Supplementary Information

Enantio- and Diastereoselective Construction of Vicinal C(sp^3) Centers via Nickel-Catalysed Hydroalkylation of Alkenes

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Table of Contents

Supplementary Methods

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1. Instrumentation and chemicals:

All reactions for the Ni-catalysed hydroalkylation were set up in 10 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen (N_2) atmosphere using glove-box techniques. Solvents were either purified using a two-column solid-state purification system (Innovative Technology, NJ, USA) or bought from the commercial sources and transferred to the glovebox without exposure to air.

NMR: ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Advance 400 Spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts were referenced internally to residual solvent peaks relative to TMS (δ = 0 ppm) at 299 K. Chemical shifts (δ (ppm)) are reported relative to TMS (δ(1H) 0.0 ppm, δ(13C) 0.0 ppm). The solvent's residual proton resonance and the respective carbon resonance (for $CHCl_3$; δ(1H) 7.26 ppm, δ(13C) 77.0 ppm were used for calibration. The boron-bound carbon peaks were very weak due to quadrupolar coupling and were not assigned.

TLC: Merck silica gel 60 F 254 plates; detection with UV light or by dipping into a solution of $KMnO_4$ (1.5 g in 400 mL H_2O, 5.0 g $NaHCO_3$) or a solution of $Ce(SO_4)_2$ x H_2O (10 g), phosphomolybdic acid hydrate (25 g), and conc. H_2SO_4 (60 mL) in H_2O (940 mL), followed by heating.

Flash column chromatography (FC): Flash column chromatography was performed using silica gel (Silicycle, ultra-pure grade). Preparative Thin Layer Chromatography (PTLC) was performed using glass plates from Merck KGaA, Darmstadt, Germany. The eluents for column chromatography and PTLC were presented as ratios of solvent volumes.

GC and GC-MS: All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with a FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector.

IR spectra were recorded on a *Bruker Vertex 80* FT-IR spectrometer.

HPLC spectra were recorded on an *Agilent* HPLC. Column, eluent, and retention times for HPLC analysis used for the determination of enantiomeric excess (*ee*) are given below in the details of the relevant experiments.

Optical rotations were measured on a *Polartronic M* polarimeter using a 0.5 cm cell with a Na 589 nm filter.

Melting points (**M.P.**) were determined on a *SMP 30 apparatus* (*Stuart Scientific*) and are uncorrected.

High-resolution mass spectra (HRMS) by electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI) and atmospheric pressure photoionization (APPI) method were performed at the EPFL ISIC Mass Spectroscopy Service.

All reagents were either prepared according to reported methods or purchased from *Sigma Aldrich*, *TCI*, *Acros Organics*, *Alfa Aesar*, *Fluorochem*, *Enamine* and *ABCR*. Anhydrous $NiCl_2$

from *ABCR*, $(MeO)_3SiH$, anhydrous LiCl powder and $BF_3{\cdot}OEt_2$ for synthesis from *Sigma Aldrich*, anhydrous KF from *Alfa Aesar*, and anhydrous DMA from *Acros Organics* were used.

2. Optimization of reaction conditions

2.1 General procedure for the screening of racemic alkyl halides and chiral ligands (Supplementary Table 1):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6 x 15 mm) were added $NiCl_2$ (1.3 mg, 0.01 mmol, 0.10 equiv.) and ligand **L1** (4.4 mg, 0.015 mmol, 0.15 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. If additive LiCl (5.0 mg, 0.12 mmol, 1.2 equiv.) was used then it was added at this time followed by the addition of anhydrous DMA (0.5 mL). The mixture was stirred for ~1.5 hours at room temperature. Then anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) and a racemic alkyl electrophile (0.10 mmol, 1.0 equiv.) followed by (*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (40.8 mg, 0.15 mmol, 1.5 equiv.) or *trans*-1-hexenylboronic acid pinacol ester (37.5 µL, 0.15 mmol, 1.5 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, DEMS (43.0 µL, 0.25 mmol, 2.5 equiv.) was added dropwise to it. The test tube was then sealed with airtight electrical tapes, removed from the glove box, and stirred at room temperature for 45 hours, maintaining 600 rpm. The reaction was quenched by the addition of aqueous NH_4Cl (0.5 mL) and EtOAc (3.0 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (2x3.0 mL). The combined organic phases were concentrated in vacuum to obtain the crude product which was used for experimental analysis.

2.2 General procedure for the screening of chiral ligands (Supplementary Table 2):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6x15 mm) were added $NiCl_2$ (1.3 mg, 0.01 mmol, 0.10 equiv.) and a ligand **L** (15 mol%) under an inert nitrogen (N_2) atmosphere using glove-box techniques. If additive LiCl (5.0 mg, 0.12 mmol, 1.2 equiv.) was used then it was added at this time followed by the addition of anhydrous DMA (0.5 mL). The mixture was stirred for ~1.5 hours at room temperature. Then racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (24.0 mg, 0.10 mmol, 1.0 equiv.) and anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (37.5 µL, 0.15 mmol, 1.5 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, DEMS (43.0 µL, 0.25 mmol, 2.5 equiv.) was added dropwise to it. The test tube was then sealed with airtight electrical tapes, removed from the glove box, and stirred at room temperature for 45 hours, maintaining 600 rpm.

General procedure (GP1) for work-up and data analysis: The reaction was quenched by the addition of aqueous NH_4Cl (0.5 mL) and EtOAc (3.0 mL). Then internal standard dodecane (23.0 µL) was added to this mixture and the resulting mixture was well mixed. A small organic aliquot was used for the GC FID analysis to determine the yield. The remaining organic phase was separated and the aqueous phase was extracted with EtOAc (2x3.0 mL). The combined organic phases were concentrated in vacuum. The crude mixture was purified by flash column chromatography. The obtained crude boronic ester product was used for the determination of enantiomeric excess (*ee*) and diastereomeric ratio (*dr*) by chiral HPLC analysis.

2.3 General procedure for the screening of hydride donors (Supplementary Table 3):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6 x 15 mm) were added $NiCl_2$ (1.3 mg, 0.01 mmol, 0.10 equiv.), ligand **L2** (5.6 mg, 0.015 mmol, 0.15 equiv.), and LiCl (5.0 mg, 0.12 mmol, 1.2 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. Then anhydrous DMA (0.5 mL) was added and the mixture was stirred for ~1.5 hours at room temperature until it became a clear solution. Then racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (24.0 mg, 0.10 mmol, 1.0 equiv.) and anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (37.5 µL, 0.15 mmol, 1.5 equiv.) [or racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (28.8 mg, 0.12 mmol, 1.2 equiv.) and anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (25.0 µL, 0.10 mmol, 1.0 equiv.)] were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, hydride donor/donors (0.25 mmol, 2.5 equiv.) were added dropwise to it [in the case of two hydride donors, the hydrosilane was added first followed by HBpin]. The test tube was then sealed with airtight electrical tapes, removed from the glove box, and stirred at room temperature or in an ice-water bath at 0 °C for 45 hours, maintaining 600 rpm. Afterward, the general procedure (**GP1**) for work-up and data analysis was followed for further analysis.

2.4 General procedure for the evaluation of boron-based Lewis acids (Supplementary Table 4-6):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6x15 mm) were added $NiCl_2$ (1.3 mg, 0.01 mmol, 0.10 equiv.), ligand **L2** (5.6 mg, 0.015 mmol, 0.15 equiv.), and LiCl (5.0 mg, 0.12 mmol, 1.2 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. Then anhydrous DMA (0.5 mL) was added and the mixture was stirred for ~1.5 hours at room temperature until it became a clear solution. Then racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (28.8 mg, 0.12 mmol, 1.2 equiv.) and anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (25.0 µL, 0.10 mmol, 1.0 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, a hydride donor (0.25 mmol, 2.5 equiv.) was added dropwise to it followed by the addition of a boron-based Lewis acid (x mol%). The test tube was then sealed with airtight electrical tapes, removed from the glove box, and stirred in an ice-water bath at 0 °C for 45 hours, maintaining 600 rpm. Afterward, the general procedure (**GP1**) for work-up and data analysis was followed for further analysis.

2.5 General procedure for the screening of Ni-salts (Supplementary Table 7):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6x15 mm) were added Ni-salt (0.01 mmol, 0.10 equiv.), ligand **L2** (5.6 mg, 0.015 mmol, 0.15 equiv.), and LiCl (5.0 mg, 0.12 mmol, 1.2 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. Then anhydrous DMA (0.5 mL) was added and the mixture was stirred for ~1.5 hours at room temperature until it became a clear solution. Then racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (28.8 mg, 0.12 mmol, 1.2 equiv.) and anhydrous KF (14.5 mg, 0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (25.0 µL, 0.10 mmol, 1.0 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point,

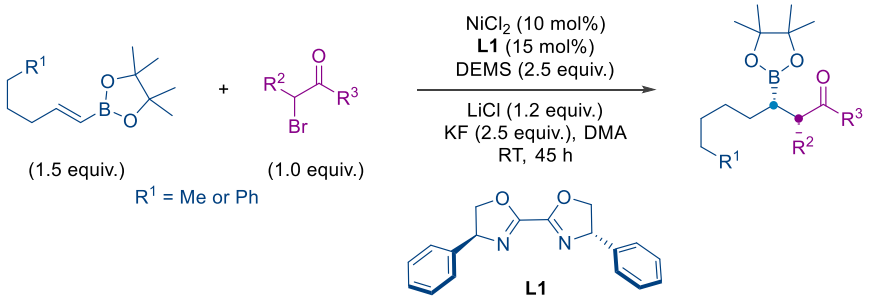
$(MeO)_3SiH$ (33.5 µL, 0.25 mmol, 2.5 equiv.) was added dropwise to it followed by the addition of $BF_3.OEt_2$ (3.6 µL, 0.03 mmol, 0.30 equiv.). The test tube was then sealed with airtight electrical tapes, removed from the glove box immediately, and stirred in an ice-water bath at 0 °C for 45 hours, maintaining 600 rpm. Afterward, the general procedure (**GP1**) for work-up and data analysis was followed for further analysis.

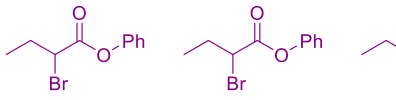
2.6 General procedure (GP2) for the investigation of the effect of different parameters (Supplementary Table 8):

To an oven-dried 10 mL Teflon-screw capped vial equipped with a magnetic stir bar (6x15 mm) were added Ni-salt (0.01 mmol, 0.10 equiv.), ligand **L** (0.015 mmol, 0.15 equiv.), and LiX (0.12 mmol, 1.2 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. Then anhydrous solvent (0.5 mL) was added and the mixture was stirred for ~1.5 hours at room temperature. Then racemic 3-bromo-1-phenylpyrrolidin-2-one **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.) and anhydrous base (0.25 mmol, 2.5 equiv.) followed by *trans*-1-hexenylboronic acid pinacol ester **1a** (25.0 µL, 0.10 mmol, 1.0 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, a hydride donor (0.25 mmol, 2.5 equiv.) was added dropwise to it followed by the addition of B-based Lewis acid (0.03 mmol, 0.30 equiv.). The test tube was then sealed with airtight electrical tapes, removed from the glove box immediately, and stirred in an ice-water bath at 0 °C for 45 hours, maintaining 600 rpm. Afterward, the general procedure (**GP1**) for work-up and data analysis was followed for further analysis.

Supplementary Tables

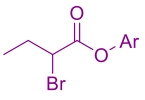
Supplementary Table 1. Evaluation of Secondary Racemic Alkyl Electrophile



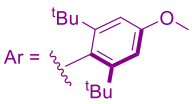


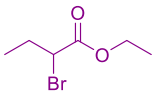
56%, 73% ee
73:27 dr
without LiCl

71%, 78% ee
74:26 dr

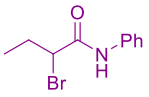


<5%, ee = n.d.
dr = n.d.

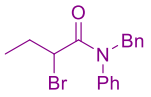




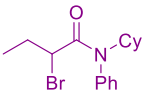
76%, 86% ee
72:28 dr



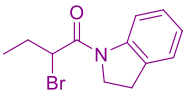
55%, ee = n.d.
dr = 34:66



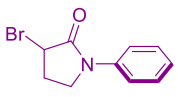
<5%, ee = n.d.
dr = n.d.



<5%, ee = n.d.
dr = n.d.

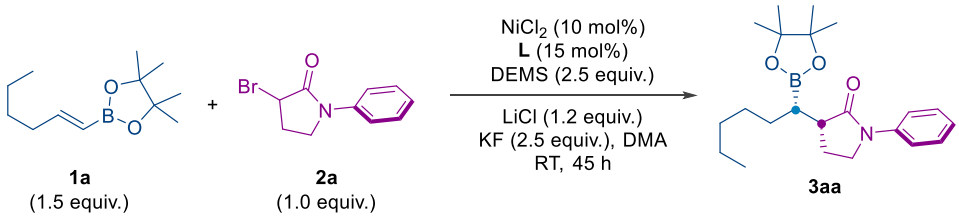


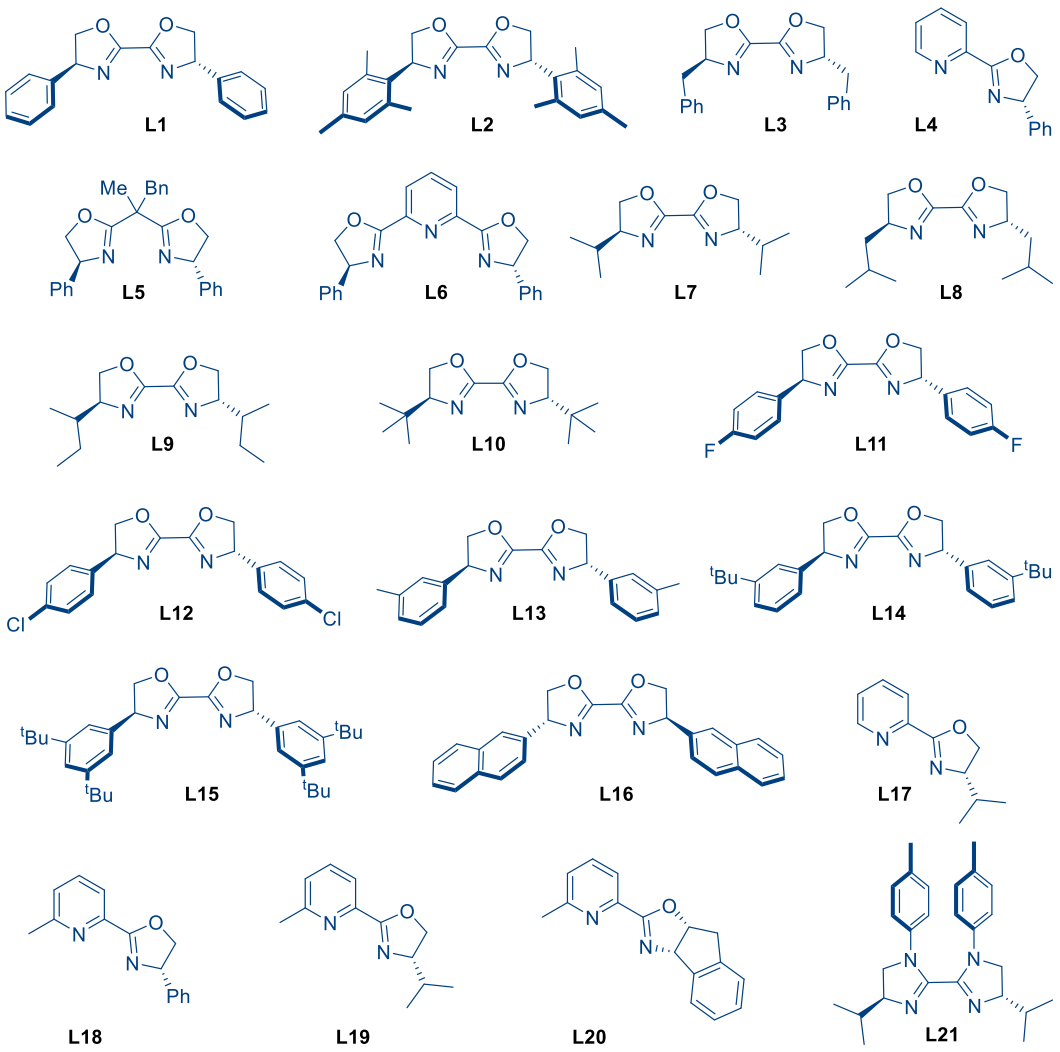
<5%, ee = n.d.
dr = n.d.



40%, 83% ee
76:24 dr
with R^1 = Me

Supplementary Table 2. Screening of Ligands (L)



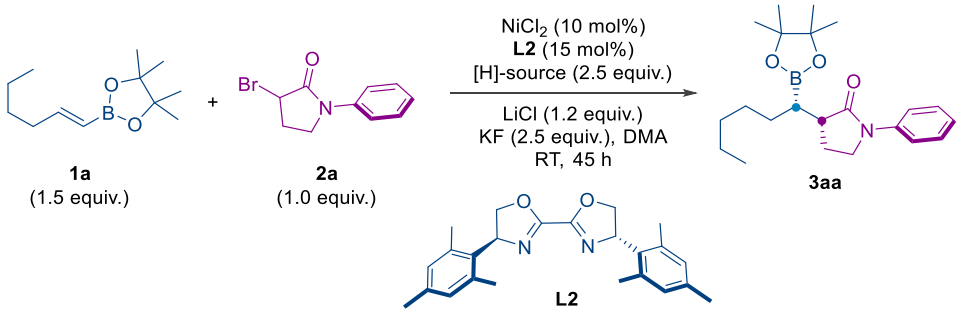


Entry	Ligand (L)	Yield (%)	ee (%)	dr
1[a]	**L1**	30	82	54:46
2	**L1**	40	83	76:24
3	**L2**	56	95	80:20
4	**L4**	trace	n.d.	n.d.
5	**L7**	48	72	61:39
6	**L8**	16	5	75:25

7	**L9**	63	72	65:35
8	**L10**	16	2	66:34
9	**L11**	22	82	62:38
10	**L12**	51	80	75:25
11	**L13**	40	89	77:23
12	**L14**	33	72	70:30
13	**L15**	43	88	84:16
14[b]	**L16**	39	-83	74:26
15	**L17**	trace	n.d.	n.d.
16	**L18**	trace	n.d.	n.d.
17	**L19**	trace	n.d.	n.d.
18	**L20**	trace	n.d.	n.d.
19	**L21**	trace	n.d.	n.d.

[a] The reaction was conducted without LiCl. DEMS = Diethoxy-methylsilane; DMA = *N*,*N*-Dimethylacetamide; RT = room temperature. [b] The opposite enantiomer was formed.

Supplementary Table 3. Screening of Hydride Donors

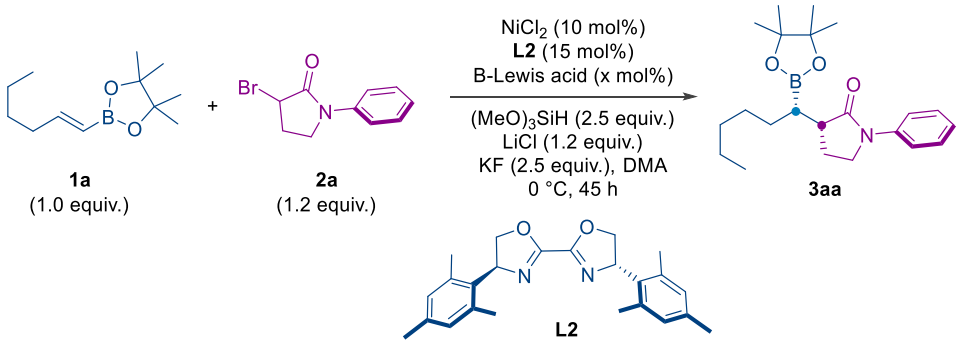


Entry	Hydride donor	Yield (%)	ee (%)	dr
1	DEMS	56	95	80:20
2	$(EtO)_3SiH$	35	96	84:16
3	PMHS	49	94	85:15
4	DMMS	67	95	86:14
5	HBpin	30	92	94:6
6	DMMS:HBpin (1:1)	49	93	96:4

7	DMMS:HBpin (2:1)	47	94	95.5:4.5
8[a]	DMMS:HBpin (1:1)	65	89	93:7
9[b]	DMMS:HBpin (1:1)	57	92	95:5
10[b]	DMMS:HBpin (1:1.5)	54	92	95:5
11[b]	DMMS:HBpin (1.5:1)	52	91	94:6
12[b]	$(MeO)_3SiH$	89	96	85:15
13[b]	$(MeO)_3SiH$:HBpin (2:0.5)	75	95	92:8
14[b,c]	$(MeO)_3SiH$:HBpin (2:0.5)	76	96	95:5
15[b,c]	$(MeO)_3SiH$:HBpin (2.0:0.3)	82	96	90.5:9.5
16[b,c]	$(MeO)_3SiH$:HBpin (2.2:0.5)	77	96	95:5

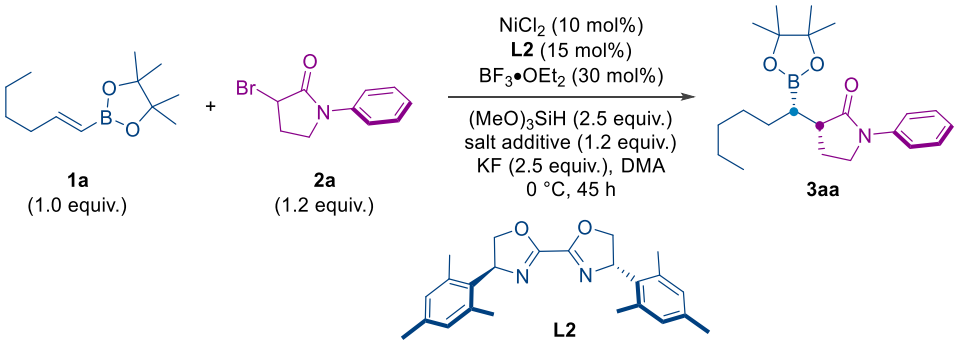
[a] The reaction was conducted with **1a** (1.0 equiv.) and **2a** (1.5 equiv.). [b] The reaction was conducted with **1a** (1.0 equiv.) and **2a** (1.2 equiv.). [c] The reaction was conducted at 0 °C.

Supplementary Table 4. Screening of Boron Lewis Acids



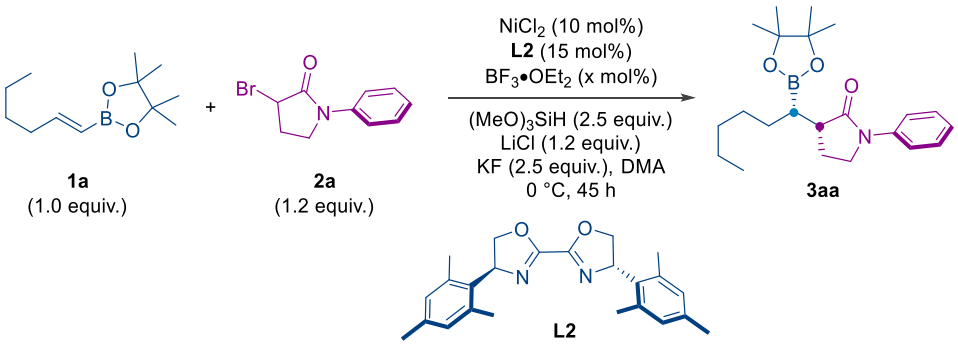
Entry	Boron-based Lewis acid (mol%)	Yield (%)	ee (%)	dr
17[b,c]	$(MeO)_3SiH + BF_3.OEt_2$ (100 mol%)	50	92	96:4
18[b,c]	$(MeO)_3SiH + BF_3.OEt_2$ (50 mol%)	74	92	95:5
19[b,c]	$(MeO)_3SiH + BF_3.OEt_2$ (30 mol%)	78	94	95:5
20[b,c]	$(MeO)_3SiH + BF_3.OEt_2$ (20 mol%)	83	97	92:8
21[b,c]	$(MeO)_3SiH + BPh_3$ (30 mol%)	16	96	95:5

Supplementary Table 5. Evaluation of the Effect of LiCl and $BF_3.OEt_2$ on the Reaction



Entry	Variation of Li-salt and $BF_3.OEt_2$	Yield (%)	ee (%)	dr
1	No variation	78	94	95:5
2	Without LiCl and $BF_3.OEt_2$	74	82	75:25
3	With LiCl and without $BF_3.OEt_2$	90	95	88:12
4	Without LiCl and with $BF_3.OEt_2$	73	86	88:12
5	With LiCl (30 mol%) and with $BF_3.OEt_2$	76	88	84:16
6	With LiBr and $BF_3.OEt_2$	70	86	87:13
7	With LiI and $BF_3.OEt_2$	63	85	88:12
8	With KCl and $BF_3.OEt_2$	74	88	84:16
9	$LiBF_4$ (1.2 equiv.) instead LiCl + $BF_3.OEt_2$	77	90	78:12

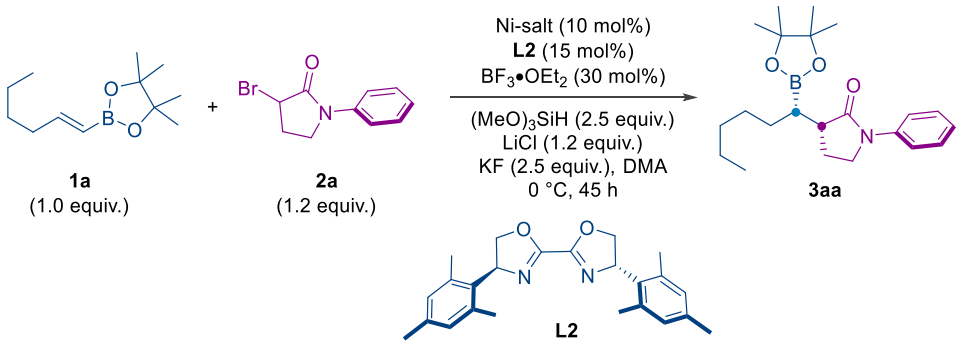
Supplementary Table 6. The Effect of $BF_3.OEt_2$ on the Reaction



Entry	$BF_3.OEt_2$ (mol%)	Yield (%)	ee (%)	dr
1	0	90	95	88:12

2	20	84	95	92:8
3	25	80	95	94:6
4	30	78	94	95:5
5	50	74	93	95:5
6	100	50	93	97:3

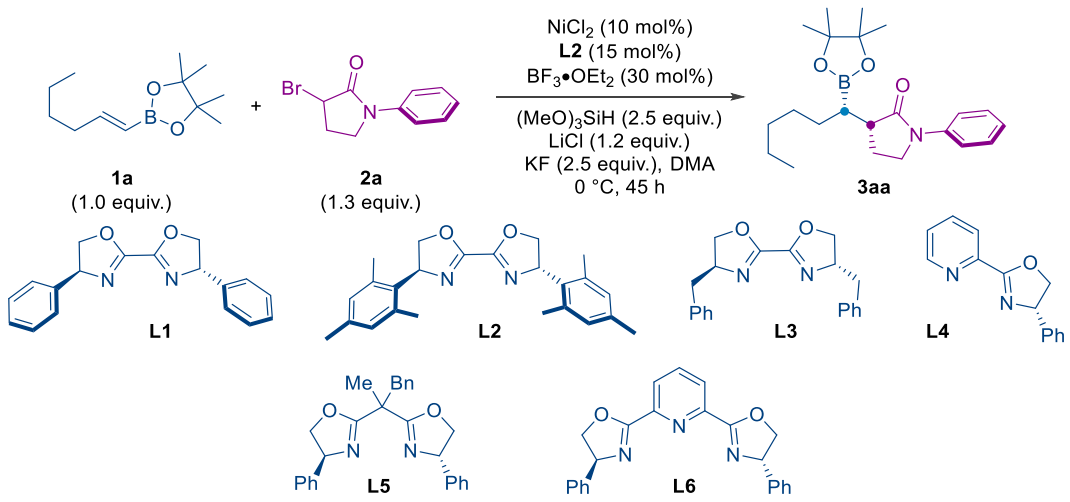
Supplementary Table 7. Screening of Ni-salts



Entry	Ni-salt	Yield (%)	ee (%)	dr
1	$NiCl_2$	78	94	95:5
2[a]	**$NiCl_2$**	**80(75)**	**94**	**95:5**
3	$NiBr_2$	77	92	95:5
4	NiI_2	72	93	95:5
5	$NiCl_2$.dme	76	94	95:5
6	$NiBr_2$.dme	49	92	95:5
7	$NiBr_2$.diglyme	75	92	95:5
8	$Ni(NO_3)_2.6H_2O$	82	94	86:14
9	$NiCl_2.6H_2O$	71	96	88:12

[a] The reaction was conducted with **1a** (1.0 equiv.) and **2a** (1.3 equiv.). Isolated yield in the parenthesis.

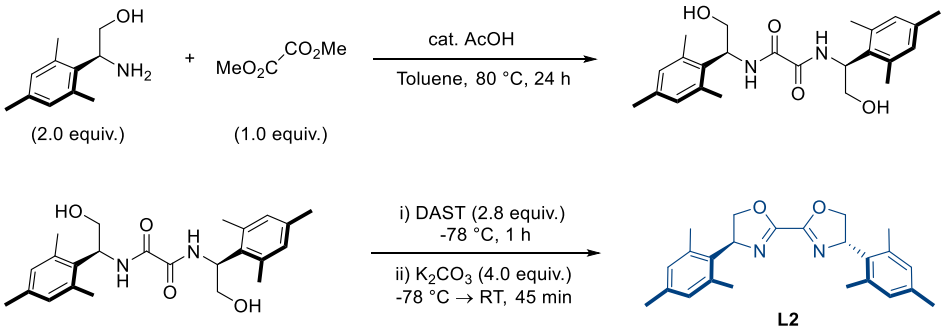
Supplementary Table 8. A Concise Summary of the Effects of Different Parameters



Entry	Deviation	Yield (%)	ee (%)	dr
1[a]	*none*	80 (75)	94	95:5
2	**L1**	40	87	84:16
3	**L3**	22	0	40:60
4	**L4**	trace	n.d.	n.d.
5	**L5**	trace	n.d.	n.d.
6	**L6**	trace	n.d.	n.d.
7	w/o LiCl	73	86	88:12
8	w/o $BF_3{\cdot}OEt_2$	90	95	88:12
9	w/o LiCl + $BF_3{\cdot}OEt_2$	73	82	75:25
10	$NiBr_2$.diglyme	75	92	95:5
11	$NiCl_2.6H_2O$	71	96	88:12
12	DEMS	73	93	87:13
13	LiBr	69	86	87:13
14	BPh_3	16	96	95:5
15	K_2CO_3	18	84	88:12
16	DMF	23	68	82:18

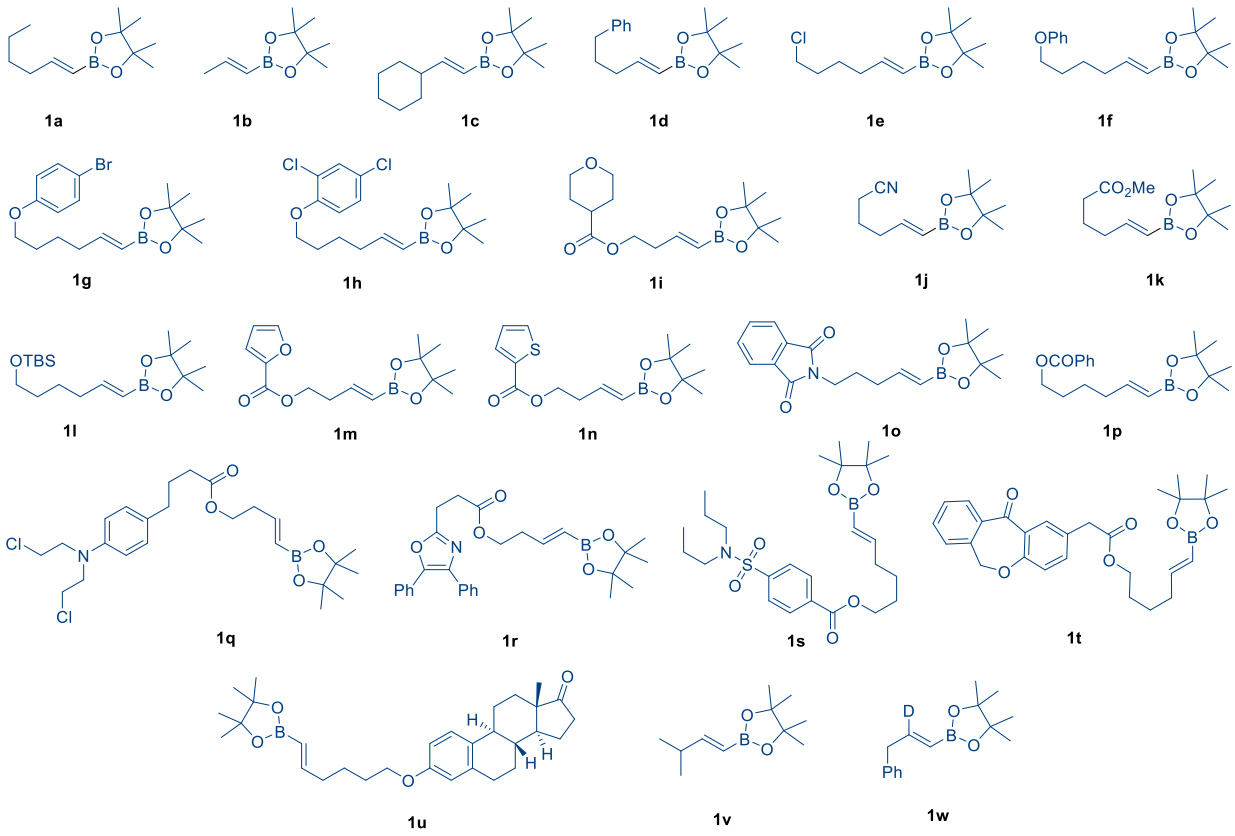
[c]Isolated yield is shown in the parenthesis

3. Synthesis of ligand (L2):



At first (*S*)-2-amino-2-mesitylethan-1-ol was synthesized according to a known literature procedure.[1] Then it was used for the synthesis of chiral ligand **L2** following a slightly modified version of a reported method.[2] To an oven-dried schlenk tube under N_2 atmosphere (*S*)-2-amino-2-mesitylethan-1-ol (1.51 g, 8.46 mmol, 2.0 equiv.) and dimethyloxalate (500 mg, 4.23 mmol, 1.0 equiv.) followed by anhydrous PhMe (40 mL) and catalytic acetic acid (40 µL) were added. The reaction mixture was sealed and stirred at 80 °C for 24 hours. The reaction mixture was then allowed to cool to room temperature and concentrated in vacuum to afford the crude diamide, which was directly used in the next step without further purification. To an oven-dried schlenk tube the diamide (1.47 g, 3.56 mmol, 1.0 equiv.) and DCM (50 mL) were added under N_2 atmosphere. The tube was cooled to -78 °C in a dry-ice/acetone bath, and diethylaminosulfur trifluoride (1.39 mL, 9.97 mmol, 2.8 equiv.) was added dropwise. The reaction mixture was stirred for 1 h, then K_2CO_3 (1.96 g, 14.2 mmol, 4.0 equiv.) was added slowly. The flask was removed from the cold bath and allowed to warm to room temperature. The stirring was continued for an additional 45 minutes. After that, the reaction mixture was diluted with DCM (30 mL) and water (30 mL). The organic layer was washed with aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc (2:1) as eluent to afford the ligand **L2** as a white solid (650 mg, 48%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.84 (s, 4H), 5.85 (t, *J* = 10.8 Hz, 2H), 4.76 (dd, *J* = 10.8, 8.7 Hz, 2H), 4.35 (dd, *J* = 10.8, 8.7 Hz, 2H), 2.30 (s, 12H), 2.25 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 155.41, 137.55, 137.09, 132.40, 130.49, 72.90, 66.80, 20.91, 20.36. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{24}H_{29}N_2O_2^+$ 377.2224; Found 377.2219.

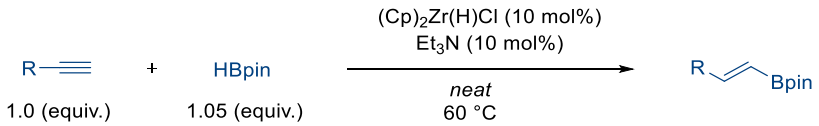
4. Synthesis of alkenyl boronic esters



Supplementary Figure 1. Alkenyl boronic esters

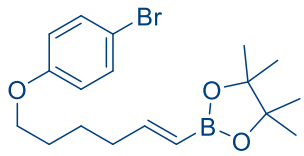
Alkenyl boronic esters **1a** and **1b** are commercially available. Compound **1c**–**1f**[3], **1j**–**1k**[3], **1p**[3], and **1v**[3] were prepared according to previously reported procedures. Alkenyl pinacol boronates **1g**–**1i**, **1l**–**1o**, **1q**, and **1r** were synthesized following the general procedure (**GP3**). Compound **1w** was synthesized following a known literature method.[4]

General Procedure (GP3) for the synthesis of alkenyl boronates:



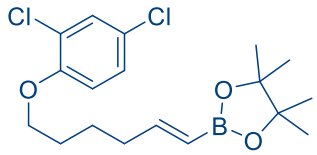
To an oven-dried 30 mL Teflon-screw capped test tube equipped with a magnetic stir were added Schwartz's reagent (136 mg, 0.5 mmol, 0.10 equiv.), pinacolborane (0.78 mL, 5.25 mmol, 1.05 equiv.), alkyne (5.0 mmol, 1.0 equiv.) and Et_3N (70.0 µL, 0.50 mmol, 0.10 equiv.) under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test tube was then sealed with airtight electrical tapes and removed from the glove box and stirred at 60 °C for 24 hours. The reaction was allowed to cool to room temperature, diluted with Et_2O, passed through a pad of silica gel, and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc as eluent to afford the desired compound.

(*E*)-2-(6-(4-Bromophenoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1g):



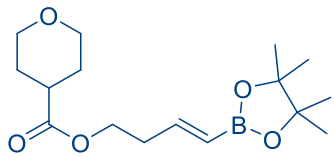
Prepared according to **GP3** from 1-bromo-4-(hex-5-yn-1-yloxy)benzene (1.27 g, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **1g** as a white solid (1.26 g, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.41 – 7.31 (m, 2H), 6.79 – 6.72 (m, 2H), 6.63 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.46 (dt, *J* = 17.9, 1.6 Hz, 1H), 3.91 (t, *J* = 6.4 Hz, 2H), 2.22 (tdd, *J* = 7.5, 6.3, 1.6 Hz, 2H), 1.78 (dq, *J* = 8.7, 6.2 Hz, 2H), 1.65 – 1.55 (m, 2H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.31, 153.95, 132.32, 116.41, 112.74, 83.20, 68.07, 35.46, 28.76, 24.92, 24.70. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 29.85. **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M]^+$ Calcd for $C_{18}H_{26}BBrO_3^+$ 380.1153; Found 380.1155. **M.P.** = < 40 °C.

(*E*)-2-(6-(2,4-Dichlorophenoxy)hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h):



Prepared according to **GP3** from 2,4-dichloro-1-(hex-5-yn-1-yloxy)benzene (1.21 g, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **1h** as a viscous oil (1.32 g, 71%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.34 (d, *J* = 2.5 Hz, 1H), 7.14 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.80 (d, *J* = 8.8 Hz, 1H), 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.46 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 2H), 2.23 (tdd, *J* = 7.5, 6.4, 1.6 Hz, 2H), 1.83 (dq, *J* = 8.4, 6.5 Hz, 2H), 1.68 – 1.57 (m, 2H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 153.89, 153.53, 130.02, 127.58, 125.55, 123.85, 114.09, 83.17, 69.29, 35.40, 28.60, 24.90, 24.62. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 29.30. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{25}BCl_2NaO_3^+$ 393.1166; Found 393.1148.

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl tetrahydro-2H-pyran-4-carboxylate (1i):

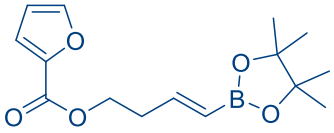


Prepared according to **GP3** from but-3-yn-1-yl tetrahydro-2H-pyran-4-carboxylate (911 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **1i** as a colorless oil (1.19 g, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.54 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.51 (dt, *J* = 18.0, 1.6 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.93 (dt, *J* = 11.5, 3.8 Hz, 2H), 3.41 (ddd, *J* = 11.5, 10.5, 3.2 Hz, 2H), 2.56 – 2.42 (m, 3H), 1.83 – 1.72 (m, 4H), 1.25 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.52, 148.97, 83.34, 67.19, 62.98, 40.17, 35.01, 28.75, 24.87. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 29.25. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{16}H_{28}BO_5^+$ 311.2024; Found 311.2019.

(*E*)-*tert*-Butyldimethyl((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)oxy)silane (1l):

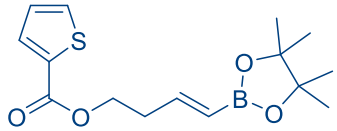
Prepared according to **GP3** from *tert*-butyl(hex-5-yn-1-yloxy)dimethylsilane (1.0g g, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **1l** as a colorless oil (1.31 g, 77%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.62 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.42 (dt, *J* = 17.9, 1.6 Hz, 1H), 3.59 (t, *J* = 6.2 Hz, 2H), 2.16 (tdd, *J* = 6.4, 4.6, 1.6 Hz, 2H), 1.55 – 1.43 (m, 4H), 1.25 (s, 12H), 0.88 (s, 9H), 0.03 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 154.62, 83.12, 63.12, 35.69, 32.47, 26.12, 24.91, 24.60, 18.50, -5.15. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 29.61. **HRMS (APCI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{18}H_{38}BO_3Si^+$ 341.2678; Found 341.2674.

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl furan-2-carboxylate (1m):



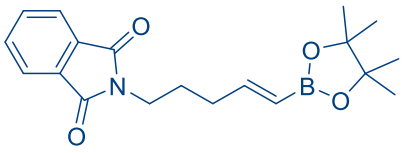
Prepared according to **GP3** from but-3-yn-1-yl furan-2-carboxylate (821 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **1m** as a colorless oil (1.08 g, 74%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.15 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.60 (dt, *J* = 18.0, 6.4 Hz, 1H), 6.48 (dd, *J* = 3.5, 1.8 Hz, 1H), 5.56 (dt, *J* = 18.0, 1.6 Hz, 1H), 4.36 (t, *J* = 6.8 Hz, 2H), 2.59 (qd, *J* = 6.8, 1.6 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.75, 148.65, 146.39, 144.77, 118.03, 111.90, 83.33, 63.52, 34.99, 24.87. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 29.24. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{15}H_{21}BNaO_5^+$ 315.1374; Found 315.1383.

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl thiophene-2-carboxylate (1n):



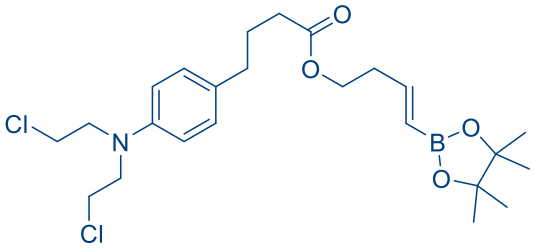
Prepared according to **GP3** from but-3-yn-1-yl thiophene-2-carboxylate (901 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **1n** as a colorless oil (989 mg, 64%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.77 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.61 (dt, *J* = 18.0, 6.5 Hz, 1H), 5.57 (dt, *J* = 18.0, 1.6 Hz, 1H), 4.35 (t, *J* = 6.8 Hz, 2H), 2.59 (qd, *J* = 6.8, 1.6 Hz, 2H), 1.25 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 162.25, 148.76, 133.94, 133.48, 132.44, 127.78, 83.30, 63.70, 35.03, 24.86. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 29.27. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{15}H_{21}BNaO_4S^+$ 331.1146; Found 331.1150.

(*E*)-2-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl)isoindoline-1,3-dione (1o):



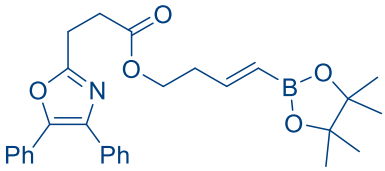
Prepared according to **GP3** from 2-(pent-4-yn-1-yl)isoindoline-1,3-dione (1.10 g, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **1o** as a white solid (1.0 g, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 – 7.79 (m, 2H), 7.73 – 7.67 (m, 2H), 6.60 (dt, *J* = 18.0, 6.3 Hz, 1H), 5.46 (dt, *J* = 18.0, 1.6 Hz, 1H), 3.69 (t, *J* = 6.5 Hz, 2H), 2.22 (dtd, *J* = 8.0, 6.5, 1.7 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.23 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.51, 152.67, 134.00, 132.28, 123.33, 83.18, 37.87, 33.19, 27.19, 24.89. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 30.14. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{24}BNNaO_4^+$ 364.1691; Found 364.1698. **M.P.** = 63.7 – 69.0 ºC

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl 4-(4-(bis(2-chloroethyl)amino)phenyl)butanoate (1q):



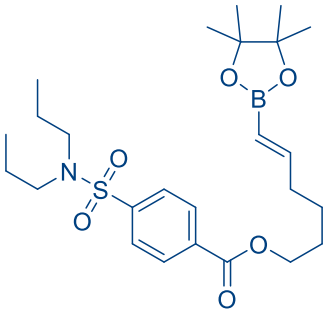
Prepared according to **GP3** from chlorambucil (1.06 g, 3.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **1q** as a colorless viscous oil (914 mg, 63%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.13 – 7.03 (m, 2H), 6.64 – 6.52 (m, 3H), 5.53 (dt, *J* = 18.0, 1.5 Hz, 1H), 4.14 (t, *J* = 6.7 Hz, 2H), 3.72 – 3.67 (m, 4H), 3.63 – 3.59 (m, 4H), 2.55 (t, *J* = 7.5 Hz, 2H), 2.48 (qd, *J* = 6.7, 1.6 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 1.89 (p, *J* = 7.5 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.65, 149.15, 144.40, 130.75, 129.83, 112.26, 83.32, 62.91, 53.73, 40.63, 35.00, 34.09, 33.70, 26.84, 24.89. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 29.19. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{24}H_{37}BCl_2NO_4^+$ 484.2187; Found 484.2196.

(*E*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl 3-(4,5-diphenyloxazol-2-yl)propanoate (1r):



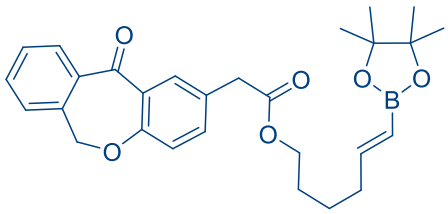
Prepared according to **GP3** from oxaprozin (1.04 g, 3.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **1r** as a colorless viscous oil (960 mg, 68%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.61 (m, 2H), 7.58 – 7.55 (m, 2H), 7.39 – 7.29 (m, 7H), 6.57 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.54 (dt, *J* = 18.0, 1.6 Hz, 1H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.21 – 3.14 (m, 2H), 2.91 (dd, *J* = 8.6, 6.7 Hz, 2H), 2.50 (qd, *J* = 6.7, 1.6 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.09, 161.86, 148.90, 145.53, 135.25, 132.59, 129.11, 128.76, 128.67, 128.55, 128.16, 128.03, 126.60, 83.35, 63.43, 34.93, 31.25, 24.90, 23.65. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 29.70. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{28}H_{33}BNO_5^+$ 474.2446; Found 474.2459.

(*E*)-6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (1s):



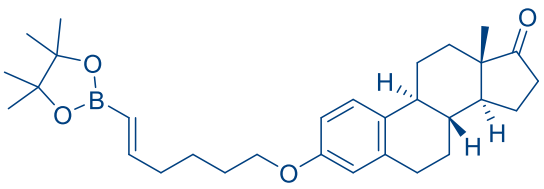
To a stirred solution of probenecid (571 mg, 2.00 mmol, 1.0 equiv.) in dry DCM (8.0 mL) at 0 °C under a N_2 atmosphere was added *N*,*N*′-diisopropylcarbodiimide (0.34 mL, 2.20 mmol, 1.10 equiv.). After 10 minutes, (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-ol (452 mg, 2.00 mmol, 1.0 equiv.) was added to it. The resulting reaction mixture was allowed to warm to room temperature and the stirring was continued overnight. The solution was diluted with DCM and filtered through a plug of silica gel. The solvent was removed in vacuo. The crude product was purified by flash column chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain **1s** as a white solid (649 mg, 66%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.16 – 8.11 (m, 2H), 7.88 – 7.83 (m, 2H), 6.61 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.45 (dt, *J* = 17.9, 1.6 Hz, 1H), 4.33 (t, *J* = 6.5 Hz, 2H), 3.12 – 3.04 (m, 4H), 2.22 (tdd, *J* = 7.6, 6.5, 1.6 Hz, 2H), 1.84 – 1.73 (m, 2H), 1.62 – 1.47 (m, 6H), 1.25 (s, 12H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 165.38, 153.59, 144.23, 133.80, 130.29, 127.09, 83.21, 65.57, 50.06, 35.30, 28.27, 24.89, 24.69, 22.05, 11.27. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 29.25. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{40}BNNaO_6S^+$ 516.2562; Found 516.2569.

(*E*)-6-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (1t):



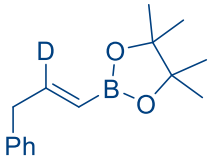
To a stirred solution of isoxepac (536 mg, 2.00 mmol, 1.0 equiv.) in dry DCM (8.0 mL) at 0 °C under a N_2 atmosphere was added *N*,*N*′-diisopropylcarbodiimide (0.34 mL, 2.20 mmol, 1.1 equiv.). After 10 minutes, (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-ol (452 mg, 2.00 mmol, 1.0 equiv.) was added to it. The resulting reaction mixture was allowed to warm to room temperature and the stirring was continued overnight. The solution was diluted with DCM and filtered through a plug of silica gel. The solvent was removed in vacuo. The crude product was purified by flash column chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain **1t** as a white solid (324 mg, 34%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 (td, *J* = 7.6, 1.4 Hz, 1H), 7.47 (td, *J* = 7.6, 1.4 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.59 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.43 (dt, *J* = 18.0, 1.6 Hz, 1H), 5.19 (s, 2H), 4.09 (t, *J* = 6.6 Hz, 2H), 3.63 (s, 2H), 2.17 (tdd, *J* = 7.6, 6.4, 1.6 Hz, 2H), 1.69 – 1.60 (m, 2H), 1.52 – 1.41 (m, 2H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.98, 171.62, 160.59, 153.80, 140.62, 136.48, 135.70, 132.88, 132.58, 129.64, 129.39, 128.06, 127.92, 125.25, 121.18, 83.20, 73.78, 65.03, 40.39, 35.33, 28.19, 24.92, 24.61. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 30.82. HRMS (ESI/QTOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{35}O_6^+$ 479.2428; Found 479.2423. **M.P.** = 142.5 – 144.5 ºC.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(((*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl)oxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (1u):



A mixture of estrone (405 mg, 1.50 mmol, 1.0 equiv.), (*E*)-2-(6-bromohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (477 mg, 1.65 mmol, 1.1 equiv.) and K_2CO_3 (621 mg, 4.50 mmol, 3.0 equiv.) in anhydrous MeCN (4.0 mL) under N_2 atmosphere was heated at 85 °C for 24 hours. Then the mixture was allowed to cool to room temperature and diluted with EtOAc (15 mL) and water (15 mL). The organic phase was separated and the aqueous phase was extracted with EtOAc (3x10 mL). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, 30:1 hexane:EtOAc) to obtain **1u** as a white solid (600 mg, 84%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.18 (dd, *J* = 8.7, 1.1 Hz, 1H), 6.72 – 6.59 (m, 3H), 5.46 (dt, *J* = 18.0, 1.5 Hz, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 2.92 – 2.86 (m, 2H), 2.55 – 2.46 (m, 1H), 2.43 – 2.35 (m, 1H), 2.28 – 1.92 (m, 7H), 1.82 – 1.73 (m, 2H), 1.66 – 1.52 (m, 5H), 1.49 – 1.39 (m, 3H), 1.27 (s, 12H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 221.12, 157.24, 154.13, 137.82, 132.00, 126.42, 114.69, 112.27, 83.18, 67.75, 50.57, 48.17, 44.14, 38.53, 36.03, 35.52, 31.74, 29.79, 28.95, 26.72, 26.07, 24.92, 24.79, 21.74, 14.00. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 30.65. **HRMS (APPI/LTQ-Orbitrap) m/z:** $[M]^+$ Calcd for $C_{30}H_{43}BO_4^+$ 478.3249; Found 478.3257.

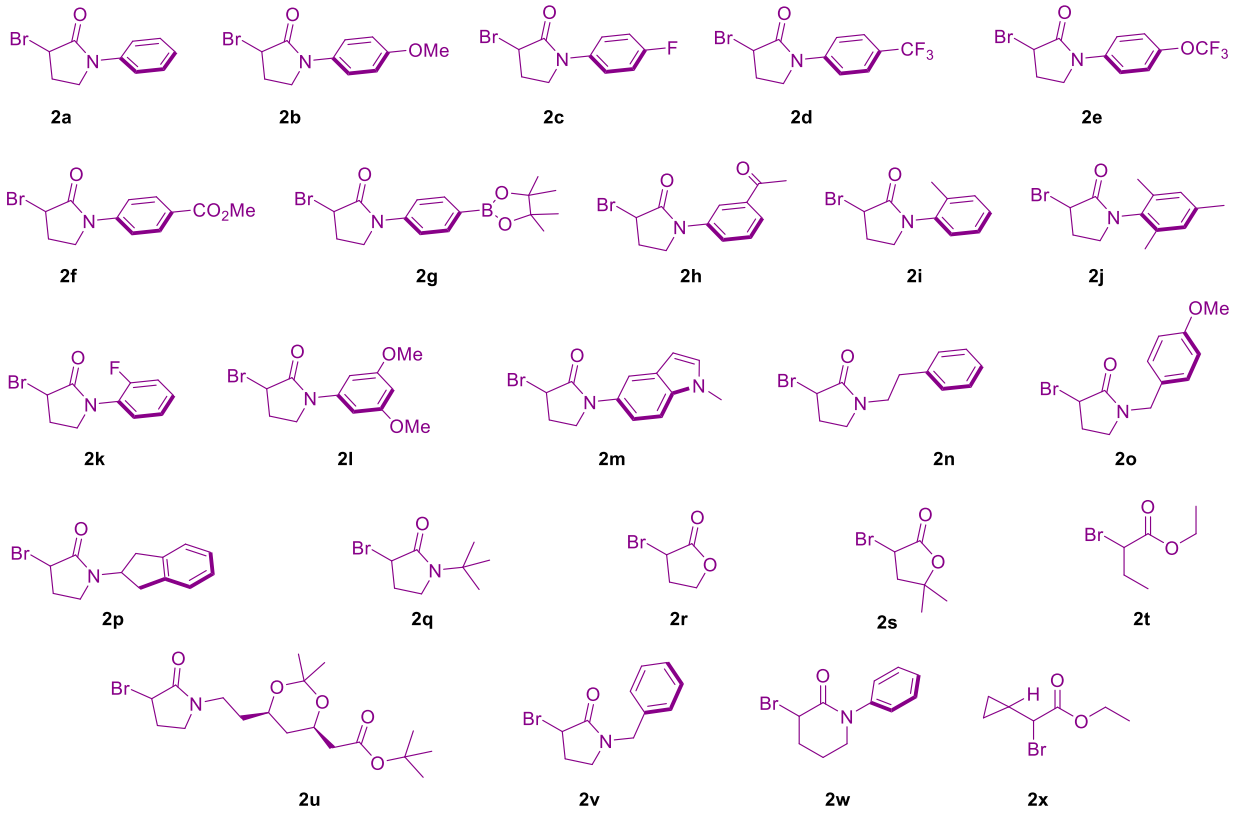
(*E*)-4,4,5,5-Tetramethyl-2-(3-phenylprop-1-en-1-yl-2-d)-1,3,2-dioxaborolane (1w):



The title compound was synthesized from 2-phenylacetaldehyde-1-d following a known literature procedure.[4] At first 2-phenylacetaldehyde-1-d was prepared then it was used in the synthesis of **1w**.[5]

In a N_2 filled glove box, an oven-dried schelnk flask with a magnetic stir bar was charged with LiTMP (889 mg, 6.0 mmol, 1.2 equiv.). The flask was sealed with a septum cap, and removed from the glovebox. Anhydrous THF (6 mL) was added to the flask under N_2 atmosphere and the mixture was cooled to 0 ℃. A solution of bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methane (1.61 g, 6.0 mmol, 1.2 equiv.) in THF (10 mL) was added slowly to the solution. The reaction mixture was stirred for 5 minutes at 0 ℃. After that, it was cooled to -78 ℃. A solution of 2-phenylacetaldehyde-1-d (606 mg, 5.0 mmol, 1 equiv.) in THF (6 mL) was added to the reaction mixture. After 4 hours of stirring at this temperature, the reaction mixture was concentrated under reduced pressure to remove the volatiles. The crude mixture was purified by flash column chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain **1w** as a yellowish oil (370 mg, 41%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.05 (m, 5H), 5.36 (s, 1H), 3.39 (s, 2H), 1.17 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 152.36, 152.12, 151.88, 137.85, 128.95, 128.45, 126.55, 83.12, 40.37, 24.85. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{15}H_{20}DBO_2^+$ 246.1775; Found 246.1779.

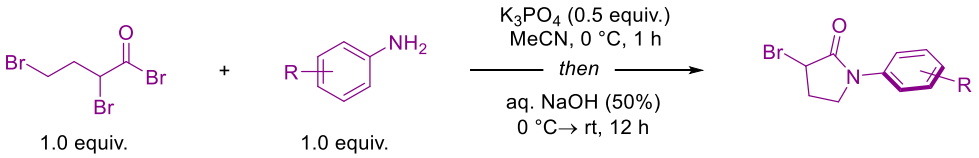
5. Preparation of racemic alkyl halides:



Supplementary Figure 2. Racemic alkyl bromides

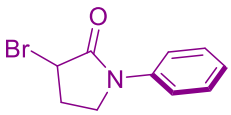
Compounds **2a**–**2m** were synthesized following a slightly modified literature procedure.[6] Compounds **2n**–**2q**, **2u**, and **2v** were prepared according to the general procedure (**GP5**). **2w** was prepared following a known literature procedure.[6] Alkyl bromides **2r**, **2t**, and **2x** were purchased from commercial sources.

General Procedure (GP4) for the synthesis of 2a–2m:



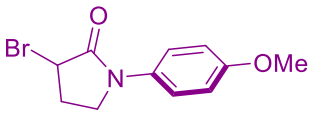
2,4-Dibromobutyryl chloride (0.73 mL, 5.00 mmol, 1.0 equiv.) was added over 10 minutes to a mixture of an amine (5.00 mmol, 1.0 equiv.) and anhydrous K_3PO_4 (504 mg, 2.50 mmol, 0.5 equiv.) in MeCN (50 mL) at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 1 h, and then freshly prepared aqueous NaOH (50%; 1.0 mL) was added. The reaction mixture was left on the ice bath and stirred overnight. The mixture was then filtered, and the solid was washed with DCM (50 mL). The combined organic layers were concentrated in vacuum. The crude mixture was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc as eluent to afford the desired compound.

3-Bromo-1-phenylpyrrolidin-2-one (2a):



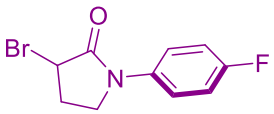
Prepared according to **GP4** using aniline (0.45 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **2a** as a white solid (807 mg, 67%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.66 – 7.60 (m, 2H), 7.42 – 7.36 (m, 2H), 7.23 – 7.17 (m, 1H), 4.58 (dd, *J* = 7.0, 2.9 Hz, 1H), 4.05 (ddd, *J* = 9.9, 7.9, 6.7 Hz, 1H), 3.83 (ddd, *J* = 9.9, 7.9, 2.7 Hz, 1H), 2.72 (dtd, *J* = 14.8, 7.9, 7.0 Hz, 1H), 2.45 (ddt, *J* = 14.8, 6.7, 2.8 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.63, 138.95, 129.12, 125.48, 120.19, 46.83, 45.55, 30.08. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{10}H_{10}BrNNaO^+$ 261.9838; Found 261.9837. **M.P.** = 101 – 102 ºC.

3-Bromo-1-(4-methoxyphenyl)pyrrolidin-2-one (2b):



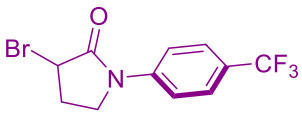
Prepared according to **GP4** using aniline (615 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 4:1 hexane:EtOAc) afforded the desired product **2b** as a white solid (800 mg, 59%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.55 – 7.50 (m, 2H), 6.95 – 6.88 (m, 2H), 4.57 (dd, *J* = 7.0, 2.8 Hz, 1H), 4.01 (ddd, *J* = 9.9, 7.8, 6.7 Hz, 1H), 3.82 – 3.74 (m, 4H), 2.72 (dtd, *J* = 14.8, 7.9, 7.0 Hz, 1H), 2.49 – 2.40 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.37, 157.29, 132.10, 122.04, 114.31, 55.63, 47.25, 45.57, 30.18. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{11}H_{13}BrNO_2^+$ 270.0124; Found 270.0120. **M.P.** = 109.9 – 111.9 ºC.

3-Bromo-1-(4-fluorophenyl)pyrrolidin-2-one (2c):



Prepared according to **GP4** using 4-fluoroaniline (0.48 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2c** as a white solid (935 mg, 72%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 – 7.57 (m, 2H), 7.11 – 7.04 (m, 2H), 4.58 (dd, *J* = 7.0, 2.8 Hz, 1H), 4.03 (ddd, *J* = 9.8, 7.9, 6.7 Hz, 1H), 3.80 (ddd, *J* = 9.8, 7.9, 2.8 Hz, 1H), 2.73 (dtd, *J* = 14.8, 7.8, 7.0 Hz, 1H), 2.45 (ddt, *J* = 14.4, 6.7, 2.8 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.62, 160.09 (d, *J* = 245.5 Hz), 135.03 (d, *J* = 3.0 Hz), 122.06 (d, *J* = 8.1 Hz), 115.88 (d, *J* = 22.4 Hz), 47.10, 45.22, 30.06. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -116.33. **HRMS (ESI/Ion Trap) m/z:** $[M + H]^+$ Calcd for $C_{10}H_{10}BrFNO^+$ 257.9924; Found 257.9923. **M.P.** = 67.1 – 72.1 ºC.

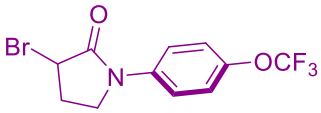
3-Bromo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one (2d):



Prepared according to **GP4** using 4-(trifluoromethyl)aniline (0.73 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2d** as a white solid (986 mg, 64%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.77 (m, 2H), 7.66 – 7.62 (m, 2H), 4.60 (dd, *J* = 6.9, 2.8 Hz, 1H), 4.08 (ddd, *J* = 9.7, 7.9, 6.9 Hz, 1H), 3.86 (ddd, *J* = 9.7, 7.8, 2.7 Hz, 1H), 2.76 (dtd, *J* = 14.8, 7.9, 6.9 Hz, 1H), 2.48 (ddt, *J* = 14.8, 6.9, 2.8 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.09, 141.89, 127.02 (q, *J* = 32.9 Hz), 126.30 (q, *J* = 3.8 Hz), 124.07 (q, *J* = 271.7 Hz), 119.59, 46.56, 44.94, 29.89. **^{19}F NMR (376 MHz,**

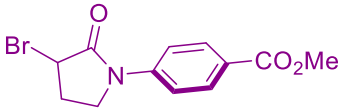
Chloroform-*d*) δ -62.27. **HRMS (ESI/QTOF) m/z:** [M + H]$^+$ Calcd for $C_{11}H_{10}BrF_3NO^+$ 307.9892; Found 307.9898. **M.P.** = 55.1 – 60.2 ºC.

3-Bromo-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-one (2e):



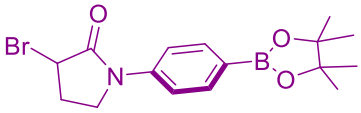
Prepared according to **GP4** using 4-(trifluoromethoxy)aniline (0.68 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **2e** as a white solid (876 mg, 54%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.72 – 7.67 (m, 2H), 7.28 – 7.22 (m, 2H), 4.59 (dd, *J* = 7.0, 2.8 Hz, 1H), 4.05 (ddd, *J* = 9.8, 7.9, 6.7 Hz, 1H), 3.83 (ddd, *J* = 9.8, 7.9, 2.8 Hz, 1H), 2.74 (dtd, *J* = 14.8, 7.9, 7.0 Hz, 1H), 2.47 (ddt, *J* = 14.8, 6.7, 2.8 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.79, 146.13 (d, *J* = 2.1 Hz), 137.56, 121.77, 121.28, 120.55 (d, *J* = 257.2 Hz), 46.81, 45.06, 29.96. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.07. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** [M + H]$^+$ Calcd for $C_{11}H_{10}BrF_3NO_2^+$ 323.9842; Found 323.9836. **M.P.** = 40.0 – 40.8 ºC.

Methyl 4-(3-bromo-2-oxopyrrolidin-1-yl)benzoate (2f):



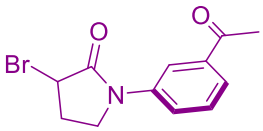
Prepared according to **GP4** using methyl 4-aminobenzoate (756 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2f** as a white solid (939 mg, 63%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 – 8.02 (m, 2H), 7.78 – 7.71 (m, 2H), 4.59 (dd, *J* = 7.0, 2.9 Hz, 1H), 4.08 (ddd, *J* = 9.8, 7.9, 6.7 Hz, 1H), 3.94 – 3.83 (m, 4H), 2.81 – 2.68 (m, 1H), 2.52 – 2.43 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.03, 166.55, 142.88, 130.73, 126.56, 119.04, 52.26, 46.56, 45.08, 29.89. **HRMS (ESI/QTOF) m/z:** [M + H]$^+$ Calcd for $C_{12}H_{13}BrNO_3^+$ 298.0073; Found 298.0079. **M.P.** = 129.0 – 130.2 ºC.

3-Bromo-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolidin-2-one (2g):



Prepared according to **GP4** using methyl 4-aminophenylboronic acid pinacol ester (547 mg, 2.50 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 4:1 hexane:EtOAc) afforded the desired product **2g** as a white solid (676 mg, 74%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.88 – 7.80 (m, 2H), 7.69 – 7.63 (m, 2H), 4.59 (dd, *J* = 7.0, 3.0 Hz, 1H), 4.06 (ddd, *J* = 9.8, 7.8, 6.7 Hz, 1H), 3.85 (ddd, *J* = 9.8, 7.8, 3.0 Hz, 1H), 2.73 (dtd, *J* = 14.7, 7.8, 7.0 Hz, 1H), 2.45 (ddt, *J* = 14.7, 6.7, 3.0 Hz, 1H), 1.34 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.73, 141.48, 135.78, 118.90, 83.99, 46.64, 45.49, 30.03, 25.00. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 31.78. **HRMS (ESI/QTOF) m/z:** [M + Na]$^+$ Calcd for $C_{16}H_{21}BBrNNaO_3^+$ 388.0690; Found 388.0691. **M.P.** = 141.5 – 147.3 ºC.

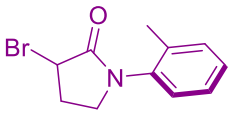
1-(3-Acetylphenyl)-3-bromopyrrolidin-2-one (2h):



Prepared according to **GP4** using 3′-aminoacetophenone (676 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2h** as a white solid (857 mg, 61%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.12 – 8.11 (m, 1H), 8.02 – 7.99 (m, 1H), 7.77 – 7.74 (m, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 4.59 (dd, *J* = 7.1, 2.8 Hz, 1H), 4.09

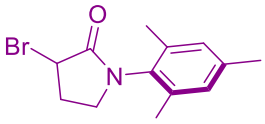
(ddd, *J* = 9.8, 7.8, 6.7 Hz, 1H), 3.88 (ddd, *J* = 9.8, 7.8, 2.8 Hz, 1H), 2.75 (dtd, *J* = 14.4, 7.8, 7.1 Hz, 1H), 2.61 (s, 3H), 2.47 (ddt, *J* = 14.4, 6.7, 2.8 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 197.74, 169.95, 139.43, 137.84, 129.42, 125.25, 124.68, 119.09, 46.73, 45.16, 29.95, 26.83. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{13}BrNO_2^+$ 282.0124; Found 282.0118. **M.P.** = 49.8 – 52.6 ºC.

3-Bromo-1-(o-tolyl)pyrrolidin-2-one (2i):



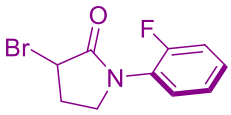
Prepared according to **GP4** using 2-toluidine (0.53 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2i** as a colorless viscous oil (987 mg, 78%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.33 – 7.25 (m, 3H), 7.21 – 7.16 (m, 1H), 4.59 (dd, *J* = 6.9, 2.1 Hz, 1H), 3.96 (ddd, *J* = 10.2, 8.3, 6.3 Hz, 1H), 3.68 (ddd, *J* = 10.2, 7.9, 2.1 Hz, 1H), 2.83 (dtd, *J* = 14.8, 8.3, 6.9 Hz, 1H), 2.50 (ddt, *J* = 14.8, 6.3, 2.0 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.88, 136.44, 135.84, 131.40, 128.48, 127.03, 126.58, 48.81, 44.66, 31.19, 17.72. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{11}H_{13}BrNO^+$ 254.0175; Found 254.0174.

3-Bromo-1-mesitylpyrrolidin-2-one (2j):



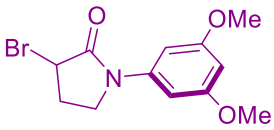
Prepared according to **GP4** using 2,4,6-trimethylaniline (0.70 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2j** as a white solid (990 mg, 76%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.91 (s, 2H), 4.55 (dd, *J* = 6.8, 1.6 Hz, 1H), 3.87 (ddd, *J* = 10.4, 8.7, 6.1 Hz, 1H), 3.47 (ddd, *J* = 10.4, 7.9, 1.6 Hz, 1H), 2.80 (dddd, *J* = 14.6, 8.7, 7.9, 6.8 Hz, 1H), 2.48 (ddt, *J* = 14.6, 6.0, 1.6 Hz, 1H), 2.28 (s, 3H), 2.25 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.94, 138.53, 136.27, 135.38, 132.08, 129.70, 129.43, 47.08, 44.45, 31.41, 21.10, 17.68, 17.52. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{13}H_{17}BrNO^+$ 282.0488; Found 282.0491. **M.P.** = 93.0 – 96.6 ºC.

3-Bromo-1-(2-fluorophenyl)pyrrolidin-2-one (2k):



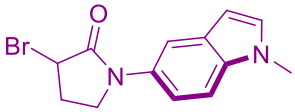
Prepared according to **GP4** using 2-fluoroaniline (0.37 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2k** as a white solid (873 mg, 68%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.46 – 7.42 (m, 1H), 7.33 – 7.24 (m, 1H), 7.22 – 7.12 (m, 2H), 4.56 (dd, *J* = 7.0, 2.6 Hz, 1H), 4.05 – 3.96 (m, 1H), 3.80 (ddd, *J* = 10.0, 7.7, 2.6 Hz, 1H), 2.78 (dq, *J* = 15.2, 7.7 Hz, 1H), 2.46 (ddt, *J* = 14.4, 6.5, 2.6 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.41, 157.12 (d, *J* = 250.8 Hz), 129.04 (d, *J* = 8.0 Hz), 127.70 (d, *J* = 1.6 Hz), 125.65 (d, *J* = 11.5 Hz), 124.69 (d, *J* = 3.6 Hz), 116.82 (d, *J* = 19.8 Hz), 48.09 (d, *J* = 4.6 Hz), 43.96, 31.05. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -120.16. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{10}H_{10}BrFNO^+$ 257.9924; Found 257.9922. **M.P.** = 77.0 – 80.5 ºC.

3-Bromo-1-(3,5-dimethoxyphenyl)pyrrolidin-2-one (2l):



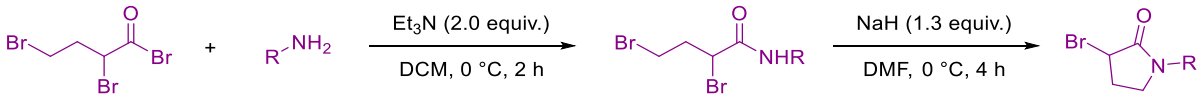
Prepared according to **GP4** using 3,5-dimethoxyaniline (766 mg, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 2:1 hexane:EtOAc) afforded the desired product **2l** as a white solid (1.12 g, 75%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.88 (d, *J* = 2.2 Hz, 2H), 6.31 (t, *J* = 2.2 Hz, 1H), 4.58 (dd, *J* = 7.1, 3.0 Hz, 1H), 4.03 – 3.96 (m, 1H), 3.83 – 3.79 (m, 7H), 2.71 (dtd, *J* = 14.3, 7.8, 7.1 Hz, 1H), 2.43 (ddt, *J* = 14.3, 6.8, 3.0 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.81, 161.08, 140.73, 98.61, 97.52, 55.61, 47.04, 45.68, 29.94. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{15}BrNO_3^+$ 300.0230; Found 300.0224. **M.P.** = 72.5 – 80.5 ºC.

3-Bromo-1-(1-methyl-1H-indol-5-yl)pyrrolidin-2-one (2m):



Prepared according to **GP4** using 1-methyl-1H-indol-5-amine (438 mg, 3.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 2:1 hexane:EtOAc) afforded the desired product **2m** as a white solid (643 mg, 73%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.73 – 7.70 (m, 1H), 7.52 – 7.48 (m, 1H), 7.34 – 7.29 (m, 1H), 7.07 (d, *J* = 3.1 Hz, 1H), 6.48 (dd, *J* = 3.1, 0.9 Hz, 1H), 4.61 (dd, *J* = 7.1, 2.8 Hz, 1H), 4.09 (ddd, *J* = 10.1, 7.8, 6.6 Hz, 1H), 3.86 (ddd, *J* = 10.1, 7.8, 2.8 Hz, 1H), 3.79 (s, 3H), 2.80 – 2.70 (m, 1H), 2.46 (ddt, *J* = 14.3, 6.6, 2.8 Hz, 1H). ^{13}C NMR (101 MHz, **Chloroform-*d***) δ 169.50, 134.89, 131.27, 130.11, 128.49, 116.13, 113.76, 109.56, 101.35, 48.22, 46.02, 33.11, 30.39. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{13}H_{14}BrN_2O^+$ 293.0284; Found 293.0277. **M.P.** = 124.0 – 127.2 ºC.

General Procedure (GP5) for the synthesis of 2n–2q, 2u, and 2v:

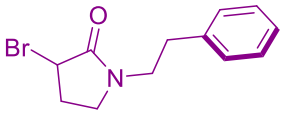


To a solution of an alkyl amine (5.00 mmol, 1.0 equiv.) and Et_3N (1.34 mL, 10.0 mmol, 2.0 equiv.) in DCM (20 mL) was added 2,4-dibromobutyryl chloride (0.73 mL, 5.00 mmol, 1.0 equiv.) over 10 minutes at 0 °C under N_2 atmosphere. The reaction mixture was stirred for 2 h until the full conversion of amine as checked by TLC. The mixture was then diluted with DCM (20 mL) and water (30 mL) and the organic layer was separated. The aqueous phase was extracted with DCM (3x20 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude amide was directly used in the next step without further purification.

An oven dried schlenk tube was charged with a crude amide (~5.00 mmol, 1.0 equiv.) and anhydrous DMF (15 mL) at 0 °C under N_2 atmosphere. Then NaH (60% in mineral oil, 260 mg, 6.50 mmol, 1.3 equiv.) was added portion-wise over 10 minutes. The reaction mixture was stirred for 4 h at this temperature until the full conversion of the amide as was checked by TLC. The mixture was then carefully quenched with aq. NH_4Cl and diluted with EtOAc (20 mL) and water

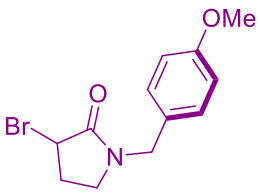
(60 mL), and the organic layer was separated. The aqueous phase was extracted with DCM (3x20 mL). The combined organic layers were washed with water (50 mL), brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The crude mixture was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc as eluent to afford the desired compound.

3-Bromo-1-phenethylpyrrolidin-2-one (2n):



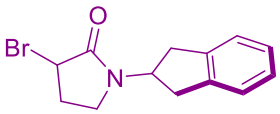
Prepared according to **GP5** using phenethylamine (0.63 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2n** as a white solid (756 mg, 56% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.33 – 7.27 (m, 3H), 7.23 – 7.20 (m, 3H), 4.37 (dd, *J* = 7.2, 2.6 Hz, 1H), 3.68 – 3.56 (m, 1H), 3.51 (dt, *J* = 13.9, 7.3 Hz, 1H), 3.36 (tdd, *J* = 9.4, 7.3, 6.4 Hz, 1H), 3.12 (ddd, *J* = 10.1, 7.9, 2.6 Hz, 1H), 2.87 (t, *J* = 7.3 Hz, 2H), 2.53 – 2.42 (m, 1H), 2.22 (ddt, *J* = 14.4, 6.7, 2.6 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.63, 138.45, 128.79, 128.70, 126.71, 45.98, 44.91, 44.46, 33.60, 30.48. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{12}H_{14}BrNNaO^+$ 290.0151; Found 290.0160. **M.P.** = 50.7 – 52.5 ºC.

3-Bromo-1-(4-methoxybenzyl)pyrrolidin-2-one (2o):



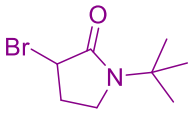
Prepared according to **GP5** using 4-methoxybenzylamine (0.65 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 2:1 hexane:EtOAc) afforded the desired product **2o** as a white solid (646 mg, 45% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.21 – 7.14 (m, 2H), 6.91 – 6.84 (m, 2H), 4.52 – 4.43 (m, 2H), 4.36 (d, *J* = 14.5 Hz, 1H), 3.80 (s, 3H), 3.40 (ddd, *J* = 10.0, 7.7, 6.7 Hz, 1H), 3.18 (ddd, *J* = 10.0, 7.9, 2.4 Hz, 1H), 2.54 (dq, *J* = 14.5, 7.9 Hz, 1H), 2.27 (ddt, *J* = 14.5, 6.7, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, **Chloroform-*d***) δ 170.69, 159.41, 129.62, 127.81, 114.30, 55.42, 46.71, 44.56, 30.28. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{12}H_{15}BrNO_2^+$ 284.0281; Found 284.0276. **M.P.** = 65.6 – 68.3 ºC.

3-Bromo-1-(2,3-dihydro-1H-inden-2-yl)pyrrolidin-2-one (2p):



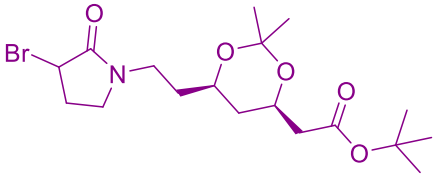
Prepared according to **GP5** using 2-aminoindan (0.67 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2p** as a white solid (586 mg, 42% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.26 – 7.16 (m, 4H), 5.06 (tt, *J* = 7.8, 4.6 Hz, 1H), 4.42 (dd, *J* = 7.1, 2.5 Hz, 1H), 3.33 – 3.19 (m, 3H), 3.07 (ddd, *J* = 10.2, 7.8, 2.5 Hz, 1H), 2.92 (ddd, *J* = 20.7, 16.5, 4.7 Hz, 2H), 2.48 (dtd, *J* = 14.4, 7.8, 7.1 Hz, 1H), 2.24 (ddt, *J* = 14.4, 6.6, 2.5 Hz, 1H). ^{13}C NMR (101 MHz, **Chloroform-*d***) δ 170.55, 140.78, 140.75, 127.10, 127.06, 124.53, 124.40, 52.16, 44.82, 41.59, 37.11, 36.52, 30.40. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{13}H_{15}BrNO^+$ 280.0332; Found 280.0327. **M.P.** = 95.0 – 98.4 ºC.

3-Bromo-1-(*tert*-butyl)pyrrolidin-2-one (2q):



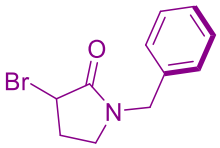
Prepared according to **GP5** using *tert*-butylamine (0.54 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2q** as a white solid (410 mg, 37% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.33 (dd, *J* = 6.9, 2.6 Hz, 1H), 3.60 – 3.53 (m, 1H), 3.43 (ddd, *J* = 10.0, 7.7, 2.3 Hz, 1H), 2.50 – 2.39 (m, 1H), 2.21 (ddt, *J* = 14.3, 6.4, 2.6 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.88, 54.72, 47.37, 43.86, 30.15, 27.44. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_8H_{14}BrNNaO^+$ 242.0151; Found 242.0147. **M.P.** = < 40 ºC.

***tert*-Butyl 2-((4R,6R)-6-(2-(3-bromo-2-oxopyrrolidin-1-yl)ethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (2u):**



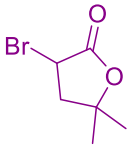
Prepared according to **GP5** using *tert*-butyl 2-[(4*R*,6*R*)-6-(2-Aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl]acetate (1.39 g, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2u** as a sticky oil (820 mg, 57% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.38 (ddd, *J* = 7.3, 4.8, 2.5 Hz, 1H), 4.24 – 4.19 (m, 1H), 3.93 – 3.84 (m, 1H), 3.61 – 3.43 (m, 2H), 3.33 – 3.28 (m, 2H), 2.60 – 2.51 (m, 1H), 2.39 (ddd, *J* = 15.1, 7.3, 1.5 Hz, 1H), 2.32 – 2.25 (m, 2H), 1.71 – 1.64 (m, 2H), 1.57 (ddt, *J* = 17.5, 12.7, 2.5 Hz, 1H), 1.45 – 1.41 (m, 12H), 1.34 – 1.33 (m, 3H), 1.24 – 1.13 (m, 1H). **13C NMR (101 MHz, Chloroform-*d*)** δ 170.71, 170.26, 98.91, 80.74, 66.82, 66.72, 66.21, 45.61, 45.39, 44.69, 42.78, 42.76, 39.93, 39.82, 36.56, 36.38, 33.81, 33.63, 30.51, 30.48, 30.19, 28.20, 19.82, 19.79. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{18}H_{30}BrNNaO_5^+$ 442.1200; Found 442.1206.

1-Benzyl-3-bromopyrrolidin-2-one (2v):



Prepared according to **GP5** using benzylamine (0.55 mL, 5.00 mmol, 1.0 equiv.). Flash column chromatography (SiO_2, 2:1 hexane:EtOAc) afforded the desired product **2v** as a white solid (663 mg, 52% over two steps). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.12 (m, 5H), 4.44 (d, *J* = 14.7 Hz, 1H), 4.40 – 4.29 (m, 2H), 3.32 (ddd, *J* = 10.1, 7.7, 6.7 Hz, 1H), 3.10 (ddd, *J* = 10.1, 8.0, 2.5 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.18 (ddt, *J* = 14.5, 6.7, 2.5 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.79, 135.71, 128.91, 128.16, 127.95, 47.22, 44.67, 44.38, 30.25. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{11}H_{13}BrNO^+$ 254.0175; Found 254.0171. **M.P.** = 40.0 – 45.8 ºC.

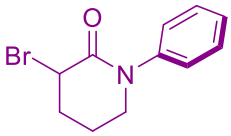
Synthesis of 3-bromo-5,5-dimethyldihydrofuran-2(3H)-one (2s):



The title compound was synthesized from the corresponding γ,γ-dimethyl-γ-butyrolactone. To a solution of lithium diisopropylamide (1M, 10.5 mL, 10.5 mmol, 1.05 equiv.) in anhydrous THF (10 mL) at -78 °C under N_2 atmosphere was added a solution of γ,γ-dimethyl-γ-butyrolactone (1.14 g, 10.0 mmol, 1.0 equiv.) in anhydrous THF (5 mL) dropwise over 3 minutes. After 45 minutes of stirring at -78 °C, TMSCl (1.36 mL, 10.8 mmol, 1.08 equiv.) was added dropwise via syringe over 1 min. The

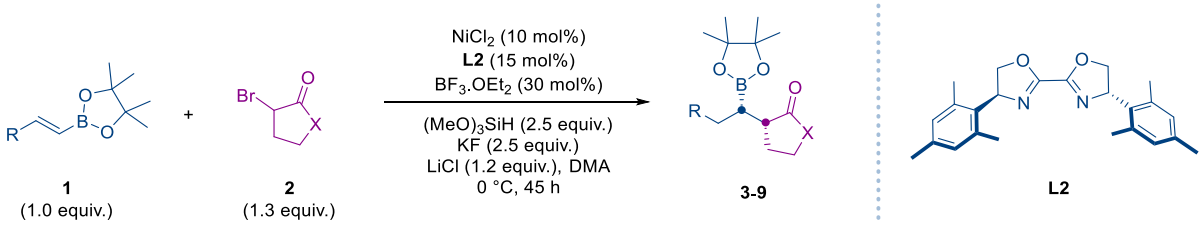
reaction mixture was stirred at -78 °C for 1 h, then it was allowed to slowly warm to room temperature over ~2 h. Next, the reaction mixture was cooled to 0 °C and NBS (2.66 g, 15.0 mmol, 1.5 equiv.) was added as a solid in five portions. The mixture was stirred at 0 °C for 2 h, and then the reaction was quenched by the addition of a saturated aq. $Na_2S_2O_3$ (20 mL). The mixture was extracted with DCM (2x25 mL), and the combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by flash column chromatography (SiO_2, 6:1 hexane:EtOAc) to afford the desired compound **2s** as a brownish oil (990 mg, 52%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 4.61 (dd, *J* = 8.7, 6.6 Hz, 1H), 2.72 (dd, *J* = 14.2, 8.7 Hz, 1H), 2.45 (dd, *J* = 14.2, 6.6 Hz, 1H), 1.60 (s, 3H), 1.44 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.38, 84.38, 45.39, 38.32, 28.51, 28.39. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_6H_9BrNaO_2^+$ 214.9678; Found 214.9681.

Synthesis of 3-bromo-1-phenylpiperidin-2-one (2w):



The title compound was synthesized from the corresponding 1-phenylpiperidin-2-one.[6] To a solution of 1-phenylpiperidin-2-one (876 mg, 5.0 mmol, 1.0 equiv.) in anhydrous THF (100 mL) at -78 °C under N_2 atmosphere was added sec-BuLi (1.4 M, 3.9 mL, 5.5 mmol, 1.1 equiv.) dropwise over 5 minutes. After 30 minutes of stirring at -78 °C, the mixture further cooled down to -100 °C and Br_2 (0.26 mL, 5.0 mmol, 5.0 equiv.) was added over 2 minutes. The reaction was immediately quenched at -100 °C by the addition of water (5 mL). The reaction mixture was allowed to slowly warm to room temperature, and then it was washed with saturated aq. $Na_2S_2O_3$ (20 mL) and then with aq. NH_4Cl (10 mL). The organic layer was dried over Na_2SO_4, and concentrated in vacuo. The crude mixture was purified by flash column chromatography (SiO_2, 2:1 hexane:EtOAc) to afford the desired compound **2w** as a white solid (1.13 g, 89%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.32 – 7.24 (m, 2H), 7.19 – 7.11 (m, 3H), 4.59 – 4.57 (m, 1H), 3.73 – 3.64 (m, 1H), 3.62 – 3.55 (m, 1H), 2.40 – 2.22 (m, 3H), 1.86 – 1.81 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.36, 142.77, 129.31, 127.21, 125.88, 51.37, 45.90, 31.52, 19.52. **HRMS (nanochip-ESI/LTQ-Orbitrap) m/z:** $[M + H]^+$ Calcd for $C_{11}H_{13}BrNO^+$ 254.0175; Found 254.0172.

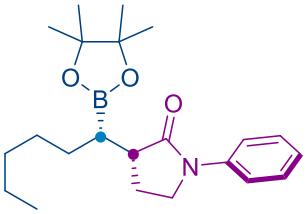
6. General Procedure (GP6) for probing the scope of enantio- and diastereoselective alkyl–alkyl cross-coupling reaction:



To an oven-dried 10 mL Teflon-screw capped vial was added $NiCl_2$ (2.6 mg, 0.02 mmol, 0.10 equiv.) and ligand **L2** (11.2 mg, 0.03 mmol, 0.15 equiv.). The vial was introduced in a nitrogen-filled glovebox. A magnetic stir bar (6x15 mm), LiCl (10.0 mg, 0.24 mmol, 1.2 equiv.) and anhydrous DMA (1.0 mL) were added and the mixture was stirred for ~1.5 hours at room temperature until it became a clear blue solution. Then racemic electrophile **2** (0.26 mmol, 1.3

equiv.) and anhydrous KF (29.0 mg, 0.50 mmol, 2.5 equiv.) followed by alkenyl boronic acid pinacol ester **1** (0.20 mmol, 1.0 equiv.) were added to it and the resulting mixture was stirred for approximately 1 minute. At this point, $(MeO)_3SiH$ (67.0 µL, 0.50 mmol, 2.5 equiv.) was added dropwise to it followed by the addition of $BF_3.OEt_2$ (7.2 µL, 0.06 mmol, 0.30 equiv.). The test tube was then sealed with airtight electrical tapes, removed from the glove box immediately, and stirred in an ice-water bath at 0 °C for 45 hours, maintaining 600 rpm. After that, the reaction was quenched by the addition of aqueous NH_4Cl (1.0 mL) and EtOAc (3.0 mL). The aqueous phase was extracted with EtOAc (3x3.0 mL). The combined organic phases were concentrated in vacuum. The crude reaction mixture was then subjected to flash column chromatography by using a mixture of hexane and EtOAc as eluent to obtain **3** – **9**.

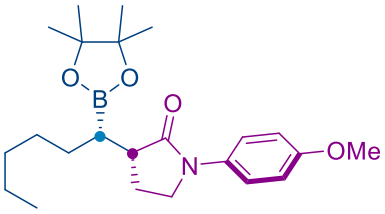
(*R*)-1-Phenyl-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3aa):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.) and **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3aa** as a white solid (56 mg, 75%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.66 – 7.59 (m, 2H), 7.36 – 7.32 (m, 2H), 7.15 – 7.04 (m, 1H), 3.84 – 3.69 (m, 2H), 2.79 (td, *J* = 9.4, 4.4 Hz, 1H), 2.28 – 2.13 (m, 1H), 2.02 (dq, *J* = 12.6, 9.4 Hz, 1H), 1.63 – 1.55 (m, 2H), 1.45 – 1.25 (m, 7H), 1.20 (s, 12H), 0.88 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.34, 140.07, 128.79, 128.76, 124.05, 119.83, 119.68, 83.15, 46.99, 44.53, 32.12, 28.89, 28.41, 24.92, 24.83, 23.25, 22.70, 14.17. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.41. **FTIR (neat):** $\tilde{\nu}$ = 2923.6, 2854.9, 1693.9, 1499.3, 1388.2, 1311.7, 1267.4, 1224.2, 1142.5, 757.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{22}H_{35}BNO_3^+$ 372.2705; Found 372.2699. $\mathbf{[\alpha]_D^{20}}$ = +42.0 (c = 1.00 in $CHCl_3$). **M.P.** = 50.0 – 54.8 ºC.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 9.0 min and t_{minor} = 15.0 min.

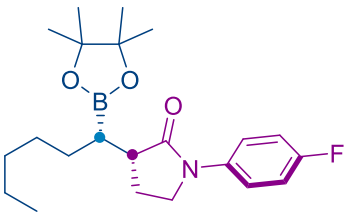
(*R*)-1-(4-Methoxyphenyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3ab):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2b** (70.2 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ab** as a white solid (66 mg, 82%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.52 – 7.49 (dd, *J* = 8.8, 1.4 Hz, 2H), 6.91 – 6.82 (m, 2H), 3.77 (s, 3H), 3.77 – 3.63 (m, 2H), 2.83 – 2.67 (m, 1H), 2.24 – 2.11 (m, 1H), 2.07 – 1.94 (m, 1H), 1.62 – 1.50 (m, 2H), 1.47 – 1.26 (m, 7H), 1.19 (s, 12H), 0.87 (t, *J* = 6.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.94, 156.27, 133.37, 121.56, 113.97, 83.10, 55.51, 47.35, 44.23, 32.10, 28.87, 28.43, 24.89, 24.84, 23.24, 22.67, 14.14. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 32.99. **FTIR (neat):** $\tilde{\nu}$ = 2924.0, 2854.9, 1686.7, 1510.8, 1388.7, 1319.4, 1246.0, 1143.1, 1036.1, 829.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{23}H_{37}BNO_4^+$ 402.2810; Found 402.2817. **$[\alpha]_D^{20}$** = +39.5 (c = 1.00 in $CHCl_3$). **M.P.** = 82.9 – 87.8 ºC.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 13.1 min and t_{minor} = 38.2 min.

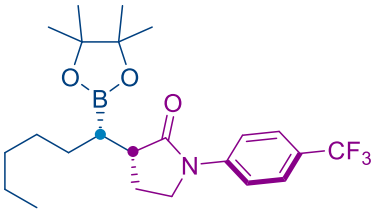
(*R*)-1-(4-Fluorophenyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3ac):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2c** (67.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3ac** as a white solid (59 mg, 76%) in 97:3 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.59 – 7.54 (m, 2H), 7.05 – 6.96 (m, 2H), 3.79 – 3.64 (m, 2H), 2.78 (td, *J* = 9.3, 4.1 Hz, 1H), 2.24 – 2.14 (m, 1H), 2.07 – 1.95 (m, 1H), 1.61 – 1.54 (m, 2H), 1.40 – 1.24 (m, 7H), 1.19 (s, 12H), 0.87 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.28, 160.51, 158.10, 136.18, 136.15, 121.52, 121.45, 115.49, 115.27, 83.17, 47.24, 44.27, 32.10, 28.86, 28.38, 24.90, 24.83, 23.15, 22.68, 14.15. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.27. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -118.59. **FTIR (neat):** $\tilde{\nu}$ = 2922.5, 2853.2, 1680.9, 1508.6, 1394.3, 1317.8, 1223.5, 1143.5, 829.9 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{22}H_{34}BFNO_3^+$ 390.2610; Found 390.2612. **$[\alpha]_D^{20}$** = +33.7 (c = 1.00 in $CHCl_3$). **M.P.** = 78.9 – 82.5 ºC.

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (97:3) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 5.4 min and t_{minor} = 6.6 min.

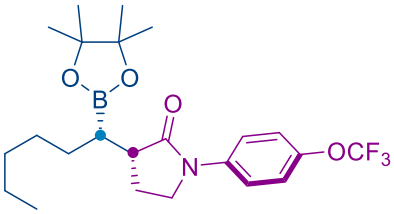
(*R*)-3-((*S*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-(4-(trifluoromethyl)phenyl)pyrrolidin-2-one ((+) 3ad):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2d** (80.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(+) 3ad** as a white solid (57 mg, 65%) in 97:3 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.77 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 3.83 – 3.72 (m, 2H), 2.82 (td, *J* = 9.5, 4.4 Hz, 1H), 2.26 – 2.18 (m, 1H), 2.10 – 2.00 (m, 1H), 1.64 – 1.53 (m, 2H), 1.45 – 1.26 (m, 7H), 1.19 (s, 12H), 0.88 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.00, 142.96, 126.04, 126.00, 125.96, 125.92, 125.75, 125.70, 125.42, 125.10, 83.27, 46.81, 44.57, 32.10, 28.86, 28.35, 24.94, 24.81, 23.05, 22.71, 14.18. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.29. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.06. **FTIR (neat):** $\tilde{\nu}$ = 2924.9, 2856.8, 1686.4, 1611.4, 1518.9, 1388.6, 1315.1, 1268.5, 1161.8, 1145.3, 1115.9, 842.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{23}H_{34}BF_3NO_3^+$ 440.2578; Found 440.2588. $\mathbf{[\alpha]_D^{20}}$ = +43.8 (c = 1.00 in $CHCl_3$). **M.P.** = 107.7 – 112.5 ºC.

HPLC: The enantiomeric excess (92%) and diastereomeric ratio (97:3) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 5.8 min and t_{minor} = 6.4 min.

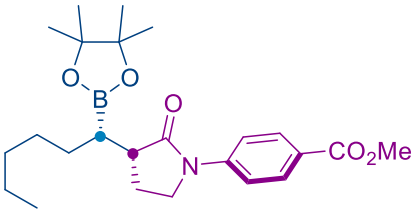
(*R*)-3-((*S*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-(4-(trifluoromethoxy)phenyl)pyrrolidin-2-one ((+) 3ae):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2e** (84.3 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ae** as a white solid (59 mg, 65%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.70 – 7.61 (m, 2H), 7.23 – 7.11 (m, 2H), 3.81 – 3.68 (m, 2H), 2.80 (td, *J* = 9.4, 4.6 Hz, 1H), 2.25 – 2.16 (m, 1H), 2.10 – 1.97 (m, 1H), 1.65 – 1.49 (m, 2H), 1.47 – 1.27 (m, 7H), 1.20 (s, 12H), 0.88 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.58, 145.16, 138.71, 121.91, 121.53, 120.77, 120.68, 119.36, 83.25, 47.06, 44.42, 32.13, 28.89, 28.36, 24.94, 24.85, 23.15, 22.72, 14.19. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.84. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -58.08. **FTIR (neat):** $\tilde{\nu}$ = 2924.9, 2856.6, 1682.4, 1508.2, 1390.2, 1321.4, 1257.2, 1221.4, 1161.1, 1118.6, 848.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{33}BF_3NNaO_4^+$ 478.2347; Found 478.2356. $\mathbf{[\alpha]_D^{20}}$ = +31.0 (c = 1.00 in $CHCl_3$). **M.P.** = 81.5 – 86.0 ºC.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 12.1 min and t_{minor} = 14.0 min.

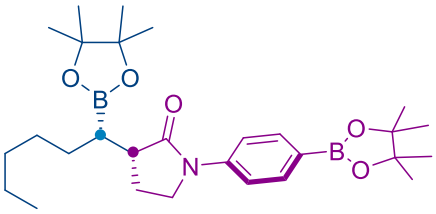
Methyl 4-((*R*)-2-oxo-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-1-yl)benzoate ((+) 3af):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2f** (77.5 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3af** as a white solid (59 mg, 69%) in 98:2 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.03 – 7.97 (m, 2H), 7.74 – 7.69 (m, 2H), 3.87 (s, 3H), 3.79 – 3.75 (m, 2H), 2.80 (td, *J* = 9.4, 4.3 Hz, 1H), 2.20 (ddt, *J* = 12.7, 9.4, 5.1 Hz, 1H), 2.03 (dq, *J* = 12.7, 9.3 Hz, 1H), 1.62 – 1.51 (m, 2H), 1.42 – 1.23 (m, 7H), 1.17 (s, 12H), 0.86 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.98, 166.81, 144.00, 130.47, 125.09, 118.54, 83.20, 52.02, 46.79, 44.61, 32.06, 28.82, 28.31, 24.89, 24.76, 22.97, 22.66, 14.14. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 32.69. **FTIR (neat):** $\tilde{\nu}$ = 2955.8, 2922.6, 2854.0, 1715.4, 1689.2, 1605.2, 1514.7, 1428.5, 1384.3, 1321.4, 1272.8, 1223.2, 1189.5, 1140.1, 1112.7, 964.8, 850.1, 772.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{24}H_{37}BNO_5^+$ 430.2759; Found 430.2768. $\mathbf{[\alpha]_D^{20}}$ = +63.0 (c = 1.00 in $CHCl_3$). **M.P.** = 124.2 – 130.5 ºC.

HPLC: The enantiomeric excess (95%) and diastereomeric ratio (98:2) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 9.1 min and t_{minor} = 10.6 min.

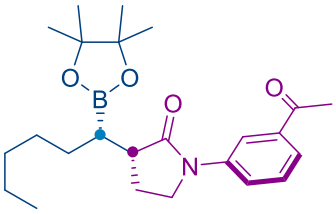
(*R*)-3-((*S*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolidin-2-one ((+) 3ag):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2g** (94.9 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3ag** as a white solid (51 mg, 51%) in 90:10 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.74 (m, 2H), 7.69 – 7.57 (m, 2H), 3.79 – 3.73 (m, 2H), 2.85 – 2.74 (m, 1H), 2.21 – 2.16 (m, 1H), 2.09 – 1.95 (m, 1H), 1.65 – 1.51 (m, 2H), 1.38 – 1.26 (m, 19H), 1.18 (s, 12H), 0.88 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.62, 142.64, 135.55, 135.52, 118.55, 83.77, 83.18, 46.84, 44.64, 32.11, 28.88, 28.45, 24.98, 24.95, 24.92, 24.81, 23.12, 22.70, 14.18. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 30.50. **FTIR (neat):** $\tilde{\nu}$ = 2976.4, 2924.6, 2855.5, 1684.1, 1605.5, 1387.2, 1359.5, 1313.8, 1268.8, 1218.2, 1142.3, 1087.5, 963.6, 860.8, 830.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{28}H_{45}B_2NNaO_5^+$ 520.3376; Found 520.3396. $\mathbf{[\alpha]_D^{20}}$ = +37.7 (c = 1.00 in $CHCl_3$). **M.P.** = 143.1 – 147.2 ºC.

HPLC: The enantiomeric excess (91%) and diastereomeric ratio (90:10) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 15.1 min and t_{minor} = 19.6 min.

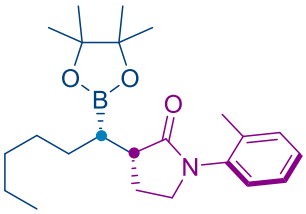
(*R*)-1-(3-Acetylphenyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3ah):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2h** (73.3 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3ah** as a sticky oil (42 mg, 51%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (s, 1H), 8.03 – 7.98 (m, 1H), 7.70 – 7.68 (m, 1H), 7.45 – 7.40 (m, 1H), 3.90 – 3.73 (m, 2H), 2.81 (td, *J* = 9.4, 4.3 Hz, 1H), 2.60 (s, 3H), 2.27 – 2.16 (m, 1H), 2.09 – 1.99 (m, 1H), 1.69 – 1.50 (m, 2H), 1.42 – 1.27 (m, 7H), 1.19 (s, 12H), 0.87 (t, *J* = 6.2 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 198.16, 176.81, 140.49, 137.66, 129.06, 124.49, 123.94, 118.90, 83.23, 46.99, 44.48, 32.09, 28.85, 28.40, 26.82, 24.93, 24.82, 23.13, 22.70, 14.17. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 35.03. **FTIR (neat):** $\tilde{\nu}$ = 2923.4, 2854.5, 1684.2, 1598.6, 1582.9, 1485.5, 1445.6, 1380.4, 1317.9, 1247.0, 1215.9, 1142.6, 965.6, 858.3, 792.2 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{36}BNNaO_4^+$ 436.2630; Found 436.2633. **$[\alpha]_D^{20}$** = +37.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 37.7 min and t_{minor} = 50.3 min.

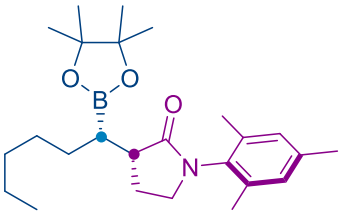
(*R*)-3-((*S*)-1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-(o-tolyl)pyrrolidin-2-one ((+) 3ai):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2i** (66.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ai** as a sticky oil (53 mg, 69%) in 92:8 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 6.97 (m, 4H), 3.71 – 3.55 (m, 2H), 2.77 (td, *J* = 9.5, 4.7 Hz, 1H), 2.28 – 2.19 (m, 4H), 2.16 – 2.02 (m, 1H), 1.62 – 1.56 (m, 1H), 1.50 – 1.28 (m, 8H), 1.23 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.27, 138.25, 135.87, 131.10, 127.53, 126.69, 126.65, 83.17, 48.98, 43.04, 32.11, 28.79, 28.56, 25.00, 24.86, 24.68, 22.70, 18.17, 14.18. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 32.64. **FTIR (neat):** $\tilde{\nu}$ = 2923.2, 2855.1, 1693.4, 1494.4, 1460.7, 1371.9, 1313.5, 1267.1, 1142.1, 966.0, 857.0, 763.2 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{36}BNNaO_3^+$ 408.2680; Found 408.2670. **$[\alpha]_D^{20}$** = +15.3 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (92:8) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 21.2 min and t_{minor} = 26.4 min.

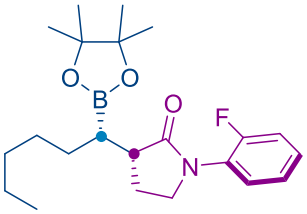
(*R*)-1-Mesityl-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3aj):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2j** (73.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3aj** as a sticky oil (60 mg, 73%) in 89:11 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.88 (d, *J* = 3.8 Hz, 2H), 3.53 – 3.43 (m, 2H), 2.74 (ddd, *J* = 10.6, 8.5, 4.9 Hz, 1H), 2.25 (s, 3H), 2.22 – 2.17 (m, 4H), 2.15 – 2.09 (m, 4H), 1.67 – 1.52 (m, 2H), 1.51 – 1.28 (m, 7H), 1.22 (s, 12H), 0.89 (t, *J* = 6.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.20, 137.52, 136.08, 135.93, 133.84, 129.20, 129.18, 83.14, 47.23, 42.73, 32.16, 28.79, 28.62, 25.09, 24.98, 24.76, 22.70, 21.05, 17.84, 17.81, 14.18. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.27. **FTIR (neat):** $\tilde{\nu}$ = 2924.4, 2857.4, 1689.8, 1489.8, 1405.2, 1378.5, 1316.1, 1268.4, 1144.1, 966.0, 851.6, 752.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{25}H_{41}BNO_3^+$ 414.3174; Found 414.3186. $\mathbf{[\alpha]_D^{20}}$ = +16.3 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (89:11) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 18.5 min and t_{minor} = 22.8 min.

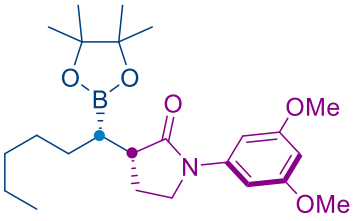
(*R*)-1-(2-Fluorophenyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3ak):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2k** (67.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ak** as a sticky oil (55 mg, 71%) in 91:9 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.45 (td, *J* = 7.7, 1.8 Hz, 1H), 7.23 – 7.05 (m, 3H), 3.81 (tdd, *J* = 9.3, 7.8, 1.6 Hz, 1H), 3.68 (td, *J* = 9.3, 2.8 Hz, 1H), 2.76 (dt, *J* = 9.3, 4.6 Hz, 1H), 2.27 – 2.19 (m, 1H), 2.05 (dq, *J* = 12.4, 9.0 Hz, 1H), 1.62 – 1.56 (m, 2H), 1.51 – 1.28 (m, 7H), 1.23 (s, 12H), 0.89 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.88, 158.41, 155.93, 128.05, 128.03, 127.88, 127.83, 127.80, 127.75, 127.13, 127.02, 124.39, 124.36, 116.70, 116.50, 83.24, 48.33, 48.29, 42.87, 32.14, 28.84, 28.55, 25.09, 24.98, 24.91, 24.43, 22.74, 14.20. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.25. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -120.08. **FTIR (neat):** $\tilde{\nu}$ = 2923.3, 2854.7, 1701.2, 1611.2, 1589.5, 1503.7, 1458.4, 1379.4, 1318.9, 1267.7, 1240.1, 1143.2, 1109.0, 966.4, 857.4, 755.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{22}H_{33}BFNNaO_3^+$ 412.2430; Found 412.2423. $\mathbf{[\alpha]_D^{20}}$ = +29.4 (c = 0.94 in $CHCl_3$).

HPLC: The enantiomeric excess (92%) and diastereomeric ratio (91:9) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 17.3 min and t_{minor} = 23.5 min.

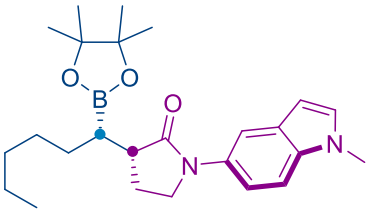
(*R*)-1-(3,5-Dimethoxyphenyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3al):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2l** (78.0 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3al** as a sticky oil (64 mg, 76%) in 97:3 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 6.89 (s, 2H), 6.24 (s, 1H), 3.77 (s, 6H), 3.73 – 3.70 (m, 2H), 2.77 (td, *J* = 9.3, 4.5 Hz, 1H), 2.21 – 2.13 (m, 1H), 2.05 – 1.95 (m, 1H), 1.62 – 1.53 (m, 2H), 1.43 – 1.28 (m, 7H), 1.19 (s, 12H), 0.87 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.61, 160.85, 141.88, 98.20, 96.39, 83.19, 55.48, 47.25, 44.86, 32.09, 28.89, 28.47, 24.93, 24.81, 23.11, 22.70, 14.17. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.13. **FTIR (neat):** $\tilde{\nu}$ = 2924.1, 2854.5, 1696.2, 1596.0, 1459.9, 1388.0, 1321.1, 1271.0, 1245.3, 1206.9, 1151.8, 1060.9, 967.0, 833.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{38}BNNaO_5^+$ 454.2735; Found 454.2740. $\mathbf{[\alpha]_D^{20}}$ = +42.7 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (97:3) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 9.4 min and t_{minor} = 24.2 min.

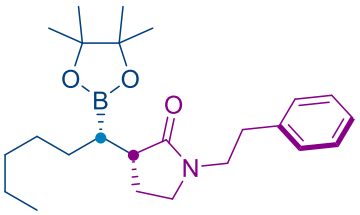
(*R*)-1-(1-Methyl-1H-indol-5-yl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3am):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2m** (76.2 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3am** as a white solid (54 mg, 64%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (d, *J* = 2.0 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.03 (d, *J* = 3.1 Hz, 1H), 6.44 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.86 (dt, *J* = 9.1, 7.9 Hz, 1H), 3.80 – 3.73 (m, 4H), 2.82 (td, *J* = 9.4, 4.9 Hz, 1H), 2.26 – 2.18 (m, 1H), 2.10 – 1.96 (m, 1H), 1.67 – 1.56 (m, 2H), 1.51 – 1.29 (m, 7H), 1.22 (d, *J* = 2.0 Hz, 12H), 0.89 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.01, 134.34, 132.65, 129.57, 128.42, 116.39, 113.06, 109.19, 101.13, 83.15, 48.32, 44.34, 33.05, 32.18, 28.96, 28.58, 24.95, 23.54, 22.75, 14.21. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.05. **FTIR (neat):** $\tilde{\nu}$ = 2923.6, 2855.4, 1681.9, 1574.5, 1490.8, 1454.3, 1422.9, 1402.3, 1371.8, 1313.1, 1269.2, 1247.0, 1234.7, 1143.2, 966.5, 854.7, 799.8, 755.9 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{25}H_{38}BN_2O_3^+$ 425.2970; Found 425.2971. $\mathbf{[\alpha]_D^{20}}$ = +37.6 (c = 0.94 in $CHCl_3$). **M.P.** = 112.0 – 115.8 °C.

HPLC: The enantiomeric excess (91%) and diastereomeric ratio (90:10) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 85:15 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 12.9 min and t_{minor} = 35.7 min.

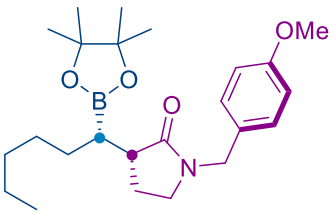
(*R*)-1-Phenethyl-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((+) 3an):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2n** (71.8 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 4:1 hexane:EtOAc) afforded the desired product **(+) 3an** as a sticky oil (58 mg, 73%) in 93:7 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.34 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 3.57 (dt, *J* = 14.6, 7.5 Hz, 1H), 3.45 (dt, *J* = 14.6, 7.5 Hz, 1H), 3.26 – 3.08 (m, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.58 (td, *J* = 9.1, 5.0 Hz, 1H), 2.12 – 2.00 (m, 1H), 1.91 – 1.76 (m, 1H), 1.54 – 1.28 (m, 9H), 1.24 (s, 12H), 0.90 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.77, 139.27, 128.83, 128.56, 126.40, 83.05, 46.14, 44.32, 42.87, 34.04, 32.12, 28.90, 28.38, 24.89, 23.73, 22.69, 14.16. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.30. **FTIR (neat):** $\tilde{\nu}$ = 2922.8, 2854.6, 1682.1, 1604.2, 1494.1, 1455.5, 1426.3, 1371.2, 1318.0, 1268.0, 1214.5, 1144.0, 967.2, 880.2, 857.9, 832.3, 748.2 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{38}BNNaO_3^+$ 422.2837; Found 422.2839. **$[\alpha]_D^{20}$** = +2.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (93:7) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 22.8 min and t_{minor} = 29.9 min.

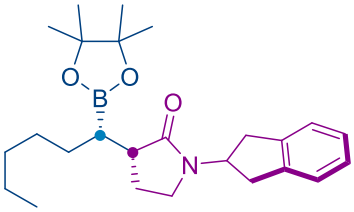
(*R*)-1-(4-Methoxybenzyl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((-) 3ao):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2o** (73.9 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 4:1 hexane:EtOAc) afforded the desired product **(-) 3ao** as a sticky oil (61 mg, 73%) in 92:8 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.19 – 7.14 (m, 2H), 6.85 – 6.79 (m, 2H), 4.52 (d, *J* = 14.6 Hz, 1H), 4.18 (d, *J* = 14.6 Hz, 1H), 3.77 (s, 3H), 3.19 – 3.04 (m, 2H), 2.61 (td, *J* = 9.2, 3.8 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.82 – 1.74 (m, 1H), 1.50 – 1.26 (m, 9H), 1.20 (s, 12H), 0.86 (t, *J* = 6.5 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.76, 158.96, 129.43, 129.21, 113.95, 83.08, 55.34, 46.01, 44.87, 43.00, 32.09, 28.83, 28.53, 24.90, 24.82, 23.56, 22.68, 14.15. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.22. **FTIR (neat):** $\tilde{\nu}$ = 2922.7, 2853.9, 1681.6, 1611.2, 1512.6, 1458.0, 1437.3, 1418.4, 1371.6, 1318.1, 1302.7, 1245.1, 1174.6, 1143.7, 1034.9, 967.1, 847.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{38}BNNaO_4^+$ 438.2786; Found 438.2794. **$[\alpha]_D^{20}$** = -11.9 (c = 0.95 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (92:8) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 44.4 min and t_{minor} = 37.8 min.

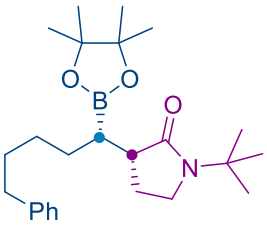
(*R*)-1-(2,3-Dihydro-1H-inden-2-yl)-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidin-2-one ((-) 3ap):



Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2p** (72.8 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(-) 3ap** as a sticky oil (54 mg, 66%) in 91:9 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.23 – 7.12 (m, 4H), 5.07 (td, *J* = 8.1, 4.0 Hz, 1H), 3.20 – 3.12 (m, 2H), 3.09 – 3.03 (m, 2H), 2.89 (dt, *J* = 16.2, 4.7 Hz, 2H), 2.61 – 2.56 (m, 1H), 2.06 – 1.94 (m, 1H), 1.84 – 1.69 (m, 1H), 1.47 – 1.27 (m, 9H), 1.23 (s, 12H), 0.86 (t, *J* = 6.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.61, 141.42, 141.34, 126.73, 126.71, 124.41, 124.29, 83.07, 51.21, 43.10, 41.68, 36.85, 36.35, 32.09, 28.84, 28.44, 24.93, 24.89, 23.53, 22.68, 14.15. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.32. **FTIR (neat):** $\tilde{\nu}$ = 2922.9, 2853.5, 1681.1, 1457.9, 1424.7, 1371.0, 1316.8, 1265.4, 1214.0, 1143.3, 966.8, 857.2, 743.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{38}BNNaO_3^+$ 434.2837; Found 434.2852. **$[\alpha]_D^{20}$** = -9.6 (c = 0.90 in $CHCl_3$).

HPLC: The enantiomeric excess (92%) and diastereomeric ratio (91:9) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 37.4 min and t_{minor} = 26.3 min.

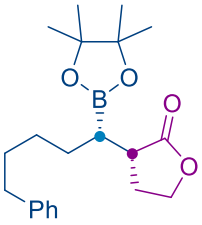
(*R*)-1-(tert-Butyl)-3-((*S*)-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)pyrrolidin-2-one ((+) 3dq):



Prepared according to **GP6** with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2q** (57.2 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3dq** as a sticky oil (56 mg, 68%). **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.38 – 7.31 (m, 2H), 7.26 – 7.22 (m, 3H), 3.54 – 3.45 (m, 1H), 3.36 (q, *J* = 8.4 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.56 (dt, *J* = 9.6, 4.8 Hz, 1H), 2.11 – 2.01 (m, 1H), 1.88 – 1.63 (m, 4H), 1.61 – 1.48 (m, 4H), 1.46 (s, 9H), 1.28 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.22, 143.00, 128.57, 128.30, 125.61, 83.03, 53.70, 44.57, 43.95, 36.01, 31.71, 28.88, 28.77, 27.83, 24.99, 24.89, 23.59. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.71. **FTIR (neat):** $\tilde{\nu}$ = 2973.1, 2923.9, 2854.0, 1680.5, 1455.2, 1404.3, 1370.0, 1318.3, 1285.1, 1247.4, 1215.7, 1143.8, 967.2, 860.4, 746.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{25}H_{41}BNO_3^+$ 414.3174; Found 414.3183. **$[\alpha]_D^{20}$** = +7.5 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (88%) and diastereomeric ratio (83:17) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 14.9 min and t_{minor} = 14.2 min.

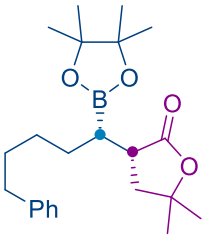
(*R*)-3-((*S*)-5-Phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)dihydrofuran-2(3H)-one ((+) 3dr):



Prepared according to **GP6** with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2r** (29.0 µL, 0.30 mmol, 1.5 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **(+) 3dr** as a sticky oil (49 mg, 68%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.36 – 7.33 (m, 2H), 7.26 – 7.22 (m, 3H), 4.42 (td, *J* = 8.7, 2.8 Hz, 1H), 4.22 (td, *J* = 8.7, 7.3 Hz, 1H), 2.76 – 2.66 (m, 3H), 2.38 – 2.16 (m, 2H), 1.78 – 1.58 (m, 4H), 1.52 – 1.41 (m, 2H), 1.37 – 1.32 (m, 1H), 1.28 (d, *J* = 2.8 Hz, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 179.86, 142.70, 128.51, 128.32, 125.69, 83.51, 66.63, 40.23, 35.85, 31.48, 28.57, 28.53, 27.26, 24.86, 24.73. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.56. **FTIR (neat):** $\tilde{\nu}$ = 2976.4, 2924.4, 2854.8, 1766.9, 1602.9, 1453.9, 1378.9, 1324.0, 1263.6, 1212.6, 1140.8, 1025.3, 967.4, 859.0, 748.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{21}H_{31}BNaO_4^+$ 381.2208; Found 381.2215. $[\alpha]_D^{20}$ = +6.7 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 93:7 at a flow rate 0.5 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 16.5 min and t_{minor} = 19.3 min.

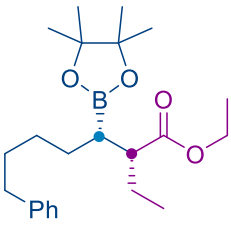
(*R*)-5,5-Dimethyl-3-((*S*)-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)dihydrofuran-2(3H)-one ((+) 3ds:



Prepared according to **GP6** with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2s** (57.9 mg, 0.30 mmol, 1.5 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ds** as a sticky oil (56 mg, 72%) in 92:8 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.24 (m, 2H), 7.18 – 7.14 (m, 3H), 2.89 – 2.83 (m, 1H), 2.63 – 2.59 (m, 2H), 2.09 – 1.92 (m, 2H), 1.67 – 1.62 (m, 2H), 1.57 – 1.51 (m, 2H), 1.45 (s, 3H), 1.41 – 1.37 (m, 2H), 1.35 (s, 3H), 1.28 – 1.25 (m, 1H), 1.20 (d, *J* = 4.5 Hz, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 179.10, 142.73, 128.54, 128.34, 125.71, 83.48, 82.08, 41.60, 39.60, 35.85, 31.48, 28.96, 28.65, 28.51, 27.52, 24.96, 24.73. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.49. **FTIR (neat):** $\tilde{\nu}$ = 2975.3, 2925.9, 2855.1, 1759.8, 1454.0, 1371.8, 1322.8, 1263.4, 1140.8, 1029.8, 954.7, 925.2, 865.5, 847.2, 748.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{35}BNaO_4^+$ 409.2521; Found 409.2529. $[\alpha]_D^{20}$ = +7.5 (c = 0.60 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (92:8) were determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 93:7 at a flow rate 0.3 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 22.9 min and t_{minor} = 27.0 min.

Ethyl (2*R*,3*S*)-2-ethyl-7-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate ((-) 3dt):

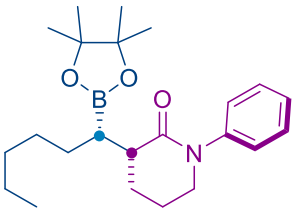


Prepared according to **GP6** with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2t** (44.8 µL, 0.30 mmol, 1.5 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **(-) 3dt** as a clear oil (46 mg, 59%) in 65:35 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 – 7.21 (m, 2H), 7.17 – 7.12 (m, 3H), 4.17 – 4.08 (m, 2H), 2.63 – 2.54 (m, 2H), 2.44 – 2.33 (m, 1H), 1.70 – 1.50 (m, 4H), 1.49 – 1.30 (m, 4H), 1.28 – 1.22 (m, 4H), 1.20 (s, 12H), 0.88 – 0.84 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.54, 176.43, 142.89, 142.83, 128.55, 128.32, 125.65, 83.28, 83.12, 60.10, 59.97, 49.36, 48.43, 35.96, 35.89, 31.77, 31.68, 29.50, 28.84, 28.73, 28.67, 25.39, 25.02, 24.96, 24.92, 24.79, 23.89, 14.54, 14.51, 12.35, 11.76. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.45. **FTIR (neat):** $\tilde{\nu}$ = 2975.6, 2927.0, 2855.9, 1729.1, 1603.9, 1496.1, 1455.7, 1370.1, 1318.7, 1264.5, 1229.9, 1212.9, 1141.2, 1111.0, 1029.1, 965.7, 847.3, 746.2 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{37}BNaO_4^+$ 411.2677; Found 411.2681. **$[\alpha]_D^{20}$** = -9.1 (c = 0.95 in $CHCl_3$).

