

–Supporting Information for–

N-Heterocyclic carbene boranes are good hydride donors

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Table of Contents

General Remarks, Kinetic Experiments.....	S2
Rate Constants, Figures S1–S6.....	S2
General Remarks, Preparative Experiments	S8
Experimental Procedures and Compound Characterization	S9
References.....	S19
Copies of NMR Spectra	S20

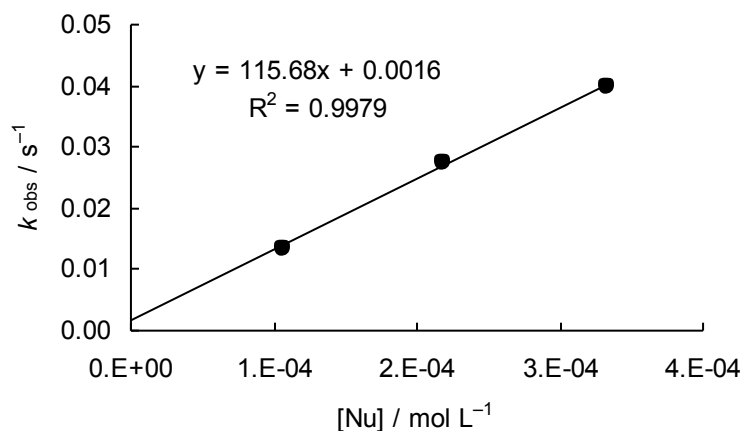
General Remarks, Kinetic Experiments

Reactions were either followed by conventional or stopped-flow photospectrometry. The conventional method employed a J&M TIDAS instrument equipped with an insertion quartz probe (Hellma) and a halogen light source. A SX.18MV-R stopped-flow device (Applied Photophysics) was used for the fast reaction between **E1** and 1,3-dimethyl-imidazol-2-ylidene borane **2**. In all experiments, the temperature was controlled to be 20 °C by water baths and water circuits. CH₂Cl₂ was dried over CaCl₂ and refluxed over CaH₂ before use.

Rate Constants

Figure S1. Reaction of **E1** with carbene-borane **1** (conventional UV-vis spectrometry, 612 nm, CH₂Cl₂, 20 °C).

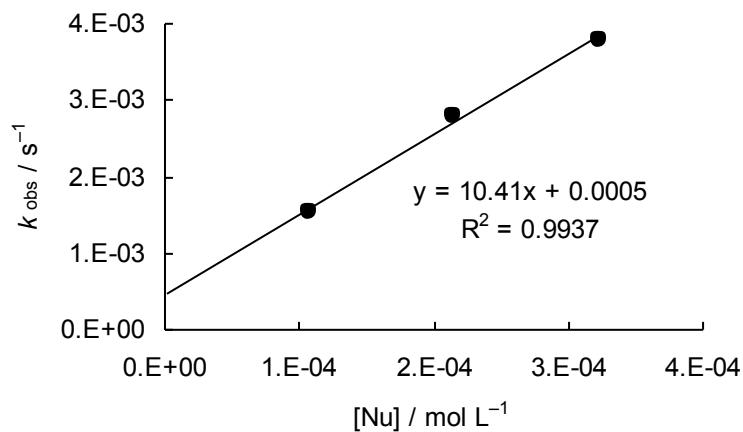
[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	$k_{\text{obs}} / \text{s}^{-1}$
1.02×10^{-5}	1.06×10^{-4}	10	1.35×10^{-2}
1.05×10^{-5}	2.18×10^{-4}	21	2.75×10^{-2}
1.07×10^{-5}	3.33×10^{-4}	31	3.98×10^{-2}



$$k = 1.16 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure S2. Reaction of **E2** with carbene-borane **1** (conventional UV-vis spectrometry, 627 nm, CH₂Cl₂, 20 °C).

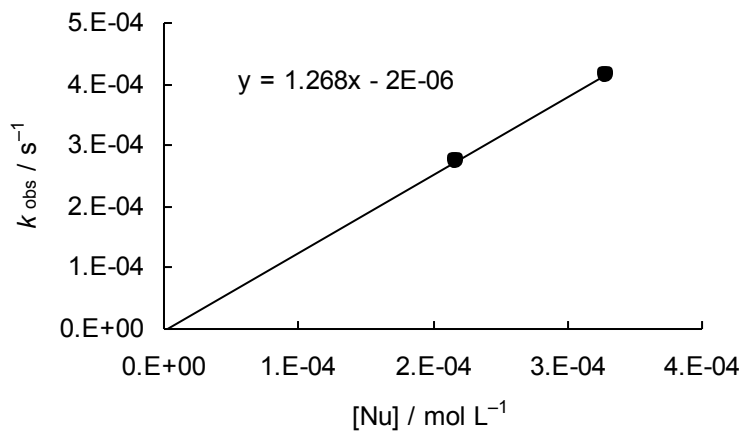
[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	$k_{\text{obs}} / \text{s}^{-1}$
1.09×10^{-5}	1.07×10^{-4}	10	1.53×10^{-3}
1.09×10^{-5}	2.14×10^{-4}	20	2.80×10^{-3}
2.18×10^{-5}	3.23×10^{-4}	15	3.78×10^{-3}



$$k = 1.04 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure S3. Reaction of **E3** with carbene-borane **1** (conventional UV-vis spectrometry, 643 nm, CH₂Cl₂, 20 °C).

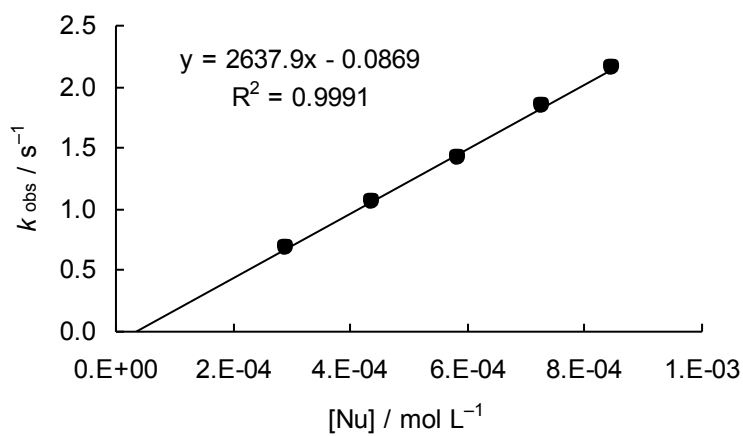
[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	<i>k</i> _{obs} / s ⁻¹
1.38 × 10 ⁻⁵	2.17 × 10 ⁻⁴	16	2.73 × 10 ⁻⁴
1.40 × 10 ⁻⁵	3.29 × 10 ⁻⁴	24	4.15 × 10 ⁻⁴



$$k = 1.27 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure S4. Reaction of **E1** with carbene-borane **2** (stopped-flow UV-vis spectrometry, 613 nm, CH₂Cl₂, 20 °C).

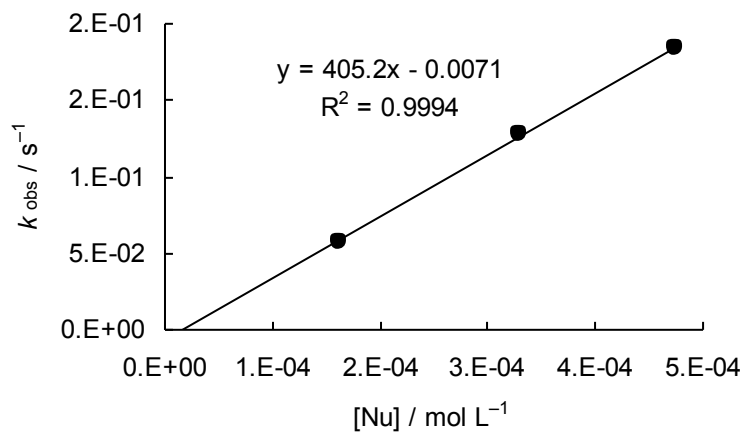
[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	<i>k</i> _{obs} / s ⁻¹
1.47 × 10 ⁻⁵	2.91 × 10 ⁻⁴	20	6.93 × 10 ⁻¹
1.47 × 10 ⁻⁵	4.36 × 10 ⁻⁴	30	1.06
1.47 × 10 ⁻⁵	5.82 × 10 ⁻⁴	40	1.42
1.47 × 10 ⁻⁵	7.28 × 10 ⁻⁴	50	1.85
1.47 × 10 ⁻⁵	8.47 × 10 ⁻⁴	58	2.15



$$k = 2.64 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure S5. Reaction of **E2** with carbene-borane **2** (conventional UV-vis spectrometry, 627 nm, CH₂Cl₂, 20 °C).

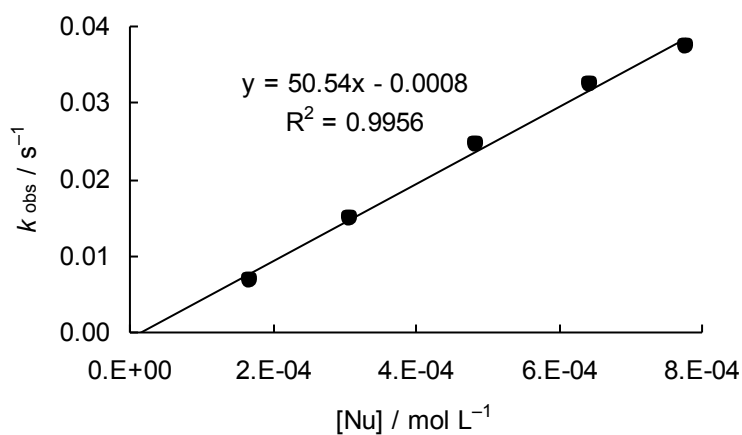
[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	<i>k</i> _{obs} / s ⁻¹
1.10 × 10 ⁻⁵	1.61 × 10 ⁻⁴	15	5.73 × 10 ⁻²
1.12 × 10 ⁻⁵	3.29 × 10 ⁻⁴	29	1.28 × 10 ⁻¹
1.62 × 10 ⁻⁵	4.74 × 10 ⁻⁴	29	1.84 × 10 ⁻¹



$$k = 4.05 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$$

Figure S6. Reaction of **E3** with carbene-borane **2** (conventional UV-vis spectrometry, 643 nm, CH₂Cl₂, 20 °C).

[E] / mol L ⁻¹	[Nu] / mol L ⁻¹	[Nu]/[E]	<i>k</i> _{obs} / s ⁻¹
1.44 × 10 ⁻⁵	1.68 × 10 ⁻⁴	12	6.89 × 10 ⁻³
1.32 × 10 ⁻⁵	3.08 × 10 ⁻⁴	23	1.50 × 10 ⁻²
1.38 × 10 ⁻⁵	4.84 × 10 ⁻⁴	35	2.45 × 10 ⁻²
1.38 × 10 ⁻⁵	6.44 × 10 ⁻⁴	47	3.23 × 10 ⁻²
1.34 × 10 ⁻⁵	7.78 × 10 ⁻⁴	58	3.75 × 10 ⁻²



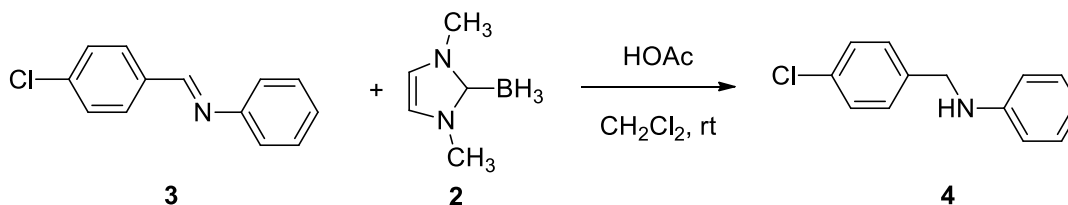
$$k = 5.05 \times 10^1 \text{ L mol}^{-1} \text{ s}^{-1}$$

General Remarks, Preparative Reactions: Chemicals were purchased from commercial suppliers and used as received. THF, CH₂Cl₂, and toluene 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 (CH₂Cl₂) on NaCl plates. Proton (¹H) and carbon (¹³C) 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 (CDCl₃: ¹H = 7.26 ppm, ¹³C = 77.0 ppm; acetone-*d*₆: ¹H = 2.05 ppm, ¹³C = 29.84 ppm). Boron (¹¹B) NMR spectra were measured on Bruker Avance III 400 instruments at 128.4 MHz. The ¹¹B chemical shifts are given relative to BF₃·OEt₂ (¹¹B = 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 carbon atoms connected to the boron atom were not observed in ¹³C 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).

Complexes dipp-Imd-BH₃ **1**¹ and diMe-Imd-BH₃ **2**² have been prepared according to the literature procedures. Their spectroscopic data were consistent with reported data.

Experimental Procedures and Compound Characterization:



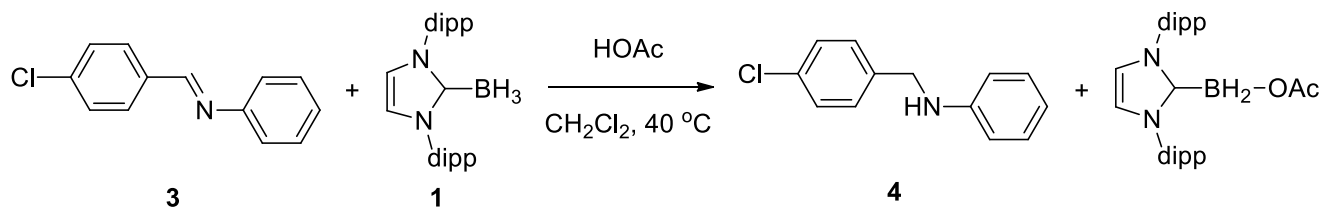
General Procedure 1 (GP1) for the reduction of *N*-(4-chlorobenzylidene)aniline **3:** A solution of *N*-(4-chlorobenzylidene)aniline **3**,³ 1,3-dimethylimidazol-2-ylidene-borane **2**, and acetic acid in CH₂Cl₂ (2 mL) was stirred at room temperature until no starting imine was detected by the TLC analysis. The solvent and volatiles were removed under reduced pressure and the residue was purified by flash chromatography. Elution with hexane:EtOAc 85:15 gave *N*-(4-chlorobenzyl)aniline **4** as yellow oil. The NMR spectroscopic data were identical with those previously reported in the literature.⁴

- 1) *Reduction with 1.3 equiv of 2 and no AcOH:* Following the GP1 with *N*-(4-chlorobenzylidene)aniline **3** (50 mg, 0.23 mmol), diMe-Imd-BH₃ **2** (34 mg, 0.31 mmol, 1.3 equiv) and no acetic acid, no product **4** was detected by the TLC analysis after 3 days of stirring.
- 2) *Reduction with 1.3 equiv of 2 and 1.3 equiv of AcOH:* Following the GP1 with *N*-(4-chlorobenzylidene)aniline **3** (50 mg, 0.23 mmol), diMe-Imd-BH₃ **2** (34 mg, 0.31 mmol, 1.3 equiv) and acetic acid (18 μL, 0.31 mmol, 1.3 equiv), *N*-(4-chlorobenzyl)aniline **4** was isolated (42 mg, 84%).

