SUPPORTING INFORMATION

Ni-Catalyzed C(sp^3)–C(sp^3) Cross-Coupling to Access γ-Carbonyl Alkylboronates and Alkylsilicons Enabled by Cyclopropanol-Derived Homoenolates

Linfei Zhu, Yang Sun, and Hui Wang*

Key Laboratory of Functional Molecular Solids (Ministry of Education), Anhui Key Laboratory of Molecular Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, P. R. China.

E-mail: wanghui29085@ahnu.edu.cn

TABLE OF CONTENTS

1. MATERIALS AND GENERAL METHODS

1.1. Glassware, Solvents, and Reagents

All manipulations were performed with oven-dried (130 °C for a minimum of 12 h) glassware under air or an atmosphere of nitrogen, unless otherwise stated.

All anhydrous solvents were commercially supplied. Reagents were purchased from commercial sources and used as received.

1.2. Chromatography and Instrumentation

Thin layer chromatography (TLC) was performed using Merck Kieselgel 60 F254 fluorescent treated silica, which was visualised under UV light, or by staining with aqueous basic potassium permanganate followed by heating, or Hanessian's stain (CAM stain) followed by heating, as stated.

Flash column chromatography (FCC) was carried out using Sili Corey silica gel (200-300 mesh), or boric acid impregnated silica gel.[1]

NMR spectra were recorded, using Bruker 400 MHz for ^{1}H, ^{11}B, ^{13}C and ^{19}F acquisitions. All NMR spectra were recorder at 25 °C unless otherwise stated. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to $CDCl_3$ (^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm). Coupling constants (J) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad signal, dd = doublet of doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons).

IR spectra were recorded were recorded on Bruker INVENIO. Selected absorption maxima (ν_{max}) are reported in wavenumbers (cm^{-1}).

High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicrOTOF II by Electrospray Ionisation (ESI).

Gas chromatography–mass spectrometry (**GC-MS**) was recorded on an Agilent 6890 Series GC and 5973 detector using a HP-5MS UI column (15 m x 0.25 mm x 0.25 μm).

1.3. Naming of Compounds

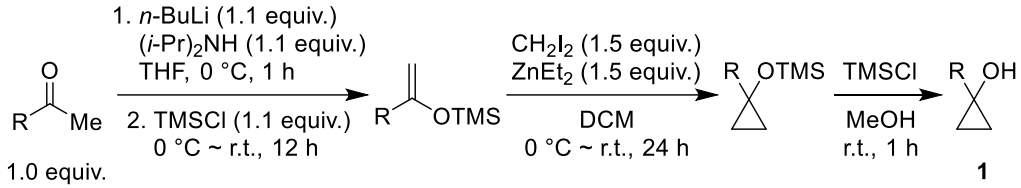
Compound names are those generated by ChemDraw Professional 20.0 software (PerkinElmer), following the IUPAC nomenclature.

2. EXPERIMENTAL DATA

2.1. Synthesis of Starting Materials

2.1.1. Synthesis of Cyclopropanols (1a-1w)

Procedure A: Simmons-Smith Reaction



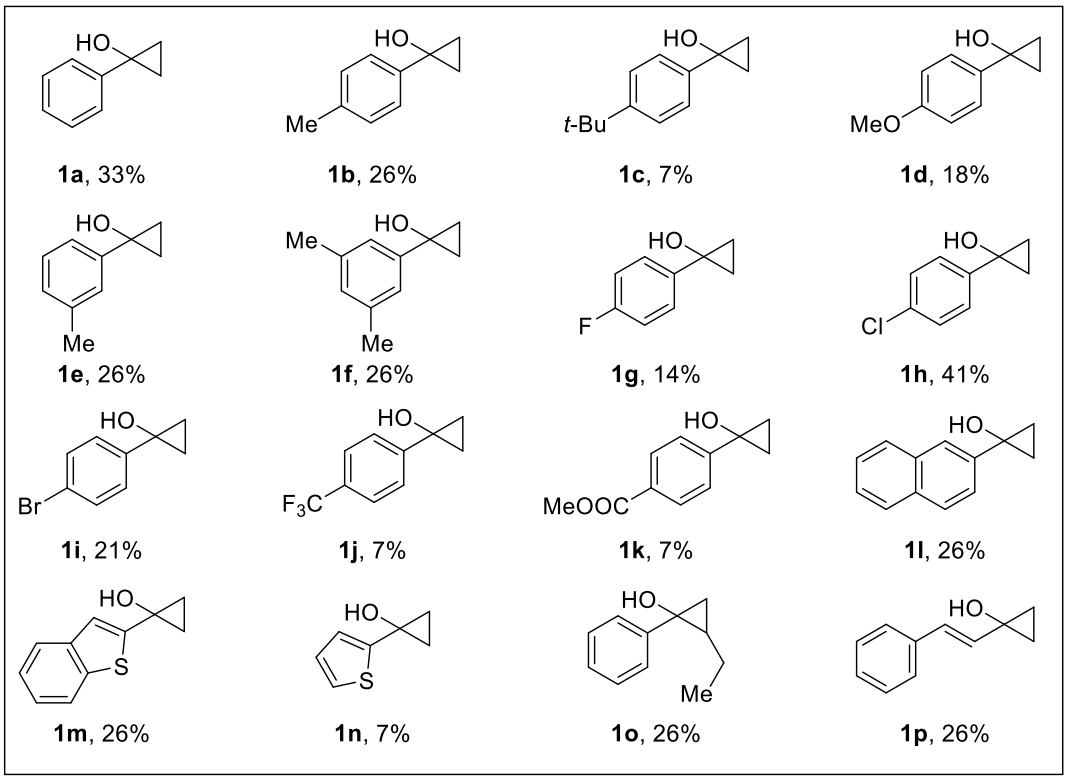
Following a modified literature procedure:[2]

To an oven-dried round-bottom flask containing a stir bar was added diisopropylamine (1.1 equiv.) and THF (0.5 M) under nitrogen atmosphere. Then *n*-BuLi (2.5 M in hexane, 1.1 equiv.) was added to the stirring mixture dropwise at 0 °C. The mixture was allowed to warmed to room temperature and stirred for 1 hour. After that the corresponding ketone (1.0 equiv.) was added at 0 °C followed by TMSCl (1.1 equiv.). The mixture was stirred for 12 hours at room temperature. Then the mixture was quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The enol ether was used in the next step without further purification.

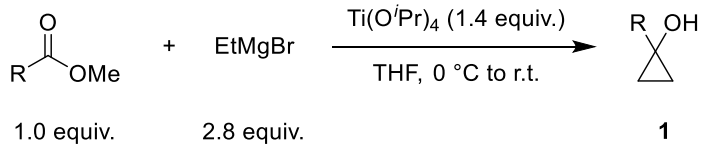
To an oven-dried round-bottom flask containing a stir bar was added the crude enol ether (1.0 equiv.). The flask was evacuated and backfilled with N_2 for three times. Then DCM (0.5 M) was added and the solution was cooled to 0 ºC. After that the diiodomethane (1.5 equiv.) was added, followed by diethylzinc (1.0 M in hexanes, 1.5 equiv.). The reaction was allowed to warm to room temperature and stirred for 24 hours. Then the mixture was quenched with saturated $NaHCO_3$, filtered through Celite and washed with DCM. The organic phase was separated and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The crude TMS ether was also used in the next step without further purification.

To an oven-dried round-bottom flask containing a stir bar was added the crude TMS ether and MeOH (0.5 M). Then TMSCl (1 drop) was added and the reaction was stirred at room temperature for 1 hour. After that the solution was directly concentrated under vacuum and the residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc) to afford **1**.

The following cyclopropanols were synthesized by **procedure A** according to literature known procedures.[2-4]



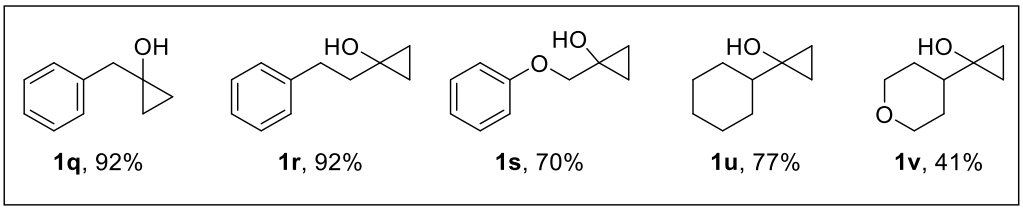
Procedure B: Kulinkovich Rreaction



Following a modified literature procedure:[2]

To an oven-dried round-bottom flask containing a stir bar was added corresponding ester (1.0 equiv.) and THF (0.25 M) under nitrogen atmosphere. Then titanium tetraisopropoxide (1.4 equiv.) was added at 0 °C, followed by the addition of ethylmagnesium bromide (2.8 equiv., 2.0 M in THF) dropwise. After that the reaction was allowed to warm to room temperature and stirred until the ester was completely consumed (detected by TLC). Then the mixture was quenched with water, filtered through Celite and washed with ethyl acetate. The organic layer was separated and the aqueous layer was washed with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuum. The residue was purified by silica gel column chromatography (Petroleum ether/EtOAc) to afford **1**.

The following cyclopropanols were synthesized by **procedure B** according to literature known procedures.[2]



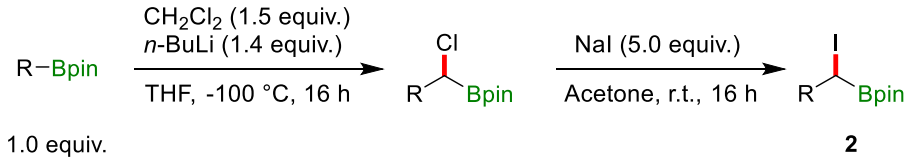
1q, 92% **1r**, 92% **1s**, 70% **1u**, 77% **1v**, 41%

The cyclopropanols **1t** and **1w** were synthesized according to literature known procedures.[5]

The cyclopropanol was purchased from commercial sources.

2.1.2. Synthesis of α-Halo Boronic Esters (2b-2q)

Procedure C: 1,2-Migration of Boronates and Exchange Reactions with NaI



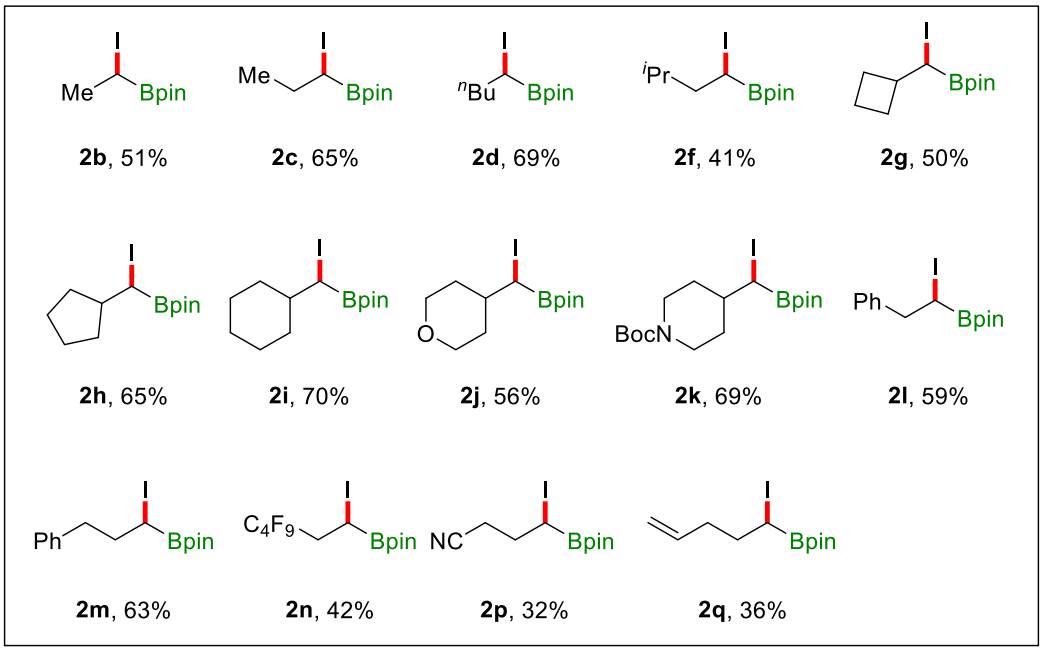
Following a modified literature procedure:[6]

To a flame-dried three necked flask equipped with a stir bar, cooled under N_2 and fitted with a thermometer and septum, was added a solution of dry CH_2Cl_2 (0.96 mL, 15.0 mmol, 1.5 equiv.) in THF (20 mL) which was cooled to -110 °C in an absolute EtOH/liq. N_2 slush bath. *n*-BuLi (2.5 M in hexane, 5.6 mL, 14.0 mmol, 1.4 equiv.) was precooled to 0 °C and lightly shaken before used to ensure homogeneity, then added dropwise over 15 min. *The needle containing the n-BuLi was placed such that the solution ran down the side of the flask before contacting the reaction mixture to ensure adequate cooling.* After 30 min stirring at -110 °C, a solution of RBpin (10.0 mmol, 1.0 equiv.) in THF (5.0 mL), precooled to -80 °C (acetone/ liq. N_2 slush bath), was added to the center of the reaction flask in one portion. The solution was stirred for a further 15 min at -110 °C, then the cooling bath was removed and the reaction mixture was stirred at rt overnight. The solution was concentrated at reduced pressure then resuspended in hexane 150.0 mL and insoluble salts were filtered off, washing the LiCl filter cake with hexane (2 x 40.0 mL). The solution was concentrated at reduced pressure to afford a cream which was subject to vacuum distillation to afford a yellow liquid.

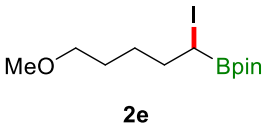
To a round bottom flask wrapped in foil and equipped with a stir bar was added NaI (7.5 g, 50.0 mmol, 10.0 equiv.) and acetone (20.0 mL), and the reaction stirred at rt for 3 min until compound α-chloro boronic ester (10.0 mmol, 1.0 equiv.) was added in one portion. The reaction mixture was stirred at rt for 16 hours. After that, the reaction mixture was filtered and concentrated at reduced pressure to afford a yellow solid which was triturated with CH_2Cl_2 (50.0 mL) and the solid was filtered off and washed with

CH_2Cl_2 (20.0 mL portions until the filtered solid turned white, excess NaI). The liquor was concentrated at reduced pressure to afford the desired product as a yellow oil.

The following cyclopropanols were synthesized by **procedure C** according to literature known procedures.[6-12]



2-(1-Iodo-5-methoxypentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2e)



2e

Prepared following **Procedure C**, using 2-(4-methoxybutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.14 g, 10.0 mmol, 1.0 equiv.), DCM (0.96 mL, 15.0 mmol, 1.5 equiv.), *n*-butyllithium (2.5 M in THF, 5.6 mL, 14.0 mmol, 1.4 equiv.), and NaI (7.50 g, 50.0 mmol, 5.0 equiv.). Purification by vacuum distillation gave boronic ester **2e** (2.21 g, 62%) as a yellow oil.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.34 (t, J = 6.4 Hz, 2H), 3.30 (s, 3H), 3.19 (t, J = 8.2 Hz, 1H), 1.94 – 1.71 (m, 2H), 1.65 – 1.43 (m, 3H), 1.41 – 1.22 (m, 1H), 1.25 (s, 12H) ppm;

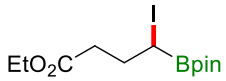
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 84.0, 72.6, 58.6, 34.7, 28.9, 28.0, 24.5, 24.3 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 31.34 ppm.

IR (film): ν_{max} 2978, 2934, 2865, 1408, 1381, 1337, 1268, 1215, 1167, 1144, 1120, 967, 873, 846, cm^{-1}.

HRMS (ESI$^+$): m/z calculated for $C_{12}H_{25}BIO_3$ $[M+H]^+$, 355.0936; found, 355.0946.

Ethyl 4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (2o)



2o

Prepared following **Procedure C**, using ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate (2.28 g, 10.0 mmol, 1.0 equiv.), DCM (0.96 mL, 15.0 mmol, 1.5 equiv.), *n*-butyllithium (2.5 M in THF, 5.6 mL, 14.0 mmol, 1.4 equiv.) and NaI (7.50 g, 50.0 mmol, 5.0 equiv.). Purification by vacuum distillation gave boronic ester **2o** (2.36 g, 64%) as a yellow oil.

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.10 (q, J = 7.1 Hz, 2H), 3.25 (dd, J = 8.6, 7.0 Hz, 1H), 2.68 – 2.29 (m, 2H), 2.19 – 1.99 (m, 2H), 1.24 (s, 12H), 1.22 (d, J = 7.3 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 172.6, 84.2, 60.6, 35.7, 29.7, 24.5, 24.3, 14.3 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

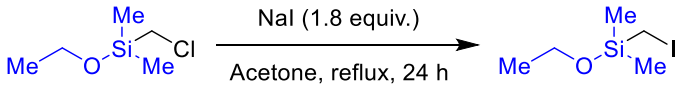
^{11}B NMR (128 MHz, $CDCl_3$): δ_B 31.38 ppm.

IR (film): ν_{max} 2980, 2936, 1735, 1382, 1338, 1270, 1143, 1096, 1035, 968, 846, 768, 671 cm^{-1}.

HRMS (ESI$^+$): m/z calculated for $C_{12}H_{23}BIO_4$ $[M+H]^+$, 369.0729; found, 369.0727.

2.1.3. Synthesis of Requisite Iodomethylsilanes

Procedure D: Synthesis of Ethoxy(iodomethyl)dimethylsilane (4b)



1.0 equiv. **4b**

To an oven-dried round-bottom flask containing a stir bar was added (chloromethyl)(ethoxy)dimethylsilane (1.0 equiv.), dry acetone (1.0 M) and sodium iodide (1.8 equiv.). The reaction was allowed to reflux for 24 hours. After that, the reaction was cooled to room temperature and the solvent was removed via rotary evaporation. Then the resulting slurry was filtered through Celite and washed with hexanes three twice. The combined organic layers were concentrated in vacuum to afford product as a colorless oil.

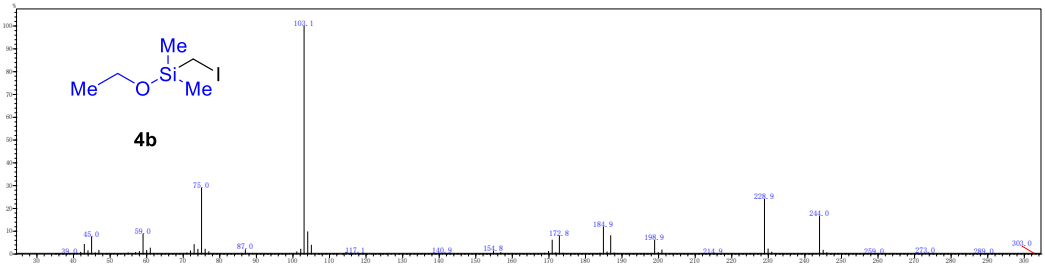
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.73 (q, J = 7.0 Hz, 2H), 2.04 (s, 2H), 1.21 (t, J = 7.0 Hz, 3H),

0.29 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 59.1, 18.6, -2.5, -14.6 ppm;

GC-MS (ESI) calculated for $C_5H_{13}IOSi$, 244.0; found, 244.0.



(Iodomethyl)trimethylsilane were purchased from commercial sources.

Triethoxy(iodomethyl)silane and (Iodomethyl)dimethyl(phenyl)silane were synthesized according to literature known procedures.[13, 14]

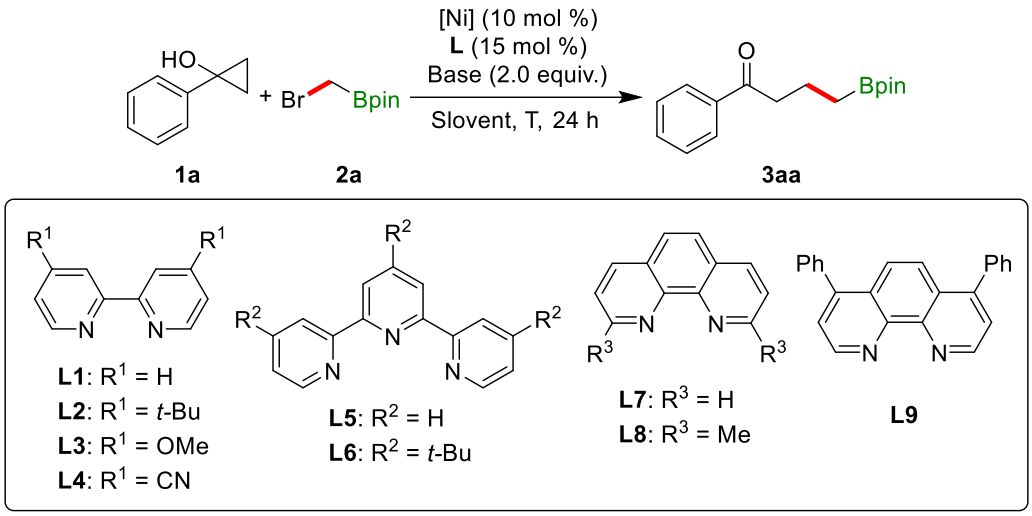
Purification of benzyl boronic esters using boric acid-capped silica (B-SiO_2)

Note: Some of the substrates synthesized showed a loss of material (up to 30%) upon column chromatography. To remedy this, the separation of any compound containing a Bpin ester was achieved using B-SiO_2, which also maintained good isolated yields of the products in comparison to obtained NMR yields (yield loss typically < 15%).

Preparation of boric acid-capped silica (B-SiO_2):[1] A solution of 5% w/v solution of boric acid in ethanol was made by dissolving 27.5 g of boric acid in 550 mL of absolute ethanol and stirred until the mixture became homogenous (ca. 30–45 min). 150 g of SiO_2 was slowly added and the suspension stirred for 1 hour. The silica was filtered off using a 600 mL fritted funnel and washed with Et_2O. This was then transferred to a 1 L round bottom flask and dried under vacuum at 60 °C for several hours. B-SiO_2 should be equally as free-flowing as standard SiO_2. If the B-SiO_2 does not give satisfactory yields, this is most likely due to residual ethanol. To remove it, transfer the B-SiO_2 to a beaker and place it in the oven at 120 °C overnight.

