Supplementary Information

Enantioselective C(sp^3)–C(sp^3) Cross-Coupling of Non-activated Alkyl Electrophiles via Nickel Hydride Catalysis

Srikrishna Bera[†], Runze Mao[†], and Xile Hu*

Laboratory of Inorganic Synthesis and Catalysis, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), ISIC-LSCI, BCH 3305, Lausanne 1015, Switzerland.

*Correspondence to: xile.hu@epfl.ch; [†]Equal contributions.

Table of Contents

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

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

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

GC and GC-MS: All GC analyses were performed on a Perkin-Elmer Clarus 400 GC system with 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(sp^3)–C(sp^3) 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 (N_2) 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 Na_2SO_4, 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.):

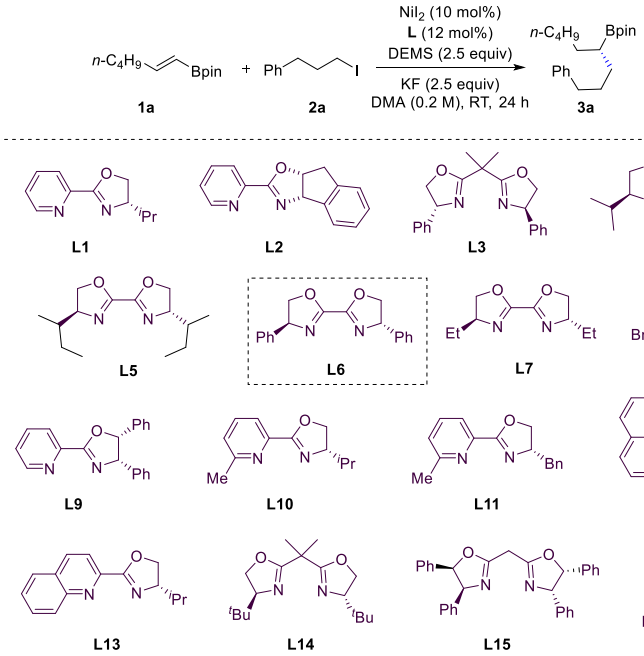
The boronic ester product was oxidized to the corresponding alcohol following **GP2**. Then, the alcohol was purified by PTLC and the enantiomeric excess (e.e.) was determined by HPLC analysis.

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:H_2O (2.0 mL) and then $NaBO_3$•$4H_2O$ (40 mg) was added to it at room temperature. After stirring for 4 hours at room temperature, H_2O (1.0 mL) was added. The reaction mixture was extracted with Et_2O (3x2.0 mL). The combined organic phases were dried over Na_2SO_4, 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

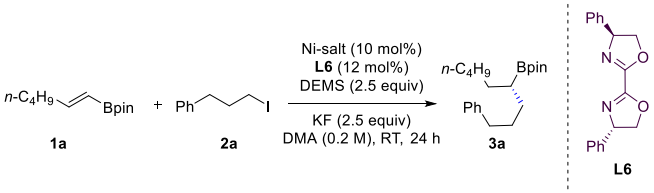
Table 1. Screening of ligands:



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.

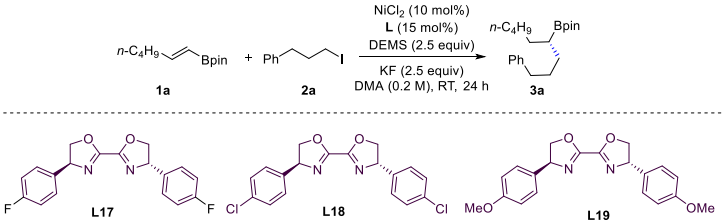
Table 2. Screening of Ni-salts:



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	$NiI_2.6H_2O$	38	60
12	$NiCl_2.6H_2O$	51	76
13	$Ni(NO_3)_2.6H_2O$	65	72
14	$Ni(BF_4)_2.6H_2O$	51	68
15	$NiSO_4.6H_2O$	16	26
16	$NiF_2.4H_2O$	n.r.	n.d.
17	$Ni(ClO_4)_2.6H_2O$	48	52

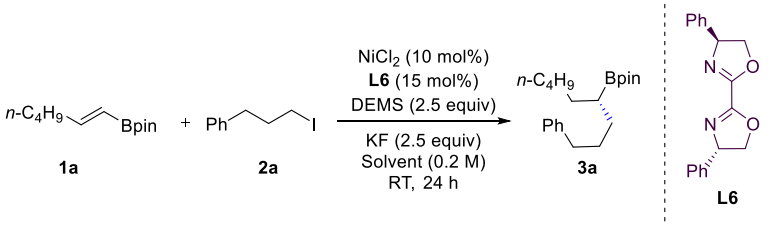
[a]15 mol% Ligand was used. [b]The reaction was conducted at 0 °C for 48 hours. n.r. = no reaction, n.d. = not determined.

Table 3. Further screening of ligands:



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

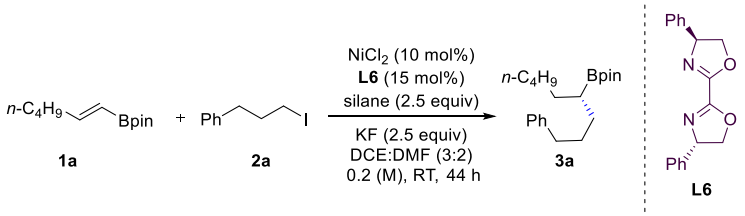
Table 4. Screening of solvents:



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

[a]Reaction time = 44 hours. n.r. = no reaction, n.d. = not determined.

Table 5. Screening of silanes:

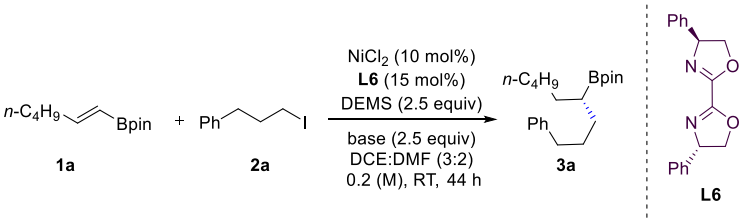


1a 2a 3a L6

Entry	Silanes	Yield(%)	e.e.(%)
1	DEMS	55	92
2	$(MeO)_2MeSiH$	55	85
3	$(MeO)Me_2SiH$	31	80
4	$(EtO)_3SiH$	42	89
5	$Me(OTMS)_2SiH$	trace	n.d.
6	PMHS	48	91
7	Et_3SiH	trace	n.d.
8	Ph_2SiH_2	14	n.d.
9	Ph_3SiH	trace	n.d.
10	$PhSiH_3$	trace	n.d.
11	$PhMe_2SiH$	n.r.	n.d.

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

Table 6. Screening of bases:

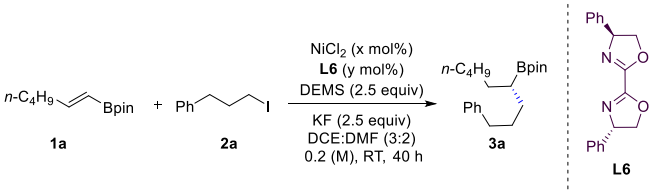


1a 2a 3a L6

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_2CO_3	10	n.d.
7	Na_2CO_3	10	n.d.
5	K_3PO_4	n.r.	n.d.

n.r. = no reaction, n.d. = not determined. [a]Reaction 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

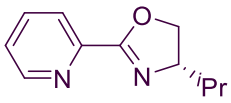
[a]10 mol% $NiCl_2$ and 15 mol% ligand. [b]15 mol% $NiCl_2$ and 20 mol% ligand. [c]17.5 mol% $NiCl_2$ and 22 mol% ligand. Isolated yield in the parenthesis.

3. Synthesis of ligands (L):

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

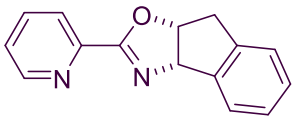
Ligands **L1**, **L2**, **L9**, **L10**, **L11** and **L12** were synthesised according to a known literature procedure.[1]

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



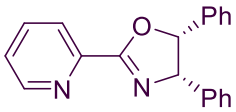
The title compound was synthesized from 2-cyanopyridine and L-valinol following a known literature procedure.[1] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.65 – 8.64 (m, 1H), 8.01 – 7.99 (m, 1H), 7.73 – 7.69 (m, 1H), 7.34 – 7.31 (m, 1H), 4.51 – 4.42 (m, 1H), 4.21 – 4.06 (m, 2H), 1.84 (hept, *J* = 6.7 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 1H), 0.89 (d, *J* = 6.7 Hz, 3H). **^{13}C 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]

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



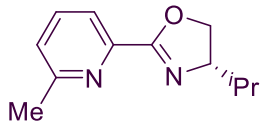
The title compound was synthesized from 2-cyanopyridine and (1*S*,2*R*)-(-)-*cis*-1-amino-2-indanol following a known literature procedure.[3] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.68 – 8.66 (m, 1H), 8.04 – 8.02 (m, 1H), 7.74 – 7.70 (m, 1H), 7.59 – 7.57 (m, 1H), 7.35 – 7.32 (m, 1H), 5.80 (d, *J* = 7.9 Hz, 1H), 5.57 (td, *J* = 7.3, 6.4, 2.1 Hz, 1H), 3.57 – 3.41 (m, 2H). **^{13}C 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):



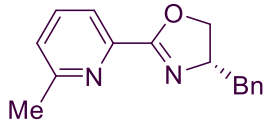
The title compound was synthesized from 2-cyanopyridine and (1*R*,2*S*)-2-amino-1,2-diphenylethan-1-ol following a known literature procedure.[3] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.80 (d, *J* = 4.8 Hz, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 7.8, 4.8 Hz, 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). ^{13}C 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):



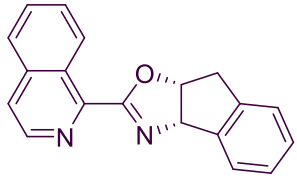
The title compound was synthesized from 2-cyano-6-methylpyridine and L-valinol following a known literature procedure.[1] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.62 (td, *J* = 7.8, 1.7 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 4.53 – 4.43 (m, 1H), 4.24 – 4.14 (m, 1H), 4.18 – 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). ^{13}C 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):



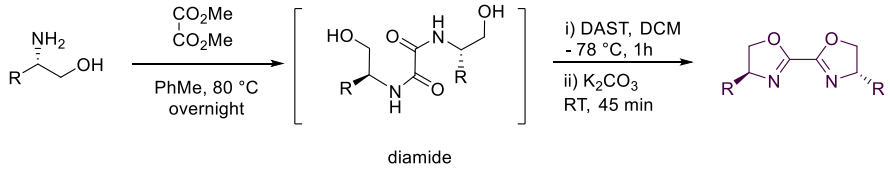
The title compound was synthesized from 2-cyano-6-methylpyridine and L-phenylalaninol following a known literature procedure.[1] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 – 7.88 (m, 1H), 7.69 – 7.65 (m, 1H), 7.36 – 7.19 (m, 6H), 4.69 – 4.61 (m, 1H), 4.44 (t, *J* = 9.0 Hz, 1H), 4.24 (t, *J* = 8.2 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). **^{13}C 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]

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



The title compound was synthesized from isoquinoline-1-carbonitrile and (1*S*,2*R*)-(-)-*cis*-1-amino-2-indanol following a known literature procedure.[1] **^{1}H 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). **^{13}C 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.

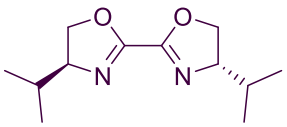
Ligands **L4**, **L5**, **L6**, **L7**, **L17**, **L18** and **L19** were synthesized according to a slightly modified known literature procedure.[6]



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 N_2 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 K_2CO_3 (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 $NaHCO_3$ (20 mL)

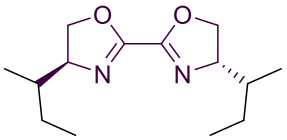
and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc as eluent to afford the desired Bi-Ox ligands.

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



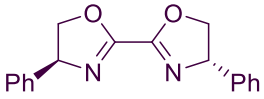
The title compound was synthesized from L-valinol following the above mentioned procedure.Yield: 68%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.47 – 4.36 (m, 2H), 4.15 – 4.03 (m, 4H), 1.83 (h, *J* = 6.7 Hz, 2H), 1.00 (d, *J* = 8.2 Hz, 6H), 0.90 (d, *J* = 8.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) 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):



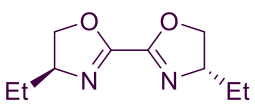
The title compound was synthesized from (*S*)-(+)-isoleucinol following the above mentioned procedure. Yield: 62%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.42 (dd, *J* = 9.5, 7.9 Hz, 2H), 4.21 (td, *J* = 9.2, 6.2 Hz, 2H), 4.13 (dd, *J* = 8.9, 7.9 Hz, 2H), 1.76 – 1.56 (m, 4H), 1.21 (ddt, *J* = 13.9,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



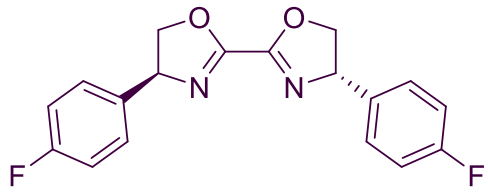
Ligand (**L6**) was synthesized according to slightly modified known literature.[6] (*S*)-(+)-2-Phenylglycinol (823 mg, 6.00 mmol, 2.00 equiv.) and dimethyloxalate (354 mg, 3.00 mmol, 1.00 equiv.), followed by anhydrous PhMe (70 mL), were added to an oven-dried schlenk tube under an inert atmosphere. 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 N_2 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 K_2CO_3 (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 $NaHCO_3$ (20 mL) and brine (30 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using a mixture of hexane/EtOAc (2:1) as eluent to afford the desired ligand **L6** as a crystalline white powder (600 mg, 82%). **^{1}H 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).**^{13}C 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):



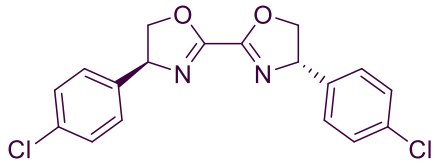
The title compound was synthesized from (*S*)-(+)-2-amino-1-butanol following the above mentioned procedure. Yield: 73%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.49 (dd, *J* = 9.7, 8.4 Hz, 2H), 4.24 (ddt, *J* = 9.7, 8.4, 6.6 Hz, 2H), 4.05 (t, *J* = 8.4 Hz, 2H), 1.82 – 1.69 (m, 2H), 1.66 – 1.54 (m,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



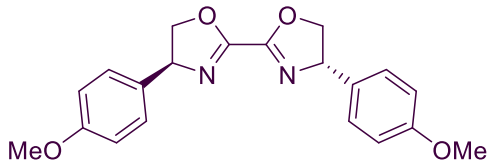
The title compound was synthesized from (*S*)-2-amino-2-(4-fluorophenyl)ethan-1-ol following the above mentioned procedure. Yield: 67%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.25 (m, 4H), 7.10 – 7.03 (m, 4H), 5.44 (dd, *J* = 10.4, 9.1 Hz, 2H), 4.85 (dd, *J* = 10.4, 8.8 Hz, 2H), 4.33 (t, *J* = 8.8 Hz, 2H). **^{13}C 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. **^{19}F 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):



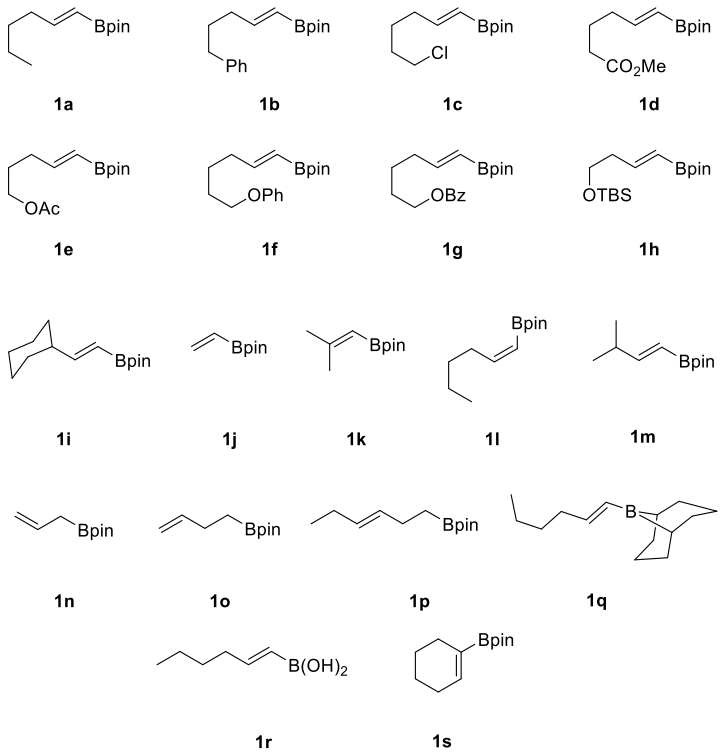
The title compound was synthesized from (*S*)-2-amino-2-(4-chlorophenyl)ethan-1-ol following the above mentioned procedure. Yield: 55%. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 4H), 7.28 – 7.22 (m, 4H), 5.44 (t, *J* = 9.8 Hz, 2H), 4.91 – 4.83 (m, 2H), 4.32 (m, 2H). **^{13}C NMR** (101 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%. **^{1}H 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). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.48, 155.64, 132.85, 128.09, 114.36, 75.51, 70.11, 55.47.

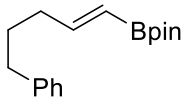
4. Synthesis of alkenyl boronic esters



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

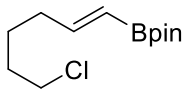
Compound **1b**–**1h**[8], **1l**[9], **1m**[11], **1o**[12], **1p**[12] and **1q**[14] were prepared according to the previously reported procedures.

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



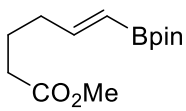
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 7.18 – 7.15 (m, 3H), 6.64 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.45 (d, *J* = 18.0 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.19 (q, *J* = 7.0, 6.6 Hz, 2H), 1.75 (p, *J* = 7.6 Hz, 2H), 1.26 (s, 12H). **^{13}C 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):



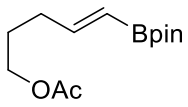
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.68 – 6.55 (m, 1H), 5.45 (d, *J* = 18.0 Hz, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.19 (q, *J* = 6.9 Hz, 2H), 1.78 (p, *J* = 6.8 Hz, 2H), 1.62 – 1.52 (m, 2H), 1.26 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 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):



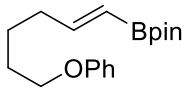
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.65 – 6.53 (m, 1H), 5.45 (d, *J* = 18.0 Hz, 1H), 3.66 (s, 3H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.19 (q, *J* = 6.9 Hz, 2H), 1.76 (p, *J* = 7.4 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 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):



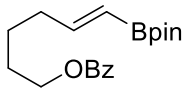
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.60 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.46 (d, *J* = 18.0 Hz, 1H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.22 (q, *J* = 7.6 Hz, 2H), 2.03 (s, 3H), 1.77 (q, *J* = 6.9 Hz, 2H), 1.26 (s, 12H). **^{13}C NMR** (101 MHz, 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):



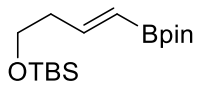
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.30 – 7.22 (m, 2H), 6.93 – 6.87 (m, 3H), 6.64 (dt, *J* = 17.9, 6.4 Hz, 1H), 5.46 (d, *J* = 18.0 Hz, 1H), 3.94 (t, *J* = 6.4 Hz, 2H), 2.22 (q, *J* = 7.0 Hz, 2H), 1.79 (p, *J* = 6.5 Hz, 2H), 1.60 (p, *J* = 7.6 Hz, 2H), 1.26 (s, 12H). **^{13}C 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):



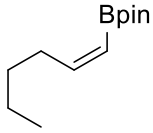
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 6.63 (dt, *J* = 18.0, 6.4 Hz, 1H), 5.47 (d, *J* = 18.0 Hz, 1H), 4.32 (t, *J* = 6.5 Hz, 2H), 2.24 (q, *J* = 7.0 Hz, 2H), 1.79 (p, *J* = 6.7 Hz, 2H), 1.59 (p, *J* = 7.6 Hz, 2H), 1.26 (s, 12H). **^{13}C 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):



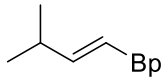
Prepared according to the known literature procedure.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.59 (dt, *J* = 17.9, 6.6 Hz, 1H), 5.49 (d, *J* = 18.0 Hz, 1H), 3.69 (t, *J* = 7.0 Hz, 2H), 2.38 (q, *J* = 6.9 Hz, 2H), 1.26 (s, 12H), 0.88 (s, 9H), 0.04 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 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):



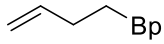
Prepared according to the known literature procedure.[9] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.42 (dt, *J* = 14.6, 7.6 Hz, 1H), 5.32 (d, *J* = 14.6 Hz, 1H), 2.39 (q, *J* = 7.6 Hz, 2H), 1.42 – 1.29 (m, 4H), 1.26 (s, 12H), 0.93 – 0.86 (m, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.38, 82.91, 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] **^{1}H 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). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.09, 83.14, 33.72, 24.94, 21.56. Spectral data match those previously reported.[11]

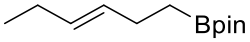
2-(But-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1o):



Prepared according to the known literature procedure.[12] **^{1}H 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). **^{13}C NMR** (101 MHz,

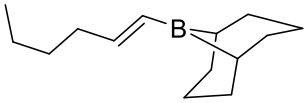
Chloroform-*d*) δ 140.81, 113.29, 83.15, 28.12, 24.97. Spectral data match those previously reported.[12]

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



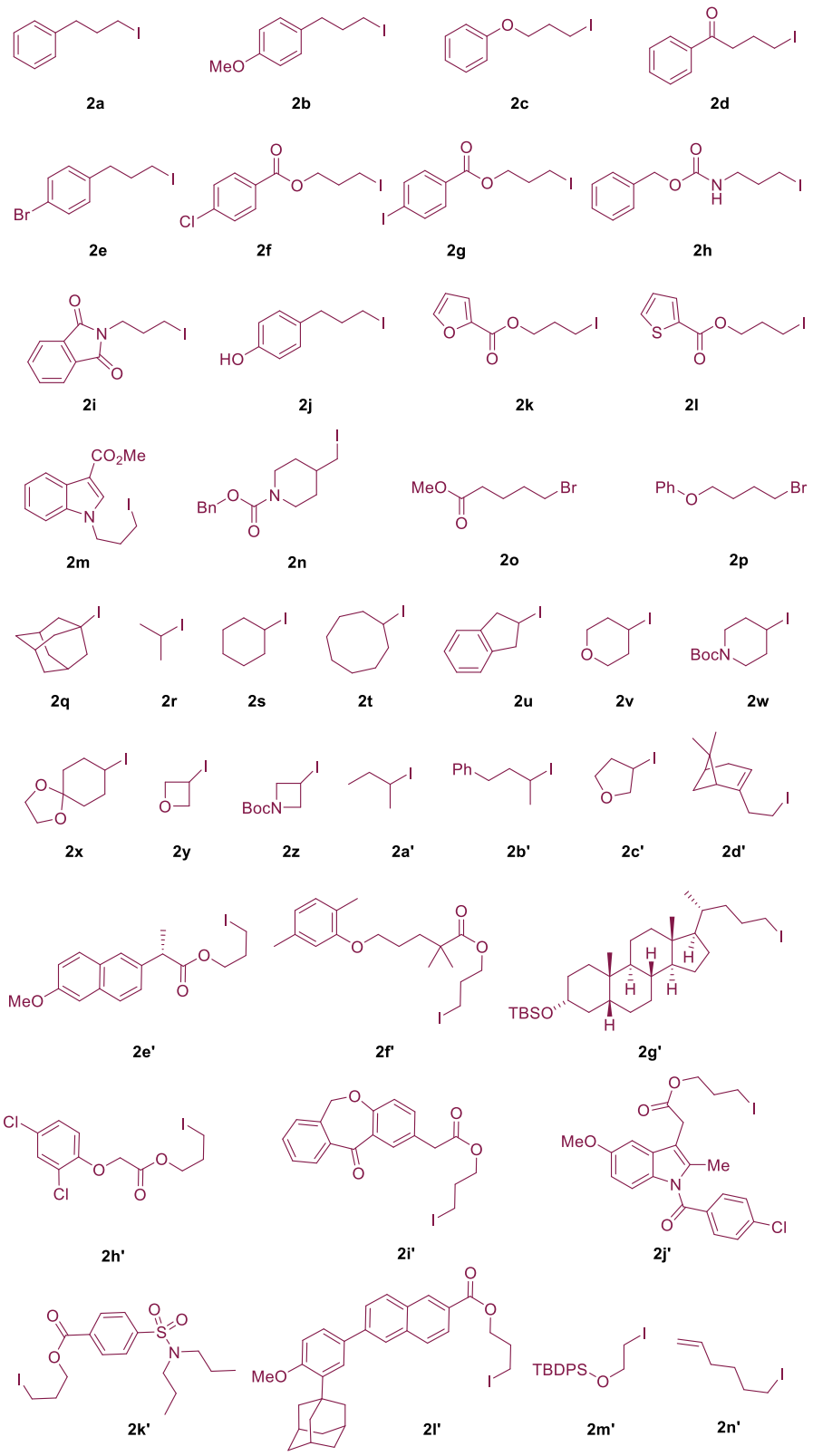
Prepared according to the modified literature procedure from (*E*)-1-bromohex-3-ene.[12] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.49 – 5.37 (m, 2H), 2.12 – 2.07 (m, 2H), 2.01 – 1.93 (m, 2H), 1.23 (s, 12H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*)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

(1s,5s)-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:

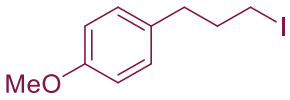


Compound **2a**, **2o**, **2p**, **2q**, **2r**, **2s**, **2v**, **2w**, **2y**, **2z**, **2a'** and **2c'** were purchased from commercial sources. Alkyl halides **2b**[15], **2c**[16], **2d**[17], **2e**[18], **2f**[8], **2h**[19], **2i**[20], **2j**[21], **2k**[8], **2m**[22], **2n**[15], **2t**[23], **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:

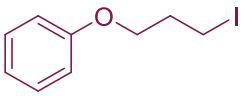
To a stirred solution of carboxylic acid (5.00 mmol, 1.0 equiv.) in dry DCM (15 mL) at 0 °C under a N_2 atmosphere was added *N*,*N*′-diisopropylcarbodiimide (0.86 mL, 5.50 mmol, 1.1 equiv.). After 10 minutes, 3-iodo-1-propanol (0.53 mL, 5.50 mmol, 1.1 equiv.) and Et_3N (0.77 mL, 5.5 mmol 1.1 equiv.) 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):



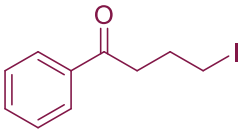
Prepared according to the known literature method.[15] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.18 – 7.06 (m, 2H), 6.90 – 6.80 (m, 2H), 3.80 (s, 3H), 3.17 (t, *J* = 6.8 Hz, 2H), 2.68 (t, *J* = 7.3 Hz, 2H), 2.10 (p, *J* = 6.7 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.15, 132.53, 129.59,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

(3-Iodopropoxy)benzene (2c):



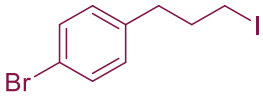
Prepared according to the known literature method.[16] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.26 (m, 2H), 7.01 – 6.89 (m, 3H), 4.05 (t, *J* = 5.8 Hz, 2H), 3.38 (t, *J* = 6.7 Hz, 2H), 2.33 – 2.25 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.78, 129.62, 121.05, 114.67, 67.28, 33.16,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

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



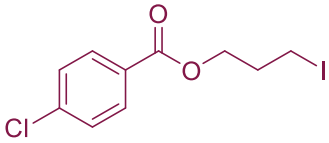
Prepared according to the known literature method.[17] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 2H), 7.65 – 7.54 (m, 1H), 7.53 – 7.42 (m, 2H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.26 (p, *J* = 6.8 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 198.70, 136.84, 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):



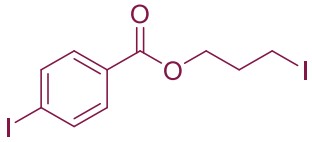
Prepared according to the known literature method.[18] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.48 – 7.36 (m, 1H), 7.13 – 7.01 (m, 1H), 3.15 (t, *J* = 6.7 Hz, 1H), 2.69 (t, *J* = 7.3 Hz, 1H), 2.17 – 2.04 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 139.45, 131.69, 130.44, 120.10, 35.70, 34.69,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

3-Iodopropyl 4-chlorobenzoate (2f):



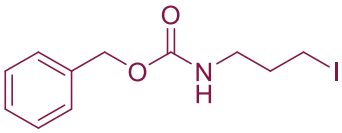
Prepared according to the known literature method.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 4.40 (t, *J* = 6.1 Hz, 2H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.29 (p, *J* = 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 165.58, 139.64, 131.08,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

3-Iodopropyl 4-iodobenzoate (2g):



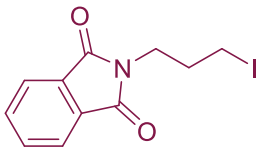
Prepared according to **GP3** with 4-iodobenzoic acid (1.20 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 40:1 hexane:EtOAc) afforded the desired product **2g** as a white solid (1.37 g, 66%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.84 – 7.75 (m, 2H), 7.77 – 7.68 (m, 2H), 4.39 (t, *J* = 6.1 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.33 – 2.22 (m, 2H). **^{13}C 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 $C_{10}H_{11}I_2O_2^+$ 416.8843; Found 416.8838.

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



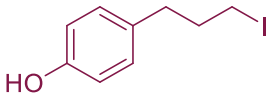
Prepared according to the known literature method.[19] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 5H), 5.10 (s, 2H), 4.92 (s, 1H), 3.29 (q, *J* = 6.4 Hz, 2H), 3.19 (t, *J* = 6.8 Hz, 2H), 2.03 (p, *J* = 6.9 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.53, 136.51, 128.67, 128.31, 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):



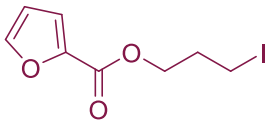
Prepared according to the known literature method.[20] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (ddd, *J* = 7.7, 4.6, 3.0 Hz, 2H), 7.77 – 7.66 (m, 2H), 3.77 (t, *J* = 6.8 Hz, 2H), 3.16 (t, *J* = 7.2 Hz, 2H), 2.24 (p, *J* = 7.0 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.37, 134.19, 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):



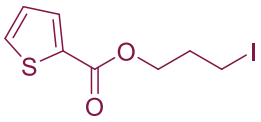
Prepared according to the known literature method.[21] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.16 – 6.98 (m, 2H), 6.87 – 6.66 (m, 2H), 3.16 (t, *J* = 6.8 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.19 – 1.99 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.93, 132.77, 129.81, 115.45, 35.39, 35.18,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

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



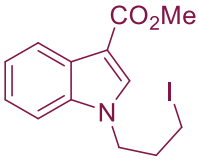
Prepared according to the known literature method.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (s, 1H), 7.19 (d, *J* = 3.5 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.38 (t, *J* = 6.1 Hz, 2H), 3.28 (t, *J* = 6.8 Hz, 2H), 2.27 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.57, 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):



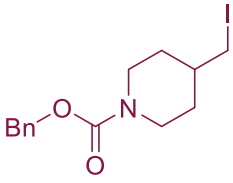
Prepared according to **GP3** with 2-thiophenecarboxylic acid (640 mg, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **2l** as a colorless oil (1.15 g, 78%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.81 (dd, *J* = 3.9, 1.3 Hz, 1H), 7.57 (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). **^{13}C 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 $C_8H_{10}IO_2S^+$ 296.9441; Found 296.9436.

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



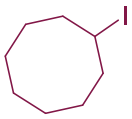
Prepared according to the known literature method.[22] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.23 – 8.06 (m, 1H), 7.83 (s, 1H), 7.42 – 7.34 (m, 1H), 7.32 – 7.22 (m, 2H), 4.25 (t, *J* = 6.5 Hz, 2H), 3.90 (s, 3H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.30 (p, *J* = 6.5 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) 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):



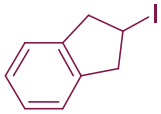
Prepared according to the known literature method.[15] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.41 – 7.28 (m, 5H), 5.13 (s, 2H), 4.21 (s, 2H), 3.10 (d, *J* = 6.5 Hz, 2H), 2.77 (s, 2H), 1.85 (d, *J* = 13.0 Hz, 2H), 1.71 – 1.57 (m, 1H), 1.29 – 1.08 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 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):



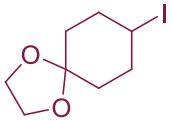
Prepared according to the known literature method.[23] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.60 (ddd, *J* = 13.0, 7.3, 5.7 Hz, 1H), 2.31 – 2.19 (m, 4H), 1.75 – 1.39 (m, 10H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 38.48, 38.07, 27.58, 26.79, 25.28. Spectral data match those previously reported.[23]

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



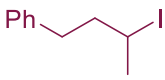
Prepared according to the known literature method.[15] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.14 (m, 4H), 4.71 (p, *J* = 5.7, 5.3 Hz, 1H), 3.52 – 3.46 (m, 2H), 3.44 – 3.35 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 141.56, 127.05, 124.42, 46.69, 23.96. Spectral data match those previously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

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



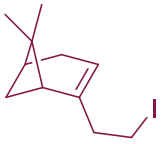
Prepared according to the known literature method.[16] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.45 – 4.39 (m, 1H), 4.01 – 3.88 (m, 4H), 2.19 – 2.04 (m, 4H), 1.84 – 1.78 (m, 2H), 1.64 – 1.57 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 107.60, 64.50, 64.43, 36.38, 34.89. Spectral data match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

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



Prepared according to the known literature method.[24] **^{1}H 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). **^{13}C 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]

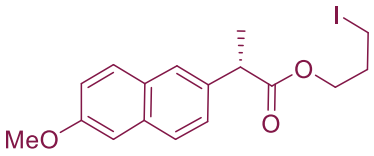
(1*R*,5*S*)-2-(2-Iodoethyl)-6,6-dimethylbicyclo[3.1.1]hept-2-ene (2d'):



Prepared according to the known literature method.[25] **^{1}H 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). **^{13}C NMR** (101 MHz,

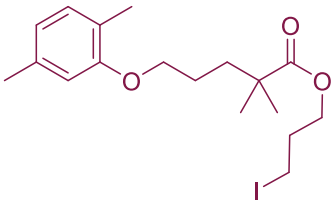
Chloroform-*d*) δ 146.89, 118.85, 45.48, 41.61, 40.83, 38.28, 31.90, 31.44, 26.41, 21.52, 3.83. Spectral data match those previously reported.[26]

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



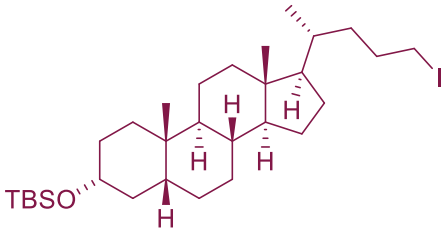
Prepared according to **GP3** with naproxen (1.15 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **2e'** as a white solid (1.39 g, 70%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.76 – 7.67 (m, 2H), 7.66 (d, *J* = 2.0 Hz, 1H), 7.39 (dd, *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). **^{13}C 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 $C_{17}H_{19}INaO_3^+$ 421.0271; Found 421.0277.

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



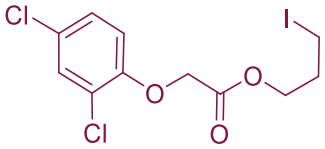
Prepared according to **GP3** with gemfibrozil (1.25 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **2f'** as a colorless oil (1.13 g, 54%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.01 (d, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 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). **^{13}C 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 $C_{18}H_{28}IO_3^+$ 419.1078; Found 419.1082.

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



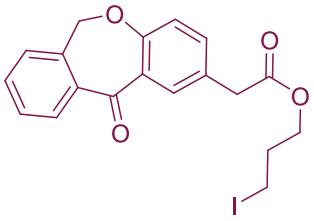
Prepared according to the known literature method.[8] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 3.57 (td, *J* = 10.5, 4.9 Hz, 1H), 3.15 (dt, *J* = 16.2, 7.7 Hz, 2H), 1.95 – 1.70 (m, 7H), 1.59 – 1.51 (m, 2H), 1.49 – 1.30 (m, 9H), 1.27 – 1.17 (m, 3H), 1.16 – 1.00 (m, 6H), 0.92 – 0.87 (m, 16H), 0.63 (s, 3H), 0.05 (s, 6H). **^{13}C 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'):



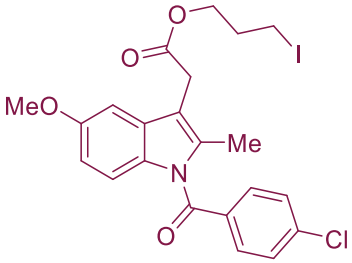
Prepared according to **GP3** with 2,4-dichlorophenoxyacetic acid (1.10 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **2h'** as a white solid (1.27 g, 65%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.40 (d, *J* = 2.5 Hz, 1H), 7.18 (dd, *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). **^{13}C 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 $C_{11}H_{11}Cl_2INaO_3^+$ 410.9022; Found 410.9020.

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



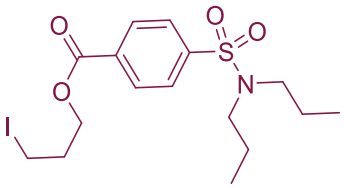
Prepared according to **GP3** with isoxepac (1.34 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2i'** as a white solid (1.32 g, 61%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.12 (d, *J* = 2.3 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.6 Hz, 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). **^{13}C 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 $C_{19}H_{18}IO_4^+$ 437.0244; Found 437.0248.

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



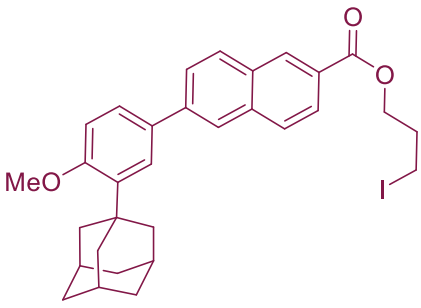
Prepared according to **GP3** with indomethacin (1.78 g, 5.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **2j'** as a white solid (1.29 g, 49%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.55 – 7.40 (m, 2H), 6.95 (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). **^{13}C 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 $C_{22}H_{22}ClINO_4^+$ 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 (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **2k'** as a white solid (930 g, 68%). **^{1}H 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). **^{13}C 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 $C_{16}H_{25}INO_4S^+$ 454.0544; Found 454.0553.

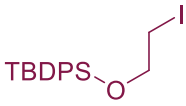
3-Iodopropyl 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (2l'):



Prepared according to **GP3** with adapalene (412 mg, 1.00 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **2l'** as a white solid (398 mg, 69%). **^{1}H 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). **^{13}C 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'):

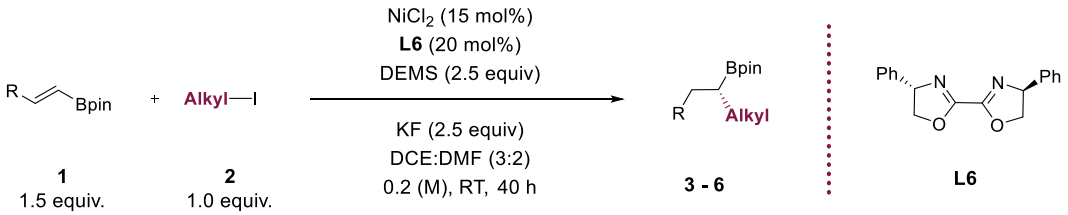


Prepared according to the known literature method.[27] **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.74 – 7.67 (m, 4H), 7.52 – 7.37 (m, 6H), 3.89 (t, *J* = 6.8 Hz, 2H), 3.24 (t, *J* = 6.8 Hz, 2H), 1.10 (s, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 135.70, 133.43, 129.96, 127.90, 64.76, 26.94, 19.40,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

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

Prepared according to the known literature method.[15] **^{1}H 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(sp^3)–C(sp^3) cross-coupling of non-activated alkyl electrophiles:

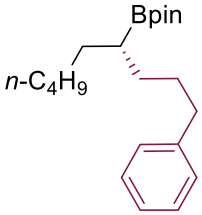


To an oven-dried 10 mL Teflon-screw capped test tube were added $NiCl_2$ (1.9 mg, 15 µmol, 0.15 equiv.) and **L6** (5.8 mg, 0.02 mmol, 0.20 equiv.). The vial was introduced in a nitrogen-filled glovebox. A magnetic stir bar (6x15 mm), anhydrous DCE (0.30 mL) and DMF (0.20 mL) were added, and the mixture 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.

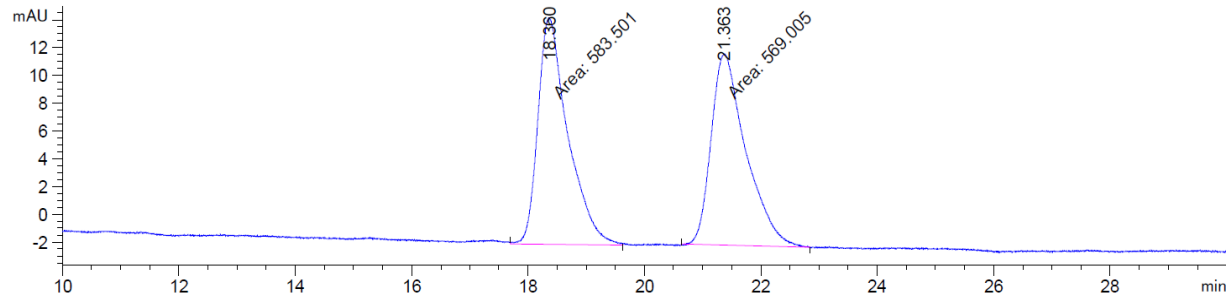
Adding all the reagents together after the catalyst formation (40 minutes later) without a waiting period resulted in 66% yield and 91% e.e. of the desired product **3a**. When the sequence of addition was changed, the product still can be obtained in 66% yield and 91% e.e.. However, when the base was added together with $NiCl_2$ 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)

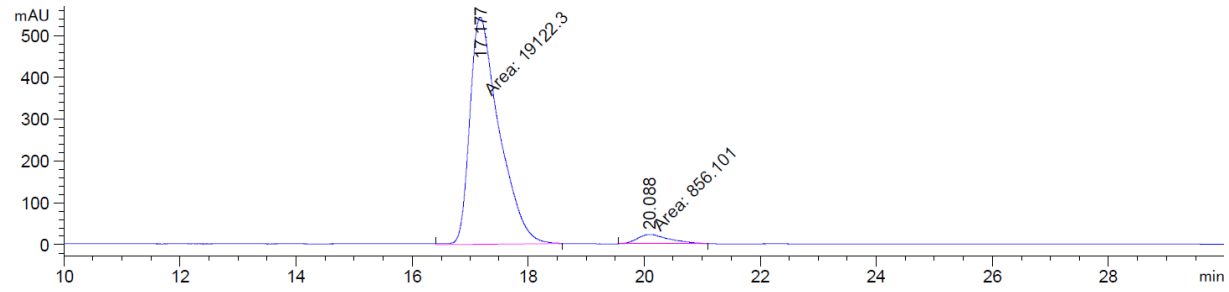


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2a** (25.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **(+) 3a** as a colorless oil (23 mg, 69%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.31 – 7.27 (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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.23. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{21}H_{35}BNaO_2^+$ 353.2622, Found 353.2623. $[\alpha]_D^{20}$ = +5.3 (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 210 nm wavelength. Elution time: t_{major} = 17.2 min and t_{minor} = 20.1 min.

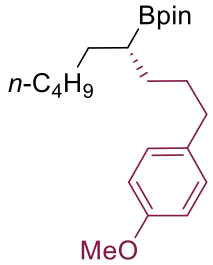


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.360	MM	0.5962	583.50098	16.31192	50.6289
2	21.363	MM	0.6897	569.00507	13.74922	49.3711



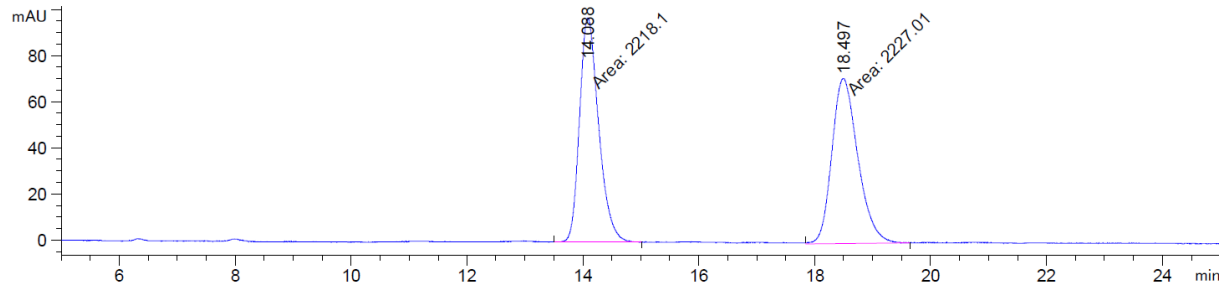
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.177	MM	0.5871	1.91223e4	542.83295	95.7149
2	20.088	MM	0.6429	856.10077	22.19448	4.2851

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

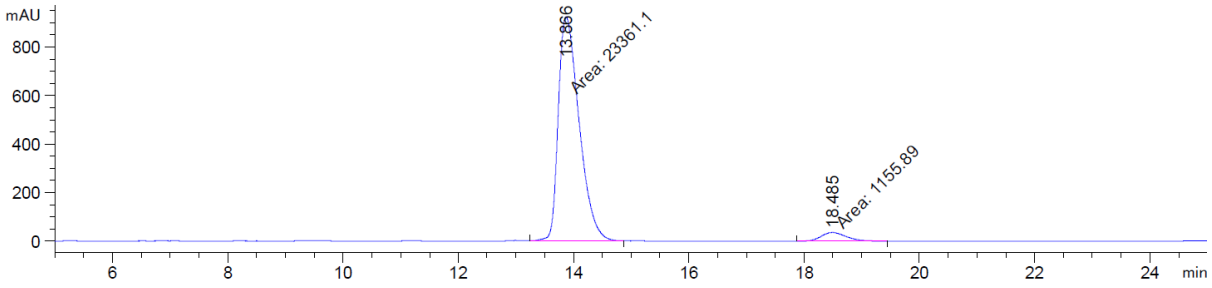


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 3b** as a colorless oil (29 mg, 80%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.13 – 7.01 (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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.00. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{22}H_{37}BNaO_3^+$ 383.2728, Found 383.2731. $[\alpha]_D^{20}$ = +5.0 (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 = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 13.8 min and t_{minor} = 18.5 min.

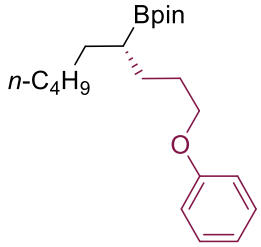


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.088	MM	0.3810	2218.09961	97.03416	49.8998
2	18.497	MM	0.5196	2227.00757	71.42858	50.1002



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.866	MM	0.4205	2.33611e4	926.03101	95.2854
2	18.485	MM	0.5277	1155.88586	36.51034	4.7146

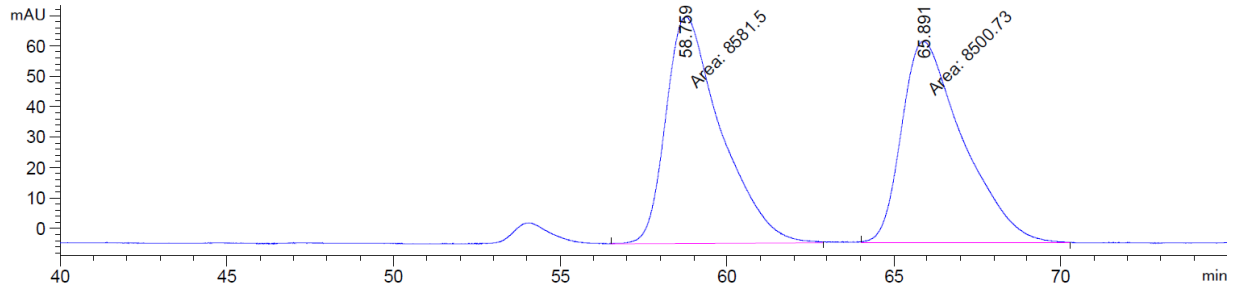
(S)-4,4,5,5-Tetramethyl-2-(1-phenoxynonan-4-yl)-1,3,2-dioxaborolane ((+) 3c)



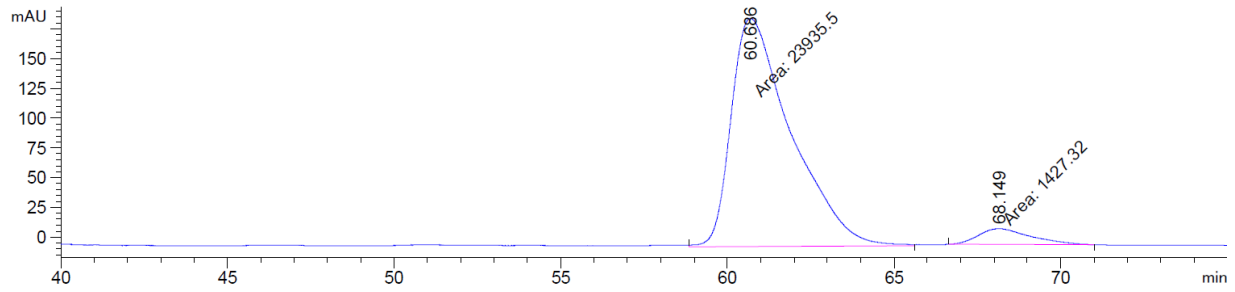
Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2c** (28.0 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **(+) 3c** as a colorless oil (25 mg, 72%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.32 – 7.27 (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.

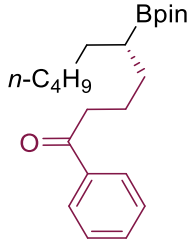


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	58.759	MM	1.9174	8581.50391	74.59299	50.2364
2	65.891	MM	2.1365	8500.73047	66.31226	49.7636



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	60.686	MM	2.0817	2.39355e4	191.63322	94.3724
2	68.149	MM	1.8154	1427.31873	13.10391	5.6276

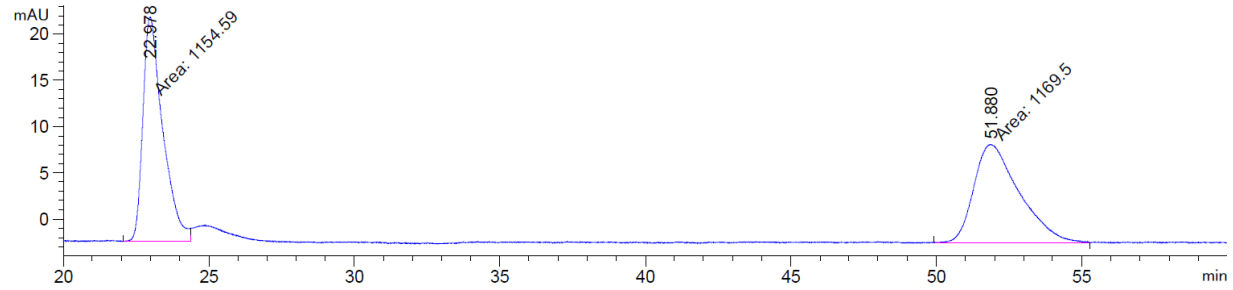
(*S*)-1-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one ((+) 3d)



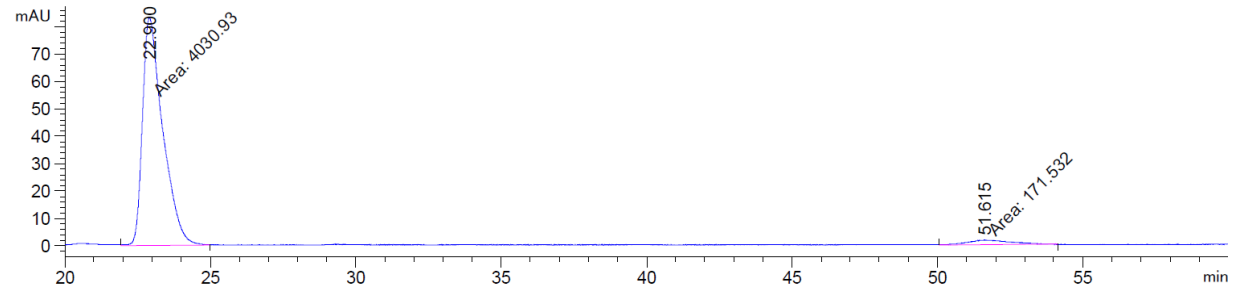
Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2d** (27.4 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 3d** as a colorless oil (24 mg, 67%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.95 (d, *J* = 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.

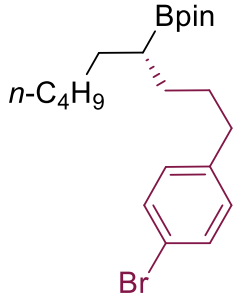


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.978	MF	0.7919	1154.59485	24.30030	49.6794
2	51.880	MM	1.8214	1169.49829	10.70122	50.3206



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.900	MM	0.8079	4030.93286	83.15546	95.9183
2	51.615	MM	1.6755	171.53233	1.70629	4.0817

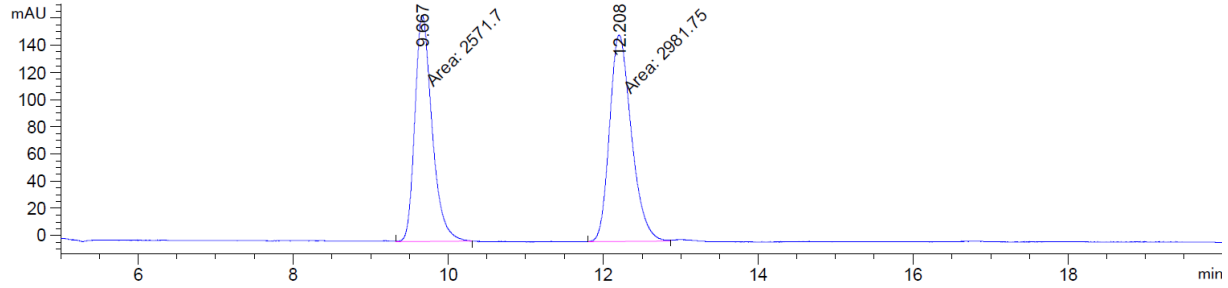
(*S*)-2-(1-(4-Bromophenyl)nonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) 3e)



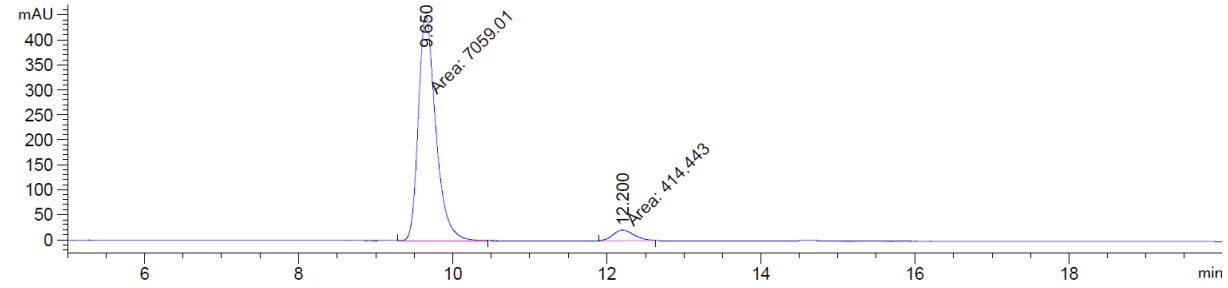
Prepared according to **GP4** with **1a** (25.0 µL, 0.10 mmol, 1.00 equiv.), **2e** (48 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **(+) 3e** as a colorless oil (30 mg, 73%).**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.39 – 7.34 (m, 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.59. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{35}BBrO_2^+$ 409.1908; Found 409.1919. **$[\alpha]_D^{20}$** = +3.0 (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} = 9.6 min and t_{minor} = 12.2 min.



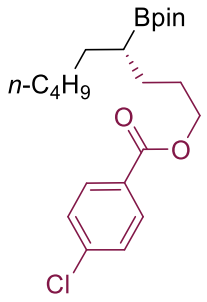
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.667	MM	0.2573	2571.70117	166.60675	46.3082
2	12.208	MM	0.3266	2981.74707	152.13881	53.6918



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.650	MM	0.2617	7059.00879	449.47610	94.4545
2	12.200	MM	0.3210	414.44342	21.51644	5.5455

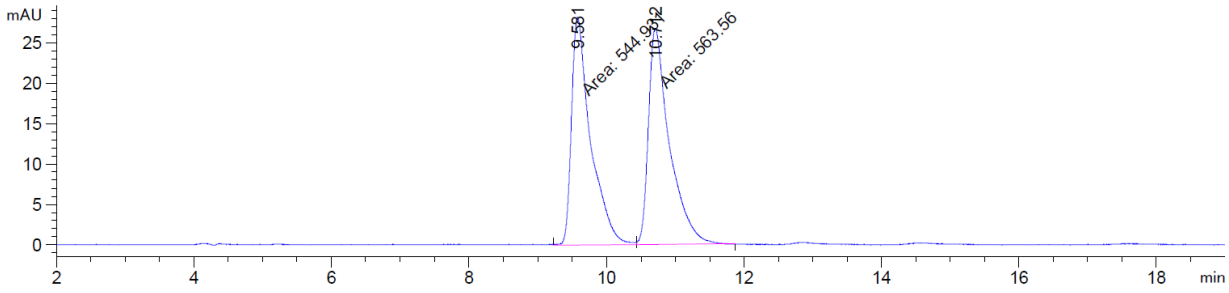
(*S*)-4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 4-chlorobenzoate ((+) 3f)

Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2f** (33 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 25:1 hexane:EtOAc) afforded the desired product

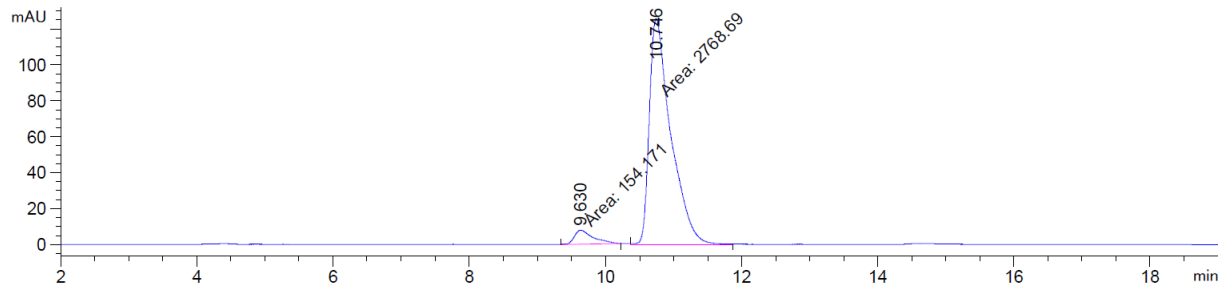


(+) 3f as a colorless oil (26 mg, 64%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.06 – 7.88 (m, 2H), 7.49 – 7.31 (m, 2H), 4.29 (t, *J* = 6.5 Hz, 2H), 1.75 (p, *J* = 7.2, 6.7 Hz, 2H), 1.57 – 1.22 (m, 22H), 1.02 (ddd, *J* = 8.8, 7.2, 4.3 Hz, 1H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.76. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{22}H_{34}BClNaO_4^+$ 431.2131, Found 431.2130. $[\alpha]_D^{20}$ = +1.5 (c = 1.00 in $CHCl_3$).

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.

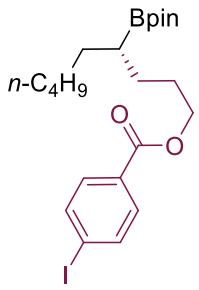


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.581	MF	0.3215	544.93121	28.24557	49.1597
2	10.712	FM	0.3513	563.56030	26.73437	50.8403



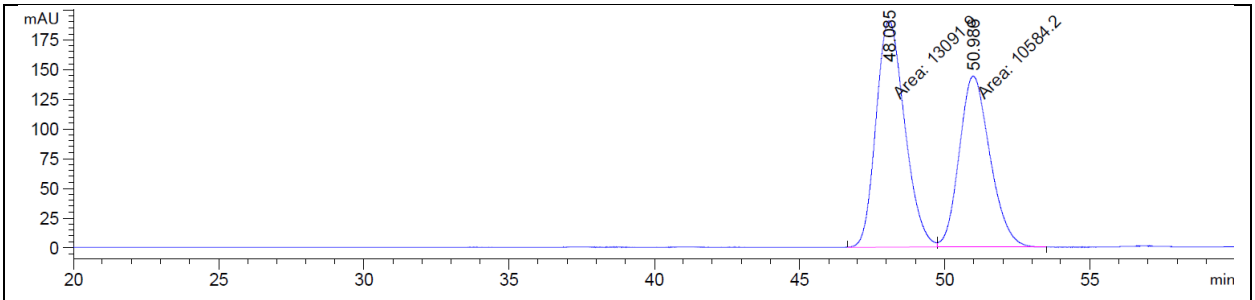
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.630	MM	0.3260	154.17059	7.88233	5.2747
2	10.746	MM	0.3669	2768.68652	125.78008	94.7253

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

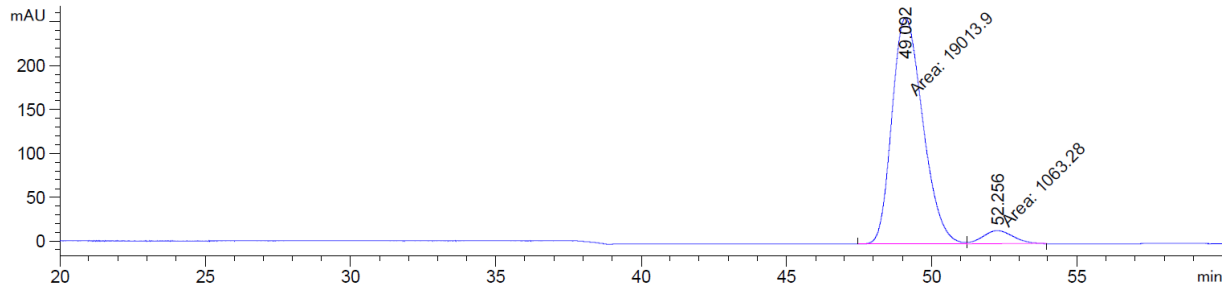


Prepared according to **GP4** with **1a** (25.0 µL, 0.10 mmol, 1.00 equiv.), **2g** (62 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 25:1 hexane:EtOAc) afforded the desired product **(+) 3g** as a colorless oil (23 mg, 46%). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.74 (m, 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: $[M + Na]^+$ Calcd for $C_{22}H_{34}BINaO_4^+$ 523.1487; Found 523.1504. **$[\alpha]_D^{20}$** = +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.

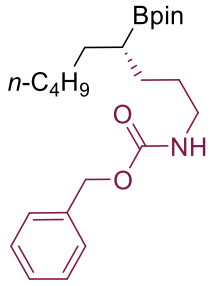


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	48.085	MF	1.1454	1.30919e4	190.49394	55.2957
2	50.986	FM	1.2259	1.05842e4	143.89952	44.7043



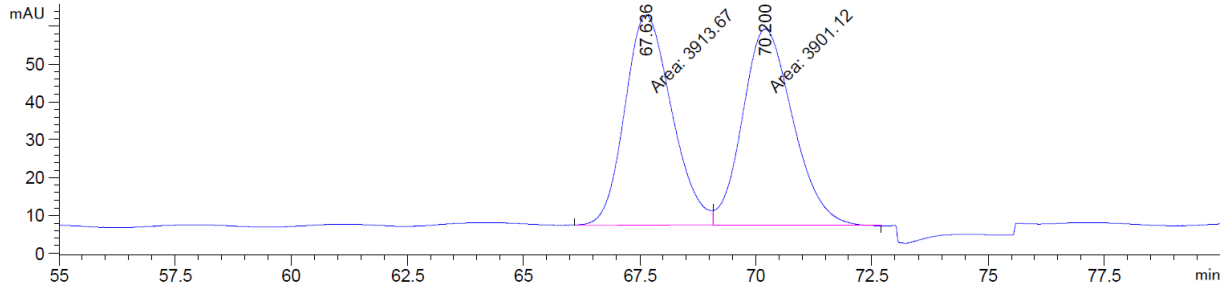
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	49.092	MF	1.2275	1.90139e4	258.17252	94.7040
2	52.256	FM	1.1929	1063.28040	14.85546	5.2960

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

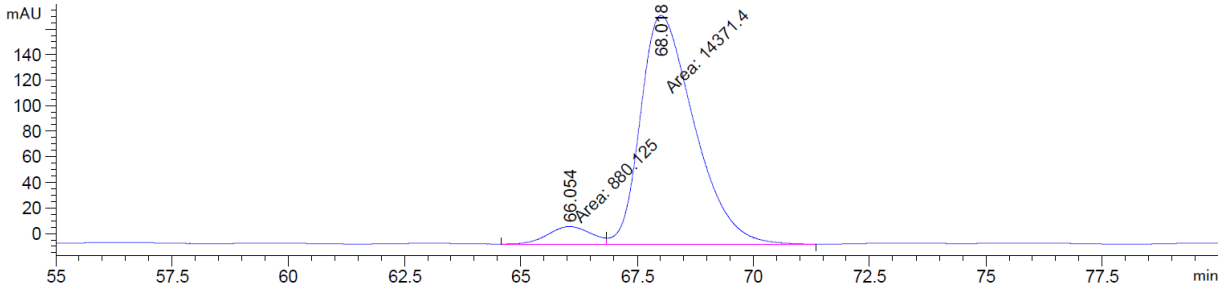


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2h** (32 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **(-) 3h** as a colorless oil (28 mg, 70%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.40 – 7.26 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.46. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{23}H_{38}BNNaO_4^+$ 426.2786; Found 426.2784. **$[\alpha]_D^{20}$** = -1.2 (c = 1.00 in $CHCl_3$).

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.

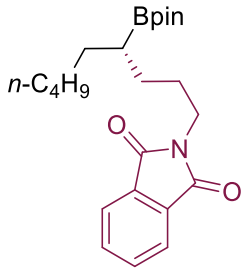


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	67.636	MF	1.1743	3913.66992	55.54537	50.0803
2	70.200	FM	1.2556	3901.11963	51.78297	49.9197



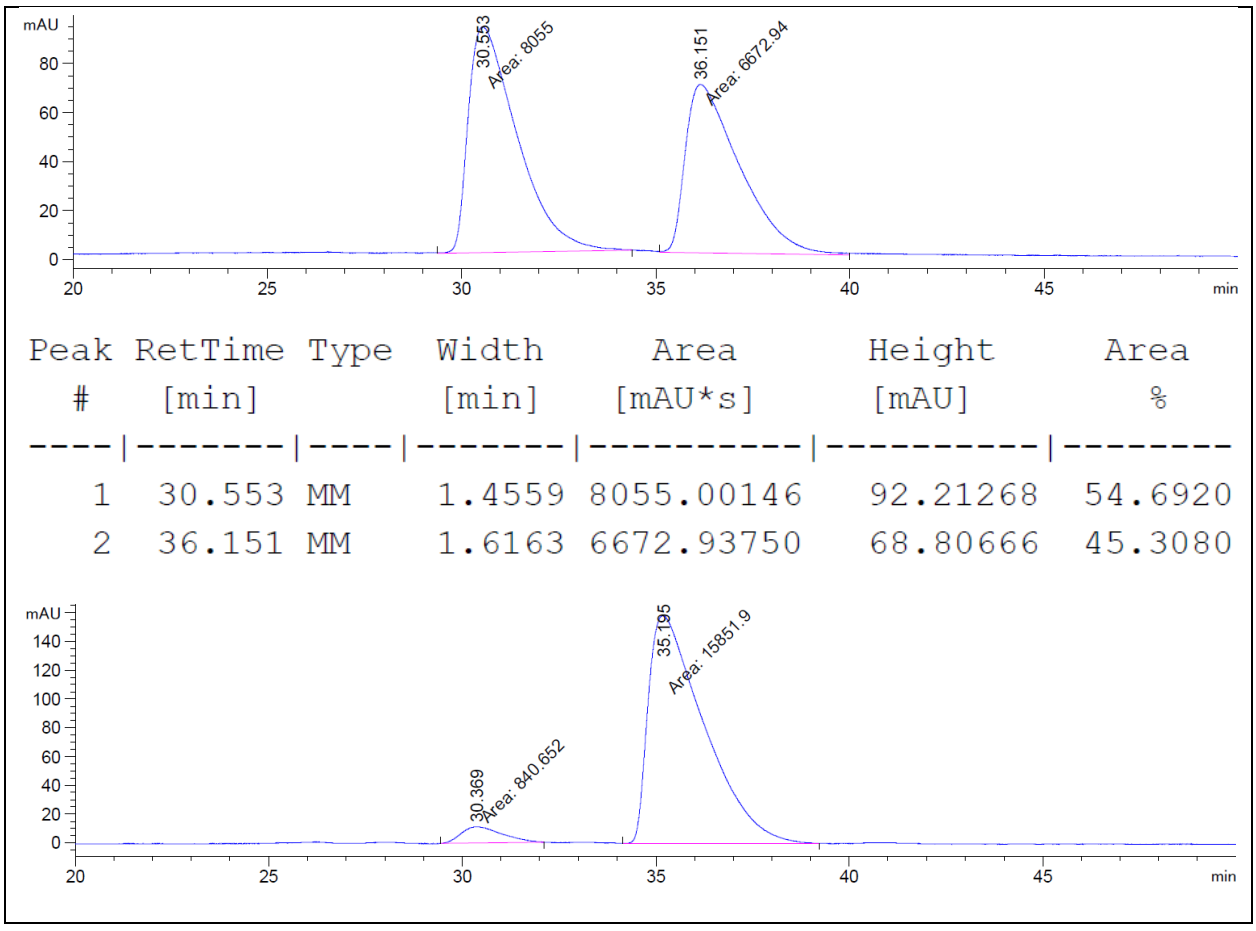
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	66.054	MF	1.0759	880.12518	13.63425	5.7707
2	68.018	FM	1.3375	1.43714e4	179.08083	94.2293

(*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 µL, 0.15 mmol, 1.50 equiv.), **2i** (31.5 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3i** as a colorless oil (30 mg, 75%). **^{1}H 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). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ ^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.88. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{23}H_{34}BNNaO_4^+$ 422.2473, Found 422.2471. **$[\alpha]_D^{20}$** = +3.0 (c = 1.00 in $CHCl_3$).

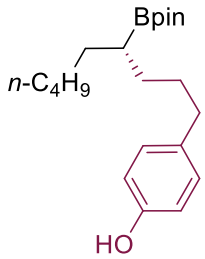
HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALCEL® OD-H column, with hexane:isopropanol = 96:4 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 35.2 min and t_{minor} = 30.4 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.553	MM	1.4559	8055.00146	92.21268	54.6920
2	36.151	MM	1.6163	6672.93750	68.80666	45.3080

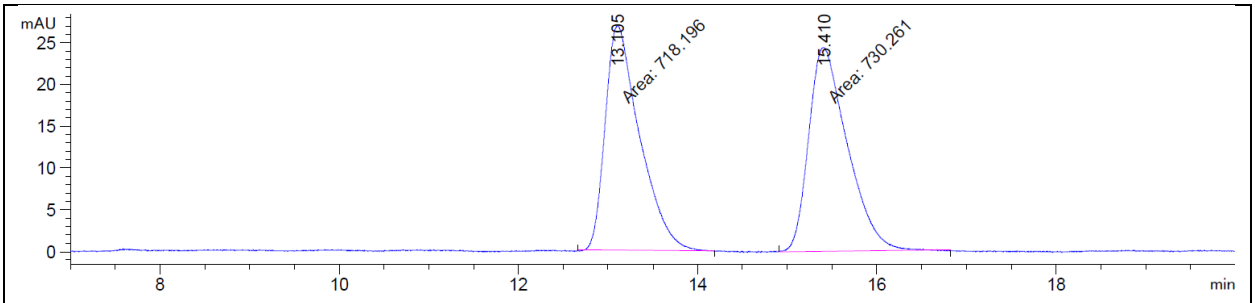
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.369	MM	1.2330	840.65161	11.36321	5.0361
2	35.195	MM	1.6677	1.58519e4	158.42488	94.9639

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

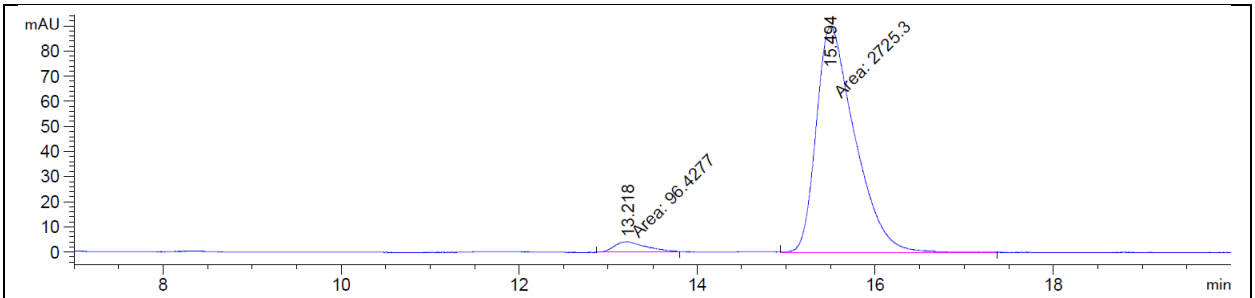


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2j** (26 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(+) 3j** as a colorless oil (19 mg, 55%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.14 – 6.94 (m, 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). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ ^{13}C 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 $C_{21}H_{35}BO_3^+$ 346.2674; Found 346.2674. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 36.02. $[\alpha]_D^{20}$ = +0.3 (c = 1.00 in $CHCl_3$).

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.

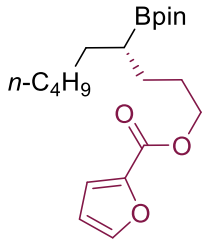


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.105	MM	0.4443	718.19611	26.93867	49.5835
2	15.410	MM	0.4988	730.26135	24.39973	50.4165



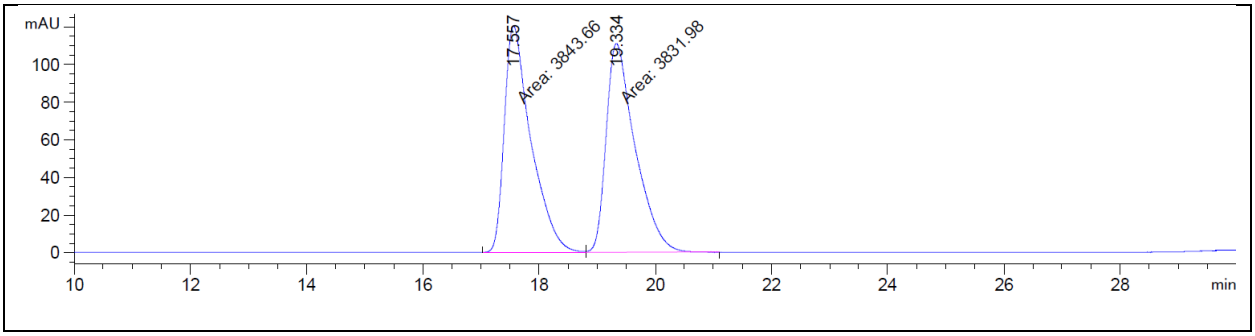
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.218	MM	0.4014	96.42765	4.00350	3.4173
2	15.494	MM	0.5048	2725.30249	89.98342	96.5827

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

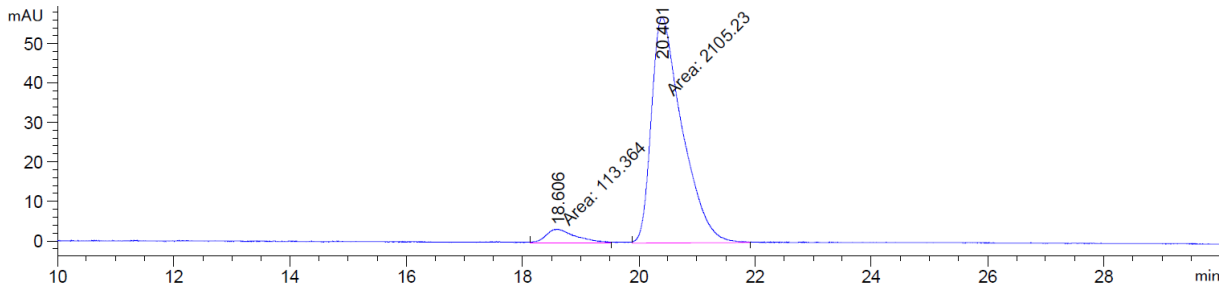


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2k** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(-) 3k** as a colorless oil (26 mg, 71%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.56 (dd, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.39. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{20}H_{33}BNaO_5^+$ 387.2313, Found 387.2313. $[\alpha]_D^{20}$ = -2.3 (c = 1.00 in $CHCl_3$).

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.

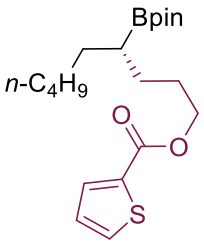


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.557	MF	0.5306	3843.66113	120.73885	50.0761
2	19.334	FM	0.5754	3831.97998	111.00167	49.9239



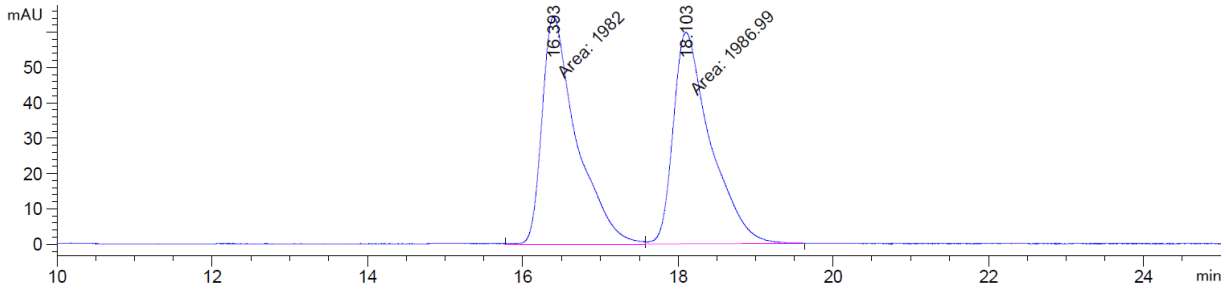
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.606	MM	0.5619	113.36444	3.36265	5.1097
2	20.401	MM	0.6129	2105.23022	57.24960	94.8903

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

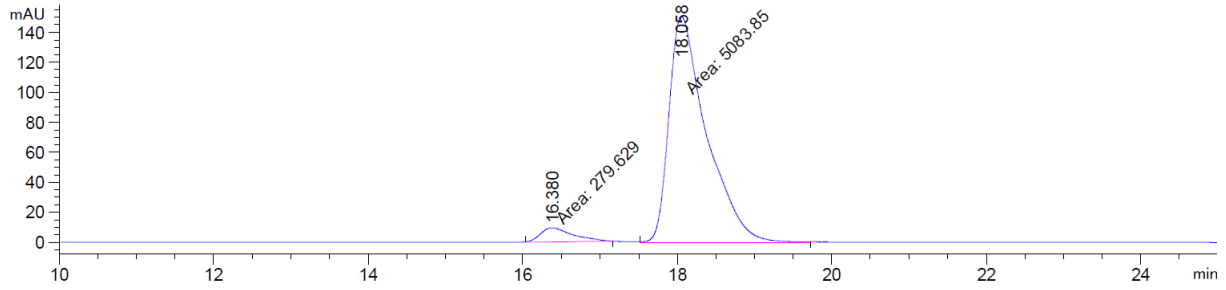


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2l** (30 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(+) 3l** as a colorless oil (23 mg, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.79 (dd, *J* = 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). **^{13}C 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 $C_{20}H_{33}BNaO_4S^+$ 403.2085; Found 403.2080. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.35. $[\alpha]_D^{20}$ = +1.3 (c = 1.00 in $CHCl_3$).

HPLC: The enantiomeric excess (90%) was determined after oxidation (**GP2**) via HPLC analysis using a 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.

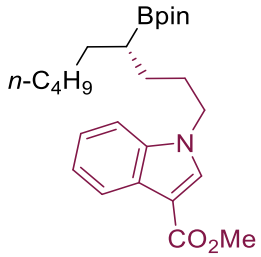


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.393	MF	0.5131	1981.99866	64.37580	49.9371
2	18.103	FM	0.5535	1986.99487	59.83447	50.0629



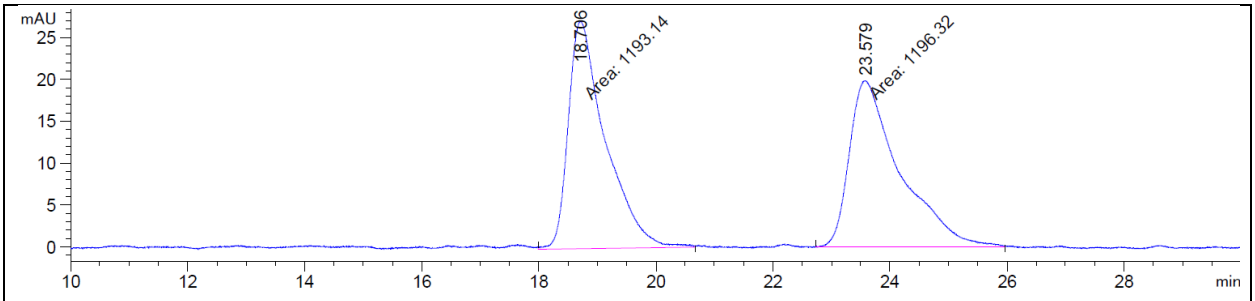
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.380	MM	0.4906	279.62924	9.50039	5.2136
2	18.058	MM	0.5616	5083.84961	150.88083	94.7864

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

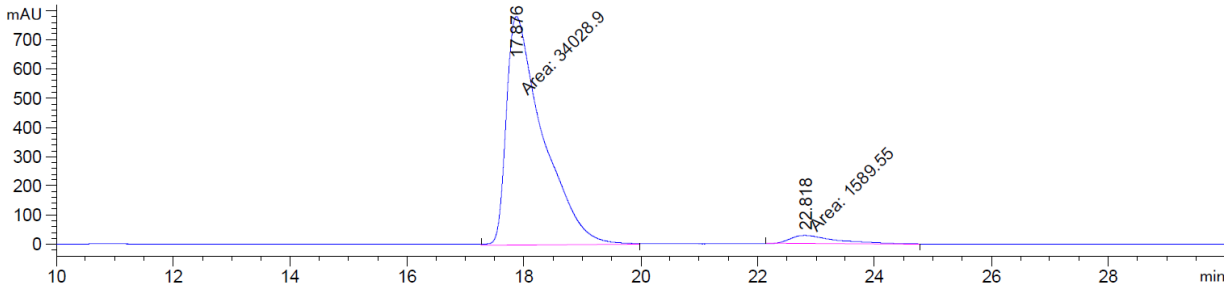


Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2m** (34 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(+) 3m** as a colorless oil (22 mg, 50%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.20 (dd, *J* = 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: $[M + Na]^+$ Calcd for $C_{25}H_{38}BNNaO_4^+$ 450.2786; Found 450.2793. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.39. $[\alpha]_D^{20}$ = +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_{major} = 17.9 min and t_{minor} = 22.8 min.

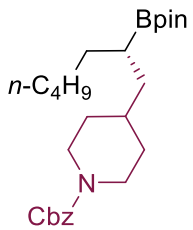


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.721	BB	0.4530	179.95532	4.65531	59.7858
2	23.600	BB	0.4722	121.04473	3.00331	40.2142



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.876	MM	0.7249	3.40289e4	782.33160	95.5373
2	22.818	MM	0.9391	1589.55420	28.21208	4.4627

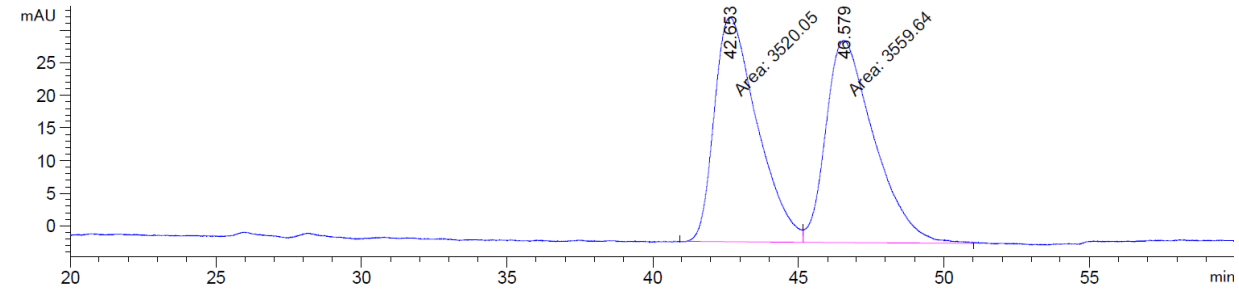
Benzyl (*S*)-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)piperidine-1-carboxylate ((+) 3n)



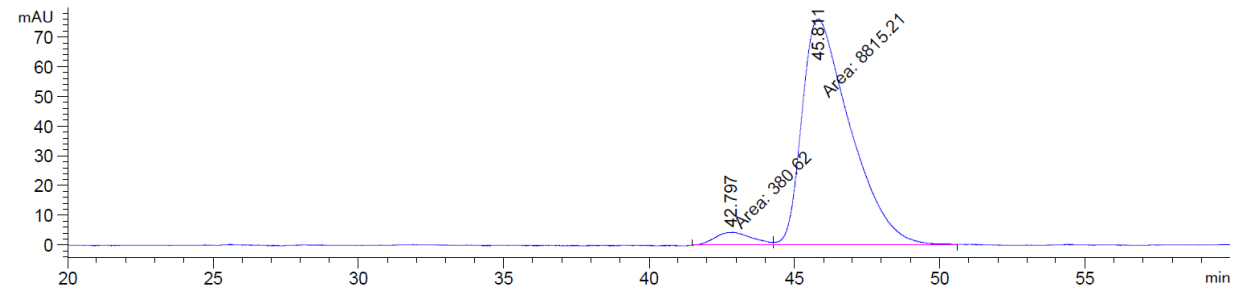
Prepared according to **GP4** with **1a** (38.0 µL, 0.15 mmol, 1.50 equiv.), **2n** (36 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(+) 3n** as a colorless oil (35 mg, 79%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.41 – 7.16 (m, 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: $[M + Na]^+$ 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.

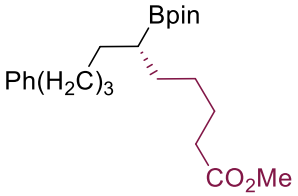


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.653	MF	1.7075	3520.05249	34.35902	49.7204
2	46.579	FM	1.9182	3559.64478	30.92876	50.2796



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.797	MF	1.4807	380.61963	4.28419	4.1390
2	45.811	FM	1.9321	8815.21289	76.04021	95.8610

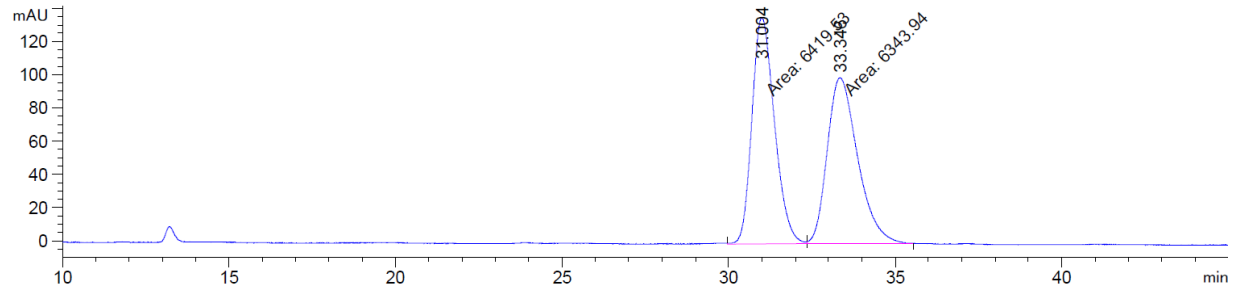
Methyl (*S*)-10-phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decanoate ((-) 3o)



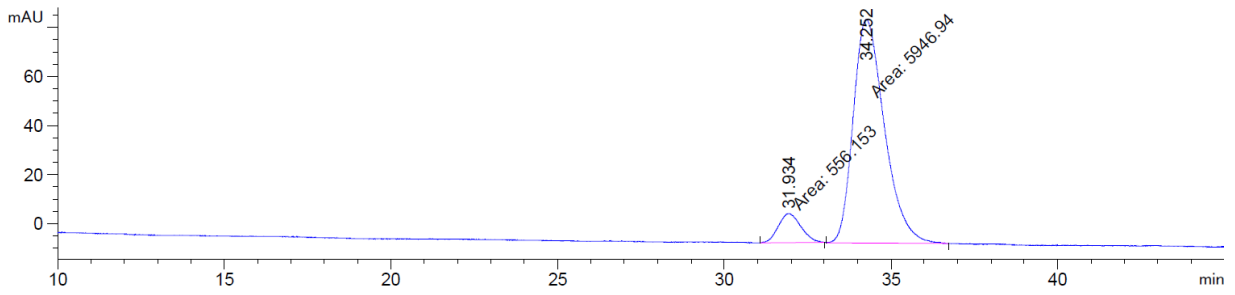
Prepared according to **GP4** with **1b** (54 mg, 0.20 mmol, 1.00 equiv.), **2o** (43 µL, 0.30 mmol, 1.50 equiv.) and KI (13.2 mg, 0.08 mmol, 0.40 equiv.) in 3:2 DCE:DMF (1.0 mL). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(-) 3o** as a colorless oil (42 mg, 54%). **^{1}H 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: $[M + Na]^+$ Calcd for $C_{23}H_{37}BNaO_4^+$ 411.2677; Found 411.2672. $[\alpha]_D^{20}$ = -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_{major} = 34.2 min and t_{minor} = 31.9 min.

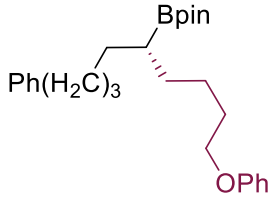


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.004	MF	0.7845	6419.52686	136.39043	50.2961
2	33.346	FM	1.0567	6343.93994	100.06331	49.7039



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.934	MM	0.7808	556.15253	11.87081	8.5521
2	34.252	MM	1.0856	5946.93604	91.30250	91.4479

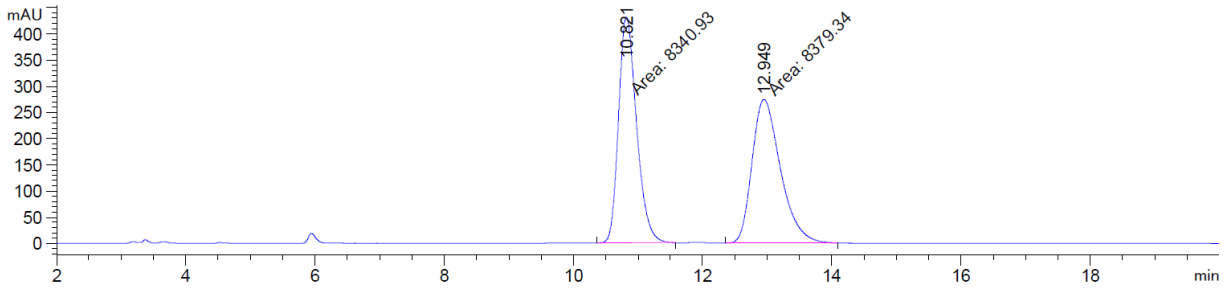
(*S*)-4,4,5,5-Tetramethyl-2-(1-phenoxy-9-phenylnonan-5-yl)-1,3,2-dioxaborolane ((-) 3p)



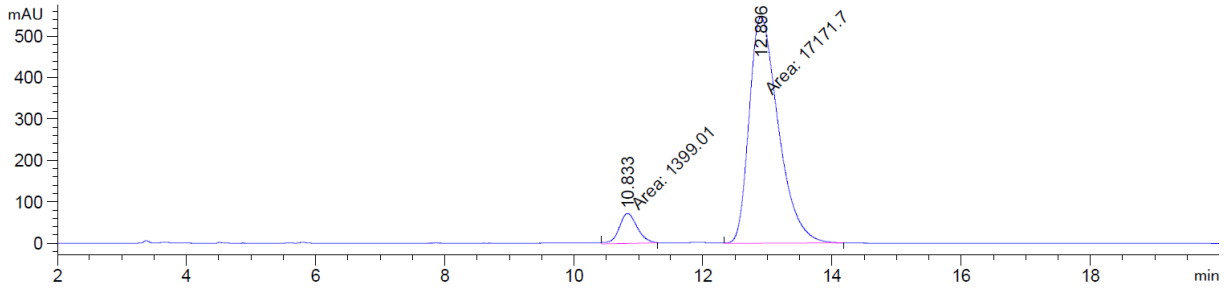
Prepared according to **GP4** with **1b** (54 mg, 0.20 mmol, 1.00 equiv.), **2p** (71 mg, 0.30 mmol, 1.50 equiv.) and KI (13.2 mg, 0.08 mmol, 0.40 equiv.) in 3:2 DCE:DMF (1.0 mL). Flash column chromatography (SiO_2, 40:1 hexane:EtOAc) afforded the desired product **(-) 3p** as a colorless oil (46 mg, 54%). **^{1}H 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: $[M]^+$ Calcd for $C_{27}H_{39}BO_3^+$ 422.2987; Found 422.3004. **$[\alpha]_D^{20}$** = -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_{major} = 12.9 min and t_{minor} = 10.8 min.



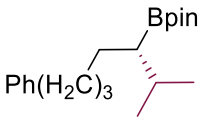
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.821	MM	0.3225	8340.93359	431.01965	49.8851
2	12.949	MM	0.5096	8379.34180	274.06198	50.1149



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.833	MM	0.3230	1399.01270	72.19270	7.5334
2	12.896	MM	0.5227	1.71717e4	547.54865	92.4666

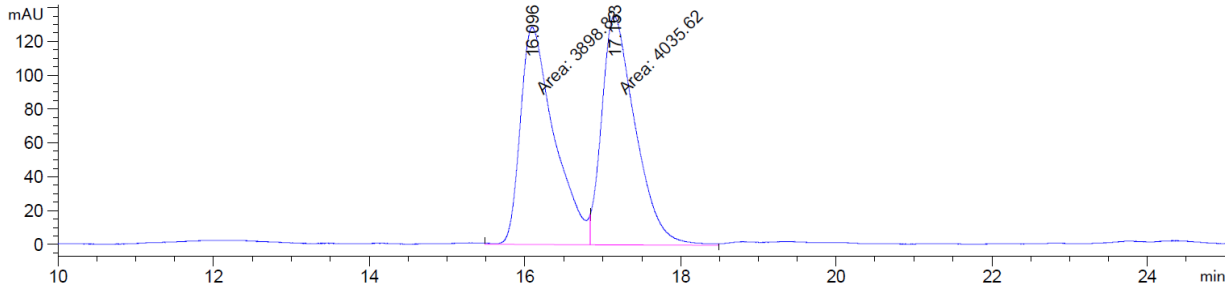
(*S*)-4,4,5,5-Tetramethyl-2-(2-methyl-7-phenylheptan-3-yl)-1,3,2-dioxaborolane ((-) 4a)

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

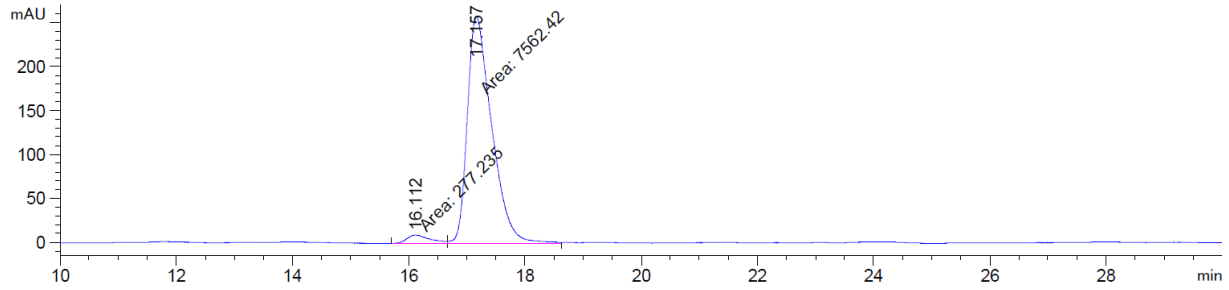


(-) 4a as a colorless oil (22 mg, 70%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.68 (ddd, *J* = 28.7, 14.3, 7.2 Hz, 3H), 1.24 (d, *J* = 4.5 Hz, 16H), 0.94 (2d, 4.7 Hz, 6H), 0.84 (dt, *J* = 11.4, 5.9 Hz, 1H). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.97. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{20}H_{33}BO_2^+$ 316.2568; Found 316.2566. **$[\alpha]_D^{20}$** = -6.0 (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} = 17.2 min and t_{minor} = 16.1 min.



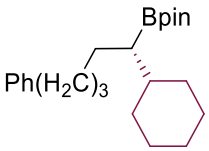
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.096	MF	0.5062	3898.82935	128.35954	49.1380
2	17.153	FM	0.4976	4035.62207	135.15623	50.8620



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.112	MF	0.4814	277.23474	9.59796	3.5363
2	17.157	FM	0.4879	7562.41943	258.33633	96.4637

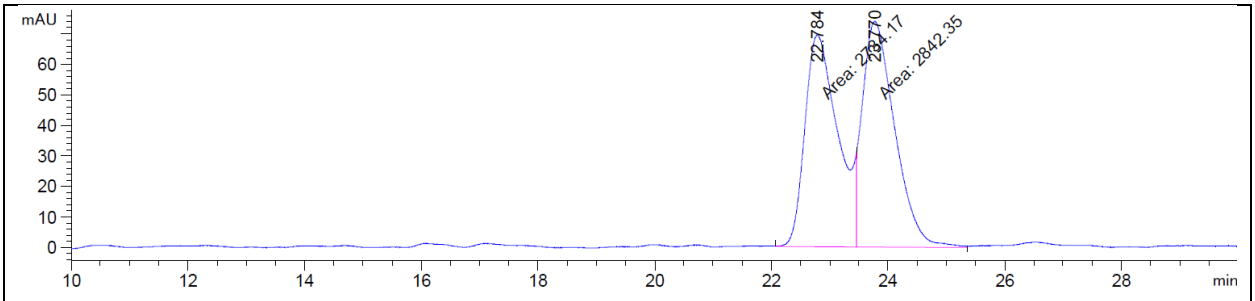
(*S*)-2-(1-Cyclohexyl-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 4b)

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 (SiO_2, 150:1 hexane:EtOAc) afforded the desired product

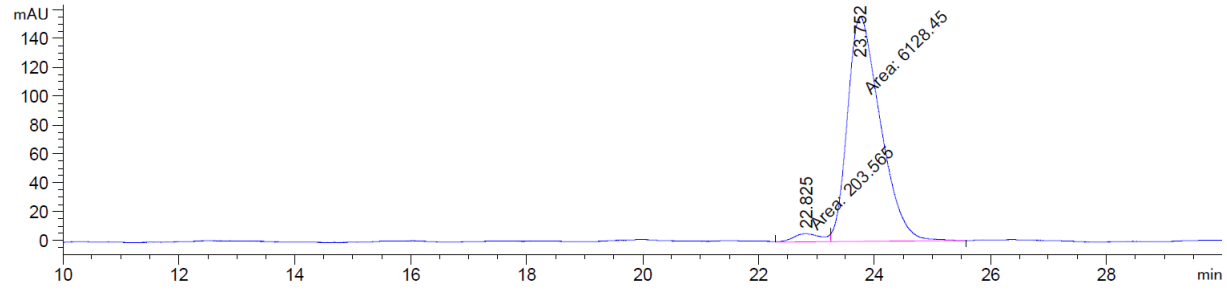


(-) 4b as a colorless oil (24 mg, 67%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 3H), 2.62 (t, *J* = 7.8 Hz, 2H), 1.85 – 1.55 (m, 7H), 1.52 – 1.41 (m, 2H), 1.36 (dq, *J* = 13.4, 6.9, 5.6 Hz, 2H), 1.24 (m, 15H), 1.16 – 0.82 (m, 4H). **^{13}C NMR** (101 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: $[M]^+$ Calcd for $C_{23}H_{37}BO_2^+$ 356.2881; Found 356.2878. $[\alpha]_D^{20}$ = -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.



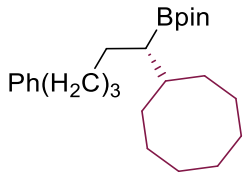
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.784	MF	0.6563	2734.17017	69.43768	49.0301
2	23.770	FM	0.6398	2842.34692	74.04537	50.9699



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.825	MF	0.5901	203.56491	5.74925	3.2149
2	23.752	FM	0.6547	6128.44775	156.02312	96.7851

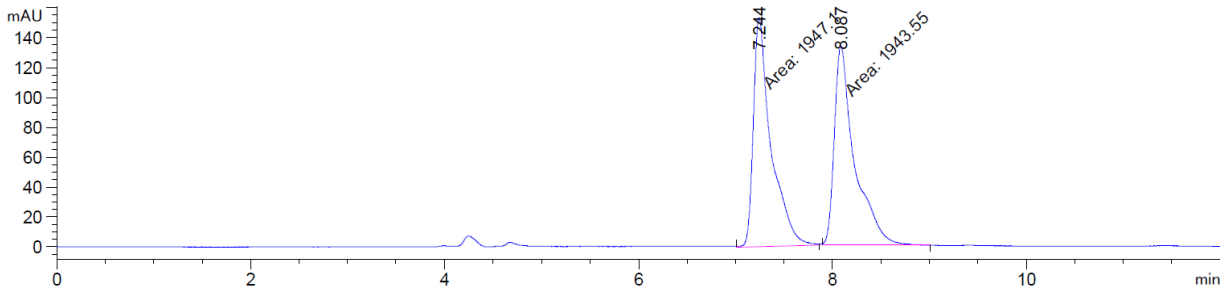
(*S*)-2-(1-Cyclooctyl-5-phenylpentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 4c)

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

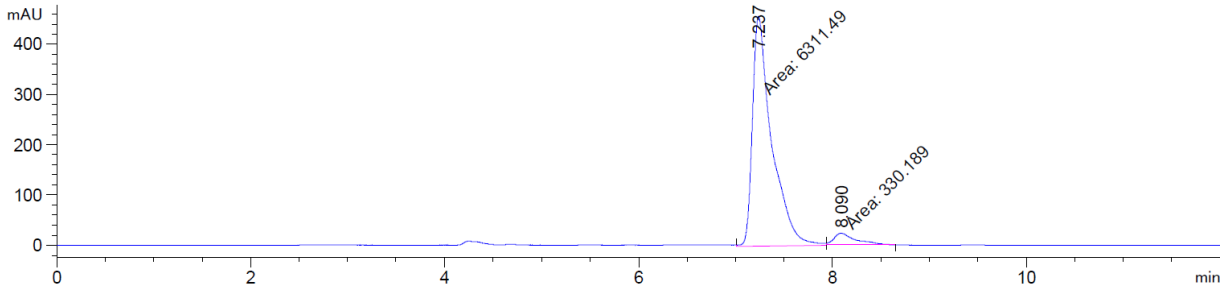


(-) 4c as a colorless oil (30 mg, 78%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.23 – 7.12 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 1.66 – 1.22 (m, 33H), 0.94 – 0.86 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*): δ 143.03, 128.57, 128.30, 125.61, 82.86, 39.22, 36.05, 32.72, 32.59, 31.91, 29.47, 29.26, 27.10, 27.07, 26.70, 26.64, 25.96, 25.07, 24.93. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.82. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{25}H_{41}BO_2^+$ 384.3194; Found 384.3192. $[\alpha]_D^{20}$ = -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.

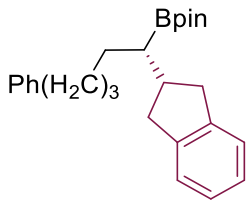


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.244	MM	0.2117	1947.09717	153.30200	50.0456
2	8.087	MM	0.2427	1943.54895	133.48889	49.9544



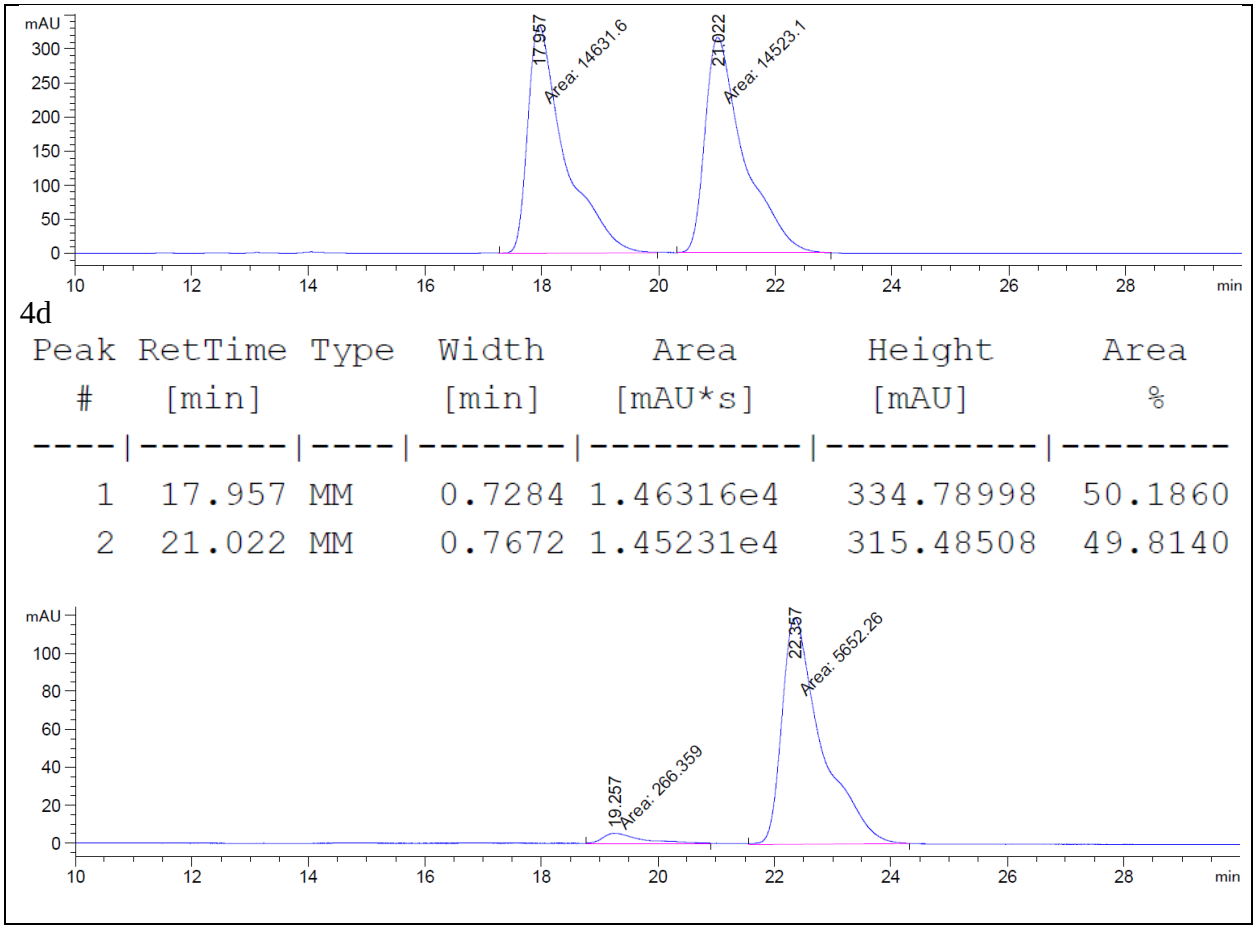
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.237	MM	0.2301	6311.48779	457.16031	95.0285
2	8.090	MM	0.2460	330.18912	22.37132	4.9715

(*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 (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **(-) 4d** as a colorless oil (27 mg, 69%). **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.68. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{26}H_{35}BO_2^+$ 390.2725; Found 390.2724. $[\alpha]_D^{20}$ = -5.8 (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 = 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.

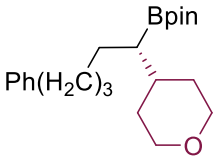


4d

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.957	MM	0.7284	1.46316e4	334.78998	50.1860
2	21.022	MM	0.7672	1.45231e4	315.48508	49.8140

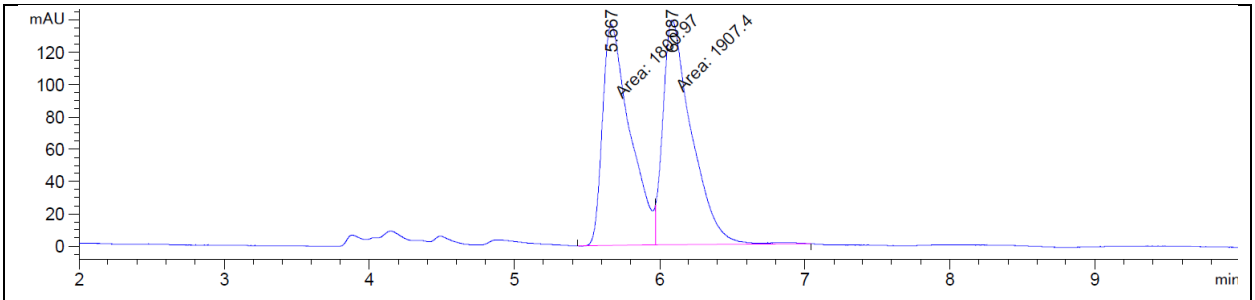
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.257	MM	0.7927	266.35928	5.60041	4.5004
2	22.357	MM	0.7888	5652.26172	119.42857	95.4996

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

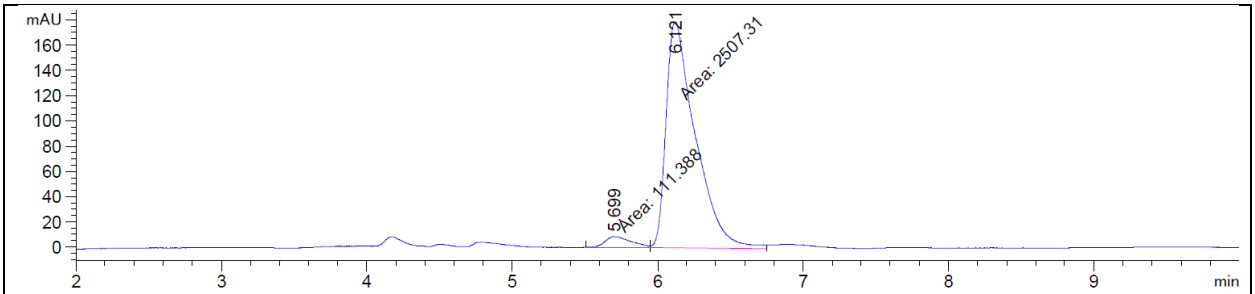


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2v** (18 µL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(-) 4e** as a colorless oil (25 mg, 70%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (dd, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.62. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + H]^+$ Calcd for $C_{22}H_{36}BO_3^+$ 359.2752; Found 359.2753. $[\alpha]_D^{20}$ = -3.5 (c = 1.00 in $CHCl_3$).