3) *Reduction with 0.7 equiv of 2 and 1 equiv of AcOH*: Following the GP1 with *N*-(4-chlorobenzylidene)aniline **3** (40 mg, 0.19 mmol), diMe-Imd-BH₃ **2** (15 mg, 0.14 mmol, 0.7 equiv) and acetic acid (11 μL, 0.19 mmol, 1 equiv), *N*-(4-chlorobenzyl)aniline **4** was isolated (36 mg, 86%).

4) *Reduction with 0.5 equiv of 2 and 1 equiv of AcOH*: Following the GP1 with *N*-(4-chlorobenzylidene)aniline **3** (39 mg, 0.18 mmol), diMe-Imd-BH₃ **2** (10 mg, 0.09 mmol, 0.5 equiv) and acetic acid (11 μL, 0.19 mmol, 1 equiv), *N*-(4-chlorobenzyl)aniline **4** was isolated (37 mg, 94%).

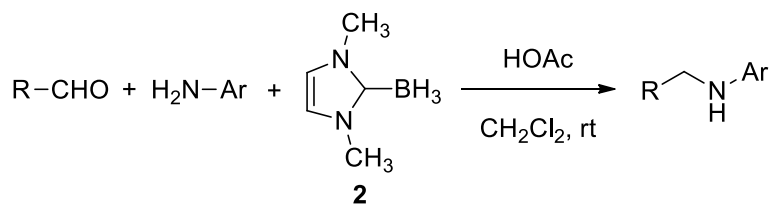
5) *Reduction with 0.33 equiv of 2 and 1 equiv of AcOH*: Following the GP1 with *N*-(4-chlorobenzylidene)aniline **3** (40 mg, 0.19 mmol), diMe-Imd-BH₃ **2** (7 mg, 0.06 mmol, 0.33 equiv) and acetic acid (11 μL, 0.19 mmol, 1 equiv), *N*-(4-chlorobenzyl)aniline **4** was isolated (35 mg, 86%).



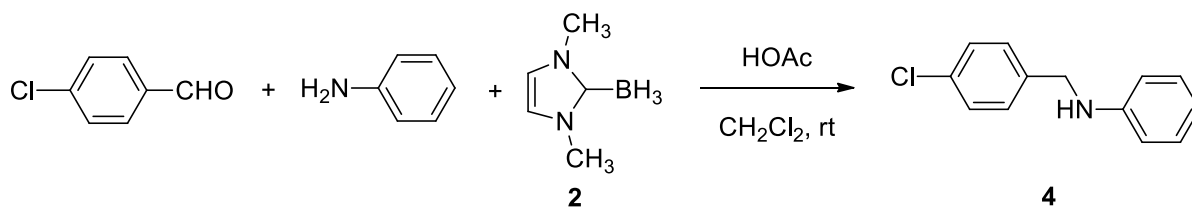
***N*-(4-Chlorobenzyl)aniline (4)**: A solution of *N*-(4-chlorobenzylidene)aniline **3**³ (110 mg, 0.51 mmol, 1 equiv), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene-borane **1** (260 mg, 0.65 mmol, 1.3 equiv), and acetic acid (38 μL, 0.65 mmol, 1.3 equiv) in 1,2-dichloroethane (2 mL) was heated at 80 °C for 48 h. The solvent and volatiles were removed under reduced pressure and the residue was purified by flash chromatography. Elution with hexane:EtOAc gave *N*-(4-

chlorobenzyl)aniline **4** as light yellow oil (85 mg, 77%). The NMR spectroscopic data were identical with those of previously isolated sample.

Further elution gave dipp-Imd-BH₂OAc as a white solid (160 mg, 69%). The complete characterization of this compound will be reported soon (Solovyev, A.; Lacôte, E.; Curran, D. P., manuscript in preparation).

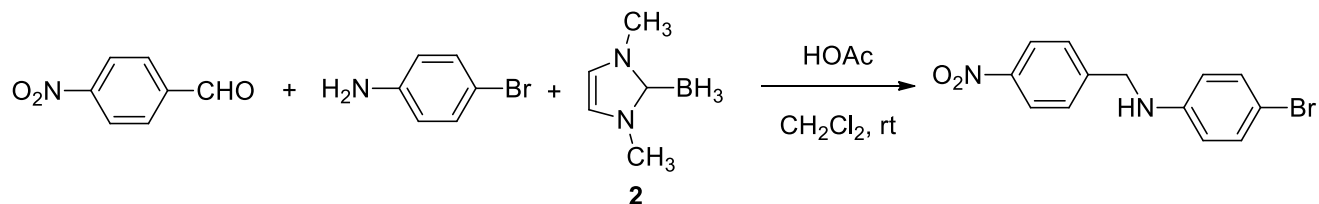


General Procedure 2 (GP2) for the imine formation and reduction: A solution of an aldehyde (1 equiv) and aniline (1 equiv) in CH₂Cl₂ (2 mL) was stirred over 4 Å molecular sieves at room temperature for 1 h. Then acetic acid (1 equiv or 1.3 equiv) and 1,3-dimethylimidazol-2-ylidene-borane **2** (0.5 equiv or 1.3 equiv) were added to the reaction mixture. The resulting solution was stirred for 1 h. The solvent and volatiles were removed under reduced pressure and the residue was purified by flash chromatography. Elution with hexane:EtOAc gave the amine product.



N-(4-Chlorobenzyl)aniline: Following the GP2 with 4-chlorobenzaldehyde (50 mg, 0.36 mmol), aniline (33 μL, 0.36 mmol), diMe-Imd-BH₃ **2** (52 mg, 0.47 mmol, 1.3 equiv) and acetic

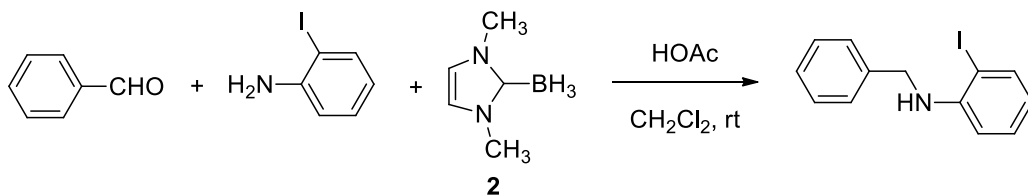
acid (27 μ L, 0.47 mmol, 1.3 equiv), elution with hexane:EtOAc 85:15 gave the product **4** as light yellow oil (71 mg, 91%). The NMR spectroscopic data were identical with those of previously isolated sample.



4-Bromo-N-(4-nitrobenzyl)aniline:

1) *Reduction with 1.3 equiv of 2*: Following the GP2 with 4-nitrobenzaldehyde (44.5 mg, 0.294 mmol), 4-bromoaniline (51 mg, 0.30 mmol), diMe-Imd-BH₃ **2** (43 mg, 0.39 mmol, 1.3 equiv) and acetic acid (22 μ L, 0.38 mmol, 1.3 equiv), elution with hexane:EtOAc 80:20 gave the product a yellow solid (89 mg, 98%): IR (thin film, cm^{-1}) ν_{max} 3055, 2987, 2684, 1596, 1500, 1422, 1346, 1265, 896, 740, 706; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.45 (d, J = 8.8 Hz, 2H), 4.45 (d, J = 5.6 Hz, 2H), 4.28 (br s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 147.2, 146.8, 146.2, 132.1, 127.6, 123.9, 114.5, 109.9, 47.5; HRMS (ESI) calcd. for C₁₃H₁₂⁷⁹BrN₂O₂ ([M + H]⁺) 307.0082, found 307.0102.

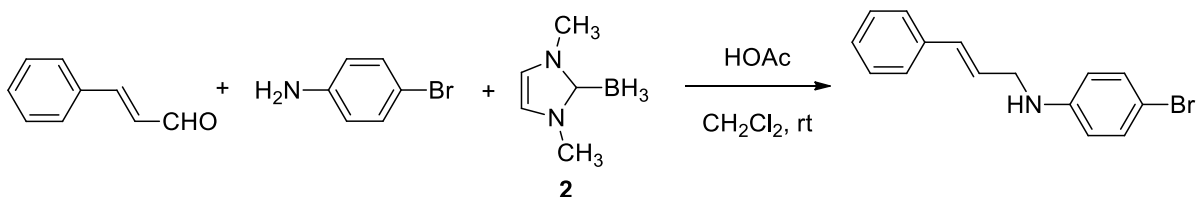
2) *Reduction with 0.5 equiv of 2*: Following the GP2 with 4-nitrobenzaldehyde (0.50 g, 3.3 mmol), 4-bromoaniline (0.57 mg, 3.3 mmol), diMe-Imd-BH₃ **2** (0.185 g, 1.68 mmol, 0.5 equiv) and acetic acid (0.19 mL, 3.3 mmol, 1 equiv) in CH₂Cl₂ (10 mL), the product was obtained as a yellow solid (0.93 g, 92%).



***N*-Benzyl-2-iodoaniline:**

1) *Reduction with 1.3 equiv of 2*: Following the GP2 with benzaldehyde (18 μ L, 0.18 mmol), 2-iodoaniline (40 mg, 0.18 mmol), diMe-Imd-BH₃ **2** (26 mg, 0.24 mmol, 1.3 equiv) and acetic acid (14 μ L, 0.24 mmol, 1.3 equiv), elution with hexane:EtOAc 97:3 gave the product as pale oil (41 mg, 73%). The NMR spectroscopic data were identical with those previously reported in the literature.⁵

2) *Reduction with 0.5 equiv of 2*: Following the GP2 with benzaldehyde (23 μ L, 0.23 mmol), 2-iodoaniline (50 mg, 0.23 mmol), diMe-Imd-BH₃ **2** (13 mg, 0.12 mmol, 0.5 equiv) and acetic acid (17 μ L, 0.30 mmol, 1.3 equiv), the product was obtained as pale oil (48 mg, 68%).

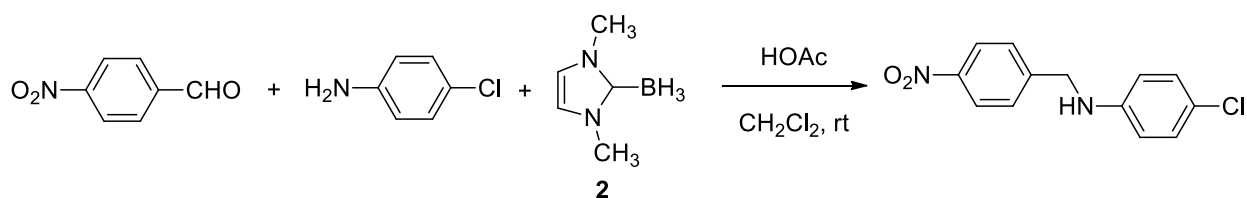


4-Bromo-*N*-cinnamylaniline:

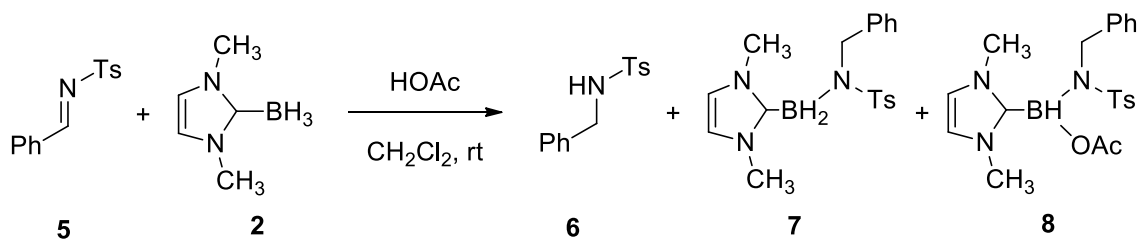
1) *Reduction with 1.3 equiv of 2*: Following the GP2 with *trans*-cinnamaldehyde (40 μ L, 0.32 mmol), 4-bromoaniline (55 mg, 0.32 mmol), diMe-Imd-BH₃ **2** (46 mg, 0.42 mmol, 1.3 equiv) and acetic acid (24 μ L, 0.42 mmol, 1.3 equiv), elution with hexane:EtOAc 90:10 gave the

product a light yellow solid (70 mg, 76%). The NMR spectroscopic data were identical with those previously reported in the literature.⁶

2) *Reduction with 0.5 equiv of 2*: Following the GP2 with *trans*-cinnamaldehyde (40 μ L, 0.32 mmol), 4-bromoaniline (55 mg, 0.32 mmol), diMe-Imd-BH₃ **2** (18 mg, 0.16 mmol, 0.5 equiv) and acetic acid (24 μ L, 0.42 mmol, 1.3 equiv), the product was obtained as a light yellow solid (65 mg, 70%).



4-Chloro-*N*-(4-nitrobenzyl)aniline: Following the GP2 with 4-nitrobenzaldehyde (57 mg, 0.38 mmol, 1 equiv), 4-chloroaniline (48 mg, 0.38 mmol, 1 equiv), diMe-Imd-BH₃ **2** (54 mg, 0.49 mmol, 1.3 equiv) and acetic acid (28 μ L, 0.49 mmol, 1.3 equiv), the product was obtained as light yellow oil (57 mg, 57%). The NMR spectroscopic data were identical with those previously reported in the literature.⁷



General Procedure 3 (GP3) for the reduction of *N*-benzylidene-4-methylbenzenesulfonamide **5**: A solution of *N*-benzylidene-4-methylbenzenesulfonamide **5**,⁸ 1,3-dimethylimidazol-2-ylidene-borane **2**, and acetic acid in CH₂Cl₂ (3 mL) was stirred over 4 Å molecular sieves at room temperature for 16 h. The solvent and volatiles were removed under

reduced pressure and the residue was purified by flash chromatography. Elution with hexane:EtOAc gave three products **6–8** as white solids.

