[3.3.1]non-9-yl)-2-pyridin-2-yl]-2,3-dihydroindole (4): A yellow crystal; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (br, 2H), 1.39-1.49 (m, 2H), 1.52-1.68 (m, 6H), 1.83-1.97 (m, 2H), 2.04-2.11 (m, 2H), 3.36 (t, *J* = 8.0 Hz, 2H), 3.98 (t, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 8.0 Hz 1H), 6.92 (t, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 7.12 (t, *J* = 6.8 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 2H), 8.39 (d, *J* = 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8, 28.4, 31.3, 33.2, 48.0,

108.4, 113.4, 120.2, 124.0, 125.1, 130.7, 138.2, 143.9, 144.6, 153.0. ^{11}B NMR (130 MHz, $CDCl_3$): δ -2.48. IR (KBr / cm^{-1}): 2920, 2860, 2839, 1622, 1556, 1502, 1467, 1458, 1422, 1263, 1159, 1032, 953, 764. HRMS (FAB^+): calcd for $C_{21}H_{25}BN_2$ ($[M]^+$) 316.2111; found. 316.2111.



[*N*-benzyl-*N*-(9-Borabicyclo[3.3.1]non-9-ylmethyl)]pyridin-2-yl amine (6): A colorless crystal; mp 127.5-128.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.70 (br, 2H), 1.34-1.42 (m, 1H), 1.63-1.70 (m, 4H), 1.71-1.79 (m, 3H), 1.80-1.89 (m, 1H), 1.96-2.08 (m, 3H), 2.77 (s, 2H), 4.53 (s, 2H), 6.33 (d, *J* = 8.8 Hz, 1H), 6.41 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.22 (d, *J* = 6.8 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 2H), 7.39 (dt, *J* = 1.6, 8.8 Hz, 1H), 8.25 (d, *J* = 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.0, 24.6, 29.7, 33.1, 52.4, 105.1, 109.0, 126.7, 127.3, 128.8, 136.7, 139.5, 143.1, 158.2. ^{11}B NMR (130 MHz, $CDCl_3$): δ -1.44. IR (KBr / cm^{-1}): 2916, 2870, 2837, 1634, 1543, 1449, 1435, 1356, 1292, 1263, 1238, 1157, 1105, 1063, 1026, 947, 905, 802, 764, 729, 694, 529. HRMS (FAB^+): calcd for $C_{21}H_{27}BN_2$ ($[M]^+$) 318.2267; found. 318.2276.

References

1. (a) D. Vitali, F. Calderazzo, *Gazz. Chim. Ital.* 1972, **102**, 587. (b) S. Du, J. A. Kautz, T. D. McGrath, F. G. A. Stone, *Organometallics*, 2003, **22**, 2842.
2. T. Mita, K. Michigami, Y. Sato, *Chem. Asian J.* 2013, **8**, 2970.
3. L. Pasumansky, A. R. Hernández, S. Gamsey, C. T. Goralski, B. Singaram, *Tetrahedron Lett.* 2004, **45**, 6417.
4. (a) H. Oikawa, Y. Suzuki, K. Katayama, A. Naya, C. Sakano, A. Ichihara, *J. Chem. Soc., Perkin Trans. 1* 1999, 1225. (b) S.-r. Choi, M. Breugst, K. N. Houk, C. D. Poulter, *J. Org. Chem.* 2014, **79**, 3572.

X-ray Crystallographic Studies of N–B Coordinated Heterocycle 2d (CCDC 1035997)**:** Yellow crystal of N–B coordinated heterocycle **2d** suitable for X-ray analysis was obtained by recrystallization from Et_2O. All measurements were made on a Rigaku R-AXIS imaging plate area detector with multi-layer monochromated Mo-Kα radiation. Details of crystal and data collection parameters are summarized in Table S1. The positions of non-hydrogen atoms were determined by direct methods (SHELX97) and subsequent Fourier syntheses. An ORTEP drawing of **2d** is shown in Figure S1.

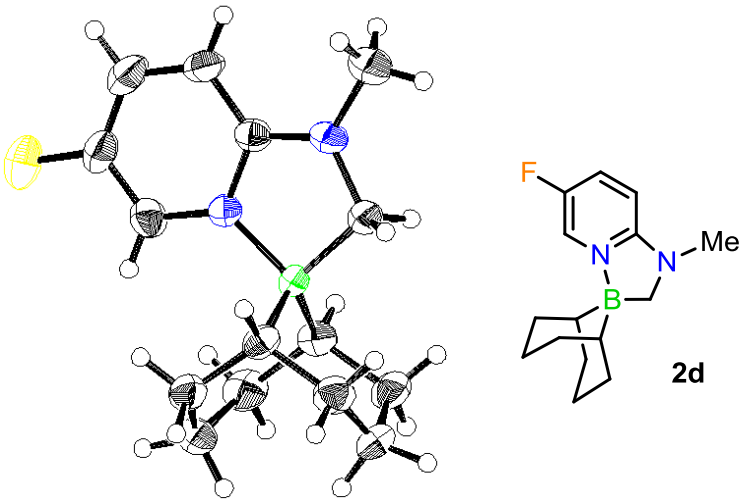


Figure S1. ORTEP drawing of N–B coordinated heterocycle **2d**. Thermal ellipsoids are drawn at the 50% probability level.

Table S1. Summary of Crystallographic Data of **2d**

Empirical formula: $C_{15}H_{22}BFN_2$
Formula weight: 260.16
Crystal system: triclinic
Space group: P-1 (#2)
Crystal color: yellow
Lattice parameters:
a (Å) = 7.486(7), b (Å) = 9.564(9), c (Å) = 10.597(11)
V (Å^3) = 700.8(12), β = 76.99(4)^o, Z = 2
D_{calc} (g cm^{-3}): 1.233
μ (Mo K α) (cm^{-1}): 0.809
Goodness of fit (GOF) = 1.218
F(000): 280.00
Diffractometer: Saturn724
Radiation: MoK α (λ = 0.71075 Å), Multi-layer Mirror Monochromated
Temp (^{o}C): 20
Scan type: ω–2 θ
Max. 2 θ (^{o}): 54.9
No. of reflections measured total: 11219
No. of observns (I > 3.00 σ (I)): 3173
Structure solution: Direct Methods (SHELX97)
Refinement: Full-Matrix Least-Squares on F^2
No. of variables: 172
Reflection/parameter ratio: 18.45
Residuals: R = 0.1194, wR2 = 0.1989
Max Shift/Error in Final Cycle: 0.000
Maximum peak in Final Diff Map (e (Å^{-3}): 0.23
Minimum peak in Final Diff Map (e (Å^{-3}): -0.26

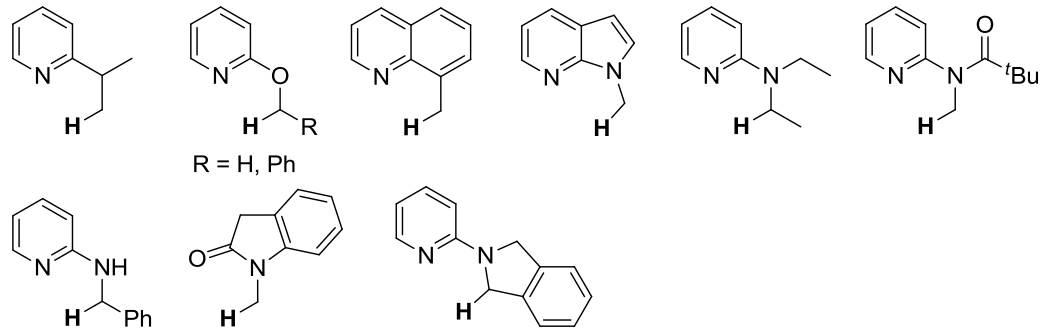


Figure S2. Ineffective substrates for the current catalytic reaction

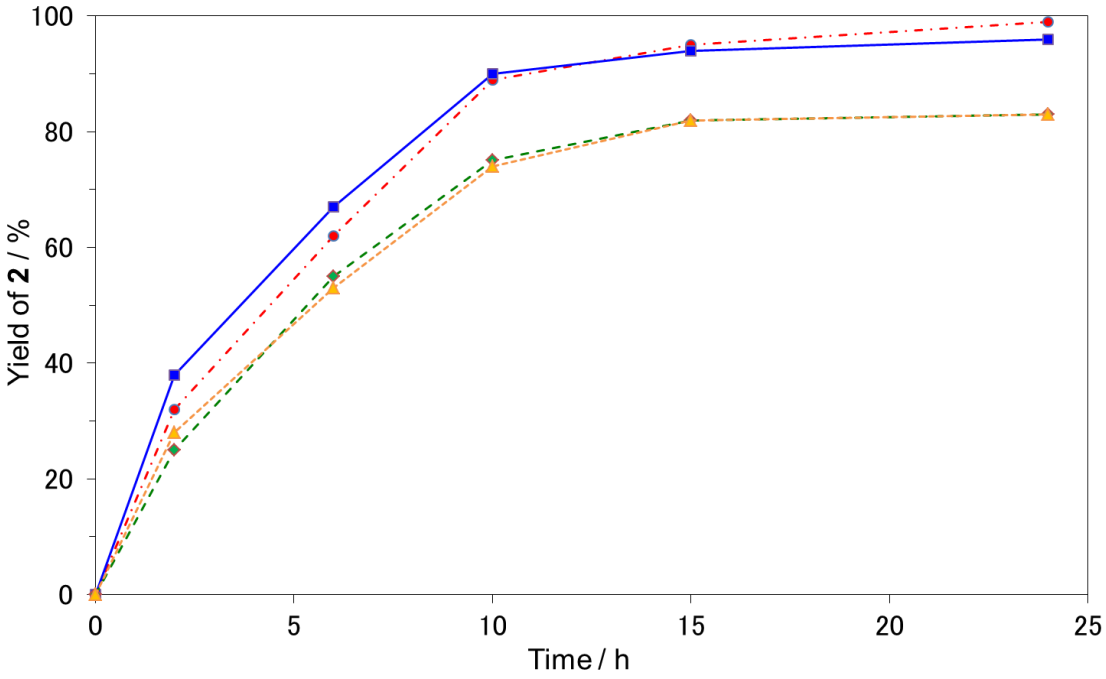


Figure S3. Time-course of the formation of **2a** (red), **2b** (blue), **2d** (green), **2g** (yellow)