2.2. Reaction Optimization

Table S1: Optimization of the Reaction Conditions[a]



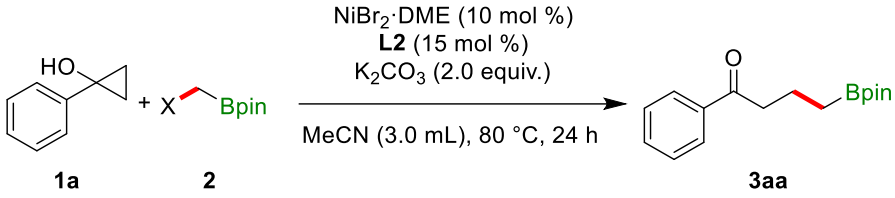
Entry	[Ni]	L	Base	Solvent	T (°C)	Yield (%)[b]
1	$NiCl_2$·DME	**L2**	K_2CO_3	MeCN	80	53
2	$NiCl_2$·DME	**L2**	K_2CO_3	DMF	80	trace
3	$NiCl_2$·DME	**L2**	K_2CO_3	DME	80	11
4	$NiCl_2$·DME	**L2**	K_2CO_3	EtOAc	80	trace
5	$NiCl_2$·DME	**L2**	K_2CO_3	Benzene	80	17
6	$NiCl_2$·DME	**L2**	K_2CO_3	Toluene	80	trace
7	$NiCl_2$·DME	**L2**	K_2CO_3	THF	80	8
8	$NiCl_2$·DME	**L1**	K_2CO_3	MeCN	80	41
9	$NiCl_2$·DME	**L3**	K_2CO_3	MeCN	80	37
10	$NiCl_2$·DME	**L4**	K_2CO_3	MeCN	80	31
11	$NiCl_2$·DME	**L5**	K_2CO_3	MeCN	80	trace
12	$NiCl_2$·DME	**L6**	K_2CO_3	MeCN	80	17
13	$NiCl_2$·DME	**L7**	K_2CO_3	MeCN	80	39
14	$NiCl_2$·DME	**L8**	K_2CO_3	MeCN	80	trace
15	$NiCl_2$·DME	**L9**	K_2CO_3	MeCN	80	26
16	$NiCl_2$·DME	**L2**	K_2CO_3	MeCN	100	36
17	$NiCl_2$·DME	**L2**	K_2CO_3	MeCN	60	33
18	$NiCl_2$·DME	**L2**	K_2CO_3	MeCN	40	14
19	$NiCl_2$·DME	**L2**	- -	MeCN	80	- -

Continued Table S1

20	$NiCl_2$·DME	**L2**	K_3PO_4	MeCN	80	46
21	$NiCl_2$·DME	**L2**	K_2HPO_4	MeCN	80	43
22	$NiCl_2$·DME	**L2**	Na_3PO_4	MeCN	80	51
23	$NiCl_2$·DME	**L2**	Na_2CO_3	MeCN	80	45
24	$NiCl_2$·DME	**L2**	$KHCO_3$	MeCN	80	43
25	$NiCl_2$·DME	**L2**	Cs_2CO_3	MeCN	80	trace
26	$NiCl_2$·DME	**L2**	DMAP	MeCN	80	trace
27	$NiBr_2$·DME	**L2**	K_2CO_3	MeCN	80	71
28	NiI_2	**L2**	K_2CO_3	MeCN	80	11
29	$Ni(COD)_2$	**L2**	K_2CO_3	MeCN	80	36
30[c]	$NiBr_2$·DME	**L2**	K_2CO_3	MeCN	80	79
31[d]	$NiBr_2$·DME	**L2**	K_2CO_3	MeCN	80	62

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ni] (10 mol %), **L** (15 mol %), base (2.0 equiv.), solvent (2.0 mL), N_2, 24 hours. [b]Yield was determined by GC-Fid analysis using 4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane as internal standard. [c]MeCN (3.0 mL). [d]MeCN (4.0 mL). MeCN = Acetonitrile, DMF = *N*, *N*-Dimethylformamide, DME = 1,2-Dimethoxyethane, EtOAc = Ethyl Acetate, THF = Tetrahydrofuran.

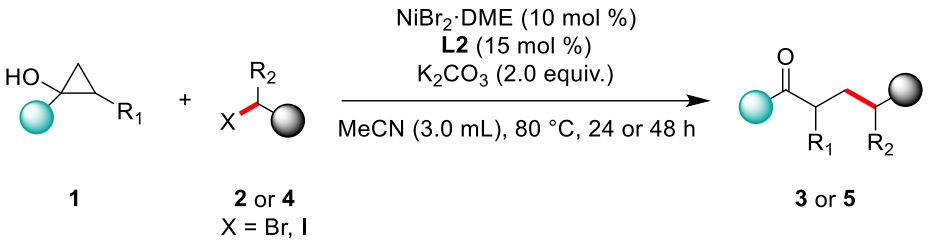
Table S2: Optimize the Substrate 2 of the Reaction[a]



Entry	**X**	**Yield (%)[b]**
1	Br	79 (82)[c]
2	I	82 (80)[c]
3	Cl	63 (66)[c]

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $NiBr_2$·DME (10 mol %), **L2** (15 mol %), K_2CO_3 (2.0 equiv.), MeCN (3.0 mL), N_2, 80 ºC, 24 hours. [b]Yield was determined by GC-Fid analysis using 4,4,5,5-tetramethyl-2-(*p*-tolyl)-1,3,2-dioxaborolane as internal standard. [c]Isolated yield.

2.3. General Procedure E: Reactions of Cyclopropanol 1 with 2 or 4

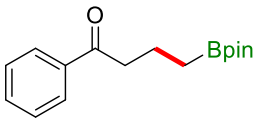


1 **2** or **4** X = Br, I **3** or **5**

To a 10 mL vial equipped with a magnetic stir bar was added cyclopropanol (**1**) (0.2 mmol, 1.0 equiv.), **2** or **4** (0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 10 mol %), **L2** (8.0 mg, 15 mol %), K_2CO_3 (55.3 mg, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 or 48 hours. Upon completion, the mixture was diluted with ethyl acetate (3.0 mL) and quenched with H_2O (3.0 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (3 × 3.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc) to afford desired product **3** or **5**.

2.4. Characterization Data

1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3aa)



3aa

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (26.8 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (43.9 mg, 80%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

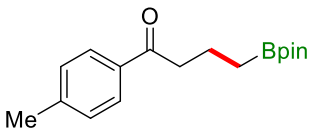
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 – 7.96 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 2.98 (t, *J* = 7.4 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.25 (s, 12H), 0.89 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.8, 137.2, 133.0, 128.7, 128.3, 83.2, 41.1, 25.0, 19.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.92 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)butan-1-one (3ba)



3ba

Prepared following **General Procedure E** using 1-(p-tolyl)cyclopropan-1-ol (29.6 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (50.5 mg, 88%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

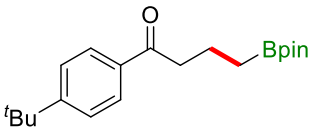
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.87 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.88 – 1.80 (m, *J* = 7.7 Hz, 2H), 1.25 (s, 12H), 0.88 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.4, 143.7, 134.7, 129.3, 128.4, 83.2, 41.0, 25.0, 21.8, 19.5 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.84 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

1-[4-(*tert*-Butyl)phenyl]-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ca)



3ca

Prepared following **General Procedure E** using 1-[4-(tert-butyl)phenyl]cyclopropan-1-ol (38.0 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (56.2 mg,

85%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7 7.91 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.81 (m, 2H), 1.33 (s, 9H), 1.24 (s, 12H), 0.88 (t, *J* = 7.8 Hz, 2H) ppm;

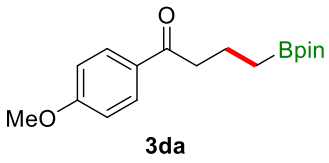
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.4, 156.6, 134.7, 128.2, 125.6, 83.2, 41.0, 35.2, 31.2, 25.0, 19.5 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.90 ppm.

IR (film): ν_{max} 3451, 2970, 1682, 1607, 1467, 1375, 1321, 1274, 1224, 1146, 1088, 973, 847, 580 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{32}BO_3$ $[M+H]^+$, 331.2439; found, 331.2441.

1-(4-Methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3da)



3da

Prepared following **General Procedure E** using 1-(4-methoxyphenyl)cyclopropan-1-ol (32.8 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 10:1) to afford the title compound (48.4 mg, 80%) as a colorless oil.

R_f = 0.4 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

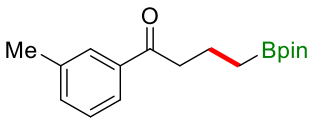
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.92 (t, *J* = 7.5 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.25 (s, 12H), 0.88 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.4, 163.4, 130.6, 130.4, 113.8, 83.2, 55.6, 40.8, 25.0, 19.7 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.81 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*m*-tolyl)butan-1-one (3ea)



3ea

Prepared following **General Procedure E** using 1-(m-tolyl)cyclopropan-1-ol (29.6 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (47.3 mg, 79%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.77 – 7.74 (m, 2H), 7.36 – 7.30 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.88 – 1.80 (m, 2H), 1.24 (s, 12H), 0.87 (t, *J* = 7.8 Hz, 2H) ppm;

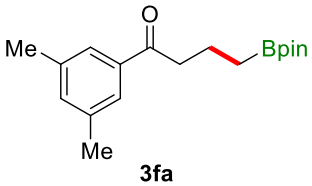
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 138.4, 137.2, 133.7, 128.8, 128.5, 125.5, 83.2, 41.1, 25.0, 21.5, 19.5. ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.91 ppm.

IR (film): ν_{max} 3452, 2980, 2933, 1684, 1596, 1376, 1319, 1146, 971, 844, 779, 691 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{26}BO_3$ $[M+H]^+$, 289.1970; found, 289.1974.

1-(3,5-Dimethylphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3fa)



3fa

Prepared following **General Procedure E** using 1-(3,5-dimethylphenyl)cyclopropan-1-ol (32.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (41.7 mg, 69%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 (s, 2H), 7.18 (s, 1H), 2.94 (t, J = 7.4 Hz, 2H), 2.36 (s, 6H), 1.87 – 1.80 (m, 2H), 1.25 (s, 12H), 0.87 (t, J = 7.8 Hz, 2H) ppm;

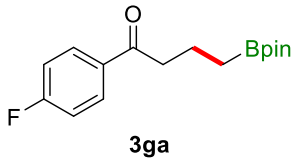
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 201.2, 138.2, 137.4, 134.6, 126.1, 83.2, 41.2, 25.0, 21.4, 19.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.92 ppm.

IR (film): ν_{max} 3421, 2979, 2930, 1683, 1605, 1452, 1376, 1316, 1269, 1146, 970, 852, 683 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{28}BO_3$ $[M+H]^+$, 303.2126; found, 303.2131.

1-(4-Fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ga)



3ga

Prepared following **General Procedure E** using 1-(4-fluorophenyl)cyclopropan-1-ol (30.4 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (42.8 mg, 73%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 (dd, J = 8.9, 5.4 Hz, 2H), 7.11 (t, J = 8.6 Hz, 2H), 2.94 (m, 2H), 1.88 – 1.80 (m, 2H), 1.25 (s, 12H), 0.88 (t, J = 7.7 Hz, 2H) ppm;

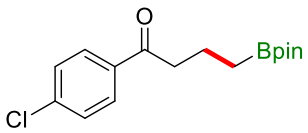
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.1, 165.7 (d, $^1J_{C\text{-}F}$ = 255.2 Hz), 133.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 130.9 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 83.2, 41.0, 25.0, 19.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{19}F NMR (377 MHz, $CDCl_3$): δ_F -105.91 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.81 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

1-(4-Chlorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ha)



3ha

Prepared following **General Procedure E** using 1-(4-chlorophenyl)cyclopropan-1-ol (33.7 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (40.2 mg, 65%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

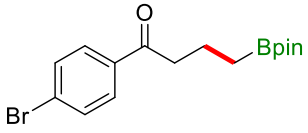
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.91 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.25 (s, 12H), 0.88 (t, *J* = 7.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.5, 139.4, 135.5, 129.7, 129.0, 83.3, 41.0, 25.0, 19.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.88 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[16]

1-(4-Bromophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ia)



3ia

Prepared following **General Procedure E** using 1-(4-bromophenyl)cyclopropan-1-ol (42.6 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (35.5 mg, 50%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 (dt, J = 8.6, 2.2 Hz, 2H), 7.59 (dt, J = 8.6, 2.3 Hz, 2H), 2.94 (t, J = 7.4 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.25 (s, 12H), 0.87 (t, J = 7.7 Hz, 2H) ppm;

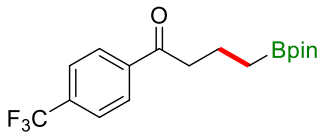
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.7, 135.9, 132.0, 129.9, 128.1, 83.3, 41.0, 25.0, 19.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.88 ppm.

IR (film): ν_{max} 3451, 2979, 2831, 1684, 1593, 1364, 1217, 1145, 1073, 975, 844, 774, 534 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{16}H_{23}BBrO_3$ $[M+H]^+$, 353.0918; found, 353.0920.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-[4-(trifluoromethyl)phenyl]butan-1-one (3ja)



3ja

Prepared following **General Procedure E** using 1-[4-(trifluoromethyl)phenyl]cyclopropan-1-ol (40.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 40:1) to afford the title compound (29.7 mg, 43%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.07 (d, J = 8.2 Hz, 2H), 7.71 (d, J = 8.2 Hz, 2H), 3.00 (t, J = 7.4 Hz, 2H), 1.90 – 1.82 (m, 2H), 1.25 (s, 13H), 0.89 (t, J = 7.7 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.7, 139.8, 134.3 (d, $^2J_{C\text{-}F}$ = 129.5 Hz), 128.6, 125.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.8 (d, $^1J_{C\text{-}F}$ = 273.7 Hz), 83.3, 41.3, 25.0, 19.2 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

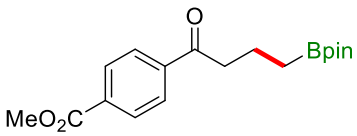
^{19}F NMR (377 MHz, $CDCl_3$): δ_F 63.06 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.78 ppm.

IR (film): ν_{max} 3750, 2986, 2362, 2357, 1691, 1653, 1541, 1377, 1325, 1162, 1139, 1068, 802 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{23}BF_3O_3$ $[M+H]^+$, 343.1687; found, 343.1693.

Methyl 4-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoyl]benzoate (3ka)



3ka

Prepared following **General Procedure E** using methyl 4-(1-hydroxycyclopropyl)benzoate (38.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 10:1) to afford the title compound (32.0 mg, 48%) as a colorless oil.

R_f = 0.4 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.10 (d, J = 8.5 Hz, 2H), 8.01 (d, J = 8.8 Hz, 2H), 3.94 (s, 3H), 3.00 (t, J = 7.4 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.24 (s, 12H), 0.89 (t, J = 7.7 Hz, 2H) ppm;

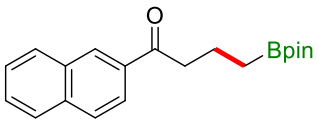
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.2, 166.5, 140.4, 133.7, 129.9, 128.2, 83.3, 52.6, 41.4, 25.0, 19.2 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.91 ppm.

IR (film): ν_{max} 3432, 2979, 1728, 1689, 1440, 1376, 1319, 1279, 1217, 1145, 1110, 1016, 972, 869, 761, 732 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{26}BO_5$ $[M+H]^+$, 333.1868; found, 333.1872.

1-(Naphthalen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3la)



3la

Prepared following **General Procedure E** using 1-(naphthalen-2-yl)cyclopropan-1-ol (36.8 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (54.3 mg, 84%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

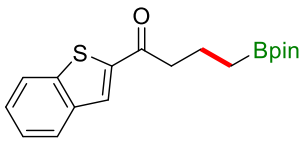
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.49 (s, 1H), 8.04 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.88 (dd, *J* = 8.6, 6.0 Hz, 2H), 7.61 – 7.52 (m, 2H), 3.11 (t, *J* = 7.4 Hz, 2H), 1.96 – 1.88 (m, 2H), 1.26 (s, 12H), 0.93 (t, *J* = 7.8 Hz, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.7, 135.6, 134.6, 132.7, 129.9, 129.7, 128.5, 128.4, 127.9, 126.8, 124.2, 83.2, 41.2, 25.0, 19.7 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.85 ppm.

All recorded spectroscopic data matched those previously reported in the literature.[15]

1-(Benzo[*b*]thiophen-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ma)



3ma

Prepared following **General Procedure E** using 1-(benzo[b]thiophen-2-yl)cyclopropan-1-ol (38.1 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 2:1) to afford the title compound (26.5 mg, 40%) as a yellowish oil.

R_f = 0.5 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 (s, 1H), 7.87 (dd, *J* = 7.6, 4.8 Hz, 2H), 7.45 (t, *J* = 7.1 Hz, 1H), 7.40 (t, *J* = 7.0 Hz, 1H), 3.01 (t, *J* = 7.5 Hz, 2H), 1.95 – 1.88 (m, 2H), 1.26 (s, 12H), 0.92 (t, *J* = 7.7 Hz, 2H) ppm;

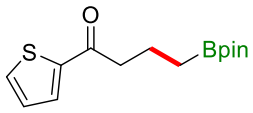
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 195.3, 144.2, 142.6, 139.4, 129.1, 127.4, 126.0, 125.0, 123.2, 83.3, 41.7, 25.0, 20.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.84 ppm.

IR (film): ν_{max} 3468, 2977, 2933, 1664, 1516, 1460, 1376, 1318, 1219, 1144, 968, 844, 750, 726 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{24}BO_3S$ $[M+H]^+$, 331.1534; found, 331.1543.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)butan-1-one (3na)



3na

Prepared following **General Procedure E** using 1-(thiophen-2-yl)cyclopropan-1-ol (28.0 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (47.9 mg, 85%) as a colorless oil.

$\mathbf{R_f}$ = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.72 (d, J = 3.8 Hz, 1H), 7.60 (d, J = 5.0 Hz, 1H), 7.11 (t, J = 4.4 Hz, 1H), 2.90 (t, J = 7.6 Hz, 2H), 1.93 – 1.77 (m, 2H), 1.24 (s, 12H), 0.88 (t, J = 7.8 Hz, 2H) ppm;

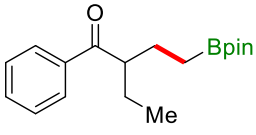
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 193.7, 144.8, 133.4, 131.9, 128.1, 83.2, 41.8, 25.0, 19.9 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.79 ppm.

IR (film): ν_{max} 3449, 2978, 2830, 2362, 1661, 1601, 1415, 1365, 1231, 1145, 969, 848, 775, 724 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{14}H_{22}BO_3S$ $[M+H]^+$, 281.1377; found, 281.1379.

2-Ethyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3oa)



3oa

Prepared following **General Procedure E** using 2-ethyl-1-phenylcyclopropan-1-ol (32.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (42.8 mg, 71%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.97 (m, 2H), 7.54 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 3.40 – 3.33 (m, 1H), 1.91 – 1.72 (m, 2H), 1.66 – 1.51 (m, 3H), 1.22 (s, 12H), 0.86 (t, *J* = 7.4 Hz, 3H), 0.78 – 0.74 (m, 2H) ppm;

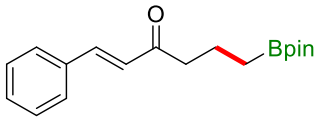
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 204.9, 138.1, 132.9, 128.6, 128.4, 83.2, 49.6, 26.6, 25.0, 25.0, 24.9, 12.2. ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.64 ppm.

IR (film): ν_{max} 2975, 2933, 2363, 1680, 1598, 1452, 1375, 1320, 1270, 1217, 1145, 969, 846, 703 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{28}BO_3$ $[M+H]^+$, 303.2126; found, 303.2136.

(*E*)-1-Phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-3-one (3pa)



3pa

Prepared following **General Procedure E** using (*E*)-1-styrylcyclopropan-1-ol (32.0 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (31.9 mg, 53%) as a yellowish solid.

M. P.: 54 – 56 °C.

R_f = 0.5 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.57 – 7.52 (m, 3H), 7.41 – 7.37 (m, 3H), 6.73 (d, *J* = 16.2 Hz, 1H), 2.68 (t, *J* = 7.4 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.25 (s, 12H), 0.86 (t, *J* = 7.8 Hz, 2H) ppm;

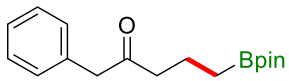
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 142.5, 134.8, 130.5, 129.1, 128.4, 126.6, 83.2, 43.3, 25.0, 19.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.67 ppm.

IR (film): ν_{max} 3058, 2976, 2363, 2339, 1658, 1615, 1454, 1373, 1318, 1197, 1145, 967, 750, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{26}BO_3$ $[M+H]^+$, 301.1970; found, 301.1979.

1-Phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-one (3qa)



3qa

Prepared following **General Procedure E** using 1-benzylcyclopropan-1-ol (29.6 mg, 0.2 mmol, 1.0 equiv.), 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (70 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (43.2 mg, 75%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34 – 7.30 (m, 2H), 7.27 – 7.22 (m, 1H), 7.21 – 7.18 (m, 2H), 3.67 (s, 2H), 2.45 (t, *J* = 7.4 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.21 (s, 12H), 0.75 (t, *J* = 7.8 Hz, 2H). ppm;

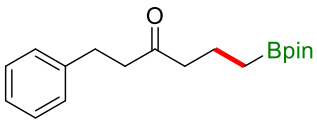
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 208.7, 134.6, 129.6, 128.8, 127.0, 83.2, 50.2, 44.3, 24.9, 18.5 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.69 ppm.

IR (film): ν_{max} 2978, 2931, 2362, 1714, 1495, 1455, 1376, 1321, 1214, 1145, 1086, 968, 847, 701 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{26}BO_3$ $[M+H]^+$, 289.1970; found, 289.1979.