1) *Reduction with 1 equiv of 2 and 1 equiv of AcOH*: Following the GP3 with *N*-benzylidene-4-methylbenzenesulfonamide **5** (30 mg, 0.12 mmol), diMe-Imd-BH₃ **2** (13 mg, 0.12 mmol, 1 equiv) and acetic acid (6.7 μ L, 0.12 mmol, 1 equiv), *N*-benzyl-4-methylbenzenesulfonamide **6** was isolated as a white solid (16.3 mg, 54%). The NMR spectroscopic data were identical with those previously reported in the literature.⁹

Further elution with hexane:EtOAc (30:70) gave diMe-Imd-BH₂-N(Ts)CH₂Ph **7** as a white solid (8.1 mg, 19%).

1,3-Dimethylimidazol-2-ylidene (*N*-benzyl-4-methylphenylsulfonamido)borane (7): mp 159–163 °C; IR (thin film, cm⁻¹) ν_{\max} 3135, 3055, 2986, 2410, 2306, 1690, 1600, 1492, 1423, 1372, 1301, 1266, 1235, 1204, 1155, 1132, 1089, 1025, 947, 920, 873, 815, 739; ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.0 Hz, 2H), 7.08 (t, *J* = 7.0 Hz, 1H), 6.58 (s, 2H), 4.22 (s, 2H), 3.57 (s, 6H), 2.39 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1, 140.2, 139.7, 128.9, 128.3, 127.7, 127.0, 126.5, 120.5, 55.4, 35.9, 21.4; ¹¹B NMR (128.4 MHz, CDCl₃) δ -18.9 (t, *J* = 91 Hz); HRMS (ESI) calcd. for C₁₉H₂₃¹¹BN₃O₂S ([M - H]⁺) 368.1604, found 368.1580.

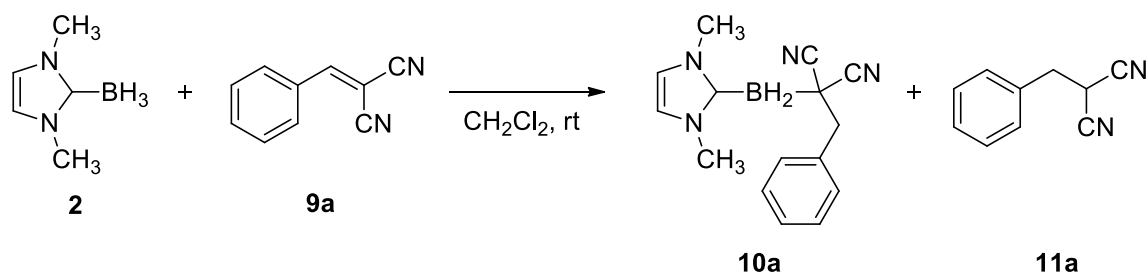
Further elution with pure EtOAc gave diMe-Imd-BH(OAc)-N(Ts)CH₂Ph **8** as a white solid (12.4 mg, 25%).

1,3-Dimethylimidazol-2-ylidene acetoxy-(*N*-benzyl-4-methylphenylsulfonamido)borane (8): mp 145–148 °C; IR (thin film, cm⁻¹) ν_{\max} 3055, 2986, 2684, 2410, 2306, 1690, 1491, 1423, 1372, 1301, 1265, 1204, 1156, 1132, 1089, 1025, 895, 739, 705; ¹H NMR (500 MHz, CDCl₃) δ

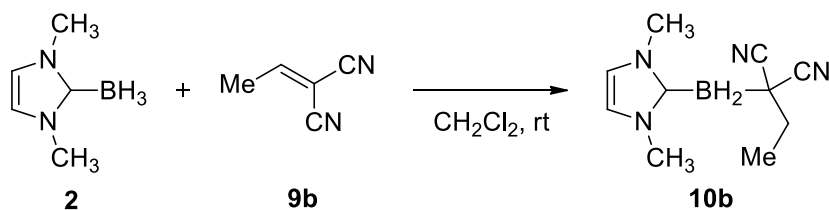
7.76 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 7.5$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.20 (t, $J = 7.5$ Hz, 2H), 7.13 (t, $J = 7.3$ Hz, 1H), 6.62 (s, 2H), 4.42 (d, $J = 15.0$ Hz, 1H), 4.29 (d, $J = 14.5$ Hz, 1H), 3.52 (s, 6H), 2.40 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 141172.7, 141.6, 140.3, 140.0, 129.0, 129.0, 127.8, 127.1, 126.7, 121.2, 51.8, 35.9, 23.0, 21.4; ^{11}B NMR (128.4 MHz, CDCl_3) δ -6.0 (br d, $J = 80$ Hz); HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{26}^{11}\text{BNaN}_3\text{O}_4\text{S}$ ($[\text{M} + \text{Na}]^+$) 450.1635, found 450.1682.

2) *Reduction with 0.33 equiv of 2 and 10 equiv of AcOH*: Following the GP3 with *N*-benzylidene-4-methylbenzenesulfonamide **5** (30 mg, 0.12 mmol), diMe-Imd-BH₃ **2** (4.2 mg, 0.038 mmol, 0.33 equiv) and acetic acid (69 μL , 1.2 mmol, 10 equiv), *N*-benzyl-4-methylbenzenesulfonamide **6** (24.0 mg, 79%) and diMe-Imd-BH₂-N(Ts)CH₂Ph **7** (8.0 mg, 19%) were obtained as white solids. The NMR spectroscopic data of all products were identical with those of previously isolated samples.

3) *Reduction with 1 equiv of 2 and no AcOH*: Following the GP3 with *N*-benzylidene-4-methylbenzenesulfonamide **5** (30 mg, 0.12 mmol) and diMe-Imd-BH₃ **2** (13 mg, 0.12 mmol, 1 equiv), *N*-benzyl-4-methylbenzenesulfonamide **6** (8 mg, 26 %) and diMe-Imd-BH₂-N(Ts)CH₂Ph **7** (17 mg, 40%) were obtained as white solids. The NMR spectroscopic data of both products were identical with those of previously isolated samples.



1,3-Dimethylimidazol-2-ylidene (1,1-dicyano-2-phenylethyl)borane (10a): A solution of benzylidenemalonitrile **9a**¹⁰ (250 mg, 1.62 mmol, 1.16 equiv) and diMe-Imd-BH₃ **2** (154 mg, 1.40 mmol) in CH₂Cl₂ (25 mL) was stirred at room temperature for 15 min. The solvent and volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography (elution with hexane:EtOAc = 25:75) to yield benzylmalononitrile **11a**¹¹ (29 mg, 13%) and diMe-Imd-BH₂C(CN)₂CH₂Ph **10a** as a white solid (210 mg, 57%): mp 140–145 °C; IR (thin film, cm⁻¹) ν_{\max} 3150, 2960, 2393, 2253, 2229, 1820, 1795, 1483, 1381, 1232, 1096, 910, 732; ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 1H), 6.97 (s, 2H), 4.00 (s, 6H), 3.13 (s, 2H), 1.99 (br q, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 137.2, 129.6, 128.4, 127.4, 121.9, 121.5, 43.7, 37.2; ¹¹B NMR (128.4 MHz, CDCl₃) δ -22.7 (t, *J* = 100 Hz); HRMS (ESI) calcd. for C₁₅H₁₇¹¹BN₄Na ([M + Na]⁺) 287.1444, found 287.1449.



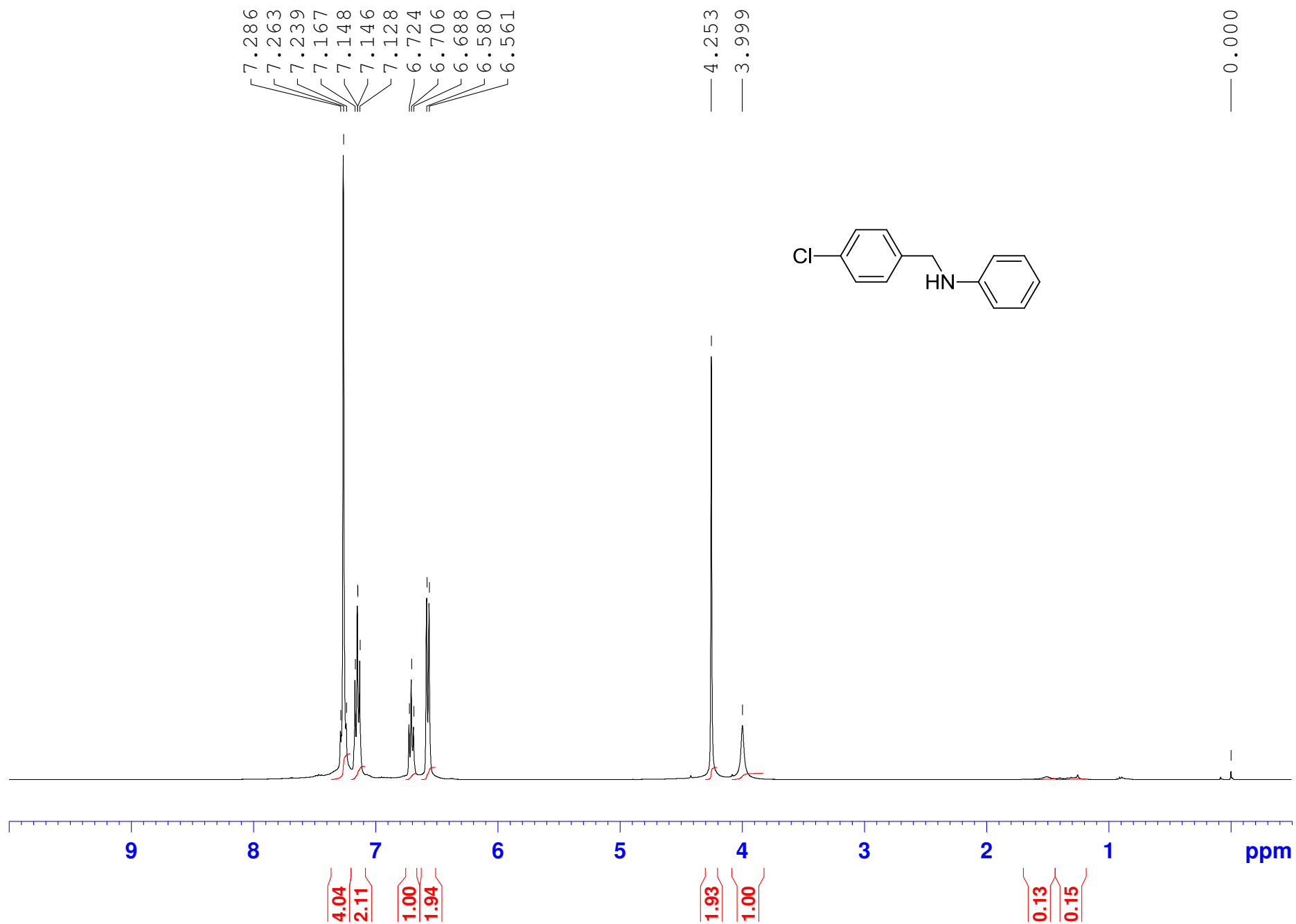
1,3-Dimethylimidazol-2-ylidene (1,1-dicyanopropyl)borane (10b): A solution of 2-ethylidenemalonitrile **9b**¹² (280 mg, 3.0 mmol, 2 equiv) and diMe-Imd-BH₃ **2** (167 mg, 1.52 mmol) in CH₂Cl₂ (25 mL) was stirred at room temperature for 18 h. The solvent and volatiles were removed under vacuum and the residue was loaded onto silica gel. The product was purified by flash chromatography (elution with hexane:EtOAc = 25:75) to yield diMe-Imd-BH₂C(CN)₂Et **10b** as a white solid (129 mg, 42%): mp 141–142 °C; IR (thin film, cm⁻¹) ν_{\max}

3152, 2973, 2254, 1789, 1470, 1382, 1096, 909, 734; ^1H NMR (500 MHz, CDCl_3) δ 7.02 (s, 2H), 3.96 (s, 6H), 1.92 (q, $J = 7.5$ Hz, 2H), 1.23 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 121.8, 121.7, 36.9, 31.5, 11.4; ^{11}B NMR (128.4 MHz, CDCl_3) δ -23.3 (t, $J = 98$ Hz); HRMS (ESI) calcd. for $\text{C}_{10}\text{H}_{14}^{11}\text{BN}_4$ [$\text{M} - \text{H}$] $^+$) 201.1312, found 201.1329.

