Electronic Supplementary Material (ESI) for ChemComm.

Towards depeptidized aminoboronic acid derivatives through the use of borylated iminium ions

Supplementary information

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1. General experiment information

General: All solvents and reagents were purchased from commercial sources and used as received unless stated otherwise. Acetonitrile (MeCN), dichloromethane (DCM) and aniline were freshly distilled from calcium hydride before use. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl prior to use. 2,2,2-Trifluoroethanol (TFE) was stored over 4Å molecular sieves prior to use. 2-(MIDA boryl)acetaldehyde (**2a**)[1], 2-(MIDA)boryl-2-cyclohexylacetaldehyde (**2b**)[2], 2-(MIDA)boryl-2-phenylacetaldehyde (**2c**)[2], , 4-methyl-2-(MIDA boryl)pentanal (**2d**)[3], and 1-(benzyloxycarbonyl)-2-pyrroline (**4c**)[4] were synthesized according to literature procedures.

Chromatography: Thin-layer chromatography was carried out on Merck Aluminum-backed TLC Silica gel 60 F_{254} plates and visualized using a UV lamp (254 μM) and curcumin stain (for boron-containing compounds). Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel or on a Teledyne-Isco Combiflash system using RediSep Gold Normal-Phase Silica. Reverse-phase chromatography was carried out using RediSep Rf Gold C18 Columns on a Biotage Isolera System.

NMR: ^{1}H, ^{11}B, and ^{13}C, and NMR spectra were recorded on Bruker 400 MHz, Varian 500 MHz, or Varian 600 MHz spectrometers at 25 ˚C unless otherwise stated. Spectral data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) and referenced to residual protonated solvent peak (MeCN-d3: δ = 1.94; DMSO-d6: δ = 2.50, CD_3OD = δ = 3.31). ^{11}B NMR chemical shifts (δ) are reported in ppm and referenced to an external standard of $BF3 \cdot OEt_2$ (δ = 0.0). ^{13}C NMR chemical shifts (δ) are reported in ppm and referenced to the corresponding solvent peaks (MeCN-d3: δ = 118.2; DMSO-d6: δ = 39.5, CD_3OD = δ = 49.00). *Carbon atoms exhibiting significant line broadening brought about by boron substituents were not reported due to quadrupolar relaxation.*

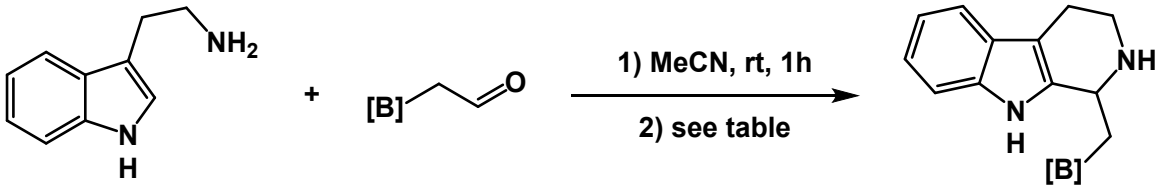
HRMS: High-resolution mass spectra (HRMS) were obtained on a VG 70−250 S (double focusing) mass spectrometer at 70 eV or on an ABI/Sciex Qstar mass spectrometer with an electrospray ionization (ESI) source, tandem mass spectrometry, and accurate mass capabilities

pH measurements: Carried using a Thermo ScientificTM OrionTM 8103BNUWP ROSS UltraTM pH Electrode coupled to VWR Symphony SB20 meter. The instrument was calibrated with Orion Buffer solutions of pH = 4.01, 7.00, and 10.01 prior to measurement.

Infrared spectroscopy: FTIR analysis of representative compounds was carried out on a Bruker Alpha Platinum ATP spectrometer and peaks below 1500 cm^{-1} are not reported.

2. Reaction optimization

a) Pictet-Spengler reaction

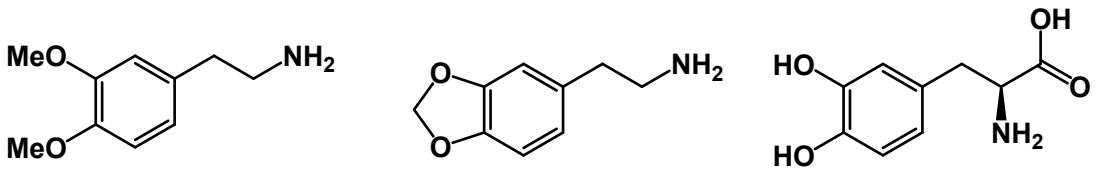


In an oven-dried 1-dram vial was added 2-(MIDA boryl)acetaldehyde **2a** (9.9 mg, 0.05 mmol) and tryptamine (see table). Dissolved in MeCN and stirred at room temperature for 1h. Added the acid by micropipette, sealed the vial and stirred at RT for 24h. The reaction was stopped by evaporation of the volatiles *in vacuo*. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the crude reaction product, the mixture was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR.

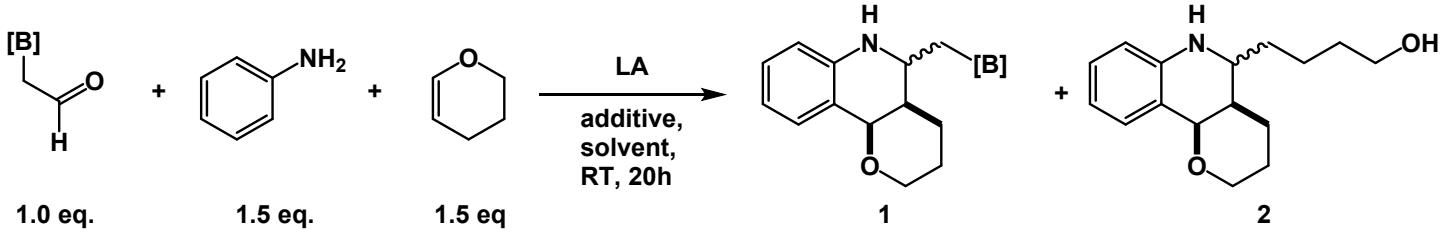
Entry	Equivalents of tryptamine	Acid	Solvent	NMR yield[a]
1	2.0	AcOH (1.0 eq)	MeCN	0%
2	2.0	TFA (1.0 eq)	MeCN	0%
3	2.0	TFA (5 vol%)	MeCN	94%
4	2.0	AcOH (1.0 eq)	DCM[b]	0%
5	2.0	TFA (1.0 eq)	DCM[b]	0%
6	2.0	TFA (5 vol%)	DCM[b]	84%
7	1.0	TFA (5 vol%)	MeCN	>95%
8	**1.2**	**TFA (5 vol%)**	**MeCN**	**>95%**
9	1.5	TFA (5 vol%)	MeCN	>95%

[a] NMR Yield determined by analysis of ^{1}H NMR spectrum of the crude reaction mixture with 1,3,5-trimethoxybenzene as internal standard.
[b]Solvent switch was performed by first removing MeCN *in vacuo*, then adding DCM prior to addition of acid.

- Unsuccesful amine derivatives:



b) Povarov reaction



In an oven-dried 1-dram vial was added 2-(MIDA boryl)acetaldehyde (9.9 mg, 0.05 mmol), followed by the solvent (0.1M). Then, aniline (6.9 µL, 0.075 mmol), the Lewis acid (20 mol%) and $MgSO_4$ (160 mg) were added and the mixture was stirred at RT for 1h. 3,4-Dihydropyran (6.8 µL, 0.075 mmol) was then added, and the reaction was stirred at RT for 20h. The reaction mixtures were filtered through a pipette plug and washed with MeCN. The volatiles were removed *in vacuo*. 1,3,5-Trimethoxybenzene (8.4 mg, 0.05 mmol) was added to the crude reaction product, and the mixture was dissolved in DMSO-d_{6i} and analyzed by ^{1}H NMR.

Entry	Lewis acid	Additive	Solvent	NMR yield (**1**)[a]	NMR yield (**2**)[a]
1	$Bi(OTf)_3$ (20 mol%)	$MgSO_4$	CH_3CN	37 % (91:9 dr)	32 % (52:48 dr)
2	$Sc(OTf)_3$ (20 mol%)	$MgSO_4$	CH_3CN	33 % (92:8 dr)	26 % (54:46 dr)
3	N/A	$MgSO_4$	TFE	37 % (86:14 dr)	< 5%

[a]NMR yield and diastereomeric ratio determined by ^{1}H NMR analysis of the crude reaction mixture with 1,3,5-trimethoxybenzene as internal standard.

3. General reaction procedures

a) General Procedure 1 (**GP1**) – Pictet-Spengler reaction

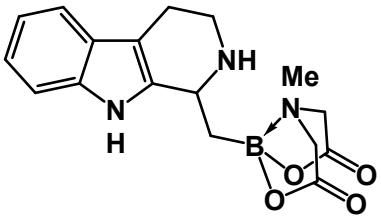
To an oven-dried round-bottom flask equipped with a stir-bar was added the corresponding α-boryl aldehyde (1.0 equiv.) and amine (1.2 equiv). The vial was capped with a septum and put under a stream of N_2. MeCN (0.1 M) was added and the mixture was stirred 1h at room temperature to dissolve the aldehyde fully. Then, TFA (5 vol%) was added slowly via syringe at room temperature. The reaction mixture turns deep green upon addition of the TFA. Stirred the reaction at room temperature under N_2 overnight (16h). The disappearance of the aldehyde was monitored by TLC (50/50 EtOAc/MeCN with 1% Et_3N, visualized boron compounds with curcumin stain). Upon completion, the volatiles were removed *in vacuo* to obtain an oily orange crude product. The crude product was redissolved in EtOAc and washed with an ice-cold saturated $NaHCO_3$ solution. The organic layer was rapidly separated and the aqueous layer was extracted three more times with EtOAc. The organic layers were combined and the crude product was loaded on celite. The purification was done by chromatography as indicated for each compound. The product fractions were combined and the volatiles were removed *in vacuo*. The pure product was redissolved in a minimal amount of THF or MeCN, then Et_2O was added to crash the product which was finally filtered and dried under vacuum.

b) General Procedure 2 (**GP2**) – Povarov reaction

In an oven-dried 2-dr screw top vial, added the corresponding α-(MIDA boryl) aldehyde (0.25 mmol, 1.0 equiv.) and $MgSO_4$ (400 mg). Added 2,2,2-trifluoroethanol (2.5 mL, 0.1 M) and stirred 5 minutes to dissolve the aldehyde. Added the corresponding aniline (0.375 mmol, 1.5 equiv.), stirred for 30 minutes, then added the corresponding alkene (0.375 mmol, 1.5 equiv.). Stirred at room temperature overnight (16h), diluted the reaction mixture with an equal volume of MeCN. Filtered $MgSO_4$ through a pipette plug, then evaporated the volatiles on a rotary evaporator. Took an aliquot for analysis of the diastereomeric ratio (dr) by ^1H NMR analysis of the crude reaction mixture in DMSO-*d*6. Recombined the crude NMR sample with the crude reaction mixture and loaded the mixture on celite. The purification was performed as indicated for each compound. The final product was lyophilized from a MeCN/H_2O mixture.

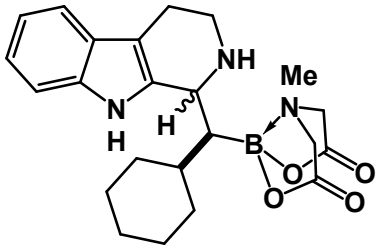
4 Synthesis and characterization of β-aminoboronates

MIDA (2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)methyl)boronate (3a)



Compound **3a** was synthesized according to **GP1** with 2-(MIDA boryl)acetaldehyde **2a** (497 mg, 2.5 mmol) and tryptamine **1a** (480.6 mg, 3.0 mmol). Purification by normal-phase chromatography with a gradient of 75% to 100% acetone (in hexanes with 1% Et_3N) afforded the product as a beige solid (737 mg, 2.16 mmol, 87% yield).

^{1}H NMR (400 MHz, CD_3CN) δ 9.60 (s, 1H), 7.47 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.39 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.15 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.07 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 4.76 (t, *J* = 7.0 Hz, 1H), 4.08 – 3.88 (m, 4H), 3.63 (ddd, *J* = 12.6, 5.5, 4.0 Hz, 1H), 3.31 (ddd, *J* = 12.6, 9.3, 5.3 Hz, 1H), 3.01 (ddd, *J* = 9.3, 5.5, 1.7 Hz, 1H), 2.93 (s, 3H), 2.94 – 2.85 (m, 1H), 1.54 (d, *J* = 7.0 Hz, 2H).
^{13}C NMR (126 MHz, CD_3CN) δ 169.0, 168.6, 137.3, 133.4, 127.4, 123.0, 120.4, 119.1, 112.3, 107.2, 62.9, 62.8, 52.1, 46.9, 42.7, 19.7.
^{11}B NMR (128 MHz, CD_3CN) δ 11.9.
HRMS (ESI+) m/z calculated for $C_{17}H_{21}BN_3O_4$ [M+H]+: 342.1623; found: 342.1622.
FTIR (neat): ν = 3407, 3216, 3004, 1761, 1670, 1623.



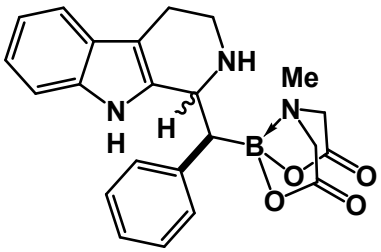
MIDA (cyclohexyl(2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)methyl)boronate (3b)

Compound **3b** was synthesized according to **GP1** with 2-(MIDA)boryl-2-cyclohexylacetaldehyde **2b** (70.3 mg, 0.25 mmol) and tryptamine **1a** (48.1 mg, 0.3 mmol). Purification by normal-phase chromatography with a gradient of 50% to 100% acetone (in hexanes with 1% Et_3N) afforded the product as a beige solid (58.9 mg, 0.14 mmol, 56% yield).

Characterized as mixture of diastereomers.

^{1}H NMR (500 MHz, CD_3CN) δ 9.07 (s, 1H), 7.60 (dt, *J* = 6.2, 1.3 Hz, 1H), 7.56 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.38 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.07 – 7.00 (m, 2H), 3.82 (d, *J* = 17.3 Hz, 1H), 3.71 (d, *J* = 17.3 Hz, 1H), 3.65 (dddd, *J* = 8.7, 5.1, 2.5, 1.0 Hz, 2H), 3.59 (d, *J* = 16.5 Hz, 1H), 3.31 (d, *J* = 16.4 Hz, 1H), 2.96 (t, *J* = 6.7 Hz, 2H), 2.78 (s, 3H), 1.78 – 1.73 (m, 2H), 1.71 – 1.63 (m, 3H), 1.61 – 1.56 (m, 1H), 1.51 – 1.45 (m, 1H), 1.27 – 1.13 (m, 2H), 1.09 – 0.94 (m, 3H).
^{13}C NMR (126 MHz, CD_3CN) δ 169.7, 169.2, 168.8, 137.5, 128.5, 123.7, 122.4, 119.7, 119.6, 114.2, 112.3, 63.6, 63.2, 62.2, 46.6, 39.3, 34.2, 31.0, 27.9, 27.8, 27.3, 27.1.
^{11}B NMR (128 MHz, CD_3CN) δ 12.1.
HRMS (ESI+) m/z calculated for $C_{23}H_{31}BN_3O_4$ [M+H]+: 424.2406; found: 424.2410.

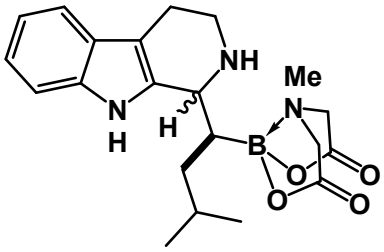
MIDA (phenyl(2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)methyl)boronate (3c)



Compound **3c** was synthesized according to **GP1** with 2-(MIDA)boryl-2-phenylacetaldehyde **2c** (103.6 mg, 0.38 mmol) and tryptamine **1a** (74.8 mg, 0.47 mmol). Purification by normal-phase chromatography with a gradient of 25 to 100% acetonitrile (in ethyl acetate) afforded the product as a white solid (72.9 mg, 0.175 mmol, 46% yield)

Characterized as mixture of diastereomers.

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.53 (s, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.18 – 7.06 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 2H), 5.12 (s, 1H), 4.45 (d, *J* = 17.2 Hz, 1H), 4.30 (d, *J* = 17.2 Hz, 1H), 4.23 (d, *J* = 17.2 Hz, 1H), 4.18 (d, *J* = 17.2 Hz, 1H), 3.54 (s, 1H), 3.35 – 3.27 (m, 1H), 3.27 – 3.19 (m, 1H), 2.77 (s, 3H), 2.72 – 2.65 (m, 2H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 168.5, 168.4, 136.1, 130.9, 128.5, 126.7, 125.9, 121.6, 118.8, 117.8, 111.4, 107.1, 62.2, 61.8, 55.8, 55.1, 46.2, 43.6.
^{11}B NMR (128 MHz, DMSO-d_6) δ 14.7.
HRMS (DART+) m/z calculated for $C_{23}H_{25}BN_3O_4$ [M+H]+: 418.19326; found: 418.19401.



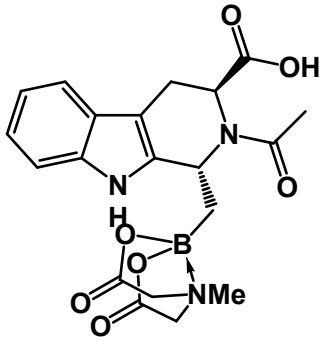
MIDA (3-methyl-1-(2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)butyl)boronate (3d)

Compound **3d** was synthesized according to **GP1** with 4-methyl-2-(MIDA boryl)pentanal **2d** (62 mg, 0.24 mmol) and tryptamine **1a** (47.5 mg, 0.30 mmol). Purification by normal-phase chromatography with a gradient of 25% to 100% acetone (in ethyl acetate) afforded the product as a white solid (38.1 mg, 0.095 mmol, 40% yield).

Characterized as mixture of diastereomers.

^{1}H NMR (500 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.09 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.00 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 4.87 (br s, 1H), 4.44 (d, *J* = 17.6 Hz, 1H), 4.28 (d, *J* = 17.2 Hz, 1H), 4.18 (d, *J* = 17.1 Hz, 1H), 4.12 (d, *J* = 17.5 Hz, 1H), 3.59 – 3.52 (m, 1H), 3.25 – 3.16 (m, 1H), 3.13 (s, 3H), 3.01 – 2.91 (m, 1H), 2.88 – 2.81 (m, 1H), 2.02 – 1.95 (m, 1H), 1.21 – 1.13 (m, 2H), 1.06 – 0.99 (m, 1H), 0.97 – 0.89 (m, 1H), 0.71 (d, *J* = 6.4 Hz, 3H), 0.62 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 169.0, 136.2, *121.2, 118.7, 117.7, 111.3, *62.3, 61.8, *45.7, *43.3, *33.9, 25.8, *22.8, 22.3, *21.9, *17.9.
^{11}B NMR (128 MHz, DMSO) δ 9.3.
HRMS (ESI+) m/z calculated for $C_{21}H_{29}BN_3O_4$ [M+H]+: 398.2249; found: 398.2259.
**Signal was observed by HSQC.*

2-acetyl-1-(MIDA-boronomethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole-3-carboxylic acid (3e)



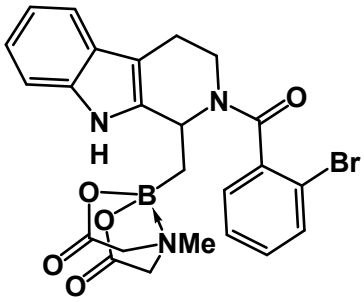
Compound **3e** was synthesized according to **GP1** with 2-(MIDA boryl)acetaldehyde **2a** (497 mg, 2.5 mmol) and L-tryptophan **1b** (613 mg, 3.0 mmol). After evaporating the volatiles from the reaction *in vacuo*, took an aliquot for analysis of the dr by ^{1}H NMR (70:30 dr). Then, re-dissolved the

crude product in MeCN (25 mL). Cooled to 0°C and added Et_3N (1020 µL, 7.5 mmol) then AcCl (533 µL, 7.5 mmol). Stirred at RT until completion. Evaporated the volatiles *in vacuo*. Dissolved the crude residue with 3/1 $CHCl_3$/IPA and washed the organic solution with ice-cold 0.1M HCl. Extracted the aqueous layer two more times with 3/1 $CHCl_3$/IPA. Loaded the product on celite and purified by reverse-phase chromatography with a gradient of 5% to 100% MeCH (in H_2O). Isolated the product as an off-white solid (251 mg, 0.589 mmol, 24% yield) as a mixture of diastereomers.

Characterized pure product fractions of the minor diastereomer (*trans*).

*Denotes the minor rotamer
^{1}H NMR (500 MHz, DMSO-d_6) δ 10.22 (s, 1H), *10.11 (s, 1H), *7.45 (d, *J* = 4.5 Hz, 1H), 7.43 (d, *J* = 4.7 Hz, 1H), *7.35 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.30 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.06 (dddd, *J* = 8.2, 7.1, 3.3, 1.2 Hz, 1H), 6.98 (tt, *J* = 7.1, 1.3 Hz, 1H), *5.65 – 5.59 (m, 1H), *5.59 (dd, *J* = 6.9, 3.0 Hz, 1H), 5.18 (dd, *J* = 8.1, 5.2 Hz, 1H), 5.04 (dd, *J* = 6.7, 1.8 Hz, 1H), 4.34 – 4.18 (m, 2H), 4.13 – 3.94 (m, 2H), *3.36 – 3.28 (m, 1H), 3.24 (dd, *J* = 15.4, 3.1 Hz, 1H), *3.01 (s, 3H), 2.88 (ddd, *J* = 15.4, 6.8, 1.7 Hz, 1H), 2.84 – 2.81 (m, 1H), 2.81 (s, 3H), 2.22 (s, 3H), *2.19 (s, 3H), 1.39 (dd, *J* = 14.6, 5.2 Hz, 1H), *1.29 (dd, *J* = 15.3, 6.1 Hz, 1H), 1.22 (dd, *J* = 14.6, 8.1 Hz, 1H), *1.09 (dd, *J* = 15.2, 7.5 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 173.5, *173.0, *170.3, 169.6, *169.1, 168.9, *168.5, 168.4, *135.9, 135.8, 135.4, *135.3, *126.2, 126.1,*121.0, 120.9, 118.6, *118.5, 117.7, *117.7, *111.2, 111.1, 104.7, *104.0, *62.0, *61.8, 61.5, 61.4, 53.7, 50.4, *49.1, 45.9, *45.9, *45.3, 22.5, *22.1, 22.0, *21.5.
^{11}B NMR (128 MHz, DMSO-d_6) δ 9.2.
HRMS (ESI+) m/z calculated for $C_{20}H_{23}BN_3O_7$ [M+H]+: 428.1627; found: 428.1623.

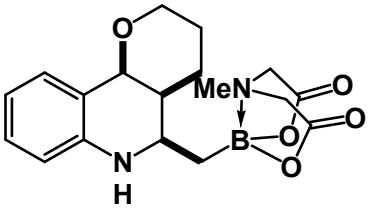
MIDA ((2-(2-bromobenzoyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)methyl)boronate (3f)



Compound **3f** was synthesized according to **GP1** with 2-(MIDA boryl)acetaldehyde **2a** (300 mg, 1.5 mmol) and tryptamine **1a** (361 mg, 2.25 mmol). After full consumption of the boryl aldehyde, the volatiles were removed *in vacuo*. The crude reaction product was re-dissolved in MeCN (15 mL) and cooled to 0°C. DIPEA was added (1306 µL, 7.5 mmol), followed by 2-bromobenzoyl chloride (312 µL, 3.0 mmol). Purification by normal-phase chromatography with a gradient of 75% to 100% acetone afforded the product as a light-yellow solid (565.8 mg, 1.08 mmol, 72% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.92 (s, 1H), 7.76 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.69 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.49 (td, *J* = 7.5, 1.1 Hz, 1H), 7.38 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.32 (dd, *J* = 13.1, 7.8 Hz, 2H), 7.04 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.95 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 5.97 (dd, *J* = 9.2, 5.5 Hz, 1H), 4.26 (t, *J* = 17.4 Hz, 2H), 4.02 (dd, *J* = 17.0, 2.4 Hz, 2H), 3.52 – 3.43 (m, 2H), 3.06 (s, 3H), 2.90 – 2.76 (m, 1H), 2.60 (d, *J* = 14.5 Hz, 1H), 1.39 – 1.22 (m, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 169.2, 168.9, 166.6, 138.9, 137.5, 135.8, 132.6, 130.3, 128.0, 127.7, 126.4, 120.7, 118.5, 118.4, 117.6, 111.0, 106.9, 104.9, 61.6, 61.6, 45.9, 45.4, 22.1.
^{11}B NMR (128 MHz, DMSO-d_6) δ 9.8.
HRMS (ESI+) m/z calculated for $C_{24}H_{24}BBrN_3O_5$ [M+H]+: 524.0991; found: 524.0982.

MIDA ((3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-5-yl)methyl)boronate (6a)

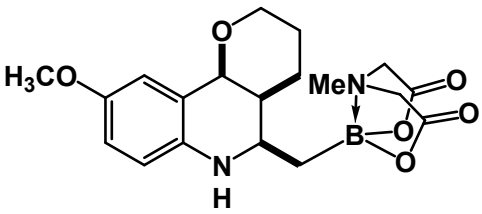


Compound **6a** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (49.7 mg, 0.25 mmol), aniline **4a** (34.2 µL, 0.375 mmol) and 3,4-dihydropyran **5a** (34.2 µL, 0.375 mmol). Crude dr = 89:11 *(endo*:*exo*). Purification by reverse-phase chromatography afforded a white solid after lyophilization. A first fraction was isolated as a single diastereomer (28.0 mg, *endo*) and the second fraction as a mixture of diastereomers (7.0 mg, 0.7/1 *endo*/*exo*). The combined fractions were a total of 35.0 mg, 0.098 mmol, 39% yield.

*Major diastereomer *(endo*) characterized

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.13 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 6.8 Hz, 1H), 6.54 (t, *J* = 7.4 Hz, 1H), 6.47 (d, *J* = 8.1 Hz, 1H), 4.98 – 4.93 (m, 2H), 4.22 (dd, *J* = 17.1, 8.5 Hz, 2H), 4.02 (dd, *J* = 17.0, 4.0 Hz, 2H), 3.52 – 3.43 (m, 2H), 3.22 (td, *J* = 11.7, 2.6 Hz, 1H), 2.88 (s, 3H), 1.95 (dt, *J* = 12.1, 5.2 Hz, 1H), 1.69 (d, *J* = 9.9 Hz, 1H), 1.53 (dt, *J* = 12.7, 4.1 Hz, 1H), 1.50 – 1.43 (m, 1H), 1.25 – 1.12 (m, 1H), 0.82 (dd, *J* = 14.1, 7.9 Hz, 1H), 0.76 (dd, *J* = 14.2, 6.6 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 169.4, 169.3, 146.3, 127.9, 127.0, 119.2, 116.4, 113.7, 72.2, 61.9, 61.9, 60.2, 51.2, 46.1, 36.3, 25.7, 18.0.
^{11}B NMR (128 MHz, DMSO-d_6) δ 11.0.
HRMS (ESI+) m/z calculated for $C_{18}H_{24}BN_2O_5$ [M+H]+: 359.1776; found: 359.1772.