HPLC: The enantiomeric excess of the major isomer (88%) and diastereomeric ratio (65:35) were determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 99.2:0.8 at a flow rate 0.5 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 14.9 min and t_{minor} = 13.8 min.

The enantiomeric excess of the minor isomer (47%) was determined (after stereospecific oxidation of the boronate to alcohol using $NaBO_3$•$4H_2O$ in THF/H_2O) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at the 210 nm wavelength. Retention time: t_{major} = 10.9 min and t_{minor} = 12.1 min.

(*R*)-1-Phenyl-3-((S)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)piperidin-2-one ((+) 3aw):



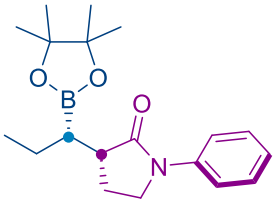
Prepared according to **GP6** with **1a** (50.0 µL, 0.20 mmol, 1.0 equiv.), **2w** (66.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(+) 3aw** as a sticky oil (21 mg, 27%) in 60:40 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.42 – 7.33 (m, 2H), 7.31 – 7.19 (m, 3H), 3.76 – 3.65 (m, 1H), 3.64 – 3.56 (m, 1H), 2.73 – 2.57 (m, 1H), 2.24 – 1.87 (m, 3H), 1.83 – 1.47 (m, 3H), 1.44 – 1.29 (m, 7H), 1.25 (s, 12H), 0.93 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.45, 173.23, 144.22, 143.45, 128.96, 128.84, 126.32, 126.27, 125.88, 82.90, 82.31, 51.65, 51.11, 45.30, 43.54, 32.50, 32.20, 29.04, 28.95, 28.86, 27.52, 26.52, 25.90, 25.28, 25.25, 25.22, 24.85, 23.53, 23.25, 22.79, 22.77, 14.26, 14.25. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 32.89. **FTIR (neat):** $\tilde{\nu}$ = 2952.7, 2925.6, 2857.2, 1645.0, 1594.9, 1493.4, 1458.0, 1417.6, 1376.8, 1350.3, 1302.6, 1144.2, 967.1, 840.5, 757.1 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{36}BNNaO_3^+$ 408.2680; Found 408.2687. **$[\alpha]_D^{20}$** = +17.6 (c = 0.98 in $CHCl_3$).

HPLC: The enantiomeric excess of the major isomer (89%) and diastereomeric ratio (60:40) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with

hexane:isopropanol = 99:1 at a flow rate 0.5 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 31.3 min and t_{minor} = 38.5 min.

The enantiomeric excess of the minor isomer (52%) was determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 99:1 at a flow rate 0.5 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 24.4 min and t_{minor} = 27.2 min.

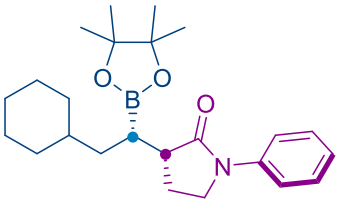
(*R*)-1-Phenyl-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)pyrrolidin-2-one ((+) 3ba):



Prepared according to **GP6** with **1b** (40.0 µL, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3ba** as a white solid (46 mg, 70%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.59 (m, 2H), 7.38 – 7.31 (m, 2H), 7.14 – 7.08 (m, 1H), 3.83 – 3.70 (m, 2H), 2.86 – 2.77 (m, 1H), 2.25 – 2.17 (m, 1H), 2.08 – 1.97 (m, 1H), 1.65 – 1.58 (m, 1H), 1.56 – 1.48 (m, 2H), 1.21 (s, 12H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.38, 140.07, 128.82, 124.14, 119.92, 83.22, 47.06, 44.42, 24.96, 24.88, 23.31, 21.57, 13.91. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.62. **FTIR (neat):** $\tilde{\nu}$ = 2978.1, 2955.7, 2925.6, 2870.8, 1681.0, 1596.8, 1503.1, 1485.4, 1458.6, 1390.5, 1310.7, 1268.1, 1215.3, 1144.8, 966.9, 891.3, 858.2, 757.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{28}BNNaO_3^+$ 352.2054; Found 352.2061. **$[\alpha]_D^{20}$** = +40.6 (c = 0.66 in $CHCl_3$). **M.P.** = n.d.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 27.3 min and t_{minor} = 34.2 min.

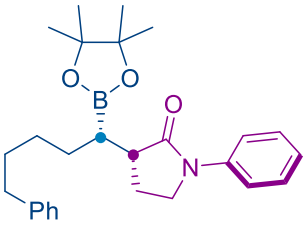
(*R*)-3-((*S*)-2-Cyclohexyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-1-phenylpyrrolidin-2-one ((+) 3ca):



Prepared according to **GP6** with **1c** (47.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 8:1 hexane:EtOAc) afforded the desired product **(+) 3ca** as a white solid (50 mg, 63%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.61 (m, 2H), 7.36 – 7.32 (m, 3H), 7.12 – 7.08 (m, 1H), 3.79 – 3.71 (m, 2H), 2.76 (td, *J* = 9.5, 5.1 Hz, 1H), 2.20 – 2.15 (m, 1H), 2.11 – 1.97 (m, 1H), 1.82 – 1.60 (m, 6H), 1.48 – 1.42 (m, 1H), 1.38 – 1.26 (m, 3H), 1.22 – 1.14 (m, 14H), 0.88 (q, *J* = 10.5, 9.9 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.31, 140.07, 128.76, 124.04, 119.81, 83.13, 46.99, 44.55, 36.58, 35.75, 33.57, 33.47, 26.81, 26.57, 26.52, 24.91, 24.82, 23.05. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.80. **FTIR (neat):** $\tilde{\nu}$ = 2975.3, 2919.4, 2848.9, 1693.1, 1598.3, 1500.0, 1448.3, 1388.3, 1310.5, 1267.9, 1224.8, 1141.9, 966.9, 890.3, 857.5, 757.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{24}H_{36}BNNaO_3^+$ 420.2680; Found 420.2689. **$[\alpha]_D^{20}$** = +20.8 (c = 1.00 in $CHCl_3$). **M.P.** = 99.9 – 105.3 °C.

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 5.6 min and t_{minor} = 8.6 min.

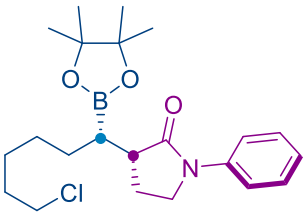
(*R*)-1-Phenyl-3-((*S*)-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)pyrrolidin-2-one ((+) 3da):



Prepared according to **GP6** with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3da** as a white solid (63 mg, 73%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.73 – 7.66 (m, 2H), 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 7.28 – 7.14 (m, 4H), 3.90 – 3.75 (m, 2H), 2.86 (td, *J* = 9.3, 4.5 Hz, 1H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.29 – 2.22 (m, 1H), 2.13 – 2.03 (m, 1H), 1.79 – 1.63 (m, 4H), 1.59 – 1.47 (m, 3H), 1.26 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.22, 142.84, 140.01, 128.75, 128.51, 128.27, 125.61, 124.07, 119.81, 83.17, 46.95, 44.52, 35.92, 31.64, 28.84, 28.28, 24.87, 24.81, 23.28. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.96. **FTIR (neat):** $\tilde{\nu}$ = 2974.8, 2925.3, 2854.8, 1693.5, 1598.4, 1496.2, 1456.5, 1388.9, 1312.3, 1266.6, 1226.0, 1142.8, 967.0, 857.4, 757.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{27}H_{37}BNO_3^+$ 434.2861; Found 434.2877. **$[\alpha]_D^{20}$** = +31.2 (c = 1.00 in $CHCl_3$). **M.P.** =88.5 – 93.4 °C.

HPLC: The enantiomeric excess (91%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 10.9 min and t_{minor} = 13.4 min.

(*R*)-3-((*S*)-6-Chloro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 3ea):

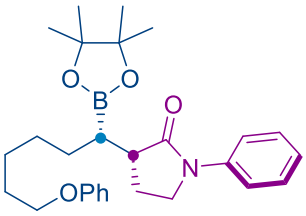


Prepared according to **GP6** with **1e** (49.0 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3ea** as a white solid (59 mg, 73%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.68 – 7.59 (m, 2H), 7.38 – 7.29 (m, 2H), 7.14 – 7.05 (m, 1H), 3.82 – 3.69 (m, 2H), 3.52 (t, *J* = 6.8 Hz, 2H), 2.79 (td, *J* = 9.3, 4.5 Hz, 1H), 2.25 – 2.14 (m, 1H), 2.06 – 1.96 (m, 1H), 1.82 – 1.75 (m, 2H), 1.58 – 1.40 (, 5H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.15, 139.98, 128.77, 124.12, 119.84, 83.23, 46.96, 45.17, 44.53, 32.59, 28.44, 28.17, 27.11, 24.90, 24.84, 23.30. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.92. **FTIR (neat):** $\tilde{\nu}$ = 2975.0, 2926.4, 2856.2, 1692.7, 1598.1, 1497.9, 1460.1, 1388.9, 1311.2, 1268.6, 1225.9, 1142.8, 966.8, 856.1, 758.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{22}H_{34}BClNO_3^+$ 406.2315; Found 406.2324. **$[\alpha]_D^{20}$** = +28.0 (c = 1.00 in $CHCl_3$). **M.P.** = 61.2 – 64.9 °C.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 92:8 at a flow

rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 7.9 min and t_{minor} = 11.9 min.

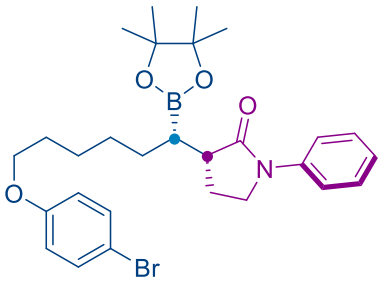
(*R*)-3-((*S*)-6-Phenoxy-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 3fa):



Prepared according to **GP6** with **1f** (60.4 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3fa** as a white solid (69 mg, 74%) in 98:2 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.18 – 7.06 (m, 1H), 6.98 – 6.86 (m, 3H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.84 – 3.69 (m, 2H), 2.82 (td, *J* = 9.4, 4.2 Hz, 1H), 2.27 – 2.16 (m, 1H), 2.09 – 1.99 (m, 1H), 1.86 – 1.78 (m, 2H), 1.55 – 1.42 (m, 5H), 1.21 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.21, 159.19, 140.00, 129.46, 128.76, 124.09, 120.49, 119.83, 114.56, 83.20, 67.85, 46.97, 44.54, 29.28, 28.96, 28.29, 26.28, 24.89, 24.82, 23.26. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 34.09. **FTIR (neat):** $\tilde{\nu}$ = 2974.6, 2926.8, 2856.7, 1693.4, 1598.4, 1495.9, 1388.9, 1311.6, 1243.9, 1143.0, 1032.6, 967.3, 856.7, 755.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + H]$^+$ Calcd for $C_{28}H_{39}BNO_4^+$ 464.2967; Found 464.2967. **$[\alpha]_D^{20}$** = +26.5 (c = 1.00 in $CHCl_3$). **M.P.** = 62.3 – 69.2 °C.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (98:2) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 15.1 min and t_{minor} = 42.2 min.

(*R*)-3-((*S*)-6-(4-Bromophenoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 3ga):

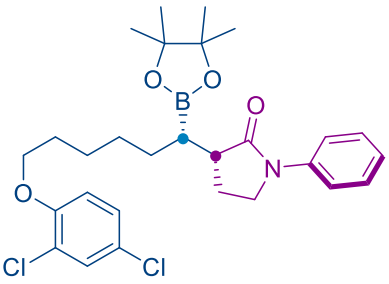


Prepared according to **GP6** with **1g** (76.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3ga** as a white solid (68 mg, 63%) in 97:3 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.59 (m, 2H), 7.37 – 7.32 (m, 4H), 7.15 – 7.07 (m, 1H), 6.80 – 6.72 (m, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.83 – 3.69 (m, 2H), 2.80 (td, *J* = 9.4, 4.6 Hz, 1H), 2.26 – 2.14 (m, 1H), 2.07 – 1.98 (m, 1H), 1.82 – 1.75 (m, 2H), 1.54 – 1.39 (m, 5H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.19, 158.33, 139.98, 132.24, 128.77, 124.12, 119.83, 116.39, 112.59, 83.22, 68.23, 46.97, 44.52, 29.12, 28.89, 28.25, 26.19, 24.90, 24.84, 23.30. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.34. **FTIR (neat):** $\tilde{\nu}$ = 2974.6, 2926.7, 2856.6, 1692.3, 1597.5, 1488.3, 1388.6, 1311.1, 1286.2, 1241.9, 1169.4, 1142.6, 1112.9, 1071.3, 1001.3, 967.4, 856.5, 822.4, 758.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + H]$^+$ Calcd for $C_{28}H_{38}BBrNO_4^+$ 542.2072; Found 542.2089. **$[\alpha]_D^{20}$** = +23.5 (c = 1.00 in $CHCl_3$). **M.P.** = 80.9 – 84.5 °C.

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (97:3) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 92:8 at a flow

rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 13.1 min and t_{minor} = 18.9 min.

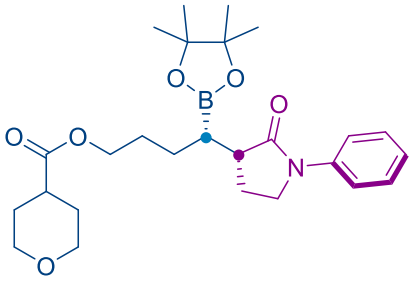
(*R*)-3-((*S*)-6-(2,4-Dichlorophenoxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 3ha):



Prepared according to **GP6** with **1h** (74.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3ha** as a white solid (86 mg, 81%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.61 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.19 – 7.05 (m, 2H), 6.86 – 6.78 (m, 1H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.83 – 3.68 (m, 2H), 2.87 – 2.74 (m, 1H), 2.25 – 2.15 (m, 1H), 2.07 – 1.99 (m, 1H), 1.87 – 1.80 (m, 2H), 1.54 – 1.42 (m, 5H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.18, 153.55, 139.95, 129.92, 128.74, 127.55, 125.39, 124.10, 123.74, 119.82, 114.09, 83.19, 69.45, 46.96, 44.51, 28.96, 28.83, 28.21, 26.10, 24.87, 24.81, 23.26. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.21. **FTIR (neat):** $\tilde{\nu}$ = 2974.9, 2926.4, 2856.4, 1691.8, 1598.0, 1484.0, 1467.2, 1388.5, 1310.8, 1288.8, 1265.3, 1227.0, 1142.5, 1103.8, 1060.4, 967.5, 857.5, 804.1, 758.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{28}H_{36}BCl_2NNaO_4^+$ 554.2007; Found 554.2021. $\mathbf{[\alpha]_D^{20}}$ = +22.2 (c = 1.00 in $CHCl_3$). **M.P.** = 82.4 – 84.8 °C.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 18.6 min and t_{minor} = 22.2 min.

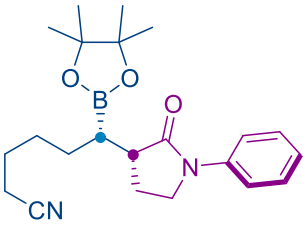
(*S*)-4-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl tetrahydro-2H-pyran-4-carboxylate ((+) 3ia):



Prepared according to **GP6** with **1i** (62.0 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **(+) 3ia** as a sticky oil (71 mg, 75%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.53 (m, 2H), 7.39 – 7.30 (m, 2H), 7.15 – 7.07 (m, 1H), 4.10 (t, *J* = 6.3 Hz, 2H), 3.99 – 3.91 (m, 2H), 3.84 – 3.70 (m, 2H), 3.42 (td, *J* = 11.1, 3.0 Hz, 2H), 2.86 – 2.77 (m, 1H), 2.53 (tt, *J* = 10.6, 4.5 Hz, 1H), 2.25 – 2.17 (m, 1H), 2.06 – 1.93 (m, 1H), 1.88 – 1.74 (m, 5H), 1.74 – 1.62 (m, 2H), 1.60 – 1.46 (m, 2H), 1.21 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.92, 174.66, 139.95, 128.86, 124.27, 119.91, 83.42, 67.26, 64.87, 47.00, 44.63, 40.29, 28.83, 28.40, 24.94, 24.92, 24.72, 23.36. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.01. **FTIR (neat):** $\tilde{\nu}$ = 2953.0, 2926.6, 2851.0, 1728.1, 1692.7, 1598.0, 1496.7, 1459.0, 1388.7, 1313.1, 1278.2, 1239.8, 1227.1, 1183.9, 1168.1, 1141.1, 1092.1, 1040.6, 983.7, 967.3, 857.9, 759.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{26}H_{38}BNNaO_6^+$ 494.2684; Found 494.2685. $\mathbf{[\alpha]_D^{20}}$ = +19.8 (c = 0.83 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 94:6 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 29.7 min and t_{minor} = 38.4 min.

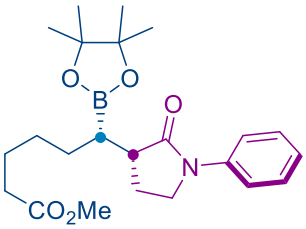
(*S*)-6-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanenitrile ((+) 3ja):



Prepared according to **GP6** with **1j** (44.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 4:1 hexane:EtOAc) afforded the desired product **(+) 3ja** as a white solid (58 mg, 76%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.56 (m, 2H), 7.39 – 7.31 (m, 2H), 7.13 – 7.09 (m, 1H), 3.84 – 3.70 (m, 2H), 2.86 – 2.75 (m, 1H), 2.35 (t, *J* = 7.0 Hz, 2H), 2.26 – 2.18 (m, 1H), 2.06 – 1.94 (m, 1H), 1.73 – 1.65 (m, 2H), 1.64 – 1.46 (m, 5H), 1.22 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.95, 139.91, 128.83, 124.25, 119.92, 119.90, 83.44, 46.96, 44.49, 28.25, 27.39, 25.58, 24.92, 24.90, 23.46, 17.14. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.45. **FTIR (neat):** $\tilde{\nu}$ = 2975.6, 2928.9, 2863.7, 1689.0, 1597.7, 1496.0, 1460.2, 1389.5, 1312.6, 1266.2, 1226.1, 1166.1, 1142.3, 1111.9, 966.9, 856.1, 760.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{22}H_{31}BN_2NaO_3^+$ 405.2320; Found 405.2323. $\mathbf{[\alpha]_D^{20}}$ = +31.0 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 94:6 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 30.7 min and t_{minor} = 42.7 min.

Methyl (*S*)-6-((*R*)-2-oxo-1-phenylpyrrolidin-3-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoate ((+) 3ka):

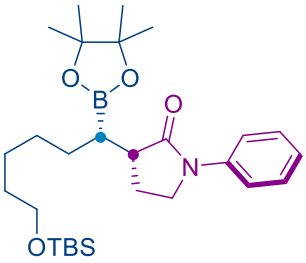


Prepared according to **GP6** with **1k** (50.8 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3ka** as a sticky oil (58 mg, 70%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.81 – 3.69 (m, 2H), 3.64 (s, 3H), 2.78 (td, *J* = 9.4, 4.4 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.14 (m, 1H), 2.05 – 1.95 (m, 1H), 1.70 – 1.52 (m, 4H), 1.47 – 1.35 (m, 3H), 1.19 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.12, 174.28, 139.96, 128.75, 124.11, 119.84, 83.22, 51.49, 46.96, 44.48, 34.10, 28.73, 27.97, 25.21, 24.88, 24.81, 23.23. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.97. **FTIR (neat):** $\tilde{\nu}$ = 2975.2, 2927.7, 2858.6, 1735.2, 1692.6, 1598.1, 1496.6, 1459.6, 1389.3, 1371.8, 1311.6, 1266.2, 1226.1, 1213.9, 1166.7, 1142.8, 1115.6, 967.2, 856.1, 759.2 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{23}H_{34}BNNaO_5^+$ 438.2422; Found 438.2432. $\mathbf{[\alpha]_D^{20}}$ = +29.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow

rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 15.8 min and t_{minor} = 18.9 min.

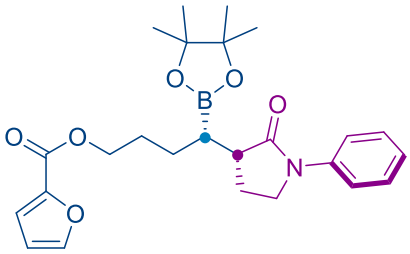
(*R*)-3-((*S*)-6-((tert-Butyldimethylsilyl)oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 3la):



Prepared according to **GP6** with **1l** (68.1 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(+) 3la** as a sticky oil (70 mg, 70%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.58 (m, 2H), 7.38 – 7.30 (m, 2H), 7.14 – 7.05 (m, 1H), 3.85 – 3.68 (m, 2H), 3.59 (t, *J* = 6.6 Hz, 2H), 2.79 (td, *J* = 9.4, 3.9 Hz, 1H), 2.24 – 2.14 (m, 1H), 2.08 – 1.96 (m, 1H), 1.63 – 1.47 (m, 4H), 1.46 – 1.30 (m, 5H), 1.20 (s, 12H), 0.89 (s, 9H), 0.04 (s, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.27, 140.03, 128.76, 124.07, 119.83, 83.16, 63.39, 46.99, 44.54, 32.95, 29.11, 28.41, 26.10, 24.91, 24.83, 23.22, 18.47, -5.15. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.83. **FTIR (neat):** $\tilde{\nu}$ = 2927.2, 2855.2, 1694.9, 1598.6, 1500.3, 1461.3, 1388.5, 1312.3, 1254.5, 1226.6, 1143.4, 1099.7, 967.6, 834.9, 777.7, 757.8 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{28}H_{48}BNNaO_4Si^+$ 524.3338; Found 524.3357. $\mathbf{[\alpha]_D^{20}}$ = +24.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (92%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 5.6 min and t_{minor} = 6.9 min.

(*S*)-4-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl furan-2-carboxylate ((+) 3ma):

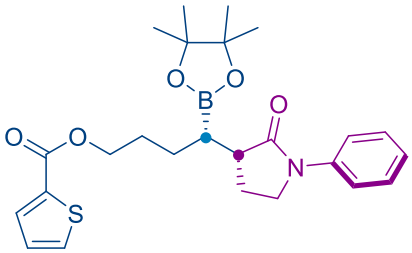


Prepared according to **GP6** with **1m** (58.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **(+) 3ma** as a sticky oil (72 mg, 79%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.63 – 7.58 (m, 2H), 7.56 – 7.55 (m, 1H), 7.37 – 7.31 (m, 2H), 7.18 – 7.16 (m, 1H), 7.13 – 7.08 (m, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.77 (dtd, *J* = 15.9, 9.3, 6.9 Hz, 2H), 2.89 – 2.79 (m, 1H), 2.25 – 2.17 (m, 1H), 2.08 – 1.98 (m, 1H), 1.95 – 1.66 (m, 3H), 1.63 – 1.55 (m, 2H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.92, 158.94, 146.26, 145.00, 139.94, 128.82, 124.22, 119.92, 117.83, 111.88, 83.39, 65.32, 47.00, 44.66, 28.43, 24.90, 24.88, 24.67, 23.28. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.71. **FTIR (neat):** $\tilde{\nu}$ = 2975.3, 2928.4, 2869.0, 1715.8, 1690.8, 1597.9, 1580.5, 1496.4, 1475.0, 1372.7, 1294.8, 1229.5, 1178.7, 1142.8, 1118.1, 1076.0, 1013.0, 967.2, 937.9, 884.7, 856.6, 757.9 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{32}BNNaO_6^+$ 476.2215; Found 476.2227. $\mathbf{[\alpha]_D^{20}}$ = +32.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow

rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 34.8 min and t_{minor} = 47.4 min.

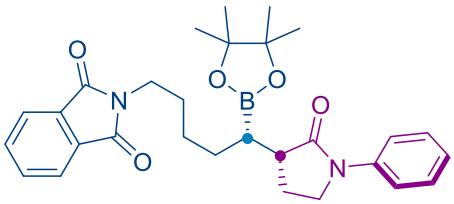
(*S*)-4-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl thiophene-2-carboxylate ((+) 3na):



Prepared according to **GP6** with **1n** (61.6 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 8:1 hexane:EtOAc) afforded the desired product **(+) 3na** as a white solid (77 mg, 82%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.81 – 7.80 (m, 1H), 7.63 – 7.61 (m, 2H), 7.54 – 7.53 (m, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.15 – 7.05 (m, 2H), 4.31 (t, *J* = 6.5 Hz, 2H), 3.85 – 3.69 (m, 2H), 2.85 (td, *J* = 9.5, 4.3 Hz, 1H), 2.28 – 2.18 (m, 1H), 2.09 – 1.97 (m, 1H), 1.97 – 1.77 (m, 2H), 1.74 – 1.68 (m, 1H), 1.65 – 1.56 (m, 2H), 1.22 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.89, 162.34, 139.89, 134.17, 133.31, 132.23, 128.76, 127.75, 124.16, 119.86, 83.33, 65.41, 46.95, 44.61, 28.40, 24.86, 24.83, 24.65, 23.21. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.93. **FTIR (neat):** $\tilde{\nu}$ = 2974.8, 2928.7, 2870.3, 1693.0, 1597.8, 1524.7, 1496.6, 1459.4, 1417.6, 1389.1, 1310.9, 1259.1, 1226.0, 1142.4, 1096.1, 1076.3, 1037.1, 966.4, 901.6, 857.8, 752.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{25}H_{32}BNNaO_5S^+$ 492.1986; Found 492.1993. **$[\alpha]_D^{20}$** = +20.8 (c = 1.00 in $CHCl_3$). **M.P.** = 80.1 – 90.1 °C.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 28.2 min and t_{minor} = 54.6 min.

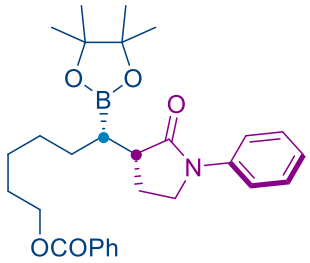
2-((*S*)-5-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)isoindoline-1,3-dione ((+) 3oa):



Prepared according to **GP6** with **1o** (68.2 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(+) 3oa** as a white solid (85 mg, 84%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.84 – 7.80 (m, 2H), 7.74 – 7.67 (m, 2H), 7.63 – 7.55 (m, 2H), 7.37 – 7.30 (m, 2H), 7.13 – 7.07 (m, 1H), 3.82 – 3.72 (m, 2H), 3.69 (td, *J* = 7.1, 1.9 Hz, 2H), 2.80 (td, *J* = 9.5, 4.5 Hz, 1H), 2.24 – 2.16 (m, 1H), 2.06 – 1.95 (m, 1H), 1.73 – 1.54 (m, 4H), 1.51 – 1.36 (m, 3H), 1.17 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.13, 168.54, 140.03, 133.94, 132.32, 128.80, 124.15, 123.26, 119.92, 83.27, 47.03, 44.60, 38.09, 28.92, 27.92, 26.59, 24.89, 24.85, 23.26. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.54. **FTIR (neat):** $\tilde{\nu}$ = 2974.2, 2924.8, 2855.3, 1770.6, 1708.5, 1598.0, 1496.8, 1464.6, 1437.1, 1393.6, 1371.2, 1311.8, 1269.4, 1215.3, 1142.6, 1034.9, 966.3, 858.0, 758.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{29}H_{35}BN_2NaO_5^+$ 525.2531; Found 525.2547. **$[\alpha]_D^{20}$** = +25.0 (c = 0.80 in $CHCl_3$).

HPLC: The enantiomeric excess (93%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 94:6 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 43.5 min and t_{minor} = 49.9 min.

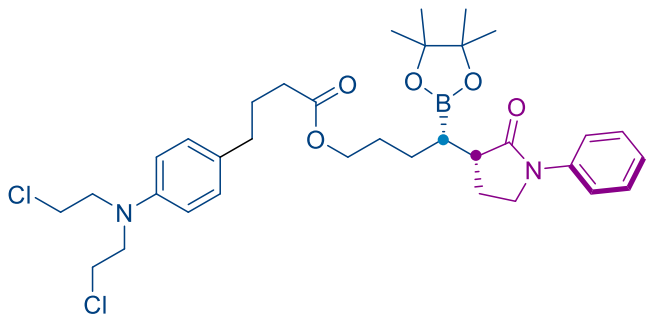
(*S*)-6-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate ((+) 3pa):



Prepared according to **GP6** with **1p** (66.0 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 3pa** as a white solid (75 mg, 76%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.07 – 8.02 (m, 2H), 7.62 – 7.60 (m, 2H), 7.57 – 7.50 (m, 1H), 7.45 – 7.40 (m, 2H), 7.38 – 7.30 (m, 2H), 7.13 – 7.07 (m, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 3.81 – 3.68 (m, 2H), 2.80 (td, *J* = 9.5, 4.2 Hz, 1H), 2.25 – 2.14 (m, 1H), 2.06 – 1.96 (m, 1H), 1.82 – 1.75 (m, 2H), 1.65 – 1.57 (m, 2H), 1.50 – 1.42 (m, 5H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.15, 166.71, 139.96, 132.83, 130.57, 129.59, 128.73, 128.37, 124.07, 119.80, 83.19, 65.11, 46.93, 44.51, 28.87, 28.72, 28.23, 26.30, 24.87, 24.80, 23.25. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.45. **FTIR (neat):** $\tilde{\nu}$ = 2974.6, 2926.6, 2856.5, 1715.5, 1693.5, 1598.5, 1497.7, 1451.7, 1388.8, 1312.5, 1271.8, 1227.0, 1142.8, 1112.6, 1070.4, 1026.6, 966.8, 857.0, 758.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{29}H_{38}BNNaO_5^+$ 514.2735; Found 514.2753. **$[\alpha]_D^{20}$** = +24.8 (c = 1.00 in $CHCl_3$). **M.P.** = 82.8 – 86.9 °C.

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 18.6 min and t_{minor} = 30.2 min.

(*S*)-4-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 4-(4-(bis(2-chloroethyl)amino)phenyl)butanoate ((+) 4):

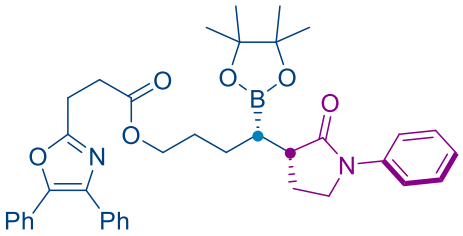


Prepared according to **GP6** with **1q** (48.4 mg, 0.10 mmol, 1.0 equiv.), **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 4** as a sticky oil (40 mg, 62%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.58 (m, 2H), 7.38 – 7.32 (m, 2H), 7.15 – 7.03 (m, 3H), 6.65 – 6.59 (m, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 3.83 – 3.72 (m, 2H), 3.72 – 3.67 (m, 4H), 3.63 – 3.58 (m, 4H), 2.88 – 2.78 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.24 – 2.17 (m, 1H), 2.08 – 1.97 (m, 1H), 1.96 – 1.86 (m, 2H), 1.80 – 1.48 (m, 5H), 1.21 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.93, 173.77, 144.41, 139.94, 130.80, 129.82, 128.83, 124.23, 119.90, 112.26, 83.38, 64.72, 53.72, 46.98, 44.63, 40.65, 34.13, 33.82, 28.40, 26.93, 24.91, 24.74, 23.28. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.19.

FTIR (neat): $\tilde{\nu}$ = 2973.5, 2926.2, 2857.3, 1727.8, 1691.7, 1614.8, 1598.0, 1518.2, 1497.3, 1457.6, 1388.9, 1370.5, 1311.8, 1270.5, 1246.8, 1227.2, 1179.6, 1142.2, 966.4, 856.5, 827.0, 803.1, 758.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{34}H_{48}BCl_2N_2O_5^+$ 645.3028; Found 645.3041. $[\alpha]_D^{20}$ = +18.3 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 80:20 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 23.0 min and t_{minor} = 33.9 min.

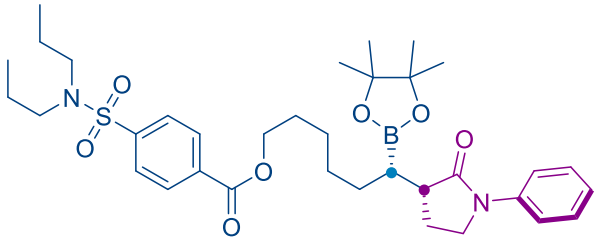
(*S*)-4-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl 3-(4,5-diphenyloxazol-2-yl)propanoate ((+) 5):



Prepared according to **GP6** with **1r** (47.3 mg, 0.10 mmol, 1.0 equiv.), **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **(+) 5** as a sticky oil (41 mg, 65%) in 97:3 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.66 – 7.55 (m, 6H), 7.40 – 7.28 (m, 8H), 7.14 – 7.08 (m, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.79 – 3.67 (m, 2H), 3.19 (dd, *J* = 8.5, 6.7 Hz, 2H), 2.92 (dd, *J* = 8.5, 6.7 Hz, 2H), 2.79 (ddd, *J* = 10.0, 8.9, 4.6 Hz, 1H), 2.22 – 2.11 (m, 1H), 2.04 – 1.92 (m, 1H), 1.84 – 1.48 (m, 5H), 1.21 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.93, 172.17, 161.96, 145.51, 139.97, 135.25, 132.62, 129.12, 128.82, 128.76, 128.66, 128.55, 128.16, 128.02, 126.58, 124.20, 119.89, 83.38, 65.23, 46.97, 44.62, 31.32, 28.32, 24.92, 24.90, 24.69, 23.69, 23.23. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.24. **FTIR (neat):** $\tilde{\nu}$ = 2975.1, 2925.1, 2854.9, 1732.8, 1692.5, 1597.8, 1499.0, 1389.9, 1371.3, 1312.4, 1267.8, 1216.6, 1165.8, 1142.4, 1072.0, 1057.8, 1025.6, 963.1, 856.2, 758.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{38}H_{44}BN_2O_6^+$ 635.3287; Found 635.3288. $[\alpha]_D^{20}$ = +14.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (93%) and diastereomeric ratio (97:3) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 28.3 min and t_{minor} = 37.2 min.

(*S*)-6-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl 4-(N,N-dipropylsulfamoyl)benzoate ((+) 6):

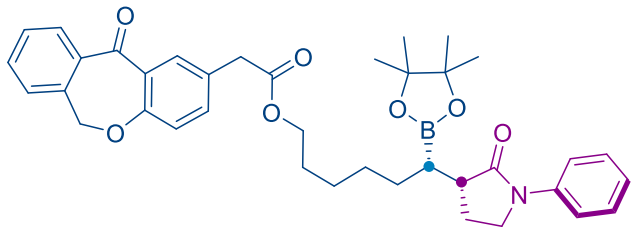


Prepared according to **GP6** with **1s** (49.3 mg, 0.10 mmol, 1.0 equiv.), **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 6** as a sticky oil (45 mg, 69%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.19 – 8.12 (m, 2H), 7.90 – 7.84 (m, 2H), 7.66 – 7.58 (m, 2H), 7.38 – 7.31 (m, 2H), 7.16 – 7.07 (m, 1H), 4.34 (t, *J* = 6.6 Hz, 2H), 3.83 – 3.70 (m, 2H), 3.12 – 3.06 (m, 4H), 2.80 (td, *J* = 9.5, 4.9 Hz, 1H), 2.26 – 2.15 (m, 1H), 2.06 – 1.95 (m, 1H), 1.82 –

1.76 (m, 2H), 1.65 – 1.41 (m, 11H), 1.20 (s, 12H), 0.86 (t, *J* = 7.4 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.20, 165.44, 144.21, 139.99, 133.92, 130.31, 128.82, 127.10, 124.19, 119.88, 83.30, 65.83, 50.07, 47.00, 44.54, 28.87, 28.70, 28.26, 26.28, 24.93, 24.88, 23.39, 22.07, 11.28. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 34.56. **FTIR (neat):** $\tilde{\nu}$ = 2969.5, 2927.9, 2874.3, 2857.0, 1719.5, 1693.0, 1598.2, 1497.5, 1459.8, 1389.1, 1341.7, 1311.1, 1271.3, 1227.4, 1157.5, 1143.4, 1107.3, 1087.5, 1017.0, 991.7, 858.5, 759.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + Na]$^+$ Calcd for $C_{35}H_{51}BN_2NaO_7S^+$ 677.3402; Found 677.3420. **$[\alpha]_D^{20}$** = +17.8 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 85:15 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 14.6 min and t_{minor} = 21.2 min.

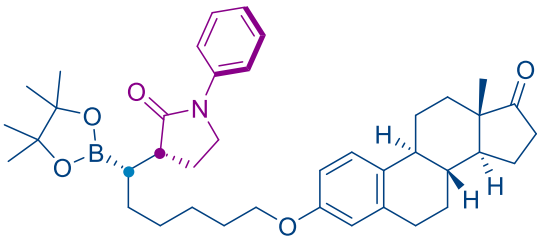
(*S*)-6-((*R*)-2-Oxo-1-phenylpyrrolidin-3-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate ((+) 7):



Prepared according to **GP6** with **1t** (47.6 mg, 0.10 mmol, 1.0 equiv.), **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 7** as a sticky oil (40 mg, 64%) in 94:6 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.4 Hz, 1H),7.63 – 7.59 (m, 2H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 7.13 – 7.09 (m, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.82 – 3.69 (m, 2H), 3.63 (s, 2H), 2.78 (td, *J* = 9.6, 4.5 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.06 – 1.95 (m, 1H), 1.69 – 1.53 (m, 4H), 1.48 – 1.32 (m, 5H), 1.20 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 190.96, 176.23, 171.64, 160.57, 140.60, 140.03, 136.52, 135.70, 132.87, 132.57, 129.61, 129.37, 128.81, 128.12, 127.92, 125.23, 124.14, 121.15, 119.88, 83.26, 73.76, 65.24, 47.01, 44.57, 40.40, 28.84, 28.60, 28.24, 26.15, 24.98, 24.94, 24.88, 23.30. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.37. **FTIR (neat):** $\tilde{\nu}$ = 2973.9, 2923.1, 2854.2, 1731.2, 1691.4, 1647.2, 1611.0, 1597.8, 1490.1, 1457.3, 1389.1, 1299.7, 1256.4, 1223.5, 1163.0, 1140.3, 1120.8, 1015.0, 967.0, 856.7, 830.3, 757.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + Na]$^+$ Calcd for $C_{38}H_{44}BNNaO_7^+$ 660.3103; Found 660.3109. **$[\alpha]_D^{20}$** = +16.5 (c = 0.94 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (94:6) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 80:20 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 33.9 min and t_{minor} = 40.1 min.

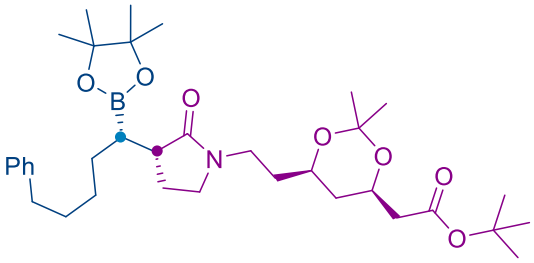
(3*R*)-3-((1*S*)-6-(((8*R*,9*S*,13*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)-1-phenylpyrrolidin-2-one ((+) 8):



Prepared according to **GP6** with **1u** (47.8 mg, 0.10 mmol, 1.0 equiv.), **2a** (31.2 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 6:1 hexane:EtOAc) afforded the desired product **(+) 8** as a white solid (40 mg, 63%) in 96:4 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.39 – 7.30 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.76 – 6.69 (m, 1H), 6.65 – 6.61 (m, 1H), 3.92 (t, *J* = 6.6 Hz, 2H), 3.75 (dt, *J* = 13.2, 9.3 Hz, 2H), 2.91 – 2.87 (m, 2H), 2.80 (td, *J* = 9.5, 4.3 Hz, 1H), 2.50 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.43 – 2.35 (m, 1H), 2.29 – 1.91 (m, 7H), 1.79 – 1.74 (m, 2H), 1.66 – 1.42 (m, 11H), 1.32 – 1.25 (m, 2H), 1.20 (s, 12H), 0.91 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 221.10, 176.26, 157.27, 140.03, 137.77, 131.90, 128.80, 126.38, 124.14, 119.88, 114.65, 112.27, 83.24, 67.98, 50.54, 48.14, 47.01, 44.55, 44.11, 38.51, 36.00, 31.71, 29.77, 29.37, 29.00, 28.31, 26.70, 26.33, 26.04, 24.94, 24.87, 23.30, 21.71, 13.98. ^{11}B NMR (128 MHz, **Chloroform-*d***) δ 34.21. **FTIR (neat):** $\tilde{\nu}$ = 2974.3, 2924.8, 2856.4, 1736.3, 1692.7, 1598.5, 1574.7, 1498.1, 1457.3, 1380.0, 1311.0, 1281.1, 1253.8, 1232.7, 1214.7, 1142.5, 1054.6, 1006.1, 966.2, 857.5, 818.5, 752.9 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + Na]$^+$ Calcd for $C_{40}H_{54}BNNaO_5^+$ 662.3987; Found 662.4007. **$[\alpha]_D^{20}$** = +90.0 (c = 1.00 in $CHCl_3$).

HPLC: The diastereomeric ratio (96:4) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 85:15 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 19.9 min and t_{minor} = 32.9 min.

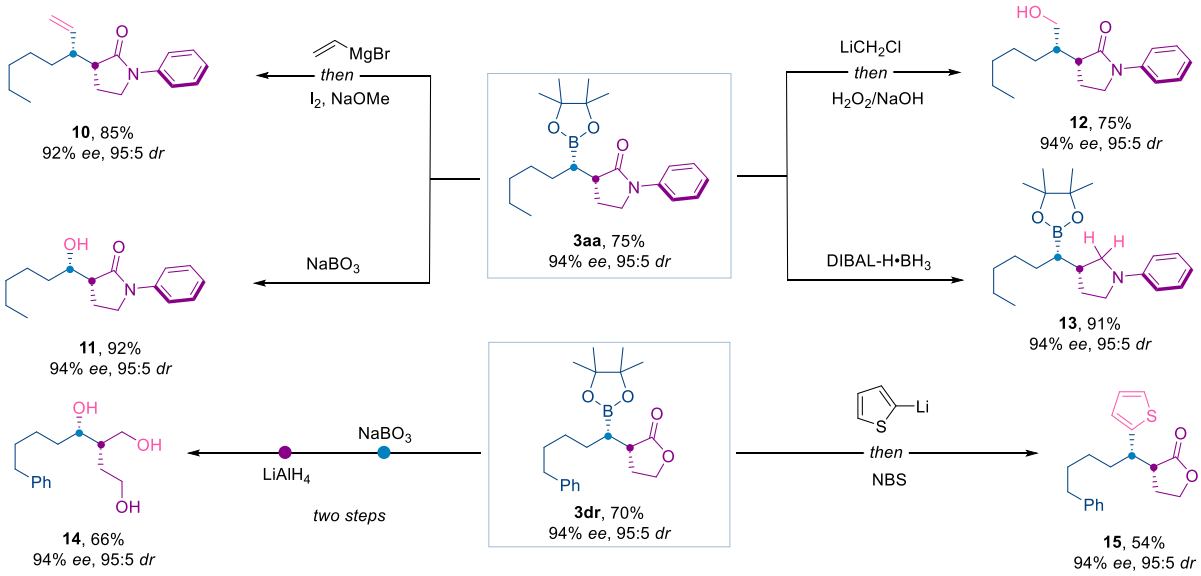
***tert*-Butyl 2-((4*R*,6*R*)-2,2-dimethyl-6-(2-((*R*)-2-oxo-3-((*S*)-5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)pyrrolidin-1-yl)ethyl)-1,3-dioxan-4-yl)acetate ((+) 9):**



Prepared according to **GP6** with **1d** (27.2 mg, 0.10 mmol, 1.0 equiv.), **2u** (50.4 mg, 0.13 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **(+) 9** as a sticky oil (39 mg, 64%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.27 – 7.22 (m, 2H), 7.18 – 7.11 (m, 3H), 4.28 – 4.17 (m, 1H), 3.88 – 3.84 (m, 1H), 3.39 – 3.21 (m, 4H), 2.61 – 2.54 (m, 3H), 2.39 (dd, *J* = 15.1, 7.3 Hz, 1H), 2.28 (dd, *J* = 15.1, 5.8 Hz, 1H), 2.12 – 2.02 (m, 1H), 1.84 – 1.77 (m, 1H), 1.73 – 1.50 (m, 7H), 1.48 – 1.27 (m, 19H), 1.18 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.75, 170.33, 142.97, 128.57, 128.30, 125.63, 98.83, 83.12, 80.69, 67.26, 66.29, 45.90, 42.89, 42.86, 39.33, 36.56, 35.98, 34.19, 31.71, 30.24, 30.22, 28.93, 28.30, 28.23, 24.94, 24.89, 23.72, 19.85. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 35.54. **FTIR (neat):** $\tilde{\nu}$ = 2975.8, 2924.1, 2855.1, 1728.8, 1682.8, 1494.6, 1455.2, 1431.1, 1378.7, 1316.2, 1260.3, 1200.6, 1144.1, 966.6, 951.2, 860.8, 844.9, 749.5 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + H]$^+$ Calcd for $C_{35}H_{57}BNO_7^+$ 614.4223; Found 614.4243. **$[\alpha]_D^{20}$** = +7.1 (c = 0.94 in $CHCl_3$).

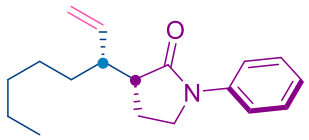
HPLC: The diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 210 nm wavelength. Retention time: t_{major} = 41.2 min and t_{minor} = 36.6 min.

7. Product diversification:



Supplementary Figure 3. Functional group transformations of the products.

(*R*)-3-((*R*)-Oct-1-en-3-yl)-1-phenylpyrrolidin-2-one ((+) 10):

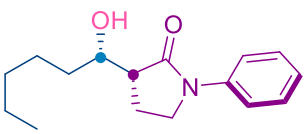


The title compound was prepared following a reported method with a slight modification.[7] A Schlenk flask was charged with **3aa** (37.1 mg, 0.10 mmol, 1.0 equiv.), backfilled with N_2, dissolved in anhydrous THF (1.5 ml) and cooled to −78 °C. vinylmagnesium bromide (1M, 400 µL, 0.40 mmol, 4.0 equiv.) was added dropwise, and the mixture was stirred for 0.5 h. A solution of iodine (102 mg, 0.40 mmol, 4.0 equiv.) in anhydrous methanol (1.0 mL) was added dropwise, and the mixture was stirred for 0.5 h. A solution of NaOMe (30.4 mg, 0.80 mmol, 8 equiv.) in anhydrous methanol (1.5 mL) was added dropwise, and the mixture was stirred for 1.5 h. The mixture was monitored by TLC, quenched with saturated aqueous $Na_2S_2O_3$ (15 mL) at this temperature, and extracted with EtOAc (3×20 ml). The combined organic phases were washed with brine (60 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude mixture was purified by flash column chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain the desired product **(+) 10** as a colorless oil (23 mg, 85%) in 95:5 diastereomeric ratio. **^{1}H NMR** (400 MHz, **Chloroform-*d***) δ 7.65 – 7.58 (m, 2H), 7.39 – 7.32 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 5.74 – 5.62 (m, 1H), 5.16 – 5.06 (m, 2H), 3.80 – 3.68 (m, 2H), 2.78 – 2.68 (m, 2H), 2.17 – 2.07 (m, 1H), 2.02 – 1.92 (m, 1H), 1.55 – 1.44 (m, 1H), 1.40 – 1.25 (m, 4H), 0.92 – 0.85 (m, 3H). **^{13}C NMR** (101 MHz, **Chloroform-*d***) δ 175.15, 139.57, 138.21, 128.77, 124.39, 119.97, 117.26, 47.34, 47.07, 43.38, 31.91, 31.86, 26.99, 22.64, 19.81, 14.09. **FTIR (neat):** $\tilde{\nu}$ = 2953.8, 2923.4, 2854.6, 1692.9, 1637.9, 1598.1, 1498.0, 1459.2, 1392.0, 1300.0, 1226.3, 1185.4, 1115.3, 1074.4,

998.6, 916.2, 757.3 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{18}H_{26}NO^+$ 272.2009; Found 272.2017. $[\alpha]_D^{20}$ = +62.8 (c = 0.90 in $CHCl_3$).

HPLC: The enantiomeric excess (92%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 11.9 min and t_{minor} = 19.8 min.

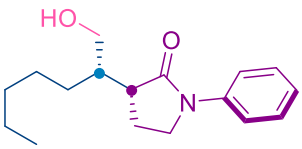
(*R*)-3-((*S*)-1-Hydroxyhexyl)-1-phenylpyrrolidin-2-one ((+) 11):



The title compound was prepared following a previous literature procedure.[8] Compound **3aa** (18.6 mg, 0.05 mmol, 1.0 equiv.) was dissolved in a 1:1 mixture of THF and H_2O (1.0 mL) at room temperature. Then $NaBO_3$•$4H_2O$ (19.2 mg, 0.125 mmol, 2.5 equiv.) was added to it. The resulting mixture was stirred for 6 hours. After the completion of the reaction as checked by TLC, the reaction mixture was diluted with water (5.0 mL) and Et_2O (5.0 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3x5.0 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, 5:1, hexane/EtOAc) to obtain the desired product **(+) 11** as a colorless oil (12.0 mg, 92%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 – 7.61 (m, 2H), 7.39 – 7.33 (m, 3H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.27 – 4.21 (m, 1H), 3.86 – 3.75 (m, 3H), 2.78 (td, *J* = 9.5, 2.9 Hz, 1H), 2.38 (brs, 1H), 2.28 – 2.07 (m, 2H), 1.61 – 1.43 (m, 3H), 1.40 – 1.28 (m, 5H), 0.93 – 0.87 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.91, 139.31, 128.84, 124.67, 119.97, 69.89, 49.17, 47.16, 34.08, 31.78, 25.73, 22.64, 18.13, 14.06. **FTIR (neat):** $\tilde{\nu}$ = 3418.3, 2952.3, 2920.1, 2852.2, 1672.3, 1597.9, 1496.1, 1460.8, 1403.6, 1377.5, 1308.7, 1276.5, 1229.4, 1138.4, 1122.1, 1091.6, 993.6, 923.0, 757.9 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{23}NNaO_2^+$ 284.1621, Found 284.1629. $[\alpha]_D^{20}$ = +16.1 (c = 0.28 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 10.2 min and t_{minor} = 12.5 min.

(*R*)-3-((*S*)-1-Hydroxyheptan-2-yl)-1-phenylpyrrolidin-2-one ((+) 12):

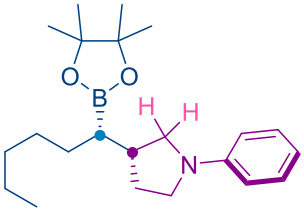


The title compound was prepared following a previous procedure.[8] A mixture of **3aa** (37.1 mg, 0.10 mmol, 1.0 equiv.) and chloroiodomethane (14.6 µL, 0.20 mmol, 2.0 equiv.) in THF (1.0 mL) was cooled to -78°C under N_2 atmosphere. Then n-butyllithium (2.4M, 83.3 µL, 0.20 mmol, 2.0 equiv.) was added slowly to it. The resulting reaction mixture was stirred for 30 mins at -78°C and then allowed to warm to room temperature overnight. The reaction flask was then transferred to an ice bath and NaOH (1.0 mL, 2.0 M) and H_2O_2 (0.50 mL, >30% w/v) were added. The reaction mixture was stirred for an additional 2 hours at this temperature and was then diluted with H_2O (5.0 mL) and EtOAc (5.0 mL) and extracted with EtOAc (3x4.0 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (SiO_2, 2:1 hexane:EtOAc) to obtain the

desired product **(+) 12** as a colorless oil (21 mg, 75%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 – 7.58 (m, 2H), 7.42 – 7.33 (m, 2H), 7.20 – 7.10 (m, 1H), 3.89 – 3.71 (m, 4H), 3.57 (dd, *J* = 7.7, 3.9 Hz, 1H), 2.95 (td, *J* = 9.7, 2.9 Hz, 1H), 2.28 – 2.16 (m, 1H), 2.11 – 1.96 (m, 2H), 1.64 – 1.54 (m, 1H), 1.53 – 1.39 (m, 1H), 1.37 – 1.21 (m, 6H), 0.95 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.35, 139.18, 128.87, 124.95, 120.35, 64.33, 47.60, 47.47, 41.40, 32.04, 27.22, 26.60, 24.86, 22.64, 21.62, 14.08. **FTIR (neat):** $\tilde{\nu}$ = 3364.6, 2953.1, 2923.0, 2855.3, 1668.3, 1597.7, 1496.9, 1459.5, 1396.1, 1302.1, 1226.8, 1116.1, 1046.4, 970.6, 897.7, 758.4 cm^{-1}. **HRMS (ESI/QTOF) m/z:** [M + Na]$^{+}$ Calcd for $C_{17}H_{25}NNaO_2^{+}$ 298.1777; Found 298.1783. **$[\alpha]_D^{20}$** = +4.2 (c = 0.88 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 13.7 min and t_{minor} = 20.0 min.

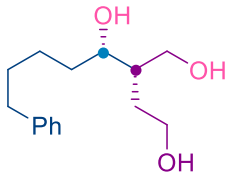
(*R*)-1-Phenyl-3-((*S*)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)pyrrolidone ((-) 13):



The title compound was prepared following a reported method with a slight modification.[9] A solution of **3aa** (18.6 mg, 0.05 mmol, 1 eq.) in THF (1.0 mL) was cooled to 0 °C under N_2 atmosphere. Then DIBAL-H•BH_3 complex (0.75M, 270 μL, 0.20 mmol, 4.0 equiv.) was added dropwise to the solution. The reaction mixture was stirred for 1 h at this temperature and monitored by TLC. Then the reaction was quenched with MeOH (1 mL) and water (2 mL). The mixture was extracted with Et_2O (3x4 mL). The organic extract was concentrated in vacuum. The crude product was purified by preparative thin layer chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain the desired product **(-) 13** as a colorless oil (16 mg, 91%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.24 – 7.17 (m, 2H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 2H), 3.52 – 3.43 (m, 1H), 3.34 (td, *J* = 8.8, 2.1 Hz, 1H), 3.28 – 3.20 (m, 1H), 2.91 (t, *J* = 9.0 Hz, 1H), 2.39 – 2.26 (m, 1H), 2.15 – 2.05 (m, 1H), 1.73 – 1.59 (m, 1H), 1.52 – 1.40 (m, 2H), 1.37 – 1.21 (m, 17H), 1.07 (td, *J* = 9.7, 4.8 Hz, 1H), 0.92 – 0.85 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 147.95, 129.10, 115.15, 111.38, 83.12, 53.64, 47.62, 40.57, 32.16, 31.29, 30.63, 29.13, 24.90, 24.88, 22.58, 14.05. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 37.19. **HRMS (ESI/QTOF) m/z:** [M + H]$^{+}$ Calcd for $C_{22}H_{37}BNO_2^{+}$ 358.2912; Found 358.2921. **$[\alpha]_D^{20}$** = -0.5 (c = 0.66 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined after stereospecific oxidation (boronate to alcohol by $NaBO_3$) via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 94:6 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 20.5 min and t_{minor} = 23.7 min.

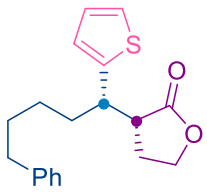
(3*S*,4*S*)-3-(Hydroxymethyl)-8-phenyloctane-1,4-diol ((-) 14):



The title compound was prepared in two steps. At first the alkyl boronate was oxidized to obtain the secondary alcohol. Then the lactone was reduced to the diol. Compound **3dr** (71.6 mg, 0.20 mmol, 1.0 equiv.) was dissolved in a 1:1 mixture of THF and H_2O (2.0 mL) at room temperature. Then $NaBO_3$•$4H_2O$ (78.0 mg, 0.50 mmol, 2.5 equiv.) was added to it. The resulting mixture was stirred for 8 hours. After the completion of the reaction as checked by TLC, the reaction mixture was diluted with water (5.0 mL) and Et_2O (5.0 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3x5.0 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, 3:1, hexane/EtOAc) to obtain the desired alcohol as a colorless oil (42 mg, 84%). Then this product was used in the next step. To a solution of alcohol (30.0 mg, 0.12 mmol, 1.0 equiv.) in anhydrous THF (1.5 mL) under N_2 atmosphere was added $LiAlH_4$ (22.8 mg, 0.60 mmol, 5.0 equiv.) at 0 °C. The reaction mixture was stirred for 6 hours and quenched with saturated aq. NH_4Cl solution (1.0 mL) and diluted with EA (3.0 mL). The layers were separated, the aqueous phase was extracted with EA (5×3.0 mL), the combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, 1:1 1:2, hexane/EtOAc) to obtain the desired product **(-) 14** as a colorless oil (24 mg, 79%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.30 – 7.24 (m, 2H), 7.22 – 7.13 (m, 3H), 3.88 – 3.62 (m, 5H), 3.36 (s, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.78 – 1.59 (m, 5H), 1.58 – 1.41 (m, 3H), 1.39 – 1.30 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 142.64, 128.52, 128.41, 125.81, 74.57, 64.99, 60.89, 42.87, 36.01, 34.00, 31.55, 29.03, 25.98. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{15}H_{24}NaO_3^+$ 275.1618; Found 275.1621. $\mathbf{[\alpha]_D^{20}}$ = -3.2 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 33.9 min and t_{minor} = 40.7 min.

(*R*)-3-((*S*)-5-Phenyl-1-(thiophen-2-yl)pentyl)dihydrofuran-2(3H)-one ((+) 15):

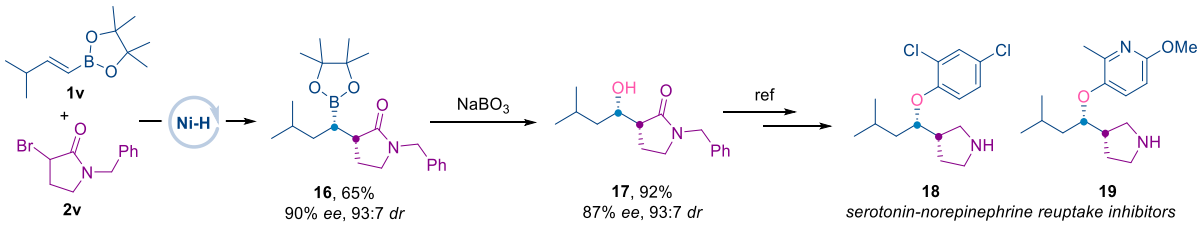


The title compound was prepared following a literature procedure with a slight modification.[8] To a solution of thiophene (10.4 µL, 0.13 mmol, 1.3 equiv.) in THF (1.0 mL) at –78 °C was added n-BuLi (1.6 M in hexane; 81.0 µL, 0.13 mmol, 1.3 equiv.) dropwise under an inert atmosphere. The mixture was then warmed to room temperature and stirred for 30 min. Then the mixture was cooled to -78 °C again. A solution of **3dr** (35.8 mg, 0.10 mmol, 1.0 equiv.) in THF (1.0 mL) was added dropwise to it. The reaction mixture was further stirred for 1.5 hours at this temperature. Then a solution of *N*-bromosuccinimide (23.4 mg, 0.13 mmol, 1.3 equiv.) in THF (1.0 mL) was added dropwise and the mixture was stirred at -78 °C for additional 1.5 hours. Then the reaction was quenched with a saturated aqueous sodium thiosulfate solution (2.0 mL) and the reaction mixture was

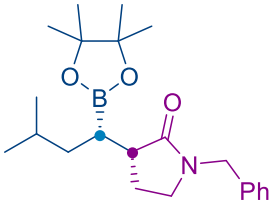
allowed to warm to room temperature. The resulting mixture was diluted with water (5.0 mL) and ethyl acetate (5.0 mL). The aqueous layer was extracted with ethyl acetate (3x5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (SiO_2, 30:1 7:1 hexane:EtOAc) to obtain the desired product **(+) 15** as a colorless oil (17 mg, 54%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.29 – 7.23 (m, 2H), 7.20 – 7.12 (m, 4H), 6.97 – 6.94 (m, 1H), 6.89 – 6.86 (m, 1H), 4.15 – 4.06 (m, 1H), 3.96 (td, *J* = 8.7, 4.2 Hz, 1H), 3.51 (dt, *J* = 9.5, 5.5 Hz, 1H), 2.79 (td, *J* = 9.2, 5.4 Hz, 1H), 2.64 – 2.52 (m, 2H), 2.22 – 2.13 (m, 1H), 2.12 – 1.92 (m, 2H), 1.85 – 1.75 (m, 1H), 1.71 – 1.60 (m, 2H), 1.41 – 1.33 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 178.24, 144.01, 142.52, 128.49, 128.41, 126.93, 126.16, 125.82, 124.16, 66.62, 45.33, 40.72, 35.81, 34.90, 31.25, 27.24, 24.91. **FTIR (neat):** $\tilde{\nu}$ = 2923.4, 2854.8, 1763.3, 1602.5, 1495.0, 1453.5, 1372.4, 1212.5, 1157.2, 1025.4, 952.2, 849.5, 748.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{19}H_{22}NaO_2S^+$ 337.1233; Found 337.1232. **$[\alpha]_D^{20}$** = +28.0 (c = 0.75 in $CHCl_3$).

HPLC: The enantiomeric excess (94%) and diastereomeric ratio (95:5) were determined via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 75:25 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Retention time: t_{major} = 39.4 min and t_{minor} = 28.7 min.

8. Synthesis of compound 17, a key intermediate to drug molecules 18 and 19:



(*R*)-1-Benzyl-3-((*S*)-3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)pyrrolidin-2-one ((-) 16):

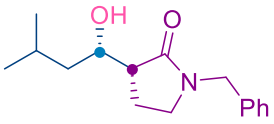


Prepared according to **GP6** with **1v** (39.2 mg, 0.20 mmol, 1.0 equiv.), **2v** (66.1 mg, 0.26 mmol, 1.3 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **(-) 16** as a sticky oil (48 mg, 65%) in 93:7 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.34 – 7.21 (m, 5H), 4.64 (d, *J* = 14.9 Hz, 1H), 4.23 (d, *J* = 14.9 Hz, 1H), 3.22 – 3.08 (m, 2H), 2.62 (td, *J* = 9.3, 5.1 Hz, 1H), 2.08 – 2.00 (m, 1H), 1.90 – 1.80 (m, 1H), 1.70 – 1.57 (m, 2H), 1.49 – 1.42 (m, 1H), 1.31 – 1.26 (m, 1H), 1.21 (s, 12H), 0.90 (dd, *J* = 6.6, 3.9 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.82,

137.11, 128.55, 128.09, 127.33, 83.06, 46.60, 44.98, 42.89, 37.49, 26.78, 24.88, 24.80, 23.37, 22.80, 22.77. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.73. **FTIR (neat):** $\tilde{\nu}$ = 2952.3, 2924.3, 2866.7, 1682.6, 1605.5, 1494.7, 1454.2, 1428.5, 1371.3, 1318.8, 1259.9, 1203.6, 1166.1, 1141.7, 1111.9, 1080.1, 967.3, 858.9, 834.0 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{22}H_{35}BNO_3^+$ 372.2705; Found 372.2699. **$[\alpha]_D^{20}$** = -10.0 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) and diastereomeric ratio (93:7) were determined via HPLC analysis using a CHIRALPAK® OD-H column, with hexane:isopropanol = 98:2 at a flow rate 0.5 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 27.3 min and t_{minor} = 32.7 min.

(*R*)-1-Benzyl-3-((*S*)-1-hydroxy-3-methylbutyl)pyrrolidin-2-one ((-) 17):

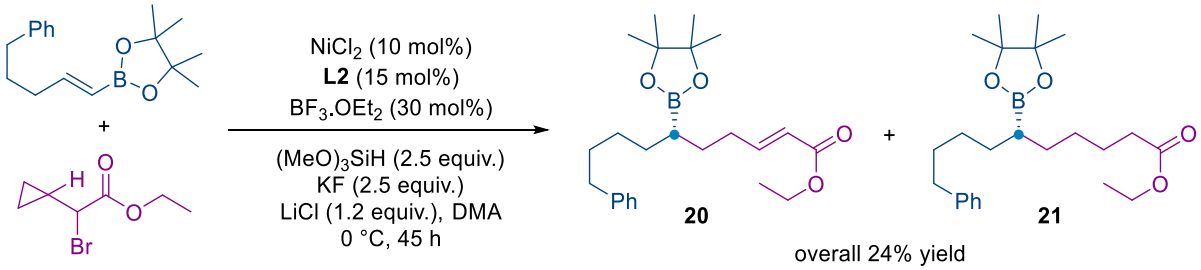


Compound **16** (37.1 mg, 0.10 mmol, 1.0 equiv.) was dissolved in a 1:1 mixture of THF and H_2O (1.0 mL) at room temperature. Then $NaBO_3$•$4H_2O$ (39.0 mg, 0.25 mmol, 2.5 equiv.) was added to it. The resulting mixture was stirred for 8 hours. After the completion of the reaction as checked by TLC, the reaction mixture was diluted with water (5.0 mL) and Et_2O (5.0 mL). The organic layer was separated and the aqueous phase was extracted with Et_2O (3x5.0 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, 2:1, hexane/EtOAc) to obtain the desired product **(-) 17** as a colorless oil (21 mg, 80%) in 95:5 diastereomeric ratio. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.36 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 4.54 – 4.42 (m, 2H), 4.30 (ddt, *J* = 9.3, 7.1, 3.8 Hz, 1H), 3.30 – 3.15 (m, 2H), 2.64 (td, *J* = 9.3, 3.0 Hz, 1H), 2.38 (d, *J* = 5.5 Hz, 1H), 2.12 – 1.92 (m, 2H), 1.86 – 1.77 (m, 1H), 1.51 – 1.44 (m, 1H), 1.22 – 1.15 (m, 1H), 0.96 (dd, *J* = 6.7, 4.3 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.55, 136.45, 128.83, 128.12, 127.69, 68.10, 48.01, 46.79, 45.31, 43.01, 24.75, 23.63, 22.12, 18.47. **FTIR (neat):** $\tilde{\nu}$ = 3383.4, 2952.0, 2922.2, 2867.2, 1663.2, 1494.6, 1454.0, 1436.4, 1364.7, 1291.8, 1261.3, 1172.2, 1143.4, 1080.6, 1029.1, 994.8, 978.4, 953.7 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + Na]^+$ Calcd for $C_{16}H_{23}NNaO_2^+$ 284.1621; Found 284.1625. **$[\alpha]_D^{20}$** = -0.93 (c = 0.72 in $CHCl_3$).

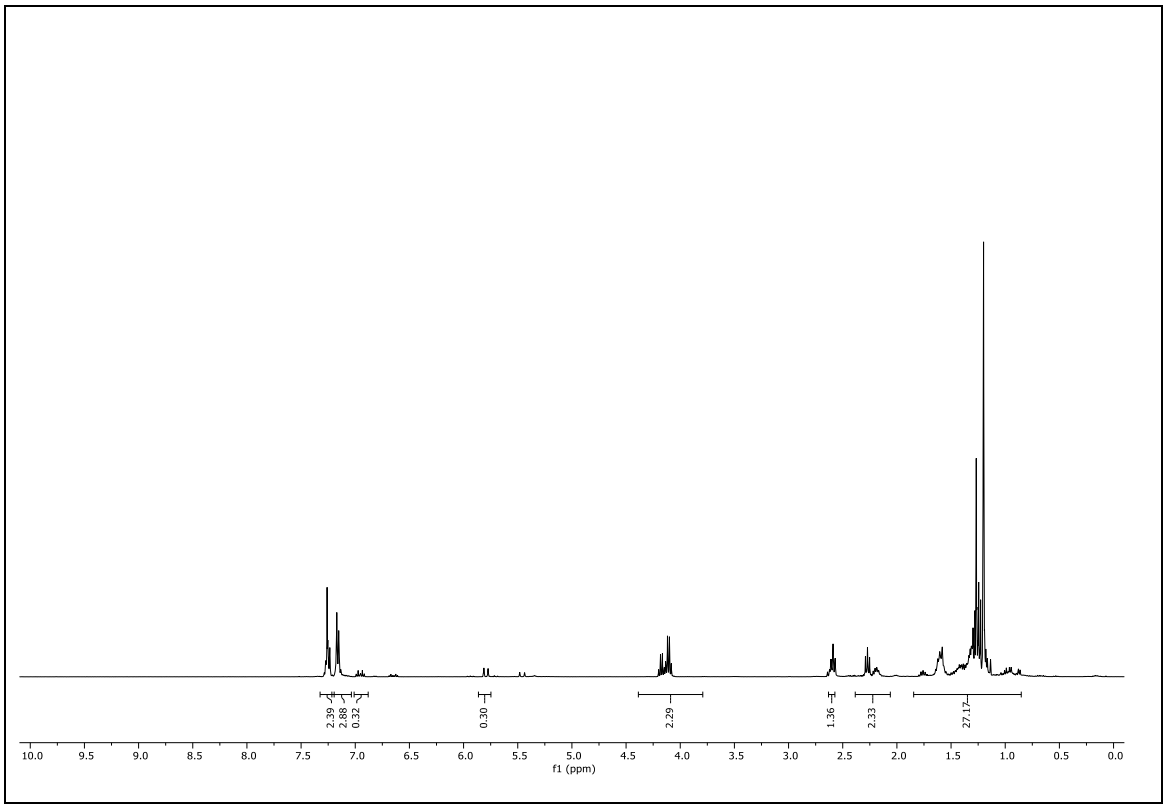
HPLC: The enantiomeric excess (87%) and diastereomeric ratio (93:7) were determined via HPLC analysis using a CHIRALPAK® IA column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Retention time: t_{major} = 14.2 min and t_{minor} = 12.7 min.

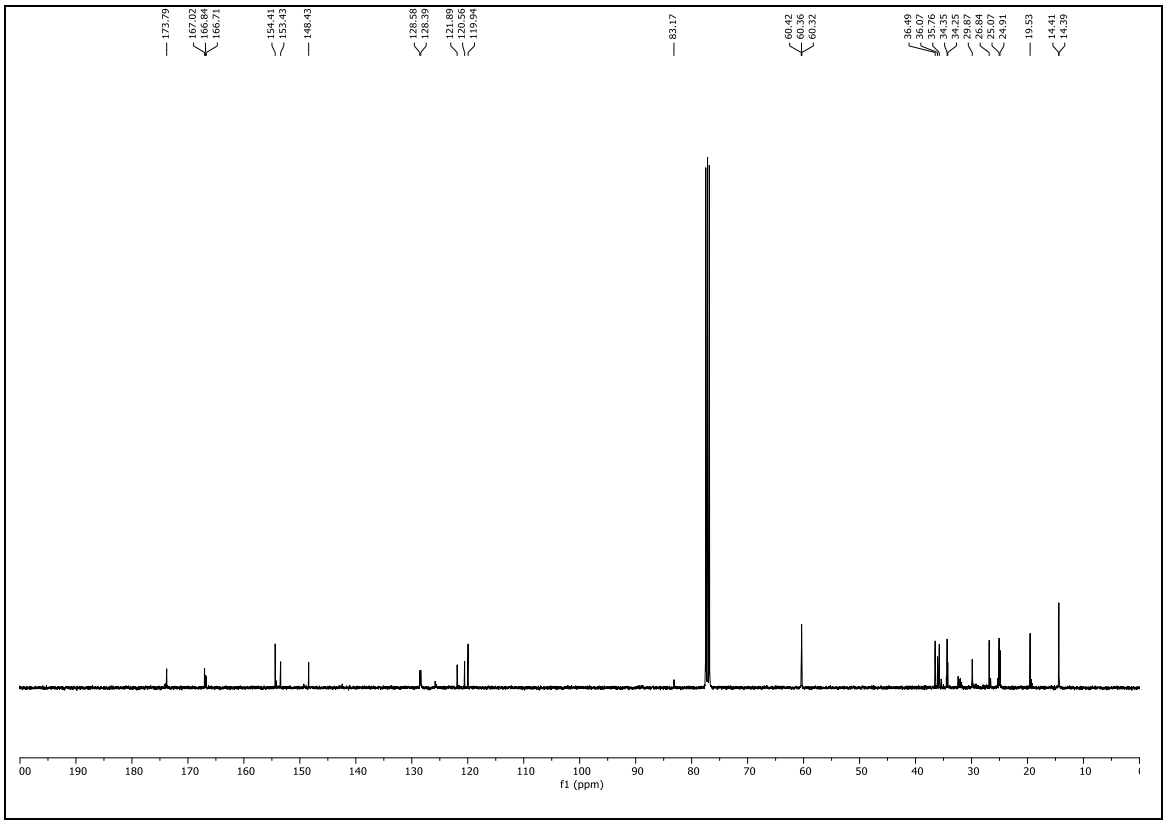
9. Mechanistic Investigations.

9a. Radical Clock Experiment.

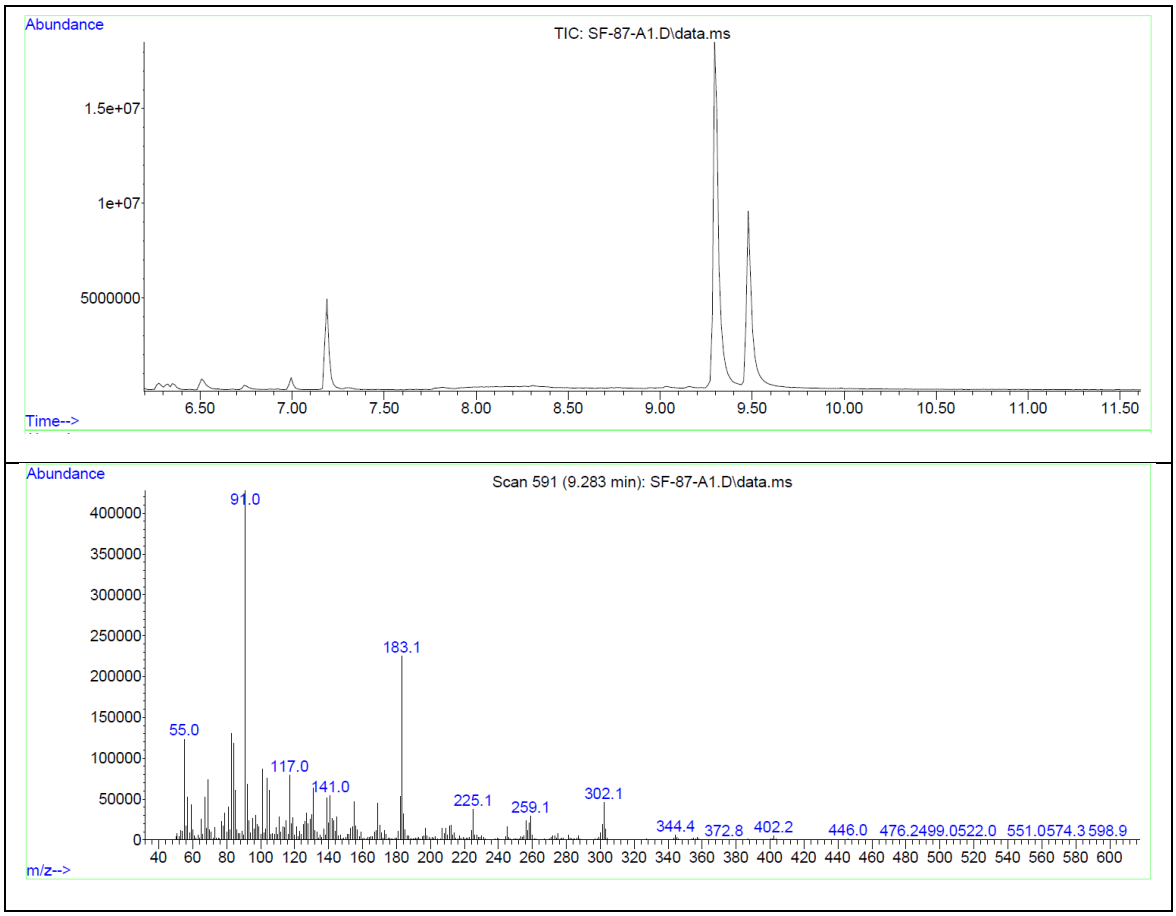


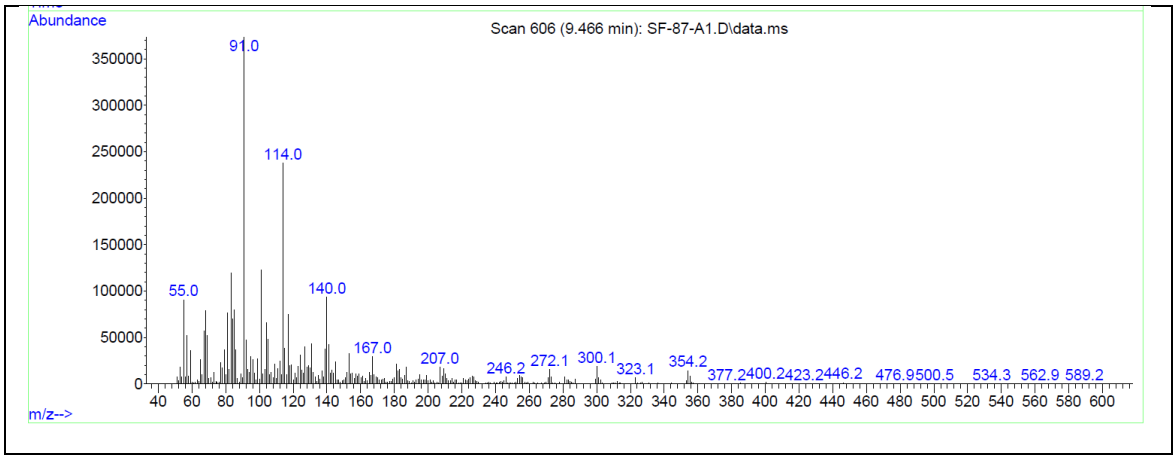
The reaction was conducted in a 0.2 mmol scale following **GP6**, with **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.) and ethyl 2-bromo-2-cyclopropyl ester (**2v**) (43.8 µL, 0.30 mmol, 1.5 equiv.) as coupling partners. Purification by preparative TLC (SiO_2, 20:1 hexane:EtOAc) afforded the mixture of ring-opening products **20** and **21** as a colorless oil (19 mg, ~24%). These two products cannot be purified separately. The supporting spectra (NMR and GC-MS) are shown below. For **20**, HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{37}BNaO_4^+$ 423.2677; Found 423.2679. For **21**, HRMS (ESI/QTOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{39}BNaO_4^+$ 425.2834; Found 425.2845.





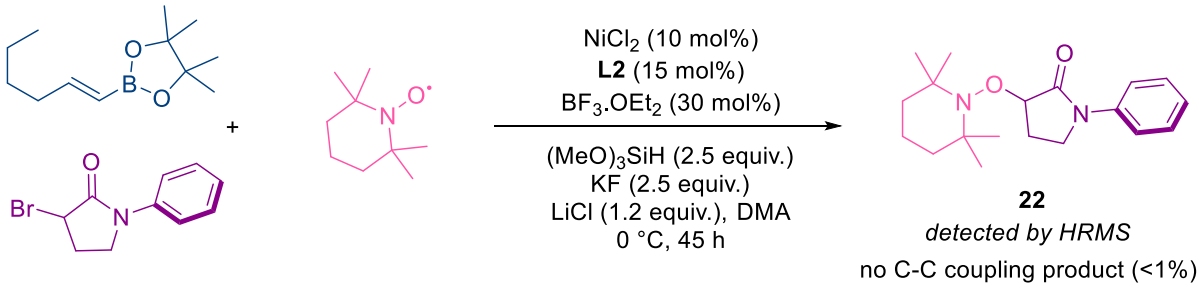
Supplementary Figure 4. NMR spectra of **20** and **21**.



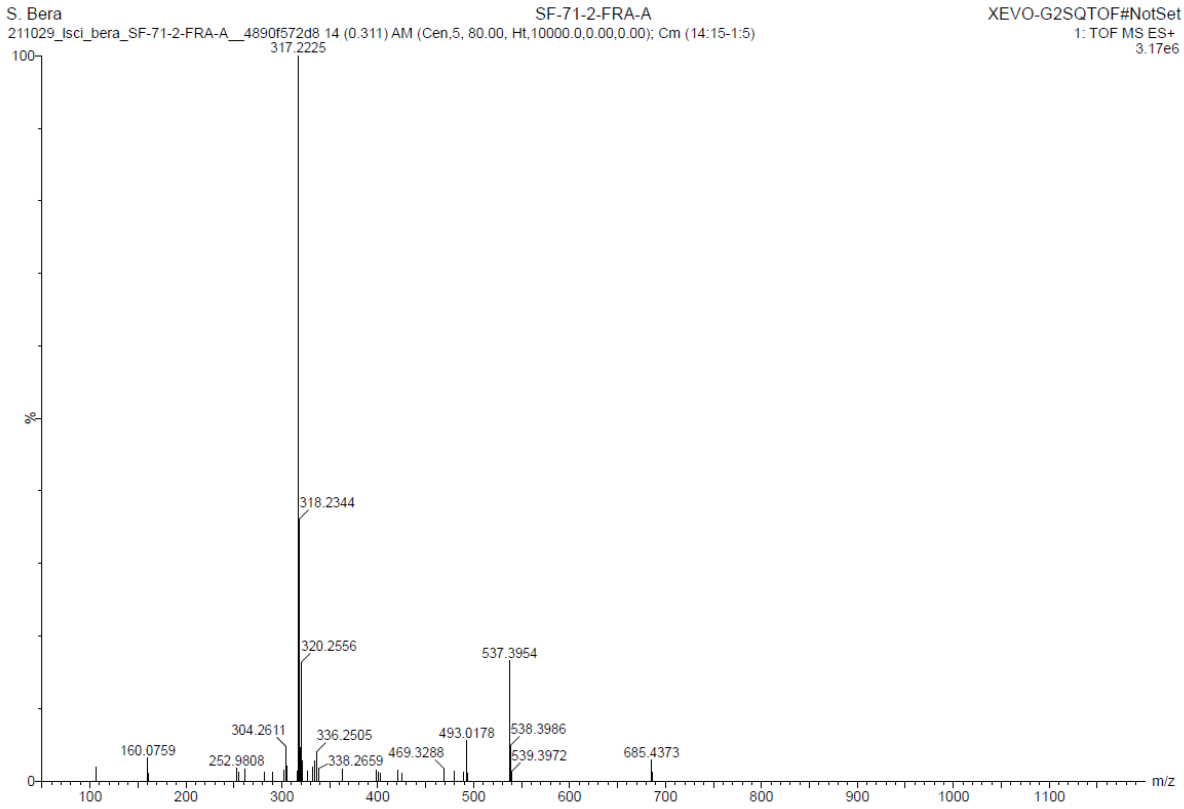


Supplementary Figure 5. GC-MS spectra of **20** and **21**.

9b. TEMPO Trapping Experiment.



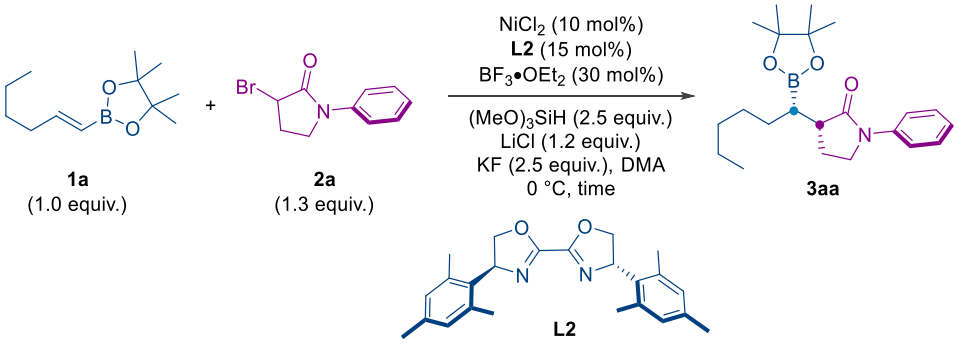
The reaction was conducted in a 0.1 mmol scale following **GP6**. TEMPO (20.7 mg, 0.13 mmol, 1.3 equiv.) was added after the addition of all reagents. The C-C coupling was not detected and an alkyl-TEMPO adduct **22** was detected by HRMS. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{19}H_{29}N_2O_2^+$ 317.2224; Found 317.2220.



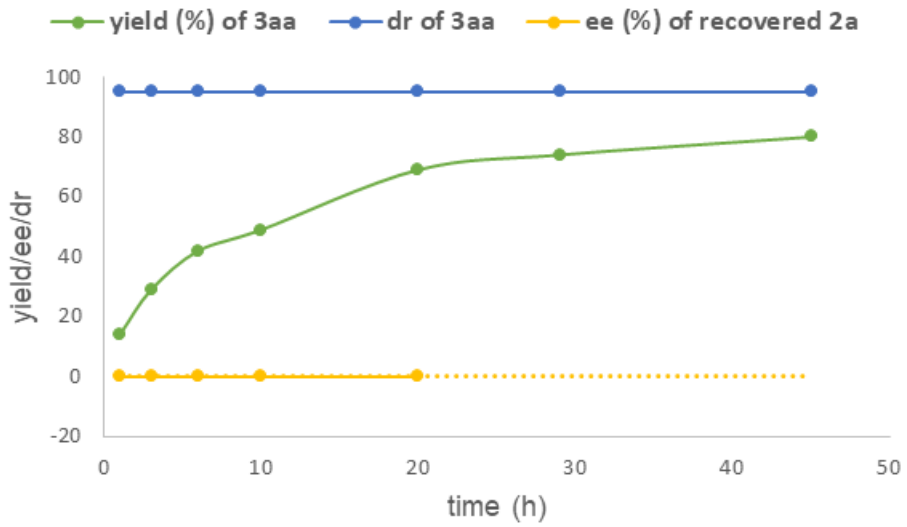
Supplementary Figure 5. High Resolution Mass Spectrometric analysis of **22**.

9c. Time-Dependent Reaction Study.

Seven parallel experiments of our model reaction between **1a** and **2a** at a 0.1 mmol scale with respect to **1a** were performed following **GP6**. The reactions were stopped at the indicated reaction time. After that, the reaction was quenched by the addition of aqueous NH_4Cl (1.0 mL) and EtOAc (3.0 mL). The aqueous phase was extracted with EtOAc (3x3.0 mL). Dodecane (23.0 μL) was added as an internal standard for GC FID analysis to this mixture and the resulting mixture was mixed well. A small organic aliquot was used for the GC FID analysis to determine the yield. The remaining organic phase was separated and the aqueous phase was extracted with EtOAc (2x3.0 mL). The combined organic phases were dried over Na_2SO_4, and the volatiles were removed to afford the crude product. The crude product was purified using flash column chromatography to obtain unreacted **2a** and crude **3aa** which were subjected to chiral HPLC analysis to determine the ee of **2a** and dr of **3aa**.

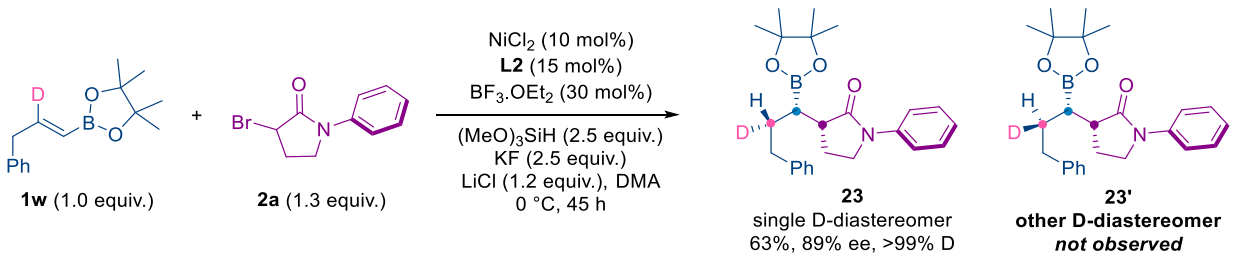


Entry	Time (h)	Yield (%) of 3aa	ee (%) of recovered 2a	dr
1	1	14	0	95:5
2	3	29	0	95:5
3	6	42	0	95:5
4	10	49	0	95:5
5	20	69	0	95:5
6	29	74	n.d.	95:5
7	45	80	n.d.	95:5



Supplementary Figure 6. Reaction profile of the model reaction.

9d. D-Labelling Experiment to Probe the Origin of Enantio-Determining Step.

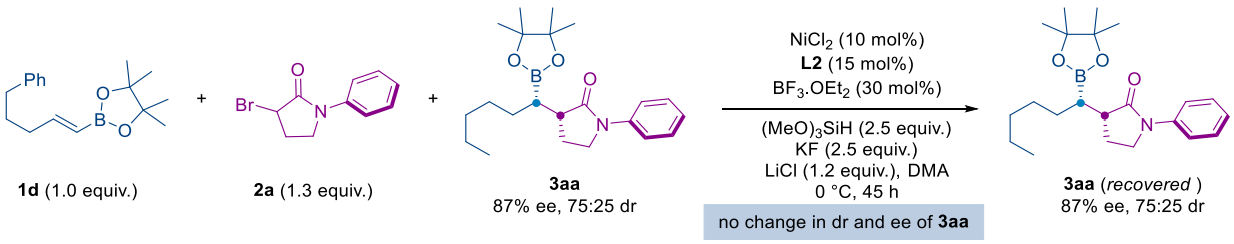


A deuterium-labelling experiment using a deuterium-labelled alkene substrate was conducted to evaluate the enantio-determining step. The reaction was performed following **GP6** with D-labelled alkenyl pinacol boronate **1w** (49.0 mg, 0.20 mmol, 1.00 equiv.) and 2-bromolactam **2a** (62.4 mg, 0.26 mmol, 1.30 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **23** as a sticky oil (51 mg, 63%) in 92:8 diastereomeric ratio. The ^{1}H NMR spectra of **23** revealed the formation of the single D-labelled diastereomer **23** with >99% D-incorporation where deuterium and Bpin group are on the same side. This result confirmed that the syn-selective Ni-H insertion step is the enantio-determining step. The formation of the other diastereomer **23´** in the product was not observed. Note that the diastereoselectivity (dr = 92:8) refers to the diastereomeric cross-coupled products.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.30 – 7.01 (m, 8H), 3.60 – 3.76 (m, 2H),2.80 (td, *J* = 9.4, 5.1 Hz, 1H), 2.70 (dd, *J* = 13.6, 10.6 Hz, 1H), 2.58 (dd, *J* = 13.4, 5.9 Hz, 1H), 2.20 – 2.08 (m, 1H), 2.02 – 1.90 (m, 1H), 1.69 – 1.61 (m, 1H), 1.55 (d, *J* = 16.3 Hz, 2H), 1.31 – 1.22 (m, 2H), 1.16 (s, 12H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.31, 142.19, 139.89, 129.70, 128.47, 128.30, 126.30, 124.78, 119.81, 84.12, 50.26, 45.00, 37.31, 29.72, 24.85, 24.83, 22.69. **^{11}B NMR (128 MHz, Chloroform-*d*)** δ 33.61. **FTIR (neat):** $\tilde{\nu}$ = 2974.4, 2923.4, 2854.2, 1692.6, 1598.1, 1495.8, 1454.3, 1389.9, 1371.9, 1311.4, 1265.8, 1214.8, 1165.0, 1142.2, 1111.9, 1030.3, 966.4, 852.3, 756.6 cm^{-1}. **HRMS (ESI/QTOF) m/z:** $[M + H]^+$ Calcd for $C_{25}H_{32}[^2H]BNO_3^+$ 407.2611; Found 407.2612. $[\alpha]_D^{20}$ = +42.1 (c = 1.00 in $CHCl_3$). **M.P.** = 71.1 – 74.0 °C.

HPLC: The enantiomeric excess (89%) and diastereomeric ratio (92:8) were determined via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Retention time: t_{major} = 9.9 min and t_{minor} = 12.9 min.

9e. Control Experiment.

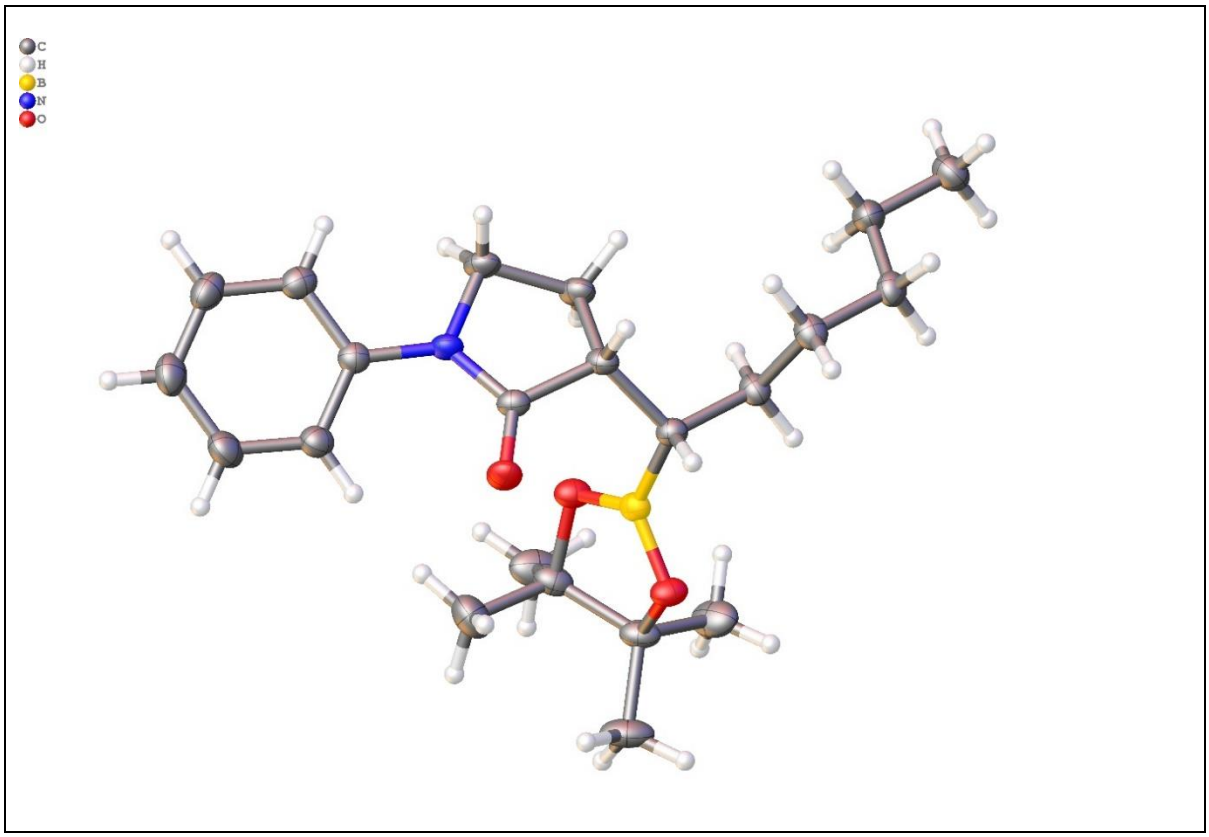


Product **3aa** with 87% ee and 75:25 dr (37.1 mg, 0.10 mmol, 1.0 equiv.) was subjected to a reaction containing substrates **1d** (54.4 mg, 0.20 mmol, 1.0 equiv.), **2a** (62.4 mg, 0.26 mmol, 1.3 equiv.) under the standard reaction conditions following **GP6**. No change in enantioselectivity and diastereoselectivity of **3aa** was observed after 45 hours of reaction time.

10. Crystallography details

Compound (+) 3aa:

Experimental details. Single clear pale colourless prism-shaped crystals of **3aa** were used as supplied. A suitable crystal with dimensions 0.86 × 0.13 × 0.07 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 139.98(10) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.



Supplementary Figure 7. Crystal structure of **3aa.**

Compound	**3aa**
Formula	$C_{22}H_{34}BNO_3$
Dcalc	1.153
μ/mm^{-1}	0.584
Formula Weight	371.31
Colour	clear pale colourless

Shape	prism-shaped
Size/mm^3	0.86×0.13×0.07
T/K	139.98(10)
Crystal System	orthorhombic
Flack Parameter	-0.11(5)
Hooft Parameter	-0.11(5)
Space Group	$P2_12_12_1$
a/Å	6.41165(6)
b/Å	13.24029(12)
c/Å	25.2063(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	2139.81(3)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu Kα
Θ_{min}/°	3.507
Θ_{max}/°	75.470
Measured Refl's.	40226
Indep't Refl's	4306
Refl's I≥2 σ(I)	4191
R_{int}	0.0396
Parameters	250
Restraints	0
Largest Peak	0.187
Deepest Hole	-0.128

GooF	1.025
wR_2 (all data)	0.0719
wR_2	0.0715
R_1 (all data)	0.0292
R_1	0.0285

Structure Quality Indicators

Reflections:	d min (Cu\a) 2Θ=150.9°	0.80	I/σ(I)	66.8	Rint	3.96%	CAP 133.9° 98% to 150.9°	100	
Refinement:	Shift	-0.001	Max Peak	0.2	Min Peak	-0.1	GooF	1.025	Hooft -.11(5)

A clear pale colourless prism-shaped-shaped crystal with dimensions 0.86 × 0.13 × 0.07 mm^3 was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at T = 139.98(10) K.

Data were measured using ω scans with Cu K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.119a (Rigaku OD, 2021). The maximum resolution that was achieved was Θ = 75.470˚ (0.80 Å).

The unit cell was refined using CrysAlisPro 1.171.41.119a (Rigaku OD, 2021) on 30693 reflections, 76% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.119a (Rigaku OD, 2021). The final completeness is 100.00 % out to 75.470˚ in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.41.119a (Rigaku Oxford Diffraction, 2021). The numerical absorption correction was based on gaussian integration over a multifaceted crystal model. The empirical absorption correction was carried out using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this crystal is 0.584 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.632 and 1.000.

The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

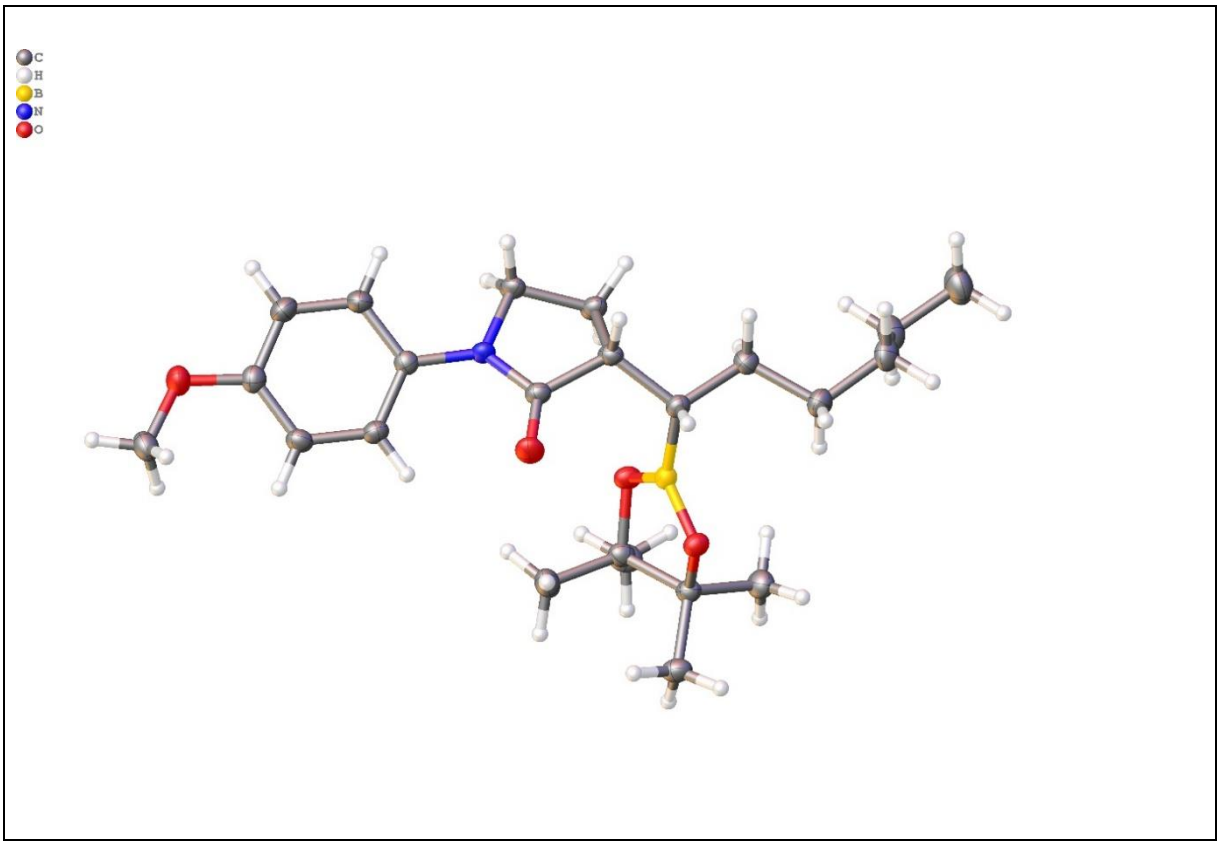
The Flack parameter was refined to -0.11(5). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.11(5). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be

near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

CCDC- 2165076 contains the supplementary crystallographic data for **3aa**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Compound (+) 3ab:

Experimental details. Single clear pale colourless prism-shaped crystals of **3ab** were used as supplied. A suitable crystal with dimensions 0.47 × 0.13 × 0.06 mm^3 was selected and mounted on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at a steady T = 139.92(14) K during data collection. The structure was solved with the **ShelXT** (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.



Supplementary Figure 8. Crystal structure of **3ab.**

Compound	**3ab**
Formula	$C_{23}H_{36}BNO_4$
Dcalc	1.184

μ/mm^{-1}	0.626
Formula Weight	401.34
Colour	clear pale colourless
Shape	prism-shaped
Size/mm^3	0.47×0.13×0.06
T/K	139.92(14)
Crystal System	monoclinic
Flack Parameter	0.0(2)
Hooft Parameter	0.13(9)
Space Group	$P2_1$
a/Å	9.9317(2)
b/Å	6.3863(2)
c/Å	17.7667(5)
α/°	90
β/°	92.939(3)
γ/°	90
V/Å^3	1125.40(5)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu Kα
Θ_{min}/°	4.458
Θ_{max}/°	72.665
Measured Refl's.	10367
Indep't Refl's	4110
Refl's I≥2 σ(I)	3903
R_{int}	0.0298
Parameters	269
Restraints	1
Largest Peak	0.252
Deepest Hole	-0.157
GooF	1.048
wR_2 (all data)	0.0842
wR_2	0.0826
R_1 (all data)	0.0346
R_1	0.0324

Structure Quality Indicators

Reflections:	d min (Cu\a) 2Θ=145.3° 0.81	I/σ(I) 29.9	Rint 2.98%	CAP 133.9° 99% to 145.3° 100
Refinement:	Shift 0.000	Max Peak 0.2	Min Peak -0.2	GooF 1.048

A clear pale colourless prism-shaped-shaped crystal with dimensions 0.47 × 0.13 × 0.06 mm^3 was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at T = 139.92(14) K.

Data were measured using ω scans with Cu K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.119a (Rigaku OD, 2021). The maximum resolution that was achieved was Θ = 72.665˚ (0.81 Å).

The unit cell was refined using CrysAlisPro 1.171.41.119a (Rigaku OD, 2021) on 6201 reflections, 60% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.119a (Rigaku OD, 2021). The final completeness is 100.00 % out to 72.665˚ in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.41.119a (Rigaku Oxford Diffraction, 2021). The numerical absorption correction was based on gaussian integration over a multifaceted crystal model. The empirical absorption correction was obtained using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this crystal is 0.626 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.807 and 1.000.

The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT (Sheldrick, 2015) structure solution program using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: Refined as a 2-component inversion twin.

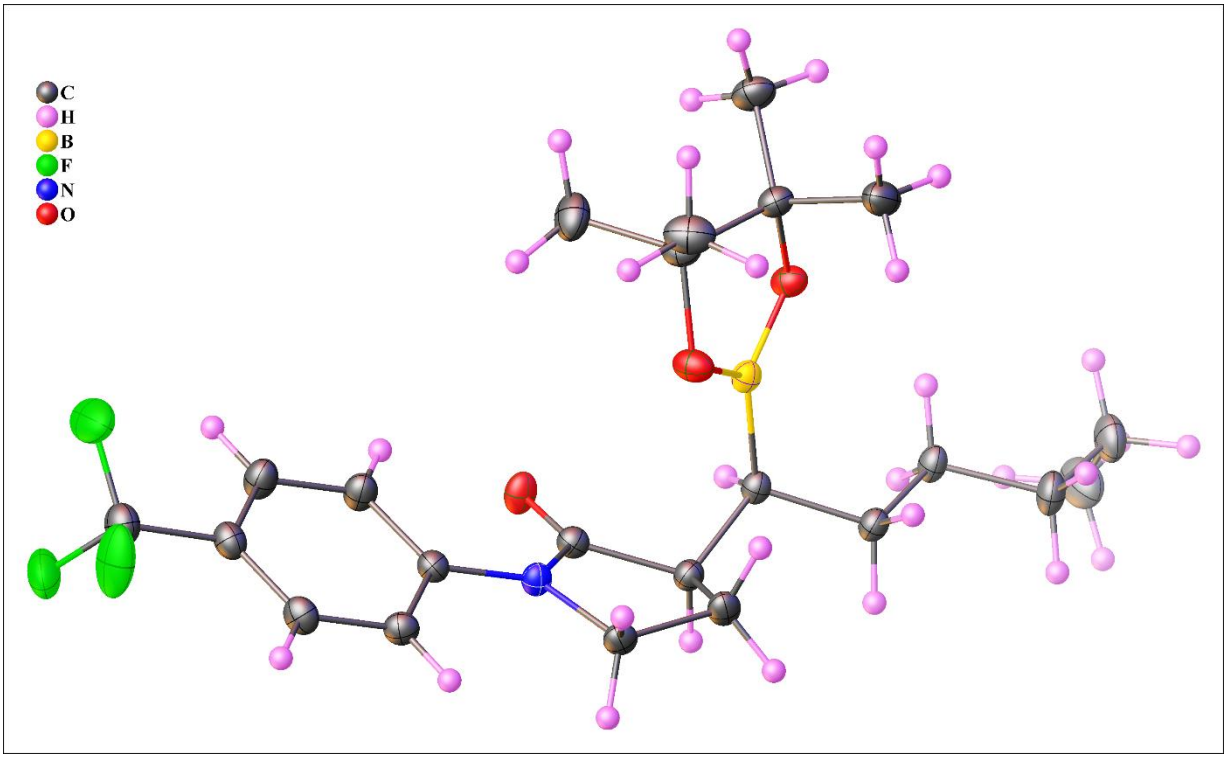
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

The Flack parameter was refined to 0.0(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in 0.13(9). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

CCDC- 2165081 contains the supplementary crystallographic data for **3ab**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Compound (+) 3ad:

Experimental details. Single colourless needle-shaped crystals of **3ad** were used as supplied. A suitable crystal with dimensions 0.47 × 0.04 × 0.04 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.



Supplementary Figure 9. Crystal structure of **3ad.**

Compound	**3ad**
Formula	$C_{23}H_{33}BF_3NO_3$
$D_{calc.}$/ g cm^{-3}	1.242
μ/mm^{-1}	0.802
Formula Weight	439.31
Colour	colourless
Shape	needle-shaped
Size/mm^3	0.47×0.04×0.04
T/K	140.00(10)
Crystal System	orthorhombic
Flack Parameter	0.04(7)
Space Group	$P2_12_12_1$
a/Å	7.53258(13)
b/Å	16.0539(3)

c/Å	19.4319(4)
α/°	90
β/°	90
γ/°	90
V/Å^3	2349.85(8)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$
Θ_{min}/°	3.571
Θ_{max}/°	75.594
Measured Refl's.	26611
Indep't Refl's	4836
Refl's I≥2σ(I)	4274
R_{int}	0.0477
Parameters	286
Restraints	0
Largest Peak/e Å^{-3}	0.249
Deepest Hole/e Å^{-3}	-0.195
GooF	1.070
wR_2 (all data)	0.1016
wR_2	0.0987
R_1 (all data)	0.0458
R_1	0.0394
CCDC number	2118223

Structure Quality Indicators

Reflections: d min (Cu\a) 2Θ=151.2° 0.80 | I/σ(I) CIF 29.3 | Rint CIF 4.77% | Full 135.4° CIF 100

Refinement: Shift CIF 0.000 | Max Peak CIF 0.2 | Min Peak CIF -0.2 | GooF CIF 1.070 | Hooft CIF .04(7)

A colourless needle-shaped-shaped crystal with dimensions 0.47 × 0.04 × 0.04 mm^3 was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at T = 140.00(10) K.

Data were measured using ω scans with Cu Kα radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.118a (Rigaku OD, 2021). The maximum resolution achieved was Θ = 75.594° (0.80 Å).

The unit cell was refined using CrysAlisPro 1.171.41.118a (Rigaku OD, 2021) on 15225 reflections, 57% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.118a (Rigaku OD, 2021). The final completeness is 100.00 % out to 75.594° in Θ. A Gaussian absorption correction was performed using CrysAlisPro 1.171.41.118a (Rigaku Oxford Diffraction, 2021) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 0.802 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.725 and 1.000.

The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT 2018/2 (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

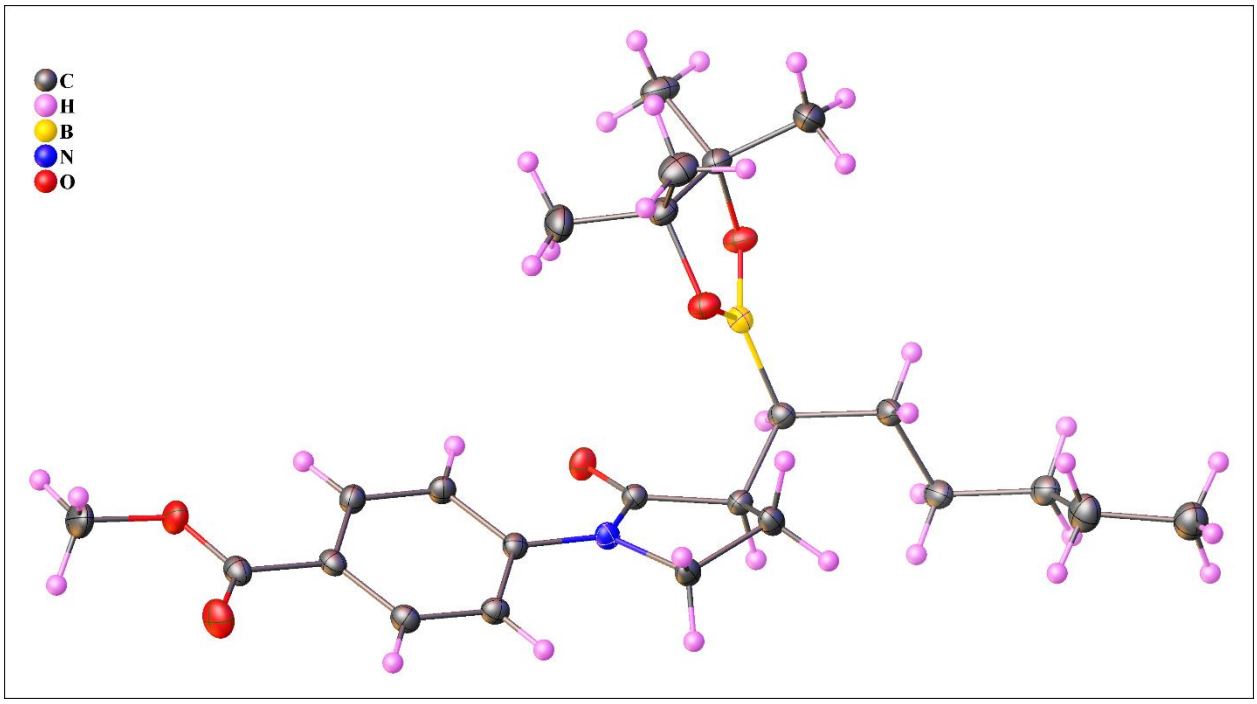
There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to 0.04(7). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in None. Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

CCDC- 2118223 contains the supplementary crystallographic data for **3ad**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Compound (+) 3af:

Experimental detail. Single colourless needle-shaped crystals of **3af** were used as supplied. A suitable crystal with dimensions 0.46 × 0.05 × 0.04 mm^3 was selected and mounted on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 140.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2015) solution program using dual methods and by using **Olex2** 1.5 (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.



Supplementary Figure 10. Crystal structure of **3af.**

Compound	**3af**
Formula	$C_{24}H_{36}BNO_5$
$D_{calc.}$/ g cm^{-3}	1.190
μ/mm^{-1}	0.654
Formula Weight	429.35
Colour	colourless
Shape	needle-shaped
Size/mm^3	0.46×0.05×0.04
T/K	140.00(10)
Crystal System	monoclinic
Flack Parameter	0.07(16)
Space Group	$P2_1$
a/Å	11.9500(2)
b/Å	6.33351(11)
c/Å	16.6233(4)
α/°	90
β/°	107.788(2)
γ/°	90
V/Å^3	1198.00(4)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu$K\alpha$
Θ_{min}/°	3.885

Θ_{max}/°	75.588
Measured Refl's.	18105
Indep't Refl's	4843
Refl's I≥2σ(I)	4352
R_{int}	0.0682
Parameters	287
Restraints	1
Largest Peak/e Å^{-3}	0.231
Deepest Hole/e Å^{-3}	-0.150
GooF	1.053
wR_2 (all data)	0.1150
wR_2	0.1126
R_1 (all data)	0.0485
R_1	0.0435
CCDC number	2118224

Structure Quality Indicators

Reflections: d min (Cu\a) 2Θ=151.2° 0.80 | I/σ(I) CIF 19.4 | Rint CIF 6.82% | Full 135.4° 98% to 151.2° 100

Refinement: Shift CIF 0.000 | Max Peak CIF 0.2 | Min Peak CIF -0.1 | GooF CIF 1.053 | Hooft CIF .07(16)

A colourless needle-shaped-shaped crystal with dimensions 0.46 × 0.05 × 0.04 mm^3 was mounted. Data were collected using a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer operating at T = 140.00(10) K.

Data were measured using ω scans with Cu K$_\alpha$ radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.41.118a (Rigaku OD, 2021). The maximum resolution achieved was Θ = 75.588° (0.80 Å).

The unit cell was refined using CrysAlisPro 1.171.41.118a (Rigaku OD, 2021) on 12151 reflections, 67% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.41.118a (Rigaku OD, 2021). The final completeness is 100.00 % out to 75.588° in Θ. A Gaussian absorption correction was performed using CrysAlisPro 1.171.41.118a (Rigaku Oxford Diffraction, 2021) Numerical absorption correction based on Gaussian integration over a multifaceted crystal model. Empirical absorption correction using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm. The absorption coefficient μ of this material is 0.654 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.718 and 1.000.