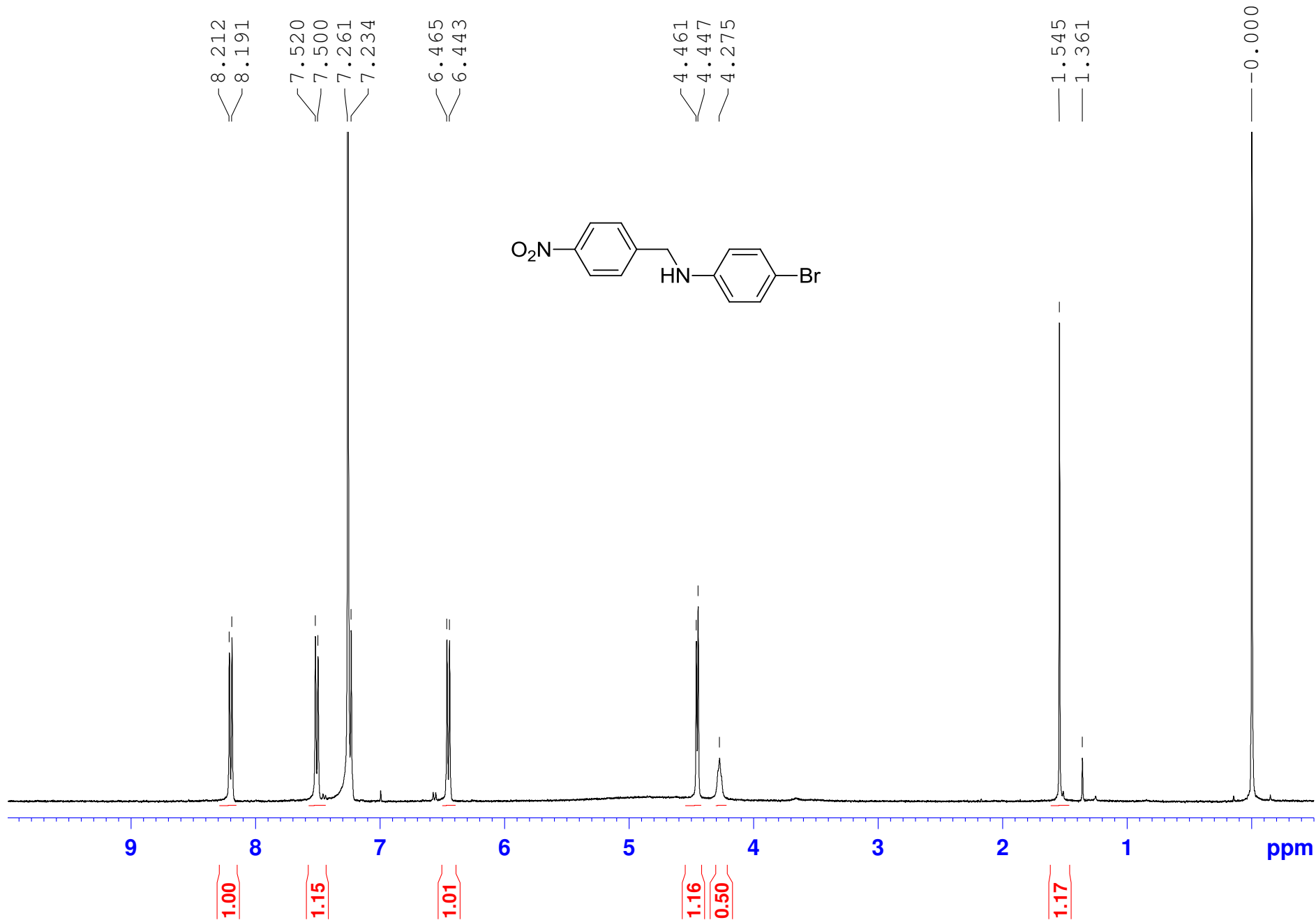
References:

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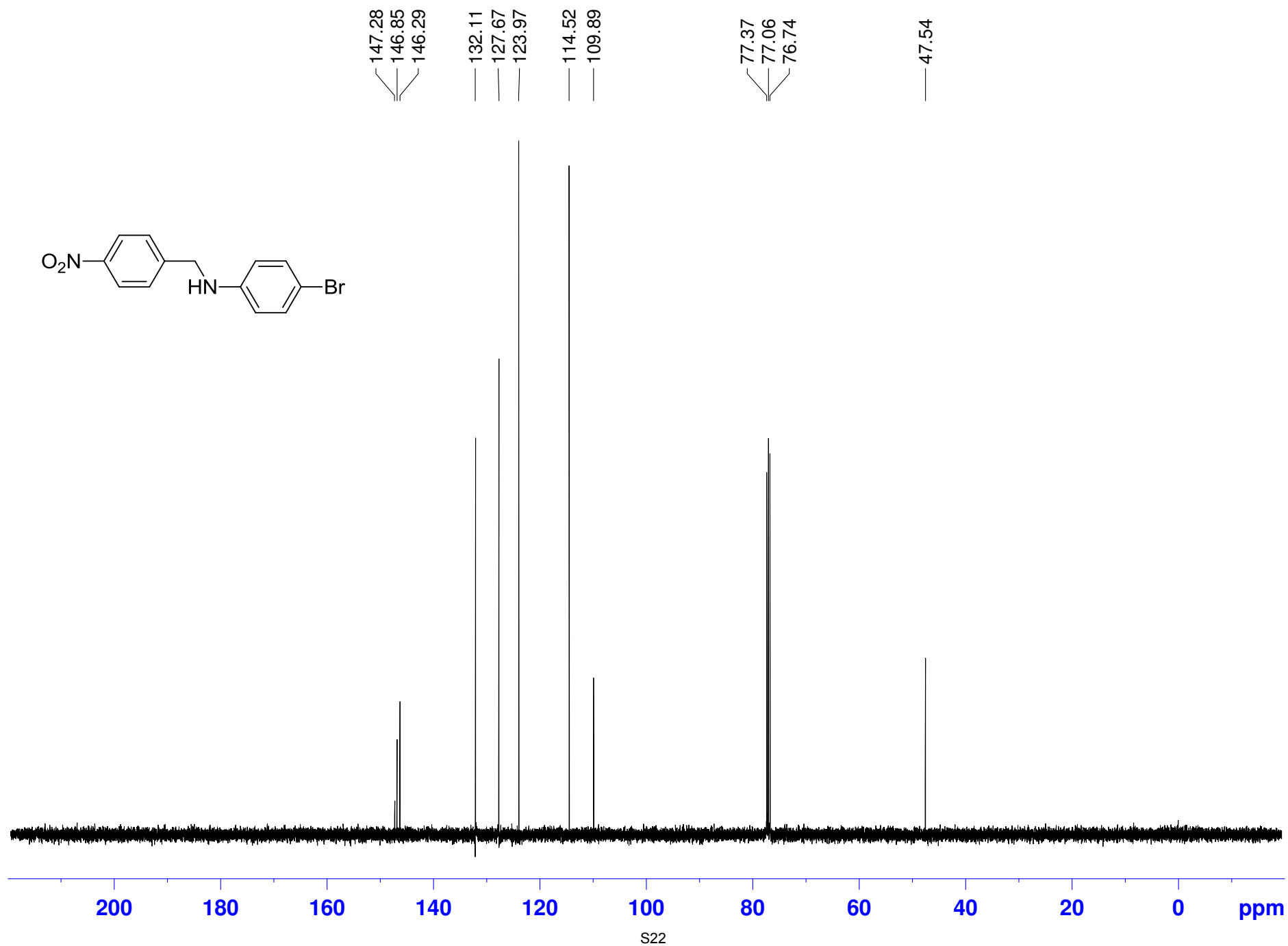
SW.01.1 400b 1H after column 5.25.11



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SW88.27 13C final2



SW88.11 final 400a

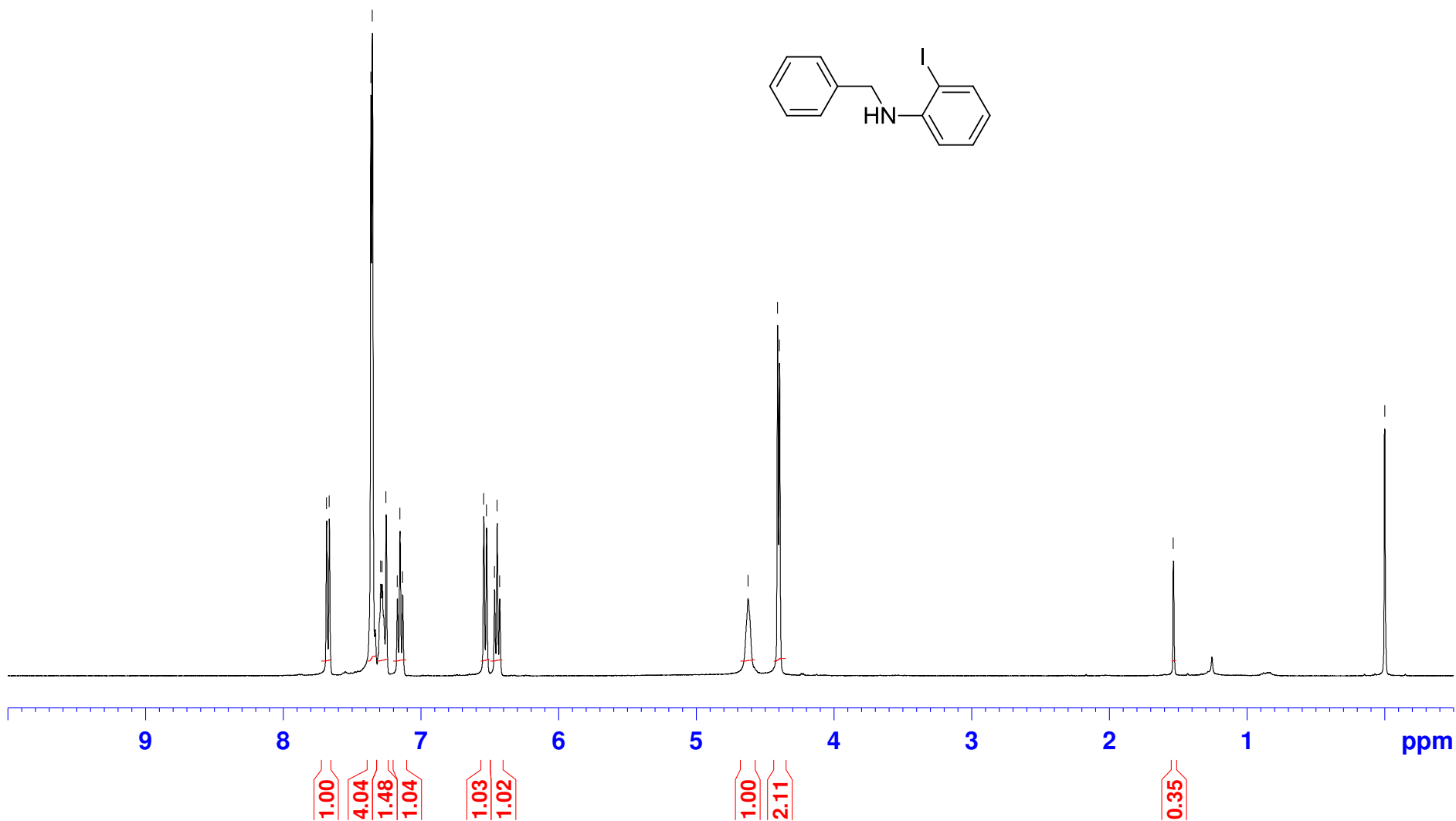
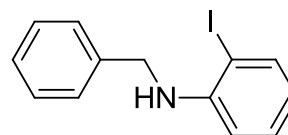
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7.364
7.354
7.293
7.283
7.255
7.172
7.153
7.134
6.545
6.524
6.466
6.448
6.429

4.625
4.410
4.397

1.537

0.000



SW88.13 final 400a

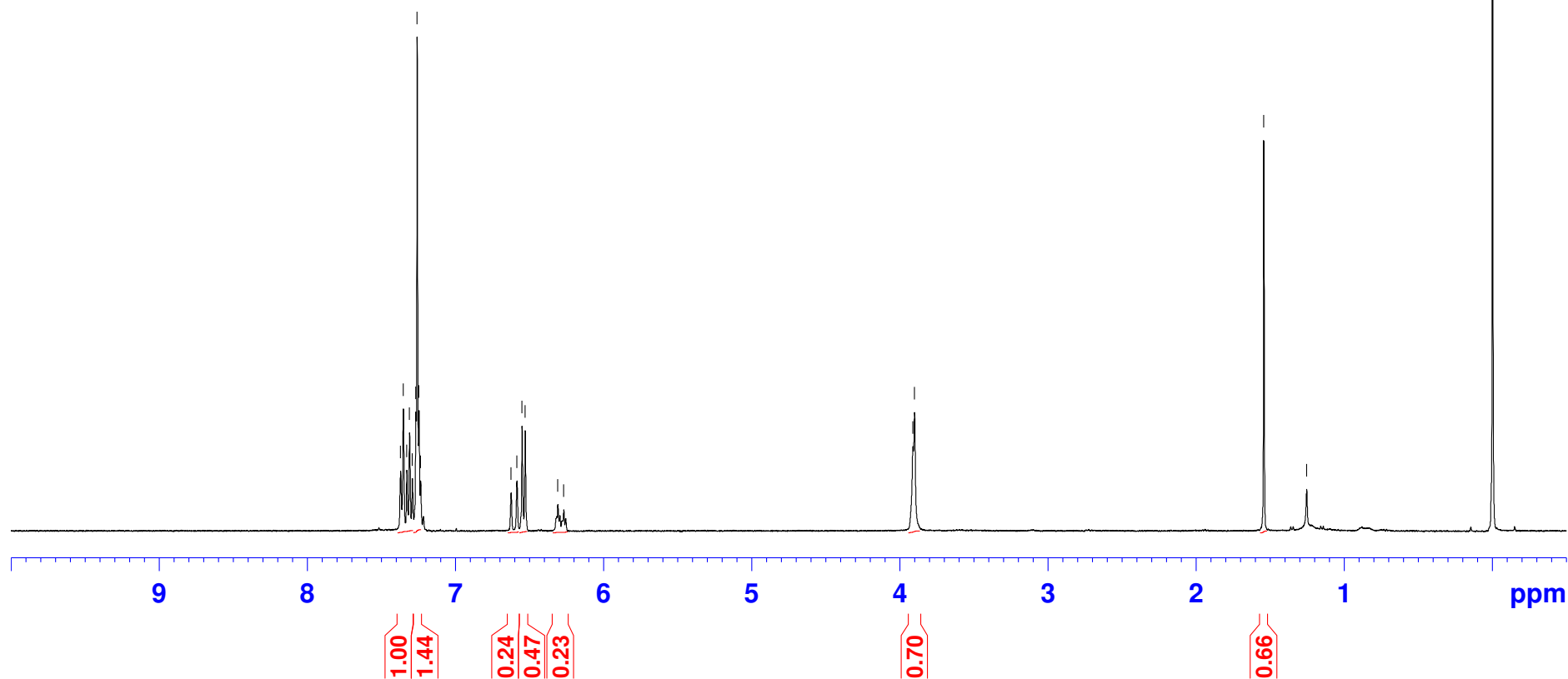
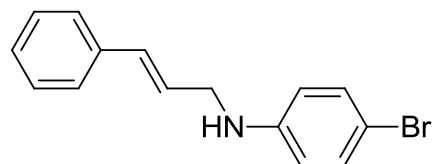
PROTON CDCl3 C:\Bruker\TOPSPIN curran 9