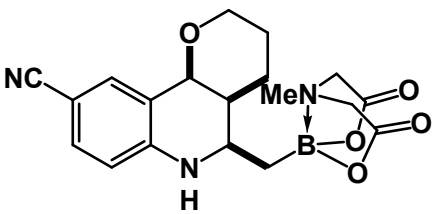
MIDA ((9-methoxy-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-5-yl)methyl)boronate (6b)



Compound **6b** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (49.7 mg, 0.25 mmol), *p*-anisidine **4b** (46.2 mg, 0.375 mmol) and 3,4-dihydropyran **5a** (34.2 µL, 0.375 mmol). Crude dr = 92:8 *(endo*:*exo*). Purification by reverse-phase chromatography with a gradient of 0% to 50% MeCN (in H_2O with 0.1% formic acid) afforded a beige solid after lyophilization (40.7 mg,105 mmol, 42% yield) as a mixture of diastereomers (89:11 *endo*:*exo*).

*Major diastereomer *(endo*) characterized.
^{1}H NMR (500 MHz, DMSO-d_6) δ 6.74 (dd, *J* = 2.9, 1.0 Hz, 1H), 6.58 (ddd, *J* = 8.7, 2.9, 0.8 Hz, 1H), 6.44 (d, *J* = 8.6 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 1H), 4.21 (dd, *J* = 17.1, 6.6 Hz, 2H), 4.02 (dd, *J* = 17.0, 2.5 Hz, 2H), 3.63 (s, 3H), 3.54 – 3.47 (m, 1H), 3.40 (td, *J* = 7.5, 7.0, 1.9 Hz, 1H), 3.22 (td, *J* = 11.7, 2.6 Hz, 1H), 2.87 (s, 3H), 1.96-1.91 (m, 1H), 1.71 – 1.65 (m, 1H), 1.53 (dt, *J* = 12.7, 4.2 Hz, 1H), 1.49-1.45 (m, 1H), 1.43-1.40 (m, 1H), 1.21 (qd, *J* = 12.9, 4.3 Hz, 1H), 0.80 (dd, *J* = 14.2, 7.6 Hz, 1H), 0.74 (dd, *J* = 14.1, 6.8 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 168.9, 168.9, 151.2, 140.0, 120.1, 114.6, 114.2, 111.3, 72.0, 61.5, 61.4, 59.9, 55.3, 51.0, 45.6, 36.2, 25.2, 17.5.
^{11}B NMR (128 MHz, DMSO-d_6) δ 12.2.
HRMS (ESI+) m/z calculated for $C_{19}H_{26}BN_2O_6$ [M+H]+: 389.1882; found: 389.1879.

MIDA((9-cyano-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-5-yl)methyl)boronate (6c)

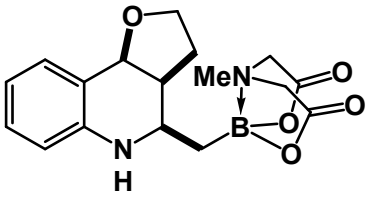


Compound **6c** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (0.25 mmol), 4-aminobenzonitrile **4c** (0.375

mmol) and 3,4-dihydropyran **5a** (0.375 mmol). Crude dr = 90:10 *(endo*:*exo*). Purification by reverse-phase chromatography with a gradient of 0% to 50% MeCN (in H_2O with 0.1% formic acid) afforded an off-white solid (44.1 mg, 0.115 mmol, 46% yield).

*Major diastereomer *(endo*) was characterized.
^{1}H NMR (600 MHz, DMSO-d_6) δ 7.36 (s, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 4.94 (d, *J* = 5.6 Hz, 1H), 4.22 (dd, *J* = 17.1, 12.1 Hz, 2H), 4.03 (dd, *J* = 17.2, 4.9 Hz, 2H), 3.58 – 3.50 (m, 3H), 3.20 (td, *J* = 11.8, 2.9 Hz, 1H), 2.89 (s, 3H), 2.05 – 2.00 (m, 1H), 1.72 (d, *J* = 12.7 Hz, 1H), 1.57 – 1.47 (m, 2H), 1.00 (qd, *J* = 12.7, 4.1 Hz, 1H), 0.88 (dd, *J* = 14.0, 9.7 Hz, 1H), 0.79 (dd, *J* = 14.1, 5.4 Hz, 1H).
^{13}C NMR (151 MHz, DMSO-d_6) δ 168.9, 168.8, 149.5, 131.6, 130.8, 120.8, 118.7, 113.1, 95.6, 70.8, 61.5, 61.5, 59.8, 50.5, 45.6, 34.3, 25.1, 17.4.
^{11}B NMR (128 MHz, DMSO-d_6) δ 13.6.
HRMS (ESI+) m/z calculated for $C_{19}H_{23}BN_3O_5$ [M+H]+: 384.1729; found: 384.1736.
FTIR (neat): ν = 3410, 3011, 2947, 2958, 2211, 1749, 1672, 1606, 1509.

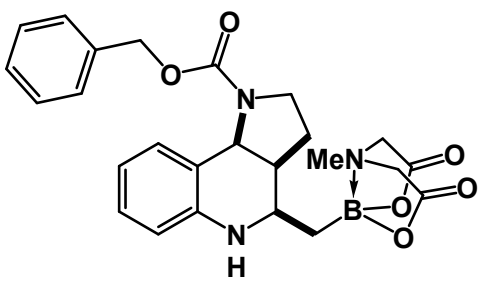
MIDA ((2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinolin-4-yl)methyl)boronate (6d)



Compound **6d** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (49.7 mg, 0.25 mmol), aniline **4a** (34.2 µL, 0.375 mmol) and 2,3-dihydrofuran **5b** (28.4 µL, 0.375 mmol). Crude dr = 82:18 *(endo*:*exo*). Purification by normal-phase chromatography on Teledyne-Isco Combiflash system using a gradient of 0% MeOH/DCM to 10% MeOH/DCM afforded a yellow solid after lyophilization (29.4 mg, 0.085 mmol, 34% yield) as a mixture of diastereomers (85:15 *endo*:*exo*).

*Major diastereomer *(endo*) characterized.
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.07 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.92 (ddd, *J* = 8.5, 7.2, 1.6 Hz, 1H), 6.55 (td, *J* = 7.4, 1.2 Hz, 1H), 6.51 (dd, *J* = 8.1, 1.2 Hz, 1H), 4.98 (d, *J* = 8.1 Hz, 1H), 4.92 (s, 1H), 4.22 (dd, *J* = 17.1, 10.2 Hz, 2H), 4.03 (dd, *J* = 17.1, 7.2 Hz, 2H), 3.64 (q, *J* = 7.9 Hz, 1H), 3.58 (td, *J* = 7.8, 5.1 Hz, 1H), 3.47 (ddd, *J* = 8.7, 5.9, 2.8 Hz, 1H), 2.88 (s, 3H), 2.60 (qd, *J* = 8.9, 2.6 Hz, 1H), 1.88 – 1.78 (m, 2H), 0.87 (dd, *J* = 14.0, 6.0 Hz, 1H), 0.78 (dd, *J* = 14.0, 8.6 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 168.9, 168.9, 146.1, 129.6, 127.6, 122.1, 116.8, 114.0, 75.0, 65.6, 61.5, 61.4, 49.3, 45.6, 43.3, 23.9.
^{11}B NMR (128 MHz, DMSO-d_6) δ 13.6.
HRMS (ESI+) m/z calculated for $C_{17}H_{22}BN_2O_5$ [M+H]+: 345.1619; found: 345.1615.

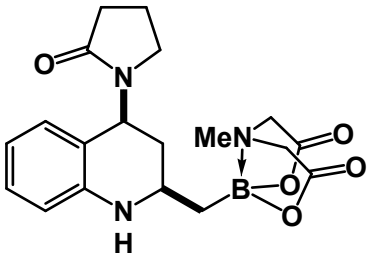
MIDA ((1-((benzyloxy)carbonyl)-2,3,3a,4,5,9b-hexahydro-1H-pyrrolo[3,2-c]quinolin-4-yl)methyl)boronate (6e)



Compound **6e** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (49.7 mg, 0.25 mmol), aniline **4a** (34.2 µL, 0.375 mmol) and 1-(benzyloxycarbonyl)-2-pyrroline **4c** (500 µL of 0.75 M solution in TFE, 0.375 mmol). Crude dr = 91:9 *(endo*:*exo*). Purification by reverse-phase chromatography with a gradient of 0% to 50% MeCN (in H_2O with 0.1% formic acid) afforded a off-white solid after lyophilization (43.6 mg, 0.088 mmol, 36% yield) as a mixture of diastereomers (91:9 *endo*:*exo*).

*Major diastereomer *(endo)* characterized.
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 7.1 Hz, 1H), 7.42 – 7.36 (m, 4H), 7.34 – 7.29 (m, 1H), 6.92 – 6.84 (m, 1H), 6.49 (q, *J* = 6.6 Hz, 2H), 5.14 (s, 1H), 5.10 (d, *J* = 7.5 Hz, 1H), 5.07 (br s, 1H), 4.23 (dd, *J* = 17.1, 7.2 Hz, 2H), 4.04 (d, *J* = 17.0 Hz, 2H), 3.59 – 3.50 (m, 1H), 3.42 (td, *J* = 10.6, 7.6 Hz, 2H), 3.30 (t, *J* = 9.9 Hz, 1H), 2.89 (s, 3H), 2.50 – 2.43 (m, 1H), 1.96 – 1.87 (m, 1H), 1.85 – 1.67 (m, 1H), 0.88 – 0.81 (m, 1H), 0.81 – 0.75 (m, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 168.9, 155.7, 144.6, 137.2, 129.4, 128.4, 128.4, 127.9, 127.7, 127.4, 127.4, 121.6, 120.3, 116.7, 113.9, 66.0, 61.5, 61.5, 56.2, 48.0, 45.7, 44.7, 41.8, 22.0.
^{11}B NMR (128 MHz, DMSO-d_6) δ 10.8.
HRMS (ESI+) m/z calculated for $C_{25}H_{29}BN_3O_6$ [M+H]+: 478.2148; found: 478.2148.

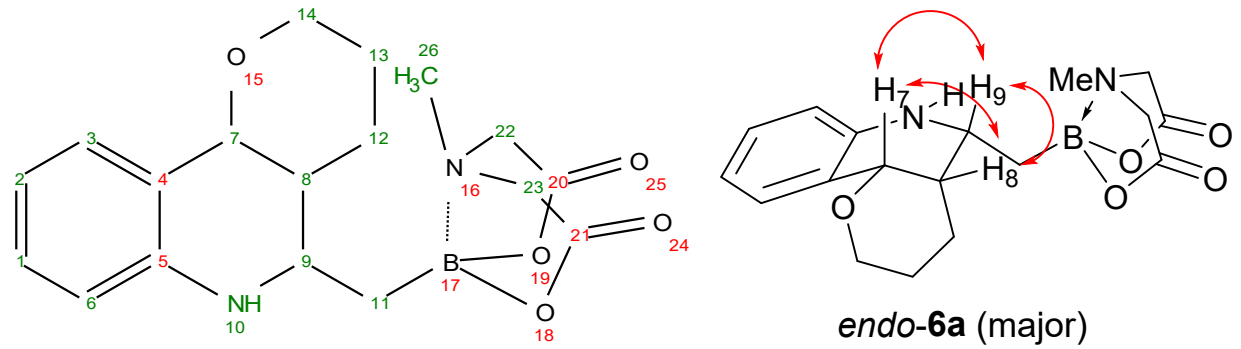
MIDA ((4-(2-oxopyrrolidin-1-yl)-1,2,3,4-tetrahydroquinolin-2-yl)methyl)boronate (6f)

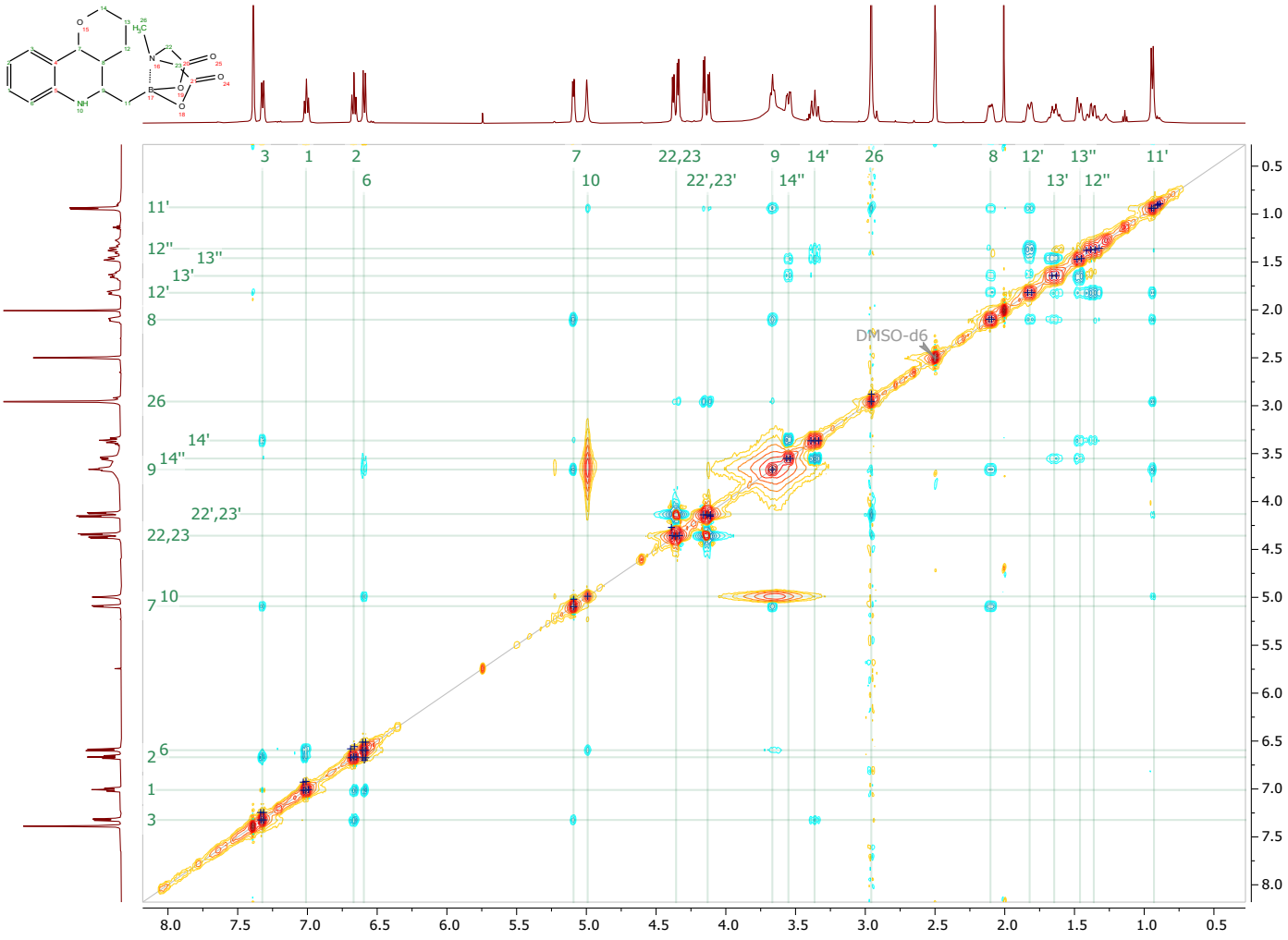


Compound **6f** was synthesized according to **GP2** with 2-(MIDA boryl)acetaldehyde **2a** (49.7 mg, 0.25 mmol), aniline **4a** (34.2 µL, 0.375 mmol) and 1-vinyl-2-pyrrolidinone **5d** (40.1 µL, 0.375 mmol). After 16h, added an extra 0.375 mmol of both aniline and the alkene and stirred another 8h to push the reaction. Crude dr = 88:12 *(endo*:*exo*). Purification by reverse-phase chromatography using a gradient of 0% to 50% MeCN (in H_2O with 0.1% formic acid) a white solid after lyophilization (26.6 mg, 0.069 mmol, 28% yield) as a mixture of diastereomers (91:9 *endo*:*exo*).

*Major diastereomer *(endo)* characterized.
^{1}H NMR (500 MHz, DMSO-d_6) δ 6.90 (td, *J* = 7.6, 1.6 Hz, 1H), 6.63 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.53 – 6.44 (m, 2H), 5.28 (d, *J* = 5.2 Hz, 1H), 5.25 (d, *J* = 5.8 Hz, 1H), 4.22 (d, *J* = 17.1 Hz, 2H), 4.02 (dd, *J* = 17.1, 15.3 Hz, 2H), 3.50 (tdd, *J* = 10.6, 4.4, 2.2 Hz, 1H), 3.23 – 3.15 (m, 1H), 2.97 (ddt, *J* = 11.5, 7.9, 4.0 Hz, 1H), 2.88 (s, 3H), 2.39 – 2.34 (m, 2H), 2.03 – 1.87 (m, 3H), 1.59 (q, *J* = 12.0 Hz, 1H), 0.92 (dd, *J* = 14.1, 4.6 Hz, 1H), 0.78 (dd, *J* = 14.1, 9.0 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 174.6, 169.0, 168.8, 146.4, 127.6, 125.8, 118.0, 115.7, 114.0, 61.5, 61.5, 54.9, 48.3, 47.7, 45.7, 33.4, 30.8, 17.7.
^{11}B NMR (128 MHz, DMSO-d_6) δ 13.8.
HRMS (ESI+) m/z calculated for $C_{19}H_{25}BN_3O_5$ [M+H]+: 386.1885; found: 386.1888.

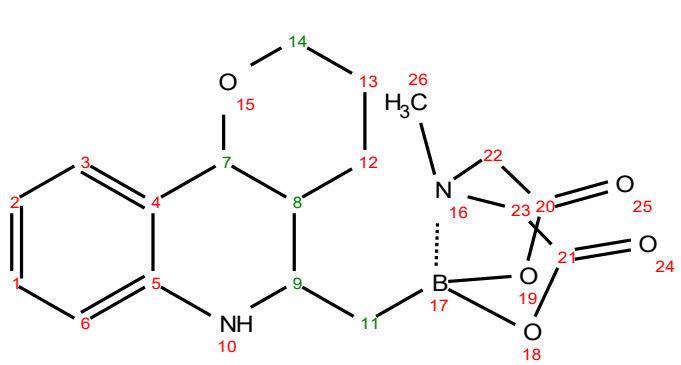
5. Diastereomer assignment of 6a (2D-NOESY spectra)

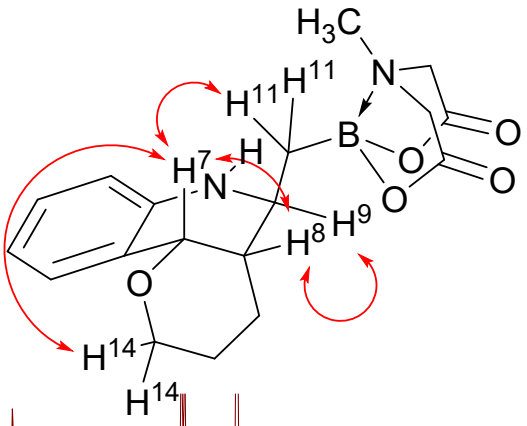




2D NOESY spectrum (400 MHz) of *endo*-**6a** diastereomer in 4/1 DMSO-d_6/benzene-d_6. The signals were assigned based on ^{1}H, ^{13}C, COSY, and HSQC NMR.

The proton signals are labelled and the NOESY correlations can be observed at the intersection of the corresponding lines. The key NOESY correlations used in the identification of the diastereomer are H_7-H_8, H_8-H_9 and H_7-H_9.



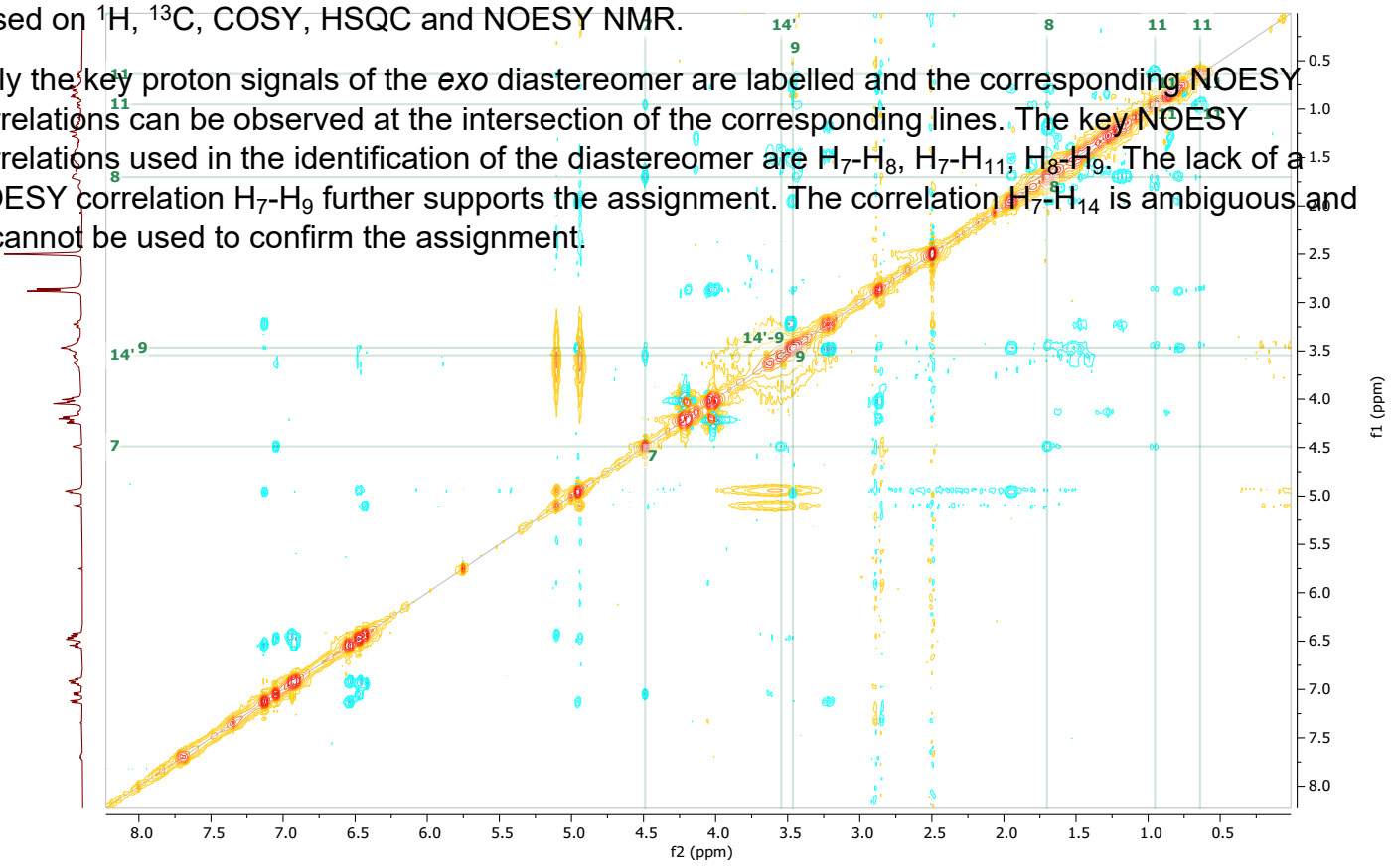


2D NOESY spectrum (400 MHz) of 0.7/1 diastereomers in DMSO-d_6. The signals were assigned based on ^{1}H, ^{13}C, COSY, HSQC and NOESY NMR.

exo-**6a** (minor)

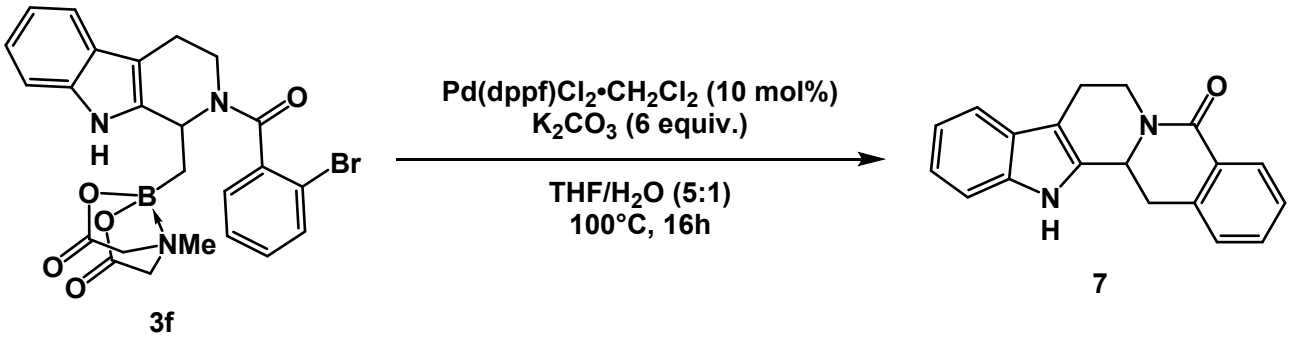
endo/*exo*

Only the key proton signals of the *exo* diastereomer are labelled and the corresponding NOESY correlations can be observed at the intersection of the corresponding lines. The key NOESY correlations used in the identification of the diastereomer are H_7-H_8, H_7-H_{11}, H_8-H_9. The lack of a NOESY correlation H_7-H_9 further supports the assignment. The correlation H_7-H_{14} is ambiguous and is cannot be used to confirm the assignment.



6. Suzuki-Miyaura cross-coupling

8,13,13b,14-tetrahydroindolo[2',3':3,4]pyrido[1,2-b]isoquinolin-5(7H)-one (7)

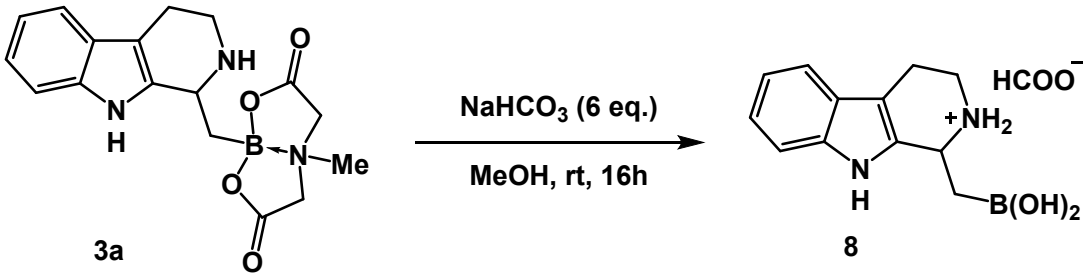


In an oven-dried 5-mL microwave vial charged with a stir bad, added **3f** (105 mg, 0.20 mmol), K_2CO_3 (82.9 mg, 1.20 mmol), then $Pd(dppf)Cl_2•CH_2Cl_2$ (16.0 mg, 0.02 mmol). Sealed the vial, then purged the vial with N_2. Added 1.66 mL of THF, followed by 0.32 mL of H_2O (0.1 M total). Heated the vial to 100°C and stirred for 16h. Cooled the reaction to room temperature, added 2 mL of H_2O, and extracted three times with 3 mL of EtOAc, followed by once with 3 mL of DCM. Combined the organic fractions and loaded the crude product on celite. Purified the product using a CombiFlash instrument with a solvent gradient of 0% to 100% EtOAc (in hexanes). Product **7** was isolated as a light yellow solid (26.1 mg, 0.091 mmol, 45% yield).

^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H), 7.99 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (td, *J* = 7.4, 1.5 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.43 (tt, *J* = 7.6, 1.1 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.39 – 7.33 (m, 1H), 7.10 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.01 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1H), 5.11 – 5.02 (m, 1H), 5.06 – 4.98 (m, 1H), 3.60 (dd, *J* = 15.8, 3.9 Hz, 1H), 3.02 – 2.83 (m, 3H), 2.76 (dddd, *J* = 15.2, 11.8, 5.1, 2.1 Hz, 1H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 163.8, 136.9, 136.4, 133.6, 132.0, 128.8, 127.9, 127.3, 127.1, 126.2, 121.2, 118.7, 118.0, 111.2, 107.3, 51.7, 34.3, 20.6.
HRMS (DART+) m/z calculated for $C_{19}H_{17}N_2O$ [M+H]+: 289.13354; found: 289.13409.