1-Phenyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-3-one (3ra)



3ra

Prepared following **General Procedure E** using 1-phenethylcyclopropan-1-ol (32.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 2:1) to afford the title compound (44.0 mg, 73%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.29 – 7.25 (m, 2H), 7.20 – 7.16 (m, 3H), 2.90 – 2.86 (m, 2H), 2.75 – 2.70 (m, 2H), 2.40 (t, J = 7.4 Hz, 2H), 1.72 – 1.65 (m, 2H), 1.23 (s, 12H), 0.76 (t, J = 7.8 Hz, 2H) ppm;

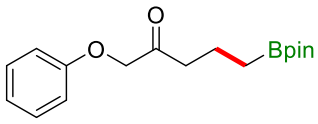
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 210.4, 141.4, 128.6, 128.5, 126.2, 83.2, 45.4, 44.4, 29.9, 25.0, 18.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.71 ppm.

IR (film): ν_{max} 2978, 2934, 2362, 1713, 1455, 1376, 1321, 1145, 1089, 969, 847, 748, 700 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{28}BO_3$ $[M+H]^+$, 303.2126; found, 303.2133.

1-Phenoxy-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-2-one (3sa)



3sa

Prepared following **General Procedure E** using 1-(phenoxymethyl)cyclopropan-1-ol (32.8 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (39.9 mg, 66%) as a colorless oil.

R_f = 0.5 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32 – 7.26 (m, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.89 – 6.86 (m, 2H), 4.54 (s, 2H), 2.61 (t, J = 7.4 Hz, 2H), 1.79 – 1.72 (m, 2H), 1.22 (s, 12H), 0.81 (t, J = 7.8 Hz, 2H) ppm;

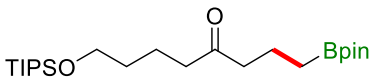
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 208.1, 158.0, 129.8, 121.7, 114.7, 83.2, 72.9, 41.4, 25.0, 18.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.72 ppm.

IR (film): ν_{max} 3453, 2978, 2363, 1721, 1599, 1496, 1377, 1322, 1243, 1144, 1036, 755, 692 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{26}BO_4$ $[M+H]^+$, 305.1919; found, 305.1914.

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-8-[(triisopropylsilyl)oxy]octan-4-one (3ta)



3ta

Prepared following **General Procedure E** using 1-{4-[(triisopropylsilyl)oxy]butyl}cyclopropan-1-ol (57.3 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 50:1) to afford the title compound (62.3 mg, 73%) as a colorless oil.

R_f = 0.8 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.67 (t, J = 6.4 Hz, 2H), 2.41 (q, J = 7.4 Hz, 4H), 1.72 – 1.60 (m, 4H), 1.55 – 1.50 (m, 2H), 1.23 (s, 12H), 1.07 – 1.03 (m, 21H), 0.77 (t, J = 7.8 Hz, 2H) ppm;

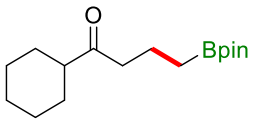
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 211.6, 83.2, 63.2, 45.2, 42.7, 32.6, 25.0, 20.5, 18.7, 18.2, 12.1 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.87 ppm.

IR (film): ν_{max} 2912, 2867, 2362, 1715, 1463, 1377, 1321, 1146, 1107, 1069, 969, 883, 683 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{23}H_{48}BO_4Si$ $[M+H]^+$, 427.3409; found, 427.3417.

1-Cyclohexyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ua)



3ua

Prepared following **General Procedure E** using 1-cyclohexylcyclopropan-1-ol (28.0 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (42.5 mg, 76%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.43 (t, J = 7.4 Hz, 2H), 2.35 – 2.28 (m, 1H), 1.85 – 1.74 (m, 4H), 1.70 – 1.62 (m, 2H), 1.33 – 1.21 (m, 18H), 0.76 (t, J = 7.8 Hz, 2H) ppm;

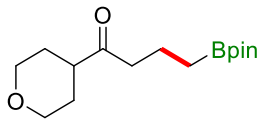
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 214.5, 83.1, 50.9, 43.0, 28.6, 26.0, 25.9, 25.0, 18.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.77 ppm.

IR (film): ν_{max} 2978, 2931, 2856, 2362, 1708, 1452, 1376, 1320, 1146, 970, 847 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{16}H_{30}BO_3$ $[M+H]^+$, 281.2283; found, 281.2288.

1-(Tetrahydro-2*H*-pyran-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3va)



3va

Prepared following **General Procedure E** using 1-(tetrahydro-2H-pyran-4-yl)cyclopropan-1-ol (28.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react at 100 ºC for 72 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 2:1) to afford the title compound (41.7 mg, 74%) as a colorless oil.

R_f = 0.5 (1:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 3.98 (dd, J = 11.6, 4.2 Hz, 2H), 3.41 (td, J = 11.3, 2.9 Hz, 2H), 2.53 (tt, J = 10.9, 4.3 Hz, 1H), 2.45 (t, J = 7.3 Hz, 2H), 1.77 – 1.62 (m, 6H), 1.23 (s, 12H), 0.77 (t, J = 7.8 Hz, 2H) ppm;

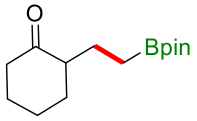
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 212.3, 83.2, 67.5, 47.6, 42.6, 28.3, 25.0, 18.5. ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.70 ppm.

IR (film): ν_{max} 2971, 2950, 2847, 2362, 1708, 1377, 1321, 1239, 1145, 1108, 1021, 971, 845 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{15}H_{28}BO_4$ $[M+H]^+$, 283.2075; found, 283.2081.

2-[2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl]cyclohexan-1-one (3wa)



3wa

Prepared following **General Procedure E** using bicyclo[4.1.0]heptan-1-ol (22.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (25.9 mg, 51%) as a colorless oil.

R_f = 0.5 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 2.39 – 2.33 (m, 1H), 2.30 – 2.18 (m, 2H), 2.12 – 2.05 (m, 1H), 2.02 – 1.95 (m, 1H), 1.92 – 1.80 (m, 2H), 1.69 – 1.56 (m, 2H), 1.41 – 1.28 (m, 2H), 1.22 (s, 12H), 0.83 – 0.67 (m, 2H) ppm;

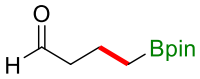
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 213.7, 83.1, 52.8, 42.1, 33.5, 28.2, 25.0, 24.8, 23.8 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.06 ppm.

IR (film): ν_{max} 3450, 2978, 2934, 2862, 2363, 1710, 1451, 1376, 1320, 1216, 1146, 968, 885, 874 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{14}H_{26}BO_3$ $[M+H]^+$, 253.1970; found, 253.1976.

4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butanal (3xa)



3xa

Prepared following **General Procedure E** using cyclopropanol (13 µL, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (8.7 mg, 22%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 9.75 (t, J = 1.8 Hz, 1H), 2.44 (td, J = 7.4, 1.8 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.24 (s, 12H), 0.83 (t, J = 7.7 Hz, 2H) ppm;

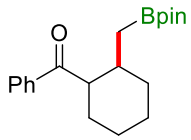
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 203.3, 83.3, 46.2, 25.0, 17.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.72 ppm.

IR (film): ν_{max} 3447, 2925, 1683, 2362, 1700, 1651, 1558, 1541, 1514, 1457, 1397, 1319, 673 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{10}H_{20}BO_3$ $[M+H]^+$, 199.1500; found, 199.1499.

Phenyl{2-[(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]cyclohexyl}methanone (3ya)



3ya

Prepared following **General Procedure E** using 7-phenylbicyclo[4.1.0]heptan-7-ol (37.6 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 48 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 40:1) to afford the title compound (32.5 mg, 50%) as a colorless oil.

R*f* = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.93 – 7.90 (m, 2H), 7.51 (tt, J = 7.3, 1.5 Hz, 1H), 7.44 – 7.40 (m, 2H), 3.59 – 3.54 (m, 1H), 2.34 – 2.27 (m, 1H), 1.92 – 1.80 (m, 2H), 1.72 – 1.62 (m, 2H), 1.61 – 1.53 (m, 2H), 1.45 – 1.38 (m, 1H), 1.36 – 1.30 (m, 1H), 1.13 (s, 6H), 1.12 (s, 6H), 0.93 (dd, J = 16.0, 9.7 Hz, 1H), 0.67 (dd, J = 16.0, 5.8 Hz, 1H) ppm;

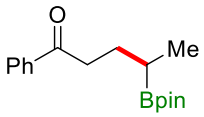
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 203.6, 137.4, 132.5, 128.6, 128.4, 83.0, 48.2, 33.6, 32.2, 25.0, 24.7, 24.3, 22.1 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.97 ppm.

IR (film): ν_{max} 3424, 2941, 2816, 2716, 2362, 1597, 1354, 1154, 1028, 776, 708, 518 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{30}BO_3$ $[M+H]^+$, 329.2283; found, 329.2291.

1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (3ab)



3ab

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodoethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (94 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (48.9 mg, 85%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.00 – 7.97 (m, 2H), 7.53 (tt, J = 7.3, 1.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 3.05 – 2.92 (m, 2H), 1.91 – 1.82 (m, 1H), 1.78 – 1.69 (m, 1H), 1.24 (s, 12H), 1.16 – 1.07 (m, 1H), 1.04 – 1.02 (m, 3H) ppm;

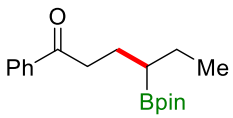
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 201.0, 137.2, 132.9, 128.6, 128.3, 83.2, 38.3, 28.2, 25.0, 24.9, 15.7 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.26 ppm.

IR (film): ν_{max} 3452, 2977, 2872, 1695, 1458, 1378, 1317, 1267, 1144, 969, 859, 745, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{17}H_{26}BO_3$ $[M+H]^+$, 289.1970; found, 289.1970.

1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3ac)



3ac

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (99.6 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (47.1 mg, 78%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.3, 1.2 Hz, 1H), 7.45 (tt, *J* = 7.8, 1.9 Hz, 2H), 3.05 – 2.89 (m, 2H), 1.89 – 1.75 (m, 2H), 1.55 – 1.40 (m, 2H), 1.26 (s, 12H), 1.04 – 0.98 (m, 1H), 0.95 – 0.91 (m, 3H) ppm;

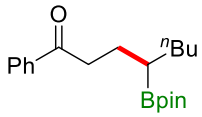
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 137.2, 132.9, 128.6, 128.3, 83.2, 38.5, 25.9, 25.0, 25.0, 24.2, 13.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.41 ppm.

IR (film): ν_{max} 3451, 2972, 2929, 1685, 1454, 1382, 1316, 1266, 1212, 1144, 970, 855, 745, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{28}BO_3$ $[M+H]^+$, 303.2126; found, 303.2128.

1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-1-one (3ad)



3ad

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodopentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (129.6 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (47.2 mg, 72%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.32, 1.4 Hz, 1H), 7.46 – 7.43 (m, 2H), 3.04 – 2.89 (m, 2H), 1.81 (q, *J* = 7.7 Hz, 2H), 1.52 – 1.34 (m, 2H), 1.32 – 1.28 (m, 4H), 1.25 (s, 12H), 1.08 – 1.01 (m, 1H), 0.89 – 0.86 (m, 3H) ppm;

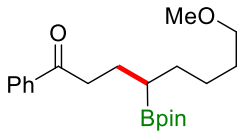
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 137.2, 132.9, 128.6, 128.3, 83.2, 38.5, 31.4, 31.0, 26.2, 25.0, 24.9, 23.1, 14.2 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.30 ppm.

IR (film): ν_{max} 2959, 2928, 2860, 2362, 1687, 1599, 1453, 1377, 1317, 1269, 1200, 1144, 969, 851, 745, 694 cm^{-1}.

HRMS (ESI$^+$): m/z calculated for $C_{20}H_{32}BO_3$ $[M+H]^+$, 331.2439; found, 331.2447.

8-Methoxy-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)octan-1-one (3ae)



3ae

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodo-5-methoxypentyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (146.1 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (32.5 mg, 45%) as a colorless oil.

R$_f$ = 0.5 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 3.35 (t, *J* = 6.7 Hz, 2H), 3.31 (s, 3H), 3.04 – 2.89 (m, 2H), 1.81 (q, *J* = 7.8 Hz, 2H), 1.60 – 1.52 (m, 2H), 1.48 – 1.32 (m, 4H), 1.25 (s, 12H), 1.09 – 1.02 (m, 1H) ppm;

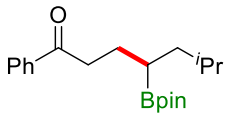
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 137.2, 133.0, 128.7, 128.3, 83.2, 72.9, 58.6, 38.5, 31.1, 30.0, 26.1, 25.6, 25.0, 25.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.48 ppm.

IR (film): ν_{max} 2978, 2930, 2861, 2363, 1685, 1454, 1386, 1318, 1268, 1215, 1144, 1118, 968, 863, 746, 693 cm^{-1}.

HRMS (ESI$^+$): m/z calculated for $C_{21}H_{34}BO_4$ $[M+H]^+$, 361.2545; found, 361.2554.

6-Methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptan-1-one (3af)



3af

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodobutyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (129.6 mg, 0.4 mmol, 2.0 equiv.),

$NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (46.5 mg, 70%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.3, 1.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 3.04 – 2.90 (m, 2H), 1.86 – 1.71 (m, 2H), 1.66 – 1.56 (m, 1H), 1.43 – 1.36 (m, 1H), 1.25 (s, 12H), 1.22 – 1.09 (m, 2H), 0.87 (dd, *J* = 8.0, 1.8 Hz, 6H) ppm;

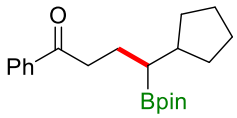
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 137.2, 132.9, 128.6, 128.3, 83.2, 40.5, 38.5, 27.1, 26.3, 25.0, 24.9, 23.0, 22.8 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.24 ppm.

IR (film): ν_{max} 3451, 2956, 2910, 1686, 1456, 1380, 1318, 1260, 1211, 1144, 972, 859, 746, 695 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{32}BO_3$ $[M+H]^+$, 331.2439; found, 331.2443.

4-Cyclopentyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ag)



3ag

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(cyclopentyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (134.4 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (35.9 mg, 52%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.99 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.3, 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 3.01 (ddd, *J* = 14.2, 10.5, 5.2 Hz, 1H), 2.89 (ddd, *J* = 16.0, 10.3, 5.8 Hz, 1H), 1.95 – 1.82 (m, 2H), 1.82 – 1.72 (m, 2H), 1.63 – 1.56 (m, 2H), 1.53 – 1.45 (m, 2H), 1.26 (s, 12H), 1.23 – 1.17 (m, 2H), 1.16 – 1.14 (m, 1H), 0.97 (dq, *J* = 12.6, 4.6 Hz, 1H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.8, 137.2, 132.9, 128.7, 128.3, 83.2, 41.9, 38.8, 32.5, 32.2,

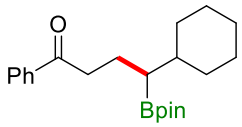
25.7, 25.5, 25.3, 25.1, 25.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.78 ppm.

IR (film): ν_{max} 2949, 2867, 2362, 1686, 1452, 1375, 1318, 1267, 1214, 1144, 968, 849, 745, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{32}BO_3$ $[M+H]^+$, 343.2439; found, 343.2448.

4-Cyclohexyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ah)



3ah

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(cyclohexyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (140.0 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (38.3 mg, 54%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 – 7.96 (m, 2H), 7.54 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.46 – 7.96 (m, 2H), 3.05 – 2.98 (m, 1H), 2.89 – 2.81 (m, 1H), 1.83 (q, *J* = 7.8 Hz, 2H), 1.75 – 1.60 (m, 4H), 1.48 – 1.40 (m, 1H), 1.27 (s, 12H), 1.21 – 1.11 (m, 3H), 1.09 – 1.01 (m, 3H), 0.94 (q, *J* = 7.8 Hz, 1H) ppm;

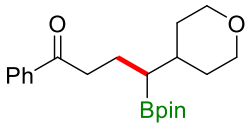
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.9, 137.2, 132.9, 128.6, 128.3, 83.2, 39.9, 39.0, 32.8, 32.5, 26.9, 26.9, 26.8, 25.2, 25.0, 23.8 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.93 ppm.

IR (film): ν_{max} 3751, 3446, 2979, 2925, 2852, 2363, 1685, 1451, 1377, 1313, 1144, 970, 845, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{22}H_{34}BO_3$ $[M+H]^+$, 357.2596; found, 357.2600.

1-Phenyl-4-(tetrahydro-2*H*-pyran-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (3ai)



3ai

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-[iodo(tetrahydro-2*H*-pyran-4-yl)methyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (140.08 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 10:1) to afford the title compound (33.2 mg, 46%) as a white solid.

Melting point: 96 – 98 °C.

R_f = 0.2 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (d, *J* = 7.0 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.47 – 7.43 (m, 2H), 3.97 – 3.92 (m, 2H), 3.36 (td, *J* = 11.9, 1.7 Hz, 2H), 3.06 – 2.98 (m, 1H), 2.93 – 2.85 (m, 1H), 1.92 – 1.78 (m, 2H), 1.72 – 1.60 (m, 3H), 1.84 – 1.36 (m, 2H), 1.27 (s, 12H), 0.98 (dt, *J* = 9.4, 6.1 Hz, 1H) ppm;

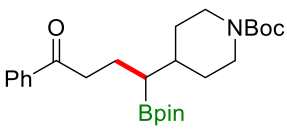
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.5, 137.1, 133.0, 128.7, 128.2, 83.4, 68.6, 68.5, 38.6, 37.2, 32.7, 32.3, 25.2, 25.0, 23.4 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.81 ppm.

IR (film): ν_{max} 3750, 2927, 2854, 2362, 1603, 1454, 1373, 1371, 1266, 1208, 1142, 1094, 967, 845, 750, 693 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{32}BO_4$ $[M+H]^+$, 359.2388; found, 359.2391.

***tert*-Butyl 4-[4-oxo-4-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl]piperidine-1-carboxylate (3aj)**



3aj

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), *tert*-butyl 4-[iodo(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl]piperidine-1-carboxylate (180.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (32.6 mg, 36%) as a colorless oil.

R_f = 0.4 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.79 – 7.74 (m, 2H), 7.56 – 7.51 (m, 1H), 7.46 – 7.43 (m, 2H), 4.08 (d, *J* = 14.0 Hz, 2H), 3.06 – 2.98 (m, 1H), 2.91 – 2.83 (m, 1H), 2.64 (t, *J* = 12.2 Hz, 2H), 1.87 – 1.81 (m, 2H), 1.70 – 1.61 (m, 2H), 1.59 – 1.53 (m, 1H), 1.44 (s, 9H), 1.25 (s, 12H), 0.98 (q, *J* = 8.2 Hz, 1H) ppm;

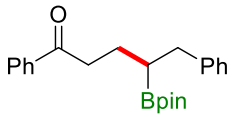
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.5, 155.0, 137.1, 133.0, 128.7, 128.2, 83.4, 79.2, 38.7, 38.2, 31.7, 31.2, 29.8, 28.6, 25.2, 25.0, 23.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.75 ppm.

IR (film): ν_{max} 3750, 2977, 2929, 2363, 1694, 1421, 1368, 1317, 1271, 1168, 969, 869, 748, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{26}H_{41}BNO_5$ $[M+H]^+$, 458.3072; found, 458.3091.

1,5-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentan-1-one (3ak)



3ak

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodo-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (143.2 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (53.7 mg, 74%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 – 7.93 (m, 2H), 7.54 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.27 – 7.20 (m, 4H), 7.17 – 7.13 (m, 1H), 3.07 – 2.90 (m, 2H), 2.82 (dd, *J* = 13.7, 8.3 Hz, 1H),

2.71 (dd, *J* = 13.7, 7.8 Hz, 1H), 1.85 (q, *J* = 7.8 Hz, 2H), 1.50 – 1.42 (m, 1H), 1.18 (s, 6H), 1.16 (s, 6H) ppm;

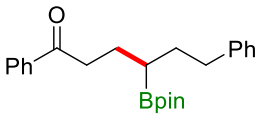
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.5, 141.9, 137.1, 133.0, 129.0, 128.6, 128.3, 125.9, 83.3, 38.4, 37.3, 25.8, 25.0, 24.9 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.73 ppm.

IR (film): ν_{max} 3062, 3028, 2978, 2929, 2363, 1965, 1492, 1383, 1321, 1268, 1213, 1143, 969, 858, 744, 695 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{23}H_{30}BO_3$ $[M+H]^+$, 365.2283; found, 365.2289.

1,6-Diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3al)



3al

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodo-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (148.8 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (51.6 mg, 68%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.00 – 7.97 (m, 2H), 7.54 (tt, *J* = 7.4, 1.1 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.29 – 7.25 (m, 2H), 7.20 – 7.15 (m, 3H), 3.07 – 2.91 (m, 2H), 2.71 – 2.58 (m, 2H), 1.89 (q, *J* = 7.7 Hz, 2H), 1.85 – 1.78 (m, 1H), 1.76 – 1.66 (m, 1H), 1.28 (s, 12H), 1.18 – 1.11 (m, 1H) ppm;

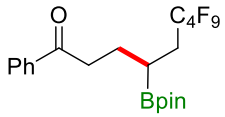
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.7, 143.0, 137.1, 133.0, 128.7, 128.6, 128.4, 128.3, 125.8, 83.3, 38.4, 35.5, 33.5, 26.0, 25.0, 25.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.07 ppm.

IR (film): ν_{max} 3062, 3027, 2978, 2928, 2860, 2362, 1685, 1600, 1453, 1383, 1318, 1270, 1217, 1143, 967, 850, 746, 696 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{25}H_{31}BO_3$ $[M+H]^+$, 379.2439; found, 379.2446.

6,6,7,7,8,8,9,9,9-Nonafluoro-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-1-one (3am)



3am

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 4,4,5,5-tetramethyl-2-(3,3,4,4,5,5,6,6,6-nonafluoro-1-iodohexyl)-1,3,2-dioxaborolane (194.4 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 30:1) to afford the title compound (63.4 mg, 61%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 (dt, *J* = 7.0, 1.1 Hz, 2H), 7.55 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.48 – 7.44 (m, 2H), 3.04 (t, *J* = 7.2 Hz, 2H), 2.48 – 2.32 (m, 1H), 2.19 – 2.04 (m, 1H), 1.96 – 1.90 (m, 2H), 1.51 – 1.44 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.7, 137.0, 133.2, 128.8, 128.2, 83.9, 37.7, 32.4 (t, *J* = 21.9 Hz), 25.9, 24.9, 24.8 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

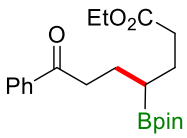
^{19}F NMR (377 MHz, $CDCl_3$): δ_F -81.07 (t, *J* = 9.6 Hz), -111.93 – -113.86 (m), -124.59 – -125.69 (m), -125.92 – -126.03 (m) ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.24 ppm.