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7.237
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6.586
6.552
6.530
6.310
6.270

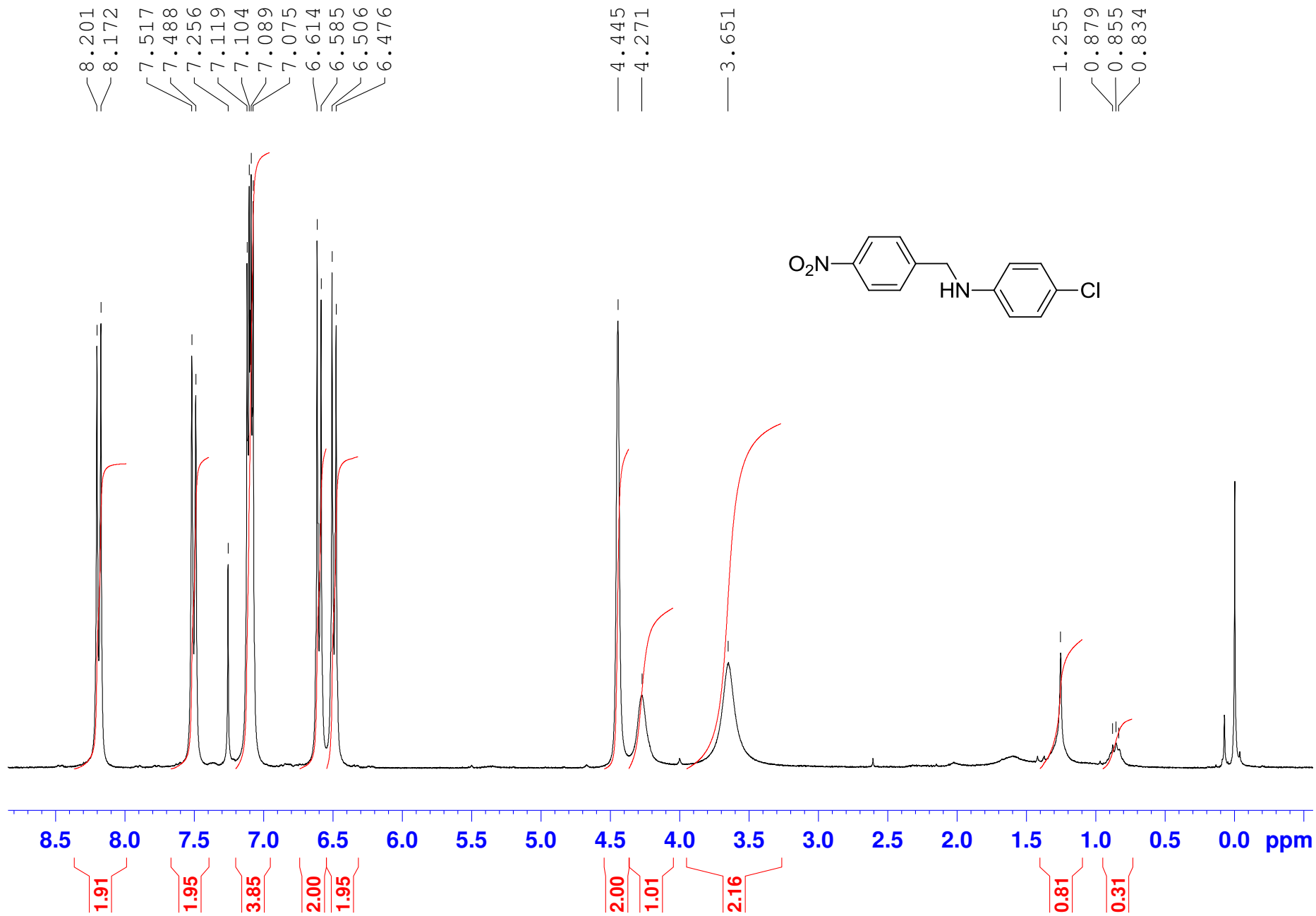
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3.902

1.544
1.254

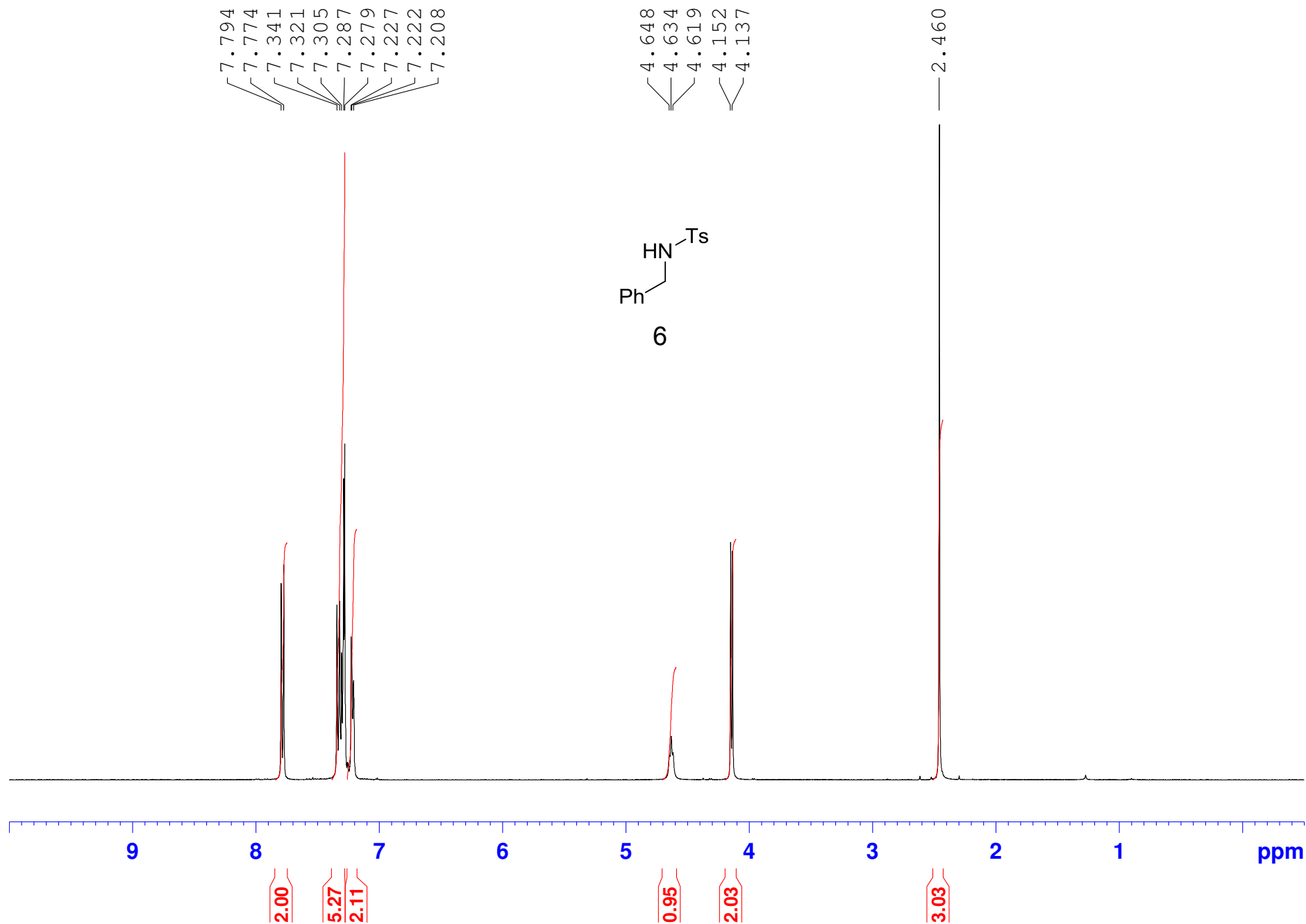
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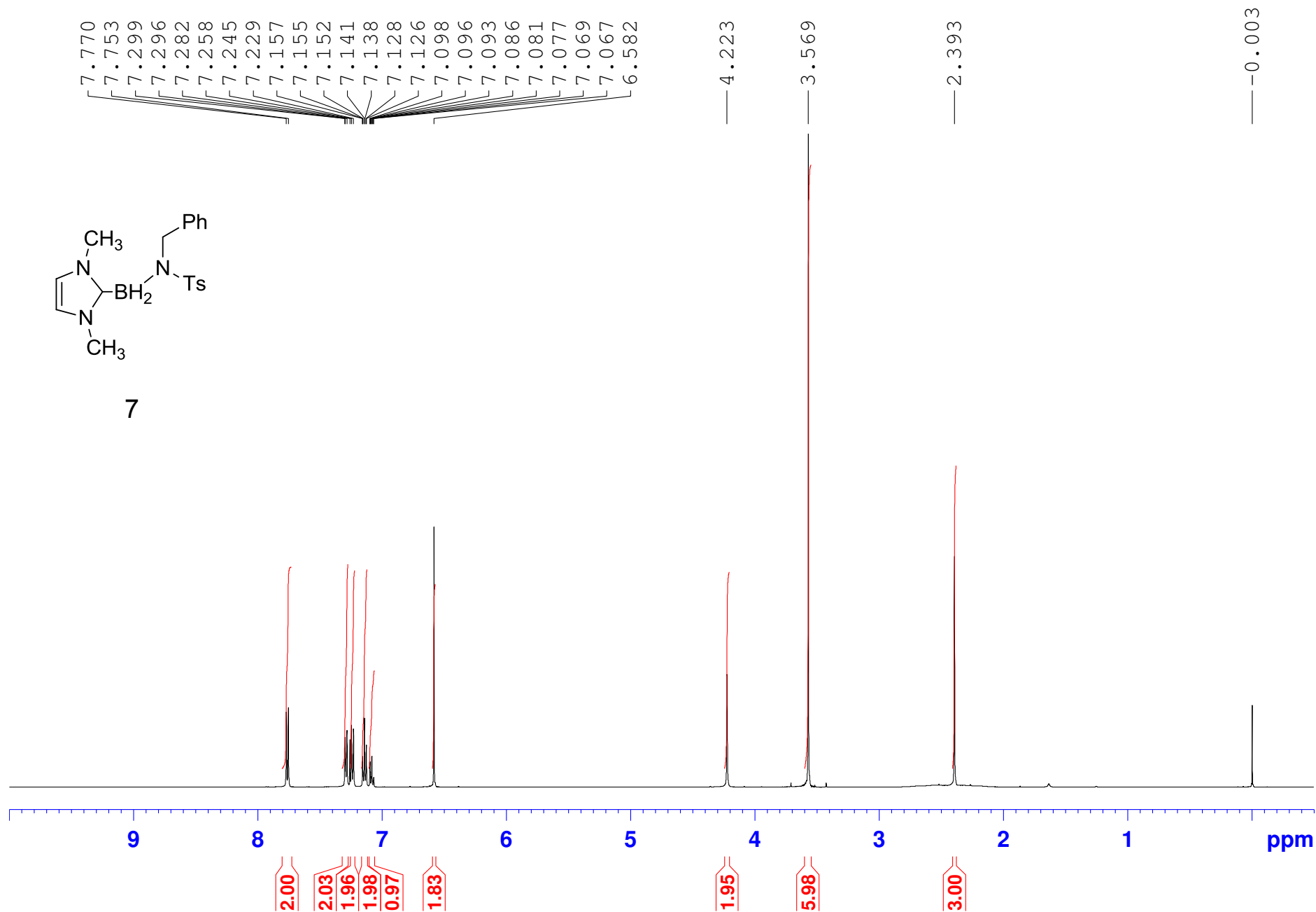
JD-38-75 4/7/11 301B 1H CDC13 Combined Fractions Post Vac



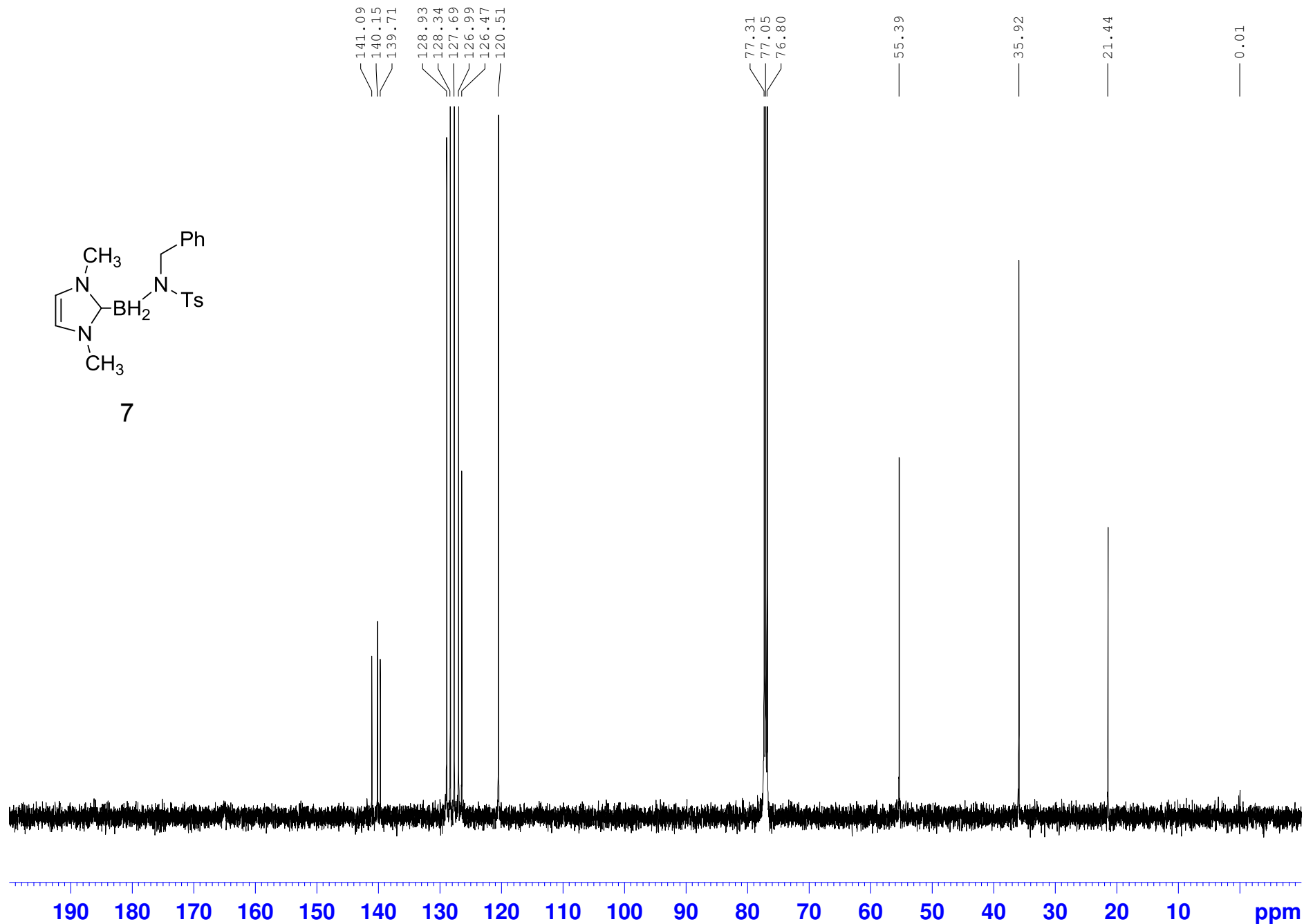
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TM.89.7.0.2 Fractions 9-12 Recrystallized, 1H, CDCl3, 8/12/11, 500 MHz