7. MIDA deprotection

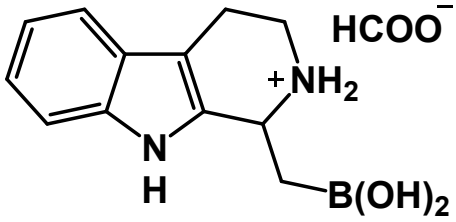
1-(boronomethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-2-ium formate (8)



In a 20-mL scintillation vial equipped with a stir bad was added **3a** (68.2 mg, 0.2 mmol). The compound was dissolved in MeOH (5 mL, 0.04 M) and the vial was capped with a septum. The reaction was put under a stream of N_2 and stirred at RT overnight for 16h. After completion, the solvent was evaporated by bubbling with a stream of N_2 gas from a needle. The crude product was suspended in 10 mL of MeCN, centrifuged and the supernatant containing the product was removed. This procedure was repeated three times. The supernatant layers were combined and the solvent was removed by bubbling with a stream of N_2 gas. The crude product was dissolved in a minimal amount of 1:1 MeCN/H_2O mixture and purified by reverse-phase chromatography via a liquid loading on the column. A gradient of 5% to 100 % MeCN (0.1% A) in water (0.1% FA) was used, and the product fractions were lyophilized to afford the formate salt **8** as white solid (30.5 mg, 0.110 mmol, 55% yield).

^{1}H NMR (500 MHz, CD_3OD) δ 8.47 (s, 1H), 7.44 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.35 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.12 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.03 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 4.76 – 4.68 (m, 1H), 3.66 (dt, *J* = 12.6, 5.2 Hz, 1H), 3.46 – 3.37 (m, 1H), 3.11 – 2.94 (m, 2H), 1.63 (dd, *J* = 16.3, 5.7 Hz, 1H), 1.35 (dd, *J* = 16.4, 8.8 Hz, 1H).
^{13}C NMR (126 MHz, CD_3OD) δ 169.4, 138.1, 132.8, 127.5, 123.1, 120.4, 118.9, 112.3, 106.2, 52.8, 42.4, 19.6.
^{11}B NMR (160 MHz, CD_3OD) δ 25.0.
HRMS (ESI+) m/z calculated for $C_{12}H_{16}BN_2O_2$ [M+H]+: 231.1302; found: 231.1302.

8. pH titration procedure and data



8

The pH titration procedure was adapted from a previous report.[5] Boronic acid **8** (27.6 mg, 0.1 mmol) was added to a 2-dram vial. The compound was dissolved in 4.1 mL of MeOD and 1.2 mL of HEPES buffer (0.1 M in D_2O). The pH was adjusted to ~3 by the dropwise addition of HCl (2.0 M in D_2O). A 200 µL aliquot was taken and set aside for NMR analysis. The pH was increased by ~1 pH unit by the addition of NaOH (2.0M in D_2O) and another 200 µL aliquot was set aside for analysis. This pH increase procedure was repeated until a pH of ~13 was reached (12 aliquot total). The aliquots were analyzed by ^1H NMR.

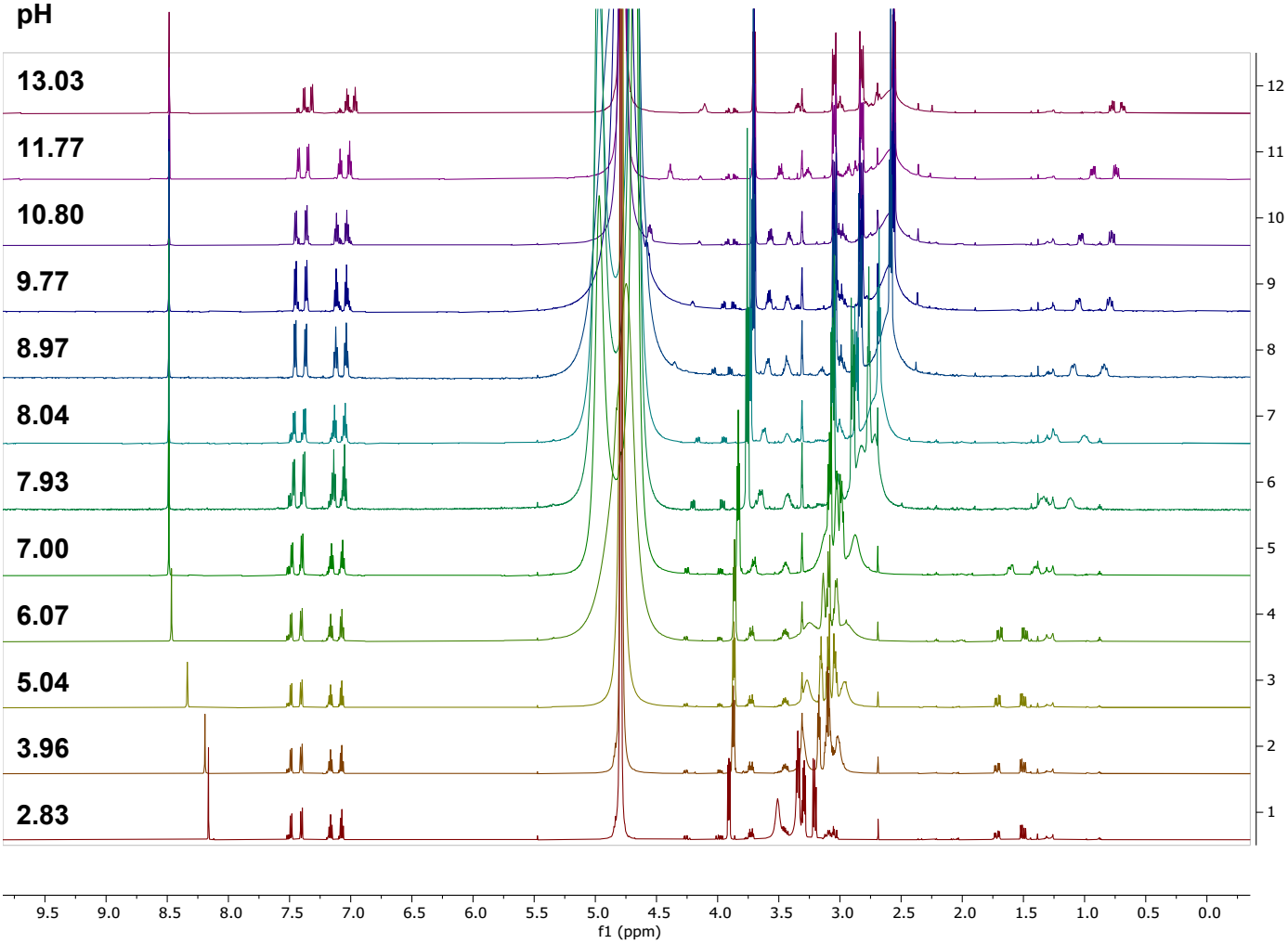


Figure 1 ^1H NMR (600 MHz) spectra at various pH (25 °C)

Aliquot	p(H,D)[1]	pH	^{1}H chemical shift	(Δshift)/(ΔpH)
A	2.83	2.83	1.50	
B	3.96	3.96	1.50	0.00
C	5.04	5.04	1.50	0.00
D	6.07	6.07	1.49	0.01
E	7	7.00	1.39	0.11
F	7.93	7.93	1.12	0.29
G	8.25	8.04	1.00	1.09
H	9.18	8.97	0.84	0.17
I	9.98	9.77	0.79	0.06
J	11.01	10.80	0.78	0.01
K	11.98	11.77	0.74	0.04
L	13.24	13.03	0.69	0.04

Table 1 Tabulated pH titration data.[1]Measured pH in buffered mixture of D_2O and H_2O. [2]Corrected p(H,D) data to pH according to a literature report.[6]

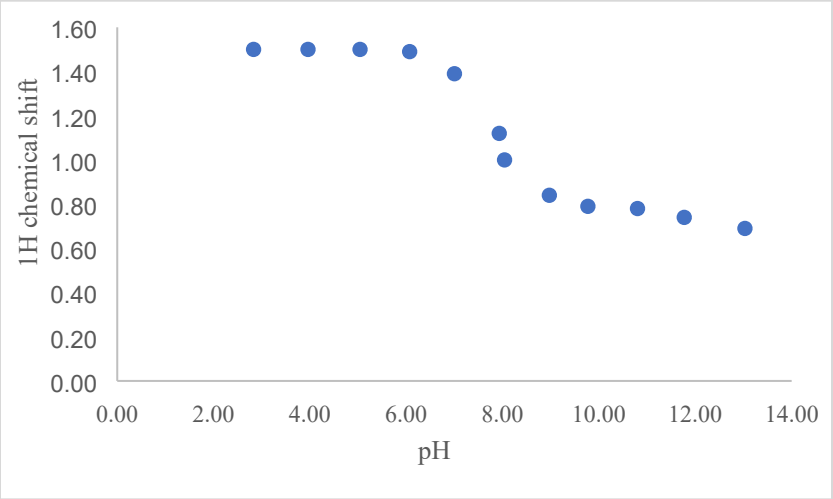


Figure 2. Plotted pH titration results with data from Table 1.

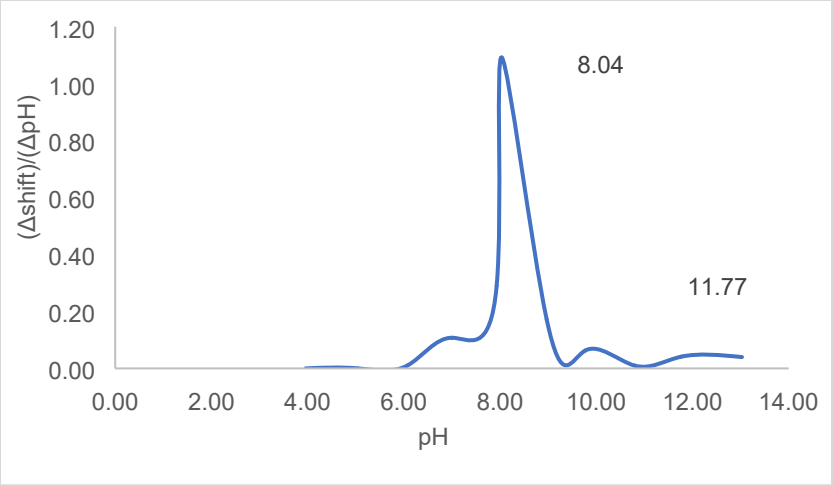


Figure 3. First derivative of the pH titration with data from Table 1. The two inflection points are labelled on the curve.

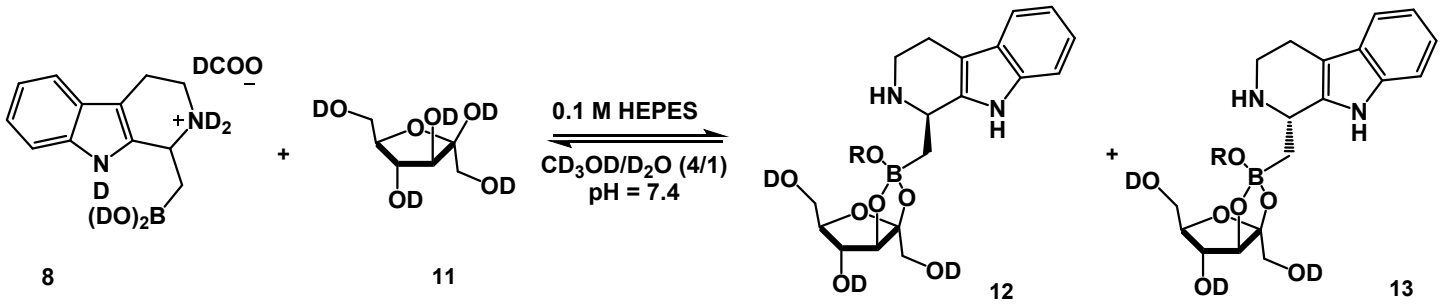
9. Fructose binding assay.

The binding assay was adapted from the literature.[7] A solvent stock solution was prepared from CD_3OD (6.0 mL) and D_2O (1.5 mL).

For the preparation of a first solution (**Solution A**), boronic acid **8** (20.7 mg, 0.075 mmol, 0.015 M) was added to a 2-dram vial, followed by HEPES (119 mg, 0.5 mmol). The solids were dissolved in 4.2 mL of the solvent stock solution. The pH was adjusted to 7.4 using NaOH (2.0 M in D_2O). The solution was transferred to a 5-mL volumetric flask using a syringe. The 2-dram vial was rinsed with several 0.1 mL portions of the solvent stock solutions, and the rinses were transferred to the volumetric flask until the 5.00 mL line was reached.

For the preparation of a second solution (**Solution B**), D-fructose **11** (54 mg, 0.3 mmol, 0.150 M) was added to a 2-dram vial. A 1.25 mL portion of Solution A was added to the vial. The pH was was adjusted to 7.4 using NaOH (2.0 M in D_2O) (1.0 µL total added). The solution was transferred to a 2-mL volumetric flask using a syringe. The 2-dram vial was rinsed with several 0.1 mL portions of the solvent stock solutions, and the rinses were transferred to the volumetric flask until the 2.00 mL line was reached.

A 200 µL aliquot of each solution was taken for analysis by ^1H NMR.



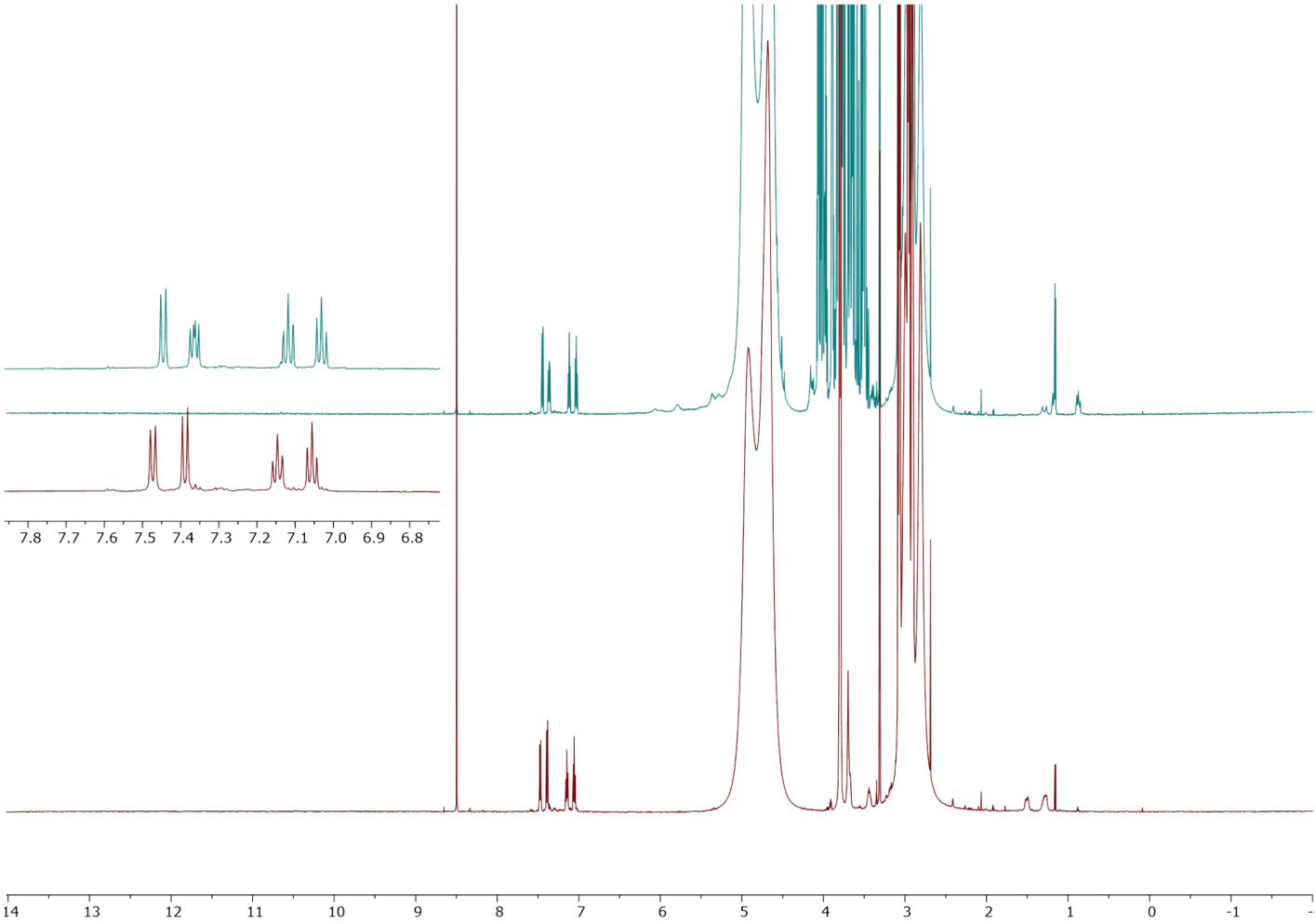


Figure 4 - Top (Green): ^{1}H NMR (600 MHz) of **Solution B**. Bottom (Red): 1H NMR (600 MHz) of **Solution A**.

10. References

(1) J. D. St. Denis, A. Zajdlik, J. Tan, P. Trinchera, C. F. Lee, Z. He, S. Adachi and A. K. Yudin, *J. Am. Chem. Soc.*, 2014, **136**, 17669–17673.

(2) Z. He and A. K. Yudin, *J. Am. Chem. Soc.*, 2011, **133**, 13770–13773.

(3) Z. He, A. Zajdlik, J. D. St. Denis, N. Assem and A. K. Yudin, *J. Am. Chem. Soc.*, 2012, **134**, 9926–9929.

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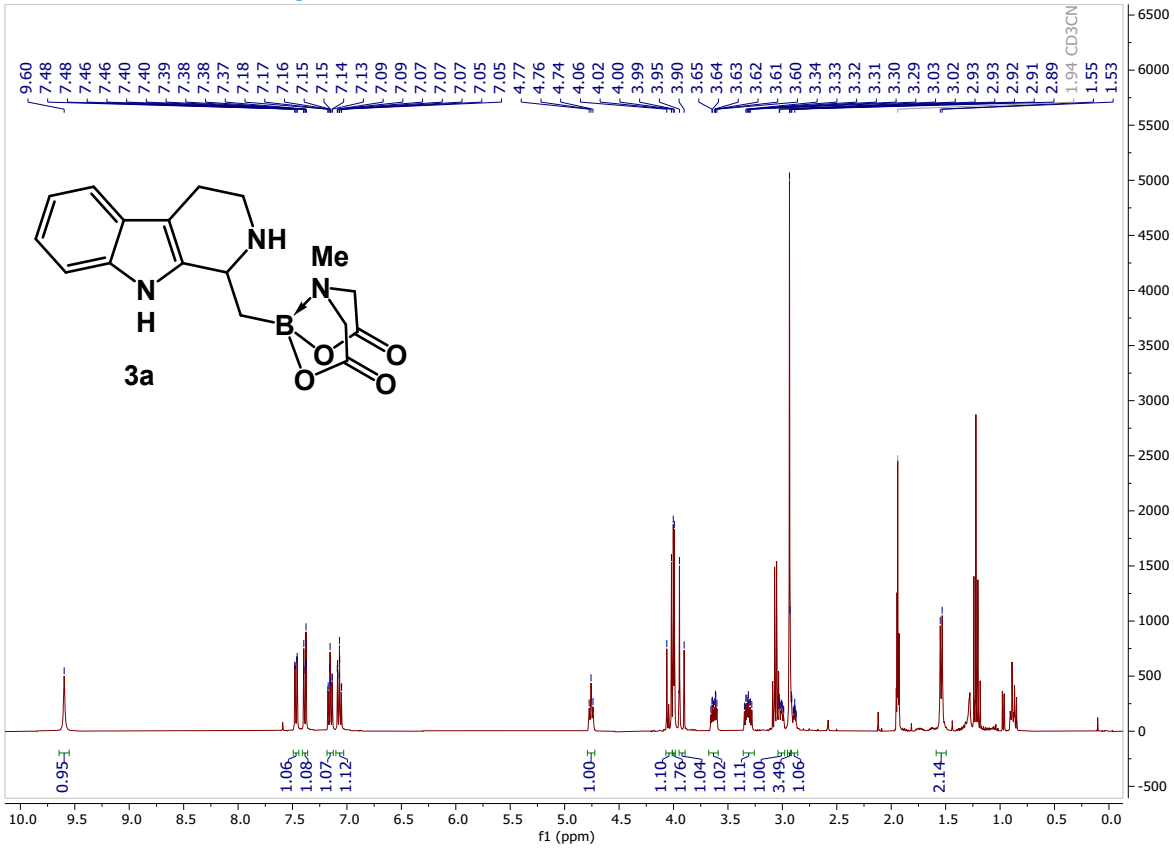
(5) . E. Garrett, D. B. Diaz, A. K. Yudin and M. S. Taylor, *Chem. Commun.*, 2017, **53**, 1809–1812.

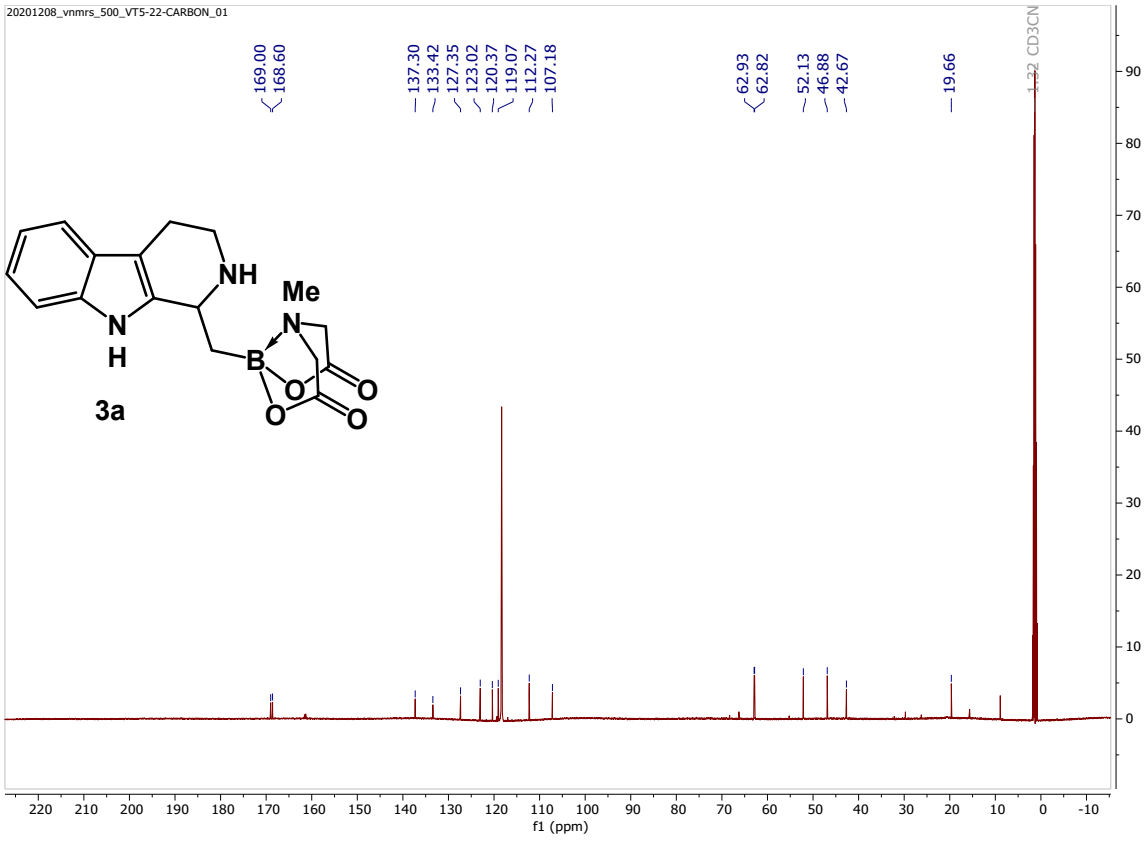
(6) K. A. Rubinson, *Anal. Methods*, 2017, **9**, 2744–2750.

(7) G. A. Ellis, M. J. Palte and R. T. Raines, *J. Am. Chem. Soc.*, 2012, **134**, 3631–3634.