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 m/min detected at 210 nm wavelength. Elution time: t_{major} = 6.1 min and t_{minor} = 5.7 min.

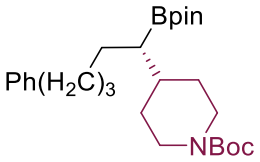


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.667	MF	0.2191	1800.97412	137.01515	48.5651
2	6.087	FM	0.2286	1907.39783	139.03949	51.4349



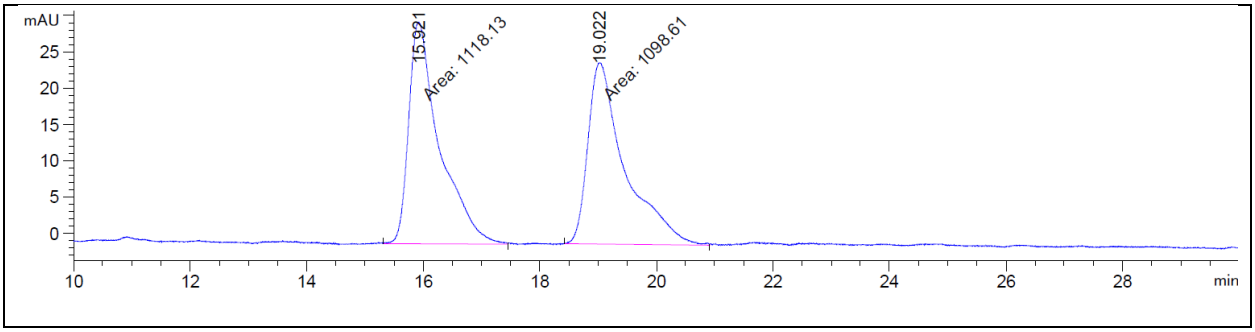
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.699	MF	0.2135	111.38789	8.69651	4.2536
2	6.121	FM	0.2330	2507.30566	179.38290	95.7464

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

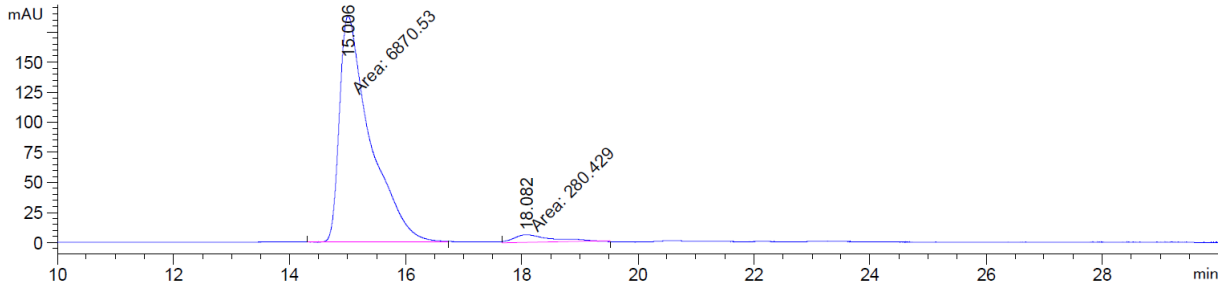


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2w** (47 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(+) 4f** as a colorless oil (28 mg, 61%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.28 (dd, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 36.14. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{27}H_{44}BNNaO_4^+$ 480.3256; Found 480.3263. $[\alpha]_D^{20}$ = +1.0 (c = 1.00 in $CHCl_3$).

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.

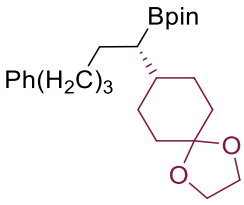


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.921	MM	0.6108	1118.12720	30.50814	50.4403
2	19.022	MM	0.7342	1098.60767	24.94016	49.5597



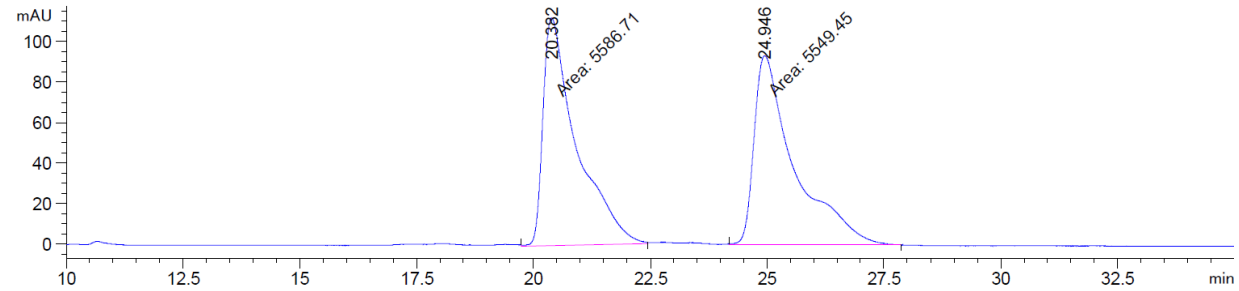
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.006	MM	0.6106	6870.53320	187.52461	96.0784
2	18.082	MM	0.7479	280.42938	6.24909	3.9216

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

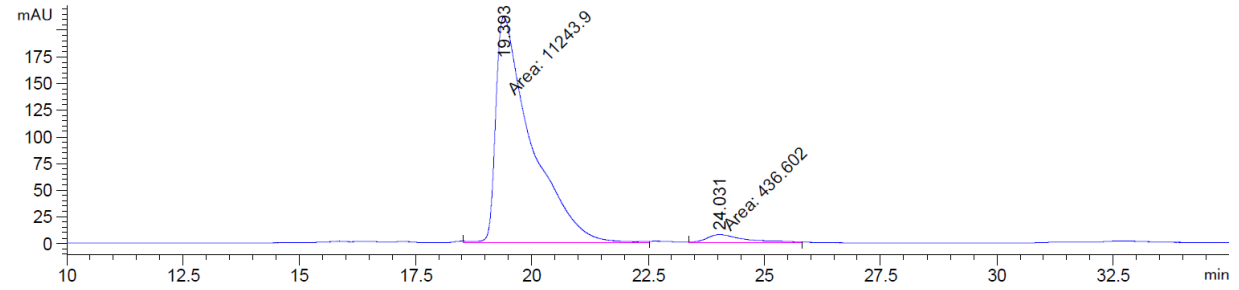


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2x** (40 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(-) 4g** as a colorless oil (26 mg, 63%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.22 (dd, *J* = 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). **^{13}C 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 $C_{25}H_{40}BO_4^+$ 415.3014; Found 415.3016. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.38. **$[\alpha]_D^{20}$** = -2.2 (c = 1.00 in $CHCl_3$).

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.

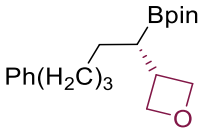


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.382	MM	0.8274	5586.71240	112.53159	50.1673
2	24.946	MM	0.9913	5549.44971	93.29922	49.8327



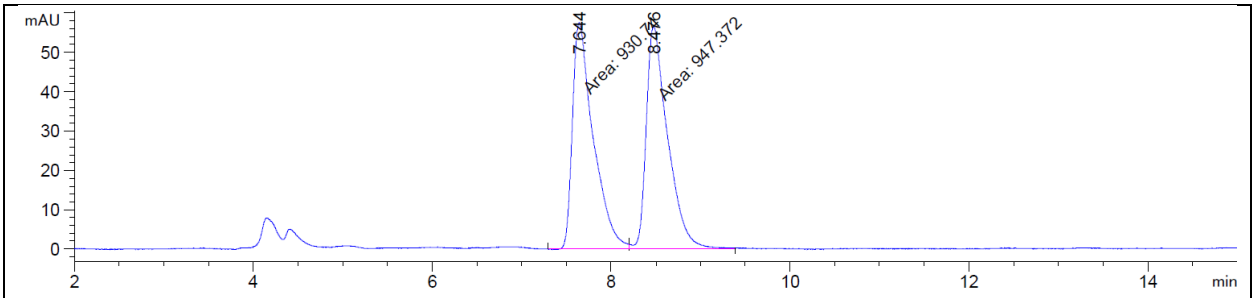
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.393	MM	0.8840	1.12439e4	211.98592	96.2621
2	24.031	MM	0.9660	436.60159	7.53260	3.7379

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

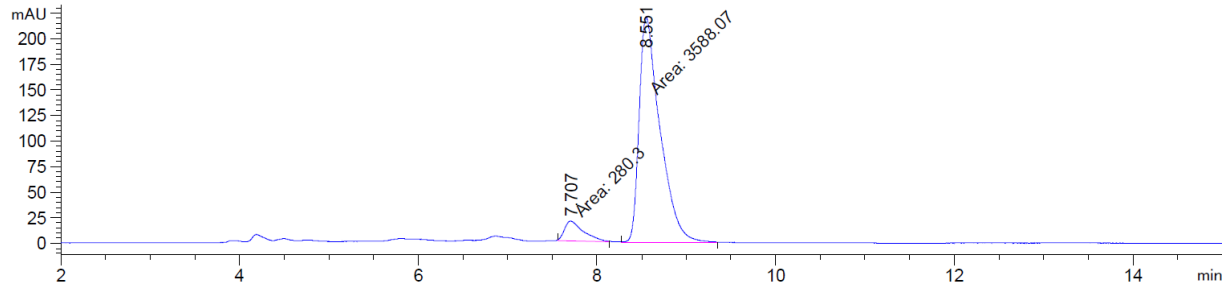


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2y** (13 µL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(-) 4h** as a colorless oil (19 mg, 58%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.34 – 7.15 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.49. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{32}BO_3^+$ 331.2439; Found 331.2438. $[\alpha]_D^{20}$ = -10.8 (c = 1.00 in $CHCl_3$).

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.

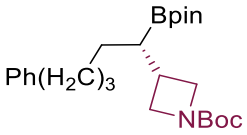


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.644	MF	0.2690	930.73950	57.65742	49.5572
2	8.476	FM	0.2788	947.37195	56.63308	50.4428



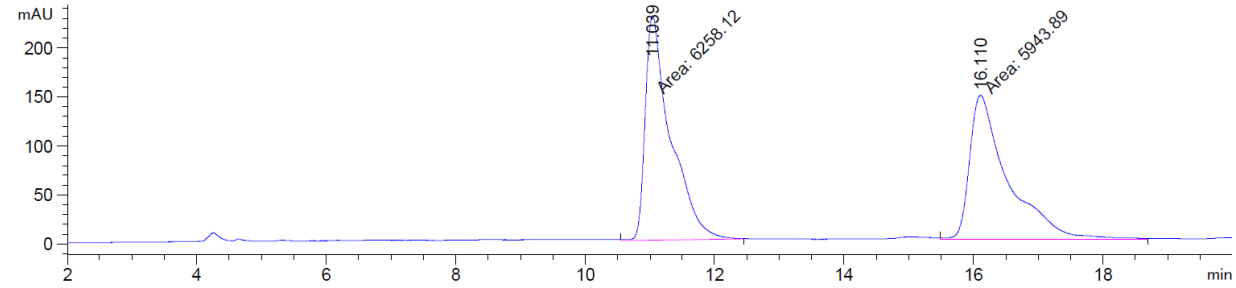
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.707	MM	0.2423	280.30038	19.28118	7.2459
2	8.551	MM	0.2707	3588.07373	220.89662	92.7541

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

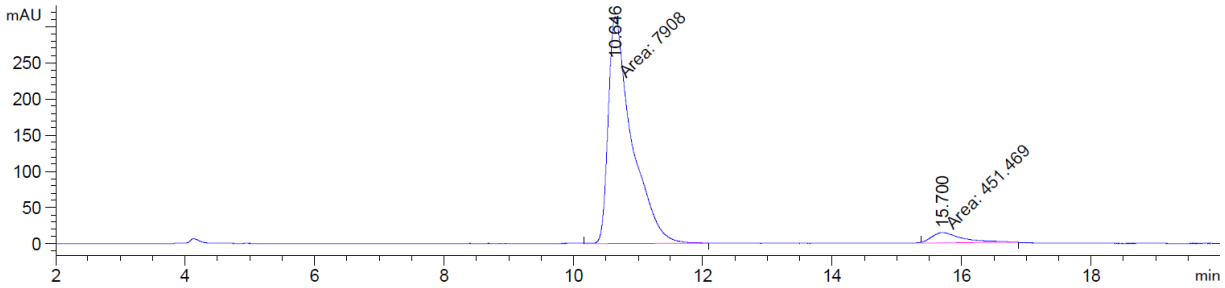


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2z** (28 µL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(-) 4i** as a colorless oil (22 mg, 51%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.30 – 7.15 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.28. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{25}H_{40}BNNaO_4^+$ 452.2943; Found 452.2948. $[\alpha]_D^{20}$ = -4.0 (c = 1.00 in $CHCl_3$).

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_{major} = 10.6 min and t_{minor} = 15.7 min.

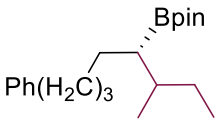


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.039	MM	0.4555	6258.11719	228.96535	51.2876
2	16.110	MM	0.6762	5943.88574	146.50420	48.7124



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.646	MM	0.4201	7907.99756	313.70868	94.5993
2	15.700	MM	0.5381	451.46872	13.98264	5.4007

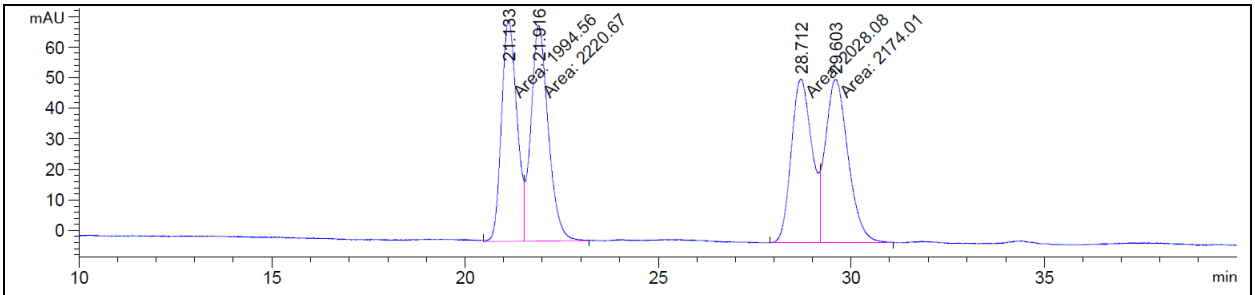
4,4,5,5-Tetramethyl-2-((4S)-3-methyl-8-phenyloctan-4-yl)-1,3,2-dioxaborolane (4j)



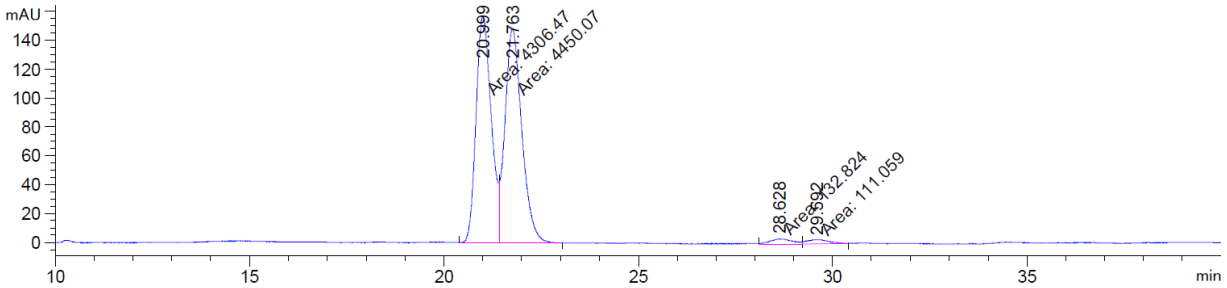
Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2a'** (18 µL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **4j** as an inseparable mixture of diastereomers (dr = 1:1.04) and a colorless oil (23 mg, 70%). The diastereomeric ratio was determined by chiral HPLC. **^{1}H 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). **^{13}C 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. **^{11}B 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.

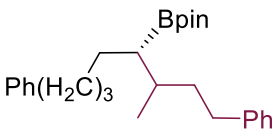


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.133	MF	0.4586	1994.55847	72.48192	23.6959
2	21.916	FM	0.5246	2220.67480	70.55004	26.3822
3	28.712	MF	0.6298	2028.08398	53.66684	24.0942
4	29.603	FM	0.6766	2174.00757	53.55584	25.8278



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.999	MF	0.4575	4306.46680	156.89224	47.8474
2	21.763	FM	0.5005	4450.07471	148.19080	49.4429
3	28.628	MF	0.6340	132.82445	3.49193	1.4758
4	29.592	FM	0.6456	111.05887	2.86715	1.2339

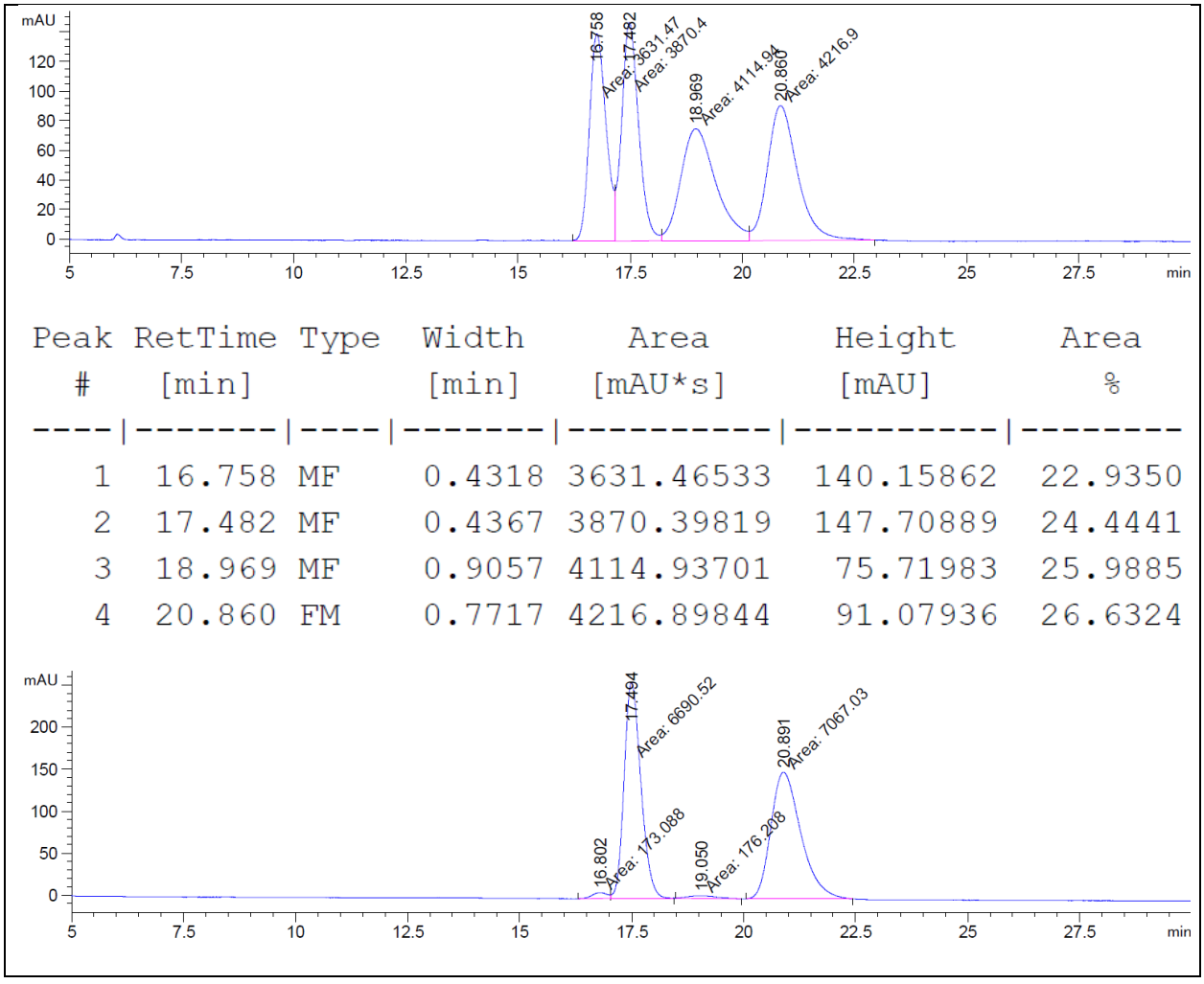
4,4,5,5-Tetramethyl-2-((4S)-3-methyl-1,8-diphenyloctan-4-yl)-1,3,2-dioxaborolane (4k)



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 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. **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.61. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + Na]^+$ Calcd for $C_{27}H_{39}BNaO_2^+$ 429.2935; Found 429.2947.

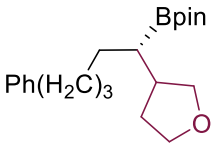
HPLC: The enantiomeric excesses (94% and 94%) were determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: t_{major} = 17.5 min, 20.9 min and t_{minor} = 16.8 min, 19.0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



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.758	MF	0.4318	3631.46533	140.15862	22.9350
2	17.482	MF	0.4367	3870.39819	147.70889	24.4441
3	18.969	MF	0.9057	4114.93701	75.71983	25.9885
4	20.860	FM	0.7717	4216.89844	91.07936	26.6324

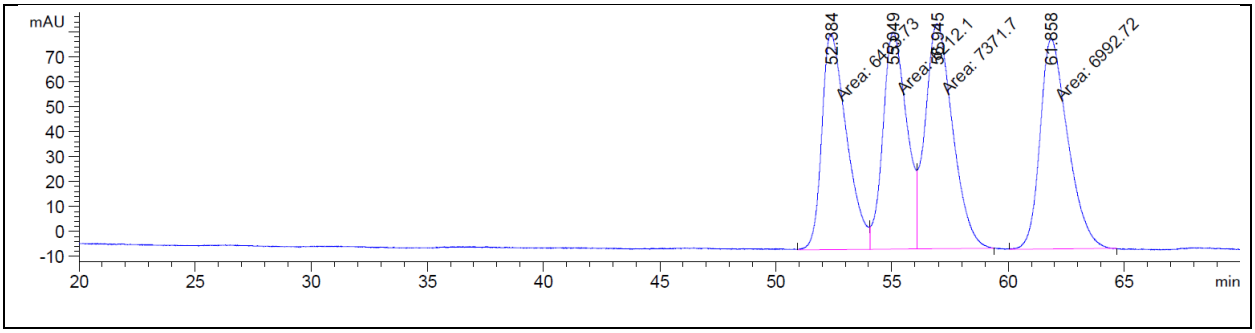
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.802	MF	0.3957	173.08803	7.29061	1.2270
2	17.494	FM	0.4333	6690.52002	257.32394	47.4275
3	19.050	MM	0.7896	176.20824	3.71941	1.2491
4	20.891	MM	0.7801	7067.03076	150.98814	50.0965

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

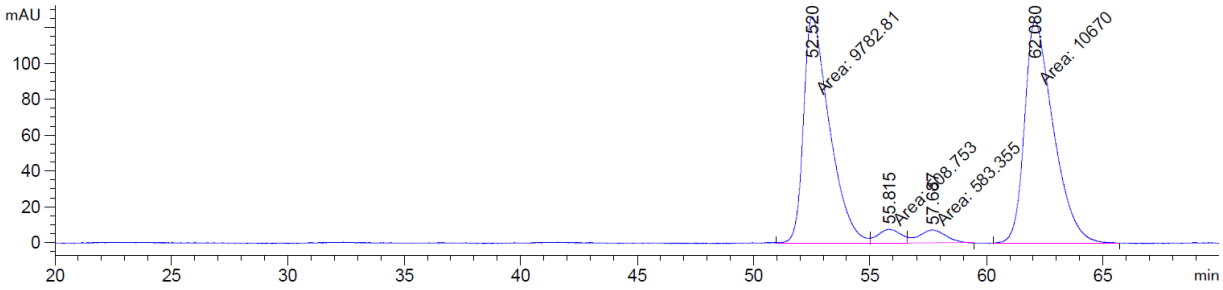


Prepared according to **GP4** with **1b** (27 mg, 0.10 mmol, 1.00 equiv.), **2c'** (30 mg, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded afforded the desired product **4l** as an inseparable mixture of diastereomers (dr = 1:1.1) and a colorless oil colorless oil (26 mg, 75%). The diastereomeric ratio was determined by chiral HPLC. **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 32.74. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{34}BO_3^+$ 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.

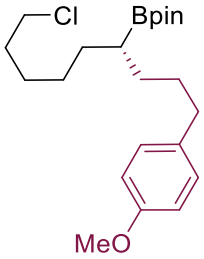


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.384	MF	1.2373	6433.73486	86.66511	23.8196
2	55.049	MF	1.1911	6212.09570	86.92649	22.9990
3	56.945	FM	1.3623	7371.70020	90.18723	27.2922
4	61.858	MM	1.3860	6992.71777	84.08586	25.8891



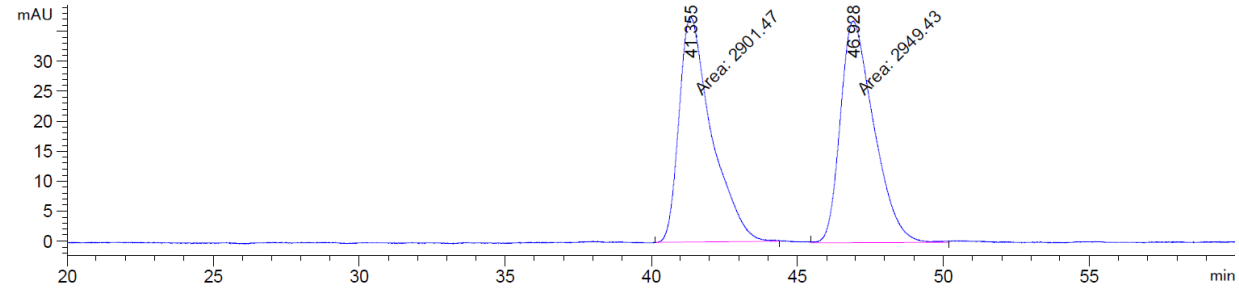
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	52.520	MF	1.2906	9782.80859	126.33604	45.4066
2	55.815	MF	1.1029	508.75348	7.68788	2.3614
3	57.687	FM	1.3363	583.35461	7.27594	2.7076
4	62.080	MM	1.4378	1.06700e4	123.68741	49.5244

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

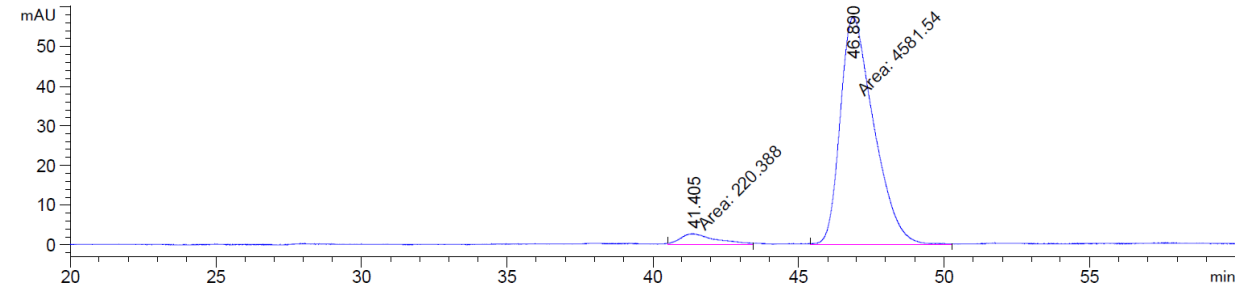


Prepared according to **GP4** with **1c** (37 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 5a** as a colorless oil (24 mg, 61%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.13 – 6.99 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.73. **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{22}H_{36}BClNaO_3^+$ 417.2338; Found 417.2340. **$[\alpha]_D^{20}$** = +1.7 (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_{major} = 46.9 min and t_{minor} = 41.4 min.

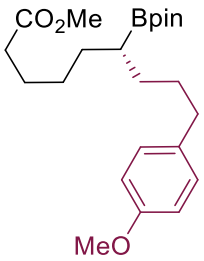


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.355	MM	1.2857	2901.47168	37.61305	49.5901
2	46.928	MM	1.3270	2949.43457	37.04493	50.4099



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.405	MM	1.3927	220.38760	2.63743	4.5896
2	46.890	MM	1.3311	4581.53955	57.36748	95.4104

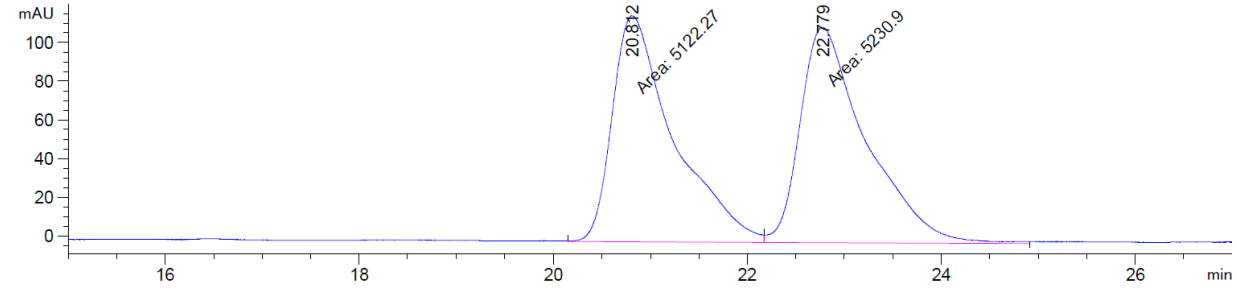
Methyl (*S*)-9-(4-methoxyphenyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate ((+) 5b)



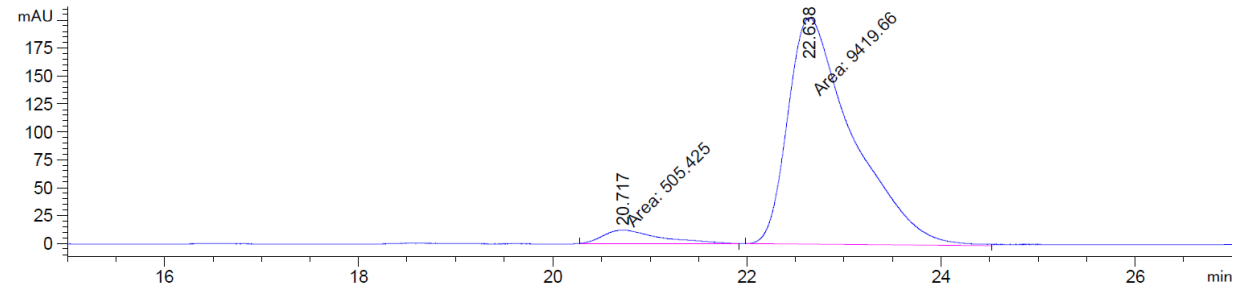
Prepared according to **GP4** with **1d** (38 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **(+) 5b** as a colorless oil (23 mg, 57%). **^{1}H NMR** (400 MHz, Chloroform-*d*): **^{1}H NMR** (400 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 36.32. **HRMS (APCI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{23}H_{37}BNaO_5^+$ 427.2626; Found 427.2633. $[\alpha]_D^{20}$ = +3.5 (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 = 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.

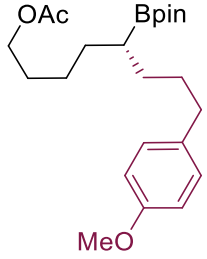


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.812	MF	0.7308	5122.26514	116.82148	49.4753
2	22.779	FM	0.7836	5230.90479	111.25119	50.5247



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.717	MM	0.6864	505.42514	12.27155	5.0924
2	22.638	MM	0.7737	9419.66309	202.91452	94.9076

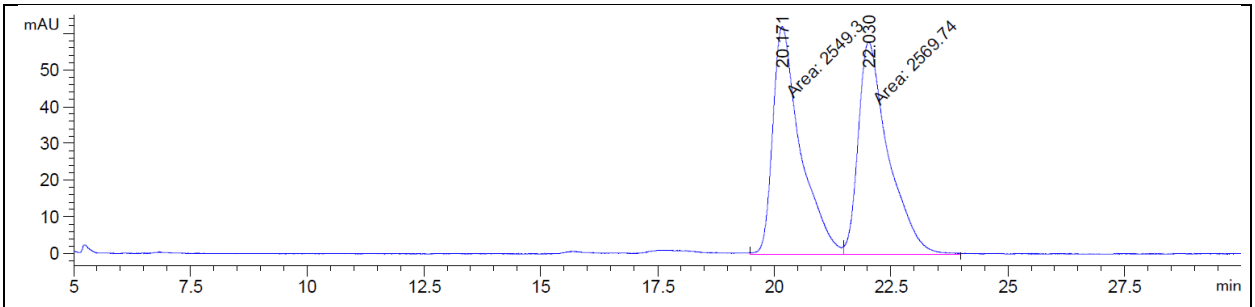
(*R*)-8-(4-Methoxyphenyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl acetate ((+) 5c)



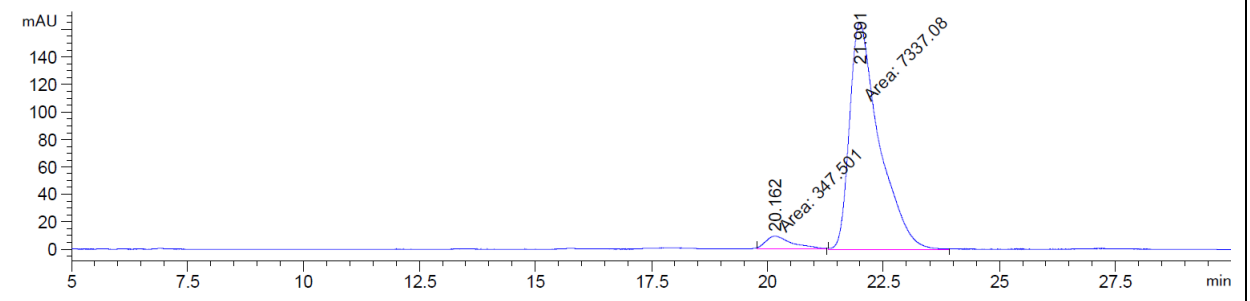
Prepared according to **GP4** with **1e** (38 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 20:1 hexane:EtOAc) afforded the desired product **(+) 5c** as a colorless oil (31 mg, 77%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.10 (d, *J* = 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: $[M + Na]^+$ Calcd for $C_{23}H_{37}BNaO_5^+$ 427.2626; Found 427.2627. $[\alpha]_D^{20}$ = +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_{major} = 21.9 min and t_{minor} = 20.2 min.



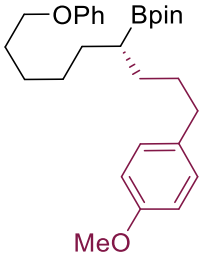
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.171	MF	0.6847	2549.29932	62.05222	49.8004
2	22.030	FM	0.7411	2569.73755	57.79004	50.1996



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.162	MM	0.6336	347.50140	9.14149	4.5221
2	21.991	MM	0.7415	7337.07617	164.92491	95.4779

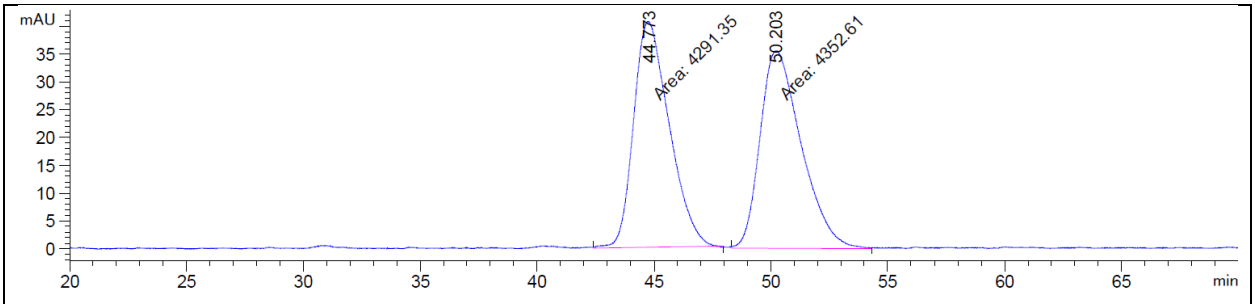
(*S*)-2-(1-(4-Methoxyphenyl)-9-phenoxynonan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 5d)

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

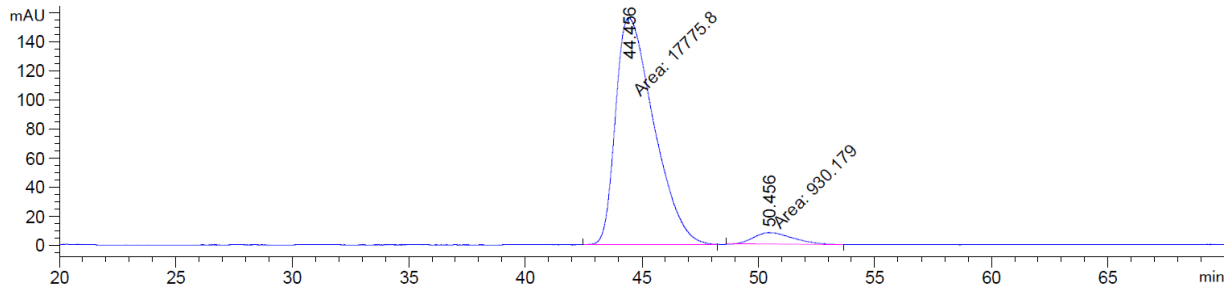


(-) 5d as a colorless oil (31 mg, 69%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.29 (t, *J* = 7.1 Hz, 3H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 2H), 6.88 (dd, *J* = 29.9, 7.8 Hz, 4H), 3.96 (t, *J* = 6.5 Hz, 2H), 3.81 (d, *J* = 1.9 Hz, 3H), 2.57 (t, *J* = 7.7 Hz, 2H), 1.79 (p, *J* = 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: $[M]^+$ Calcd for $C_{28}H_{41}BO_4^+$ 452.3092; Found 452.3081. $[\alpha]_D^{20}$ = -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.

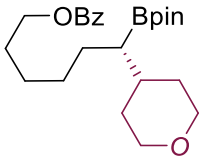


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.773	MM	1.7627	4291.35254	40.57667	49.6457
2	50.203	MM	2.0421	4352.61084	35.52348	50.3543



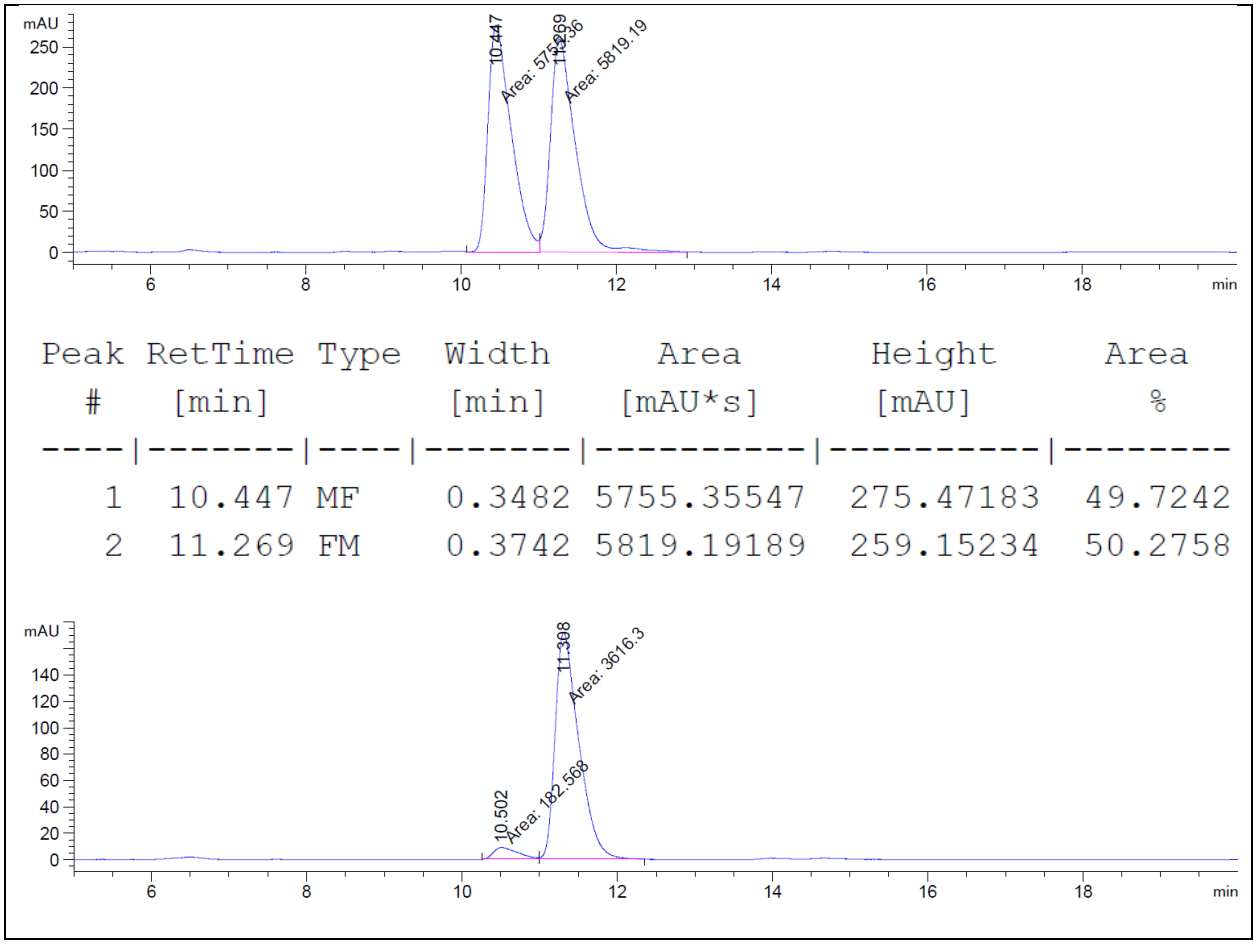
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.456	MM	1.8970	1.77758e4	156.17520	95.0274
2	50.456	MM	1.9580	930.17871	7.91796	4.9726

(*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 µL, 0.15 mmol, 1.50 equiv.). Flash column chromatography (SiO_2, 10:1 hexane:EtOAc) afforded the desired product **(-) 5e** as a colorless oil (33 mg, 79%). **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.35. **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{24}H_{38}BO_5^+$ 417.2807; Found 417.2804. **$[\alpha]_D^{20}$** = -0.5 (c = 1.00 in $CHCl_3$).

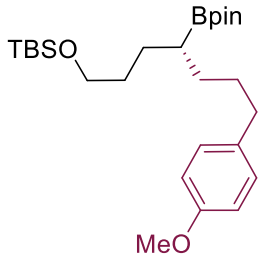
HPLC: The enantiomeric excess (90%) was determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 98:2 at a flow rate 1.0 mL/min detected at 214 nm wavelength. Elution time: t_{major} = 11.3 min and t_{minor} = 10.5 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.447	MF	0.3482	5755.35547	275.47183	49.7242
2	11.269	FM	0.3742	5819.19189	259.15234	50.2758

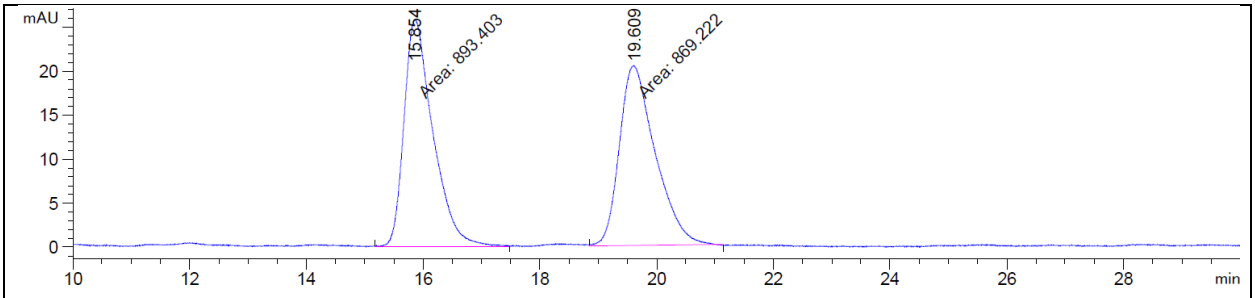
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.502	MF	0.3544	182.56752	8.58649	4.8058
2	11.308	FM	0.3516	3616.30103	171.42809	95.1942

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

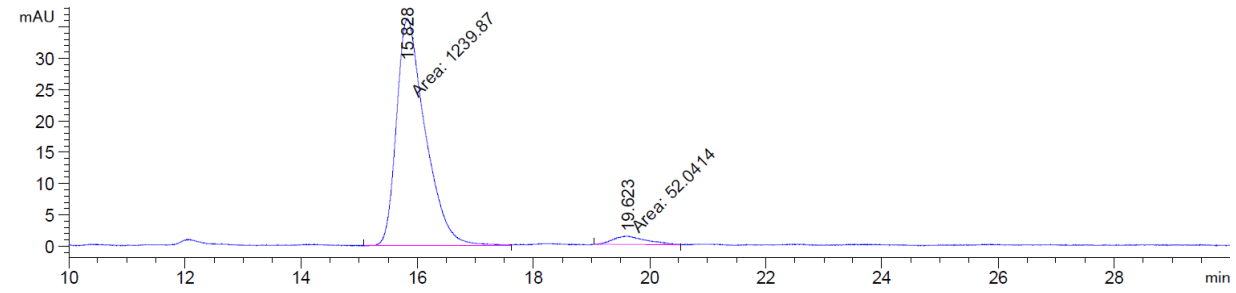


Prepared according to **GP4** with **1h** (47 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 5f** as a colorless oil (26 mg, 56%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.07 (d, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 33.63. **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{26}H_{48}BO_4Si^+$ 463.3409; Found 463.3408. $[\alpha]_D^{20}$ = +1.2 (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} = 15.8 min and t_{minor} = 19.6 min.

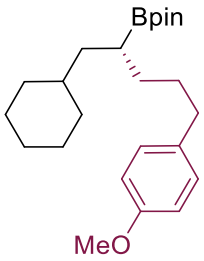


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.854	MM	0.5765	893.40259	25.82875	50.6859
2	19.609	MM	0.7094	869.22192	20.42143	49.3141



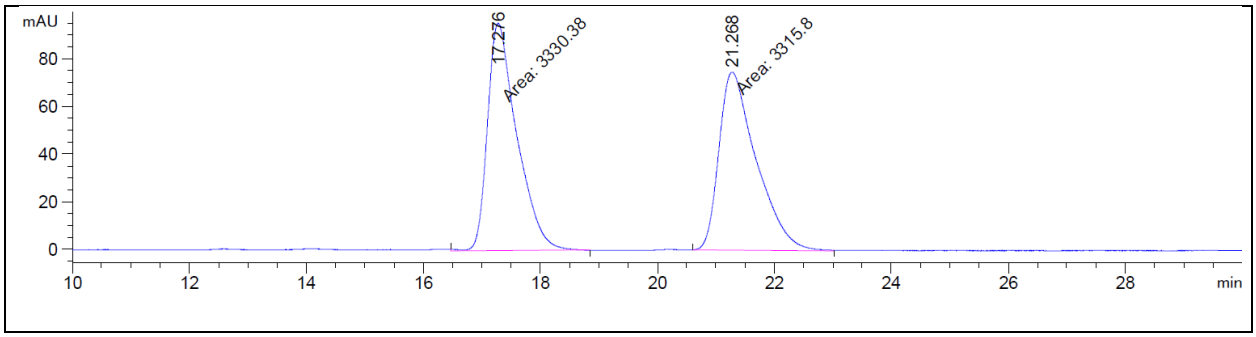
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.828	MM	0.5705	1239.87317	36.22004	95.9718
2	19.623	MM	0.6472	52.04137	1.34012	4.0282

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

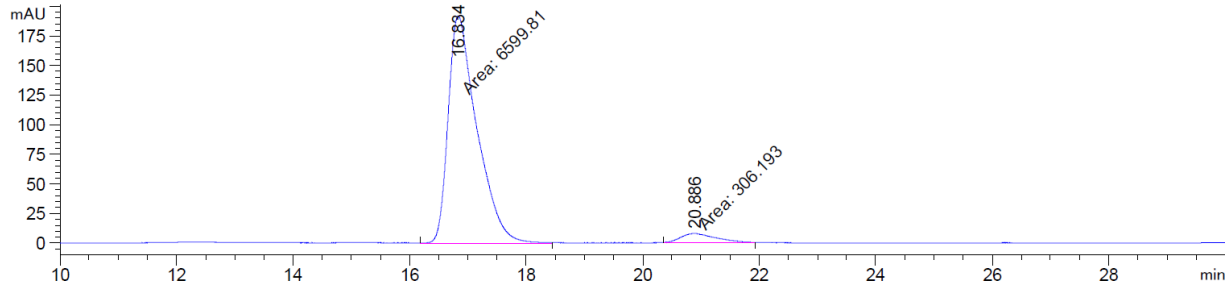


Prepared according to **GP4** with **1i** (36 mg, 0.15 mmol, 1.50 equiv.), **2b** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 5g** as a colorless oil (20 mg, 54%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.08 (d, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.31. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{24}H_{39}BO_3^+$ 386.2987; Found 386.2999. **$[\alpha]_D^{20}$** = +1.2 (c = 1.00 in $CHCl_3$).

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.

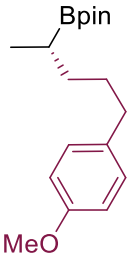


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.276	MM	0.5813	3330.38159	95.48704	50.1097
2	21.268	MM	0.7387	3315.79956	74.81236	49.8903



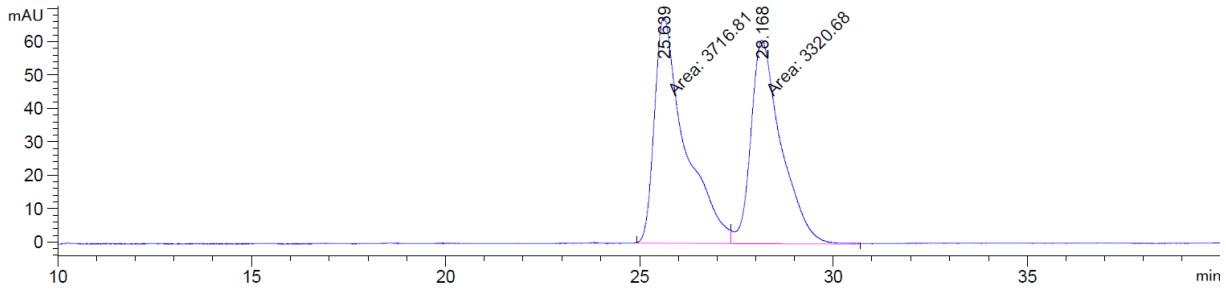
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.834	MM	0.5723	6599.80664	192.20392	95.5663
2	20.886	MM	0.6790	306.19308	7.51567	4.4337

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

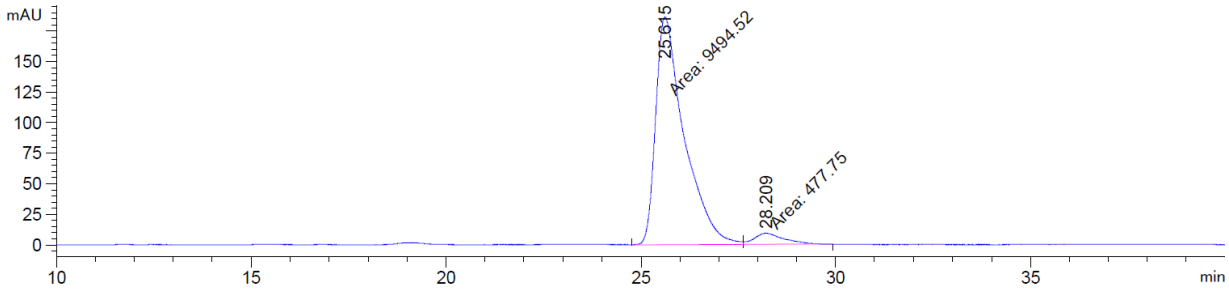


Prepared according to **GP4** with **1j** (51 µL, 0.30 mmol, 1.50 equiv.), **2b** (56 mg, 0.20 mmol, 1.00 equiv.), DEMS (86 µL, 0.50 mmol, 2.50 equiv.), KF (29 mg, 0.50 mmol, 2.5 equiv.) and DCE/DMF (1.0 mL). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 5h** as a colorless oil (41 mg, 68%). **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.31. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{18}H_{29}BO_3^+$ 304.2204; Found 304.2209. $[\alpha]_D^{20}$ = +4.3 (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 = 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.

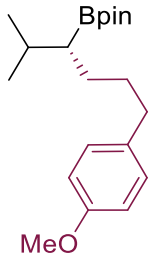


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.639	MF	0.9158	3716.80762	67.64159	52.8144
2	28.168	FM	0.9079	3320.67944	60.95637	47.1856



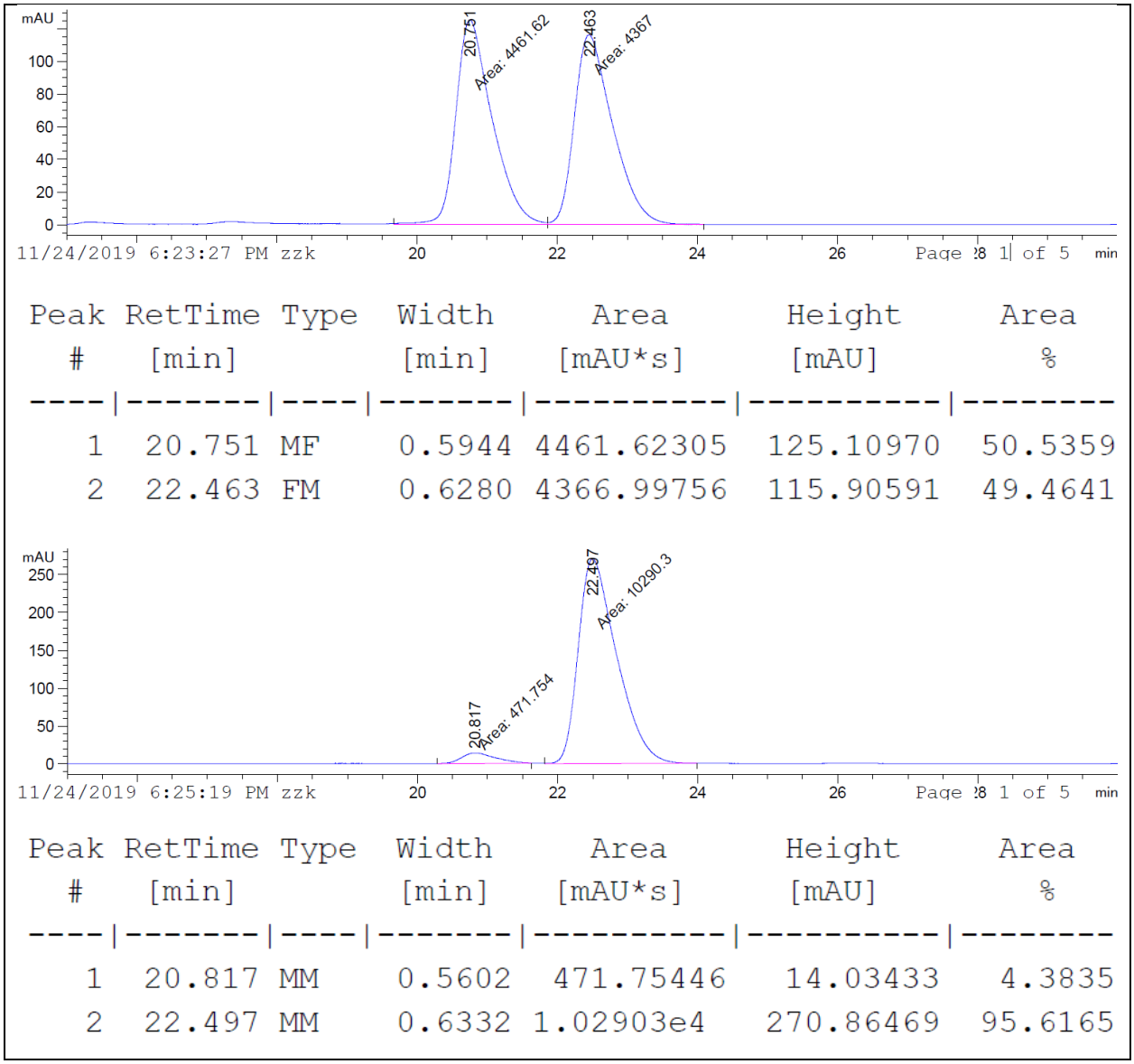
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.615	MF	0.8489	9494.51563	186.40912	95.2092
2	28.209	FM	0.8748	477.74991	9.10241	4.7908

(*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 µL, 0.30 mmol, 1.50 equiv.), **2b** (56 mg, 0.20 mmol, 1.00 equiv.), DEMS (86 µL, 0.50 mmol, 2.50 equiv.), KF (29 mg, 0.50 mmol, 2.5 equiv.) and DCE/DMF (1.0 mL). Flash column chromatography (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 5i** as a colorless oil (20 mg, 30%). **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.85. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{20}H_{33}BO_3^+$ 332.2517; Found 332.2526. $[\alpha]_D^{20}$ = +3.61 (c = 1.00 in $CHCl_3$).

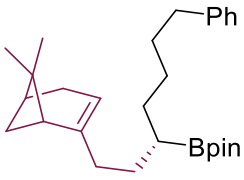
HPLC: The enantiomeric excess (91%) was determined after oxidation (**GP2**) via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 230 nm wavelength. Elution time: t_{major} = 22.5 min and t_{minor} = 20.8 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.751	MF	0.5944	4461.62305	125.10970	50.5359
2	22.463	FM	0.6280	4366.99756	115.90591	49.4641

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.817	MM	0.5602	471.75446	14.03433	4.3835
2	22.497	MM	0.6332	1.02903e4	270.86469	95.6165

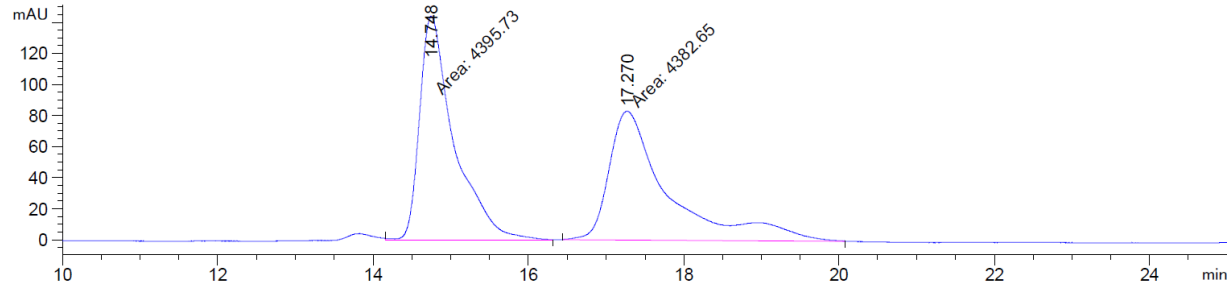
2-((*S*)-1-((*1R,5S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)-7-phenylheptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((-) 6a)



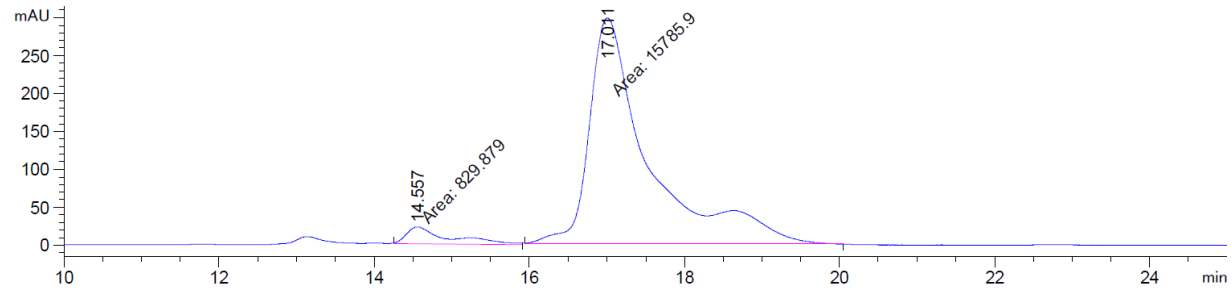
Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2d'** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 100:1 hexane:EtOAc) afforded the desired product **(-) 6a** as a colorless oil (20 mg, 54%) in 95:5 diastereomeric ratio. **^{1}H NMR** (400 MHz, Chloroform-*d*): 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.26. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{28}H_{43}BO_2^+$ 422.3351; Found 422.3352. **$[\alpha]_D^{20}$** = -11.7 (c = 1.00 in $CHCl_3$).

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.



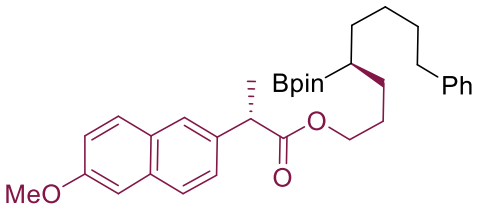
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.748	MM	0.5099	4395.73291	143.66977	50.0745
2	17.270	MM	0.8828	4382.64746	82.74044	49.9255



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.557	MM	0.6230	829.87946	22.20256	4.9945
2	17.011	MM	0.8837	1.57859e4	297.71661	95.0055

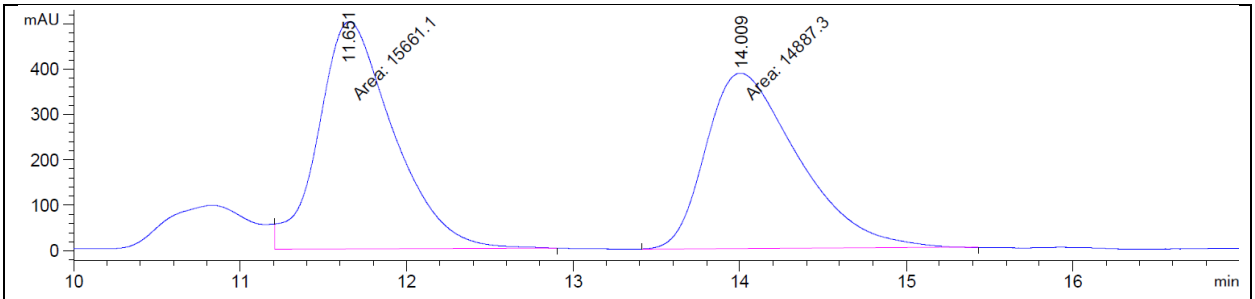
(*S*)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate ((+) 6b):

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 (SiO_2, 30:1 hexane:EtOAc) afforded the desired product

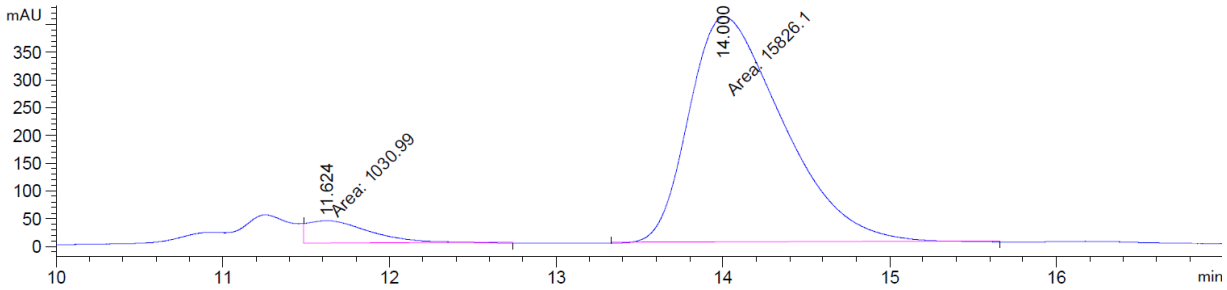


(+) 6b as a colorless oil (37 mg, 68%) in 94:6 diastereomeric ratio. **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.75 – 7.69 (m, 3H), 7.44 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.20 – 7.11 (m, 5H), 4.08 (t, *J* = 6.6 Hz, 2H), 3.92 (s, 3H), 3.87 (q, *J* = 7.2 Hz, 1H), 2.59 (t, *J* = 7.7 Hz, 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: $[M + Na]^+$ Calcd for $C_{34}H_{45}BNaO_5^+$ 567.3252; Found 567.3265. $[\alpha]_D^{20}$ = +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.

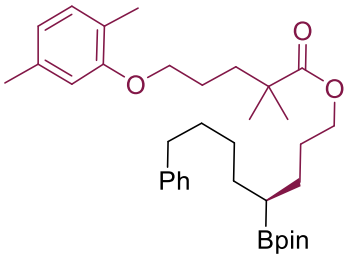


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.651	FM	0.5212	1.56611e4	500.75705	51.2666
2	14.009	MM	0.6424	1.48873e4	386.22513	48.7334



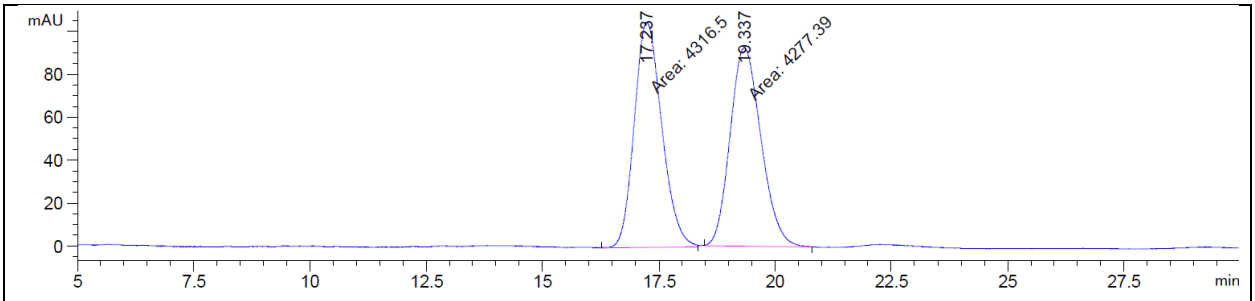
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.624	FM	0.4263	1030.99438	40.31121	6.1161
2	14.000	MM	0.6508	1.58261e4	405.26898	93.8839

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

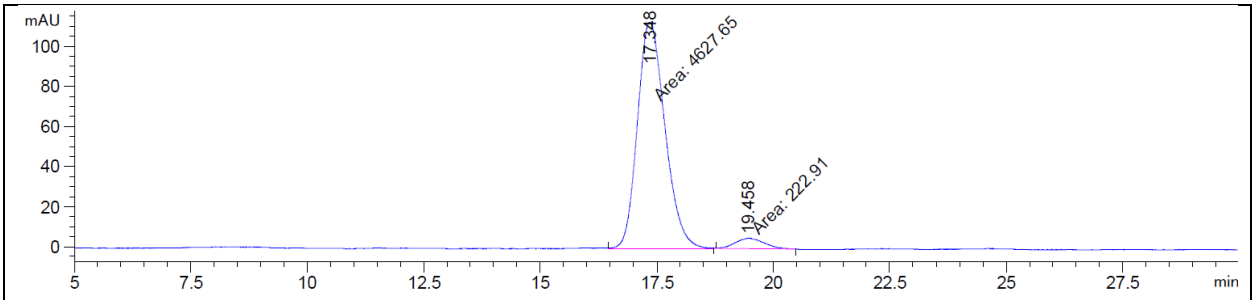


Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2f'** (28 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **(+) 6c** as a colorless oil (32 mg, 57%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.30 – 7.26 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.07. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{35}H_{53}BNaO_5^+$ 587.3878; Found 587.3892. $[\alpha]_D^{20}$ = +1.2 (c = 1.00 in $CHCl_3$).

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.

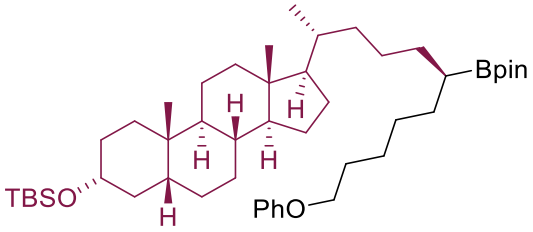


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.237	MM	0.6862	4316.50146	104.84542	50.2275
2	19.337	MM	0.7709	4277.39404	92.47763	49.7725



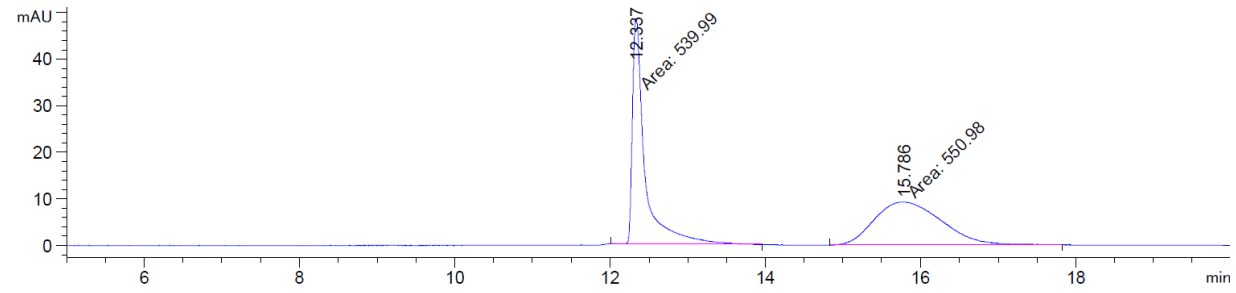
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.348	MM	0.6836	4627.65234	112.82446	95.4044
2	19.458	MM	0.7164	222.91049	5.18610	4.5956

***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)**

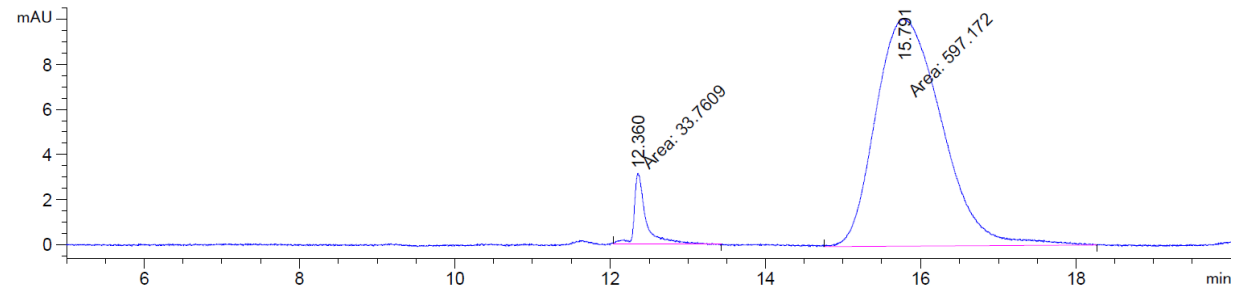


Prepared according to **GP4** with **1f** (45 mg, 0.15 mmol, 1.50 equiv.), **2g'** (59 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 30:1 hexane:EtOAc) afforded the desired product **(+) 6d** as a white solid (33 mg, 43%) in 95:5 diastereomeric ratio. **^{1}H NMR** (400 MHz, Chloroform-*d*): 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). **^{13}C 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 $C_{48}H_{83}BNaO_4Si^+$ 785.6046; Found 785.6050. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 37.90. $[\alpha]_D^{20}$ = +23.0 (c = 1.00 in $CHCl_3$).

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.

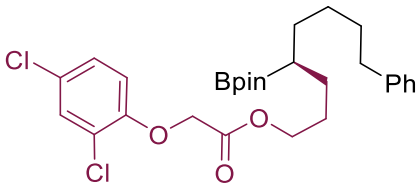


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.337	MM	0.1862	539.98956	48.33888	49.4963
2	15.786	MM	0.9984	550.97998	9.19735	50.5037



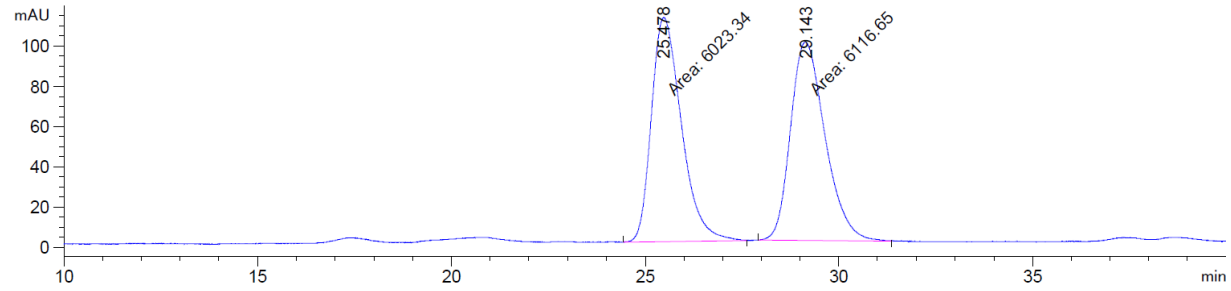
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.360	MM	0.1784	33.76090	3.15323	5.3510
2	15.791	MM	0.9837	597.17194	10.11783	94.6490

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



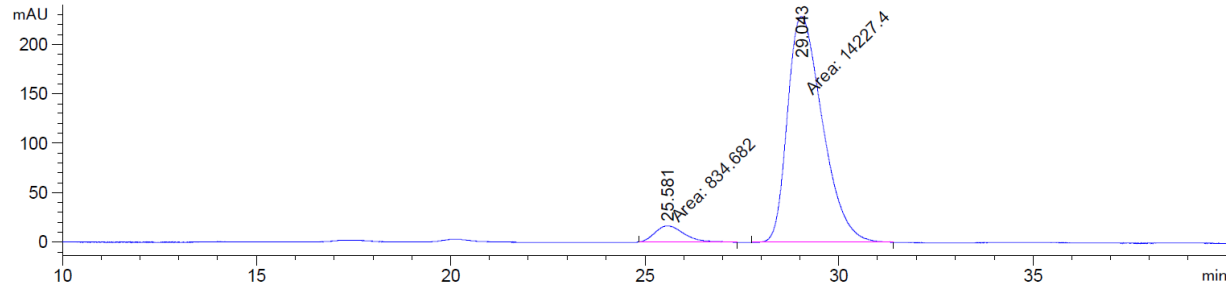
Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2h'** (39 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 15:1 hexane:EtOAc) afforded the desired product **(-) 6e** as a colorless oil (34 mg, 64%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 7.41 (d, *J* = 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.13. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{28}H_{37}BCl_2NaO_5^+$ 557.2003; Found 557.2012. $[\alpha]_D^{20}$ = -1.2 (c = 1.00 in $CHCl_3$).

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_{major} = 29.0 min and t_{minor} = 25.6 min.



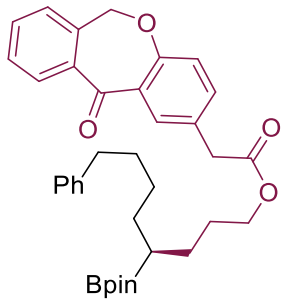
6e

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.478	MM	0.8995	6023.34326	111.60850	49.6157
2	29.143	MM	1.0343	6116.65088	98.55893	50.3843



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.581	MM	0.8502	834.68176	16.36313	5.5416
2	29.043	MM	1.0387	1.42274e4	228.28233	94.4584

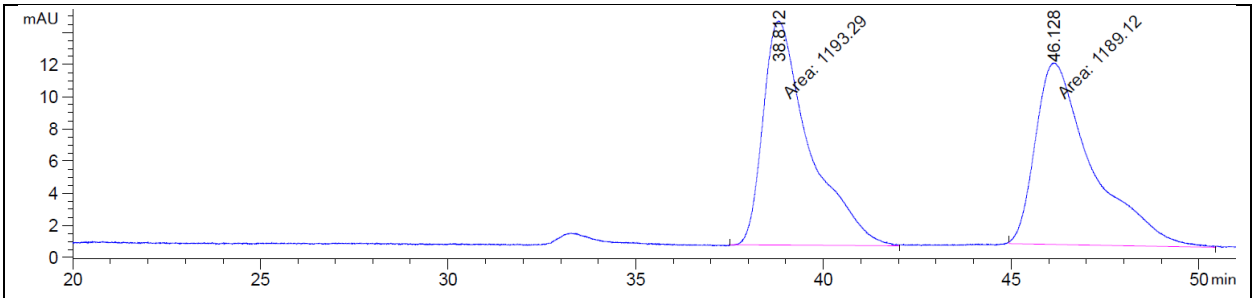
(*S*)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 2-(11-oxo-6,11-dihydrodibenzo[*b*,*e*]oxepin-2-yl)acetate ((-) 6f)



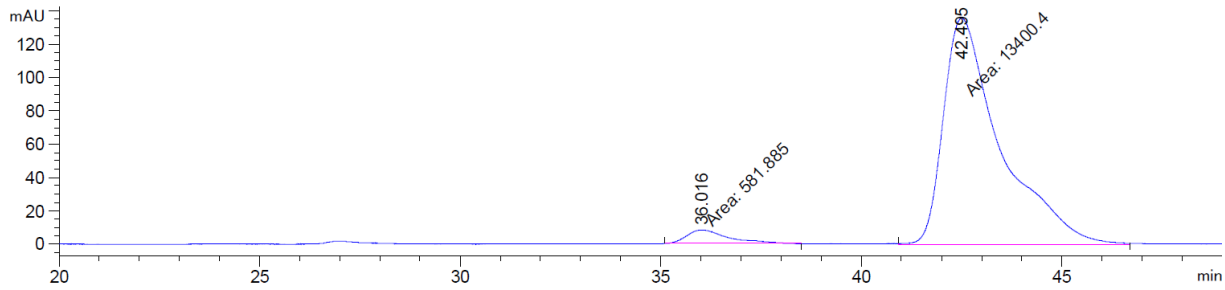
Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2i'** (44 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 7:1 hexane:EtOAc) afforded the desired product **(-) 6f** as a colorless oil (34 mg, 58%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.14 (d, *J* = 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).

^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.70. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{36}H_{43}BNaO_6^+$ 605.3045; Found 605.3057. $[\alpha]_D^{20}$ = -0.3 (c = 1.00 in $CHCl_3$).

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.



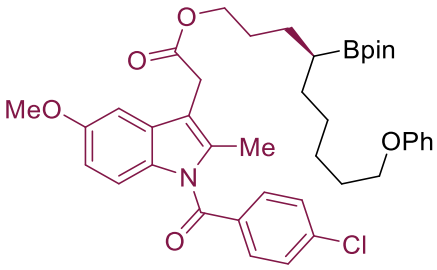
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.812	MM	1.4273	1193.29309	13.93437	50.0875
2	46.128	MM	1.7529	1189.12170	11.30647	49.9125



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.016	MM	1.1830	581.88513	8.19762	4.1616
2	42.495	MM	1.6417	1.34004e4	136.04102	95.8384

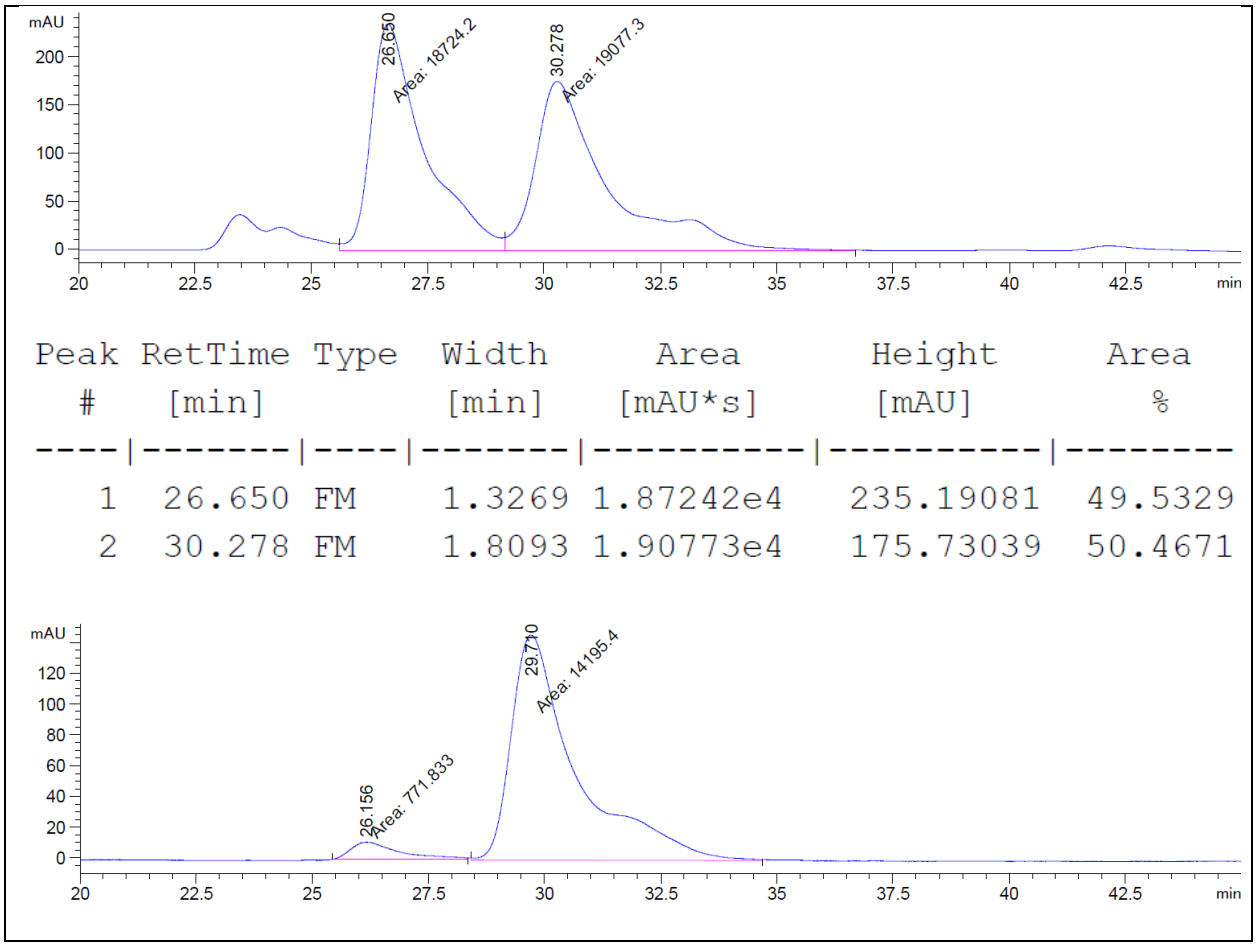
(*S*)-9-Phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate ((-) 6g)

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 (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(-)**



6g as a colorless oil (37 mg, 53%). **^{1}H 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). **^{13}C 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.. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 36.50. **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{40}H_{49}BClNNaO_7^+$ 724.3183; Found 724.3189. **$[\alpha]_D^{20}$** = -0.67 (c = 1.00 in $CHCl_3$).

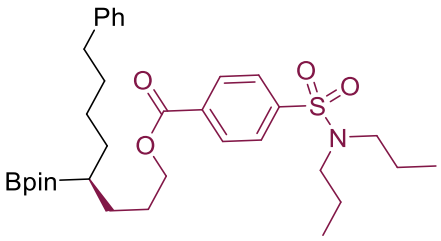
HPLC: The enantiomeric excess (90%) was determined via HPLC analysis using a CHIRALPAK® AD-H column, with hexane:isopropanol = 95:5 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 29.7 min and t_{minor} = 26.1 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.650	FM	1.3269	1.87242e4	235.19081	49.5329
2	30.278	FM	1.8093	1.90773e4	175.73039	50.4671

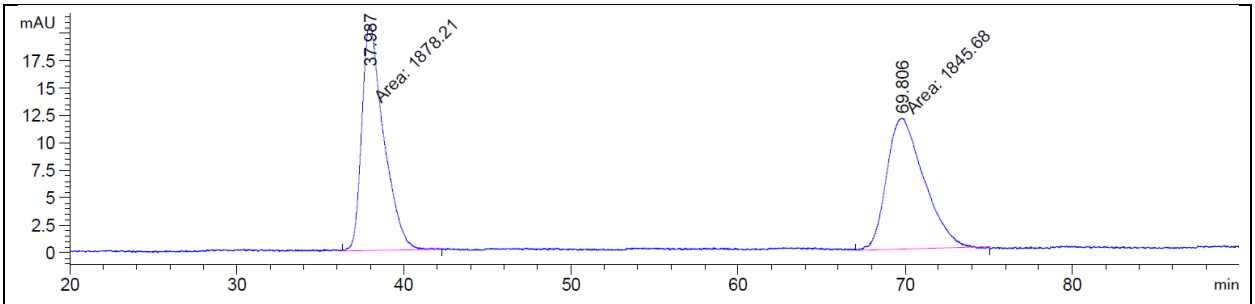
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.156	MM	1.1791	771.83325	10.90991	5.1568
2	29.710	MM	1.6194	1.41954e4	146.09392	94.8432

(*S*)-8-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate ((-) 6h)

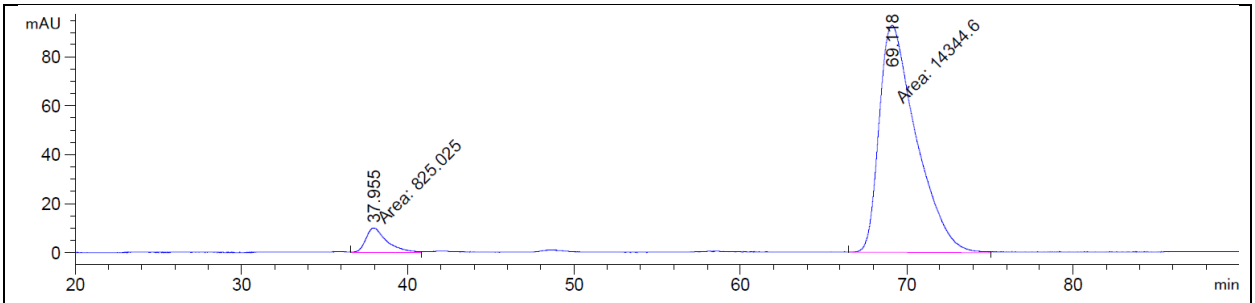


Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2k'** (46 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 3:1 hexane:EtOAc) afforded the desired product **(-) 6h** as a colorless oil (36 mg, 60%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.22 – 8.13 (m, 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.11. **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{33}H_{51}BNO_6S^+$ 600.3525; Found 600.3537. **$[\alpha]_D^{20}$** = -0.7 (c = 1.00 in $CHCl_3$).

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.

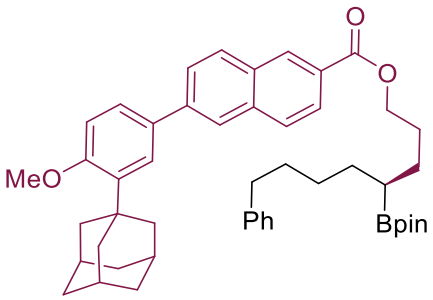


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.987	MM	1.5193	1878.21240	20.60425	50.4368
2	69.806	MM	2.5743	1845.68103	11.94955	49.5632



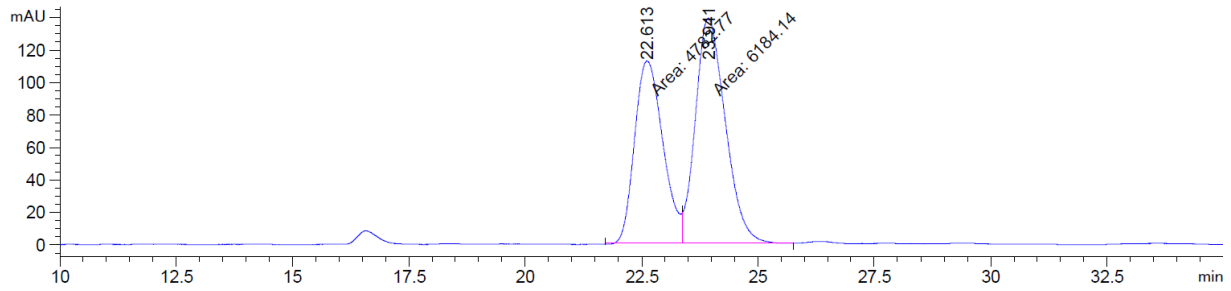
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.955	MM	1.3925	825.02527	9.87456	5.4387
2	69.118	MM	2.5741	1.43446e4	92.87648	94.5613

(*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)

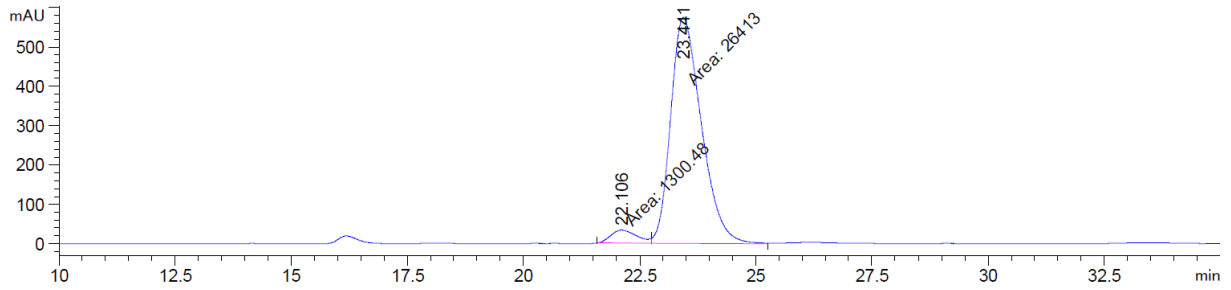


Prepared according to **GP4** with **1b** (41 mg, 0.15 mmol, 1.50 equiv.), **2l'** (58 mg, 0.10 mmol, 1.00 equiv.). Flash column chromatography (SiO_2, 5:1 hexane:EtOAc) afforded the desired product **(+) 6i** as a colorless oil (43 mg, 59%). **^{1}H NMR** (400 MHz, Chloroform-*d*): δ 8.64 (s, 1H), 8.11 (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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 34.12. **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{48}H_{60}BO_5^+$ 727.4528; Found 727.4526. $[\alpha]_D^{20}$ = +1.5 (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 = 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.

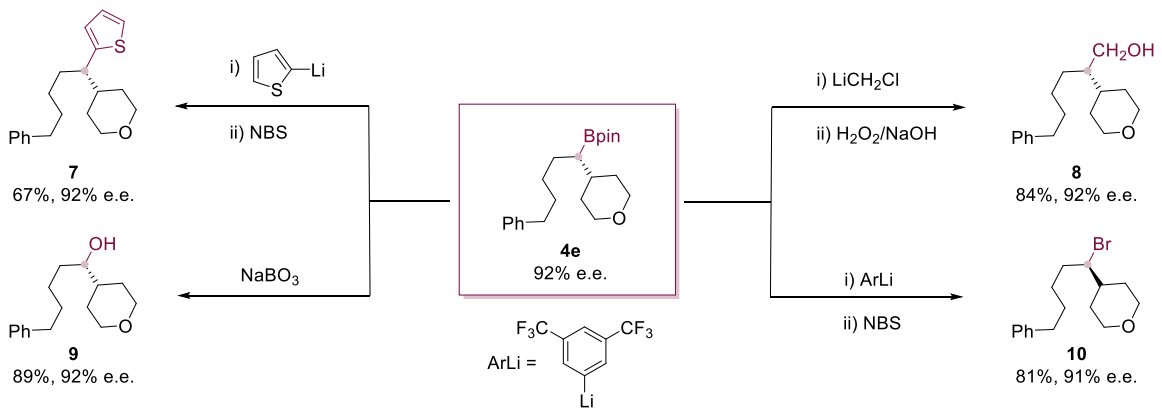


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.613	MF	0.7087	4782.77490	112.48418	43.6110
2	23.941	FM	0.7422	6184.13623	138.86404	56.3890

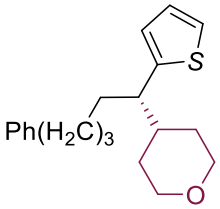


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.106	MF	0.6591	1300.47522	32.88686	4.6926
2	23.441	FM	0.7664	2.64130e4	574.36633	95.3074

7. Functional group transformations:

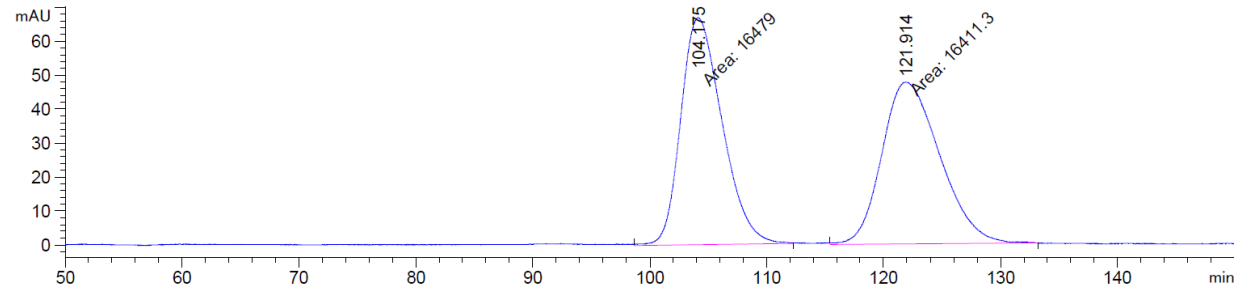


(*S*)-4-(5-Phenyl-1-(thiophen-2-yl)pentyl)tetrahydro-2H-pyran ((-) 7)

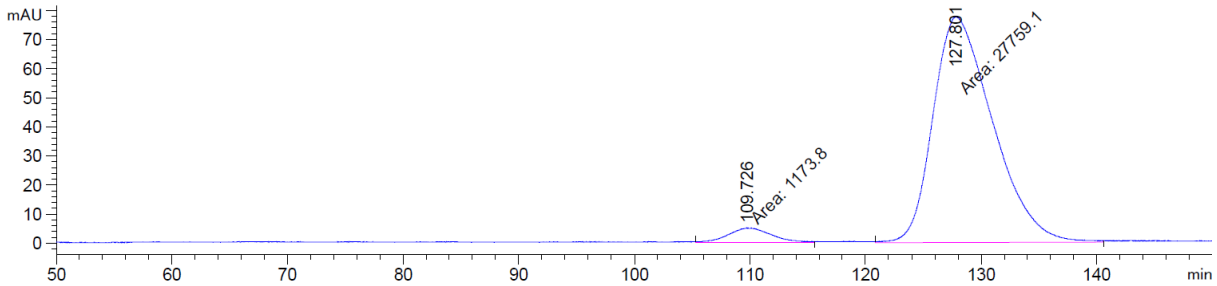


The title compound was prepared following a known literature procedure with slight modification.[28] To a solution of thiophene (14.0 µL, 0.18 mmol, 1.20 equiv.) in THF (1.0 mL) at –78 °C was added n-BuLi (1.6 M in hexane; 112 µL, 0.18 mmol, 1.20 equiv.) dropwise under an inert atmosphere. The mixture was then warmed to room temperature and stirred for 30 min. Then the mixture was cooled to -78 °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 °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. **^{1}H 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). **^{13}C 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: $[M]^+$ Calcd for $C_{20}H_{26}OS^+$ 314.1699; Found 314.1699. $[\alpha]_D^{20}$ = -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_{major} = 127.8 min and t_{minor} = 109.7 min.

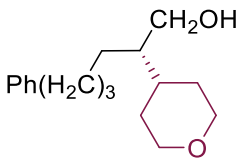


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	104.175	MM	4.1013	1.64790e4	66.96680	50.1029
2	121.914	MM	5.7298	1.64113e4	47.73660	49.8971



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	109.726	MM	4.0663	1173.80347	4.81109	4.0570
2	127.801	MM	5.9686	2.77591e4	77.51400	95.9430

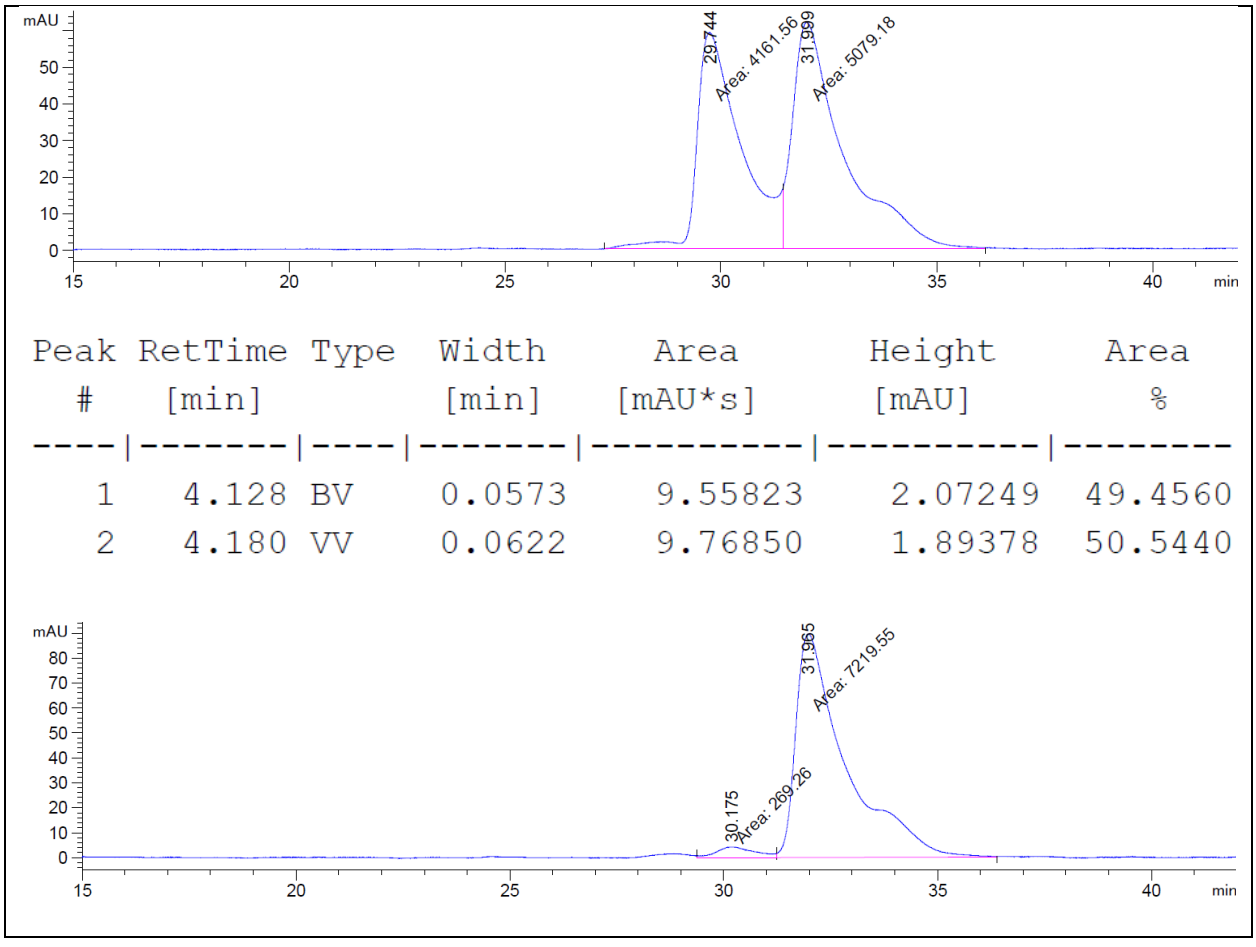
(*S*)-6-Phenyl-2-(tetrahydro-2H-pyran-4-yl)hexan-1-ol ((-) 8)



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 chloroiodomethane (22.0 µL, 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 µL, 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 H_2O_2 (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 H_2O (5.0 mL) and EtOAc (5.0 mL) and extracted with EtOAc (3x4.0 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash column chromatography (SiO_2, 2:1 hexane:EtOAc) to obtain the desired product (-) **8** (33 mg, 84%) as a colorless oil. **^{1}H 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). **^{13}C 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 $C_{17}H_{27}O_2^+$ 263.2006; Found 263.2008. $[\alpha]_D^{20}$ = -10.0 (c = 1.00 in $CHCl_3$).

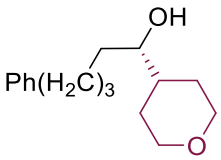
HPLC: The enantiomeric excess (92%) was determined via HPLC analysis using a CHIRALPAK® IB column, with hexane:isopropanol = 97:3 at a flow rate 1.0 mL/min detected at 210 nm wavelength. Elution time: t_{major} = 31.9 min and t_{minor} = 30.1 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.128	BV	0.0573	9.55823	2.07249	49.4560
2	4.180	VV	0.0622	9.76850	1.89378	50.5440

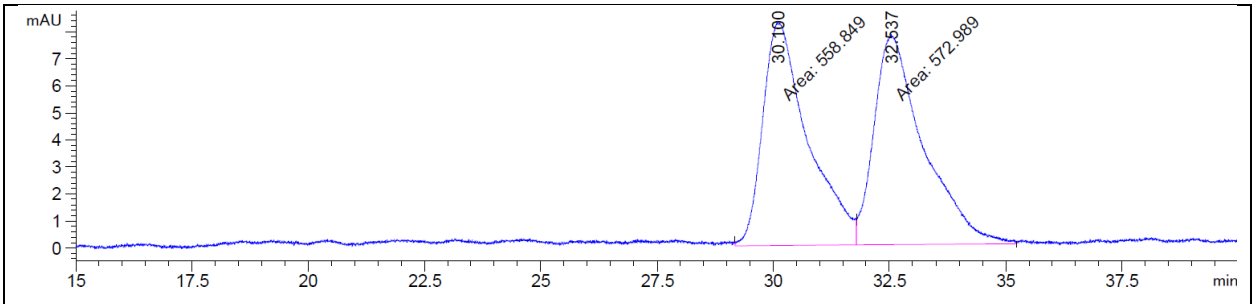
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.175	MF	1.0303	269.26025	4.35569	3.5955
2	31.965	FM	1.3405	7219.55078	89.75989	96.4045

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

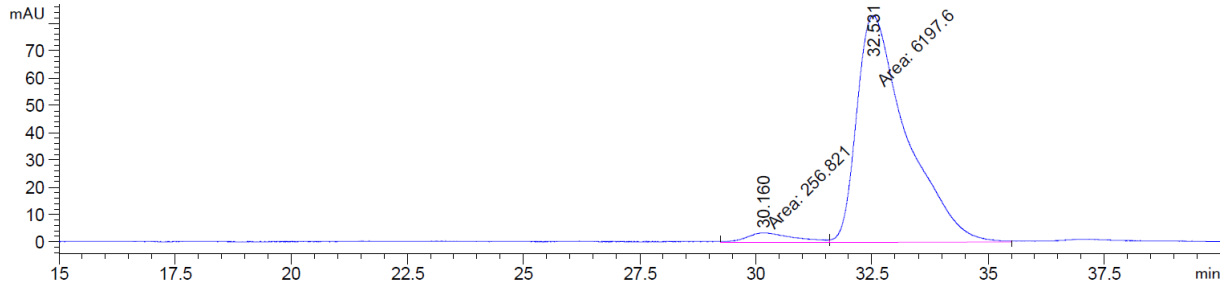


(*S*)-4,4,5,5-tetramethyl-2-(5-phenyl-1-(tetrahydro-2H-pyran-4-yl)pentyl)-1,3,2-dioxaborolane (**4e**) (36.0 mg, 0.10 mmol, 1.00 equiv.) was dissolved in a 1:1 mixture of THF and H_2O (2.0 mL) at room temperature. Then $NaBO_3$•$4H_2O$ (39 mg, 0.25 mmol, 2.50 equiv.) was added. The resulting mixture 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 Et_2O (5.0 mL). The organic layer was separated and aqueous phase was extracted with Et_2O (3x5.0 mL), and the combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by flash column chromatography (SiO_2, 3:1 hexane:EtOAc) to obtain the desired product (-) **9** (22 mg, 89%) as a colorless oil. **^{1}H 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. **^{13}C 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 $C_{16}H_{23}O_2^-$ 247.1704; Found 247.1693. $[\alpha]_D^{20}$ = -8.0 (c = 1.00 in $CHCl_3$).

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.

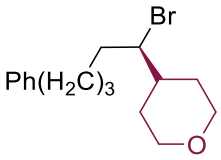


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.100	MF	1.1264	558.84937	8.26930	49.3753
2	32.537	FM	1.2277	572.98944	7.77885	50.6247



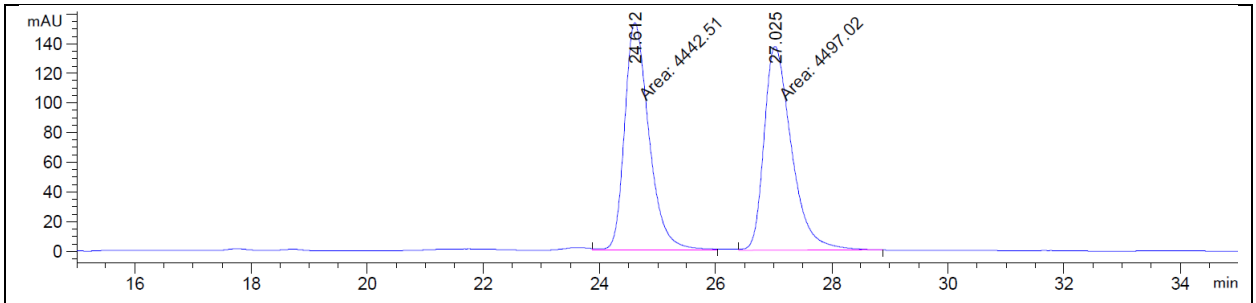
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.160	MF	1.1911	256.82108	3.59365	3.9790
2	32.531	FM	1.2431	6197.60303	83.09115	96.0210

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

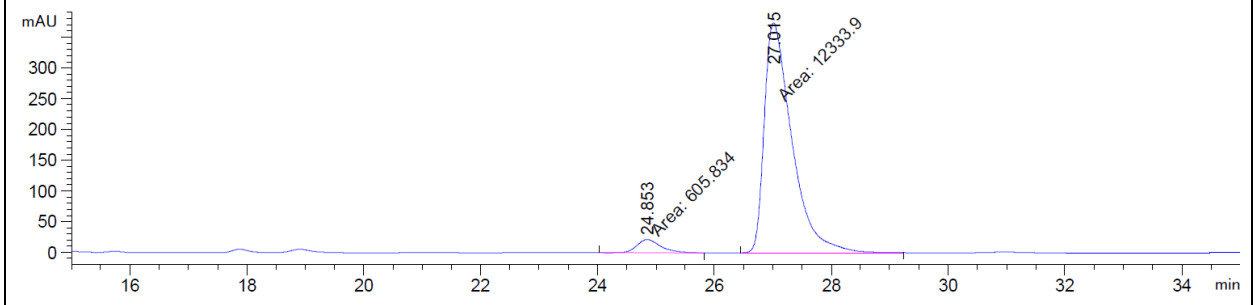


The title compound was prepared following a known literature procedure with slight modification.[30] To a solution of 1-bromo-3,5-bis(trifluoromethyl)benzene (66 mg, 0.23 mmol, 1.50 equiv.) in THF (2 mL) at –78 °C was added n-BuLi (1.6 M in hexane; 144 µL, 0.23 mmol, 1.50 equiv.) dropwise. The mixture was stirred at –78 °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 °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. **^{1}H 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: $[M + H]^+$ Calcd for $C_{16}H_{24}BrO^+$ 311.1005; Found 311.1004. $\mathbf{[\alpha]_D^{20}}$ = +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_{major} = 27.0 min and t_{minor} = 24.8 min.

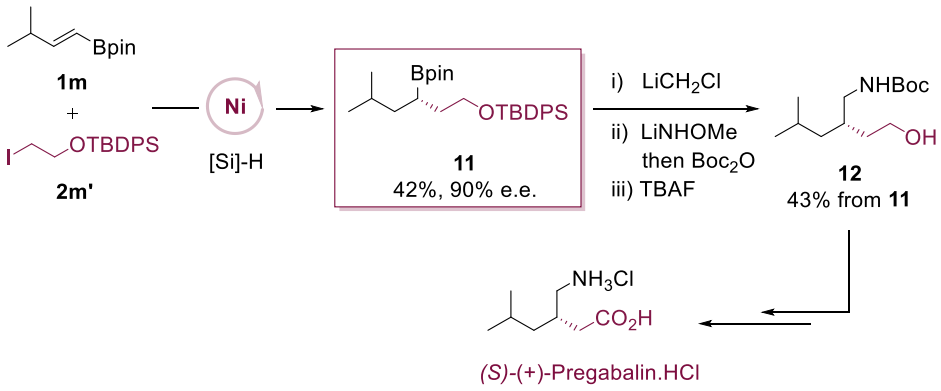


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.612	MM	0.4842	4442.51074	152.90222	49.6951
2	27.025	MM	0.5458	4497.02246	137.31042	50.3049

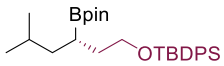


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.853	MM	0.4722	605.83405	21.38309	4.6820
2	27.015	MM	0.5496	1.23339e4	374.01254	95.3180

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

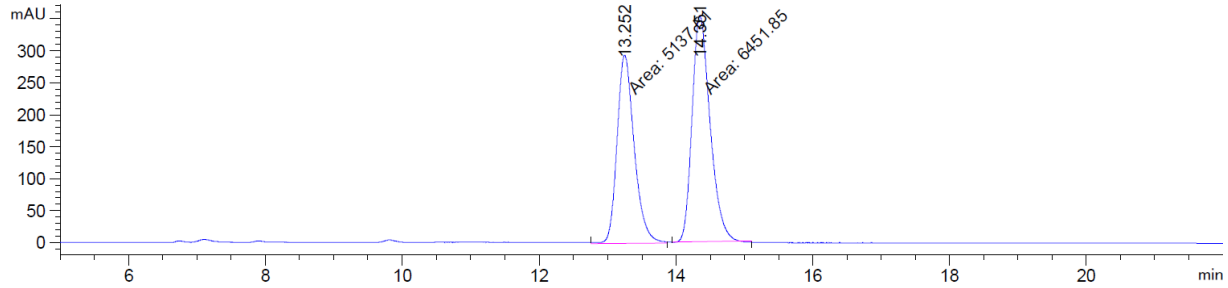


(*S*)-*tert*-Butyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)diphenylsilane ((+) 11)

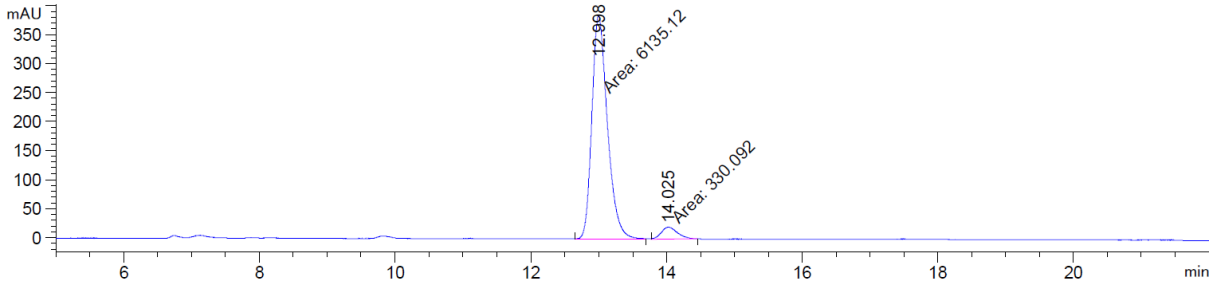


The title compound was prepared according to **GP4** with **1m** (29.4 mg, 0.15 mmol, 1.50 equiv.), **2m'** (41.0 mg, 0.10 mmol, 1.00 equiv.) in a mixture of DCE (0.40 mL) and DMF (0.14 mL) after stirring for 48 hours. Flash column chromatography (SiO_2, 150:1 hexane:EtOAc) afforded the desired product **(+) 11** as a colorless oil (20 mg, 42%). **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.12. **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{29}H_{46}BO_3Si^+$ 481.3304; Found 481.3310. $[\alpha]_D^{20}$ = +4.5 (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 = 99.5:05 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.