^{11}B NMR Study for the Reaction of $[ReBr(CO)_3(thf)]_2$ with 9-BBN

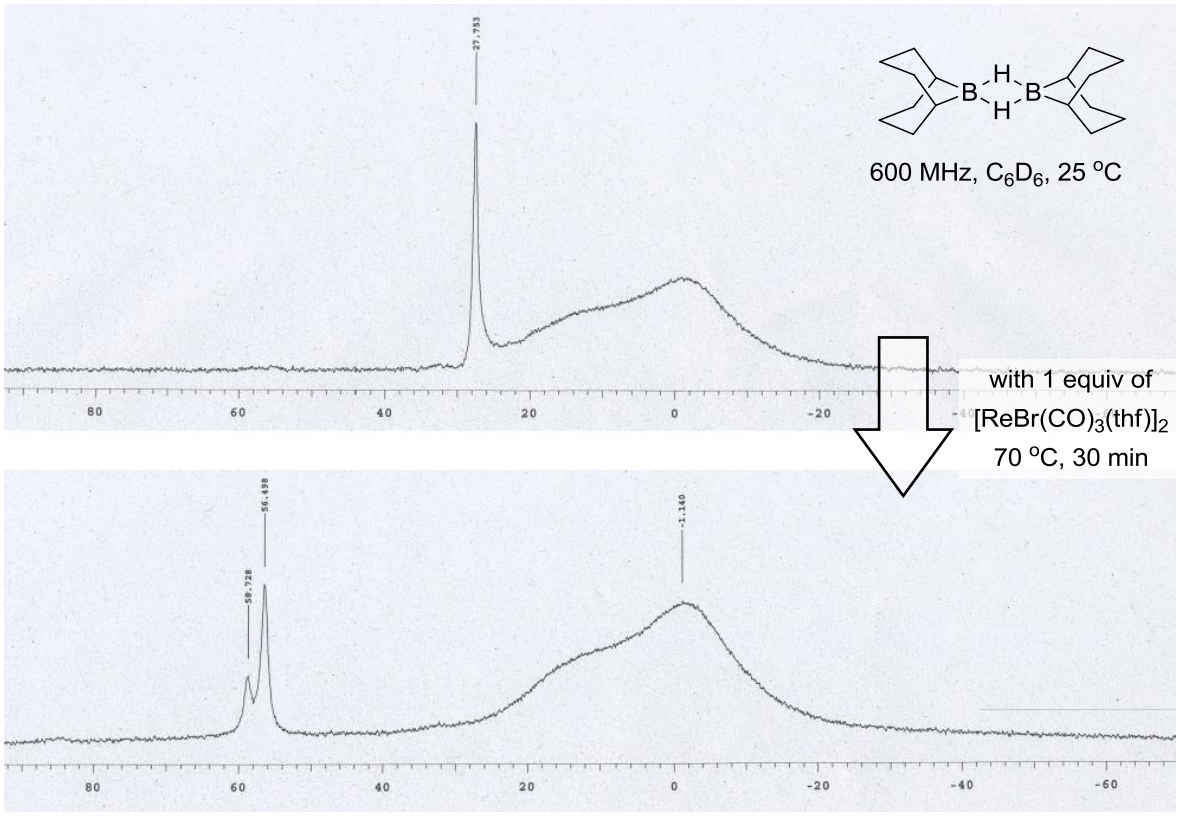
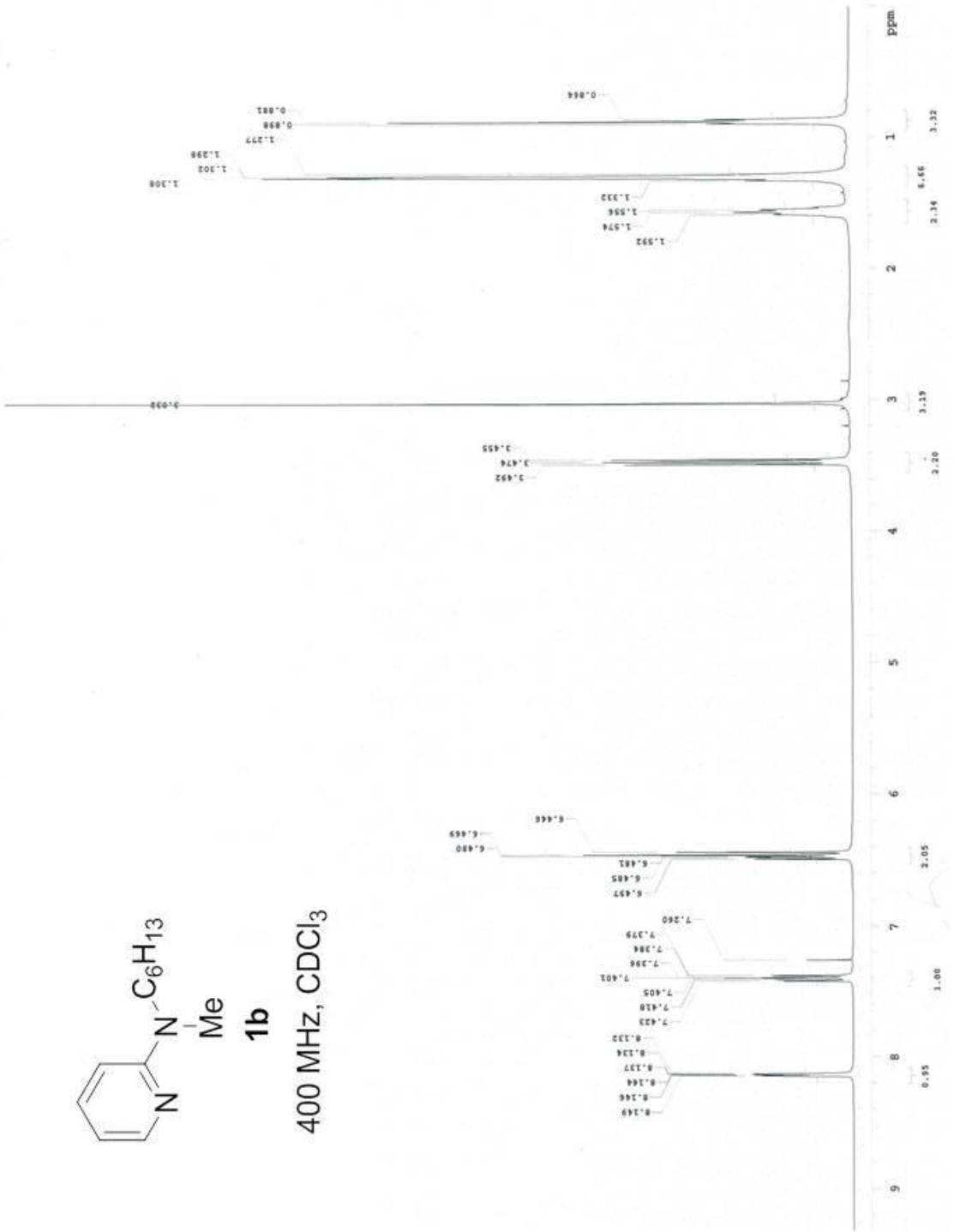
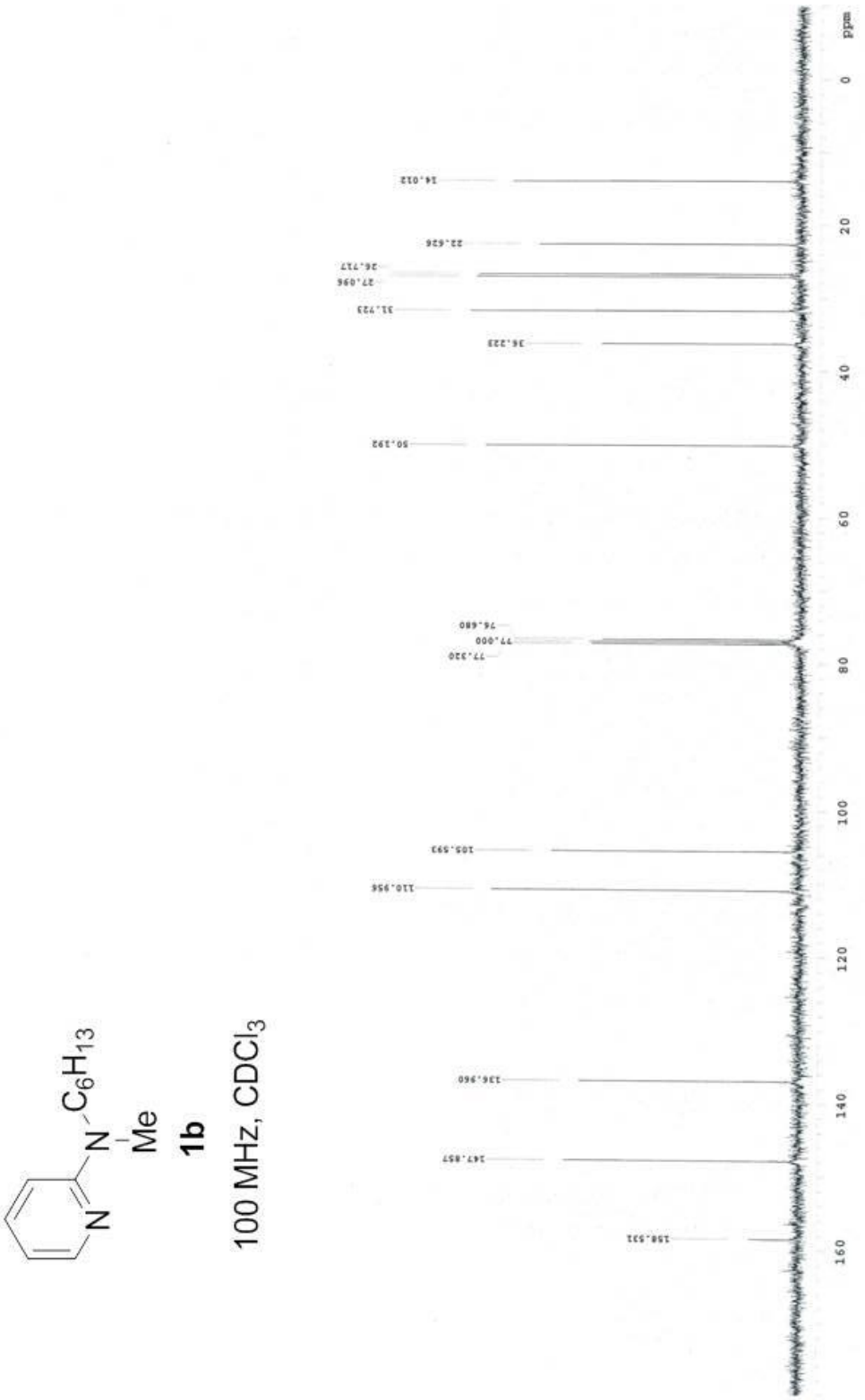


Figure S4. ^{11}B NMR study for the reaction of $[ReBr(CO)_3(thf)]_2$ with a stoichiometric amount of 9-BBN in C_6D_6 at 70 °C for 30 min