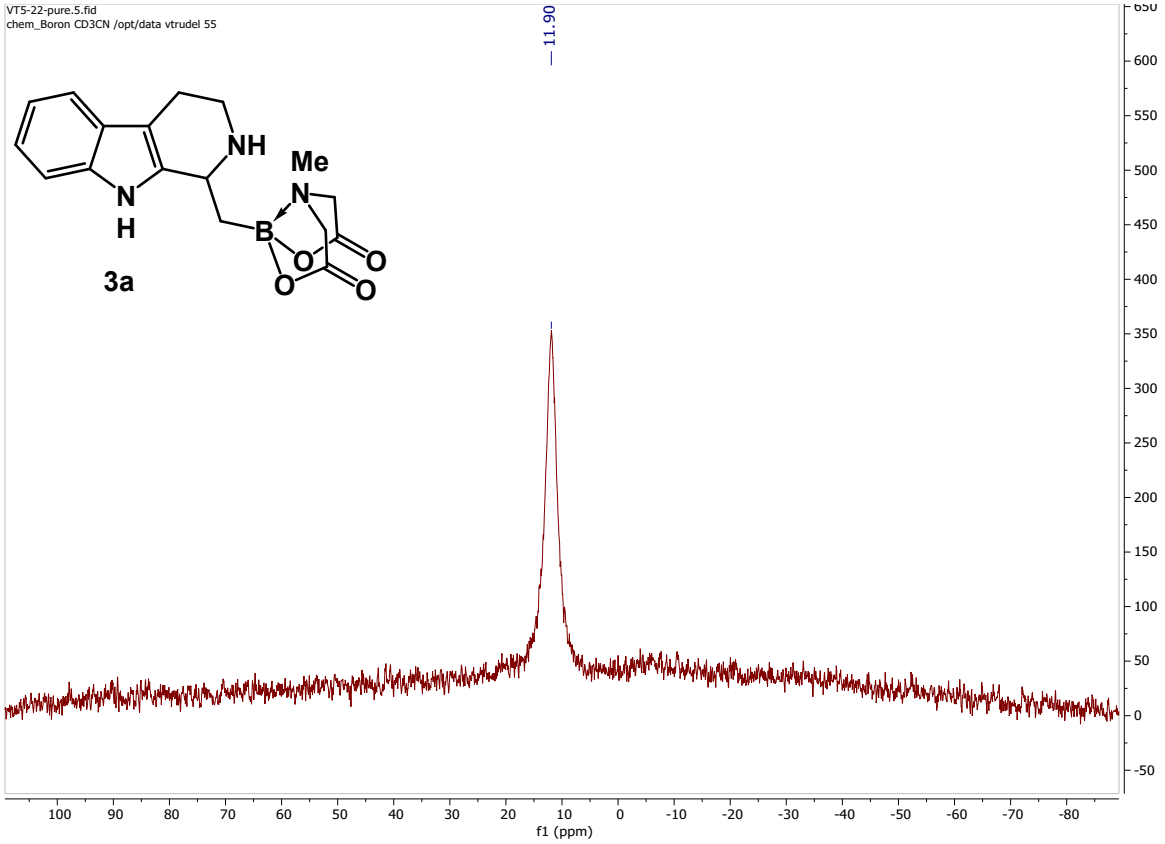
11. NMR spectra



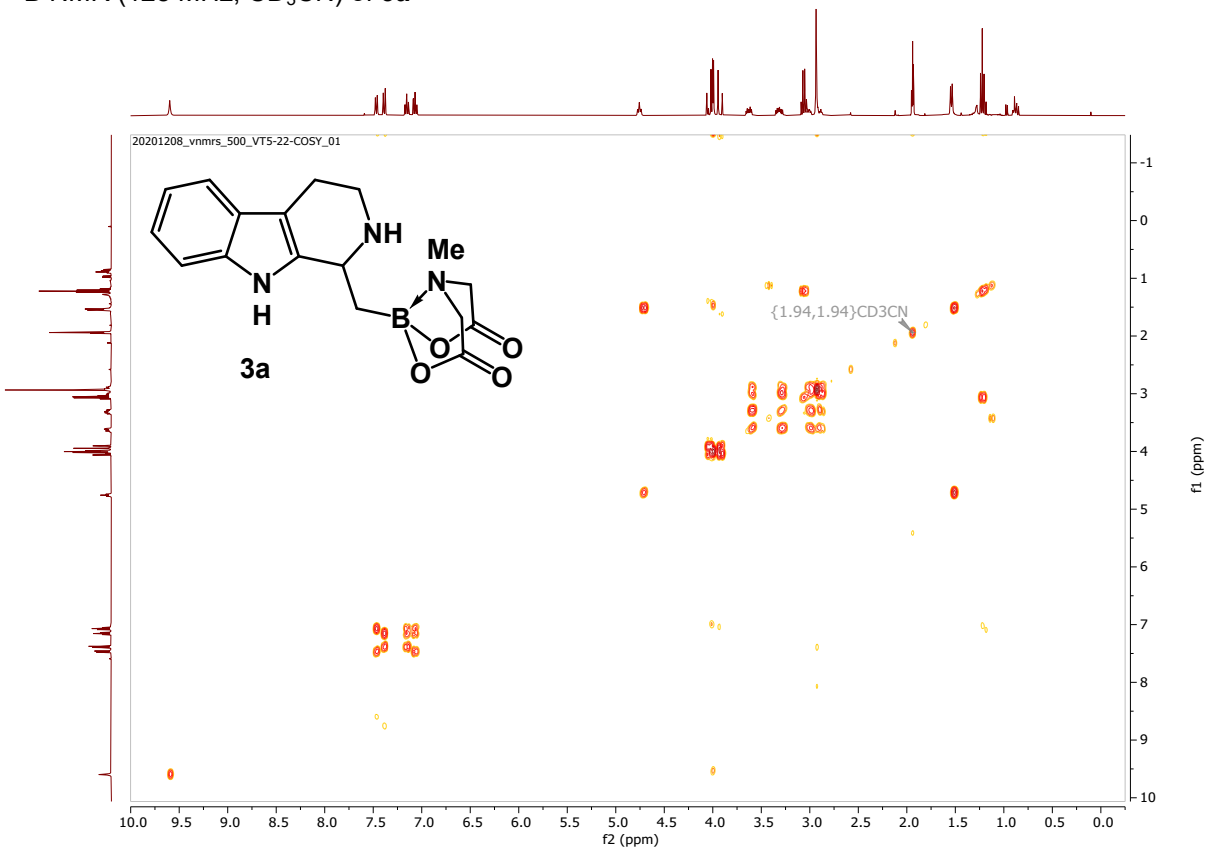
^{1}H NMR (400 MHz, CD_3CN) of **3a**



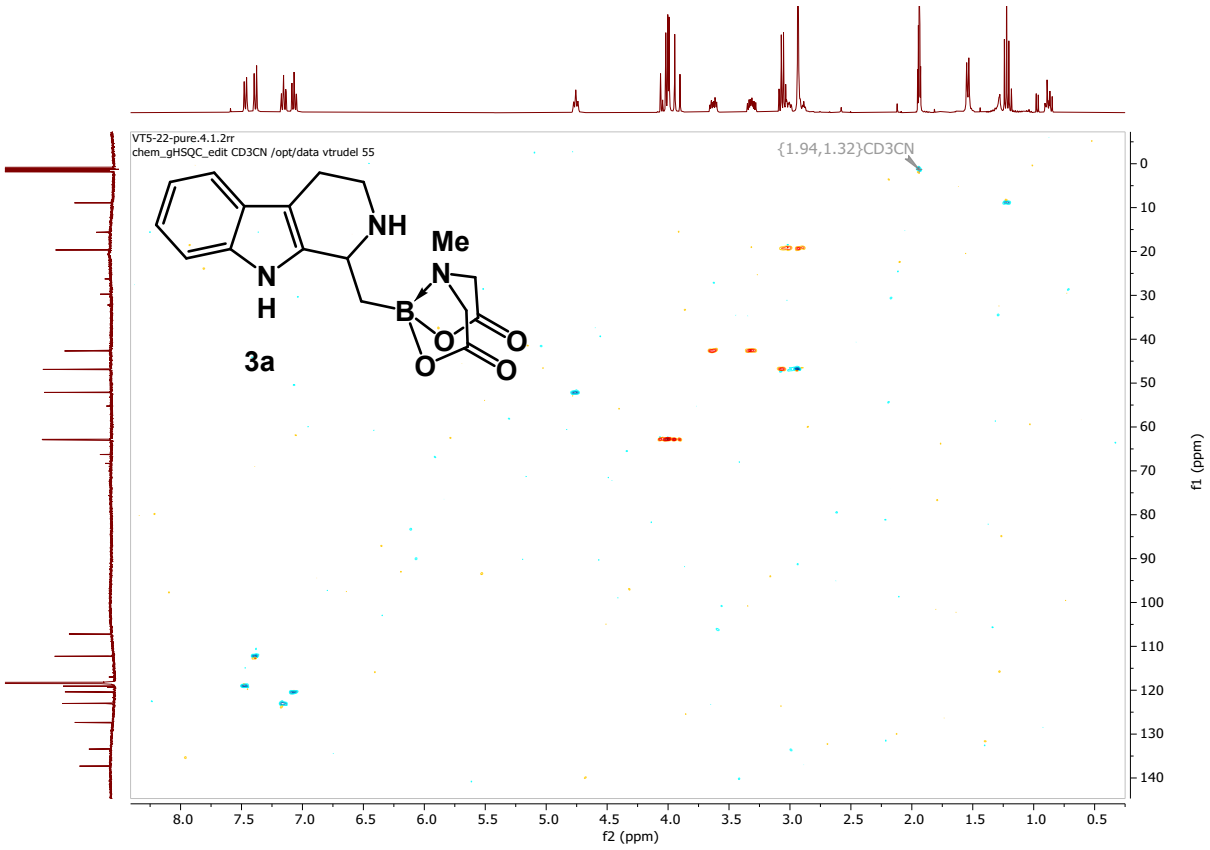
^{13}C NMR (126 MHz, CD_3CN) of **3a**



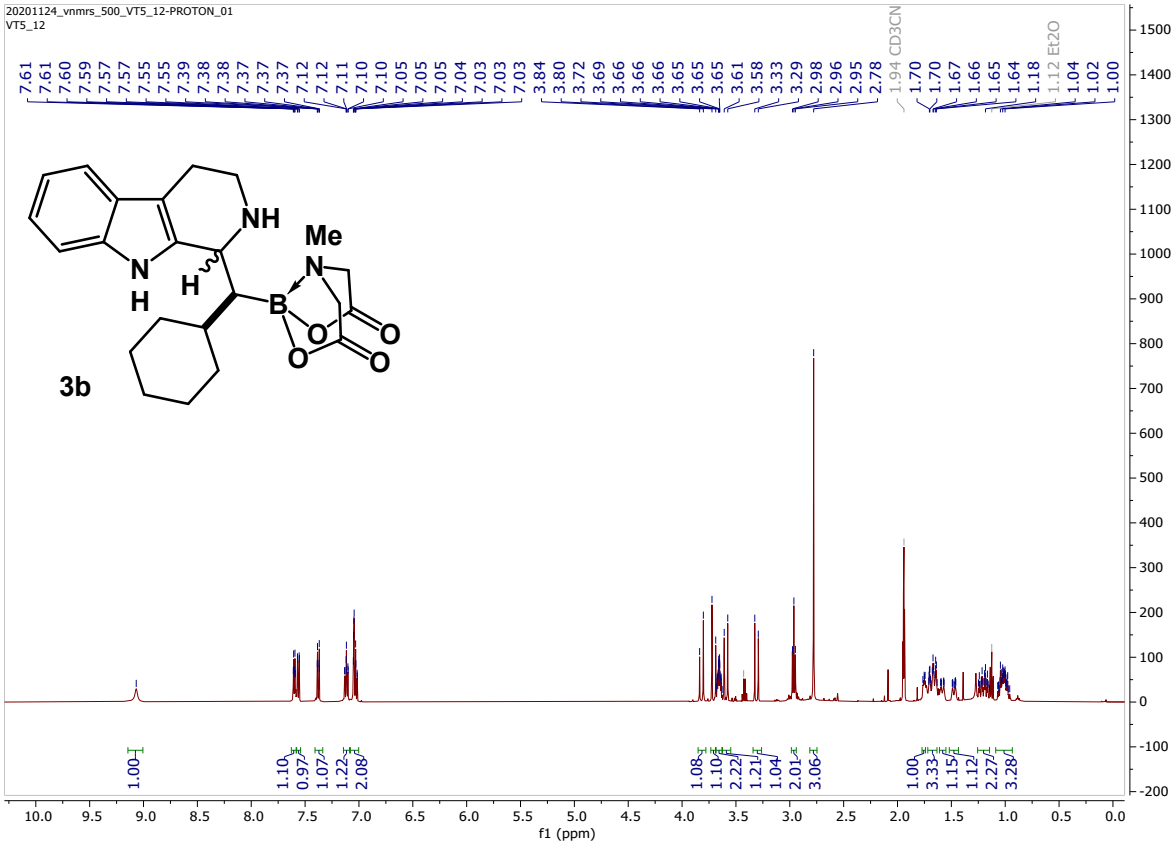
^{11}B NMR (128 MHz, CD_3CN) of **3a**



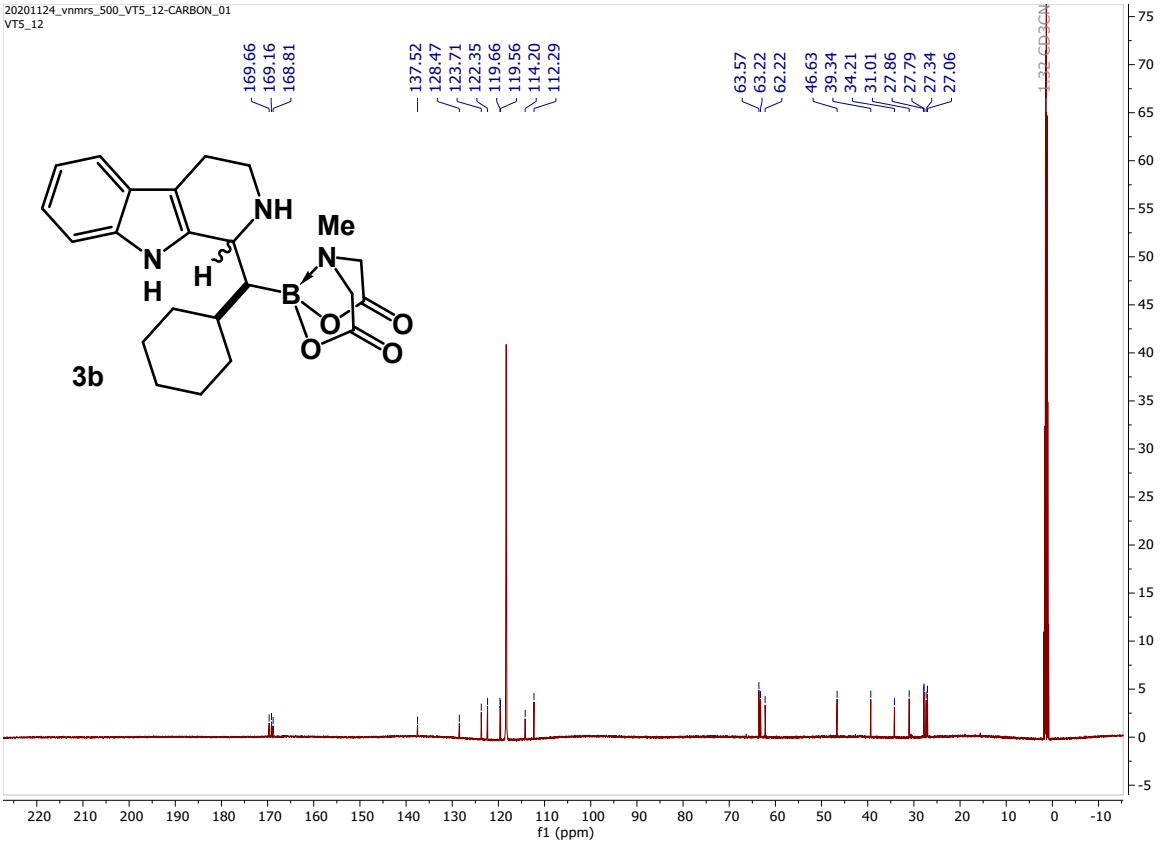
COSY NMR of **3a**



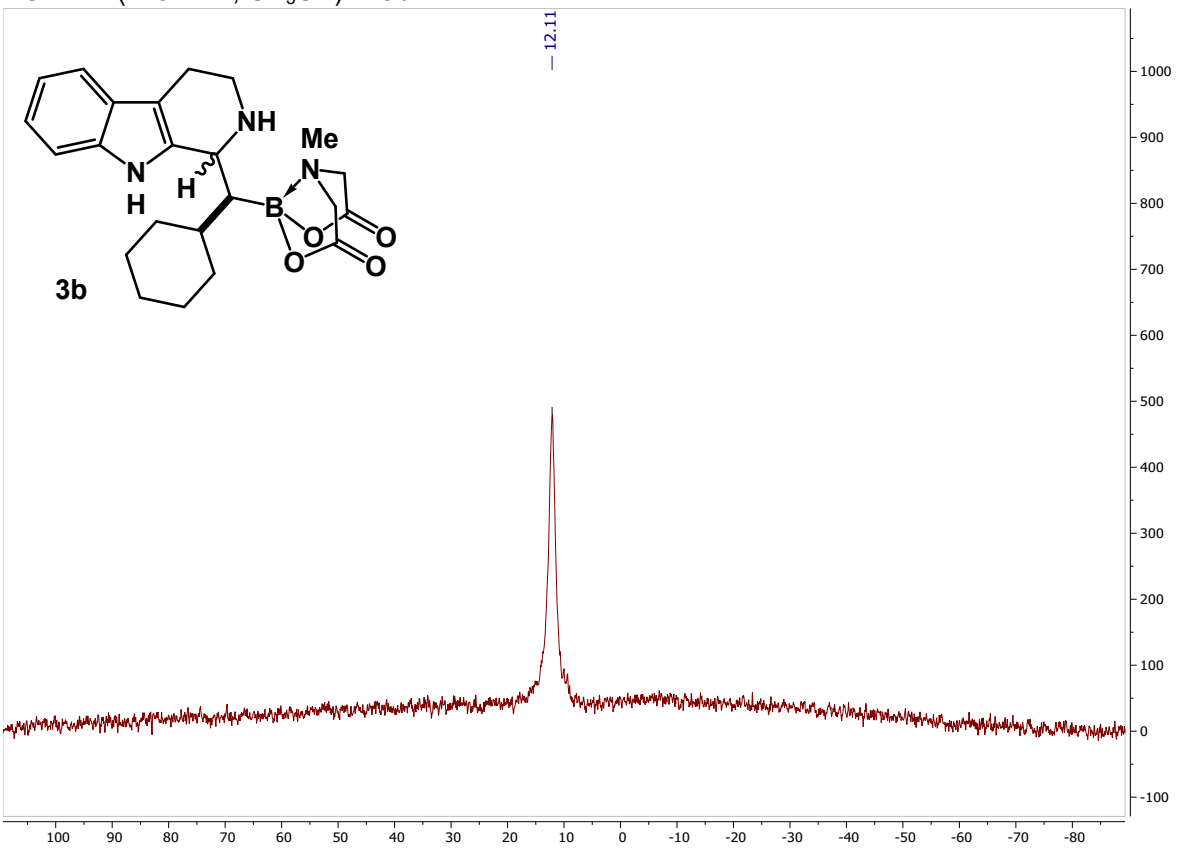
HSQC NMR of **3a**



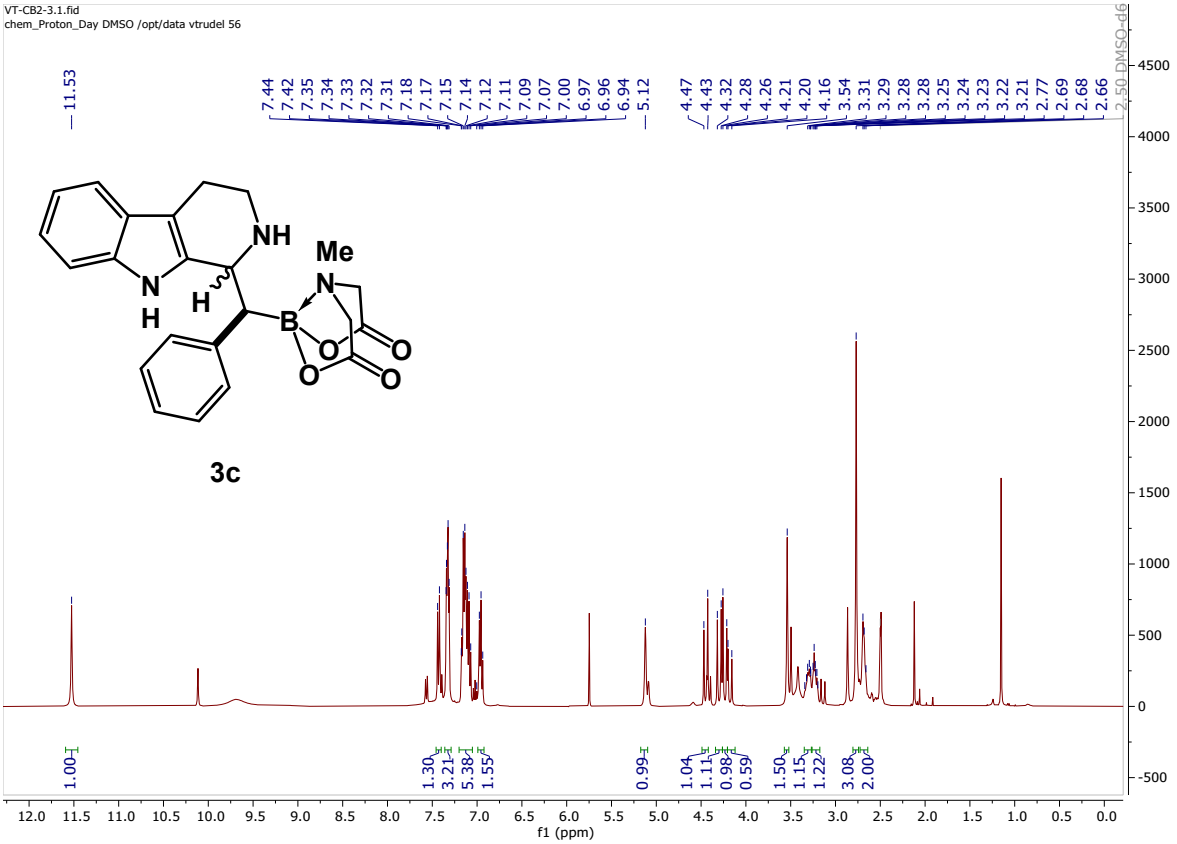
^{1}H NMR (500 MHz, CD_3CN) of **3b**



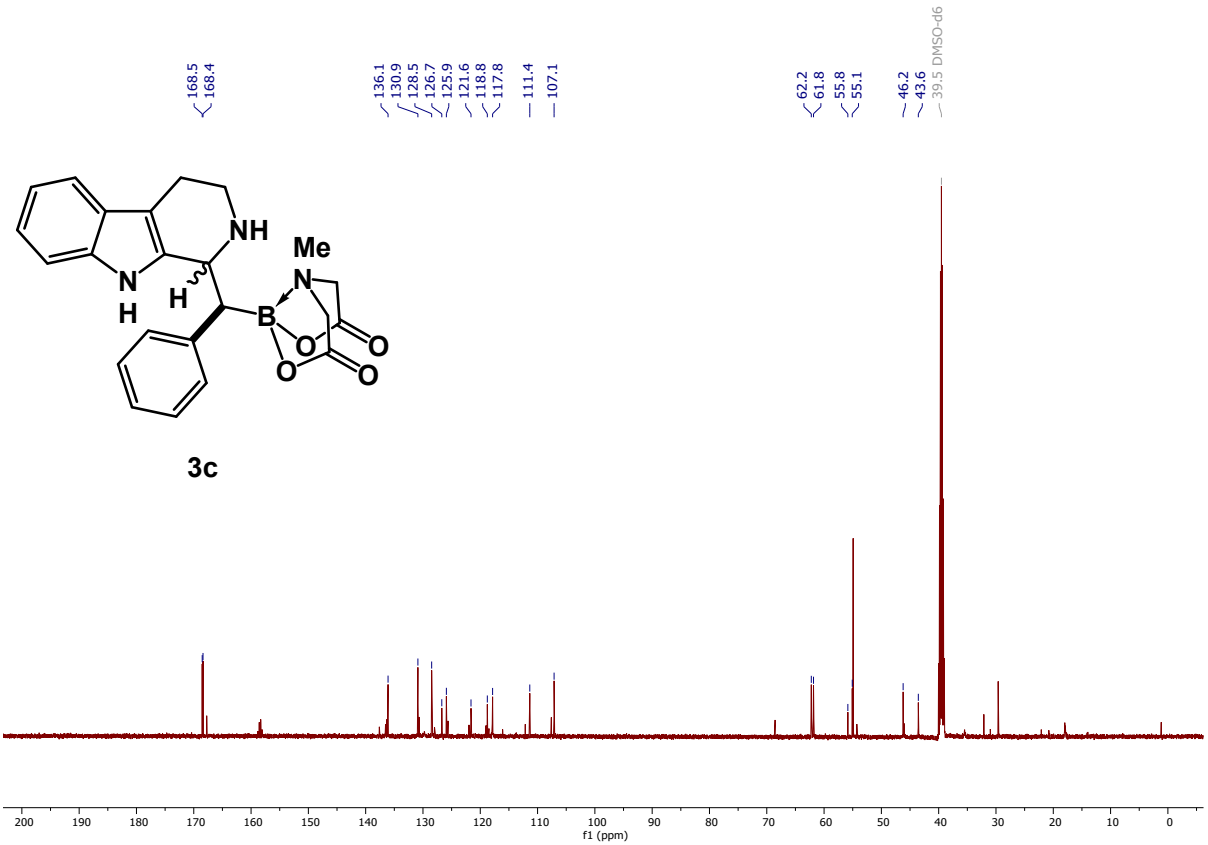
^{13}C NMR (126 MHz, CD_3CN) of **3b**.



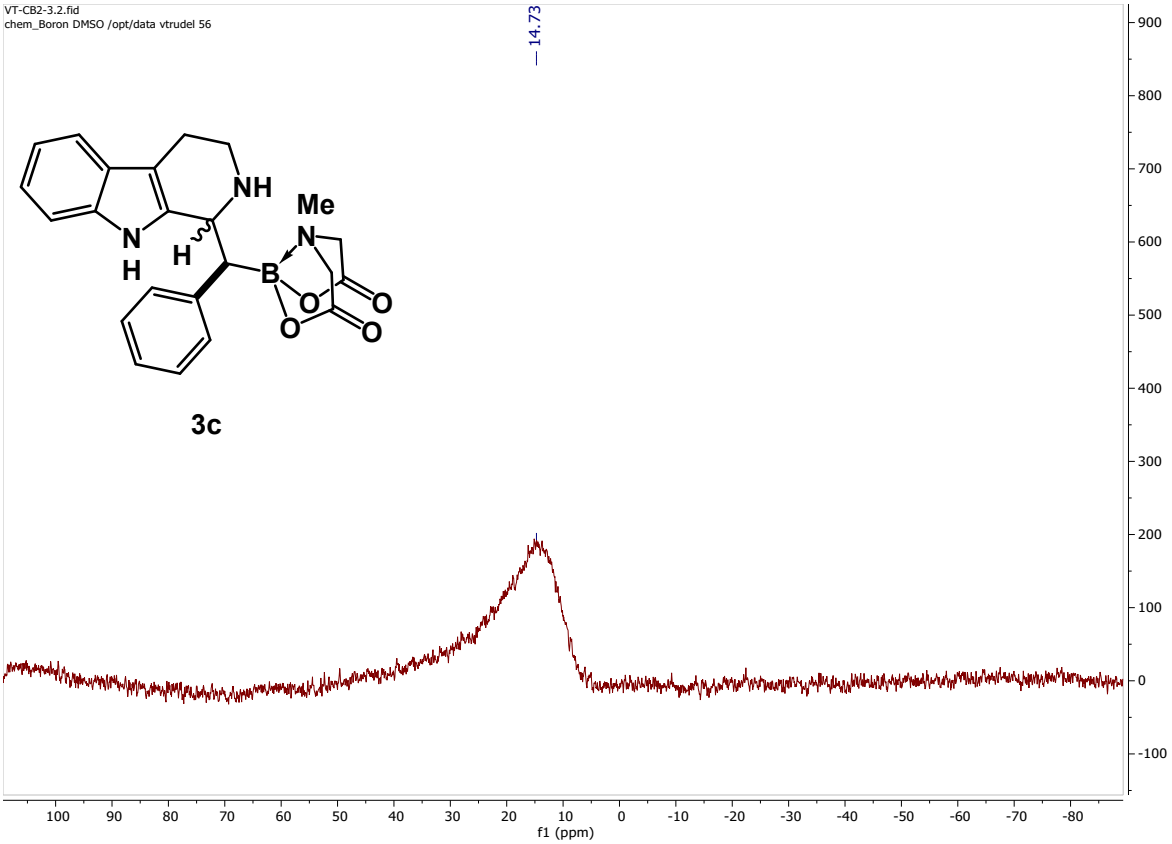
^{11}B NMR (128 MHz, CD_3CN) of **3b**



^{1}H NMR (400 MHz, DMSO-d_6) of **3c**.



^{13}C NMR (126 MHz, DMSO-d_6) of **3c**.