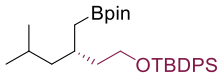


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.252	MM	0.2909	5137.50879	294.29605	44.3295
2	14.351	MM	0.3044	6451.84863	353.31107	55.6705



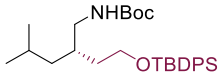
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.998	MM	0.2652	6135.11523	385.49411	94.8943
2	14.025	MM	0.2714	330.09207	20.27290	5.1057

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



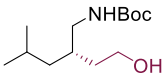
The title compound was prepared following a known literature procedure with slight modification.[29] A solution of (*S*)-*tert*-butyl((5-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl)oxy)diphenylsilane (**11**) (90.0 mg, 0.19 mmol, 1.00 equiv.) and chloroiodomethane (29.1 µL, 0.38 mmol, 2.00 equiv.) in THF (1.0 mL) was cooled to -78°C. Then n-BuLi (1.6 M in hexane; 238 µL, 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 H_2O (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 Na_2SO_4, 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**



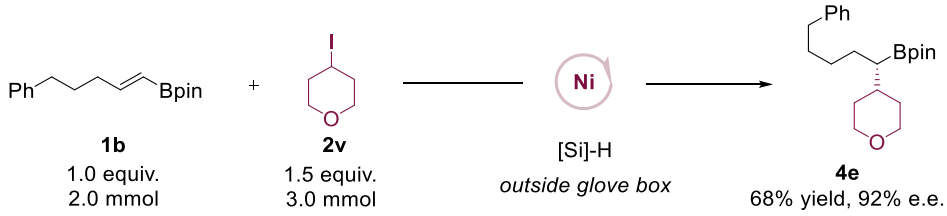
The conversion of the Bpin group to NHBoc group was conducted following a literature reported method.[31] A solution of O-methylhydroxylamine (0.28 mL, 0.52 mmol, 1.88 M in THF) was diluted with THF (1.5 mL) and the reaction flask was cooled to -78° C in a dry ice/acetone bath. Then n-BuLi (1.6 M in hexane; 330 µL, 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 Boc_2O (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 H_2O (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 Na_2SO_4, 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 N_2 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. NH_4Cl 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 Na_2SO_4 and concentrated in vacuo. The crude product was purified by flash column chromatography (SiO_2, 2:1 hexane:EtOAc) to obtain the desired product (+) **12** (20 mg, 81%, overall 43% from **11**) as a colorless oil. **^{1}H 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). **^{13}C 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 $C_{13}H_{27}NNaO_3^+$ 268.1883; Found 268.1886. $[\alpha]_D^{20}$ = +1.5 (c = 1.00 in $CHCl_3$).

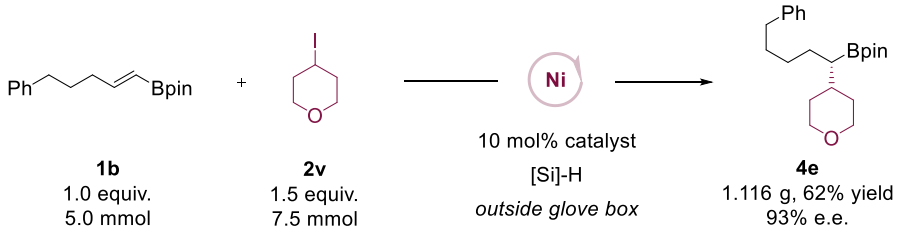
9. Large Scale Reaction (with 15 mol% catalyst loading):



A heat gun dried schlenk tube equipped with a magnetic stir bar (6x15 mm) was charged with $NiCl_2$ (38.0 mg, 0.30 mmol, 0.15 equiv.) and **L6** (116 mg, 0.40 mmol, 0.20 equiv.) under N_2. 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 H_2O (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 Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash

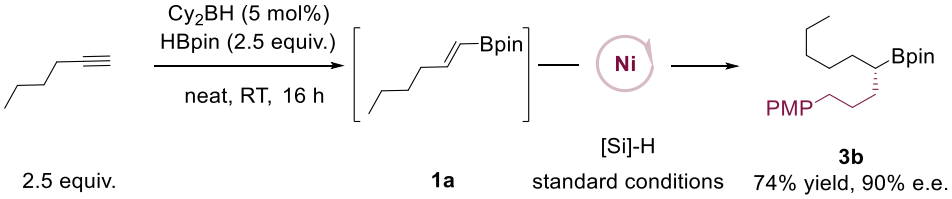
column chromatography (SiO_2, 10:1 hexane:EtOAc) to obtain the desired product **4e** as colourless oil (488 mg, 68% yield, 92% e.e.).

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 $NiCl_2$ (64.5 mg, 0.50 mmol, 0.10 equiv.) and **L6** (219 mg, 0.75 mmol, 0.15 equiv.) under N_2. 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 H_2O (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 Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by flash column chromatography (SiO_2, 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:

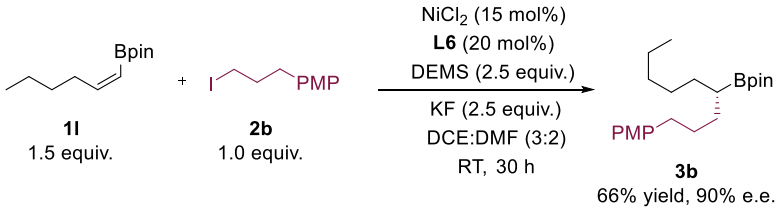


In a heat gun dried schlenk tube equipped with a magnetic stir bar (6x15 mm) freshly prepared dicyclohexylborane (3.60 mg, 20.0 µmol, 0.05 equiv.), 1-hexyne (115 µL, 1.00 mmol, 1.00 equiv.) and pinacolborane (145 µL, 1.00 mmol, 1.00 equiv.) were added successively under an N_2 atmosphere. The reaction 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

N_2. To the resulting residue was added a solution of preformed catalyst [prepared with $NiCl_2$ (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 H_2O (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 Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash column chromatography (SiO_2, 60:1 hexane:EtOAc) to obtain the desired product **3b** as colourless oil (133 mg, 74% yield, 90% e.e.).

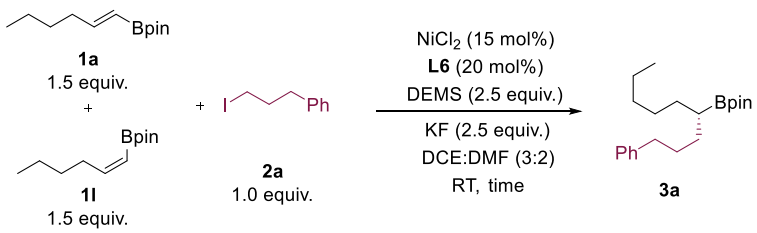
12. Mechanistic investigations:

12.1 Reaction with a cis-boronic ester:



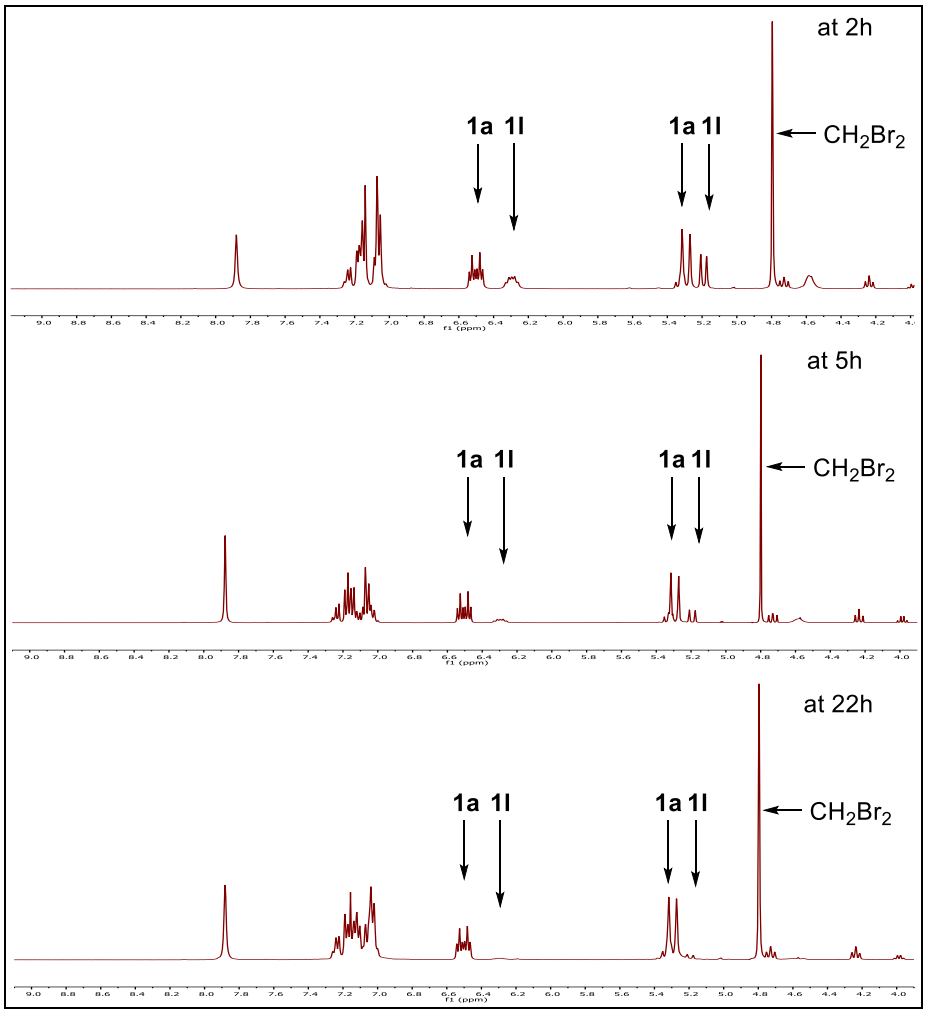
The reaction was conducted for 30 hours according to **GP4**, with (*Z*)-2-(hex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1l**) (42 mg, 0.20 mmol, 2.00 equiv.) and 1-(3-iodopropyl)-4-methoxybenzene (**2b**) (28 mg, 0.10 mmol, 1.00 equiv.) as coupling partners. Flash column chromatography (SiO_2, 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

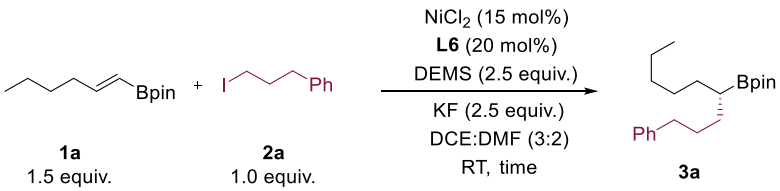
reactions were stopped at the indicated reaction time. Afterwards, water (1.0 mL) and EtOAc (3.0 mL) were added to the reaction mixture. The organic phase was separated and the aqueous phase was extracted with EtOAc (2x3.0 mL). The volatiles were removed to afford the crude product. Then dibromomethane was added as an internal standard to this mixture and the resulting mixture was mixed well. A small organic aliquot was used for ^{1}H 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-calatyst, the *cis* to *trans* conversion still occurred.



12.3 Reaction profile:

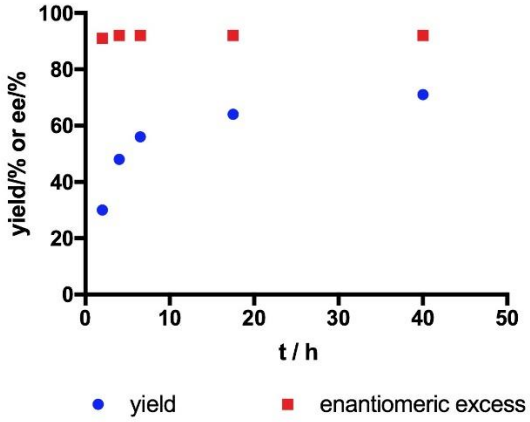
Five parallel reactions at a 0.1 mmol scale were performed following **GP4**. The reactions were stopped at the indicated reaction time. Afterwards, water (1.0 mL) and EtOAc (3.0 mL) were added to the reaction mixture. Dodecane (23.0 µL) was added as an internal standard for GC FID analysis to this mixture 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 Na_2SO_4, 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.

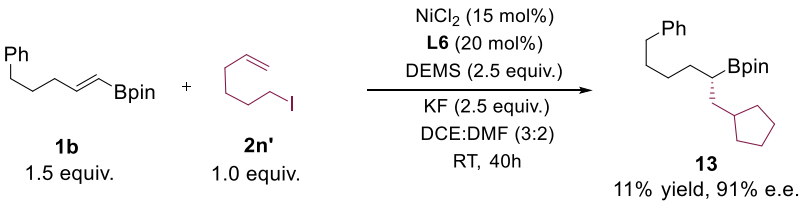


1a 1.5 equiv. **2a** 1.0 equiv. **3a**

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:

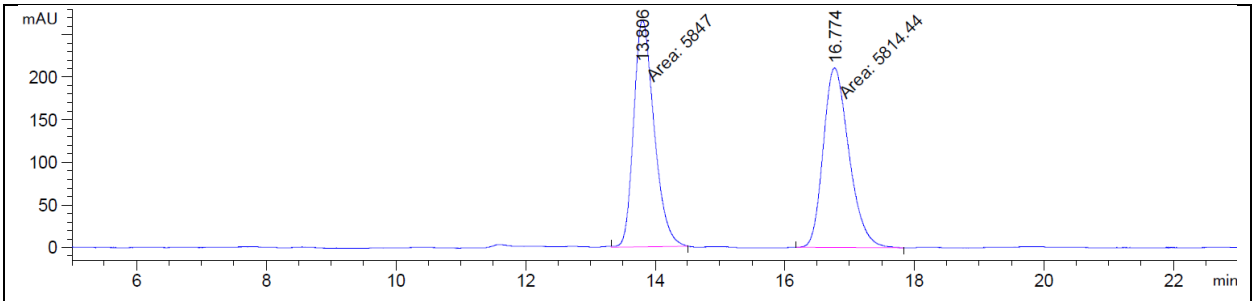


1b 1.5 equiv. **2n'** 1.0 equiv. **13** 11% yield, 91% e.e.

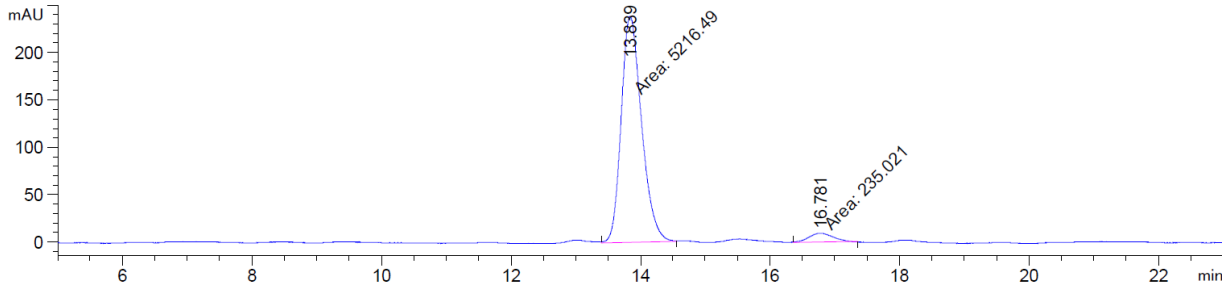
The reaction was conducted in 0.2 mmol scale following **GP4**, with **1b** (81 mg, 0.30 mmol, 1.50 equiv.) and 6-iodohex-1-ene (**2n'**) (42 mg, 0.20 mmol, 1.00 equiv.) as coupling partners. Purification by preparative TLC (SiO_2, 60:1 hexane:EtOAc) afforded compound **(-) 13** as a colorless oil (8 mg, 11%). The analogous compound with no cyclization was detected but could not be purified. **^{1}H 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). **^{13}C 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. **^{11}B NMR** (128 MHz, Chloroform-*d*) δ 35.31. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M + Na]^+$ Calcd for $C_{23}H_{37}BNaO_2^+$ 379.2779; Found 379.2788 . **$[\alpha]_D^{20}$** = -1.2 (c = 1.00 in $CHCl_3$).

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.

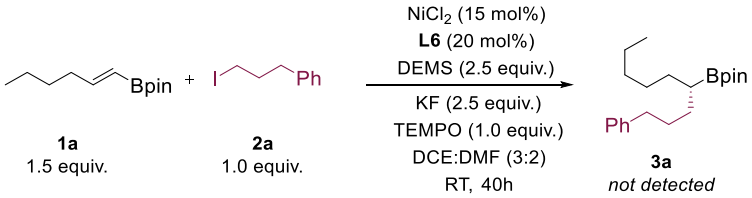


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.806	MM	0.3664	5847.00488	265.96167	50.1396
2	16.774	MM	0.4603	5814.44141	210.54149	49.8604



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.839	MM	0.3643	5216.48975	238.63029	95.6889
2	16.781	MM	0.4256	235.02074	9.20381	4.3111

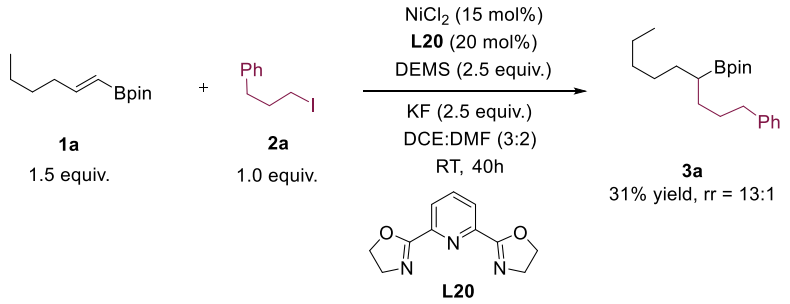
12.5 TEMPO quenching experiment:



1a 1.5 equiv. **2a** 1.0 equiv. **3a** *not detected*

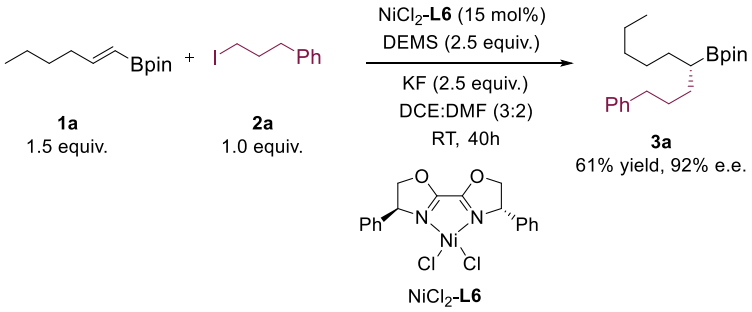
The reaction was conducted following **GP4**. TEMPO (15.6 mg, 0.10 mmol, 1.0 equiv.) was added after the addition of all reagents. The hydroalkylation product was not detected.

12.6 Probe for origin of regioselectivity:



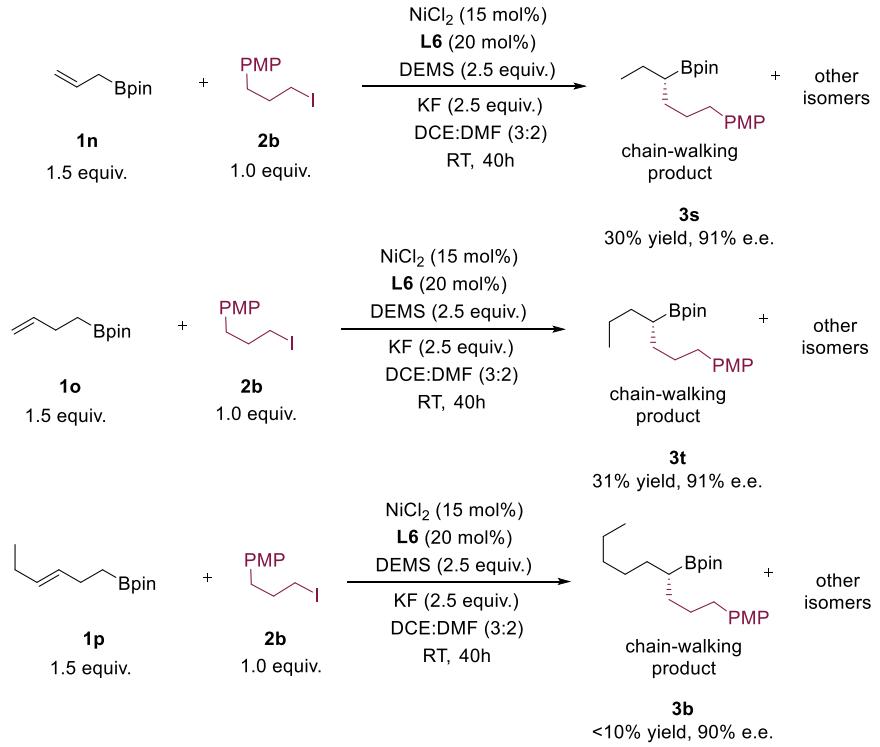
See main text for design of experiments. The reaction was conducted following **GP4** using **L20** (4.3 mg, 0.02 mmol, 0.20 equiv.) instead of **L6**. The regioselectivity was found to be 13:1 where **3a** was obtained in 31% yield.

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

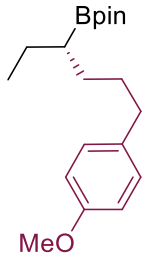


The $NiCl_2$-**L6** complex was prepared following a literature procedure with slight modification.[32] To a 20 mL oven-dried vial equipped with a magnetic stir bar in a glovebox was added $NiCl_2$•DME (46 mg, 0.21 mmol, 1.0 equiv.) and **L6** (73 mg, 0.25 mmol, 1.19 equiv.) and DCM (7.5 mL). The mixture 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:

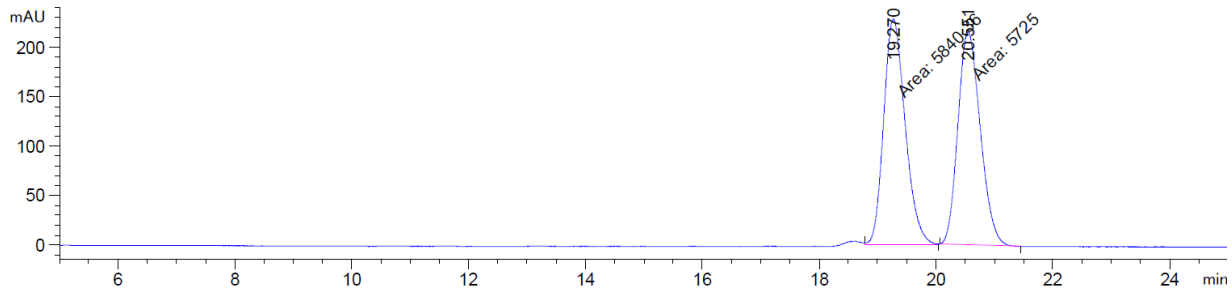


(S)-2-(6-(4-Methoxyphenyl)hexan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) 3s)

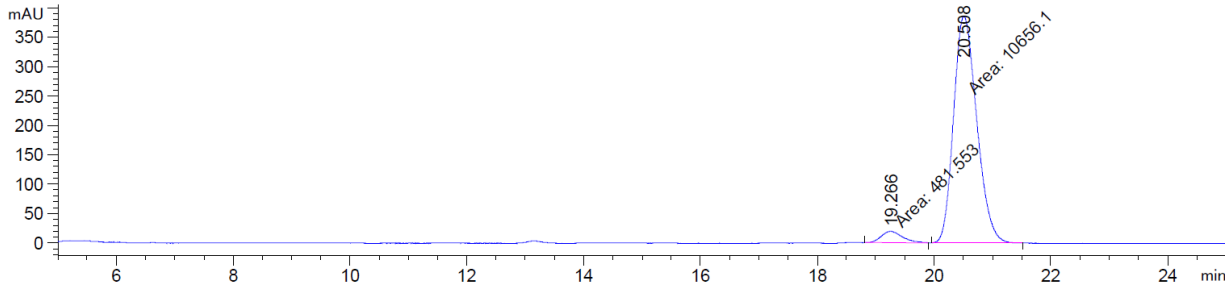


Prepared according to **GP4** with **1n** (30.0 µL, 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Purification by PTLC (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 3s** as a colorless oil (10 mg, 30%). The other regioisomeric products were also formed in this reaction 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}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}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}B NMR** (128 MHz, Chloroform-*d*) δ 35.15. **HRMS (APPI/LTQ-Orbitrap)** m/z: $[M]^+$ Calcd for $C_{19}H_{31}BO_3^+$ 318.2361; Found 318.2375. **$[\alpha]_D^{20}$** = +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_{major} = 20.5 min and t_{minor} = 19.3 min.

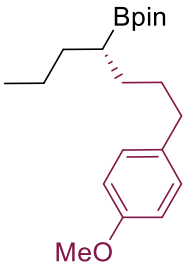


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.270	MM	0.4262	5840.36377	228.39580	50.4988
2	20.551	MM	0.4432	5724.99658	215.28188	49.5012



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.266	MM	0.4195	481.55267	19.12977	4.3236
2	20.508	MM	0.4597	1.06561e4	386.34412	95.6764

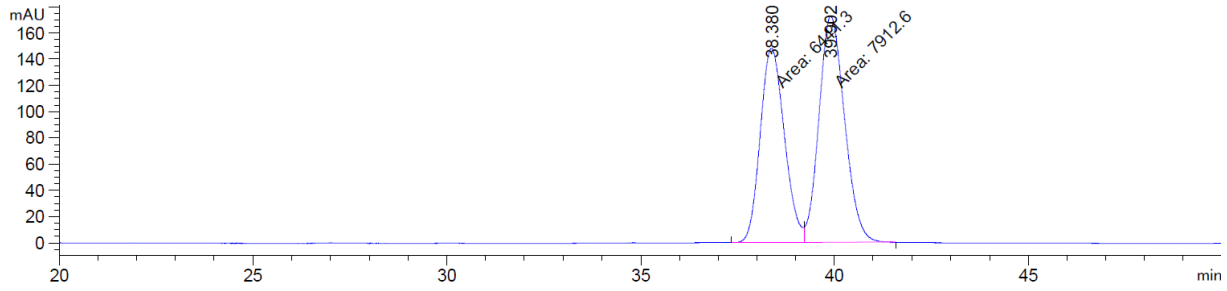
(S)-2-(1-(4-Methoxyphenyl)heptan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane ((+) 3t)



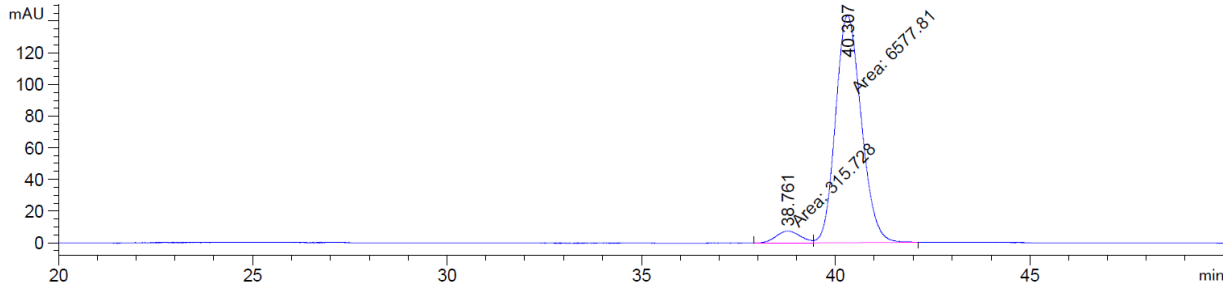
Prepared according to **GP4** with **1o** (27.0 mg, 0.15 mmol, 1.50 equiv.), **2b** (28.0 mg, 0.10 mmol, 1.00 equiv.). Purification by PTLC (SiO_2, 60:1 hexane:EtOAc) afforded the desired product **(+) 3t** as a colorless oil (11 mg, 31%). The other regioisomeric products were also formed in this reaction 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). **^{1}H 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). **^{13}C 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: $[M]^+$ Calcd for $C_{20}H_{33}BO_3^+$ 332.2517; Found 332.2527. $[\alpha]_D^{20}$ = +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_{major} = 40.3 min and t_{minor} = 38.7 min.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.380	MF	0.7240	6441.29932	148.27286	44.8749
2	39.902	FM	0.7651	7912.59912	172.36314	55.1251

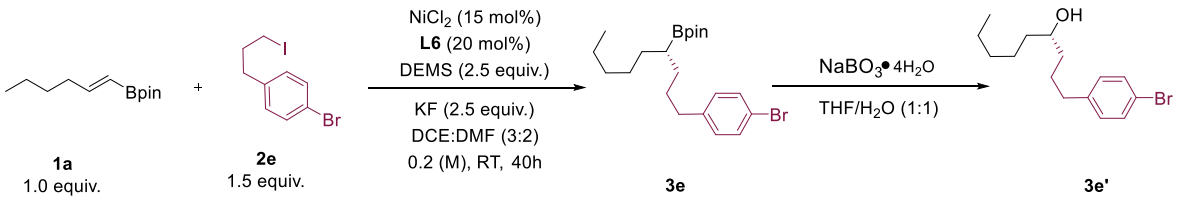


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	38.761	MF	0.7116	315.72800	7.39482	4.5801
2	40.307	FM	0.7643	6577.81006	143.44547	95.4199

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 crystalized 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.

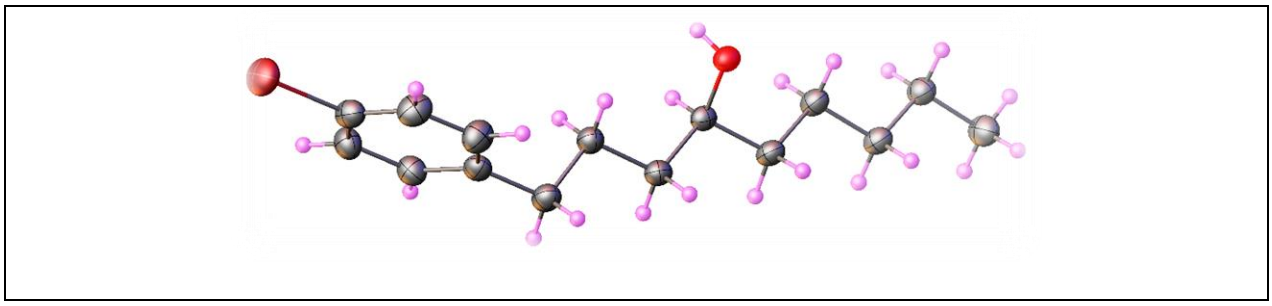
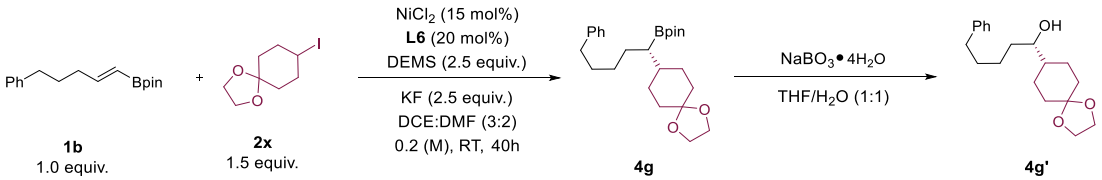


Fig. Crystal structure of **3e'**

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 crystalized 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.

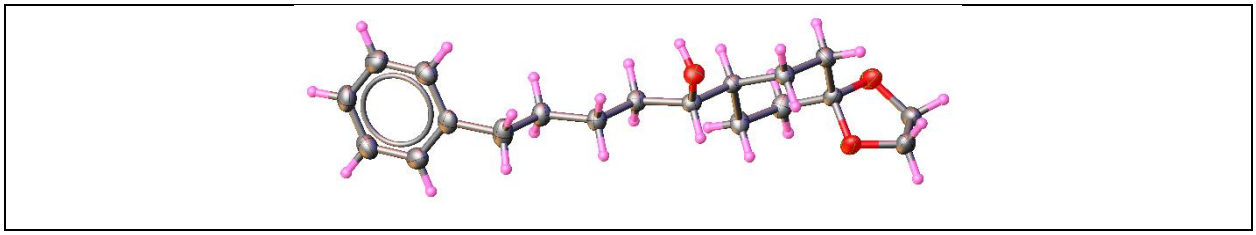


Fig. Crystal structure of **4g'**

15. Crystallography details

3e'

Experimental. Single colourless prism crystals of **3e'** were used as supplied. A suitable crystal with dimensions 0.35 × 0.17 × 0.04 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) 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 $\boldsymbol{F^2}$.

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

$\Theta_{min}/^{\circ}$	4.647
$\Theta_{max}/^{\circ}$	76.118
Measured Refl's.	14280
Ind't Refl's	3058
Refl's with I > 2σ(I)	3024
R_{int}	0.0217
Parameters	160
Restraints	1
Largest Peak/e Å^{-3}	0.226
Deepest Hole/e Å^{-3}	-0.251
GooF	1.059
wR_2 (all data)	0.0519
wR_2	0.0517
R_1 (all data)	0.0195
R_1	0.0193

Structure Quality Indicators

Reflections: d min (Cu) CIF 0.79 | I/σ CIF 68.0 | Rint 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 × 0.17 × 0.04 mm^3 was mounted. Data were collected using a SuperNova, Dual, Cu at home/near, AtlasS2 diffractometer operating at T = 140.00(10) 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 Θ = 76.118° (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 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 (λ = 1.54184Å) 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 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 0.75×0.39×0.17 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) 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 $|\boldsymbol{F}|^2$.

Compound	**4g'**
Formula	$C_{19}H_{28}O_3$
$D_{calc.}$/ g cm^{-3}	1.174
μ/mm^{-1}	0.613
Formula Weight	304.41
Colour	clear colourless
Shape	plate
Size/mm^3	0.75×0.39×0.17
T/K	139.94(12)
Crystal System	orthorhombic
Flack Parameter	0.04(16)
Space Group	$P2_12_12_1$

a/Å	5.30185(5)
b/Å	9.59127(10)
c/Å	33.8681(3)
α/°	90
β/°	90
γ/°	90
V/Å^3	1722.24(3)
Z	4
Z'	1
Wavelength/Å	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 Å^{-3}	0.215
Deepest Hole/e Å^{-3}	-0.123
GooF	1.059
wR_2 (all data)	0.0711
wR_2	0.0709
R_1 (all data)	0.0254
R_1	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 (λ = 1.542Å) and the minimum and maximum transmissions are 0.468 and 1.000.

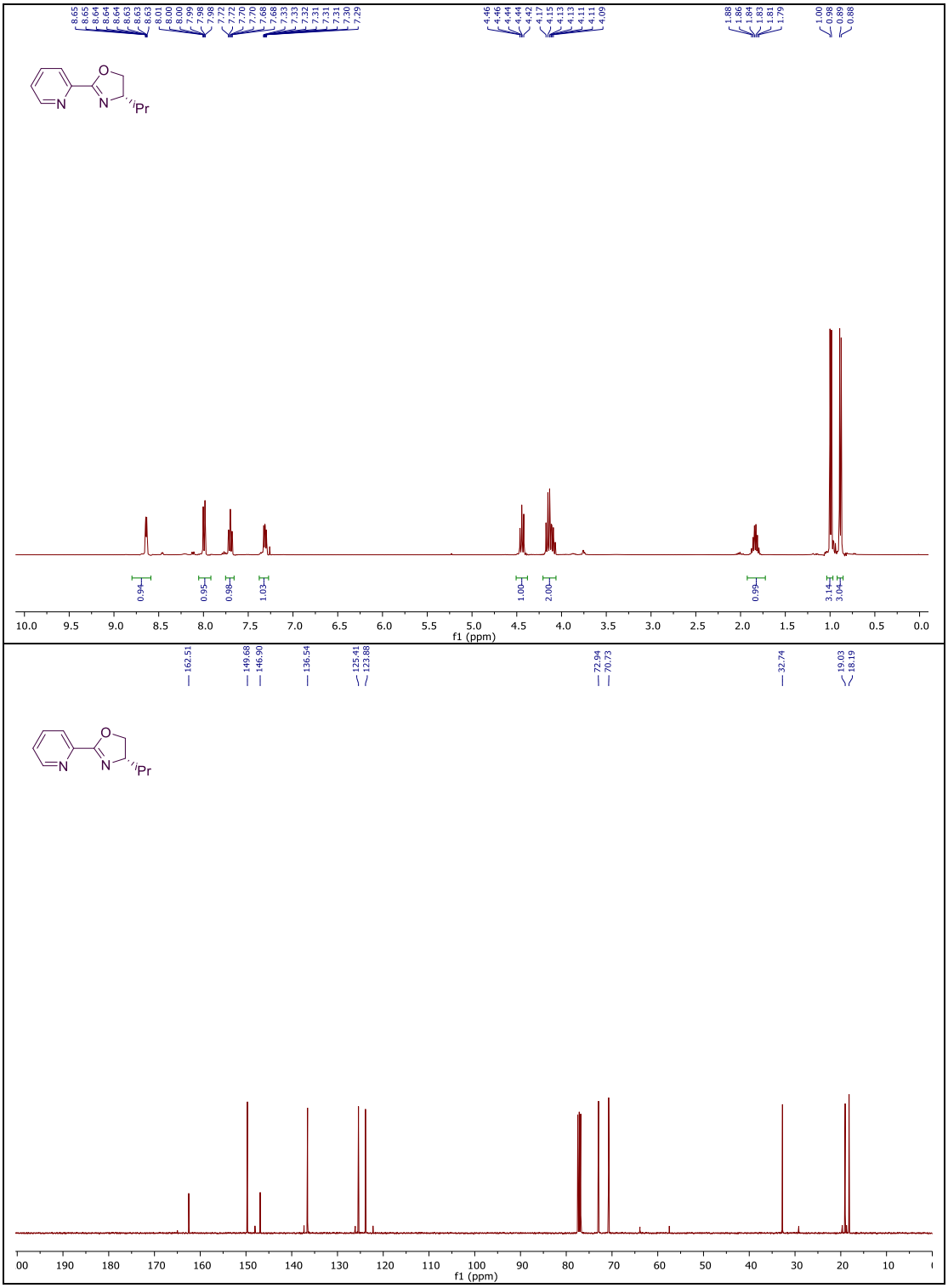
The structure was solved and the space group $P2_12_12_1$ (# 19) determined by the ShelXT 2018/2 structure solution program using dual methods and refined by full matrix least squares minimisation on $|F|^2$ using version 2018/3 of ShelXL 2018/3. All non-hydrogen atoms were refined anisotropically. Hydrogen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

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

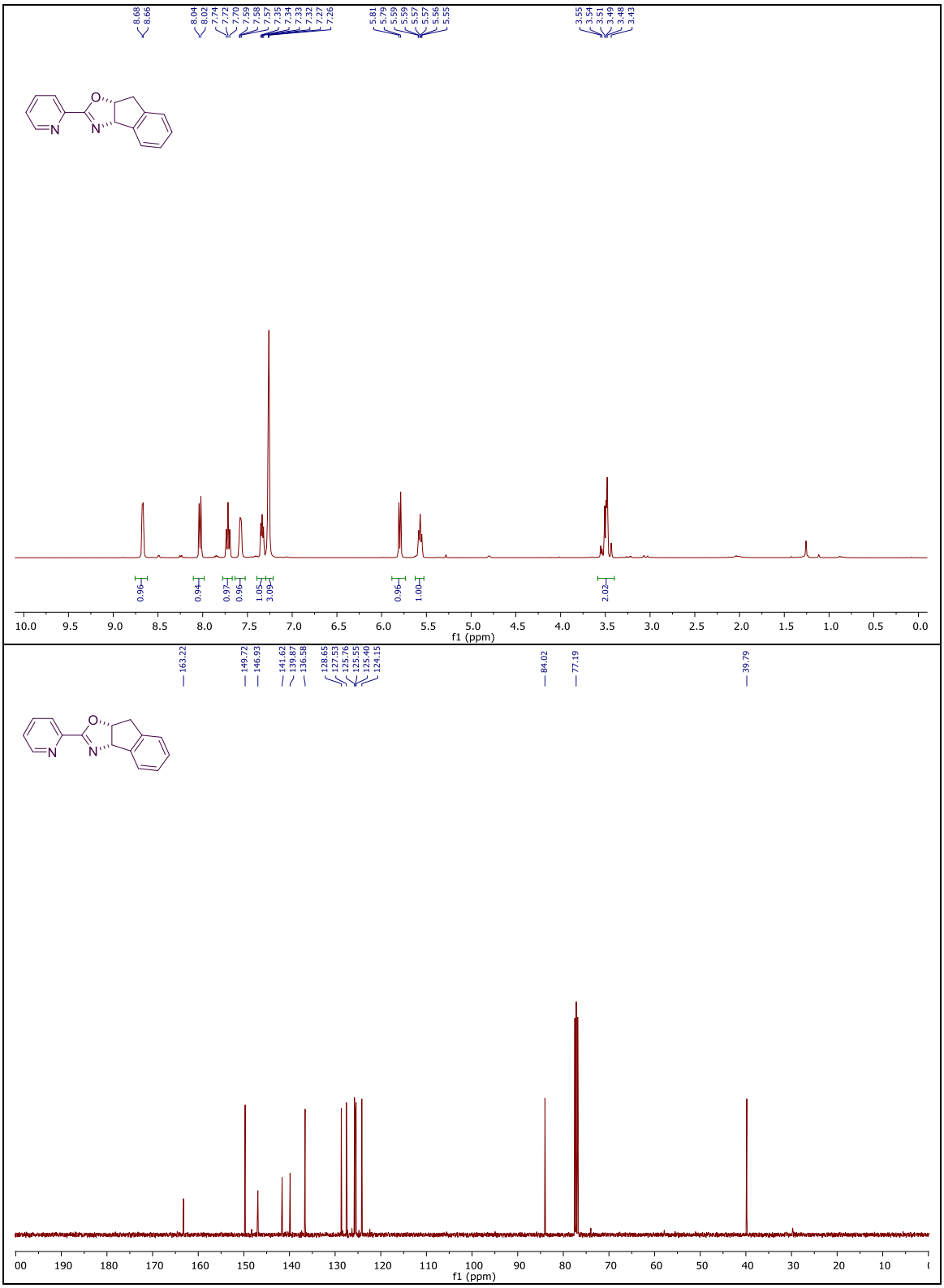
CCDC- 1971802 contains the supplementary crystallographic data for **4g'**. These data can be obtained free of charge from *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

