
Supplementary information

Enantioselective C(*sp*³)–C(*sp*³) cross-coupling of non-activated alkyl electrophiles via nickel hydride catalysis

In the format provided by the
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Enantioselective C(sp³)–C(sp³) Cross-Coupling of Non-activated Alkyl Electrophiles via Nickel Hydride Catalysis

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Table of Contents

1. Instrumentation and chemicals.....	3
2. Optimization of reaction conditions (Table 1–6).....	4-9
3. Synthesis of ligands.....	9-12
4. Synthesis of alkenyl boronic esters.....	13-15
5. Preparation of alkyl halides.....	16-22
6. General Procedure (GP4) for probing the scope of enantioselective C(sp ³)–C(sp ³) cross-coupling of non-activated alkyl electrophiles.....	23-75
7. Functional group transformations.....	76-81
8. Synthesis of 12 , a key intermediate of (S)-(+)-Pregabalin.....	81-84
9. Large scale reaction (with 15 mol% catalyst loading).....	84-85
10. Gram scale reaction (with 10 mol% catalyst loading).....	85
11. One-pot reaction from alkyne without isolation of alkenyl Bpin intermediate.....	85-86
12. Mechanistic investigations:	
12.1 Reaction with a <i>cis</i> -boronic ester.....	86
12.2 Monitoring of reactions with a mixture of <i>cis</i> - and <i>trans</i> -alkenyl boronic ester.....	86-87
12.3 Reaction profile.....	87-88
12.4 Radical-clock experiment.....	88-89
12.5 TEMPO quenching experiment.....	89
12.6 Probe for origin of regioselectivity.....	90
12.7 Reaction with a pre-complex NiCl ₂ - L6	90
13. Reactions with substrates where an alkenyl group is distal to a Bpin group.....	91-93
14. Determination of the absolute configuration of 3e and 4g	94
15. Crystallography details.....	95-99
16. ¹ H, ¹³ C and ¹¹ B NMR spectra of compounds.....	100-258
17. References.....	259-261

1. Instrumentation and chemicals:

All reactions for the Ni-catalyzed enantioselective $C(sp^3)-C(sp^3)$ coupling were set up in a 10 mL Teflon-screw capped test tubes (unless otherwise noted) under an inert nitrogen (N_2) atmosphere using glove-box techniques. The test tubes were then sealed with airtight electrical tapes and the reaction mixtures were stirred at room temperature outside the glovebox for 36 – 48 hours with 460 rpm. 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: 1H , ^{13}C , ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance 400 Spectrometer. 1H and $^{13}C\{^1H\}$ chemical shifts were referenced internally to residual solvent peaks relative to TMS ($\delta = 0$ ppm) at 299 K. Chemical shifts (δ (ppm)) are reported relative to TMS ($\delta(^1H)$ 0.0 ppm, $\delta(^{13}C)$ 0.0 ppm). The solvent's residual proton resonance and the respective carbon resonance (for $CHCl_3$; $\delta(^1H)$ 7.26 ppm, $\delta(^{13}C)$ 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 $Ce(SO_4)_2 \times H_2O$ (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 an FID detector. All GC-MS analyses were performed on an Agilent Technologies 7890A GC system equipped with a 5975C MS detector.

HPLC spectra were recorded on an *Agilent* HPLC. Column, eluent and retention times for HPLC analysis used for the determination of enantiomeric ratios 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.

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 or purchased from *Aldrich*, *TCI*, *Acros Organics*, *Alfa Aesar*, *Fluorochem*, *Enamine* and *ABCR*. Anhydrous $NiCl_2$ and DEMS from *ABCR*, anhydrous KF from *Alfa Aesar*, anhydrous DCE from *Aldrich* and anhydrous DMF from *Acros Organics* were purchased.

2. Optimization of reaction conditions

General procedure (GP1) for the Optimization of the Enantioselective C(sp³)-C(sp³) Cross-Coupling of Non-activated Alkyl Electrophiles:

To an oven-dried 10 mL Teflon-screw capped test tube equipped with a magnetic stir bar (6x15 mm) were added a Ni-salt (x mol%) and a ligand **L** (y mol%) under an inert nitrogen (N₂) atmosphere using glove-box techniques. An anhydrous solvent (0.5 mL) was added, and the mixture was stirred for 40 minutes at room temperature. Then a base (2.5 equiv.) was added to it and the stirring was continued for another 2 – 3 minutes, at which point *trans*-1-hexenylboronic acid pinacol ester **1a** (25.0 μL, 0.1 mmol, 1.0 equiv.) was added and the mixture was stirred for an additional 1 min. Then 3-phenyl-1-propyl iodide **2a** (24.4 μL, 0.15 mmol, 1.5 equiv.) was added to the resulting mixture. Stirring was further continued for 5 minutes, then a silane (2.5 equiv.) was added dropwise to it. The test tube was then sealed with airtight electrical tapes and removed from the glove box and stirred at room temperature for 24 – 48 hours maintaining 460 rpm unless otherwise noted. Afterwards, water (1.0 mL) and EtOAc (3.0 mL) were added to the reaction mixture. Dodecane (23.0 μL) was added as an internal standard for GC FID analysis 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 dried over Na₂SO₄, and the volatiles were removed to afford the crude product. The crude product was purified by flash column chromatography.

Determination of enantiomeric excess (e.e.):

The boronic ester product was oxidized to the corresponding alcohol following **GP2**. Then, the alcohol was purified by PTLC and the enantiomeric excess (e.e.) was determined by HPLC analysis.

General procedure (GP2) for the stereospecific oxidation of boronic ester to alcohol:

The purified boronic ester product (10 – 12 mg) was dissolved in a 1:1 mixture of THF:H₂O (2.0 mL) and then NaBO₃•4H₂O (40 mg) was added to it at room temperature. After stirring for 4 hours at room temperature, H₂O (1.0 mL) was added. The reaction mixture was extracted with Et₂O (3x2.0 mL). The combined organic phases were dried over Na₂SO₄, and the volatiles were removed under vacuum. The product was purified by PTLC. Afterwards, it was used for the HPLC analysis for the determination of enantiomeric excess (e.e.).

Optimization Tables

Table 1. Screening of ligands:

$n\text{-C}_4\text{H}_9\text{-CH=CH-Bpin}$ (1a) + $\text{Ph-CH}_2\text{-CH}_2\text{-CH}_2\text{-I}$ (2a) $\xrightarrow[\text{DMA (0.2 M), RT, 24 h}]{\text{NiI}_2 (10 \text{ mol\%}), \text{L (12 mol\%)}, \text{DEMS (2.5 equiv)}, \text{KF (2.5 equiv)}}$ $n\text{-C}_4\text{H}_9\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-Ph}$ (3a)

L1

L2

L3

L4

L5

L6

L7

L8

L9

L10

L11

L12

L13

L14

L15

L16

Entry	Ligand(L)	Yield(%)	e.e.(%)
1	L1	42	35
2	L2	80	24
3	L3	5	n.d.
4	L4	11	6
5	L5	30	35
6	L6	66	61
7	L7	48	29
8	L8	70	14
9	L9	61	33
10	L10	5	n.d.
11	L11	12	24
12	L12	21	11
13	L13	n.r.	n.d.
14	L14	n.r.	n.d.
15	L15	trace	n.d.
16	L16	n.r.	n.d.

n.r. = no reaction, n.d. = not determined.

Table 2. Screening of Ni-salts:

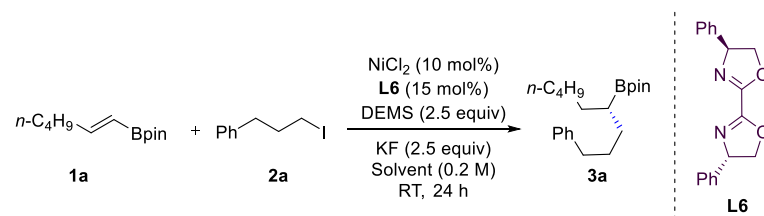
Entry	Ni-salt	Yield(%)	e.e.(%)
1	NiI ₂	66	61
2	NiBr ₂	72	64
3	NiCl ₂	71	78
4 ^a	NiCl ₂	79	80
5 ^{a,b}	NiCl ₂	33	30
6	NiCl ₂ .dme	45	78
7	NiBr ₂ .dme	44	74
8	NiBr ₂ .diglyme	41	72
9	Ni(acac) ₂	26	22
10	Ni(OTf) ₂	9	17
11	NiI ₂ .6H ₂ O	38	60
12	NiCl ₂ .6H ₂ O	51	76
13	Ni(NO ₃) ₂ .6H ₂ O	65	72
14	Ni(BF ₄) ₂ .6H ₂ O	51	68
15	NiSO ₄ .6H ₂ O	16	26
16	NiF ₂ .4H ₂ O	n.r.	n.d.
17	Ni(ClO ₄) ₂ .6H ₂ O	48	52

^a15 mol% Ligand was used. ^bThe reaction was conducted at 0 °C for 48 hours. n.r. = no reaction, n.d. = not determined.

Table 3. Further screening of ligands:

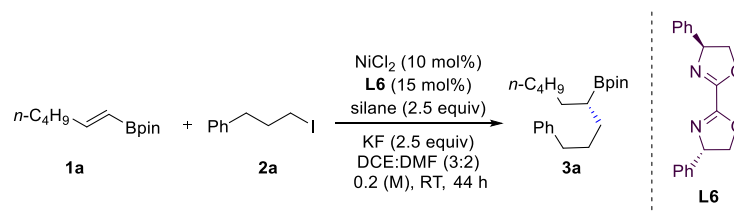
Entry	Ligand(L)	Yield(%)	e.e.(%)
1	L17	80	74
2	L18	78	78
3	L19	77	0

Table 4. Screening of solvents:



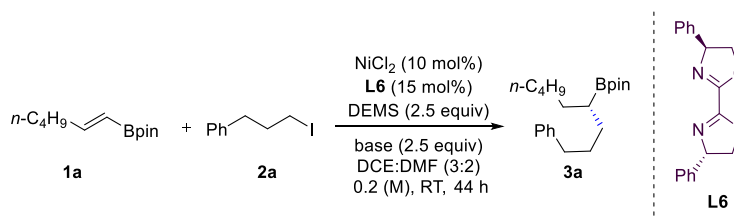
Entry	Solvents	Yield(%)	e.e.(%)
1	DMA	79	80
2	DMF	78	59
3	NMP	64	80
4	DMI	34	48
5	DMPU	25	44
6	DCE	n.r.	n.d.
7	DMA:NMP(3:2)	59	80
8	DMA:DMF (3:2)	82	83
9	DMA:DCE(3:2)	54	79
10	DMA:DMSO(3:2)	61	70
11	DMA:MeCN(3:2)	79	68
12	DMA:THF(3:2)	63	74
13	DMA:DME(3:2)	76	72
14	DMF:DMA(3.17:1)	82	69
15	DCM:DMA(3.17:1)	19	92
16	PhCF ₃ :DMA(3.17:1)	18	63
17	DCE:DMPU(3.17:1)	n.r	n.d.
18	DCE:DMA(3.17:1)	n.r	n.d.
19	DCE:NMP(3.17:1)	n.r	n.d.
20	DCE:DMF(3.17:1)	29	93
21	DCE:PhCF ₃ (3.17:1)	n.r	n.d.
22 ^a	DCE:DMF(3.17:1)	40	93
23 ^a	DCM:DMF(3.17:1)	34	92
24 ^a	PhCl:DMF(3.17:1)	51	80
25 ^a	PhCH ₃ :DMF(3.17:1)	40	73
26 ^a	PhCF ₃ :DMF(3.17:1)	71	78
27 ^a	DCE:DMF(3:2)	55	92
28 ^a	DCE:DMF(1:1)	61	88
29 ^a	DCE:DMF(2:3)	79	84
30 ^a	DCE:DMF(4:1)	30	94
31 ^a	DCE:DMF(2.57:1)	36	93
32 ^a	DCE:DMF(2.12:1)	42	93

^aReaction time = 44 hours. n.r. = no reaction, n.d. = not determined.

Table 5. Screening of silanes:

Entry	Silanes	Yield(%)	e.e.(%)
1	DEMS	55	92
2	(MeO) ₂ MeSiH	55	85
3	(MeO)Me ₂ SiH	31	80
4	(EtO) ₃ SiH	42	89
5	Me(OTMS) ₂ SiH	trace	n.d.
6	PMHS	48	91
7	Et ₃ SiH	trace	n.d.
8	Ph ₂ SiH ₂	14	n.d.
9	Ph ₃ SiH	trace	n.d.
10	PhSiH ₃	trace	n.d.
11	PhMe ₂ SiH	n.r.	n.d.

n.r. = no reaction, n.d. = not determined.

Table 6. Screening of bases:

Entry	Bases	Yield(%)	e.e.(%)
1	LiF	n.r.	n.d.
2	NaF	n.r.	n.d.
3	KF	55	92
4	RbF	65	56
5 ^a	CsF	63	53
6	K ₂ CO ₃	10	n.d.
7	Na ₂ CO ₃	10	n.d.
5	K ₃ PO ₄	n.r.	n.d.

n.r. = no reaction, n.d. = not determined. ^aReaction time = 12 hours.

Table 7. Manipulation of substrates ratio and catalyst loading:

Entry	1a:2a (equiv.)	Yield(%)	e.e.(%)
1 ^a	1:1.5	55	92
2 ^a	1.5:1	62	92
3 ^b	1.5:1	72(69)	92
4 ^b	2:1	74	92
5 ^c	2:1	78	91

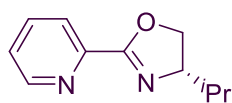
^a10 mol% NiCl₂ and 15 mol% ligand. ^b15 mol% NiCl₂ and 20 mol% ligand. ^c17.5 mol% NiCl₂ and 22 mol% ligand. Isolated yield in the parenthesis.

3. Synthesis of ligands (L):

Ligands **L3**, **L8**, **L13**, **L14**, **L15** and **L16** are commercially available.

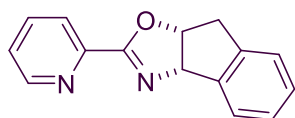
Ligands **L1**, **L2**, **L9**, **L10**, **L11** and **L12** were synthesised according to a known literature procedure.^[1]

(S)-4-Isopropyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L1):



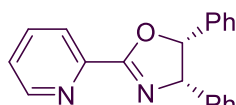
The title compound was synthesized from 2-cyanopyridine and L-valinol following a known literature procedure.^[1] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 – 8.64 (m, 1H), 8.01 – 7.99 (m, 1H), 7.73 – 7.69 (m, 1H), 7.34 – 7.31 (m, 1H), 4.51 – 4.42 (m, 1H), 4.21 – 4.06 (m, 2H), 1.84 (hept, *J* = 6.7 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.54, 149.71, 146.92, 136.56, 125.44, 123.90, 72.97, 70.75, 32.77, 19.06, 18.21. Spectral data match those previously reported.^[2]

(3aS,8aR)-2-(Pyridin-2-yl)-3a,8a-dihydro-8H-indeno[1,2-d]oxazole (L2):



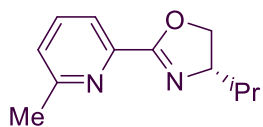
The title compound was synthesized from 2-cyanopyridine and (1*S*,2*R*)-(-)-*cis*-1-amino-2-indanol following a known literature procedure.^[3] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.68 – 8.66 (m, 1H), 8.04 – 8.02 (m, 1H), 7.74 – 7.70 (m, 1H), 7.59 – 7.57 (m, 1H), 7.35 – 7.32 (m, 1H), 5.80 (d, *J* = 7.9 Hz, 1H), 5.57 (td, *J* = 7.3, 6.4, 2.1 Hz, 1H), 3.57 – 3.41 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.22, 149.72, 146.93, 141.62, 139.87, 136.58, 128.65, 127.53, 125.76, 125.55, 125.40, 124.15, 84.02, 77.19, 39.79. Spectral data match those previously reported.^[3]

(4*S*,5*R*)-4,5-Diphenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (L9):



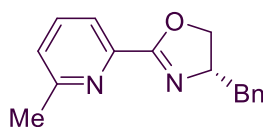
The title compound was synthesized from 2-cyanopyridine and (1*R*,2*S*)-2-amino-1,2-diphenylethan-1-ol following a known literature procedure.^[3] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.06 – 7.00 (m, 6H), 6.98 – 6.94 (m, 4H), 6.10 (d, *J* = 10.3 Hz, 1H), 5.81 (d, *J* = 10.3 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.20, 150.06, 146.66, 137.32, 136.81, 136.17, 127.96, 127.67, 127.48, 127.07, 126.50, 125.93, 124.33, 86.02, 74.61. Spectral data match those previously reported.^[3]

(S)-4-Isopropyl-2-(6-methylpyridin-2-yl)-4,5-dihydrooxazole (L10):



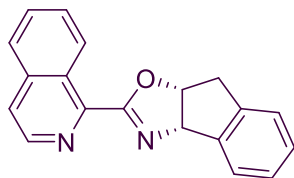
The title compound was synthesized from 2-cyano-6-methylpyridine and L-valinol following a known literature procedure.^[1] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.8, 1.7 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 4.53 – 4.43 (m, 1H), 4.24 – 4.14 (m, 1H), 4.18 – 4.06 (m, 1H), 2.61 (s, 3H), 1.96 – 1.79 (m, 1H), 1.03 (d, *J* = 8.5 Hz, 3H), 0.91 (d, *J* = 8.5 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.80, 158.81, 146.46, 136.78, 125.35, 121.26, 72.93, 70.80, 32.82, 24.77, 19.25, 18.20. Spectral data match those previously reported.^[4]

(S)-4-Benzyl-2-(6-methylpyridin-2-yl)-4,5-dihydrooxazole (L11):



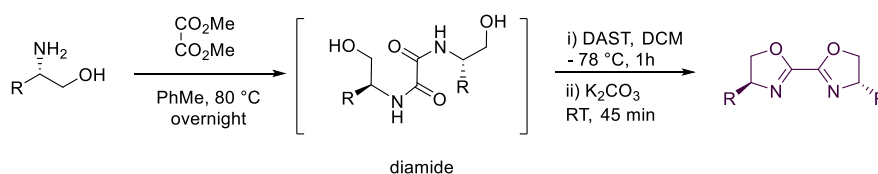
The title compound was synthesized from 2-cyano-6-methylpyridine and L-phenylalaninol following a known literature procedure.^[1] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.88 (m, 1H), 7.69 – 7.65 (m, 1H), 7.36 – 7.19 (m, 6H), 4.69 – 4.61 (m, 1H), 4.44 (t, *J* = 9.0 Hz, 1H), 4.24 (t, *J* = 8.2 Hz, 1H), 3.33 (dd, *J* = 13.8, 5.0 Hz, 1H), 2.75 (dd, *J* = 13.8, 9.2 Hz, 1H), 2.65 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.41, 158.94, 146.29, 137.98, 136.87, 129.30, 128.70, 126.65, 125.52, 121.26, 72.62, 68.19, 41.82, 24.77. Spectral data match those previously reported.^[5]

(3aS,8aR)-2-(Isoquinolin-1-yl)-3a,8a-dihydro-8H-indeno[1,2-d]oxazole (L12):



The title compound was synthesized from isoquinoline-1-carbonitrile and (1S,2R)-(-)-*cis*-1-amino-2-indanol following a known literature procedure.^[1] ¹H NMR (400 MHz, Chloroform-*d*) δ 9.20 – 9.18 (m, 1H), 8.63 – 8.61 (m, 1H), 7.83 – 7.81 (m, 1H), 7.74 – 7.61 (m, 4H), 7.34 – 7.30 (m, 3H), 5.97 (d, *J* = 7.9 Hz, 1H), 5.61 (dq, *J* = 7.9, 2.9, 1.8 Hz, 1H), 3.61 – 3.52 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 162.56, 146.42, 141.88, 141.84, 140.07, 136.83, 130.47, 128.76, 128.57, 127.66, 127.64, 127.51, 127.08, 125.75, 125.61, 123.49, 82.91, 78.04, 39.91.

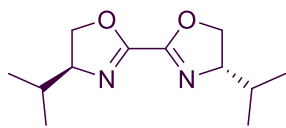
Ligands **L4**, **L5**, **L6**, **L7**, **L17**, **L18** and **L19** were synthesized according to a slightly modified known literature procedure.^[6]



Dimethyloxalate (1.00 equiv.) and chiral amino alcohol (2.00 equiv.), followed by anhydrous PhMe were added to an oven-dried schlenk tube under an inert atmosphere. The tube was heated to 80 °C. The reaction mixture was stirred overnight, during which the diamide precipitated out of solution as a white solid. The reaction mixture was cooled to room temperature and concentrated in vacuo to afford the crude diamide, which was directly used in the next step without further purification. To an oven-dried schlenk tube diamide (1.00 mmol, 1.00 equiv.) and DCM (20 mL) were added under a N₂ atmosphere. The tube was cooled to -78 °C in a dry-ice/acetone bath, and diethylaminosulfur trifluoride (0.39 mL, 2.80 mmol, 2.80 equiv.) was added dropwise. The reaction mixture was stirred for 1 h, then K₂CO₃ (552 mg, 4.00 mmol, 4.00 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 min. After that the reaction mixture was diluted with DCM (20 mL) and water (30 mL). The organic layer was washed with aqueous NaHCO₃ (20 mL)

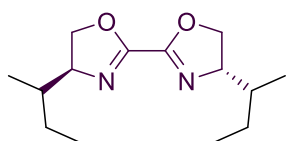
and brine (30 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc as eluent to afford the desired Bi-Ox ligands.

(4*S*,4'*S*)-4,4'-Diisopropyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (L4):



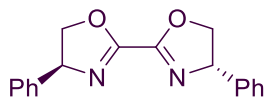
The title compound was synthesized from L-valinol following the above mentioned procedure. Yield: 68%. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.47 – 4.36 (m, 2H), 4.15 – 4.03 (m, 4H), 1.83 (h, *J* = 6.7 Hz, 2H), 1.00 (d, *J* = 8.2 Hz, 6H), 0.90 (d, *J* = 8.2 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 154.65, 73.26, 71.17, 32.54, 19.07, 18.36. Spectral data match those previously reported.^[7]

(4*S*,4'*S*)-4,4'-Di((*S*)-sec-butyl)-4,4',5,5'-tetrahydro-2,2'-bioxazole (L5):



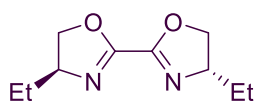
The title compound was synthesized from (*S*)-(+)-isoleucinol following the above mentioned procedure. Yield: 62%. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.42 (dd, *J* = 9.5, 7.9 Hz, 2H), 4.21 (td, *J* = 9.2, 6.2 Hz, 2H), 4.13 (dd, *J* = 8.9, 7.9 Hz, 2H), 1.76 – 1.56 (m, 4H), 1.21 (ddt, *J* = 13.9, 8.7, 7.2 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 6H), 0.86 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 154.62, 71.88, 70.80, 38.85, 26.13, 14.59, 11.46.

(4*S*,4'*S*)-4,4'-Diphenyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (L6):



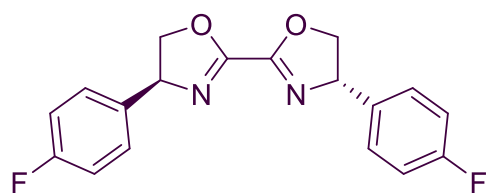
Ligand (**L6**) was synthesized according to slightly modified known literature.^[6] (*S*)-(+)-2-Phenylglycinol (823 mg, 6.00 mmol, 2.00 equiv.) and dimethyloxalate (354 mg, 3.00 mmol, 1.00 equiv.), followed by anhydrous PhMe (70 mL), were added to an oven-dried schlenk tube under an inert atmosphere. The tube was heated to 80 °C. The reaction mixture was stirred overnight, during which the diamide precipitated out of solution as a white solid. The reaction mixture was cooled to room temperature and concentrated in *vacuo* to afford the crude diamide, which was directly used in the next step without further purification. To an oven-dried schlenk tube diamide (820 mg, 2.50 mmol, 1.00 equiv.) and DCM (40 mL) were added under a N₂ atmosphere. The tube was cooled to -78 °C in a dry-ice/acetone bath, and diethylaminosulfur trifluoride (0.92 mL, 7.00 mmol, 2.80 equiv.) was added dropwise. The reaction mixture was stirred for 1 h, then K₂CO₃ (1.40 g, 10.0 mmol, 4.00 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 min. After that the reaction mixture was diluted with DCM (20 mL) and water (30 mL). The organic layer was washed with aqueous NaHCO₃ (20 mL) and brine (30 mL), dried over Na₂SO₄, 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 desired ligand **L6** as a crystalline white powder (600 mg, 82%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.34 (m, 4H), 7.33 – 7.28 (m, 6H), 5.45 (t, *J* = 9.8 Hz, 2H), 4.85 (dd, *J* = 10.4, 8.7 Hz, 2H), 4.37 (t, *J* = 8.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.73, 140.56, 128.93, 128.05, 126.85, 75.37, 70.53.

(4*S*,4'*S*)-4,4'-Diethyl-4,4',5,5'-tetrahydro-2,2'-bioxazole (L7):



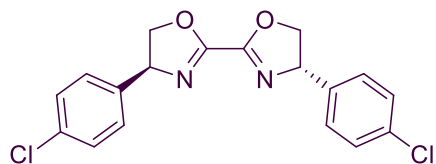
The title compound was synthesized from (*S*)-(+)-2-amino-1-butanol following the above mentioned procedure. Yield: 73%. ¹H NMR (400 MHz, Chloroform-*d*) δ 4.49 (dd, *J* = 9.7, 8.4 Hz, 2H), 4.24 (ddt, *J* = 9.7, 8.4, 6.6 Hz, 2H), 4.05 (t, *J* = 8.4 Hz, 2H), 1.82 – 1.69 (m, 2H), 1.66 – 1.54 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 154.72, 73.05, 68.62, 28.26, 10.20.

(4*S*,4'*S*)-4,4'-Bis(4-fluorophenyl)-4,4',5,5'-tetrahydro-2,2'-bioxazole (L17):



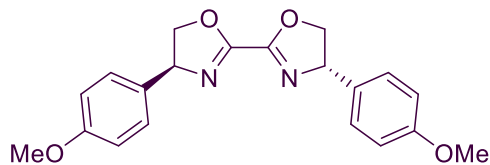
The title compound was synthesized from (*S*)-2-amino-2-(4-fluorophenyl)ethan-1-ol following the above mentioned procedure. Yield: 67%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 4H), 7.10 – 7.03 (m, 4H), 5.44 (dd, *J* = 10.4, 9.1 Hz, 2H), 4.85 (dd, *J* = 10.4, 8.8 Hz, 2H), 4.33 (t, *J* = 8.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 163.80, 161.35, 155.78, 136.35, 136.31, 128.63, 128.55, 116.00, 115.79, 75.41, 69.93. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.19.

(4*S*,4'*S*)-4,4'-bis(4-chlorophenyl)-4,4',5,5'-tetrahydro-2,2'-bioxazole (L18):



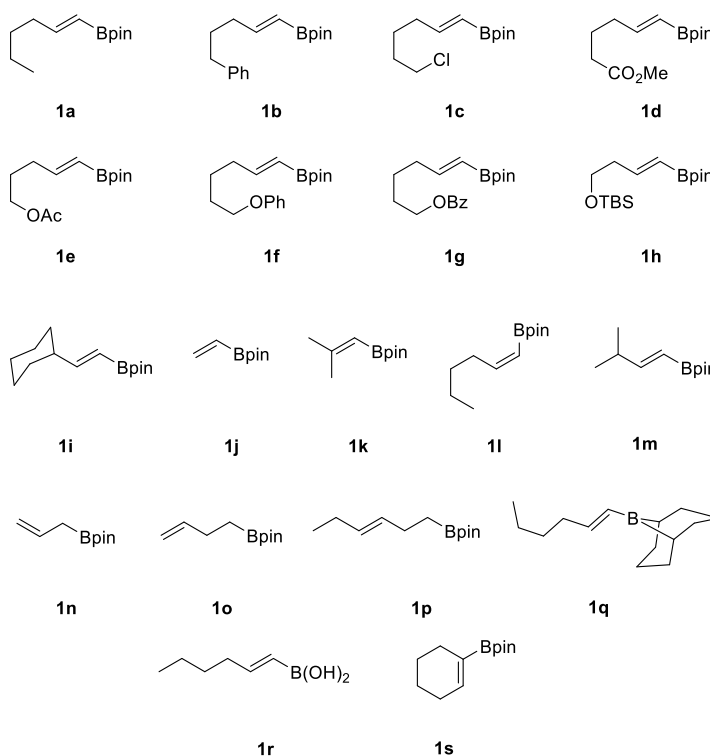
The title compound was synthesized from (*S*)-2-amino-2-(4-chlorophenyl)ethan-1-ol following the above mentioned procedure. Yield: 55%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 4H), 7.28 – 7.22 (m, 4H), 5.44 (t, *J* = 9.8 Hz, 2H), 4.91 – 4.83 (m, 2H), 4.32 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.90, 138.99, 134.02, 129.17, 128.24, 75.29, 69.93.

(4*S*,4'*S*)-4,4'-bis(4-methoxyphenyl)-4,4',5,5'-tetrahydro-2,2'-bioxazole (L19):



The title compound was synthesized from (*S*)-2-amino-2-(4-methoxyphenyl)ethan-1-ol following the above mentioned procedure. Yield: 31%. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.24 – 7.17 (m, 4H), 6.93 – 6.85 (m, 4H), 5.39 (t, *J* = 9.6 Hz, 2H), 4.86 – 4.76 (m, 2H), 4.38 – 4.28 (m, 2H), 3.80 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.48, 155.64, 132.85, 128.09, 114.36, 75.51, 70.11, 55.47.

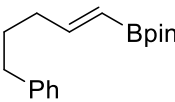
4. Synthesis of alkenyl boronic esters



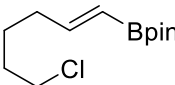
Alkenyl boronic esters **1a**, **1i**, **1j**, **1k**, **1n**, **1r** and **1s** are commercially available.

Compound **1b–1h**^[8], **1l**^[9], **1m**^[11], **1o**^[12], **1p**^[12] and **1q**^[14] were prepared according to the previously reported procedures.

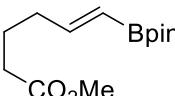
(*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-1-en-1-yl)-1,3,2-dioxaborolane (**1b**):

 Prepared according to the known literature procedure.^[8] **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 7.18 – 7.15 (m, 3H), 6.64 (dt, J = 17.9, 6.4 Hz, 1H), 5.45 (d, J = 18.0 Hz, 1H), 2.61 (t, J = 7.7 Hz, 2H), 2.19 (q, J = 7.0, 6.6 Hz, 2H), 1.75 (p, J = 7.6 Hz, 2H), 1.26 (s, 12H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 154.21, 142.44, 128.58, 128.40, 125.83, 83.17, 35.44, 35.37, 29.93, 24.93. Spectral data match those previously reported.^[8]

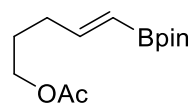
(*E*)-2-(6-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1c**):

 Prepared according to the known literature procedure.^[8] **¹H NMR** (400 MHz, Chloroform-*d*) δ 6.68 – 6.55 (m, 1H), 5.45 (d, J = 18.0 Hz, 1H), 3.53 (t, J = 6.7 Hz, 2H), 2.19 (q, J = 6.9 Hz, 2H), 1.78 (p, J = 6.8 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.26 (s, 12H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 153.60, 83.22, 45.01, 34.99, 32.14, 25.56, 24.93. Spectral data match those previously reported.^[8]

Methyl (*E*)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-enoate (**1d**):

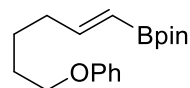
 Prepared according to the known literature procedure.^[8] **¹H NMR** (400 MHz, Chloroform-*d*) δ 6.65 – 6.53 (m, 1H), 5.45 (d, J = 18.0 Hz, 1H), 3.66 (s, 3H), 2.32 (t, J = 7.5 Hz, 2H), 2.19 (q, J = 6.9 Hz, 2H), 1.76 (p, J = 7.4 Hz, 2H), 1.26 (s, 12H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 174.05, 153.06, 83.22, 51.62, 35.08, 33.52, 24.92, 23.52. Spectral data match those previously reported.^[8]

(E)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-en-1-yl acetate (1e):



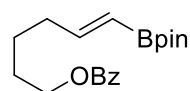
Prepared according to the known literature procedure.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 6.60 (dt, J = 17.9, 6.4 Hz, 1H), 5.46 (d, J = 18.0 Hz, 1H), 4.06 (t, J = 6.6 Hz, 2H), 2.22 (q, J = 7.6 Hz, 2H), 2.03 (s, 3H), 1.77 (q, J = 6.9 Hz, 2H), 1.26 (s, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.27, 152.86, 83.24, 64.03, 32.13, 27.27, 24.92, 21.11. Spectral data match those previously reported.^[8]

(E)-4,4,5,5-tetramethyl-2-(6-phenoxyhex-1-en-1-yl)-1,3,2-dioxaborolane (1f):



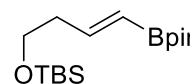
Prepared according to the known literature procedure.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 6.93 – 6.87 (m, 3H), 6.64 (dt, J = 17.9, 6.4 Hz, 1H), 5.46 (d, J = 18.0 Hz, 1H), 3.94 (t, J = 6.4 Hz, 2H), 2.22 (q, J = 7.0 Hz, 2H), 1.79 (p, J = 6.5 Hz, 2H), 1.60 (p, J = 7.6 Hz, 2H), 1.26 (s, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.19, 154.09, 129.53, 120.62, 114.62, 83.18, 67.70, 35.53, 28.92, 24.93, 24.81. Spectral data match those previously reported.^[8]

(E)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-5-en-1-yl benzoate (1g):



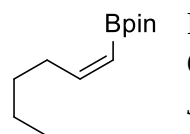
Prepared according to the known literature procedure.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 7.7 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 6.63 (dt, J = 18.0, 6.4 Hz, 1H), 5.47 (d, J = 18.0 Hz, 1H), 4.32 (t, J = 6.5 Hz, 2H), 2.24 (q, J = 7.0 Hz, 2H), 1.79 (p, J = 6.7 Hz, 2H), 1.59 (p, J = 7.6 Hz, 2H), 1.26 (s, 12H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.78, 153.84, 132.95, 130.59, 129.68, 128.47, 83.21, 64.97, 35.44, 28.42, 24.93, 24.83. Spectral data match those previously reported.^[8]

(E)-tert-butyldimethyl((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-1-yl)oxy)silane (1h):



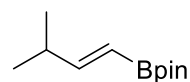
Prepared according to the known literature procedure.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 6.59 (dt, J = 17.9, 6.6 Hz, 1H), 5.49 (d, J = 18.0 Hz, 1H), 3.69 (t, J = 7.0 Hz, 2H), 2.38 (q, J = 6.9 Hz, 2H), 1.26 (s, 12H), 0.88 (s, 9H), 0.04 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 150.81, 83.20, 62.41, 39.60, 26.11, 24.91, 18.53, -5.10. Spectral data match those previously reported.^[8]

(Z)-2-(Hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1l):



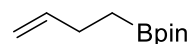
Prepared according to the known literature procedure.^[9] ¹H NMR (400 MHz, Chloroform-*d*) δ 6.42 (dt, J = 14.6, 7.6 Hz, 1H), 5.32 (d, J = 14.6 Hz, 1H), 2.39 (q, J = 7.6 Hz, 2H), 1.42 – 1.29 (m, 4H), 1.26 (s, 12H), 0.93 – 0.86 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 155.38, 82.91, 32.03, 31.79, 24.98, 22.24, 14.05. Spectral data match those previously reported.^[10]

(E)-4,4,5,5-Tetramethyl-2-(3-methylbut-1-en-1-yl)-1,3,2-dioxaborolane (1m):



Prepared according to the known literature procedure.^[11] ¹H NMR (400 MHz, Chloroform-*d*) δ 6.61 (dd, J = 18.1, 6.1 Hz, 1H), 5.38 (d, J = 18.1 Hz, 1H), 2.34 (hept, J = 6.8 Hz, 1H), 1.26 (s, 12H), 1.00 (d, J = 6.8 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 161.09, 83.14, 33.72, 24.94, 21.56. Spectral data match those previously reported.^[11]

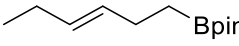
2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1o):



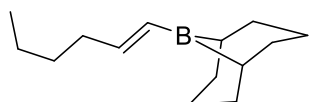
Prepared according to the known literature procedure.^[12] ¹H NMR (400 MHz, Chloroform-*d*) δ 5.88 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.03 – 4.86 (m, 2H), 2.16 (tdd, J = 7.9, 5.4, 1.6 Hz, 2H), 1.24 (s, 12H), 0.88 (t, J = 7.8 Hz, 2H). ¹³C NMR (101 MHz,

Chloroform-*d*) δ 140.81, 113.29, 83.15, 28.12, 24.97. Spectral data match those previously reported.^[12]

(*E*)-2-(Hex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1p):

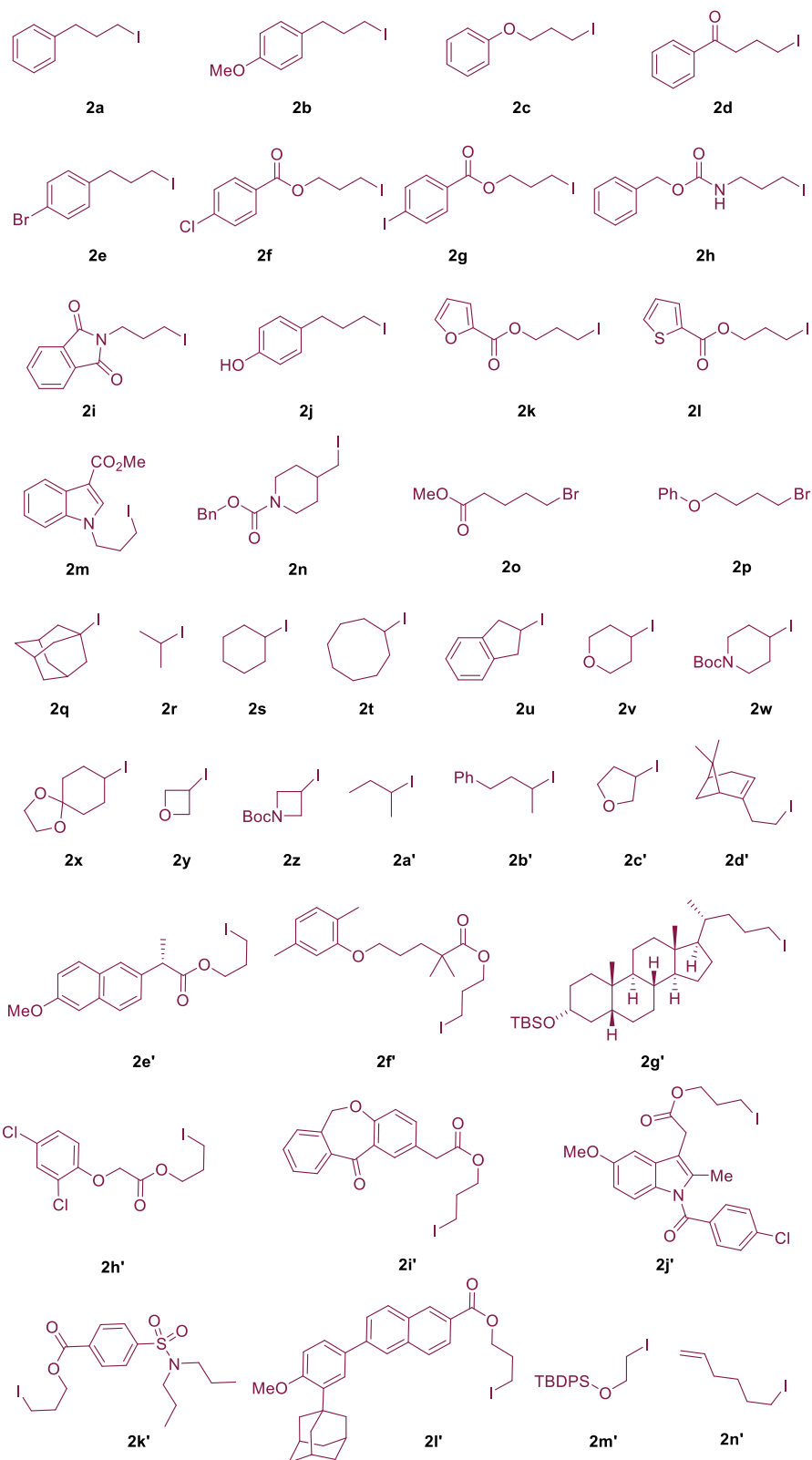
 Prepared according to the modified literature procedure from (*E*)-1-bromohex-3-ene.^[12] **¹H NMR** (400 MHz, Chloroform-*d*) δ 5.49 – 5.37 (m, 2H), 2.12 – 2.07 (m, 2H), 2.01 – 1.93 (m, 2H), 1.23 (s, 12H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.7 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 131.05, 83.07, 26.95, 25.67, 24.97, 14.09. Spectral data match those previously reported.^[13]

(1*s*,5*s*)-9-((*E*)-Hex-1-en-1-yl)-9-borabicyclo[3.3.1]nonane (1q):



The title compound was generated in situ following a known literature procedure then it was directly used in the reaction.^[14]

5. Preparation of alkyl halides:

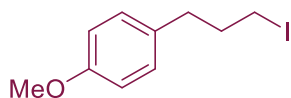


Compound **2a**, **2o**, **2p**, **2q**, **2r**, **2s**, **2v**, **2w**, **2y**, **2z**, **2a'** and **2c'** were purchased from commercial sources. Alkyl halides **2b**^[15], **2c**^[16], **2d**^[17], **2e**^[18], **2f**^[8], **2h**^[19], **2i**^[20], **2j**^[21], **2k**^[8], **2m**^[22], **2n**^[15], **2t**^[23], **2u**^[15], **2x**^[16], **2b'**^[24], **2d'**^[25], **2g**^[8], **2m'**^[27] and **2n'**^[15] were prepared according to known literature procedures.

General Procedure (GP3) for the synthesis of alkyl iodides:

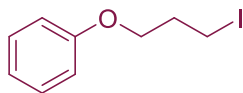
To a stirred solution of carboxylic acid (5.00 mmol, 1.0 equiv.) in dry DCM (15 mL) at 0 °C under a N₂ atmosphere was added *N,N'*-diisopropylcarbodiimide (0.86 mL, 5.50 mmol, 1.1 equiv.). After 10 minutes, 3-iodo-1-propanol (0.53 mL, 5.50 mmol, 1.1 equiv.) and Et₃N (0.77 mL, 5.5 mmol, 1.1 equiv.) were added to it. The resulting reaction mixture was allowed to warm to room temperature and the stirring was continued for 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 column chromatography on silica gel with a mixture of hexane:EtOAc as eluent to obtain the desired alkyl iodides.

1-(3-Iodopropyl)-4-methoxybenzene (2b):



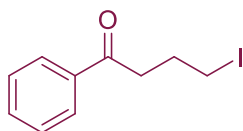
Prepared according to the known literature method.^[15] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.06 (m, 2H), 6.90 – 6.80 (m, 2H), 3.80 (s, 3H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.10 (p, *J* = 6.7 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.15, 132.53, 129.59, 114.02, 55.39, 35.38, 35.21, 6.59. Spectral data match those previously reported.^[15]

(3-Iodopropoxy)benzene (2c):



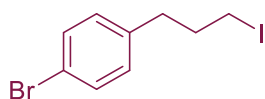
Prepared according to the known literature method.^[16] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 7.01 – 6.89 (m, 3H), 4.05 (t, *J* = 5.8 Hz, 2H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.33 – 2.25 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.78, 129.62, 121.05, 114.67, 67.28, 33.16, 2.70. Spectral data match those previously reported.^[16]

4-Iodo-1-phenylbutan-1-one (2d):



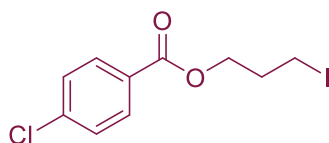
Prepared according to the known literature method.^[17] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 2H), 7.65 – 7.54 (m, 1H), 7.53 – 7.42 (m, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.26 (p, *J* = 6.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 198.70, 136.84, 133.35, 128.78, 128.13, 39.05, 27.67, 6.92. Spectral data match those previously reported.^[17]

1-Bromo-4-(3-iodopropyl)benzene (2e):



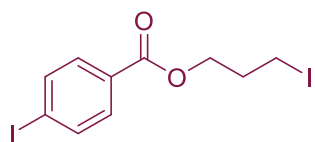
Prepared according to the known literature method.^[18] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 1H), 7.13 – 7.01 (m, 1H), 3.15 (t, *J* = 6.7 Hz, 1H), 2.69 (t, *J* = 7.3 Hz, 1H), 2.17 – 2.04 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 139.45, 131.69, 130.44, 120.10, 35.70, 34.69, 6.06. Spectral data match those previously reported.^[18]

3-Iodopropyl 4-chlorobenzoate (2f):



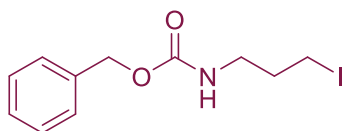
Prepared according to the known literature method.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.40 (t, *J* = 6.1 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.29 (p, *J* = 6.5 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.58, 139.64, 131.08, 128.87, 128.52, 64.92, 32.51, 1.34. Spectral data match those previously reported.^[8]

3-Iodopropyl 4-iodobenzoate (**2g**):



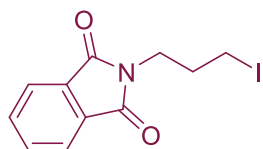
Prepared according to **GP3** with 4-iodobenzoic acid (1.20 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 40:1 hexane:EtOAc) afforded the desired product **2g** as a white solid (1.37 g, 66%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.84 – 7.75 (m, 2H), 7.77 – 7.68 (m, 2H), 4.39 (t, *J* = 6.1 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.33 – 2.22 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 165.95, 137.88, 131.12, 129.55, 101.05, 64.94, 32.50, 1.34. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₀H₁₁I₂O₂⁺ 416.8843; Found 416.8838.

Benzyl (3-iodopropyl)carbamate (**2h**):



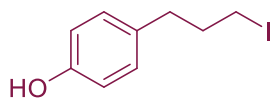
Prepared according to the known literature method.^[19] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 5.10 (s, 2H), 4.92 (s, 1H), 3.29 (q, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.03 (p, *J* = 6.9 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.53, 136.51, 128.67, 128.31, 128.27, 66.94, 41.59, 33.29, 3.03. Spectral data match those previously reported.^[19]

2-(3-Iodopropyl)isoindoline-1,3-dione (**2i**):



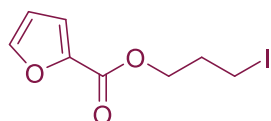
Prepared according to the known literature method.^[20] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.83 (ddd, *J* = 7.7, 4.6, 3.0 Hz, 2H), 7.77 – 7.66 (m, 2H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.24 (p, *J* = 7.0 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.37, 134.19, 134.10, 132.11, 123.47, 123.41, 38.78, 32.70, 1.31. Spectral data match those previously reported.^[20]

4-(3-Iodopropyl)phenol (**2j**):



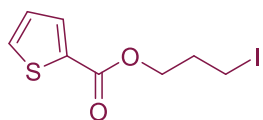
Prepared according to the known literature method.^[21] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 6.98 (m, 2H), 6.87 – 6.66 (m, 2H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.19 – 1.99 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 153.93, 132.77, 129.81, 115.45, 35.39, 35.18, 6.58. Spectral data match those previously reported.^[21]

3-Iodopropyl furan-2-carboxylate (**2k**):

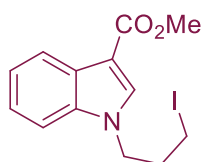


Prepared according to the known literature method.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.38 (t, *J* = 6.1 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.27 (p, *J* = 6.6 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 158.57, 146.54, 144.52, 118.25, 111.99, 64.59, 32.56, 1.28. Spectral data match those previously reported.^[8]

3-Iodopropyl thiophene-2-carboxylate (**2l**):

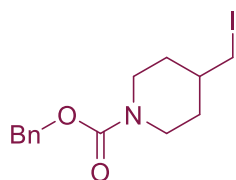


Prepared according to **GP3** with 2-thiophenecarboxylic acid (640 mg, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 30:1 hexane:EtOAc) afforded the desired product **2l** as a colorless oil (1.15 g, 78%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.81 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.57 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.9 Hz, 1H), 4.38 (t, *J* = 6.0 Hz, 2H), 3.29 (t, *J* = 6.9 Hz, 2H), 2.32 – 2.22 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 162.14, 133.74, 132.70, 127.95, 64.82, 32.64, 1.40. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₈H₁₀IO₂S⁺ 296.9441; Found 296.9436.

Methyl 1-(3-iodopropyl)-1H-indole-3-carboxylate (2m):

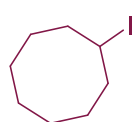
Prepared according to the known literature method.^[22] **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.23 – 8.06 (m, 1H), 7.83 (s, 1H), 7.42 – 7.34 (m, 1H), 7.32 – 7.22 (m, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.90 (s, 3H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.30 (p, *J* = 6.5 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 165.39, 136.41, 134.25, 126.84, 123.05, 122.14, 121.98, 109.97, 107.56, 51.13, 46.86, 33.05,

2.25.

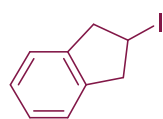
Benzyl 4-(iodomethyl)piperidine-1-carboxylate (2n):

Prepared according to the known literature method.^[15] **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 5.13 (s, 2H), 4.21 (s, 2H), 3.10 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 2H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.71 – 1.57 (m, 1H), 1.29 – 1.08 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 155.23, 136.92, 128.60, 128.10, 127.98, 67.21, 43.89, 38.64, 32.63, 13.33. Spectral data match those

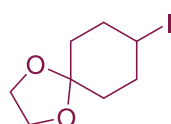
previously reported.^[15]

Iodocyclooctane (2t):

Prepared according to the known literature method.^[23] **¹H NMR** (400 MHz, Chloroform-*d*) δ 4.60 (ddd, *J* = 13.0, 7.3, 5.7 Hz, 1H), 2.31 – 2.19 (m, 4H), 1.75 – 1.39 (m, 10H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 38.48, 38.07, 27.58, 26.79, 25.28. Spectral data match those previously reported.^[23]

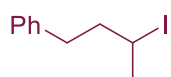
2-Iodo-2,3-dihydro-1H-indene (2u):

Prepared according to the known literature method.^[15] **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.14 (m, 4H), 4.71 (p, *J* = 5.7, 5.3 Hz, 1H), 3.52 – 3.46 (m, 2H), 3.44 – 3.35 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 141.56, 127.05, 124.42, 46.69, 23.96. Spectral data match those previously reported.^[15]

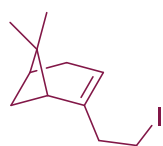
8-Iodo-1,4-dioxaspiro[4.5]decane (2x):

Prepared according to the known literature method.^[16] **¹H NMR** (400 MHz, Chloroform-*d*) δ 4.45 – 4.39 (m, 1H), 4.01 – 3.88 (m, 4H), 2.19 – 2.04 (m, 4H), 1.84 – 1.78 (m, 2H), 1.64 – 1.57 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 107.60, 64.50, 64.43, 36.38, 34.89. Spectral data match those previously

reported.^[16]

(3-Iodobutyl)benzene (2b'):

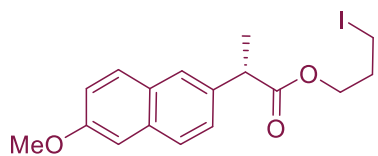
Prepared according to the known literature method.^[24] **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 3H), 4.17 – 4.08 (m, 1H), 2.89 – 2.82 (m, 1H), 2.74 – 2.67 (m, 1H), 2.21 – 2.12 (m, 1H), 1.96 (d, *J* = 6.8 Hz, 3H), 1.95 – 1.85 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 140.88, 128.65, 128.62, 126.25, 44.54, 35.98, 29.77, 29.13. Spectral data match those previously reported.^[24]

(1R,5S)-2-(2-Iodoethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (2d'):

Prepared according to the known literature method.^[25] **¹H NMR** (400 MHz, Chloroform-*d*) δ 5.32 (s, 1H), 3.18 – 3.13 (m, 2H), 2.59 – 2.53 (m, 2H), 2.39 (dt, *J* = 8.6, 5.6 Hz, 1H), 2.30 – 2.14 (m, 2H), 2.11 – 2.08 (m, 1H), 2.01 (td, *J* = 5.6, 1.6 Hz, 1H), 1.29 (s, 3H), 1.20 (d, *J* = 8.6 Hz, 1H), 0.85 (s, 3H). **¹³C NMR** (101 MHz,

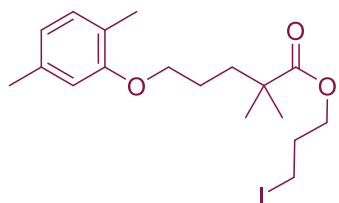
Chloroform-*d*) δ 146.89, 118.85, 45.48, 41.61, 40.83, 38.28, 31.90, 31.44, 26.41, 21.52, 3.83. Spectral data match those previously reported.^[26]

3-Iodopropyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (**2e'**):



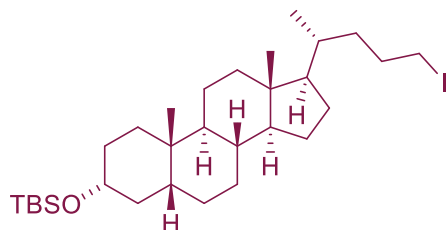
Prepared according to **GP3** with naproxen (1.15 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **2e'** as a white solid (1.39 g, 70%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.76 – 7.67 (m, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.20 – 7.07 (m, 2H), 4.15 (q, *J* = 5.5 Hz, 2H), 3.92 (s, 3H), 3.86 (q, *J* = 7.1 Hz, 1H), 3.29 – 2.88 (m, 2H), 2.14 – 1.94 (m, 2H), 1.58 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 174.59, 157.80, 135.69, 133.83, 129.40, 127.33, 126.25, 126.02, 119.17, 105.73, 64.40, 55.45, 45.56, 32.34, 18.58, 1.53. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₇H₁₉INaO₃⁺ 421.0271; Found 421.0277.

3-Iodopropyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (**2f'**):



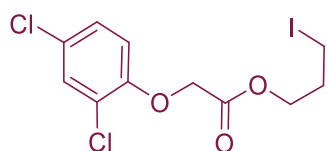
Prepared according to **GP3** with gemfibrozil (1.25 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 20:1 hexane:EtOAc) afforded the desired product **2f'** as a colorless oil (1.13 g, 54%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.01 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.63 – 6.58 (m, 1H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.99 – 3.88 (m, 2H), 3.22 (t, *J* = 6.8 Hz, 2H), 2.31 (s, 3H), 2.18 (s, 3H), 2.16 – 2.08 (m, 2H), 1.84 – 1.66 (m, 4H), 1.23 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 177.71, 157.04, 136.61, 130.45, 123.71, 120.86, 112.11, 68.01, 64.13, 42.31, 37.30, 32.39, 25.32, 21.56, 15.95, 1.59. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₁₈H₂₈IO₃⁺ 419.1078; Found 419.1082.

tert-Butyl(((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-17-((*R*)-5-iodopentan-2-yl)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)dimethylsilane (**2g'**):



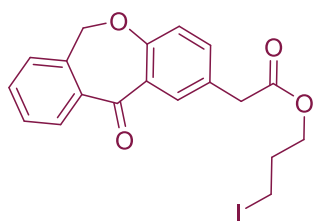
Prepared according to the known literature method.^[8] ¹H NMR (400 MHz, Chloroform-*d*) δ 3.57 (td, *J* = 10.5, 4.9 Hz, 1H), 3.15 (dt, *J* = 16.2, 7.7 Hz, 2H), 1.95 – 1.70 (m, 7H), 1.59 – 1.51 (m, 2H), 1.49 – 1.30 (m, 9H), 1.27 – 1.17 (m, 3H), 1.16 – 1.00 (m, 6H), 0.92 – 0.87 (m, 16H), 0.63 (s, 3H), 0.05 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 72.96, 56.55, 56.22, 42.86, 42.44, 40.35, 40.28, 37.07, 37.01, 36.01, 35.73, 35.25, 34.73, 31.18, 30.55, 28.47, 27.45, 26.56, 26.13, 24.37, 23.55, 20.95, 18.85, 18.47, 12.17, 8.01, -4.43. Spectral data match those previously reported.^[8]

3-Iodopropyl 2-(2,4-dichlorophenoxy)acetate (**2h'**):



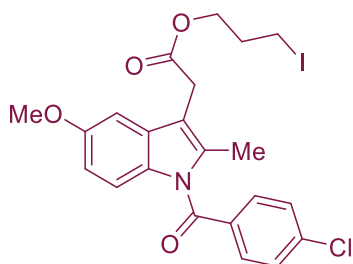
Prepared according to **GP3** with 2,4-dichlorophenoxyacetic acid (1.10 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 7:1 hexane:EtOAc) afforded the desired product **2h'** as a white solid (1.27 g, 65%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.40 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.79 (d, *J* = 8.8 Hz, 1H), 4.71 (s, 2H), 4.28 (t, *J* = 6.0 Hz, 2H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.15 (p, *J* = 6.4 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.09, 152.46, 130.57, 127.76, 127.40, 124.42, 114.84, 66.50, 65.23, 32.07. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₁H₁₁Cl₂INaO₃⁺ 410.9022; Found 410.9020.

3-Iodopropyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (2i'):



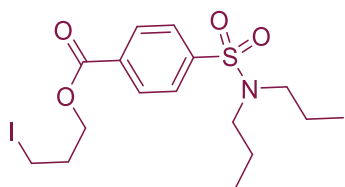
Prepared according to **GP3** with isoxepac (1.34 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 5:1 hexane:EtOAc) afforded the desired product **2i'** as a white solid (1.32 g, 61%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.56 (td, *J* = 7.5, 1.6 Hz, 1H), 7.47 (td, *J* = 7.6, 1.5 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.19 (s, 2H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.65 (s, 2H), 3.18 (t, *J* = 6.8 Hz, 2H), 2.13 (p, *J* = 6.5 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 190.92, 171.32, 160.64, 140.55, 136.37, 135.67, 132.92, 132.56, 129.64, 129.41, 127.95, 127.77, 125.30, 121.24, 73.78, 64.70, 40.32, 32.33, 1.45. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₁₉H₁₈IO₄⁺ 437.0244; Found 437.0248.

3-Iodopropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (2j'):



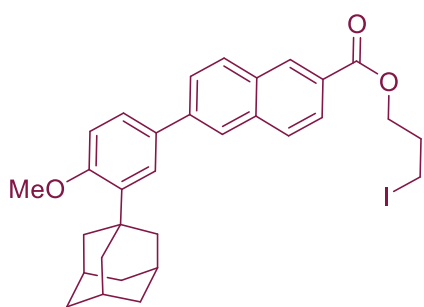
Prepared according to **GP3** with indomethacin (1.78 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 5:1 hexane:EtOAc) afforded the desired product **2j'** as a white solid (1.29 g, 49%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.40 (m, 2H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.67 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.84 (s, 3H), 3.67 (s, 2H), 3.11 (t, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 2.11 (p, *J* = 6.5 Hz, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 170.77, 156.21, 139.45, 136.07, 133.99, 131.33, 130.93, 129.28, 115.14, 112.54, 111.85, 101.35, 64.71, 55.91, 32.29, 30.47, 13.49, 1.26. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₂₂H₂₂ClINO₄⁺ 526.0277; Found 526.0282.

3-Iodopropyl 4-(*N,N*-dipropylsulfamoyl)benzoate (2k'):



Prepared according to **GP3** with probenecid (856 mg, 3.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 3:1 hexane:EtOAc) afforded the desired product **2k'** as a white solid (930 g, 68%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 8.16 – 8.06 (m, 2H), 7.91 – 7.81 (m, 2H), 4.43 (t, *J* = 6.1 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 3.13 – 3.05 (m, 4H), 2.29 (p, *J* = 6.5 Hz, 2H), 1.53 (p, *J* = 7.5 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 165.13, 144.54, 133.34, 130.33, 127.15, 65.33, 50.03, 32.41, 22.04, 11.27, 1.19. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₁₆H₂₅INO₄S⁺ 454.0544; Found 454.0553.

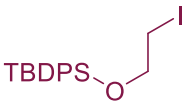
3-Iodopropyl 6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (2l'):



Prepared according to **GP3** with adapalene (412 mg, 1.00 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **2l'** as a white solid (398 mg, 69%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 8.60 (s, 1H), 8.06 (dd, *J* = 8.5, 1.7 Hz, 1H), 8.04 – 7.96 (m, 2H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.55 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.48 (t, *J* = 6.0 Hz, 2H), 3.91 (s, 3H), 3.37 (t, *J* = 6.9 Hz, 2H), 2.36 (p, *J* = 6.5 Hz, 2H), 2.19 (d, *J* = 2.8 Hz, 6H), 2.11 (s, 3H), 1.80 (d, *J* = 3.0 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 166.72, 159.07, 141.61, 139.14, 136.14, 132.61, 131.33, 131.00, 129.83, 128.41, 126.84, 126.67, 126.09, 125.86, 125.62, 124.85, 112.24, 64.81, 55.30,

40.75, 37.35, 37.27, 32.78, 31.06, 29.25, 1.65. **HRMS (ESI/QTOF)** m/z : $[M + H]^+$ Calcd for $C_{31}H_{34}IO_3^+$ 581.1547; Found 581.1552.

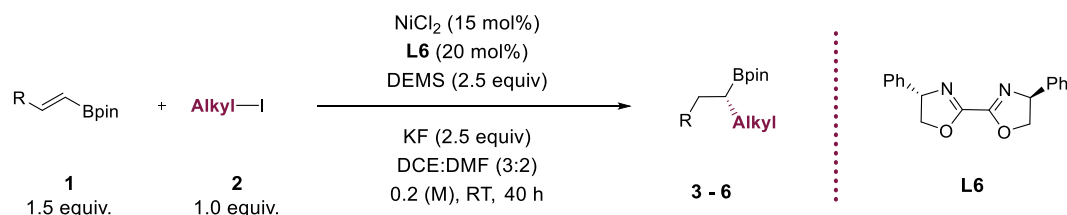
tert-Butyl(2-iodoethoxy)diphenylsilane (2m'):

 Prepared according to the known literature method.^[27] **1H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 4H), 7.52 – 7.37 (m, 6H), 3.89 (t, J = 6.8 Hz, 2H), 3.24 (t, J = 6.8 Hz, 2H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.70, 133.43, 129.96, 127.90, 64.76, 26.94, 19.40, 6.89. Spectral data match those previously reported.^[27]

6-Iodohept-1-ene (2n'):

 Prepared according to the known literature method.^[15] **1H NMR** (400 MHz, Chloroform-*d*) δ 5.91 – 5.67 (m, 1H), 5.10 – 4.91 (m, 2H), 3.19 (td, J = 7.0, 2.0 Hz, 2H), 2.08 (q, J = 7.3 Hz, 2H), 1.84 (p, J = 7.0 Hz, 2H), 1.50 (p, J = 7.3, 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 138.24, 115.13, 33.04, 32.75, 29.83, 6.98. Spectral data match those previously reported.^[15]

6. General Procedure (GP4) for probing the scope of enantioselective C(sp³)–C(sp³) cross-coupling of non-activated alkyl electrophiles:

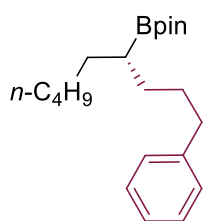


To an oven-dried 10 mL Teflon-screw capped test tube were added NiCl₂ (1.9 mg, 15 μmol, 0.15 equiv.) and **L6** (5.8 mg, 0.02 mmol, 0.20 equiv.). The vial was introduced in a nitrogen-filled glovebox. A magnetic stir bar (6x15 mm), anhydrous DCE (0.30 mL) and DMF (0.20 mL) were added, and the mixture was stirred for 40 minutes at room temperature. Then KF (14.5 mg, 0.25 mmol, 2.50 equiv.) was added to it and the stirring was continued for additional 2 – 3 minutes, at which point alkenyl boronic acid pinacol ester **1** (0.15 mmol, 1.00 equiv.) was added and the mixture was stirred for additional 1 min. Then alkyl iodide **2** (0.10 mmol, 1.50 equiv.) was added to the resulting mixture [for cross coupling with secondary alkyl iodides: alkenyl boronic acid pinacol ester **1** (0.10 mmol, 1.00 equiv.) and secondary alkyl iodide (0.15 mmol, 1.50 equiv.) were used]. Stirring was further continued for 5 minutes, then DEMS (43.0 μL, 0.25 mmol, 2.50 equiv.) was added dropwise to it. The test tube was then sealed with airtight electrical tapes and removed from the glove box and stirred at RT for 40 hours maintaining 460 rpm. The crude reaction mixture was directly subjected to flash column chromatography by using a mixture of hexane and EtOAc to obtain **3a – 6i**. A relatively low rpm was chosen to avoid the spill.

For cross-coupling with alkyl bromide 40 mol% KI was used. KI was added together with KF.

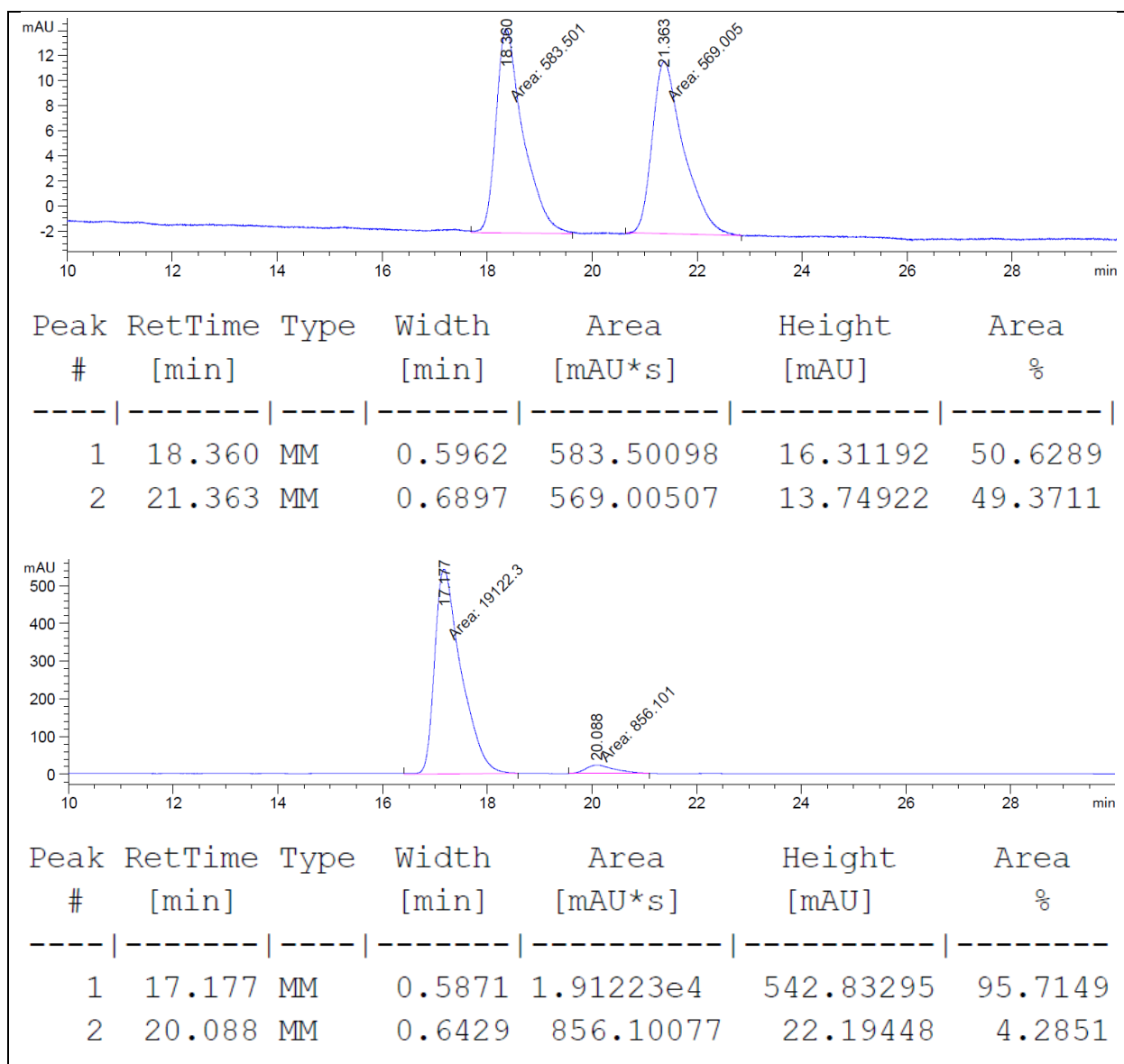
Adding all the reagents together after the catalyst formation (40 minutes later) without a waiting period resulted in 66% yield and 91% e.e. of the desired product **3a**. When the sequence of addition was changed, the product still can be obtained in 66% yield and 91% e.e.. However, when the base was added together with NiCl₂ and ligand and the mixture was stirred for 40 minutes followed by the sequential addition of the other reagents, the yield and e.e. substantially decrease to 49% and 83%, respectively.

(*S*)-4,4,5,5-Tetramethyl-2-(1-phenylnonan-4-yl)-1,3,2-dioxaborolane ((+) **3a**)

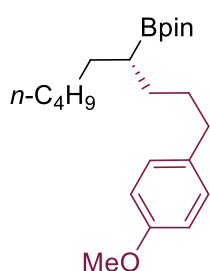


Prepared according to **GP4** with **1a** (38.0 μL, 0.15 mmol, 1.50 equiv.), **2a** (25.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 100:1 hexane:EtOAc) afforded the desired product (**+**) **3a** as a colorless oil (23 mg, 69%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.64 (q, *J* = 7.6 Hz, 2H), 1.56 – 1.38 (m, 3H), 1.29 – 1.26 (m, 19H), 1.06 – 0.99 (m, 1H), 0.90 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 143.07, 128.51, 128.32, 125.62, 82.95, 36.39, 32.29, 31.51, 31.32, 31.30, 29.08, 24.97, 24.94, 22.75, 14.21. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 34.23. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₁H₃₅BNaO₂⁺ 353.2622, Found 353.2623. [α]_D²⁰ = +5.3 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 17.2 min and *t*_{minor} = 20.1 min.

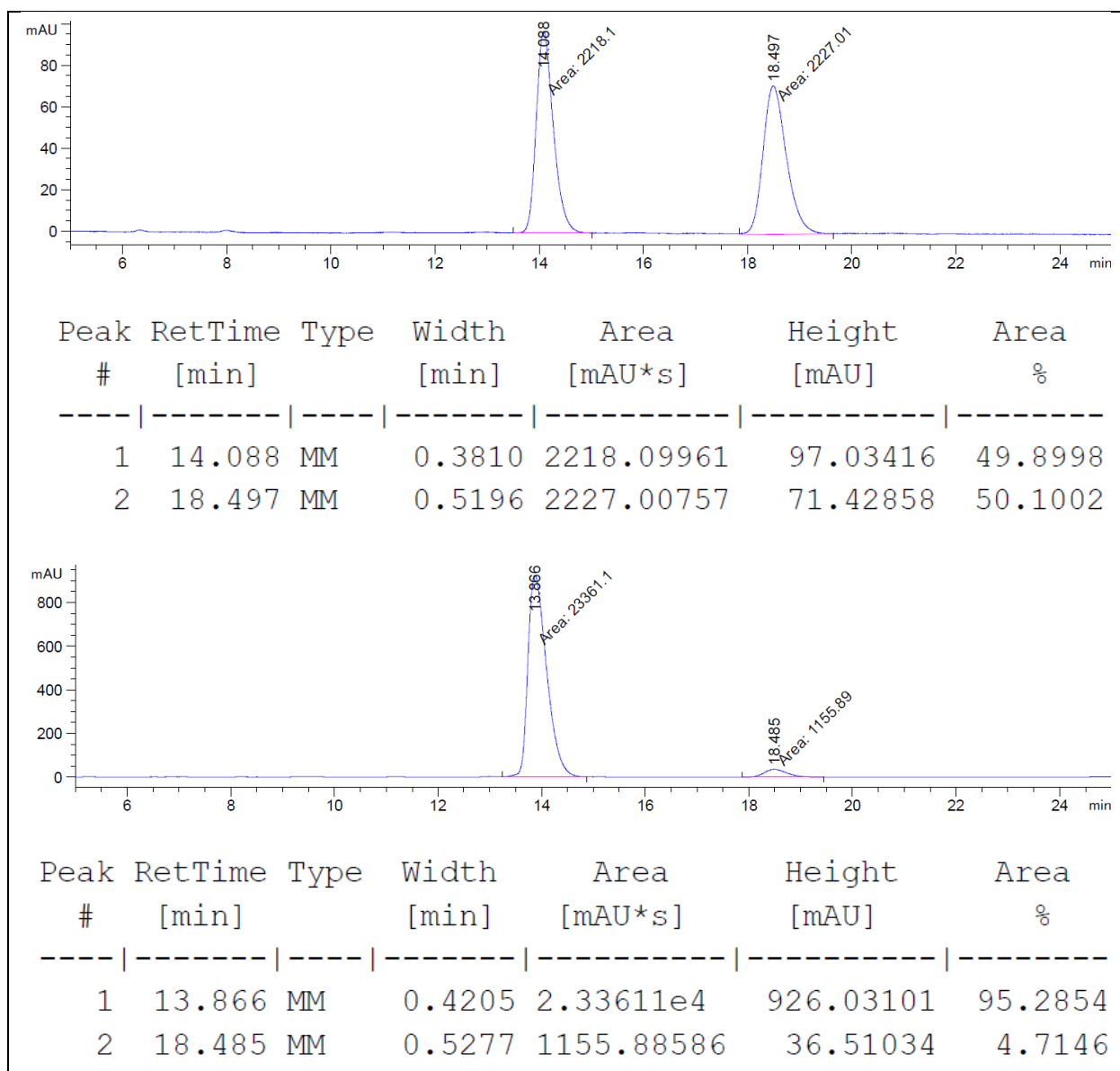


(S)-2-(1-(4-Methoxyphenyl)nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) 3b)

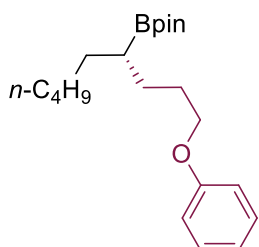


Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 3b** as a colorless oil (29 mg, 80%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.13 – 7.01 (m, 2H), 6.88 – 6.74 (m, 2H), 3.78 (s, 3H), 2.54 (t, *J* = 7.7 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.49 – 1.37 (m, 3H), 1.29 – 1.23 (m, 19H), 1.09 – 1.02 (m, 1H), 0.89 – 0.85 (m, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 157.68, 135.18, 129.34, 113.75, 82.94, 82.82, 55.37, 35.43, 32.28, 31.52, 31.24, 29.07, 24.96, 24.94, 22.74, 14.20. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.00. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₂H₃₇BNaO₃⁺ 383.2728, Found 383.2731. $[\alpha]_D^{20}$ = +5.0 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: $t_{\text{major}} = 13.8$ min and $t_{\text{minor}} = 18.5$ min.



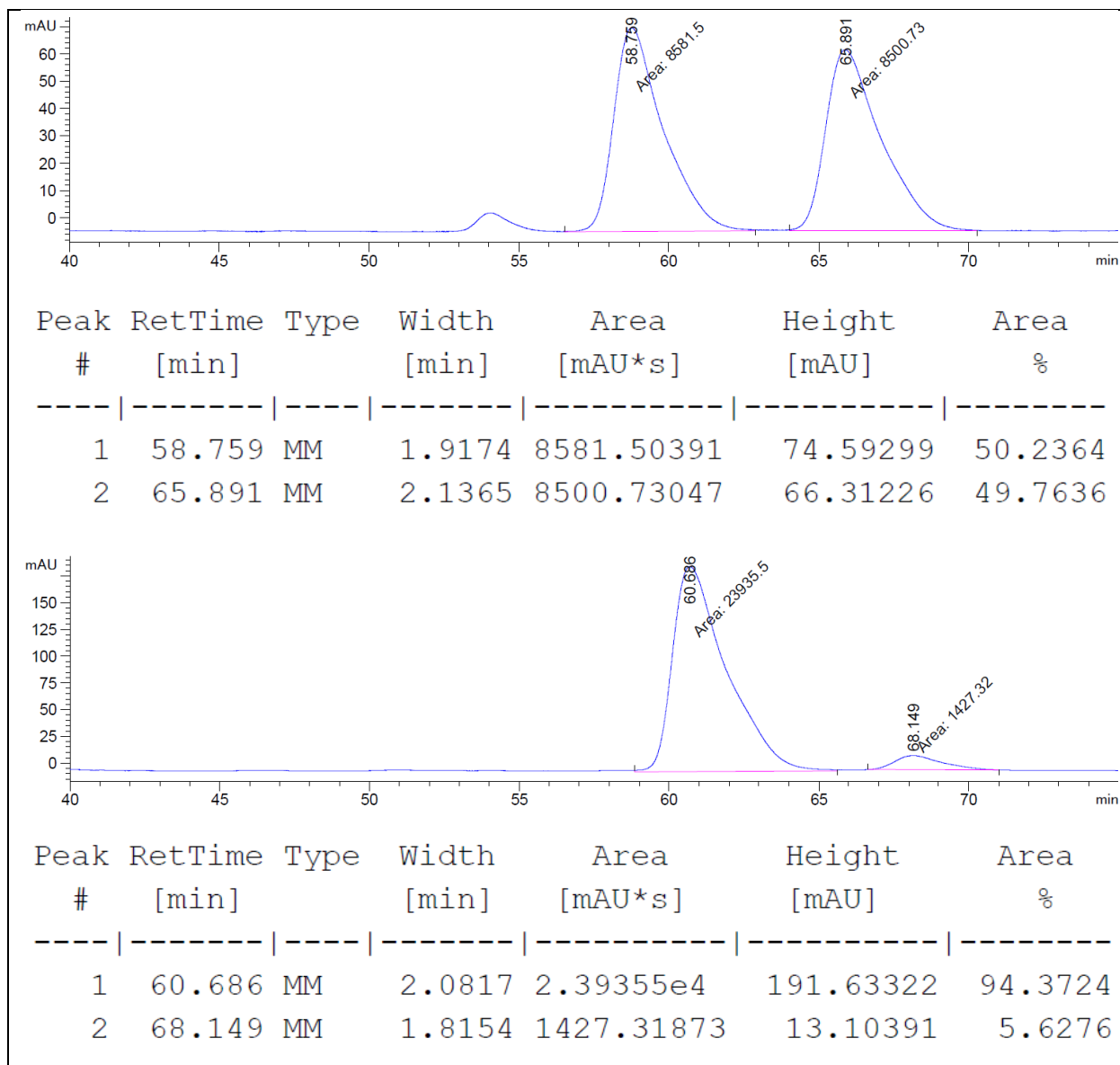
(S)-4,4,5,5-Tetramethyl-2-(1-phenoxynonan-4-yl)-1,3,2-dioxaborolane ((+) **3c)**



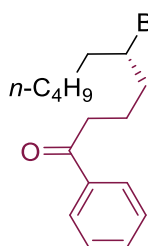
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2c** (28.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2 , 100:1 hexane:EtOAc) afforded the desired product (+) **3c** as a colorless oil (25 mg, 72%). **^1H NMR** (400 MHz, Chloroform- d): δ 7.32 – 7.27 (m, 2H), 6.98 – 6.87 (m, 3H), 3.97 (t, $J = 6.6$ Hz, 2H), 1.86 – 1.76 (m, 2H), 1.66 – 1.46 (m, 3H), 1.28 – 1.26 (m, 19H), 1.05 (ddd, $J = 8.7, 5.8, 2.7$ Hz, 1H), 0.92 – 0.88 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform- d): δ 159.25, 129.48, 120.50, 114.67, 83.05, 68.24, 32.28, 31.42, 29.85, 29.01, 28.97, 27.77, 24.98, 24.93, 22.75, 14.21. **HRMS (APPI/LTQ-Orbitrap)** m/z :

$[M]^+$ Calcd for $C_{21}H_{35}BO_3^+$ 346.2674; Found 346.2677. ^{11}B NMR (128 MHz, Chloroform- d) δ 34.21. $[\alpha]_D^{20} = +2.6$ ($c = 1.00$ in $CHCl_3$).

HPLC: The enantiomeric excess (89%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{major} = 60.7$ min and $t_{minor} = 68.1$ min.



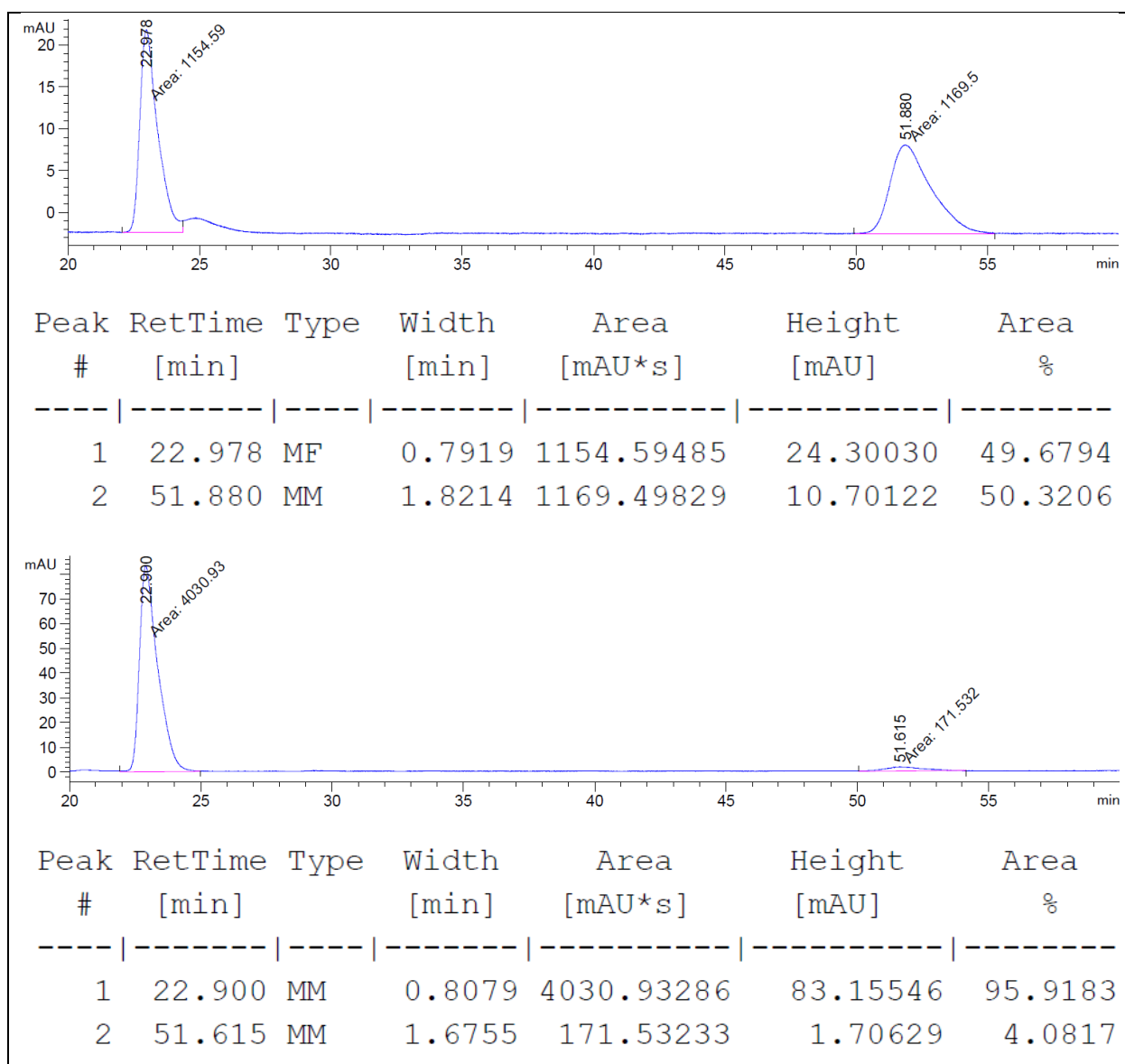
(S)-1-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one ((+) **3d)**



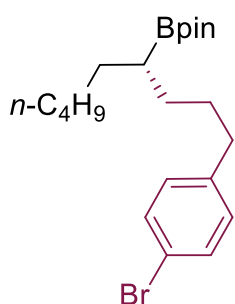
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2d** (27.4 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2 , 60:1 hexane:EtOAc) afforded the desired product **(+) 3d** as a colorless oil (24 mg, 67%). 1H NMR (400 MHz, Chloroform- d): δ 7.95 (d, $J = 7.6$ Hz, 2H), 7.53 (t, $J = 7.1$ Hz, 1H), 7.44 (t, $J = 7.4$ Hz, 2H), 2.95 (q, $J = 6.2, 5.6$ Hz, 2H), 1.73 (p, $J = 7.7$ Hz, 2H), 1.60 – 1.22 (m, 22H), 1.01 (dd, $J = 10.0, 4.8$ Hz, 1H), 0.88 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d): δ 200.66, 137.21, 132.92, 128.63, 128.22, 83.03, 39.15, 32.27, 31.36,

31.26, 28.99, 24.96, 24.93, 24.27, 22.73, 14.20. **HRMS (ESI/QTOF)** m/z : $[M + Na]^+$ Calcd for $C_{22}H_{35}BNaO_3^+$ 381.2571; Found 381.2574. **^{11}B NMR** (128 MHz, Chloroform- d) δ 34.08. $[\alpha]_D^{20} = +2.6$ ($c = 1.00$ in $CHCl_3$).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) 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. Elution time: $t_{major} = 22.9$ min and $t_{minor} = 51.6$ min.



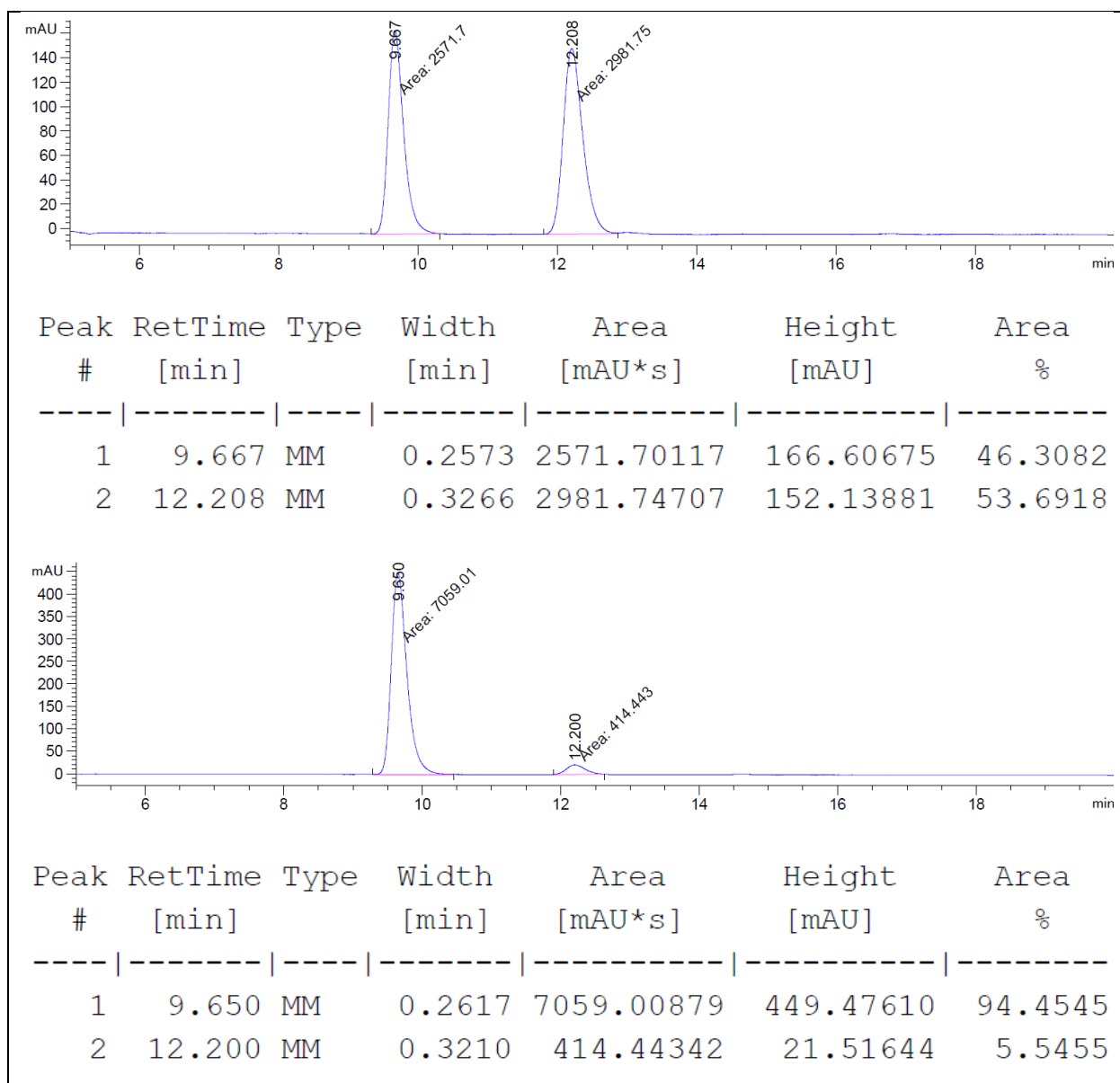
(S)-2-(1-(4-Bromophenyl)nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) **3e)**



Prepared according to **GP4** with **1a** (25.0 μ L, 0.10 mmol, 1.00 equiv.), **2e** (48 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2 , 100:1 hexane:EtOAc) afforded the desired product **(+) 3e** as a colorless oil (30 mg, 73%). **1H NMR** (400 MHz, Chloroform- d) δ 7.39 – 7.34 (m, 2H), 7.06 – 7.01 (m, 2H), 2.54 (td, $J = 7.4, 2.2$ Hz, 2H), 1.64 – 1.52 (m, 2H), 1.49 – 1.35 (m, 4H), 1.31 – 1.21 (m, 18H), 1.01 – 0.94 (m, 1H), 0.89 – 0.84 (m, 3H). **^{13}C**

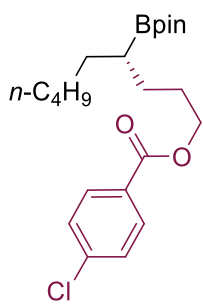
NMR (101 MHz, Chloroform-*d*) δ 141.96, 131.35, 130.29, 119.32, 82.98, 35.71, 32.25, 31.48, 31.10, 29.04, 24.95, 24.92, 22.73, 14.20. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 33.59. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + H]⁺ Calcd for C₂₁H₃₅BBrO₂⁺ 409.1908; Found 409.1919. [α]_D²⁰ = +3.0 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (89%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 9.6 min and *t*_{minor} = 12.2 min.



(S)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 4-chlorobenzoate ((+) 3f)

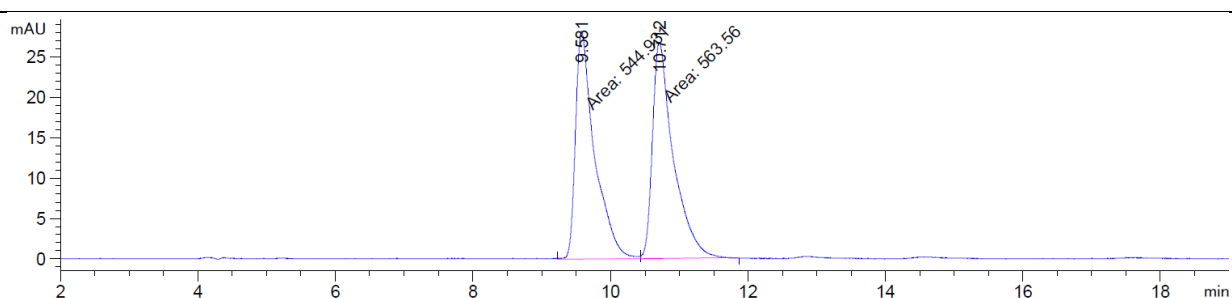
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2f** (33 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 25:1 hexane:EtOAc) afforded the desired product



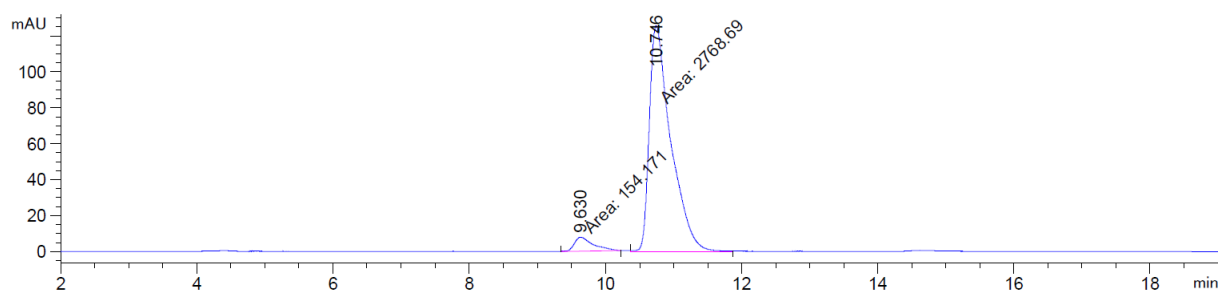
(+) **3f** as a colorless oil (26 mg, 64%). ¹H NMR (400 MHz, Chloroform-*d*): δ 8.06 – 7.88 (m, 2H), 7.49 – 7.31 (m, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 1.75 (p, *J* = 7.2, 6.7 Hz, 2H), 1.57 – 1.22 (m, 22H), 1.02 (ddd, *J* = 8.8, 7.2, 4.3 Hz, 1H), 0.87 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 165.92, 139.30, 131.11, 129.19, 128.76, 83.10, 65.79, 32.25, 31.35, 28.94, 28.46, 27.78, 24.98, 24.93, 22.74, 14.19. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 35.76. HRMS

(ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₂H₃₄BClNaO₄⁺ 431.2131, Found 431.2130. [α]_D²⁰ = +1.5 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OJ-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Elution time: *t*_{major} = 10.7 min and *t*_{minor} = 9.6 min.

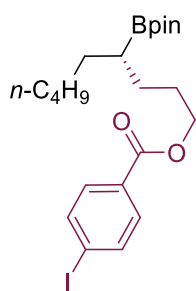


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.581	MF	0.3215	544.93121	28.24557	49.1597
2	10.712	FM	0.3513	563.56030	26.73437	50.8403



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.630	MM	0.3260	154.17059	7.88233	5.2747
2	10.746	MM	0.3669	2768.68652	125.78008	94.7253

(S)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 4-iodobenzoate ((+) 3g)

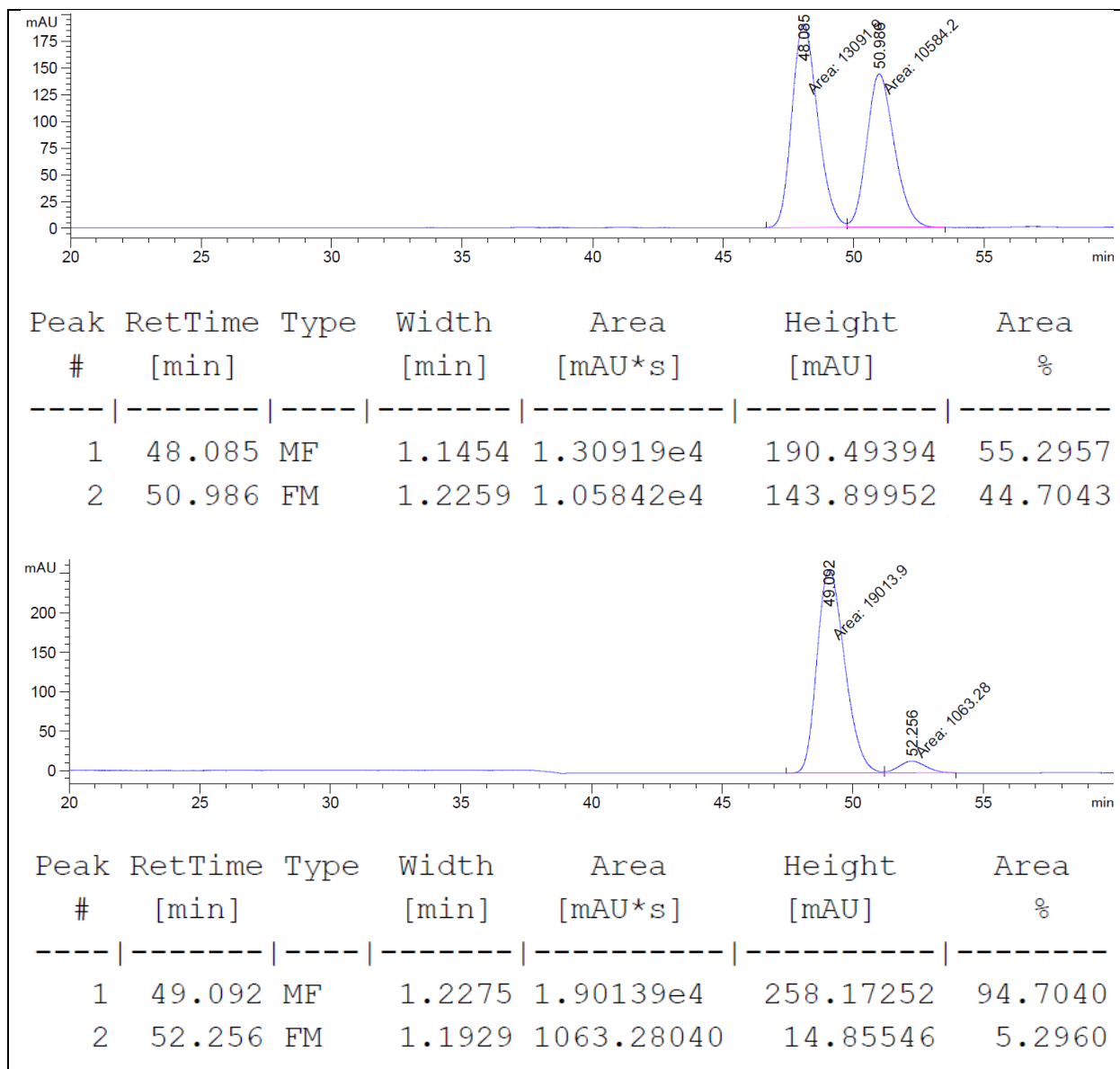


Prepared according to **GP4** with **1a** (25.0 μ L, 0.10 mmol, 1.00 equiv.), **2g** (62 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2 , 25:1 hexane:EtOAc) afforded the desired product **(+) 3g** as a colorless oil (23 mg, 46%). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 2H), 7.78 – 7.70 (m, 2H), 4.28 (t, J = 6.6 Hz, 2H), 1.81 – 1.69 (m, 2H), 1.62 – 1.32 (m, 4H), 1.29 – 1.22 (m, 18H), 1.01 (tt, J = 8.8, 5.8 Hz, 1H), 0.90 – 0.83 (m, 3H). ^{13}C NMR

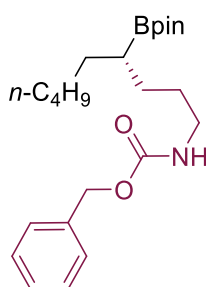
(101 MHz, Chloroform-*d*): δ 166.28, 137.77, 131.19, 130.19, 100.62, 83.09, 65.79, 32.24, 31.34, 28.93, 28.43, 27.76, 24.97, 24.92, 22.73, 14.20. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 36.03.

HRMS (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{34}\text{BINaO}_4^+$ 523.1487; Found 523.1504. $[\alpha]_{\text{D}}^{20}$ = +1.3 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Elution time: t_{major} = 49.1 min and t_{minor} = 52.2 min.



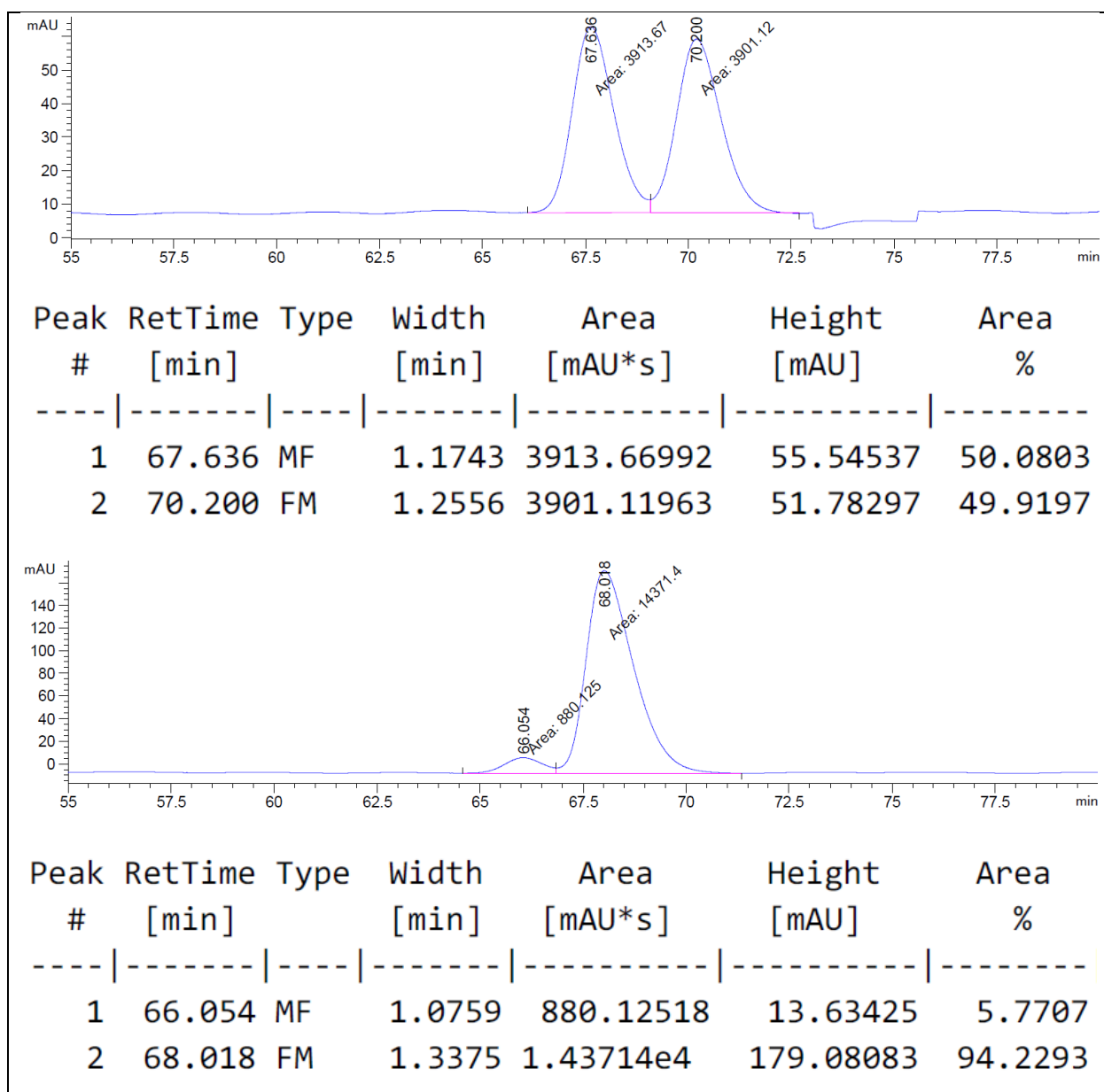
Benzyl (S)-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)carbamate ((-) 3h)



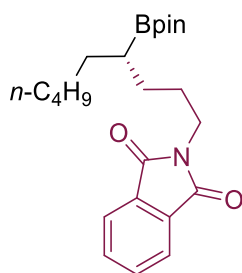
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2h** (32 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 7:1 hexane:EtOAc) afforded the desired product **(-) 3h** as a colorless oil (28 mg, 70%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.40 – 7.26 (m, 5H), 5.09 (s, 2H), 4.83 (s, 1H), 3.24 – 3.11 (m, 2H), 1.90 – 1.04 (m, 24H), 0.98 – 0.91 (m, 1H), 0.86 (t, *J* = 6.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 156.46, 136.86, 128.61, 128.22, 128.15, 83.09, 66.63, 41.44, 32.24, 31.37, 29.54, 28.89, 28.40, 24.93, 24.91, 22.71, 14.19. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 34.46.

HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₃H₃₈BNNaO₄⁺ 426.2786; Found 426.2784. [α]_D²⁰ = -1.2 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (88%) was determined via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 99:1 at a flow rate 0.3 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 68.0 min and *t*_{minor} = 66.0 min.

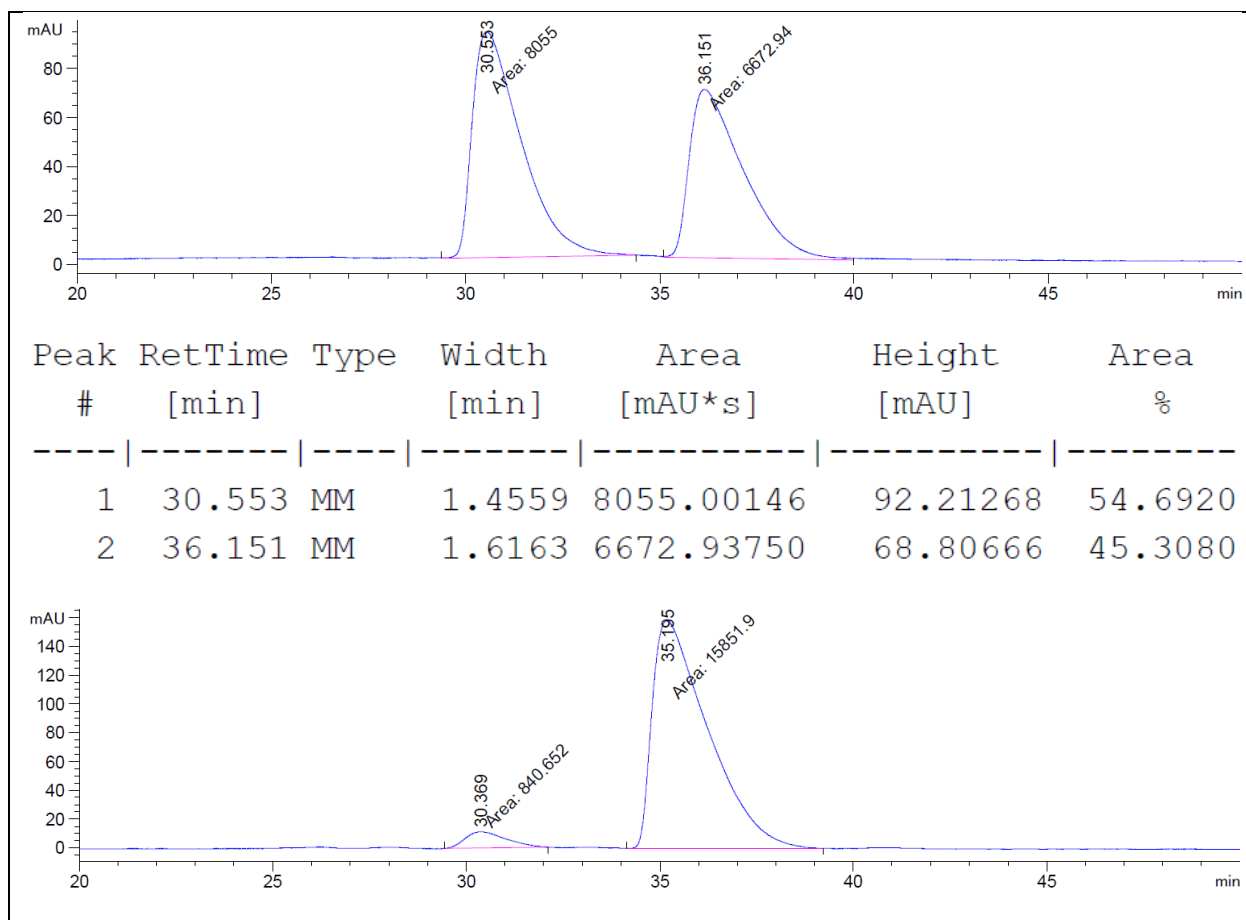


(S)-2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)isoindoline-1,3-dione ((+) 3i)



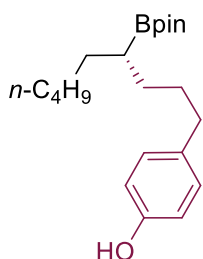
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2i** (31.5 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **(+) 3i** as a colorless oil (30 mg, 75%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.76 (dd, *J* = 5.4, 3.0 Hz, 2H), 7.62 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.59 (t, *J* = 7.2 Hz, 2H), 1.60 (dtd, *J* = 13.2, 6.5, 2.9 Hz, 2H), 1.43 – 1.14 (m, 22H), 0.91 (ddd, *J* = 8.9, 5.6, 3.1 Hz, 1H), 0.78 (t, *J* = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 168.53, 133.88, 132.40, 123.23, 83.07, 38.50, 32.23, 31.38, 28.97, 28.69, 28.39, 24.95, 24.89, 22.71, 14.18. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.88. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₃H₃₄BNNaO₄⁺ 422.2473, Found 422.2471. **[α]_D²⁰** = +3.0 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 96:4 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 35.2 min and *t*_{minor} = 30.4 min.