IR (film): ν_{max} 2983, 2937, 1689, 1452, 1390, 1332, 1235, 1136, 1075, 1020, 970, 928, 877, 742, 692 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{25}BF_9O_3$ $[M+H]^+$, 507.1748; found, 507.1754.

Ethyl 7-oxo-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3an)



3ao

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0

equiv.), ethyl 4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (147.21 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (63.6 mg, 85%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 – 7.94 (m, 2H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.10 (q, *J* = 8.0 Hz, 2H), 3.06 – 2.92 (m, 2H), 2.43 – 2.28 (m, 2H), 1.89 – 1.69 (m, 4H), 1.25 – 1.22 (m, 15H), 1.10 – 1.02 (m, 1H) ppm;

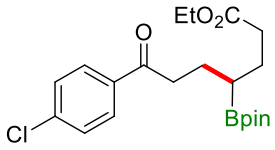
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.5, 173.9, 137.1, 133.0, 128.6, 128.2, 83.4, 60.3, 38.1, 33.8, 26.3, 25.7, 24.9, 14.6 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.80 ppm.

IR (film): ν_{max} 3453, 2978, 2931, 2363, 1721, 1599, 1496, 1377, 1322, 1243, 1170, 1144, 1036, 968, 755, 692 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{32}BO_5$ $[M+H]^+$, 375.2337; found, 375.2346.

Ethyl 7-(4-chlorophenyl)-7-oxo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanoate (3hn)



3hn

Prepared following **General Procedure E** using 1-(4-chlorophenyl)cyclopropan-1-ol (33.7 mg, 0.2 mmol, 1.0 equiv.), ethyl 4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (147.21 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (54.7 mg, 73%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.89 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.87 (m, 2H), 2.42 – 2.26 (m, 2H), 1.88 – 1.67 (m, 4H), 1.27 – 1.18 (m, 15H), 1.07 – 0.97 (m, 1H) ppm;

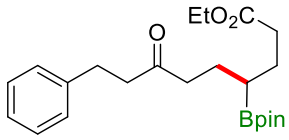
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.2, 173.8, 139.3, 135.4, 129.7, 128.9, 83.4, 60.3, 38.1, 33.7, 26.2, 25.6, 24.9, 14.3 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.81 ppm.

IR (film): ν_{max} 2980, 2934, 1734, 1688, 1590, 1458, 1376, 1319, 1265, 1212, 1143, 1092, 1035, 1011, 848, 672 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{21}H_{31}BClO_5$ $[M+H]^+$, 409.1948; found, 409.1956.

Ethyl 7-oxo-9-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonanoate (3rn)



3rn

Prepared following **General Procedure E** using 1-phenethylcyclopropan-1-ol (32.4 mg, 0.2 mmol, 1.0 equiv.), ethyl 4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate (147.21 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (55.2 mg, 69%) as a yellowish oil.

R_f = 0.4 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.28 – 2.24 (m, 2H), 7.19 – 7.15 (m, 3H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.44 – 2.39 (m, 2H), 2.37 – 2.23 (m, 2H), 1.76 – 1.62 (m, 4H), 1.25 – 1.22 (m, 15H), 0.95 – 0.88 (m, 1H) ppm;

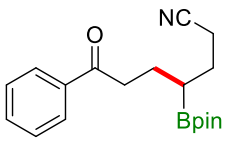
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 210.1, 173.8, 141.2, 128.5, 128.3, 126.1, 83.2, 60.2, 44.3, 42.2, 33.6, 29.8, 26.1, 24.8, 24.8, 14.3 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.68 ppm.

IR (film): ν_{max} 2979, 2933, 2363, 1734, 1455, 1375, 1320, 1248, 1144, 1103, 1034, 968, 749, 701 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{23}H_{36}BO_5$ $[M+H]^+$, 403.2650; found, 403.2661.

7-Oxo-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanenitrile (3ao)



3ao

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 4-iodo-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanenitrile (128.8 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 10:1) to afford the title compound (40.8 mg, 62%) as a white solid.

Melting point: 45 – 47 °C.

R_f = 0.4 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 – 7.95 (m, 2H), 7.55 (tt, J = 7.4, 1.5, 1H), 7.47 – 7.43 (m, 2H), 3.09 – 2.94 (m, 2H), 2.49 – 2.34 (m, 2H), 1.90 – 1.70 (m, 4H), 1.25 – 1.24 (m, 12H), 1.20 – 1.13 (m, 1H) ppm;

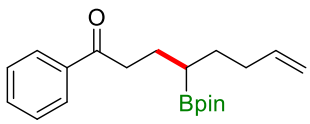
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.1, 137.0, 133.1, 128.7, 128.2, 120.1, 83.7, 37.8, 27.1, 25.1, 24.9, 24.9, 16.5 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 33.50 ppm.

IR (film): ν_{max} 2979, 2933, 2363, 1685, 1453, 1385, 1321, 1272, 1217, 1142, 968, 851, 746, 693 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{19}H_{27}BNO_3$ $[M+H]^+$, 328.2079; found, 320.2086.

1-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-one (3ap)



3ap

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(1-iodopent-4-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (128.79 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.), anhydrous acetonitrile (3.0 mL, 0.067 M) and react for 24 h. Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (36.7 mg,

56%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 – 7.96 (m, 2H), 7.57 – 7.52 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.86 – 5.76 (m, 1H), 5.00 (dq, *J* = 17.1, 1.8 Hz, 1H), 4.95 – 4.91 (m, 1H), 3.05 – 2.89 (m, 2H), 2.19 – 2.02 (m, 2H), 1.87 – 1.78 (m, 2H), 1.64 – 1.55 (m, 1H), 1.53 – 1.44 (m, 1H), 1.26 (s, 12H), 1.14 – 1.05 (m, 1H) ppm;

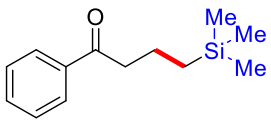
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.8, 139.1, 137.2, 133.0, 128.7, 128.3, 114.6, 83.3, 38.4, 33.4, 30.6, 26.0, 25.0, 25.0 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 34.05 ppm.

IR (film): ν_{max} 2978, 2928, 2362, 1686, 1650, 1453, 1382, 1318, 1269, 1218, 1144, 968, 911, 853, 745, 693 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{20}H_{30}BO_3$ $[M+H]^+$, 329.2283; found, 329.2291.

1-Phenyl-4-(trimethylsilyl)butan-1-one (5aa)



5aa

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)trimethylsilane (85.6 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 50:1) to afford the title compound (20.0 mg, 45%) as a colorless oil.

R_f = 0.8 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

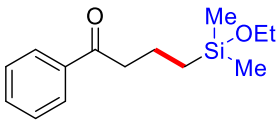
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.98 – 7.94 (m, 2H), 7.54 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.48 – 7.44 (m, 2H), 2.99 (t, *J* = 7.3 Hz, 2H), 1.79 – 1.71 (m, 2H), 0.60 – 0.56 (m, 2H), 0.00 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.8, 137.3, 133.0, 128.7, 128.2, 42.4, 19.2, 16.8, -1.6 ppm.

IR (film): ν_{max} 3448, 2953, 2892, 1687, 1362, 1248, 1220, 971, 838, 757, 737, 693 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{13}H_{21}OSi$ $[M+H]^+$, 221.1356; found, 221.1361.

4-(Ethoxydimethylsilyl)-1-phenylbutan-1-one (5ab)



5ab

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), ethoxy(iodomethyl)dimethylsilane (97.7 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 30:1) to afford the title compound (27.8 mg, 56%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

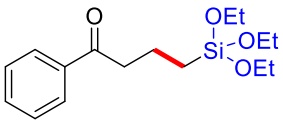
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 – 7.94 (m, 2H), 7.54 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 3.66 (q, *J* = 7.0 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.77 (m, 2H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.72 – 0.64 (m, 2H), 0.12 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.6, 137.2, 133.0, 128.7, 128.2, 58.4, 42.0, 18.7, 18.5, 16.3, -2.0 ppm.

IR (film): ν_{max} 3481, 2964, 1685, 1598, 1450, 1409, 1346, 1253, 1221, 1164, 970, 840, 794, 747, 693 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{14}H_{23}O_2Si$ $[M+H]^+$, 251.1462; found, 251.1469.

1-Phenyl-4-(triethoxysilyl)butan-1-one (5ac)



5ac

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), triethoxy(iodomethyl)silane (121.7 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound (26.3 mg, 42%) as a colorless oil.

R_f = 0.6 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.97 – 7.95 (m, 2H), 7.54 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.47 – 7.43 (m,

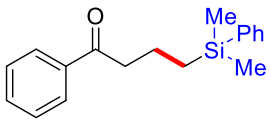
2H), 3.82 (q, *J* = 7.0 Hz, 6H), 3.03 (t, *J* = 7.2 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.22 (t, *J* = 7.0 Hz, 9H), 0.76 – 0.70 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.5, 137.2, 133.0, 128.7, 128.2, 58.5, 41.5, 18.4, 18.1, 10.2 ppm.

IR (film): ν_{max} 2975, 2928, 2889, 2362, 1687, 1451, 1392, 1223, 1167, 1104, 1080, 958, 787, 694 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{16}H_{27}O_4Si$ $[M+H]^+$, 311.1673; found, 311.1675.

4-[Dimethyl(phenyl)silyl]-1-phenylbutan-1-one (5ad)



5ad

Prepared following **General Procedure E** using 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 50:1) to afford the title compound (36.1 mg, 64%) as a colorless oil.

R_f = 0.8 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

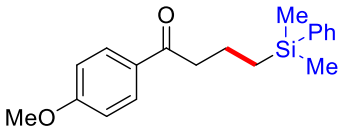
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.92 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.35 (m, 3H), 2.98 (t, *J* = 7.2 Hz, 2H), 1.84 – 1.76 (m, 2H), 0.88 – 0.84 (m, 2H), 0.31 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.6, 139.3, 137.2, 133.7, 133.0, 129.0, 128.7, 128.1, 127.9, 42.2, 19.1, 15.8, -3.0 ppm.

IR (film): ν_{max} 3067, 2954, 2890, 2363, 1695, 1450, 1425, 1362, 1250, 1220, 1113, 970, 834, 785, 734, 696, 469 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{21}OSi$ $[M-H]^-$, 281.1367; found, 281.1384.

4-[Dimethyl(phenyl)sily]-1-(4-methoxyphenyl)butan-1-one (5dd)



5dd

Prepared following **General Procedure E** using 1-(4-methoxyphenyl)cyclopropan-1-ol (32.8 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 40:1) to afford the title compound (36.2 mg, 58%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

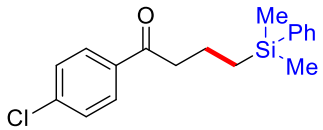
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.90 (dt, *J* = 8.8, 3.0 Hz, 2H), 7.54 – 7.50 (m, 2H), 7.37 – 7.34 (m, 3H), 6.92 (dt, *J* = 8.9, 2.9 Hz, 2H), 3.86 (s, 3H), 2.92 (t, *J* = 7.2 Hz, 2H), 1.82 – 1.74 (m, 2H), 0.87 – 0.82 (m, 2H), 0.30 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.2, 163.4, 139.3, 133.7, 130.4, 130.3, 129.0, 129.0, 113.8, 55.5, 41.9, 19.3, 15.8, -3.0 ppm.

IR (film): ν_{max} 3006, 1676, 1601, 1576, 1510, 1460, 1421, 1362, 1312, 1259, 1226, 1171, 1113, 1031, 973, 732, 702 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{19}H_{24}O_2SiNa$ $[M+Na]^+$, 335.1438; found, 335.1436.

1-(4-Chlorophenyl)-4-[dimethyl(phenyl)silyl]butan-1-one (5hd)



5hd

Prepared following **General Procedure** using 1-(4-chlorophenyl)cyclopropan-1-ol (33.7 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 50:1) to afford the title compound (27.3 mg, 43%) as a colorless oil.

R_f = 0.8 (5:1 Petroleum ether/EtOAc)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.83 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.53 – 7.49 (m, 2H), 7.41 (dt, *J* = 8.6, 2.5 Hz, 2H), 7.37 – 7.34 (m, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 1.81 – 1.73 (m, 2H), 0.85 –0.81 (m, 2H), 0.29 (s, 6H) ppm;

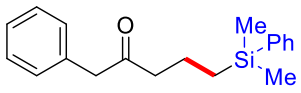
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.3, 139.4, 139.2, 135.5, 133.7, 129.6, 129.1, 129.0, 127.9, 42.2, 19.1, 15.8, -3.0 ppm.

IR (film): ν_{max} 2954, 2363, 1697, 1589, 1401, 1362, 1250, 1217, 1113, 1092, 973, 838, 732, 702, 470

cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{18}H_{21}ClOSiNa$ $[M+Na]^+$, 339.0942; found, 339.0940.

5-[Dimethyl(phenyl)silyl]-1-phenylpentan-2-one (5qd)



5qd

Prepared following **General Procedure E** using 1-benzylcyclopropan-1-ol (29.6 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 30:1) to afford the title compound (39.5 mg, 67%) as a colorless oil.

$\mathbf{R_f}$ = 0.6 (5:1 Petroleum ether/EtOAc, K_2MnO_4 stain)

NMR Spectroscopy (*see spectra*):

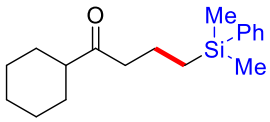
^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.49 – 7.47 (m, 2H), 7.37 – 7.27 (m, 6H), 7.18 – 7.16 (m, 2H), 3.62 (s, 2H), 2.45 (t, J = 7.2 Hz, 2H), 1.62 – 1.54 (m, 2H), 0.70 – 0.66 (m, 2H), 0.25 (s, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 208.6, 139.2, 134.5, 133.7, 129.5, 129.0, 128.8, 127.9, 127.1, 50.3, 45.6, 18.5, 15.5, -3.1 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

IR (film): ν_{max} 3447, 2955, 1713, 1494, 1454, 1426, 1366, 1251, 1186, 1082, 833, 731, 700, 469 cm^{-1}.

HRMS (ESI^+): m/z calculated for $C_{19}H_{24}OSiNa$ $[M+Na]^+$, 319.1487; found, 319.1486.

1-Cyclohexyl-4-[dimethyl(phenyl)silyl]butan-1-one (5td)



5td

Prepared following **General Procedure E** using 1-cyclohexylcyclopropan-1-ol (28.0 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M). Purification by flash column chromatography (Petroleum ether/EtOAc: 60:1) to afford the title compound (23.6 mg, 41%) as a colorless oil.

R_f = 0.7 (5:1 Petroleum ether/EtOAc, K_2MnO_4 stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H δ 7.52 – 7.50 (m, 2H), 7.36 – 7.34 (m, 3H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.27 (tt, *J* = 11.1, 3.3 Hz, 1H), 1.81 – 1.74 (m, 4H), 1.67 – 1.55 (m, 2H), 1.34 – 1.15 (m, 6H), 0.74 – 0.69 (m, 2H), 0.27 (s, 6H) ppm;

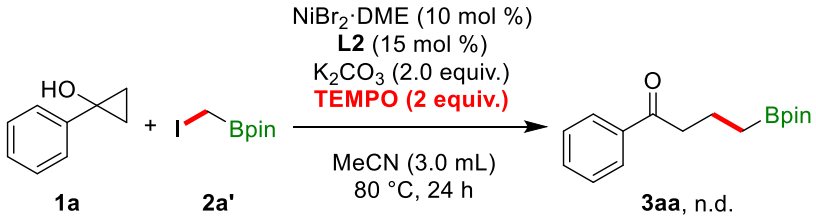
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 214.5, 139.3, 133.7, 129.0, 127.9, 50.9, 44.2, 28.6, 26.0, 25.8, 18.4, 15.7, -3.0 ppm.

IR (film): ν_{max} 2030, 2855, 1707, 1450, 1249, 1114, 985, 831, 781, 731, 702, 470 cm^{-1}.

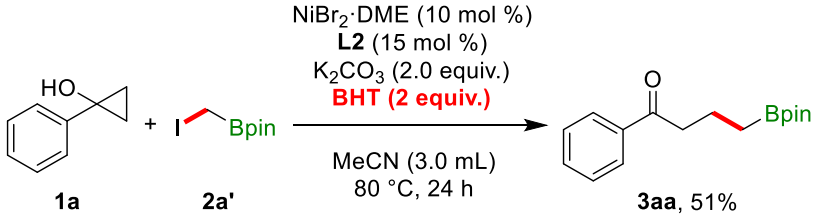
HRMS (ESI^+): m/z calculated for $C_{18}H_{28}OSiNa$ $[M+Na]^+$, 327.1541; found, 327.1538.

3. MECHANISTIC STUDIES

3.1. Radical Trap Experiment

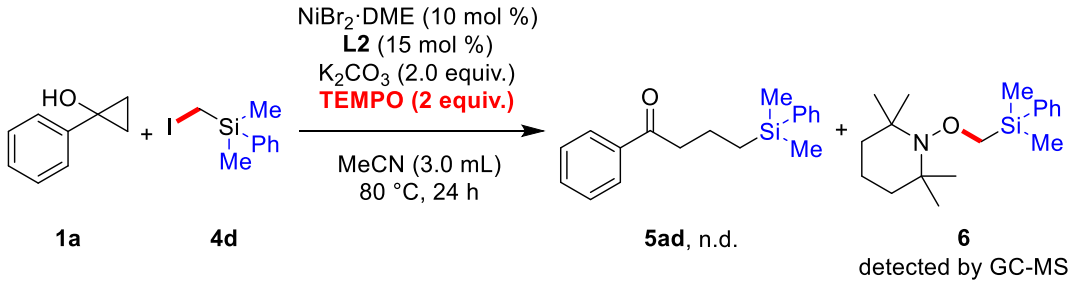


To a 10 mL vial equipped with a magnetic stir bar was added 1-phenylcyclopropan-1-ol (**1a**) (26.8 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(2a')** (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.0 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 2.0 equiv.), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (62.5 mg, 0.2 mmol. 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 hours. After the reaction, the mixture was checked by TLC and GC-Mass, and showed that the desired product **3aa** was not observed.



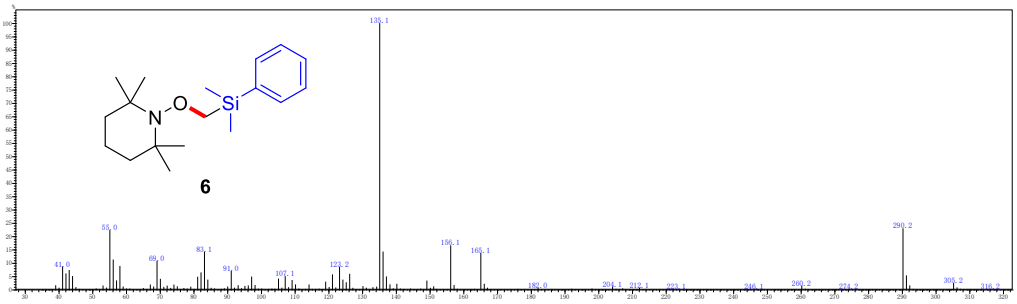
To a 10 mL vial equipped with a magnetic stir bar was added 1-phenylcyclopropan-1-ol (**1a**) (26.8 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(2a')** (73 µL, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.0 mg, 0.03 mmol, 15 mol %), K_2CO_3

(55.3 mg, 2.0 equiv.), 2,6-di-tert-butyl-4-methylphenol (BHT) (88.1 mg, 0.2 mmol. 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 hours. After the reaction, the desired product **3aa** was obtained in 51% yield by GC-Fid analysis.



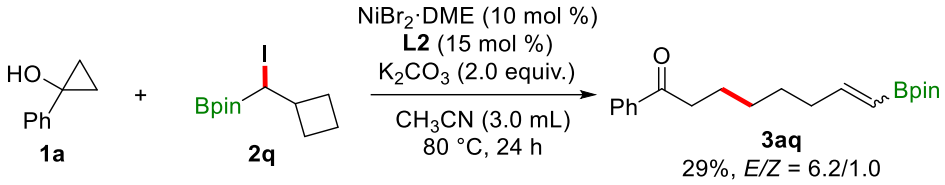
To a 10 mL vial equipped with a magnetic stir bar was added 1-phenylcyclopropan-1-ol (**1a**) (26.8 mg, 0.2 mmol, 1.0 equiv.), (iodomethyl)dimethyl(phenyl)silane **(4d)** (110.5 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.0 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 2.0 equiv.), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) (62.5 mg, 0.2 mmol. 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 hours. After the reaction, the mixture was checked by TLC and GC-Mass, and showed that the desired product **5ad** was not observed and the corresponding TEMPO-adduct was detected by GC-MS.

GC-MS (ESI) calculated for $C_{18}H_{31}NOSi$, 305.2; found, 305.2.



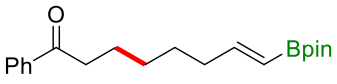
Overall, these three results indicate that a radical intermediate might be involved in this transformation.

3.2. Radical Clock Experiment



To a 10 mL vial equipped with a magnetic stir bar was added 1-phenylcyclopropan-1-ol (27.6 mg, 0.2 mmol, 1.0 equiv.), 2-(cyclobutyliodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (128.8 mg, 0.4 mmol, 2.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.1 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 0.4 mmol, 2.0 equiv.) and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 hours. After the reaction, The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 40:1) to afford desired product **3aq** (19.2 mg, 29%) as a colorless oil.