16. NMR spectra

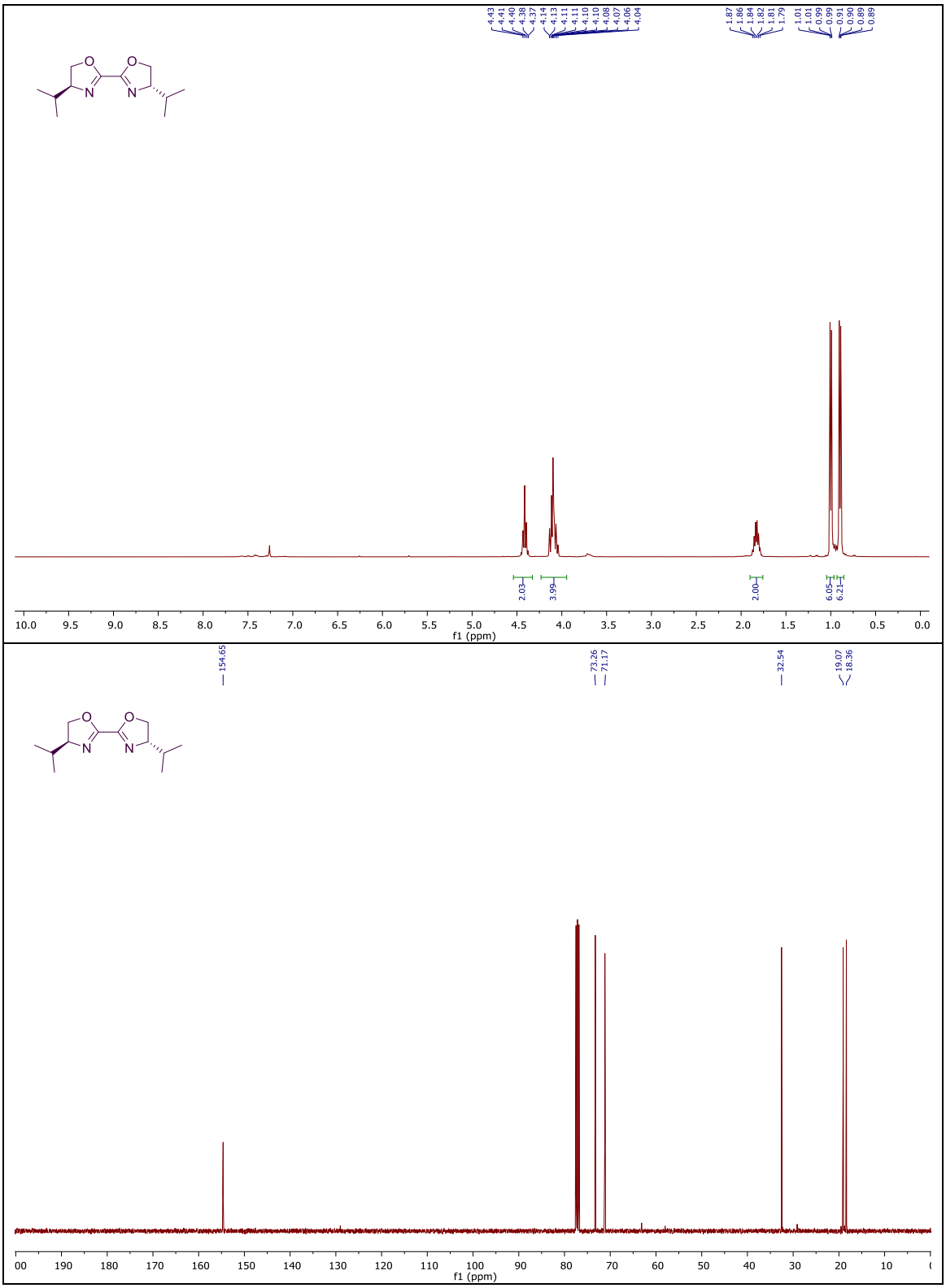
NMR spectra of L1



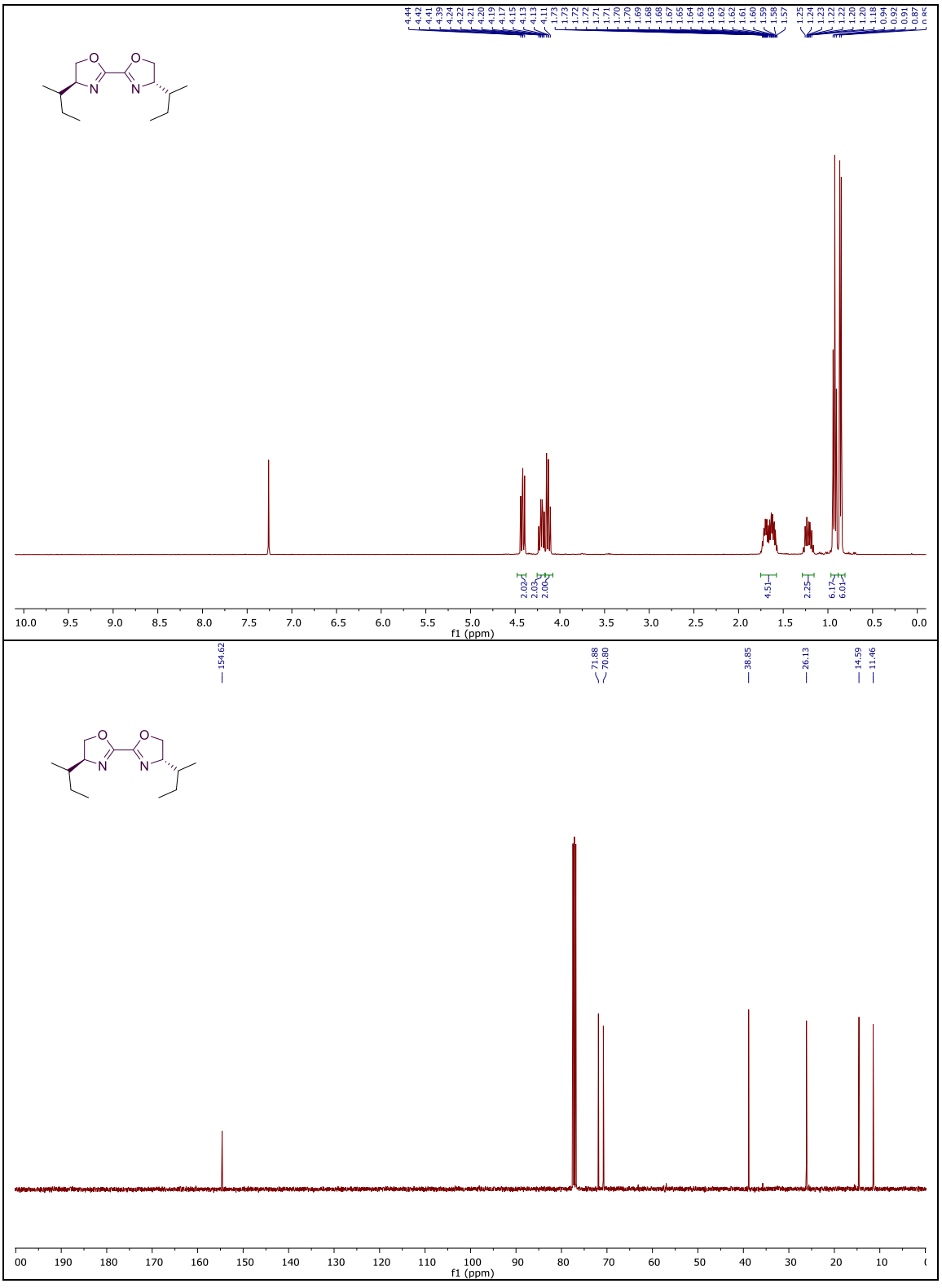
NMR spectra of L2



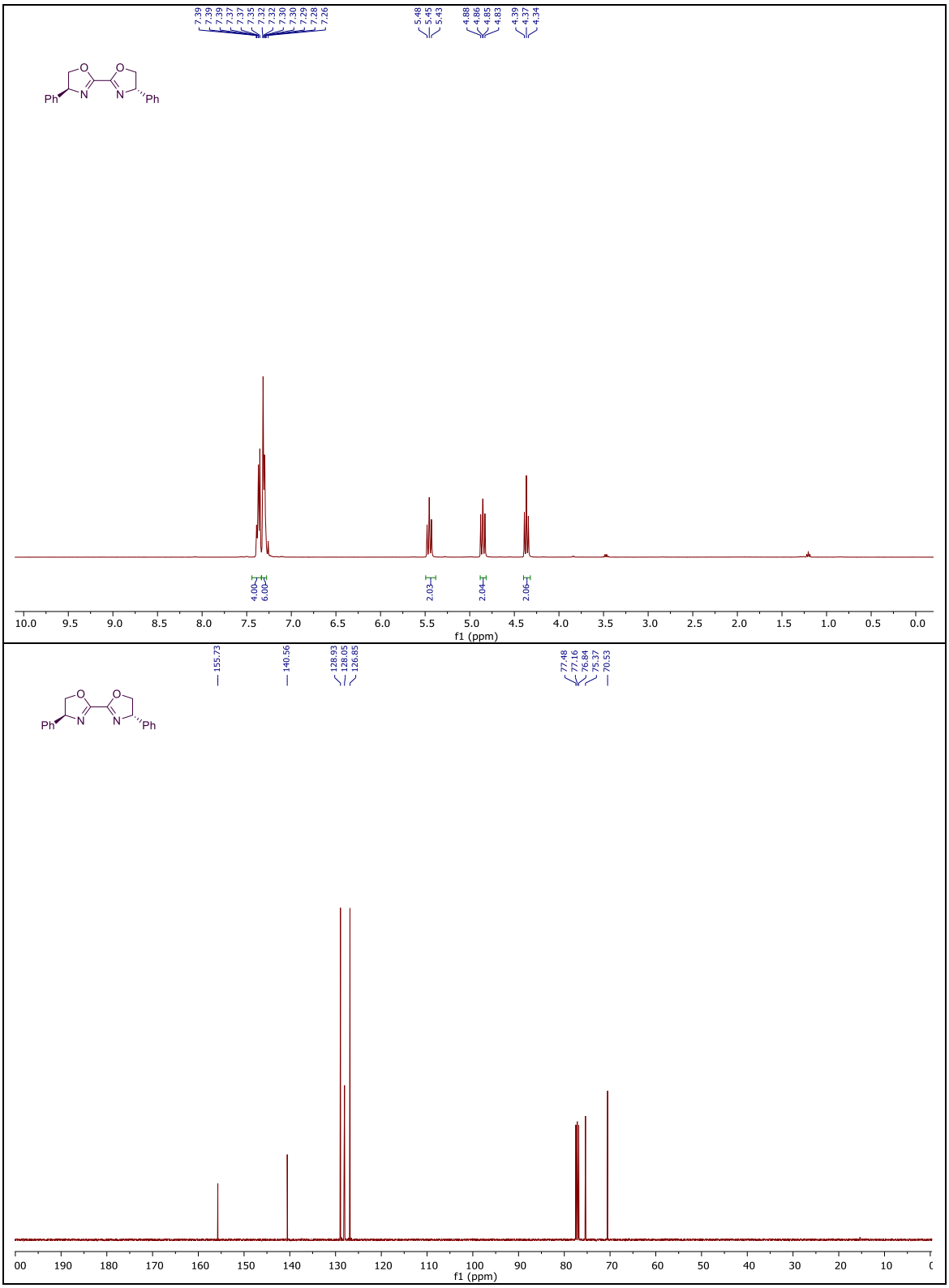
NMR spectra of L4



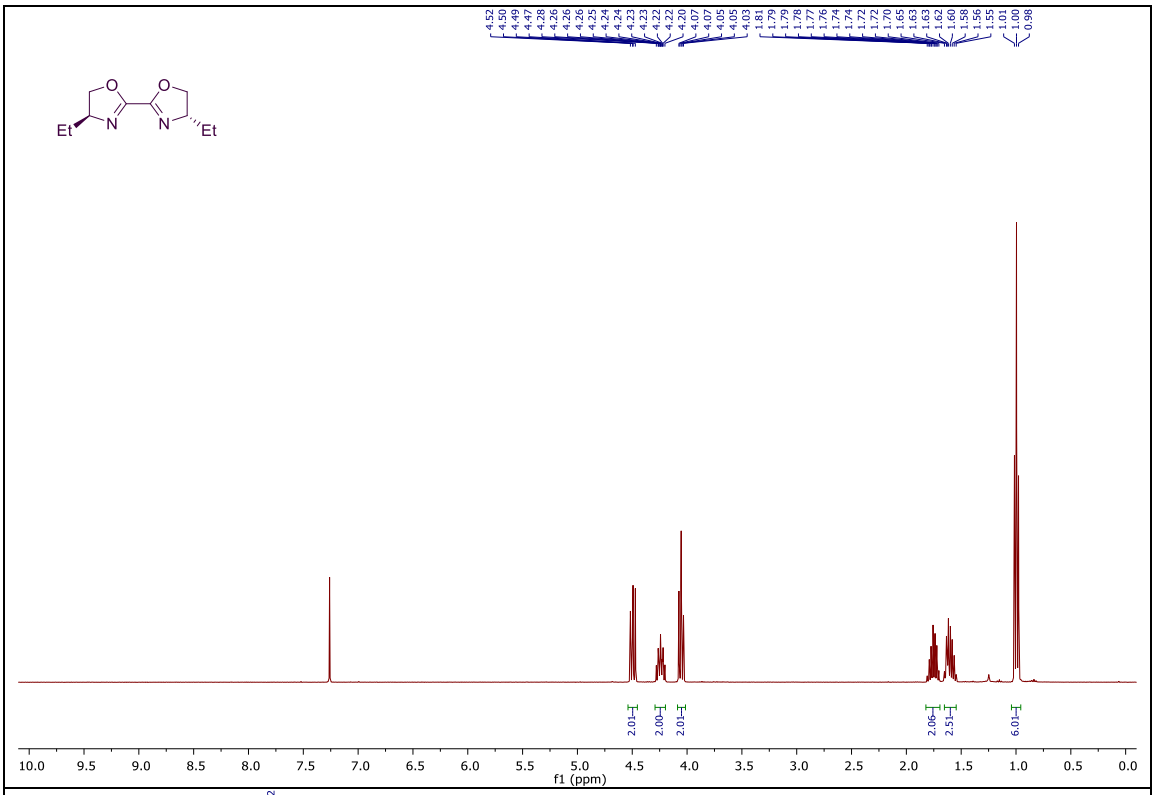
NMR spectra of L5

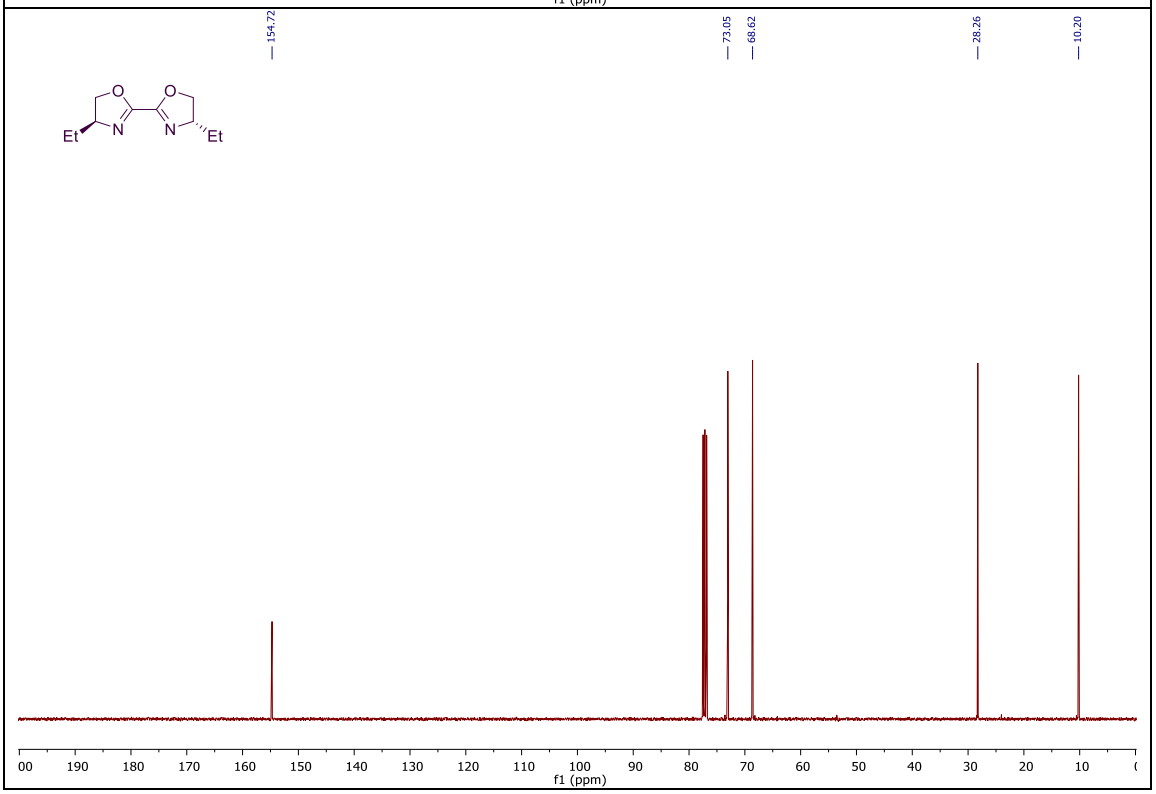


NMR spectra of L6

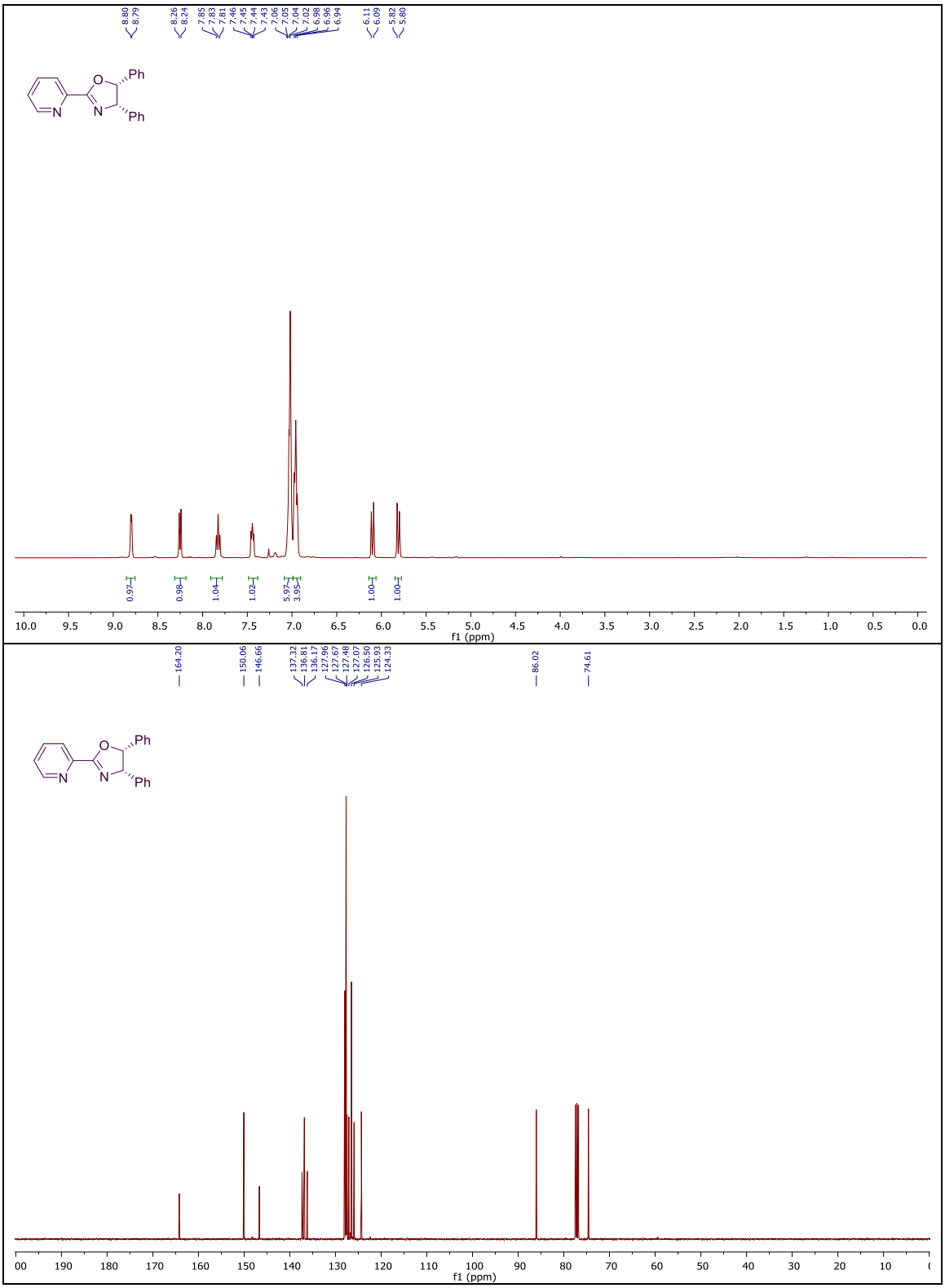


NMR spectra of L7

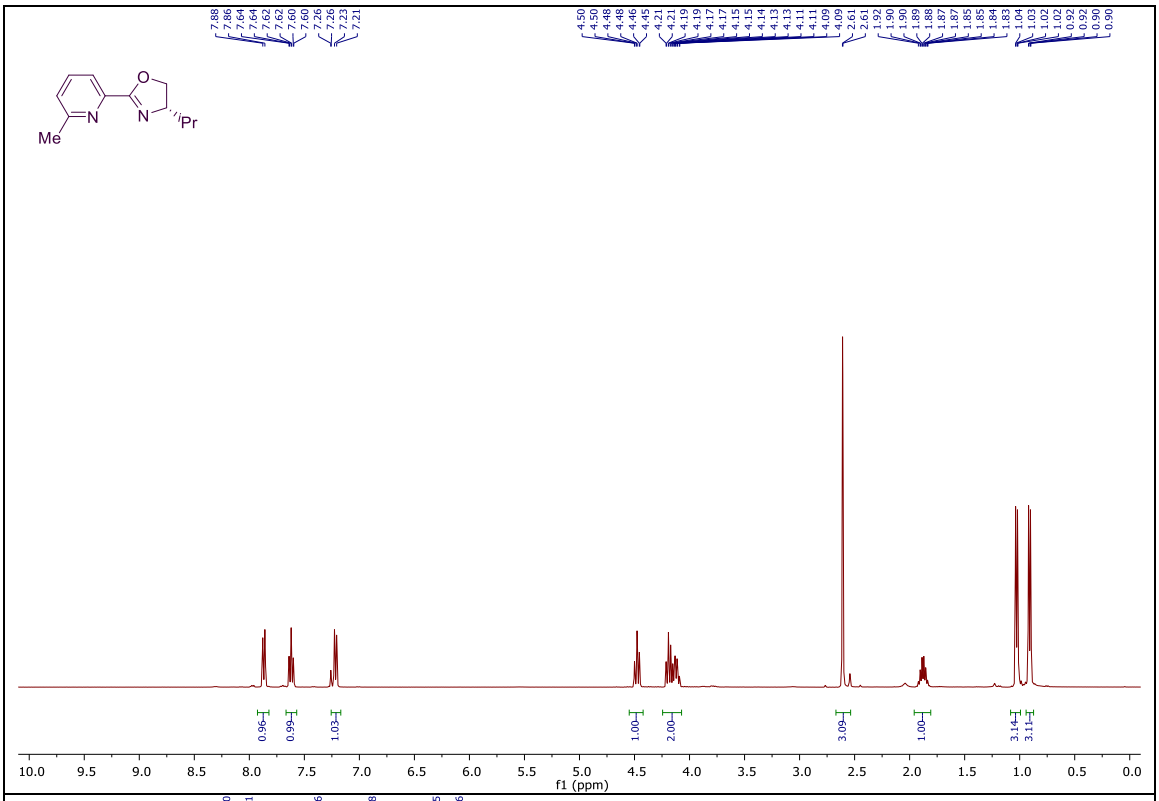


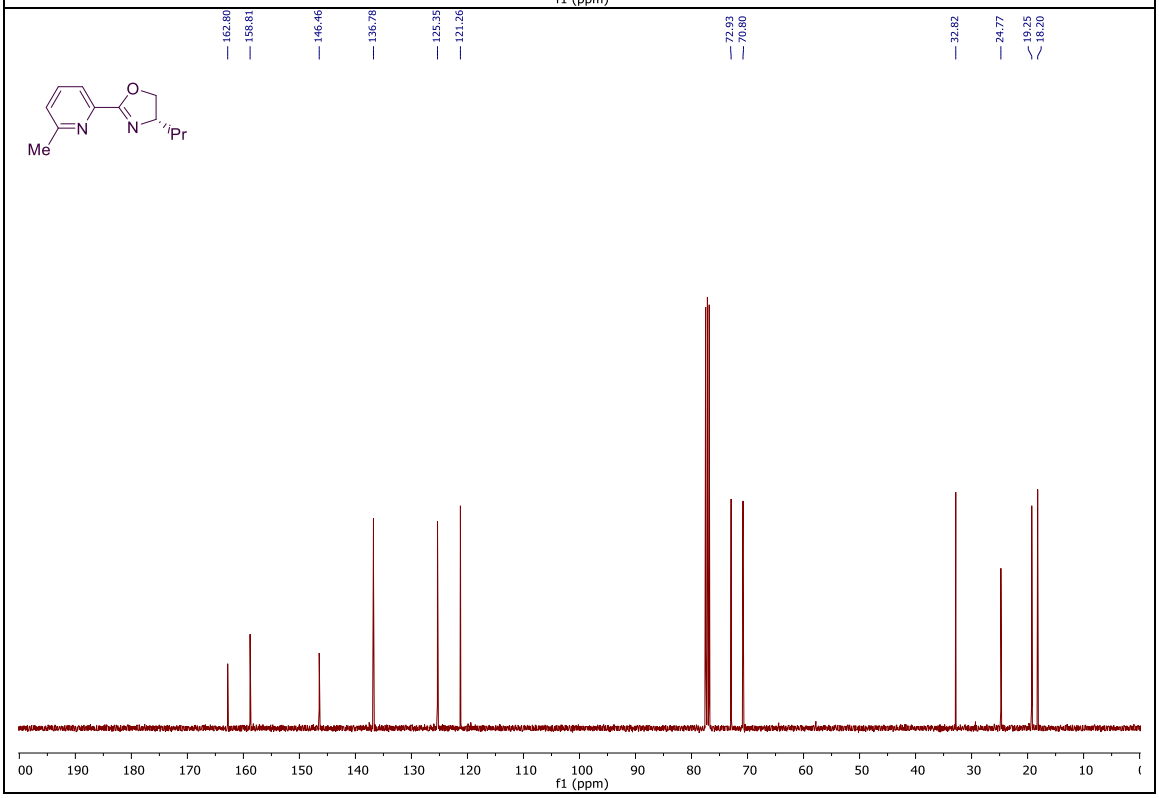


NMR spectra of L9

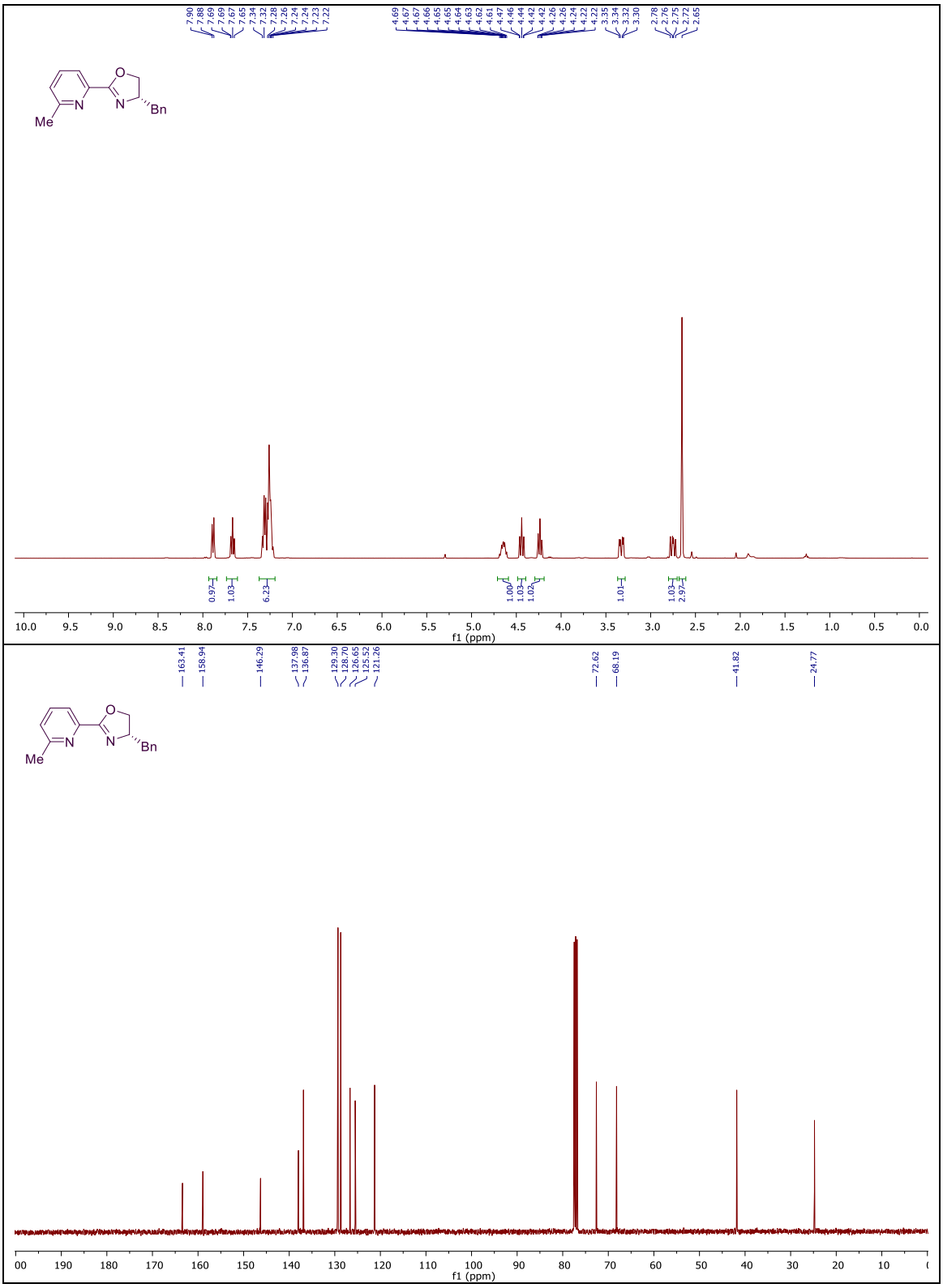


NMR spectra of L10

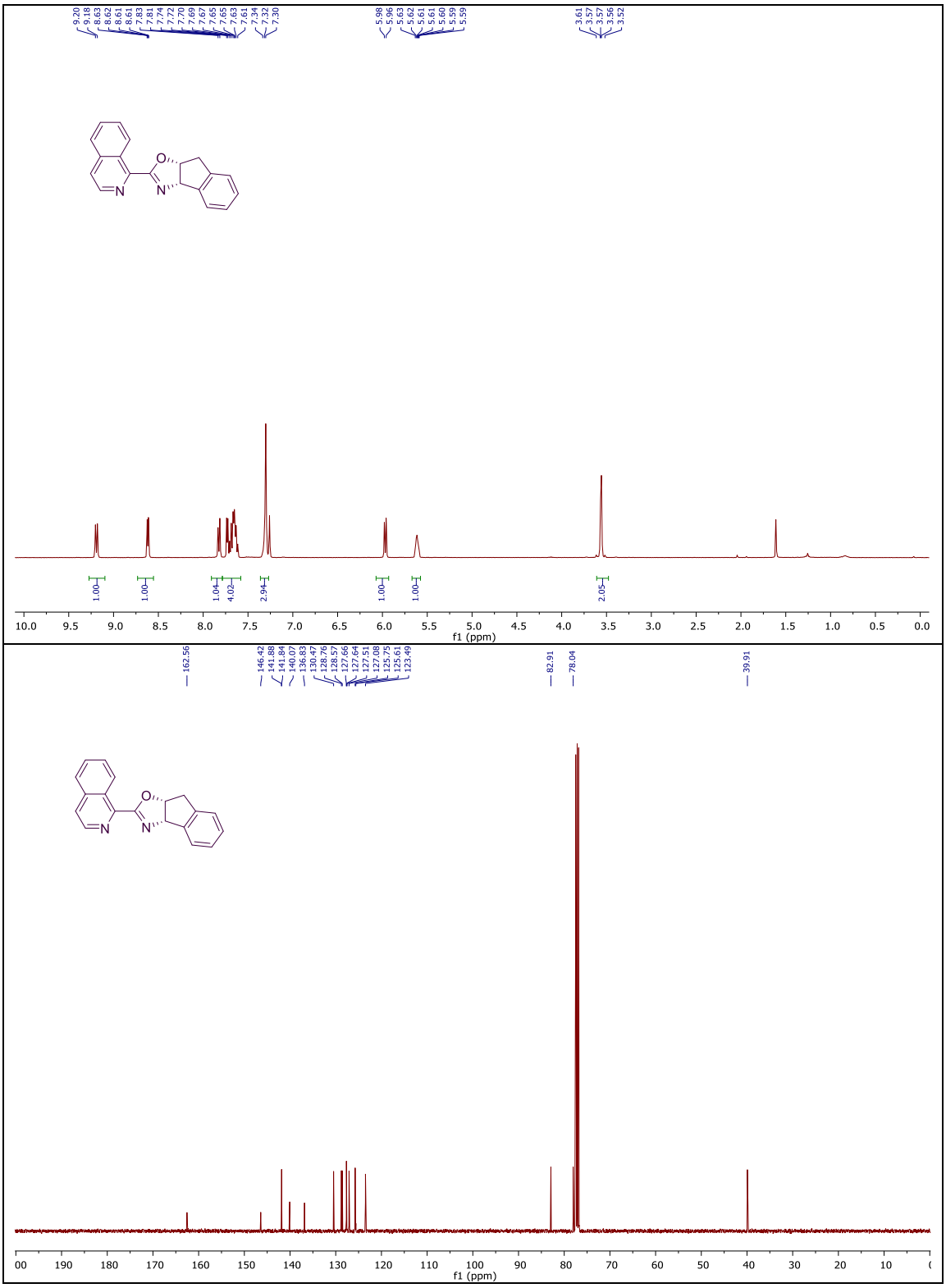




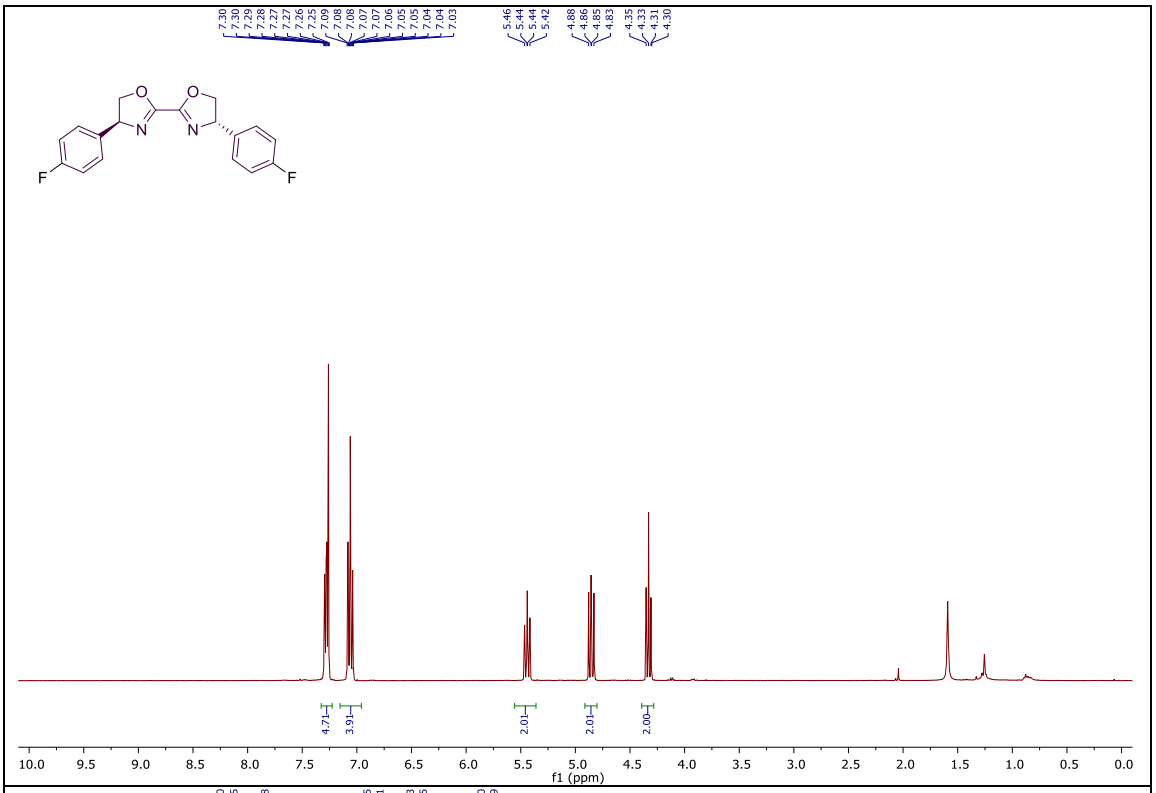
NMR spectra of L11

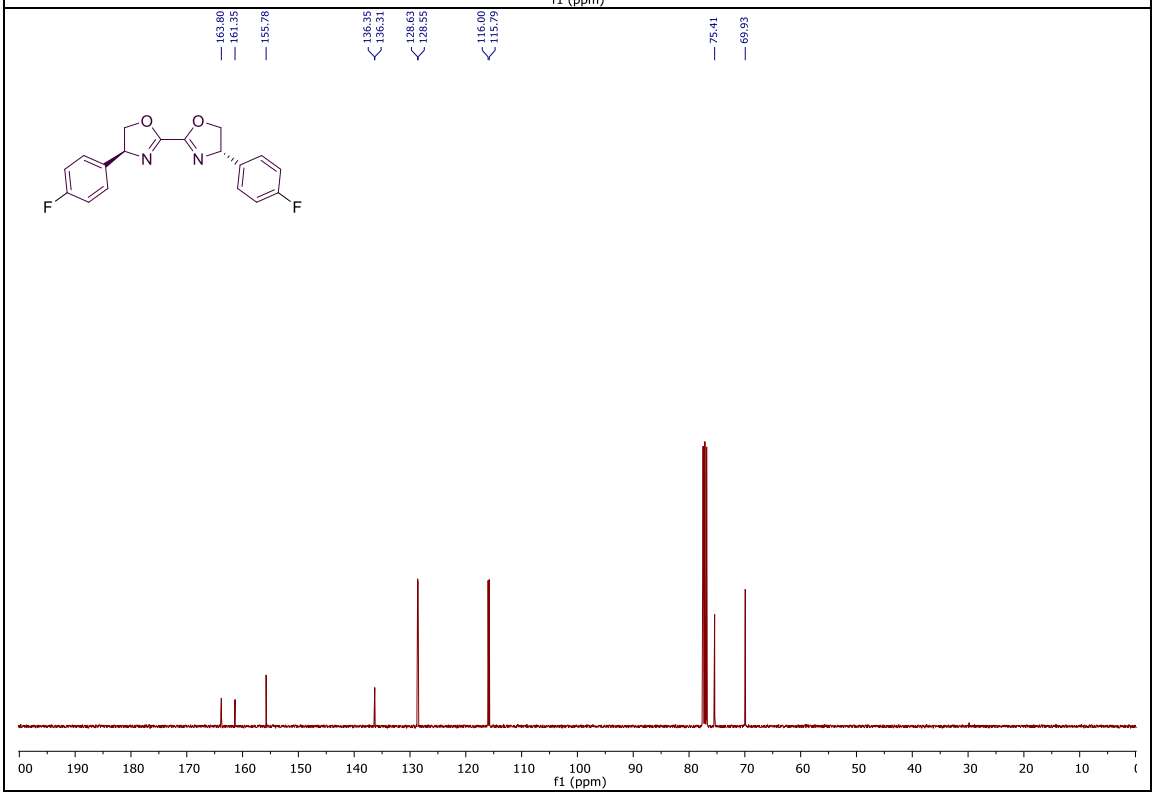


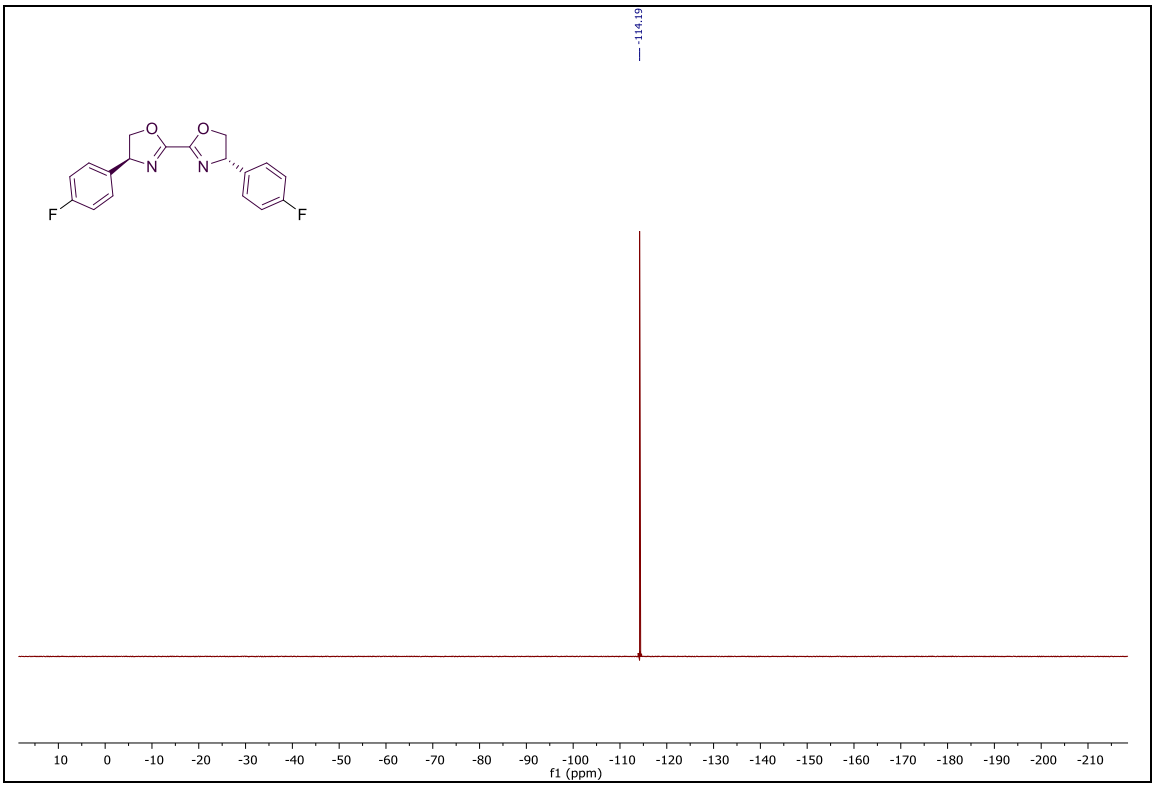
NMR spectra of L12



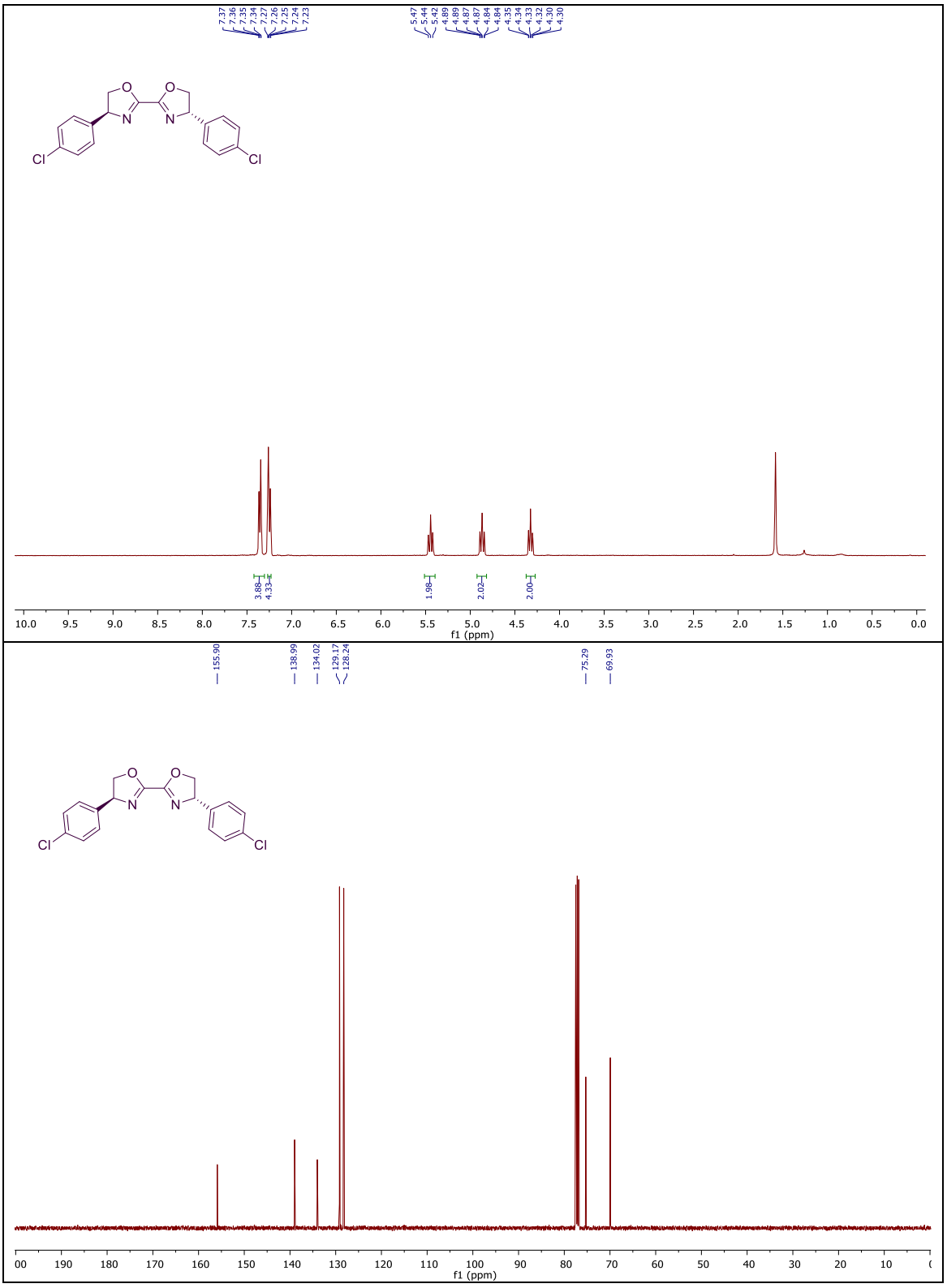
NMR spectra of L17



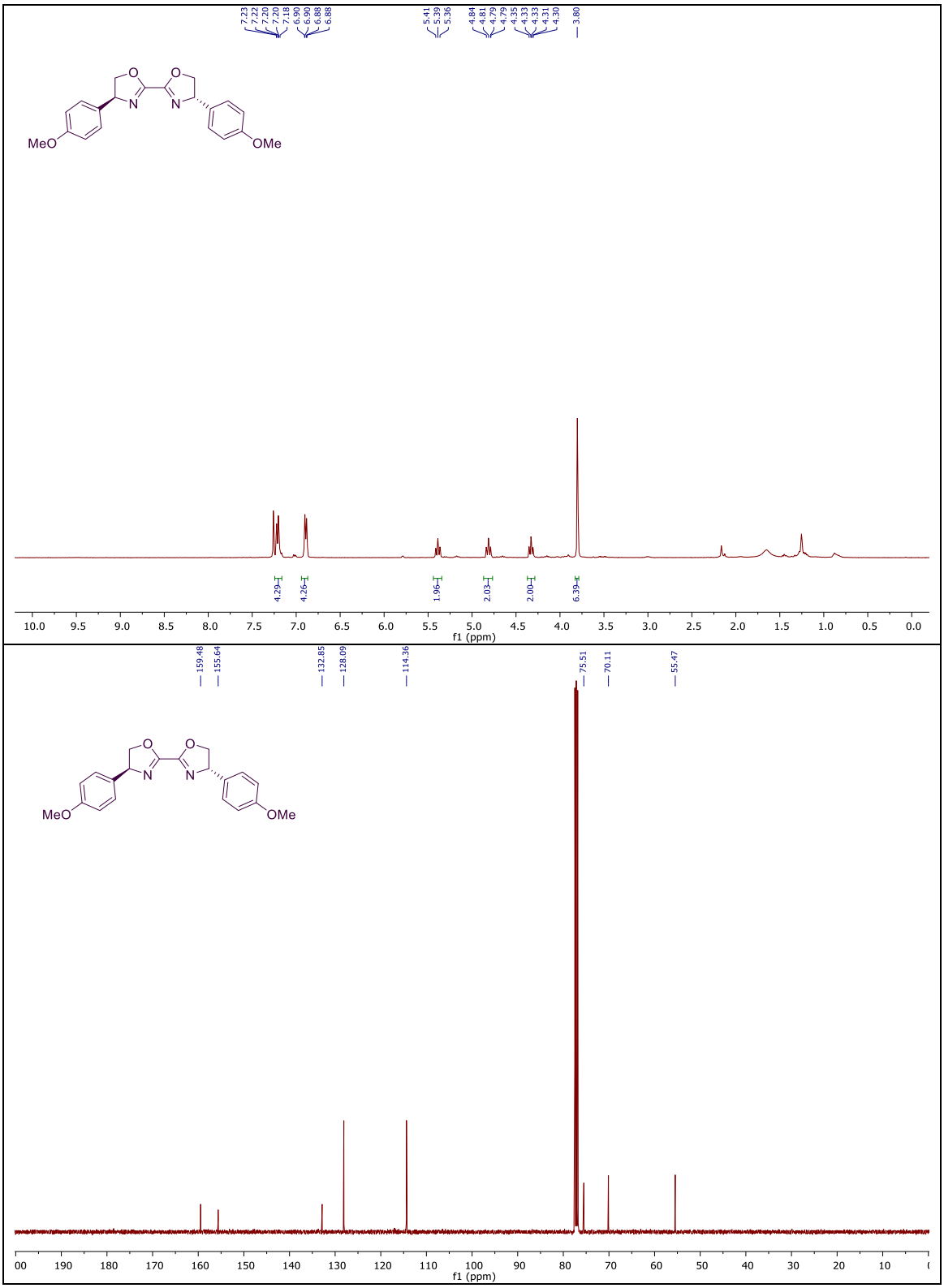



-114.19
O
O
N
N
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

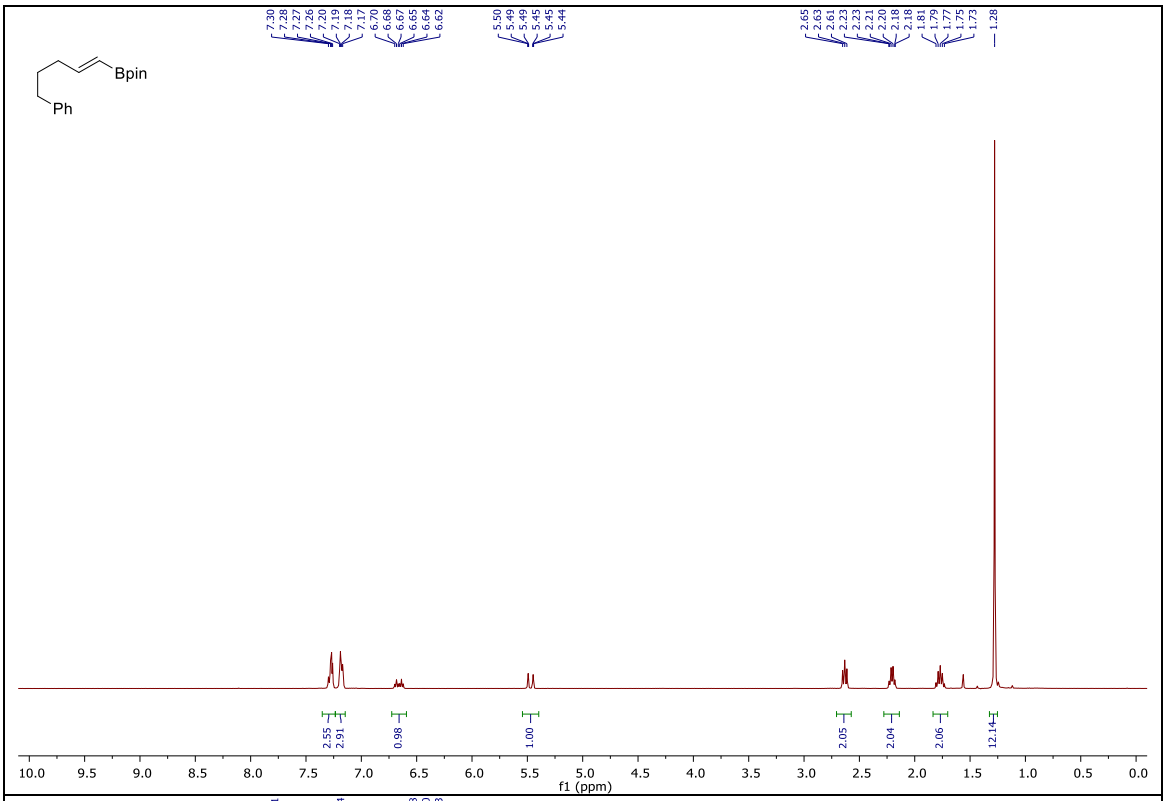
NMR spectra of L18

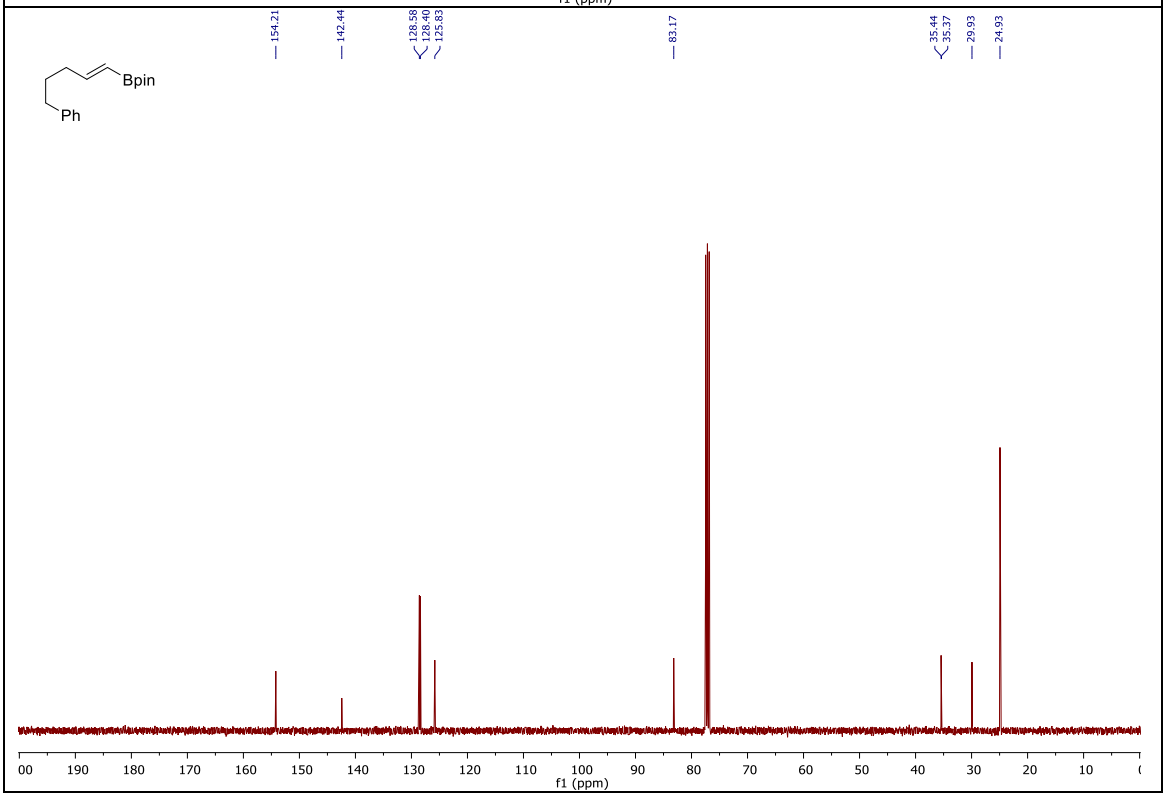


NMR spectra of L19

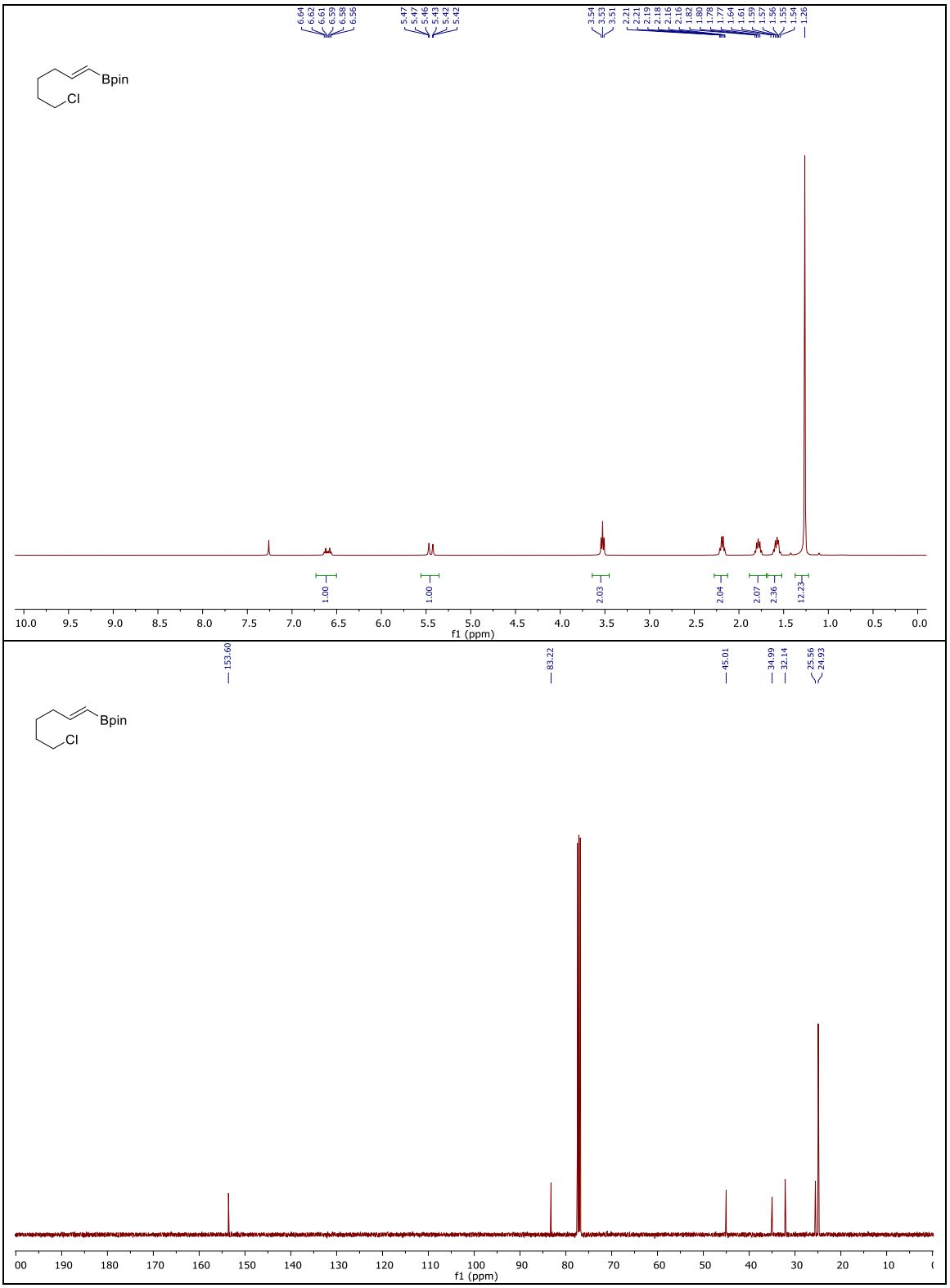


NMR spectra of 1b

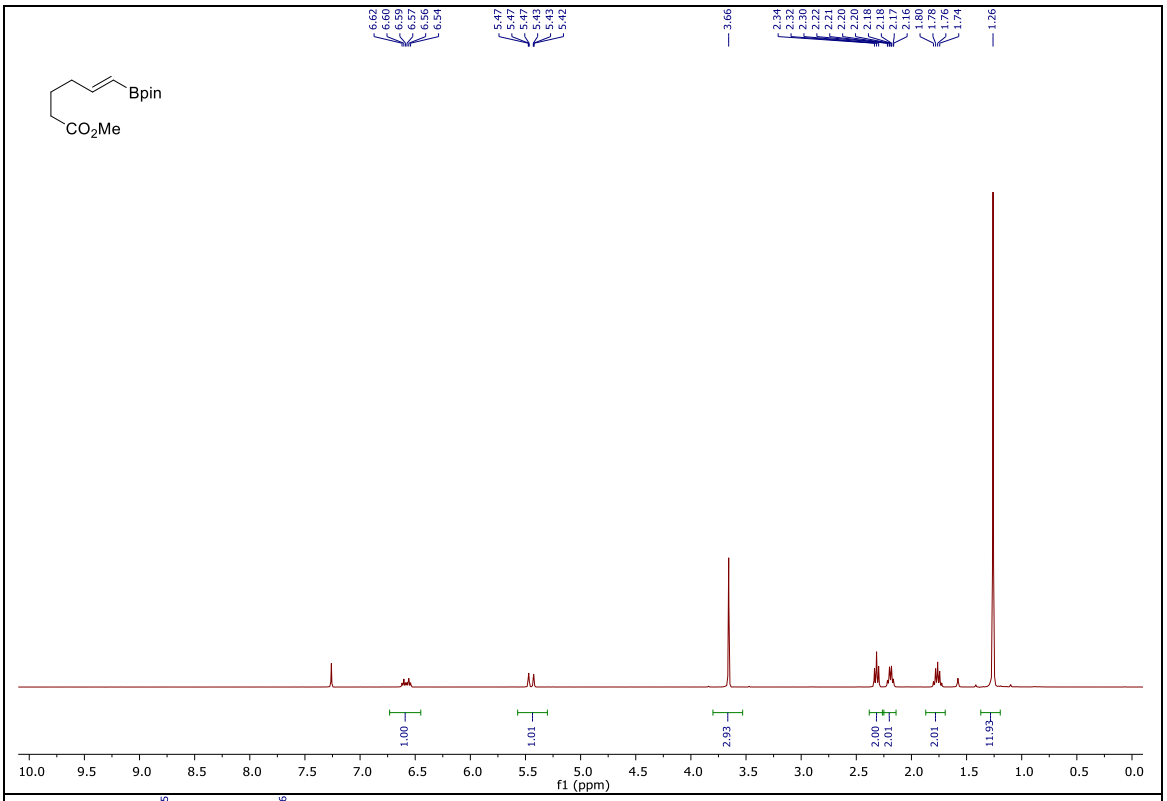


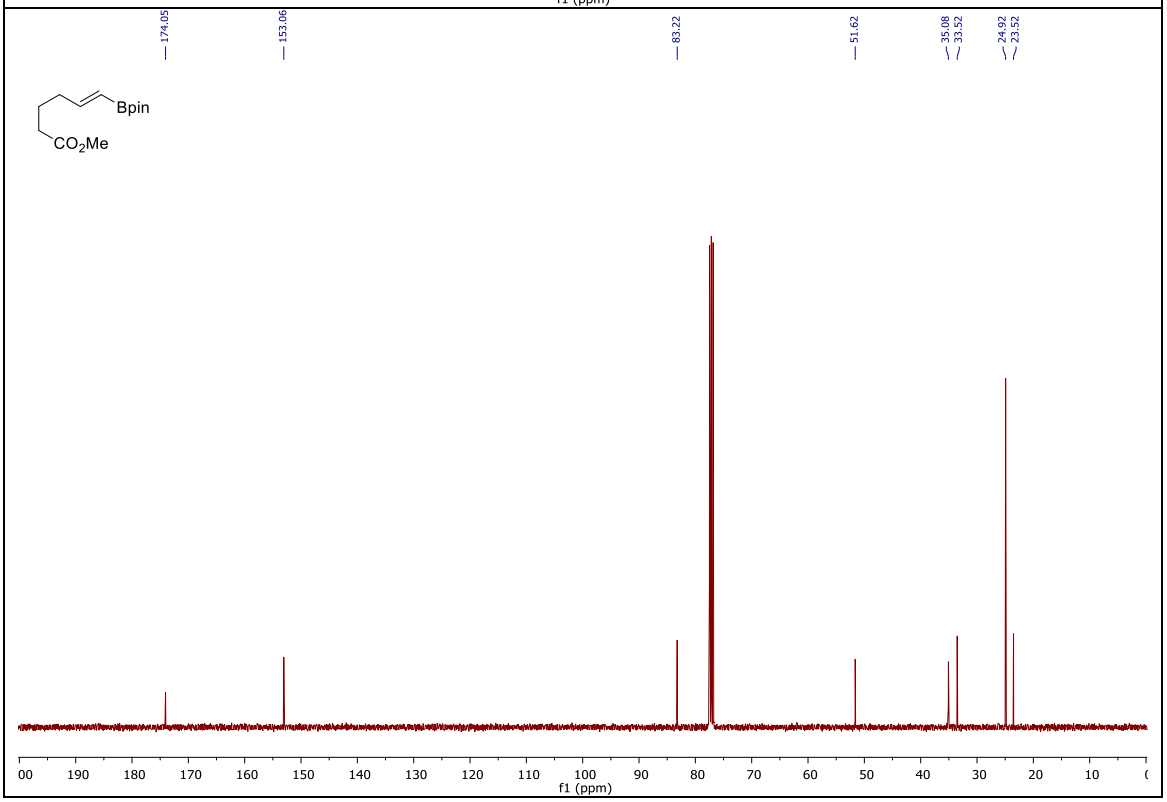


NMR spectra of 1c

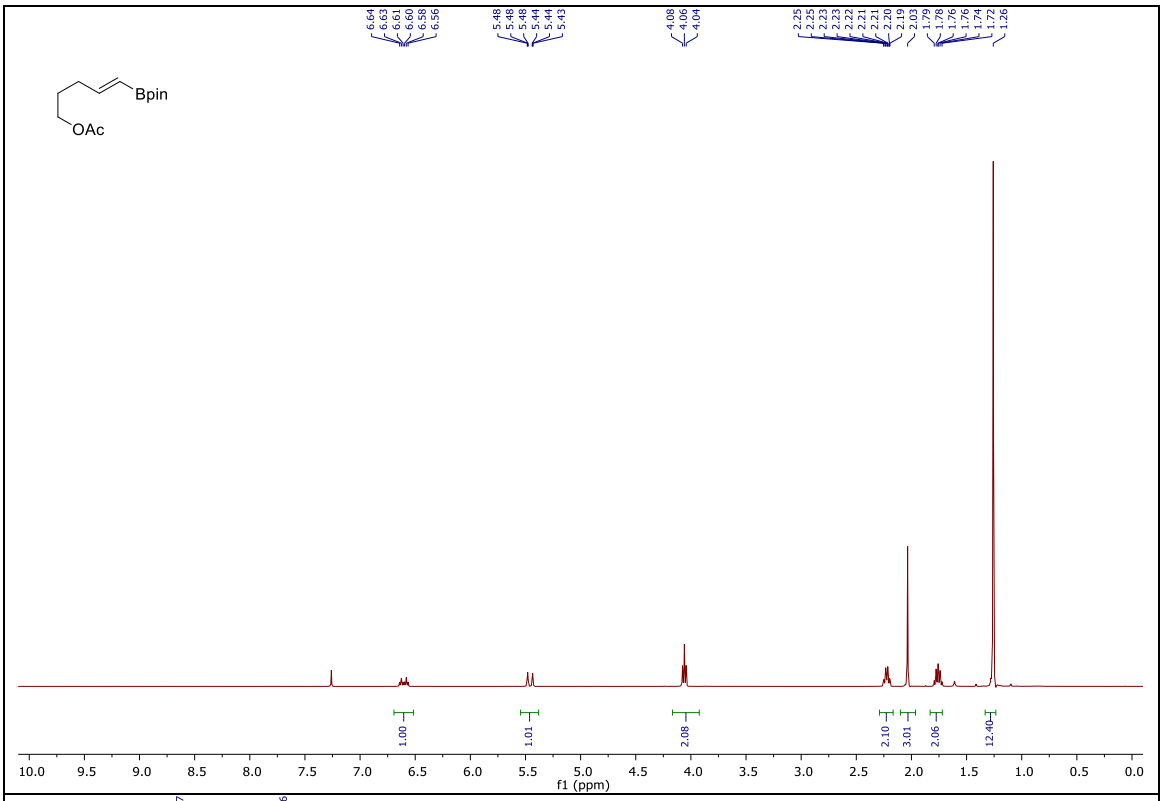


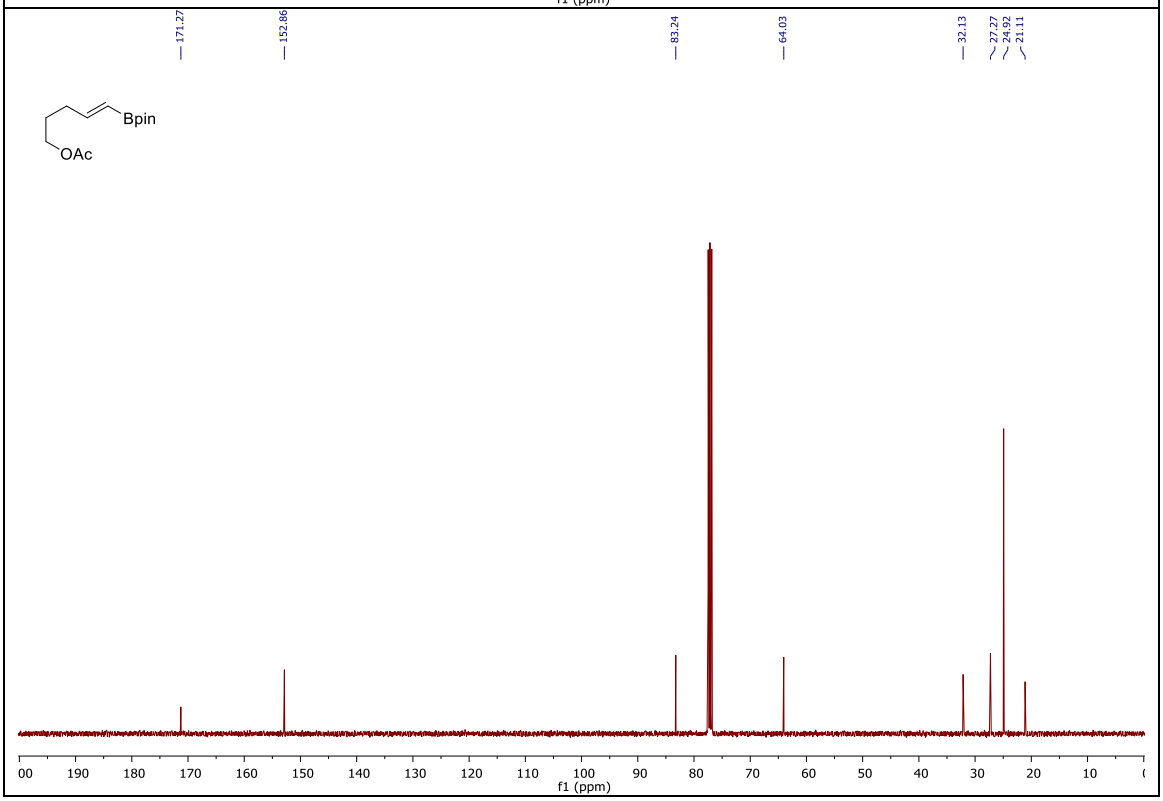
NMR spectra of 1d



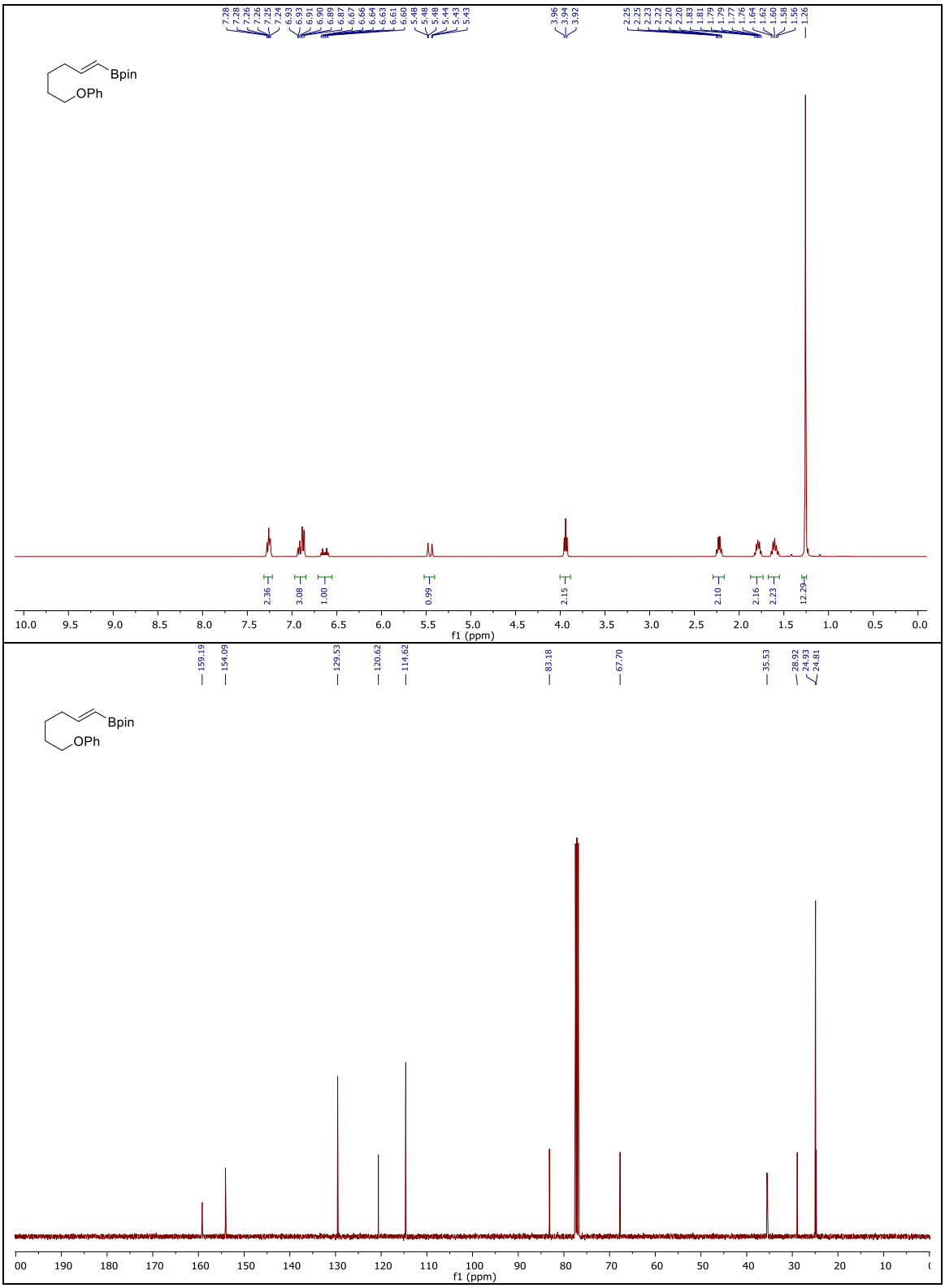


NMR spectra of 1e

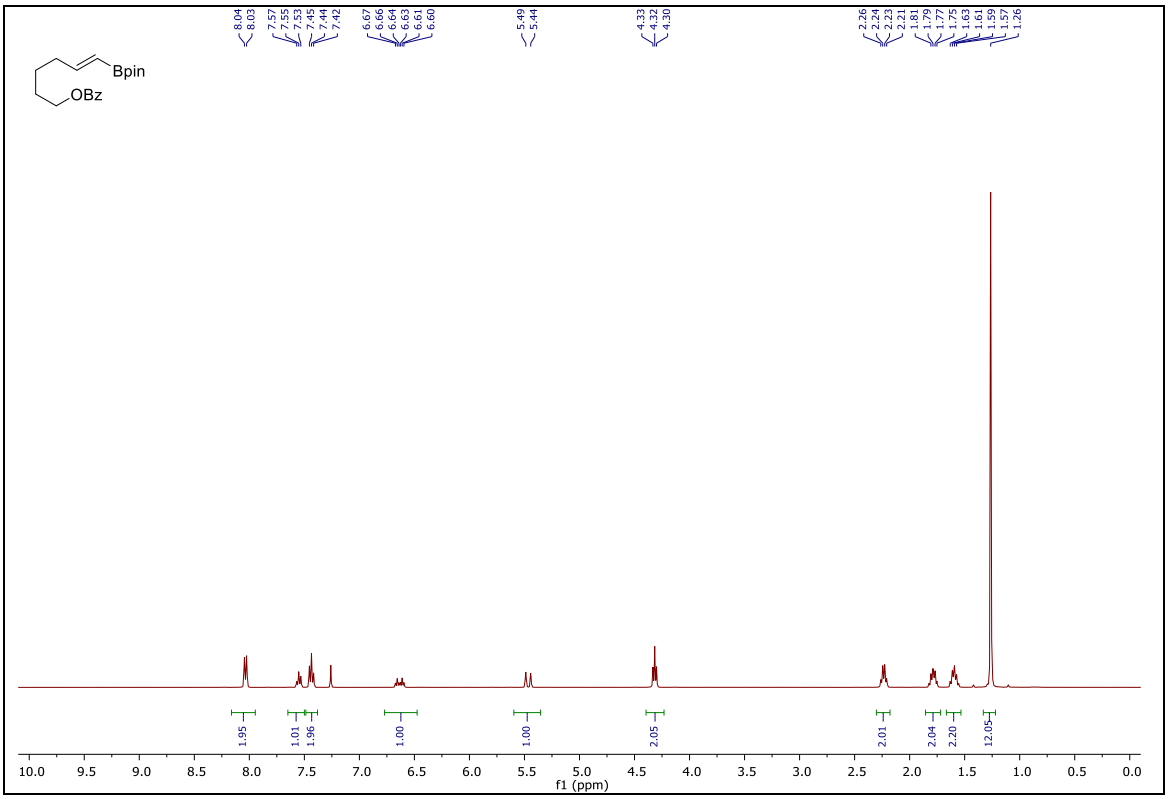


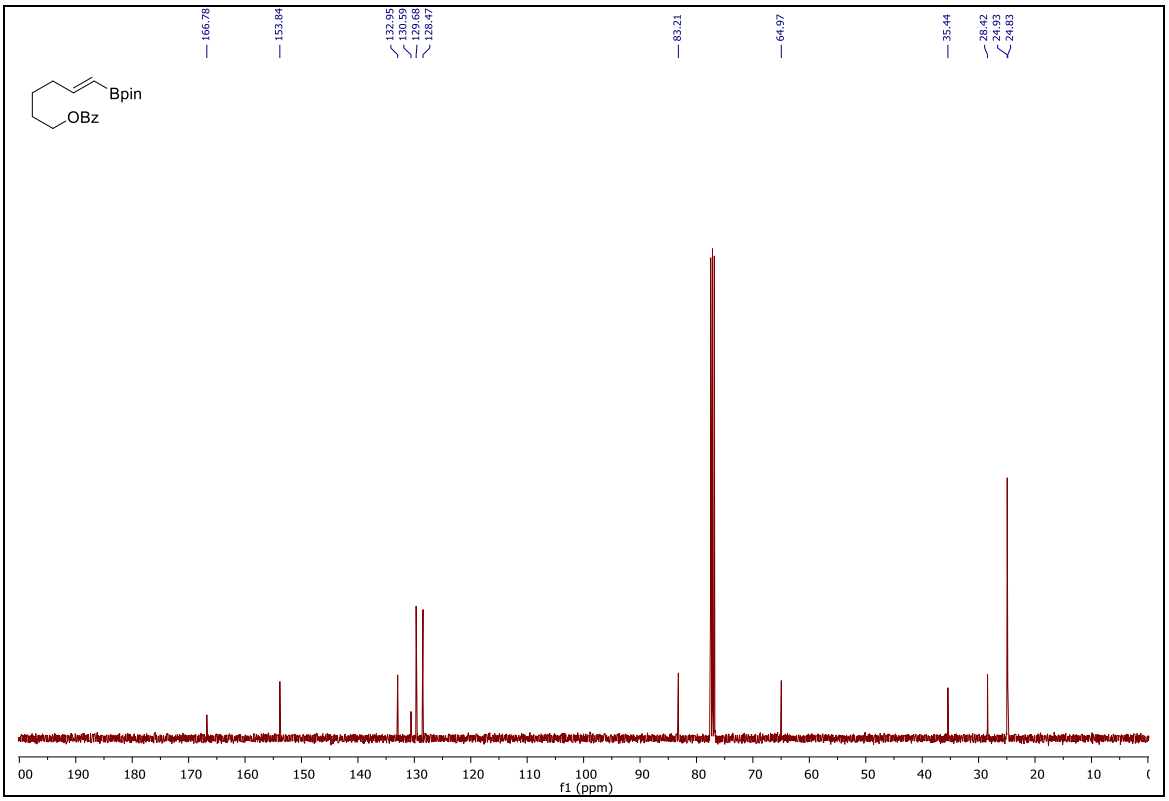


NMR spectra of 1f

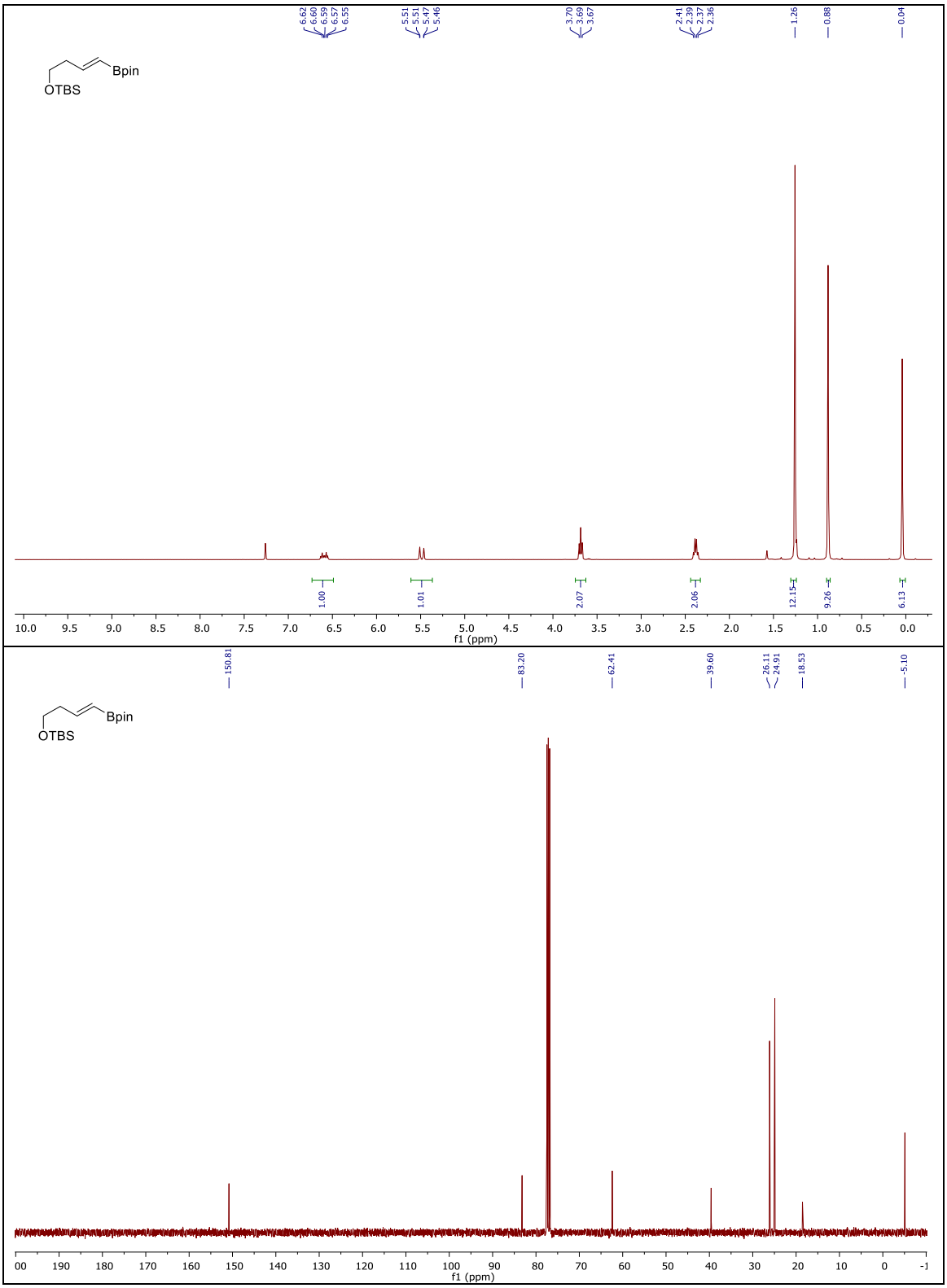


NMR spectra of 1g

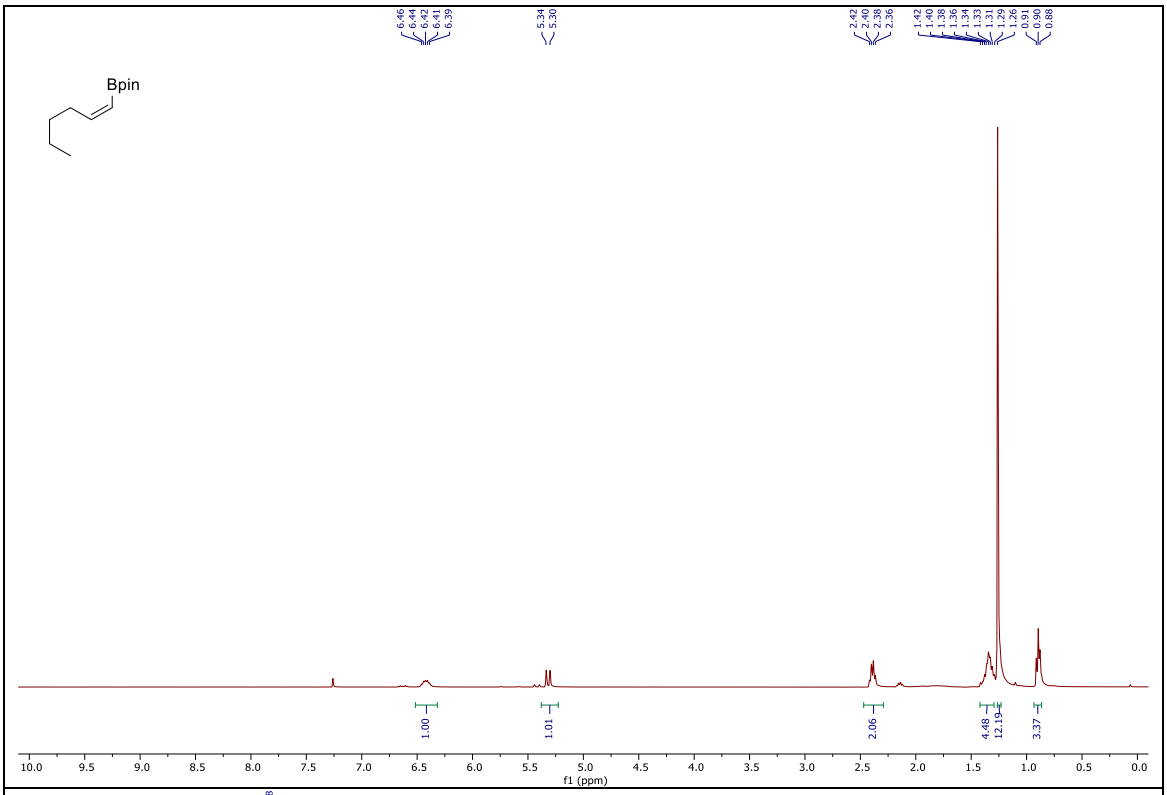


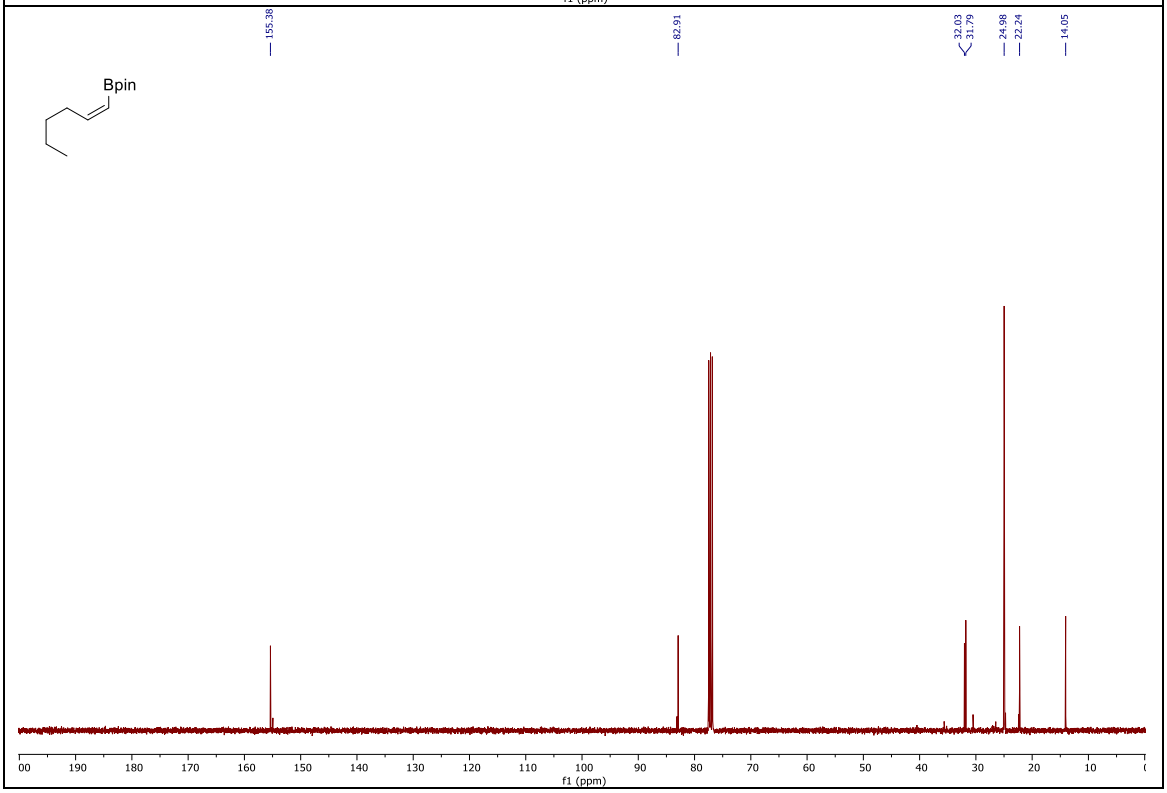

166.78
153.84
132.95
130.59
129.68
128.47
83.21
64.97
35.44
28.42
24.93
24.83
Bpin
OBz
f1 (ppm)

NMR spectra of 1h

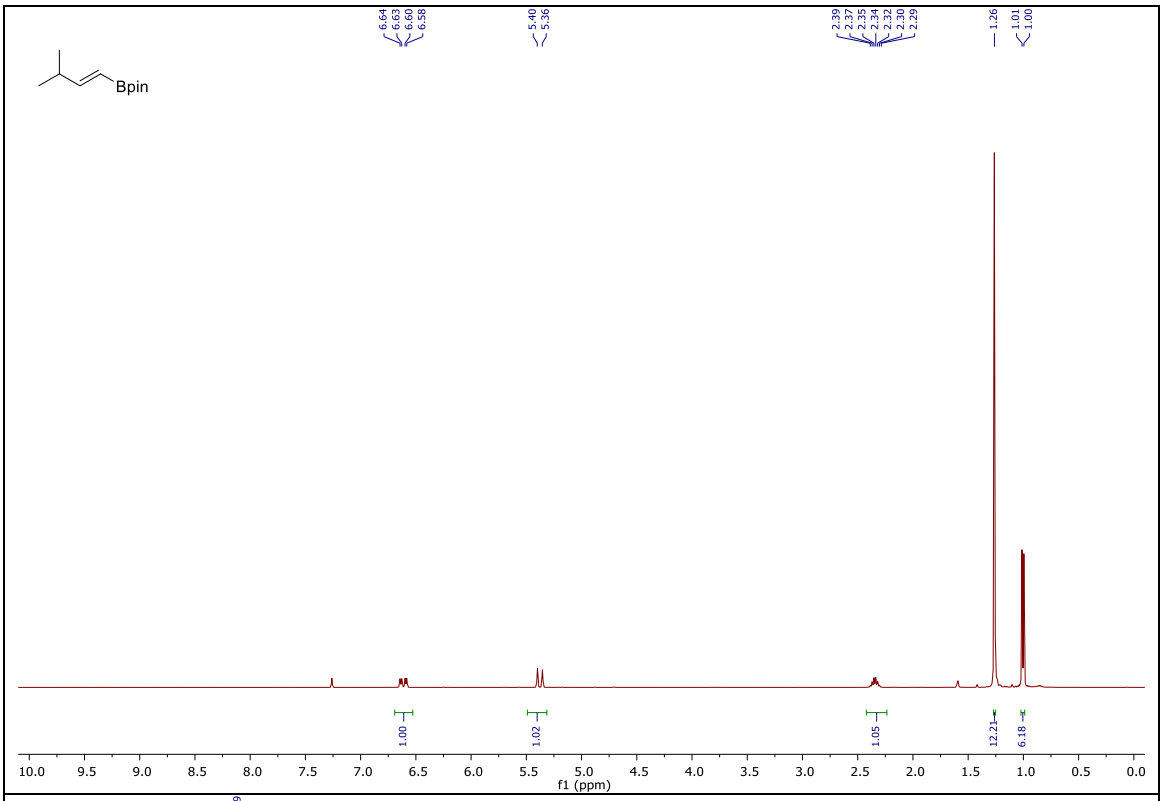


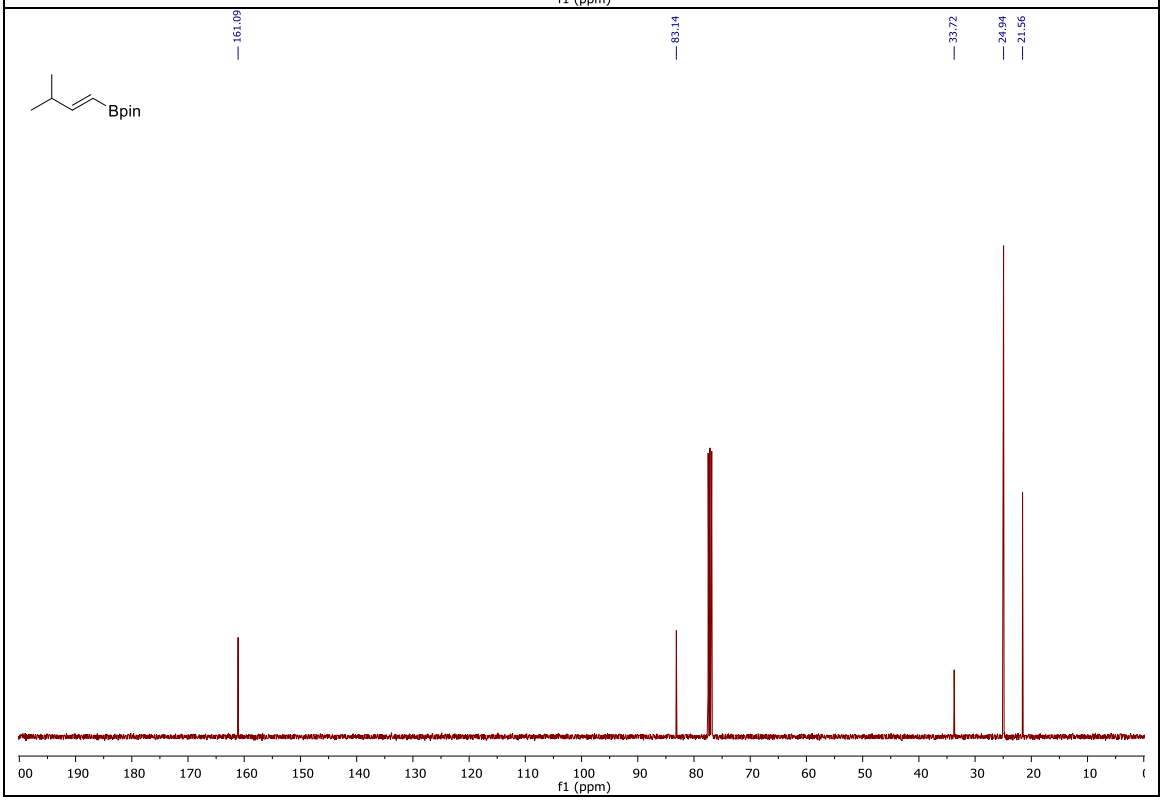
NMR spectra of 1l



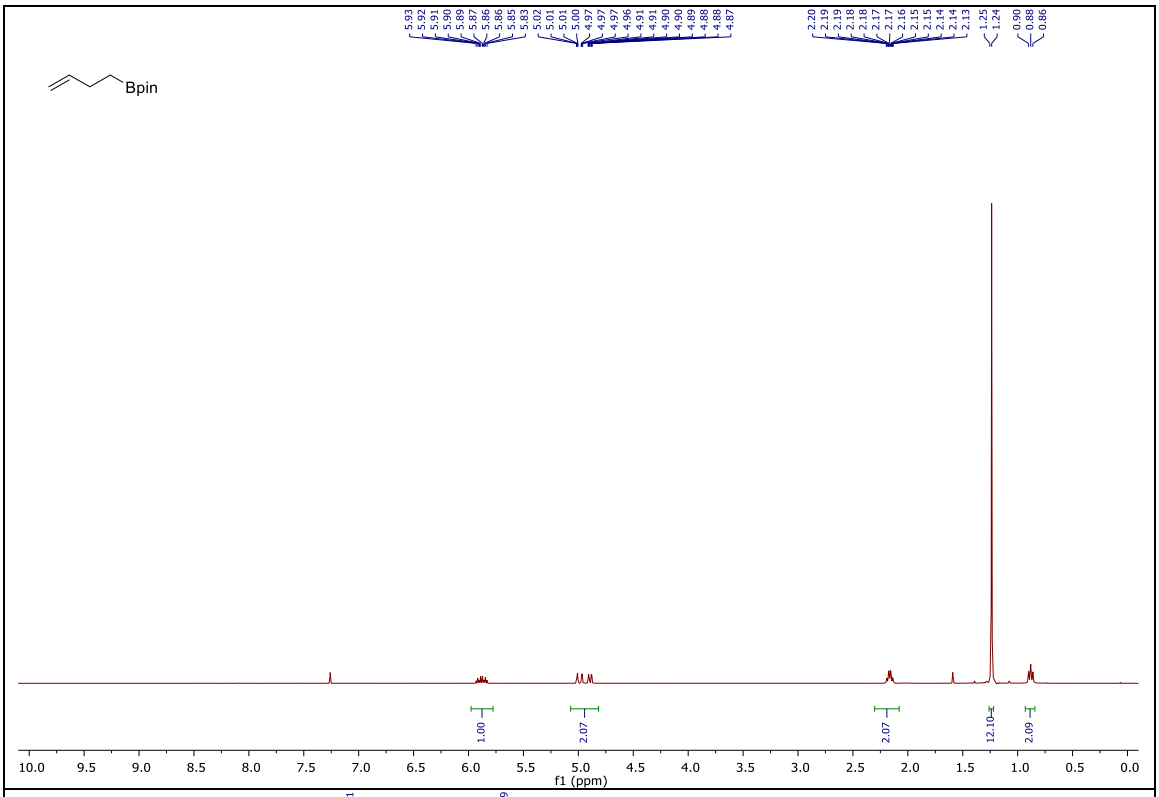


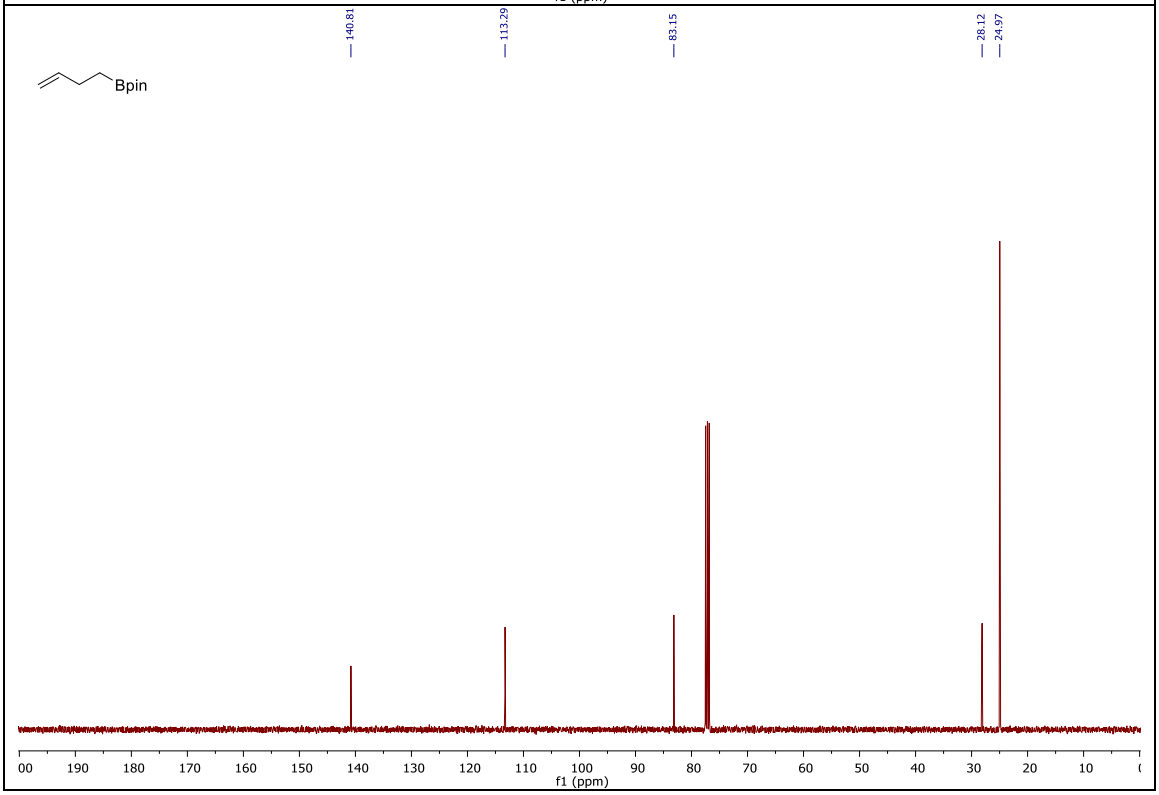
NMR spectra of 1m



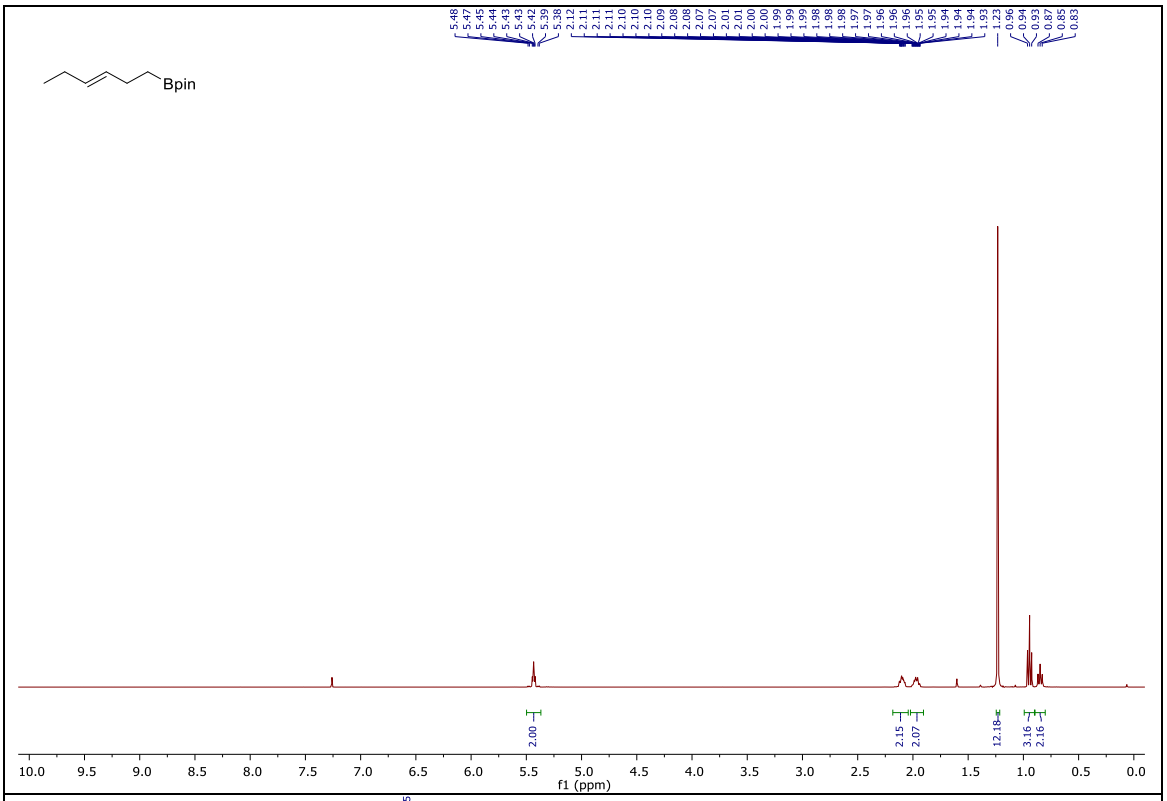


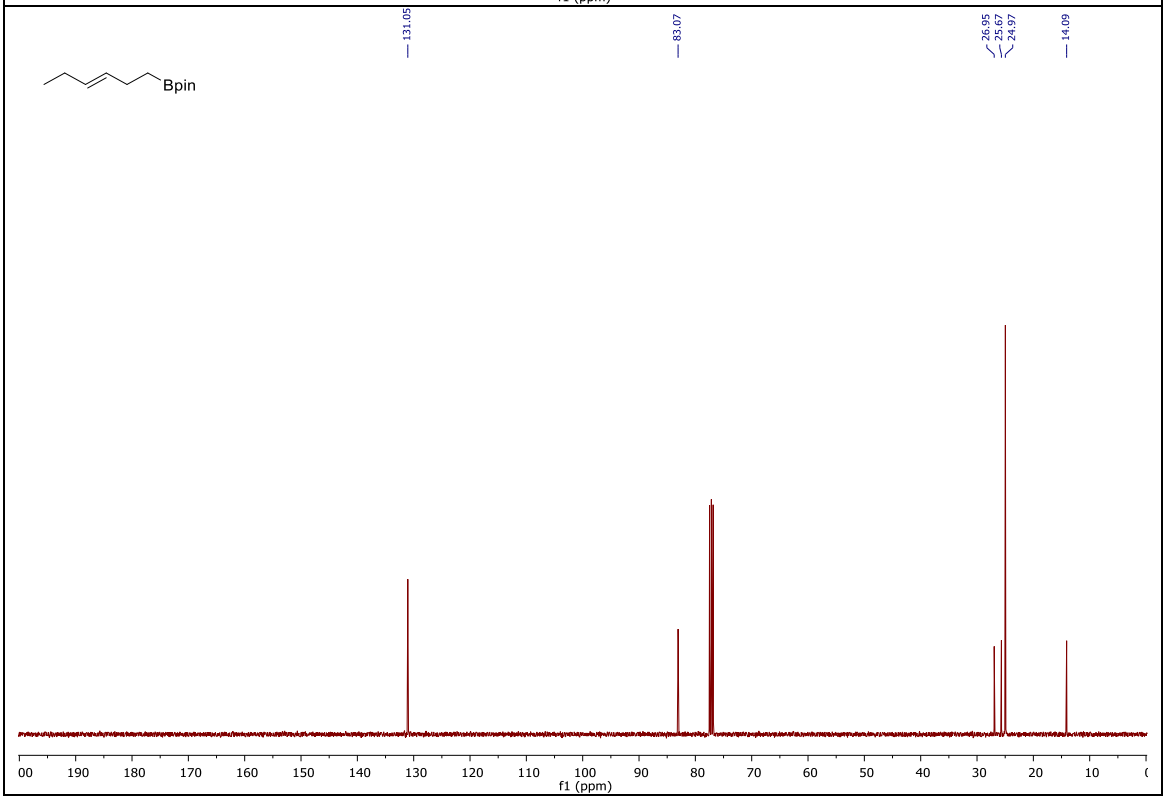
NMR spectra of 1o



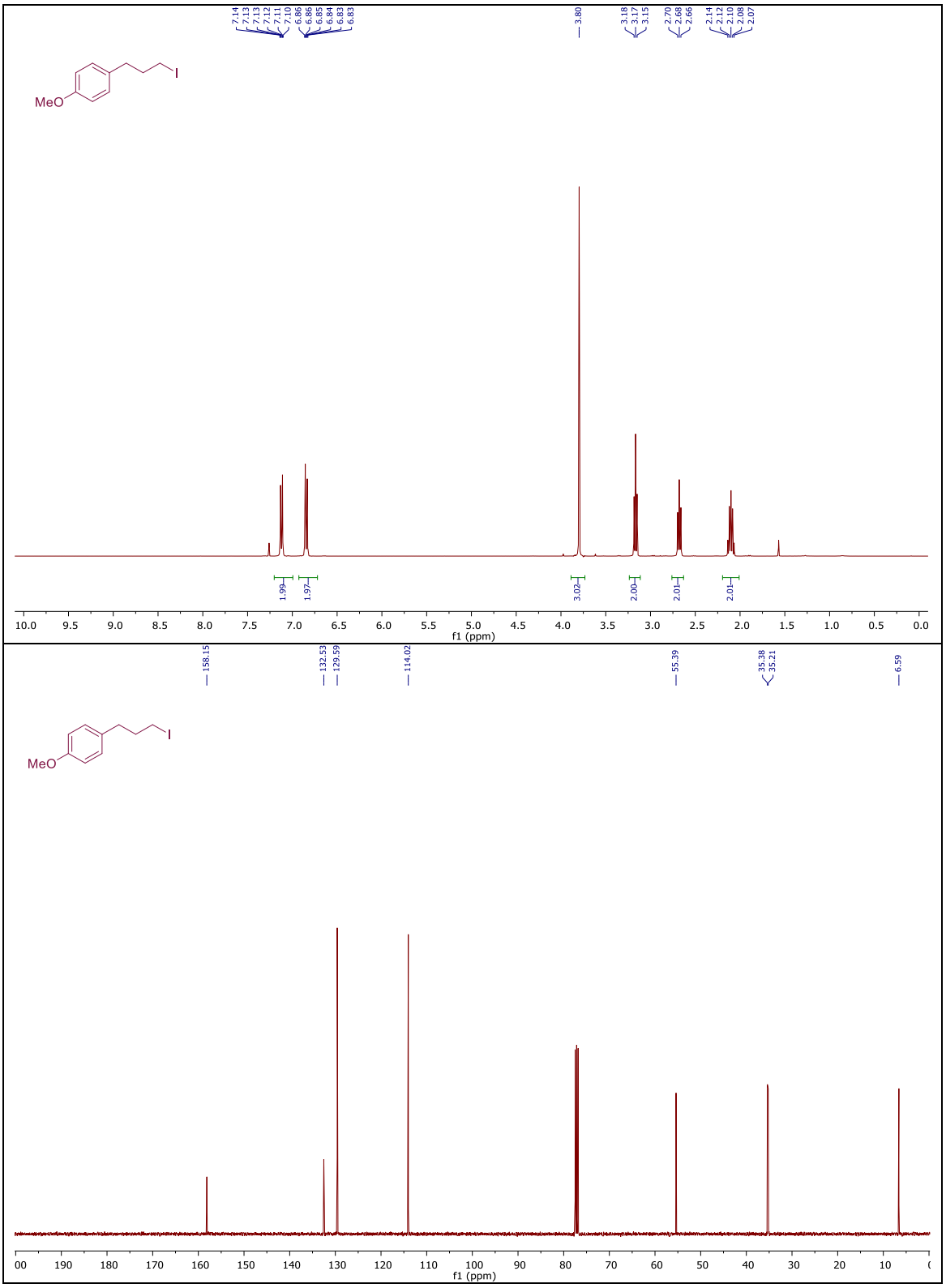


NMR spectra of 1p

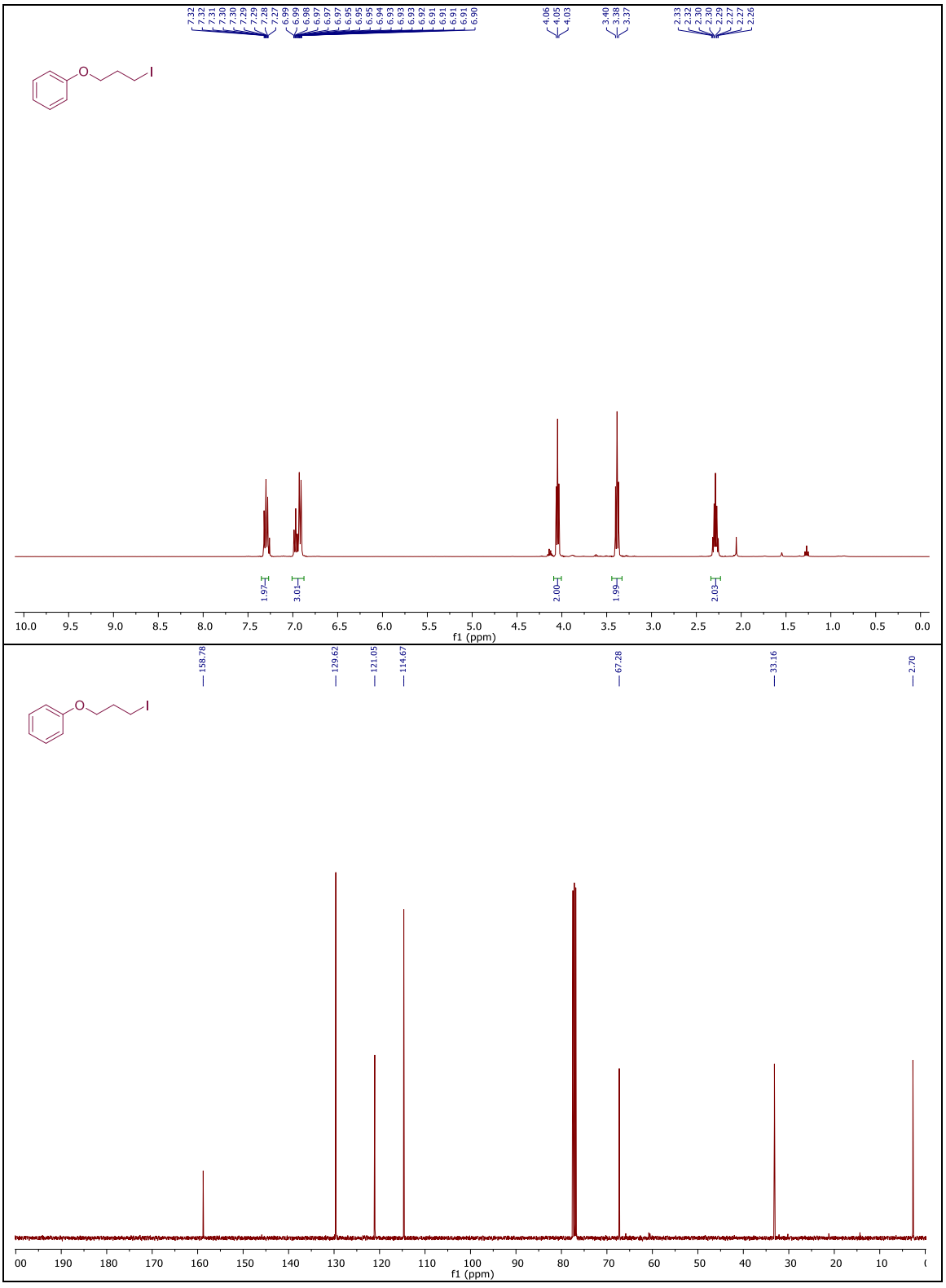




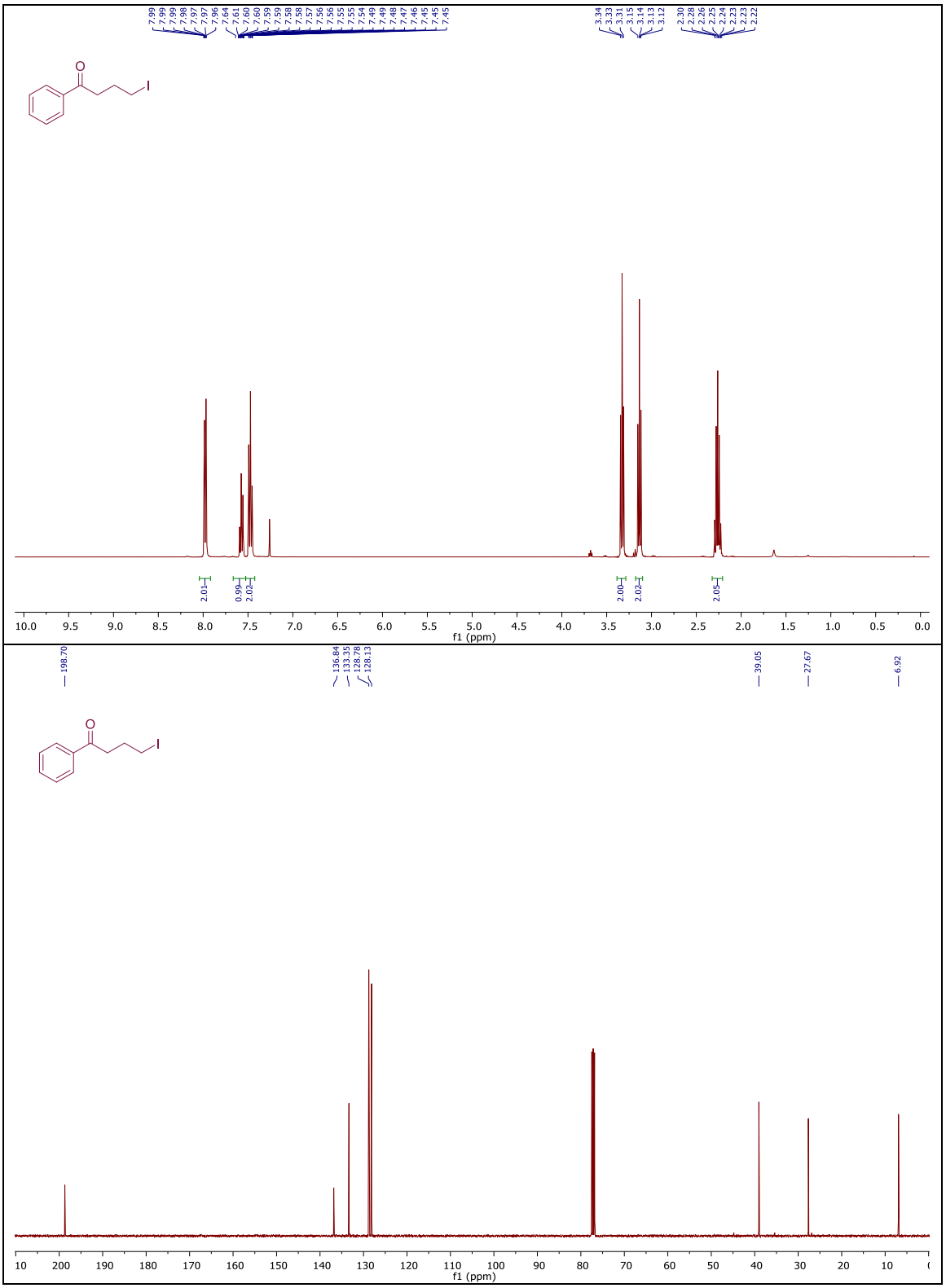
NMR spectra of 2b



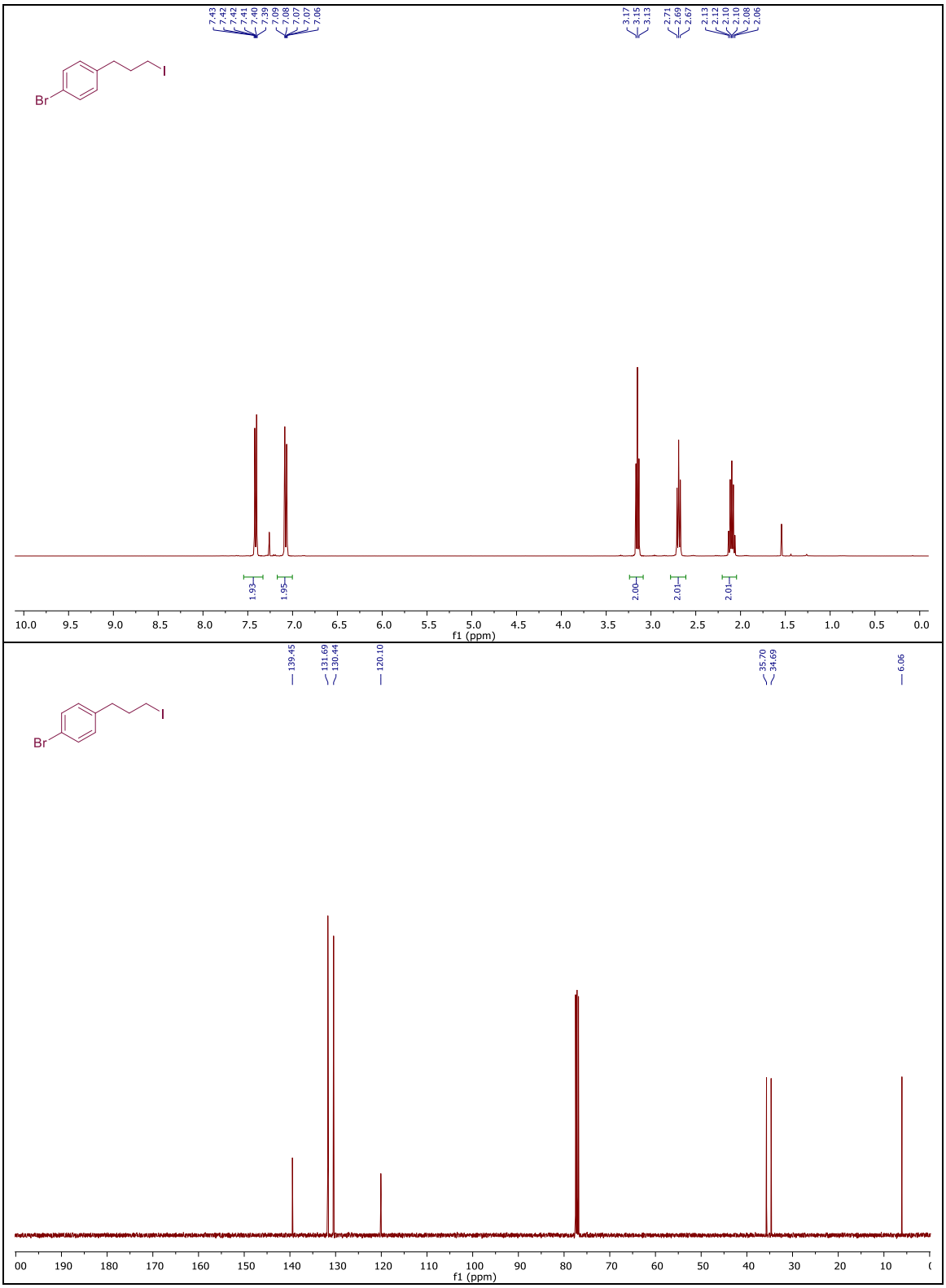
NMR spectra of 2c



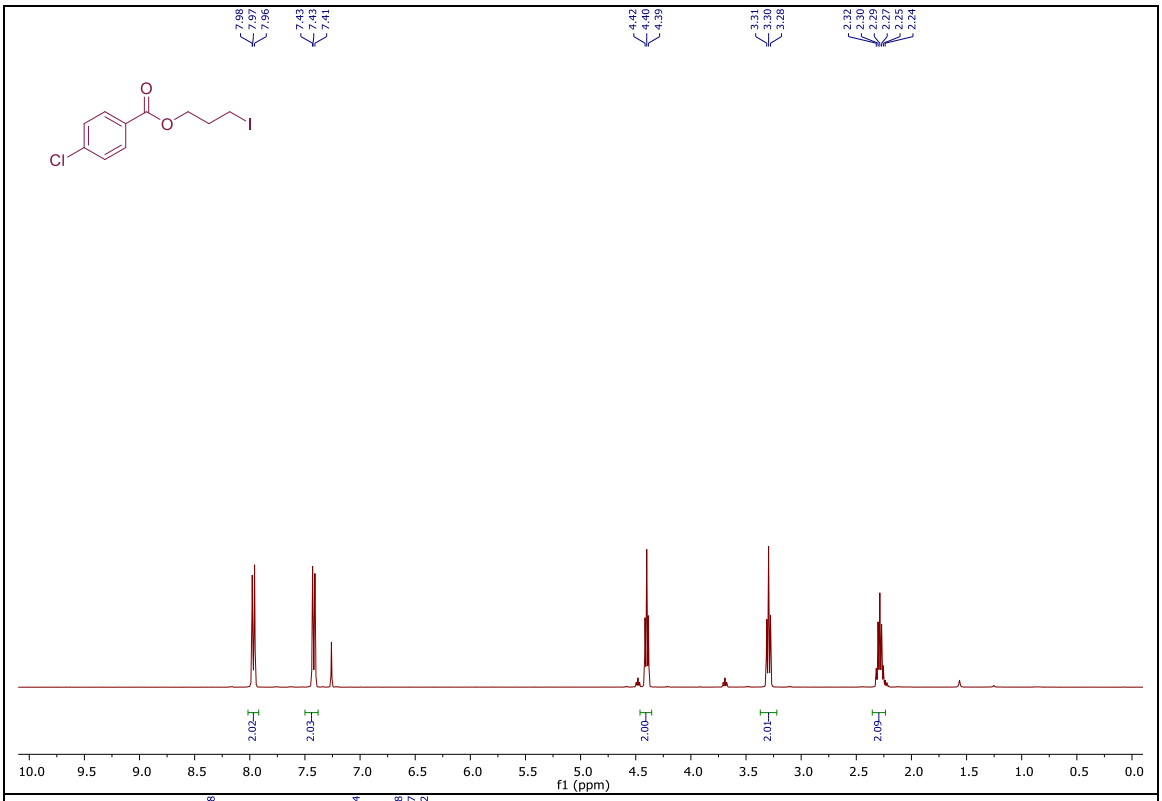
NMR spectra of 2d

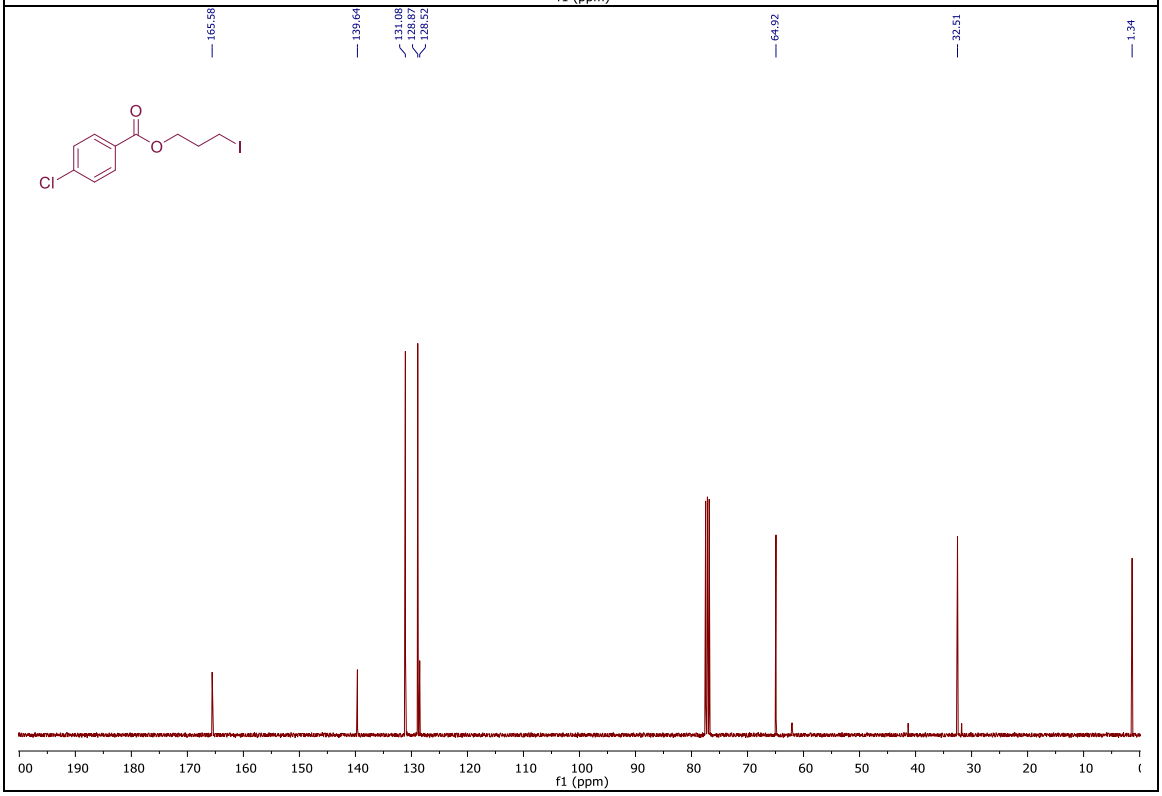


NMR spectra of 2e

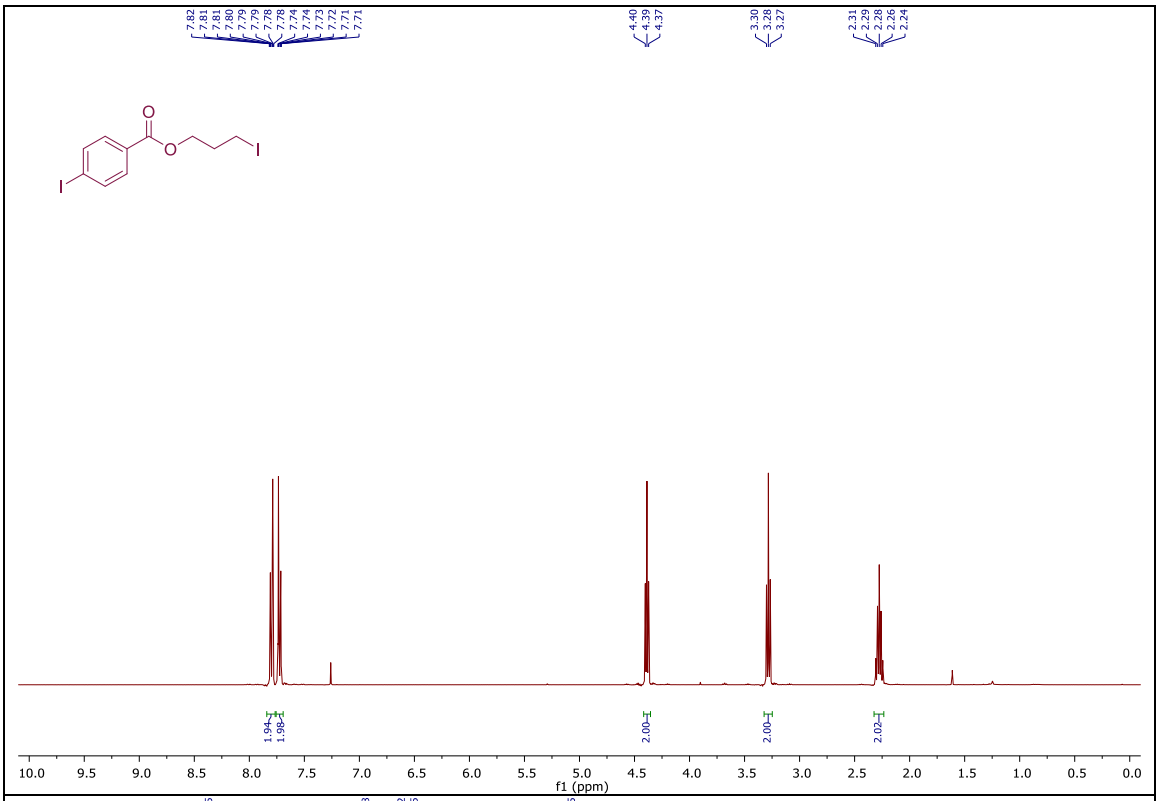


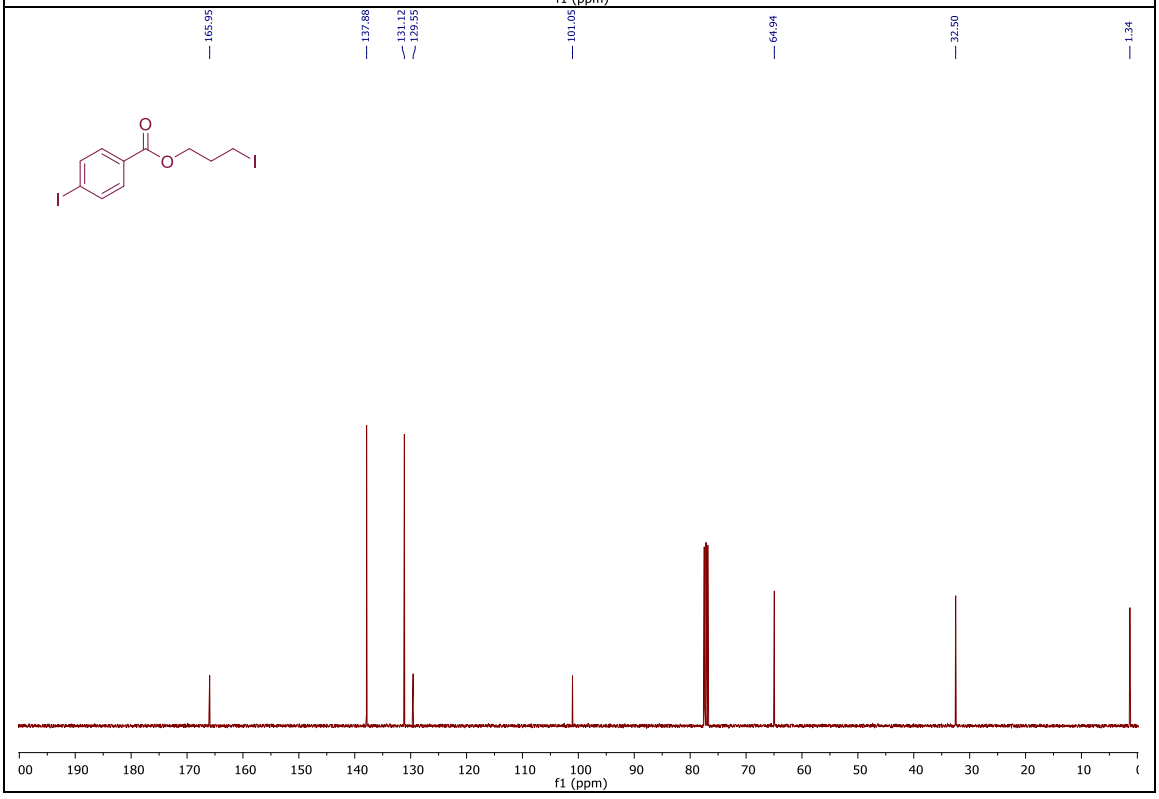
NMR spectra of 2f



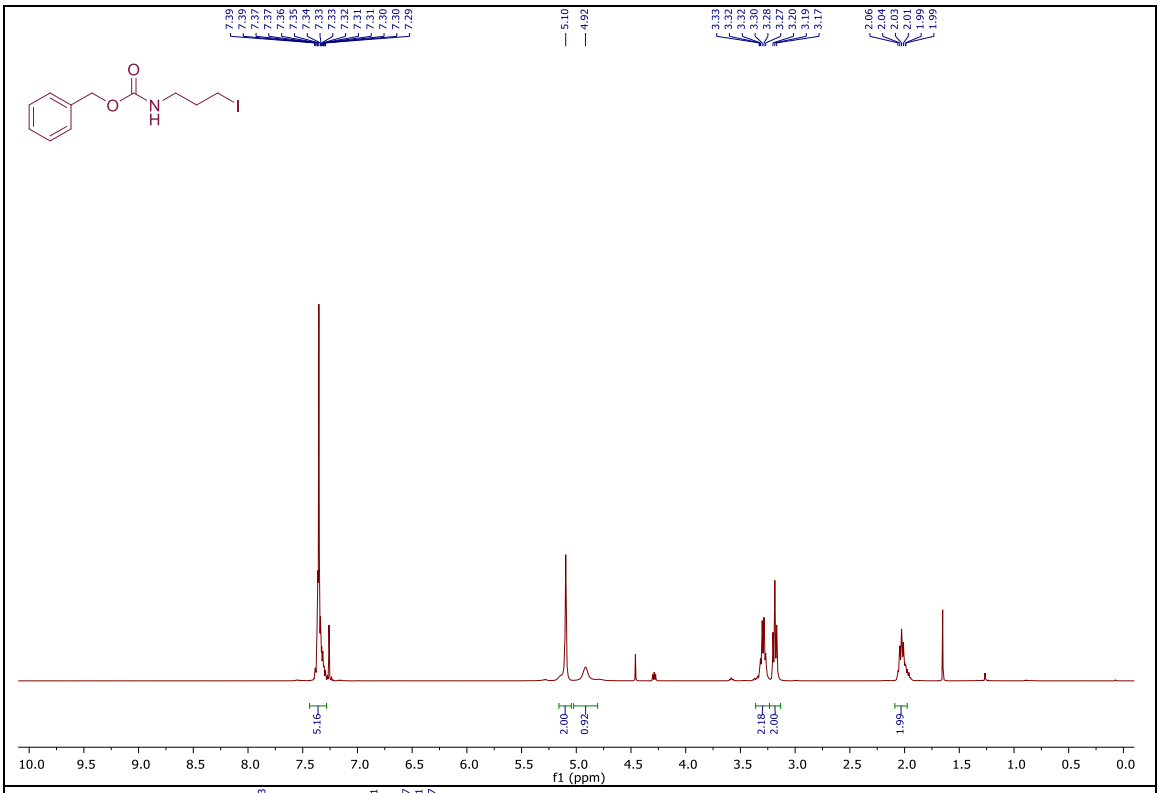


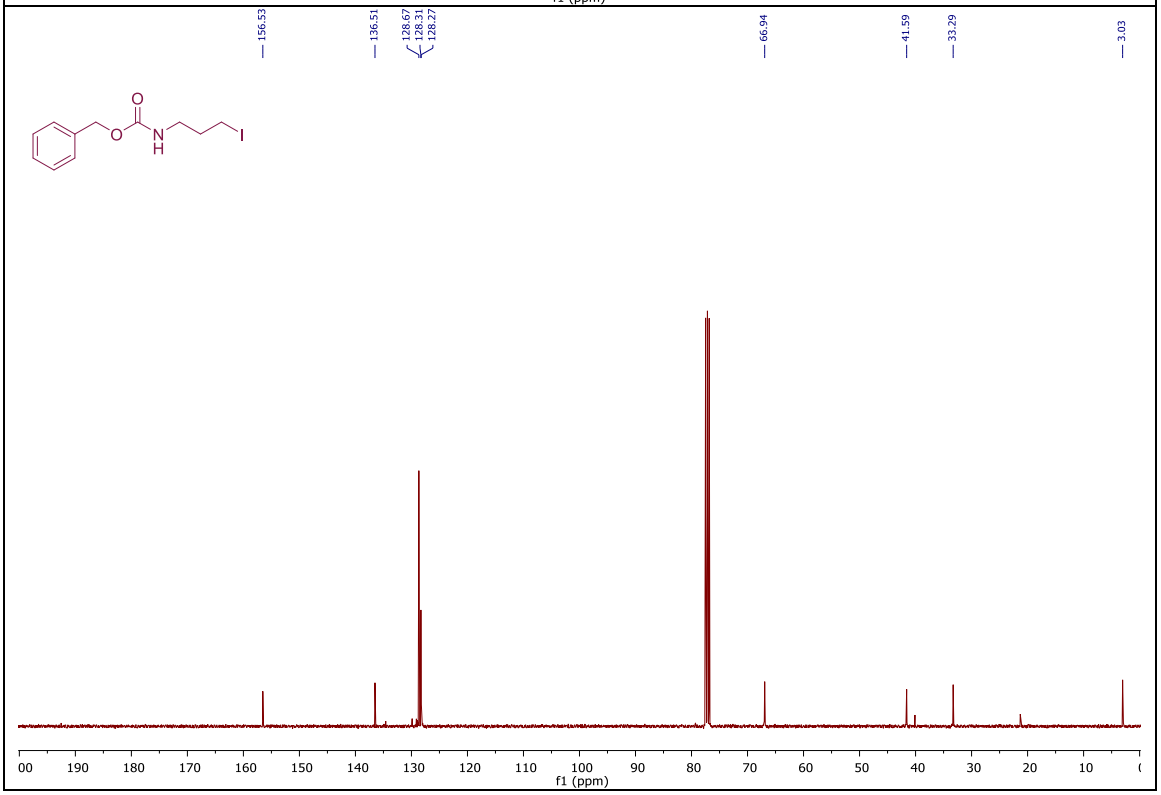
NMR spectra of 2g



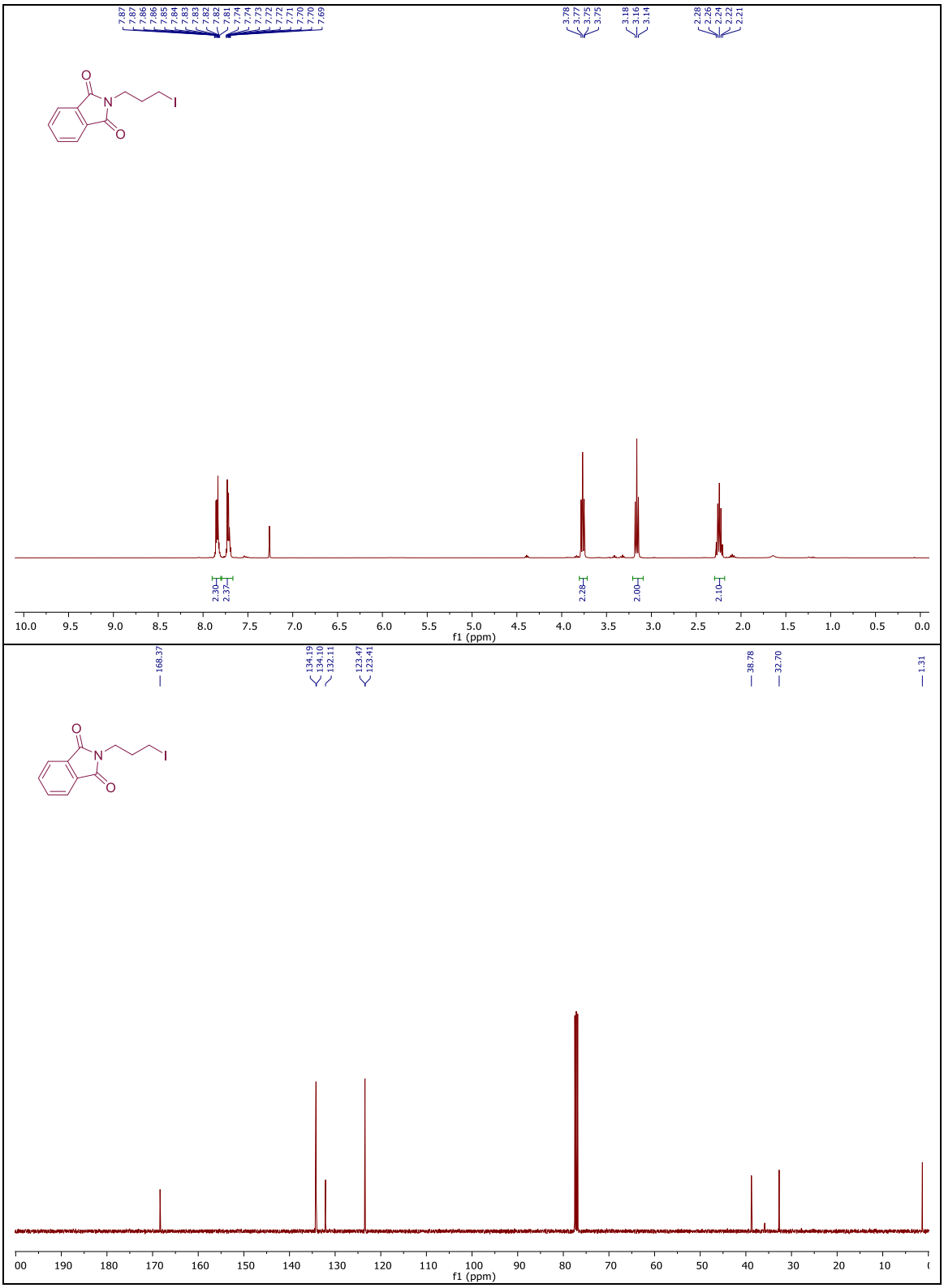


NMR spectra of 2h

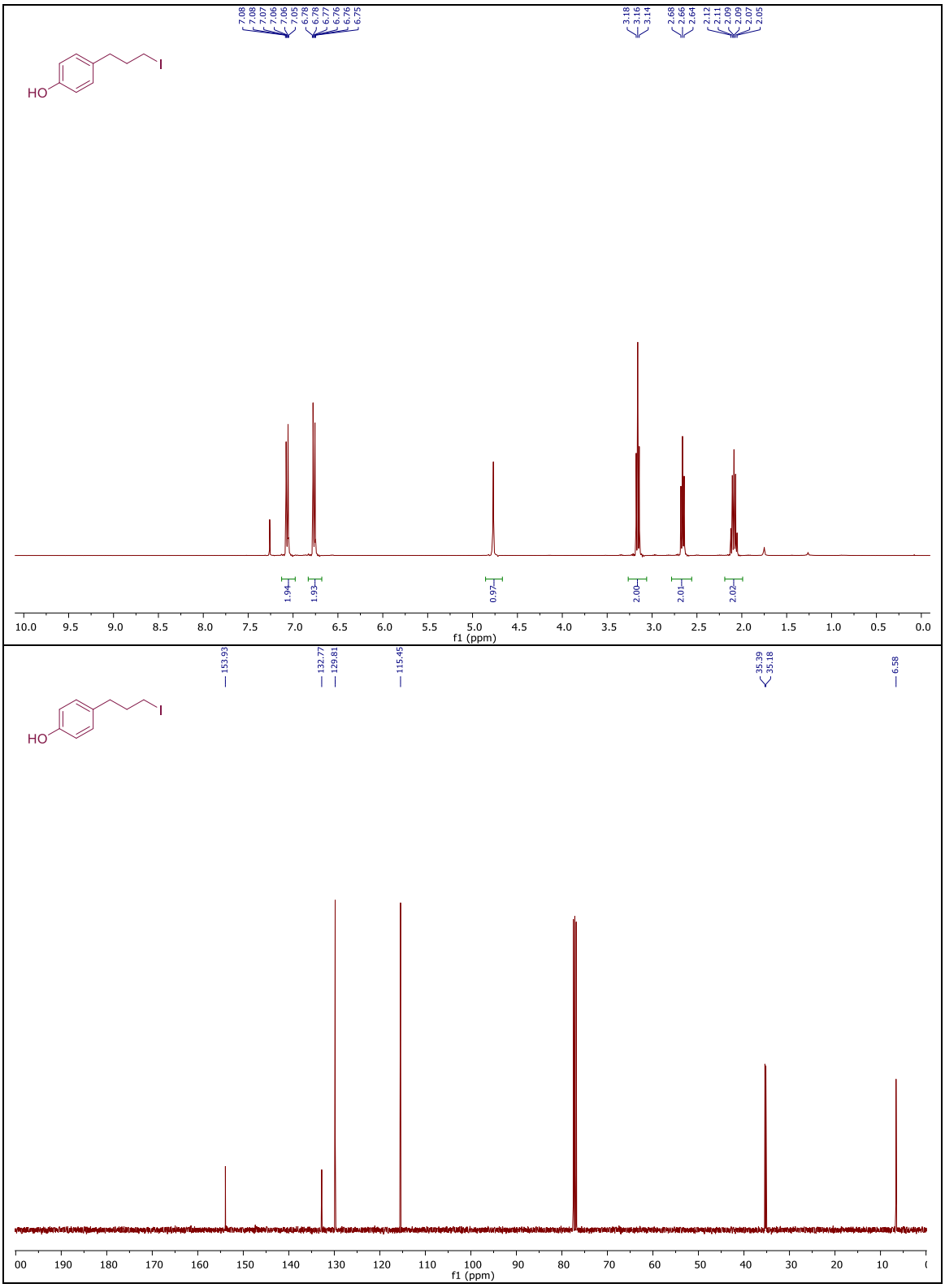




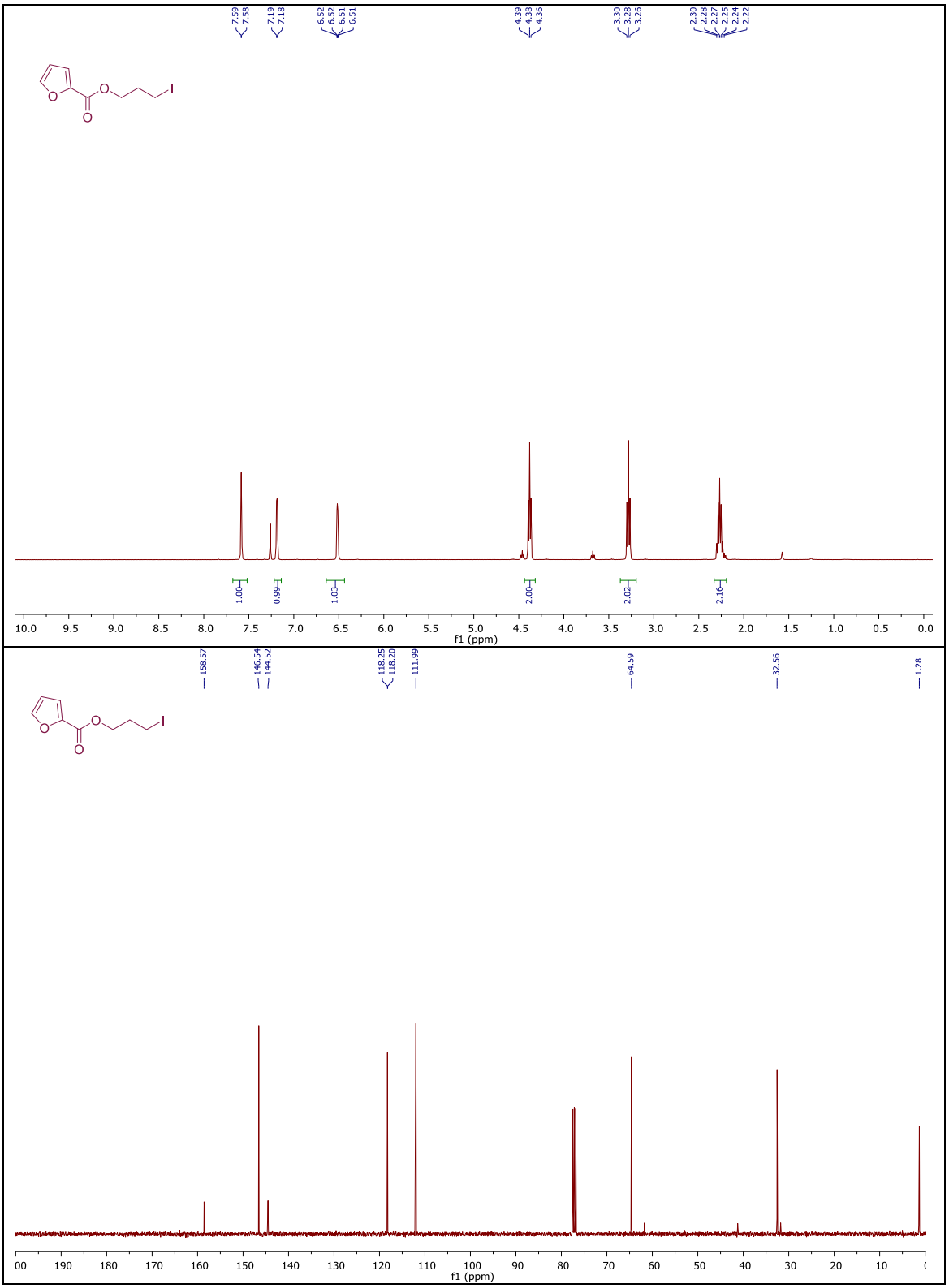
NMR spectra of 2i



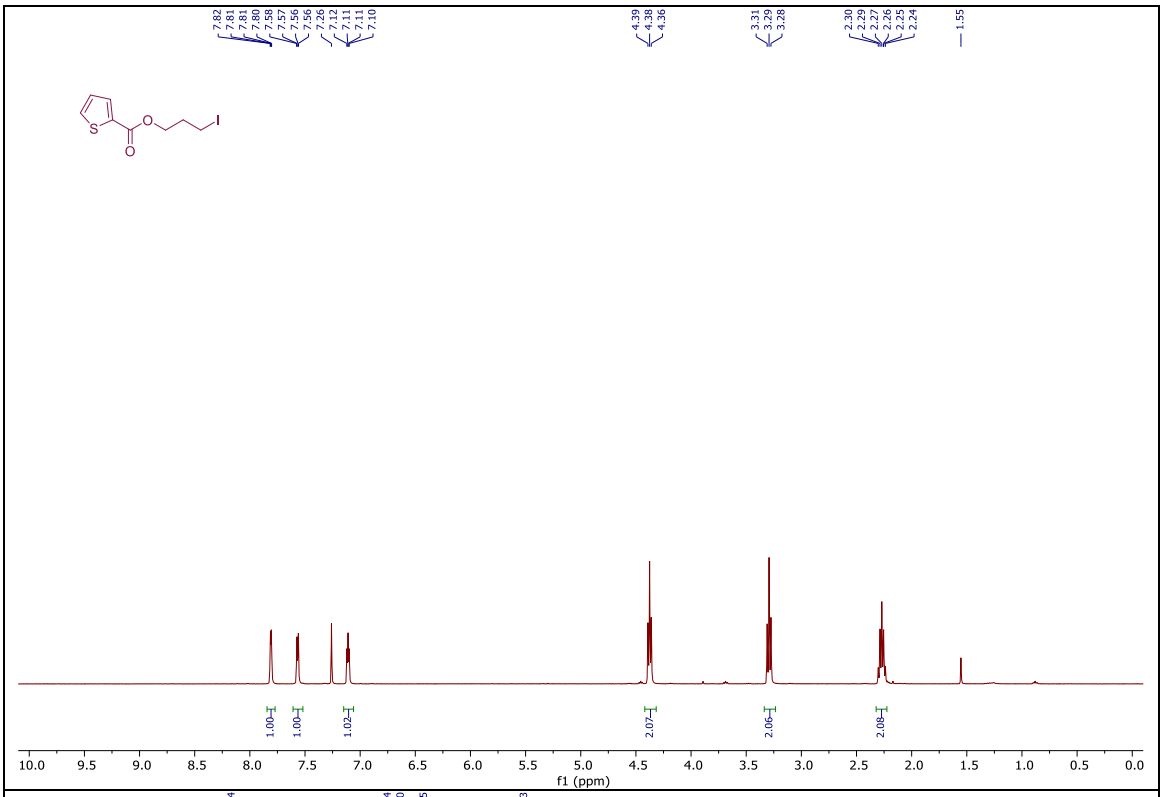
NMR spectra of 2j

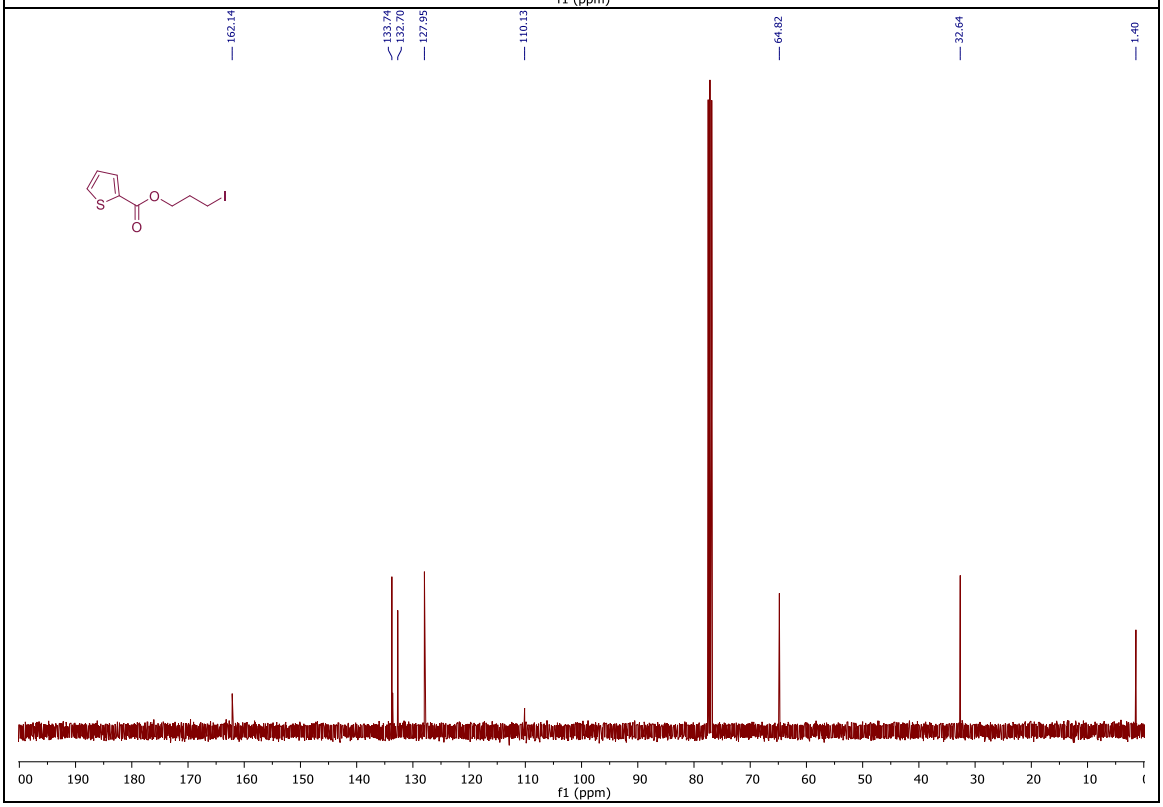


NMR spectra of 2k

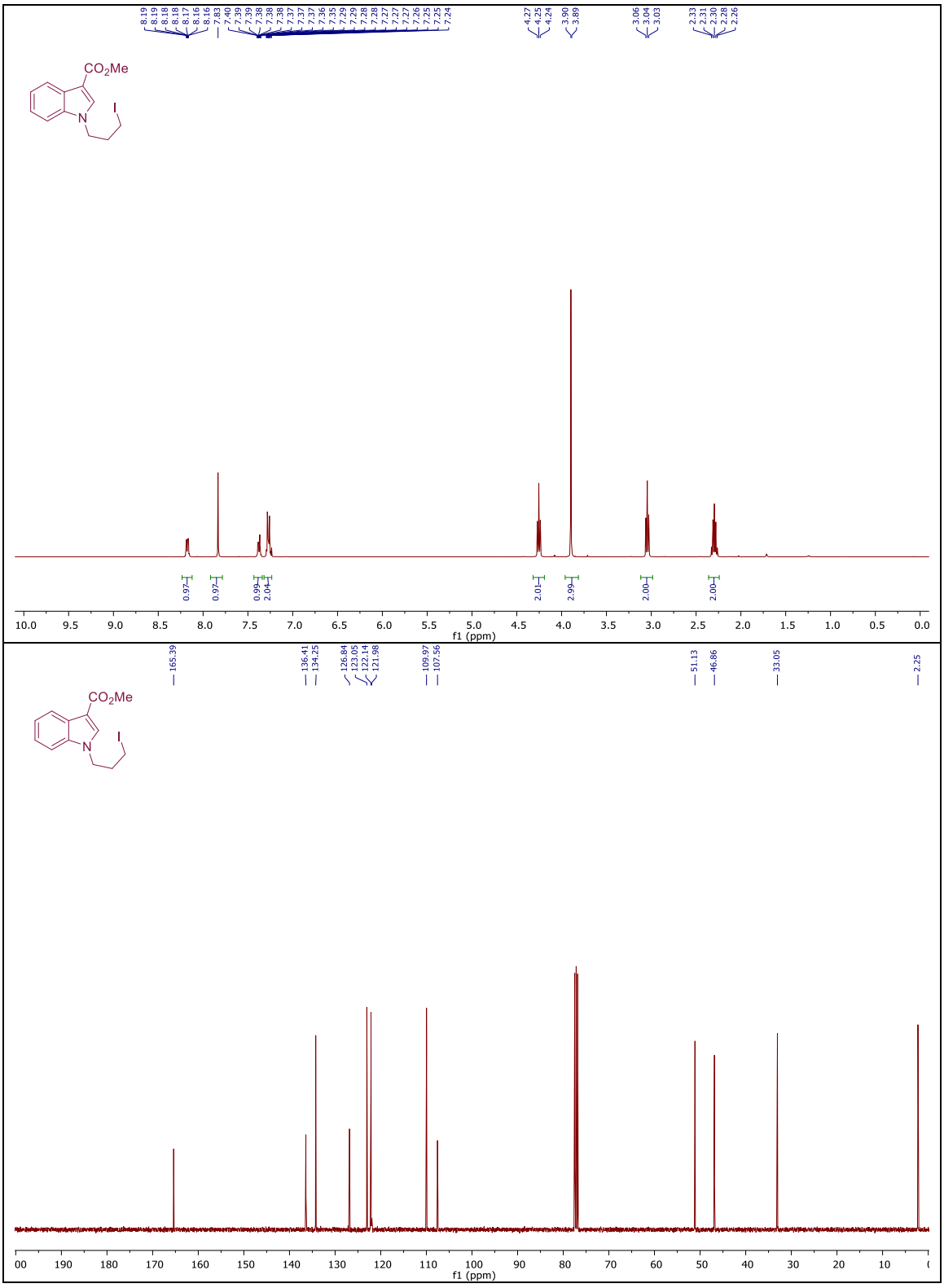


NMR spectra of 2l

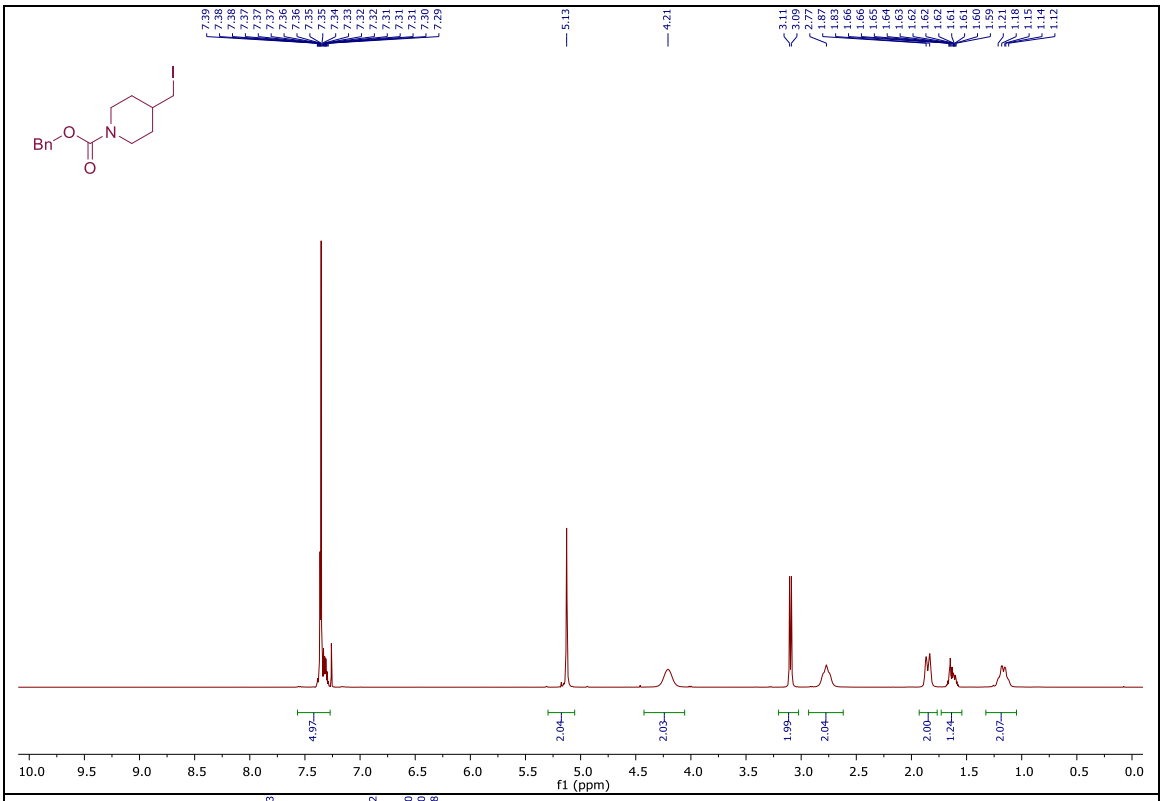


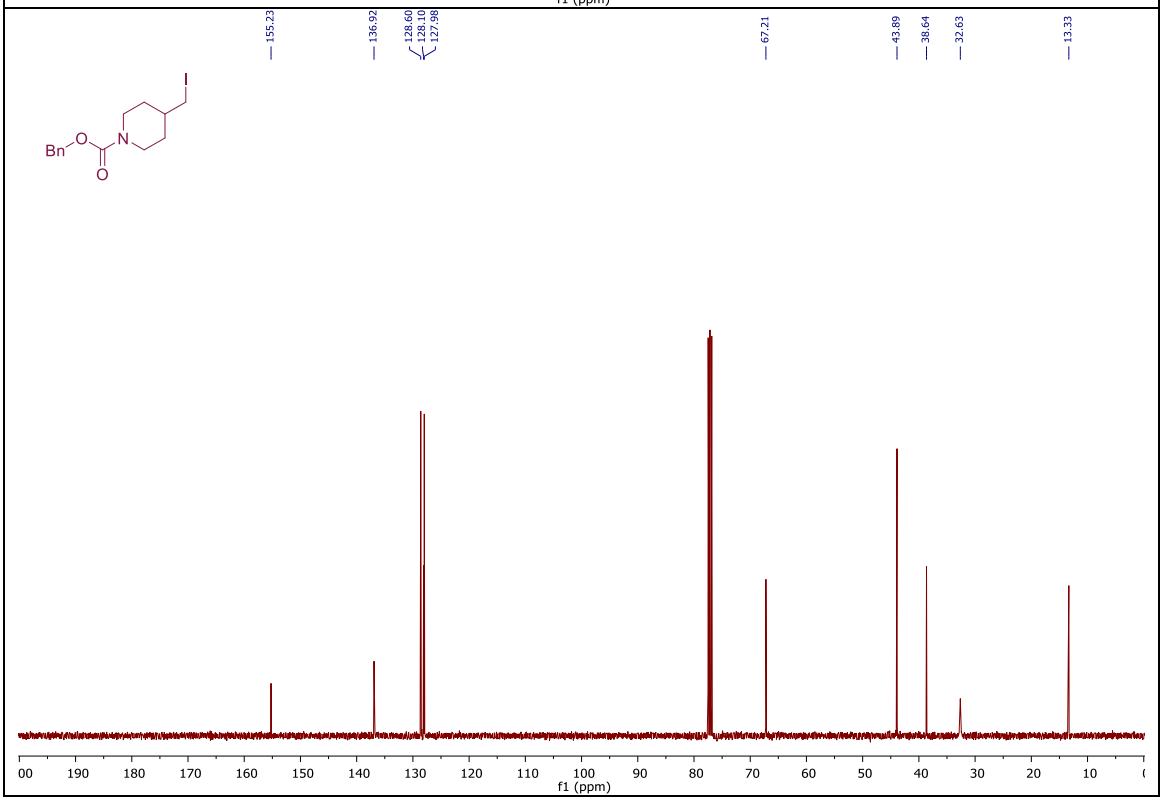


NMR spectra of 2m

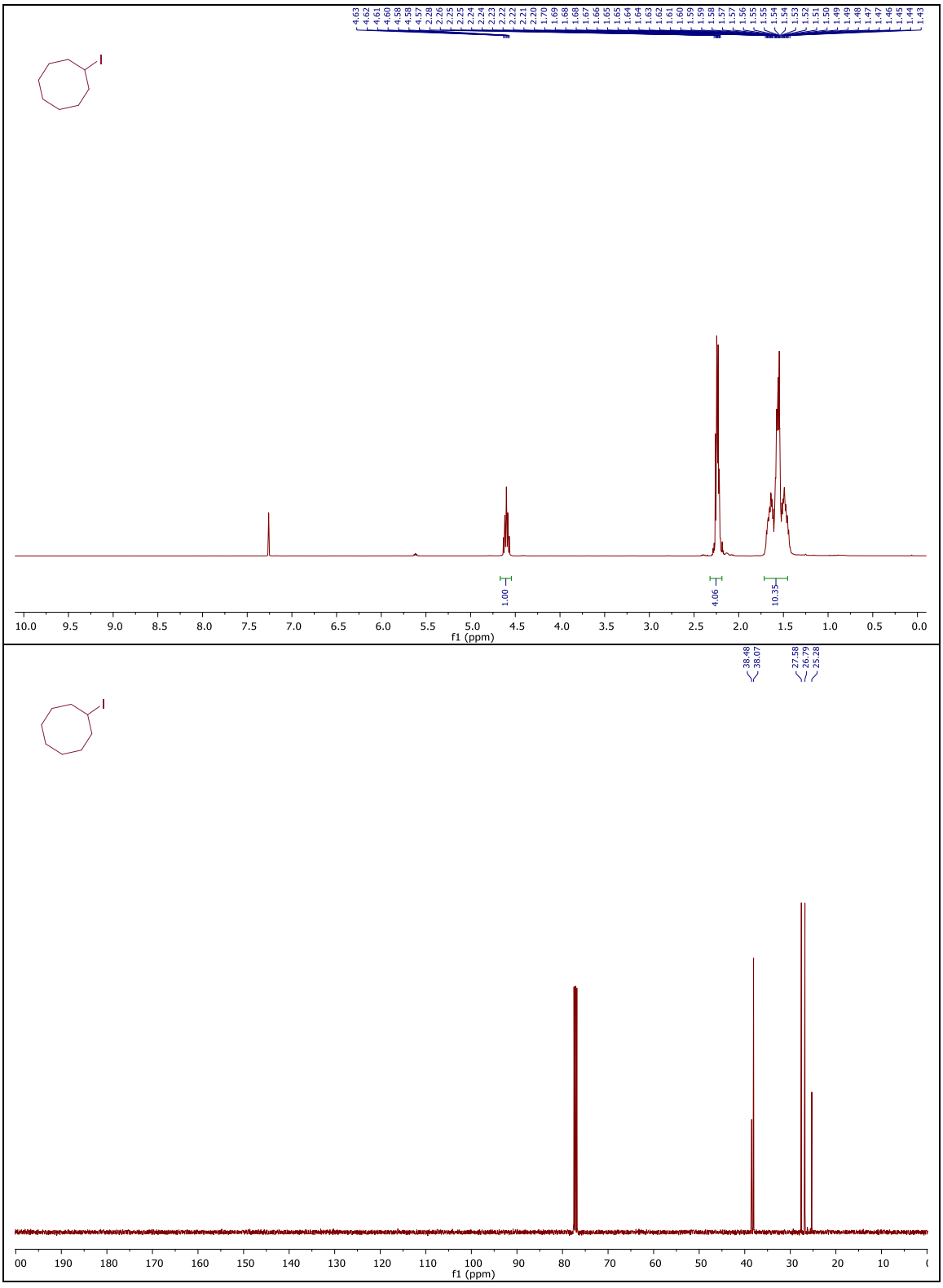


NMR spectra of 2n

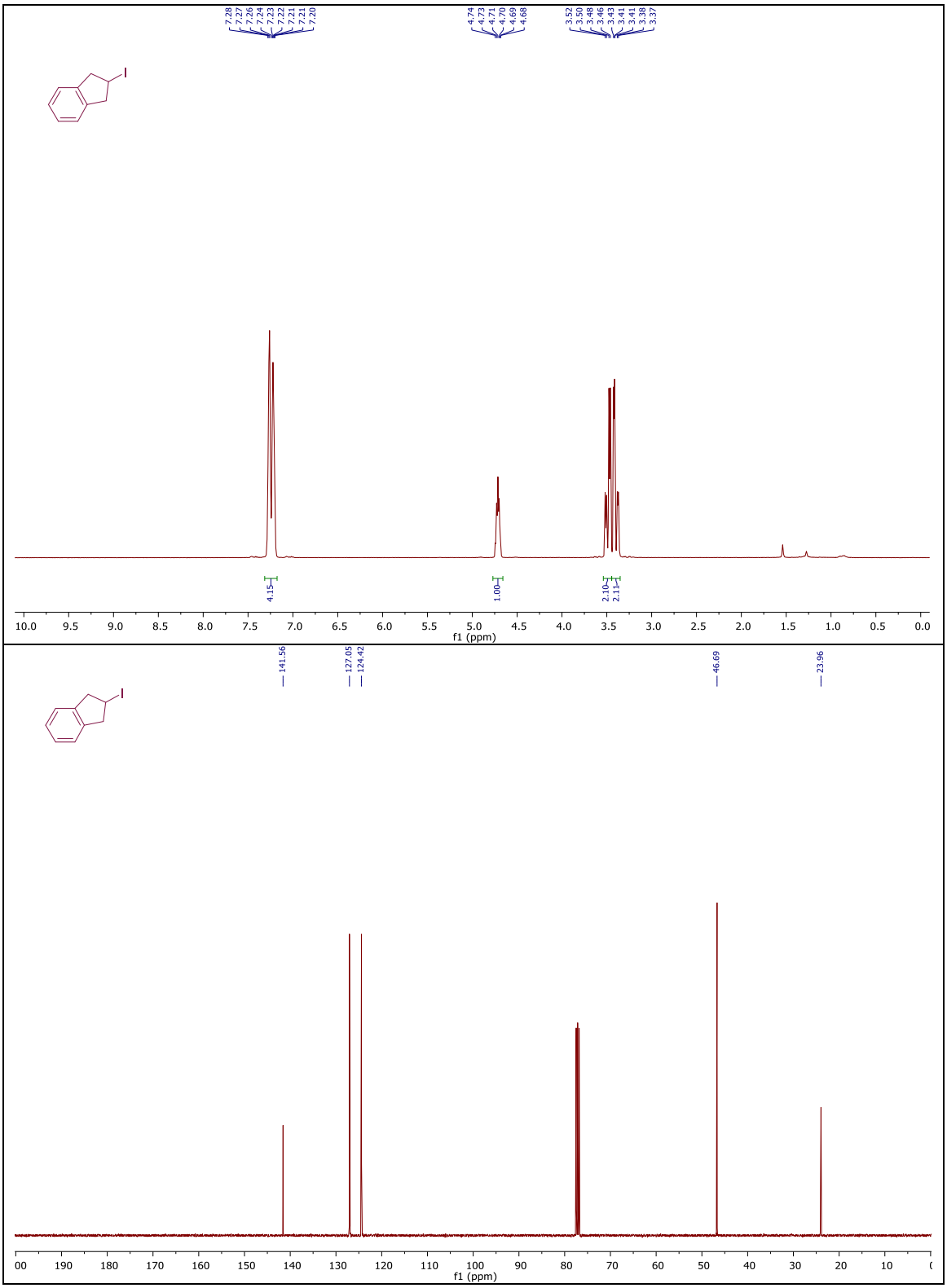




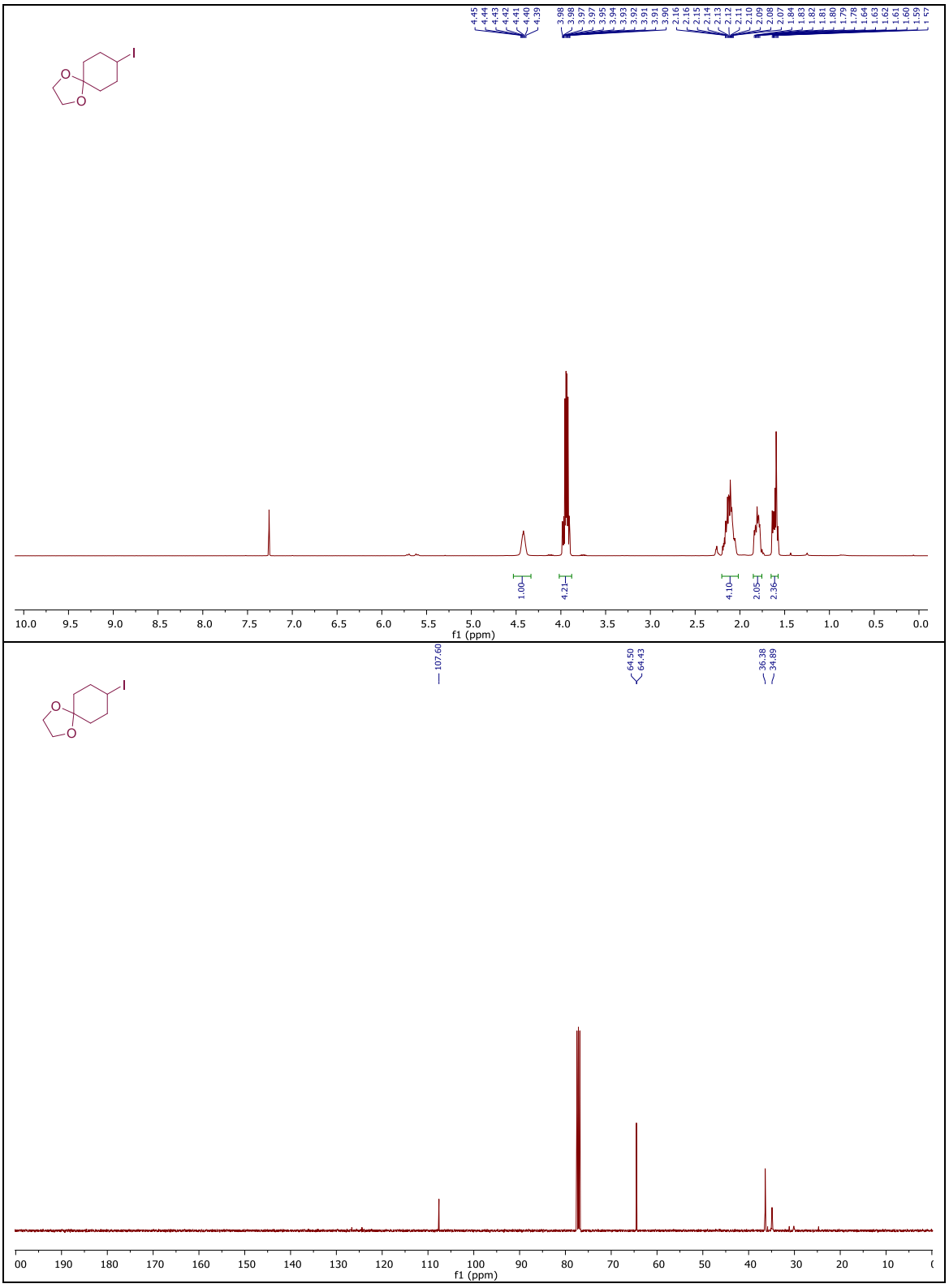
NMR spectra of 2t



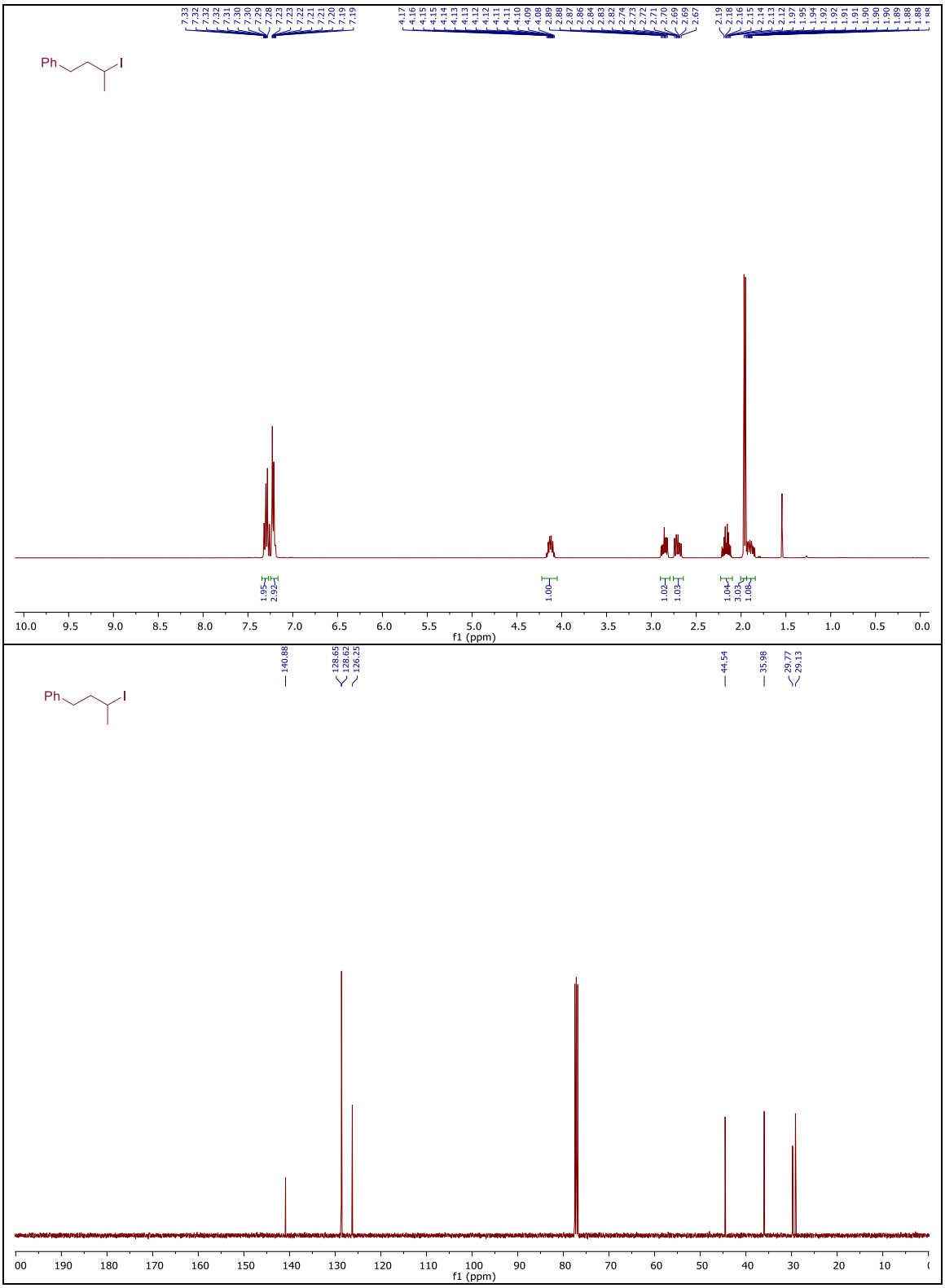
NMR spectra of 2u



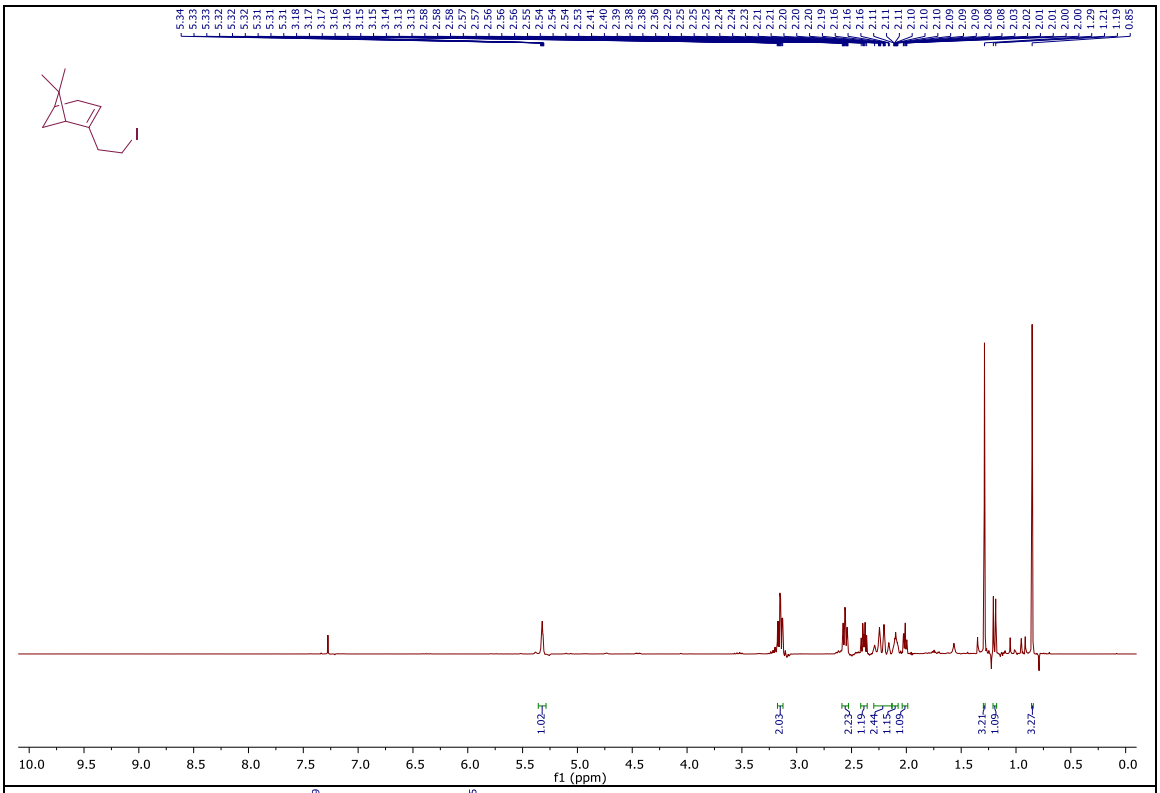
NMR spectra of 2x

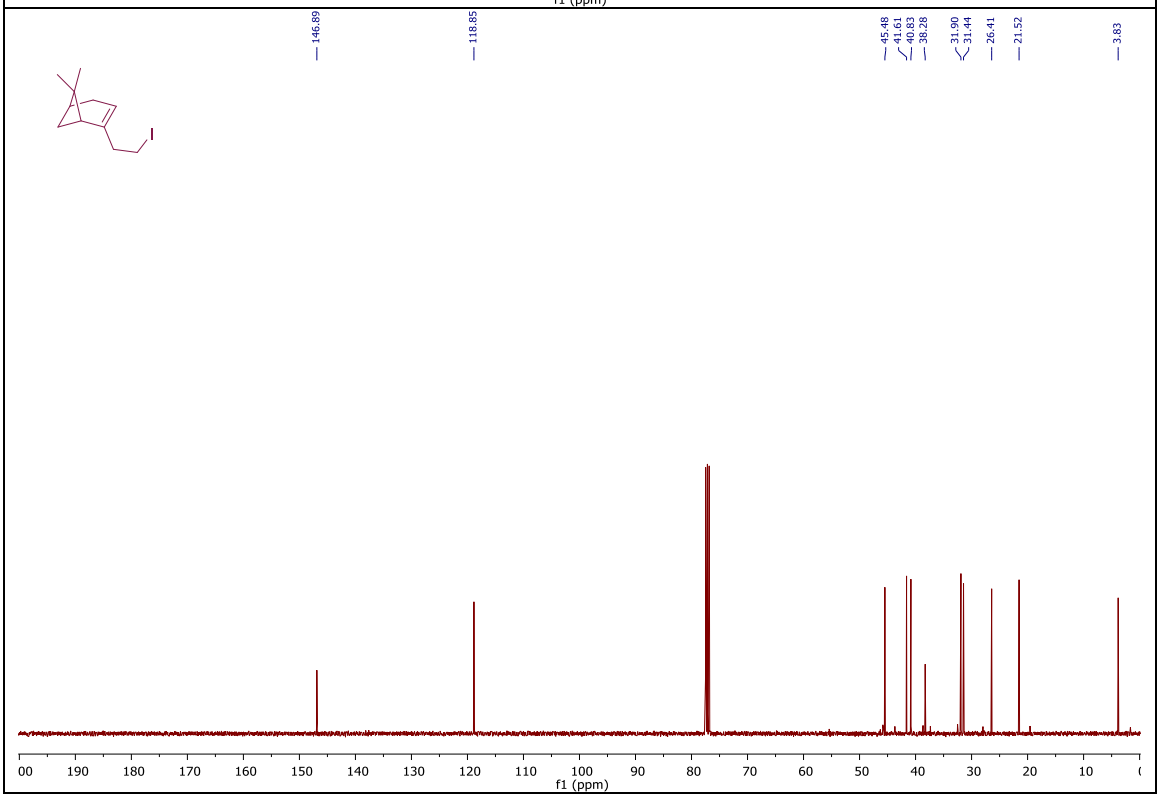


NMR spectra of 2b'