The structure was solved and the space group $P2_1$ (# 4) determined by the ShelXT 2018/2

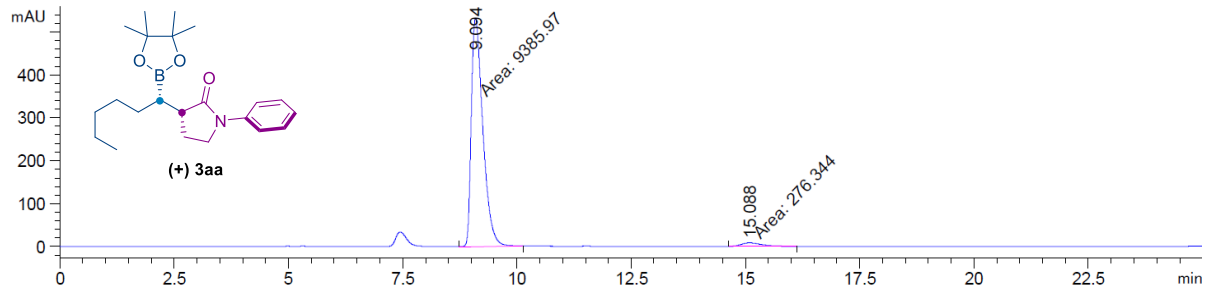
(Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of **ShelXL** 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

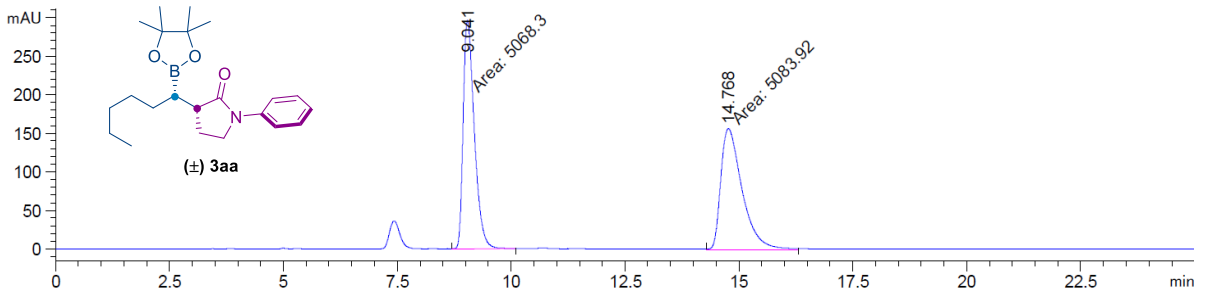
The Flack parameter was refined to 0.07(16). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in None. Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

CCDC- 2118224 contains the supplementary crystallographic data for **3af**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

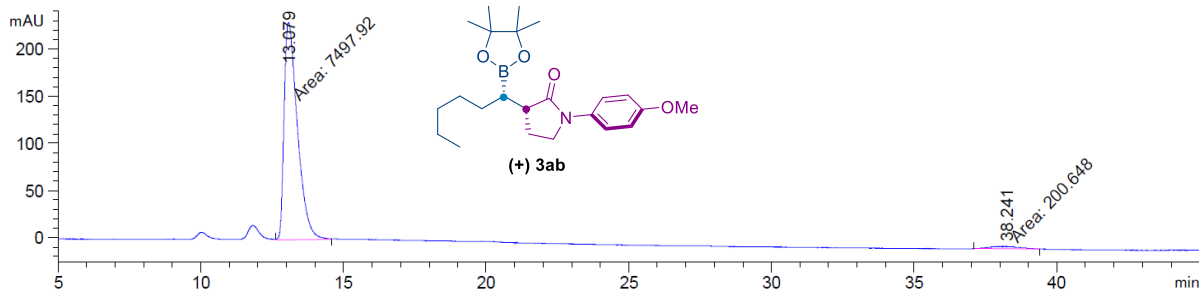
11. HPLC Spectra:



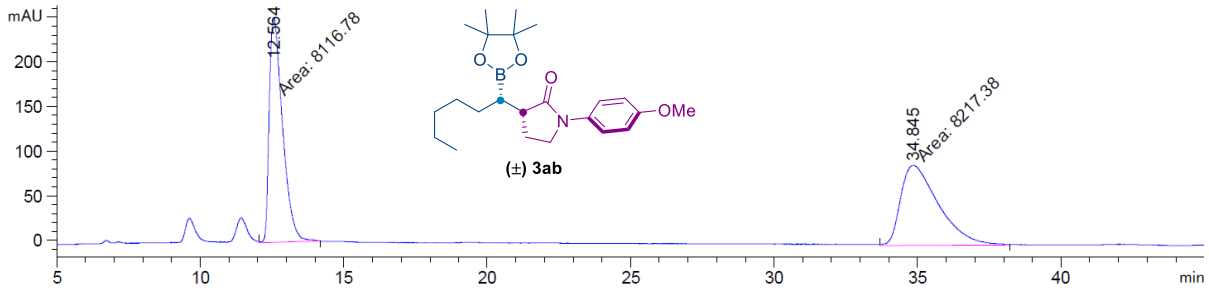
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.094	MM	0.2937	9385.97168	532.54309	97.1400
2	15.088	MM	0.5432	276.34418	8.47932	2.8600



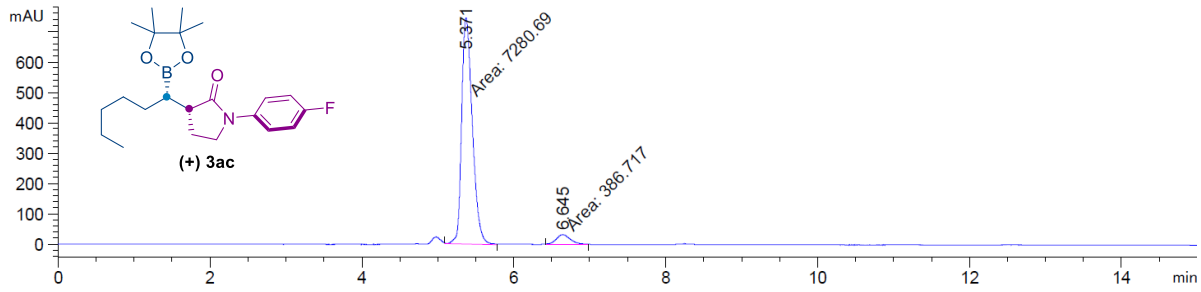
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.041	MM	0.2845	5068.29834	296.90427	49.9231
2	14.768	MM	0.5412	5083.91797	156.56822	50.0769



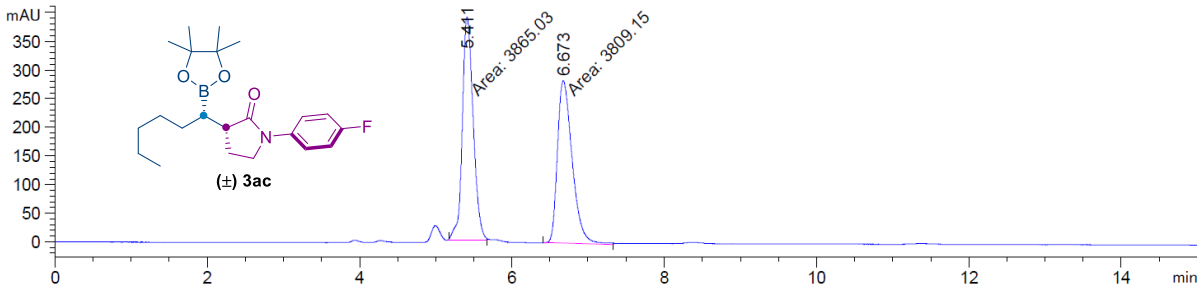
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.079	MM	0.5416	7497.91504	230.73347	97.3937
2	38.241	MM	1.2780	200.64798	2.61670	2.6063



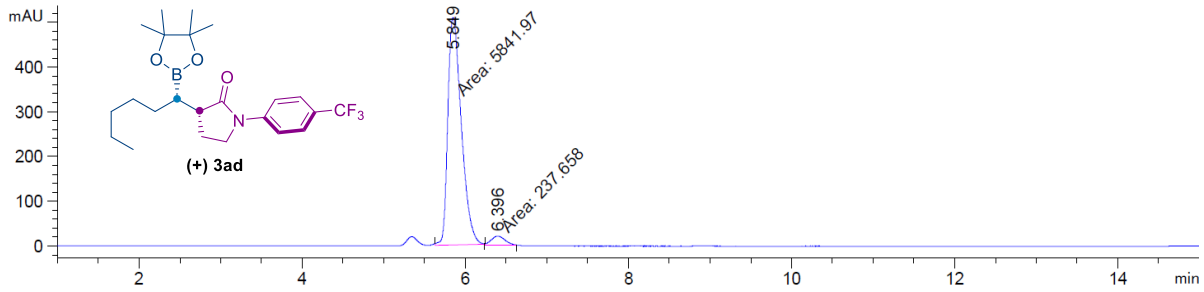
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.564	MM	0.5366	8116.78418	252.09378	49.6921
2	34.845	MM	1.5285	8217.37598	89.60329	50.3079



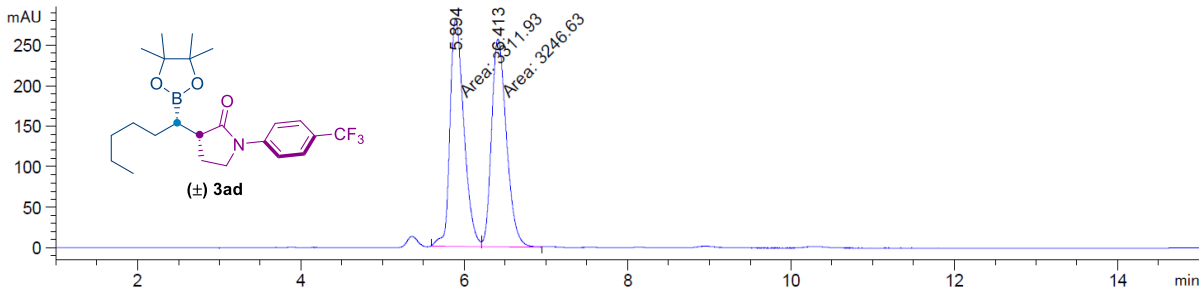
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.371	MM	0.1628	7280.68994	745.29175	94.9564
2	6.645	MM	0.2092	386.71671	30.81579	5.0436



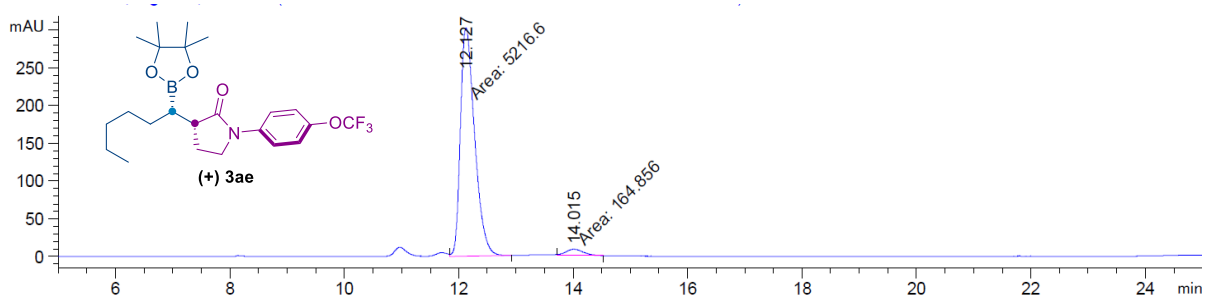
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.411	MM	0.1657	3865.03491	388.83401	50.3641
2	6.673	MM	0.2240	3809.14893	283.39978	49.6359



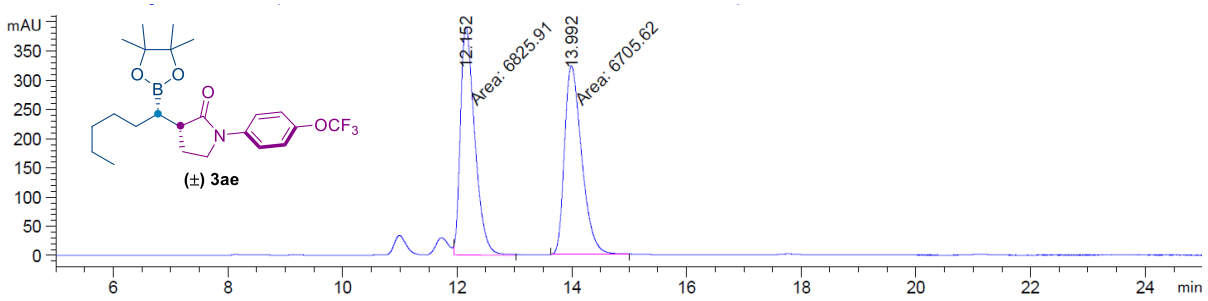
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.849	MM	0.1914	5841.96826	508.81122	96.0909
2	6.396	MM	0.1971	237.65802	20.09516	3.9091



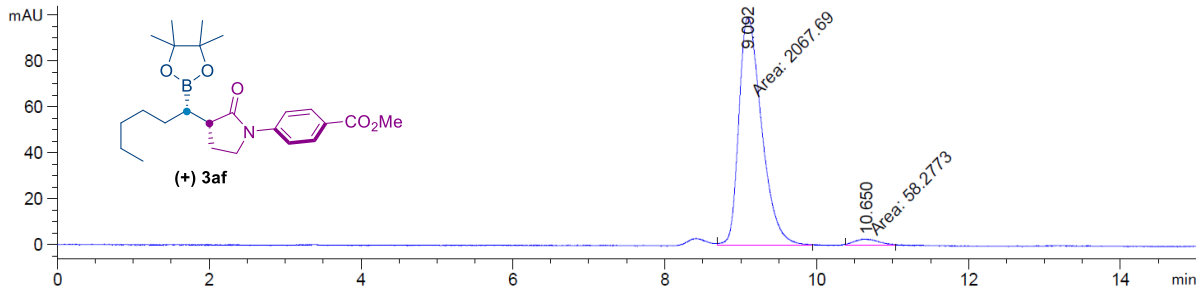
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.894	MF	0.1965	3311.92627	280.92212	50.4978
2	6.413	FM	0.2114	3246.62695	256.02112	49.5022



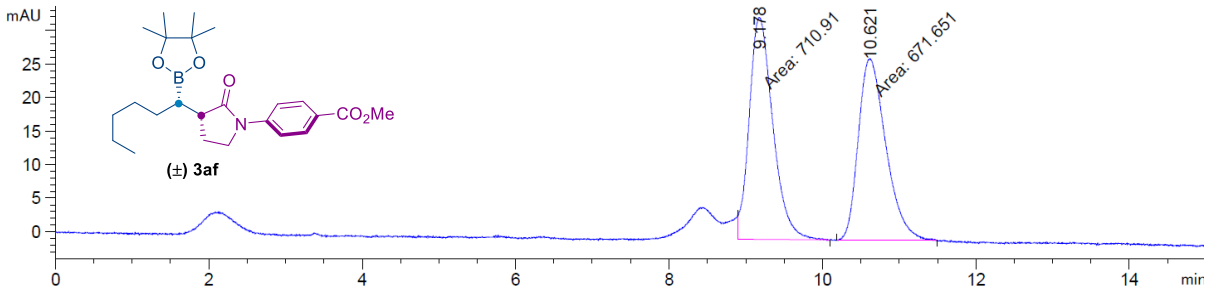
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.127	FM	0.2876	5216.60205	302.25458	96.9366
2	14.015	MM	0.3389	164.85605	8.10719	3.0634



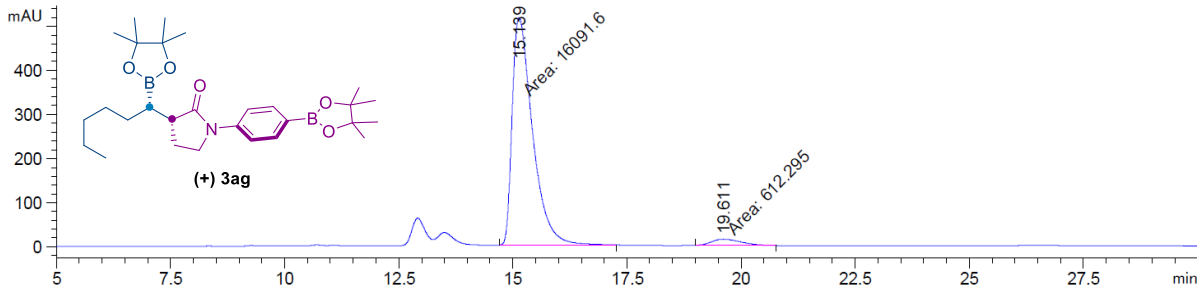
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.152	FM	0.2910	6825.91162	390.89606	50.4445
2	13.992	MM	0.3463	6705.62012	322.69064	49.5555



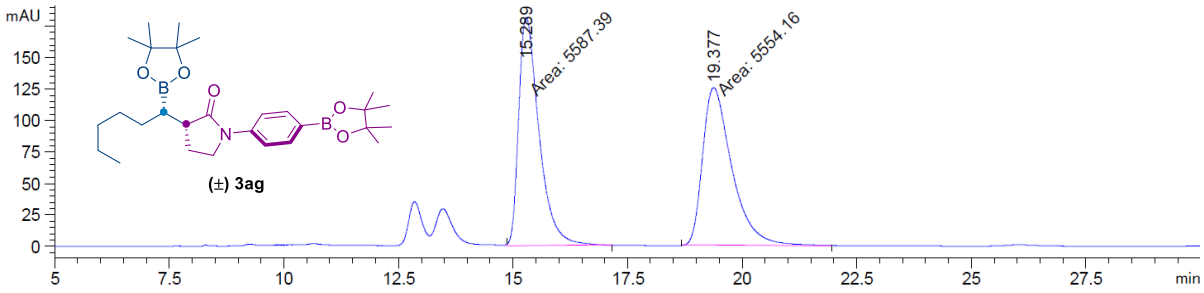
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.092	MM	0.3474	2067.68945	99.19828	97.2588
2	10.650	MM	0.3637	58.27728	2.67083	2.7412



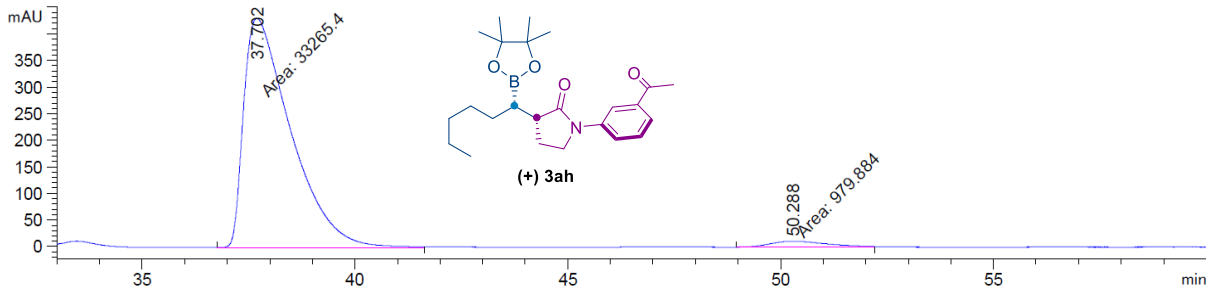
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.178	FM	0.3577	710.90973	33.12564	51.4198
2	10.621	MM	0.4137	671.65088	27.05931	48.5802



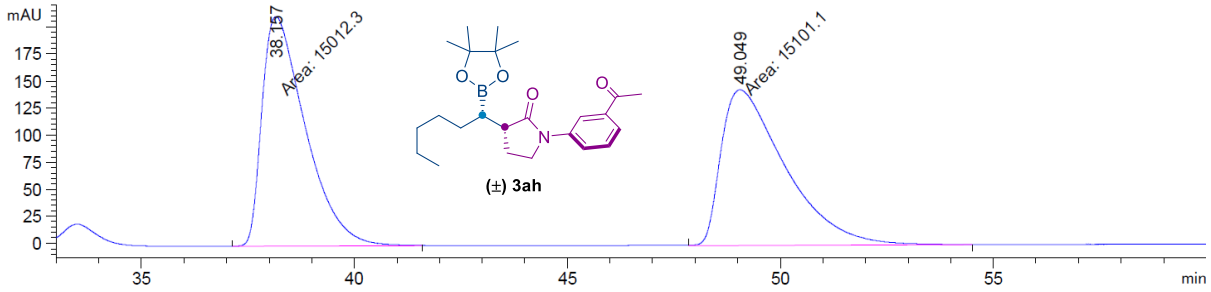
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.139	MM	0.5190	1.60916e4	516.73743	96.3344
2	19.611	MM	0.7334	612.29529	13.91473	3.6656



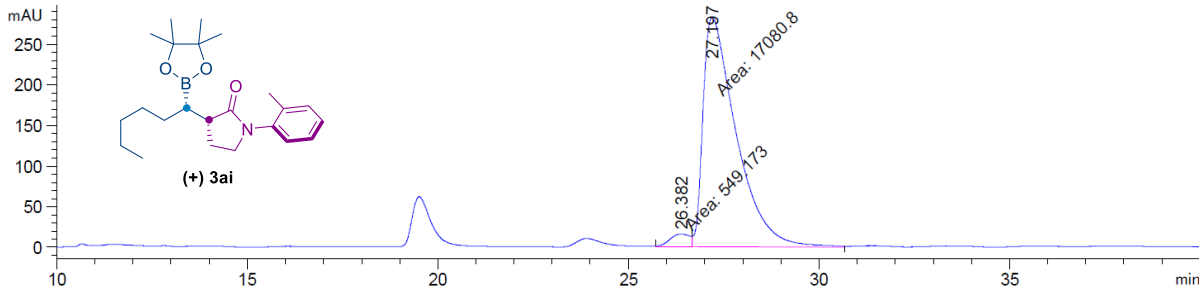
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.289	MM	0.5134	5587.39063	181.40291	50.1491
2	19.377	MM	0.7395	5554.15771	125.18571	49.8509



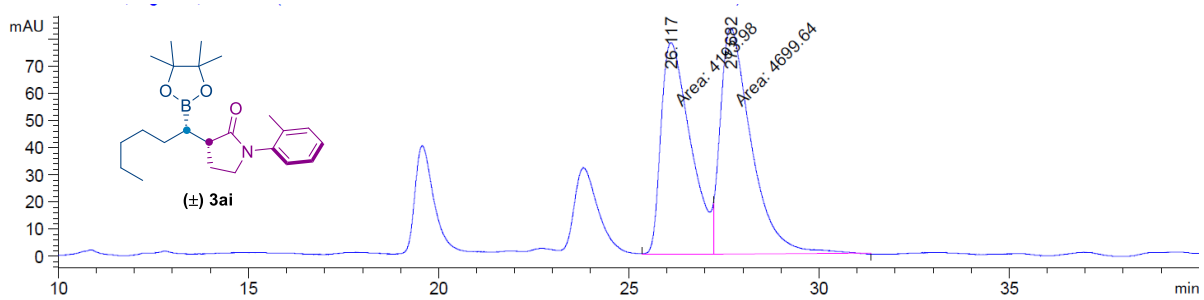
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.702	MM	1.2843	3.32654e4	431.67712	97.1386
2	50.288	MM	1.5074	979.88361	10.83385	2.8614



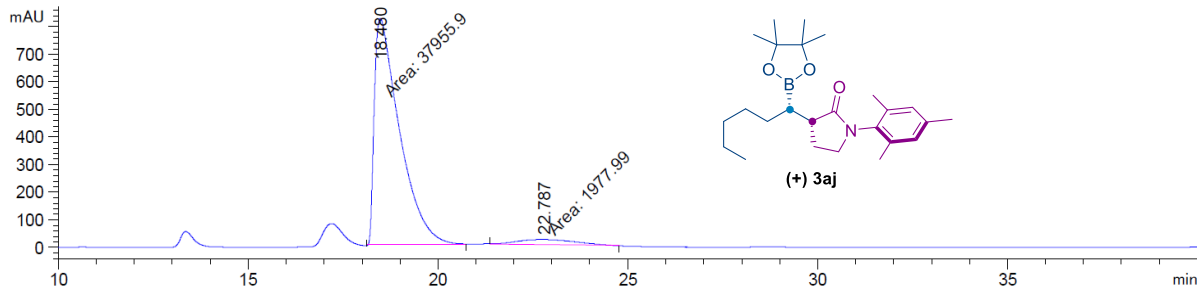
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.157	MM	1.1796	1.50123e4	212.11505	49.8526
2	49.049	MM	1.7505	1.51011e4	143.78099	50.1474



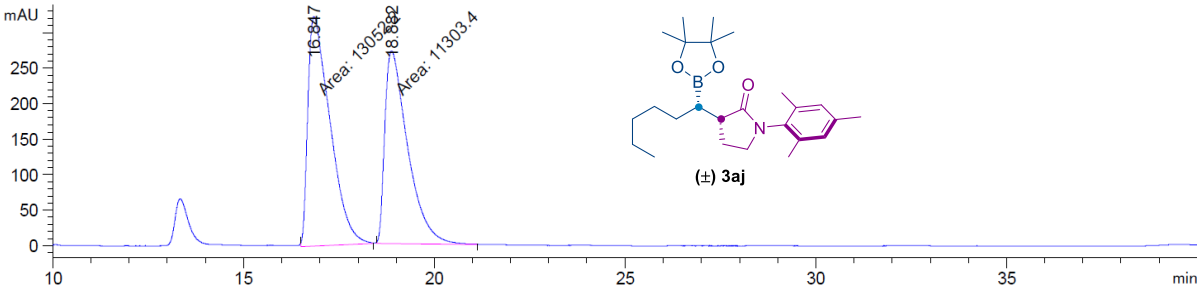
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.382	MF	0.5965	549.17291	15.34314	3.1150
2	27.197	FM	1.0068	1.70808e4	282.76984	96.8850



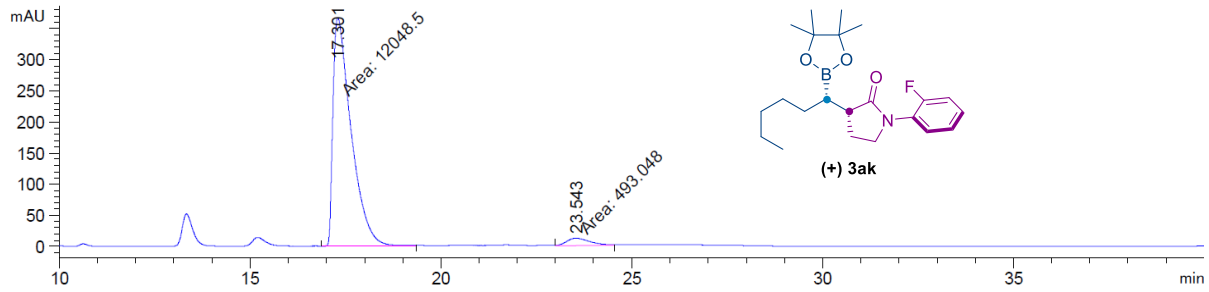
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.117	MF	0.8973	4193.98291	77.90073	47.1572
2	27.682	FM	0.9407	4699.63623	83.26147	52.8428



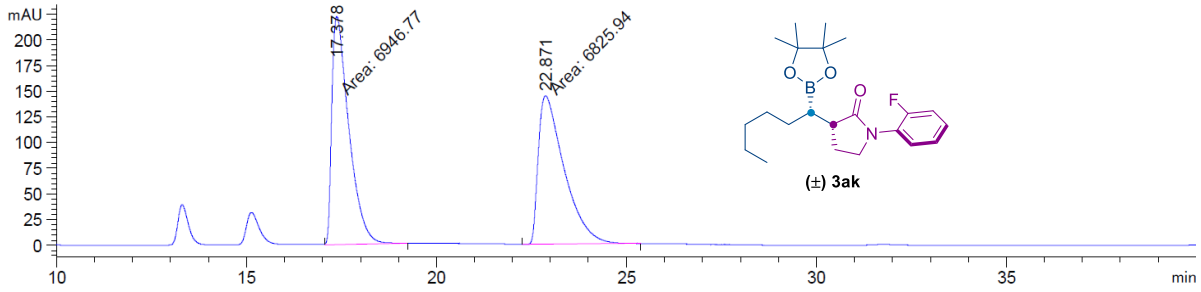
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.480	MM	0.7710	3.79559e4	820.53296	95.0468
2	22.787	MM	1.7552	1977.98840	18.78168	4.9532



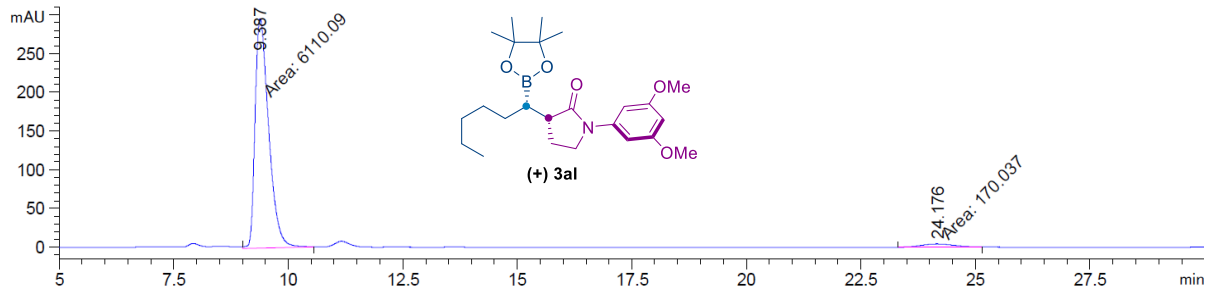
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.847	MM	0.6728	1.30522e4	323.30807	53.5901
2	18.882	MM	0.6936	1.13034e4	271.61853	46.4099



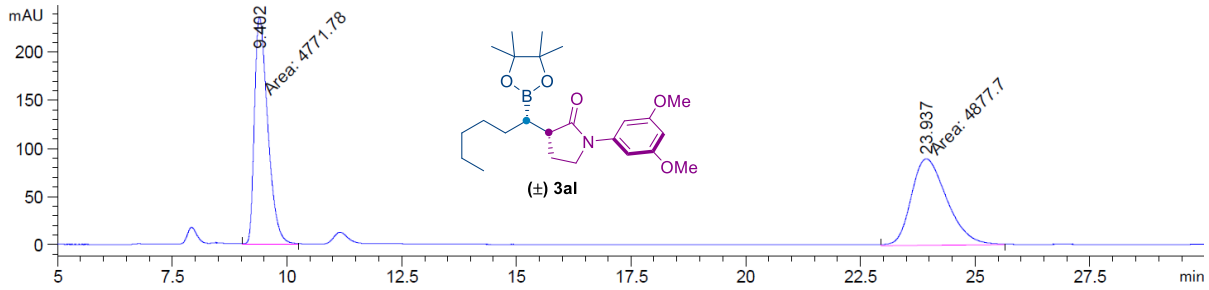
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.301	MM	0.5479	1.20485e4	366.53171	96.0687
2	23.543	MM	0.6954	493.04770	11.81677	3.9313



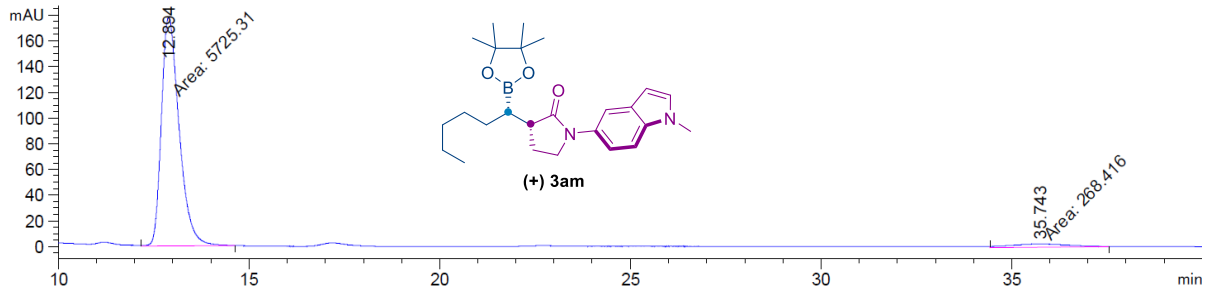
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.378	MM	0.5215	6946.77002	222.02208	50.4387
2	22.871	MM	0.7895	6825.93652	144.10368	49.5613



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.387	MM	0.3437	6110.08691	296.30750	97.2925
2	24.176	MM	0.7398	170.03699	3.83058	2.7075

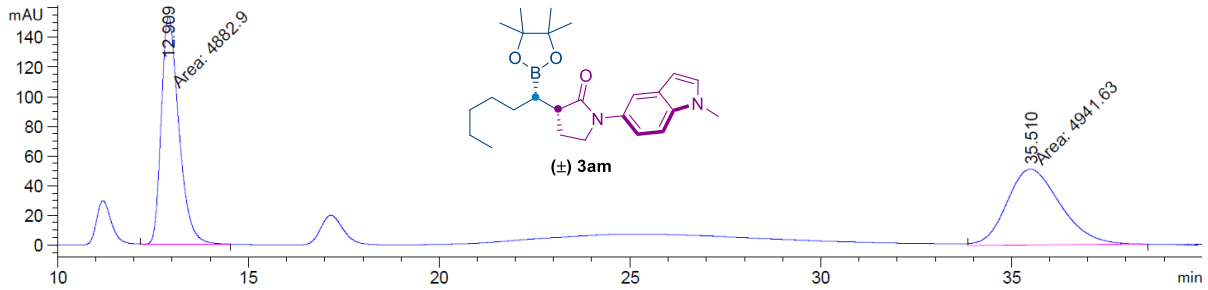


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.402	MM	0.3361	4771.78320	236.62791	49.4512
2	23.937	MM	0.9034	4877.70117	89.98909	50.5488



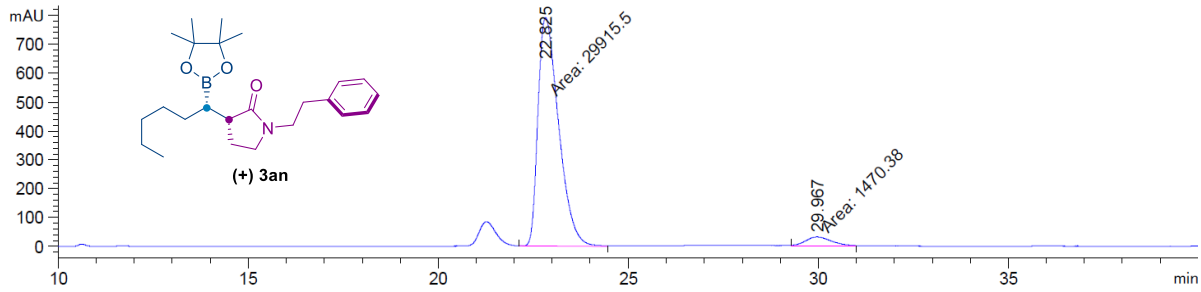
(+) 3am

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.894	MM	0.5366	5725.31055	177.81055	95.5217
2	35.743	MM	1.7865	268.41602	2.50418	4.4783

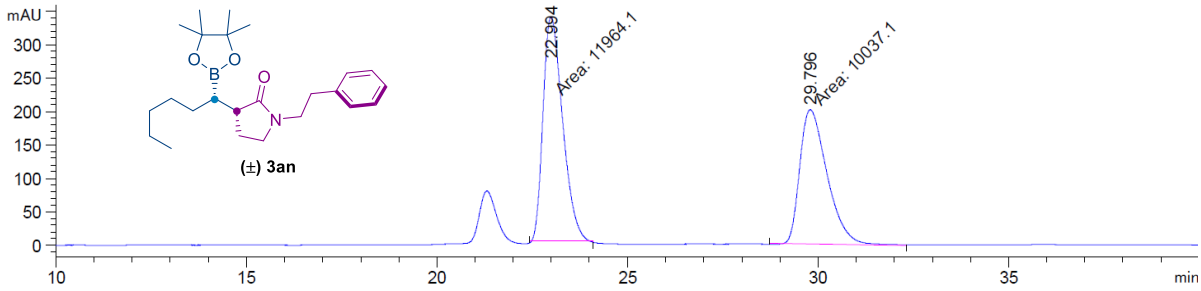


(±) 3am

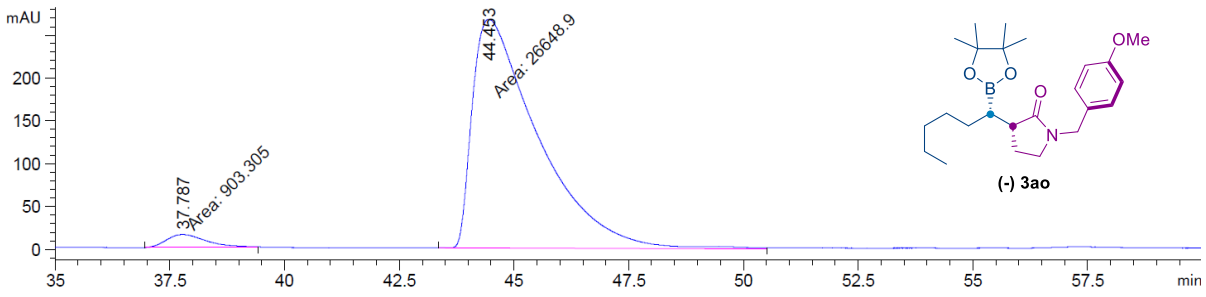
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.909	MM	0.5315	4882.89551	153.12021	49.7011
2	35.510	MM	1.6149	4941.62988	51.00124	50.2989



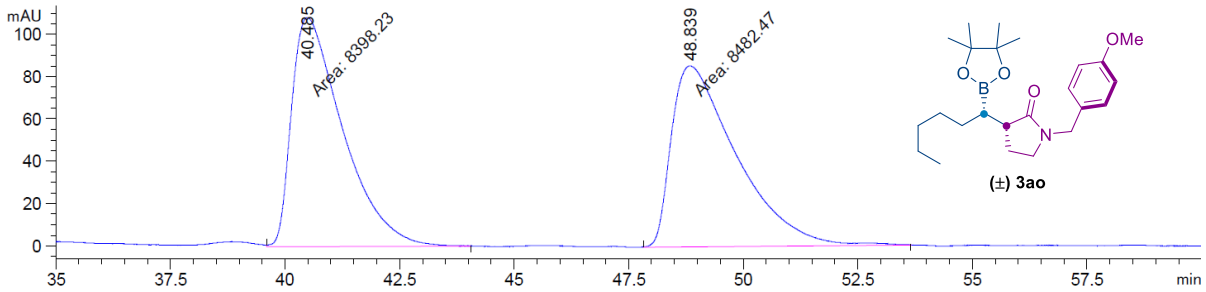
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.825	MM	0.6297	2.99155e4	791.83850	95.3152
2	29.967	MM	0.7937	1470.37512	30.87414	4.6848



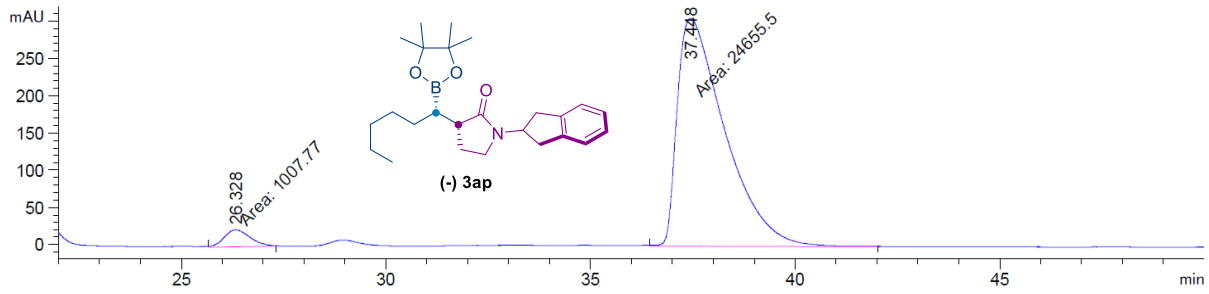
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.994	MM	0.5944	1.19641e4	335.46793	54.3793
2	29.796	MM	0.8327	1.00371e4	200.89597	45.6207



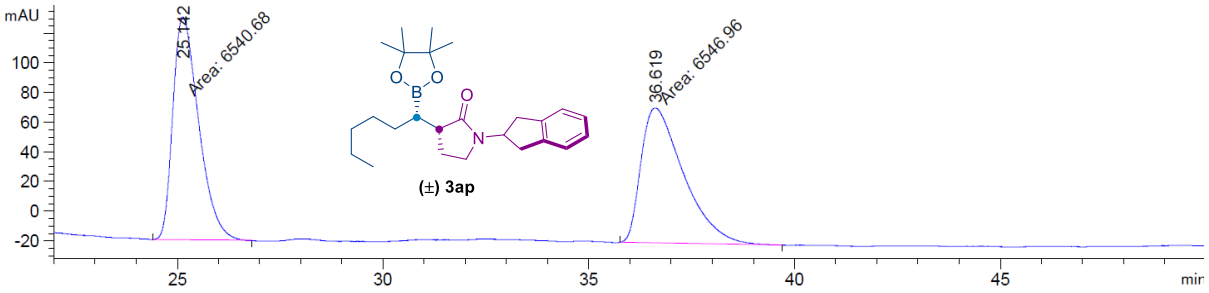
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.787	MM	1.0070	903.30463	14.94980	3.2785
2	44.453	MM	1.6623	2.66489e4	267.18762	96.7215



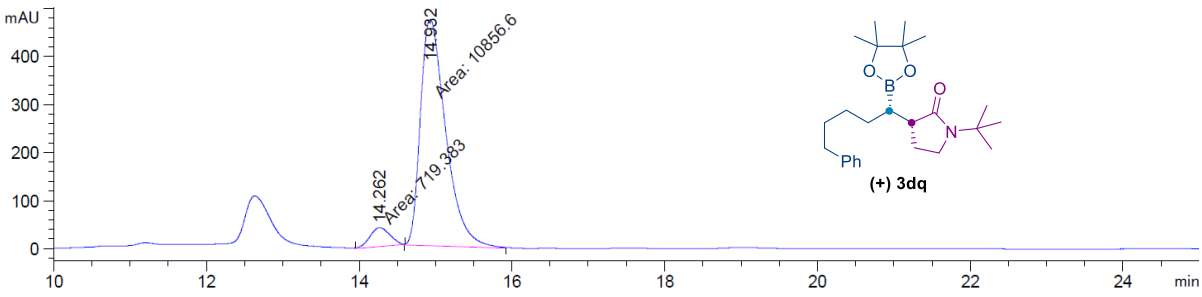
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	40.485	MM	1.2937	8398.22852	108.19526	49.7505
2	48.839	MM	1.6521	8482.47363	85.57281	50.2495



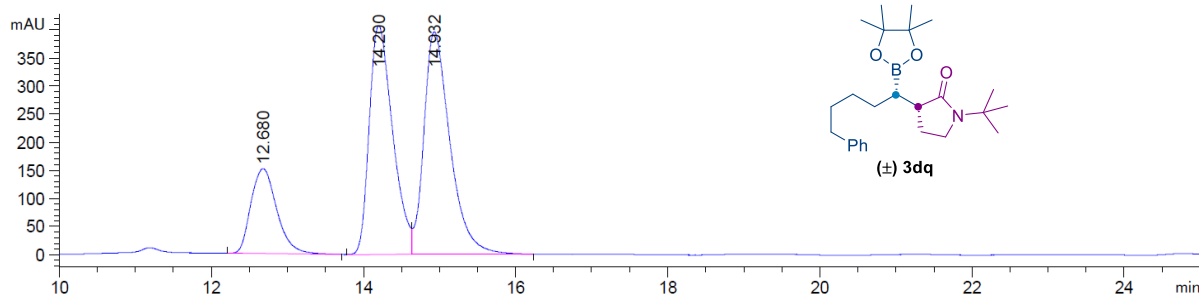
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.328	MM	0.7323	1007.77429	22.93682	3.9269
2	37.448	MM	1.3441	2.46555e4	305.72208	96.0731



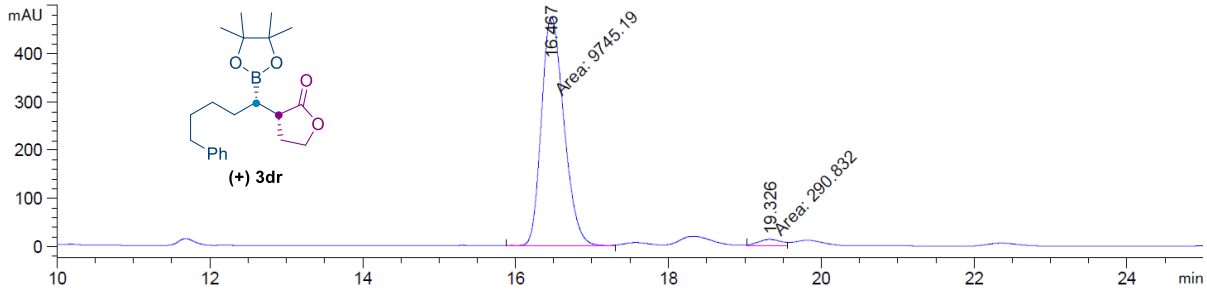
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.142	MM	0.7261	6540.67871	150.12521	49.9760
2	36.619	MM	1.2007	6546.95703	90.87841	50.0240



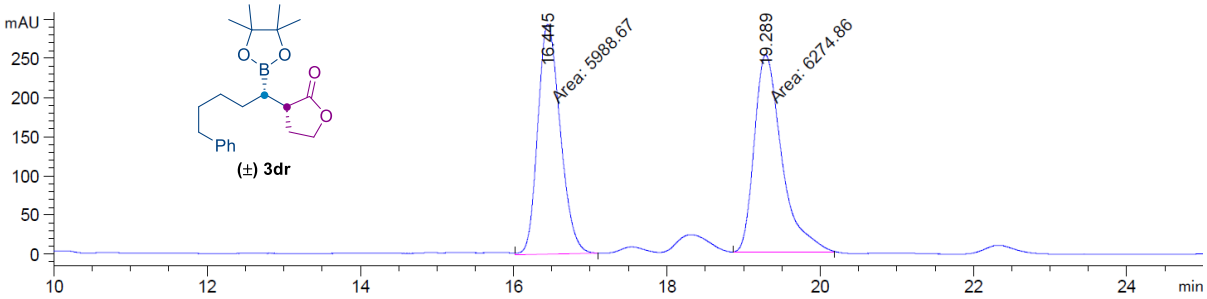
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.262	MM	0.2156	719.38293	39.27181	6.2144
2	14.932	MM	0.3838	1.08566e4	471.47153	93.7856



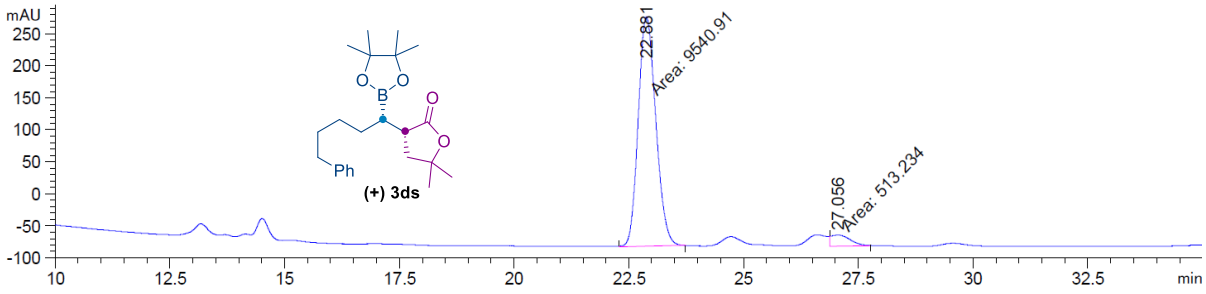
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.680	BB	0.3059	3575.91821	151.21214	16.4388
2	14.200	BV	0.3059	8710.93652	406.74878	40.0449
3	14.932	VB	0.3362	9466.09082	396.19577	43.5164



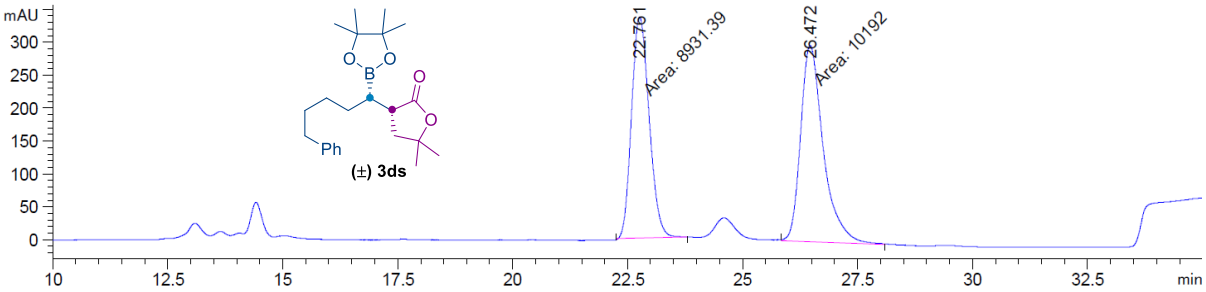
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.467	MM	0.3423	9745.19336	474.55881	97.1021
2	19.326	MM	0.3564	290.83221	13.60085	2.8979



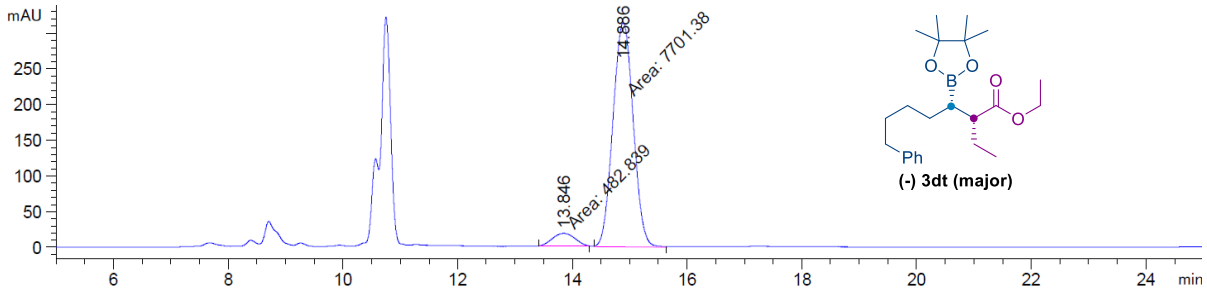
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.445	MM	0.3399	5988.66748	293.64975	48.8331
2	19.289	MM	0.4156	6274.86182	251.61076	51.1669



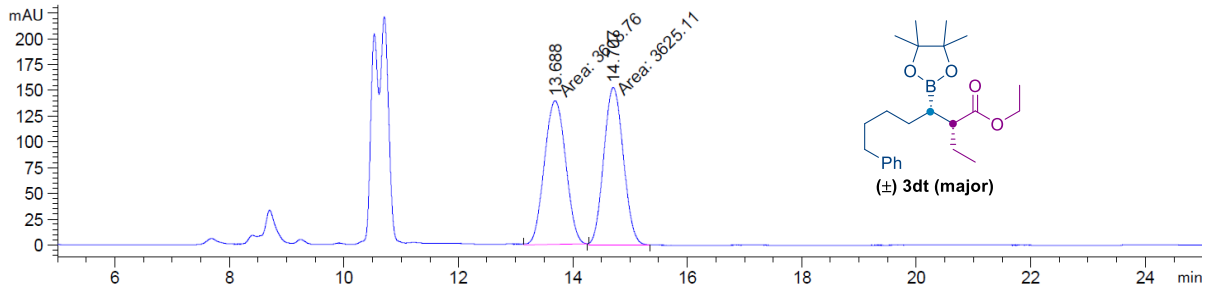
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.881	MM	0.4434	9540.90820	358.66101	94.8953
2	27.056	FM	0.4869	513.23450	17.56773	5.1047



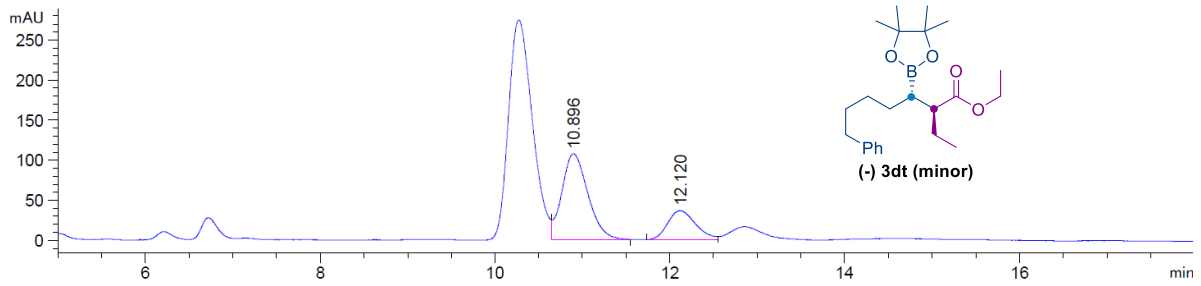
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.761	MM	0.4426	8931.38867	336.28705	46.7041
2	26.472	MM	0.5695	1.01920e4	298.28616	53.2959



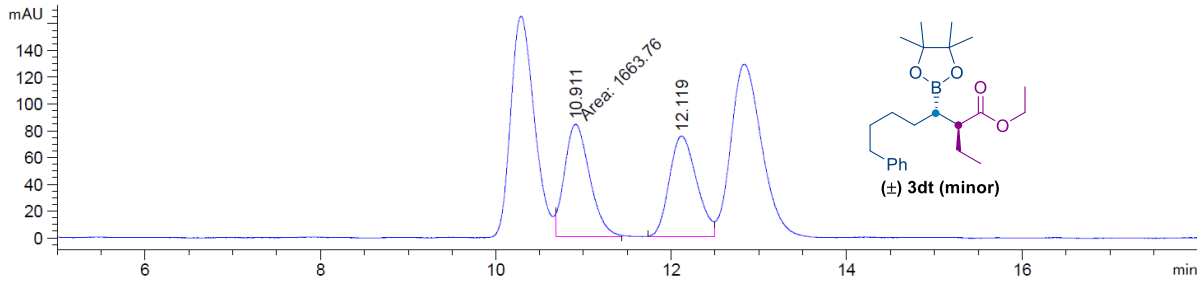
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.846	MM	0.4529	482.83936	17.76749	5.8996
2	14.886	MM	0.4089	7701.38037	313.88858	94.1004



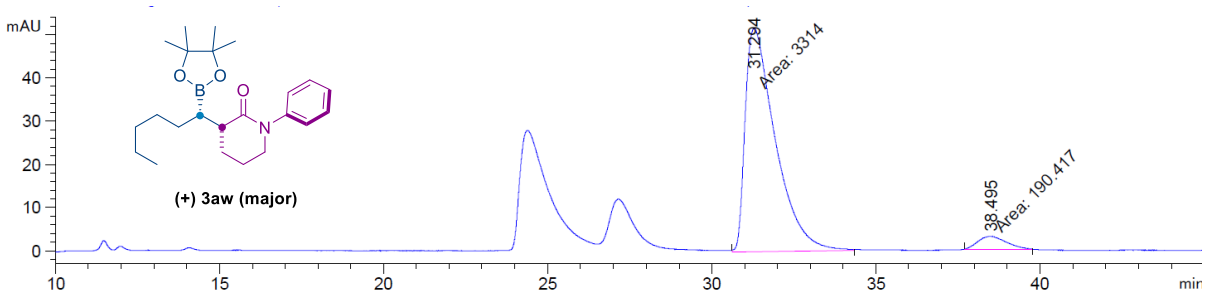
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.688	MM	0.4325	3618.75977	139.44695	49.9562
2	14.707	MM	0.3955	3625.11108	152.76118	50.0438



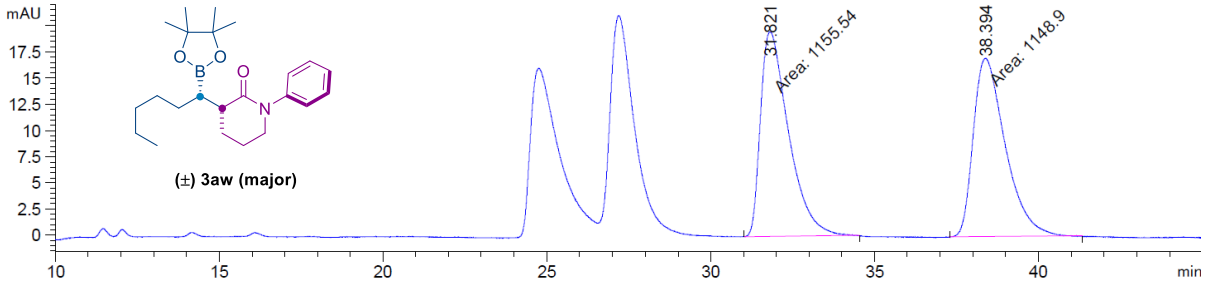
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.896	VV	0.2471	2217.96997	107.10815	73.6149
2	12.120	BV	0.2610	794.96686	35.95023	26.3851



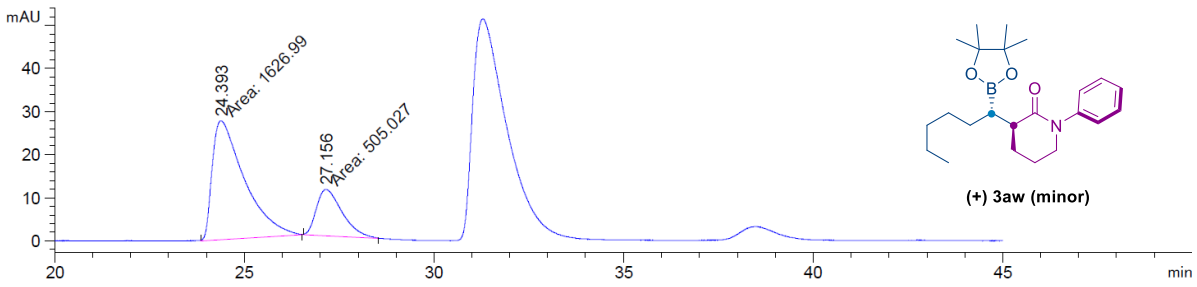
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.911	MM	0.3308	1663.75684	83.81496	50.7679
2	12.119	BV	0.2563	1613.42639	74.90170	49.2321



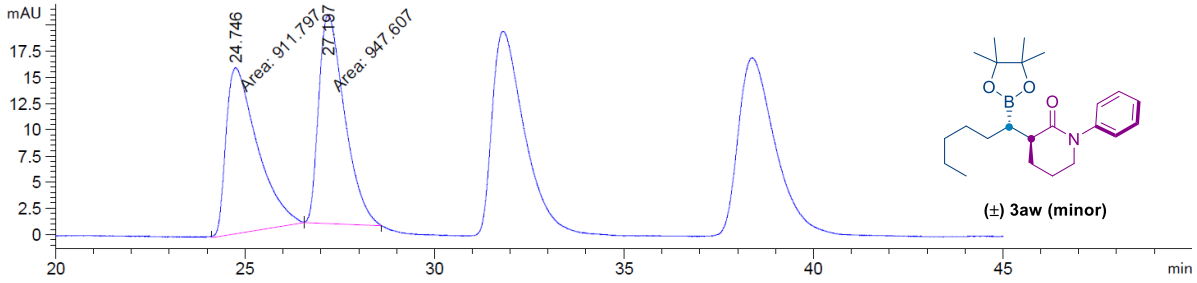
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.294	MM	1.0672	3314.00195	51.75385	94.5664
2	38.495	MM	1.0317	190.41656	3.07611	5.4336



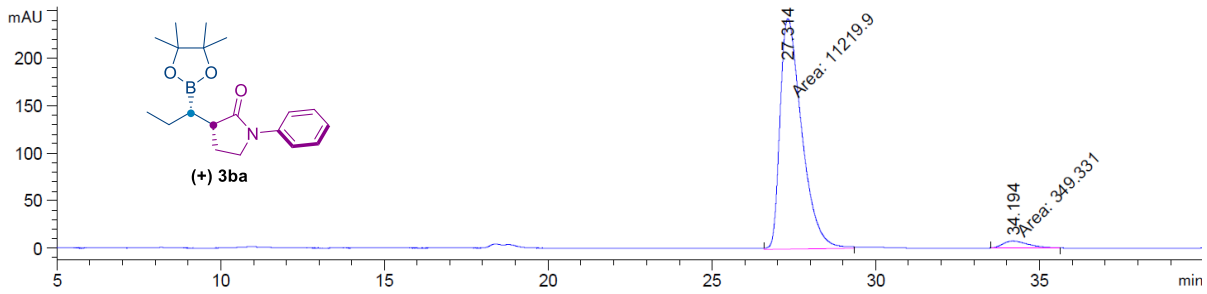
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.821	MM	0.9885	1155.53894	19.48248	50.1439
2	38.394	MM	1.1284	1148.90466	16.97013	49.8561



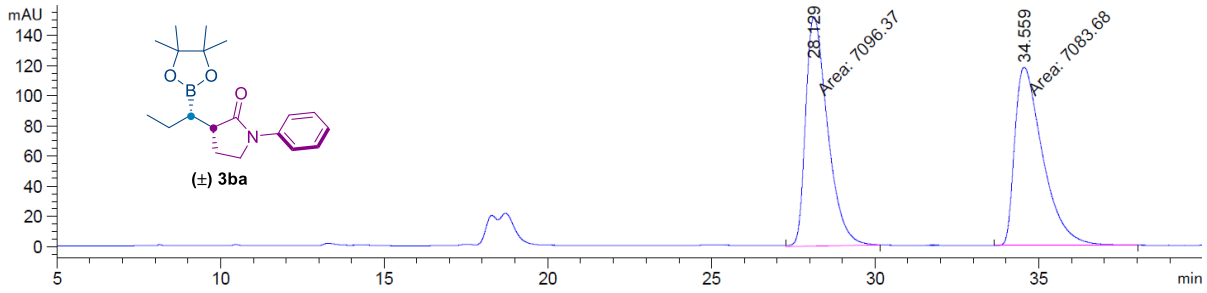
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.393	MM	0.9836	1626.99500	27.56790	76.3123
2	27.156	MM	0.7830	505.02725	10.74963	23.6877



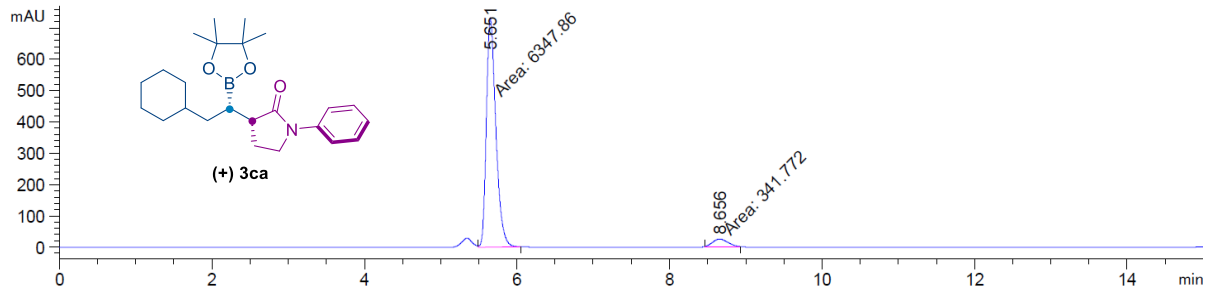
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.746	MM	0.9579	911.79706	15.86453	49.0371
2	27.197	MM	0.7935	947.60687	19.90372	50.9629



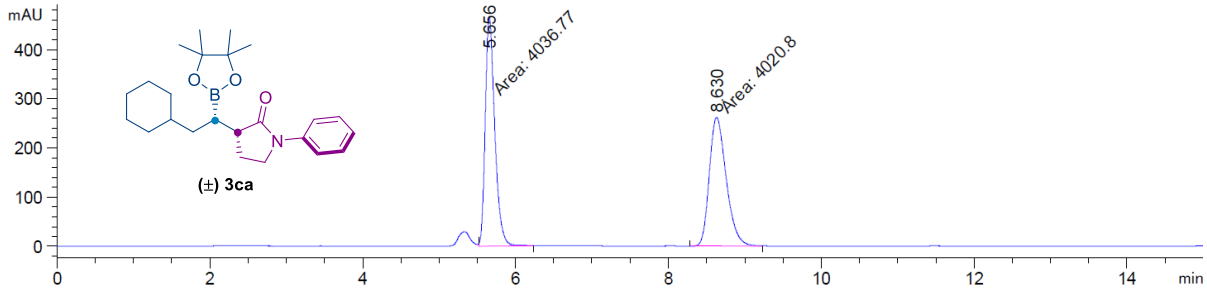
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.314	MM	0.7701	1.12199e4	242.82306	96.9805
2	34.194	MM	0.8335	349.33078	6.98527	3.0195



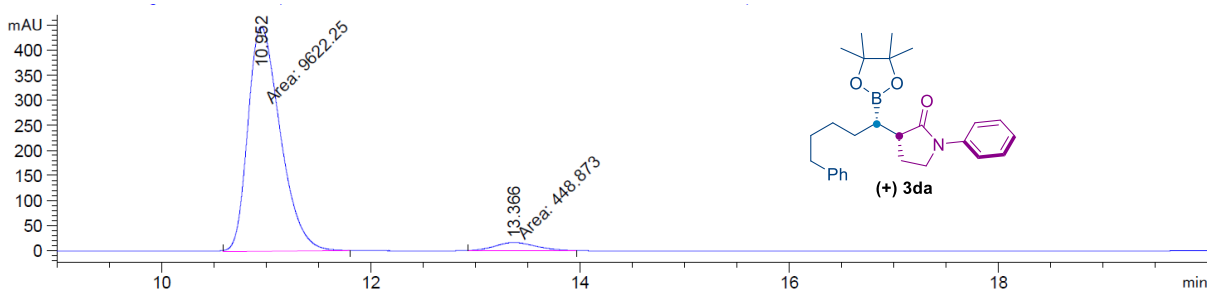
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.129	MM	0.7785	7096.37354	151.92281	50.0448
2	34.559	MM	0.9981	7083.67627	118.28110	49.9552



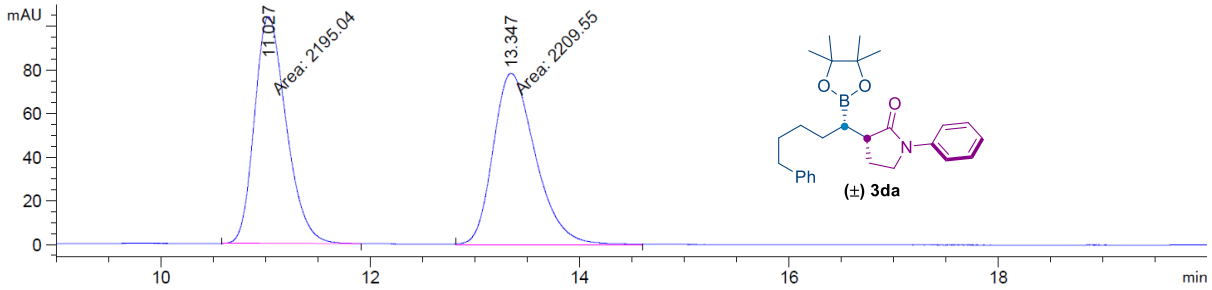
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.651	MM	0.1444	6347.86475	732.44989	94.8910
2	8.656	MM	0.2315	341.77216	24.60767	5.1090



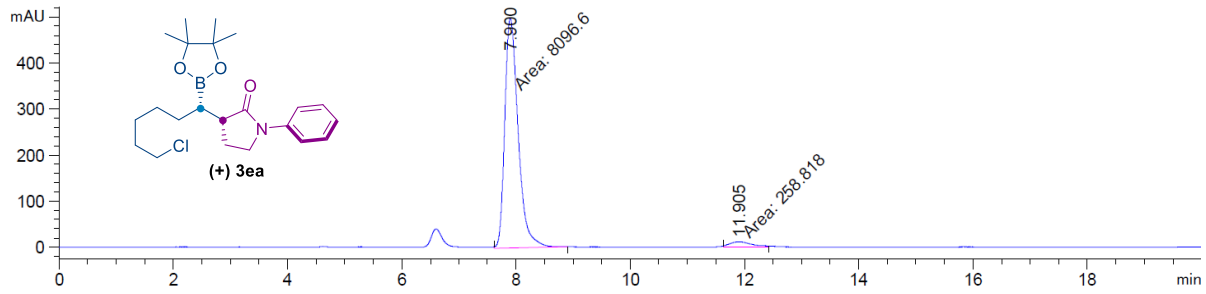
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.656	FM	0.1441	4036.77319	466.91855	50.0991
2	8.630	MM	0.2563	4020.79565	261.49023	49.9009



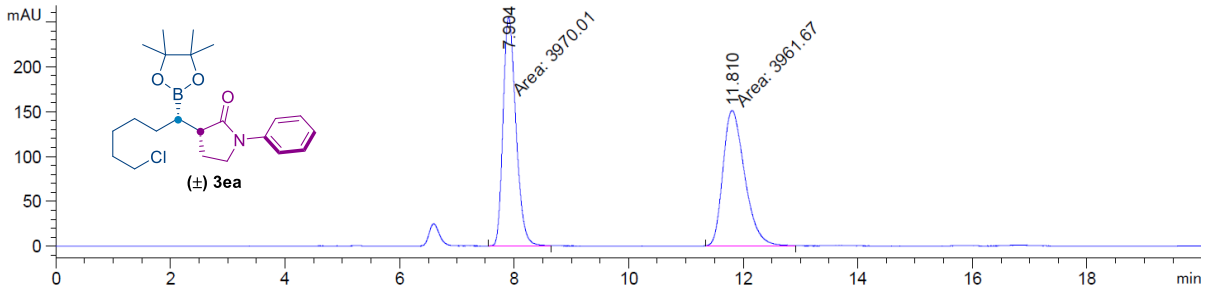
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.952	MM	0.3577	9622.25293	448.33804	95.5430
2	13.366	MM	0.4619	448.87292	16.19617	4.4570



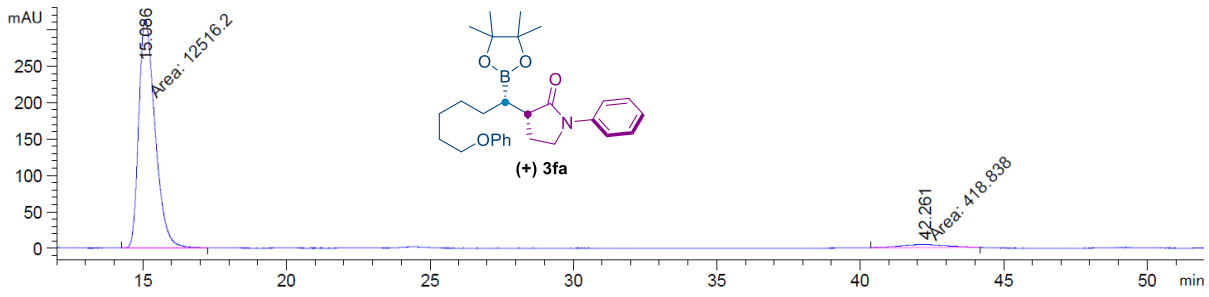
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.027	MM	0.3515	2195.04346	104.08289	49.8354
2	13.347	MM	0.4690	2209.54541	78.52073	50.1646



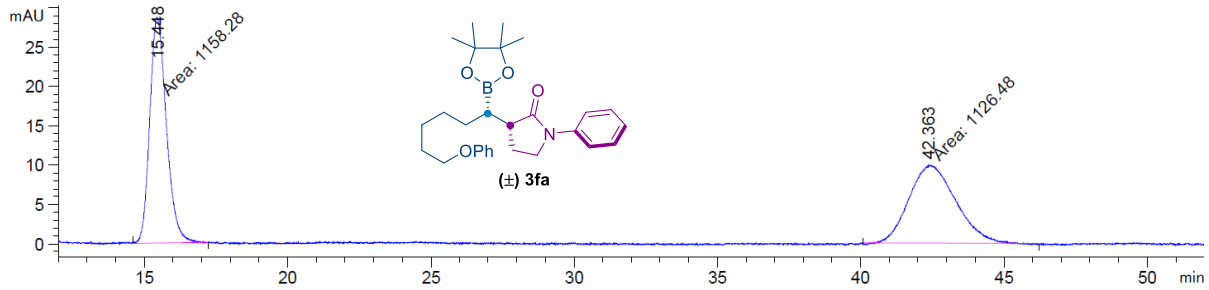
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.900	MM	0.2705	8096.60449	498.78998	96.9024
2	11.905	MM	0.4159	258.81775	10.37295	3.0976



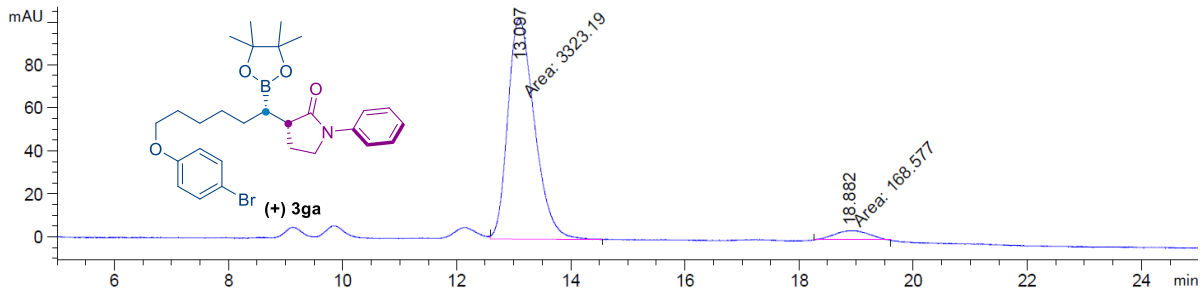
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.904	MM	0.2597	3970.01050	254.75241	50.0526
2	11.810	MM	0.4380	3961.67358	150.75473	49.9474



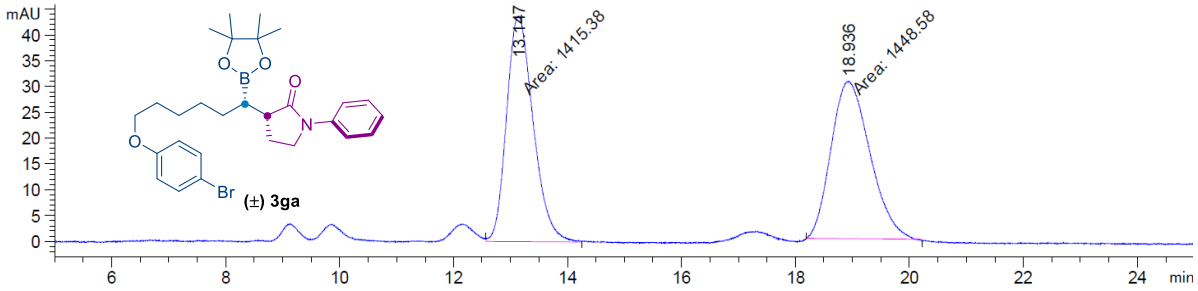
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.086	MM	0.6627	1.25162e4	314.78467	96.7620
2	42.261	MM	1.7709	418.83792	3.94196	3.2380



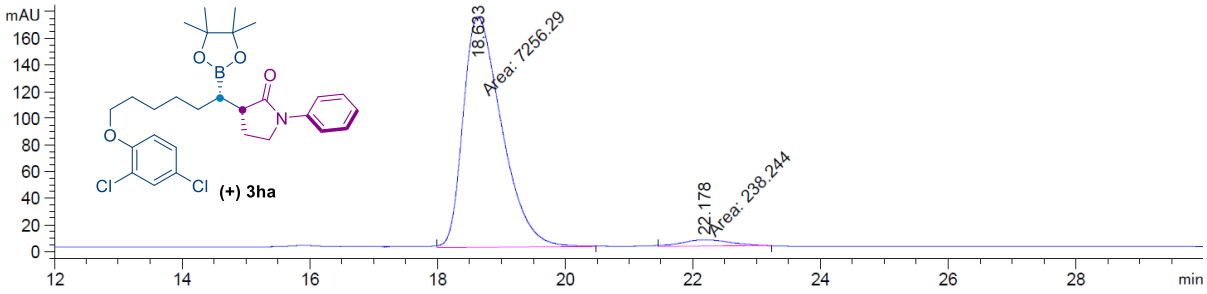
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.448	MM	0.6721	1158.27979	28.72178	50.6959
2	42.363	MM	1.8772	1126.48108	10.00131	49.3041



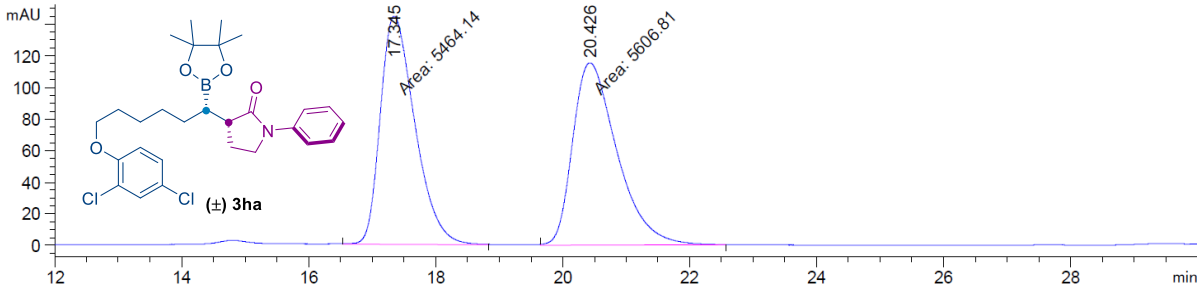
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.097	FM	0.5397	3323.19043	102.62529	95.1722
2	18.882	MM	0.6757	168.57669	4.15809	4.8278



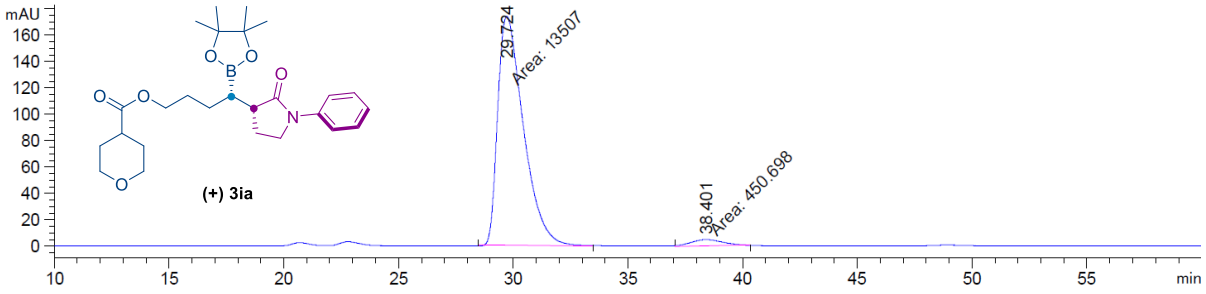
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.147	FM	0.5404	1415.37598	43.65500	49.4202
2	18.936	MM	0.7918	1448.58362	30.49292	50.5798



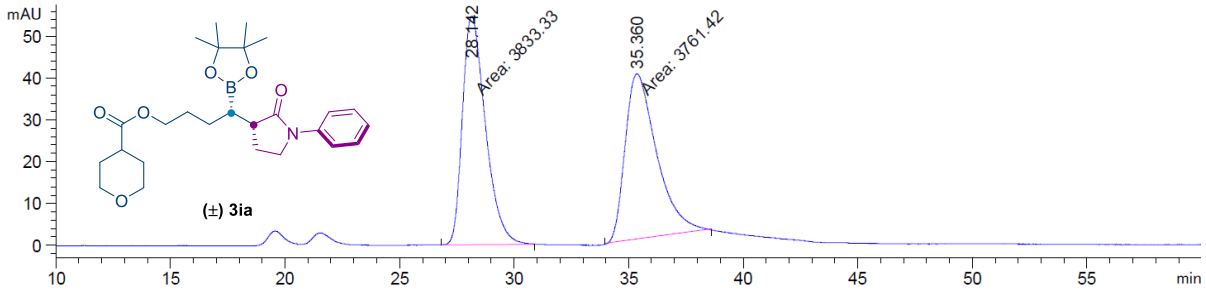
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.633	MM	0.6986	7256.28760	173.11084	96.8211
2	22.178	MM	0.8533	238.24420	4.65357	3.1789



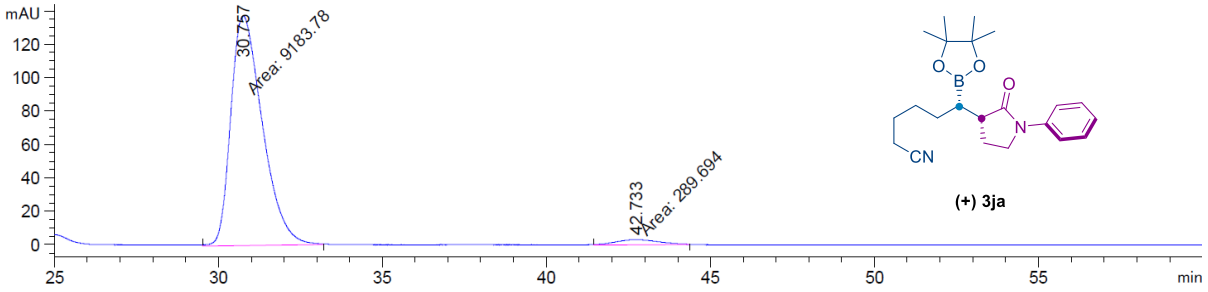
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.345	MM	0.6314	5464.13574	144.23337	49.3556
2	20.426	MM	0.8092	5606.81055	115.47496	50.6444



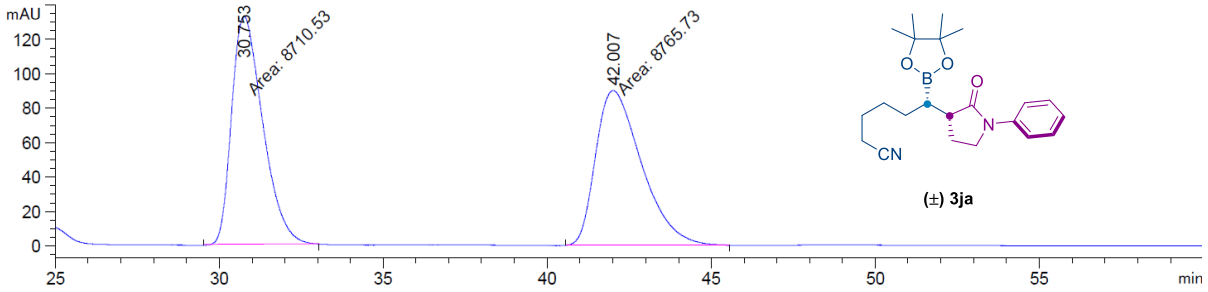
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.724	MM	1.2956	1.35070e4	173.75844	96.7710
2	38.401	MM	1.5800	450.69833	4.75423	3.2290



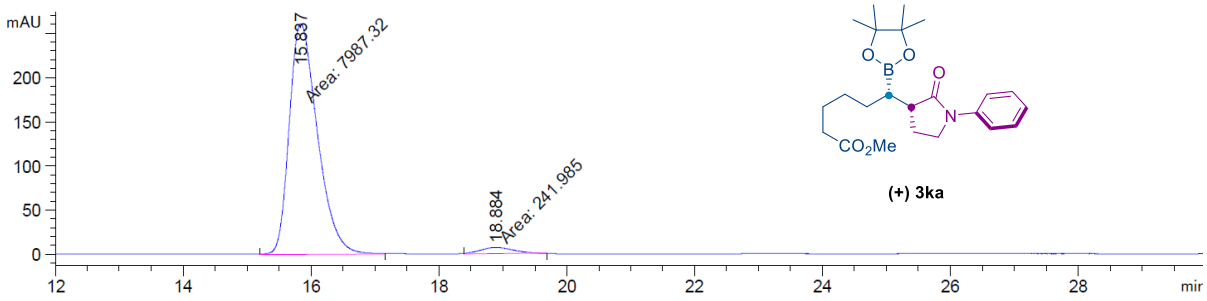
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.142	MM	1.1678	3833.32544	54.70760	50.4734
2	35.360	MM	1.5879	3761.41846	39.47984	49.5266



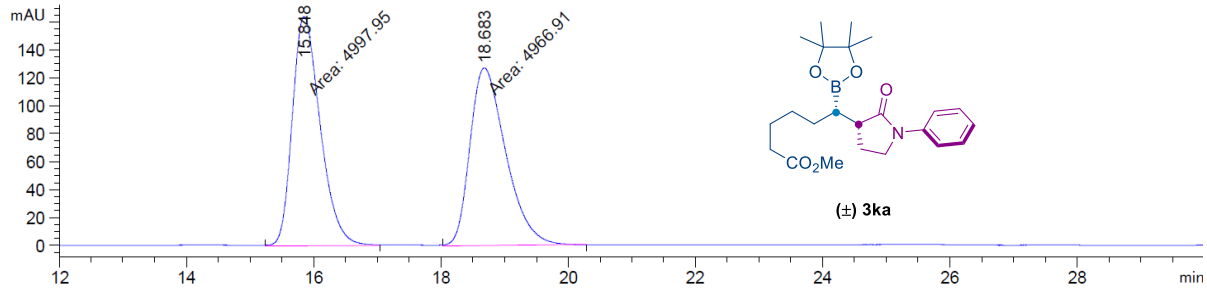
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.757	MM	1.1137	9183.78320	137.43437	96.9420
2	42.733	MM	1.5163	289.69434	3.18416	3.0580



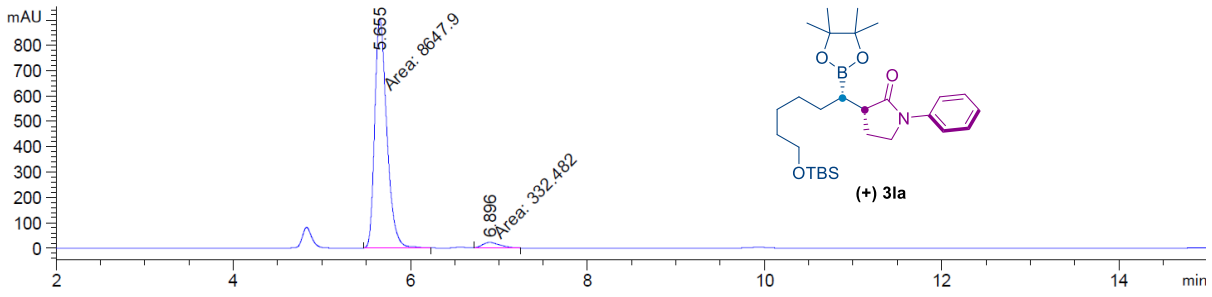
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.753	MM	1.0965	8710.52637	132.39986	49.8421
2	42.007	MM	1.6262	8765.72754	89.83585	50.1579



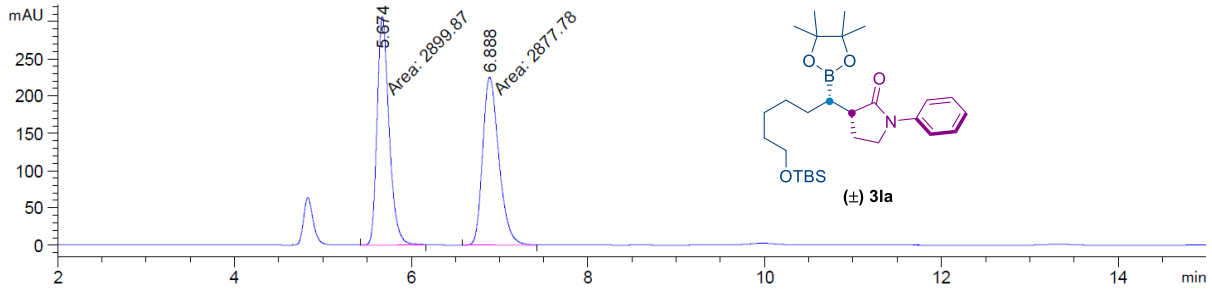
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.837	MM	0.5106	7987.32422	260.71899	97.0595
2	18.884	MM	0.5901	241.98505	6.83421	2.9405



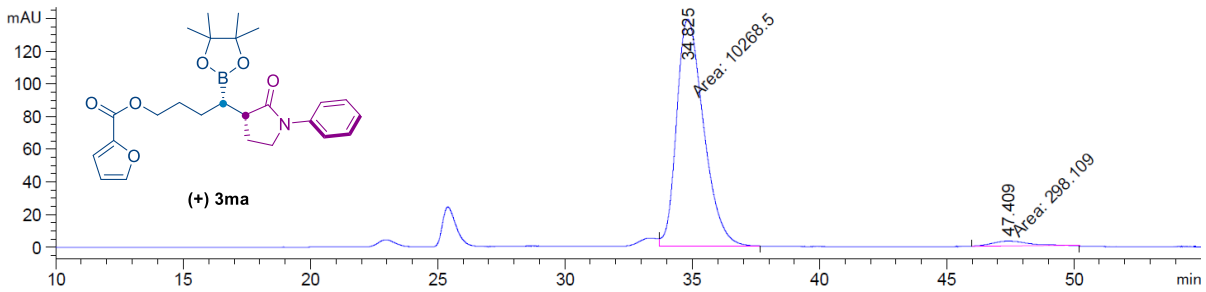
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.848	MM	0.5075	4997.95410	164.14026	50.1558
2	18.683	MM	0.6510	4966.90674	127.15783	49.8442



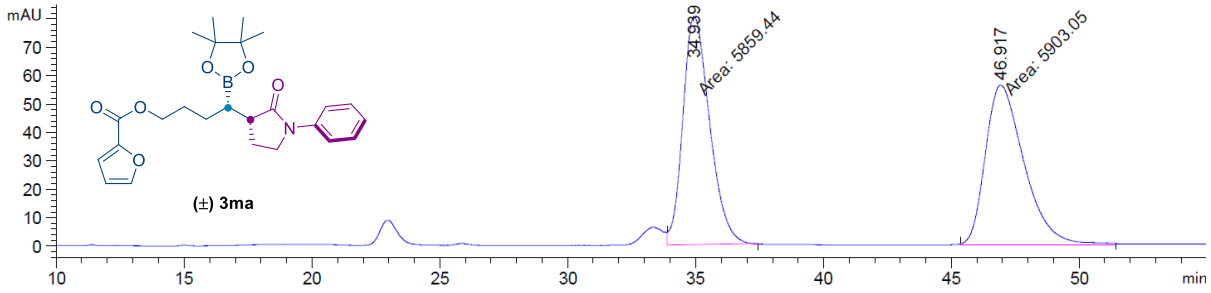
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.655	MM	0.1590	8647.90332	906.51489	96.2977
2	6.896	MM	0.2368	332.48178	23.40563	3.7023



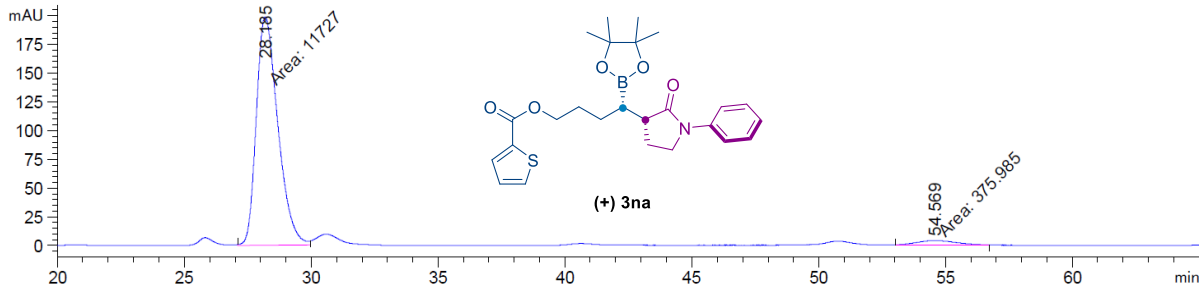
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.674	MM	0.1577	2899.86646	306.42374	50.1911
2	6.888	MM	0.2132	2877.78369	224.92429	49.8089



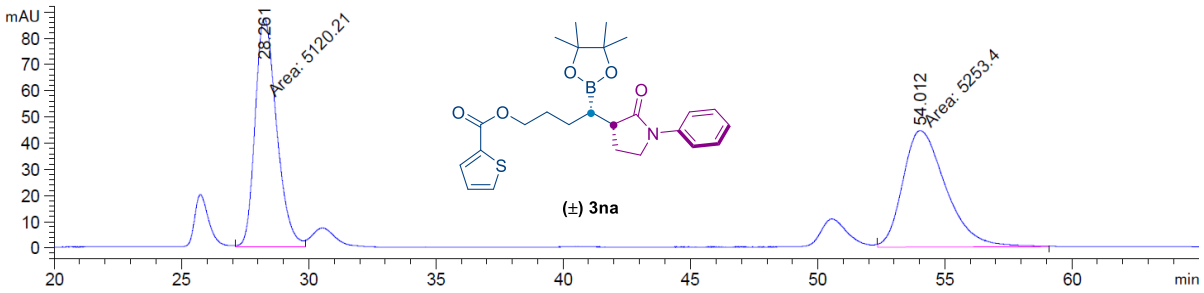
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.825	FM	1.2321	1.02685e4	138.90054	97.1788
2	47.409	MM	1.6329	298.10950	3.04281	2.8212



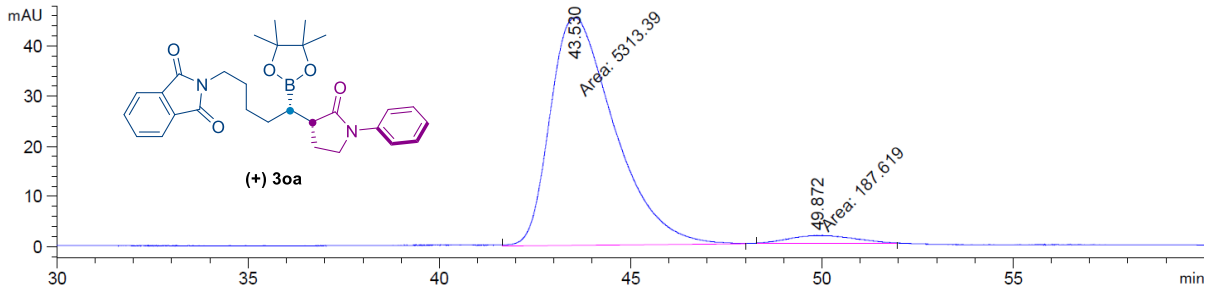
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.939	FM	1.2154	5859.43701	80.34891	49.8146
2	46.917	MM	1.7512	5903.04541	56.18028	50.1854



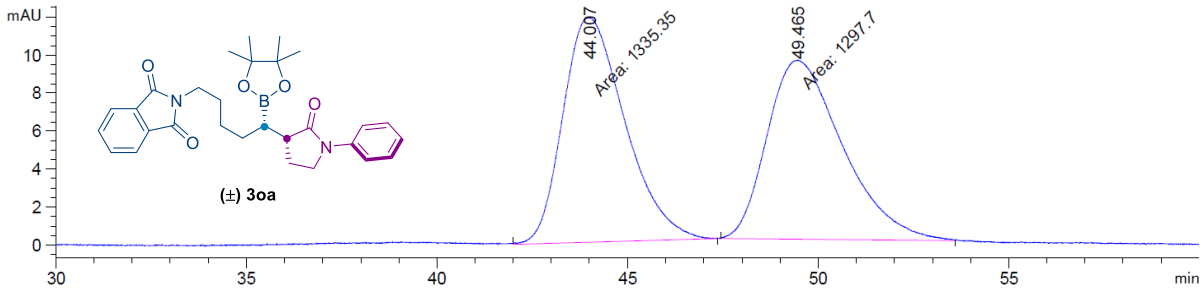
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.185	MF	0.9846	1.17270e4	198.50087	96.8934
2	54.569	MM	1.6930	375.98508	3.70131	3.1066



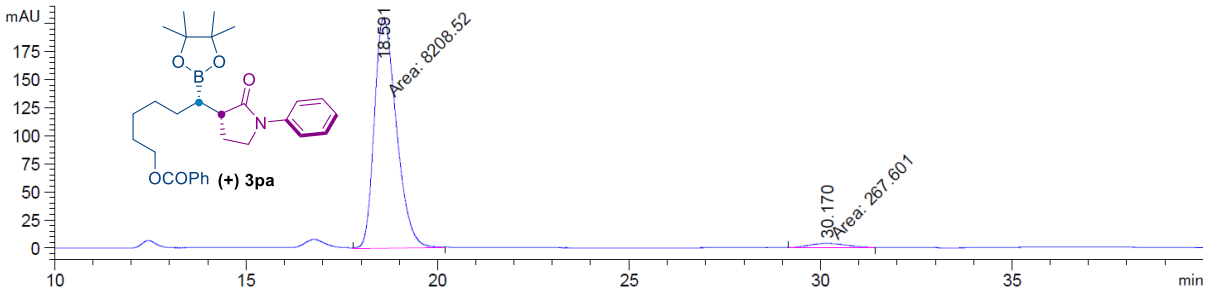
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.261	MM	0.9778	5120.21045	87.27162	49.3580
2	54.012	FM	1.9700	5253.40039	44.44412	50.6420



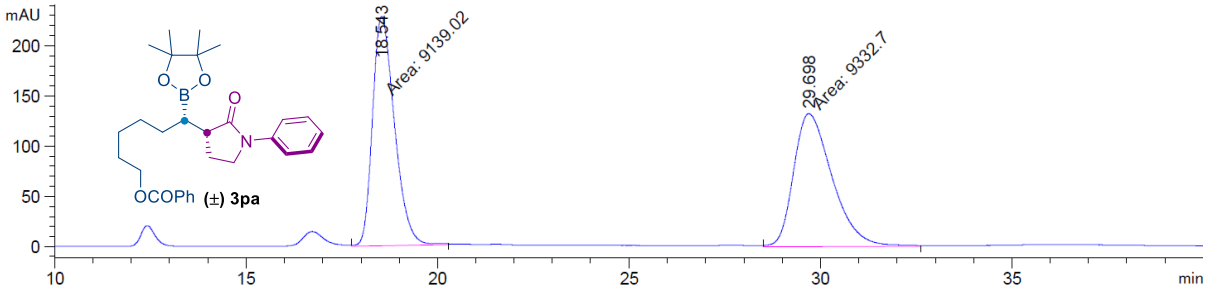
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.530	MM	1.9453	5313.39063	45.52367	96.5894
2	49.872	MM	1.9927	187.61931	1.56923	3.4106



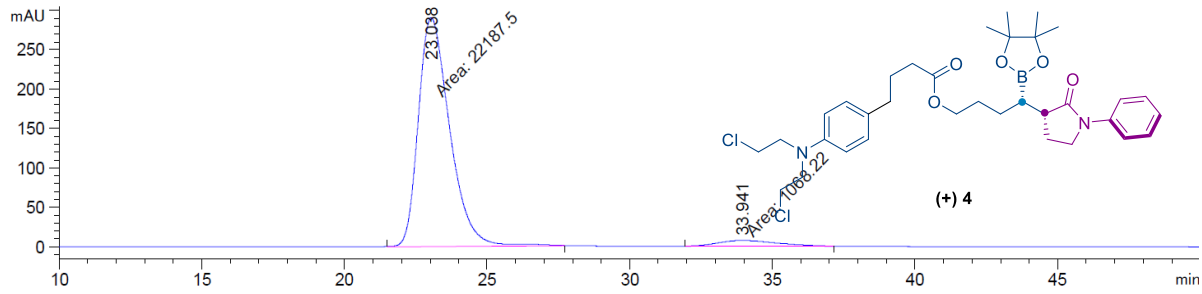
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.007	MM	1.8833	1335.34680	11.81763	50.7148
2	49.465	MM	2.2956	1297.70361	9.42170	49.2852



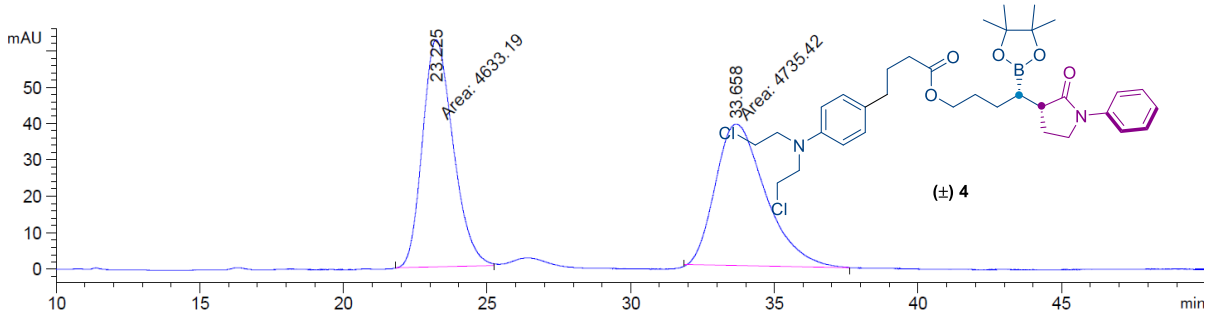
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.591	MM	0.6668	8208.52148	205.16338	96.8429
2	30.170	MM	1.1095	267.60135	4.01984	3.1571



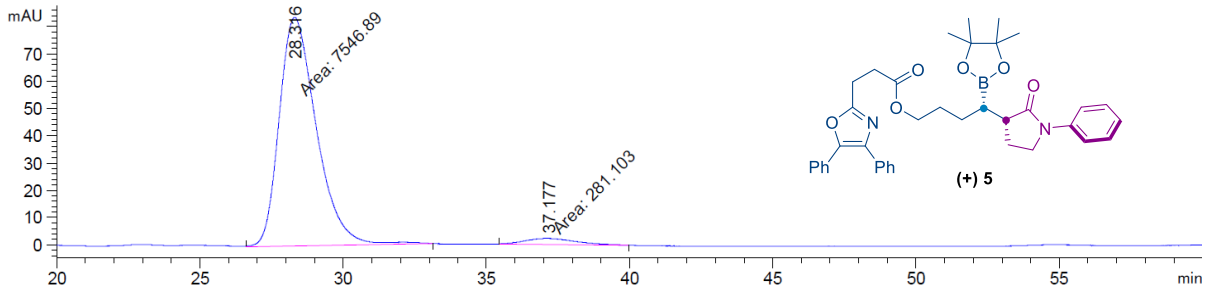
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.543	MM	0.6669	9139.01563	228.40222	49.4757
2	29.698	MM	1.1724	9332.70117	132.66791	50.5243



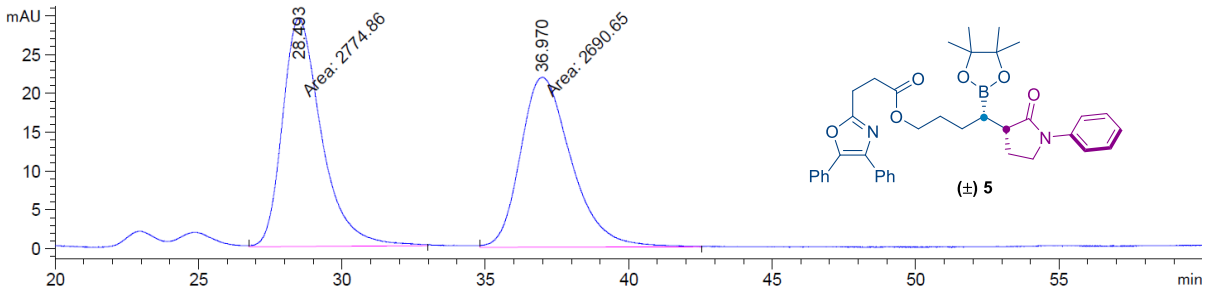
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.038	MM	1.2742	2.21875e4	290.21603	95.4067
2	33.941	MM	2.3758	1068.21729	7.49382	4.5933



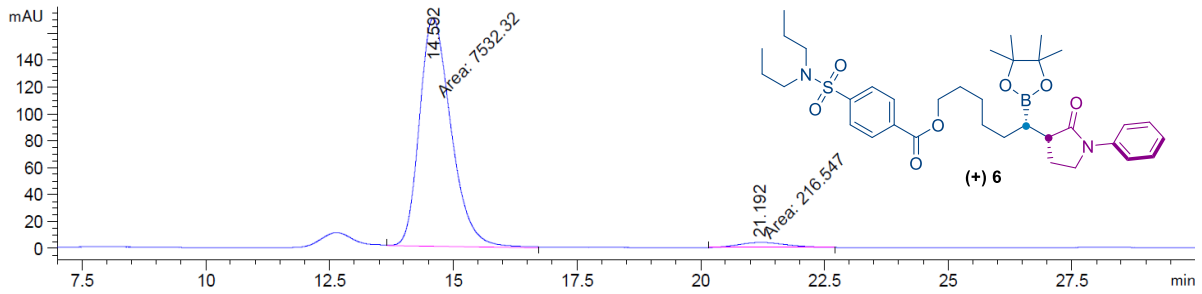
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.225	MM	1.2371	4633.18848	62.42113	49.4544
2	33.658	MM	2.0262	4735.42383	38.95099	50.5456



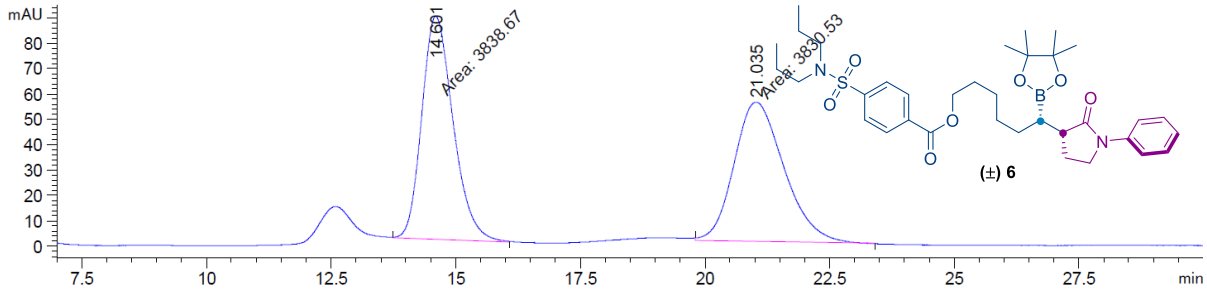
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.316	MM	1.5013	7546.88818	83.78117	96.4090
2	37.177	MM	2.0680	281.10269	2.26554	3.5910



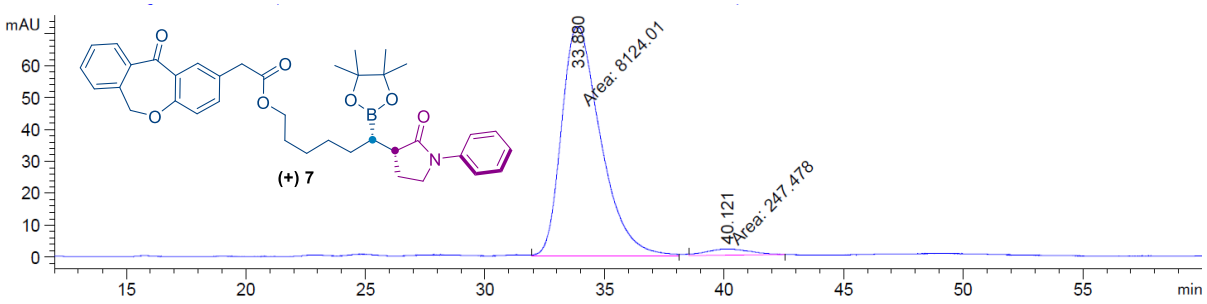
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.493	MM	1.5752	2774.85645	29.36048	50.7703
2	36.970	MM	2.0512	2690.65454	21.86239	49.2297



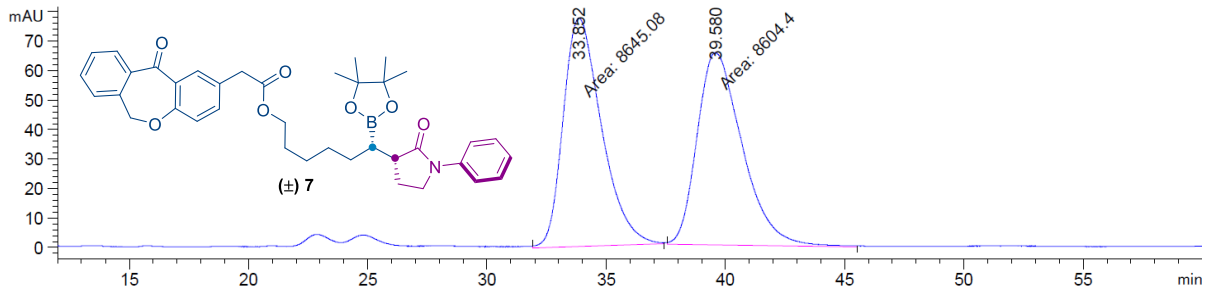
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.592	MM	0.7400	7532.32129	169.64740	97.2054
2	21.192	MM	1.0298	216.54709	3.50453	2.7946



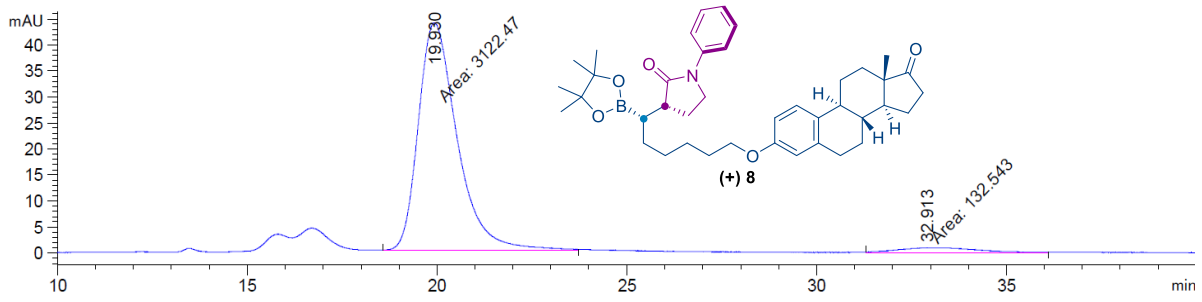
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.601	MM	0.7279	3838.67017	87.89114	50.0531
2	21.035	MM	1.1621	3830.53076	54.93533	49.9469



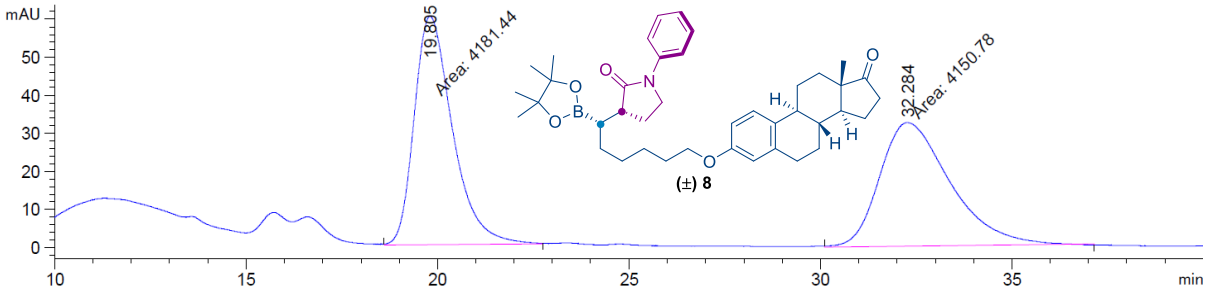
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.880	MM	1.8872	8124.00684	71.74749	97.0438
2	40.121	MM	2.1430	247.47804	1.92474	2.9562



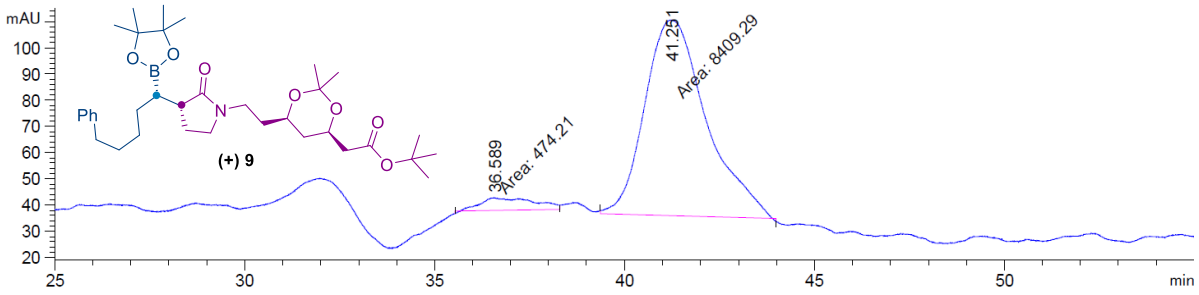
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.852	MM	1.8592	8645.07520	77.49928	50.1179
2	39.580	MM	2.1948	8604.39941	65.34071	49.8821



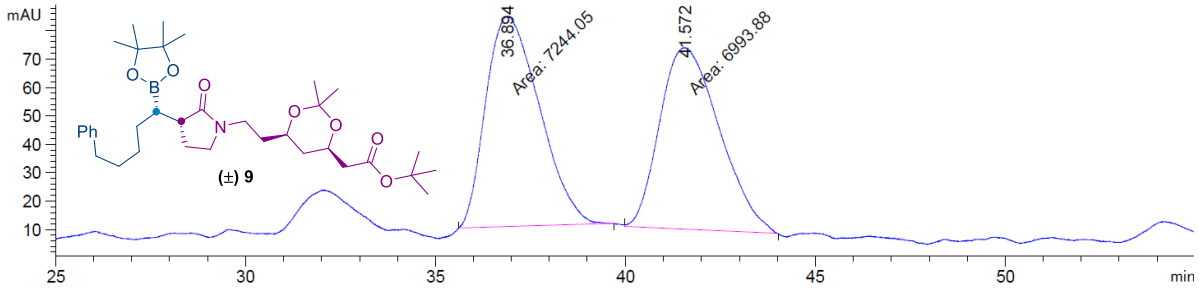
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.930	MM	1.1884	3122.46777	43.78921	95.9280
2	32.913	MM	2.3121	132.54309	9.55426e-1	4.0720



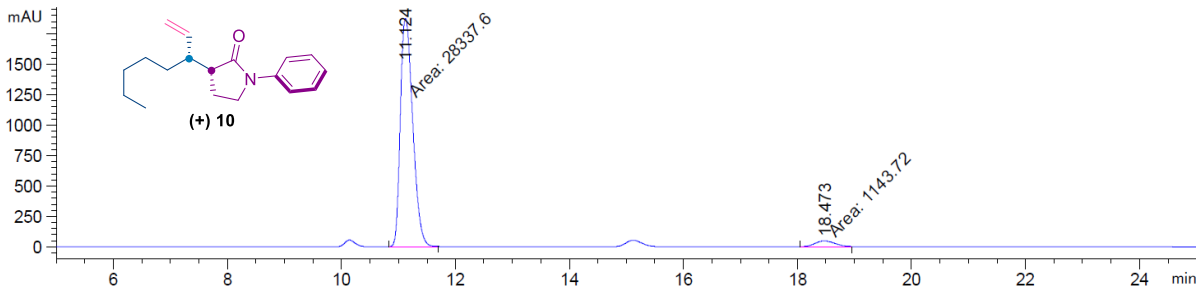
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.805	MM	1.1609	4181.43994	60.03291	50.1840
2	32.284	MM	2.1311	4150.77881	32.46224	49.8160



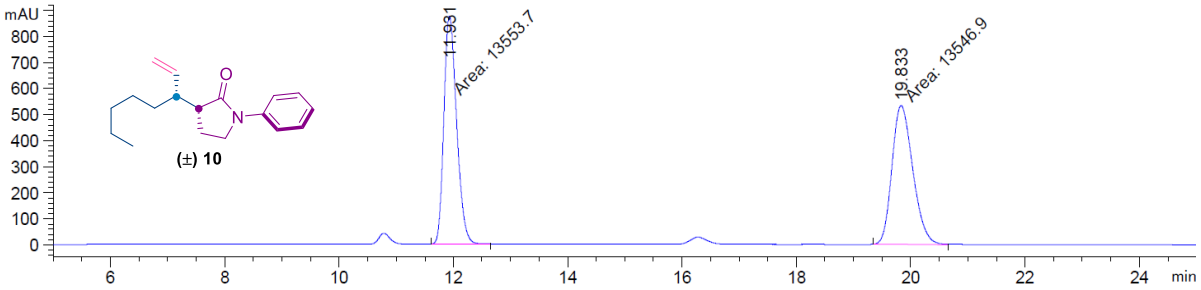
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.589	MM	1.6107	474.21005	4.90683	5.3381
2	41.251	MM	1.8776	8409.28516	74.64626	94.6619



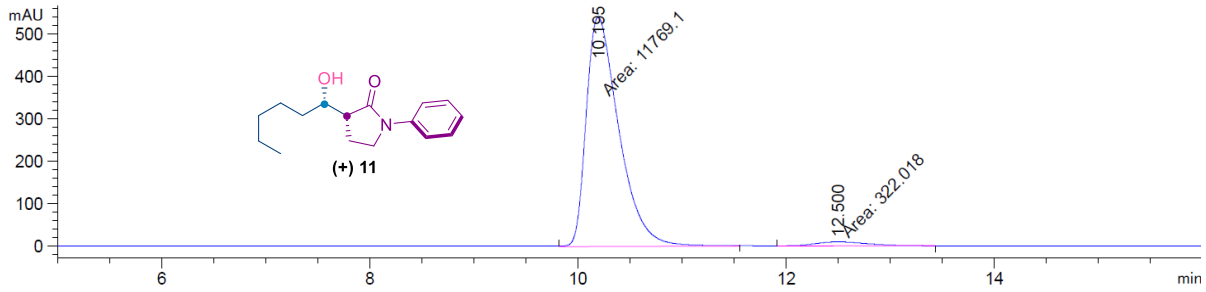
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.894	MM	1.6330	7244.05176	73.93255	50.8786
2	41.572	MM	1.8235	6993.87500	63.92266	49.1214



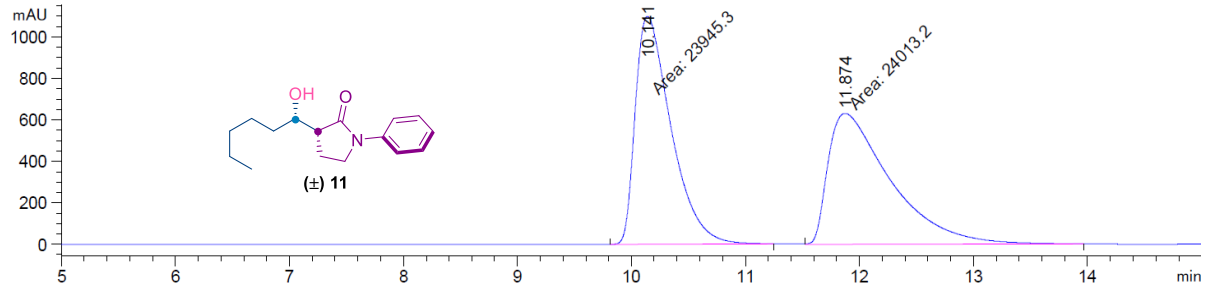
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.124	MM	0.2519	2.83376e4	1874.60583	96.1205
2	18.473	MM	0.3967	1143.72424	48.05034	3.8795



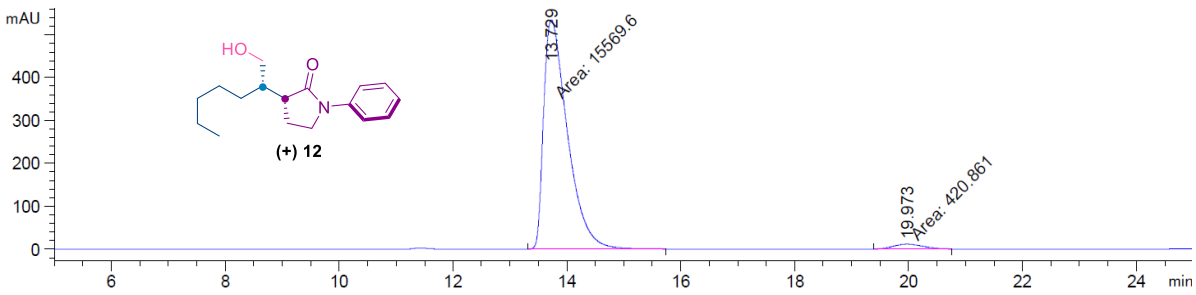
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.931	MM	0.2583	1.35537e4	874.40198	50.0126
2	19.833	MM	0.4237	1.35469e4	532.82172	49.9874



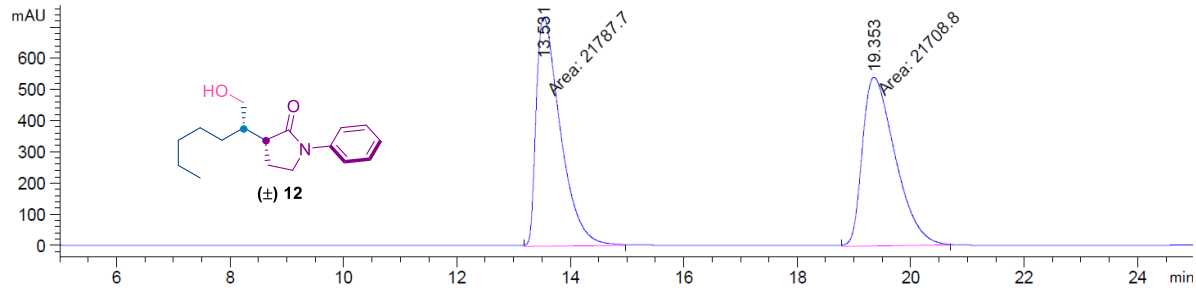
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.195	MM	0.3634	1.17691e4	539.75201	97.3367
2	12.500	MM	0.5682	322.01770	9.44586	2.6633



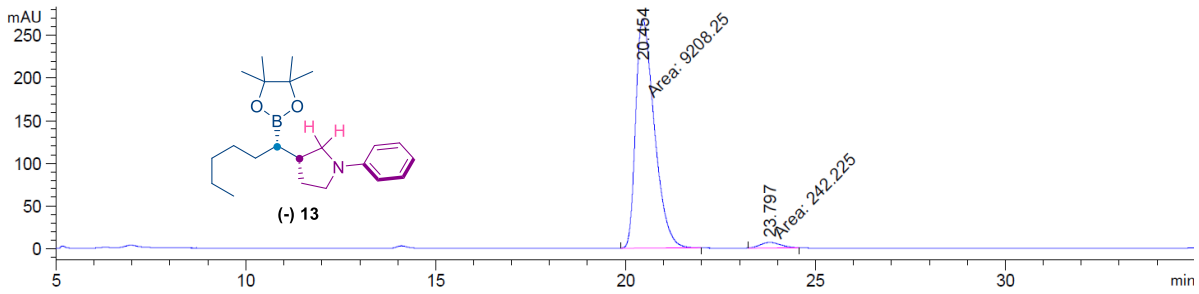
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.141	MM	0.3633	2.39453e4	1098.58142	49.9292
2	11.874	MM	0.6354	2.40132e4	629.90240	50.0708



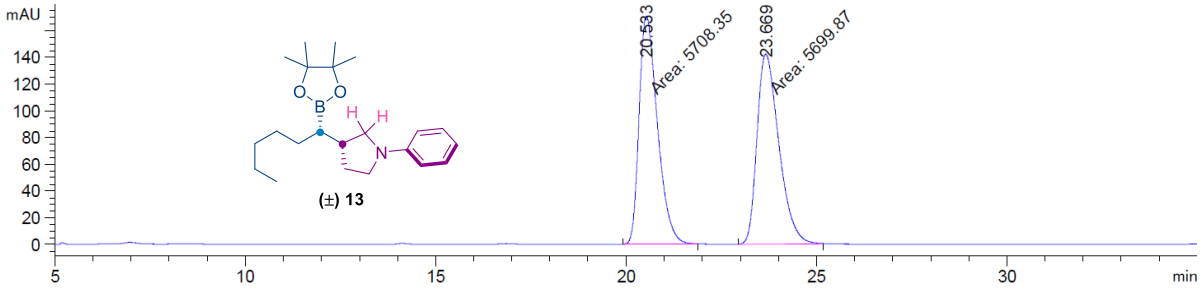
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.729	MM	0.4854	1.55696e4	534.56384	97.3680
2	19.973	MM	0.5969	420.86124	11.75095	2.6320



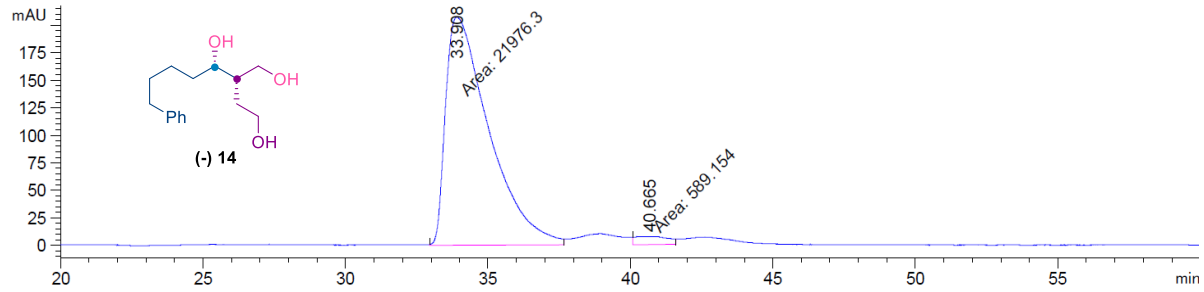
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.531	MM	0.4943	2.17877e4	734.68628	50.0907
2	19.353	MM	0.6691	2.17088e4	540.71655	49.9093



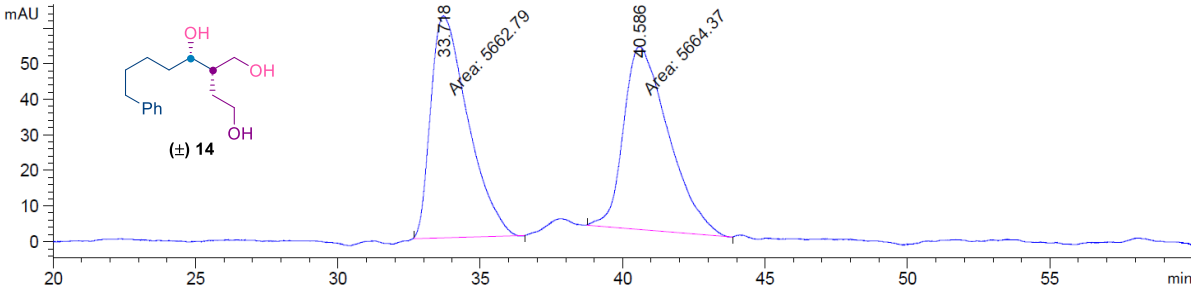
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.454	MM	0.5700	9208.24609	269.26517	97.4369
2	23.797	MM	0.6135	242.22470	6.58014	2.5631



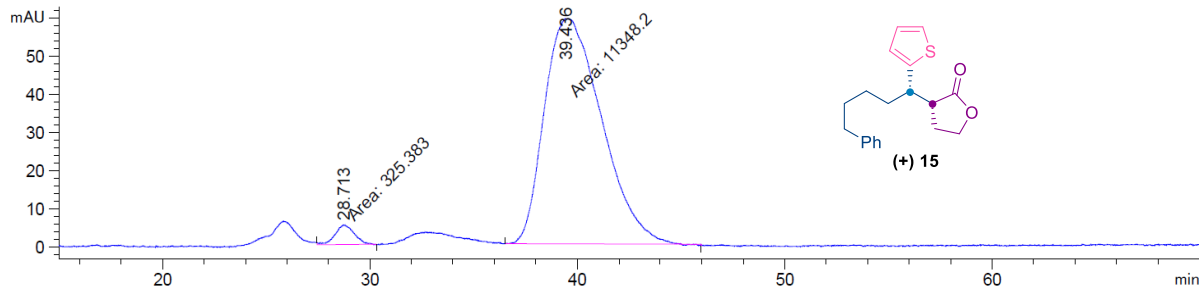
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.533	MM	0.5575	5708.35303	170.65575	50.0372
2	23.669	MM	0.6681	5699.87109	142.18613	49.9628



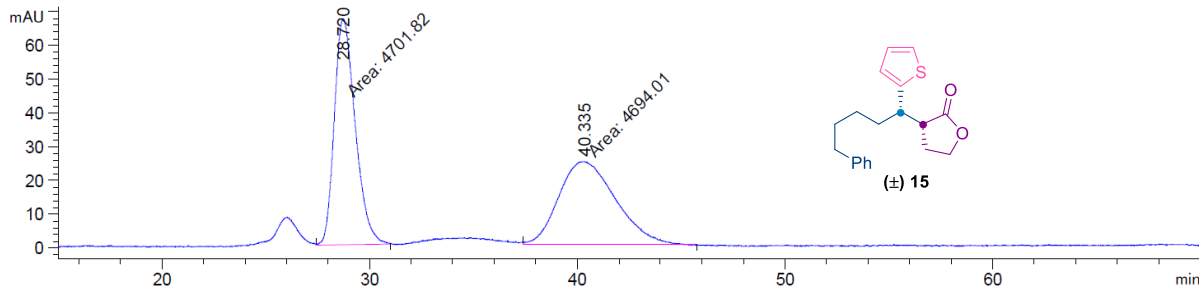
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.908	MF	1.7668	2.19763e4	207.30835	97.3891
2	40.665	MF	1.3578	589.15350	7.23184	2.6109