(*E*)-1-Phenyl-8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-7-en-1-one (3aq) (Major product)



(*E*)-3aq

R*f* = 0.6 (5:1 Petroleum ether/EtOAc, CAM stain)

NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 – 7.93 (m, 2H), 7.54 (tt, *J* = 7.3, 1.5 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 6.62 (dt, *J* = 17.9, 6.5 Hz, 1H), 5.42 (dt, *J* = 18.0, 1.7 Hz, 1H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.19 – 2.14 (m, 2H), 1.77 – 1.69 (m, 2H), 1.51 – 1.35 (m, 4H), 1.26 (s, 12H) ppm;

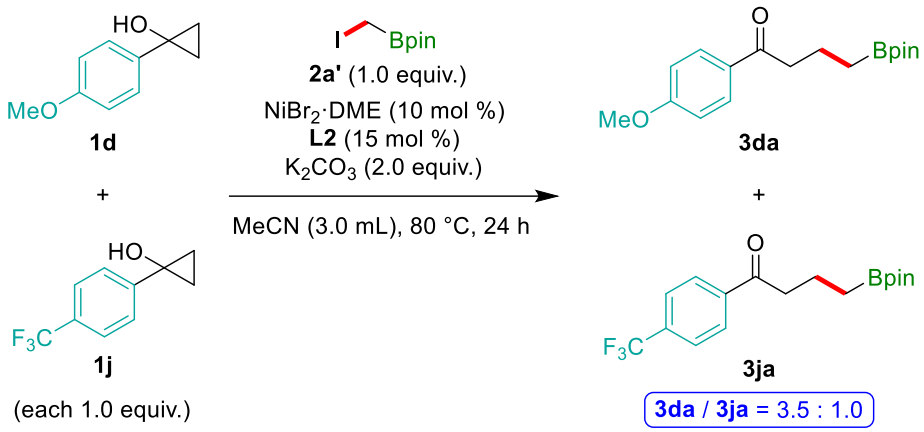
^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.6, 154.5, 137.2, 133.0, 128.7, 128.2, 83.1, 38.6, 35.8, 29.0, 28.1, 24.9, 24.3 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

^{11}B NMR (128 MHz, $CDCl_3$): δ_B 29.38 ppm.

IR (film): ν_{max} 3750, 2928, 2363, 1686, 1639, 1454, 1365, 1321, 1145, 971, 850, 693 cm^{-1}.

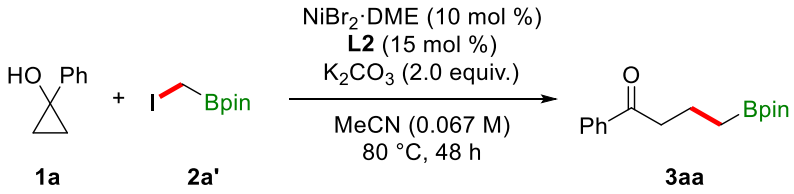
HRMS (ESI^+): m/z calculated for $C_{20}H_{30}BO_3$ $[M+H]^+$, 329.2283; found, 329.2291.

3.3. Competition Experiments



To a 10 mL vial equipped with a magnetic stir bar was added 1-(4-methoxyphenyl)cyclopropan-1-ol (**1d**) (32.8 mg, 0.2 mmol, 1.0 equiv.), 1-[4-(trifluoromethyl)phenyl]cyclopropan-1-ol (**1j**) (40.4 mg, 0.2 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(2a')** (36 μL, 0.2 mmol, 1.0 equiv.), $NiBr_2$·DME (7.1 mg, 0.02 mmol, 10 mol %), **L2** (8.0 mg, 0.03 mmol, 15 mol %), K_2CO_3 (55.3 mg, 2.0 equiv.), and anhydrous acetonitrile (3.0 mL, 0.067 M) under nitrogen atmosphere. The vial was sealed with a septum and allowed to stir at 80 °C for 24 hours. After the reaction, the mixture was checked by GC-Fid analysis, and showed that the ratio of **3da** : **3ja** was 3.5 : 1.0.

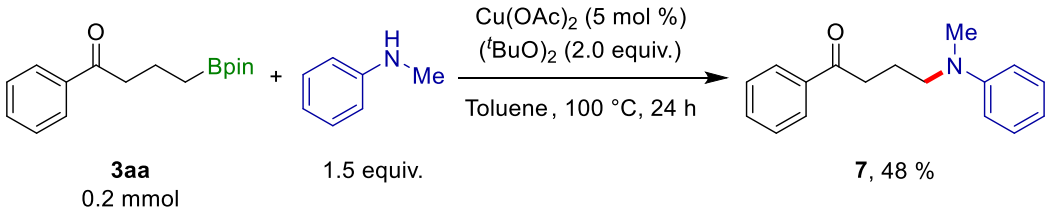
3.4. Gram-Scale Reaction



Following **General Procedure E**, in a 500 mL flame-dried Schlenk flask using 1-phenylcyclopropan-1-ol (**1a**) (1.25 g, 9.3 mmol, 1.0 equiv.), 2-(iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a'**) (3.4 mL, 18.6 mmol, 2.0 equiv.), $NiBr_2$·DME (329.8 mg, 0.93 mmol, 10 mol %), **L2** (374.4 mg, 1.4 mmol, 15 mol %), K_2CO_3 (2.6 mg, 18.6 mmol, 2.0 equiv.), acetonitrile (138.8 mL, 0.067 M) and react under nitrogen atmosphere at 80 ºC for 48 hours. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 20:1) to afford desired product **3aa** (1.9 g, 75 %) as a colorless oil.

4. SYNTHETIC APPLICATIONS

4.1. Synthesis of Compound 7



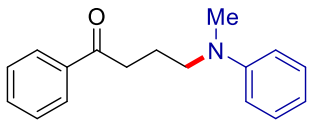
3aa
0.2 mmol

1.5 equiv.

7, 48 %

Following a known procedure.[17] To a 10 mL Schlenk flask with a magnetic stir bar was added 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3aa**) (54.8 mg, 0.2 mmol, 1.0 equiv.), *N*-methylaniline (33 µL, 0.3 mmol, 1.5 equiv.), $Cu(OAc)_2$ (1.8 mg, 0.01 mmol, 5 mol %), di-*tert*-butyl peroxide (73 µL, 0.4 mmol, 2 equiv.) and toluene (0.8 mL, 0.25 M). The reaction mixture was stirred at 100 °C for 24 h. After that, the reaction mixture was cooled to room temperature and the solvent was removed in vacuo. The resulting crude material was purified by flash column chromatography (Petroleum ether/EtOAc: 20:1) to afford the title compound **7** (24.1 mg, 48%) as a yellowish oil.

4-[Methyl(phenyl)amino]-1-phenylbutan-1-one (7)



7

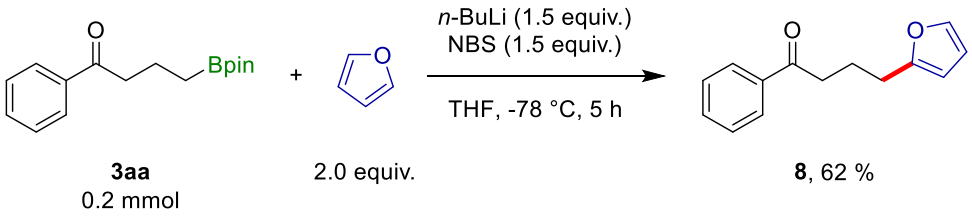
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 – 7.93 (m, 2H), 7.56 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.25 – 7.21 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 3.42 (t, *J* = 7.2 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 2.95 (s, 3H), 2.09 – 2.01 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 199.9, 149.5, 137.0, 133.2, 129.4, 128.7, 128.1, 116.4, 112.4, 52.1, 38.4, 35.7, 21.5 ppm;

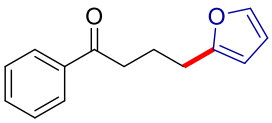
All recorded spectroscopic data matched those previously reported in the literature.[18]

4.2. Synthesis of Compound 8



Following a known procedure.[19] To a 10 mL flame-dried Schlenk flask with a magnetic stir bar was added furan (29 µL, 0.2 mmol, 2.0 equiv.) and THF (2.0 mL) and the solution was cooled to -78 °C. Then *n*-BuLi (120 µL, 2.5 M in hexane, 1.5 equiv.) was added dropwise. After that the mixture was allowed to warm to room temperature and stirred for 1 hour. Subsequently, the reaction mixture was cooled back to -78 °C and a solution of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3aa**) (54.8 mg, 0.2 mmol, 1.0 equiv.) in THF (1.0 mL) was then added dropwise. The reaction was stirred for 1 hour at -78 °C, followed by the addition of a solution of NBS (53.4 mg, 0.3 mmol, 1.5 equiv.) in THF (2.0 mL). After stirred at -78 °C for another 1 hour, a saturated aqueous $Na_2S_2O_3$ solution (4.0 mL) was added. Then the reaction mixture was allowed to warm to room temperature before the organic phase was separated, and the aqueous layer was extracted with ethyl acetate (3 × 3.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 30:1) to afford the title compound **8** (26.7 mg, 62 %) as a colorless oil.

4-(Furan-2-yl)-1-phenylbutan-1-one (8)



8

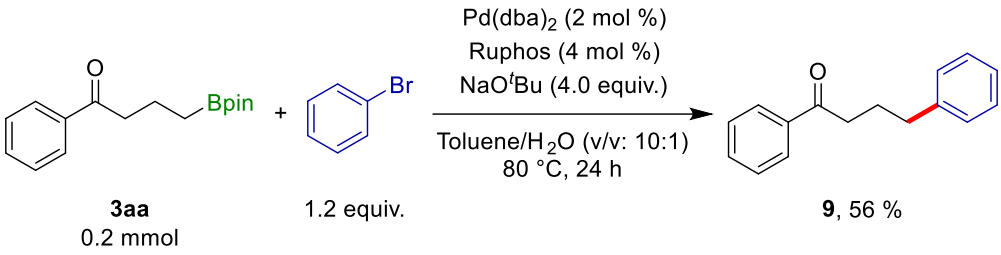
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.96 – 7.93 (m, 2H), 7.56 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.31 (d, *J* = 1.0 Hz, 1H), 6.28 (dd, *J* = 2.1, 0.8 Hz, 1H), 6.02 (d, *J* = 2.8 Hz, 1H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 7.14 – 7.07 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.0, 155.6, 141.2, 137.1, 133.1, 128.7, 128.2, 110.3, 105.5, 37.7, 27.4, 22.7 ppm;

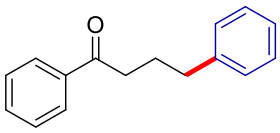
All recorded spectroscopic data matched those previously reported in the literature.[20]

4.3. Synthesis of Compound 9



Following a modified procedure.[21] To a 10 mL flame-dried Schlenk flask with a magnetic stir bar was added 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3aa**) (54.8 mg, 0.2 mmol, 1.0 equiv.), bromobenzene (25 µL, 0.24 mmol, 1.2 equiv.), $Pd(dba)_2$ (2.3 mg, 0.004 mmol, 2 mol %), Ruphos (3.7 mg, 0.008 mmol, 4 mol %), NaO^tBu (76.9 mg, 0.8 mmol, 4.0 equiv.) toluene (0.7 mL) and H_2O (70 µL) under nitrogen atmosphere. Then the reaction was stirred at 80 °C for 24 hours. After that, the mixture was cooled to room temperature, diluted with ethyl acetate (1.0 mL) and quenched with H_2O (1.0 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (3 × 1.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 50:1) to afford the title compound **9** (24.9 mg, 56 %) as a colorless oil.

1,4-Diphenylbutan-1-one (9)



9

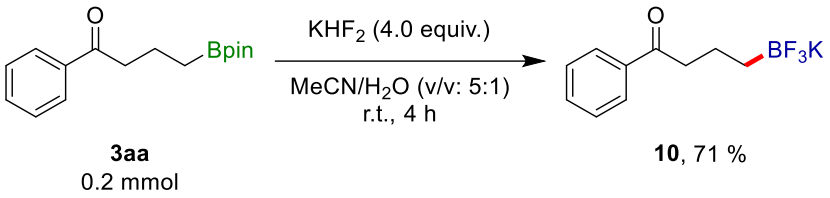
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.95 – 7.92 (m, 2H), 7.55 (tt, *J* = 7.2, 1.5 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.32 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.13 – 2.06 (m, 2H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ_C 200.3, 141.8, 137.1, 133.1, 128.7, 128.7, 128.5, 128.2, 126.1, 37.8, 35.3, 25.8 ppm;

All recorded spectroscopic data matched those previously reported in the literature.[22]

4.4. Synthesis of Compound 10

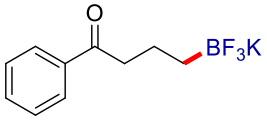


3aa
0.2 mmol

10, 71 %

Following a known procedure.[15] Saturated aq. KHF_2 (4.5 M, 0.3 mL, 0.8 mmol) was added dropwise to the solution of 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3aa**) (54.8 mg, 0.2 mmol, 1.0 equiv.) in acetonitrile (1.5 mL) at room temperature. The reaction was stirred for 4 h. After that the mixture was concentrated in vacuo. The dried solids were triturated with hot acetone (3 × 1.0 mL) and filtered to remove inorganic salts. The resulting filtrate was concentrated and washed with Et_2O (3 × 1.0 mL) to give the title compound **10** (36.2 mg, 71%) as a white solid.

Trifluoro(4-oxo-4-phenylbutyl)borate (10)



10

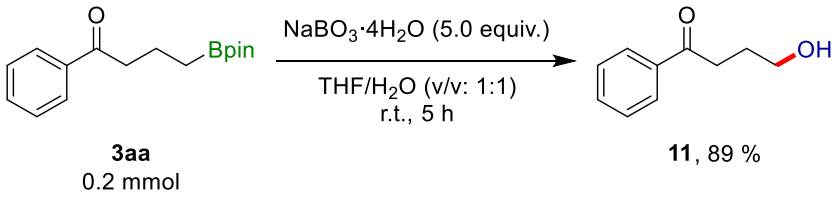
NMR Spectroscopy (*see spectra*):

^{1}H NMR (400 MHz, d_6-DMSO): 7.93 – 7.90 (m, 2H), 7.59 (tt, J = 7.3, 1.4 Hz, 1H), 7.52 – 7.48 (m, 2H), 2.85 (t, J = 7.5 Hz, 2H), 1.53 – 1.45 (m, 2H), 0.06 – -0.02 (m, 2H) ppm;

^{13}C NMR (101 MHz, d_6-DMSO): δ_C 201.7, 137.0, 132.7, 128.6, 127.9, 41.9, 21.8 ppm. The carbon attached to boron was not observed due to quadrupolar relaxation;

All recorded spectroscopic data matched those previously reported in the literature.[15]

4.5. Synthesis of Compound 11



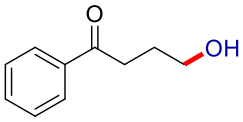
3aa
0.2 mmol

11, 89 %

Following a known procedure.[21] To a 10 mL Schlenk flask with a magnetic stir bar was added 1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-1-one (**3aa**) (54.8 mg, 0.2 mmol, 1.0 equiv.), $NaBO_3 \cdot 4H_2O$ (101.8 mg, 1 mmol, 5.0 equiv.) THF (2.0 mL) and H_2O (2.0 mL). The reaction was stirred

at room temperature for 5 h. After that, the organic phase was separated and the aqueous layer was extracted with ethyl acetate (3 × 2.0 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and the solvent was evaporated in vacuo. The residue was purified by column chromatography on silica gel (Petroleum ether/EtOAc: 2:1) to afford the title compound **11** (29.4 mg, 89 %) as a colorless oil.

4-Hydroxy-1-phenylbutan-1-one (11)



11

NMR Spectroscopy (*see spectra*):

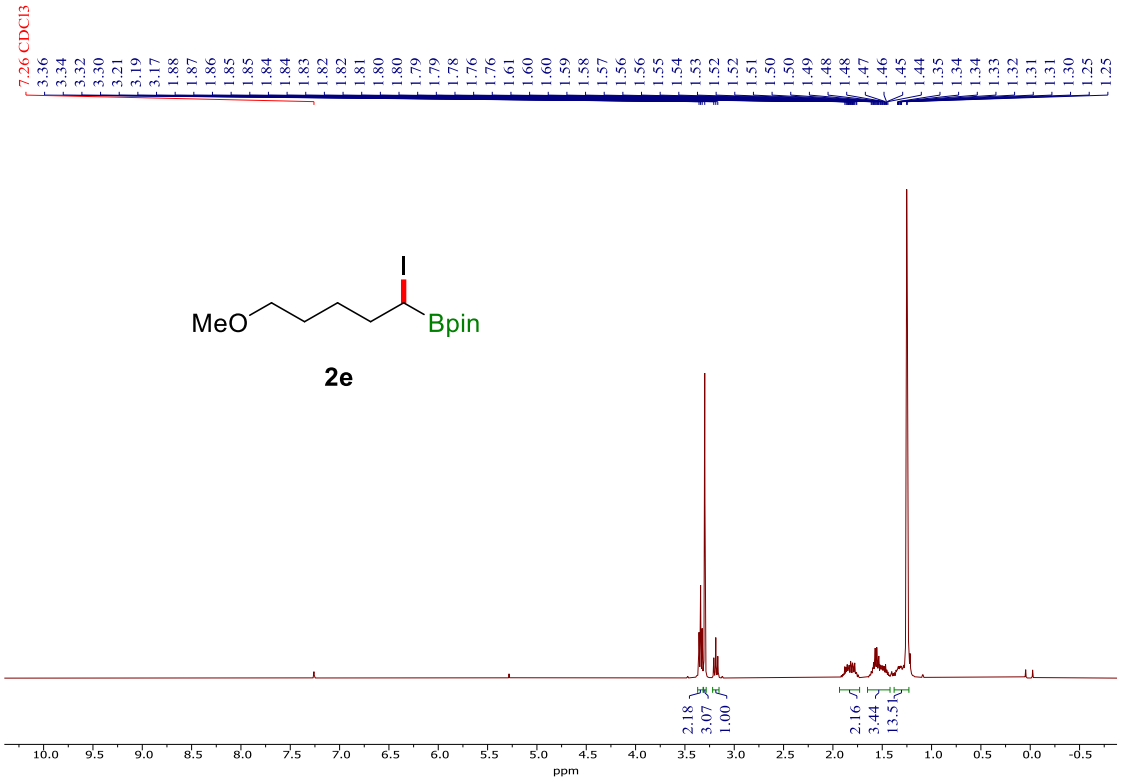
^{1}H NMR (400 MHz, CD_3OD): δ_H 8.00 – 7.97 (m, 2H), 7.58 (tt, *J* = 7.4, 1.2 Hz, 1H), 7.50 – 7.46 (m, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 1.96 – 1.89 (m, 2H) ppm;

^{13}C NMR (101 MHz, CD_3OD): δ_C 202.2, 138.3, 134.2, 129.7, 129.1, 62.2, 35.8, 28.2 ppm;

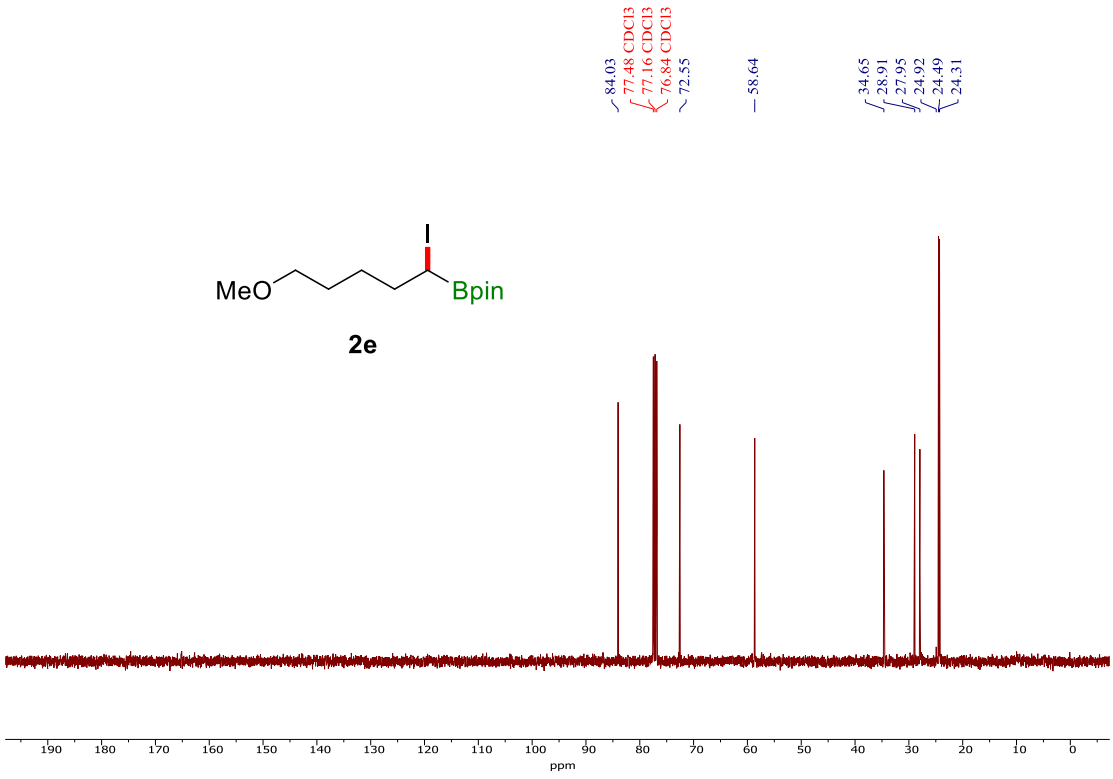
All recorded spectroscopic data matched those previously reported in the literature.[23]