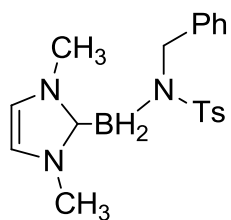


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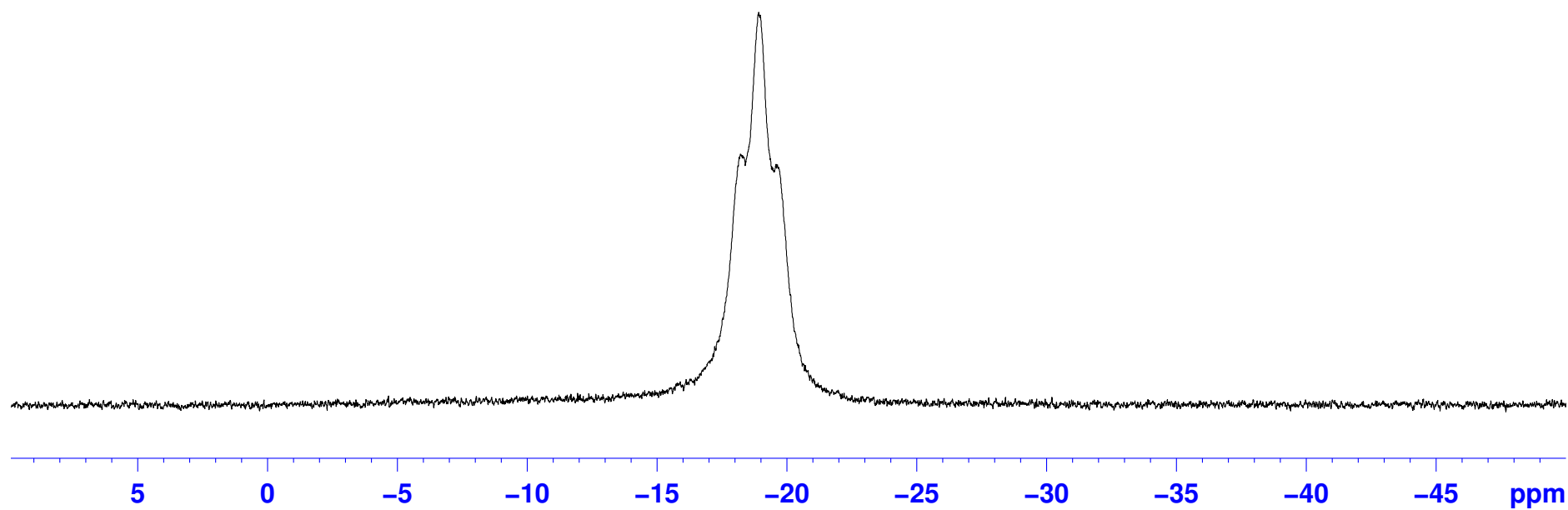


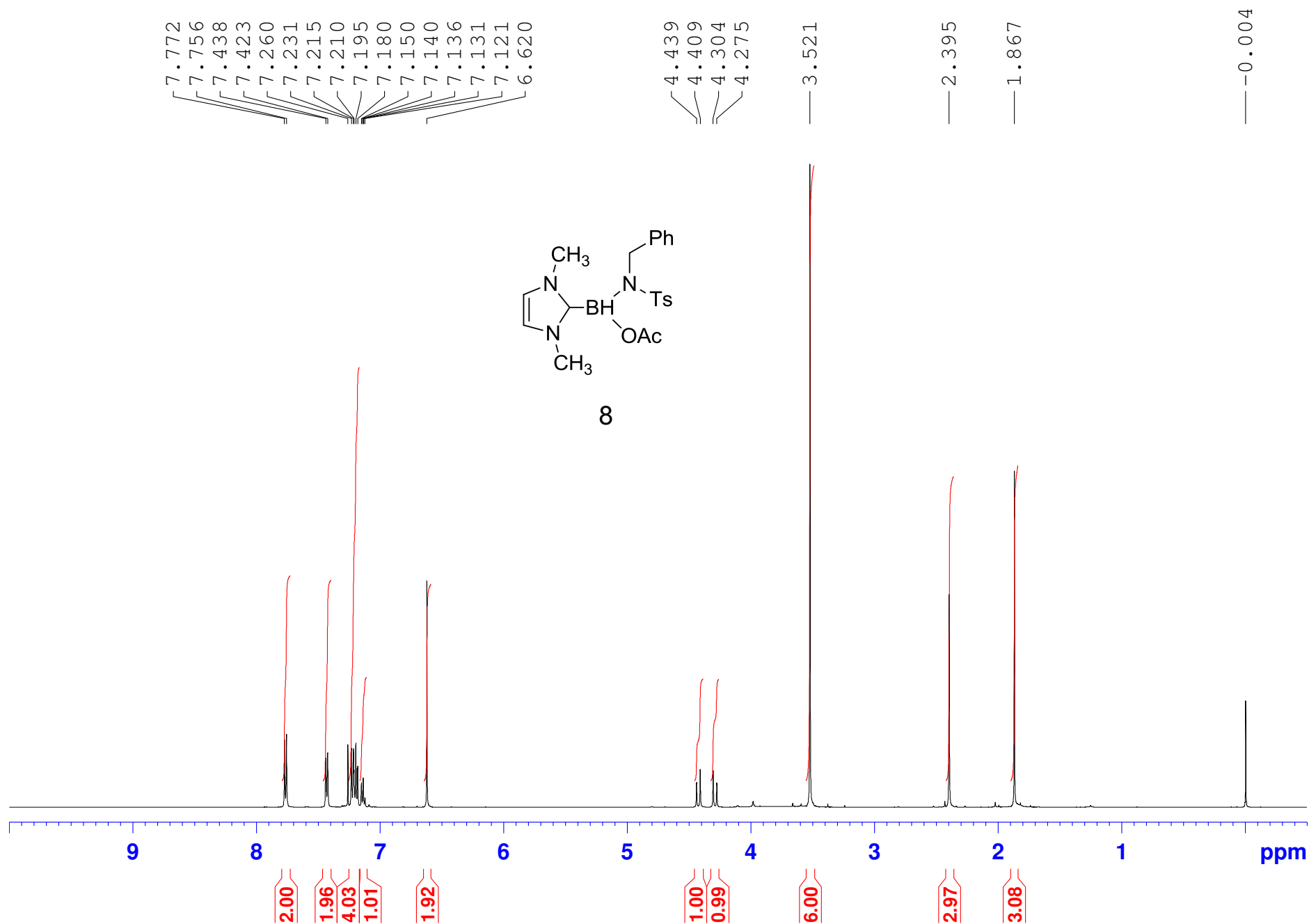
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-18.91

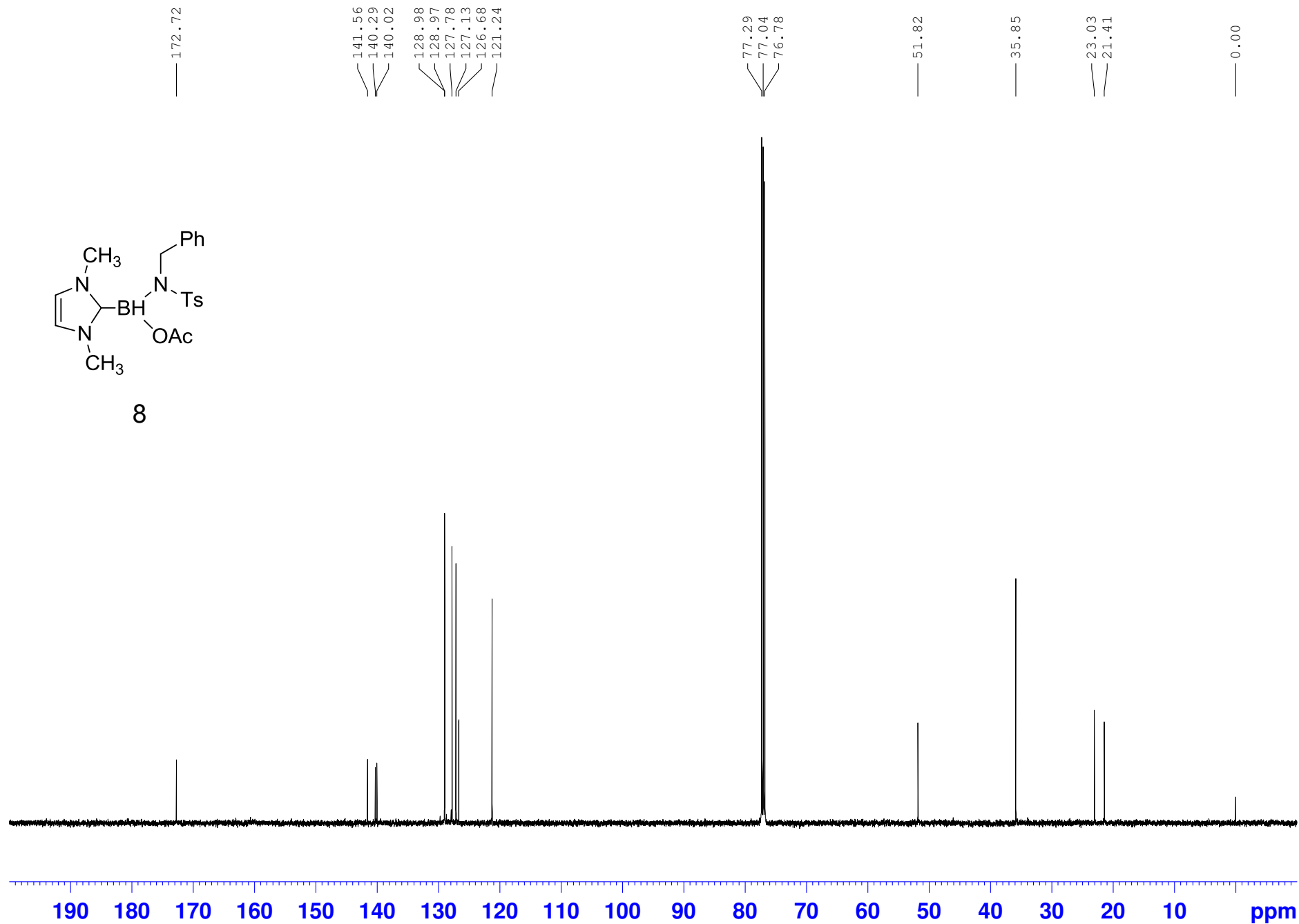
Boron-11 NMR



7

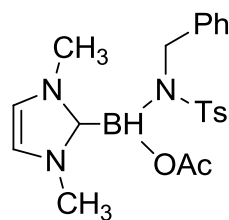


TM.89.7.0.2 Fractions 14-18 Recrystallized, ^1H , CDCl_3 , 8/12/11, 500 MHz

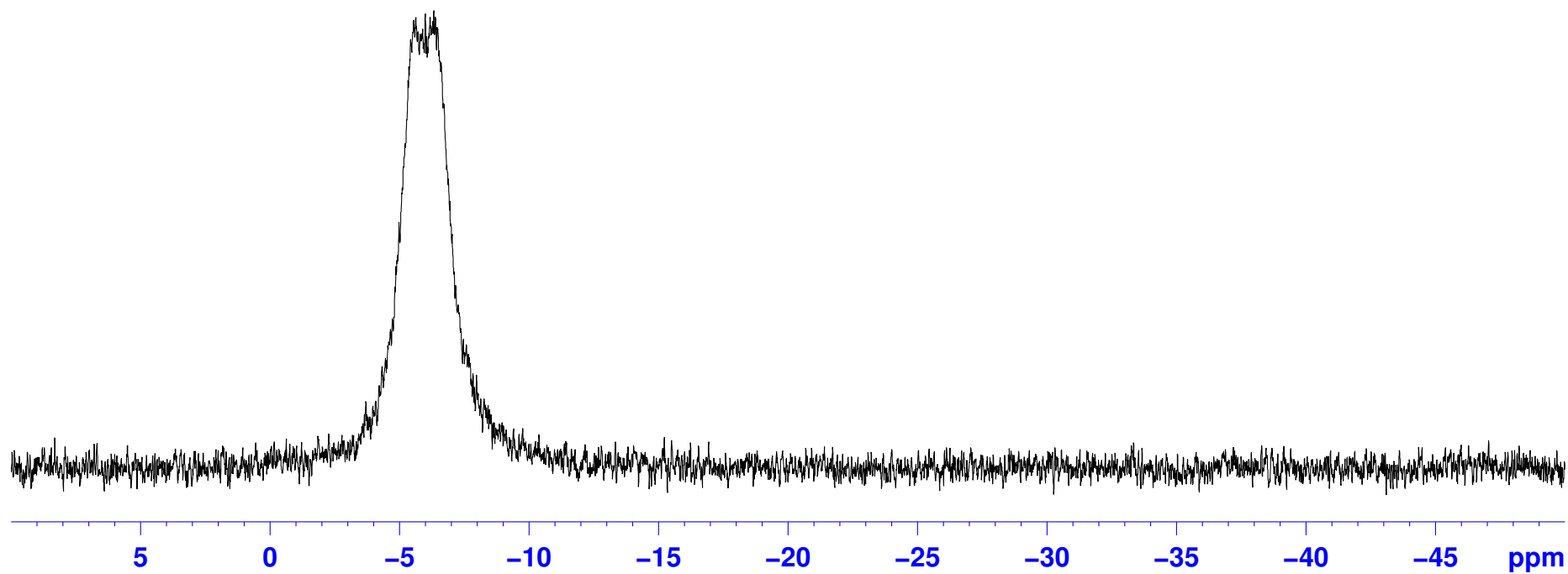
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TM.89.7.0 Fractions 10-12 Recrystallized, 11B, CDCl₃, 8/8/11-5.99
-6.31