^{1}H NMR and ^{13}C NMR Spectra of Selected Compounds

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N
Me
N
1b
100 MHz, CDCl3
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26.727
27.096
31.723
36.323
50.392
76.680
77.000
77.320
105.593
110.956
136.960
147.857
158.531
ppm
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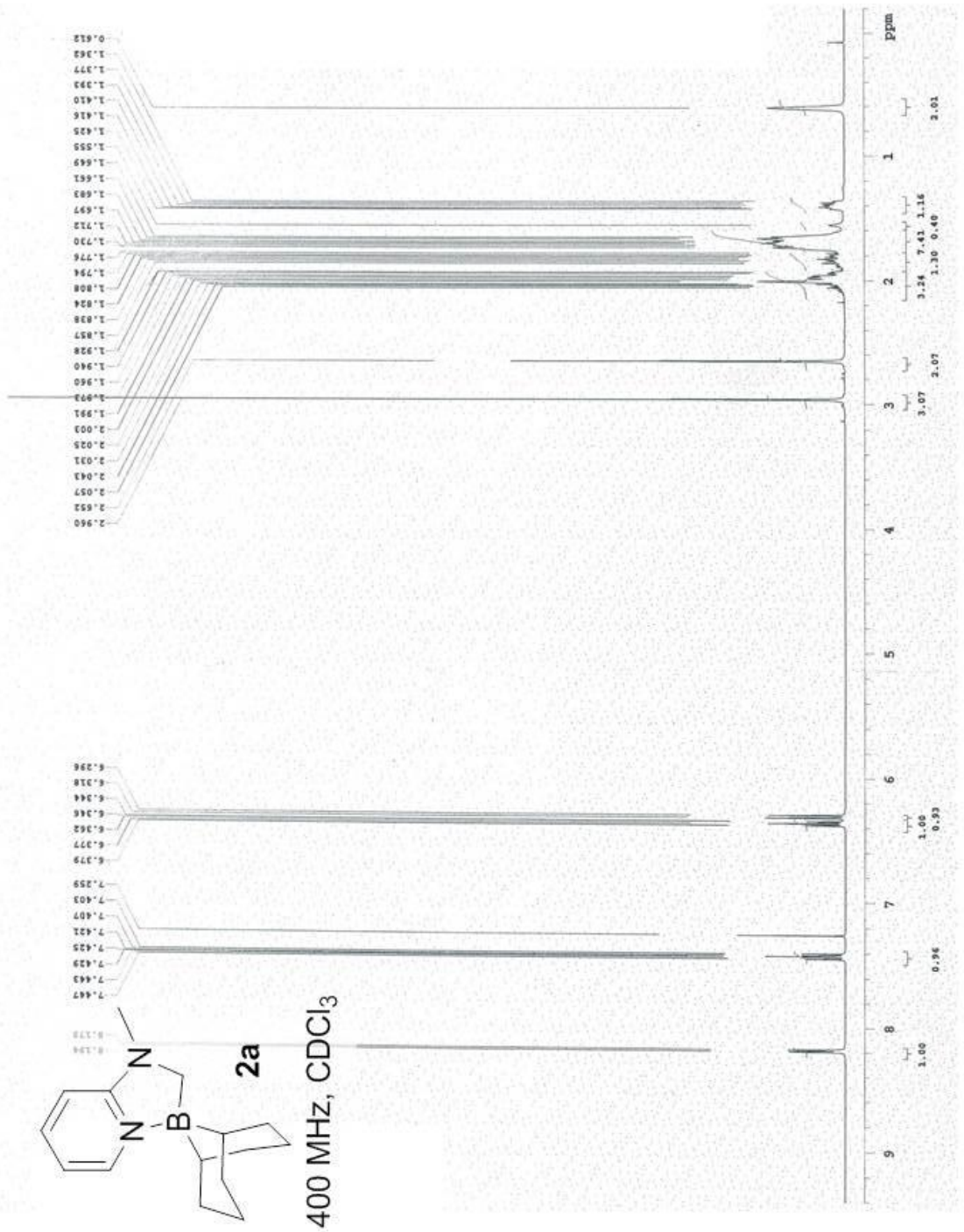
20
40
60
80
100
120
140
160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400 MHz, CDCl3
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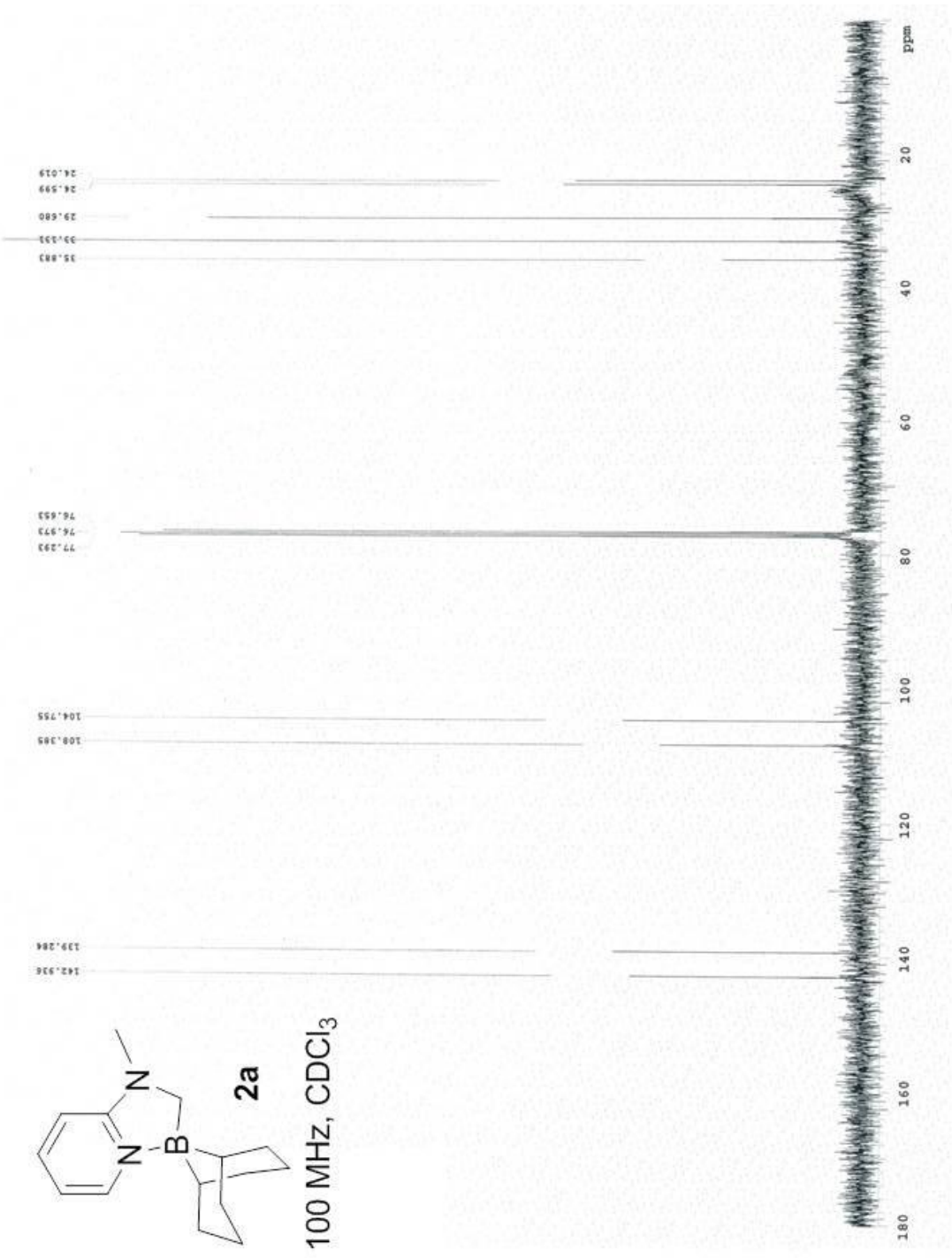
