Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Straightforward synthesis of chiral non-racemic α-boryl isocyanides

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General methods and materials.

All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions by using oven dried glassware at 120°C. CH_2Cl_2 and toluene were dried by filtering over a pad of neutral alumina prior the use. Triethylamine was distilled off from CaH_2 and stored over $KOH_{(S)}$ under argon atmosphere. Reactions were monitored by using Thin Layer chromatography (TLC) by means of Macherey-Nagel silica gel 0.20mm (60-F_{254}) under UV light (λ= 254 nm) or developed with standard stain solution: $KMnO_4$, ninhydrin, curcumin, Cerium Ammonium Molybdate (Hanessian's Stain) followed by heating. Chromatographic purification and isolation of the compounds was performed on gravimetric silica gel (particle size 0.05-0.20 mm). ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm and were calibrated to the residual signals of the deuterated solvent ($CDCl_3$, CD_3OD, DMSO-d_6, CD_3CN).[1] ^{13}C NMR were recorded with ^{1}H broadband decoupling. Multiplicity is given as s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublets, n= nonet, m = multiplet, br = broad signal and coupling constants (*J*) are given in Hz. Two-dimensional NMR techniques (COSY, HMBC, HSQC) were used to aid in the assignment of signals in ^{1}H and ^{13}C spectra. In particular the signal of the boron-bearing carbon atom in the ^{13}C spectra tends to be broadened, and the signal is often beyond the detection limit, but its resonance was unambiguously determined by HSQC and HMBC. Mass spectra were determined on an Agilent Technologies LC-MS (n) Ion Trap 6310A (ESI, 70 eV). High-resolution mass spectra were recorded on a LC-MS apparatus: Thermo Scientific UHPLC Ultimate 3000 coupled with Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer. Melting points were measured in open capillary tubes on a Stuart SMP30 Melting Point apparatus and are uncorrected. Optical rotations were determined at 20 °C on a Perkin-Elmer 241 polarimeter and are expressed in 10^{-1} deg cm^2 g^{-1}.

Unless otherwise noted all commercially available reagents were used as received. *t*-Butylsulfynilimines **4a**,[2] **ent-4a**,[2] **4b**,[3] **4c**,[4] **4d**[3] and **4e**,[5] and compound **6f**[6] were obtained following literature procedures.

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[1] H. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.* 1997, **62**, 7512–7515.

[2] D. Staas, K. Savage, C. Homnick, N. Tsou and R. Ball *J. Org. Chem.*, 2002, **67**, 8276–8279.

[3] F. Chemla, F. Ferreira, *J. Org. Chem.* 2004, **69**, 8244–8250.

[4] G. Liu, D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.* 1997, **119**, 9913

[5] M. Maji, R. Frohlich, A. Studer, *Org. Lett.* 2008, **10**, 1847–1850

[6] L. Han, C. Liu, W. Zhang, X.-X. Shi and S.-L. You, *Chem. Commun.* 2014, **50**, 1231; M. C. DiPoto, R. P. Hughes and J. Wu, *J. Am. Chem. Soc.* 2015, **137**, 14861.

Determination of enantiomeric ratio of α-boryl isocyanides 1a

The chiral purity of isocyanide **1a** has been verified by using ^{1}H NMR technique and Pirkle's alcohol as chiral shift reagent.[7]

*Condition for the visualisation of both enantiomers **1a** / **ent-1a** with CSA by using ^{1}H NMR spectroscopy.*

To a 50:50 mixture of **1a** (2.2 mg) and **ent-1a** (2.2 mg) in 0.7 mL of $CDCl_3$ was added (*R*)-1-Anthracen-9-yl-2,2,2-trifluoroethanol in proportion 1:1, 1:2, 1:4, 1:10, 1:20. After each additions an ^{1}H NMR spectrum (600 MHz) was recorded (**Figure S1**).

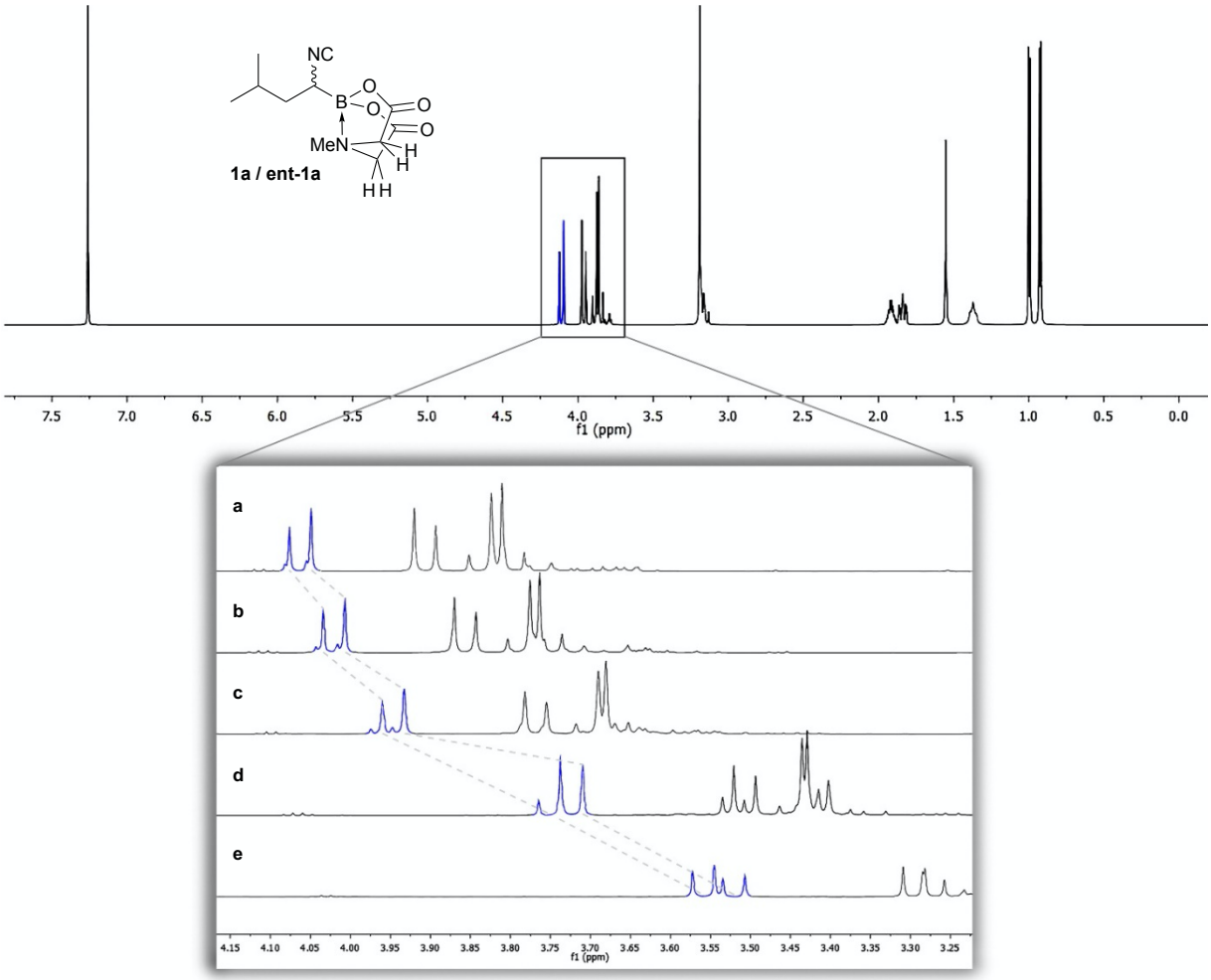


Figure S1. ^{1}H-NMR spectra (600 MHz, $CDCl_3$) of racemic mixture **1a** and **ent-1a** with different amount of Pirkle's alcohol. **a)** racemic: Pirkle 1:1; **b)** racemic: Pirkle 1:2; **c)** racemic: Pirkle 1:4; **d)** racemic: Pirkle 1:10; **e)** racemic: Pirkle 1:20.

[7] a) W. Pirkle, D. Sikkenga, M. Pavlin, *J. Org. Chem.* 1977, **42**, 384–387; b) J. Redondo, A. Capdevila, I. Latorre *Chirality*, 2010, **22**, 472

With the optimal condition in hand a second experiment has been repeated with **1a** : Pirkle's alcohol 1:20 (enlargement **c**, Figure S2) where it has been confirmed the enantiomeric ratio of **1a** of 98:2. This result has been verified by the final addition of a small amount of **ent-1a** to the sample **1a** : Pirkle's alcohol 1:20 (enlargement **d**, Figure S2).

The enantiomeric ratio remained 98:2 along the synthetic sequence.

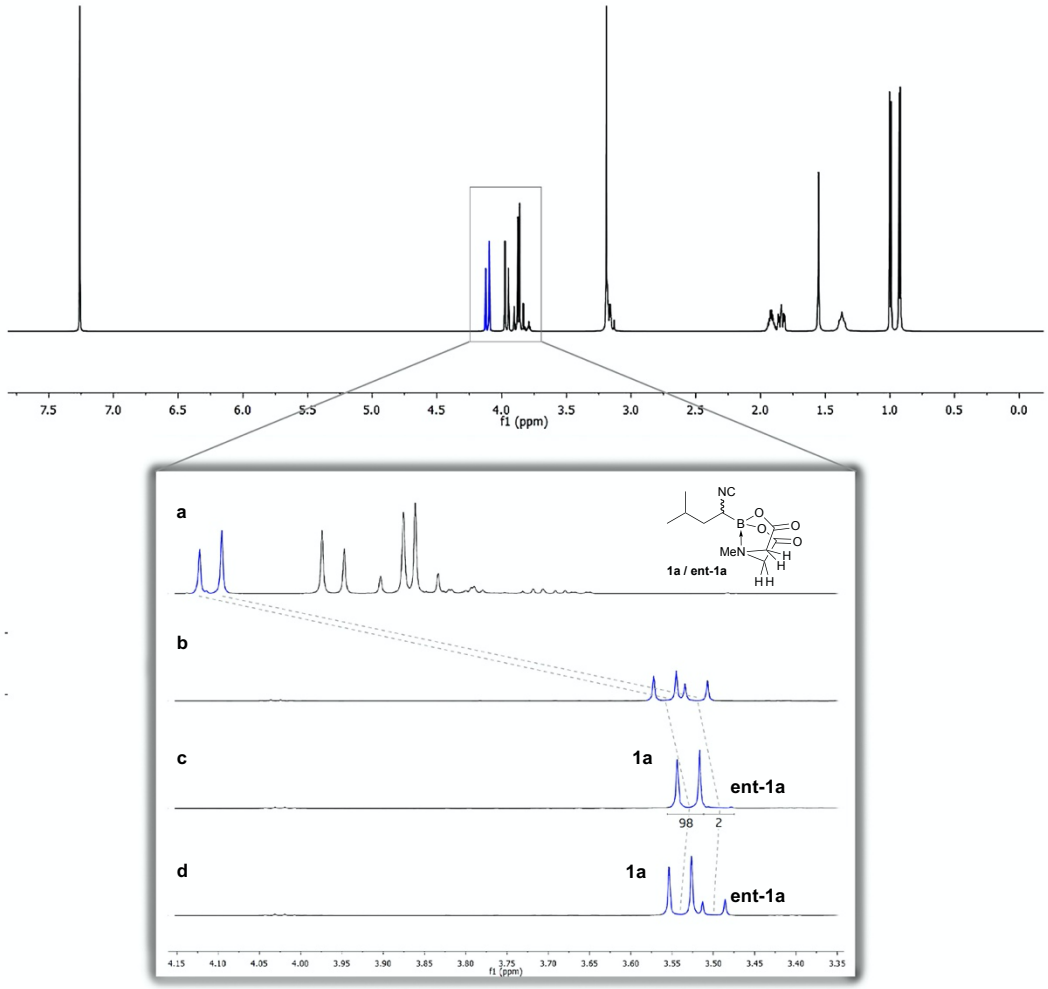
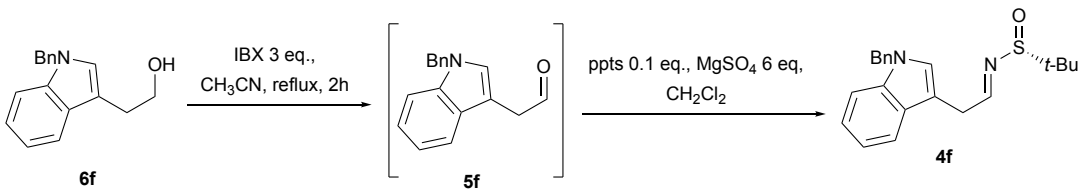


Figure S2. Determination of enantiomeric ratio. ^{1}H NMR spectra (600 MHz, $CDCl_3$): **a)** racemic; **b)** racemic : Pirkle 1:20; **c) 1a** : Pirkle 1:20; **d)** (**1a** : Pirkle 1:20) + **ent-1a**.

Synthesis of Imines 4f

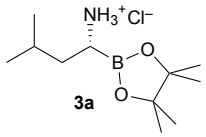


A 100 ml round bottom flasks equipped with magnetic stir bar was charged with **6f** (1.05 g, 4.18 mmol), CH_3CN (21 ml) and IBX (2-iodoxybenzoic acid, 3.51 g, 12.54 mmol). The reaction mixture was refluxed for 2 h, filtered through a thin pad of celite and concentrate under reduced pressure. The resulting residue was dissolved in CH_2Cl_2 (20 mL) and was sequentially charged with (*R*)-2-methylpropane-2-sulfinamide (405 mg, 3.34 mmol), $MgSO_4$ (2.41g, 20.04 mmol) and PPTS (pyridinium *p*-toluenesulfonate, 84 mg, 0.334 mmol). After 24 h, the resulting suspension was filtered off a pad of celite and evaporated *in vacuo*. The crude was purified by using silica gel (petroleum ether/AcOEt 8:2), obtaining 666 mg of **4f** as orange oil (1.80 mmol, 43 % from **6f**), with a purity of 95% due to the presence of ethyl acetate. The imine has been used for the next step without further manipulation.

(*R*,*E*)-*N*-(2-(1-benzyl-1*H*-indol-3-yl)ethylidene)-2-methylpropane-2-sulfinamide 4f. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (t, J = 5.2 Hz, 1H), 7.61 (dt, J = 7.8 Hz, 1.0 Hz, 1H), 7.33 – 7.24 (m, 4H), 7.23 – 7.17 (m, 1H), 7.16 – 7.08 (m, 3H), 7.03 (s, 1H), 5.29 (s, 2H), 4.00 – 3.94 (m, 2H), 1.18 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 137.5, 136.8, 128.9, 128.1, 127.8, 126.9, 126.8, 122.3, 119.6, 119.1, 109.9, 108.3, 56.9, 50.1, 32.6, 22.5. ESIMS: 353 $[M+H]^+$. $[\alpha]^{20}_D$ -153.4 (c = 0.96, $CHCl_3$).

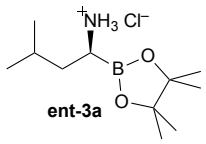
Borylation of imines 4a–f and subsequent hydrolysis for the synthesis of 3a–f.

(R)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-aminium chloride 3a



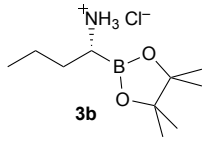
Following the general procedure, starting from imines **4a** (452 mg, 2.39 mmol), compound **3a** has been prepared as a white solid (507 mg, 1.9 mmol) with 85% yield. Spectroscopic data are in agreement with the ones reported in literature.[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (s, 3H), 2.71 – 2.61 (m, *J* = 7.4, 1H), 1.70 (n, *J* = 6.7 Hz, 1H), 1.55 – 1.38 (m, 2H), 1.242 (s, 6H), 1.236 (s, 6H), 0.86 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) *δ* 84.5, 38.2, 34.6 (CHB, br), 24.6, 24.4, 24.3, 22.4, 22.2.

(S)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-aminium chloride ent-3a



Following the general procedure, starting from imines **ent-4a** (621 mg, 3.28 mmol), compound **ent-3a** has been prepared as a white solid (603 mg, 2.42 mmol) with 74% yield. Spectroscopic data are in agreement with the ones reported in literature.[8] ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (s, 3H), 2.72 – 2.60 (m, 1H), 1.70 (n, *J* = 6.8 Hz, 1H), 1.55 – 1.38 (m, 2H), 1.24 (s, 6H), 1.23 (s, 6H), 0.86 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 84.5, 38.2, 34.6 (CHB, br), 24.6, 24.40, 24.35, 22.4, 22.2.

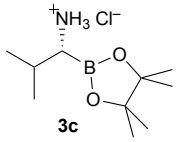
(*R*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-aminium chloride 3b



Following the general procedure, starting from imines **4b** (500 mg, 2.90 mmol), compound **3b** has been prepared as a white solid (473 mg, 2.00 mmol) with 69% yield. M.p. 124.8–126.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) *δ* 7.79 (br s, 3H), 2.76 – 2.66 (m, 1H), 1.56 (q, *J* = 7.6 Hz, 2H), 1.45 – 1.27 (m, 2H), 1.25 (s, 6H), 1.24 (s, 6H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CD_3OD) δ 86.5, 75.8, 38.8 (CHB, br), 32.8, 25.1, 20.7, 14.1. ^{11}B NMR (128 MHz, $CDCl_3$) *δ* 31.4. HRMS $[M]^+$: calc. for $C_{10}H_{23}BNO_2$ 200.1816, found 200.1820; $[\alpha]^{20}_D$ -1.3 (c = 1.1, CH_3OH).

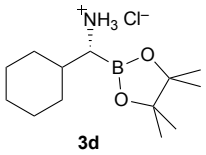
[8] M. Beenen, C. An, J. Ellman, *J. Am. Chem. Soc.* 2008, **130**, 6910–6911

***(R)*-2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-aminium chloride 3c**



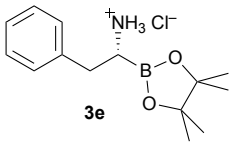
Following the general procedure, starting from imines **4c** (558 mg, 3.18 mmol), compound **3c** has been prepared as a pale yellow solid (455 mg, 1.93 mmol) with 61% yield. M.p. 159 – 161 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (br s, 3H), 2.57 (br s, 1H), 2.04 – 1.92 (m, 1H), 1.26 (s, 6H), 1.25 (s, 6H), 0.96 (d, J = 6.9 Hz, 3H), 0.94 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 84.6, 42.9 (CHB), 28.6, 24.7, 24.4, 20.0, 19.1. ^{11}B NMR (128 MHz, DMSO-d_6) δ 33.0. HRMS $[M]^+$: calc. for $C_{10}H_{23}BNO_2$ 200.1816, found 200.1817; $[\alpha]^{20}_D$ +3.6 (c = 1.0, CH_3OH).

***(R)*-cyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methanaminium chloride 3d**



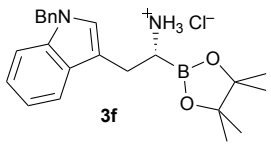
Following the general procedure, starting from imines **4d** (1.54 g, 7.15 mmol), compound **3d** has been prepared as a white solid (1.79 g, 6.49 mmol) with 91% yield. M.p. 125.1–127.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (br s, 3H), 2.78 (br s, 1H), 2.06 – 1.82 (m, 4H), 1.80 – 1.57 (m, 4H), 1.29 (s, 6H,), 1.28 (s, 6H), 1.19 – 1.01 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 84.5, 73.5, 42.2 (CHB), 38.2, 29.8, 29.3, 25.7, 25.5, 24.9, 24.4. ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.1. ESIMS: 240.1 $[M\text{-}Cl]^+$; $[\alpha]^{20}_D$ -3.4 (c = 1.2, CH_3OH).

***(R)*-2-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-aminium chloride 3e**



Following the general procedure, starting from imines **4e** (550 mg, 2.46 mmol), compound **3e** has been prepared as a pale yellow solid (419 mg, 1.48 mmol) with 60% yield. M.p. 169.5–171.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (br s, 3H), 7.38 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 3.33 – 3.12 (m, 2H+1H, C*H*B), 1.20 (s, 6H), 1.19 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.5, 129.8, 129.0, 127.4, 85.5, 39.4 (CHB), 35.4, 25.0, 24.9. ^{11}B NMR (128 MHz, DMSO-d_6) δ 32.9. ESIMS: 166 $[M\text{-}pin\text{-}Cl]^+$; $[\alpha]^{20}_D$ -11.4 (c = 1.0, CH_3OH).

***(R)*-2-(1-benzyl-1H-indol-3-yl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethan-1-aminium chloride 3f**

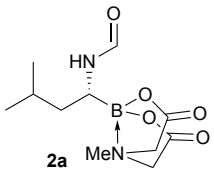


Following the general procedure, starting from imines **4f** (650 mg, 1.84 mmol), compound **3f** has been prepared as a pale yellow solid (618 mg, 1.50 mmol) with 81% yield. M.p. 202.0–203.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 (br s, 3H), 7.64 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 7.33 (s, 1H), 7.32 – 7.18 (m, 5H), 7.10 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 5.36 (s, 2H), 3.15 (dd, J = 13.3, 5.3 Hz, 1H) 3.09 – 2.94 (m, 2H,

BCHCH_2 + CHB), 1.11 (s, 6H), 1.06 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 138.2, 136.0, 128.4, 127.7, 127.6, 127.3, 127.0, 121.4, 118.8, 118.7, 110.1, 109.0, 84.4, 49.0, 37.0 (*C*HB), 24.9, 24.5, 24.4. ^{11}B NMR (128 MHz, DMSO-d_6) δ 33.1. HRMS $[M]^+$: calc. for $C_{23}H_{30}BN_2O_2$ 377.2395, found 377.2399; $[\alpha]^{20}_D$ -13.2 (c = 1.0, CH_3OH).

Synthesis and characterization of compounds 2a–f.