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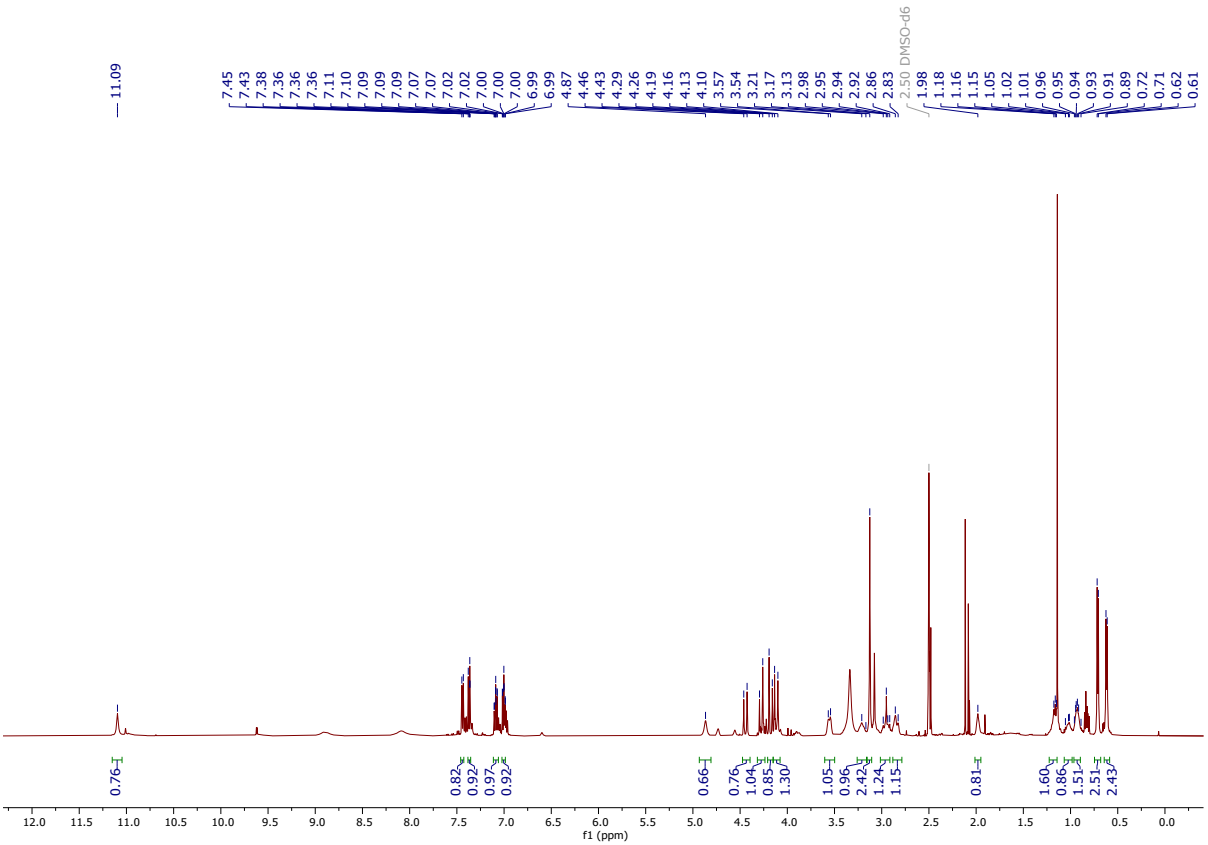
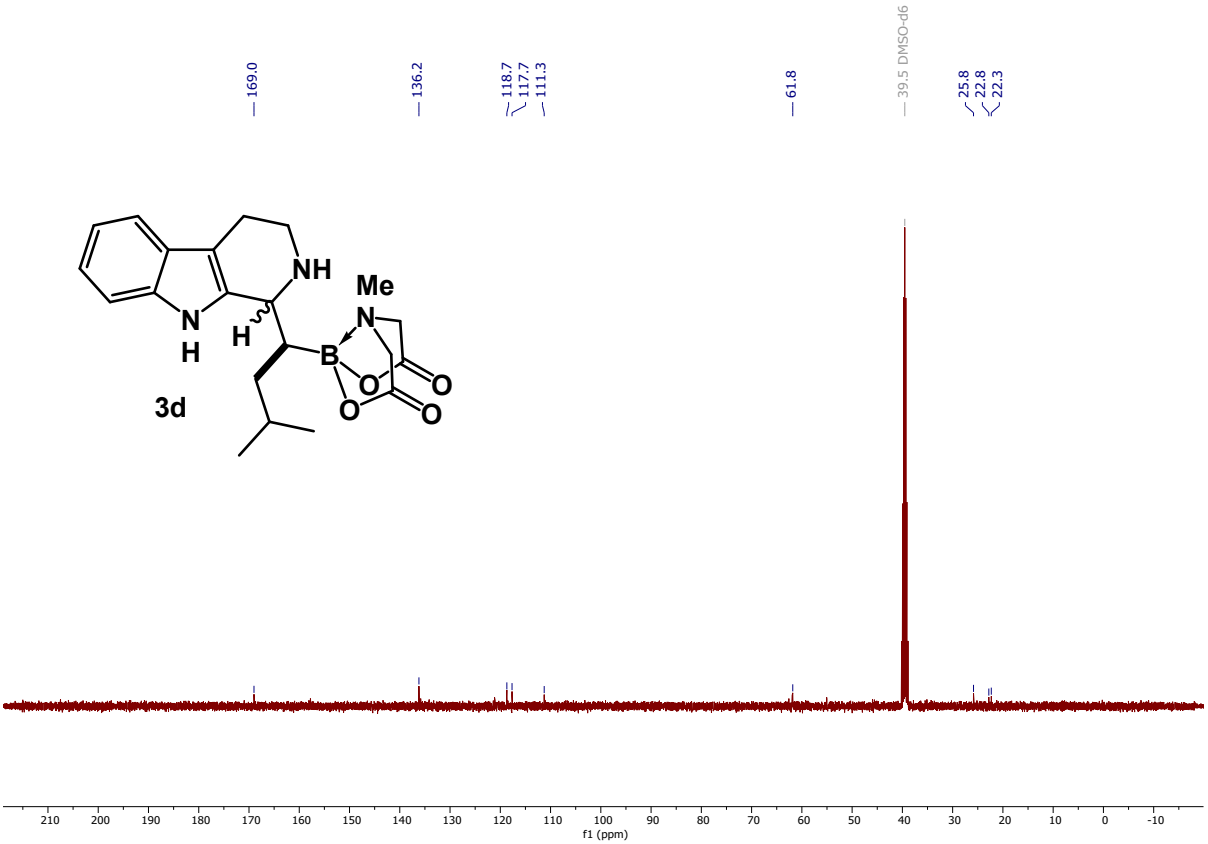
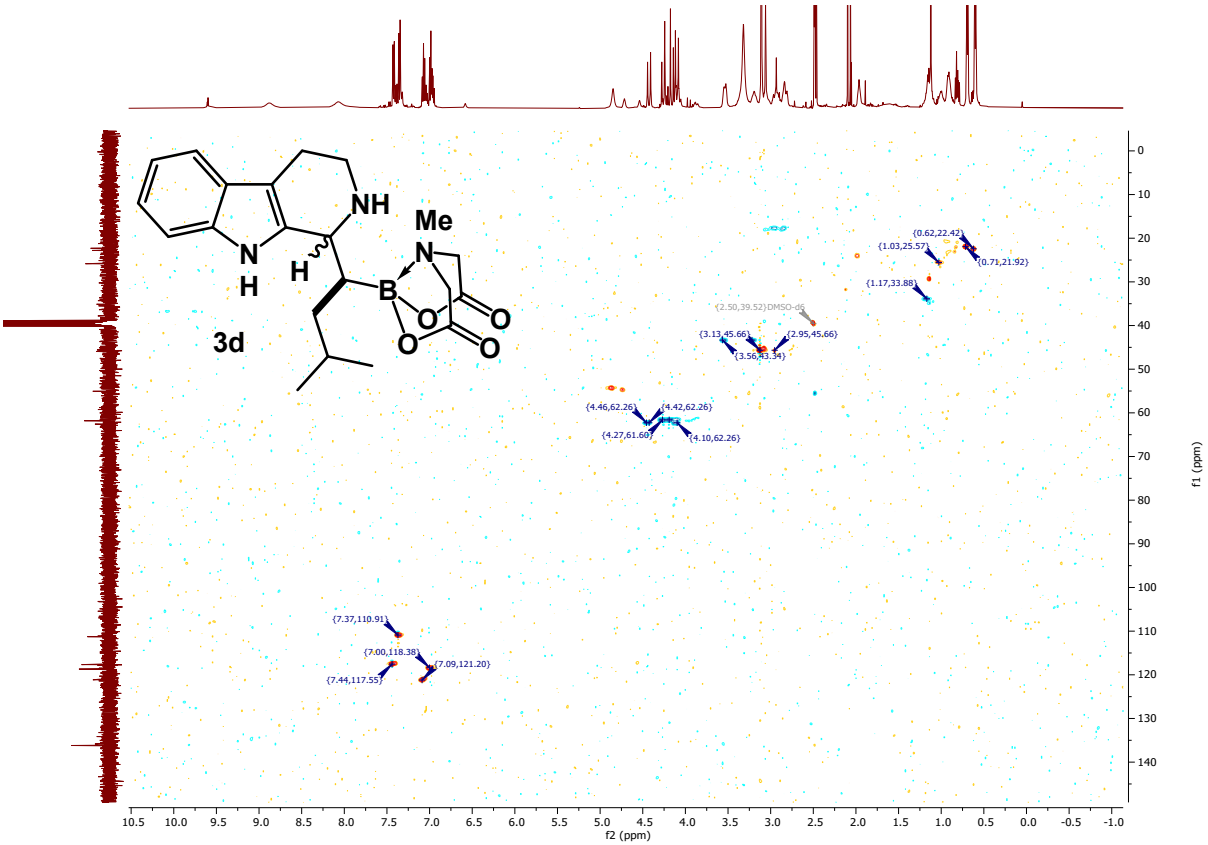


^{1}H NMR (500 MHz, DMSO-d_6) of **3d**.



^{13}C NMR (126 MHz, DMSO-d_6) of **3d**.



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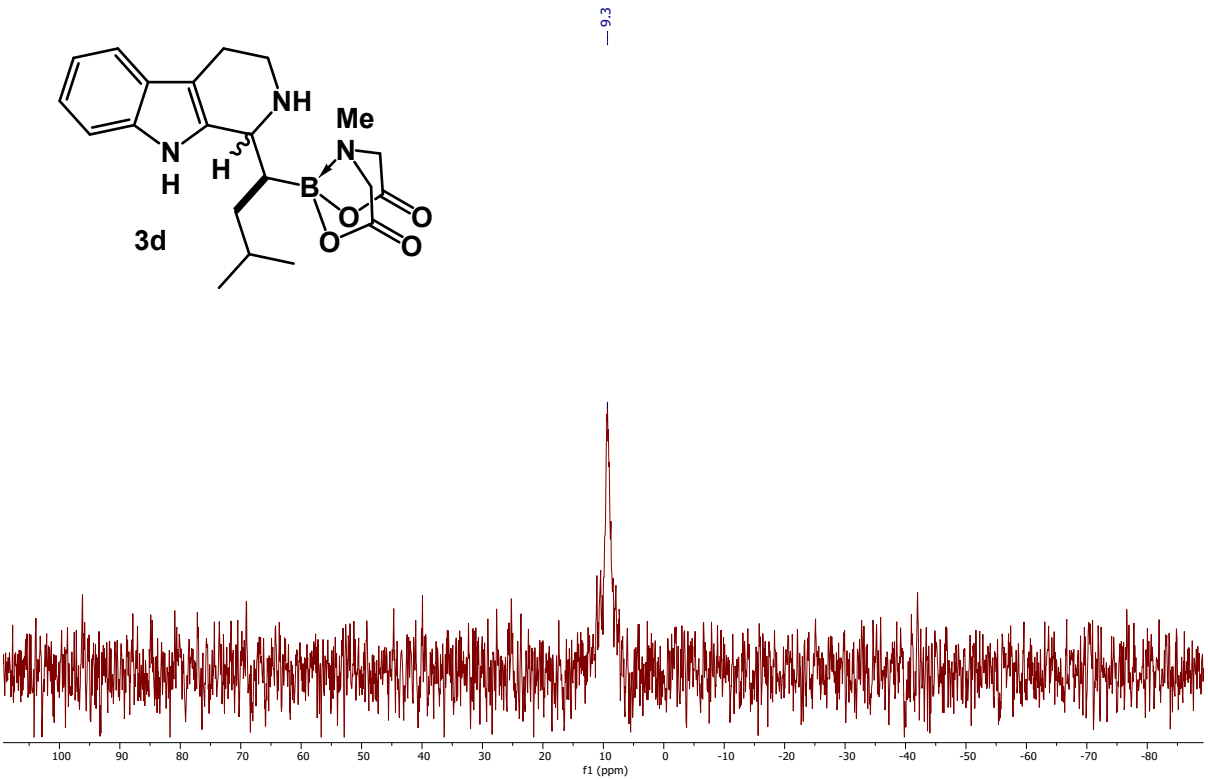
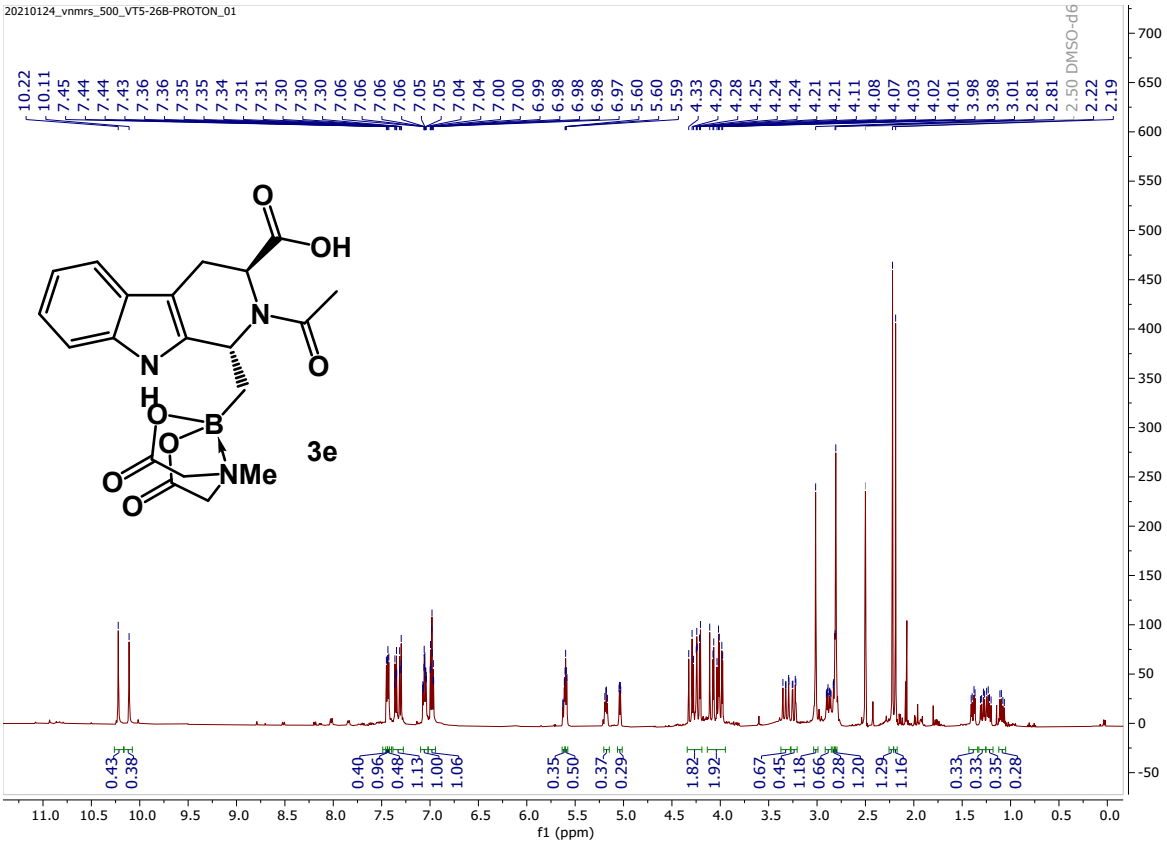
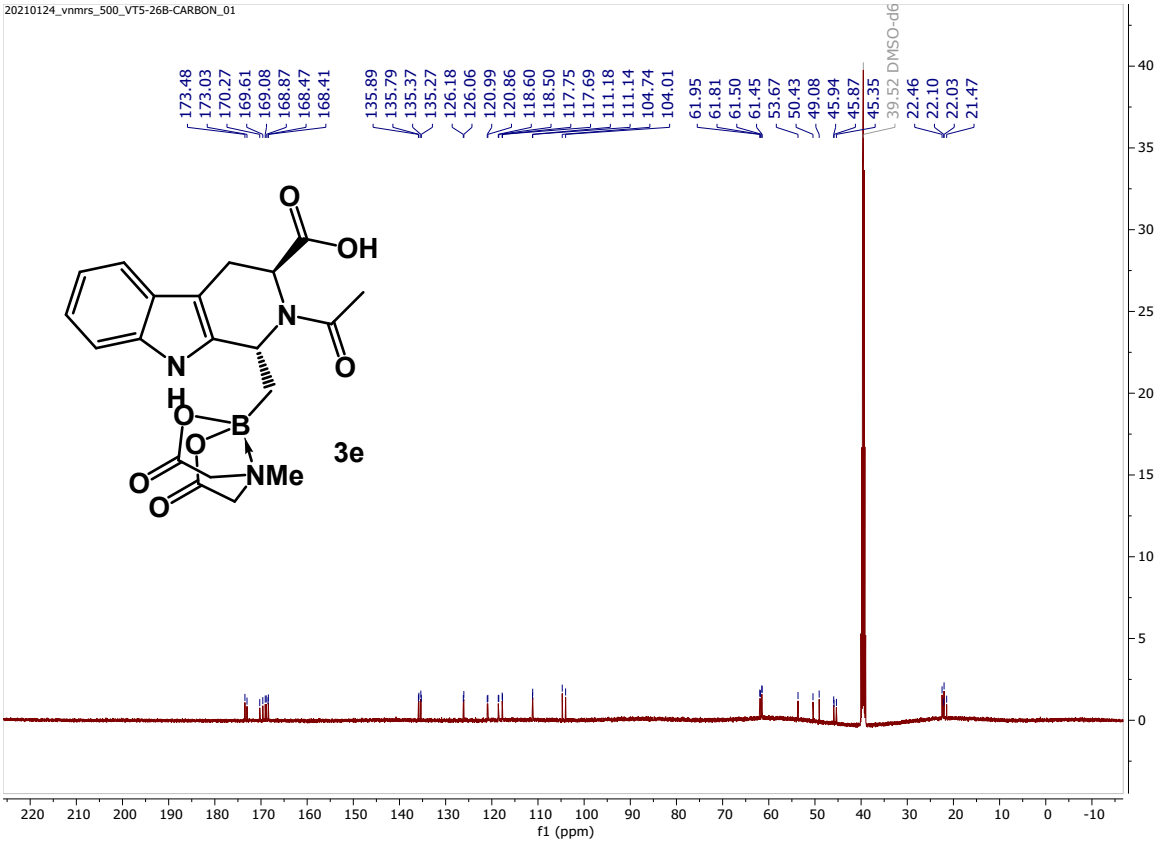


^{11}B NMR (128 MHz, DMSO) of **3d**.



^{1}H NMR (500 MHz, DMSO-d_6) of **3e**.



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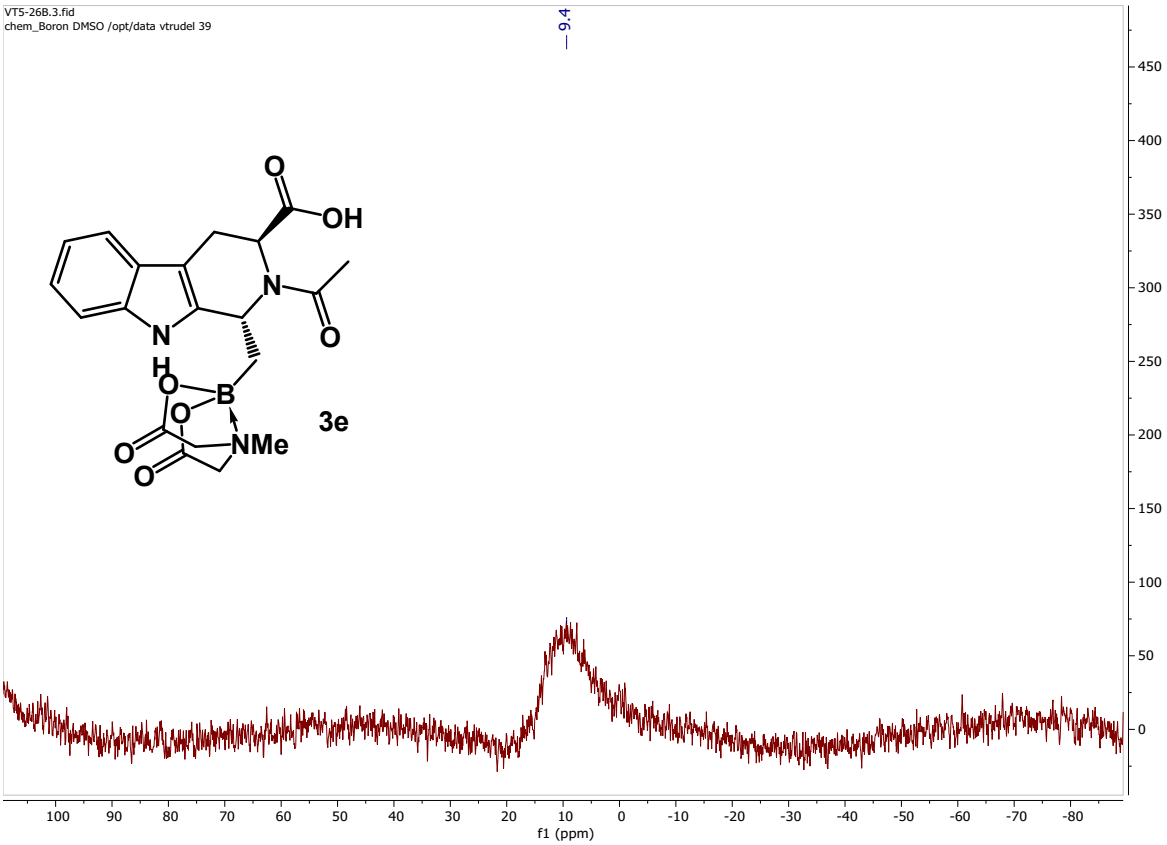
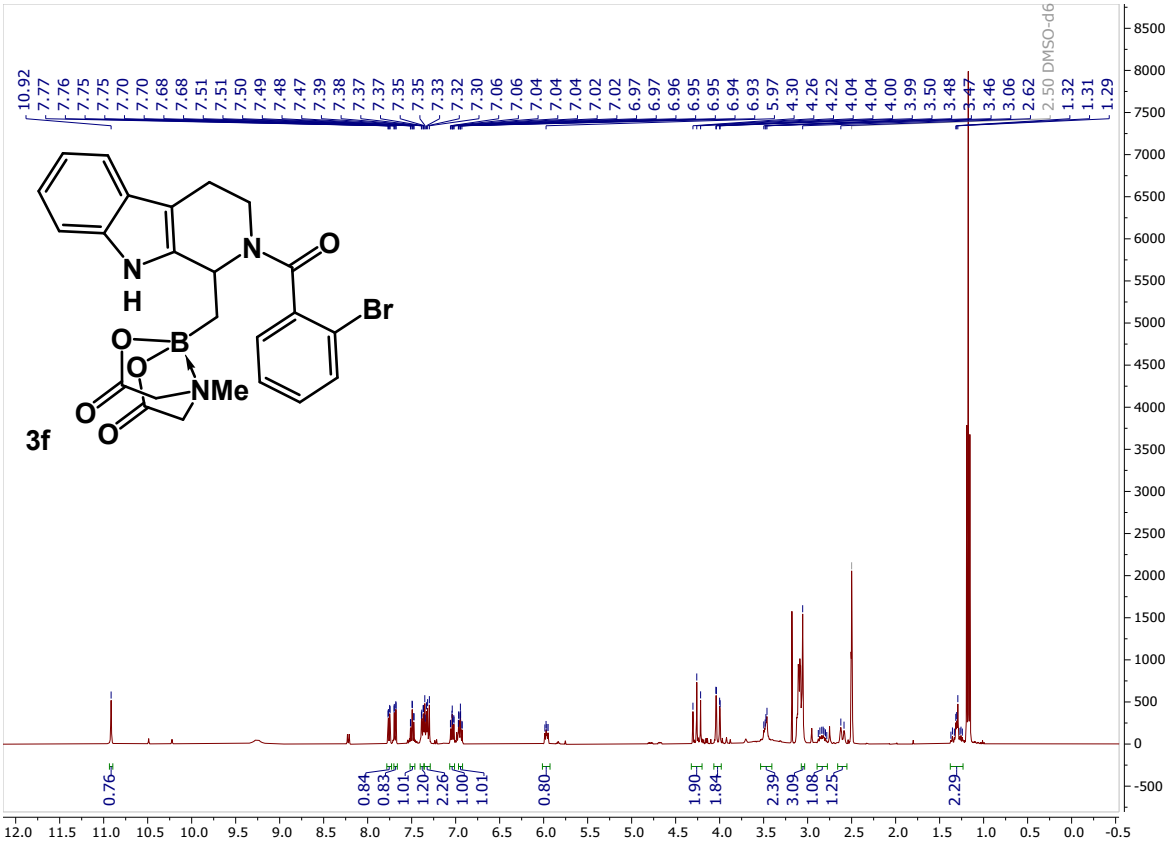
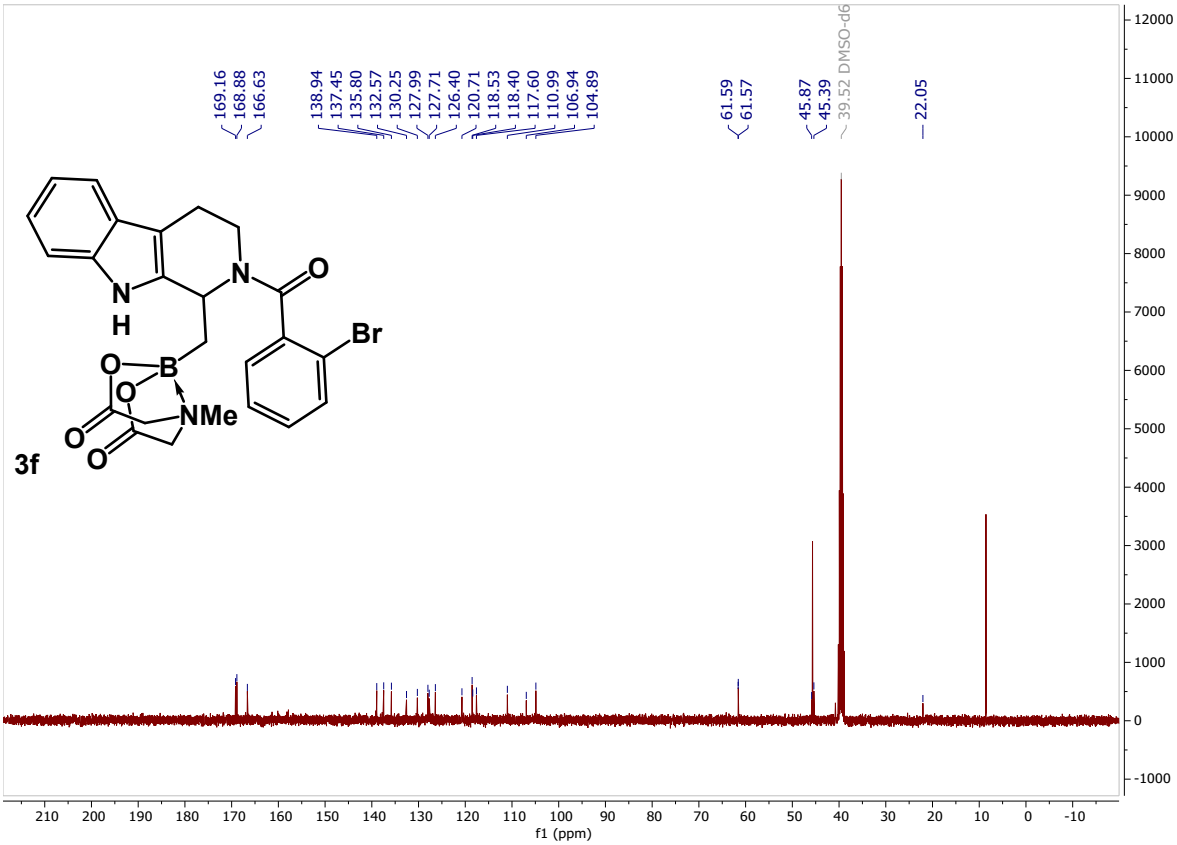


^{11}B NMR (128 MHz, DMSO-d_6) of **3e**.