N
B
ppm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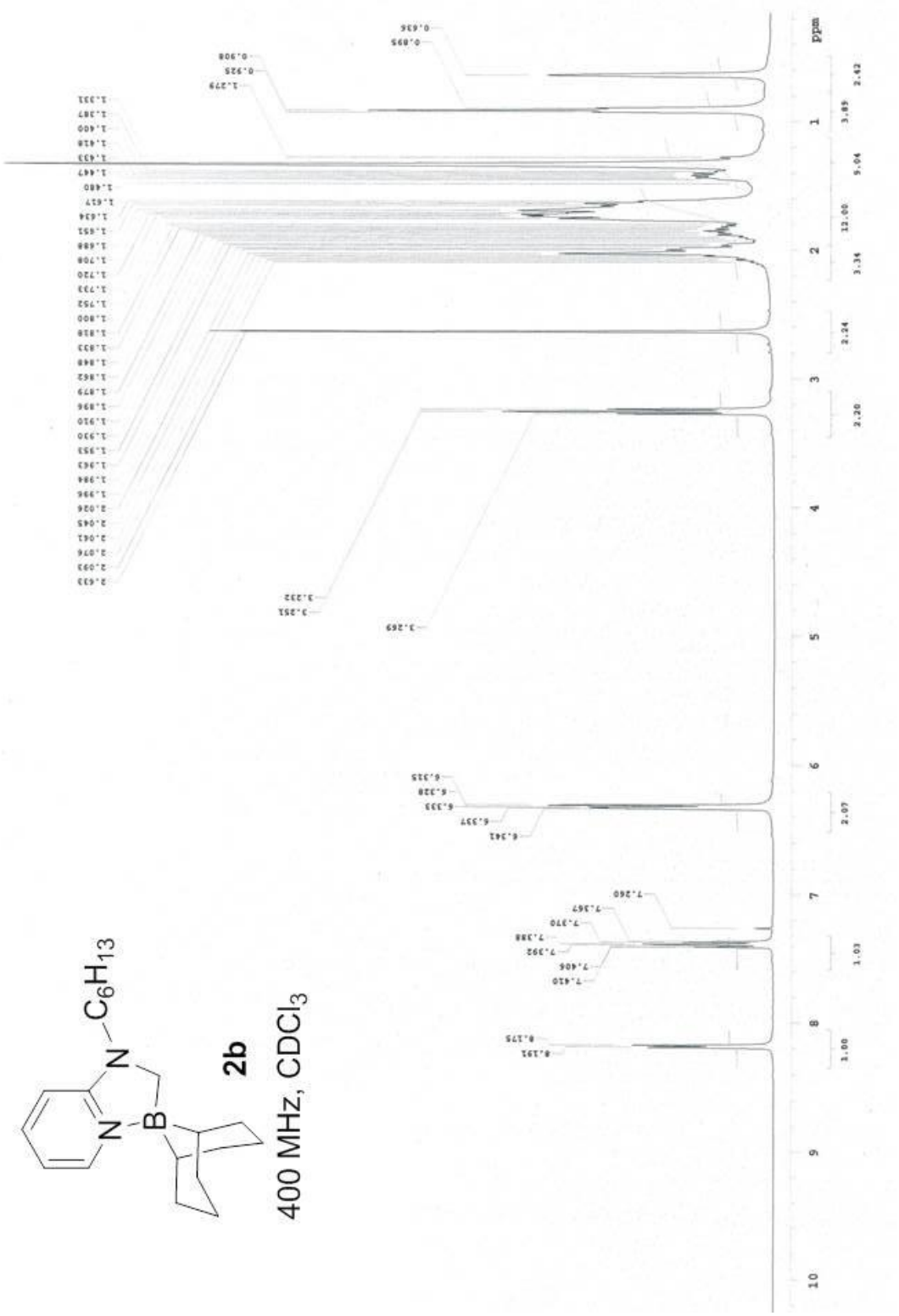
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B
2b
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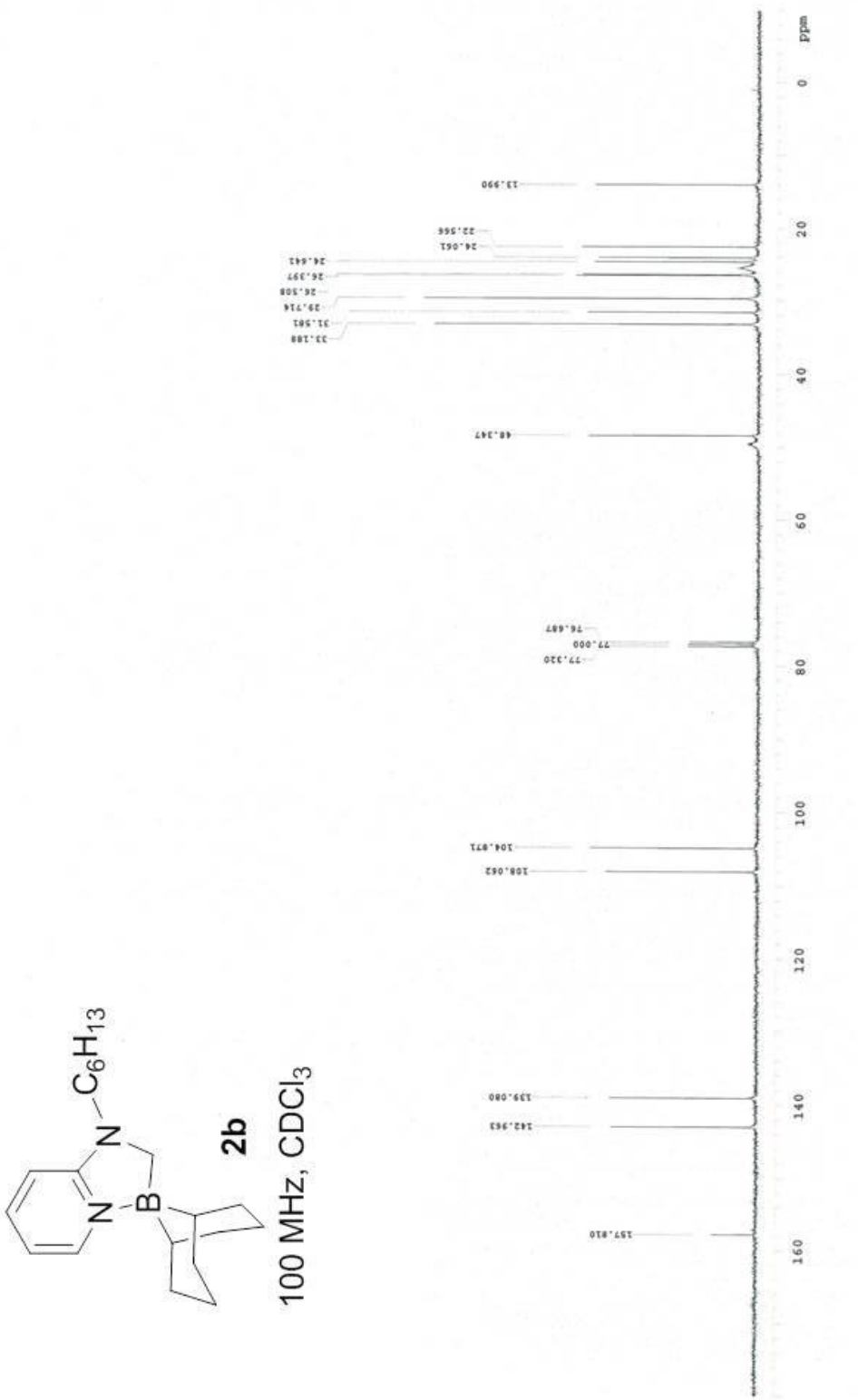
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48.347
76.687
77.000
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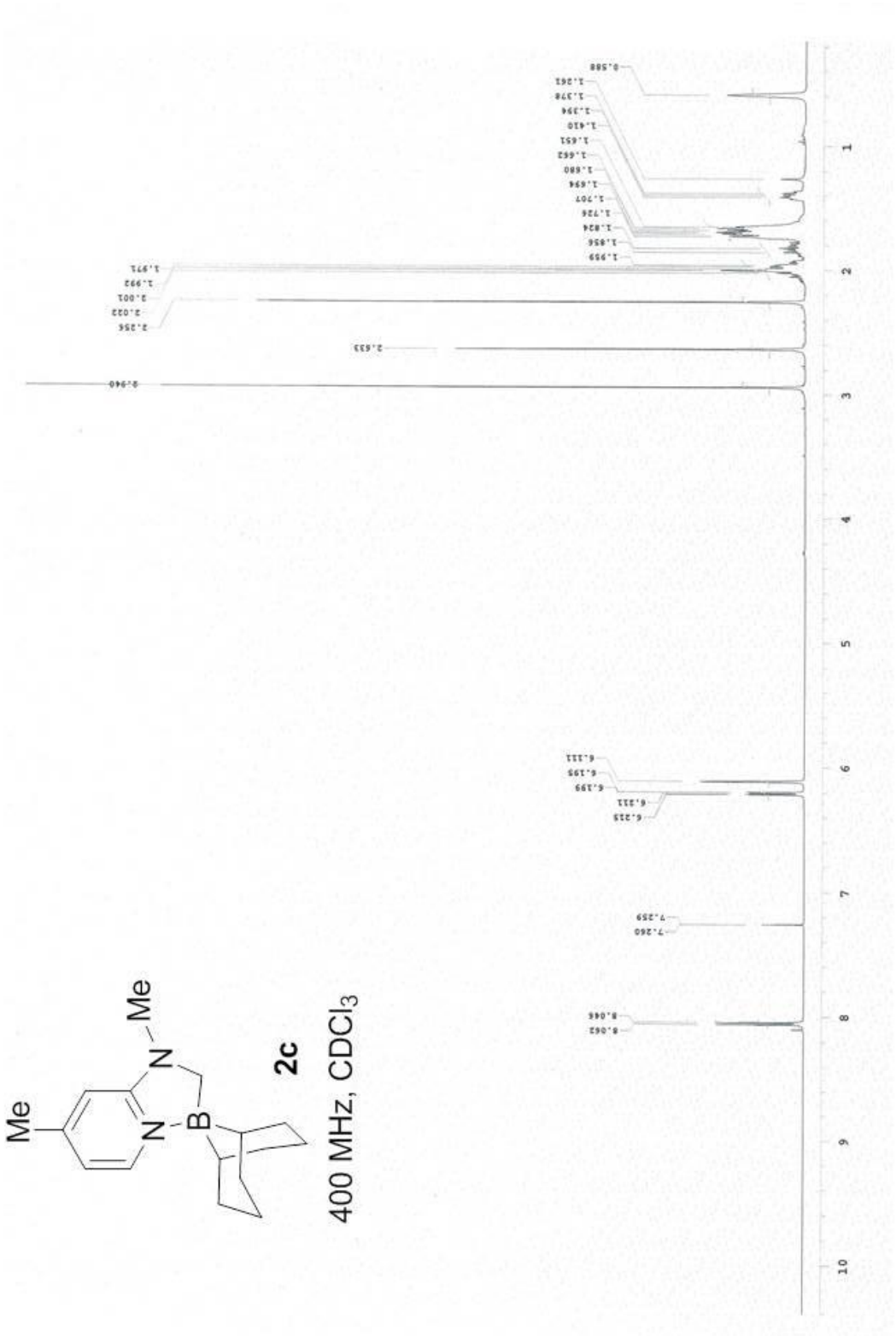
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Me
