–Supporting Information for–

Tetrahydrofuran Ring Opening and Related Reactions with Lewis Acidic N-Heterocyclic Carbene-Boryl Trifluoromethanesulfonate

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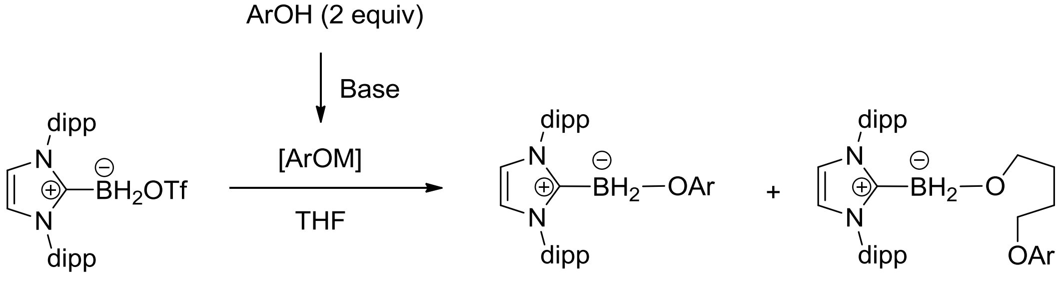
General Remarks: Chemicals were purchased from commercial suppliers and used as received. THF, toluene, and CH_2Cl_2 were dried by passing through an activated alumina column. Reactions were monitored by TLC analysis. Visualization was accomplished with a 254 nm UV lamp or by staining with a vanillin solution. The CombiFlash®R_f flash chromatography system (Teledyne ISCO) and prepacked RediSep®R_f columns were used for purification of products. Melting points (mp) were determined with a Mel-Temp II apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer as thin films (CH_2Cl_2) on NaCl plates. Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance III 400 and Bruker Avance III 500 instruments at 400 (500) and 100 (125) MHz, respectively. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak ($CDCl_3$: ^1H = 7.27 ppm, ^{13}C = 77.0 ppm). Boron (^{11}B) NMR spectra were measured on a Bruker Avance III 400 instrument at 128.4 MHz. The ^{11}B chemical shifts are given relative to $BF_3{\cdot}OEt_2$ (^{11}B = 0 ppm). All NMR spectra were recorded at 293 K. The following abbreviations are used to describe coupling: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet; br = broad; app = apparent. The resonances of hydrogen atoms connected to the boron atom often cannot be observed in ^1H NMR spectra because of quadrupole broadening. For the same reason, the resonances of carbene carbon atoms connected to the boron atom were not observed in ^{13}C NMR spectra of all NHC-boranes. High resolution mass spectra (HRMS) were obtained on a Q-Tof Ultima API, Micromass UK Limited instrument by electrospray ionization (ESI).

Compounds **1**[1] and **2**[2] have been prepared according to the literature procedures. Their spectroscopic data were consistent with those previous reported.

Experimental Procedures and Compound Characterization:



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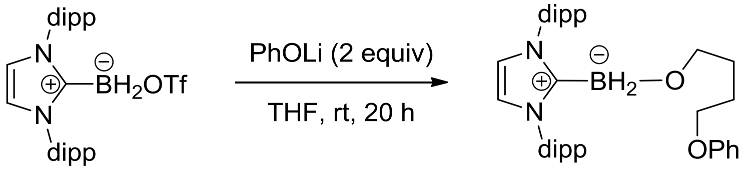
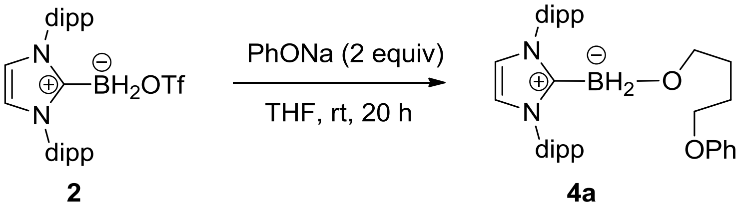
General procedure: THF ring-opening reactions (GP): A solution of a base (0.2 mmol) was added to a solution of ArOH (0.2 mmol) in THF (0.5 mL) or toluene (0.5 mL) at rt under argon. After 5 min of stirring, the formation of the phenoxide ArOM was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **1** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **2** was assumed. In several cases, CH_2Cl_2 was removed by rotary evaporation and the white residue was dissolved in THF (1 mL). Then the solution of ArOM was added to the resulting solution of dipp-Imd-BH_2OTf **2**. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography.



2 **4a**

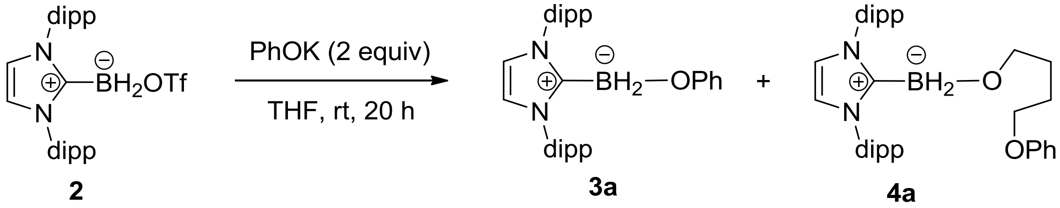
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-$BH_2O(CH_2)_4OPh$) (4a): Following GP with LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) and

PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 gave dipp-Imd-$BH_2O(CH_2)_4OPh$ **4a** as a white solid (28.9 mg, 51%): mp 121–122 °C; IR (thin film, cm^{-1}) ν_{max} 3071, 2964, 2928, 2870, 2250 (B–H), 1689, 1599, 1586, 1538, 1497, 1470, 1387, 1368, 1332, 1301, 1246, 1208, 1172, 1061, 954, 936, 883, 803, 755; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.30–7.22 (m, 6H), 7.00 (s, 2H), 6.91 (dt, *J* = 7.3, 1.0 Hz, 1H), 6.85 (dd, *J* = 8.6, 1.0 Hz, 1H), 3.70 (t, *J* = 7.0 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 2.65 (septet, *J* = 6.9 Hz, 4H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.29 (app quintet, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.07 (app quintet, *J* = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 145.2, 134.2, 129.7, 129.2, 123.6, 122.3, 120.0, 114.5, 68.8, 68.2, 28.7, 28.4, 25.8, 24.8, 22.9; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.2 (t, $J_{B–H}$ = 92 Hz); HRMS (ESI) calcd. for $C_{37}H_{52}{}^{11}BN_2O_2$ ($[M + H]^+$) 567.4122, found 567.4144.



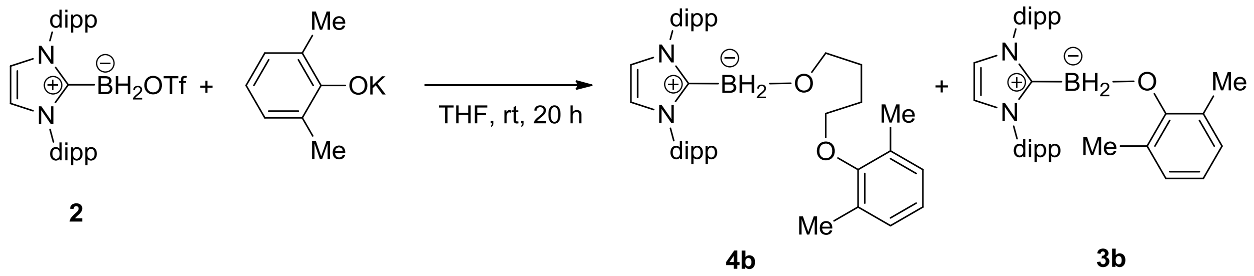
2 **4a**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-$BH_2O(CH_2)_4OPh$) (4a): Following GP with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol) and PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.35 mL), elution with hexane:EtOAc = 90:10 gave dipp-Imd-$BH_2O(CH_2)_4OPh$ **4a** as a white solid (26.4 mg, 46%). The NMR data of the isolated product were identical to those of the previously prepared sample of **4a**.



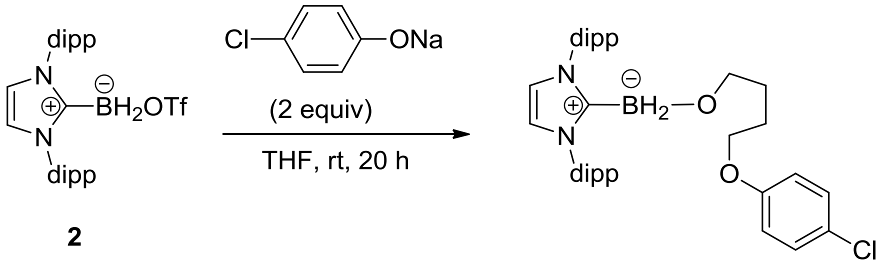
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenoxyborane (dipp-Imd-BH$_2$OPh) (3a) and 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-phenoxybutyloxy)borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OPh) (4a): Following GP with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) and PhOH (19 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 first gave dipp-Imd-BH$_2$OPh **3a** as a white solid (14.9 mg, 30%): mp 166–168 °C; IR (thin film, cm^{-1}) ν_{max} 3129, 2963, 2927, 2869, 2282 (B–H), 1596, 1496, 1471, 1460, 1427, 1385, 1364, 1331, 1293, 1173, 1158, 1070, 998, 955, 878, 803, 759; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.07 (s, 2H), 6.92 (t, *J* = 8.0 Hz, 2H), 6.48 (t, *J* = 7.2 Hz, 1H), 6.18 (d, *J* = 7.6 Hz, 2H), 2.80 (br q, 2H), 2.65 (septet, *J* = 6.9 Hz, 4H), 1.23 (d, *J* = 6.8 Hz, 12H), 1.20 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 162.1, 145.2, 134.1, 129.9, 128.1, 123.7, 122.5, 116.4, 115.5, 28.8, 24.7, 23.0; ^{11}B NMR (128.4 MHz, CDCl$_3$) δ –11.3 (t, $J_{B–H}$ = 93 Hz); HRMS (ESI) calcd. for $C_{33}H_{43}{}^{11}BN_2NaO$ ([M + Na]$^+$) 517.3366, found 517.3386.

Slightly more polar dipp-Imd-BH$_2$O(CH$_2$)$_4$OPh **4a** was eluted next and isolated as a white solid (23 mg, 40%). The NMR data of the isolated product were identical to those of the previously prepared sample of **4a**.



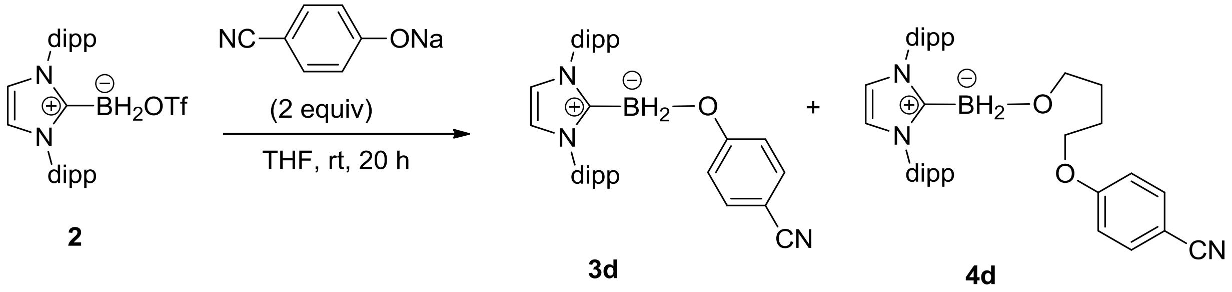
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(2,6-dimethylphenoxy)butyloxy]borane (dipp-Imd-$BH_2O(CH_2)_4O(2,6\text{-}Me_2C_6H_3)$) (4b): Following GP with KHMDS (0.5 M in toluene, 0.4 mL, 0.2 mmol) and 2,6-dimethylphenol (25 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 90:10 gave **4b** as a white solid (36.1 mg, 60%): mp 108–110 °C; IR (thin film, cm^{-1}) ν_{max} 3162, 3134, 3070, 3035, 2962, 2928, 2869, 2712, 2225 (B–H), 1699, 1593, 1562, 1472, 1426, 1384, 1361, 1332, 1296, 1262, 1207, 1172, 1123, 1108, 1091, 1060, 1044, 983, 949, 938, 863, 802, 760; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 4H), 7.00 (s, 2H), 6.99 (d, *J* = 6.4 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 2.65 (septet, *J* = 6.8 Hz, 4H), 2.23 (s, 6H), 1.40–1.30 (m, 2H), 1.32 (d, *J* = 6.8 Hz, 12H), 1.29 (app quintet, *J* = 7.8 Hz, 2H), 1.18 (d, *J* = 6.8 Hz, 12H), 1.12 (app quintet, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 145.2, 134.2, 131.0, 129.7, 128.5, 123.6, 123.2, 122.3, 72.8, 69.1, 28.7, 28.7, 27.0, 24.8, 24.8, 22.9, 16.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.2 (t, $J_{B–H}$ = 91 Hz); HRMS (ESI) calcd. for $C_{39}H_{55}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 617.4254, found 617.4227.

Dipp-Imd-$BH_2O(2,6\text{-}Me_2C_6H_3)$ **3b** was isolated as impure solid (1.3 mg, 2%) and was not characterized.



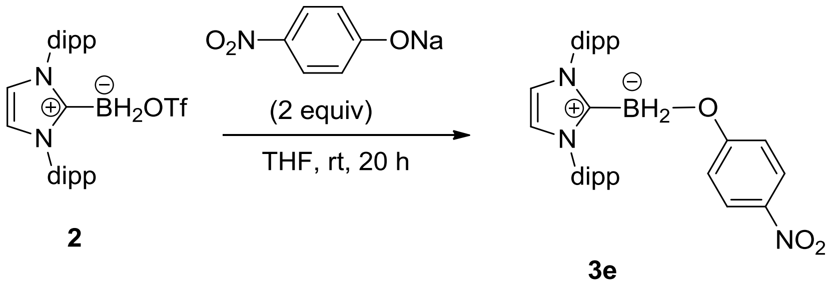
2 **4c**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-chlorophenoxy)butyloxy]borane ($dipp$-Imd-$BH_2O(CH_2)_4OC_6H_4Cl$) (4c): Following GP with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-chlorophenol (25 mg, 0.20 mmol) in THF (1.5 mL)–CH_2Cl_2 (1 mL), elution with hexane:EtOAc = 6:1 gave **4c** as a light yellow solid (30.5 mg, 50%): mp 115–120 °C; IR (thin film, cm^{-1}) ν_{max} 3073, 2963, 2929, 2869, 2359 (B–H), 2222 (B–H), 1695, 1596, 1580, 1492, 1471, 1426, 1385, 1364, 1332, 1286, 1245, 1211, 1161, 1123, 1104, 1092, 1060, 1005, 824, 823, 759; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (t, J = 7.5 Hz, 2H), 7.26 (d, J = 7.5 Hz, 4H), 7.20 (d, J = 9.0 Hz, 2H), 7.00 (s, 2H), 6.76 (d, J = 9.0 Hz, 2H), 3.66 (t, J = 6.9 Hz, 2H), 2.84 (t, J = 6.5 Hz, 2H), 2.64 (septet, J = 6.9, 4H), 1.31 (d, J = 6.9 Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, J = 7.2 Hz, 12H), 1.06 (app quintet, J = 7.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 145.2, 134.2, 129.7, 129.1, 124.7, 123.6, 122.3, 115.7, 68.7, 68.6, 28.7, 28.3, 25.6, 24.8, 22.9; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.3 (t, J_{B-H} = 84 Hz); HRMS (ESI) calcd. for $C_{37}H_{50}{}^{11}B^{35}ClN_2NaO_2$ ($[M + Na]^+$) 623.3552, found 623.3535.

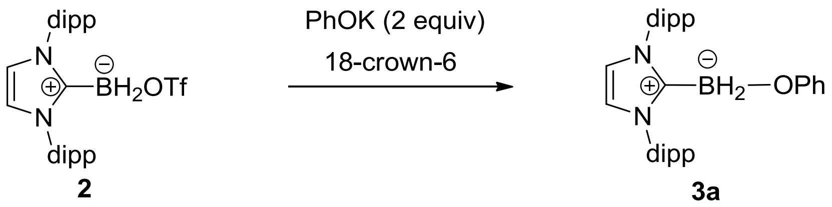


1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-cyanophenoxy)borane (dipp-Imd-BH$_2$-OC$_6$H$_4$CN) (3d) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(4-cyanophenoxy)butyloxy]borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$OC$_6$H$_4$CN) (4d): Following GP with NaHMDS (1 M in THF, 0.2 mL, 0.2 mmol) and 4-cyanophenol (24 mg, 0.20 mmol) in THF (1.5 mL)–CH$_2$Cl$_2$ (1 mL), elution with hexane:EtOAc = 8:1 to 3:1 gave dipp-Imd-BH$_2$OC$_6$H$_4$CN **3d** as a white solid (10.6 mg, 20%): mp 181–182 °C; IR (thin film, cm^{-1}) ν_{max} 2966, 2929, 2871, 2306, 2212, 1600, 1511, 1471, 1385, 1366, 1325, 1174, 1155, 1125, 1101, 1086, 1061, 937, 839, 762, 740; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.51 (t, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.5, 4H), 7.19 (d, *J* = 8.7 Hz, 2H), 7.11 (s, 2H), 6.17 (d, *J* = 9.0 Hz, 2H), 2.60 (septet, *J* = 6.9, 4H), 1.21 (d, *J* = 6.9 Hz, 12H), 1.20 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 165.8, 145.2, 133.7, 133.0, 130.2, 123.8, 122.8, 121.2, 117.1, 97.8, 28.8, 24.7, 23.0; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ –11.2 (br s); HRMS (ESI) calcd. for $C_{34}H_{42}{}^{11}BN_3NaO$ ([M + Na]$^+$) 542.3319, found 542.3342.

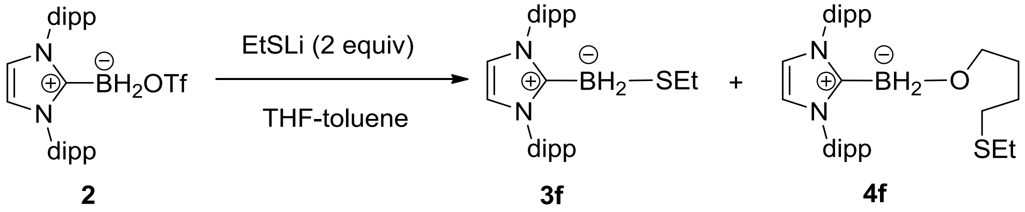
Further elution gave dipp-Imd-BH$_2$O(CH$_2$)$_4$OC$_6$H$_4$CN **4d** as yellow oil (8.2 mg, 14%). The compound **4d** was only about 75% pure and was not stable enough to be fully characterized: IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2871, 2224, 1698, 1651, 1605, 1508, 1470, 1386, 1367, 1331, 1303, 1259, 1207, 1171, 1114, 1061; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.55 (t, *J* = 6.9 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 4H), 7.08 (s, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.74 (t, *J* = 6.9 Hz, 2H), 2.84 (t, *J* = 6.3 Hz, 2H), 2.65 (septet, *J* = 6.9, 4H), 1.30 (d, *J* = 6.9 Hz, 12H), 1.30–1.20 (m, 2H), 1.17 (d, *J* = 6.9 Hz, 12H), 1.06 (app quintet, *J* = 6.9 Hz, 2H); ^{11}B NMR (96.3 MHz, CDCl$_3$) δ –9.3 (t, $J_{\mathrm{B–H}}$ = 92 Hz); HRMS (ESI) calcd. for $C_{38}H_{50}{}^{11}BN_3NaO_2$ ([M + Na]$^+$) 614.3894, found 614.3888.



1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-nitrophenoxy)borane (dipp-Imd-BH$_2$-OC$_6$H$_4$NO$_2$) (3e): Following GP with NaHMDS (0.6 M in toluene, 0.35 mL, 0.2 mmol) and 4-nitrophenol (28 mg, 0.20 mmol) in THF (2 mL)–toluene (0.4 mL), elution with hexane:EtOAc = 80:20 gave **3e** as a light yellow solid (23.5 mg, 43%): mp 175–178 °C; IR (thin film, cm^{-1}) ν_{max} 2965, 2929, 2871, 2328 (B–H), 1594, 1500, 1471, 1429, 1386, 1365, 1313, 1257, 1178, 1158, 1104, 1089, 952, 938, 849, 804, 758; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.87–7.83 (m, 2H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 4H), 7.12 (s, 2H), 6.16–6.12 (m, 2H), 2.61 (septet, *J* = 6.9, 4H), 1.22 (d, *J* = 6.9 Hz, 12H), 1.21 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 168.4, 145.2, 137.7, 133.7, 130.3, 125.5, 123.9, 122.9, 116.1, 28.9, 24.7, 23.0; ^{11}B NMR (96.3 MHz, CDCl$_3$) δ –10.9 (br s); HRMS (ESI) calcd. for $C_{33}H_{42}{}^{11}BN_3NaO_3$ ([M + Na]$^+$) 562.3217, found 562.3209.



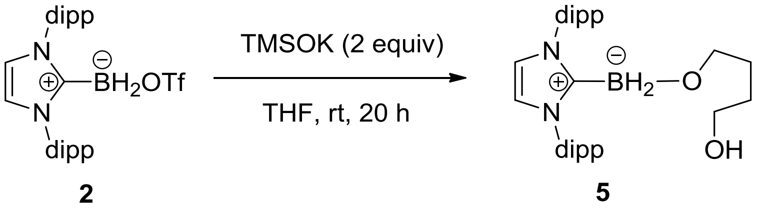
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene phenoxyborane (dipp-Imd-BH$_2$OPh) (3a): A solution of KHMDS (0.5 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) and 18-crown-6 ether (53 mg, 0.20 mmol) in toluene (0.1 mL) at rt under argon. After 5 min of stirring, the formation of PhOK was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH$_3$ **1** (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH$_2$OTf **2** was assumed. Then the solution of dipp-Imd-BH$_2$OTf **2** was added to a suspension of PhOK followed by toluene (1.5 mL). The cloudy reaction mixture was stirred at rt for 2 days. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The products were purified by flash chromatography. Elution with hexane:Et$_2$O = 95:5 gave dipp-Imd-BH$_2$OPh **3a** as a white solid (31.9 mg, 64%). The NMR data of the isolated product were identical to those of the previously prepared sample of **3a**.