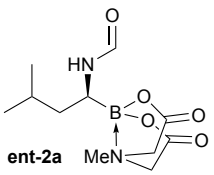
(*R*)-*N*-(3-methyl-1-(MIDA-boryl)butyl)formamide 2a



2a

Following the general procedure (reaction time= 2.5 h), starting from chloride **3a** (150 mg, 0.60 mmol), compound **2a** has been synthesised as an off white solid (105 mg, 0.39 mmol) with 65% yield. M.p. 233.5–234.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 (d, J = 2.0 Hz, 1H), 7.48 (dd, J = 10.2, 2.1 Hz, 1H), 4.25 (d, J = 17.2 Hz, 1H), 4.16 (d, J = 16.8 Hz, 1H), 4.04 (d, J = 17.2 Hz, 1H), 3.87 (d, J = 16.9 Hz, 1H), 3.61 – 3.51 (m, 1H, C*H*B), 2.89 (s, 3H), 1.62 – 1.46 (m, 1H), 1.38 – 1.27 (m, 1H), 1.24 – 1.14 (m, 1H), 0.87 (d, J = 6.7 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.5, 161.0, 62.3, 62.1, 45.6, 40.4, 34.1 (*C*HB), 24.0, 23.8, 21.2. ^{11}B NMR (128 MHz, DMSO-d$_6$) δ 11.0. ESIMS: 268.9 [M-H]$^-$; $[\alpha]^{20}_D$ -40.5 (c = 1.1, CH_3OH).

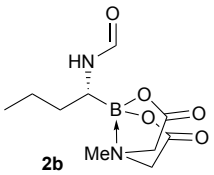
(*S*)-*N*-(3-methyl-1-(MIDA-boryl)butyl)formamide ent-2a



ent-2a

Following the general procedure (reaction time= 2.5 h), starting from chloride **ent-3a** (280 mg, 1.12 mmol), compound **ent-2a** has been synthesised as an off white solid (197 mg, 0.73 mmol) with 65% yield. Spectral data were identical to compound **2a**; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 (d, J = 1.8 Hz, 1H), 7.48 (dd, J = 10.1, 1.3 Hz, 1H), 4.24 (d, J = 17.2 Hz, 1H), 4.15 (d, J = 16.8 Hz, 1H), 4.03 (d, J = 17.2 Hz, 1H), 3.86 (d, J = 17.2 Hz, 1H), 3.60 – 3.52 (m, 1H, C*H*B), 2.88 (s, 3H), 1.62 – 1.47 (m, 1H), 1.38 – 1.27 (m, 1H), 1.24 – 1.14 (m, 1H), 0.86 (d, J = 6.6 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.5, 161.0, 62.4, 62.1, 45.6, 40.4, 34.1 (*C*HB, br), 24.0, 23.8, 21.2. ^{11}B NMR (128 MHz, DMSO-d$_6$) δ 11.0. $[\alpha]^{20}_D$ +37.3 (c = 1.0, CH_3OH).

(*R*)-*N*-(1-(MIDA-boryl)butyl)formamide 2b

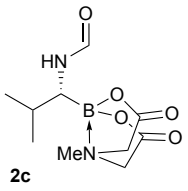


2b

Following the general procedure (reaction time= 2.5 h), starting from chloride **3b** (235 mg, 1.06 mmol), compound **2b** has been synthesised as an off white solid (220 mg, 0.86 mmol) with 81% yield. M.p. 178 – 180 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, J = 1.9 Hz, 1H), 7.50 (d, J = 10.0 Hz, 1H), 4.22 (d, J = 17.2 Hz, 1H), 4.17 (d, J = 17.0 Hz, 1H), 4.05 (d, J = 17.2 Hz, 1H), 3.86 (d, J = 17.0 Hz, 1H), 3.53 – 3.45 (m, 1H), 2.86 (s, 3H), 1.51 – 1.13 (m, 5H), 0.84 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.7, 168.6, 161.1,

62.2, 62.1, 45.5, 35.6 (br CHB), 33.4, 19.2, 13.9. ^{11}B NMR (128 MHz, DMSO-d_6) δ 10.9. HRMS [M-H]$^-$: calc. $C_{10}H_{16}BN_2O_5$ 255.11468, found 255.1157. $[\alpha]^{20}_D$ -25.1 (c = 0.59, $CH_3OH/CHCl_3$ 1:1).

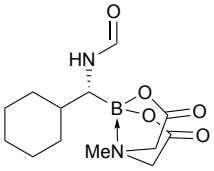
(*R*)-*N*-(2-methyl-1-(MIDA-boryl)propyl)formamide 2c



2c

Following the general procedure (reaction time= 3 h), starting from chloride **3c** (389 mg, 1.65 mmol), compound **2c** has been synthesised as an off white solid (222 mg, 0.87 mmol) with 53% yield. M.p. 210 – 212 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04 (d, J = 1.9 Hz, 1H), 7.46 (d, J = 10.3 Hz, 1H), 4.18 (d, J = 17.1 Hz, 1H), 4.16 (d, J = 17.0 Hz, 1H), 4.06 (d, J = 17.1 Hz, 1H), 3.83 (d, J = 17.0 Hz, 1H), 3.52 (dd, J = 10.5, 3.2 Hz, 1H), 2.82 (s, 3H), 1.94 – 1.80 (m, 1H), 0.84 (d, J = 6.9 Hz, 3H), 0.81 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.6, 161.5, 61.8, 61.7, 45.5, 40.6 (br, CHB), 29.5, 21.1, 18.2. ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.2. HRMS [M-H]$^-$: calc. for $C_{10}H_{16}BN_2O_5$ 255.11468, found 255.1158. $[\alpha]^{20}_D$ -25.3 (c = 0.58, $CH_3OH/CHCl_3$ 1:1).

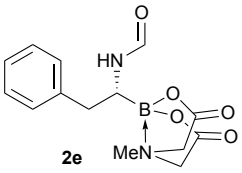
(*R*)-*N*-(cyclohexyl-(MIDA-boryl)methyl)formamide 2d



2d

Following the general procedure (reaction time= 5 h), starting from chloride **3d** (200 mg, 0.73 mmol), compound **2d** has been synthesised as an off white solid 89 mg (0.29 mmol, with 40% yield), with a purity of 95% due to the presence of ethyl ether and then used for the next step without further manipulation. M.p. 63.5–65.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.01 (d, J = 2.2 Hz, 1H), 7.44 (dd, J = 10.6, 2.3 Hz, 1H), 4.18 (d, J = 17.0 Hz, 1H), 4.15 (d, J = 17.0 Hz, 1H), 4.06 (d, J = 17.1 Hz, 1H), 3.82 (d, J = 17.1 Hz, 1H), 3.49 (dd, J = 10.6, 2.9 Hz, 1H, CHB), 2.80 (s, 3H,), 1.75 – 1.41 (m, 6H), 1.28 – 0.93 (m, 5H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.7, 161.4, 61.8, 61.7, 45.5, 40.7 (br, CHB), 39.9, 31.0, 28.0, 26.24, 26.22, 18.6. ^{11}B NMR (128 MHz, $CDCl_3$) δ 11.1. ESIMS [M-H]$^-$: 295.0. $[\alpha]^{20}_D$ +28.0 (c = 1.0, CH_3OH).

(*R*)-*N*-(1-(MIDA-boryl)-2-phenylethyl)formamide 2e

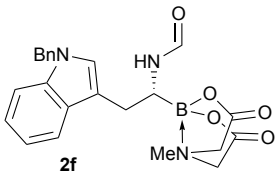


2e

Following the general procedure (reaction time= 2.5 h), starting from chloride **3e** (120 mg, 0.42 mmol), compound **2e** has been synthesised as an off white solid 81 mg (0.26 mmol, 62% yield) with a purity of 95% due to the presence of ethyl ether and then used for the next step without further manipulation. M.p. 69.5–71.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 (d, J = 1.9 Hz, 1H), 7.62 (dd, J = 10.1, 2.2 Hz, 1H), 7.24 – 7.09 (m, 5H), 4.29 (d, J = 17.2 Hz, 1H), 4.19 (d, J = 16.9 Hz, 1H), 4.08 (d, J = 17.2 Hz, 1H), 3.87 (d, J = 17.2 Hz,

1H), 3.83 – 3.76 (m, 1H, CHB), 2.90 (s, 3H), 2.54 – 2.46 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.5, 160.6, 140.2, 129.1, 127.7, 125.5, 62.4, 62.1, 45.7, 38.0 (CHB, br), 36.8. ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.5. ESIMS [M-H]$^-$: 302.9. $[\alpha]^{20}_D$ -12.3 (c = 1.0, CH_3OH).

(*R*)-*N*-(2-(1-benzyl-1H-indol-3-yl)-1-MIDAboryl)ethyl)formamide 2f

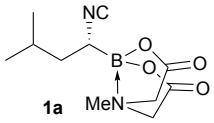


2f

Following the general procedure (reaction time= 5 h), starting from chloride **3f** (590 mg, 1.43 mmol), compound **2f** has been synthesised as an off white solid (275 mg, 0.64 mmol) with 44% yield. M.p. 102.0 –103.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.85 (d, J = 2.0 Hz, 1H), 7.65 (dd, J = 10.0, 2.0 Hz, 1H), 7.55 (d, J = 7.8 Hz, 1H), 7.39 – 7.18 (m, 6H), 7.13 (d, J = 7.7 Hz, 1H,), 7.04 (t, J = 7.6 Hz, 1H), 6.98 (t, J = 7.3 Hz, 1H), 5.34 (br s, 2H), 4.30 (d, J = 17.3 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.09 (d, J = 17.2 Hz, 1H), 3.89 (d, J = 16.9 Hz, 1H), 3.86 – 3.80 (m, 1H, CHB), 3.05 – 2.97 (m, 1H), 2.69 (s, 3H), 2.73 – 2.65 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.6, 160.9, 138.4, 135.9, 128.4, 128.3, 127.1, 127.0, 126.8, 120.8, 118.7, 118.3, 112.4, 109.7, 62.3, 62.1, 48.9, 45.6, 37.2 (br, CHB), 26.5. ^{11}B NMR (128 MHz, DMSO-d_6) δ 8.7. ESIMS [M-H]$^-$: 432.1. $[\alpha]^{20}_D$ -20.5 (c = 1.0, CH_3OH).

Synthesis and characterization of α-boryl isocyanide 1a–f.

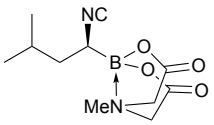
(*R*)-Isobutyl(MIDA boryl)methyl isocyanide 1a



1a

Following the general procedure, starting from **2a** (80 mg, 0.30 mmol), compound **1a** has been synthesised as an off white solid (58 mg, 0.23 mmol) with 75% yield. Spectroscopic data are in agreement with the ones reported in literature.[9] M.p. 193.3 –196.2 °C. ^{1}H NMR (400 MHz, CD_3CN) δ 4.10 (d, *J* = 17.0 Hz, 1H), 4.04 (d, *J* = 17.0 Hz, 1H), 3.94 (d, *J* = 17.4 Hz, 1H), 3.92 (d, *J* = 17.4 Hz, 1H), 3.30 (br d, *J* = 11.5 Hz, 1H, CHB), 3.09 (s, 3H), 1.9 – 1.8 (m, 1H), 1.74 – 1.66 (m, 1H), 1.34 – 1.22 (m, 1H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) *δ* 168.31, 168.27, 155.7, 62.63, 62.59, 46.1, 42.0 (CHB, br), 38.4, 24.7, 23.2, 20.4. HRMS $[M+H]^+$: calc. for $C_{11}H_{18}BN_2O_4$ 253.1356, found 253.1349. $[\alpha]^{20}_D$ -27.6 (c = 0.91, CH_3OH).

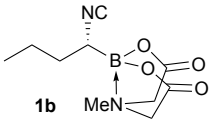
(*S*)-Isobutyl(MIDA boryl)methyl isocyanide ent-1a



ent-1a

Following the general procedure, starting from **ent-2a** (182 mg, 0.67 mmol), compound **ent-1a** has been synthesised as an off white solid (110 mg, 0.44 mmol) with 65% yield. Spectroscopic data are in agreement with **1a** and the ones reported in literature.[9] ^{1}H NMR (400 MHz, CD_3CN) δ 4.10 (d, *J* = 17.0 Hz, 1H), 4.06 (d, *J* = 17.0 Hz, 1H), 3.96 (d, *J* = 17.2 Hz, 1H), 3.92 (d, *J* = 17.2 Hz, 1H), 3.30 (br d, *J* = 11.7 Hz, 1H, CHB), 3.09 (s, 3H), 1.90 – 1.80 (m, 1H), 1.74 – 1.65 (m, 1H), 1.34 – 1.23 (m, 1H), 0.99 (d, *J* = 6.7 Hz, 3H), 0.93 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) *δ* 168.31, 168.27, 155.7, 62.62, 62.59, 46.1, 42.0, 38.4, 24.7, 23.2, 20.4. HRMS $[M-H]^-$: calc. for $C_{11}H_{16}BN_2O_4$ 251.1198, found 251.1208. $[\alpha]^{20}_D$ +24.5 (c = 1.1, CH_3OH).

(*R*)-Propyl(MIDA boryl)methyl isocyanide 1b



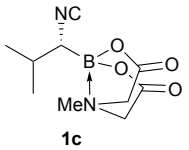
1b

Following the general procedure, starting from **2b** (50 mg, 0.2 mmol), compound **1b** has been synthesised as a pale-yellow wax (26 mg, 0.11 mmol) with 53% yield.

1H NMR (400 MHz, DMSO-d_6) *δ* 4.38 (d, *J* = 17.2 Hz, 1H), 4.35 (d, *J* = 17.3 Hz, 1H), 4.09 (d, *J* = 17.1 Hz, 1H), 4.05 (d, *J* = 17.3 Hz, 1H), 3.39 – 3.33 (m, 1H, CHB), 3.09 (s, 3H), 1.63 – 1.46 (m, 3H), 1.44 – 1.29 (m, 1H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) *δ* 168.4, 168.3, 155.6, 62.5, 46.1, 45.6, 43.3 (br, CHB), 31.80, 19.51, 13.23. ^{11}B NMR (128 MHz, DMSO-d_6) *δ* 9.9. HRMS $[M-H]^-$: calc. for $C_{10}H_{14}BN_2O_4$ 237.1041, found 237.1047. $[\alpha]^{20}_D$ -9.52 (c = 0.9, CH_3OH).

[9] A. Zajdlik, Z. Wang, J. Hickey, A. Aman, A. Schimmer, A. Yudin, A. *Angew. Chem. Int. Ed.* 2013, **52**, 8411.

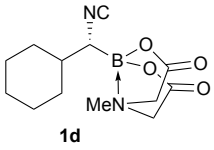
(*R*)-isopropyl(MIDA boryl)methyl isocyanide 1c



1c

Following the general procedure, starting from **2c** (100 mg, 0.4 mmol), compound **1c** has been synthesised as a pale-yellow wax (40 mg, 0.17 mmol) with 42% yield. ^{1}H NMR (400 MHz, CD_3CN) δ 4.07 (d, J = 17.1 Hz, 1H), 4.04 (d, J = 17.2 Hz, 1H), 3.92 (d, J = 17.1 Hz, 1H), 3.88 (d, J = 17.2 Hz, 1H), 3.28 – 3.20 (m, 1H, CHB), 3.05 (s, 3H), 2.08 – 1.98 (m, 1H), 1.06 (d, J = 6.8 Hz, 3H), 0.99 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 168.6, 168.5, 158.4, 63.43, 63.37, 51.9 (br, CHB), 47.1, 29.2, 21.7, 18.1.^{11}B NMR (128 MHz, CD_3CN) δ 10.0. HRMS $[M\text{-}H]^-$: calc. for $C_{10}H_{14}BN_2O_4$ 237.1041, found 237.1050. $[\alpha]^{20}_D$ -6.8 (c = 1.3, CH_3OH).

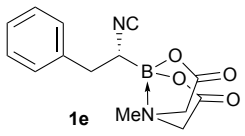
(*R*)-cyclohexyl(MIDA boryl)methyl isocyanide 1d



1d

Following the general procedure, starting from **2d** (28 mg, 0.1 mmol), compound **1d** has been synthesised as a pale-yellow solid (17 mg, 0.06 mmol) with 65% yield. Spectroscopic data are in agreement with the ones reported in literature.[9] M.p. 206.2 –209.0 °C. ^{1}H NMR (600 MHz, CD_3CN) δ 4.06 (d, J = 17.0 Hz, 1H), 4.03 (d, J = 17.0 Hz, 1H), 3.92 (d, J = 17.0 Hz, 1H), 3.88 (d, J = 17.1 Hz, 1H), 3.20 (br s, 1H, CHB), 3.05 (s, 3H), 1.85 – 1.74 (m, 2H), 1.69 – 1.61 (m, 2H), 1.42 – 1.09 (m, 7H). ^{13}C NMR (151 MHz, CD_3CN) δ 169.5 (2C), 159.3, 64.4, 64.3, 52.2 (CHB), 48.1, 39.7, 33.3, 29.9, 28.0, 27.8, 27.7. HRMS $[M\text{-}H]^-$: calc. for $C_{13}H_{18}BN_2O_4$ 277.1354, found 277.1366. $[\alpha]^{20}_D$ -42.6 (c = 0.70, CH_3OH).

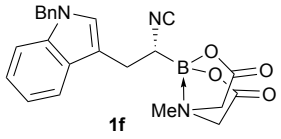
(*R*)-benzyl(MIDA boryl)methyl isocyanide 1e



1e

Following the general procedure, starting from **2e** (55 mg, 0.18 mmol), compound **1e** has been synthesised as a pale-yellow wax (37 mg, 0.13 mmol) with 70% yield. ^{1}H NMR (400 MHz, CD_3CN) δ 7.40 – 7.24 (m, 5H), 4.13 (d, J = 17.2 Hz, 1H), 4.11 (d, J = 17.3 Hz, 1H), 3.98 (d, J = 17.2 Hz, 1H), 3.96 (d, J = 17.3 Hz, 1H), 3.50 (br d, J = 11.7 Hz, 1H, CHB), 3.09 (s, 3H), 3.08 – 2.99 (m, 1H), 2.84 – 2.75 (m, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 168.43, 168.40, 158.4, 139.9, 130.1, 129.4, 127.7, 63.9, 63.8, 48.2 (br, CHB), 47.2, 37.3.^{11}B NMR (193 MHz, CD_3CN) δ 10.1. HRMS $[M\text{-}H]^-$: calc. for $C_{14}H_{14}BN_2O_4$ 285.1041, found 285.1052. $[\alpha]^{20}_D$ +42.6 (c = 0.7, CH_3OH).

(*R*)-(1-benzyl-1*H*-indol-3-yl)methyl (MIDA boryl)methyl isocyanide 1f

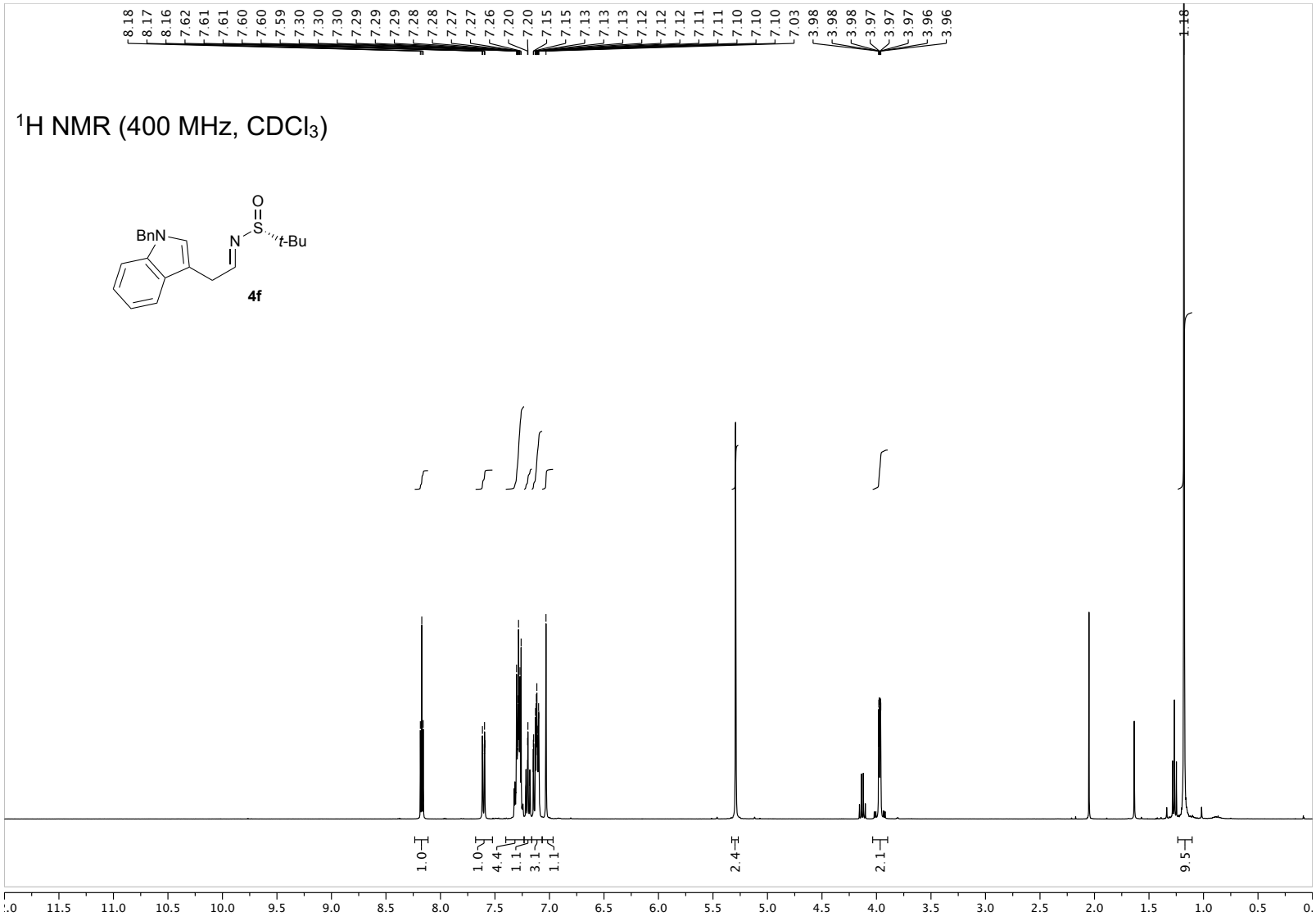


1f

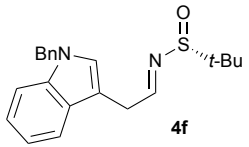
Following the general procedure, starting from **2f** (80 mg, 0.18 mmol), compound **1f** has been synthesised as a pale-yellow wax (74 mg, 0.17 mmol) with 96% yield.