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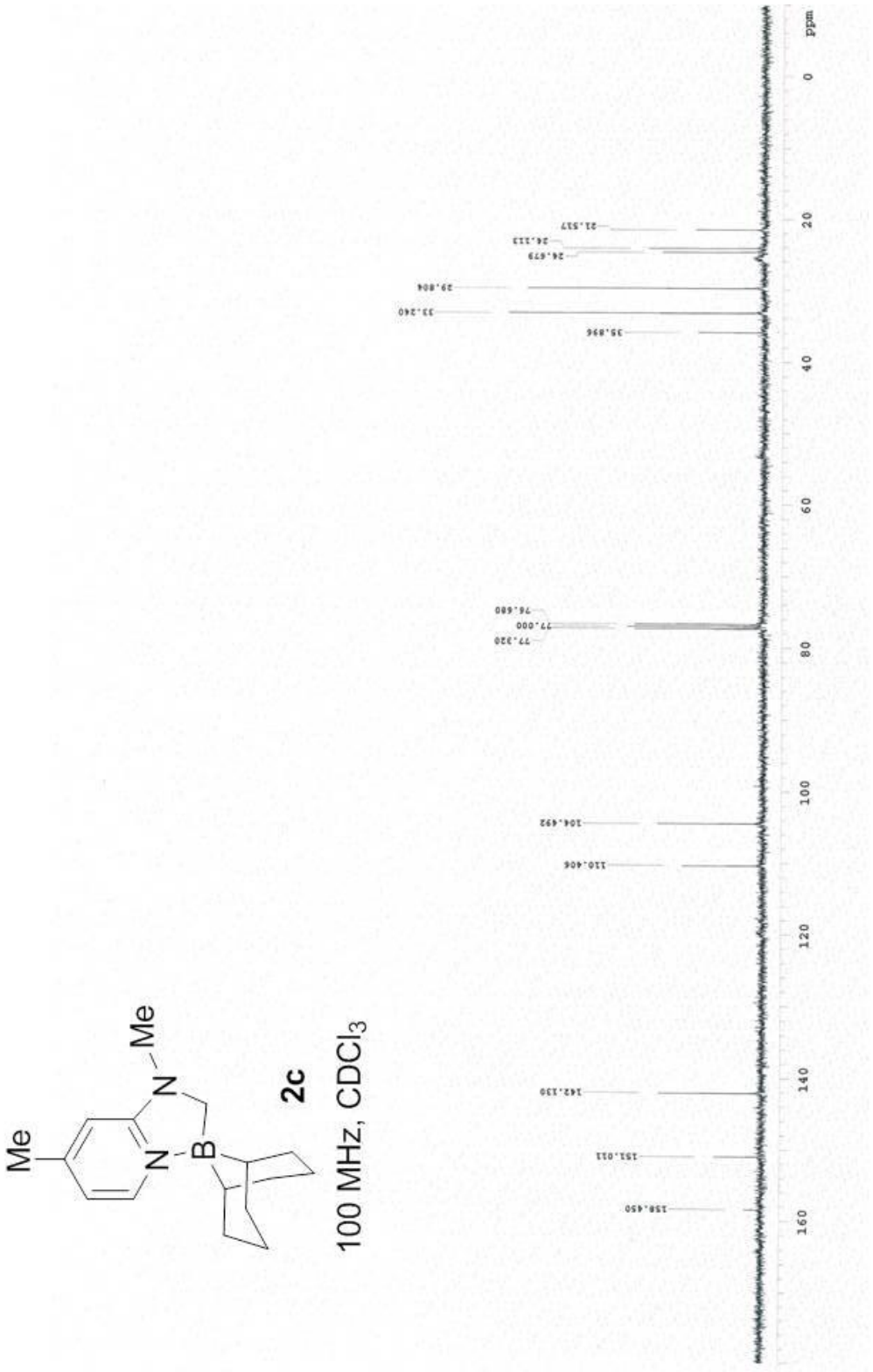
B
2c
400 MHz, CDCl3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Me
N
N
B
2c
100 MHz, CDCl3
ppm
0
20
40
60
80
100
120
140
160
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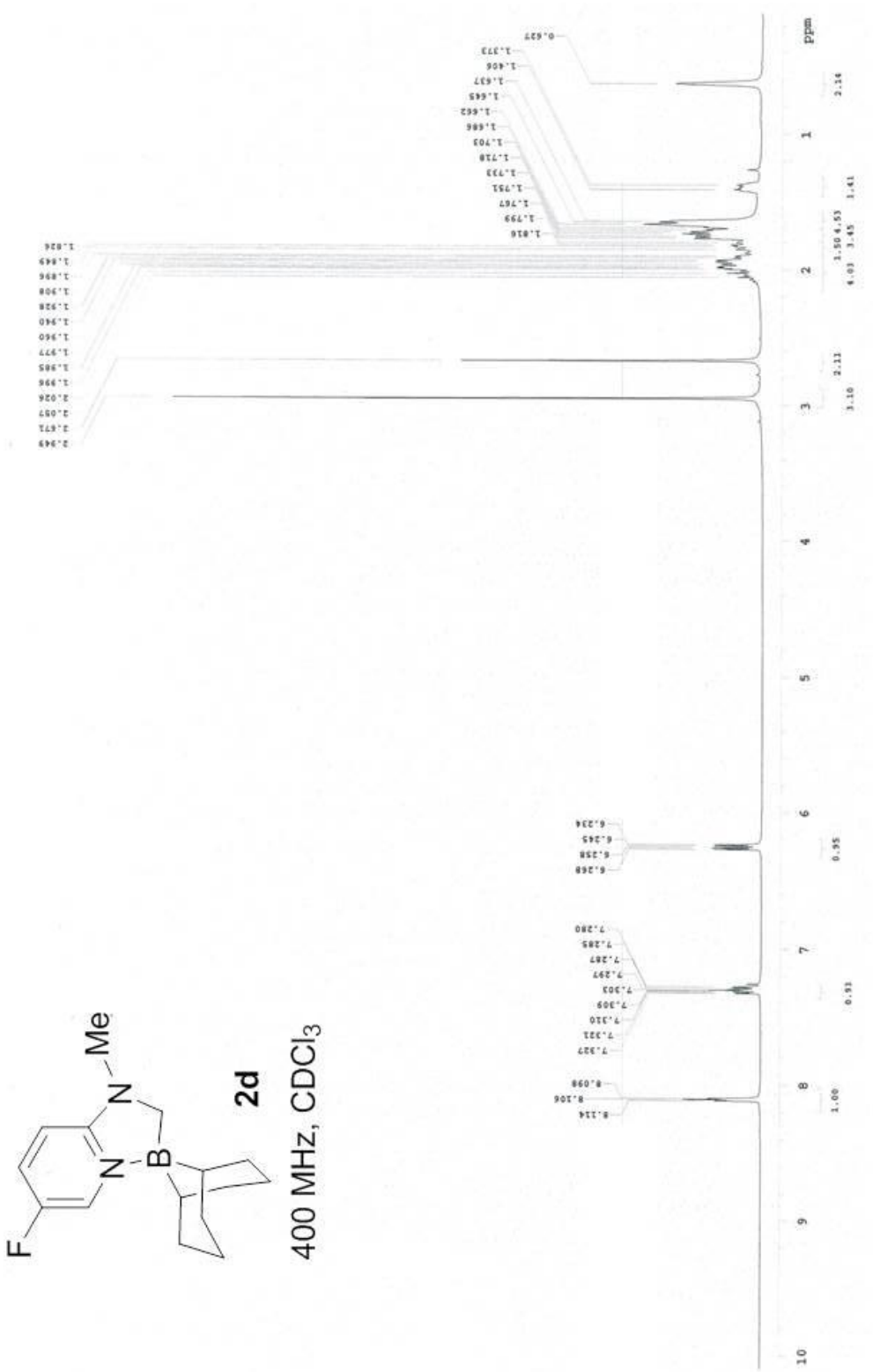
158.450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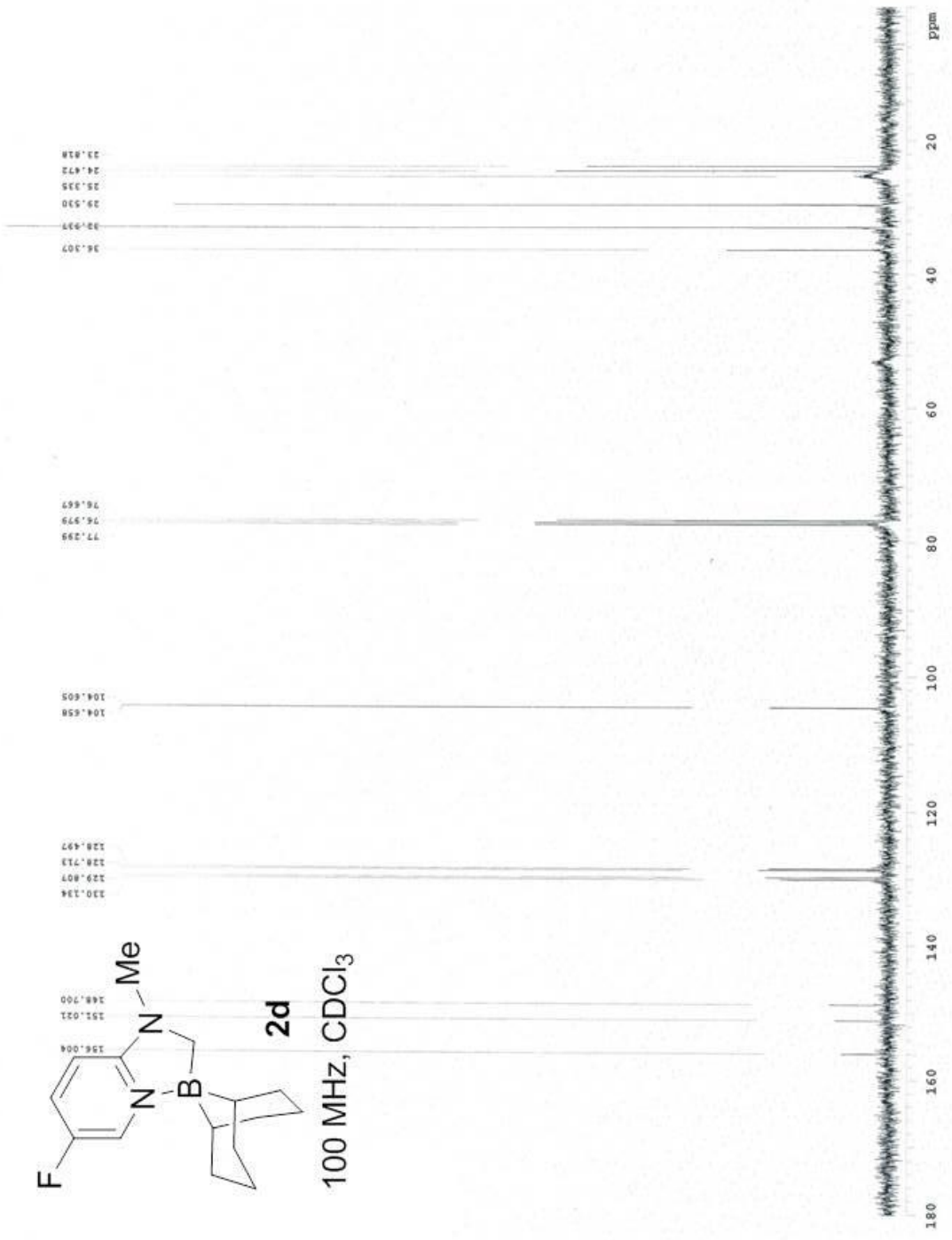
F
2d
400 MHz, CDCl3
ppm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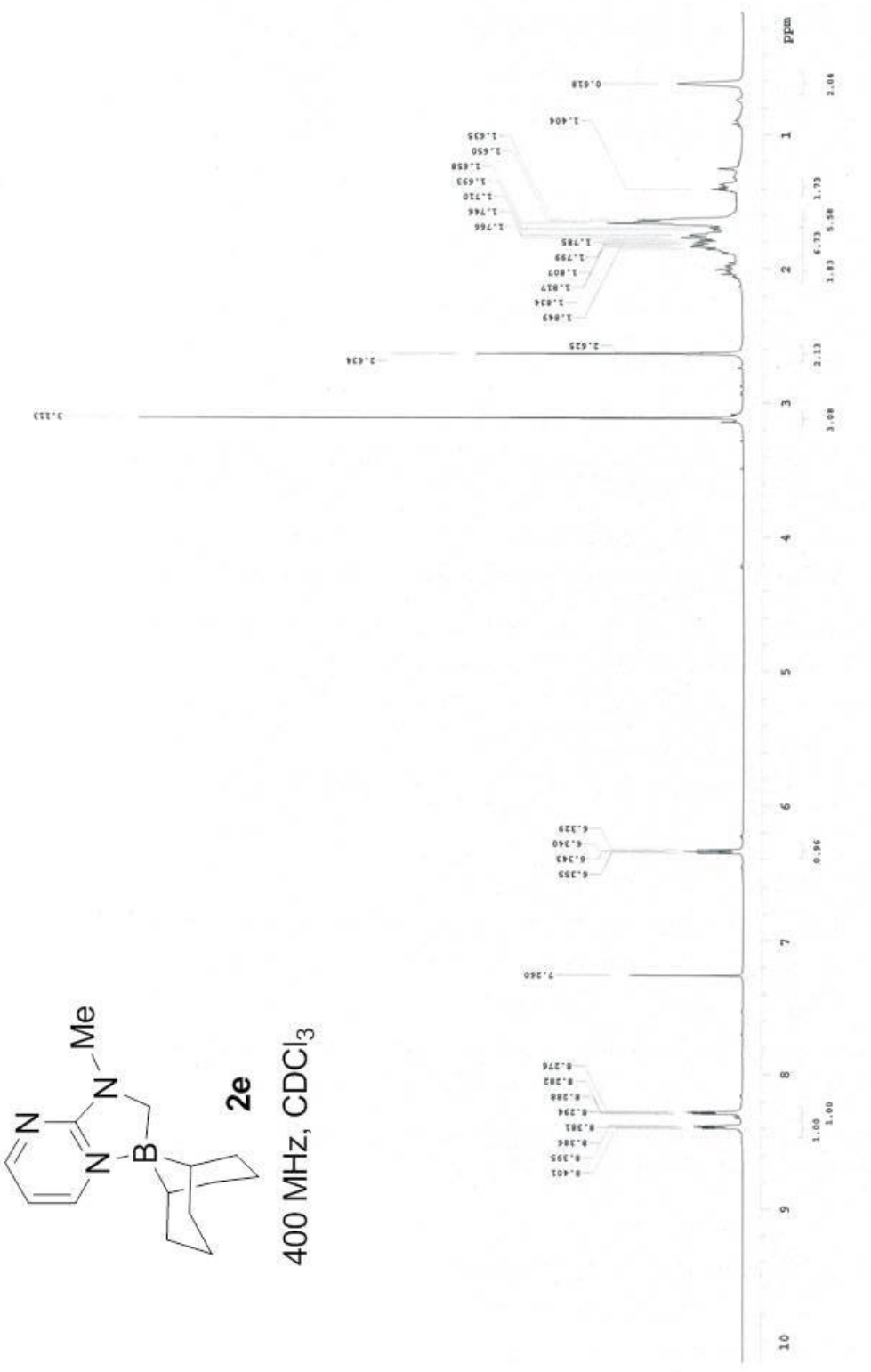
F
2d
100 MHz, CDCl3