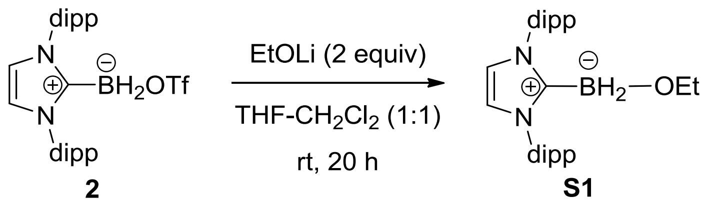
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (ethylthio)borane (dipp-Imd-BH$_2$SEt) (3f) and 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene [4-(ethylthio)butyloxy]borane (dipp-Imd-BH$_2$O(CH$_2$)$_4$SEt) (4f): A solution of LiHMDS (1 M in toluene, 0.2 mL, 0.2 mmol) was added to a solution of EtSH (15 µL, 0.20 mmol) in THF (0.5 mL) at rt. After 5 min of stirring, the formation of EtSLi was assumed. In a separate flask, triflic acid (10 µL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **1** (40.5 mg, 0.10 mmol) in toluene (1 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **2** was assumed. Toluene was removed by rotary evaporation and the white residue was dissolved in THF (1.5 mL). Then the solution of EtSLi was added to the resulting solution of dipp-Imd-BH_2OTf **2**. The cloudy reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography. Elution with hexane:EtOAc = 95:5 to 90:10 gave dipp-Imd-BH_2SEt **3f** as a white solid (7.3 mg, 16%): mp 204–207 °C; IR (thin film, cm^{-1}) ν_{max} 3156, 3053, 2963, 2926, 2869, 2365 (B–H), 1565, 1471, 1429, 1383, 1364, 1333, 1258, 1233, 1173, 1061, 1038, 937, 803, 763; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 4H), 7.04 (s, 2H), 2.62 (septet, *J* = 6.8 Hz, 4H), 1.53 (q, *J* = 7.3 Hz, 2H), 1.34 (d, *J* = 6.8 Hz, 12H), 1.16 (d, *J* = 6.8 Hz, 12H), 0.85 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.5, 133.9, 130.1, 123.8, 122.4, 28.8, 27.1, 25.3, 22.7, 17.3; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –24.0 (t, *J* = 99 Hz); HRMS (ESI) calcd. for $C_{29}H_{44}{}^{11}BN_2S$ ($[M + H]^+$) 463.3318, found 463.3301.

Further elution gave dipp-Imd-$BH_2O(CH_2)_4SEt$ **4f** as a white solid (29.3 mg, 54%): mp 66–68 °C; IR (thin film, cm^{-1}) ν_{max} 3075, 2963, 2928, 2869, 2708, 2218 (B–H), 1596, 1471, 1459, 1426, 1384, 1364, 1332, 1259, 1211, 1173, 1121, 1107, 1060, 1037, 981, 949, 937, 802, 759; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 4H), 6.98 (s, 2H), 2.78 (t, *J* = 6.6, 2H), 2.63 (septet, *J* = 6.8 Hz, 4H), 2.45 (q, *J* = 7.5 Hz, 2H), 2.26 (t, *J* = 7.8 Hz, 2H), 1.31 (d, *J* = 6.8 Hz, 12H), 1.20 (t, *J* = 7.4 Hz, 3H), 1.17 (d, *J* = 6.8 Hz, 12H), 1.12 (app. quintet, *J* = 8.0 Hz, 2H), 0.99 (app. quintet, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.2, 129.7, 123.6, 122.3, 68.9, 31.8, 31.7, 28.7, 26.4, 25.7, 24.8, 22.9, 14.8; ^{11}B NMR

(128.4 MHz, $CDCl_3$) δ –9.3 (t, *J* = 94 Hz); HRMS (ESI) calcd. for $C_{33}H_{50}{}^{11}BN_2OS$ ($[M - H]^+$) 533.3737, found 533.3749.



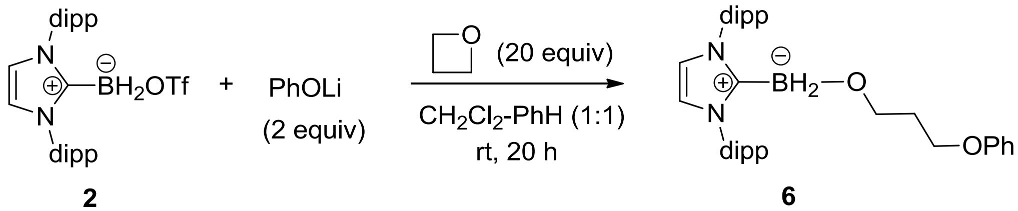
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (4-hydroxybutyloxy)borane (dipp-Imd-$BH_2O(CH_2)_4OH$) (5): A solution of TMSOK (26 mg, 0.20 mmol) and dipp-Imd-BH_2OTf **2** (55 mg, 0.10 mmol) in a THF (2 mL) was stirred for 20 h at rt. The solvent was removed and the residue was loaded on silica gel. Chromatographic separation (elution with hexane : EtOAc = 2 : 1 to 1 : 1) gave dipp-Imd-$BH_2O(CH_2)_4OH$ **5** as a white solid (18.3 mg, 37%): mp 106–108 °C; IR (thin film, cm^{-1}) ν_{max} 3159, 3073, 2963, 2928, 2870, 2287, 2228 (B–H), 1683, 1595, 1471, 1460, 1426, 1385, 1364, 1332, 1299, 1271, 1257, 1213, 1171, 1103, 1061, 1043, 949, 937, 871, 803, 759, 733; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 4H), 7.02 (s, 2H), 5.41 (t, *J* = 6.2 Hz, 1H), 3.27 (q, *J* = 5.5 Hz, 2H), 2.66 (t, *J* = 5.2 Hz, 2H), 2.62 (septet, *J* = 6.9, 4H), 1.33 (d, *J* = 6.8 Hz, 12H), 1.35–1.25 (m, 2H), 1.16 (d, *J* = 6.8 Hz, 12H), 1.06 (app quintet, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 133.9, 129.9, 123.7, 122.4, 70.0, 62.4, 32.2, 30.4, 28.7, 25.0, 22.7; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –9.3 (t, *J* = 96 Hz); HRMS (ESI) calcd. for $C_{31}H_{48}{}^{11}BN_2O_2$ ($[M]^+$) 491.3809, found 491.3828.



2 **S1**

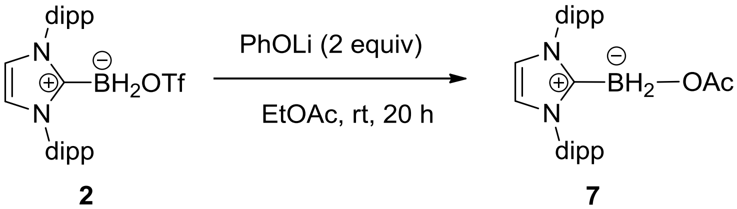
1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene ethoxyborane (dipp-Imd-BH_2OEt) (S1): Lithium ethoxide was prepared by the addition of BuLi (1.6 M solution in hexanes, 0.13 mL, 0.21 mmol) to a solution of ethanol (12 μL, 0.20 mmol) in THF (0.5 mL) at 0 °C. Then compound **S1** was prepared according to GP from resulting EtOLi (0.20 mmol) and dipp-Imd-BH_2OTf **2** (50 mg, 0.09 mmol) in a THF (1.5 mL)–CH_2Cl_2 (0.5 mL) solution. Chromatographic separation (elution with hexane:EtOAc = 8:1 to 5:1) gave dipp-Imd-BH_2OEt **S1** as a light yellow solid (14.9 mg, 33%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (t, *J* = 7.8 Hz, 2H), 7.27 (d, *J* = 7.8 Hz, 4H), 7.00 (s, 2H), 2.82 (q, *J* = 6.9 Hz, 2H), 2.65 (septet, *J* = 6.8, 4H), 1.32 (d, *J* = 6.9 Hz, 12H), 1.17 (d, *J* = 6.9 Hz, 12H), 0.52 (t, *J* = 6.9 Hz, 6H); ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.5 (t, *J* = 96 Hz).

The isolated sample of **S1** was only 90% pure and decomposed during the attempts to purify it by recrystallization.



2 **6**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene (3-phenyloxypropoxy]borane (dipp-Imd-$BH_2O(CH_2)_3OPh$) (6): A solution of BuLi (1.5 M in hexanes, 0.13 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in PhH (0.5 mL) at rt. After 5 min of stirring, the formation of a precipitate of PhOLi was observed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **1** (40.5 mg, 0.10 mmol) in CH_2Cl_2 (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **2** was assumed. Then the resulting solution of dipp-Imd-BH_2OTf **2** was added to the suspension of PhOLi followed by oxetane (0.13 mL, 2.0 mmol). The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 5:1 gave dipp-Imd-$BH_2O(CH_2)_3OPh$ **6** as yellow oil (24 mg, 43%). The product was about 90% pure: IR (thin film, cm^{-1}) ν_{max} 3071, 2963, 2929, 2869, 2224 (B–H), 1691, 1600, 1586, 1497, 1471, 1426, 1384, 1364, 1332, 1300, 1247, 1212, 1172, 1123, 1061, 1032, 950, 937, 803, 755; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.8 Hz, 2H), 7.30–7.20 (m, 6H), 6.99 (s, 2H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.79 (d, *J* = 8.4 Hz, 2H), 3.46 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 6.0 Hz, 2H), 2.64 (septet, *J* = 6.9, 4H), 1.44 (app. quintet, *J* = 6.8, 2H), 1.31 (d, *J* = 6.6 Hz, 12H), 1.30–1.20 (m, 2H), 1.18 (d, *J* = 6.9 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 145.2, 134.1, 129.8, 129.0, 123.6, 122.3, 119.8, 114.7, 66.5, 65.7, 32.1, 28.8, 24.8, 24.6, 23.0; ^{11}B NMR (96.3 MHz, $CDCl_3$) δ –9.2 (t, *J* = 87 Hz); HRMS (ESI) calcd. for $C_{36}H_{49}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 575.3785, found 575.3755.



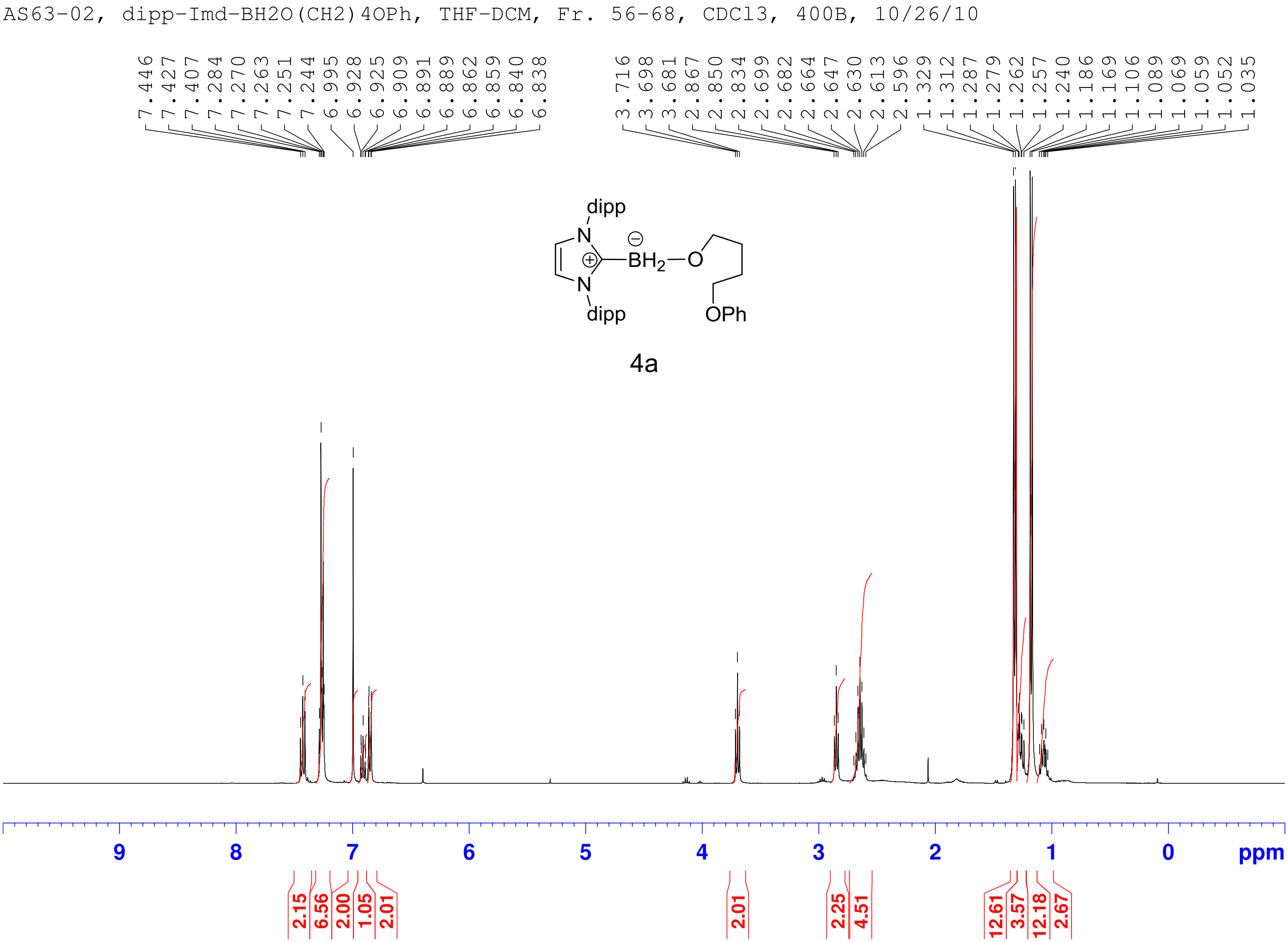
2 **7**

1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene acetoxyborane (7): A solution of BuLi (0.9 M in hexanes, 0.22 mL, 0.2 mmol) was added to a solution of PhOH (19 mg, 0.20 mmol) in EtOAc (0.5 mL) at rt. After 5 min of stirring, the formation of PhOLi was assumed. In a separate flask, triflic acid (10 μL, 0.1 mmol) was added to a solution of dipp-Imd-BH_3 **1** (40.5 mg, 0.10 mmol) in PhH (0.5 mL) at rt. After 10 min of stirring, the formation of dipp-Imd-BH_2OTf **2** was assumed. The solvent was removed by rotary evaporation and the residue was dissolved in EtOAc (0.5 mL). Then the resulting solution of dipp-Imd-BH_2OTf **2** was added to the solution of PhOLi. The reaction mixture was stirred at rt for 20 h. The volatiles were removed under vacuum and the residue was purified by column chromatography. Elution with hexane:EtOAc = 9:1 to pure EtOAc gave dipp-Imd-BH_2OAc **7** as a white solid (14.5 mg, 31%): mp 203–204 ˚C; IR (thin film, cm^{-1}) ν_{max} 3153, 3114, 3082, 2962, 2926, 2872, 2359, 2340, 1682, 1470, 1428, 1372, 1314, 1160, 1106, 802, 760; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 145.1, 133.6, 130.1, 123.8, 122.7, 28.8, 24.8, 22.9, 22.2; ^{11}B NMR (128.4 MHz, $CDCl_3$) δ –12.4 (t, *J* = 89 Hz); HRMS (ESI) calcd. for $C_{29}H_{41}{}^{11}BN_2NaO_2$ ($[M + Na]^+$) 483.3159, found 483.3150.

References:

(1) Ueng, S.-H.; Makhlouf Brahmi, M.; Derat, E.; Fensterbank, L.; Lacôte, E.; Malacria, M.; Curran, D. P. *J. Am. Chem. Soc.* **2008**, *130*, 10082-10083.

(2) Solovyev, A.; Chu, Q.; Geib, S. J.; Fensterbank, L.; Malacria, M.; Lacôte, E.; Curran, D. P. *J. Am. Chem. Soc.* **2010**, *132*, 15072-15080.


AS63-02, dipp-Imd-BH2O(CH2)4OPh, THF-DCM, Fr. 56-68, CDCl3, 400B, 10/26/10
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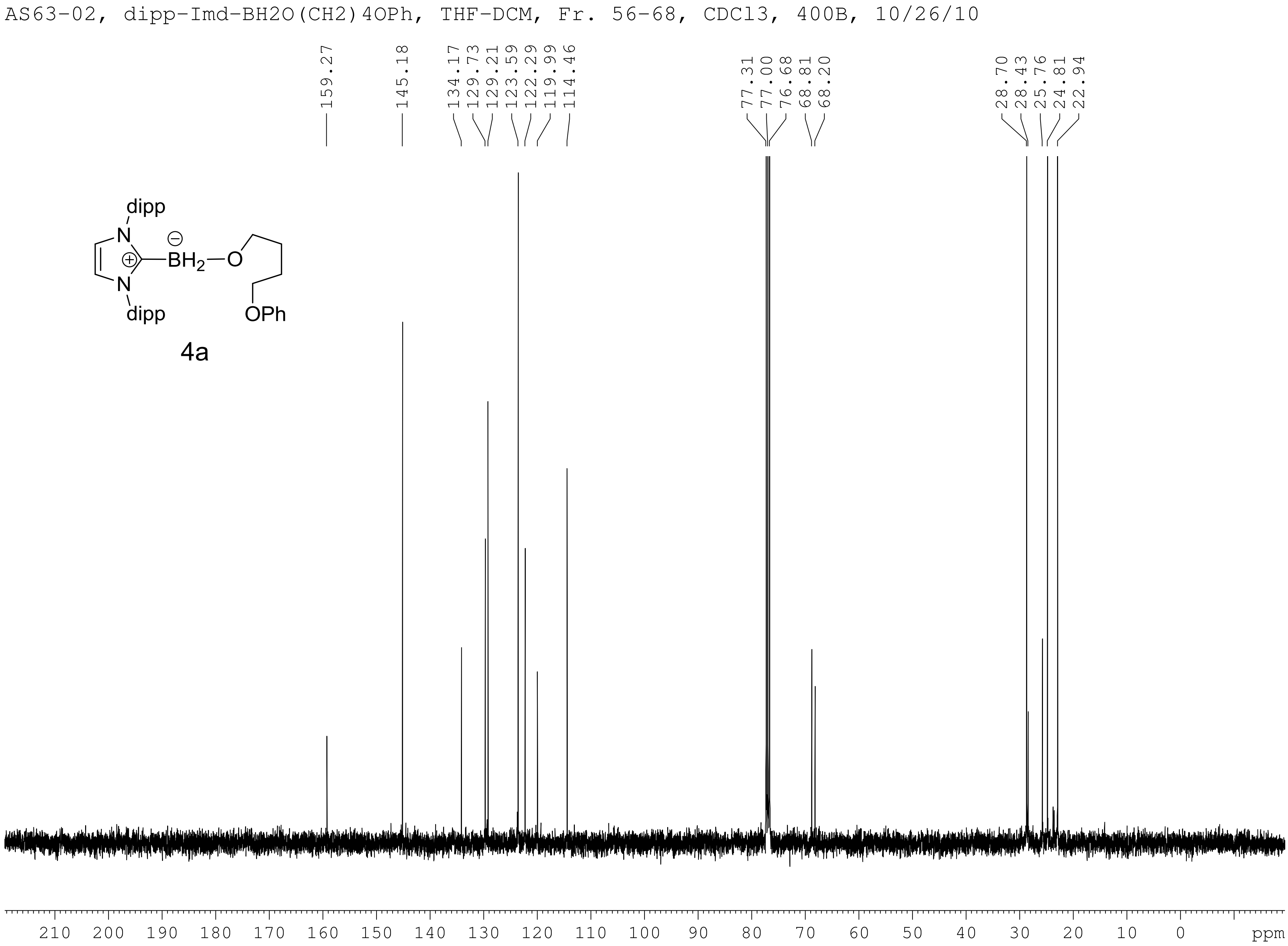
7.427
7.407
7.284
7.270
7.263
7.251
7.244
6.995
6.928
6.925
6.909
6.891
6.889
6.862
6.859
6.840
6.838
3.716
3.698
3.681
2.867
2.850
2.834
2.699
2.682
2.664
2.647
2.630
2.613
2.596
1.329
1.312
1.287
1.279
1.262
1.257
1.240
1.186
1.169
1.106
1.089
1.069
1.059
1.052
1.035
dipp
N
BH2
O
N
dipp
OPh
4a
9
8
7
6
5
4
3
2
1
0
ppm
2.15
6.56
2.00
1.05
2.01
2.01
2.25
4.51
12.61
3.57
12.18
2.67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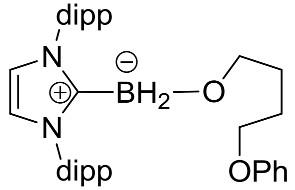
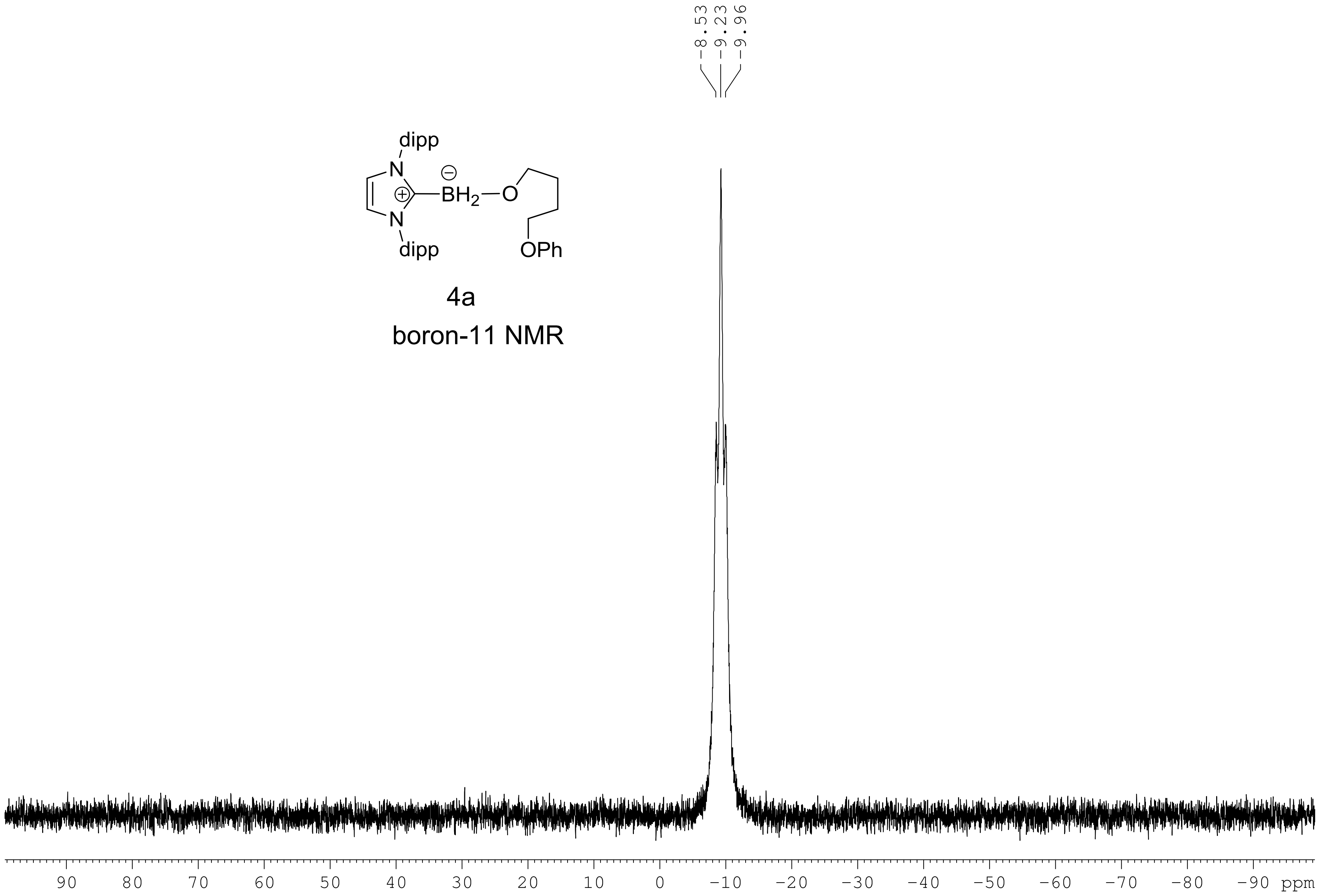
134.17
129.73
129.21
123.59
122.29
119.99
114.46
77.31
77.00
76.68
68.81
68.20
28.70
28.43
25.76
24.81
22.94
dipp
N
BH2
O
OPh
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