^{1}H NMR (400 MHz, CD_3CN) δ 7.62 (d, J = 7.7 Hz), 7.37 – 7.02 (m, 9H), 5.36 (br s, 2H), 4.14 (d, J = 17.2 Hz, 1H), 4.11 (d, J = 17.3 Hz, 1H), 3.99 (d, J = 17.2 Hz, 1H), 3.96 (d, J = 17.3 Hz, 1H), 3.61 – 3.53 (m, 1H, CHB), 3.24 – 3.14 (m, 1H), 3.09 (s, 3H), 3.06 – 2.99 (m, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 168.6, 168.5, 158.0, 139.4, 137.5, 129.6, 128.9, 128.7, 128.4, 127.9, 122.6, 119.94, 119.92, 112.5, 111.0, 63.9, 63.8, 50.5, 47.2, 46.6 (CHB), 27.5.^{11}B NMR (193 MHz, CD_3CN) δ 10.2. HRMS $[M\text{-}H]^-$: calc. for $C_{23}H_{21}BN_3O_4$ 414.1620, found 414.1634. $[\alpha]^{20}_D$ –56.9 (c = 0.51, CH_3OH).

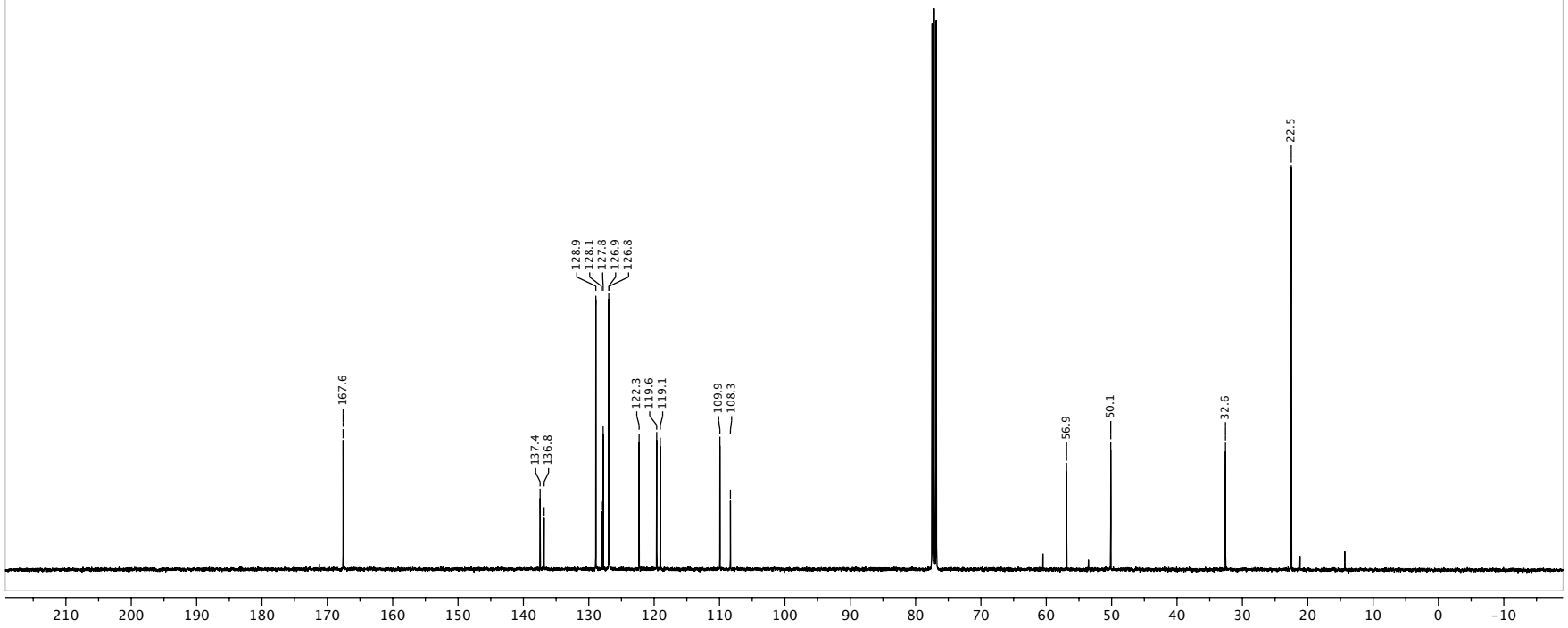
Copies of the ^{1}H NMR and ^{13}C NMR spectra of 4f, 3a–f, 2a–f, 1a–f and ent-3a, ent-2a and ent-1a and ^{1}H-^{13}C HSQC of 2a–f and 1b–f.

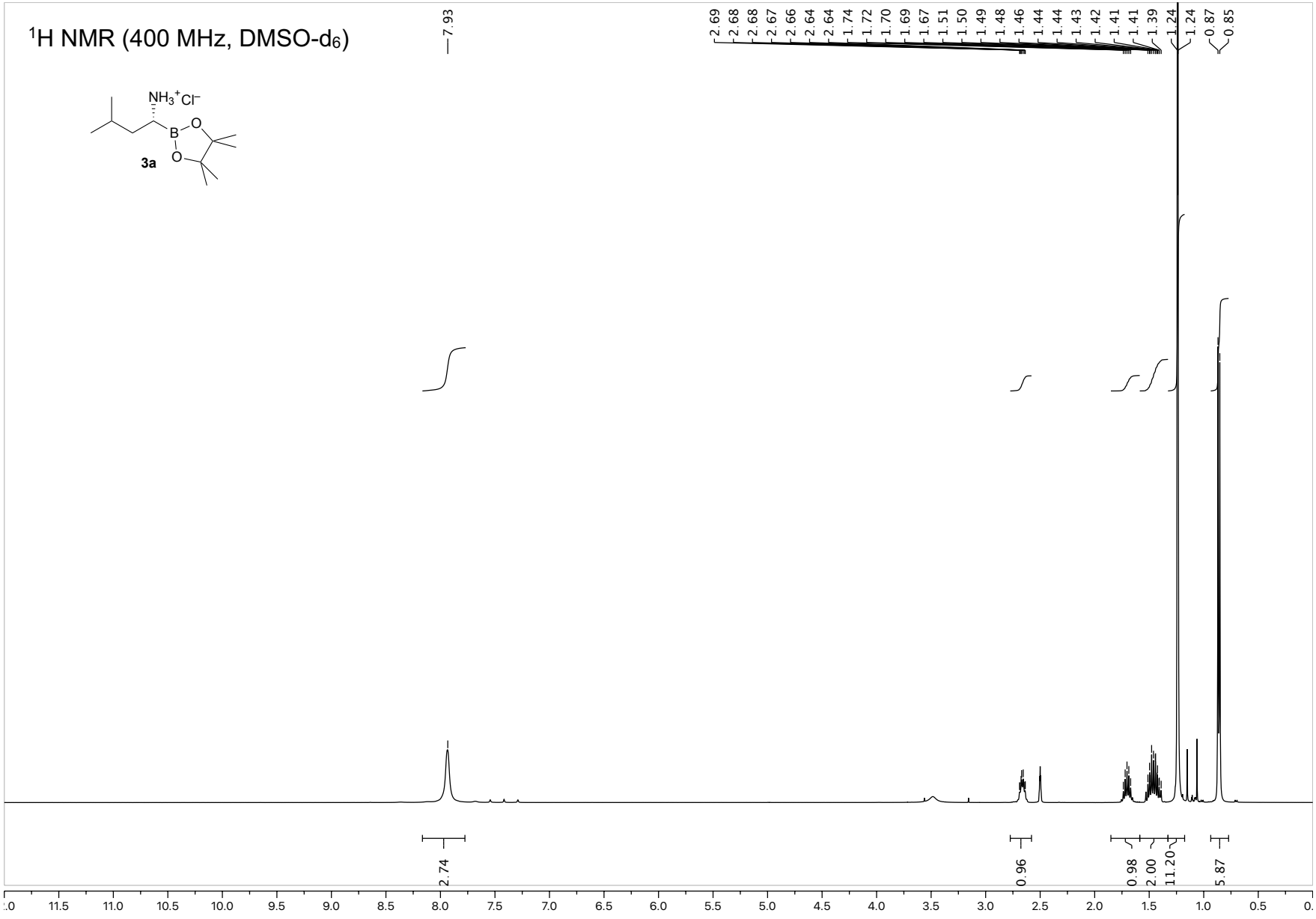


^{13}C NMR (101 MHz, $CDCl_3$)

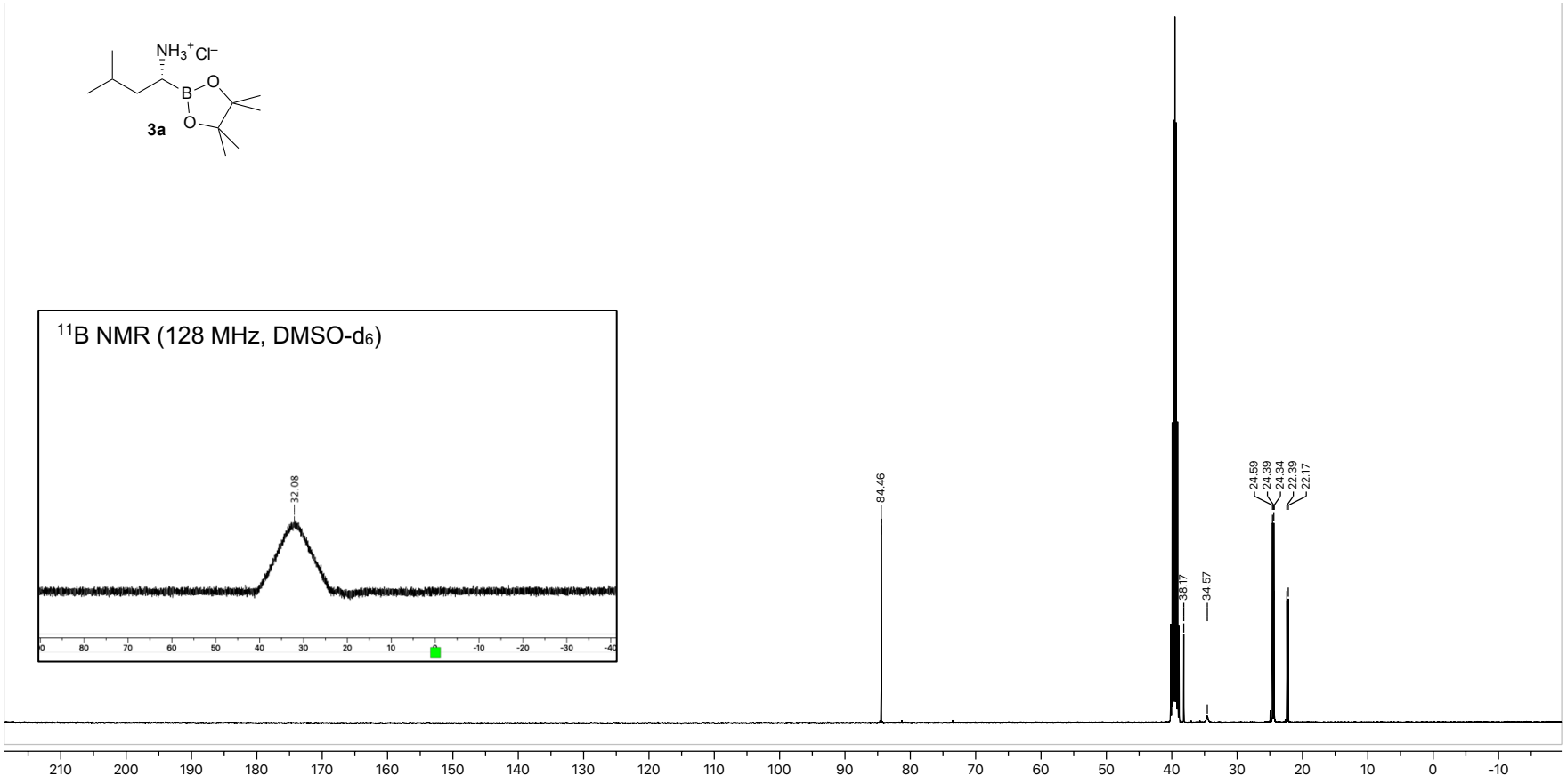


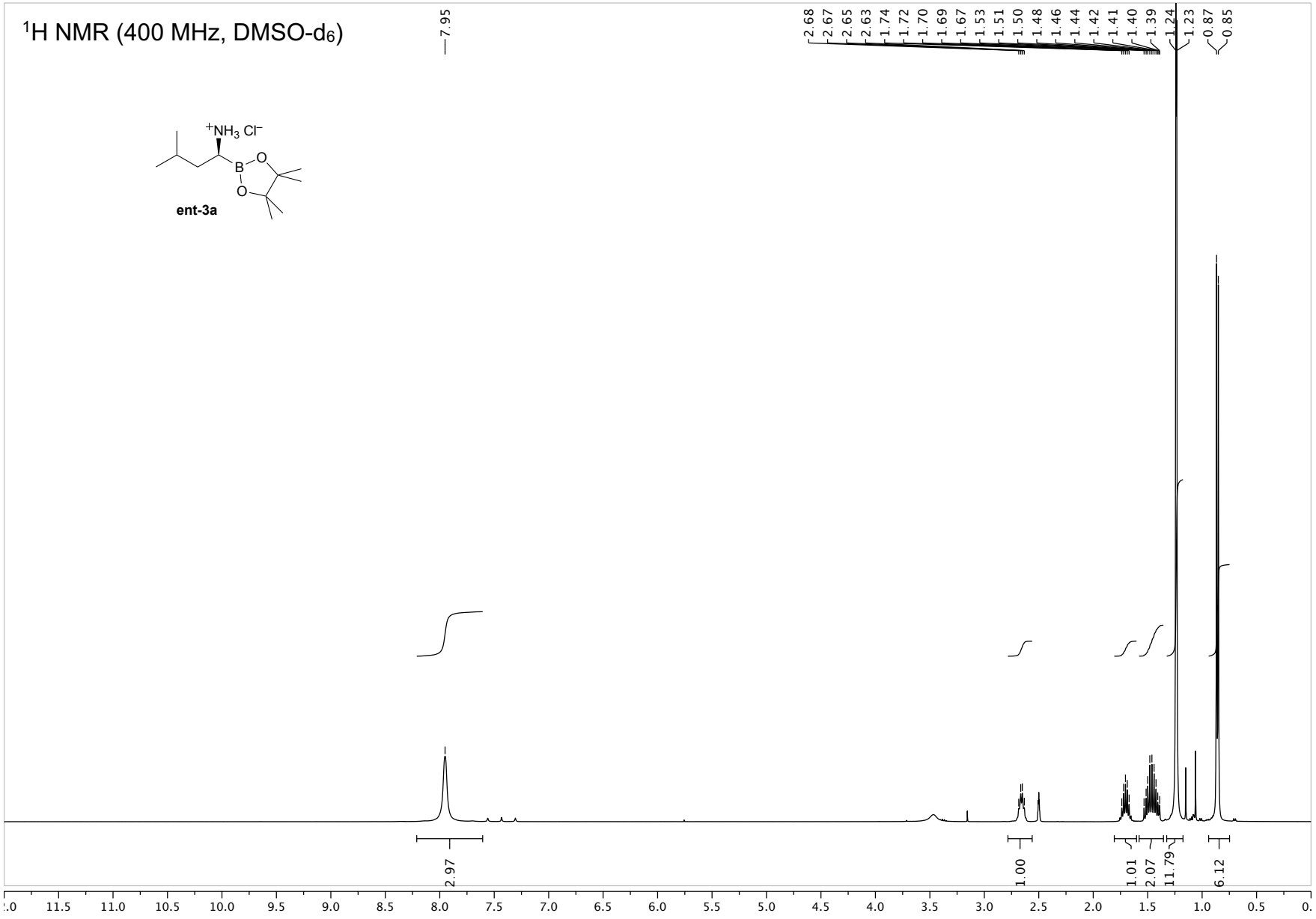
4f



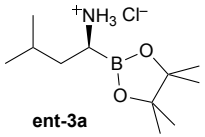

1H NMR (400 MHz, DMSO-d6)
NH3+Cl−
B
O
O
3a
7.93
2.69
2.68
2.68
2.67
2.66
2.64
2.64
1.74
1.72
1.70
1.69
1.67
1.51
1.50
1.49
1.48
1.46
1.44
1.44
1.43
1.42
1.41
1.41
1.39
1.24
1.24
0.87
0.85
2.74
0.96
0.98
2.00
11.20
5.87
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

^{13}C NMR (101 MHz, DMSO-d$_6$)



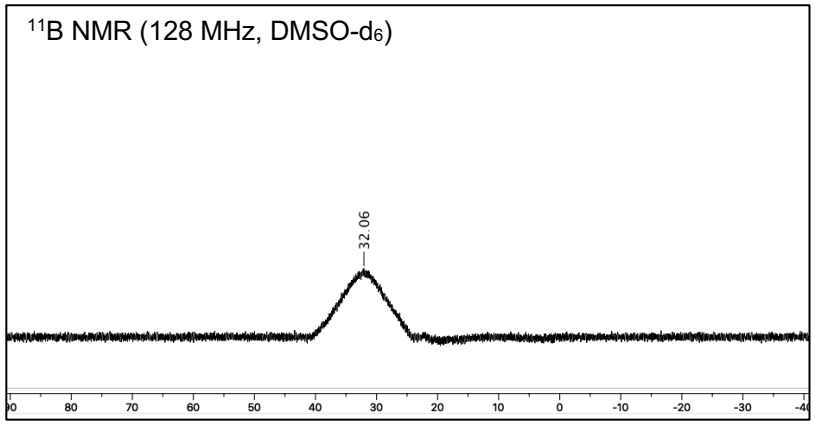

1H NMR (400 MHz, DMSO-d6)
+NH3 Cl−
B
O
O
ent-3a
7.95
2.68
2.67
2.65
2.63
1.74
1.72
1.70
1.69
1.67
1.53
1.51
1.50
1.48
1.46
1.44
1.42
1.41
1.40
1.39
1.24
1.23
0.87
0.85
2.97
1.00
1.01
2.07
11.79
6.12
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

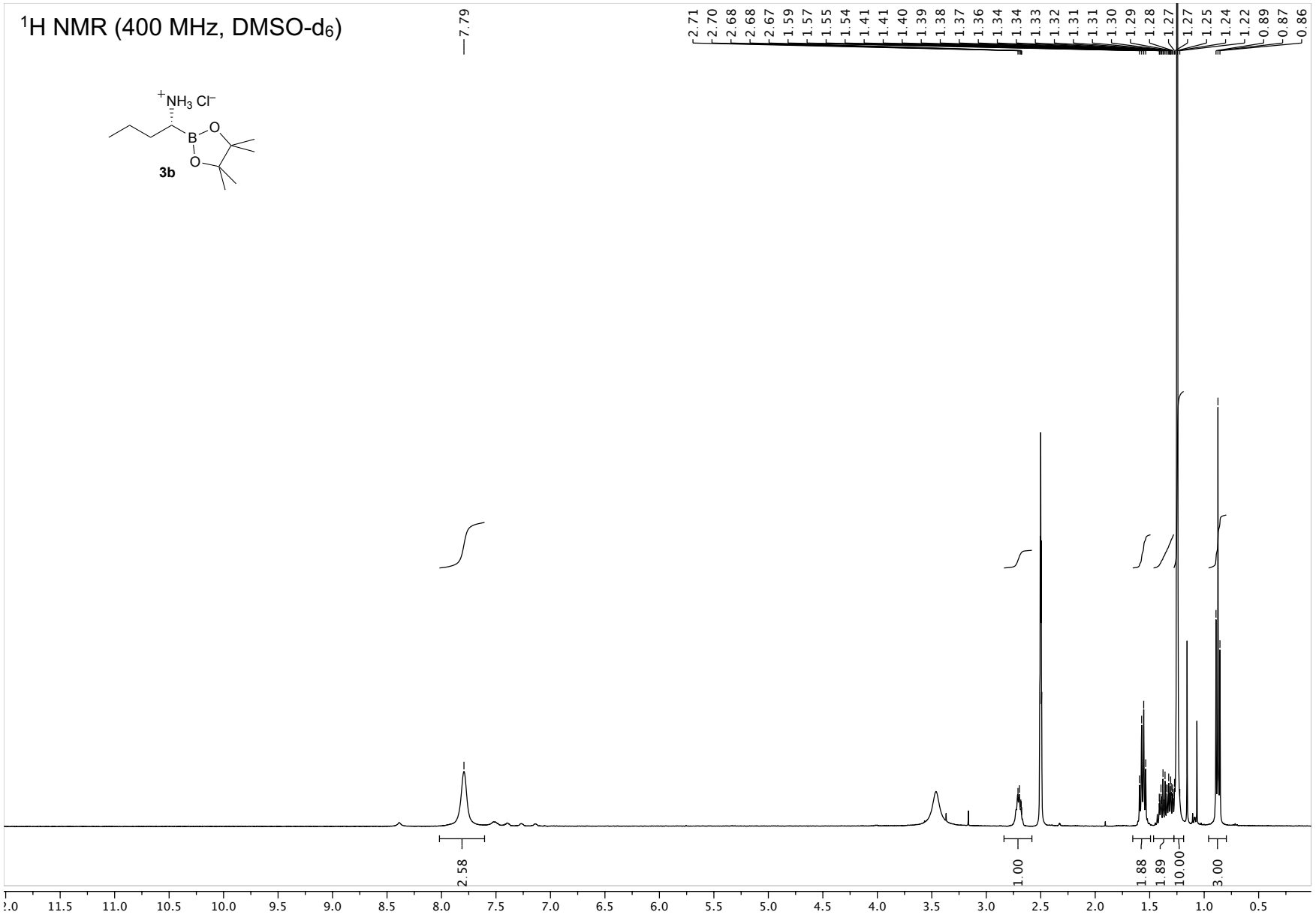
^{13}C NMR (101 MHz, DMSO-d_6)