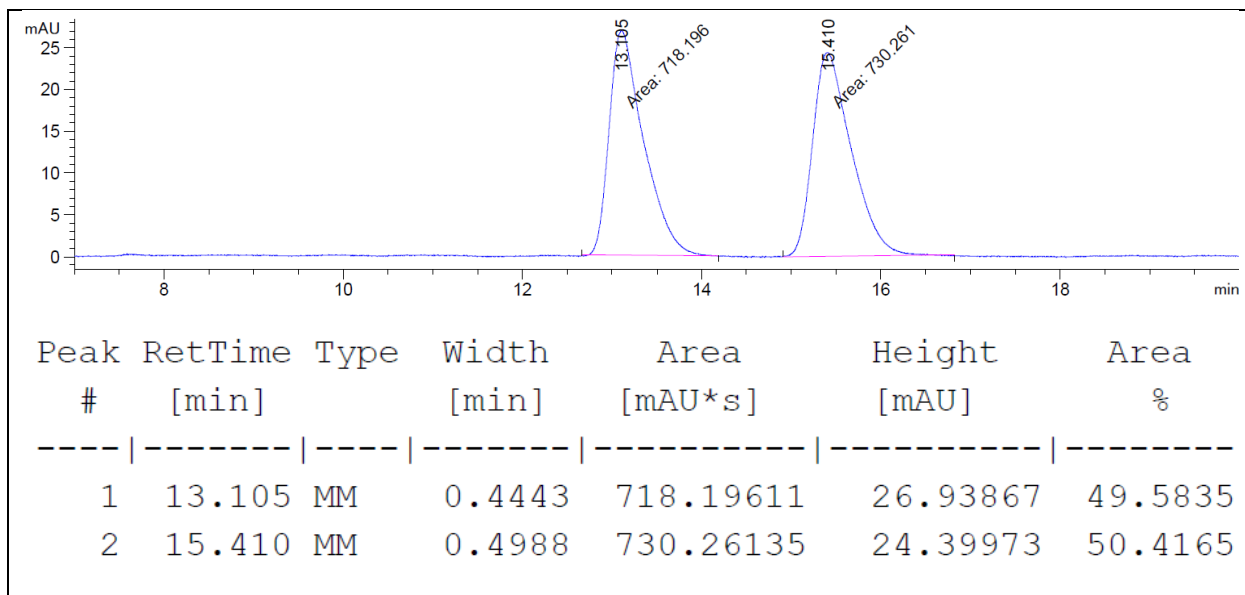
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.369	MM	1.2330	840.65161	11.36321	5.0361
2	35.195	MM	1.6677	1.58519e4	158.42488	94.9639

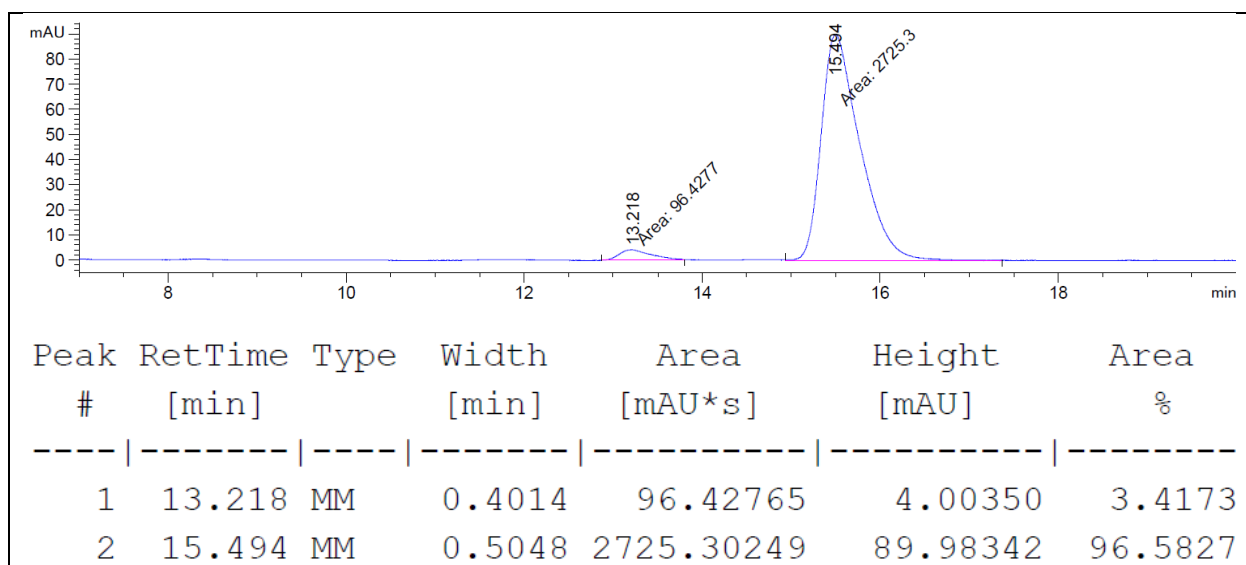
(S)-4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)phenol ((+) 3j)



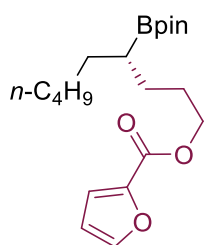
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2j** (26 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **(+) 3j** as a colorless oil (19 mg, 55%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.14 – 6.94 (m, 2H), 6.83 – 6.57 (m, 2H), 4.71 (brs, 1H), 2.52 (t, *J* = 7.7 Hz, 2H), 1.57 (p, *J* = 7.6 Hz, 2H), 1.46 – 1.23 (m, 22H), 0.99 (q, *J* = 8.3, 7.6 Hz, 1H), 0.86 (t, *J* = 5.9 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 153.54, 135.27, 129.53, 115.14, 83.02, 35.44, 32.28, 31.52, 31.22, 29.09, 24.96, 24.93, 22.74, 14.21. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₁H₃₅BO₃⁺ 346.2674; Found 346.2674. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 36.02. **[α]_D²⁰** = +0.3 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (93%) was determined via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 15.5 min and *t*_{minor} = 13.2 min.



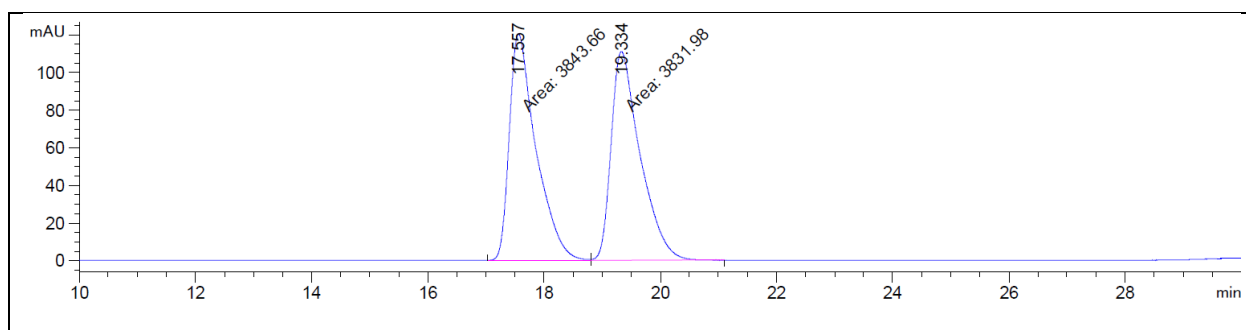


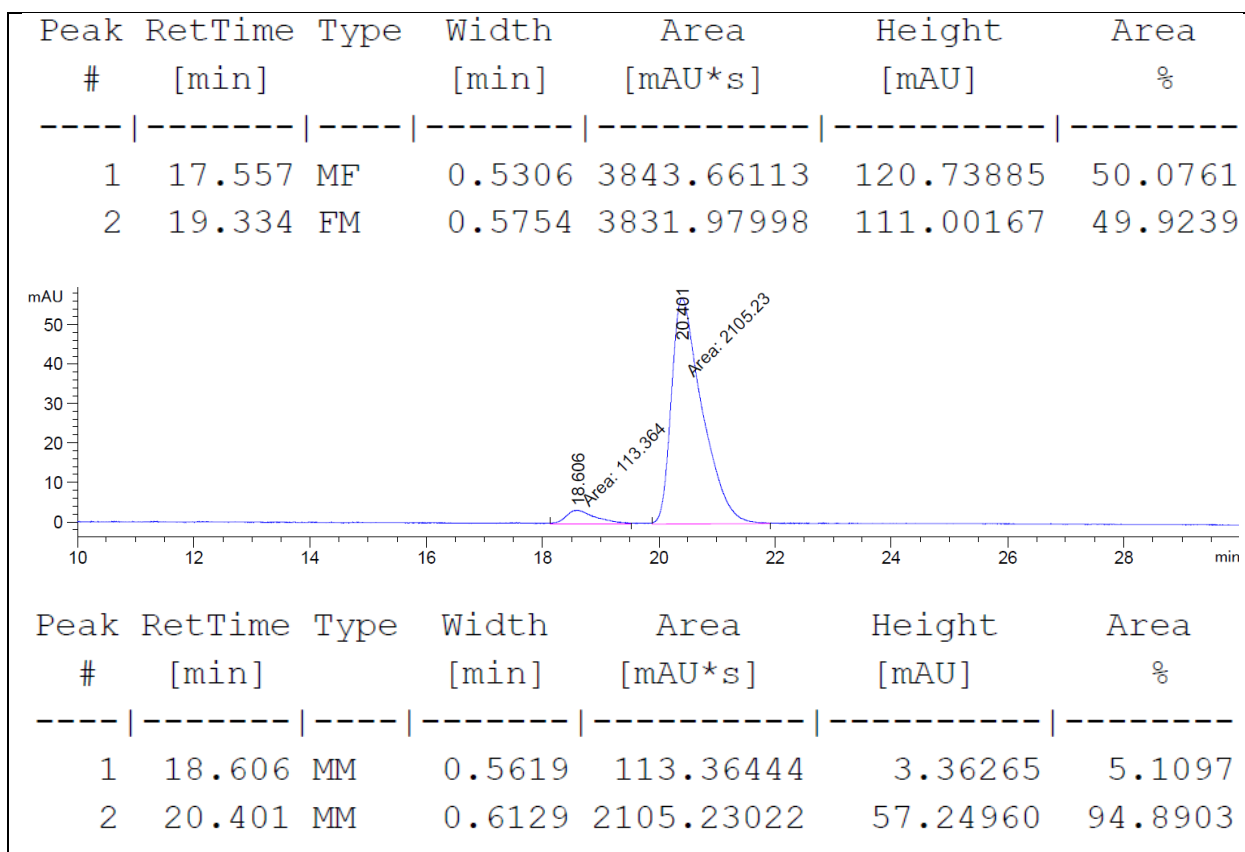
(S)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl furan-2-carboxylate ((-) 3k)



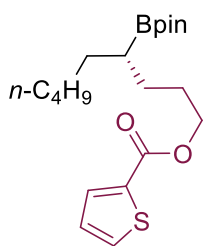
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2k** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 20:1 hexane:EtOAc) afforded the desired product **(-) 3k** as a colorless oil (26 mg, 71%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.56 (dd, *J* = 1.8, 0.9 Hz, 1H), 7.16 (dd, *J* = 3.5, 0.9 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 2H), 1.79 – 1.70 (m, 2H), 1.49 – 1.23 (m, 22H), 1.00 (ddd, *J* = 8.8, 7.2, 4.3 Hz, 1H), 0.88 – 0.84 (m, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 158.98, 146.23, 145.10, 117.74, 111.85, 83.08, 65.52, 32.25, 31.33, 28.92, 28.47, 27.61, 24.97, 24.92, 22.73, 14.19. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.39. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₀H₃₃BNaO₅⁺ 387.2313, Found 387.2313. **[α]_D²⁰** = -2.3 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OJ-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Elution time: *t*_{major} = 20.4 min and *t*_{minor} = 18.6 min.



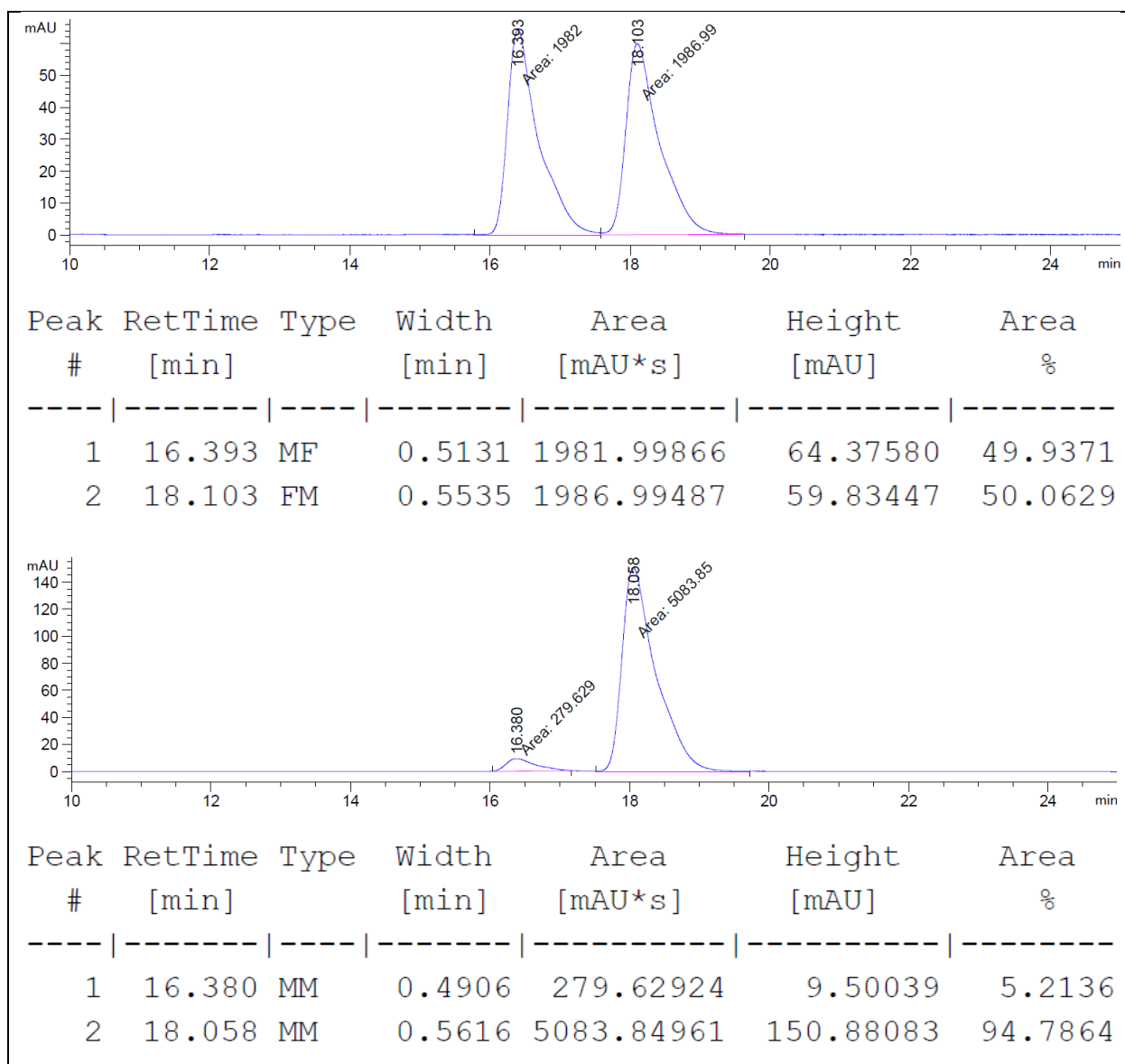


(S)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl thiophene-2-carboxylate ((+) **3l)**

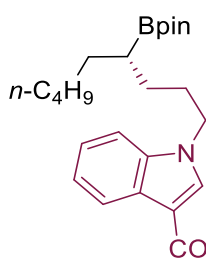


Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2l** (30 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 20:1 hexane:EtOAc) afforded the desired product (+) **3l** as a colorless oil (23 mg, 60%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.79 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.53 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1H), 4.27 (t, *J* = 6.6 Hz, 2H), 1.78 – 1.70 (m, 2H), 1.24 (s, 22H), 1.01 (ddd, *J* = 8.7, 5.8, 2.9 Hz, 1H), 0.87 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 158.98, 146.23, 145.10, 117.74, 111.85, 83.08, 65.52, 32.25, 31.33, 28.92, 28.47, 27.61, 24.97, 24.92, 22.73, 14.19. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₀H₃₃BNaO₄S⁺ 403.2085; Found 403.2080. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 35.35. [α]_D²⁰ = +1.3 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OJ-H column, with hexane:isopropanol = 96:4 at a flow rate 1.0 mL/min detected at 254 nm wavelength. Elution time: *t*_{major} = 18.1 min and *t*_{minor} = 16.4 min.

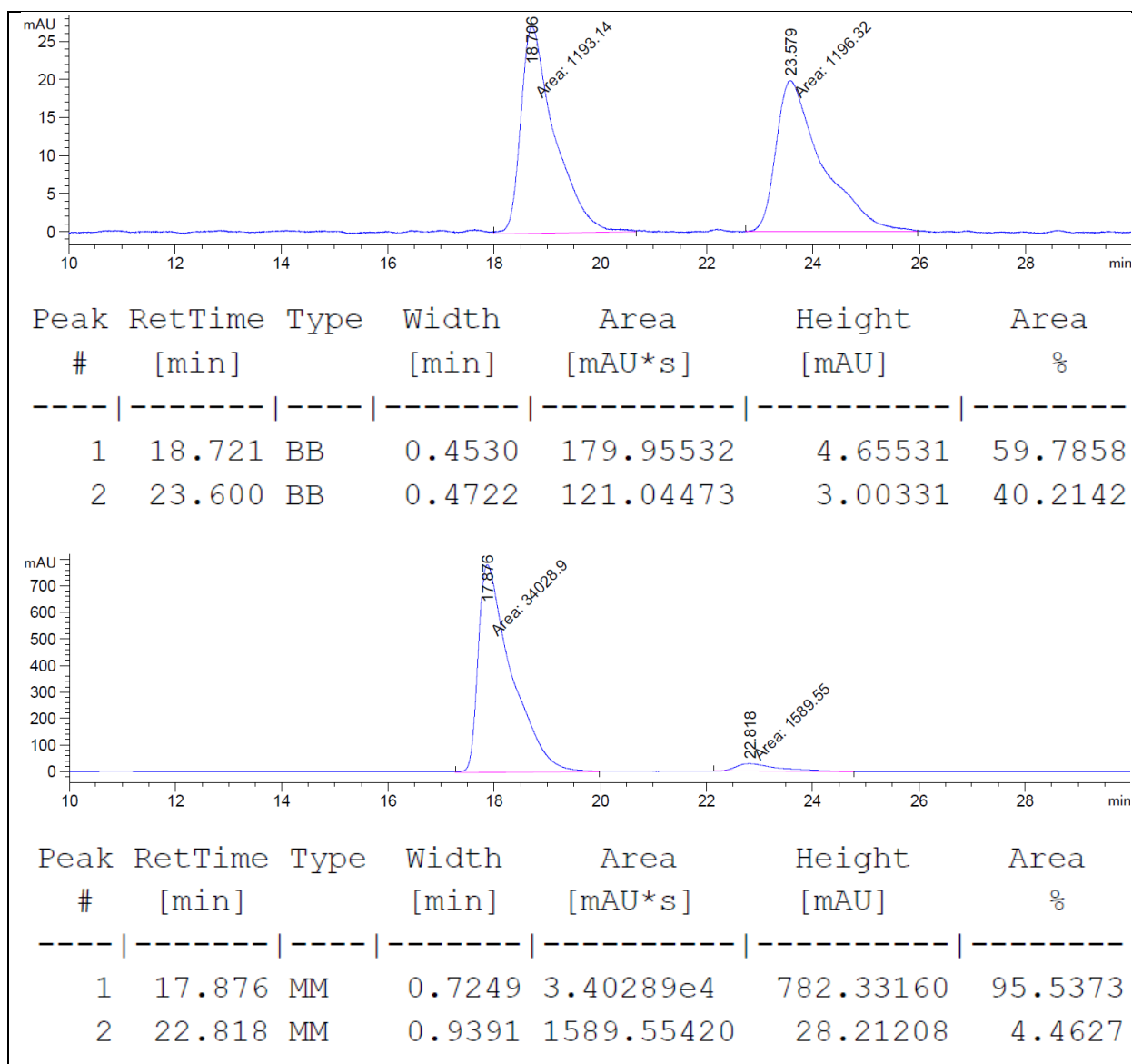


Methyl (S)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl)-1H-indole-3-carboxylate ((+) 3m)

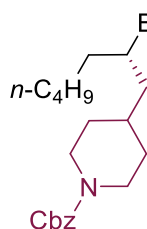


Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2m** (34 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2 , 20:1 hexane:EtOAc) afforded the desired product **(+) 3m** as a colorless oil (22 mg, 50%). **^1H NMR** (400 MHz, Chloroform-*d*): δ 8.20 (dd, J = 6.2, 3.1 Hz, 1H), 7.85 (s, 1H), 7.43 – 7.37 (m, 1H), 7.28 (dd, J = 6.0, 3.2 Hz, 2H), 4.15 (t, J = 8.0 Hz, 2H), 3.93 (s, 3H), 1.99 – 1.81 (m, 2H), 1.44 – 1.21 (m, 22H), 1.00 (dq, J = 20.3, 7.6, 6.1 Hz, 1H), 0.89 (t, J = 6.7 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ 165.70, 136.63, 134.38, 126.89, 122.66, 121.86, 121.83, 110.20, 106.88, 83.17, 51.04, 47.39, 32.19, 31.39, 29.54, 28.89, 28.60, 24.96, 24.87, 22.69, 14.17. **HRMS (ESI/QTOF)** m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{38}\text{BNNaO}_4^+$ 450.2786; Found 450.2793. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.39. **$[\alpha]_{\text{D}}^{20}$** = +4.00 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® IB column, with hexane:isopropanol = 92:8 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: $t_{\text{major}} = 17.9$ min and $t_{\text{minor}} = 22.8$ min.



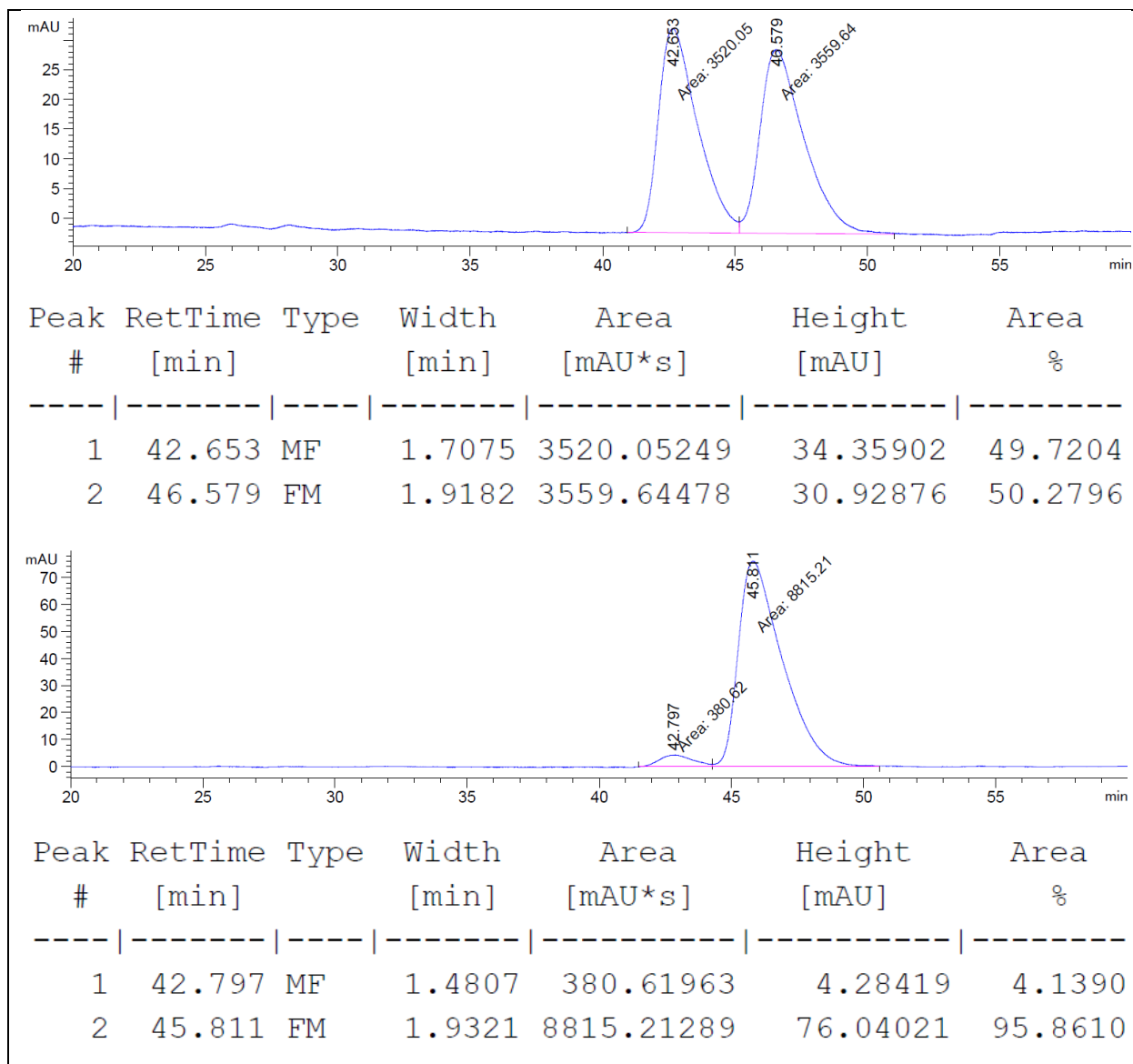
Benzyl (S)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)piperidine-1-carboxylate ((+) **3n)**



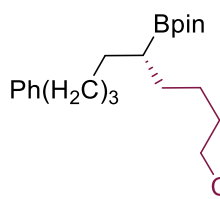
Prepared according to **GP4** with **1a** (38.0 μ L, 0.15 mmol, 1.50 equiv.), **2n** (36 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2 , 20:1 hexane:EtOAc) afforded the desired product **(+) 3n** as a colorless oil (35 mg, 79%). ^1H NMR (400 MHz, Chloroform- d): δ 7.41 – 7.16 (m, 5H), 5.12 (s, 2H), 4.24 – 4.03 (m, 4H), 2.73 (t, $J = 12.0$ Hz, 2H), 1.68 (dd, $J = 27.5, 13.5$ Hz, 2H), 1.46 – 1.22 (m, 23H), 1.14 – 0.97 (m, 3H), 0.87 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform- d): δ 155.45, 137.20, 128.58, 127.99, 127.92, 83.04, 67.00, 44.47, 38.22, 35.52, 32.27, 31.78, 29.00, 24.98, 24.91, 22.74, 14.20. **HRMS (ESI/QTOF)** m/z : $[\text{M} + \text{Na}]^+$ Calcd for

$C_{26}H_{42}BNNaO_4^+$ 466.3099; Found 466.3095. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.84. $[\alpha]_D^{20} = +4.7$ ($c = 1.00$ in $CHCl_3$).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{major} = 45.8$ min and $t_{minor} = 42.8$ min.



Methyl (*S*)-10-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate ((-)3o**)**

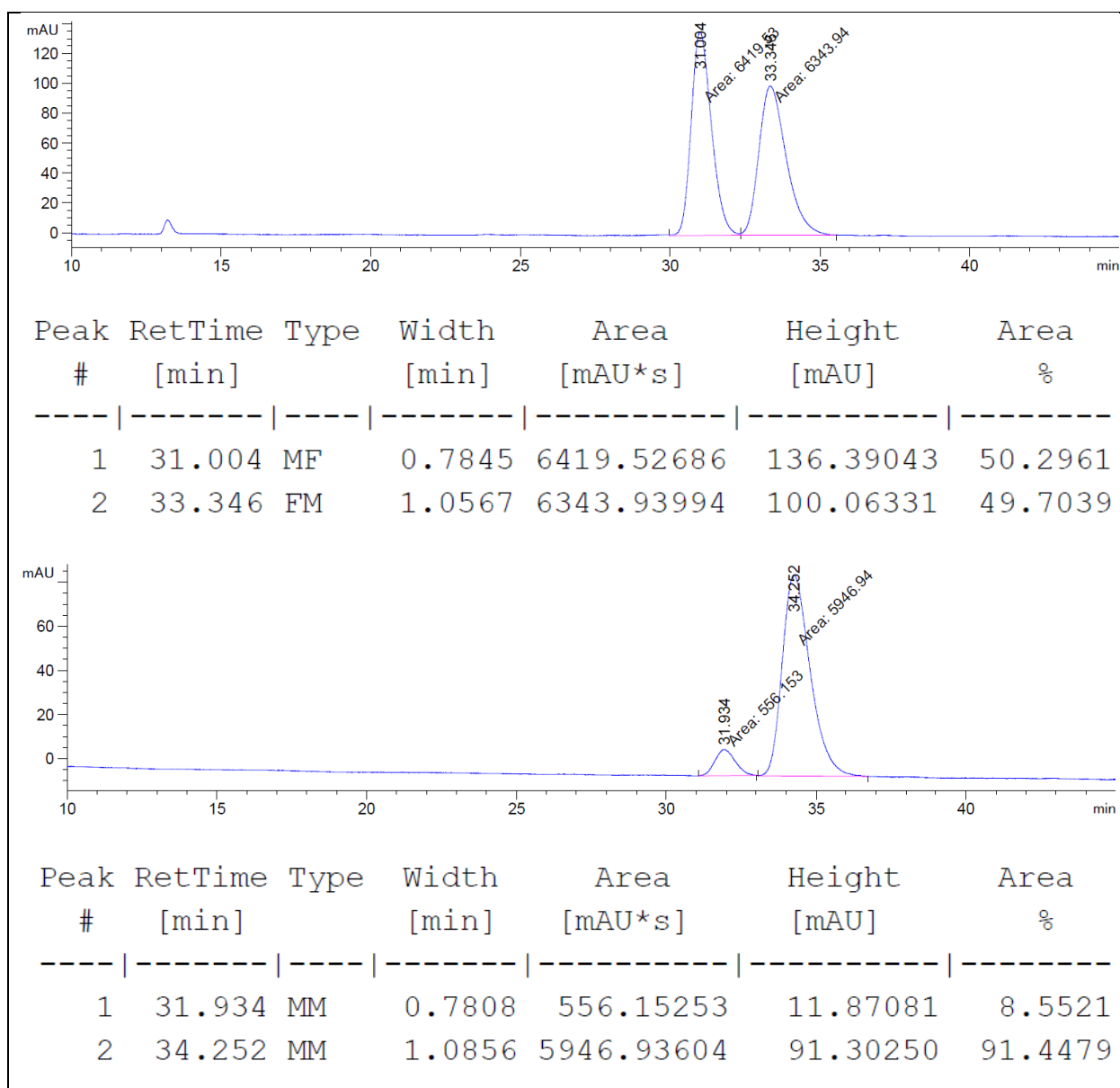


Prepared according to **GP4** with **1b** (54 mg, 0.20 mmol, 1.00 equiv.), **2o** (43 μ L, 0.30 mmol, 1.50 equiv.) and KI (13.2 mg, 0.08 mmol, 0.40 equiv.) in 3:2 DCE:DMF (1.0 mL). Flash column chromatography (SiO_2 , 15:1 hexane:EtOAc) afforded the desired product **(-)** **3o** as a colorless oil (42 mg, 54%). 1H NMR (400 MHz, Chloroform-*d*): δ 7.38 – 7.31 (m, 2H), 7.28 – 7.21 (m, 3H), 3.74 (s, 3H), 2.68 (t, $J = 7.6$ Hz, 2H), 2.42 – 2.34 (m, 2H), 1.73 – 1.65 (m, 4H), 1.56 – 1.35 (m, 8H), 1.29 (s, 12H), 1.08 – 0.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.40, 142.96, 128.54,

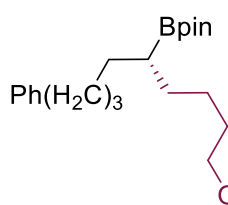
128.30, 125.62, 82.97, 51.53, 35.99, 34.21, 31.82, 31.37, 31.13, 28.97, 28.91, 25.37, 24.89, 24.87.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 33.70. **HRMS (ESI/QTOF)** m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{37}\text{BNaO}_4^+$ 411.2677; Found 411.2672. $[\alpha]_{\text{D}}^{20} = -1.2$ ($c = 1.00$ in CHCl_3).

HPLC: The enantiomeric excess (83%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{\text{major}} = 34.2$ min and $t_{\text{minor}} = 31.9$ min.



(S)-4,4,5,5-Tetramethyl-2-(1-phenoxy-9-phenylnonan-5-yl)-1,3,2-dioxaborolane ((-) 3p)

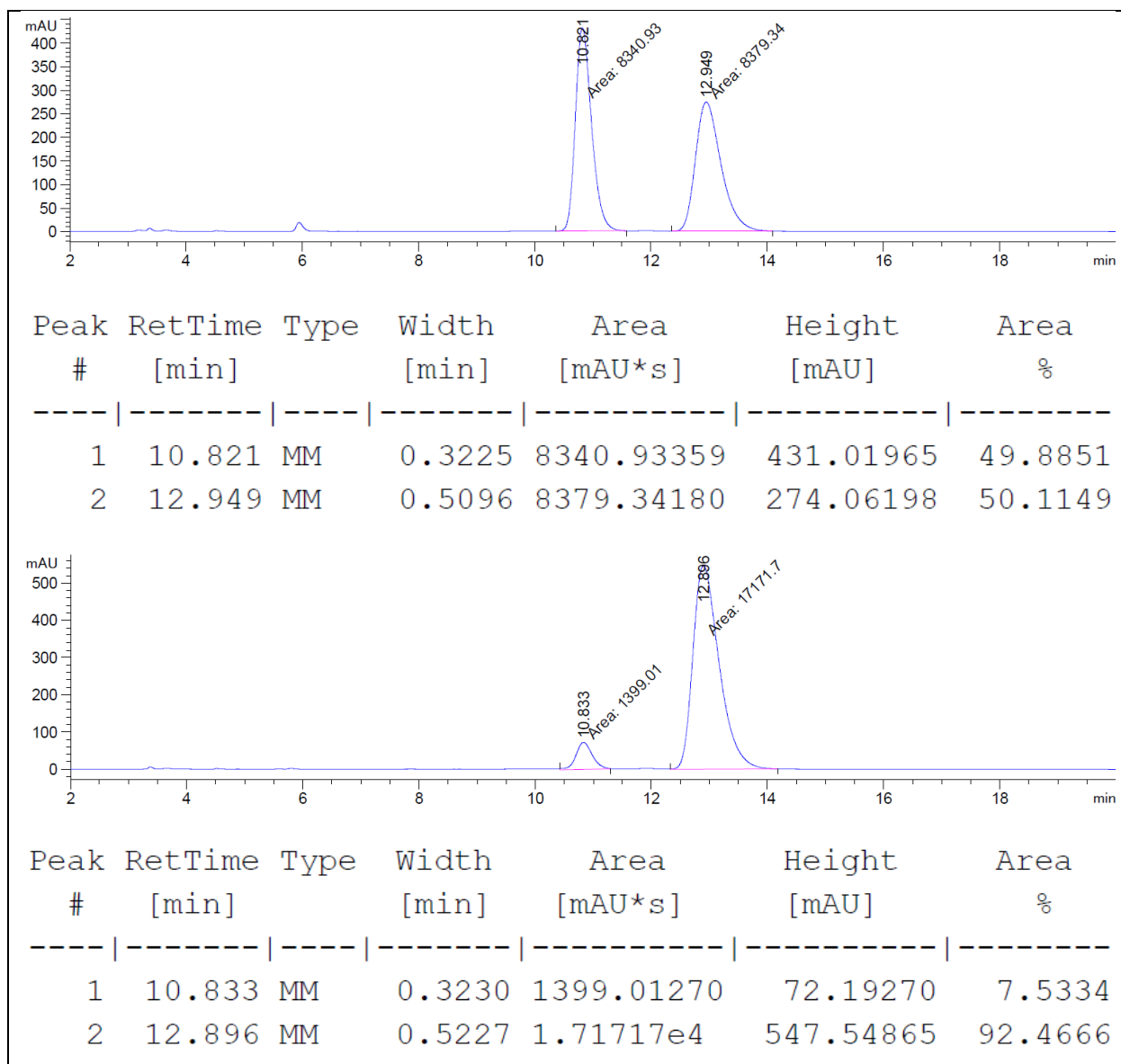


Prepared according to **GP4** with **1b** (54 mg, 0.20 mmol, 1.00 equiv.), **2p** (71 mg, 0.30 mmol, 1.50 equiv.) and KI (13.2 mg, 0.08 mmol, 0.40 equiv.) in 3:2 DCE:DMF (1.0 mL). Flash column chromatography (SiO_2 , 40:1 hexane:EtOAc) afforded the desired product **(-) 3p** as a colorless oil (46

mg, 54%). **^1H NMR** (400 MHz, Chloroform-*d*): δ 7.31 – 7.24 (m, 4H), 7.20 – 7.14 (m, 3H), 6.98

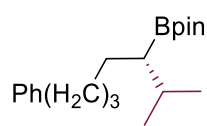
– 6.87 (m, 3H), 3.95 (t, $J = 6.5$ Hz, 2H), 2.61 (t, $J = 7.7$ Hz, 2H), 1.78 (td, $J = 6.8, 3.0$ Hz, 2H), 1.69 – 1.56 (m, 2H), 1.53 – 1.29 (m, 8H), 1.22 (s, 12H), 1.01 (ddd, $J = 8.7, 5.6, 2.9$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 159.25, 142.97, 129.52, 129.48, 128.55, 128.31, 125.63, 120.50, 114.59, 82.99, 67.84, 36.00, 31.83, 31.40, 31.30, 29.67, 28.99, 25.81, 24.90, 24.88. ^{11}B NMR (128 MHz, Chloroform- d) δ 33.72. HRMS (APPI/LTQ-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{27}\text{H}_{39}\text{BO}_3^+$ 422.2987; Found 422.3004. $[\alpha]_{\text{D}}^{20} = -0.3$ ($c = 1.00$ in CHCl_3).

HPLC: The enantiomeric excess (85%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{\text{major}} = 12.9$ min and $t_{\text{minor}} = 10.8$ min.

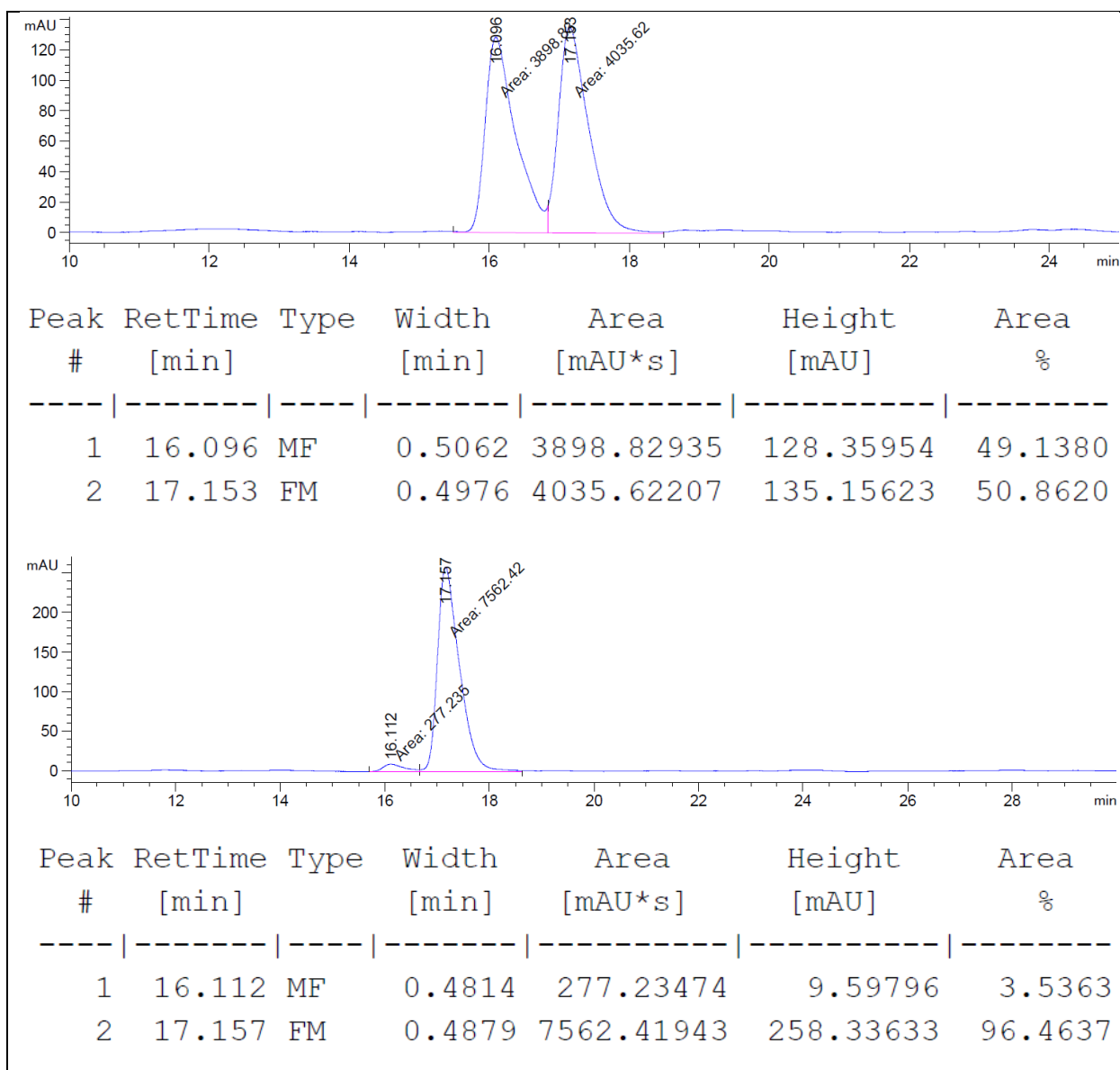


(S)-4,4,5,5-Tetramethyl-2-(2-methyl-7-phenylheptan-3-yl)-1,3,2-dioxaborolane ((-) 4a)

Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2r** (15 μL , 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2 , 150:1 hexane:EtOAc) afforded the desired product

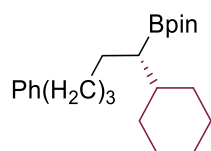

(-) 4a as a colorless oil (22 mg, 70%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.68 (ddd, *J* = 28.7, 14.3, 7.2 Hz, 3H), 1.24 (d, *J* = 4.5 Hz, 16H), 0.94 (2d, 4.7 Hz, 6H), 0.84 (dt, *J* = 11.4, 5.9 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 143.03, 128.57, 128.31, 125.62, 82.91, 36.07, 31.93, 29.84, 29.41, 29.29, 25.07, 24.97, 22.52, 22.00. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.97. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₀H₃₃BO₂⁺ 316.2568; Found 316.2566. [α]_D²⁰ = -6.0 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (93%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 99:1 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 17.2 min and *t*_{minor} = 16.1 min.



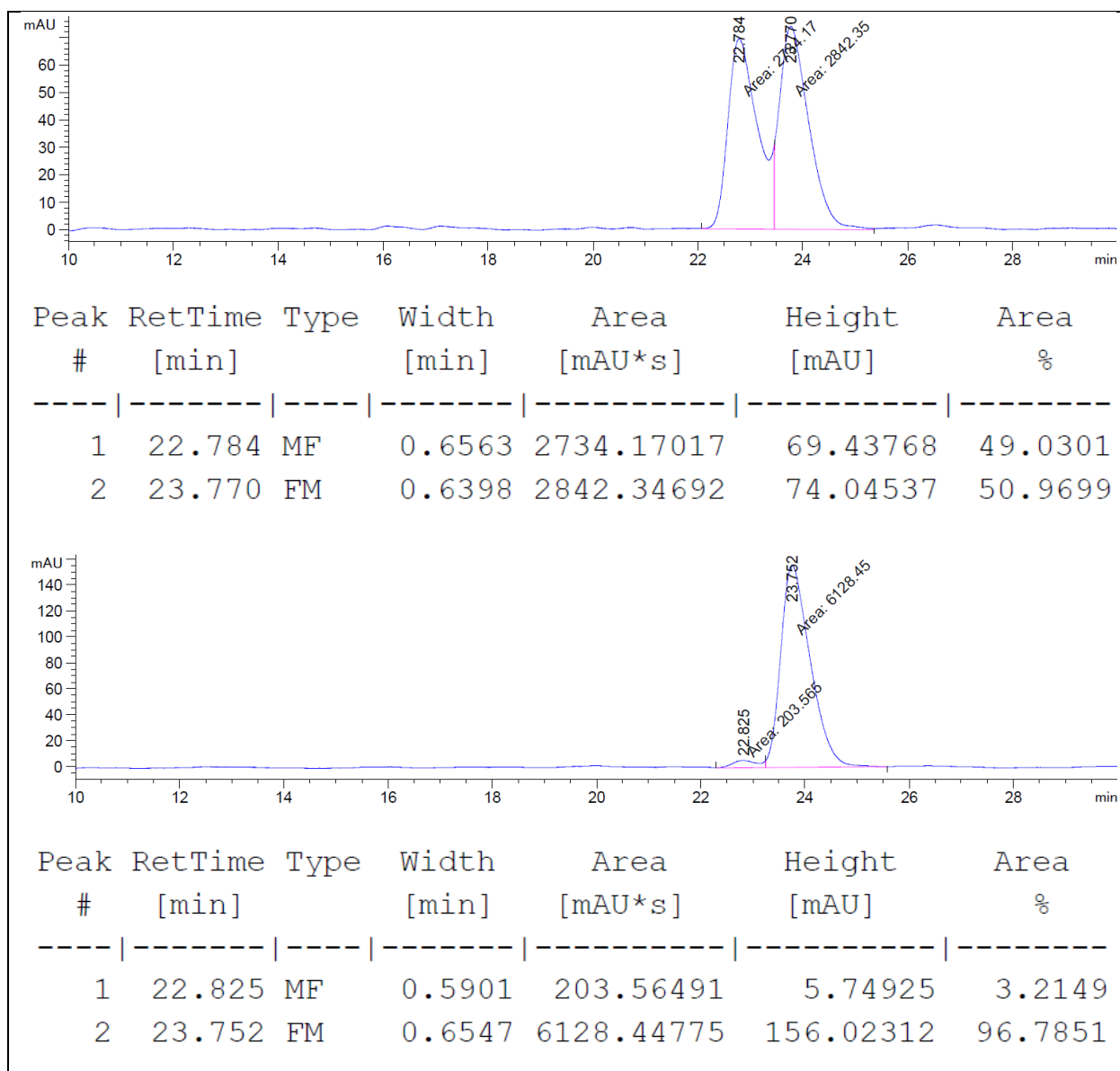
(S)-2-(1-Cyclohexyl-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 4b)

Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2s** (20 μL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 150:1 hexane:EtOAc) afforded the desired product



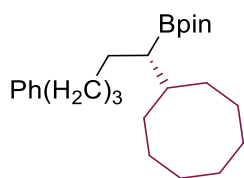
(-) 4b as a colorless oil (24 mg, 67%). ^1H NMR (400 MHz, Chloroform-*d*): δ 7.27 (d, J = 7.9 Hz, 2H), 7.19 (d, J = 7.8 Hz, 3H), 2.62 (t, J = 7.8 Hz, 2H), 1.85 – 1.55 (m, 7H), 1.52 – 1.41 (m, 2H), 1.36 (dq, J = 13.4, 6.9, 5.6 Hz, 2H), 1.24 (m, 15H), 1.16 – 0.82 (m, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*): δ 143.03, 128.57, 128.30, 125.61, 82.91, 39.90, 36.04, 33.05, 32.72, 31.91, 29.44, 28.84, 26.95, 26.93, 25.10, 24.95. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 34.18. HRMS (APPI/LTQ-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{23}\text{H}_{37}\text{BO}_2^+$ 356.2881; Found 356.2878. $[\alpha]_{\text{D}}^{20}$ = -4.33 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (93%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 99:1 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 23.7 min and t_{minor} = 22.8 min.



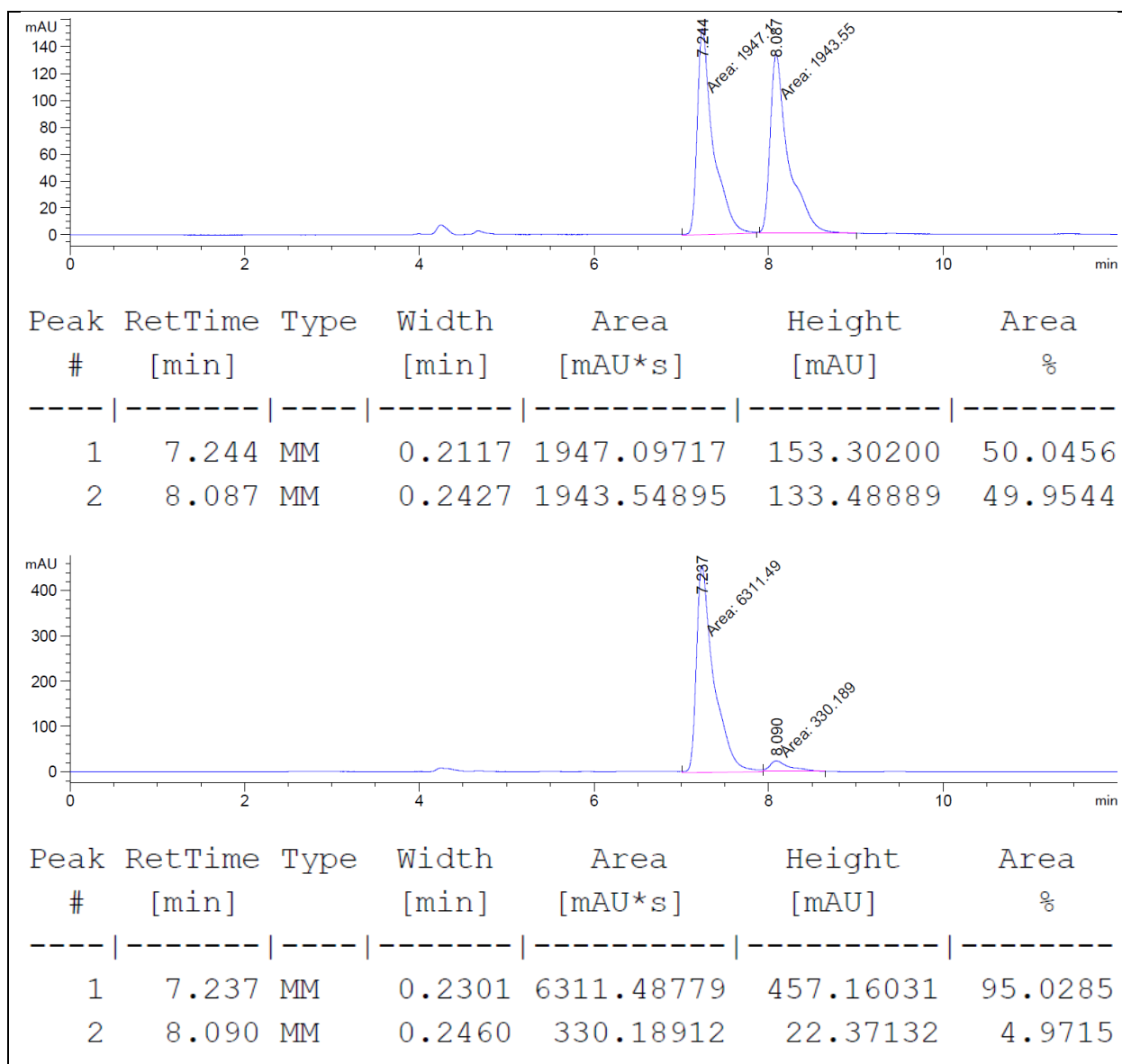
(S)-2-(1-Cyclooctyl-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 4c)

Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2t** (36 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2 , 150:1 hexane:EtOAc) afforded the desired product

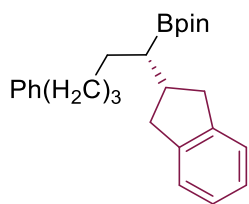


(-) **4c** as a colorless oil (30 mg, 78%). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 7.28 (t, J = 7.5 Hz, 2H), 7.23 – 7.12 (m, 3H), 2.62 (t, J = 7.7 Hz, 2H), 1.66 – 1.22 (m, 33H), 0.94 – 0.86 (m, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*): δ 143.03, 128.57, 128.30, 125.61, 82.86, 39.22, 36.05, 32.72, 32.59, 31.91, 29.47, 29.26, 27.10, 27.07, 26.70, 26.64, 25.96, 25.07, 24.93. $^{11}\text{B NMR}$ (128 MHz, Chloroform-*d*) δ 33.82. **HRMS (APPI/LTQ-Orbitrap)** m/z : $[\text{M}]^+$ Calcd for $\text{C}_{25}\text{H}_{41}\text{BO}_2^+$ 384.3194; Found 384.3192. $[\alpha]_{\text{D}}^{20}$ = -1.0 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 96:4 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 7.2 min and t_{minor} = 8.1 min.

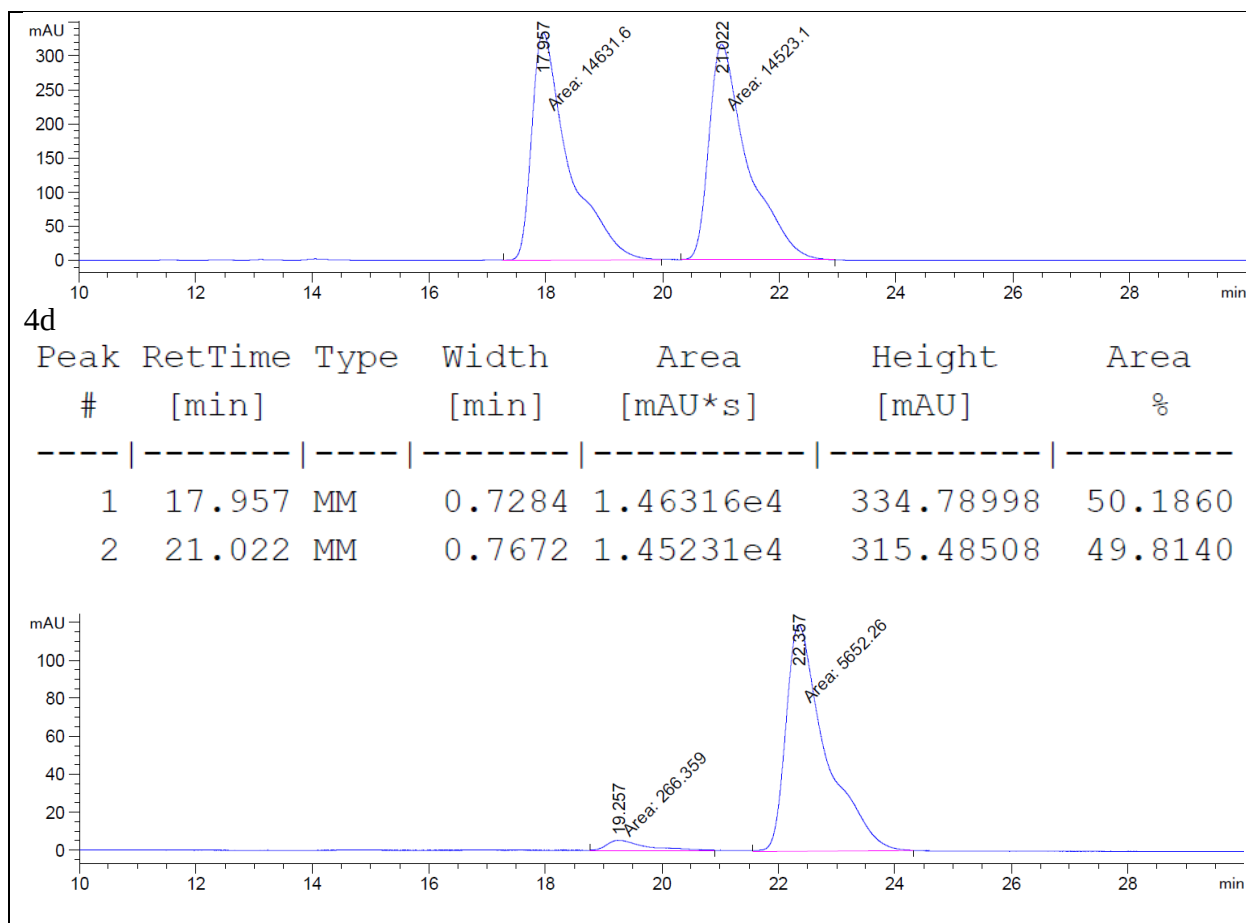


(S)-2-(1-(2,3-Dihydro-1H-inden-2-yl)-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 4d)



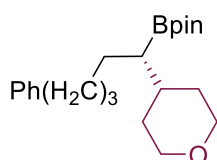
Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2u** (36 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 100:1 hexane:EtOAc) afforded the desired product **(-) 4d** as a colorless oil (27 mg, 69%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.15 – 7.11 (m, 2H), 7.08 – 7.00 (m, 5H), 6.99 – 6.92 (m, 2H), 2.89 (ddd, *J* = 36.2, 15.4, 7.7 Hz, 2H), 2.58 – 2.45 (m, 4H), 2.44 – 2.32 (m, 1H), 1.51 – 1.04 (m, 19H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 143.94, 143.74, 142.92, 128.58, 128.34, 126.04, 126.02, 125.67, 124.40, 124.38, 83.09, 42.29, 39.39, 38.77, 36.03, 31.91, 30.58, 29.23, 24.98. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 33.68. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₆H₃₅BO₂⁺ 390.2725; Found 390.2724. [α]_D²⁰ = -5.8 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 22.4 min and *t*_{minor} = 19.3 min.



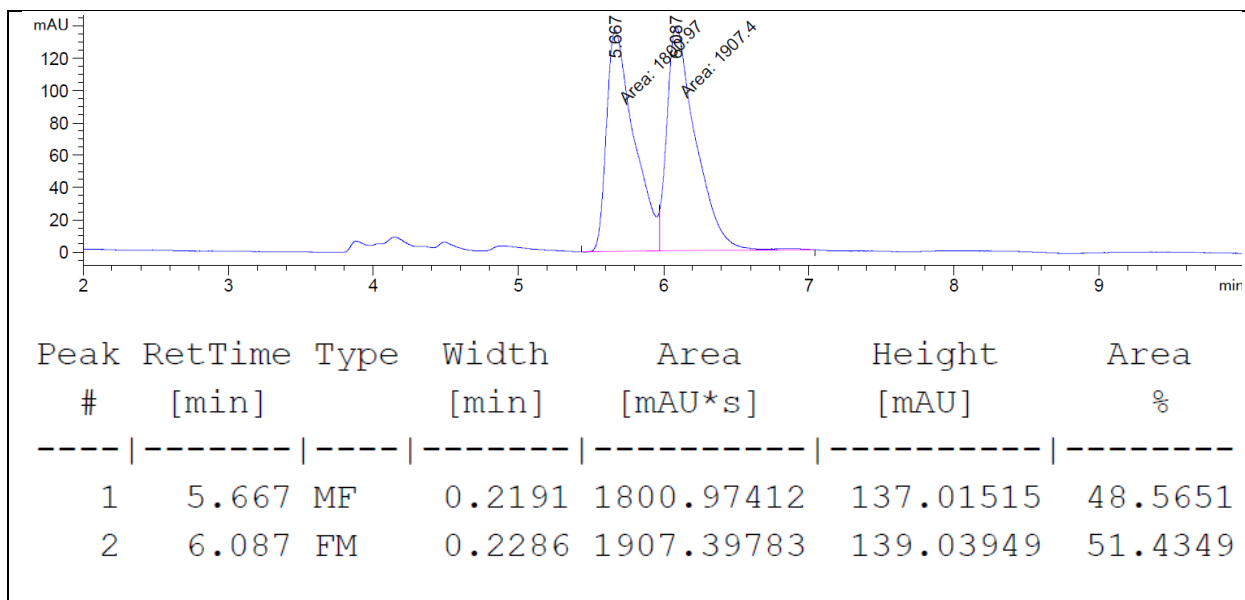
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.257	MM	0.7927	266.35928	5.60041	4.5004
2	22.357	MM	0.7888	5652.26172	119.42857	95.4996

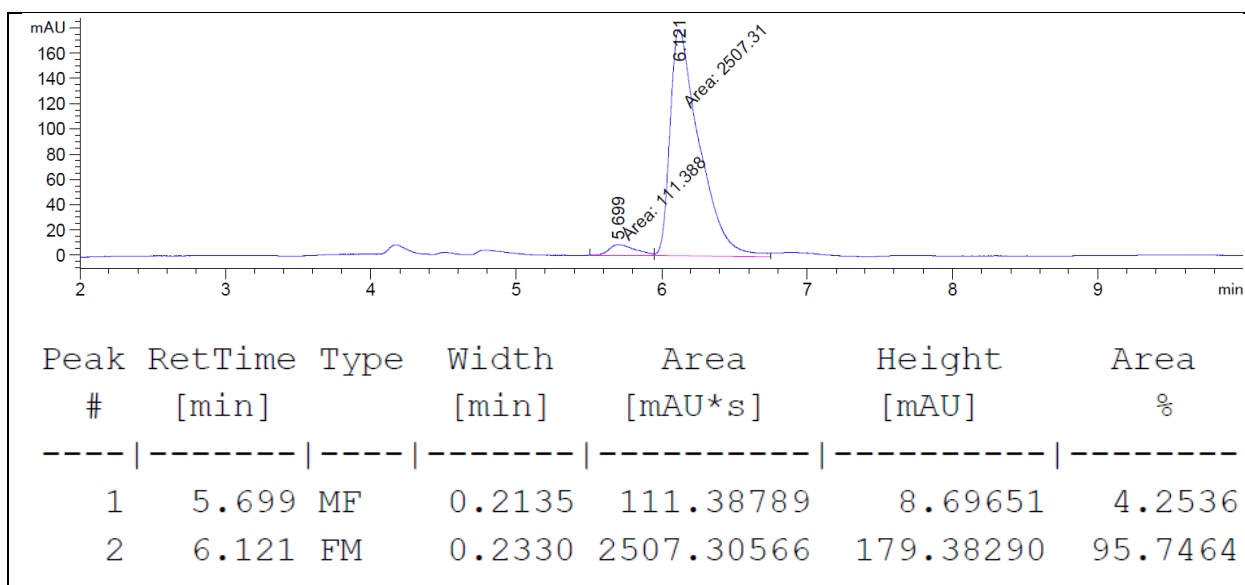
(S)-4,4,5,5-Tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane ((-) 4e)



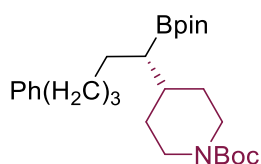
Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2v** (18 μ L, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 15:1 hexane:EtOAc) afforded the desired product **(-) 4e** as a colorless oil (25 mg, 70%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (dd, *J* = 8.6, 6.4 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 3H), 3.96 (dt, *J* = 10.5, 4.9 Hz, 2H), 3.37 (t, *J* = 11.7 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.73 – 1.23 (m, 23H), 0.95 – 0.87 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 142.86, 128.54, 128.32, 125.67, 83.13, 68.66, 68.54, 37.05, 35.99, 32.93, 32.54, 31.83, 29.14, 28.40, 25.07, 24.99. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 33.62. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + H]⁺ Calcd for C₂₂H₃₆BO₃⁺ 359.2752; Found 359.2753. [α]_D²⁰ = -3.5 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 99:1 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 6.1 min and *t*_{minor} = 5.7 min.



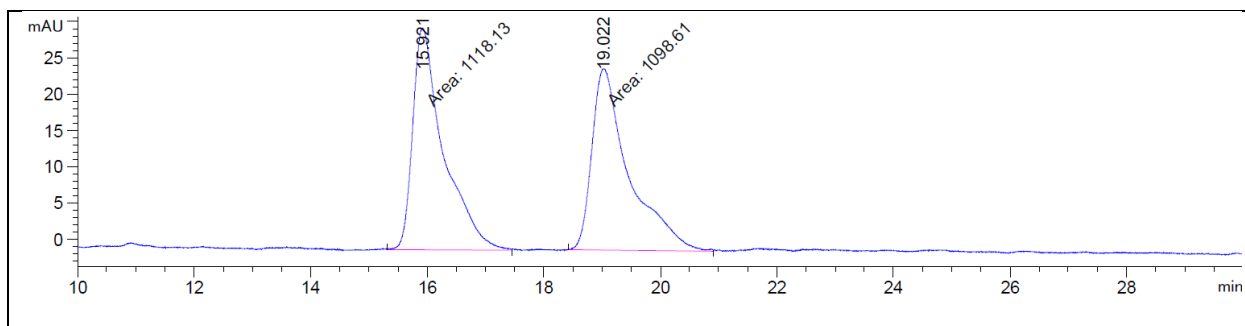


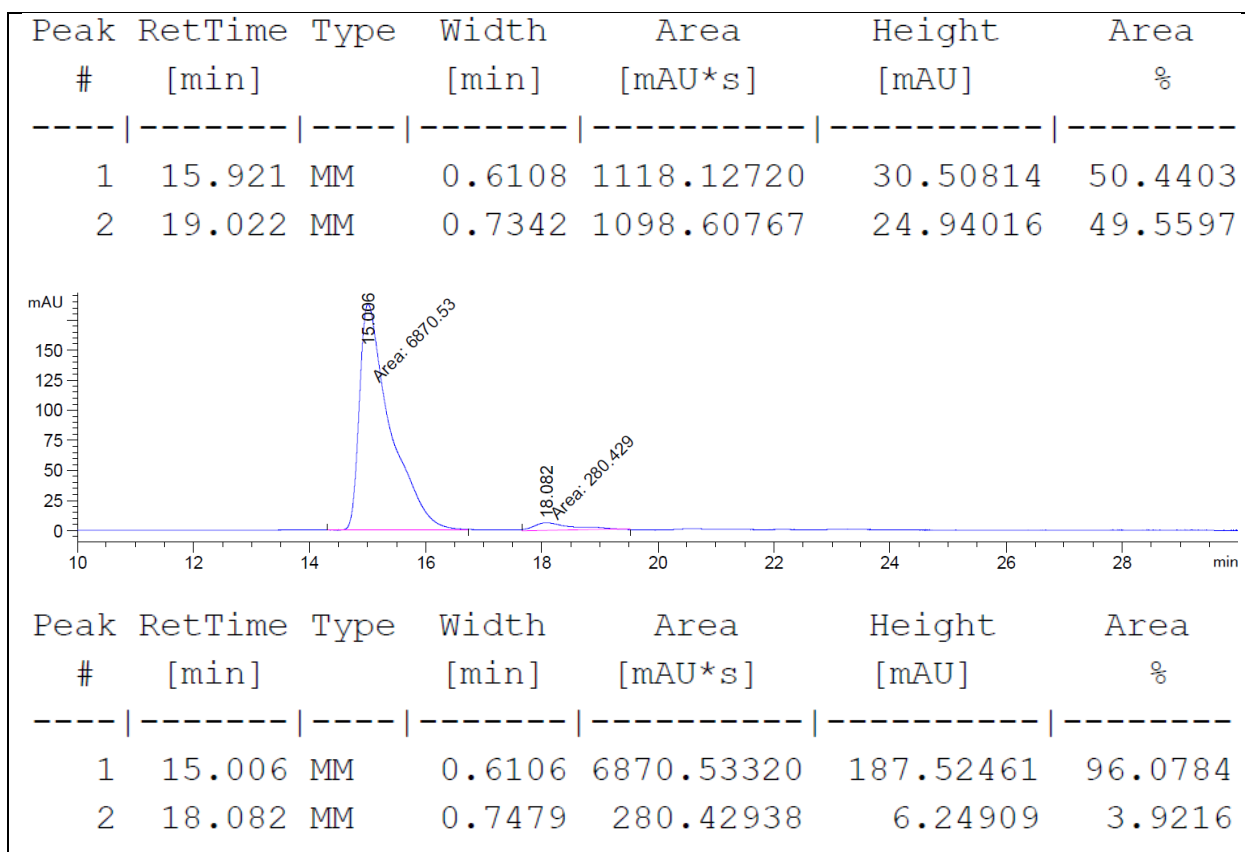
tert-Butyl (S)-4-(5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)piperidine-1-carboxylate ((+) 4f)



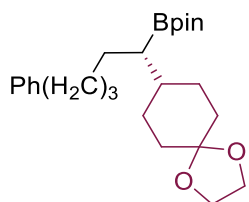
Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2w** (47 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 5:1 hexane:EtOAc) afforded the desired product **(+) 4f** as a colorless oil (28 mg, 61%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (dd, *J* = 9.5, 5.6 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 3H), 4.16 – 4.01 (m, 2H), 2.64 (dt, *J* = 15.1, 10.3 Hz, 4H), 1.72 – 1.58 (m, 4H), 1.47 (s, 9H), 1.40 – 1.08 (m, 19H), 0.94 – 0.86 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*): 155.05, 142.85, 128.55, 128.33, 125.67, 83.13, 79.19, 44.59, 38.09, 35.97, 31.89, 31.80, 31.49, 29.16, 28.65, 28.62, 25.06, 24.95. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 36.14. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₇H₄₄BNNaO₄⁺ 480.3256; Found 480.3263. [α]_D²⁰ = +1.0 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Elution time: *t*_{major} = 15.0 min and *t*_{minor} = 18.1 min.



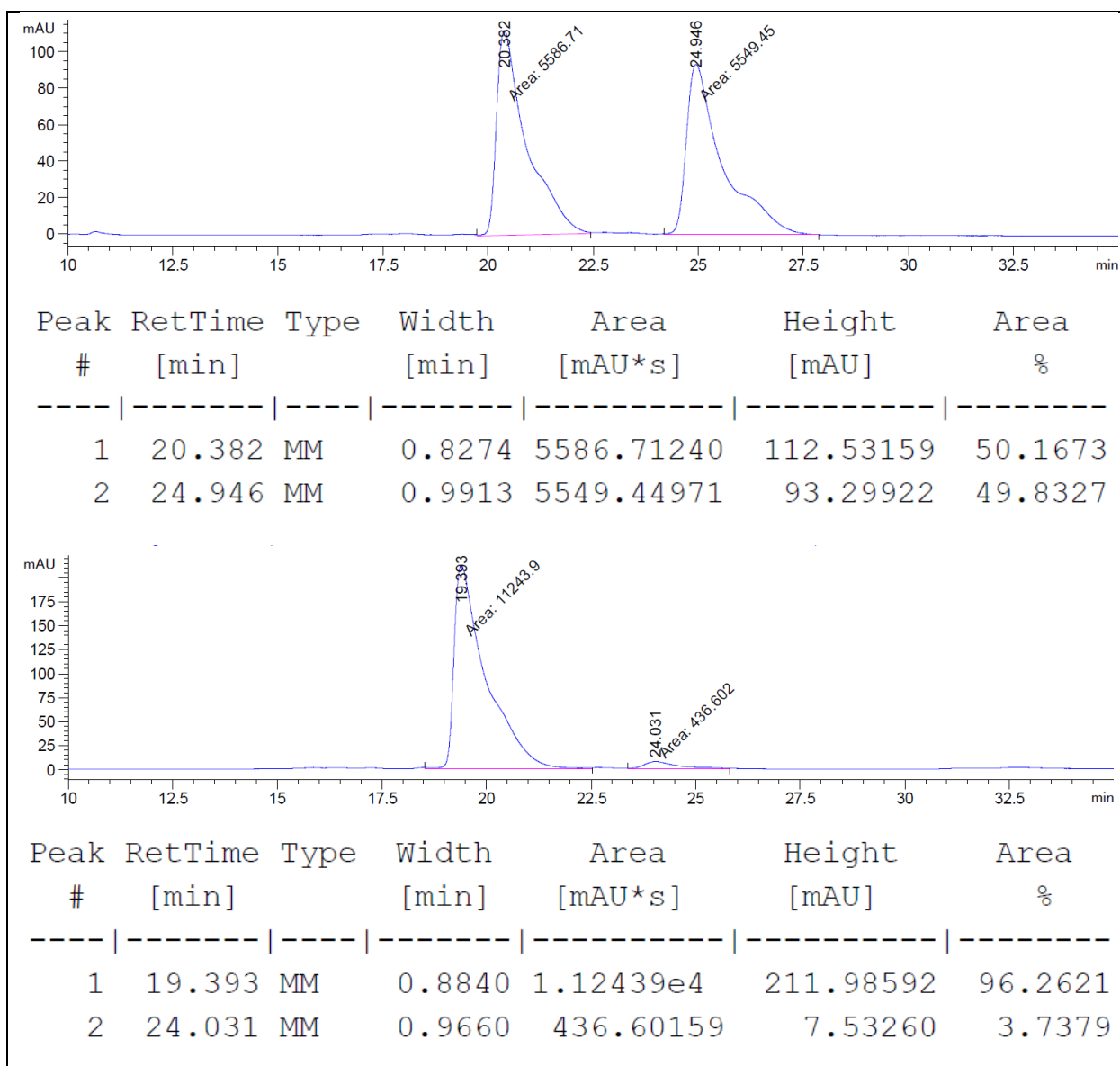


(S)-4,4,5,5-Tetramethyl-2-(5-phenyl-1-(1,4-dioxaspiro[4.5]decan-8-yl)pentyl)-1,3,2-dioxaborolane ((-) **4g)**

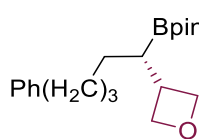


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2x** (40 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 15:1 hexane:EtOAc) afforded the desired product **(-) 4g** as a colorless oil (26 mg, 63%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.22 (dd, *J* = 33.2, 7.5 Hz, 5H), 3.94 (s, 4H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.81 – 1.71 (m, 3H), 1.71 – 1.58 (m, 3H), 1.56 – 1.28 (m, 9H), 1.24 (s, 6H), 1.23 (s, 6H), 0.95 – 0.87 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 142.94, 128.56, 128.30, 125.62, 109.22, 83.03, 64.29, 64.26, 38.44, 35.99, 35.01, 34.97, 31.84, 29.63, 29.32, 29.01, 25.07, 24.91. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₂₅H₄₀BO₄⁺ 415.3014; Found 415.3016. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.38. **$[\alpha]_D^{20}$** = -2.2 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Elution time: *t*_{major} = 19.4 min and *t*_{minor} = 24.0 min.

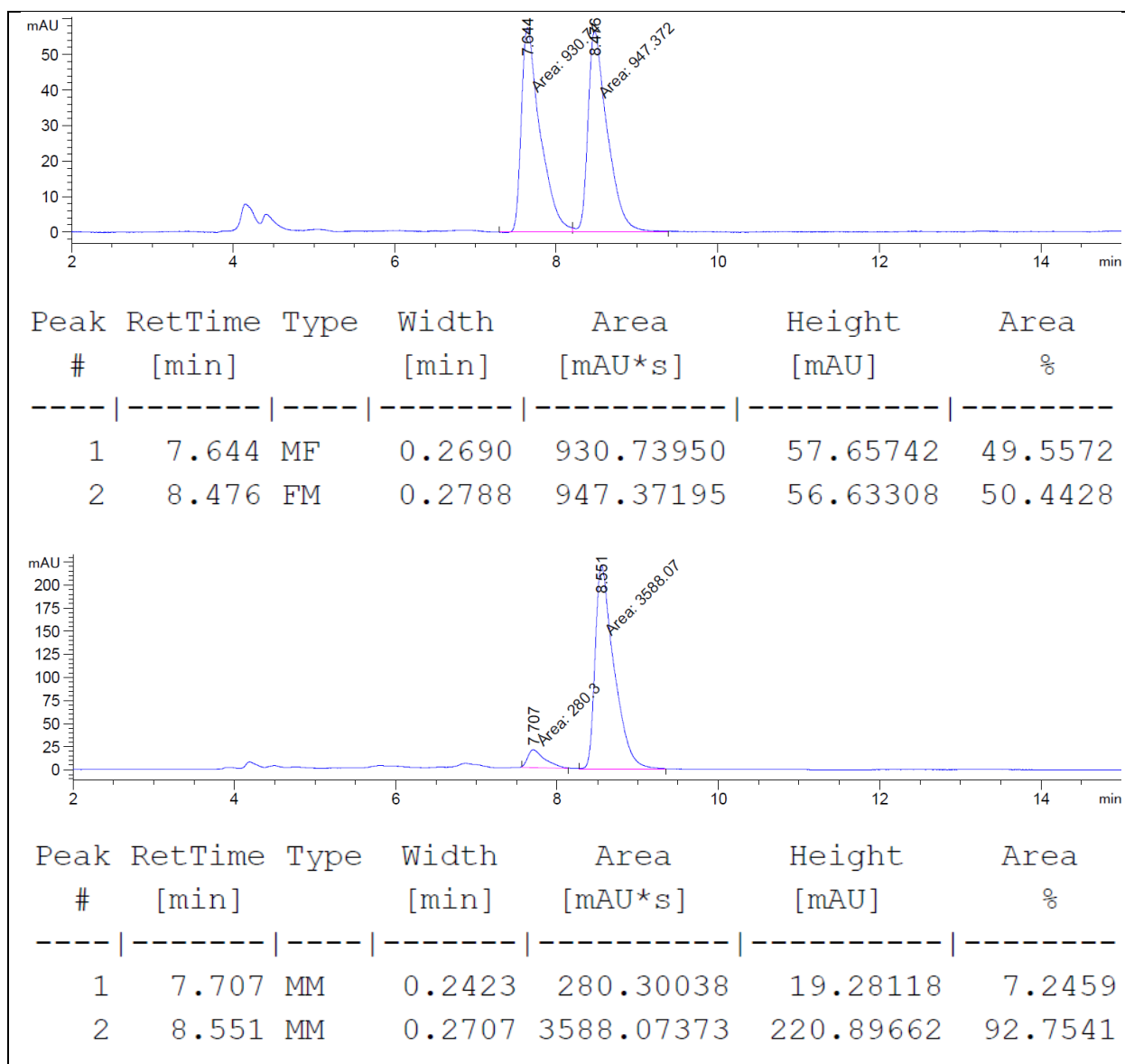


(S)-4,4,5,5-Tetramethyl-2-(1-(oxetan-3-yl)-5-phenylpentyl)-1,3,2-dioxaborolane ((-) 4h)

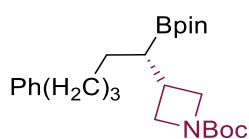


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2y** (13 μ L, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **(-) 4h** as a colorless oil (19 mg, 58%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.34 – 7.15 (m, 5H), 4.76 (ddd, *J* = 10.9, 7.9, 5.9 Hz, 2H), 4.54 – 4.35 (m, 2H), 3.06 (q, *J* = 8.0 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.63 (h, *J* = 6.9 Hz, 2H), 1.41 – 1.20 (m, 17H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 142.72, 128.53, 128.34, 125.71, 83.28, 78.91, 77.73, 37.19, 35.89, 31.77, 29.00, 28.82, 24.87, 24.77. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 33.49. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + H]⁺ Calcd for C₂₀H₃₂BO₃⁺ 331.2439; Found 331.2438. [α]_D²⁰ = -10.8 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (85%) was determined via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 99:1 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 8.5 min and *t*_{minor} = 7.7 min.

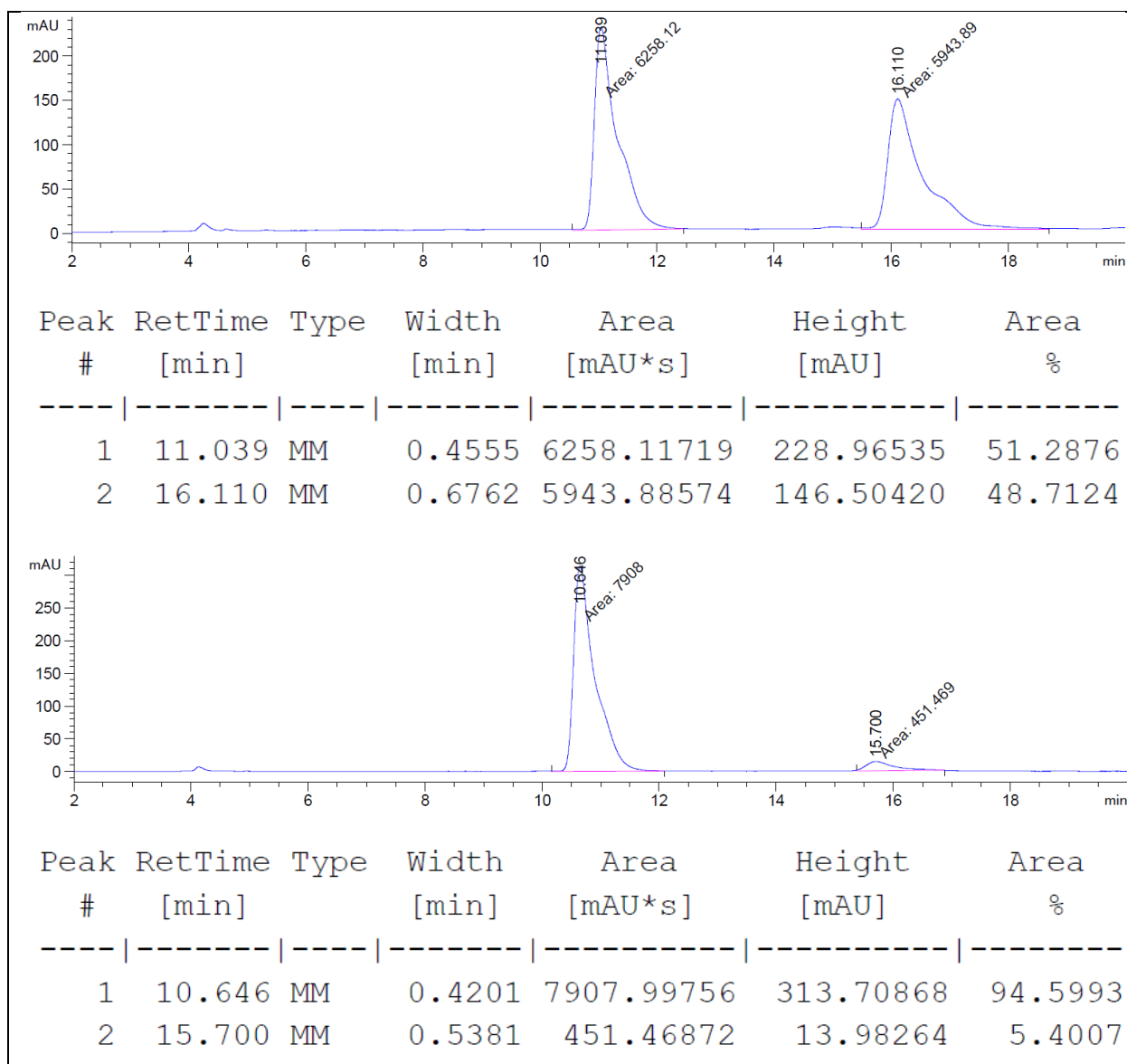


tert-Butyl (S)-3-(5-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyl)azetidine-1-carboxylate ((-) 4i)

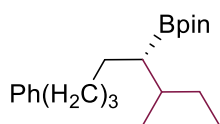


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2z** (28 μ L, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 15:1 hexane:EtOAc) afforded the desired product **(-) 4i** as a colorless oil (22 mg, 51%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.30 – 7.15 (m, 5H), 3.97 (q, *J* = 8.4 Hz, 2H), 3.60 (t, *J* = 7.3 Hz, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.58 – 2.48 (m, 1H), 1.63 (q, *J* = 7.2, 6.6 Hz, 2H), 1.45 (d, *J* = 2.1 Hz, 9H), 1.36 – 1.19 (m, 17H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 156.49, 142.72, 128.53, 128.34, 125.71, 83.33, 79.10, 55.33, 54.30, 35.89, 31.76, 30.70, 29.04, 28.78, 28.57, 24.91, 24.77. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.28. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₅H₄₀BNNaO₄⁺ 452.2943; Found 452.2948. [α]_D²⁰ = -4.0 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (89%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® IB column, with hexane:isopropanol = 93:7 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: $t_{\text{major}} = 10.6$ min and $t_{\text{minor}} = 15.7$ min.



4,4,5,5-Tetramethyl-2-((4S)-3-methyl-8-phenyloctan-4-yl)-1,3,2-dioxaborolane (**4j**)

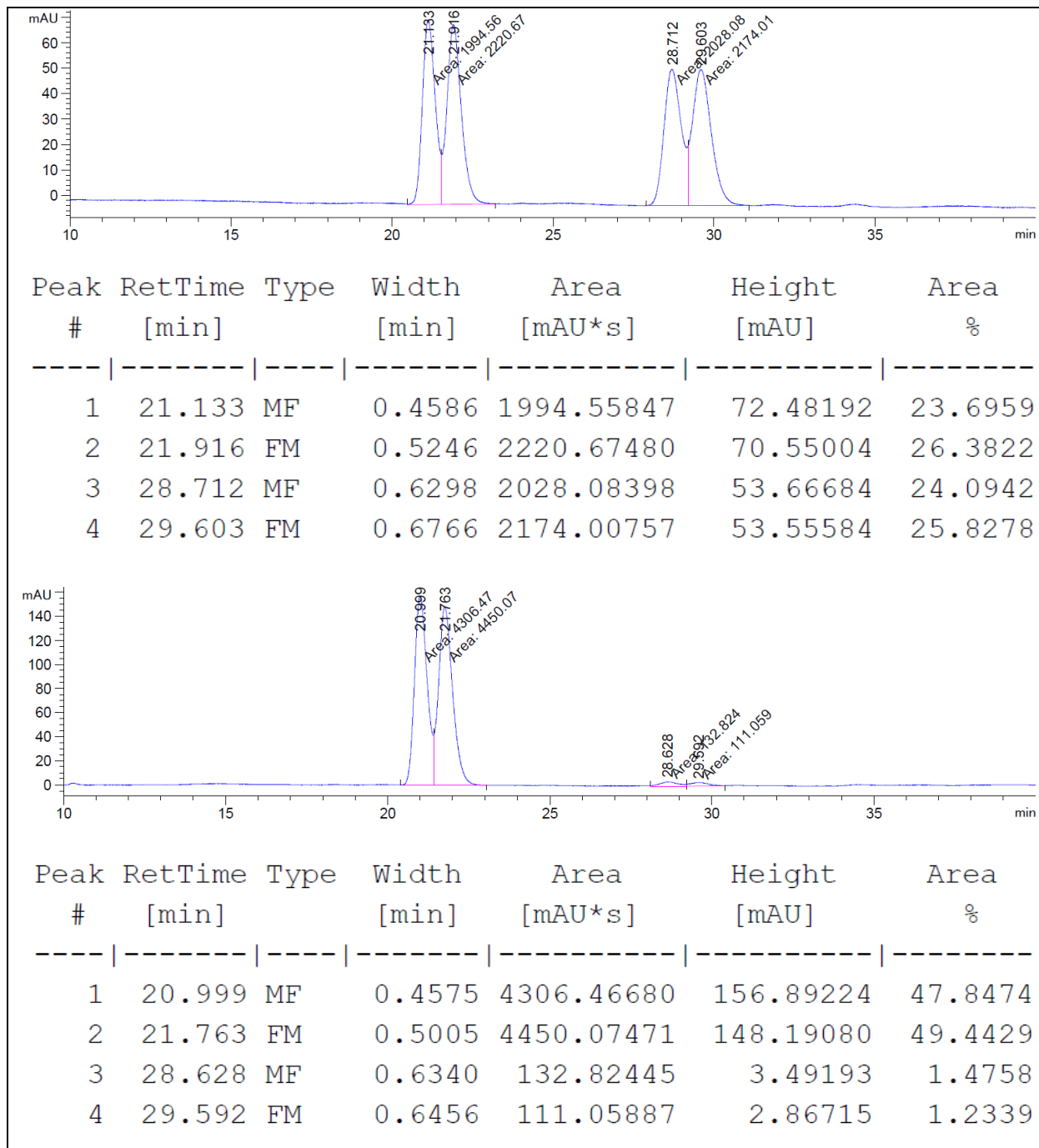


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2a'** (18 μ L, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 100:1 hexane:EtOAc) afforded the desired product **4j** as an inseparable mixture of

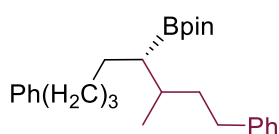
diastereomers (dr = 1:1.04) and a colorless oil (23 mg, 70%). The diastereomeric ratio was determined by chiral HPLC. **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.31 – 7.20 (m, 2H), 7.22 – 7.11 (m, 3H), 2.60 (t, $J = 7.7$ Hz, 2H), 1.71 – 1.55 (m, 2H), 1.54 – 1.28 (m, 5H), 1.31 – 1.16 (m, 14H), 1.19 – 1.02 (m, 1H), 1.01 – 0.82 (m, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 143.05, 128.57, 128.31, 125.62, 82.89, 82.87, 36.65, 36.38, 36.07, 31.94, 31.91, 29.56, 29.46, 29.11, 28.74, 28.06, 25.08, 24.94, 24.87, 18.42, 18.23, 12.23, 11.85. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ

33.67. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + Na]^+$ Calcd for $C_{21}H_{35}BNaO_2^+$ 353.2622; Found 353.2628.

HPLC: The enantiomeric excesses (94% and 95%) were determined after oxidation (**GP2**) 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. Elution time: t_{major} = 21.0 min, 21.7 min and t_{minor} = 28.6 min, 29.6 min.



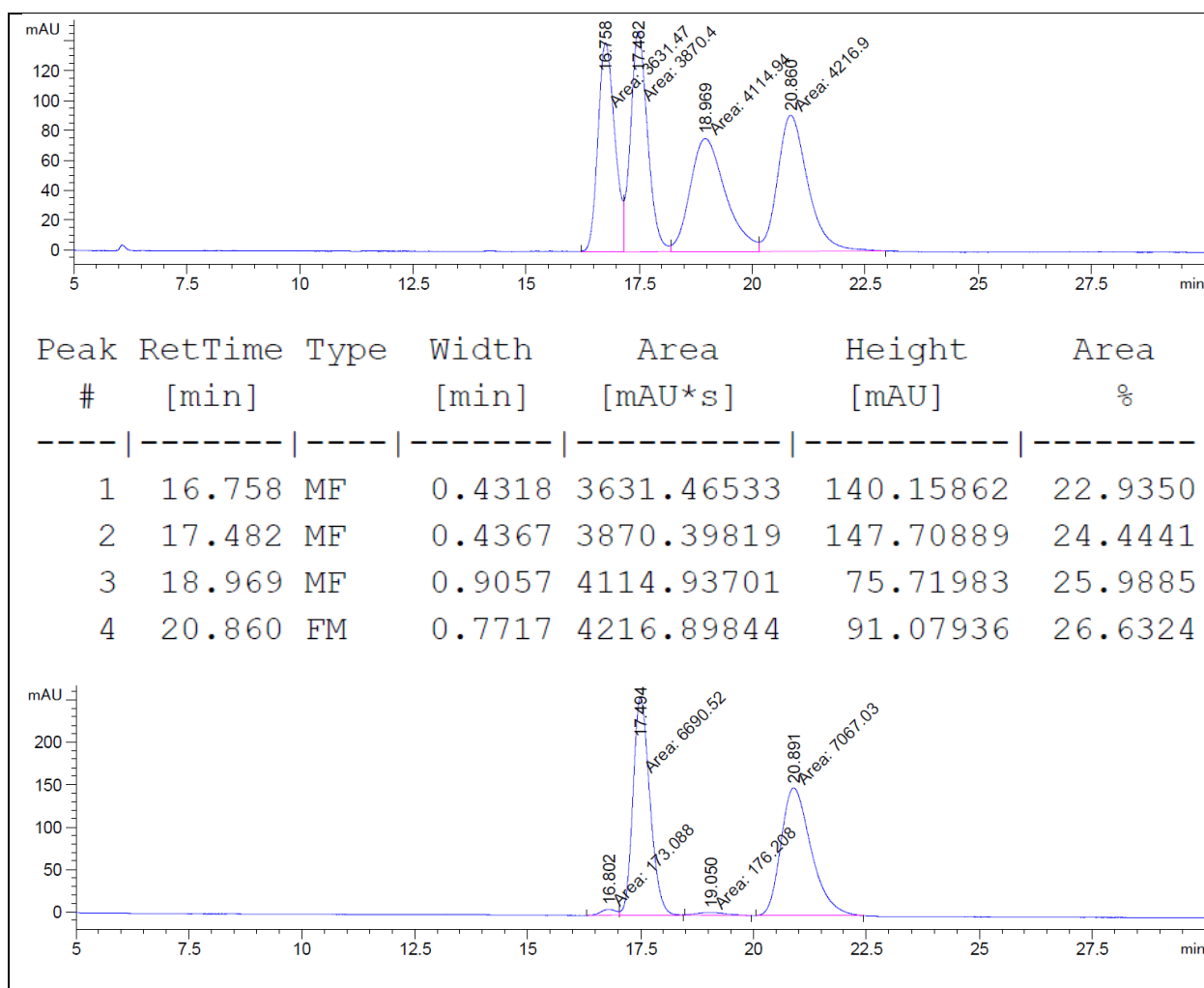
4,4,5,5-Tetramethyl-2-((4S)-3-methyl-1,8-diphenyloctan-4-yl)-1,3,2-dioxaborolane (**4k**)



Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2b'** (39 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2 ,

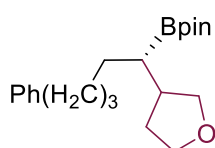
100:1 hexane:EtOAc) afforded the desired product **4k** as an inseparable mixture of diastereomers (dr = 1:1.05) and a colorless oil (28 mg, 69%). The diastereomeric ratio was determined by chiral HPLC. **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.41 – 7.30 (m, 4H), 7.30 – 7.20 (m, 6H), 2.84 – 2.54 (m, 4H), 1.87 – 1.63 (m, 4H), 1.63 – 1.47 (m, 2H), 1.51 – 1.37 (m, 2H), 1.36 – 1.24 (m, 13H), 1.16 – 0.98 (m, 4H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 143.37, 143.32, 143.00, 128.57, 128.53, 128.49, 128.39, 128.34, 128.31, 125.63, 125.59, 82.96, 82.94, 38.64, 38.10, 36.05, 35.99, 34.61, 34.35, 34.11, 33.80, 31.91, 31.88, 29.50, 29.45, 29.33, 28.01, 25.11, 25.05, 24.94, 18.85, 18.69. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.61. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + Na]⁺ Calcd for C₂₇H₃₉BNaO₂⁺ 429.2935; Found 429.2947.

HPLC: The enantiomeric excesses (94% and 94%) were determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 17.5 min, 20.9 min and *t*_{minor} = 16.8 min, 19.0 min.



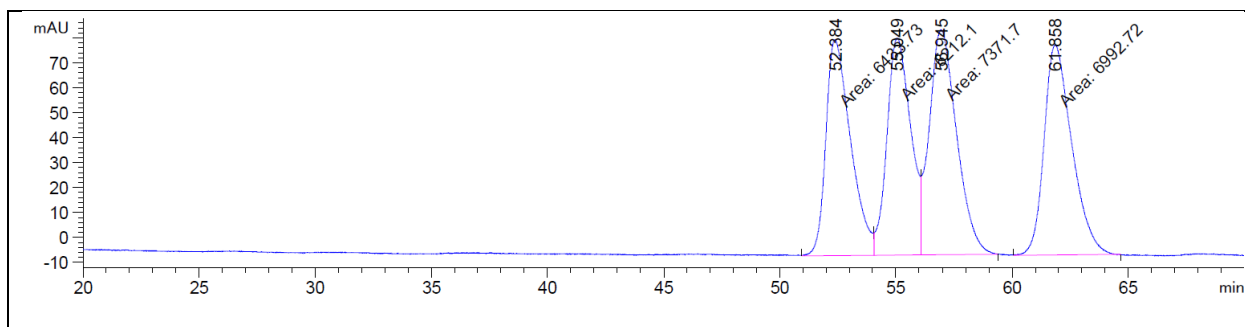
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.802	MF	0.3957	173.08803	7.29061	1.2270
2	17.494	FM	0.4333	6690.52002	257.32394	47.4275
3	19.050	MM	0.7896	176.20824	3.71941	1.2491
4	20.891	MM	0.7801	7067.03076	150.98814	50.0965

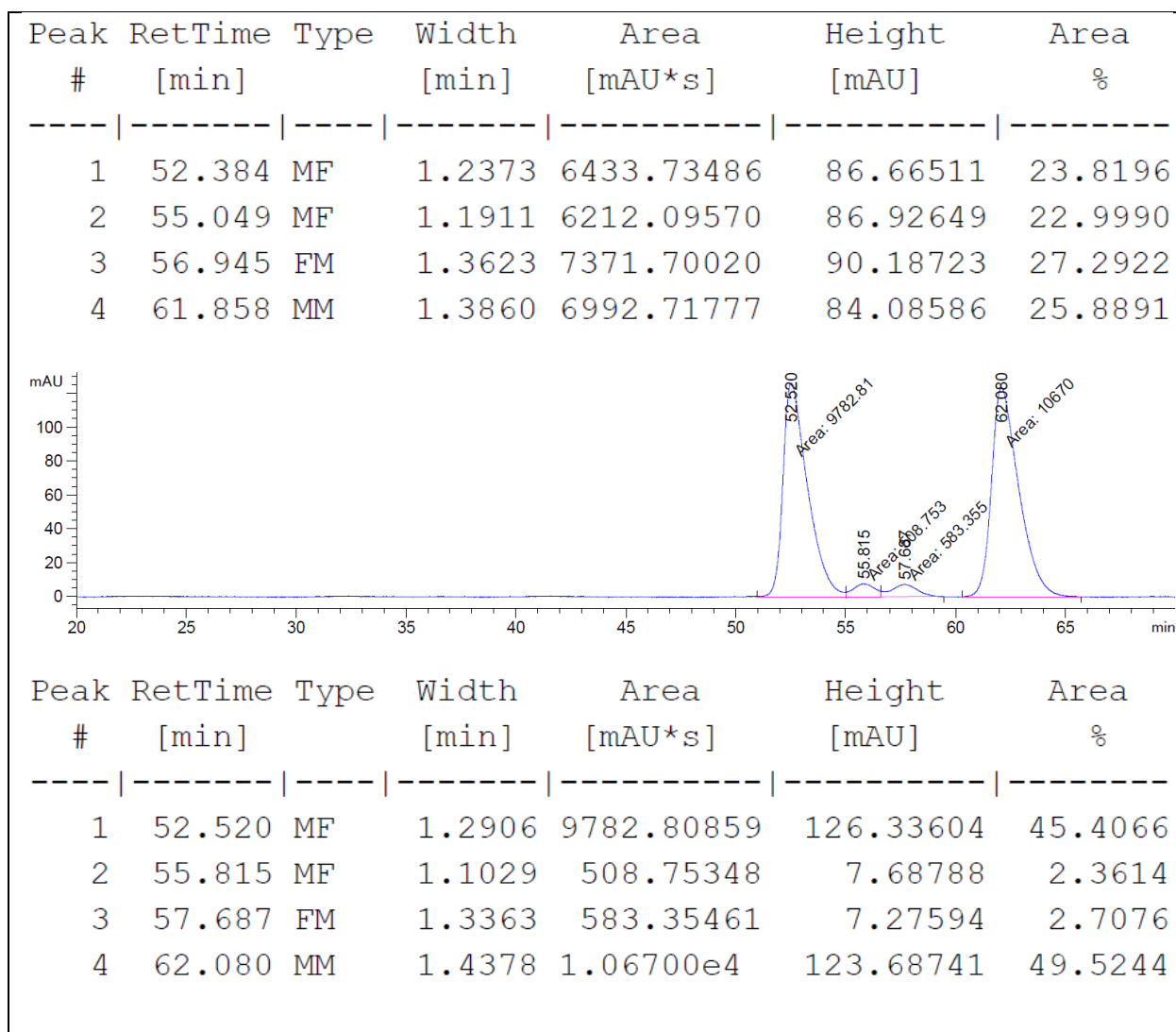
4,4,5,5-Tetramethyl-2-((1S)-5-phenyl-1-(tetrahydrofuran-3-yl)pentyl)-1,3,2-dioxaborolane (4I)



Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2c'** (30 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **4I** as an inseparable mixture of diastereomers (dr = 1:1.1) and a colorless oil (26 mg, 75%). The diastereomeric ratio was determined by chiral HPLC. **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.39 – 7.30 (m, 2H), 7.28 – 7.20 (m, 3H), 4.01 (dt, *J* = 23.1, 7.8 Hz, 1H), 3.92 (tdd, *J* = 8.4, 5.8, 4.3 Hz, 1H), 3.80 (tt, *J* = 8.4, 6.7 Hz, 1H), 3.41 (dt, *J* = 9.6, 8.3 Hz, 1H), 2.68 (td, *J* = 7.6, 3.8 Hz, 2H), 2.31 (tdt, *J* = 14.9, 10.0, 5.0 Hz, 1H), 2.10 (ddtd, *J* = 31.2, 11.8, 7.4, 4.0 Hz, 1H), 1.80 – 1.51 (m, 4H), 1.52 – 1.34 (m, 3H), 1.32 – 1.24 (m, 12H), 1.12 – 0.95 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 142.80, 142.76, 128.54, 128.33, 125.68, 83.22, 83.20, 73.79, 72.86, 68.22, 68.16, 41.35, 41.13, 35.95, 35.93, 32.54, 31.95, 31.81, 31.74, 30.79, 30.65, 29.83, 29.16, 29.01, 24.93, 24.90, 24.85. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 32.74. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + H]⁺ Calcd for C₂₁H₃₄BO₃⁺ 345.2596; Found 345.2603.

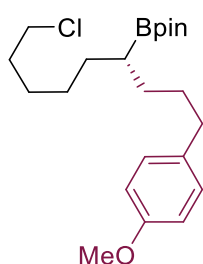
HPLC: The enantiomeric excesses (90% and 90%) were determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] IA column, with hexane:isopropanol = 98:2 at a flow rate 0.7 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 52.5 min, 62.1 min and *t*_{minor} = 55.8 min, 57.7 min.





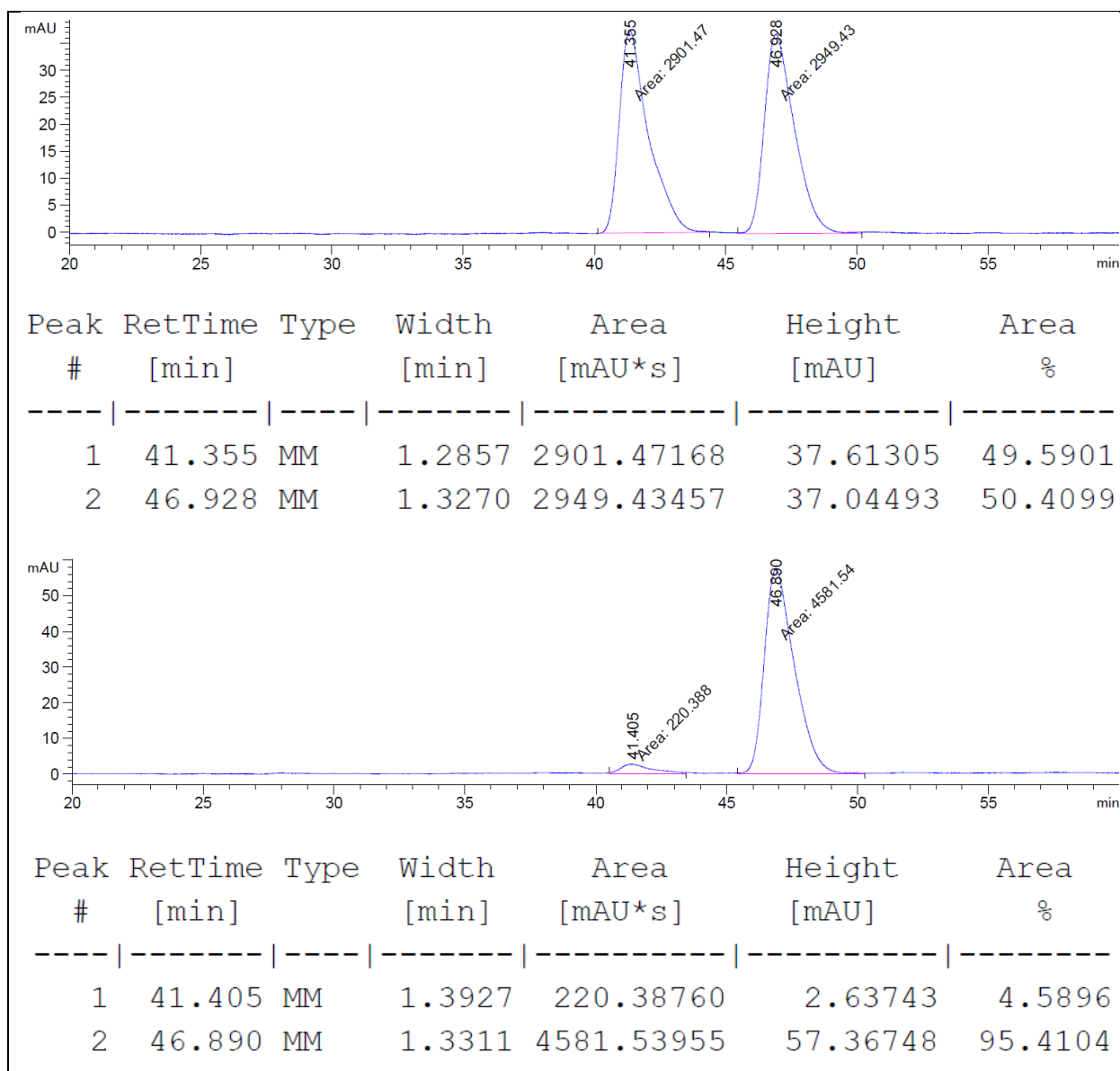
(S)-2-(9-Chloro-1-(4-methoxyphenyl)nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

(+) 5a

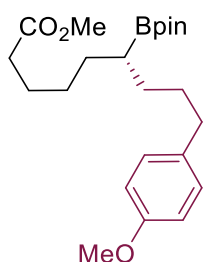


Prepared according to **GP4** with **1c** (37 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 5a** as a colorless oil (24 mg, 61%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.13 – 6.99 (m, 2H), 6.89 – 6.74 (m, 2H), 3.78 (d, *J* = 2.1 Hz, 3H), 3.51 (td, *J* = 6.9, 2.0 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.75 (h, *J* = 7.2, 6.2 Hz, 2H), 1.58 (h, *J* = 7.2, 6.8 Hz, 2H), 1.53 – 1.23 (m, 20H), 0.98 (t, *J* = 7.3 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 157.70, 135.08, 129.34, 113.76, 83.02, 55.38, 45.23, 35.40, 32.68, 31.44, 31.26, 31.12, 28.58, 27.25, 24.95. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 33.73. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₂H₃₆BClNaO₃⁺ 417.2338; Found 417.2340. [α]_D²⁰ = +1.7 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{\text{major}} = 46.9$ min and $t_{\text{minor}} = 41.4$ min.