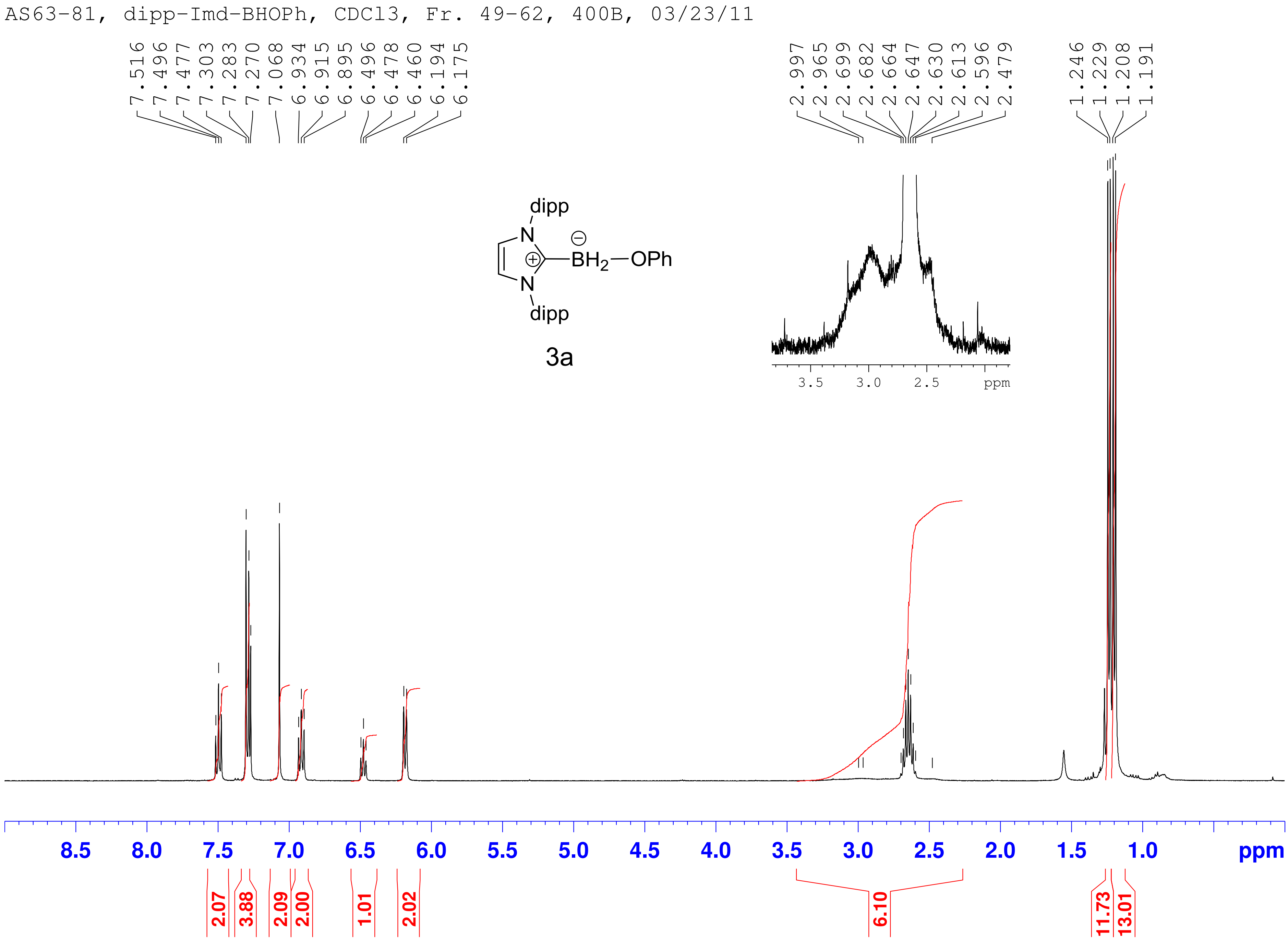
AS63-02, dipp-Imd-BH2O(CH2)4OPh, THF-DCM, Fr. 56-68, CDCl3, 400B, 10/26/10



4a

boron-11 NMR




AS63-81, dipp-Imd-BHOPh, CDCl3, Fr. 49-62, 400B, 03/23/11
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7.496
7.477
7.303
7.283
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7.068
6.934
6.915
6.895
6.496
6.478
6.460
6.194
6.175
2.997
2.965
2.699
2.682
2.664
2.647
2.630
2.613
2.596
2.479
1.246
1.229
1.208
1.191
dipp
N
BH2—OPh
N
dipp
3.5
3.0
2.5
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
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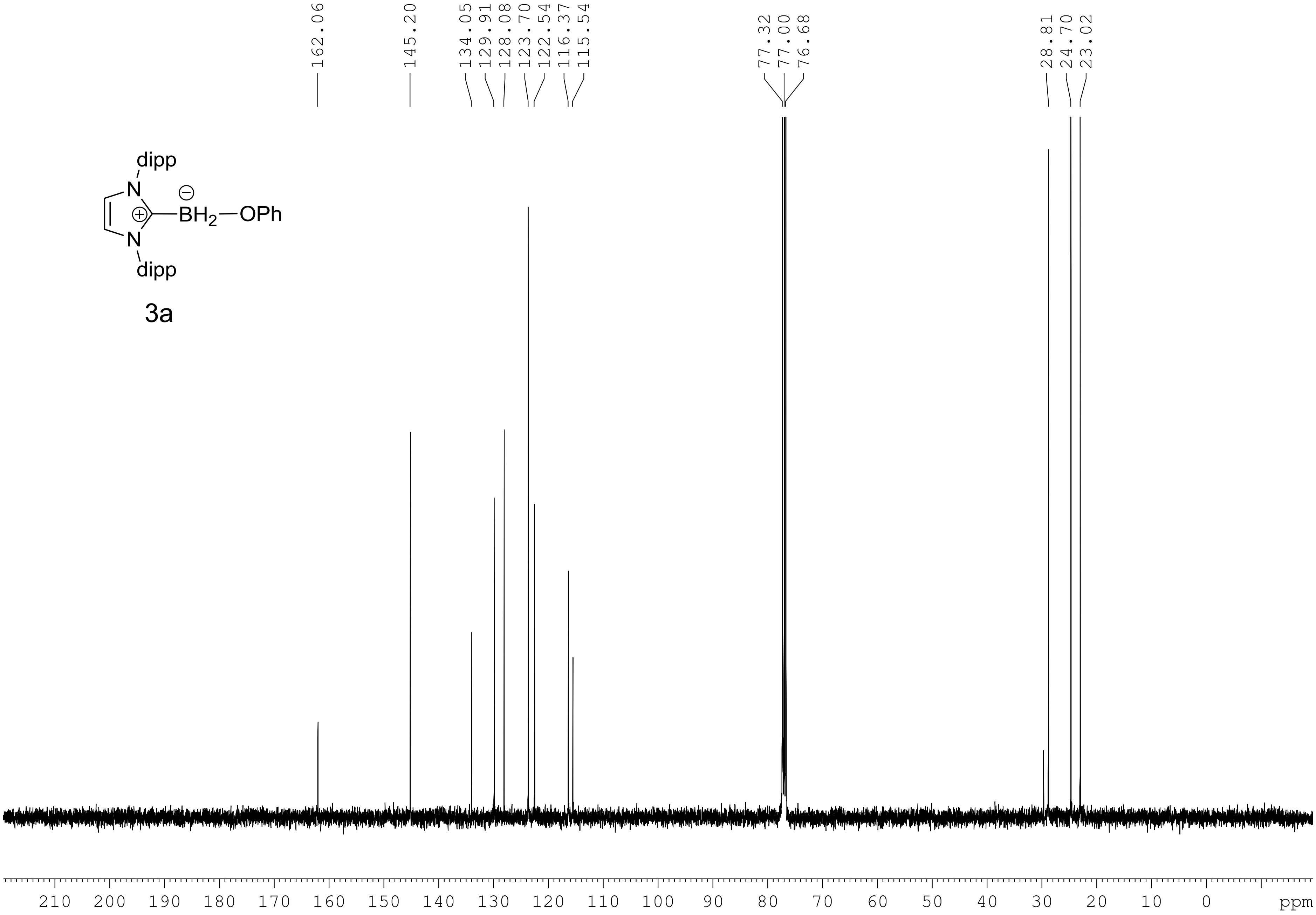
3.88
2.09
2.00
1.01
2.02
6.10
11.73
13.01

3a

AS63-81, dipp-Imd-BHOPh, CDCl3, Fr. 49-62, 400B, 03/29/11



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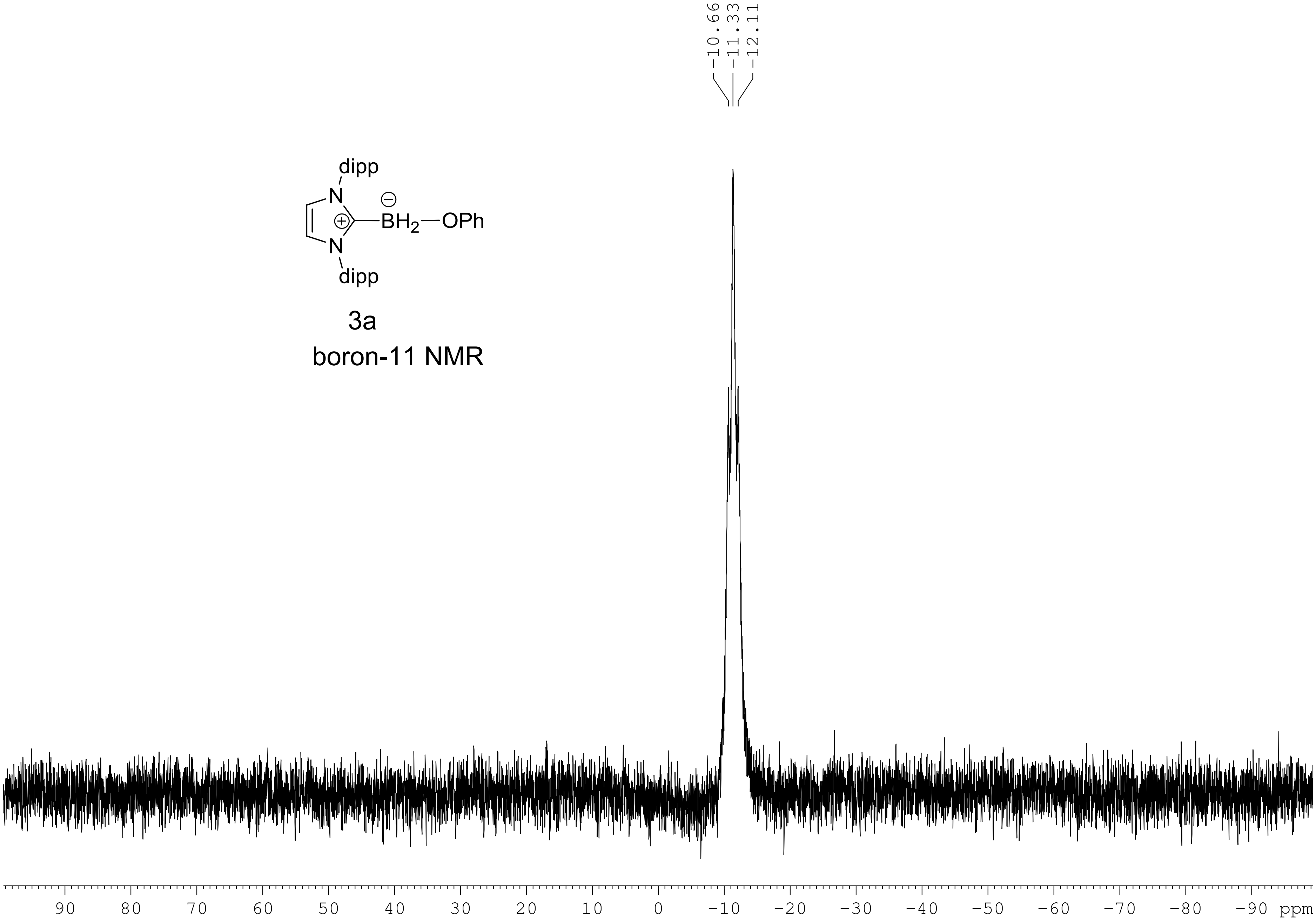
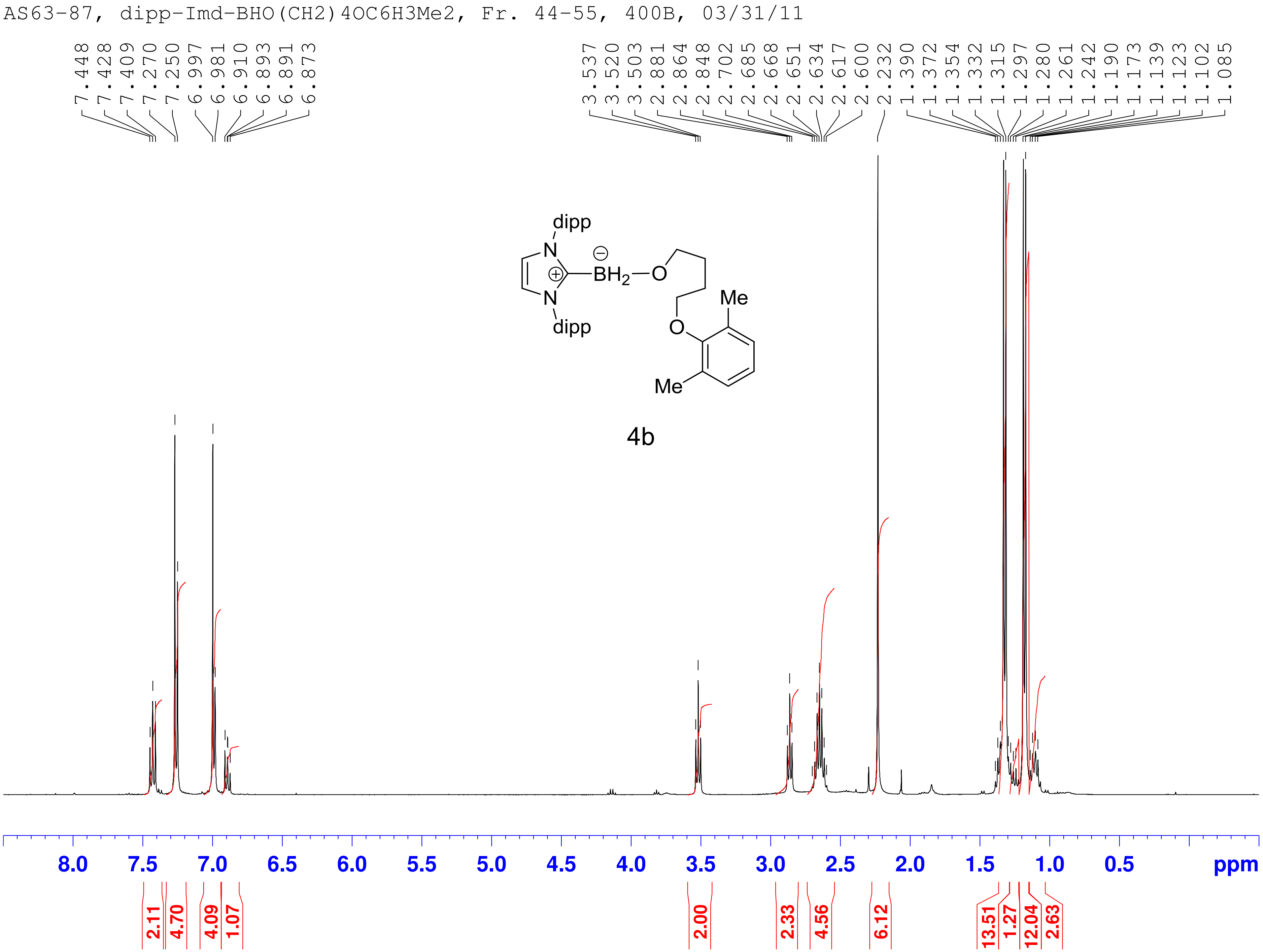