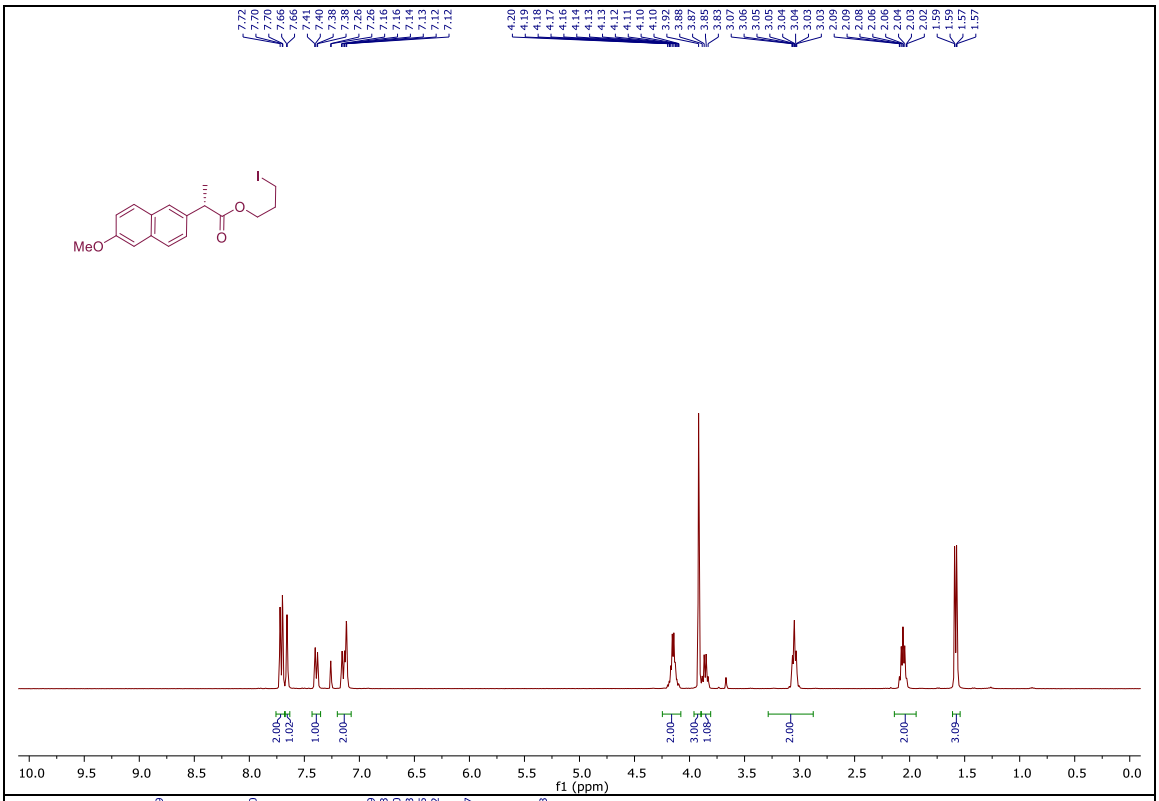


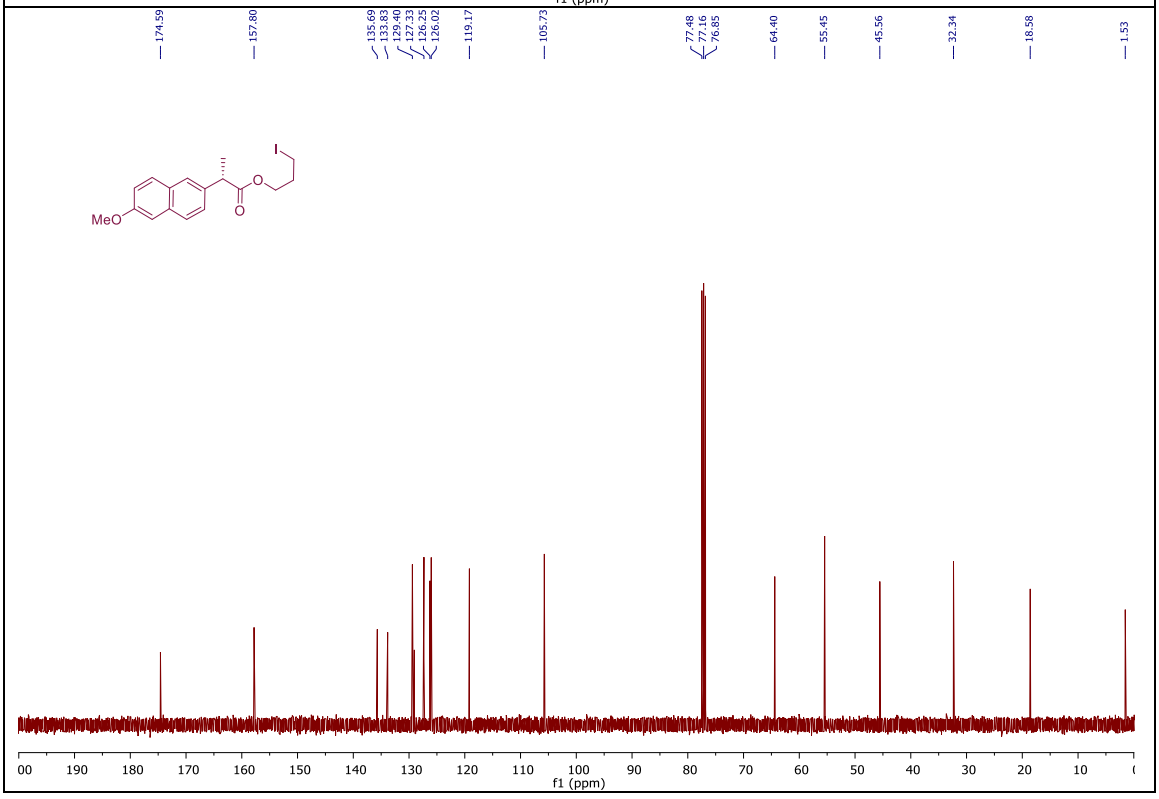
NMR spectra of 2d'



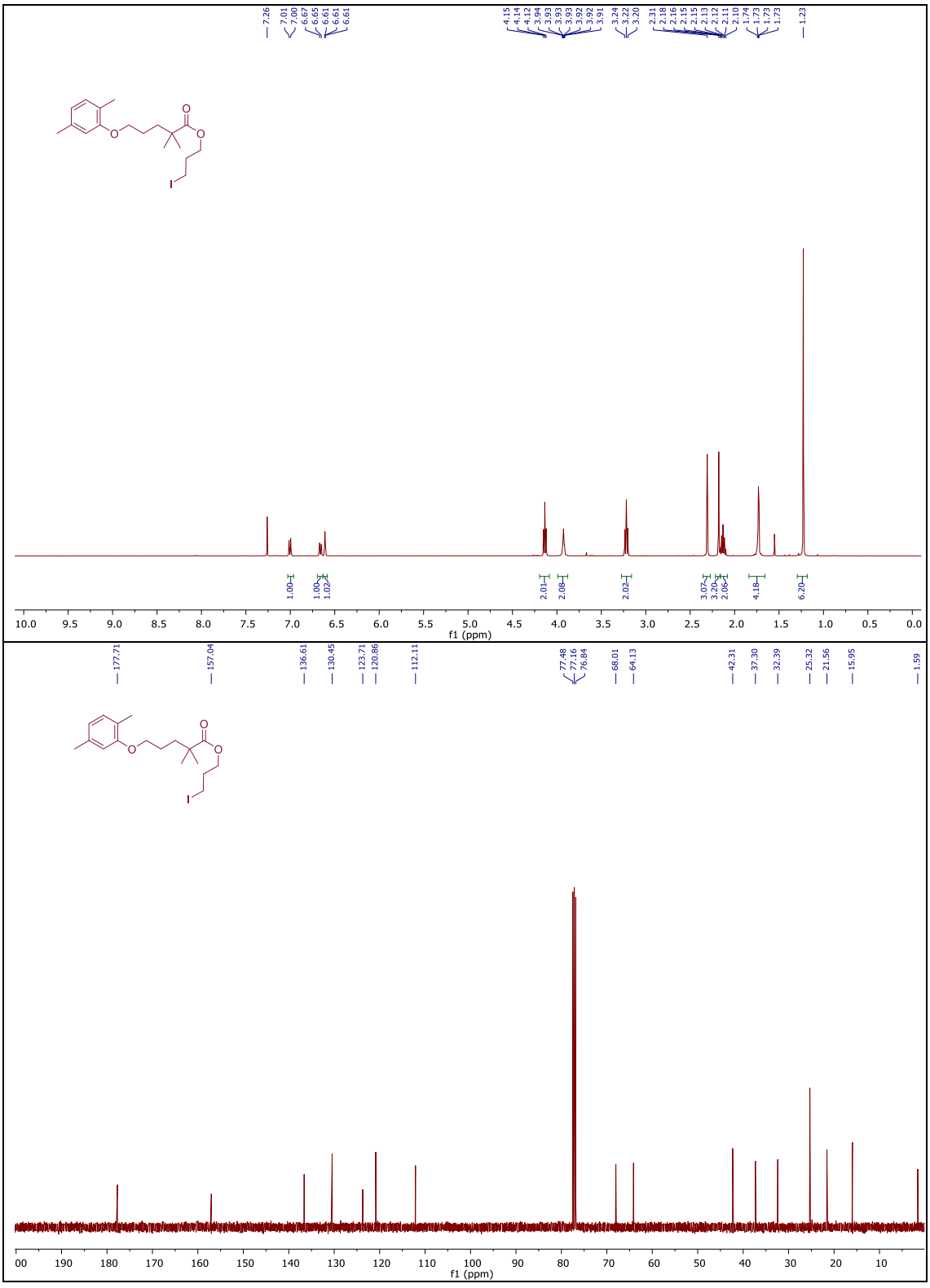


NMR spectra of 2e'

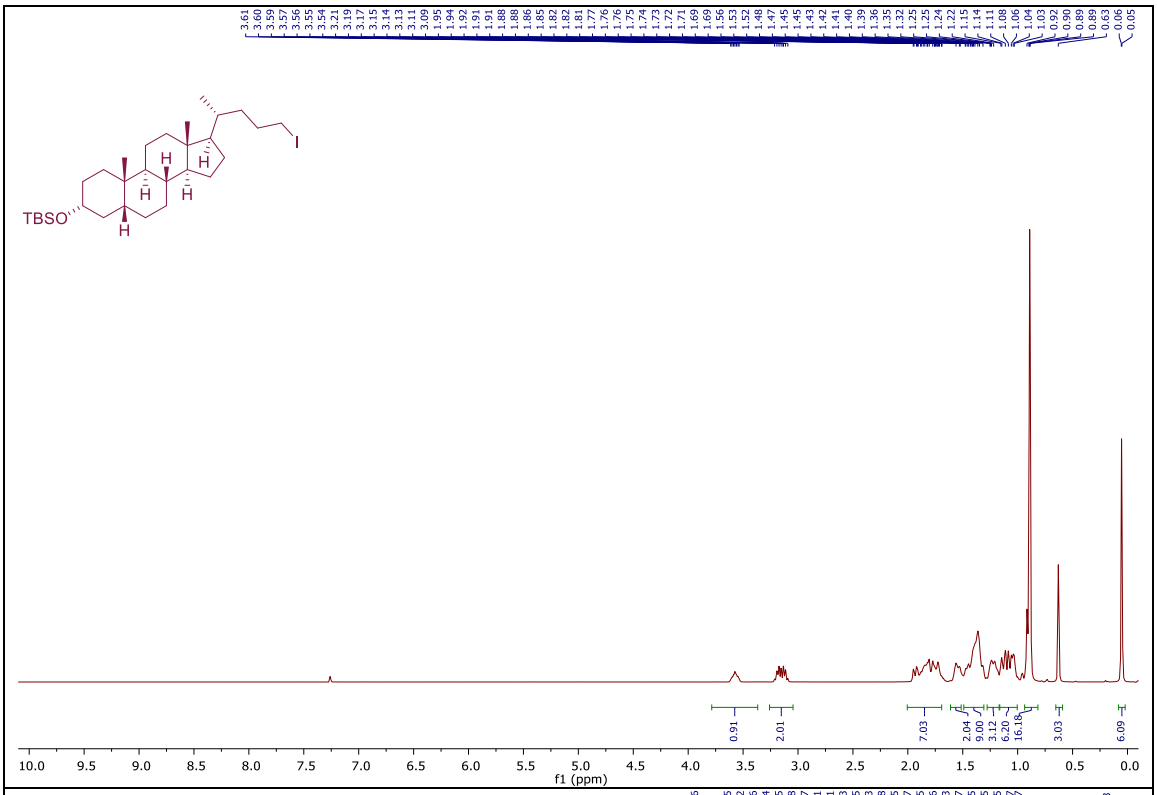


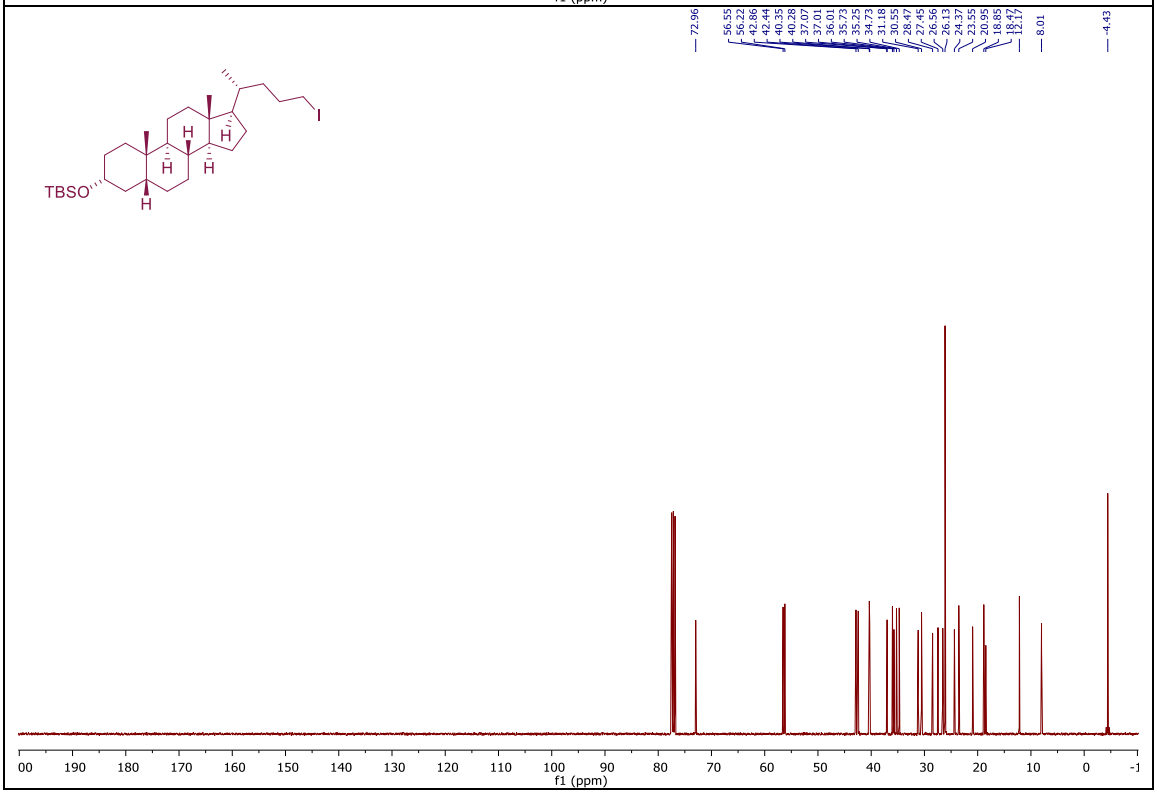


NMR spectra of 2f'

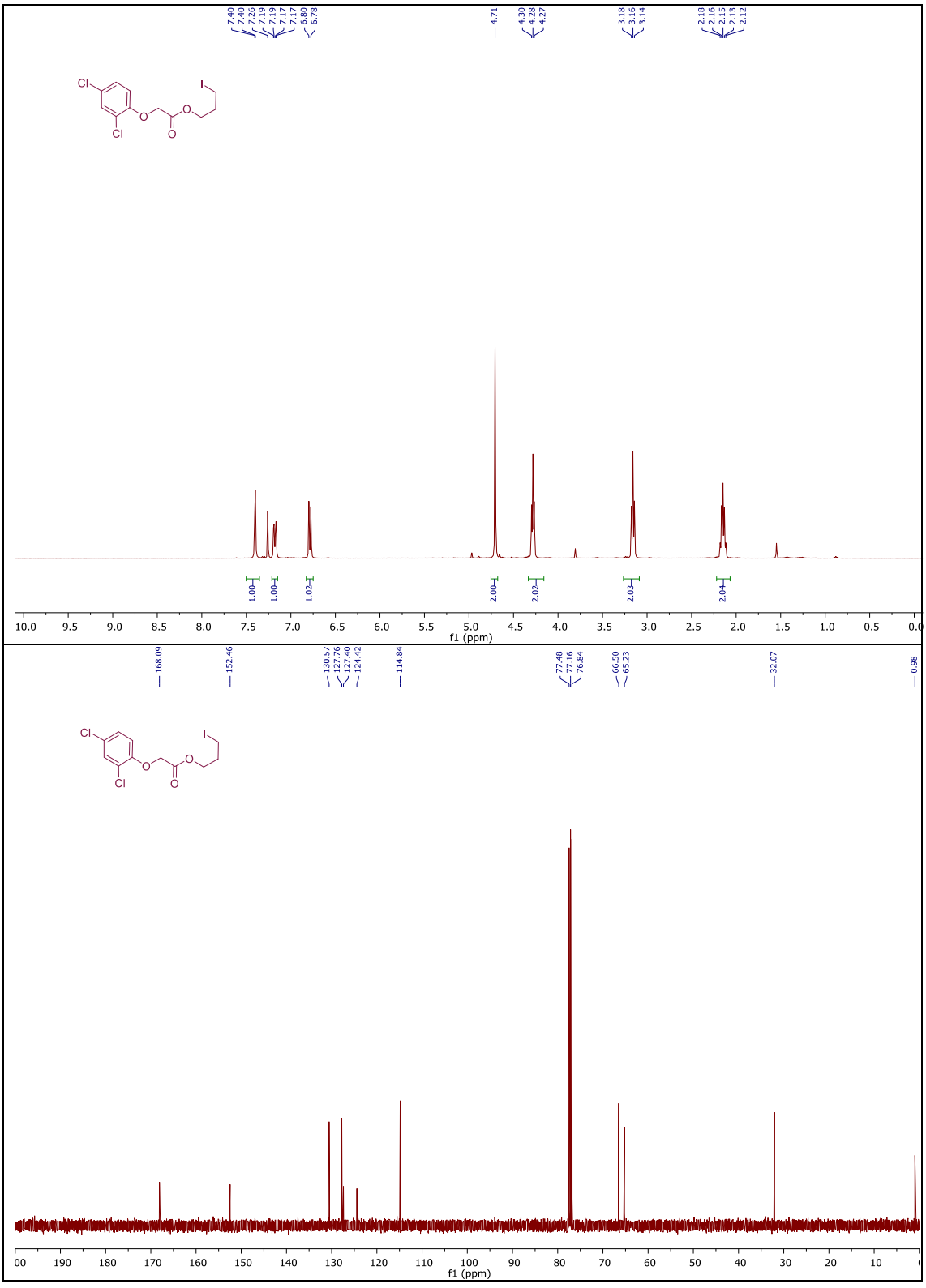


NMR spectra of 2g'

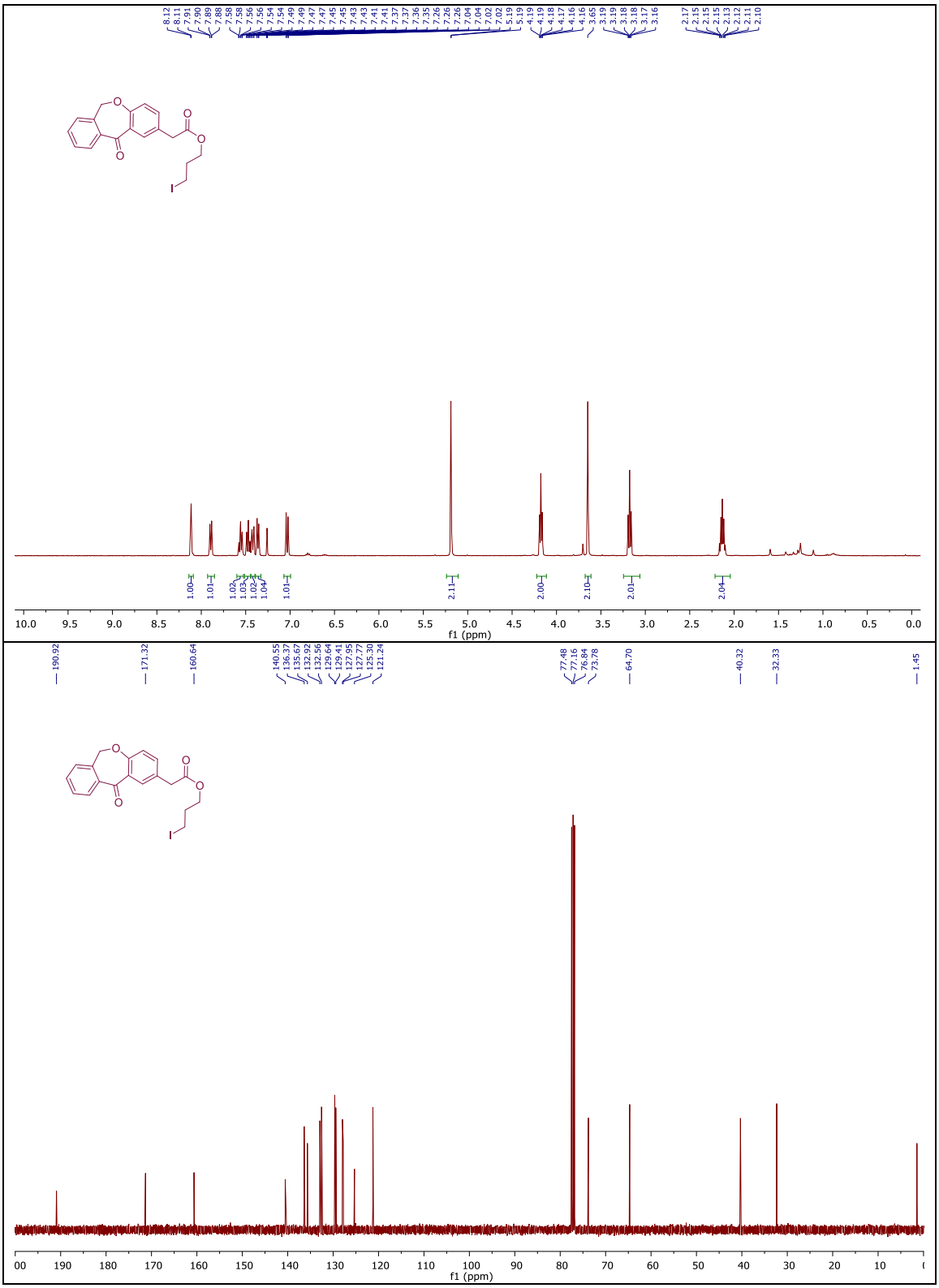




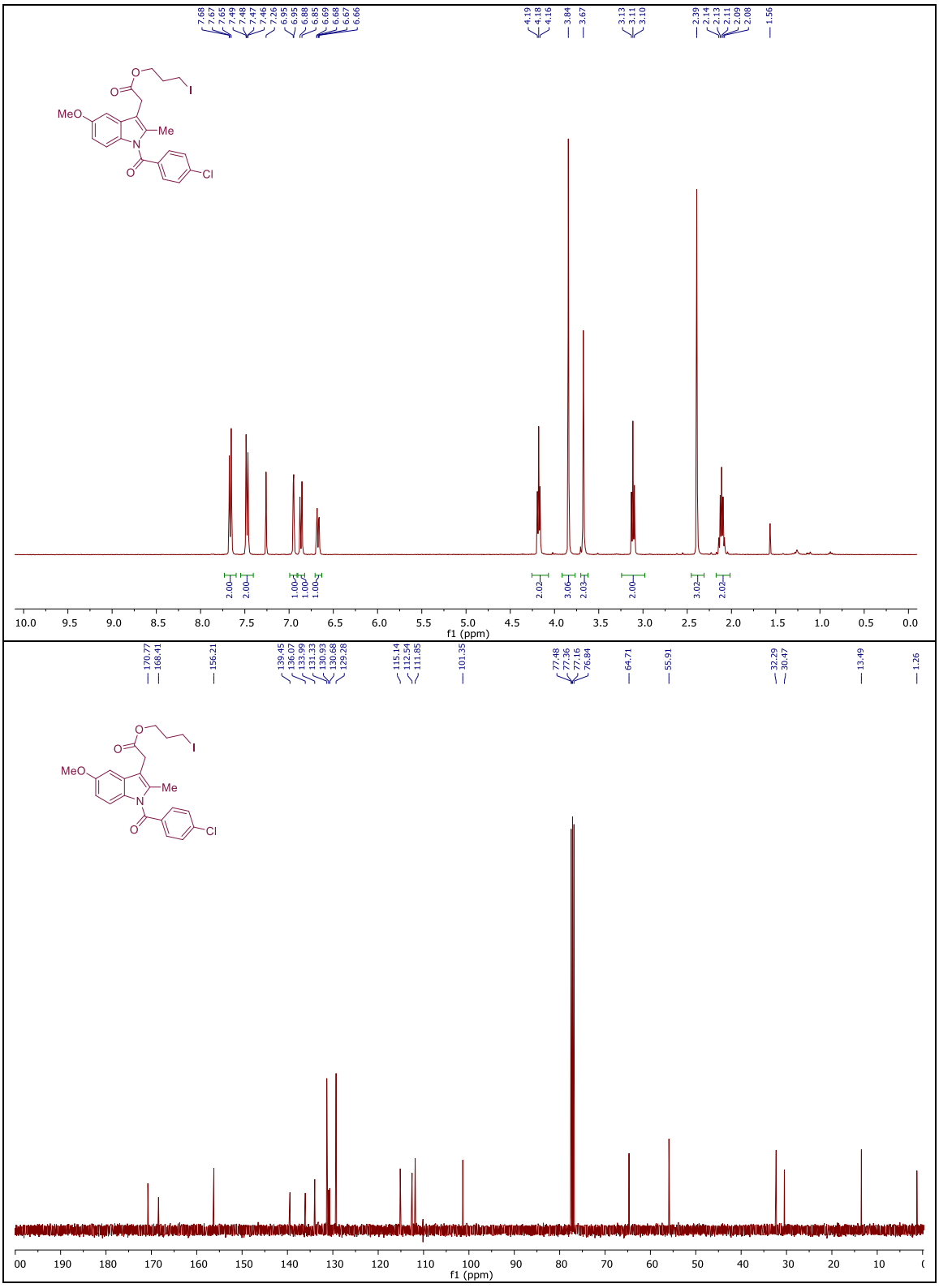
NMR spectra of 2h'



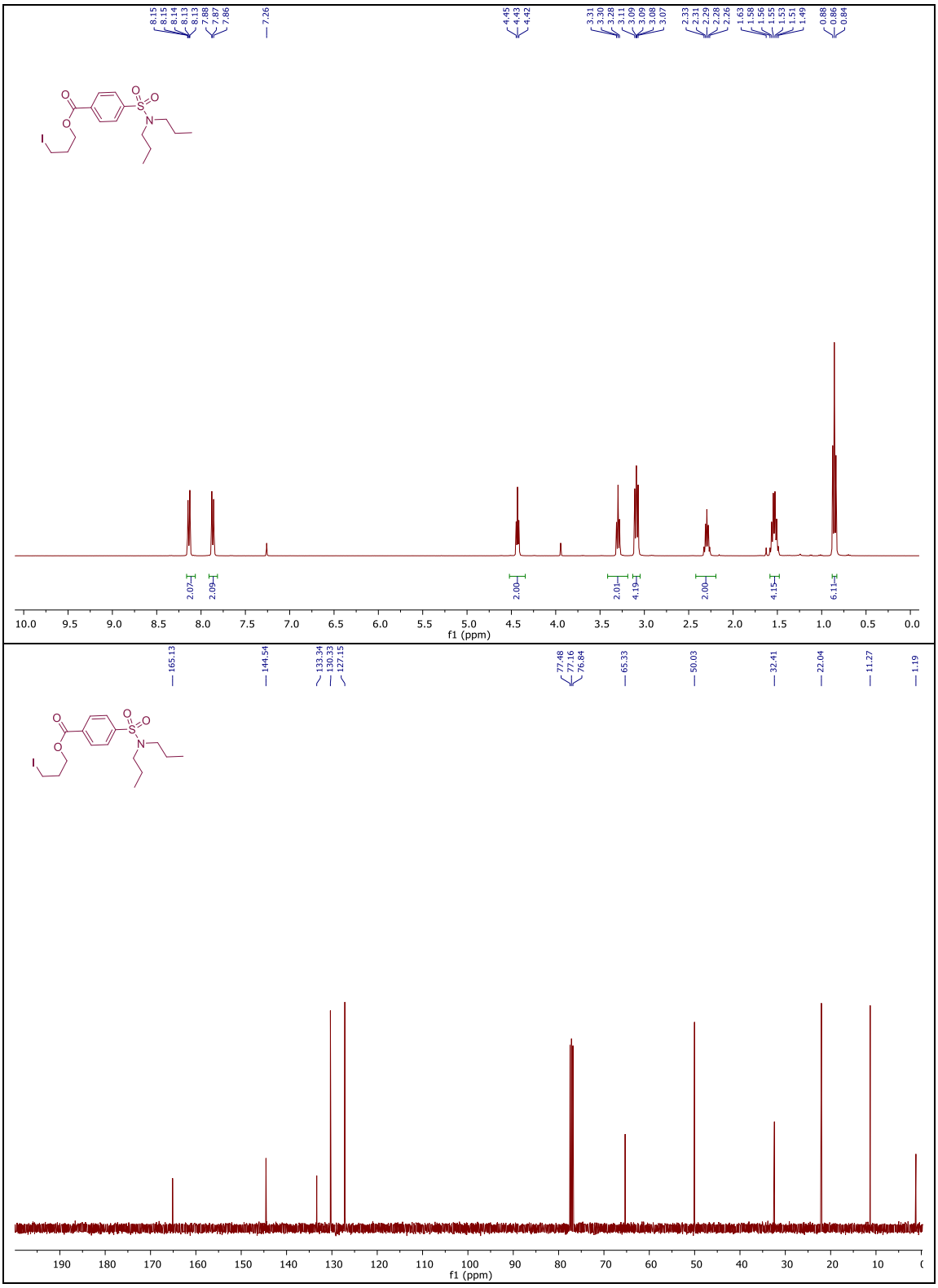
NMR spectra of 2i'



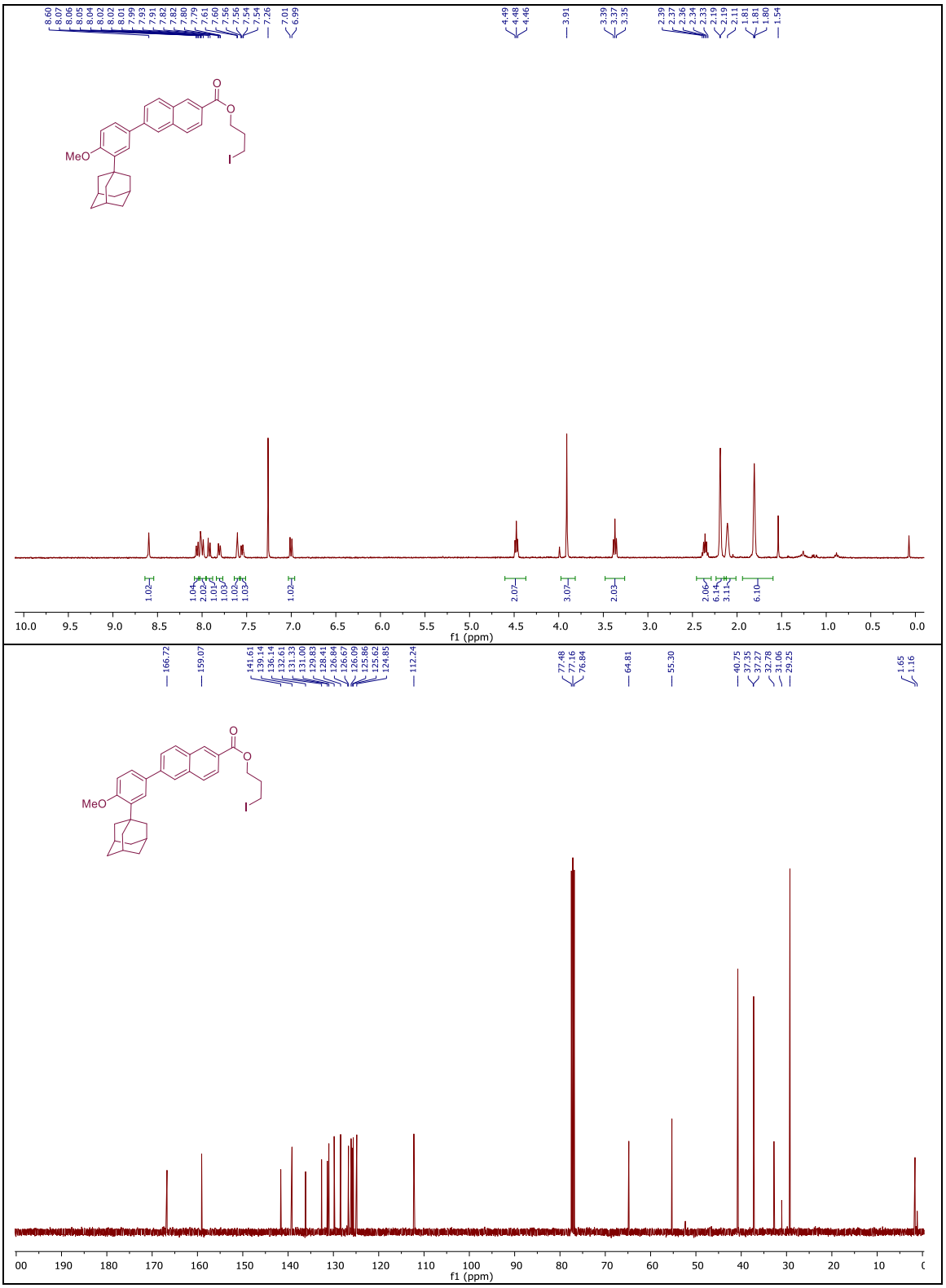
NMR spectra of 2j'



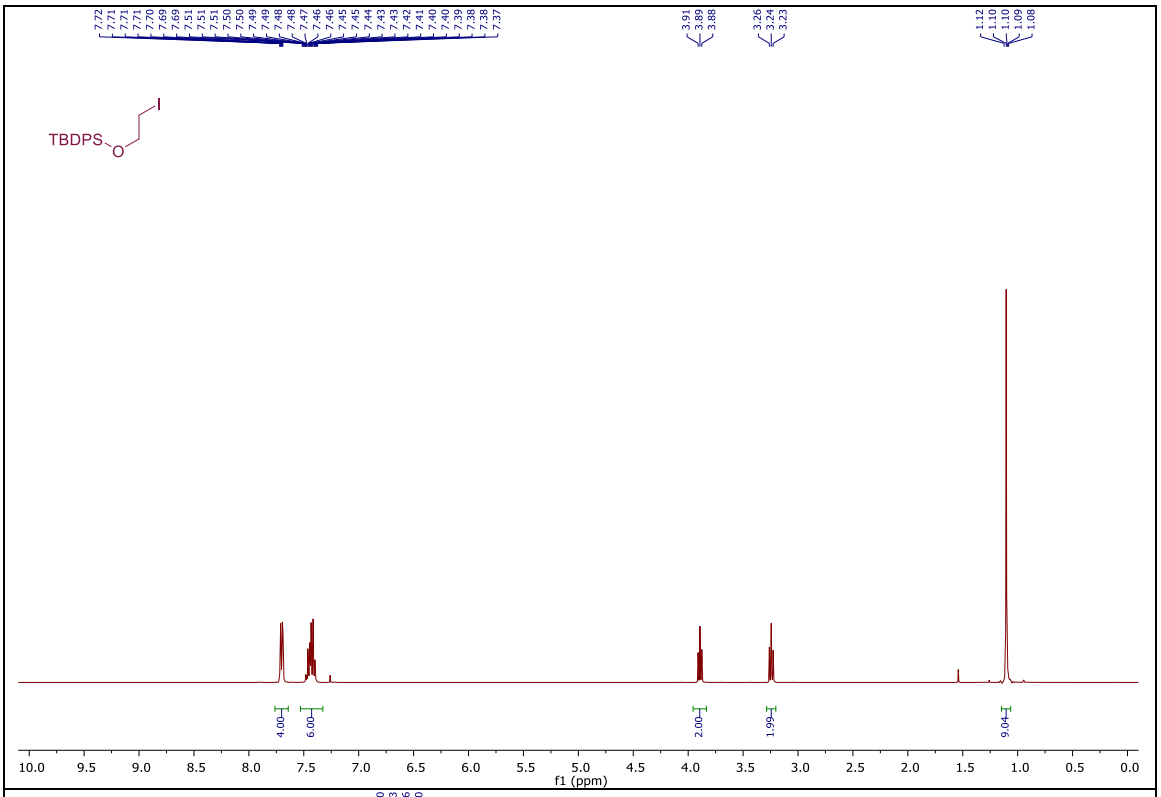
NMR spectra of 2k'

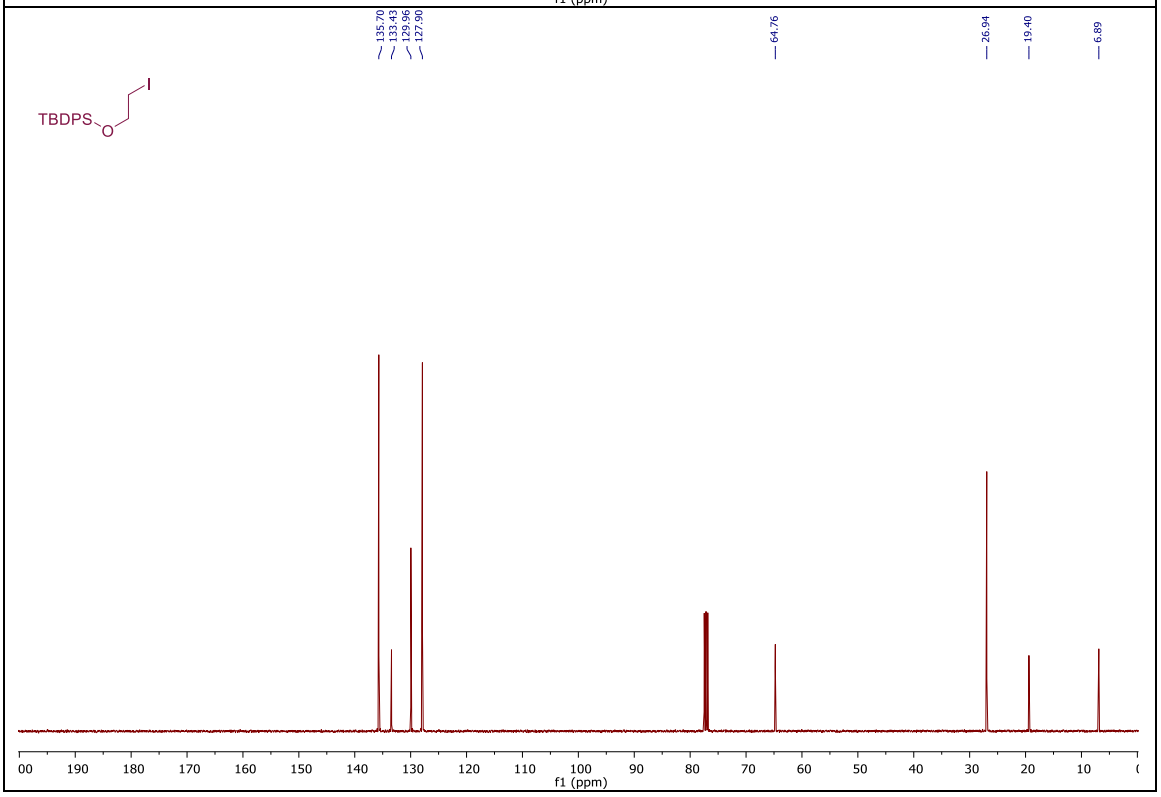


NMR spectra of 2l'

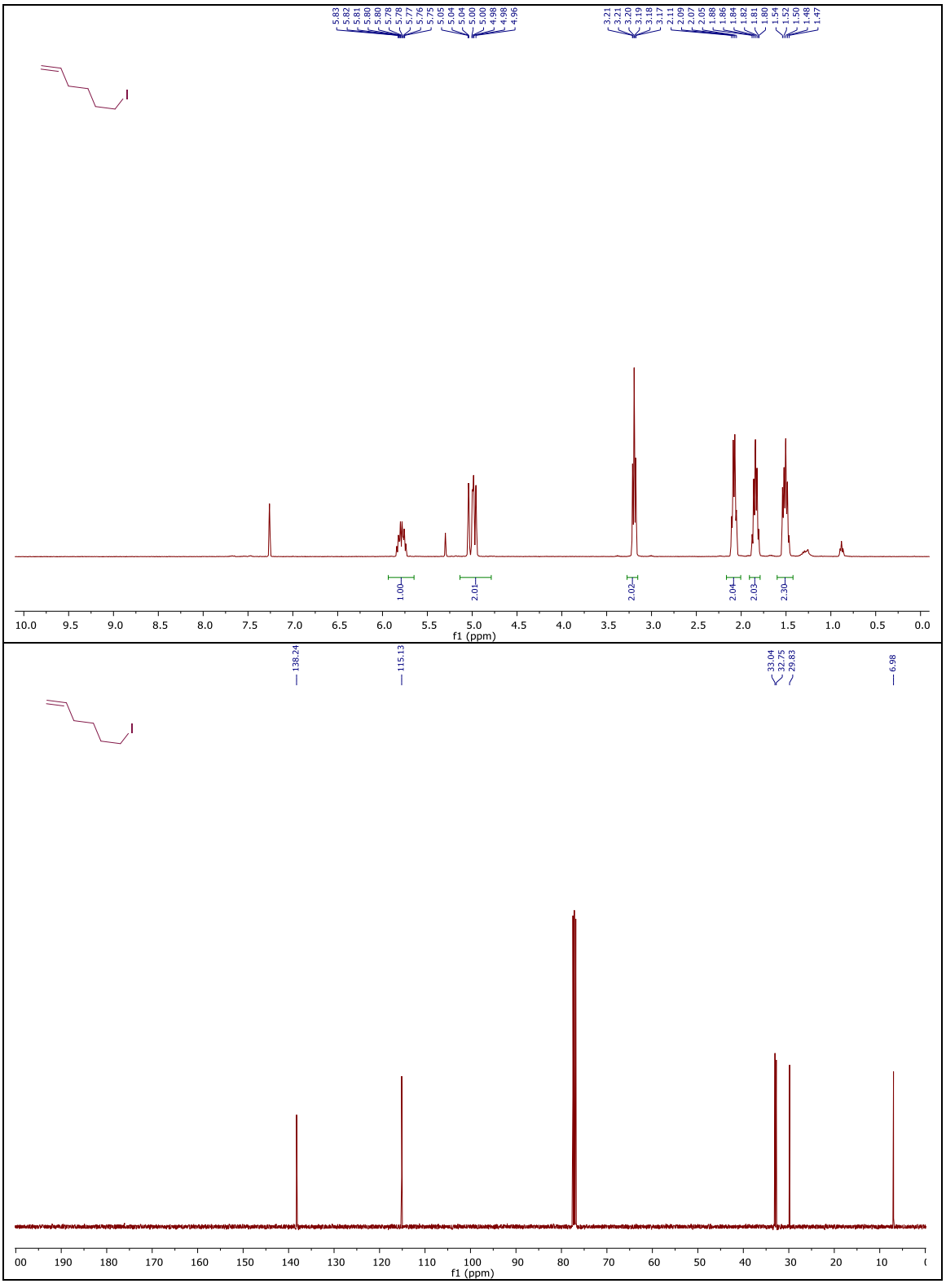


NMR spectra of 2m'

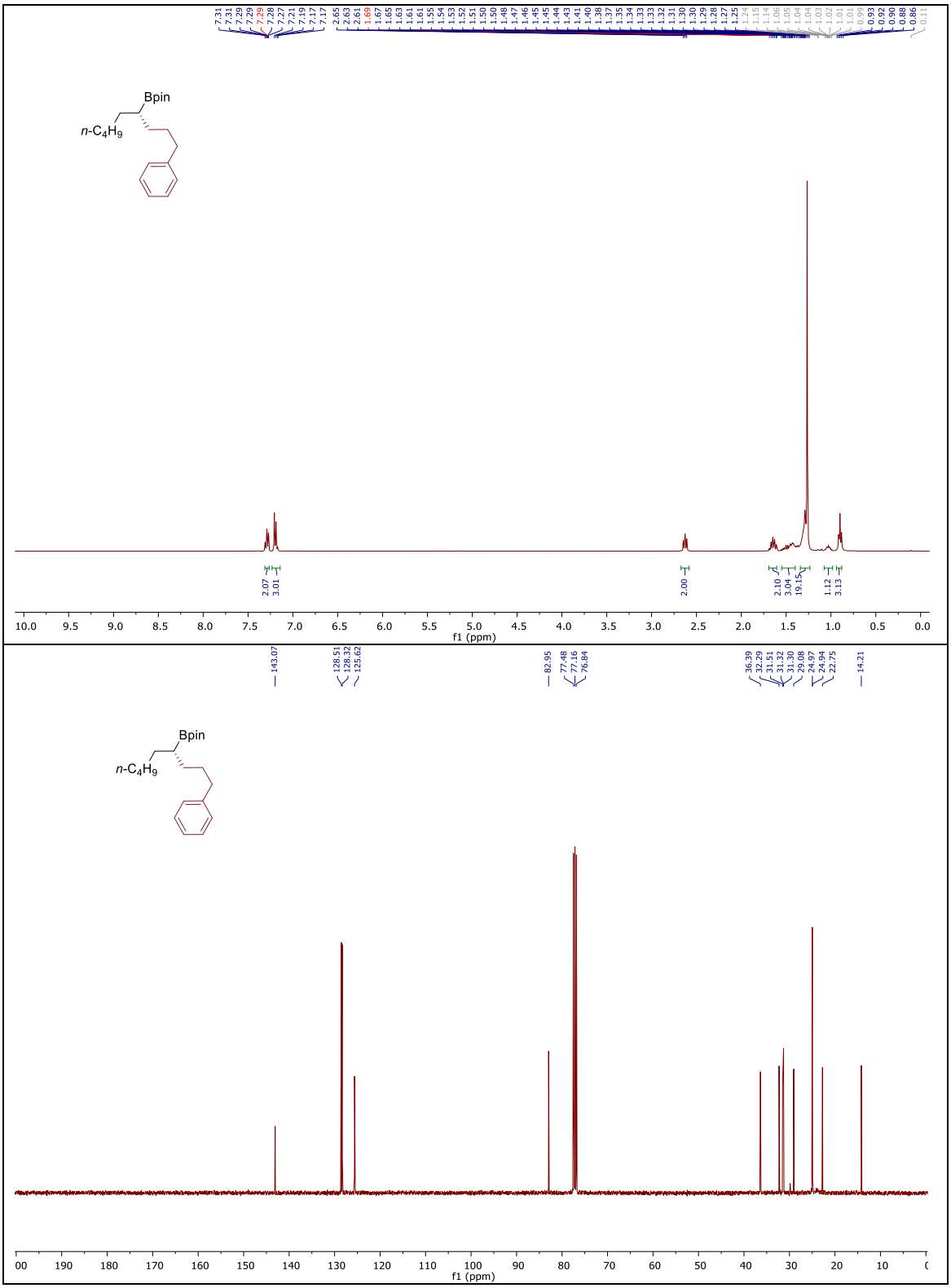


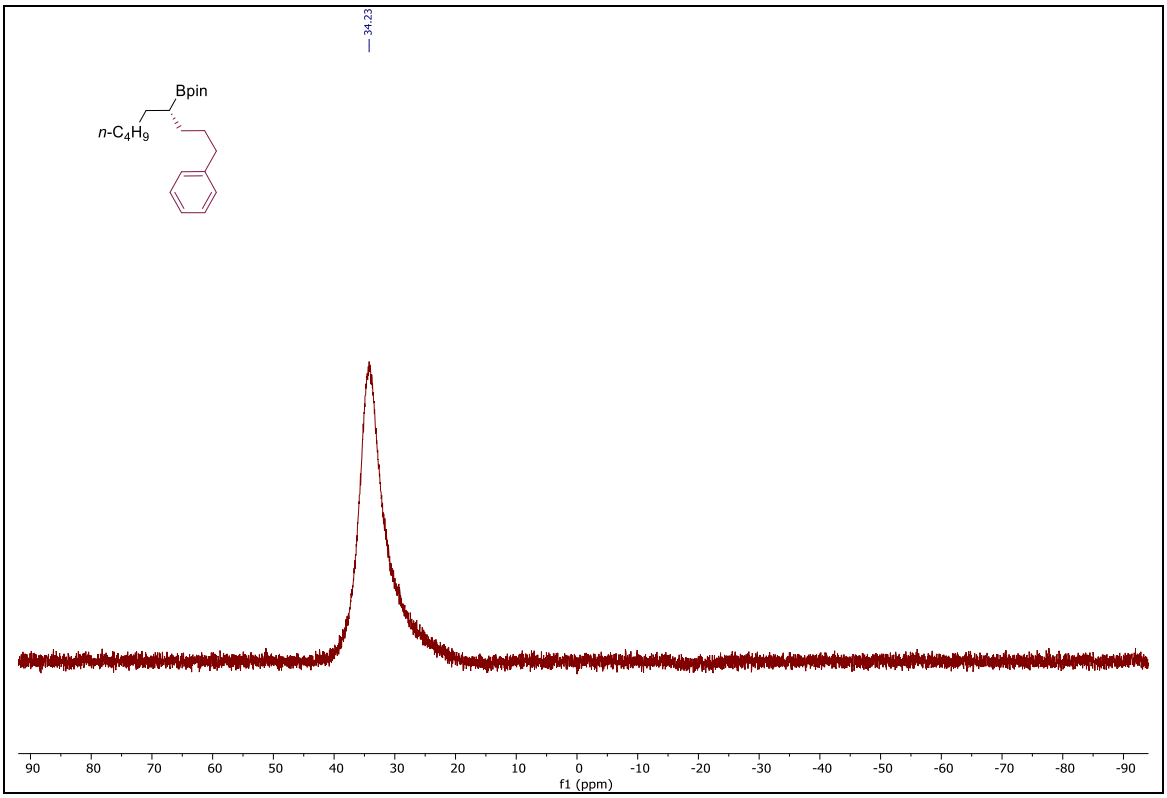


NMR spectra of 2n'