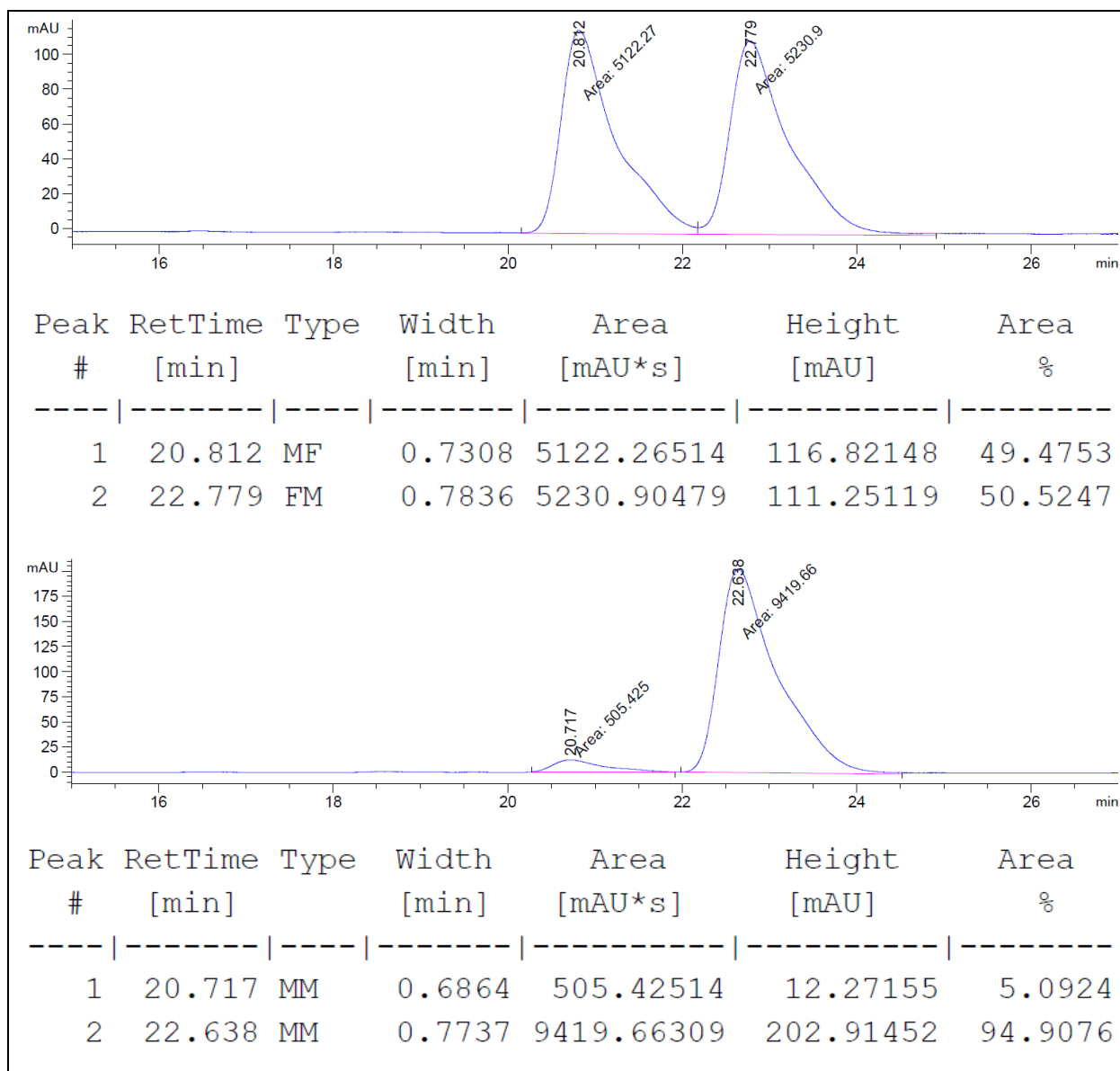
Methyl (S)-9-(4-methoxyphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate ((+) **5b)**



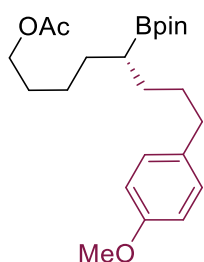
Prepared according to **GP4** with **1d** (38 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 30:1 hexane:EtOAc) afforded the desired product (+) **5b** as a colorless oil (23 mg, 57%). ¹H NMR (400 MHz, Chloroform-d): ¹H NMR (400 MHz, Chloroform-d) δ 7.07 (d, $J = 7.5$ Hz, 2H), 6.80 (d, $J = 7.4$ Hz, 2H), 3.78 (s, 3H), 3.65 (s, 3H), 2.53 (t, $J = 7.7$ Hz, 2H), 2.32 – 2.24 (m, 2H), 1.59 (td, $J = 14.7, 14.2, 7.0$ Hz, 4H), 1.47 – 1.35 (m, 3H), 1.34 – 1.26 (m, 3H), 1.23 (s, 6H), 1.22 (s, 6H), 0.97 (dd, $J = 10.0, 4.8$ Hz, 1H). ¹³C NMR (101 MHz, Chloroform-d) δ 174.38, 157.69, 135.08, 129.33, 113.76, 83.01, 55.37, 51.53, 35.39,

34.22, 31.43, 31.10, 31.07, 28.90, 25.38, 24.94. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 36.32. **HRMS (APCI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₂₃H₃₇BNaO₅⁺ 427.2626; Found 427.2633. $[\alpha]_D^{20}$ = +3.5 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 92:8 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 22.6 min and *t*_{minor} = 20.7 min.



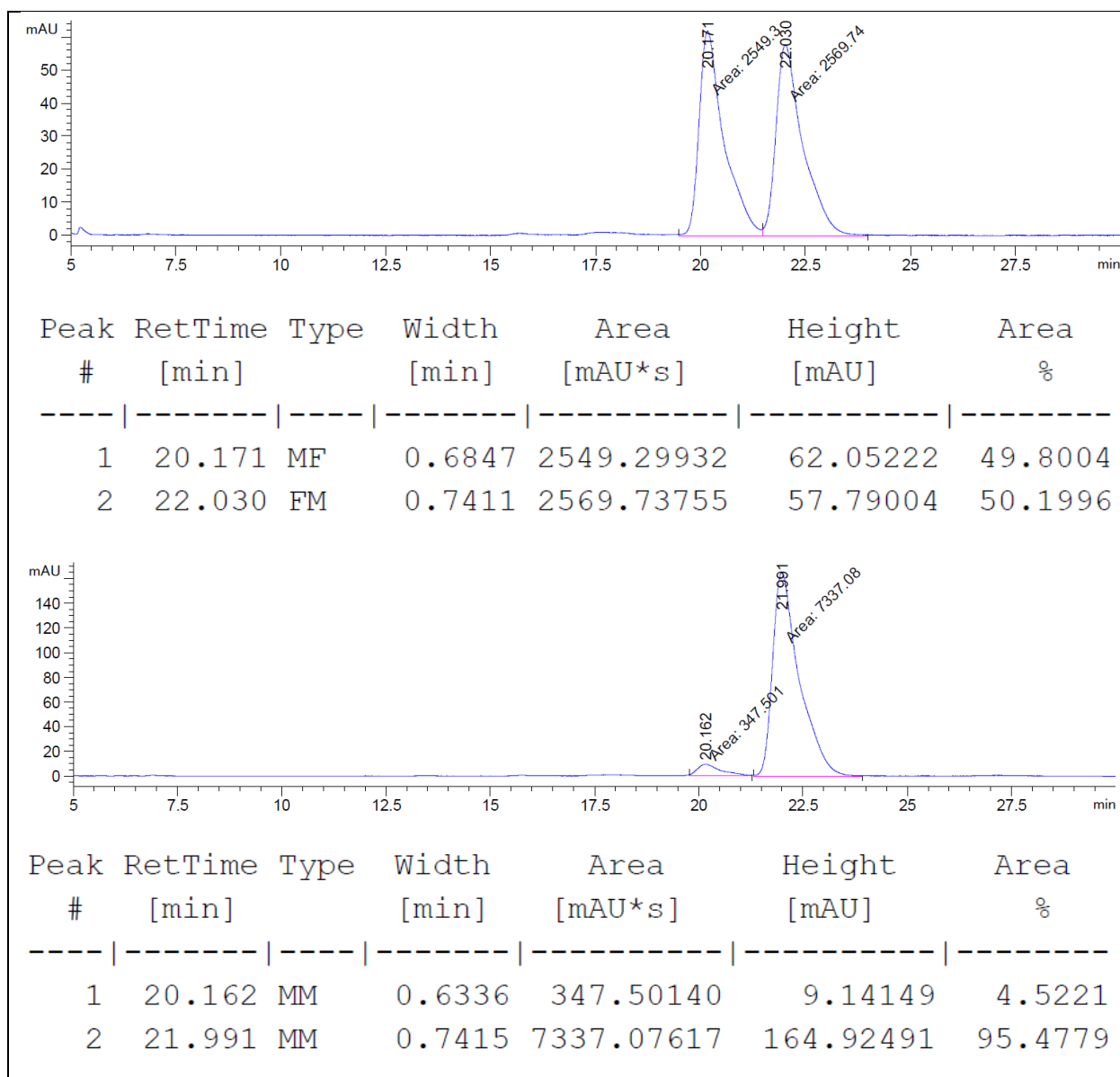
(*R*)-8-(4-Methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl acetate ((+) **5c)**



Prepared according to **GP4** with **1e** (38 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 20:1 hexane:EtOAc) afforded the desired product (**+**) **5c** as a colorless oil (31 mg, 77%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.10 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.80 (s, 3H), 2.56 (t, *J* = 7.4 Hz, 2H),

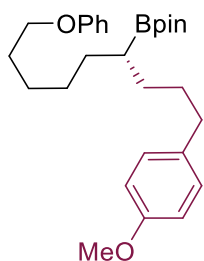
2.05 (s, 3H), 1.60 (p, $J = 7.5$ Hz, 4H), 1.48 – 1.25 (m, 18H), 1.06 – 0.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 171.30, 157.68, 135.02, 129.30, 113.74, 83.01, 64.71, 55.34, 35.36, 31.40, 31.08, 28.96, 25.67, 24.91, 21.10. ^{11}B NMR (128 MHz, Chloroform- d) δ 33.78. HRMS (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{37}\text{BNaO}_5^+$ 427.2626; Found 427.2627. $[\alpha]_{\text{D}}^{20} = +2.8$ ($c = 1.00$ in CHCl_3).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 92:8 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{\text{major}} = 21.9$ min and $t_{\text{minor}} = 20.2$ min.



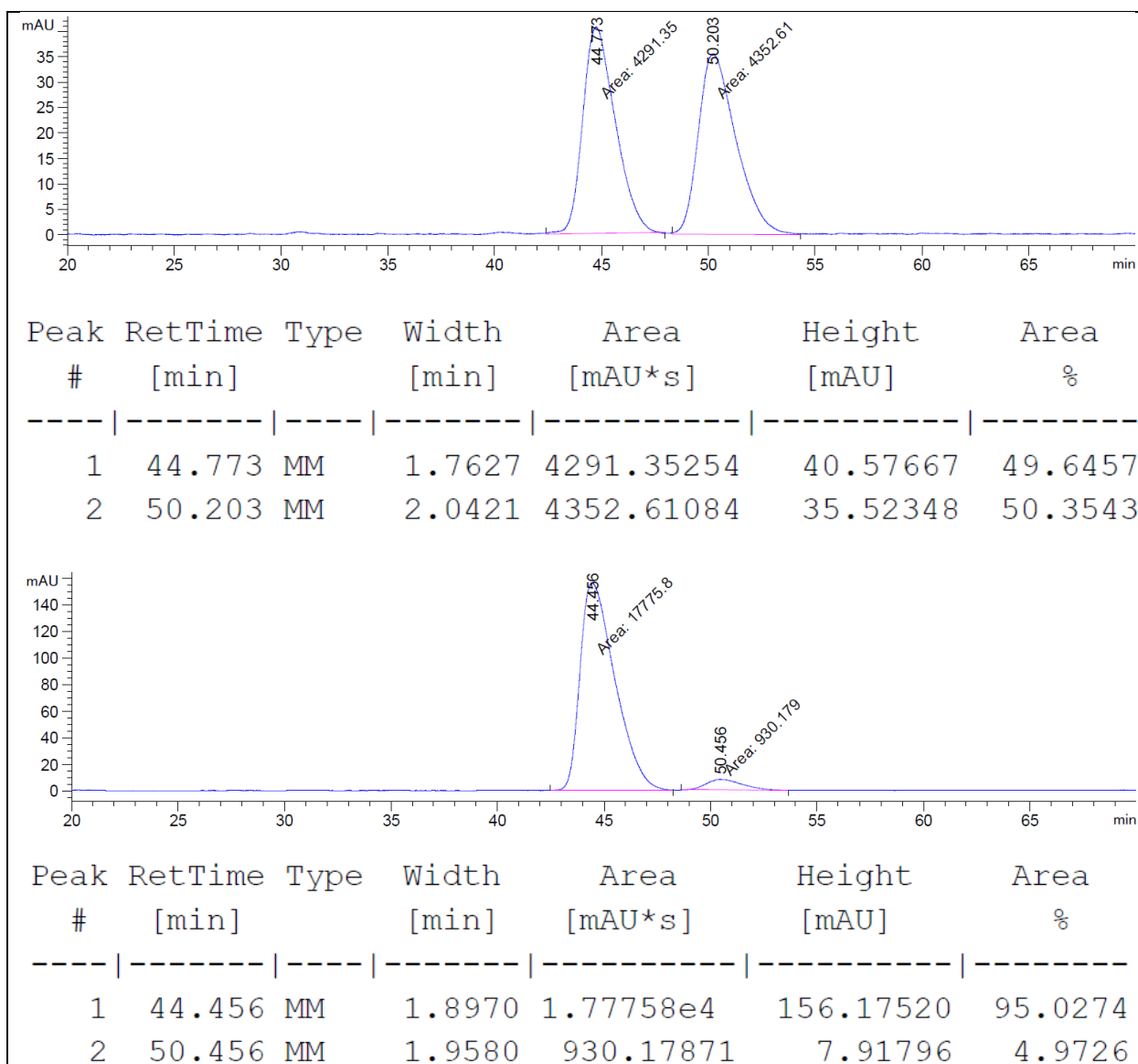
(S)-2-(1-(4-Methoxyphenyl)-9-phenoxy-nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
(-) 5d)

Prepared according to **GP4** with **1f** (45 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2 , 30:1 hexane:EtOAc) afforded the desired product

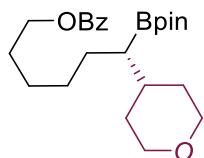


(-) **5d** as a colorless oil (31 mg, 69%). ^1H NMR (400 MHz, Chloroform-*d*): δ 7.29 (t, J = 7.1 Hz, 3H), 7.11 (d, J = 7.6 Hz, 2H), 6.95 (t, J = 7.3 Hz, 2H), 6.88 (dd, J = 29.9, 7.8 Hz, 4H), 3.96 (t, J = 6.5 Hz, 2H), 3.81 (d, J = 1.9 Hz, 3H), 2.57 (t, J = 7.7 Hz, 2H), 1.79 (p, J = 6.3 Hz, 2H), 1.60 (dd, J = 15.0, 7.5 Hz, 3H), 1.46 – 1.25 (m, 17H), 1.07 – 0.99 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.26, 157.69, 135.14, 129.51, 129.35, 120.55, 114.62, 113.77, 83.00, 67.96, 55.39, 35.42, 31.48, 31.42, 31.19, 29.36, 29.13, 26.43, 24.96, 24.94. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.50. HRMS (APPI/LTQ-Orbitrap) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{28}\text{H}_{41}\text{BO}_4^+$ 452.3092; Found 452.3081. $[\alpha]_{\text{D}}^{20}$ = -0.7 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: t_{major} = 44.4 min and t_{minor} = 55.4 min.

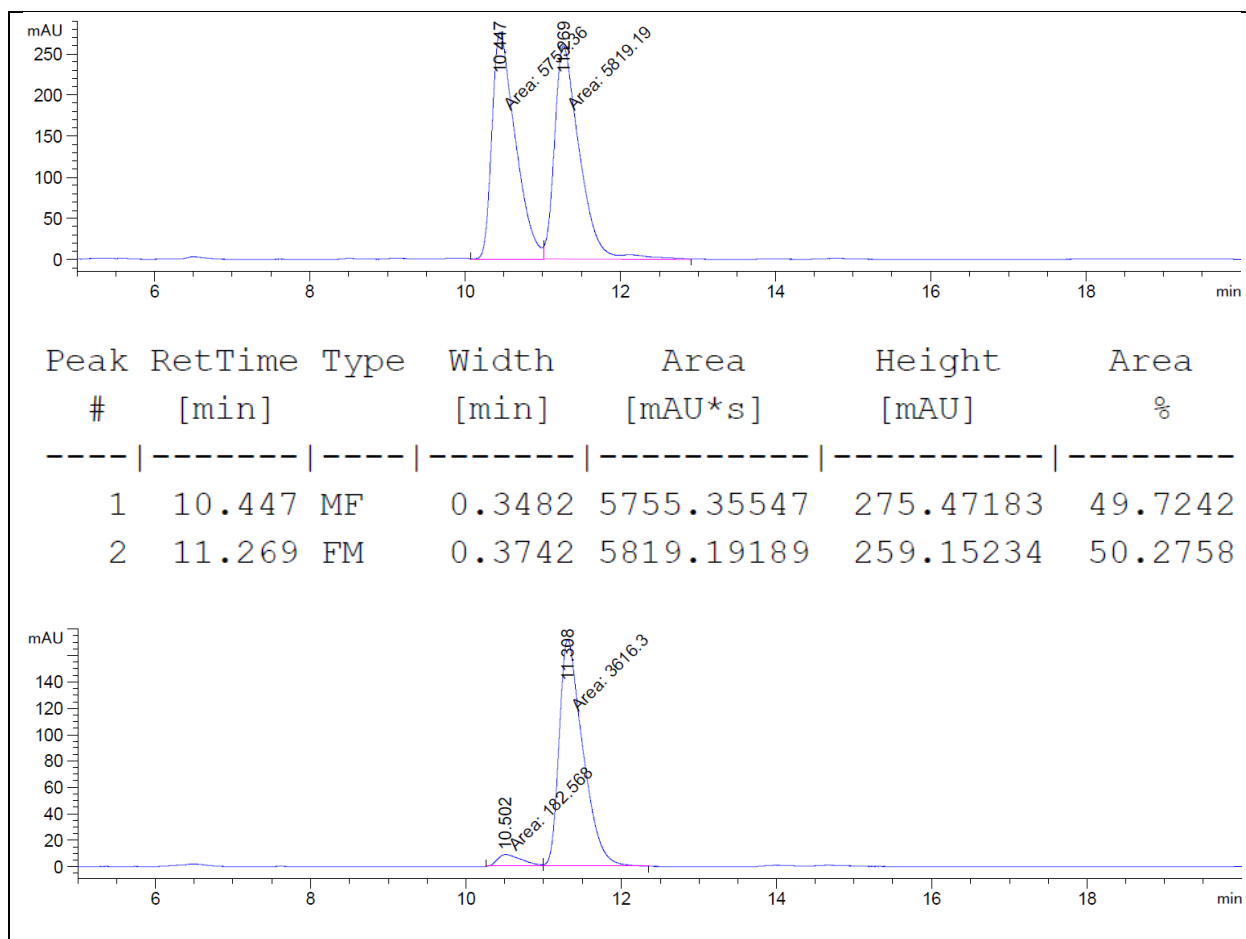


(S)-6-(Tetrahydro-2H-pyran-4-yl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl benzoate ((-) 5e)



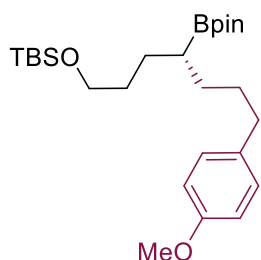
Prepared according to **GP4** with **1g** (33 mg, 0.10 mmol, 1.00 equiv.), **2v** (18 μ L, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO₂, 10:1 hexane:EtOAc) afforded the desired product **(-) 5e** as a colorless oil (33 mg, 79%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 8.03 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 4.30 (t, *J* = 6.4 Hz, 2H), 3.93 (d, *J* = 11.1 Hz, 2H), 3.34 (t, *J* = 11.6 Hz, 2H), 1.75 (p, *J* = 6.7 Hz, 2H), 1.64 – 1.23 (m, 23H), 0.94 – 0.84 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) 166.78, 132.91, 130.64, 129.66, 128.44, 83.17, 68.65, 68.54, 65.16, 37.05, 32.92, 32.47, 29.21, 28.79, 28.38, 26.48, 25.11, 25.00. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.35. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₂₄H₃₈BO₅⁺ 417.2807; Found 417.2804. [α]_D²⁰ = -0.5 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 11.3 min and *t*_{minor} = 10.5 min.



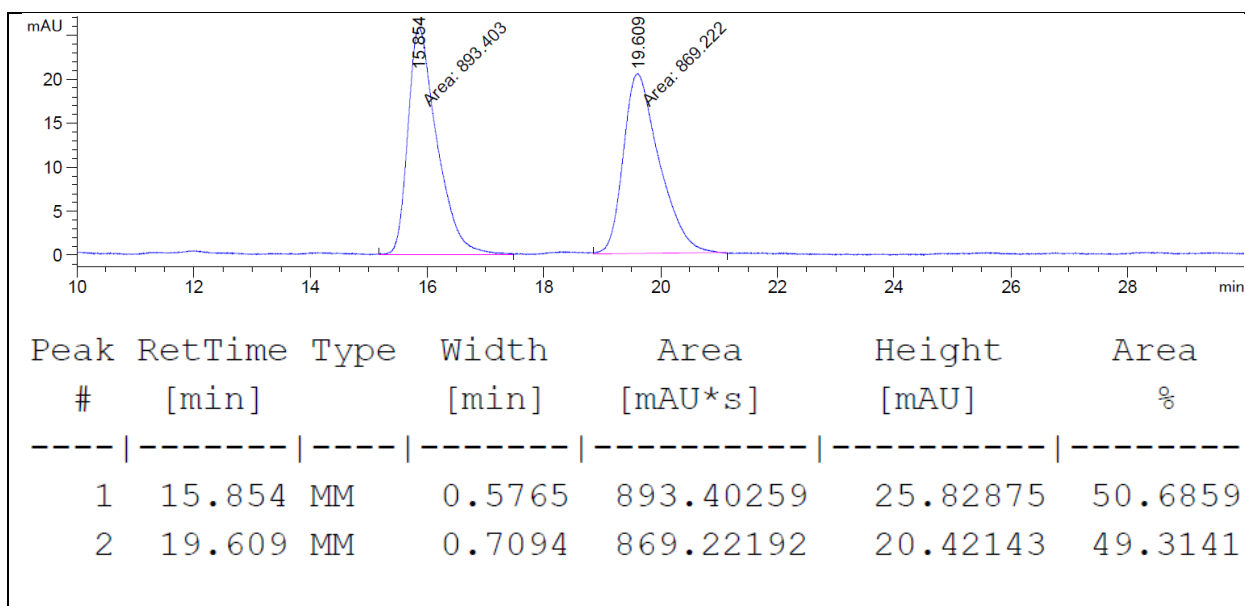
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.502	MF	0.3544	182.56752	8.58649	4.8058
2	11.308	FM	0.3516	3616.30103	171.42809	95.1942

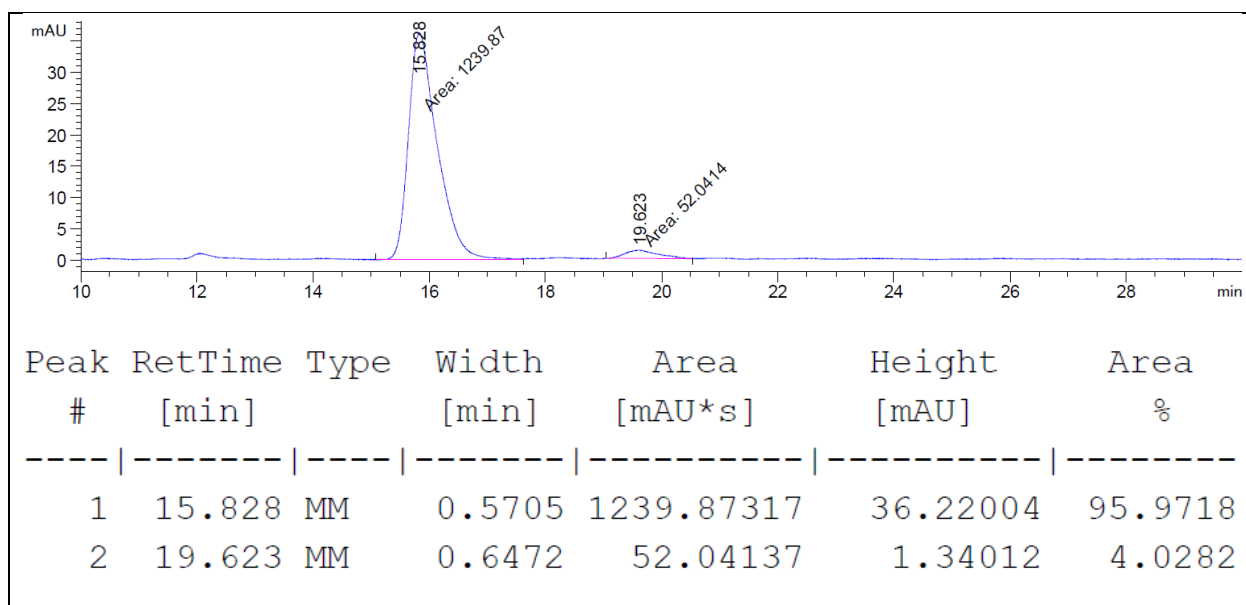
(*R*)-tert-Butyl((7-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)oxy)dimethylsilane ((+) **5f)**



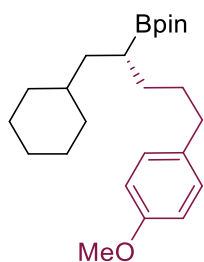
Prepared according to **GP4** with **1h** (47 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product (**+**) **5f** as a colorless oil (26 mg, 56%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.07 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 3.57 (t, *J* = 6.5 Hz, 2H), 2.53 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.36 (m, 8H), 1.23 (s, 12H), 1.05 – 0.96 (m, 1H), 0.89 (s, 9H), 0.03 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 157.69, 135.14, 129.34, 113.76, 83.00, 63.72, 55.38, 35.42, 32.67, 31.45, 31.16, 27.56, 26.15, 24.96, 18.52, -5.07. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 33.63. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₆H₄₈BO₄Si⁺ 463.3409; Found 463.3408. [α]_D²⁰ = +1.2 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 15.8 min and *t*_{minor} = 19.6 min.



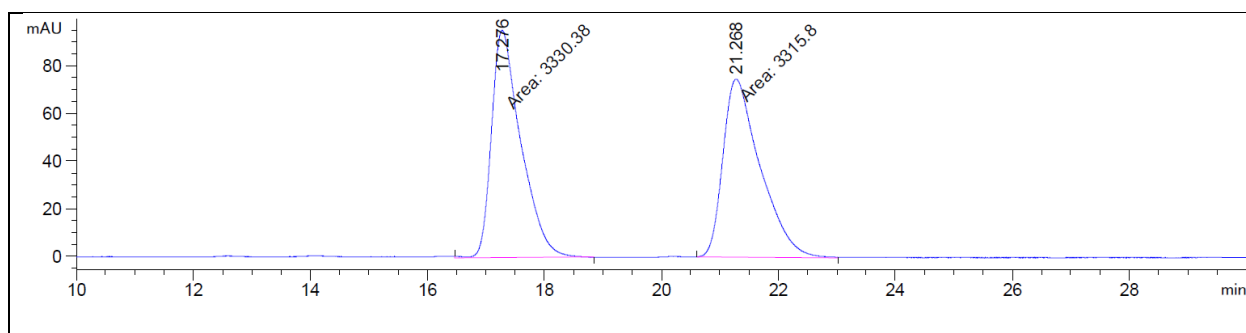


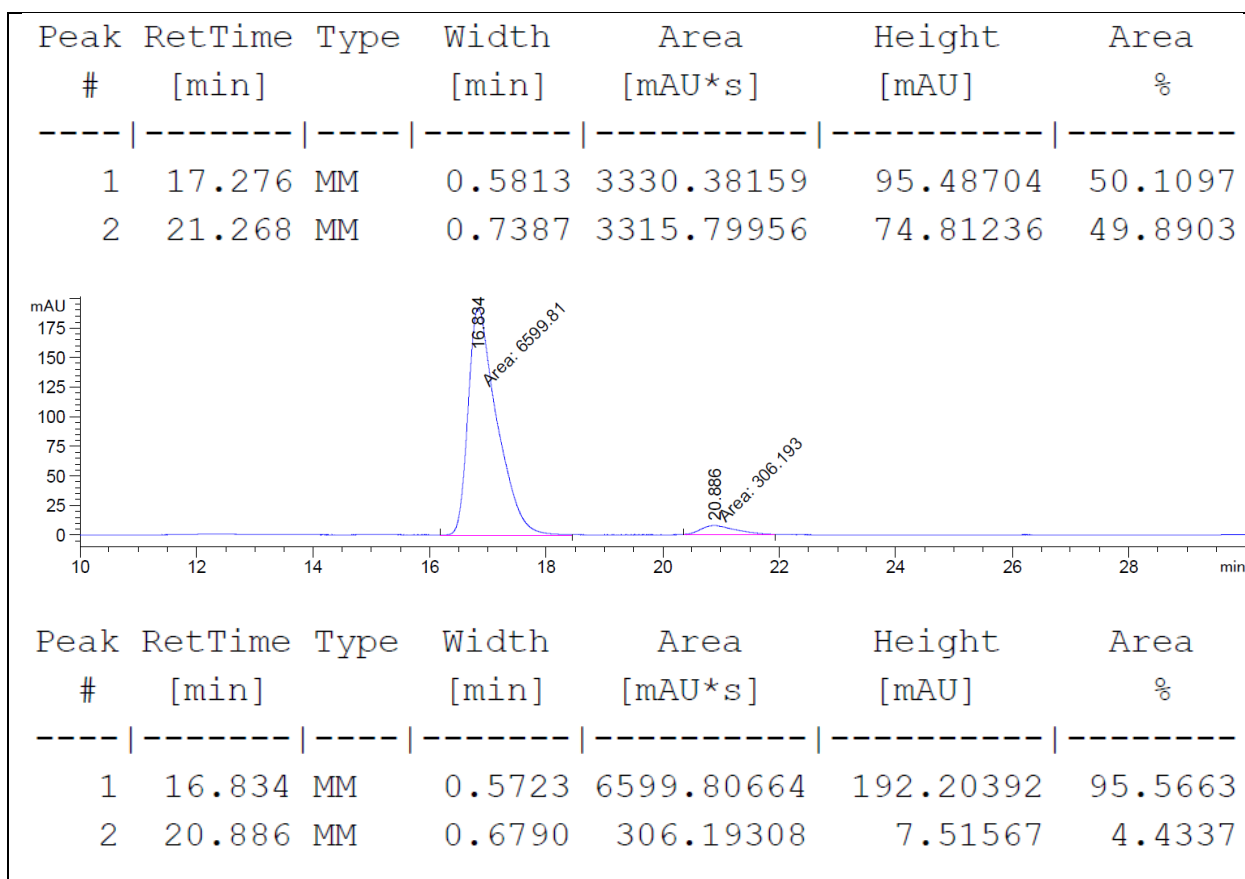
(R)-2-(1-Cyclohexyl-5-(4-methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (+) 5g



Prepared according to **GP4** with **1i** (36 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 5g** as a colorless oil (20 mg, 54%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.5 Hz, 2H), 3.78 (s, 3H), 2.53 (td, *J* = 7.4, 3.1 Hz, 2H), 1.72 – 1.19 (m, 29H), 0.88 – 0.78 (m, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 157.69, 135.17, 129.36, 113.76, 82.93, 55.39, 39.28, 37.24, 35.42, 33.96, 33.44, 31.54, 31.50, 26.87, 26.63, 26.59, 25.01, 24.89. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.31. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₄H₃₉BO₃⁺ 386.2987; Found 386.2999. [α]_D²⁰ = +1.2 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 16.8 min and *t*_{minor} = 20.9 min.



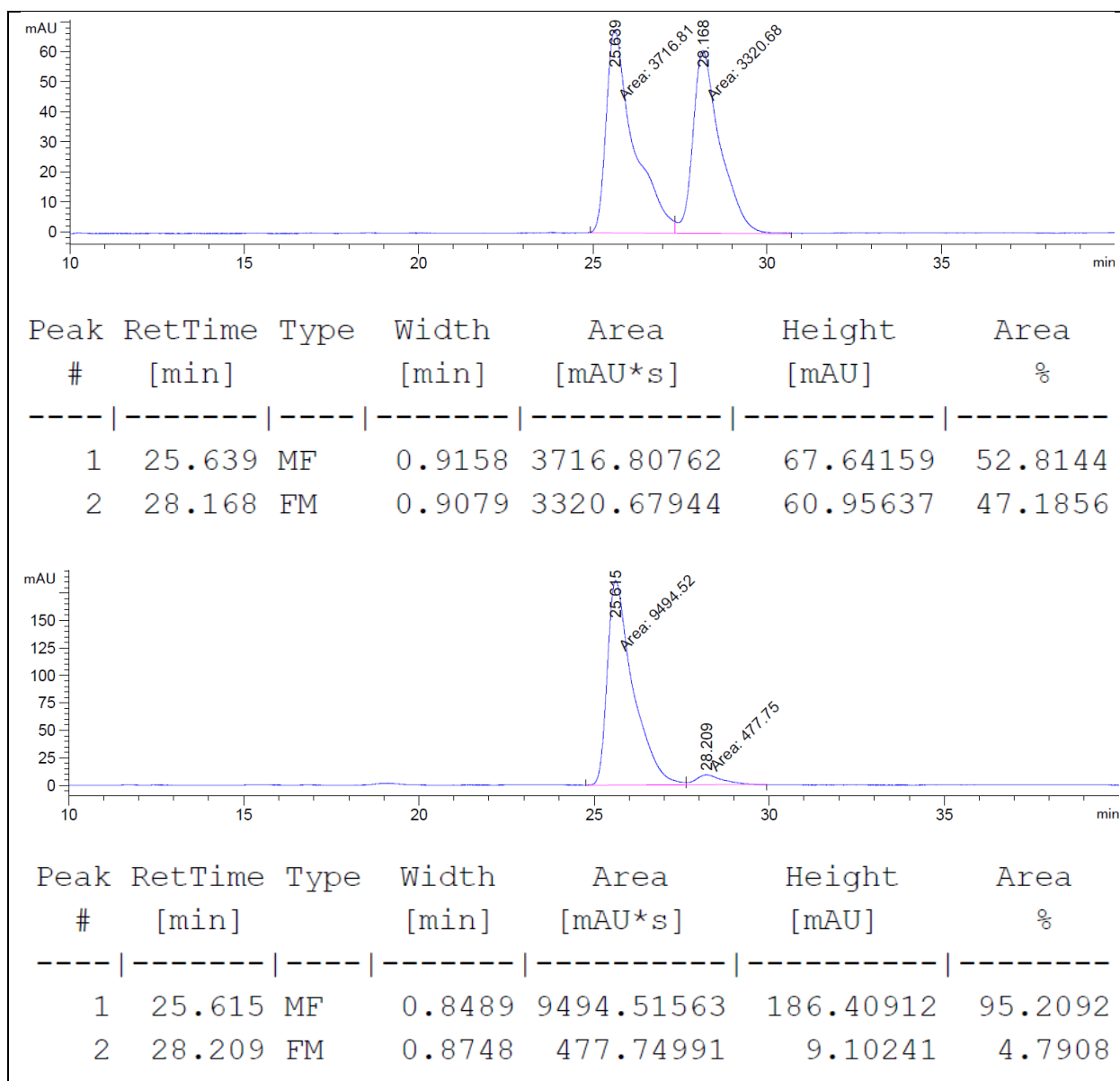


(S)-2-(5-(4-Methoxyphenyl)pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) **5h)**

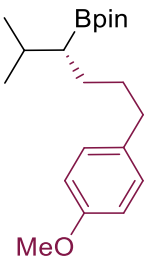


Prepared according to **GP4** with **1j** (51 μ L, 0.30 mmol, 1.50 equiv.), **2b** (56 mg, 0.20 mmol, 1.00 equiv.), DEMS (86 μ L, 0.50 mmol, 2.50 equiv.), KF (29 mg, 0.50 mmol, 2.5 equiv.) and DCE/DMF (1.0 mL). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 5h** as a colorless oil (41 mg, 68%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.19 – 7.07 (m, 2H), 6.94 – 6.79 (m, 2H), 3.81 (s, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.58 – 1.48 (m, 1H), 1.37 (dq, *J* = 9.3, 6.6 Hz, 1H), 1.26 (s, 12H), 1.07 (dd, *J* = 14.7, 7.6 Hz, 1H), 0.99 (d, *J* = 6.8 Hz, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 157.68, 135.20, 129.33, 113.75, 82.93, 55.36, 35.38, 33.03, 31.24, 24.90, 24.85, 15.63. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.31. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₁₈H₂₉BO₃⁺ 304.2204; Found 304.2209. $[\alpha]_D^{20}$ = +4.3 (*c* = 1.00 in CHCl₃).

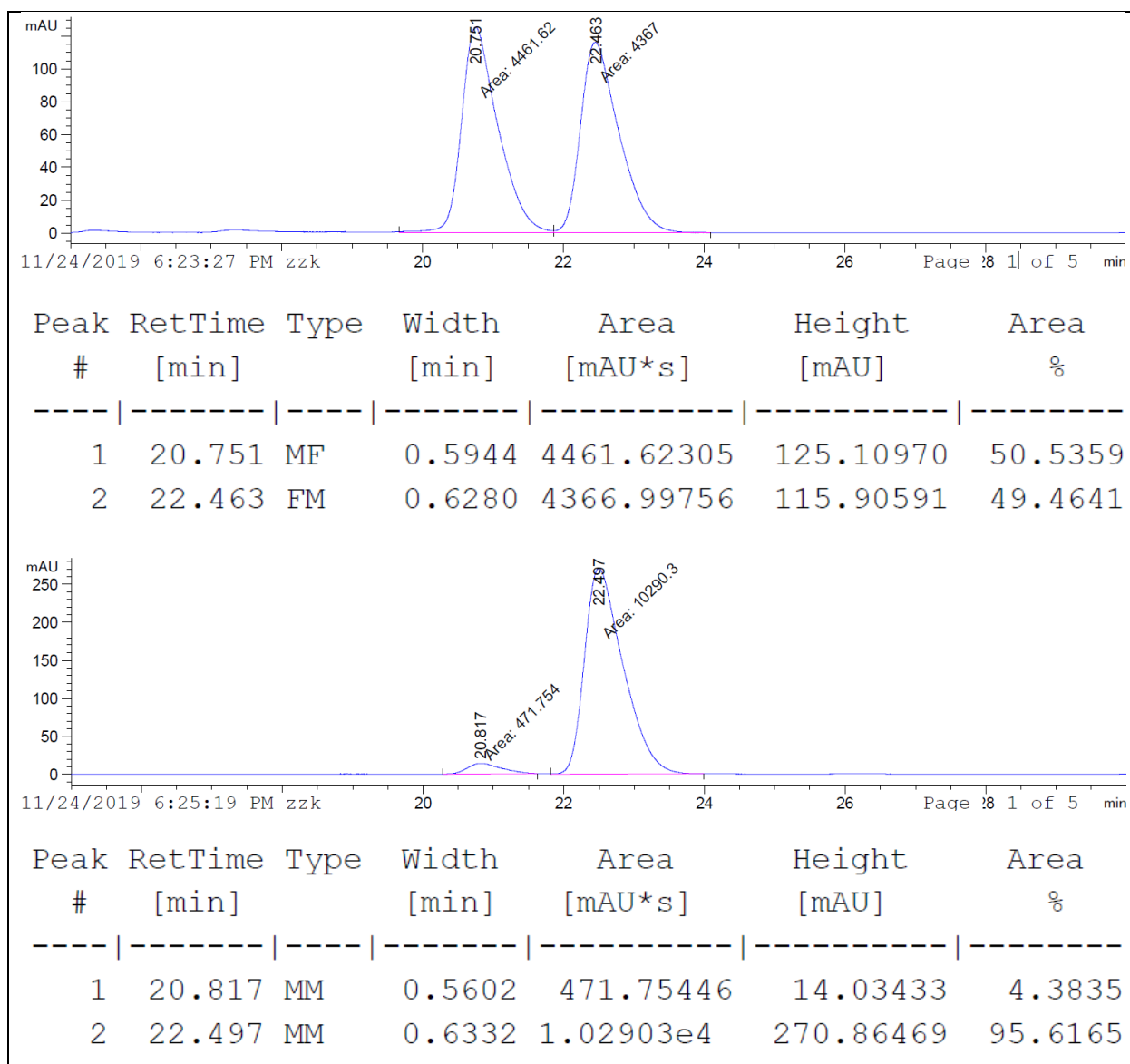
HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 25.6 min and *t*_{minor} = 28.2 min.



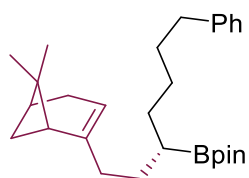
(R)-2-(6-(4-Methoxyphenyl)-2-methylhexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
(+ 5i)


 Prepared according to **GP4** with **1k** (62 μ L, 0.30 mmol, 1.50 equiv.), **2b** (56 mg, 0.20 mmol, 1.00 equiv.), DEMS (86 μ L, 0.50 mmol, 2.50 equiv.), KF (29 mg, 0.50 mmol, 2.5 equiv.) and DCE/DMF (1.0 mL). Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 5i** as a colorless oil (20 mg, 30%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.08 (d, *J* = 8.2 Hz, 2H), 6.91 – 6.73 (m, 2H), 3.78 (s, 3H), 2.55 (td, *J* = 7.9, 7.4, 4.6 Hz, 2H), 1.74 – 1.67 (m, 1H), 1.66 – 1.34 (m, 5H), 1.24 (s, 12H), 0.92 – 0.83 (m, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 157.67, 135.20, 129.36, 129.33, 113.75, 82.95, 55.38, 35.48, 31.86, 29.79, 29.05, 25.14, 24.99, 22.52, 21.95. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.85. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₀H₃₃BO₃⁺ 332.2517; Found 332.2526. **[α]_D²⁰** = +3.61 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 230 nm wavelength. Elution time: $t_{\text{major}} = 22.5$ min and $t_{\text{minor}} = 20.8$ min.



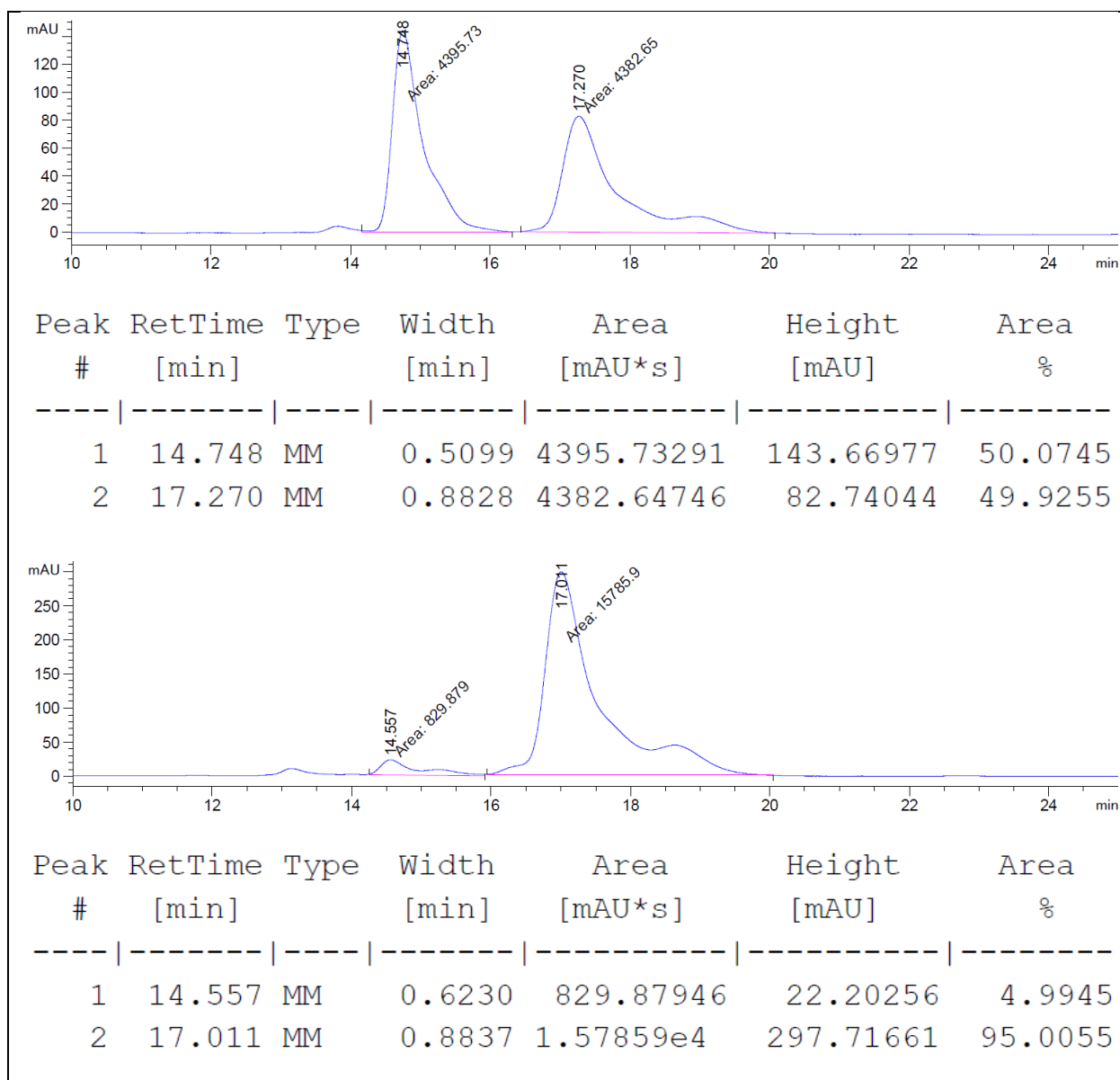
2-((*S*)-1-((*1R,5S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-7-phenylheptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-)6a**)**



Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2d'** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 100:1 hexane:EtOAc) afforded the desired product (-) **6a** as a colorless oil (20 mg, 54%) in 95:5 diastereomeric ratio. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.30 – 7.17 (m, 5H), 5.18 (s, 1H), 2.62 (t, $J = 7.7$ Hz, 2H), 2.36 (dt, $J = 8.4, 5.6$ Hz, 1H), 2.31 – 2.14 (m, 2H), 2.08 (dddd, $J = 6.8, 5.5, 3.4, 1.9$ Hz, 1H), 2.02 (td, $J = 5.6, 1.5$ Hz, 1H), 1.94 (ddt, $J = 9.1, 7.2, 1.9$ Hz, 2H), 1.62 (ddt, $J = 13.9, 7.4, 3.4$ Hz, 2H), 1.44 – 1.32 (m, 5H), 1.29 (s, 3H), 1.24 (s, 12H), 1.16 (d, $J = 8.4$ Hz, 1H), 1.06 – 0.88 (m, 2H), 0.84 (s, 3H). ¹³C NMR (101 MHz,

Chloroform-*d*) δ 148.86, 143.01, 128.56, 128.31, 125.62, 115.67, 82.95, 45.90, 41.05, 38.09, 36.78, 36.01, 31.84, 31.81, 31.41, 31.39, 29.85, 29.22, 29.02, 26.53, 24.94, 24.91, 21.36. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.26. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M]⁺ Calcd for C₂₈H₄₃BO₂⁺ 422.3351; Found 422.3352. [α]_D²⁰ = -11.7 (c = 1.00 in CHCl₃).

Determination of dr: The diastereomeric ratio (95:5) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 17.0 min and *t*_{minor} = 14.5 min.

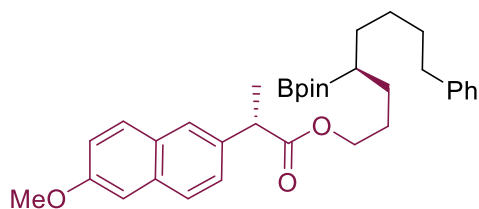


(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl

(S)-2-(6-

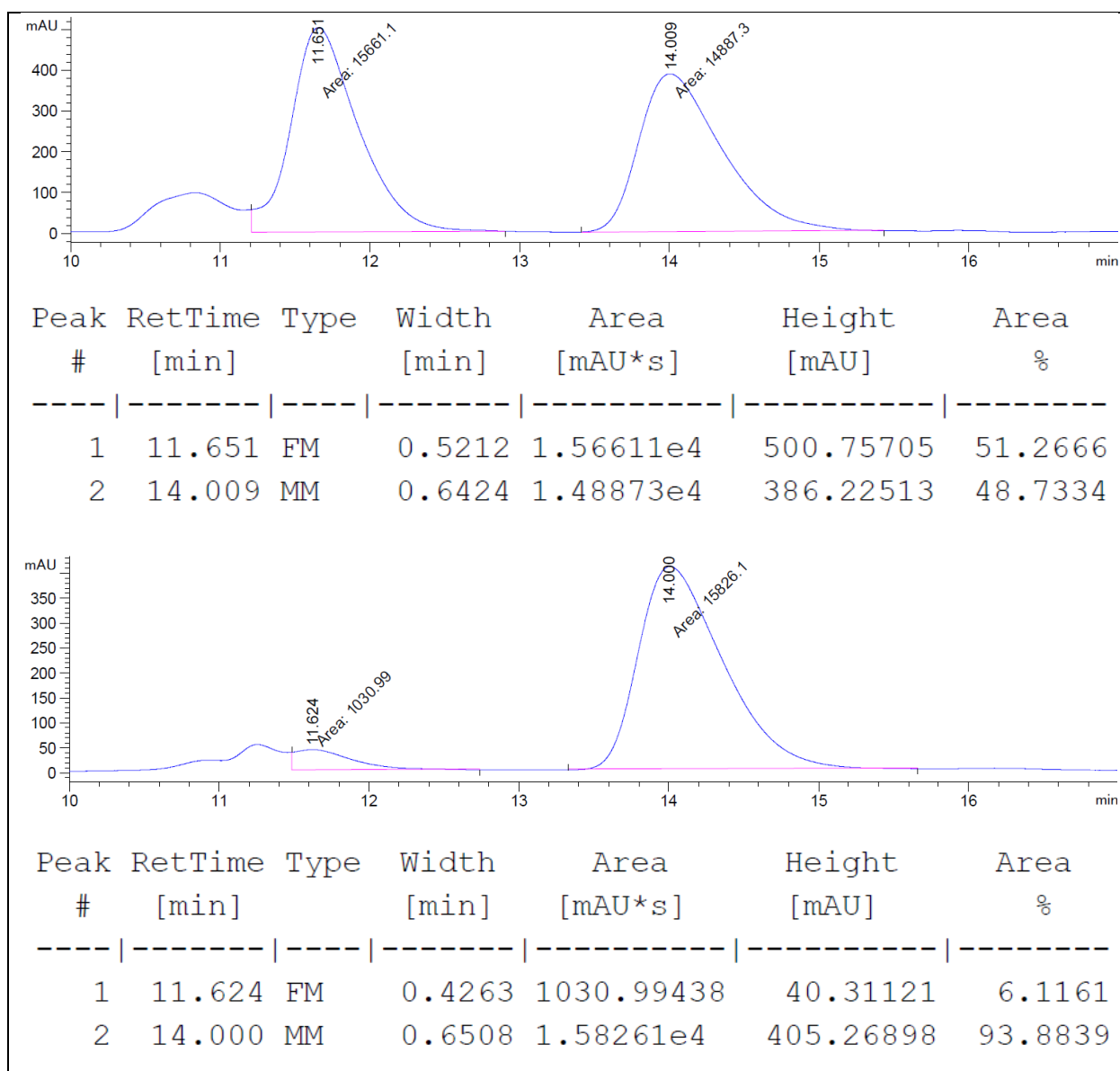
methoxynaphthalen-2-yl)propanoate ((+) 6b):

Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2e'** (40 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 30:1 hexane:EtOAc) afforded the desired product

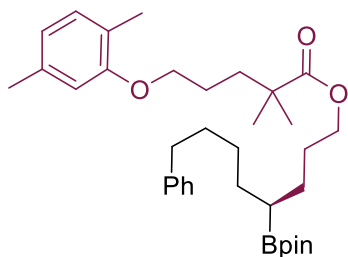


(+) **6b** as a colorless oil (37 mg, 68%) in 94:6 diastereomeric ratio. ^1H NMR (400 MHz, Chloroform-*d*): δ 7.75 – 7.69 (m, 3H), 7.44 (dd, J = 8.5, 1.9 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.20 – 7.11 (m, 5H), 4.08 (t, J = 6.6 Hz, 2H), 3.92 (s, 3H), 3.87 (q, J = 7.2 Hz, 1H), 2.59 (t, J = 7.7 Hz, 2H), 1.62 – 1.57 (m, 6H), 1.45 – 1.17 (m, 19H), 0.91 (dq, J = 8.8, 5.6, 4.5 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.80, 157.70, 142.94, 136.00, 133.77, 129.41, 129.06, 128.53, 128.31, 127.18, 126.43, 126.03, 125.64, 119.01, 105.69, 83.02, 65.21, 55.41, 45.64, 35.97, 31.79, 31.23, 28.85, 28.30, 27.57, 24.89, 24.85, 18.66. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 36.03. HRMS (ESI/QTOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{45}\text{BNaO}_5^+$ 567.3252; Found 567.3265. $[\alpha]_{\text{D}}^{20}$ = +14.0 (c = 1.00 in CHCl_3).

Determination of dr: The diastereomeric ratio (94:6) was determined via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 99:1 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: t_{major} = 14.0 min and t_{minor} = 11.6 min.

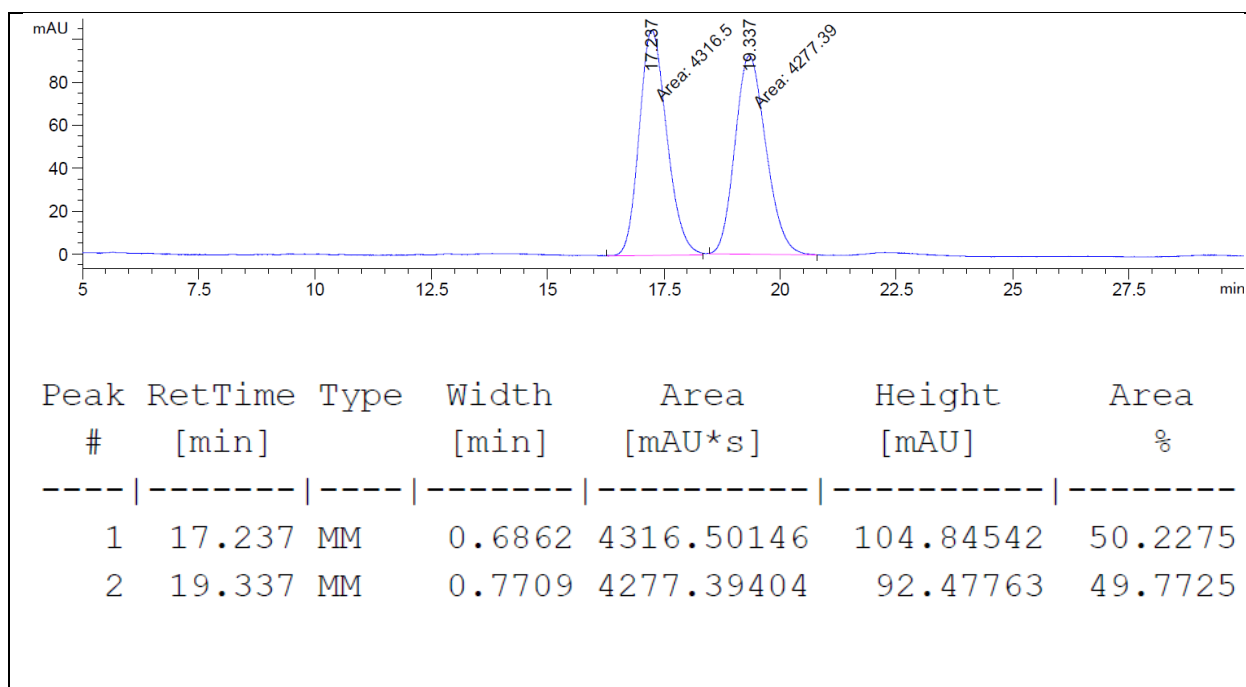


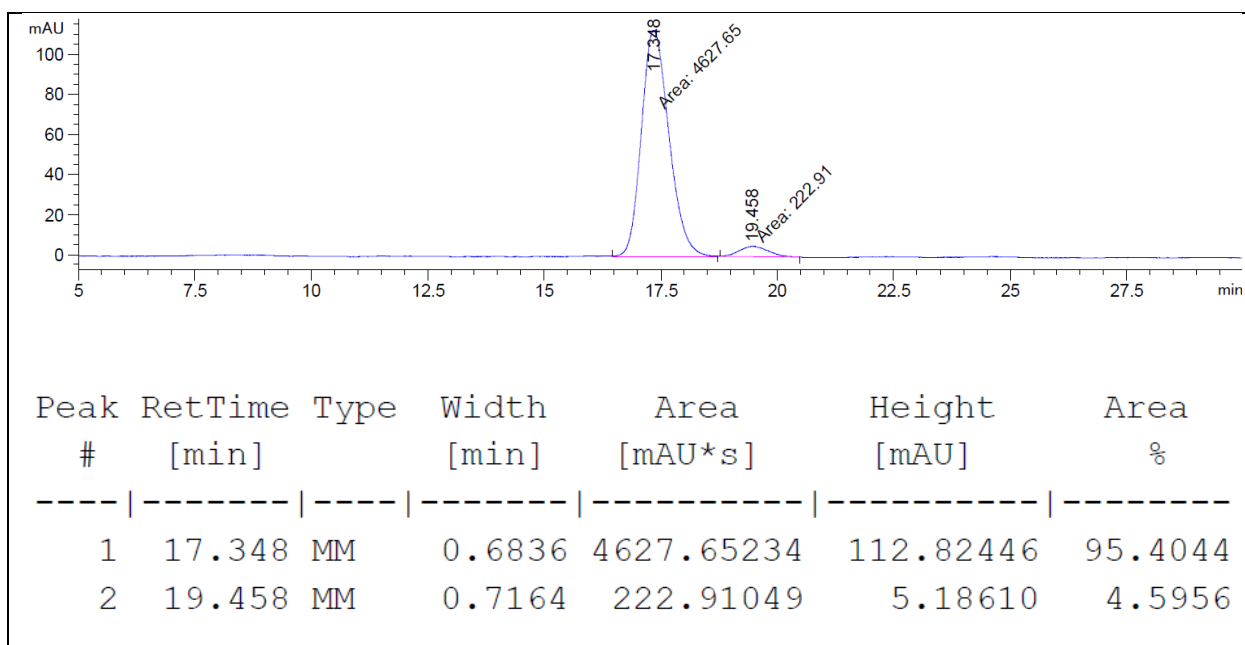
(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate ((+) **6c):**



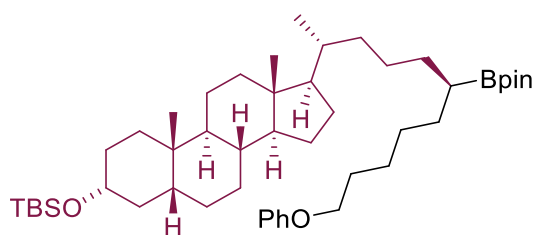
Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2f'** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 30:1 hexane:EtOAc) afforded the desired product **(+) 6c** as a colorless oil (32 mg, 57%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.30 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.71 – 6.66 (m, 1H), 6.63 (d, *J* = 1.6 Hz, 1H), 4.07 (t, *J* = 6.5 Hz, 2H), 3.94 (t, *J* = 5.5 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 2.33 (s, 3H), 2.20 (s, 3H), 1.80 – 1.72 (m, 4H), 1.68 – 1.60 (m, 4H), 1.52 – 1.40 (m, 4H), 1.39 – 1.28 (m, 5H), 1.24 (d, *J* = 5.9 Hz, 18H), 1.00 (ddd, *J* = 8.8, 5.7, 3.0 Hz, 1H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 177.93, 157.10, 142.91, 136.53, 130.39, 128.54, 128.31, 125.65, 123.71, 120.77, 112.05, 83.06, 68.11, 64.84, 42.21, 37.25, 36.00, 31.80, 31.33, 29.84, 28.92, 28.44, 27.77, 25.34, 24.91, 24.88, 21.55, 15.92. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 34.07. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₃₅H₅₃BNaO₅⁺ 587.3878; Found 587.3892. [α]_D²⁰ = +1.2 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 215 nm wavelength. Elution time: *t*_{major} = 17.3 min and *t*_{minor} = 19.4 min.





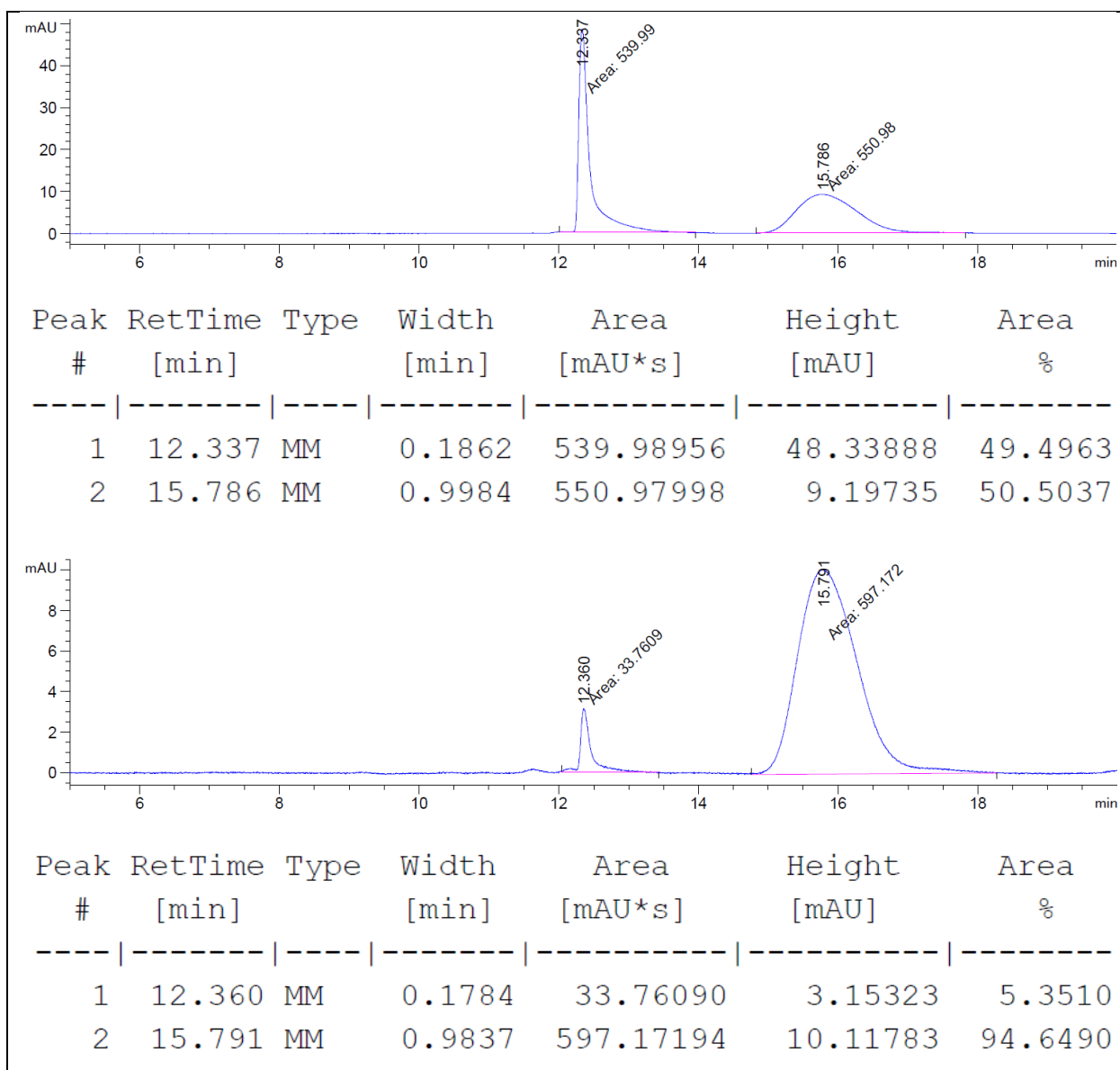
***tert*-Butyl(((3R,5R,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((2R,6S)-11-phenoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undecan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)dimethylsilane ((+) **6d**)**



Prepared according to **GP4** with **1f** (45 mg, 0.15 mmol, 1.50 equiv.), **2g'** (59 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 30:1 hexane:EtOAc) afforded the desired product **(+) 6d** as a white solid (33 mg, 43%) in 95:5 diastereomeric

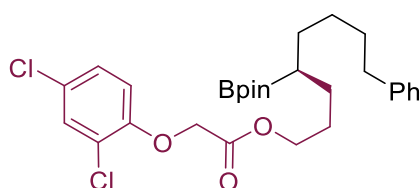
ratio. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.31 – 7.26 (m, 2H), 6.98 – 6.87 (m, 3H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.60 (tt, *J* = 10.5, 4.5 Hz, 1H), 2.00 – 1.92 (m, 1H), 1.91 – 1.74 (m, 6H), 1.63 – 0.91 (m, 59H), 0.65 (s, 3H), 0.08 (s, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.28, 129.51, 120.53, 114.63, 82.95, 73.03, 67.99, 56.59, 56.41, 42.82, 42.49, 40.38, 40.33, 37.10, 36.31, 36.04, 35.76, 34.76, 32.10, 31.61, 31.19, 29.38, 29.22, 28.46, 27.49, 26.59, 26.45, 26.14, 25.74, 24.99, 24.96, 24.40, 23.57, 20.98, 18.79, 18.50, 12.17, -4.43. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₄₈H₈₃BNaO₄Si⁺ 785.6046; Found 785.6050. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 37.90. [α]_D²⁰ = +23.0 (*c* = 1.00 in CHCl₃).

Determination of dr: The diastereomeric ratio (95:5) 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 280 nm wavelength. Elution time: *t*_{major} = 15.8 min and *t*_{minor} = 12.3 min.



**(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl
dichlorophenoxy)acetate ((-) 6e)**

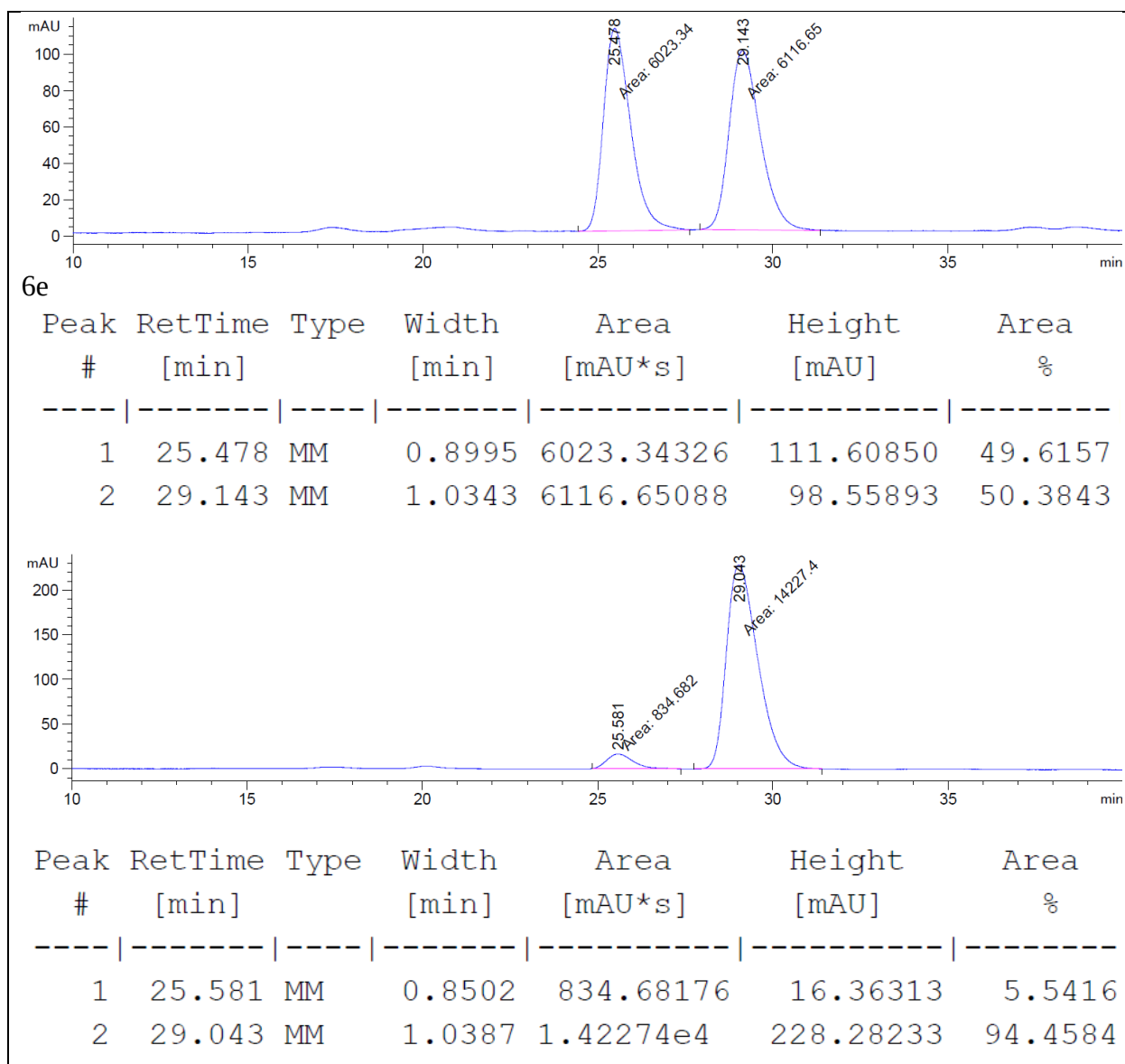
2-(2,4-



Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2h'** (39 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 15:1 hexane:EtOAc) afforded the desired product **(-) 6e** as a colorless oil (34 mg, 64%). ¹H NMR

(400 MHz, Chloroform-*d*): δ 7.41 (d, *J* = 2.6 Hz, 1H), 7.28 (td, *J* = 7.1, 1.8 Hz, 2H), 7.22 – 7.11 (m, 4H), 6.80 (d, *J* = 8.8 Hz, 1H), 4.70 (s, 2H), 4.20 (t, *J* = 6.6 Hz, 2H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.72 – 0.91 (m, 23H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.26, 152.60, 142.88, 130.44, 128.54, 128.33, 127.66, 127.14, 125.67, 124.39, 114.89, 83.13, 66.57, 66.07, 35.97, 31.79, 31.30, 28.83, 28.23, 27.57, 24.93, 24.88. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 34.13. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₂₈H₃₇BCl₂NaO₅⁺ 557.2003; Found 557.2012. [α]_D²⁰ = -1.2 (*c* = 1.00 in CHCl₃).

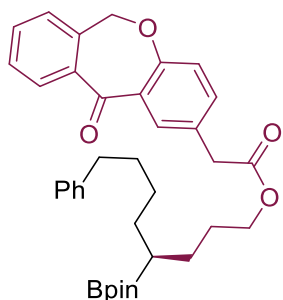
HPLC: The enantiomeric excess (89%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 70:30 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: $t_{\text{major}} = 29.0$ min and $t_{\text{minor}} = 25.6$ min.



(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl

2-(11-oxo-6,11-

dihydrodibenzo[*b,e*]oxepin-2-yl)acetate ((-)- 6f)

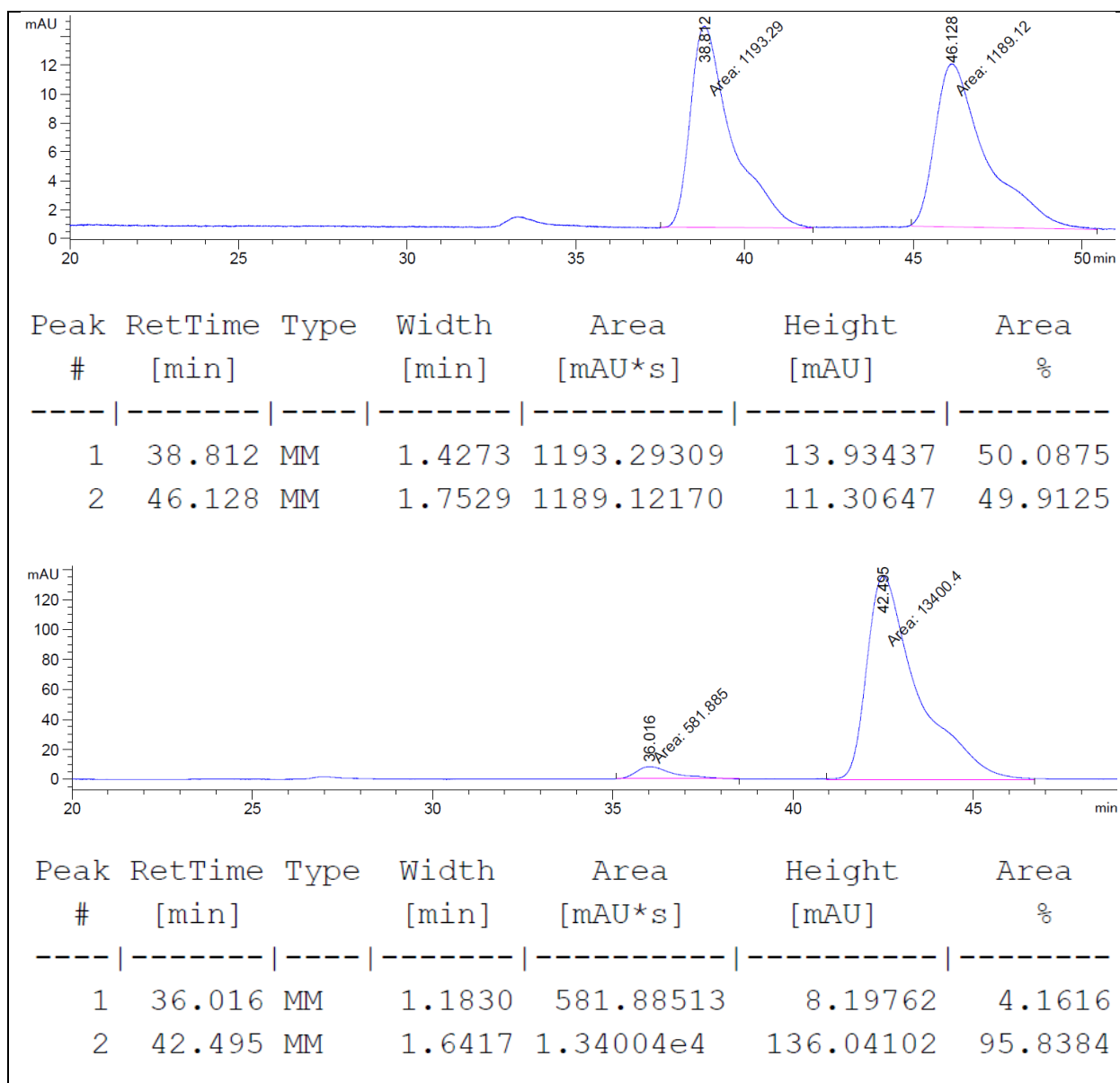


Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2i'** (44 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 7:1 hexane:EtOAc) afforded the desired product **(-)- 6f** as a colorless oil (34 mg, 58%). ¹H NMR (400 MHz, Chloroform-*d*): δ 8.14 (d, *J* = 2.5 Hz, 1H), 7.92 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.53 – 7.43 (m, 2H), 7.42 – 7.35 (m, 1H), 7.31 – 7.24 (m, 2H), 7.18 (d, *J* = 7.3 Hz, 2H),

7.05 (dd, *J* = 8.5, 6.4 Hz, 1H), 5.20 (s, 2H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.65 (s, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.63 (ddt, *J* = 10.7, 7.7, 2.8 Hz, 4H), 1.54 – 1.13 (m, 19H), 0.98 (tt, *J* = 8.8, 5.7 Hz, 1H).

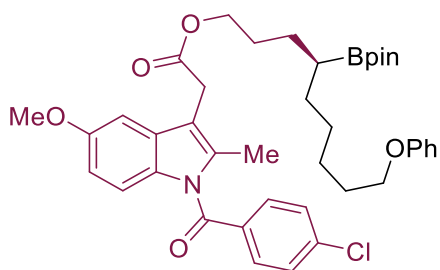
¹³C NMR (101 MHz, Chloroform-*d*) δ 190.93, 171.58, 160.55, 142.92, 140.60, 136.49, 135.69, 132.85, 132.58, 132.55, 129.62, 129.36, 128.54, 128.31, 128.15, 127.90, 125.64, 121.12, 83.07, 73.75, 65.52, 40.40, 35.98, 31.79, 31.28, 28.87, 28.31, 27.65, 24.92, 24.88. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.70. **HRMS (ESI/QTOF)** *m/z*: [M + Na]⁺ Calcd for C₃₆H₄₃BNaO₆⁺ 605.3045; Found 605.3057. [α]_D²⁰ = -0.3 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 42.5 min and *t*_{minor} = 36.0 min.



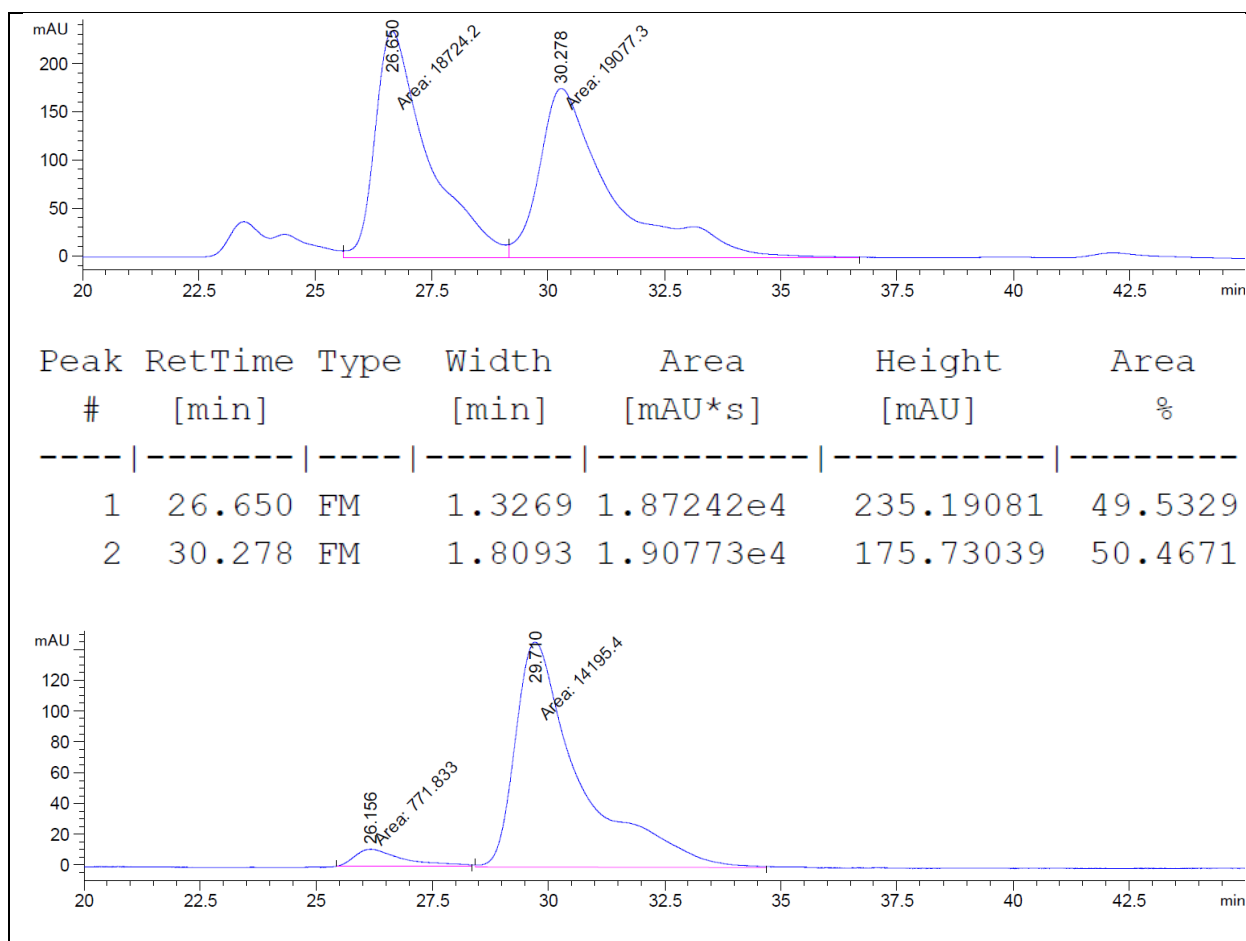
(S)-9-Phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate ((-)- 6g)

Prepared according to **GP4** with **1f** (45 mg, 0.15 mmol, 1.50 equiv.), **2j'** (53 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 5:1 hexane:EtOAc) afforded the desired product ((-)-



6g as a colorless oil (37 mg, 53%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 7.68 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 7.34 – 7.24 (m, 2H), 7.00 – 6.86 (m, 4H), 6.68 (dd, J = 9.0, 2.3 Hz, 1H), 4.03 (dt, J = 59.1, 6.7 Hz, 3H), 3.86 (s, 3H), 3.67 (s, 2H), 2.41 (s, 3H), 1.71 (dq, J = 55.1, 7.3 Hz, 4H), 1.54 – 1.17 (m, 19H), 1.05 – 0.90 (m, 2H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 171.02, 168.40, 159.23, 156.18, 139.33, 135.99, 134.10, 131.31, 130.92, 130.83, 129.51, 129.23, 120.56, 115.06, 114.60, 112.91, 111.83, 101.39, 83.11, 67.90, 65.56, 55.82, 31.32, 30.55, 29.35, 29.00, 28.36, 27.67, 26.43, 24.94, 24.90, 13.51. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 36.50. **HRMS (ESI/QTOF)** m/z : $[M + Na]^+$ Calcd for C₄₀H₄₉BClINNaO₇⁺ 724.3183; Found 724.3189. $[\alpha]_D^{20}$ = -0.67 (c = 1.00 in CHCl₃).

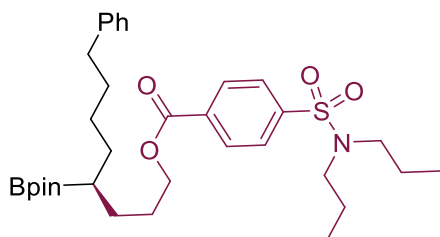
HPLC: The enantiomeric excess (90%) was determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 29.7 min and t_{minor} = 26.1 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.156	MM	1.1791	771.83325	10.90991	5.1568
2	29.710	MM	1.6194	1.41954e4	146.09392	94.8432

(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl dipropylsulfamoylbenzoate ((-) 6h)

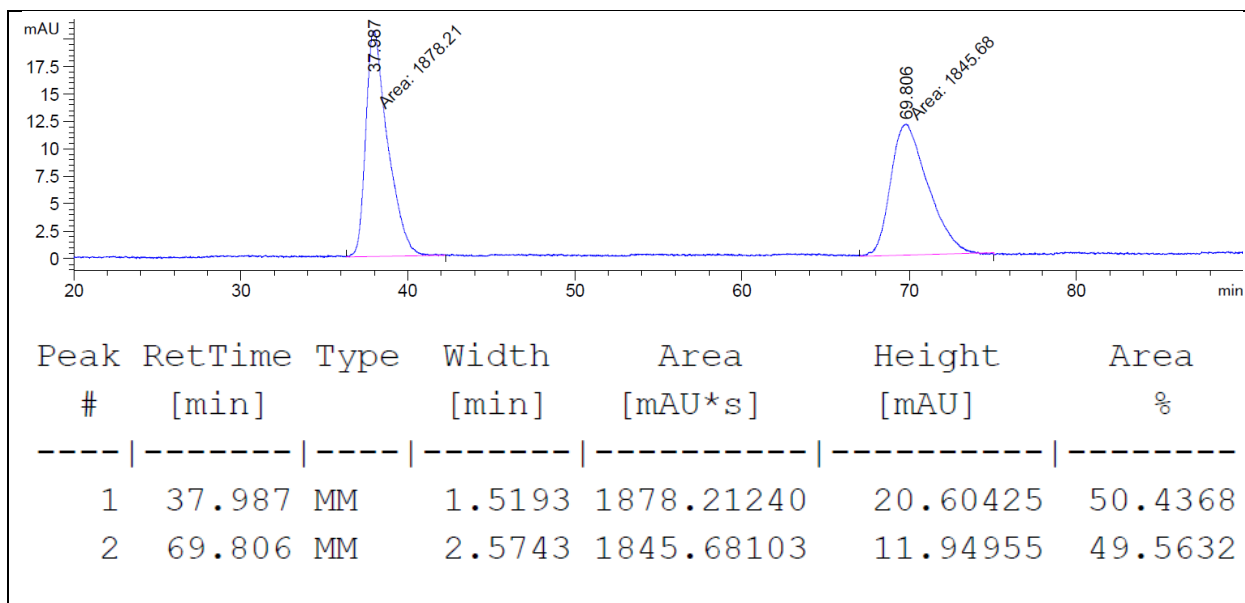
4-(N,N-

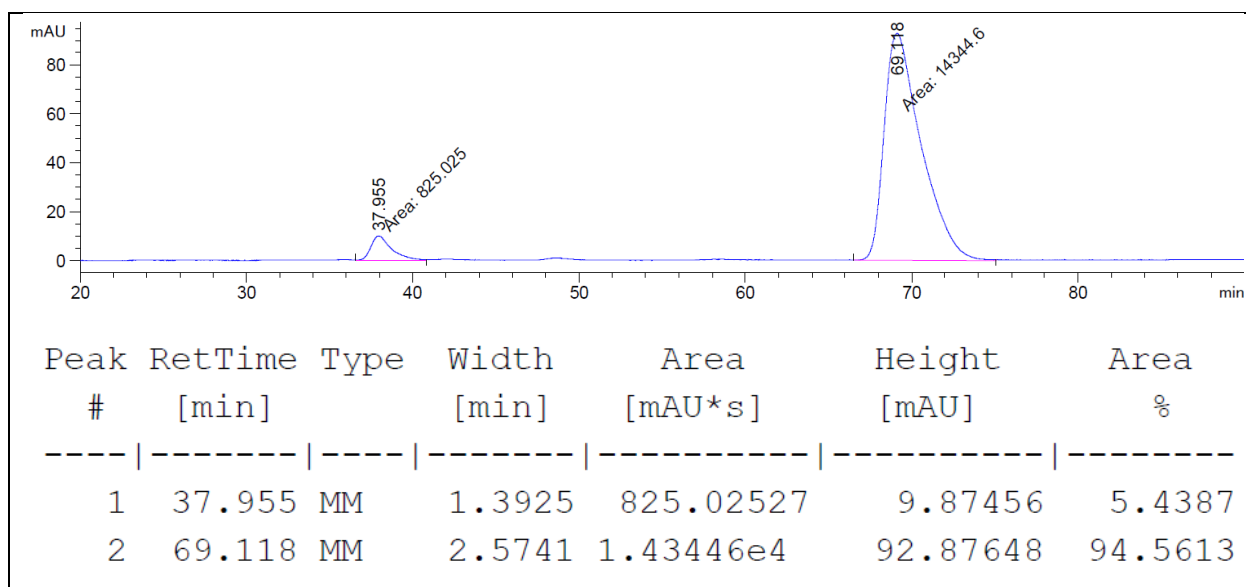


Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2k'** (46 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 3:1 hexane:EtOAc) afforded the desired product **(-) 6h** as a colorless oil (36 mg, 60%). **¹H NMR** (400 MHz, Chloroform-*d*): δ 8.22 – 8.13 (m, 2H), 7.93

– 7.85 (m, 2H), 7.35 – 7.10 (m, 5H), 4.35 (t, *J* = 6.5 Hz, 2H), 3.18 – 3.03 (m, 4H), 2.62 (t, *J* = 7.6 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.72 – 1.17 (m, 25H), 0.89 (t, *J* = 7.4 Hz, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 165.41, 144.21, 142.85, 133.99, 130.32, 128.52, 128.32, 127.07, 125.67, 83.14, 66.14, 50.06, 35.98, 31.78, 31.29, 28.86, 28.40, 27.79, 24.94, 24.89, 22.07, 11.29. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.11. **HRMS (ESI/QTOF)** *m/z*: [M + H]⁺ Calcd for C₃₃H₅₁BNO₆S⁺ 600.3525; Found 600.3537. **[α]_D²⁰** = -0.7 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (89%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 90:10 at a flow rate 1.0 mL/min detected at 230 nm wavelength. Elution time: *t*_{major} = 69.1 min and *t*_{minor} = 37.9 min.

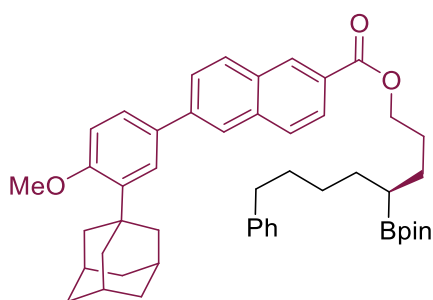




(S)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl

6-(3-((3r,5r,7r)-

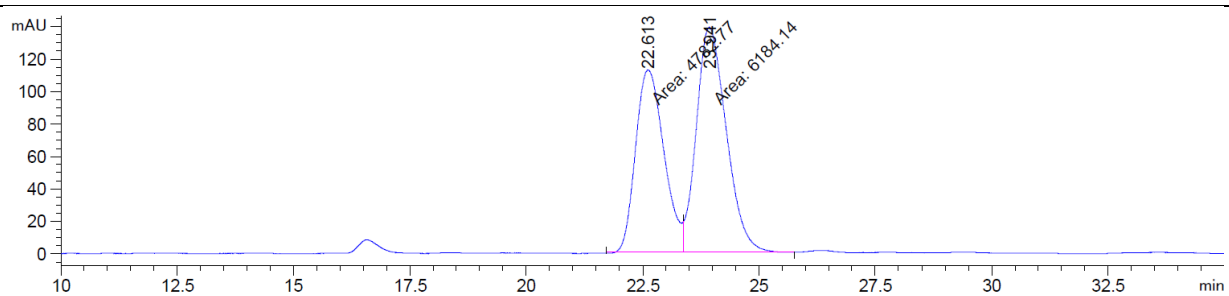
adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate ((+) **6i**)



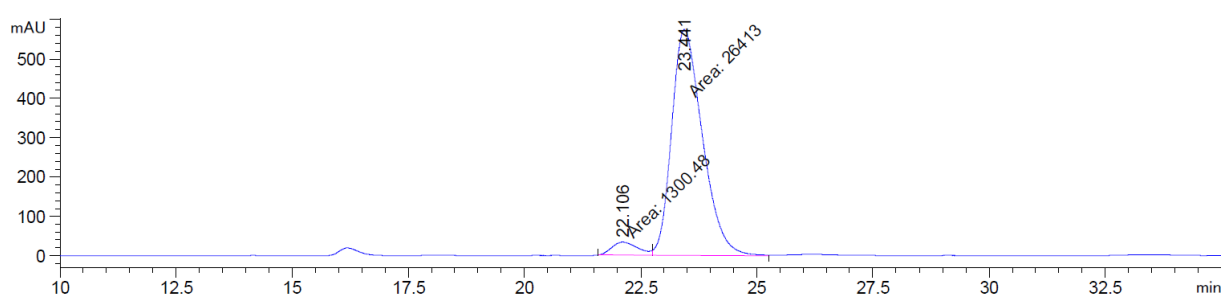
Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2I'** (58 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO₂, 5:1 hexane:EtOAc) afforded the desired product (+) **6i** as a colorless oil (43 mg, 59%). ¹H NMR (400 MHz, Chloroform-*d*): δ 8.64 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.94 (d, *J* = 8.6 Hz, 1H),

7.82 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.58 (dt, *J* = 8.5, 1.8 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 3H), 7.03 (d, *J* = 8.4 Hz, 1H), 4.40 (t, *J* = 6.6 Hz, 2H), 3.93 (s, 3H), 2.64 (t, *J* = 7.6 Hz, 2H), 2.23 (d, *J* = 2.8 Hz, 6H), 2.14 (s, 3H), 1.84 (s, 8H), 1.69 – 1.64 (m, 2H), 1.64 – 1.46 (m, 4H), 1.40 (q, *J* = 7.5 Hz, 2H), 1.26 (s, 12H), 1.10 (t, *J* = 7.1 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.00, 159.03, 142.93, 141.39, 139.12, 136.03, 132.73, 131.39, 130.84, 129.82, 128.55, 128.32, 128.25, 127.50, 126.52, 126.10, 125.85, 125.80, 125.65, 124.86, 112.24, 83.12, 65.61, 55.30, 40.75, 37.35, 37.27, 36.02, 31.83, 31.32, 29.26, 28.93, 28.57, 27.88, 24.96, 24.92. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 34.12. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₄₈H₆₀BO₅⁺ 727.4528; Found 727.4526. [α]_D²⁰ = +1.5 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 99:1 at a flow rate 0.8 mL/min detected at 230 nm wavelength. Elution time: *t*_{major} = 23.4 min and *t*_{minor} = 22.1 min.

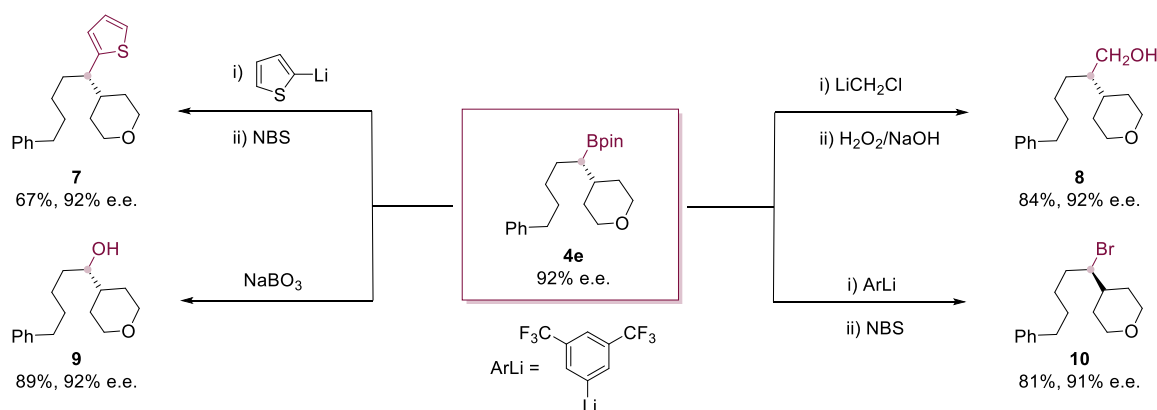


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.613	MF	0.7087	4782.77490	112.48418	43.6110
2	23.941	FM	0.7422	6184.13623	138.86404	56.3890

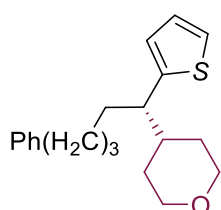


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.106	MF	0.6591	1300.47522	32.88686	4.6926
2	23.441	FM	0.7664	2.64130e4	574.36633	95.3074

7. Functional group transformations:

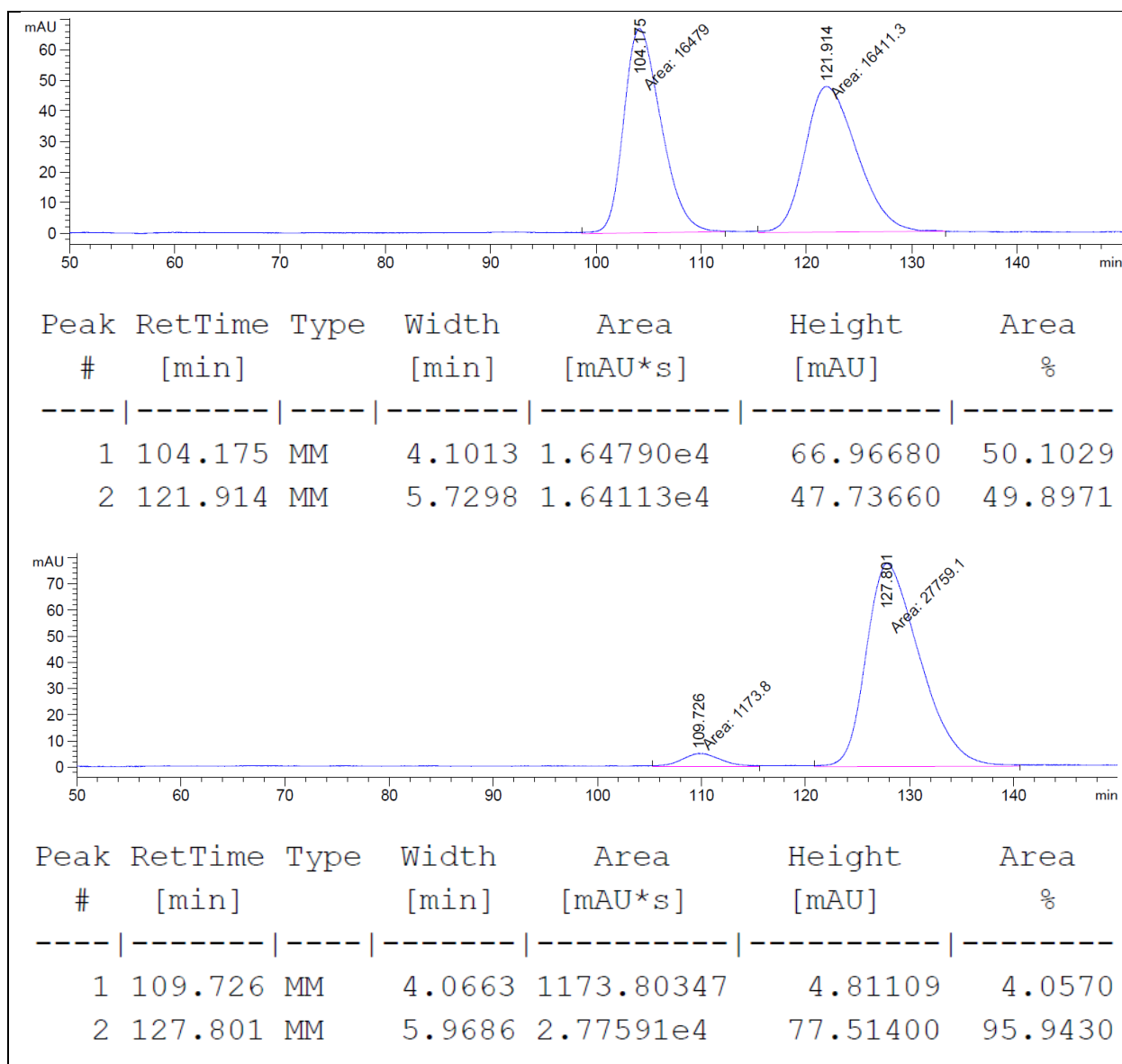


(*S*)-4-(5-Phenyl-1-(thiophen-2-yl)pentyl)tetrahydro-2H-pyran ((-) 7)

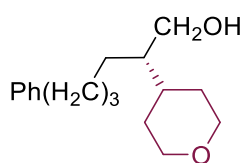


The title compound was prepared following a known literature procedure with slight modification.^[28] To a solution of thiophene (14.0 μ L, 0.18 mmol, 1.20 equiv.) in THF (1.0 mL) at -78 $^{\circ}$ C was added *n*-BuLi (1.6 M in hexane; 112 μ L, 0.18 mmol, 1.20 equiv.) dropwise under an inert atmosphere. The mixture was then warmed to room temperature and stirred for 30 min. Then the mixture was cooled to -78 $^{\circ}$ C again. A solution of (*S*)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane (**4e**) (54.0 mg, 0.15 mmol, 1.00 equiv.) in THF (2.5 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 (32.0 mg, 0.18 mmol, 1.20 equiv.) in THF (2.5 mL) was added dropwise and the mixture was stirred at -78 $^{\circ}$ 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 , 5:1 hexane:EtOAc) to obtain the desired product (–) **7** (31 mg, 67%) as a colorless oil. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (ddd, J = 7.6, 6.4, 1.3 Hz, 2H), 7.18 (ddd, J = 8.3, 5.9, 3.3 Hz, 3H), 6.96 (dd, J = 5.1, 3.4 Hz, 1H), 6.77 (dd, J = 3.5, 1.1 Hz, 1H), 4.08 – 3.87 (m, 2H), 3.39 (td, J = 11.9, 2.2 Hz, 1H), 3.32 (td, J = 11.6, 2.6 Hz, 1H), 2.67 (ddd, J = 11.3, 7.9, 3.8 Hz, 1H), 2.56 (dddd, J = 15.8, 13.7, 8.3, 4.7 Hz, 2H), 1.86 (dddd, J = 13.5, 10.1, 6.6, 3.9 Hz, 1H), 1.78 (ddq, J = 13.0, 4.2, 2.2 Hz, 1H), 1.72 – 1.49 (m, 4H), 1.45 – 1.17 (m, 6H). **¹³C NMR** (101 MHz, Chloroform-*d*) δ 147.70, 142.80, 128.46, 128.36, 126.43, 125.73, 124.86, 123.03, 68.37, 68.19, 47.16, 41.77, 35.93, 33.69, 31.59, 31.57, 31.15, 27.39. **HRMS (APPI/LTQ-Orbitrap)** m/z : $[\text{M}]^+$ Calcd for $\text{C}_{20}\text{H}_{26}\text{OS}^+$ 314.1699; Found 314.1699. $[\alpha]_{\text{D}}^{20}$ = -5.0 (c = 1.00 in CHCl_3).

HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALCEL® OJ-H column, with hexane:isopropanol = 99:1 at a flow rate 0.5 mL/min detected at 230 nm wavelength. Elution time: $t_{\text{major}} = 127.8$ min and $t_{\text{minor}} = 109.7$ min.



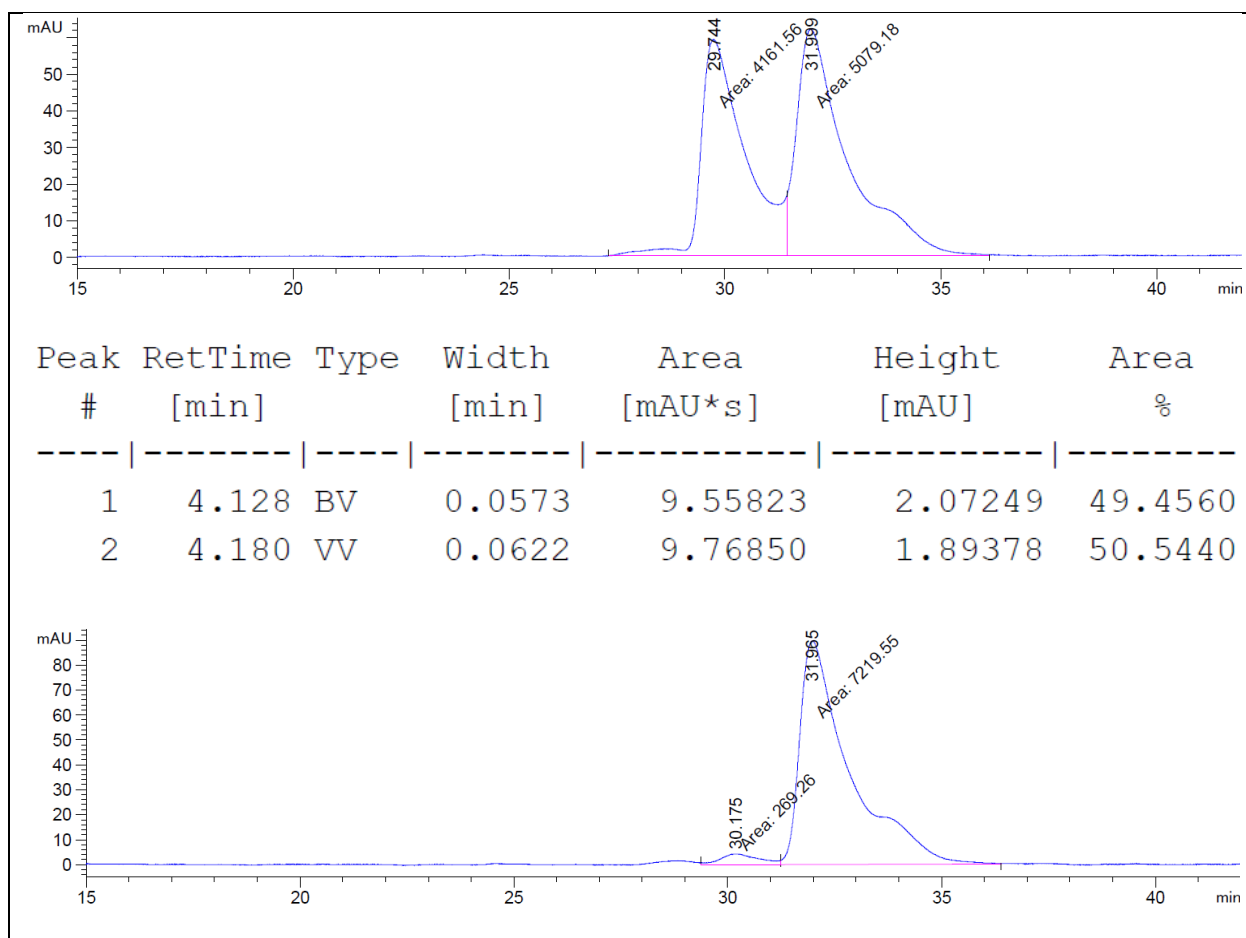
(S)-6-Phenyl-2-(tetrahydro-2H-pyran-4-yl)hexan-1-ol ((-) 8)



The title compound was prepared following a known literature procedure with slight modification.^[29] A solution of (S)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane (**4e**) (54.0 mg, 0.15 mmol, 1.00 equiv.) and chloriodomethane (22.0 μ L, 0.30 mmol, 2.00 equiv.) in THF (0.8 mL) was cooled to -78°C. Then n-BuLi (1.6 M in hexane; 188 μ L, 0.30 mmol, 2.00 equiv.) was added slowly to it. The resulting reaction mixture was stirred for 30 min at -78°C and then allowed to warm to room temperature overnight. The reaction flask was then transferred to an ice bath and NaOH (1.5 mL, 2.0 M) and H₂O₂ (0.80 mL, >30% w/v) were added. The reaction mixture was stirred for an additional 2 hours at this temperature and was then diluted

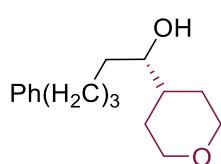
with H₂O (5.0 mL) and EtOAc (5.0 mL) and extracted with EtOAc (3x4.0 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated. The crude product was purified by flash column chromatography (SiO₂, 2:1 hexane:EtOAc) to obtain the desired product (-) **8** (33 mg, 84%) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*): δ 7.32 – 7.28 (m, 2H), 7.20 (td, *J* = 5.7, 5.2, 2.6 Hz, 3H), 4.01 (ddd, *J* = 11.6, 4.6, 1.6 Hz, 2H), 3.64 (d, *J* = 4.1 Hz, 2H), 3.39 (ddt, *J* = 13.2, 11.5, 1.6 Hz, 2H), 2.64 (t, *J* = 7.7 Hz, 2H), 2.19 (s, 1H), 1.72 – 1.61 (m, 3H), 1.61 – 1.53 (m, 2H), 1.48 – 1.41 (m, 3H), 1.32 (dd, *J* = 6.3, 3.5 Hz, 3H), 0.97 – 0.79 (m, 1H). ¹³C NMR (101 MHz, Chloroform-*d*): δ 147.70, 142.80, 128.46, 128.36, 126.43, 125.73, 124.86, 123.03, 68.37, 68.19, 47.16, 41.77, 35.93, 33.69, 31.59, 31.57, 31.15, 27.39. HRMS (APPI/LTQ-Orbitrap) *m/z*: [M + H]⁺ Calcd for C₁₇H₂₇O₂⁺ 263.2006; Found 263.2008. [α]_D²⁰ = -10.0 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: *t*_{major} = 31.9 min and *t*_{minor} = 30.1 min.