3a

boron-11 NMR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7.250
6.997
6.981
6.910
6.893
6.891
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3.537
3.520
3.503
2.881
2.864
2.848
2.702
2.685
2.668
2.651
2.634
2.617
2.600
2.232
1.390
1.372
1.354
1.332
1.315
1.297
1.280
1.261
1.242
1.190
1.173
1.139
1.123
1.102
1.085
dipp
N
N
dipp
BH2
O
O
Me
Me
4b
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.11
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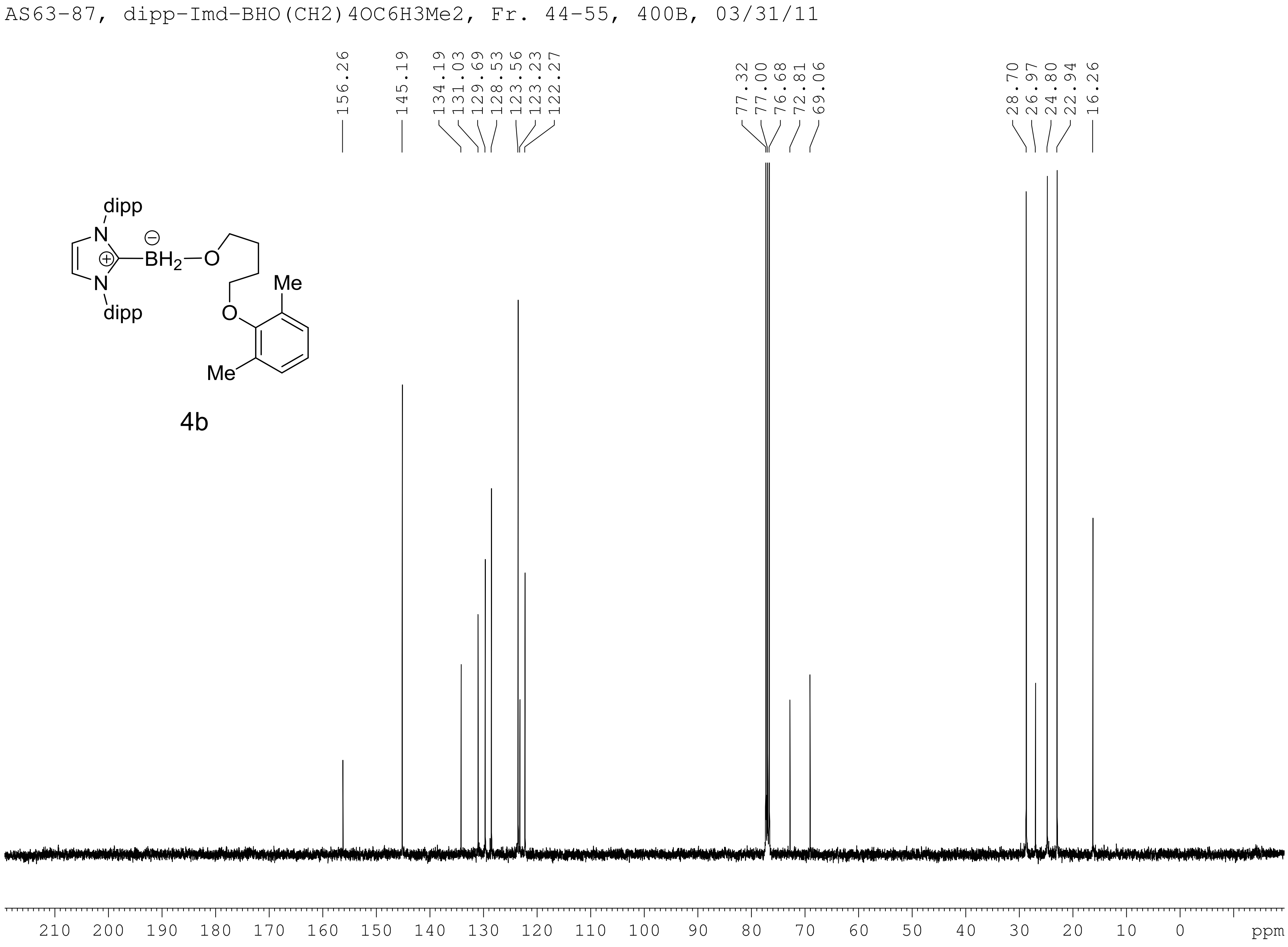
4.09
1.07
2.00
2.33
4.56
6.12
13.51
1.27
12.04
2.63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134.19
131.03
129.69
128.53
123.56
123.23
122.27
77.32
77.00
76.68
72.81
69.06
28.70
26.97
24.80
22.94
16.26
dipp
N
N
dipp
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Me
Me
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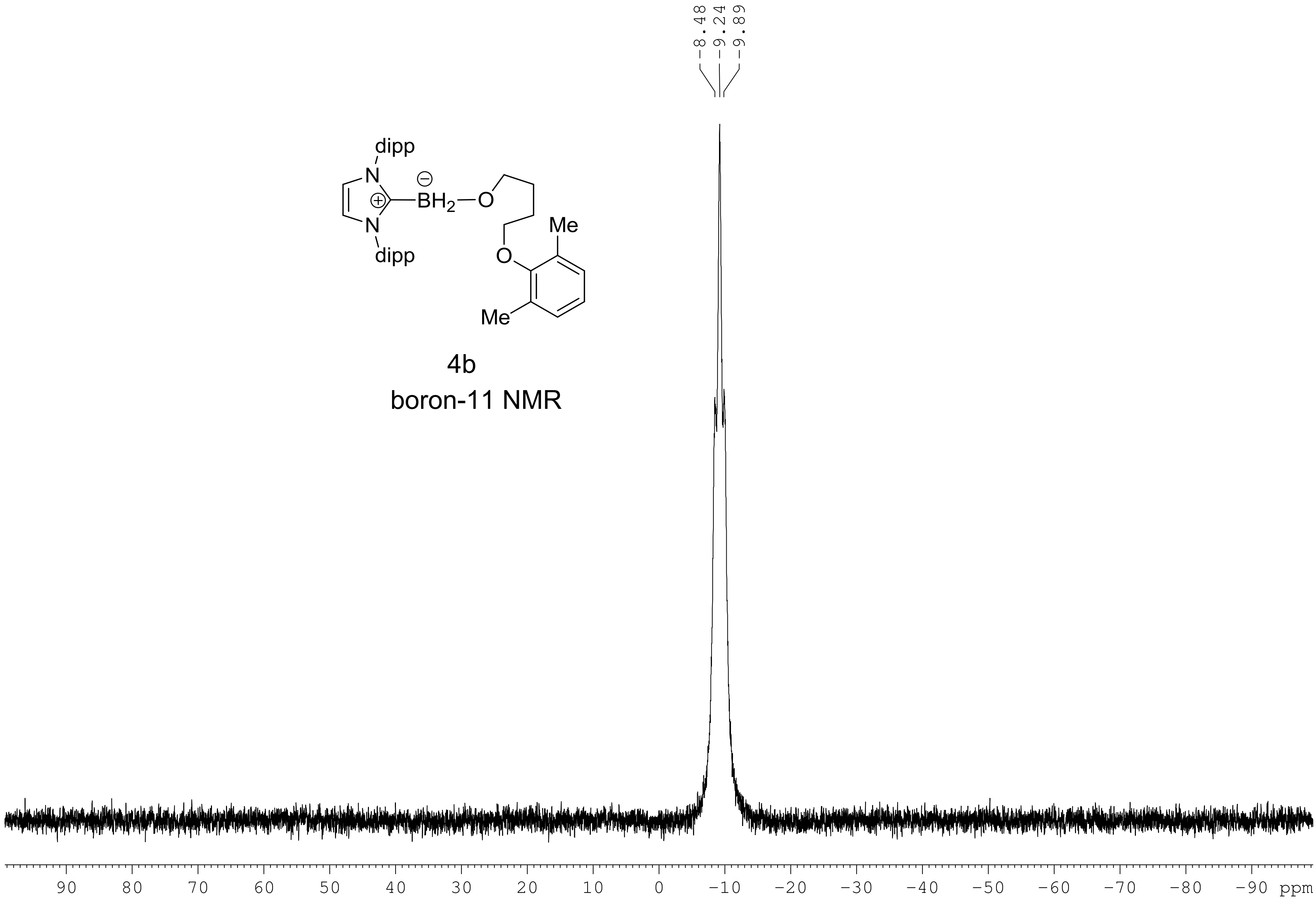
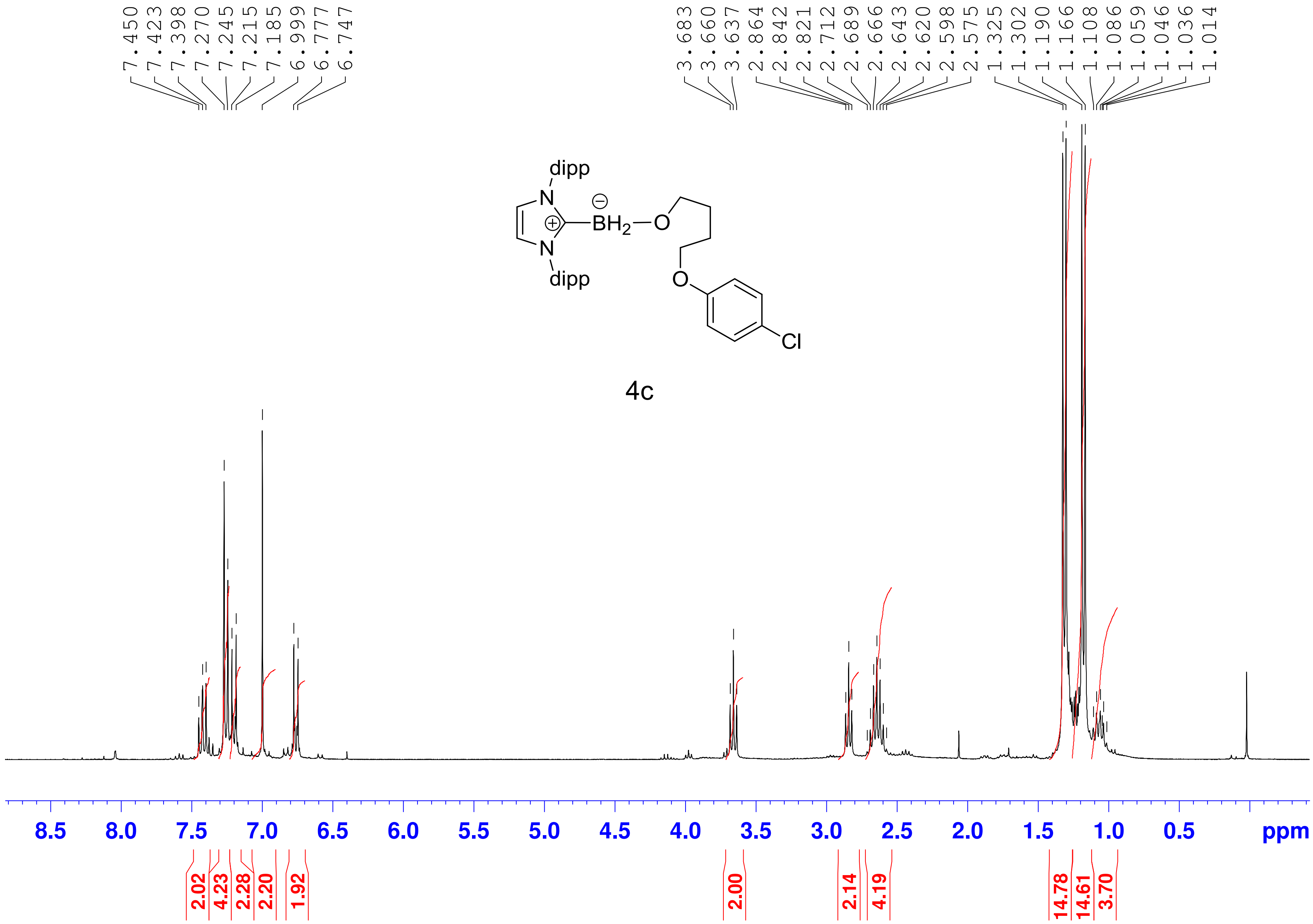
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4b

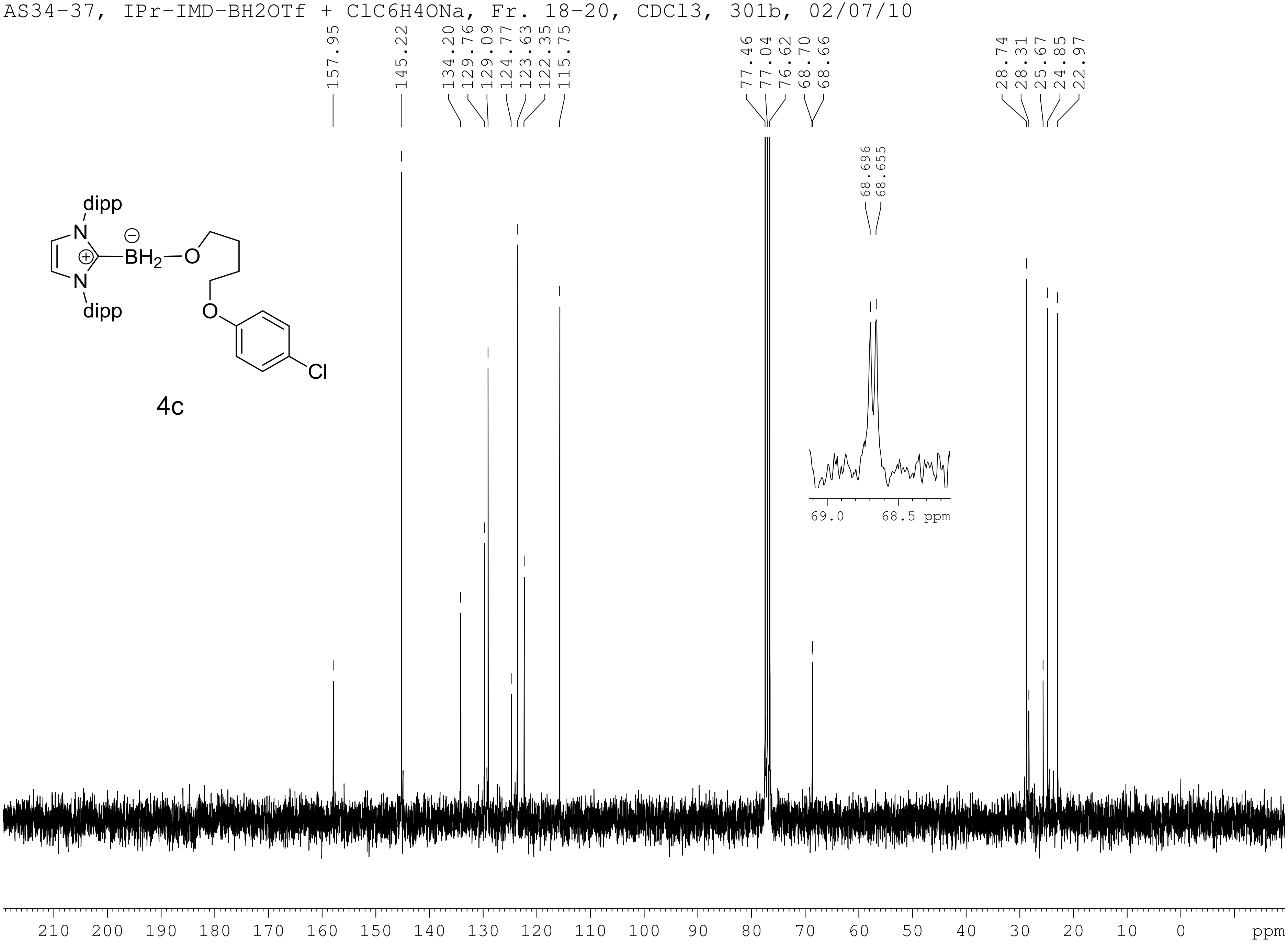
AS63-87, dipp-Imd-BHO(CH2)4OC6H3Me2, Fr. 44-55, 400B, 03/31/11



AS34-37, IPr-IMD-BH2OTf + ClC6H4ONa, Fr. 18-20, CDCl3, 301b, 02/07/10



4c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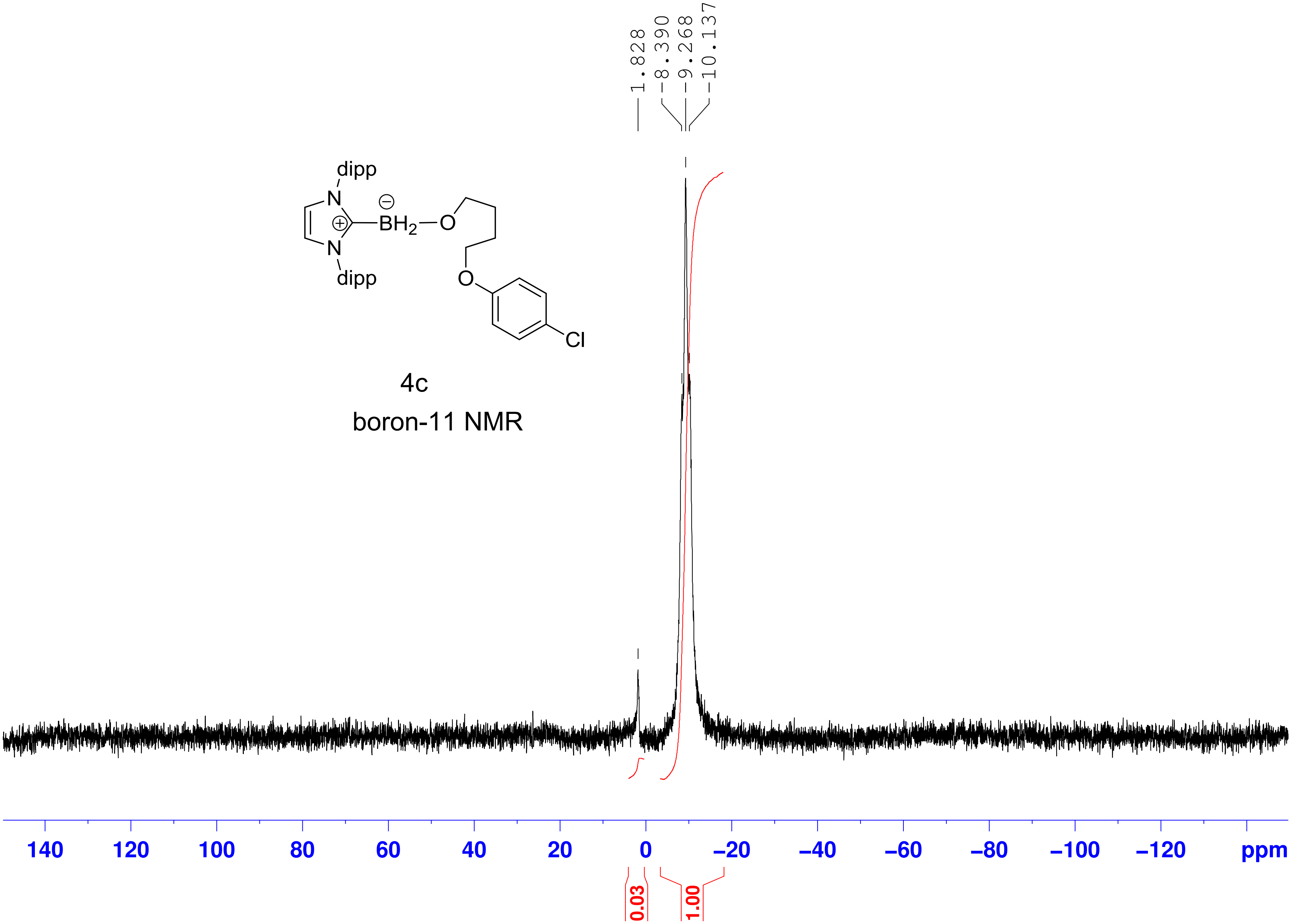
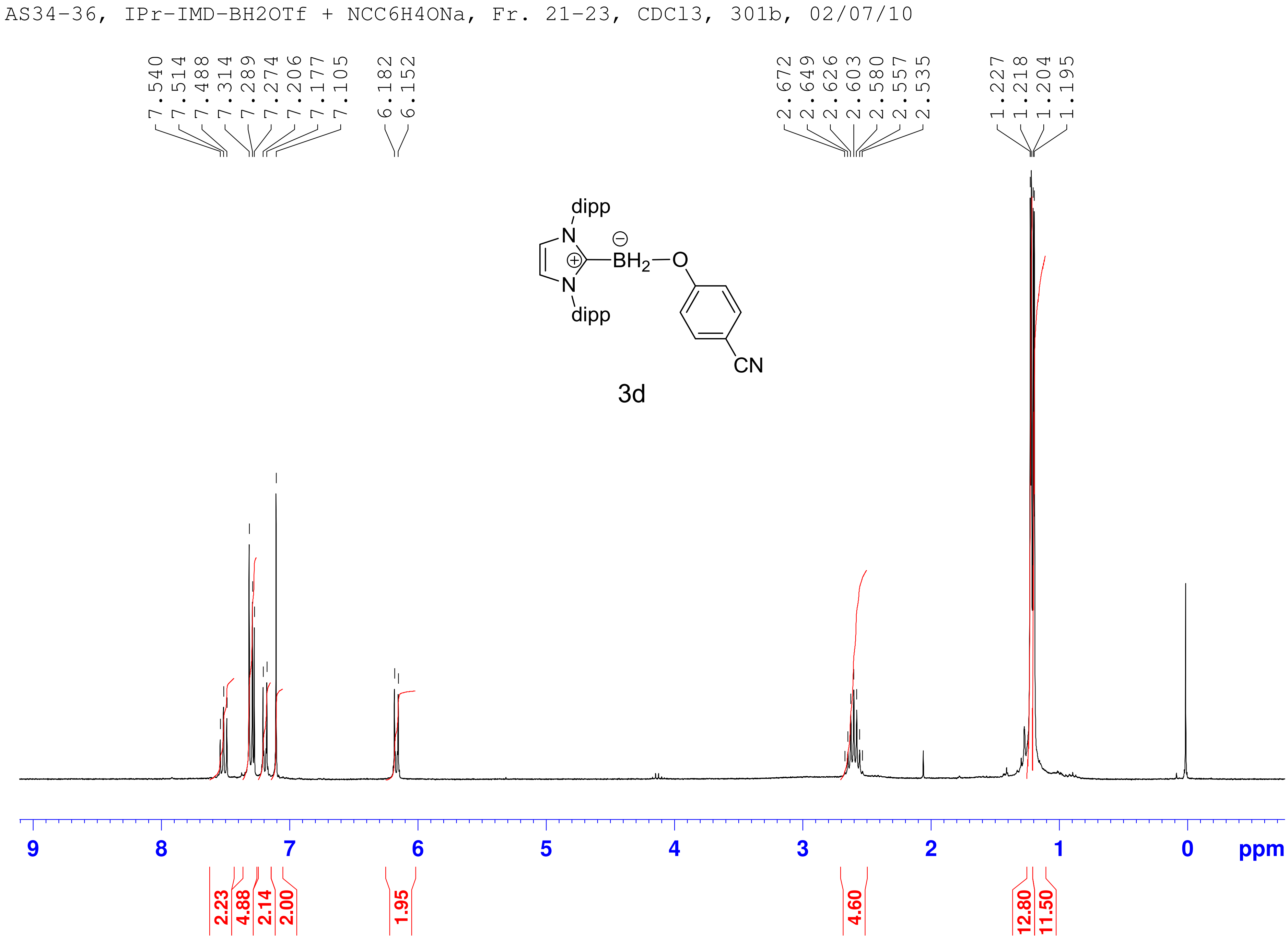
129.76
129.09
124.77
123.63
122.35
115.75
77.46
77.04
76.62
68.70
68.66
28.74
28.31
25.67
24.85
22.97
68.696
68.655
69.0
68.5 ppm
dipp
N
BH2
O
N
dipp
O
Cl
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

AS34-37, IPr-IMD-BH2OTf + ClC6H4ONa, Fr. 18-20, CDCl3, 301b, 02/07/10



4c

boron-11 NMR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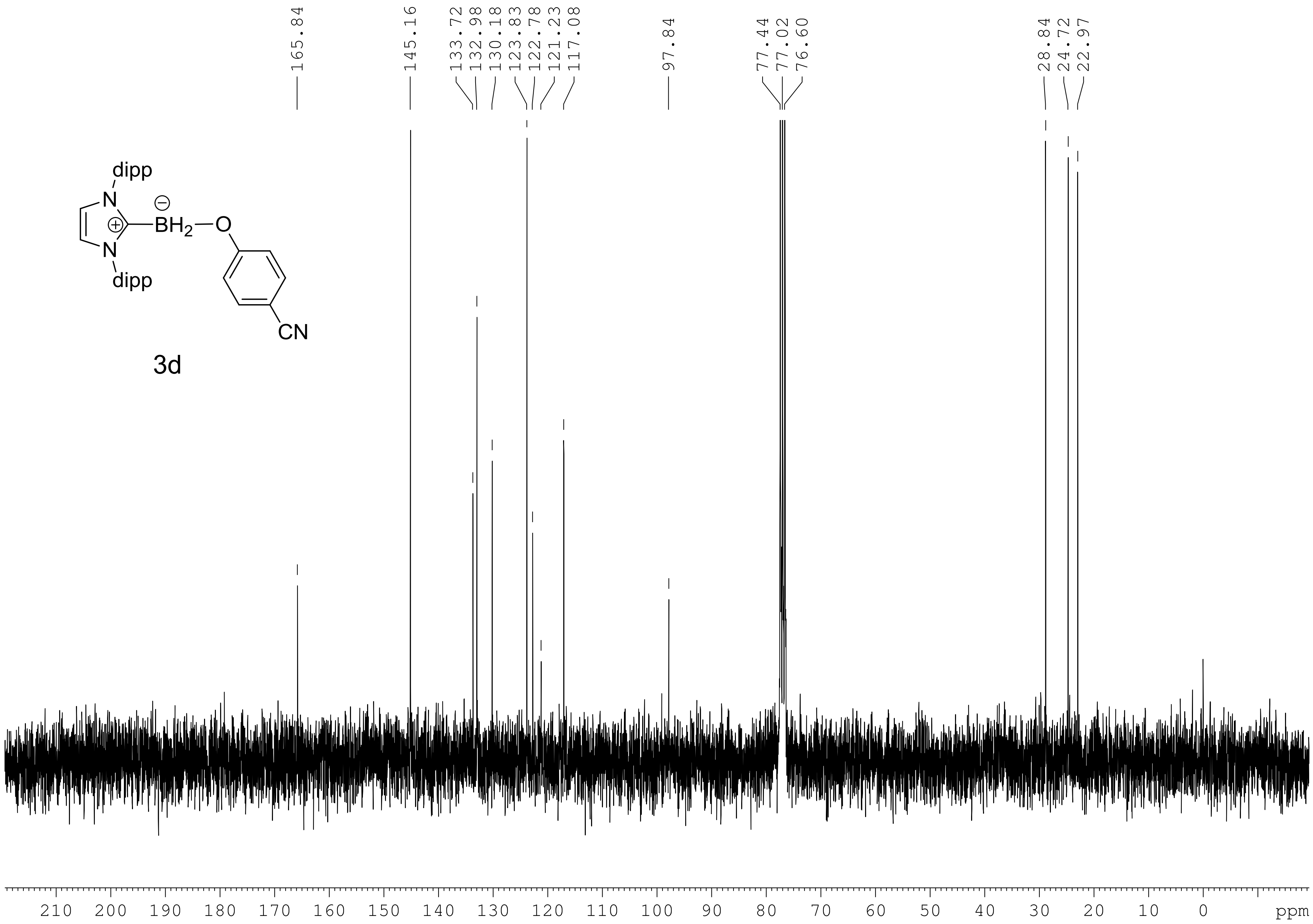
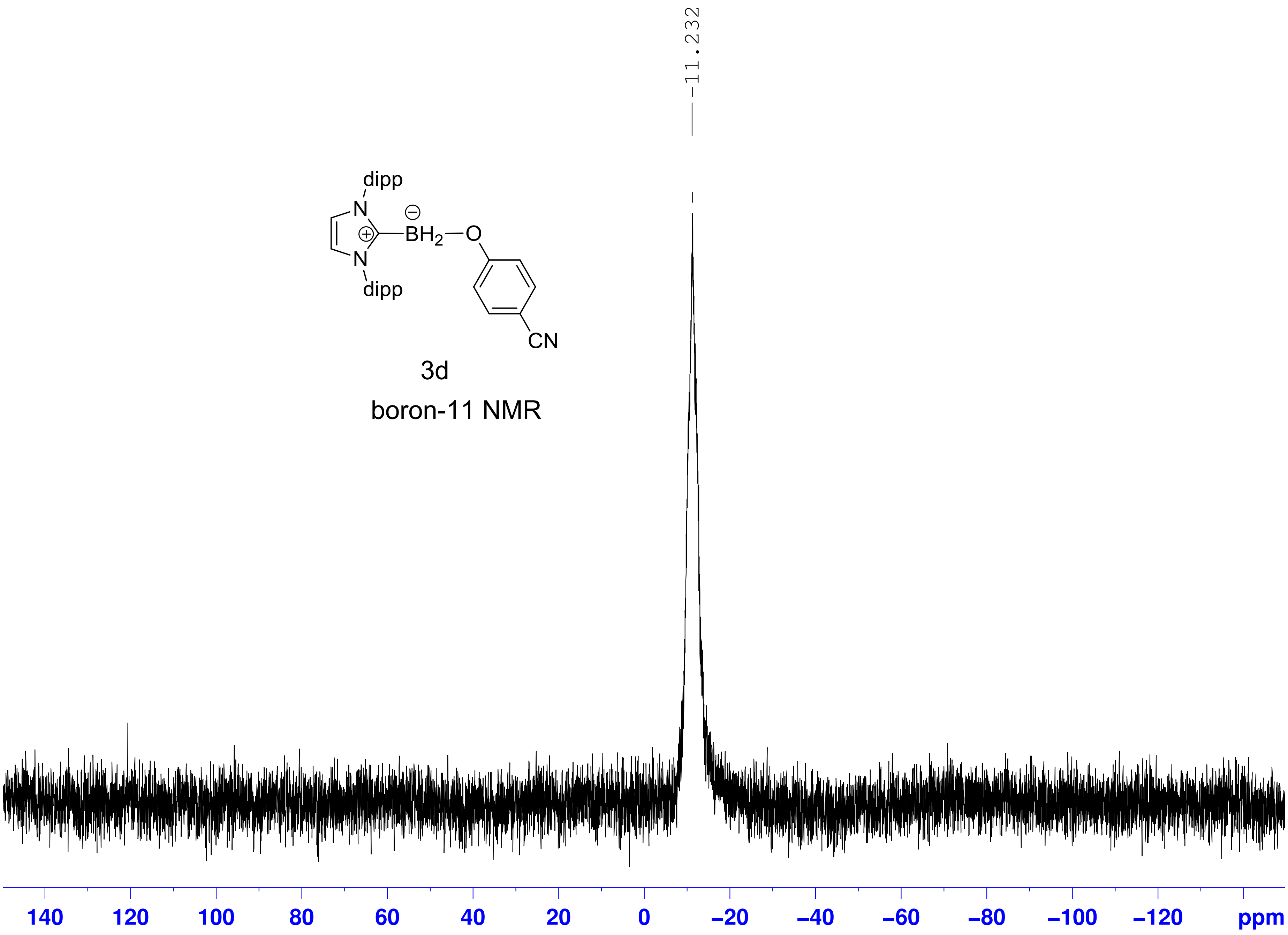
7.314
7.289
7.274
7.206
7.177
7.105
6.182
6.152
2.672
2.649
2.626
2.603
2.580
2.557
2.535
1.227
1.218
1.204
1.195
dipp
N
BH2
O
N
dipp
CN
3d
9
8
7
6
5
4
3
2
1
0
ppm
2.23
4.88
2.14
2.00
1.95
4.60
12.80
11.50

AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 21-23, CDCl3, 301b, 02/07/10



AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 21-23, CDCl3, 301b, 02/07/10



3d

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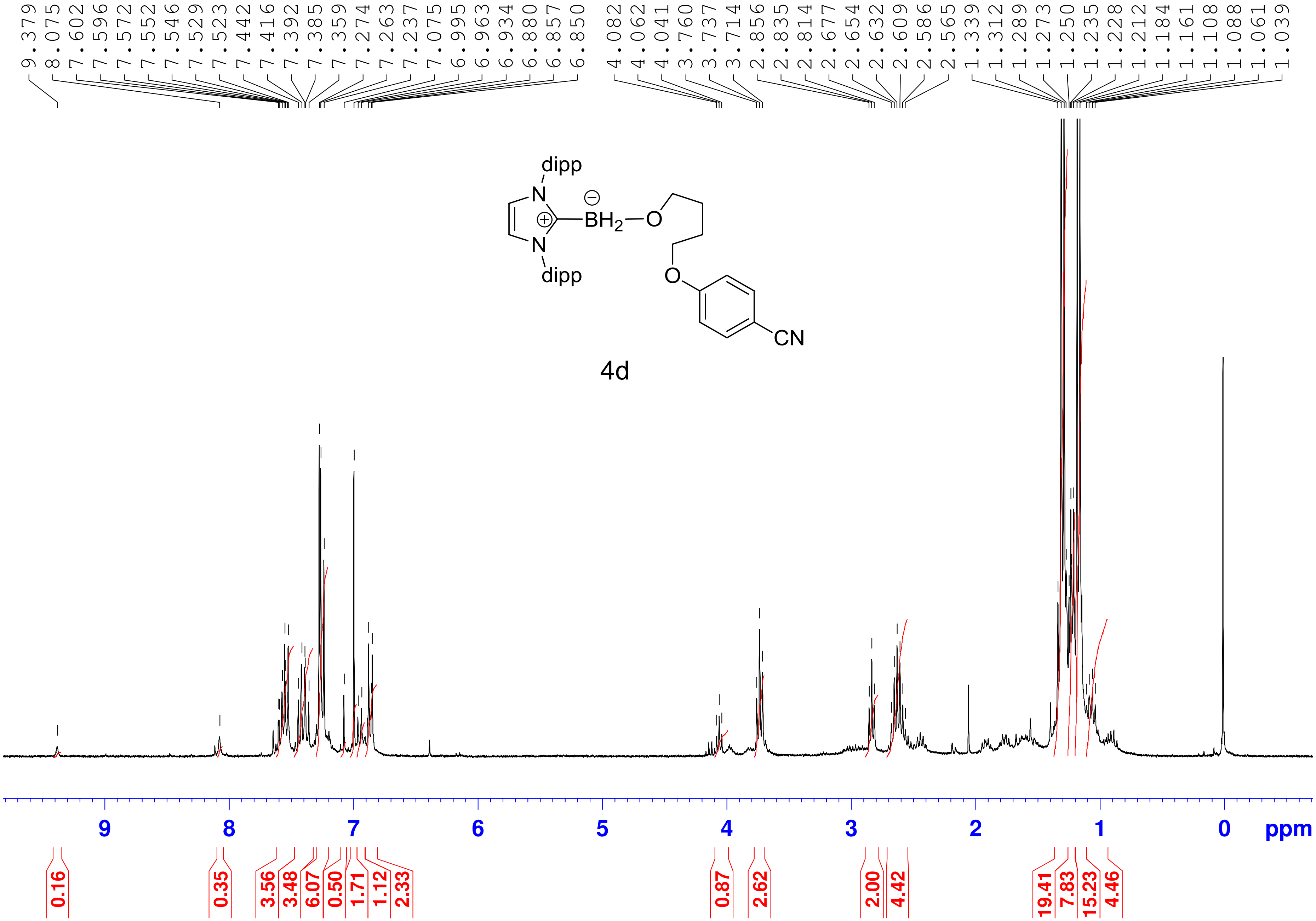
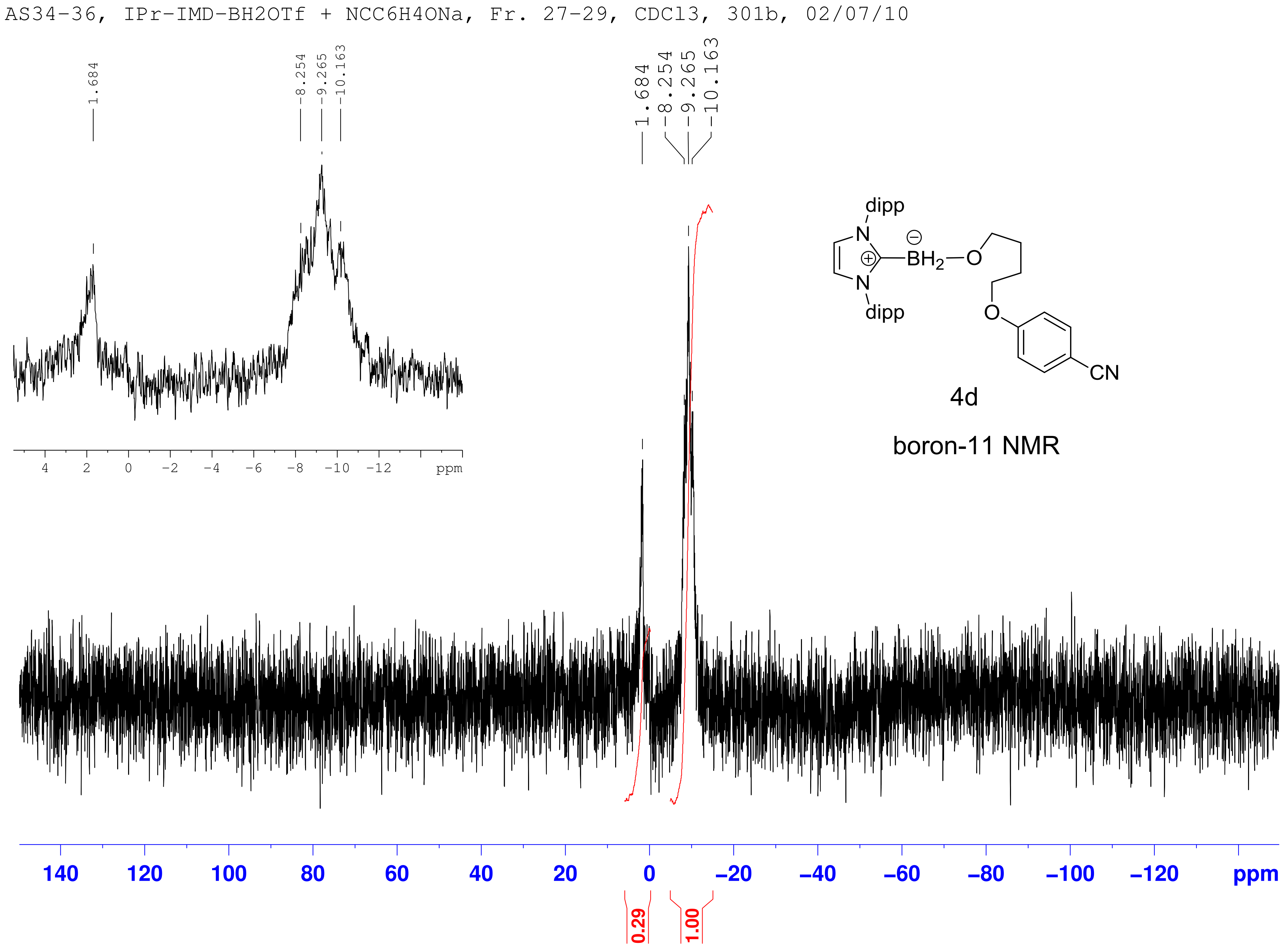
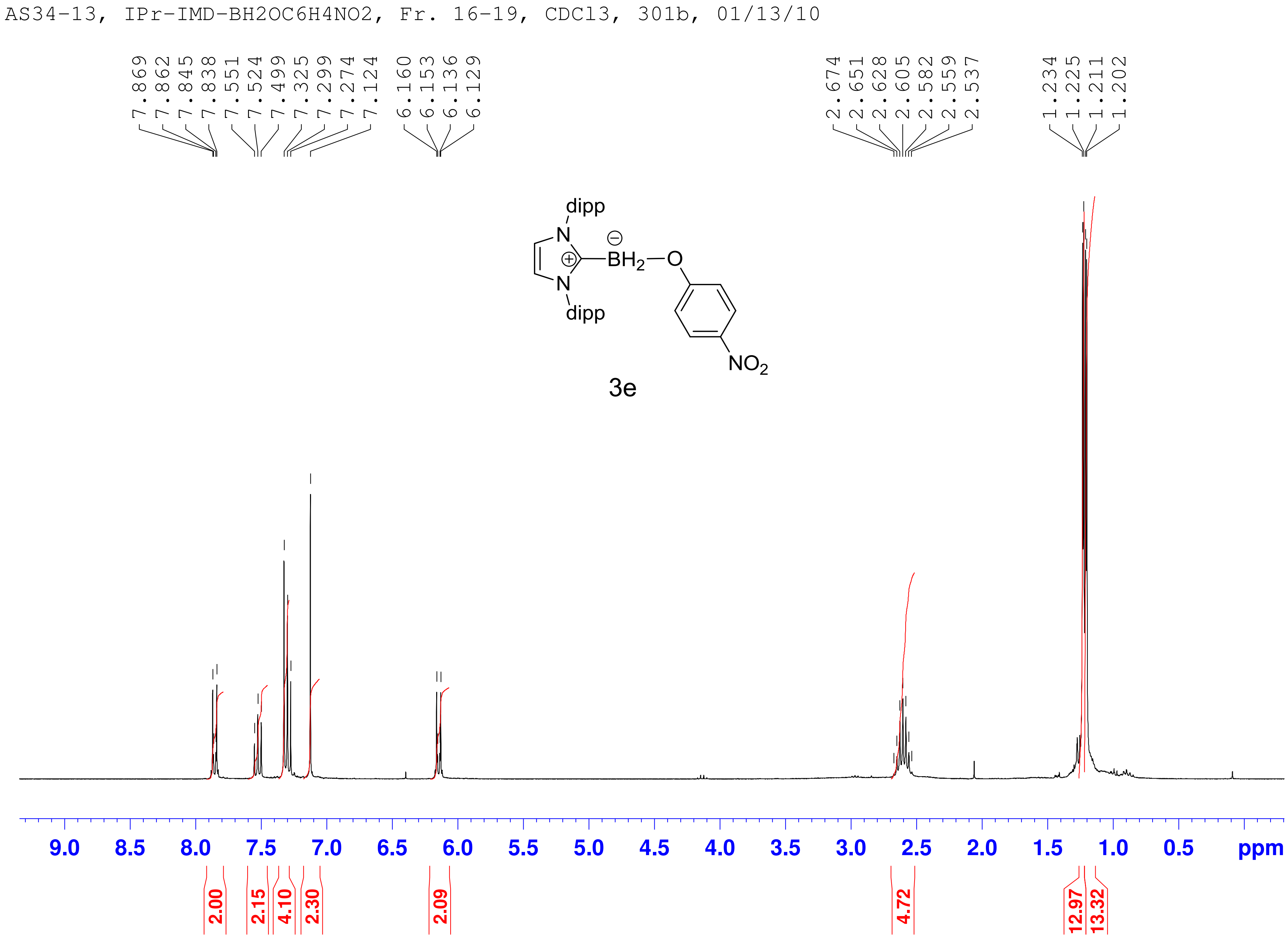
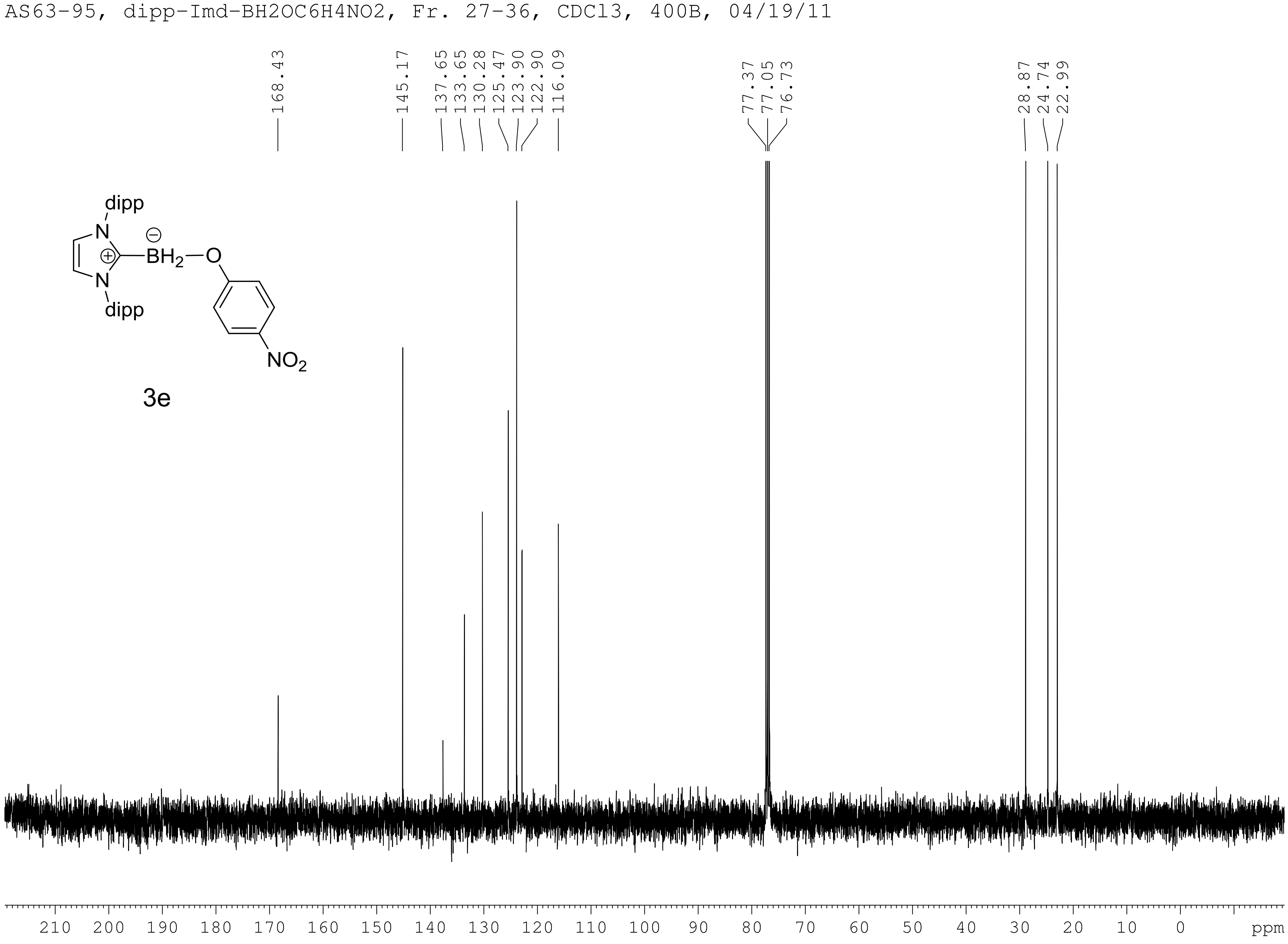
AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 27-29, CDCl3, 301b, 02/07/10



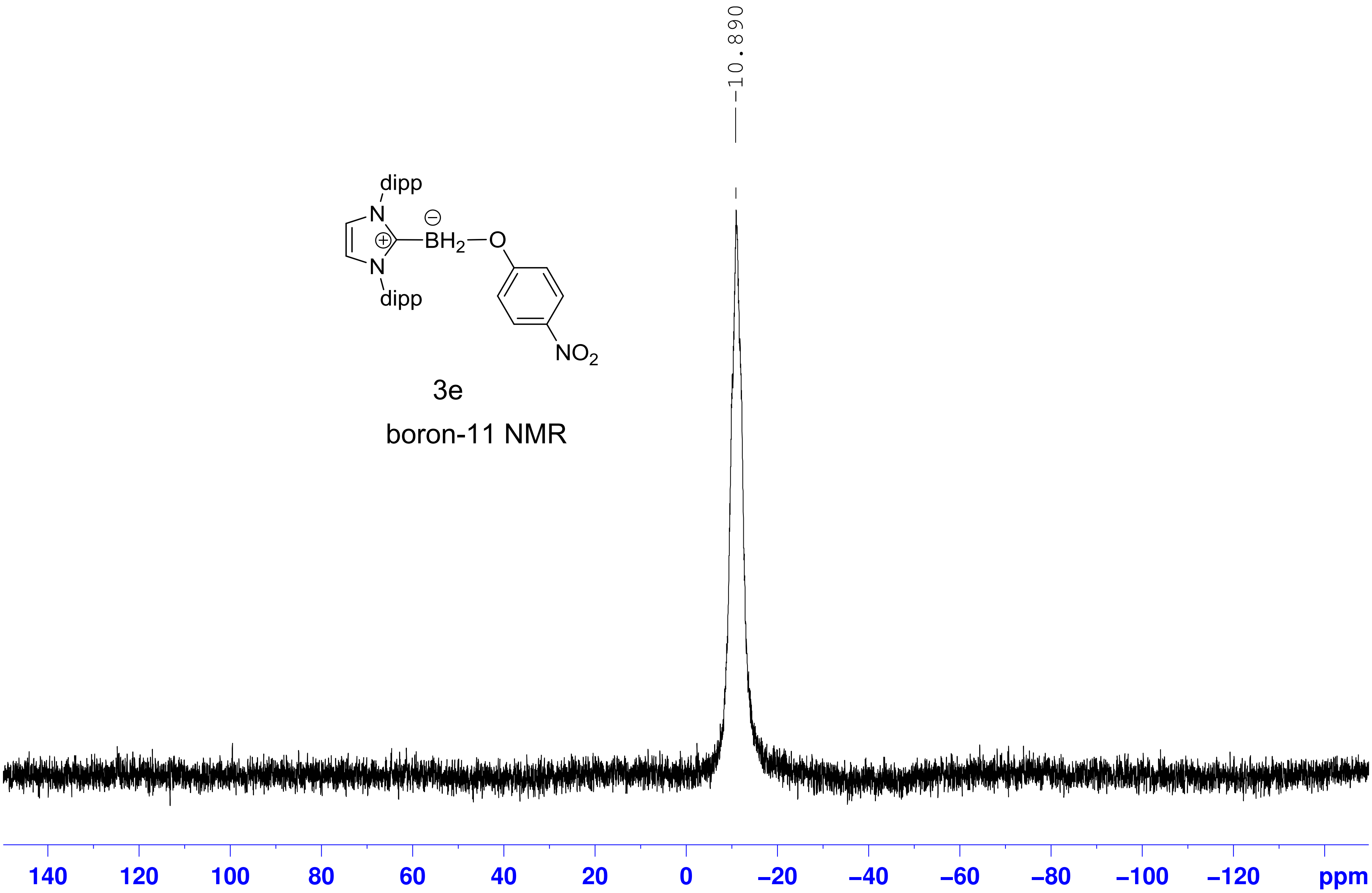

AS34-36, IPr-IMD-BH2OTf + NCC6H4ONa, Fr. 27-29, CDCl3, 301b, 02/07/10
1.684
-8.254
-9.265
-10.163
4
2
0
-2
-4
-6
-8
-10
-12
ppm
dipp
N
N
dipp
BH2
O
O
CN
4d
boron-11 NMR
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
ppm
0.29
1.00


AS34-13, IPr-IMD-BH2OC6H4NO2, Fr. 16-19, CDCl3, 301b, 01/13/10
7.869
7.862
7.845
7.838
7.551
7.524
7.499
7.325
7.299
7.274
7.124
6.160
6.153
6.136
6.129
2.674
2.651
2.628
2.605
2.582
2.559
2.537
1.234
1.225
1.211
1.202
dipp
N
BH2
O
N
dipp
NO2
3e
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.15
4.10
2.30
2.09
4.72
12.97
13.32