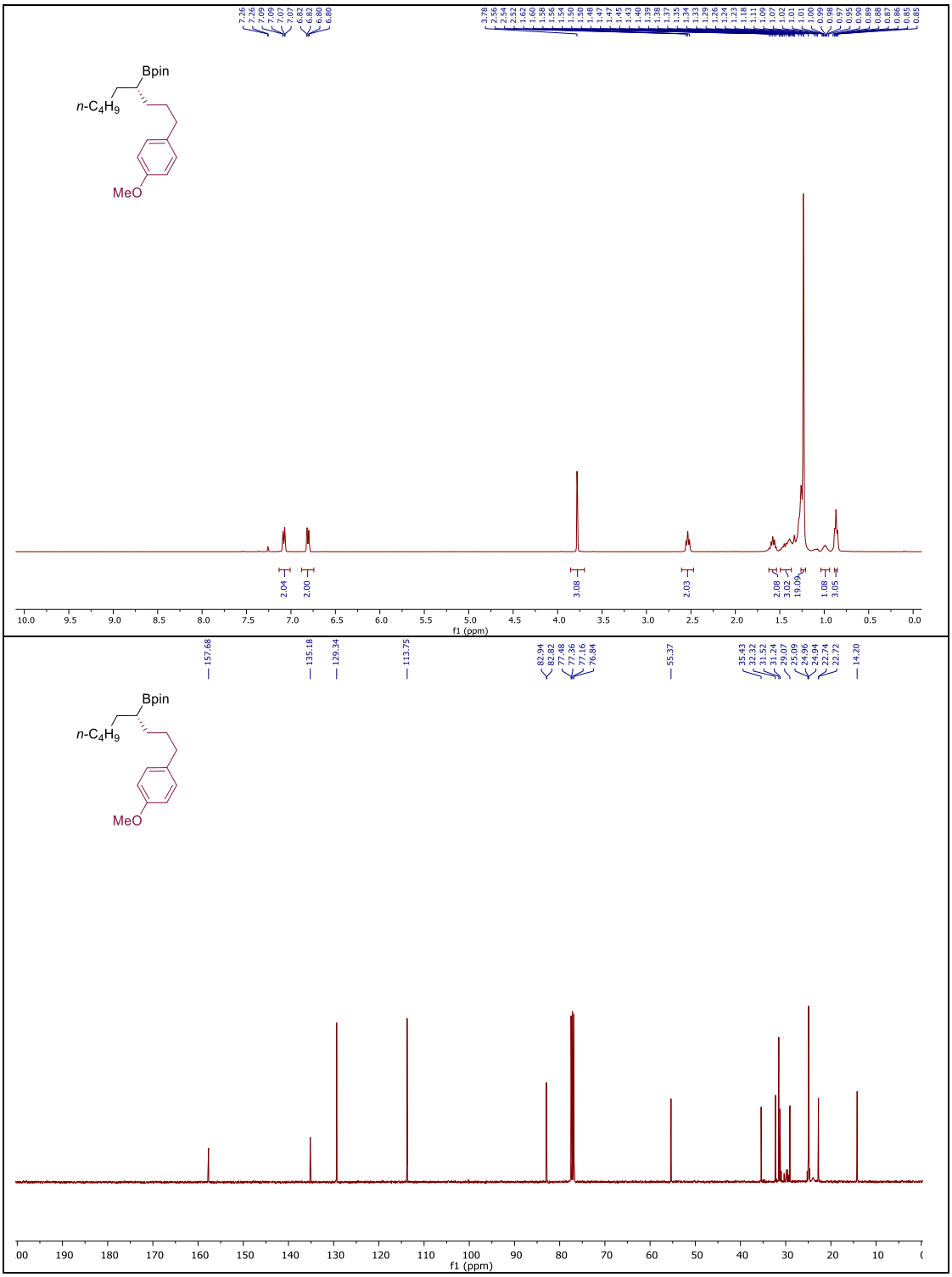


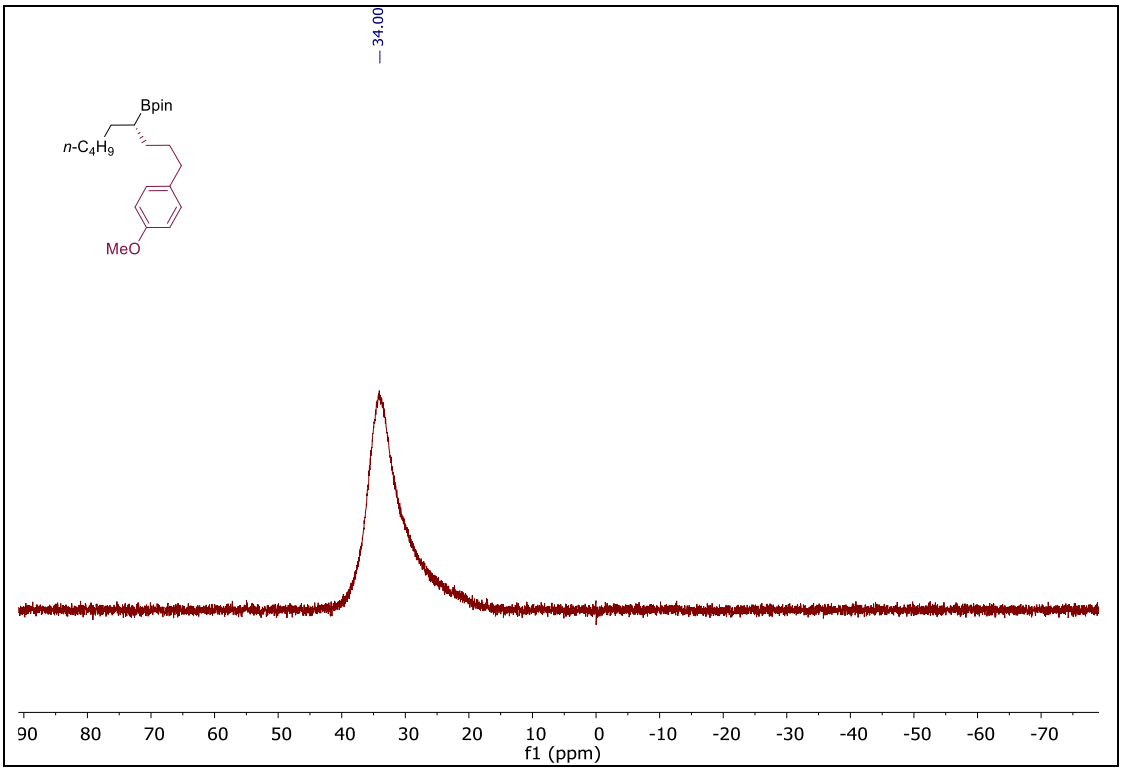
NMR spectra of 3a



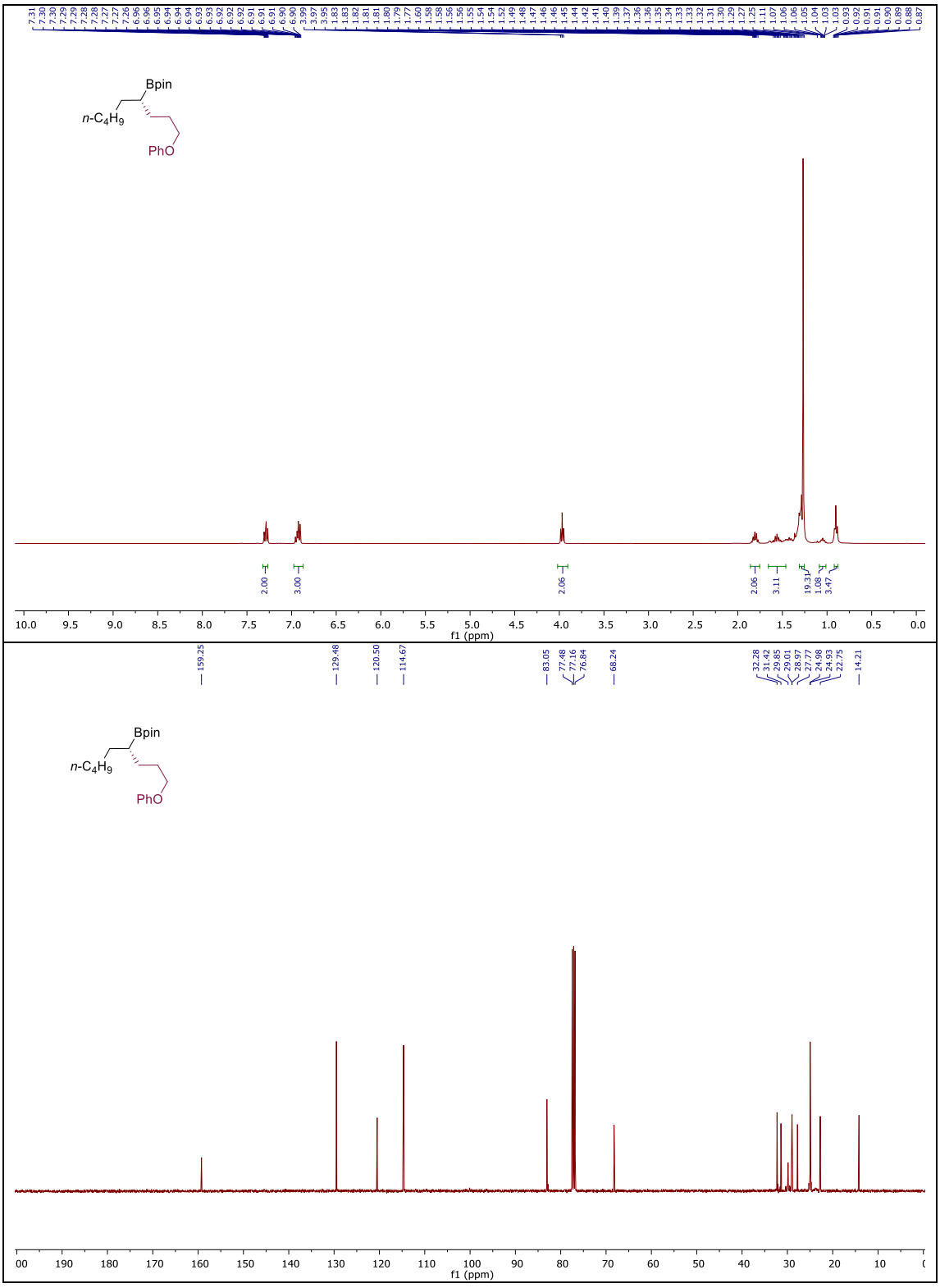

34.23
Bpin
n-C4H9
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

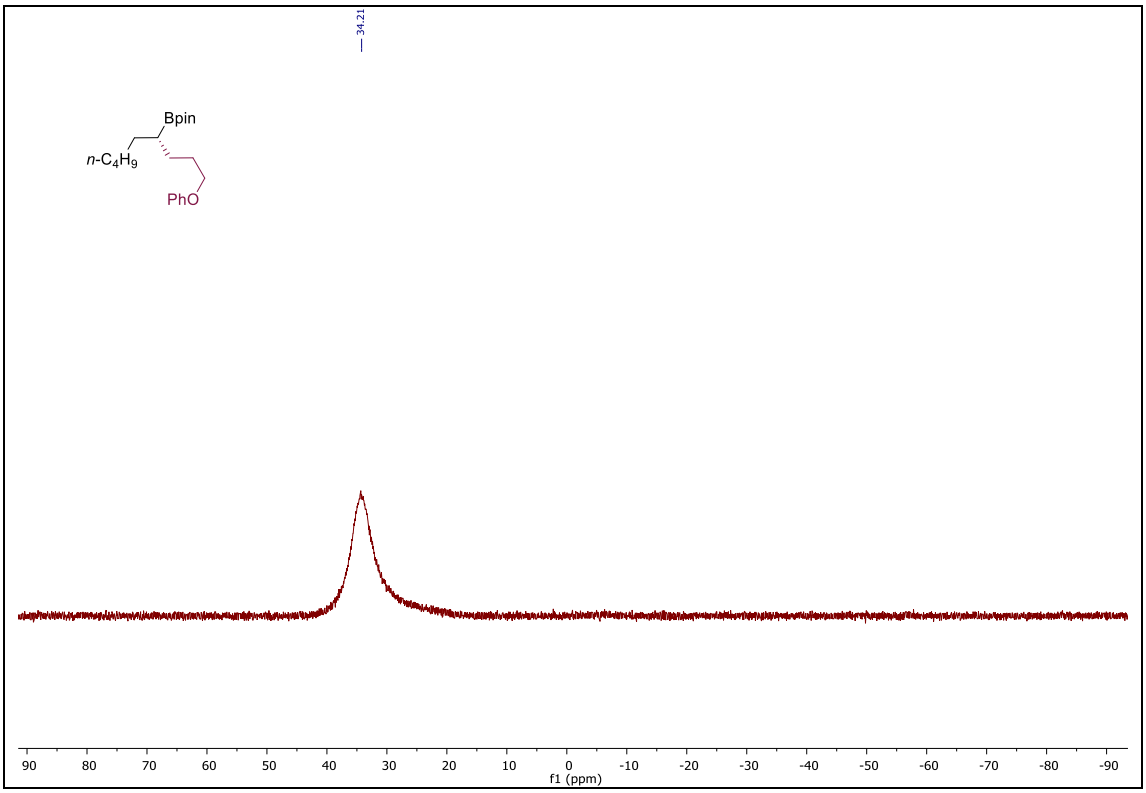
NMR spectra of 3b



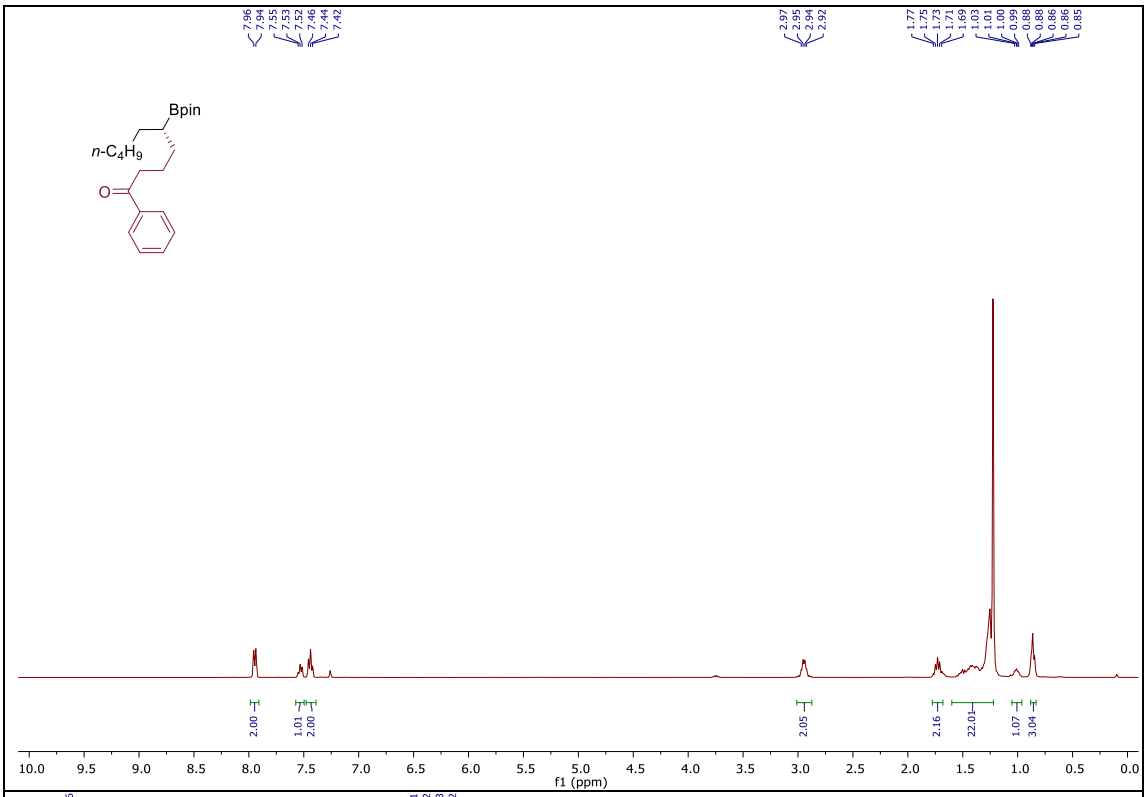

34.00
Bpin
n-C4H9
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

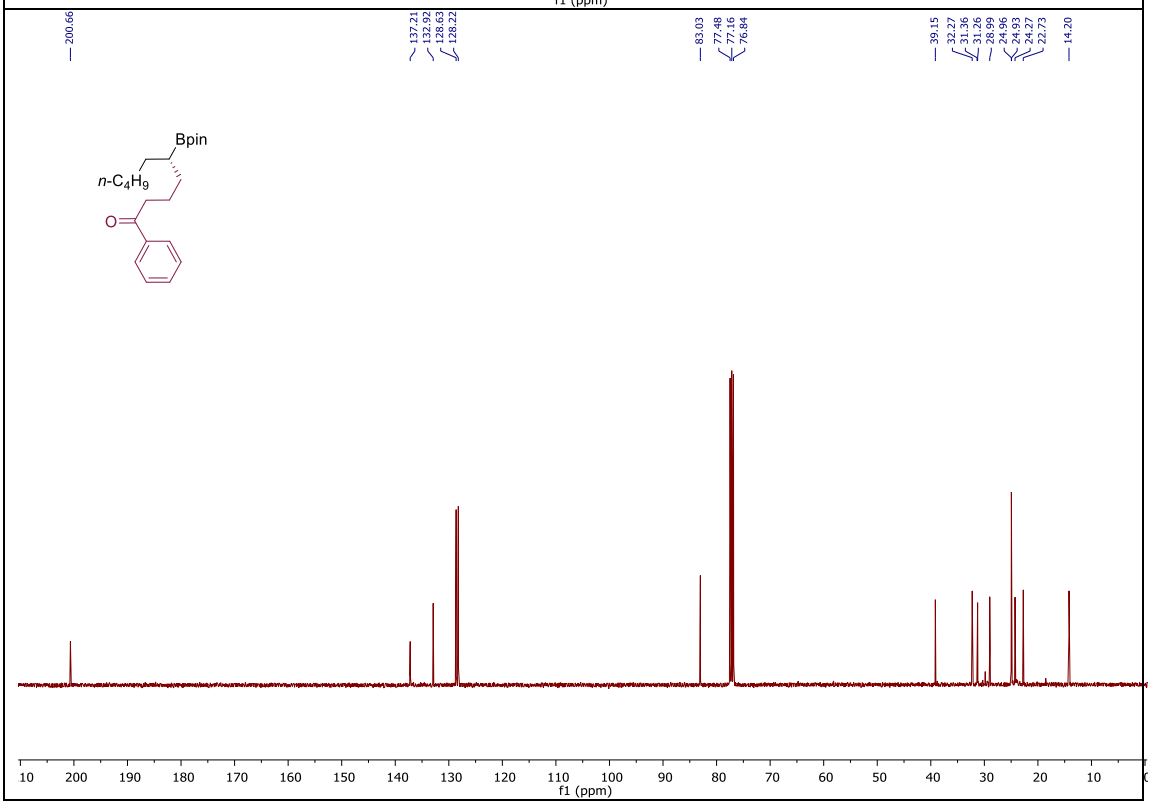
NMR spectra of 3c

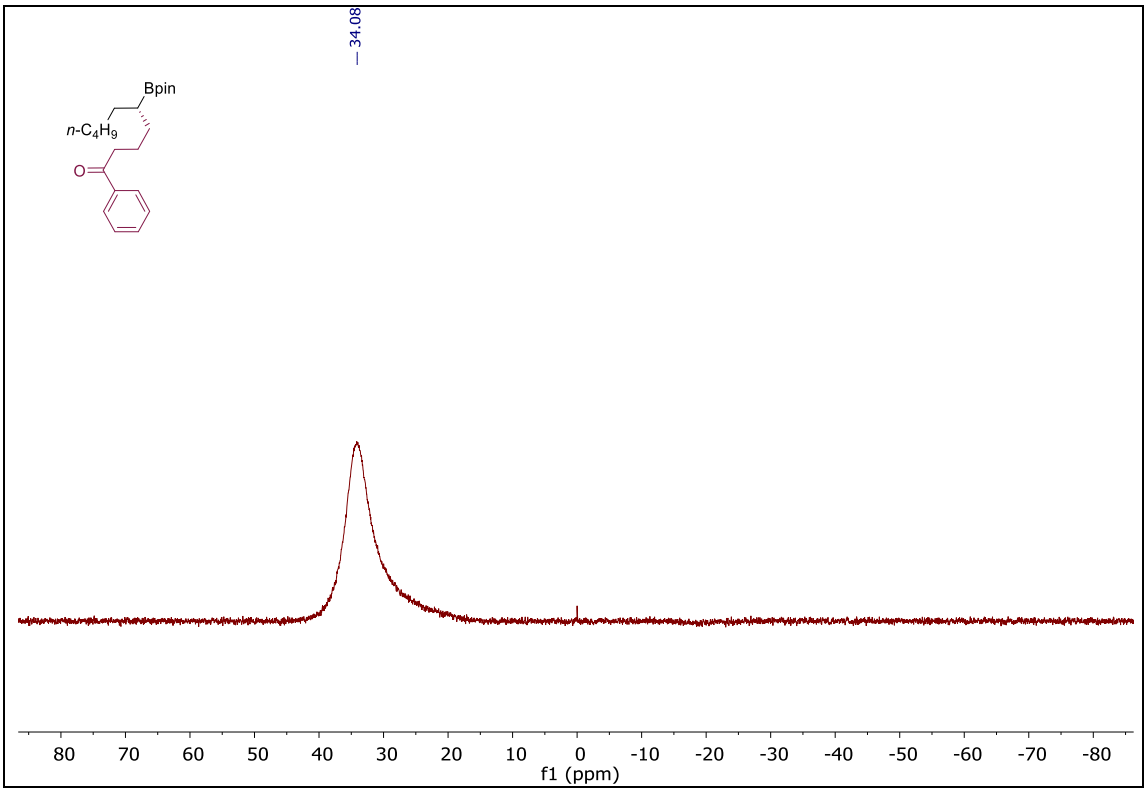



34.21
Bpin
n-C4H9
PhO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

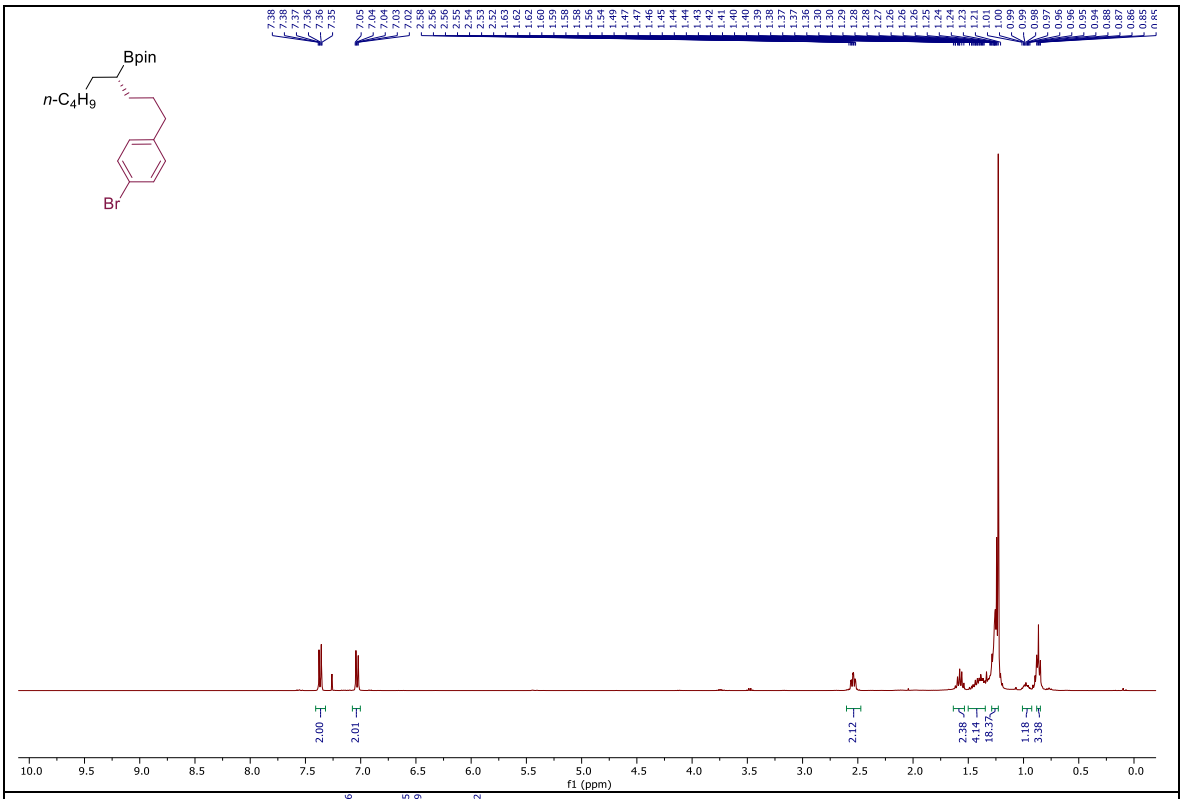
NMR spectra of 3d

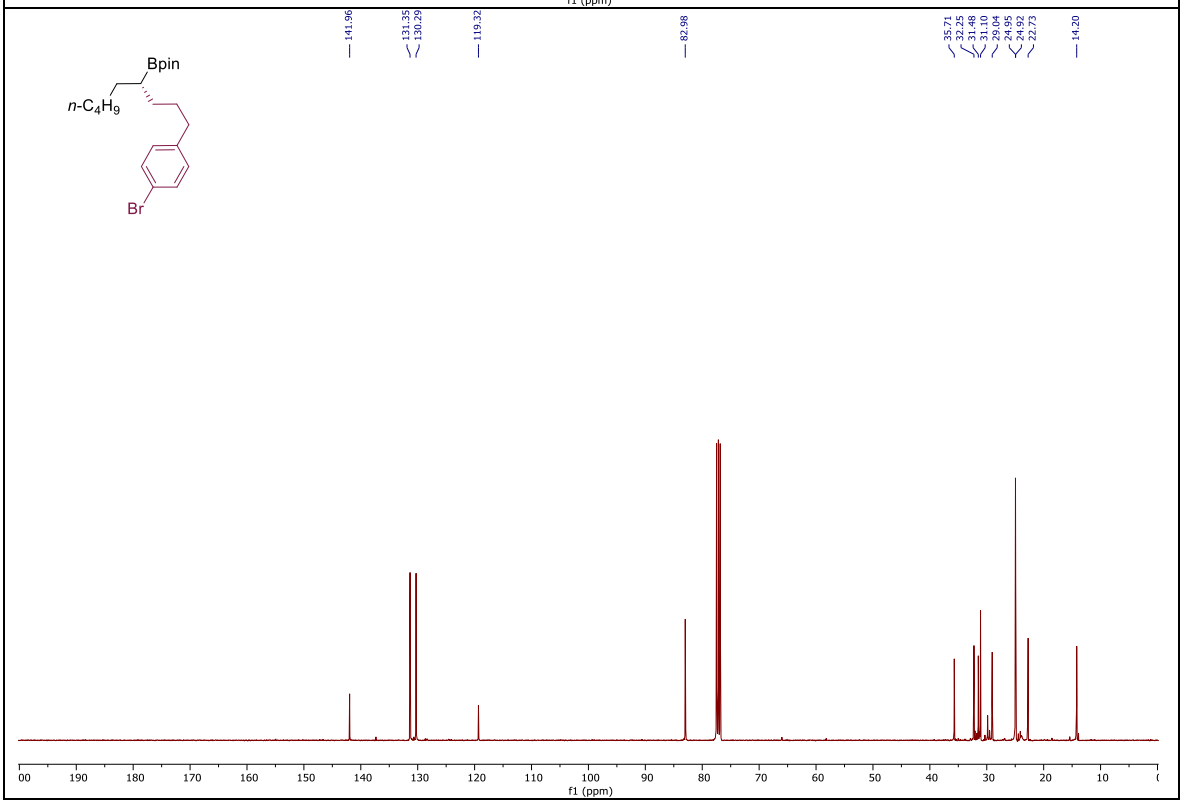


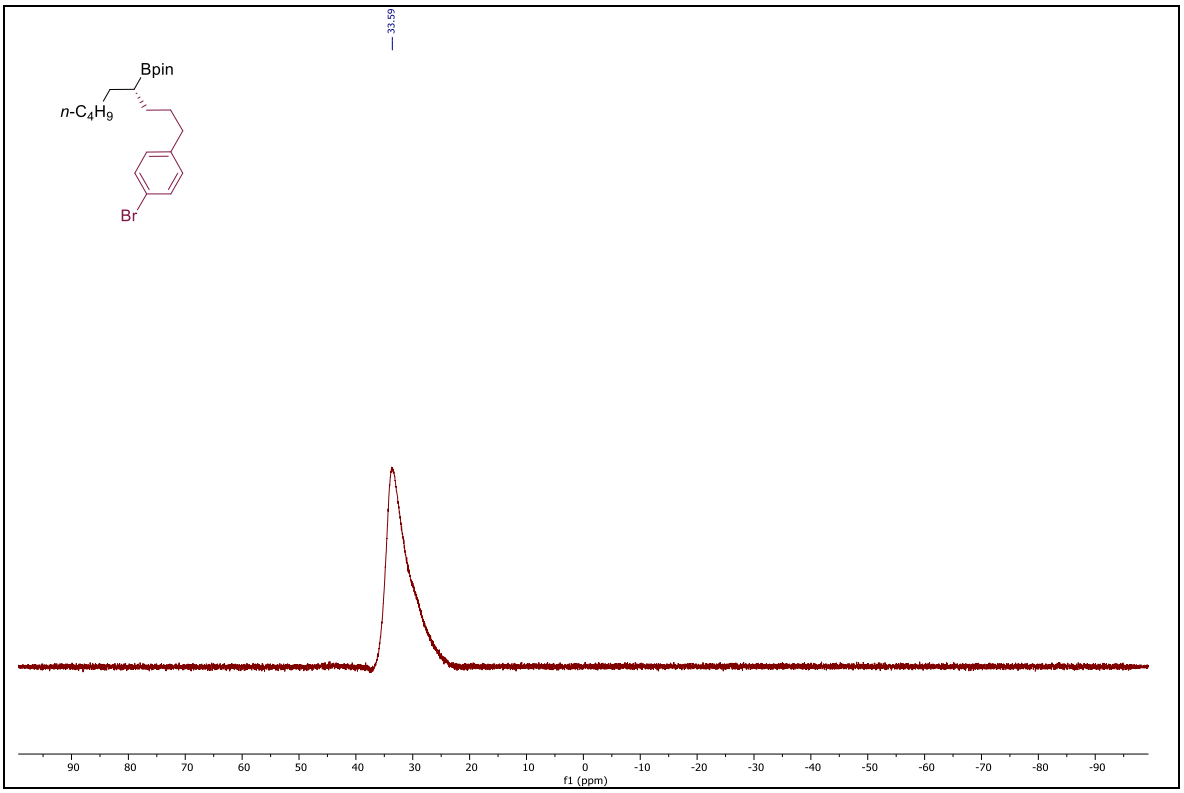



34.08
Bpin
n-C4H9
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

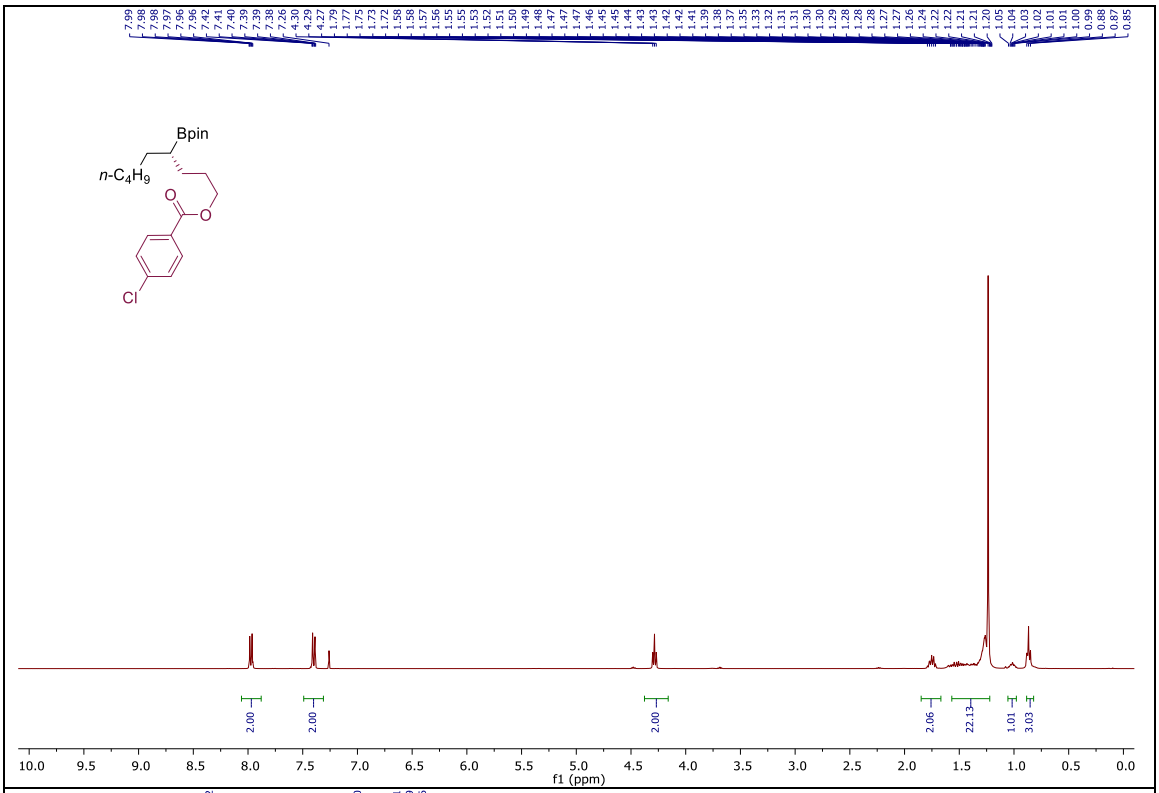
NMR spectra of 3e

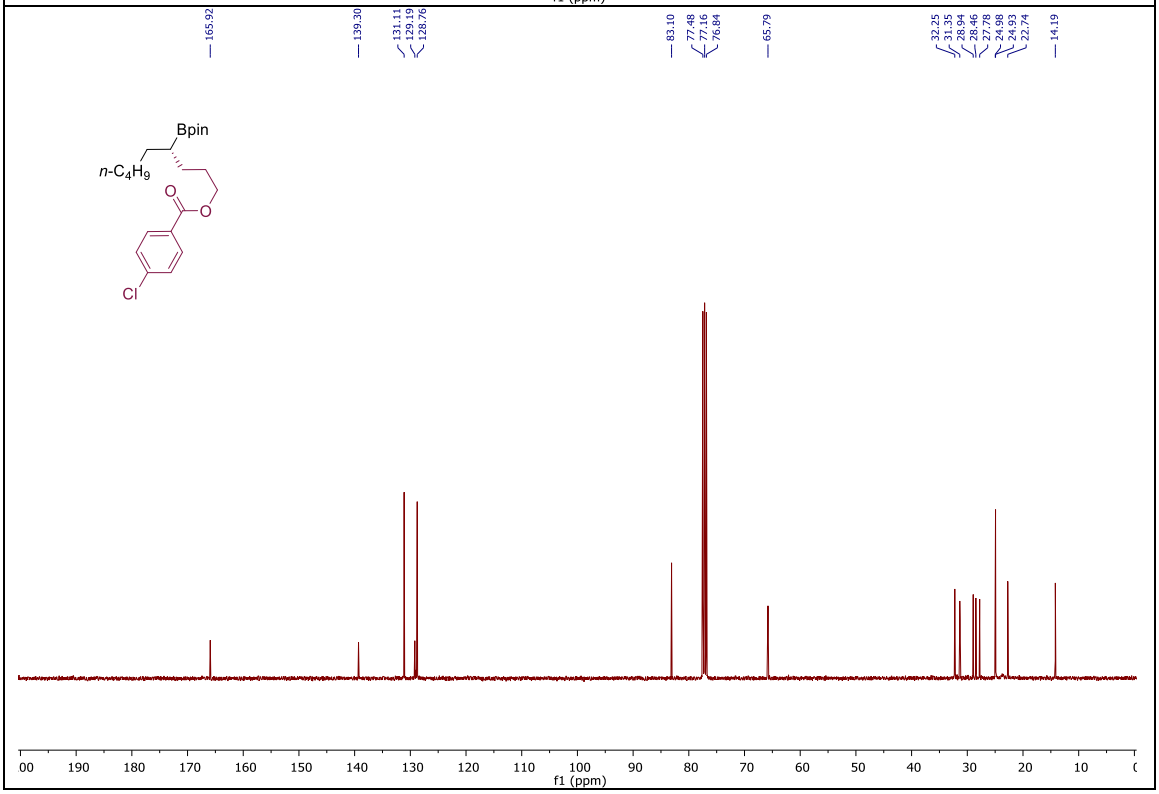


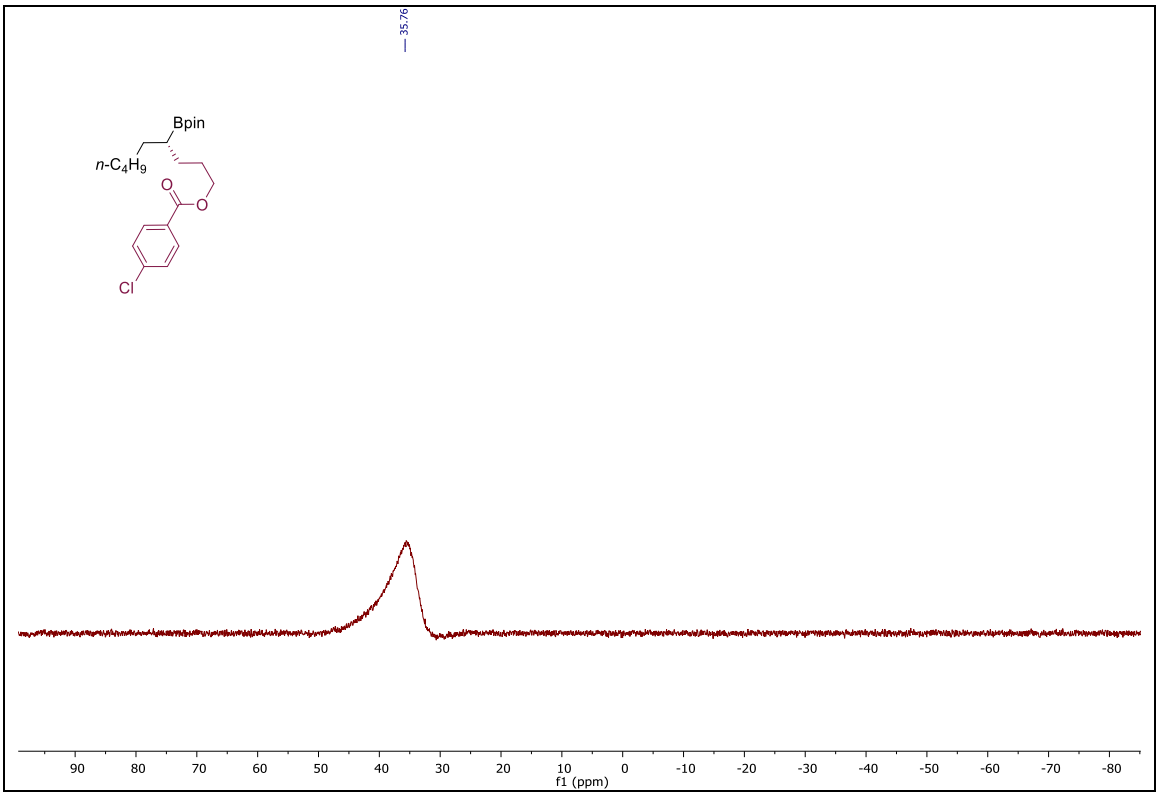



33.59
Bpin
n-C4H9
Br
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

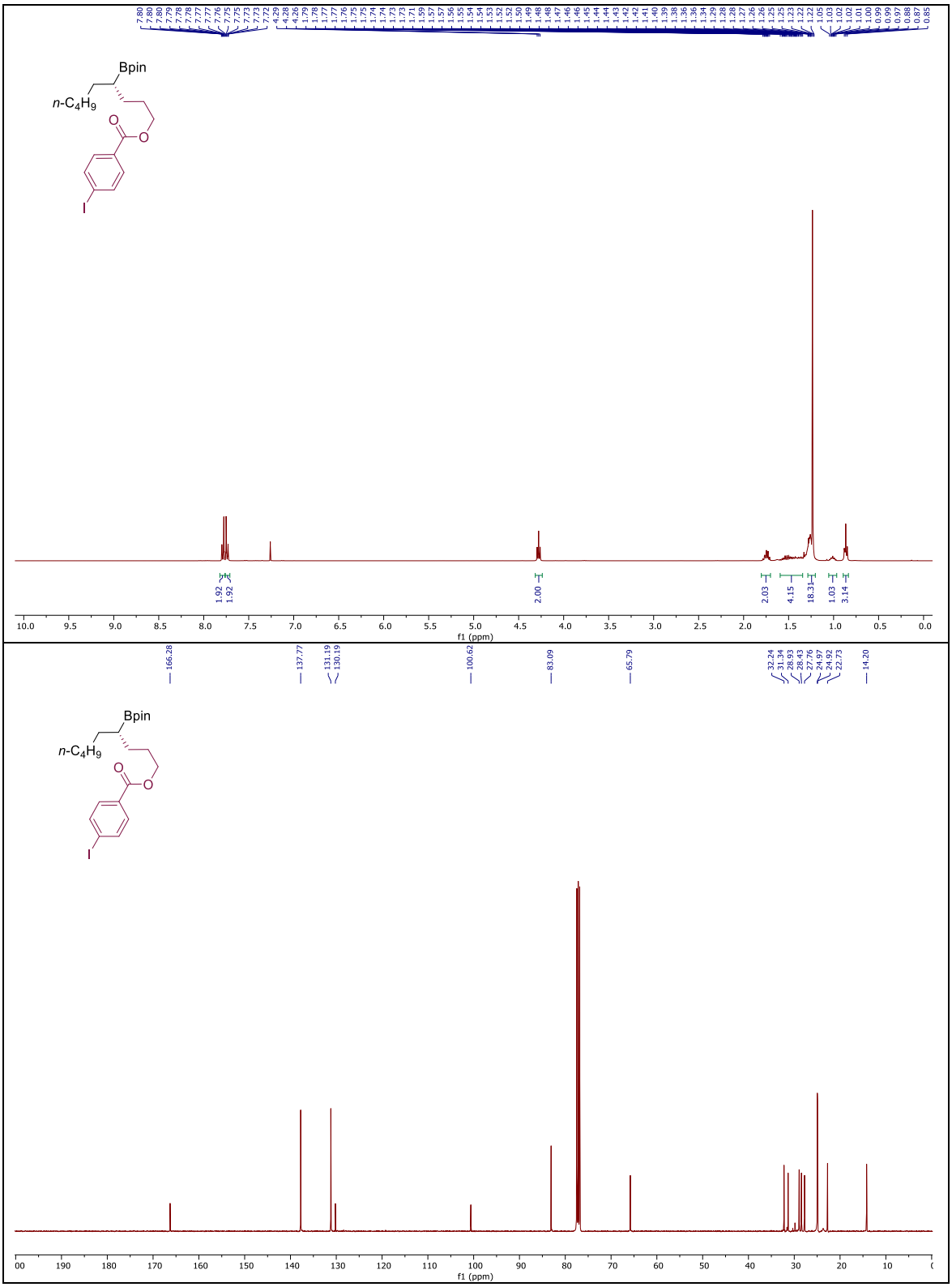
NMR spectra of 3f

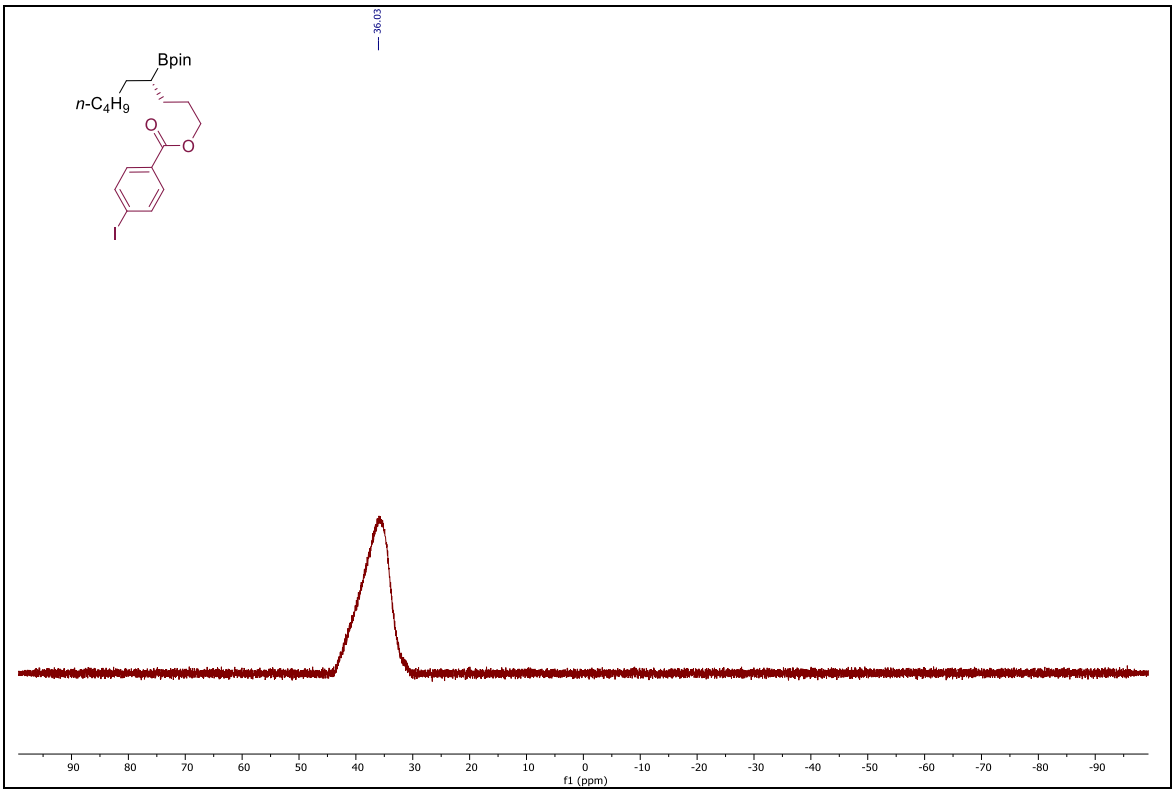




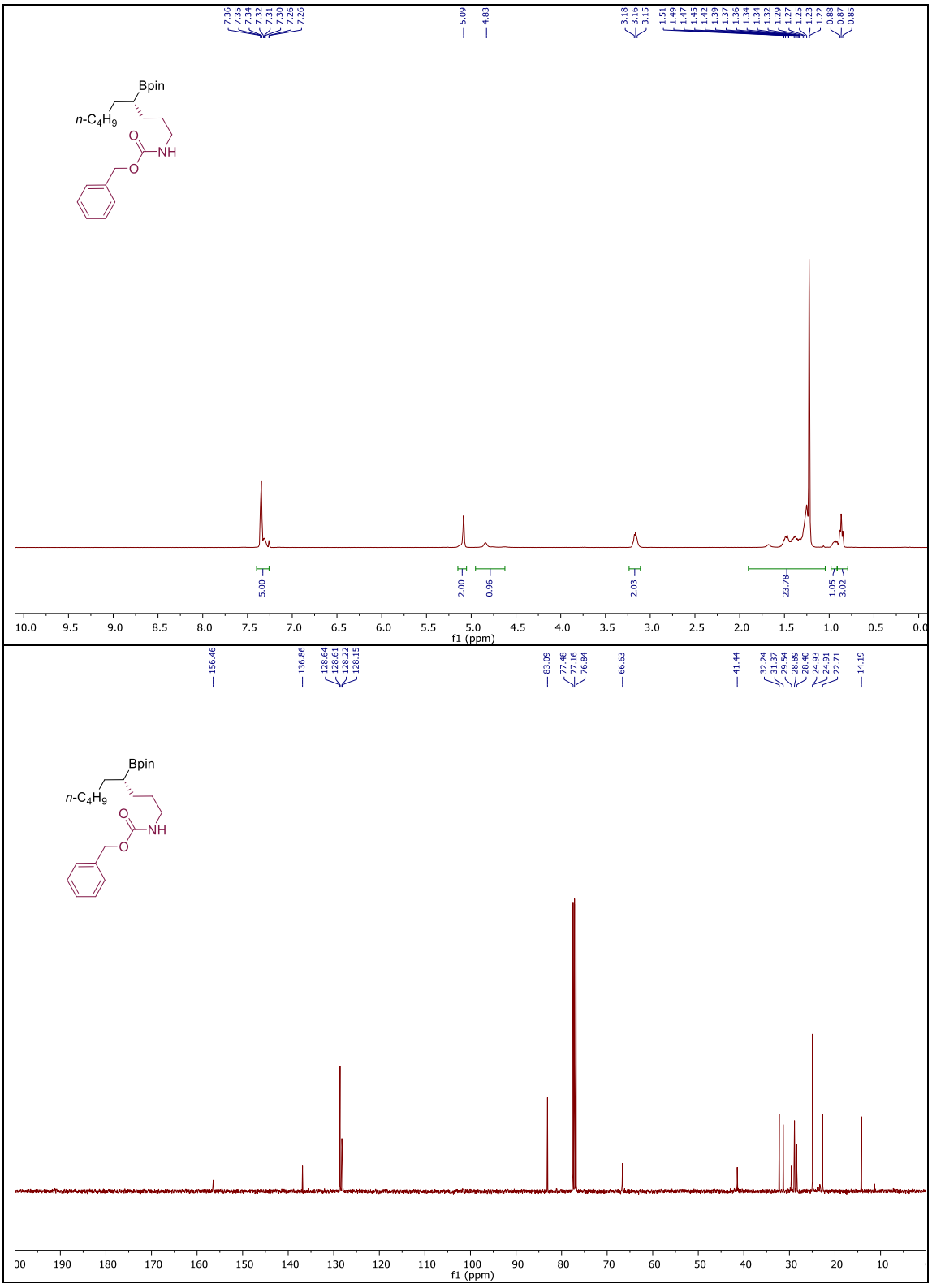

35.76
Bpin
n-C4H9
O
O
Cl
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

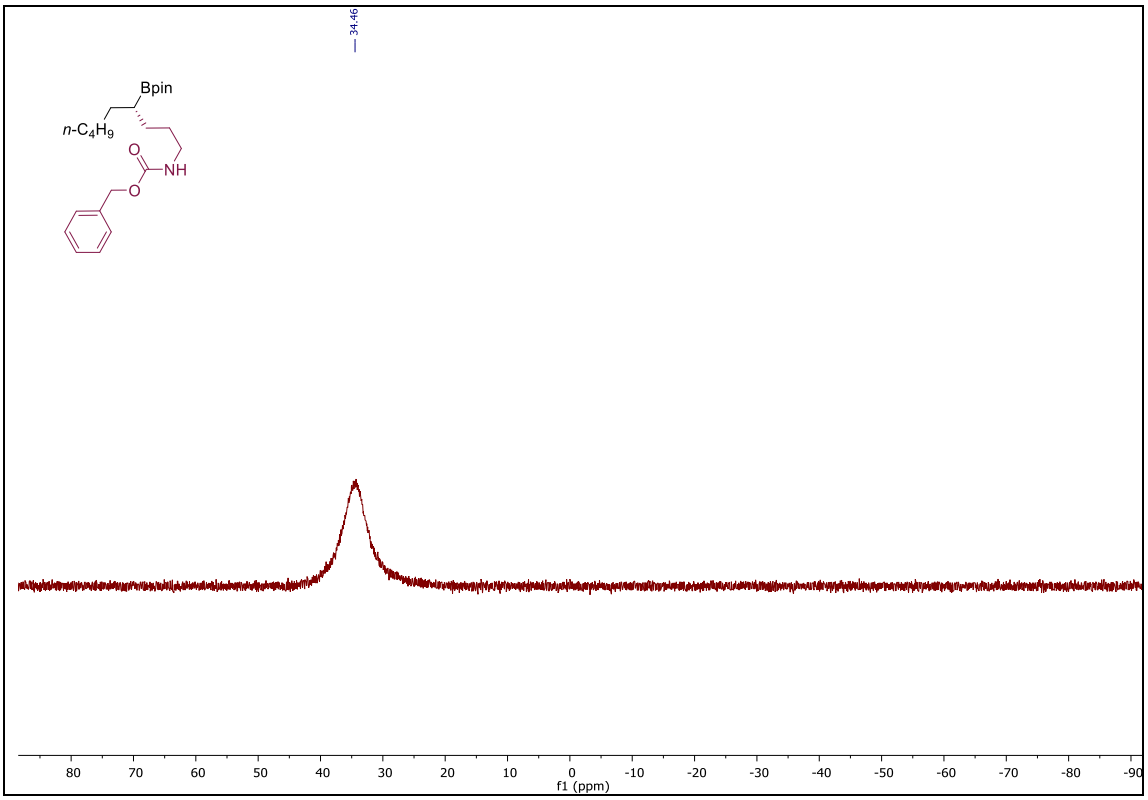
NMR spectra of 3g



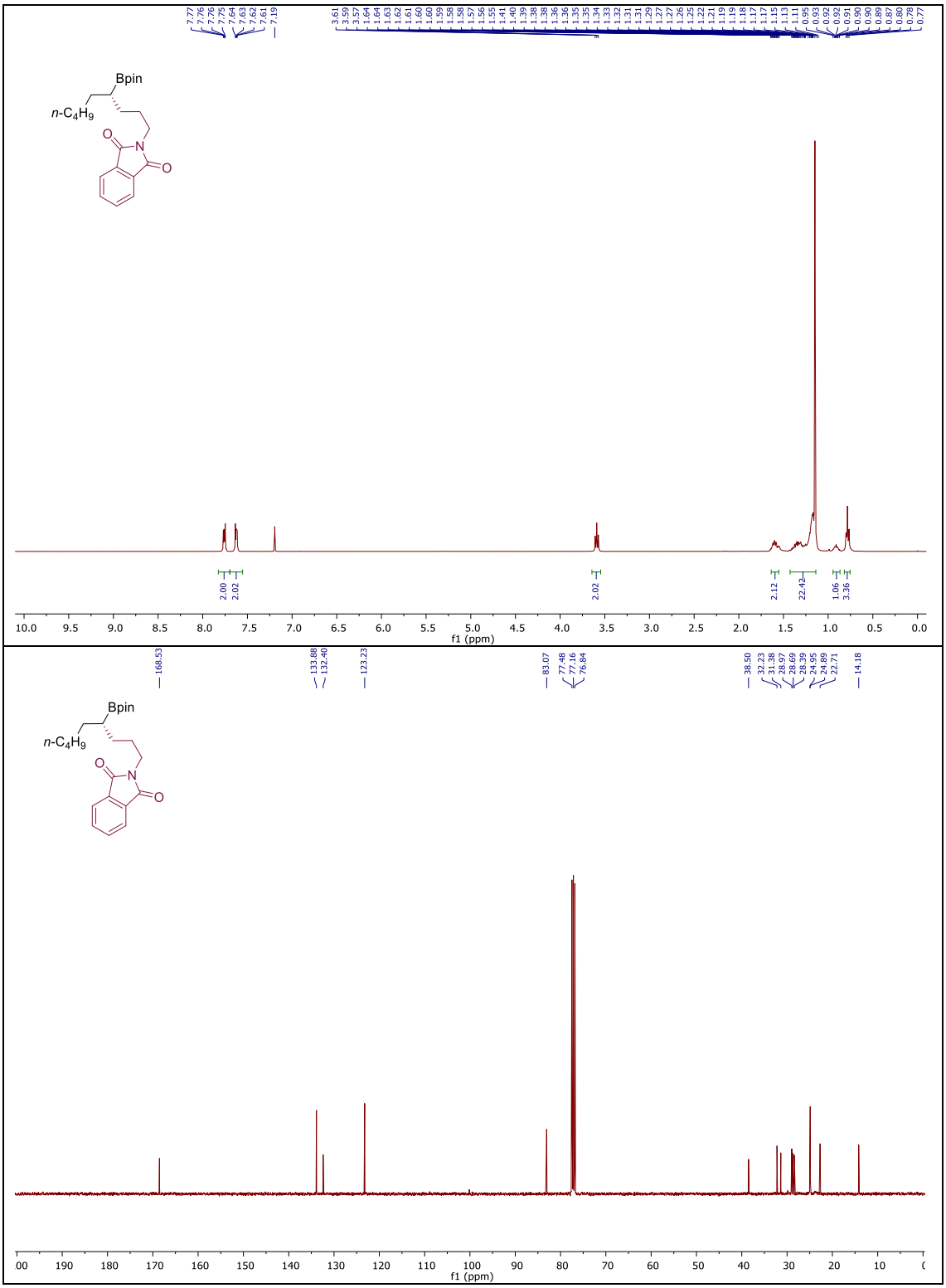

36.03
Bpin
n-C4H9
O
O
I
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

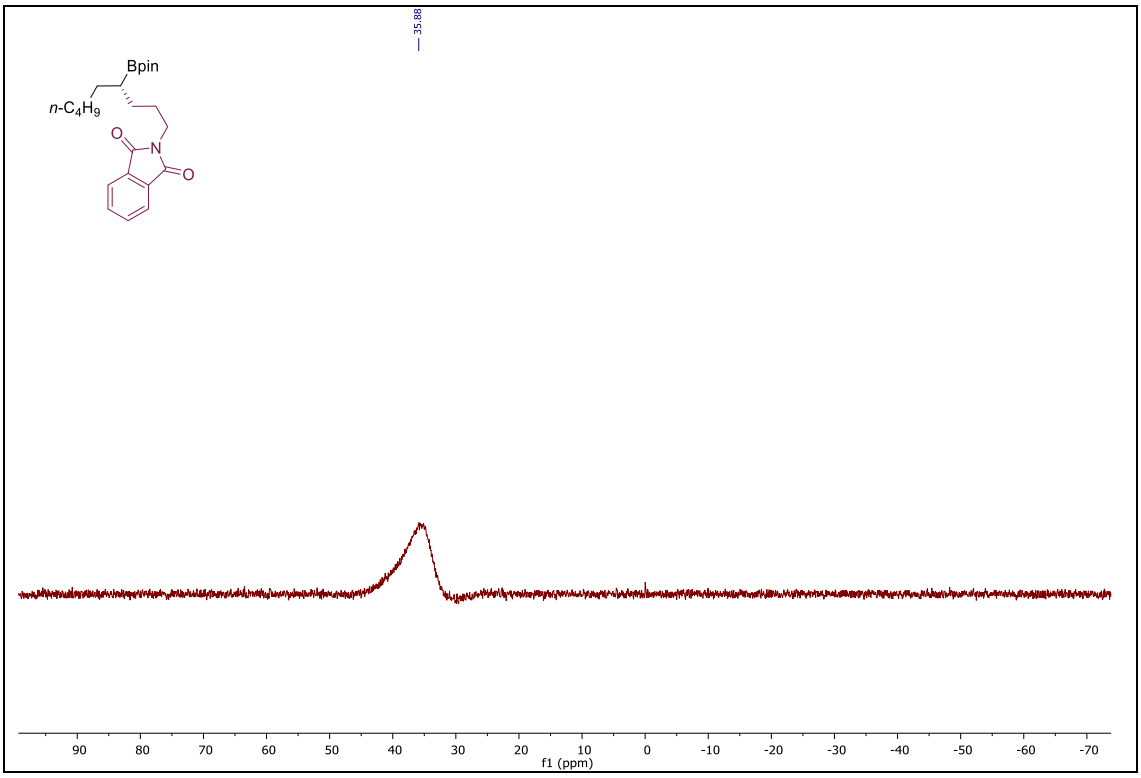
NMR spectra of 3h



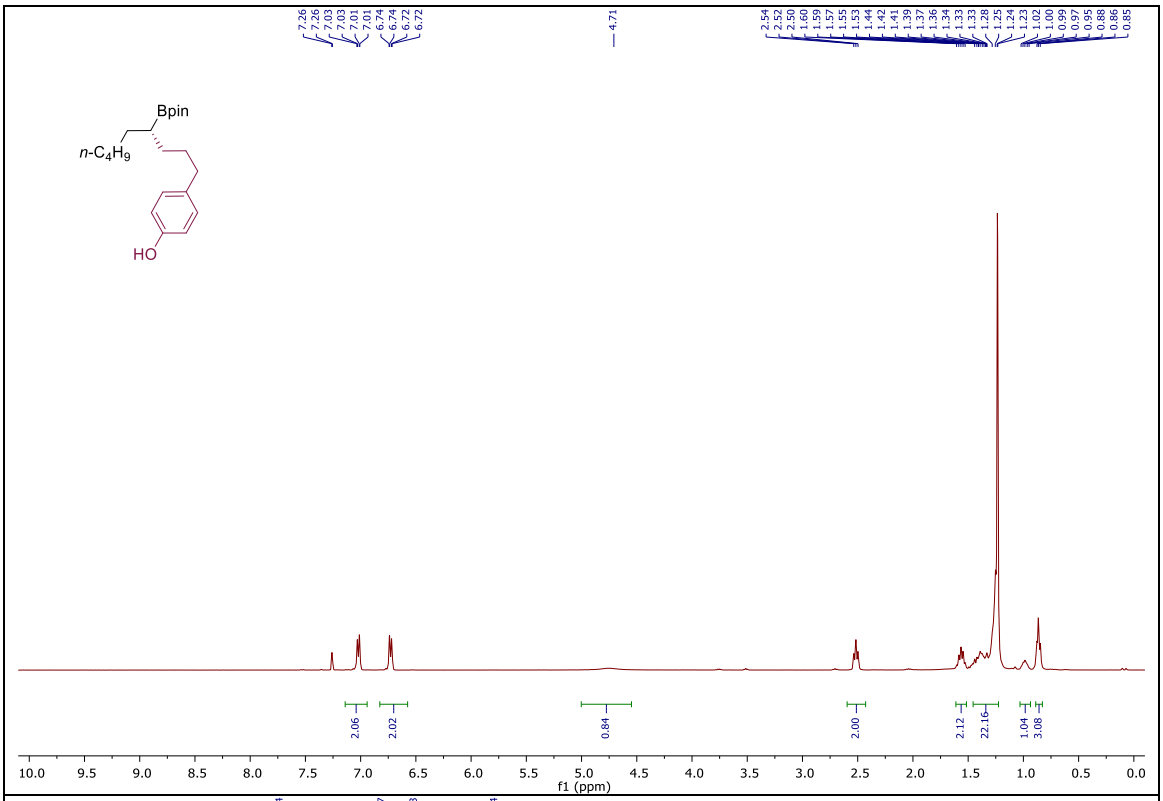

34.46
Bpin
n-C4H9
O
NH
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

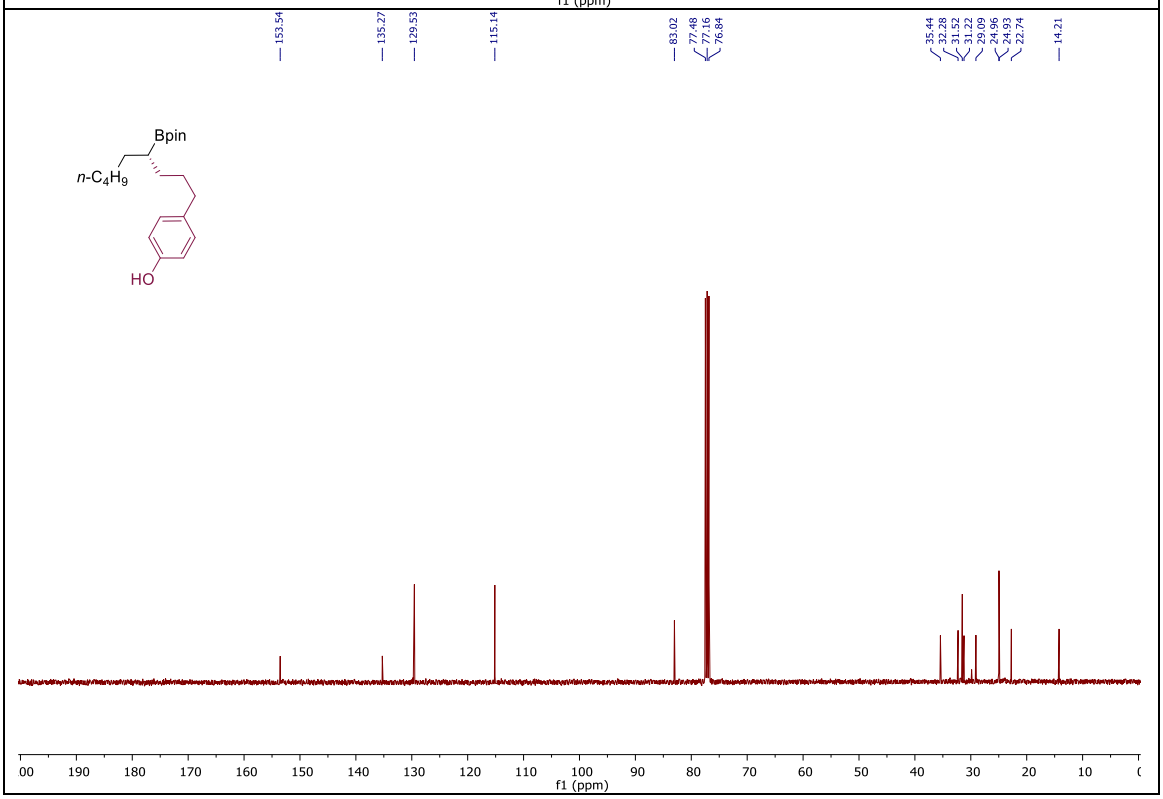
NMR spectra of 3i

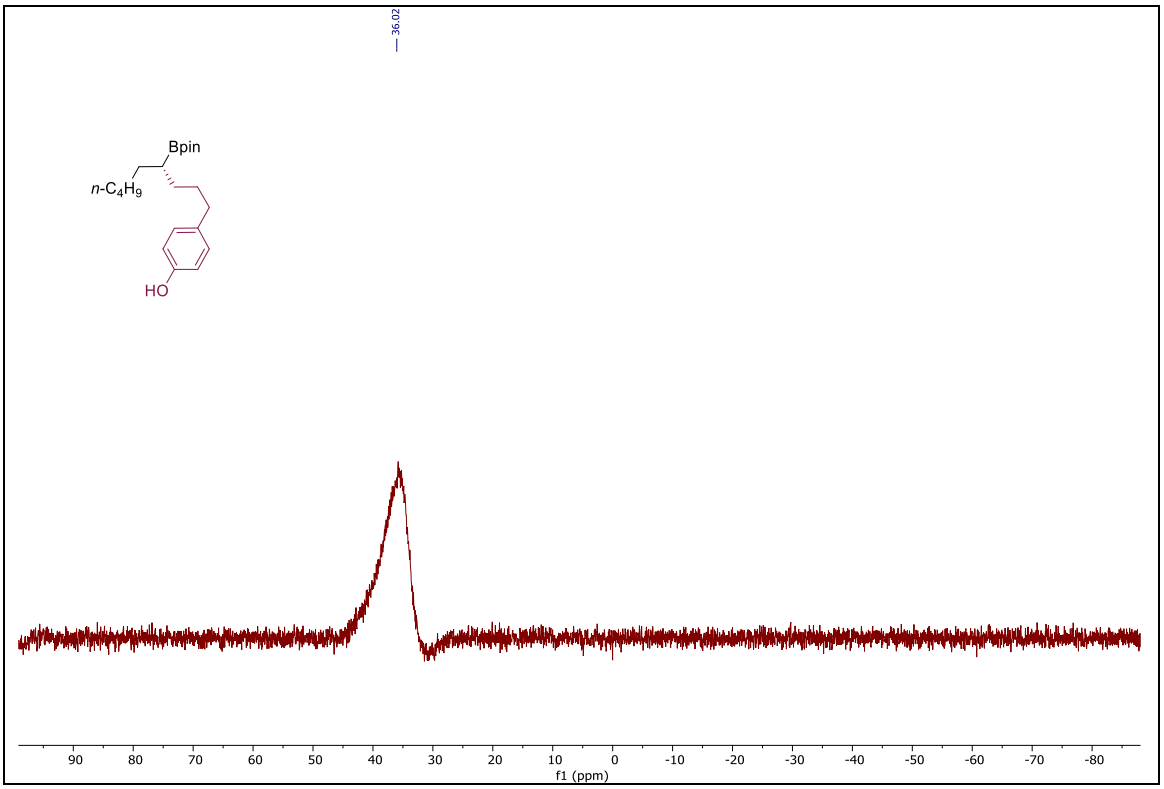



35.88
Bpin
n-C4H9
O
N
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

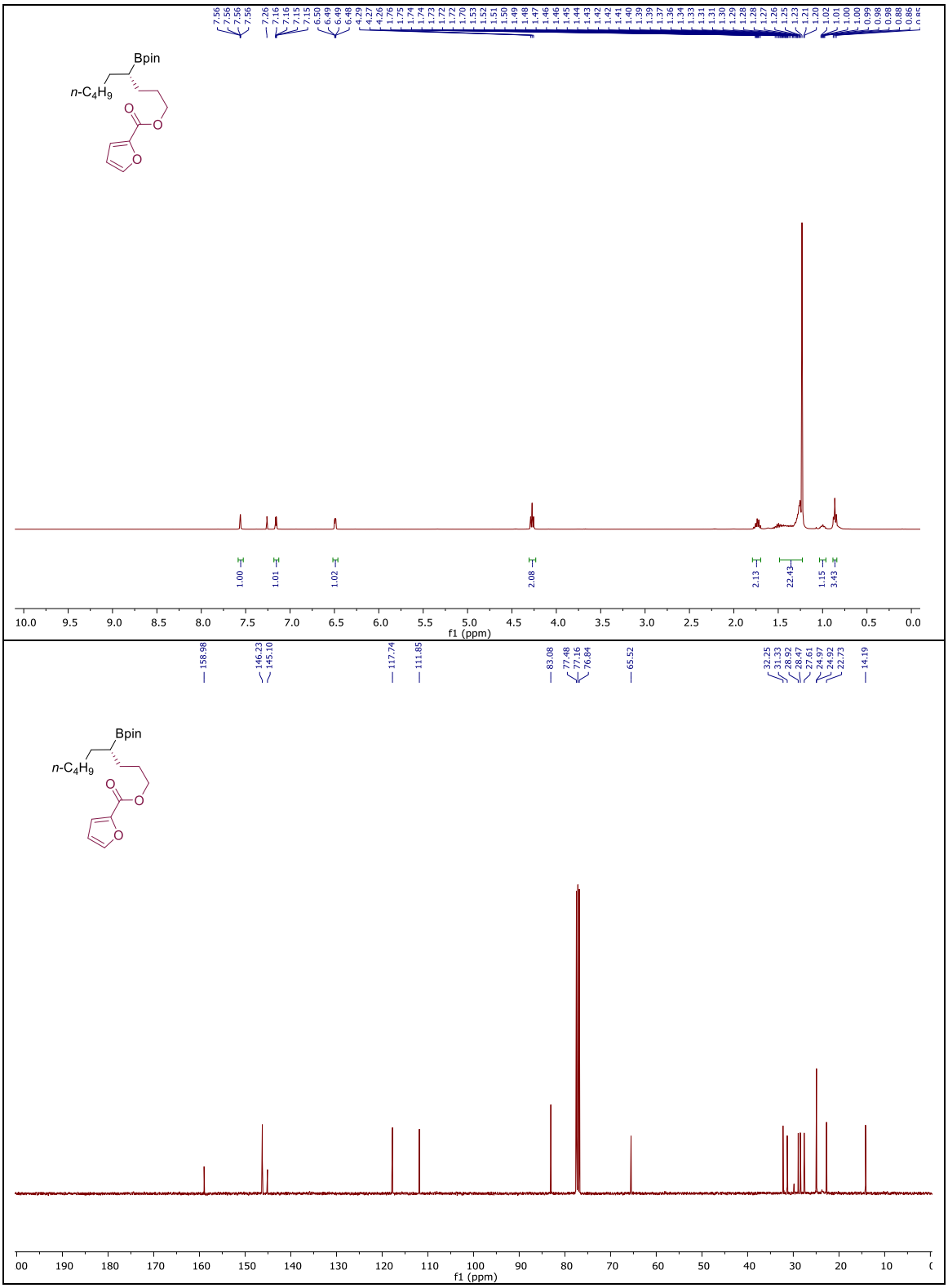
NMR spectra of 3j

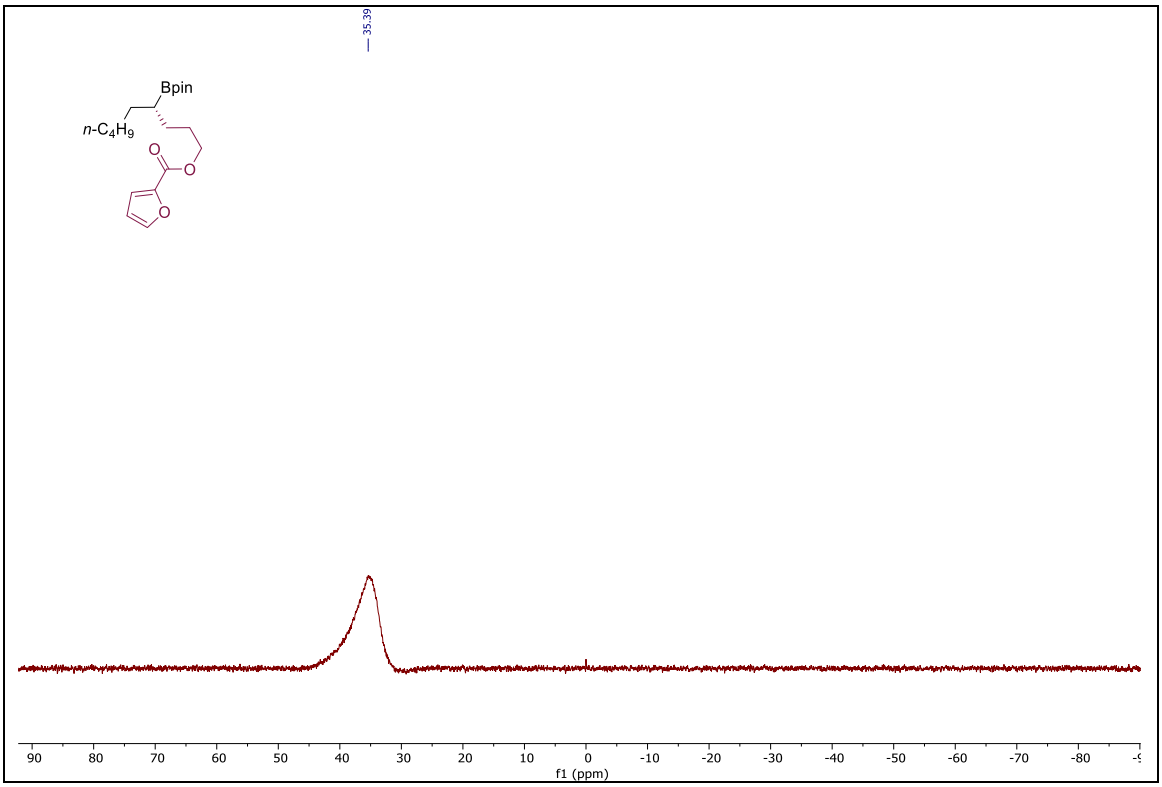




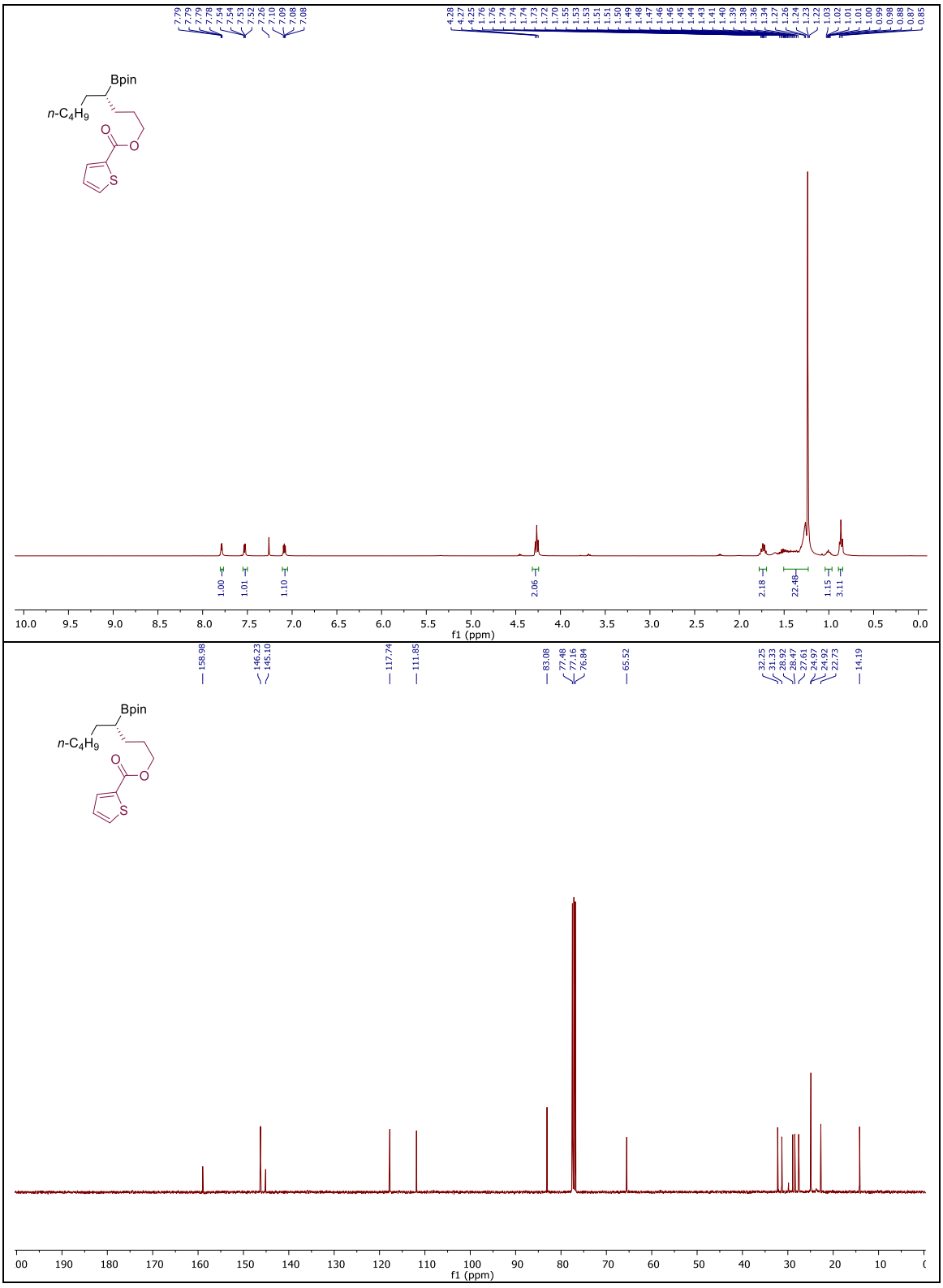

36.02
Bpin
n-C4H9
HO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

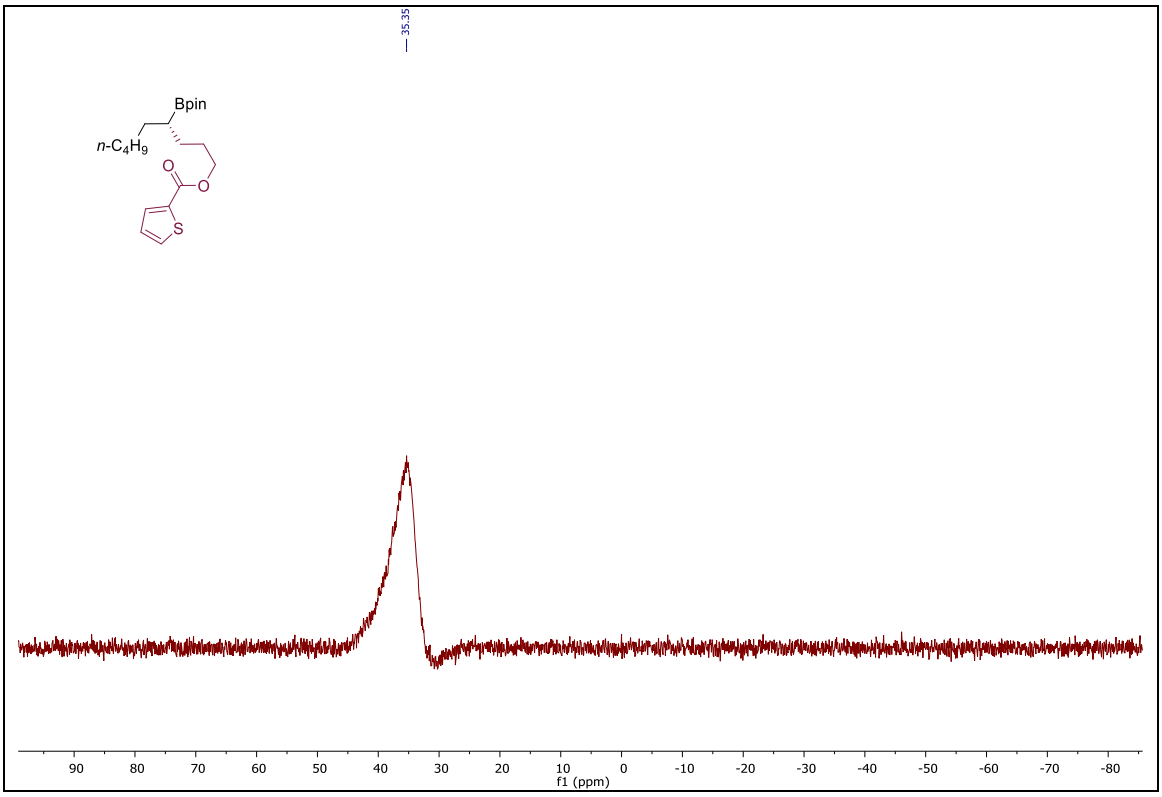
NMR spectra of 3k



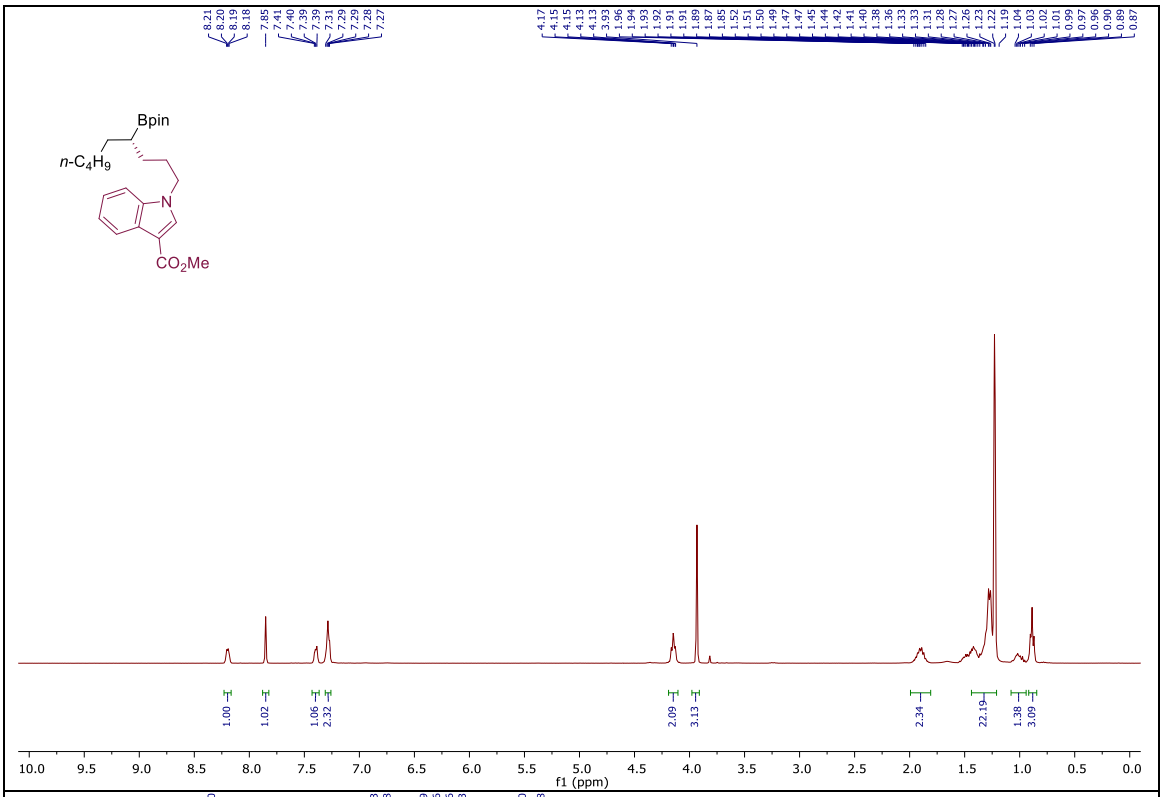

35.39
Bpin
n-C4H9
O
O
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

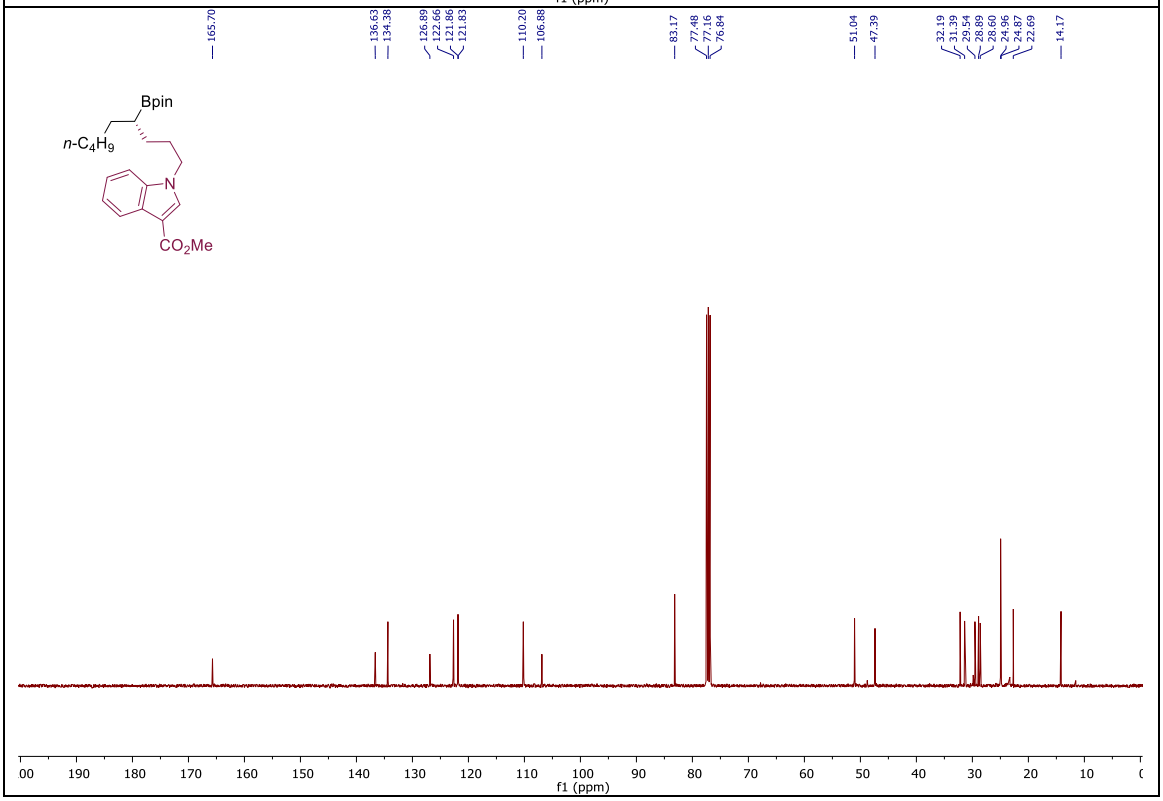
NMR spectra of 3l

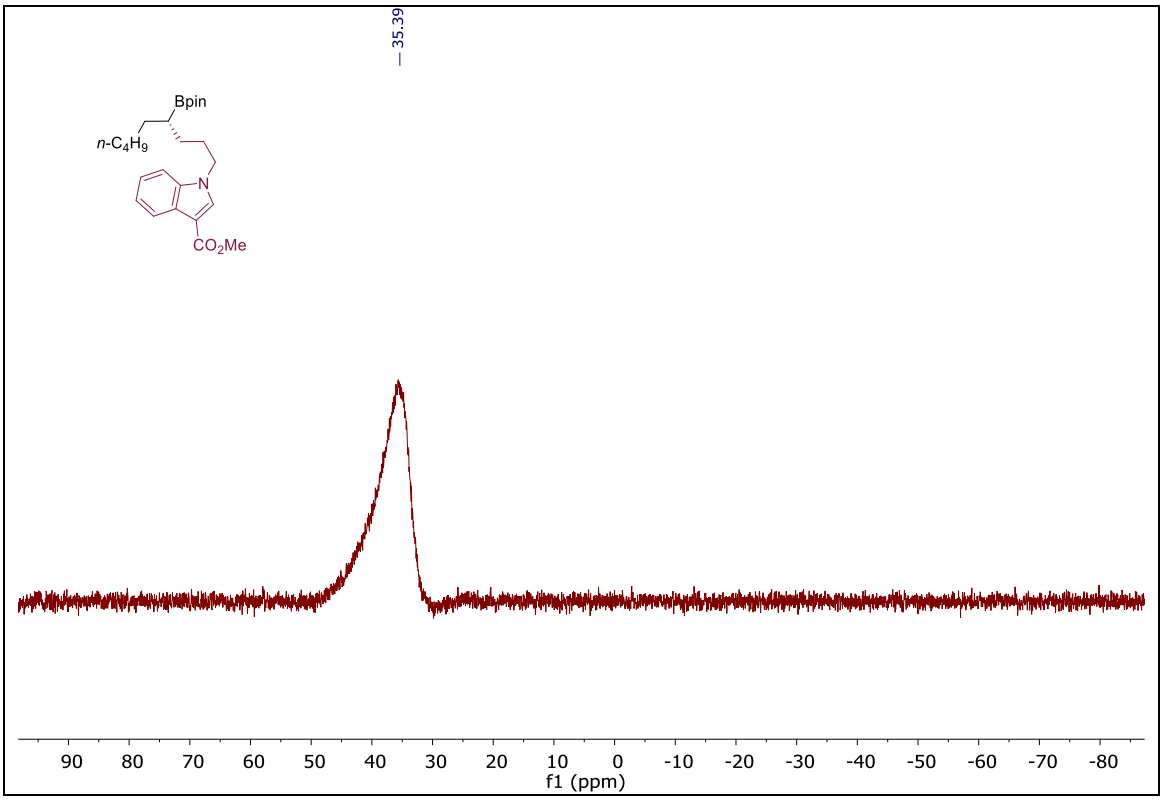



35.35
Bpin
n-C4H9
O
O
S
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

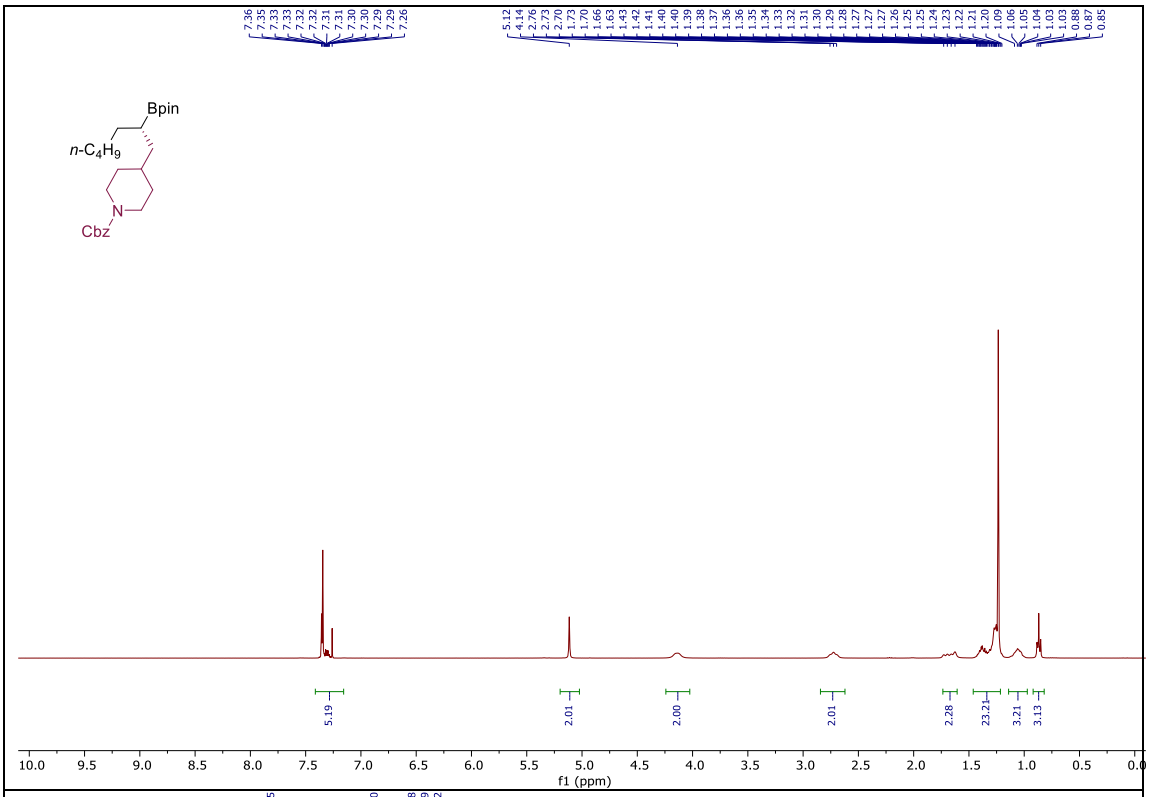
NMR spectra of 3m

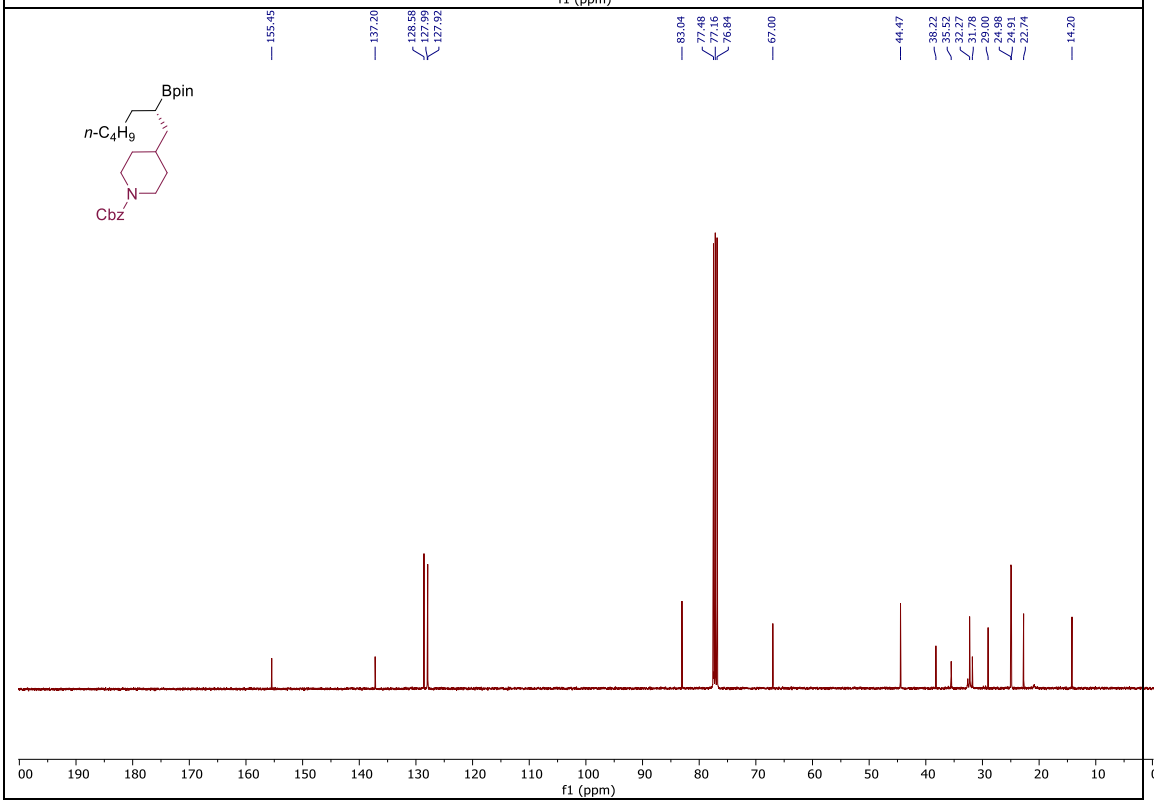


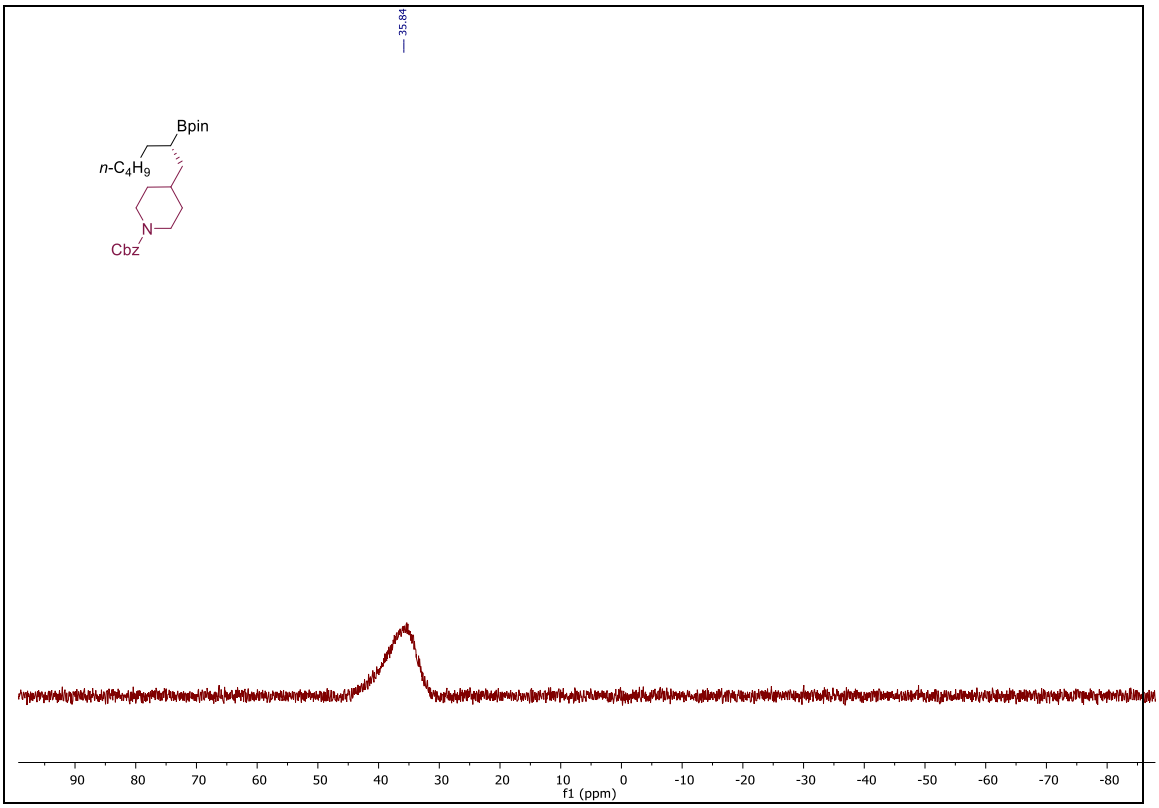



35.39
Bpin
n-C4H9
N
CO2Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

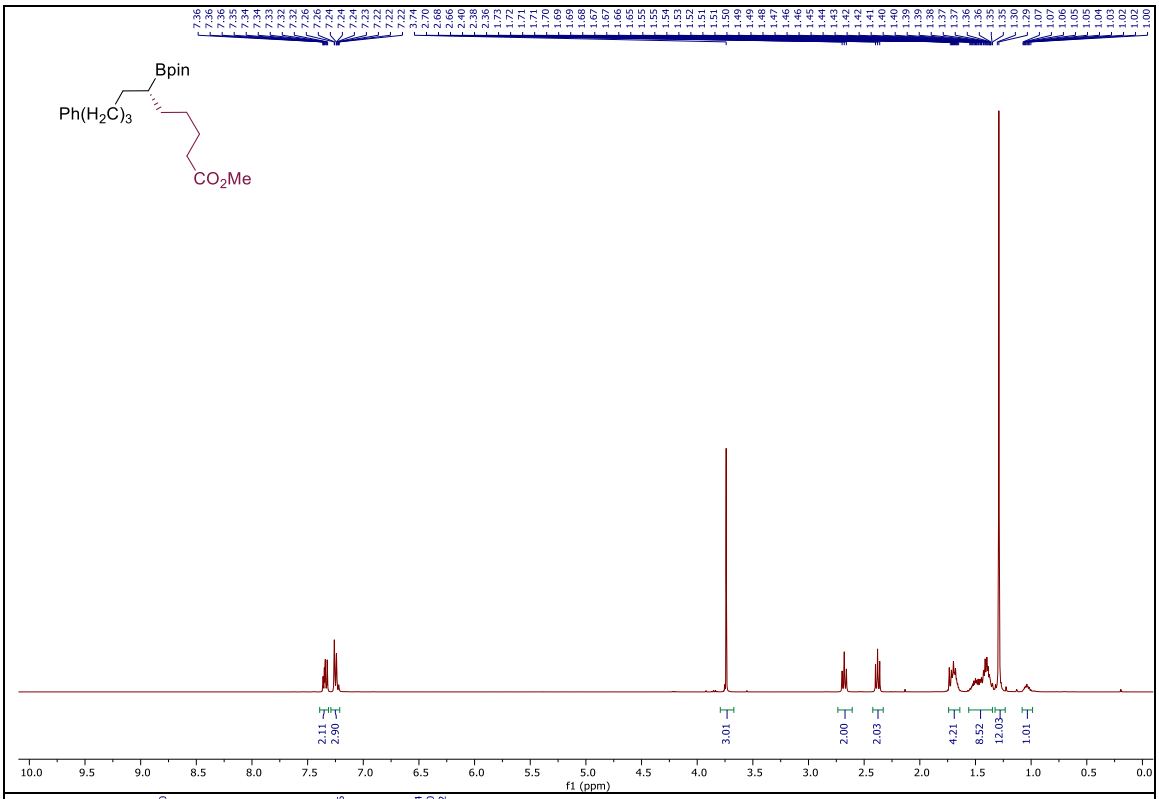
NMR spectra of 3n

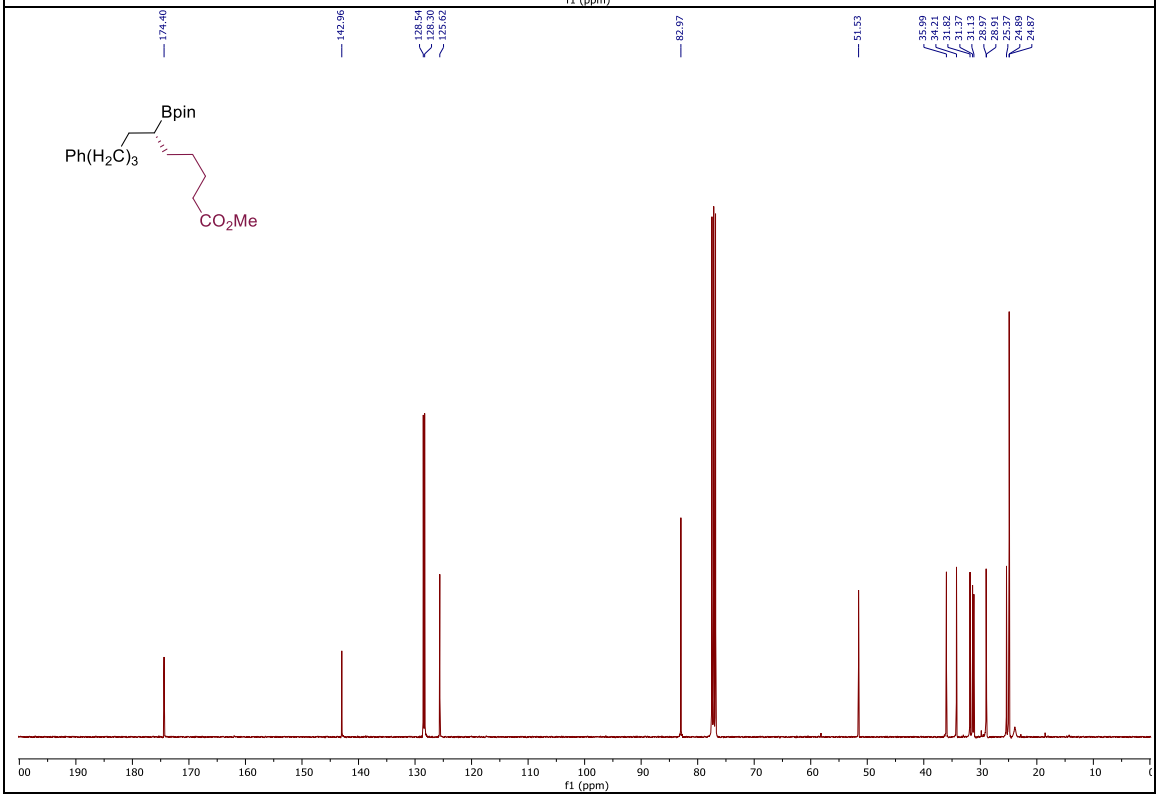


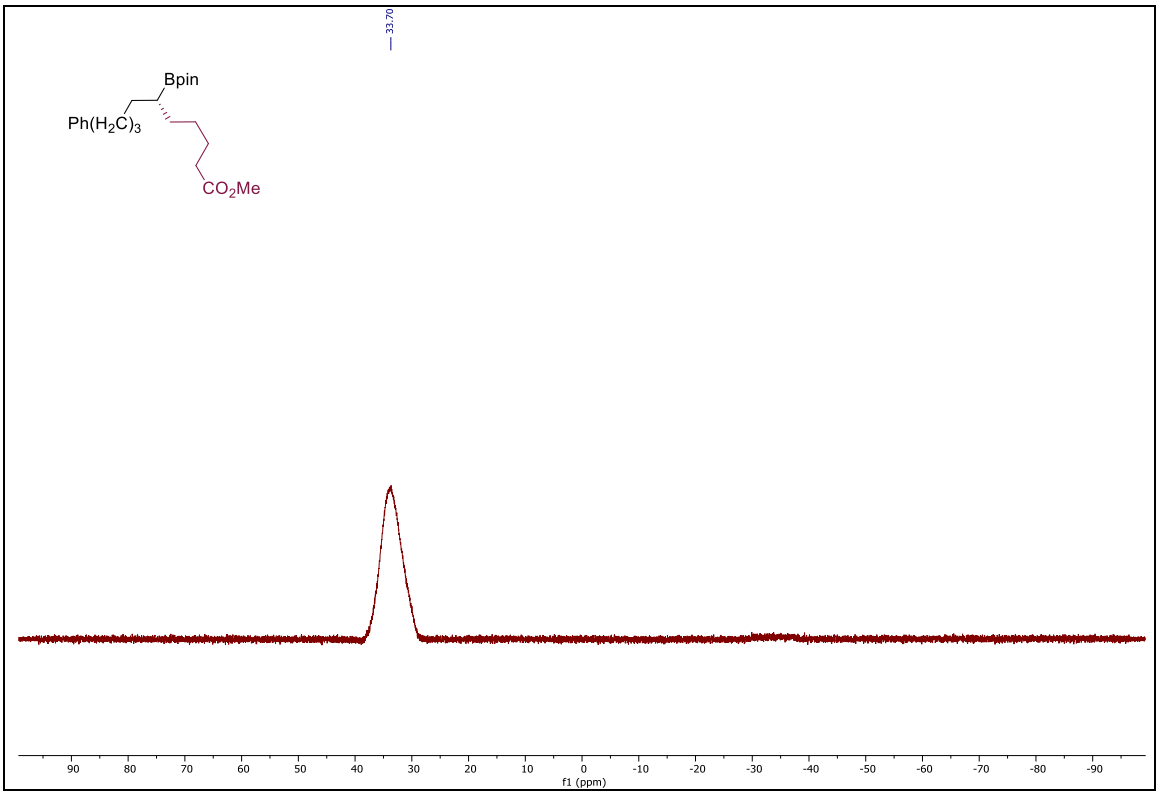



35.84
Bpin
n-C4H9
N
Cbz
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

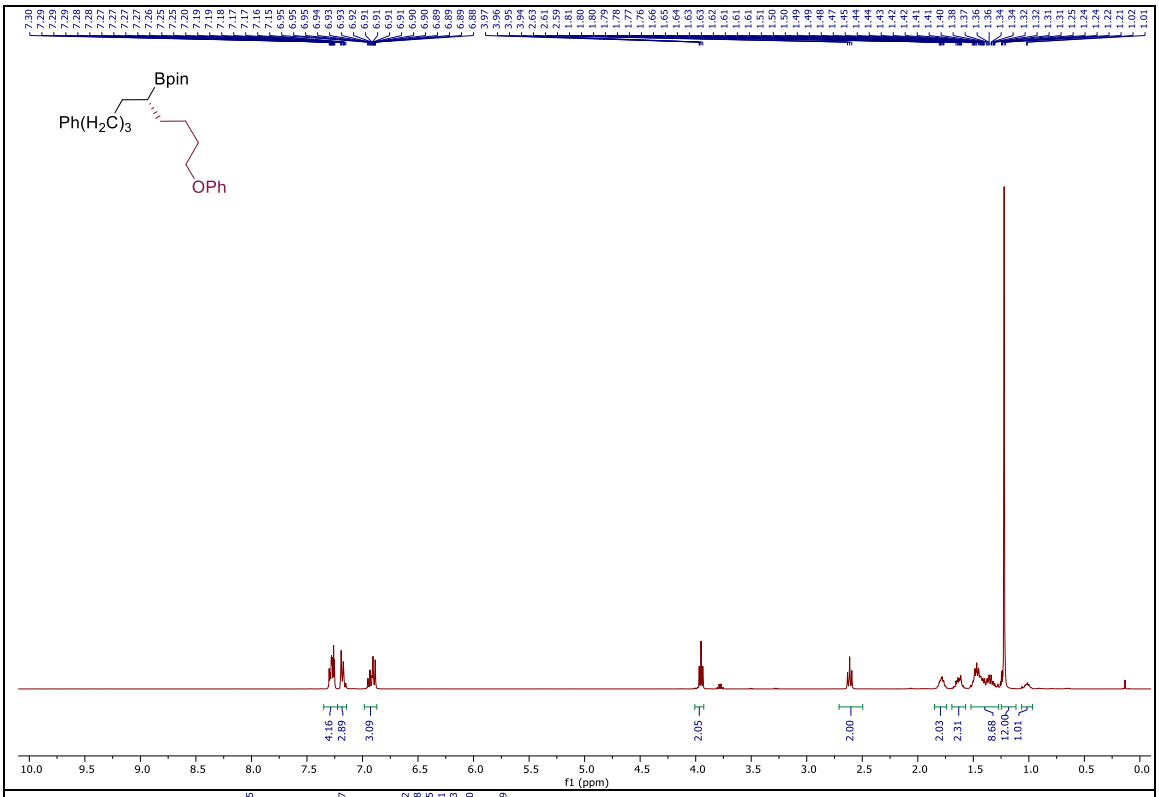
NMR spectra of 3o

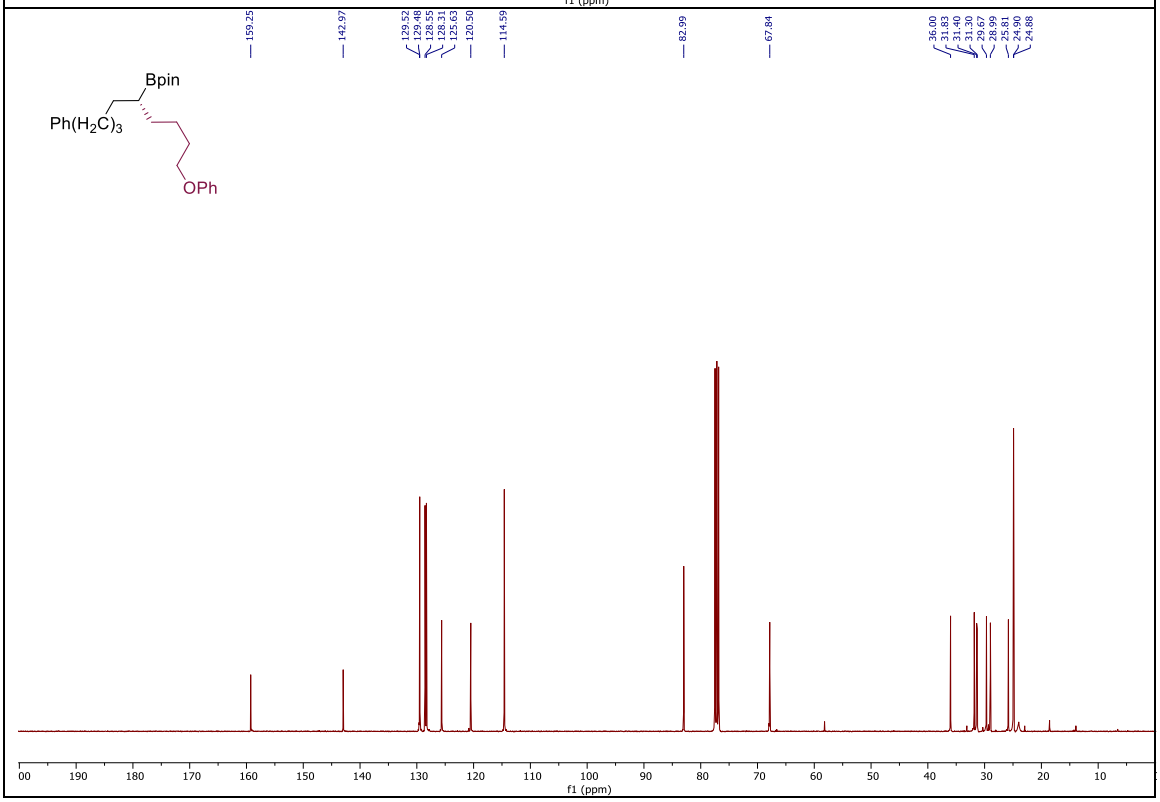


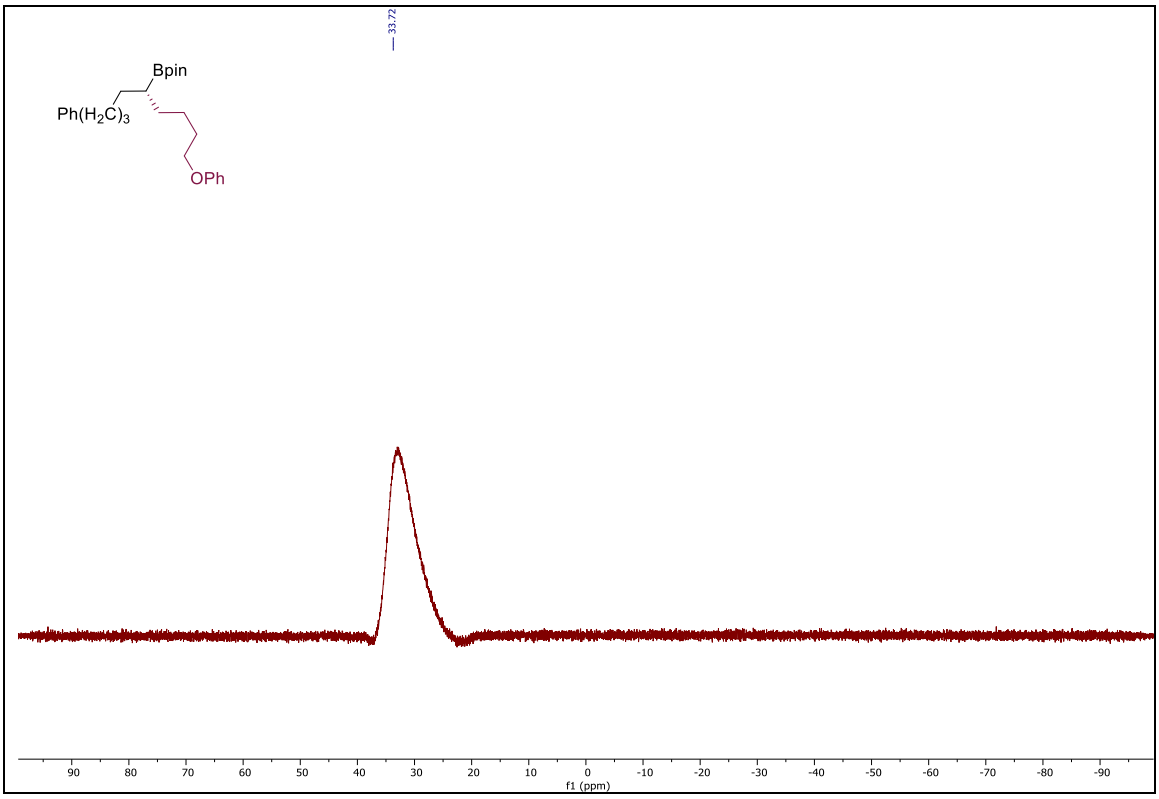



33.70
Bpin
Ph(H2C)3
CO2Me
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

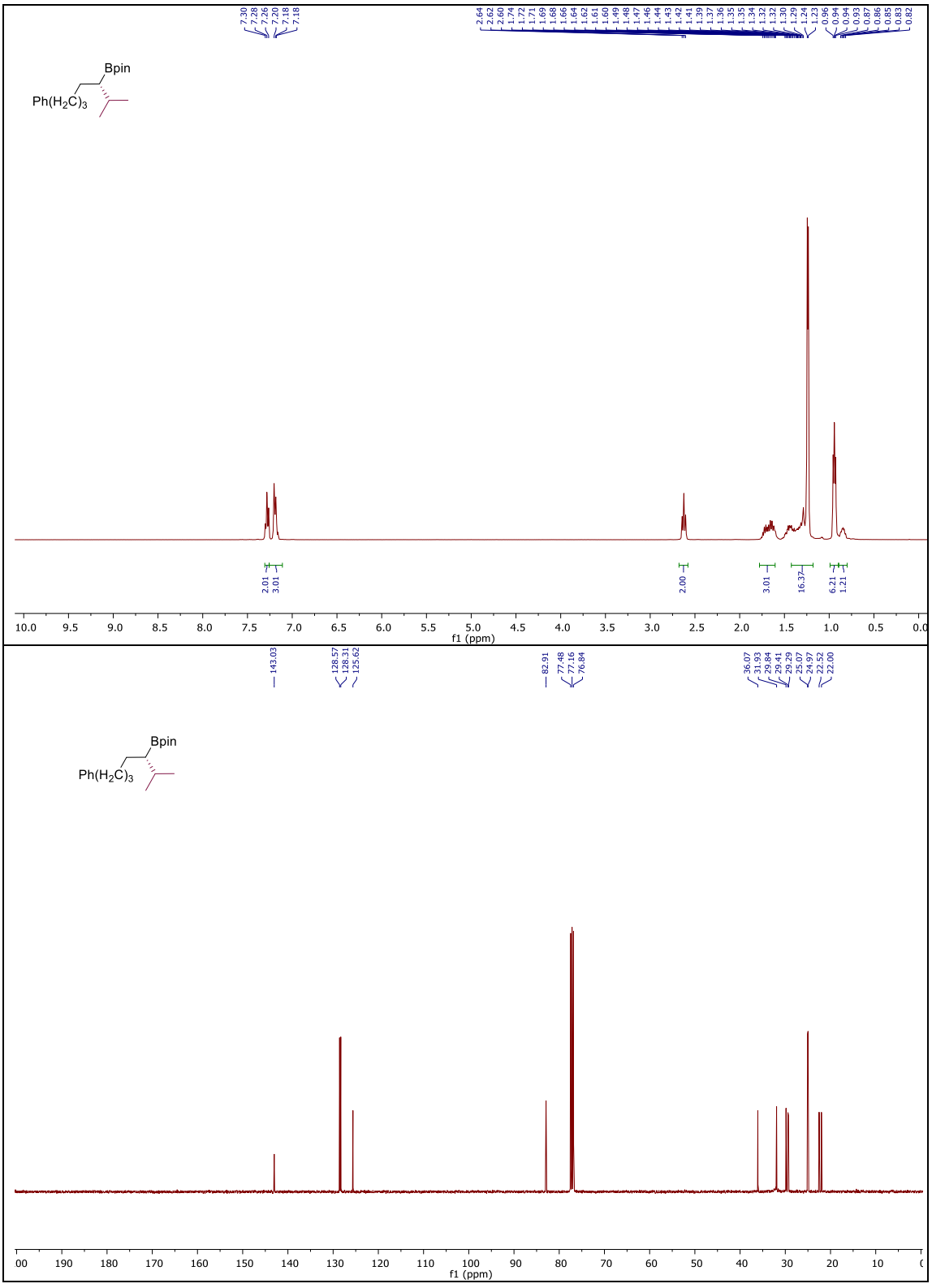
NMR spectra of 3p

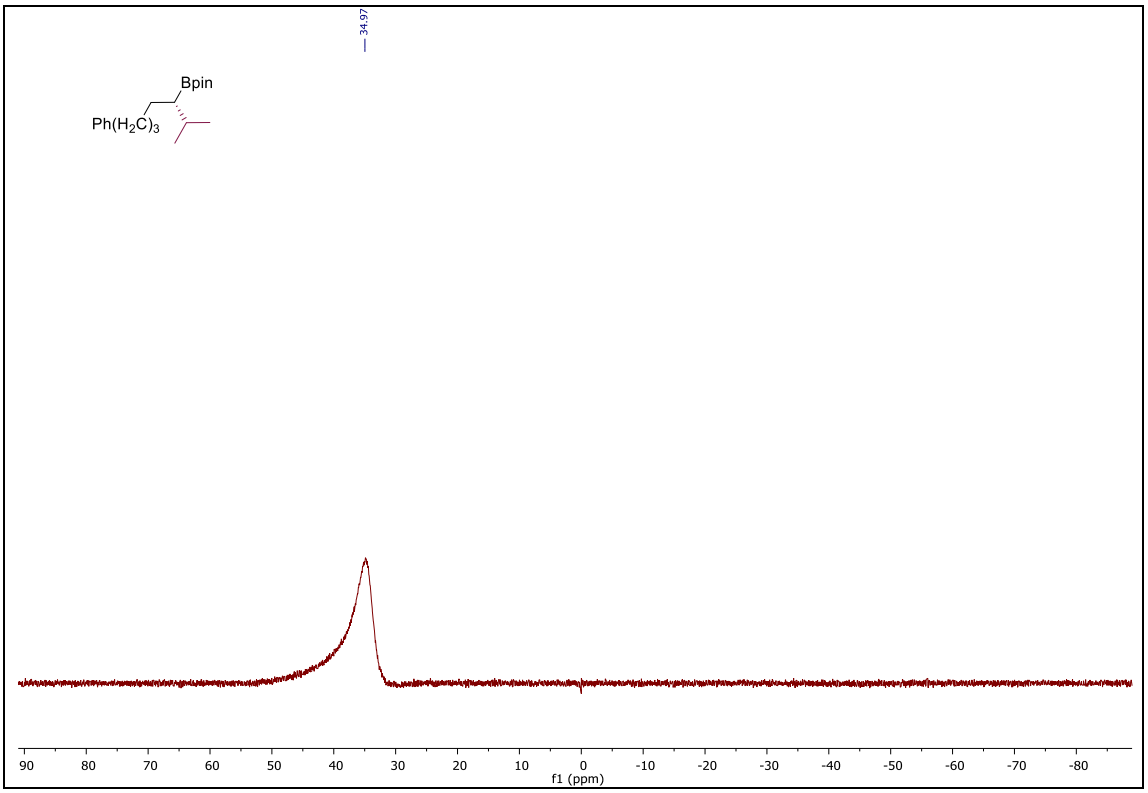




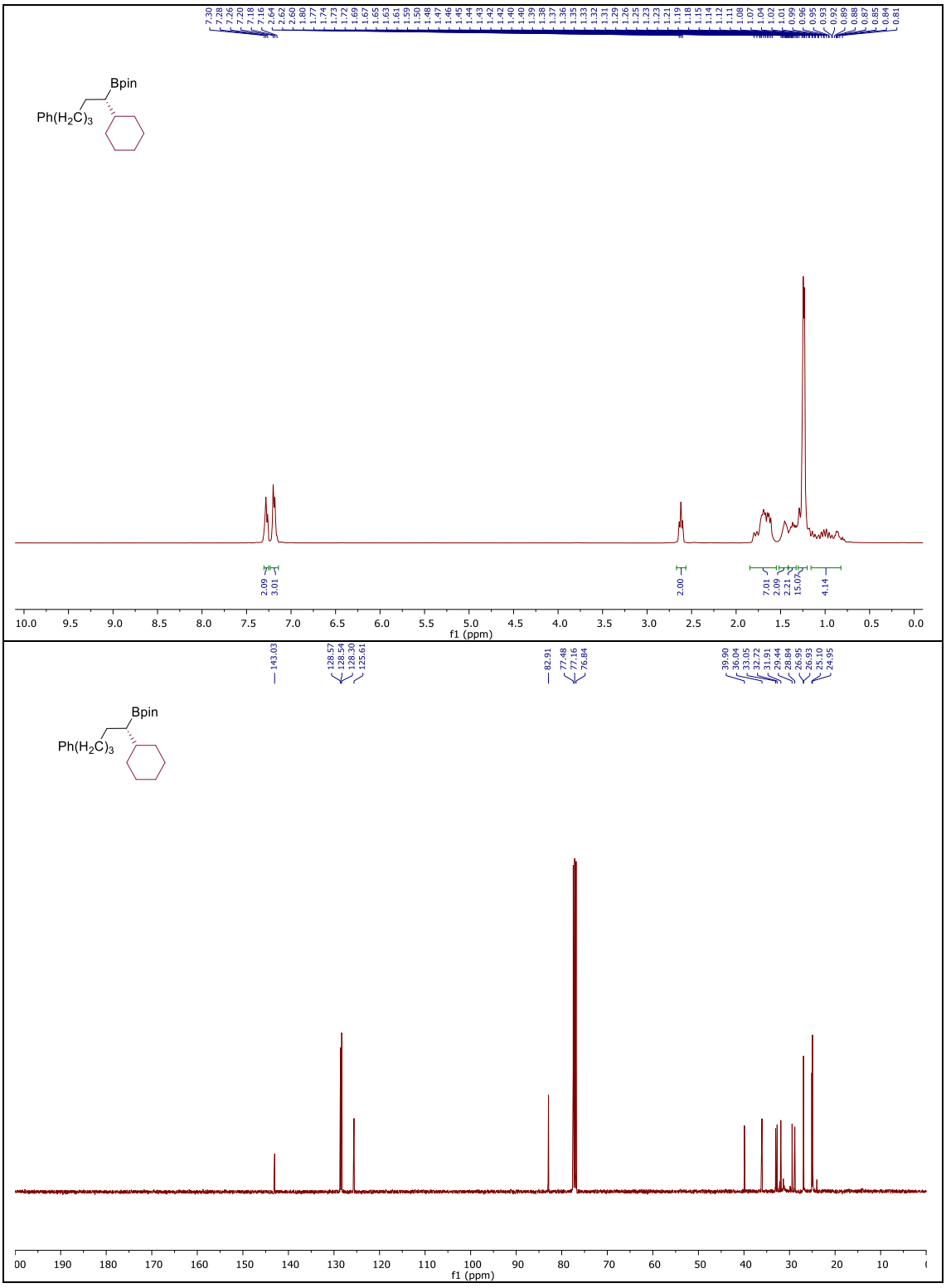

33.72
Bpin
Ph(H2C)3
OPh
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

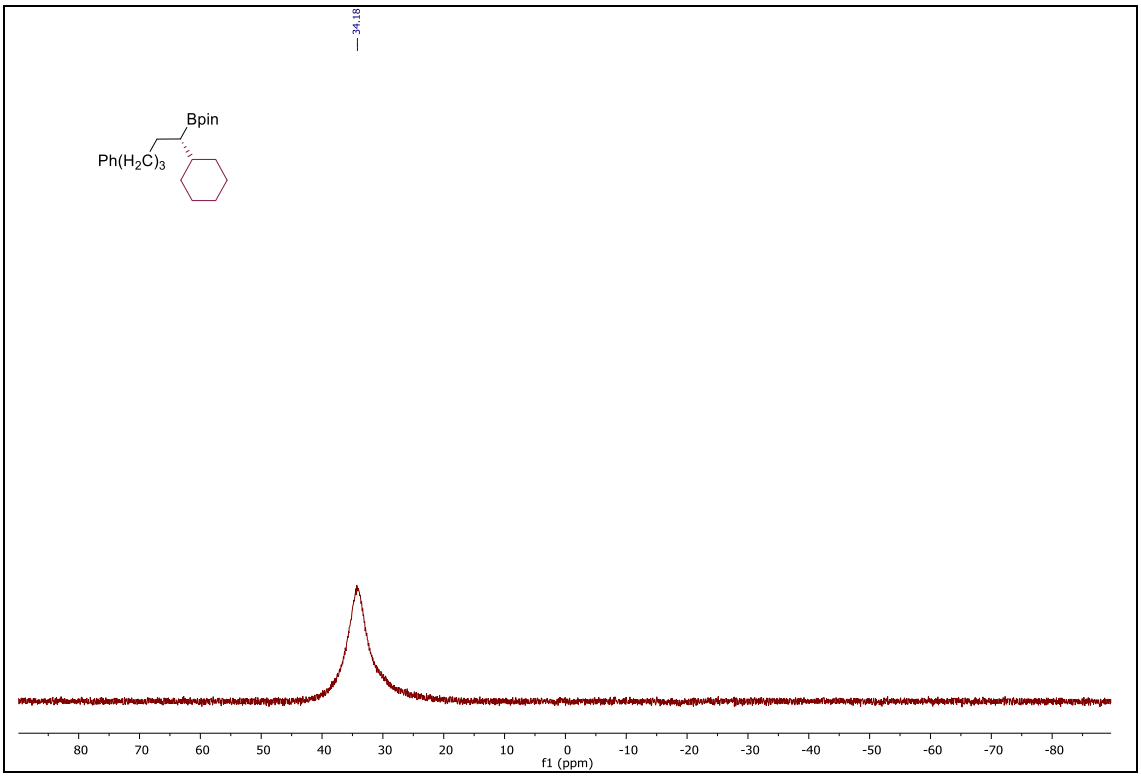
NMR spectra of 4a



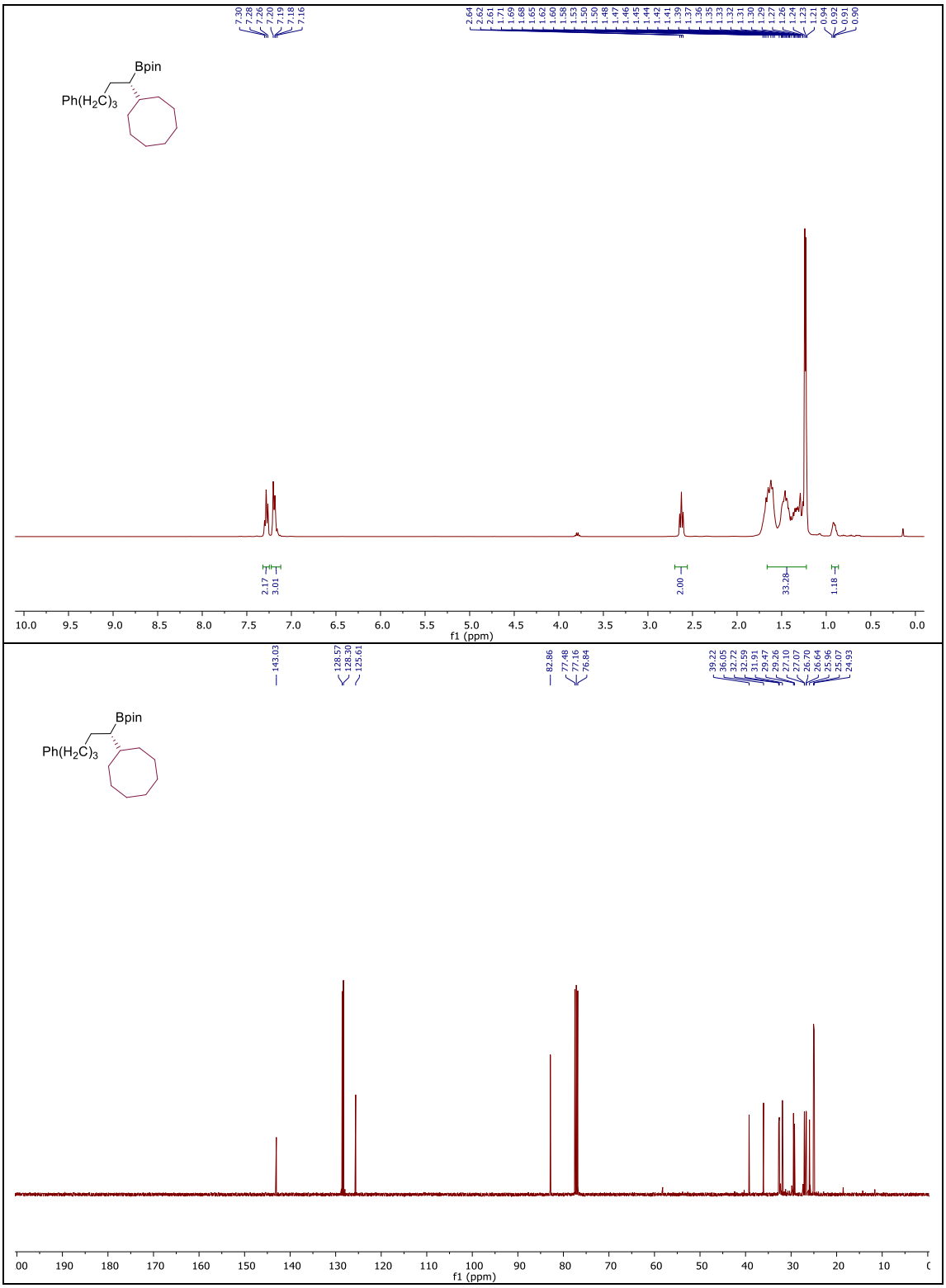

34.97
Bpin
Ph(H2C)3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

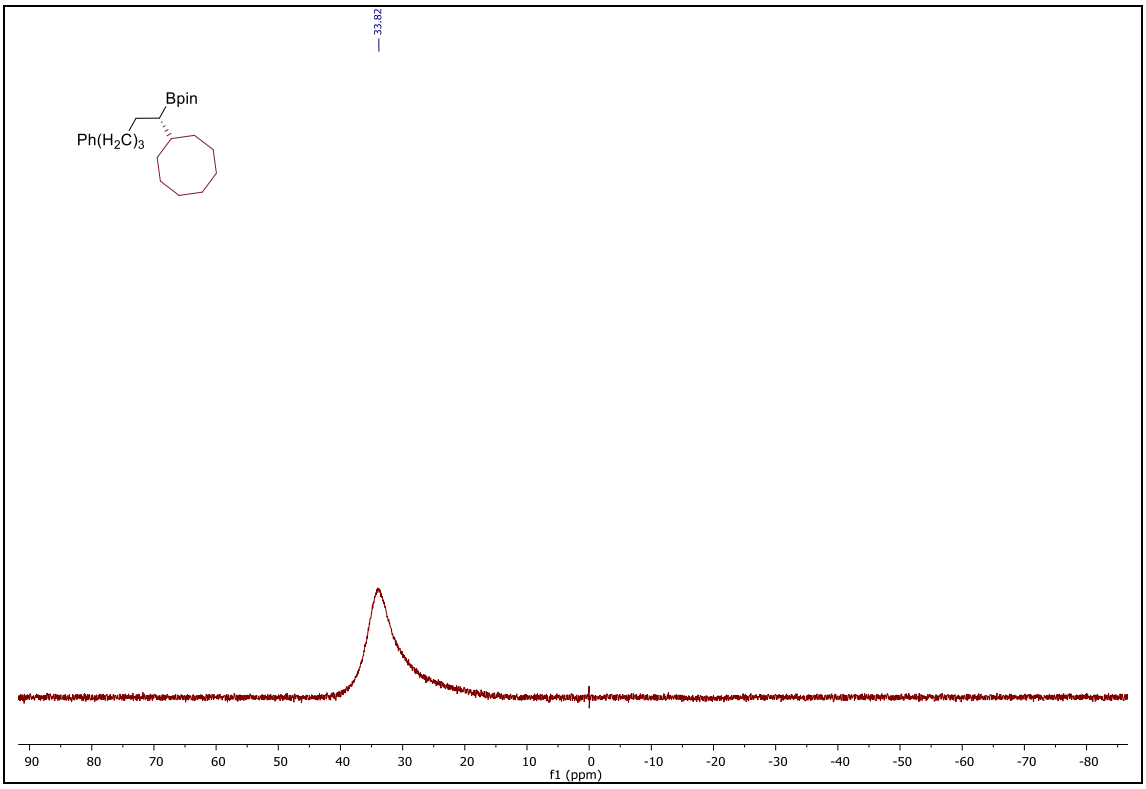
NMR spectra of 4b



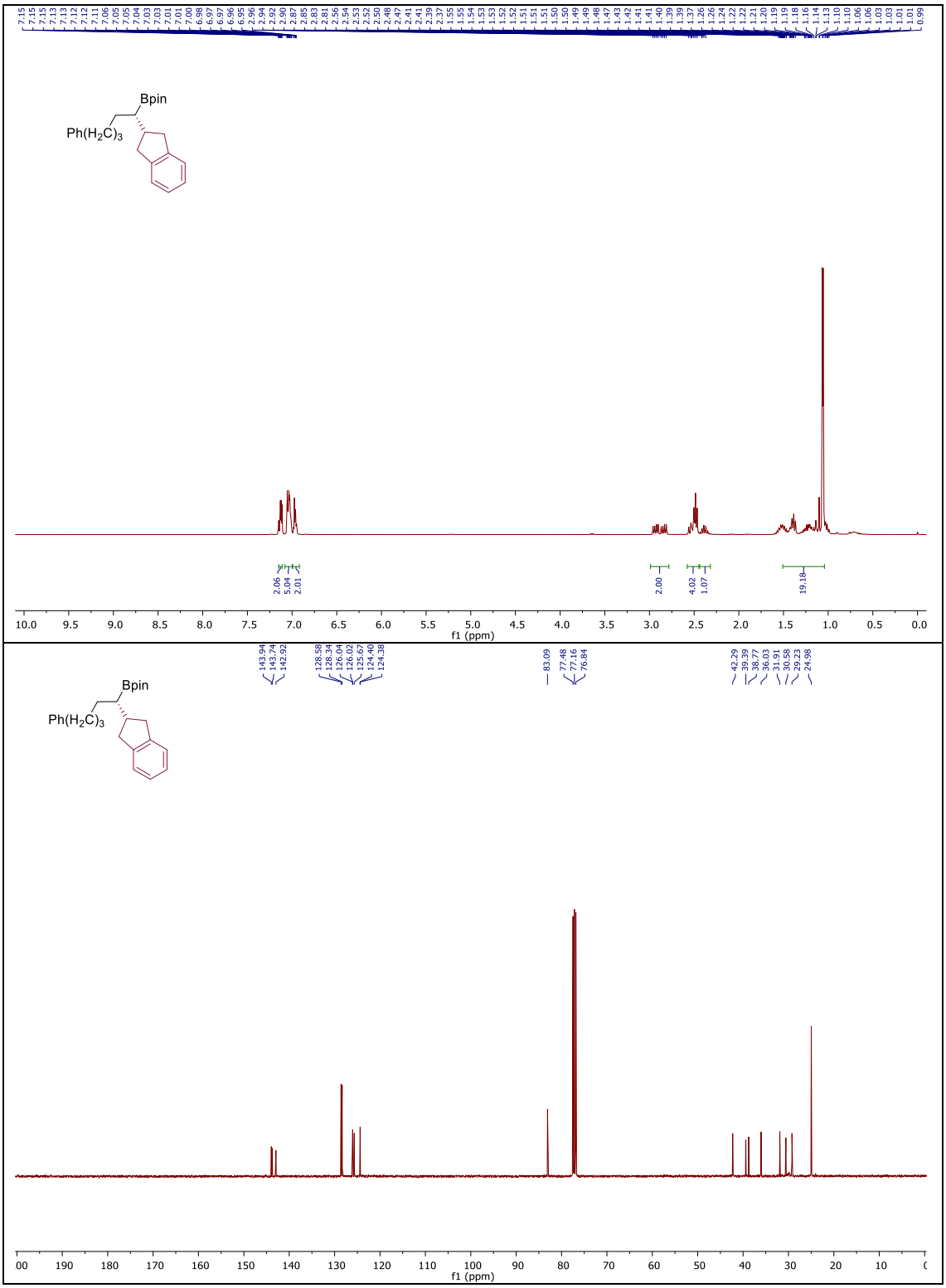

34.18
Bpin
Ph(H2C)3
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

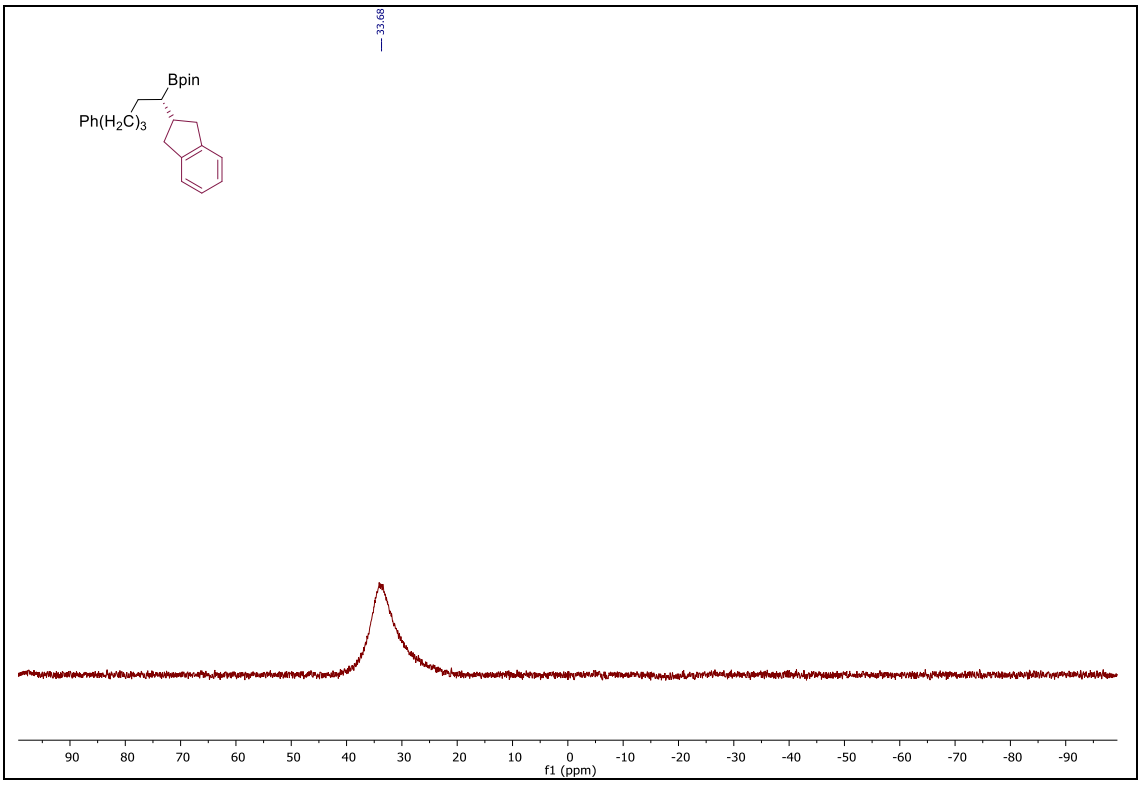
NMR spectra of 4c



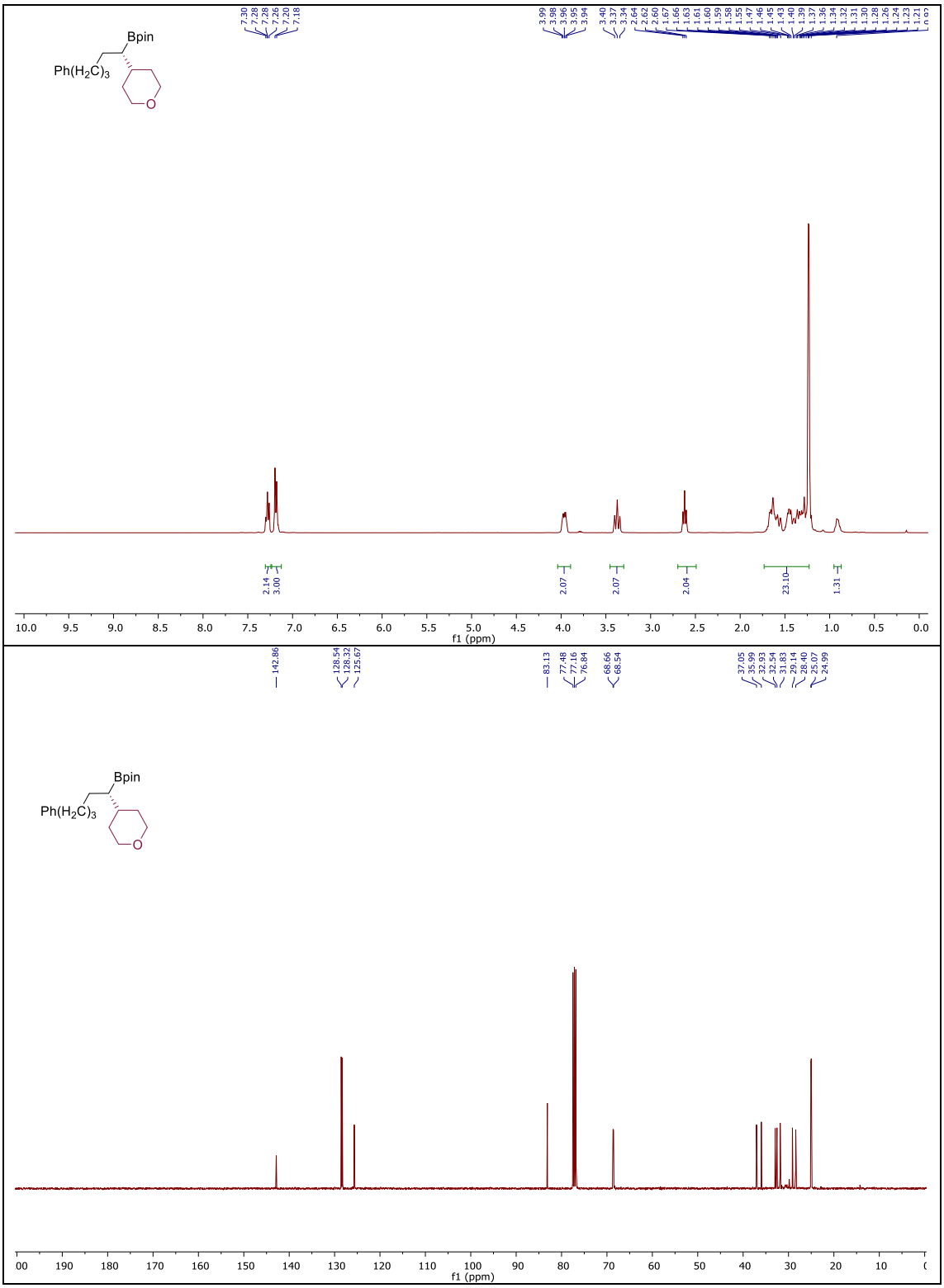

33.82
Bpin
Ph(H2C)3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

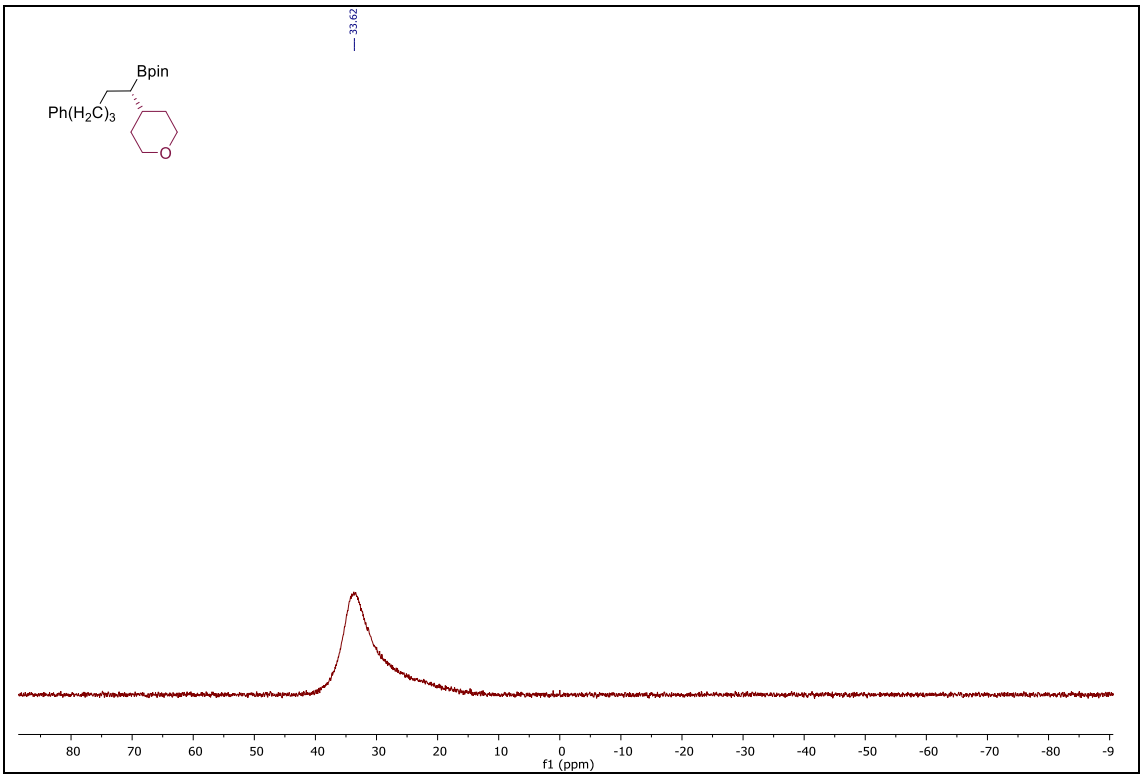
NMR spectra of 4d



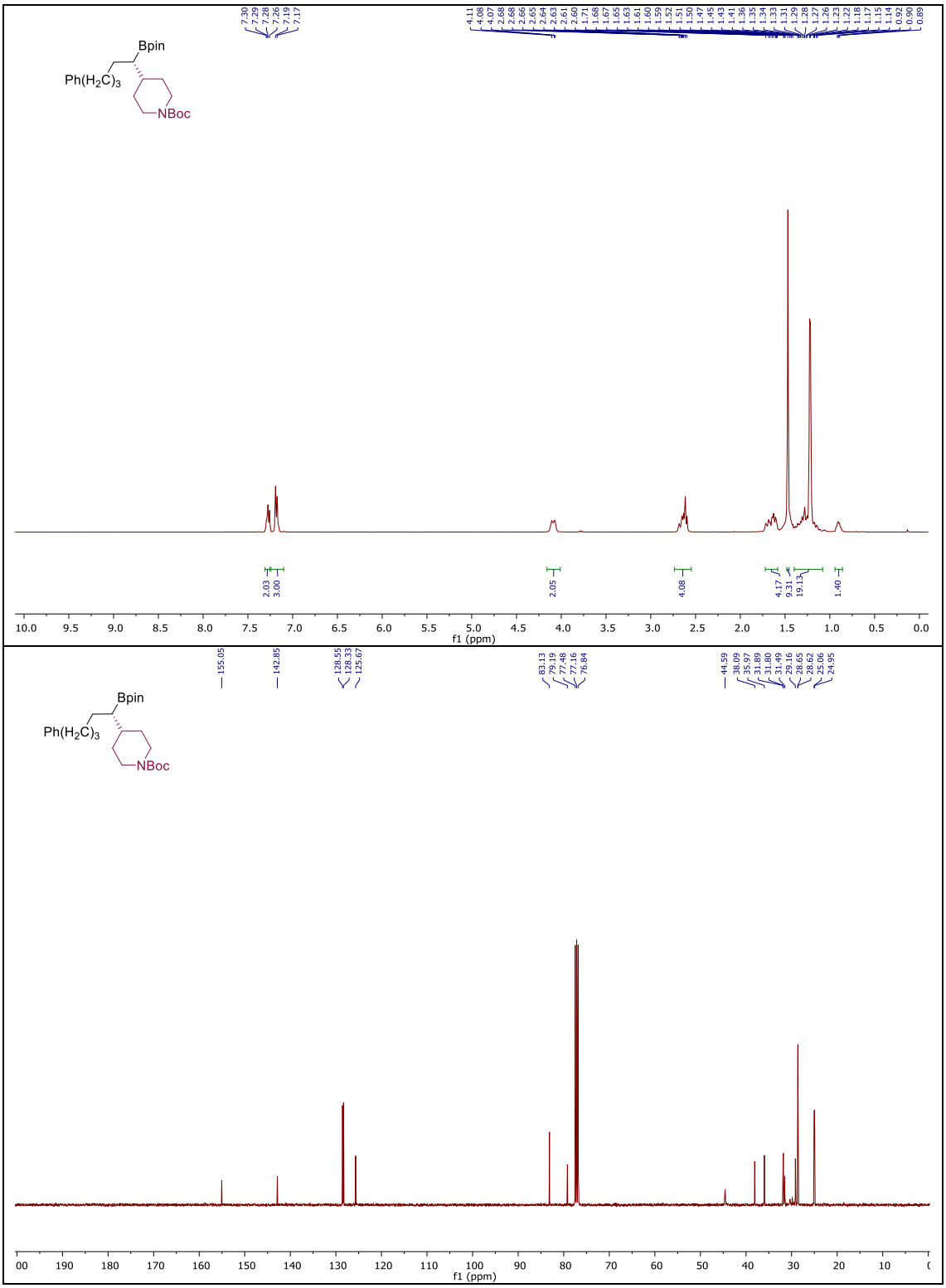

33.68
Bpin
Ph(H2C)3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

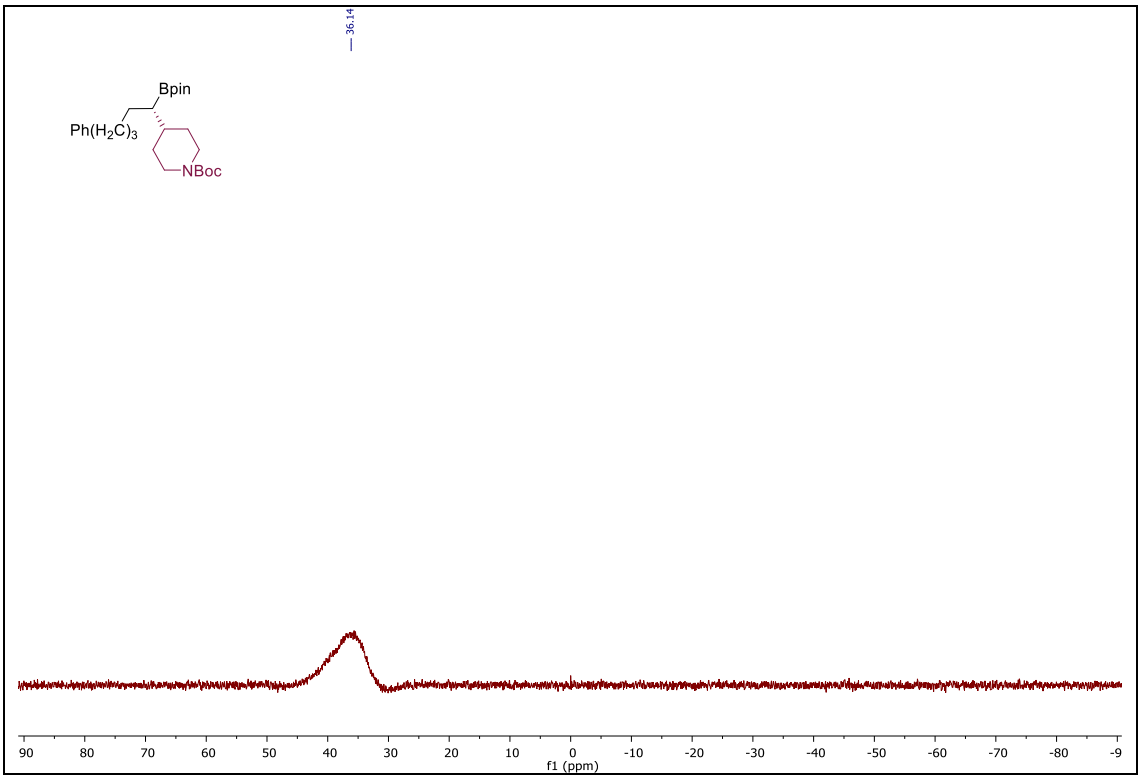
NMR spectra of 4e



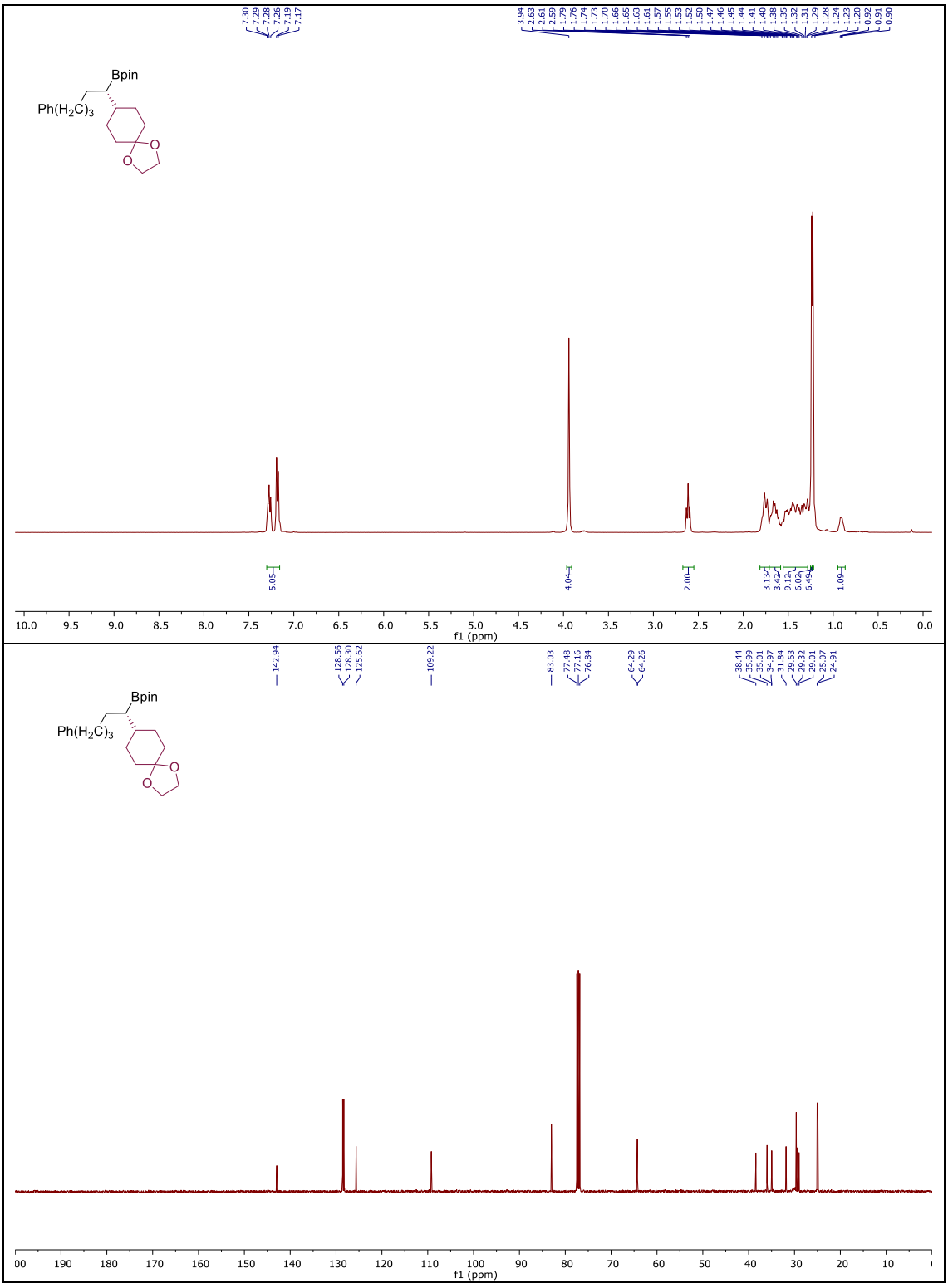

33.62
Bpin
Ph(H2C)3
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-9
f1 (ppm)

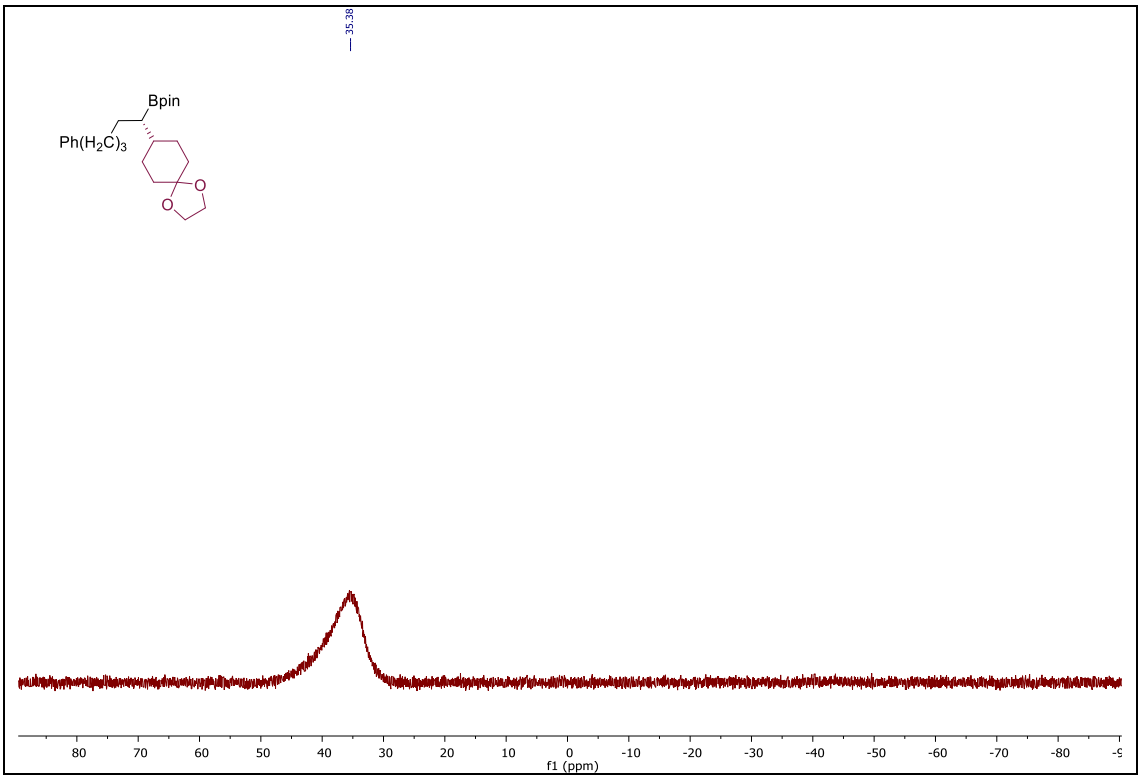
NMR spectra of 4f



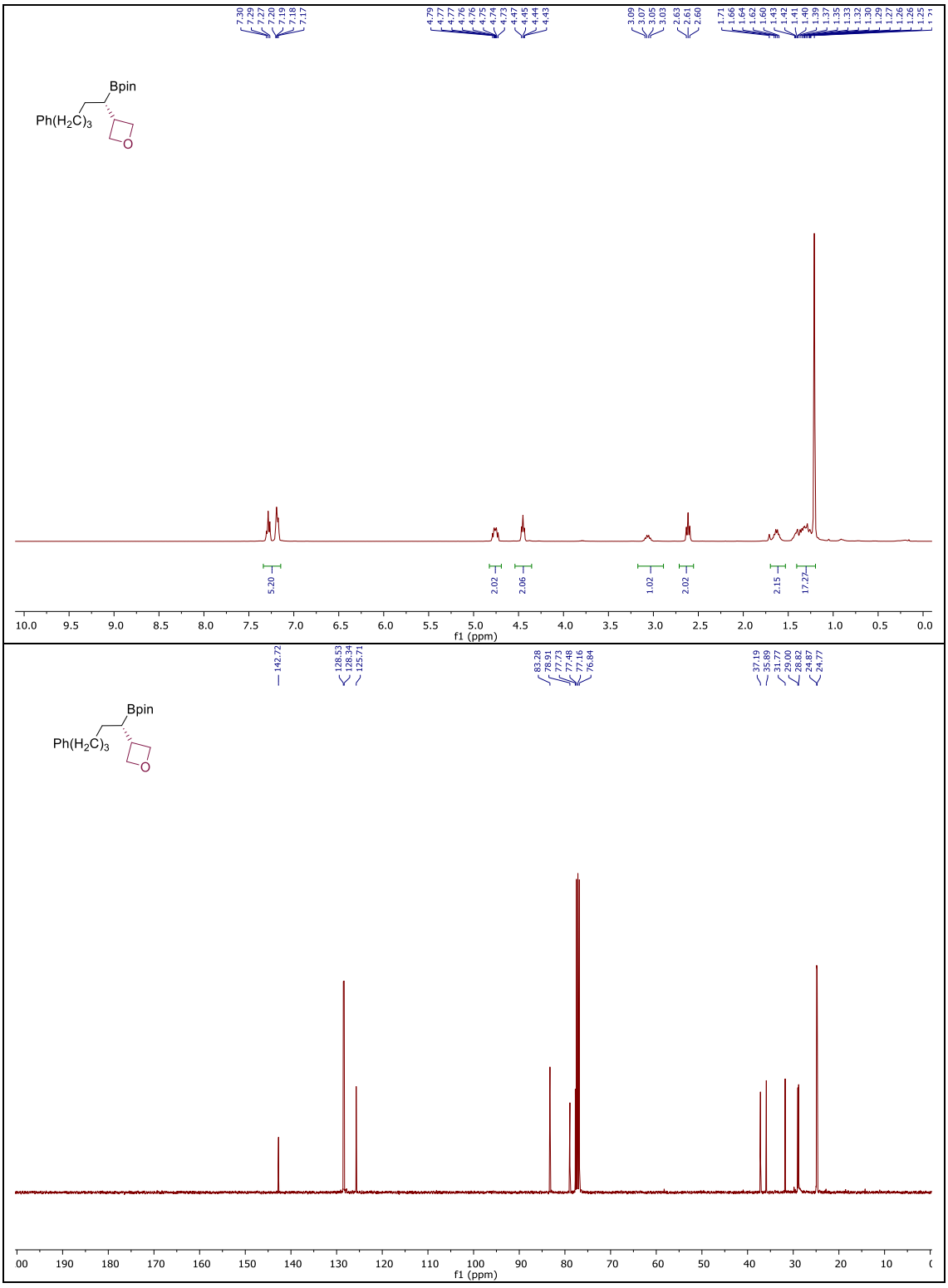

36.14
Bpin
Ph(H2C)3
NBoc
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-9
f1 (ppm)

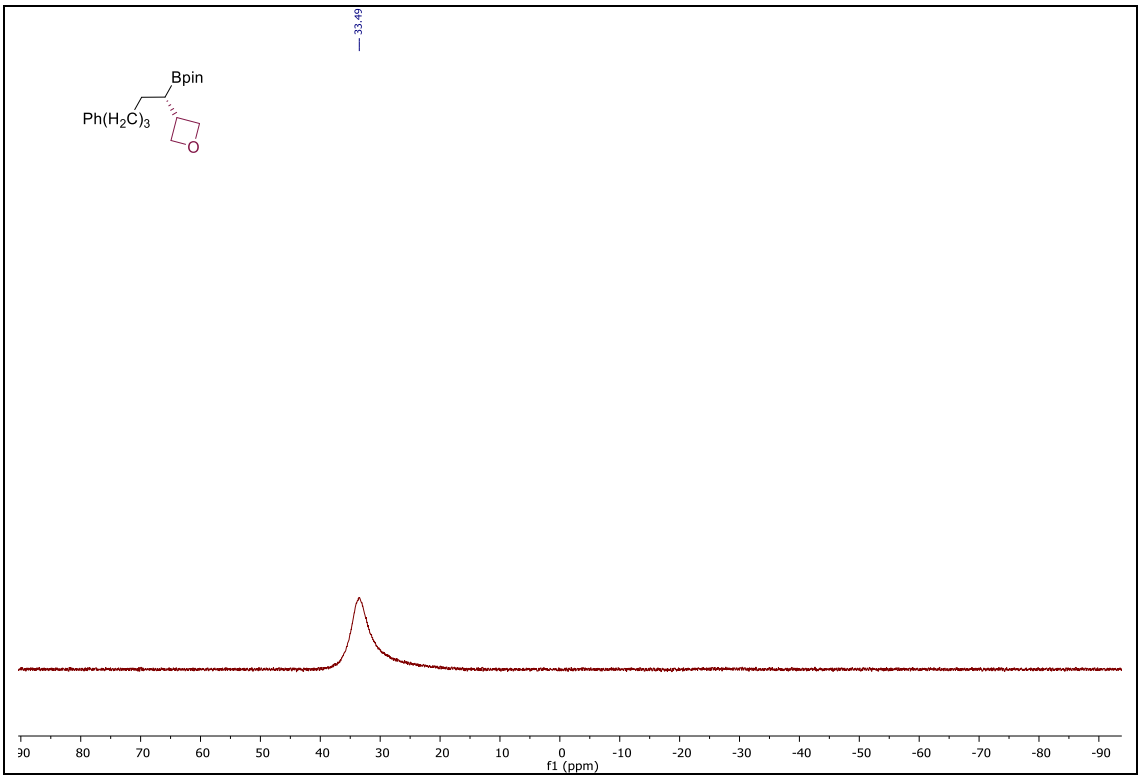
NMR spectra of 4g



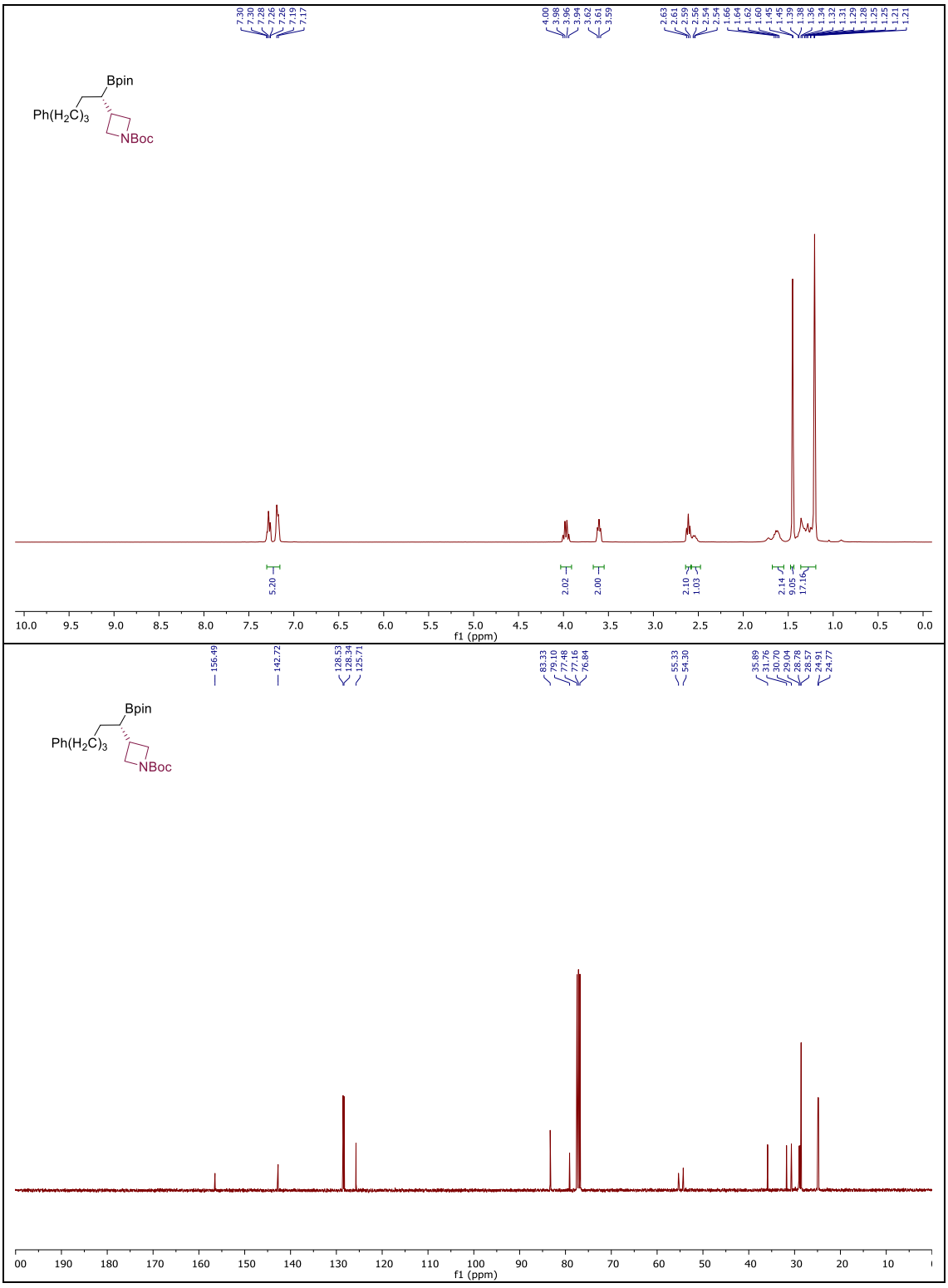

35.38
Bpin
Ph(H2C)3
O
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

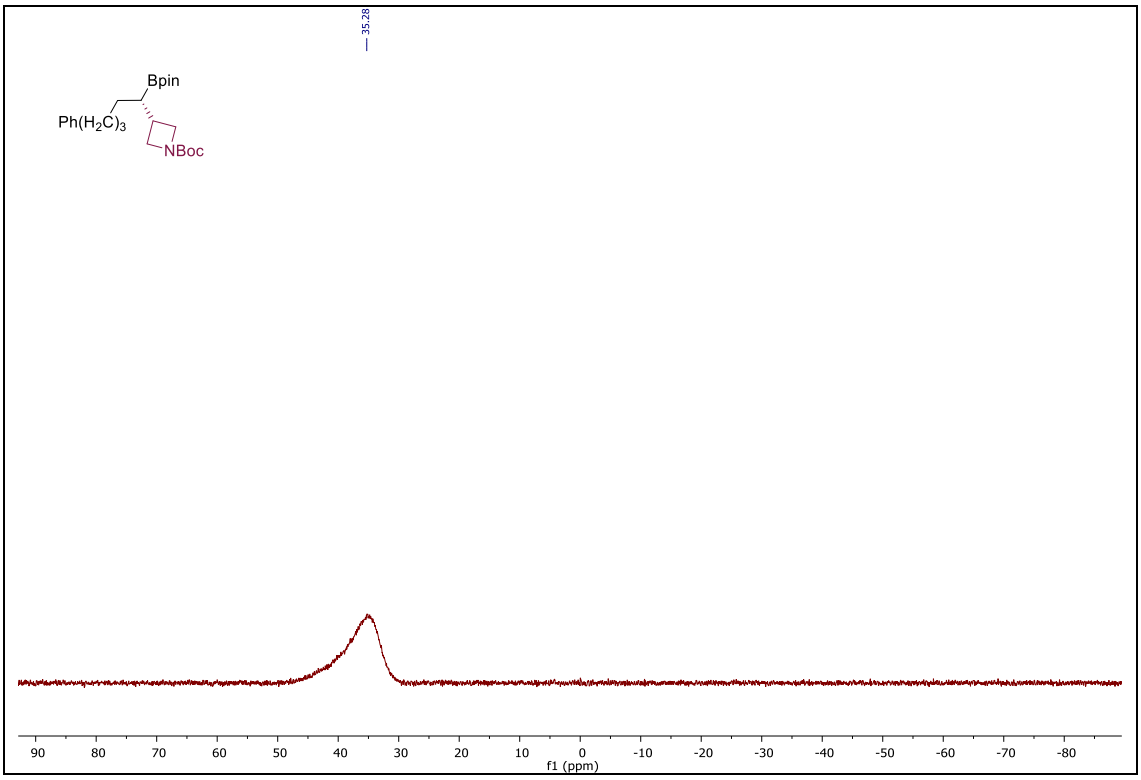
NMR spectra of 4h



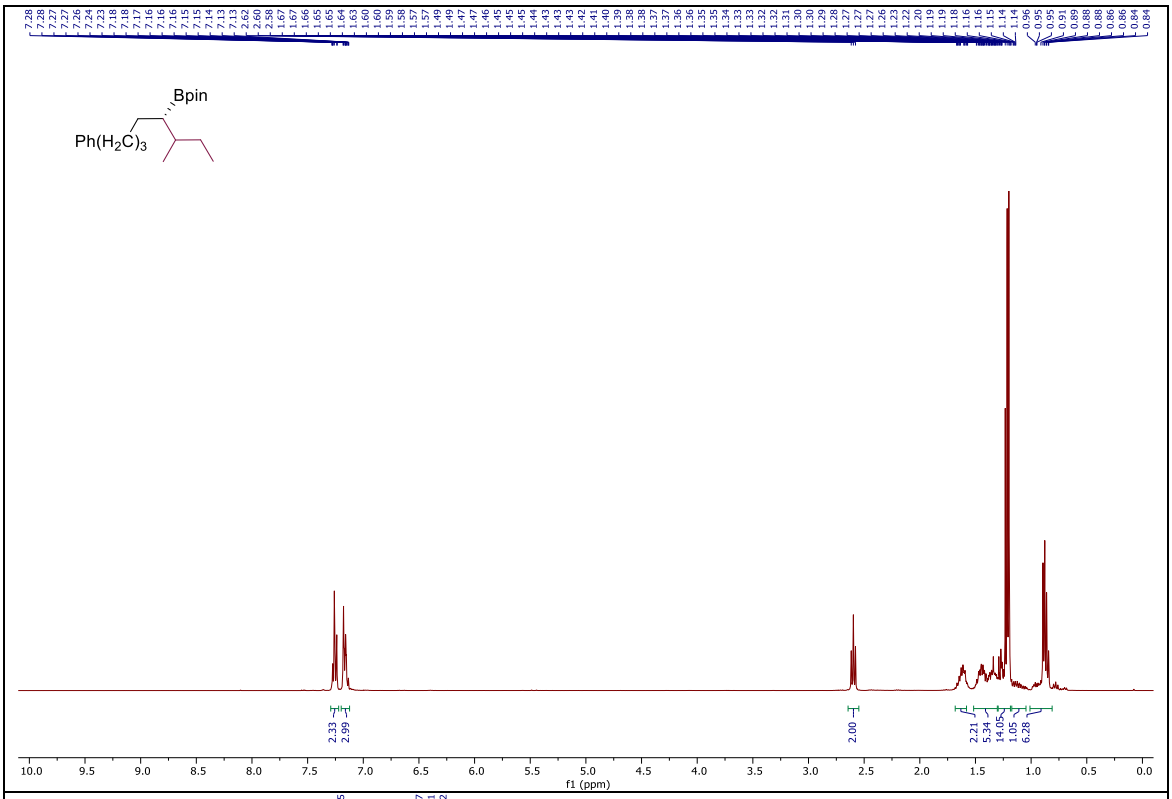

33.49
Bpin
Ph(H2C)3
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

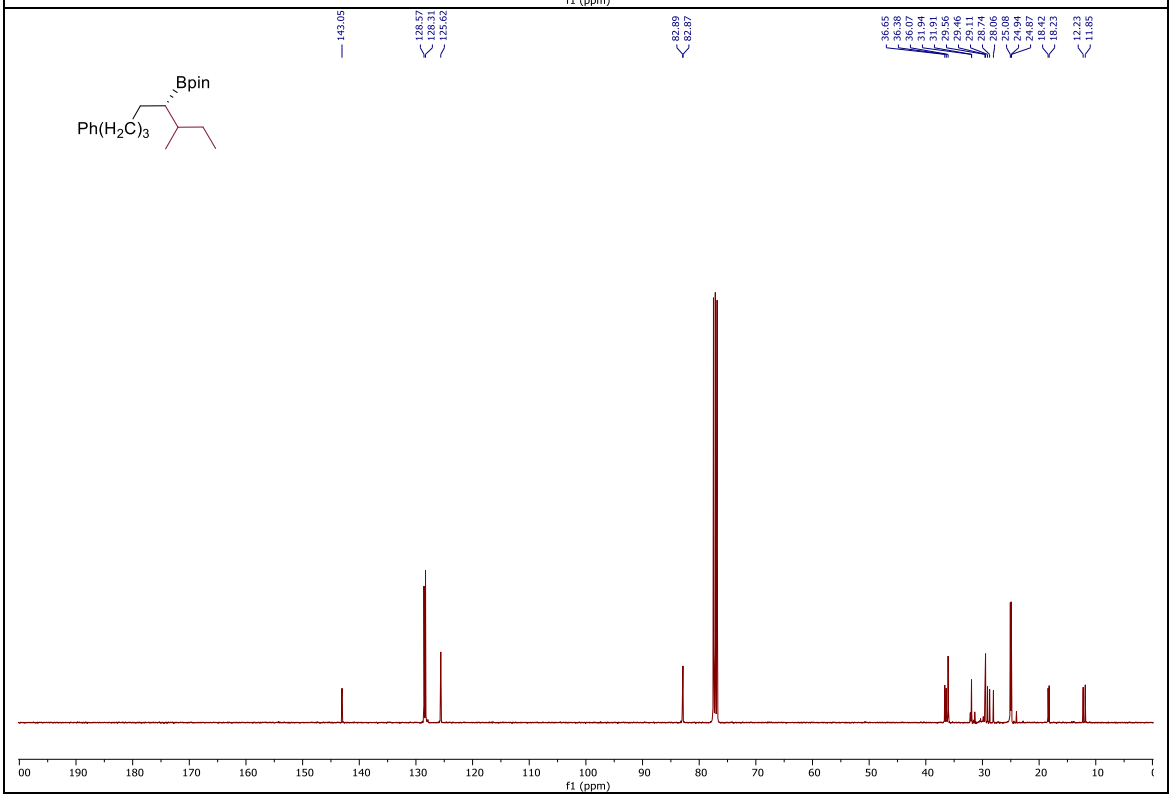
NMR spectra of 4i

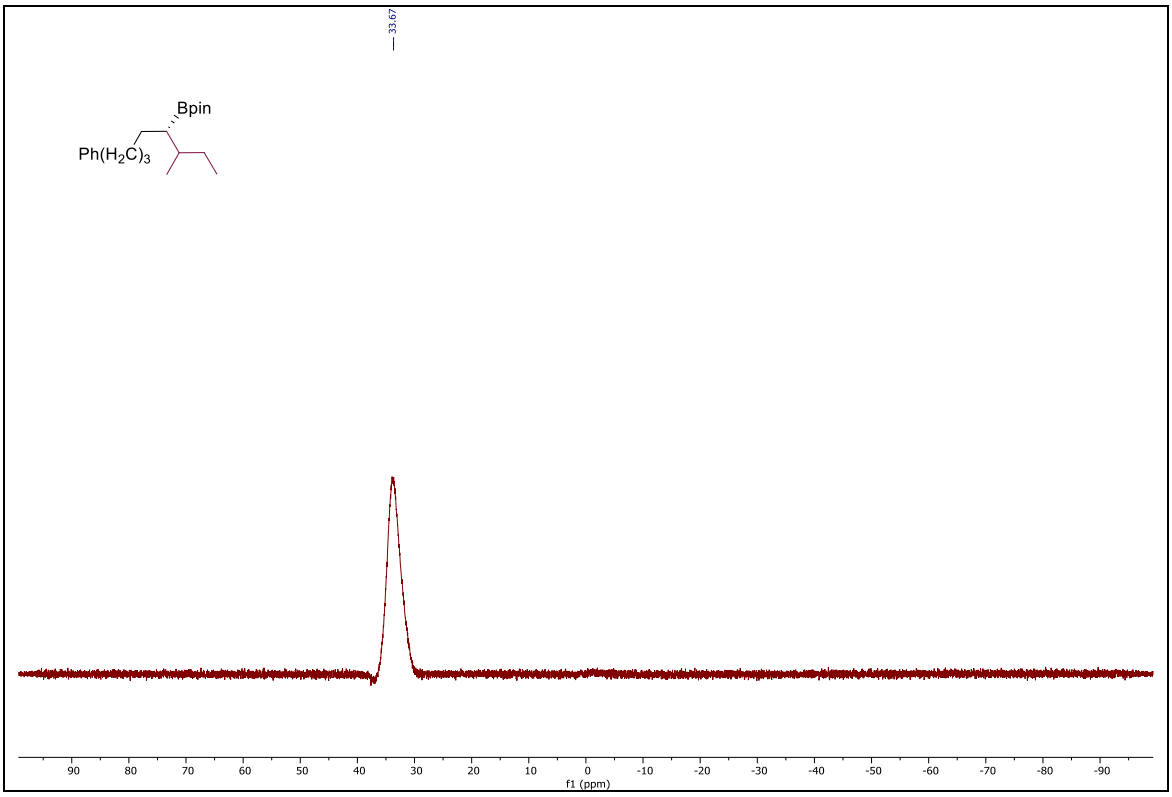



35.28
Bpin
Ph(H2C)3
NBoc
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

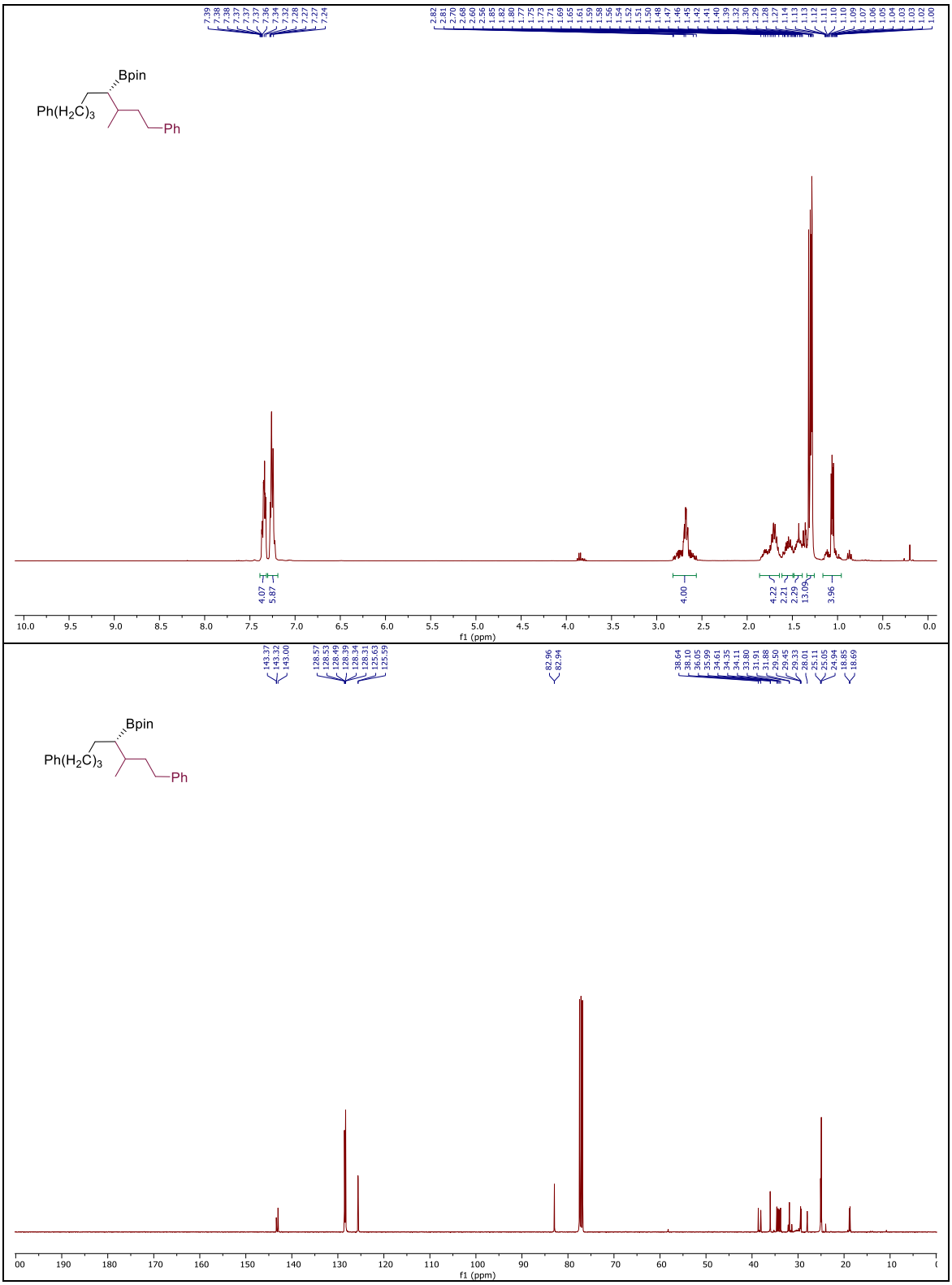
NMR spectra of 4j

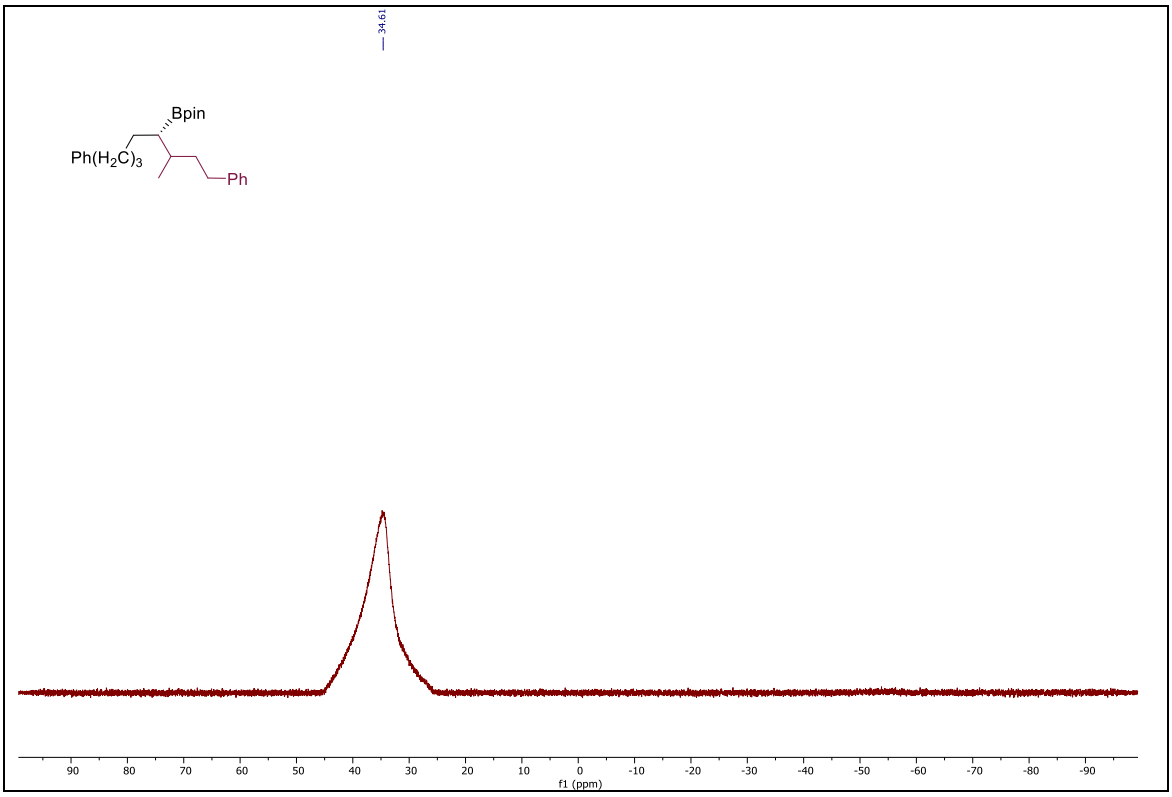




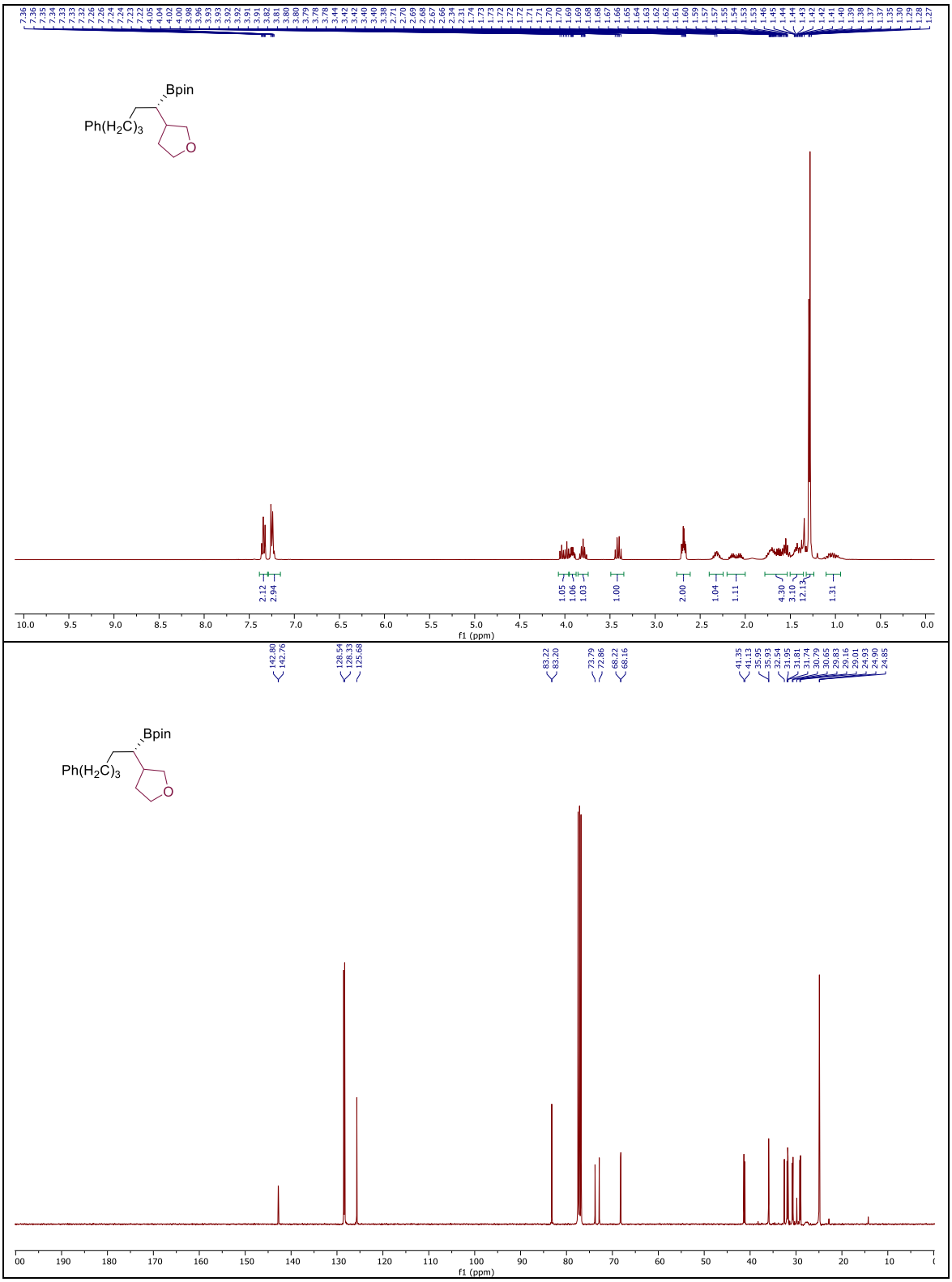

33.67
Bpin
Ph(H2C)3
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

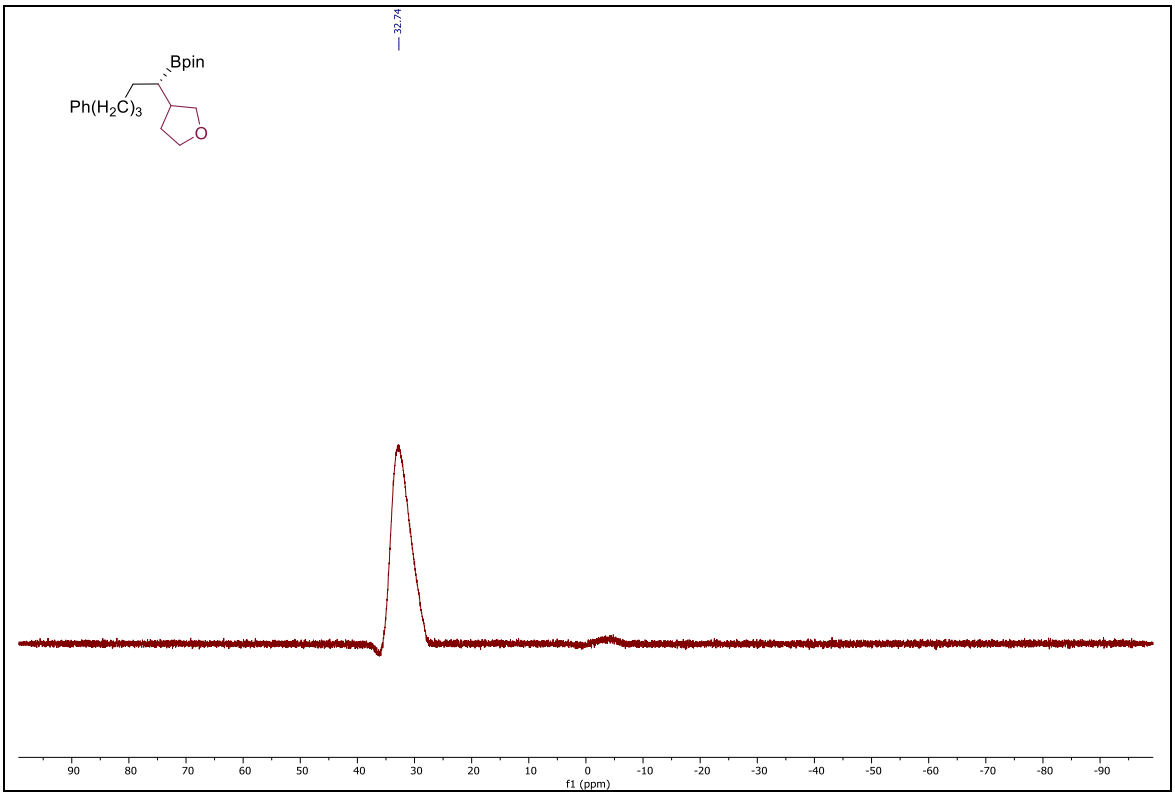
NMR spectra of 4k



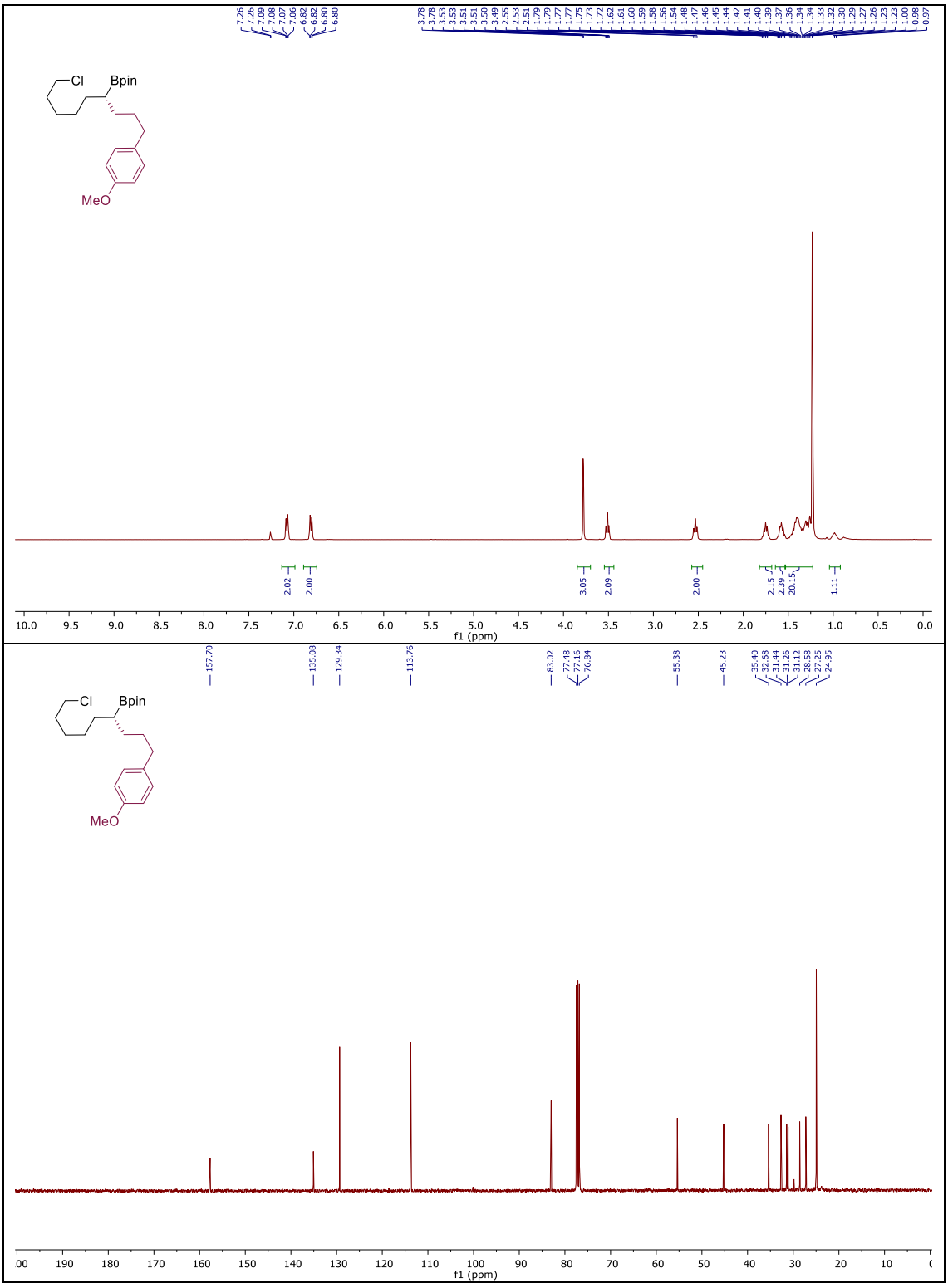

34.61
Bpin
Ph(H2C)3
Ph
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