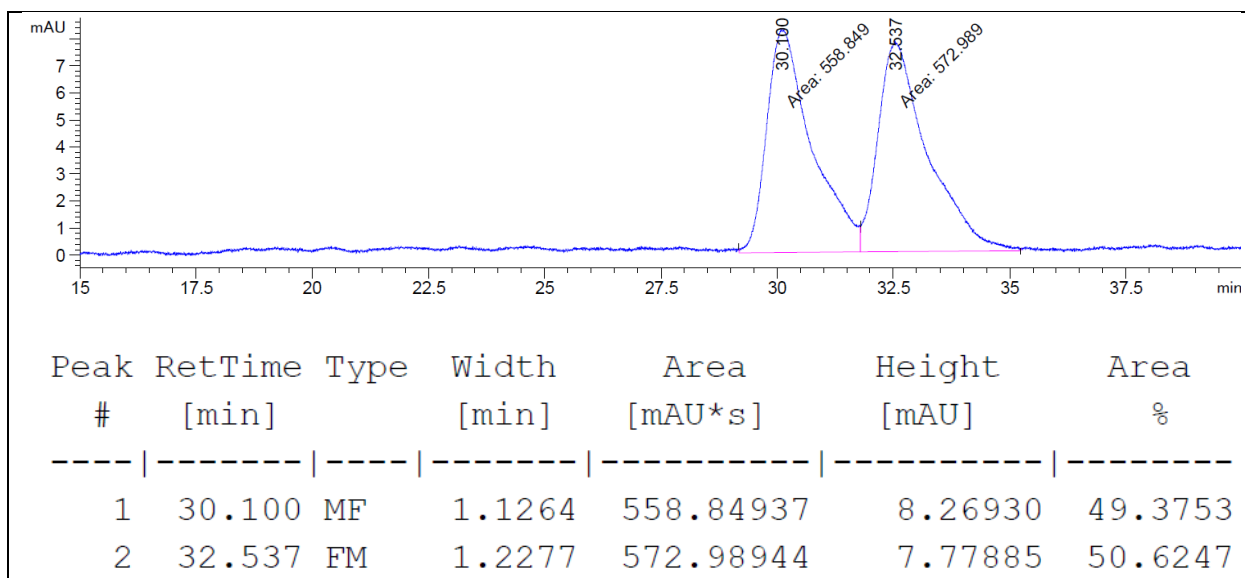
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.175	MF	1.0303	269.26025	4.35569	3.5955
2	31.965	FM	1.3405	7219.55078	89.75989	96.4045

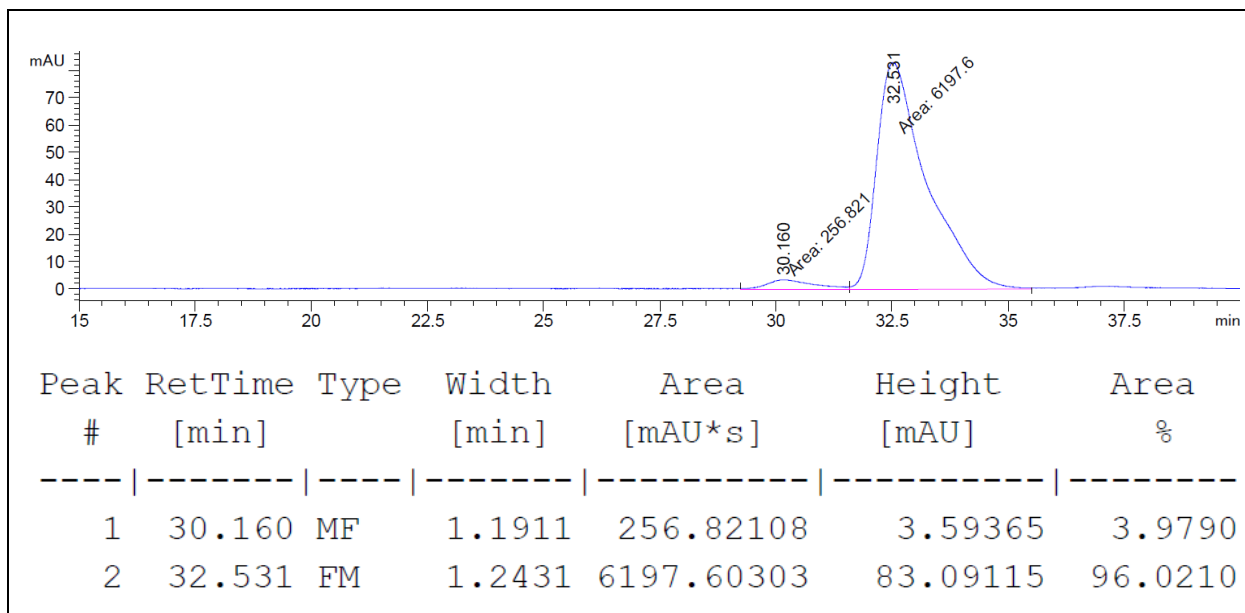
(S)-5-Phenyl-1-(tetrahydro-2H-pyran-4-yl)pentan-1-ol ((-)- 9)



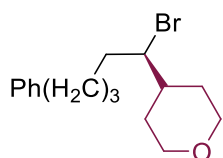
(S)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane (**4e**) (36.0 mg, 0.10 mmol, 1.00 equiv.) was dissolved in a 1:1 mixture of THF and H₂O (2.0 mL) at room temperature. Then NaBO₃•4H₂O (39 mg, 0.25 mmol, 2.50 equiv.) was added. The resulting mixture was stirred 6 hours. After the completion of the reaction as checked by TLC, the reaction mixture was diluted with water (5.0 mL) and Et₂O (5.0 mL). The organic layer was separated and aqueous phase was extracted with Et₂O (3x5.0 mL), and the combined organic phases were dried over Na₂SO₄ and concentrated. The crude product was purified by flash column chromatography (SiO₂, 3:1 hexane:EtOAc) to obtain the desired product (-) **9** (22 mg, 89%) as a colorless oil. **¹H NMR** (400 MHz, Chloroform-*d*): δ 147.70, 142.80, 128.46, 128.36, 126.43, 125.73, 124.86, 123.03, 68.37, 68.19, 47.16, 41.77, 35.93, 33.69, 31.59, 31.57, 31.15, 27.39. **¹³C NMR** (101 MHz, Chloroform-*d*): δ 142.63, 128.50, 128.41, 125.81, 75.47, 68.15, 67.99, 41.14, 36.05, 33.92, 31.63, 29.27, 28.34, 25.51. **HRMS (LTQ-Orbitrap)** m/z: [M + H-1]⁻ Calcd for C₁₆H₂₃O₂⁻ 247.1704; Found 247.1693. [α]_D²⁰ = -8.0 (c = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: t_{major} = 32.5 min and t_{minor} = 30.1 min.



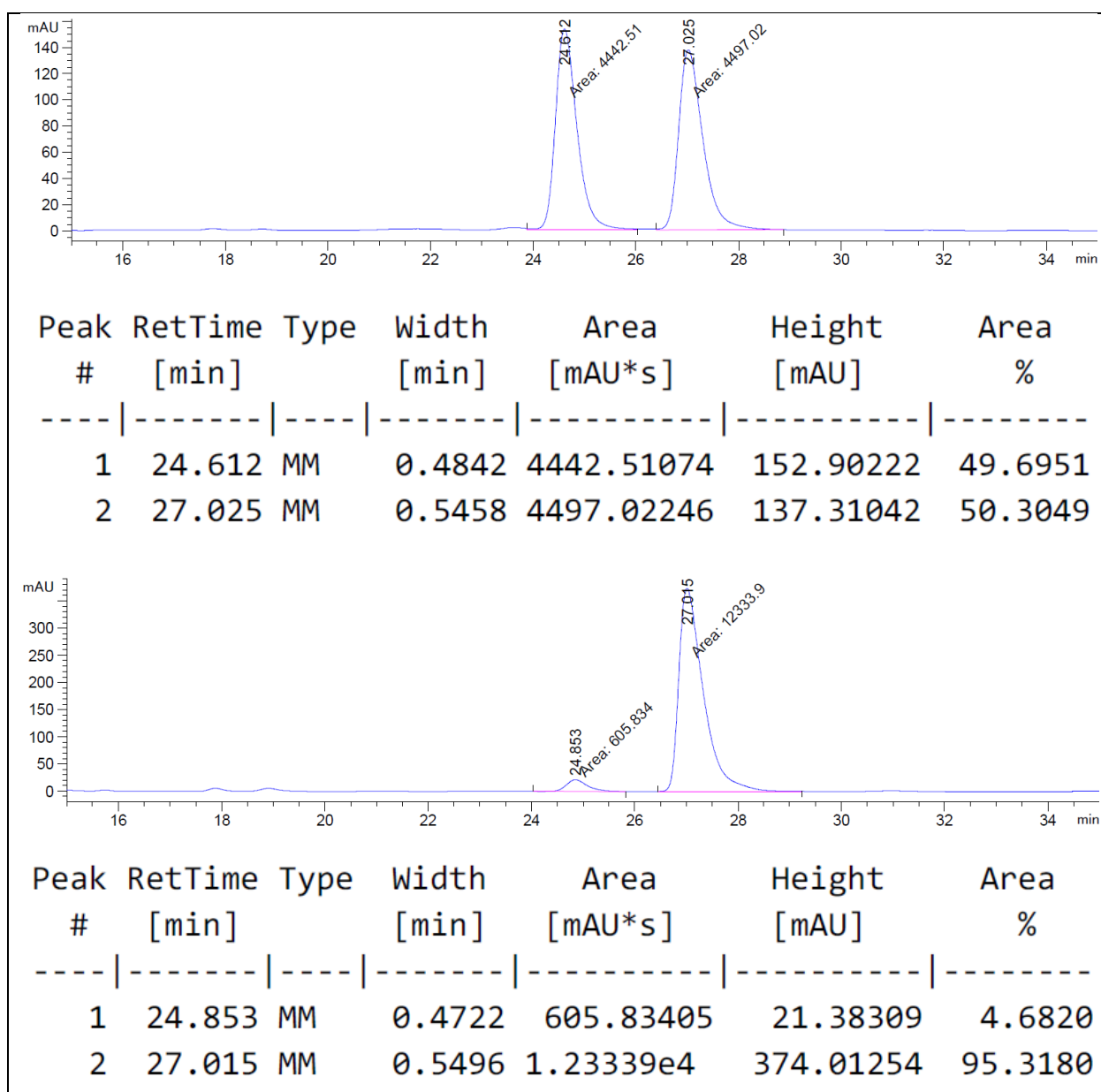


(R)-4-(1-Bromo-5-phenylpentyl)tetrahydro-2H-pyran ((+) 10)

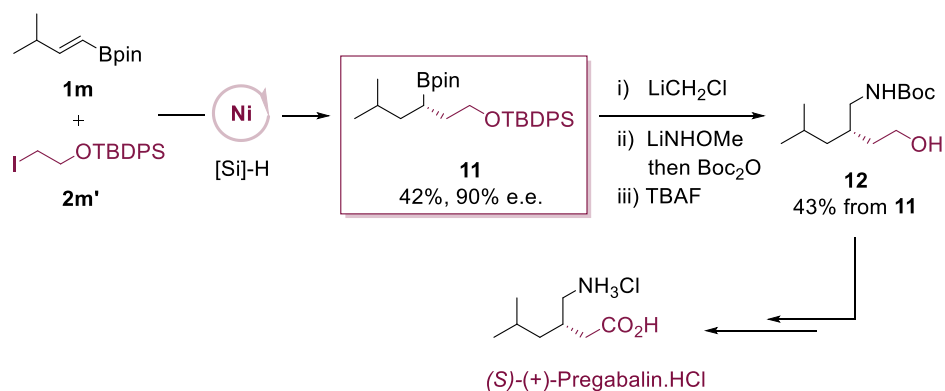


The title compound was prepared following a known literature procedure with slight modification.^[30] To a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (66 mg, 0.23 mmol, 1.50 equiv.) in THF (2 mL) at $-78\text{ }^{\circ}\text{C}$ was added *n*-BuLi (1.6 M in hexane; 144 μL , 0.23 mmol, 1.50 equiv.) dropwise. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h, at which point a solution of (*S*)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane (**4e**) (54.0 mg, 0.15 mmol, 1.00 equiv.) in THF (1.0 mL) was added. The mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. *N*-bromosuccinimide (40 mg, 0.23 mmol, 1.50 equiv.) was added as a solid to it and stirred at this temperature for another 5 minutes, and then allowed to warm to room temperature and stirred for 1 hour. Then the reaction was quenched with a saturated aqueous sodium thiosulfate solution (2.0 mL). The resulting mixture was diluted with water (5.0 mL) and ethyl acetate (5.0 mL). The aqueous layer was extracted with ethyl acetate (3 x 5 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 , 20:1 hexane:EtOAc) to obtain the desired product (+) **10** (38 mg, 81%) as a colorless oil. **^1H NMR** (400 MHz, Chloroform-*d*): δ 7.35 – 7.27 (m, 2H), 7.21 (td, J = 5.4, 3.0 Hz, 3H), 4.03 (ddt, J = 11.7, 6.9, 2.2 Hz, 2H), 3.94 (dt, J = 7.0, 5.4 Hz, 1H), 3.40 (tt, J = 11.3, 2.1 Hz, 2H), 2.66 (dt, J = 6.7, 3.5 Hz, 2H), 1.91 – 1.46 (m, 11H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ 142.44, 128.49, 128.44, 125.89, 67.96, 67.77, 63.85, 42.13, 35.90, 35.56, 31.00, 30.98, 30.23, 27.56. **HRMS (APPI/LTQ-Orbitrap)** m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{24}\text{BrO}^+$ 311.1005; Found 311.1004. $[\alpha]_{\text{D}}^{20} = +16.7$ (c = 1.00 in CHCl_3).

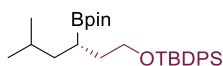
HPLC: The enantiomeric excess (91%) was determined via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 99:1 at a flow rate 0.5 ml/min detected at 210 nm wavelength. Elution time: $t_{\text{major}} = 27.0$ min and $t_{\text{minor}} = 24.8$ min.



8. Synthesis of 12, a key intermediate of (S)-(+)-Pregabalin:

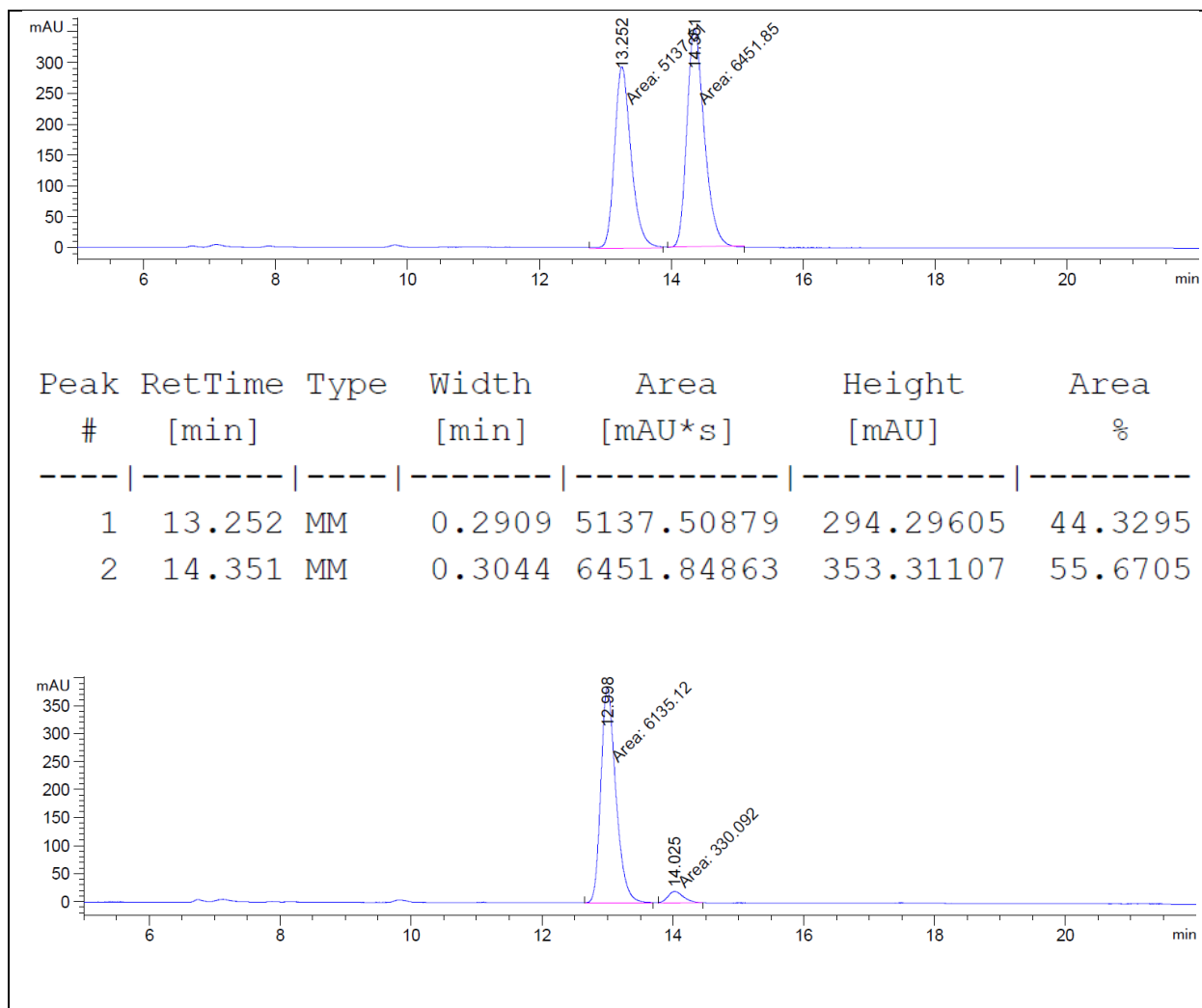


(S)-tert-Butyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)diphenylsilane ((+) 11)



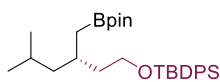
The title compound was prepared according to **GP4** with **1m** (29.4 mg, 0.15 mmol, 1.50 equiv.), **2m'** (41.0 mg, 0.10 mmol, 1.00 equiv.) in a mixture of DCE (0.40 mL) and DMF (0.14 mL) after stirring for 48 hours. Flash column chromatography (SiO₂, 150:1 hexane:EtOAc) afforded the desired product **(+) 11** as a colorless oil (20 mg, 42%). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.61 (m, 4H), 7.43 – 7.33 (m, 6H), 3.72 – 3.58 (m, 2H), 1.73 – 1.63 (m, 2H), 1.58 – 1.50 (m, 1H), 1.36 – 1.32 (m, 1H), 1.28 – 1.23 (m, 1H), 1.18 – 1.15 (m, 1H), 1.15 (s, 12H), 1.04 (s, 9H), 0.85 (d, *J* = 6.6 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 135.72, 134.37, 129.54, 127.68, 82.92, 63.85, 40.55, 34.43, 27.29, 27.04, 24.88, 24.82, 23.05, 22.73, 19.36. ¹¹B NMR (128 MHz, Chloroform-*d*) δ 35.12. HRMS (ESI/QTOF) *m/z*: [M + H]⁺ Calcd for C₂₉H₄₆BO₃Si⁺ 481.3304; Found 481.3310. [α]_D²⁰ = +4.5 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] IB column, with hexane:isopropanol = 99.5:0.5 at a flow rate 0.5 ml/min detected at 210 nm wavelength. Elution time: *t*_{major} = 12.9 min and *t*_{minor} = 14.0 min.



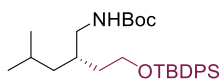
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.998	MM	0.2652	6135.11523	385.49411	94.8943
2	14.025	MM	0.2714	330.09207	20.27290	5.1057

(S)-tert-Butyl((5-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hexyl)oxy)diphenylsilane



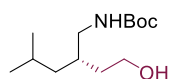
The title compound was prepared following a known literature procedure with slight modification.^[29] A solution of (S)-tert-butyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)diphenylsilane (**11**) (90.0 mg, 0.19 mmol, 1.00 equiv.) and chloriodomethane (29.1 μ L, 0.38 mmol, 2.00 equiv.) in THF (1.0 mL) was cooled to -78°C. Then n-BuLi (1.6 M in hexane; 238 μ L, 0.38 mmol, 2.00 equiv.) was added slowly to it. The resulting reaction mixture was stirred for 30 min at -78°C and then allowed to warm to room temperature overnight. The reaction was quenched with H₂O (5 mL) and diluted with dichloromethane (15 mL). The aqueous and organic layers were separated, and the aqueous layer was extracted with dichloromethane (3x15 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude reaction mixture was placed on the high-vac overnight. The crude material was subjected to amination without additional purification.

tert-Butyl (S)-(2-(2-((tert-butyldiphenylsilyl)oxy)ethyl)-4-methylpentyl)carbamate



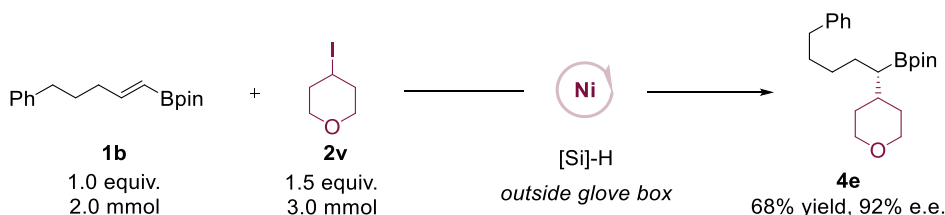
The conversion of the Bpin group to NHBoc group was conducted following a literature reported method.^[31] A solution of O-methylhydroxylamine (0.28 mL, 0.52 mmol, 1.88 M in THF) was diluted with THF (1.5 mL) and the reaction flask was cooled to -78° C in a dry ice/acetone bath. Then n-BuLi (1.6 M in hexane; 330 μ L, 0.52 mmol, 3.00 equiv.) was added slowly to it and the resulting reaction mixture was stirred for 30 min at -78°C. Afterwards a solution of (S)-tert-butyl((5-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hexyl)oxy)diphenylsilane (**11**, 85 mg, 0.17 mmol, 1.00 equiv.) was added dropwise to the solution of deprotonated O-methylhydroxylamine via syringe. The reaction tube was allowed to warm to room temperature and then heated at 60° C for 12 h. The reaction tube was then cooled to room temperature and Boc₂O (126 mg, 0.55 mmol, 3.20 equiv.) was added. After stirring at room temperature for 1 h the reaction was quenched by addition of H₂O (6 mL) and diluted with EtOAc (10 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (3x10 mL). The combined organics were dried over Na₂SO₄, filtered, and concentrated in vacuo to give the crude reaction mixture. The crude material was subjected to TBDPS deprotection (see below) without further purification.

***tert*-Butyl (S)-(2-(2-hydroxyethyl)-4-methylpentyl)carbamate ((+) 12):**



A heat-gun dried schlenk tube was charged with *tert*-butyl (S)-(2-(2-((*tert*-butyldiphenylsilyl)oxy)ethyl)-4-methylpentyl)carbamate (see above, 49 mg, 0.10 mmol, 1.00 equiv.) in THF (4 mL) under N₂ atmosphere and the flask was cooled down to 0 °C with an ice-water bath. Then TBAF (1.0 M in THF, 0.40 mL, 0.40 mmol, 4.00 equiv.) was added dropwise to it. The reaction mixture was then allowed to warm to room temperature and stirred for 2 hours and quenched with an aq. NH₄Cl solution (3 mL). The resulting mixture was diluted with EtOAc (5 mL) and brine (5 mL). The organic layer was separated and the aqueous phase was extracted with ethyl acetate (3×10 mL). The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO₂, 2:1 hexane:EtOAc) to obtain the desired product (+) **12** (20 mg, 81%, overall 43% from **11**) as a colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 3.71 (dtd, *J* = 17.0, 10.9, 5.3 Hz, 2H), 3.15 – 3.02 (m, 2H), 1.75 – 1.61 (m, 2H), 1.60 – 1.46 (m, 2H), 1.44 (s, 9H), 1.16 – 1.07 (m, 2H), 0.88 (t, *J* = 6.3 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 156.63, 79.44, 60.94, 44.32, 42.16, 34.88, 33.77, 28.56, 25.38, 22.98, 22.94. HRMS (ESI/QTOF) *m/z*: [M + Na]⁺ Calcd for C₁₃H₂₇NNaO₃⁺ 268.1883; Found 268.1886. [α]_D²⁰ = +1.5 (*c* = 1.00 in CHCl₃).

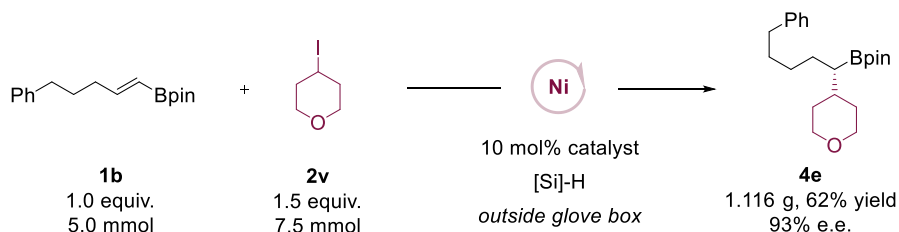
9. Large Scale Reaction (with 15 mol% catalyst loading):



A heat gun dried schlenk tube equipped with a magnetic stir bar (6x15 mm) was charged with NiCl₂ (38.0 mg, 0.30 mmol, 0.15 equiv.) and **L6** (116 mg, 0.40 mmol, 0.20 equiv.) under N₂. The tube was evacuated and backfilled with nitrogen (three cycles). Then anhydrous DCE (6.0 mL) and DMF (4.0 mL) were added via syringe and the mixture was stirred at room temperature for 40 minutes. Then KF (290 mg, 5.00 mmol, 2.50 equiv.) was added to it and the heterogeneous mixture was stirred for 3 minutes at which point alkenyl boronic acid pinacol ester **1b** (544 mg, 2.00 mmol, 1.00 equiv.) was added and the mixture was stirred for additional 2 minutes. 4-Iodotetrahydro-2H-pyran **2v** (370 μL, 3.00 mmol, 1.50 equiv.) was added to the resulting mixture, which was stirred for 5 minutes. Then DEMS (0.85 mL, 5.00 mmol, 2.5 equiv.) was added dropwise to it over a period of 5 minutes and the resulting mixture was stirred for 40 hours. Afterwards, the reaction was diluted by addition of H₂O (8.0 mL) and EtOAc (10.0 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (3x5.0 mL). The combined organic phase was dried over Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash

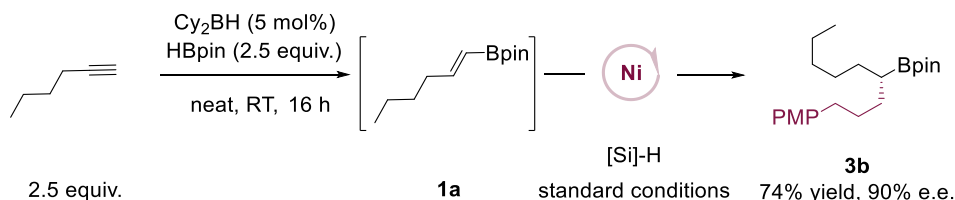
column chromatography (SiO₂, 10:1 hexane:EtOAc) to obtain the desired product **4e** as colourless oil (488 mg, 68% yield, 92% e.e.).

10. Gram Scale Reaction (with 10 mol% catalyst loading):



A heat gun dried schlenk tube (50 mL) equipped with a cylindrical magnetic stir bar was charged with NiCl₂ (64.5 mg, 0.50 mmol, 0.10 equiv.) and **L6** (219 mg, 0.75 mmol, 0.15 equiv.) under N₂. The tube was evacuated and backfilled with nitrogen (three cycles). Then anhydrous DMF (10.0 mL) and DCE (15.0 mL) were added via syringe and the mixture was stirred at room temperature for 80 minutes. Then KF (733 mg, 12.5 mmol, 2.50 equiv.) was added to it and the heterogeneous mixture was stirred for 3 minutes at which point alkenyl boronic acid pinacol ester **1b** (1.36 g, 5.00 mmol, 1.00 equiv.) was added and the mixture was stirred for additional 2 minutes. 4-Iodotetrahydro-2H-pyran **2v** (0.92 mL, 7.50 mmol, 1.50 equiv.) was added to the resulting mixture, which was stirred for 4 minutes. Then DEMS (2.10 mL, 12.5 mmol, 2.5 equiv.) was added dropwise to it over a period of 5 minutes and the resulting mixture was stirred for 46 hours. Afterwards, the reaction was diluted by addition of H₂O (15.0 mL) and EtOAc (15.0 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (3x30.0 mL). The combined organic phase was washed with brine (15.0 mL), dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography (SiO₂, 10:1 hexane:EtOAc) to obtain the desired product **4e** as colourless oil (1.116 g, 62% yield, 93% e.e.).

11. One-pot reaction from alkyne without isolation of alkenyl Bpin intermediate:

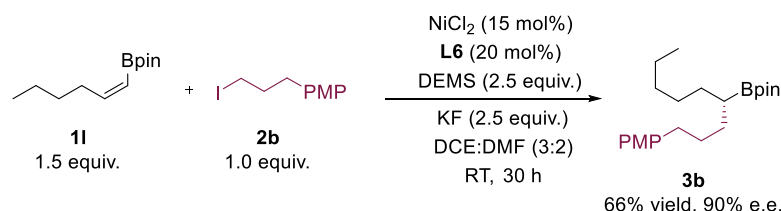


In a heat gun dried schlenk tube equipped with a magnetic stir bar (6x15 mm) freshly prepared dicyclohexylborane (3.60 mg, 20.0 μmol, 0.05 equiv.), 1-hexyne (115 μL, 1.00 mmol, 1.00 equiv.) and pinacolborane (145 μL, 1.00 mmol, 1.00 equiv.) were added successively under an N₂ atmosphere. The reaction mixture was stirred for 18 hours. Afterwards, the volatile materials were removed under reduced pressure at room temperature for 30 minutes. The tube was refilled with

N₂. To the resulting residue was added a solution of preformed catalyst [prepared with NiCl₂ (9.5 mg, 75 μmol, 0.15 equiv.), **L6** (29.3 mg, 0.10 mmol, 0.20 equiv.) in DCE (1.5 mL) and DMF (1.0 mL) after stirring for 40 minutes]. Then KF (72.5 mg, 1.25 mmol, 2.50 equiv.) was added to it and the heterogeneous mixture was stirred for 3 minutes at which point **2b** (138 mg, 0.50 mmol, 1.00 equiv.) was added. The resulting mixture was stirred for 5 minutes. Then DEMS (215 μL, 1.25 mmol, 2.5 equiv.) was added dropwise to it over a period of 5 minutes and the resulting mixture was stirred for 30 hours. Afterwards, the reaction was diluted by addition of H₂O (3.0 mL) and EtOAc (5.0 mL). The organic layer was separated and the aqueous phase was extracted with EtOAc (3x5.0 mL). The combined organic phase was dried over Na₂SO₄ and concentrated under vacuum. The crude product was purified by flash column chromatography (SiO₂, 60:1 hexane:EtOAc) to obtain the desired product **3b** as colourless oil (133 mg, 74% yield, 90% e.e.).

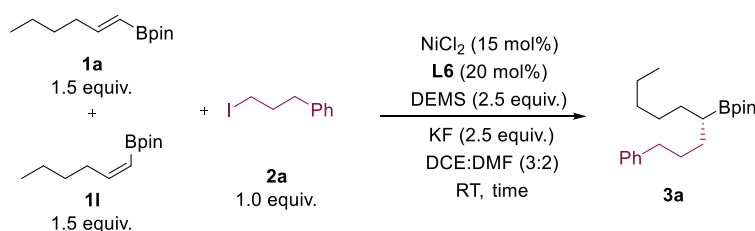
12. Mechanistic investigations:

12.1 Reaction with a *cis*-boronic ester:



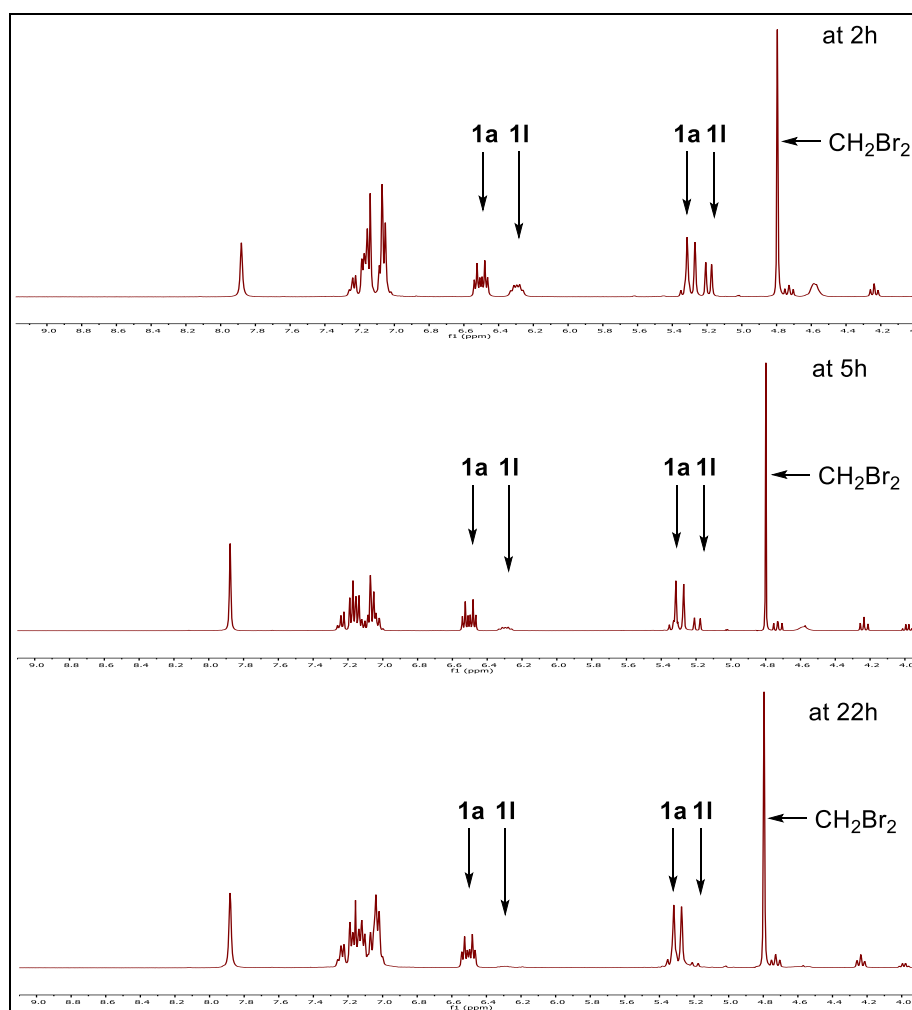
The reaction was conducted for 30 hours according to **GP4**, with (*Z*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1l**) (42 mg, 0.20 mmol, 2.00 equiv.) and 1-(3-iodopropyl)-4-methoxybenzene (**2b**) (28 mg, 0.10 mmol, 1.00 equiv.) as coupling partners. Flash column chromatography (SiO₂, 60:1 hexane:EtOAc) afforded the desired product (+) **3b** as a colorless oil (24 mg, 66%). The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis which confirmed the same enantiomer as obtained from the reaction with its *trans* analogue **1a**.

12.2 Monitoring of reactions with a mixture of *cis*- and *trans*-alkenyl boronic esters:



Three parallel reactions at a 0.1 mmol scale with an equimolar mixture (1:1) of *cis*- and *trans*-alkenyl boronic esters (**1l**) and (**1a**) were performed following **GP4**. **1a** (37.5 μL, 0.15 mmol, 1.5 equiv.), **1l** (32 mg, 0.15 mmol, 1.5 equiv.) and **2a** (16.1 μL, 0.10 mmol, 1.0 equiv.) were used. The

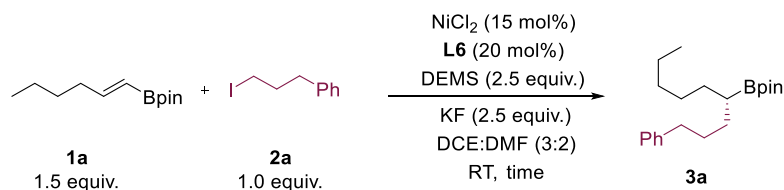
reactions were stopped at the indicated reaction time. Afterwards, water (1.0 mL) and EtOAc (3.0 mL) were added to the reaction mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc (2x3.0 mL). The volatiles were removed to afford the crude product. Then dibromomethane was added as an internal standard to this mixture and the resulting mixture was mixed well. A small organic aliquot was used for ^1H NMR analysis to determine the reactivity of *cis* and *trans* isomers. The results show that the *cis* to *trans* conversion occurs prior to the hydroalkylation. However, it was also observed that without Ni-catalyst, the *cis* to *trans* conversion still occurred.



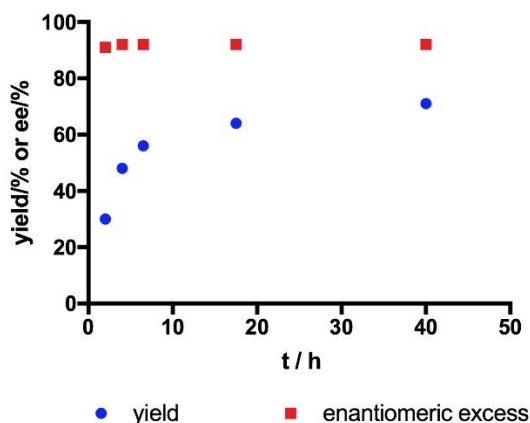
12.3 Reaction profile:

Five parallel reactions at a 0.1 mmol scale were performed following **GP4**. The reactions were stopped at the indicated reaction time. Afterwards, water (1.0 mL) and EtOAc (3.0 mL) were added to the reaction mixture. 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

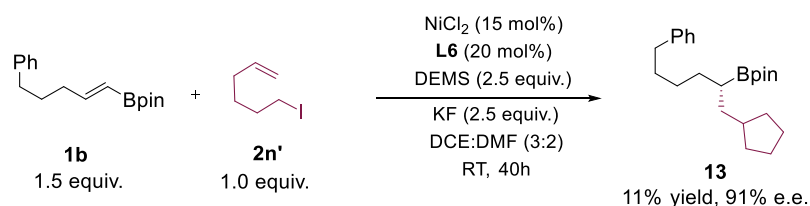
over Na₂SO₄, and the volatiles were removed to afford the crude product. The crude product was directly oxidized following **GP2** to obtain the pure alcohol which was subjected to HPLC analysis to determine the e.e.



Entry	Time (hour)	Yield (%)	e.e. (%)
1	2.0	30	91
2	4.0	48	92
3	6.5	56	92
4	17.5	64	92
5	40	71	92



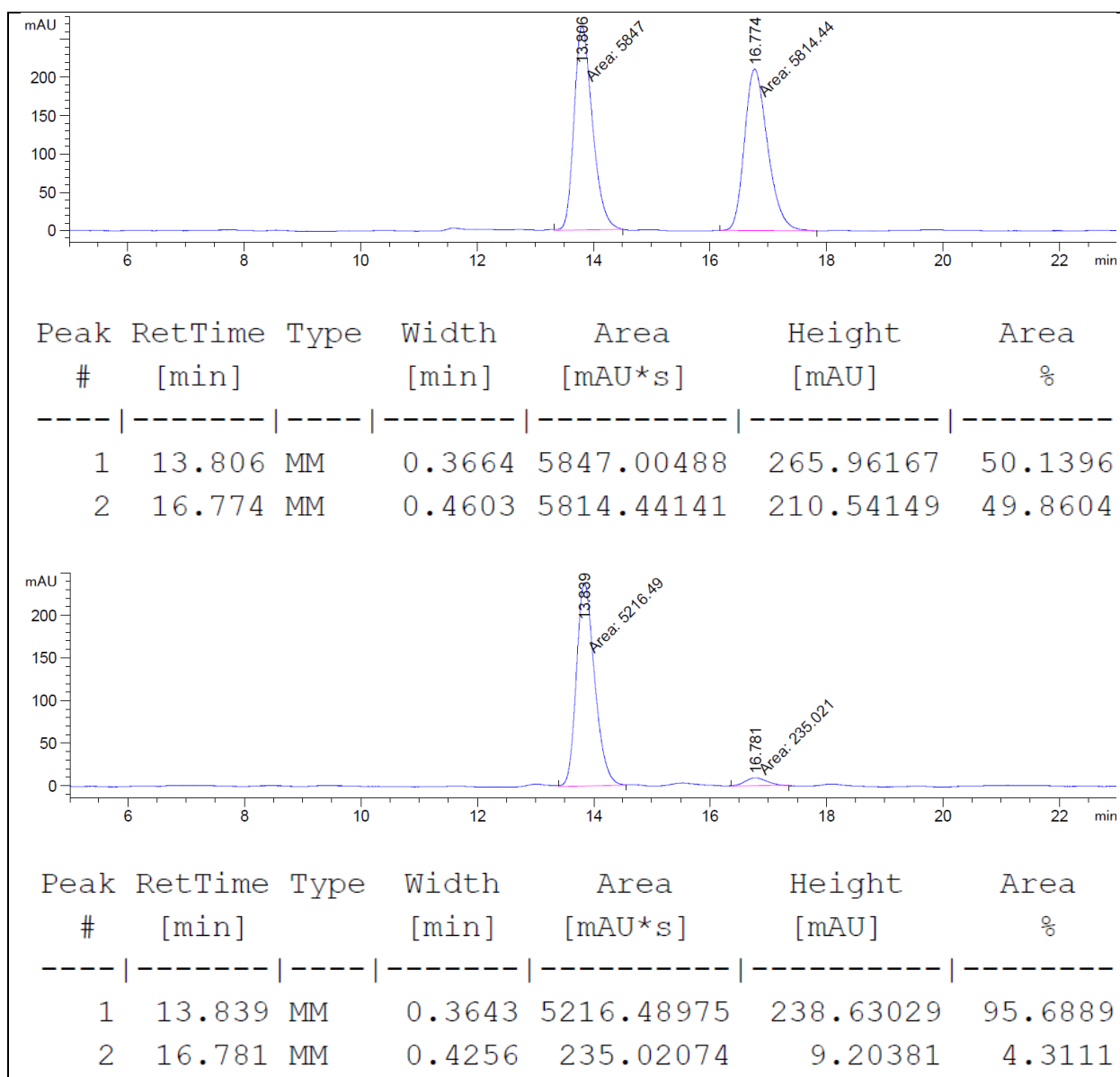
12.4 Radical-clock experiment:



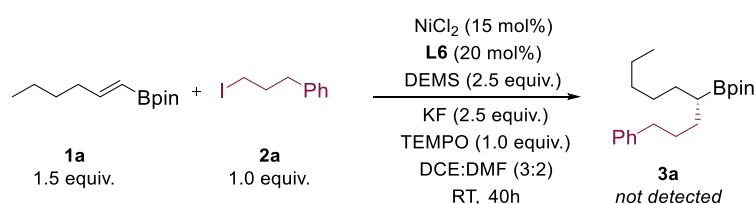
The reaction was conducted in 0.2 mmol scale following **GP4**, with **1b** (81 mg, 0.30 mmol, 1.50 equiv.) and 6-iodohex-1-ene (**2n'**) (42 mg, 0.20 mmol, 1.00 equiv.) as coupling partners. Purification by preparative TLC (SiO₂, 60:1 hexane:EtOAc) afforded compound (-) **13** as a colorless oil (8 mg, 11%). The analogous compound with no cyclization was detected but could not be purified. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.22 (m, 3H), 7.18 – 7.14 (m, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.81 – 1.69 (m, 3H), 1.69 – 1.58 (m, 4H), 1.53 – 1.42 (m, 3H), 1.40 – 1.29 (m, 5H), 1.21 (s, 12H), 1.08 – 1.00 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.04, 128.57,

128.31, 125.62, 82.91, 39.89, 38.08, 36.05, 33.23, 32.87, 31.90, 31.85, 29.07, 25.40, 25.26, 24.96, 24.91. **¹¹B NMR** (128 MHz, Chloroform-*d*) δ 35.31. **HRMS (APPI/LTQ-Orbitrap)** *m/z*: [M + Na]⁺ Calcd for C₂₃H₃₇BNaO₂⁺ 379.2779; Found 379.2788. **[α]_D²⁰** = -1.2 (*c* = 1.00 in CHCl₃).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL[®] OD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: *t*_{major} = 13.8 min and *t*_{minor} = 16.8 min.

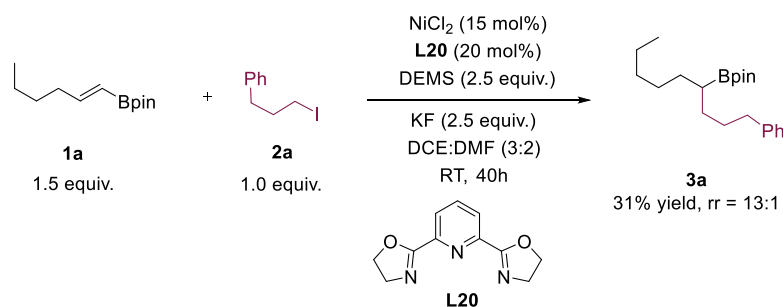


12.5 TEMPO quenching experiment:



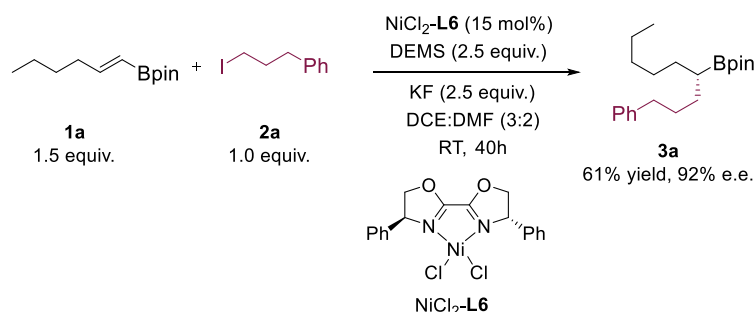
The reaction was conducted following **GP4**. TEMPO (15.6 mg, 0.10 mmol, 1.0 equiv.) was added after the addition of all reagents. The hydroalkylation product was not detected.

12.6 Probe for origin of regioselectivity:



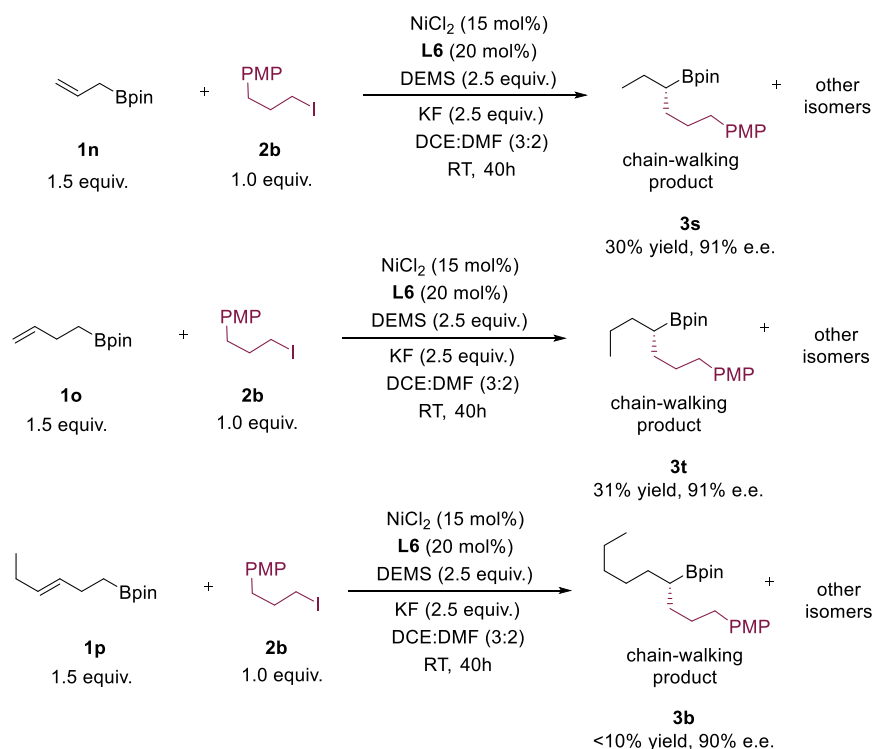
See main text for design of experiments. The reaction was conducted following **GP4** using **L20** (4.3 mg, 0.02 mmol, 0.20 equiv.) instead of **L6**. The regioselectivity was found to be 13:1 where **3a** was obtained in 31% yield.

12.7 Reaction with a pre-complex NiCl_2 -**L6**:

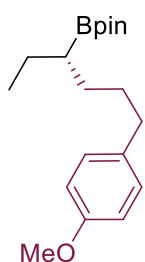


The NiCl_2 -**L6** complex was prepared following a literature procedure with slight modification.^[32] To a 20 mL oven-dried vial equipped with a magnetic stir bar in a glovebox was added $\text{NiCl}_2 \cdot \text{DME}$ (46 mg, 0.21 mmol, 1.0 equiv.) and **L6** (73 mg, 0.25 mmol, 1.19 equiv.) and DCM (7.5 mL). The mixture was stirred for 4 hours and it was then concentrated to dryness. After that DCM (1.5 mL) was added to it followed by the addition of Et_2O to precipitate a light blue solid, which was filtered off. The precipitate was then washed with pentane and Et_2O and finally dried under high vacuum to afford light blue powder (45 mg, 51%). Then it was used in the hydroalkylation reaction following **GP4**. The reaction was conducted in 0.1 mmol scale with respect to **2a** using NiCl_2 -**L6** complex (6.3 mg, 0.015 mmol, 0.15 equiv.) instead of using NiCl_2 and **L6**. The product was formed in 61% yield with 92% e.e..

13. Reactions with substrates where an alkenyl group is distal to a Bpin group:

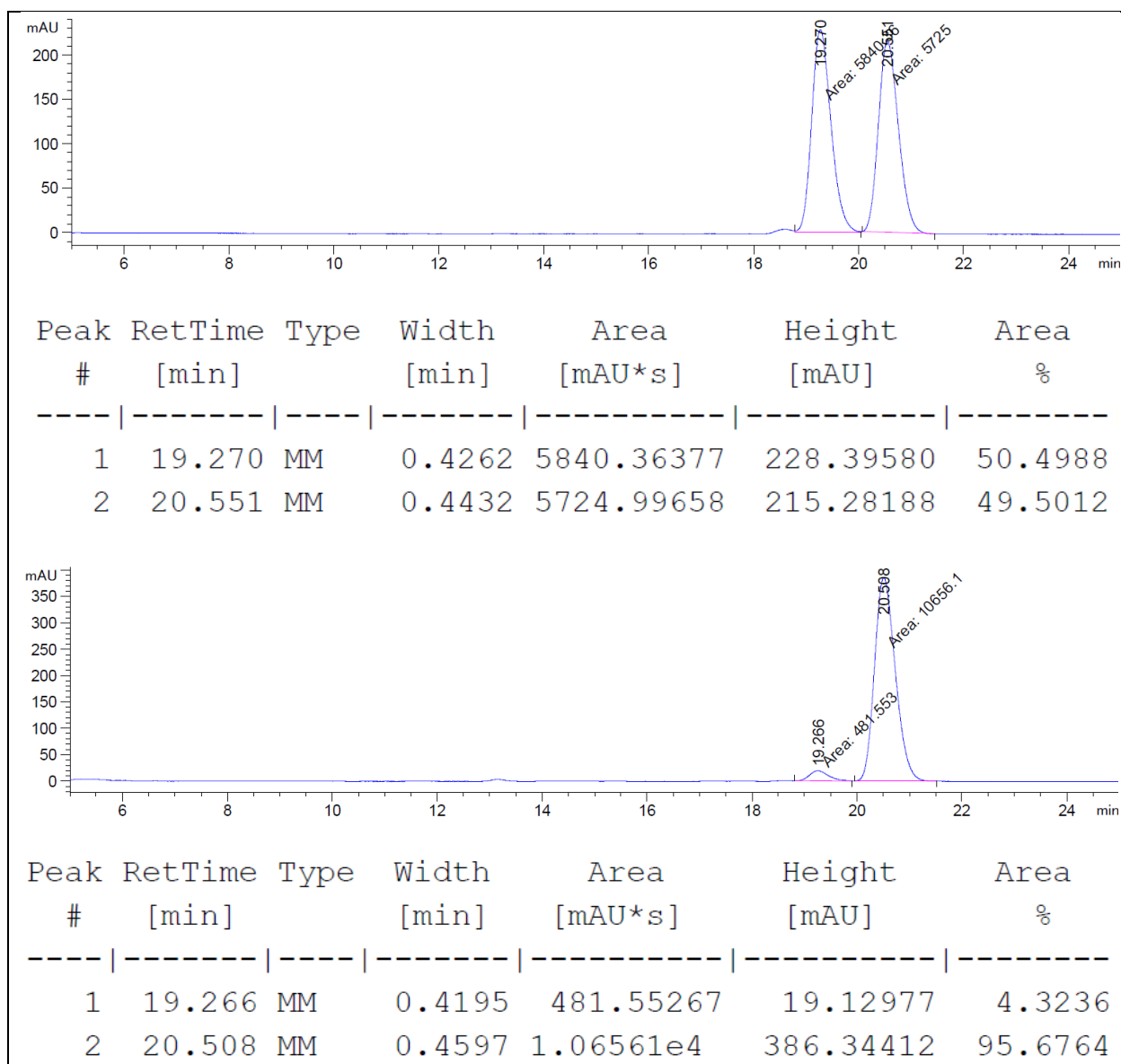


(S)-2-(6-(4-Methoxyphenyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) **3s**)

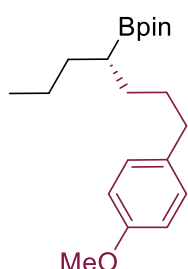


Prepared according to **GP4** with **1n** (30.0 μL , 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Purification by PTLC (SiO_2 , 60:1 hexane:EtOAc) afforded the desired product (+) **3s** as a colorless oil (10 mg, 30%). The other regioisomeric products were also formed in this reaction as observed by GC-MS. But the regioselectivity of those isomers were not determined. The overall regioselectivity of this reaction was 2.6:1 favoring the desired product as determined by using GC-FID (the minor isomers include all the other regioisomers). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 7.12 – 7.06 (m, 2H), 6.84 – 6.78 (m, 2H), 3.78 (s, 3H), 2.57 – 2.50 (m, 2H), 1.63 – 1.54 (m, 2H), 1.47 – 1.36 (m, 3H), 1.29 – 1.21 (m, 14H), 0.89 (t, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*): δ 157.67, 135.20, 129.38, 129.35, 113.75, 82.98, 55.39, 35.44, 31.50, 30.93, 29.86, 24.97, 13.85. $^{11}\text{B NMR}$ (128 MHz, Chloroform-*d*) δ 35.15. **HRMS (APPI/LTQ-Orbitrap)** m/z : $[\text{M}]^+$ Calcd for $\text{C}_{19}\text{H}_{31}\text{BO}_3^+$ 318.2361; Found 318.2375. $[\alpha]_{\text{D}}^{20} = +4.7$ ($c = 1.00$ in CHCl_3).

HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: $t_{\text{major}} = 20.5$ min and $t_{\text{minor}} = 19.3$ min.



(S)-2-(1-(4-Methoxyphenyl)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) 3t)

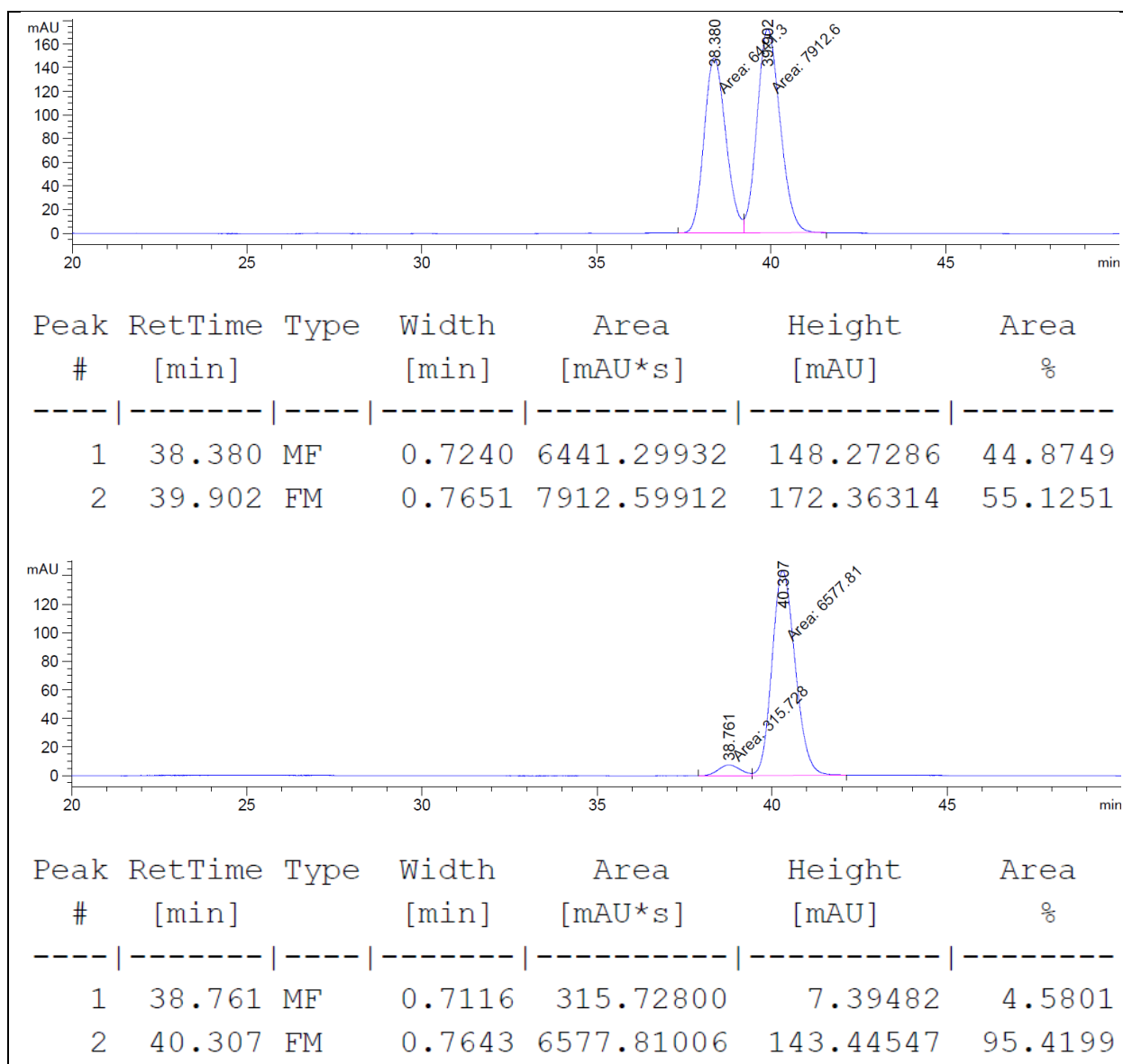


Prepared according to **GP4** with **1o** (27.0 mg, 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Purification by PTLT (SiO₂, 60:1 hexane:EtOAc) afforded the desired product **(+) 3t** as a colorless oil (11 mg, 31%). The other regioisomeric products were also formed in this reaction as observed by GC-MS.

But the regioselectivity of those isomers were not determined. The overall regioselectivity of this reaction was 2.6:1 favoring the desired product as determined by using GC-FID (the minor isomers include all the other regioisomers). **¹H NMR** (400 MHz, Chloroform-*d*): 7.12 – 7.04 (m, 2H), 6.85 – 6.77 (m, 2H), 3.78 (s, 3H), 2.53 (td, *J* = 7.9, 2.3 Hz, 2H), 1.63 – 1.53 (m, 2H), 1.47 – 1.38 (m, 2H), 1.33 – 1.27 (m, 4H), 1.24 (d, *J* = 3.3 Hz, 12H), 1.01 (ddt, *J* = 11.1, 8.7, 5.4 Hz, 1H), 0.90 – 0.85 (m, 3H). **¹³C NMR** (101 MHz, Chloroform-*d*): δ 157.67, 135.19, 129.37, 129.35, 113.75, 82.95, 55.39, 35.44, 33.87, 31.53, 31.21, 29.86, 24.97, 24.94, 22.54, 14.60.

^{11}B NMR (128 MHz, Chloroform-*d*) δ 35.15. **HRMS (APPI/LTQ-Orbitrap)** m/z : $[\text{M}]^+$ Calcd for $\text{C}_{20}\text{H}_{33}\text{BO}_3^+$ 332.2517; Found 332.2527. $[\alpha]_{\text{D}}^{20} = +4.2$ ($c = 1.00$ in CHCl_3).

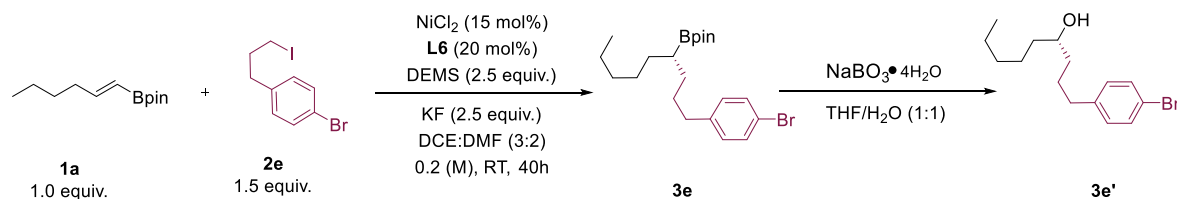
HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK[®] AD-H column, with hexane:isopropanol = 97:3 at a flow rate 0.5 mL/min detected at 230 nm wavelength. Elution time: $t_{\text{major}} = 40.3$ min and $t_{\text{minor}} = 38.7$ min.



The reaction of substrate **1p** with **2b** was conducted following **GP4**. A mixture of regioisomeric products were formed as observed by GC-MS. The yield of the desired product was very low (<10%) and the regioisomeric ratio was not determined. The enantiomeric excess (90%) was determined after oxidation (**GP2**) of the crude mixture (after work-up) via HPLC analysis which confirmed the same enantiomer as obtained from the reaction with its *trans* analogue **1a**.

14. Determination of the absolute configuration of 3e and 4g:

Absolute configuration of 3e:



(S)-1-(4-bromophenyl)nonan-4-ol (**3e'**) was obtained from the stereospecific oxidation of (S)-2-(1-(4-bromophenyl)nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**). The alcohol **3e'** was crystallized from a mixture of DCM/hexane at room temperature by slow evaporation. The crystal structure indicates the absolute configuration of **3e'** is (S). By analogy, we assign the corresponding absolute configurations to other products.

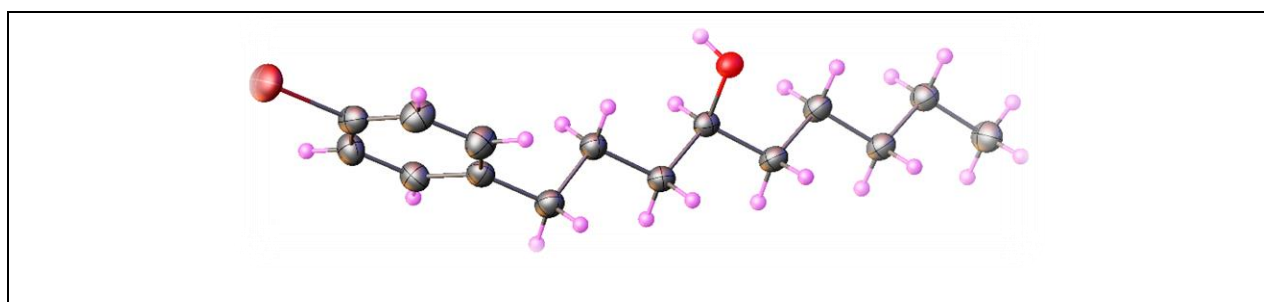
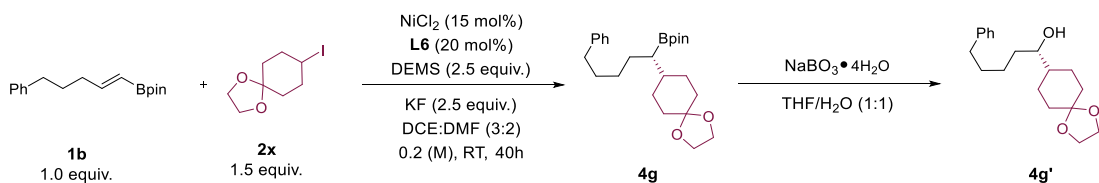


Fig. Crystal structure of **3e'**

Absolute configuration of 4g:



(S)-5-phenyl-1-(1,4-dioxaspiro[4.5]decan-8-yl)pentan-1-ol (**4g'**) was obtained from the stereospecific oxidation of (S)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(1,4-dioxaspiro[4.5]decan-8-yl)pentyl)-1,3,2-dioxaborolane (**4g**). The alcohol **4g'** was crystallized from a mixture of DCM/hexane at 4 °C. The crystal structure indicates the absolute configuration of **4g'** is (S). By analogy, we assign the corresponding absolute configurations to other products.

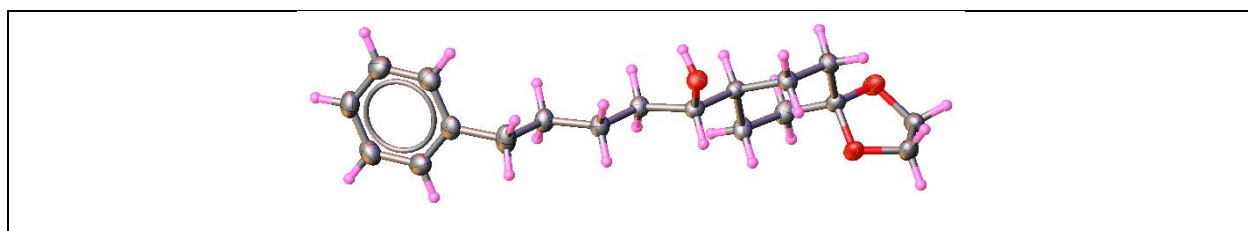


Fig. Crystal structure of **4g'**

15. Crystallography details

3e'

Experimental. Single colourless prism crystals of **3e'** were used as supplied. A suitable crystal with dimensions $0.35 \times 0.17 \times 0.04 \text{ mm}^3$ was selected and mounted on a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer. The crystal was kept at a steady $T = 140.00(10) \text{ K}$ during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2015) solution program using dual methods and by using **Olex2** (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 .

Compound	3e'
Formula	$\text{C}_{15}\text{H}_{23}\text{BrO}$
$D_{\text{calc.}}/\text{g cm}^{-3}$	1.343
μ/mm^{-1}	3.639
Formula Weight	299.24
Colour	colourless
Shape	prism
Size/ mm^3	$0.35 \times 0.17 \times 0.04$
T/K	140.00(10)
Crystal System	monoclinic
Flack Parameter	-0.034(13)
Hooft Parameter	-0.037(5)
Space Group	$P2_1$
$a/\text{\AA}$	9.52472(11)
$b/\text{\AA}$	4.93139(5)
$c/\text{\AA}$	15.77317(18)
α°	90
β°	92.4023(10)
γ°	90
$V/\text{\AA}^3$	740.216(14)
Z	2
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	$\text{CuK}\alpha$

$\Theta_{min}/^\circ$	4.647
$\Theta_{max}/^\circ$	76.118
Measured Refl's.	14280
Ind't Refl's	3058
Refl's with $I > 2\sigma(I)$	3024
R_{int}	0.0217
Parameters	160
Restraints	1
Largest Peak/e $\text{\AA}^{-3}$	0.226
Deepest Hole/e $\text{\AA}^{-3}$	-0.251
GooF	1.059
wR_2 (all data)	0.0519
wR_2	0.0517
R_I (all data)	0.0195
R_I	0.0193

Structure Quality Indicators

Reflections:	d min (Cu) CIF 0.79	I/σ CIF 68.0	R_{int} CIF 2.17%	complete 100% (IUCr)	100%
Refinement:	Shift CIF 0.000	Max Peak CIF 0.2	Min Peak CIF -0.3	GooF CIF 1.059	Flack CIF 0.034(13)

A colourless prism-shaped crystal with dimensions $0.35 \times 0.17 \times 0.04 \text{ mm}^3$ was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at $T = 140.00(10) \text{ K}$.

Data were measured using ω scans using 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 1.171.40.81a (Rigaku OD, 2020). The maximum resolution achieved was $\Theta = 76.118^\circ$ (0.79 $\text{\AA}$).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro 1.171.40.81a (Rigaku OD, 2020). The unit cell was refined using CrysAlisPro 1.171.40.81a (Rigaku OD, 2020) on 11785 reflections, 83% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro 1.171.40.81a (Rigaku OD, 2020). The final completeness is 99.90 % out to 76.118° in Θ . A Gaussian absorption correction was performed using CrysAlisPro 1.171.40.81a (Rigaku Oxford Diffraction, 2020) 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 3.639 mm^{-1} at this wavelength ($\lambda = 1.54184 \text{ \AA}$) and the minimum and maximum transmissions are 0.295 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 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. Most hydrogen atom positions were calculated geometrically and refined using the riding model, but some hydrogen atoms were refined freely.

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 -0.034(13). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.037(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- 2011678 contains the supplementary crystallographic data for **3e'**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

4g'

Experimental. Single clear intense red plate crystals of **4g'** were used as supplied. A suitable crystal with dimensions of $0.75 \times 0.39 \times 0.17 \text{ mm}^3$ was selected and mounted on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady $T = 139.94(12) \text{ K}$ during data collection. The structure was solved with the **ShelXT** 2018/2 solution program using dual methods and by using **Olex2** as the graphical interface. The model was refined with **ShelXL** 2018/3 using full matrix least squares minimisation on $|F|^2$.

Compound	4g'
Formula	$\text{C}_{19}\text{H}_{28}\text{O}_3$
$D_{\text{calc.}} / \text{g cm}^{-3}$	1.174
μ / mm^{-1}	0.613
Formula Weight	304.41
Colour	clear colourless
Shape	plate
Size/ mm^3	$0.75 \times 0.39 \times 0.17$
T / K	139.94(12)
Crystal System	orthorhombic
Flack Parameter	0.04(16)
Space Group	$P2_12_12_1$

$a/\text{\AA}$	5.30185(5)
$b/\text{\AA}$	9.59127(10)
$c/\text{\AA}$	33.8681(3)
α°	90
β°	90
γ°	90
$V/\text{\AA}^3$	1722.24(3)
Z	4
Z'	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu $K\alpha$
Θ_{min}°	2.609
Θ_{max}°	76.013
Measured Refl.	15899
Independent Refl.	3578
Reflections with $I > 2(I)$	3546
R_{int}	0.0154
Parameters	313
Restraints	0
Largest Peak/e $\text{\AA}^{-3}$	0.215
Deepest Hole/e $\text{\AA}^{-3}$	-0.123
GooF	1.059
wR_2 (all data)	0.0711
wR_2	0.0709
R_I (all data)	0.0254
R_I	0.0252

Structure Quality Indicators

Reflections:	d min (Cu) CIF 0.79	I/ σ CIF 85.9	Rint CIF 1.54%	complete CIF 100%
Refinement:	Shift CIF 0.001	Max Peak CIF 0.2	Min Peak CIF -0.1	Goof CIF 1.059

Data were measured using ω scans using Cu $K\alpha$ radiation. The total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} (Rigaku, V1.171.40.62a, 2019). The maximum resolution achieved was $\Theta = 76.013^\circ$ (0.79 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlis^{Pro} (Rigaku, V1.171.40.62a, 2019) and the unit cell was refined using CrysAlis^{Pro} (Rigaku, V1.171.40.62a, 2019) on 12356 reflections, 78% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlis^{Pro} (Rigaku, V1.171.40.62a, 2019). The final completeness is 100.00 % out to 76.013° in Θ . A Gaussian absorption correction was performed using CrysAlis^{Pro} 1.171.40.62a (Rigaku Oxford Diffraction, 2019) 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 0.613 mm^{-1} at this wavelength ($\lambda = 1.542 \text{ Å}$) and the minimum and maximum transmissions are 0.468 and 1.000.

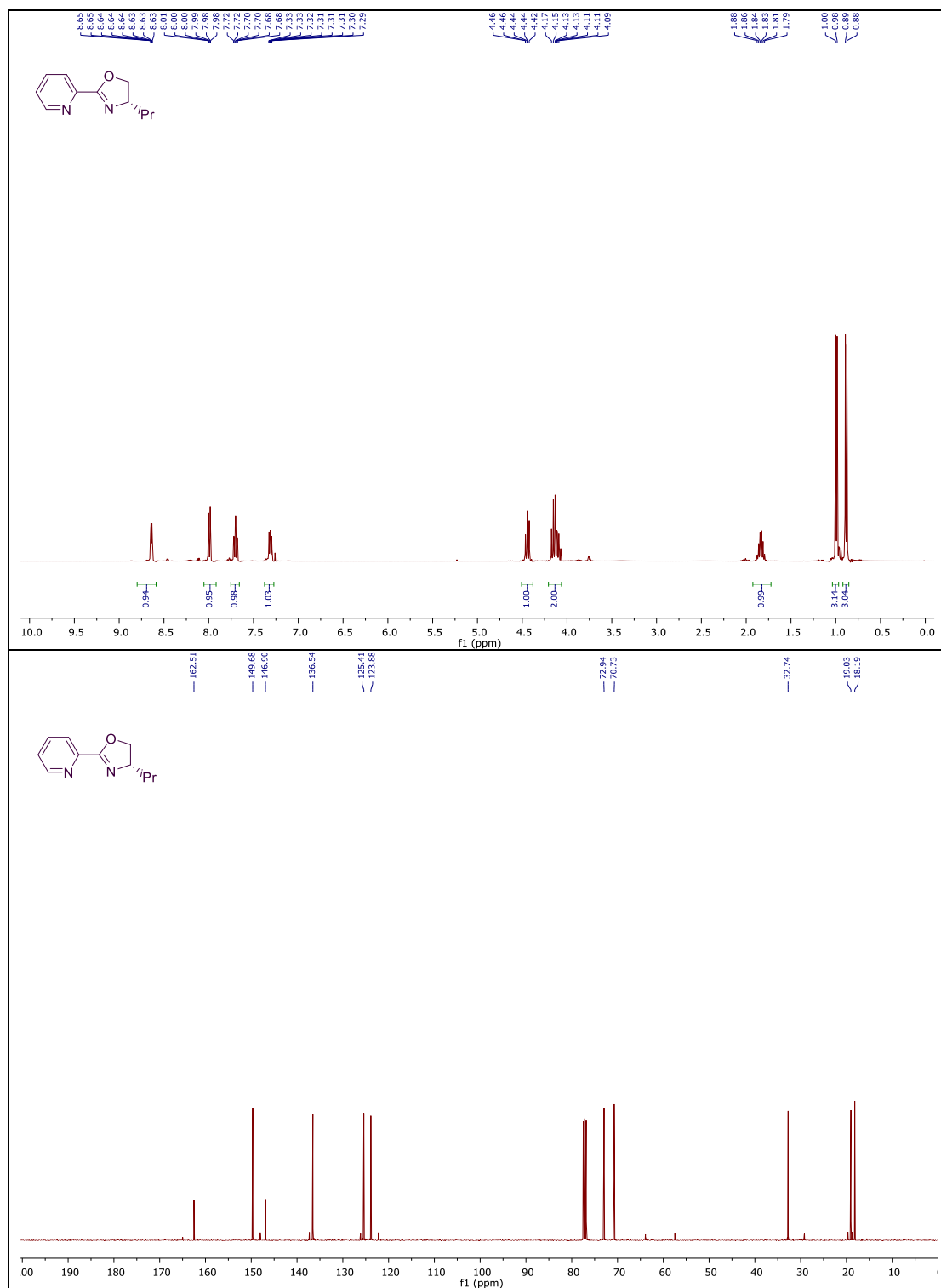
The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT 2018/2 structure solution program using dual methods and refined by full matrix least squares minimisation on $|F|^2$ using version 2018/3 of ShelXL 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were found in a difference map and refined freely.

This structure was refined as a 2-component inversion twin.

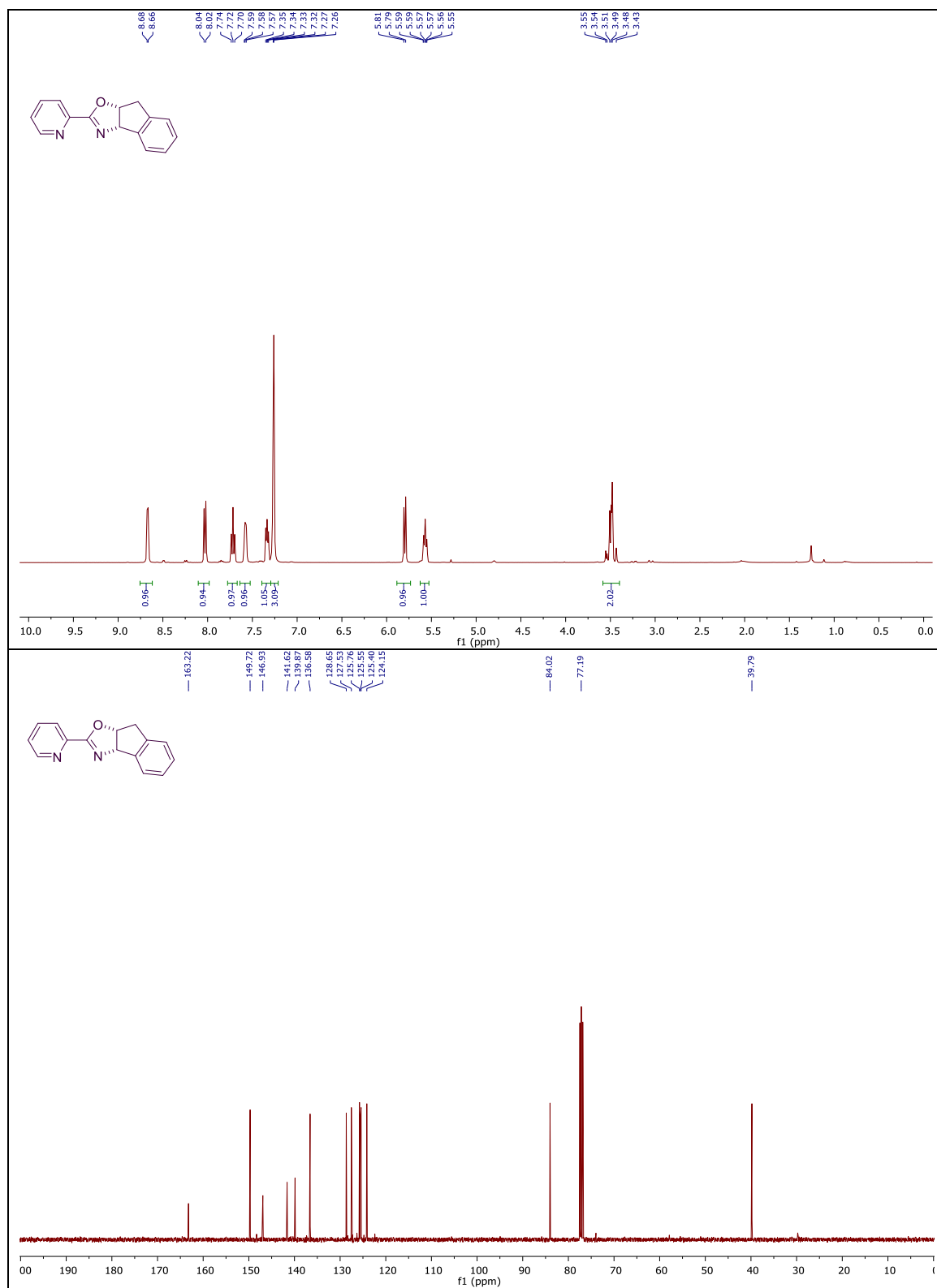
CCDC- 1971802 contains the supplementary crystallographic data for **4g'**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre* via www.ccdc.cam.ac.uk/data_request/cif.

16. NMR spectra

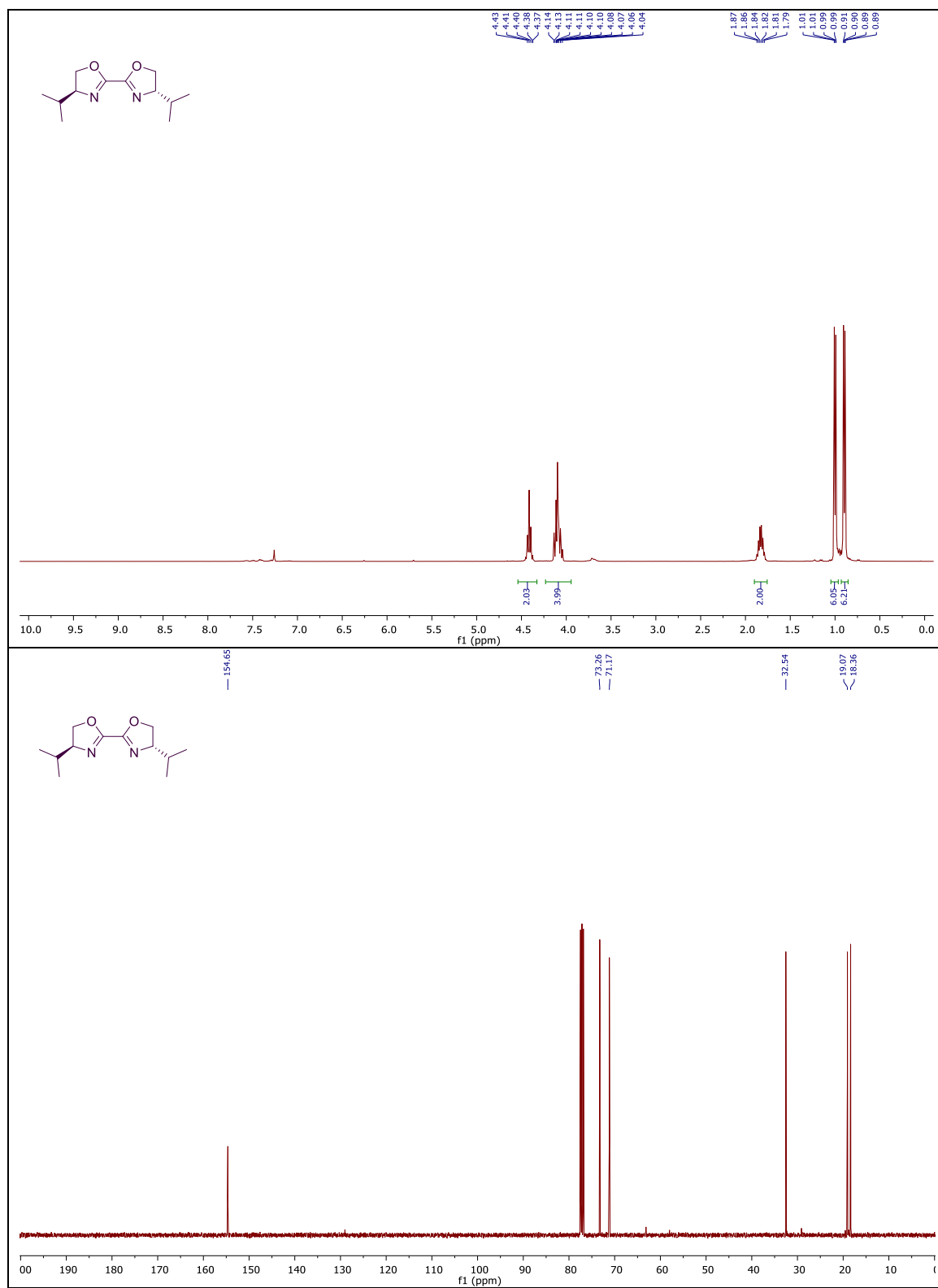
NMR spectra of L1



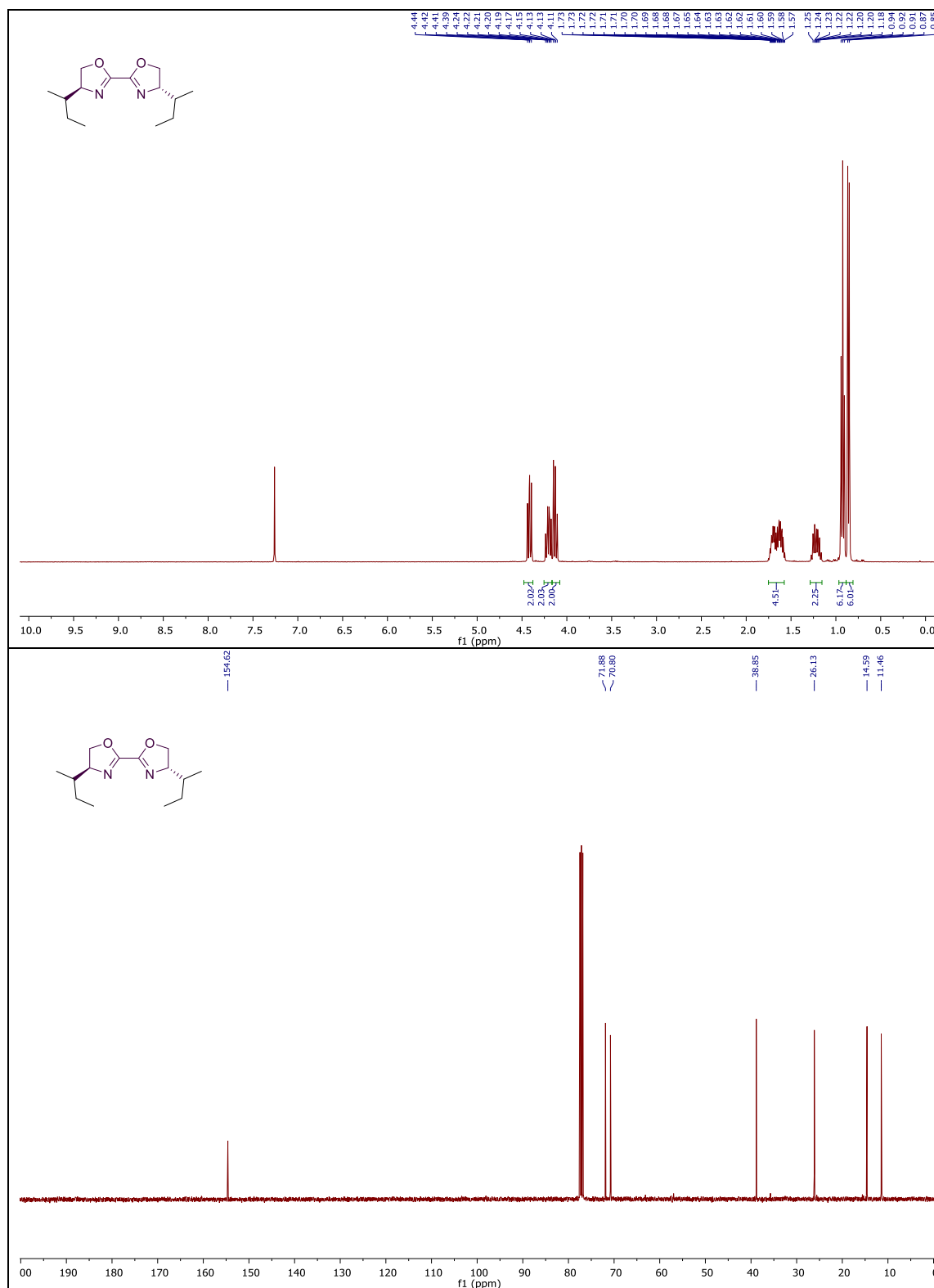
NMR spectra of L2



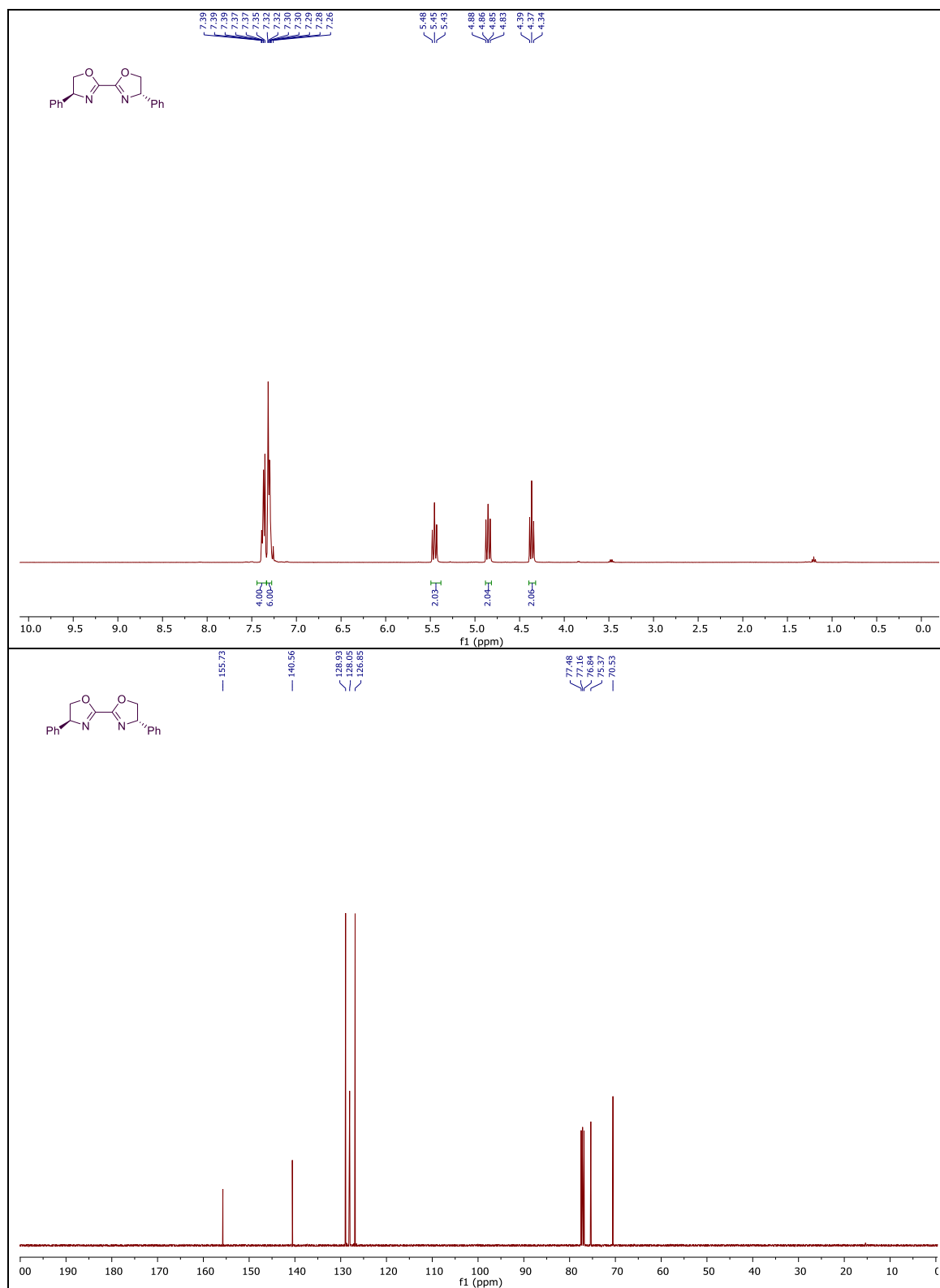
NMR spectra of L4



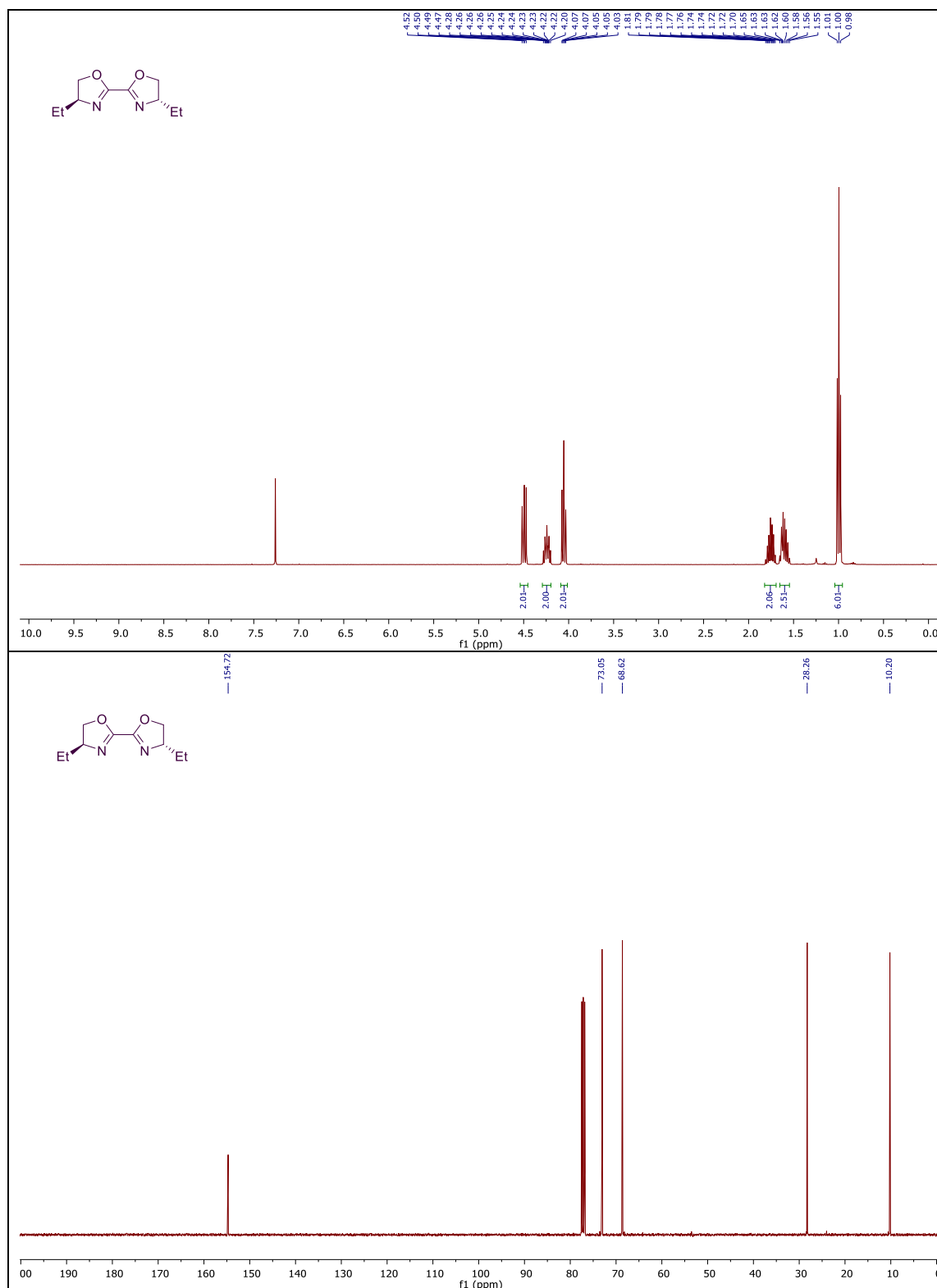
NMR spectra of L5



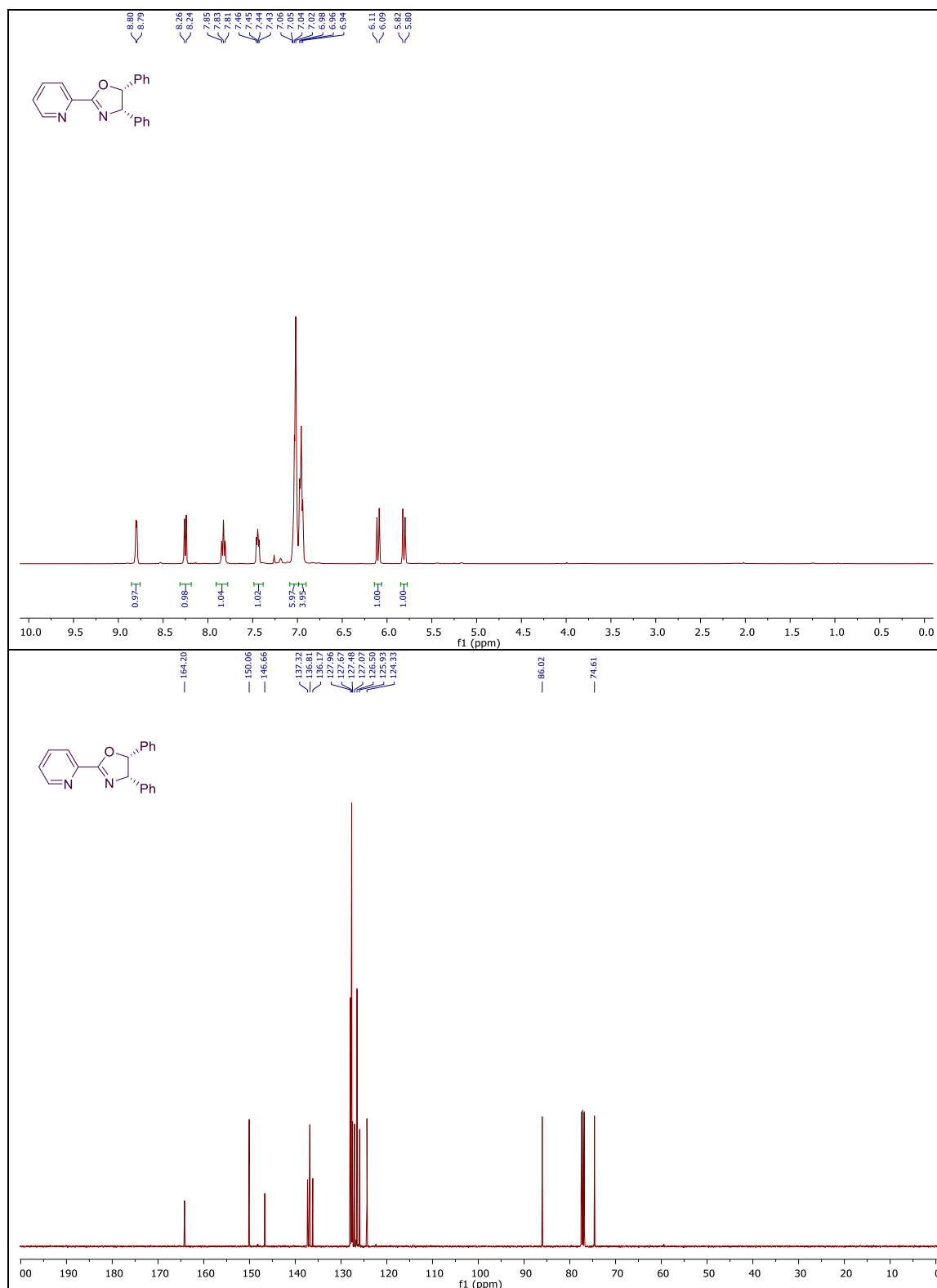
NMR spectra of L6



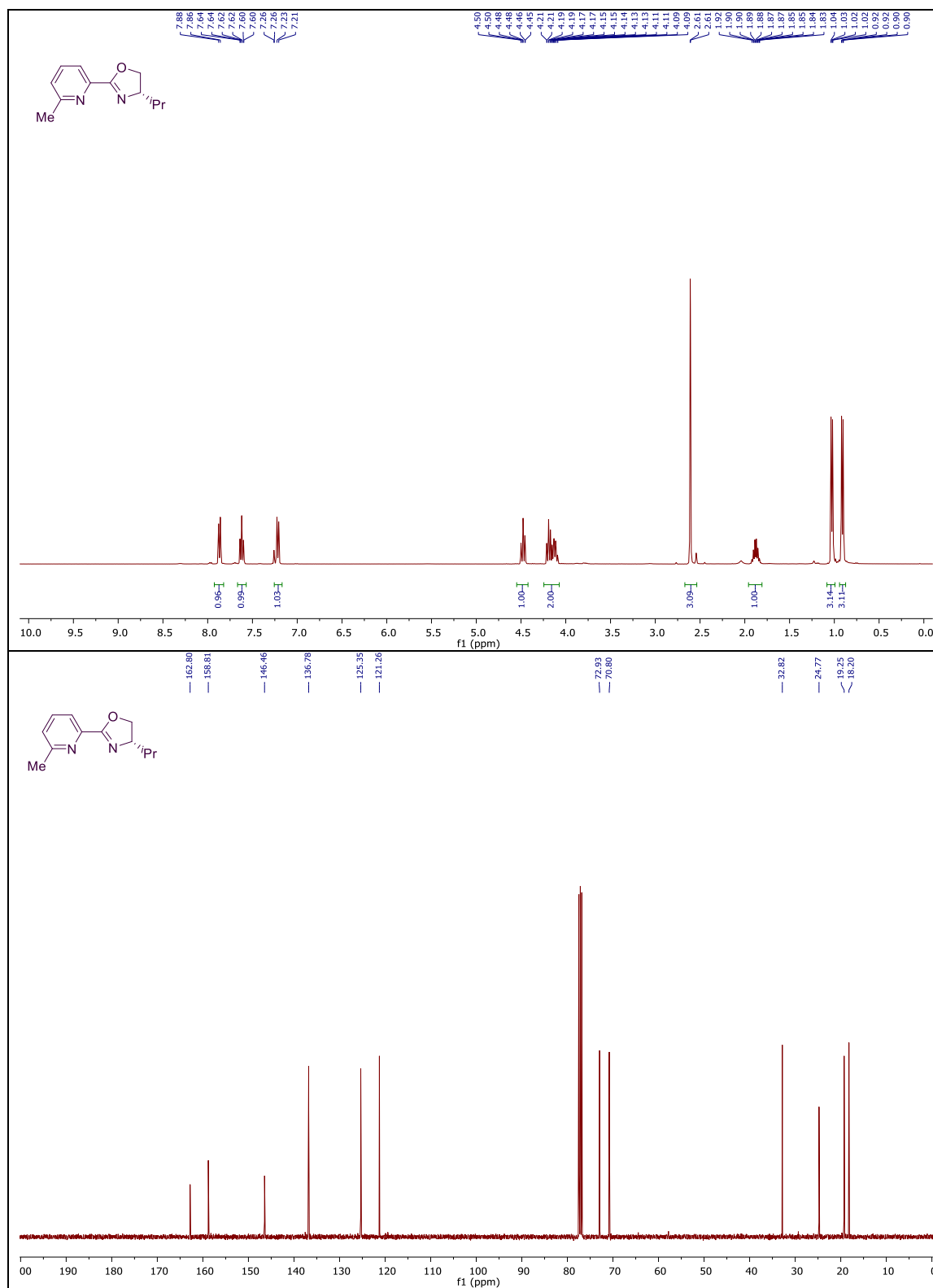
NMR spectra of L7



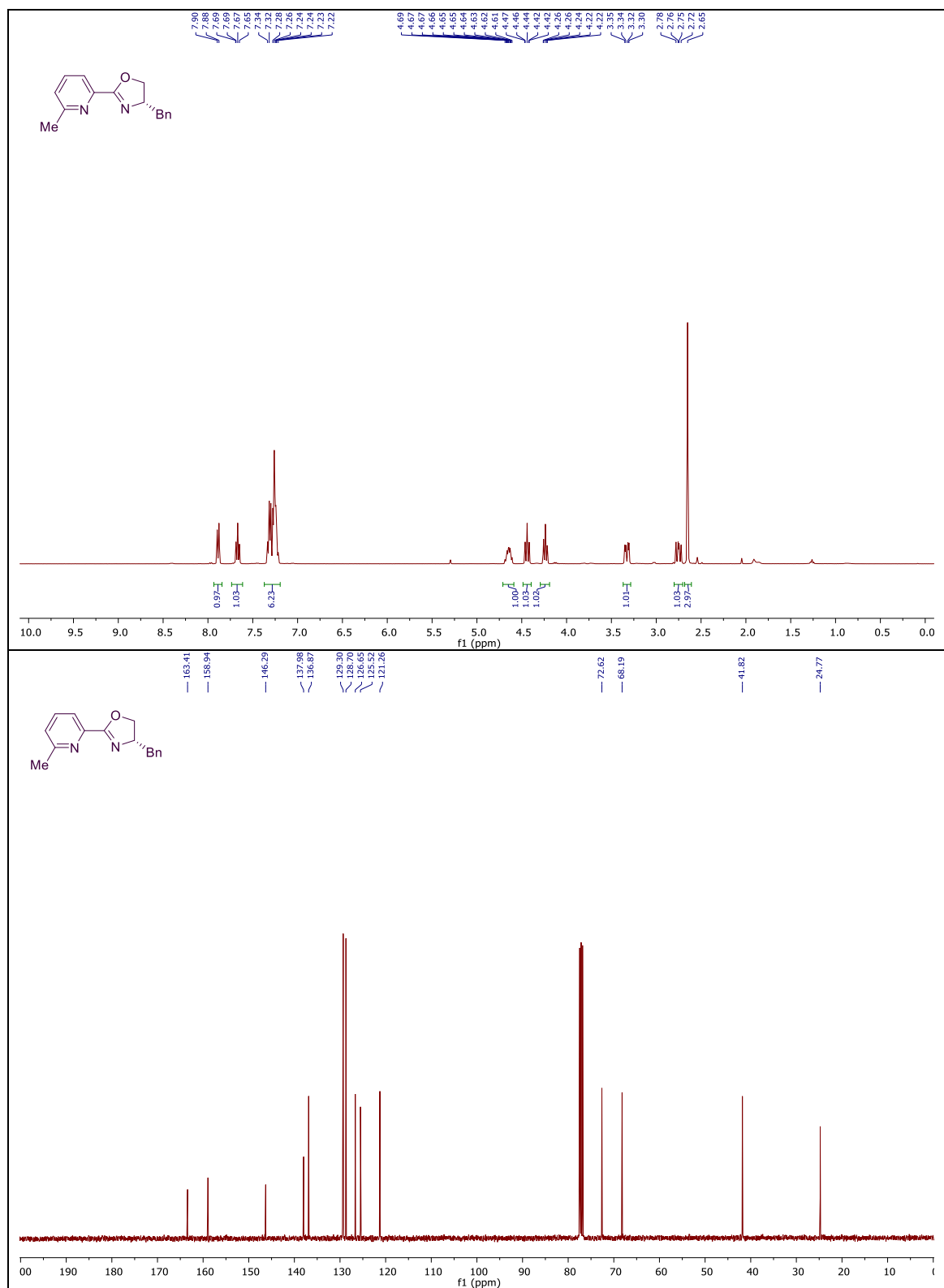
NMR spectra of L9



NMR spectra of L10



NMR spectra of L11



The figure displays the chemical structure of 2-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-indole and its corresponding ¹H and ¹³C NMR spectra.

Chemical Structure: C1=CC=C2C(=C1)C(=CN2)C3=CC=CC=C4C(=C3)CC=CC4

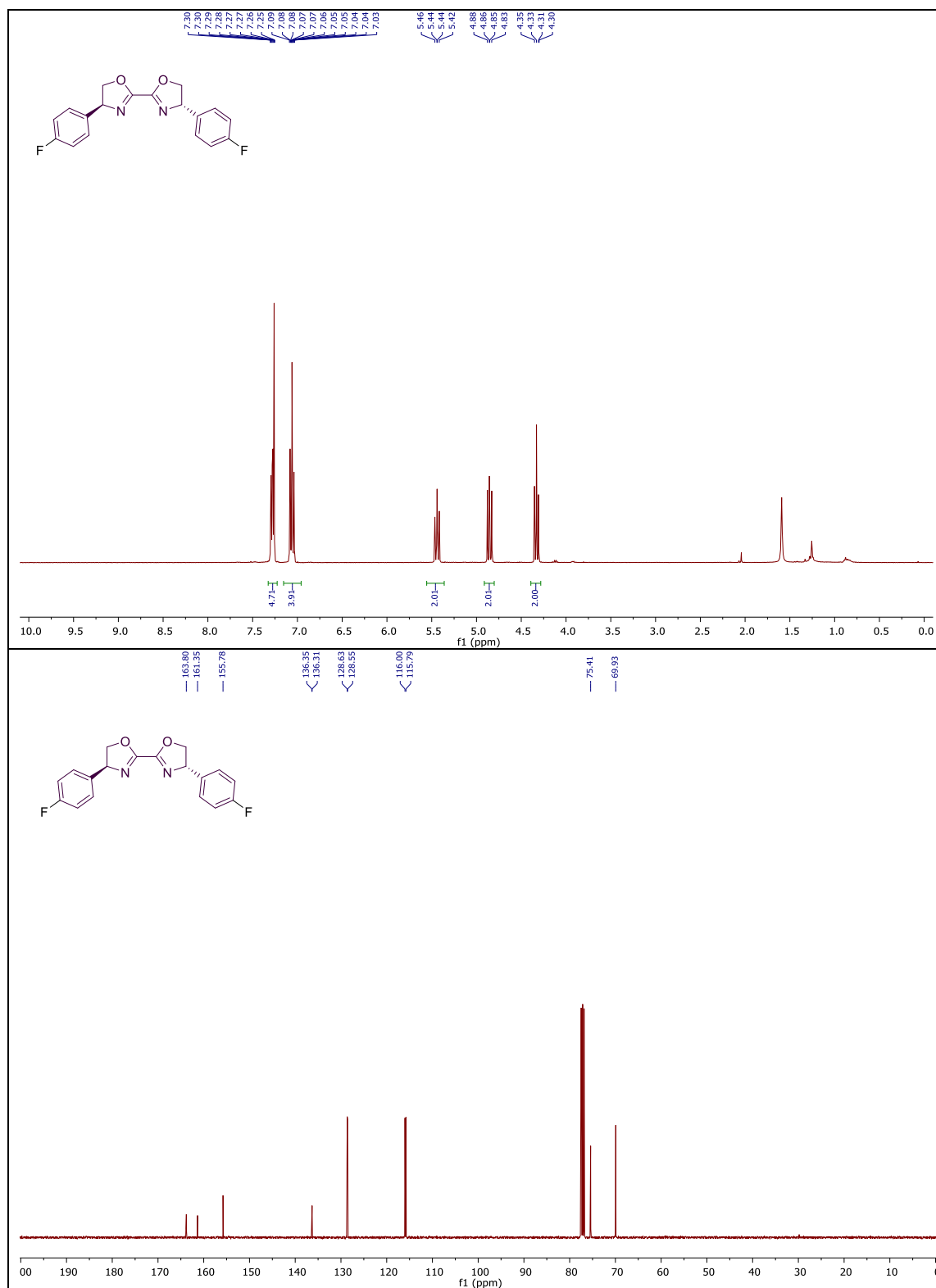
¹H NMR Spectrum (Top): The spectrum shows peaks in the aromatic region (7.30-9.20 ppm) and aliphatic region (1.50-2.00 ppm). Integration values are provided below the peaks.