AS63-95, dipp-Imd-BH2OC6H4NO2, Fr. 27-36, CDCl3, 400B, 04/19/11
168.43
145.17
137.65
133.65
130.28
125.47
123.90
122.90
116.09
77.37
77.05
76.73
28.87
24.74
22.99
dipp
N
BH2
O
N
dipp
NO2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

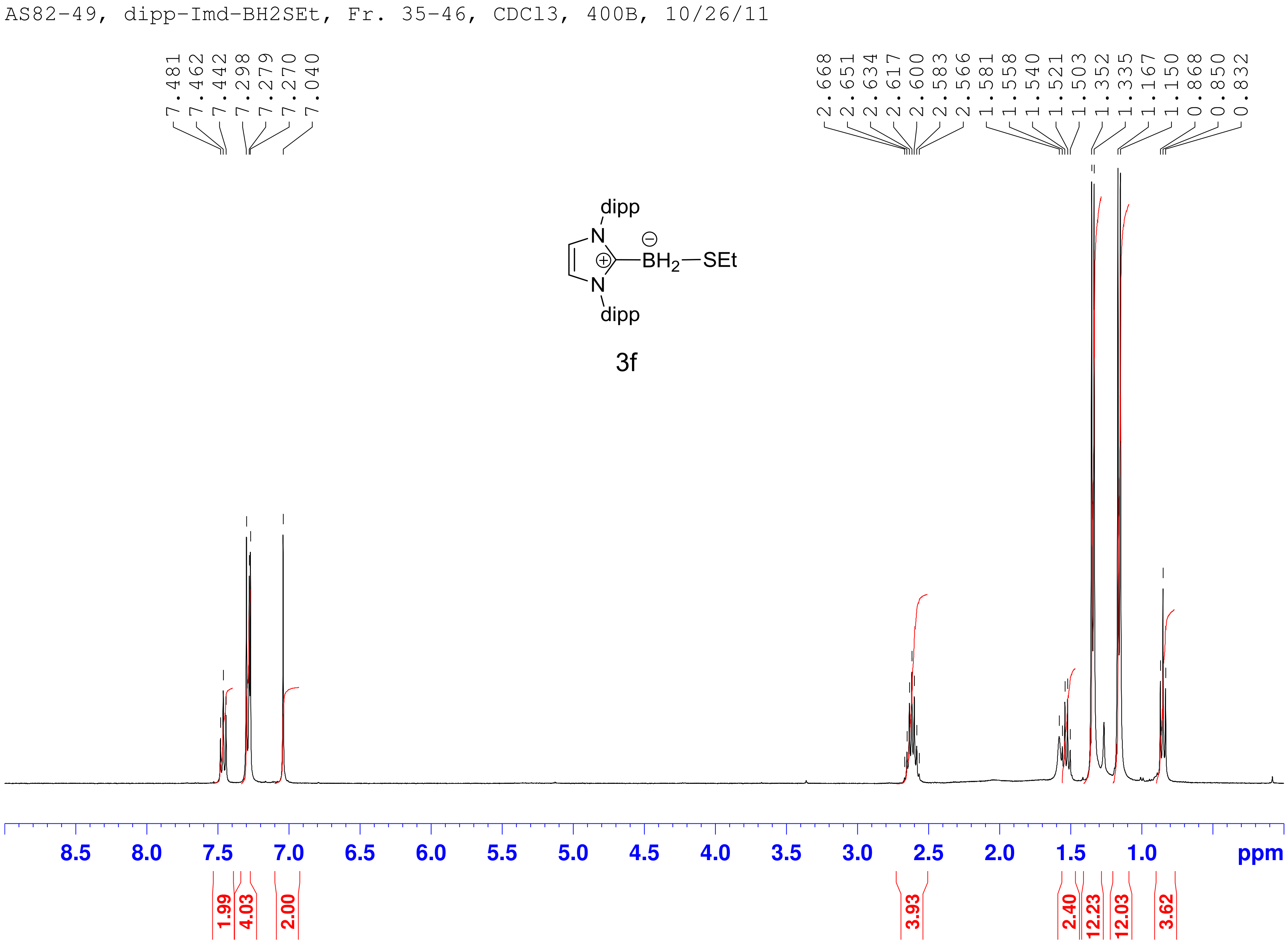
3e

AS34-13, IPr-IMD-BH2OC6H4NO2, Fr. 16-19, CDCl3, 301b, 01/13/10

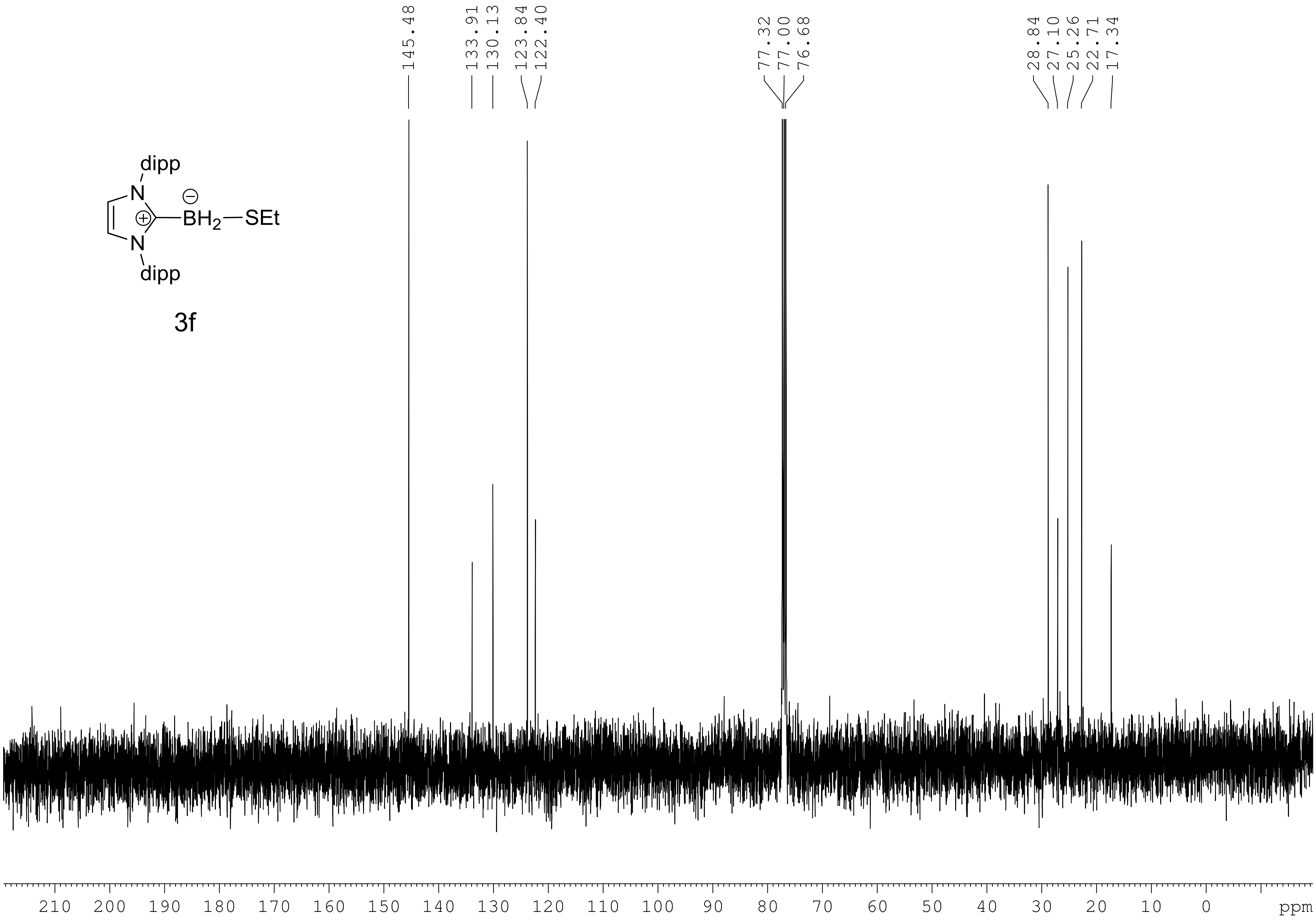


3e

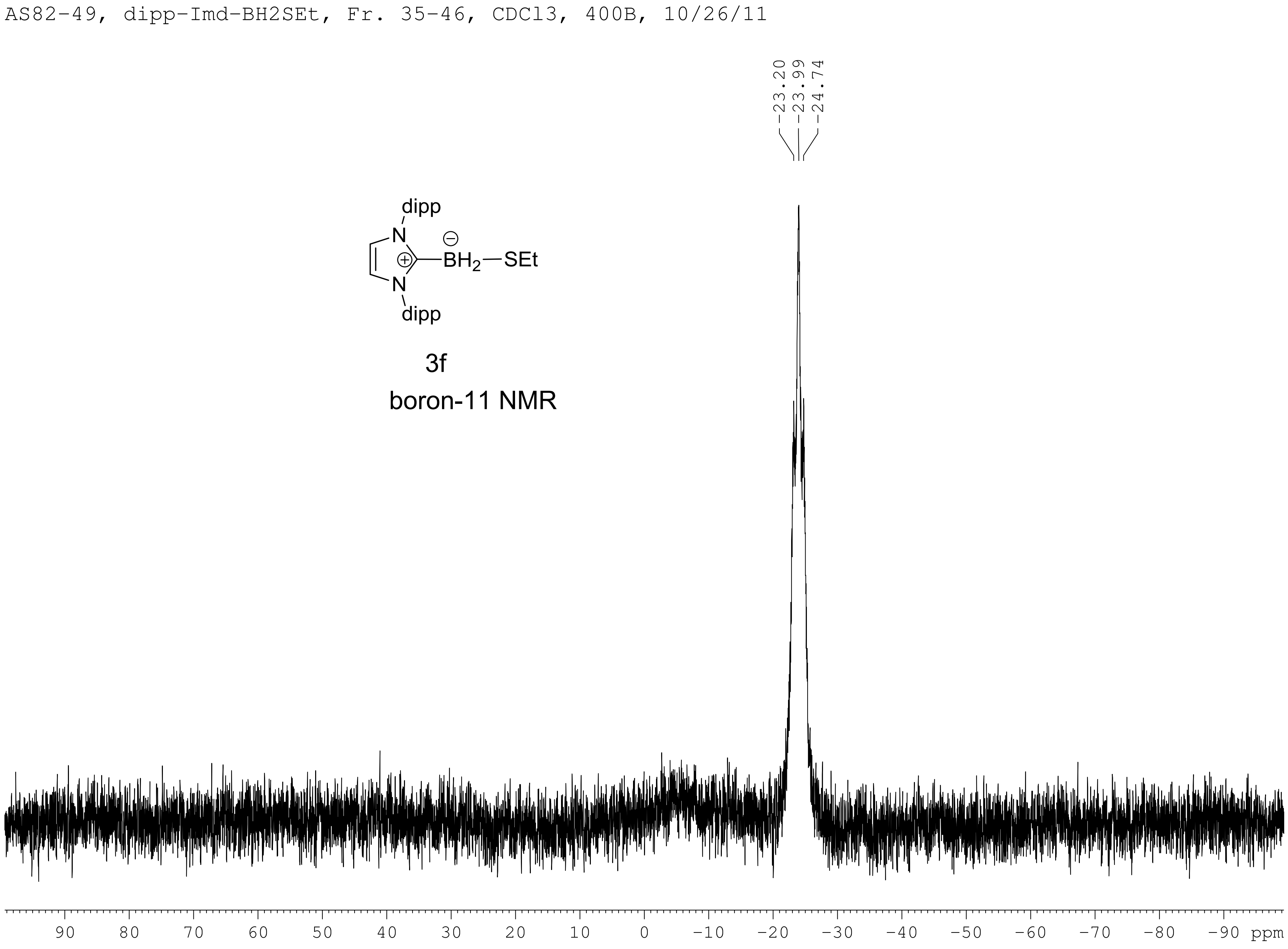
boron-11 NMR


AS82-49, dipp-Imd-BH2SEt, Fr. 35-46, CDCl3, 400B, 10/26/11
7.481
7.462
7.442
7.298
7.279
7.270
7.040
2.668
2.651
2.634
2.617
2.600
2.583
2.566
1.581
1.558
1.540
1.521
1.503
1.352
1.335
1.167
1.150
0.868
0.850
0.832
dipp
N
⊕
⊖
BH2—SEt
N
dipp
3f
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.99
4.03
2.00
3.93
2.40
12.23
12.03
3.62

AS82-49, dipp-Imd-BH2SEt, Fr. 35-46, CDCl3, 400B, 10/26/11



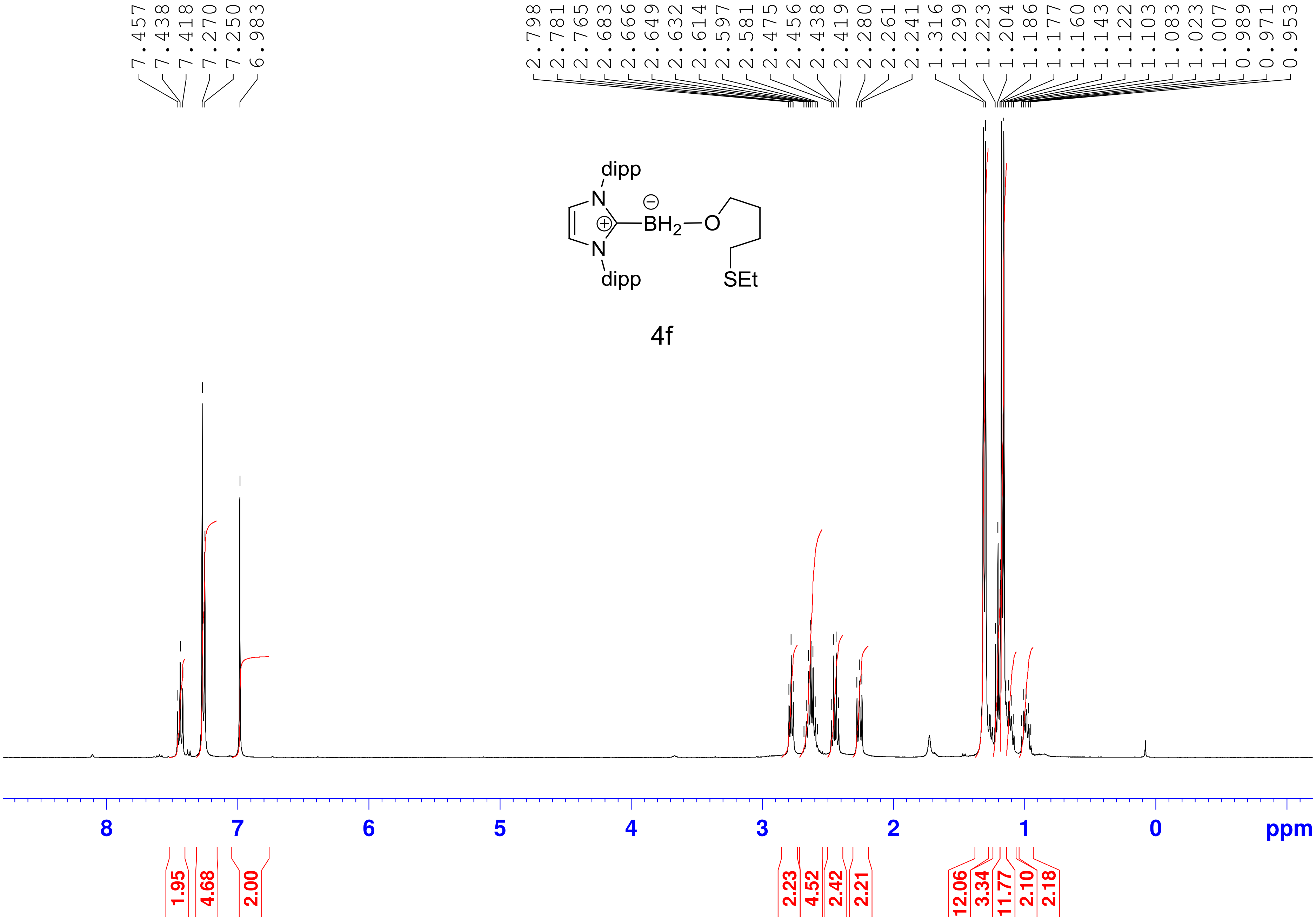
3f



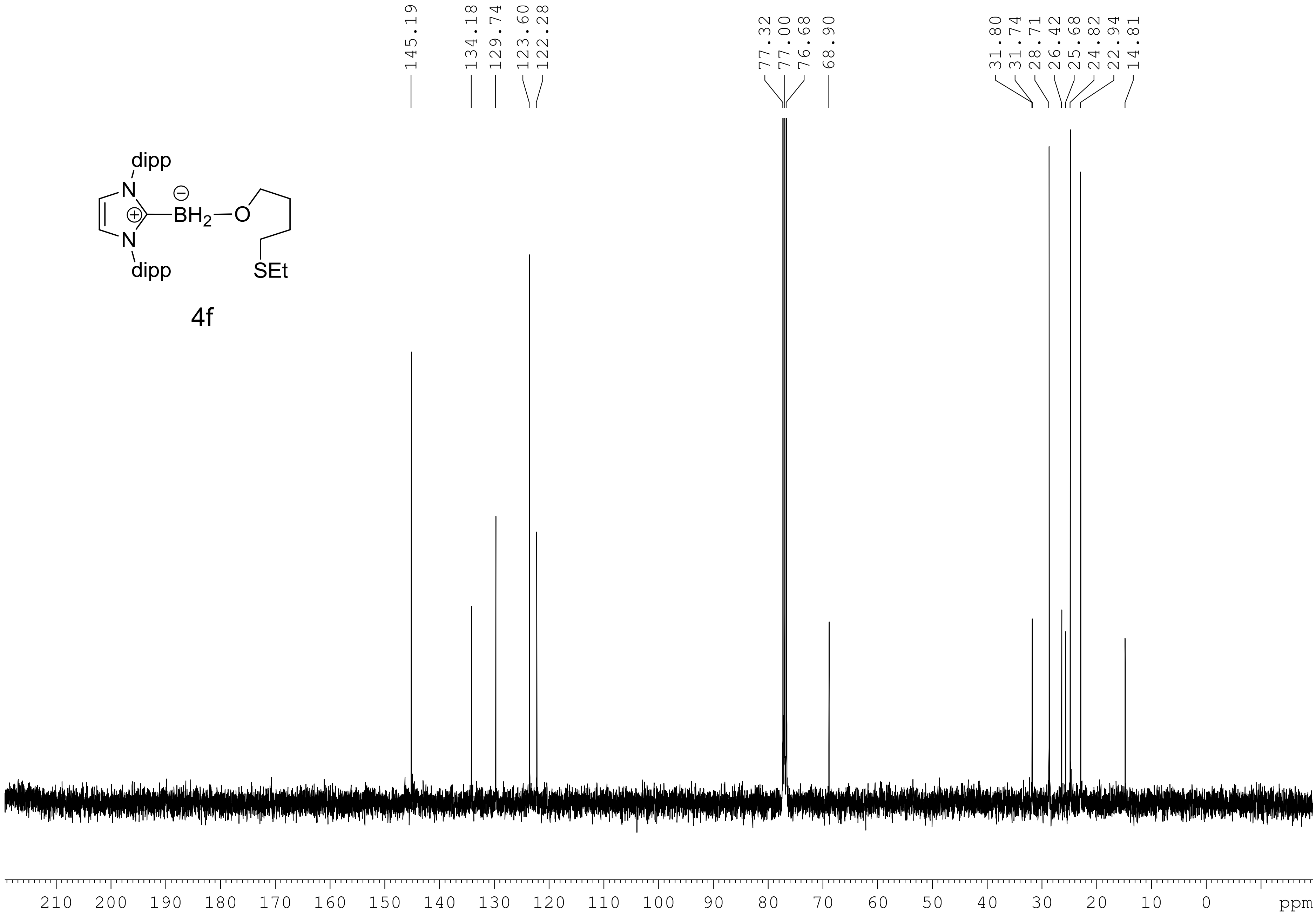
3f

boron-11 NMR

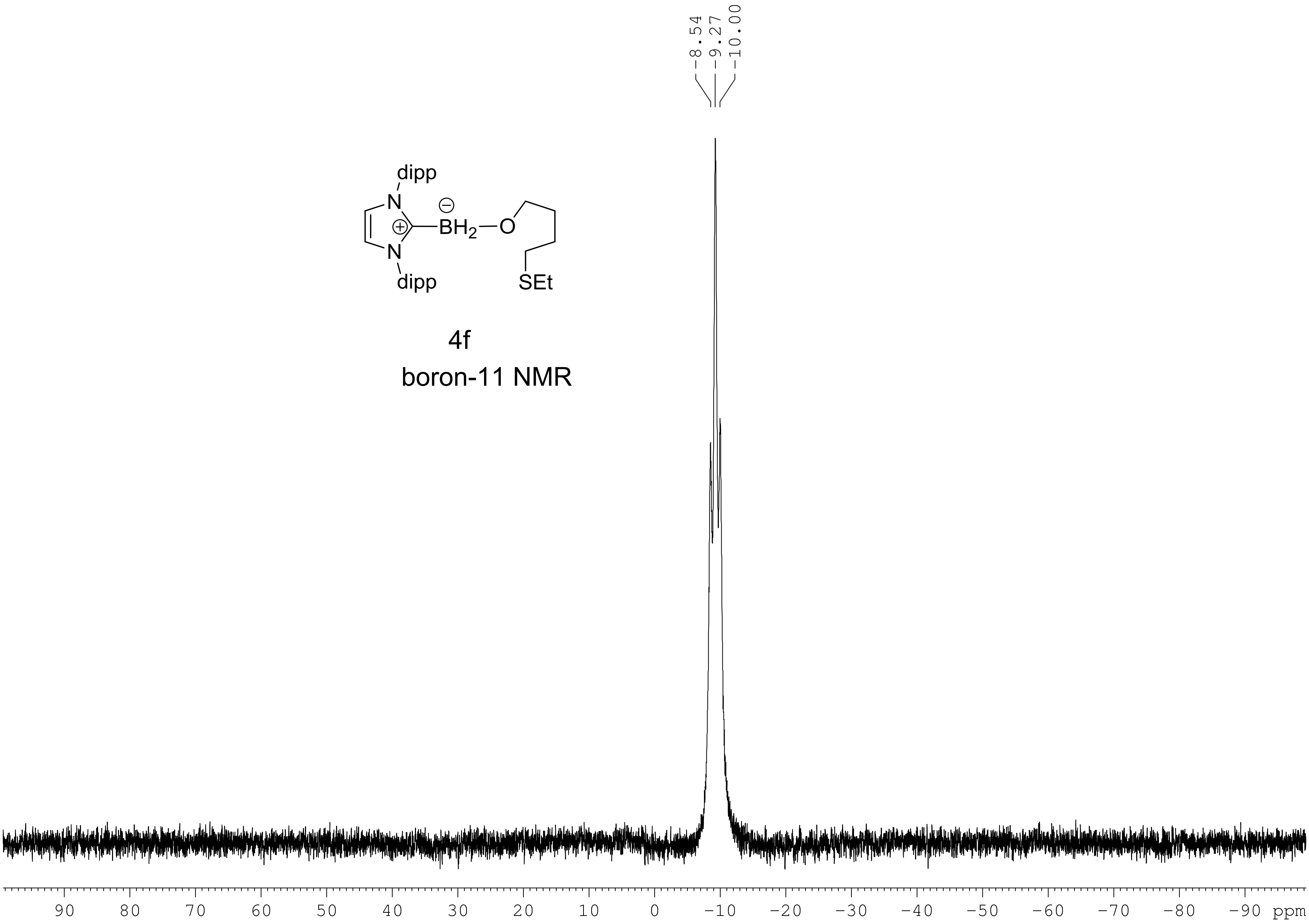
AS82-48, dipp-Imd-BH2O(CH2)4SEt, Fr. 38-46, CDCl3, 400B, 10/21/11