ppm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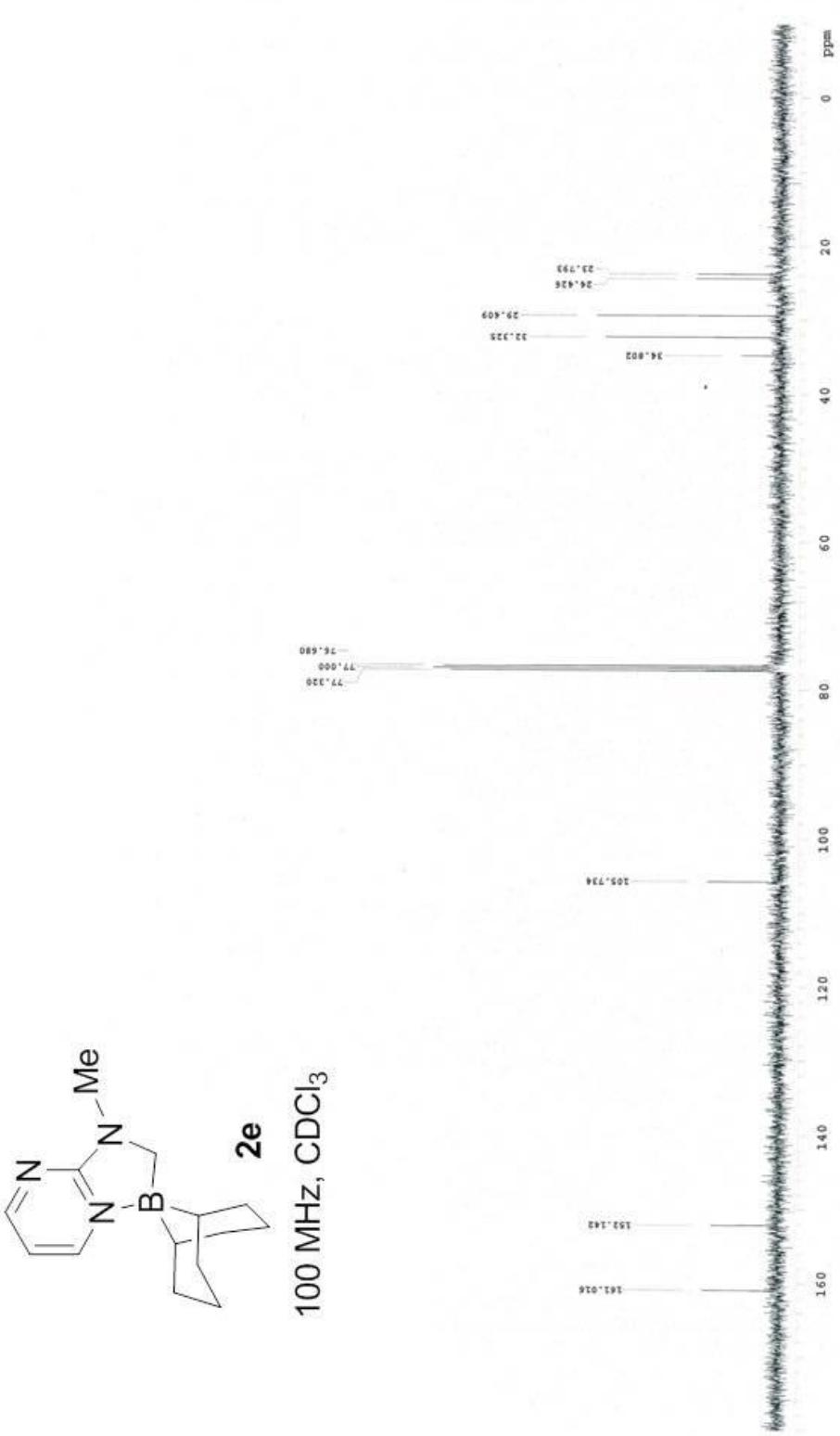
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77.320
105.734
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161.016
ppm
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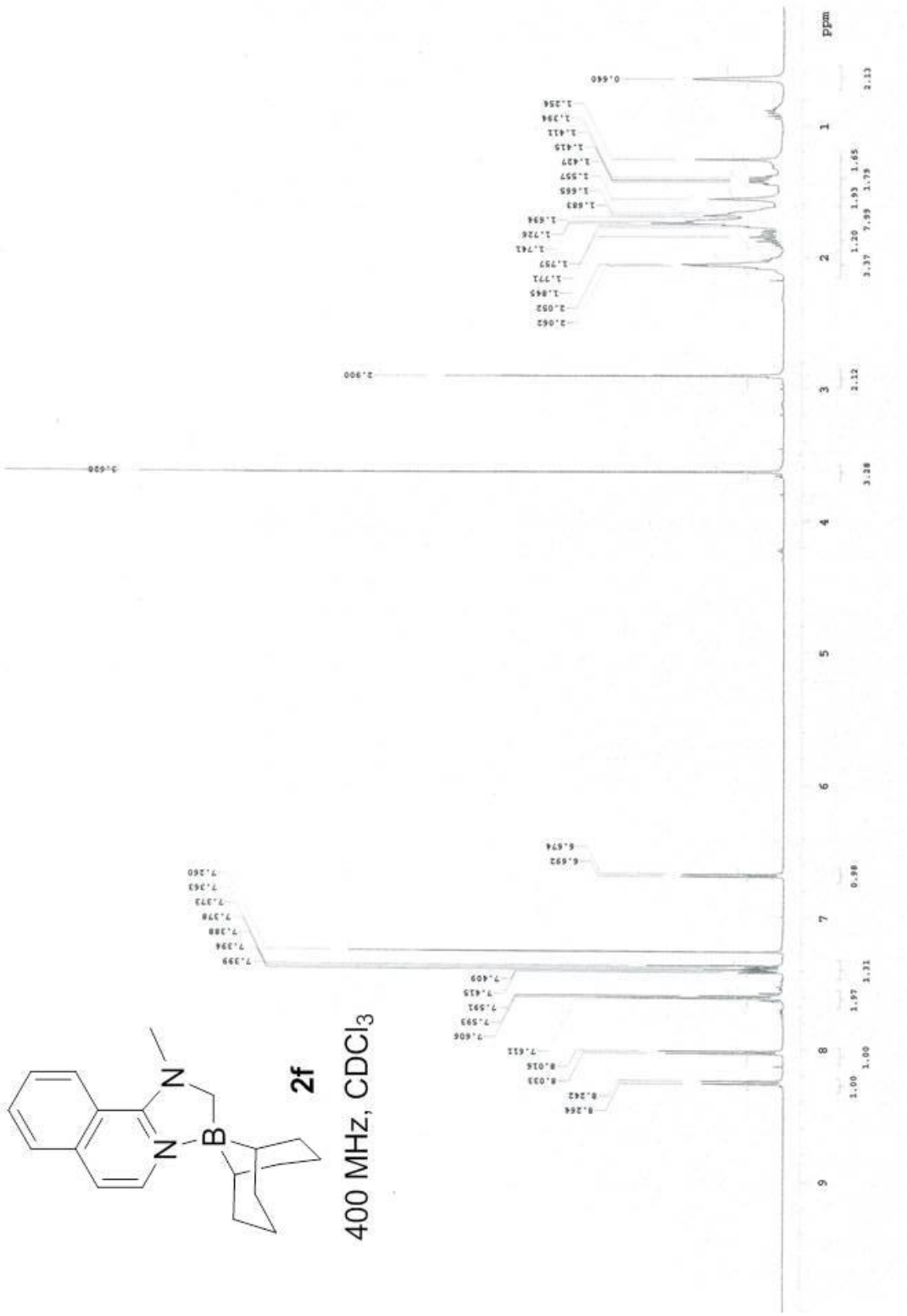
80
100
120
140
160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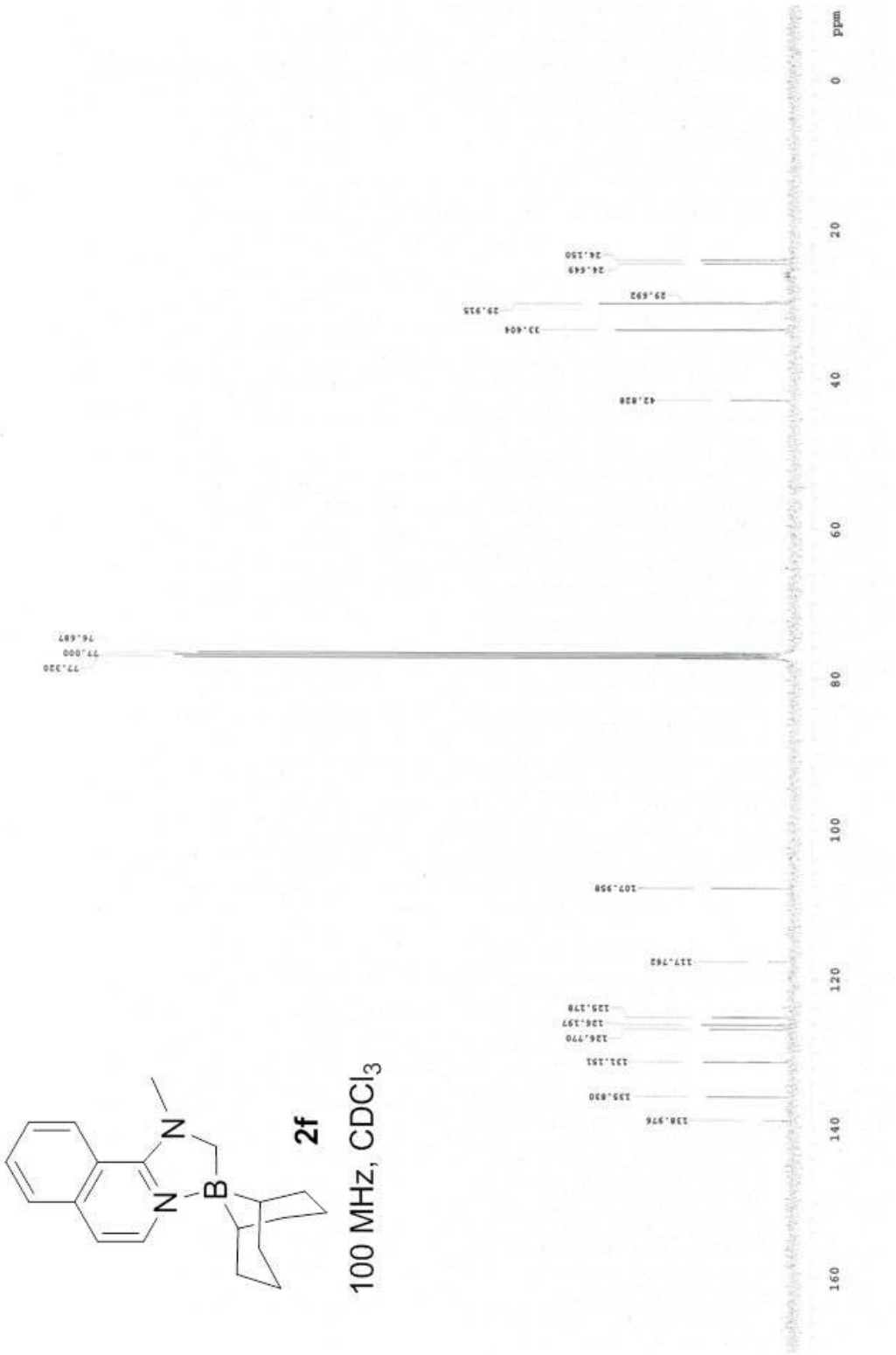
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20
40
60
80
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120
140