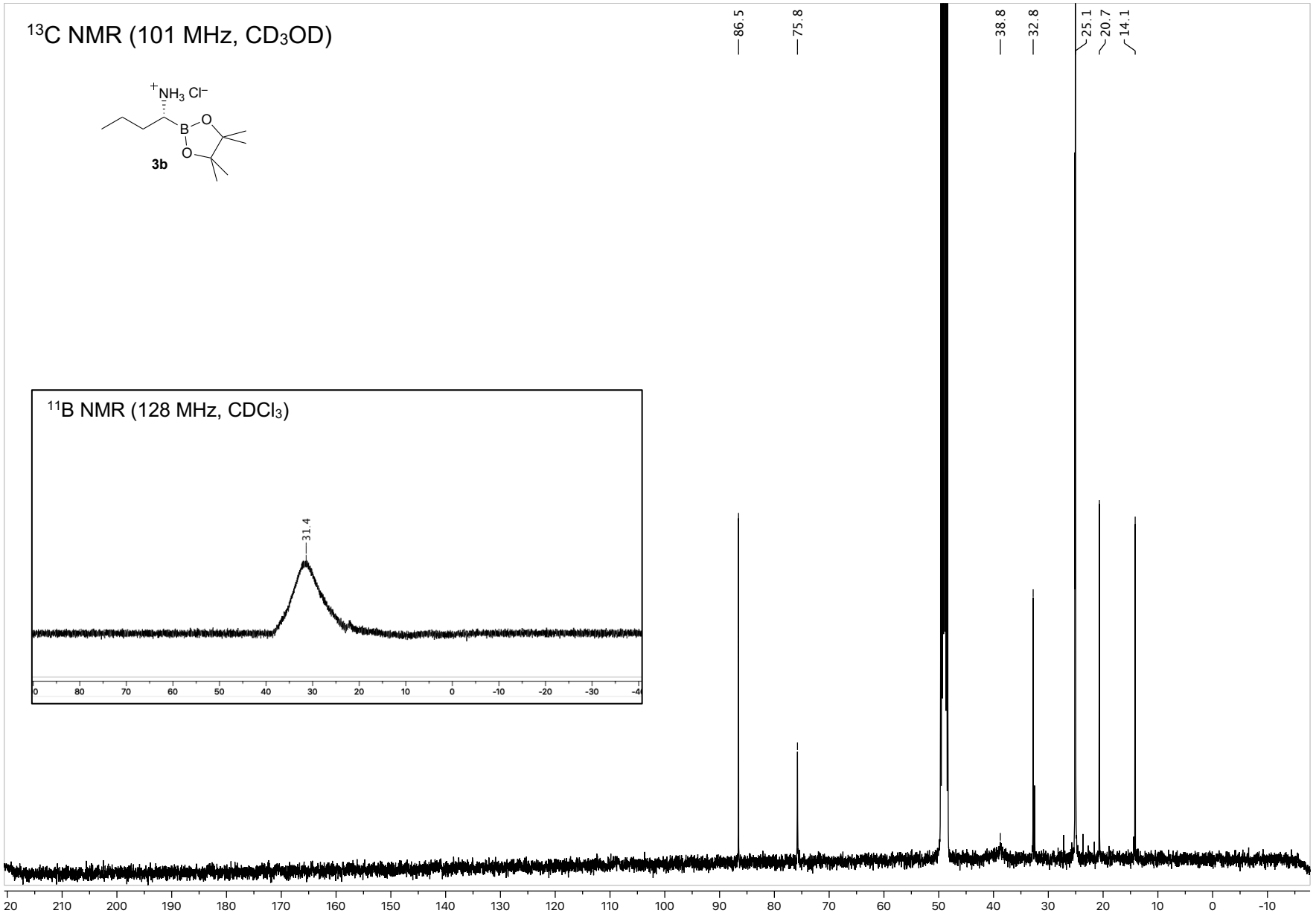


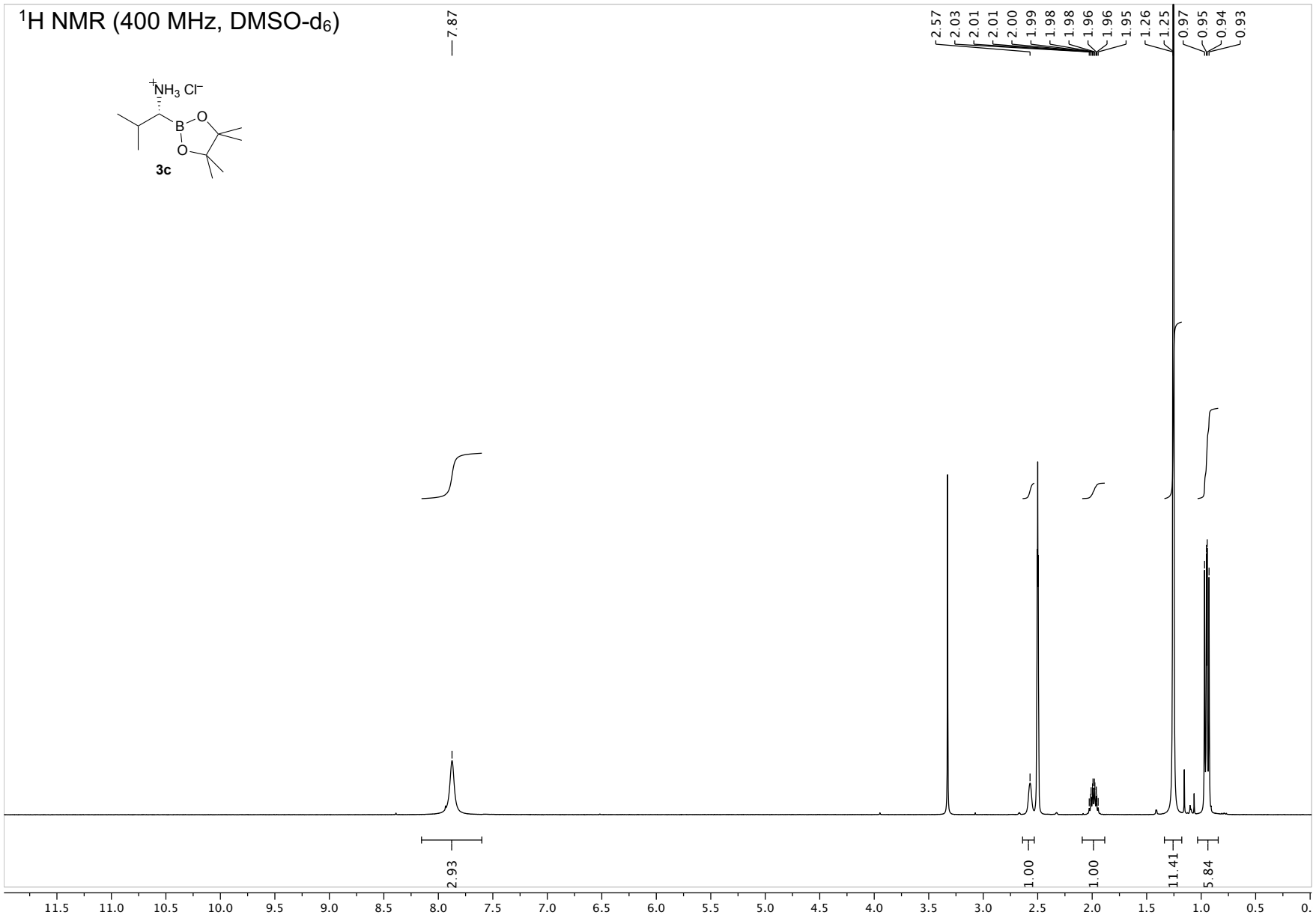
ent-3a

^{11}B NMR (128 MHz, DMSO-d_6)

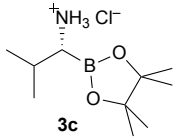



1H NMR (400 MHz, DMSO-d6)
7.79
2.71
2.70
2.68
2.68
2.67
1.59
1.57
1.55
1.54
1.41
1.41
1.40
1.39
1.38
1.37
1.36
1.34
1.34
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.27
1.27
1.25
1.24
1.22
0.89
0.87
0.86
+NH3 Cl−
B
O
O
3b
2.58
1.00
1.88
1.89
10.00
3.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


13C NMR (101 MHz, CD3OD)
+NH3 Cl−
B
O
O
3b
86.5
75.8
38.8
32.8
25.1
20.7
14.1
11B NMR (128 MHz, CDCl3)
31.4
80
70
60
50
40
30
20
10
0
-10
-20
-30
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

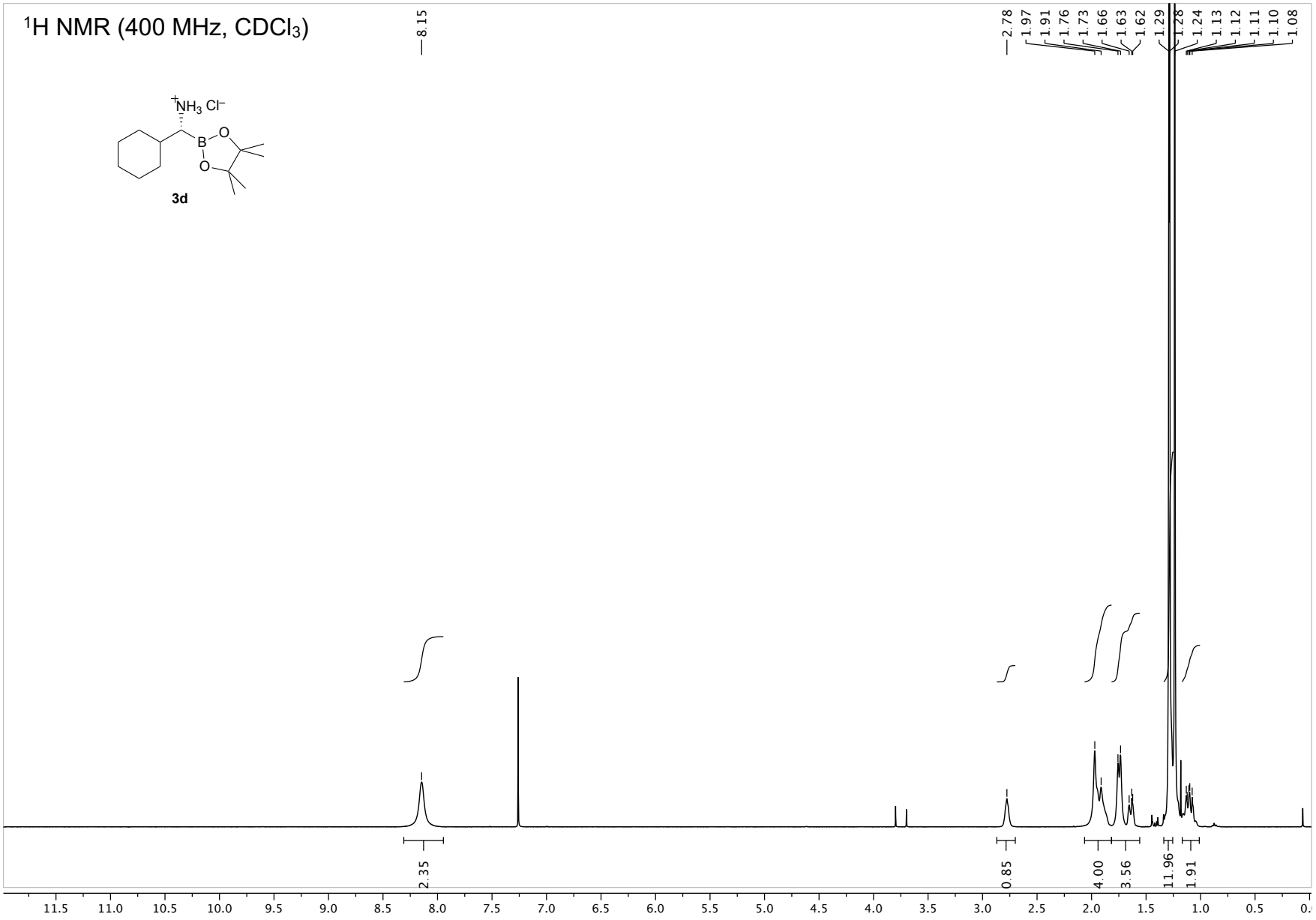

1H NMR (400 MHz, DMSO-d6)
+NH3 Cl−
B
O
O
3c
7.87
2.57
2.03
2.01
2.01
2.00
1.99
1.98
1.98
1.96
1.96
1.95
1.26
1.25
0.97
0.95
0.94
0.93
2.93
1.00
1.00
11.41
5.84
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

^{13}C NMR (101 MHz, DMSO-d_6)

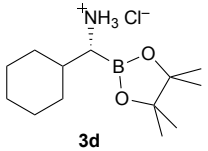


3c

^{11}B NMR (128 MHz, DMSO-d_6)

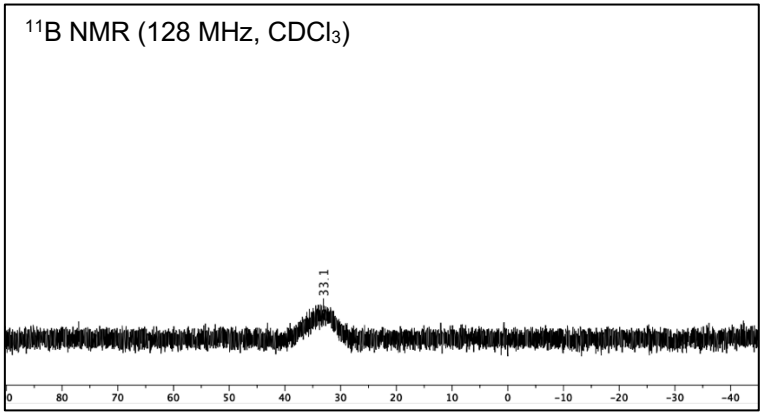

1H NMR (400 MHz, CDCl3)
8.15
2.78
1.97
1.91
1.76
1.73
1.66
1.63
1.62
1.29
1.28
1.24
1.13
1.12
1.11
1.10
1.08
NH3 Cl
B
O
O
3d
2.35
0.85
4.00
3.56
11.96
1.91
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

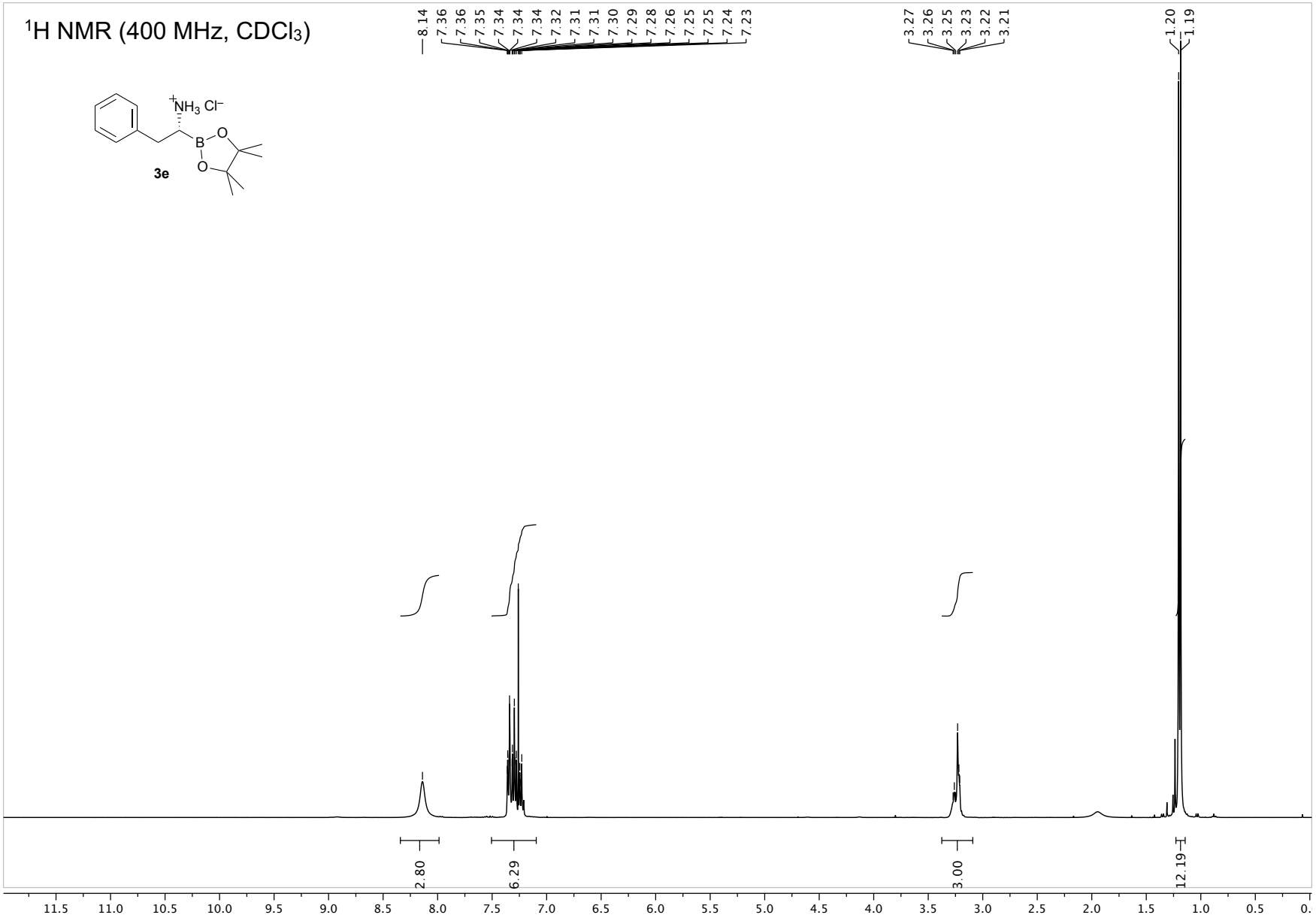
^{13}C NMR (101 MHz, DMSO-d_6)



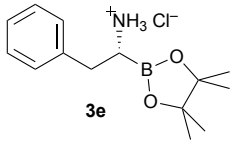
3d

^{11}B NMR (128 MHz, $CDCl_3$)

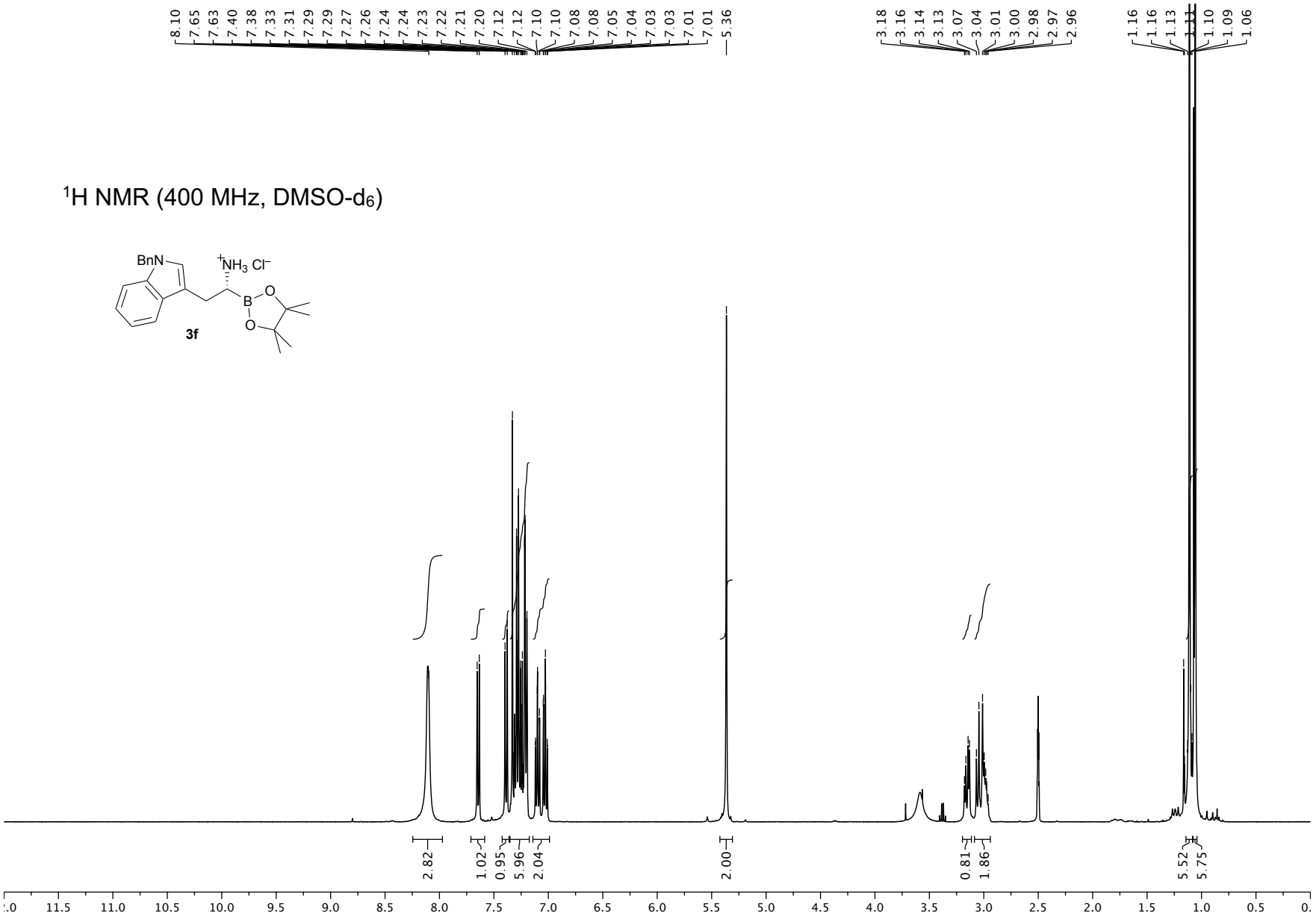



1H NMR (400 MHz, CDCl3)
8.14
7.36
7.36
7.35
7.34
7.34
7.34
7.32
7.31
7.31
7.30
7.29
7.28
7.26
7.25
7.25
7.24
7.23
3.27
3.26
3.25
3.23
3.22
3.21
1.20
1.19
NH3 Cl
B
O
O
3e
2.80
6.29
3.00
12.19
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.