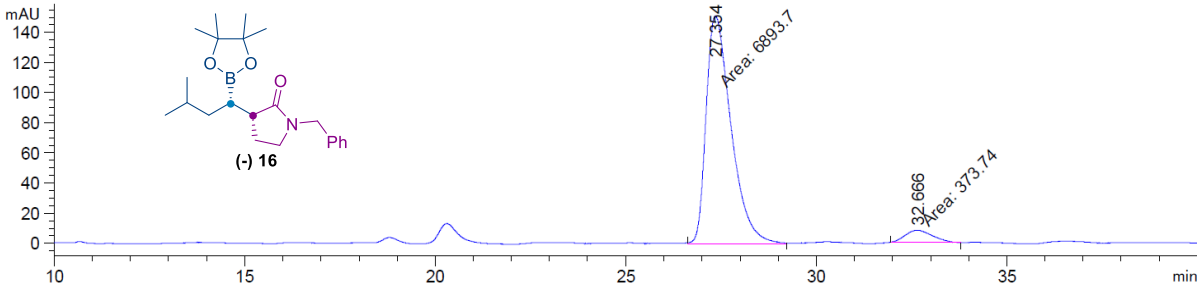
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.718	MM	1.5141	5662.79150	62.33413	49.9930
2	40.586	MM	1.8370	5664.37354	51.39104	50.0070



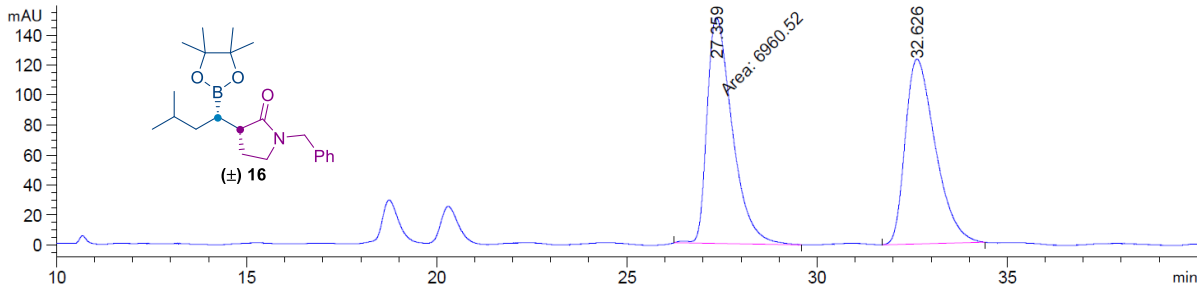
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.713	MM	1.0663	325.38269	5.08569	2.7873
2	39.436	MM	3.2022	1.13482e4	59.06487	97.2127



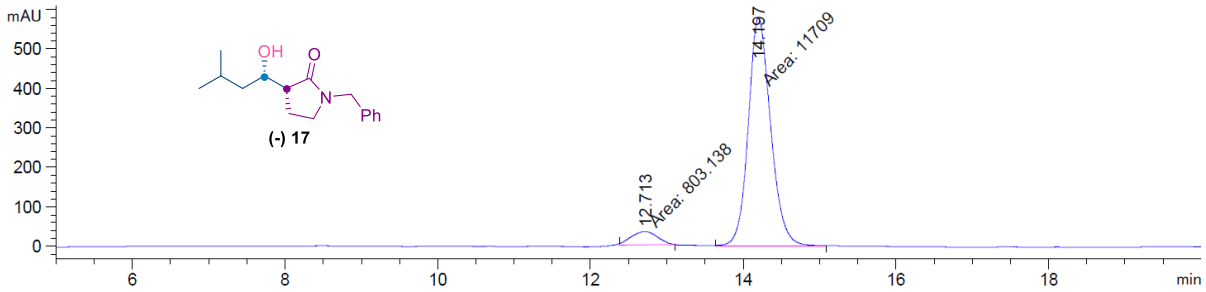
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.720	MM	1.1683	4701.82422	67.07335	50.0416
2	40.335	FM	3.1733	4694.00684	24.65377	49.9584



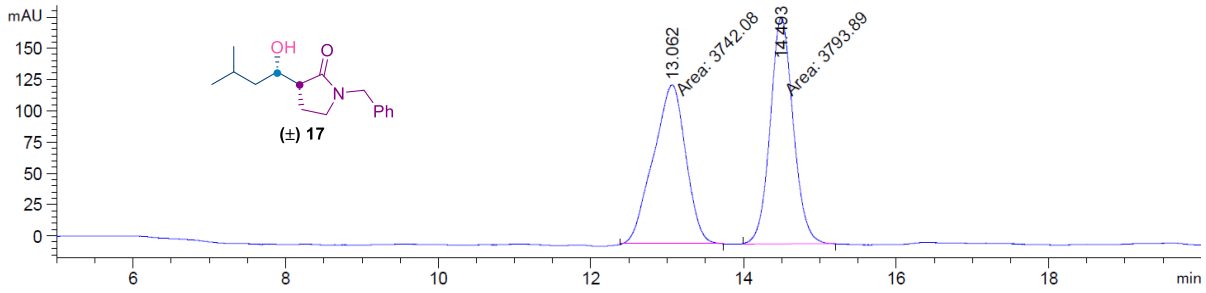
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.354	MM	0.7589	6893.69873	151.38716	94.8573
2	32.666	MM	0.7962	373.74002	7.82340	5.1427



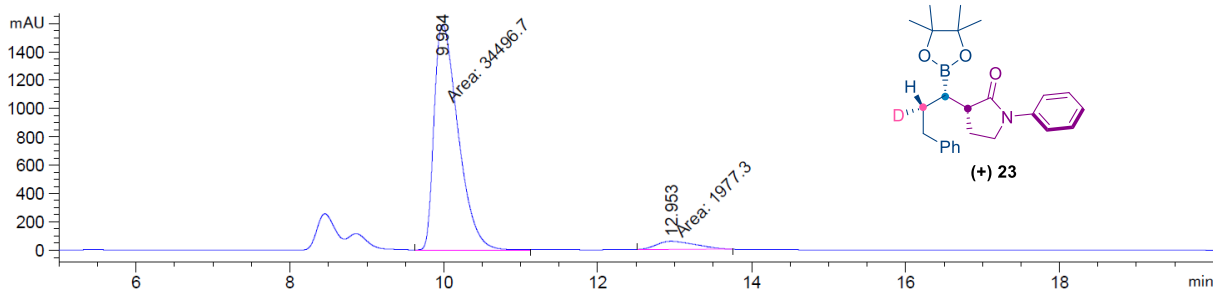
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.359	MM	0.7689	6960.51904	150.88023	50.6461
2	32.626	BB	0.6462	6782.92725	123.21529	49.3539



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.713	MM	0.3953	803.13800	33.86258	6.4188
2	14.197	MM	0.3378	1.17090e4	577.74255	93.5812

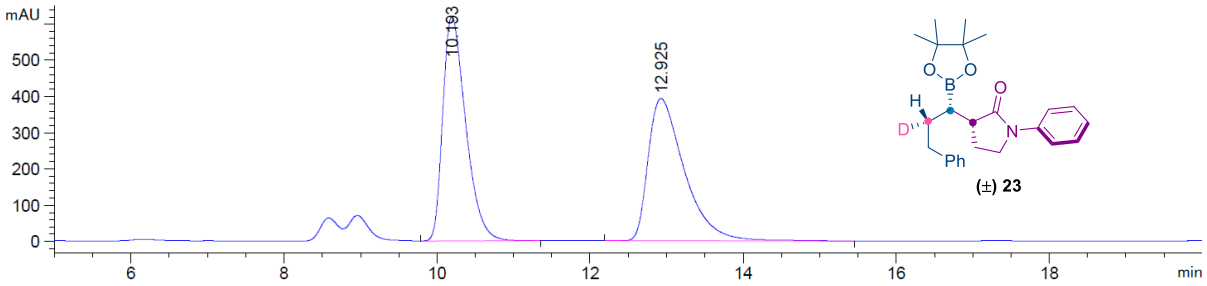


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.067	BB	0.3102	48.75586	1.84259	46.6617
2	14.491	BB	0.2372	55.73201	2.78173	53.3383



(+) **23**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.984	MM	0.3613	3.44967e4	1591.19250	94.5789
2	12.953	MM	0.5834	1977.30469	56.48365	5.4211

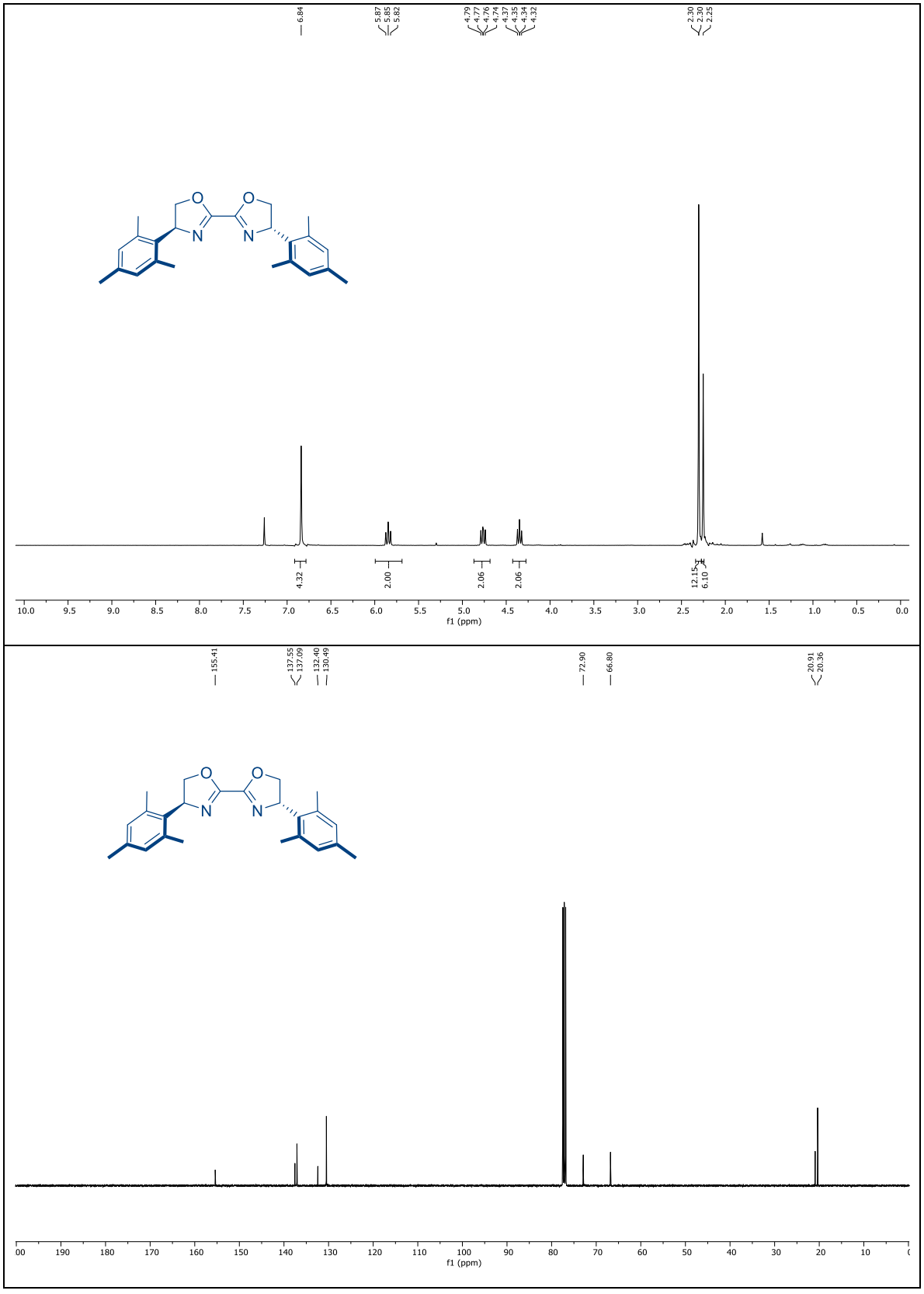


(±) **23**

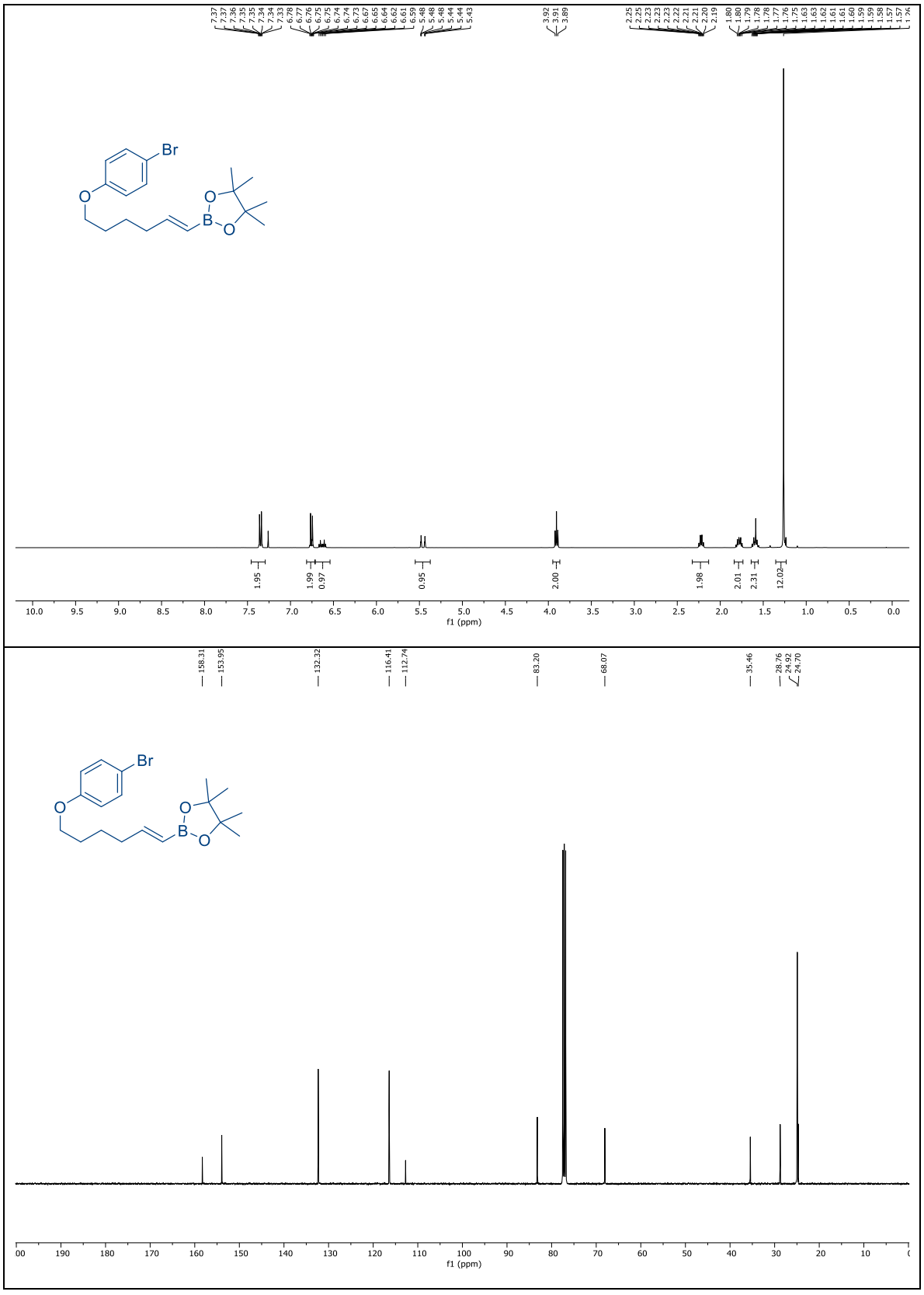
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.193	BB	0.3197	1.28937e4	619.84479	49.9158
2	12.925	BB	0.4914	1.29372e4	392.63306	50.0842

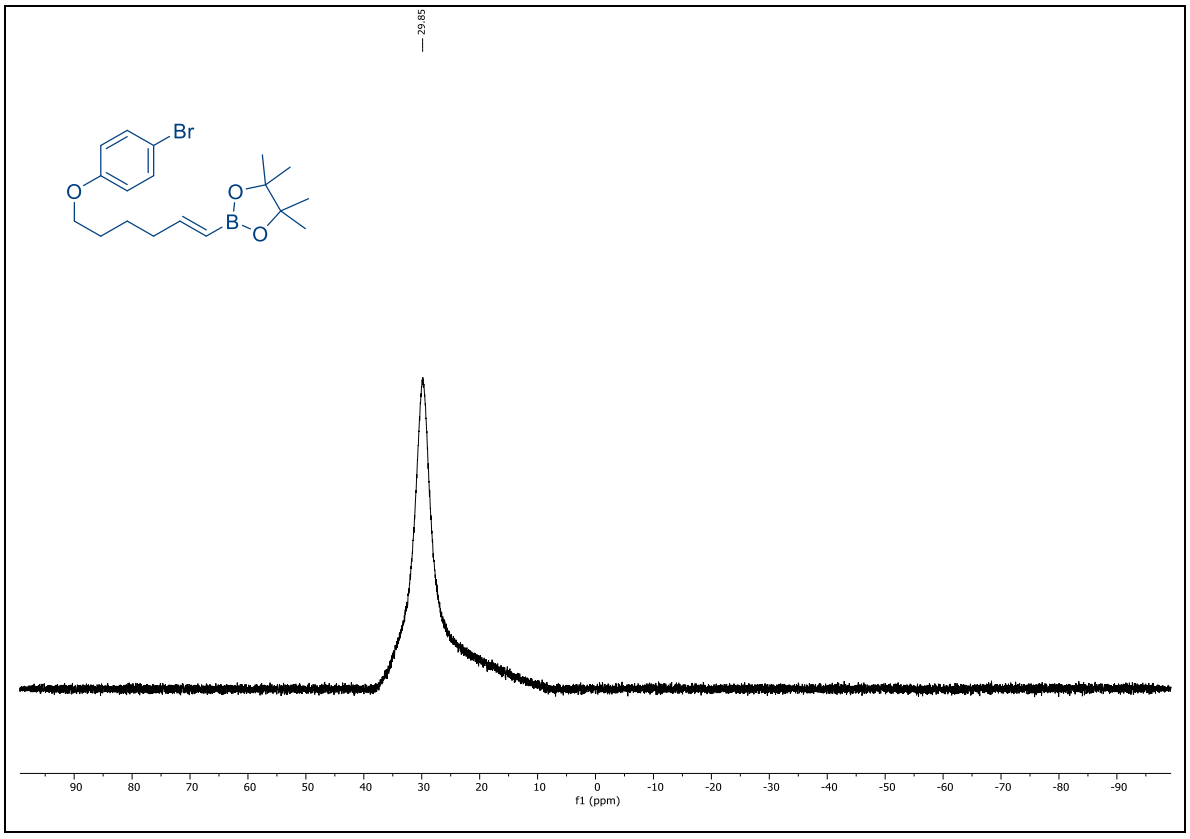
12. NMR spectra

NMR spectra of L2

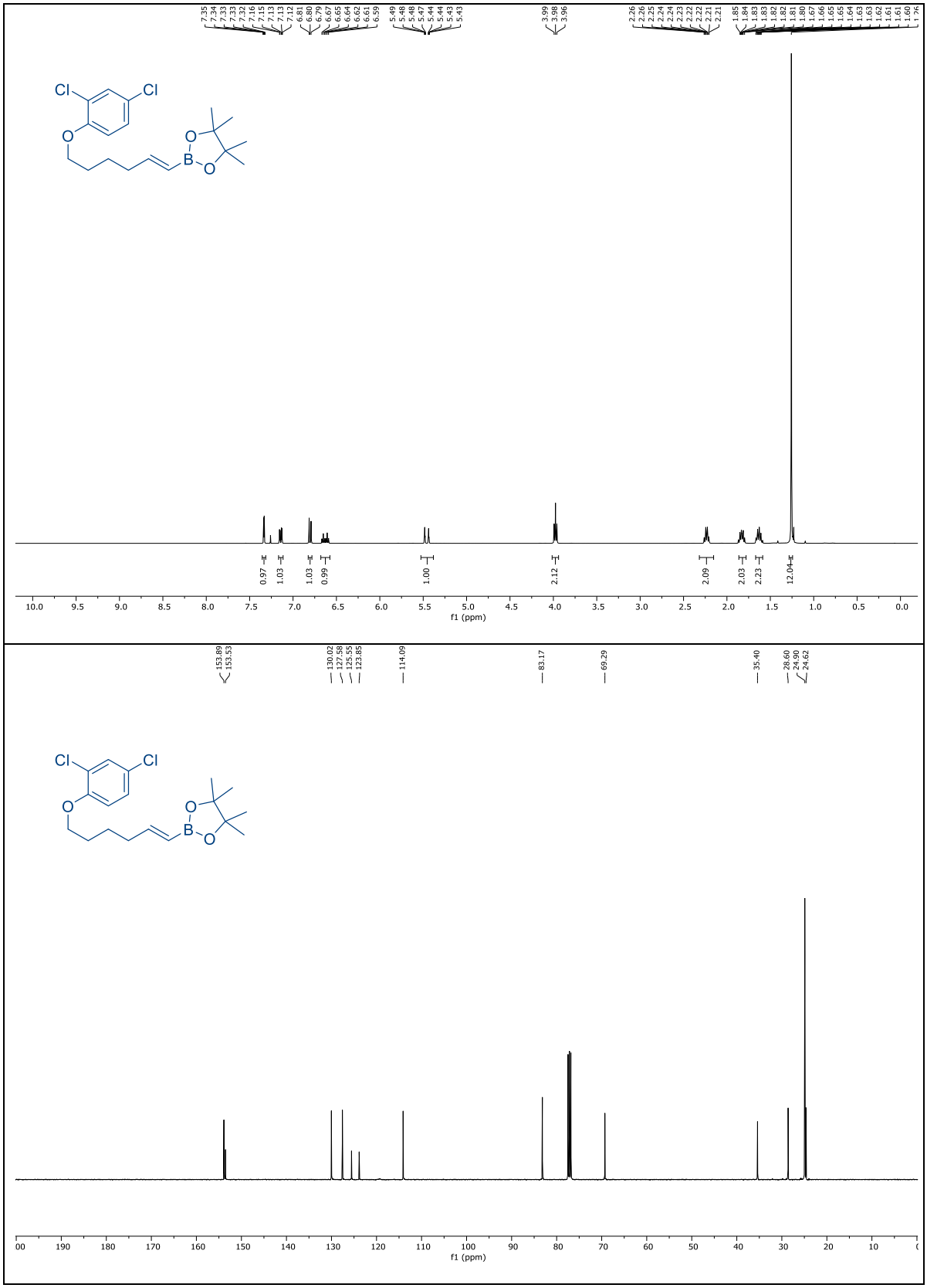


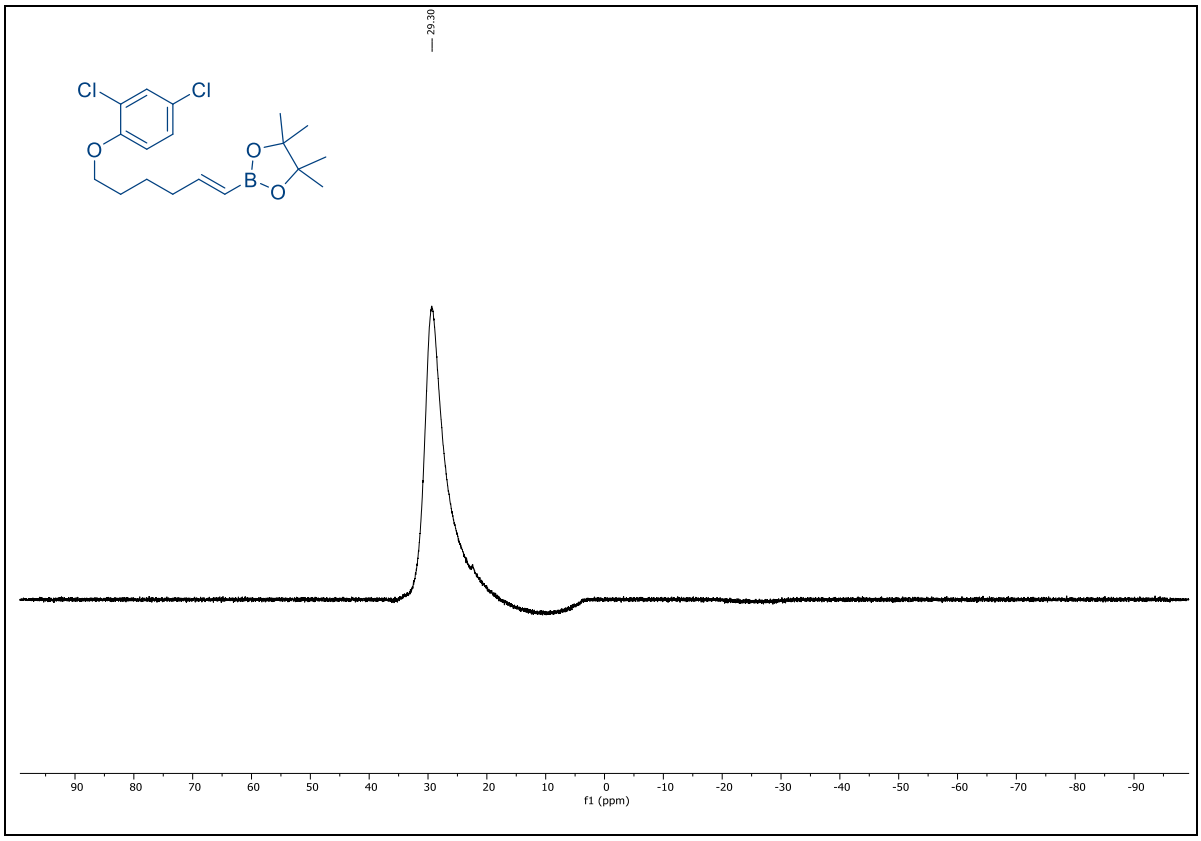
NMR spectra of 1g



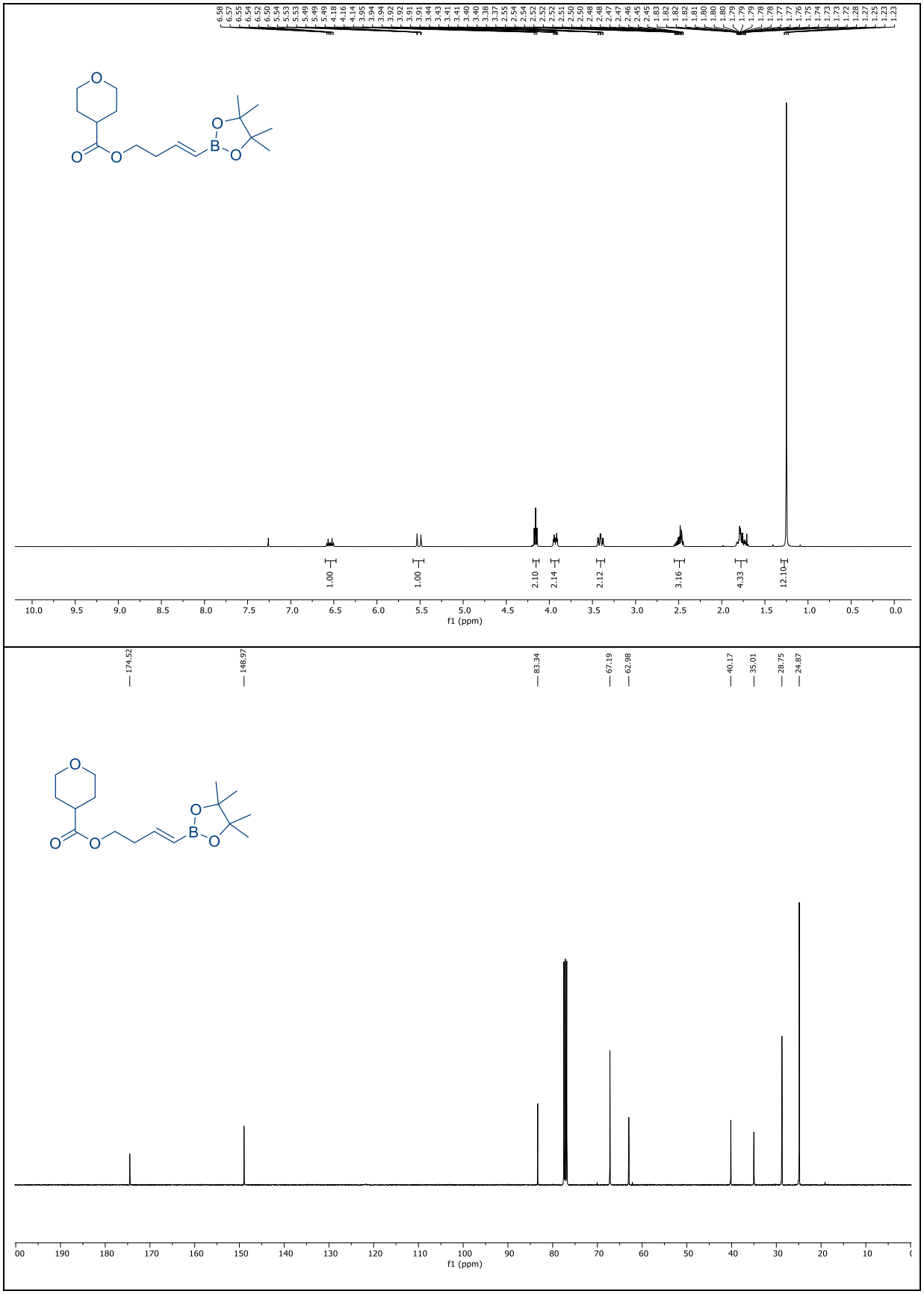

29.65
Br
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

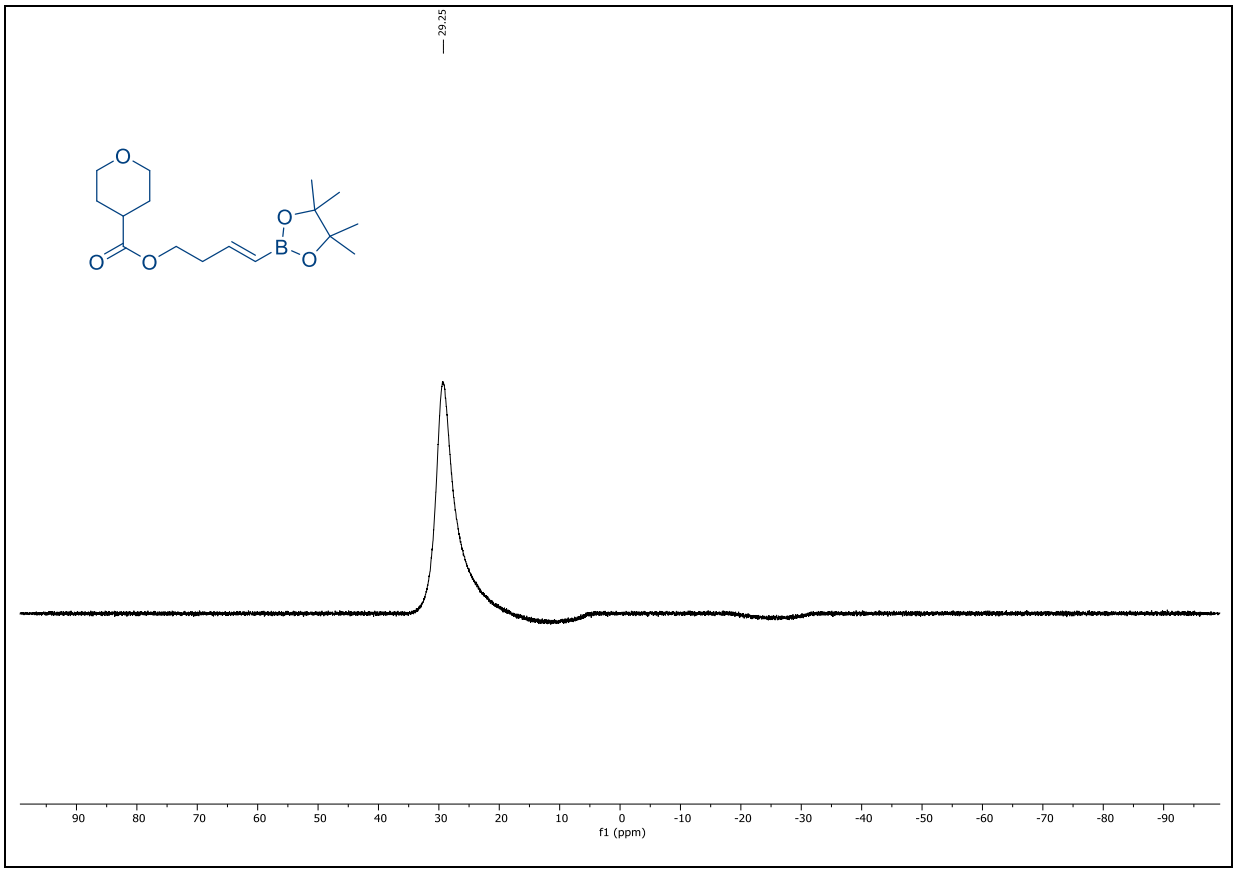
NMR spectra of 1h:



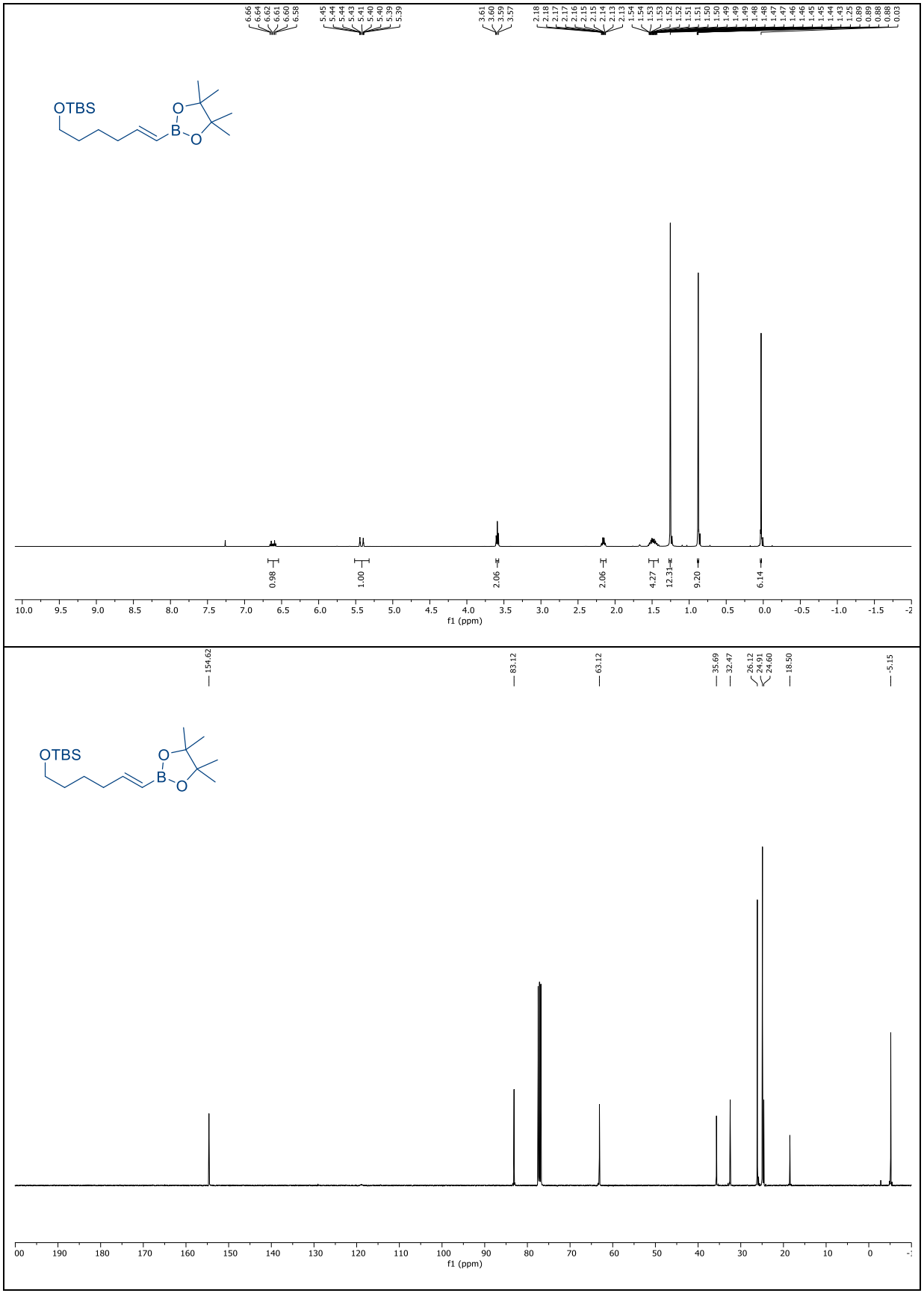

29.30
Cl
Cl
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

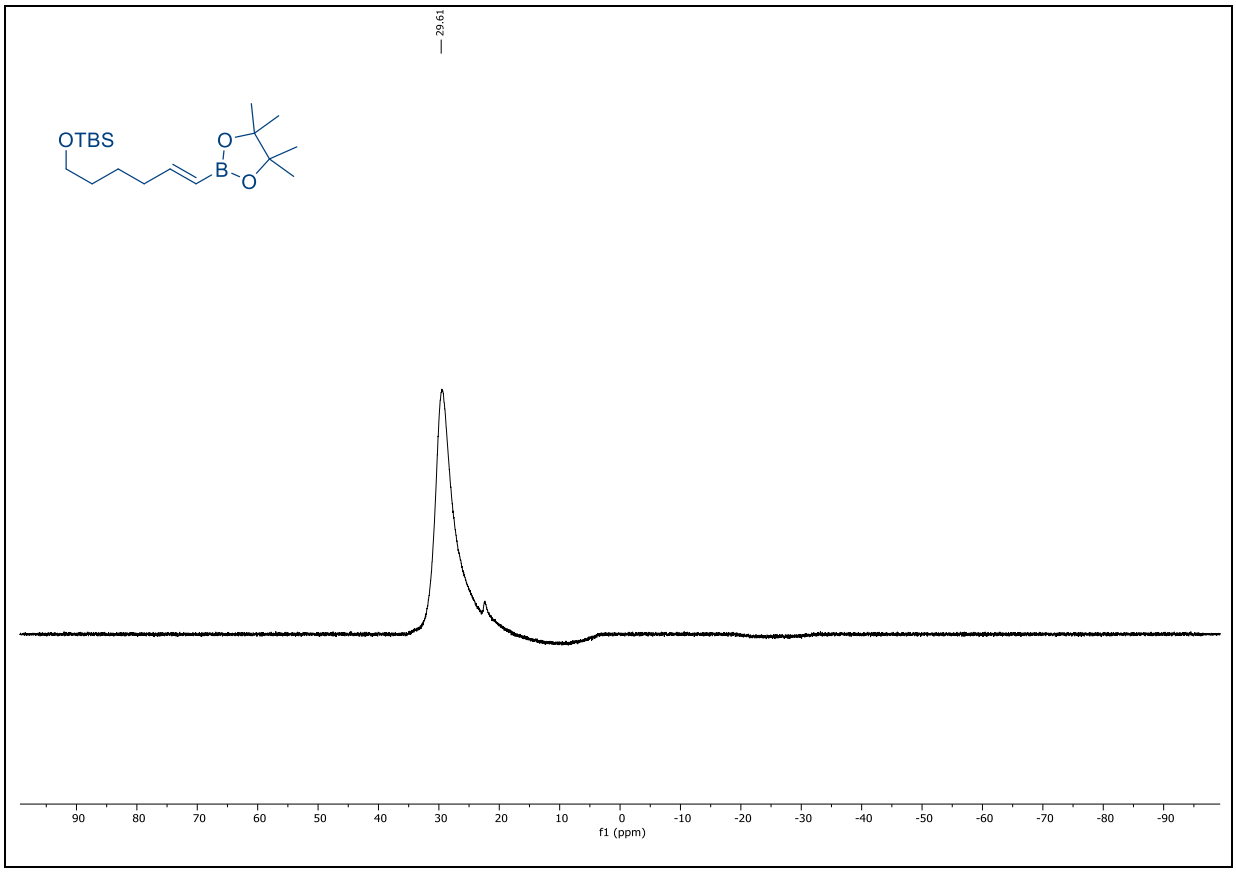
NMR spectra of 1i:



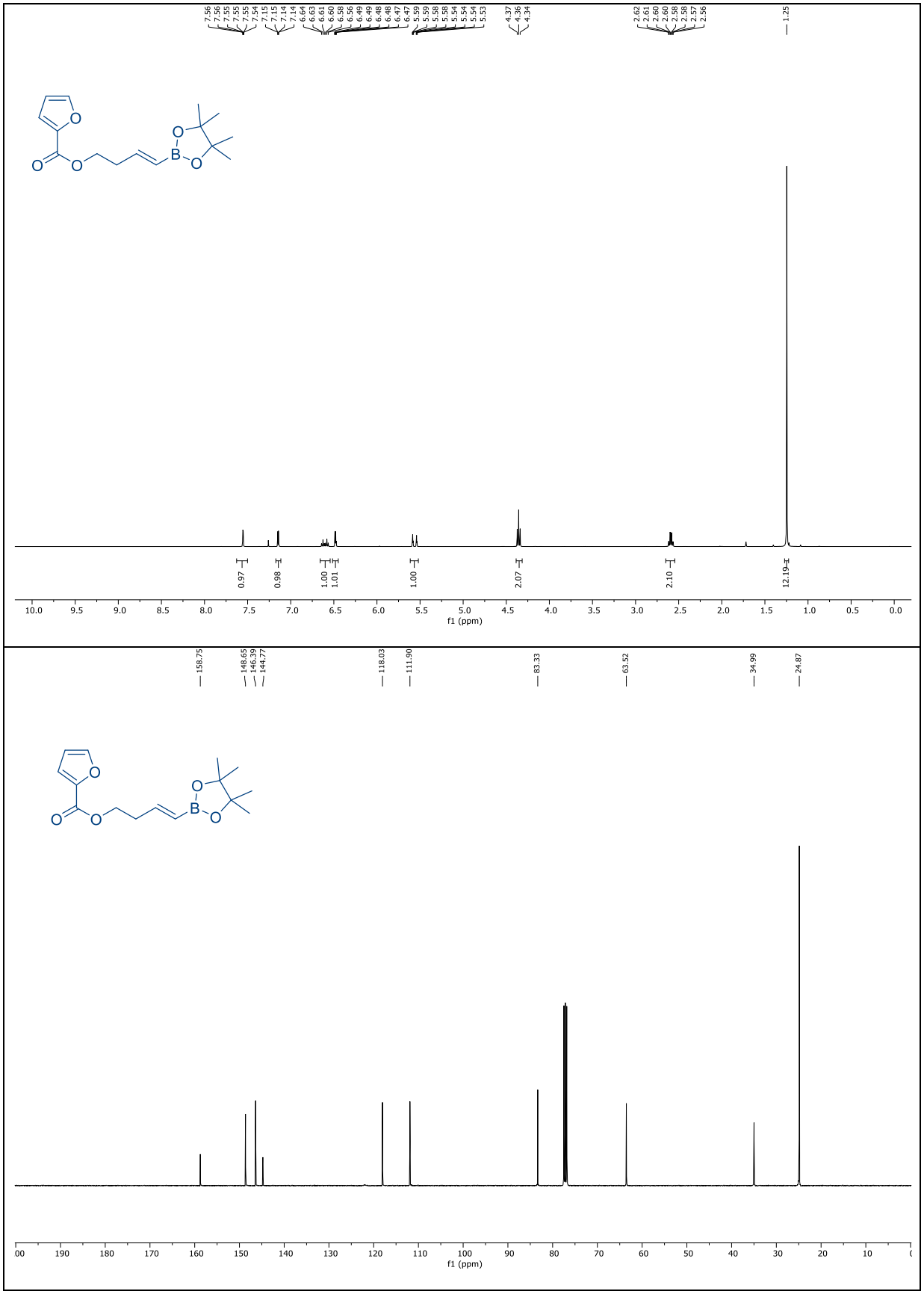

29.25
O
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

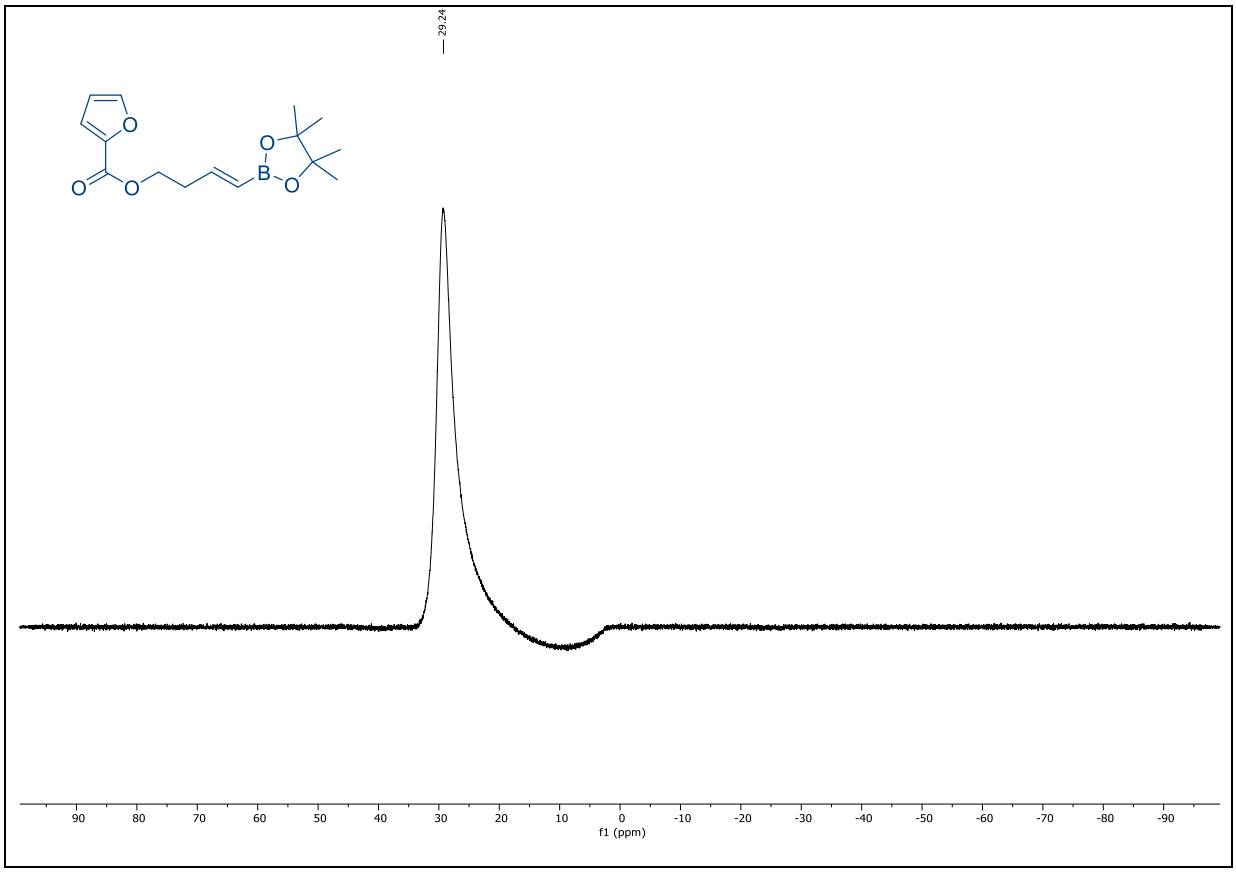
NMR spectra of 1l:



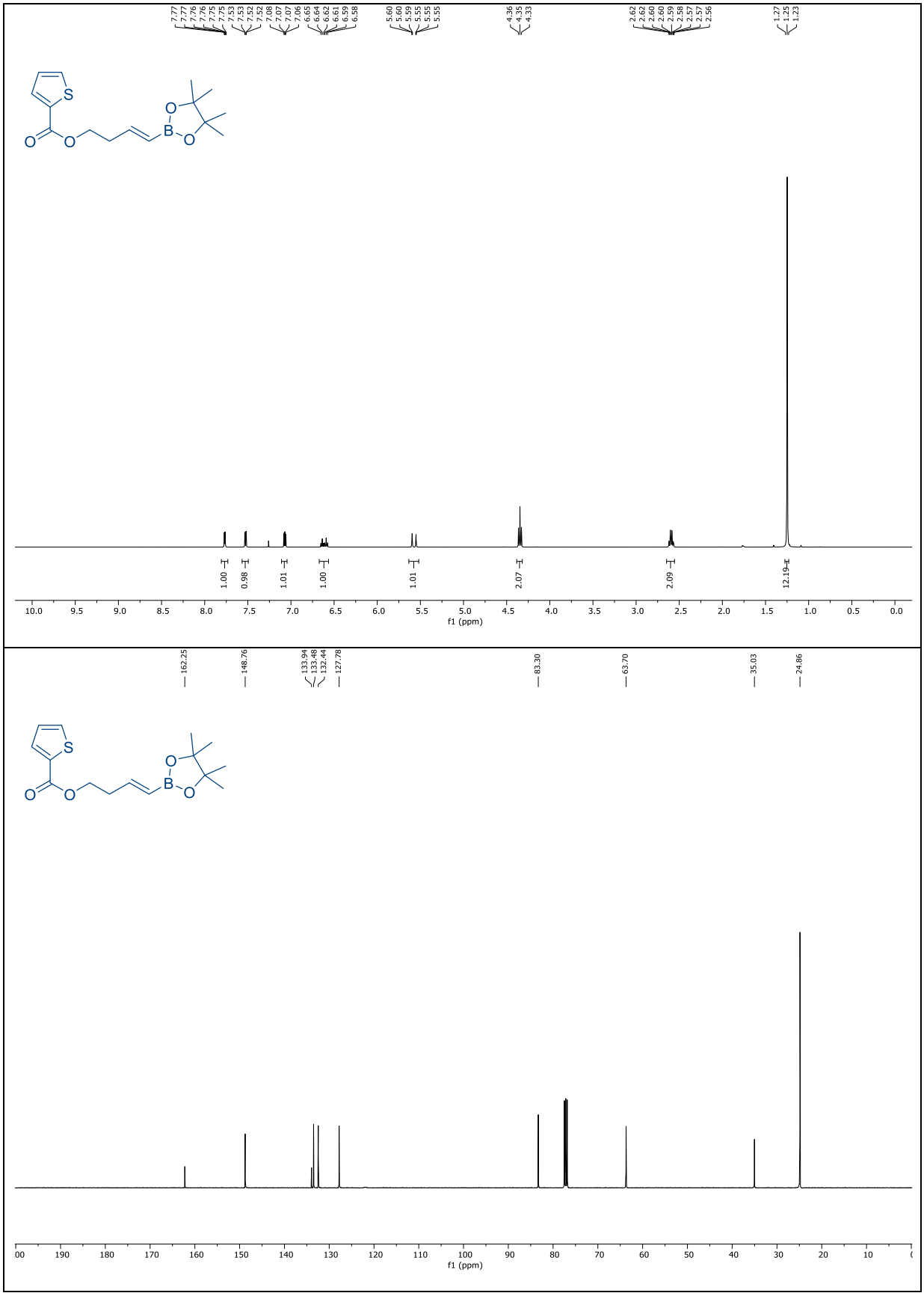

29.61
OTBS
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

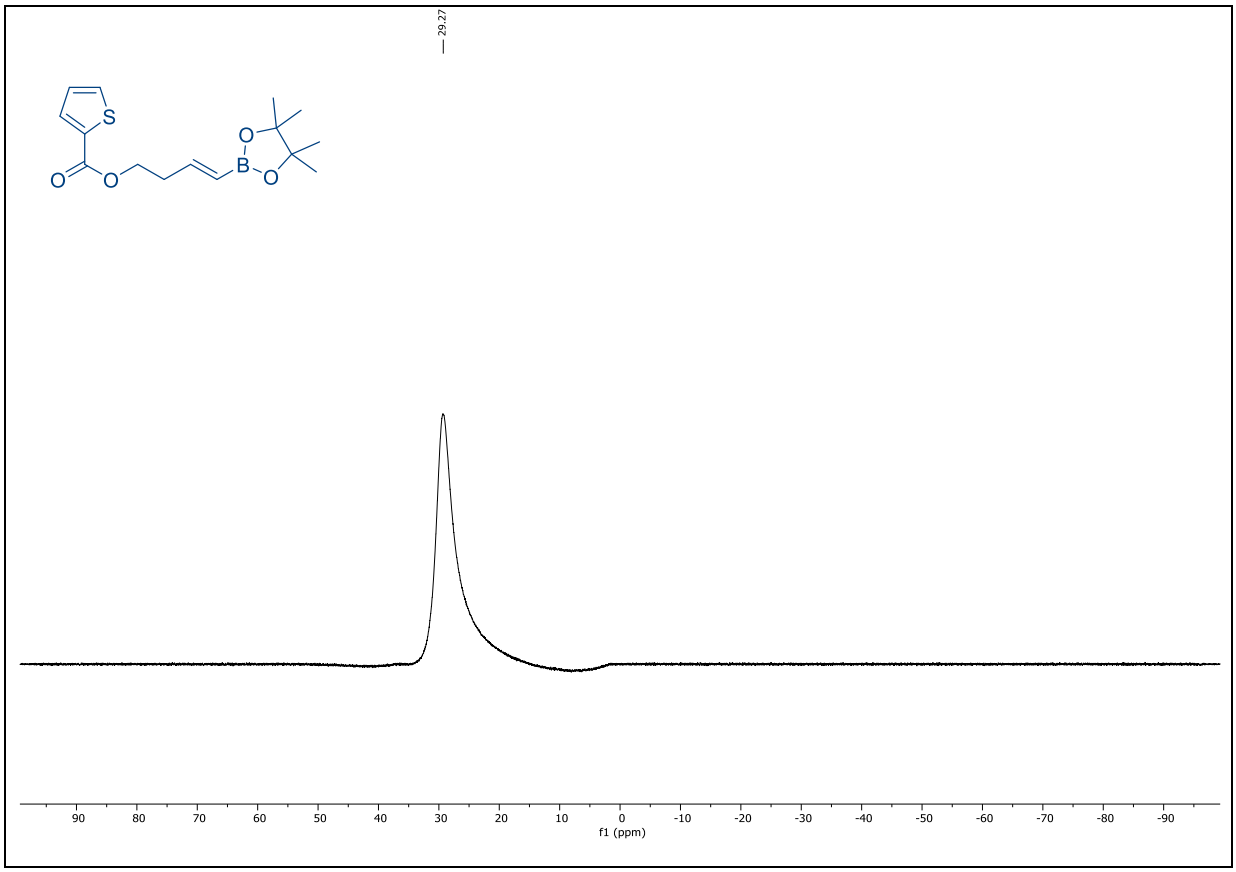
NMR spectra of 1m:



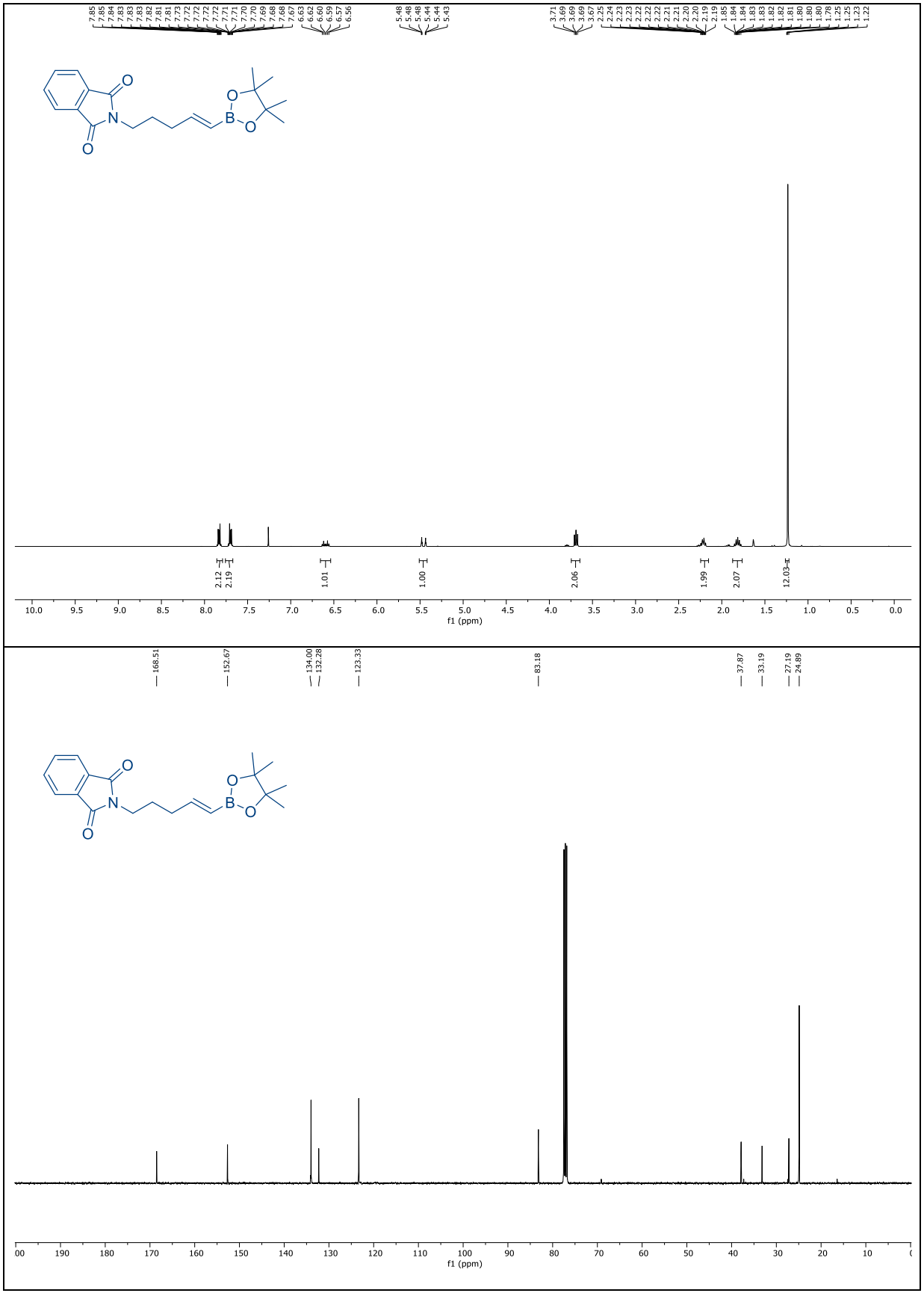

29.24
O
O
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

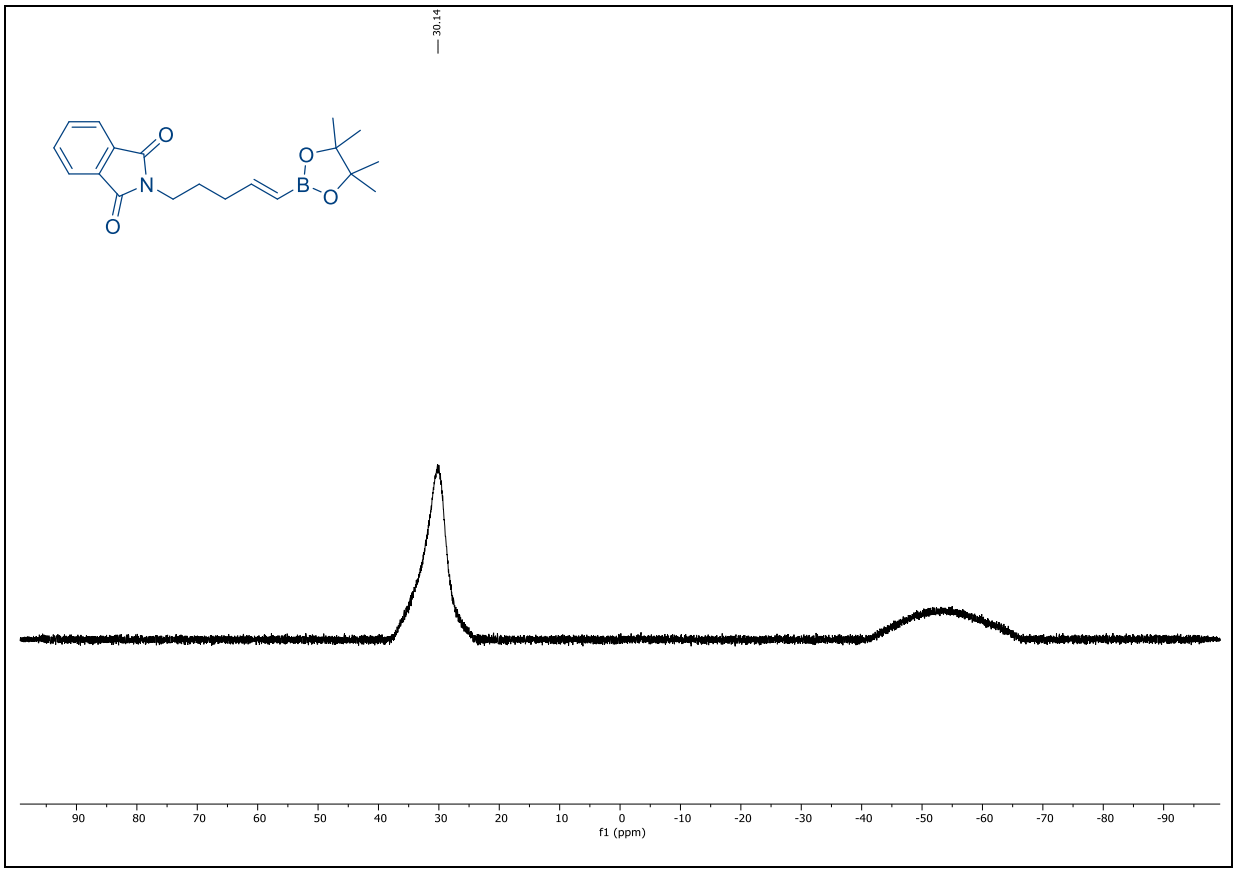
NMR spectra of 1n:



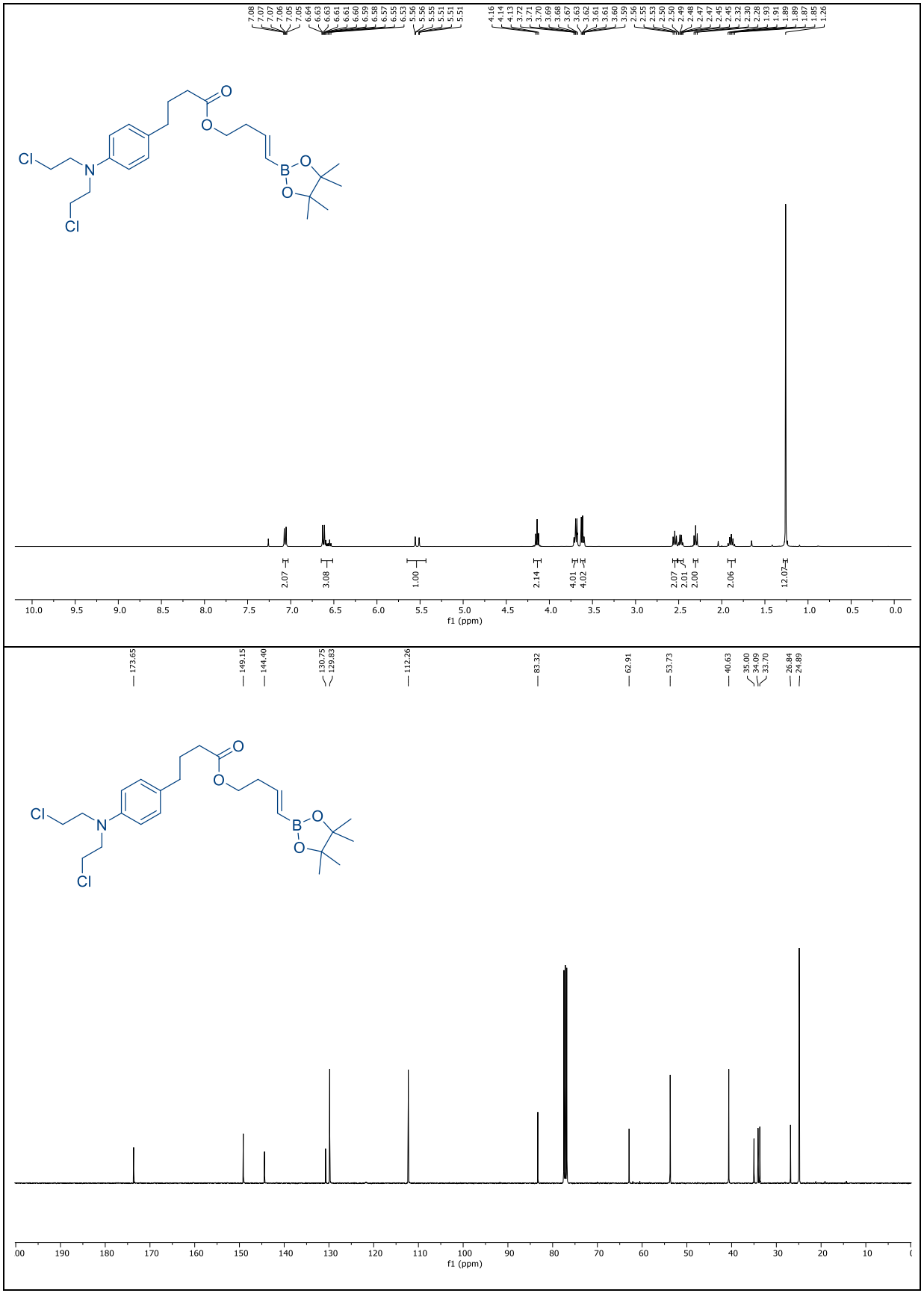

29.27
S
O
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

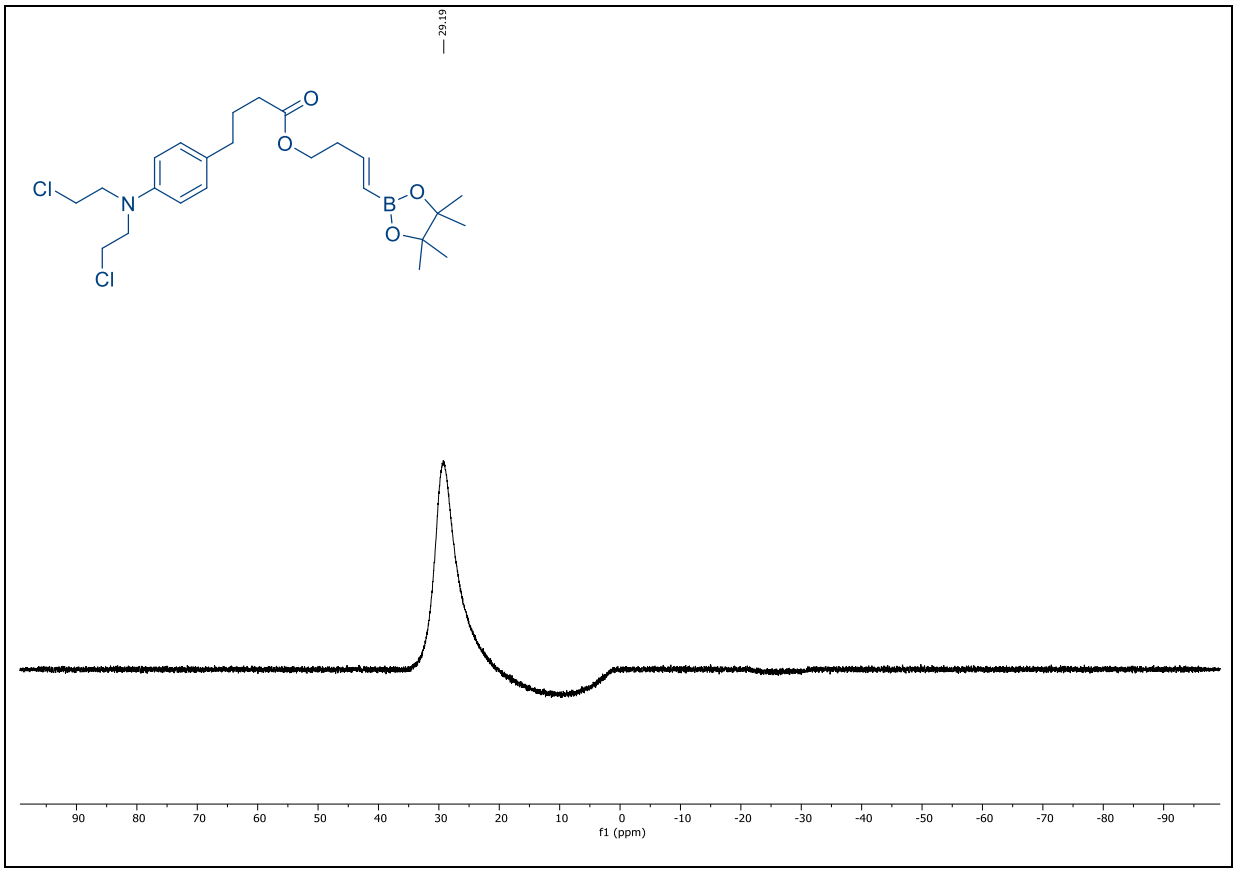
NMR spectra of 1o:



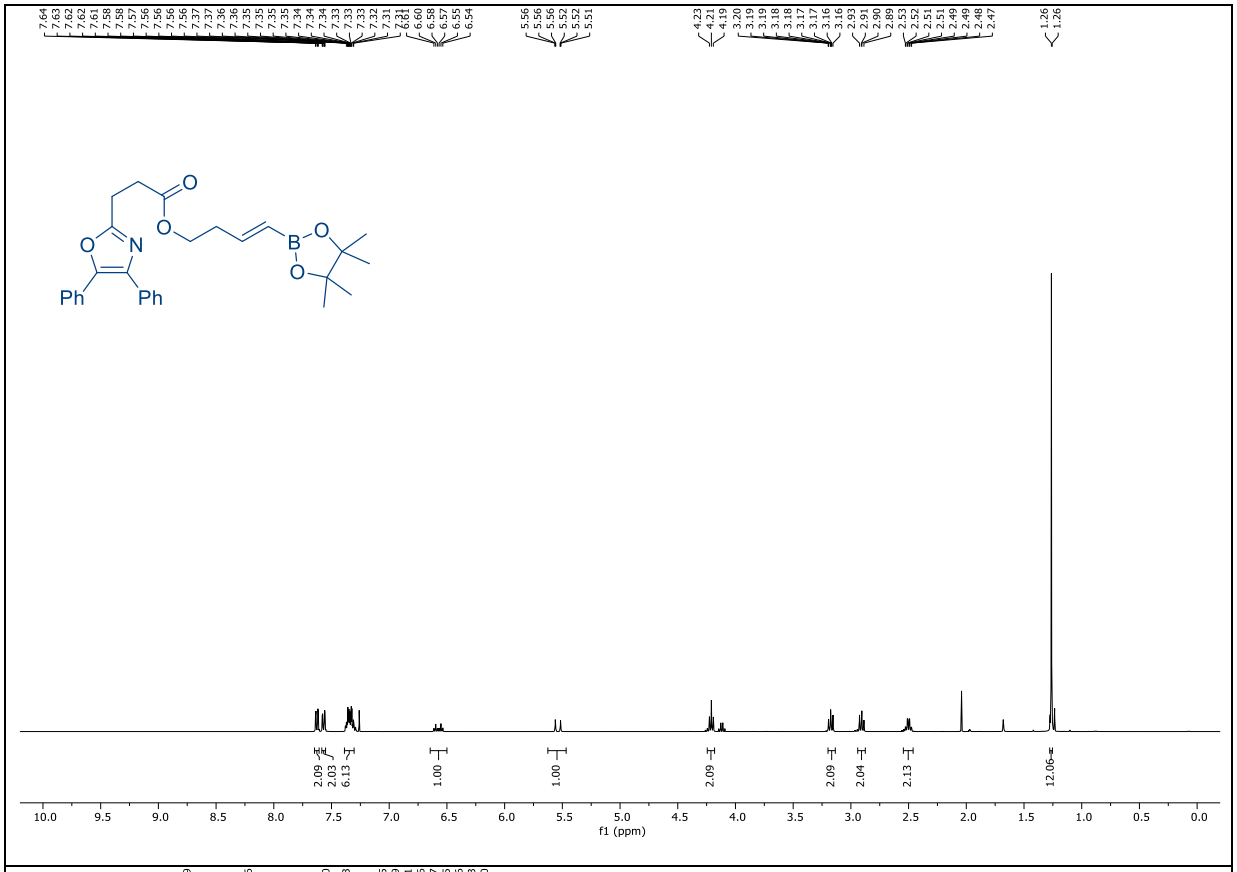

30.14
O
N
O
O
B
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

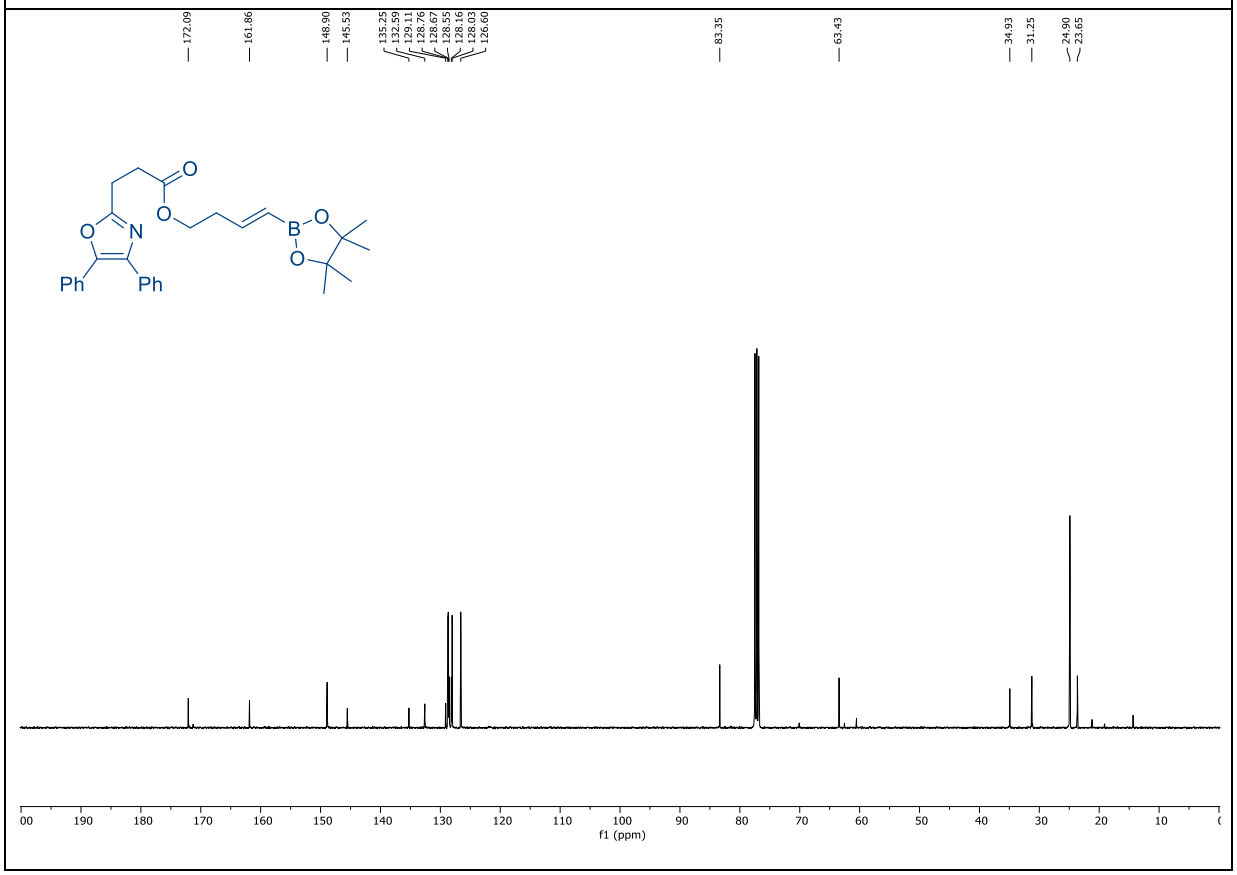
NMR spectra of 1q:

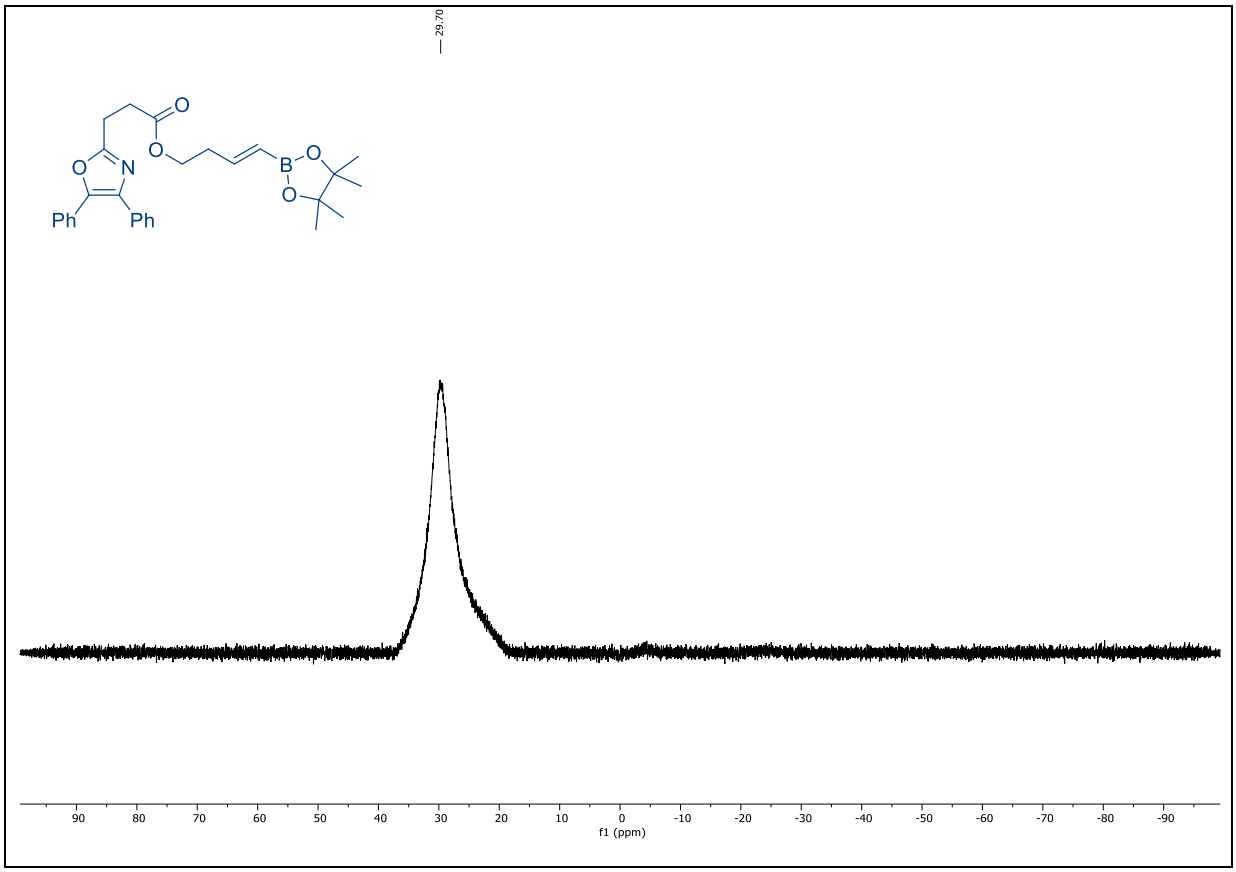



29.19
Cl
N
Cl
O
O
B
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

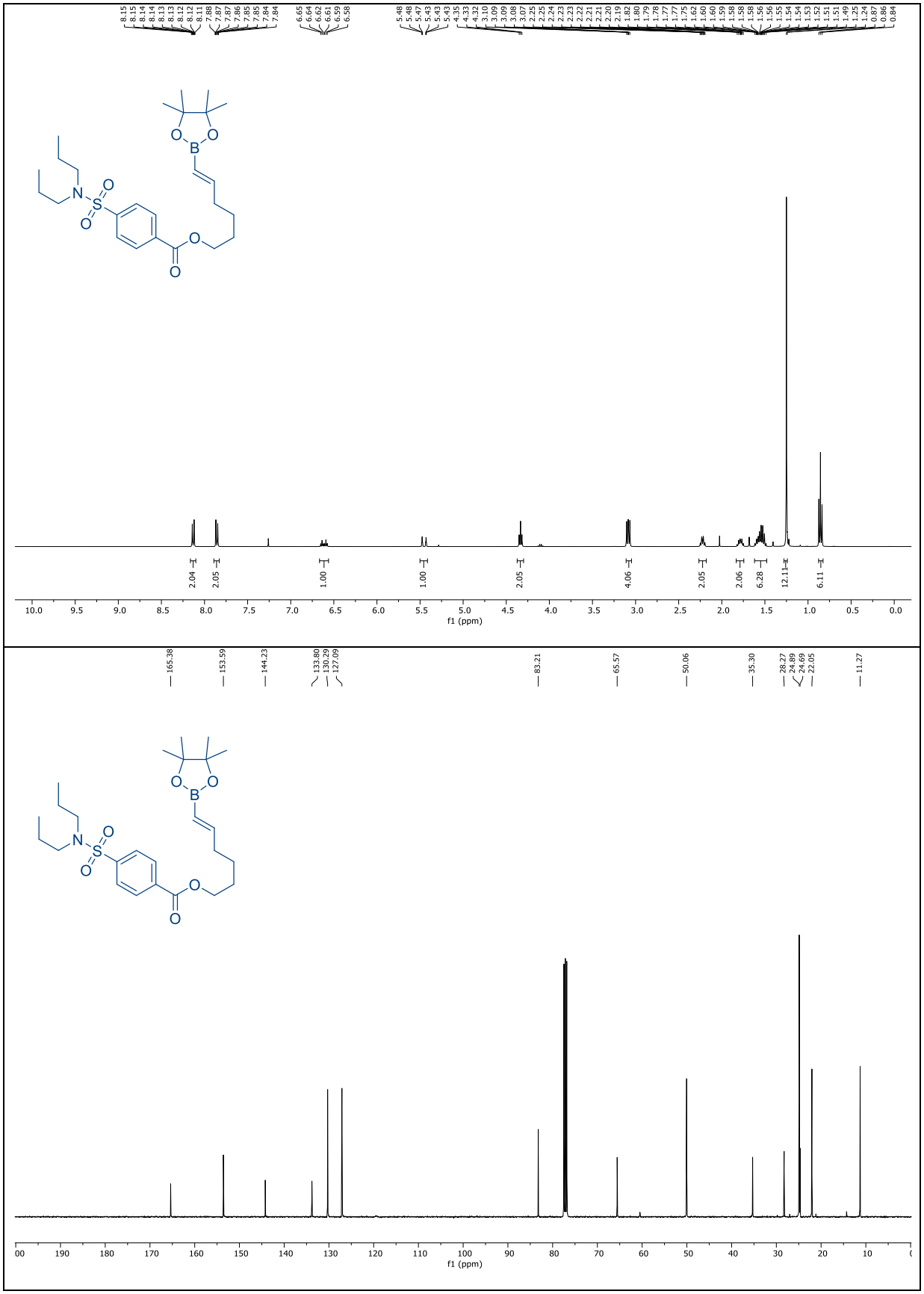
NMR spectra of 1r:

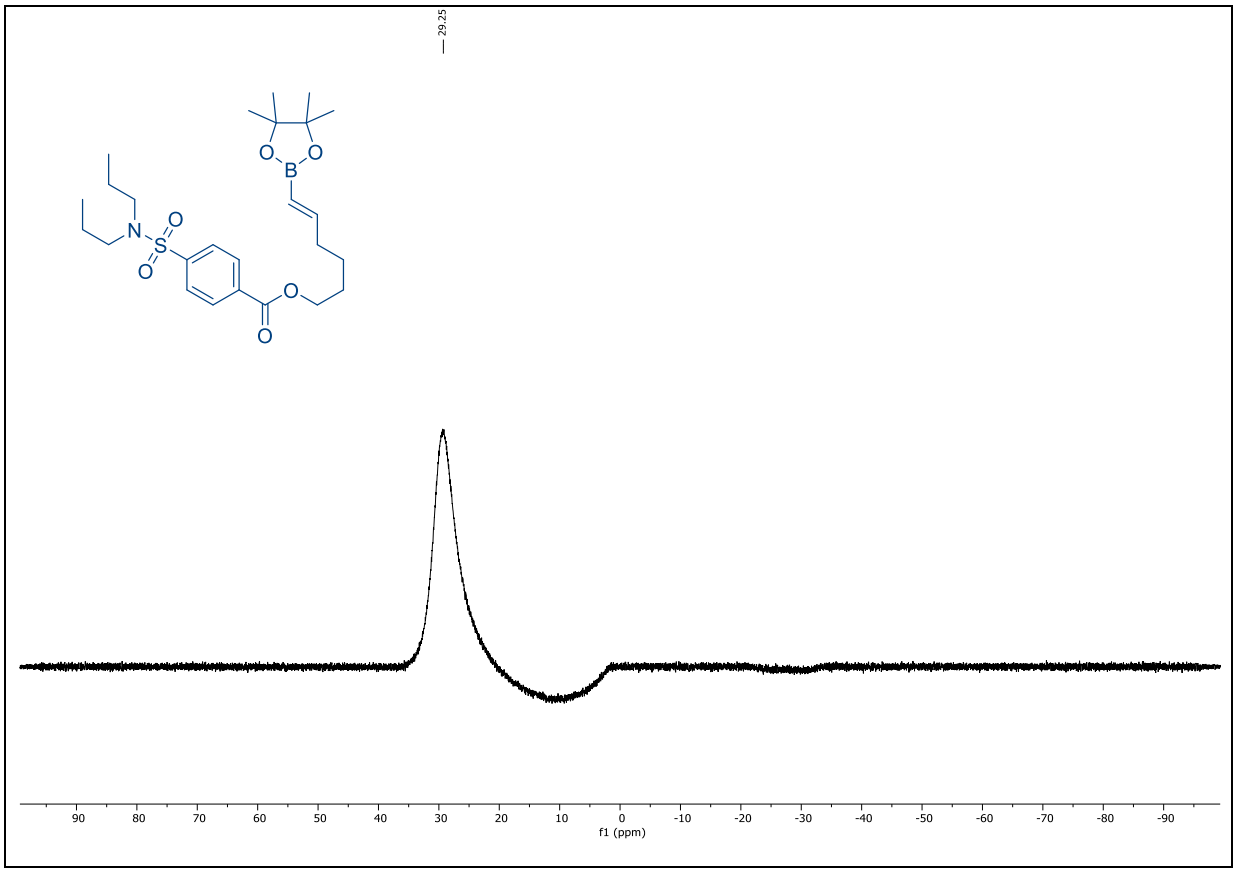




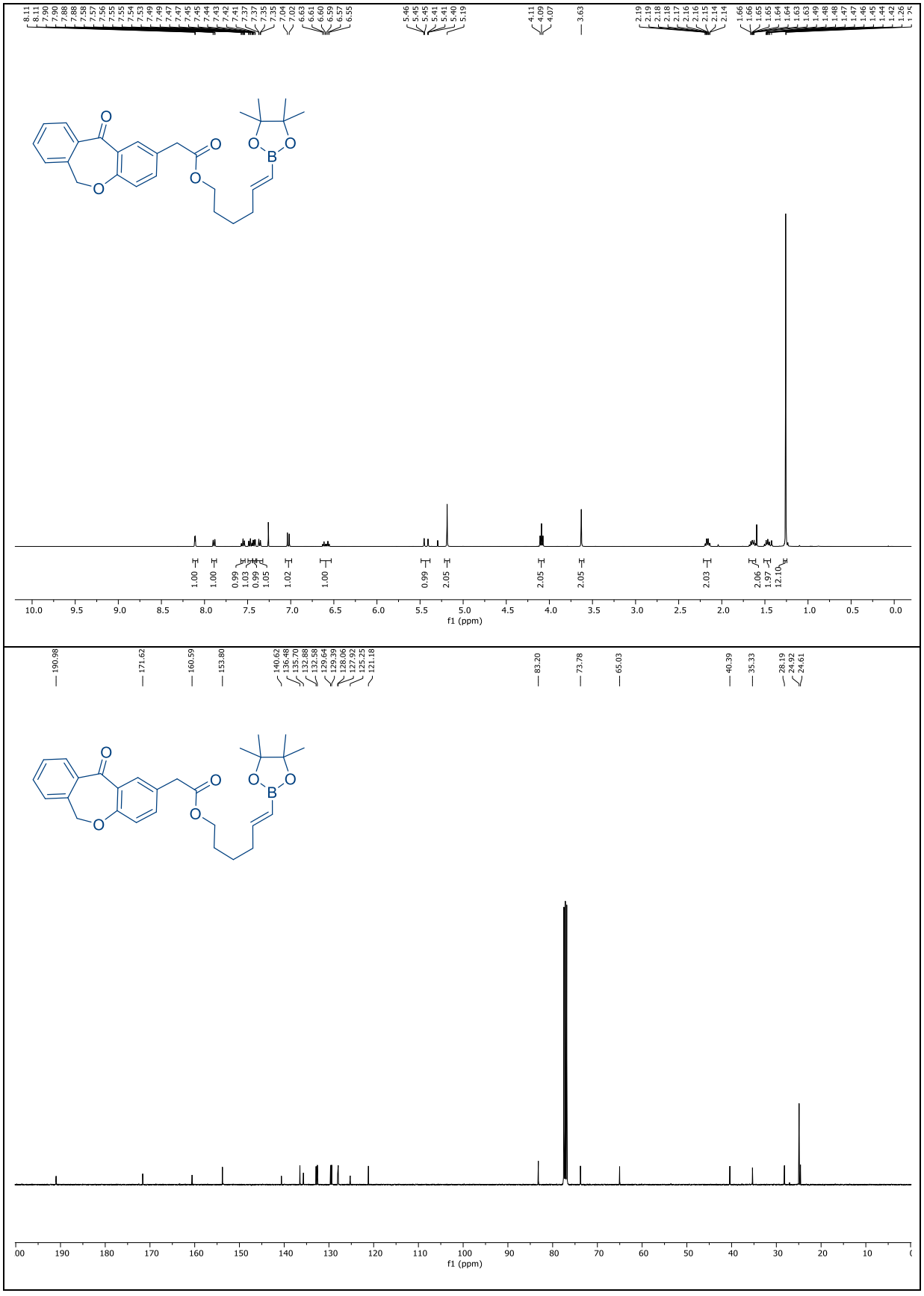

29.70
O
O
O
N
Ph
Ph
B
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

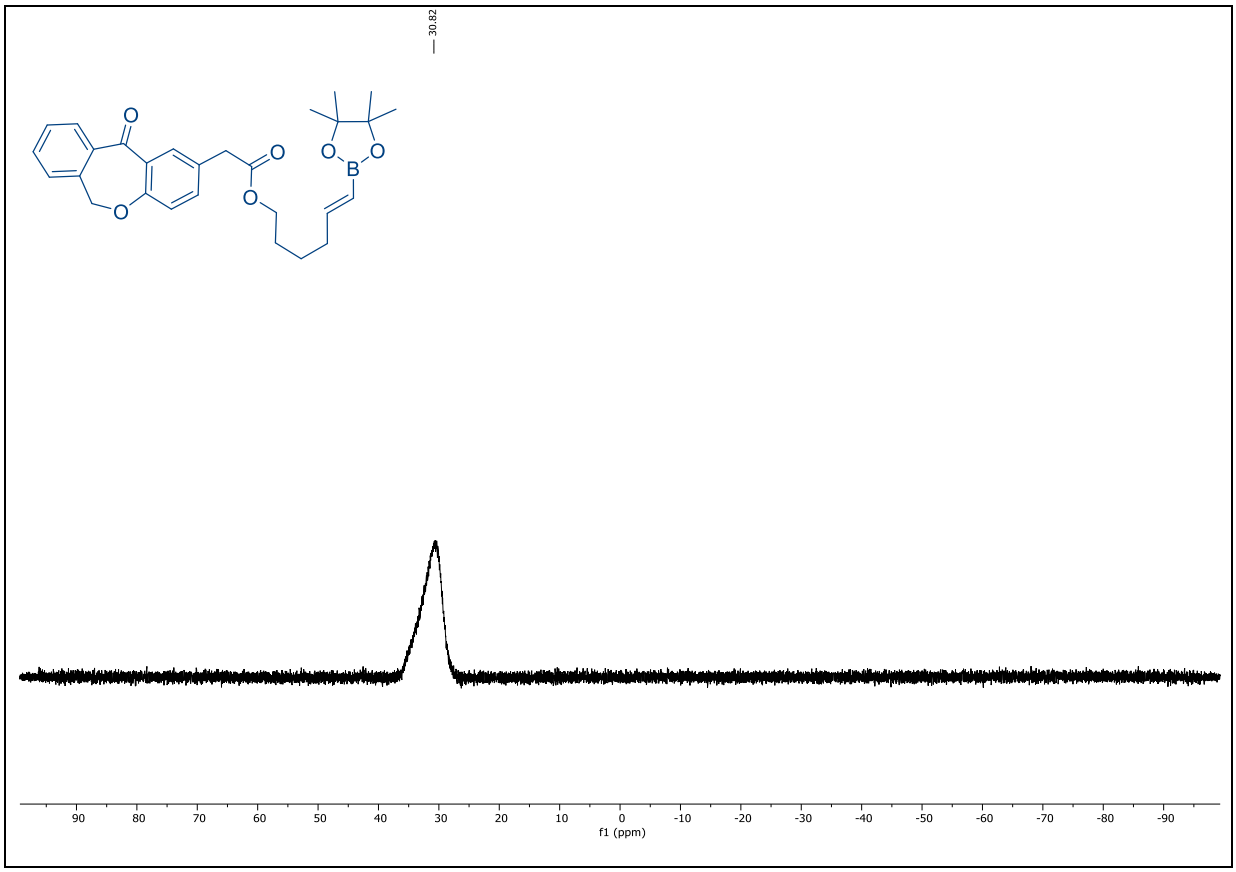
NMR spectra of 1s:



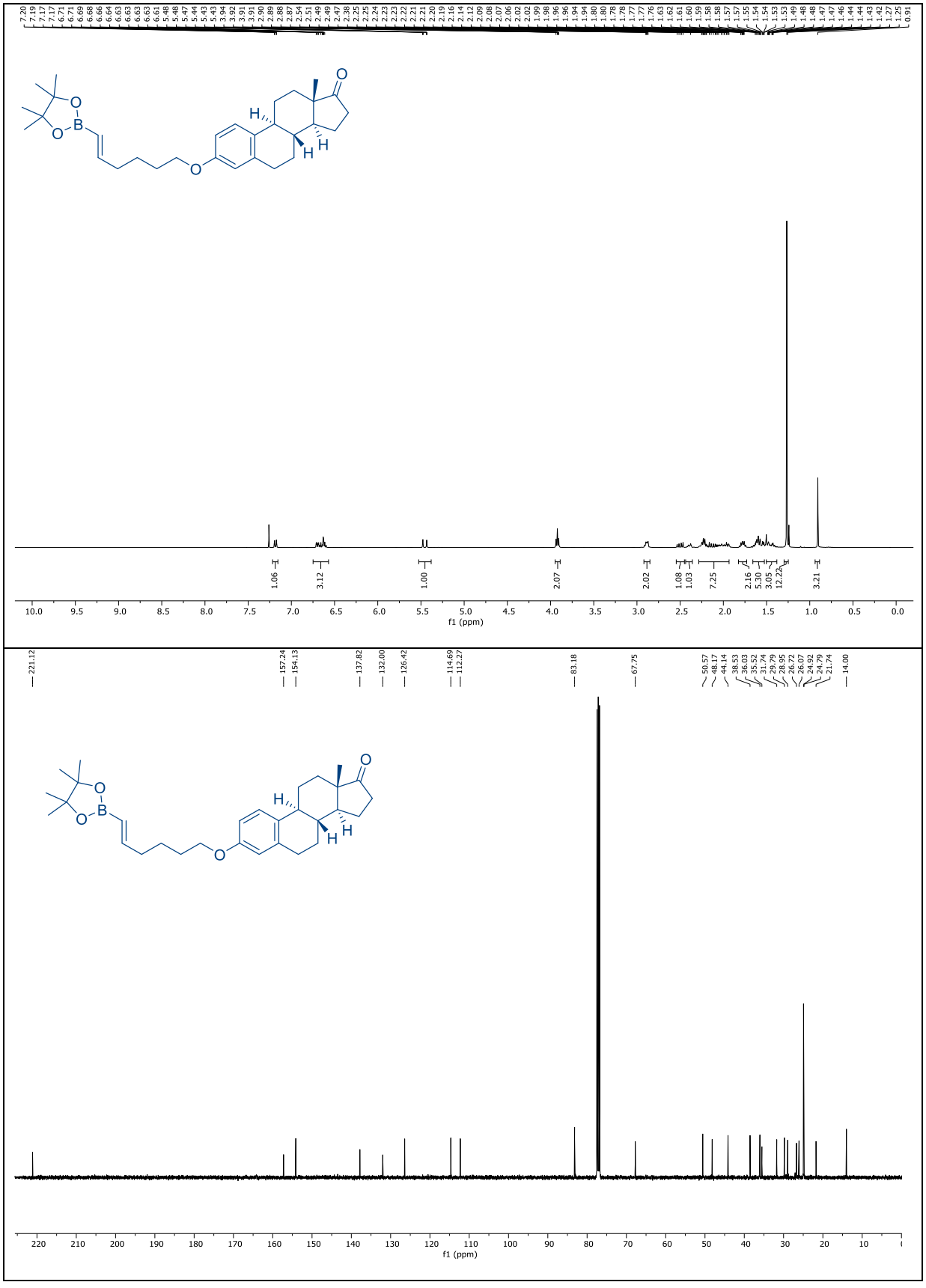

29.25
O
B
O
N
S
O
O
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

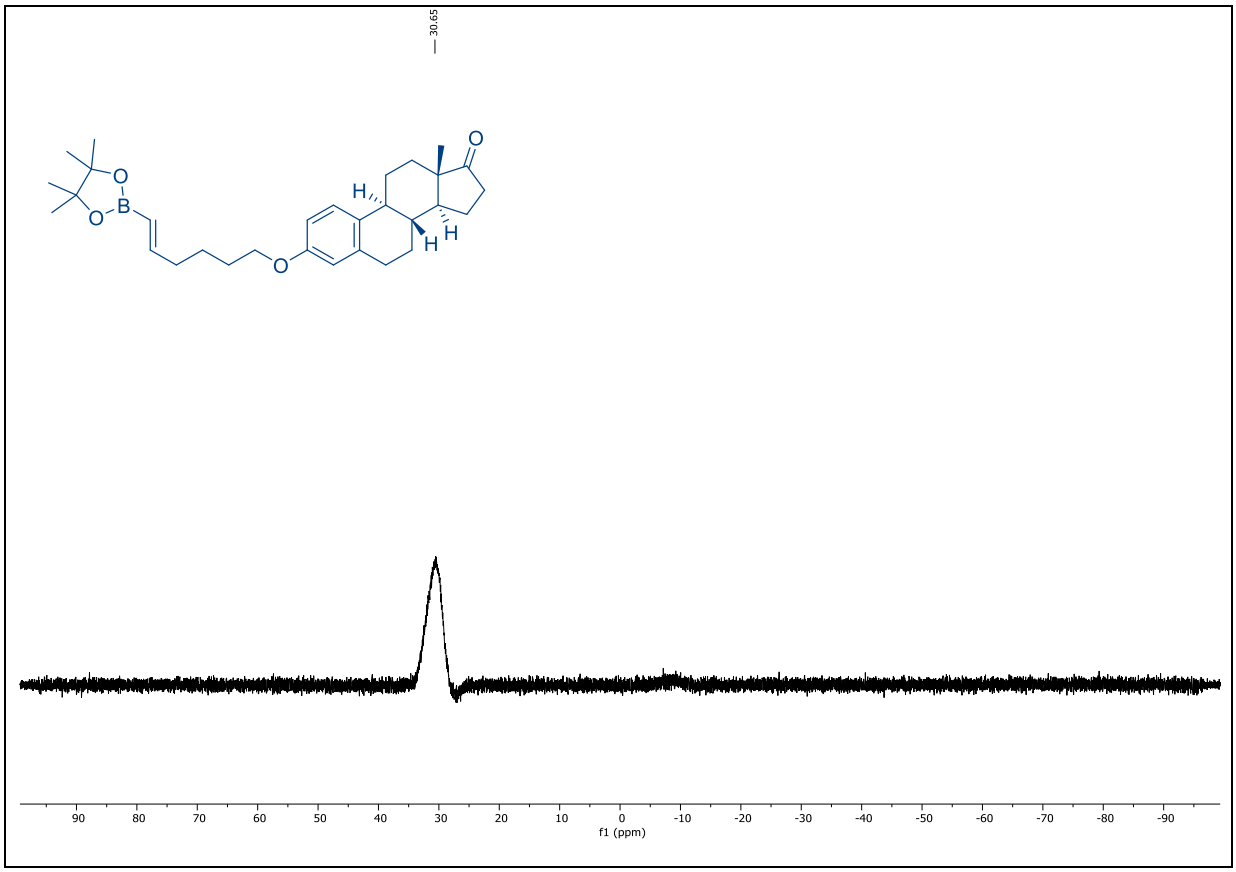
NMR spectra of 1t:



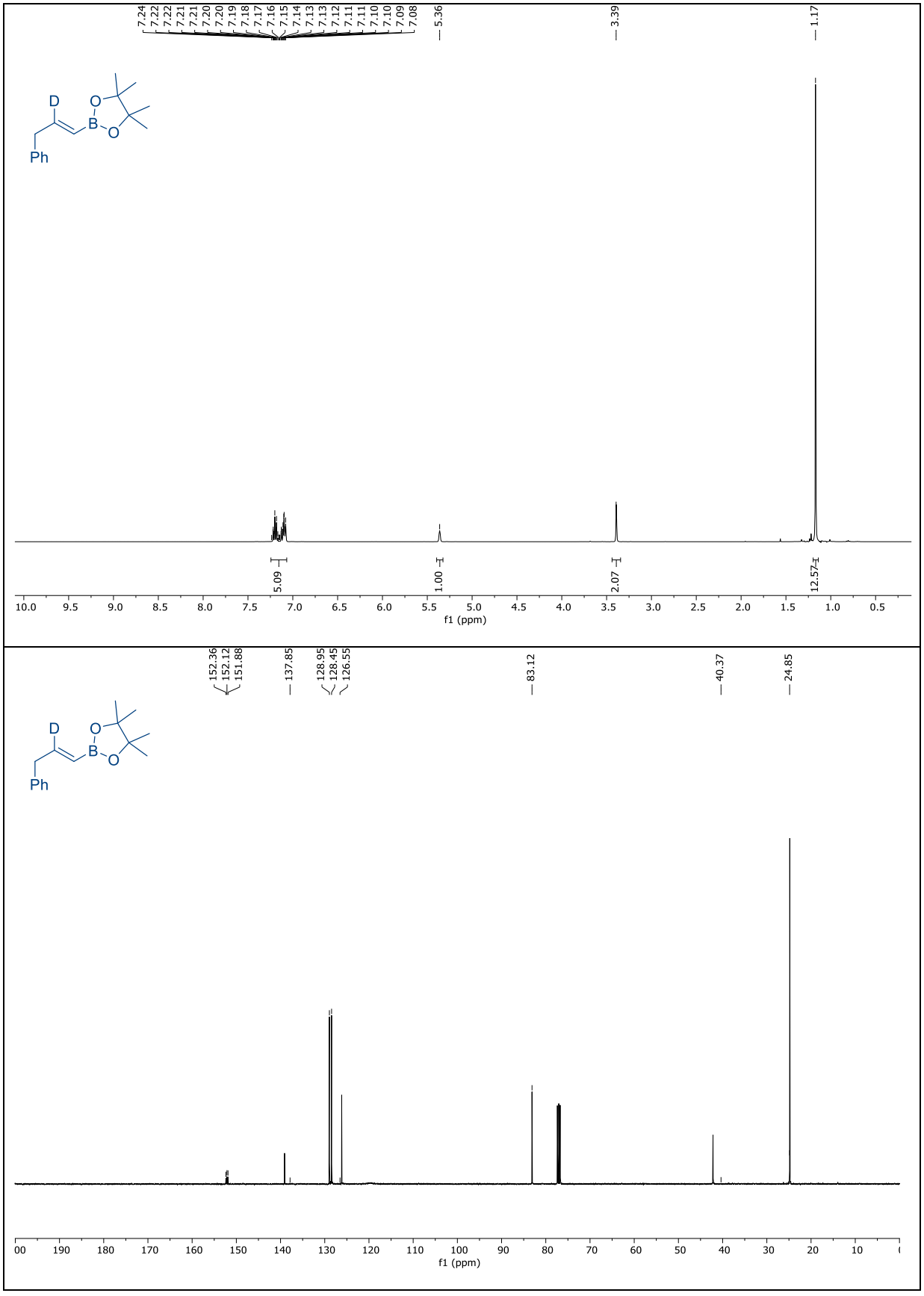

30.82
O
O
O
O
O
B
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 1u:

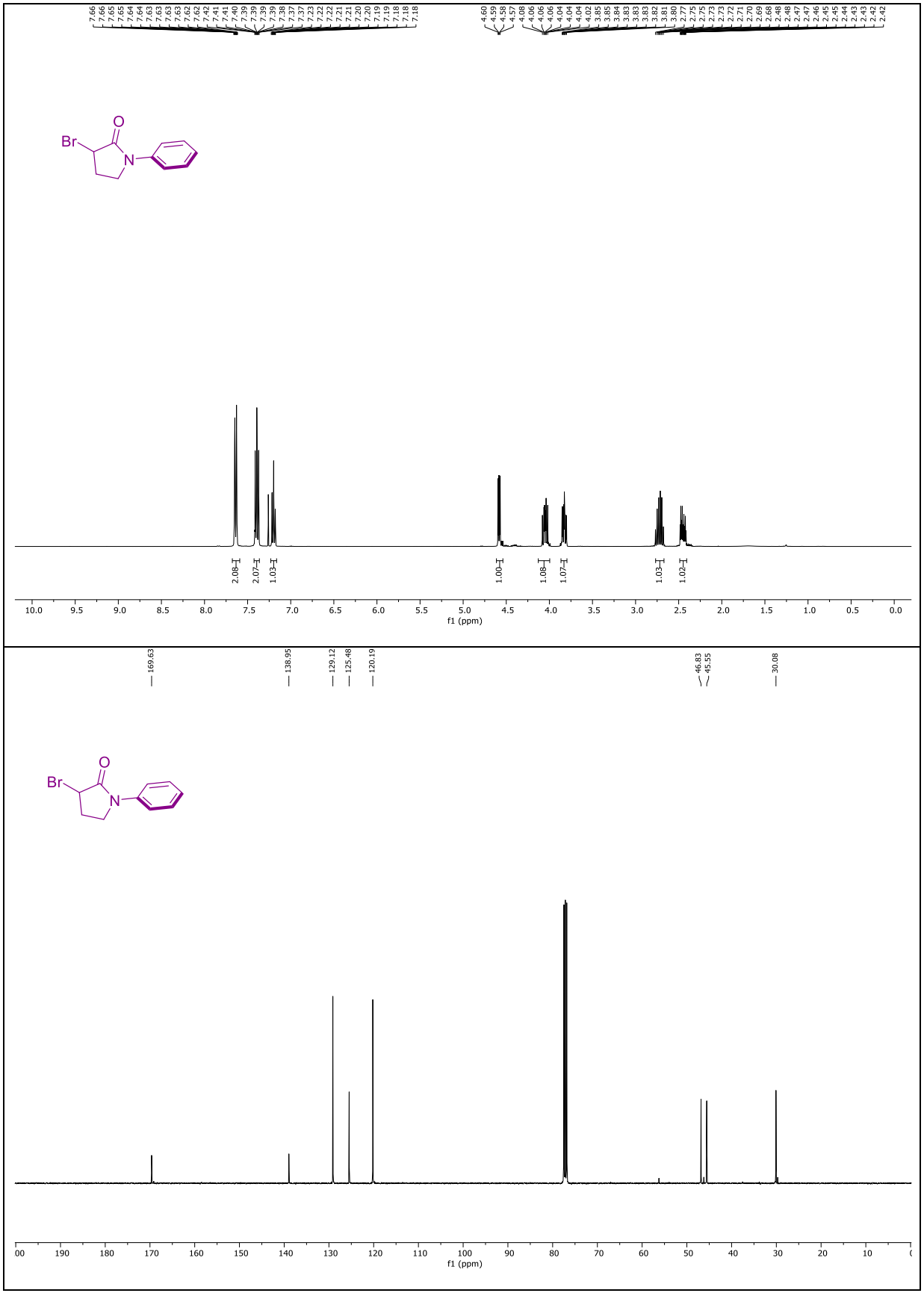



30.65
O
B
O
O
H
H
H
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

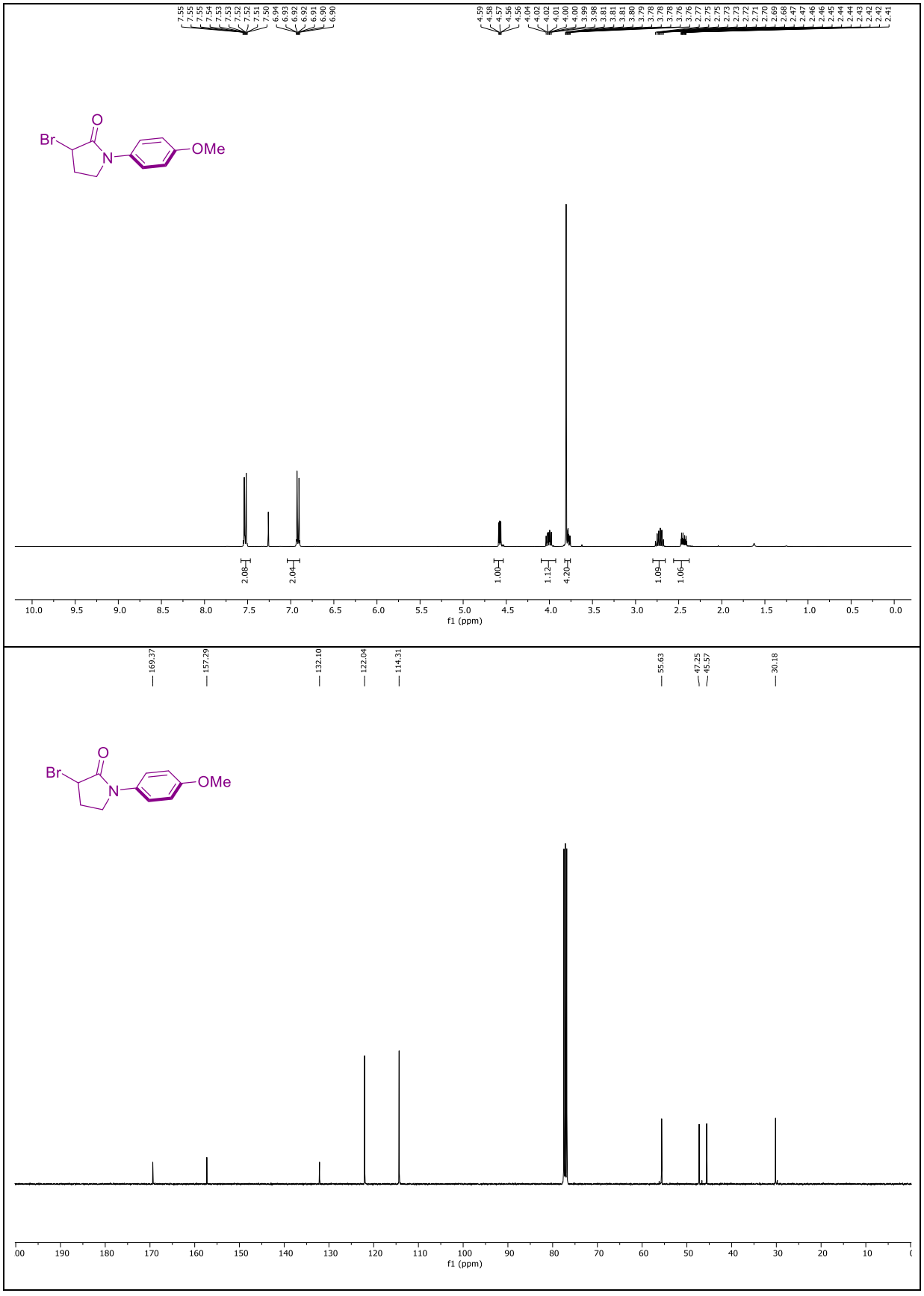
NMR spectra of 1w:



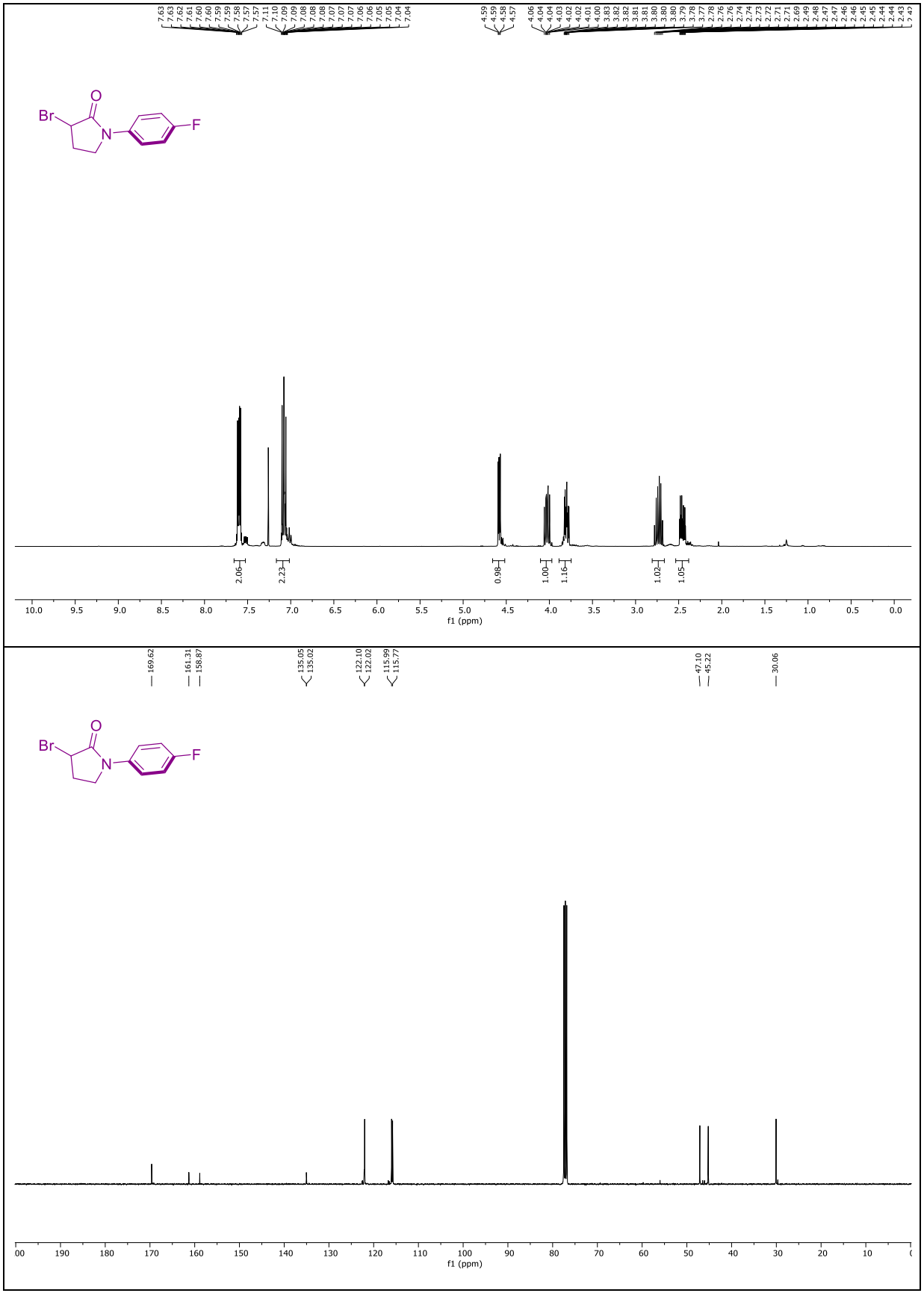
NMR spectra of 2a:

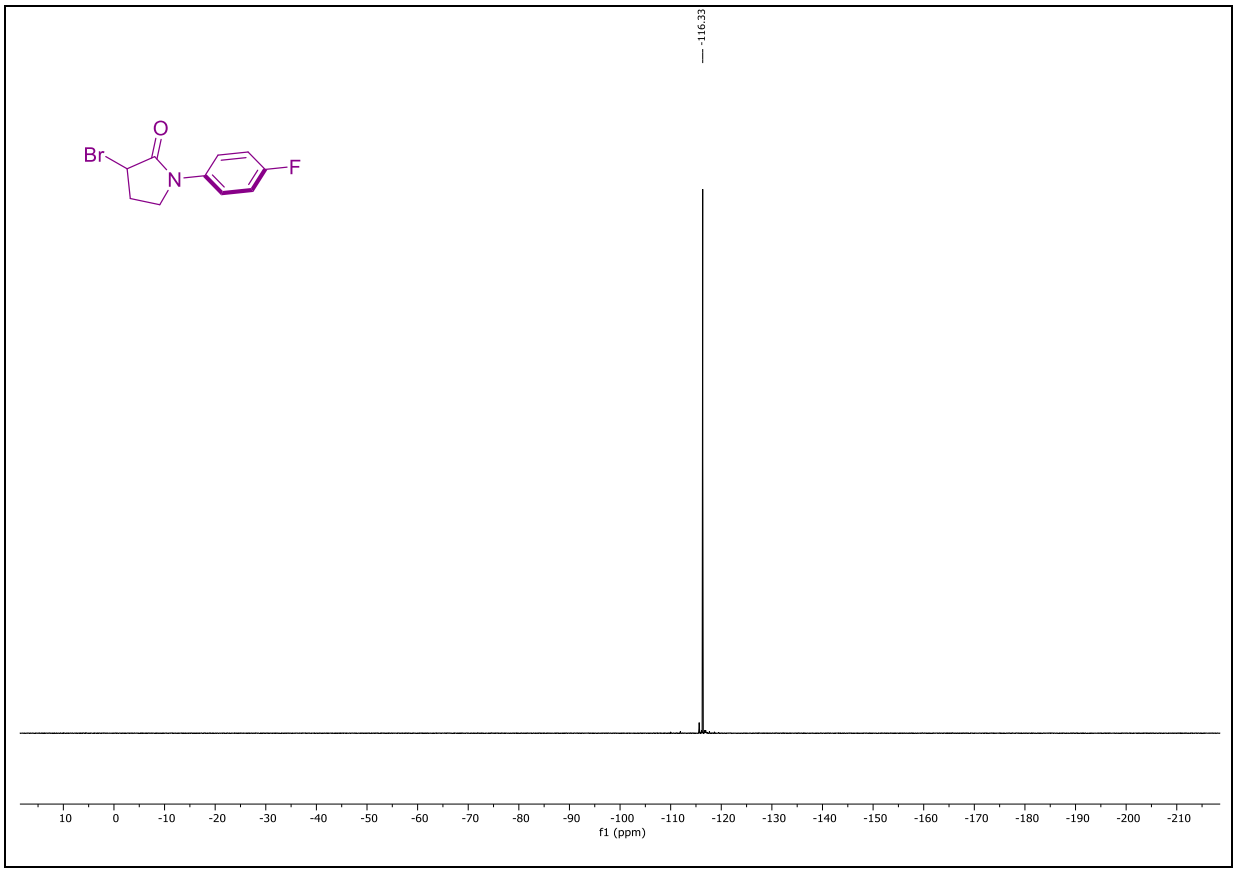


NMR spectra of 2b:

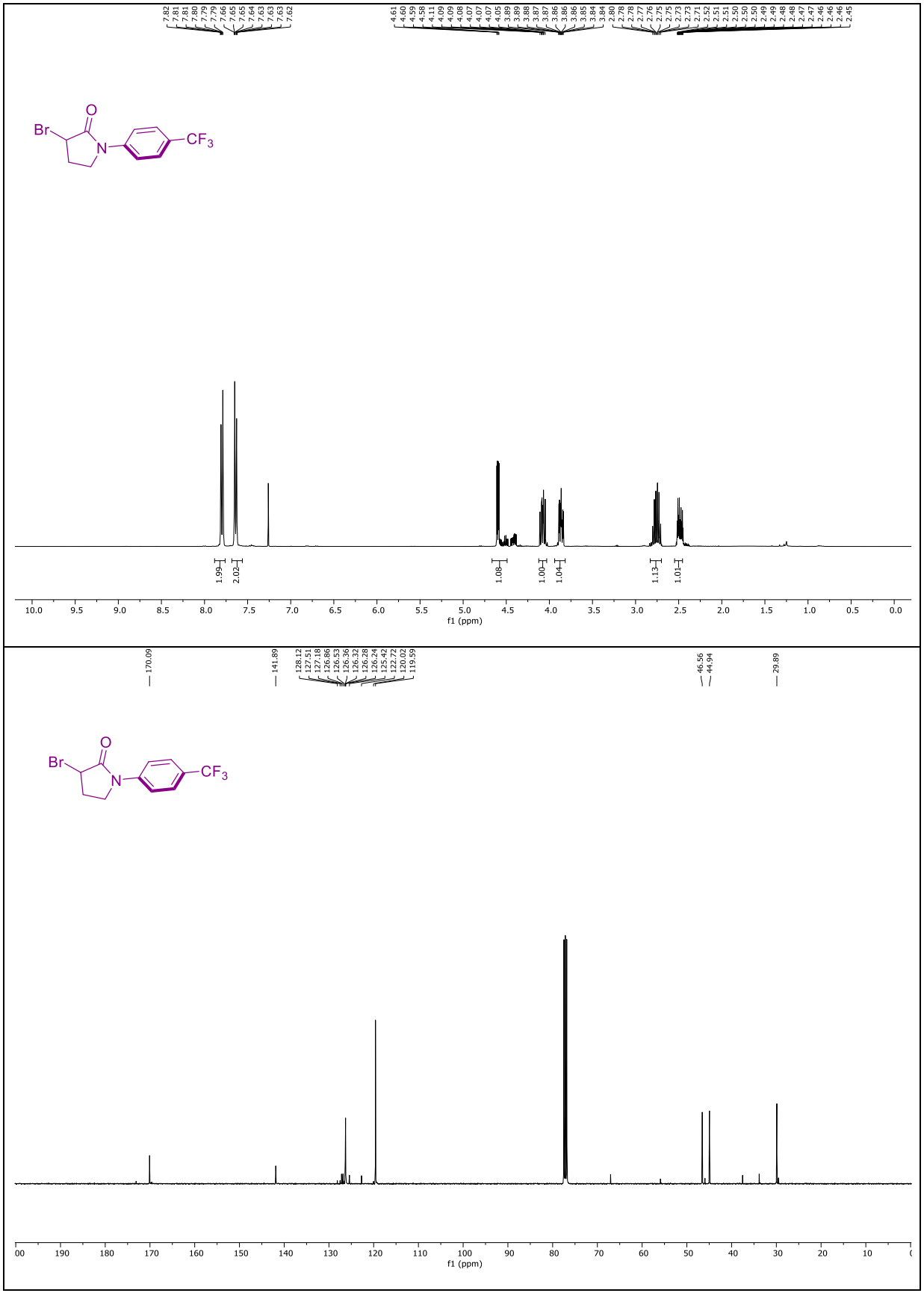


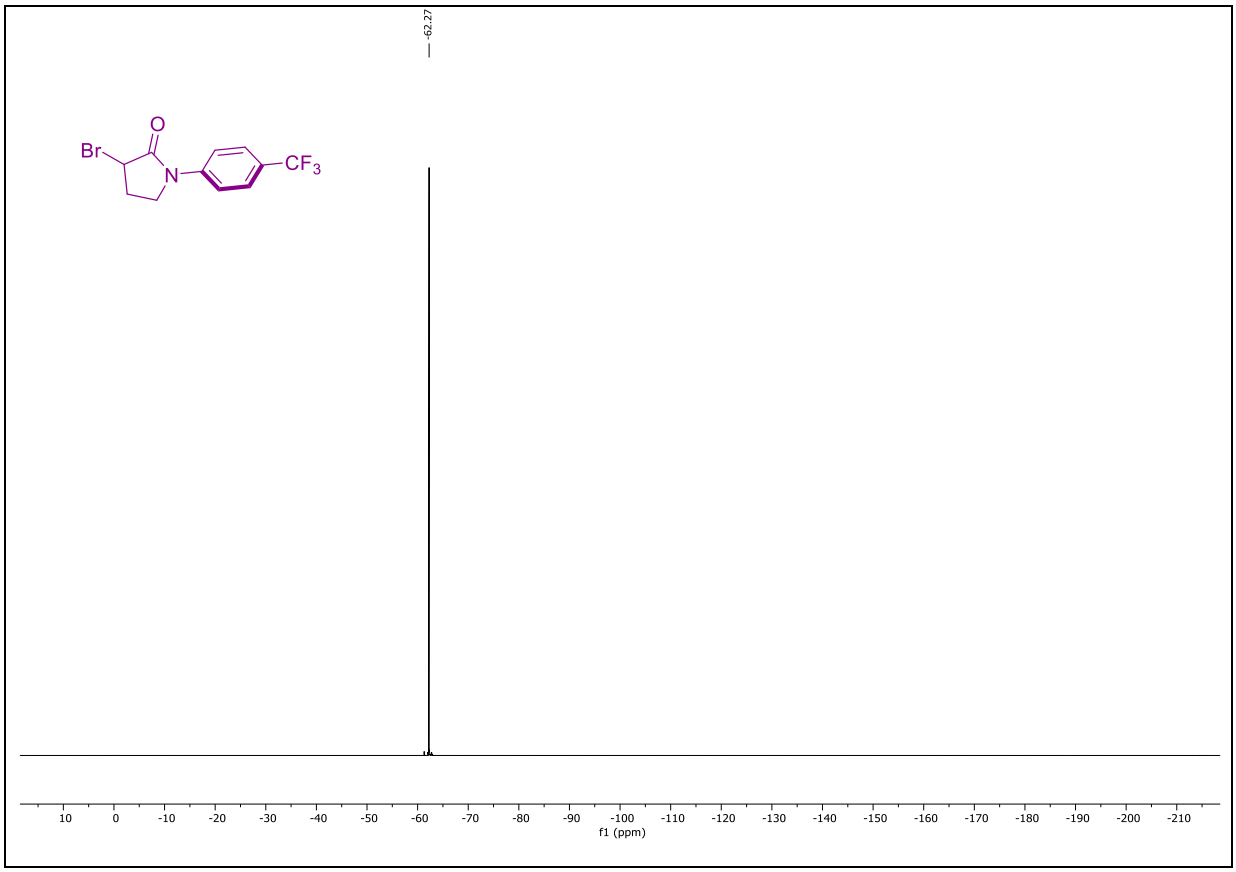
NMR spectra of 2c:



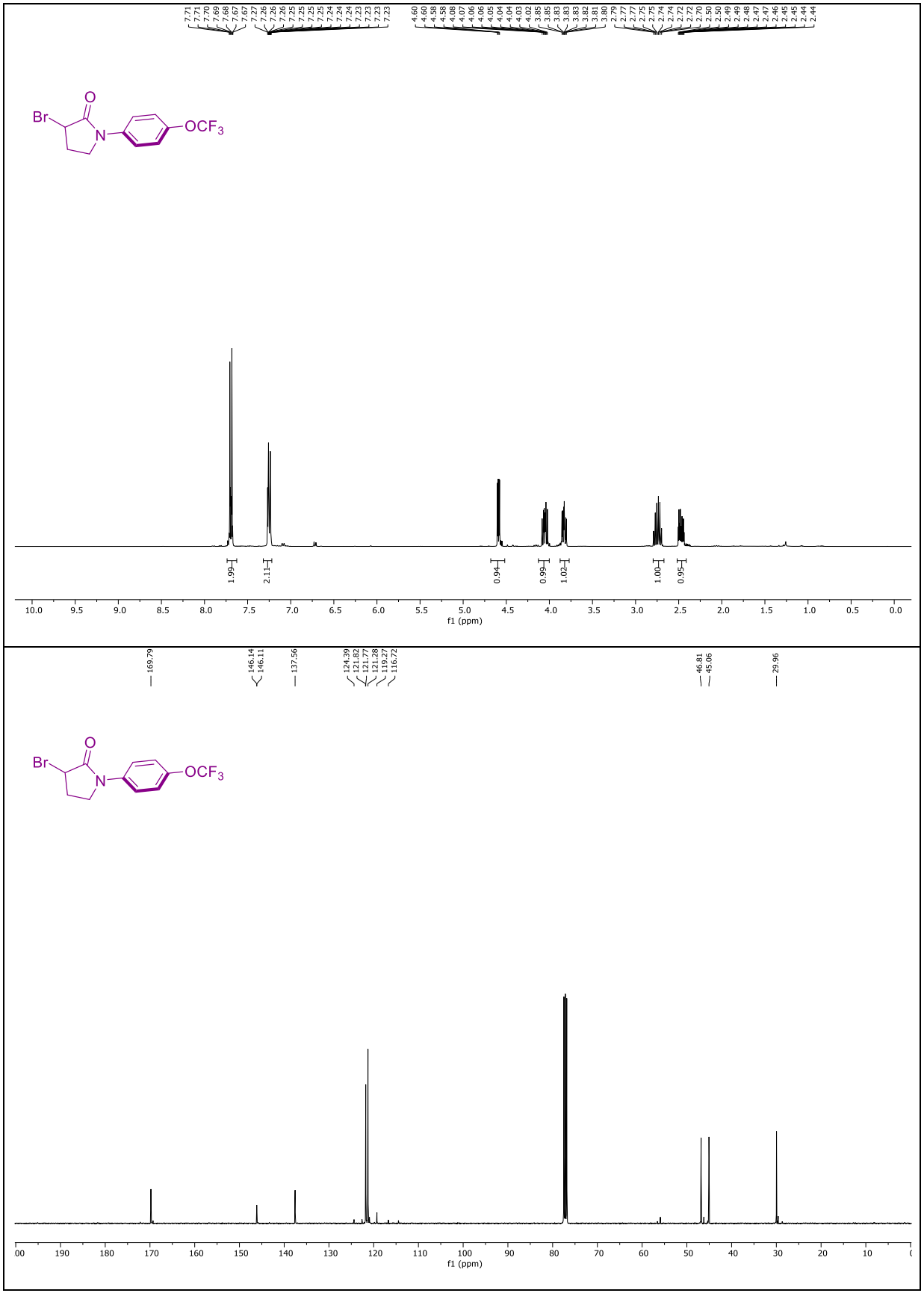

-116.33
O
Br
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

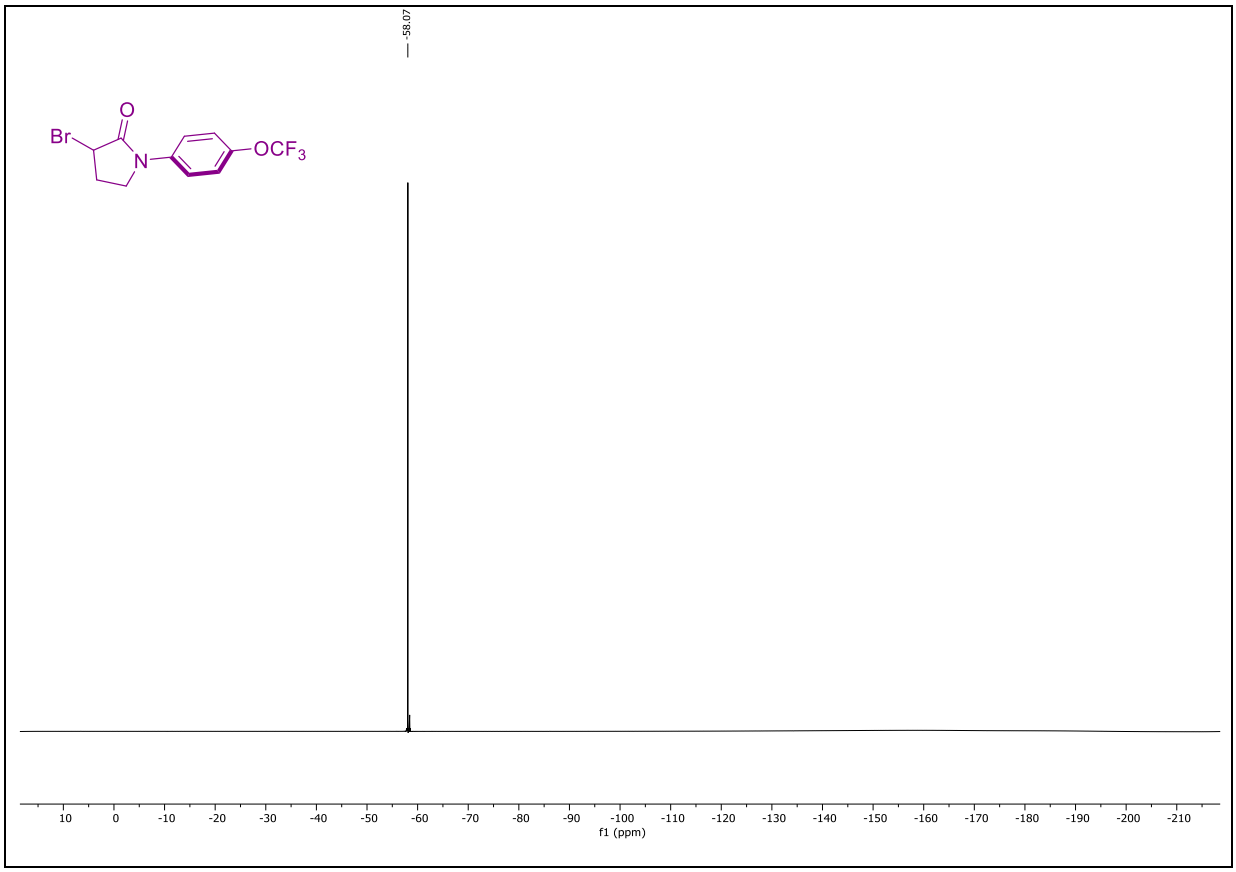
NMR spectra of 2d:



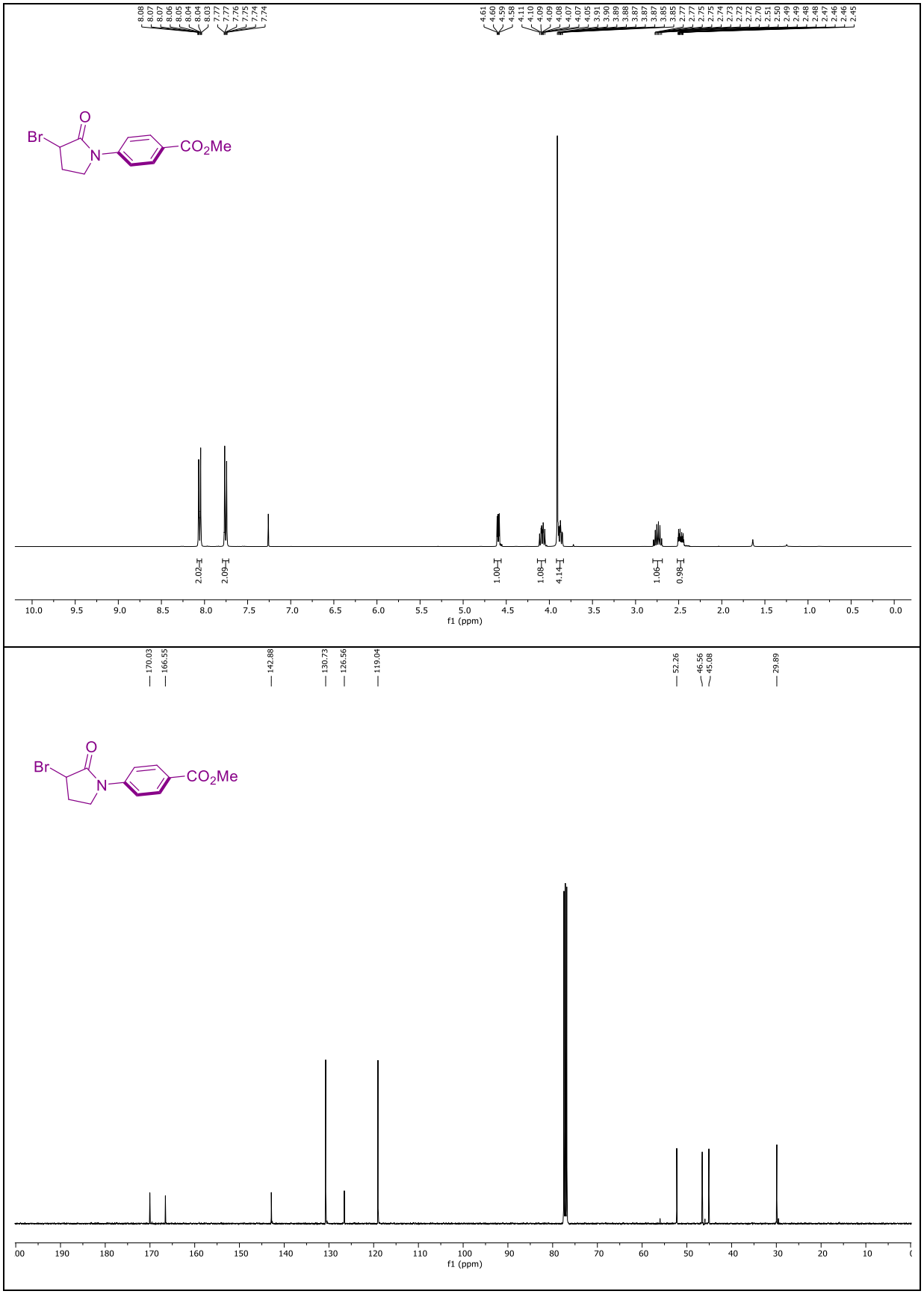

-62.27
Br
O
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

NMR spectra of 2e:

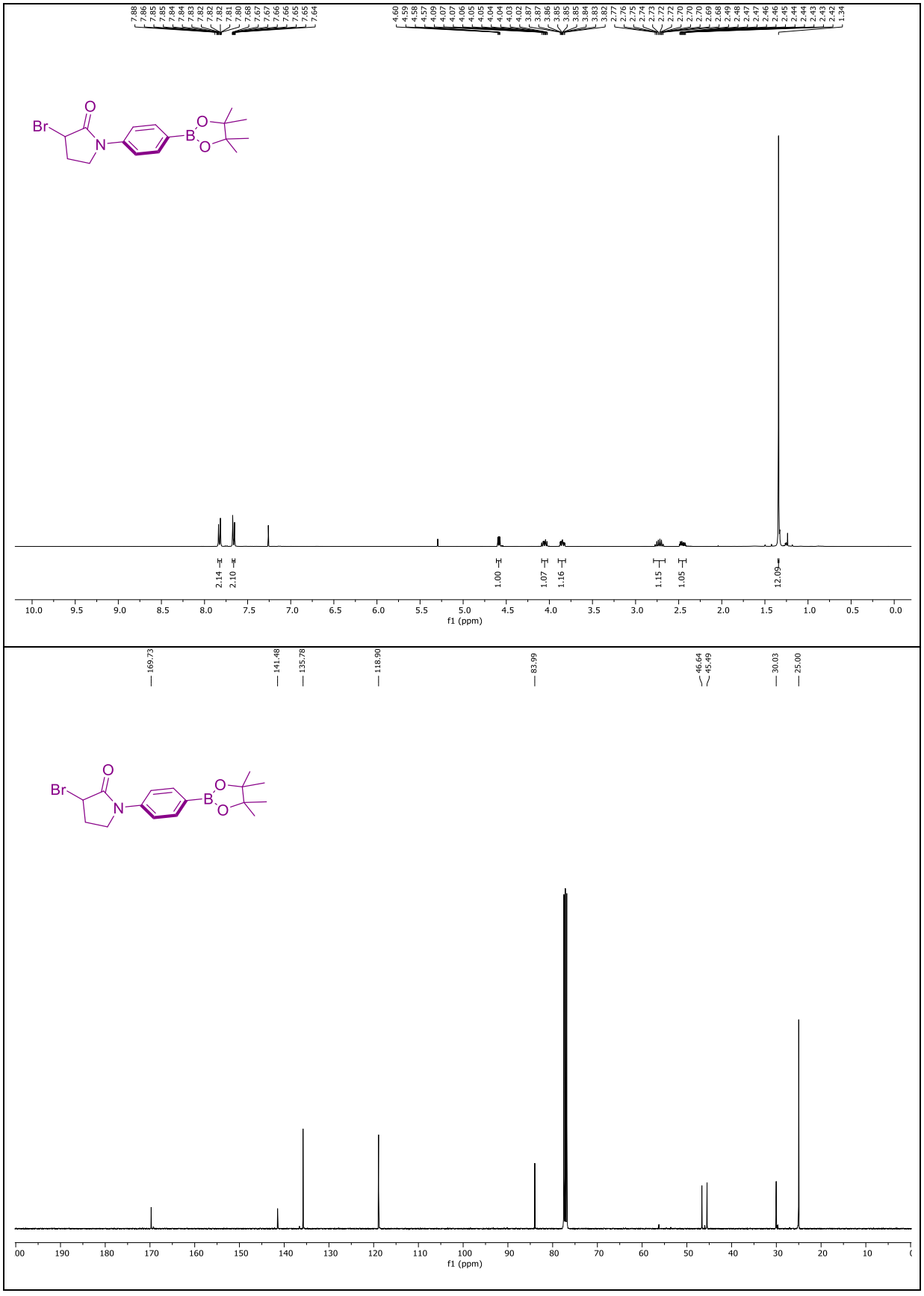


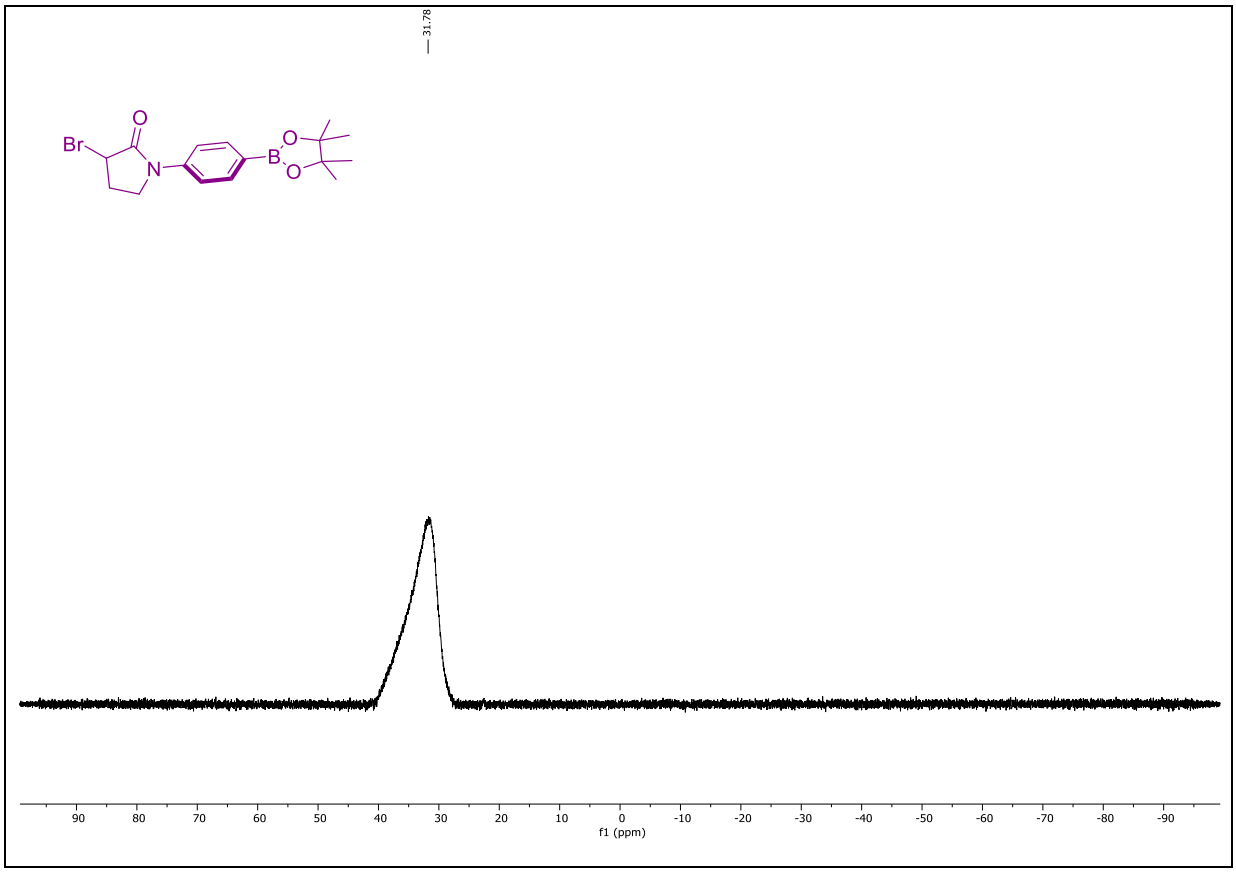

-58.07
O
Br
N
OCF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

NMR spectra of 2e:

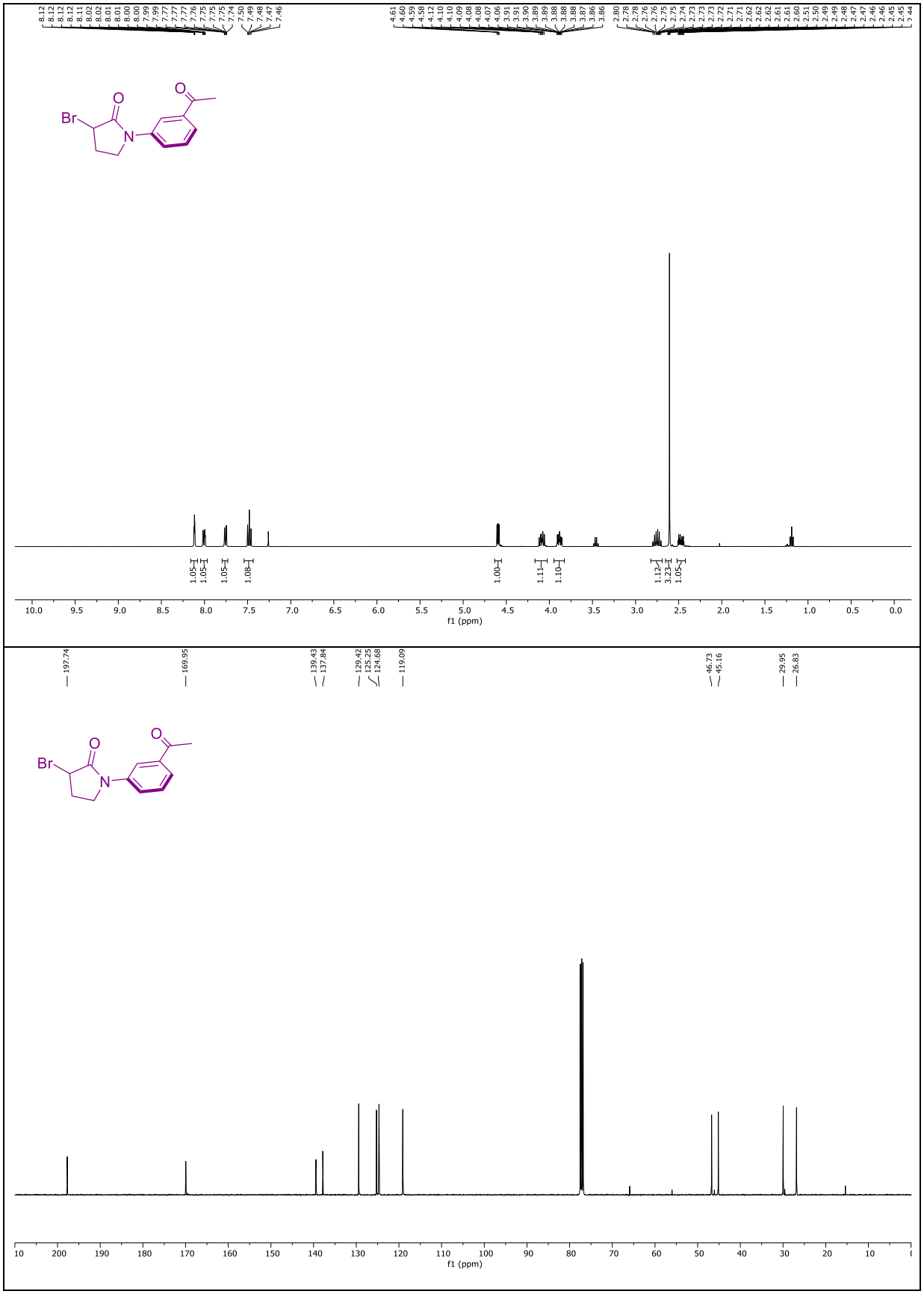


NMR spectra of 2g:

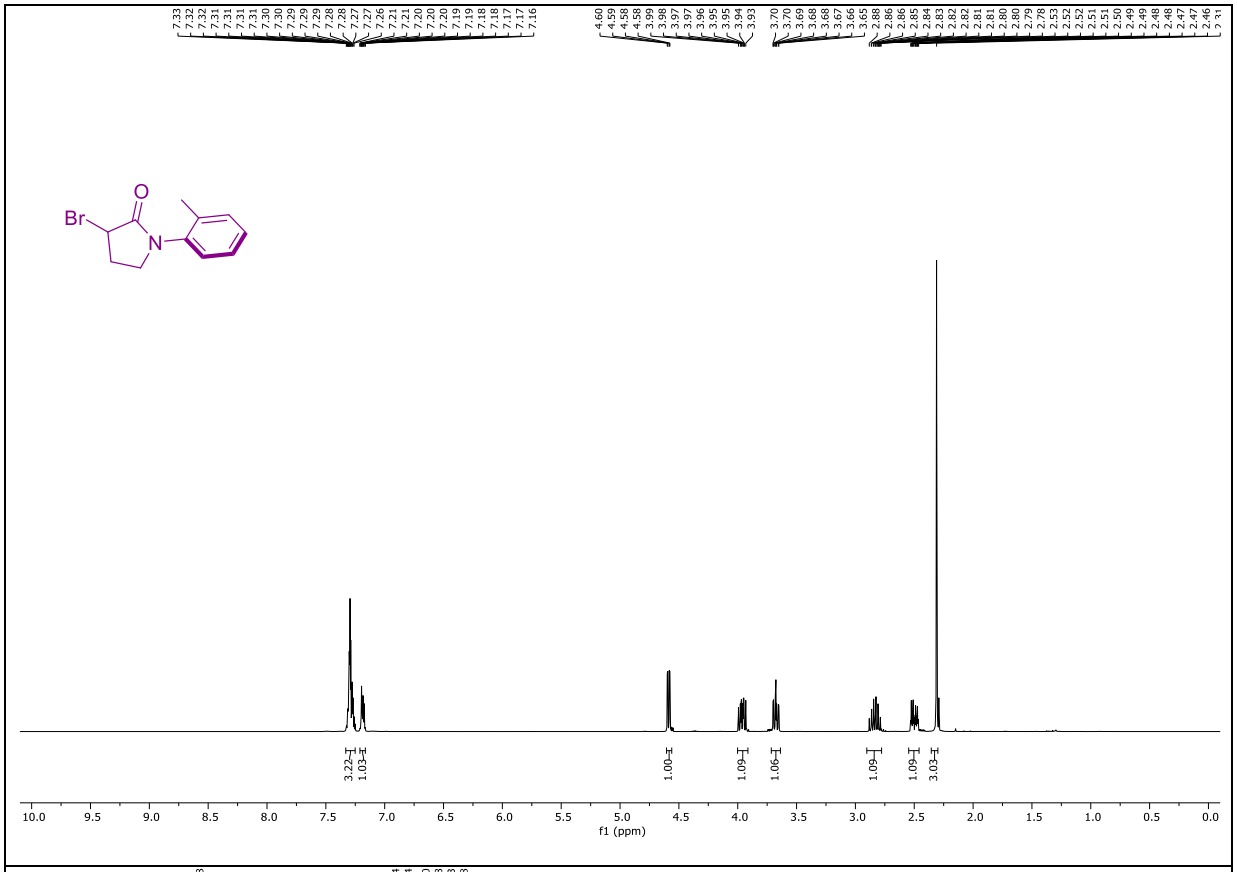


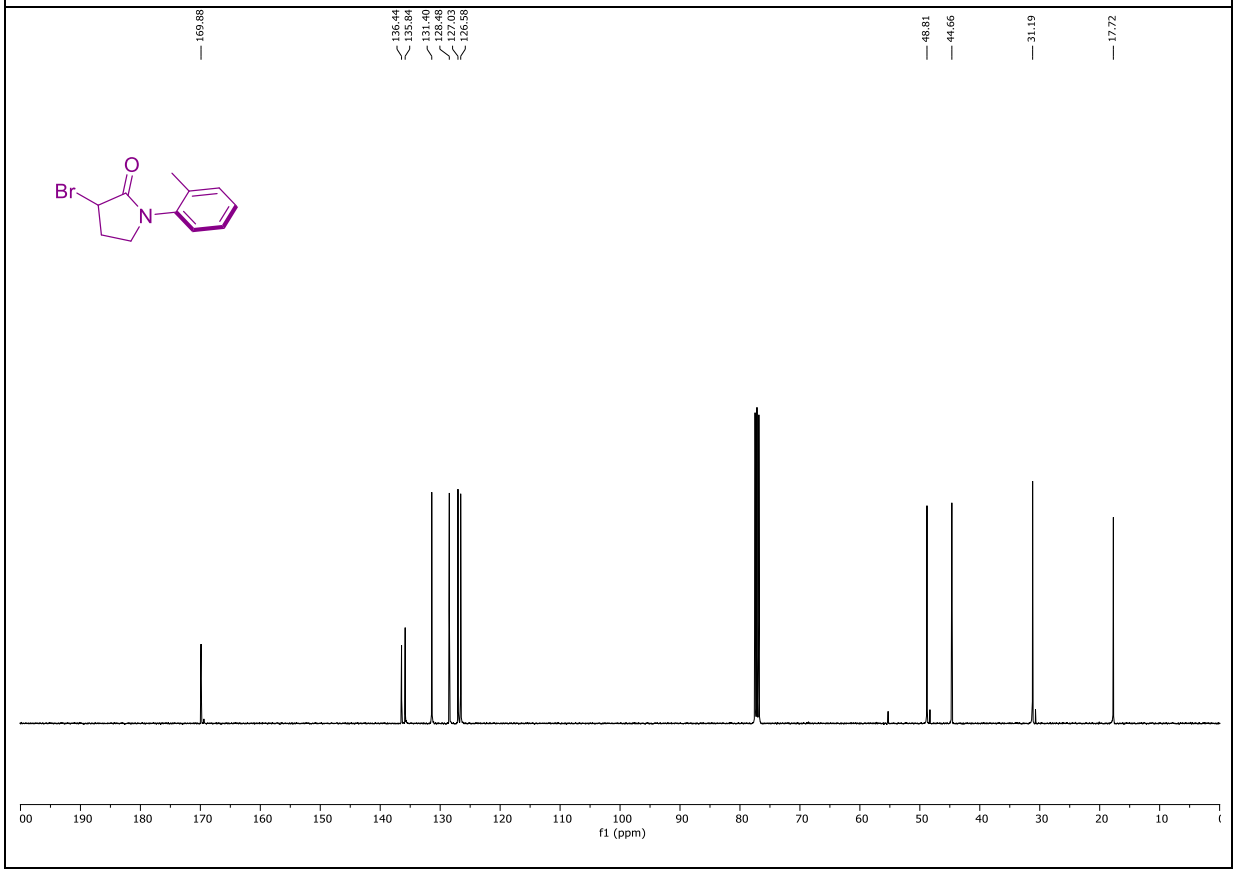

31.78
Br
O
N
B
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 2h:

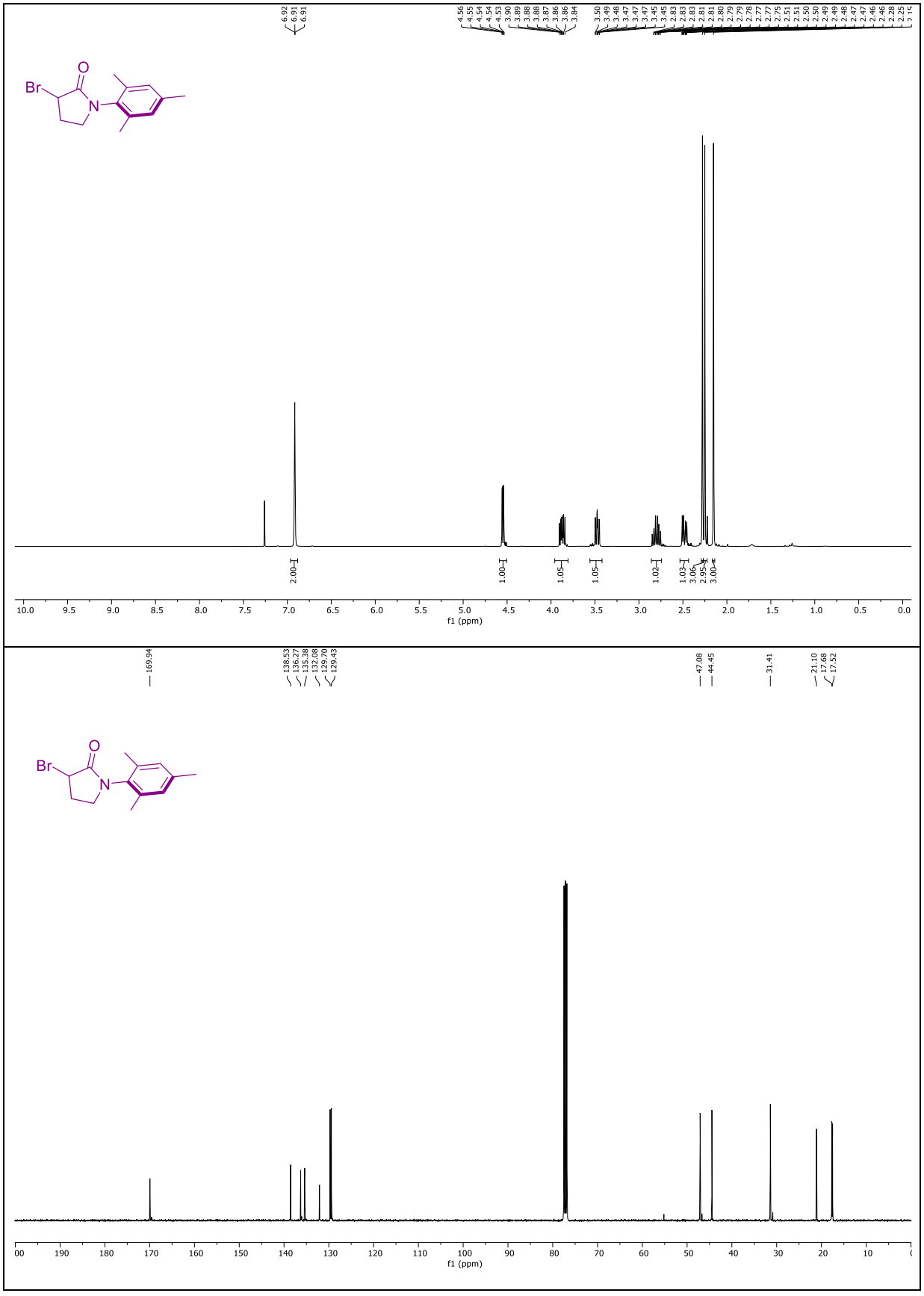


NMR spectra of 2i:

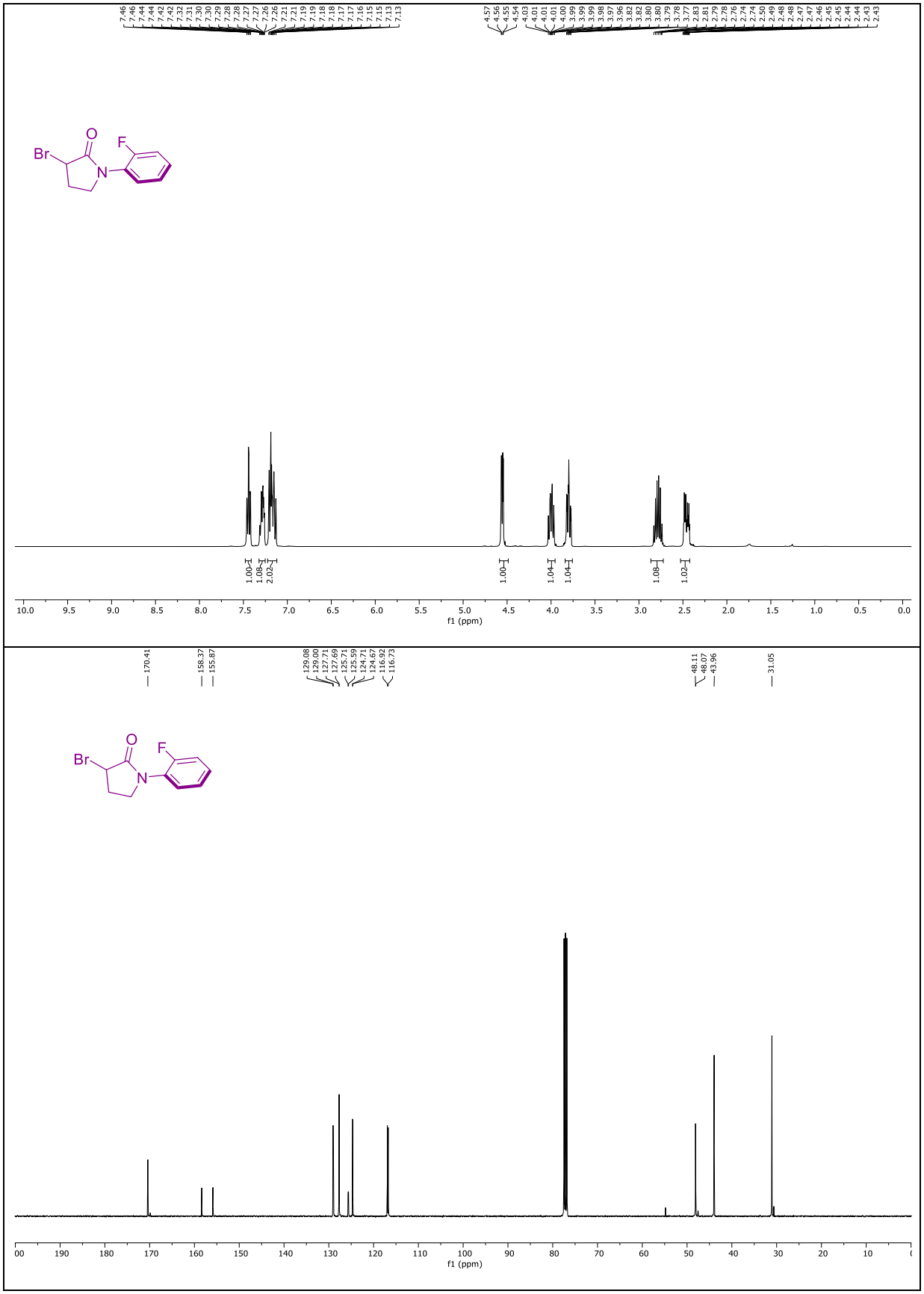


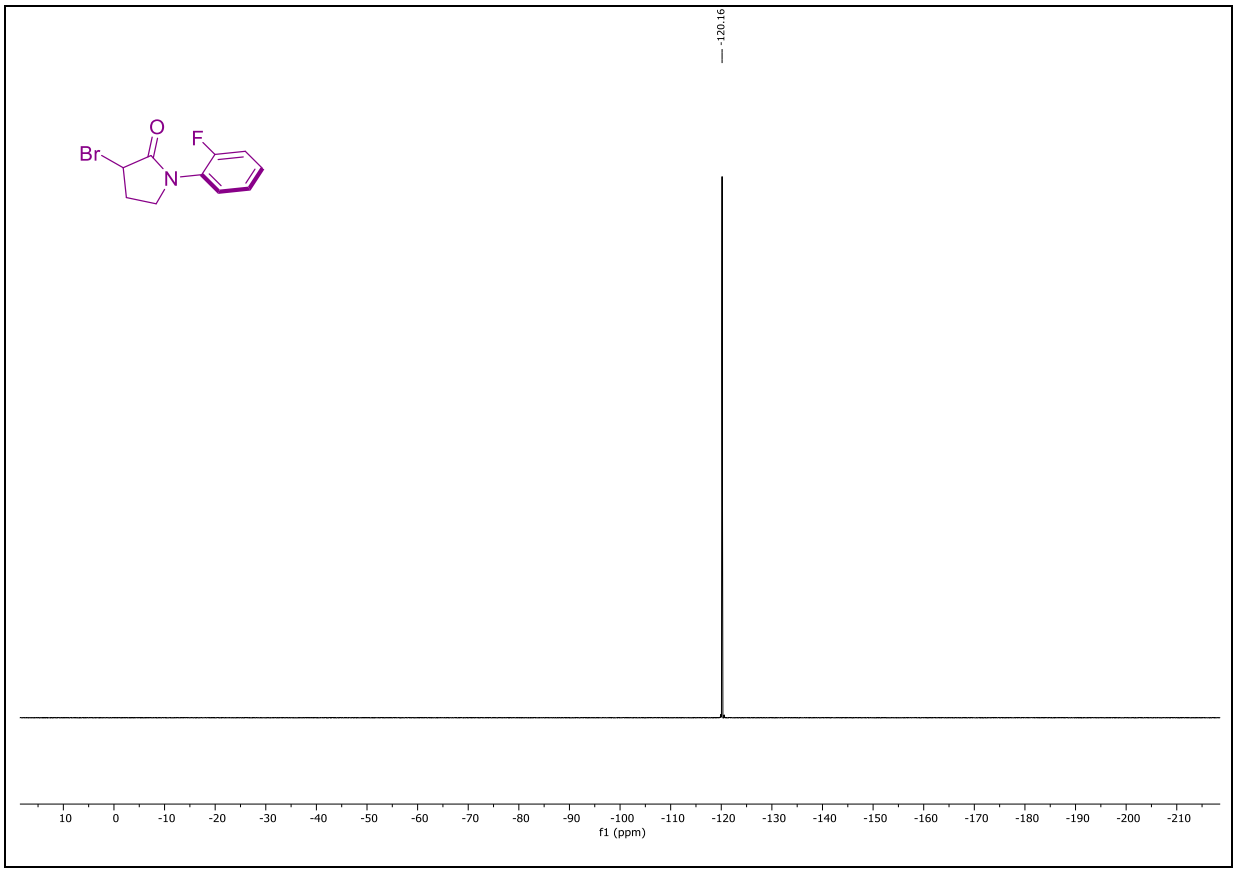


NMR spectra of 2j:

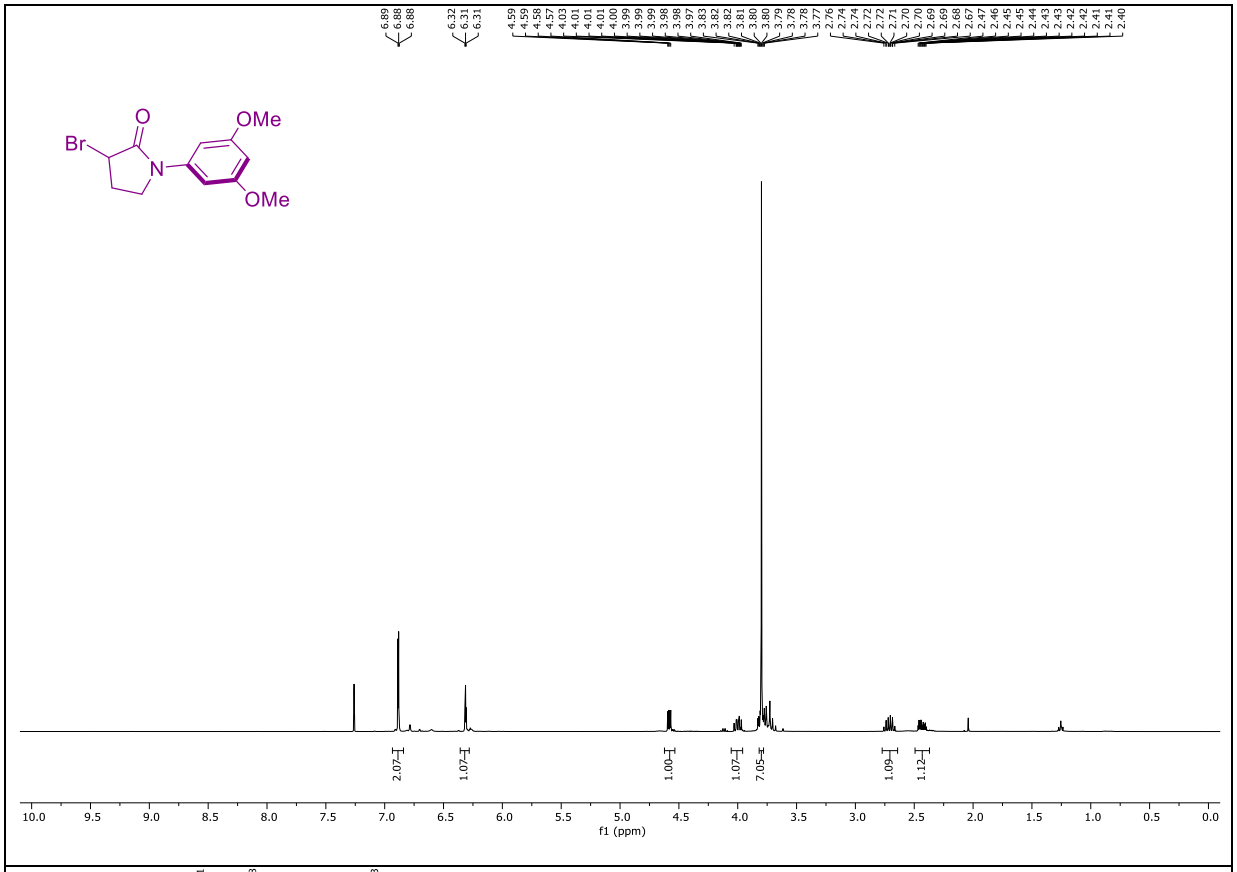


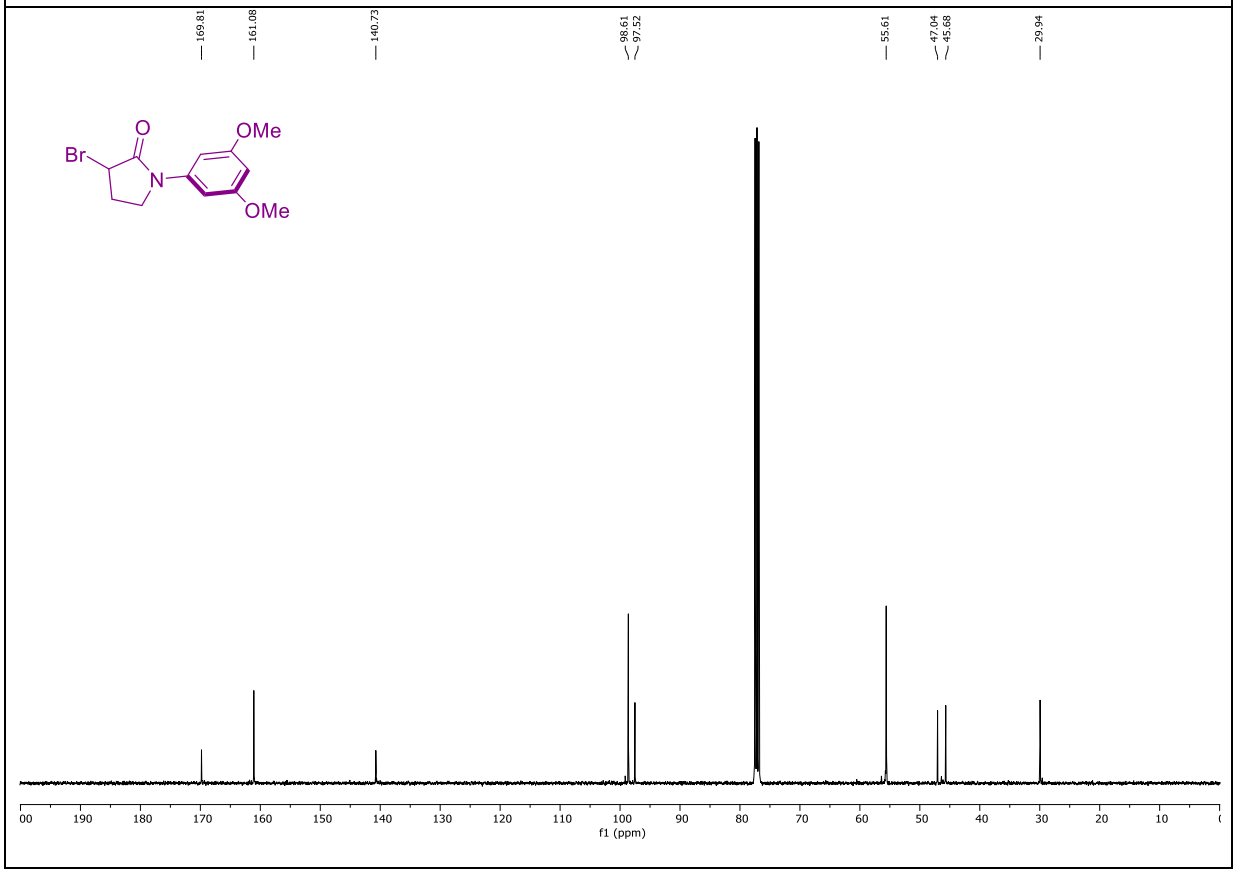
NMR spectra of 2k:



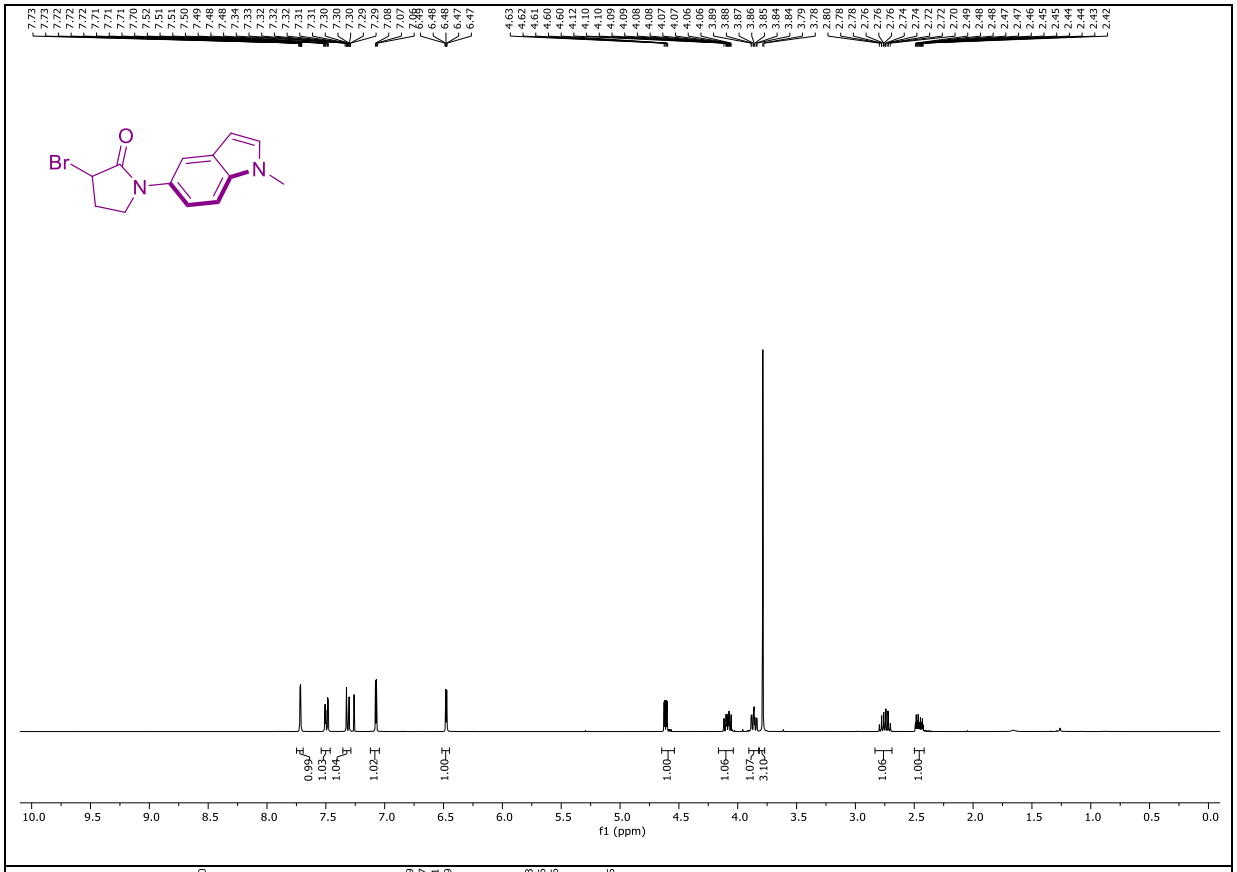

-120.16
O
Br
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

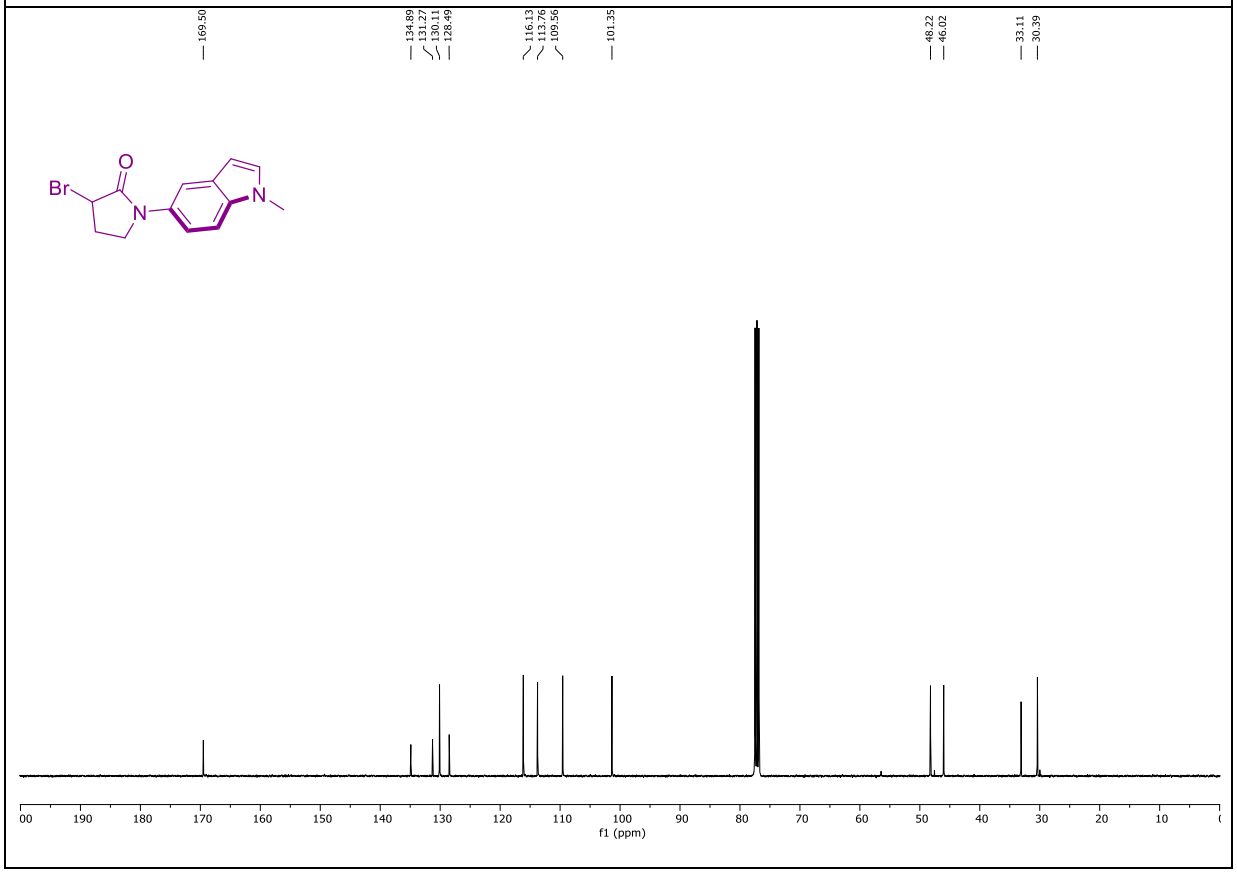
NMR spectra of 2l:



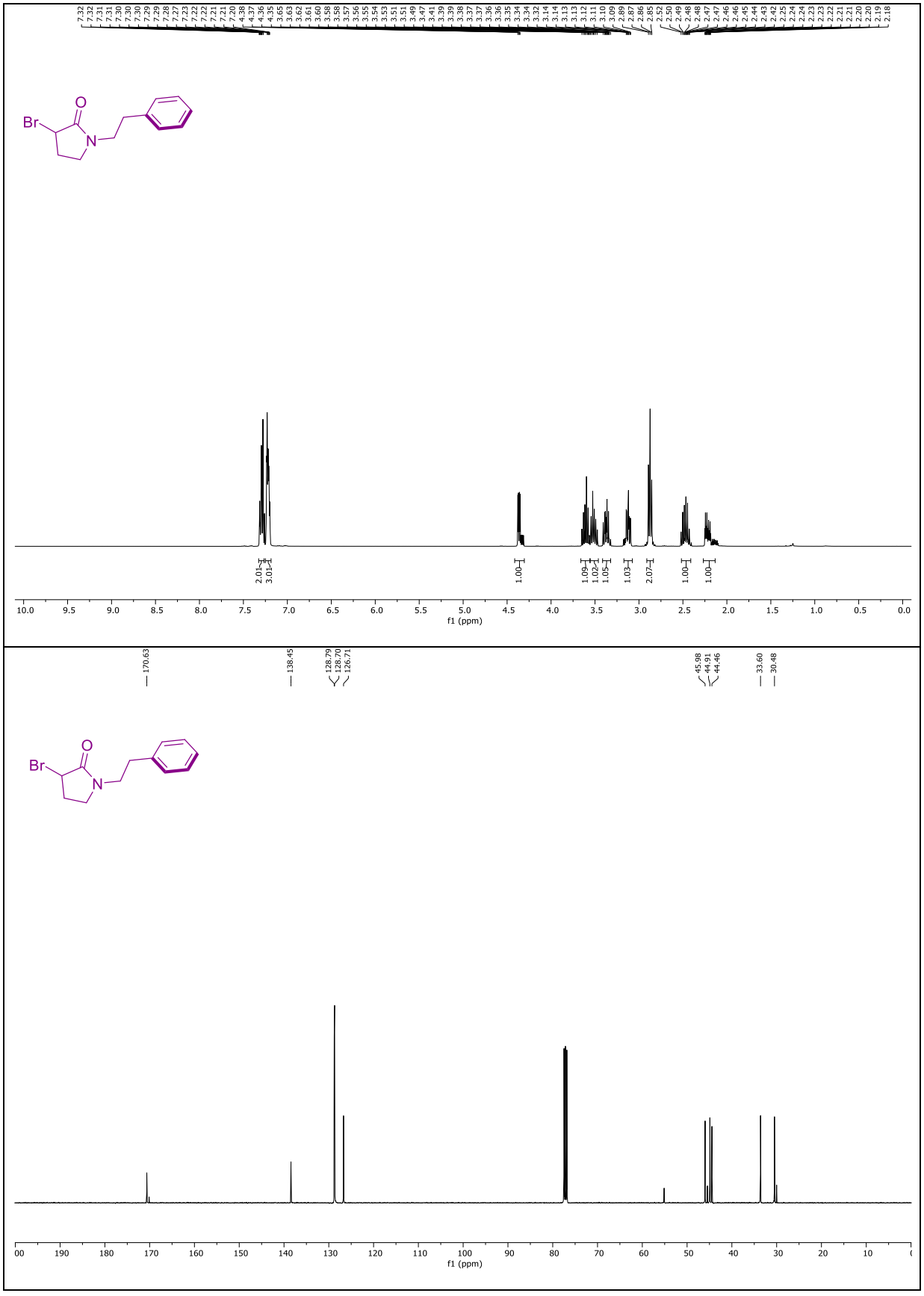


NMR spectra of 2m:

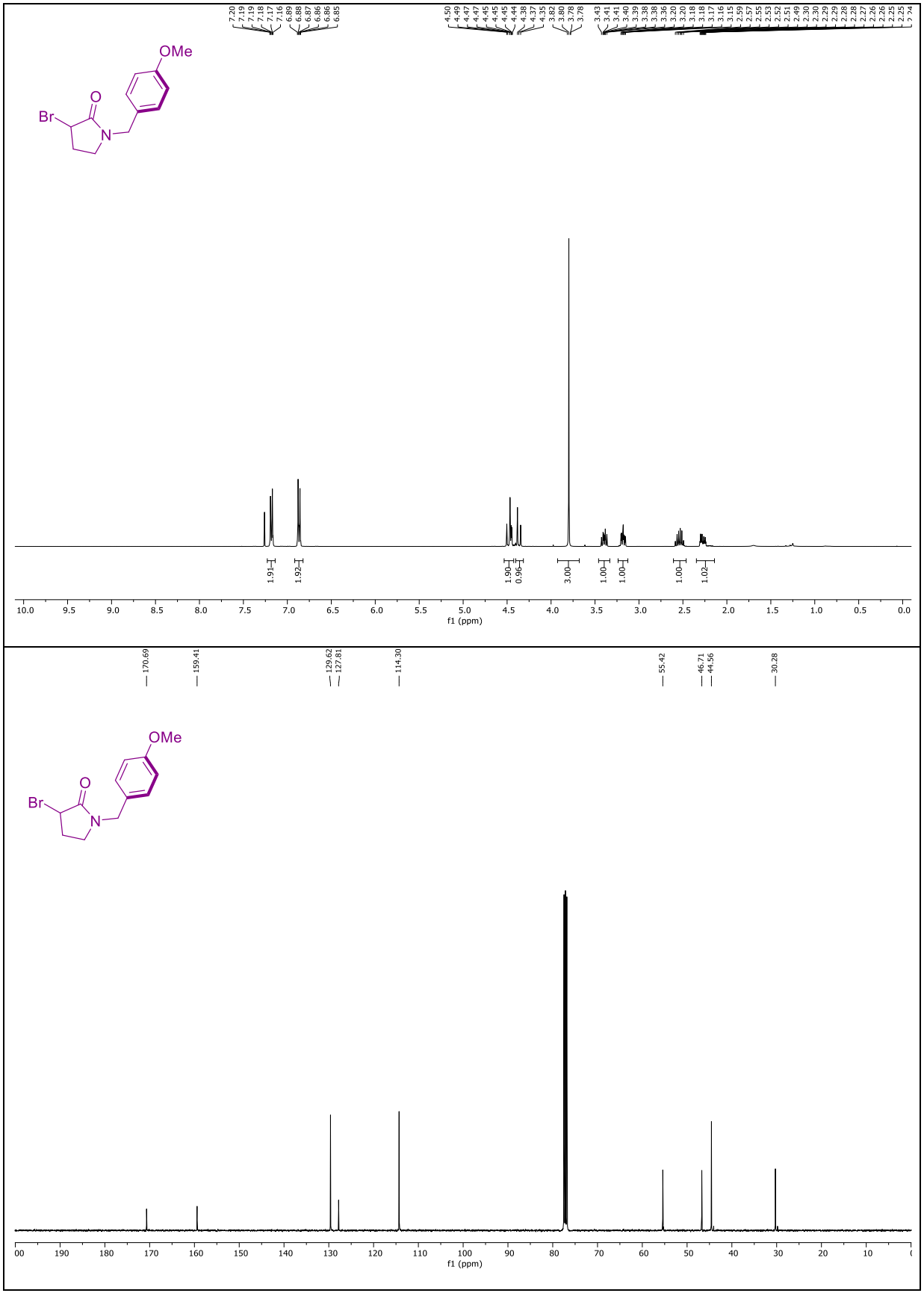




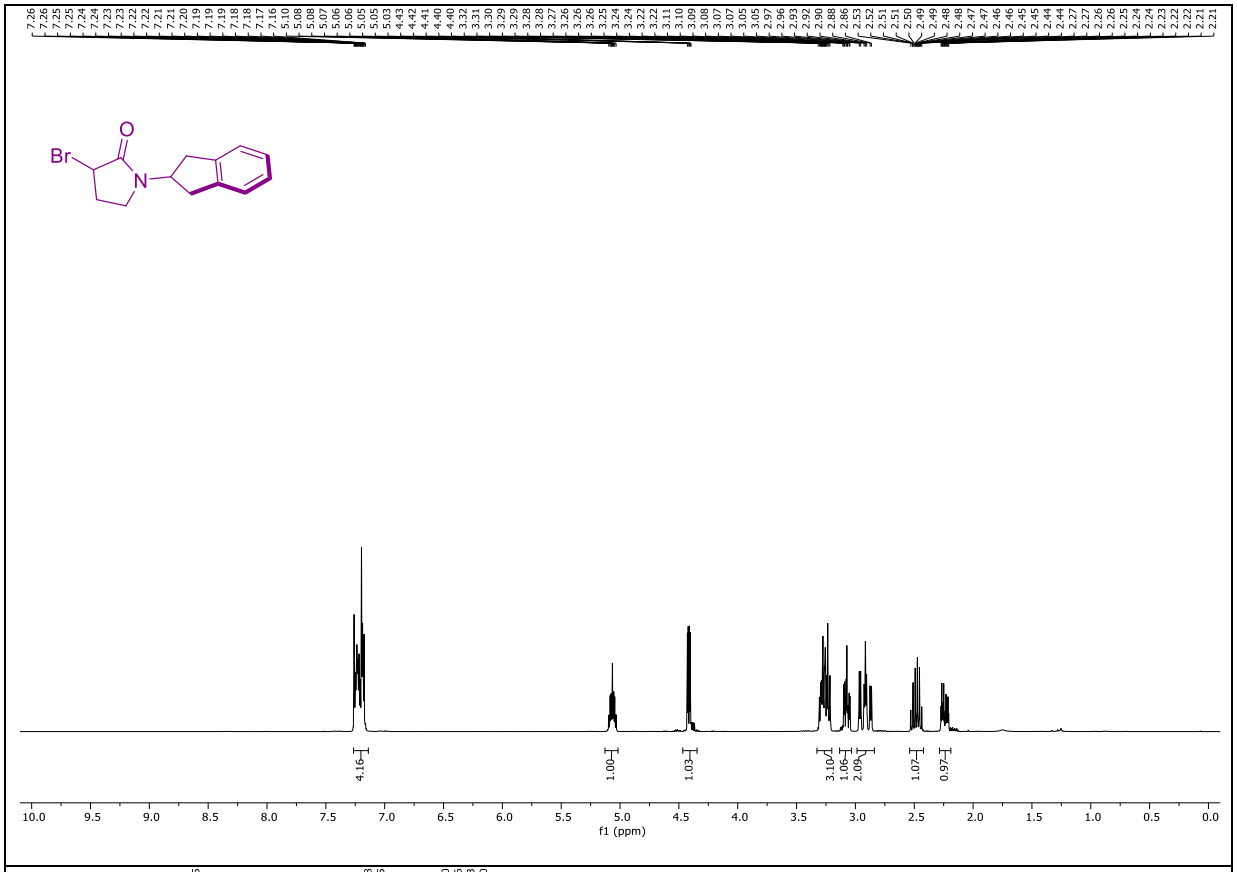
NMR spectra of 2n:

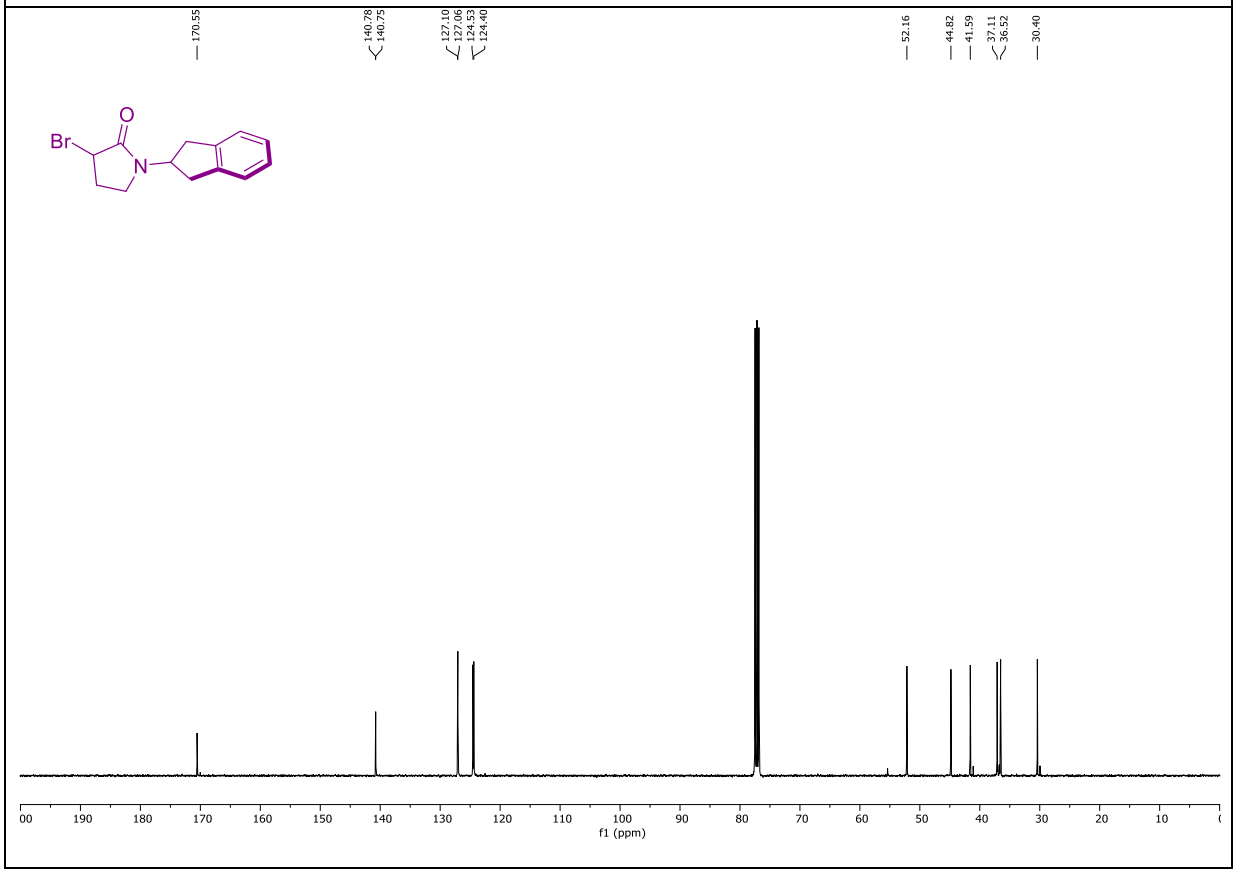


NMR spectra of 2o:

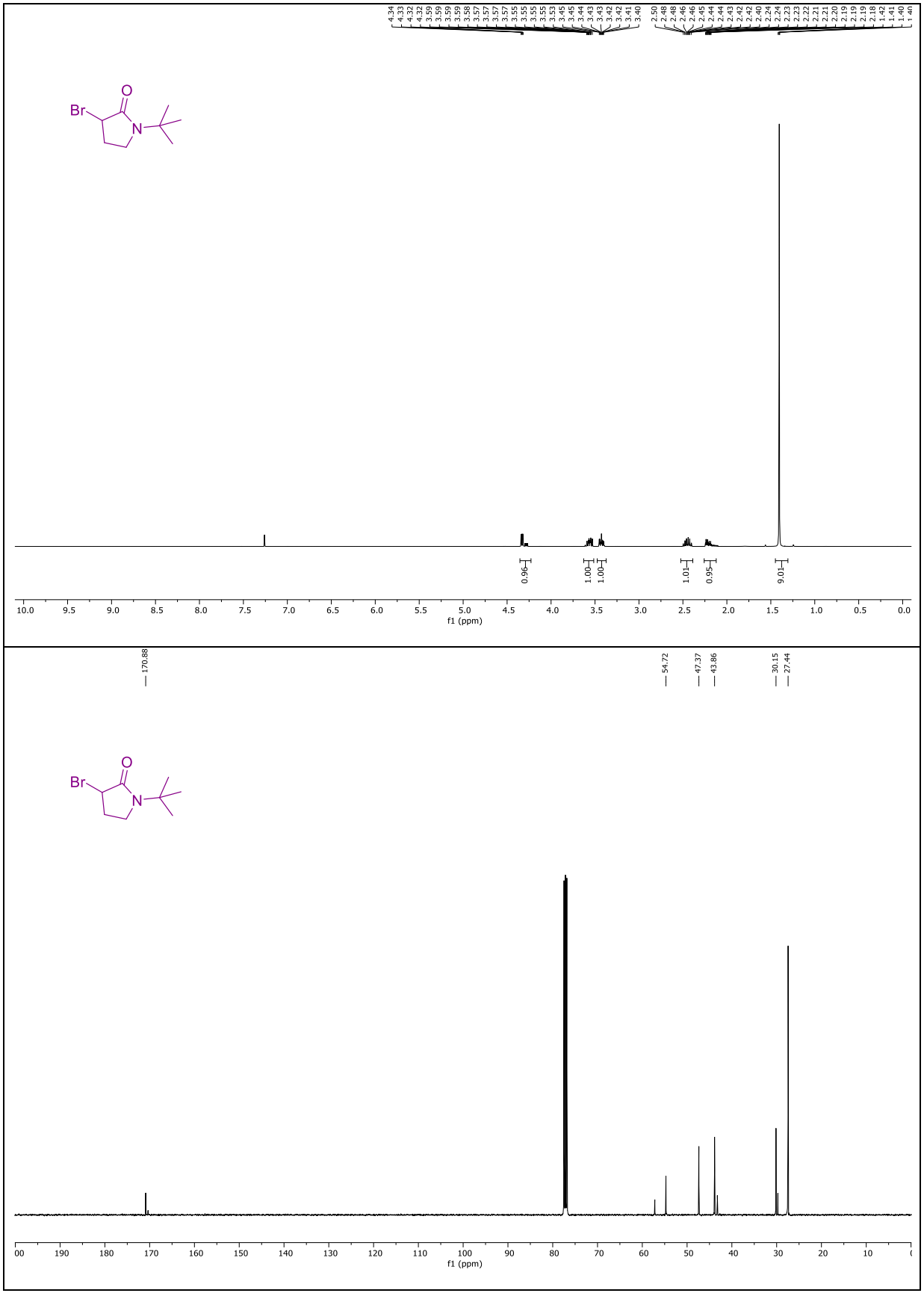


NMR spectra of 2p:

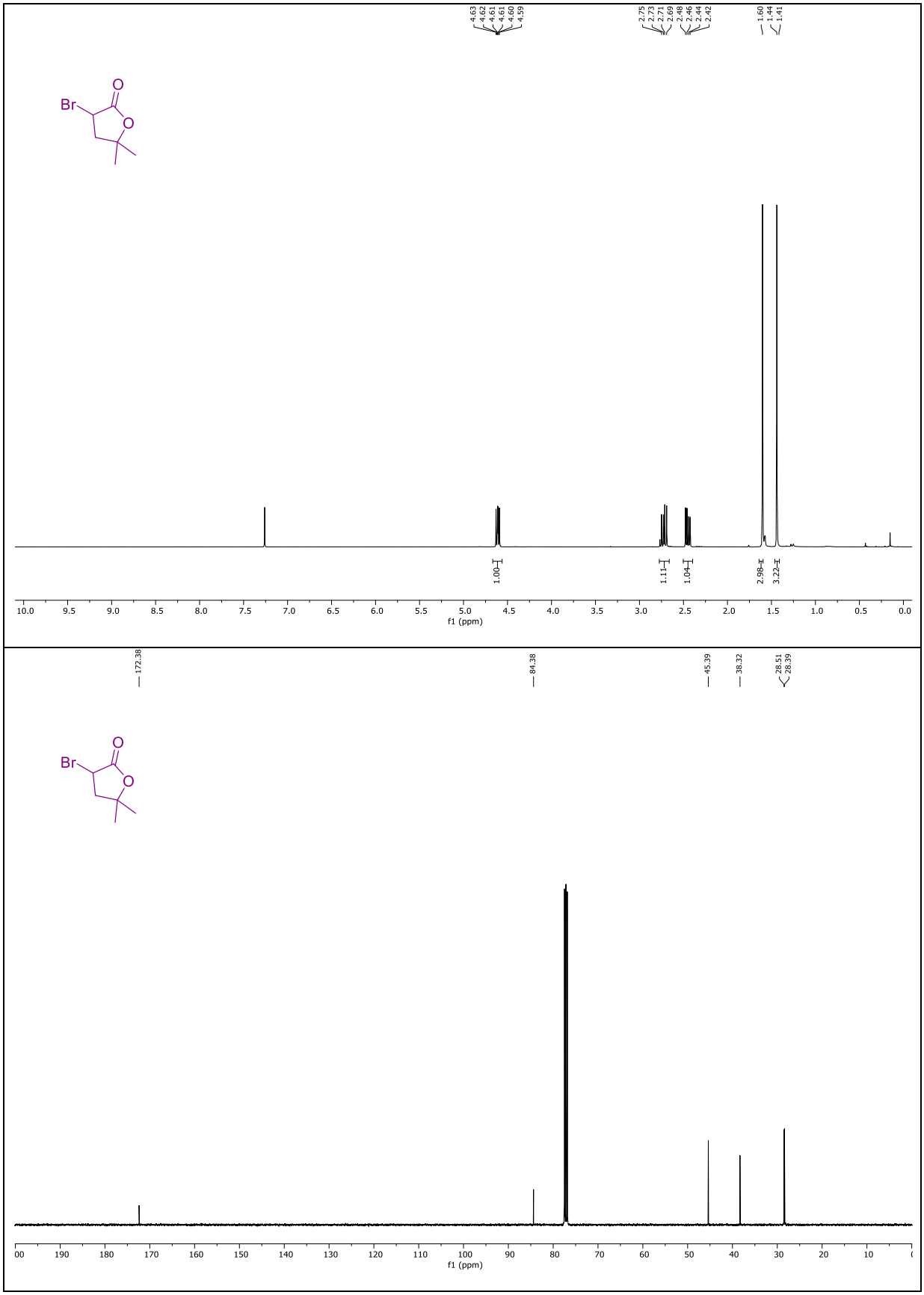




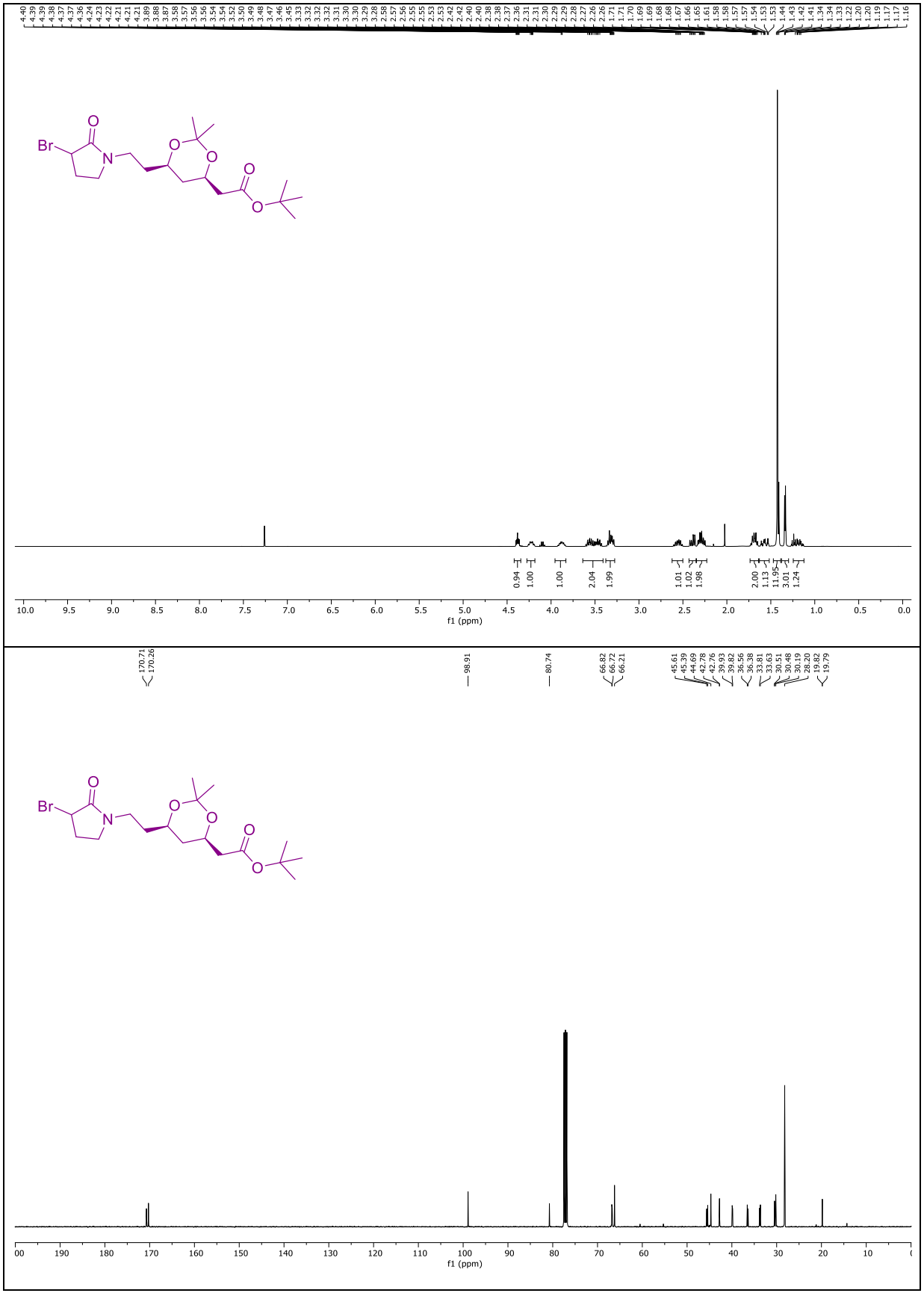
NMR spectra of 2q:



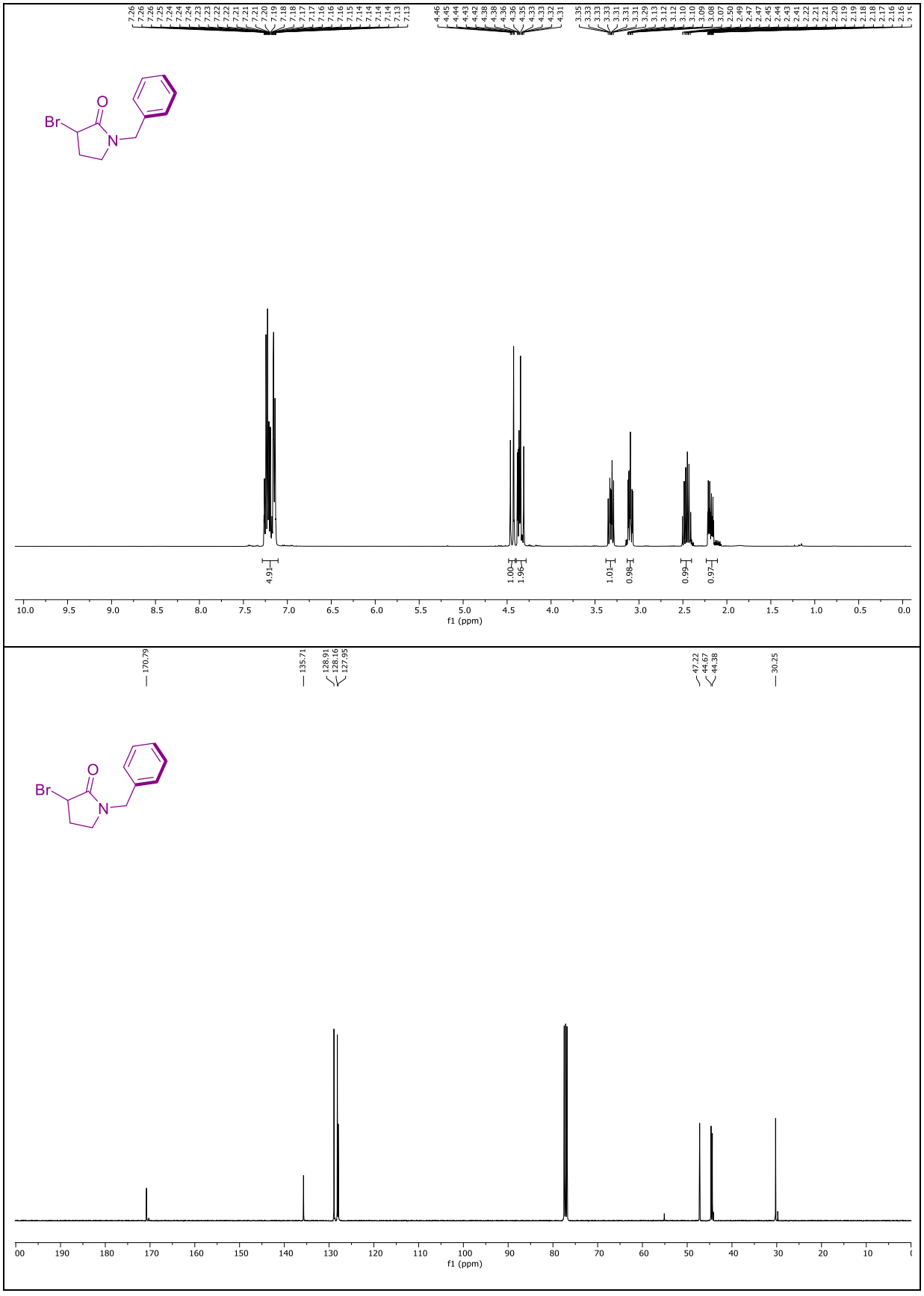
NMR spectra of 2s:



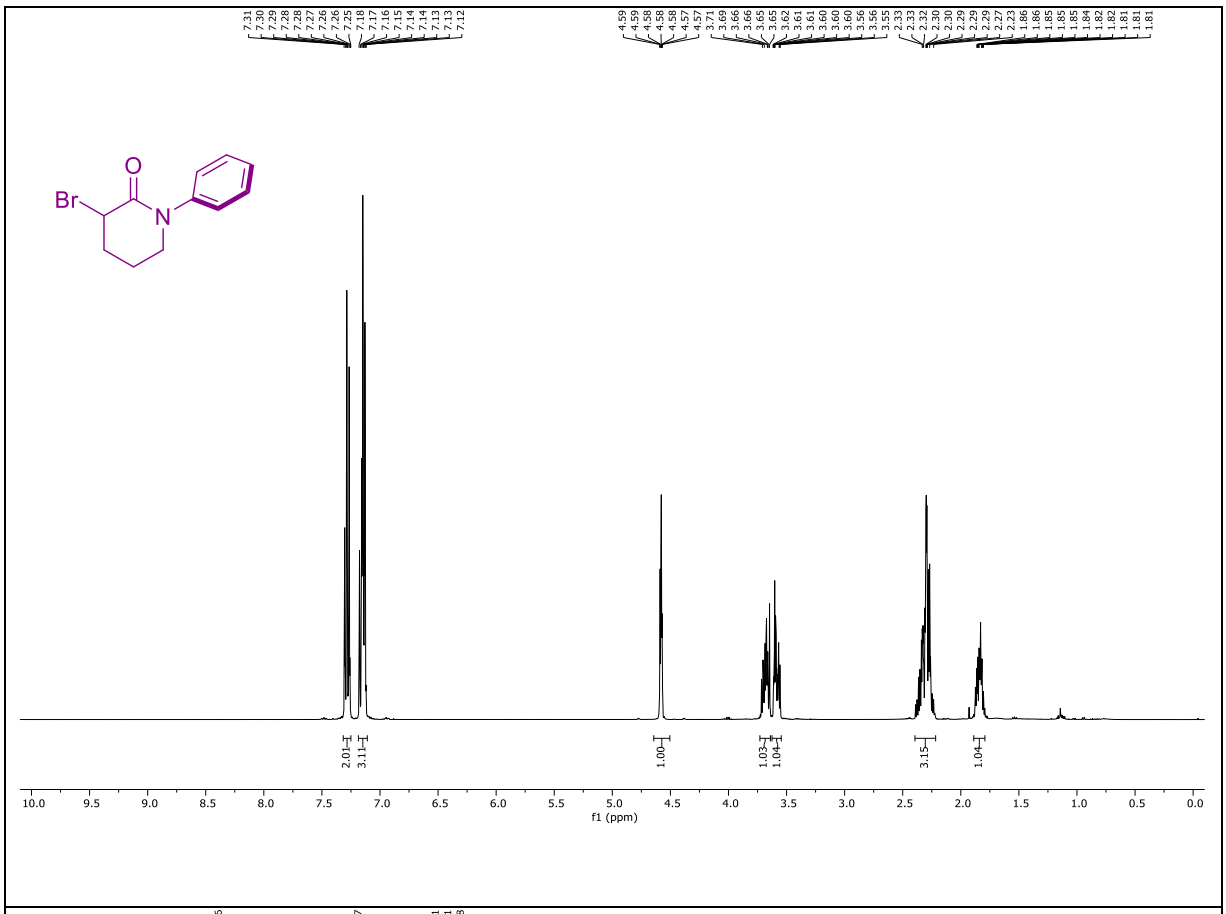
NMR spectra of 2u:

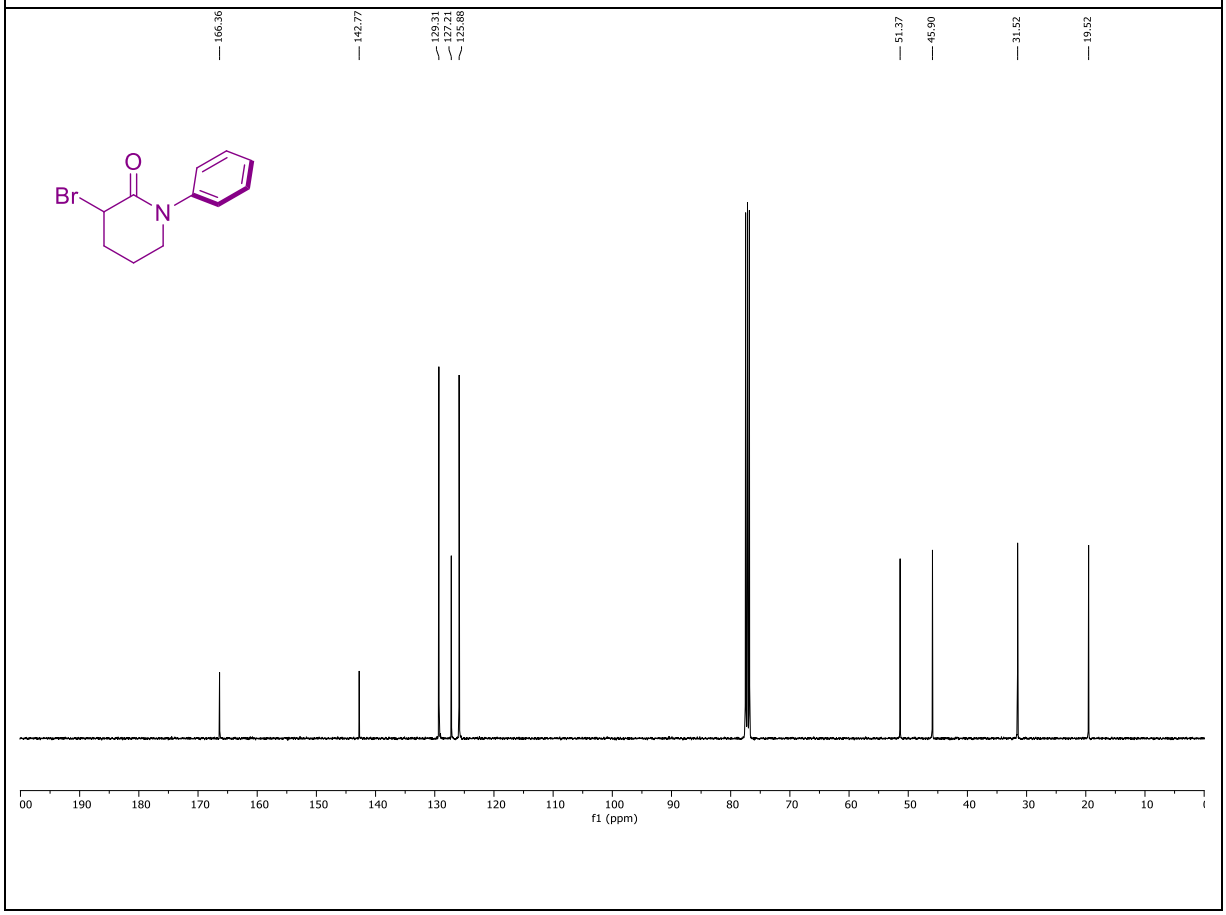


NMR spectra of 2v:

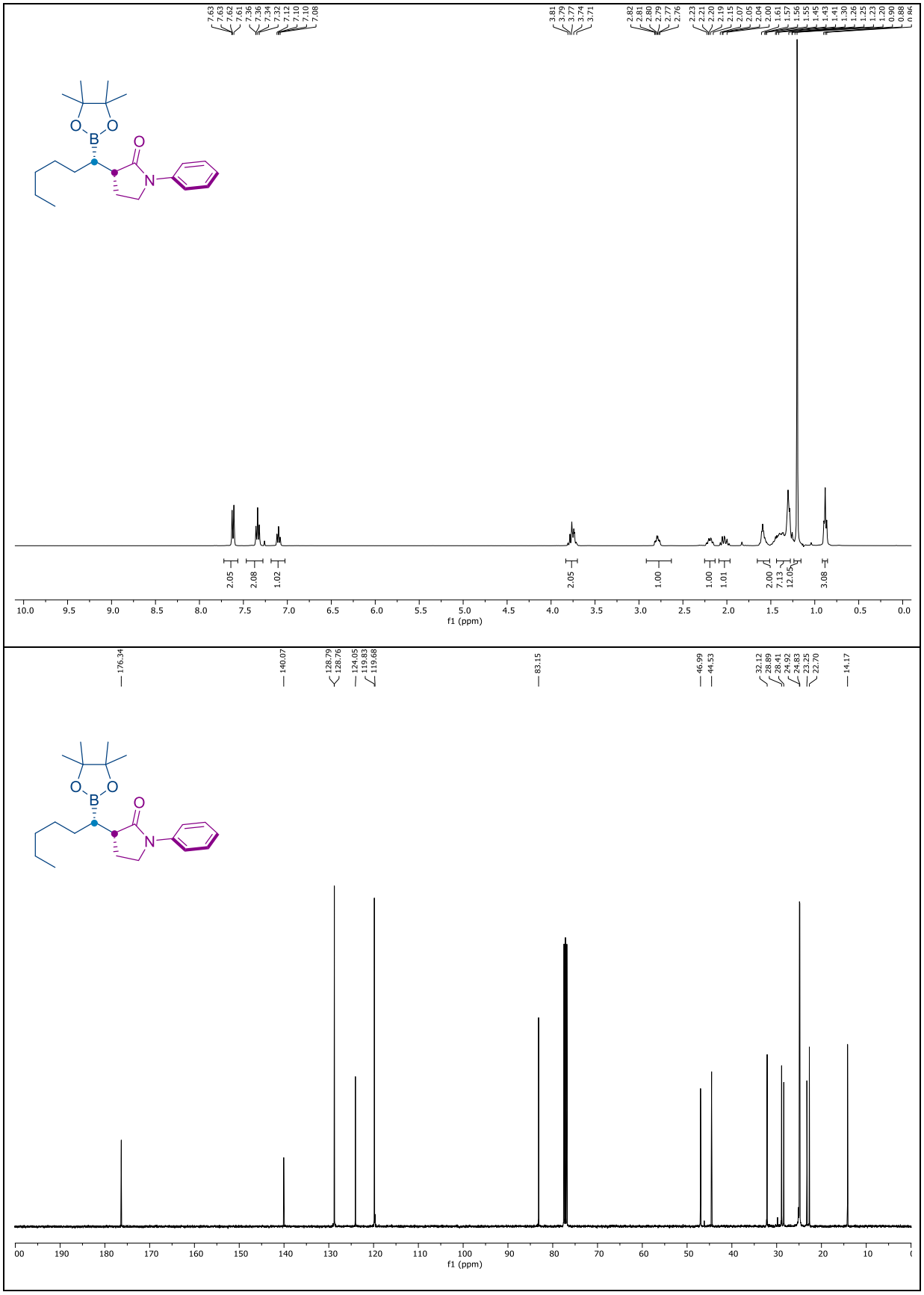


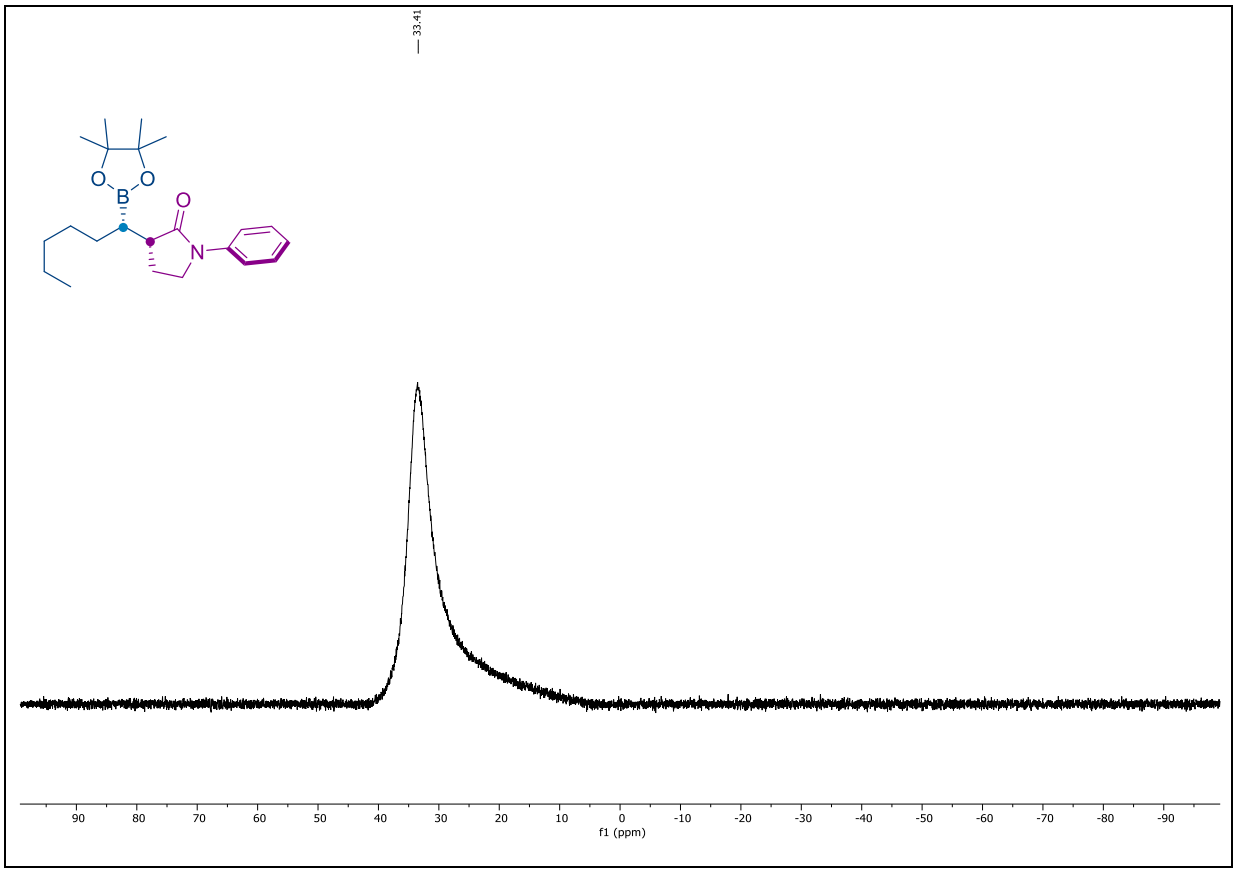
NMR spectra of 2w:



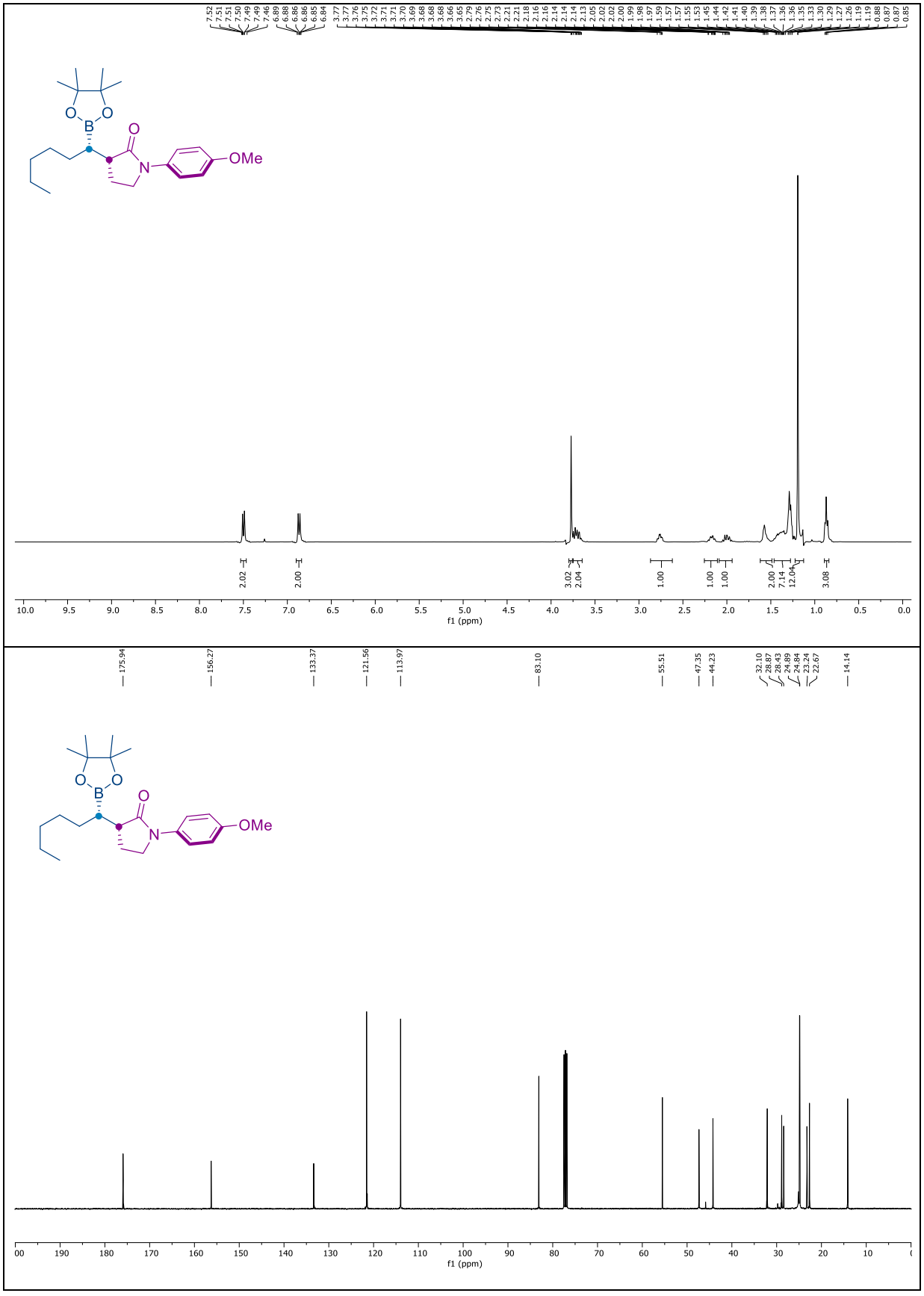


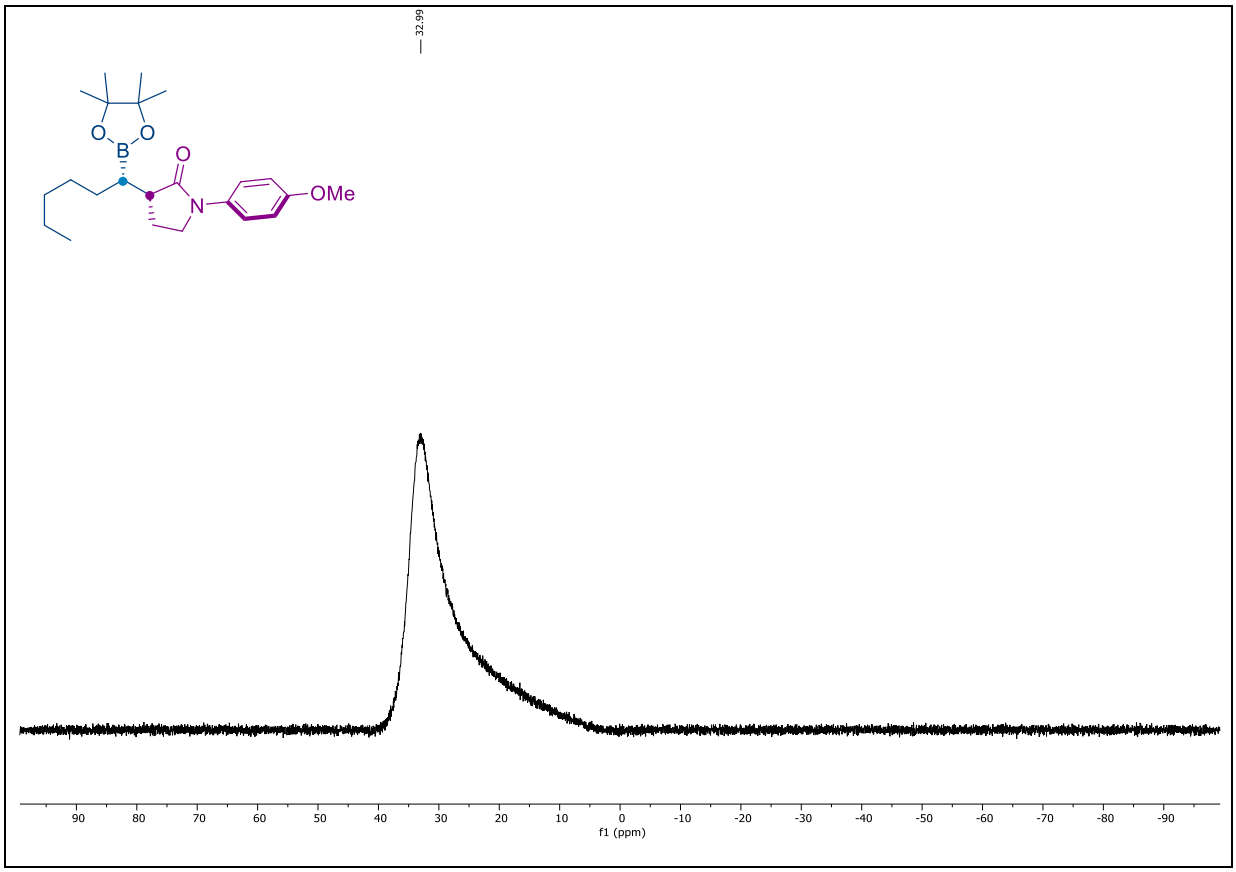
NMR spectra of 3aa:



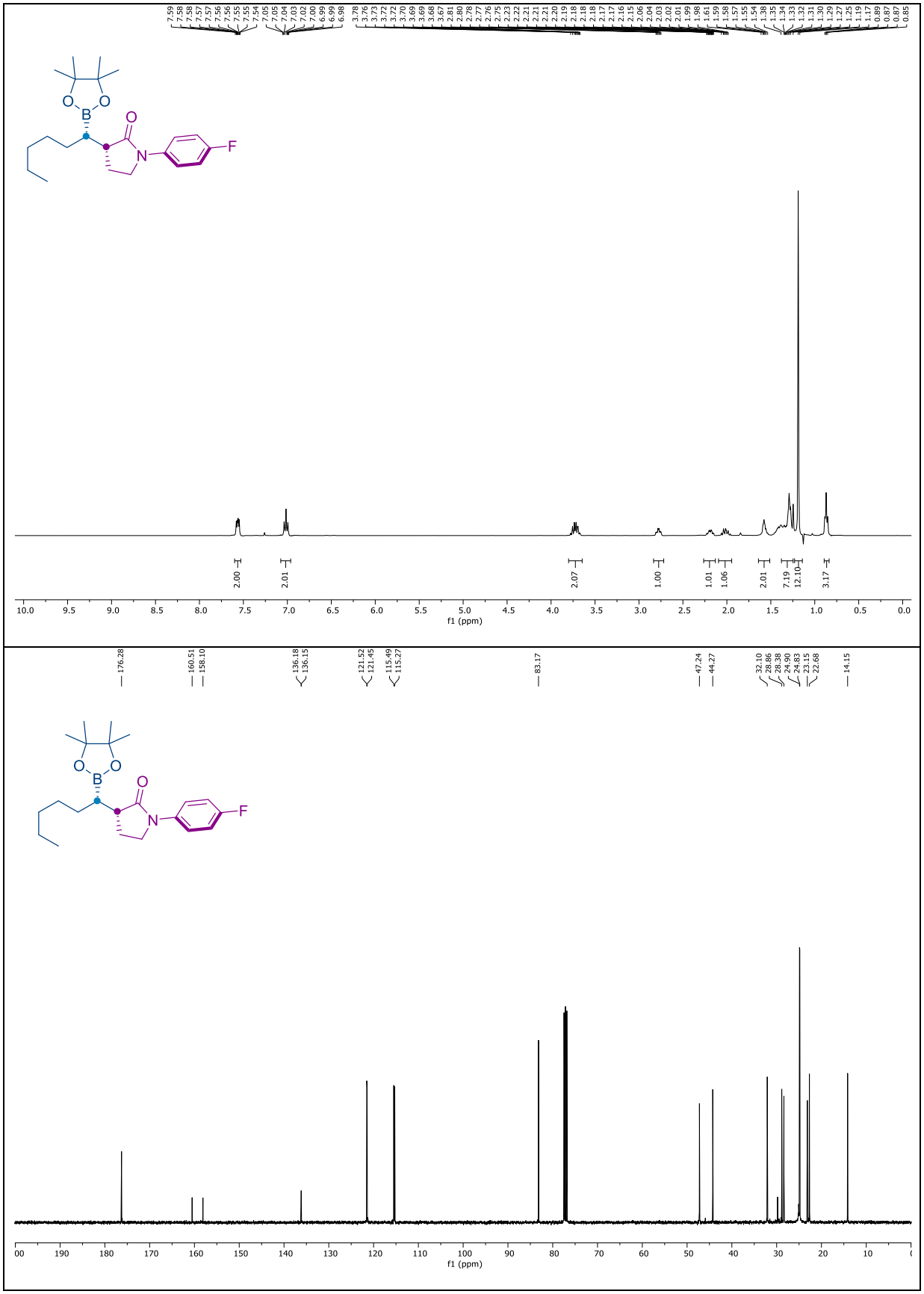

33.41
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

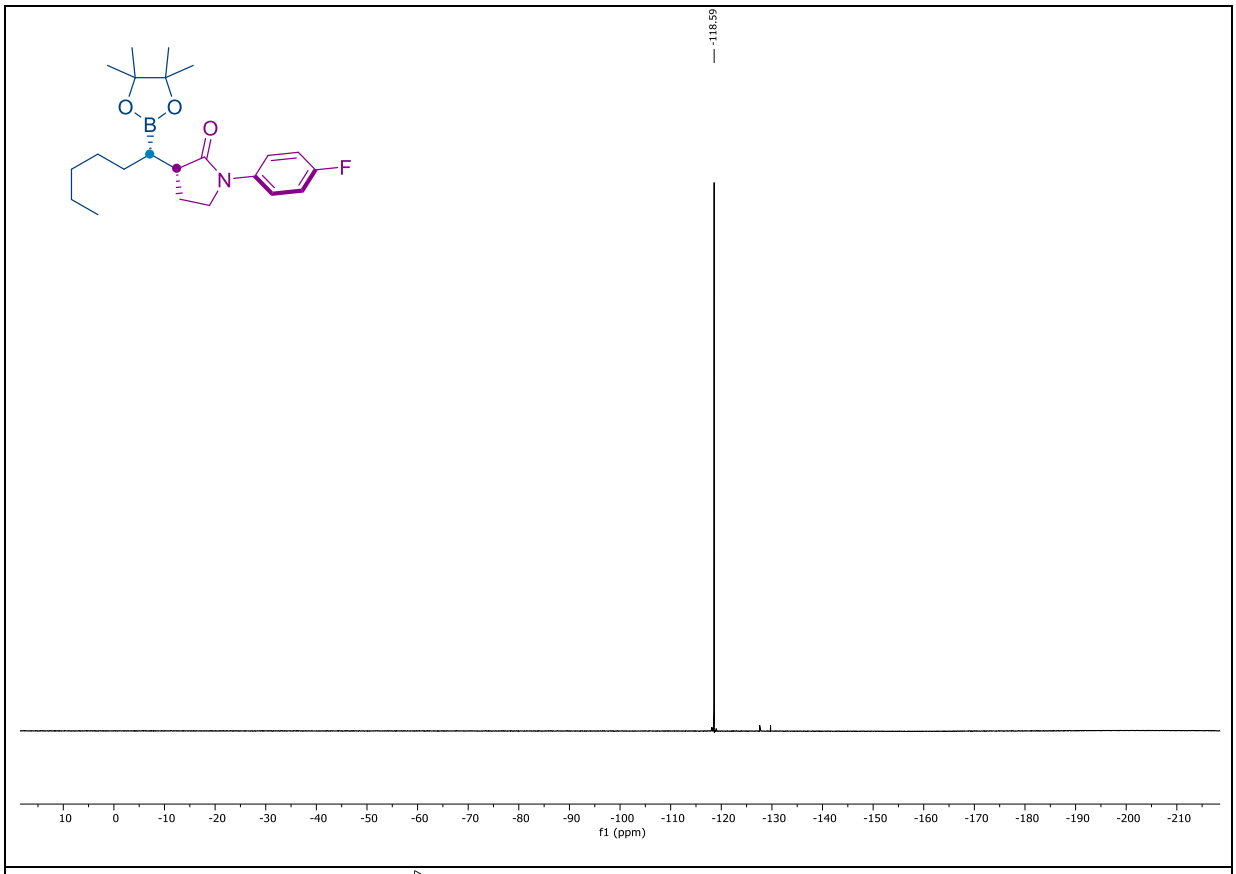
NMR spectra of 3ab:




32.99
O
B
O
O
N
OMe
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 3ac:




-118.59
O
B
O
O
N
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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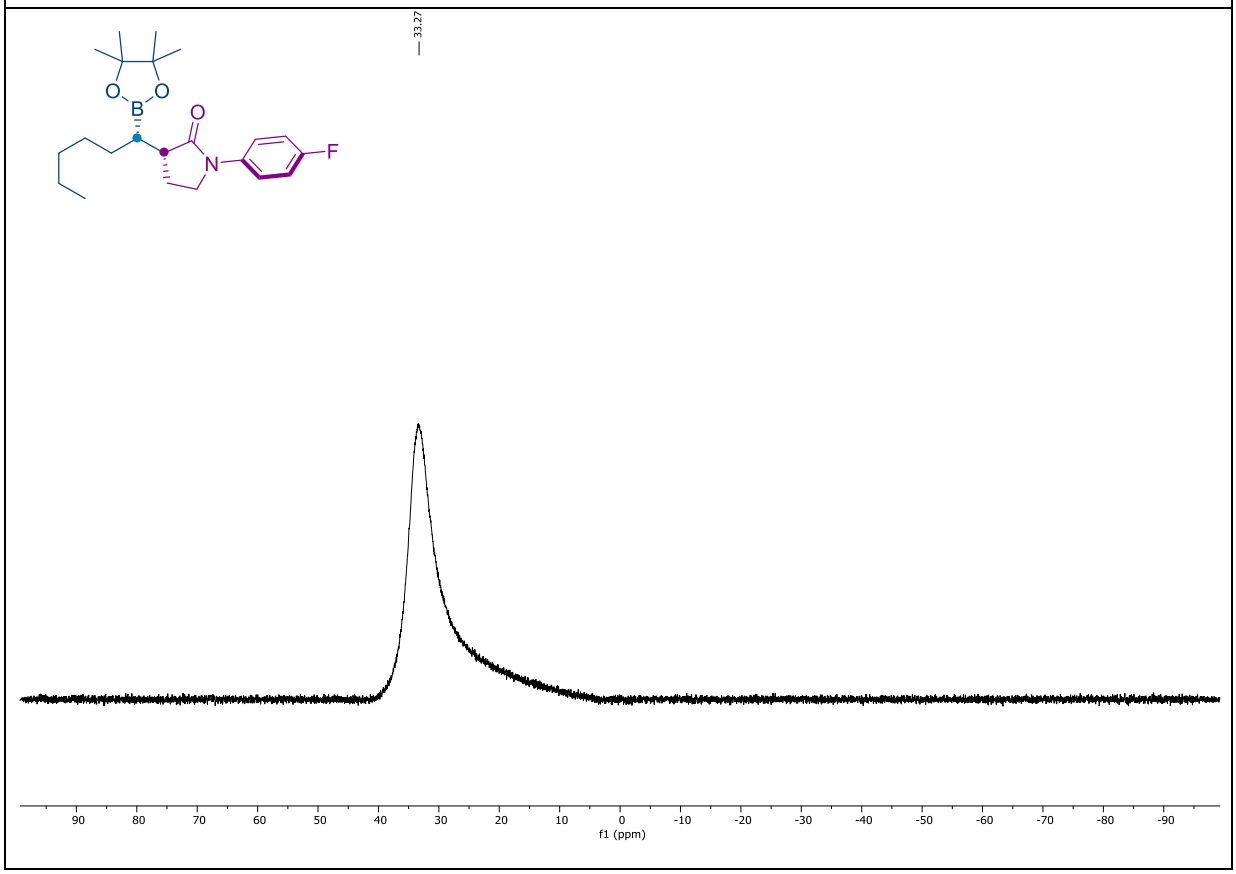
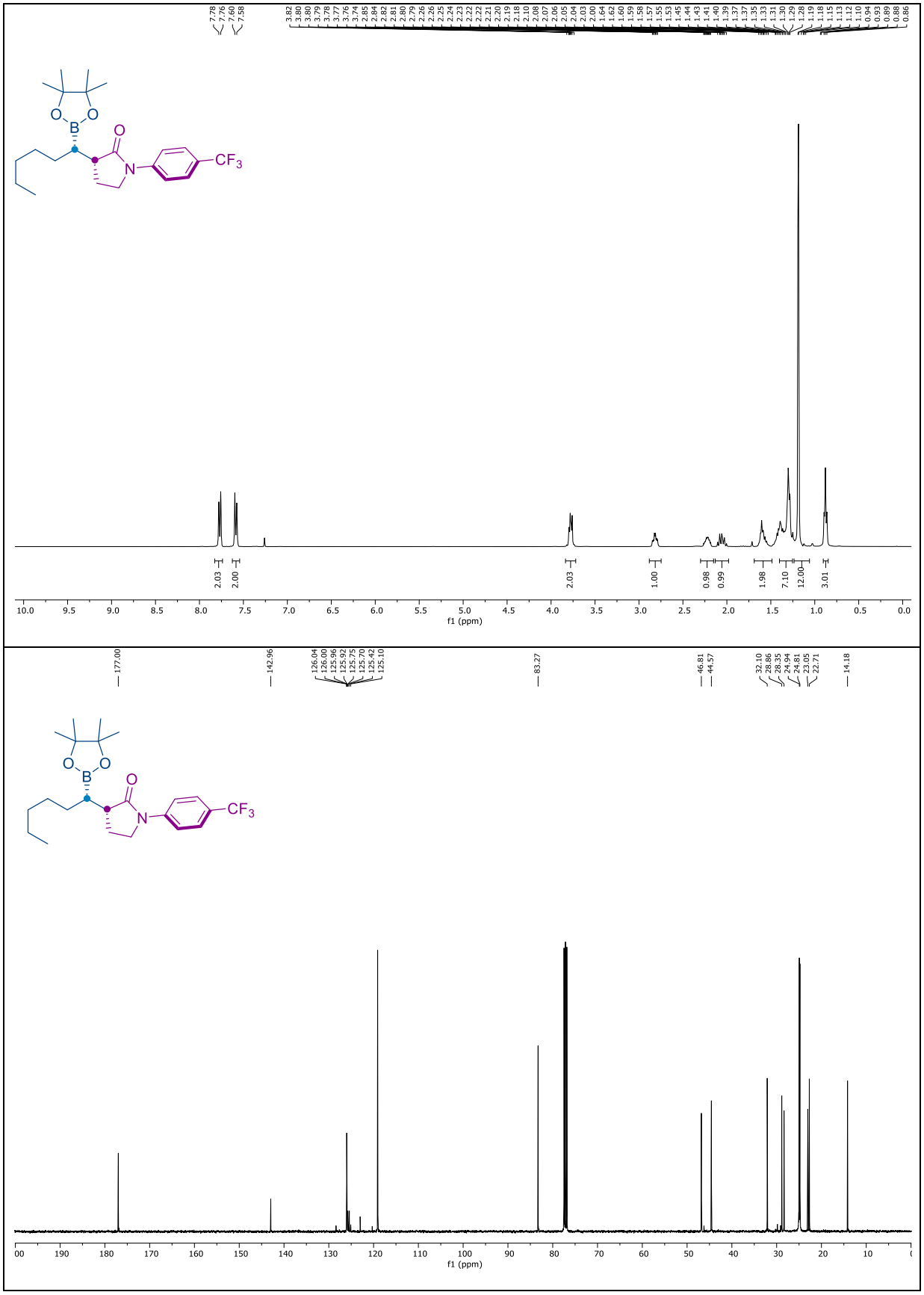
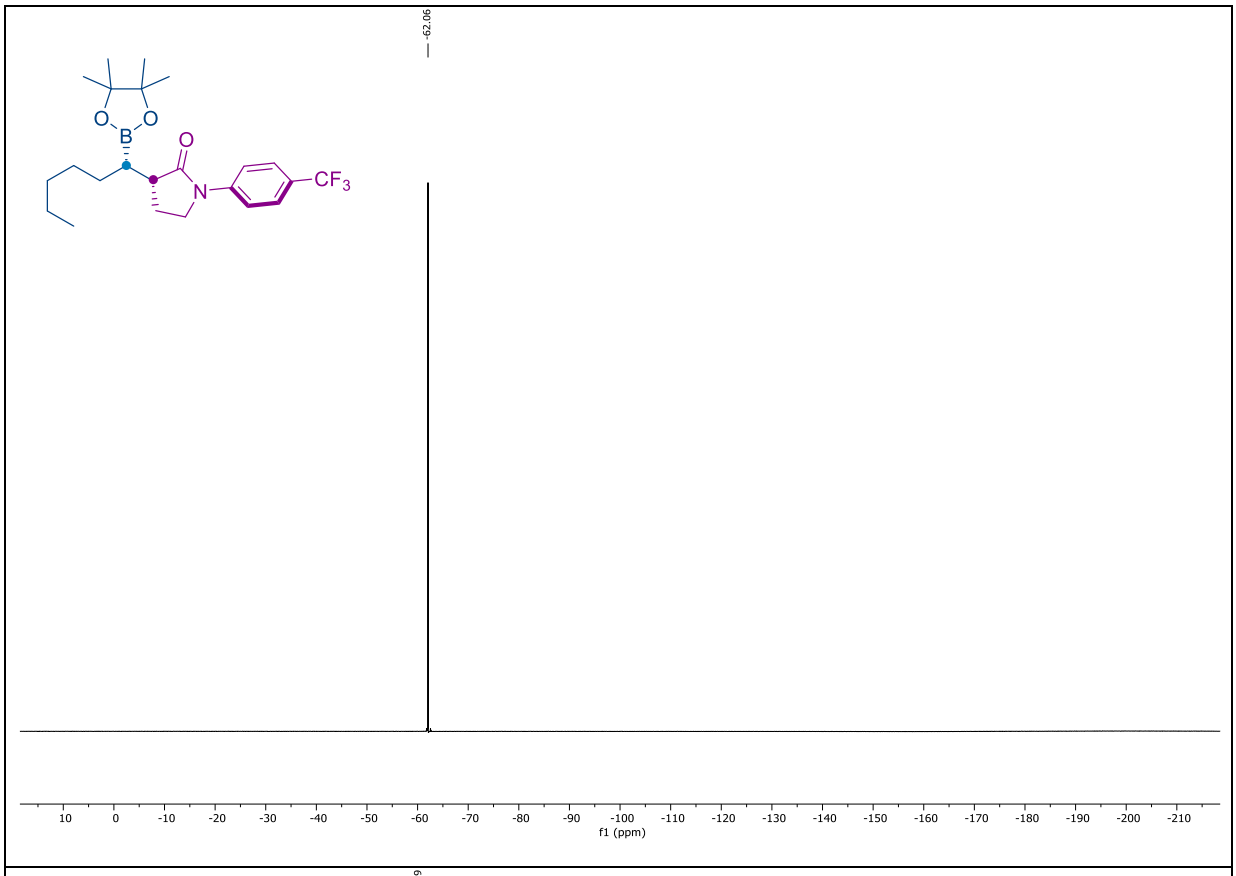
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