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33.404
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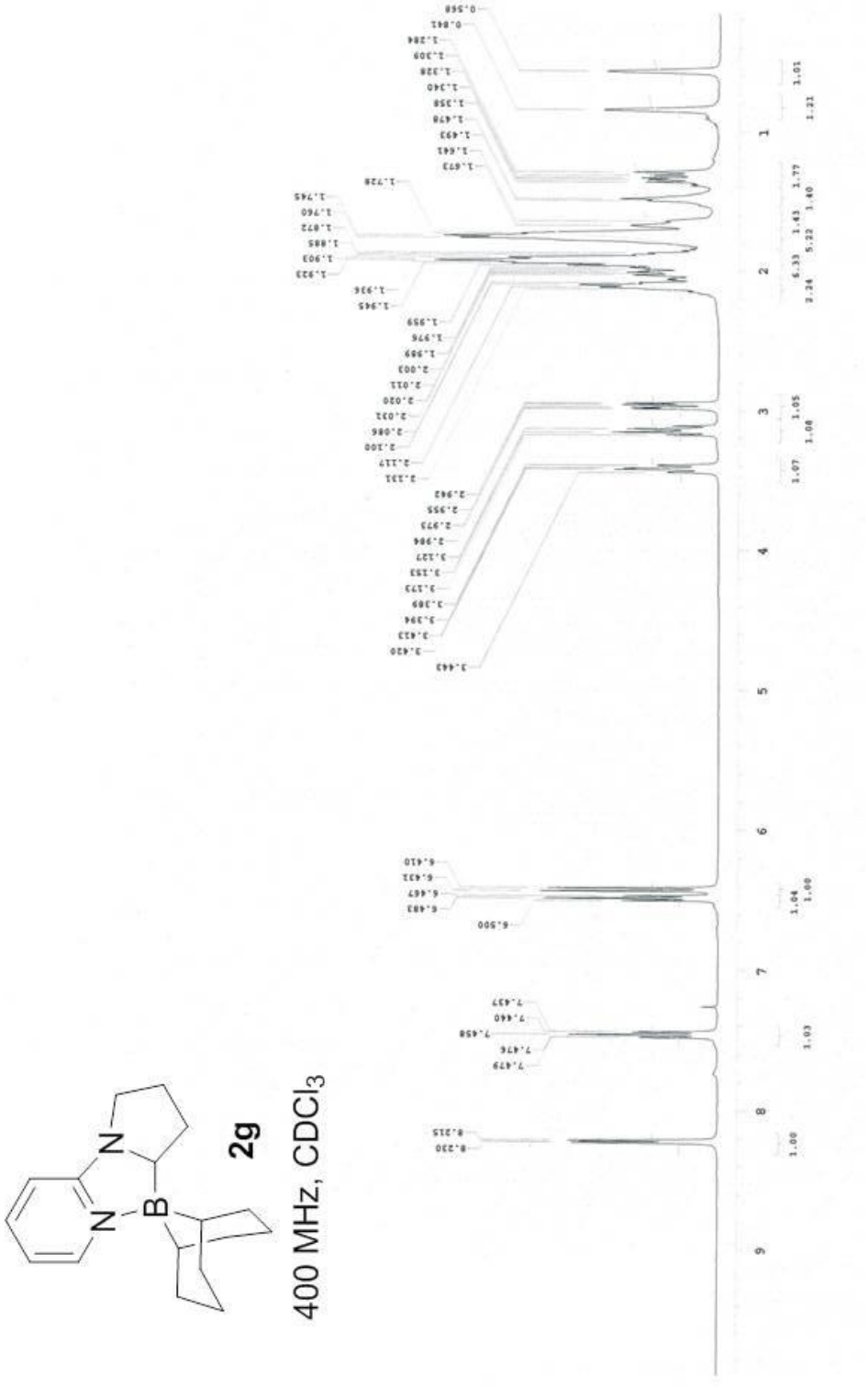
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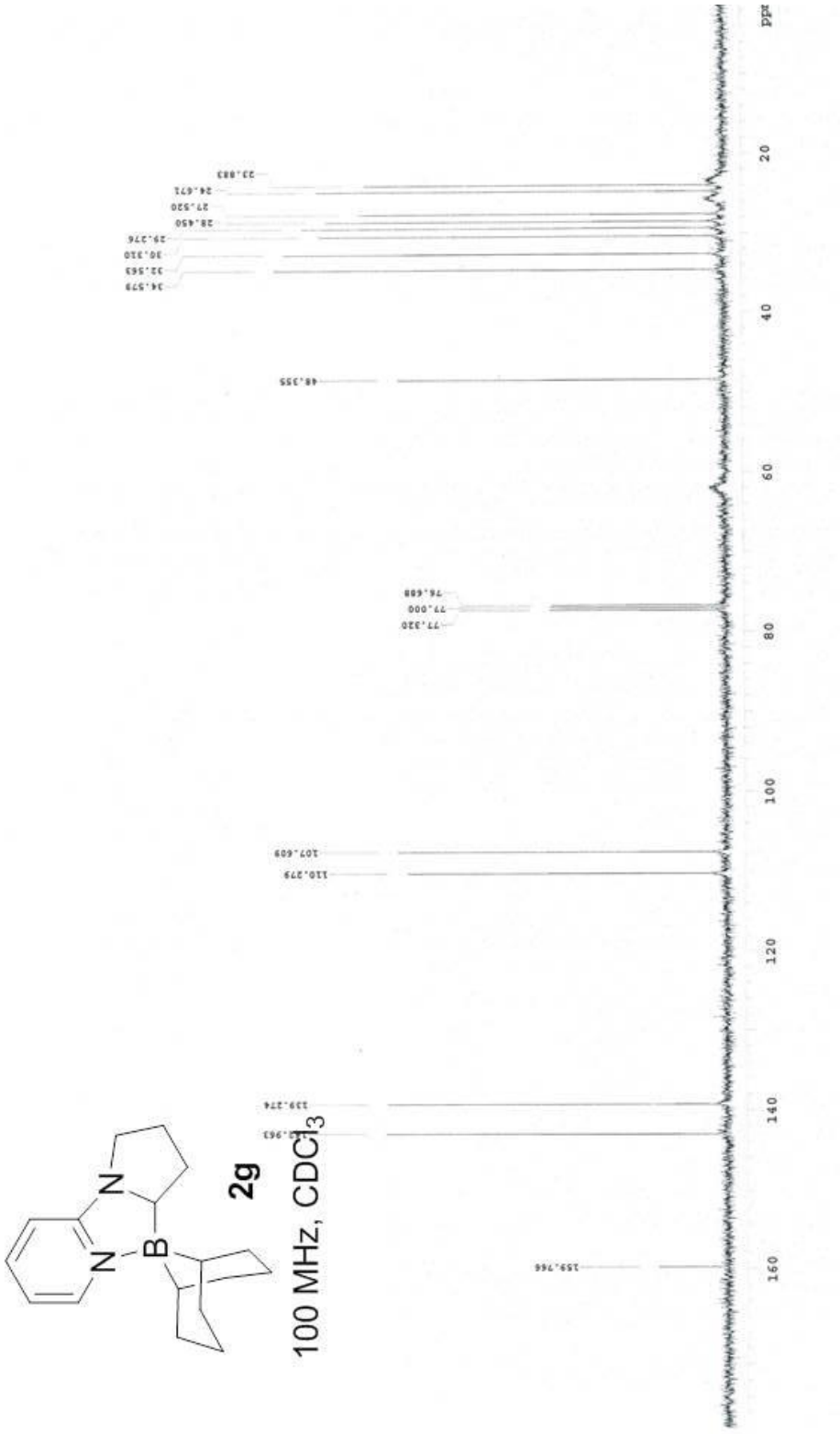
N
B
2g
400 MHz, CDCl3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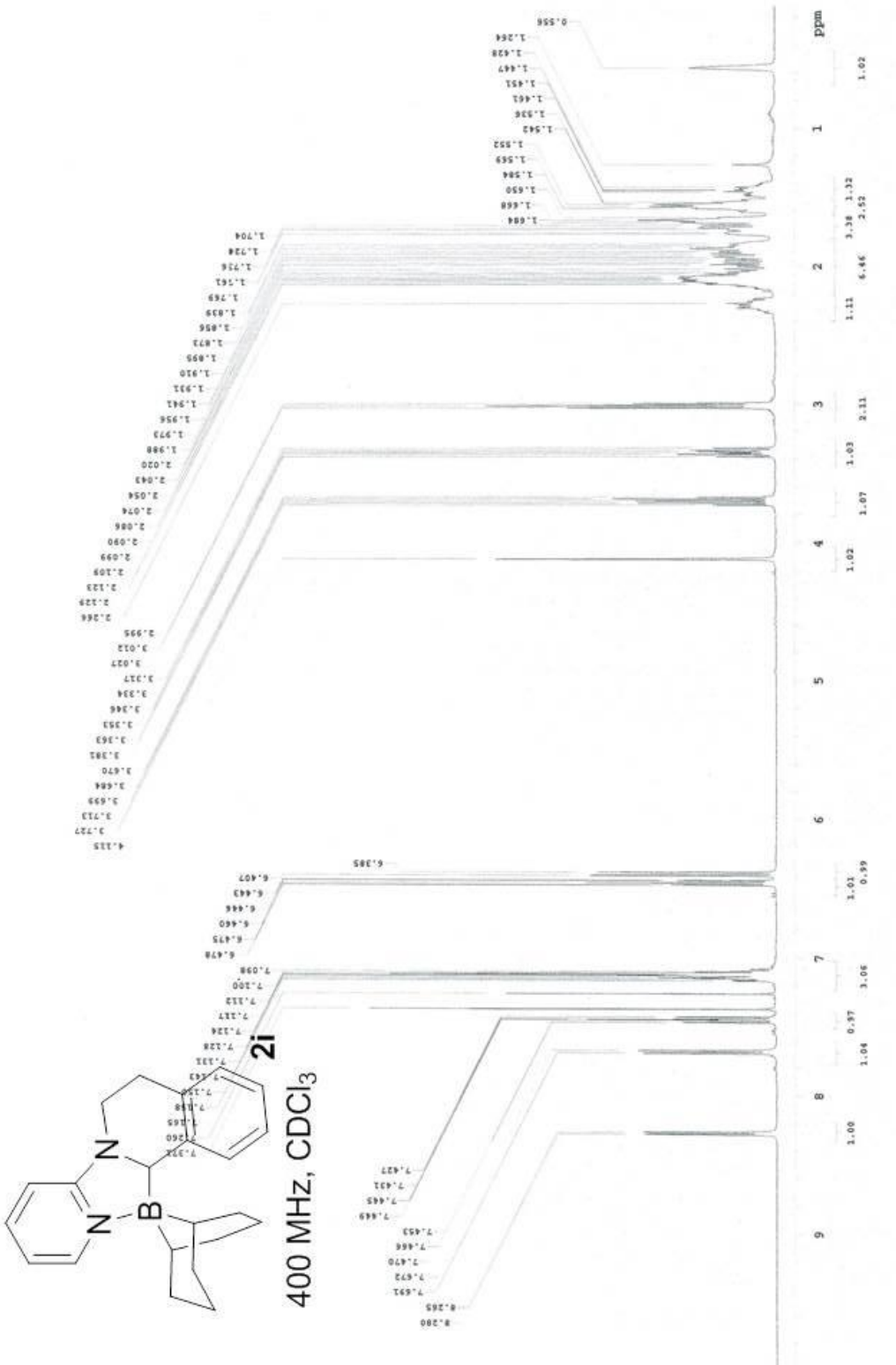
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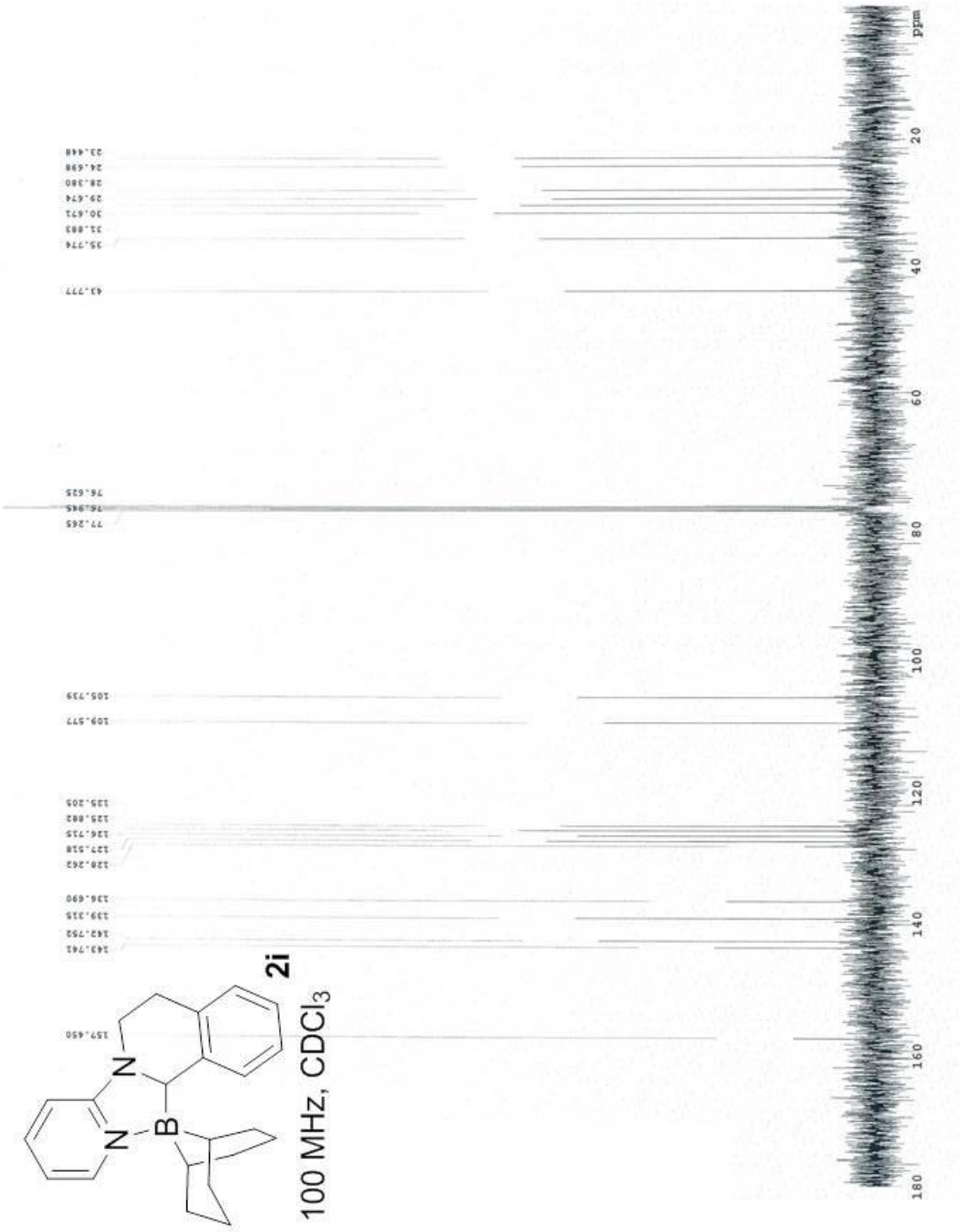
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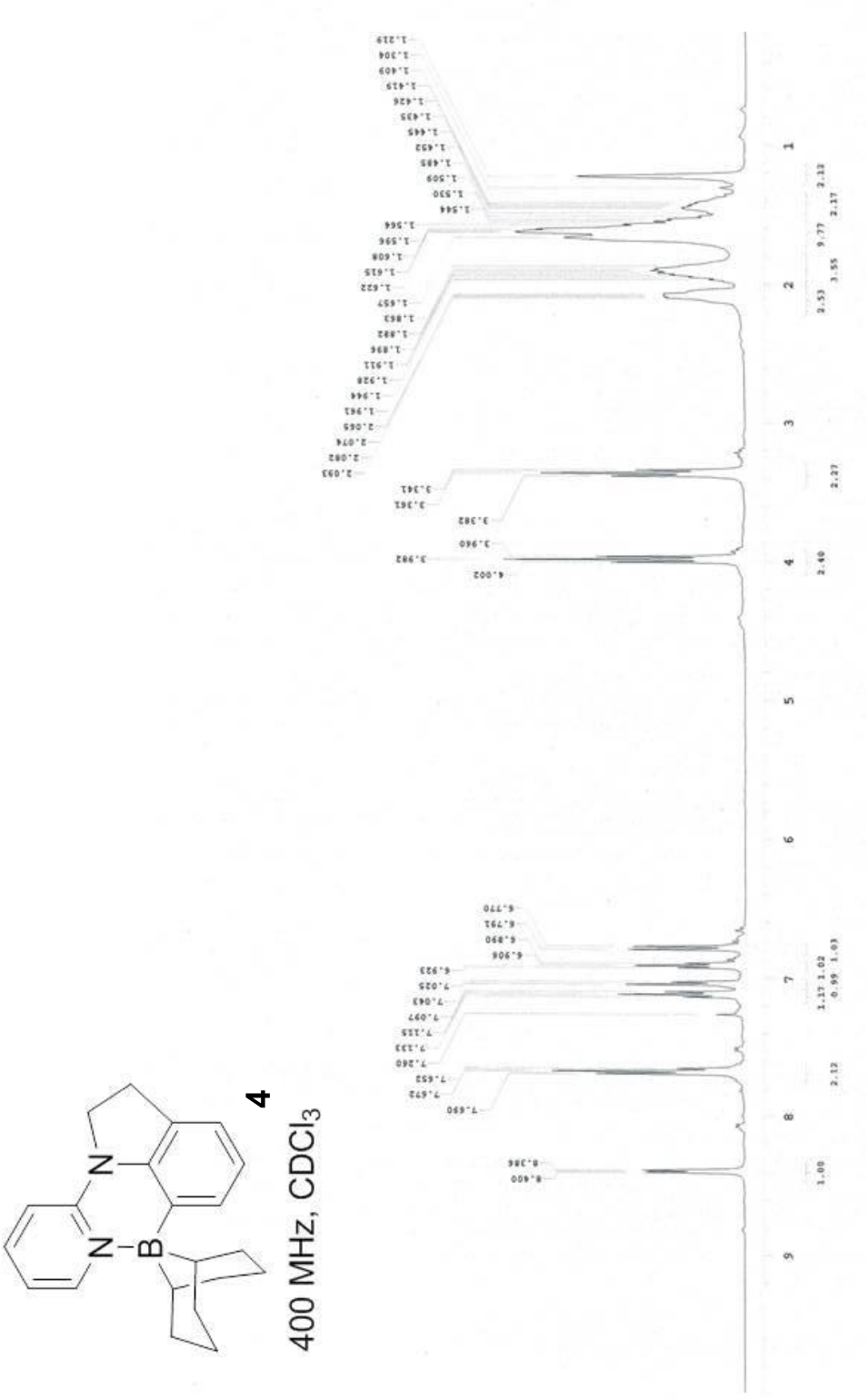