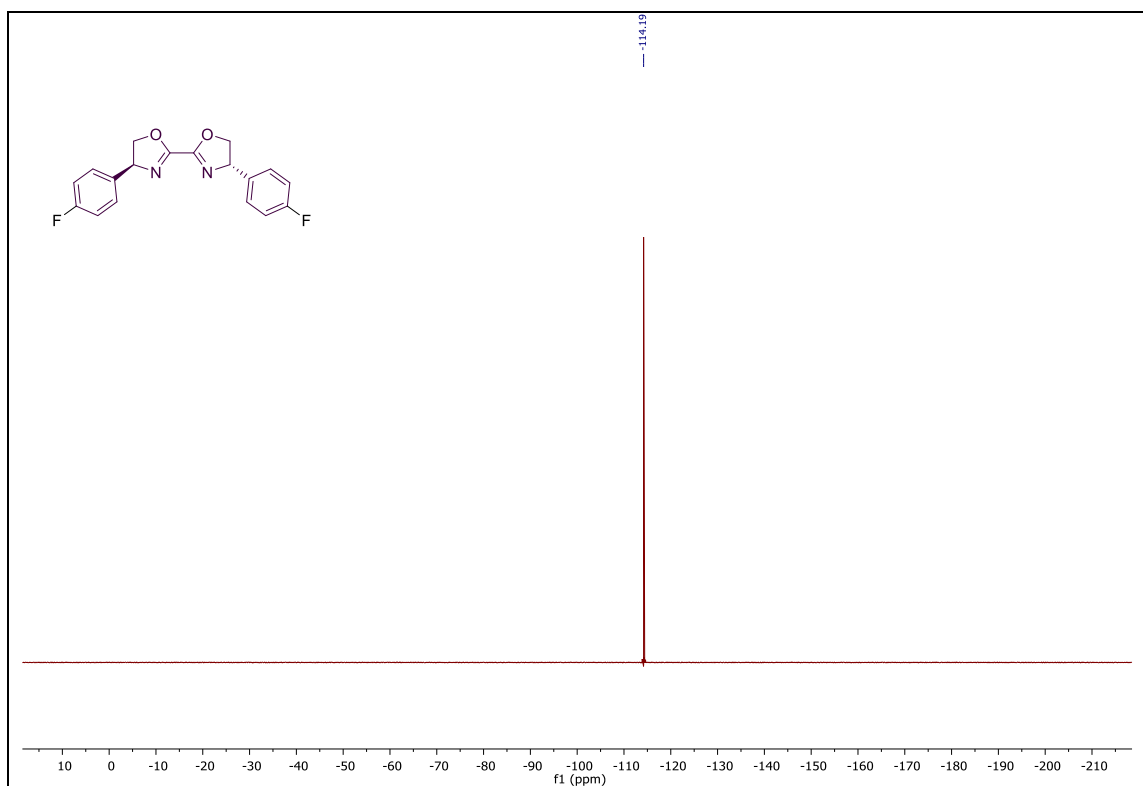
Chemical Shift (ppm)	Integration
9.20	1.00
8.61	1.00
7.72	1.04
7.65	4.02
7.30	2.94
6.00	1.00
5.61	1.00
3.57	2.05

¹³C NMR Spectrum (Bottom): The spectrum shows peaks in the aromatic region (122.49-162.56 ppm) and aliphatic region (39.91 ppm).

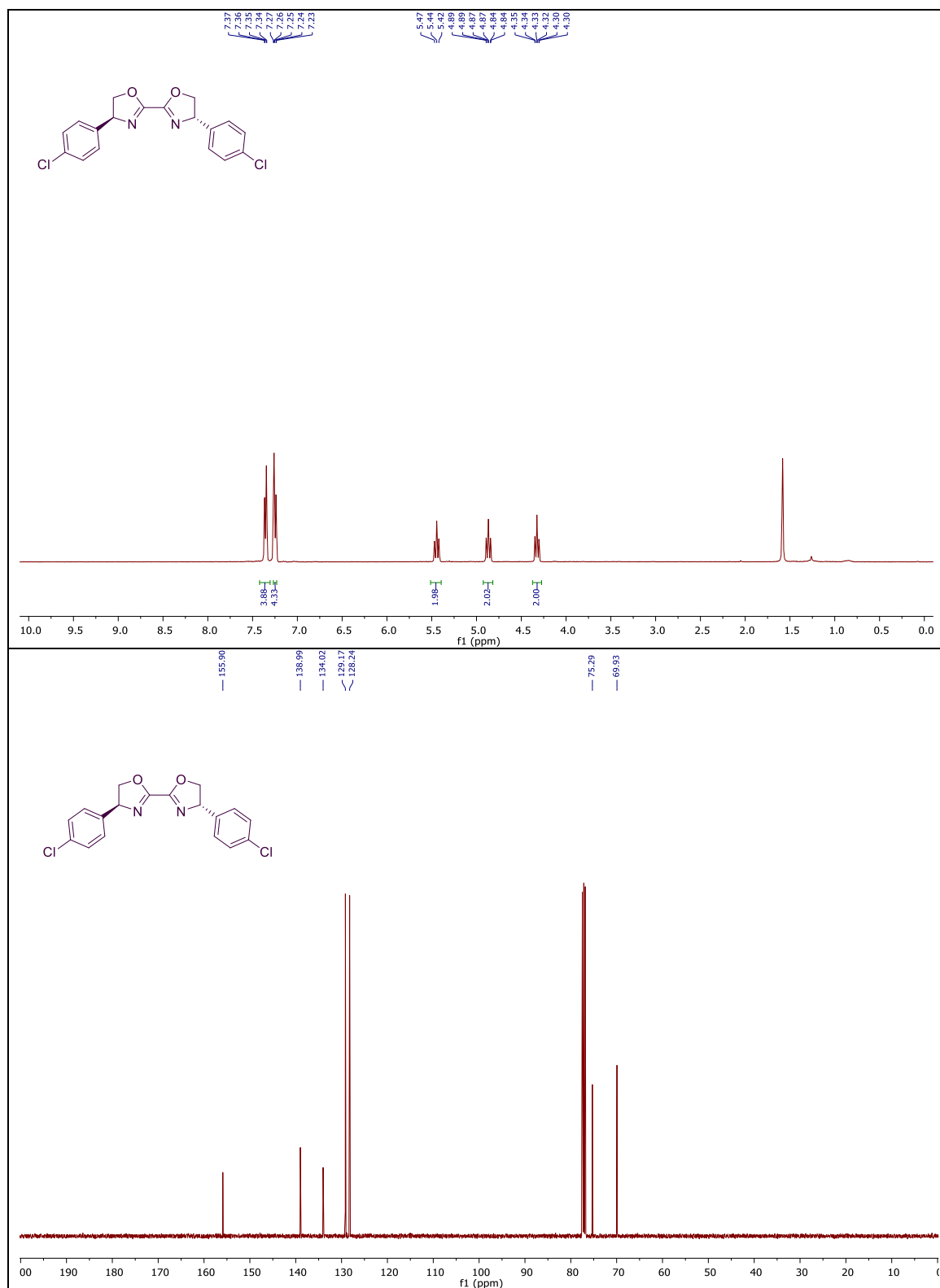
Chemical Shift (ppm)
162.56
146.42
141.88
141.84
136.83
130.47
128.76
128.57
127.64
127.51
127.08
125.75
125.61
122.49
82.91
78.04
39.91

NMR spectra of L17

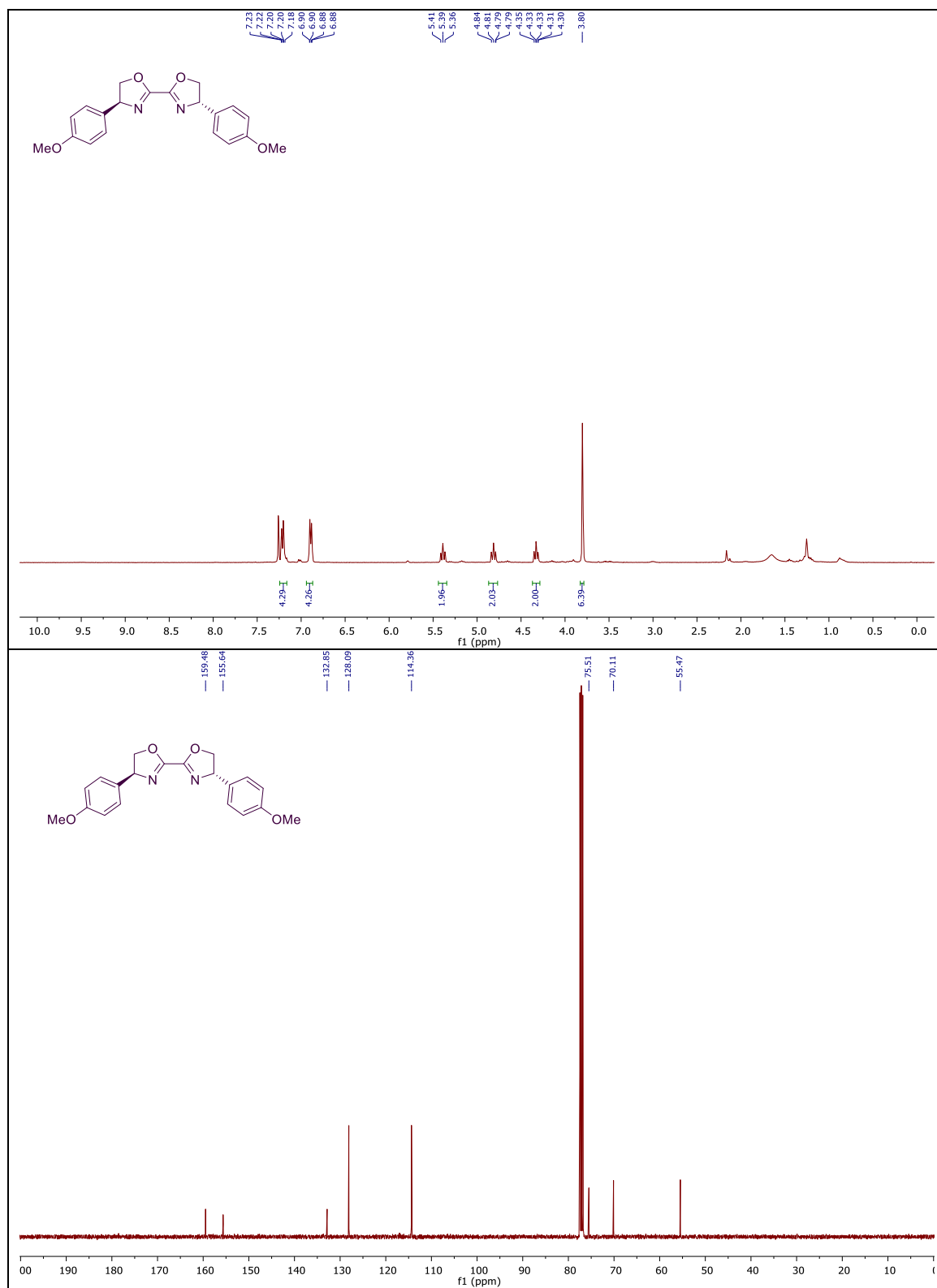




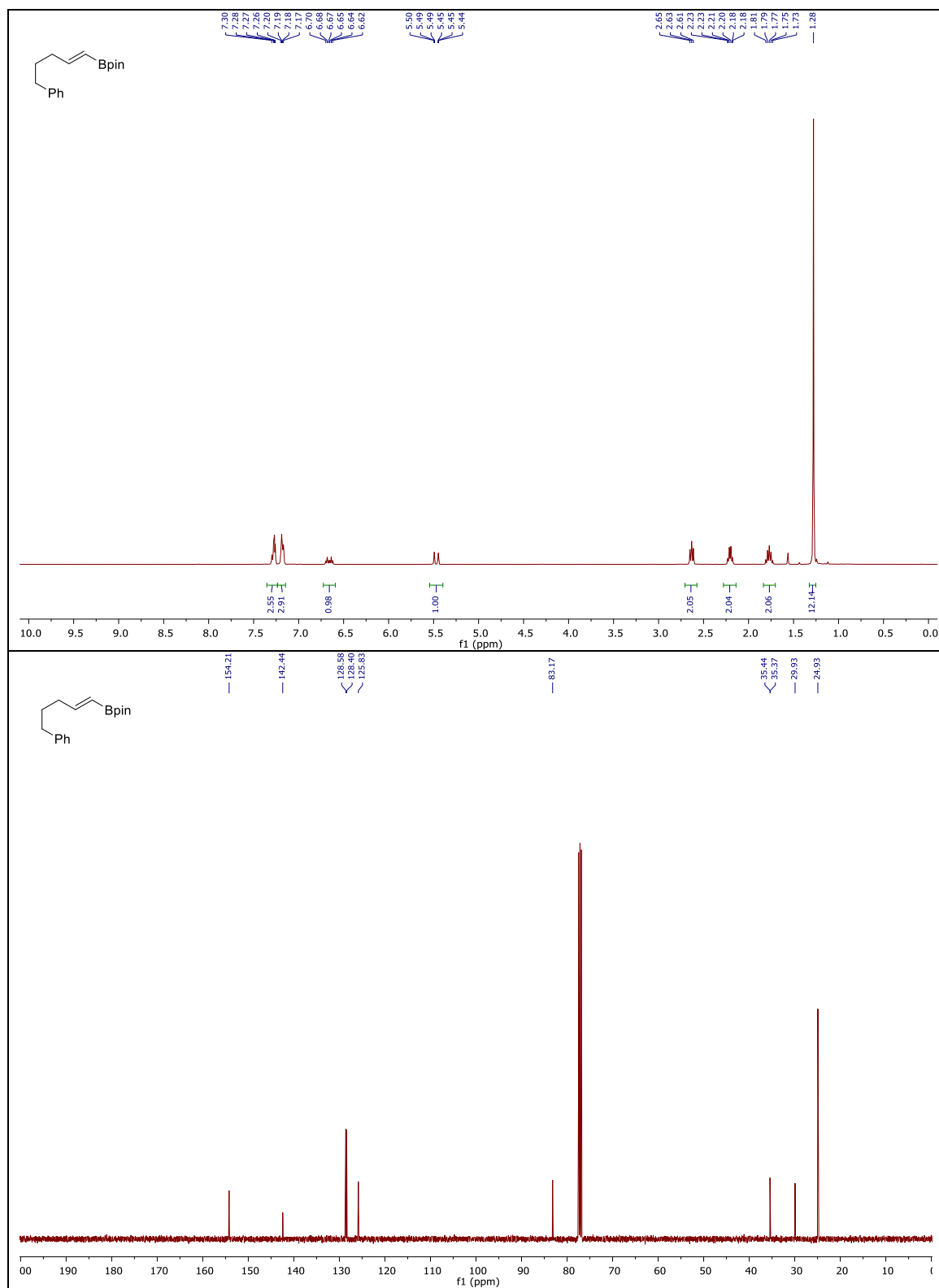
NMR spectra of L18



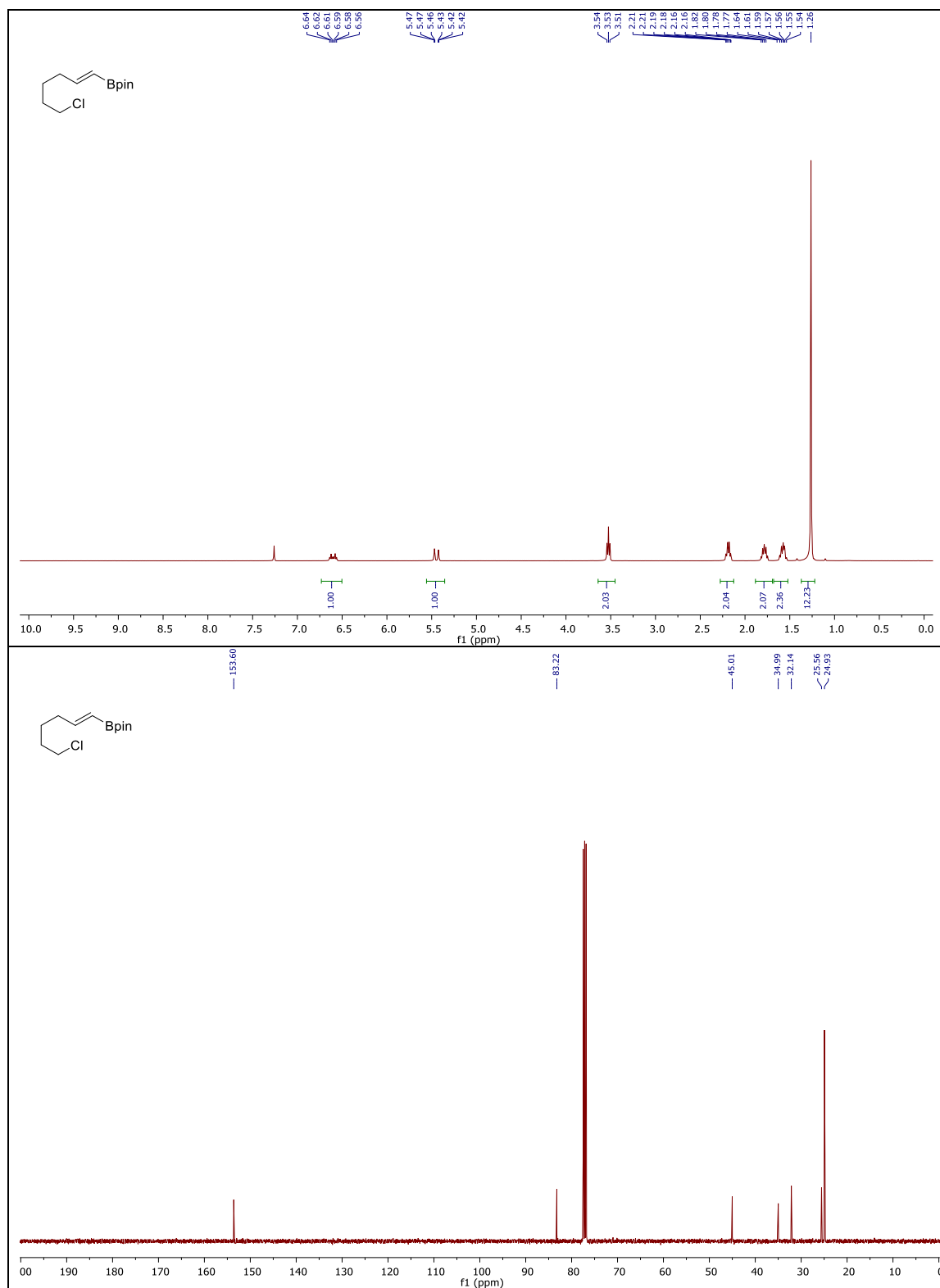
NMR spectra of L19



NMR spectra of 1b



NMR spectra of 1c



¹H NMR (400 MHz, CDCl₃)

Chemical structure: CCCCC/C=C/B1OC(C)(C)C(C)(C)C1 (Methyl 6-(pinacolat-1-en-1-yl)hexanoate)

Peak list (ppm): 6.62, 6.60, 6.59, 6.57, 6.56, 6.54, 5.47, 5.47, 5.47, 5.43, 5.43, 5.42, 3.66, 2.34, 2.32, 2.30, 2.22, 2.22, 2.21, 2.20, 2.20, 2.18, 2.18, 2.17, 2.16, 1.80, 1.78, 1.76, 1.74, 1.26.

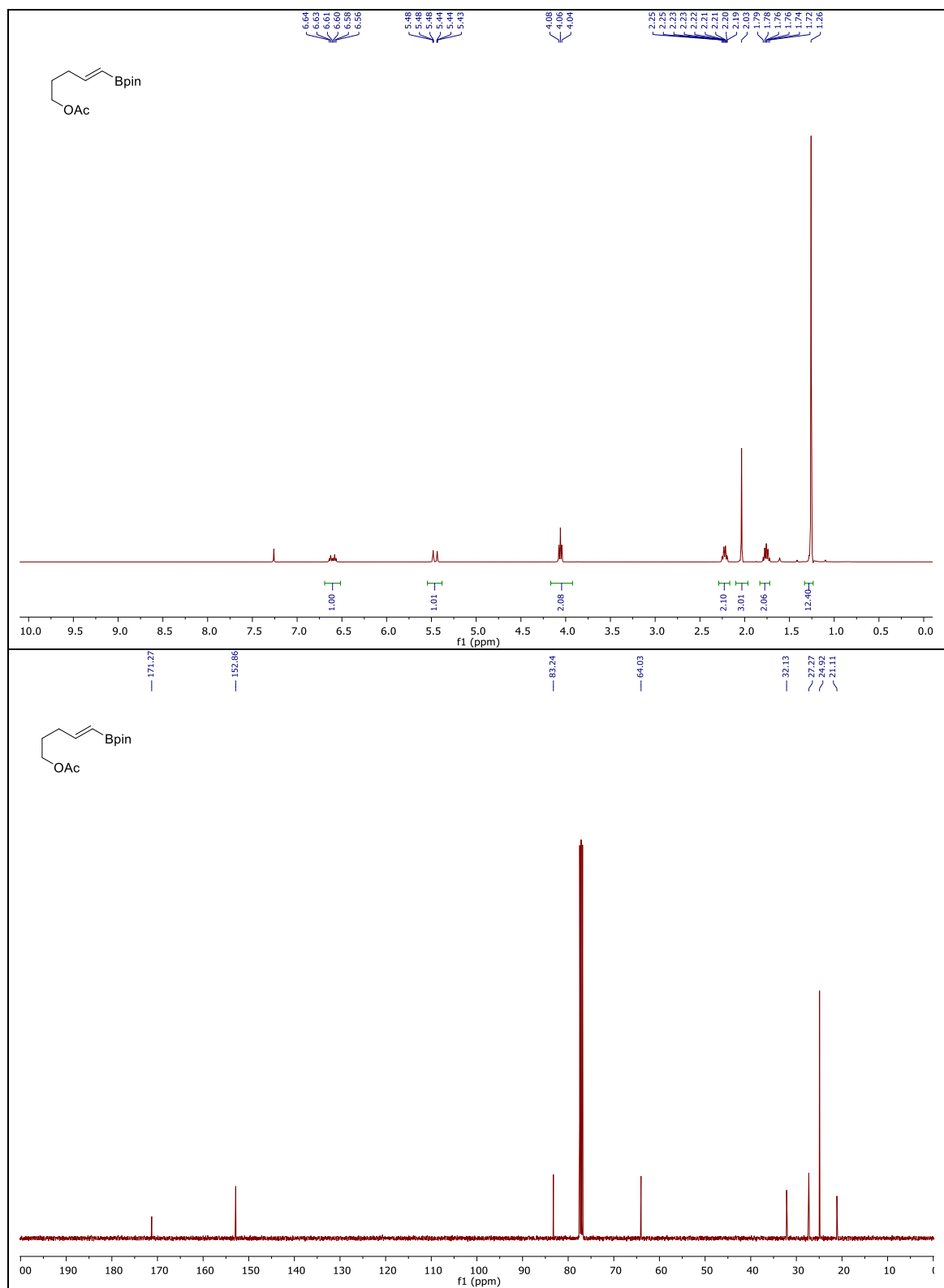
Integration values: 1.00, 1.01, 2.93, 2.00, 2.01, 2.01, 11.95.

¹³C NMR (100 MHz, CDCl₃)

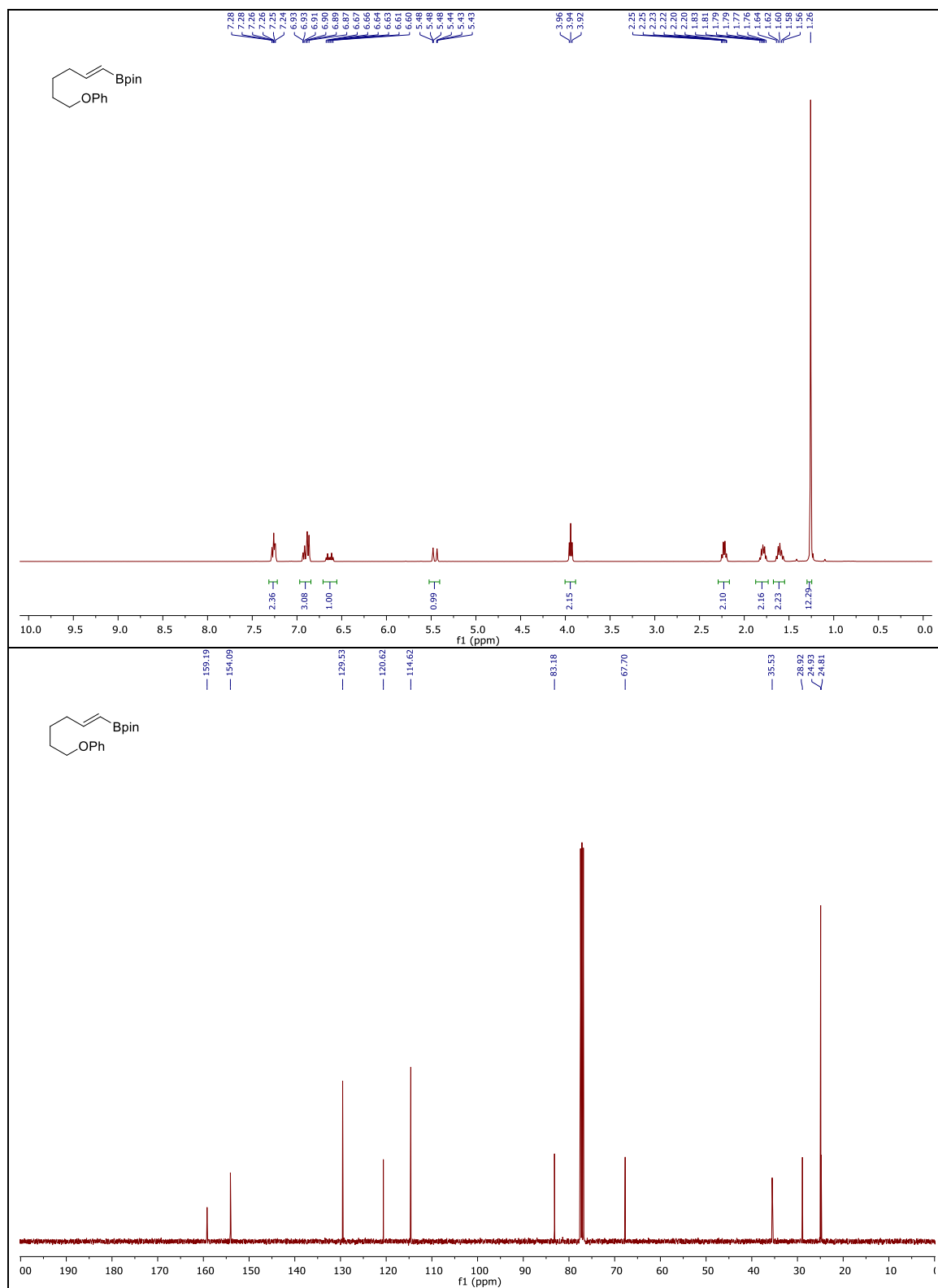
Chemical structure: CCCCC/C=C/B1OC(C)(C)C(C)(C)C1 (Methyl 6-(pinacolat-1-en-1-yl)hexanoate)

Peak list (ppm): 174.05, 153.06, 83.22, 51.62, 35.08, 33.52, 24.93, 23.52.

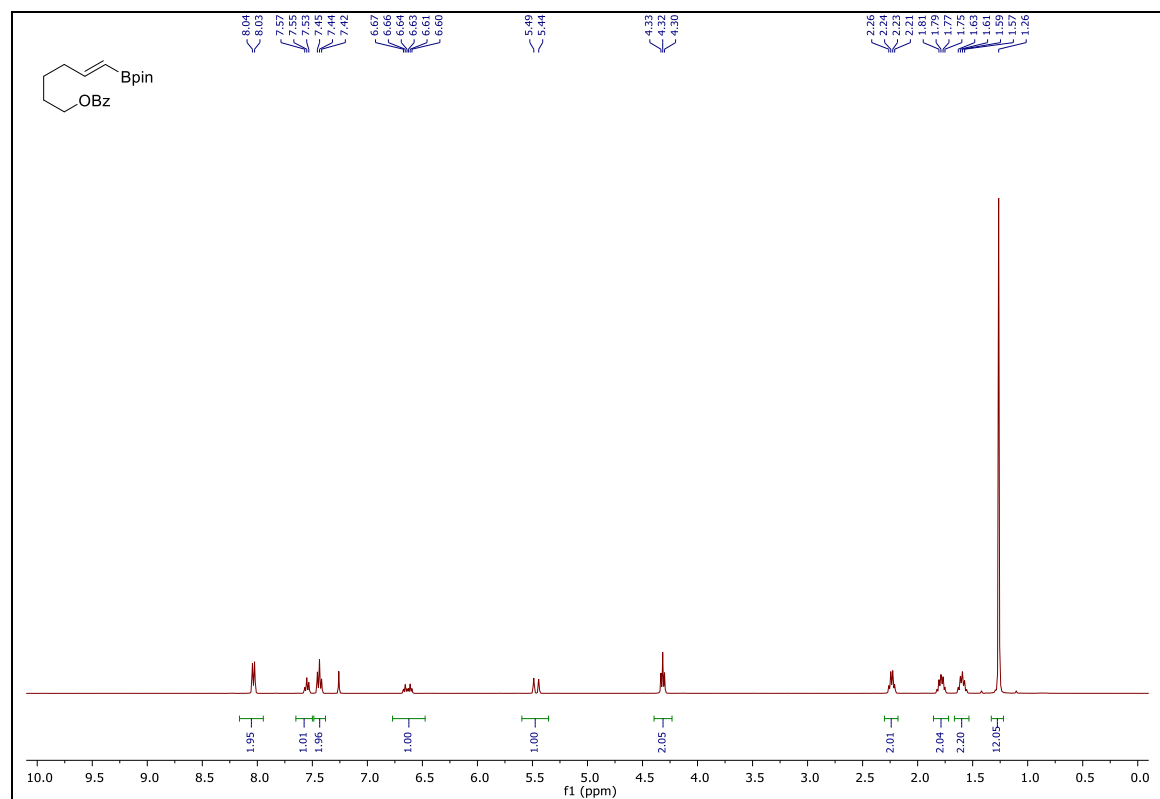
NMR spectra of 1e

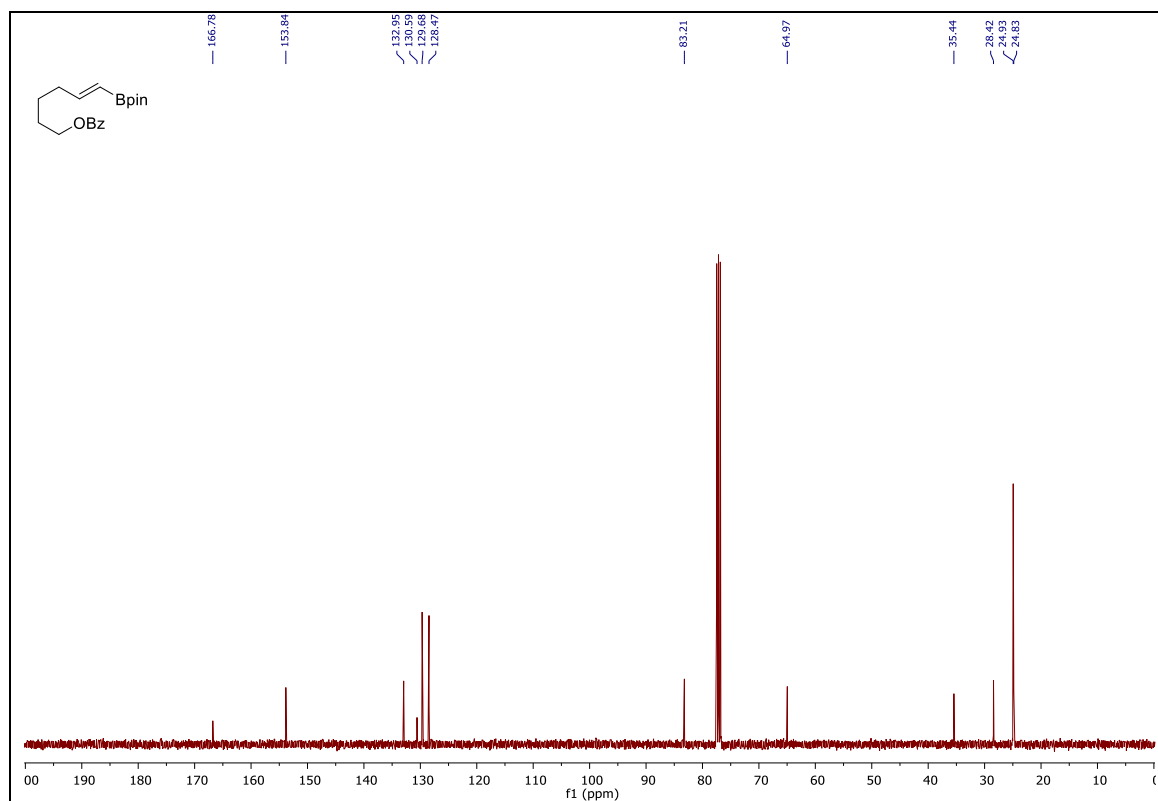


NMR spectra of 1f



NMR spectra of 1g





The figure displays two NMR spectra for the compound (E)-4-(tert-butyldimethylsilyl)-1-pentene, which is shown as a chemical structure at the top left of each spectrum.

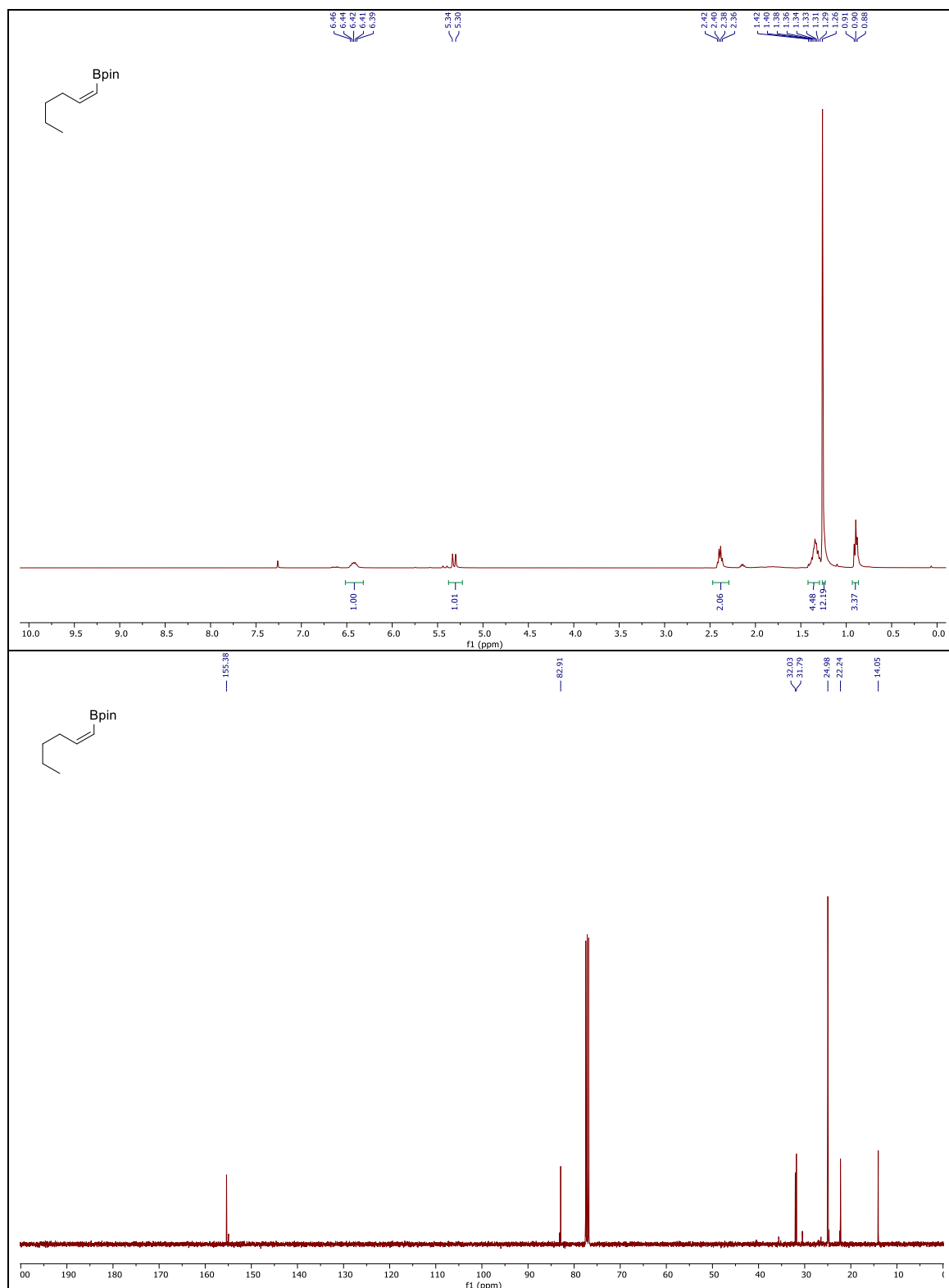
¹H NMR Spectrum (Top): The x-axis represents the chemical shift in ppm, ranging from 10.0 to 0.0. The spectrum shows several peaks with corresponding integrations and coupling constants (J values) indicated above the peaks.

Chemical Shift (ppm)	Integration	J (Hz)
~7.2	1.00	-
~6.6	1.01	-
~5.4	2.07	-
~2.4	2.06	-
~1.2	12.15	-
~0.9	9.26	-
~0.1	6.13	-

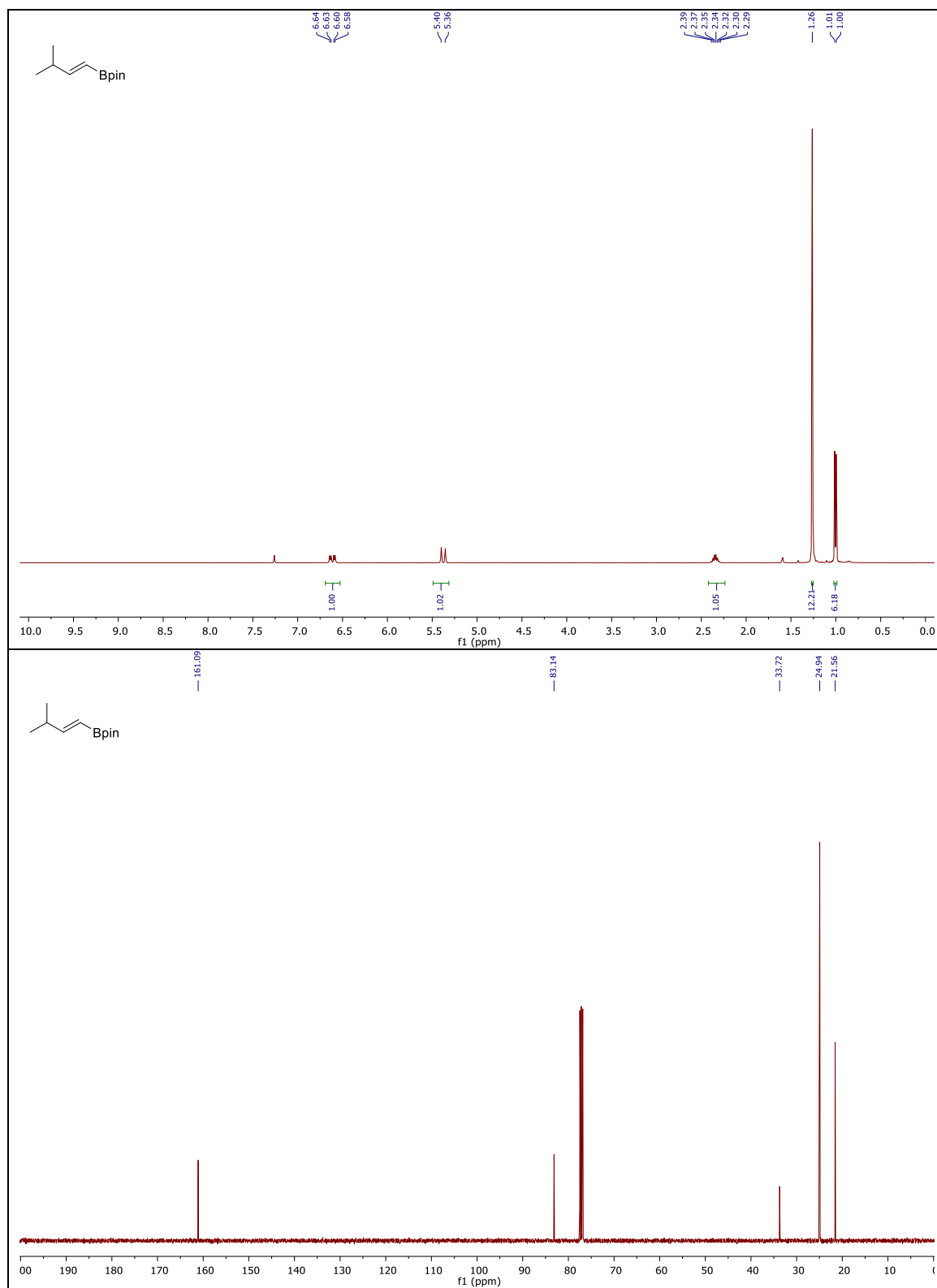
¹³C NMR Spectrum (Bottom): The x-axis represents the chemical shift in ppm, ranging from 0 to 200. The spectrum shows several peaks, with chemical shift values labeled above them.

Chemical Shift (ppm)
158.81
83.20
62.41
39.60
26.11
24.91
18.53
-5.10

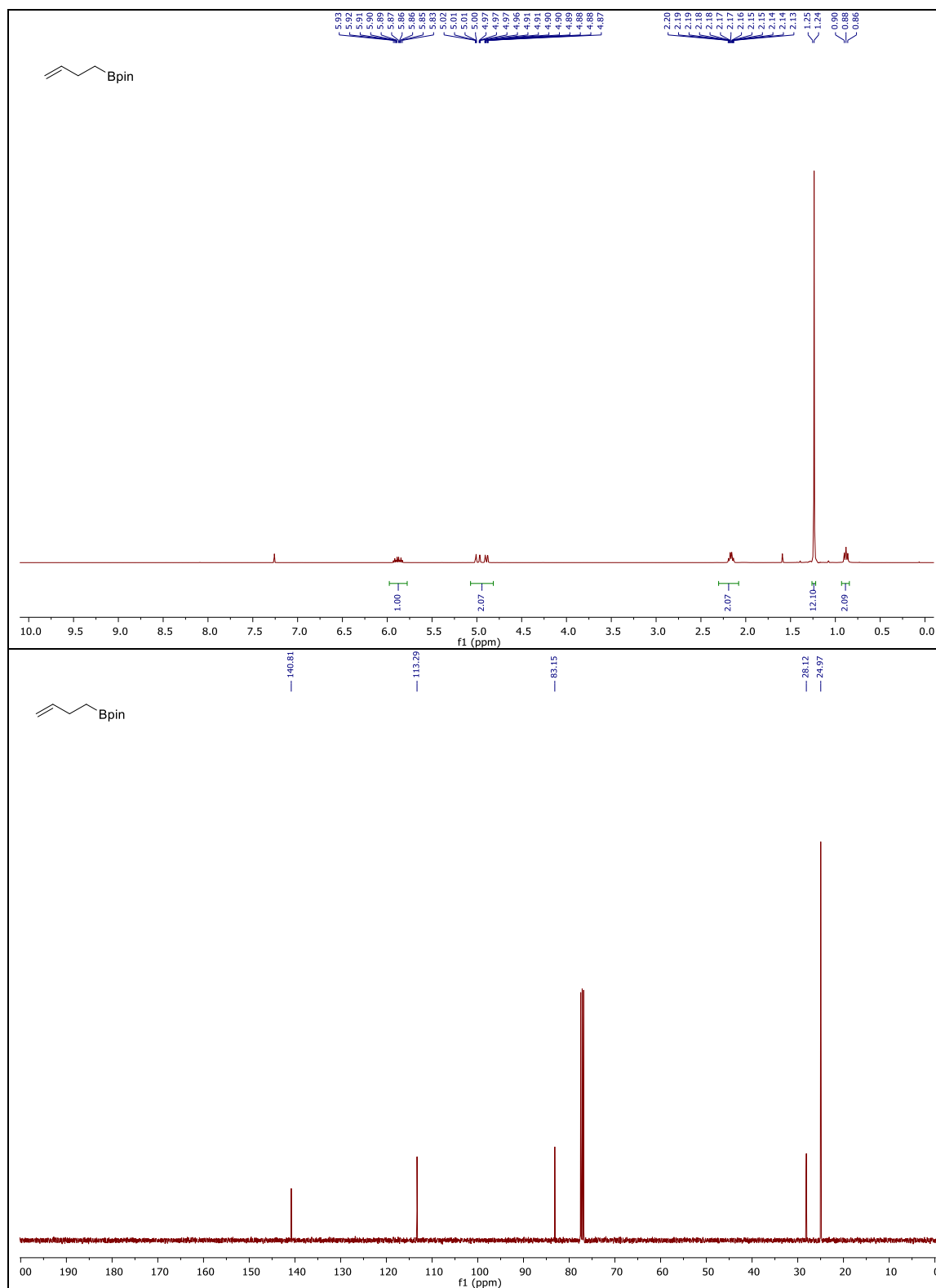
NMR spectra of 11



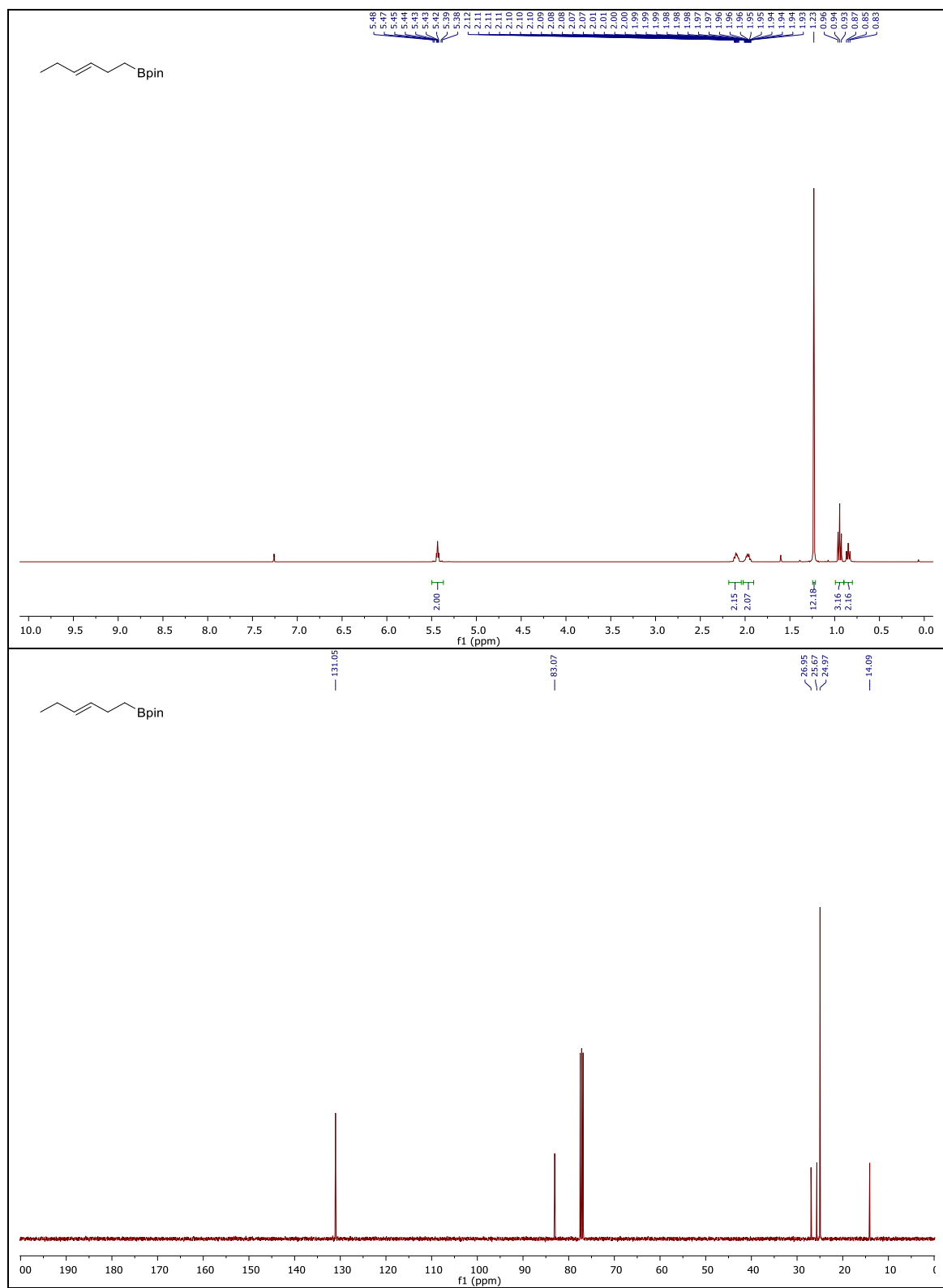
NMR spectra of 1m



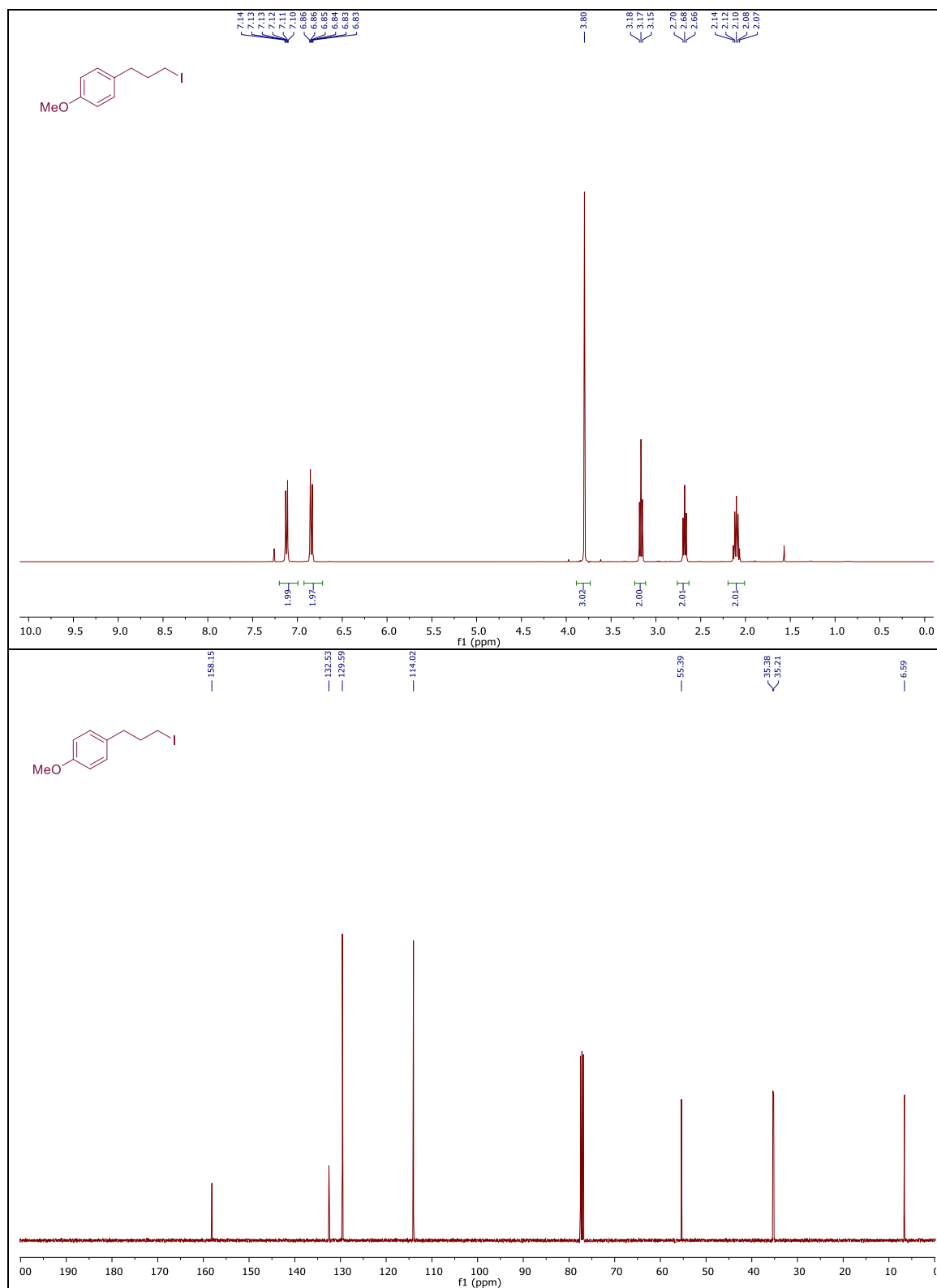
NMR spectra of 1o



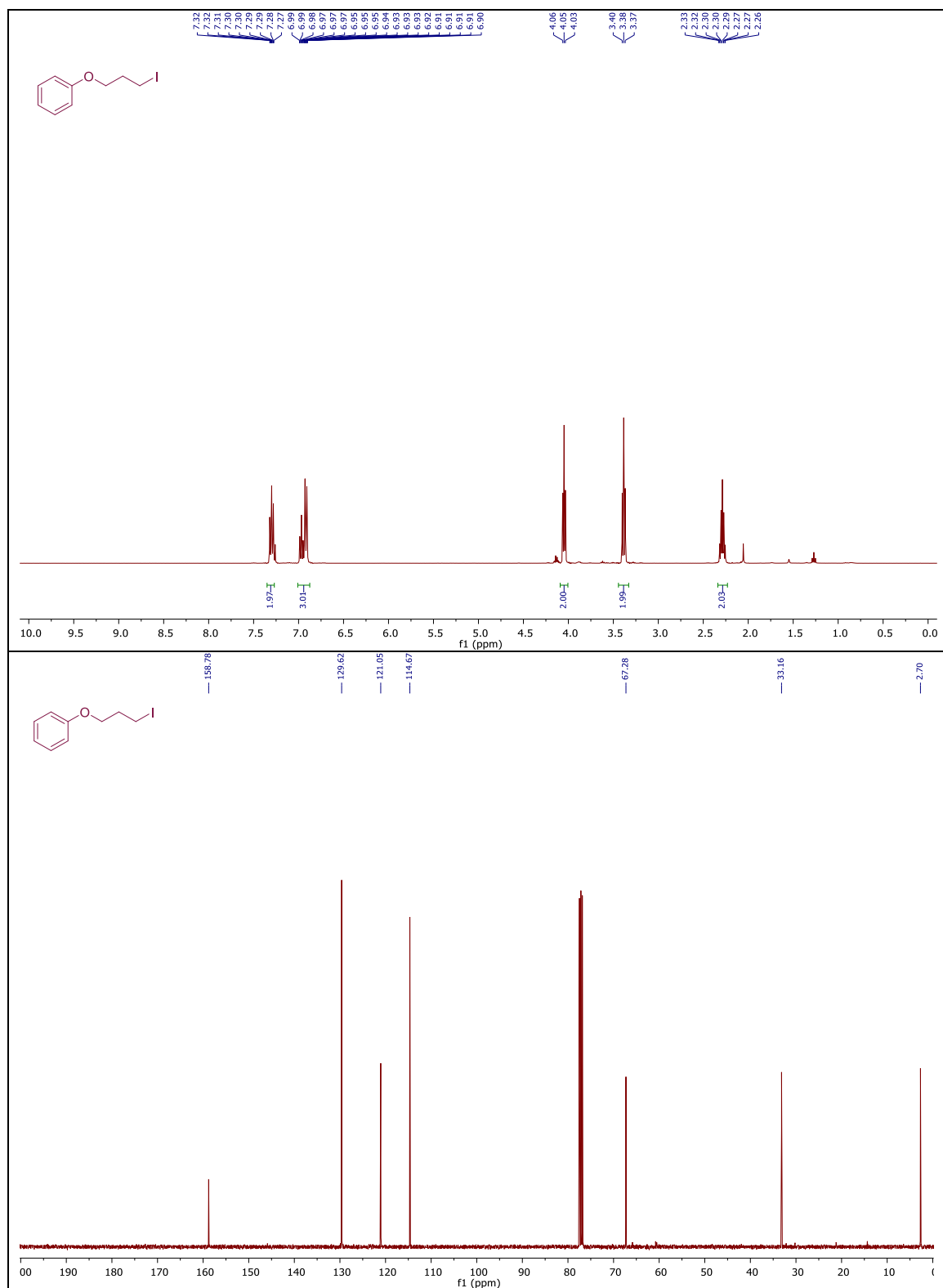
NMR spectra of 1p



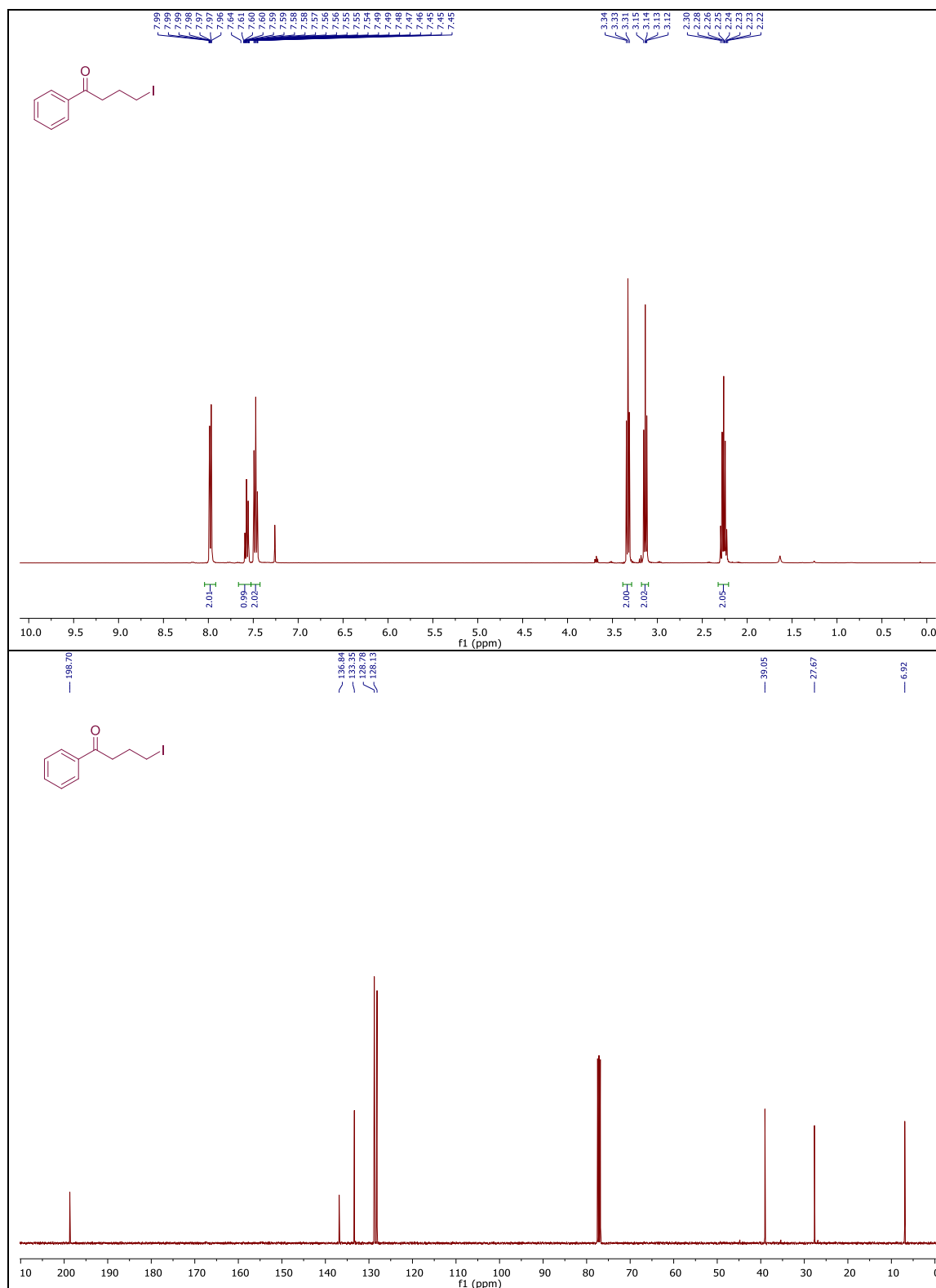
NMR spectra of 2b



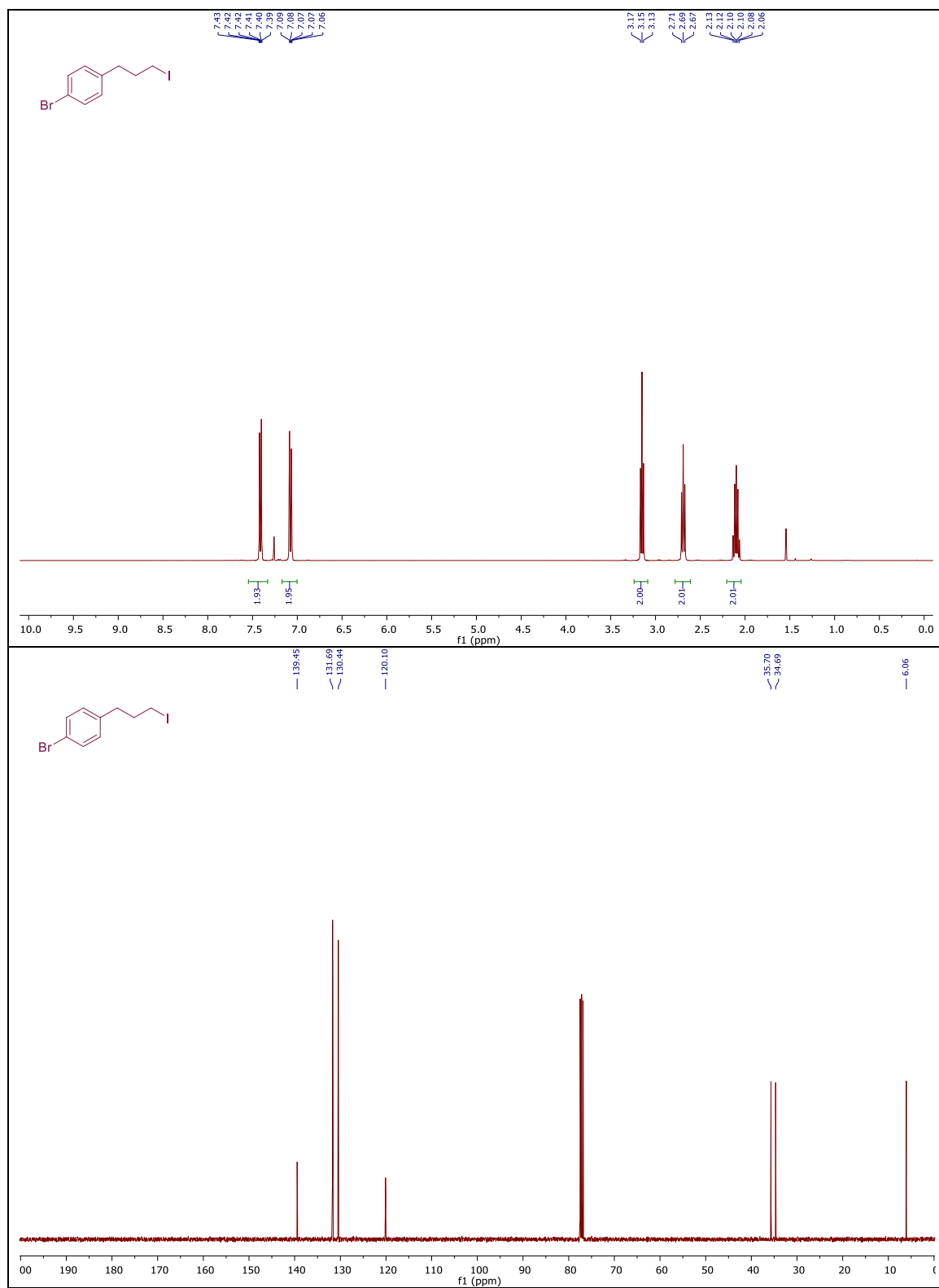
NMR spectra of 2c



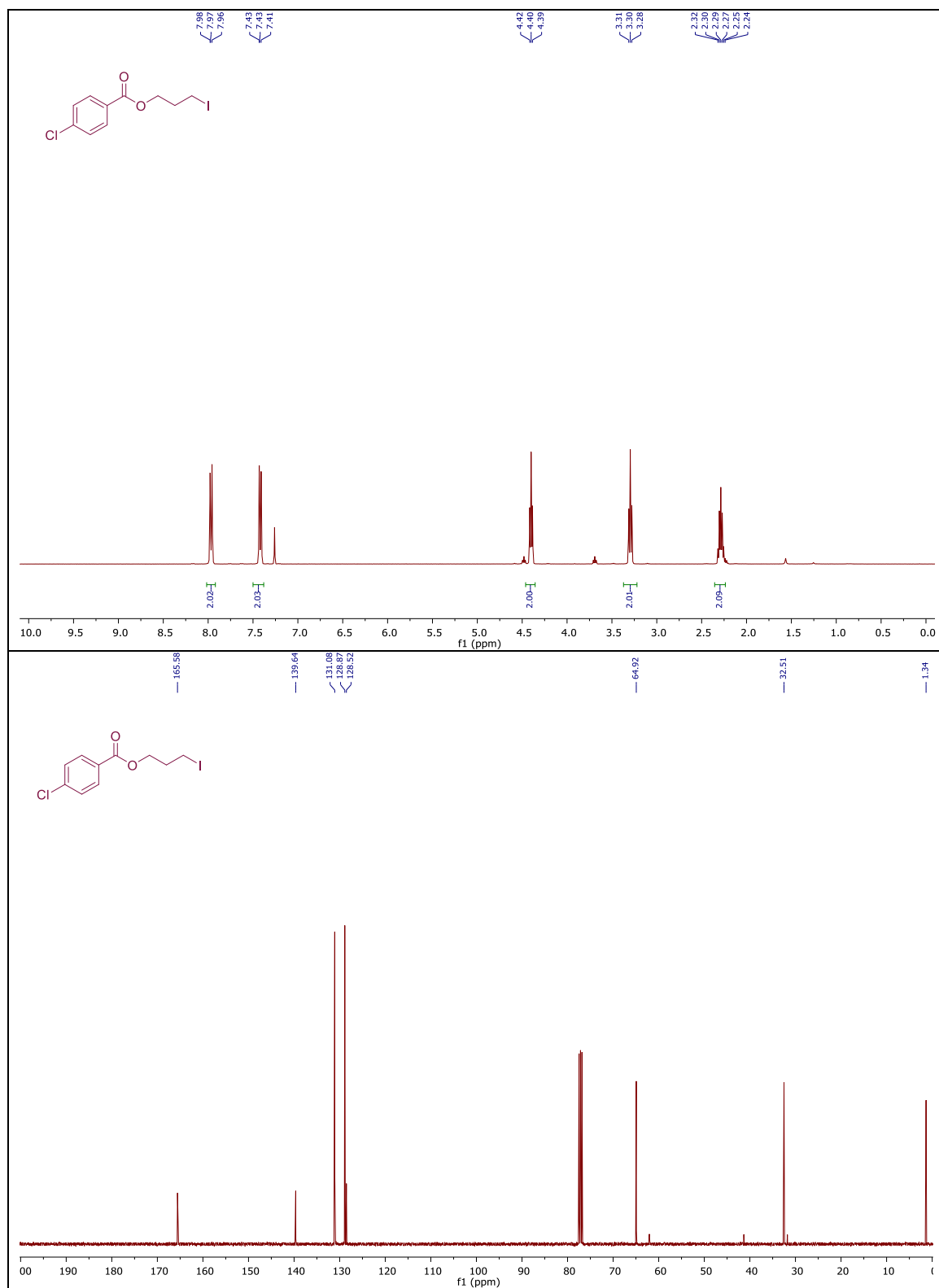
NMR spectra of 2d



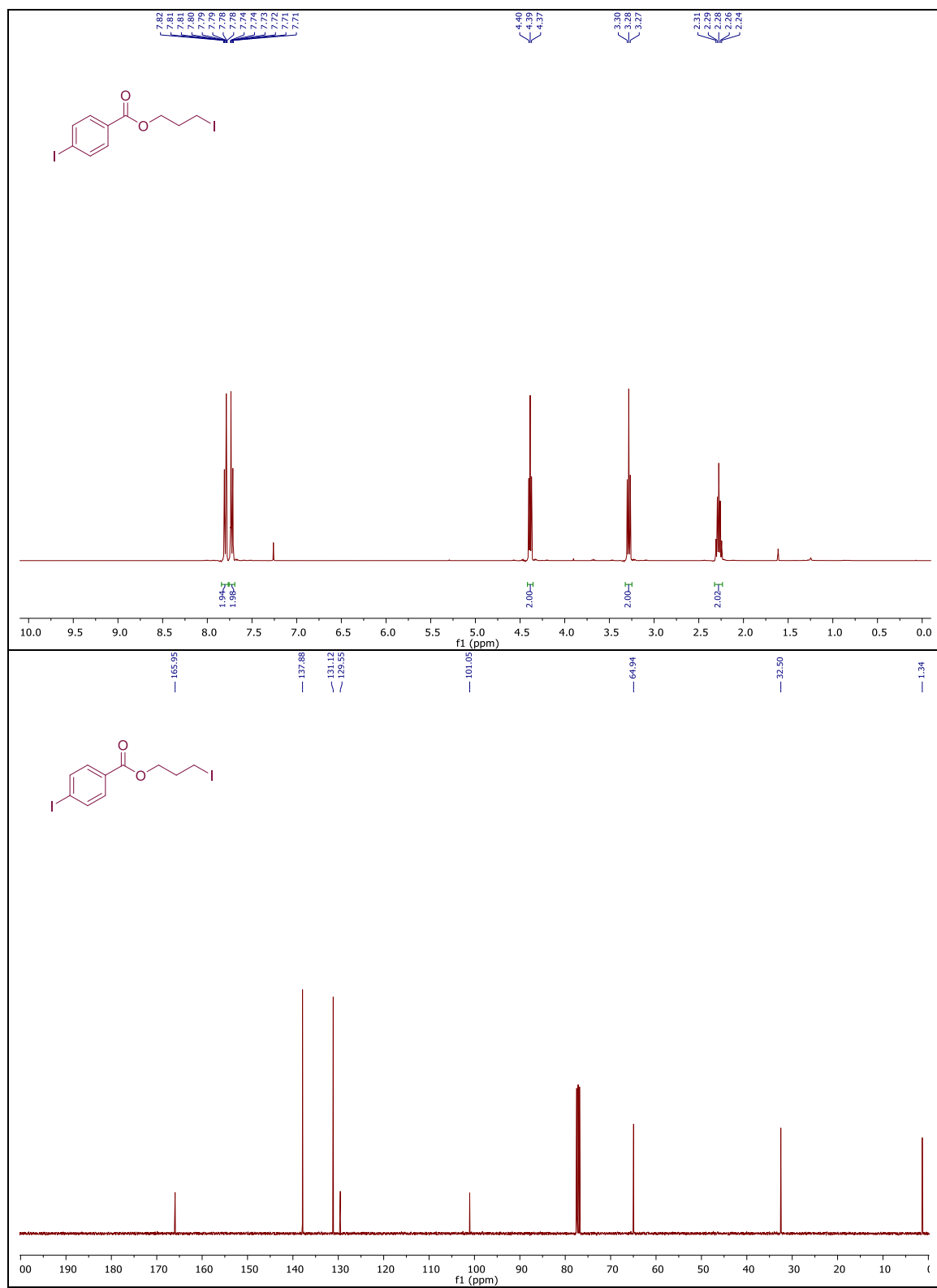
NMR spectra of 2e



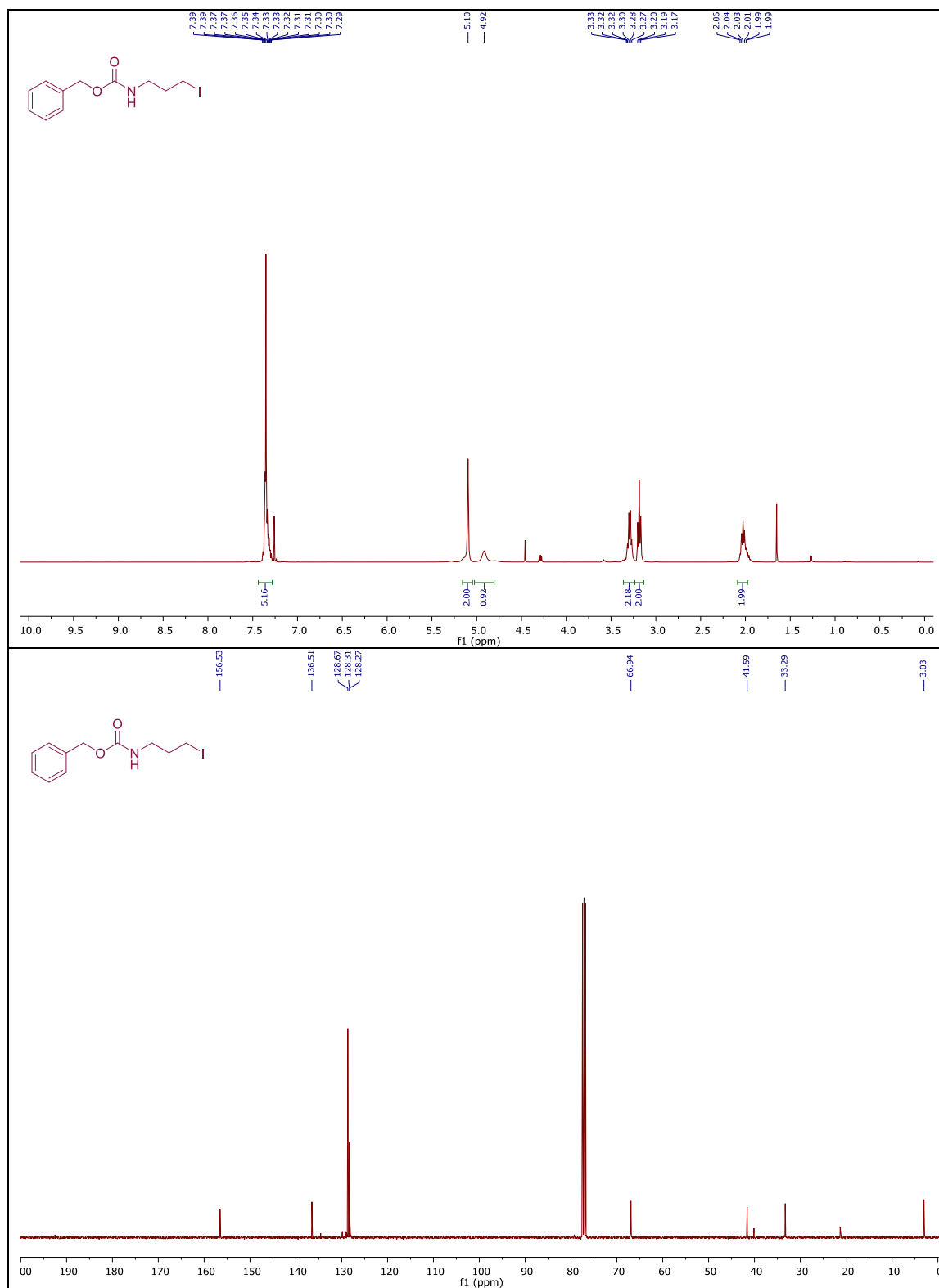
NMR spectra of 2f



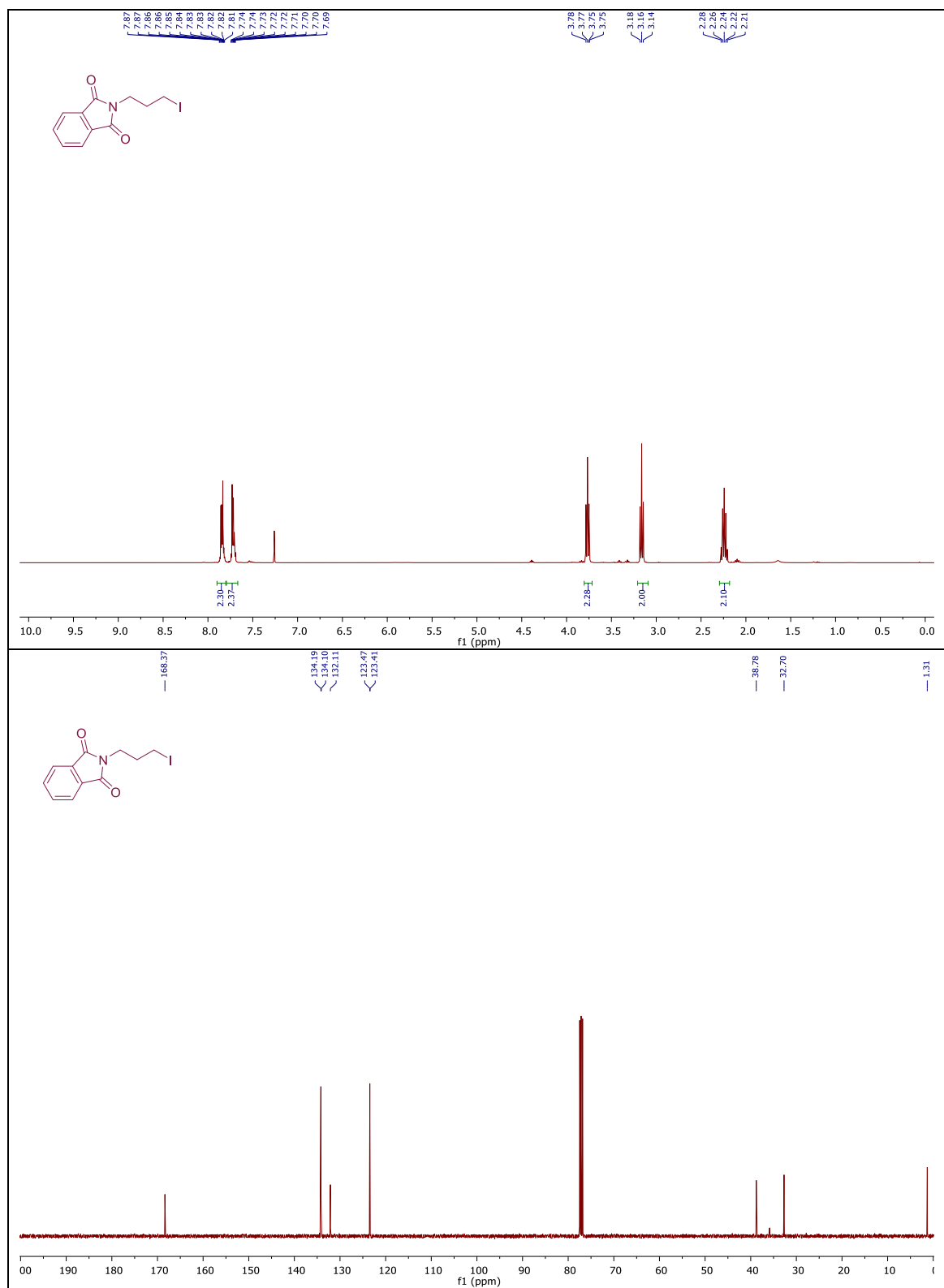
NMR spectra of 2g



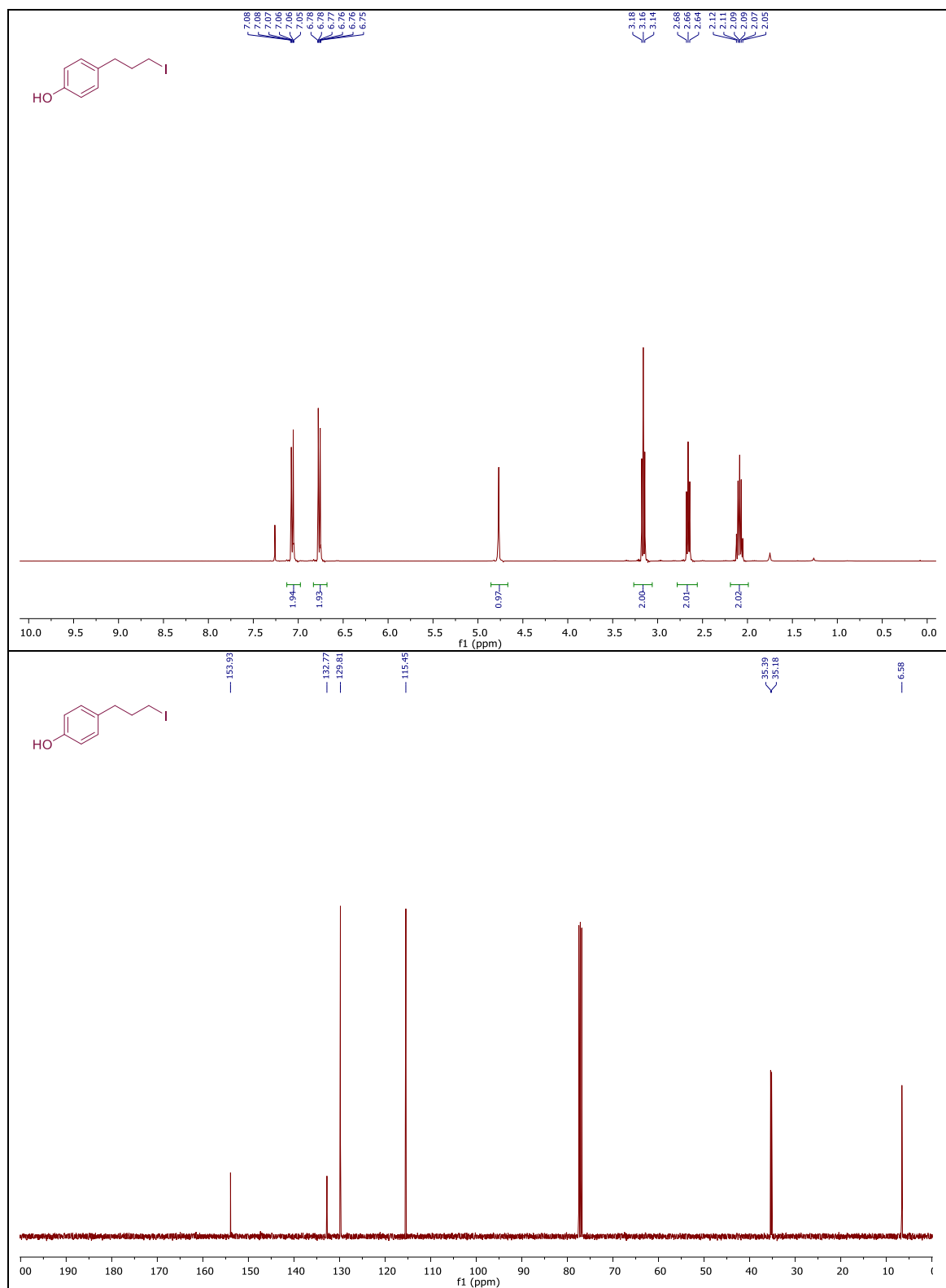
NMR spectra of 2h



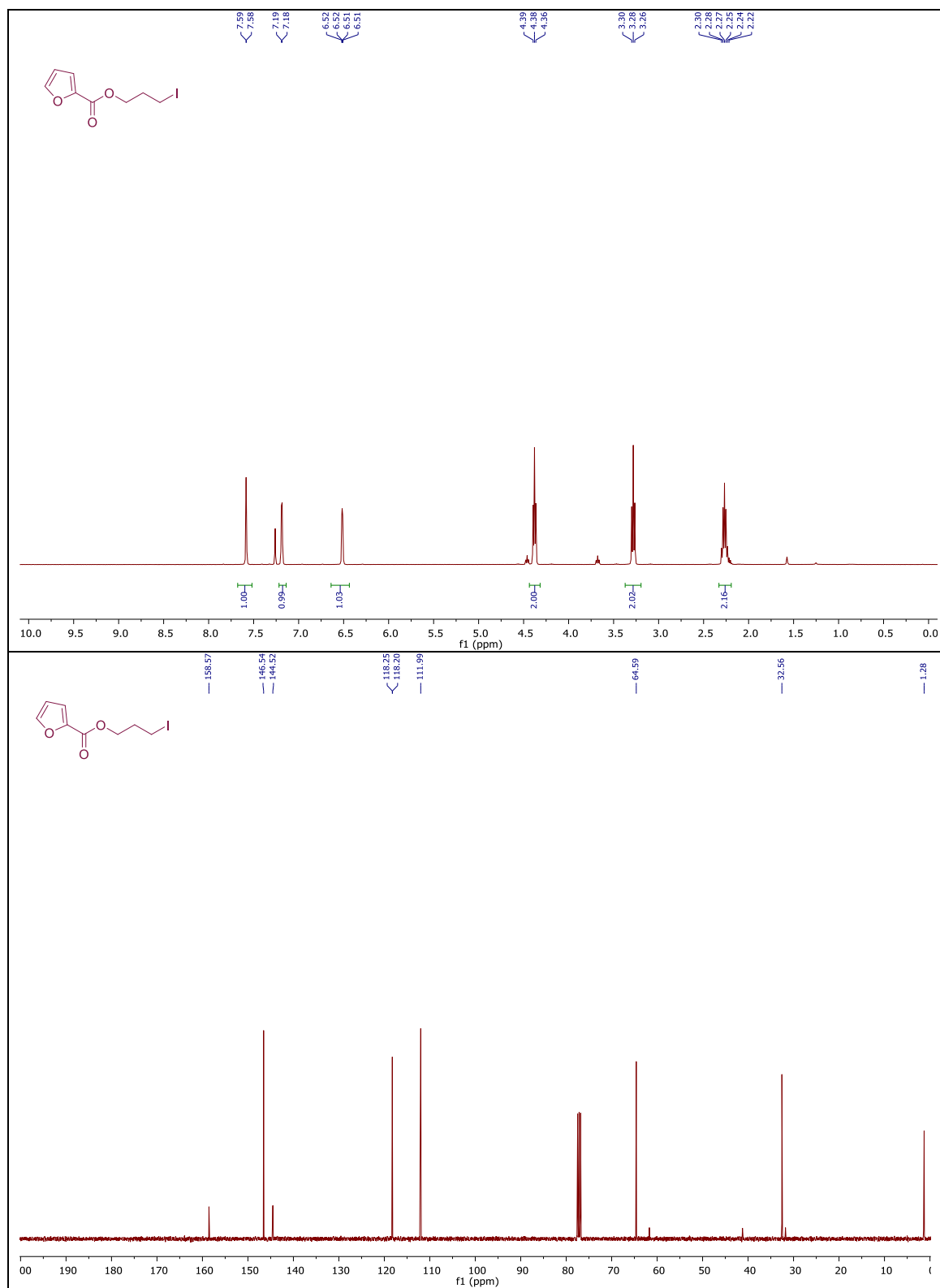
NMR spectra of 2i



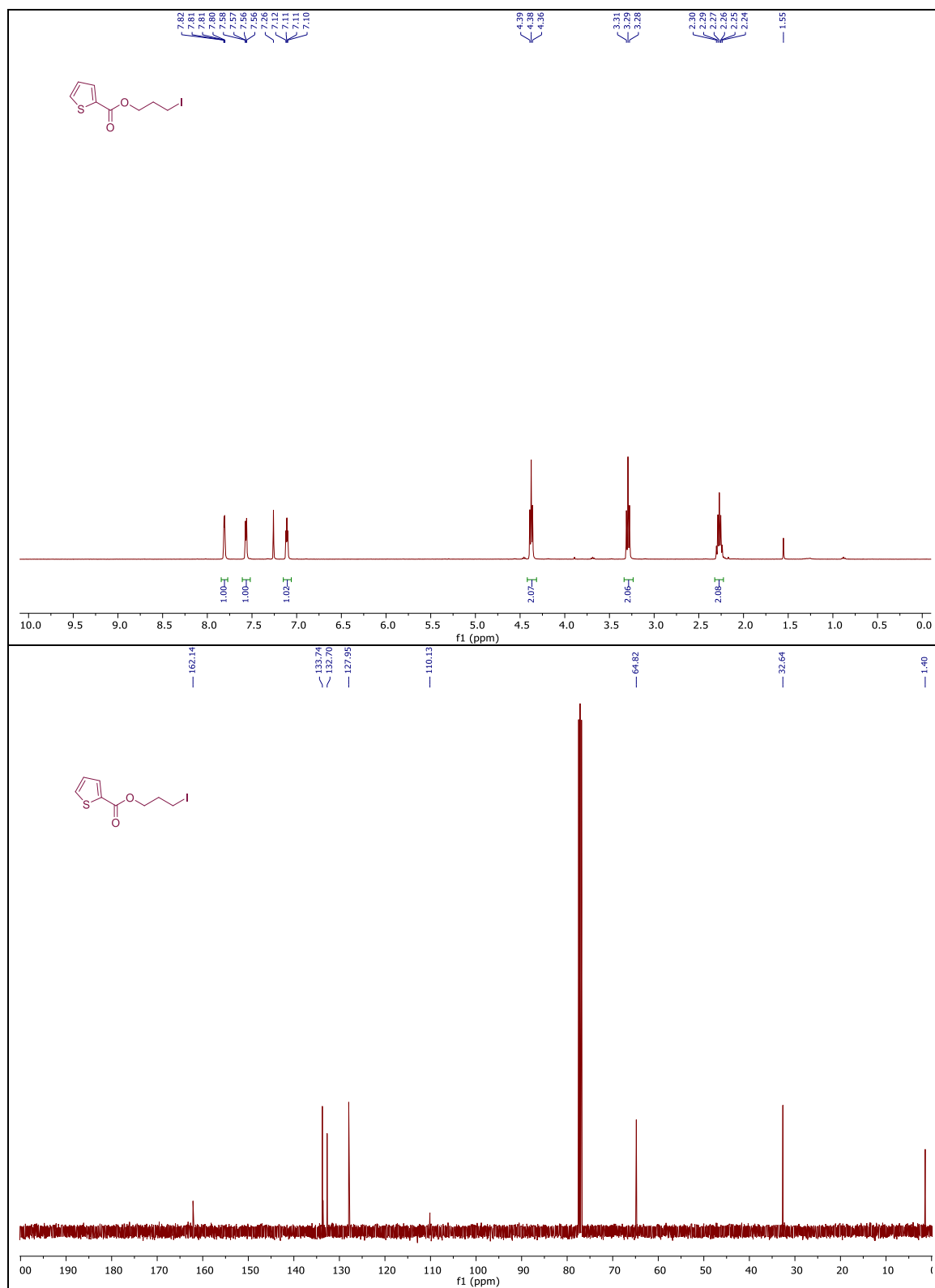
NMR spectra of 2j



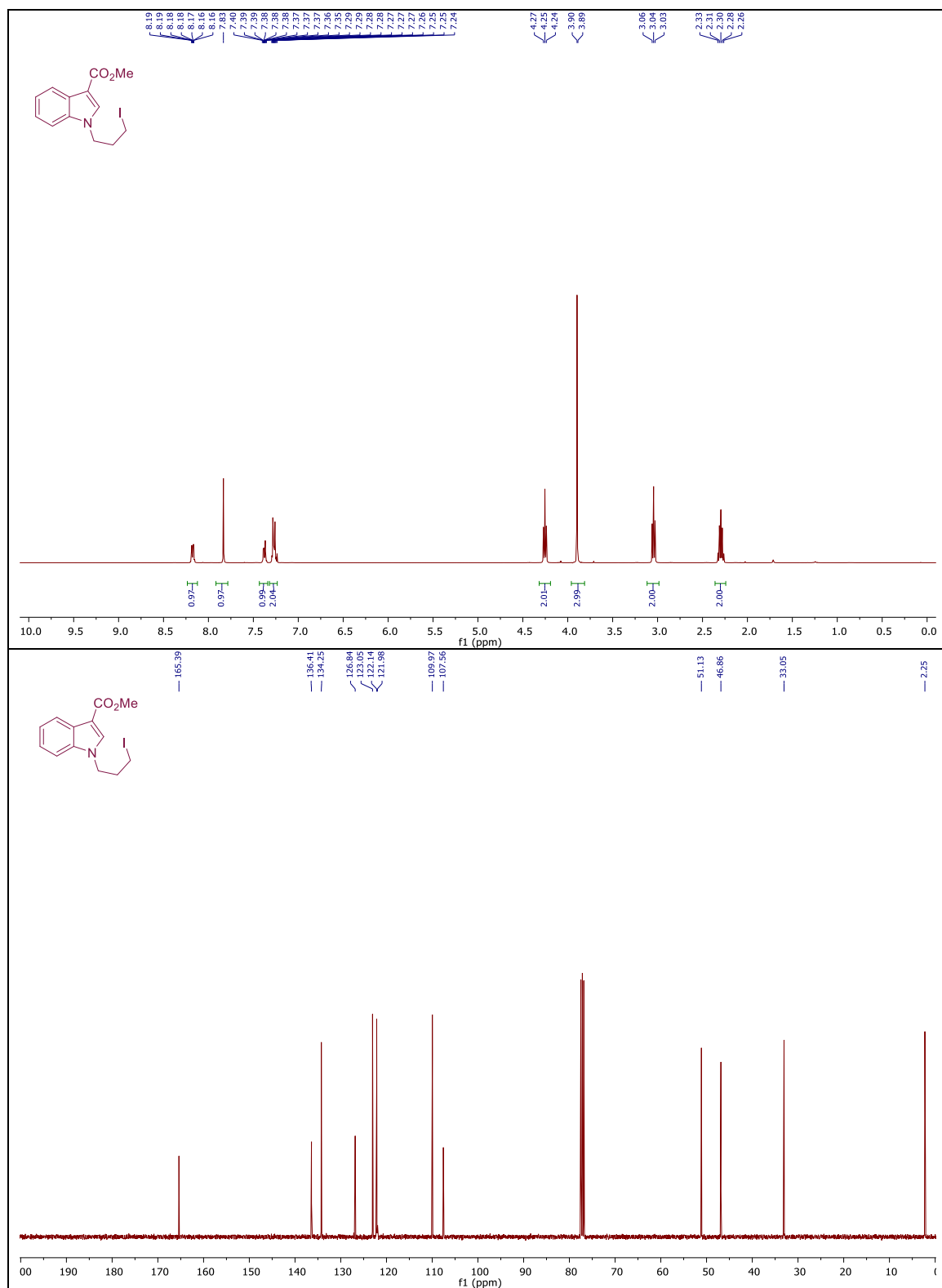
NMR spectra of 2k



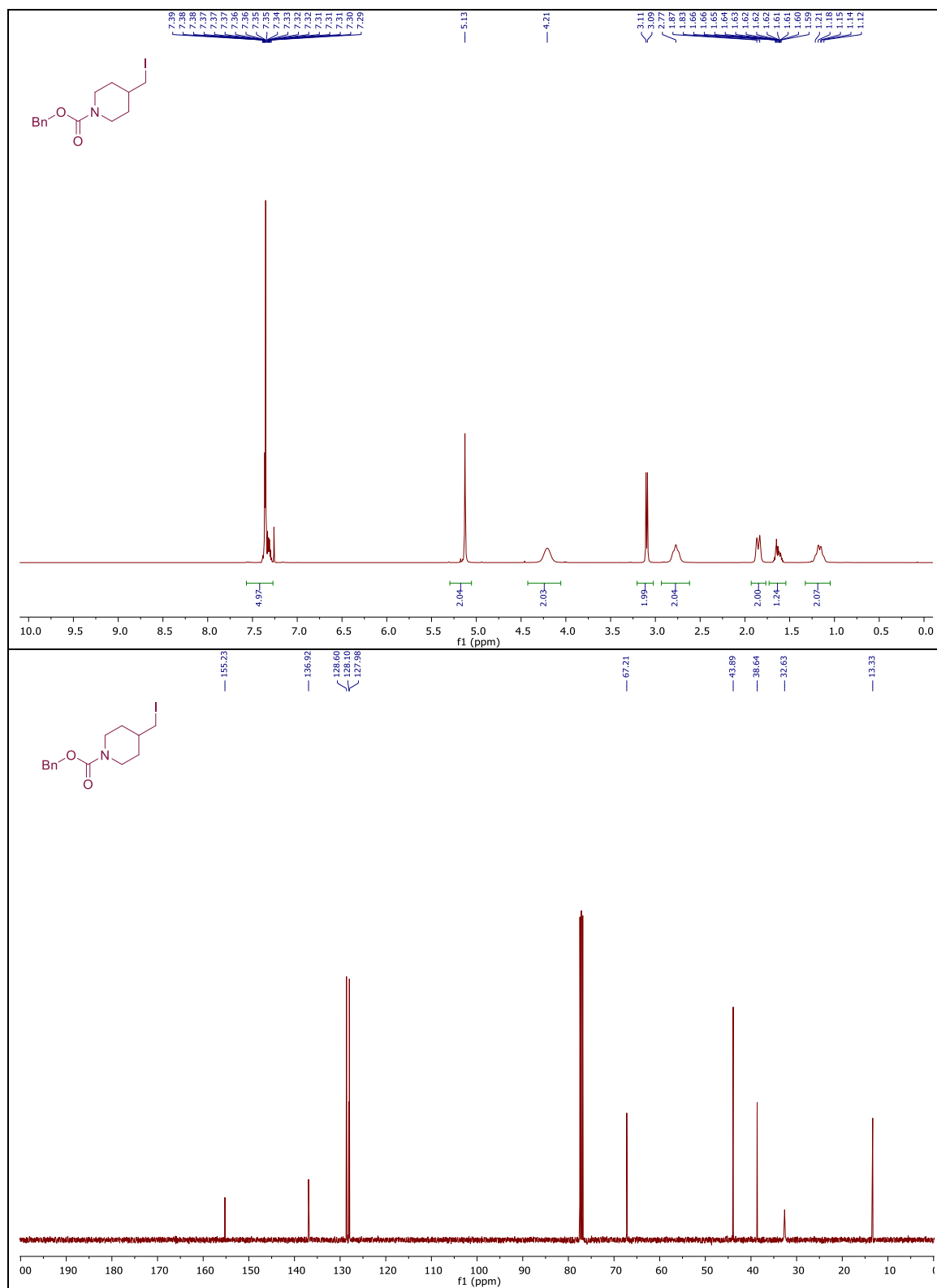
NMR spectra of 2l



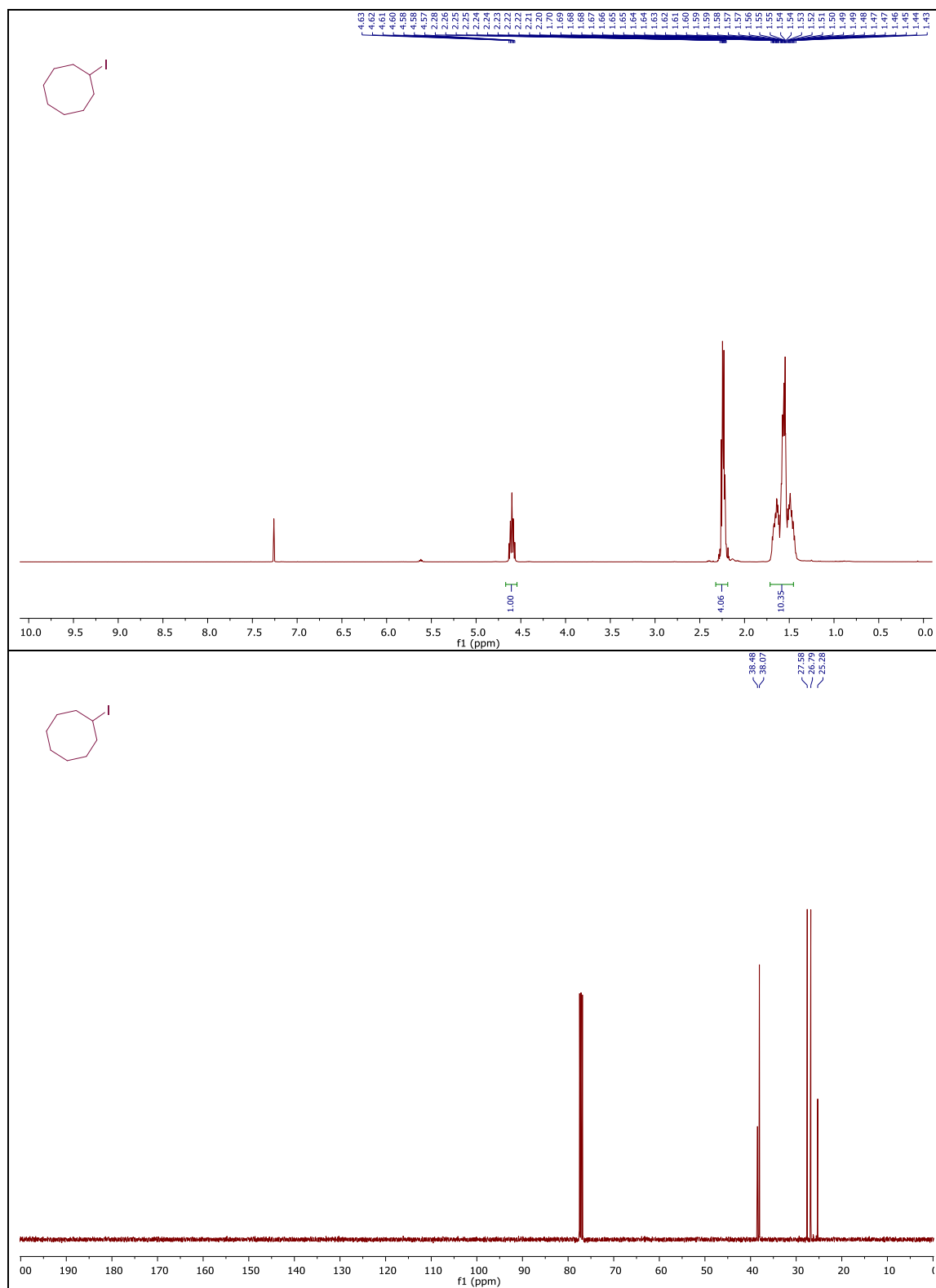
NMR spectra of 2m



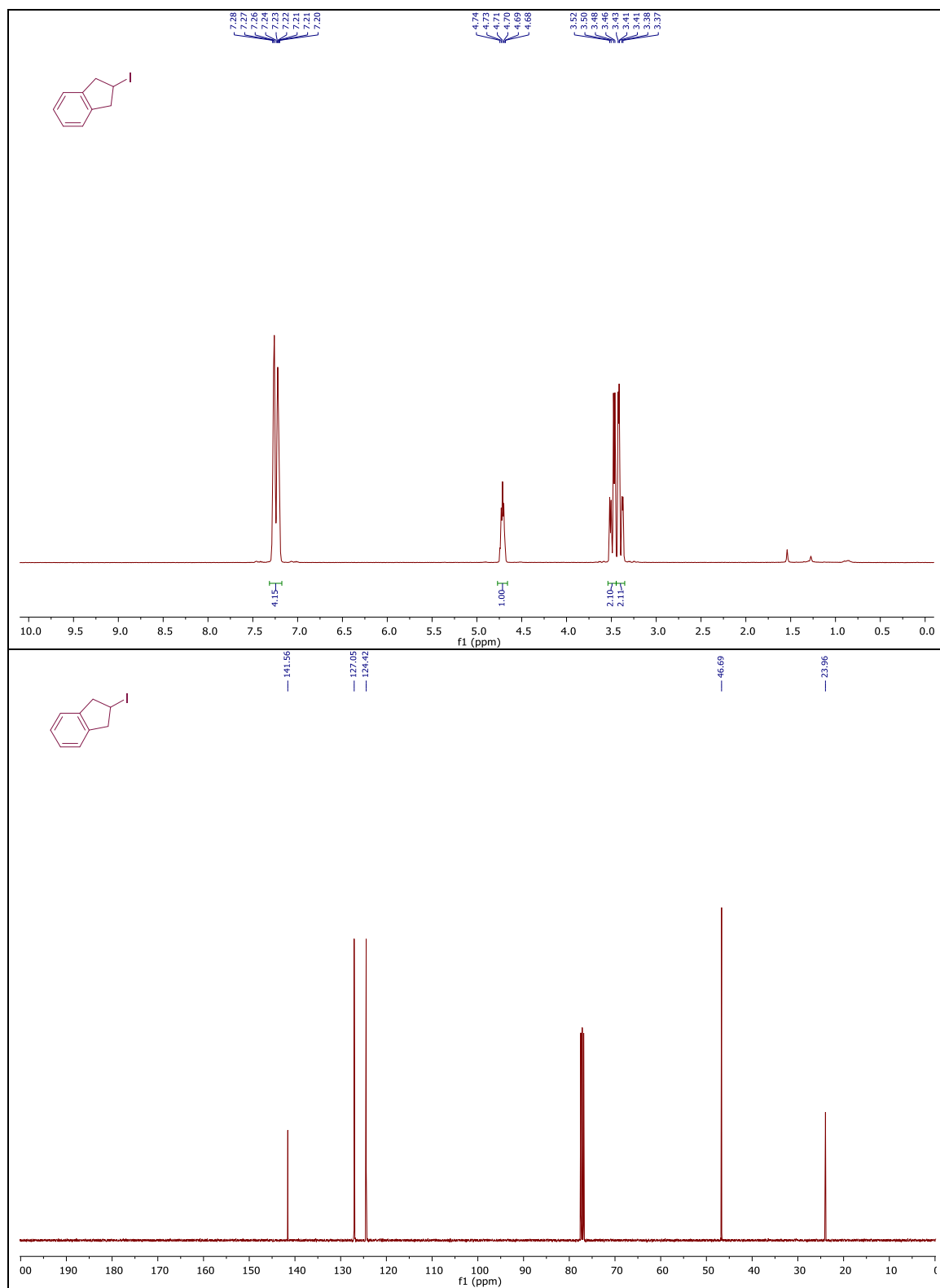
NMR spectra of 2n



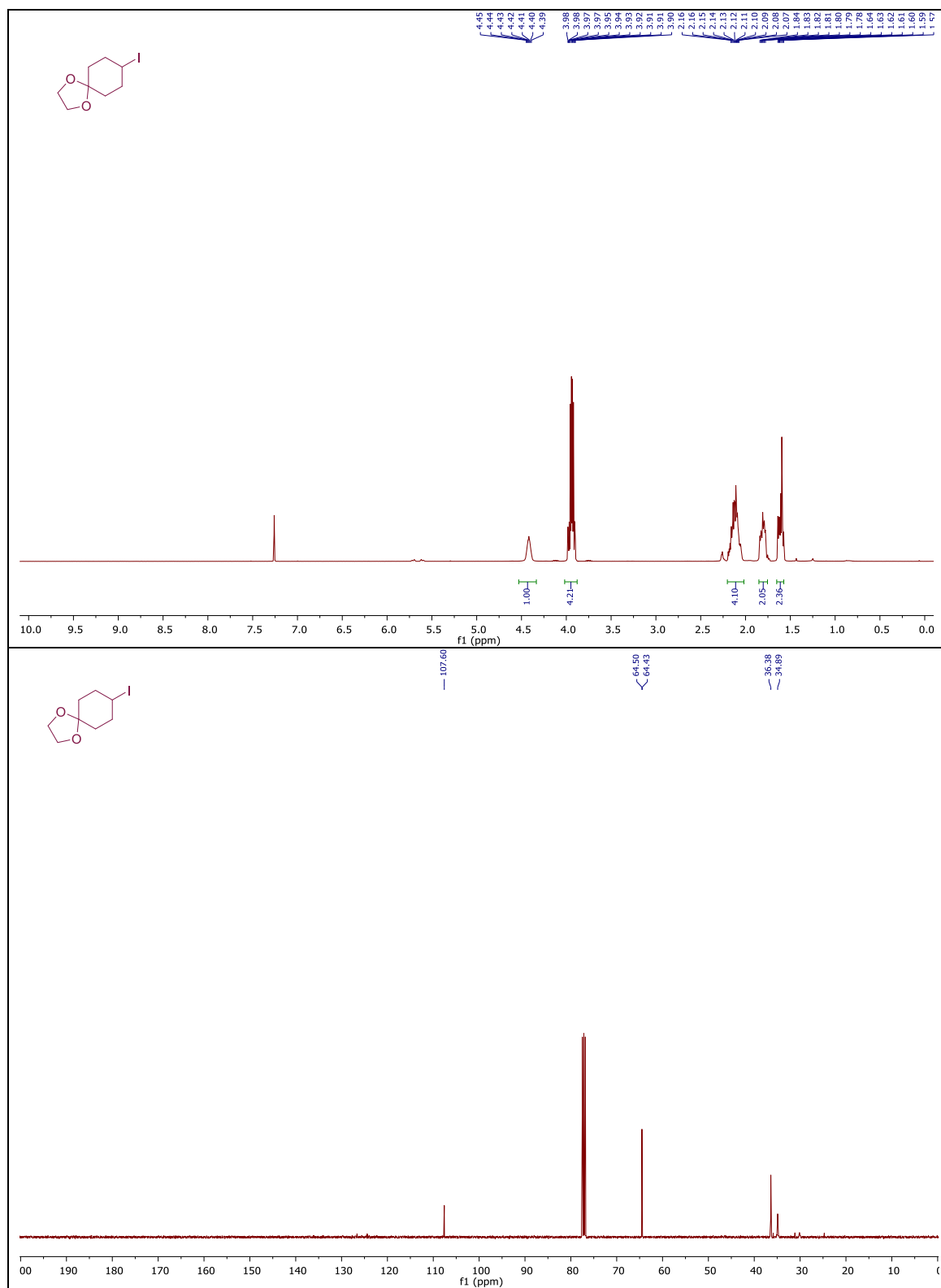
NMR spectra of 2t



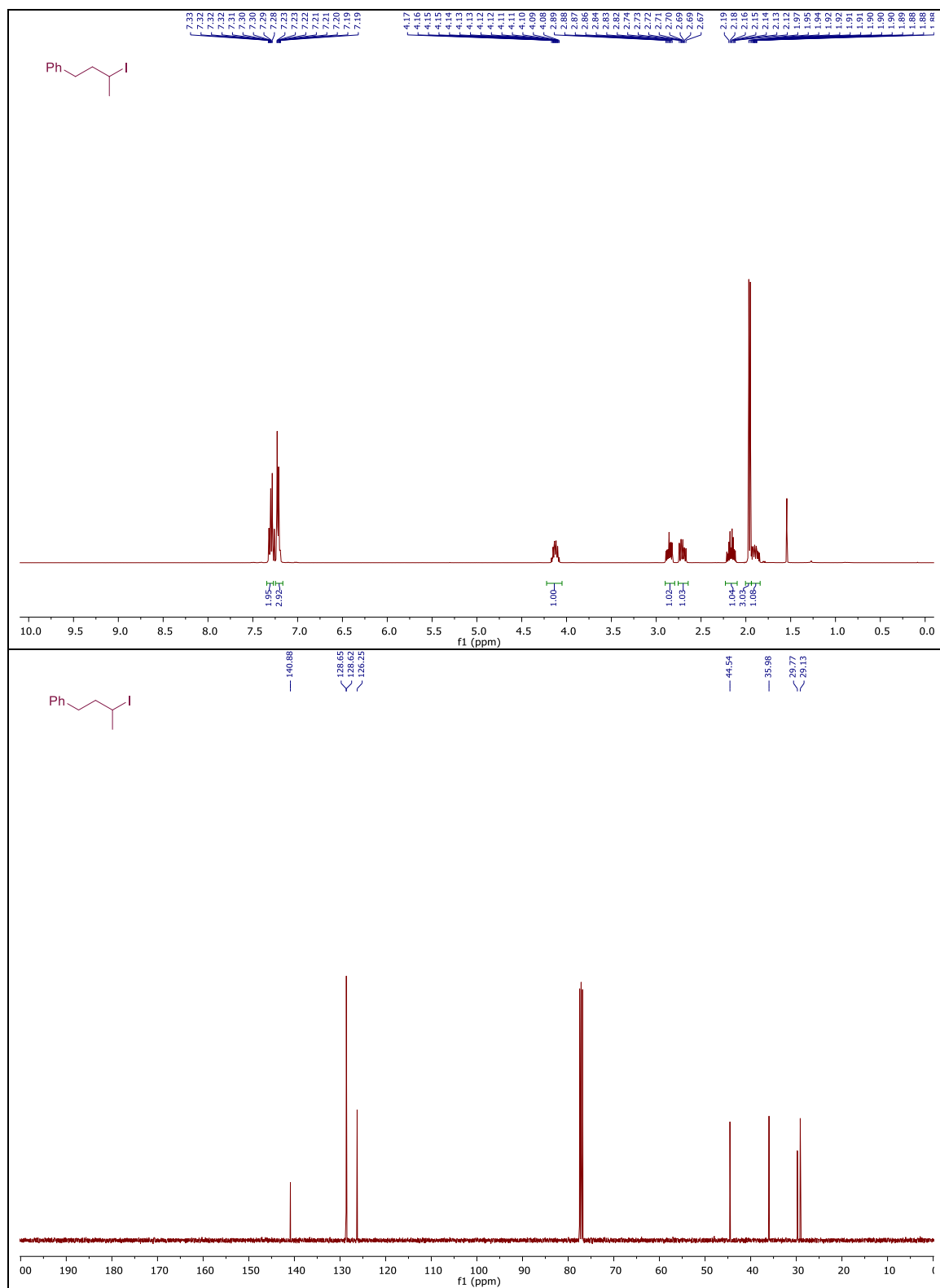
NMR spectra of 2u



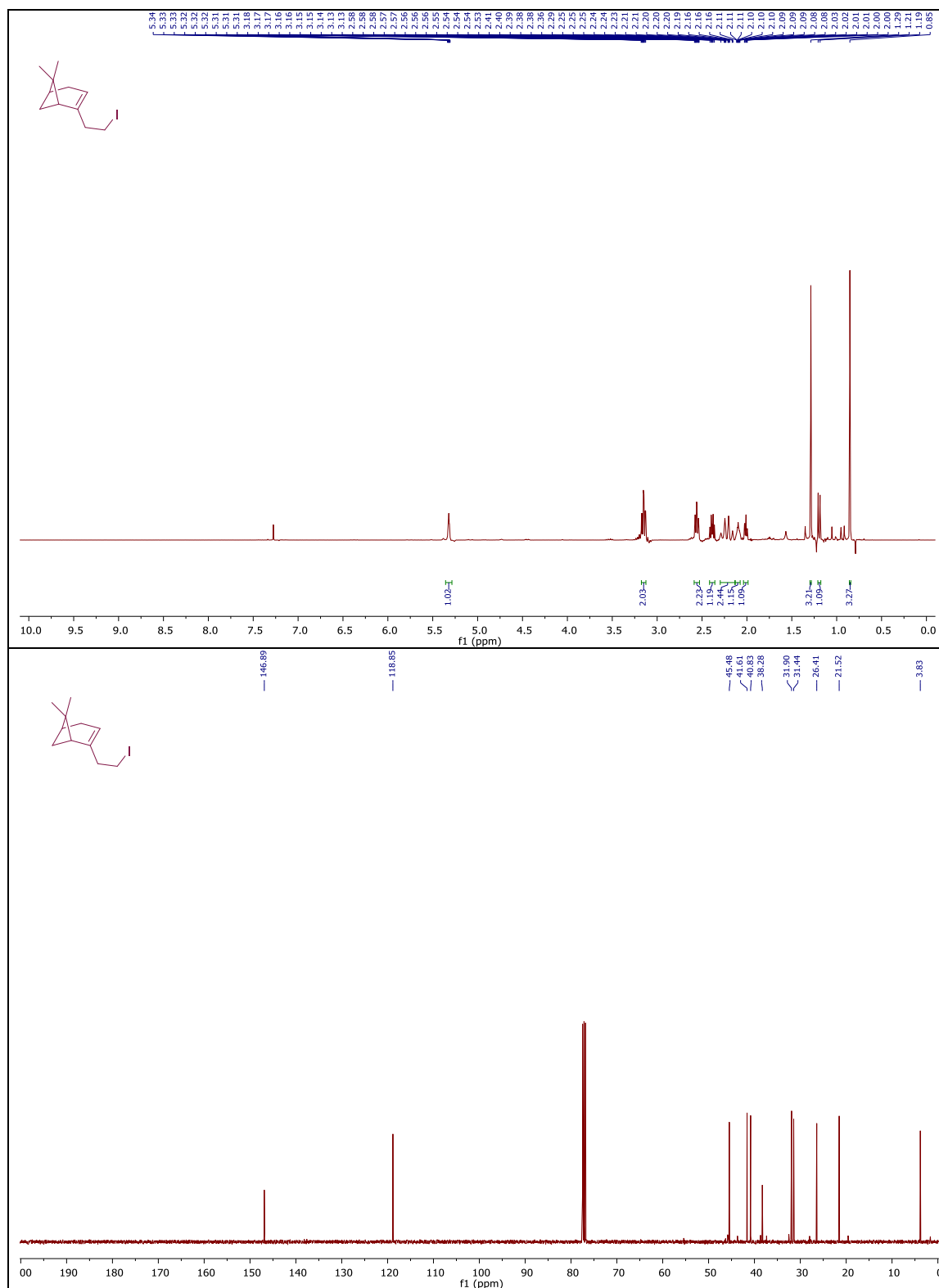
NMR spectra of 2x



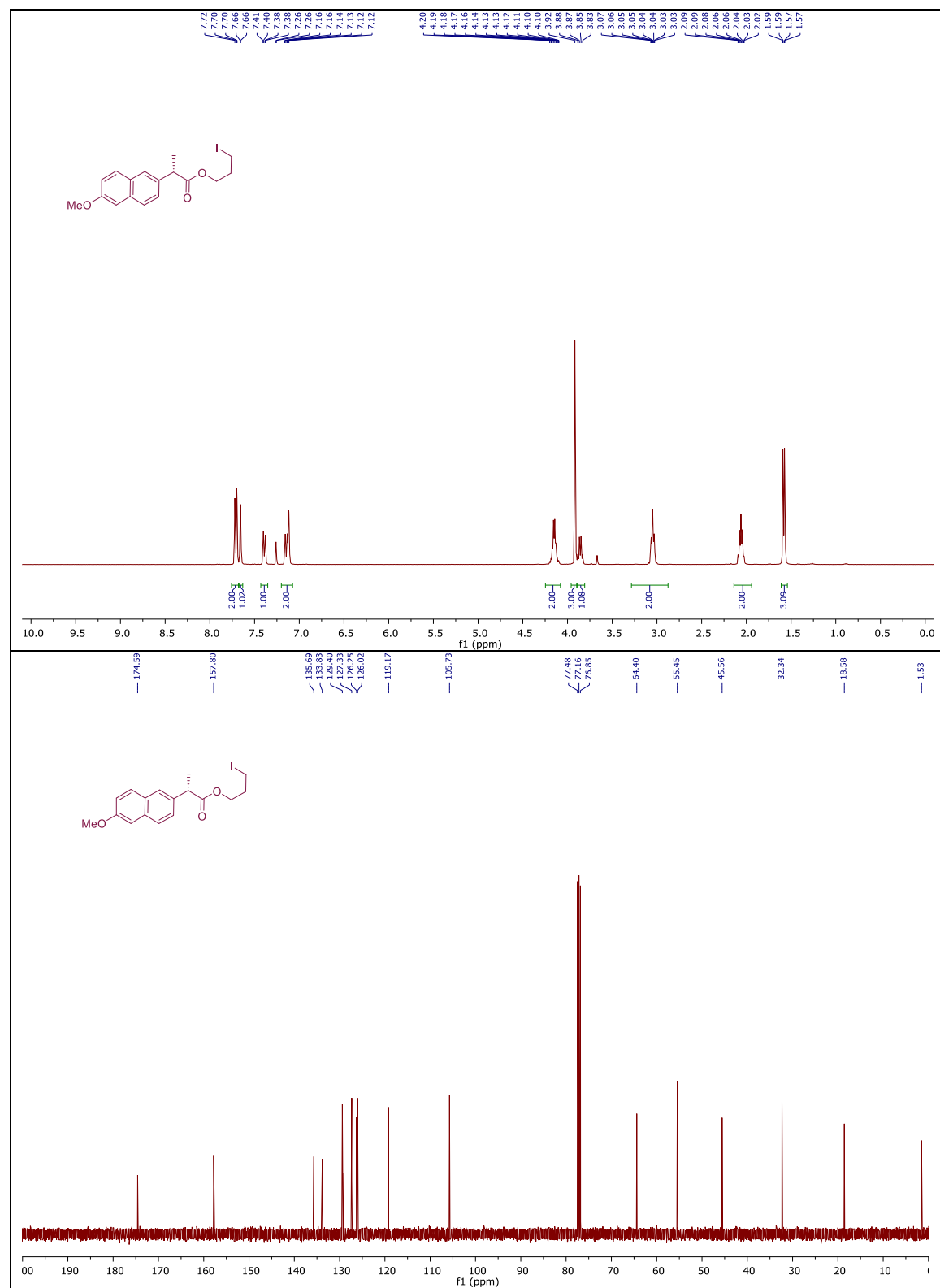
NMR spectra of 2b'