AS82-48, dipp-Imd-BH2O(CH2)4SEt, Fr. 38-46, CDCl3, 400B, 10/21/11



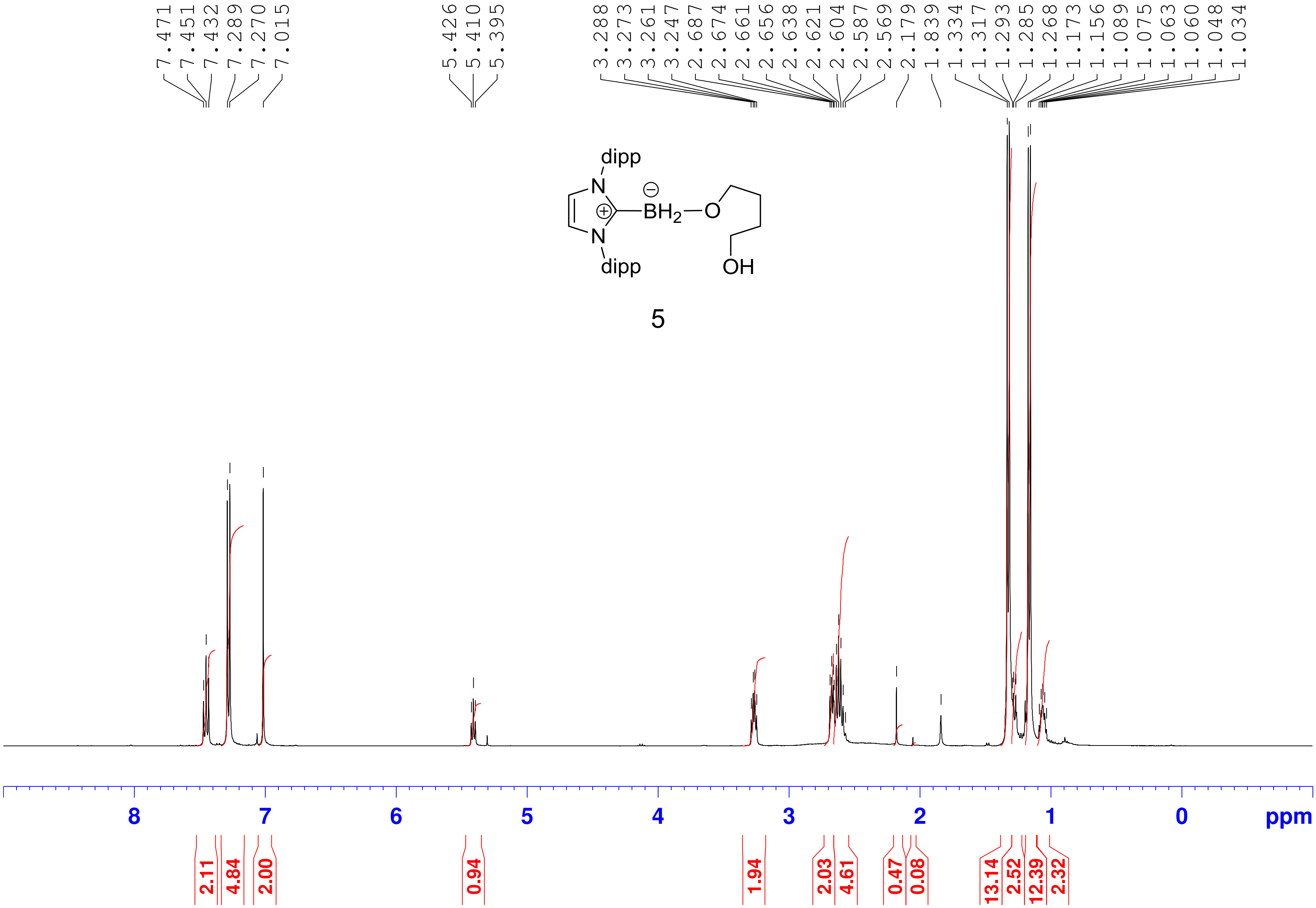
AS82-48, dipp-Imd-BH2O(CH2)4SEt, Fr. 38-46, CDCl3, 400B, 10/21/11



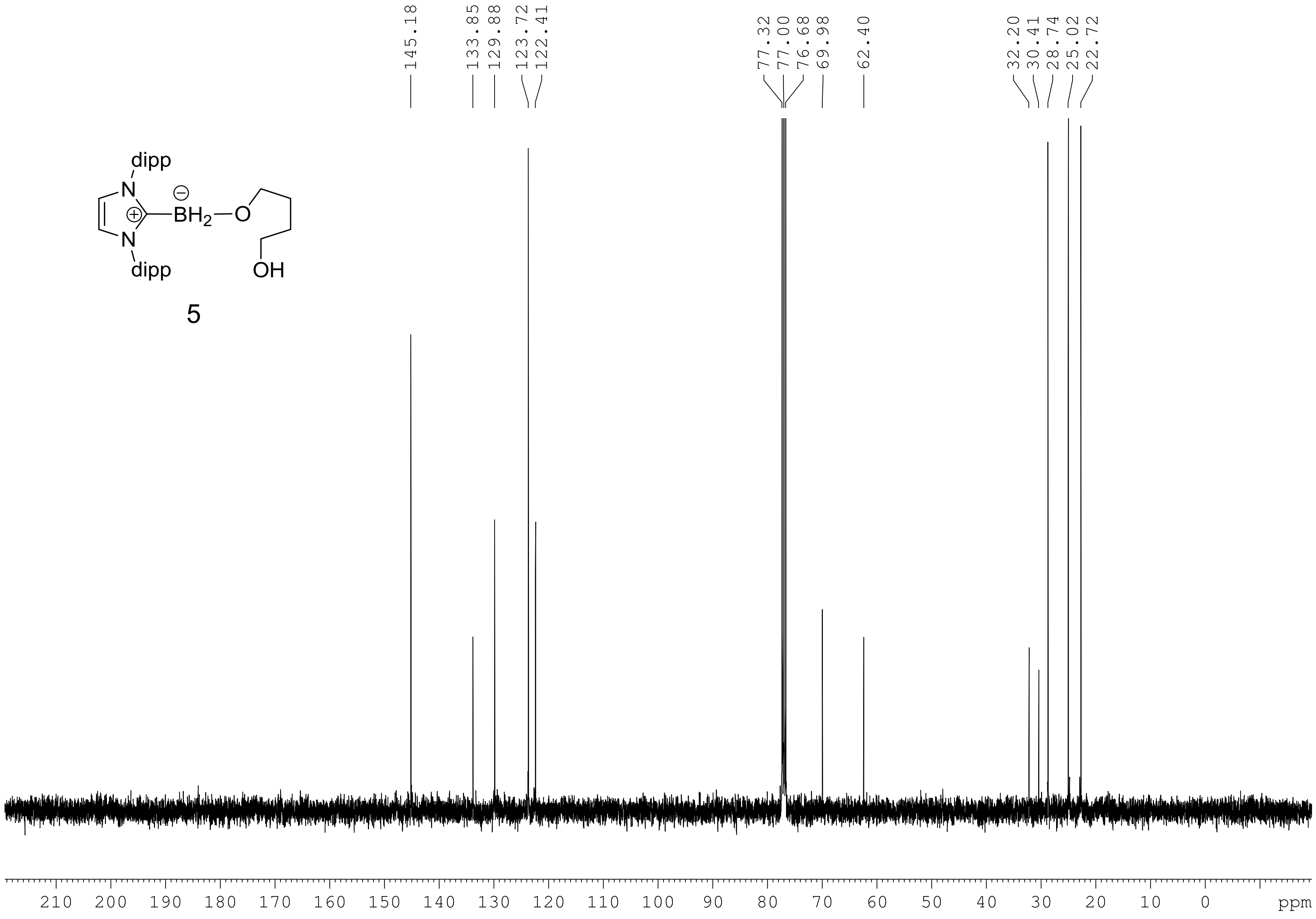
4f

boron-11 NMR

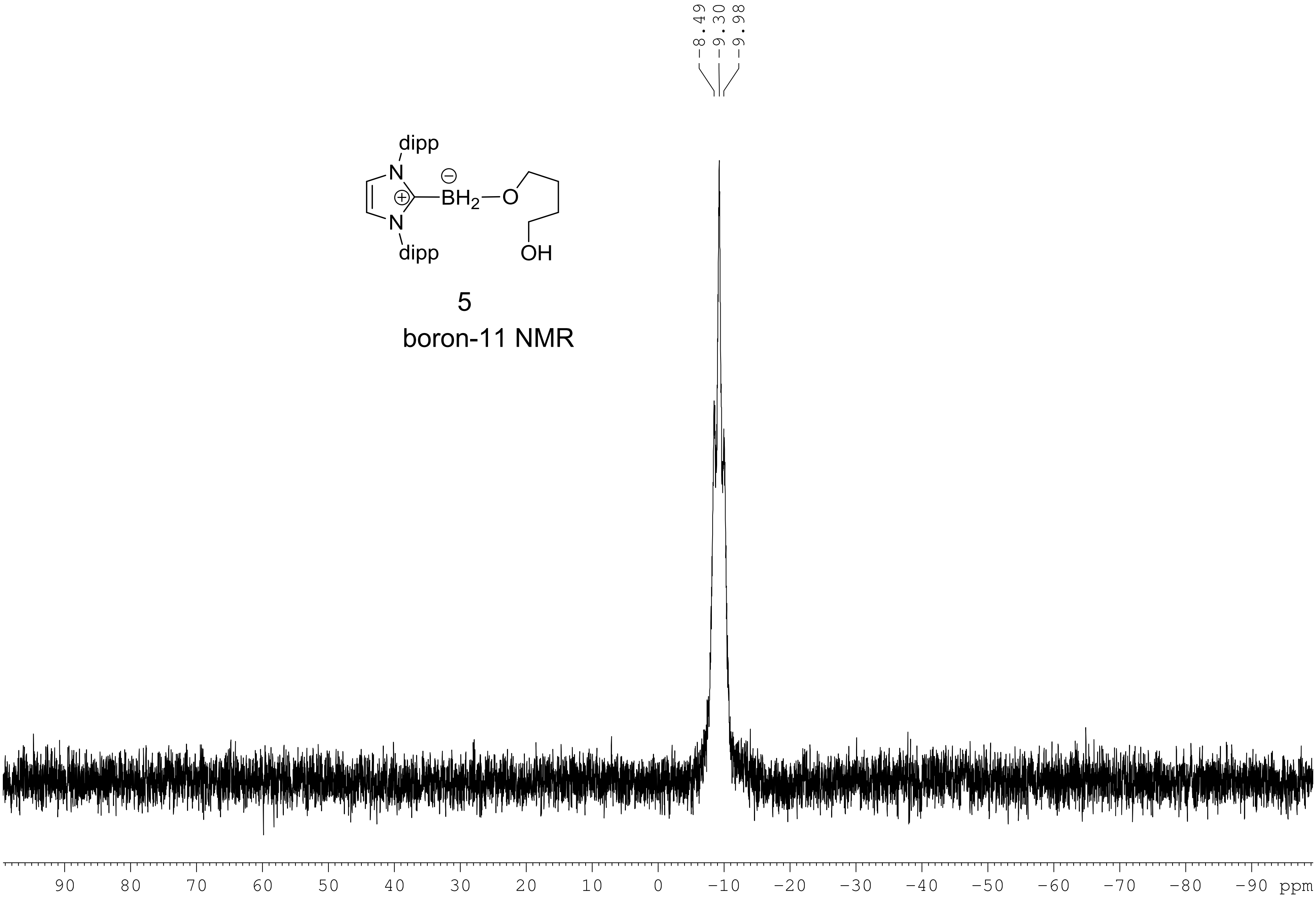
AS82-01, dipp-Imd-BH2O(CH2)4OH, Fr. 52-59, CDCl3, 400B, 04/29/11



AS82-01, dipp-Imd-BH2O(CH2)4OH, Fr. 52-59, CDCl3, 400B, 04/29/11

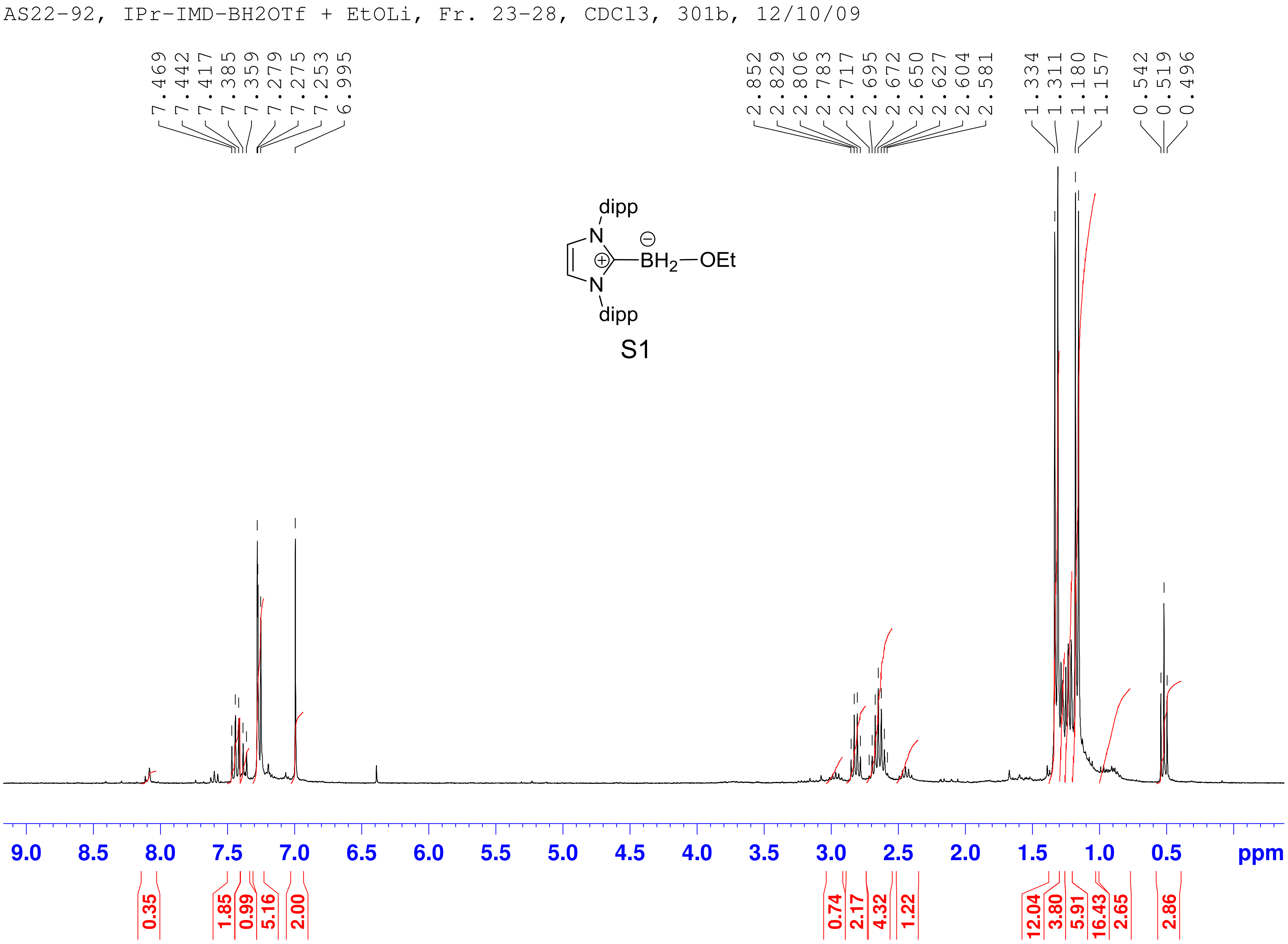


AS82-01, dipp-Imd-BH2OTf + TMSOK in THF, Fr. 52-59, CDCl3, 400B, 04/29/11

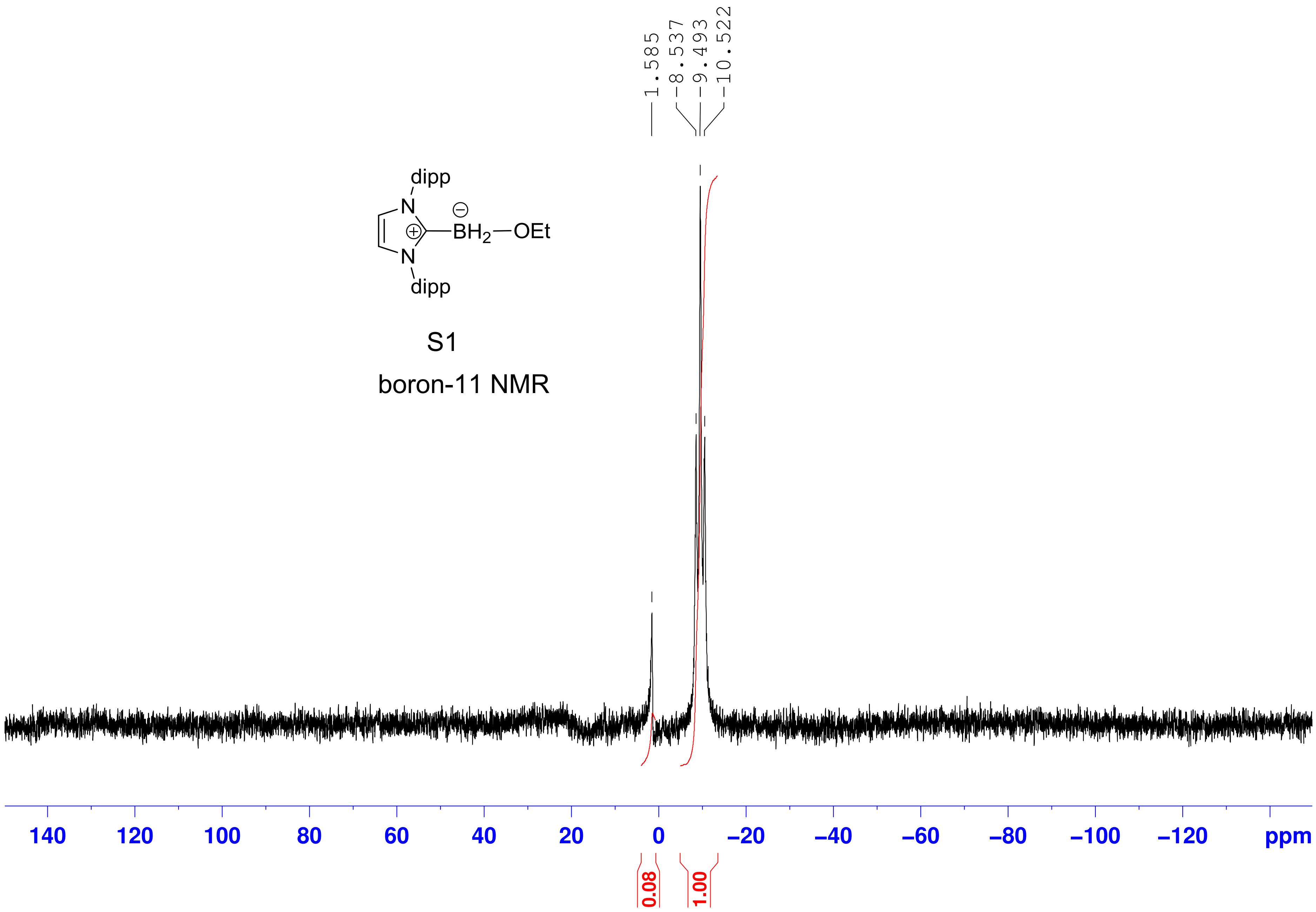


5

boron-11 NMR

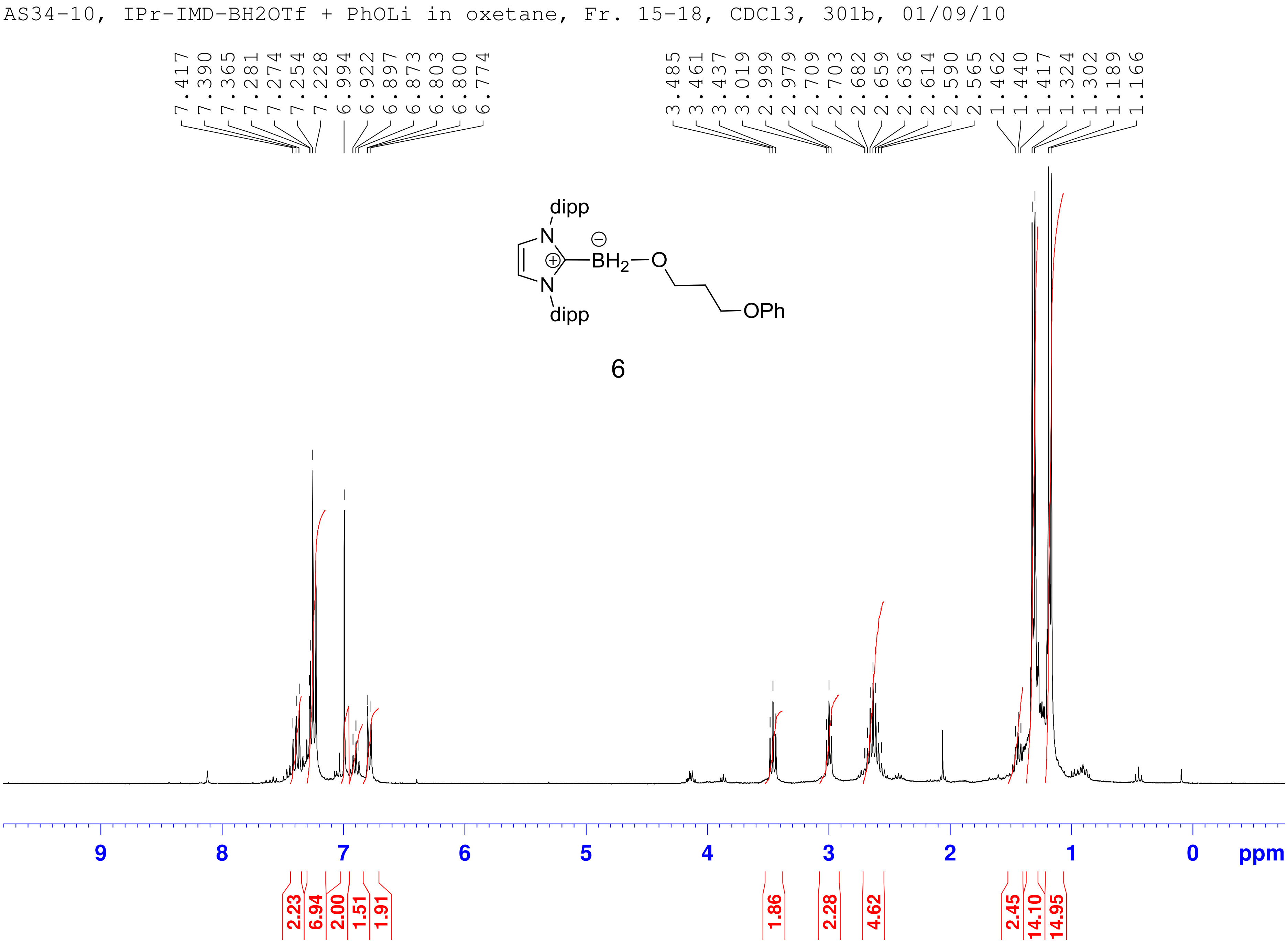

AS22-92, IPr-IMD-BH2OTf + EtOLi, Fr. 23-28, CDCl3, 301b, 12/10/09
7.469
7.442
7.417
7.385
7.359
7.279
7.275
7.253
6.995
2.852
2.829
2.806
2.783
2.717
2.695
2.672
2.650
2.627
2.604
2.581
1.334
1.311
1.180
1.157
0.542
0.519
0.496
dipp
N
⊖
⊕
BH2
OEt
N
dipp
S1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.35
1.85
0.99
5.16
2.00
0.74
2.17
4.32
1.22
12.04
3.80
5.91
16.43
2.65
2.86