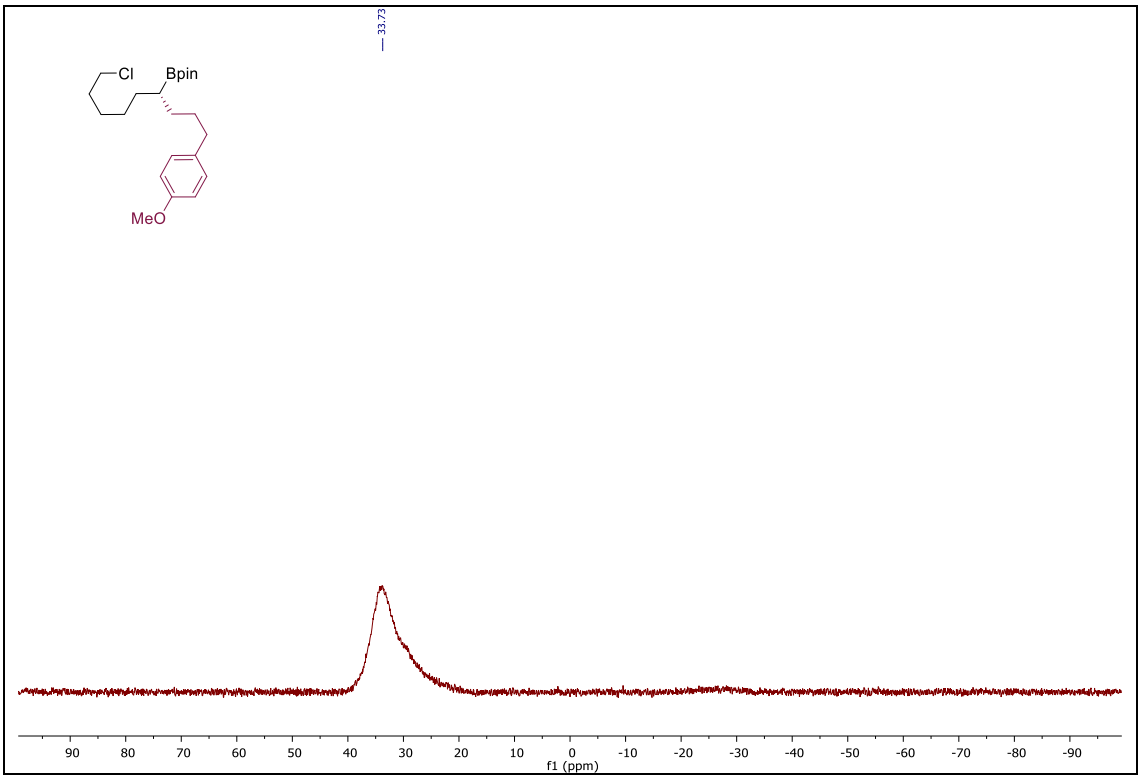
NMR spectra of 4l



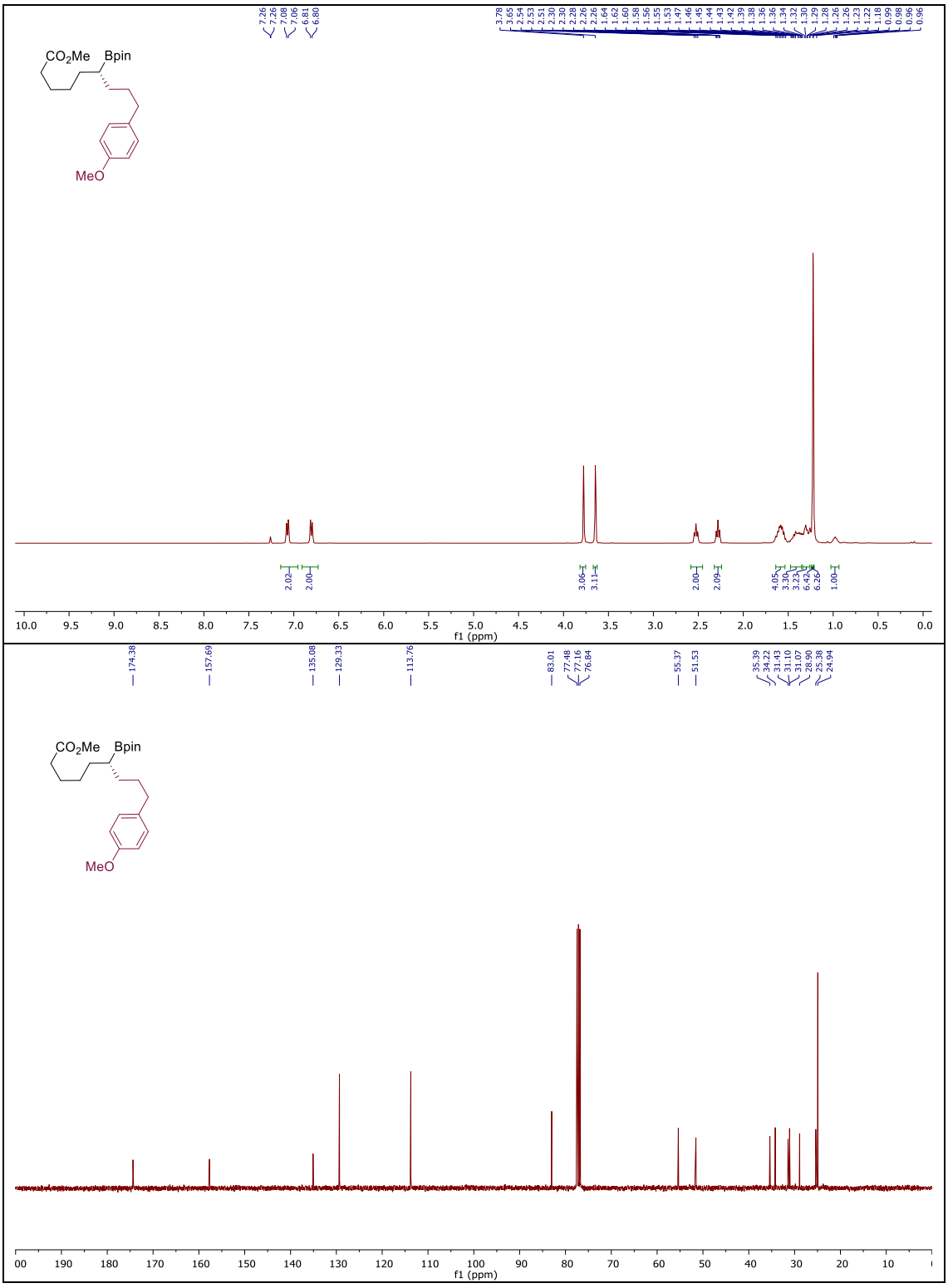

32.74
Bpin
Ph(H2C)3
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

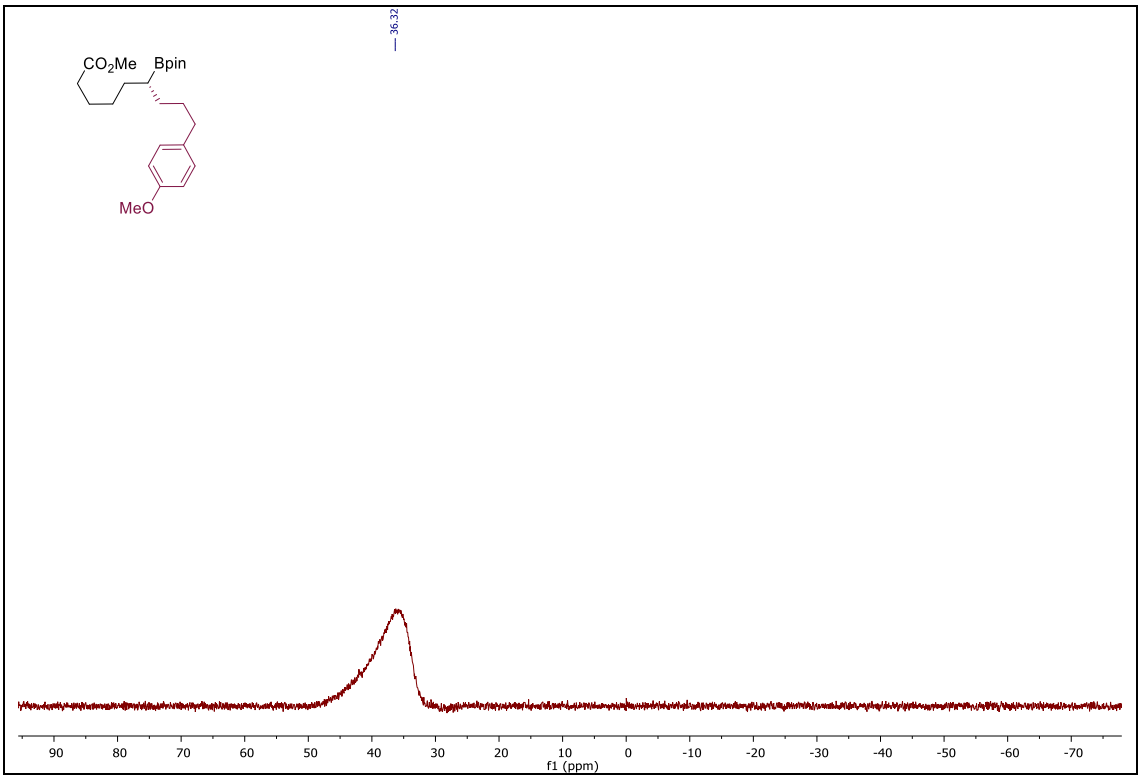
NMR spectra of 5a



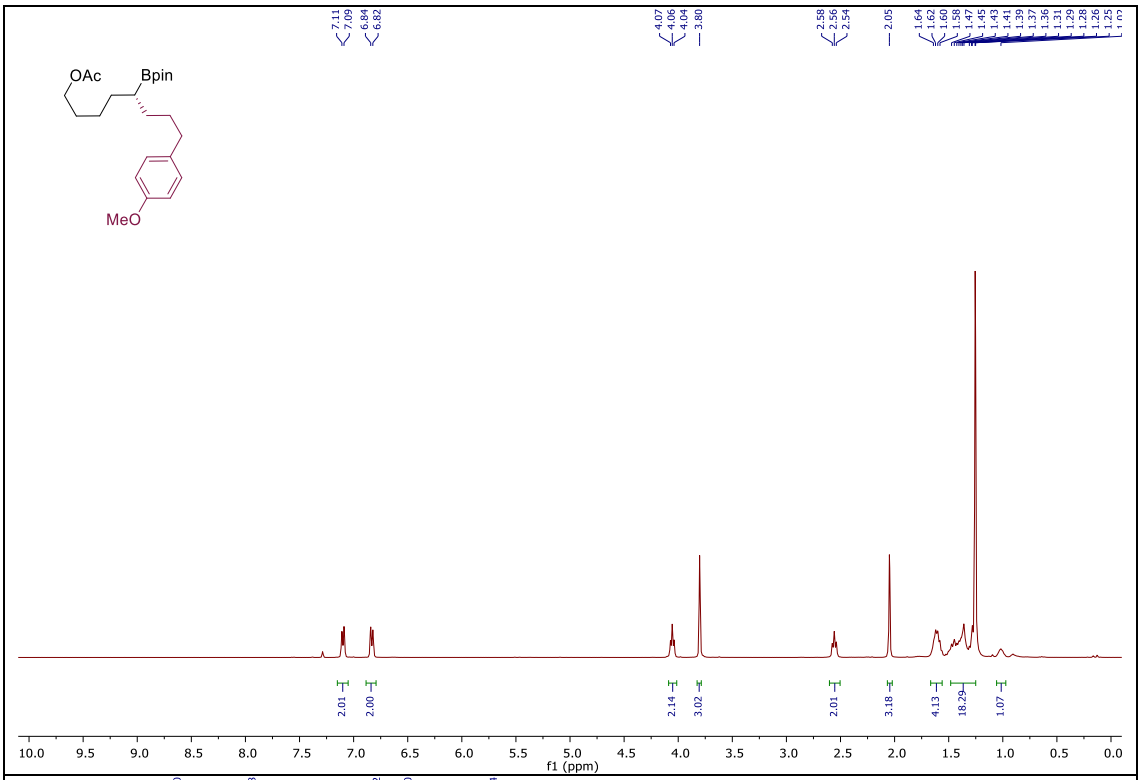

33.73
Cl
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

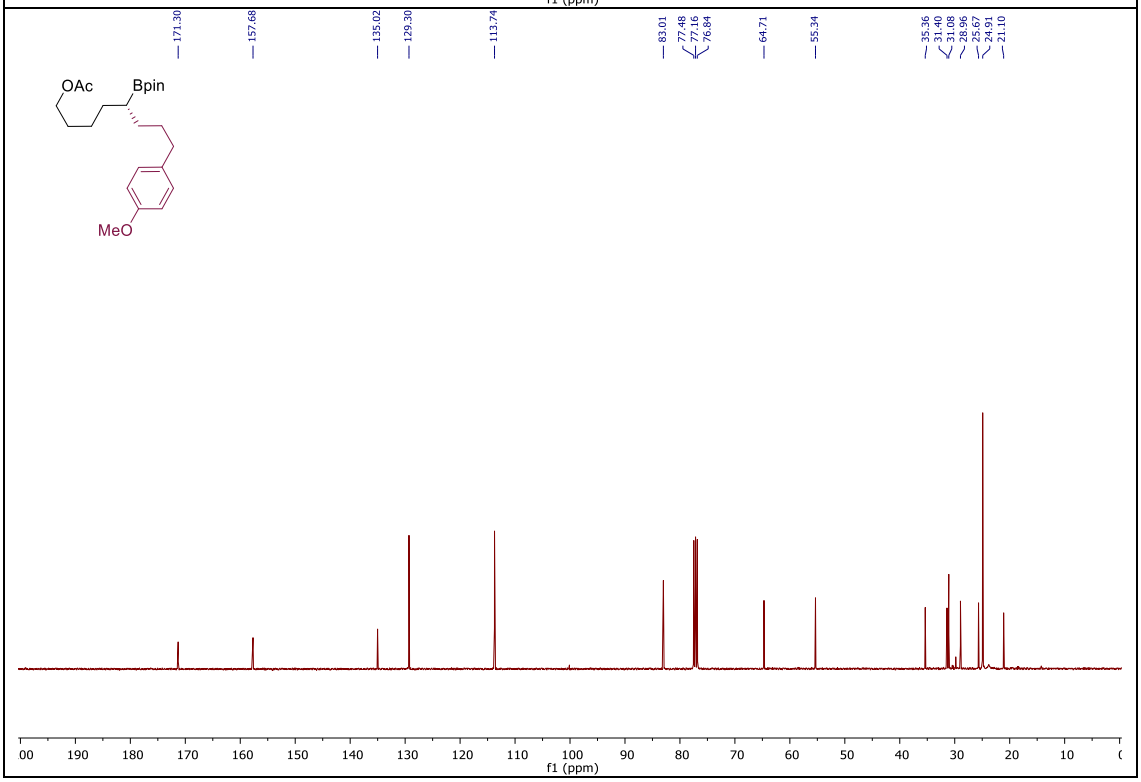
NMR spectra of 5b

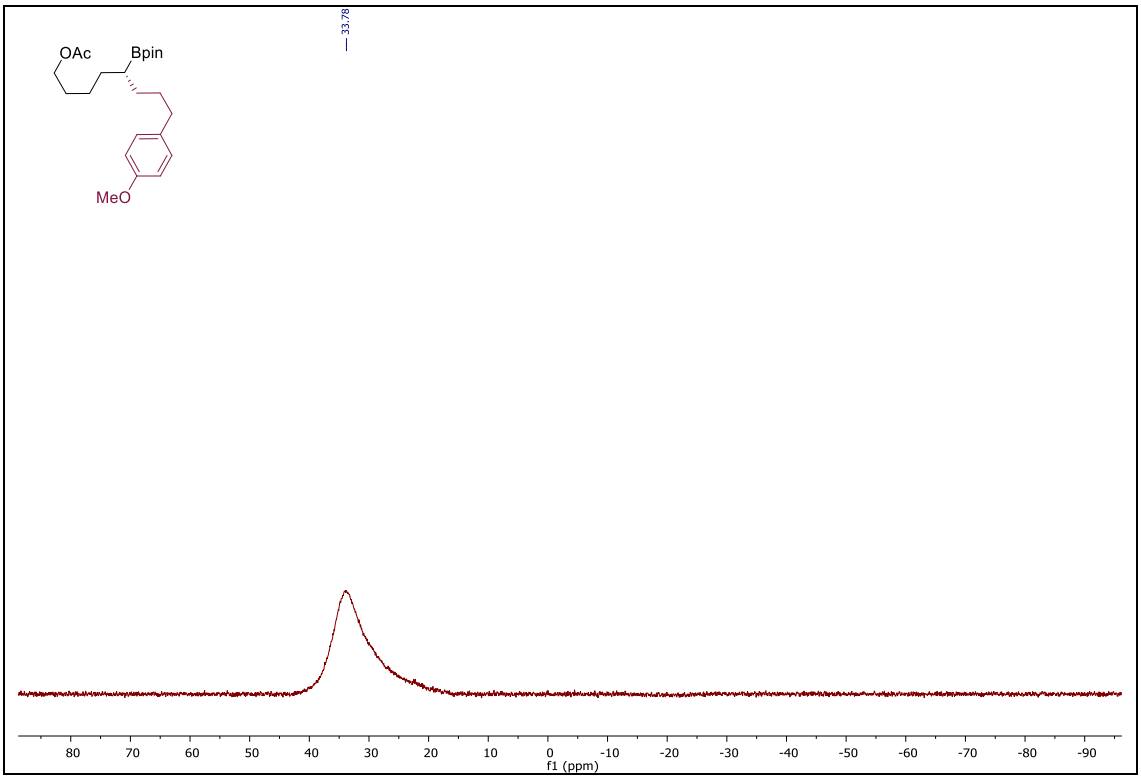



36.32
CO2Me
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

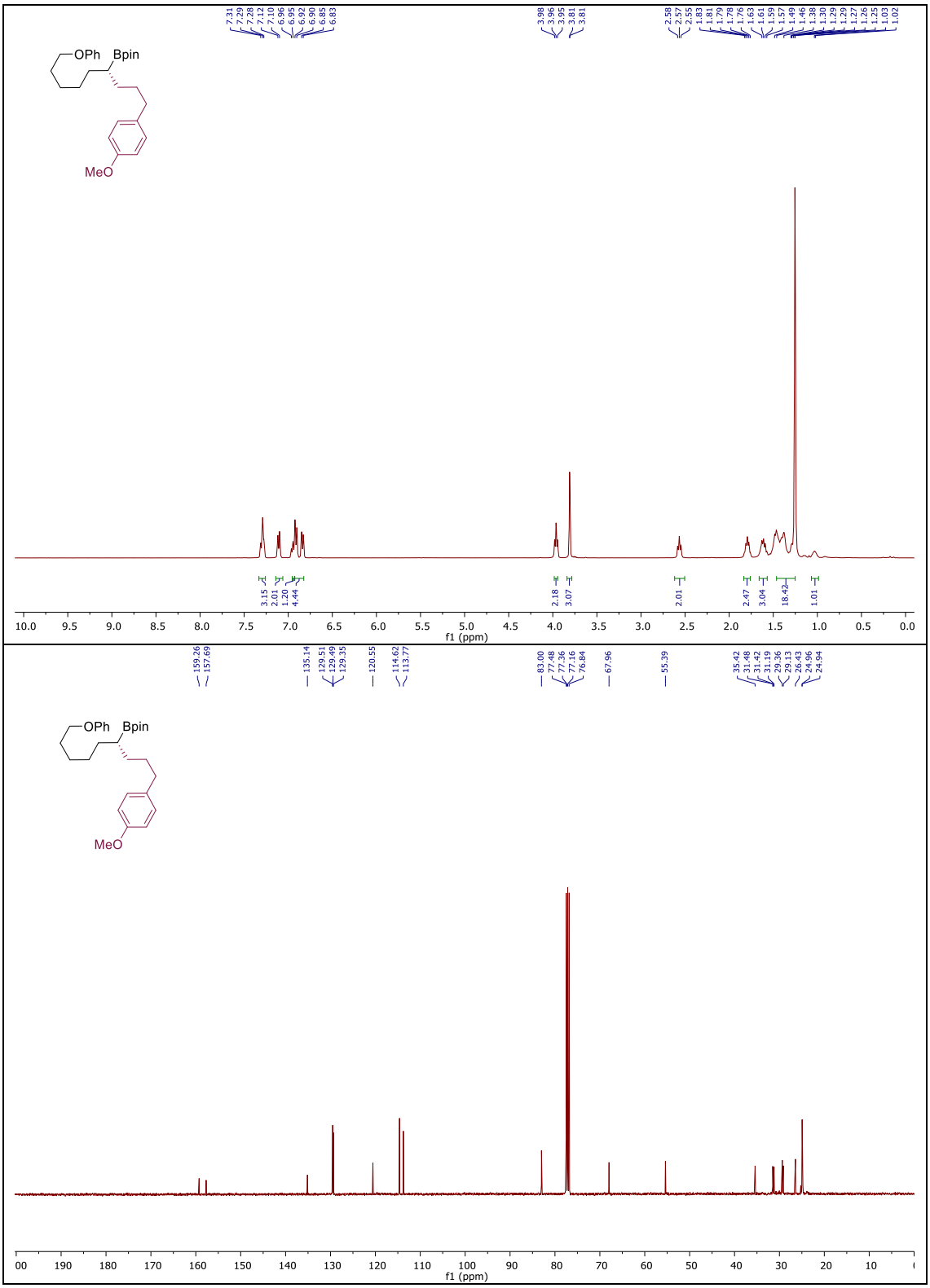
NMR spectra of 5c

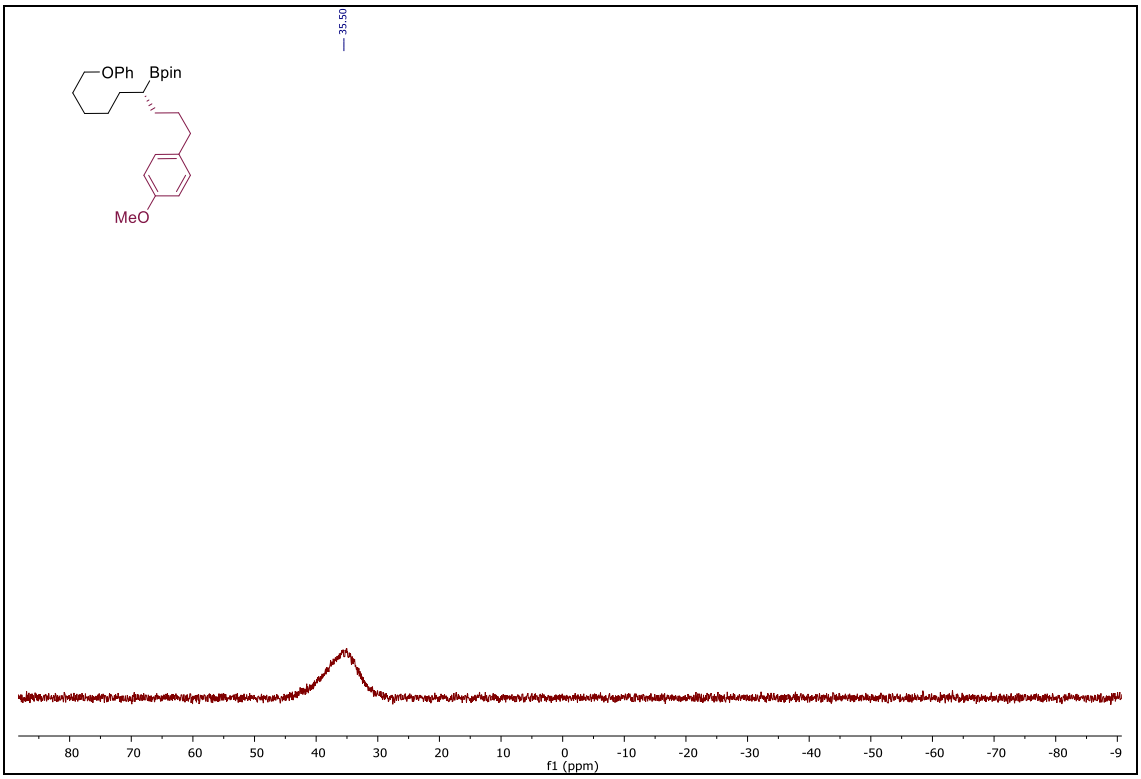




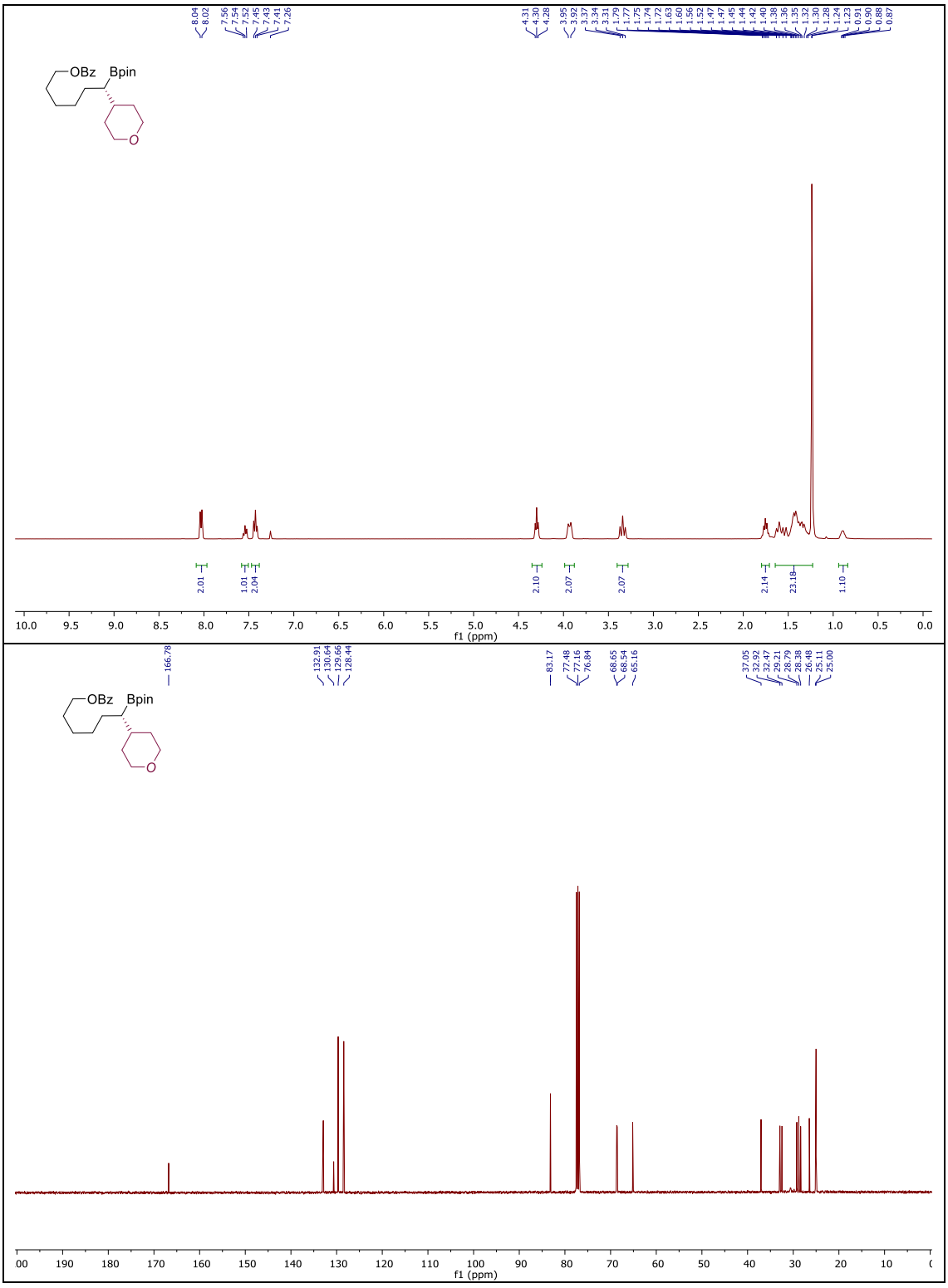

33.78
OAc
Bpin
MeO
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

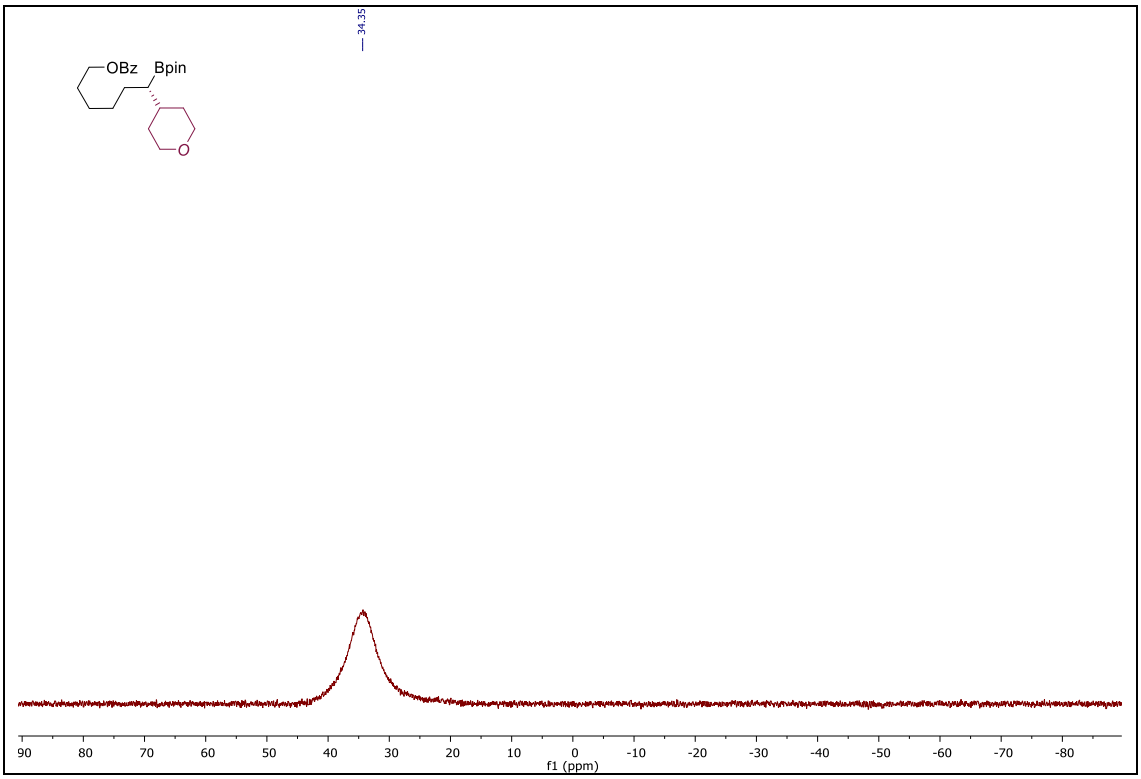
NMR spectra of 5d



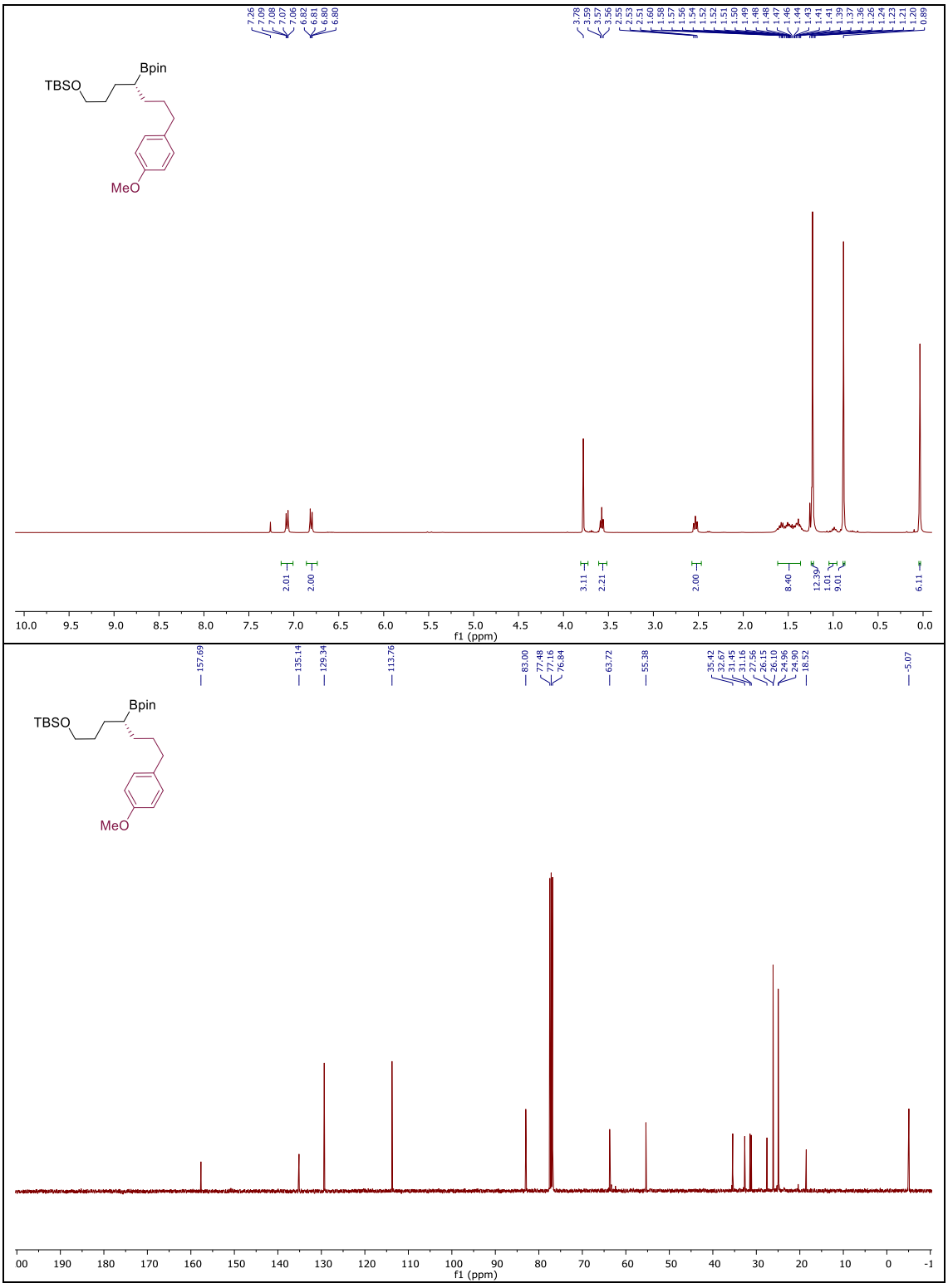

35.50
OPh
Bpin
MeO
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-9
f1 (ppm)

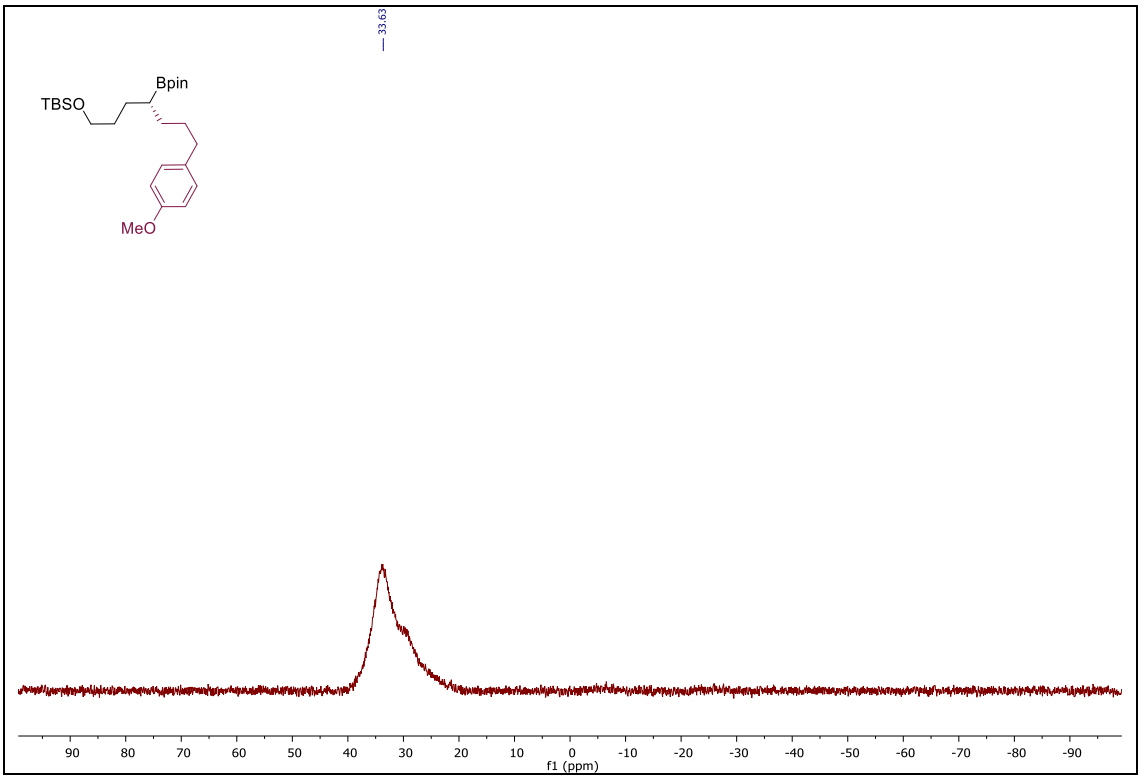
NMR spectra of 5e



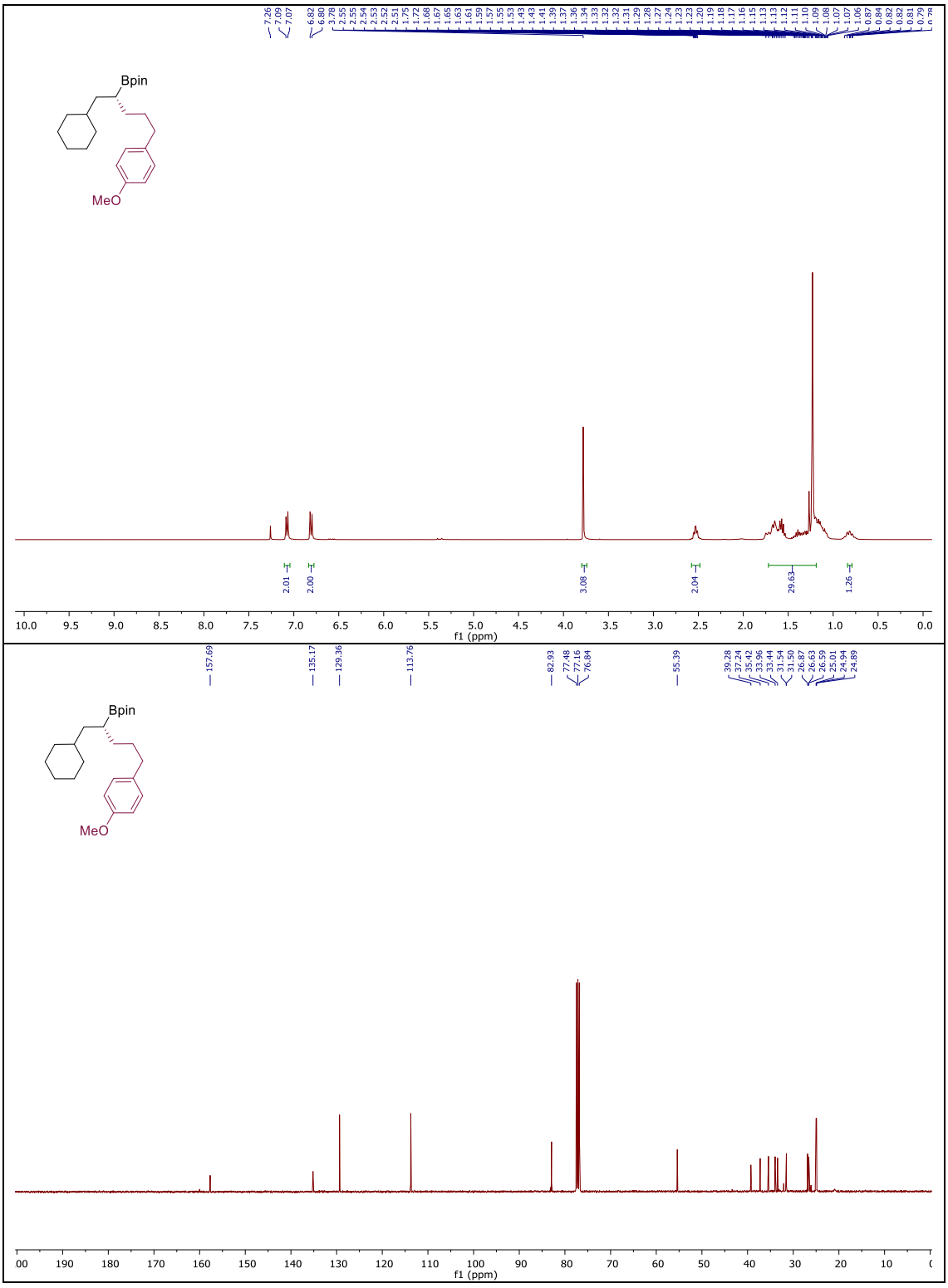

34.35
OBz
Bpin
O
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

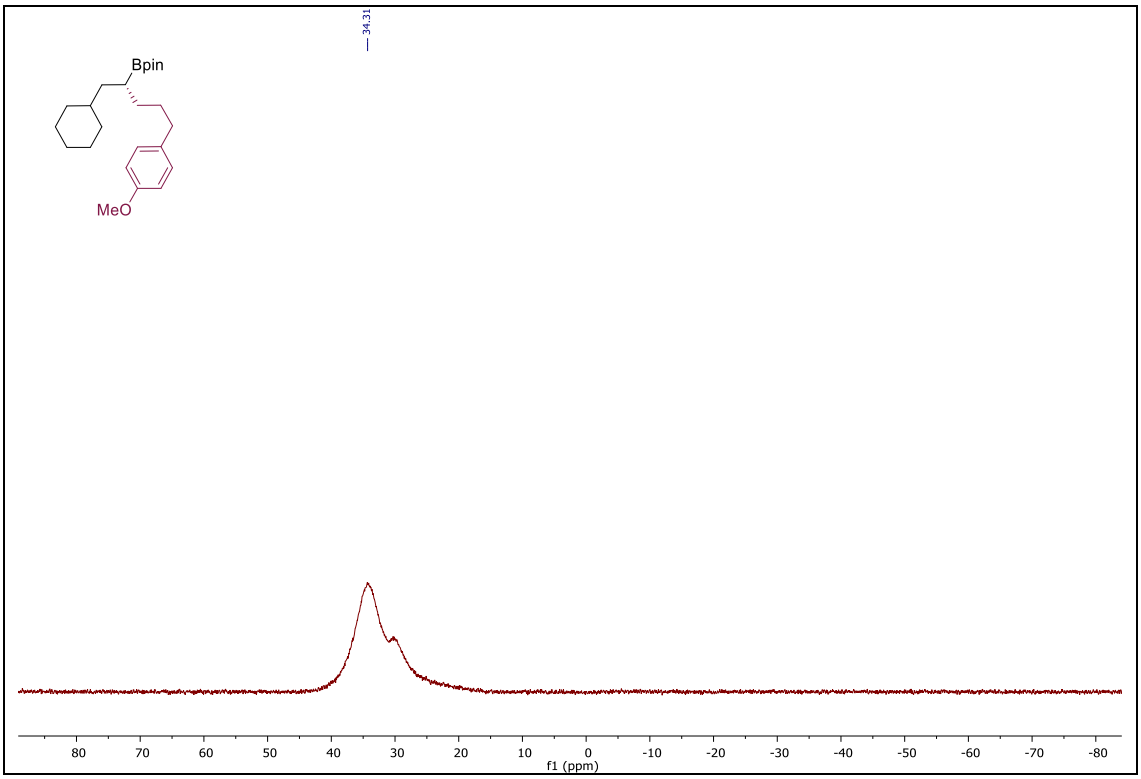
NMR spectra of 5f



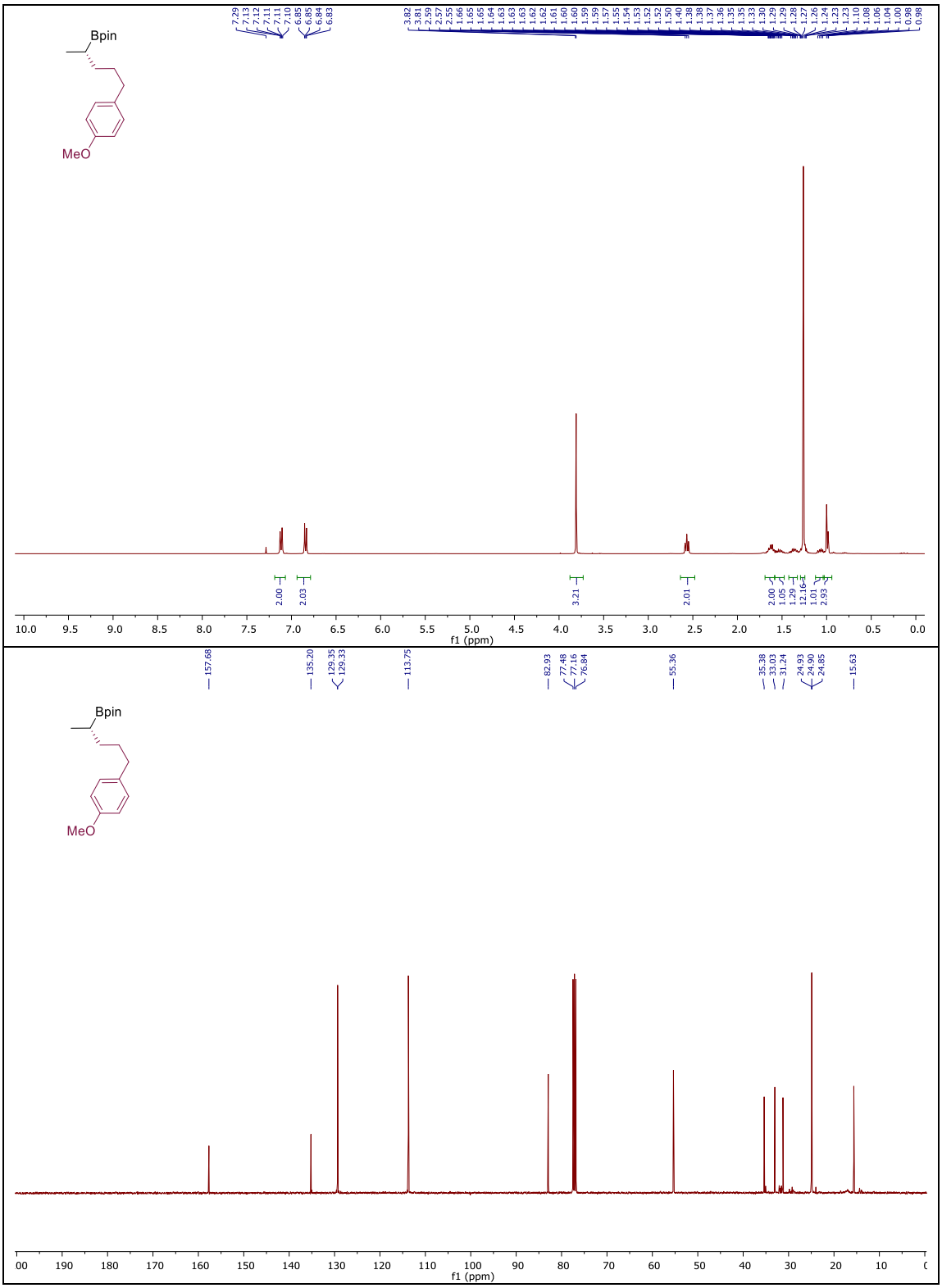

33.63
Bpin
TBSO
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

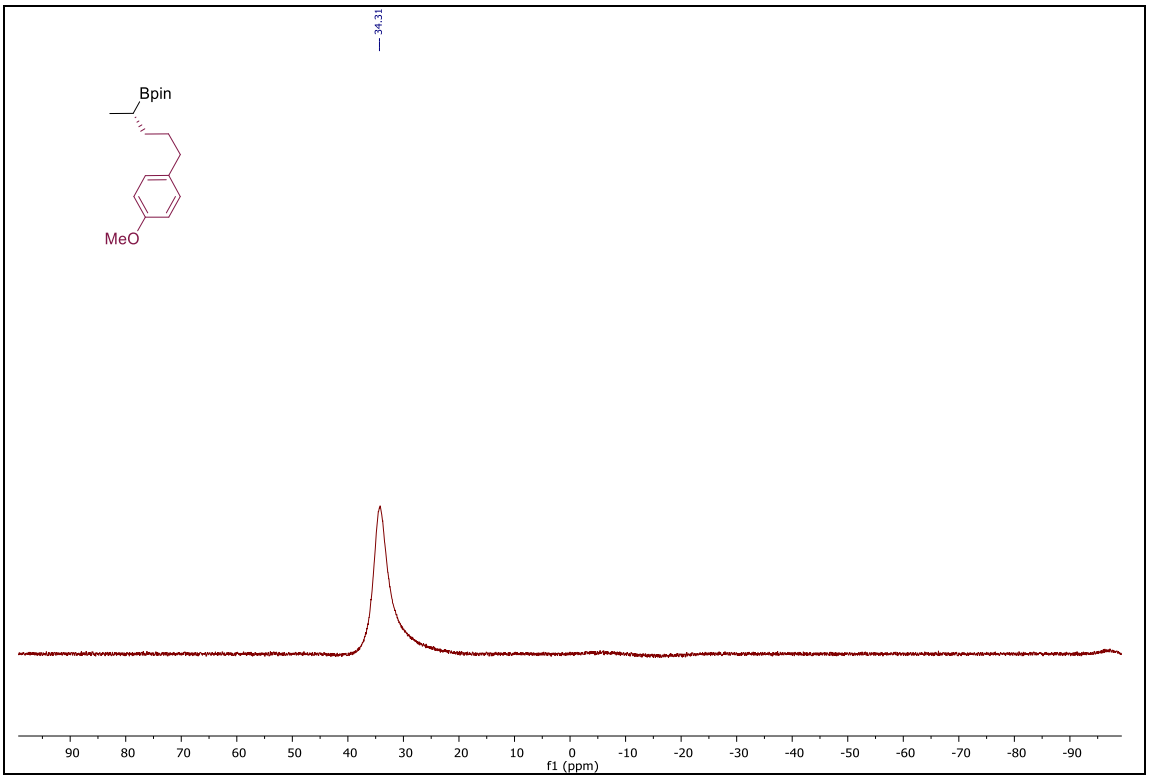
NMR spectra of 5g



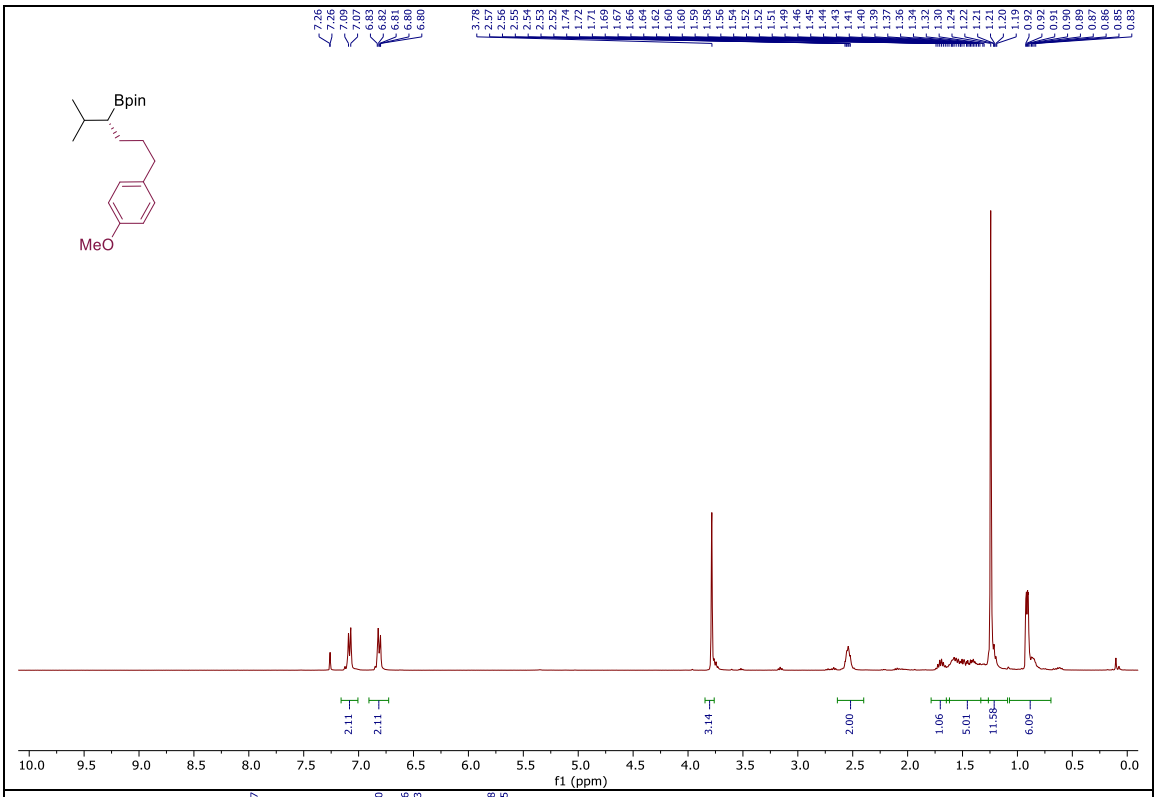

34.31
Bpin
MeO
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

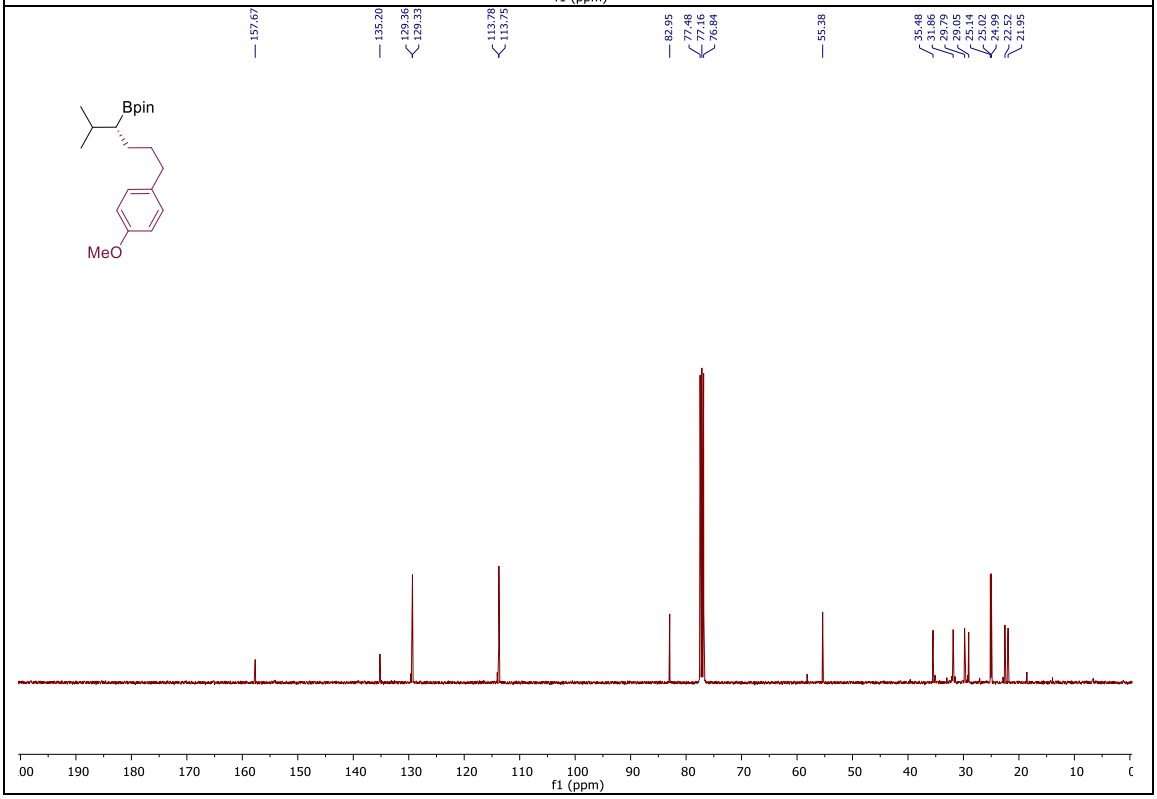
NMR spectra of 5h

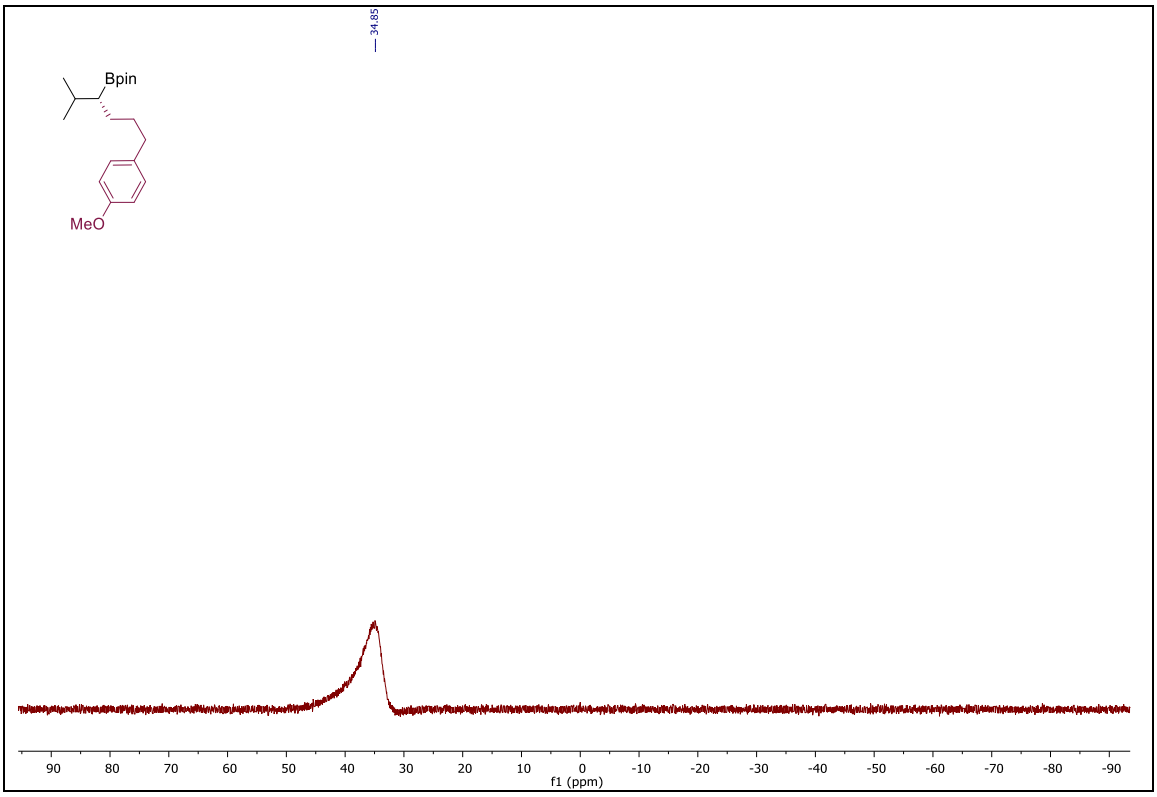



34.31
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

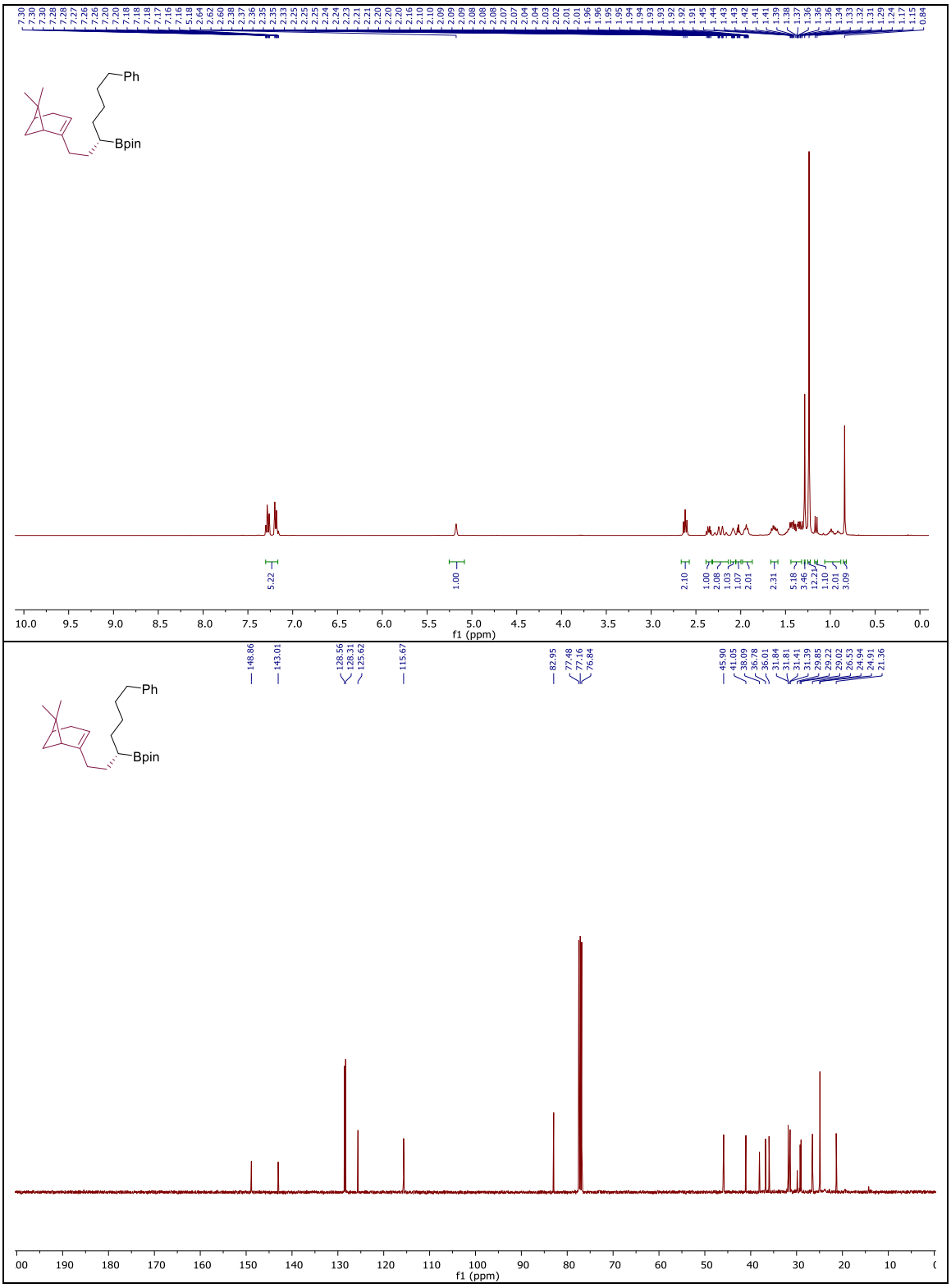
NMR spectra of 5i

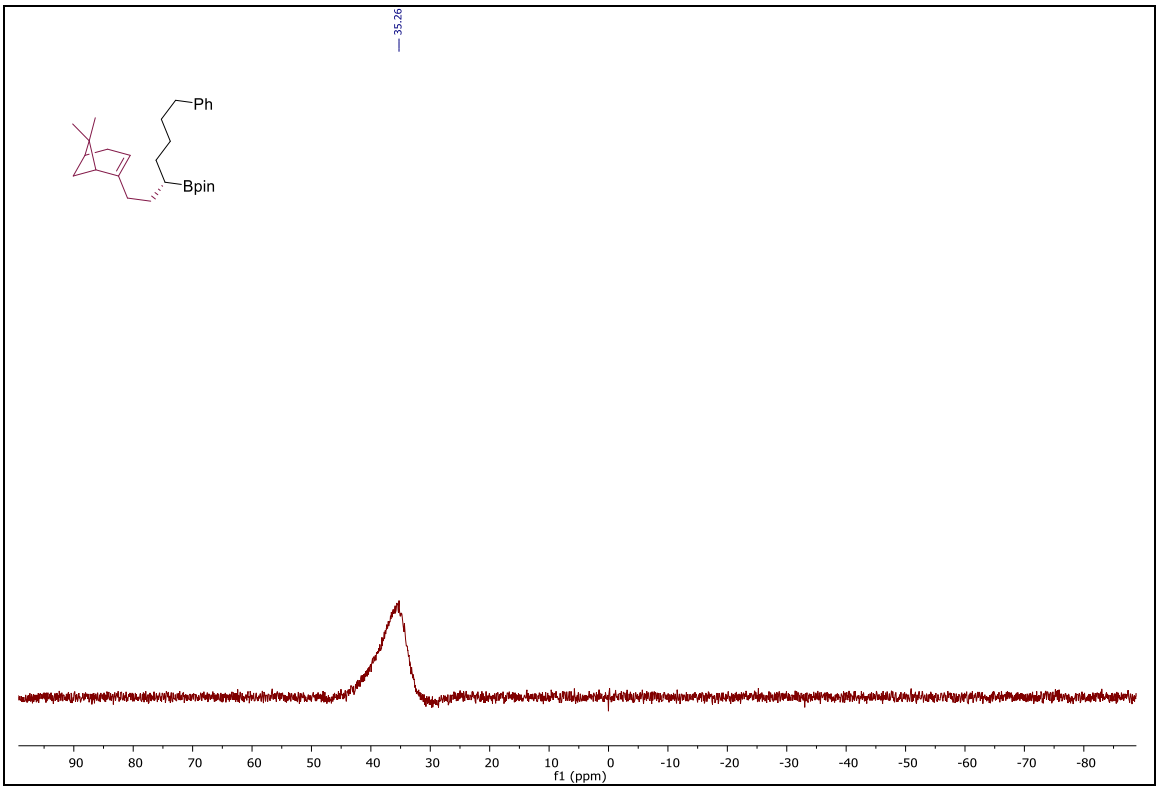




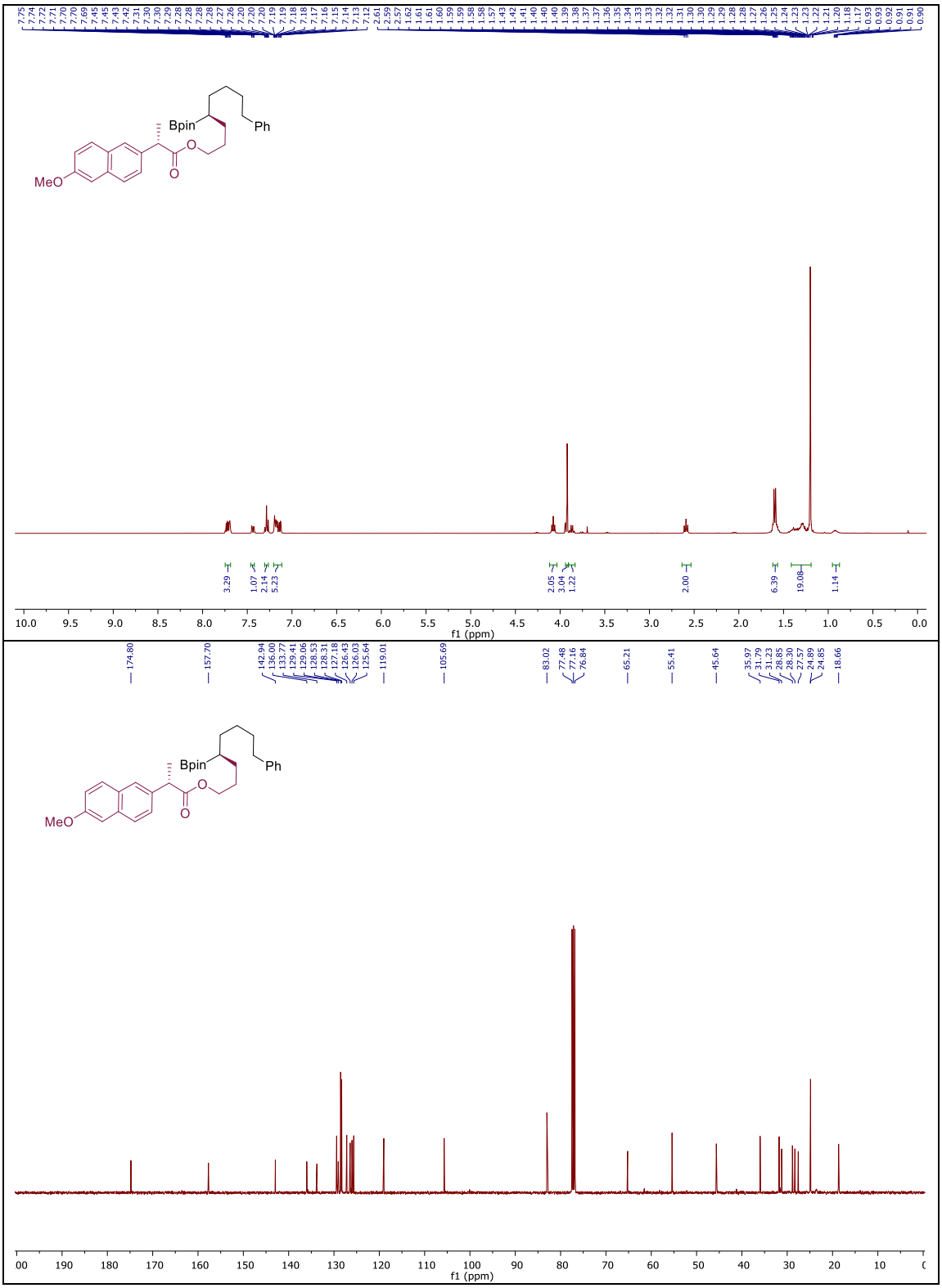

34.85
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

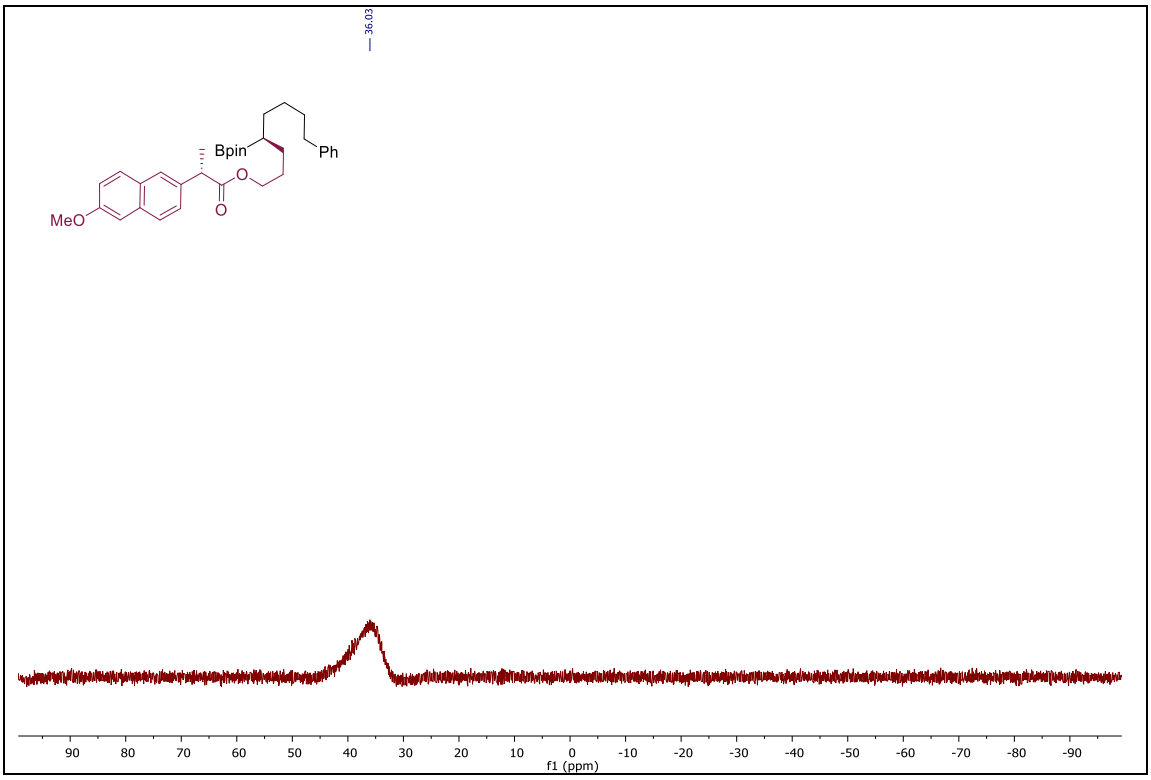
NMR spectra of 6a



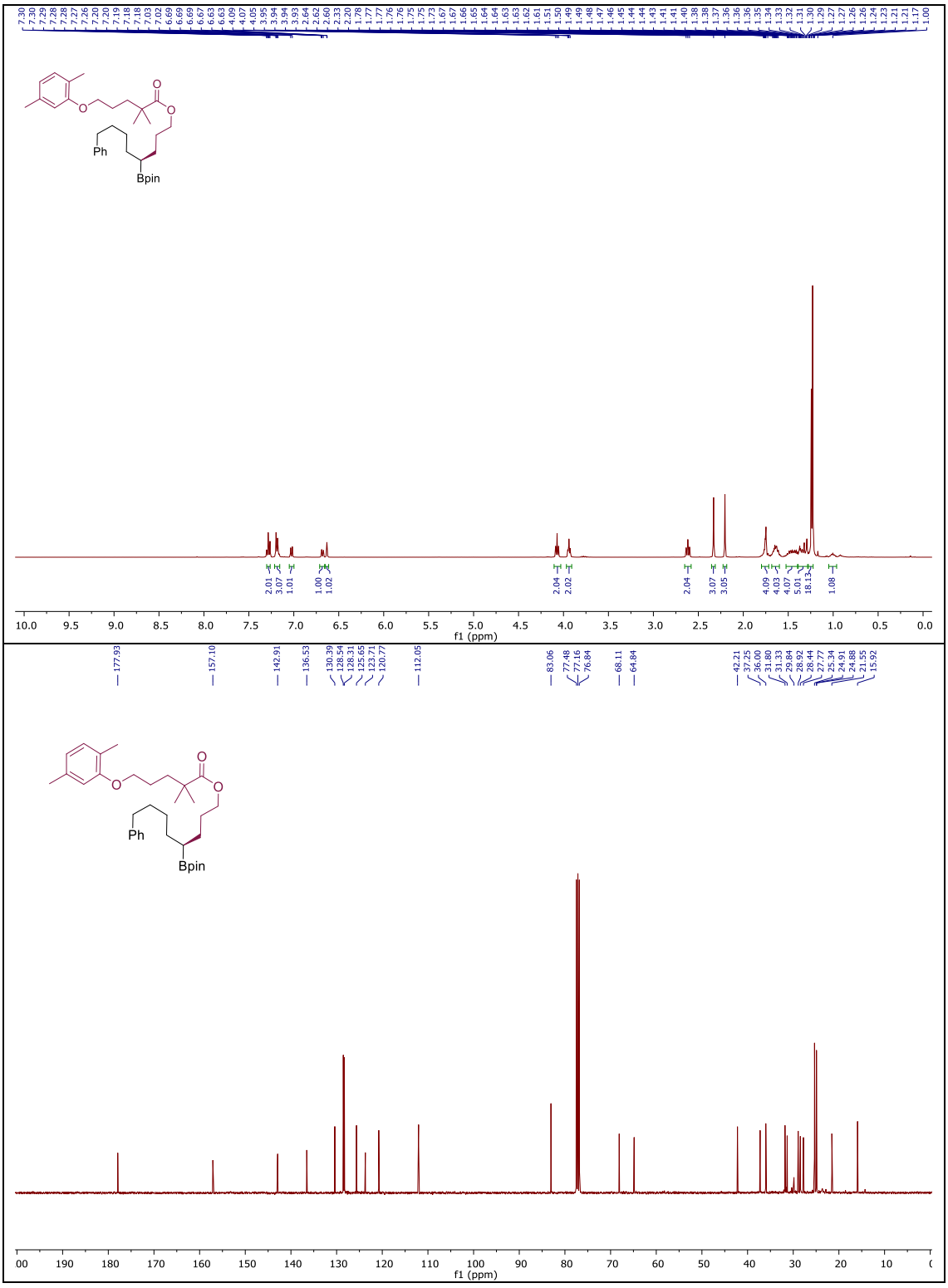

35.26
Ph
Bpin
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

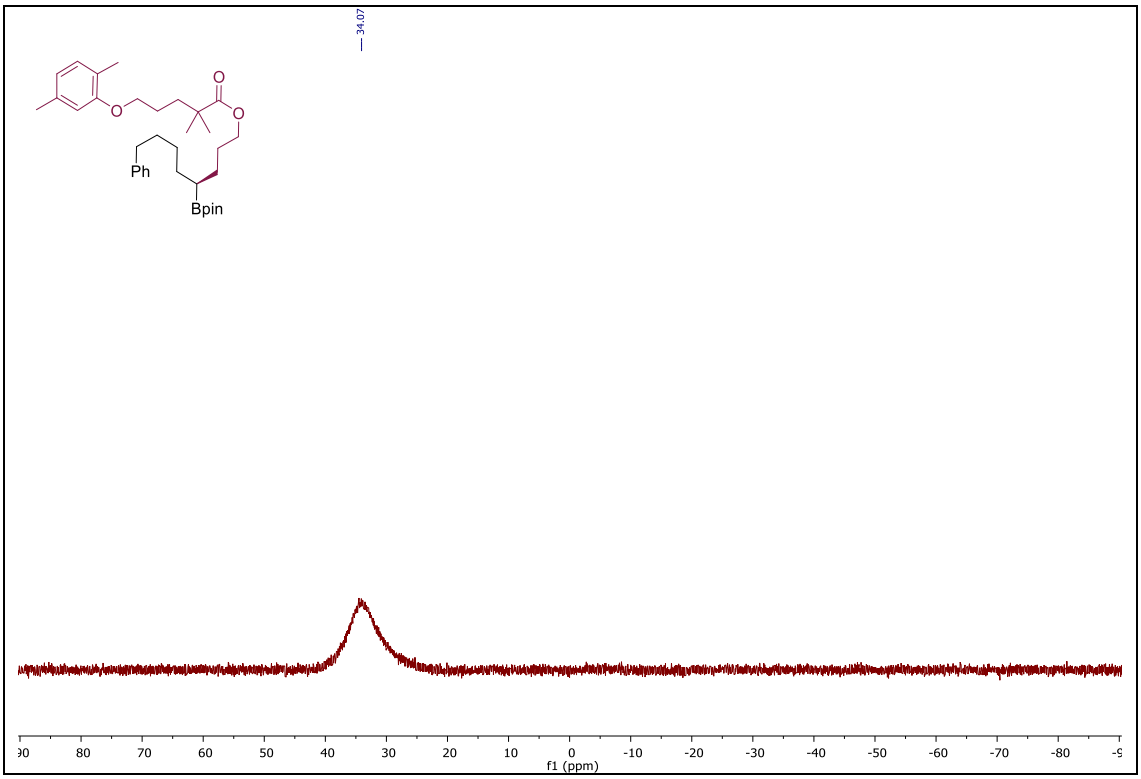
NMR spectra of 6b



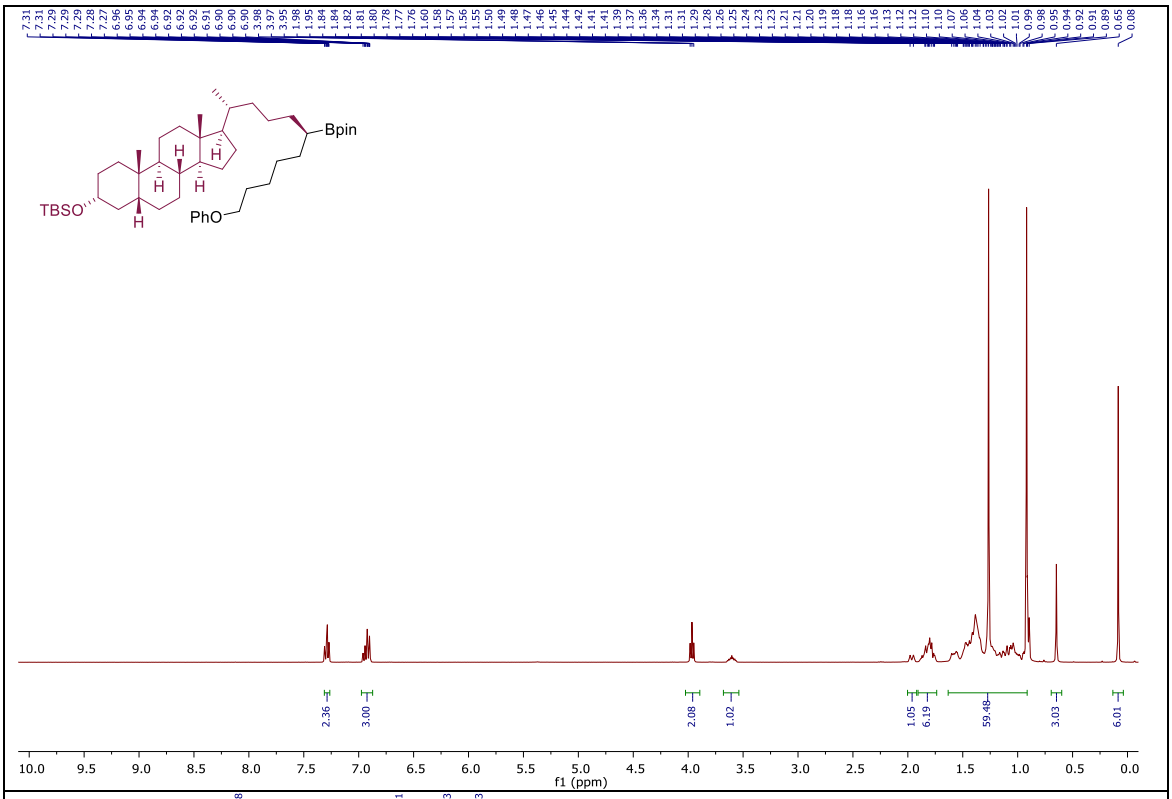

36.03
Bpin
Ph
O
O
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

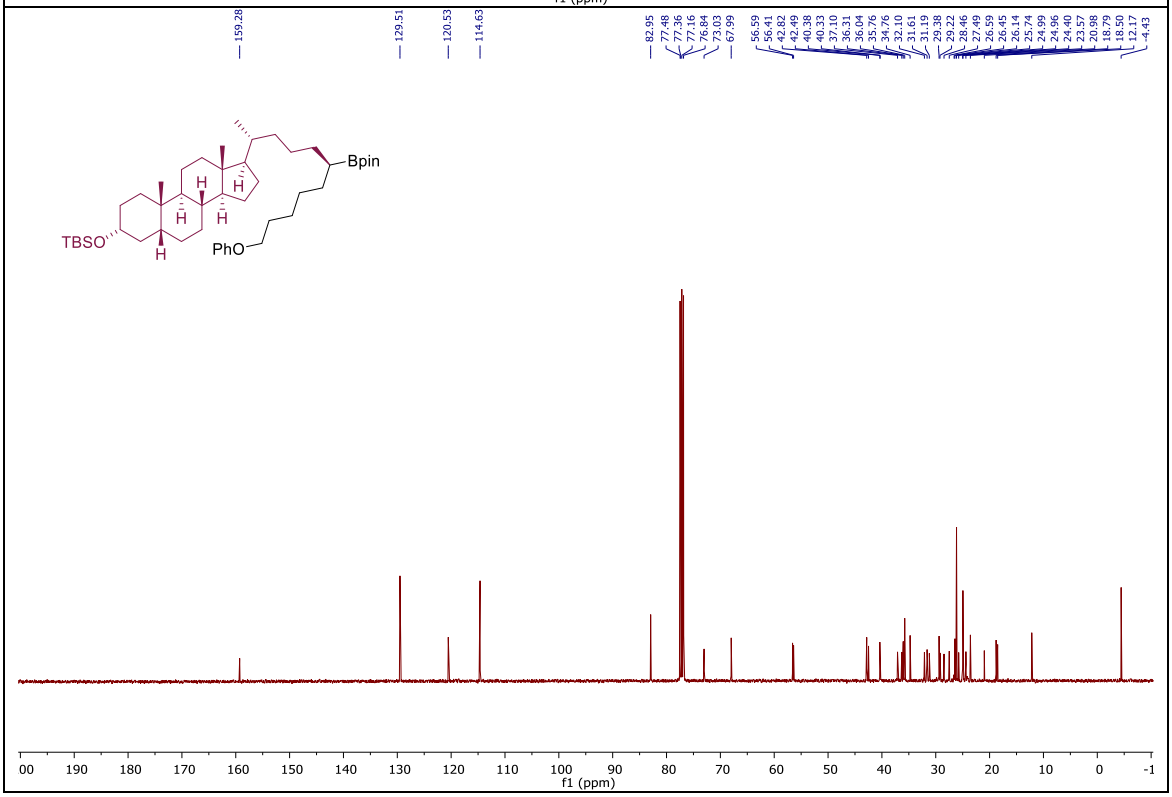
NMR spectra of 6c

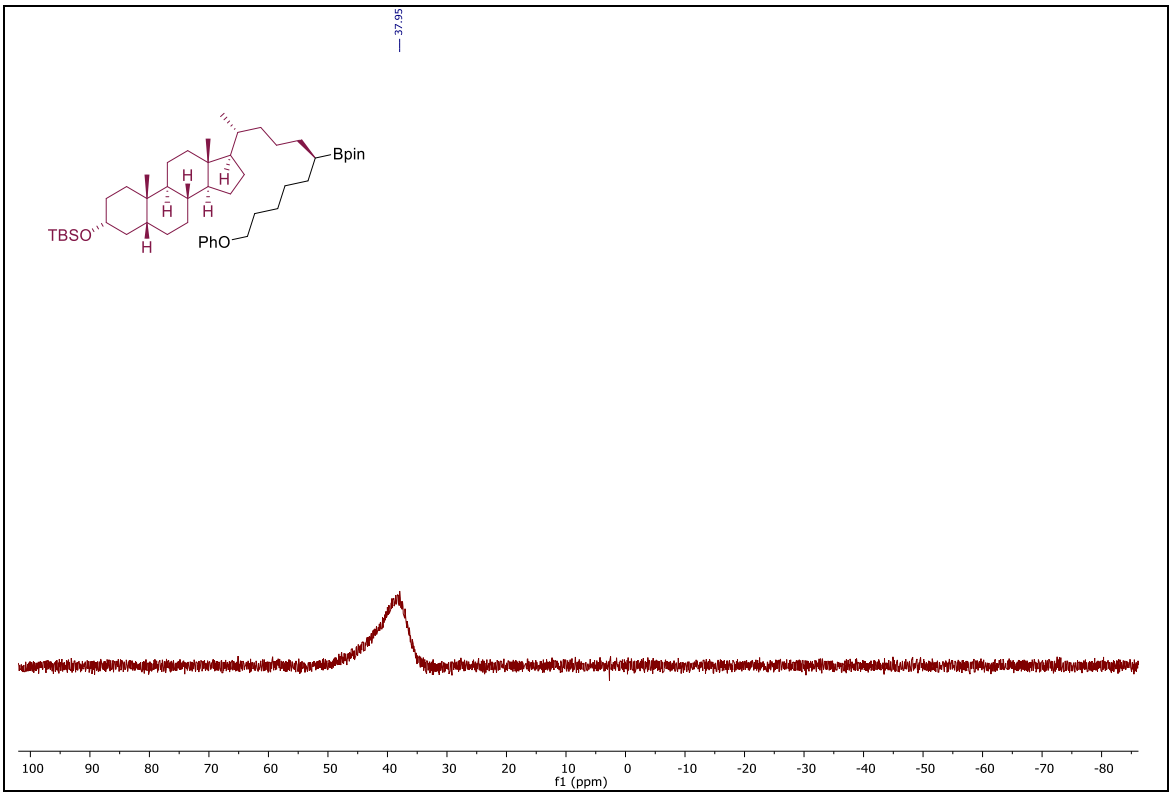



34.07
O
O
O
Ph
Bpin
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

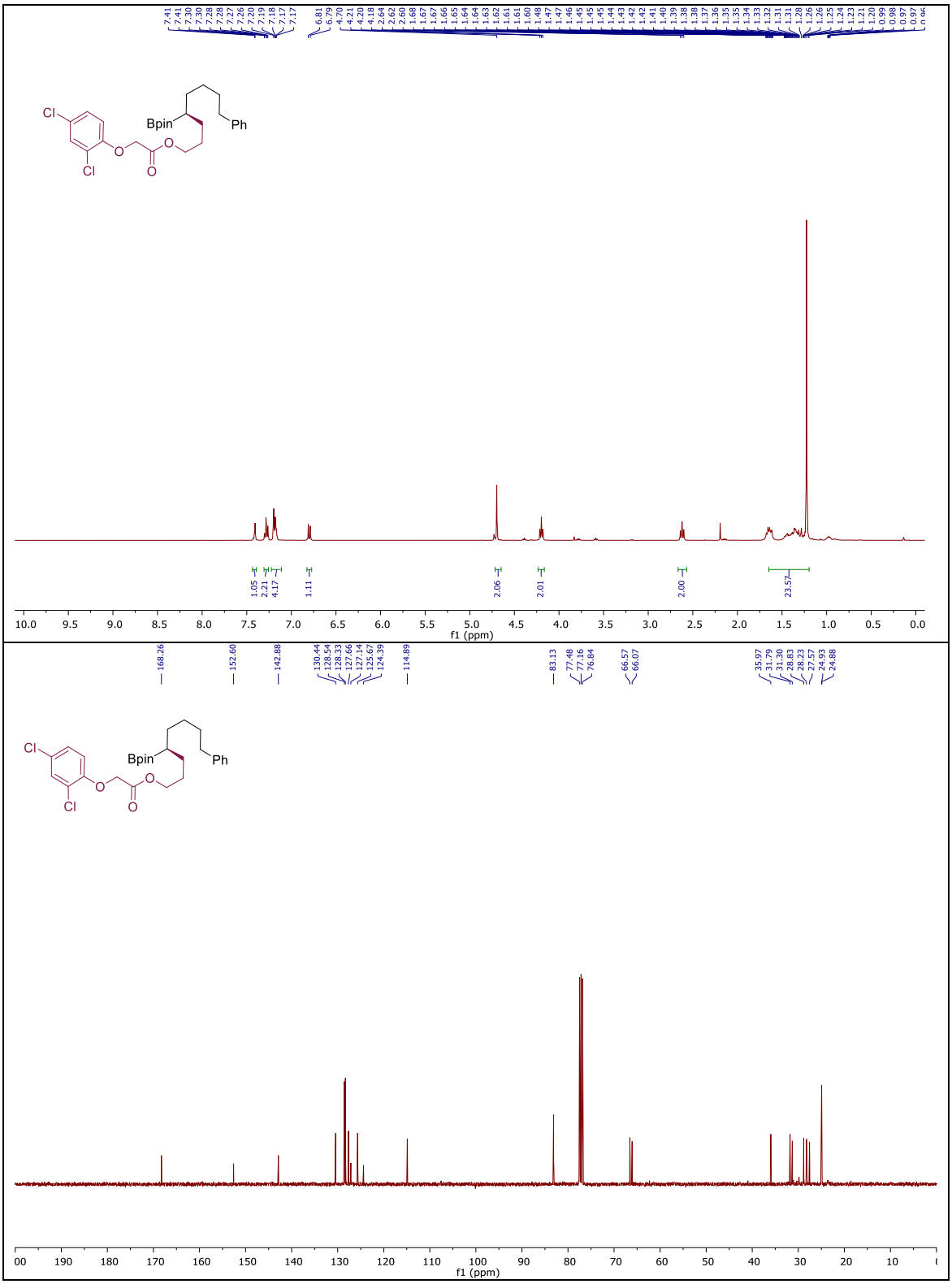
NMR spectra of 6d

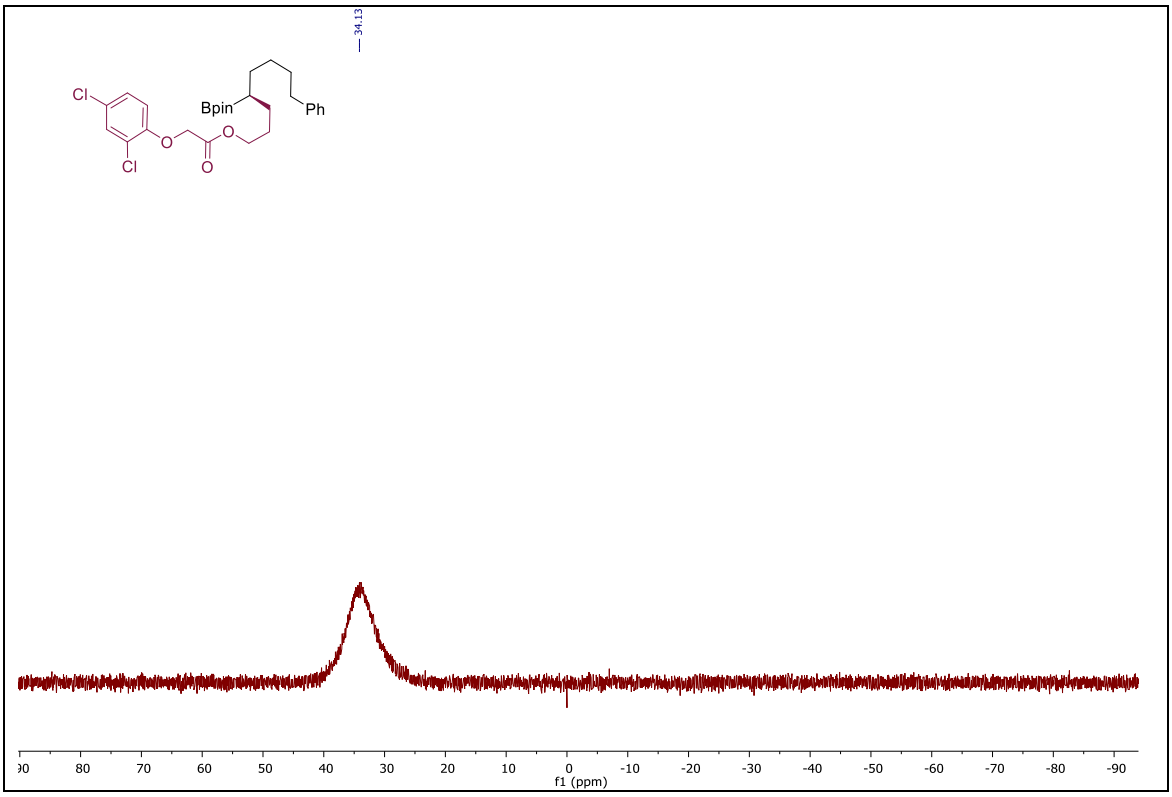




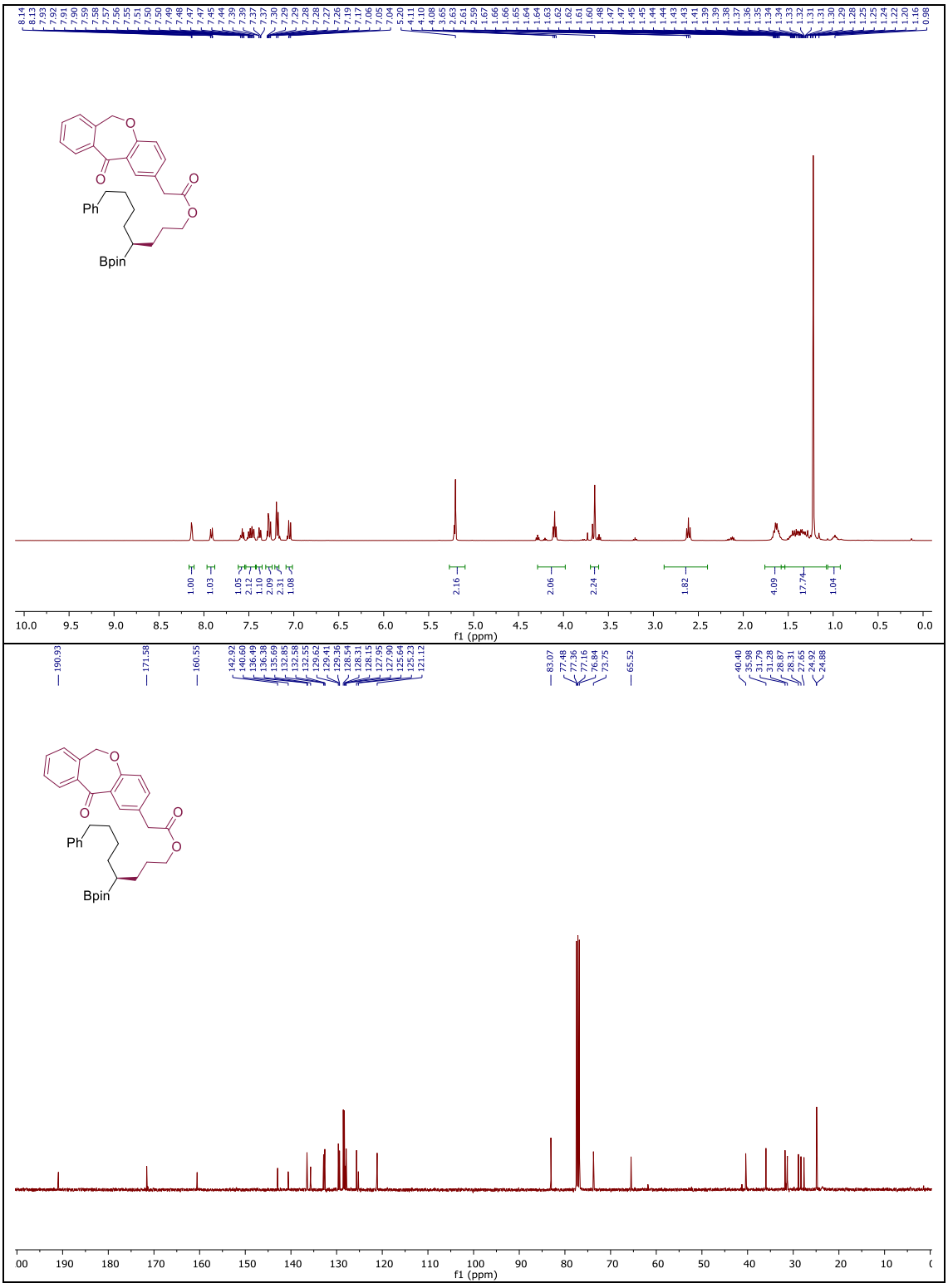

37.95
Bpin
TBSO
PhO
H
H
H
H
H
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

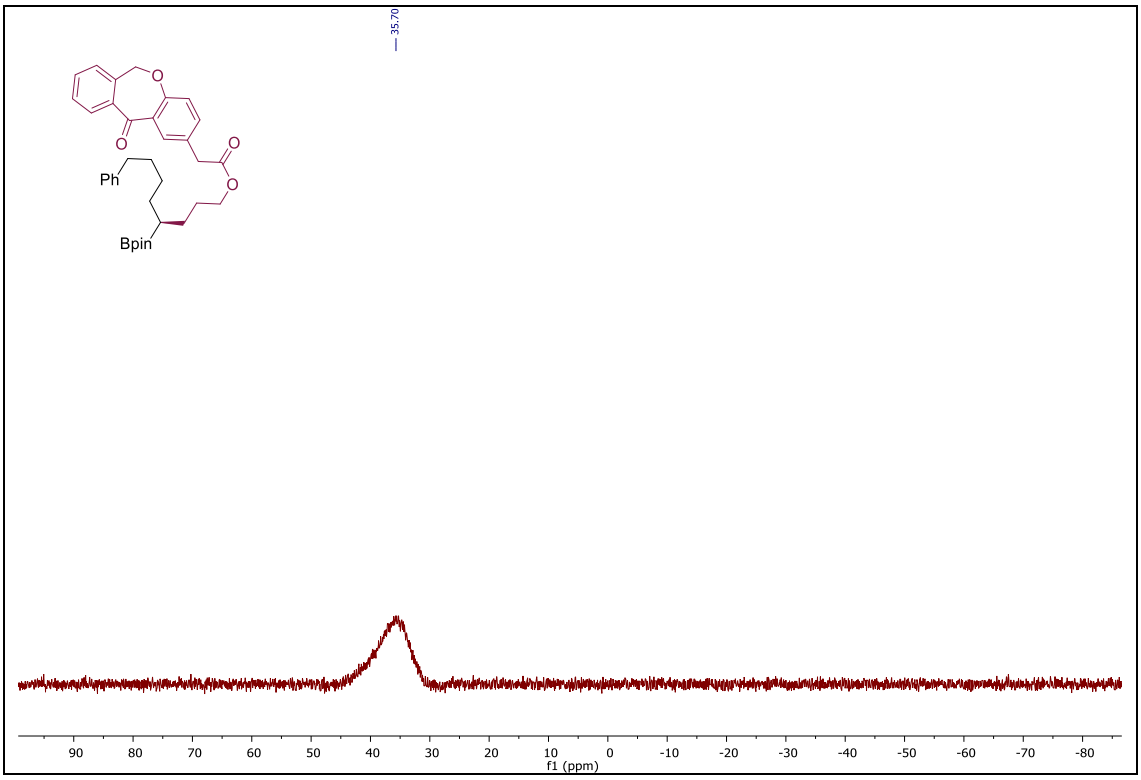
NMR spectra of 6e



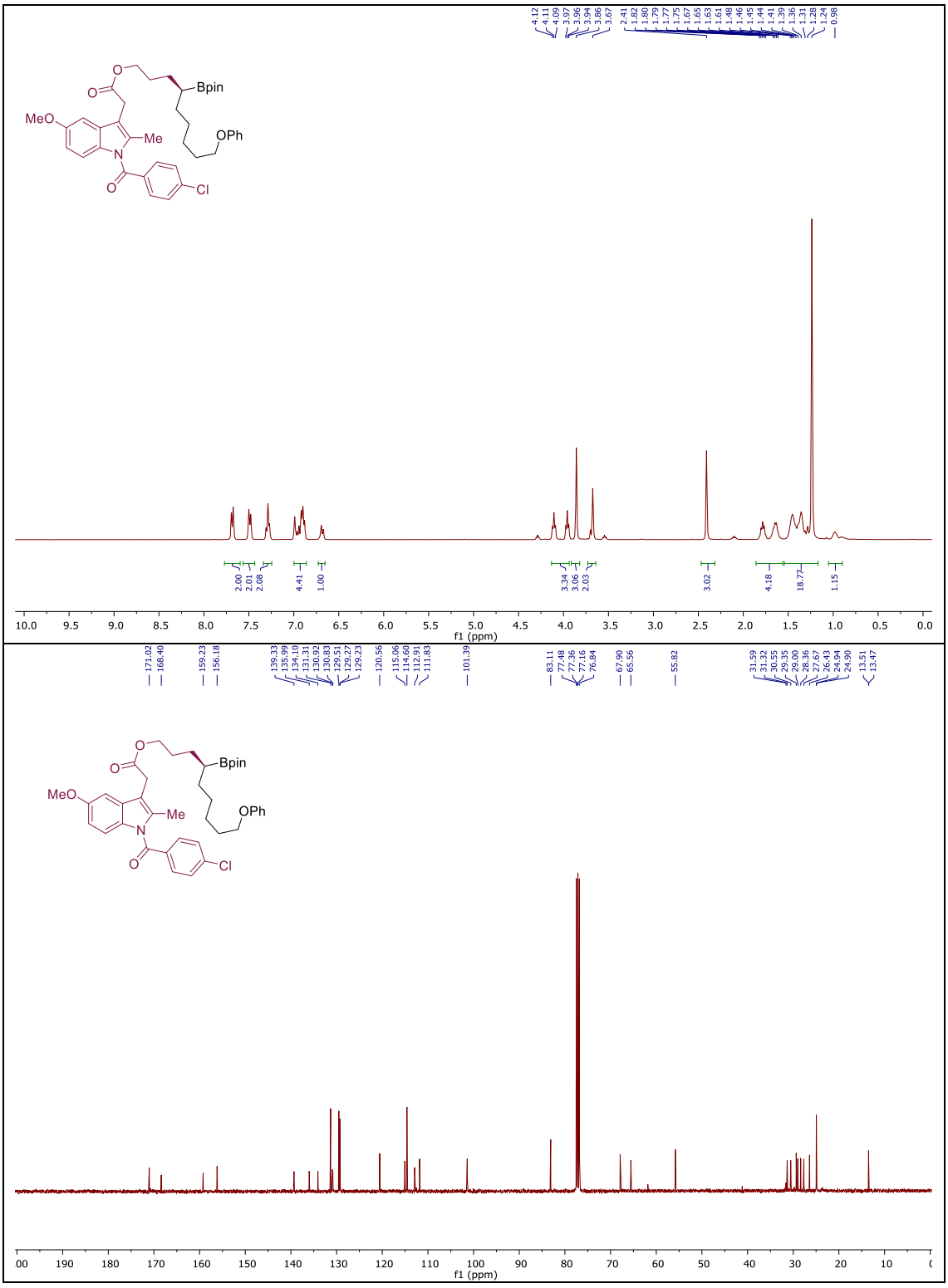

34.13
Cl
Cl
O
Bpin
O
O
Ph
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

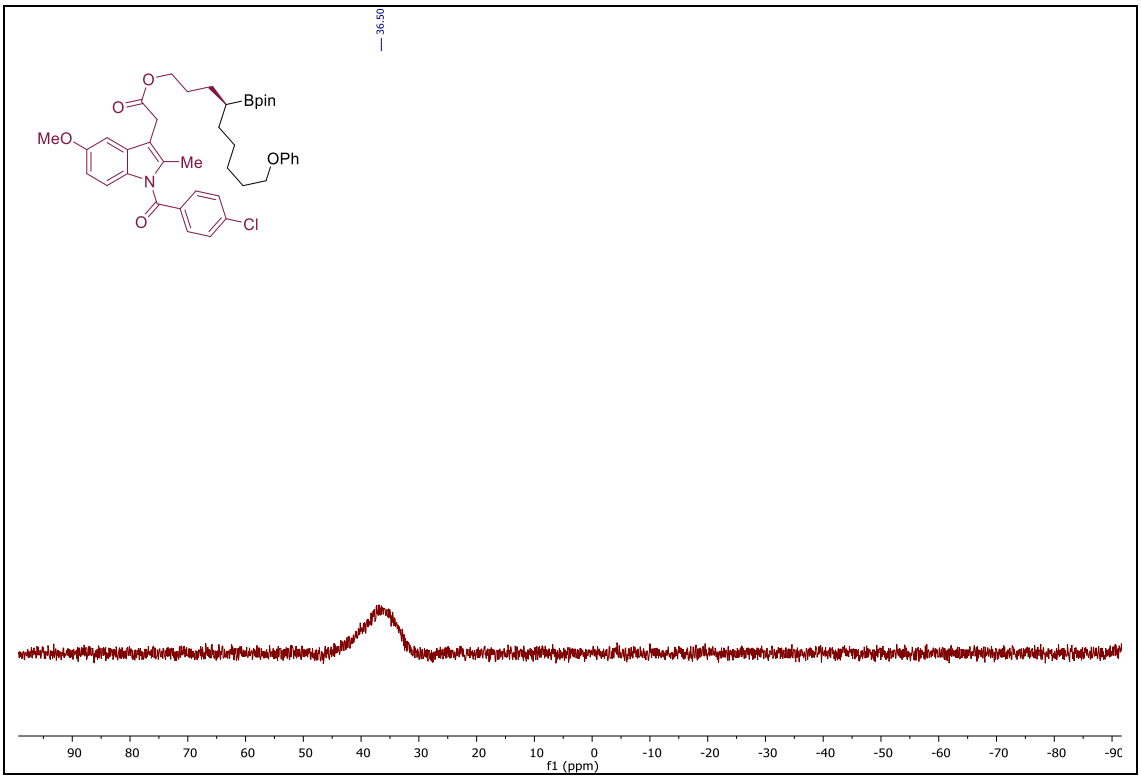
NMR spectra of 6f



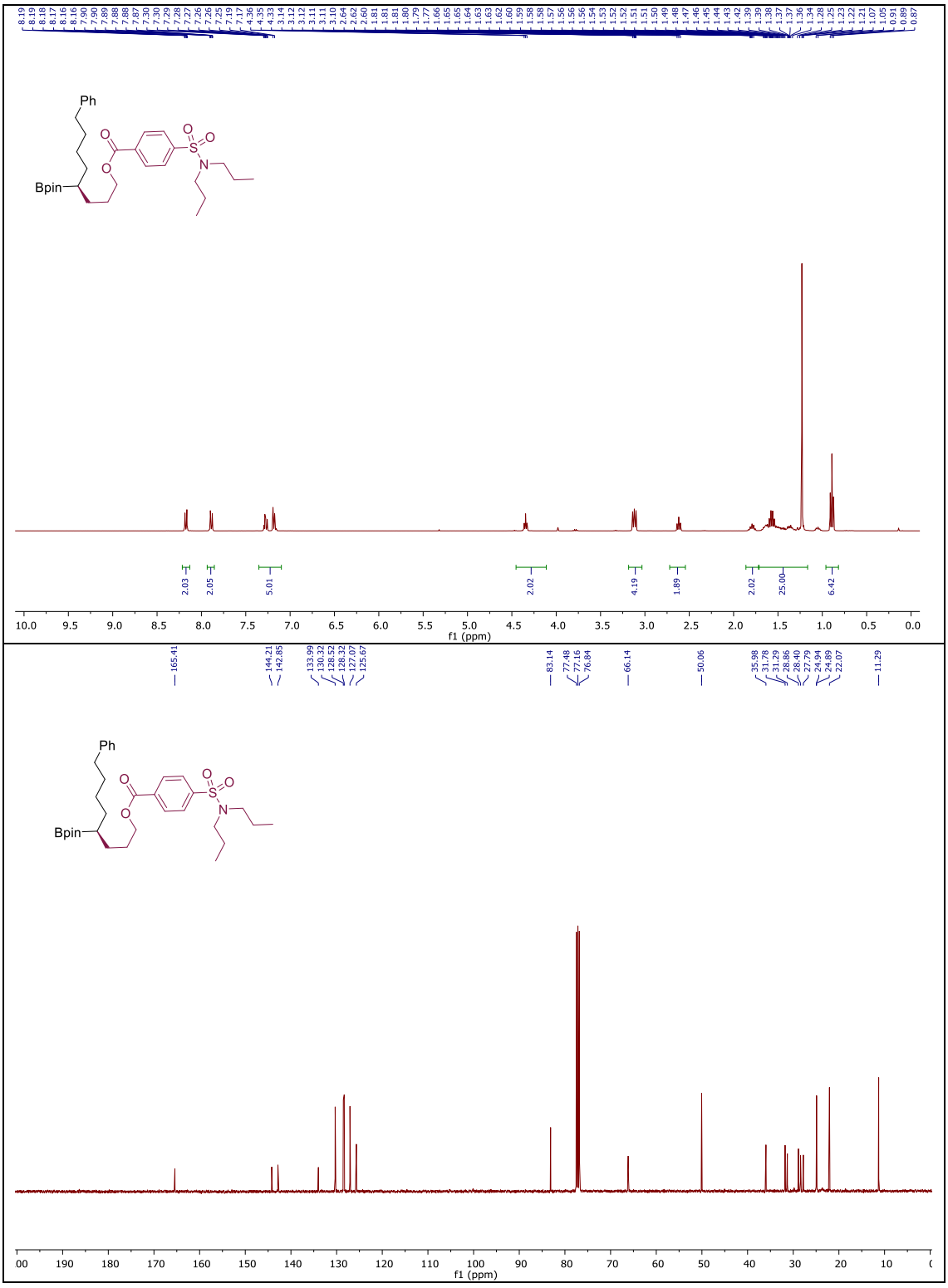

35.70
O
O
O
O
Ph
Bpin
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

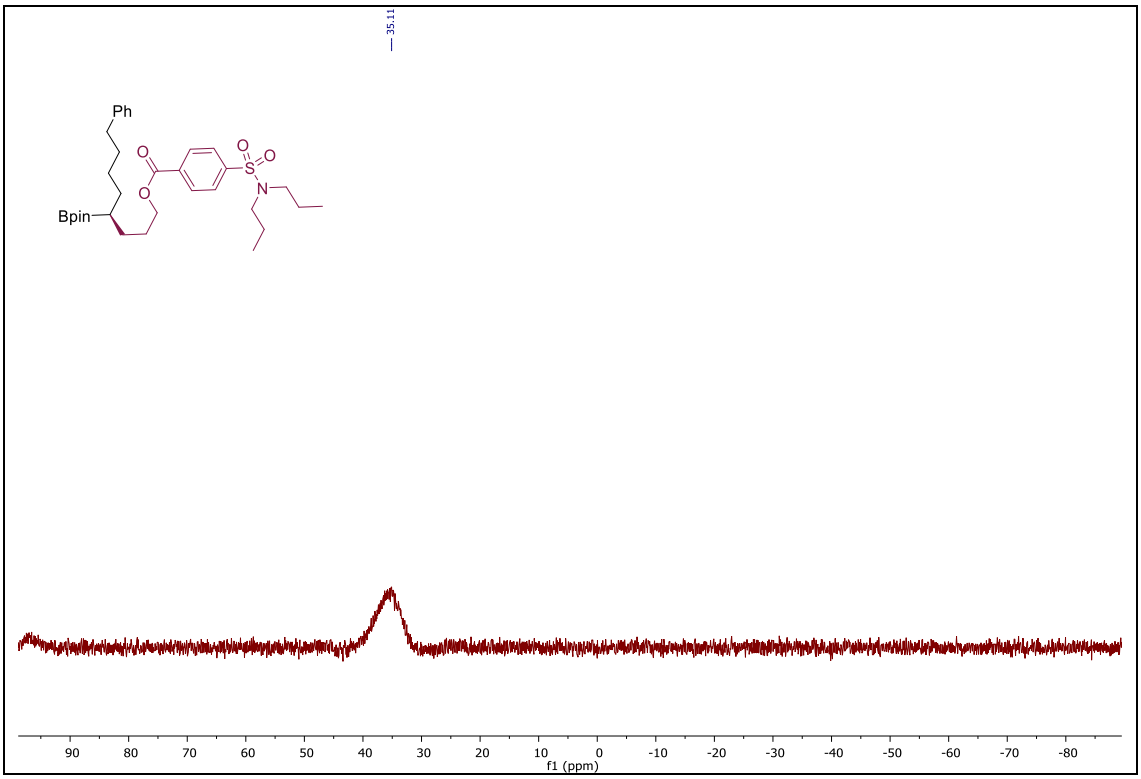
NMR spectra of 6g



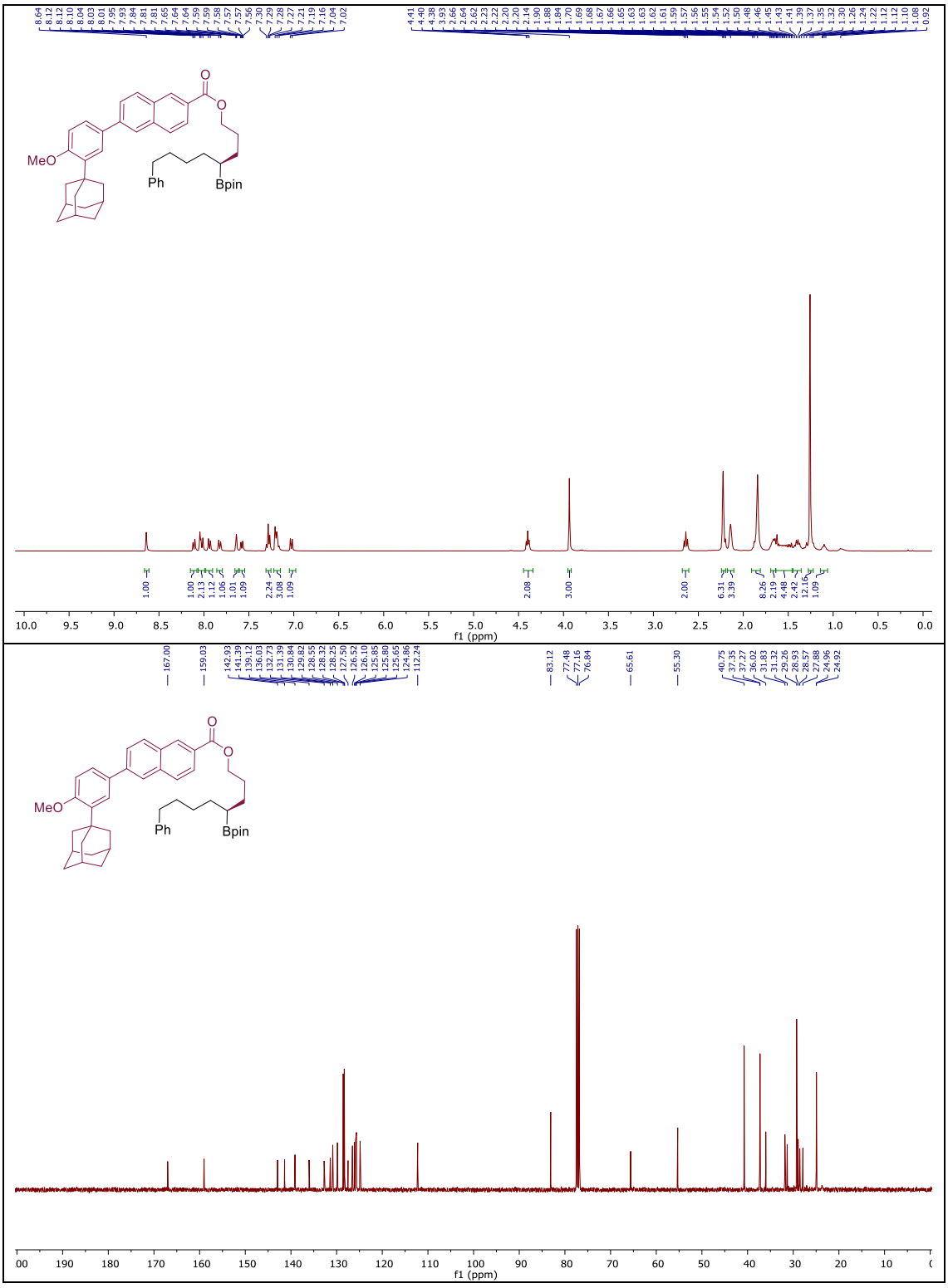

36.50
O
O
Bpin
MeO
Me
OPh
N
O
Cl
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

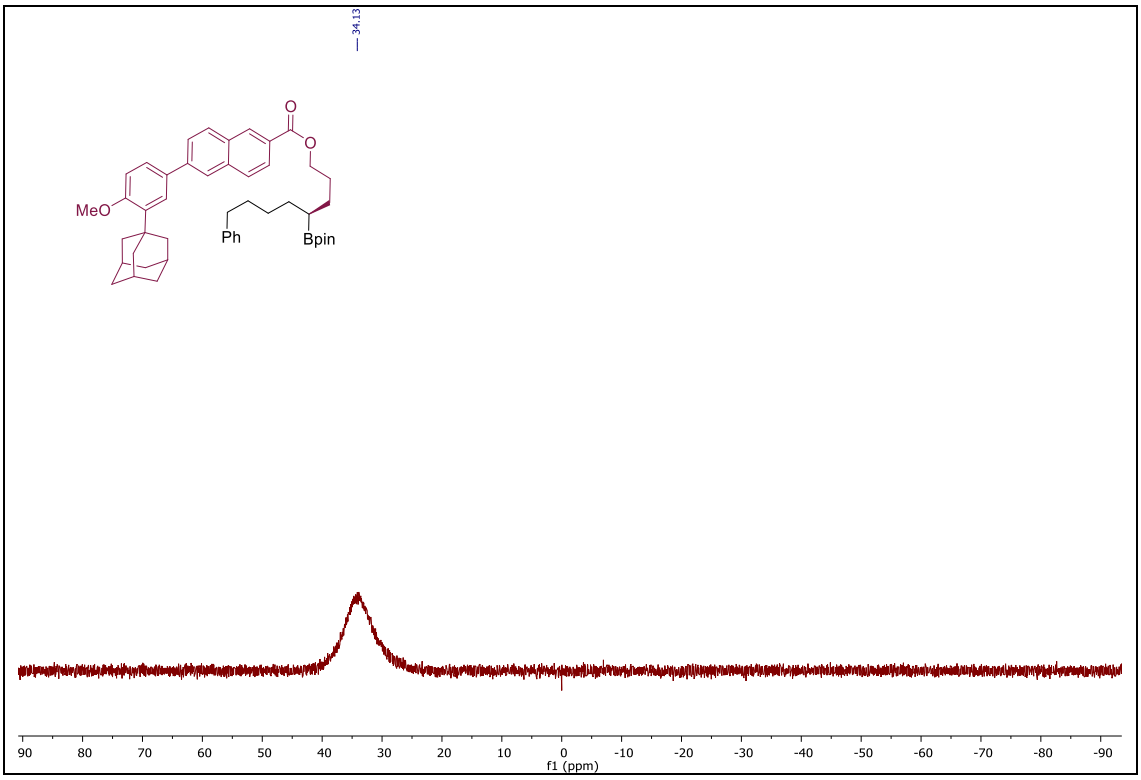
NMR spectra of 6h



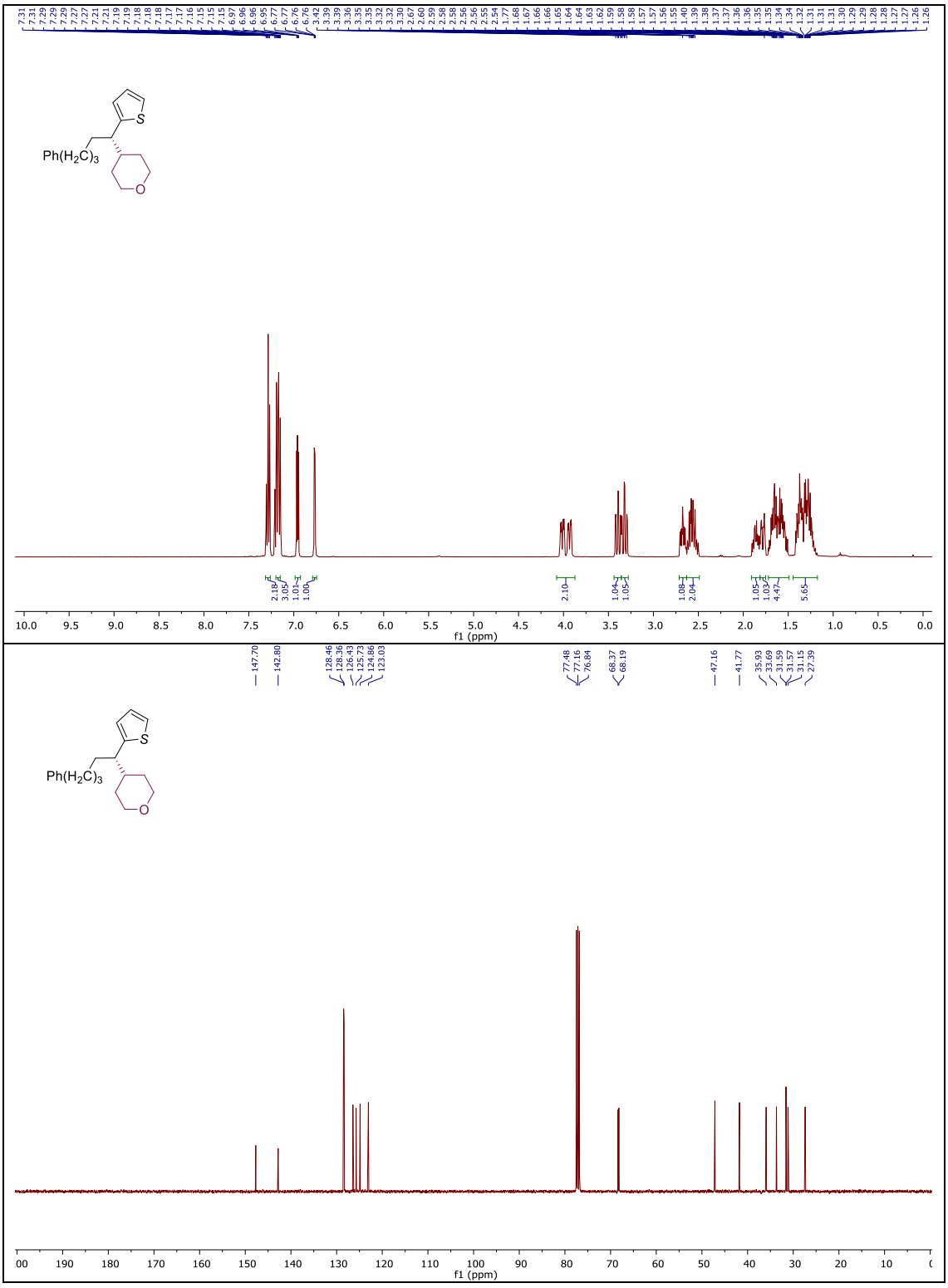

35.11
Ph
O
O
S
O
O
N
Bpin
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
f1 (ppm)

NMR spectra of 6i

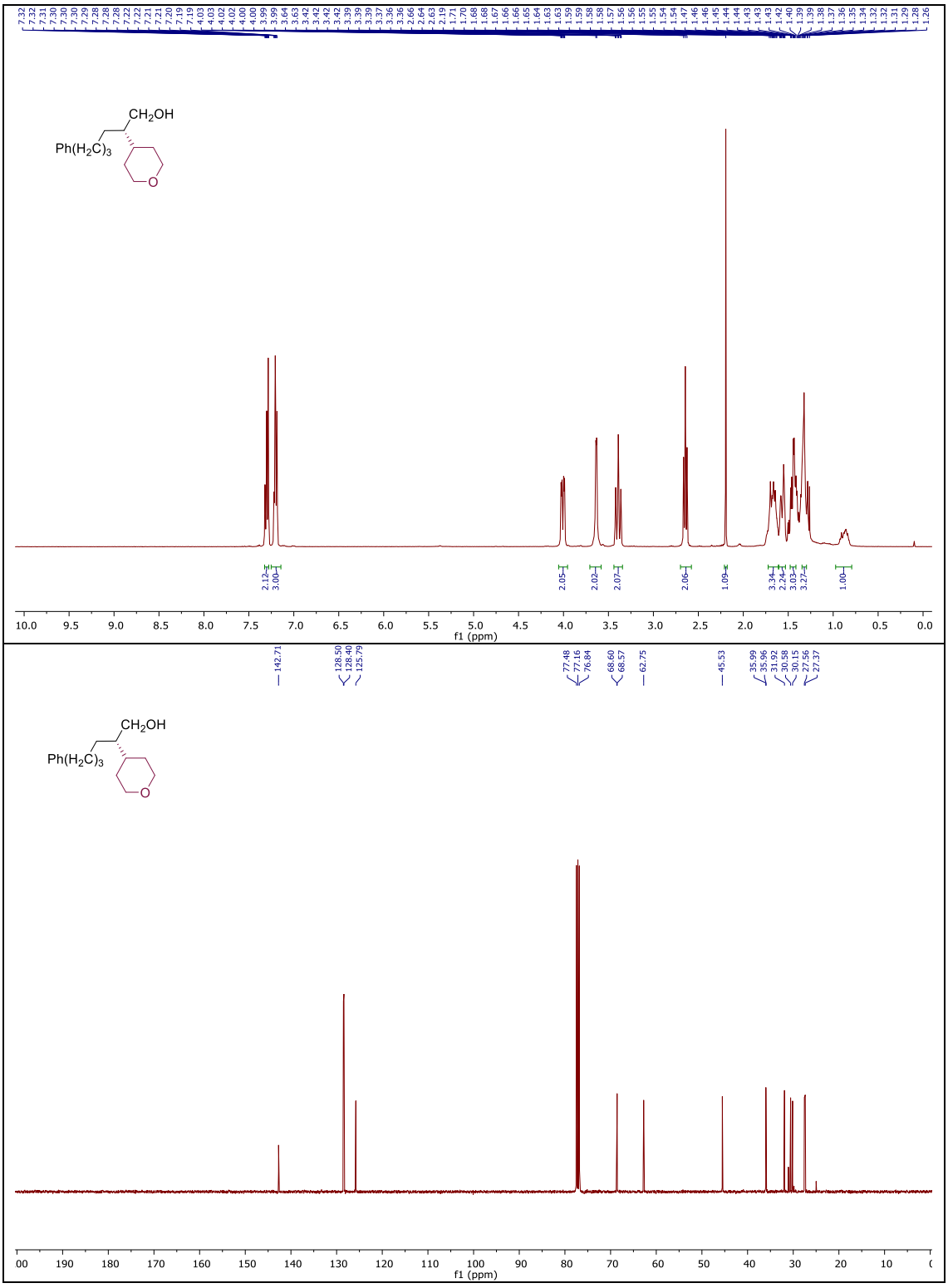



34.13
O
O
MeO
Ph
Bpin
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

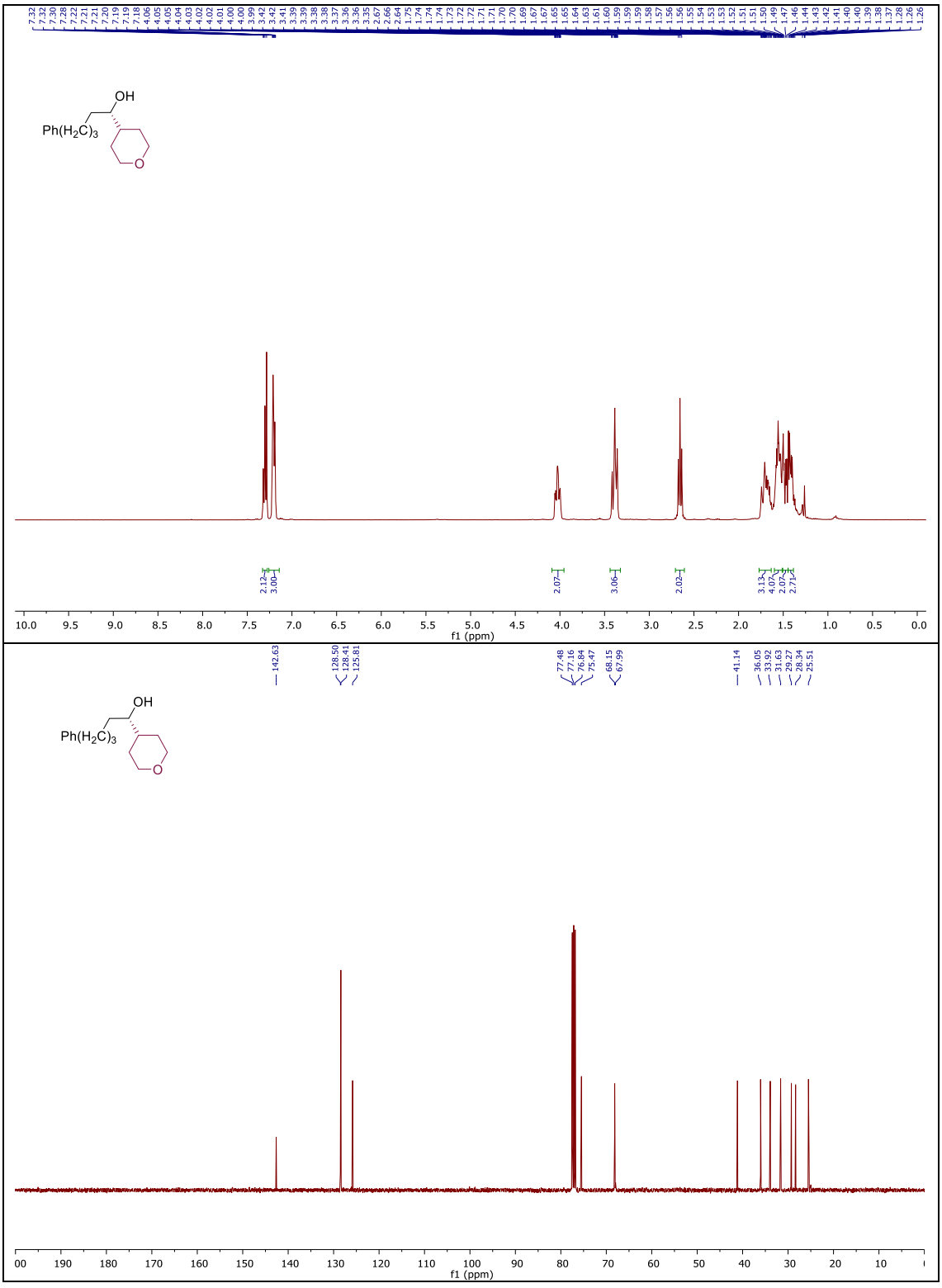
NMR spectra of 7



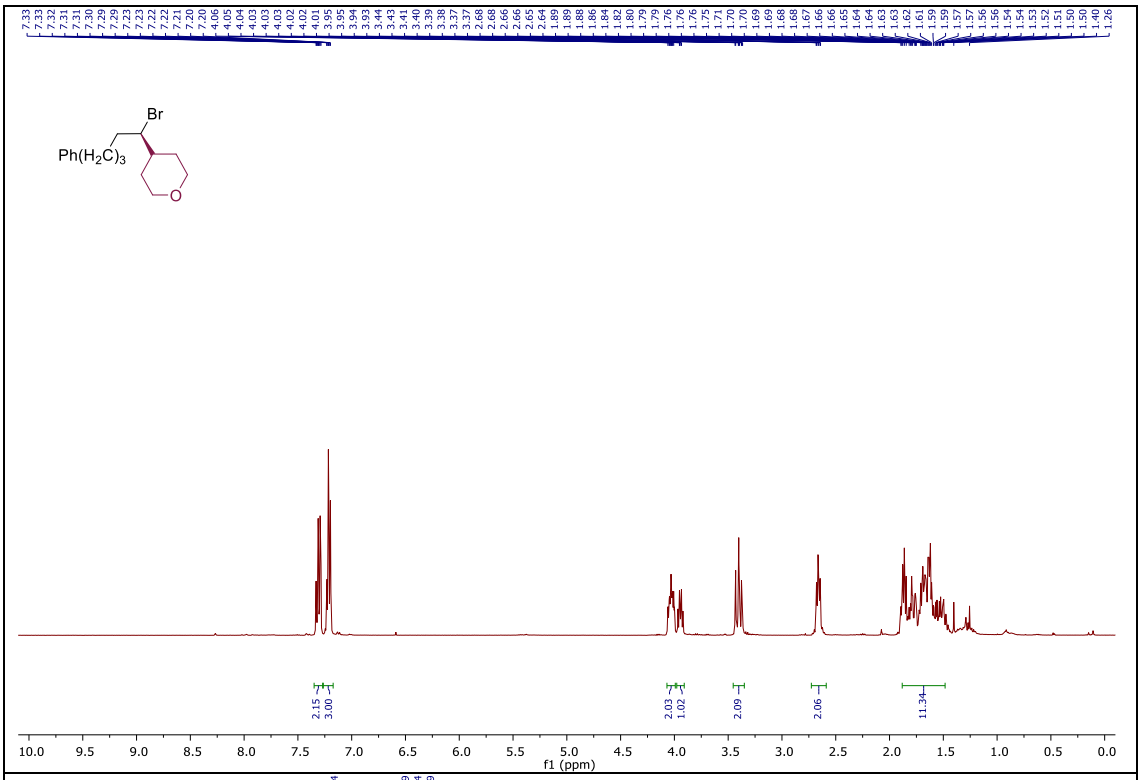
NMR spectra of 8

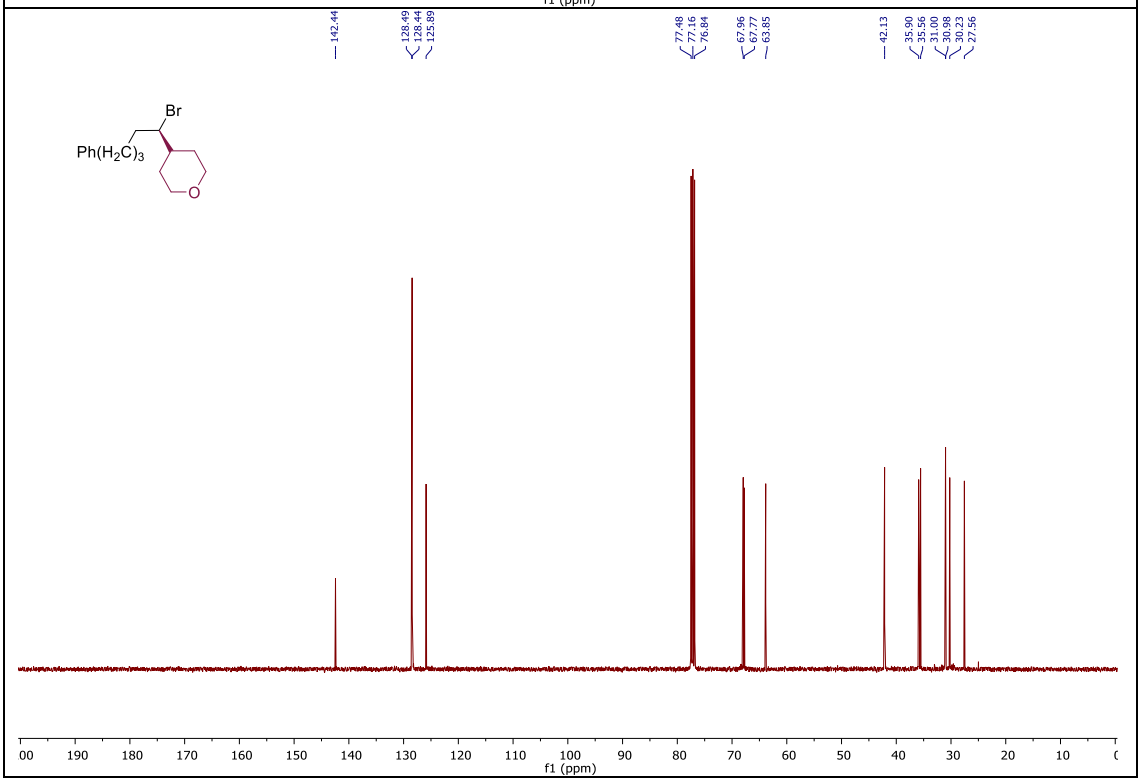


NMR spectra of 9

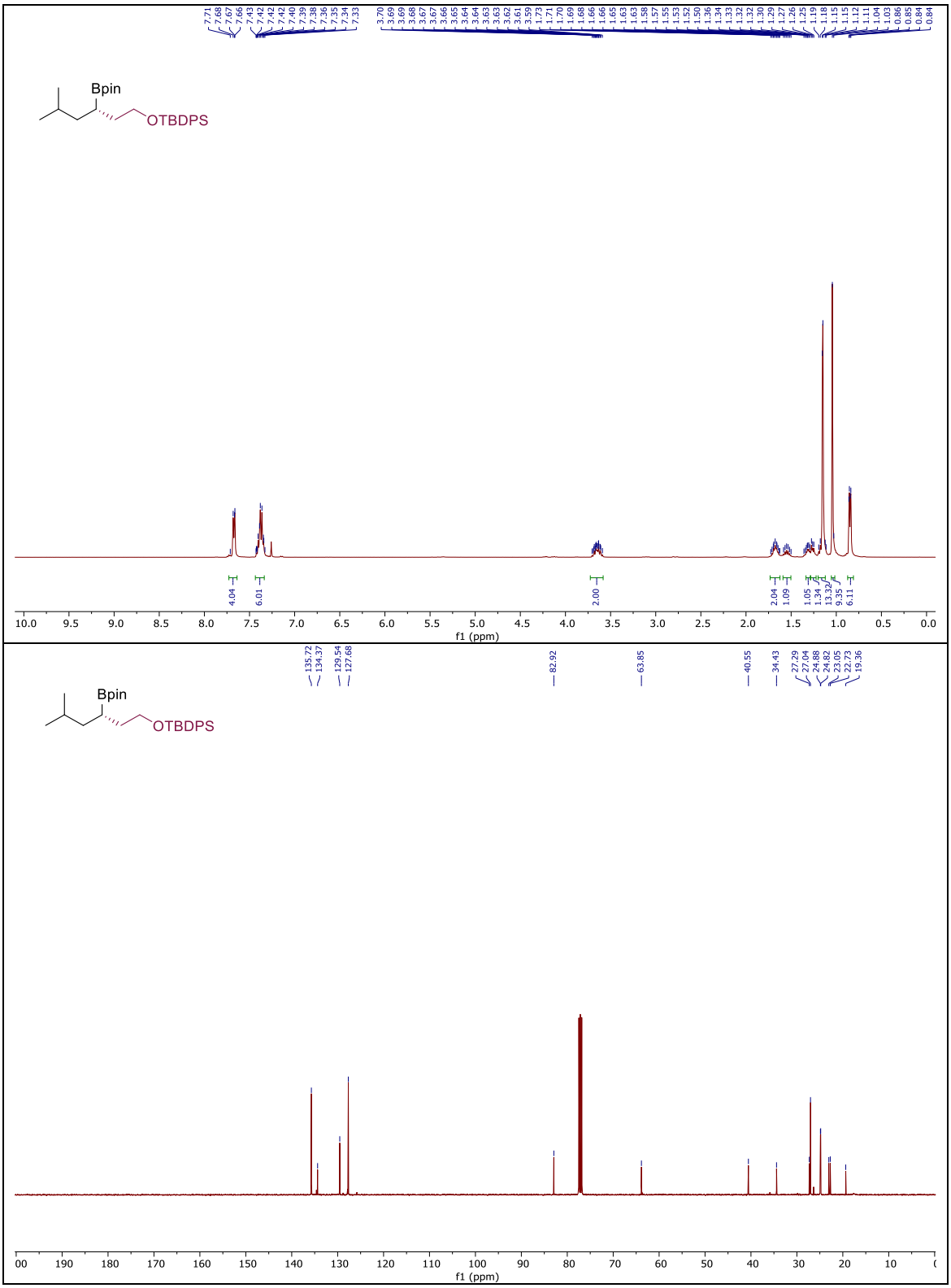


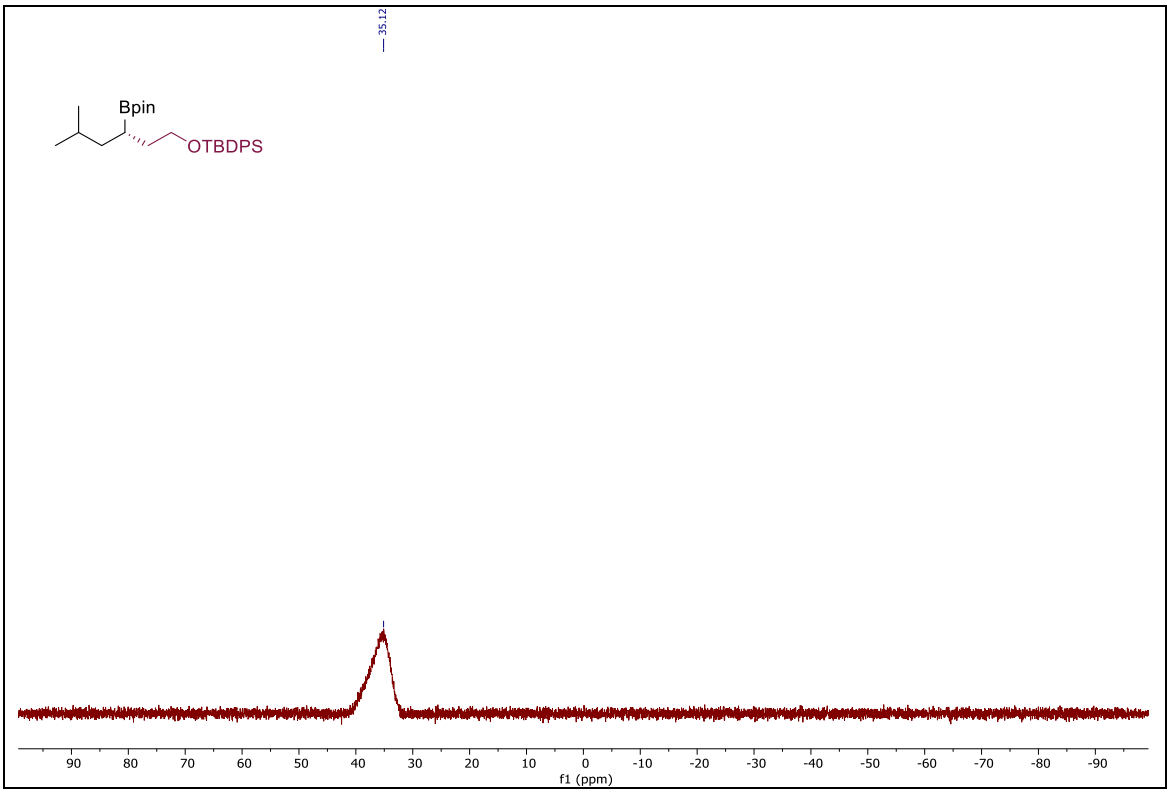
NMR spectra of 10



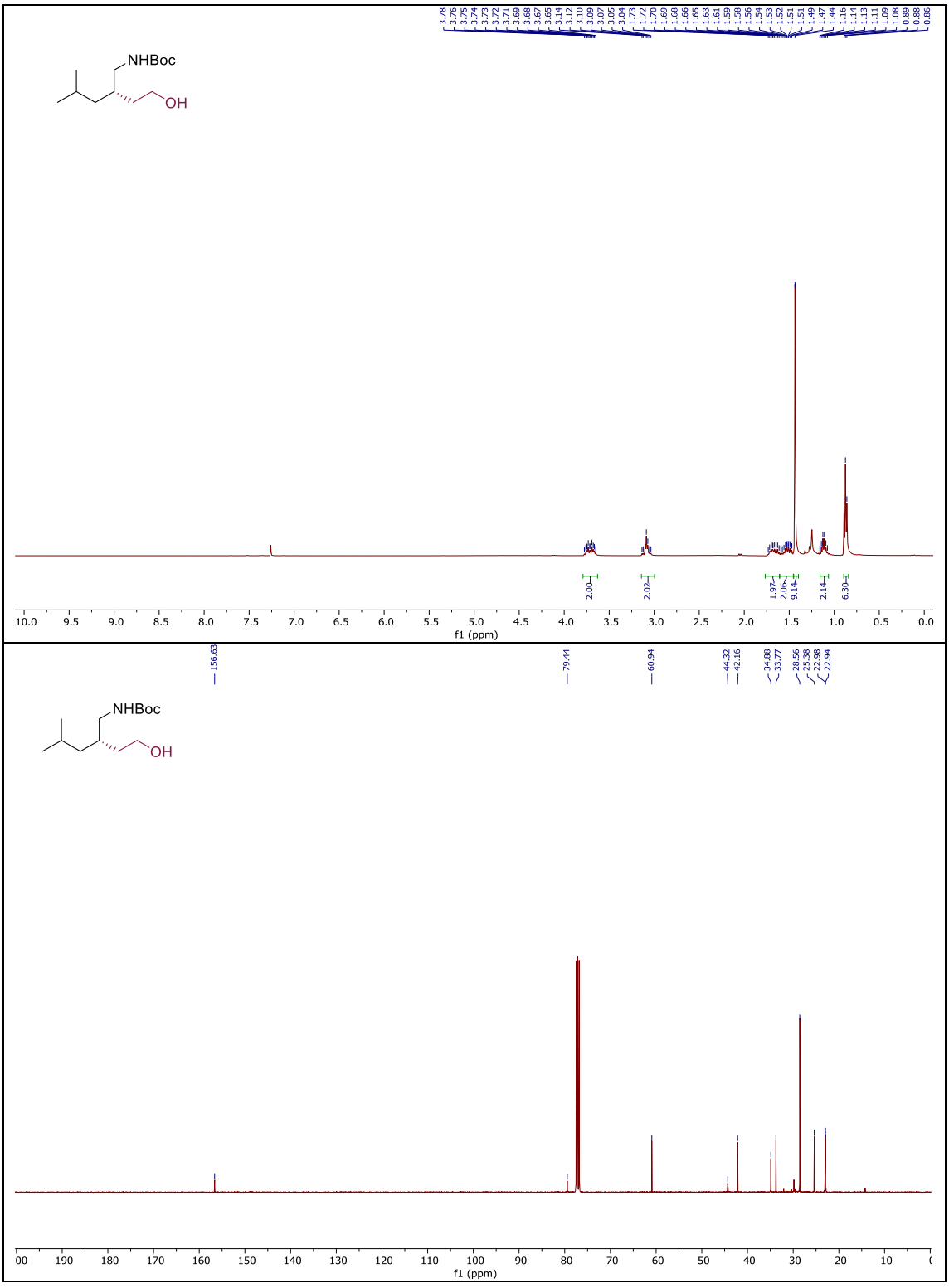


NMR spectra of 11

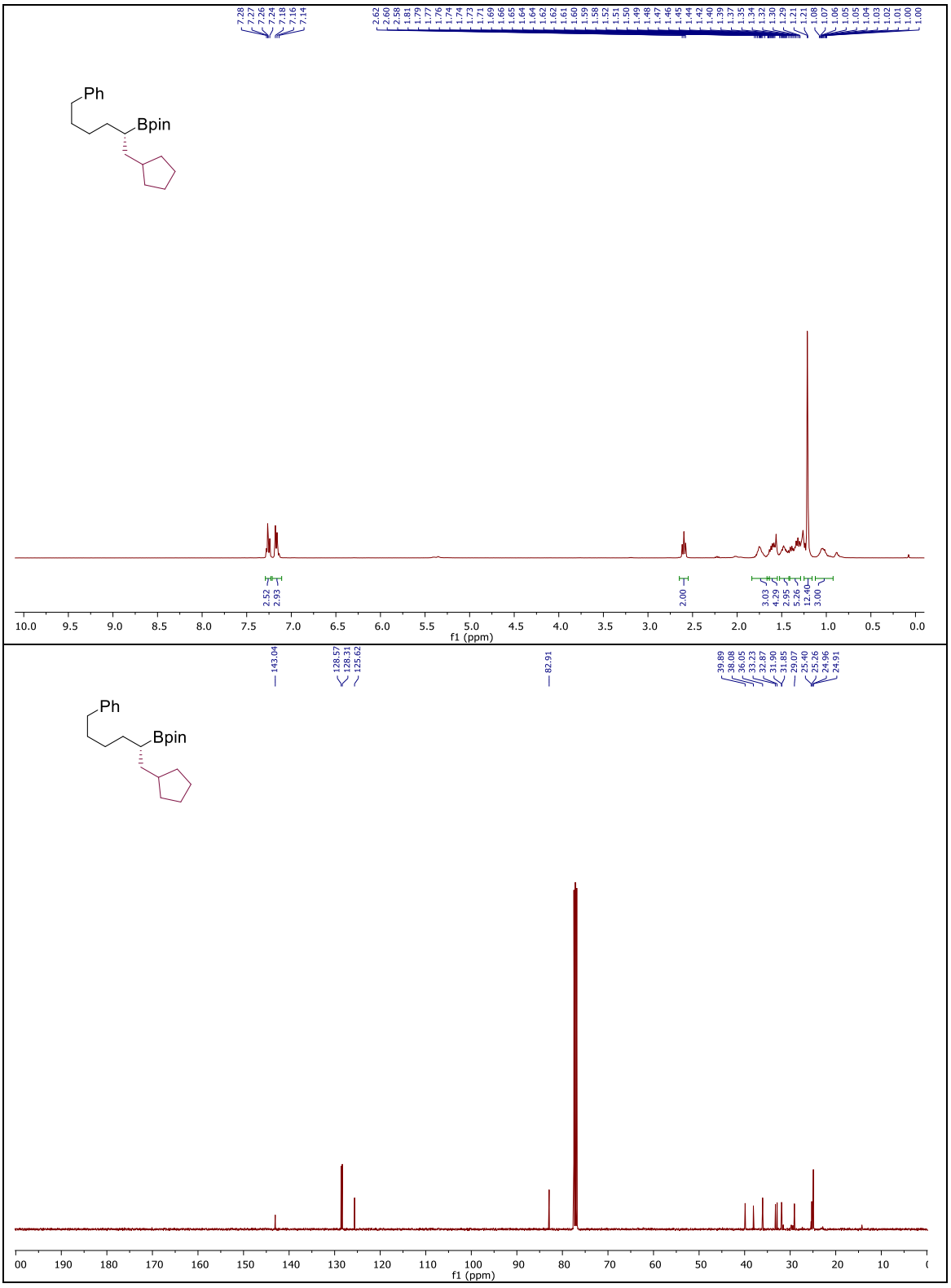


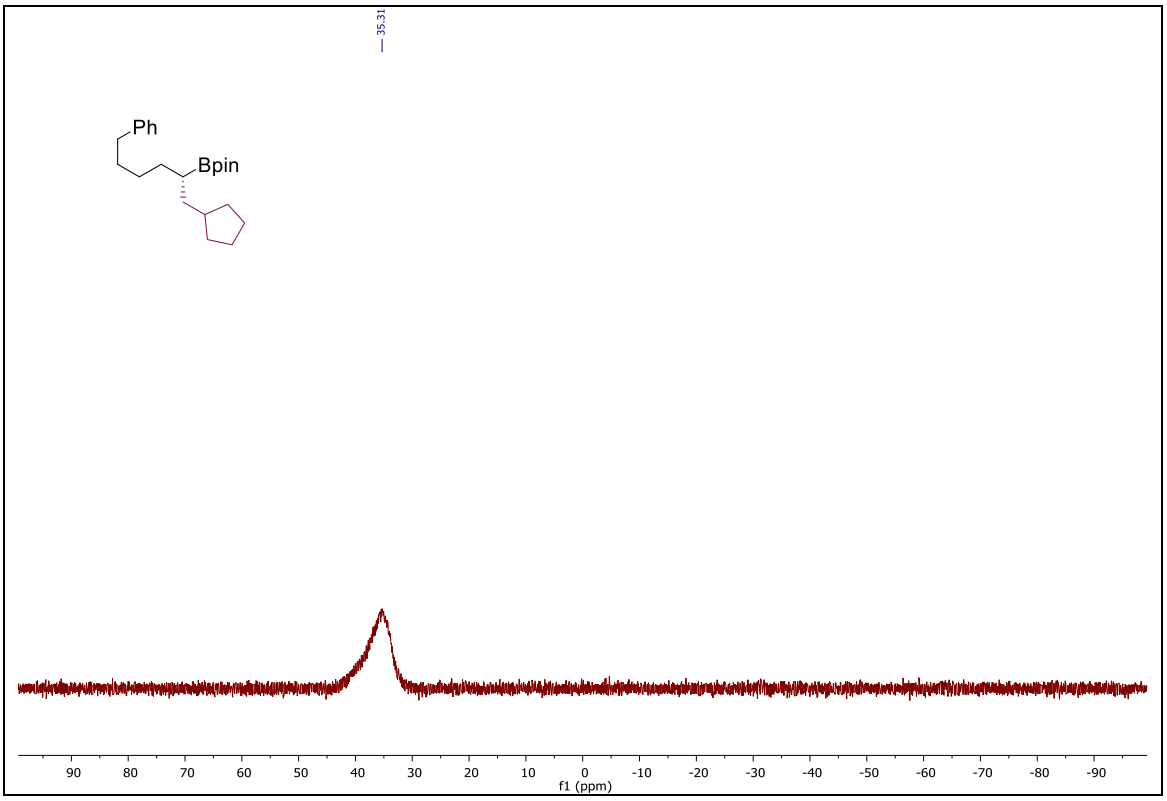

35.12
Bpin
OTBDPS
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 12

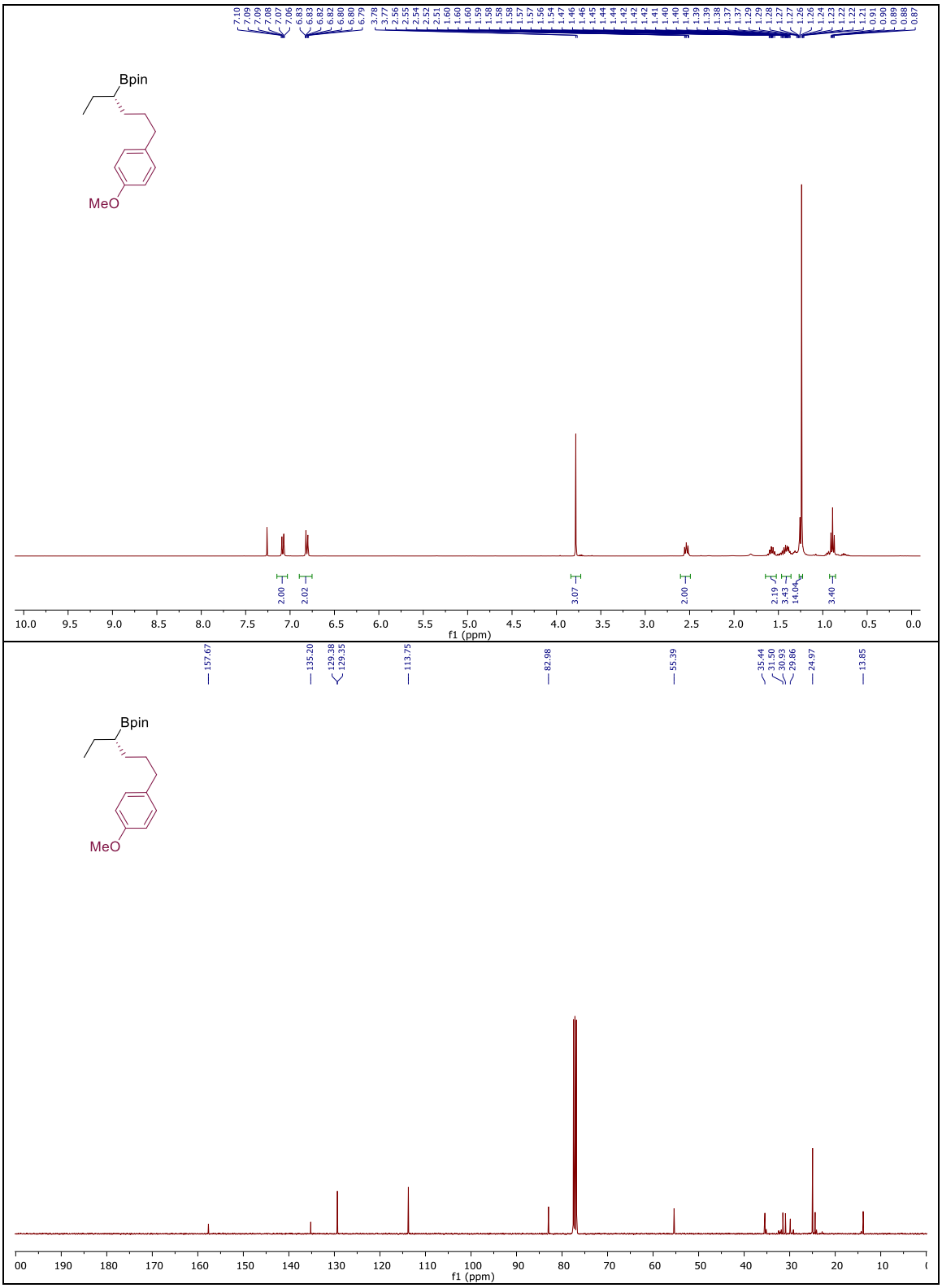


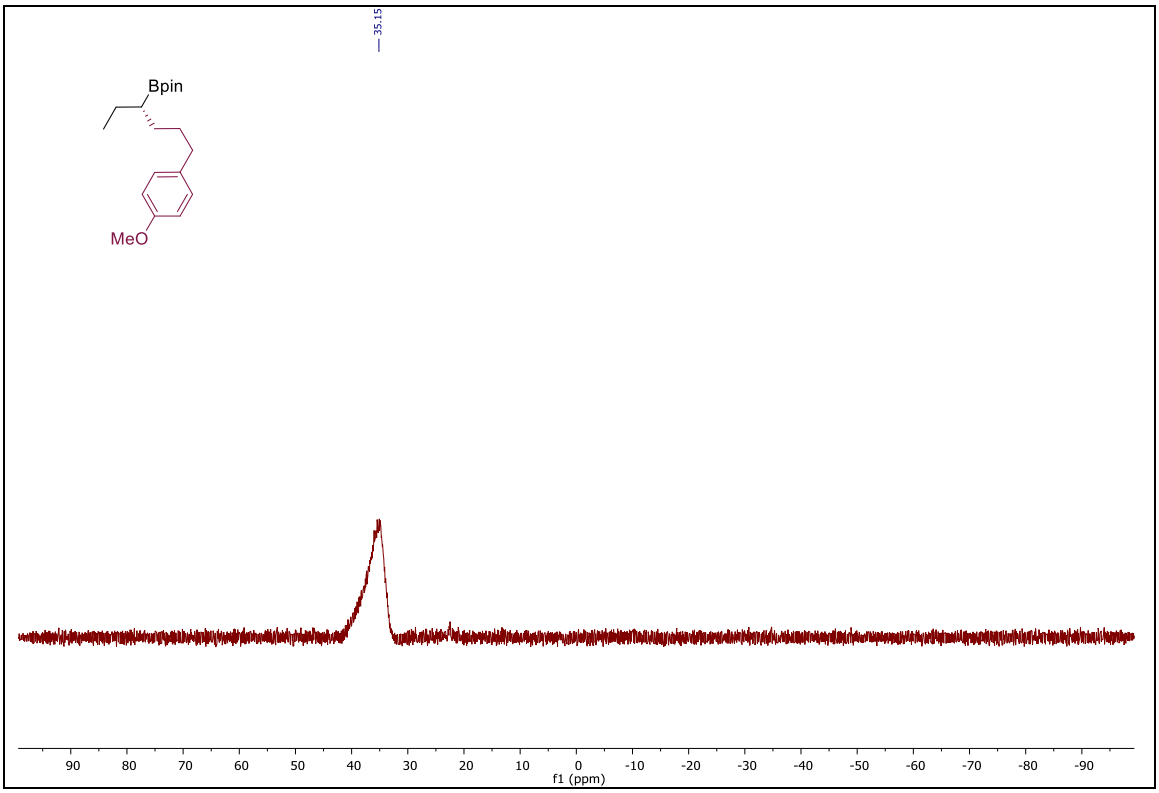
NMR spectra of 13



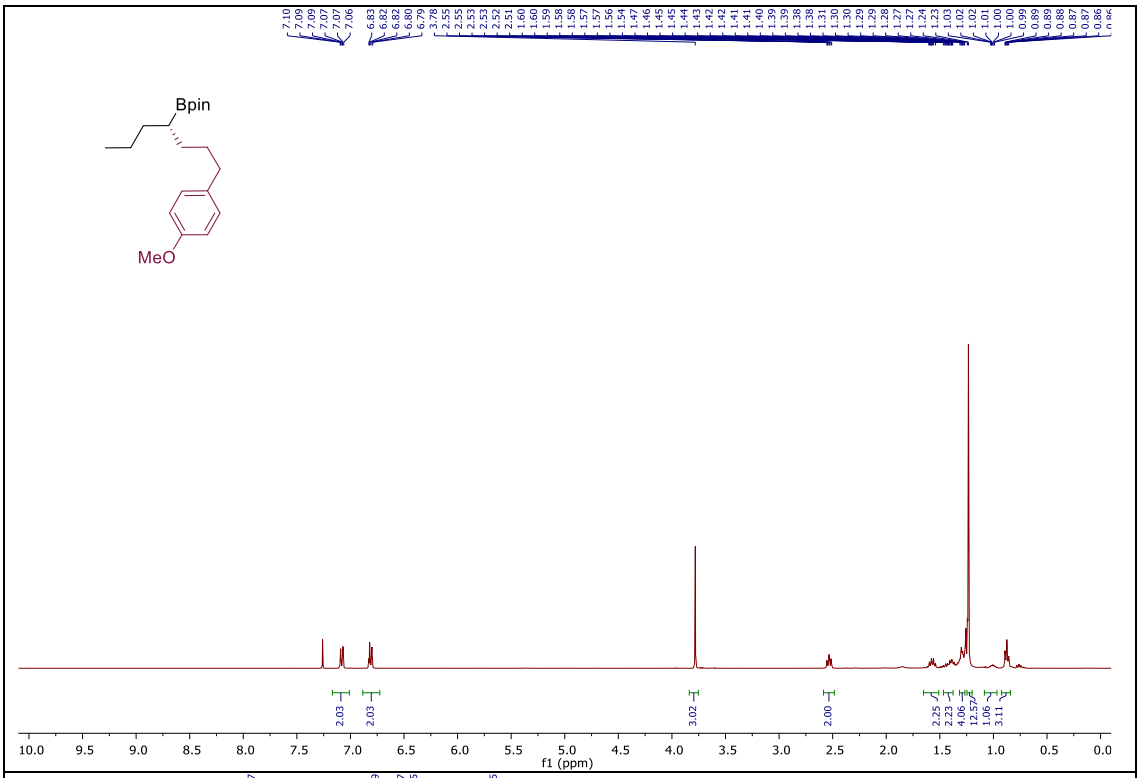

35.31
Ph
Bpin
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

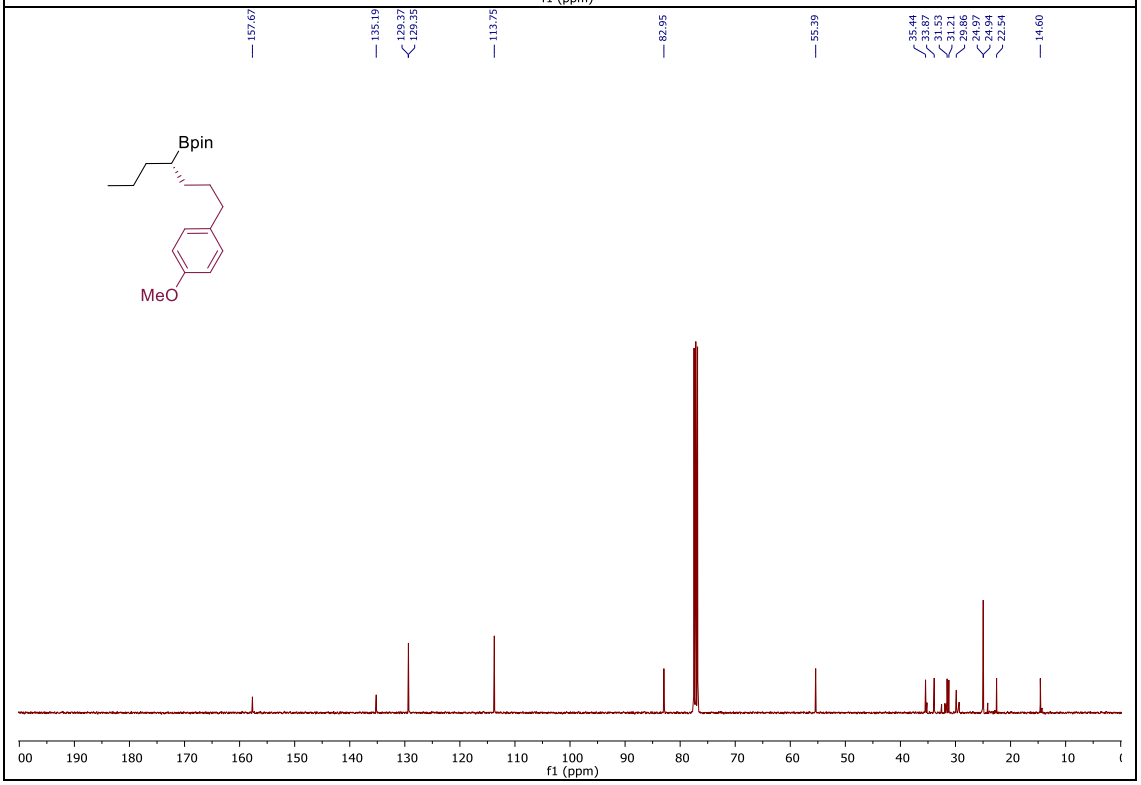
NMR spectra of 3s

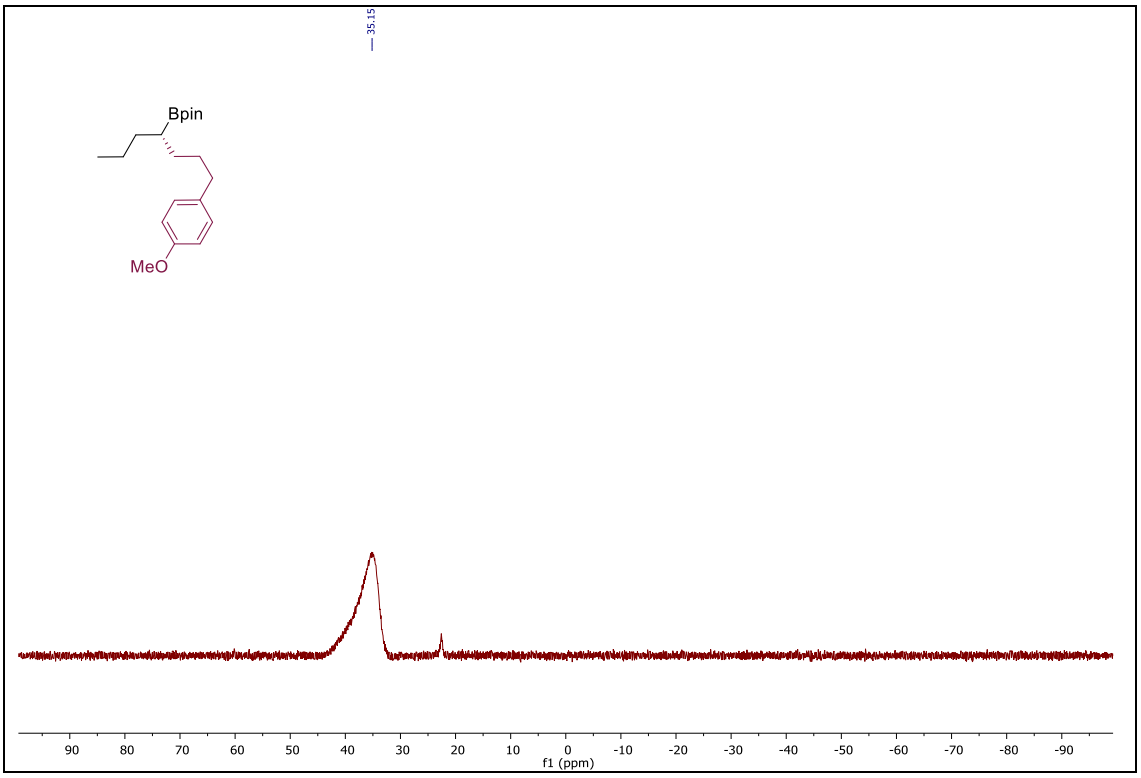



35.15
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

NMR spectra of 3t






35.15
Bpin
MeO
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

17. References

[1] Huang, W., Wan, X. & Shen, Q. Enantioselective Construction of Trifluoromethoxylated Stereogenic Centers by a Nickel-Catalyzed Asymmetric Suzuki–Miyaura Coupling of Secondary Benzyl Bromides. *Angew. Chem. Int. Ed.* **56**,11986–11989 (2017).

[2] Bolm, C., Weickhardt, K., Zehnder, M. & Ranff, T. Synthesis of Optically Active Bis(2-oxazolines): Crystal Structure of a 1,2-Bis(2-oxazolinyl)benzene $ZnCl_2$ Complex. *Chem. Ber.* **124**, 1173–1180 (1991).

[3] Pezzetta, C., Bonifazi, D. & Davidson, R. W. M. Enantioselective Synthesis of N-Benzylic Heterocycles: A Nickel and Photoredox Dual Catalysis Approach. *Org. Lett.* **21**, 8957−8961 (2019).

[4] De Crisci, A. G., Chung, K., Oliver, A. G., Solis-Ibarra, D. & Waymouth, R. M. Chemoselective Oxidation of Polyols with Chiral Palladium Catalysts. *Organometallics* **32**, 2257−2266 (2013).