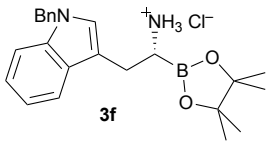
^{13}C NMR (101 MHz, $CDCl_3$)



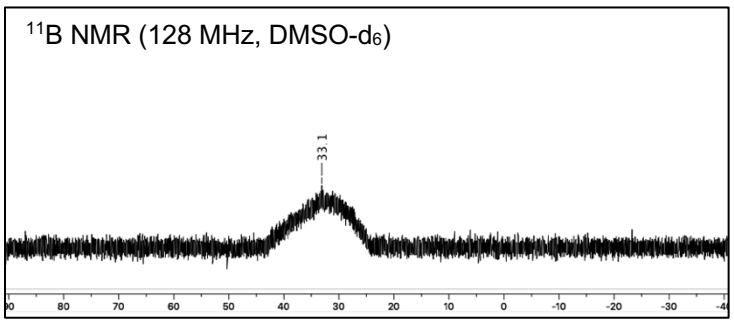
3e


8.10
7.65
7.63
7.40
7.38
7.33
7.31
7.29
7.29
7.27
7.26
7.24
7.24
7.23
7.22
7.21
7.20
7.12
7.12
7.10
7.10
7.08
7.08
7.05
7.04
7.03
7.03
7.01
7.01
5.36
3.18
3.16
3.14
3.13
3.07
3.04
3.01
3.00
2.98
2.97
2.96
1.16
1.16
1.13
1.11
1.10
1.09
1.06
1H NMR (400 MHz, DMSO-d6)
BnN
+NH3 Cl−
B
O
O
O
3f
2.82
1.02
0.95
5.96
2.04
2.00
0.81
1.86
5.52
5.75
11.5
11.0
10.5
10.0
9.5
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

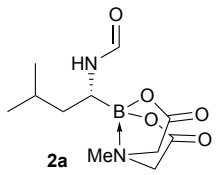
^{13}C NMR (101 MHz, DMSO-d$_6$)



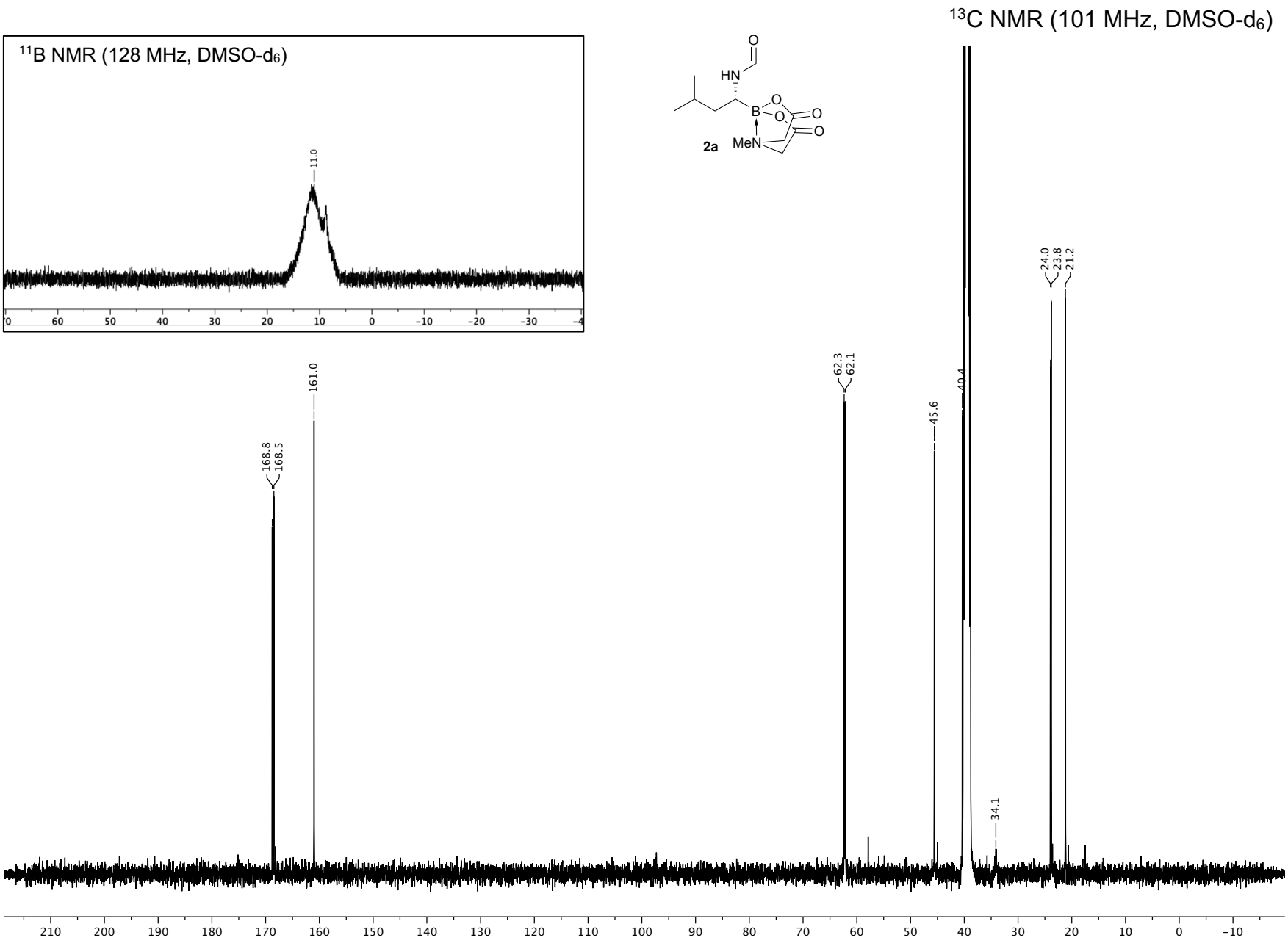
3f

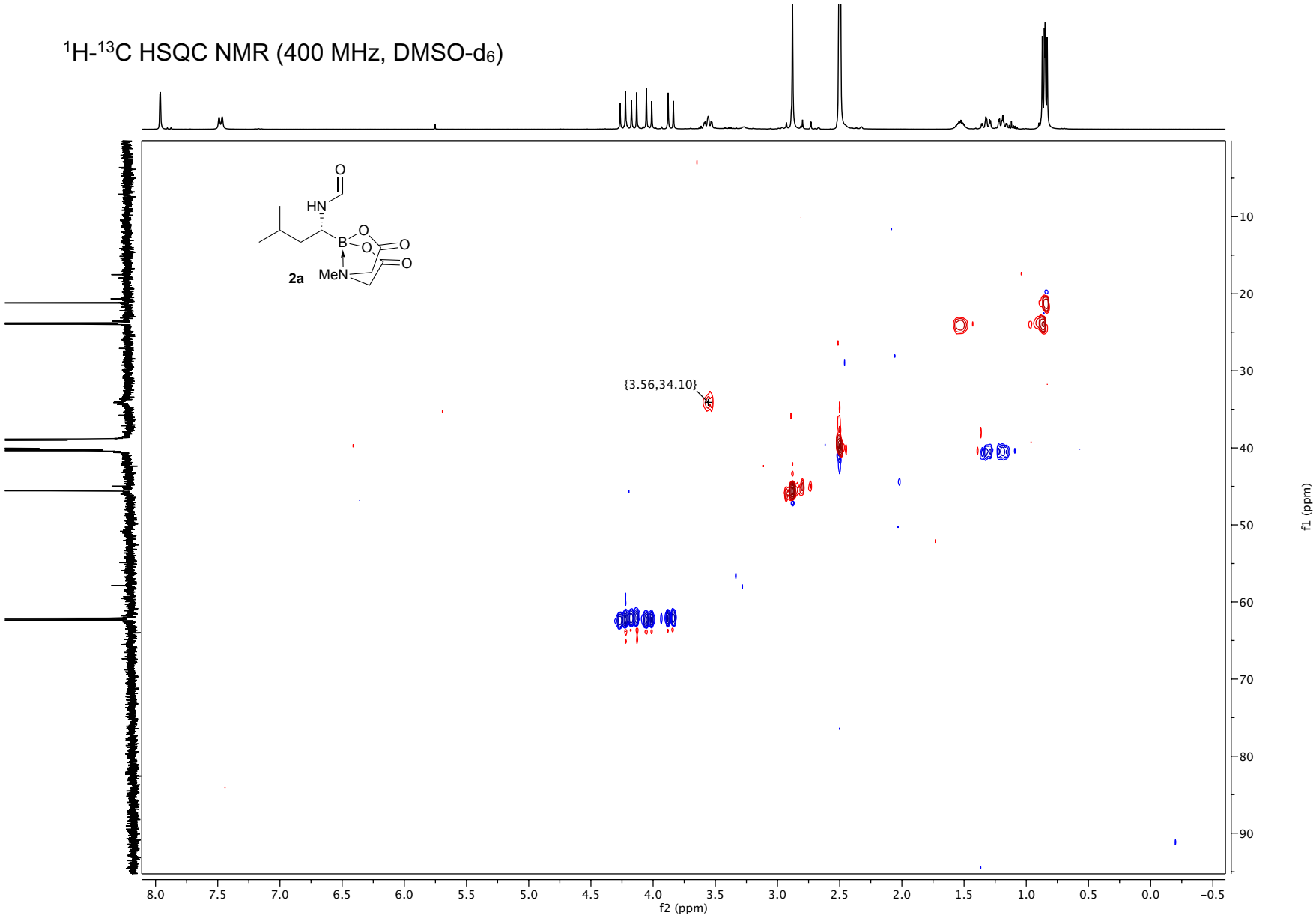


^{1}H NMR (400 MHz, DMSO-d_6)

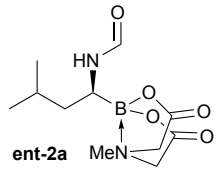


2a


^{11}B NMR (128 MHz, DMSO-d$_6$)
11.0
^{13}C NMR (101 MHz, DMSO-d$_6$)
2a
168.8
168.5
161.0
62.3
62.1
45.6
40.4
34.1
24.0
23.8
21.2

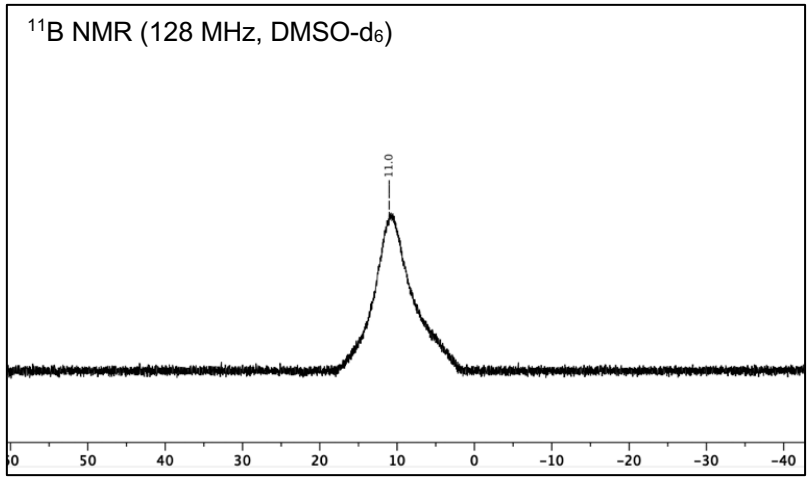

^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d$_6$)
HN
O
B
O
O
O
O
MeN
2a
{3.56,34.10}
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
f1 (ppm)

^{1}H NMR (400 MHz, DMSO-d_6)



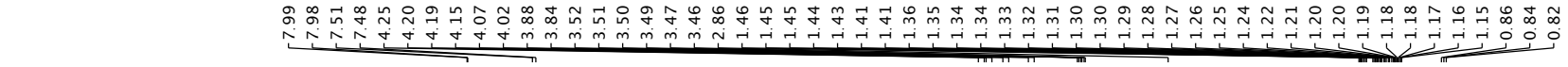
ent-2a

^{11}B NMR (128 MHz, DMSO-d$_6$)

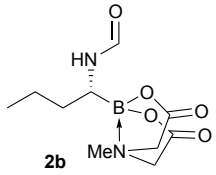


^{13}C NMR (101 MHz, DMSO-d$_6$)

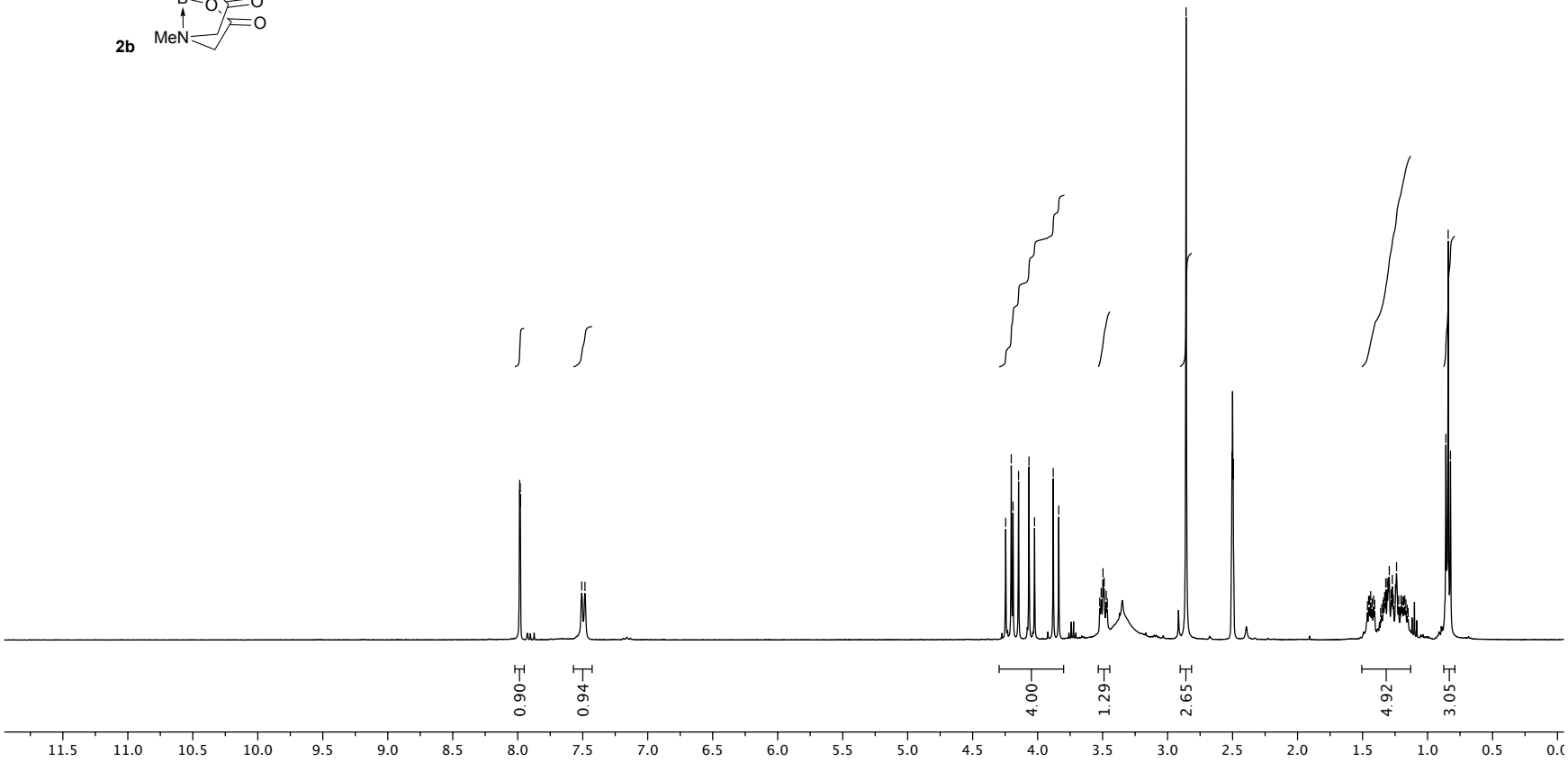
ent-2a



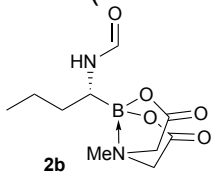
^{1}H NMR (400 MHz, DMSO-d_6)



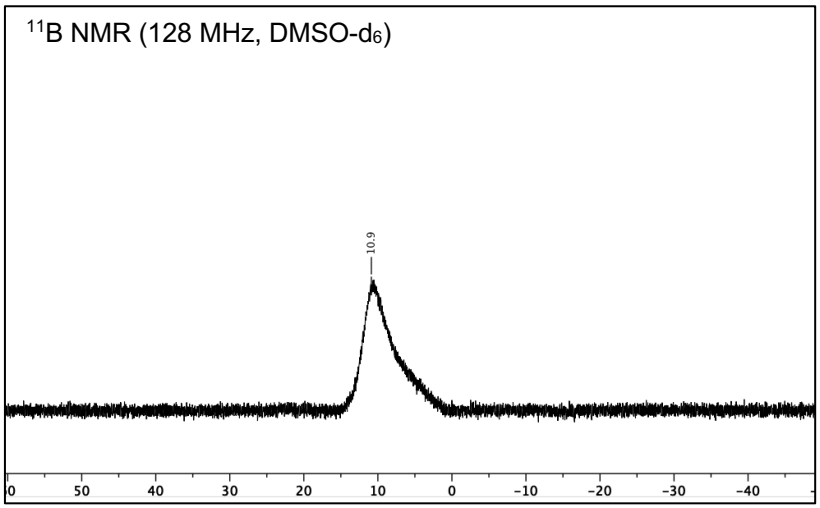
2b

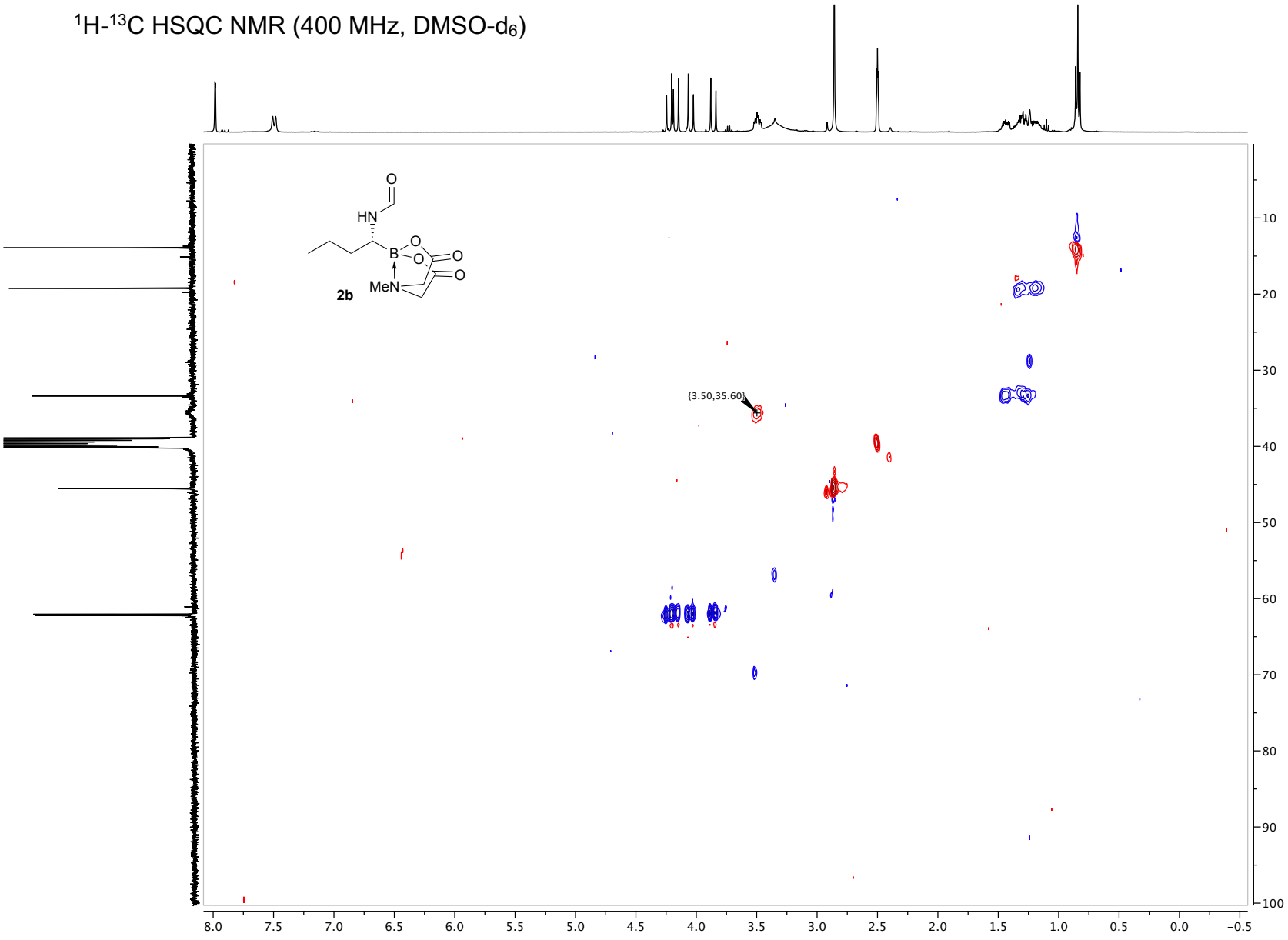


^{13}C NMR (101 MHz, DMSO-d$_6$)