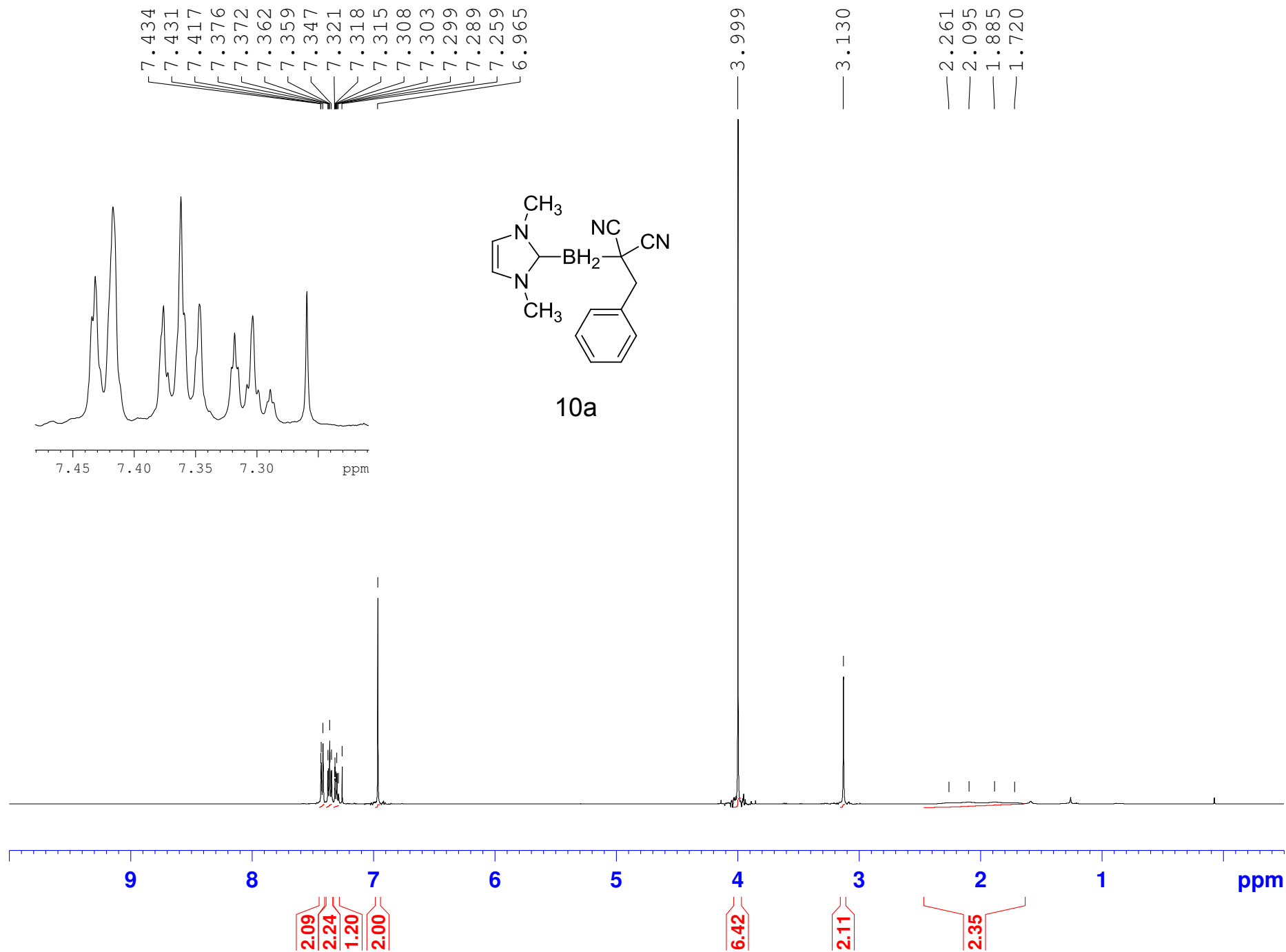
Boron-11 NMR



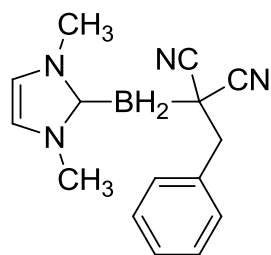
8



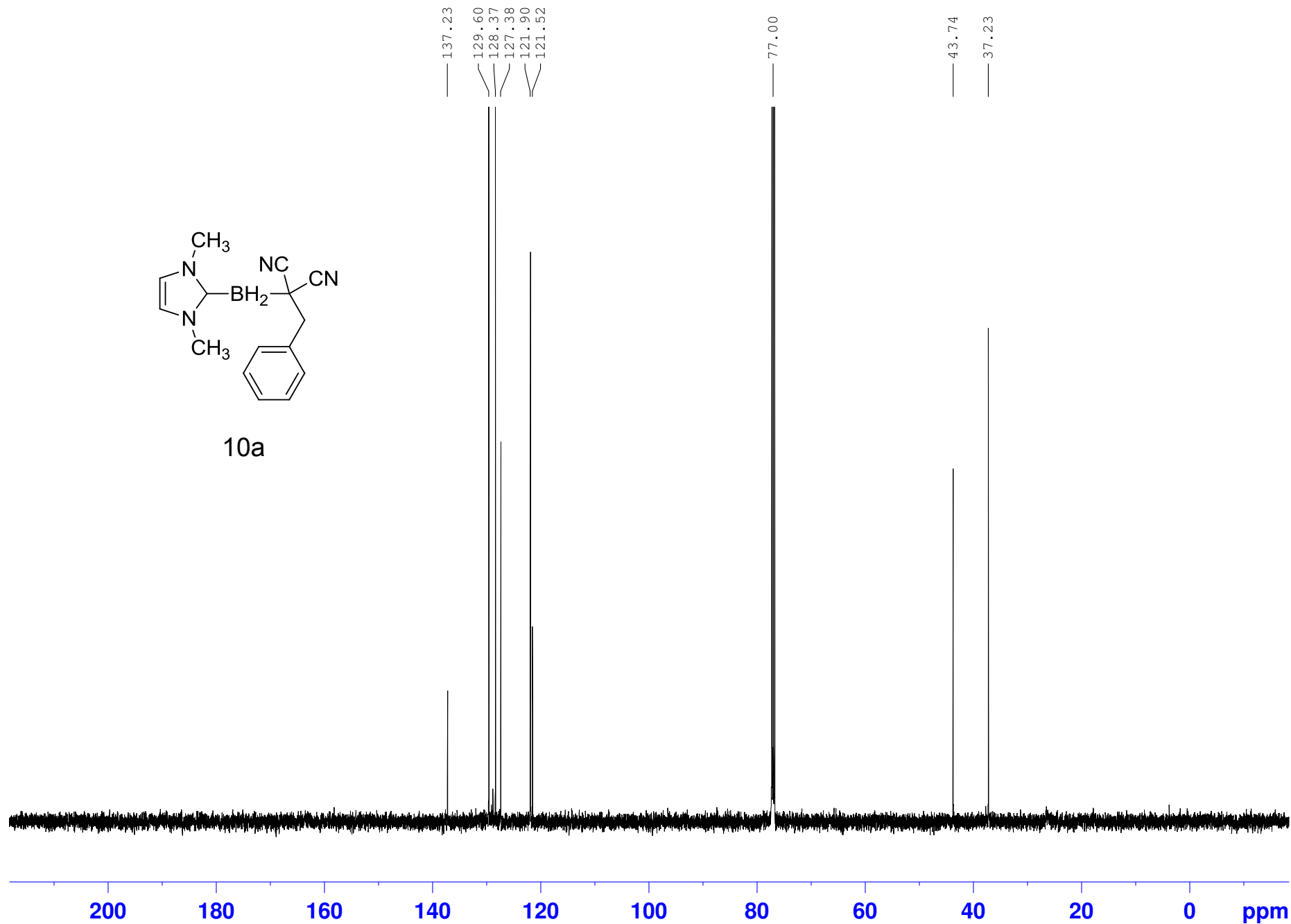
EM74.32.phenylboranemalonitrile 500 1H CDC13 9.21.11