5. SPECTROSCOPIC DATA

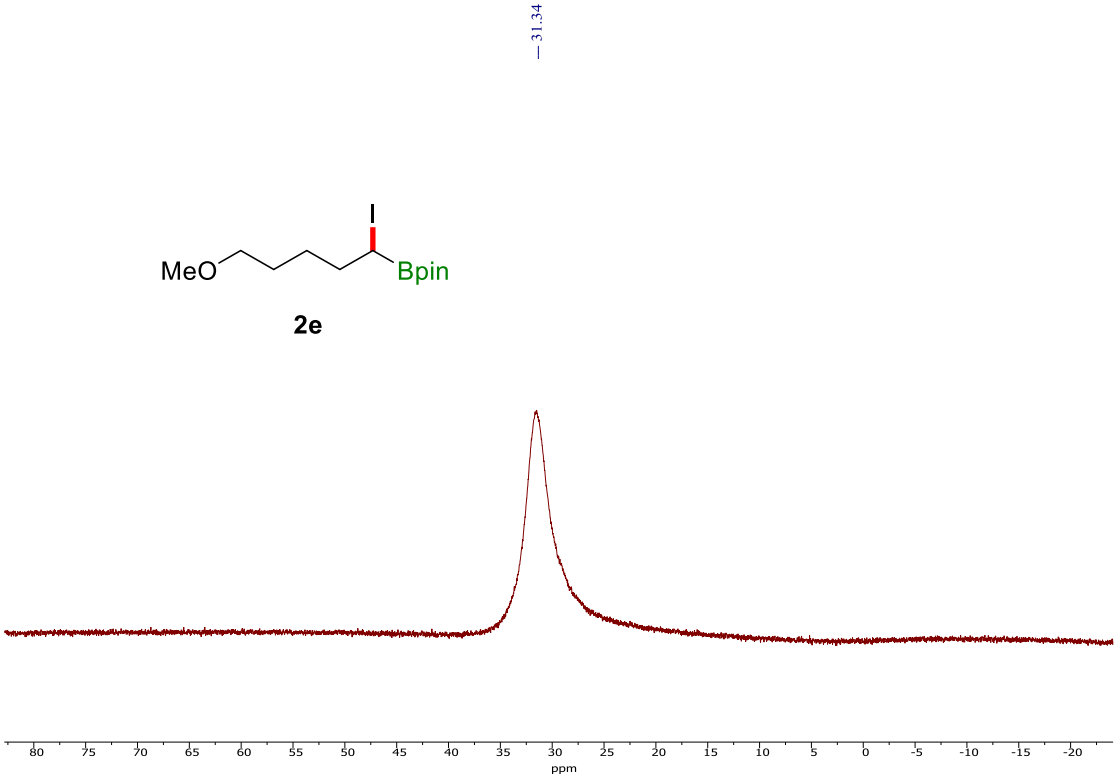
^{1}H NMR (400 MHz, $CDCl_3$) of **2e** (*see procedure*)



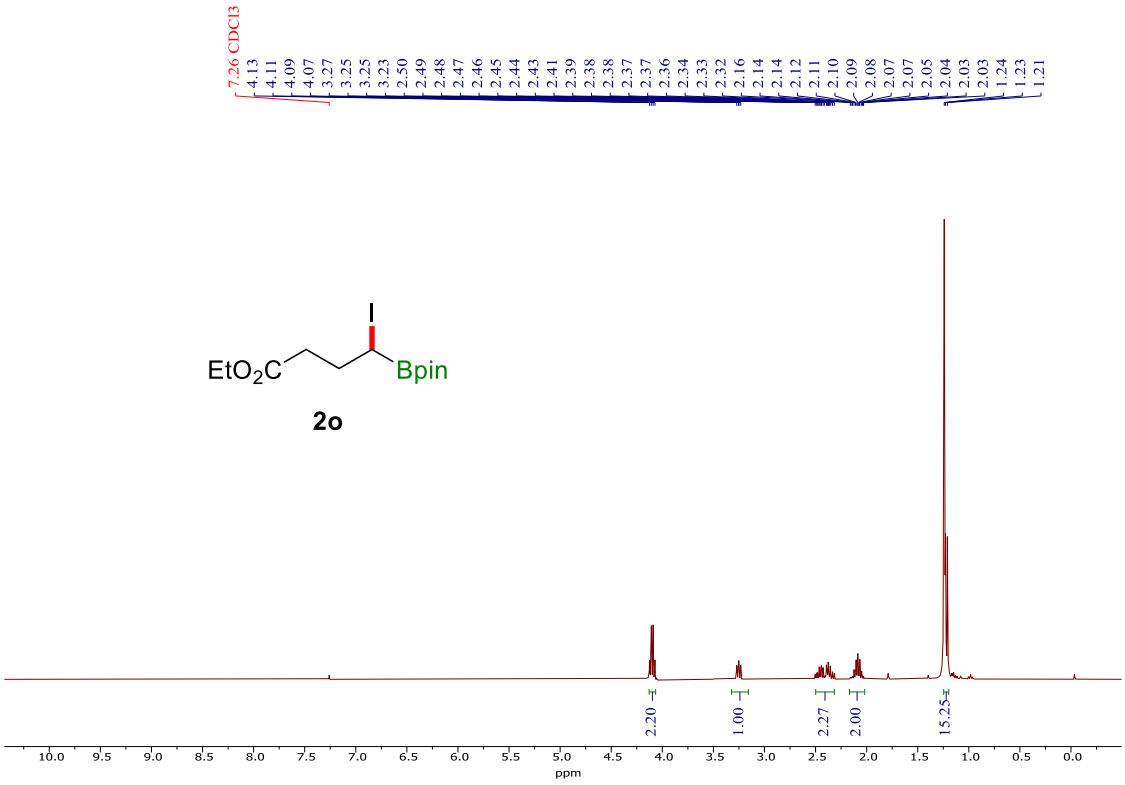
^{13}C NMR (101 MHz, $CDCl_3$) of **2e**



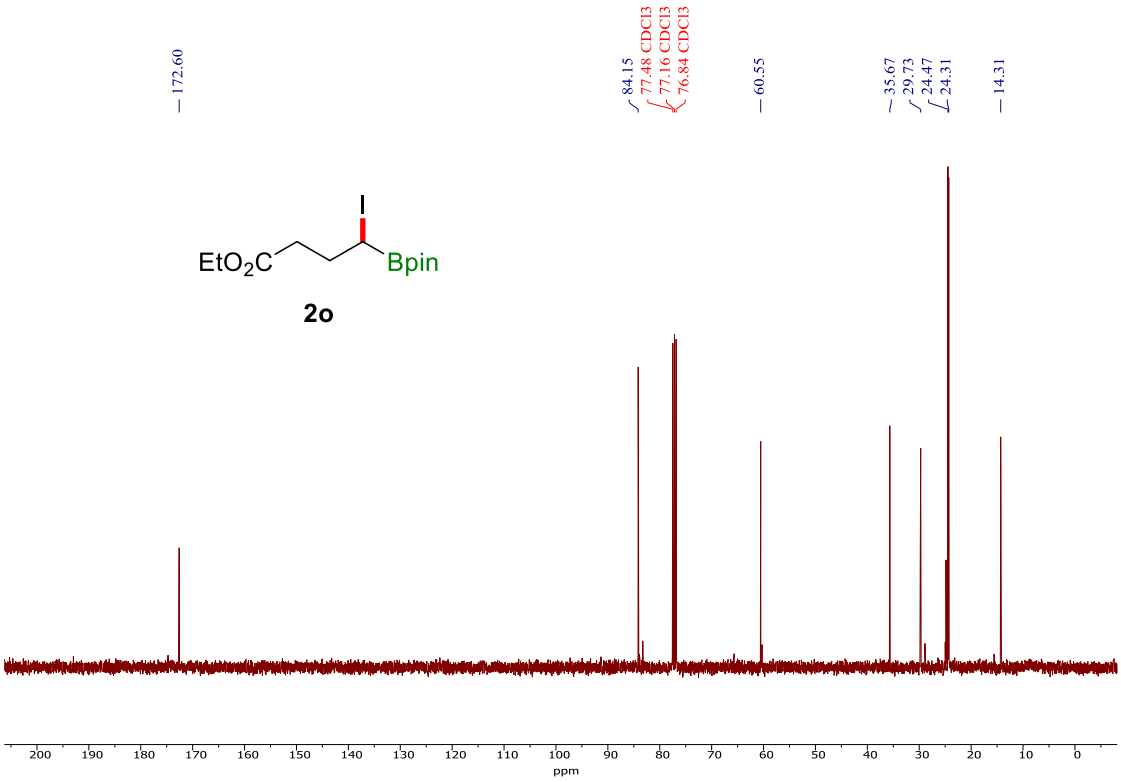
^{11}B NMR (128 MHz, $CDCl_3$) of **2e**



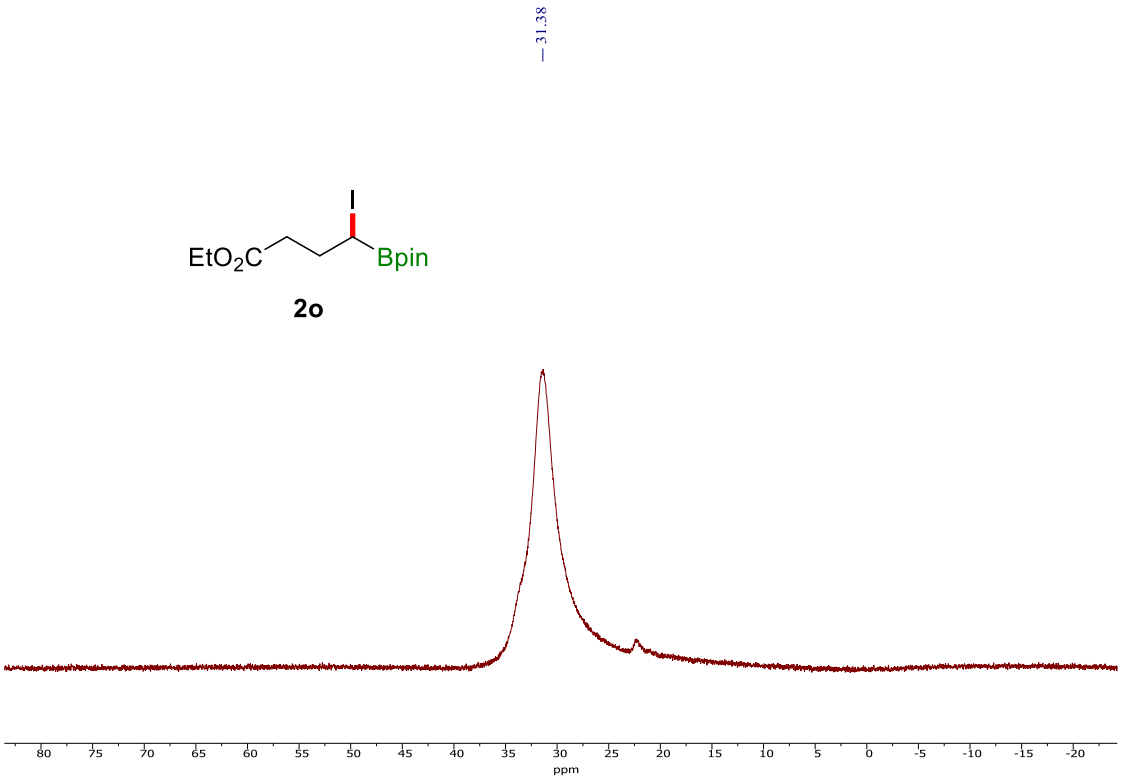
^{1}H NMR (400 MHz, $CDCl_3$) of **2o** (*see procedure*)



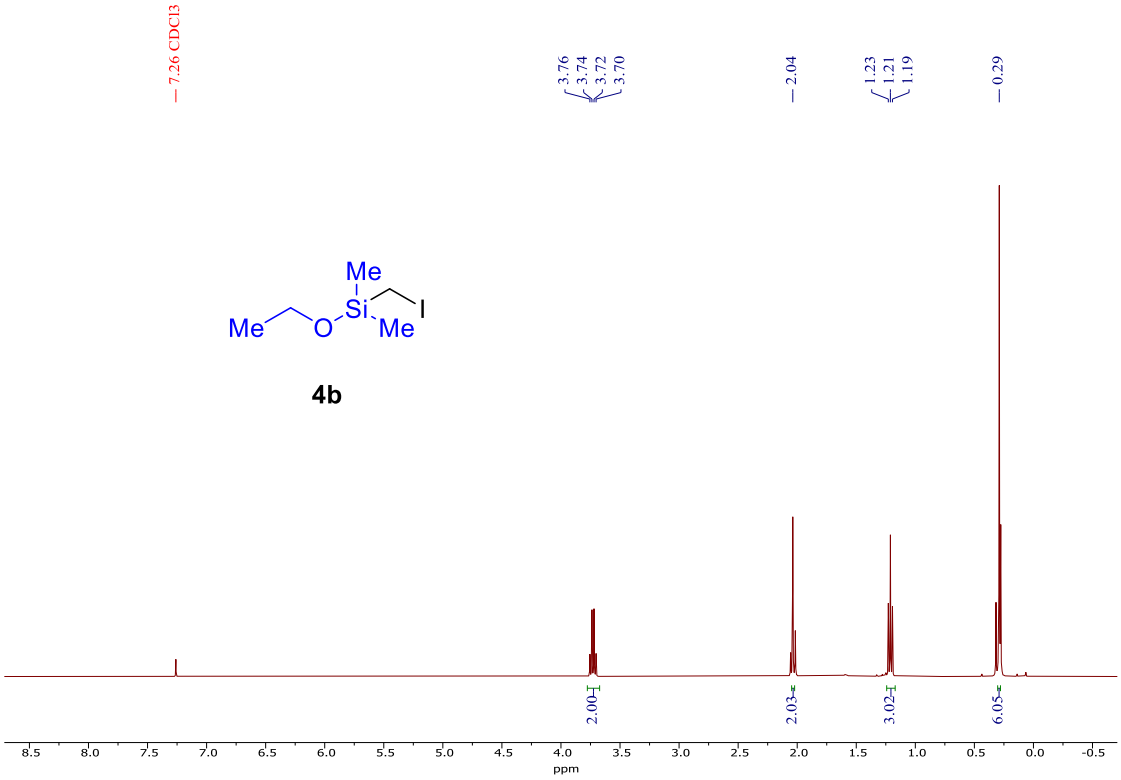
^{13}C NMR (101 MHz, $CDCl_3$) of **2o**



^{11}B NMR (128 MHz, $CDCl_3$) of **2o**

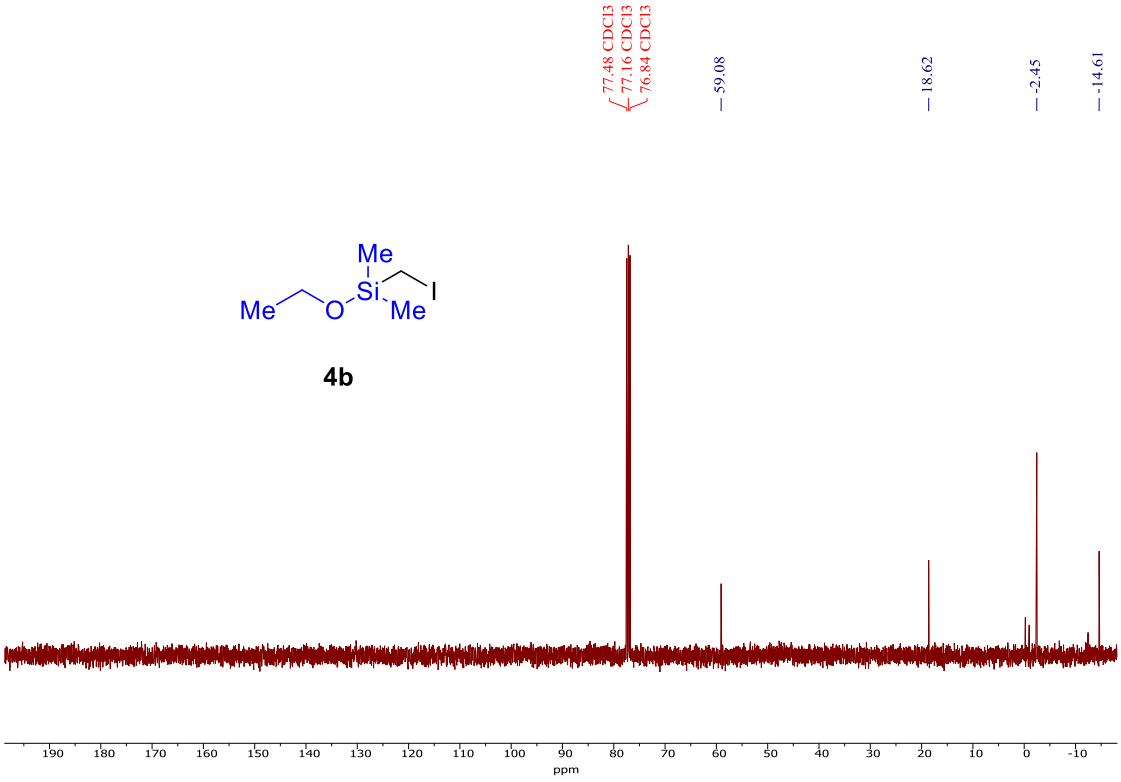


^{1}H NMR (400 MHz, $CDCl_3$) of **4b** (*see procedure*)



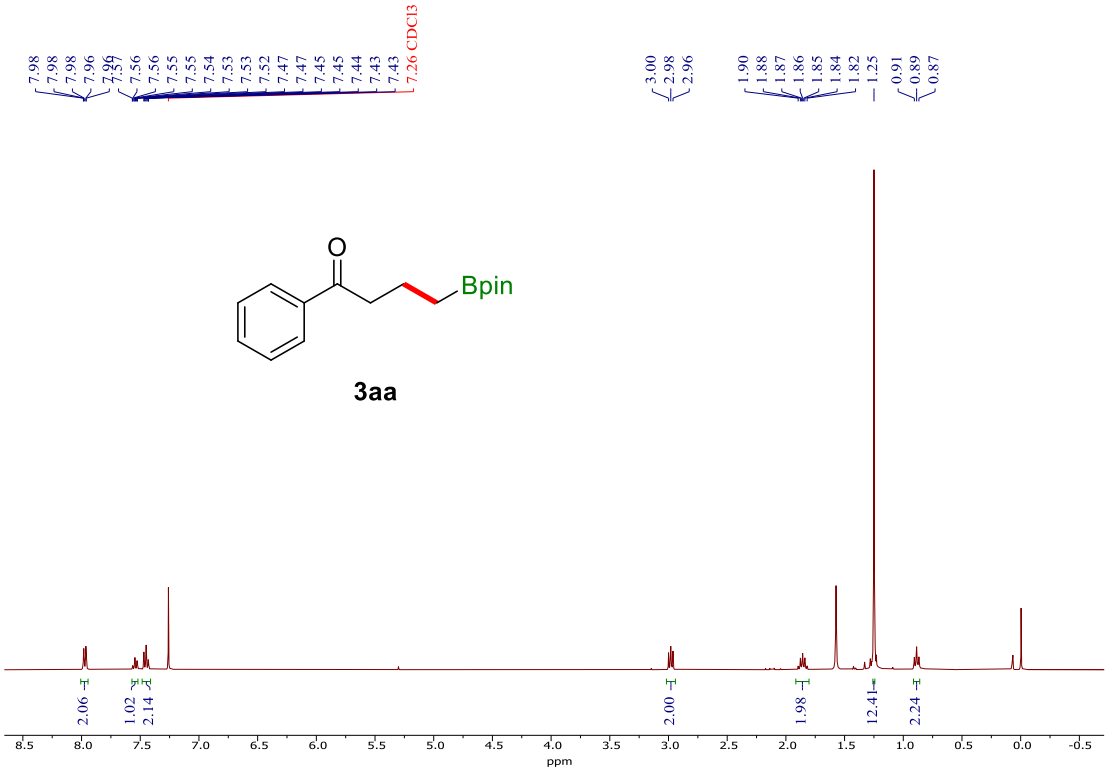
4b

^{13}C NMR (101 MHz, $CDCl_3$) of **4b**

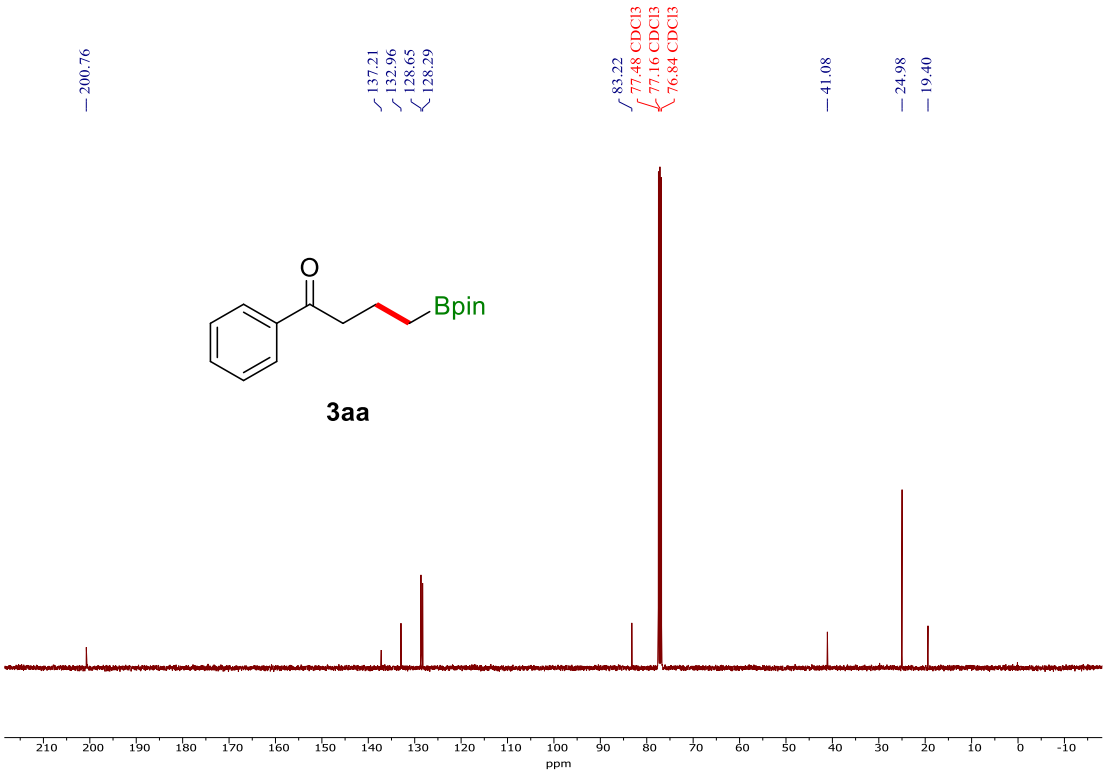


4b

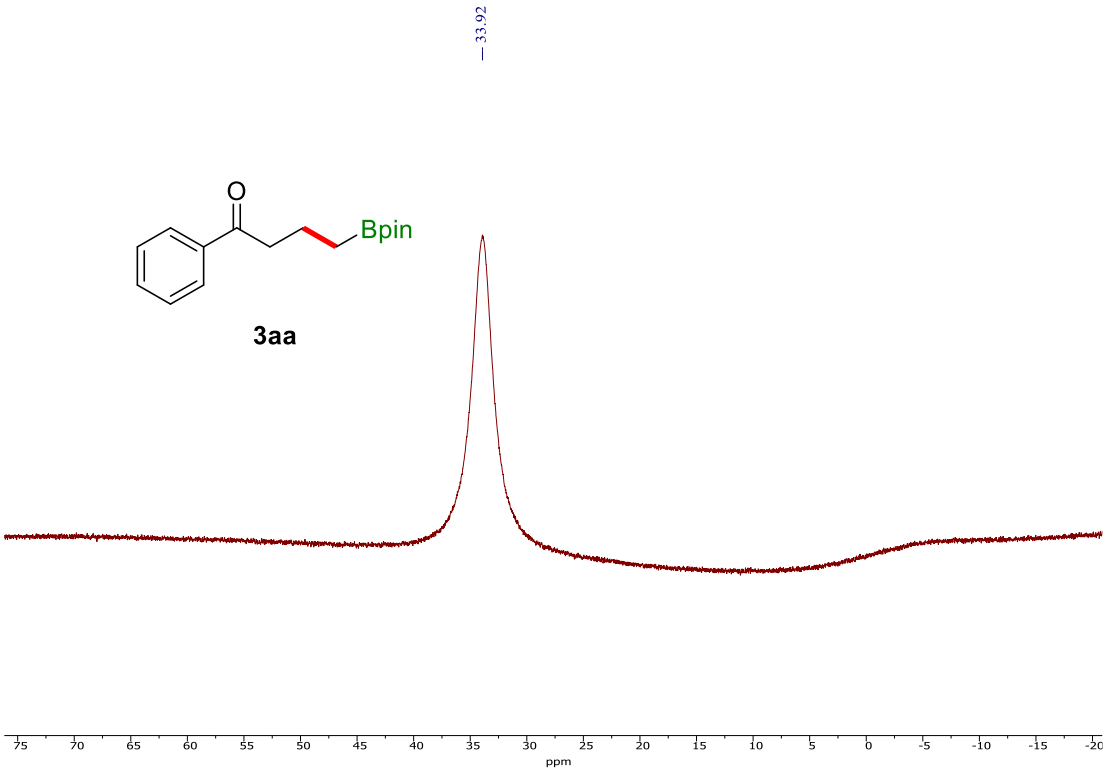
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa** (*see procedure*)