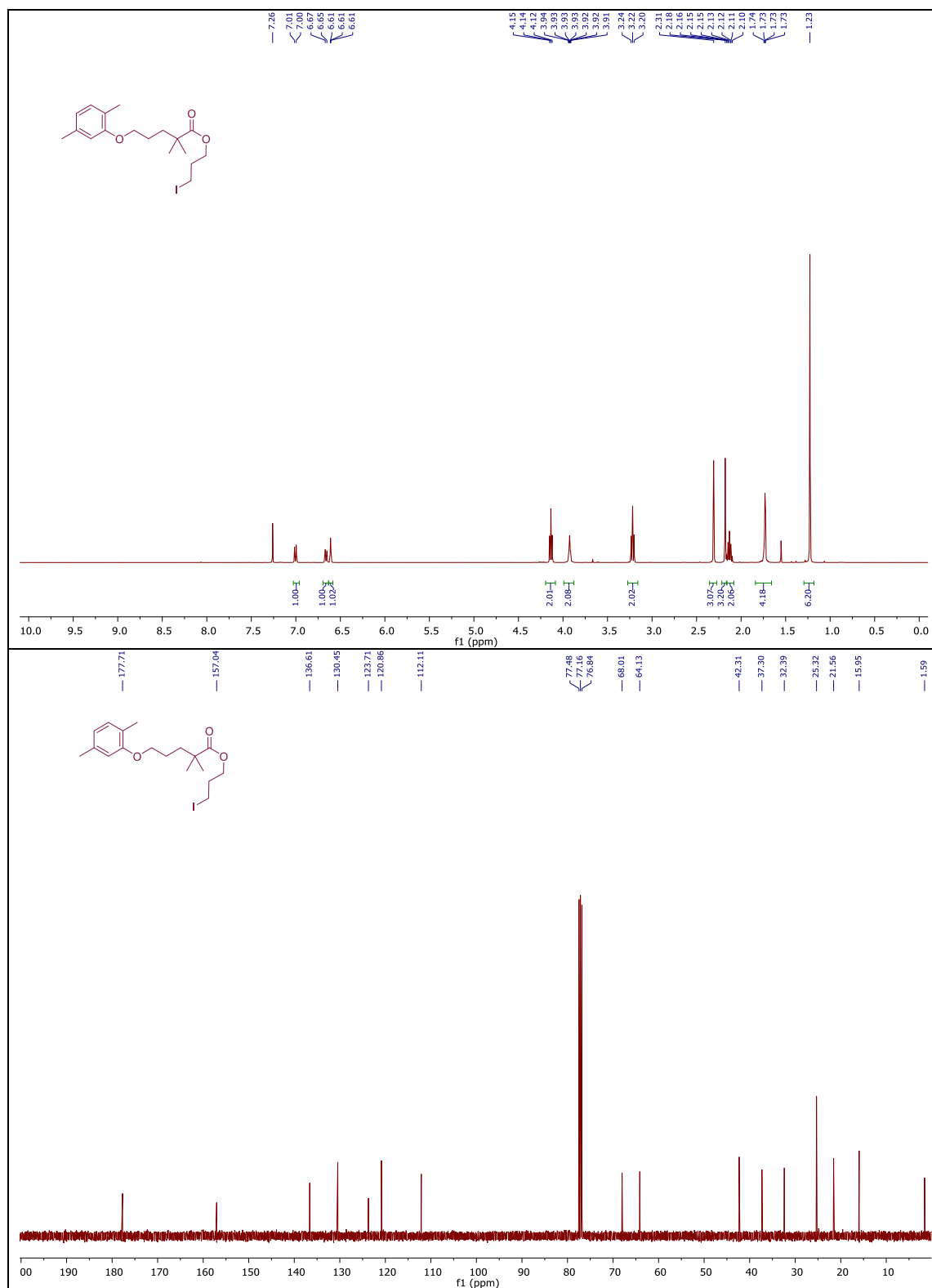
NMR spectra of 2d'



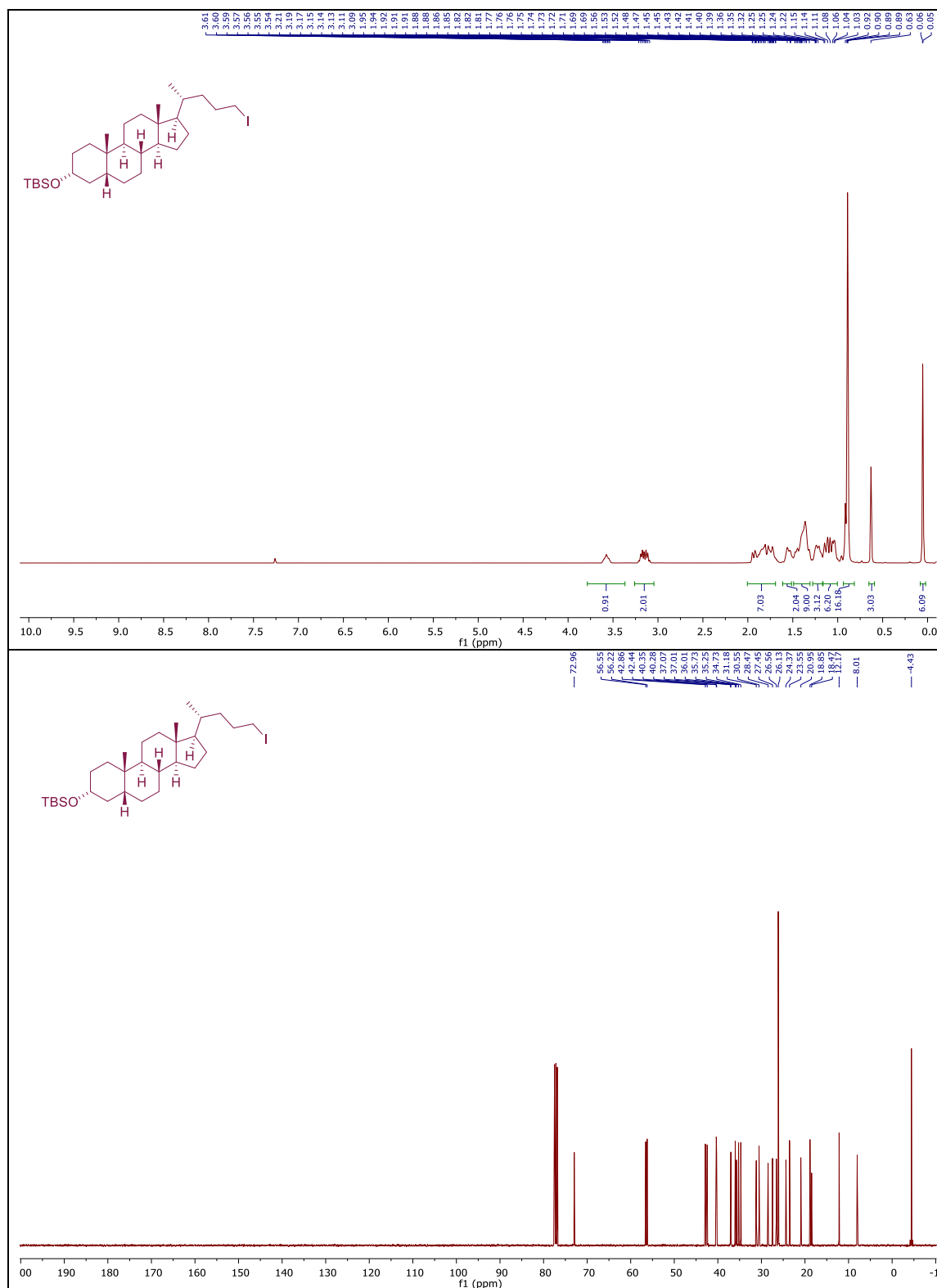
NMR spectra of 2e'



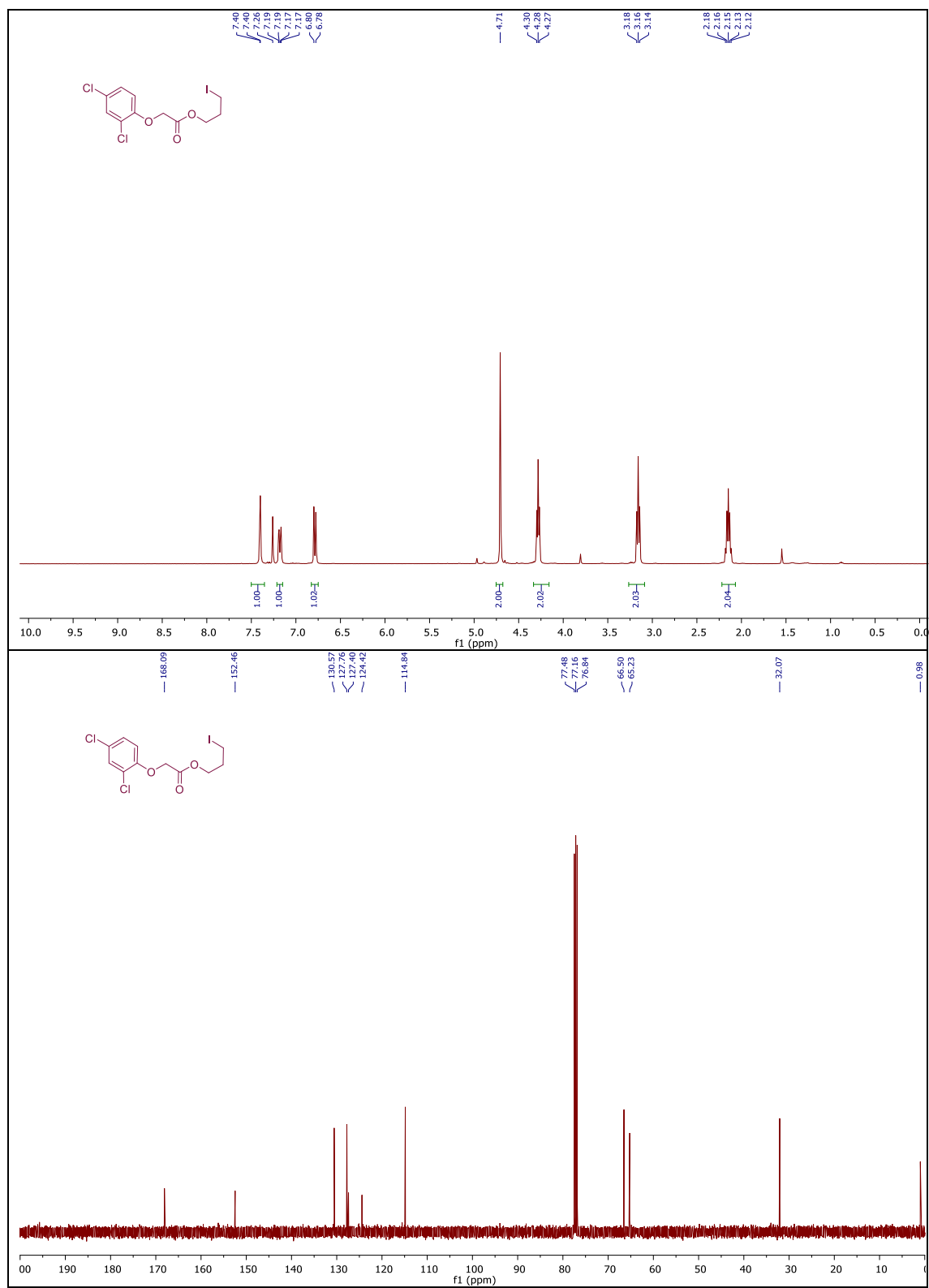
NMR spectra of 2f



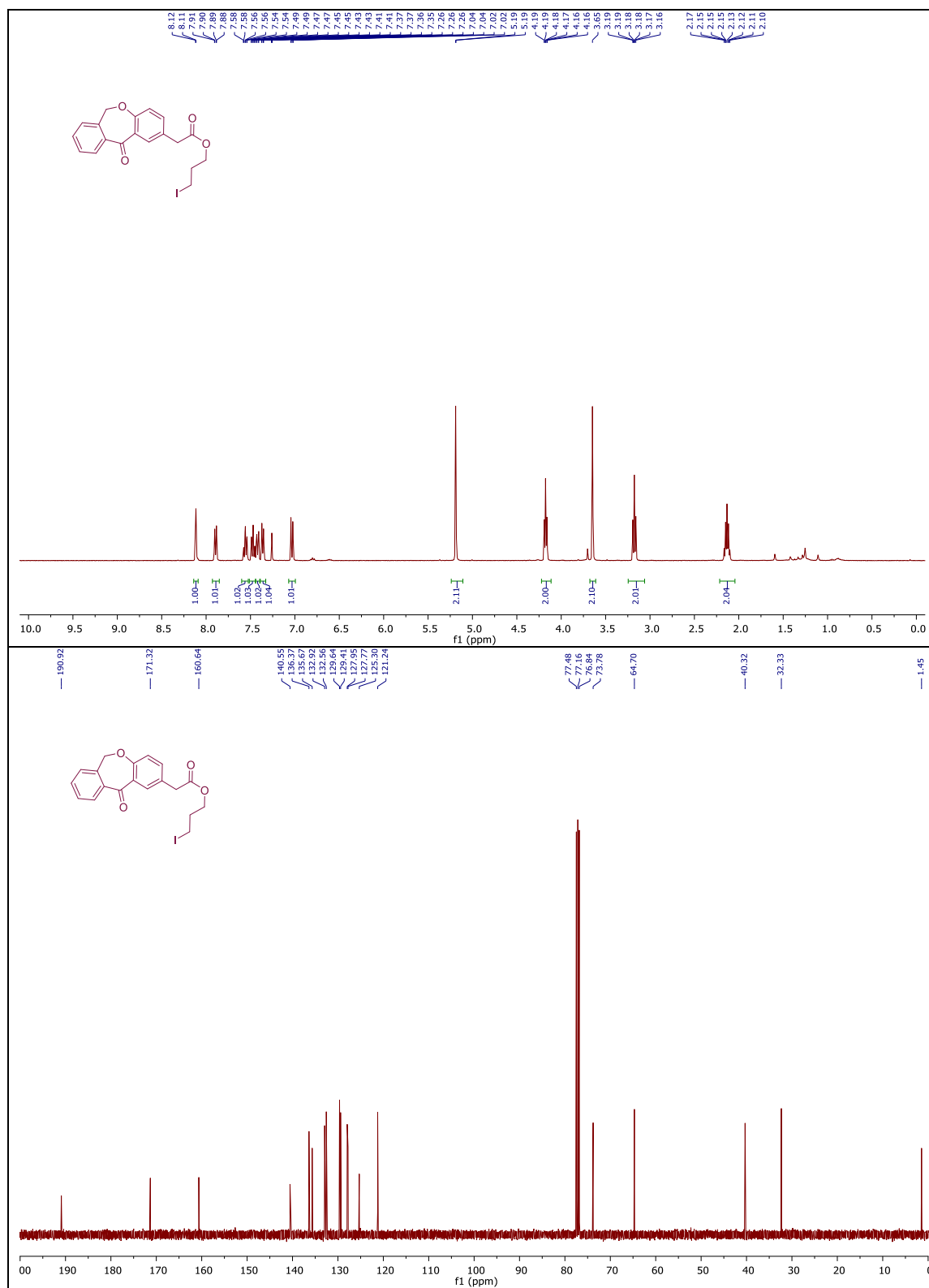
NMR spectra of 2g'



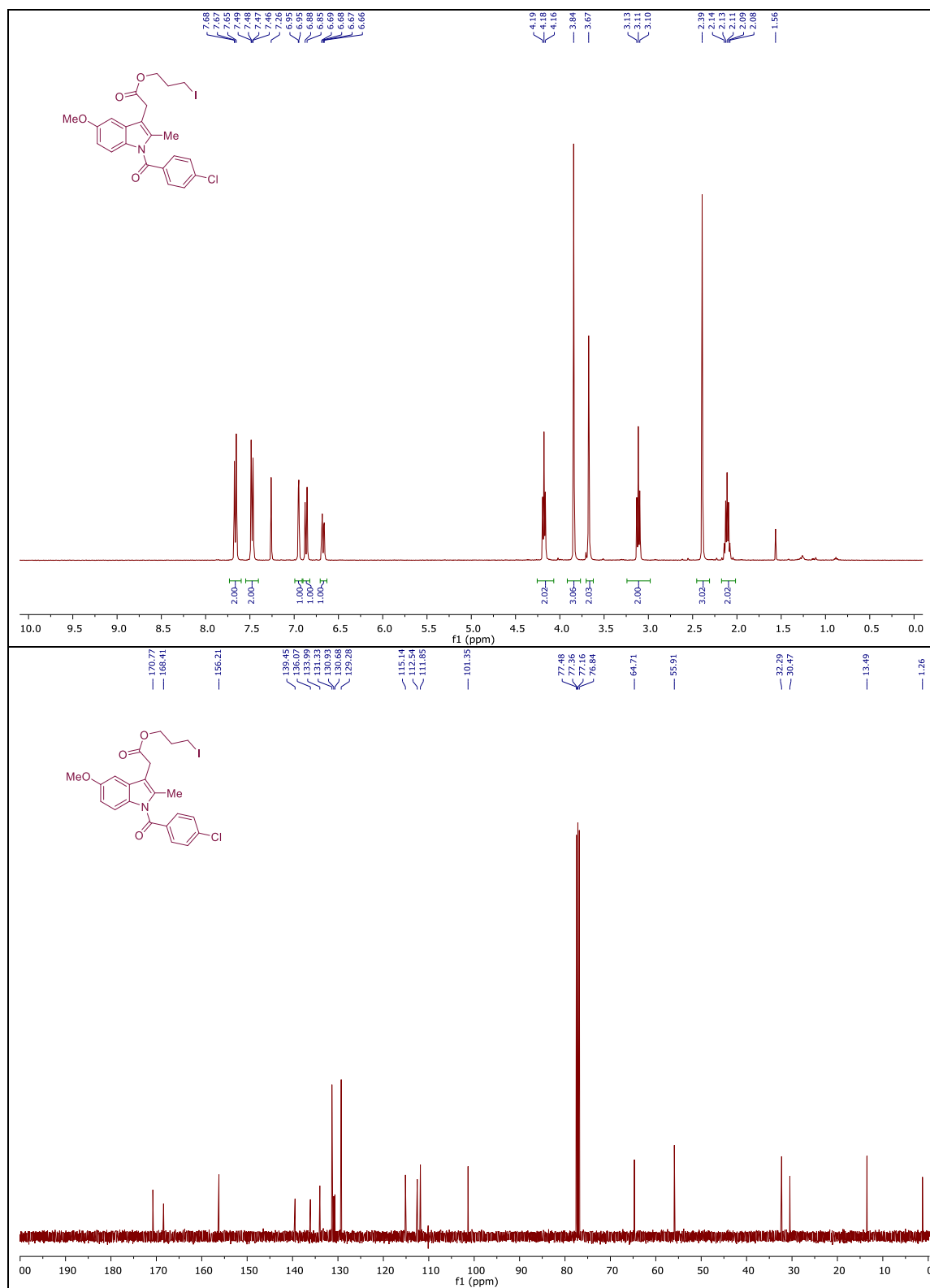
NMR spectra of 2h'



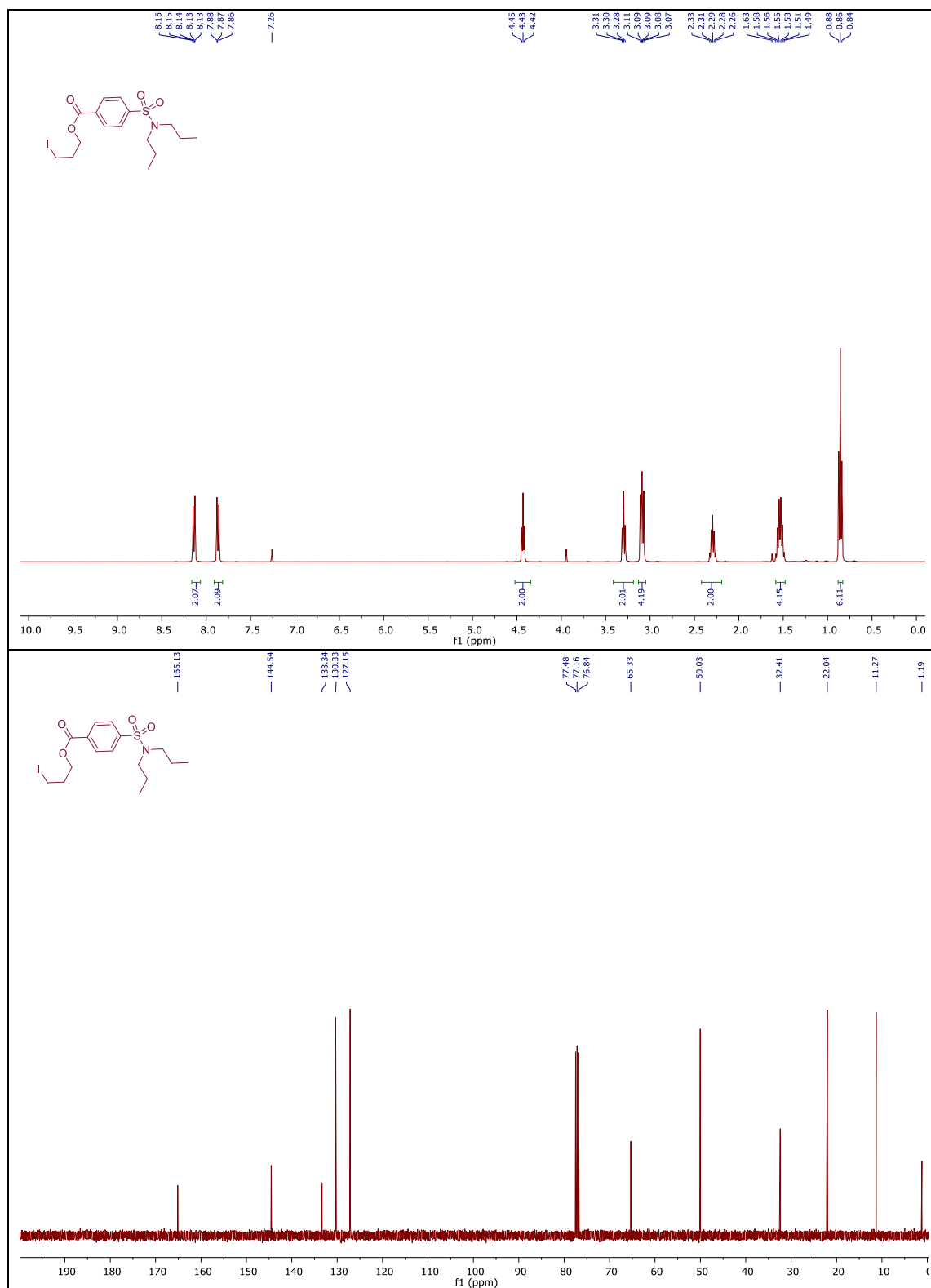
NMR spectra of 2i'



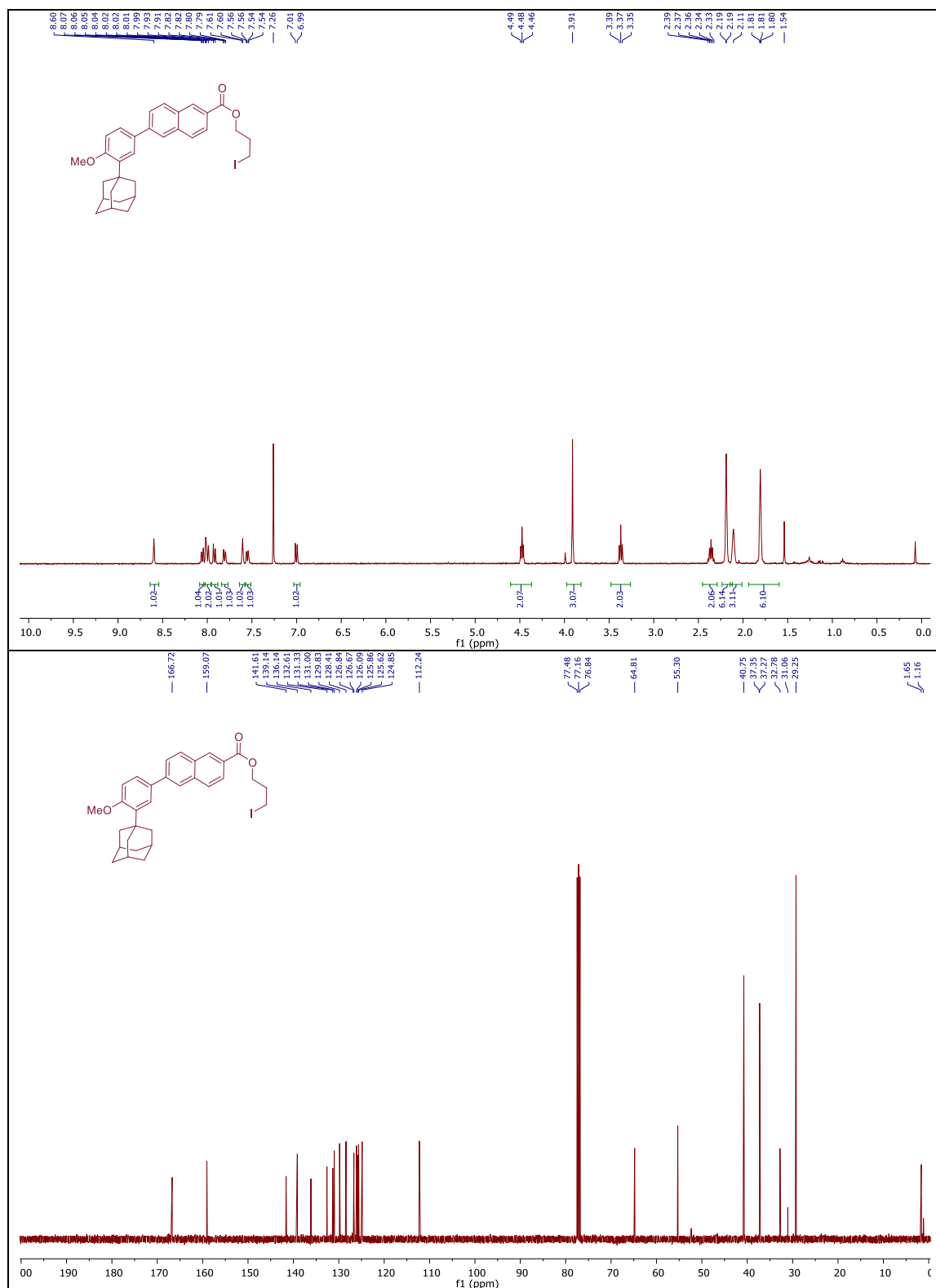
NMR spectra of 2j'



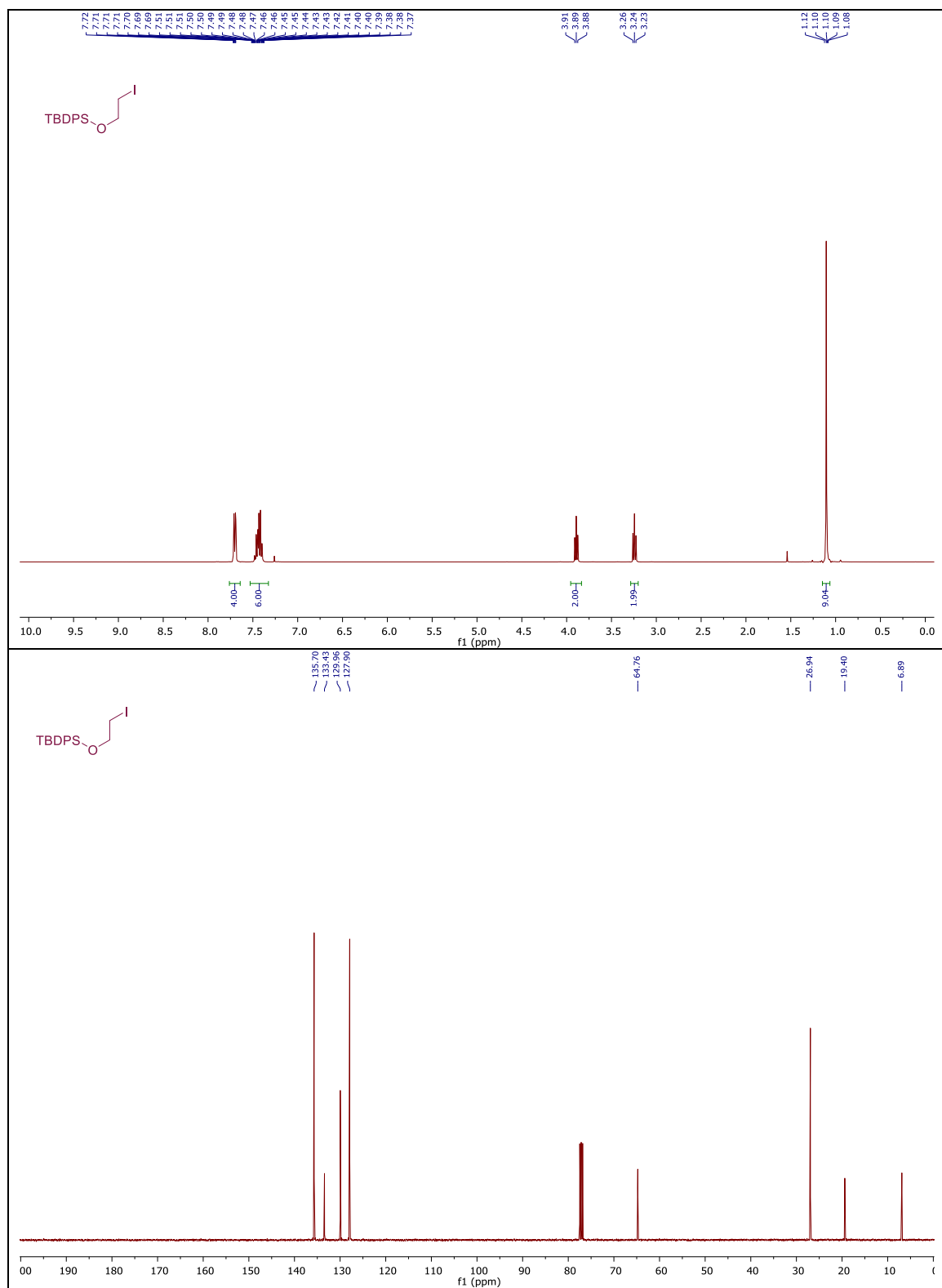
NMR spectra of 2k'



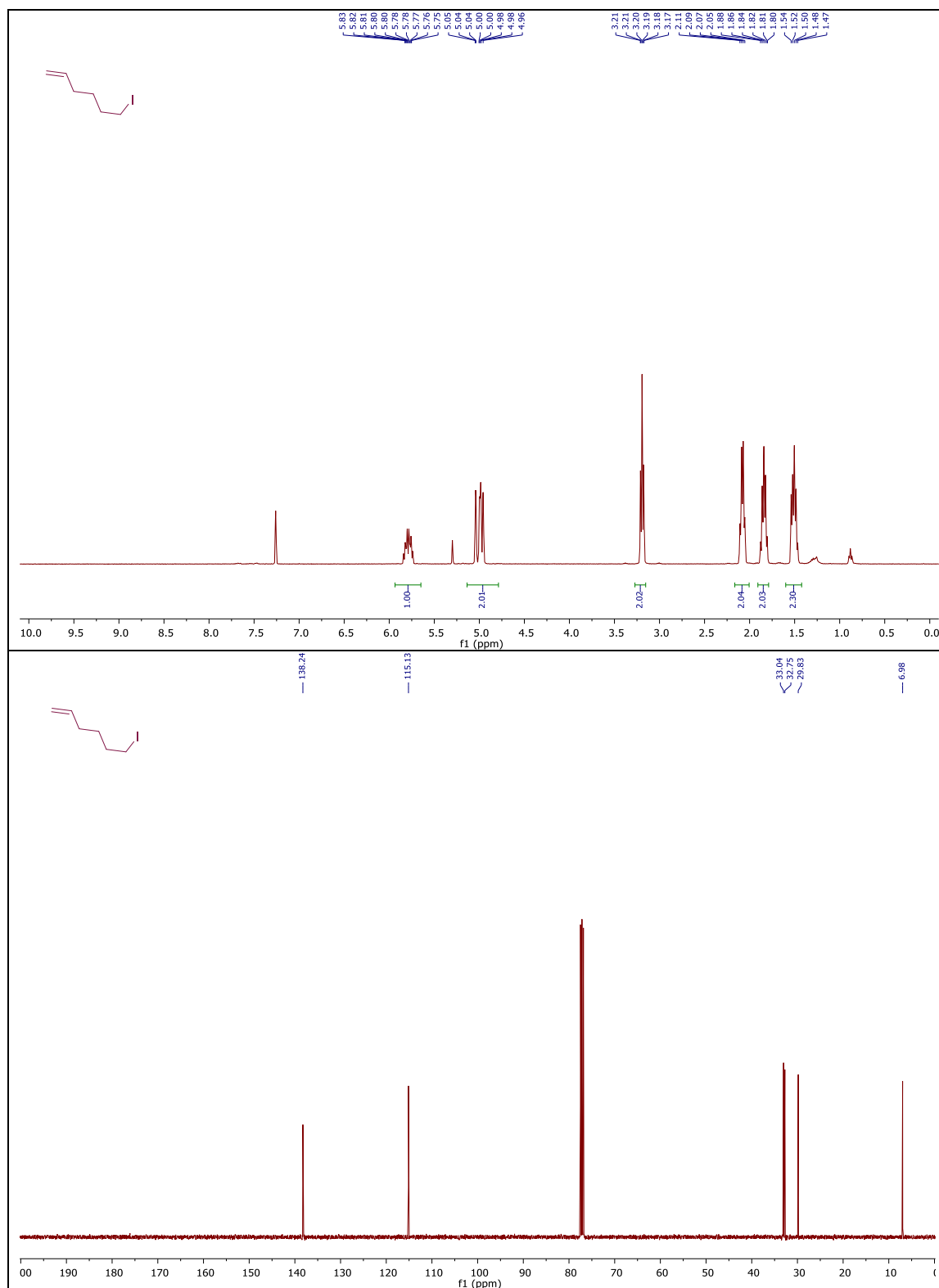
NMR spectra of 2l'



NMR spectra of 2m'



NMR spectra of 2n'



¹H NMR (400 MHz, CDCl₃)

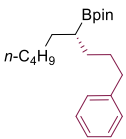
Chemical structure: (S)-1-(4-((n-butyl(phenyl)methyl)boronate)phenyl)ethan-1-ol

Chemical shift (ppm): 7.31, 7.31, 7.29, 7.29, 7.29, 7.28, 7.27, 7.27, 7.27, 7.27, 7.17, 7.17, 2.65, 2.63, 2.61, 1.69, 1.67, 1.65, 1.63, 1.61, 1.61, 1.53, 1.53, 1.52, 1.51, 1.51, 1.50, 1.50, 1.48, 1.47, 1.46, 1.45, 1.44, 1.44, 1.41, 1.41, 1.40, 1.39, 1.37, 1.35, 1.34, 1.34, 1.33, 1.33, 1.32, 1.32, 1.31, 1.31, 1.30, 1.30, 1.29, 1.29, 1.27, 1.25, 1.24, 1.15, 1.15, 1.14, 1.14, 1.05, 1.05, 1.04, 1.04, 1.03, 1.02, 1.01, 1.01, 0.99, 0.99, 0.93, 0.93, 0.90, 0.88, 0.86, 0.11.

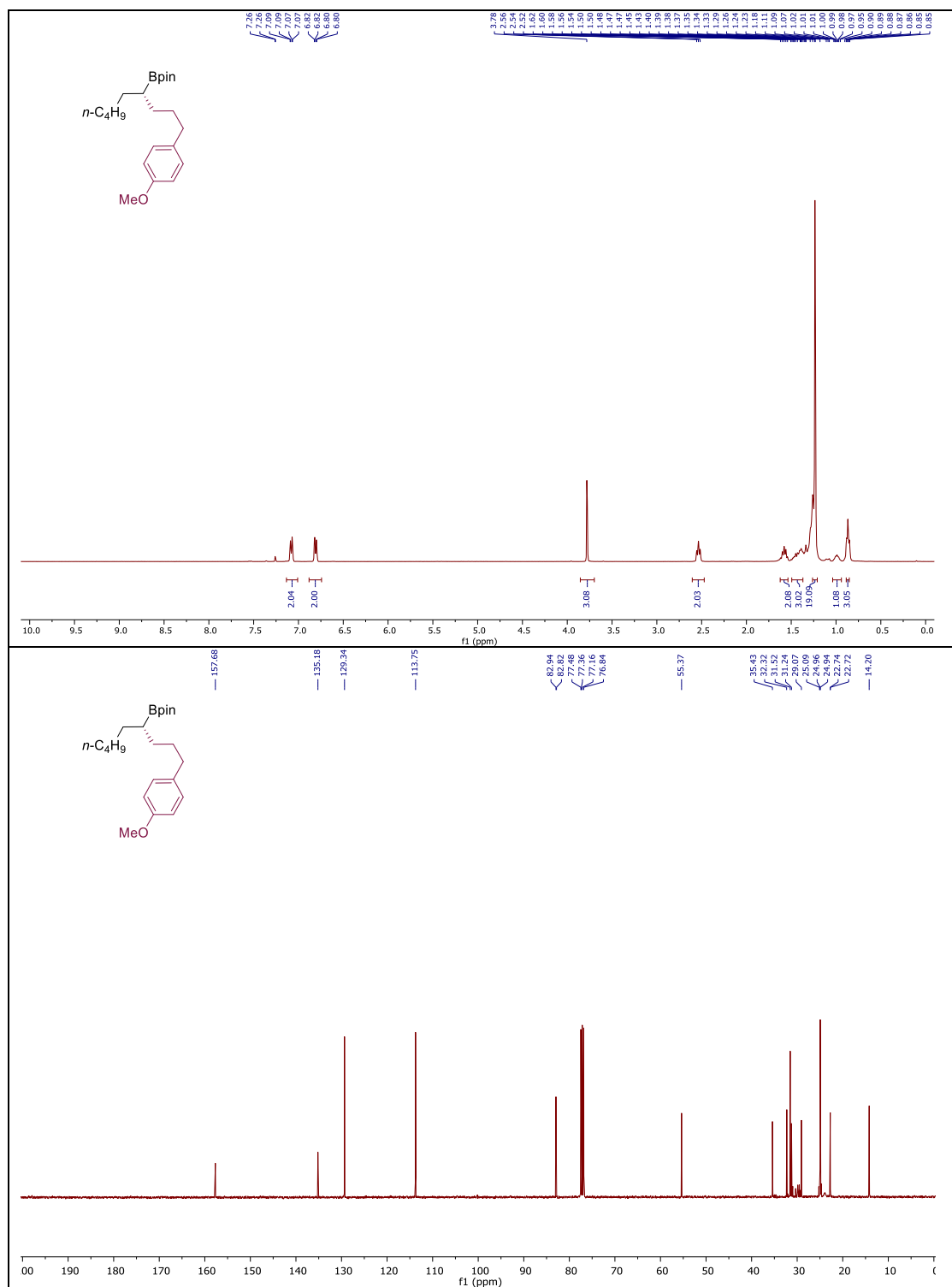
Integration: 2.07, 3.01, 2.00, 2.10, 3.04, 19.15, 1.12, 3.13.

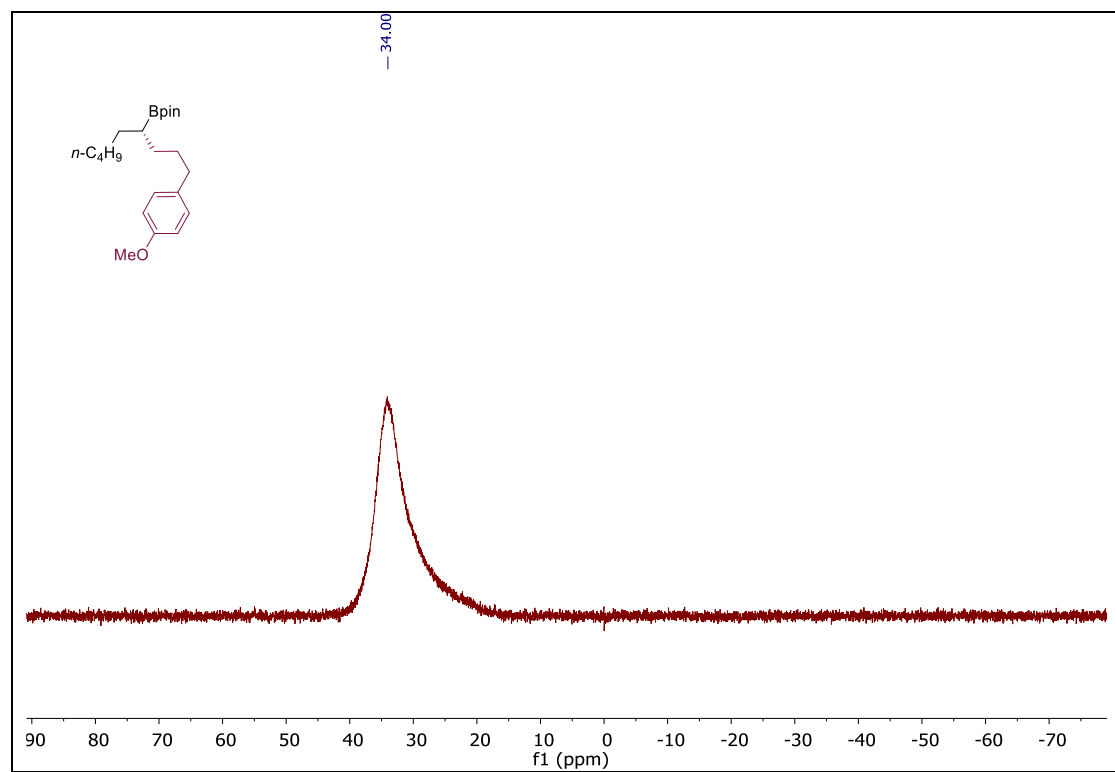
¹³C NMR (100 MHz, CDCl₃)

Chemical shift (ppm): 143.07, 128.51, 128.32, 125.62, 82.95, 77.48, 77.06, 76.84, 36.39, 32.29, 31.51, 31.22, 31.30, 29.08, 24.97, 24.94, 22.75, 14.21.



NMR spectra of 3b





¹H NMR (400 MHz, CDCl₃)

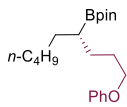
Chemical structure: (S)-1-(4-((pinacolatobenzyl)oxy)phenyl)butane

Peak list (ppm): 7.31, 7.30, 7.30, 7.29, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.26, 6.96, 6.96, 6.95, 6.94, 6.94, 6.94, 6.93, 6.93, 6.92, 6.92, 6.91, 6.91, 6.90, 6.90, 3.99, 3.99, 3.97, 3.95, 3.95, 1.83, 1.82, 1.82, 1.82, 1.81, 1.81, 1.80, 1.80, 1.79, 1.79, 1.77, 1.77, 1.60, 1.60, 1.58, 1.58, 1.56, 1.56, 1.55, 1.55, 1.54, 1.54, 1.52, 1.52, 1.49, 1.49, 1.48, 1.48, 1.47, 1.46, 1.46, 1.45, 1.45, 1.44, 1.44, 1.41, 1.41, 1.40, 1.40, 1.39, 1.39, 1.37, 1.36, 1.36, 1.36, 1.35, 1.35, 1.34, 1.34, 1.33, 1.33, 1.32, 1.32, 1.31, 1.31, 1.30, 1.30, 1.29, 1.29, 1.27, 1.27, 1.25, 1.25, 1.25, 1.25, 1.07, 1.07, 1.06, 1.06, 1.05, 1.05, 1.04, 1.04, 1.03, 1.03, 0.93, 0.93, 0.92, 0.92, 0.91, 0.91, 0.89, 0.89, 0.88, 0.87.

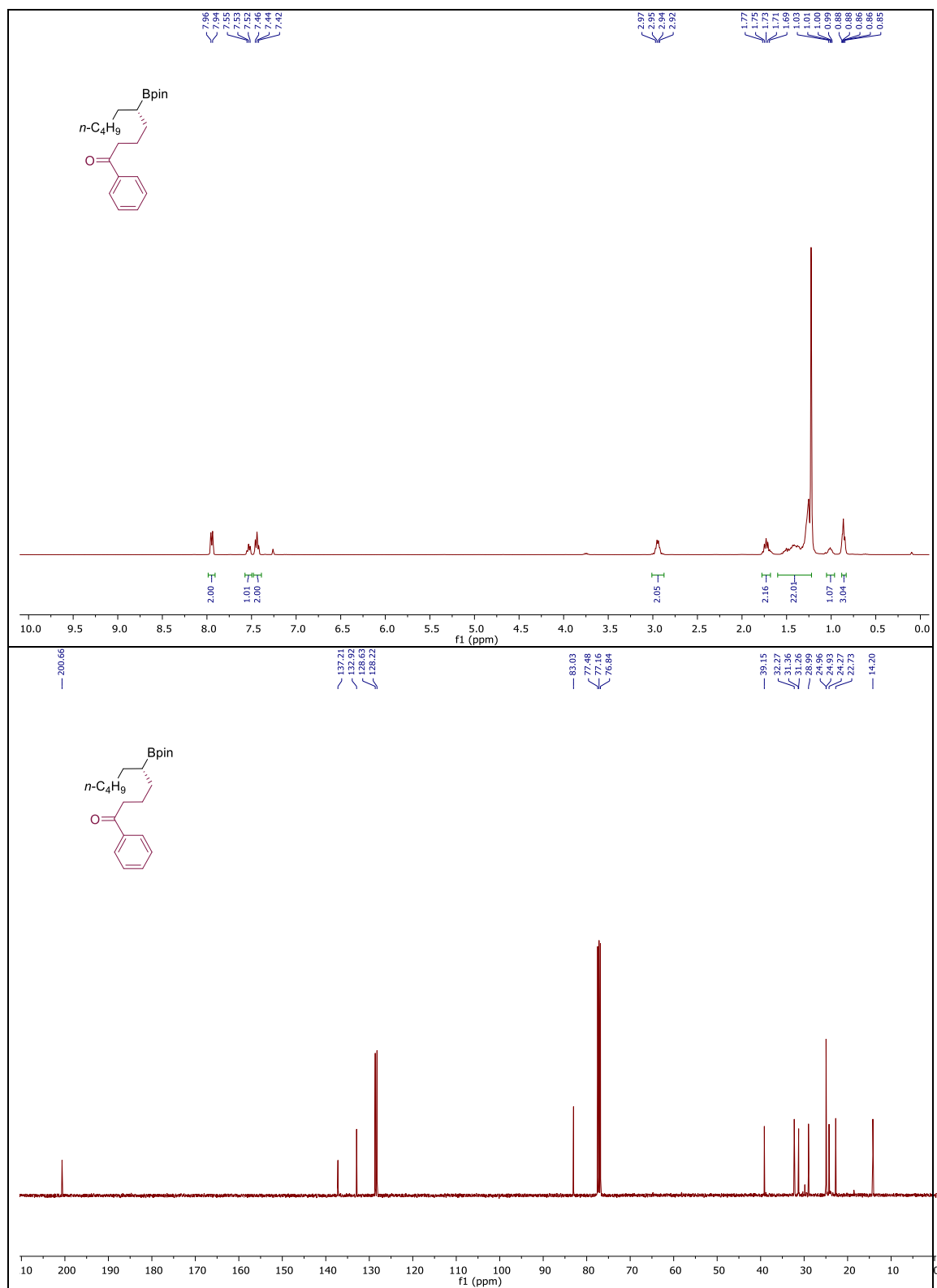
Integration values: 2.00, 3.00, 2.06, 2.06, 3.11, 19.31, 1.08, 3.47.

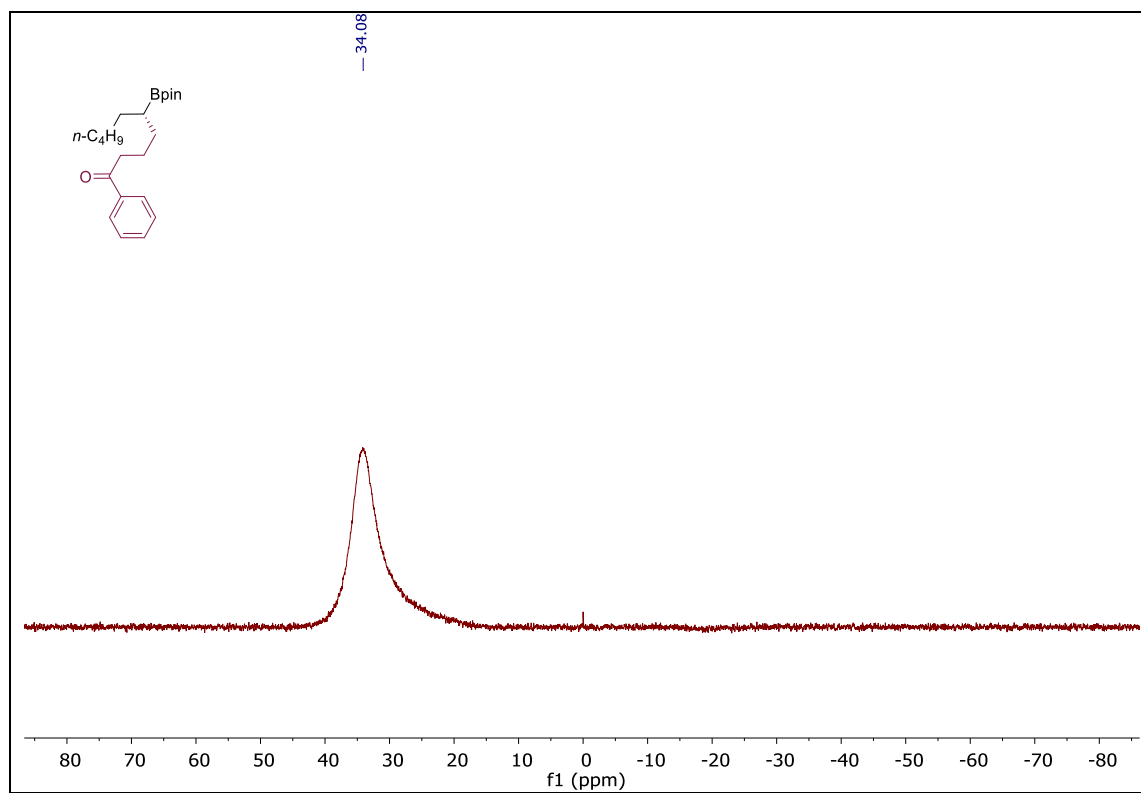
¹³C NMR (100 MHz, CDCl₃)

Peak list (ppm): 159.25, 129.48, 120.50, 114.67, 83.05, 77.48, 77.16, 76.84, 68.24, 32.28, 31.42, 29.85, 29.85, 28.97, 28.97, 27.77, 24.98, 24.93, 22.73, 14.21.



NMR spectra of 3d



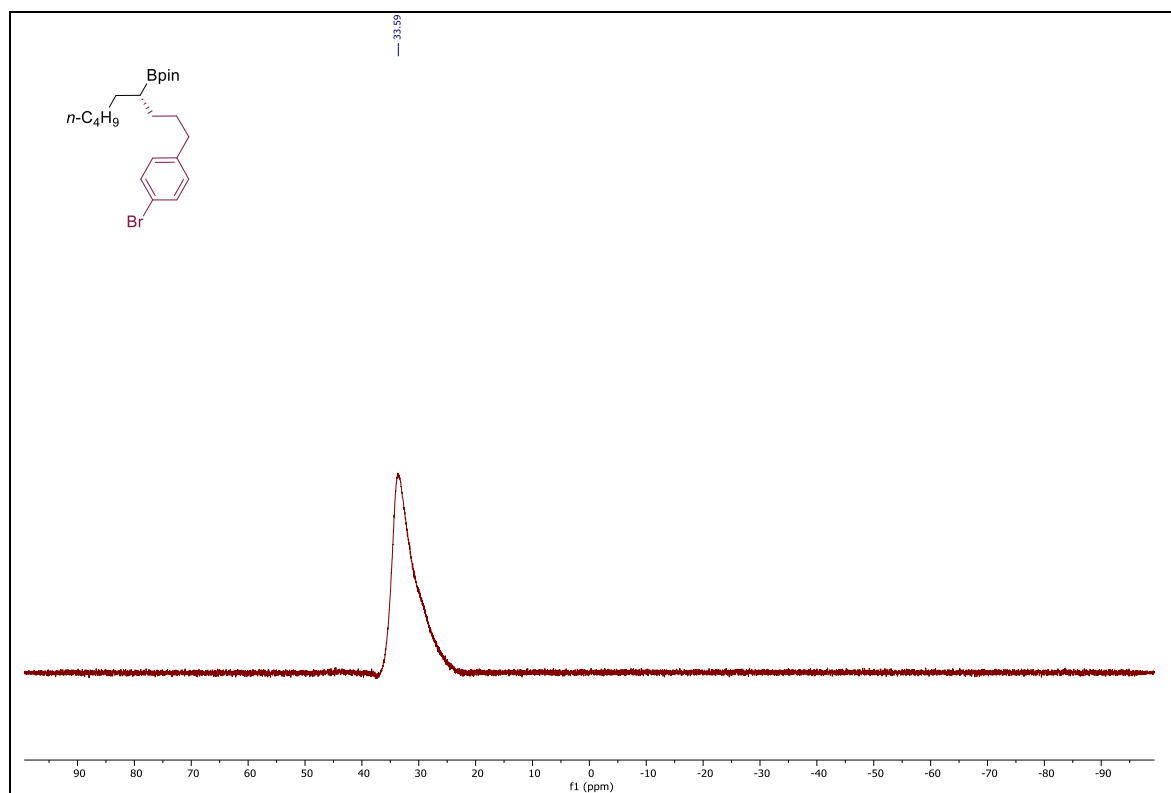


¹H NMR (400 MHz, CDCl₃)

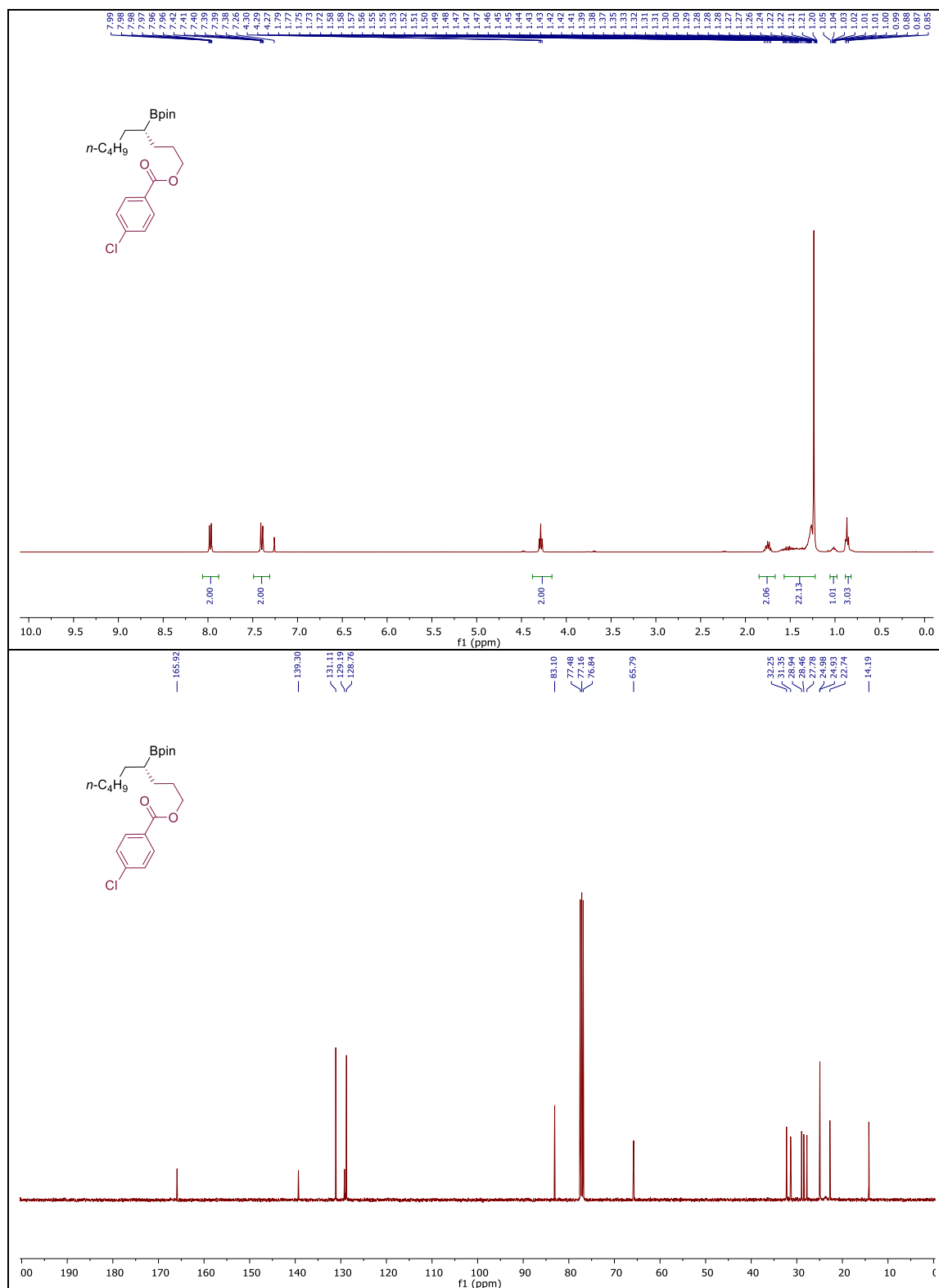
Chemical Shift (ppm)	Integration
7.38, 7.35, 7.36, 7.37	2.00
7.04, 7.03, 7.05	2.01
2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85	2.12
1.23, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85	2.38, 4.14, 18.37, 1.18, 3.38

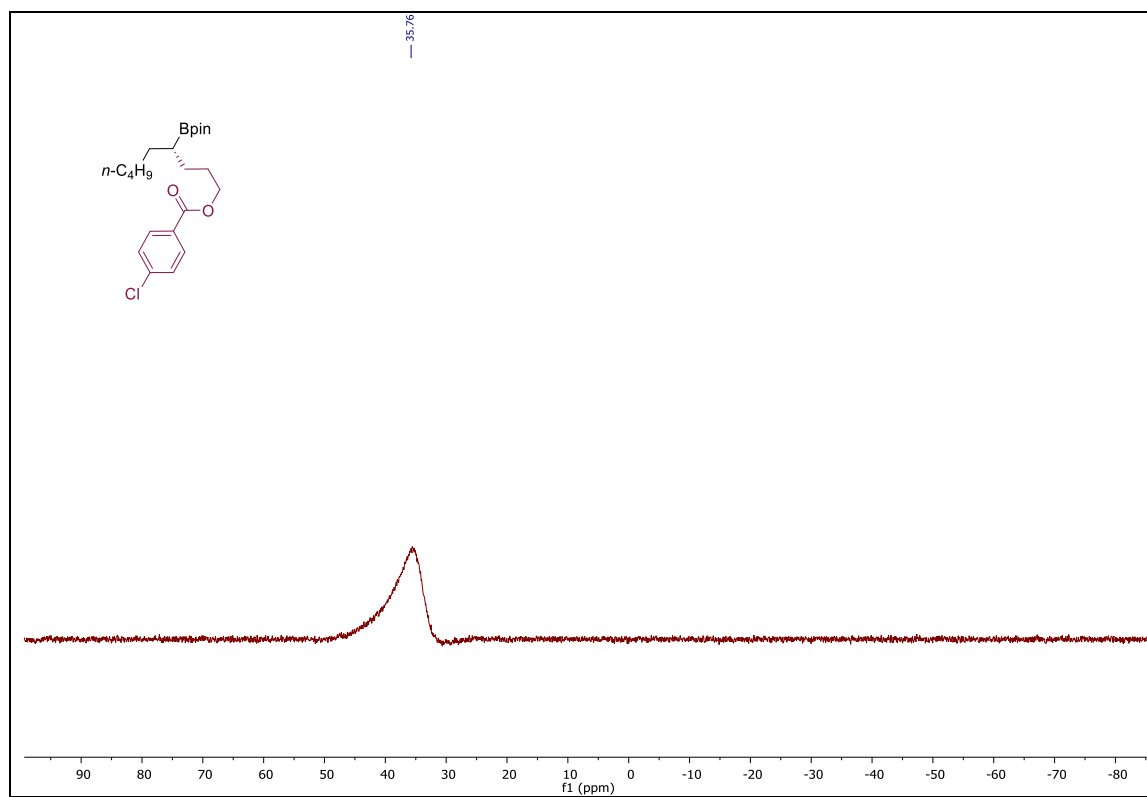
¹³C NMR (100 MHz, CDCl₃)

Chemical Shift (ppm)
141.96, 131.35, 130.26, 119.32, 85.98, 35.71, 32.25, 31.86, 31.16, 29.04, 24.95, 24.92, 22.73, 14.20



NMR spectra of 3f





¹H NMR Spectrum (Top):

Chemical structure: (S)-1-(4-iodophenyl)-4-(n-butyl(phenyl)phosphonyl)pyrrolidine

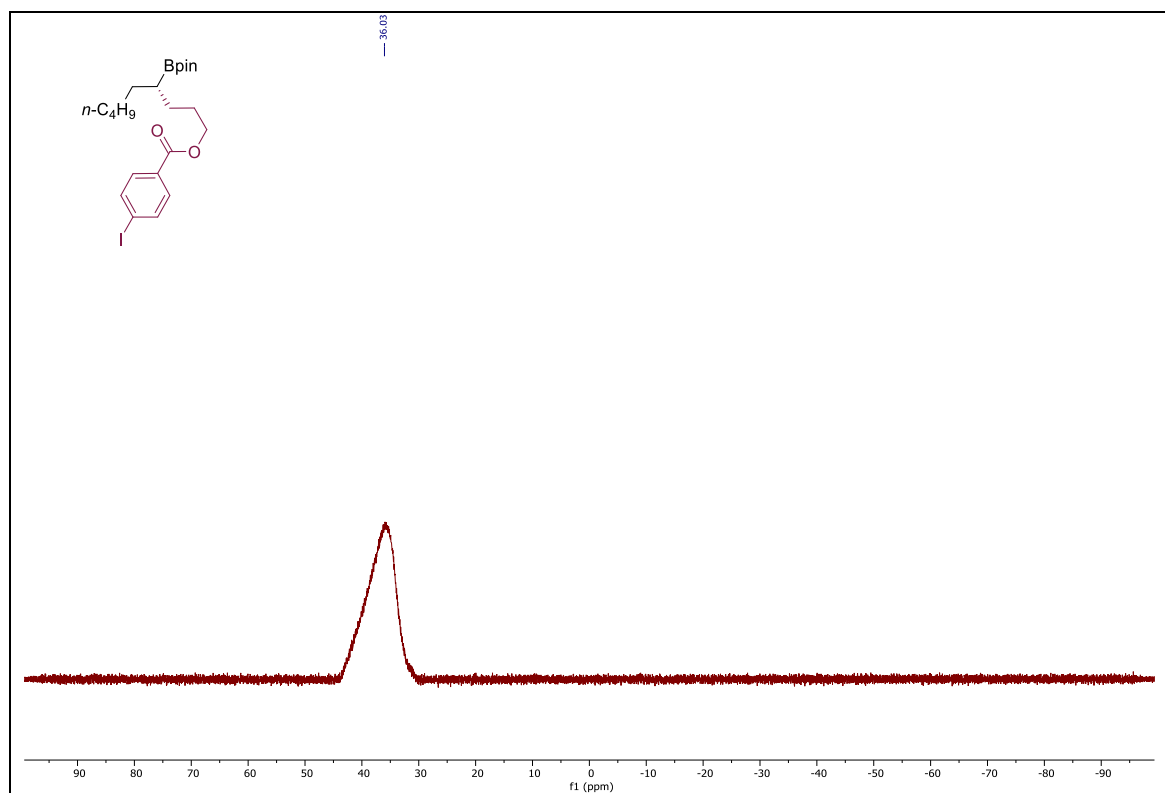
Chemical shift range: 0.85 to 7.80 ppm

Integration values: 1.92, 1.92, 2.00, 2.03, 4.15, 18.31, 1.03, 3.14

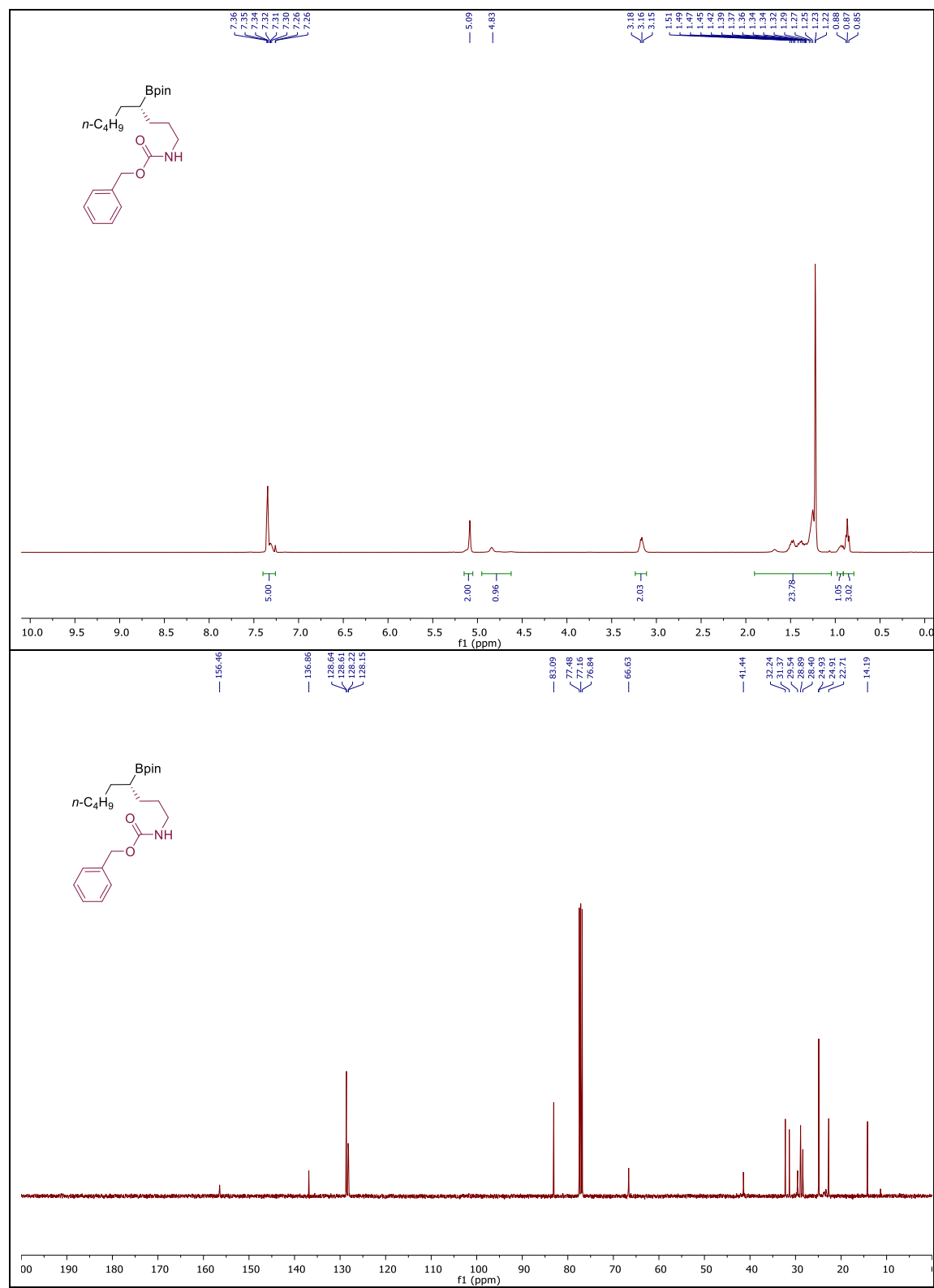
¹³C NMR Spectrum (Bottom):

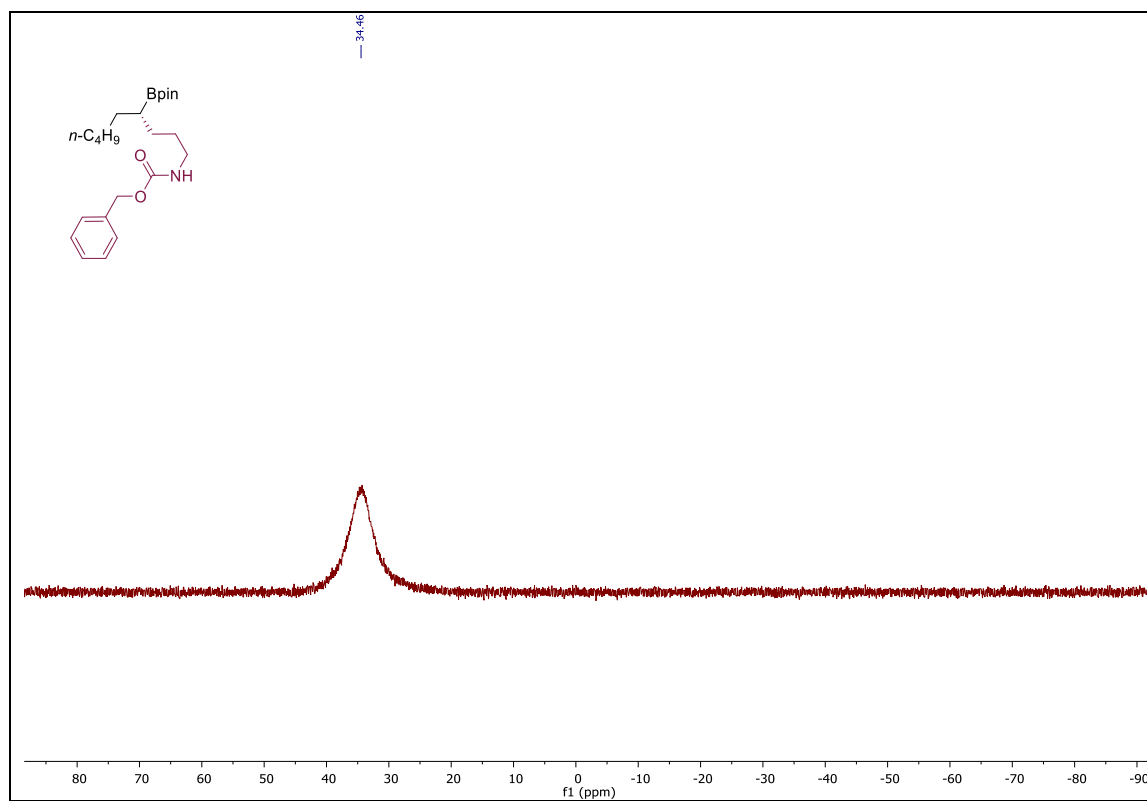
Chemical structure: (S)-1-(4-iodophenyl)-4-(n-butyl(phenyl)phosphonyl)pyrrolidine

Chemical shift range: 14.20 to 166.28 ppm

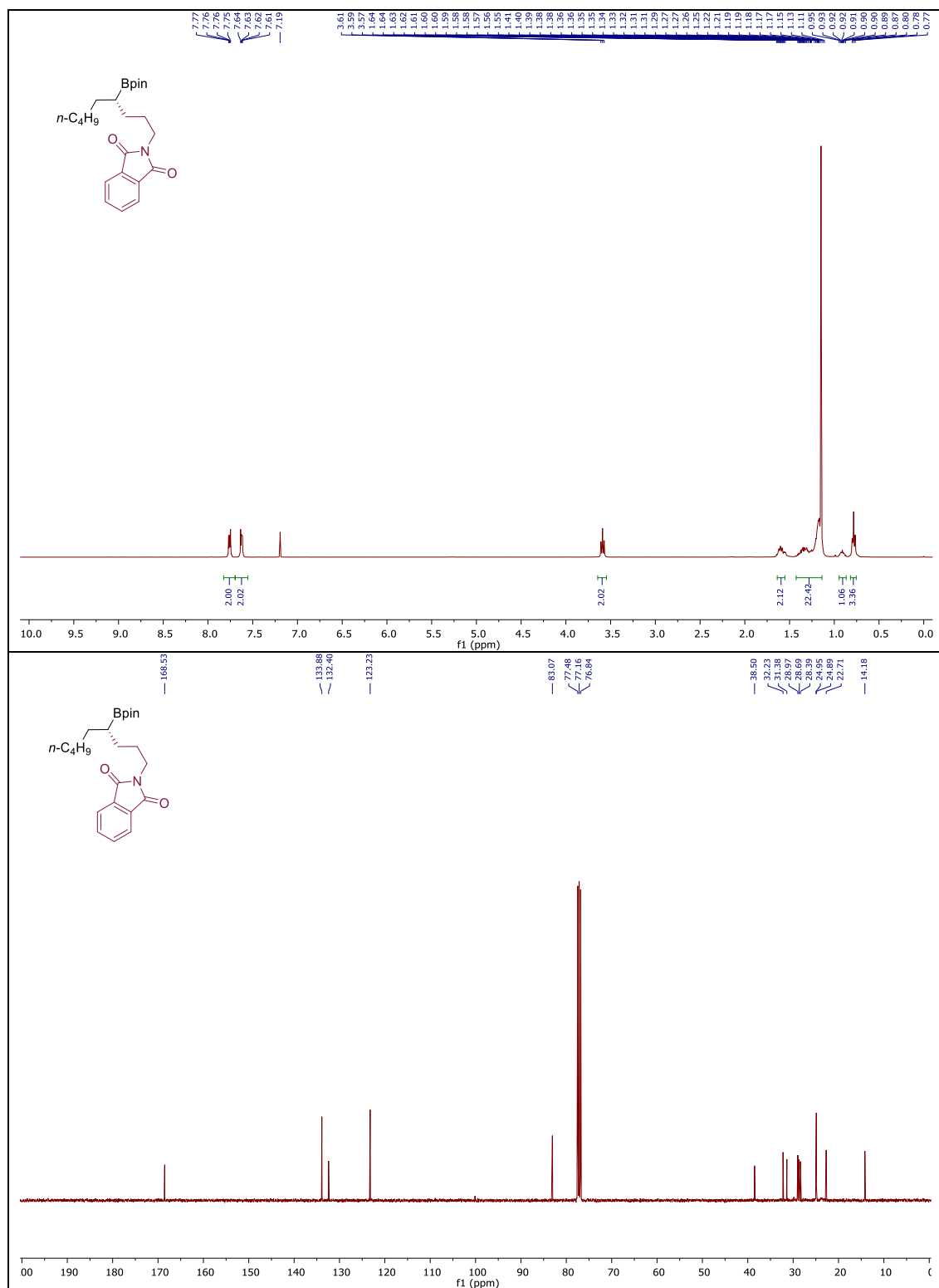


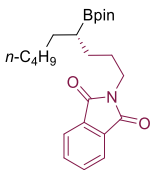
NMR spectra of 3h



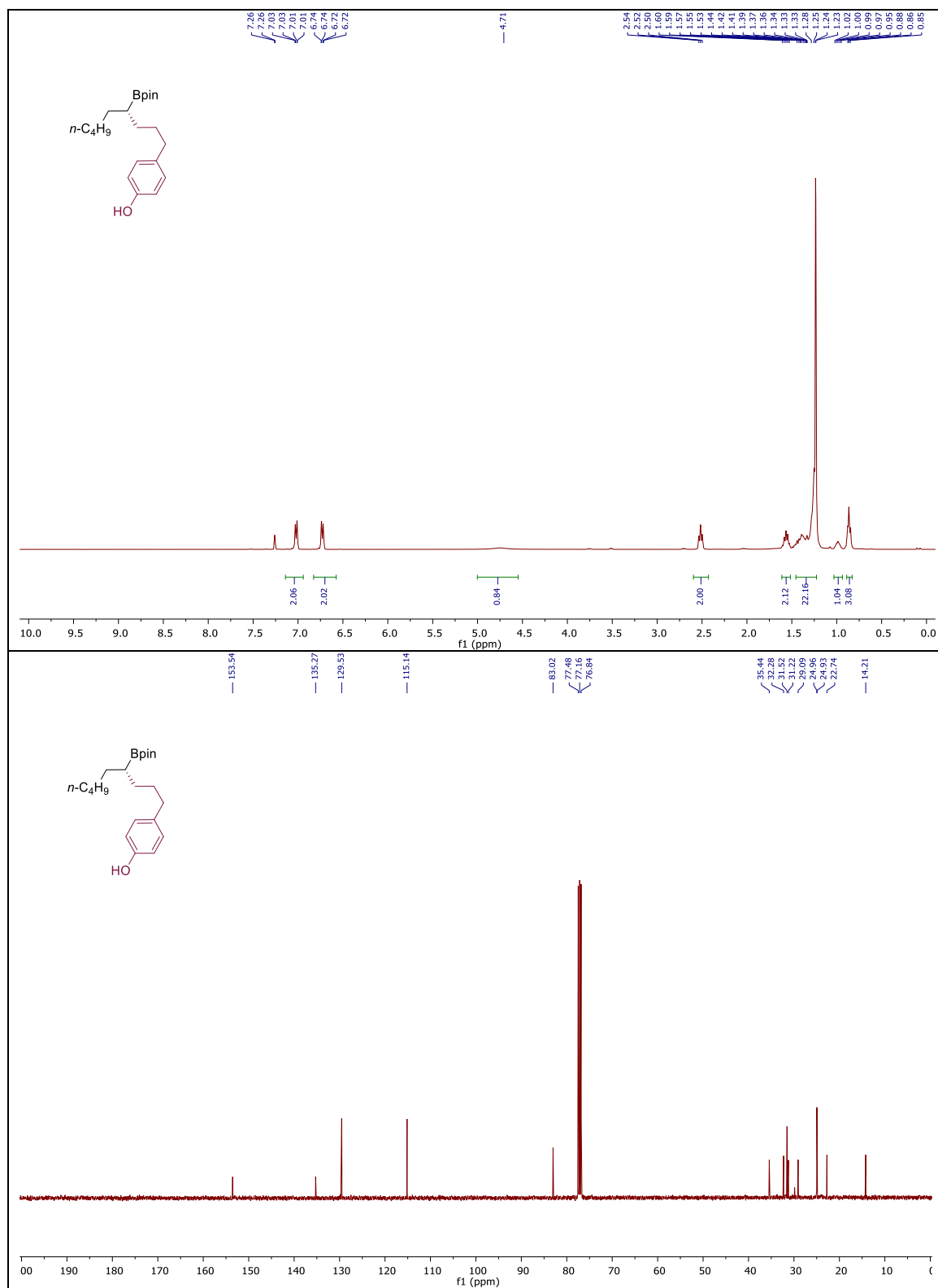


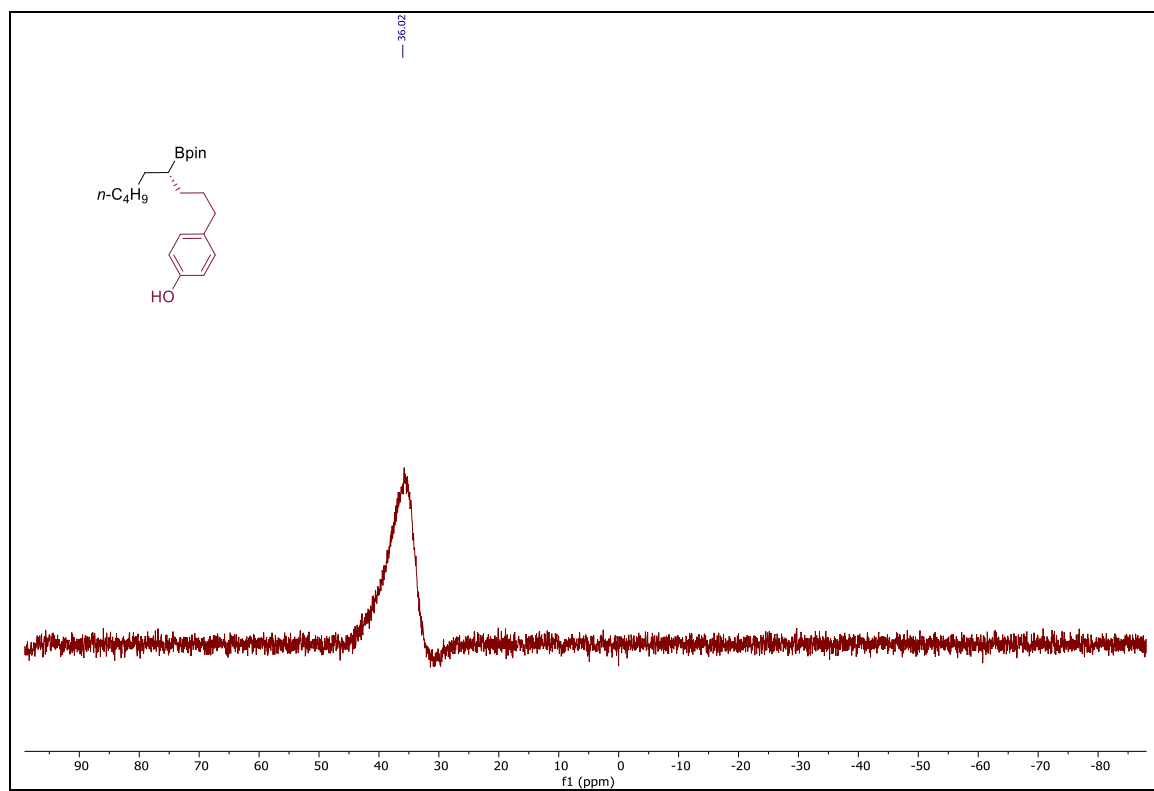
NMR spectra of 3i



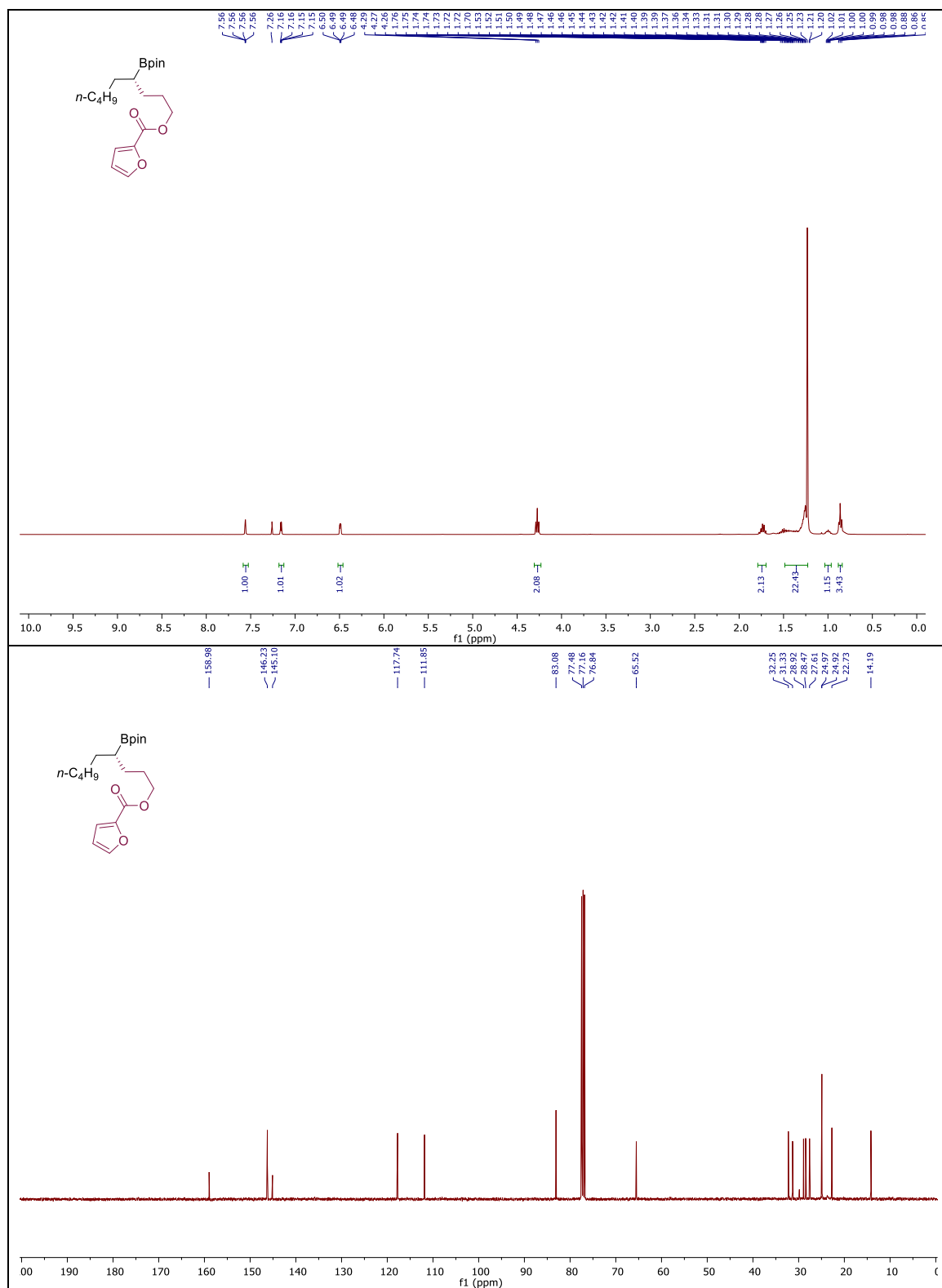


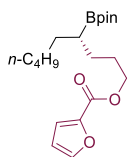
NMR spectra of 3j



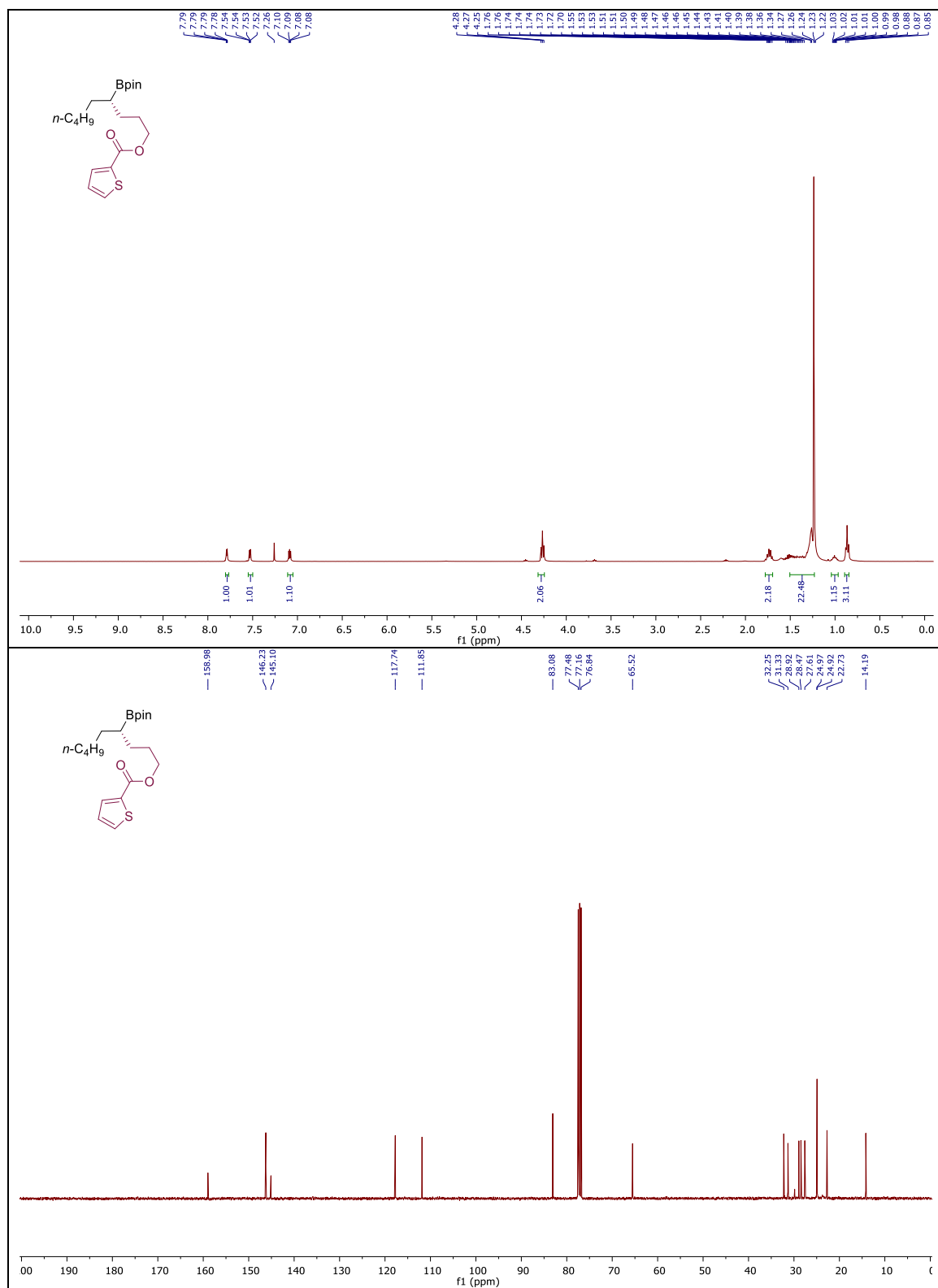


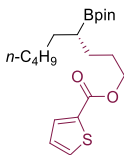
NMR spectra of 3k



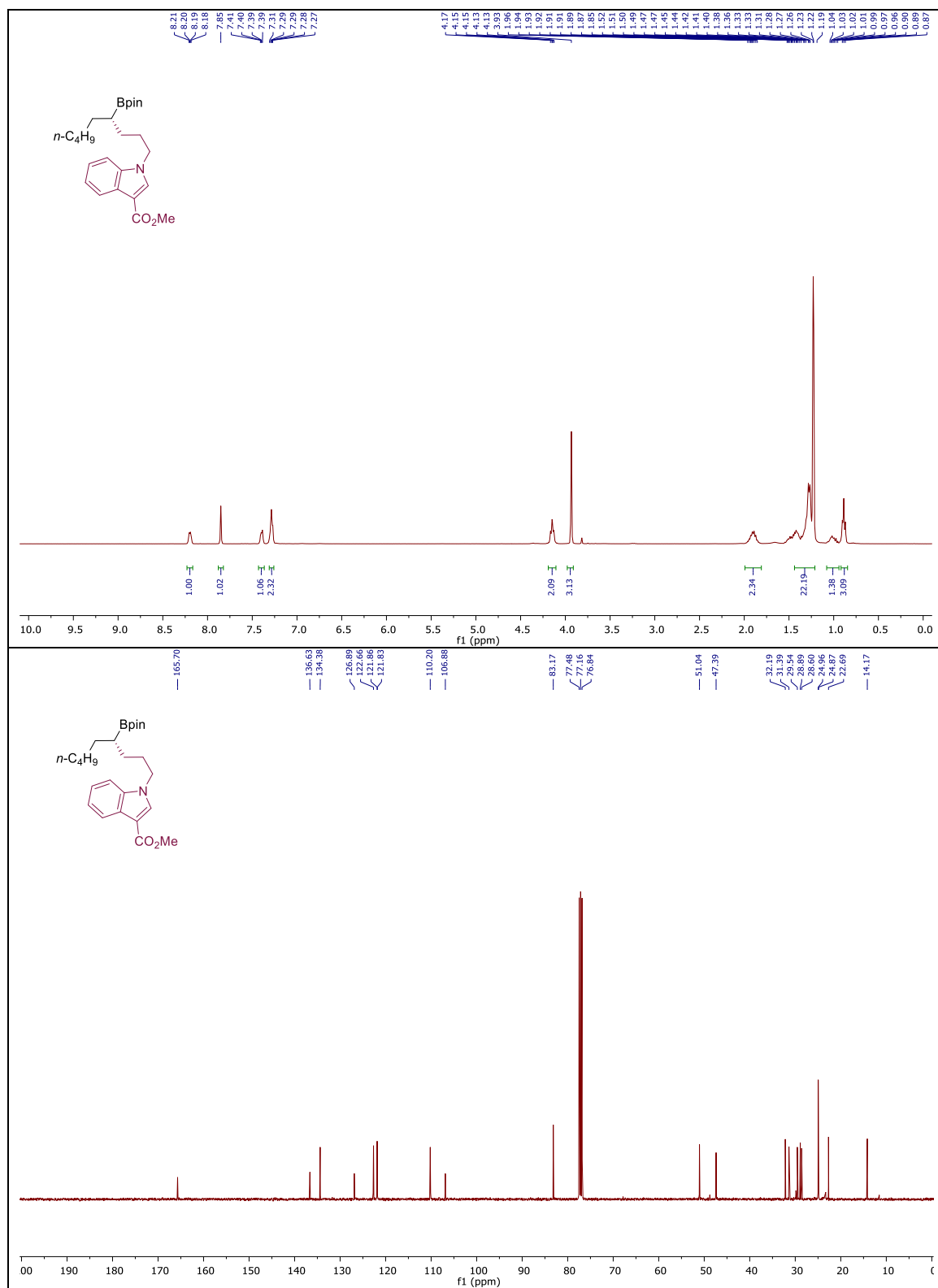


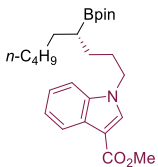
NMR spectra of 3l





NMR spectra of 3m





¹H NMR (400 MHz, CDCl₃)

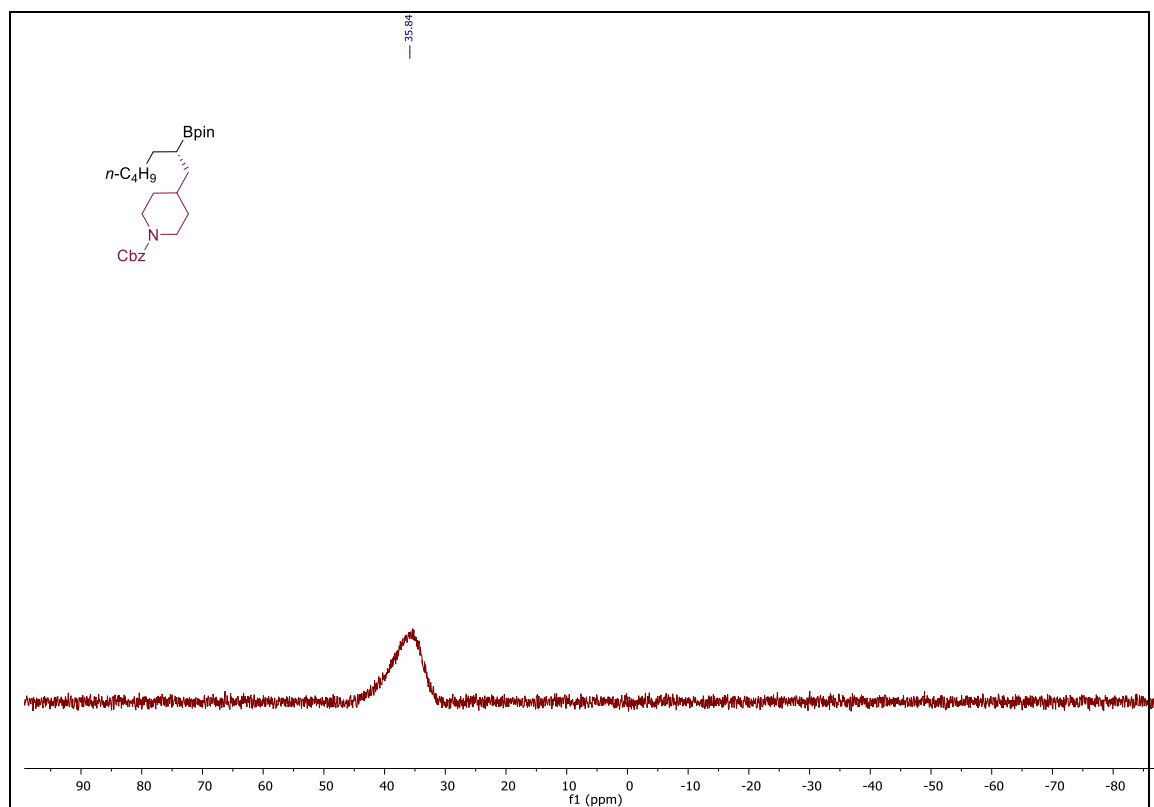
Chemical structure: (S)-1-(4-(benzyloxycarbonyl)-4,5,6,7-tetrahydropyridin-2-yl)butan-1-ol

Chemical shift (ppm): 7.36, 7.35, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.29, 7.26, 5.12, 4.14, 2.76, 2.76, 2.73, 2.70, 2.70, 1.70, 1.66, 1.63, 1.43, 1.42, 1.41, 1.40, 1.39, 1.39, 1.38, 1.38, 1.36, 1.35, 1.35, 1.34, 1.34, 1.32, 1.32, 1.31, 1.30, 1.29, 1.29, 1.27, 1.27, 1.26, 1.25, 1.25, 1.24, 1.23, 1.22, 1.22, 1.21, 1.20, 1.09, 1.06, 1.05, 1.04, 1.03, 0.88, 0.87, 0.85.