^{1}H NMR (400 MHz, DMSO-d_6) of **3f**



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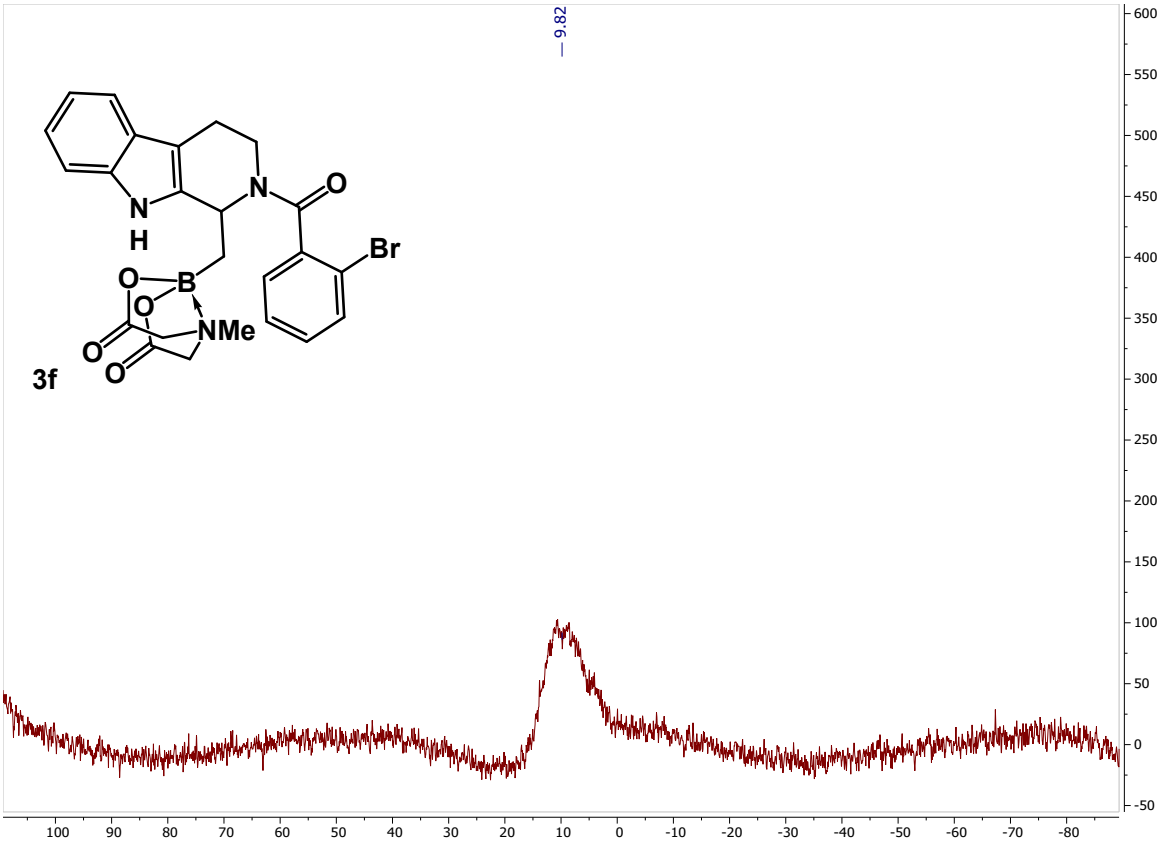
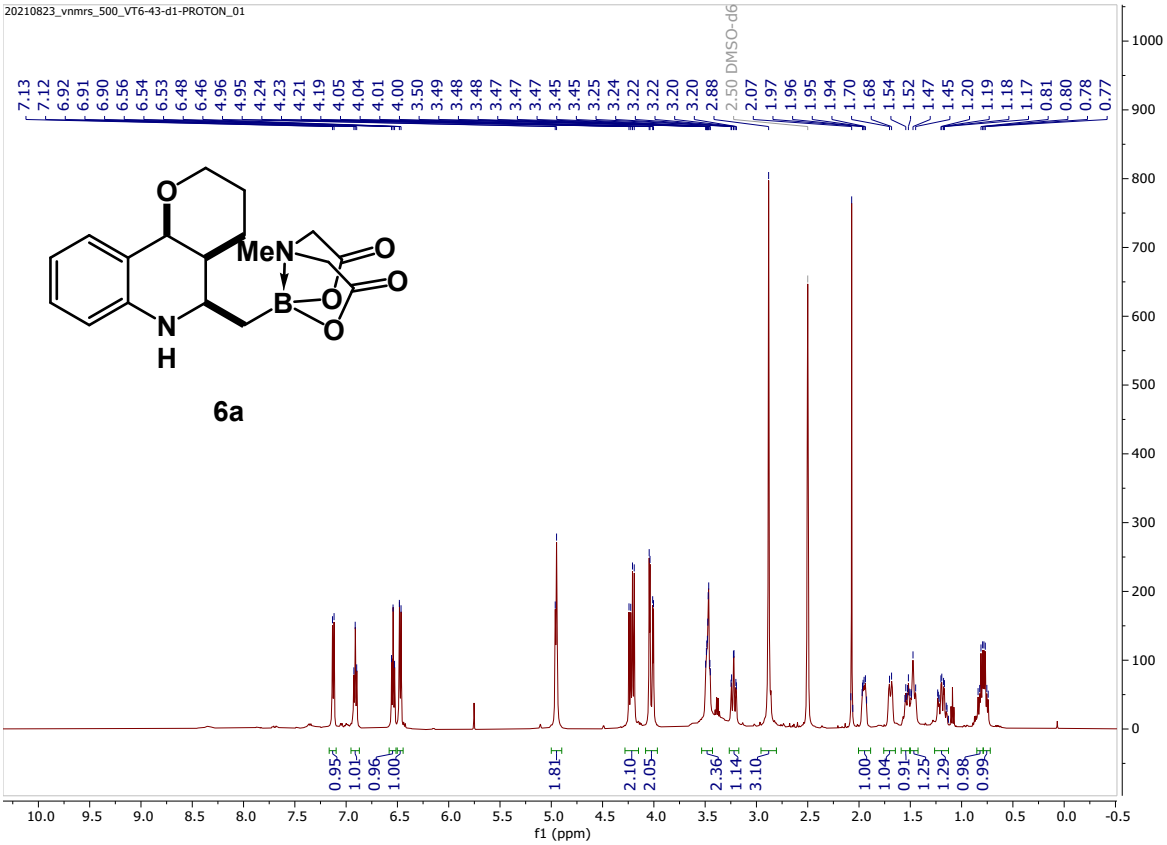
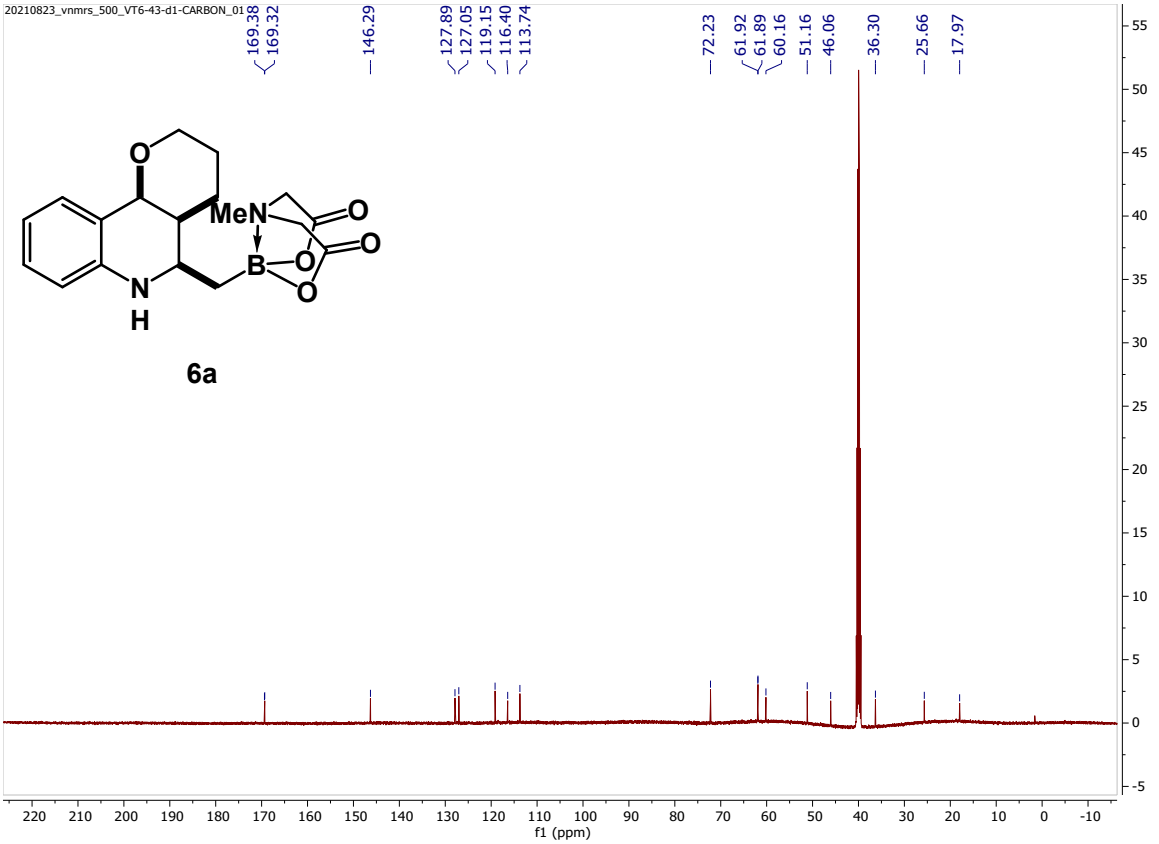


^{11}B NMR (128 MHz, DMSO-d_6) of **3f**



^{1}H NMR (500 MHz, DMSO-d_6) of *endo*-**6a**



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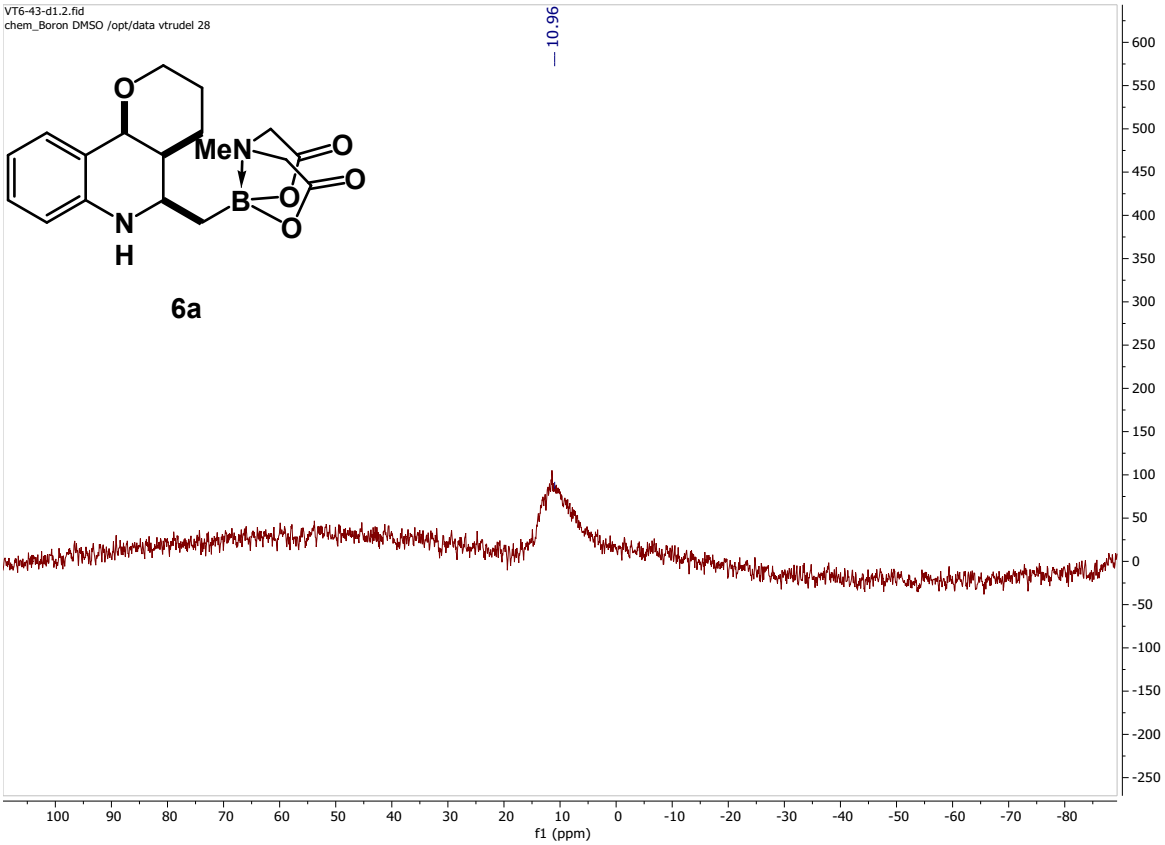

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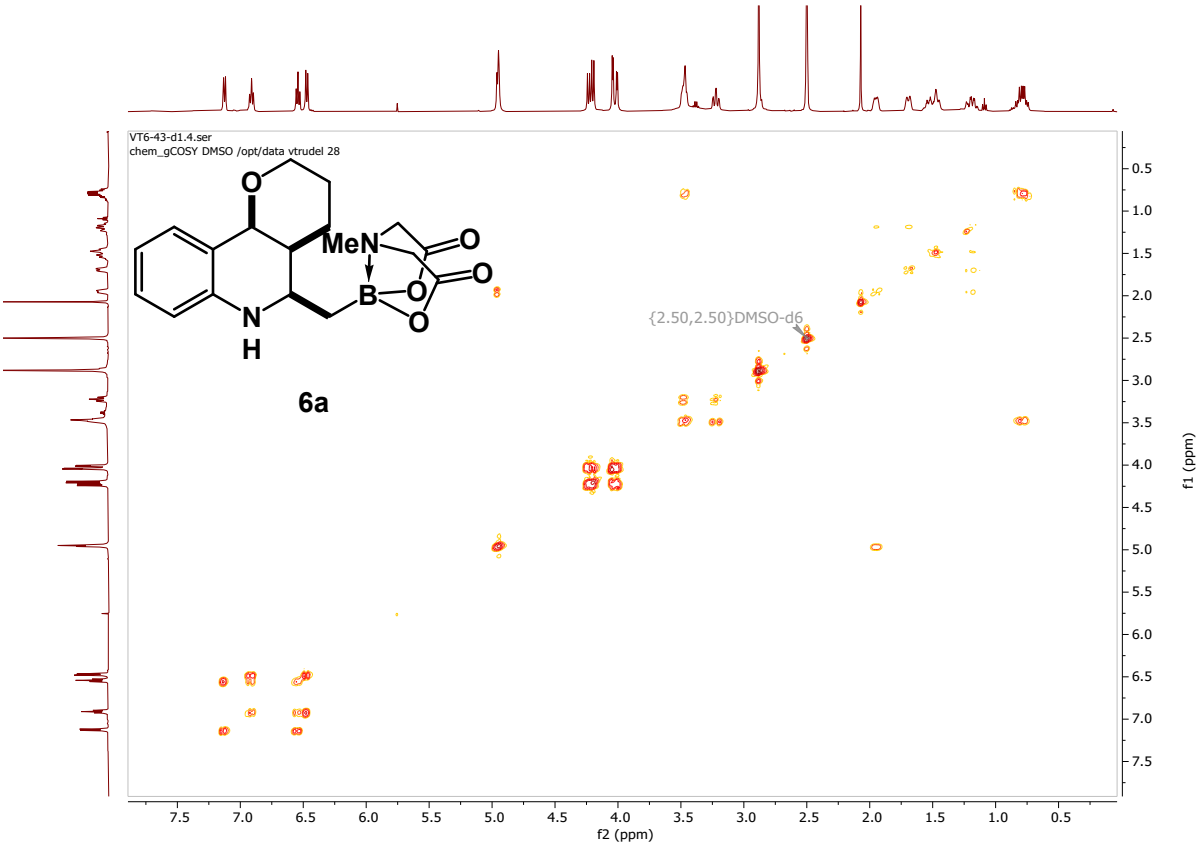
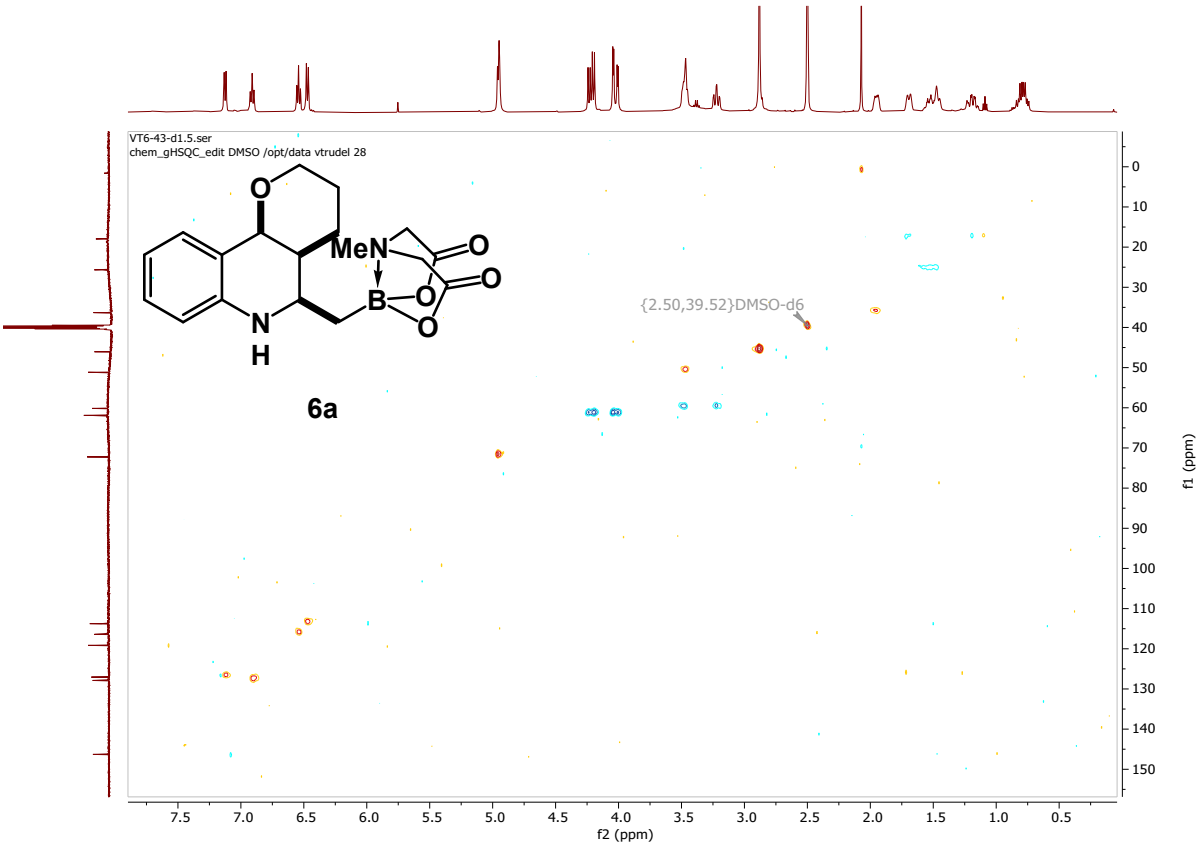


COSY NMR of *endo*-**6a**



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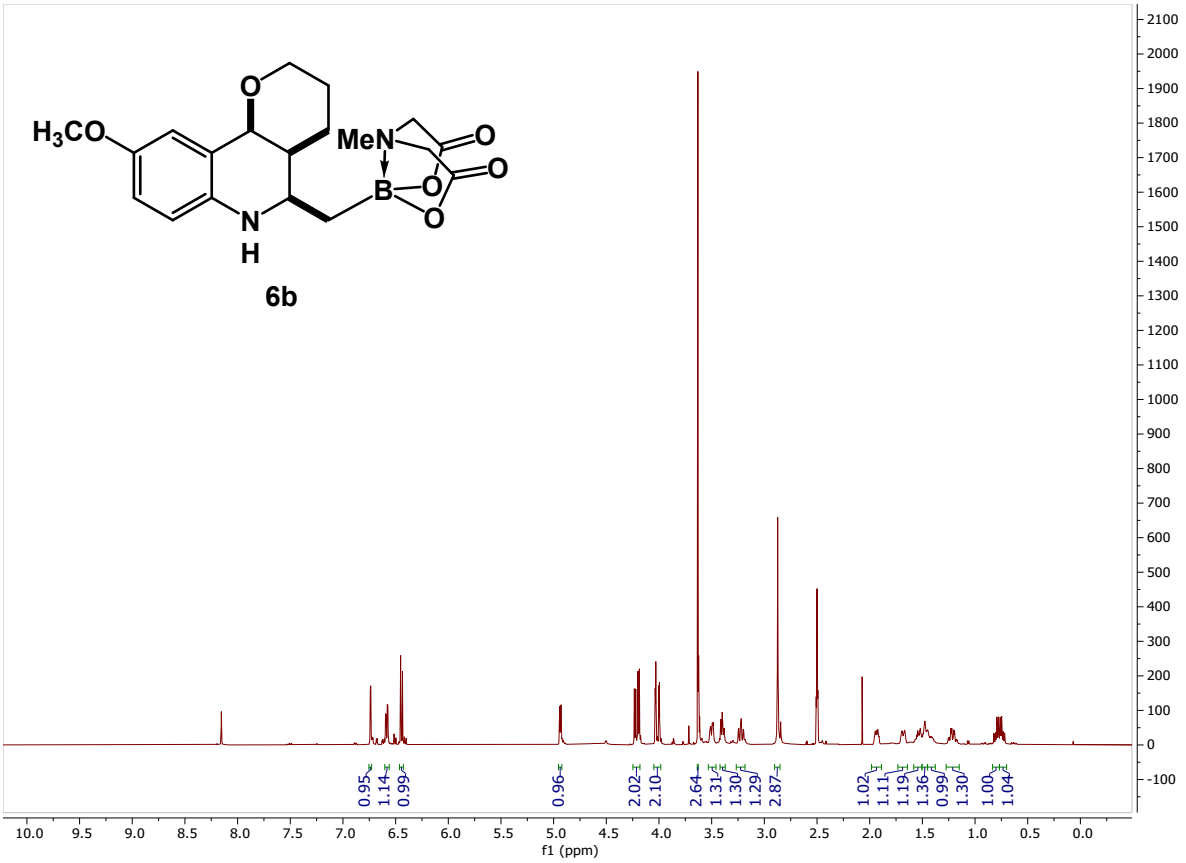

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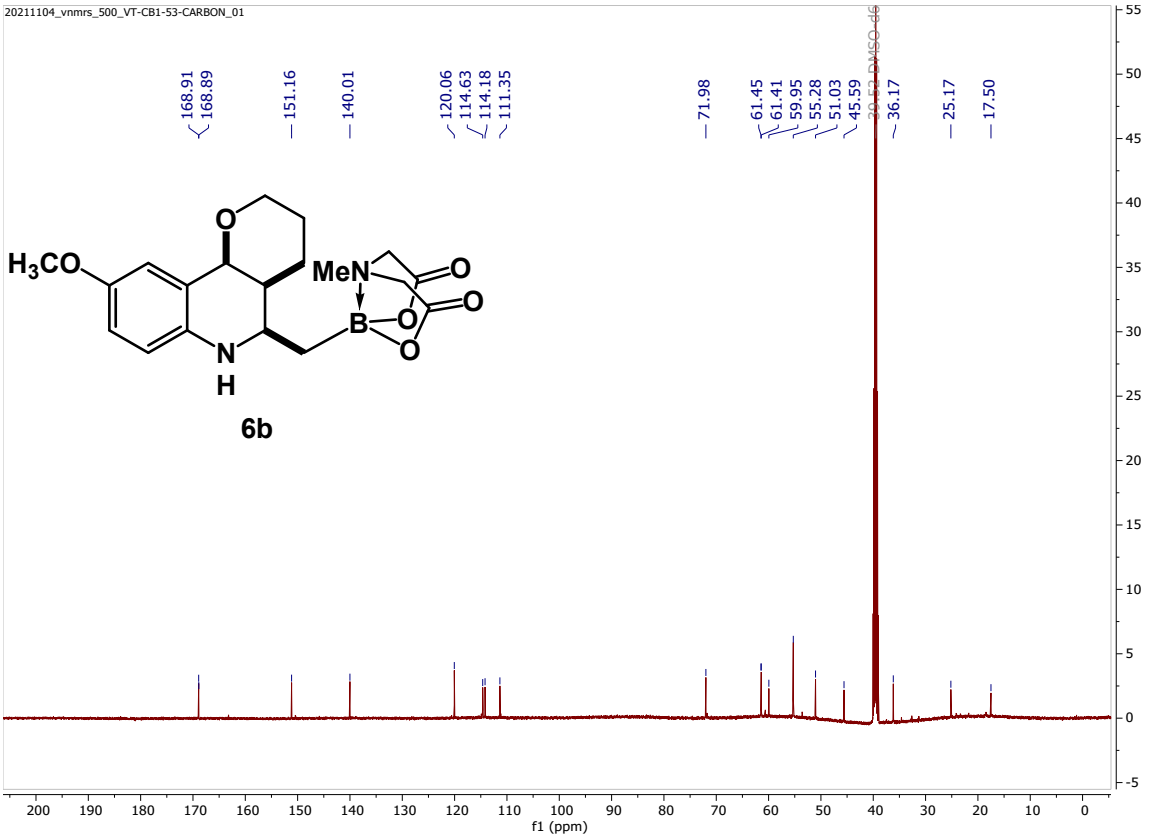
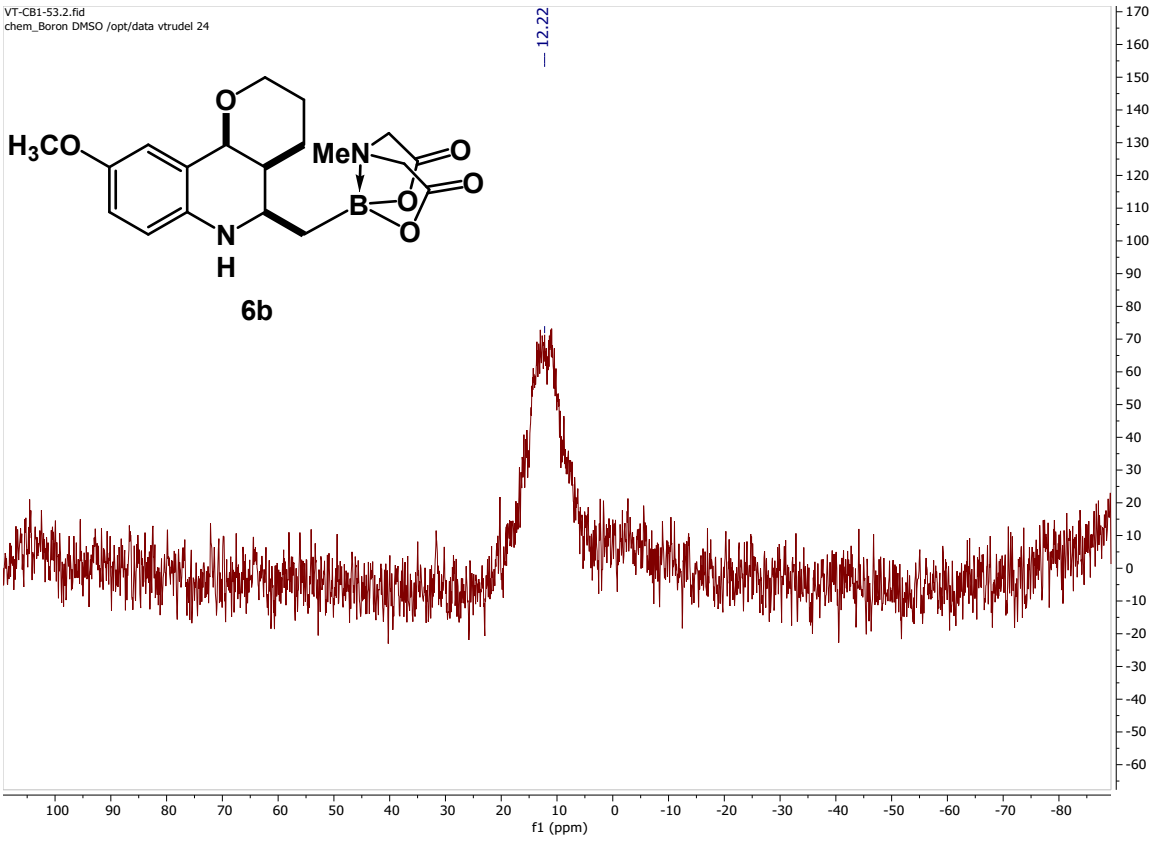
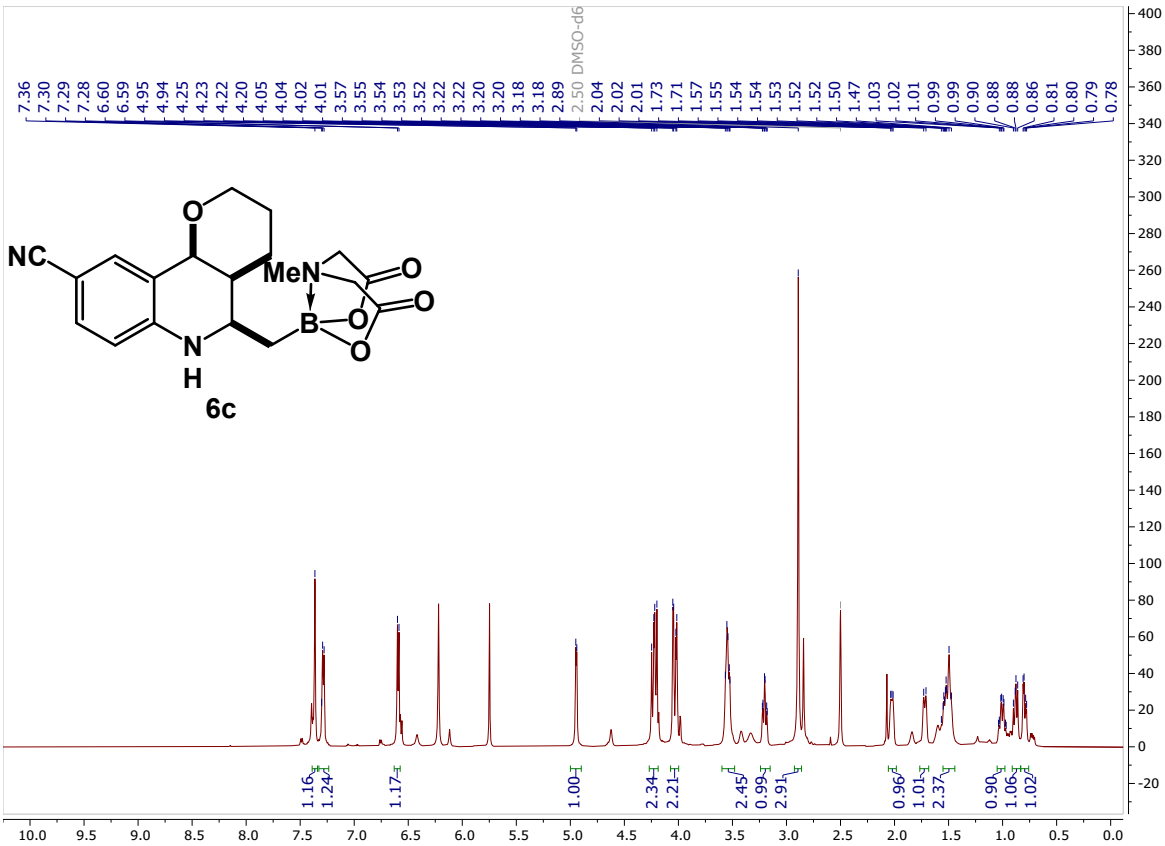