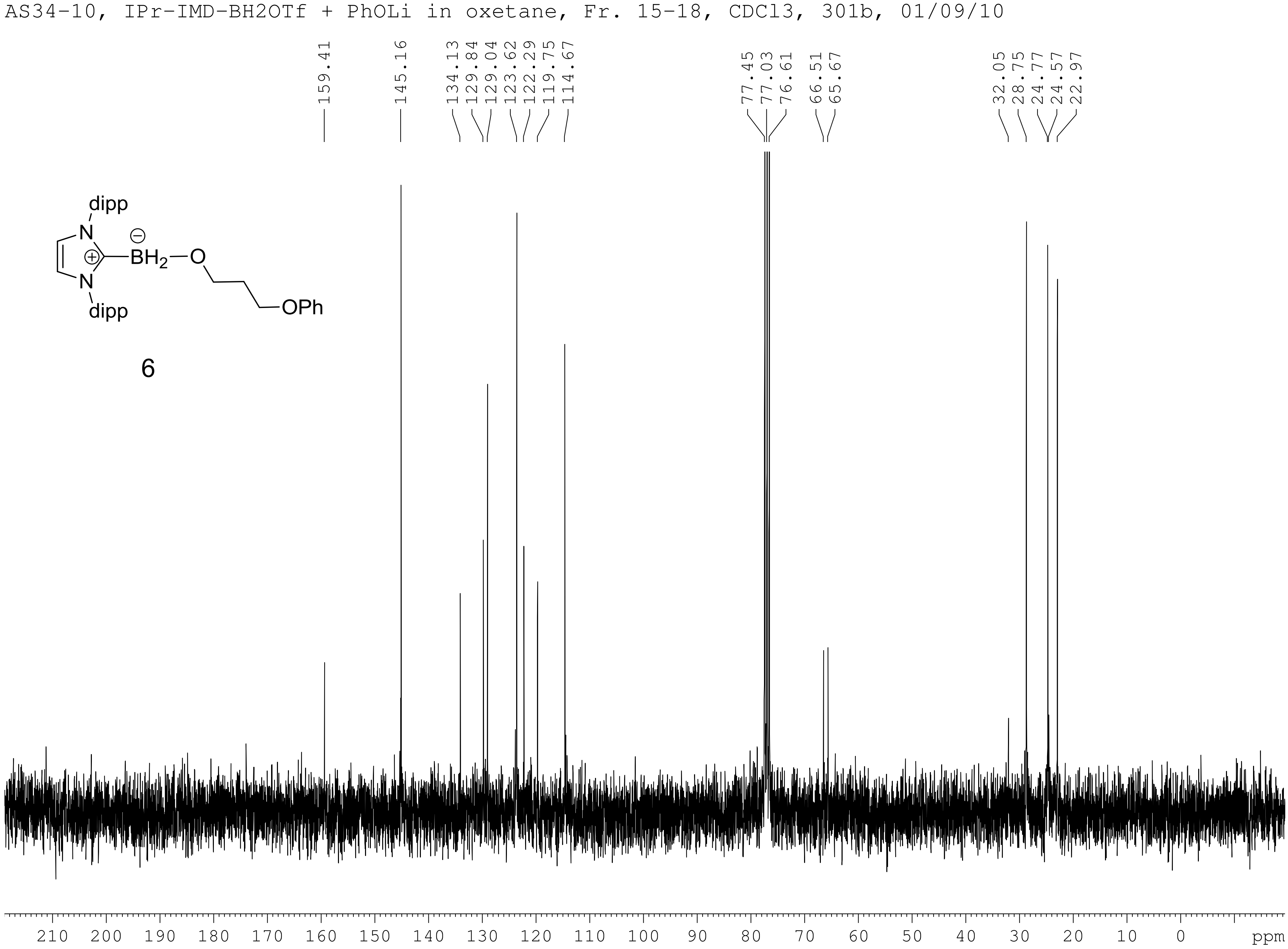
AS22-92, IPr-IMD-BH2OTf + EtOLi, Fr. 23-28, CDCl3, 301b, 12/10/09



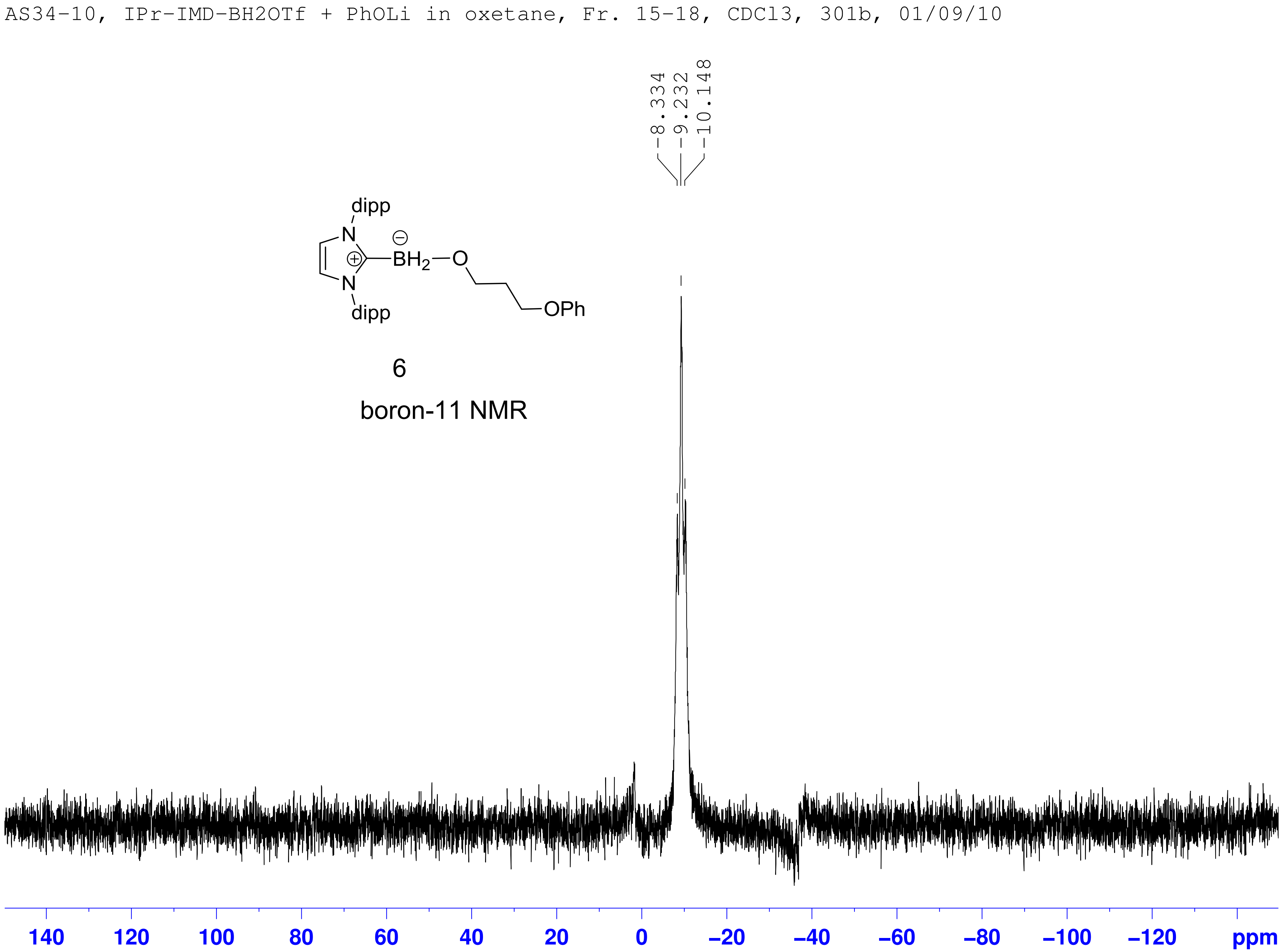
S1

boron-11 NMR

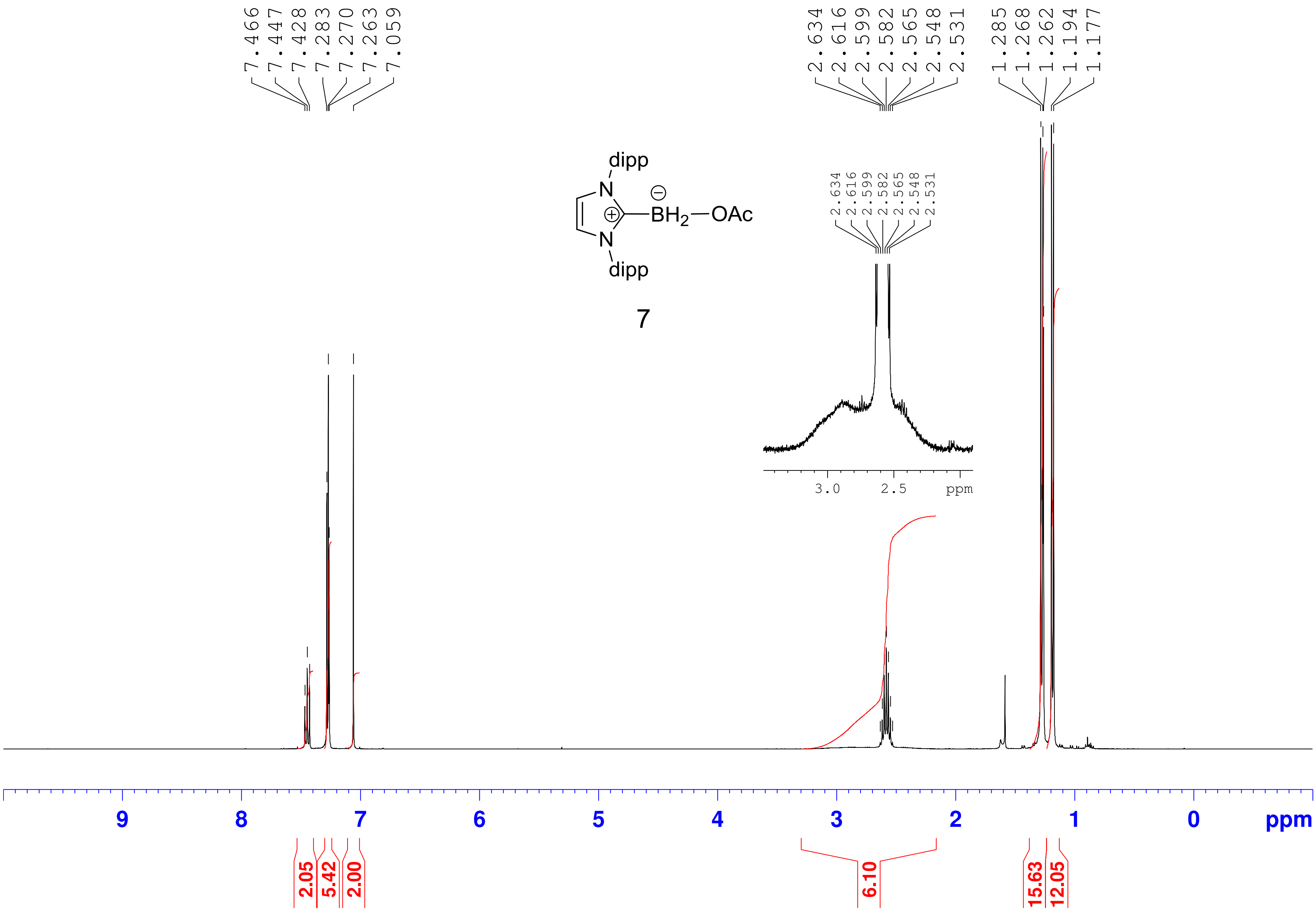

AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDCl3, 301b, 01/09/10
7.417
7.390
7.365
7.281
7.274
7.254
7.228
6.994
6.922
6.897
6.873
6.803
6.800
6.774
3.485
3.461
3.437
3.019
2.999
2.979
2.709
2.703
2.682
2.659
2.636
2.614
2.590
2.565
1.462
1.440
1.417
1.324
1.302
1.189
1.166
dipp
N
N
dipp
BH2
O
OPh
6
9
8
7
6
5
4
3
2
1
0
ppm
2.23
6.94
2.00
1.51
1.91
1.86
2.28
4.62
2.45
14.10
14.95


AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDCl3, 301b, 01/09/10
159.41
145.16
134.13
129.84
129.04
123.62
122.29
119.75
114.67
77.45
77.03
76.61
66.51
65.67
32.05
28.75
24.77
24.57
22.97
dipp
N
BH2
O
N
dipp
OPh
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

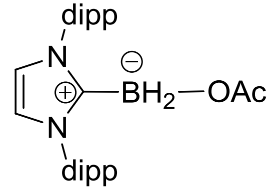
6


AS34-10, IPr-IMD-BH2OTf + PhOLi in oxetane, Fr. 15-18, CDCl3, 301b, 01/09/10
-8.334
-9.232
-10.148
dipp
N
BH2
O
N
dipp
OPh
6
boron-11 NMR
140
120
100
80
60
40
20
0
−20
−40
−60
−80
−100
−120
ppm

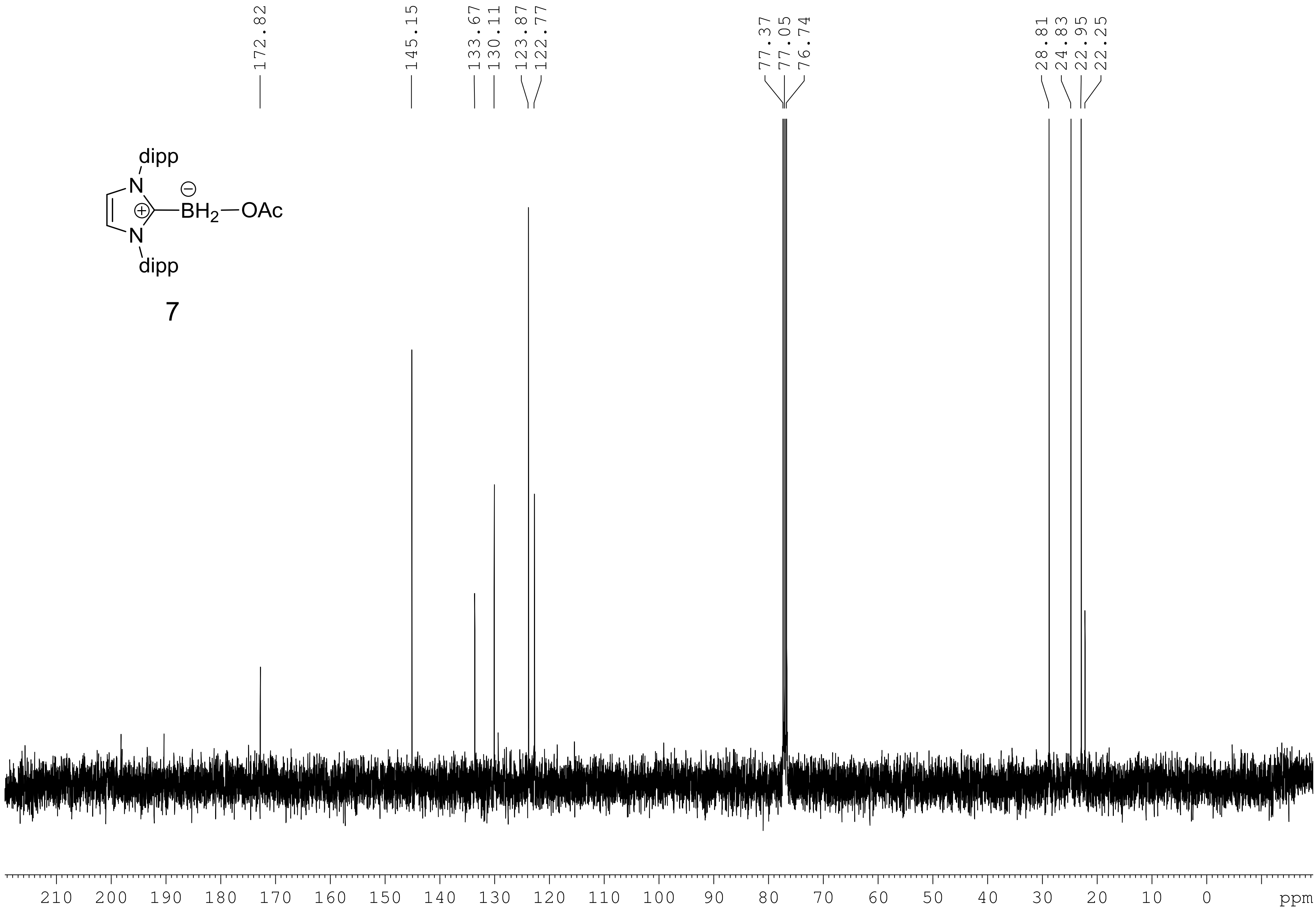
AS49-68, IPr-IMD-BH2OAc, crystal, CDCl3, 400B, 09/21/10



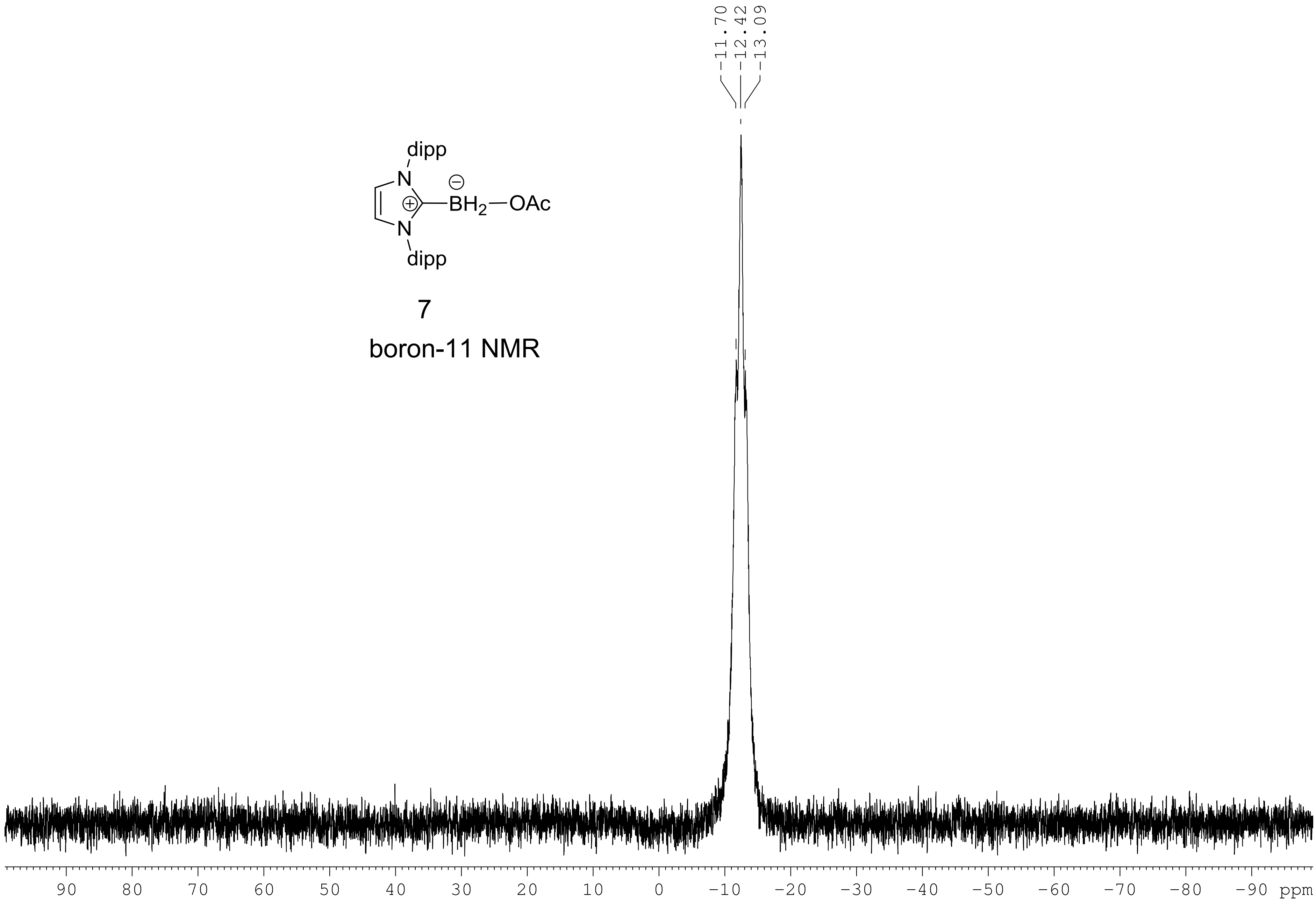
AS49-68, IPr-IMD-BH2OTf + PhOLi in EtOAc, Fr. 41-48, CDCl3, 400B, 09/16/10



7



AS49-68, IPr-IMD-BH2OTf + PhOLi in EtOAc, Fr. 41-48, CDCl3, 400B, 09/16/10



7

boron-11 NMR