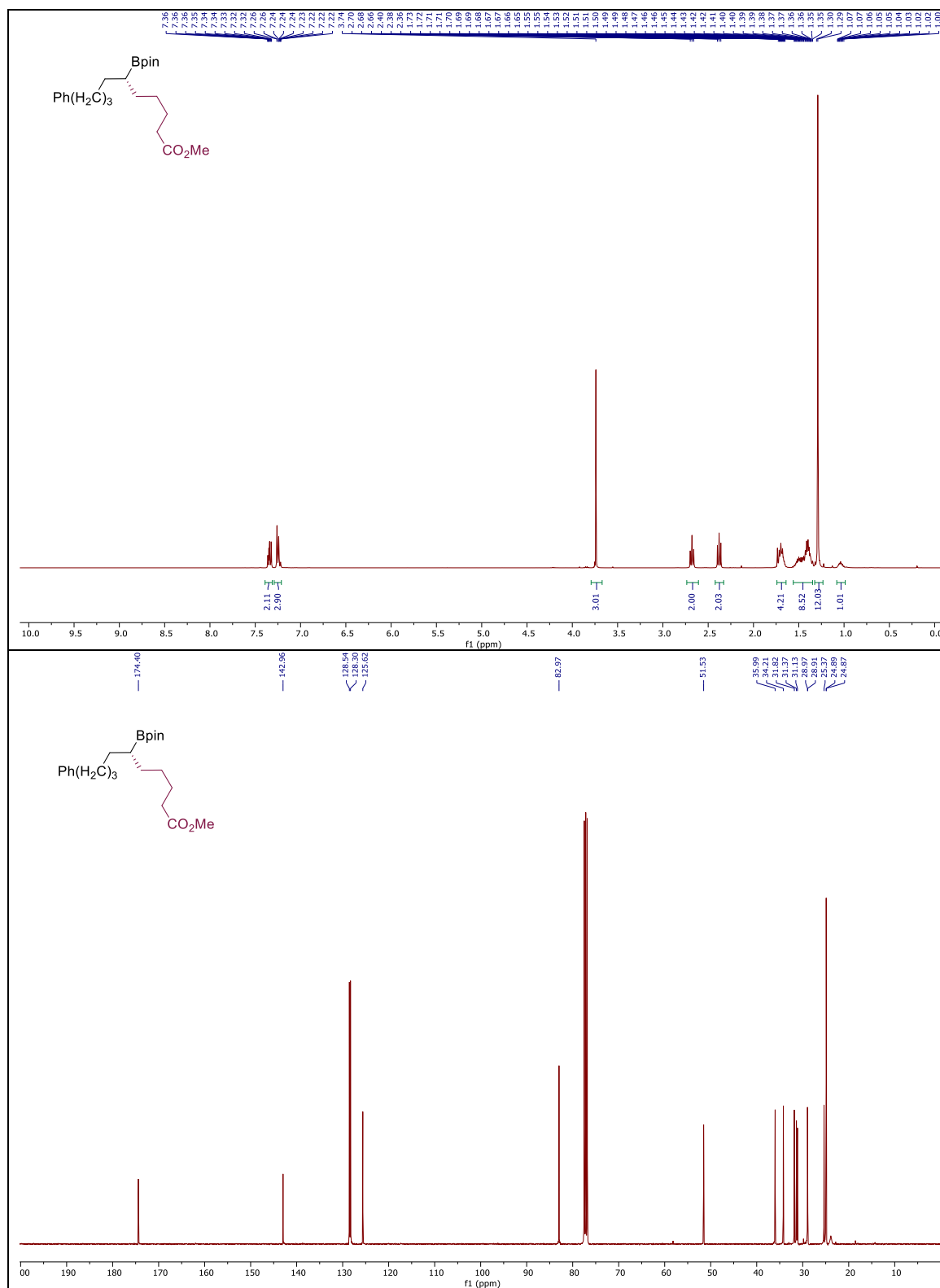
Integration values: 5.19, 2.01, 2.00, 2.01, 2.28, 23.32, 3.21, 3.13.

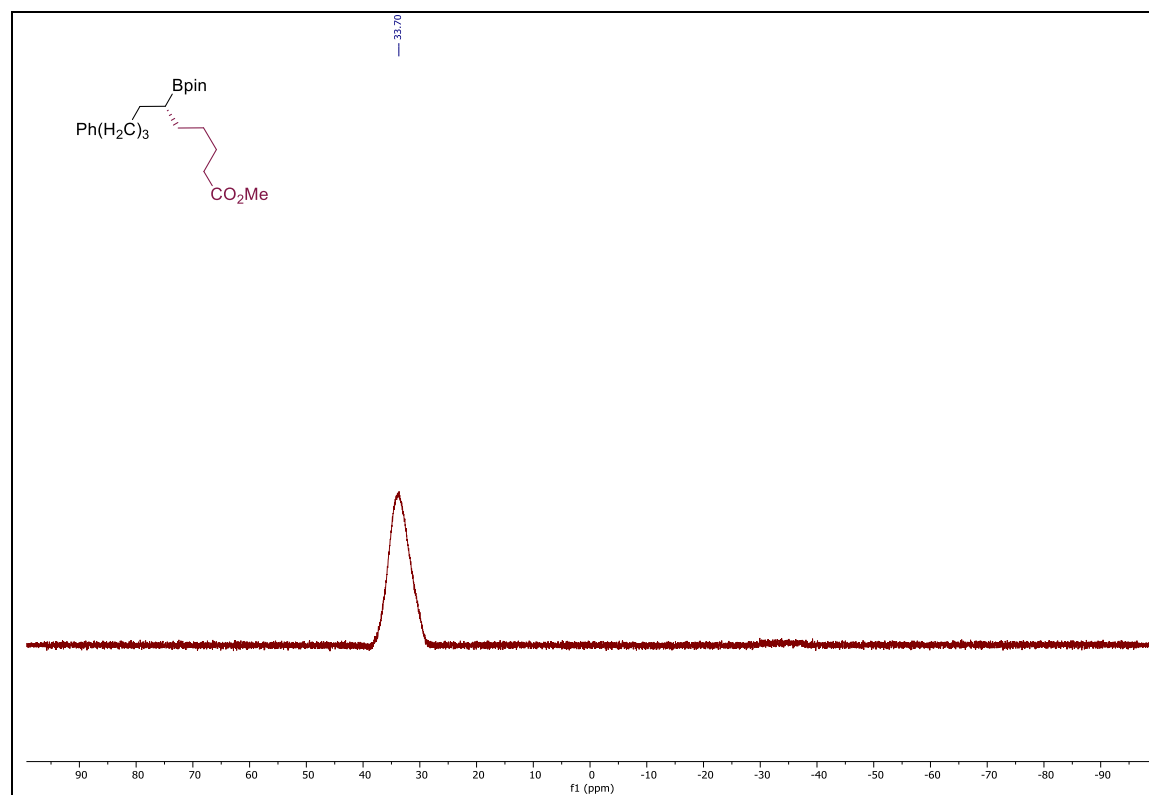
¹³C NMR (100 MHz, CDCl₃)

Chemical shift (ppm): 155.45, 137.20, 128.58, 127.92, 83.04, 77.48, 76.84, 67.00, 44.47, 38.22, 35.52, 32.27, 31.86, 29.00, 24.98, 24.91, 22.74, 14.20.