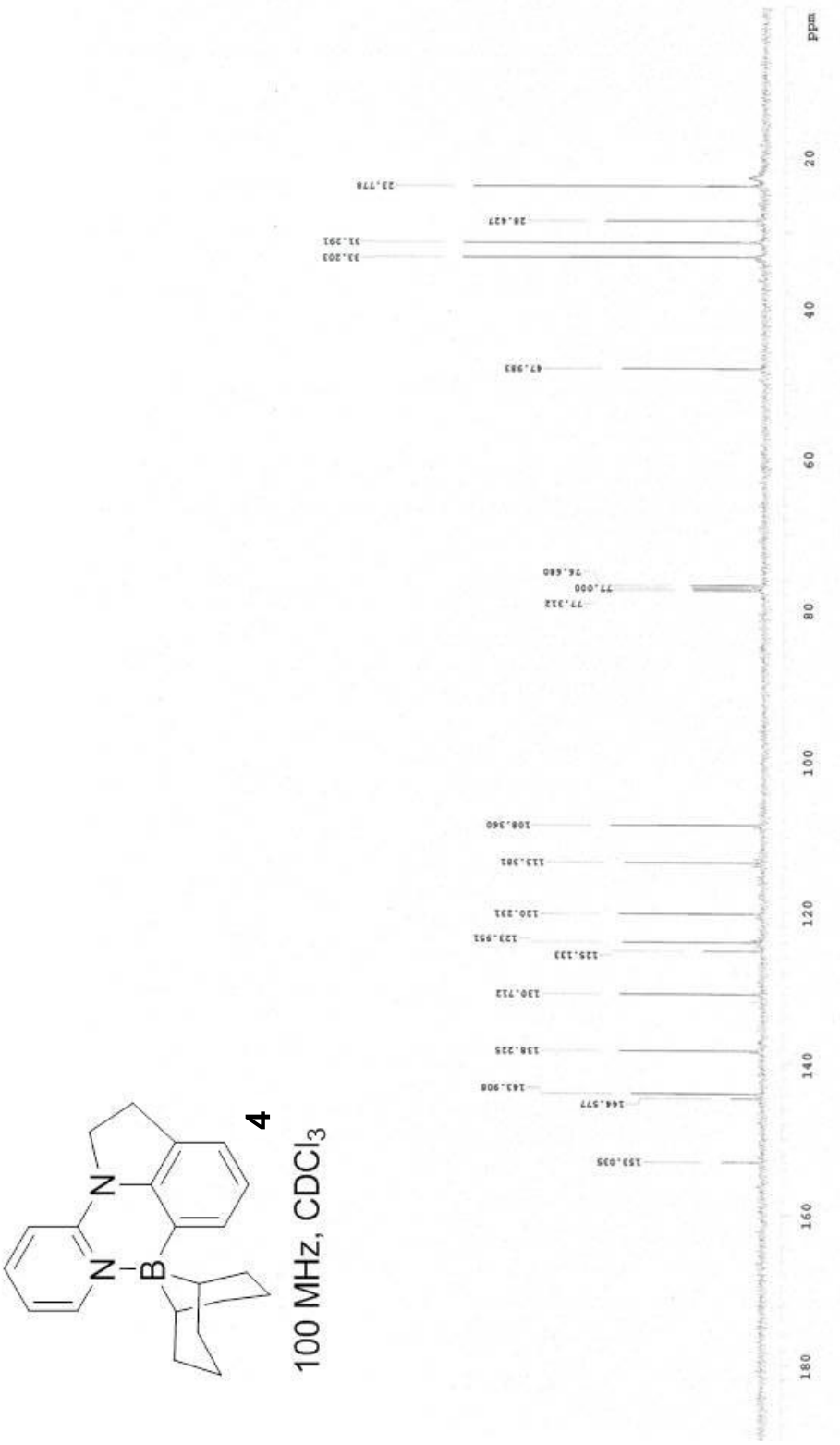
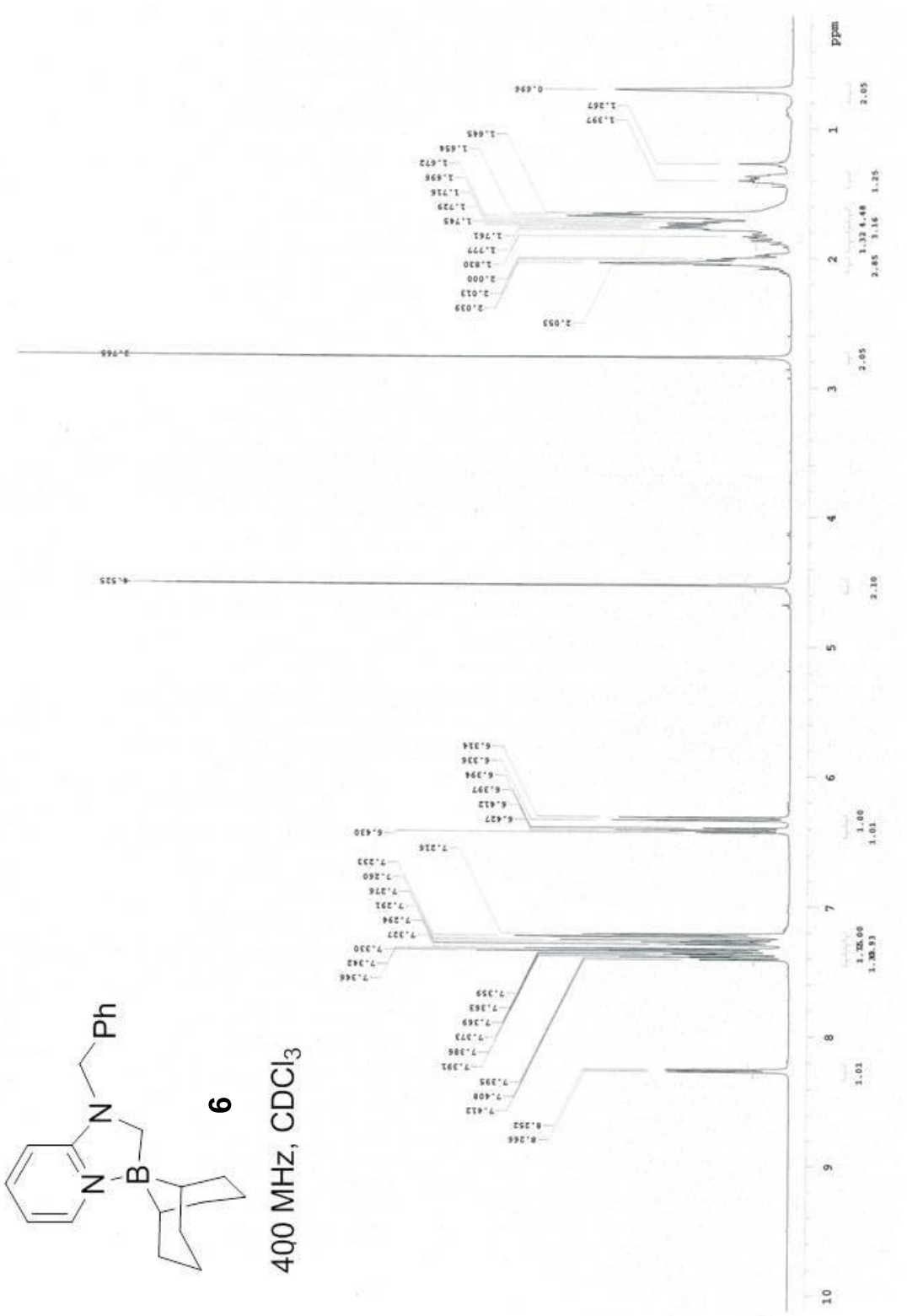
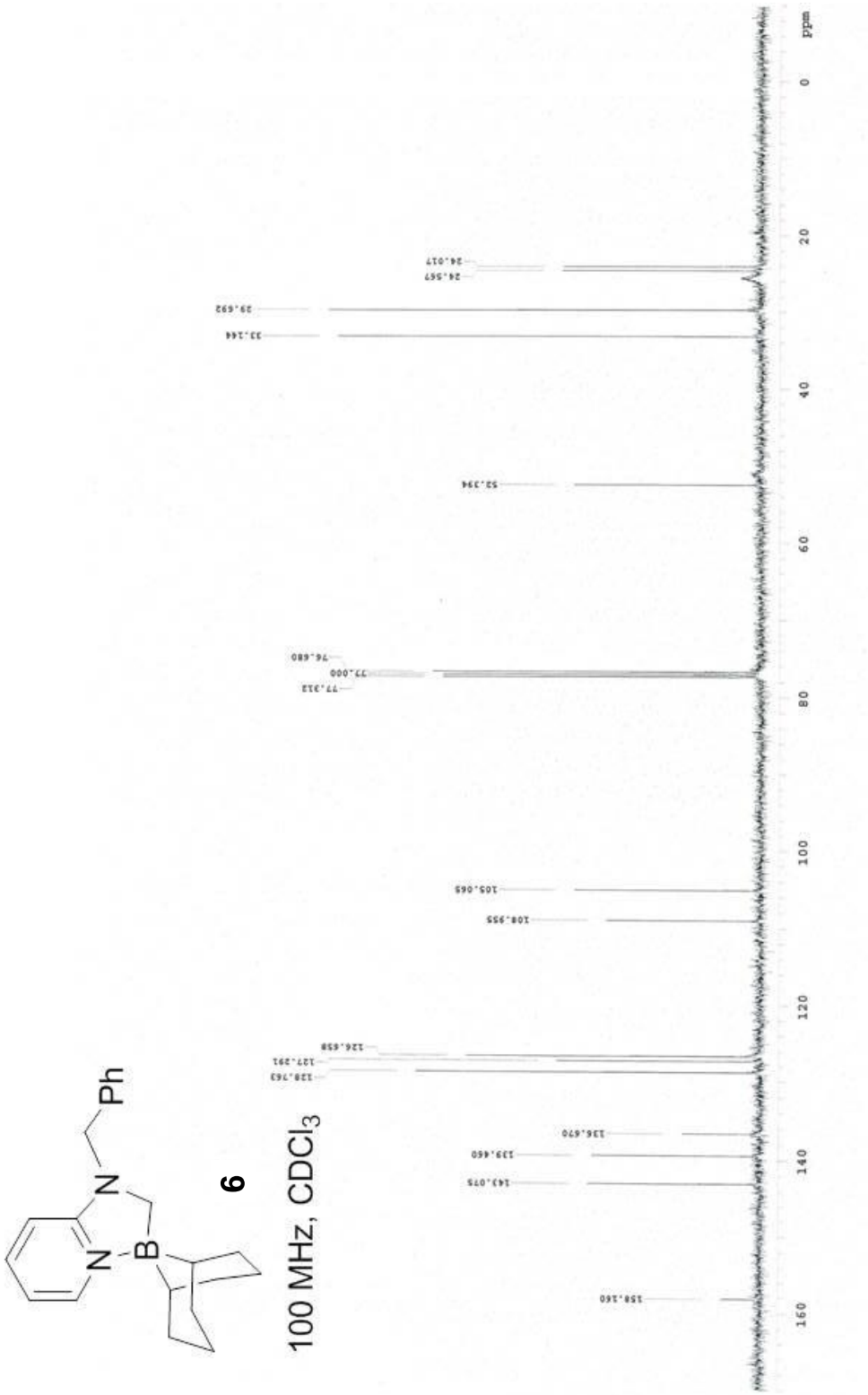

4
400 MHz, CDCl3


4
100 MHz, CDCl3
N
N
B
ppm
20
40
60
80
100
120
140
160
180
23.778
28.427
31.291
33.303
47.983
76.680
77.000
77.312
108.360
113.381
120.331
123.951
125.133
130.713
138.235
143.908
144.577
153.035


Ph
N
B
N
6
400 MHz, CDCl3
ppm


Ph
N
N
B
6
100 MHz, CDCl3
34.017
34.567
39.692
33.144
53.394
76.680
77.000
77.313
105.063
108.955
126.658
127.291
128.763
136.670
139.460
143.075
158.160
ppm
0
20
40
60
80
100
120
140
160