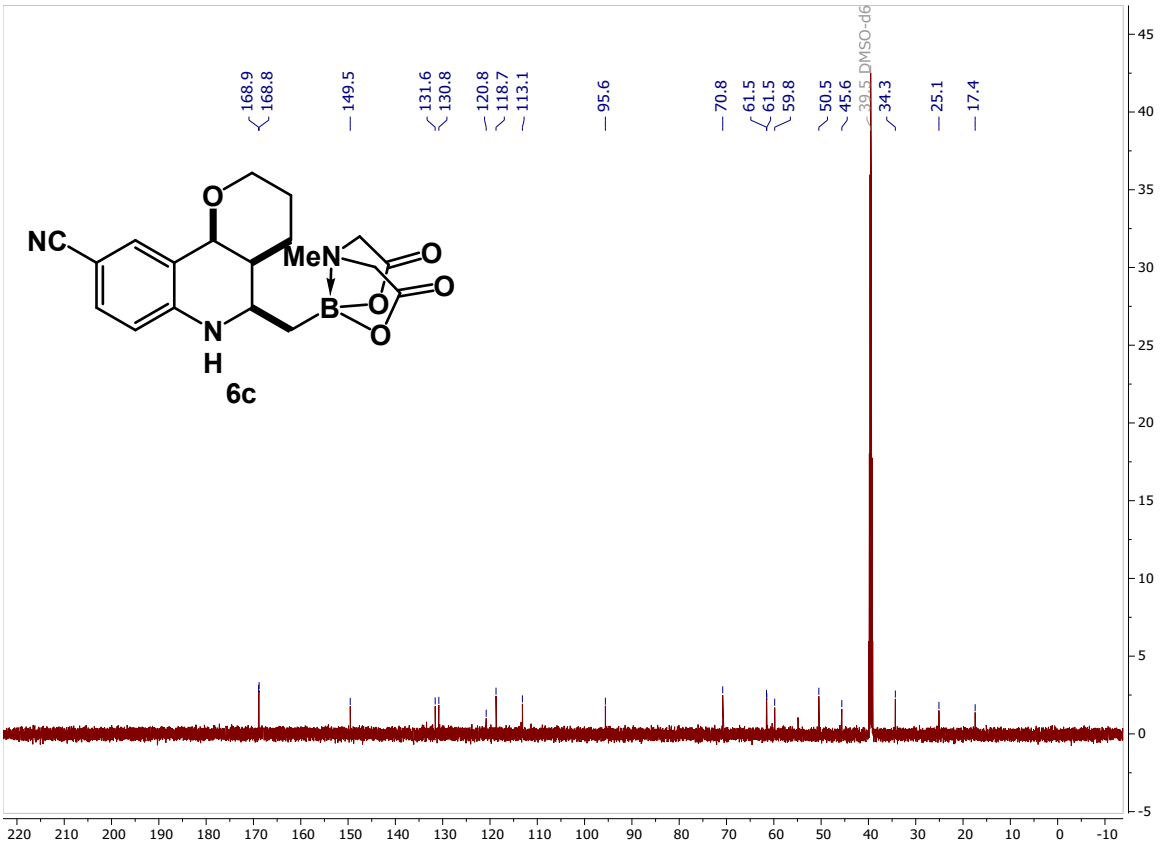
^{13}C NMR (126 MHz, DMSO-d_6) of **6b**



^{11}B NMR (128 MHz, DMSO-d_6) of **6b**



^{1}H NMR (600 MHz, DMSO-d_6) of **6c**



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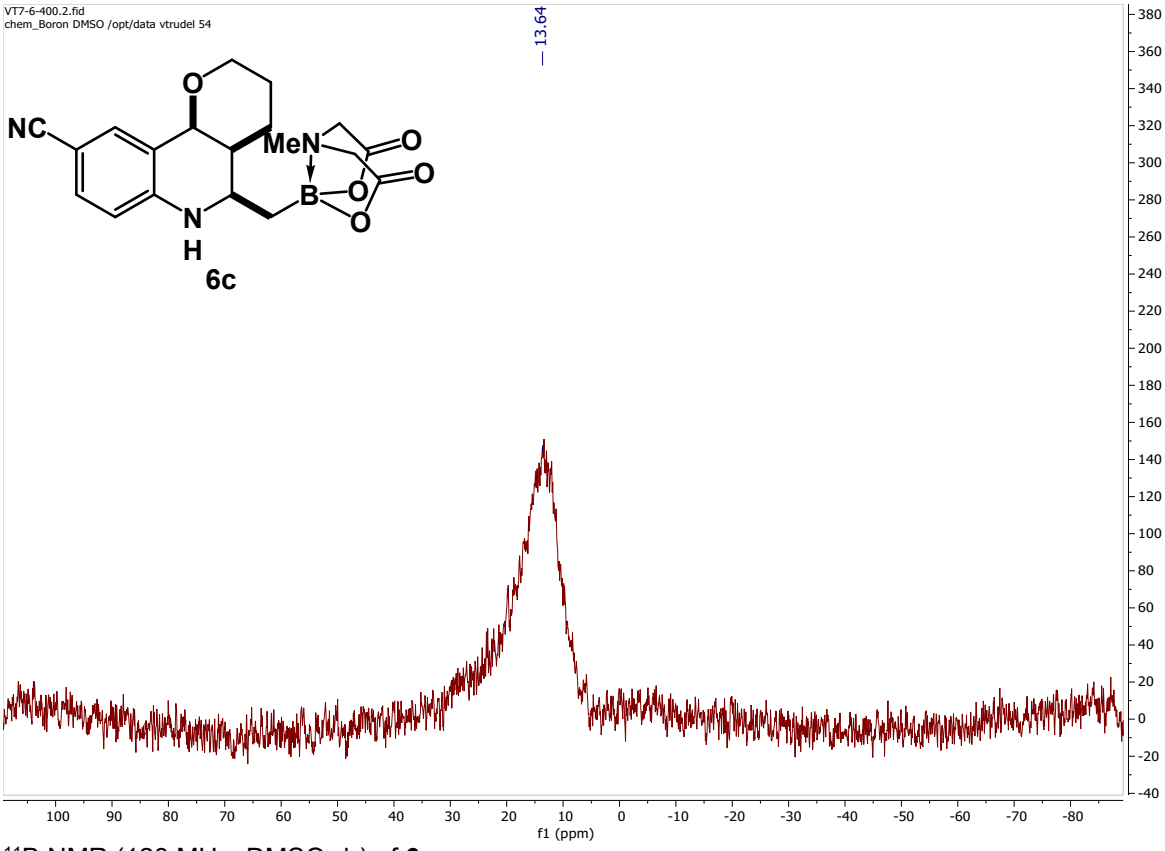
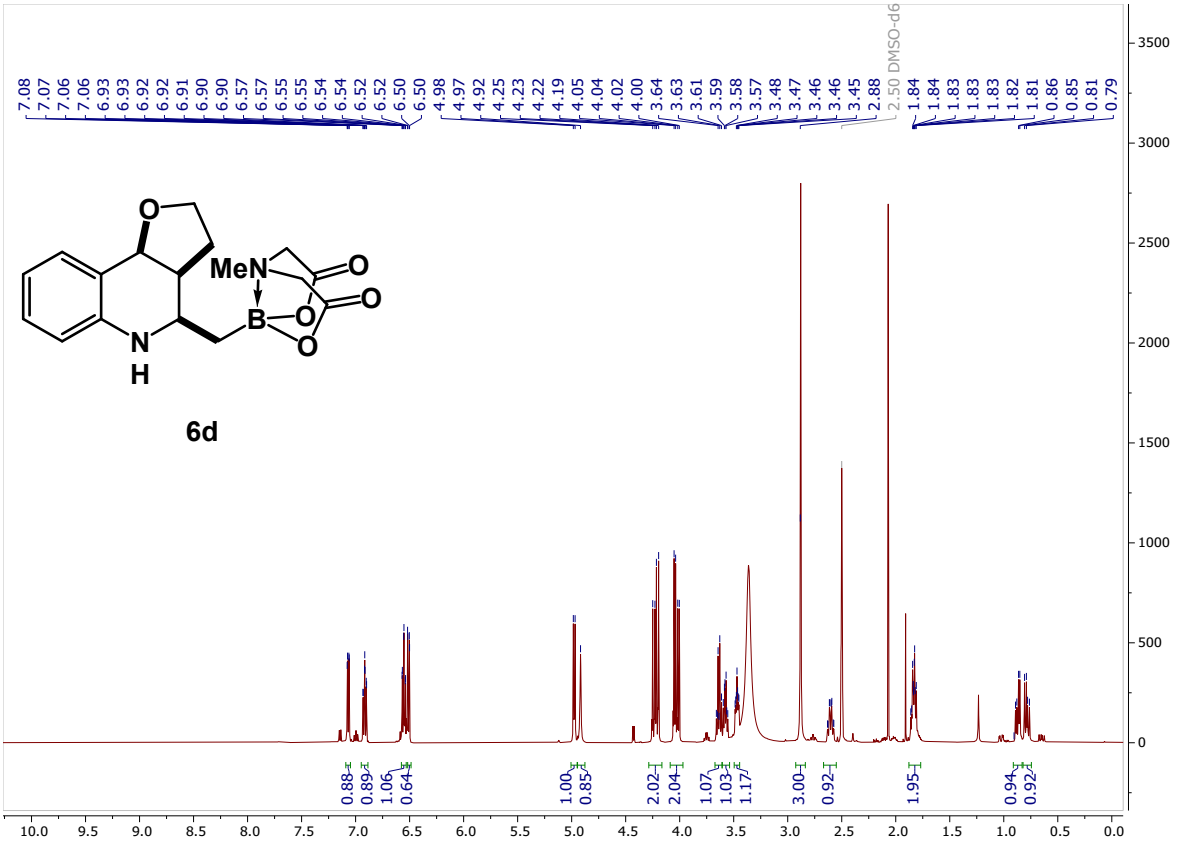
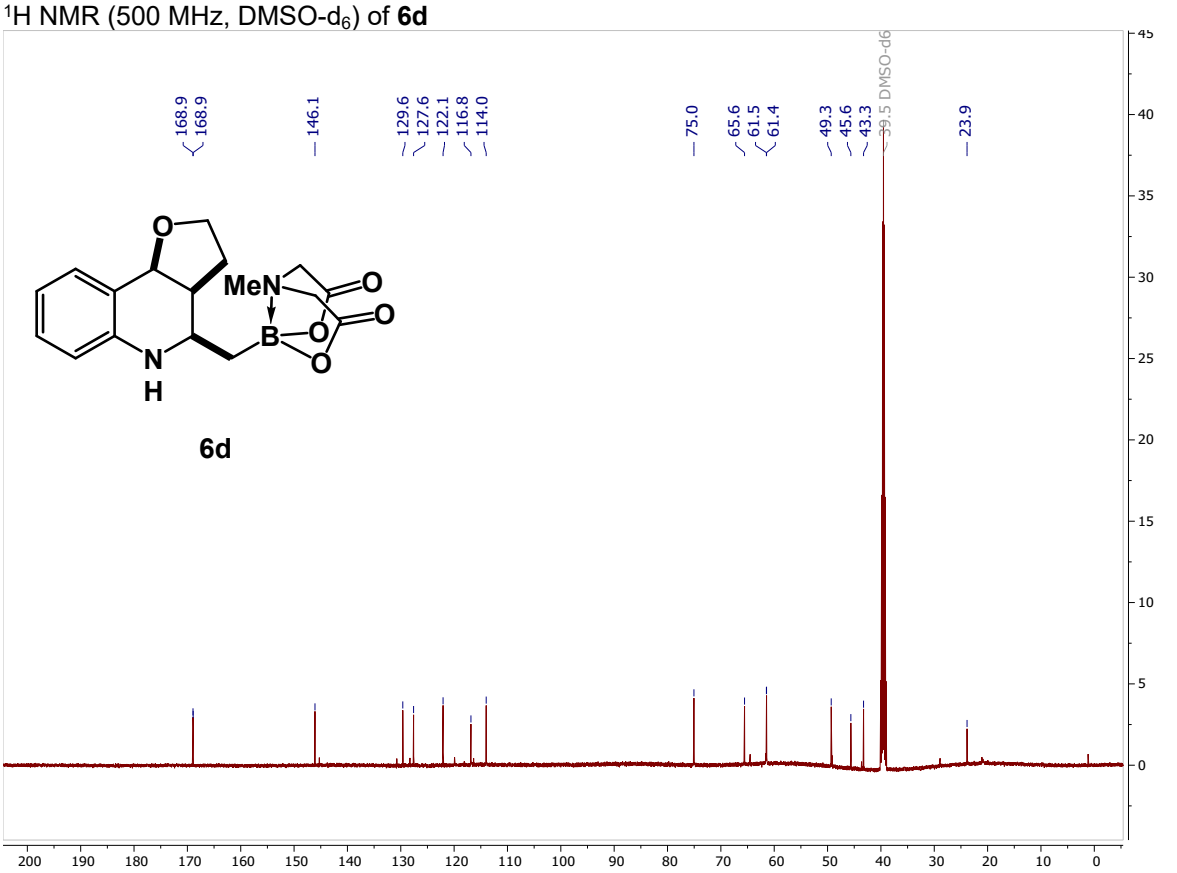


^{11}B NMR (128 MHz, DMSO-d_6) of **6c**



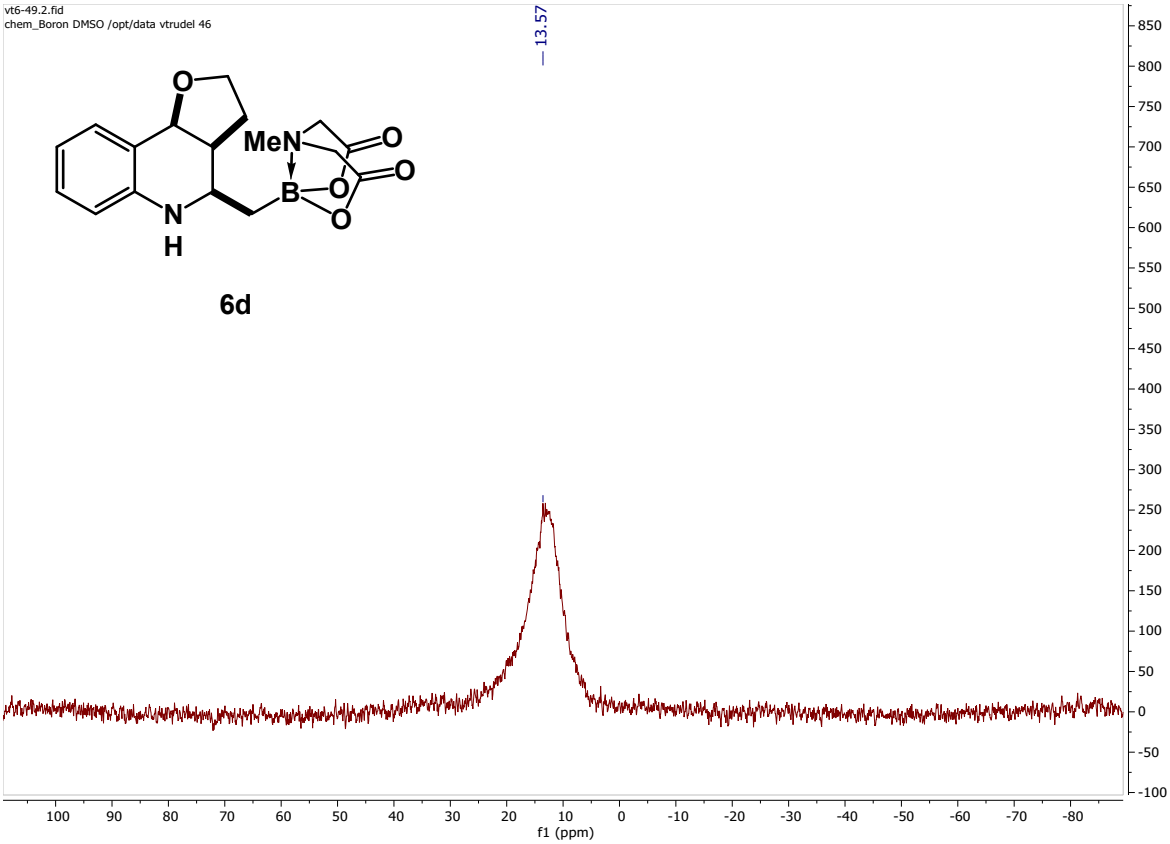
6d

^{1}H NMR (500 MHz, DMSO-d_6) of **6d**



6d

^{13}C NMR (126 MHz, DMSO-d_6 of **6d**



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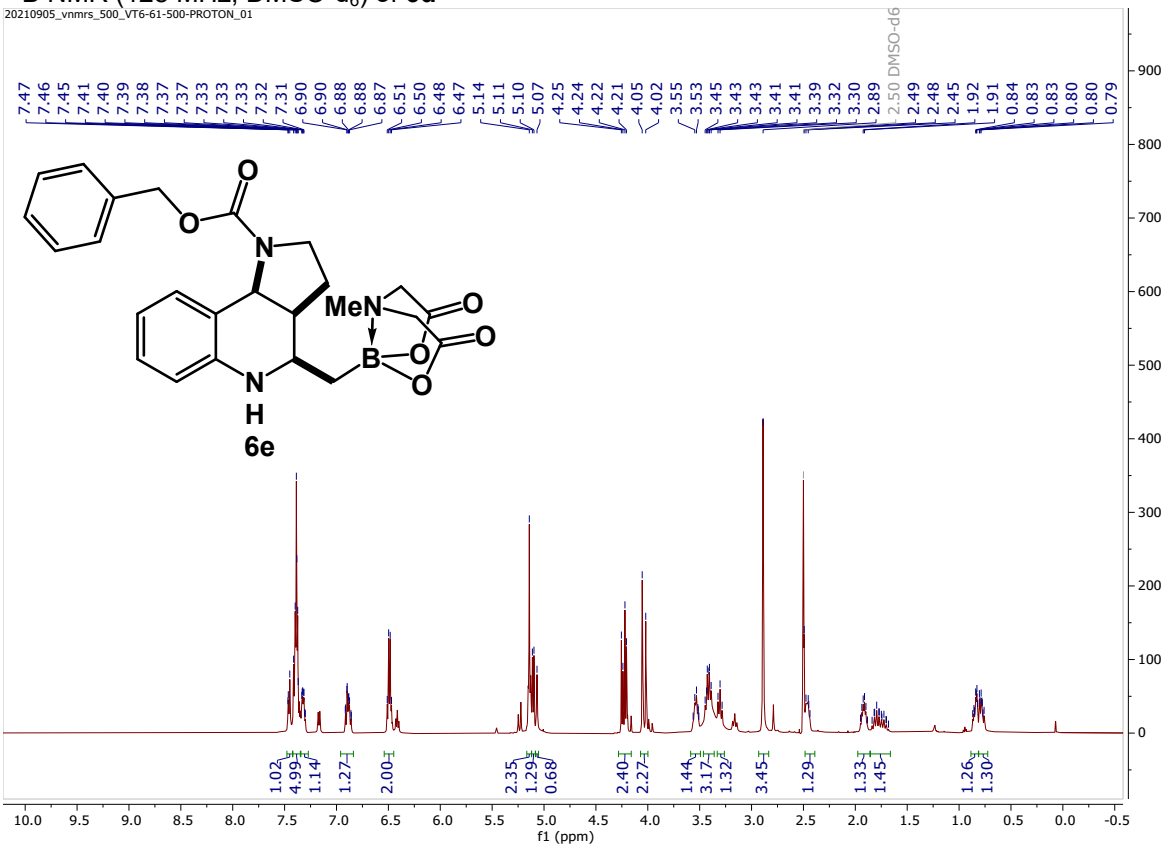

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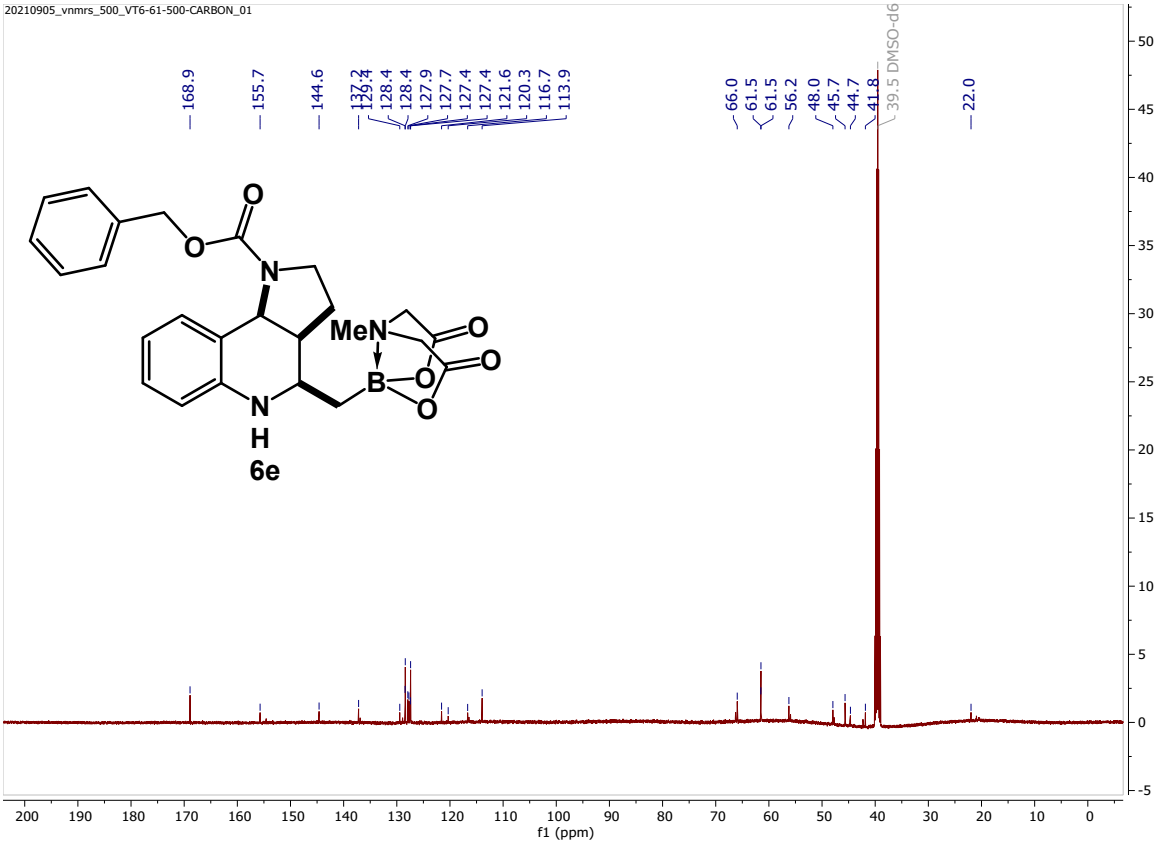