[5] Wang, H. et al. Palladium-Catalyzed Amide-Directed Enantioselective Hydrocarbofunctionalization of Unactivated Alkenes Using a Chiral Monodentate Oxazoline Ligand. *J. Am. Chem. Soc.* **140**, 3542−3546 (2018).

[6] Woods, B. P., Orlandi, M., Huang, C.-Y., Sigman, M. S. & Doyle, A. G. Nickel-Catalyzed Enantioselective Reductive Cross-Coupling of Styrenyl Aziridines. *J. Am. Chem. Soc.* **139**, 5688-5691 (2017).

[7] Cheng, X., Lu, H. & Lu, Z. Enantioselective benzylic C–H arylation via photoredox and nickel dual catalysis. *Nat Commun* **10,** 3549 (2019).

[8] Bera, S. & Hu, X. Nickel-Catalyzed Regioselective Hydroalkylation and Hydroarylation of Alkenyl Boronic Esters. *Angew. Chem. Int. Ed.* **58**, 13854-13859 (2019).

[9] H. Shimizu, T. Igarashi, T. Miura, M. Murakami, Rhodium-catalyzed reaction of 1-alkenylboronates with aldehydes leading to allylation products. *Angew. Chem., Int. Ed.* **50**, 11465-11469 (2011).

[10] Yoo, K. S., Yoon, C. H. & Jung, K. W. Oxidative Palladium(II) Catalysis: A Highly Efficient and Chemoselective Cross-Coupling Method for Carbon–Carbon Bond Formation under Base-Free and Nitrogenous-Ligand Conditions. *J. Am. Chem. Soc.* **128**, 16384–16393 (2006).

[11] Kontokosta, D., Mueller, D. S., Wang, H.-Y. & Anderson, L. L. Preparation of α-Imino Aldehydes by [1,3]-Rearrangements of O-Alkenyl Oximes. *Org. Lett.* **15**, 4830-4833 (2013).

[12] Sušnik, P. & Hilt, G. Homoallylpinacolboronic Ester as Alkene Component in Cobalt-Catalyzed Alder Ene Reactions. *Organometallics* **33**, 5907-5910 (2014).

[13] Laulhé, S., Blackburn, J. M. & Roizen, J. L. Exhaustive Suzuki–Miyaura reactions of polyhalogenated heteroarenes with alkyl boronic pinacol esters. *Chem. Commun.* **53**, 7270-7273 (2017).

[14] Franco, T. D., Epenoy, A. & Hu, X. Synthesis of *E*-Alkyl Alkenes from Terminal Alkynes via Ni-Catalyzed Cross-Coupling of Alkyl Halides with B-Alkenyl-9-borabicyclo[3.3.1]nonanes. *Org. Lett.* **17**, 4910-4913 (2015).

[15] Rezazadeh, S., Devannah, V. & Watson, D. A. Nickel-Catalyzed C-Alkylation of Nitroalkanes with Unactivated Alkyl Iodides. *J. Am. Chem. Soc.* **139**, 8110-8113 (2017).

[16] Chen, Y., Ma, G. & Gong, H. Copper-Catalyzed Reductive Trifluoromethylation of Alkyl Iodides with Togni's Reagent. *Org. Lett.* **20**, 4677-4680 (2018).

[17] Zhou, J. & Fu, G. C. Cross-Couplings of Unactivated Secondary Alkyl Halides: Room-Temperature Nickel-Catalyzed Negishi Reactions of Alkyl Bromides and Iodides. *J. Am. Chem. Soc.* **125**, 14726-14727 (2003).

[18] Andersen, C., Ferey, V., Daumas, M., Bernardelli, P., Guérinot, A. & Cossy, J. Introduction of Cyclopropyl and Cyclobutyl Ring on Alkyl Iodides through Cobalt-Catalyzed Cross-Coupling. *Org. Lett.* **21**, 2285-2289 (2019).

[19] Wotal, A. C. & Weix, D. J. Synthesis of Functionalized Dialkyl Ketones from Carboxylic Acid Derivatives and Alkyl Halides. *Org. Lett.* **14**, 1476-1479 (2012).

[20] Hea, C. & Gaunt, M. J. Ligand-assisted palladium-catalyzed C–H alkenylation of aliphatic amines for the synthesis of functionalized pyrrolidines. *Chem. Sci.* **8**, 3586-3592 (2017).

[21] Zhou, F., Zhu, J., Zhang, Y. & Zhu, S. NiH-Catalyzed Reductive Relay Hydroalkylation: A Strategy for the Remote C(sp^3)-H Alkylation of Alkenes. *Angew. Chem. Int. Ed.* **57**, 4058-4062 (2018).

[22] Vechorkin, O. & Hu, X. Nickel-catalyzed cross-coupling of non-activated and functionalized alkyl halides with alkyl Grignard reagents. *Angew. Chem. Int. Ed.* **48**, 2937-40 (2009).

[23] Ren, P., Vechorkin, O., von Allmen, K., Scopelliti, R. & Hu, X. A Structure–Activity Study of Ni-Catalyzed Alkyl–Alkyl Kumada Coupling. Improved Catalysts for Coupling of Secondary Alkyl Halides. *J. Am. Chem. Soc.* **133**, 7084-7095 (2011).

[24] Deng, W., Ye, C., Li, Y., Li, D. & Bao, H. Iron-Catalyzed Oxyalkylation of Terminal Alkynes with Alkyl Iodides. *Org. Lett.* **21**, 261-265 (2019).

[25] Hazra, A., Chen, J. & Lalic, G. Stereospecific Synthesis of E-Alkenes through Anti-Markovnikov Hydroalkylation of Terminal Alkynes. *J. Am. Chem. Soc.* **141**, 12464–12469 (2019).

[26] Dai, C., Narayanam, J. M. R. & Stephenson, C. R. J. Visible-Light-Mediated Conversion of Alcohols to Halides. *Nat. Chem.* **3**, 140–145 (2011).

[27] Fürstner, A. et al. Total Syntheses of Amphidinolides B1, B4, G1, H1 and Structure Revision of Amphidinolide H2. *Chem. Eur. J.* **15**, 3983-4010 (2009).

[28] Hoang, G. L. & Takacs, J. M. Enantioselective γ-borylation of unsaturated amides and stereoretentive Suzuki-Miyaura cross-coupling. *Chem. Sci.* **8**, 4511-4516 (2017).

[29] Vedrenne, E., Wallner, O. A., Vitale, M., Schmidt, F. & Aggarwal, V. K. Homologation of Boronic Esters with Lithiated Epoxides for the Stereocontrolled Synthesis of 1,2- and 1,3-Diols and 1,2,4-Triols. *Org. Lett.* **11**, 165-168 (2009).

[30] Schmidt, J., Choi, J., Liu, A. T., Slusarczyk, M. & Fu, G. C. A general, modular method for the catalytic asymmetric synthesis of alkylboronate esters. *Science* **354**, 1265-1269 (2016).

[31] Mlynarski, S. N., Karns, A. S. & Morken, J. P. Direct Stereospecific Amination of Alkyl and Aryl Pinacol Boronates. *J. Am. Chem. Soc.* **134**, 16449-16451 (2012).

[32] Rand, A. W. & Montgomery, J. Enantioselective α-Arylation of Benzamides via Synergistic Nickel and Metallaphotoredox Catalysis. *ChemRxiv* doi: 10.26434/chemrxiv.9978824.v1 (2019).