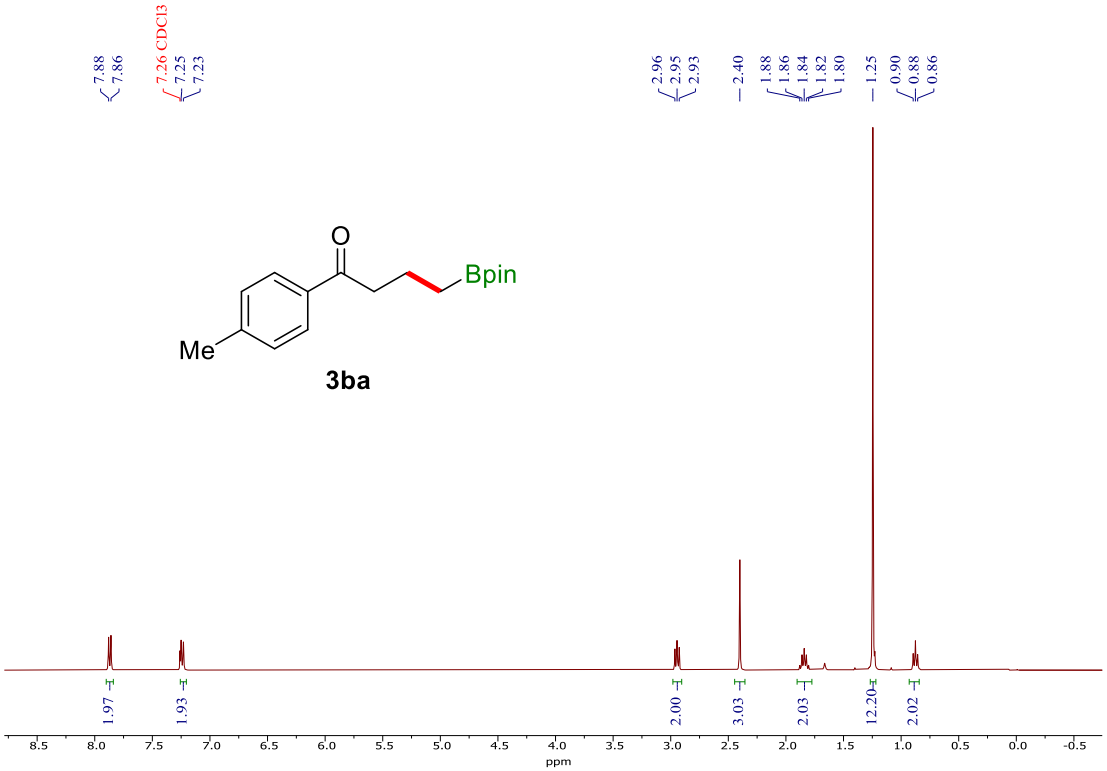
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



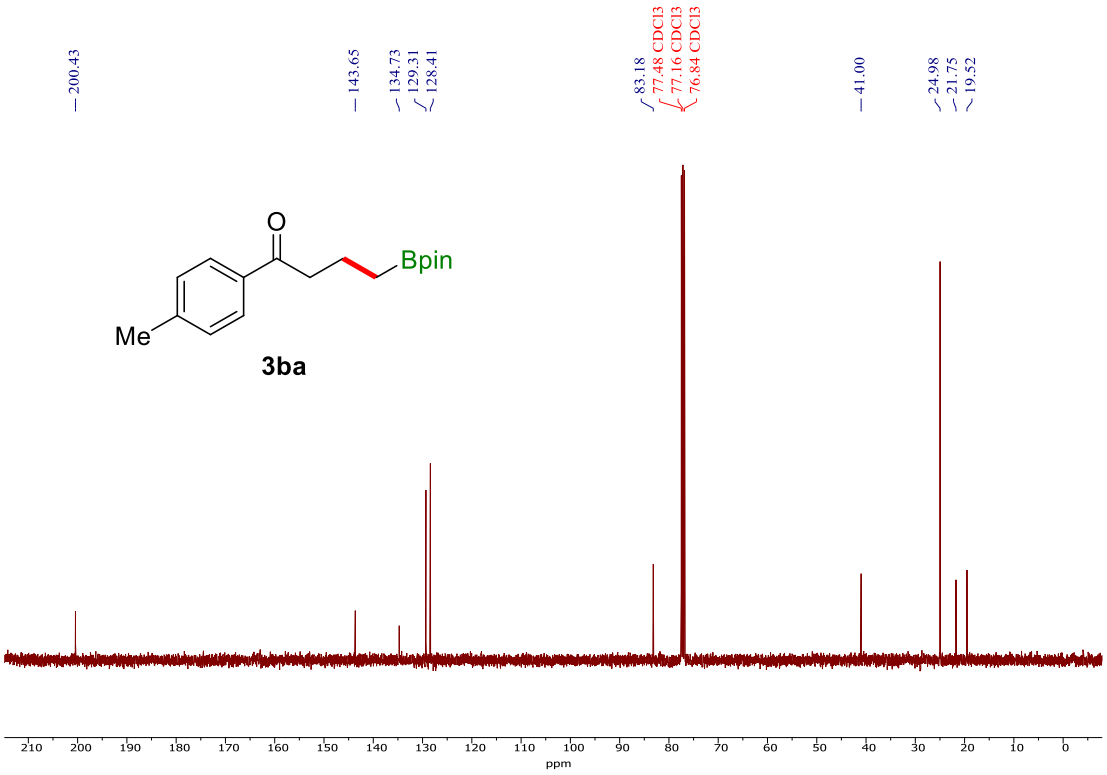
^{11}B NMR (128 MHz, $CDCl_3$) of **3aa**



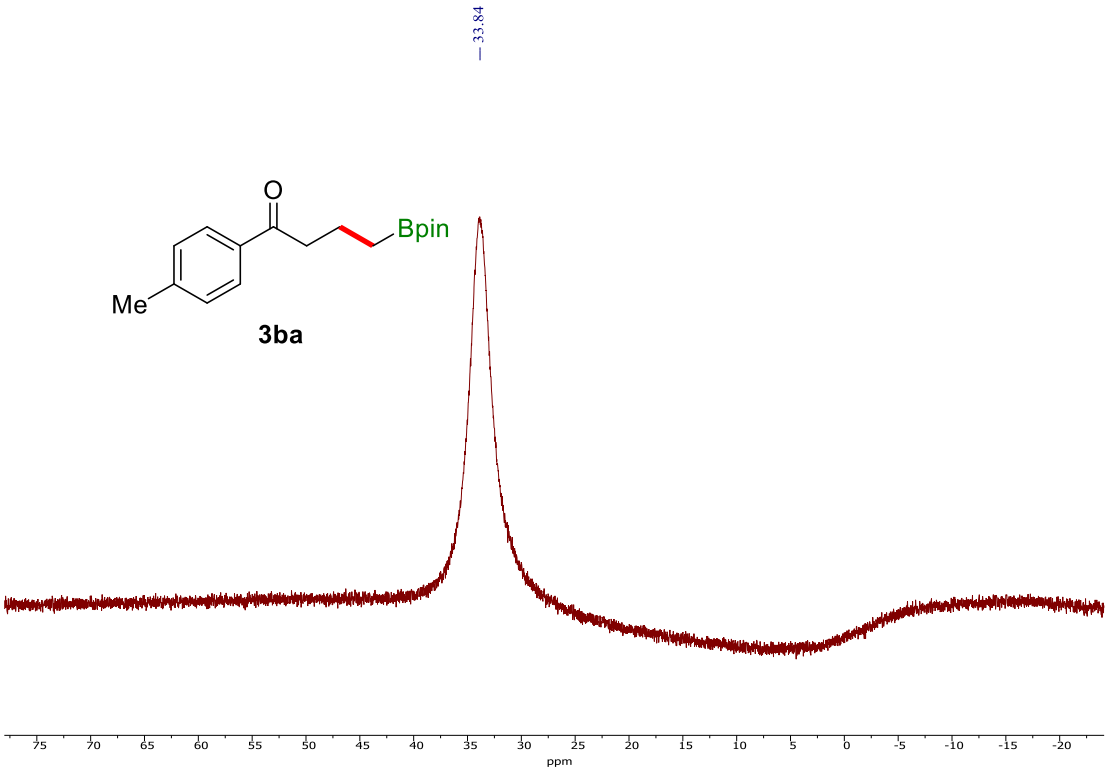
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba** (*see procedure*)



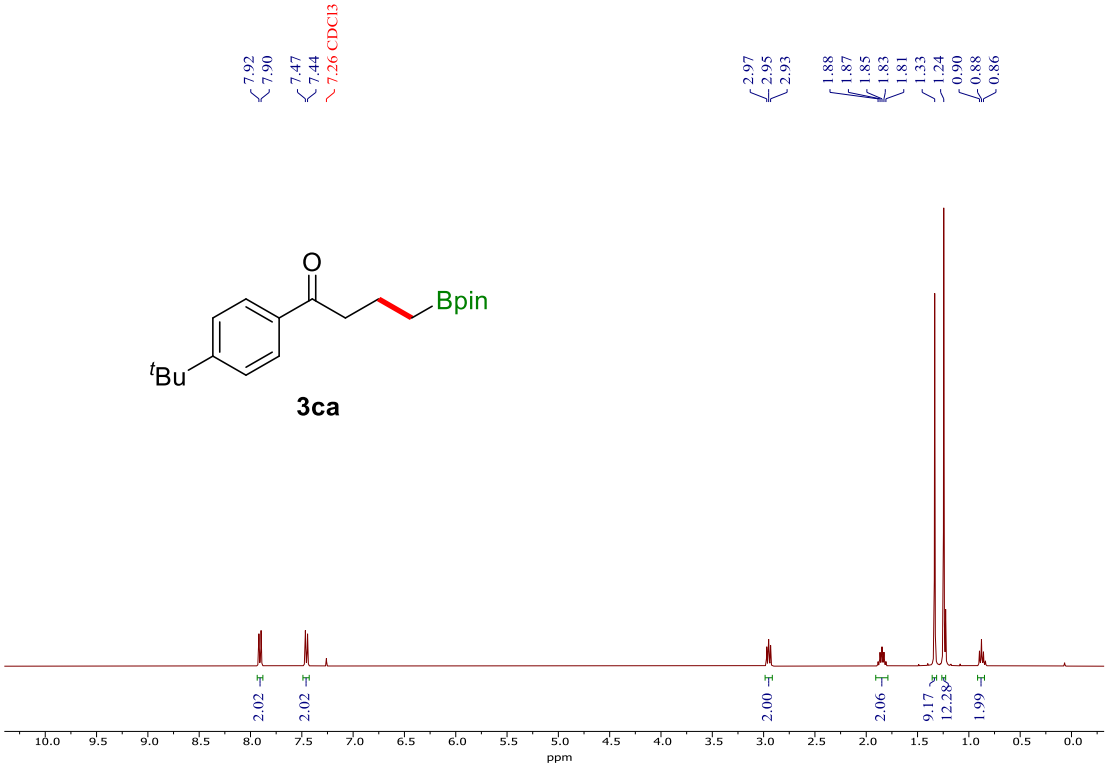
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**



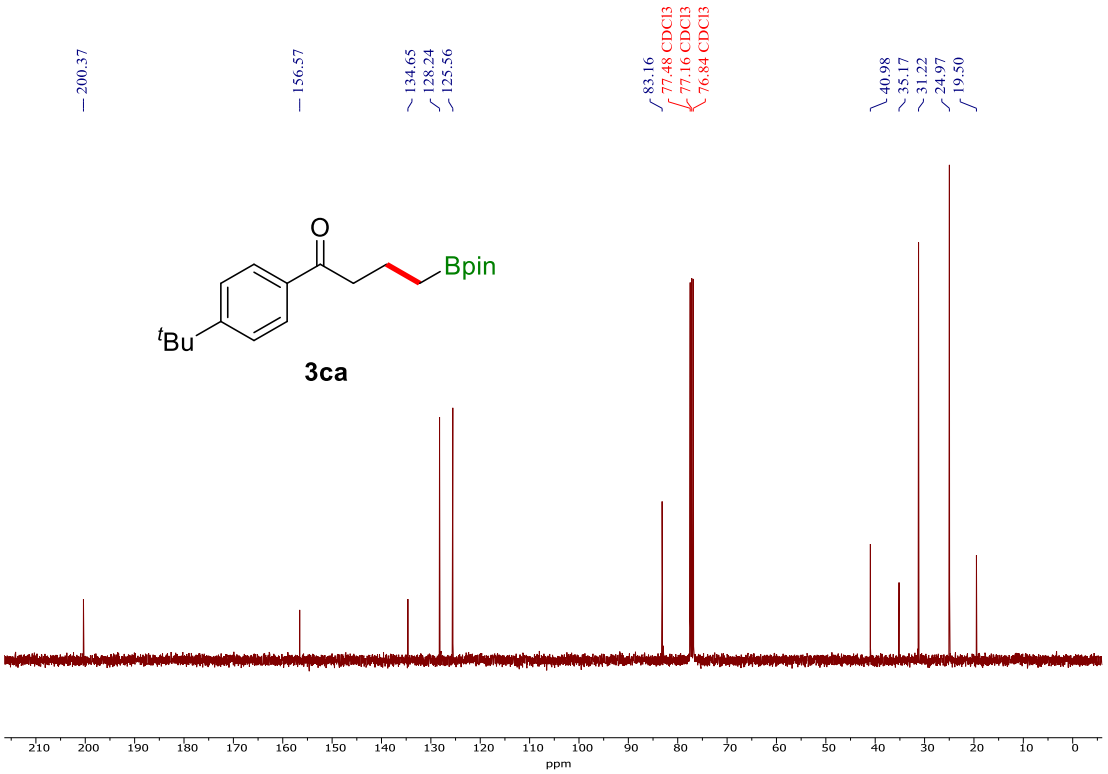
^{11}B NMR (128 MHz, $CDCl_3$) of **3ba**



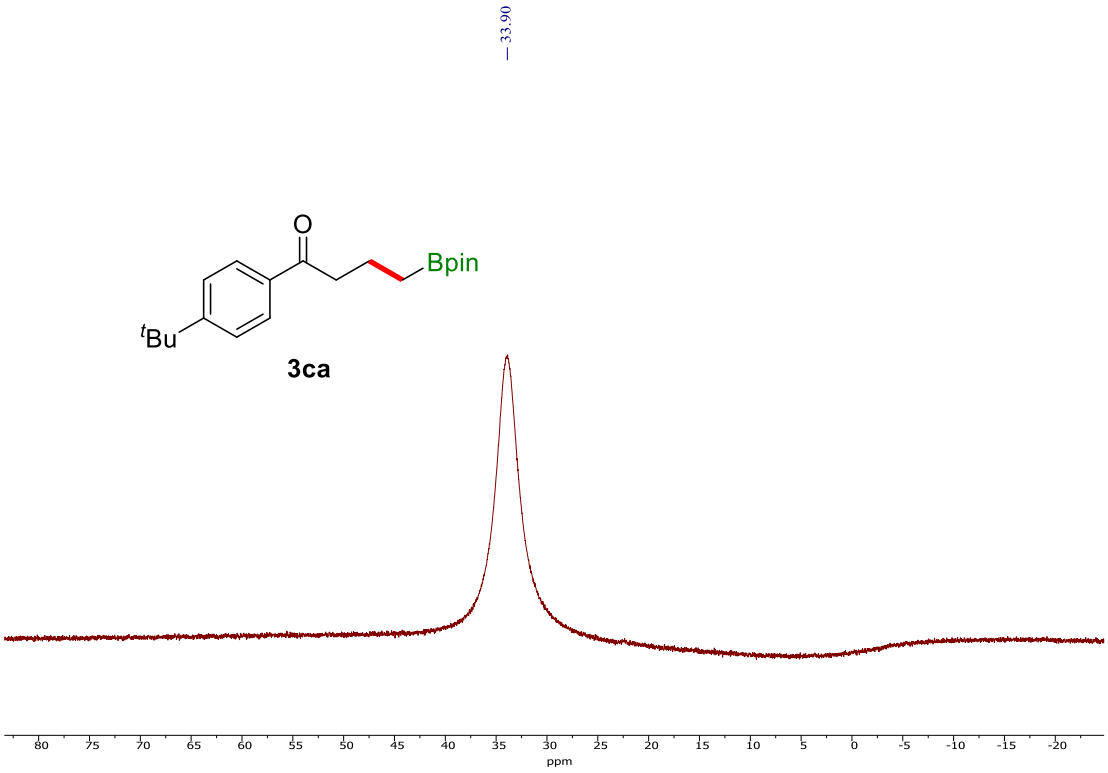
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca** (*see procedure*)



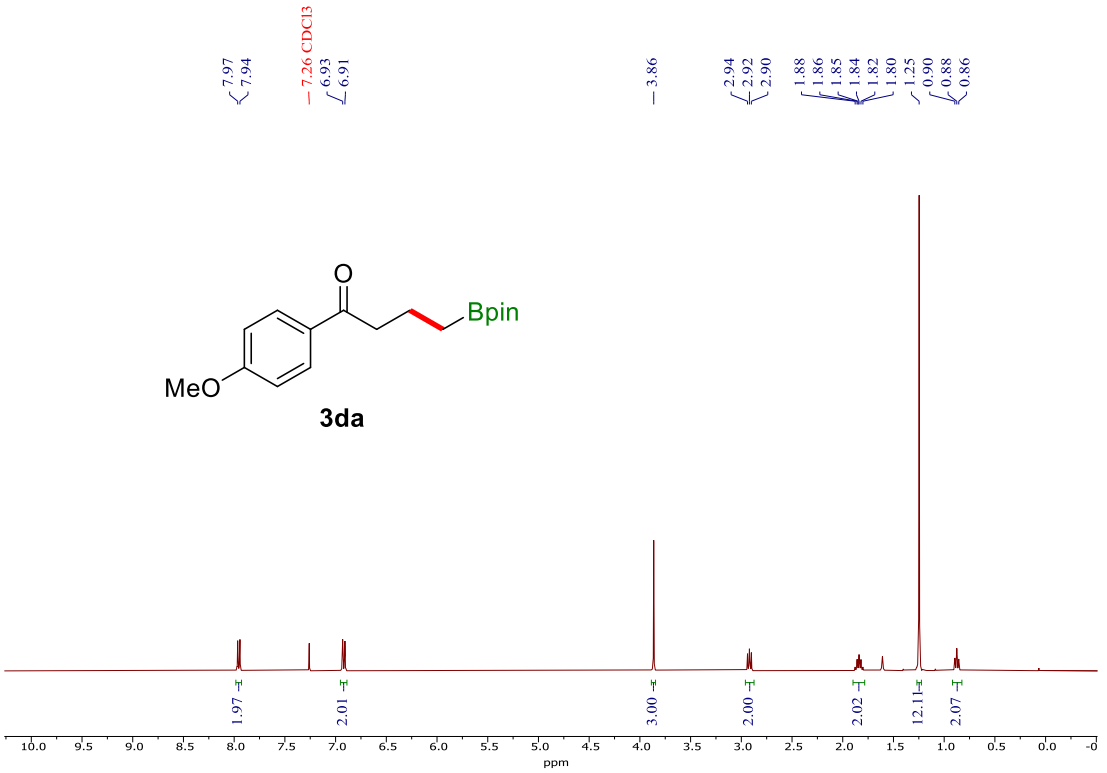
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**