33.27
O
B
O
O
N
F
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 3ad:




-62.06
O
B
O
O
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
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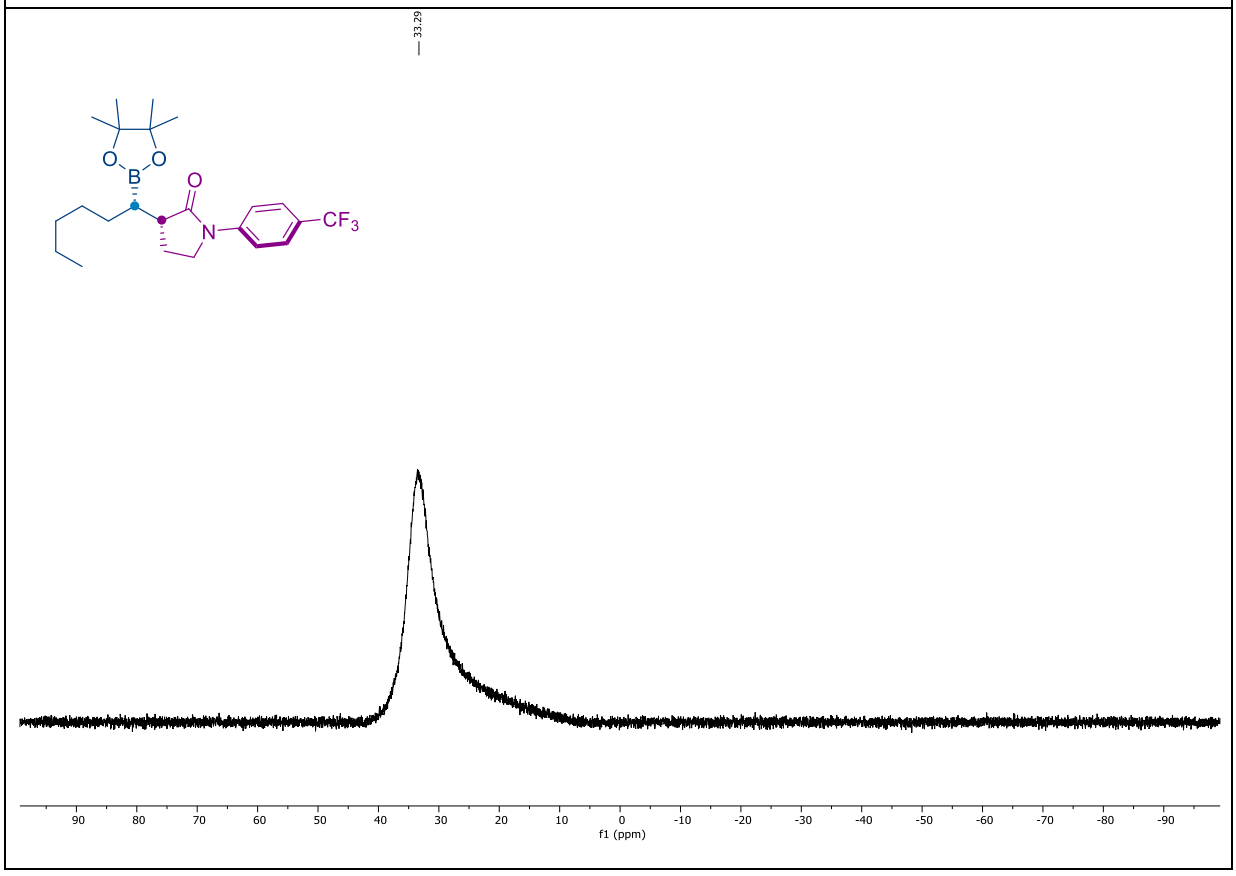
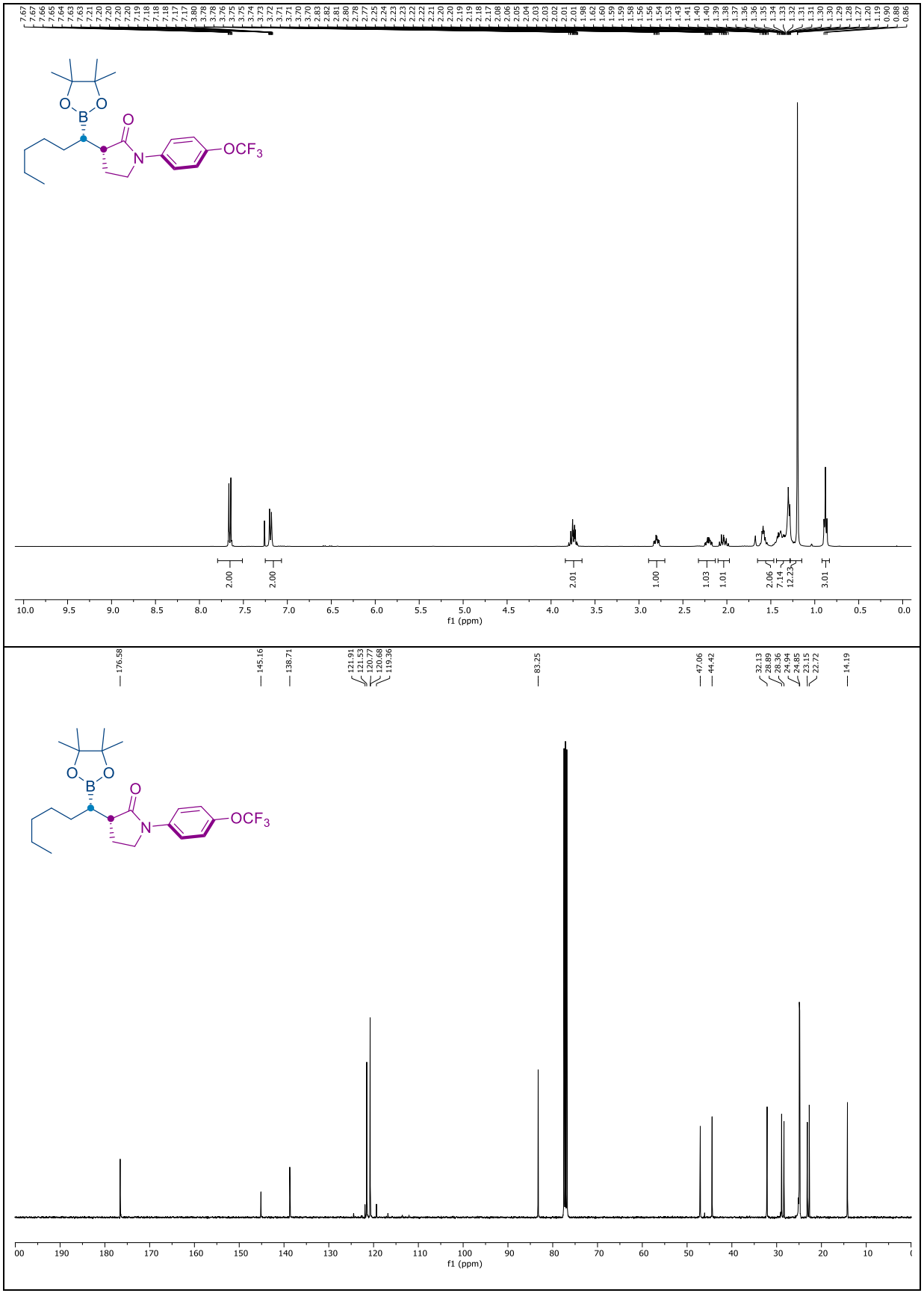
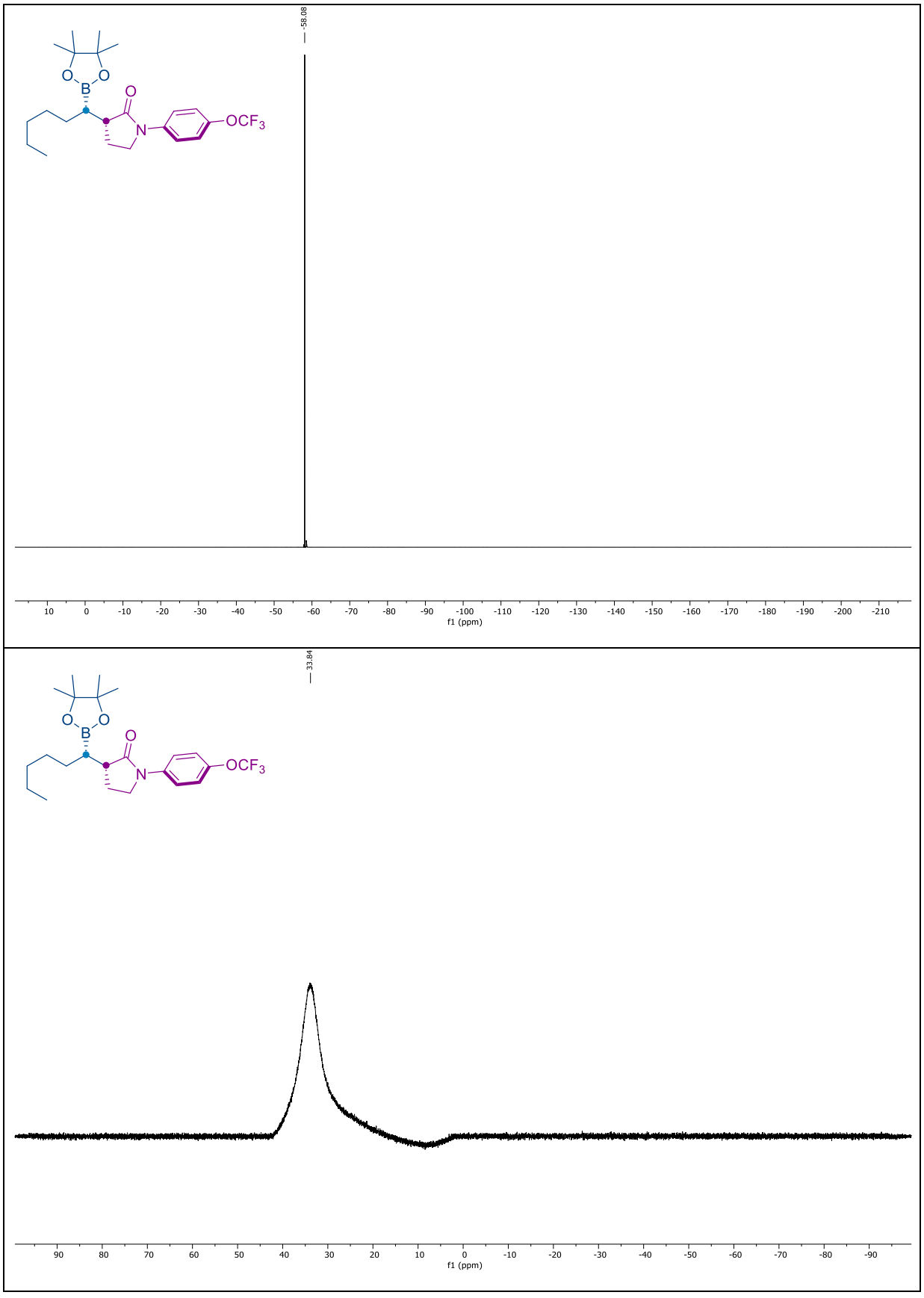
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

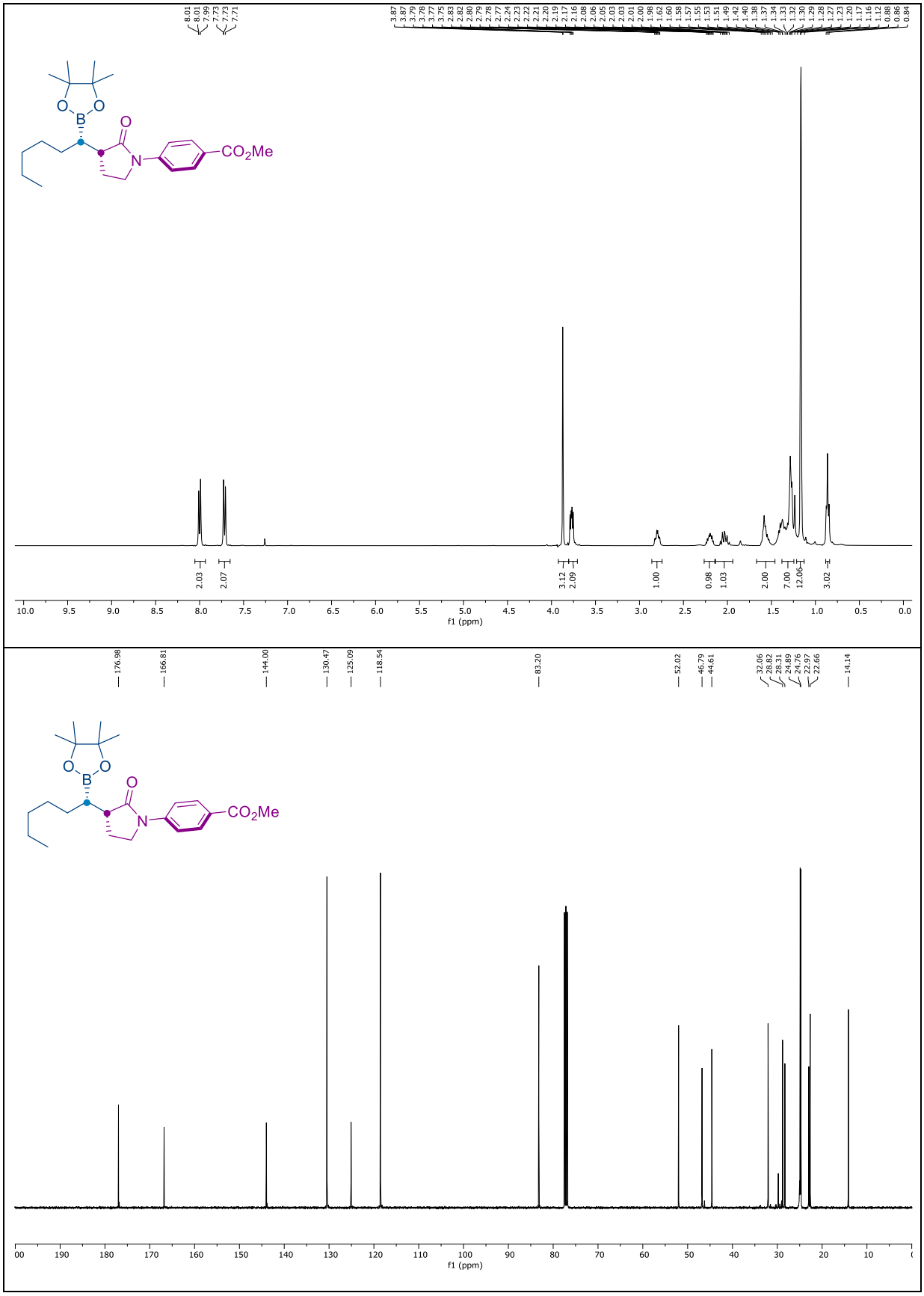

33.29
O
B
O
O
N
CF3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

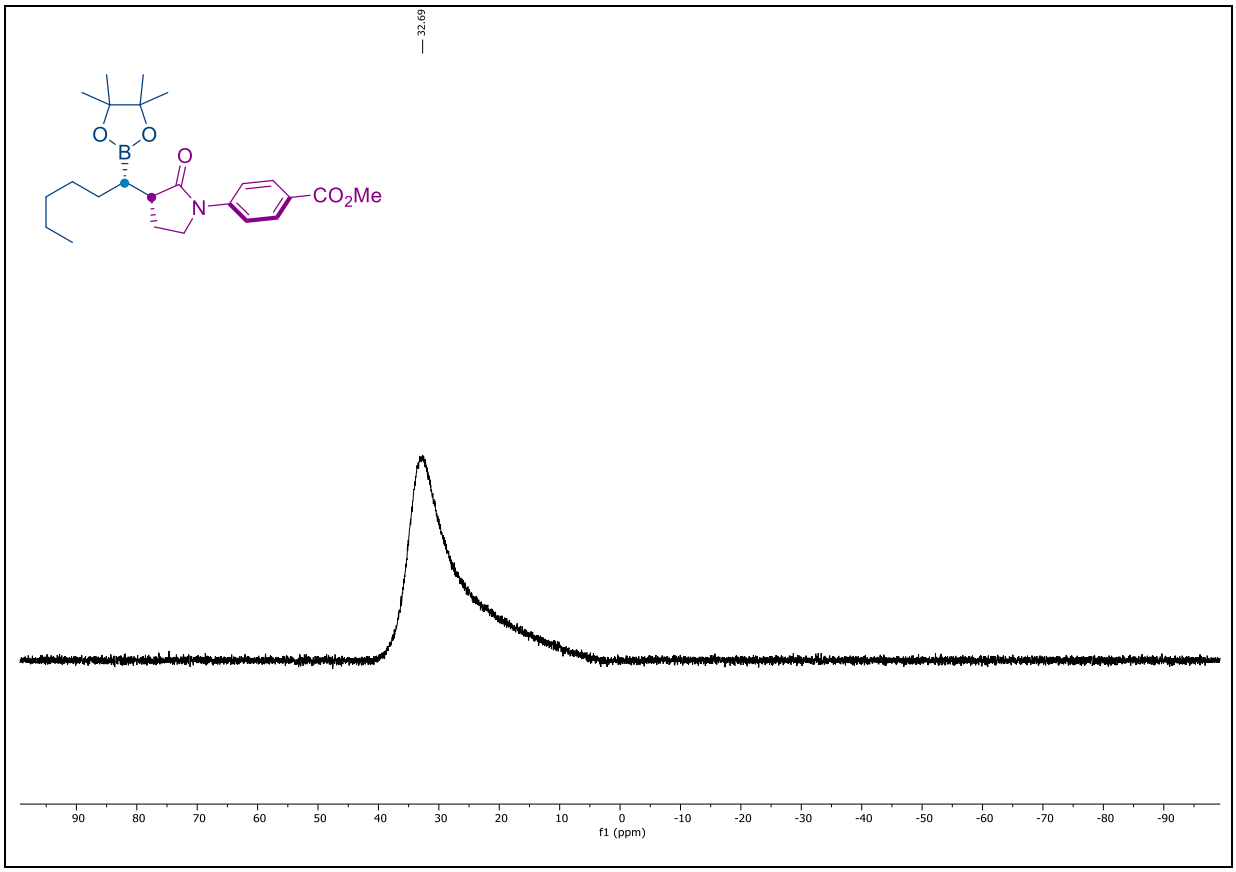
NMR spectra of 3ae:



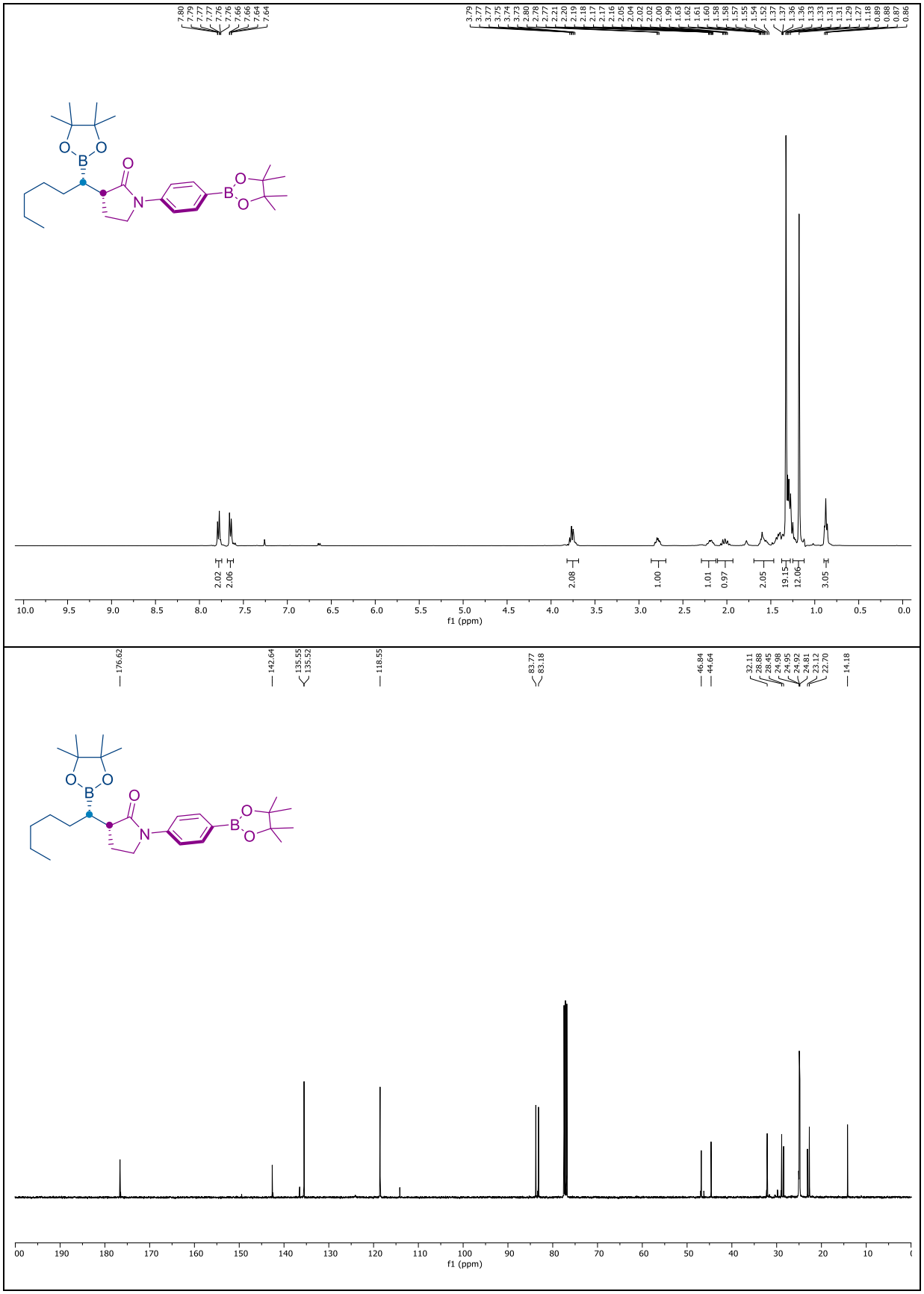

-58.08
O
B
O
O
N
OCF3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
33.84
O
B
O
O
N
OCF3
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

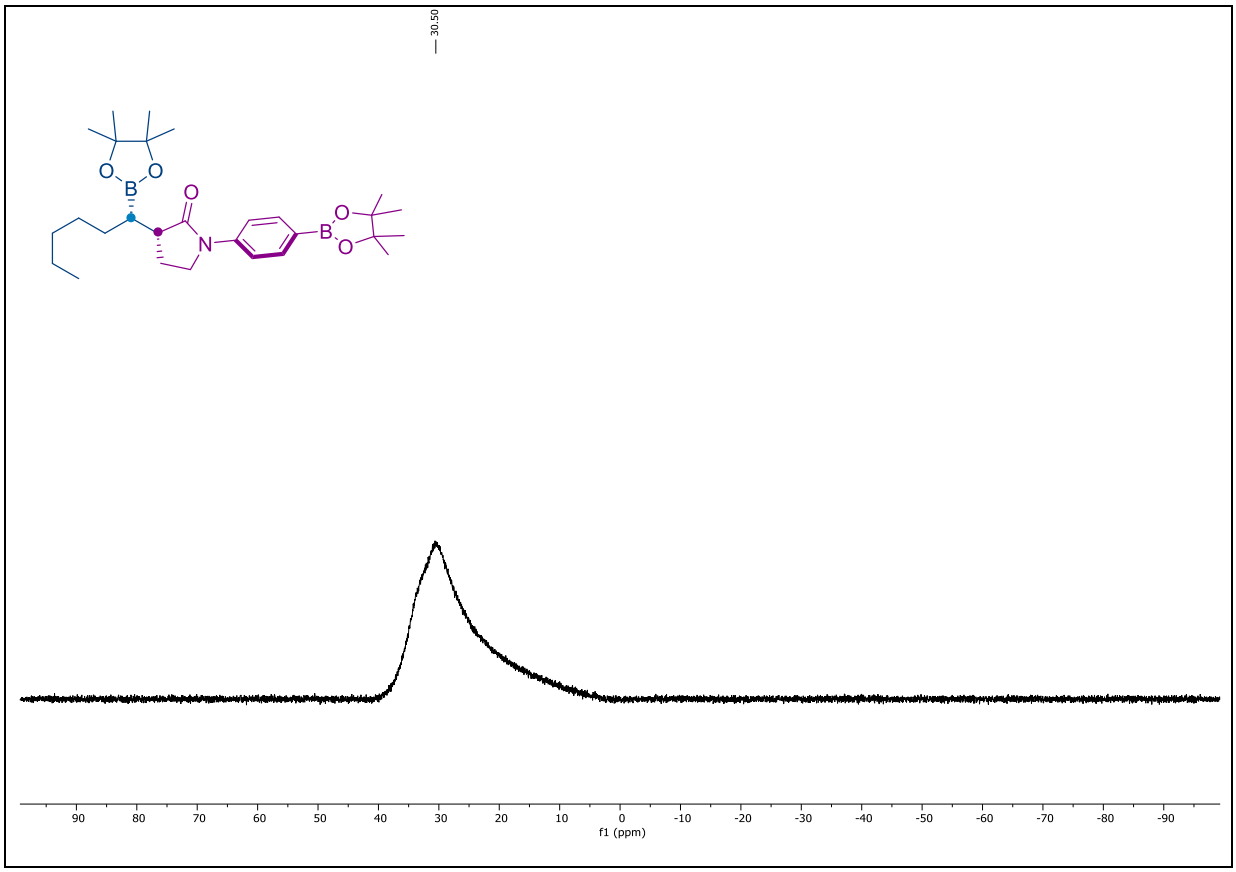
NMR spectra of 3af:



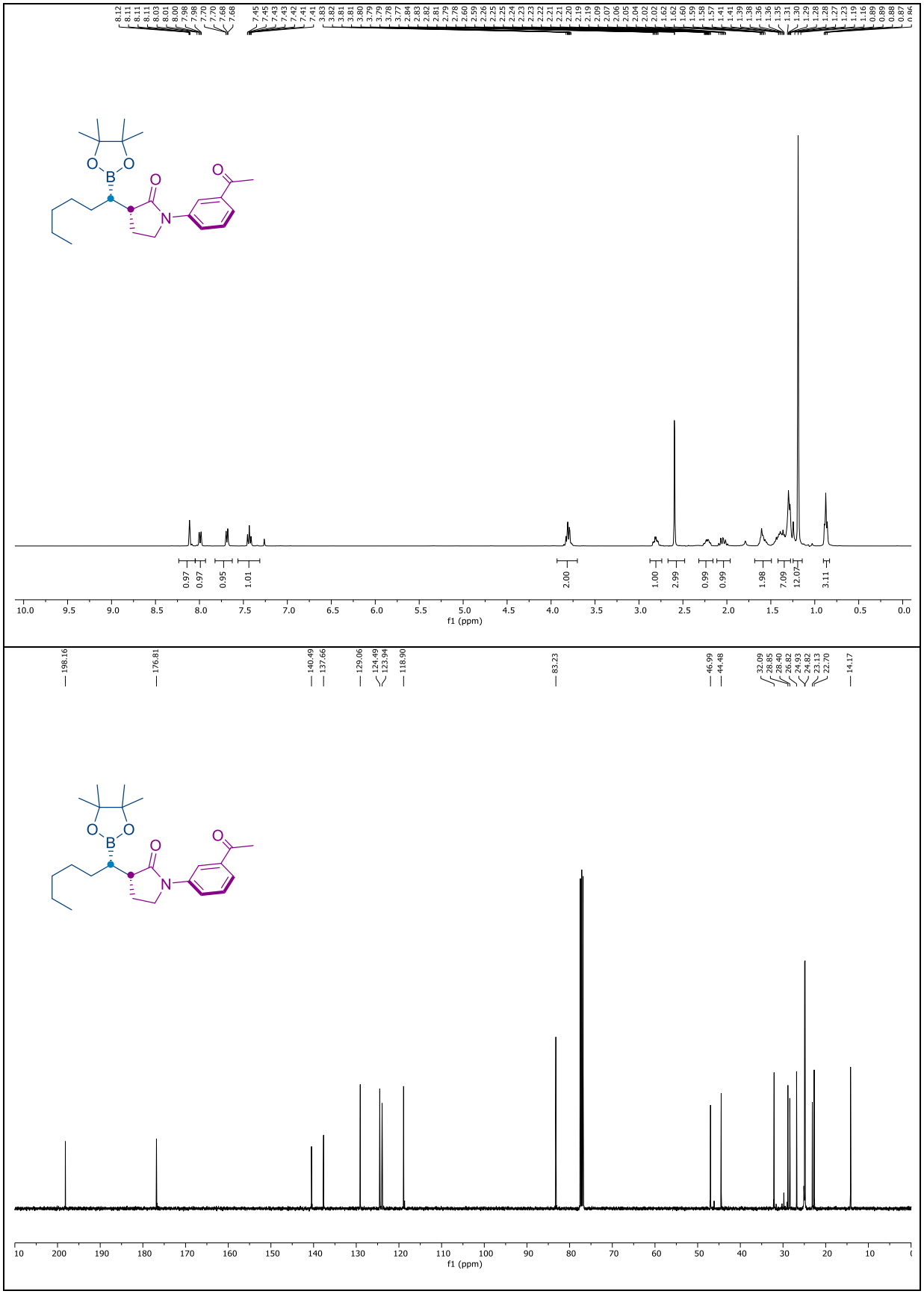

32.69
O
B
O
O
N
CO2Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

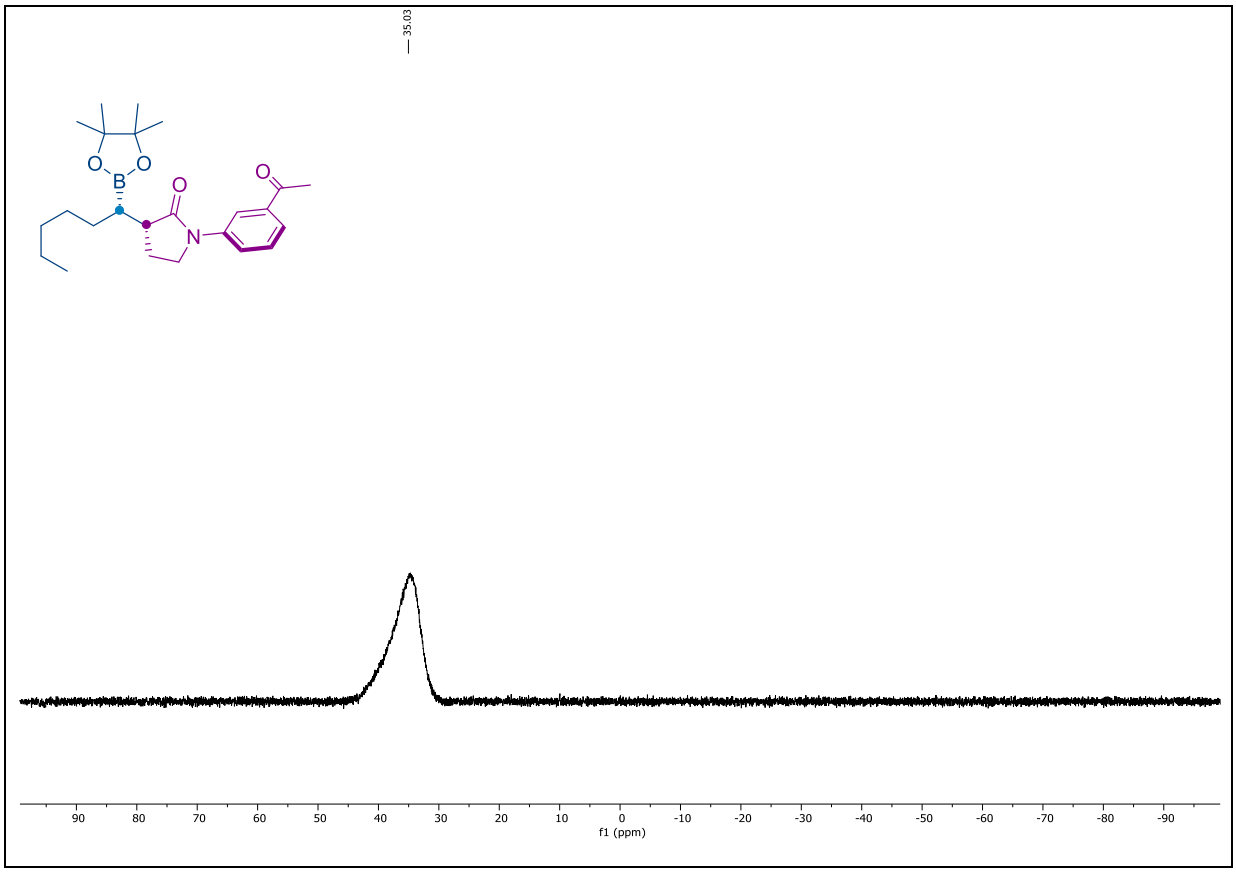
NMR spectra of 3ag:



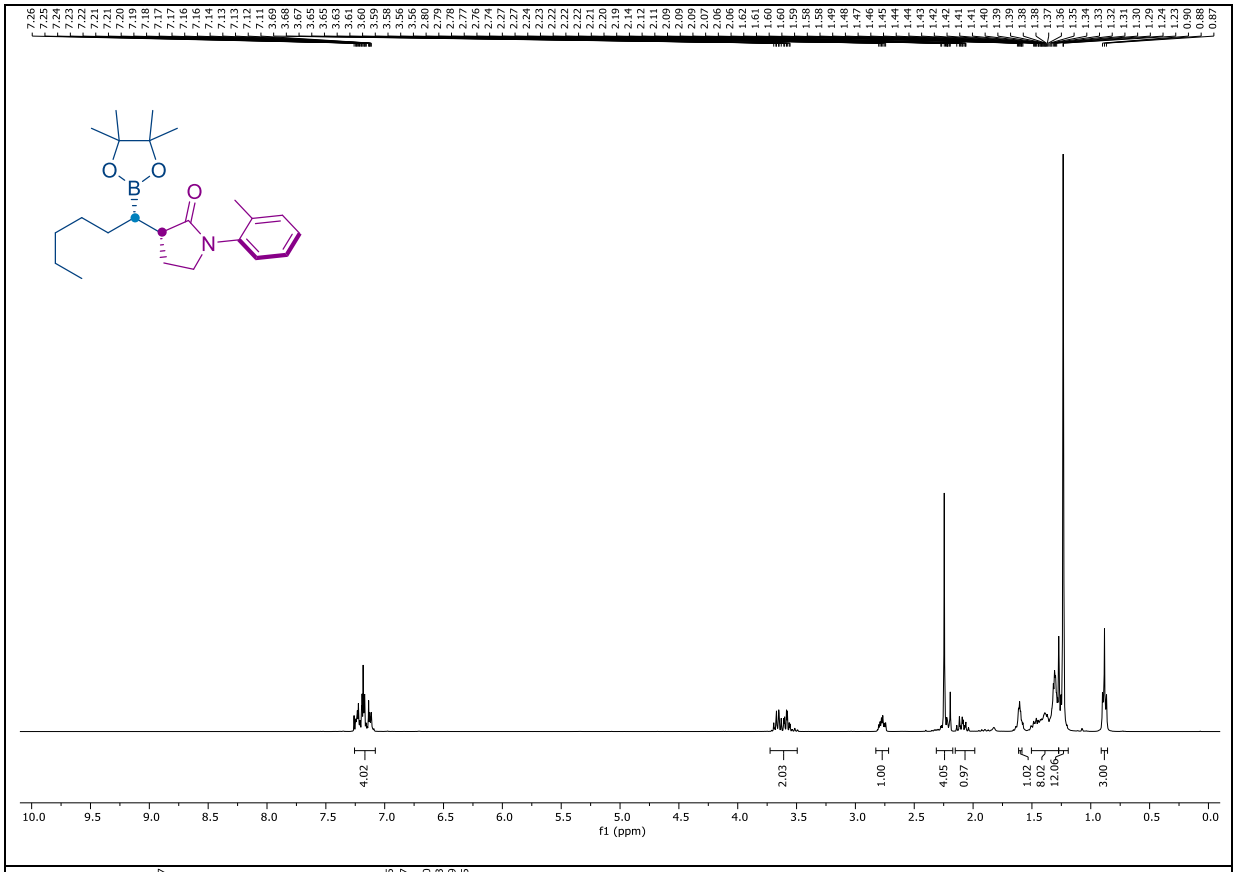

30.50
O
B
O
O
N
B
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

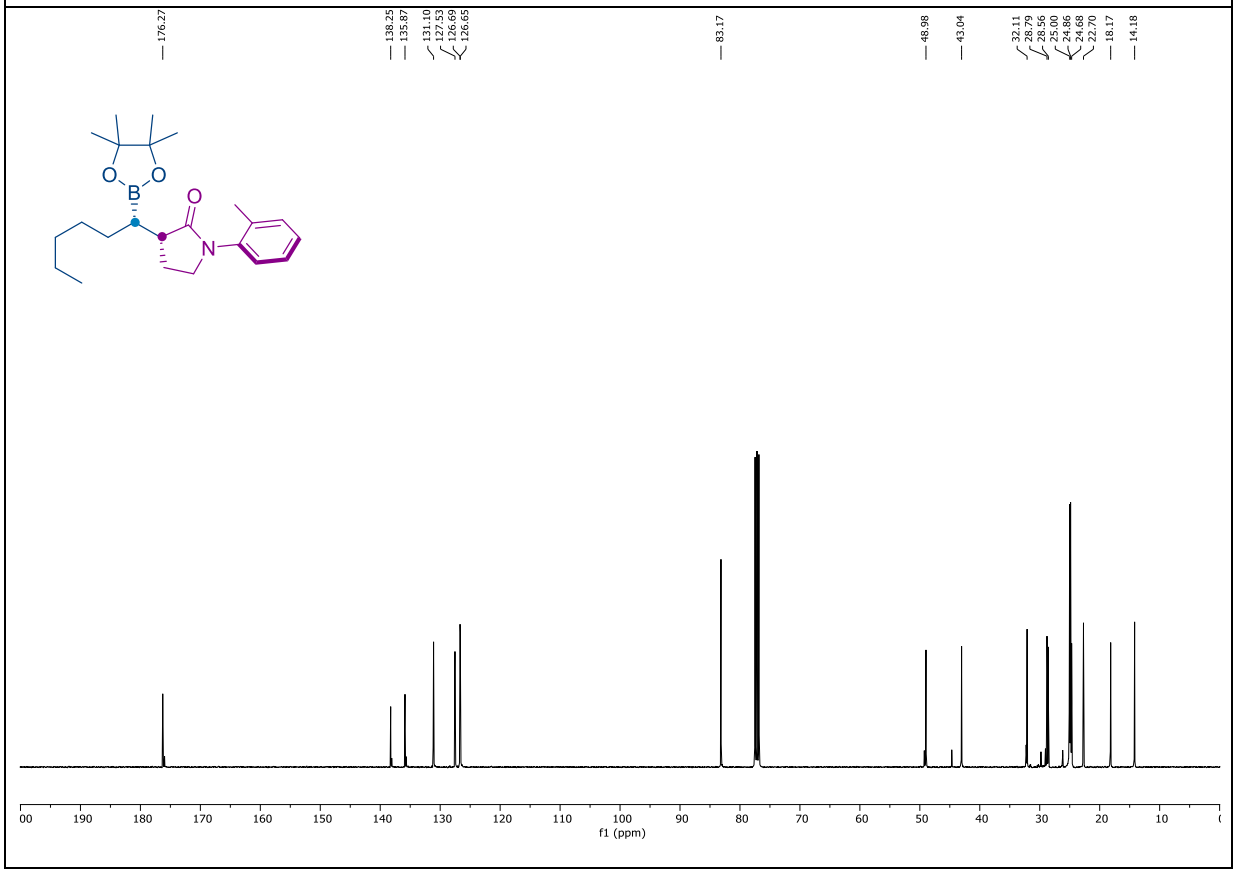
NMR spectra of 3ah:

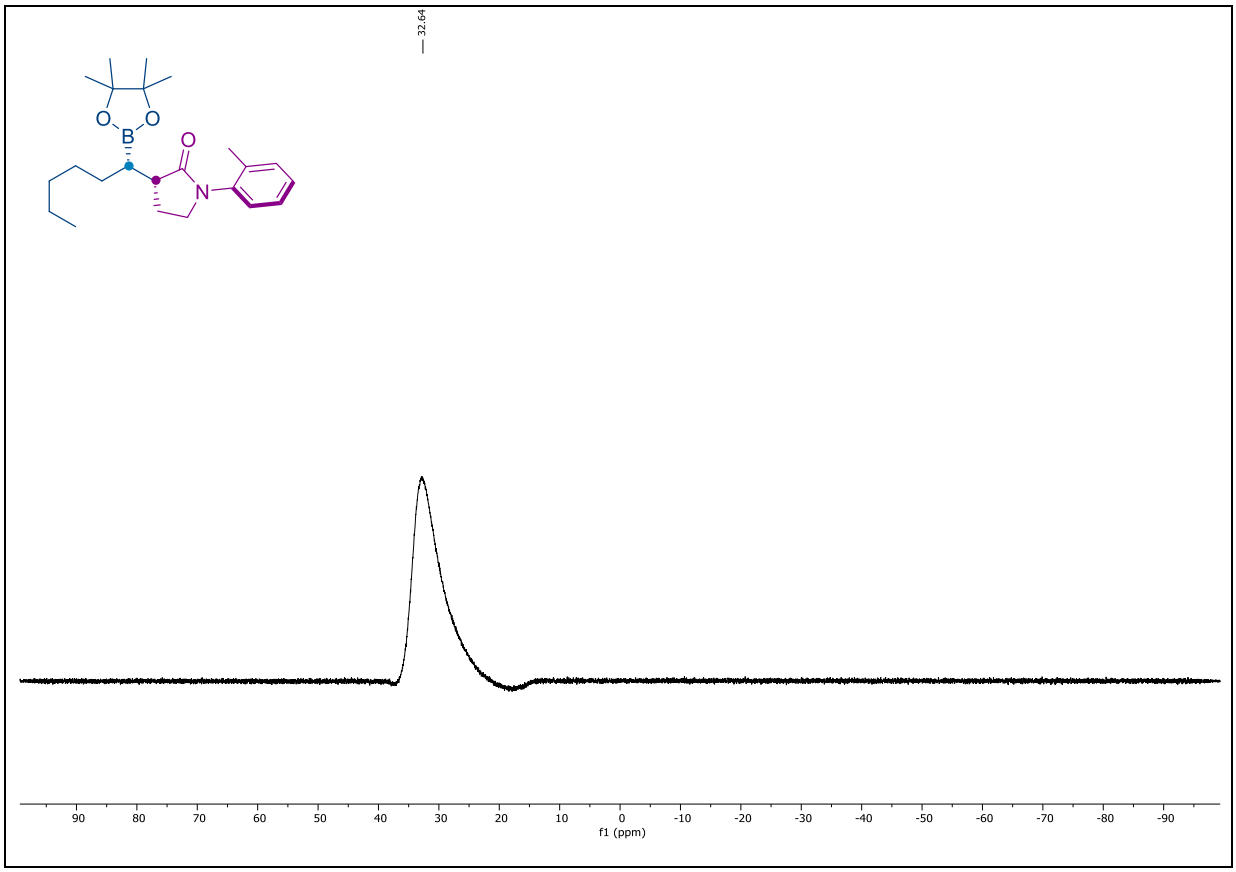



35.03
O
B
O
O
N
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

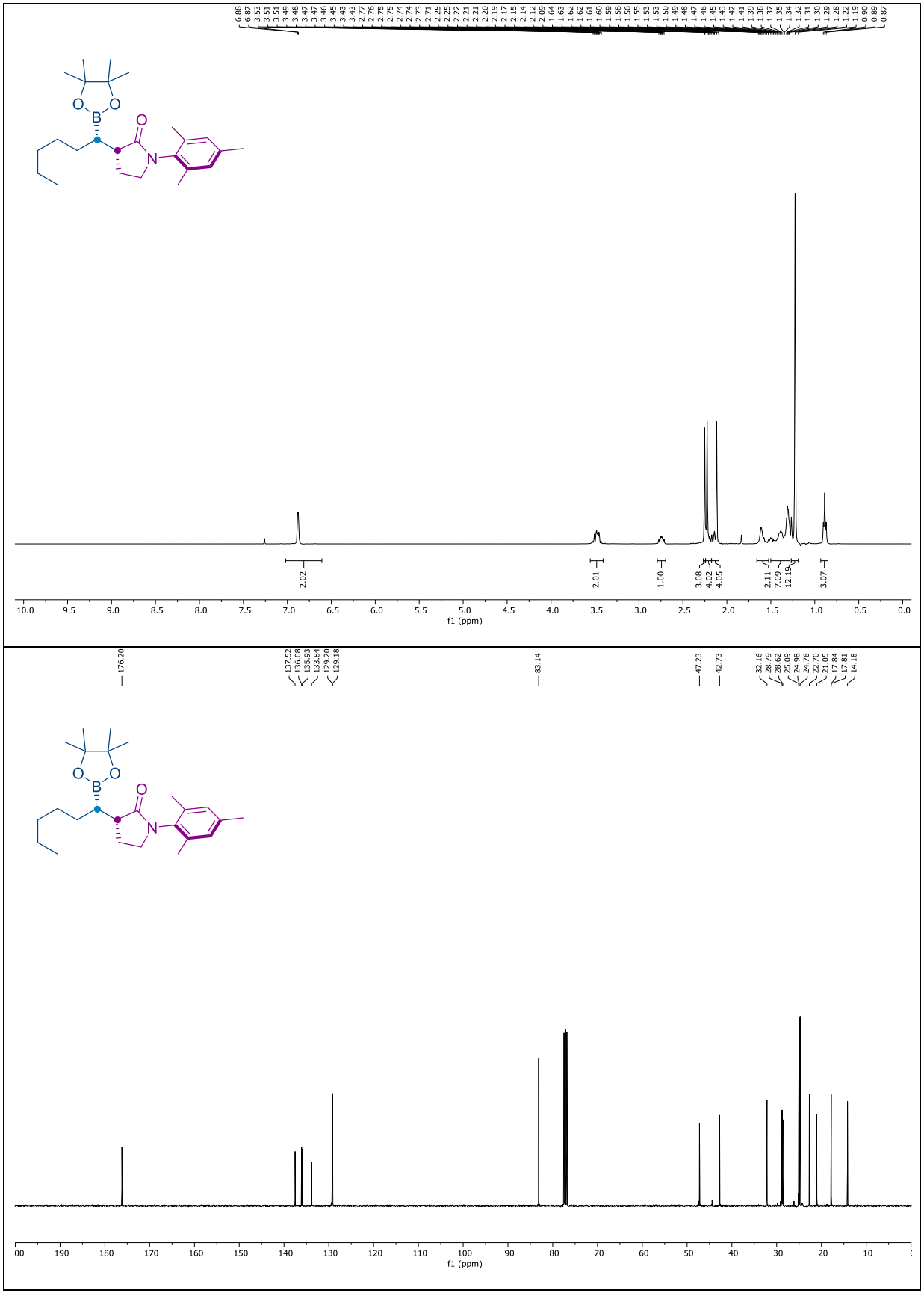
NMR spectra of 3ah:

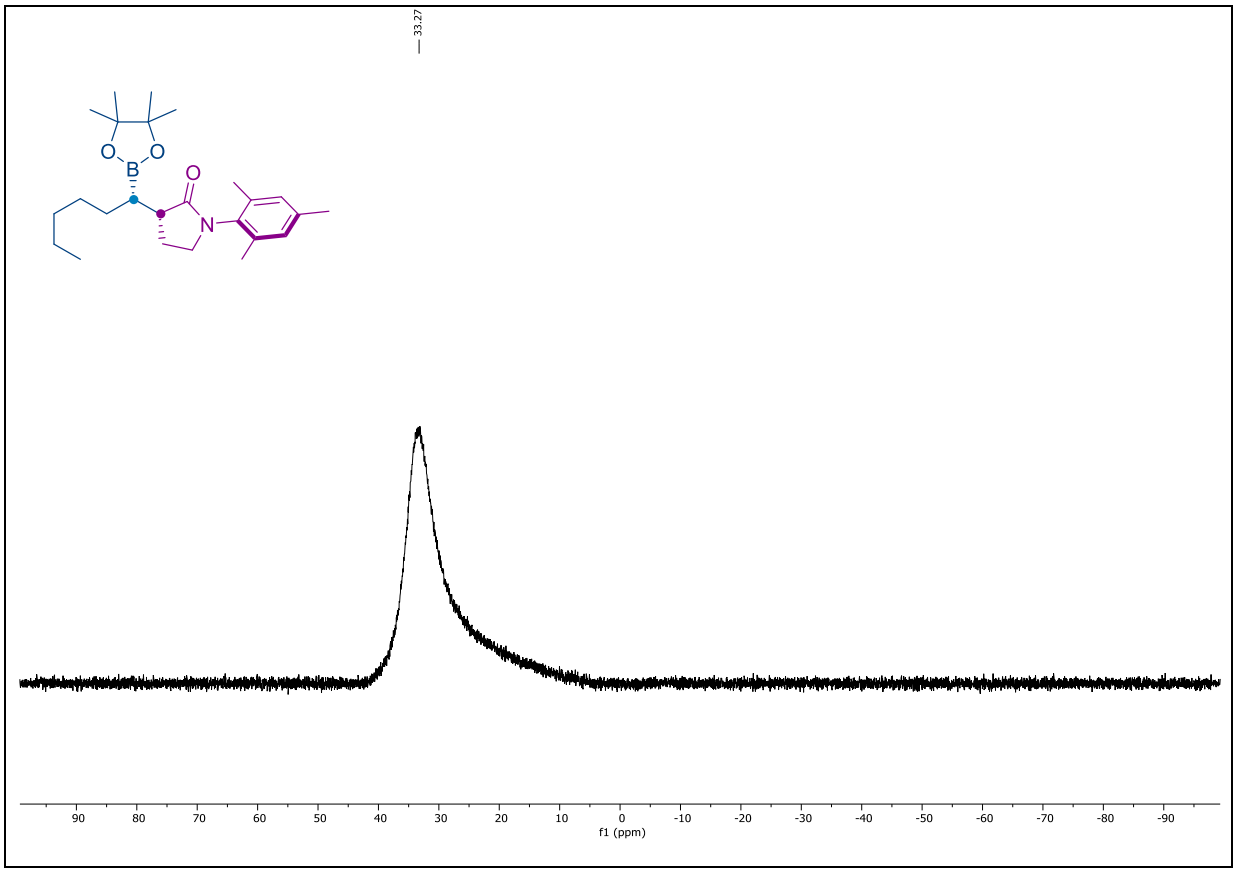




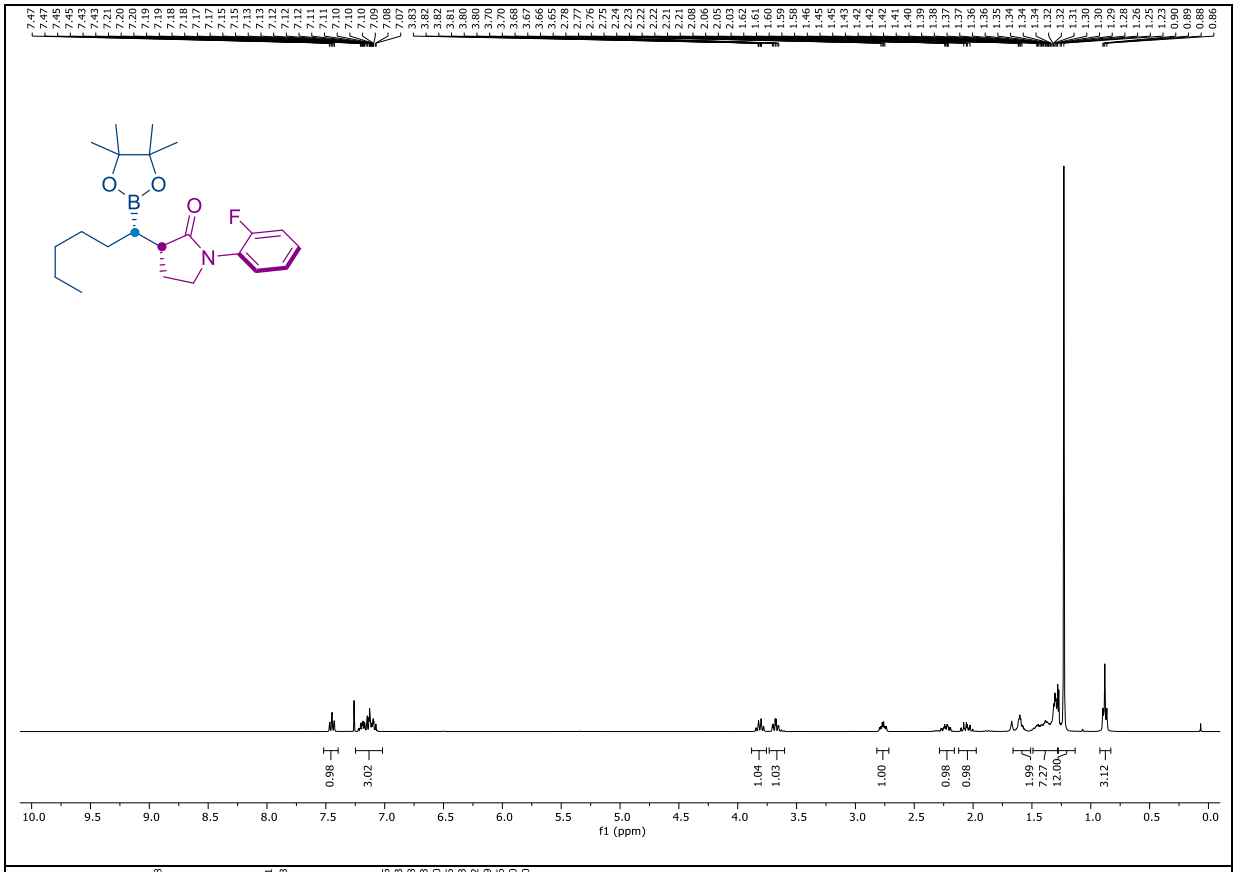

32.64
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

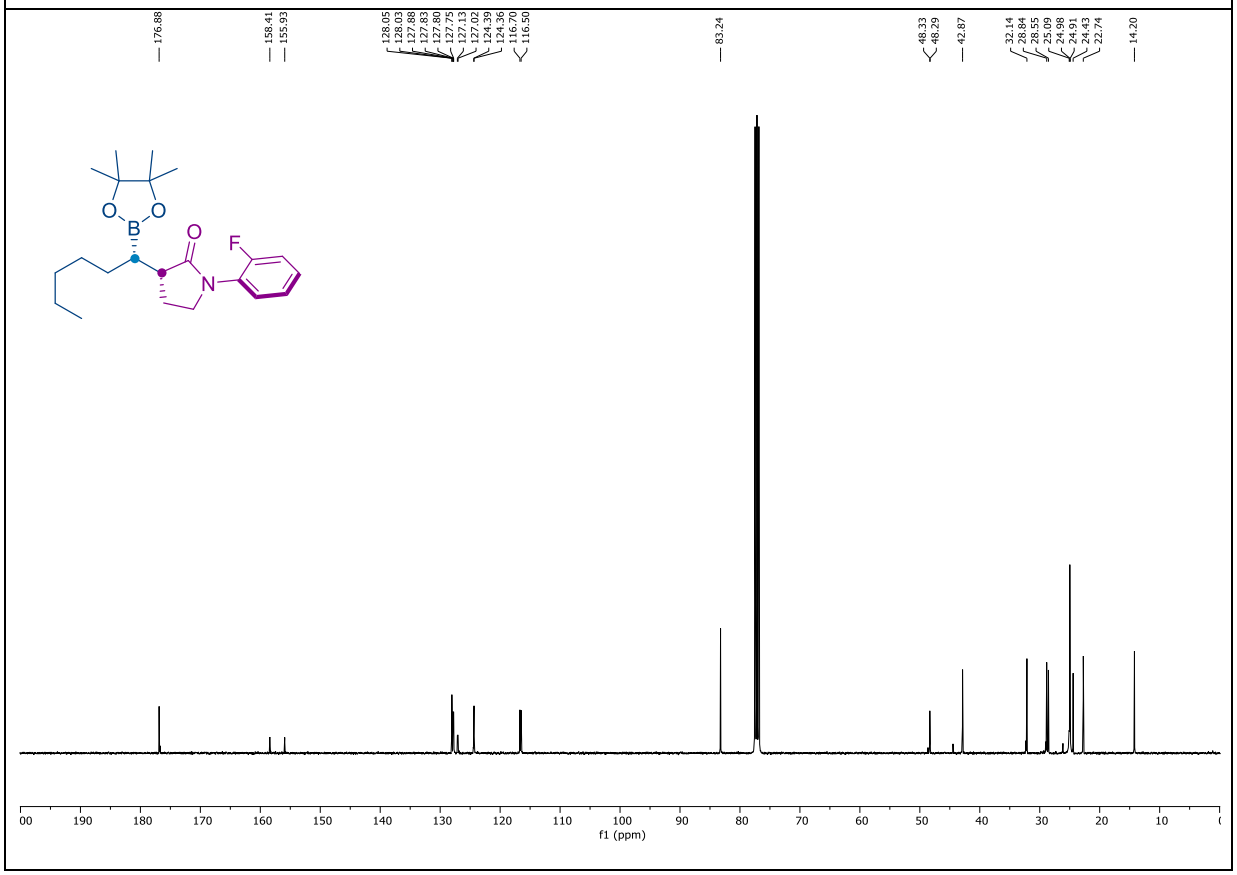
NMR spectra of 3ai:

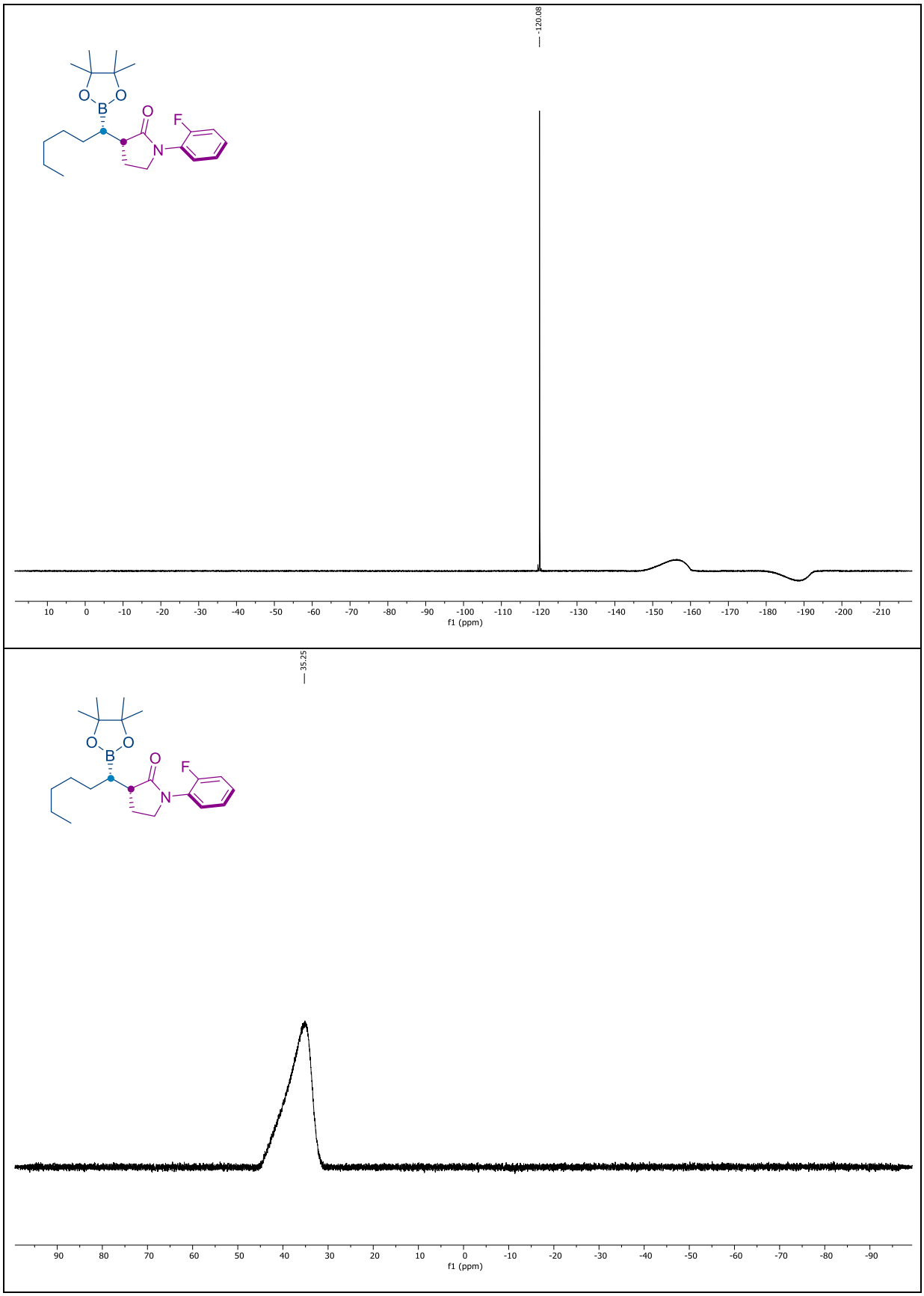



33.27
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

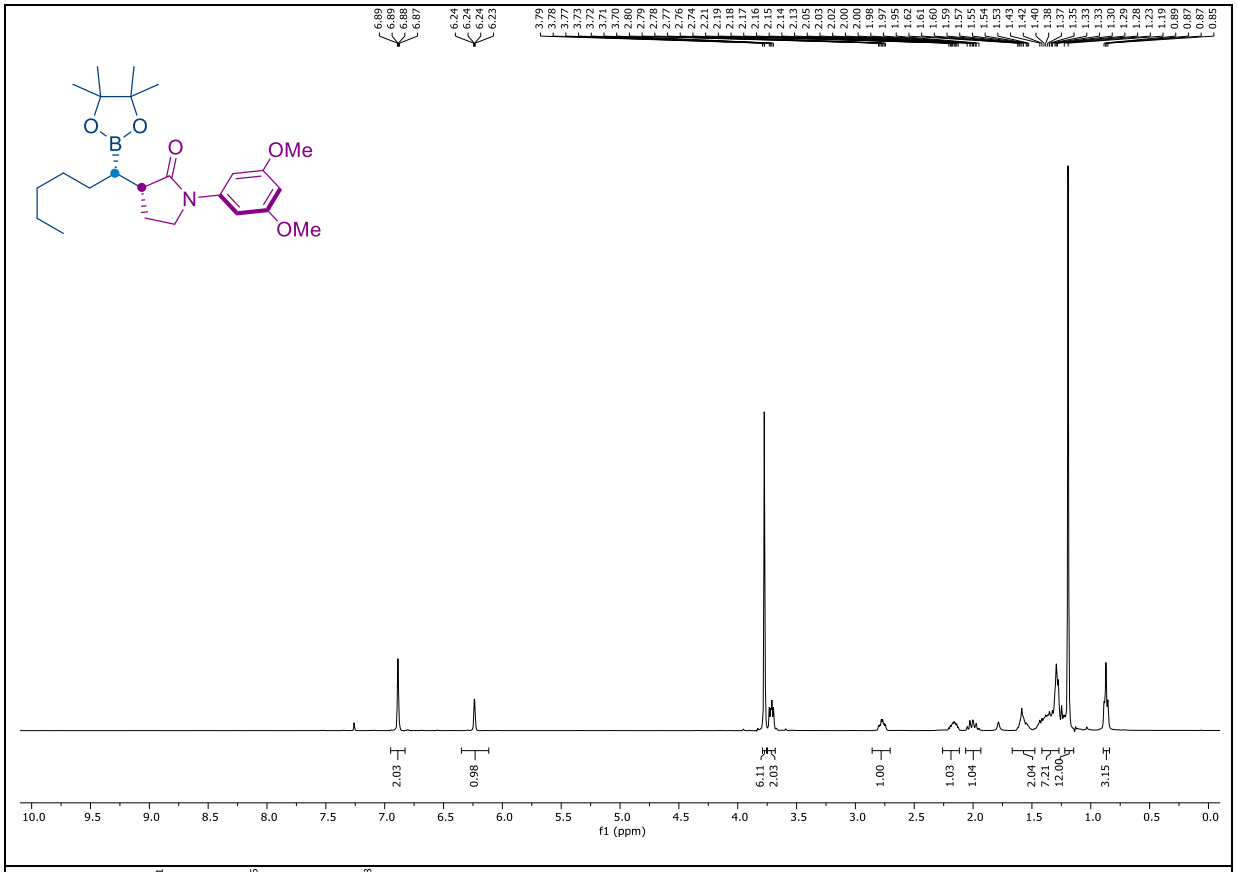
NMR spectra of 3ak:

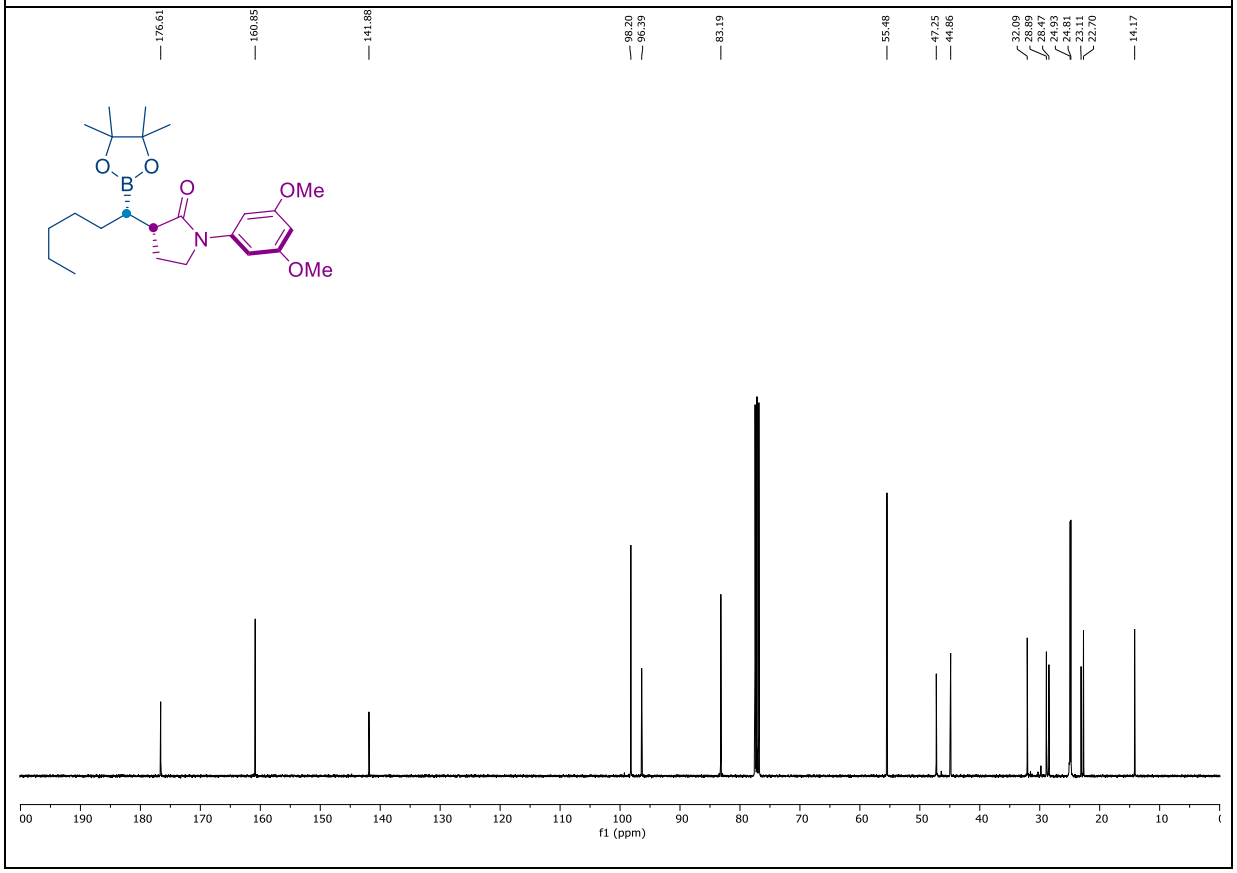


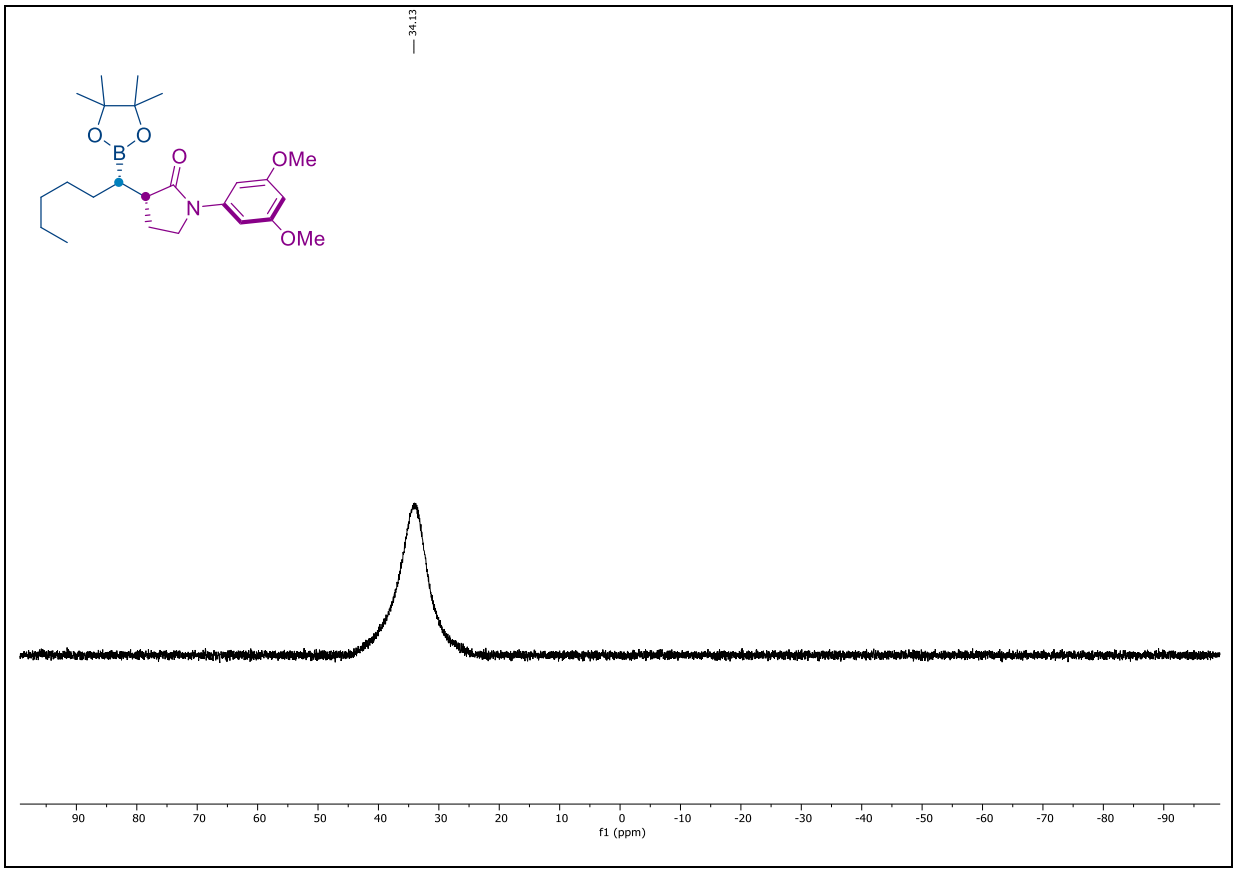



-120.08
O
B
O
O
F
N
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)
35.25
O
B
O
O
F
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

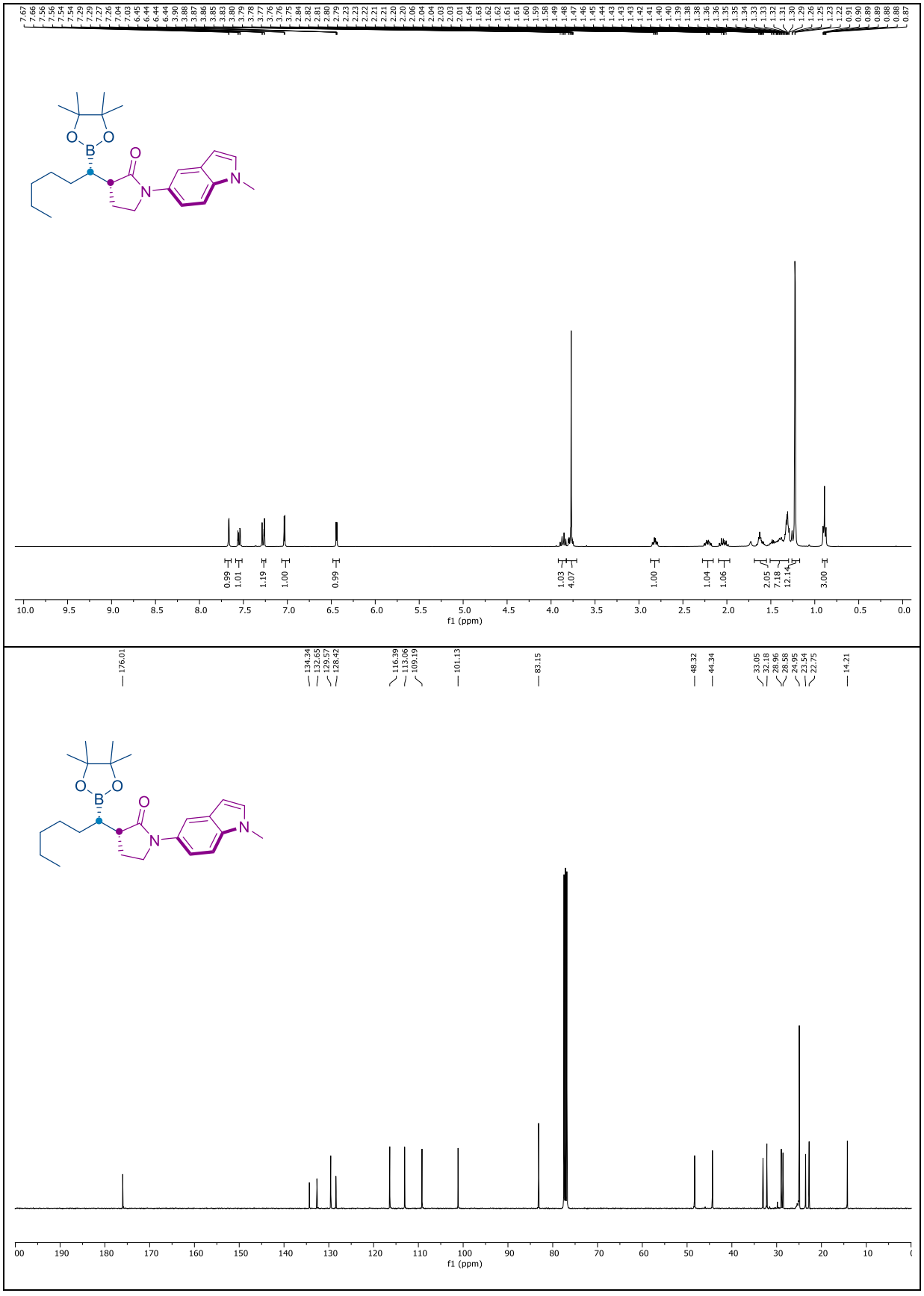
NMR spectra of 3al:

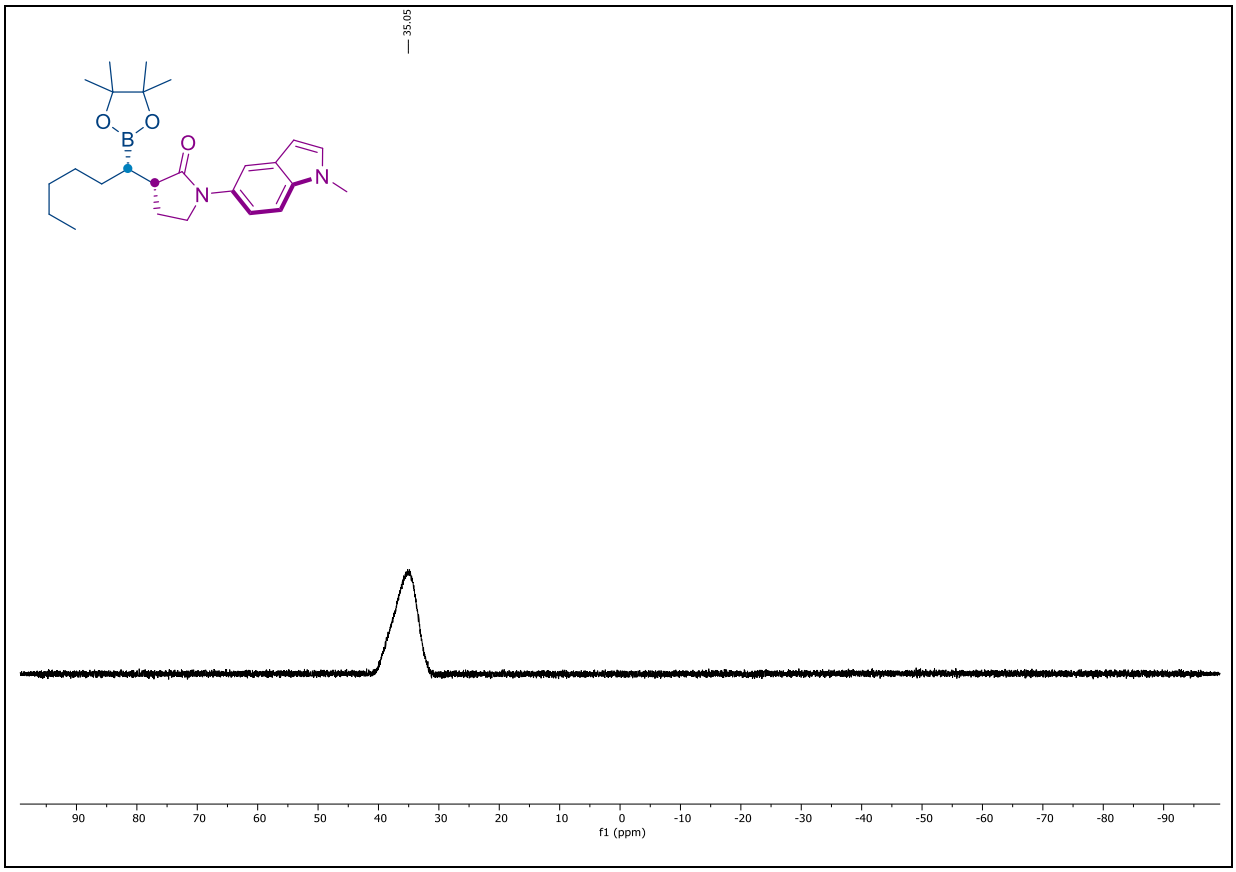




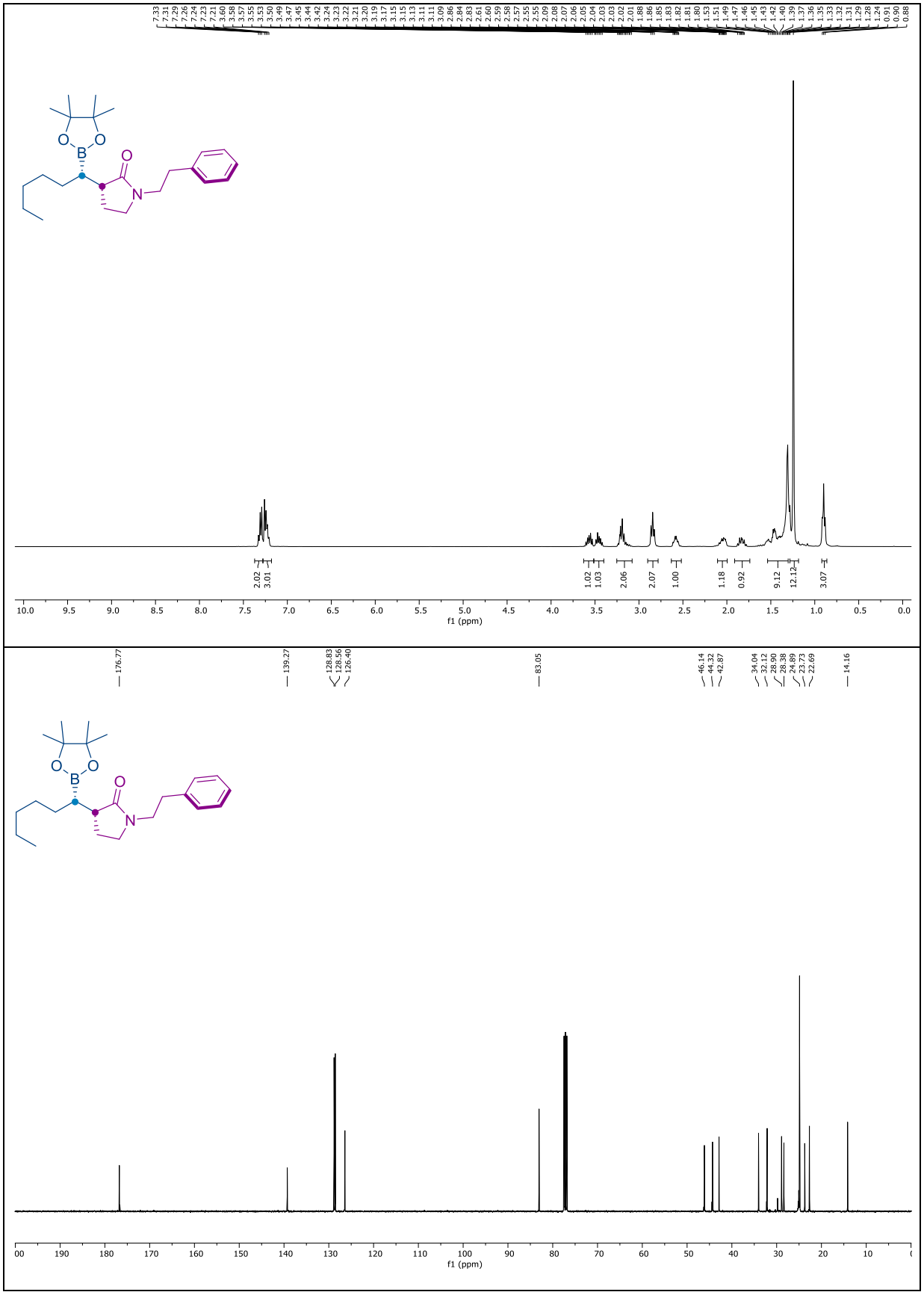

34.13
O
B
O
O
N
OMe
OMe
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

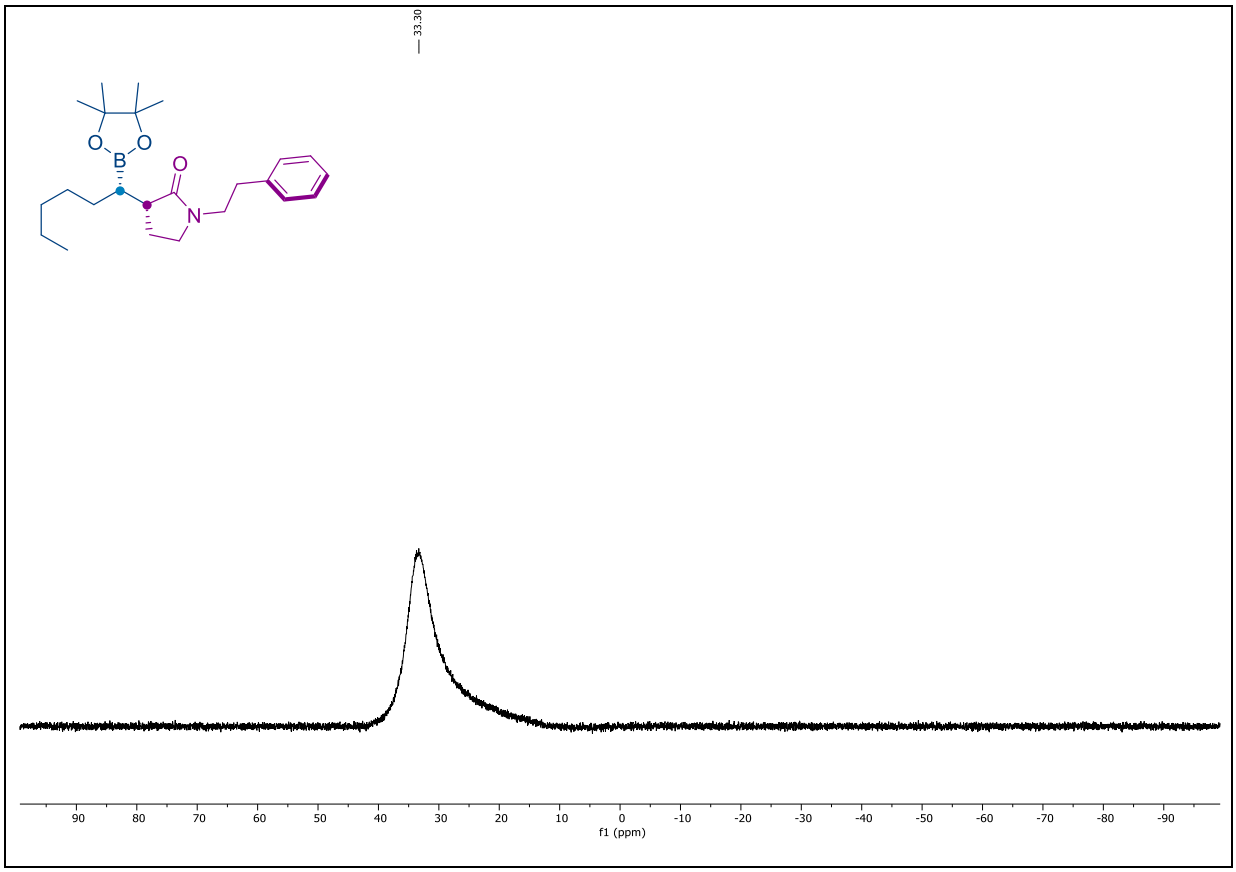
NMR spectra of 3am:



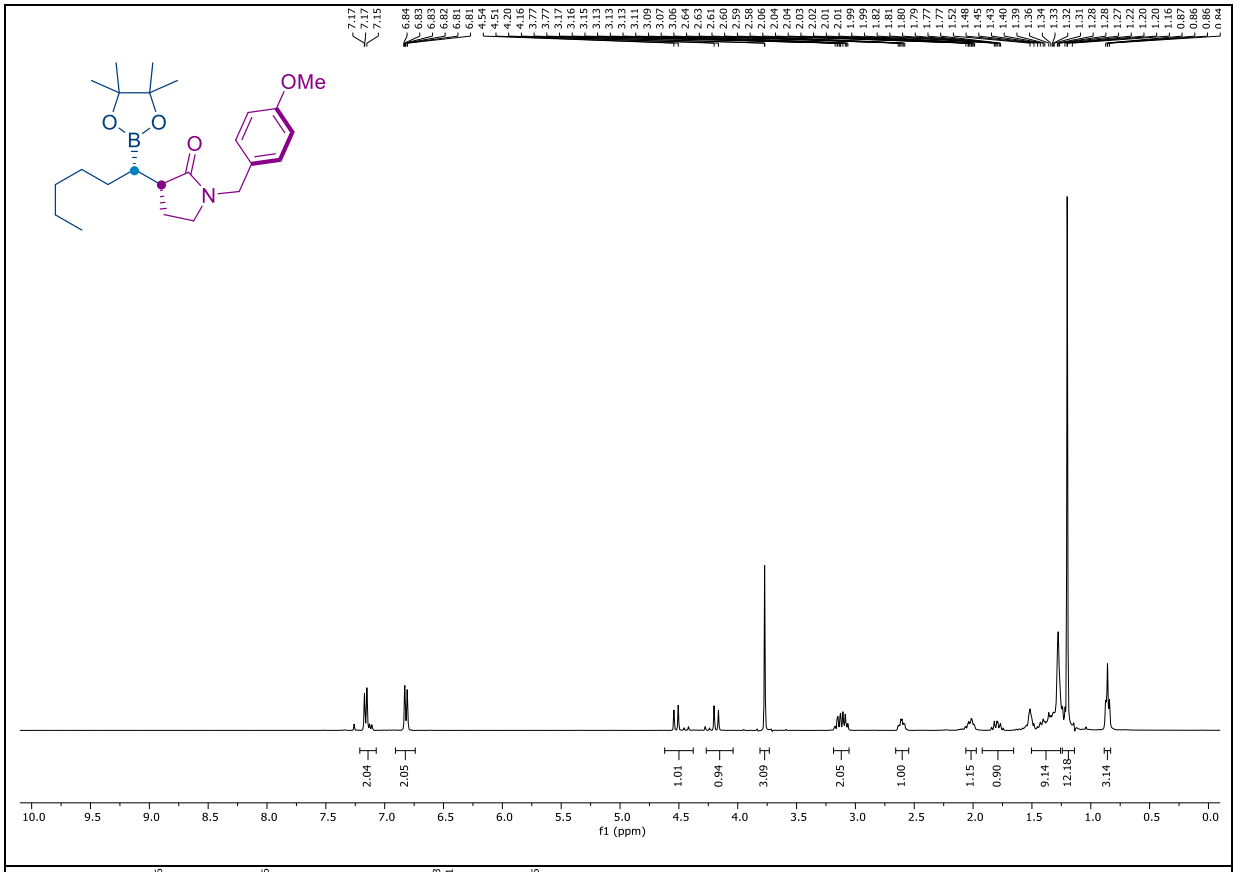

35.05
O
B
O
O
N
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

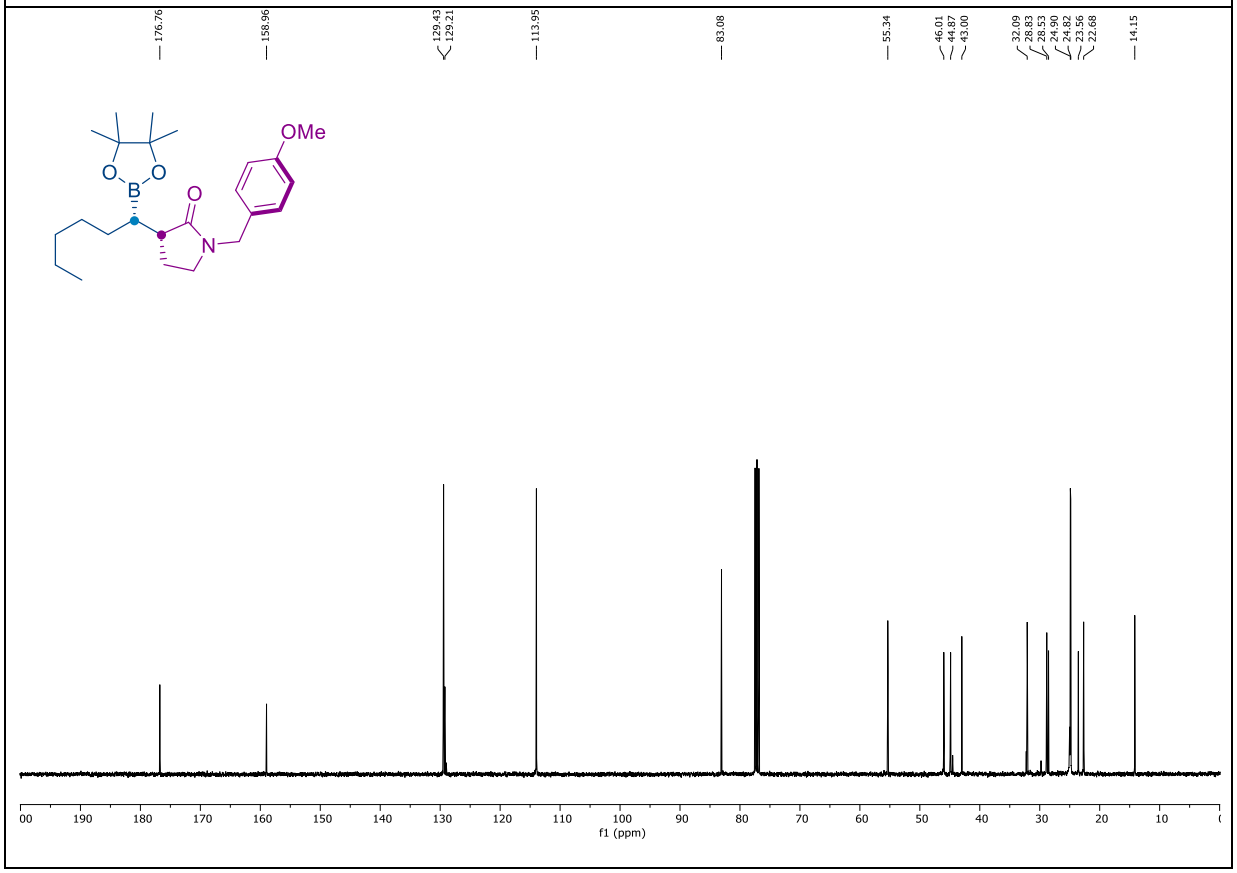
NMR spectra of 3an:

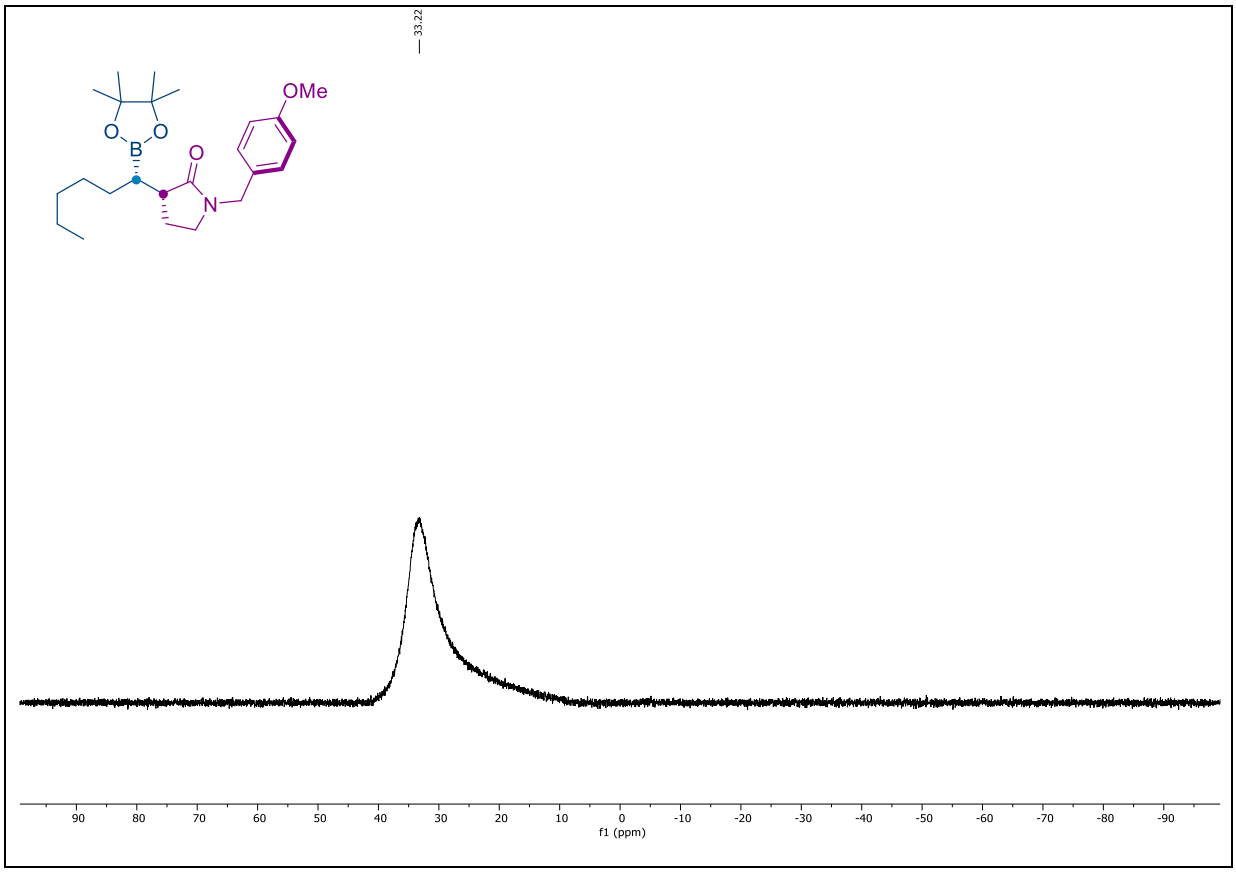



33.30
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

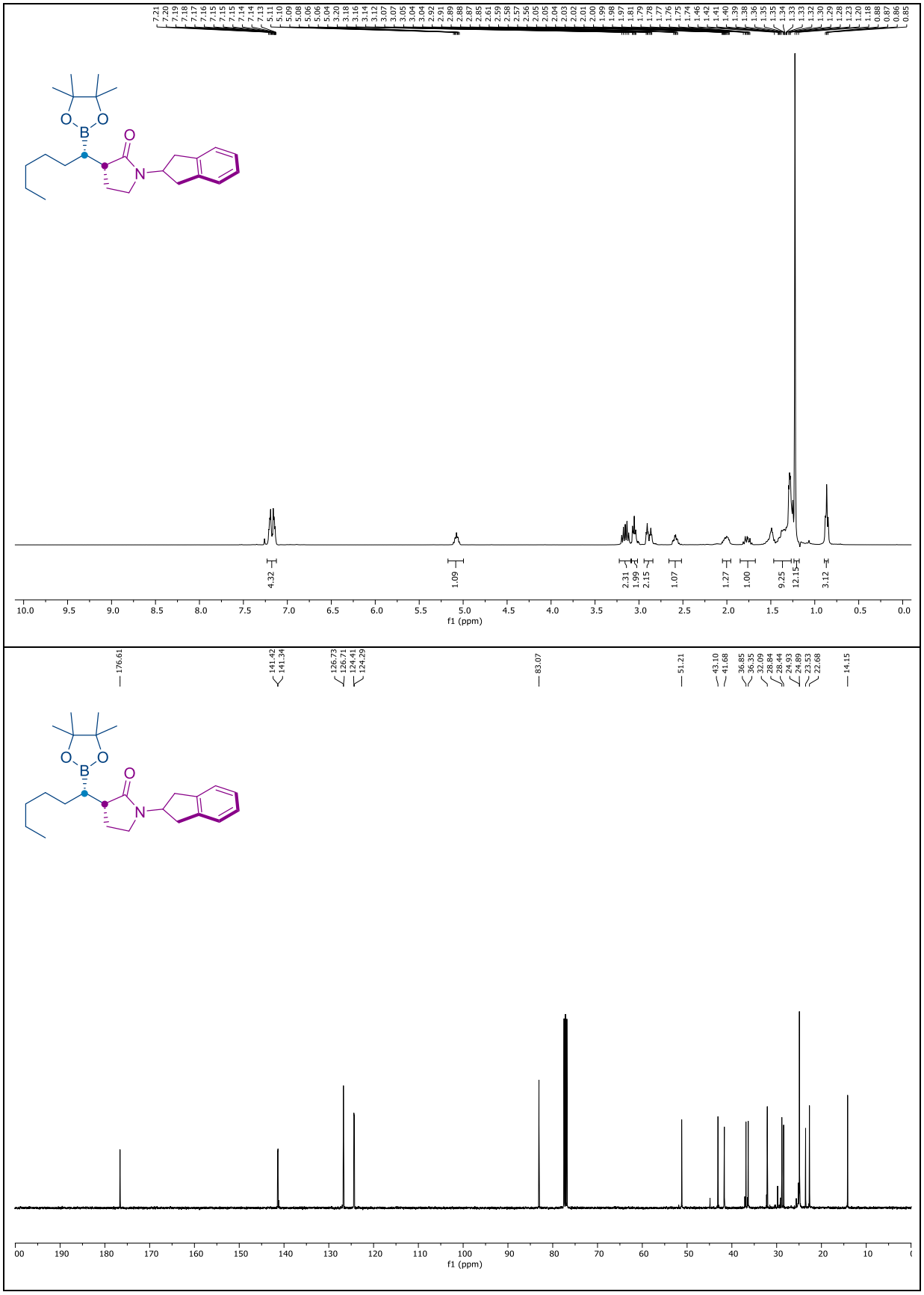
NMR spectra of 3ao:

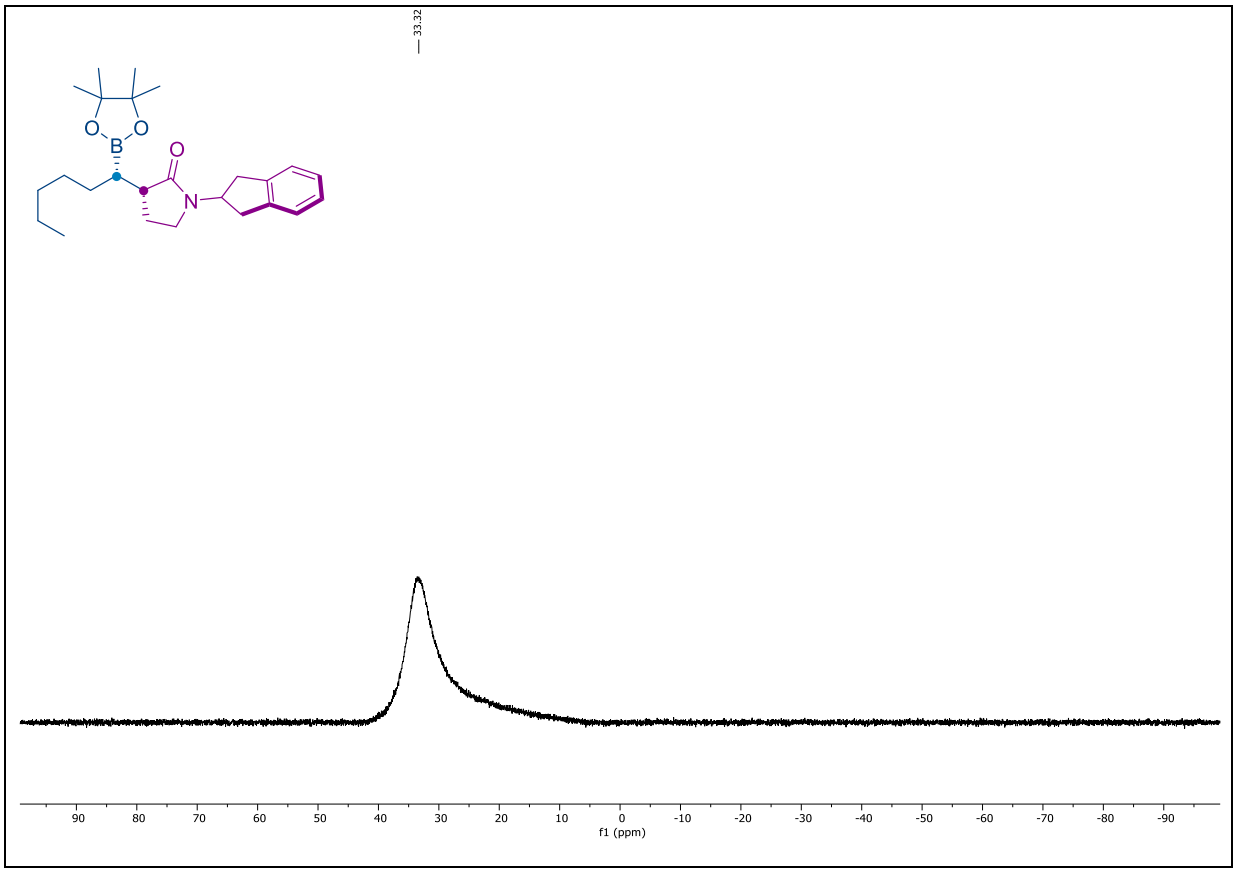




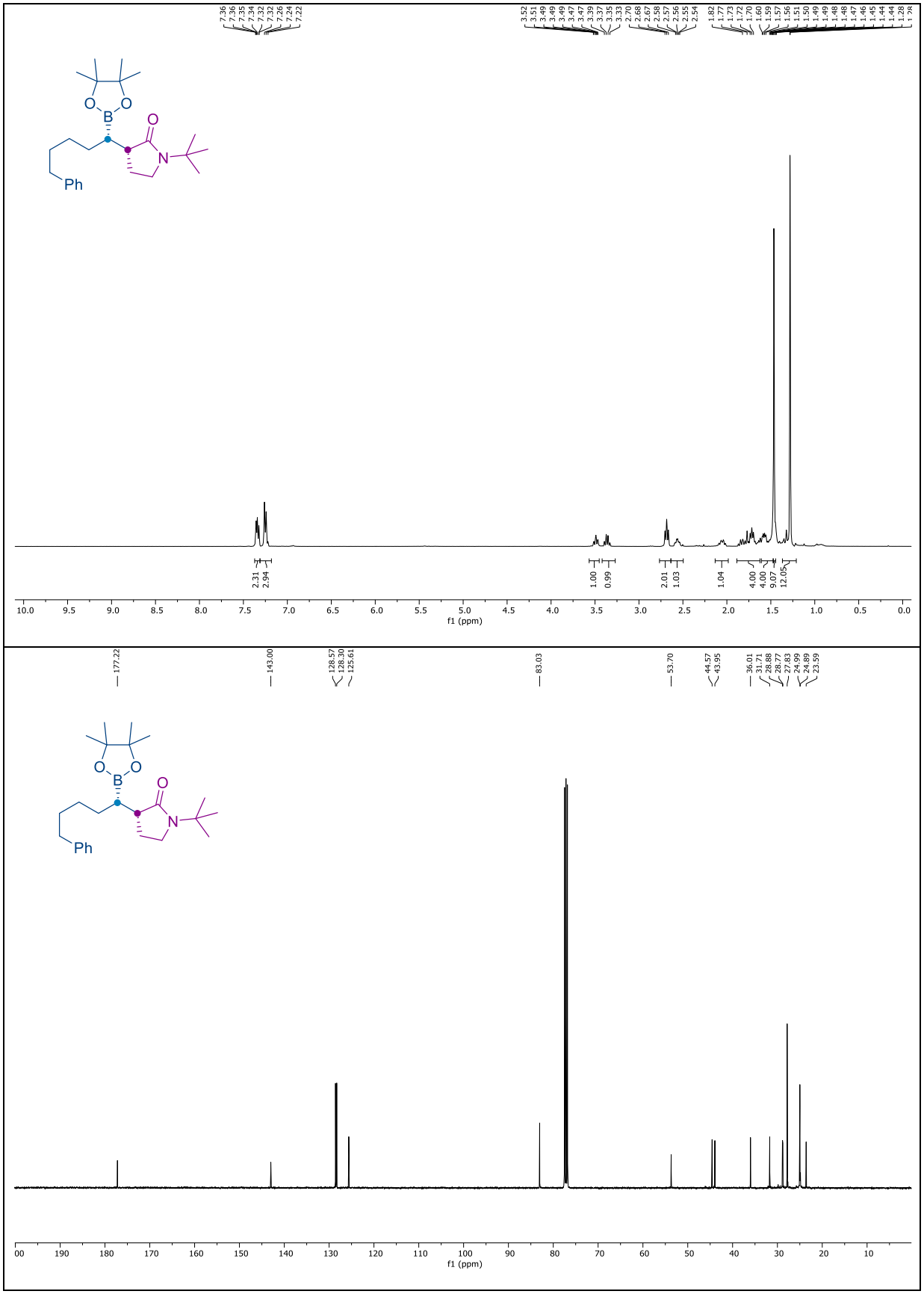

33.22
OMe
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

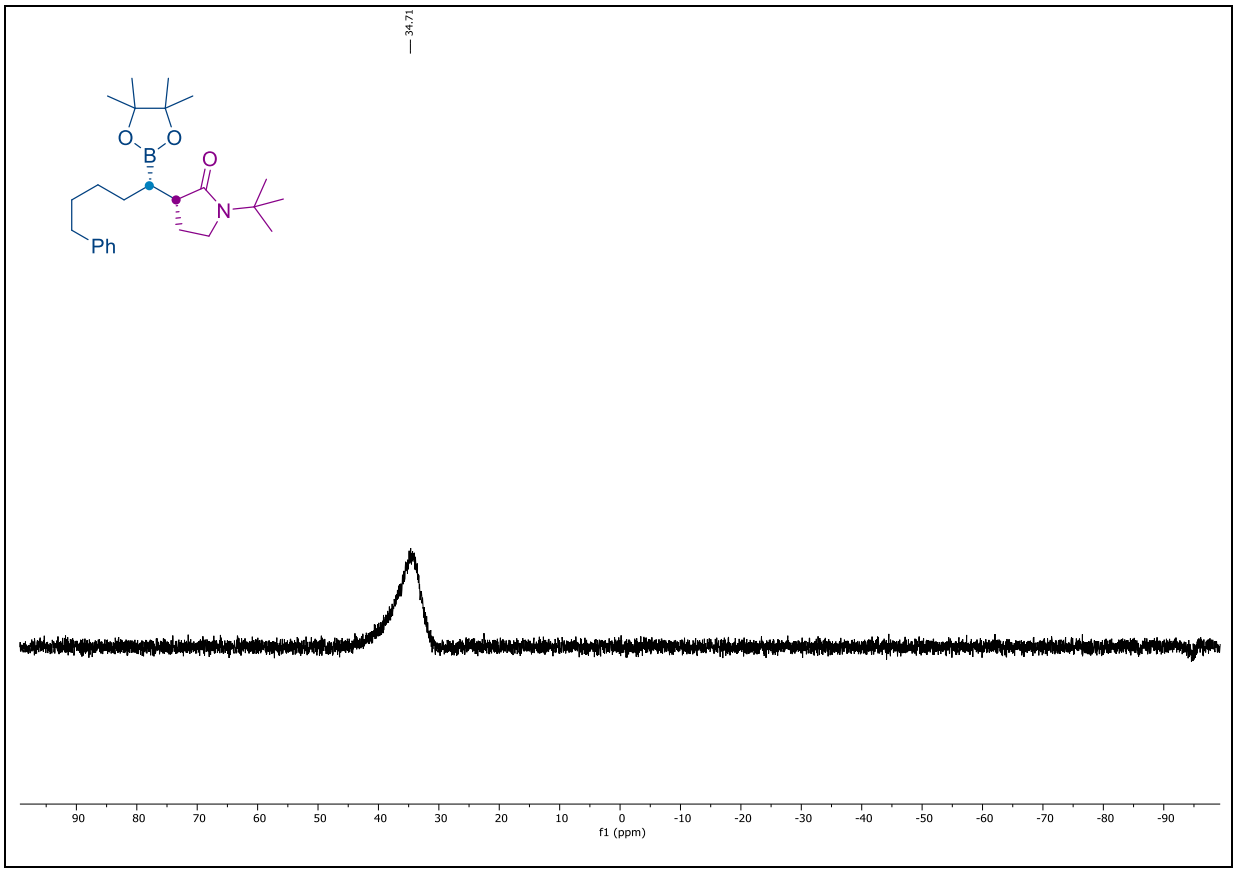
NMR spectra of 3ap:



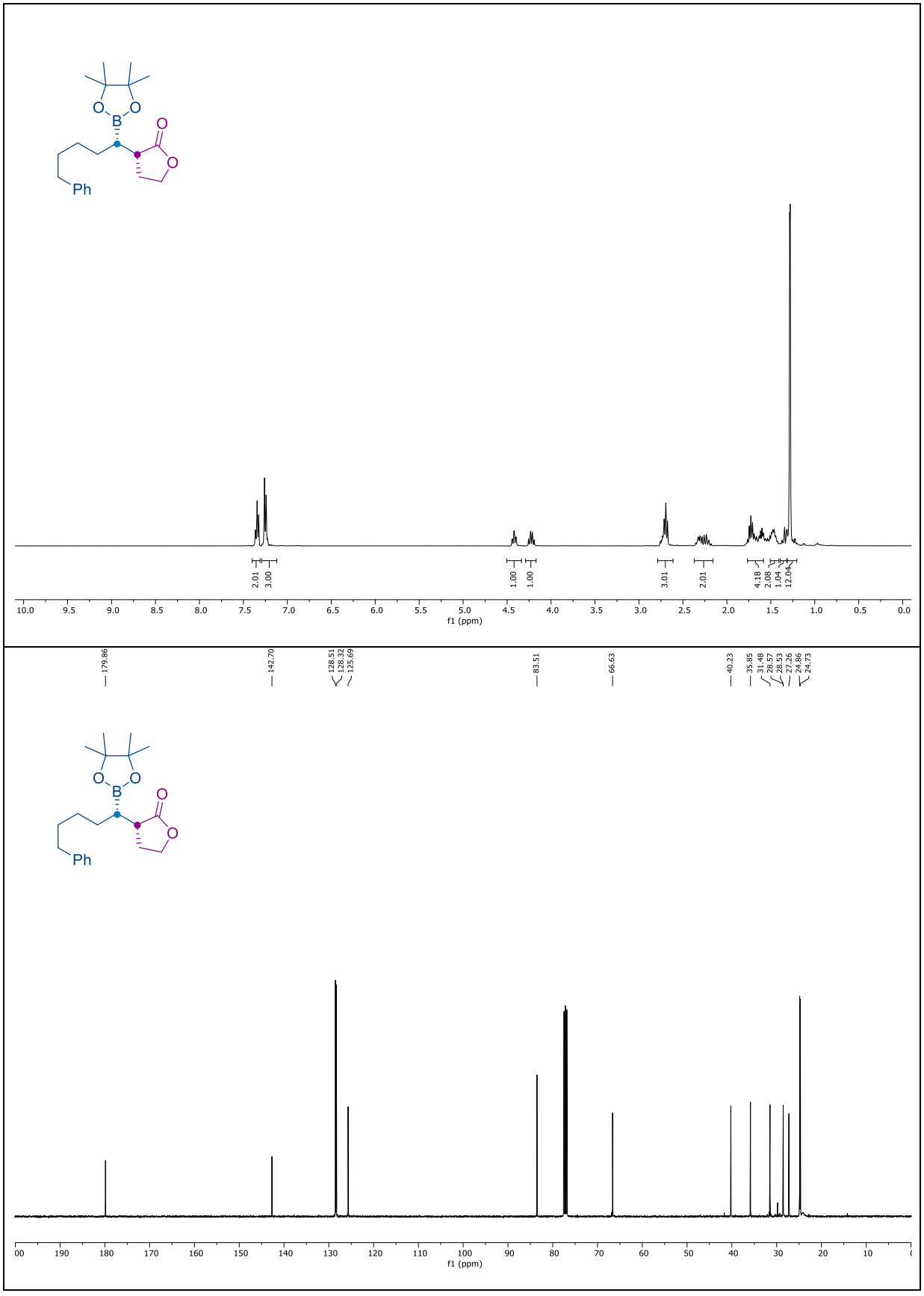

33.32
O
O
B
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

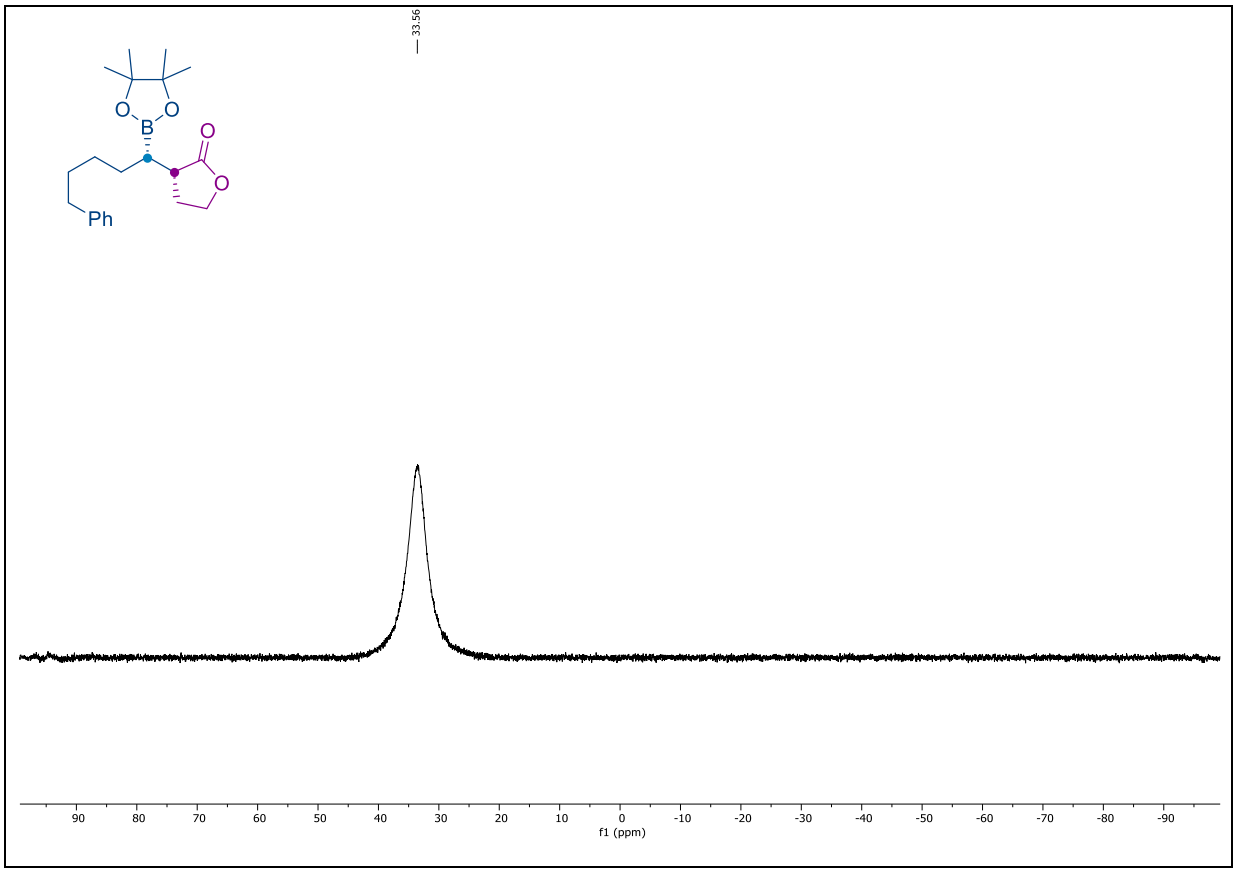
NMR spectra of 3dq:



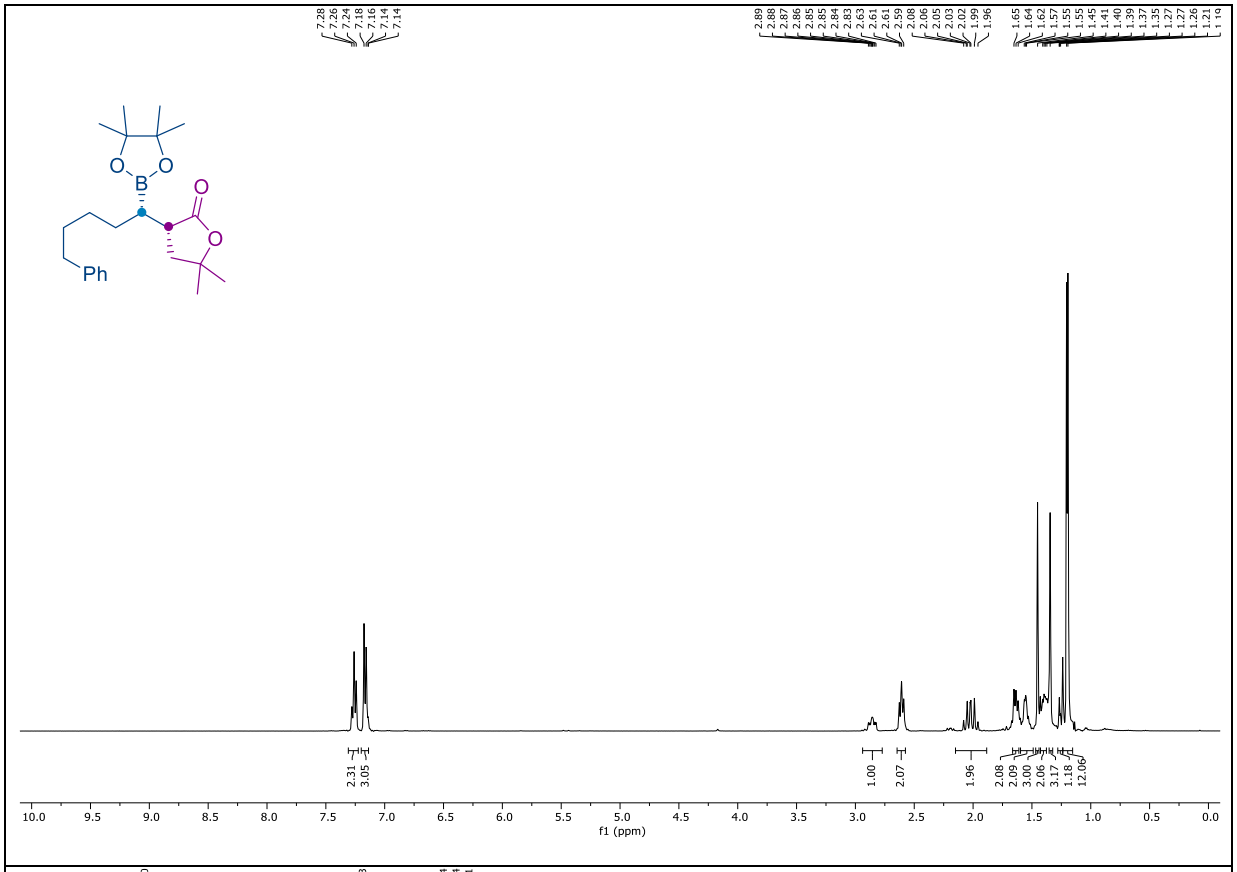

34.71
O
B
O
O
N
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

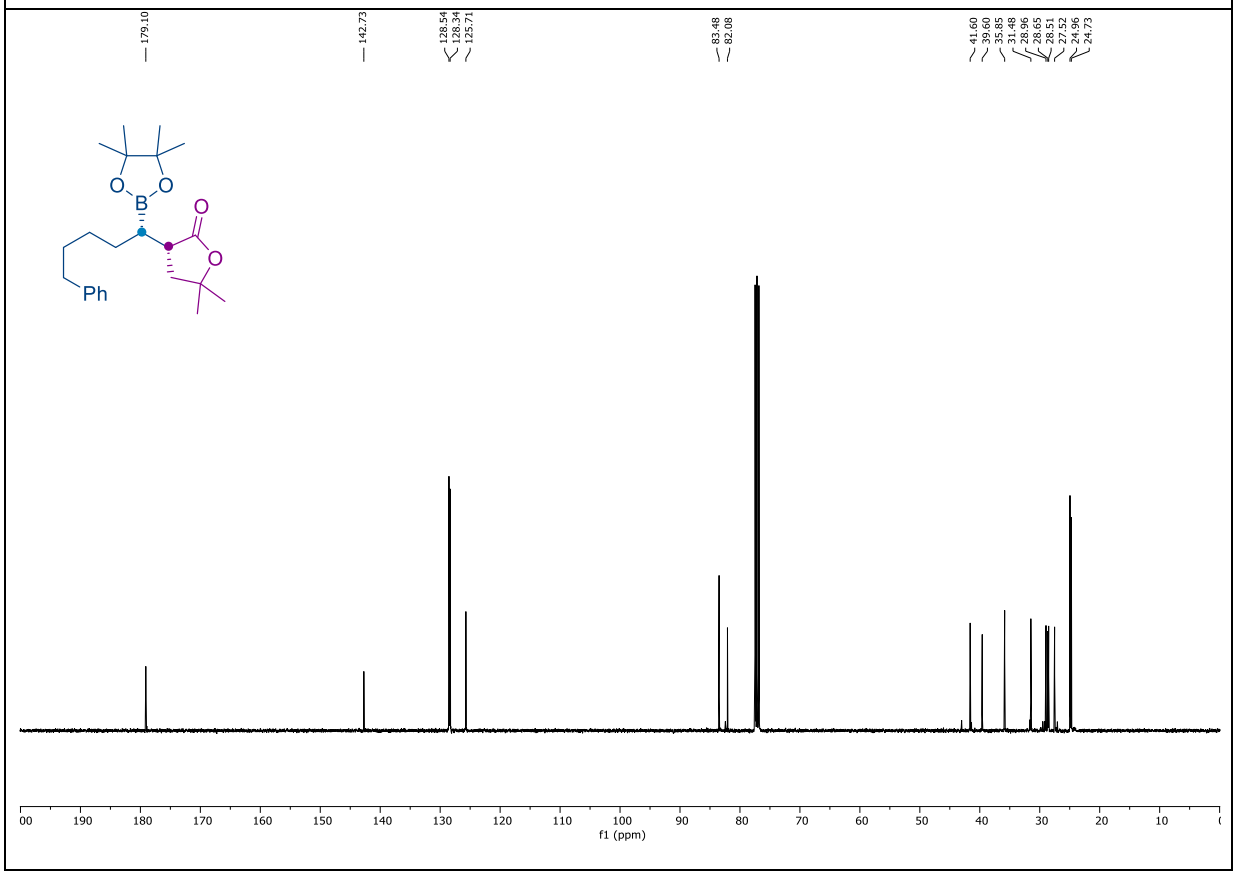
NMR spectra of 3dr:

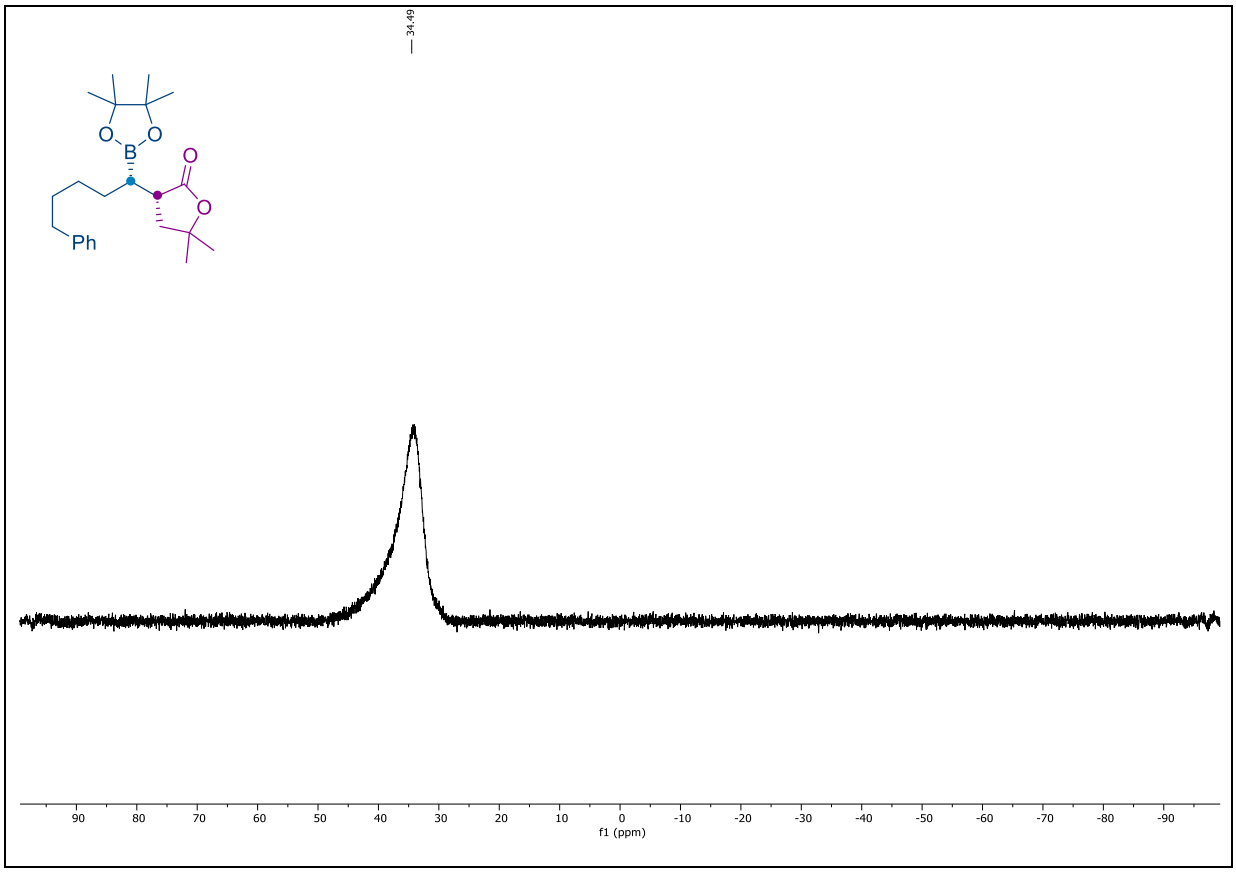



33.56
O
B
O
O
O
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

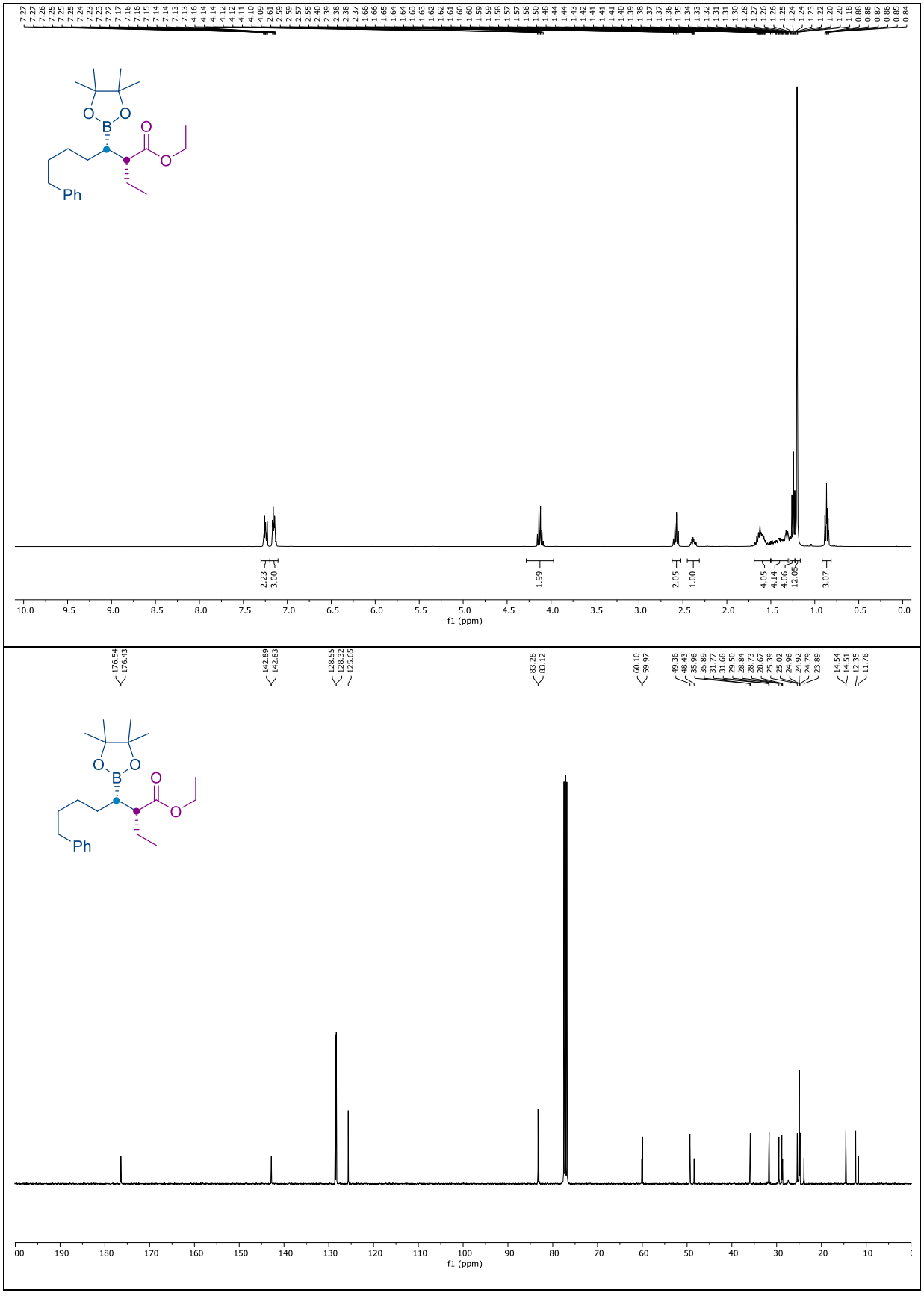
NMR spectra of 3ds:

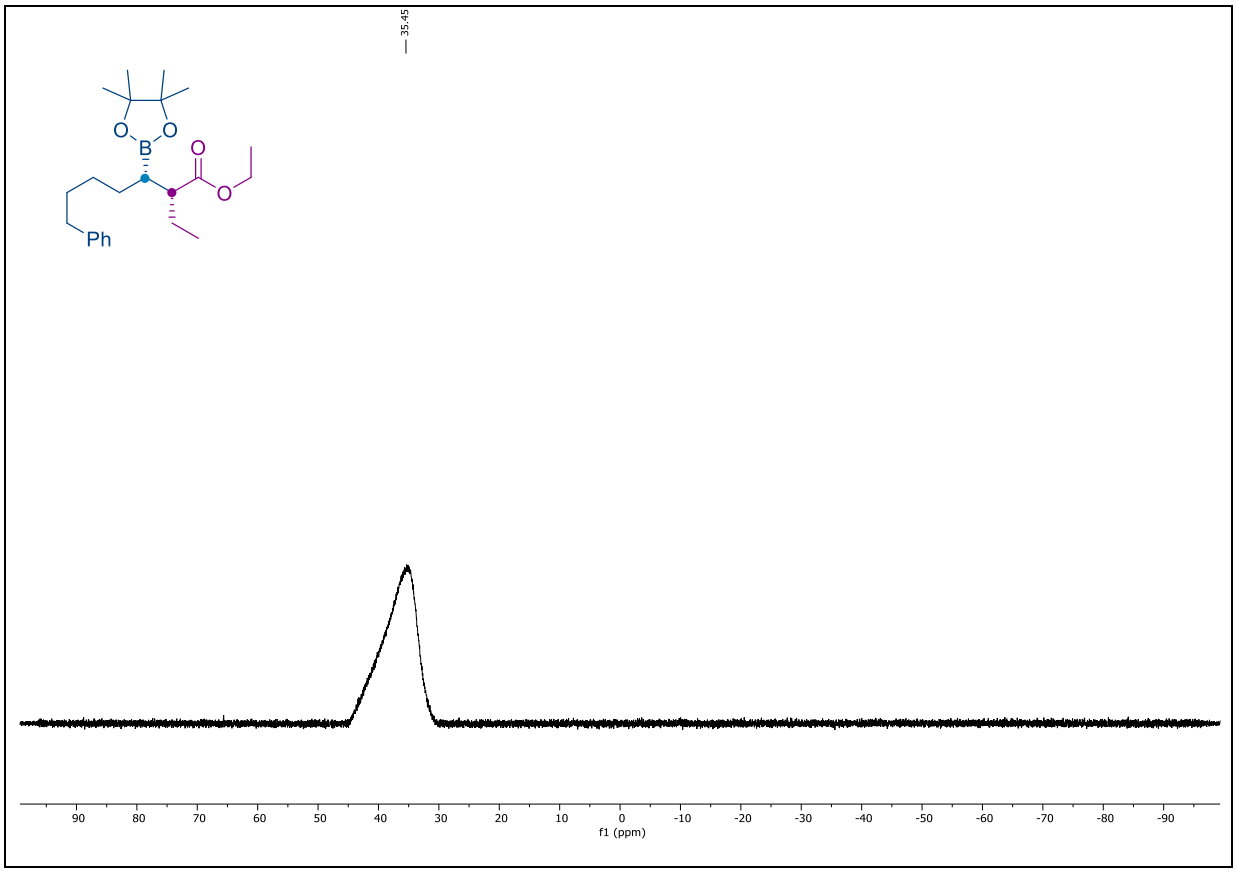




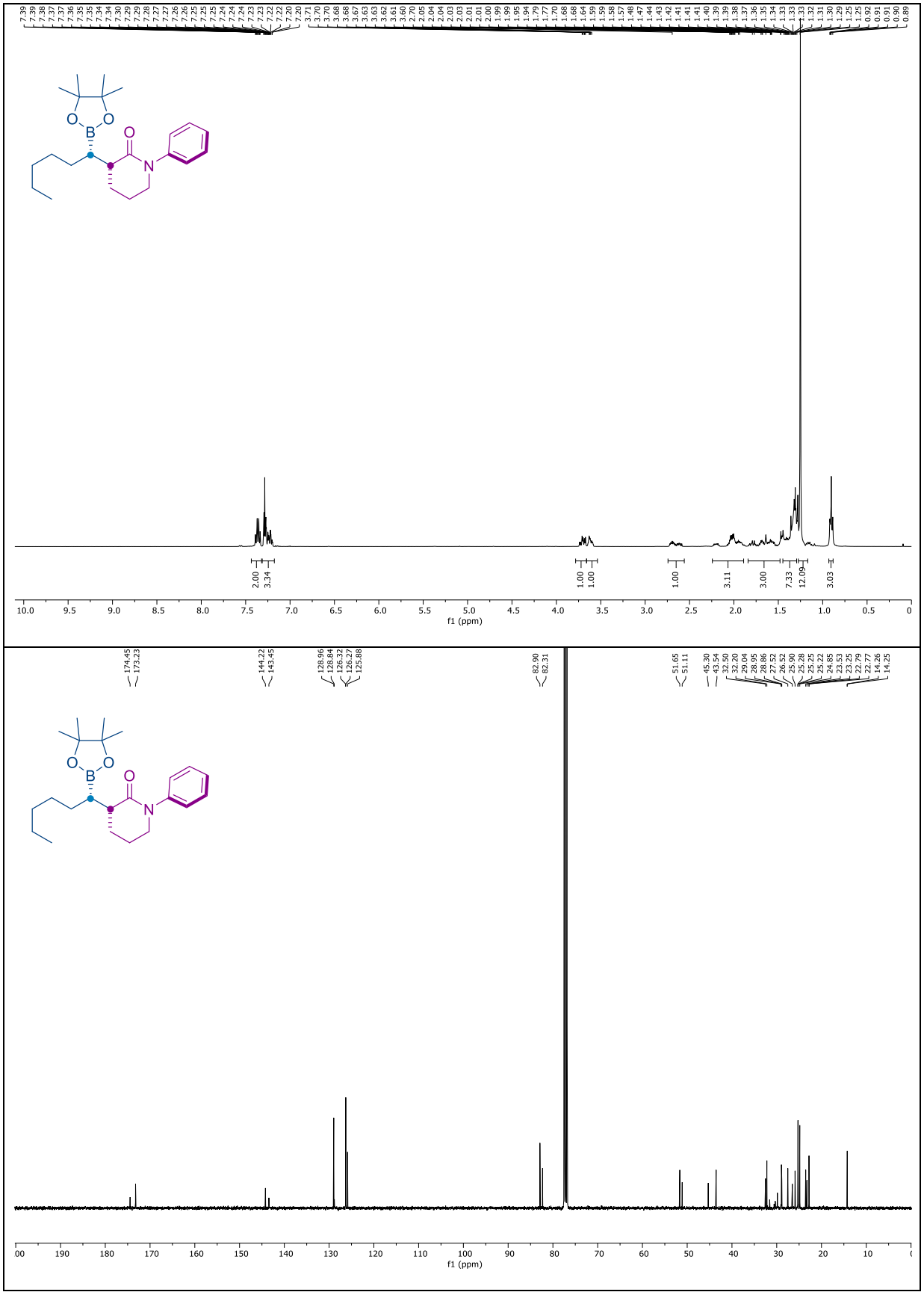

34.49
O
B
O
O
O
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

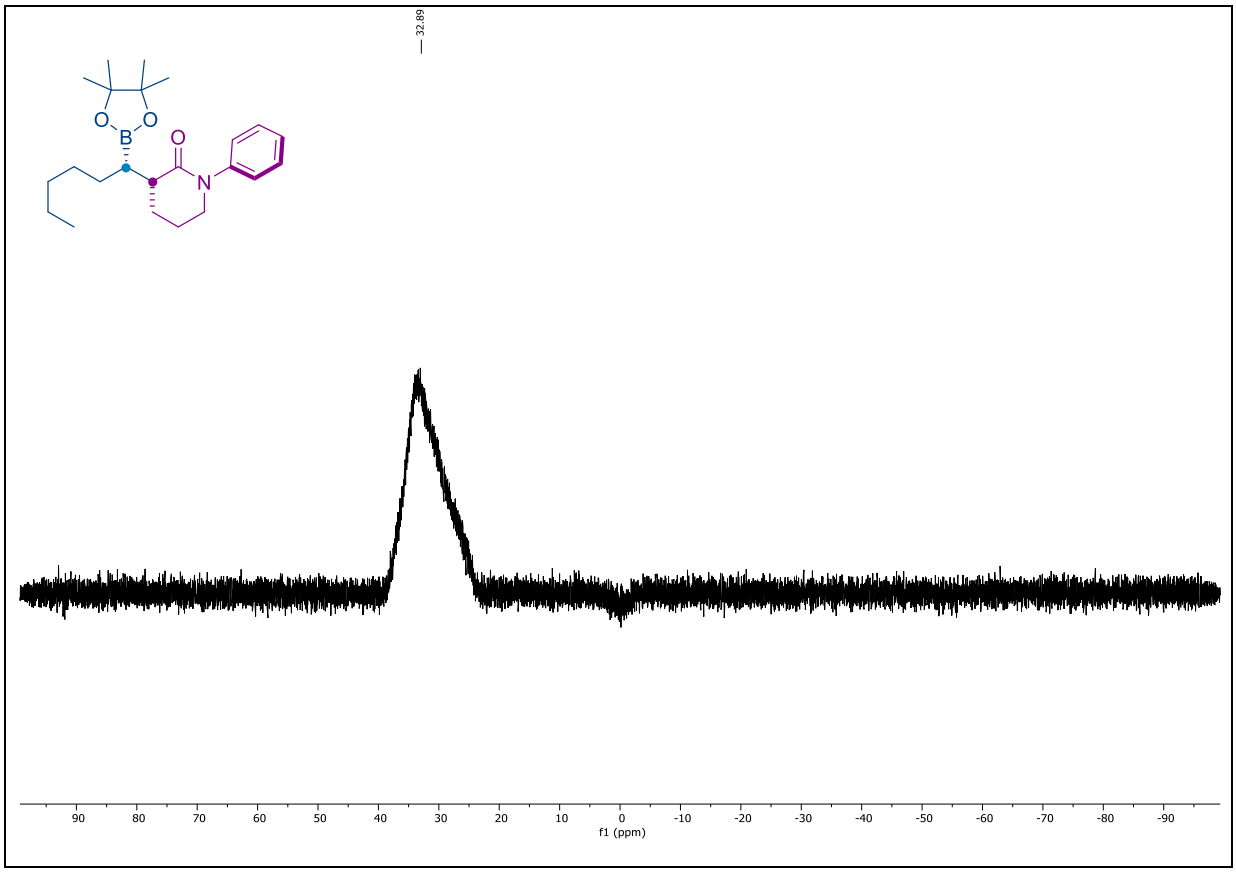
NMR spectra of 3dt:



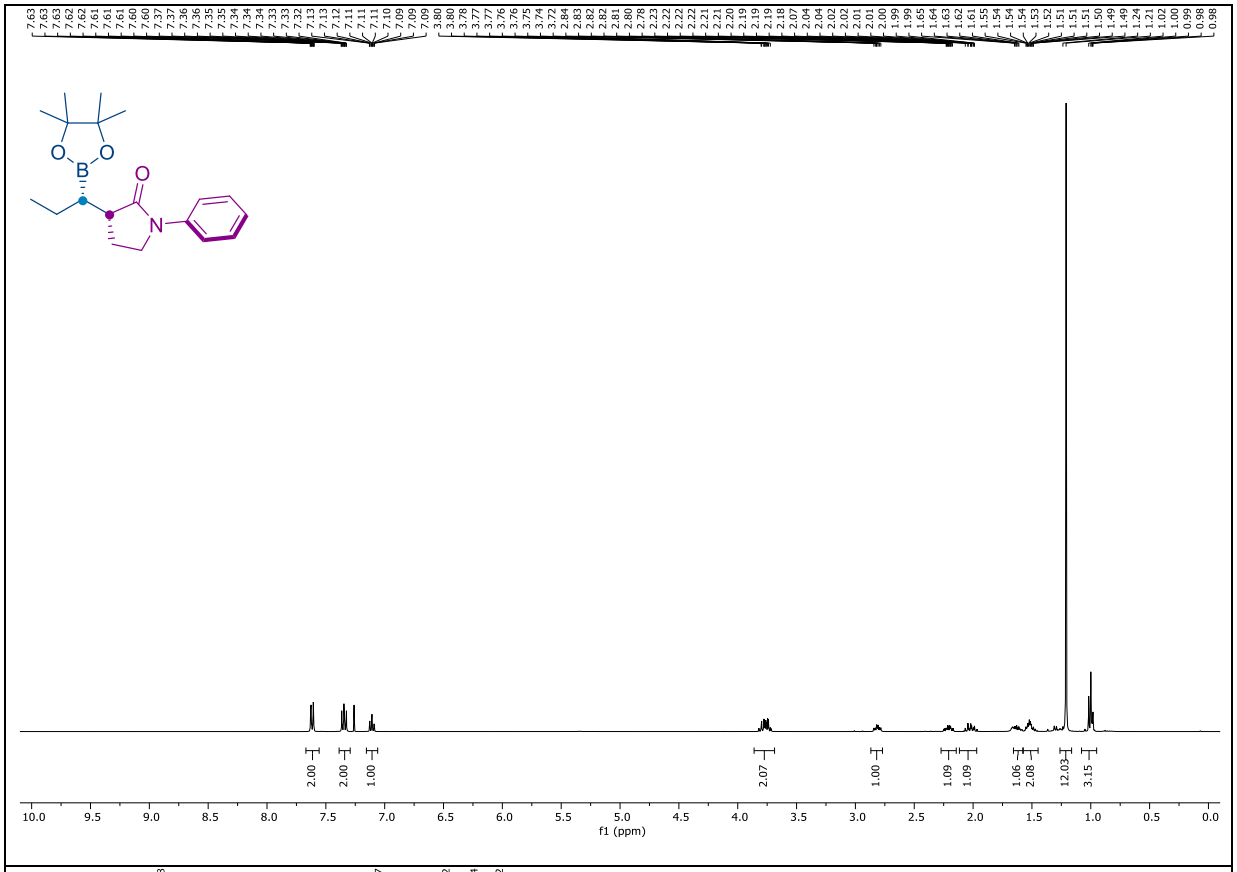

35.45
O
O
B
O
O
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

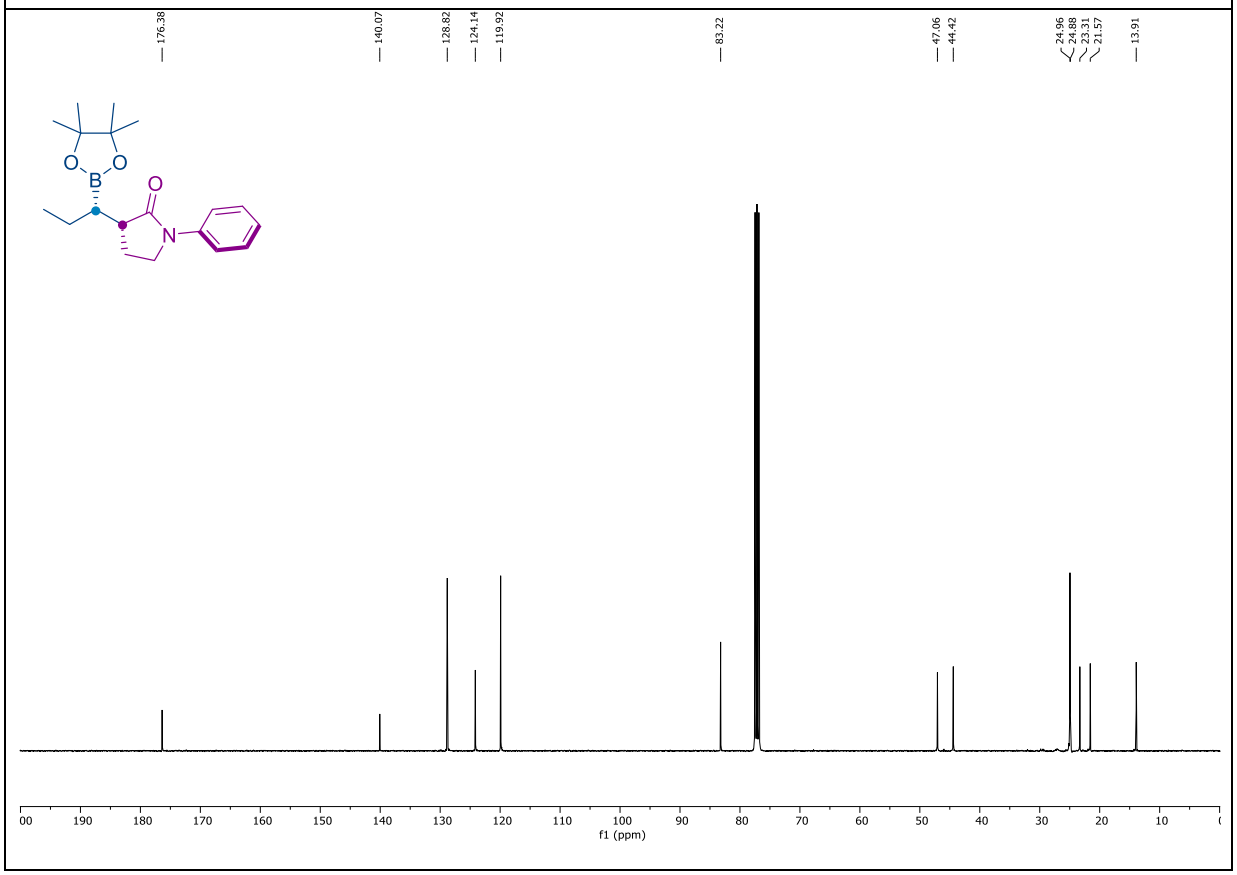
NMR spectra of 3aw:

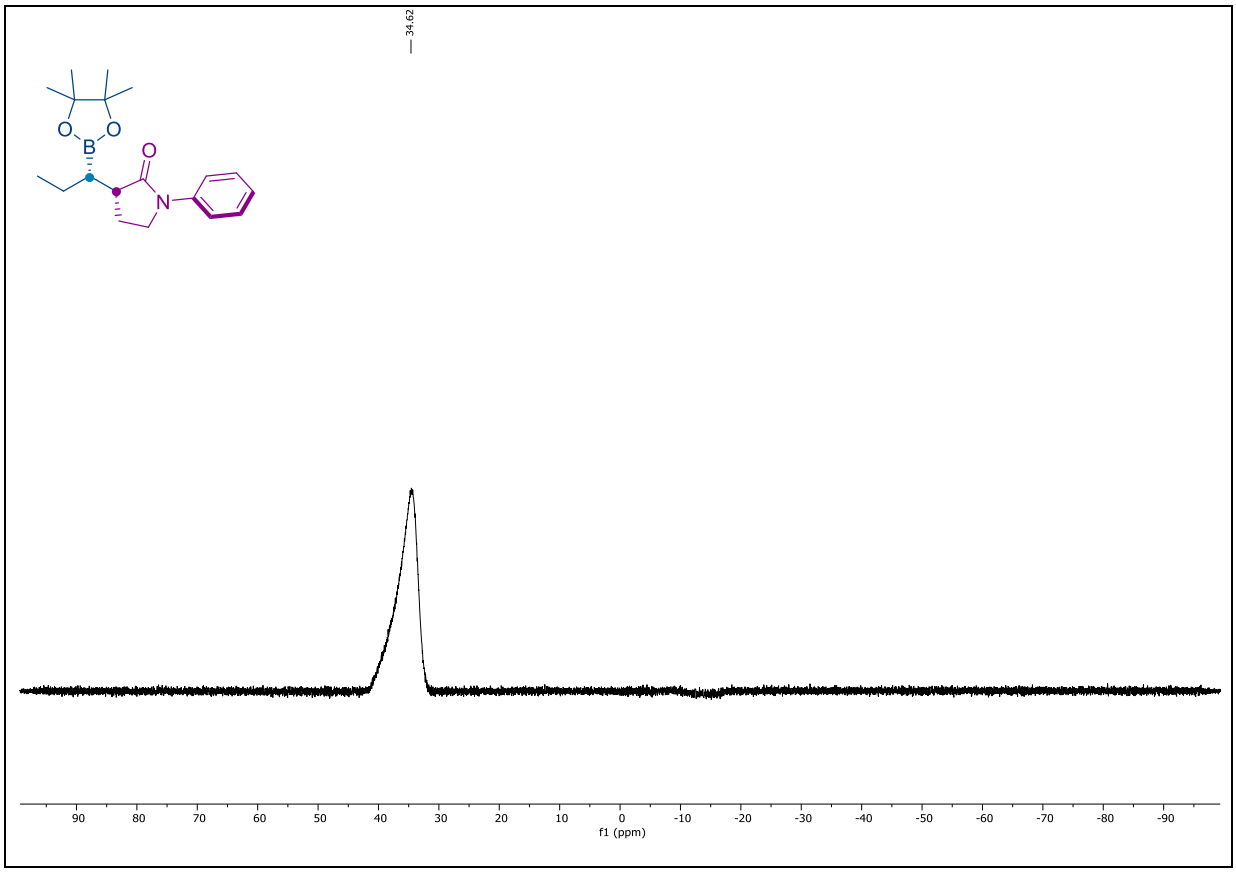



32.89
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

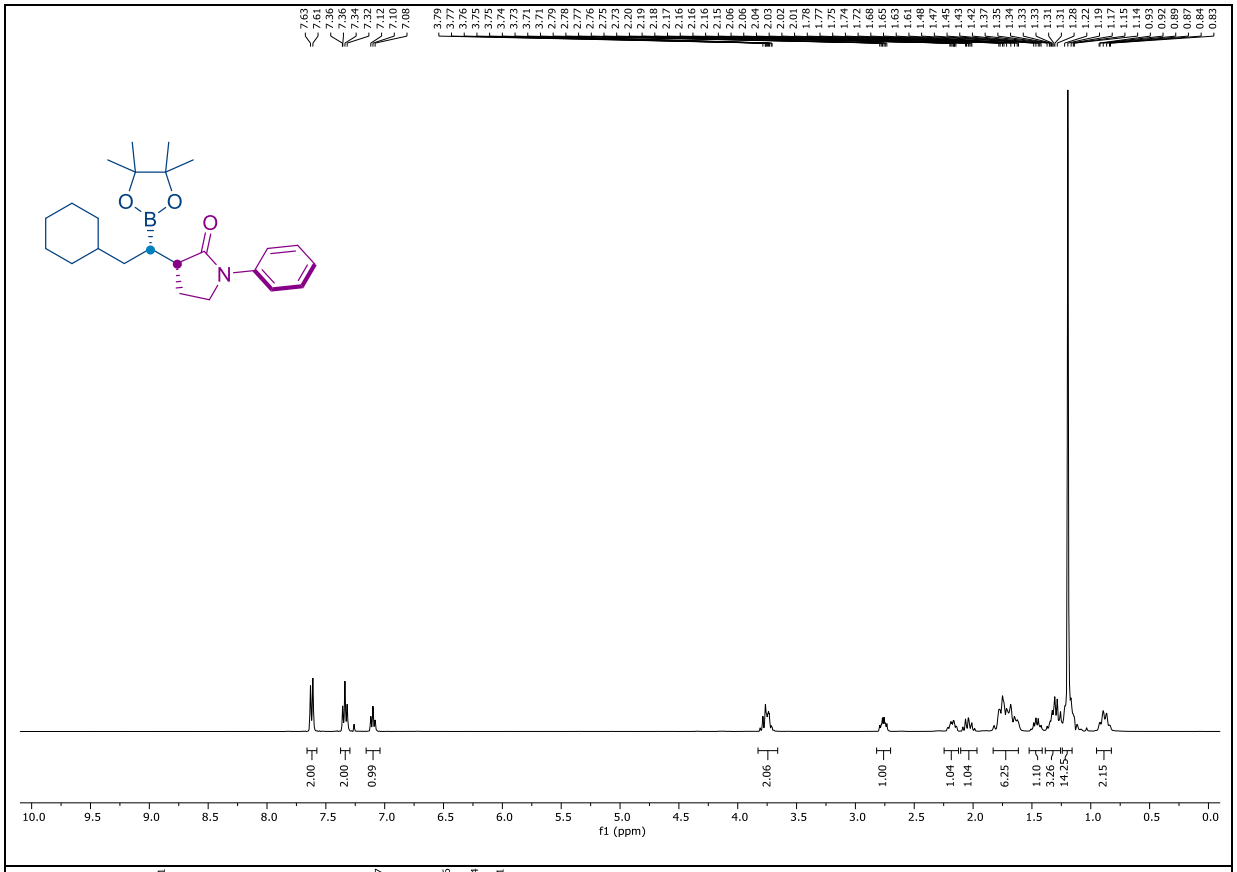
NMR spectra of 3ba:

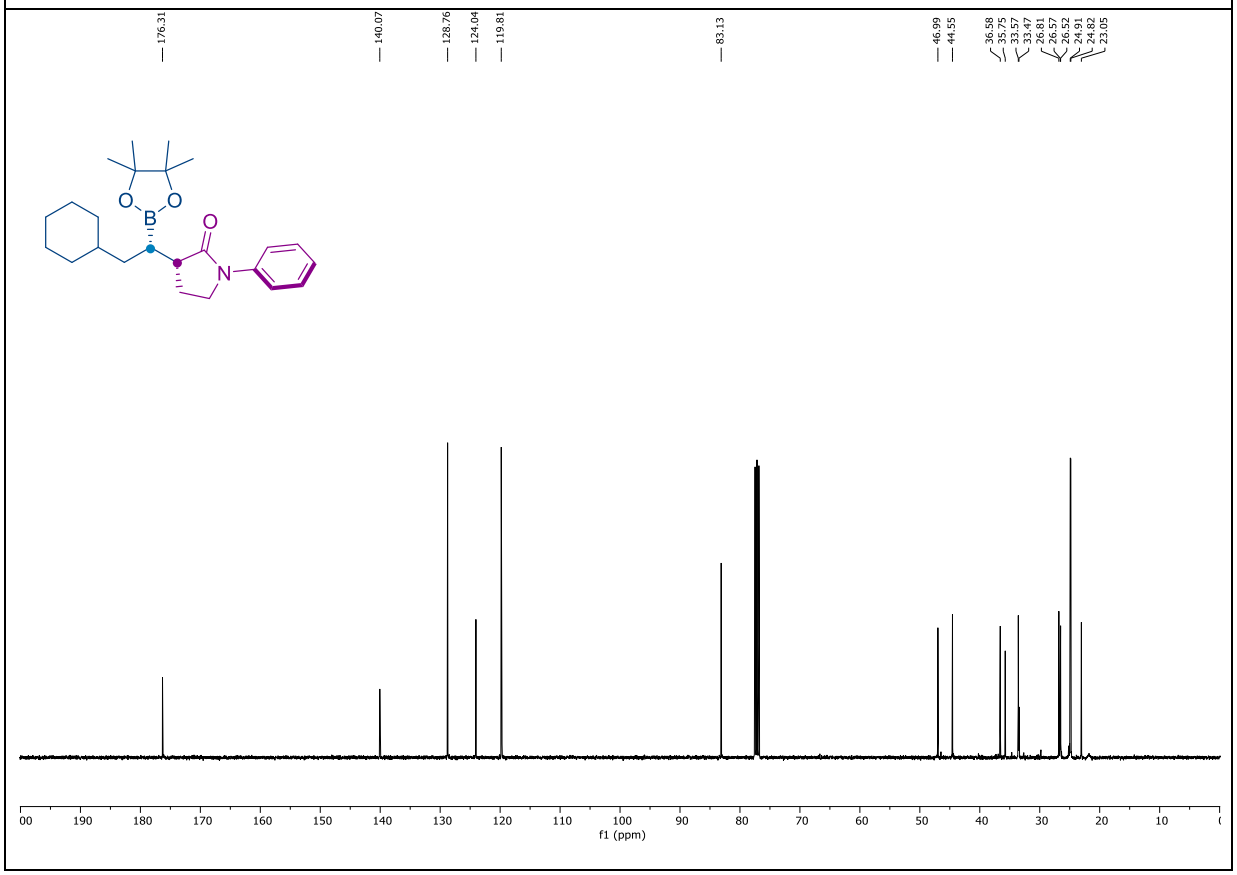


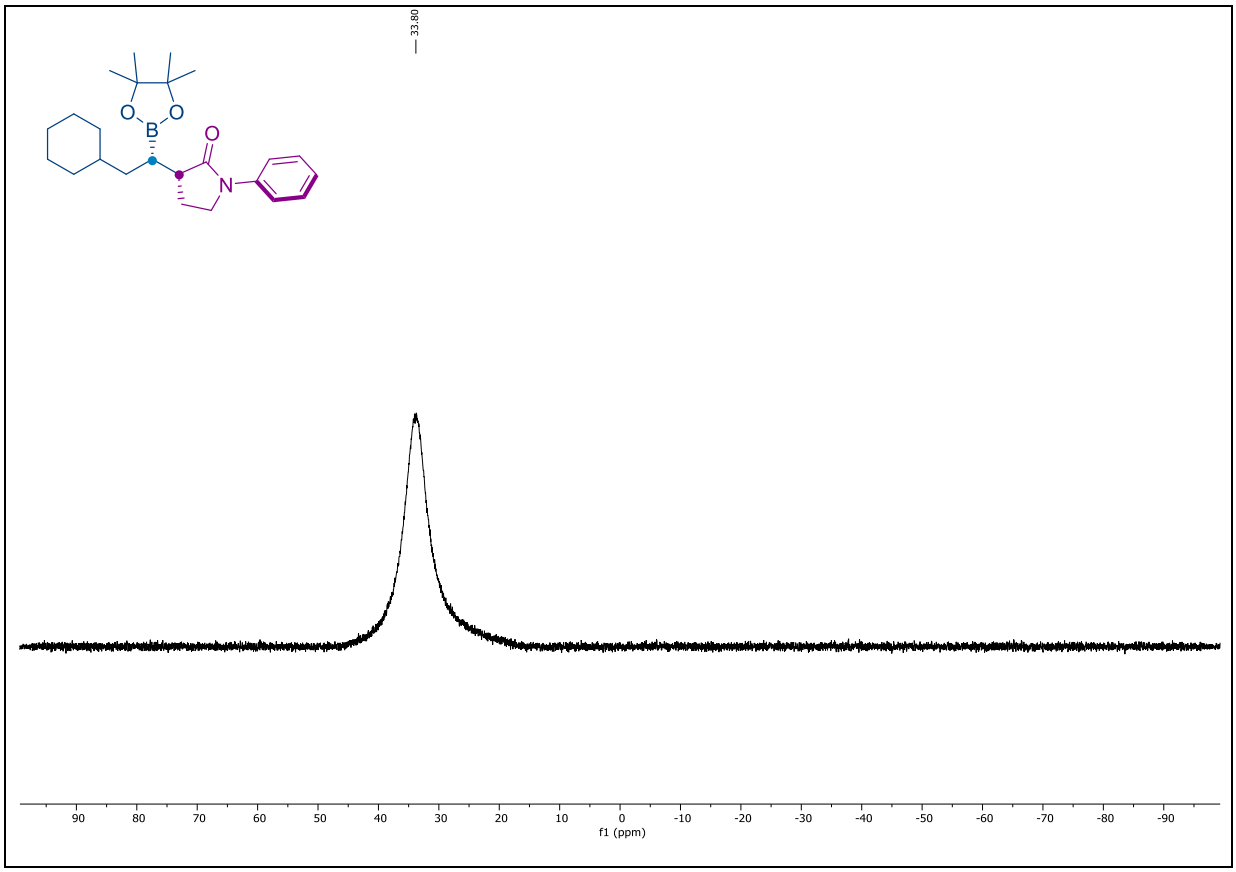



34.62
O
O
B
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

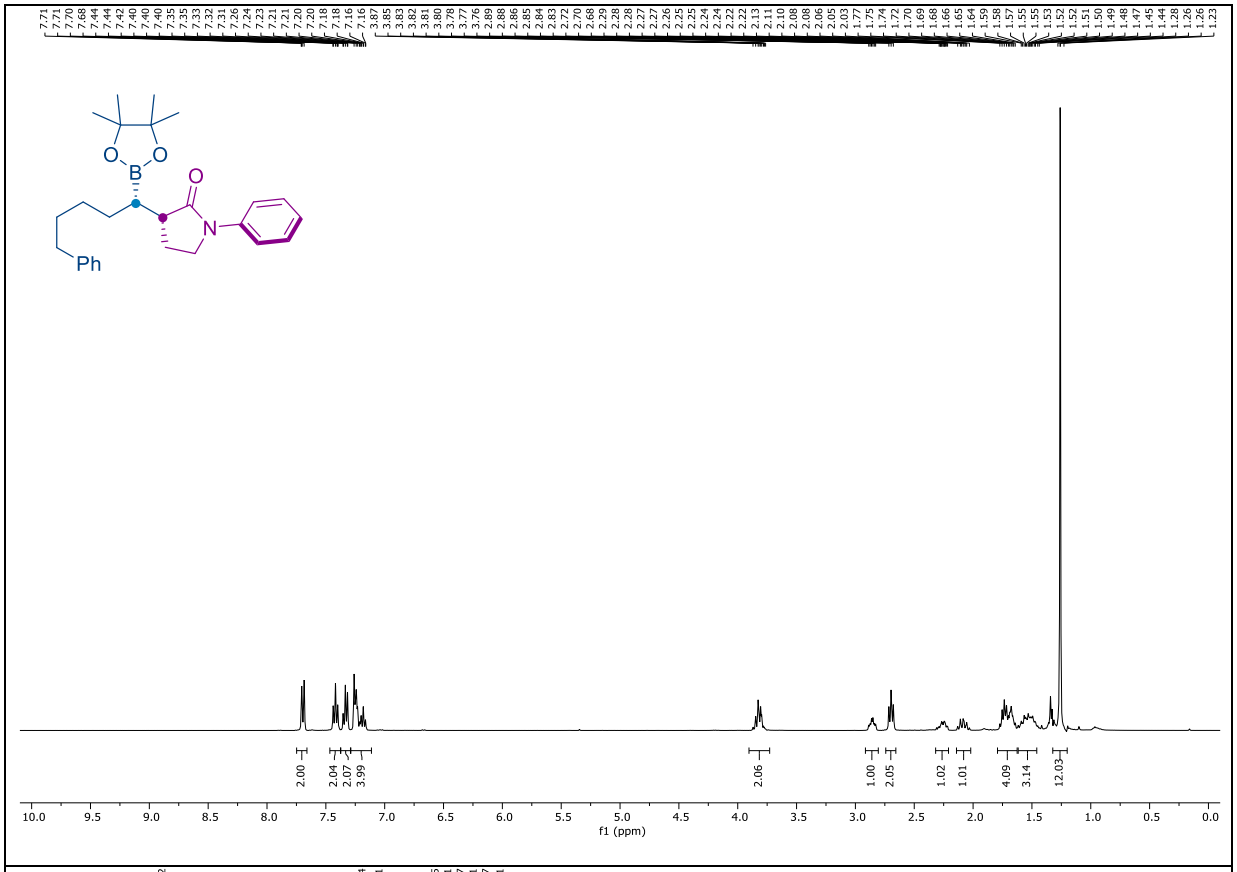
NMR spectra of 3ca:

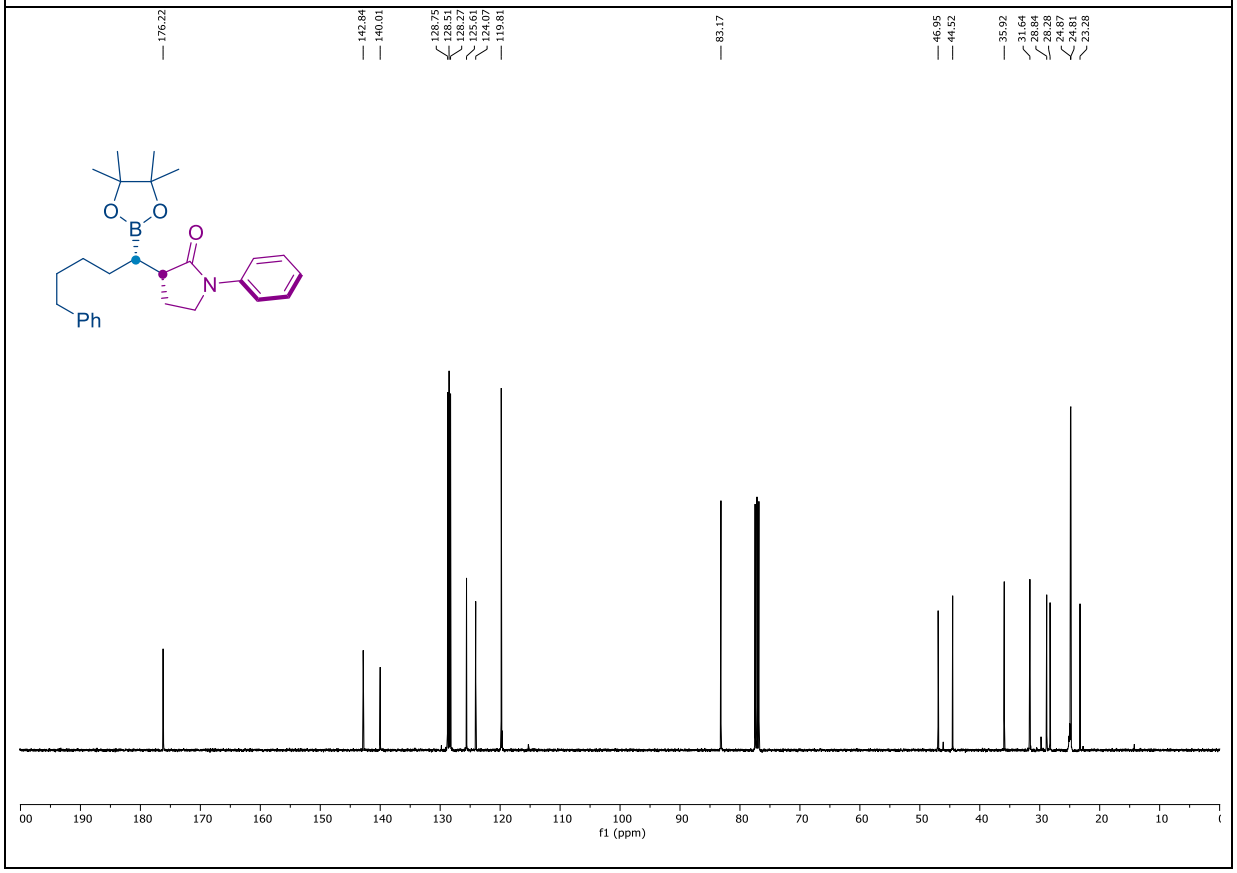


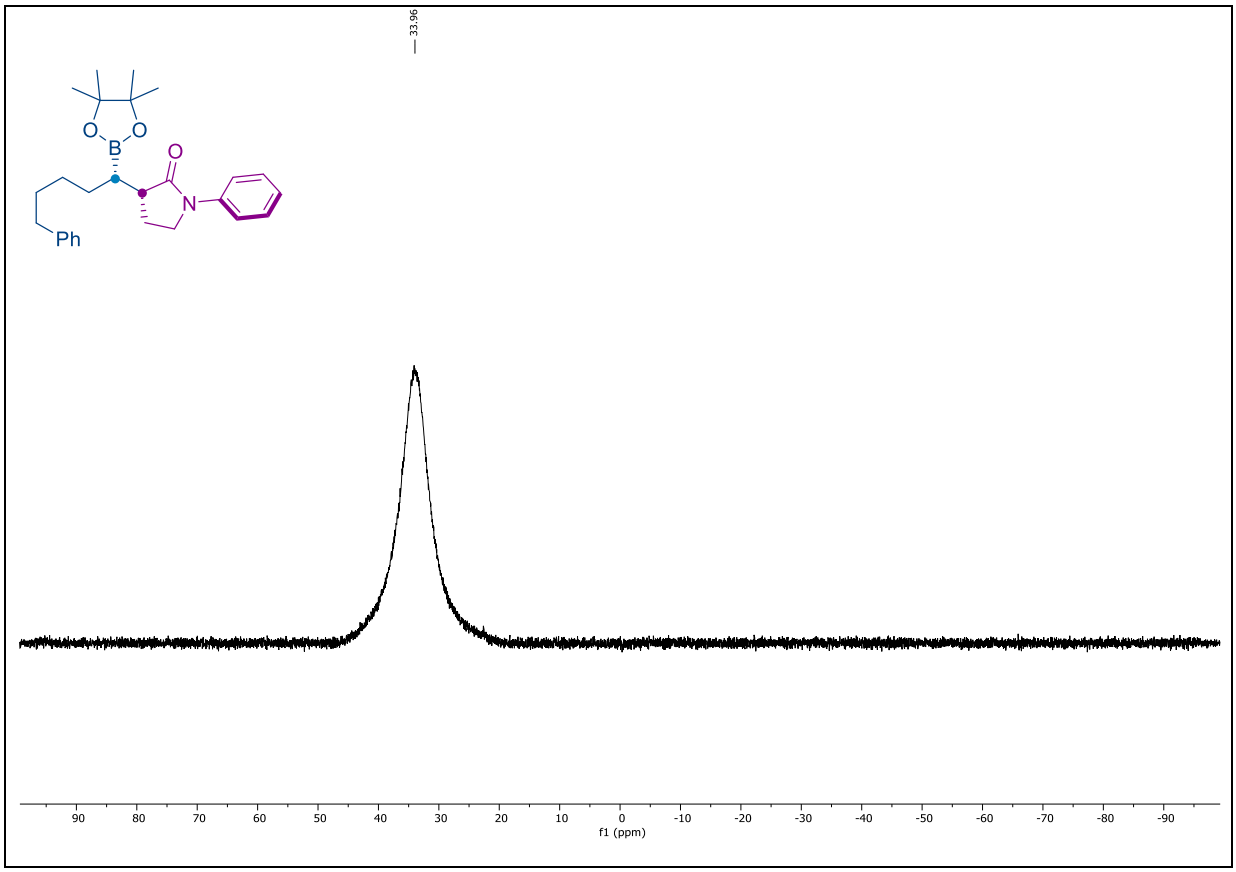



33.80
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

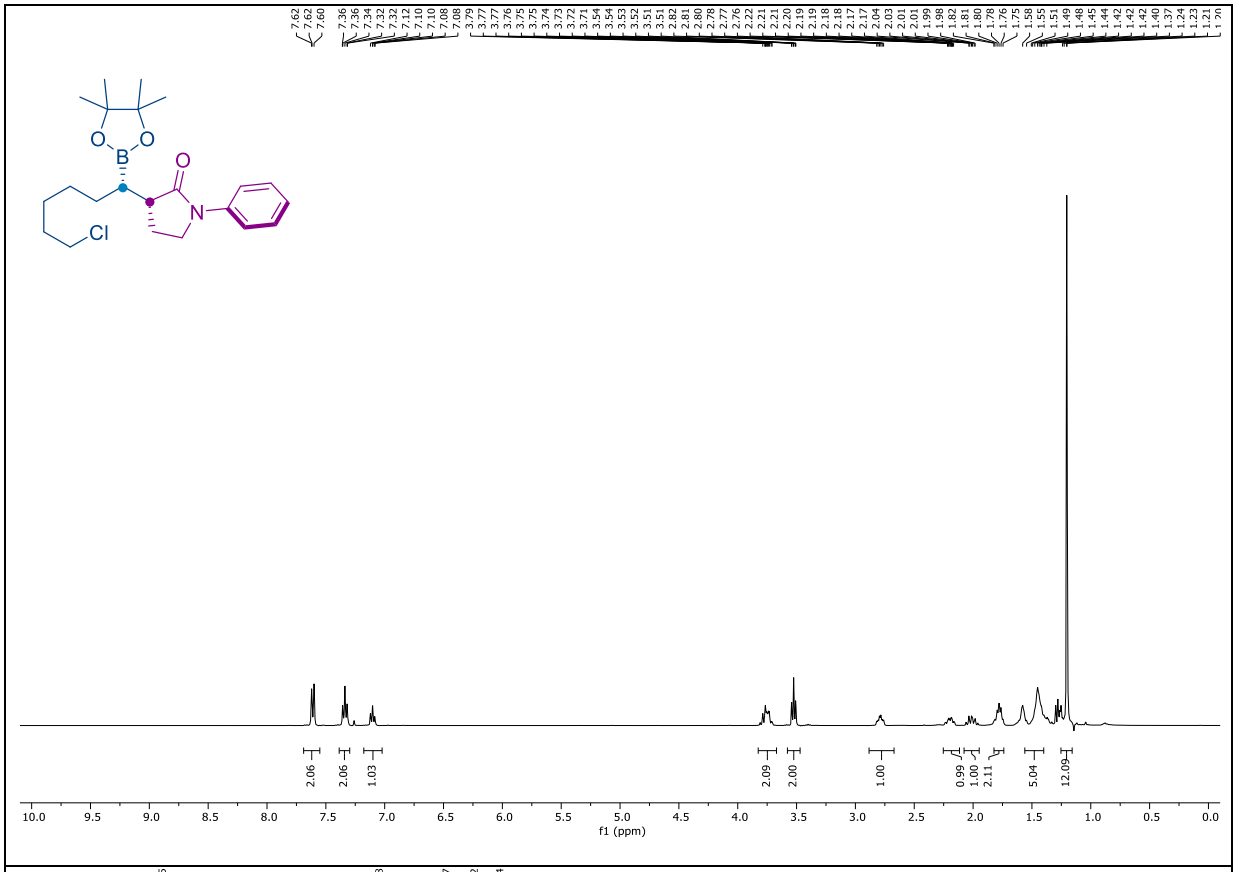
NMR spectra of 3da:

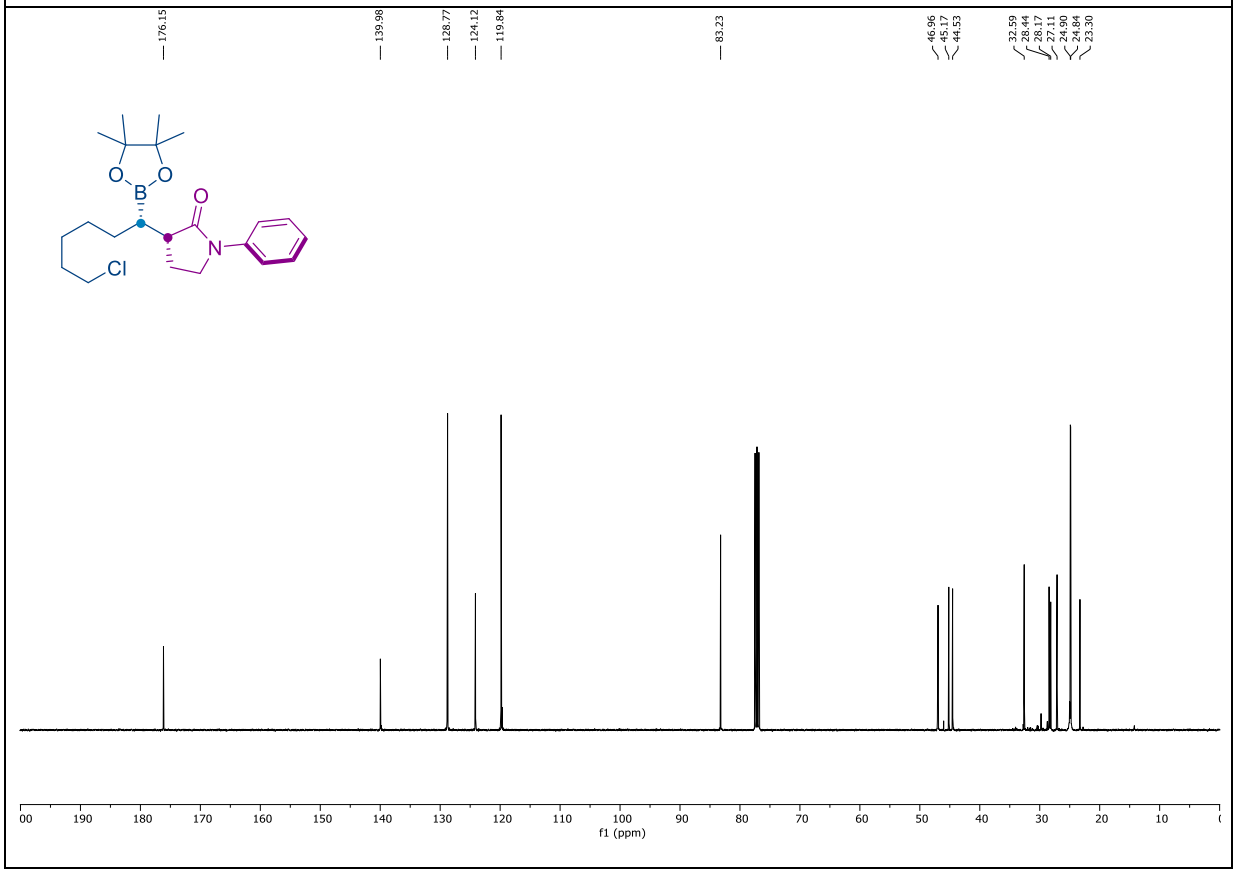


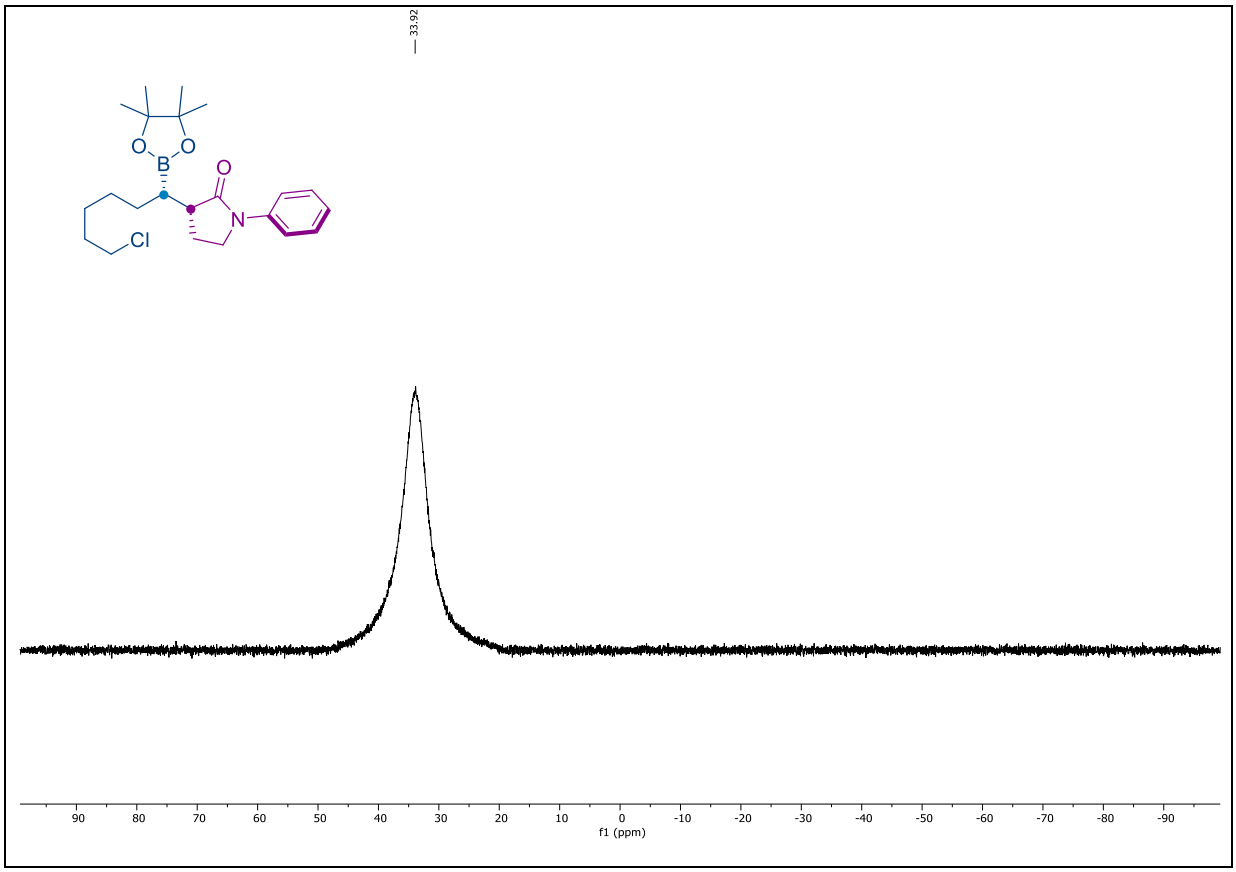



33.96
O
O
B
O
N
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

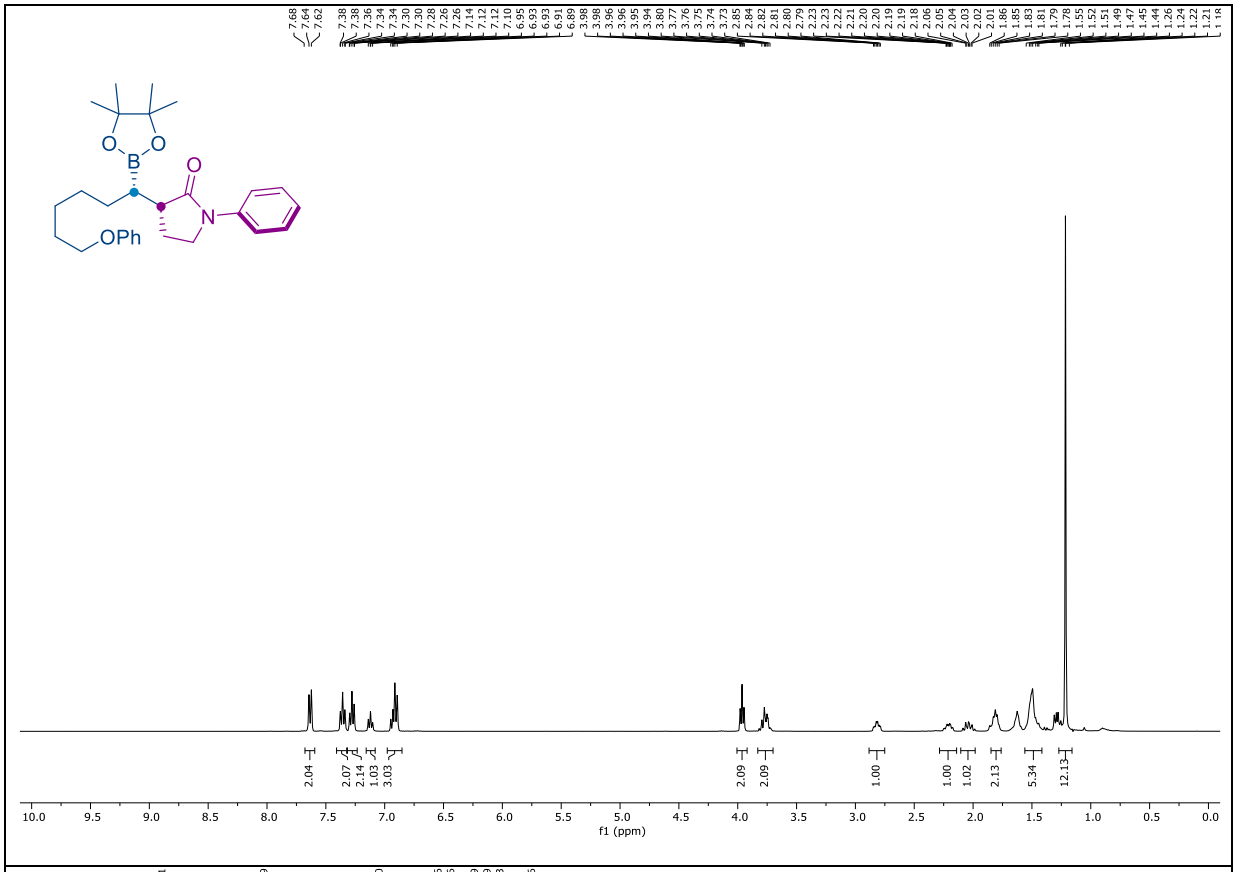
NMR spectra of 3ea:

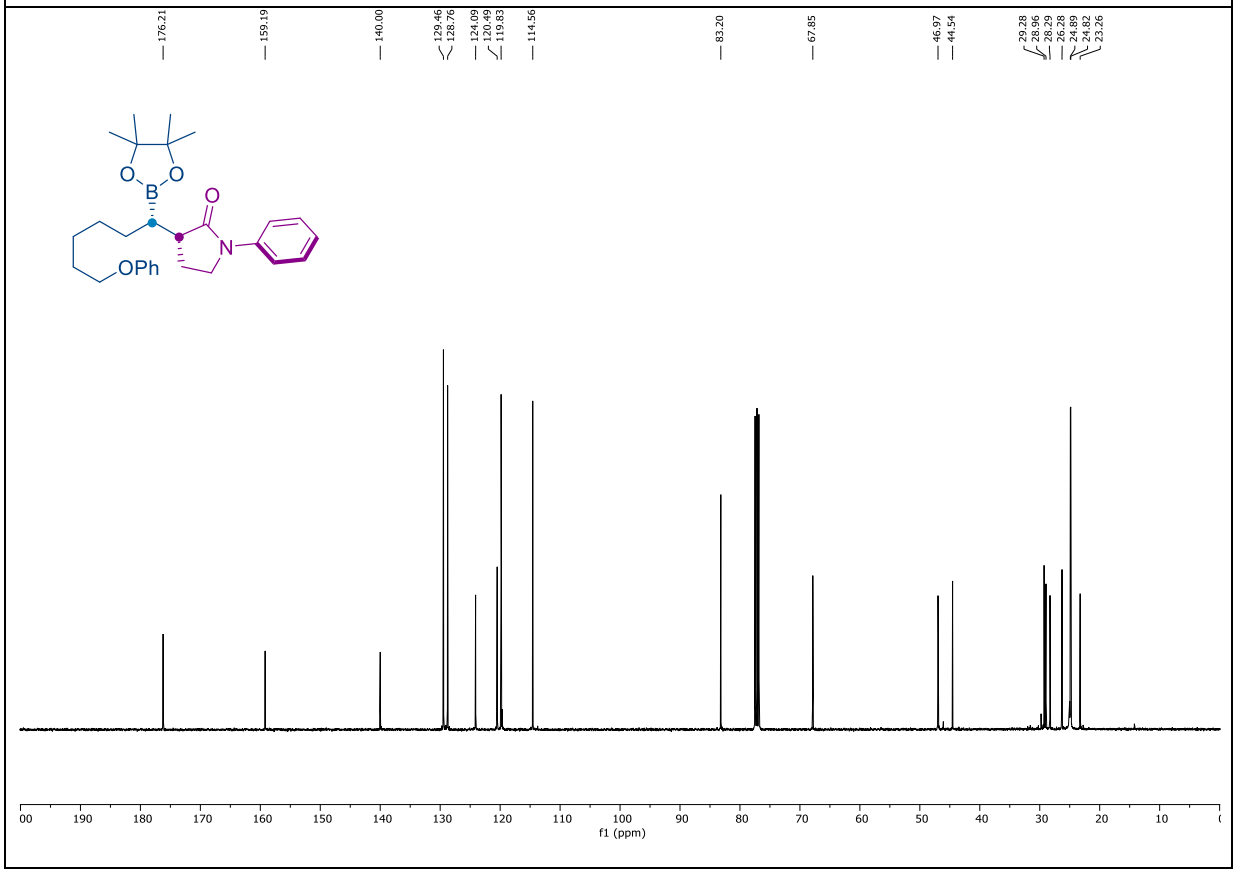


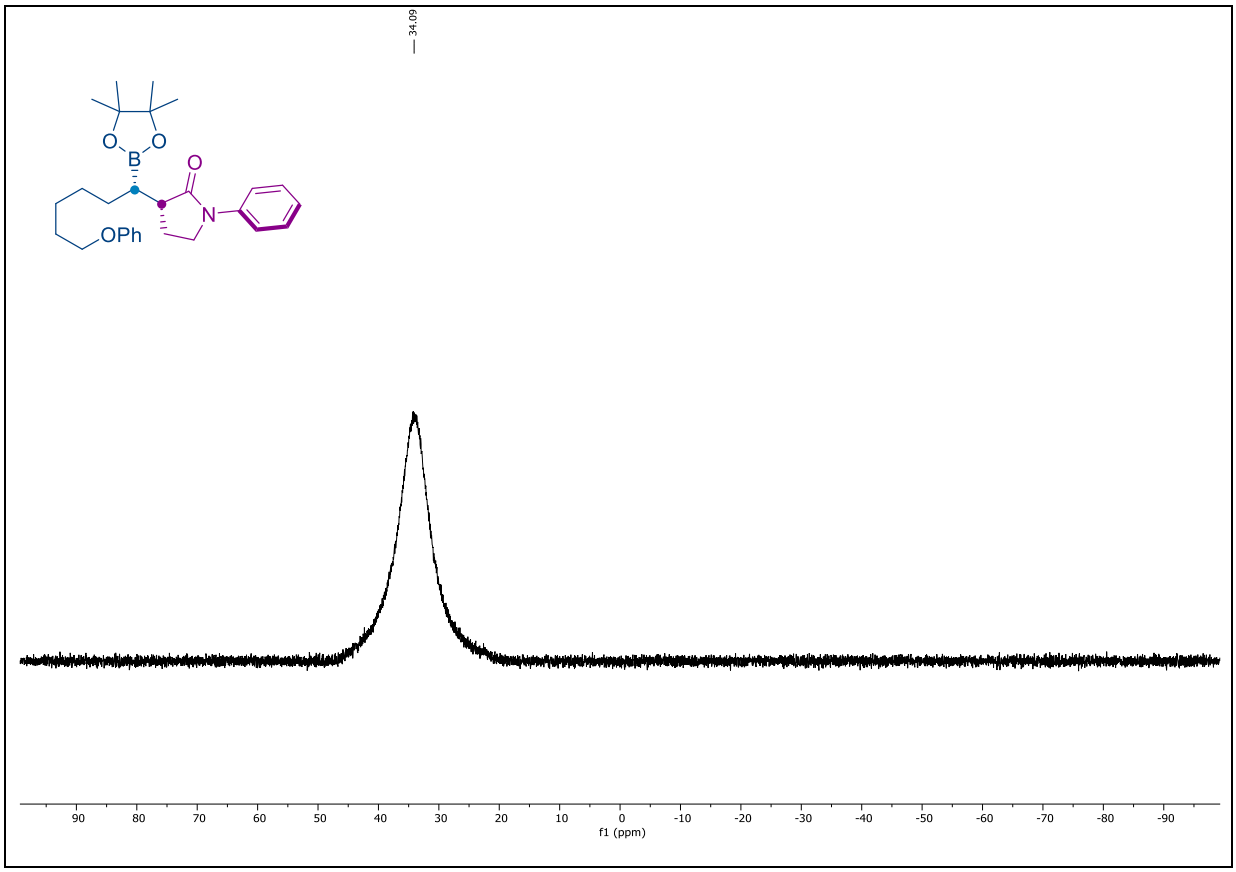



33.92
O
B
O
O
N
Cl
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

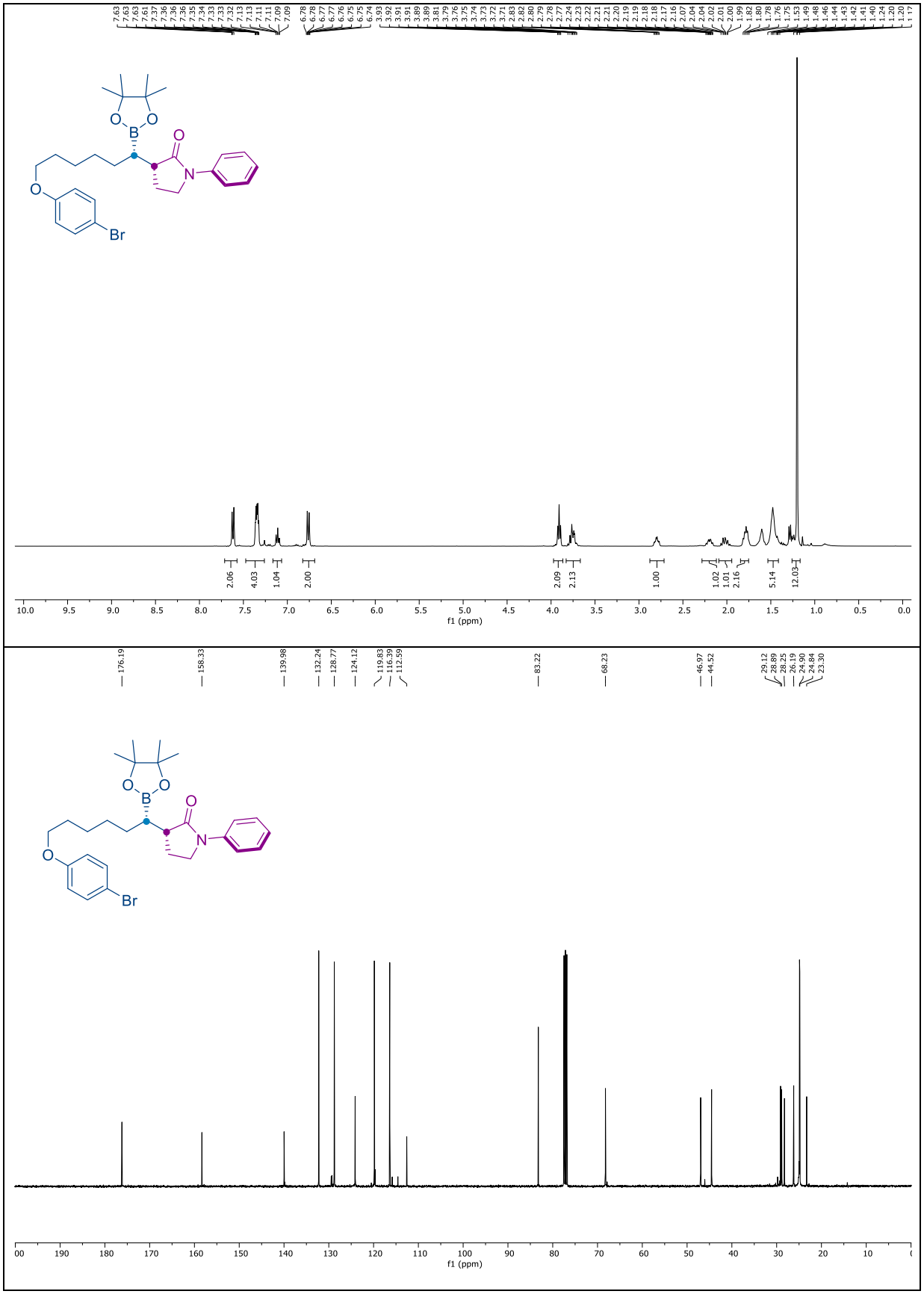
NMR spectra of 3fa:

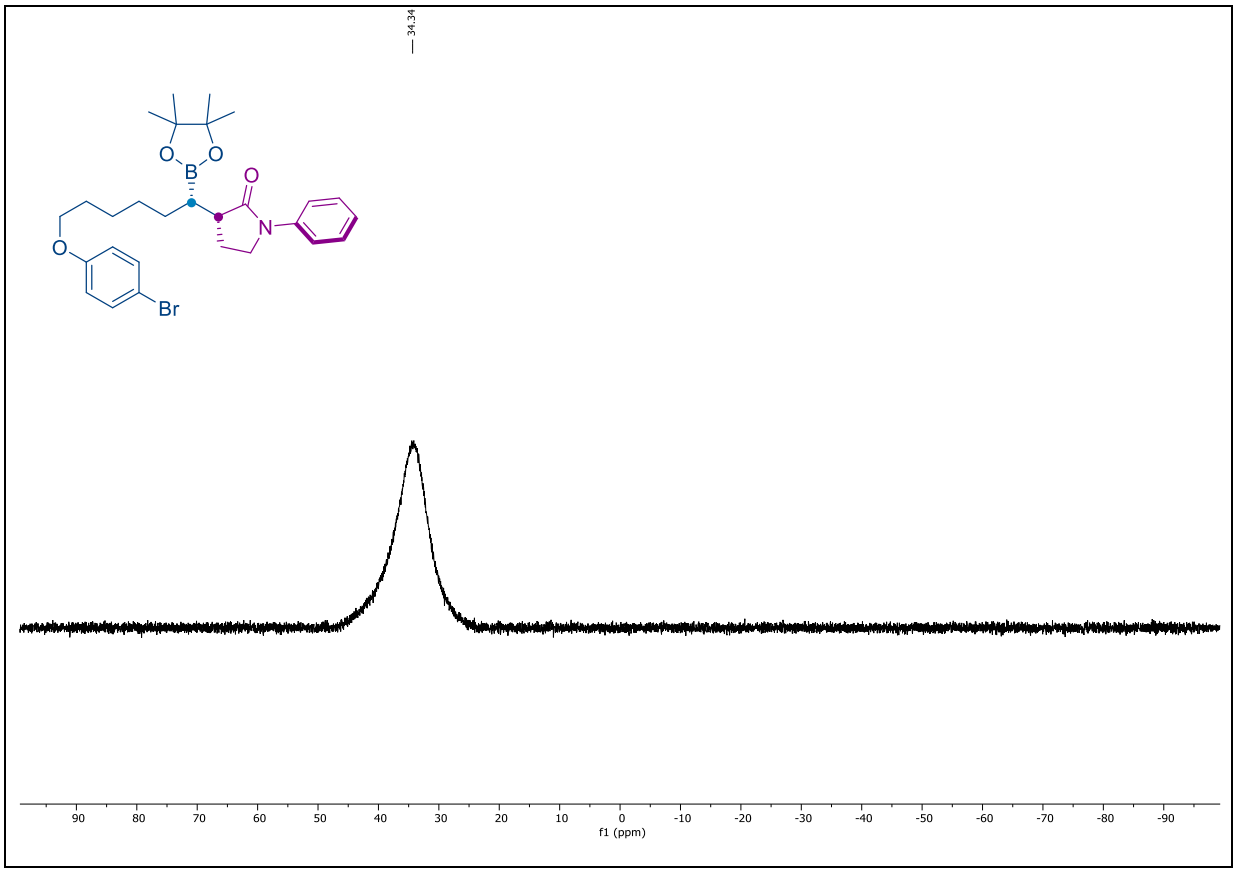




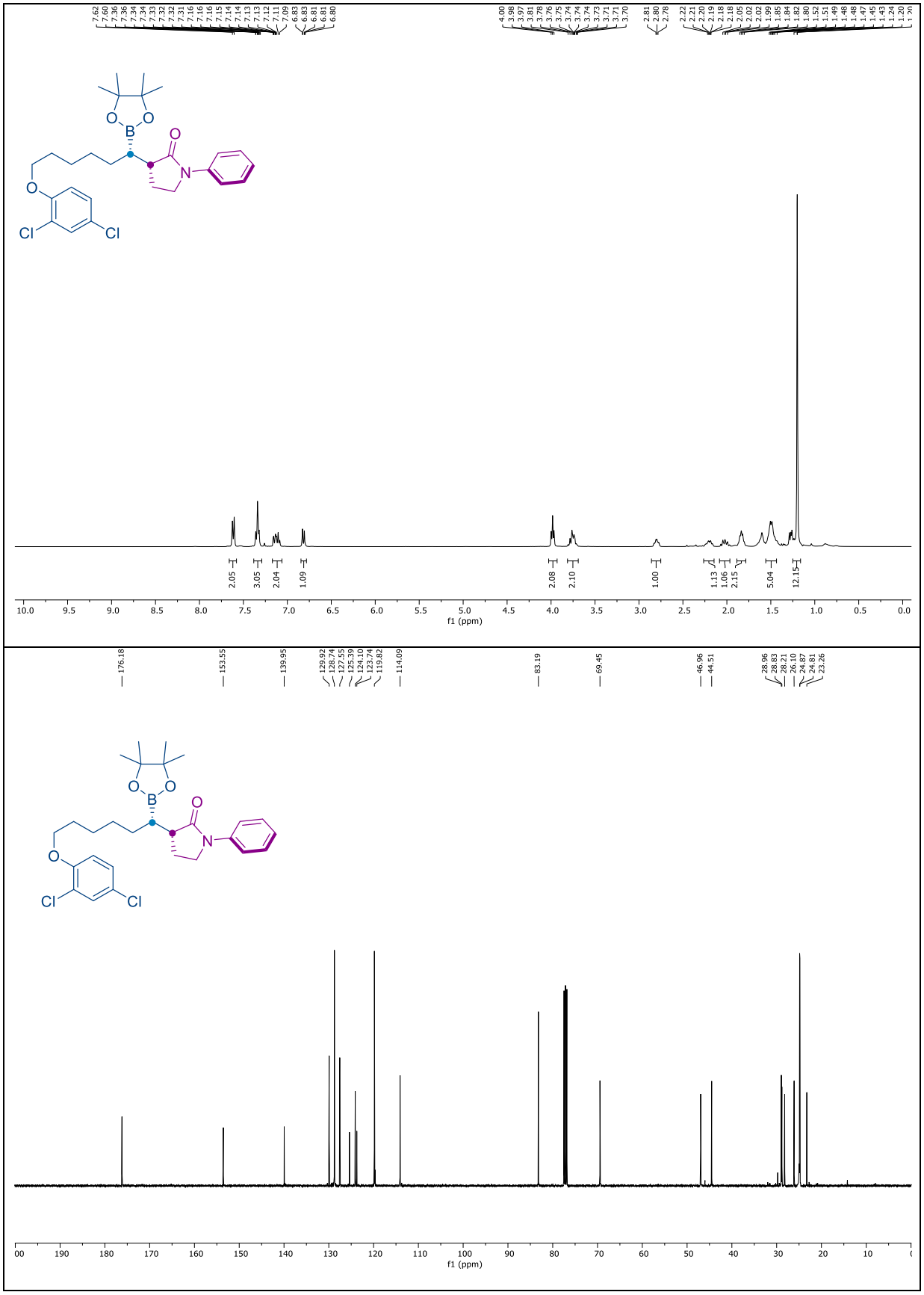

34.09
O
B
O
O
N
OPh
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

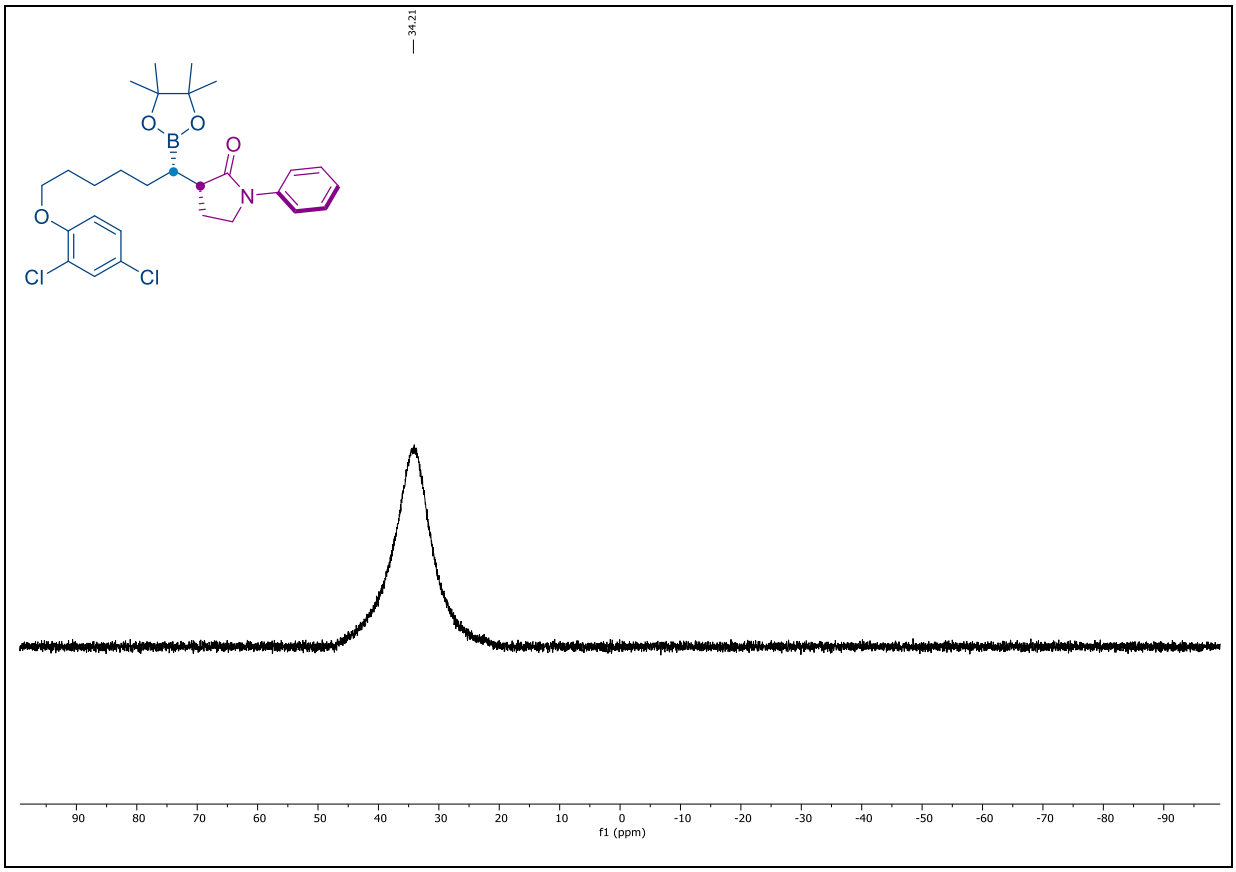
NMR spectra of 3ga:



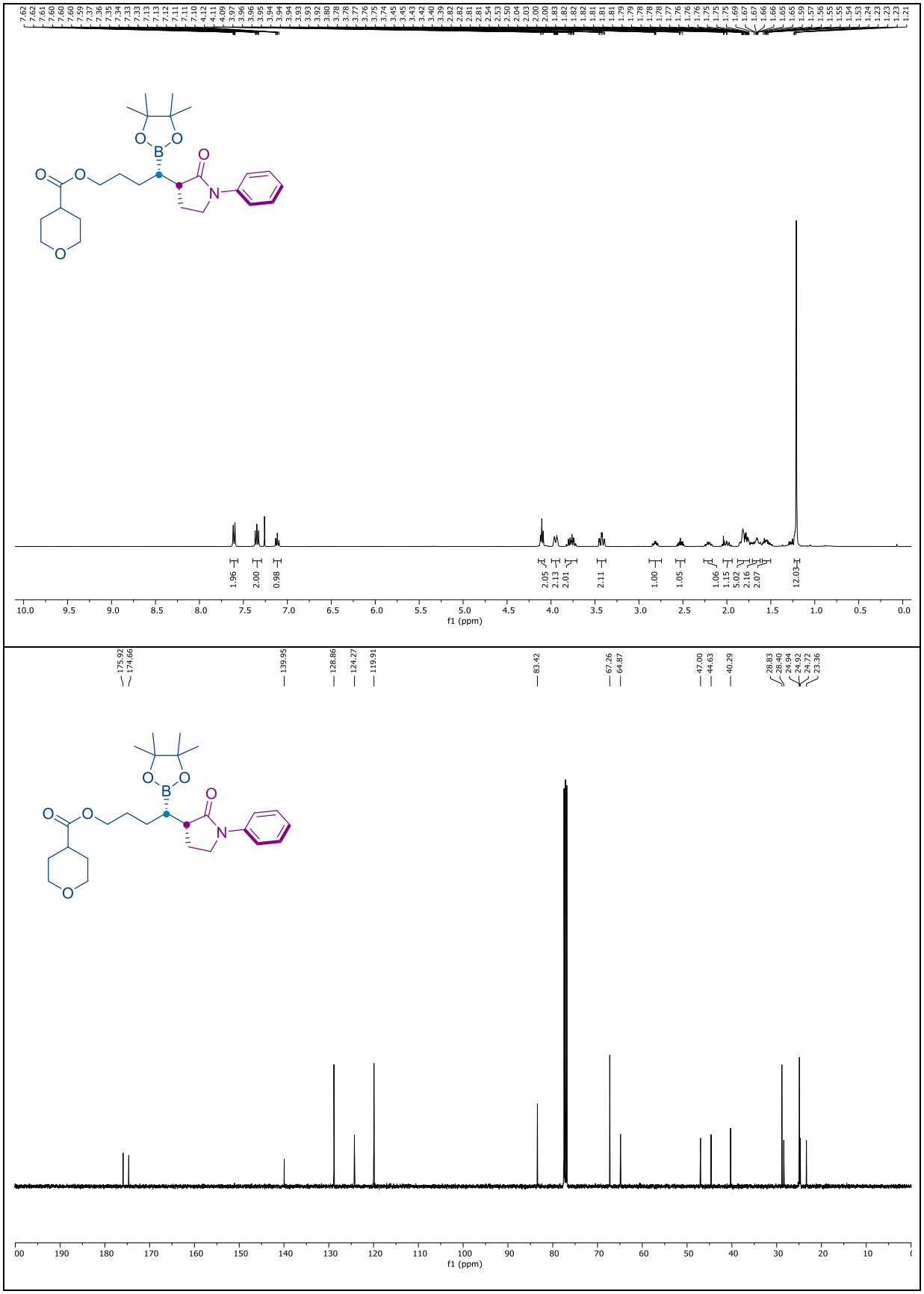

34.34
O
B
O
O
N
O
Br
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

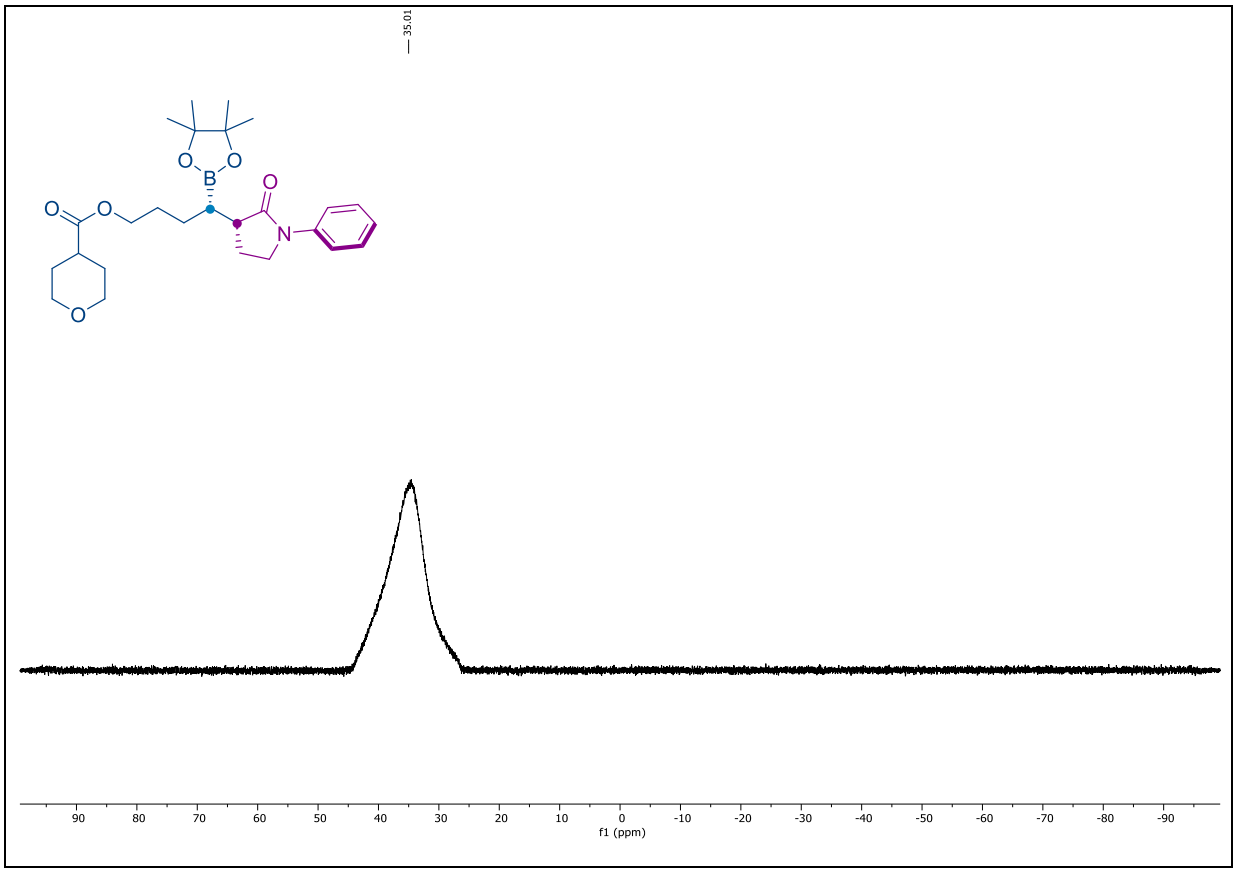
NMR spectra of 3ha:



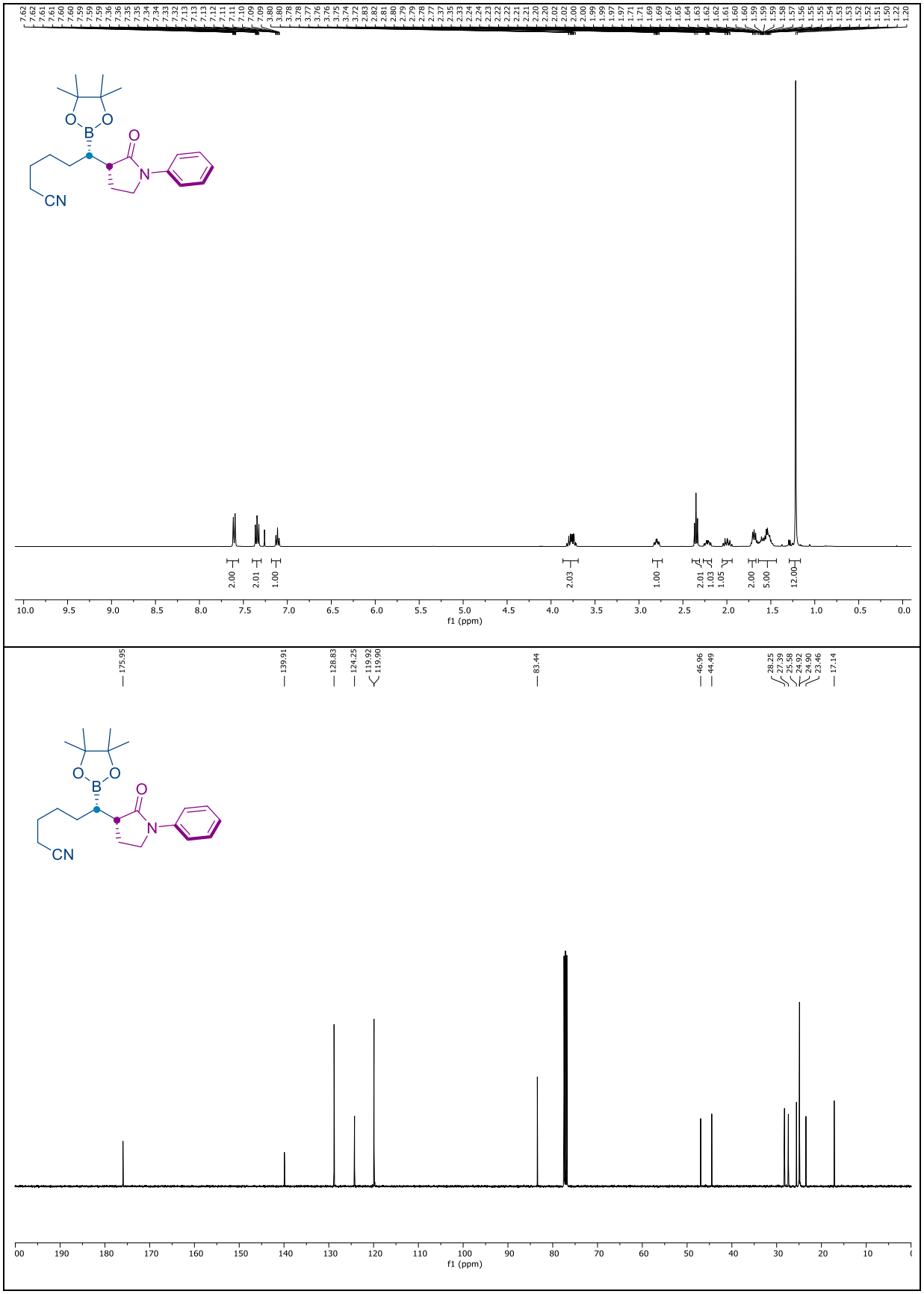

34.21
O
B
O
O
N
O
Cl
Cl
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

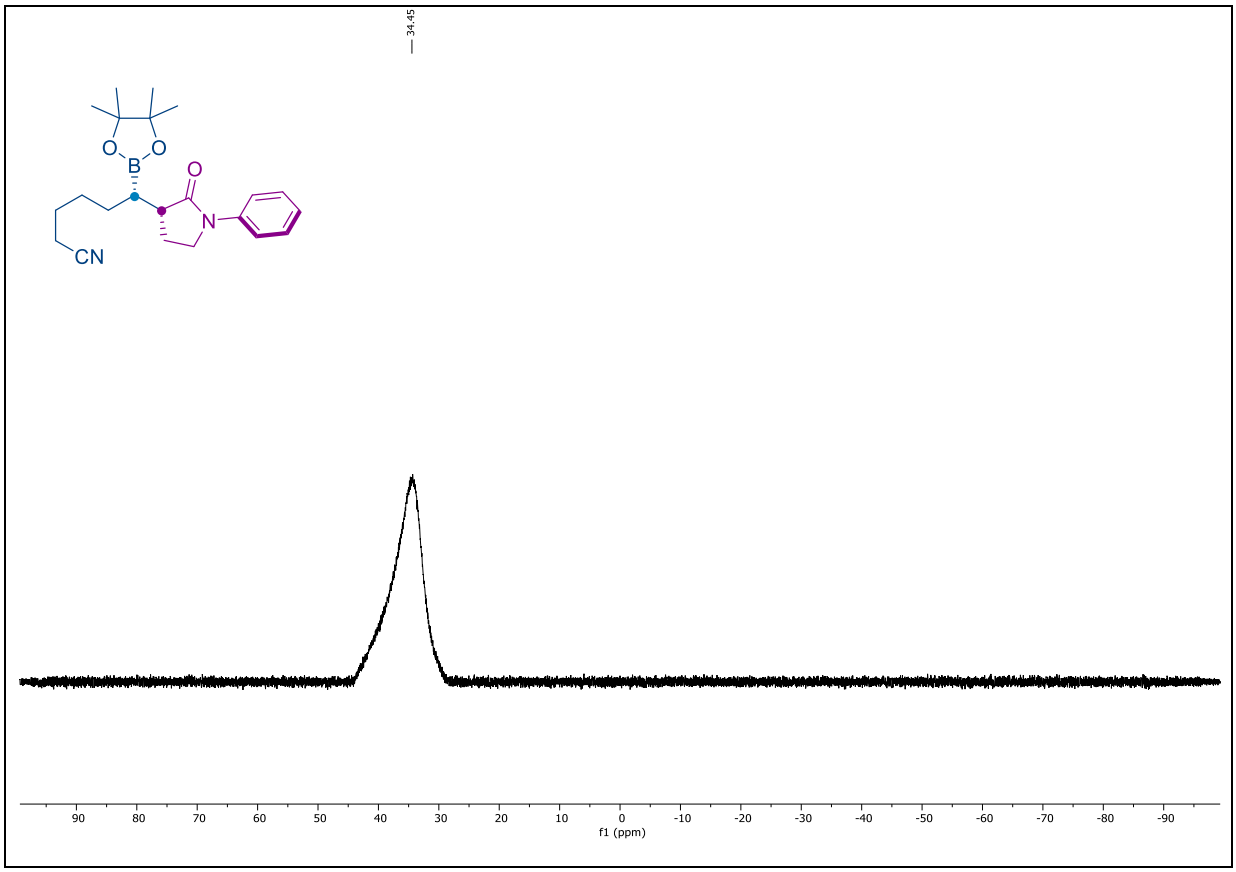
NMR spectra of 3ia:



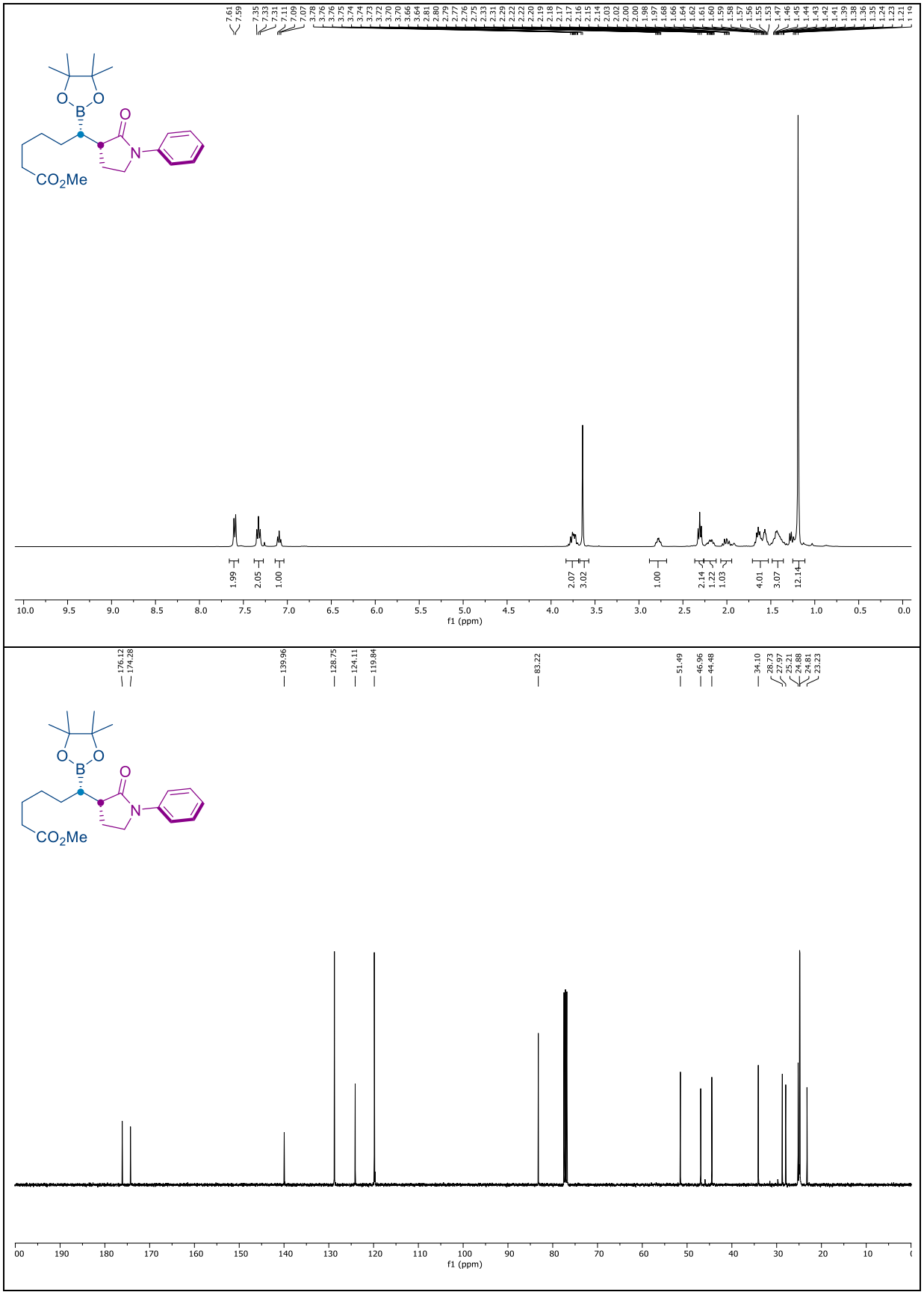

35.01
O
O
B
O
O
O
N
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

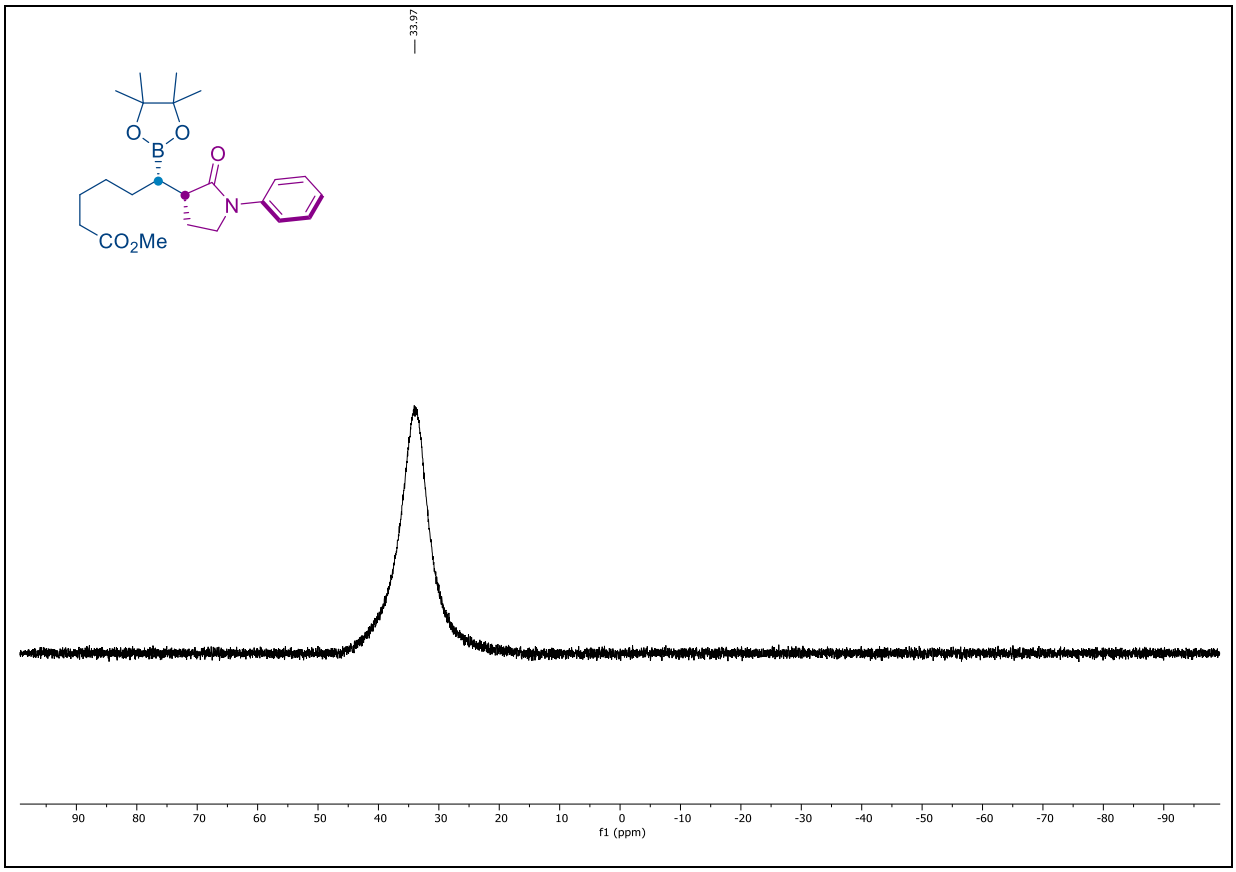
NMR spectra of 3ja:



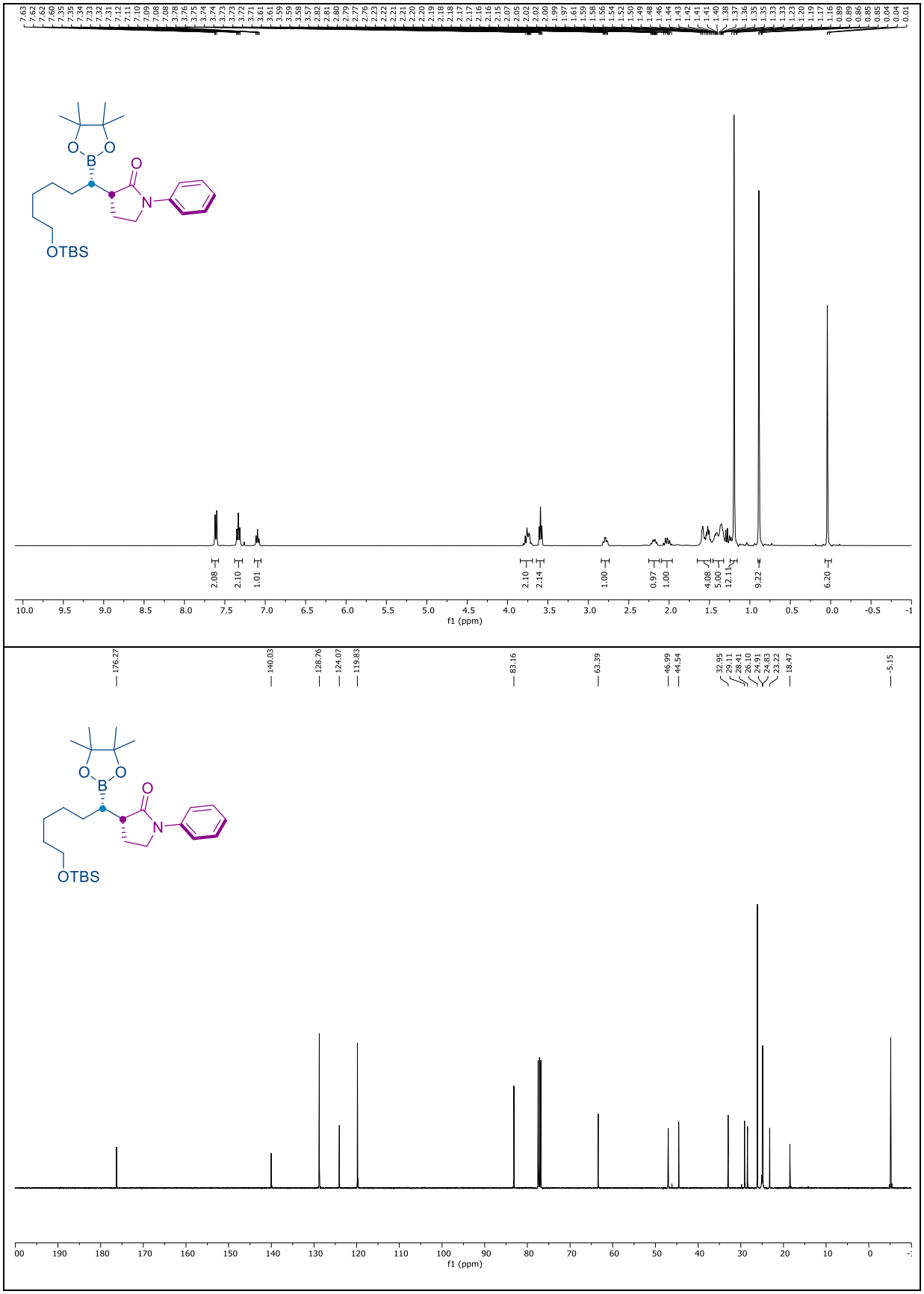

34.45
O
B
O
O
N
CN
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

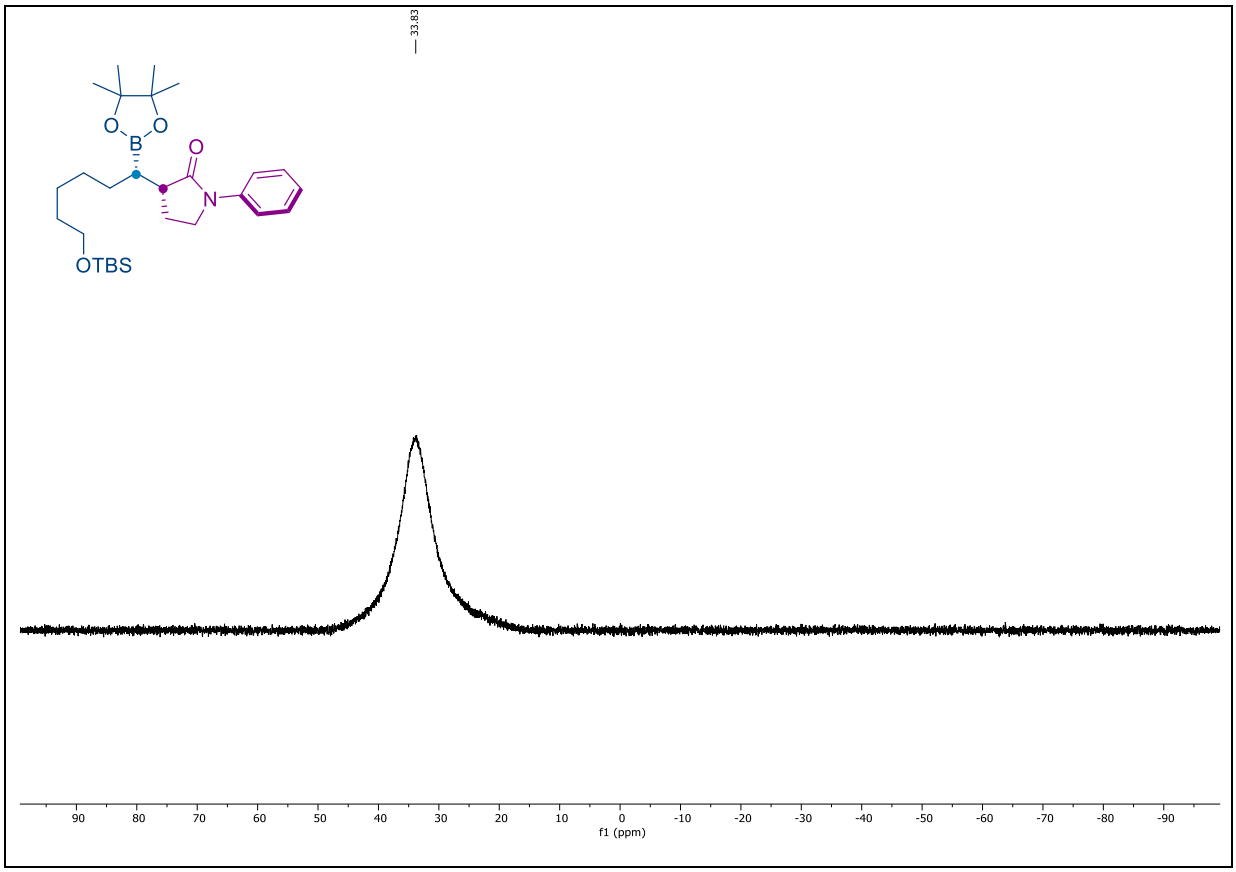
NMR spectra of 3ka:



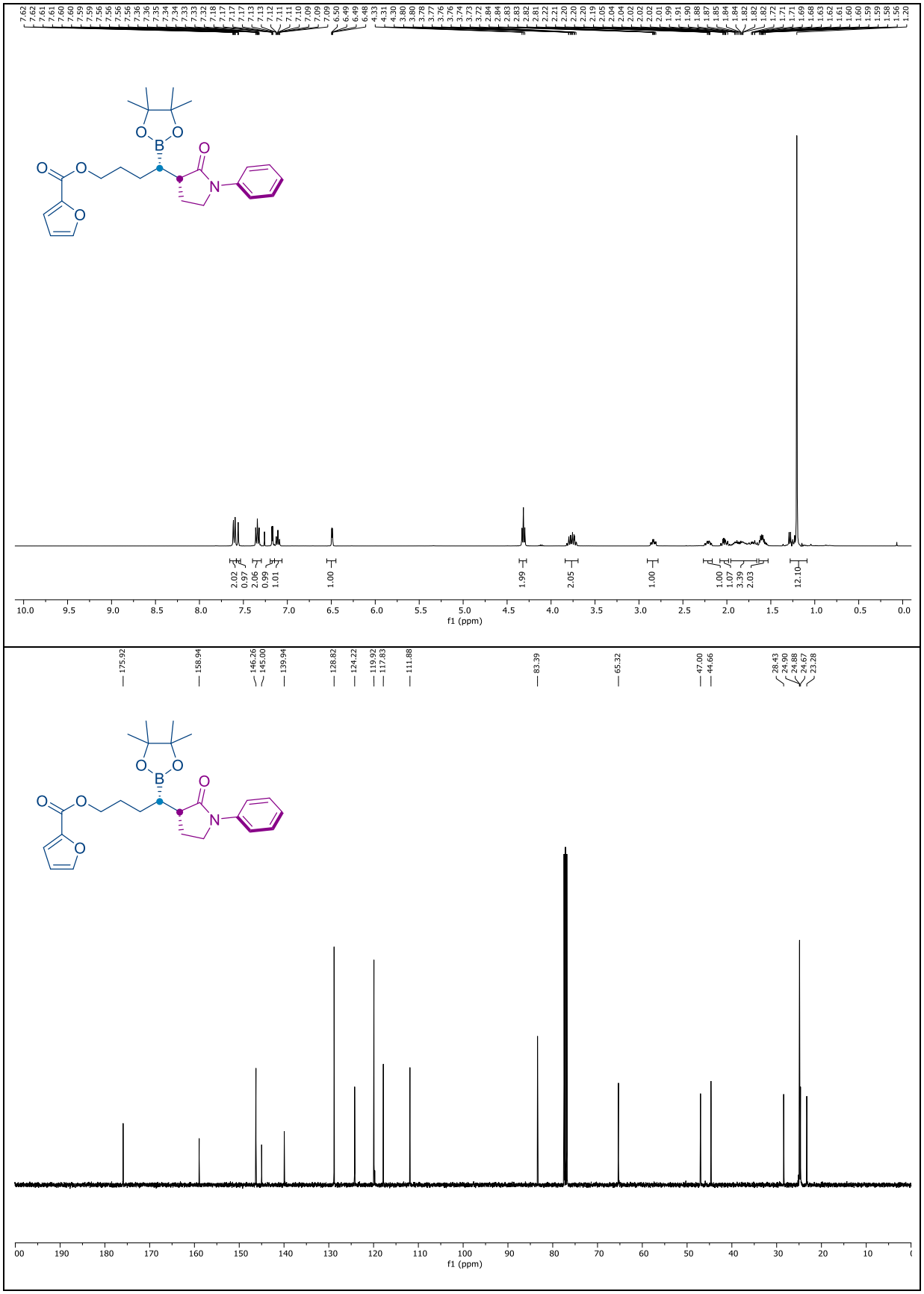

33.97
O
B
O
O
N
CO2Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

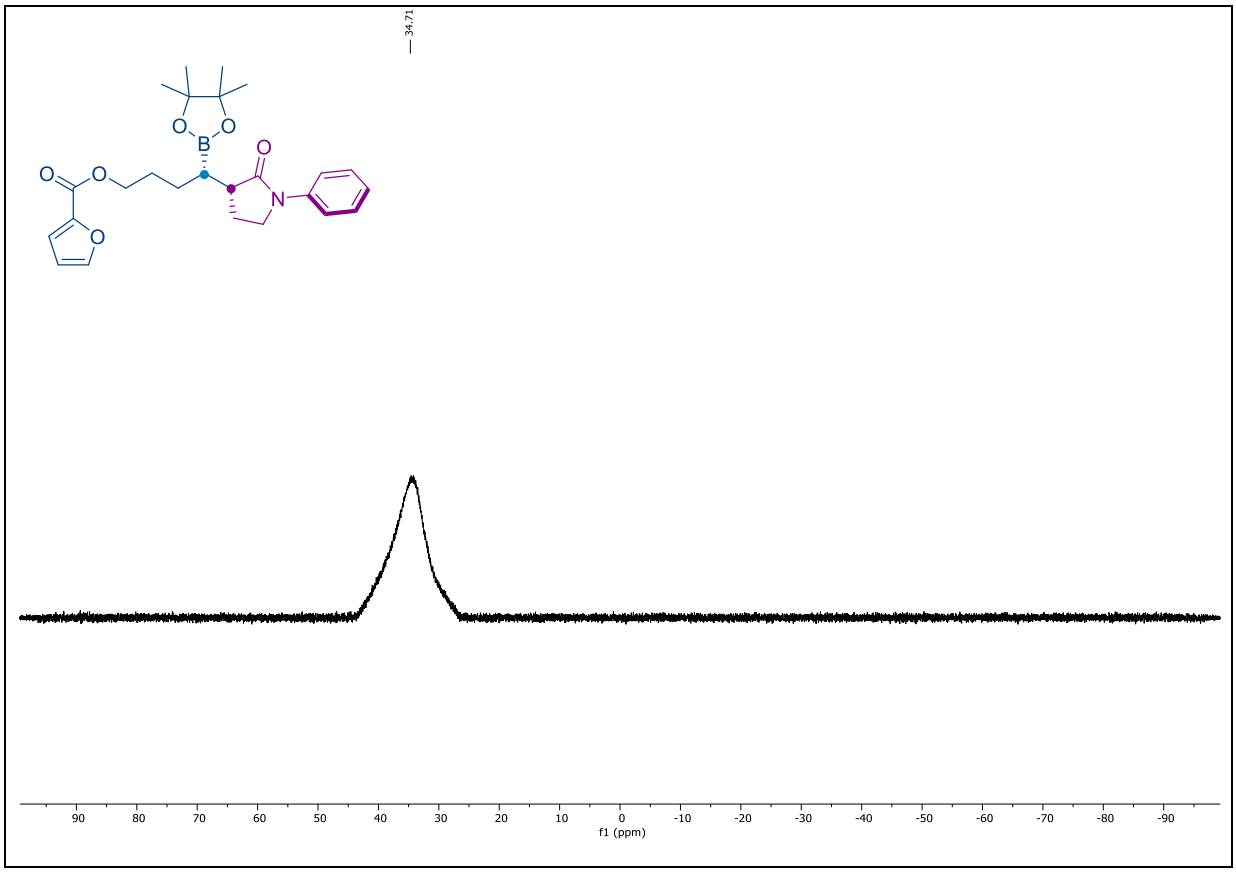
NMR spectra of 3la:



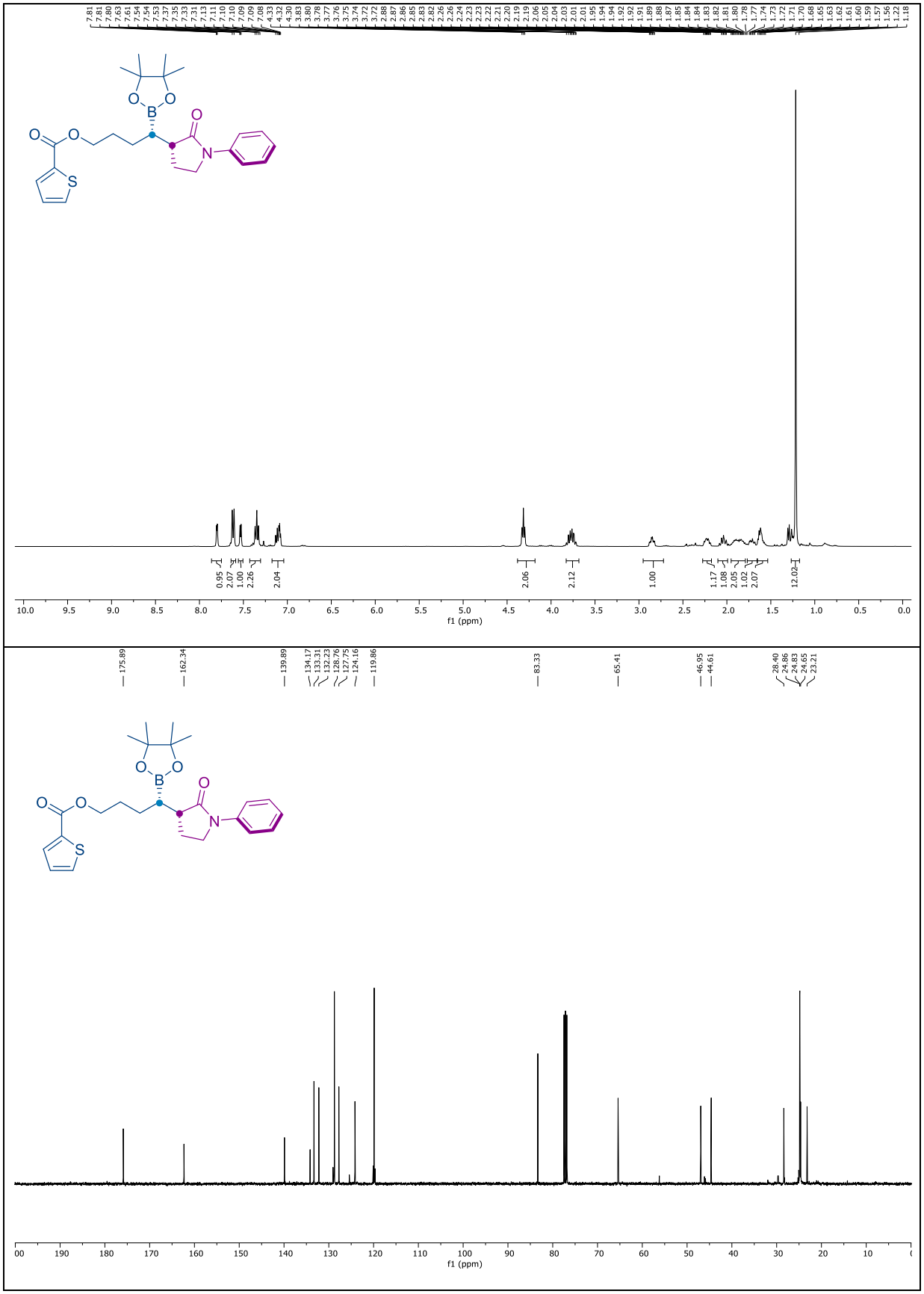

33.83
O
B
O
O
N
OTBS
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

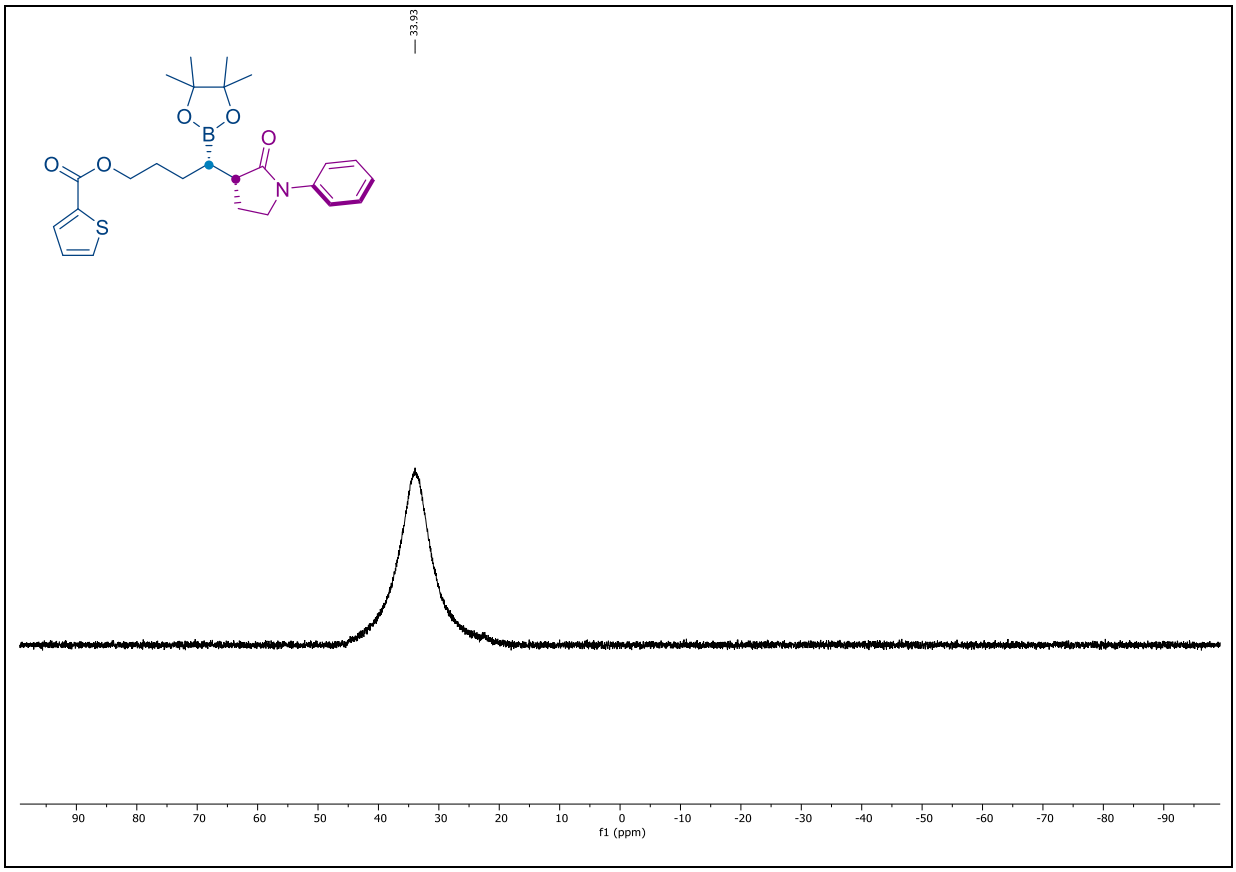
NMR spectra of 3ma:



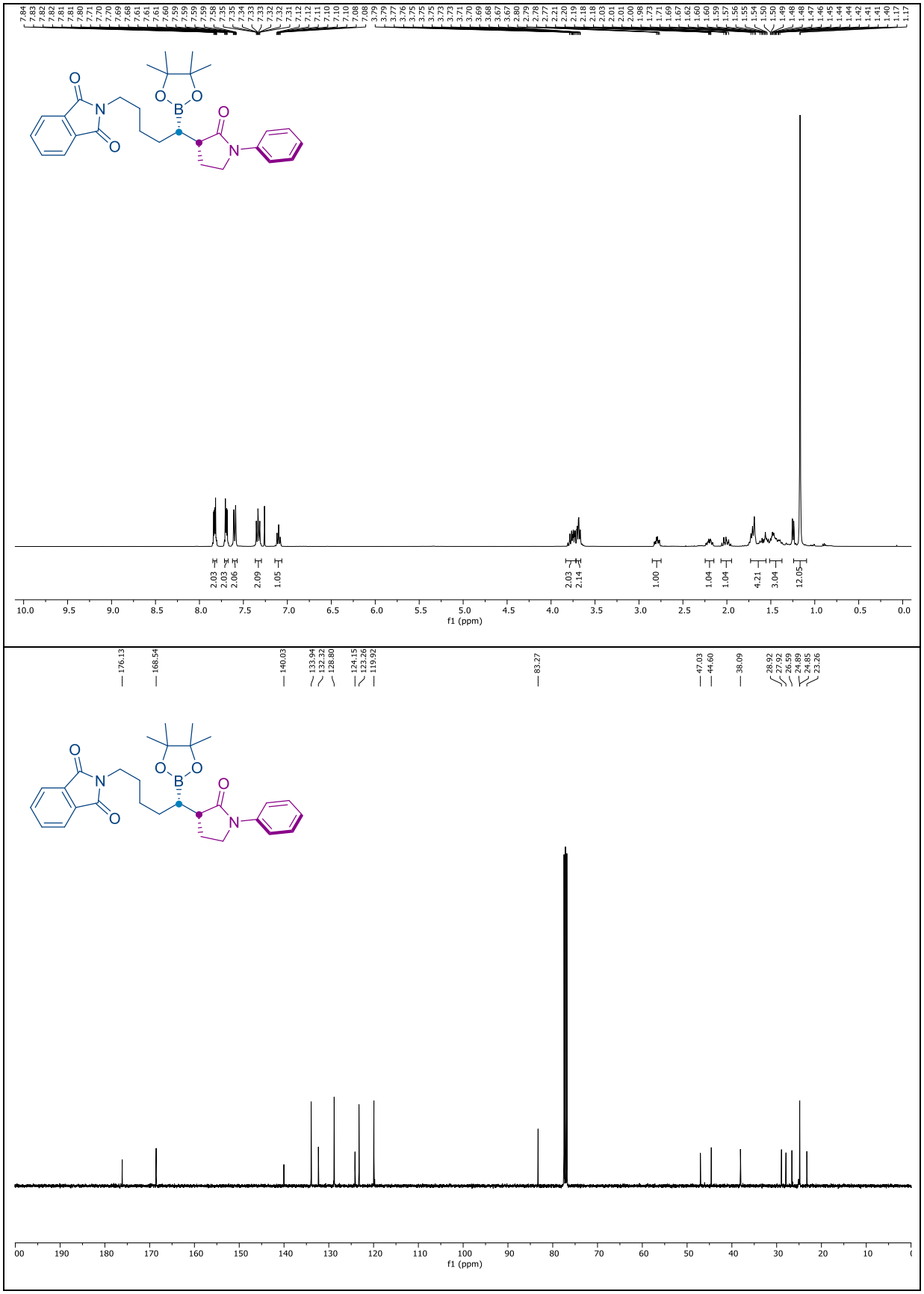

34.71
O
O
B
O
O
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

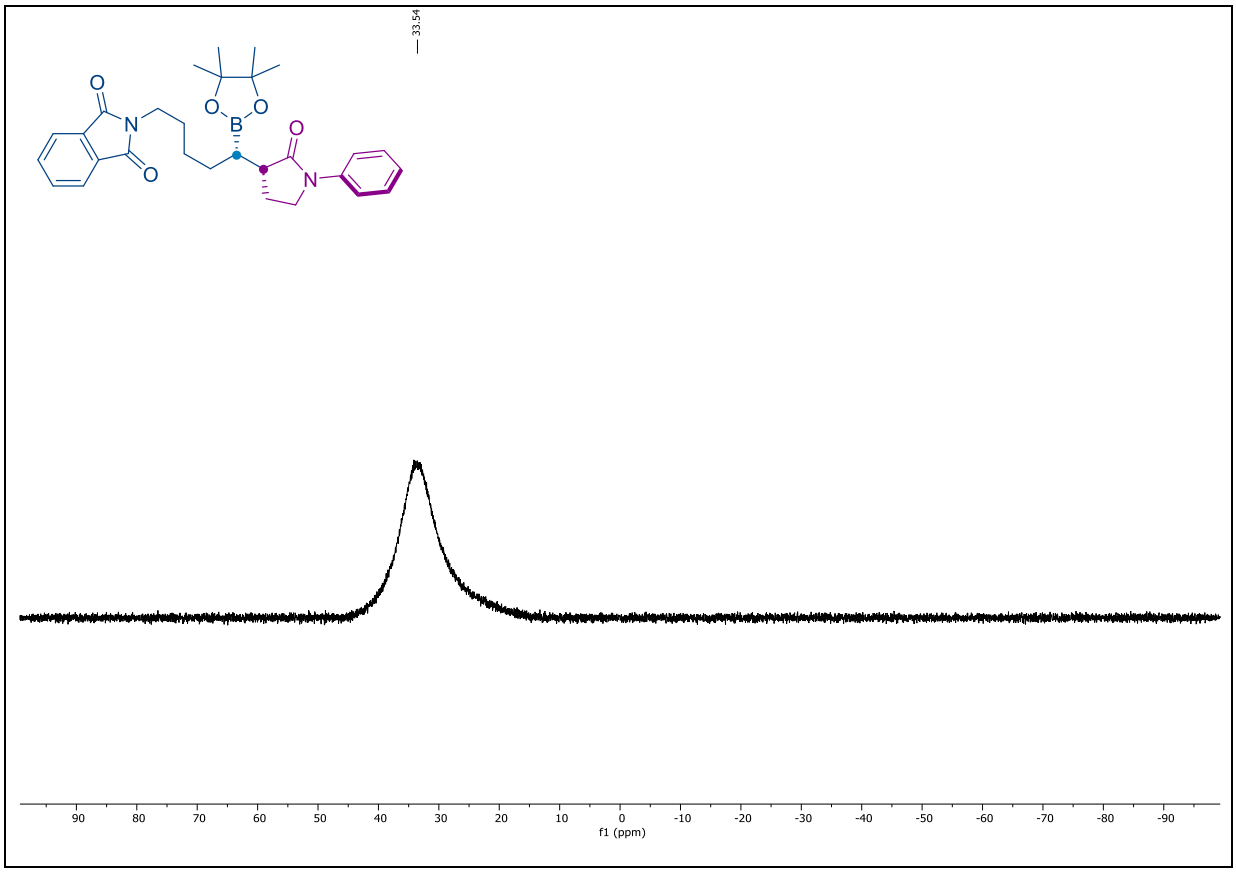
NMR spectra of 3na:



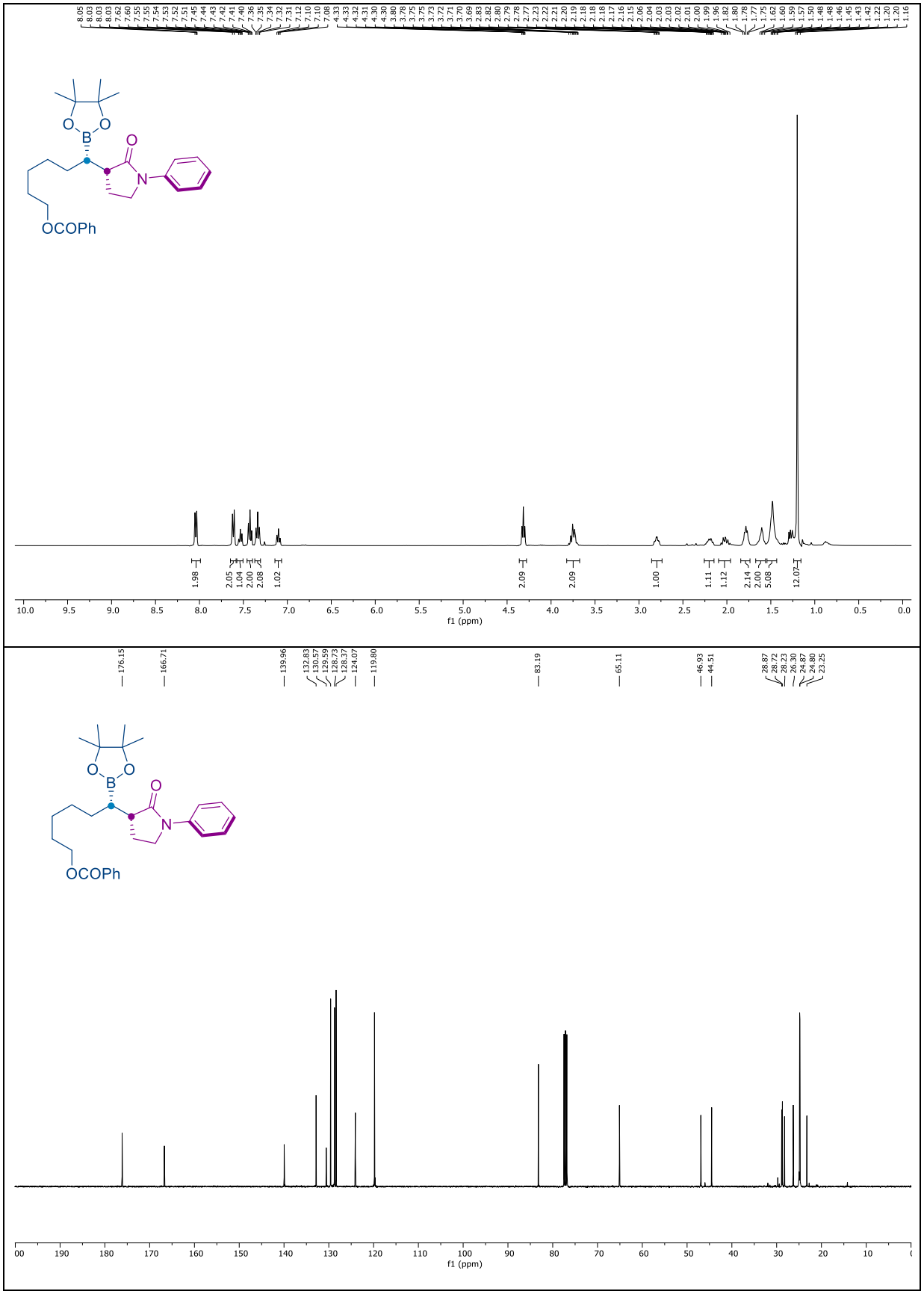

33.93
O
O
B
O
O
N
S
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

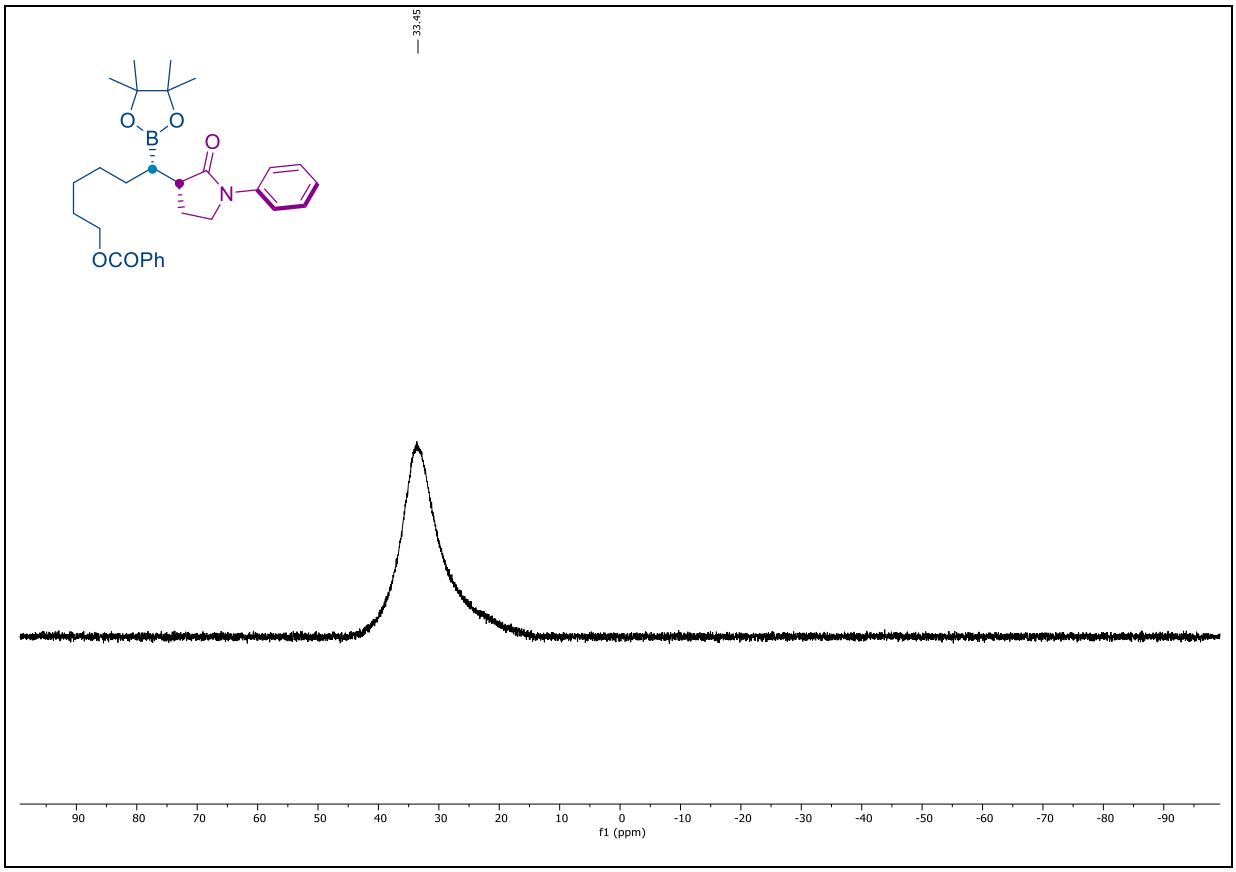
NMR spectra of 3oa:



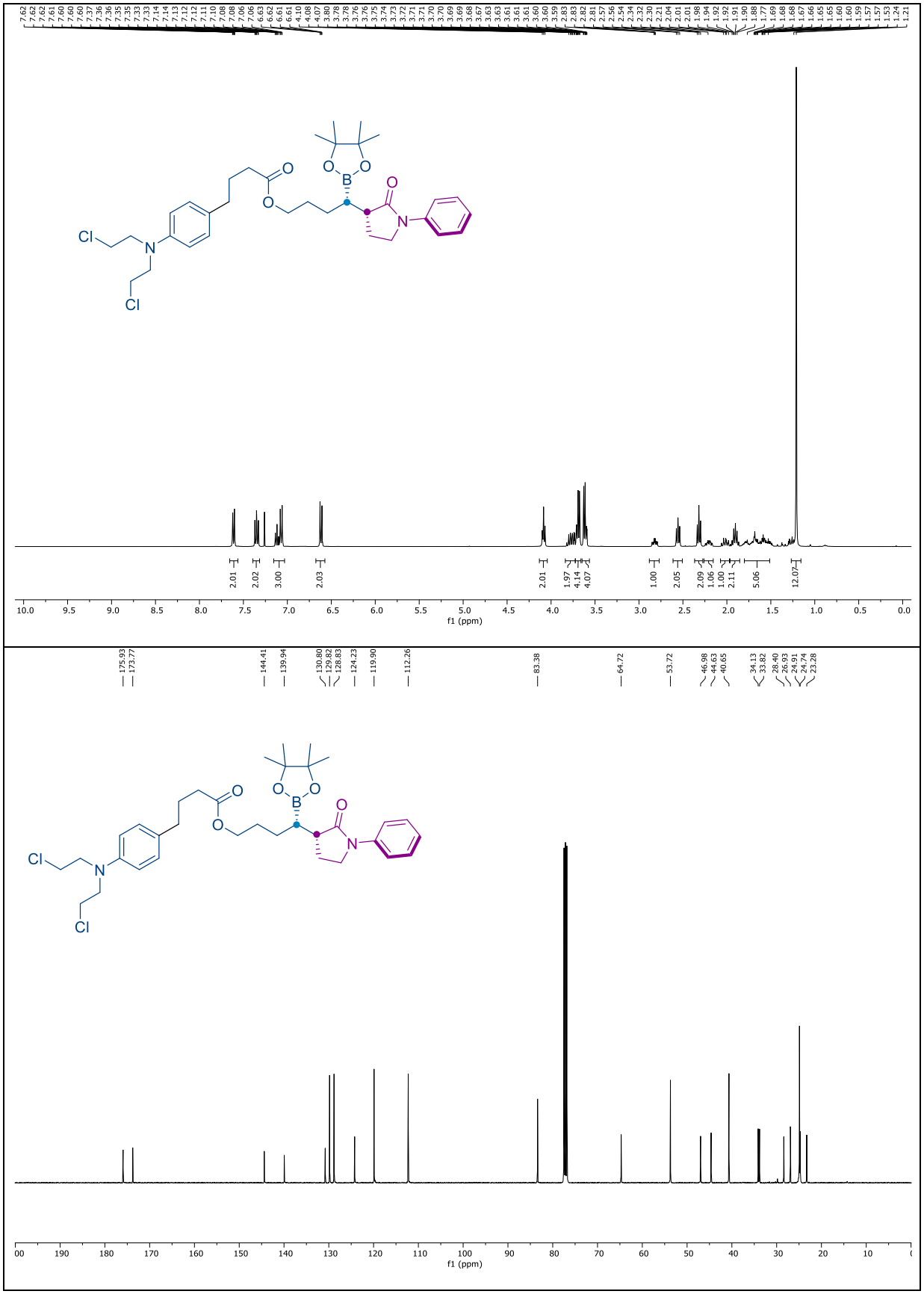

33.54
O
N
O
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

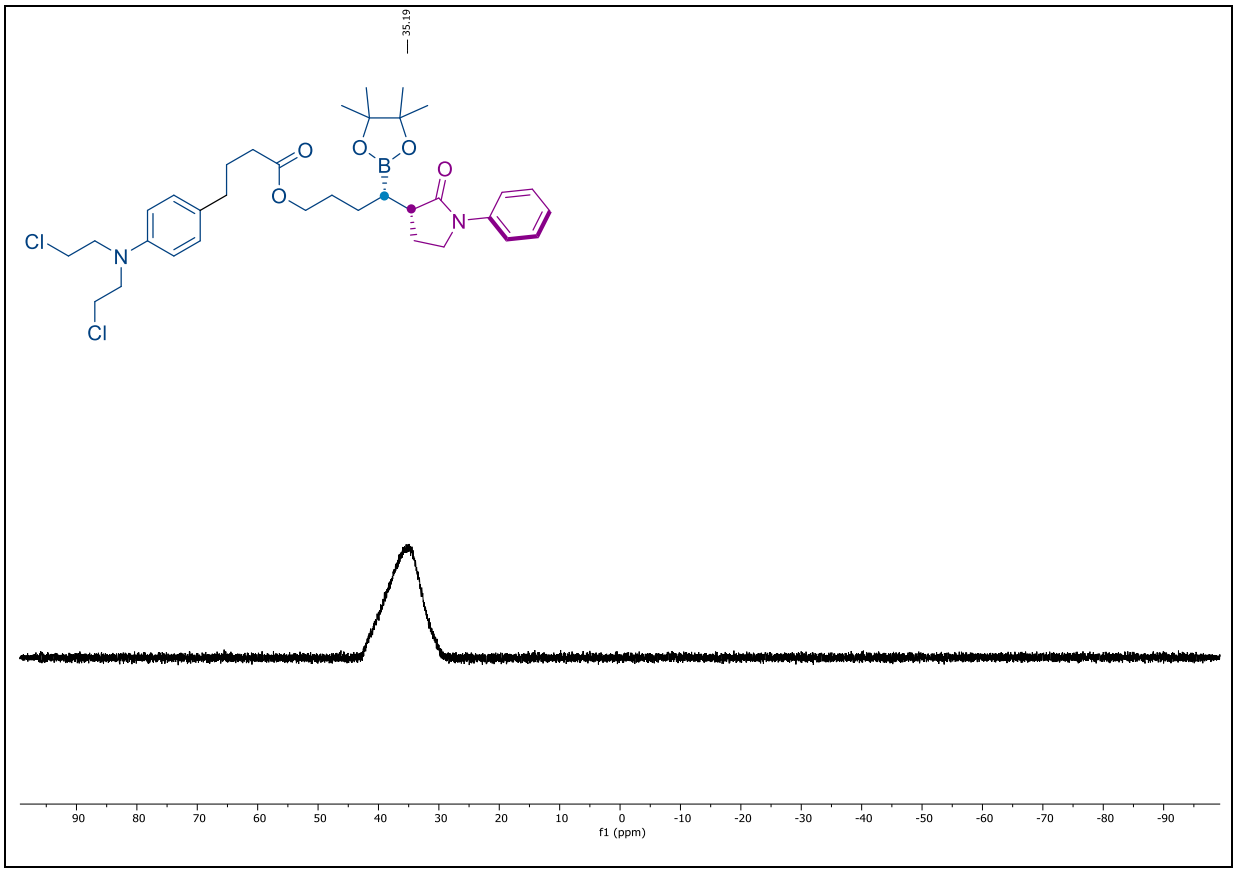
NMR spectra of 3pa:



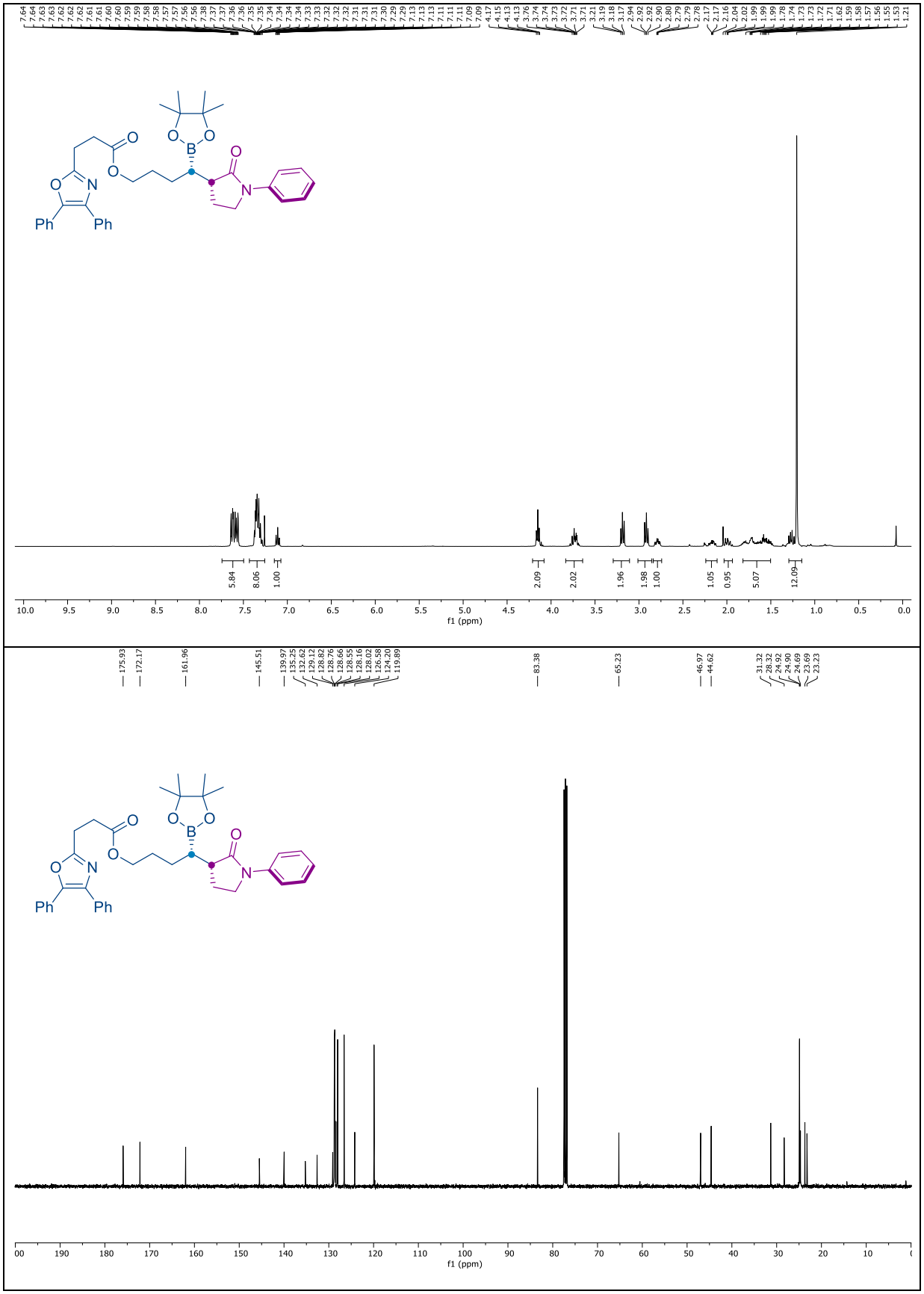

33.45
O
B
O
O
N
OCOPh
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

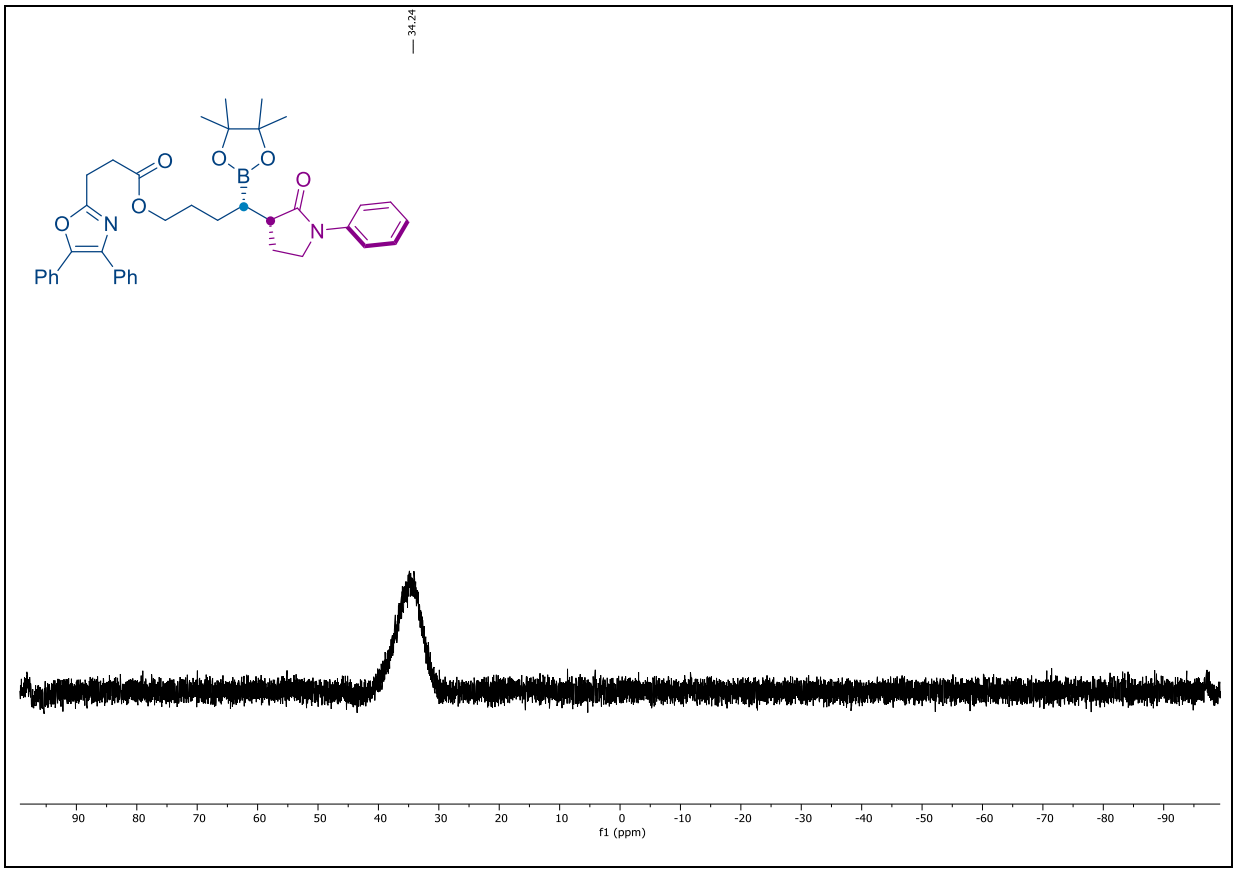
NMR spectra of 4:



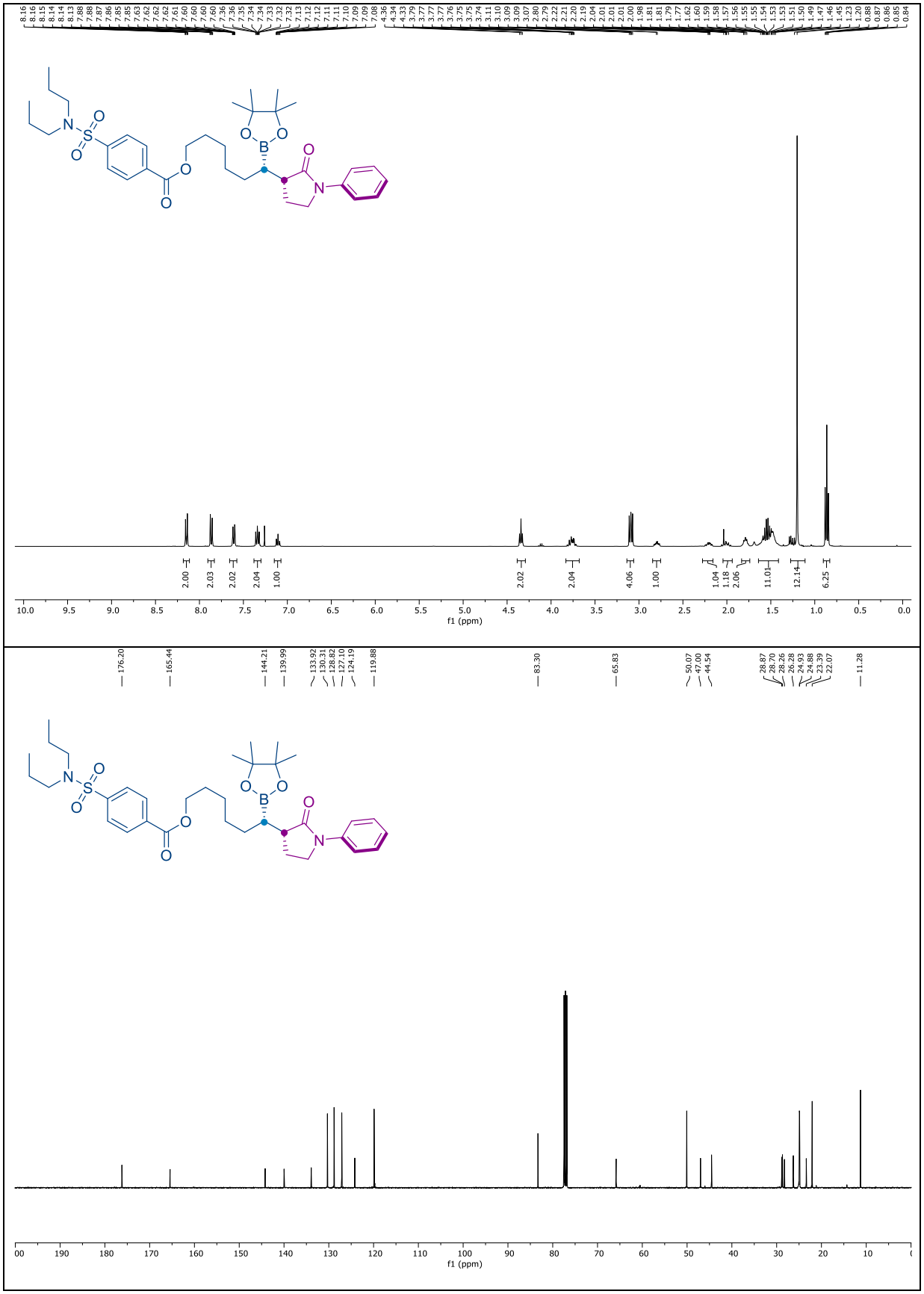

35.19
O
O
B
O
O
O
N
Cl
N
Cl
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

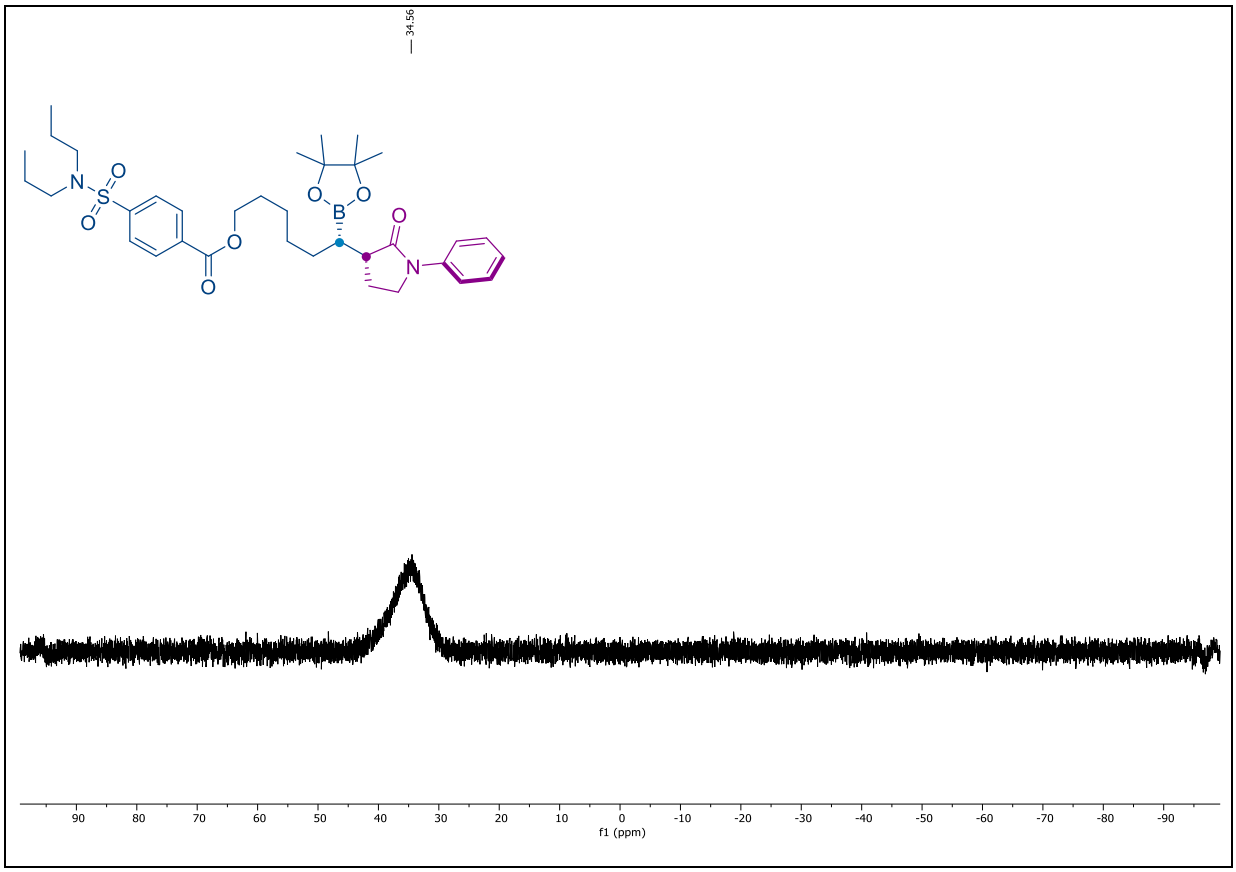
NMR spectra of 5:



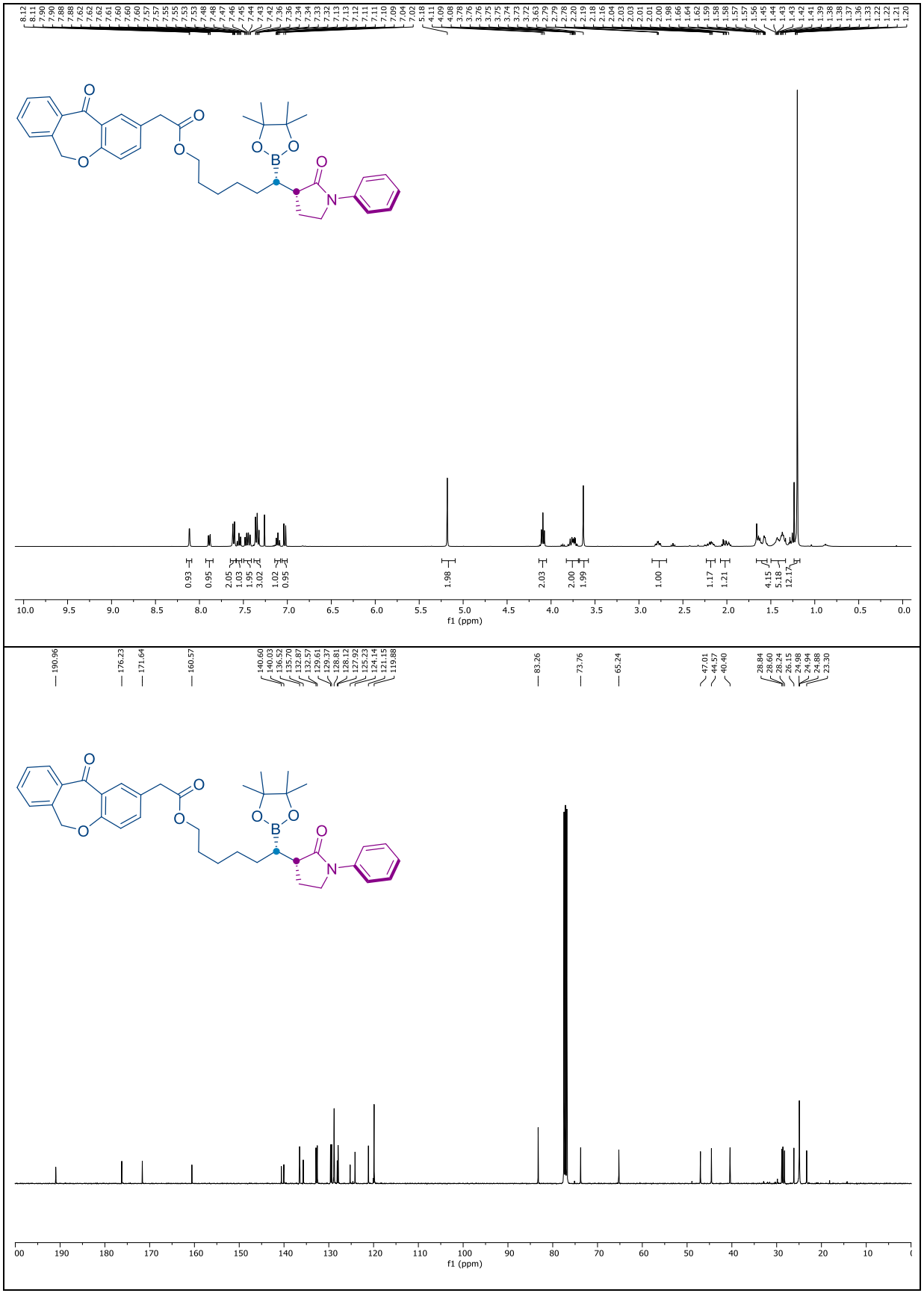

34.24
O
O
B
O
O
O
N
Ph
Ph
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

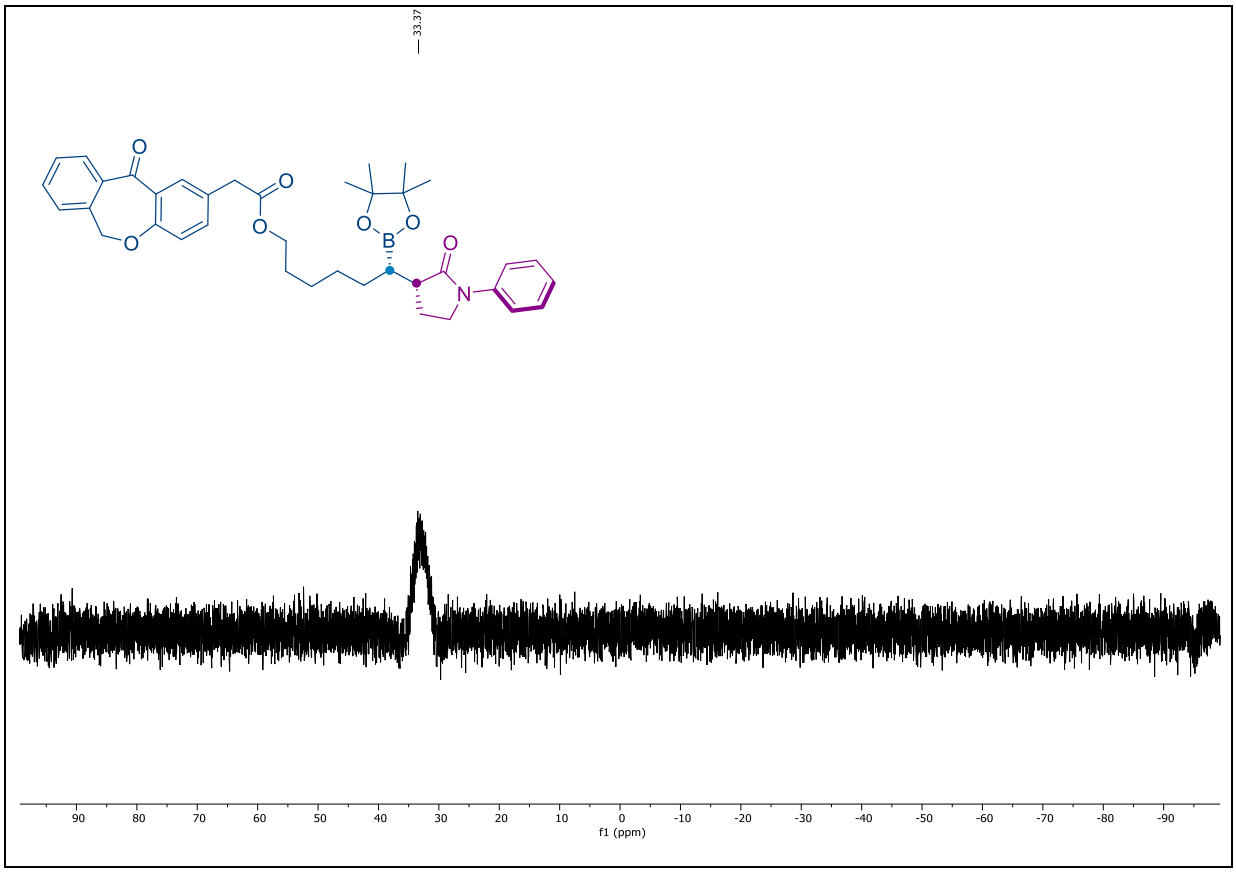
NMR spectra of 6:



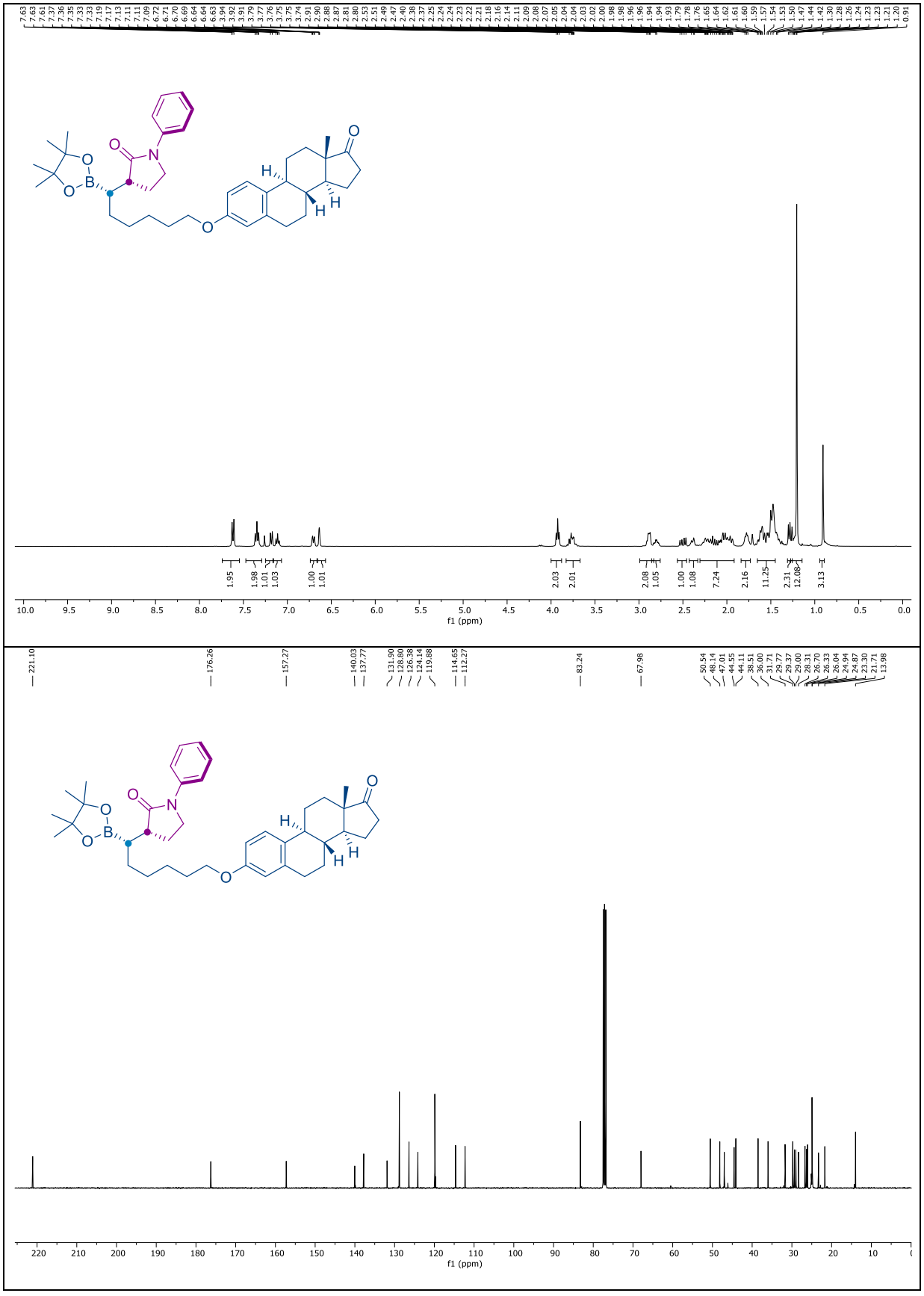

34.56
N
S
O
O
O
O
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

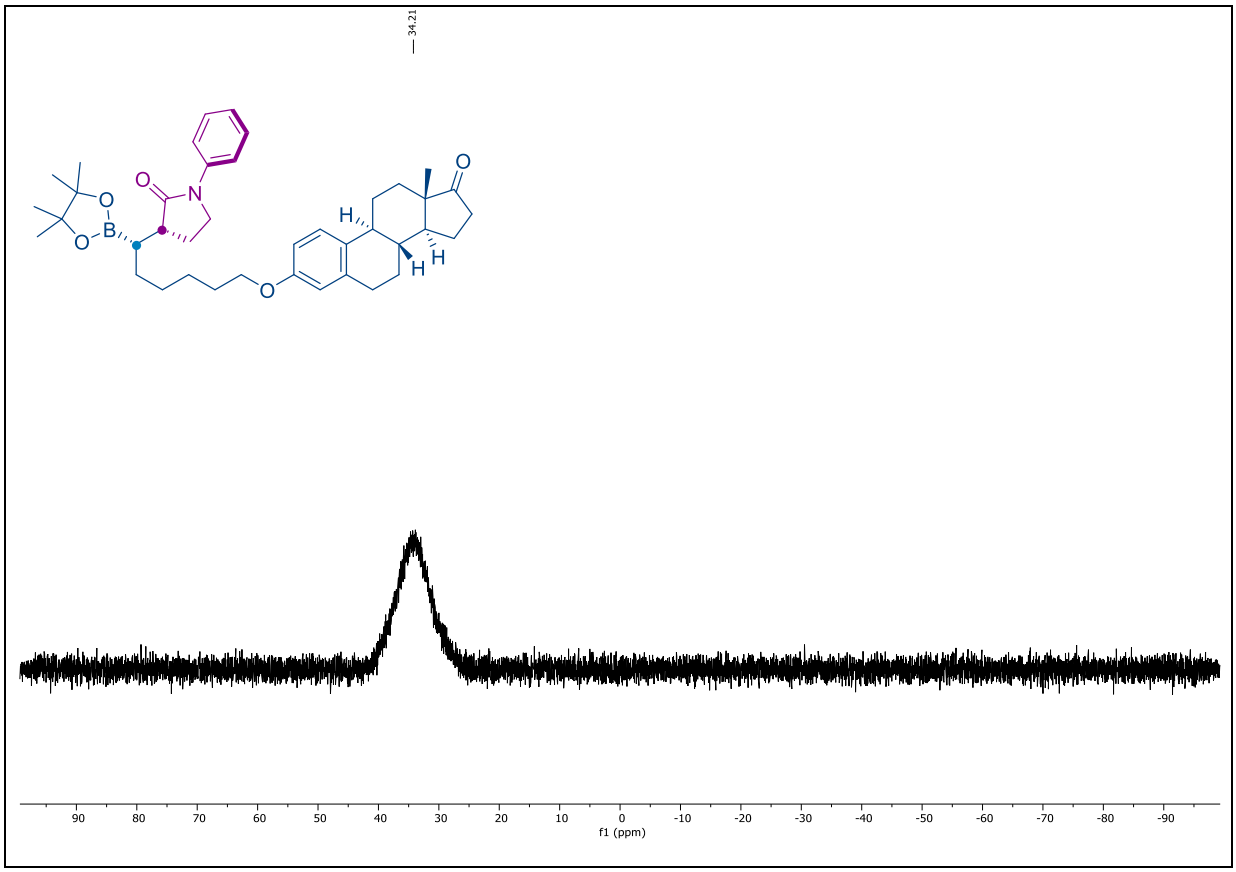
NMR spectra of 7:



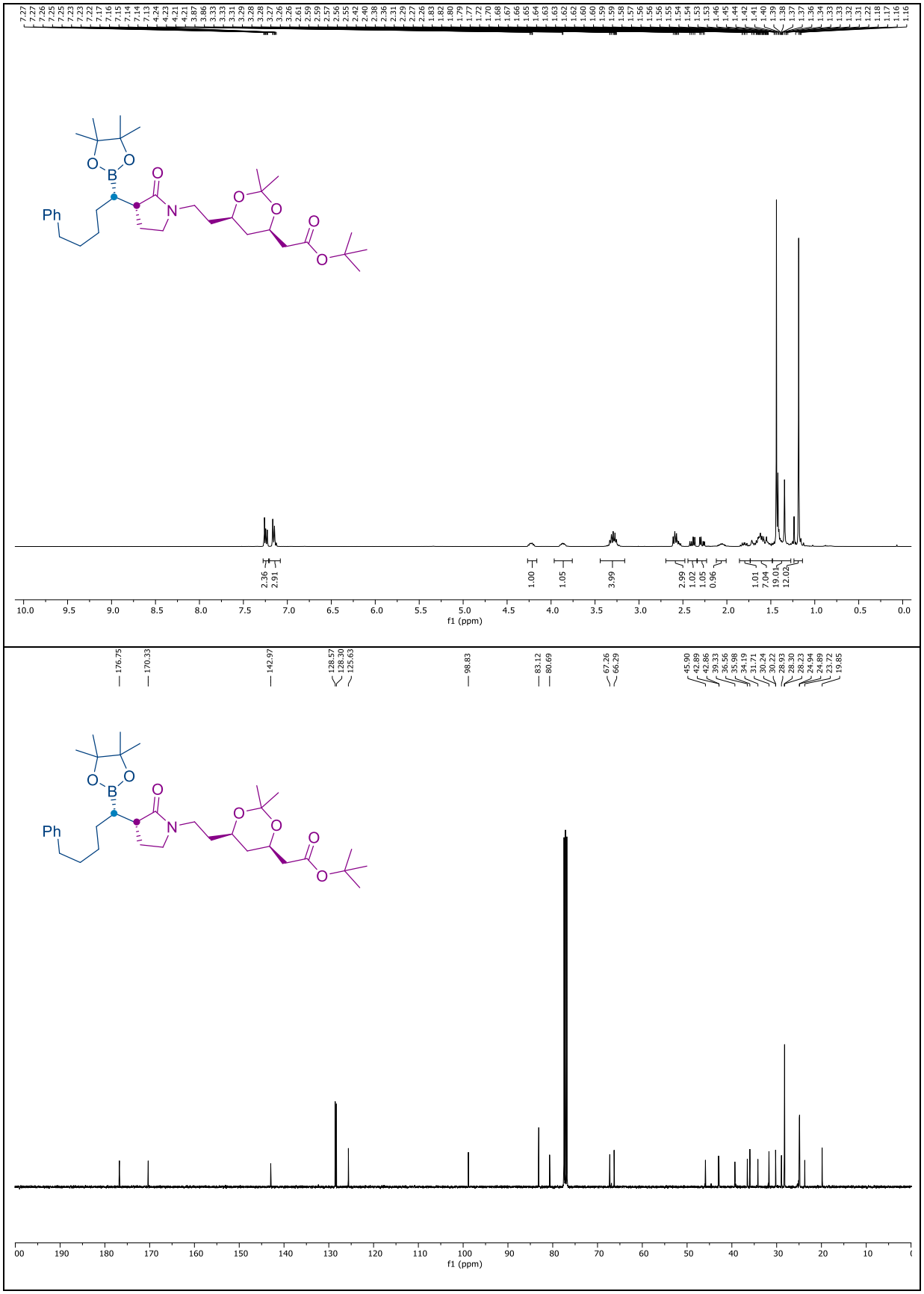

33.37
O
O
O
O
B
O
O
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

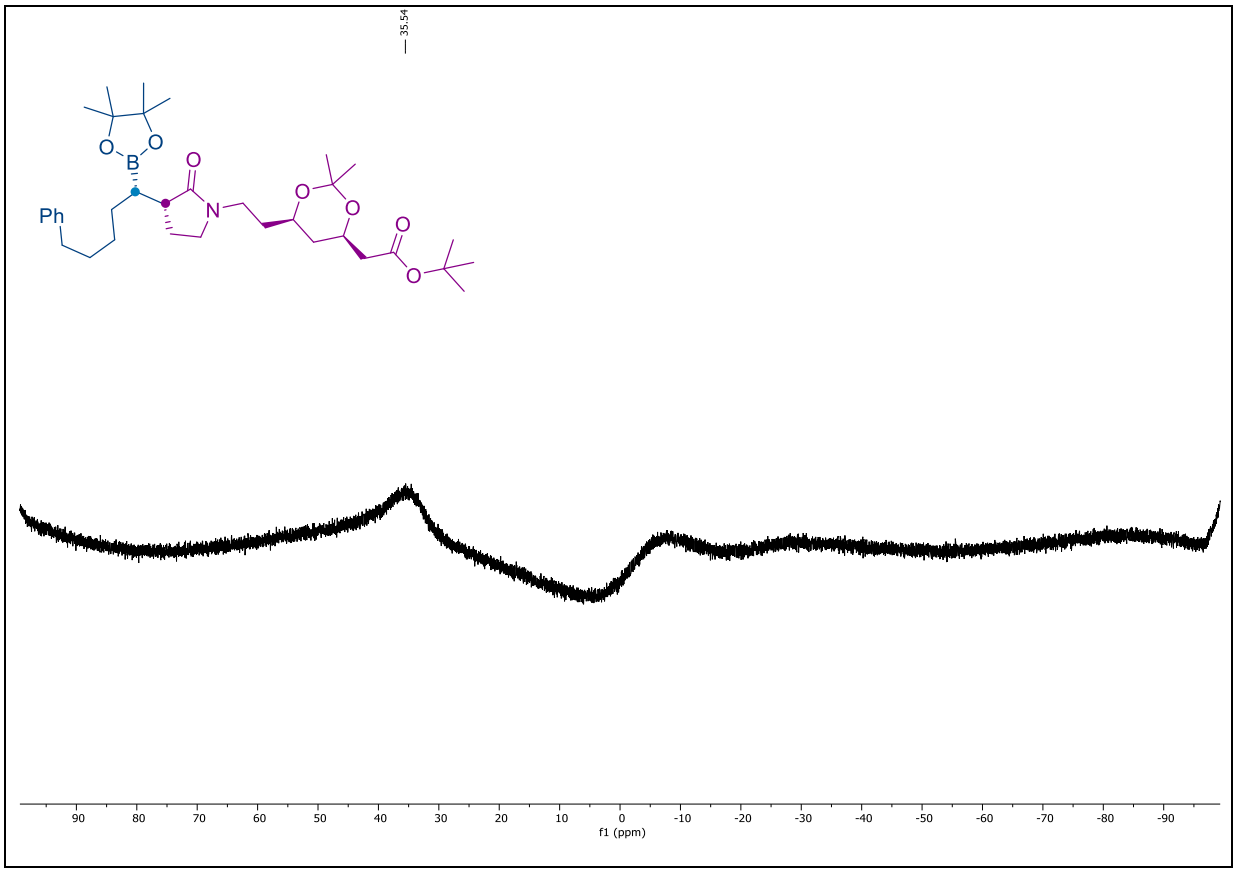
NMR spectra of 8:



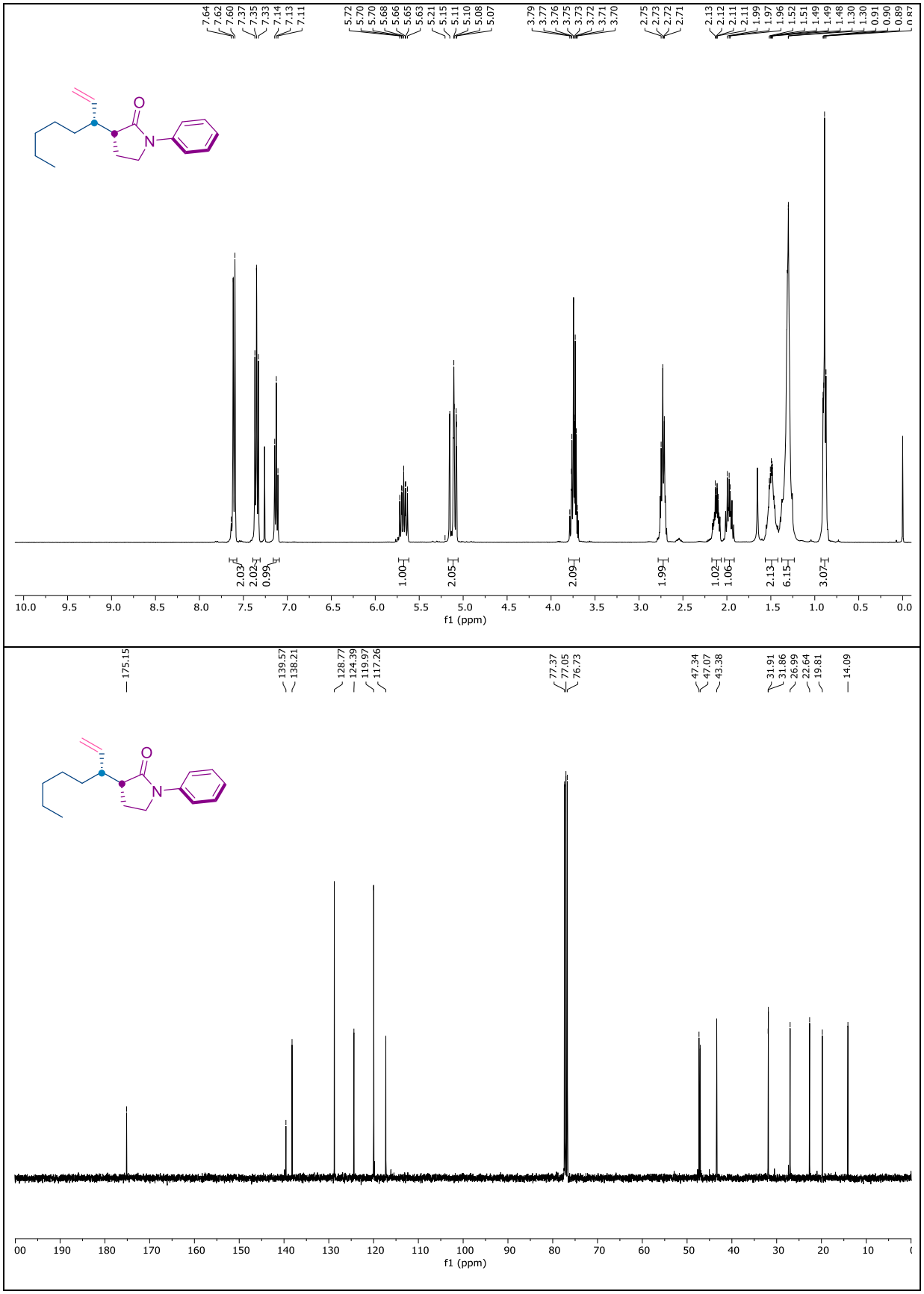

34.21
O
N
O
B
O
O
H
H
H
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 9:

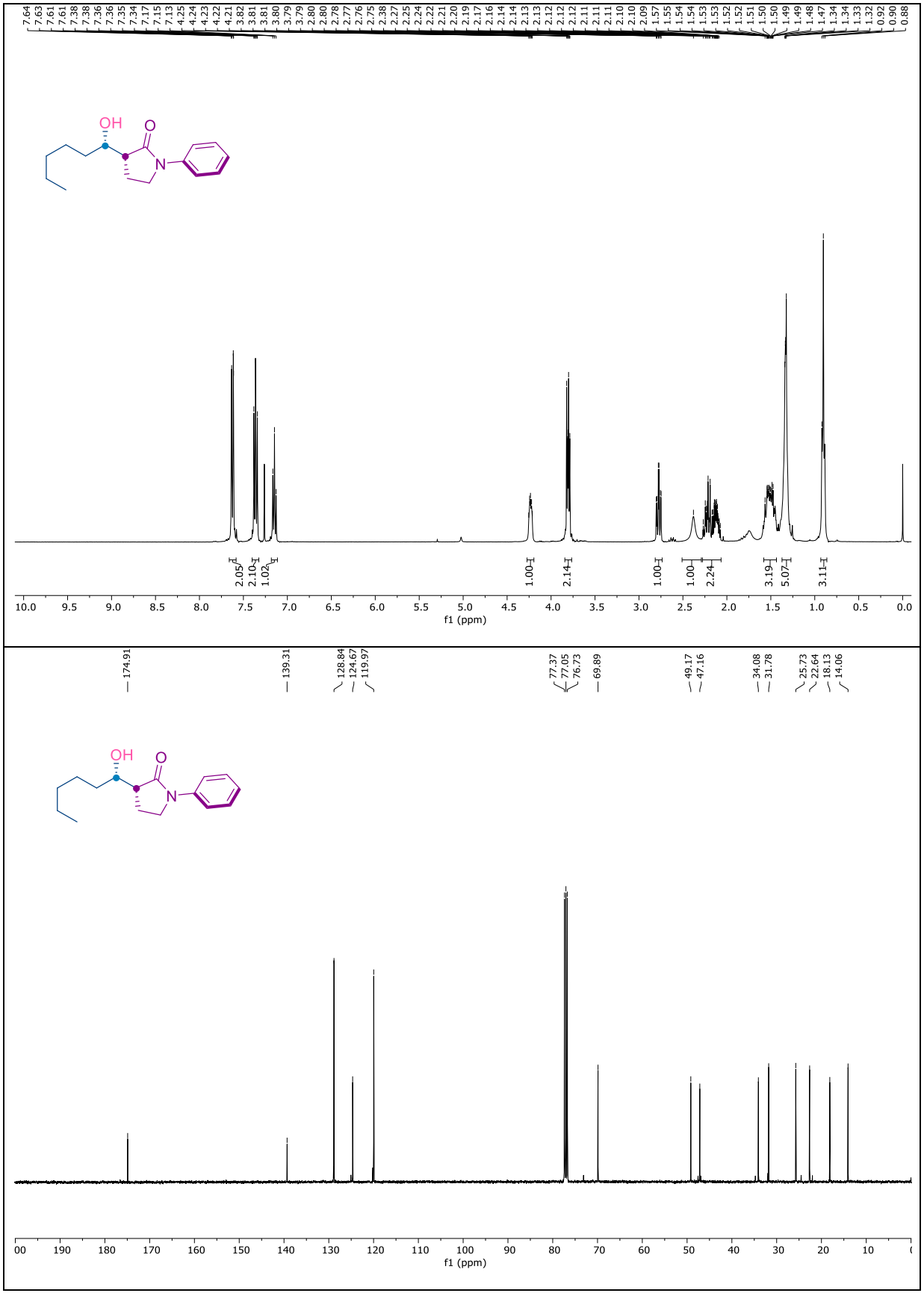



35.54
O
B
O
O
N
O
O
O
O
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

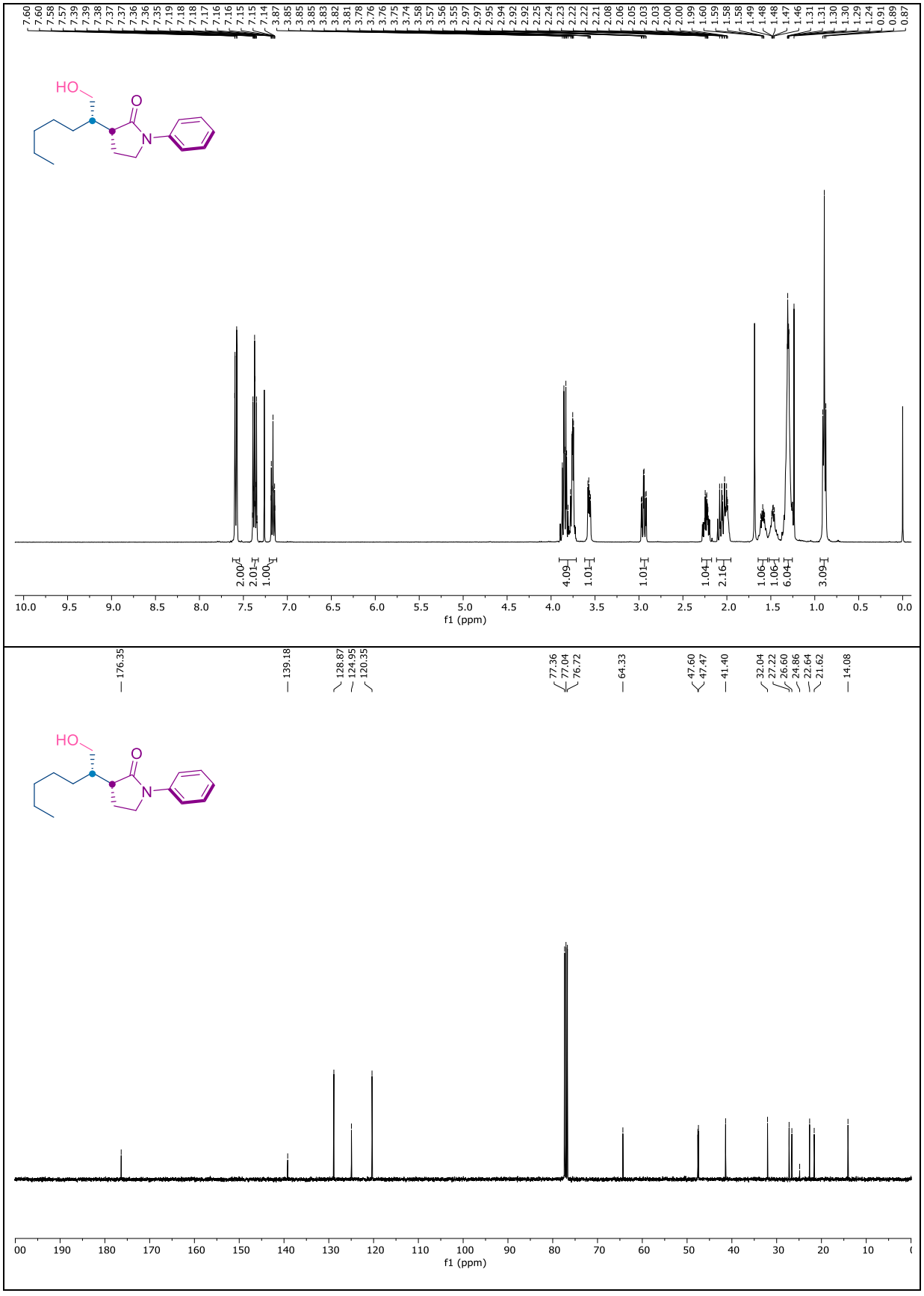
NMR spectra of 10:



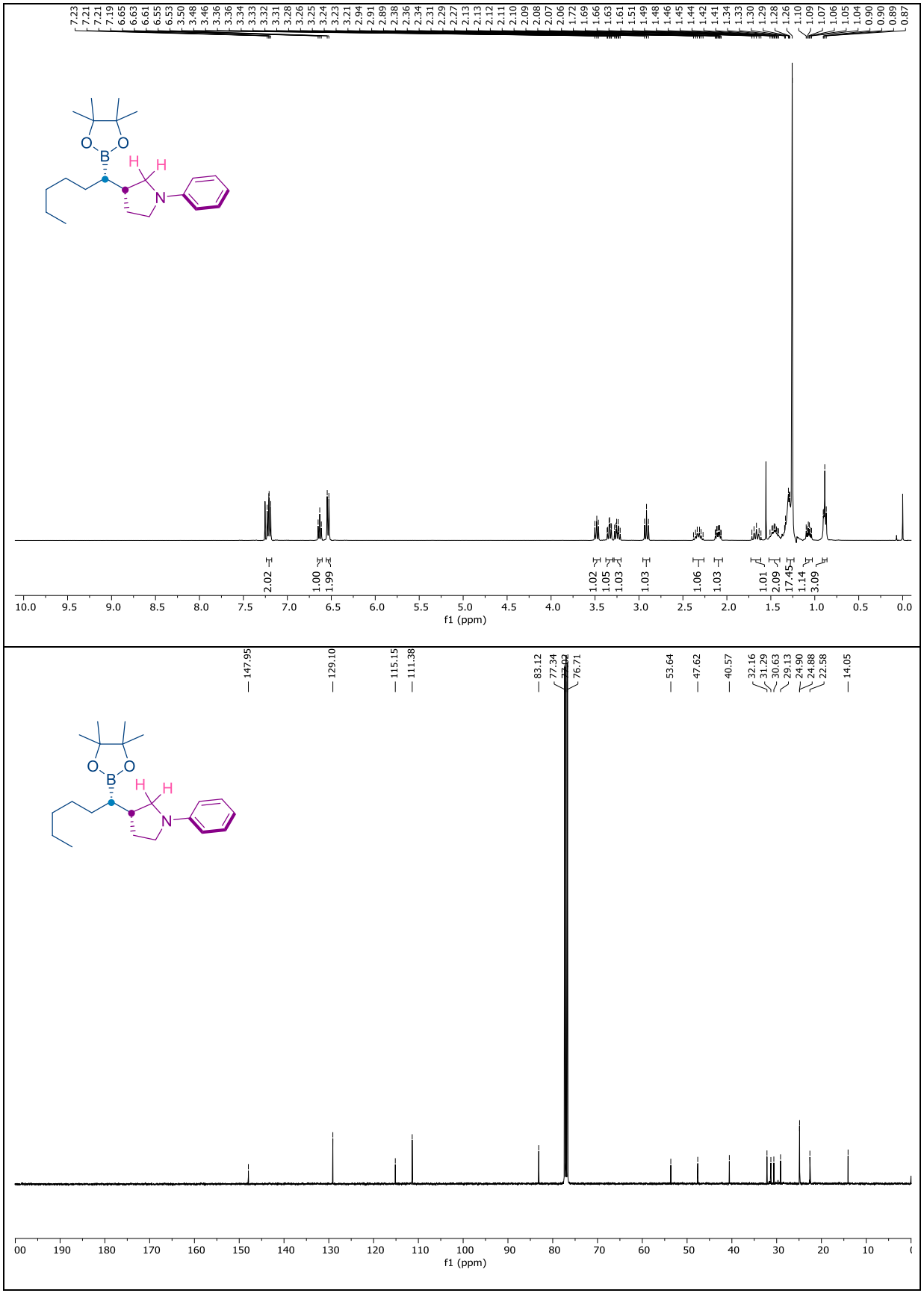
NMR spectra of 11:

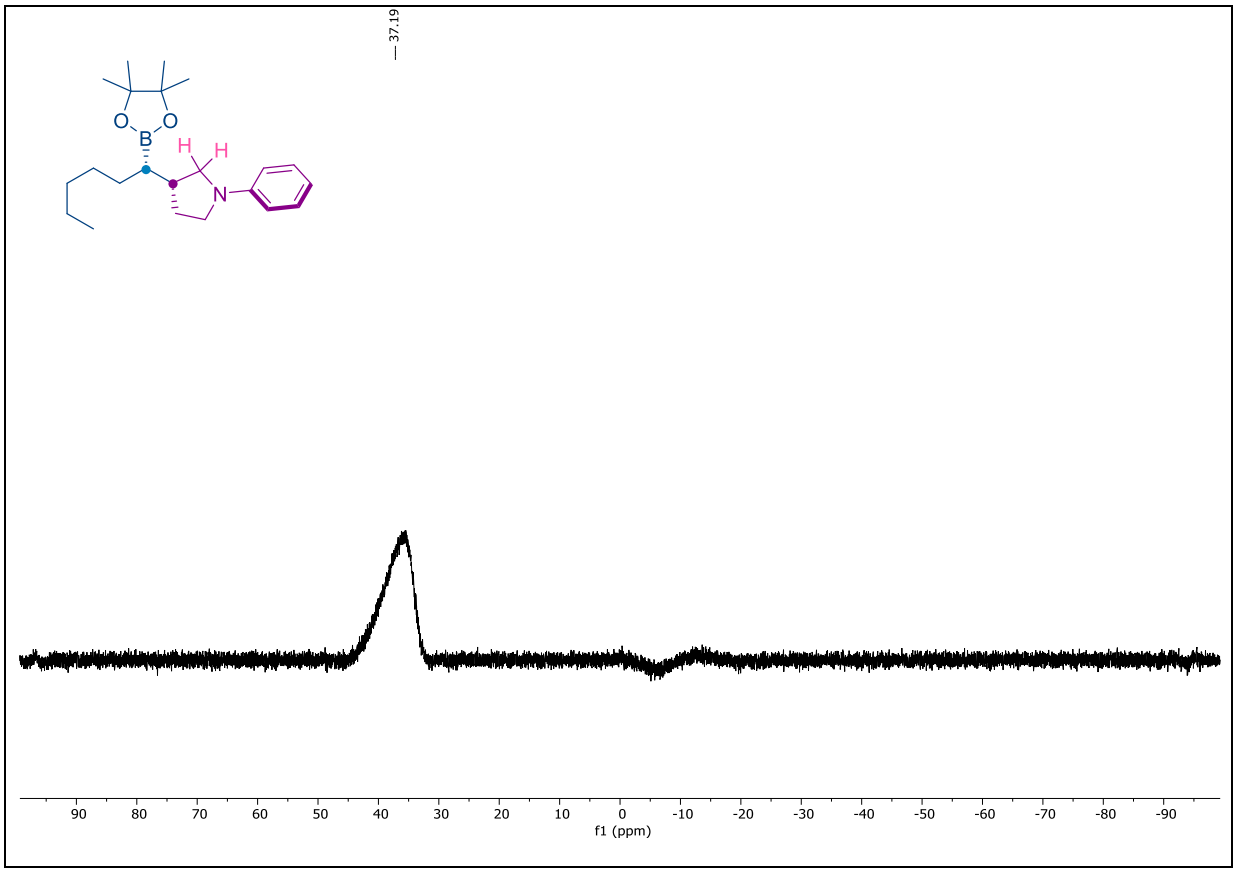


NMR spectra of 12:

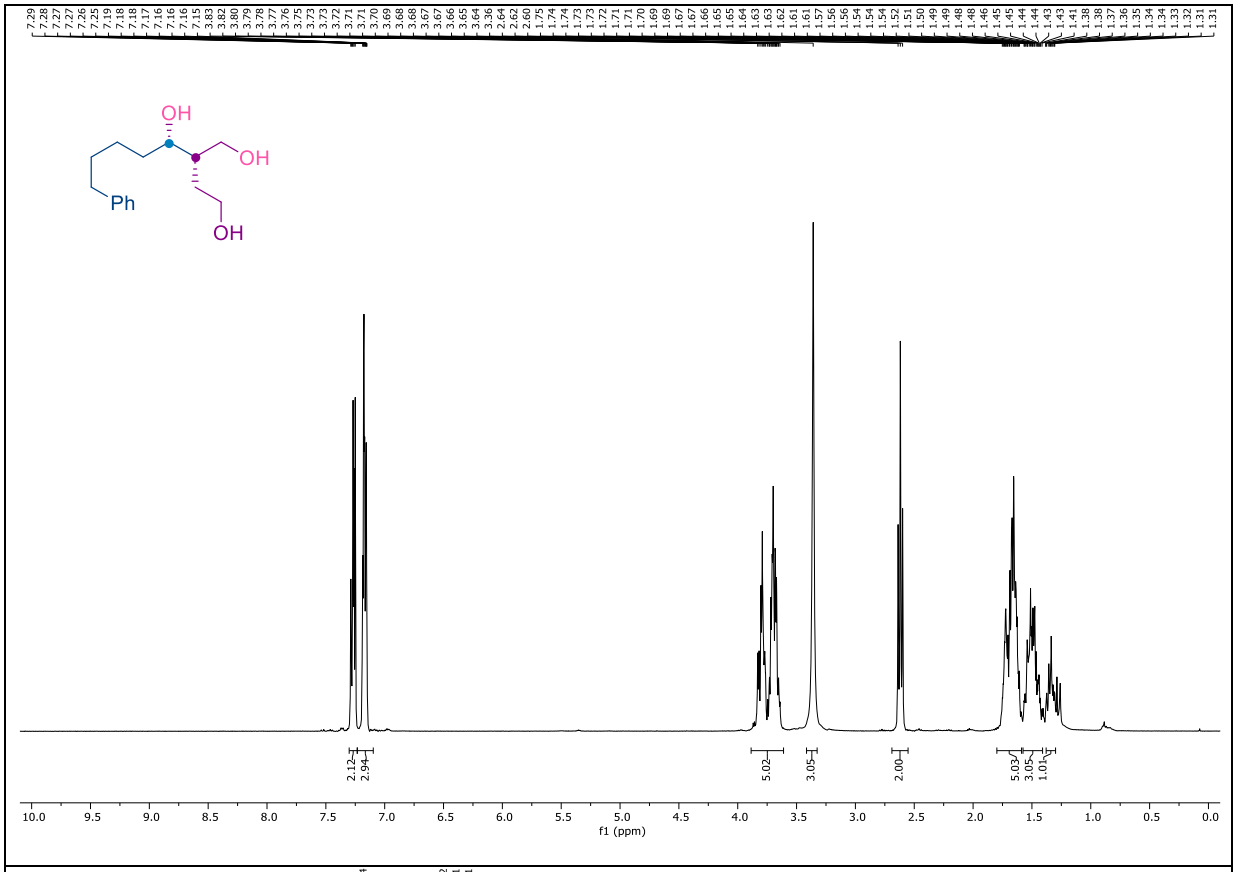


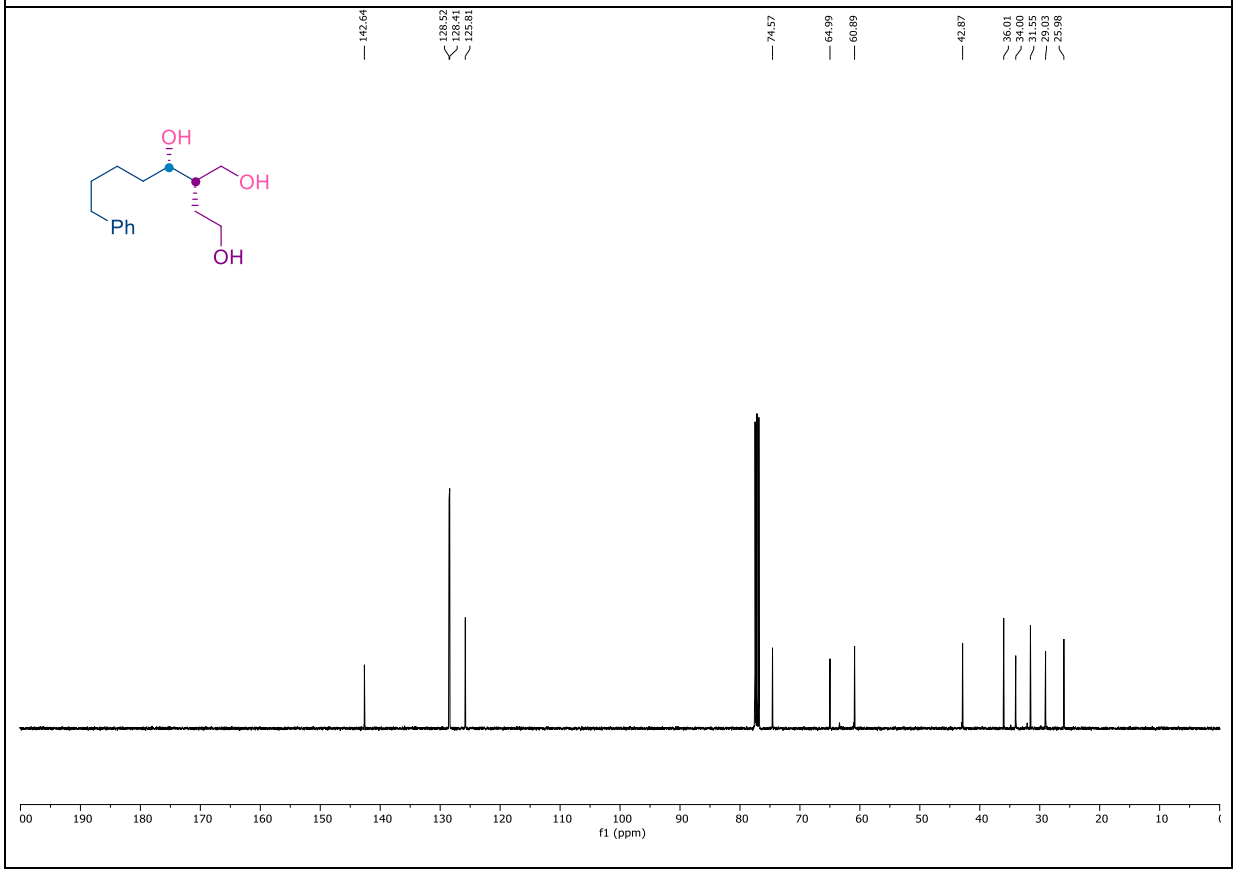
NMR spectra of 13:



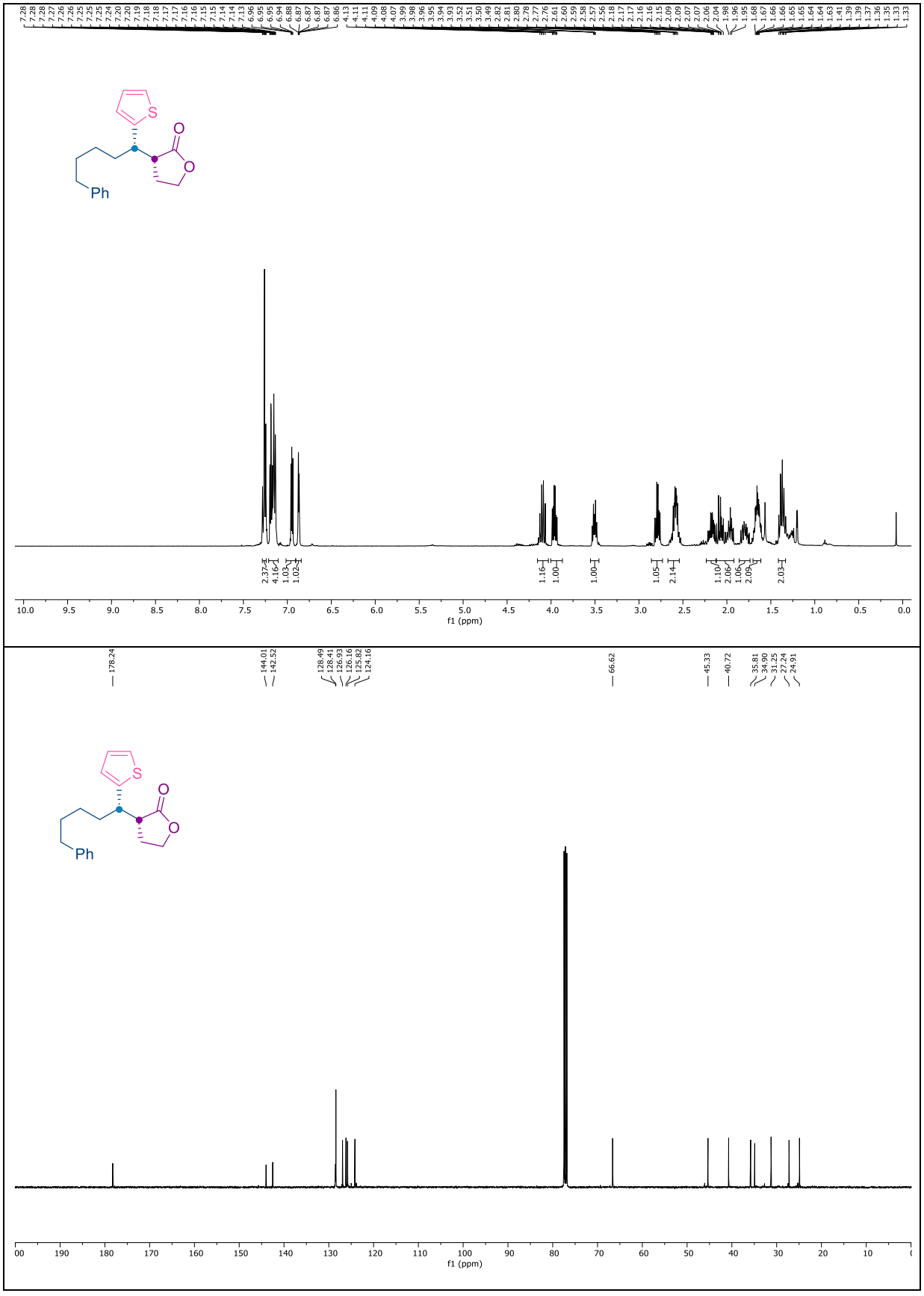

37.19
O
O
B
H
H
N
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 14:

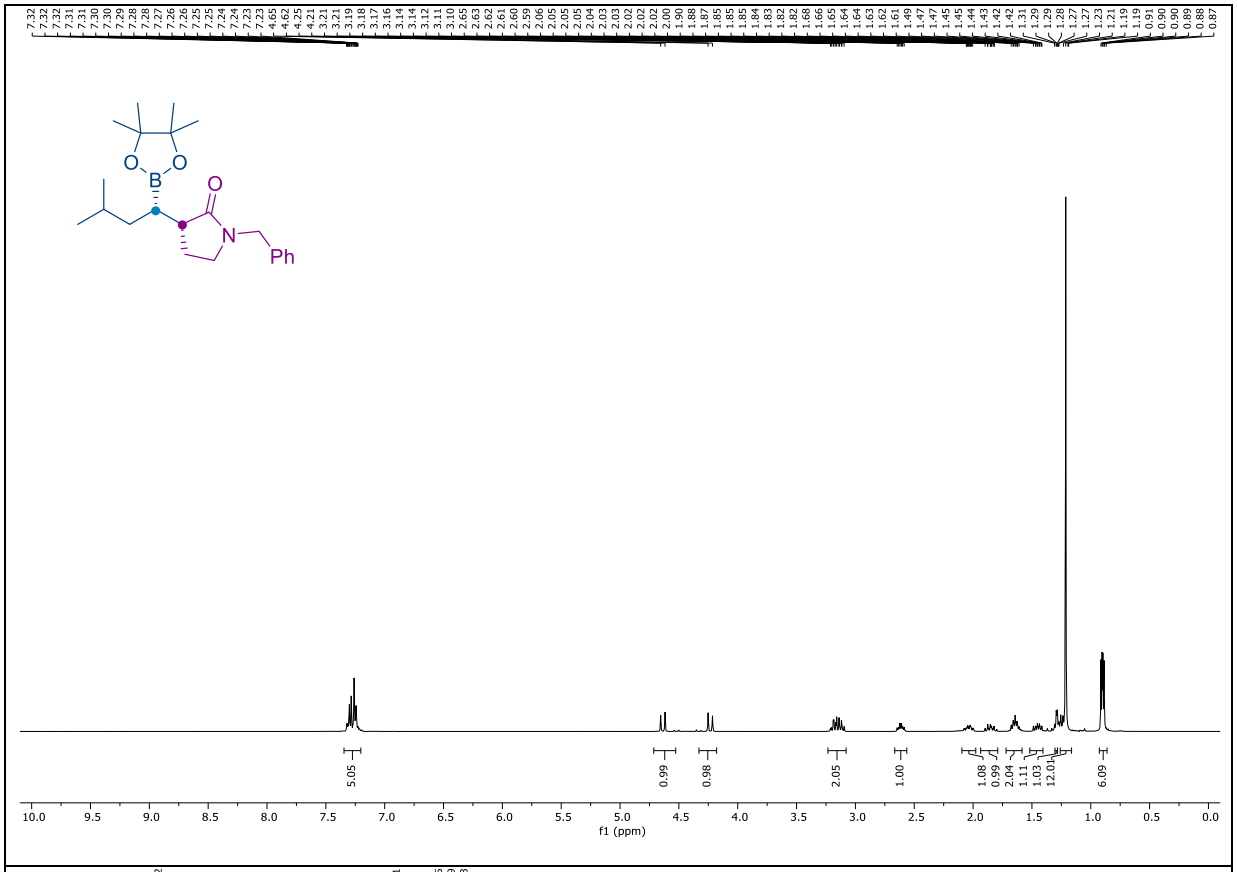


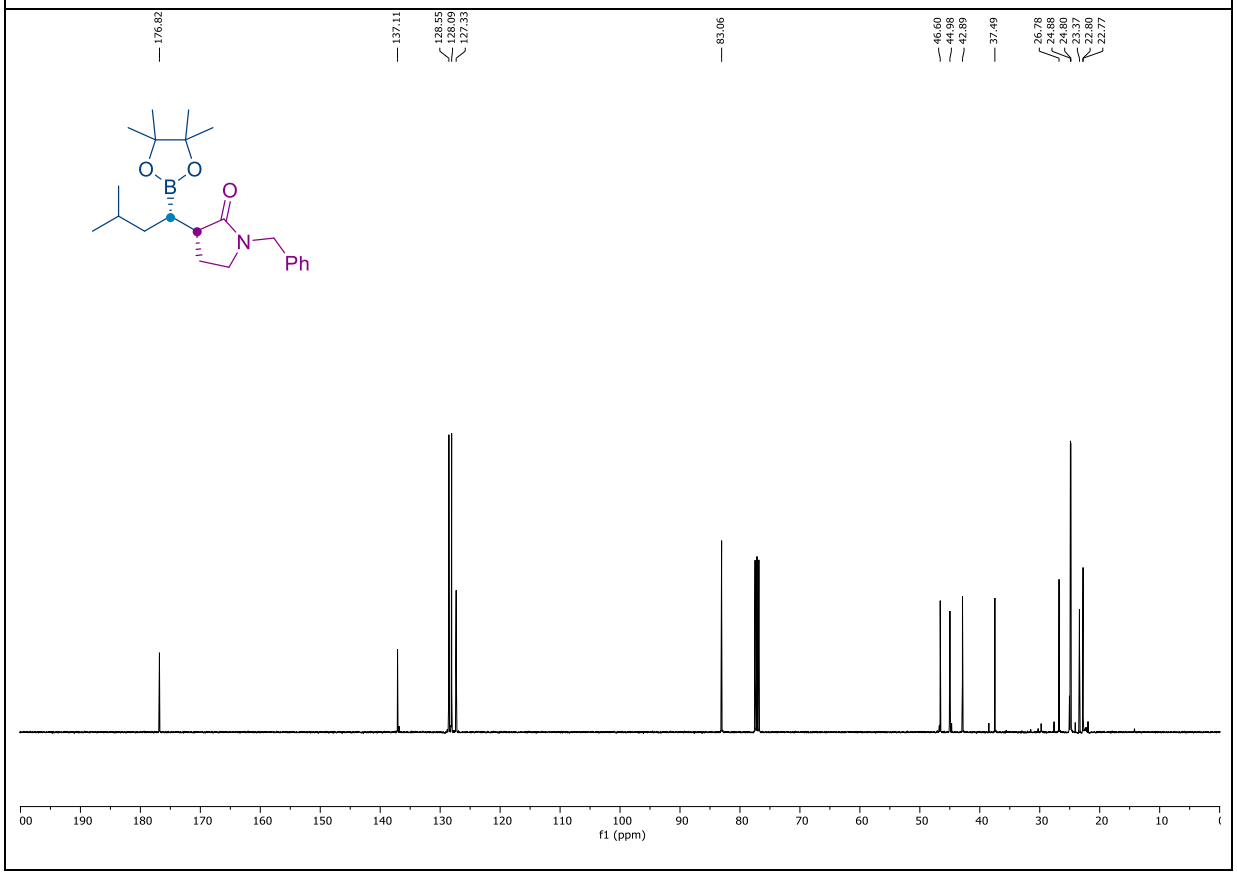


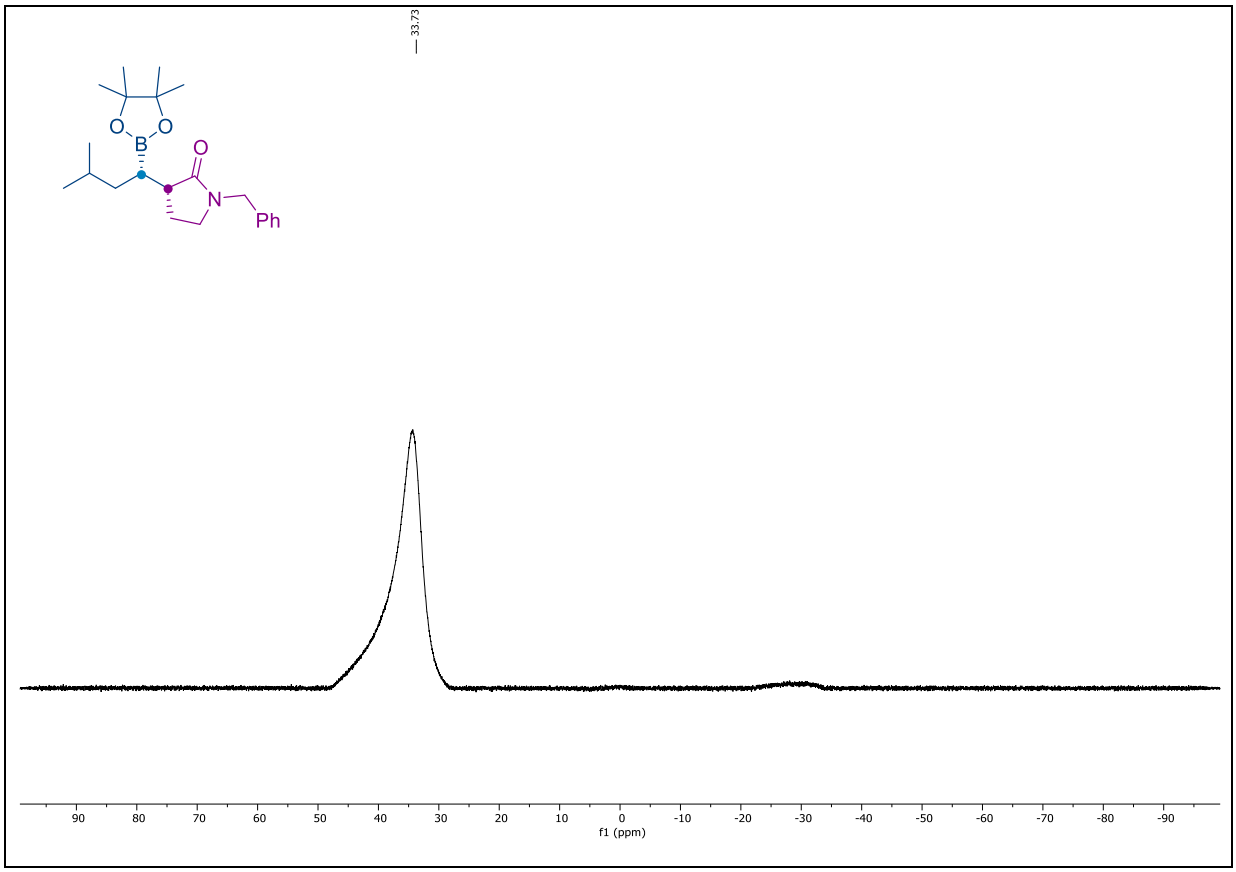
NMR spectra of 15:



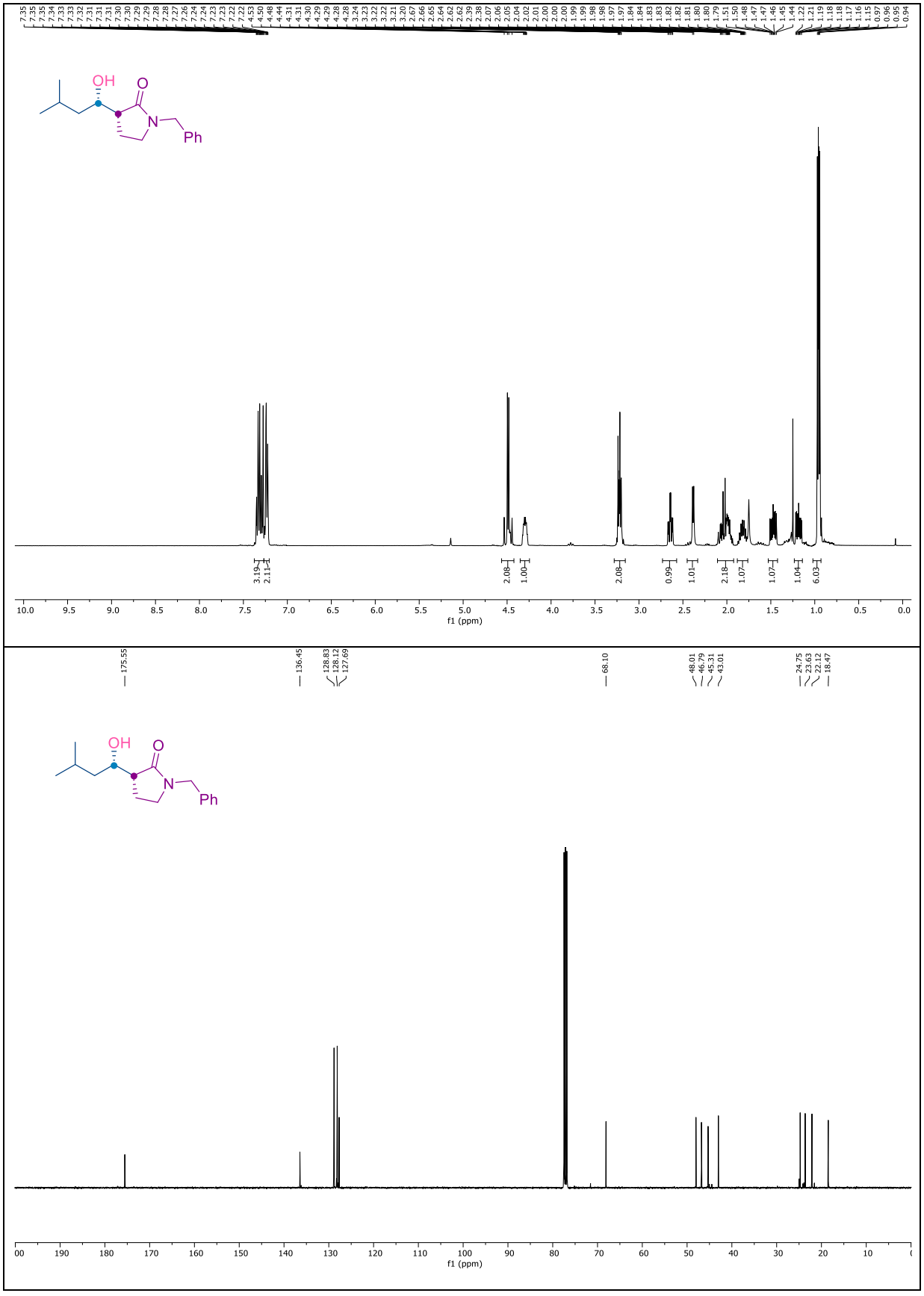
NMR spectra of 16:



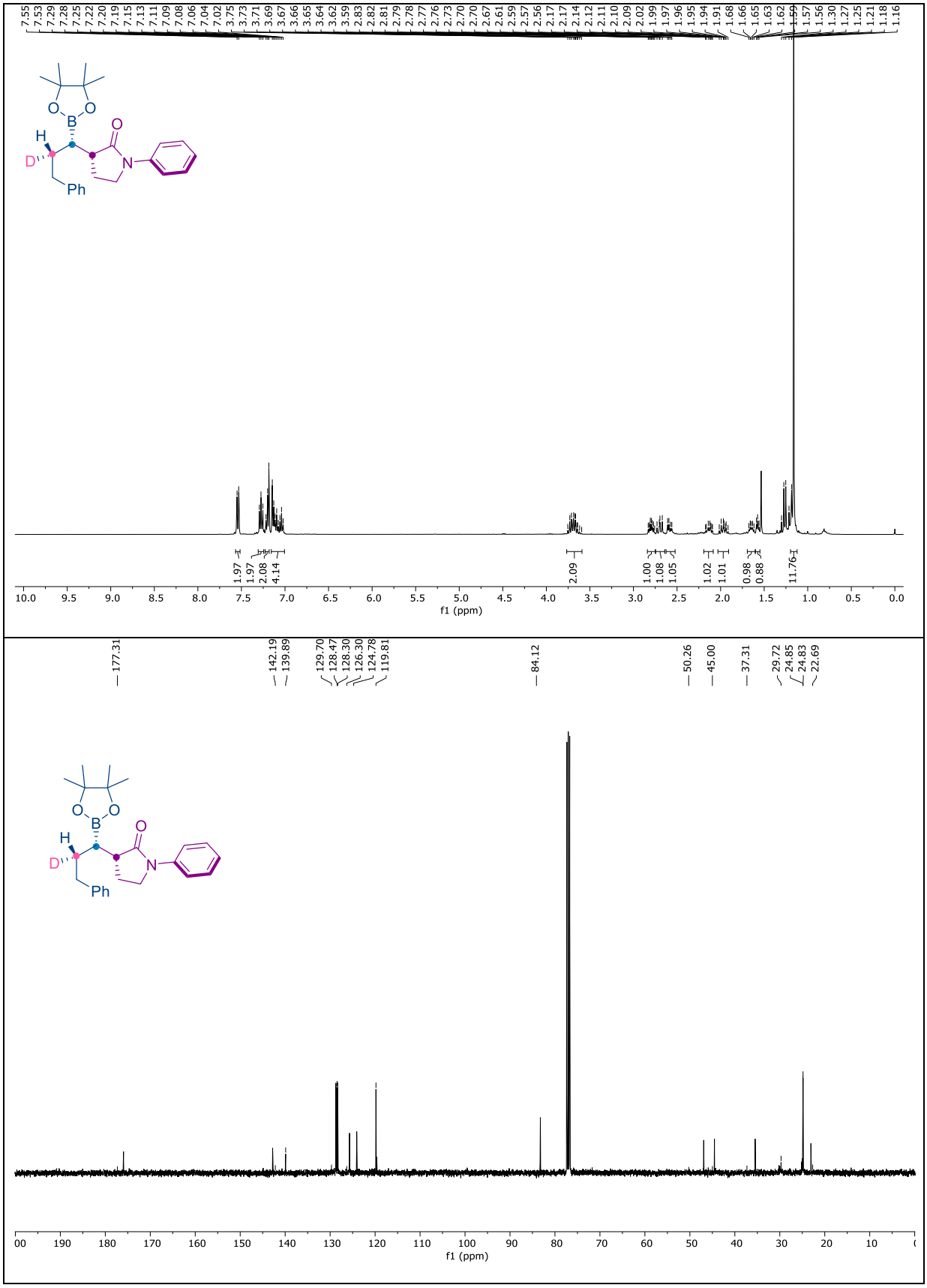


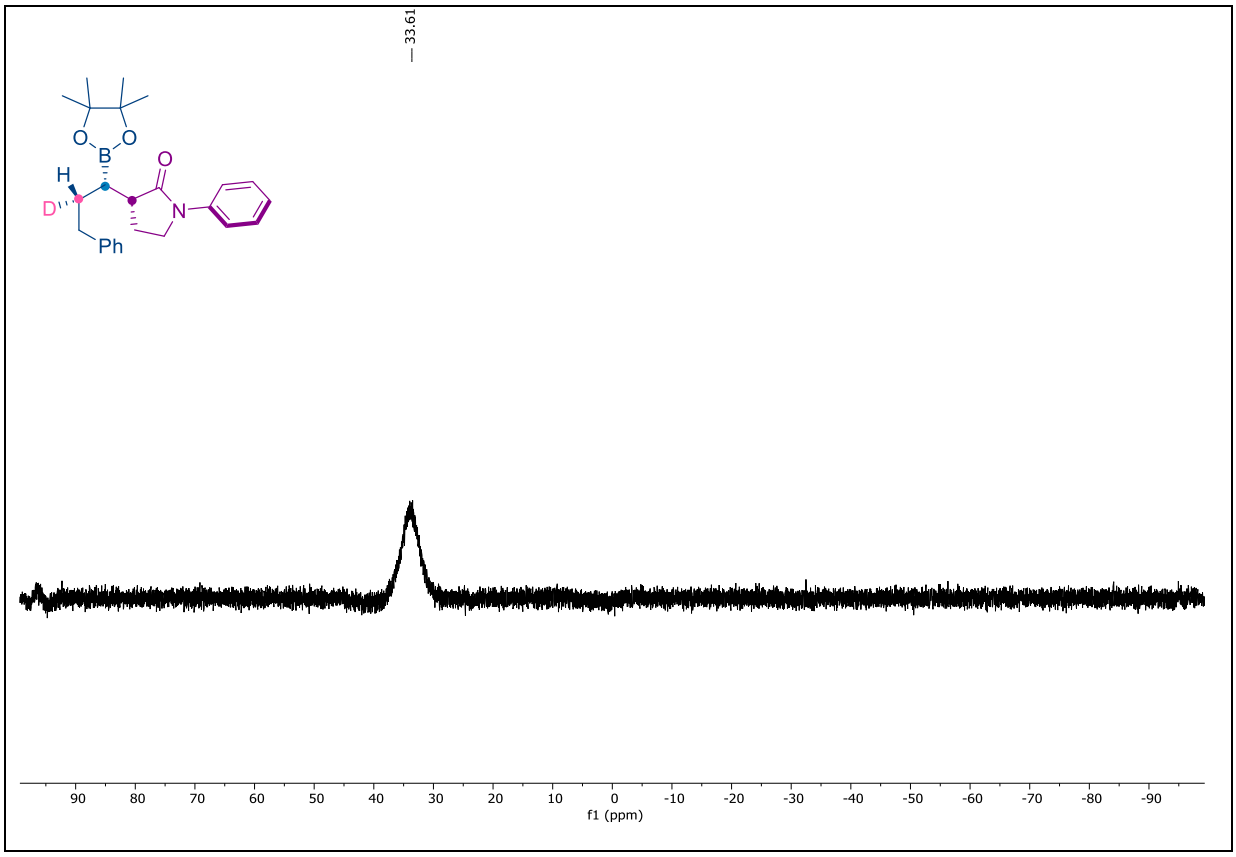

33.73
O
O
B
O
N
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 17:



NMR spectra of 23:




33.61
O
B
O
H
D
O
N
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

Supplementary References

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