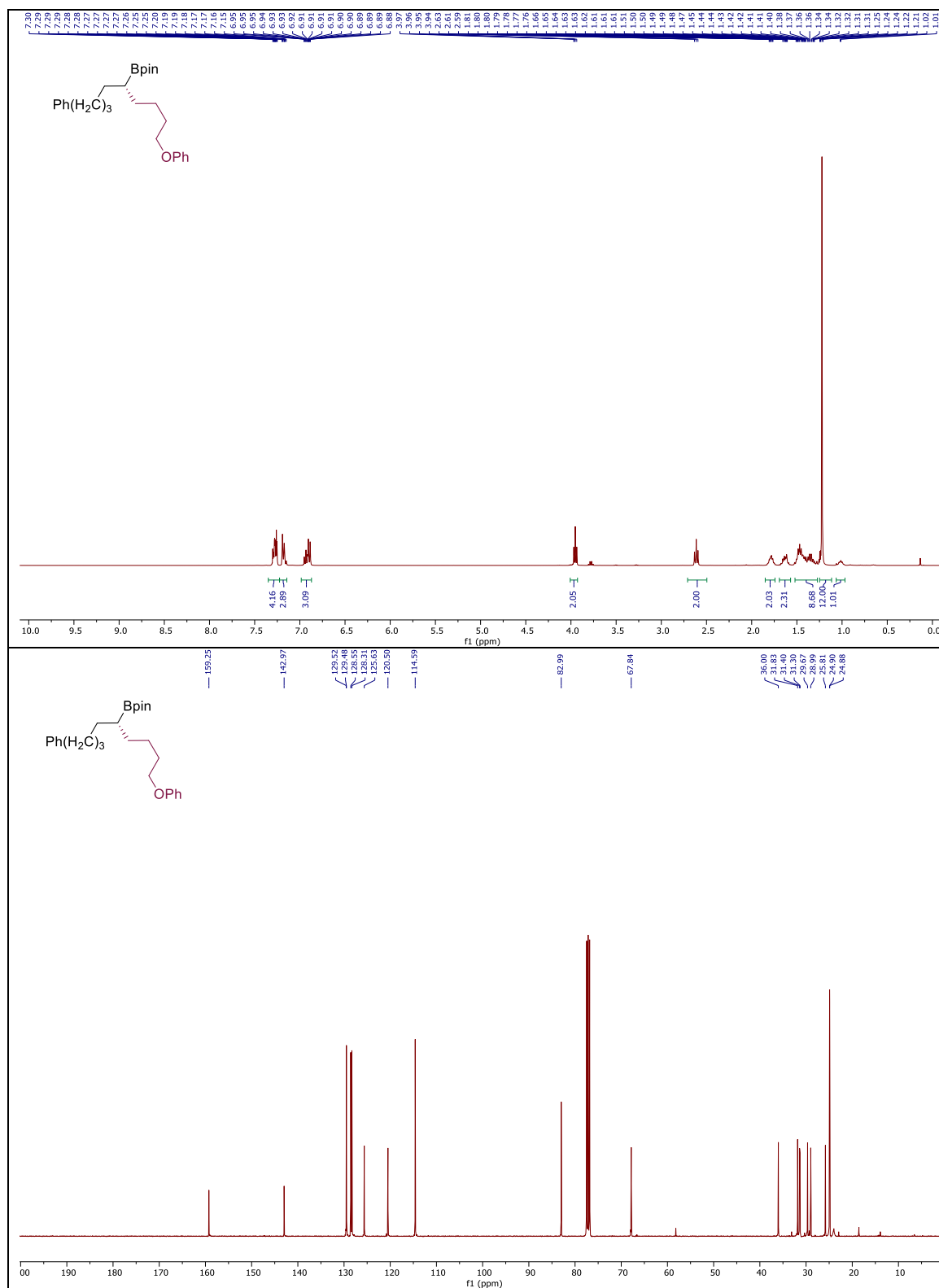


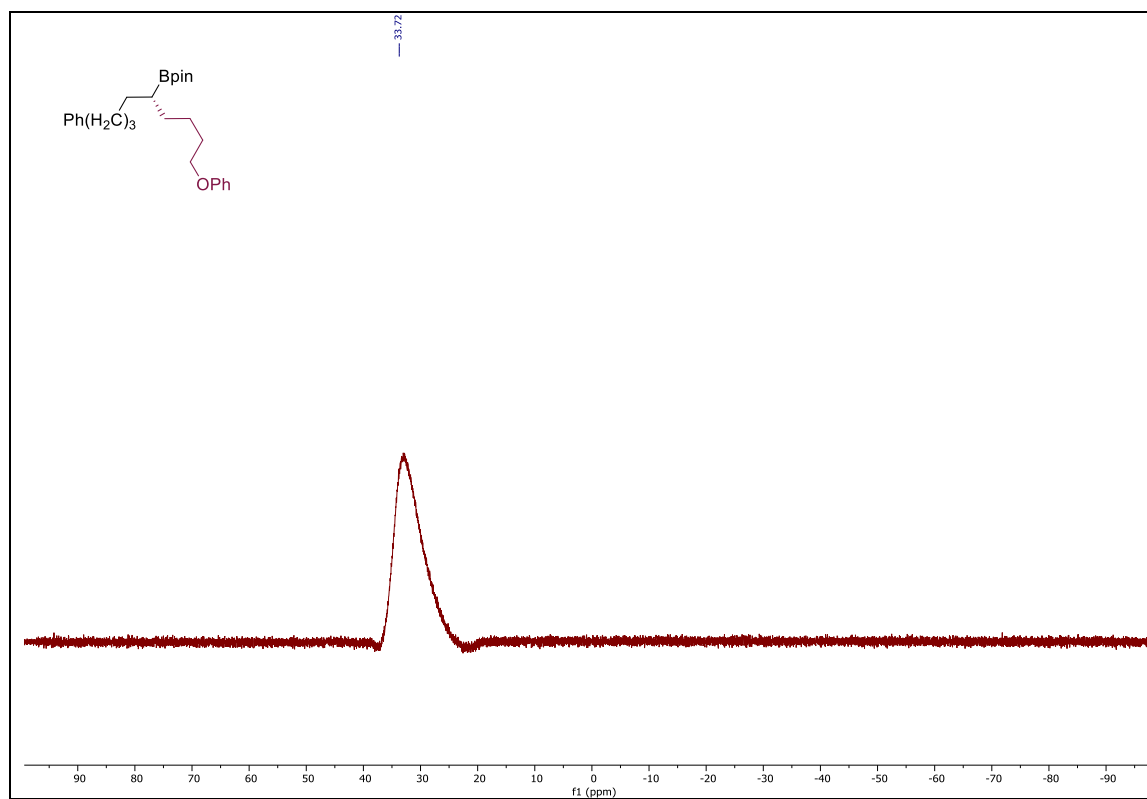
NMR spectra of 3o



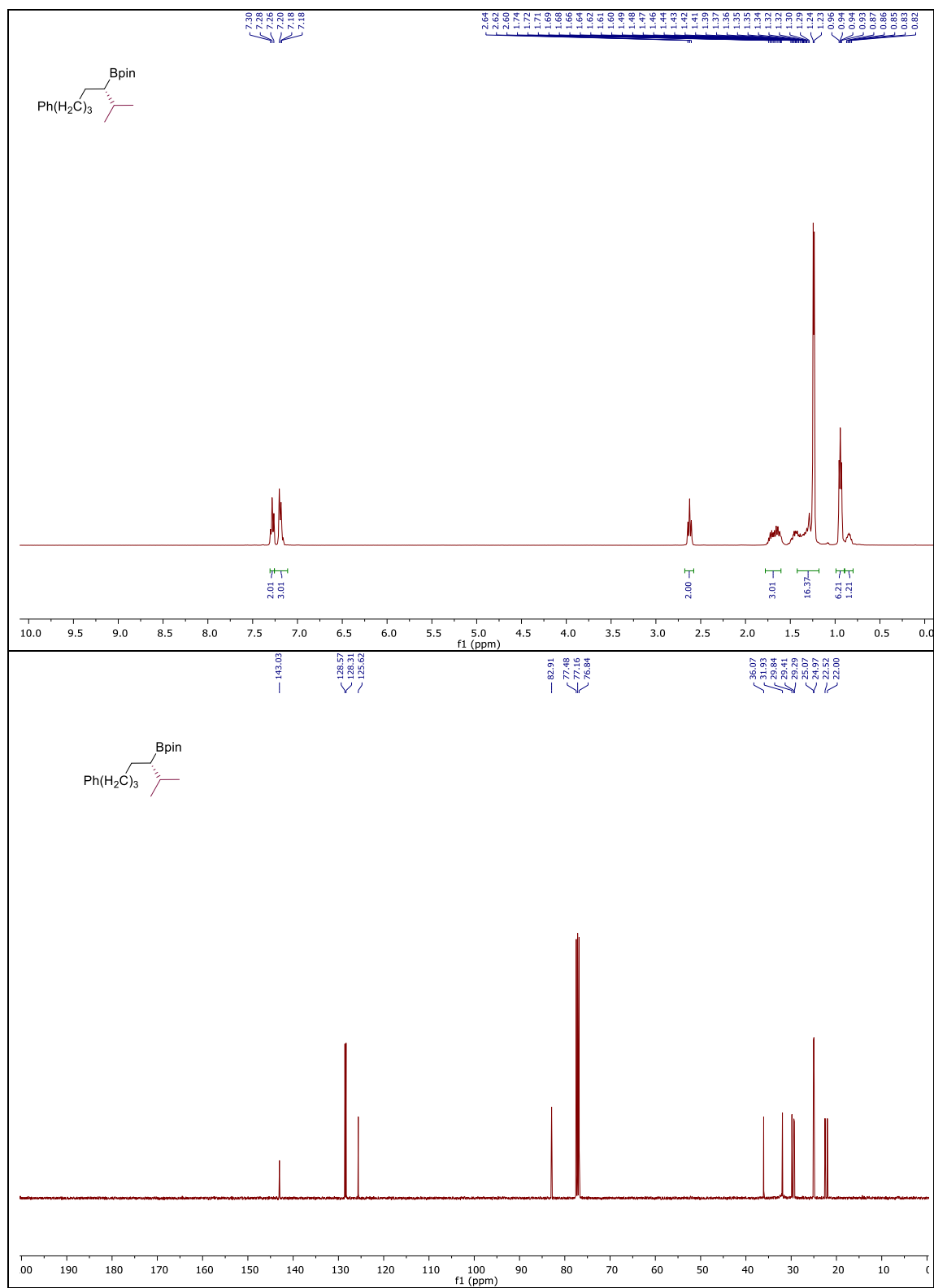


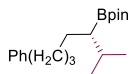
NMR spectra of 3p



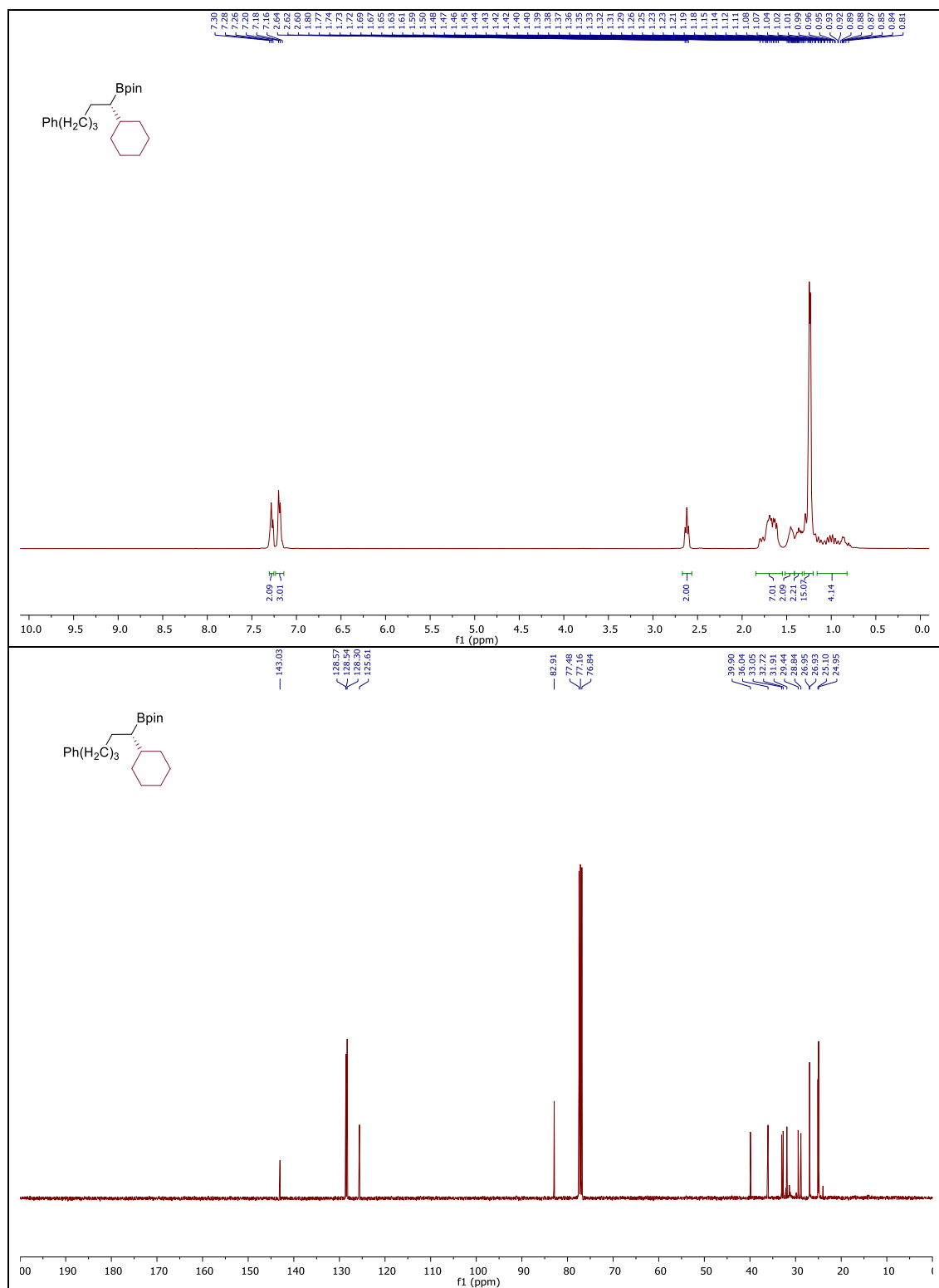


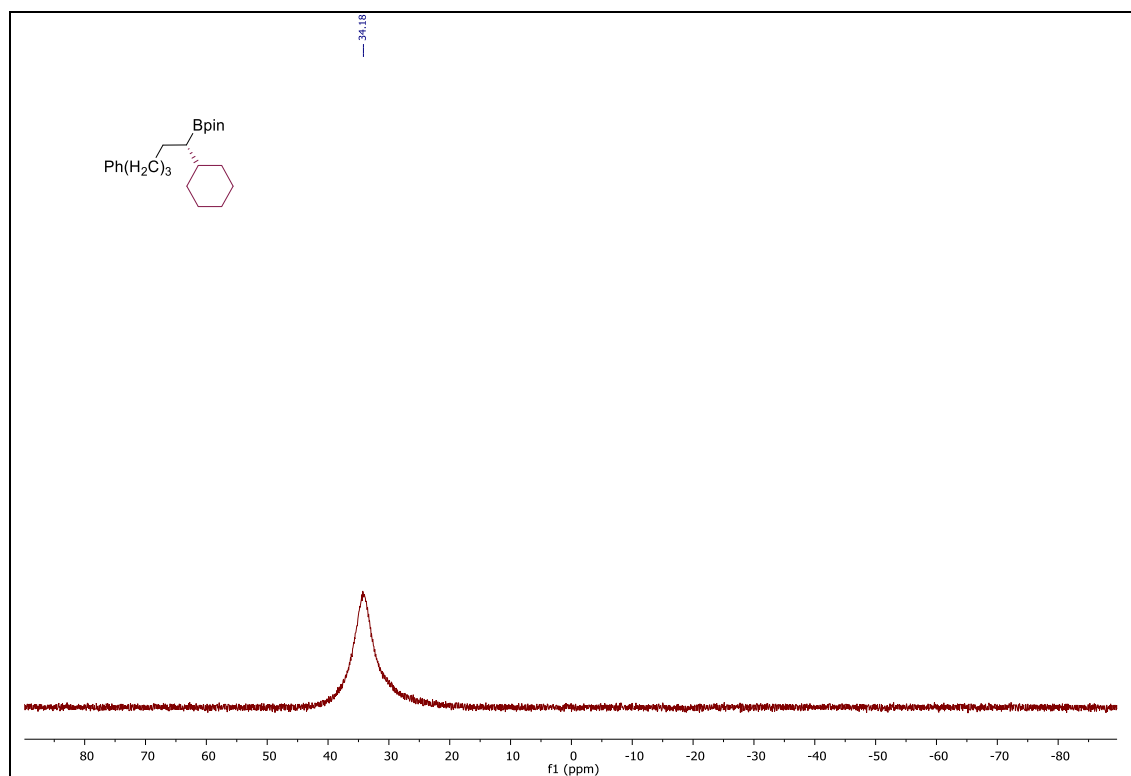
NMR spectra of 4a



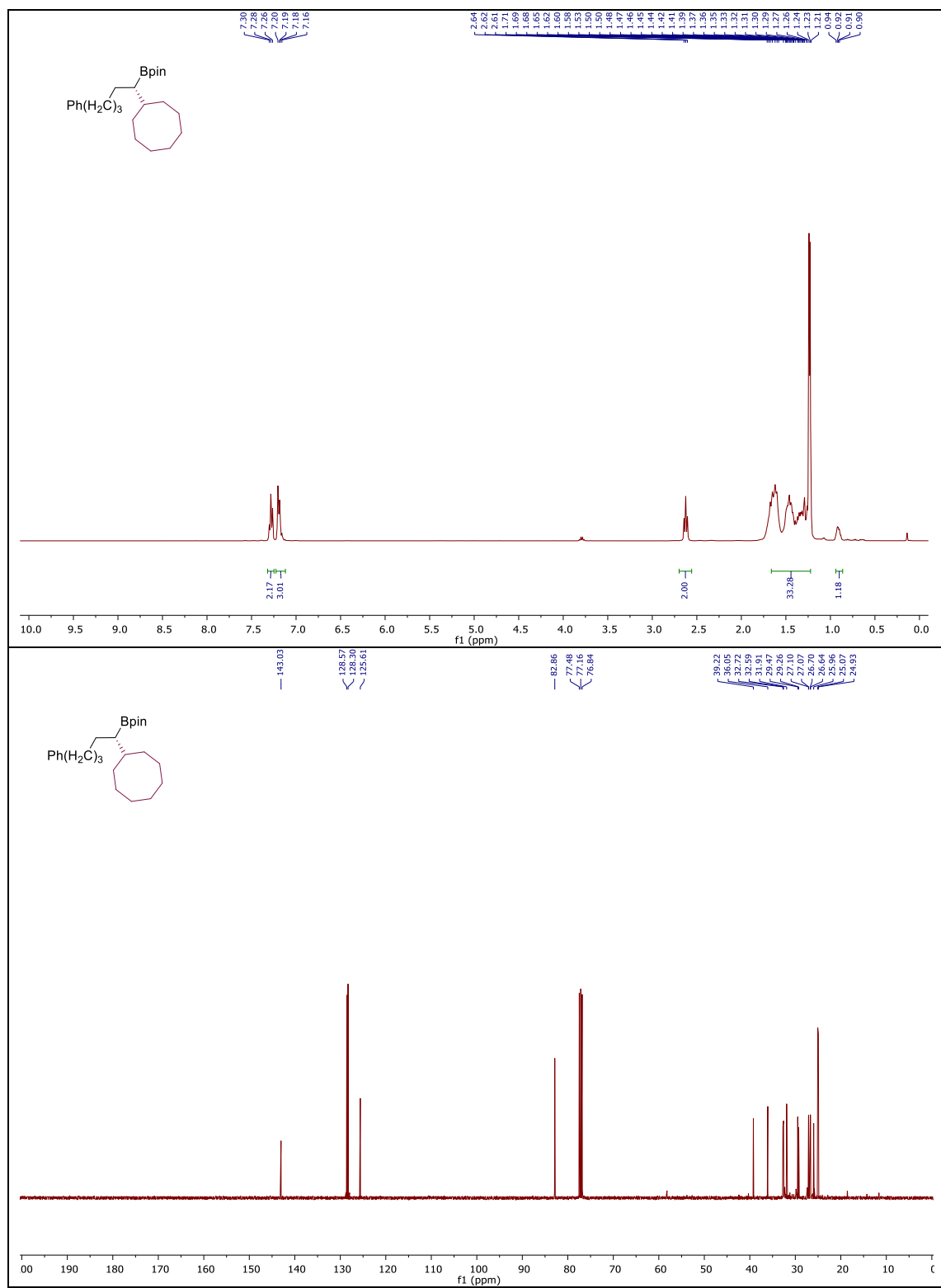


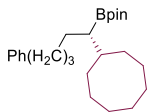
NMR spectra of 4b



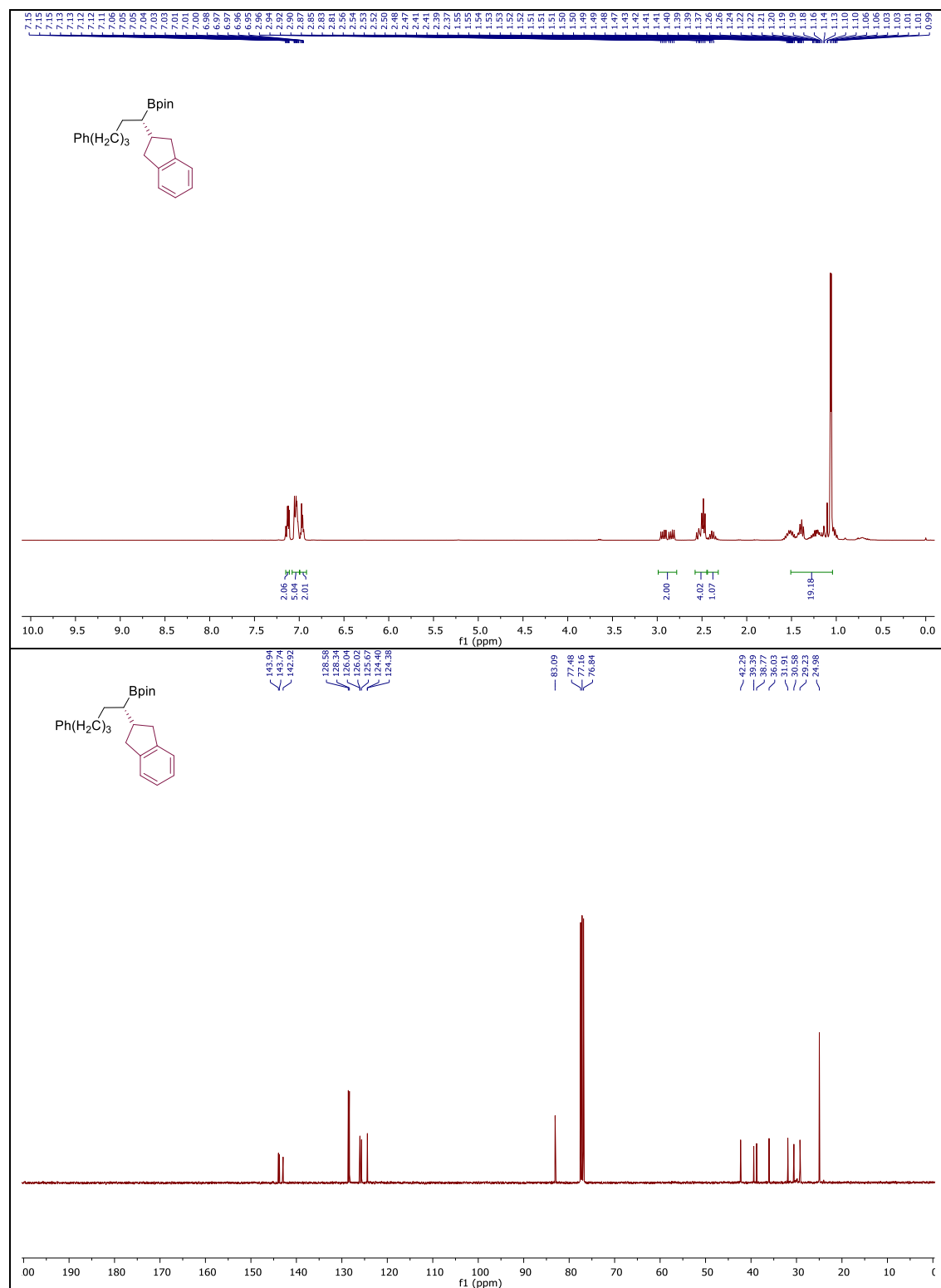


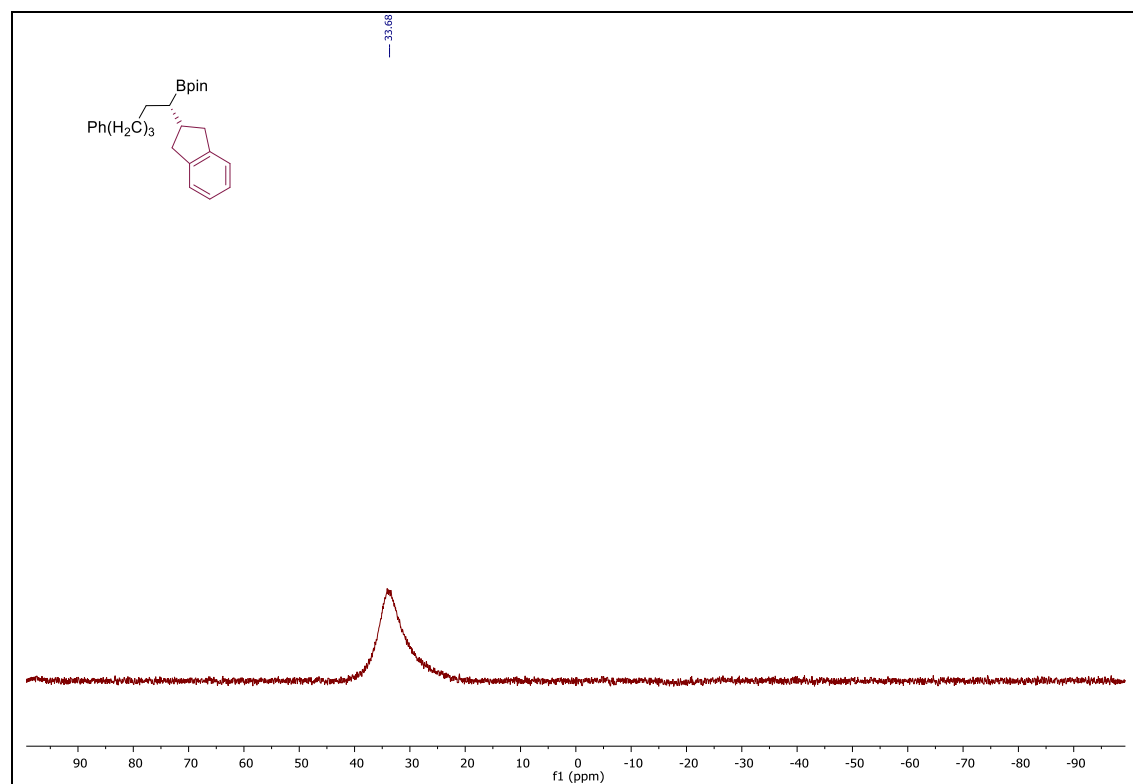
NMR spectra of 4c



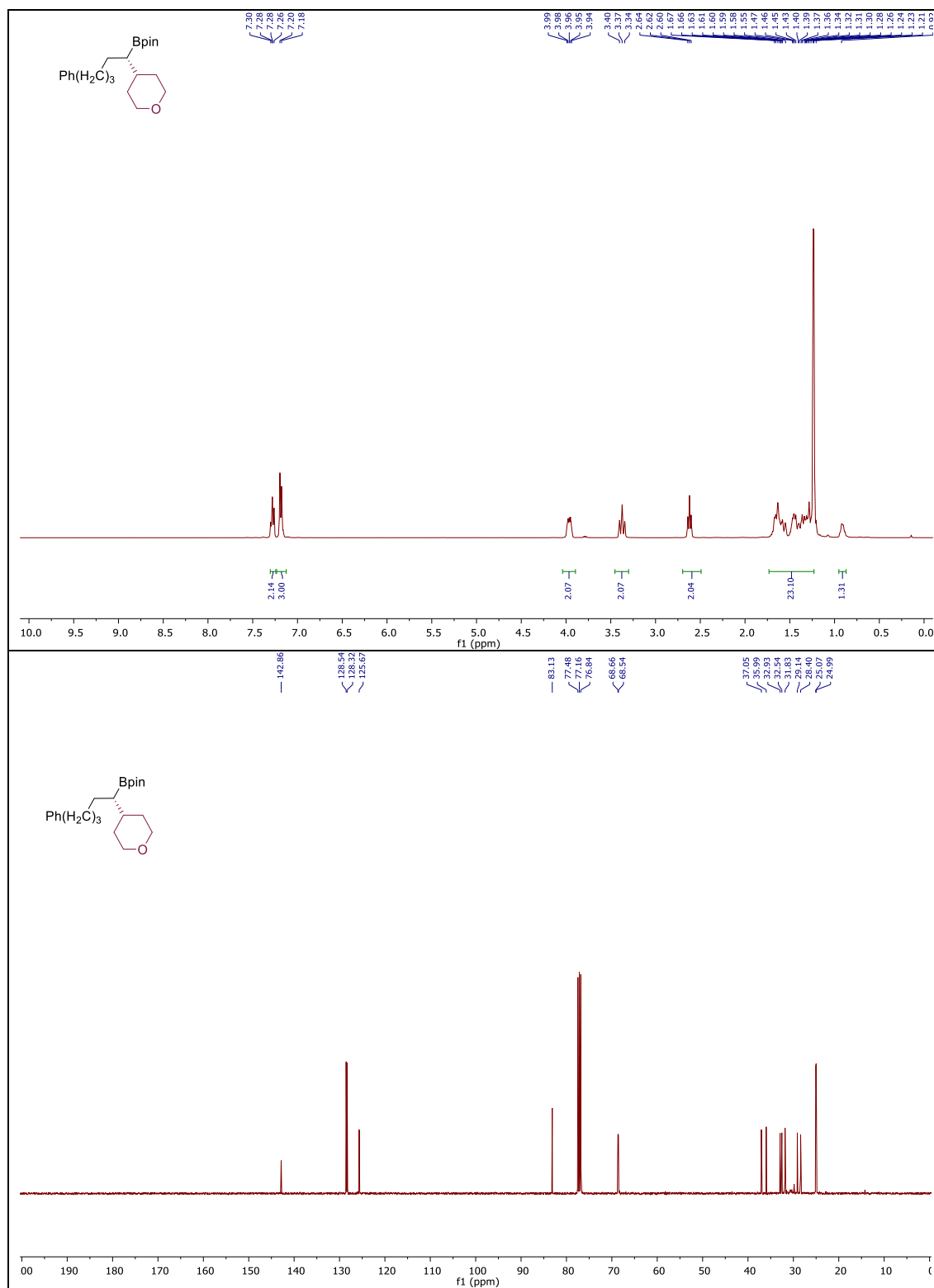


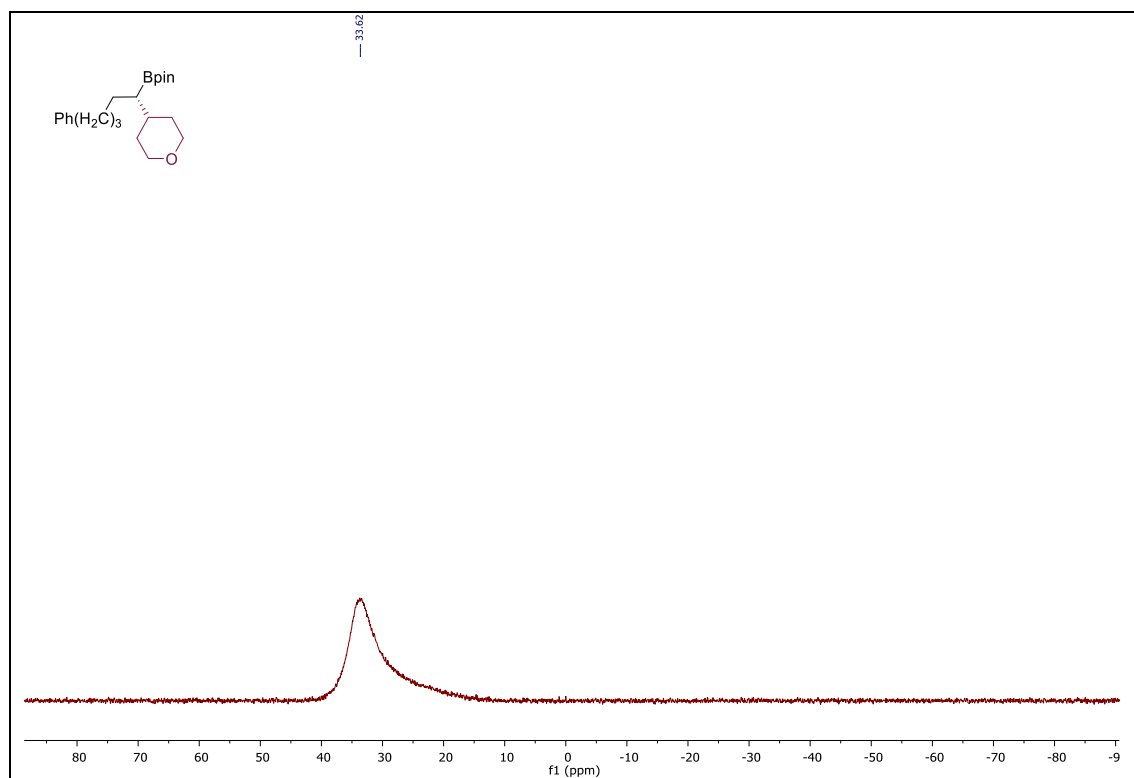
NMR spectra of 4d



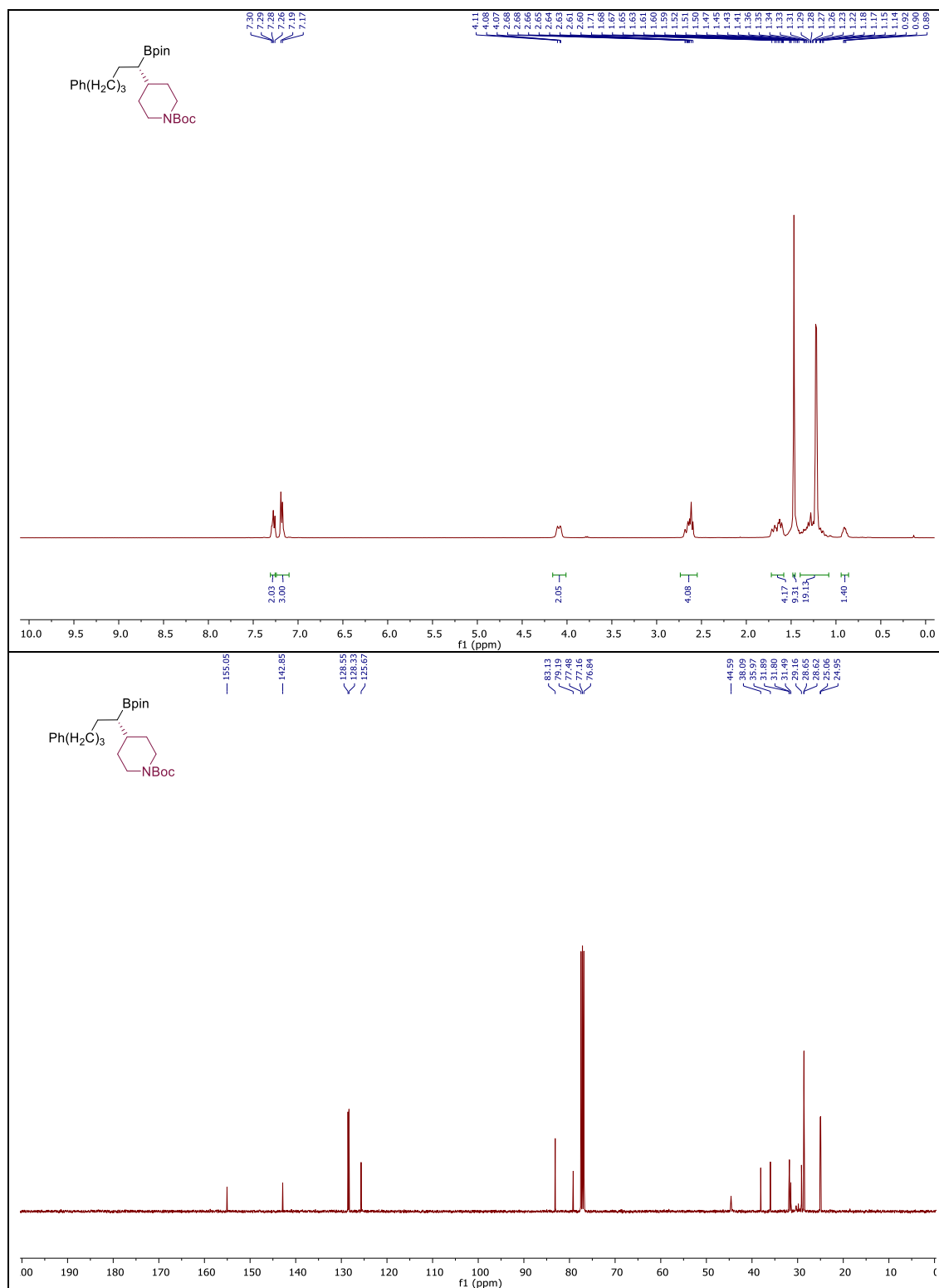


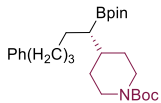
NMR spectra of 4e



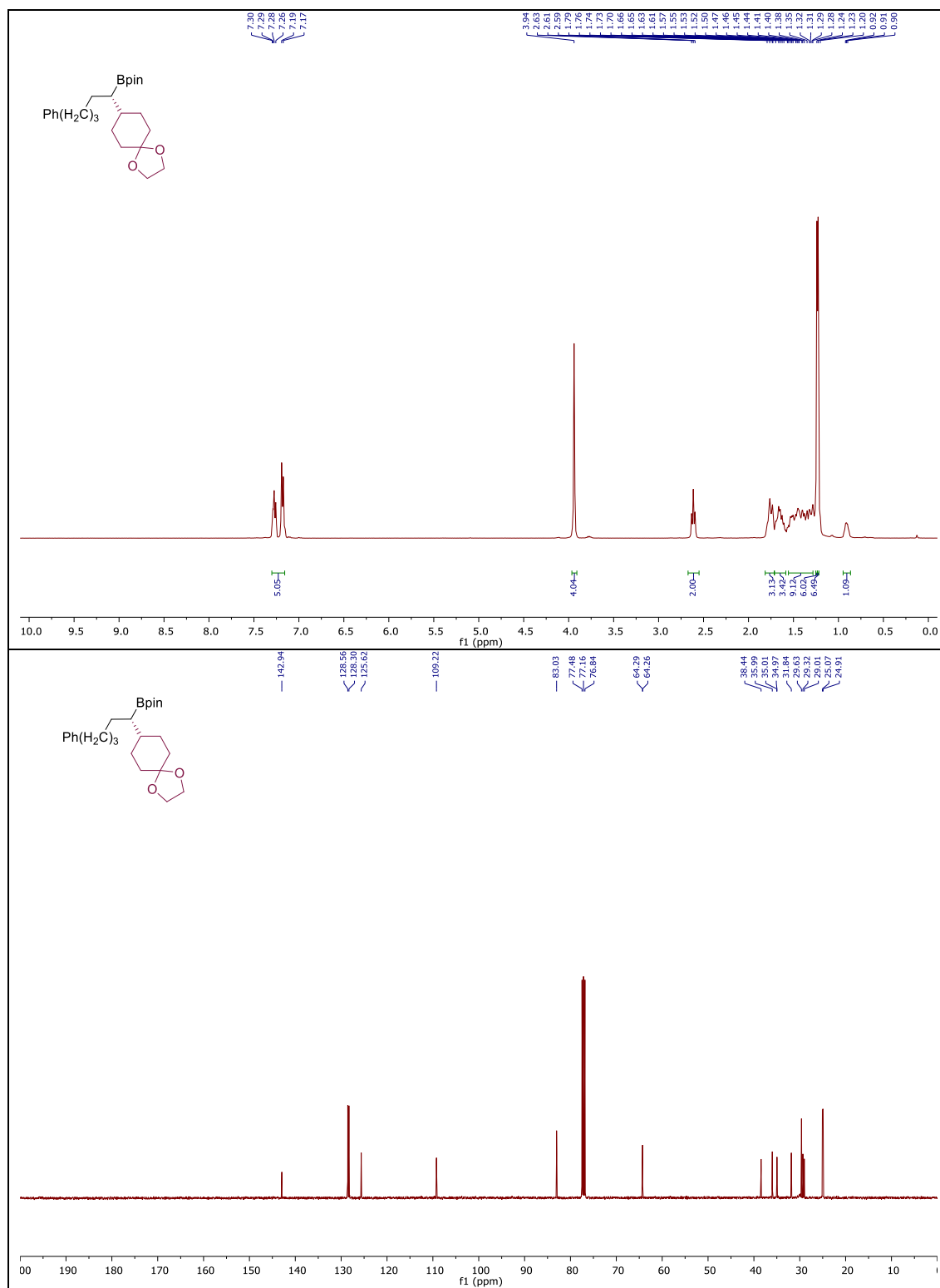


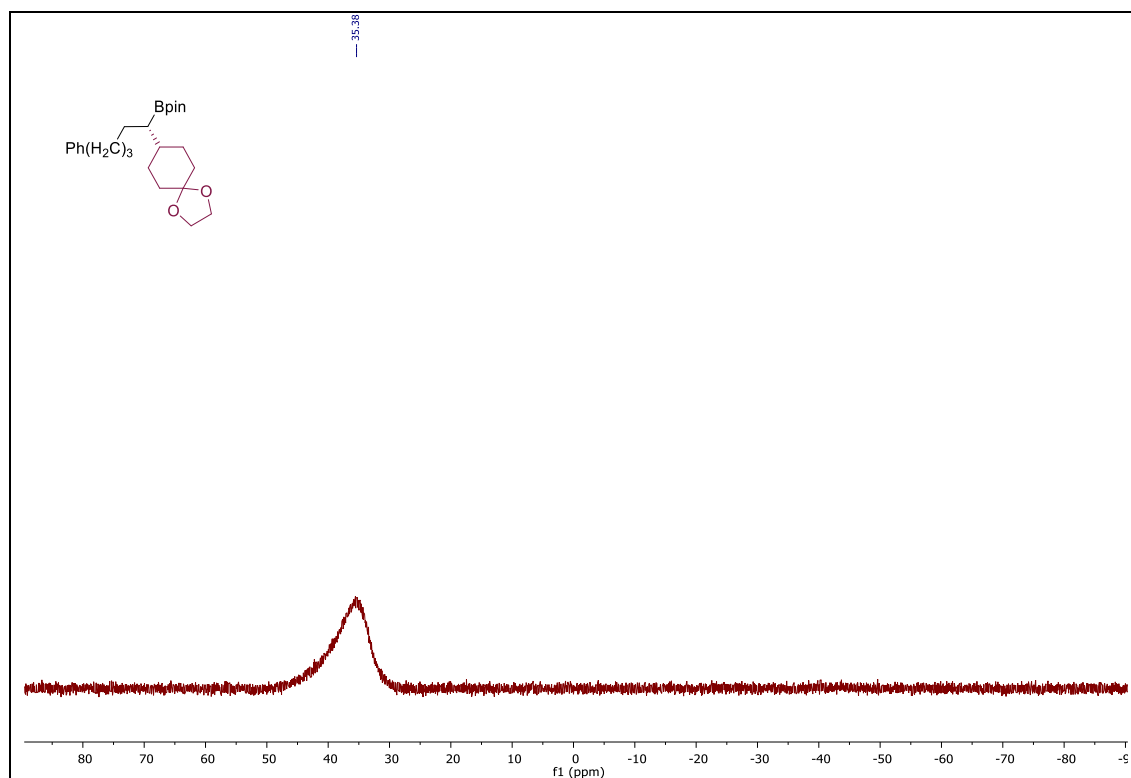
NMR spectra of 4f



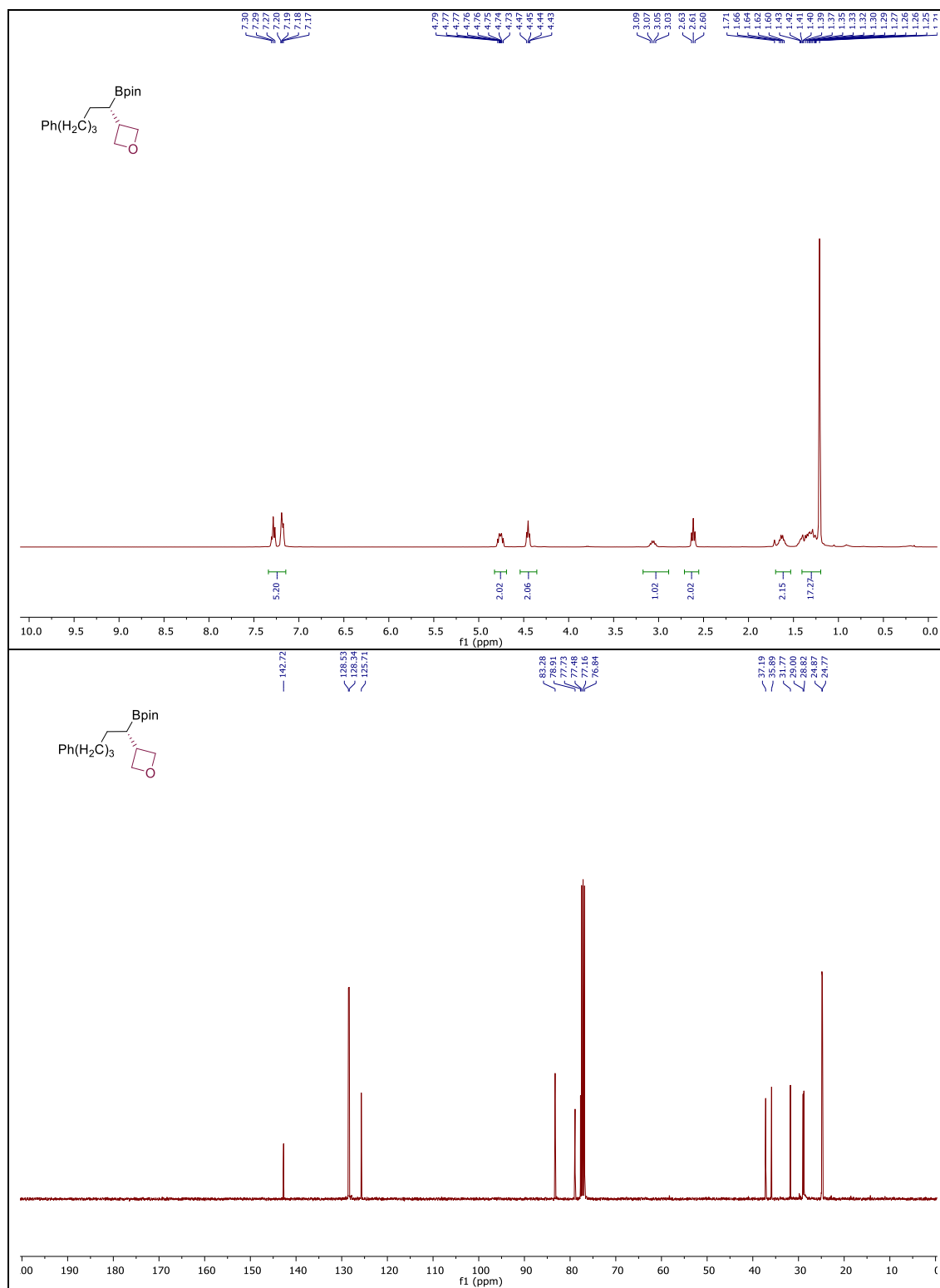


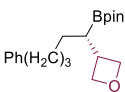
NMR spectra of 4g



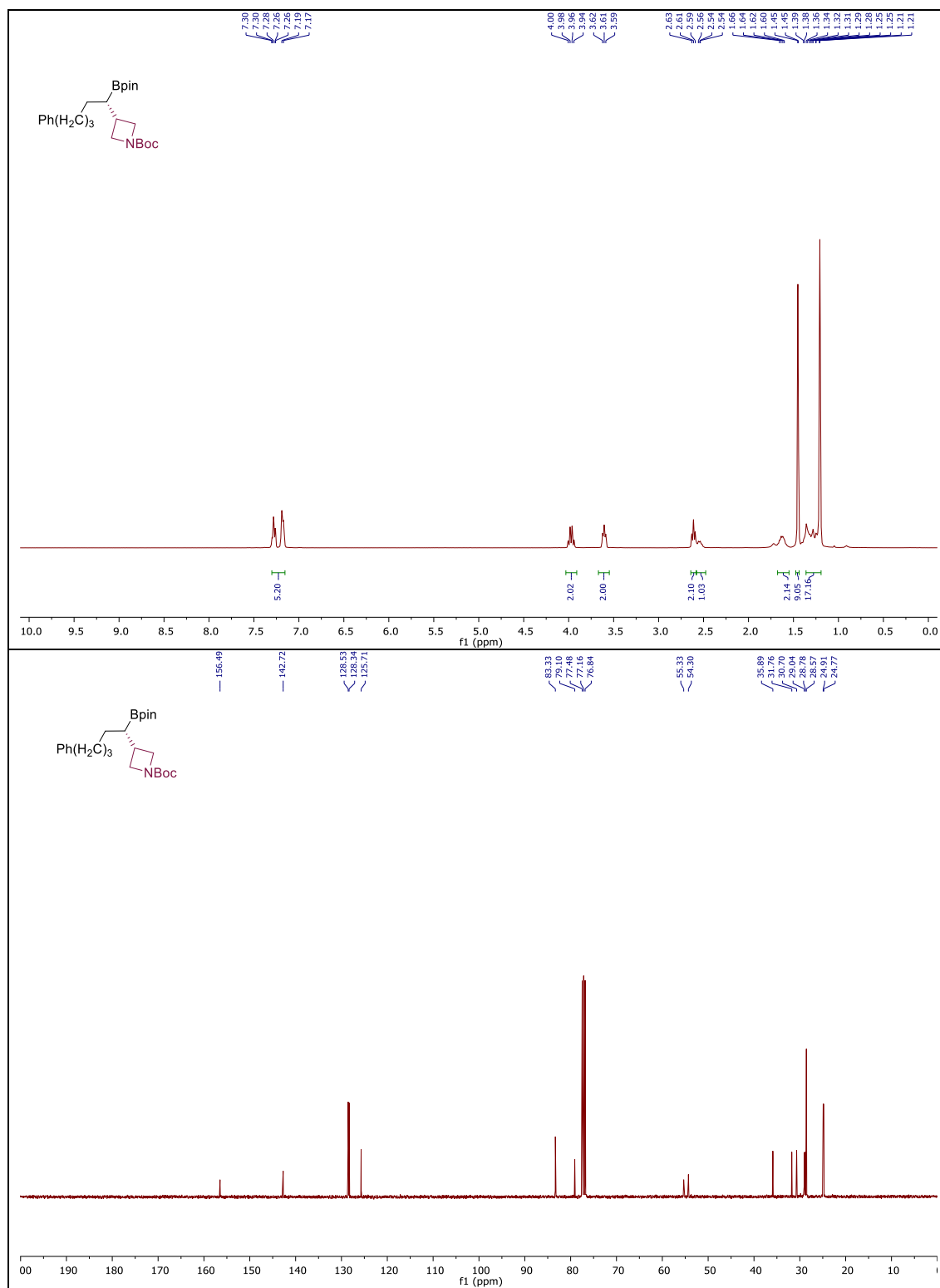


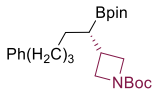
NMR spectra of 4h



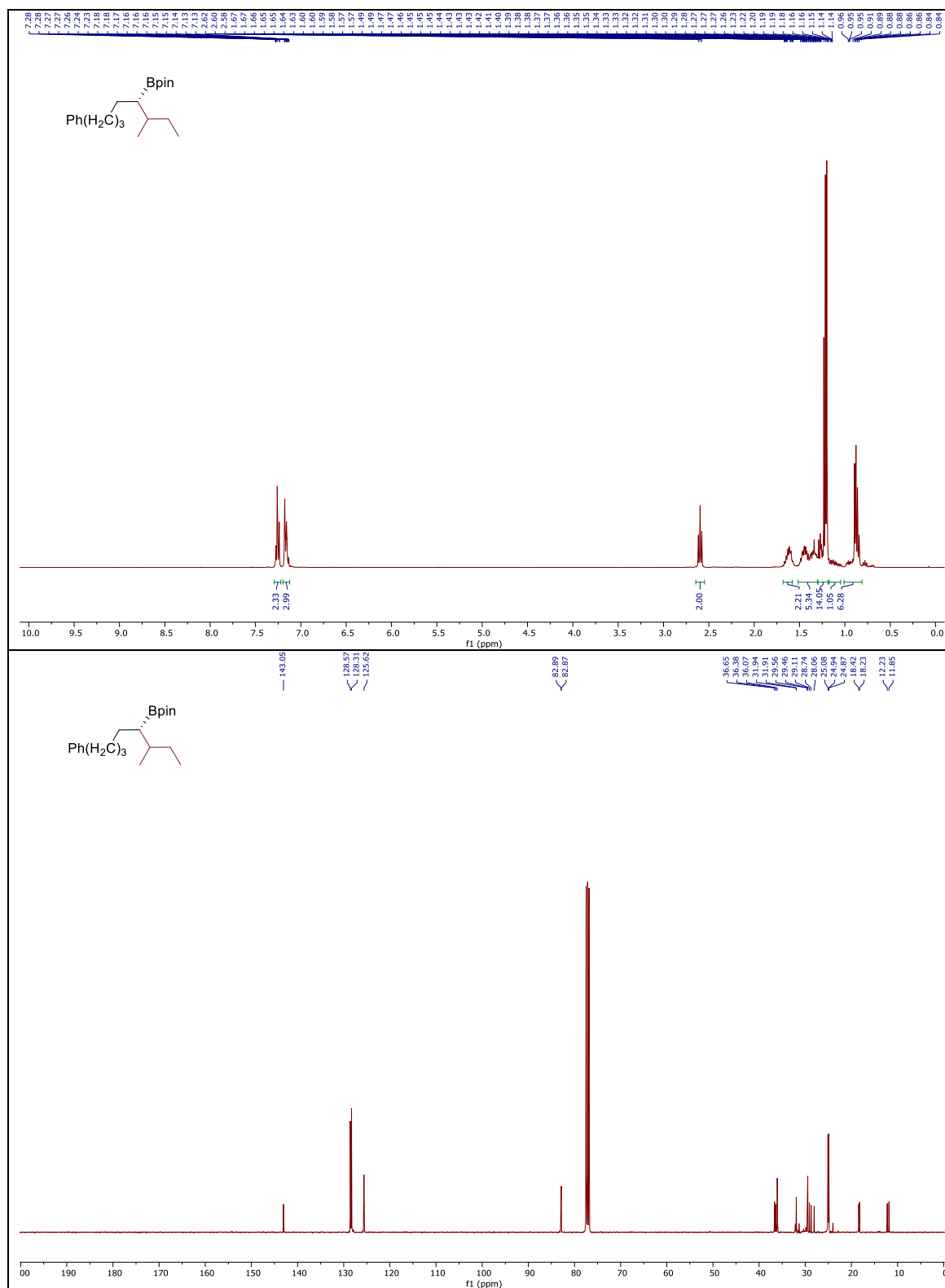


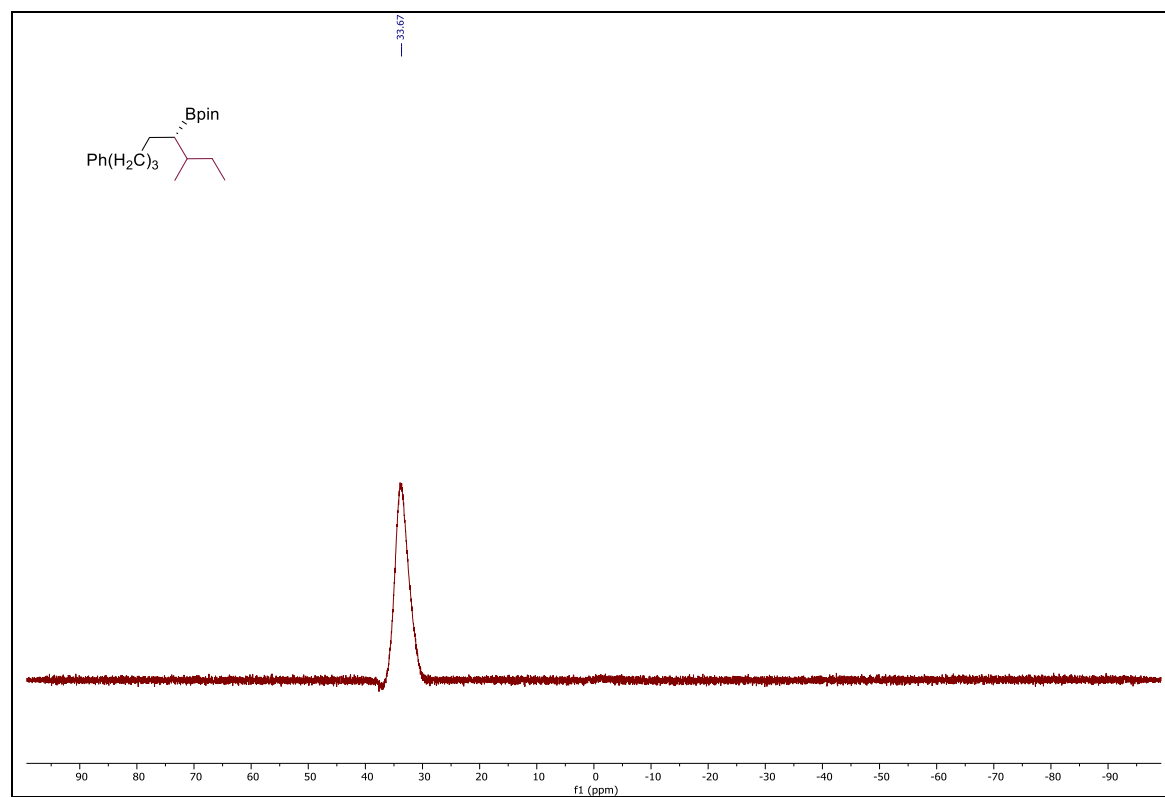
NMR spectra of 4i



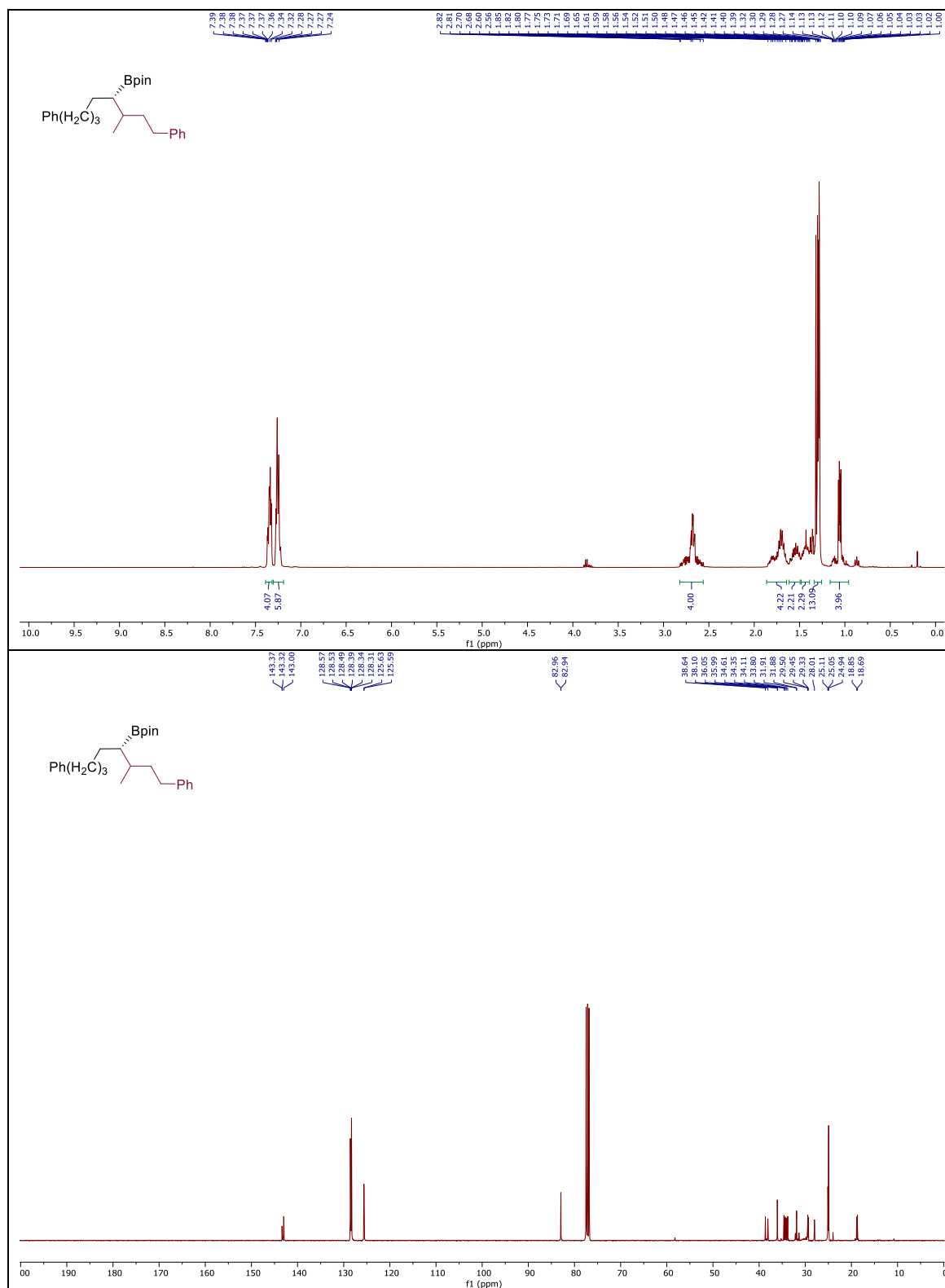


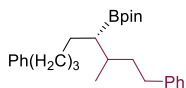
NMR spectra of 4j



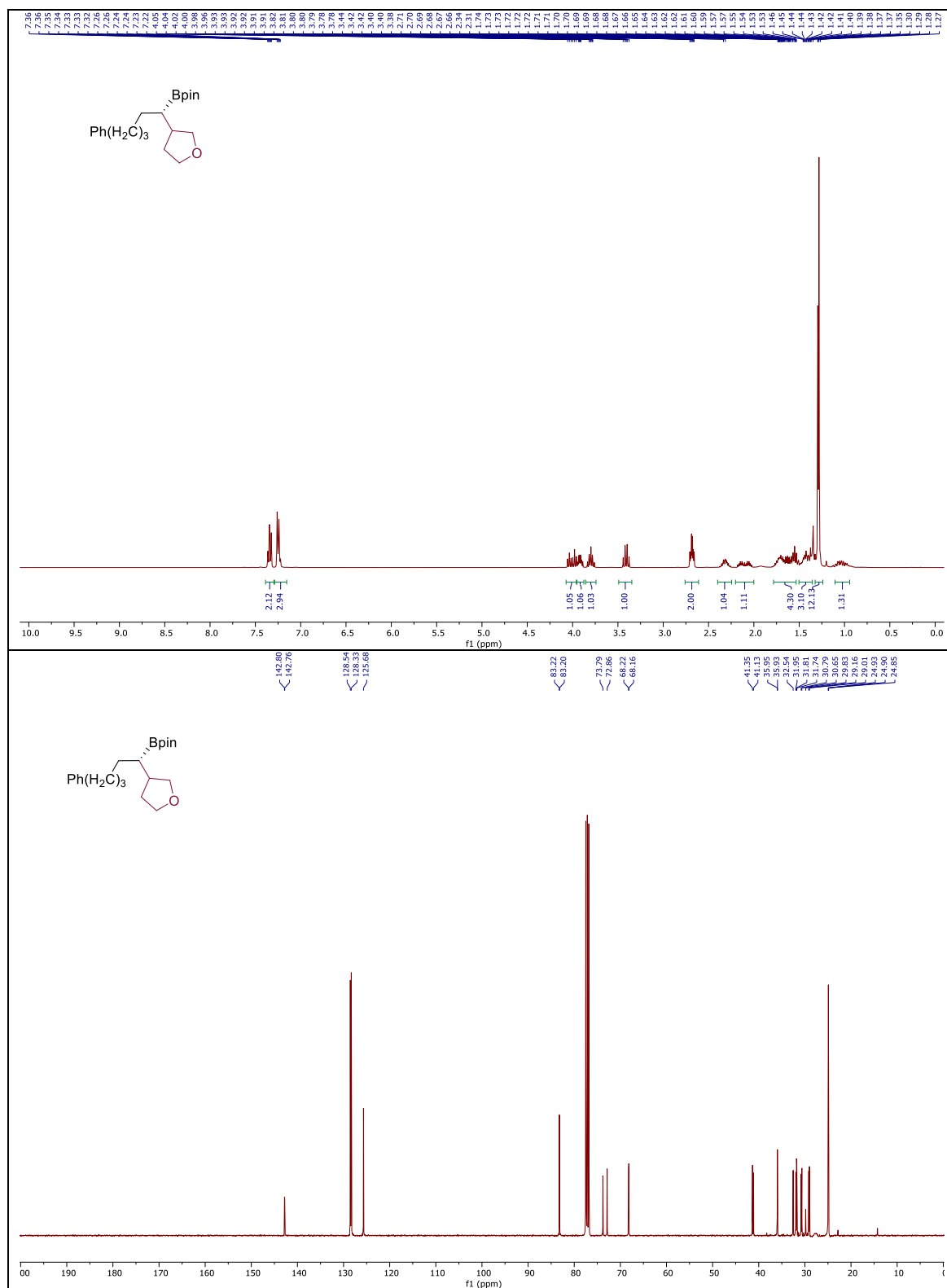


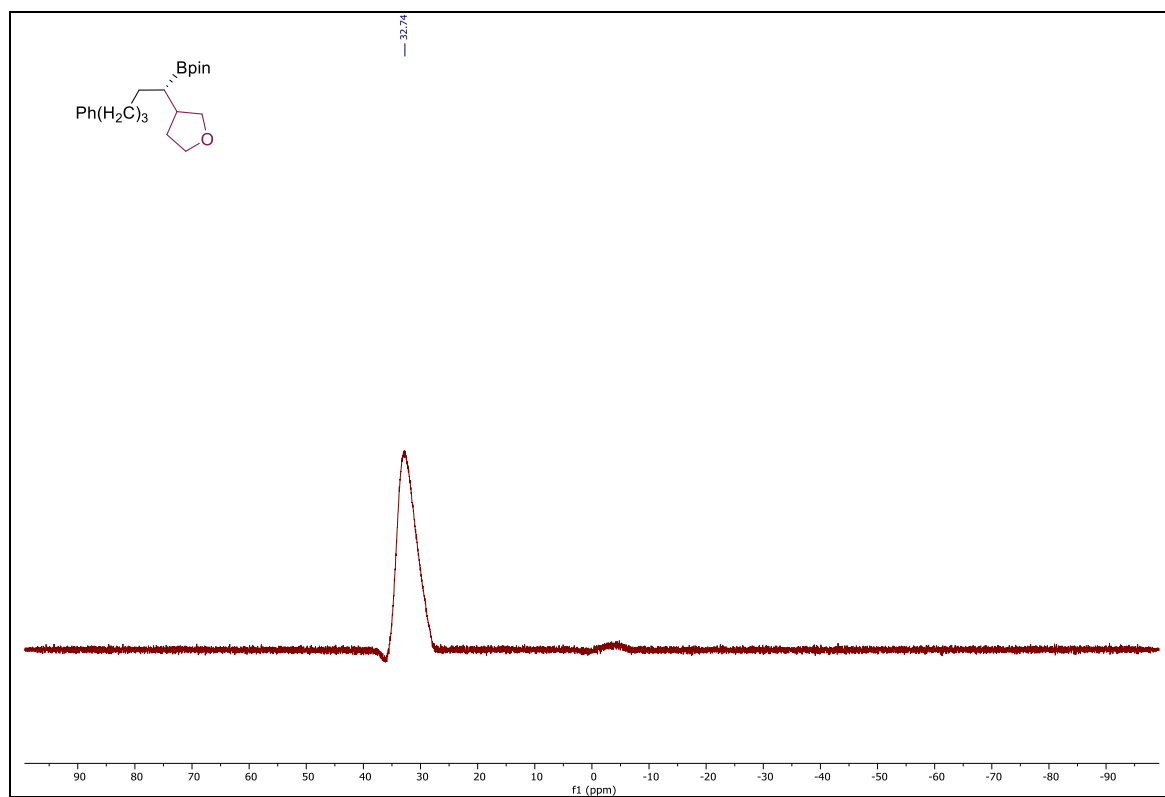
NMR spectra of 4k



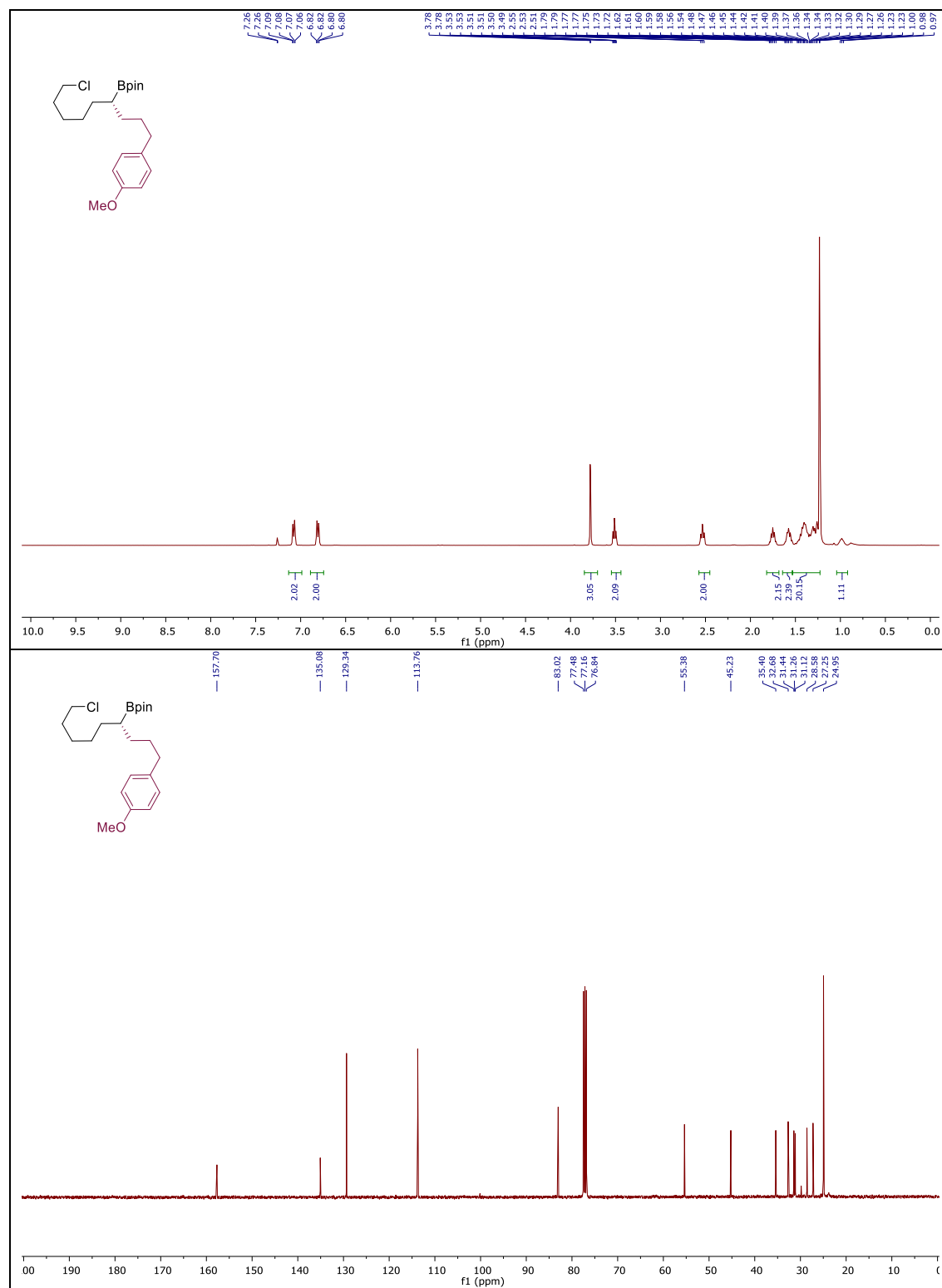


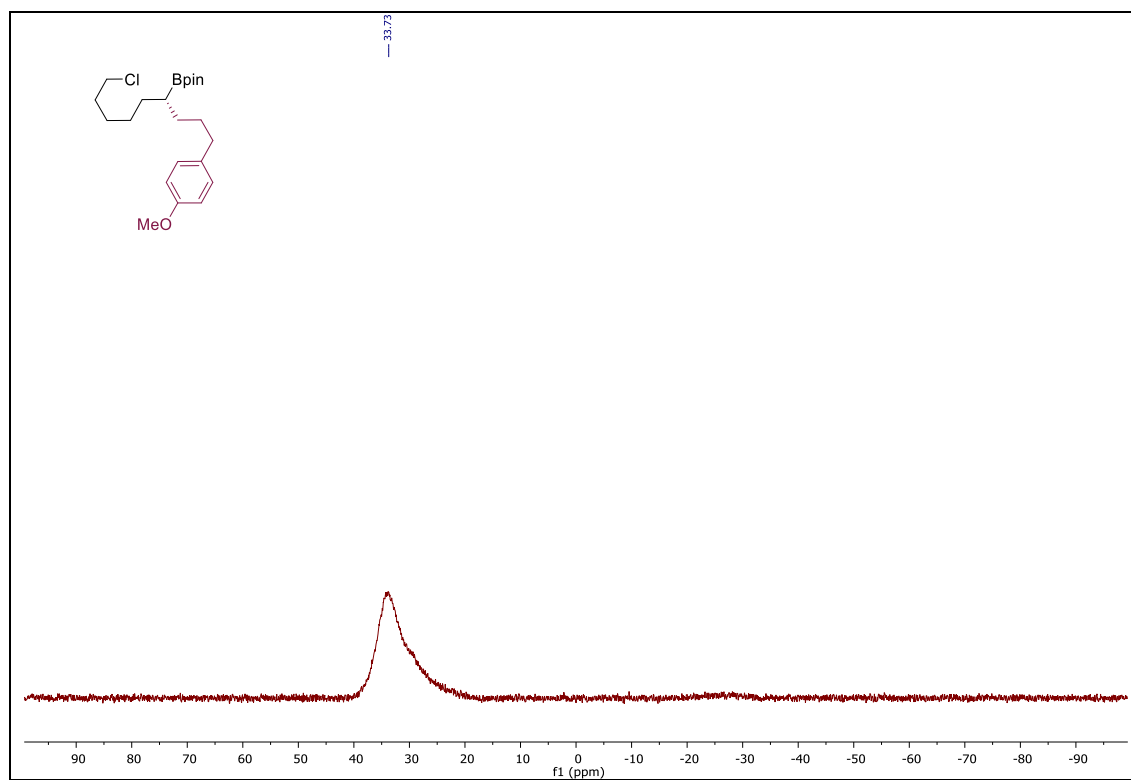
NMR spectra of 4l



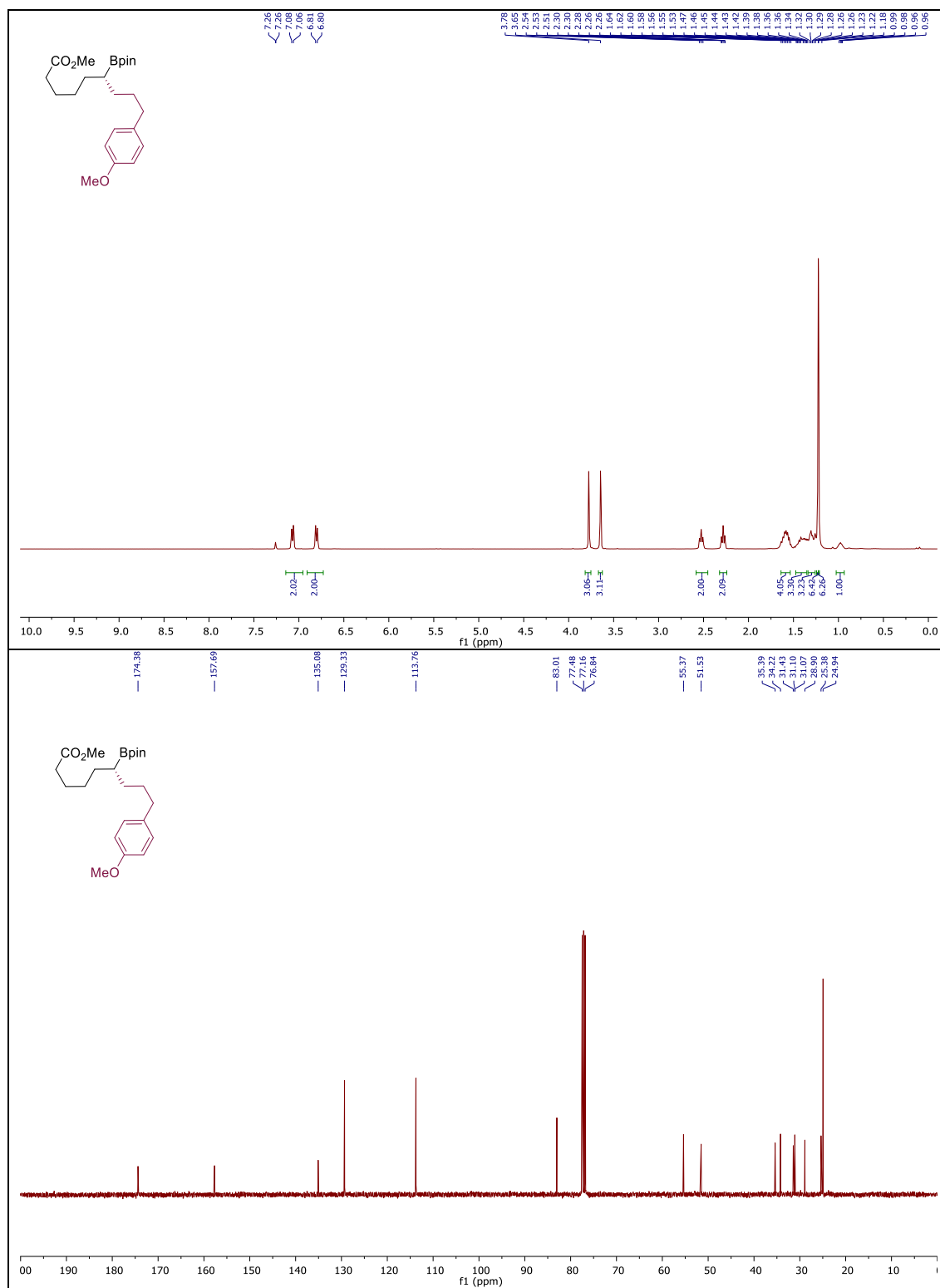


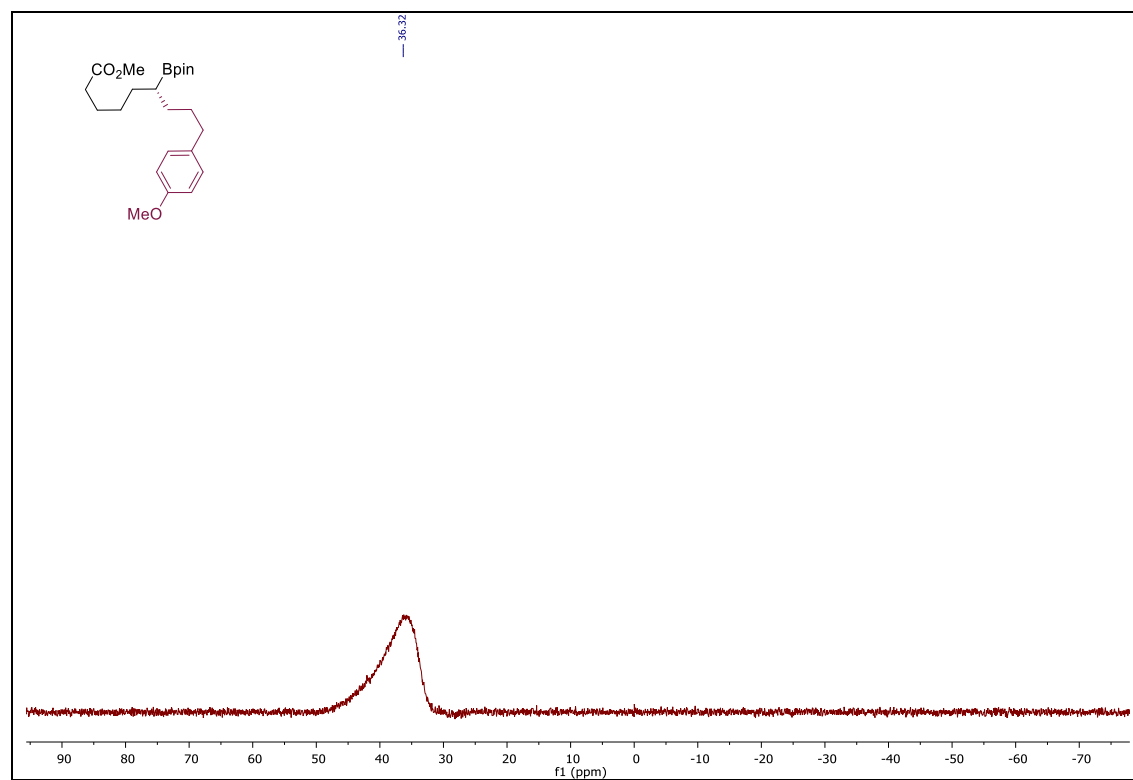
NMR spectra of 5a



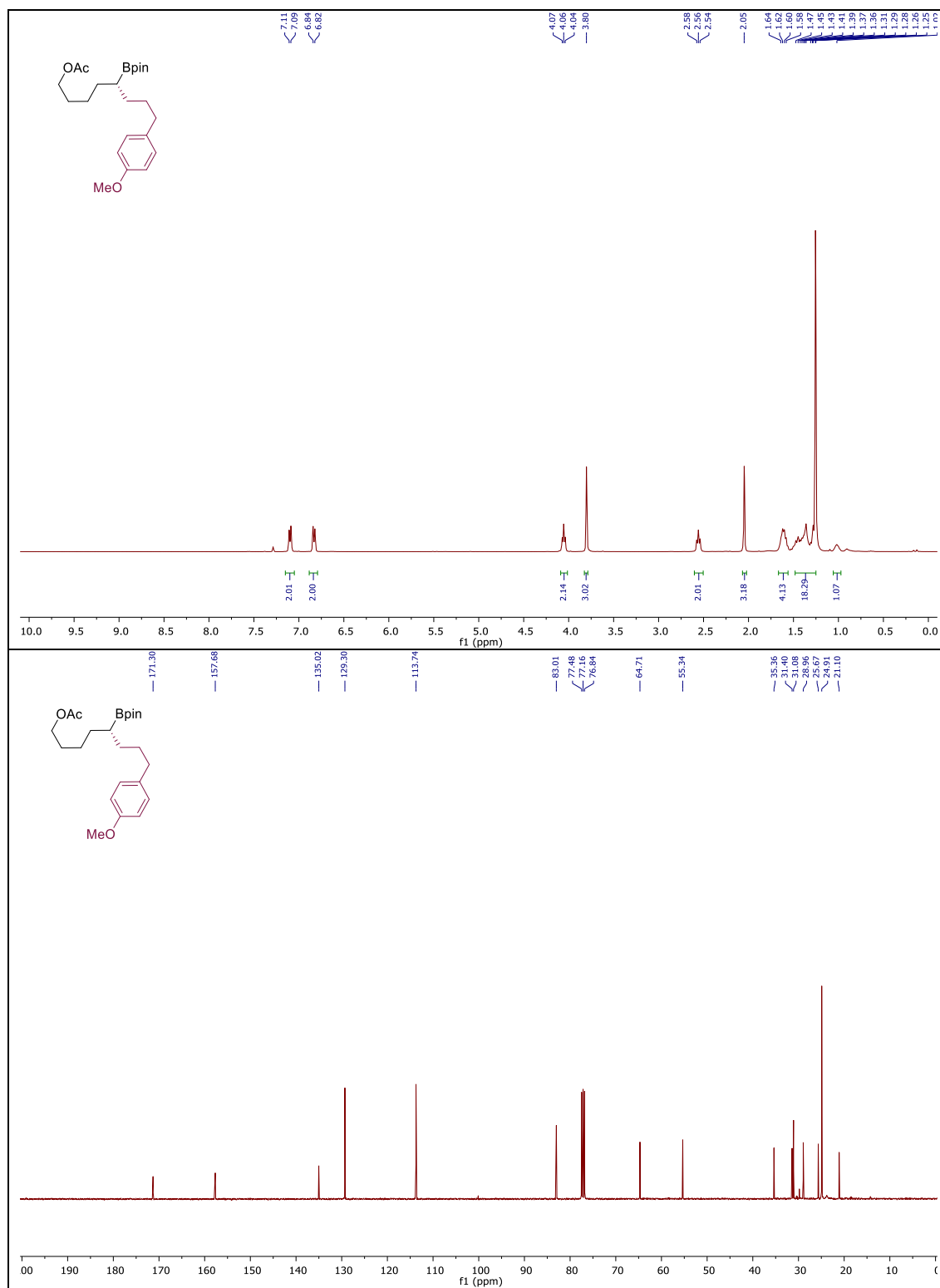


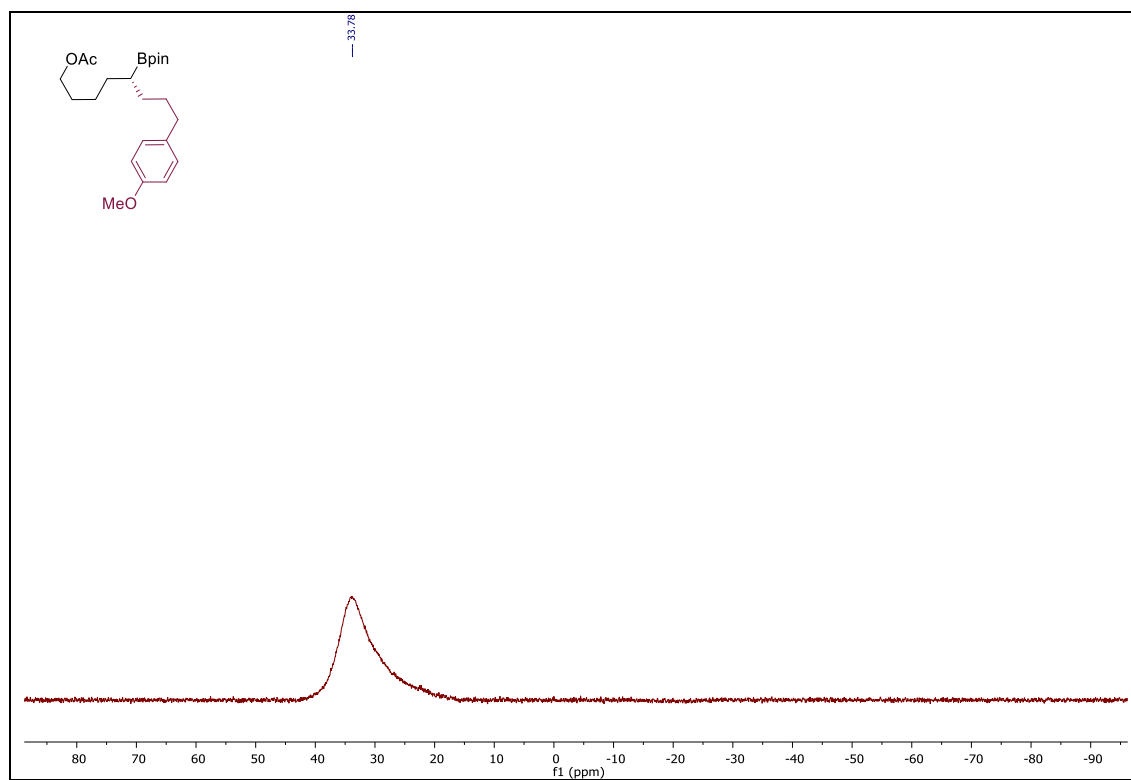
NMR spectra of 5b



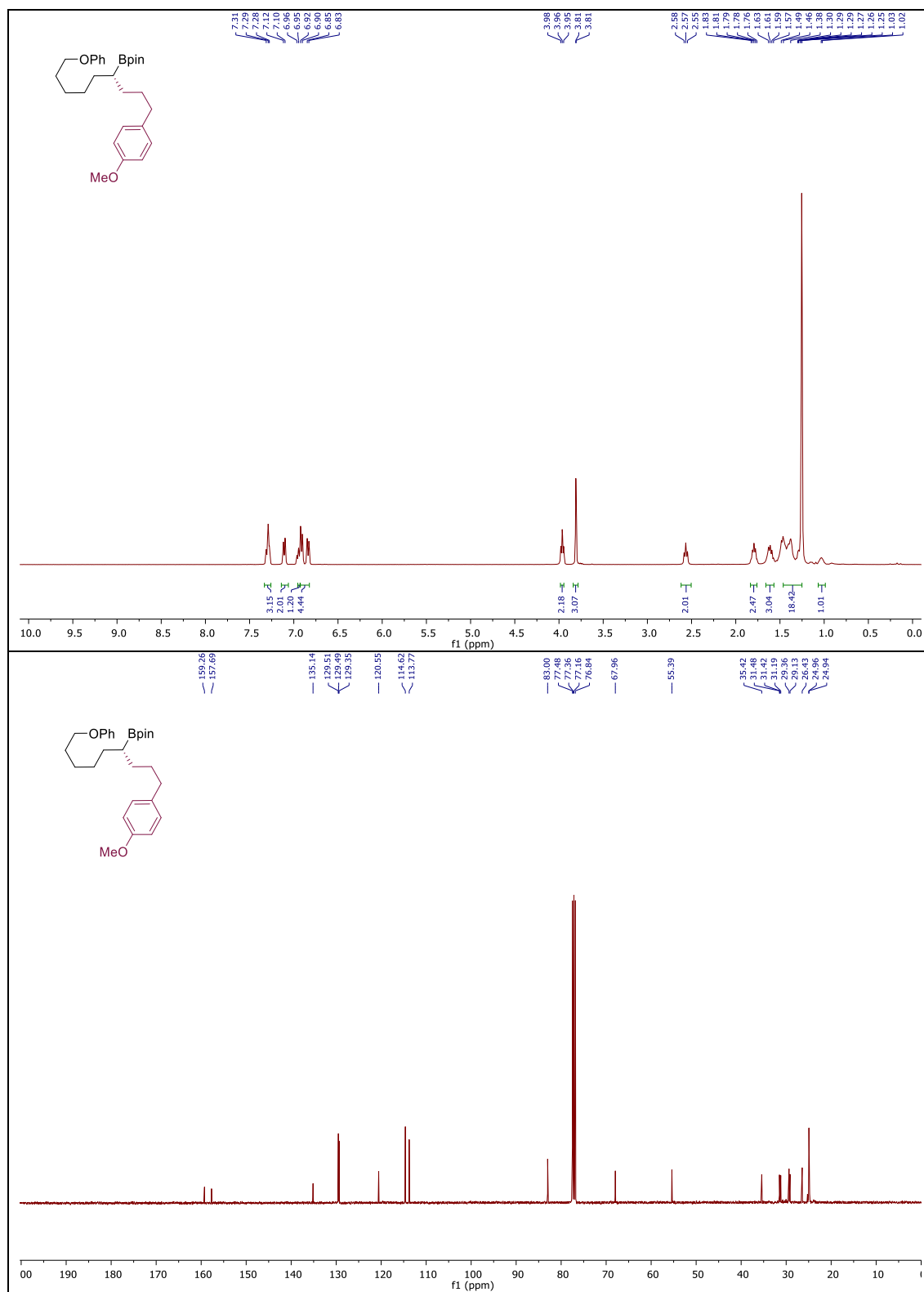


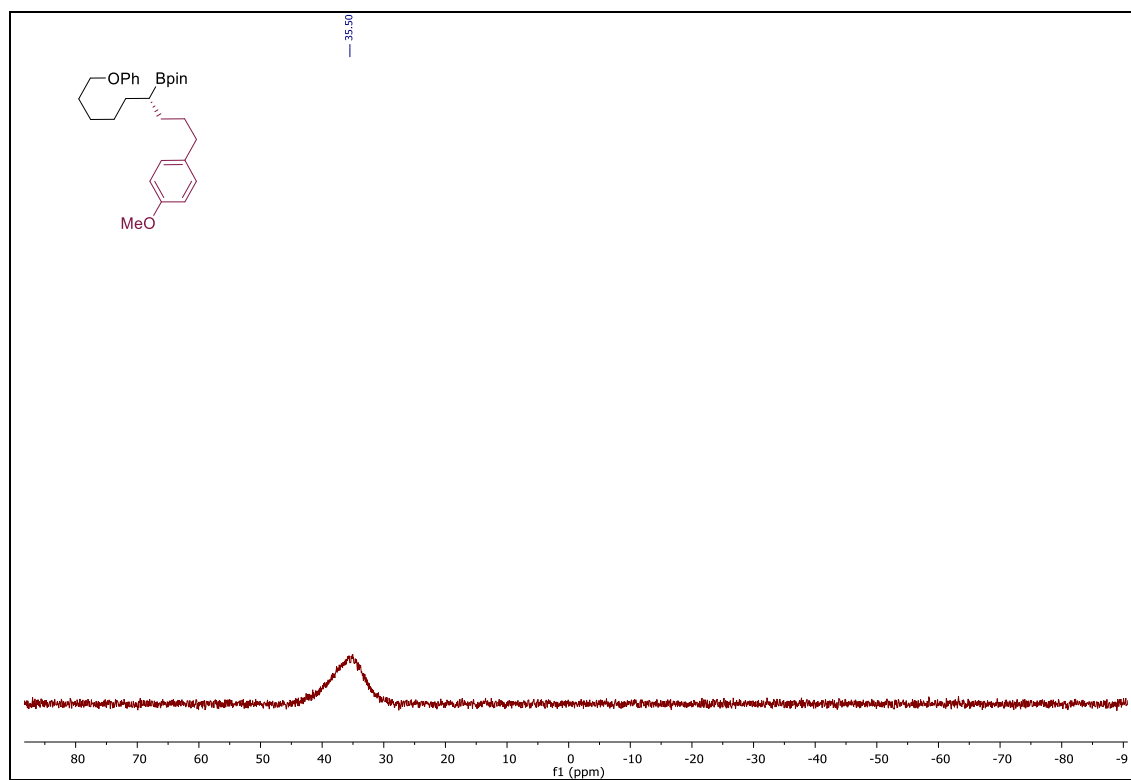
NMR spectra of 5c



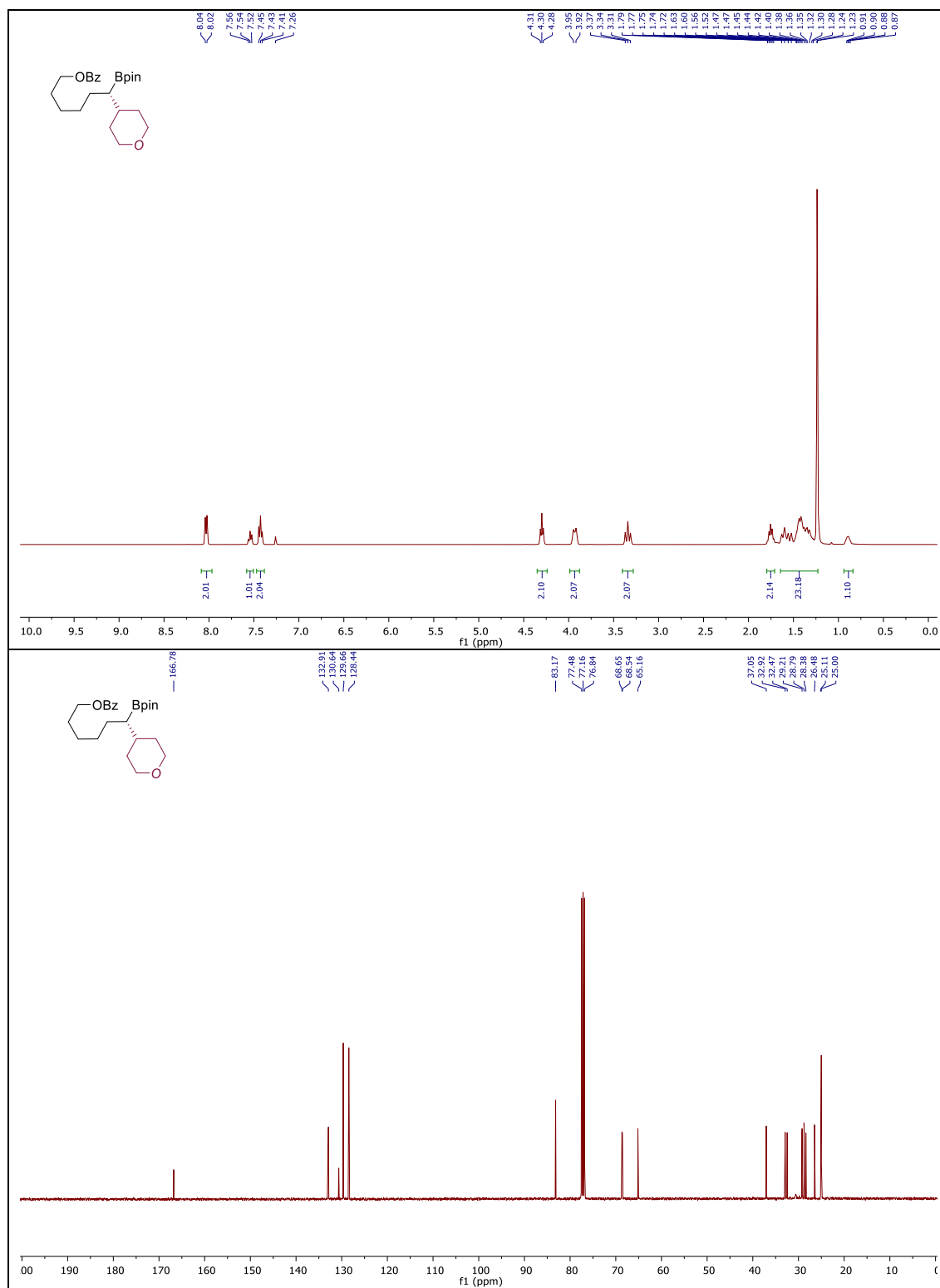


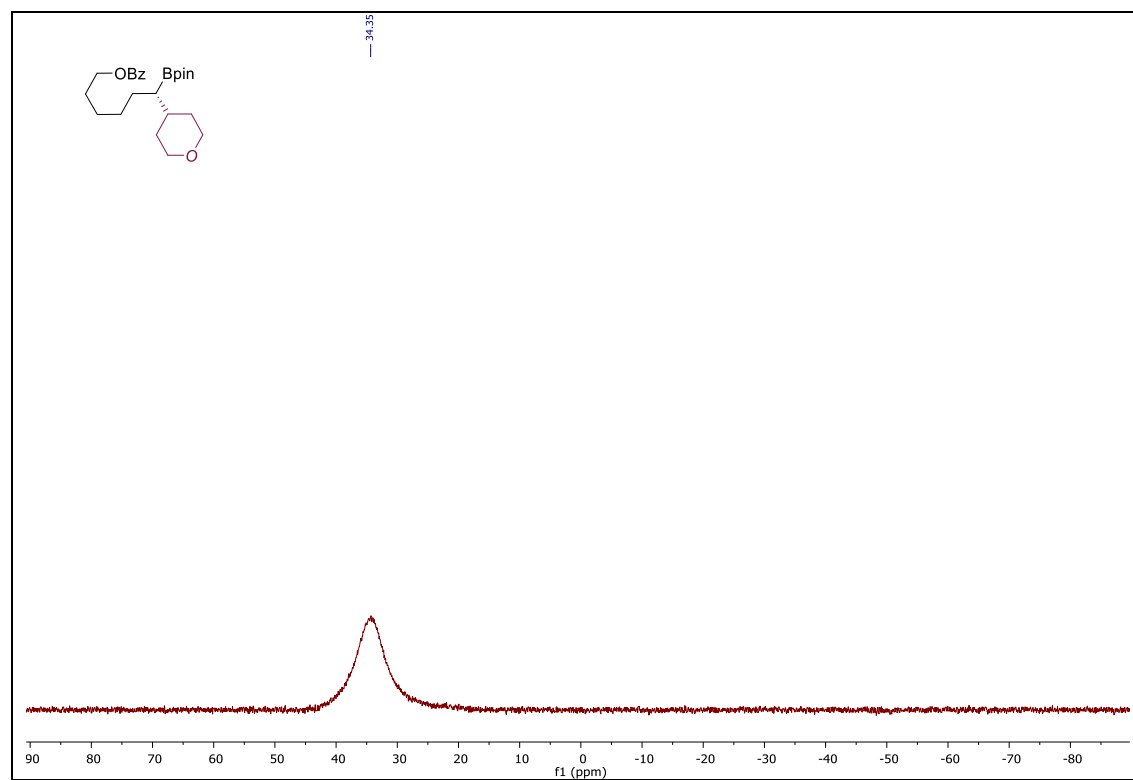
NMR spectra of 5d



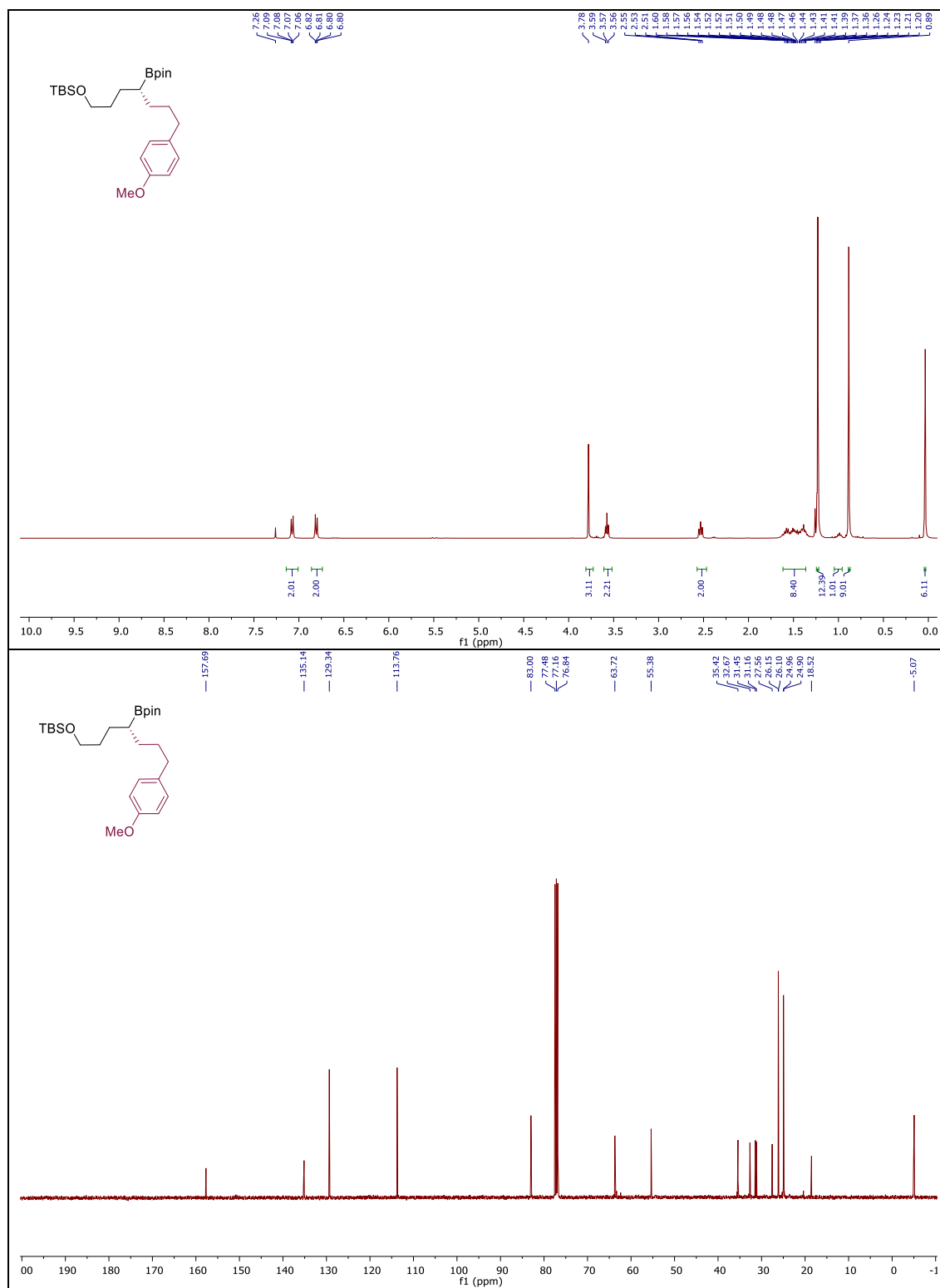


NMR spectra of 5e



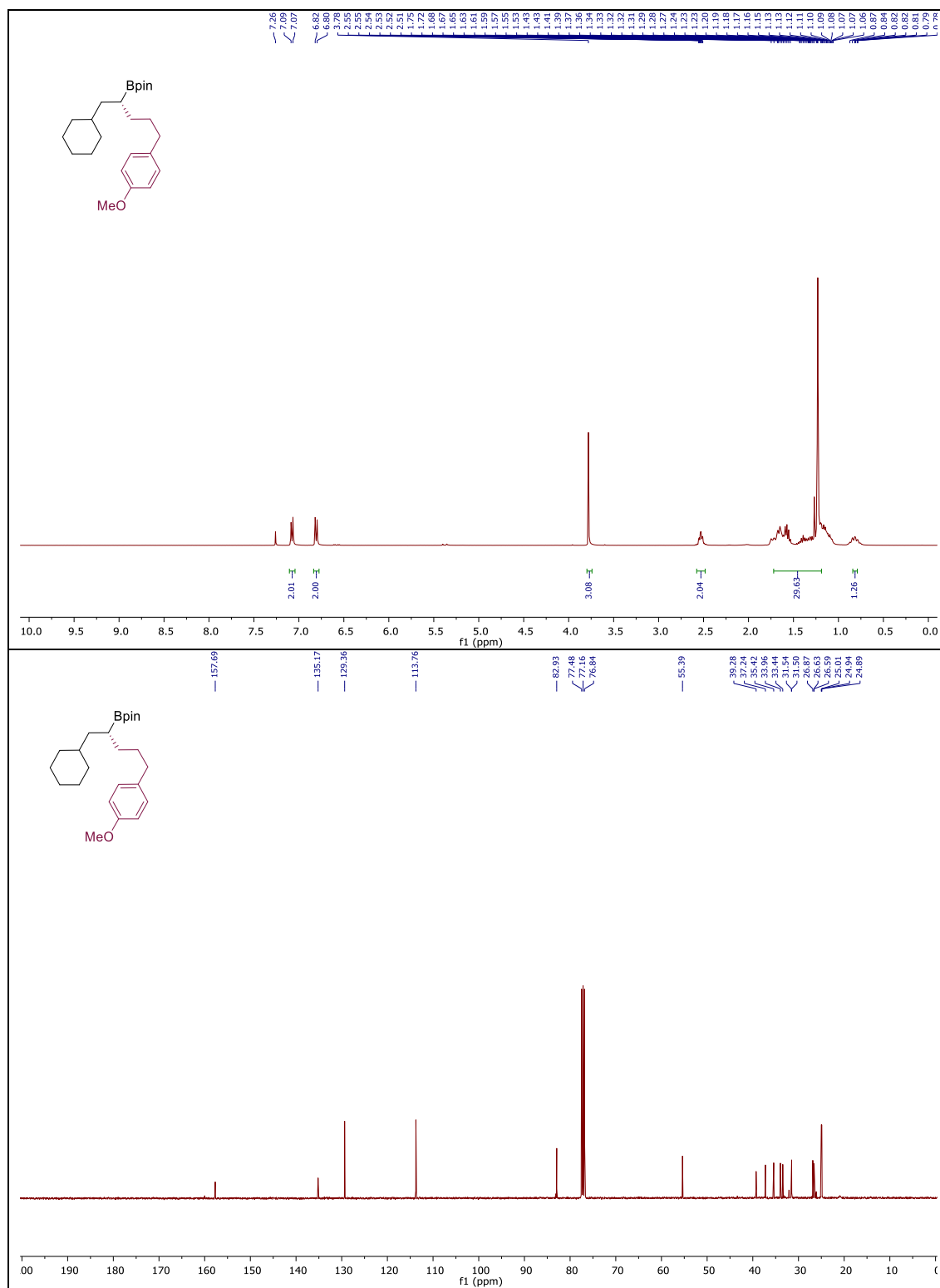


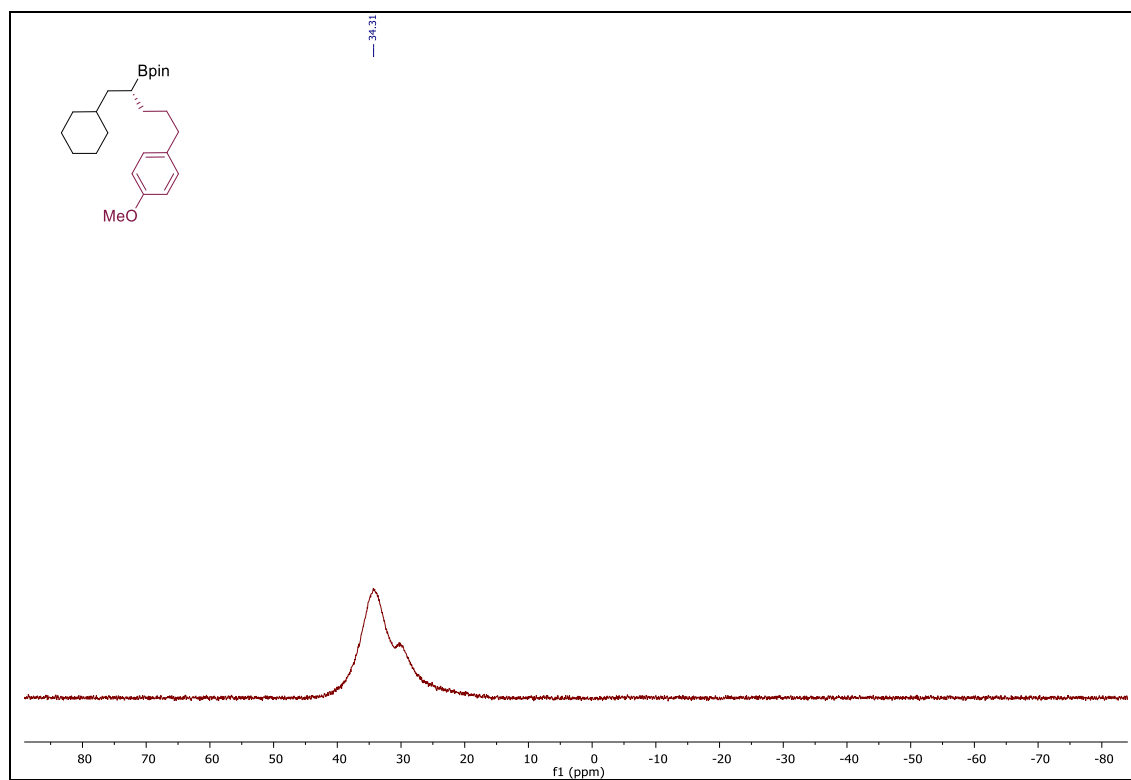
NMR spectra of 5f



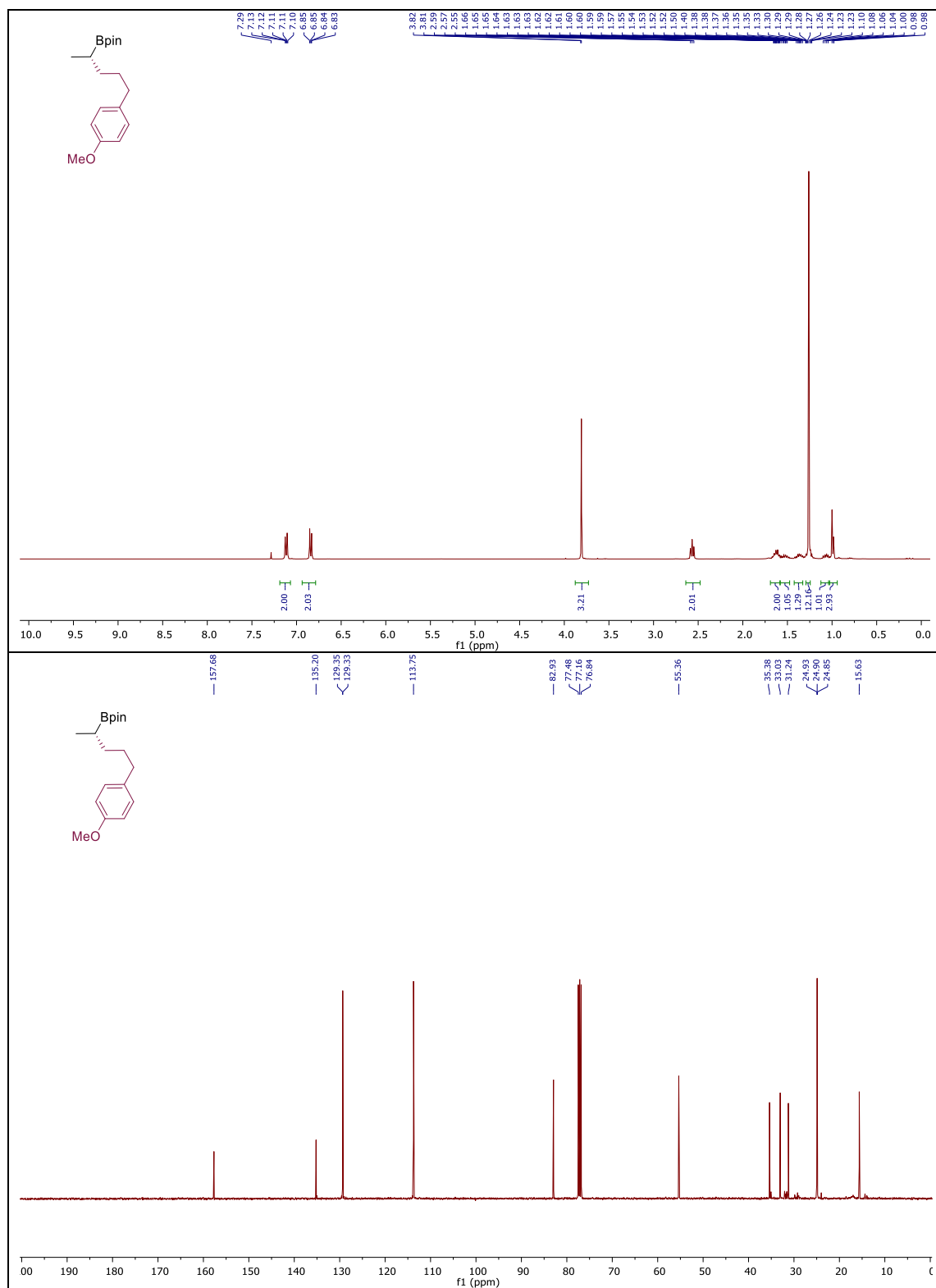


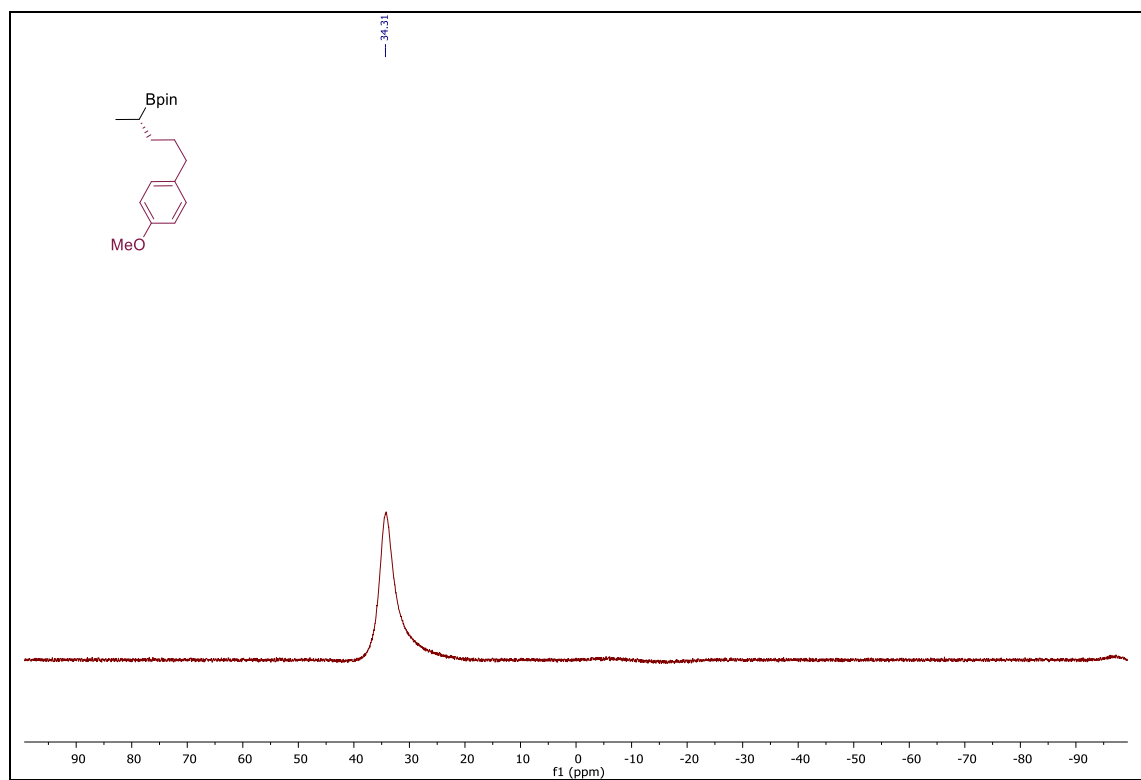
NMR spectra of 5g





NMR spectra of 5h





¹H NMR Spectrum (Top):

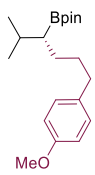
Chemical structure: (S)-1-(4-methoxyphenyl)-3-methylbutan-1-ol

Chemical Shifts (ppm): 7.26, 7.25, 7.09, 7.07, 6.83, 6.82, 6.81, 6.80, 3.79, 3.57, 3.56, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 1.74, 1.72, 1.71, 1.71, 1.69, 1.68, 1.66, 1.64, 1.62, 1.60, 1.59, 1.58, 1.56, 1.54, 1.52, 1.51, 1.49, 1.48, 1.46, 1.44, 1.43, 1.41, 1.40, 1.39, 1.37, 1.36, 1.34, 1.32, 1.30, 1.24, 1.22, 1.21, 1.20, 1.19, 0.92, 0.91, 0.90, 0.89, 0.87, 0.86, 0.85, 0.83.

Integrations: 2.11, 2.11, 3.14, 2.00, 1.06, 5.01, 11.58, 6.09.

¹³C NMR Spectrum (Bottom):

Chemical Shifts (ppm): 157.67, 135.20, 129.36, 129.33, 113.78, 113.75, 82.95, 77.48, 77.16, 76.84, 55.38, 35.48, 31.86, 28.79, 28.55, 25.15, 25.02, 24.99, 22.52, 21.95.



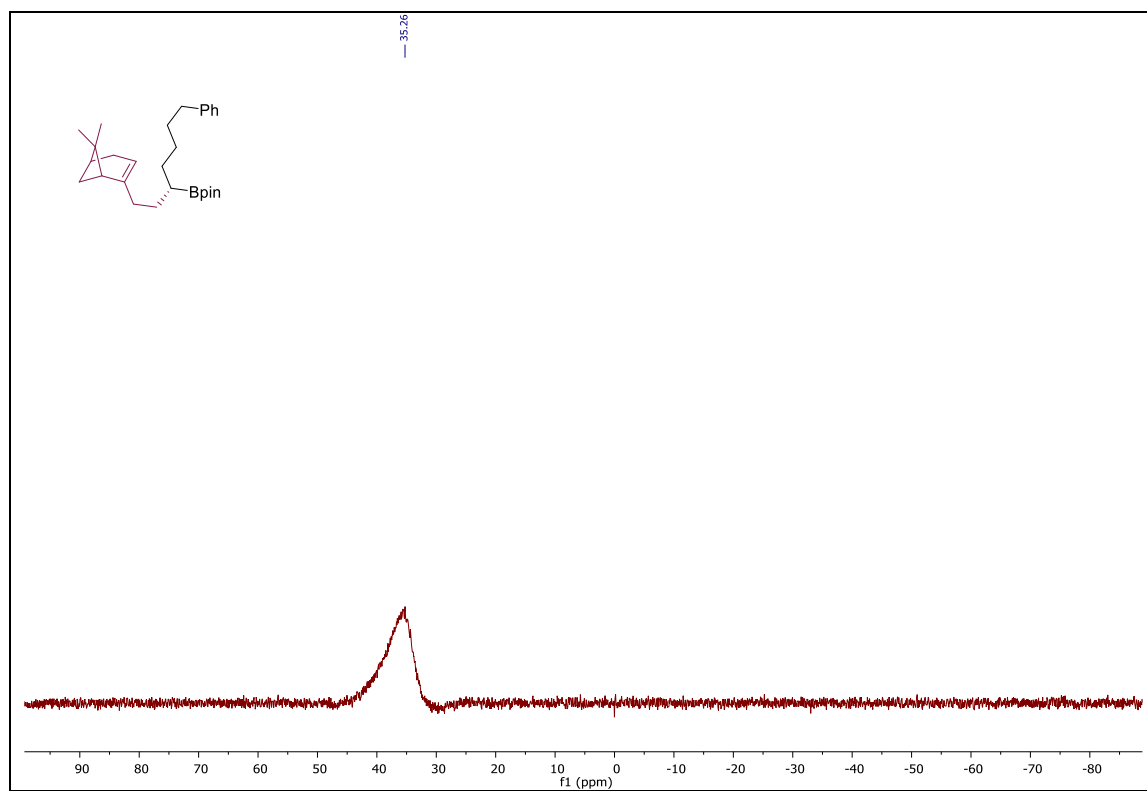
The figure displays the ^1H and ^{13}C NMR spectra of a bicyclic compound, specifically a norbornene derivative with a Bpin group and a phenyl group. The chemical structure is shown in the top left corner of each spectrum.

^1H NMR Spectrum (Top):

- X-axis:** Chemical shift in ppm, ranging from 10.0 to 0.0.
- Peaks:** Aromatic protons (7.2-7.4 ppm), Bpin protons (4.5 ppm), and aliphatic protons (1.0-2.5 ppm).
- Integration:** 5.22 (aromatic), 1.00 (Bpin), and 2.10 (aliphatic).

^{13}C NMR Spectrum (Bottom):

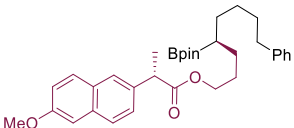
- X-axis:** Chemical shift in ppm, ranging from 200 to 0.
- Peaks:** Carbonyl carbons (143-149 ppm), aromatic carbons (123-128 ppm), Bpin carbons (77 ppm), and aliphatic carbons (21-46 ppm).



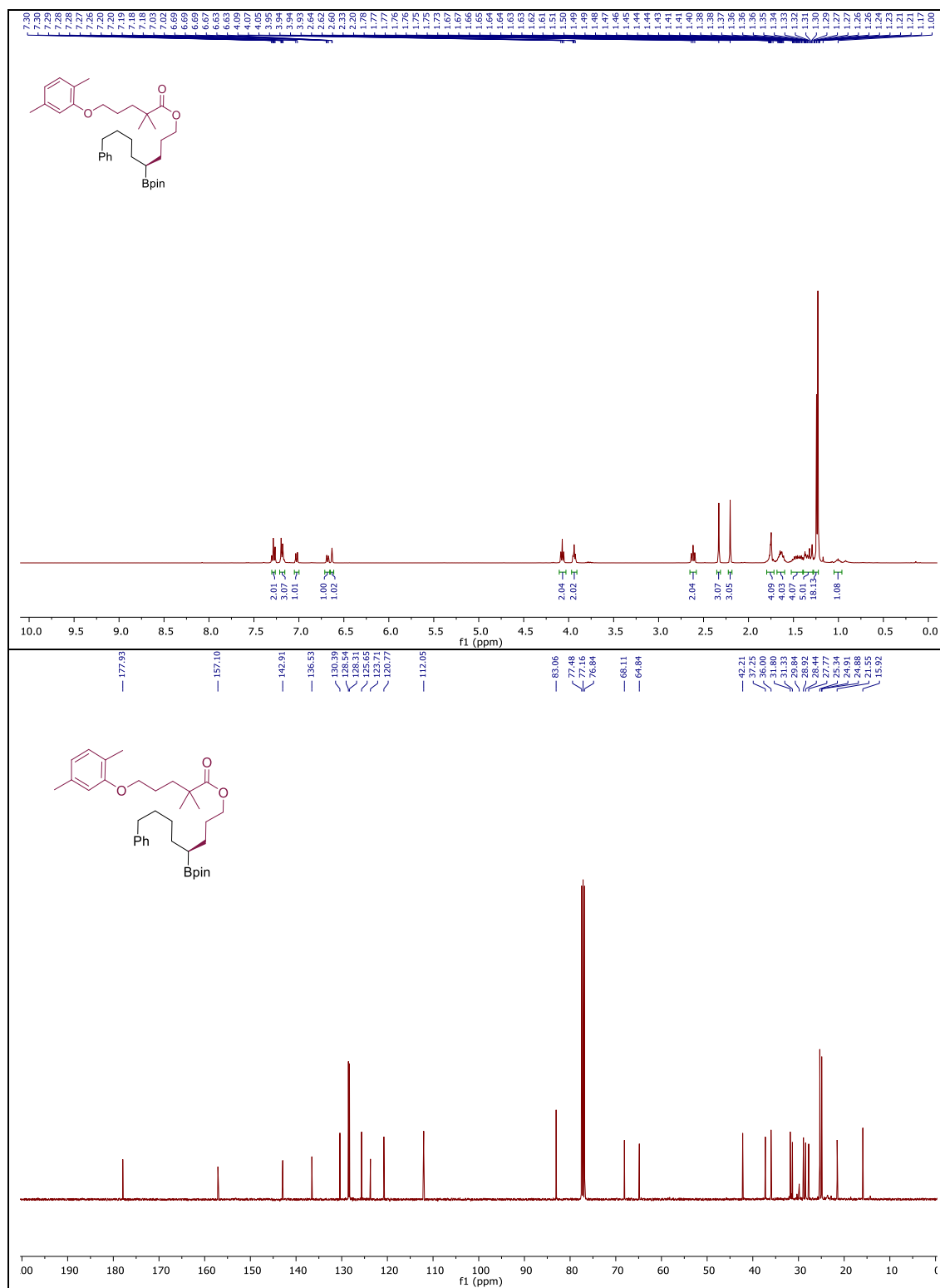
The figure displays the ¹H and ¹³C NMR spectra of compound 10, which is (S)-1-(4-methoxyphenyl)-2-(4-((S)-1-phenylbutyl)oxyphenyl)ethan-1-one. The chemical structure is shown at the top left of each spectrum.

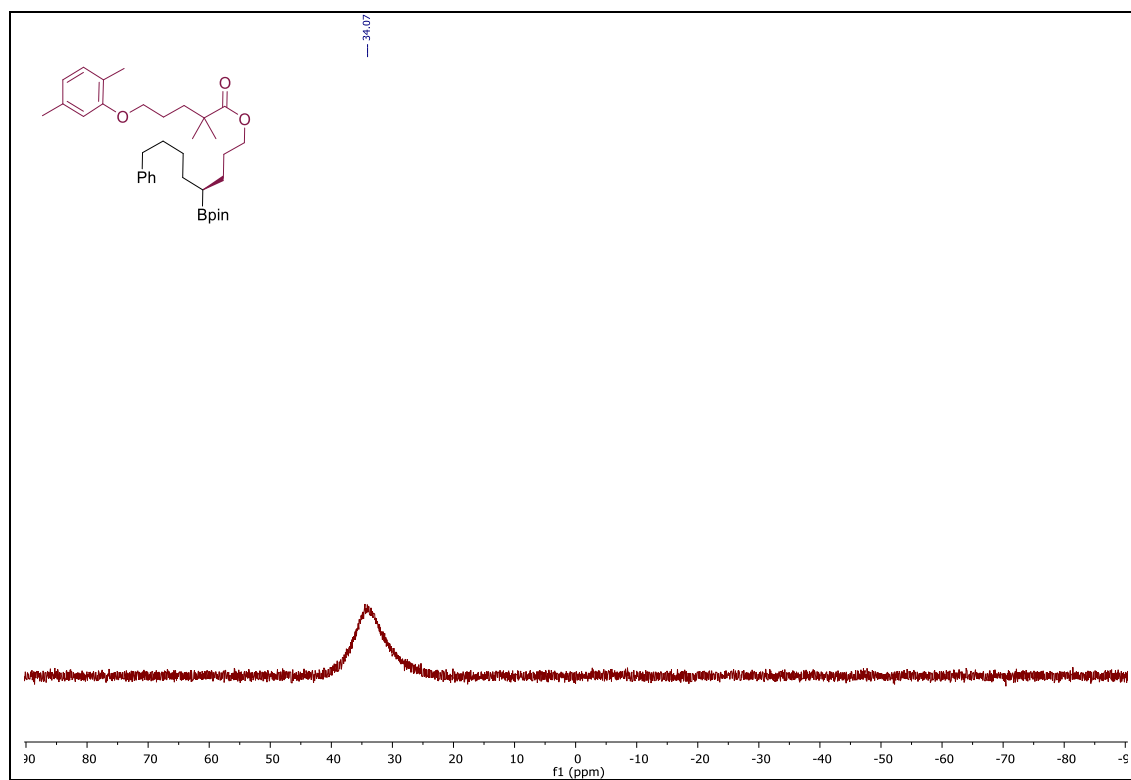
¹H NMR Spectrum (Top): The spectrum is recorded in CDCl₃ and shows peaks from 0.90 to 7.75 ppm. Integration values are provided below the baseline. The peaks are assigned as follows:

- 7.75, 7.74, 7.72, 7.71, 7.70, 7.69, 7.68, 7.65, 7.45, 7.43, 7.42, 7.41, 7.30, 7.29, 7.28, 7.28, 7.27, 7.26, 7.25, 7.20, 7.19, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61, 7.59, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.61

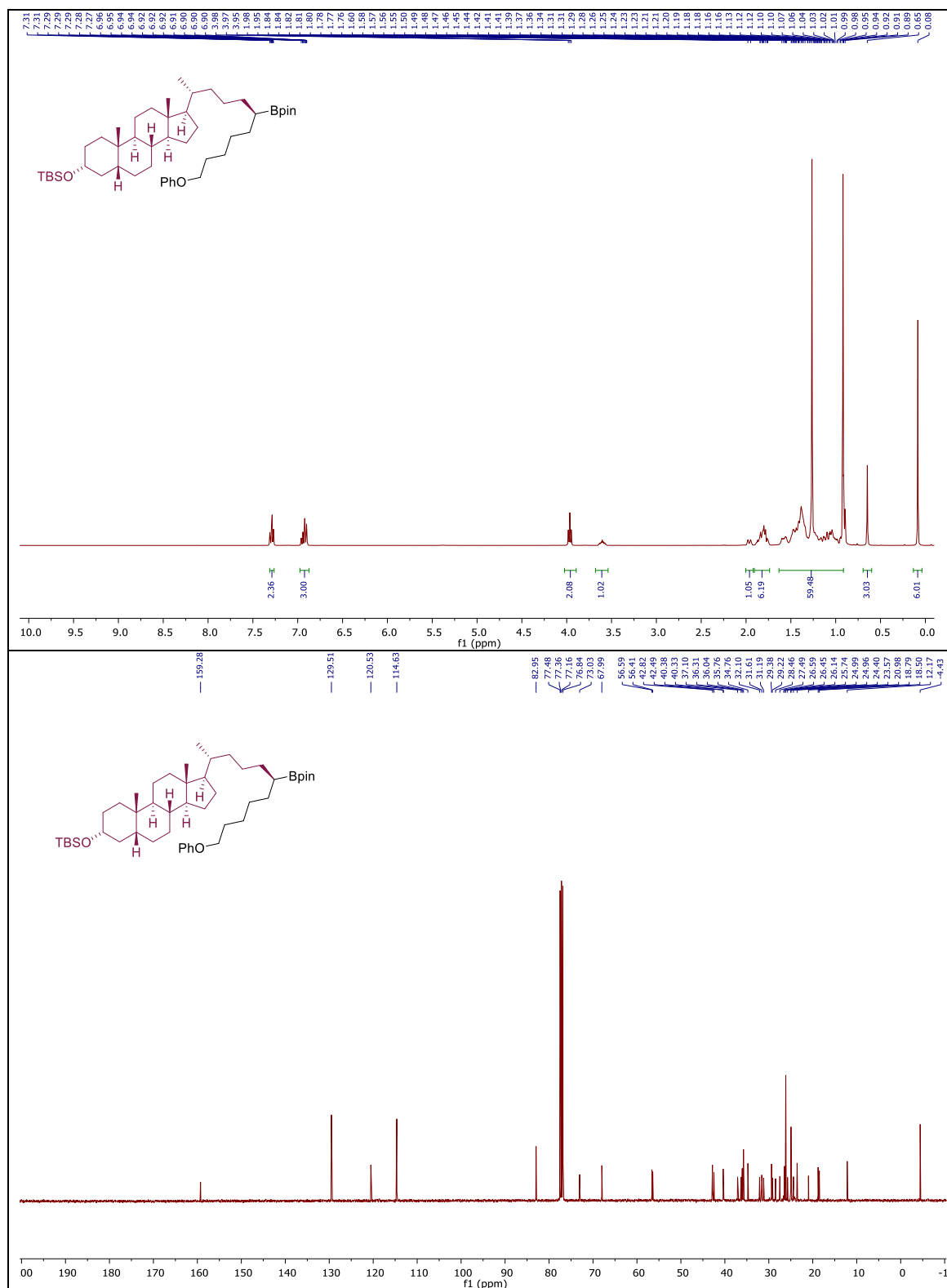


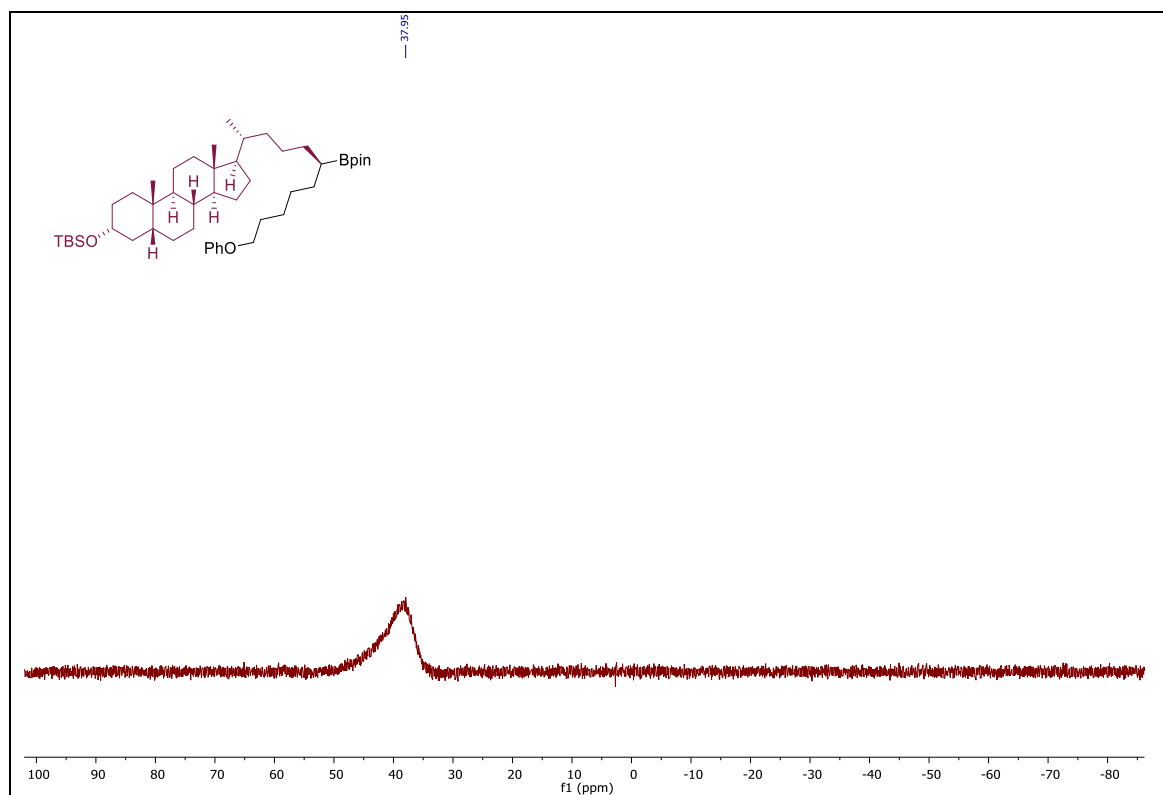
NMR spectra of 6c



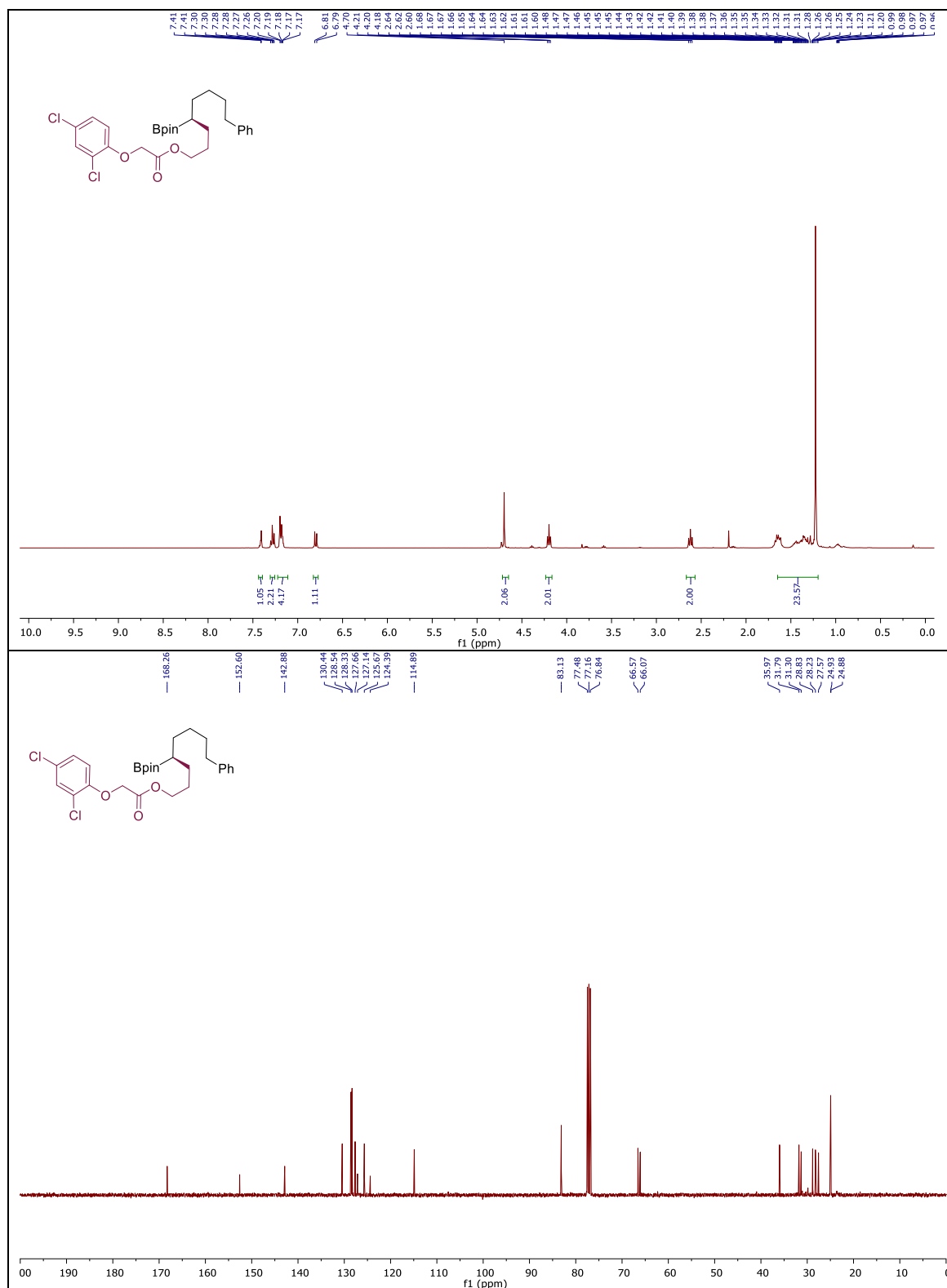


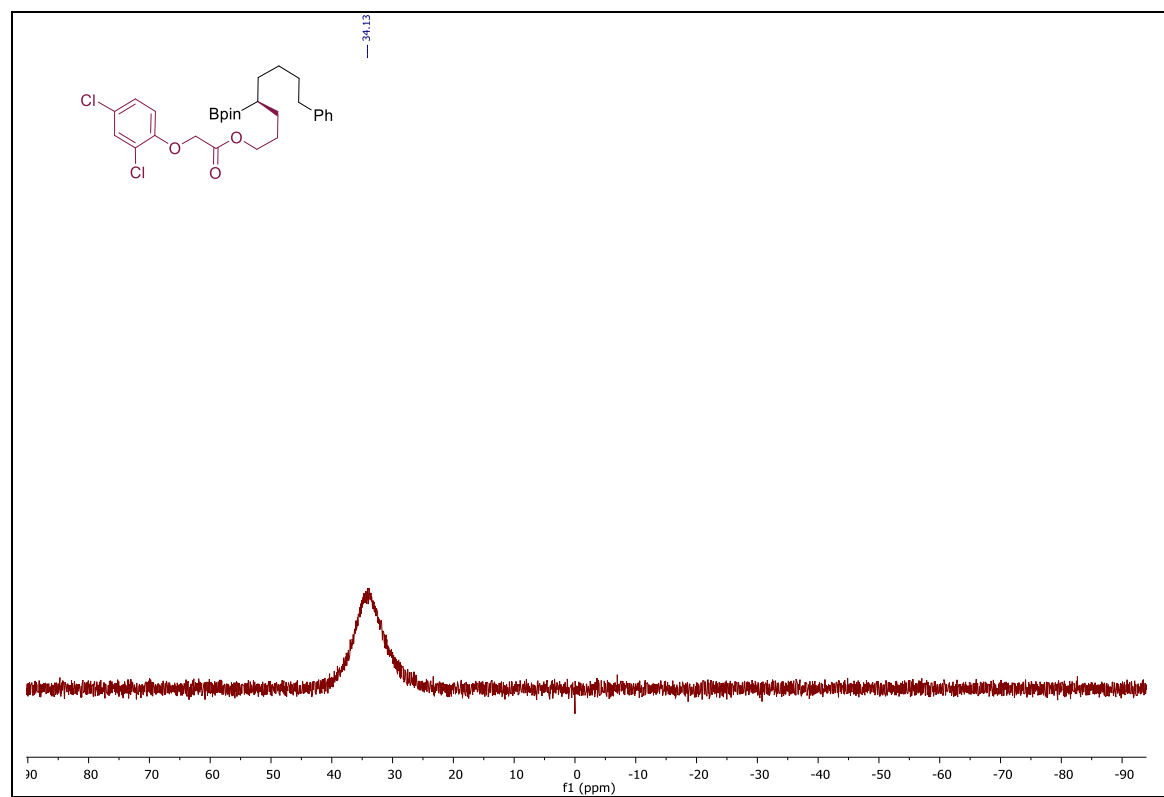
NMR spectra of 6d



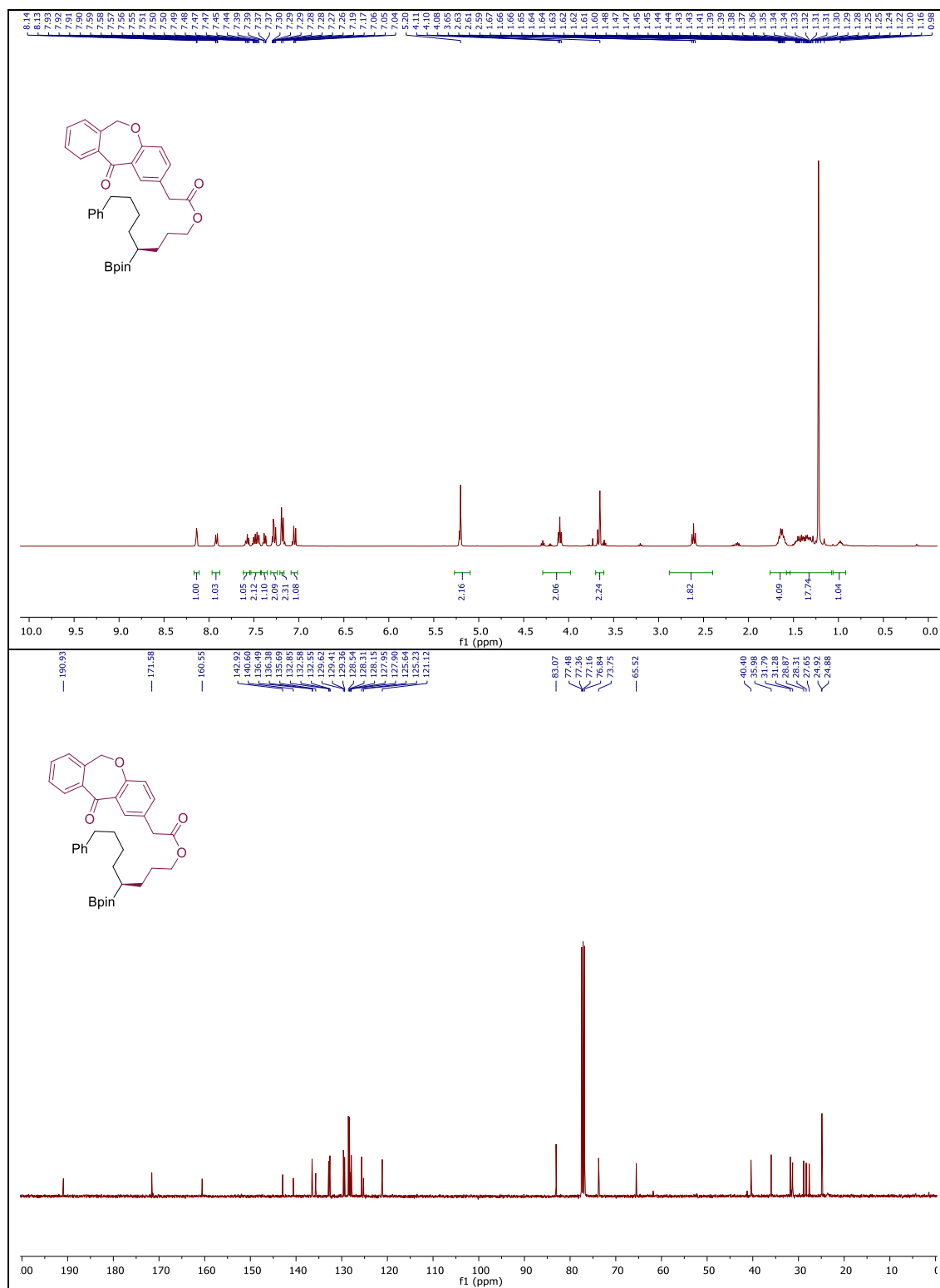


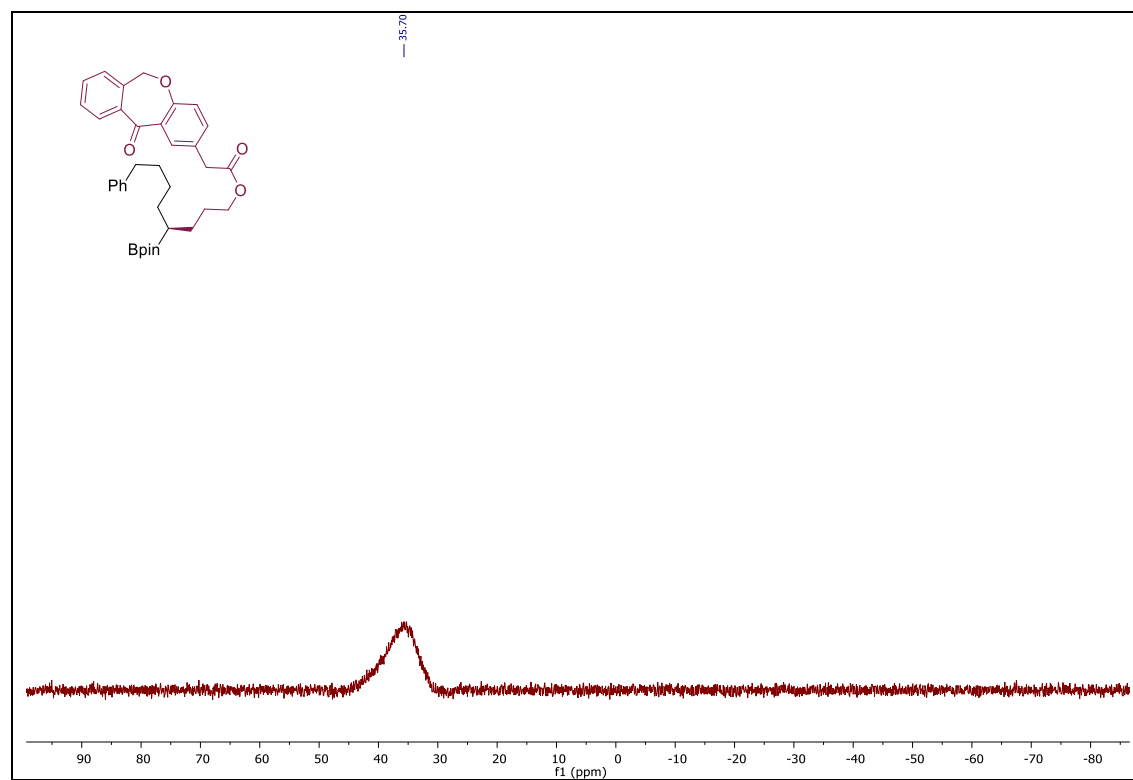
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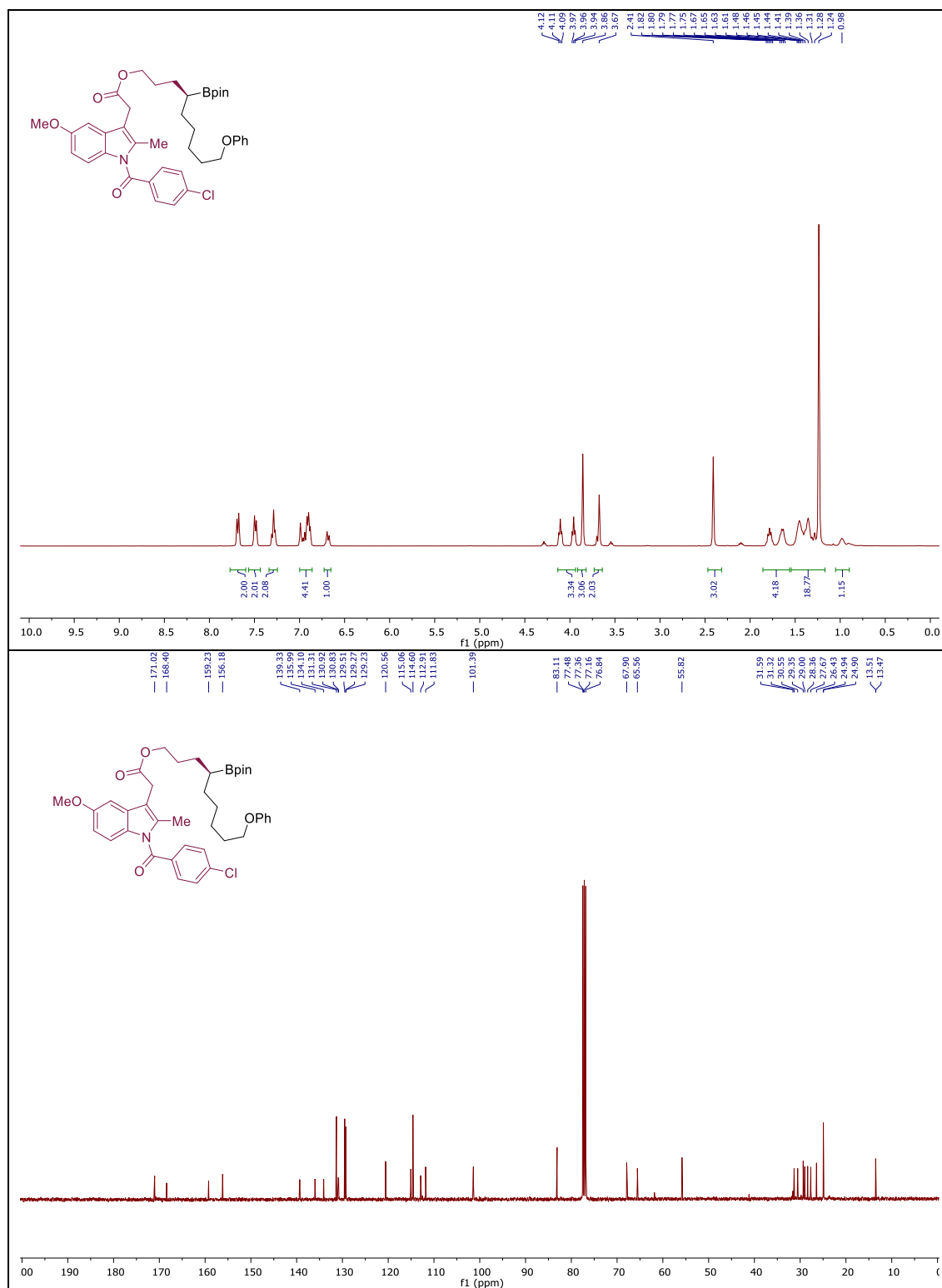


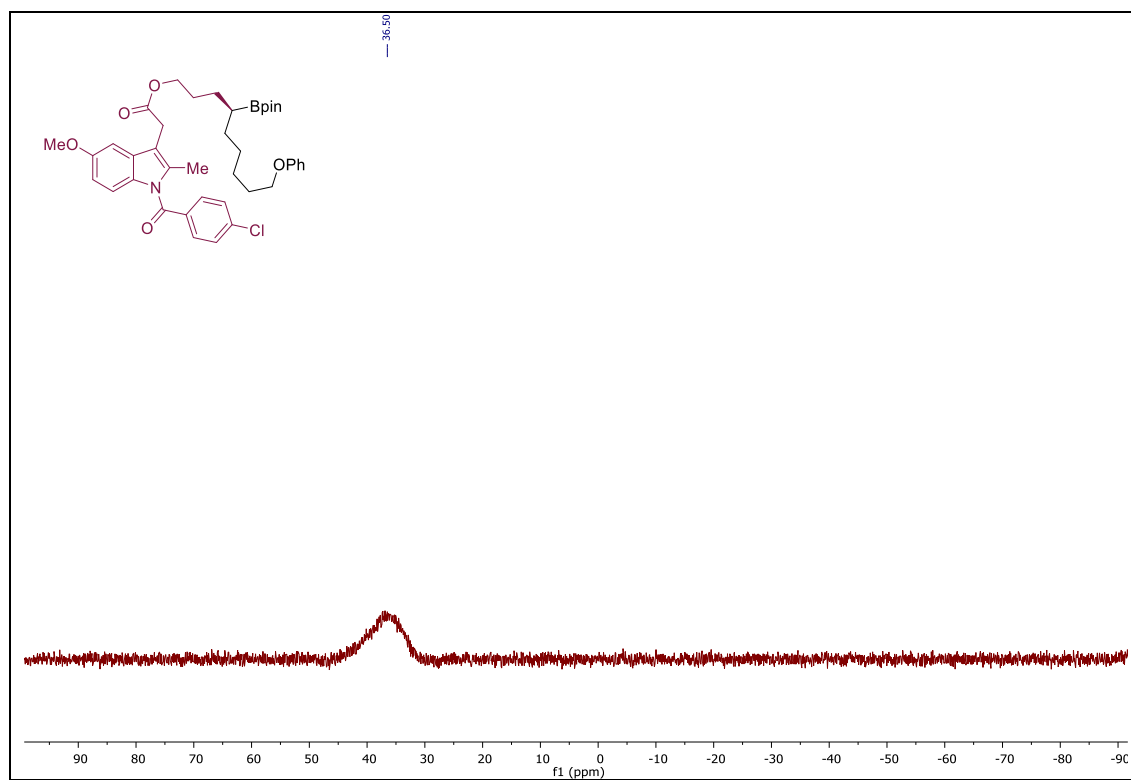
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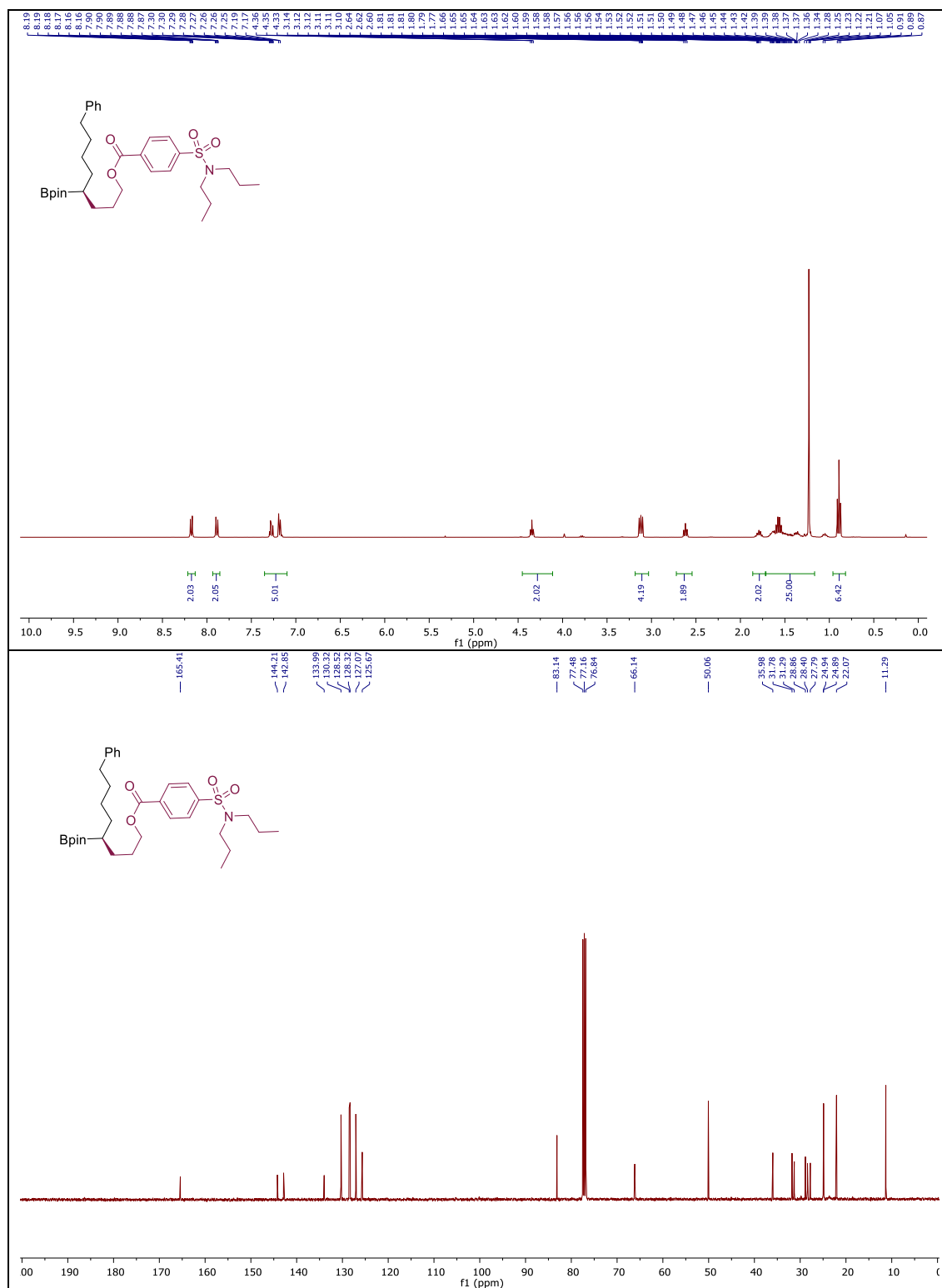


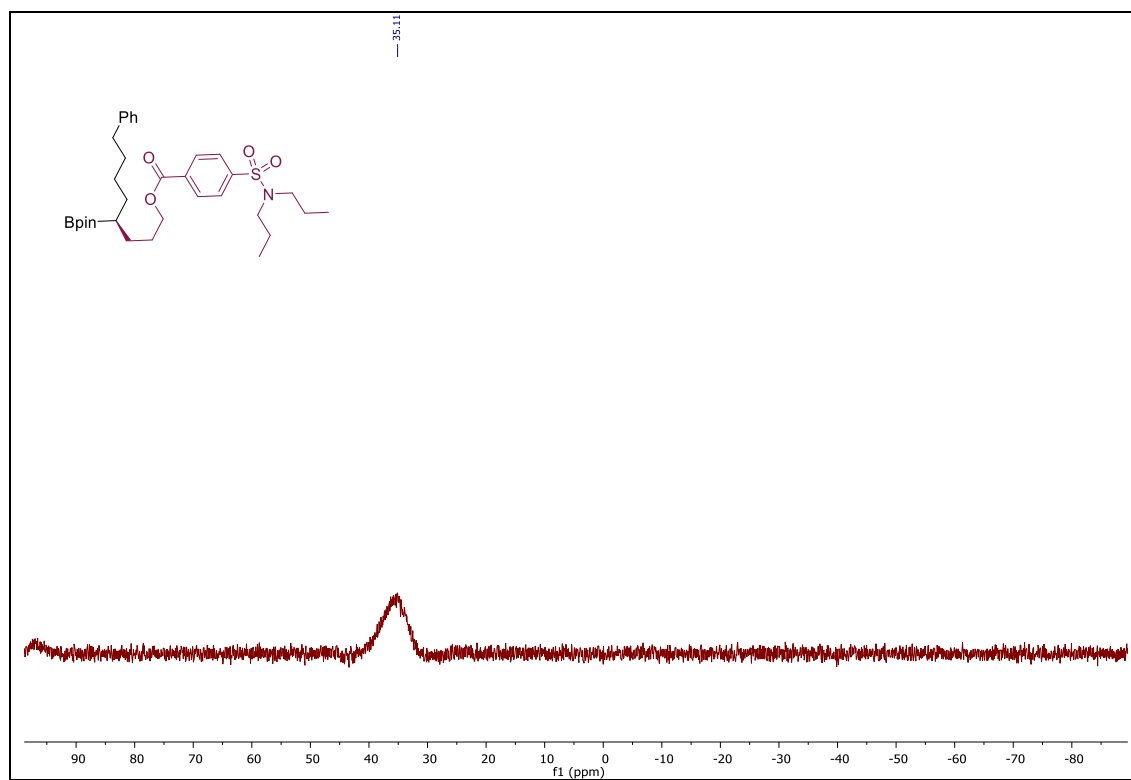
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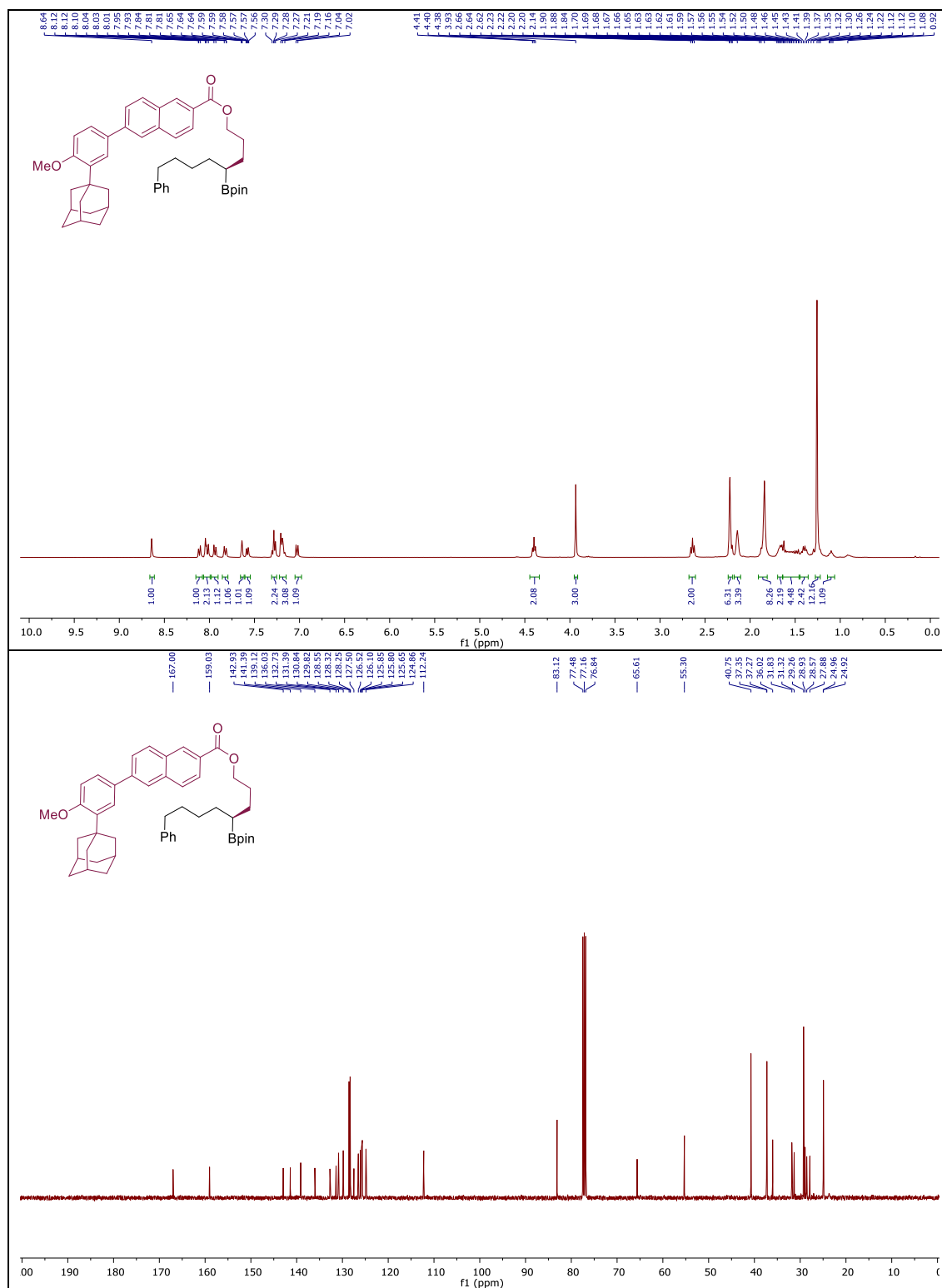


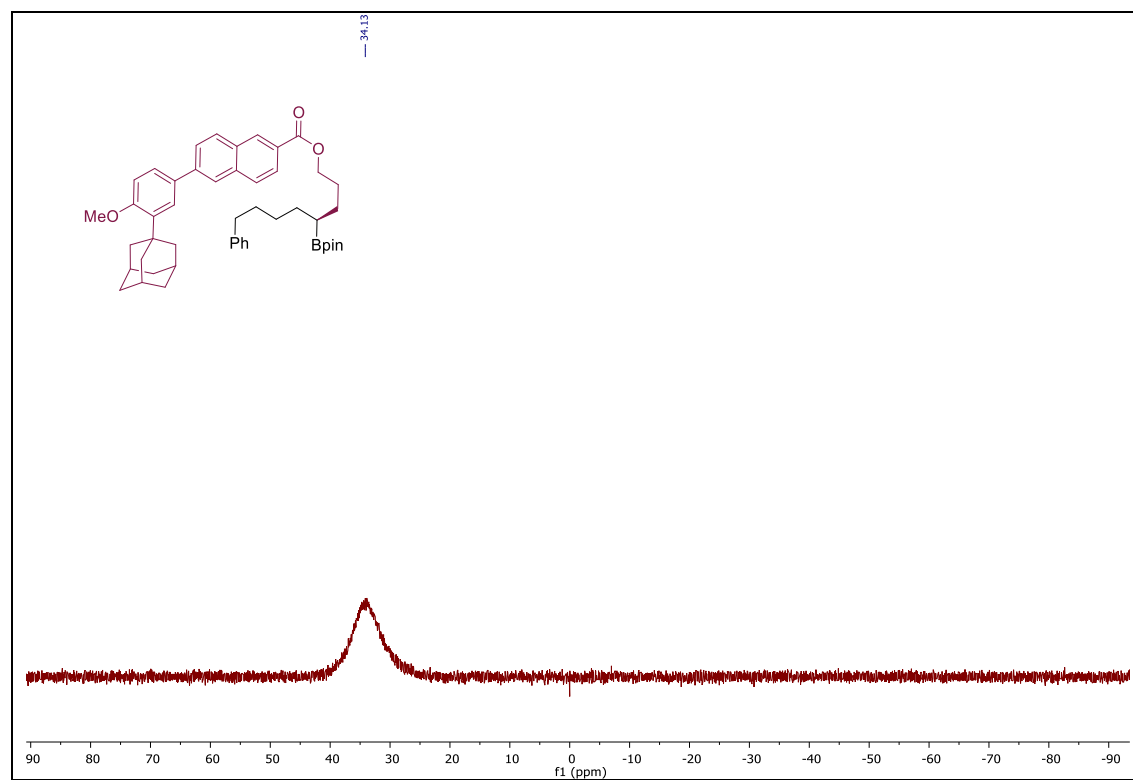
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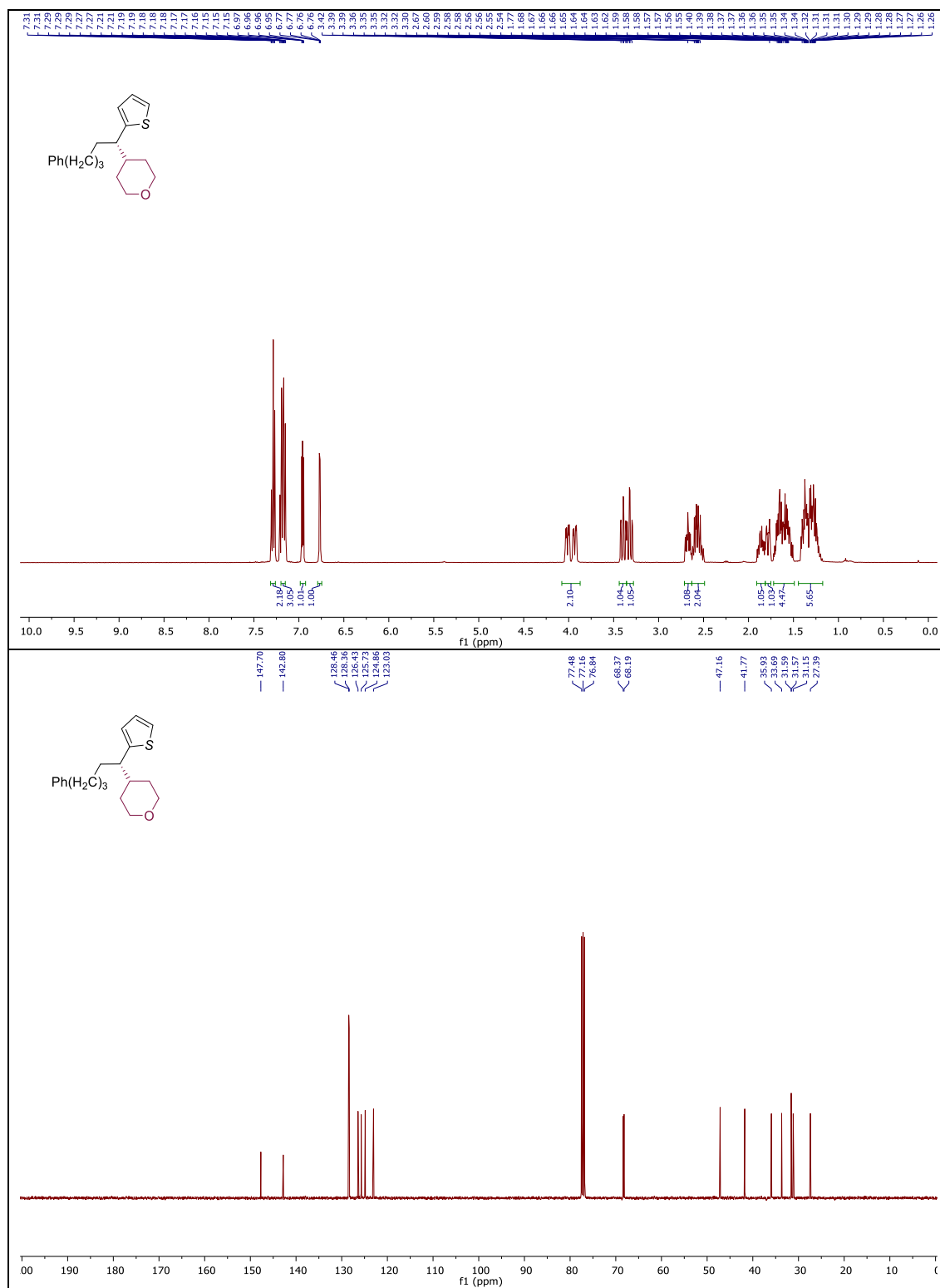


NMR spectra of 6i

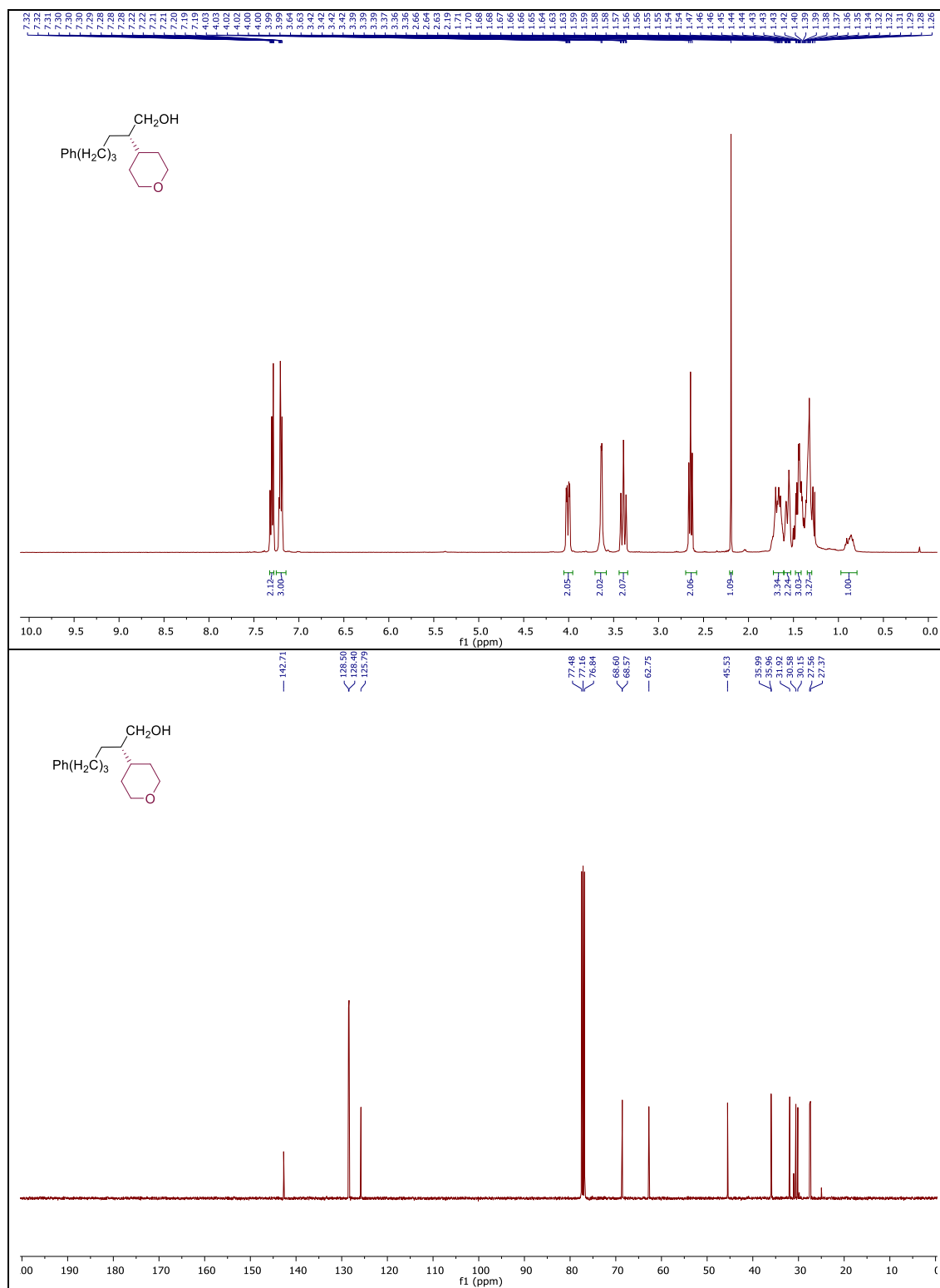




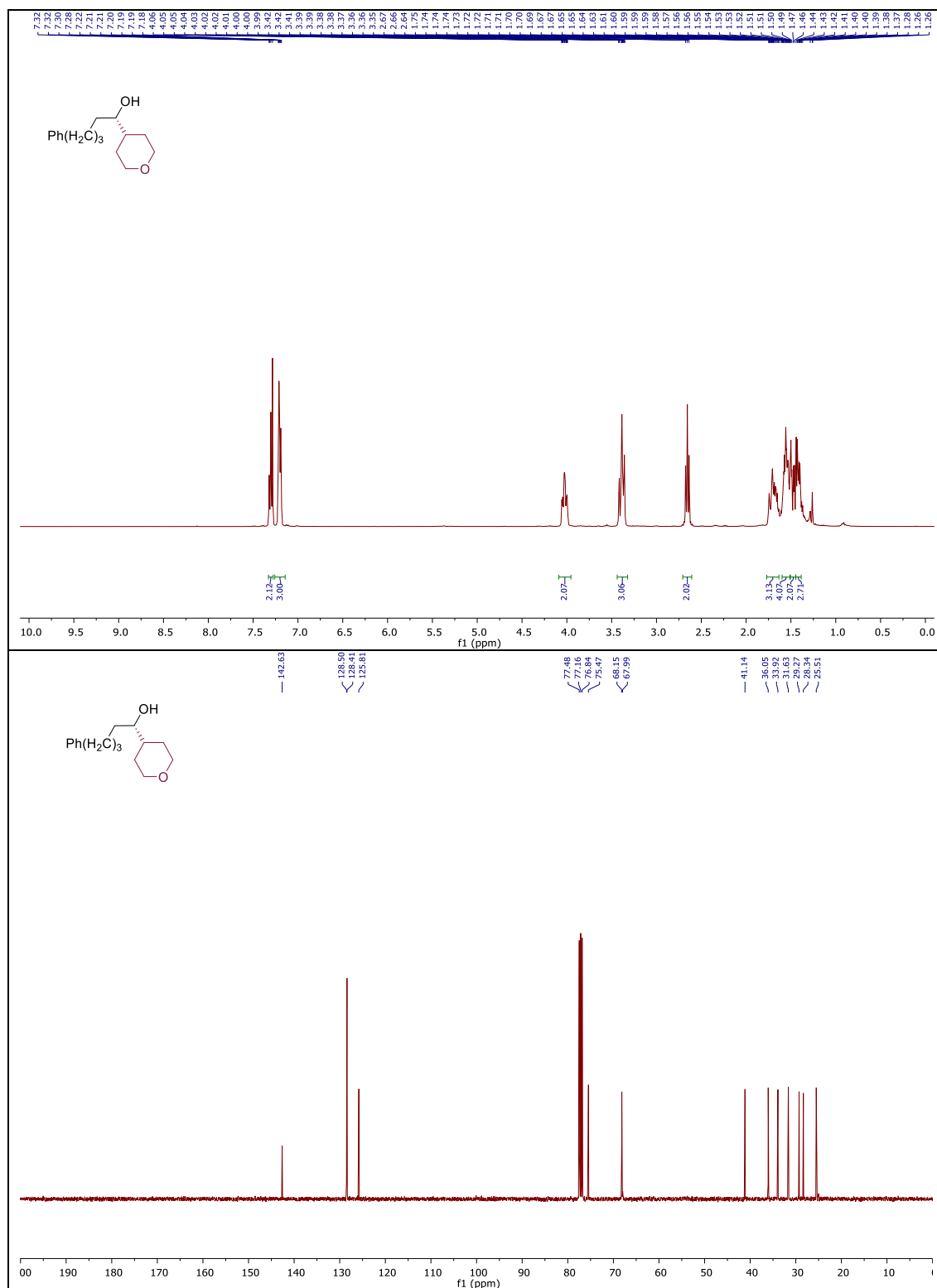
NMR spectra of 7



NMR spectra of 8

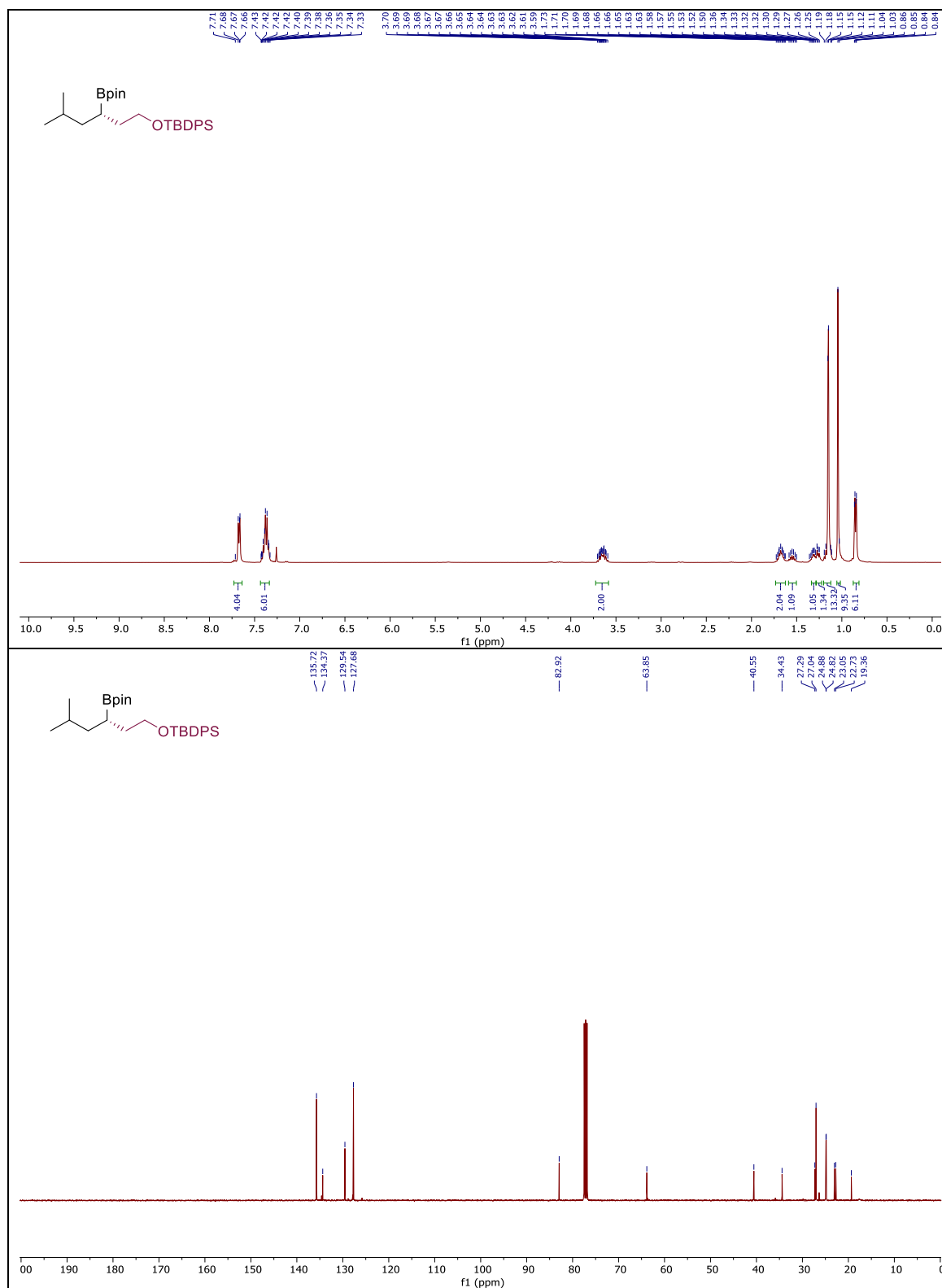


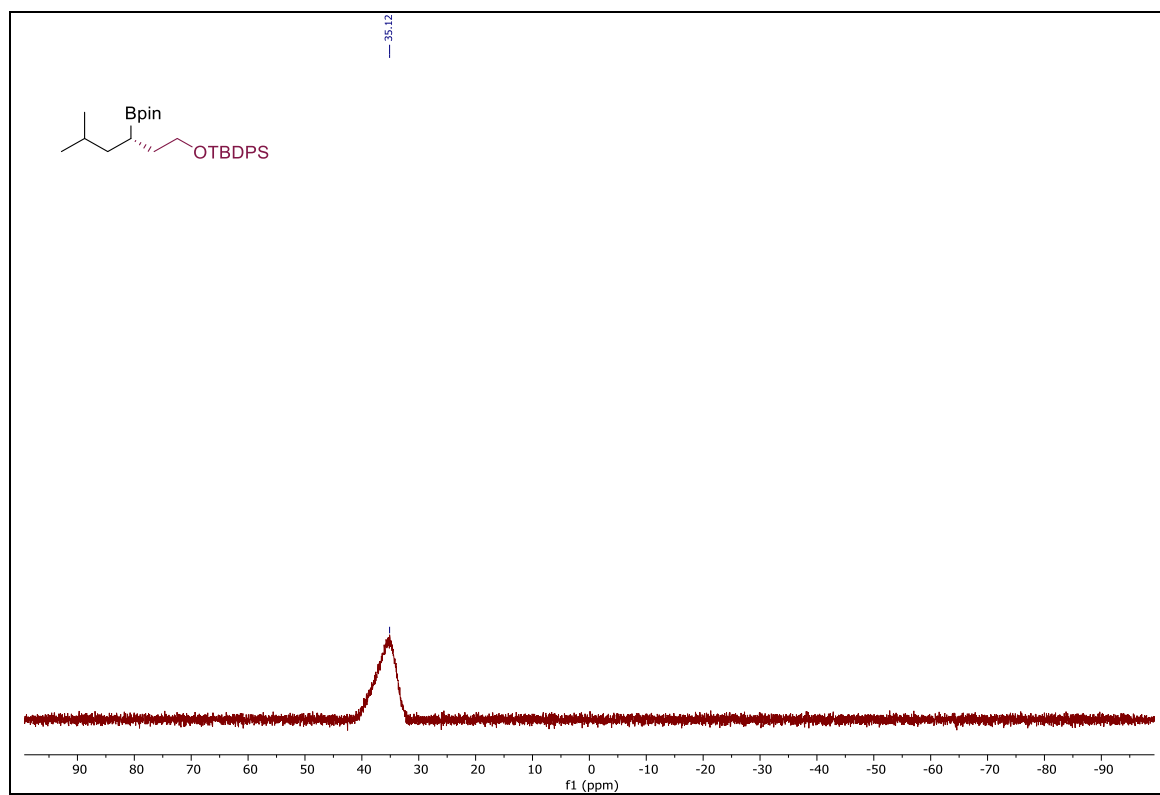
NMR spectra of 9



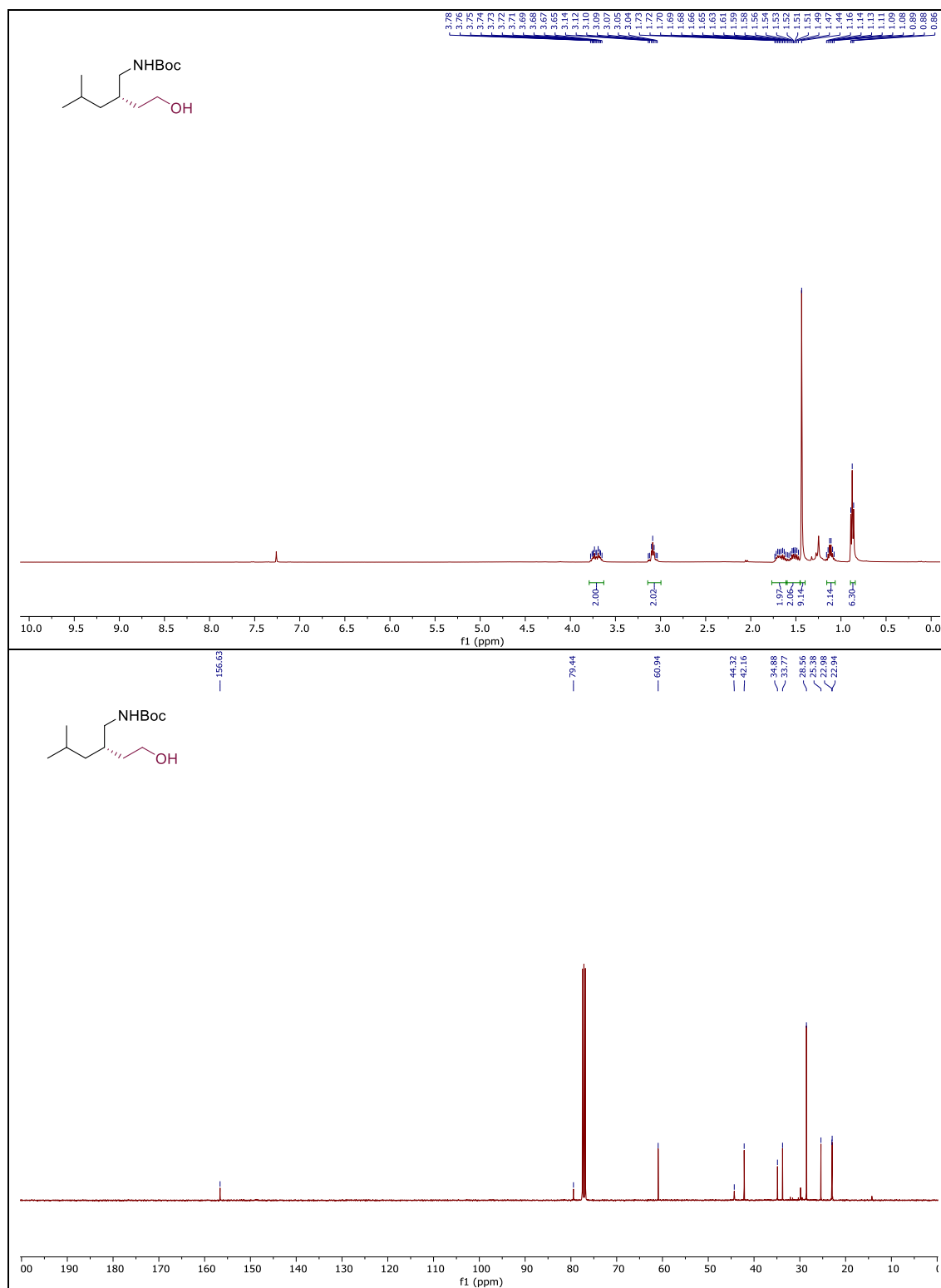
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NMR spectra of 11

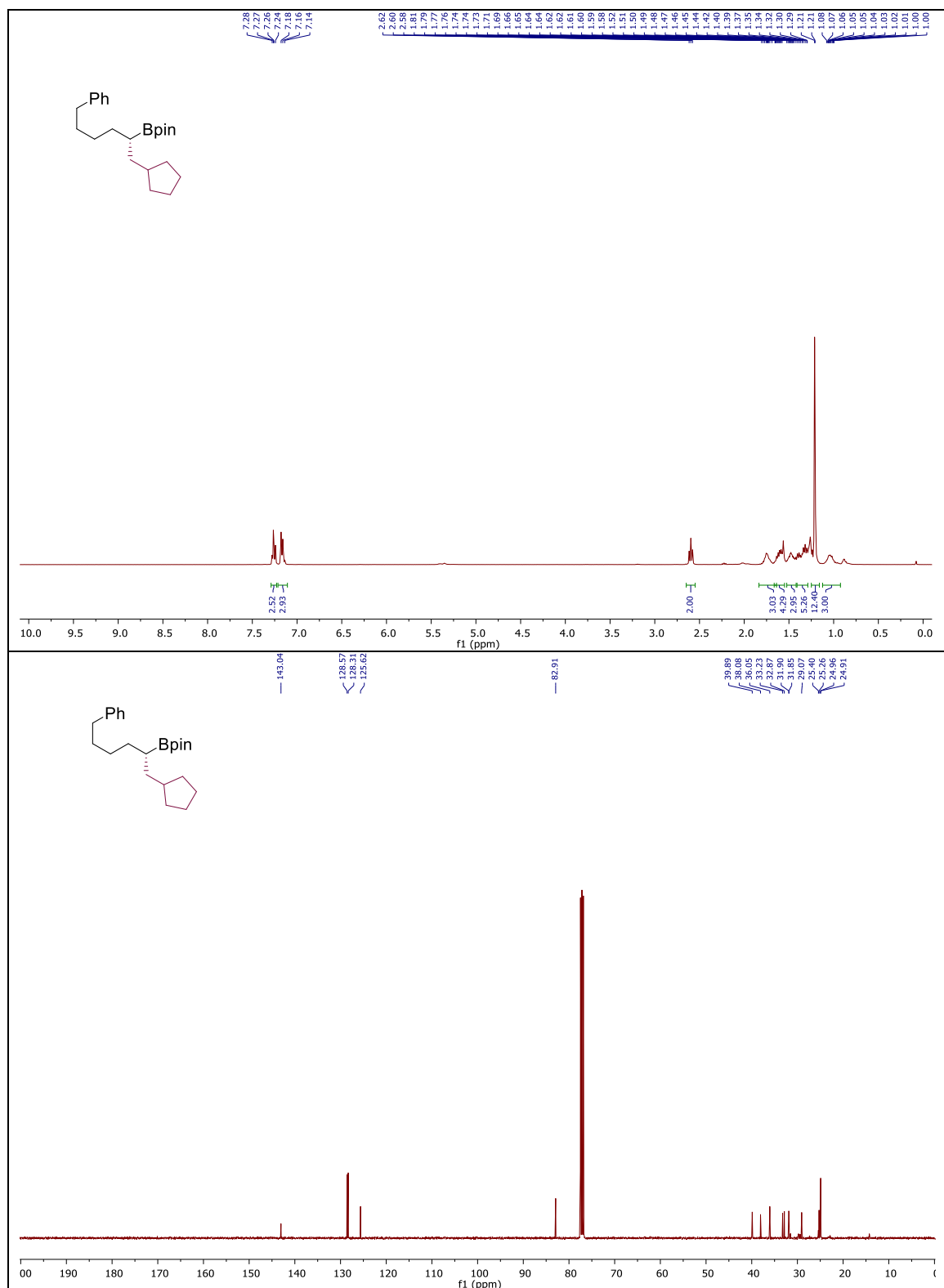


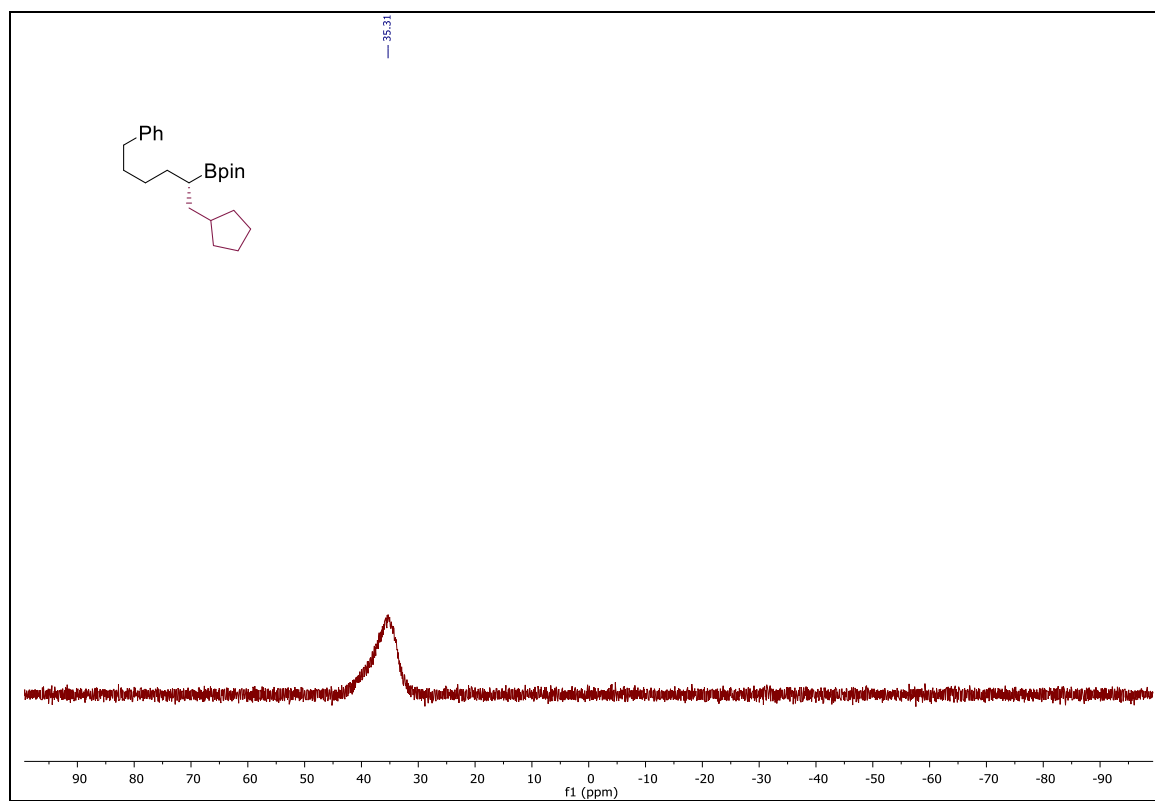


NMR spectra of 12

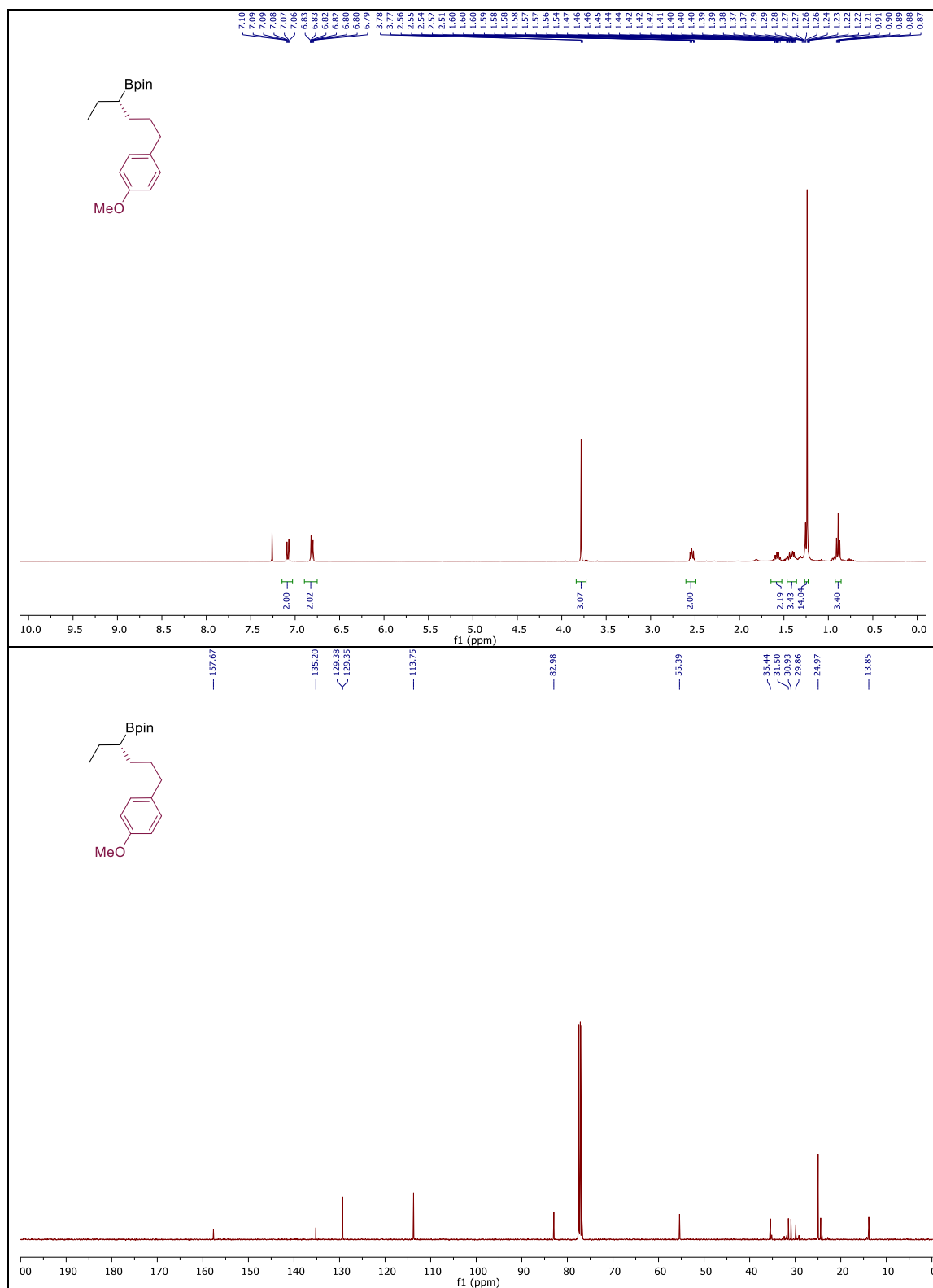


NMR spectra of 13





NMR spectra of 3s





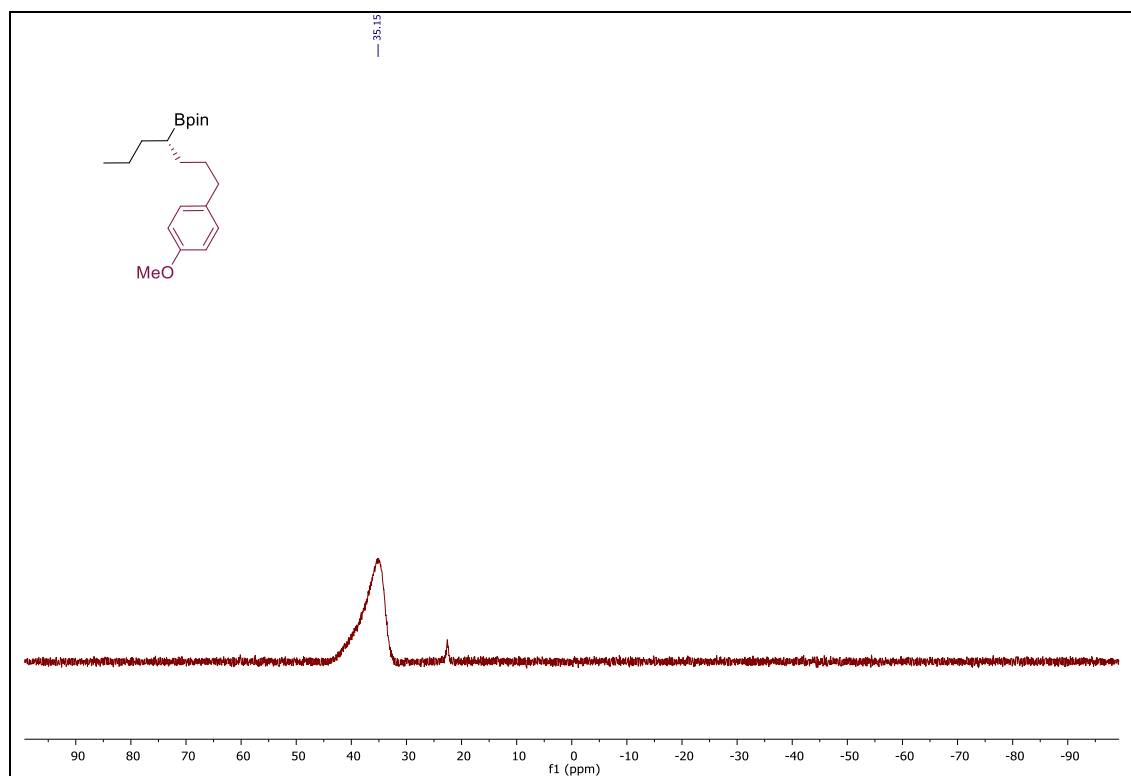
¹H NMR (400 MHz, CDCl₃)

Chemical structure: (S)-1-(4-methoxyphenyl)-3-methylbutan-1-ol

Peak list (ppm): 7.10, 7.09, 7.07, 7.06, 6.83, 6.82, 6.81, 6.80, 6.79, 3.78, 3.75, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1.55, 1.54, 1.53, 1.52, 1.51, 1.50, 1.49, 1.48, 1.47, 1.46, 1.45, 1.44, 1.43, 1.42, 1.41, 1.40, 1.39, 1.38, 1.37, 1.36, 1.35, 1.34, 1.33, 1.32, 1.31, 1.30, 1.29, 1.28, 1.27, 1.26, 1.25, 1.24, 1.23, 1.22, 1.21, 1.20, 1.19, 1.18, 1.17, 1.16, 1.15, 1.14, 1.13, 1.12, 1.11, 1.10, 1.09, 1.08, 1.07, 1.06, 1.05, 1.04, 1.03, 1.02, 1.01, 1.00, 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.89, 0.88, 0.87, 0.86, 0.85, 0.84, 0.83, 0.82, 0.81, 0.80, 0.79, 0.78, 0.77, 0.76, 0.75, 0.74, 0.73, 0.72, 0.71, 0.70, 0.69, 0.68, 0.67, 0.66, 0.65, 0.64, 0.63, 0.62, 0.61, 0.60, 0.59, 0.58, 0.57, 0.56, 0.55, 0.54, 0.53, 0.52, 0.51, 0.50, 0.49, 0.48, 0.47, 0.46, 0.45, 0.44, 0.43, 0.42, 0.41, 0.40, 0.39, 0.38, 0.37, 0.36, 0.35, 0.34, 0.33, 0.32, 0.31, 0.30, 0.29, 0.28, 0.27, 0.26, 0.25, 0.24, 0.23, 0.22, 0.21, 0.20, 0.19, 0.18, 0.17, 0.16, 0.15, 0.14, 0.13, 0.12, 0.11, 0.10, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.00.

¹³C NMR (100 MHz, CDCl₃)

Peak list (ppm): 157.67, 135.19, 129.37, 129.35, 113.75, 82.95, 55.39, 35.44, 33.87, 31.53, 31.21, 29.66, 24.97, 24.94, 22.54, 14.60.



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