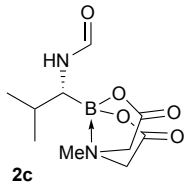


2b



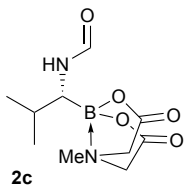

^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6)
HN
O
B
O
O
O
O
MeN
2b
{3.50,35.60}
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
10
20
30
40
50
60
70
80
90
100

^{1}H NMR (400 MHz, DMSO-d_6)

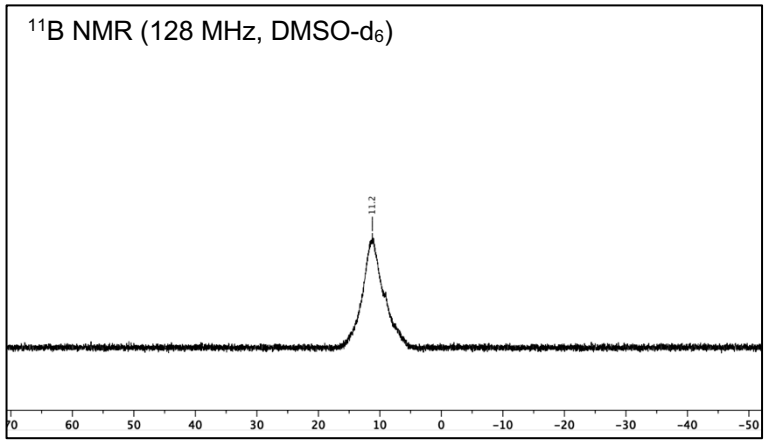


2c

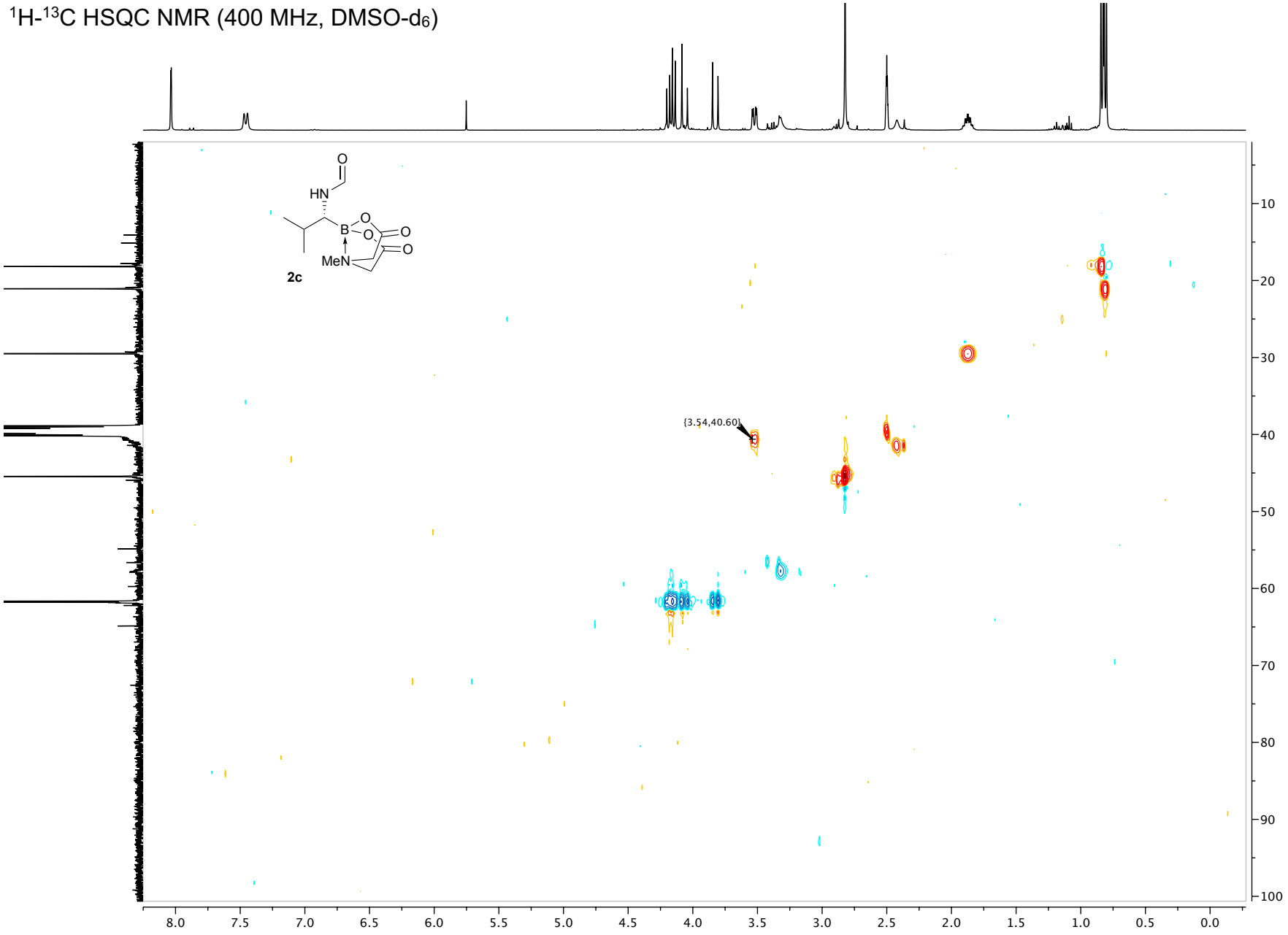
^{13}C NMR (101 MHz, DMSO-d$_6$)



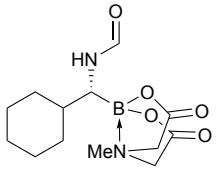
2c



^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6)

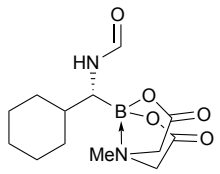


^{1}H NMR (400 MHz, DMSO-d_6)

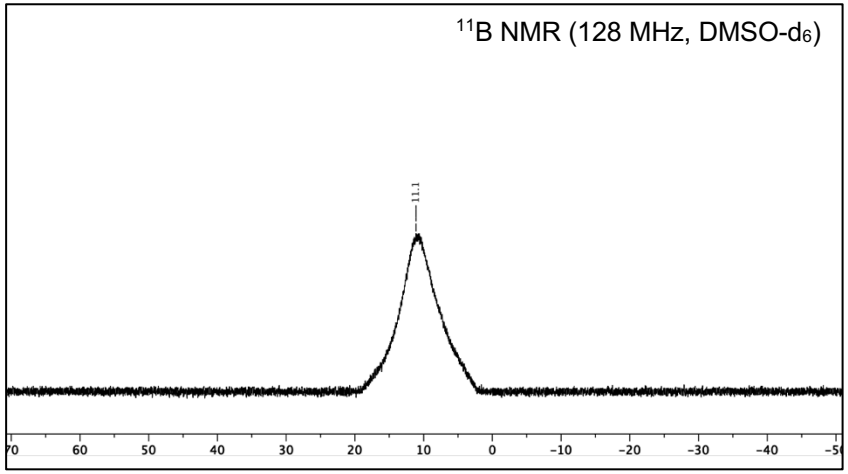


2d

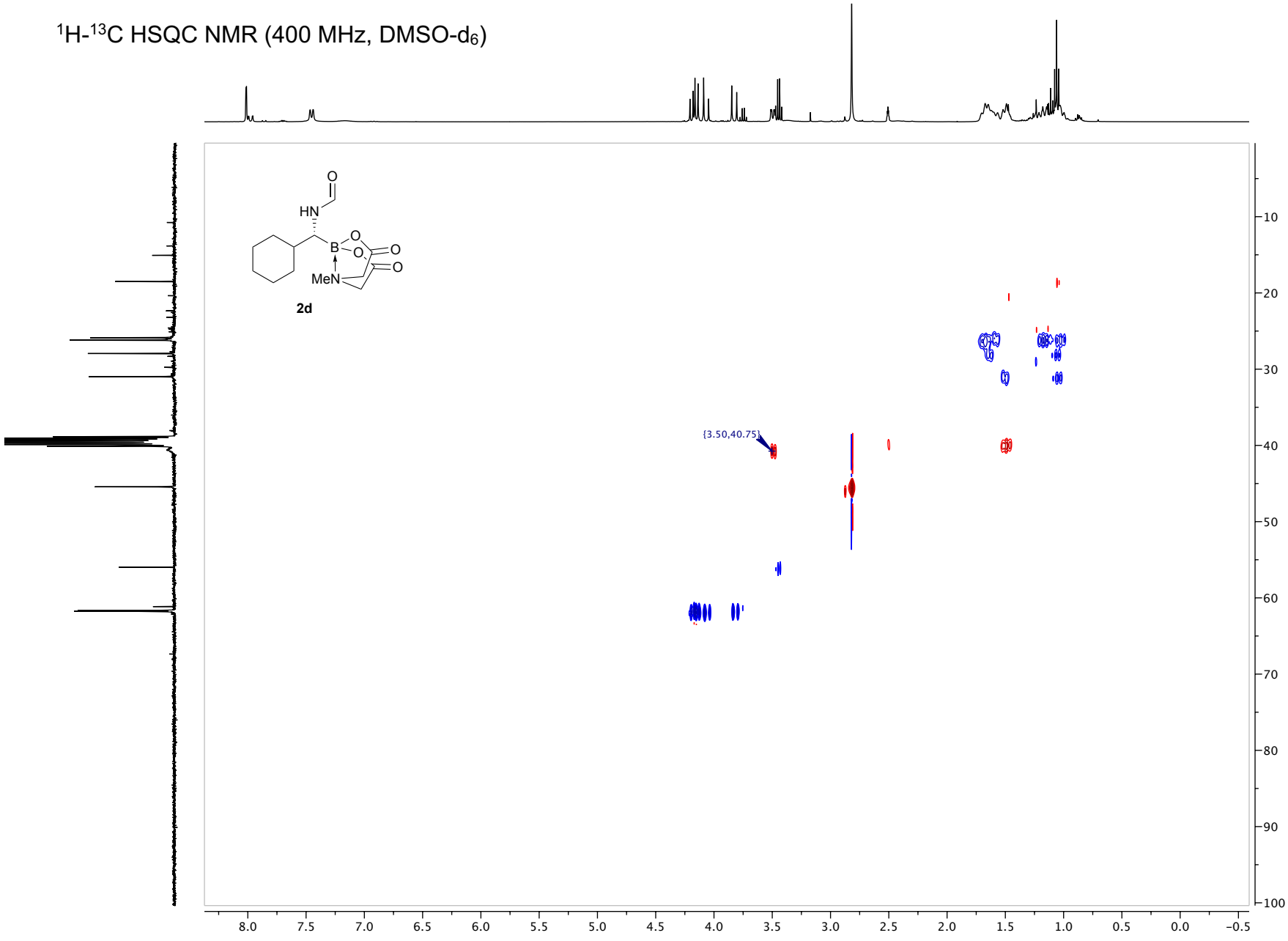
^{13}C NMR (101 MHz, DMSO-d$_6$)

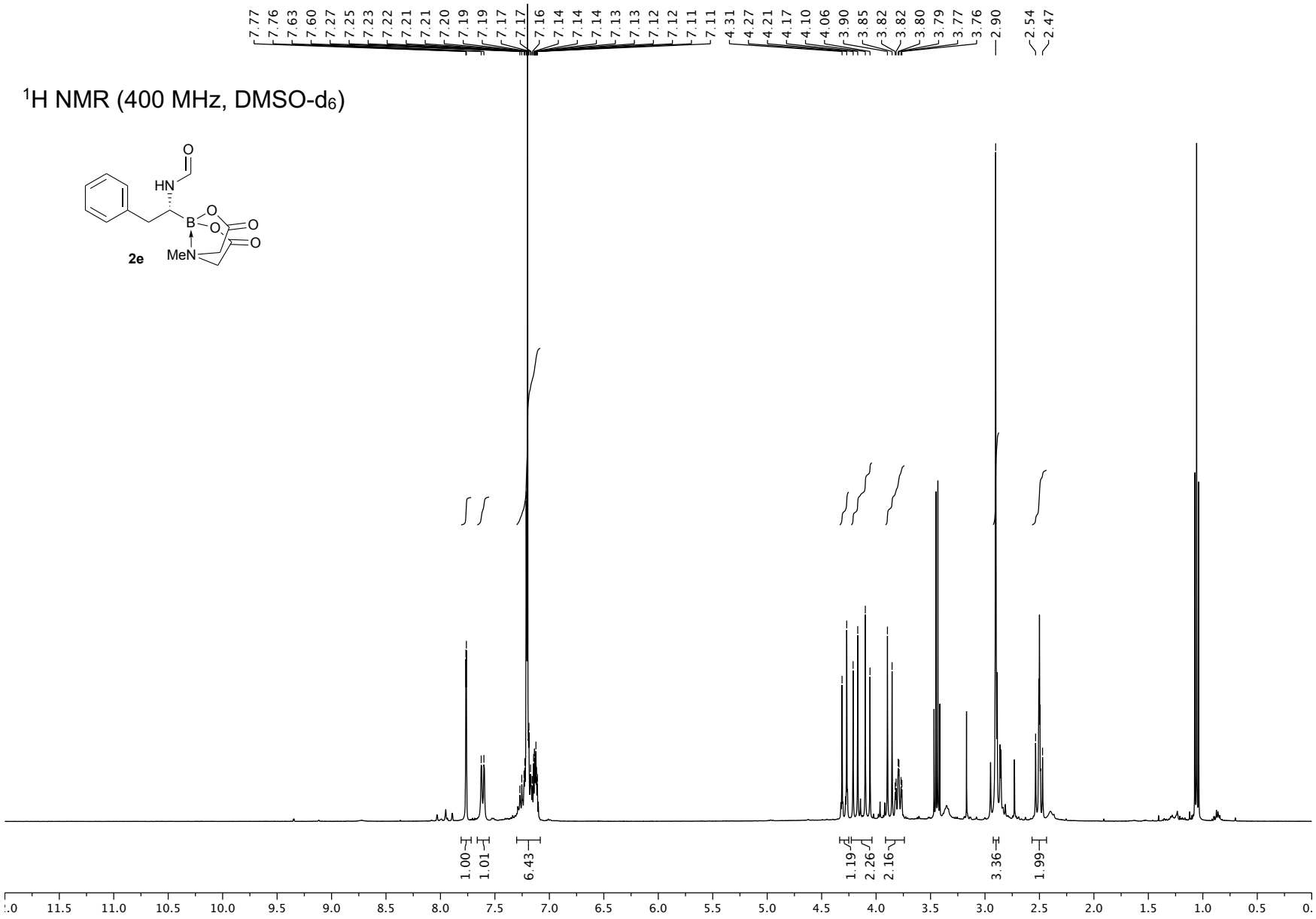


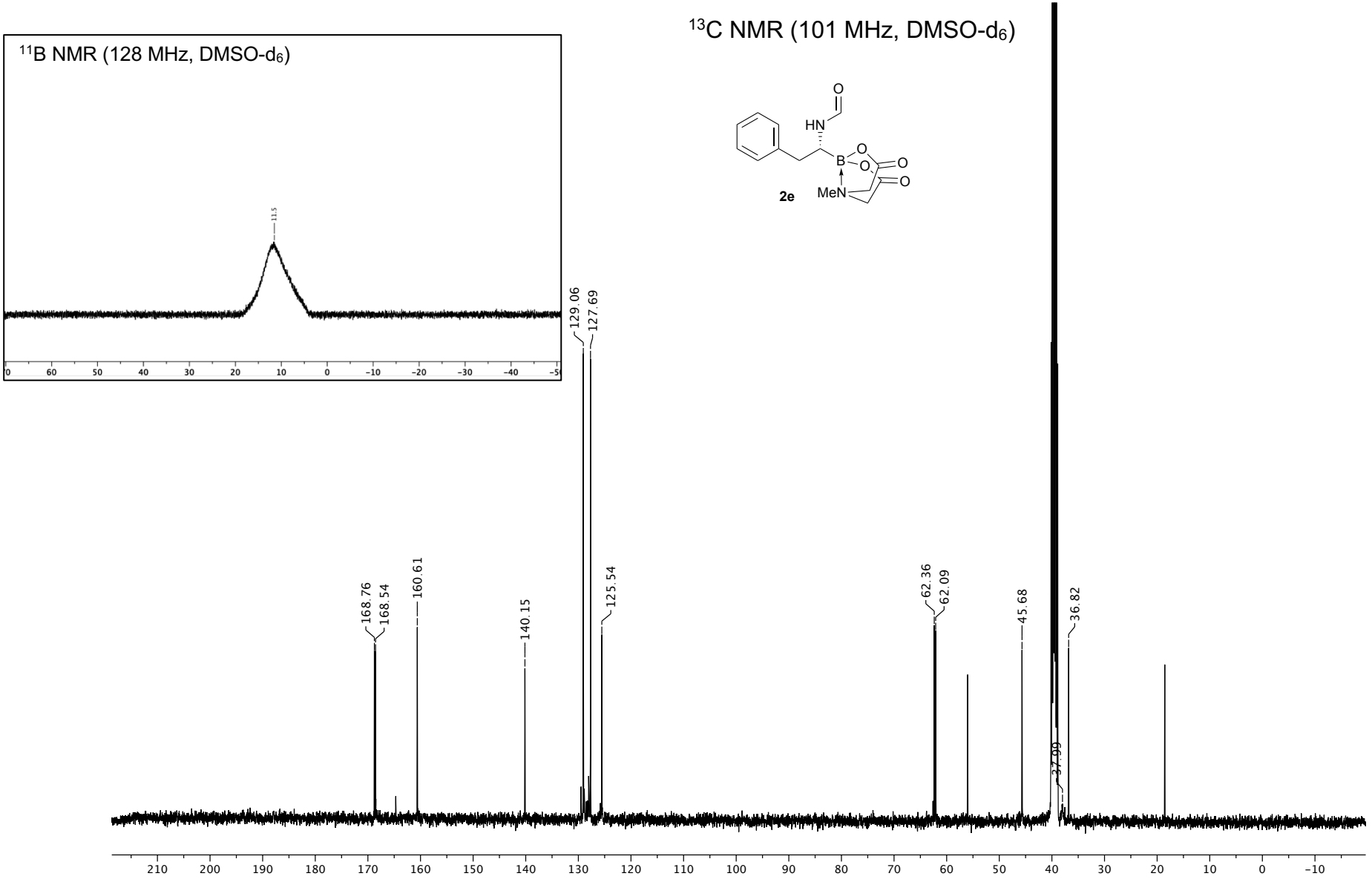
2d

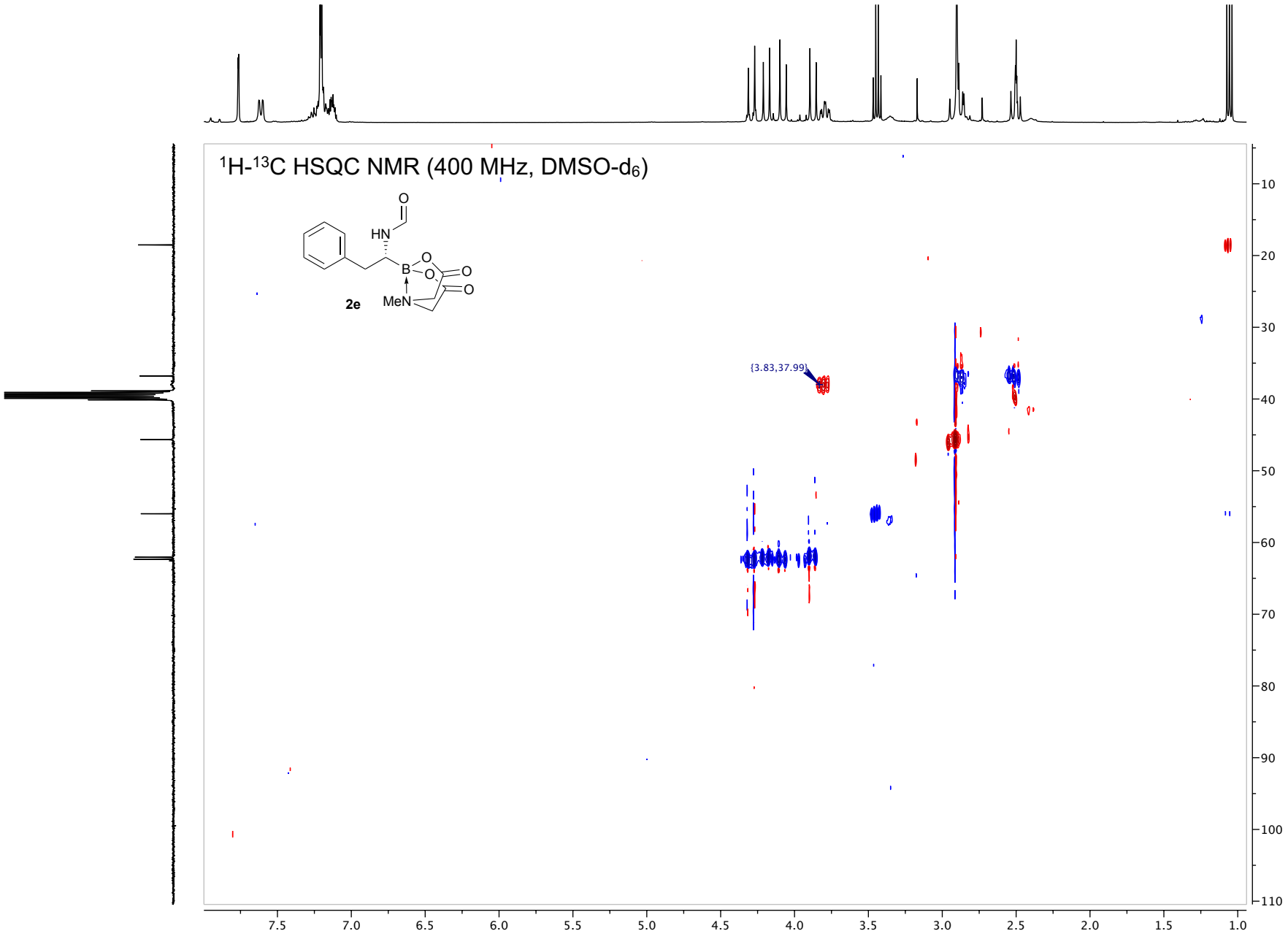


^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6)