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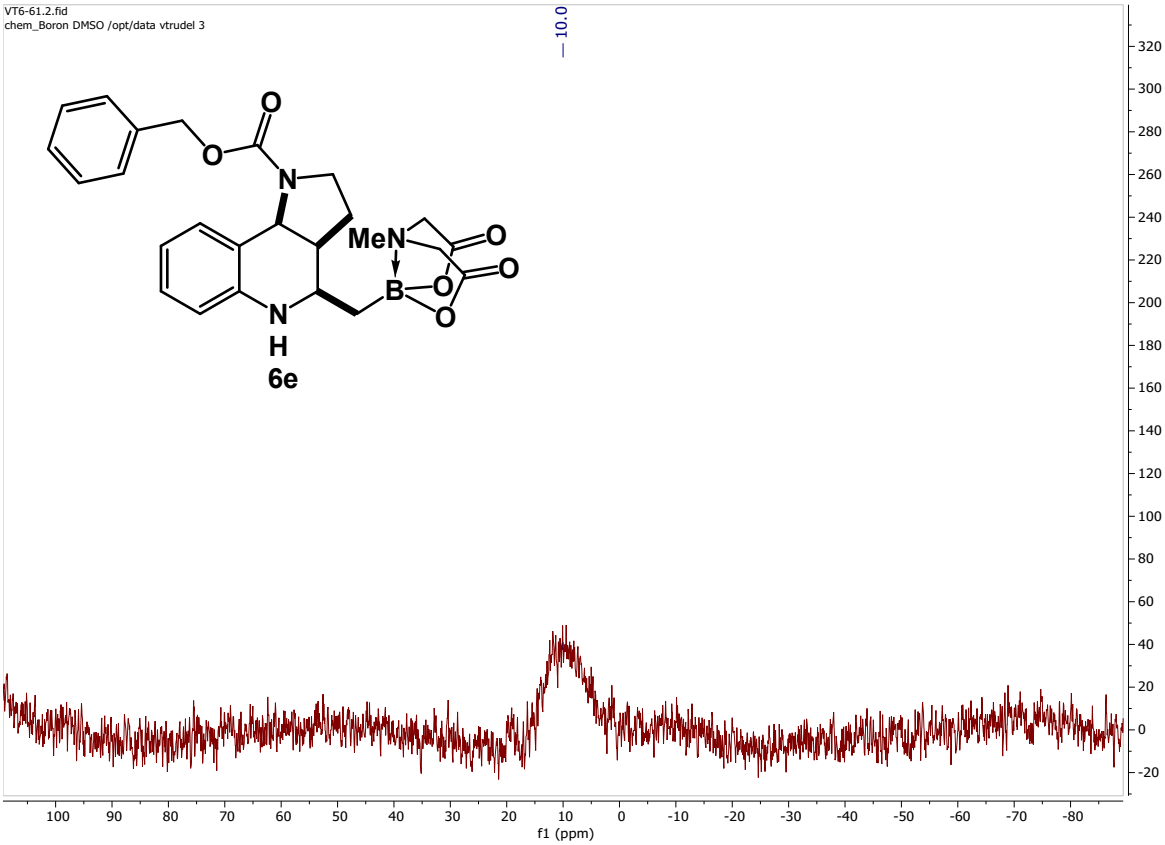
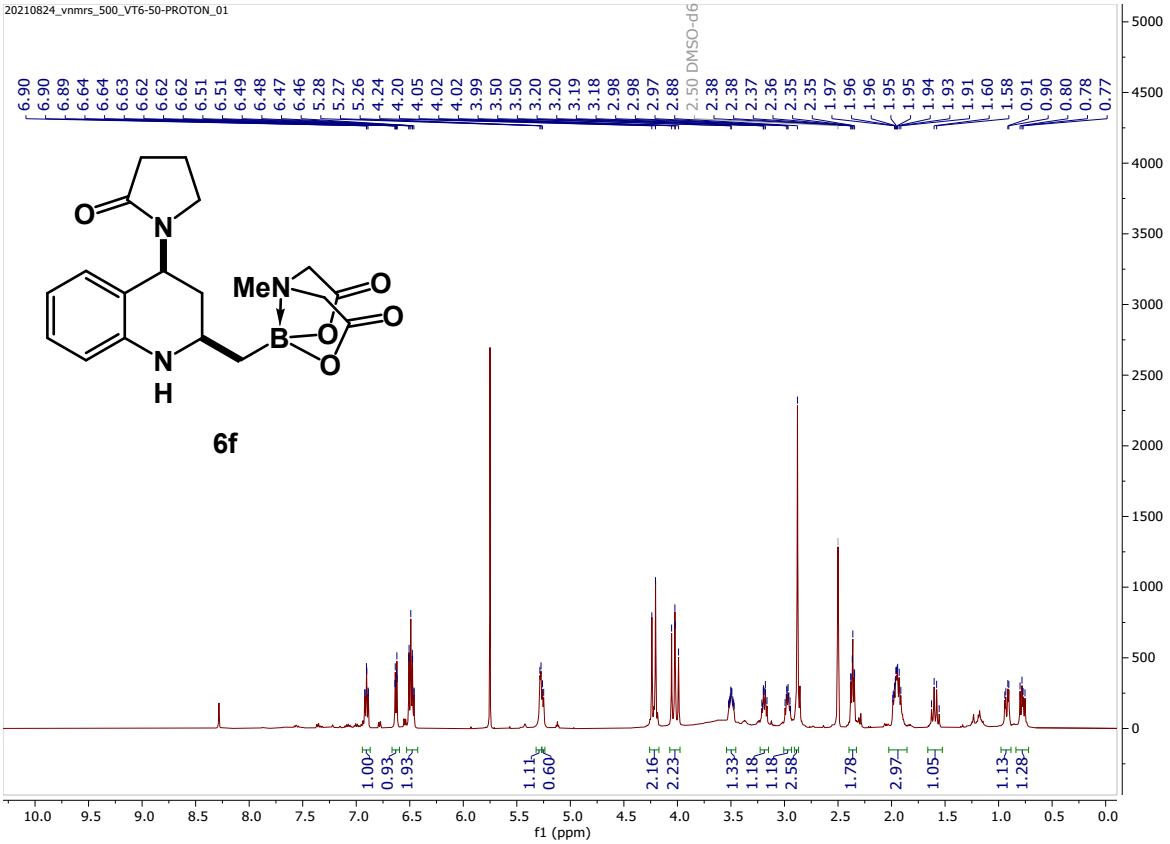
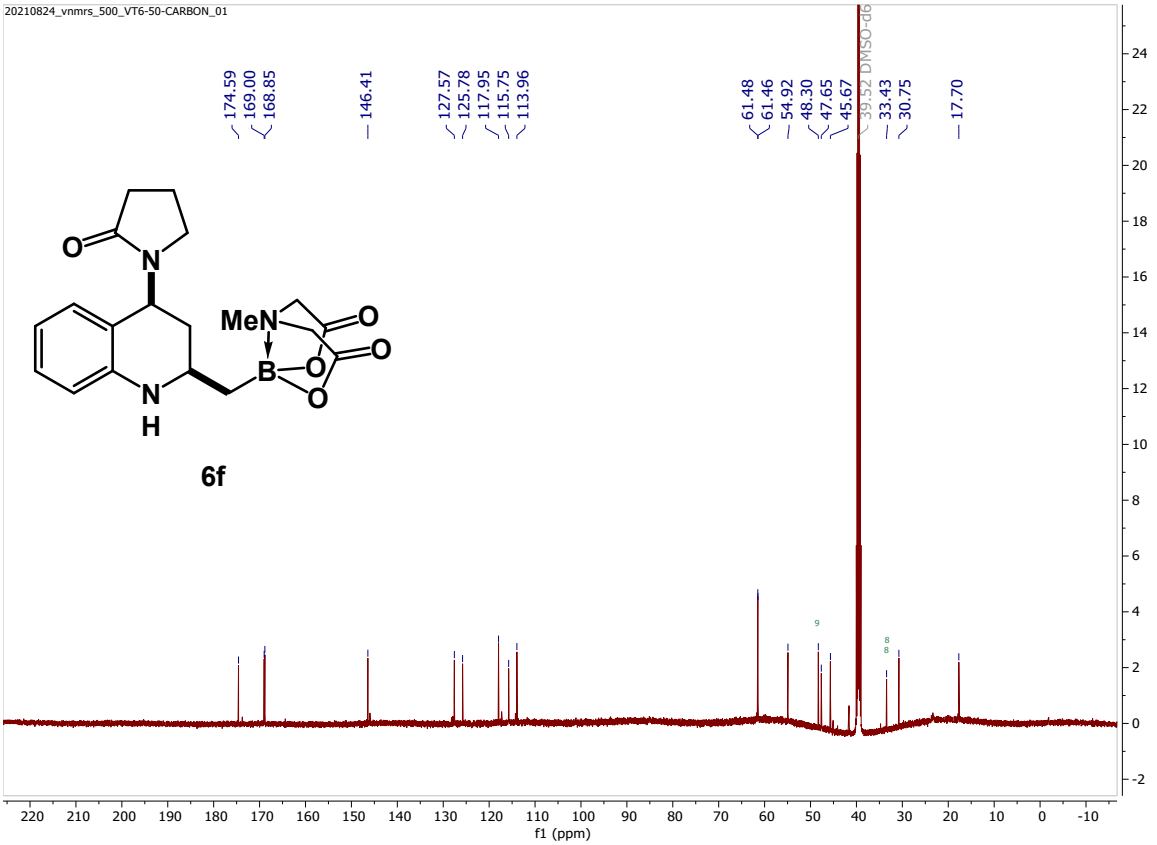


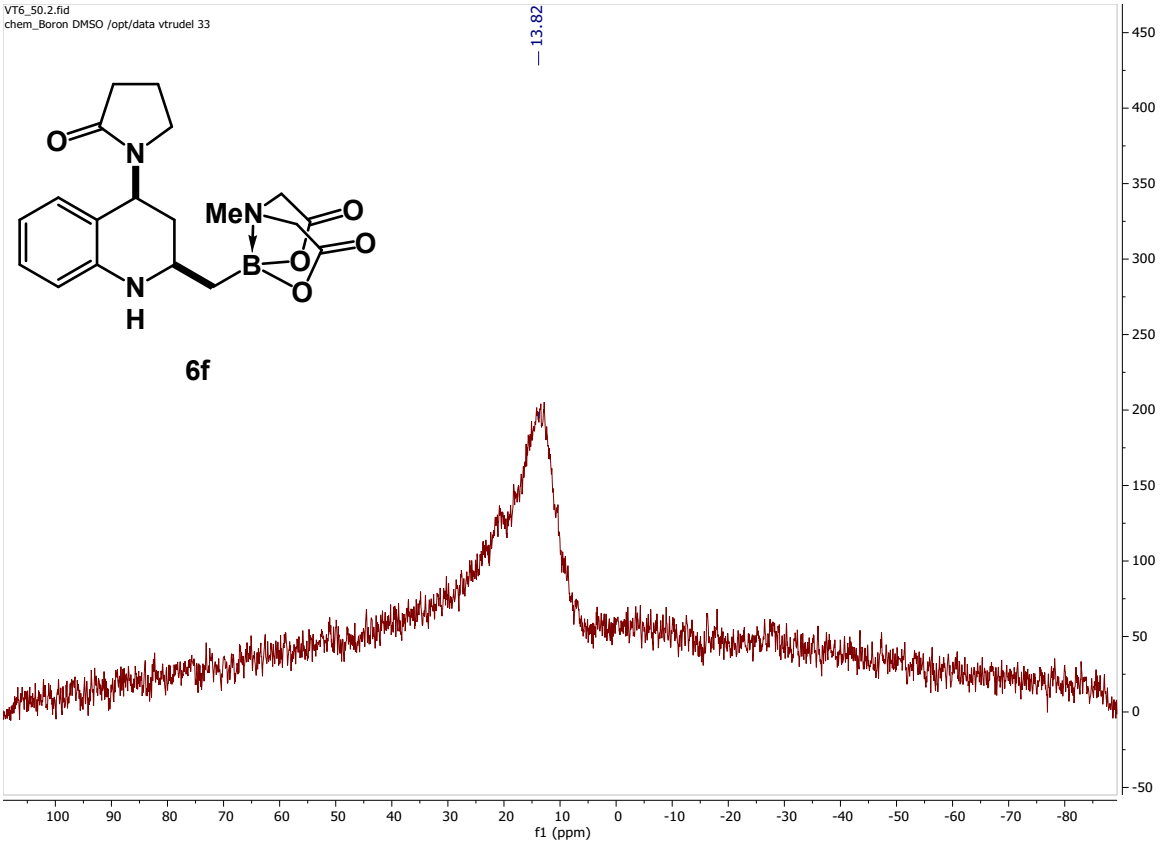
^{11}B NMR (128 MHz, DMSO-d_6) of **6e**.



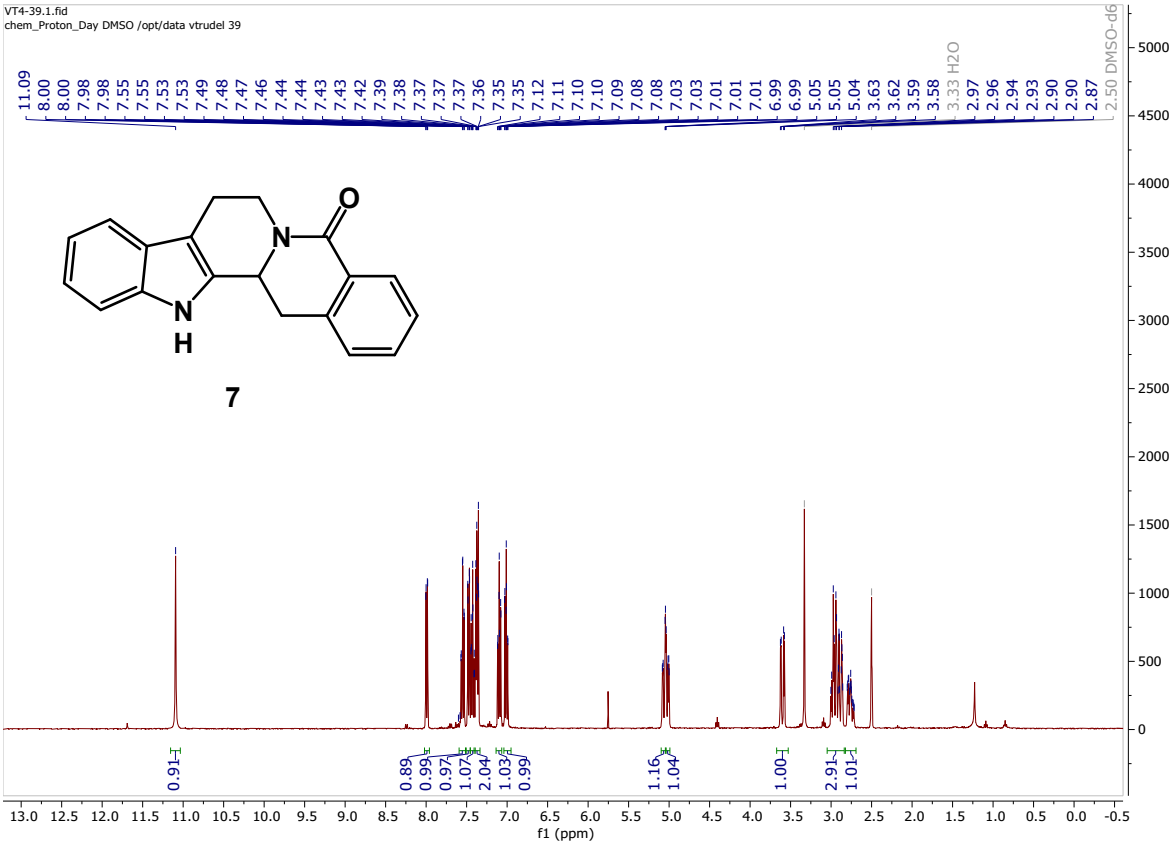
^{1}H NMR (500 MHz, DMSO-d_6) of **6f**



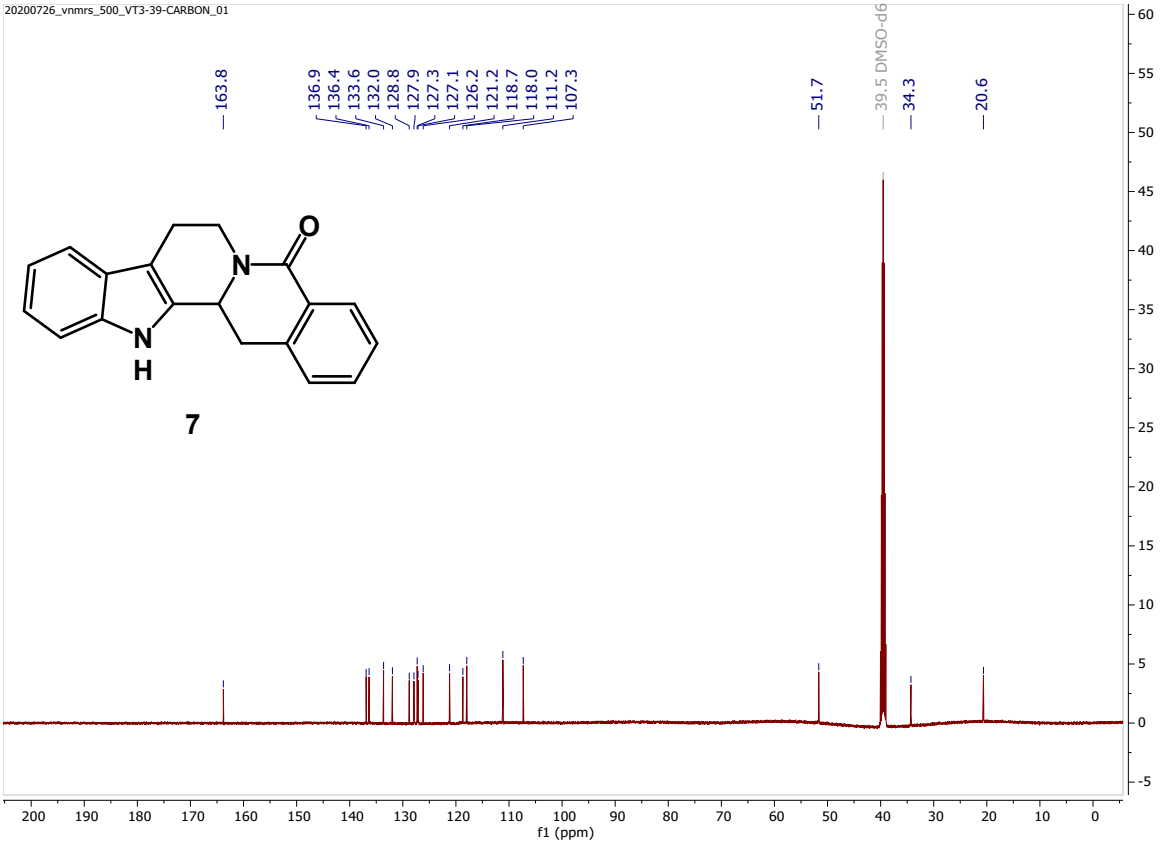
^{13}C NMR (126 MHz, DMSO-d_6) of **6f**



^{11}B NMR (128 MHz, DMSO-d_6) of **6f**

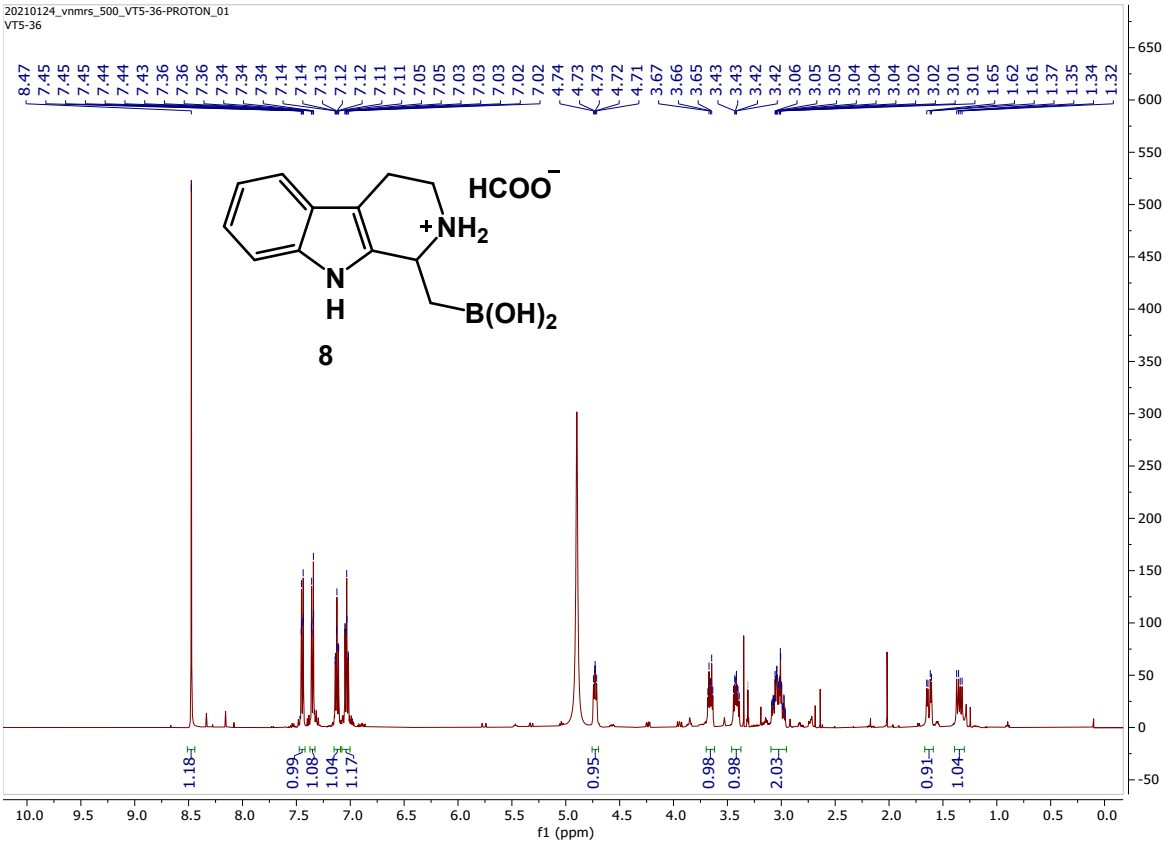


^{1}H NMR (400 MHz, DMSO-d_6) of **7**



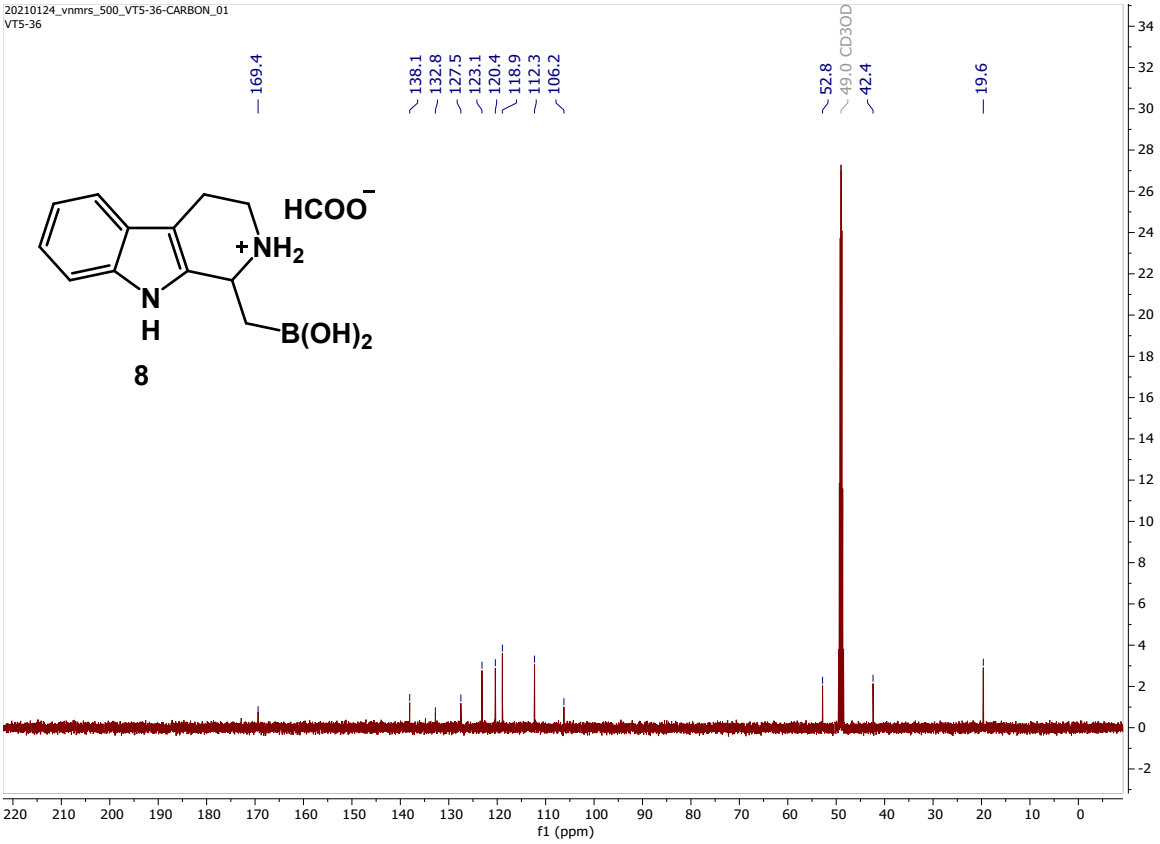
7

^{13}C NMR (126 MHz, DMSO-d_6) of **7**

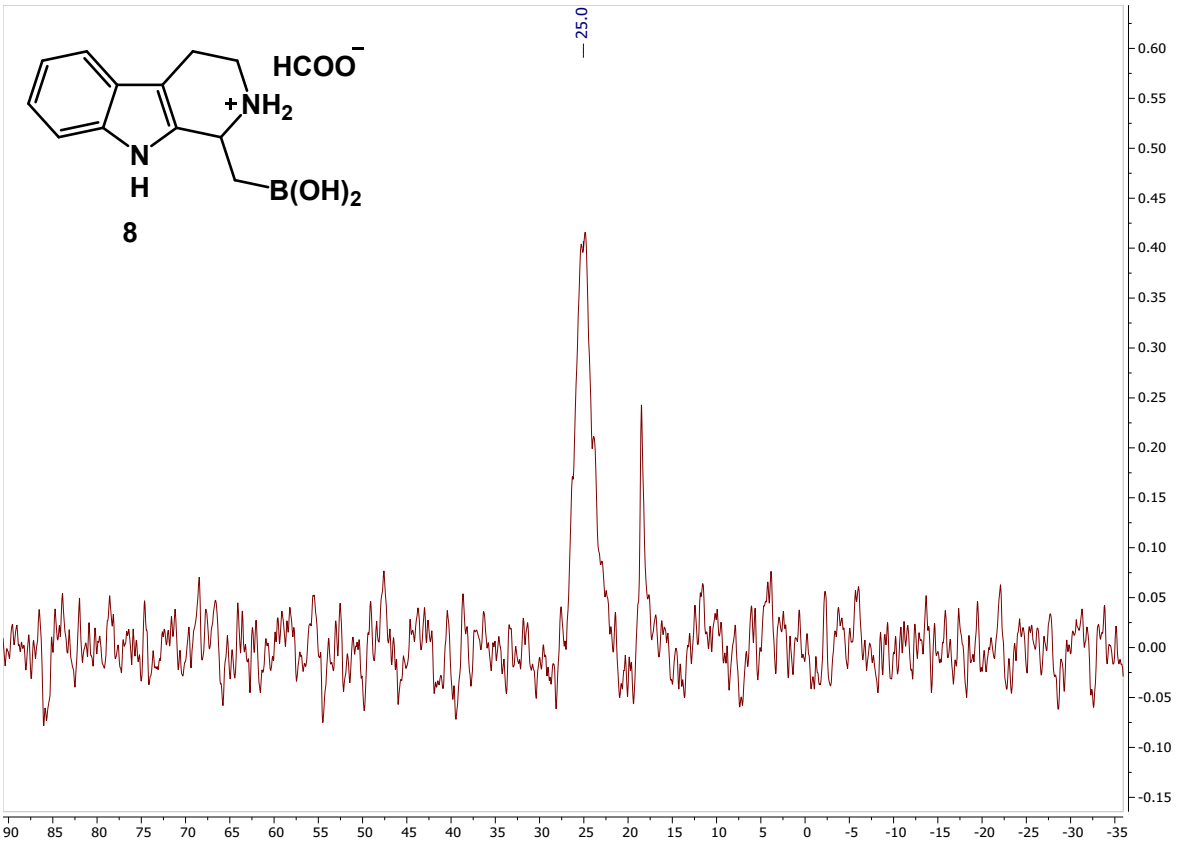


8

^{1}H NMR (500 MHz, CD_3OD) of **8**.



^{13}C NMR (126 MHz, CD_3OD) of **8**



^{11}B NMR (160 MHz, CD_3OD) of **8**.