EM74.32.phenylboranemalonitrile 500 13C CDC13 9.21.11



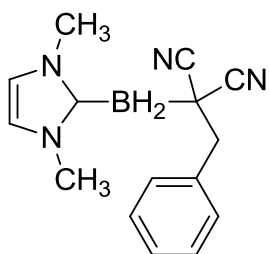
10a



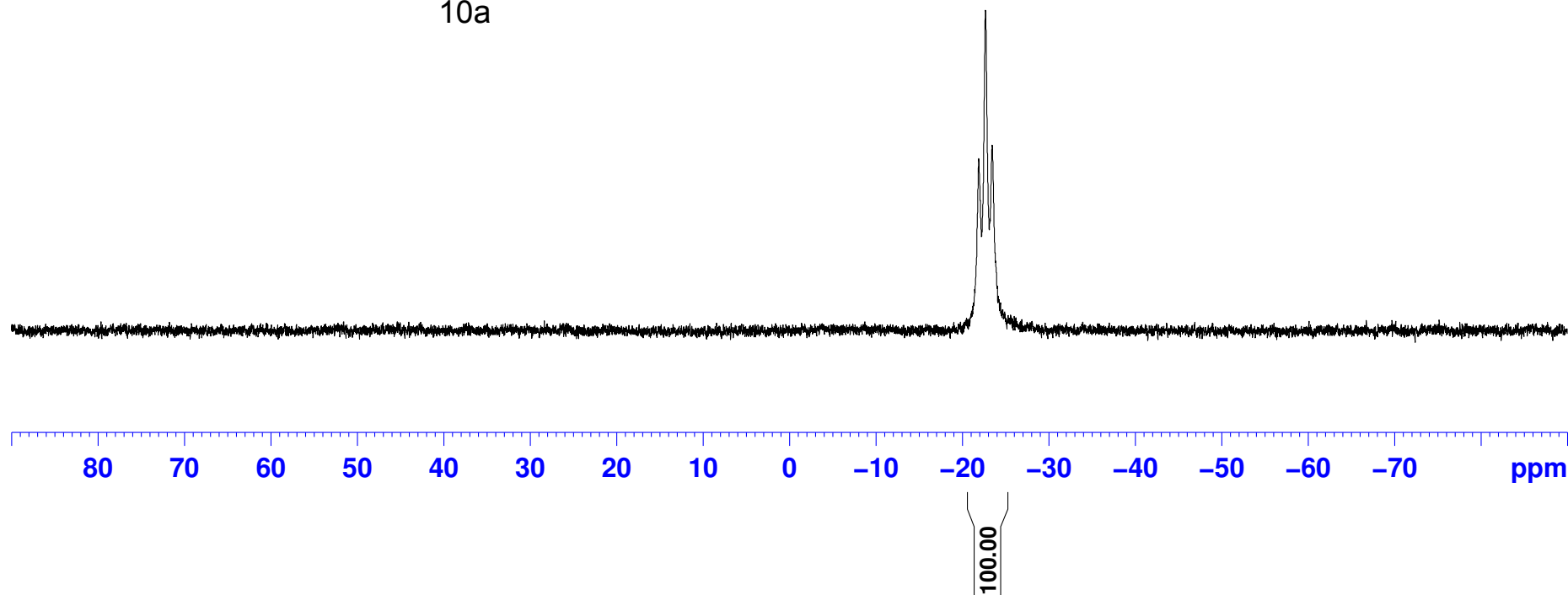
EM74.32mystery 400b 11B 10.3.11

-21.88
-22.67
-23.44

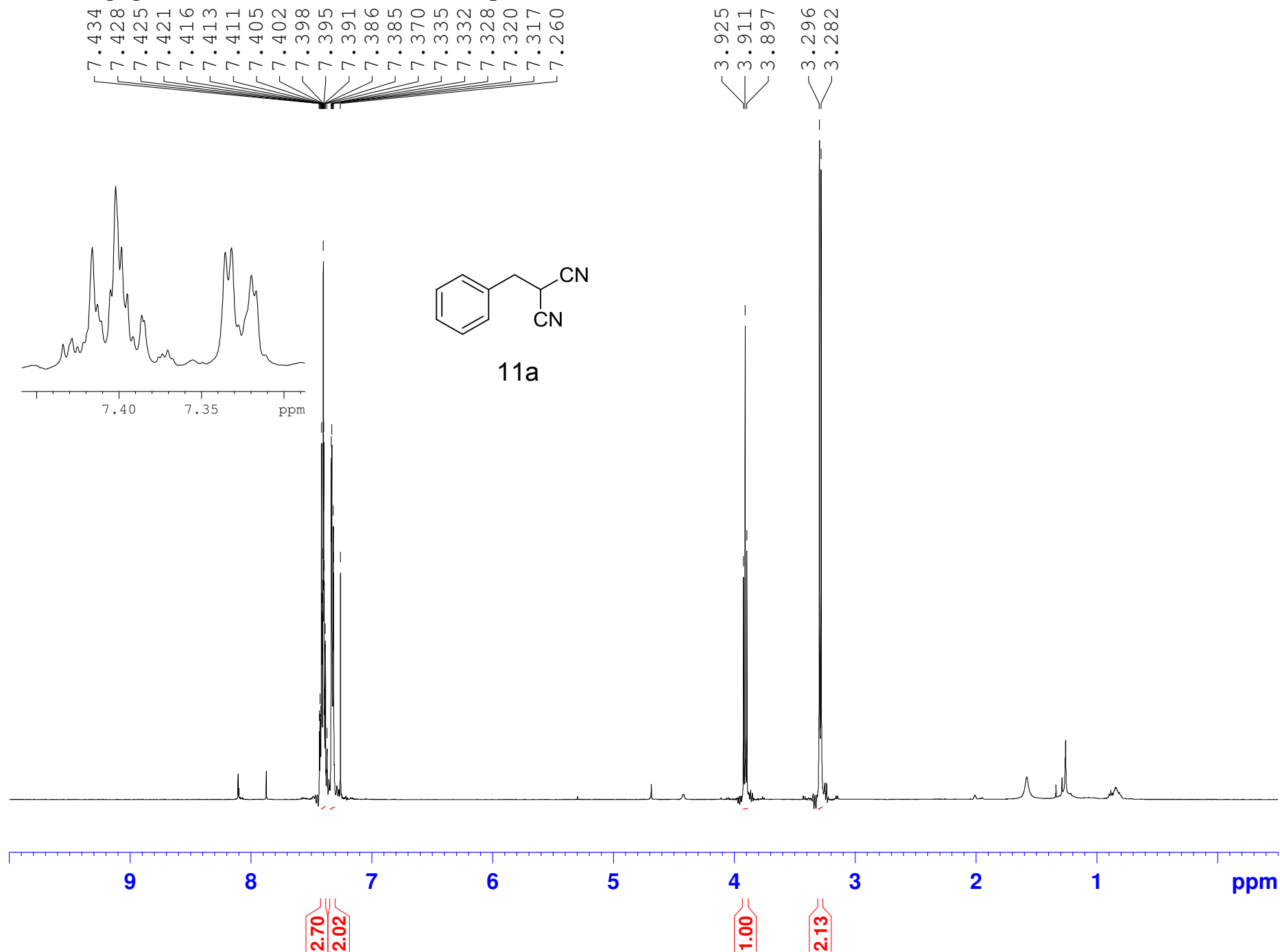
Boron-11 NMR



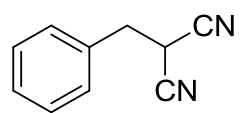
10a



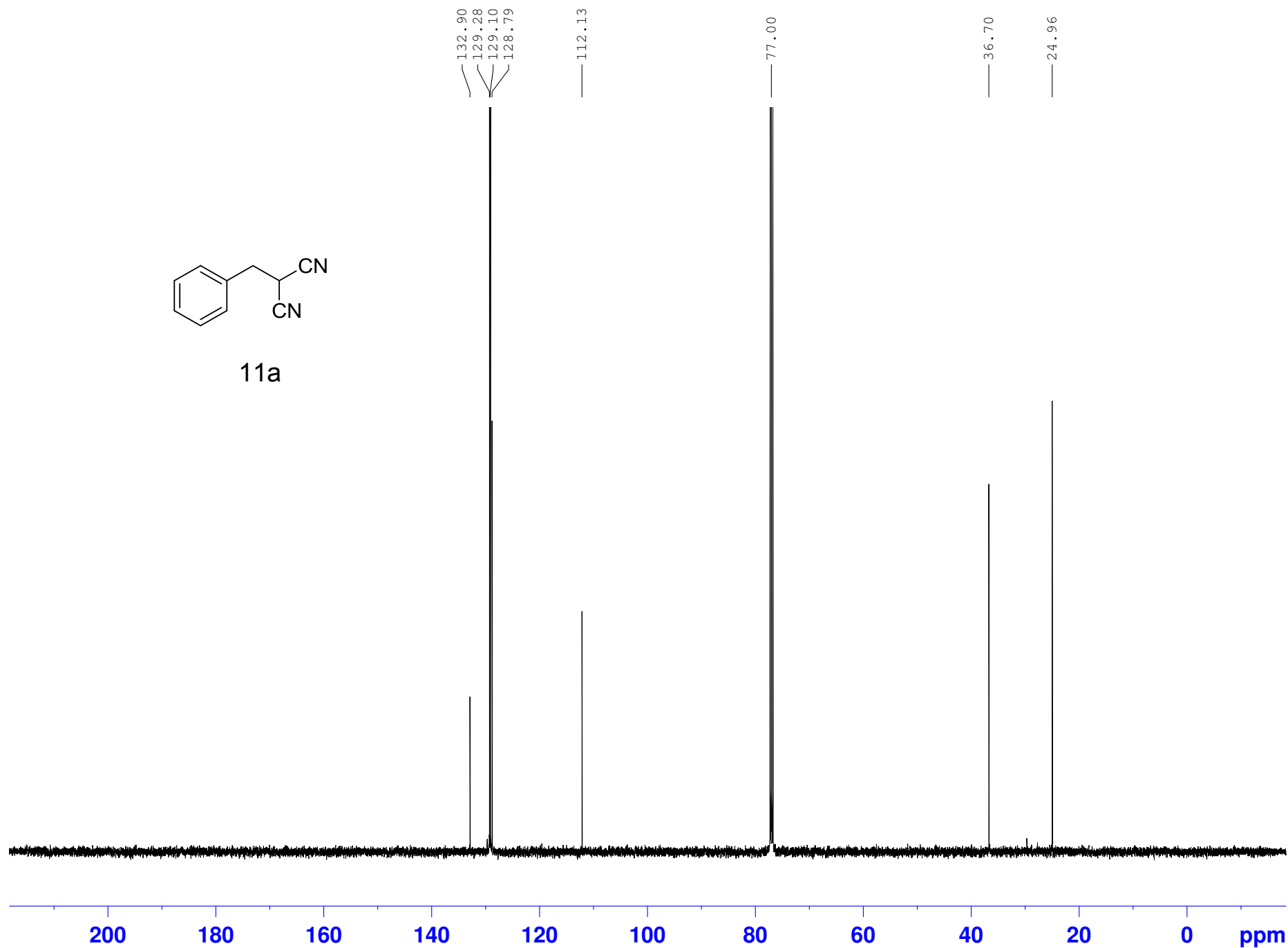
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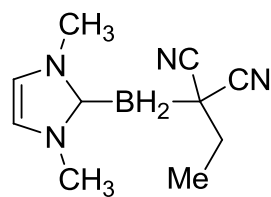
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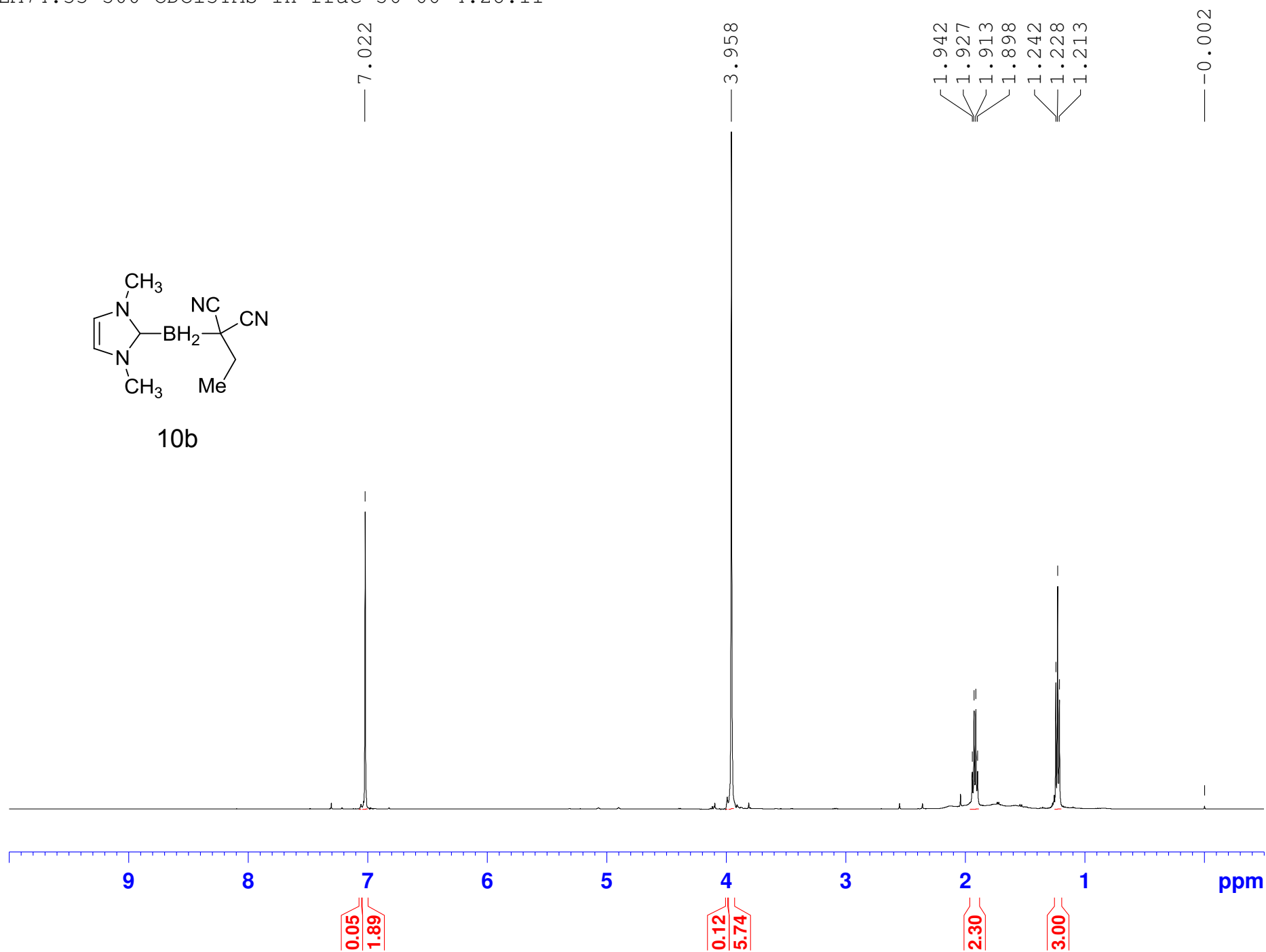
11a



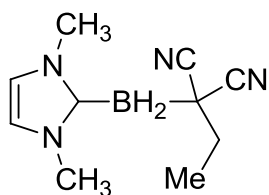
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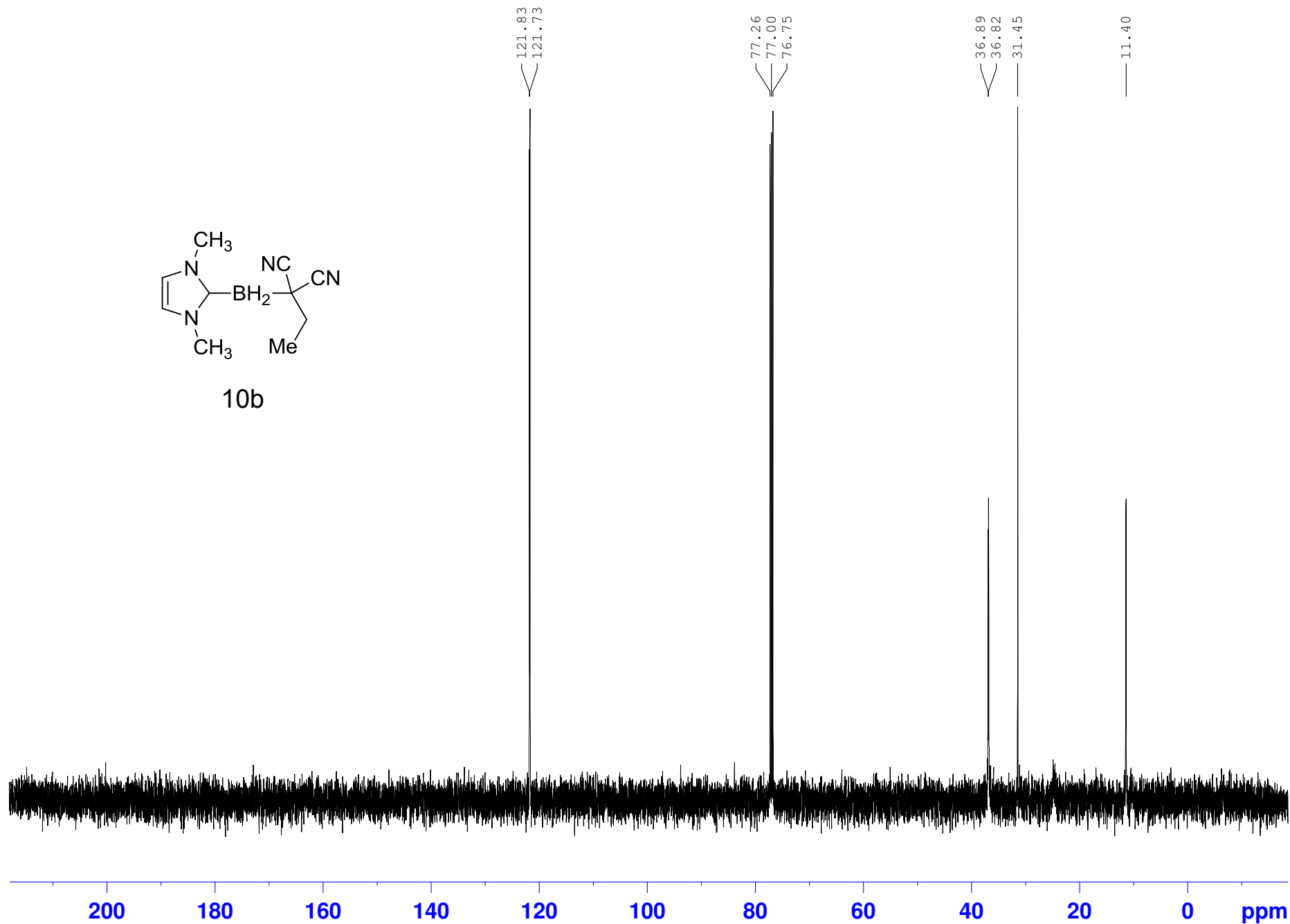
10b



EM74.33 500 CDC13TMS 13C frac 56-66 4.28.11

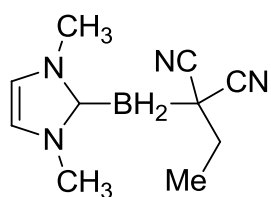


10b



EM74.purity 400b CDCl3TMS 11B methyl dicyano borane 5.9.11

Boron-11 NMR



10b