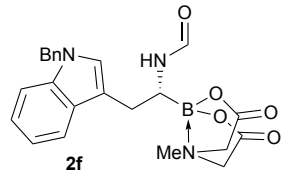



7.77
7.76
7.63
7.60
7.27
7.25
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.17
7.17
7.16
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.11
7.11
4.31
4.27
4.21
4.17
4.10
4.06
3.90
3.85
3.82
3.82
3.80
3.79
3.77
3.76
2.90
2.54
2.47
1H NMR (400 MHz, DMSO-d6)
O
HN
B
O
O
O
O
MeN
2e
1.00
1.01
6.43
1.19
2.26
2.16
3.36
1.99
11.5
11.0
10.5
10.0
9.5
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

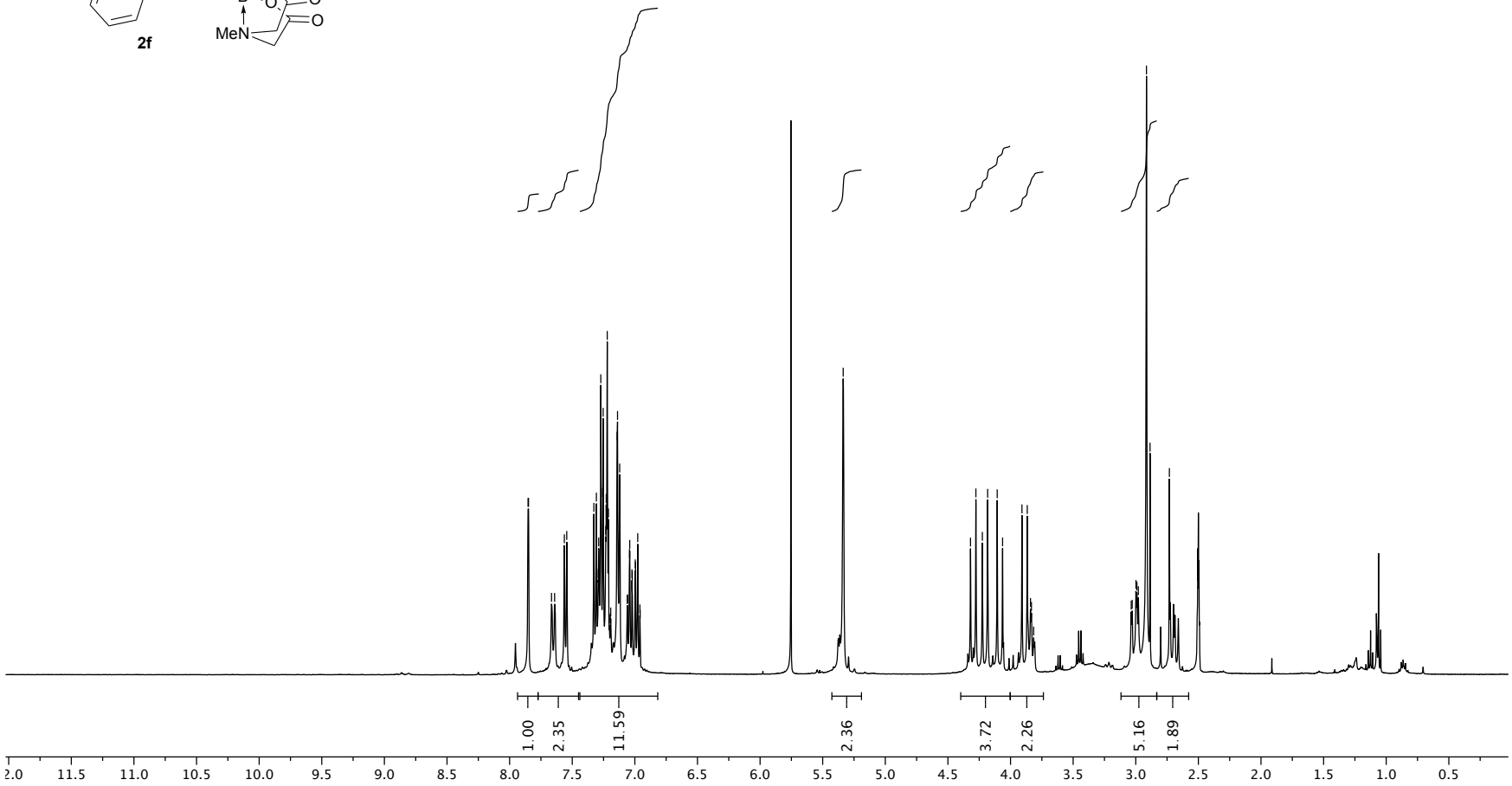

^{11}B NMR (128 MHz, DMSO-d$_6$)
^{13}C NMR (101 MHz, DMSO-d$_6$)
2e
MeN
HN
B
O
11.5
129.06
127.69
168.76
168.54
160.61
140.15
125.54
62.36
62.09
45.68
37.99
36.82

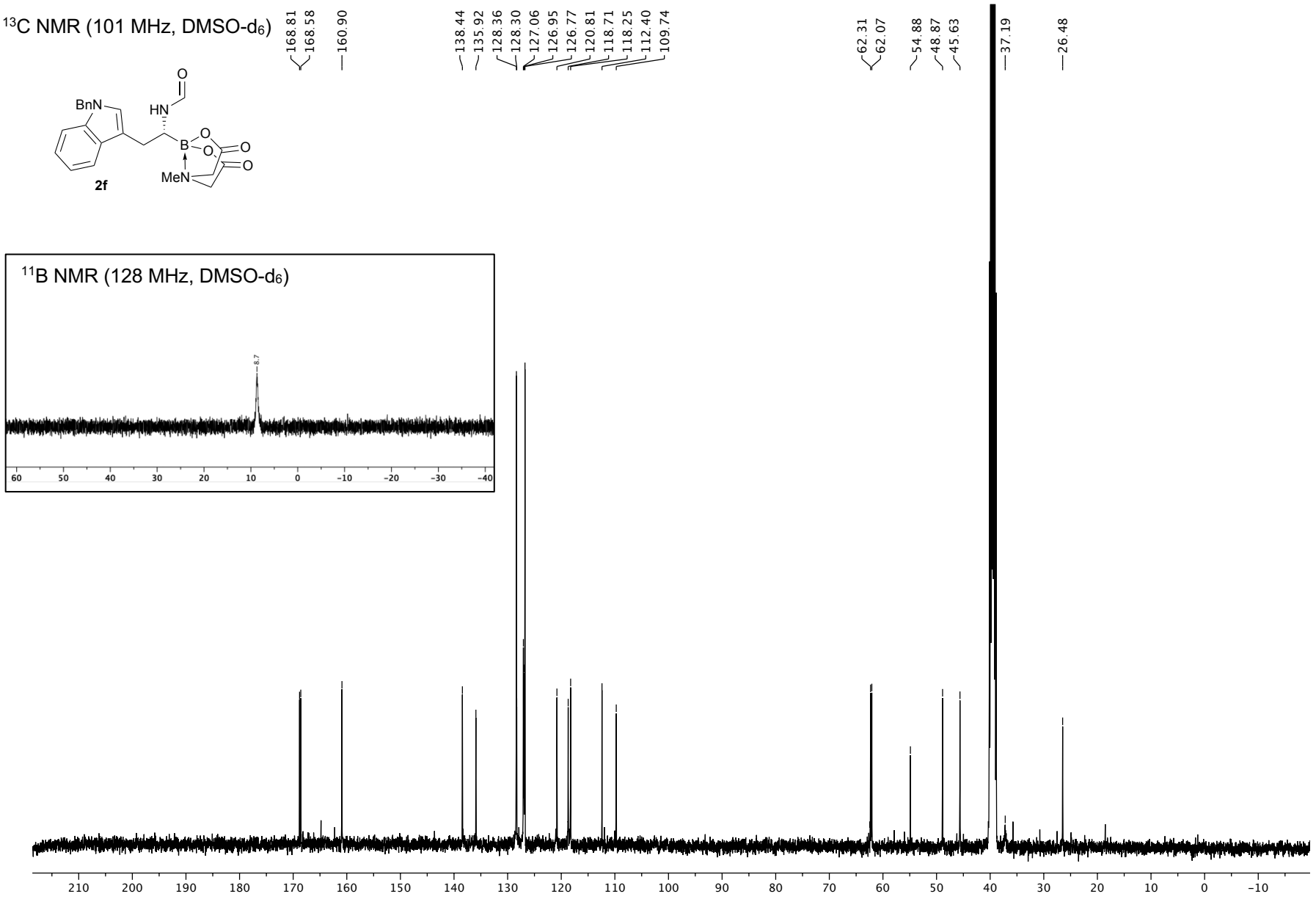

^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d$_6$)
2e
{3.83,37.99}
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
10
20
30
40
50
60
70
80
90
100
110

^{1}H NMR (400 MHz, DMSO-d$_6$)

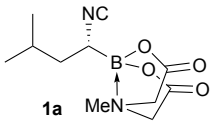


2f



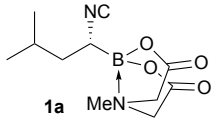

13C NMR (101 MHz, DMSO-d6)
168.81
168.58
160.90
138.44
135.92
128.36
128.30
127.06
126.95
126.77
120.81
118.71
118.25
112.40
109.74
62.31
62.07
54.88
48.87
45.63
37.19
26.48
BnN
HN
O
B
O
O
O
O
MeN
2f
11B NMR (128 MHz, DMSO-d6)
8.7
60
50
40
30
20
10
0
-10
-20
-30
-40
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

^{1}H NMR (400 MHz, CD_3CN)

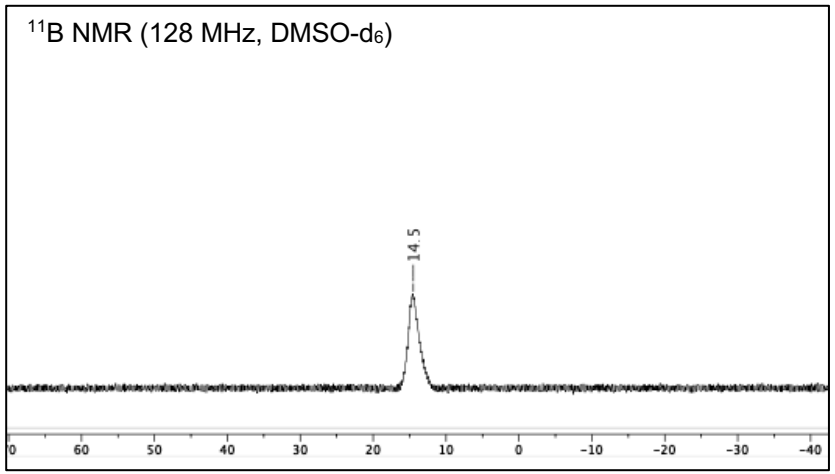


1a

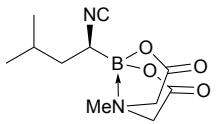
^{13}C NMR (101 MHz, DMSO-d_6)



1a

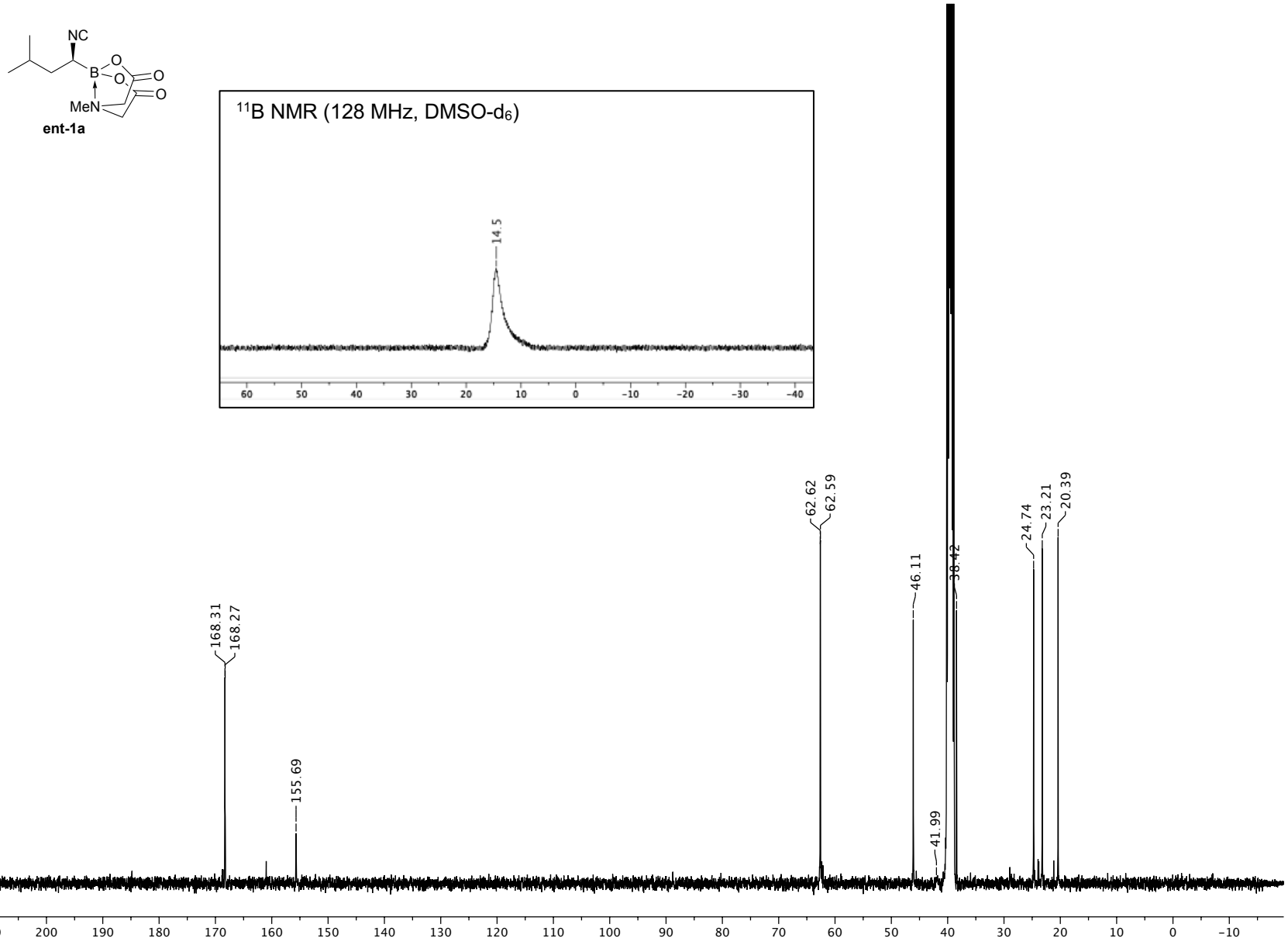


^{1}H NMR (400 MHz, CD_3CN)

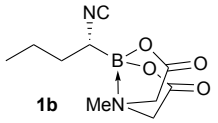


ent-1a

^{13}C NMR (101 MHz, DMSO-d_6)

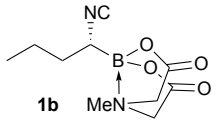


^{1}H NMR (400 MHz, DMSO-d_6)

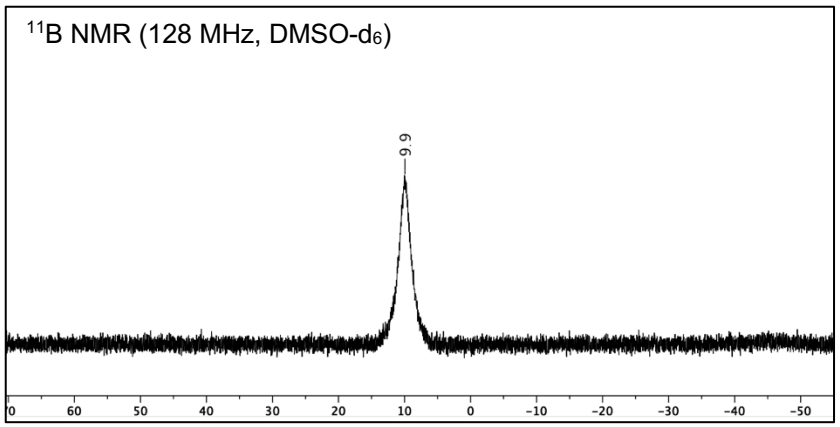


1b

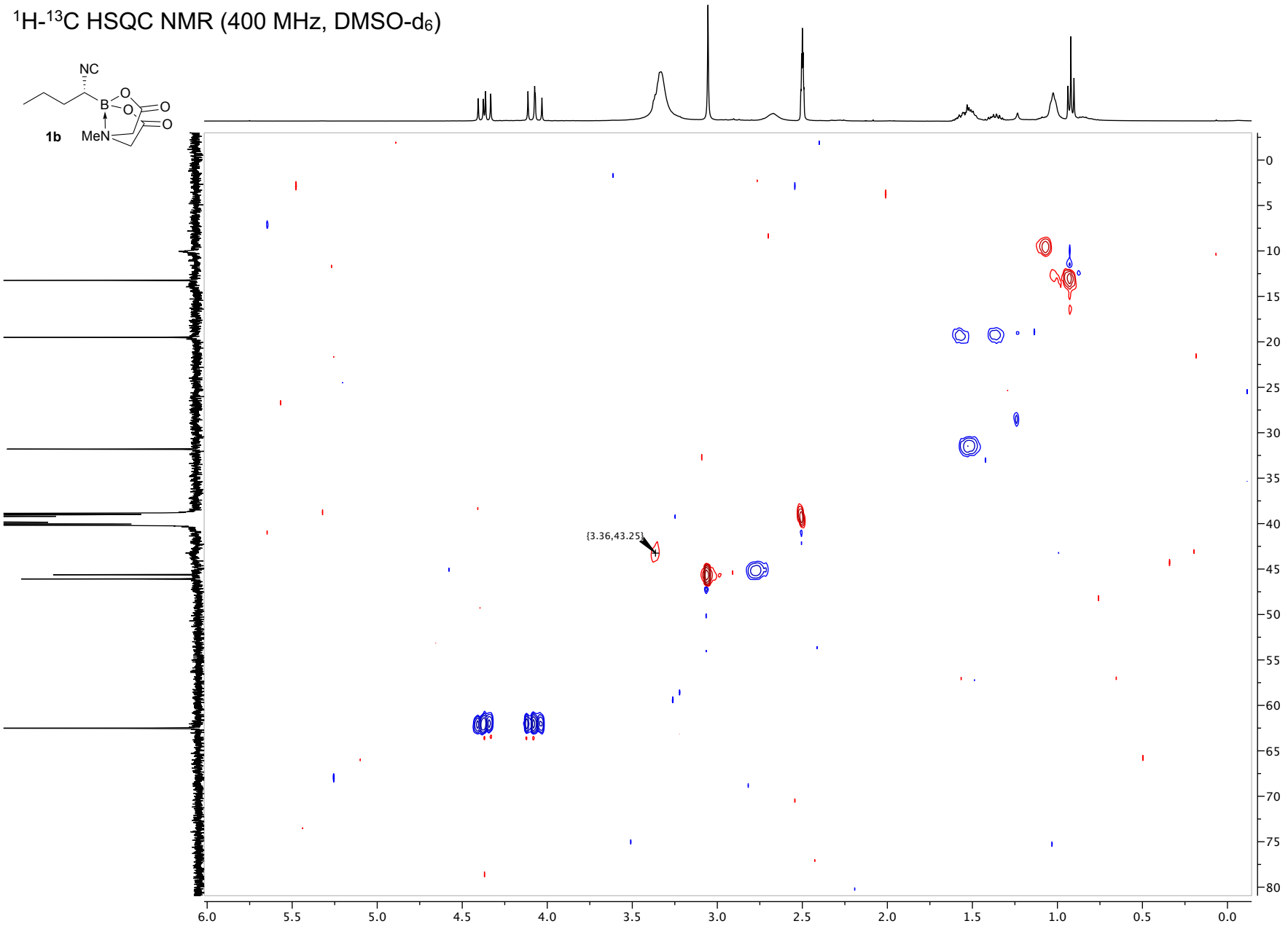
^{13}C NMR (101 MHz, DMSO-d$_6$)



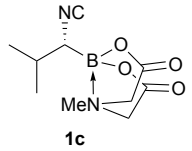
1b



^{1}H-^{13}C HSQC NMR (400 MHz, DMSO-d_6)

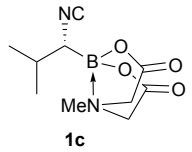


^{1}H NMR (400 MHz, CD_3CN)



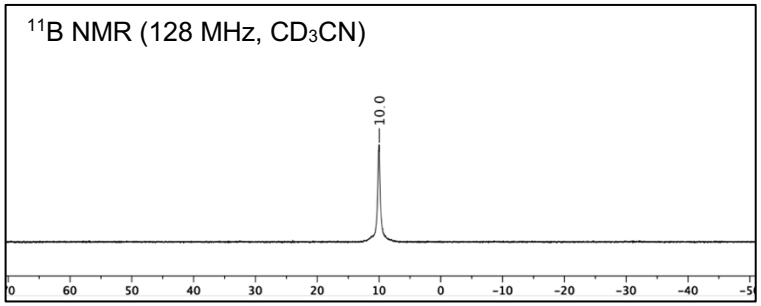
1c

^{13}C NMR (101 MHz, CD_3CN)

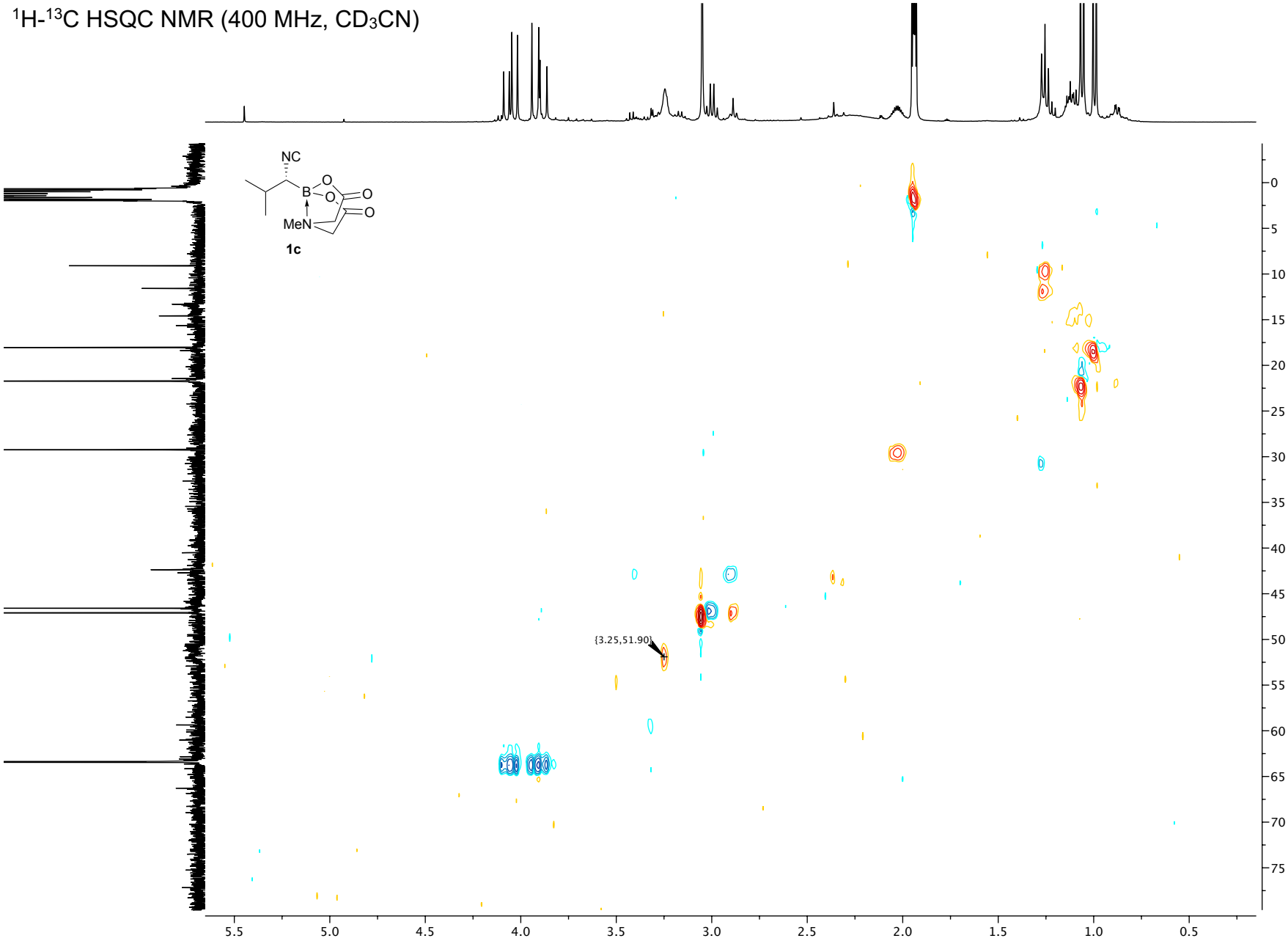


1c

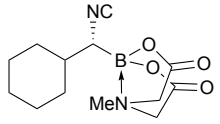
^{11}B NMR (128 MHz, CD_3CN)



^{1}H-^{13}C HSQC NMR (400 MHz, CD_3CN)

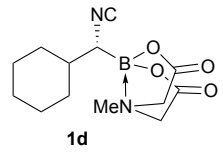


^{1}H NMR (600 MHz, CD_3CN)

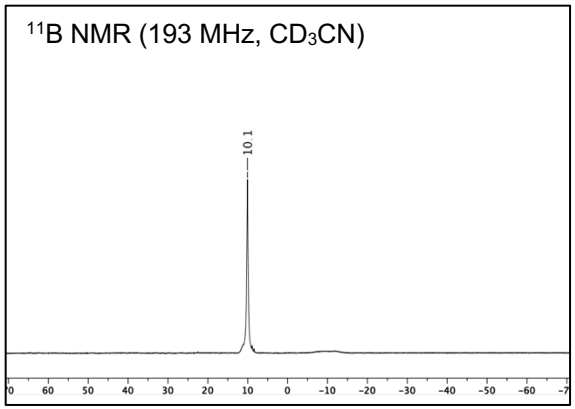


1d

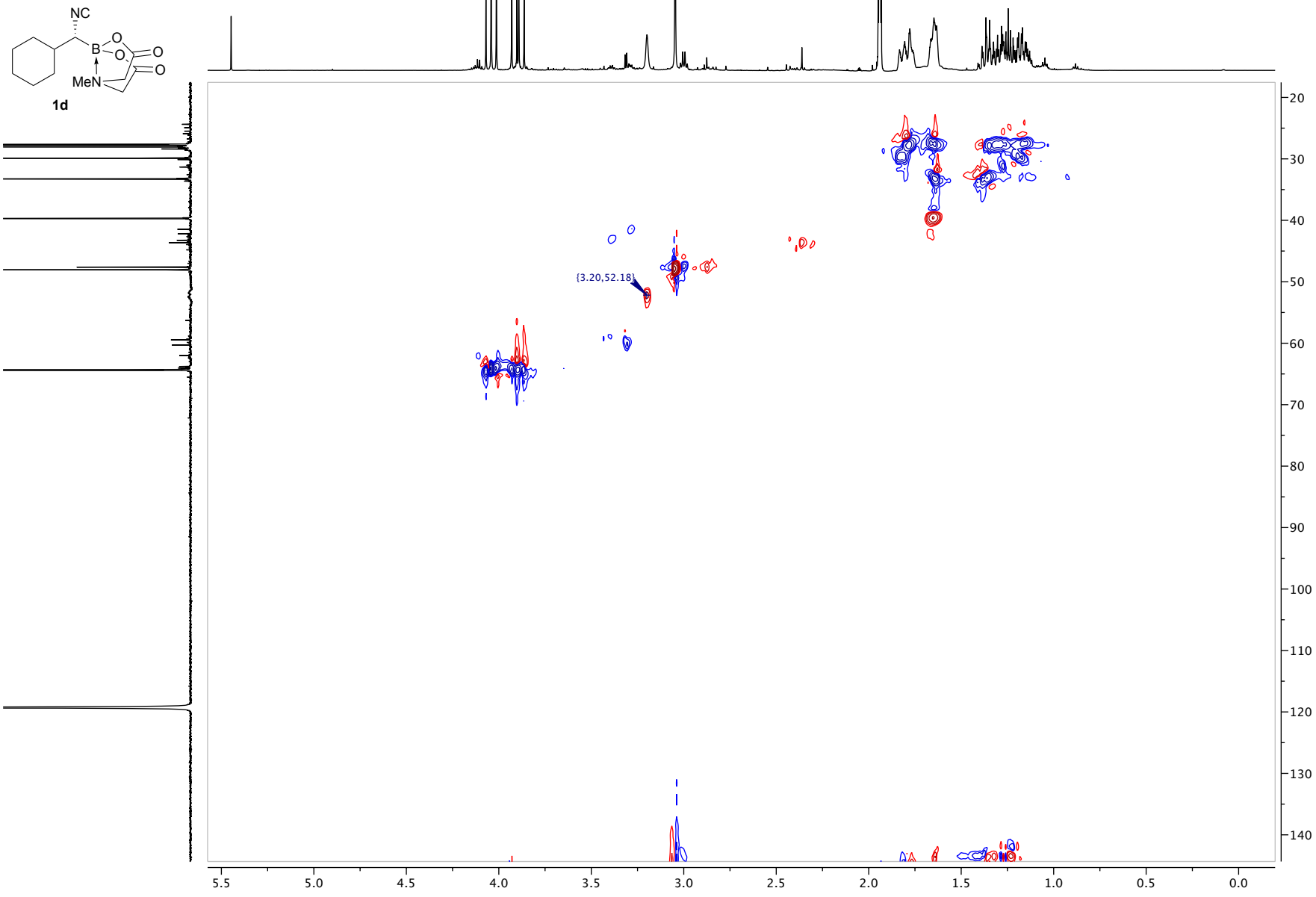
^{13}C NMR (150 MHz, CD_3CN)



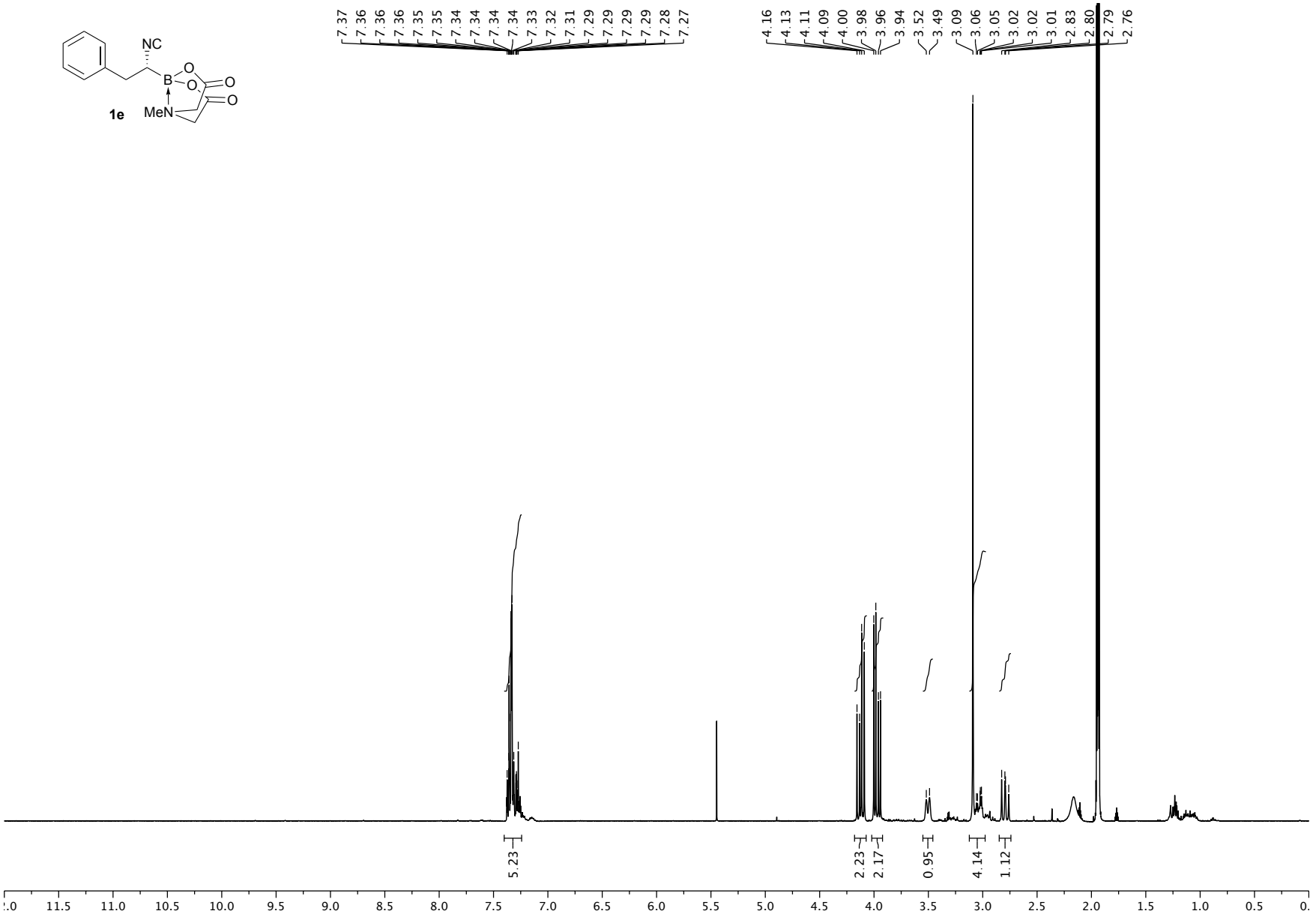
1d



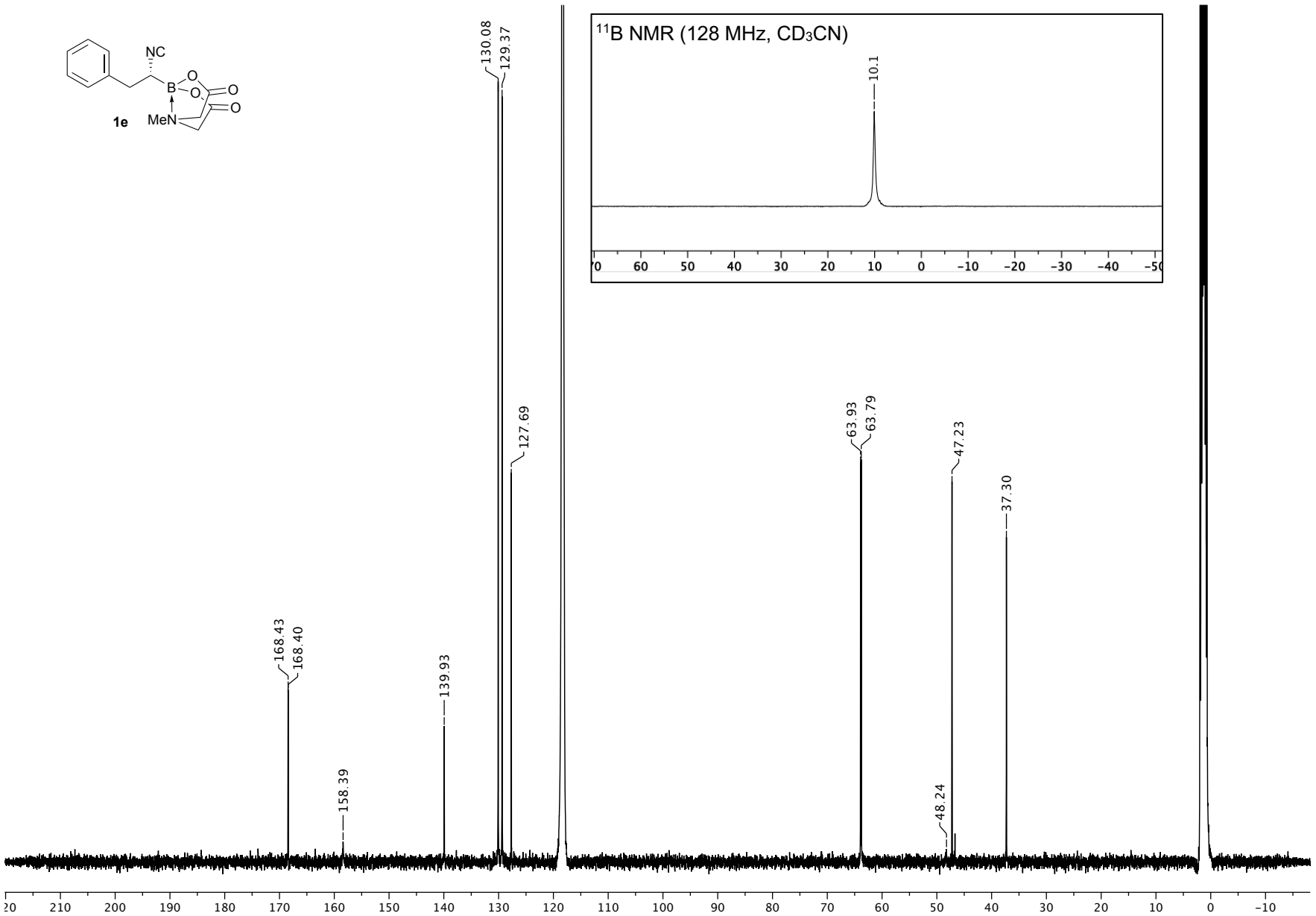
^{1}H-^{13}C HSQC NMR (600 MHz, CD_3CN)



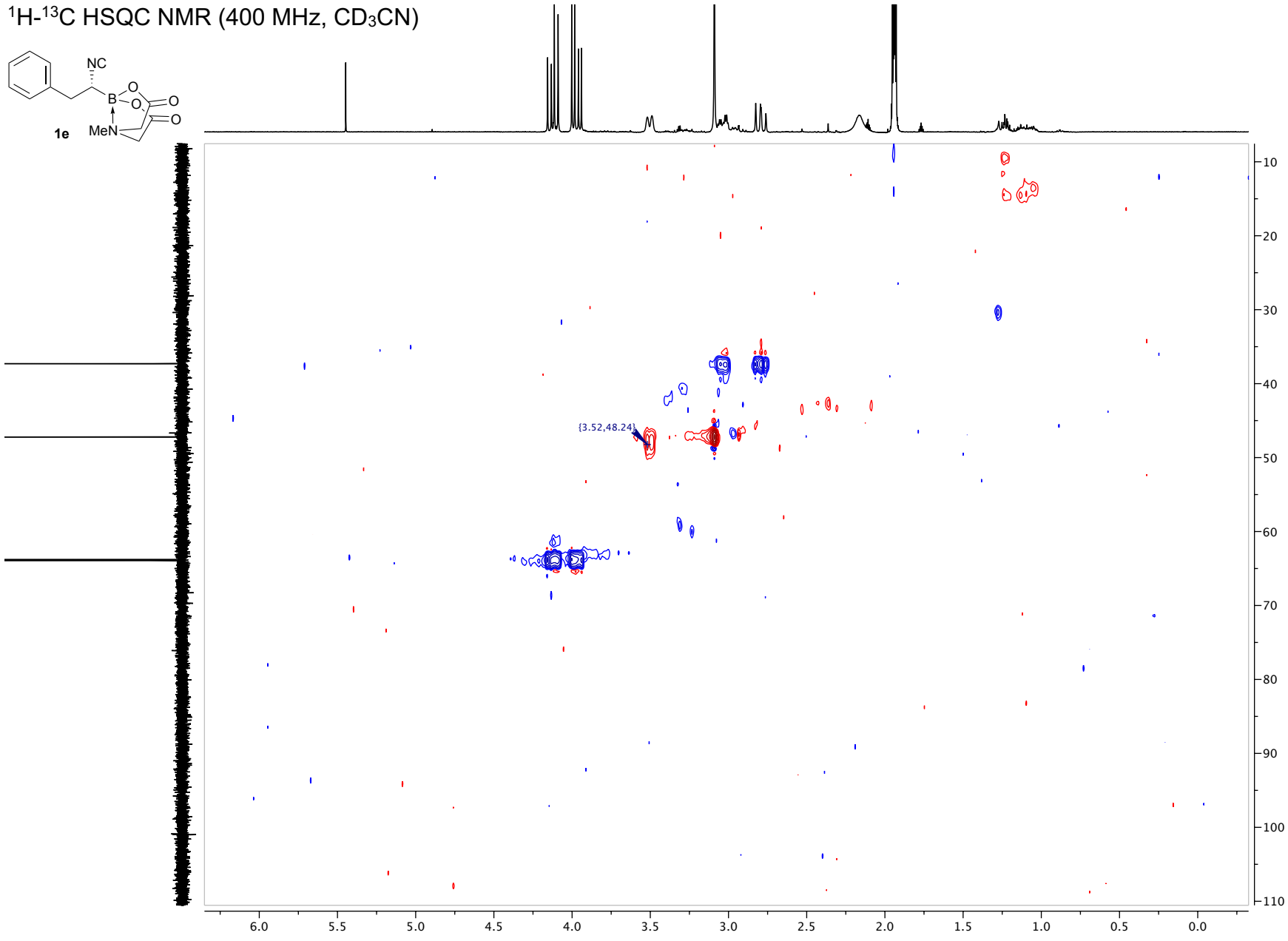
^{1}H NMR (400 MHz, CD_3CN)



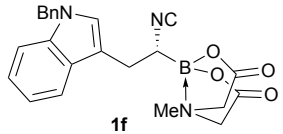
^{13}C NMR (101 MHz, CD_3CN)



^{1}H-^{13}C HSQC NMR (400 MHz, CD_3CN)

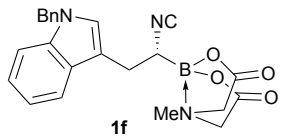


^{1}H NMR (400 MHz, CD_3CN)

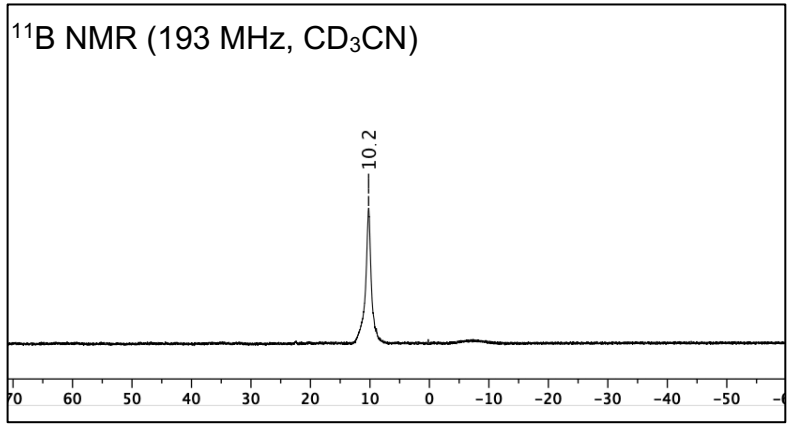


1f

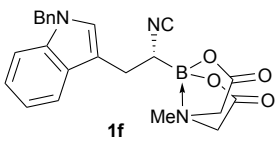
^{13}C NMR (101 MHz, CD_3CN)



1f



^{1}H-^{13}C HSQC NMR (400 MHz, CD_3CN)



1f