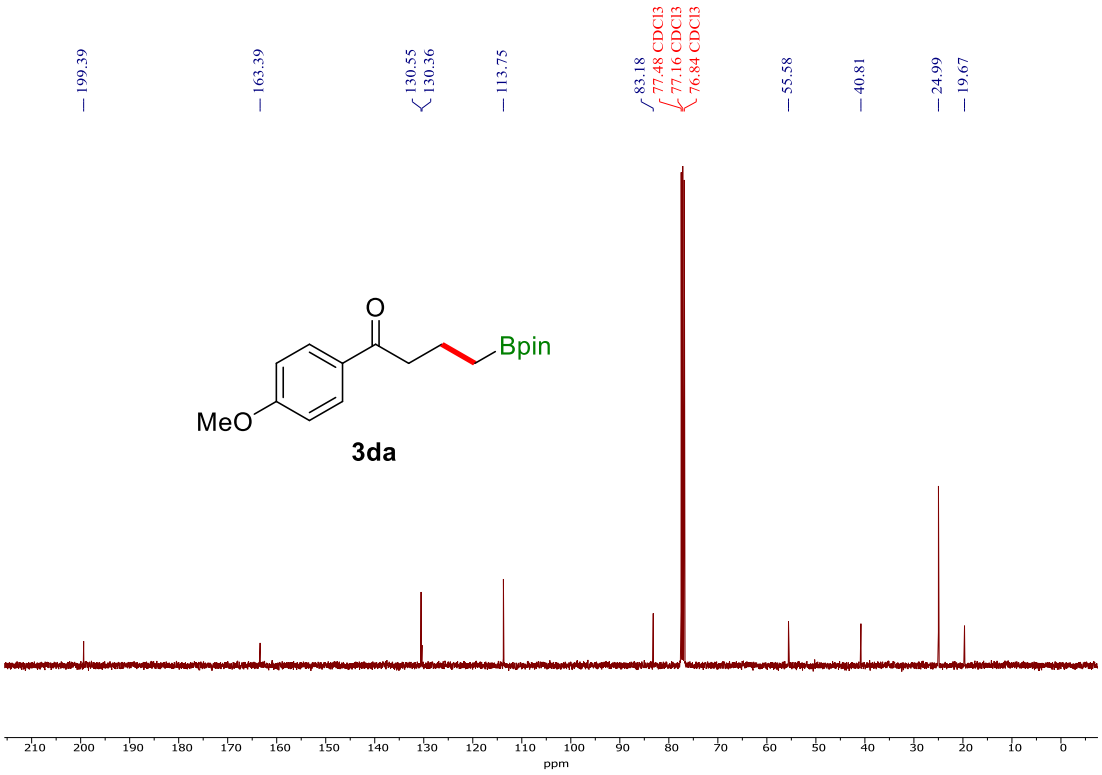
^{11}B NMR (128 MHz, $CDCl_3$) of **3ca**



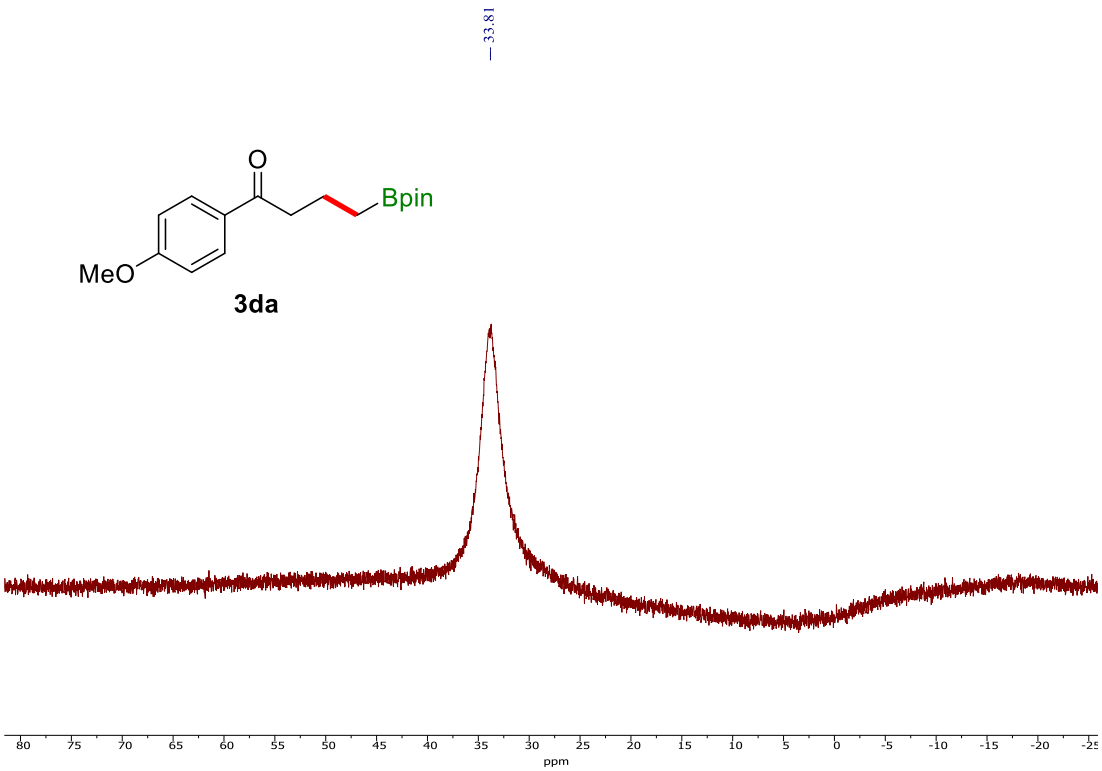
^{1}H NMR (400 MHz, $CDCl_3$) of **3da** (*see procedure*)



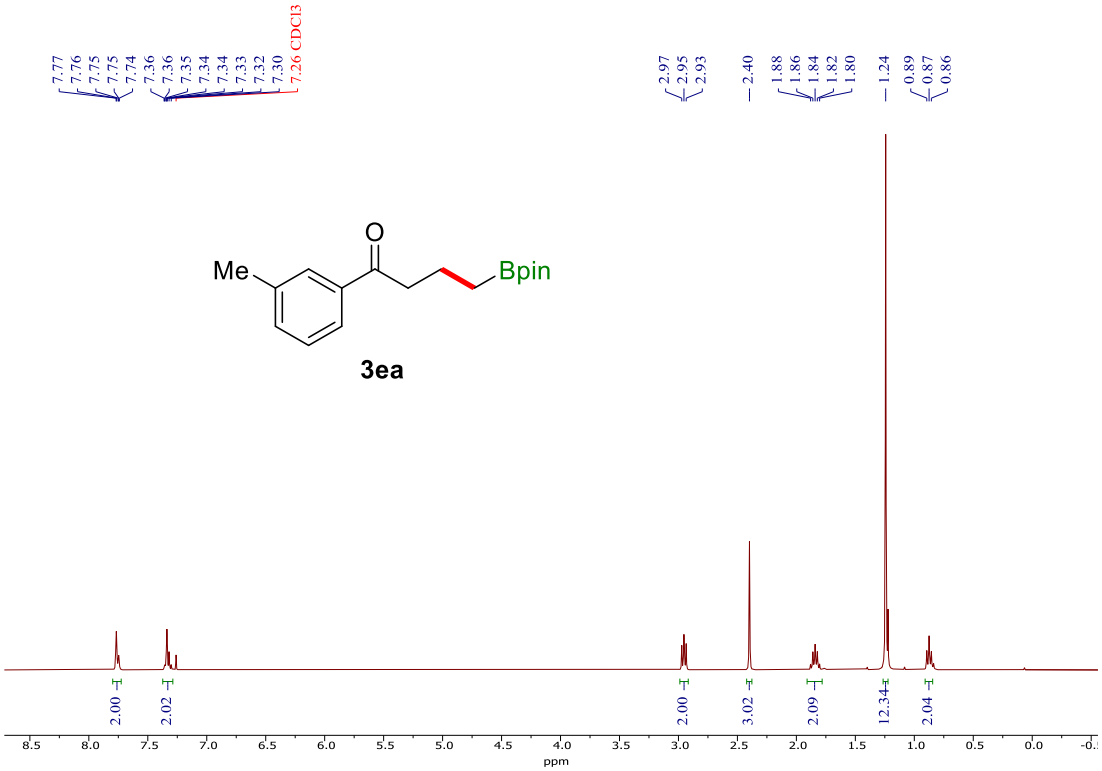
^{13}C NMR (101 MHz, $CDCl_3$) of **3da**



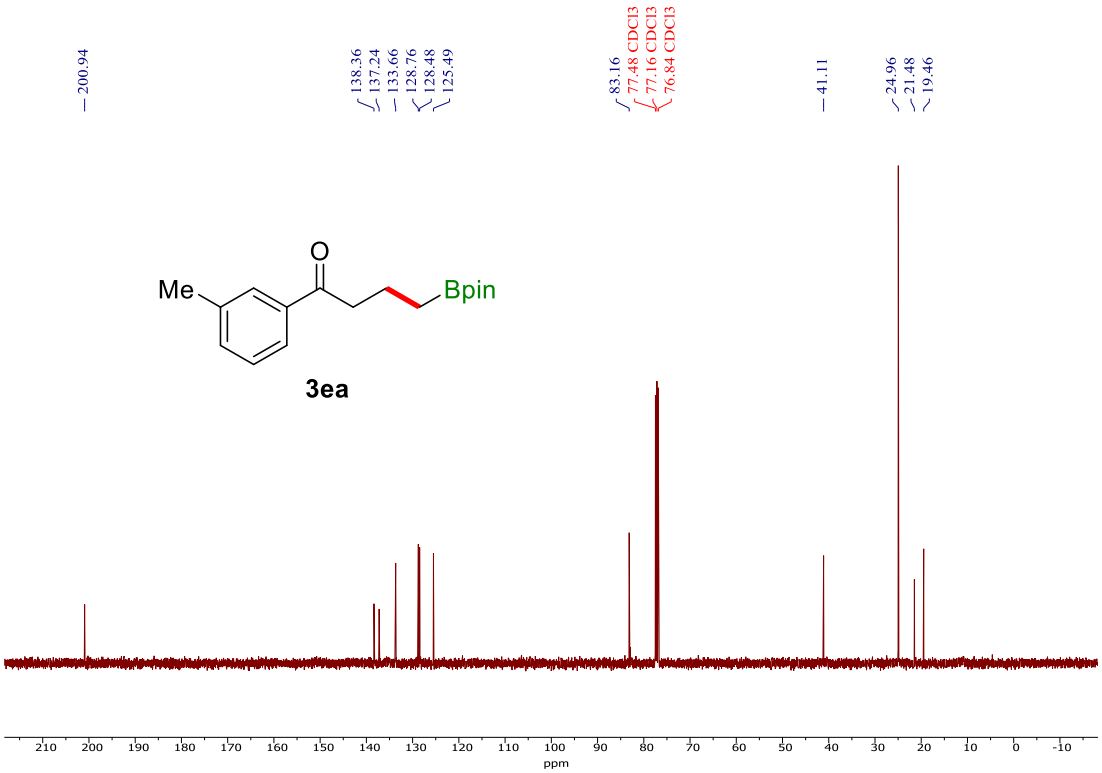
^{11}B NMR (128 MHz, $CDCl_3$) of **3da**



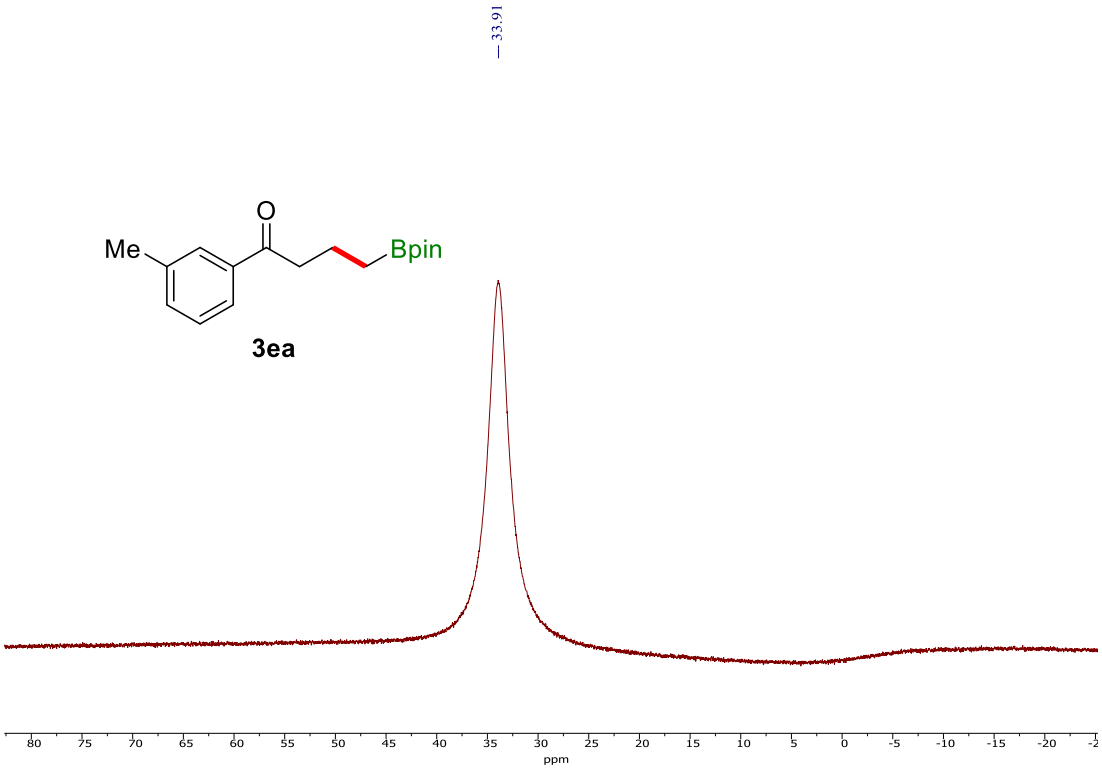
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea** (*see procedure*)



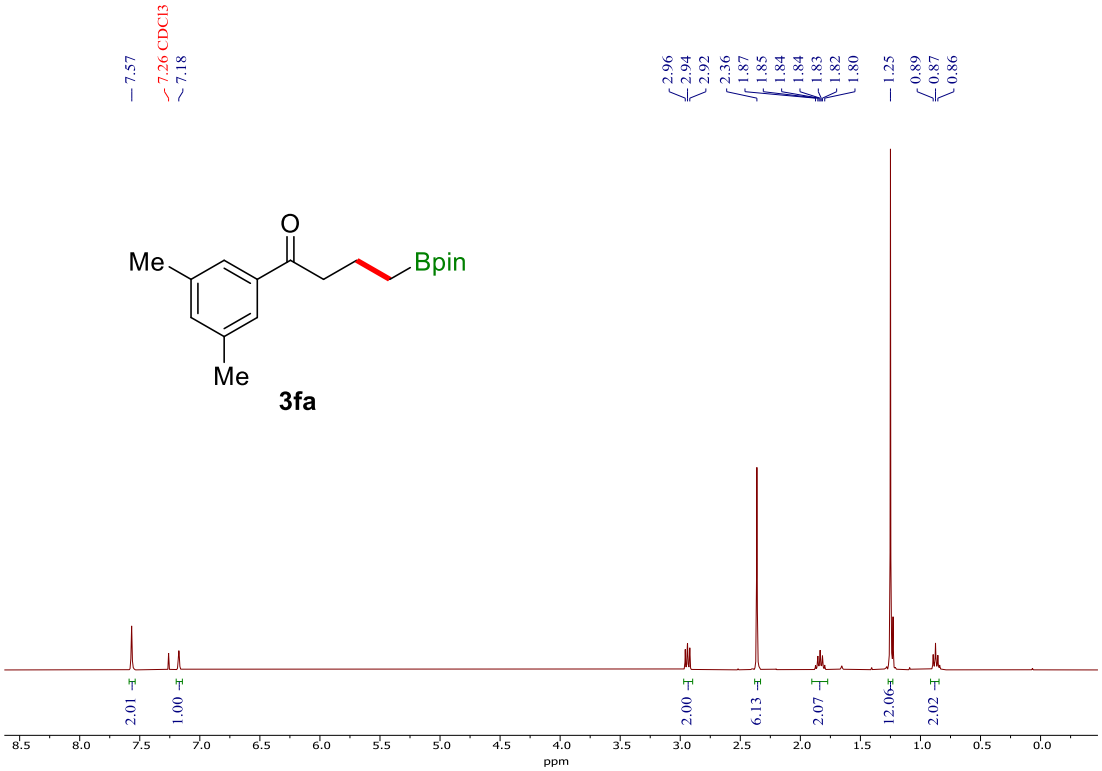
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



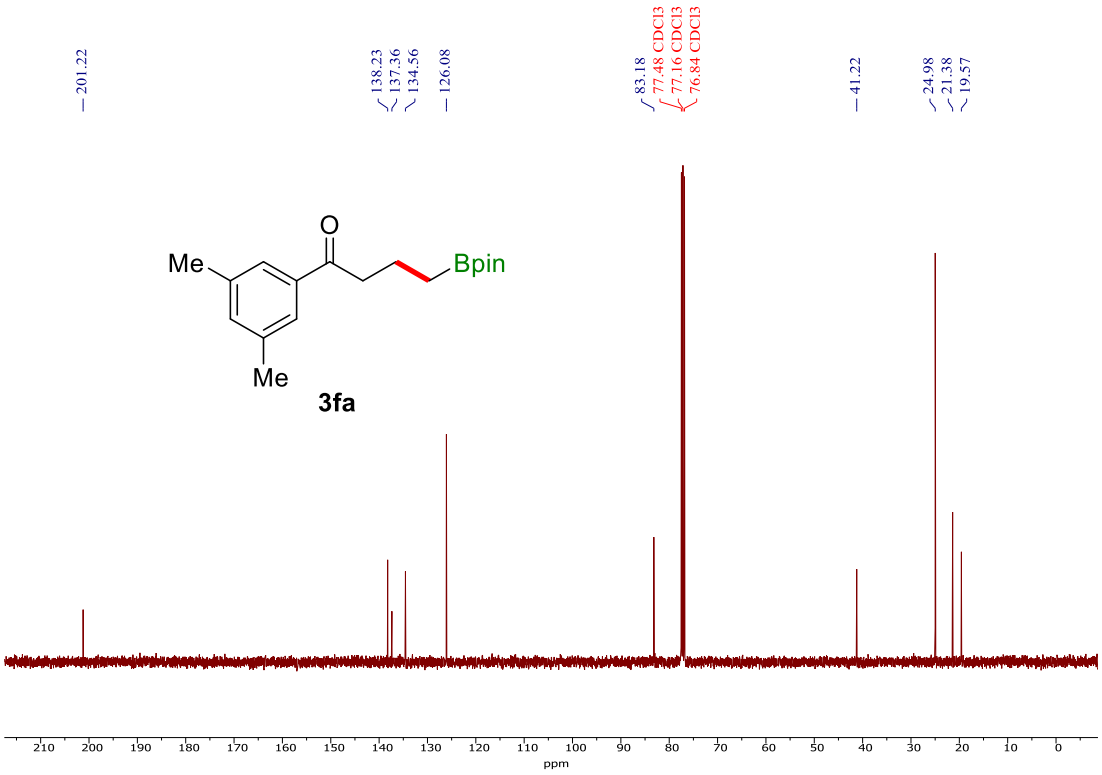
^{11}B NMR (128 MHz, $CDCl_3$) of **3ea**



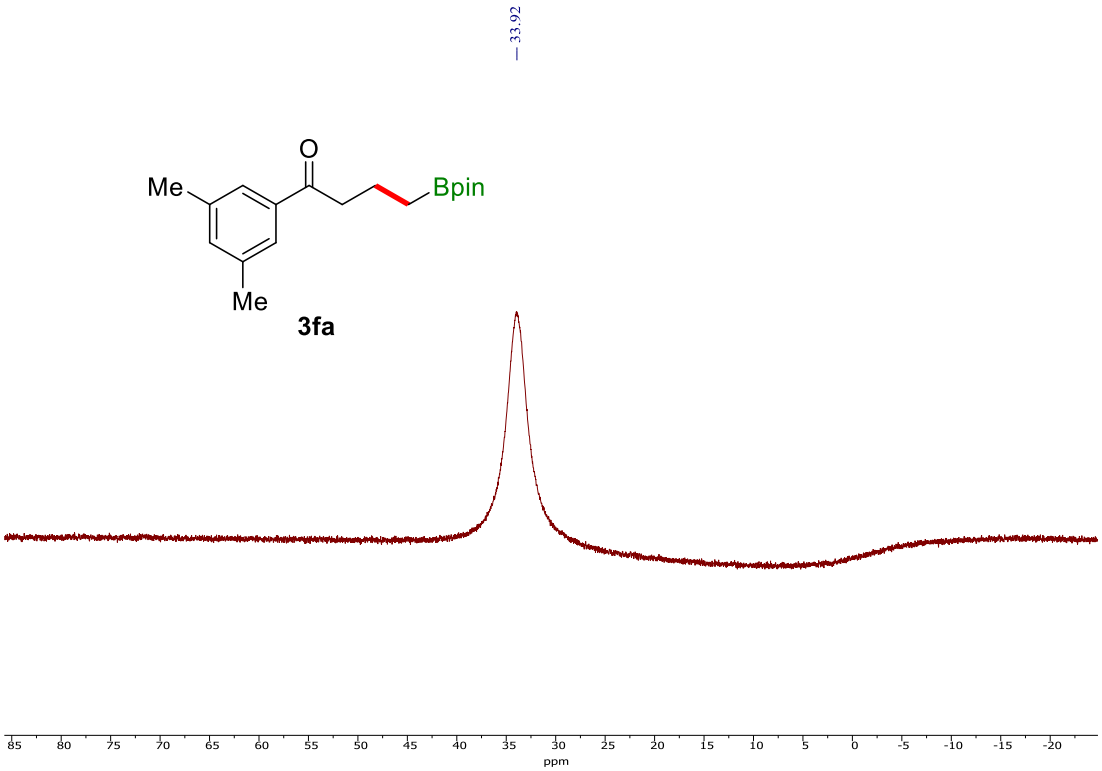
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa** (*see procedure*)



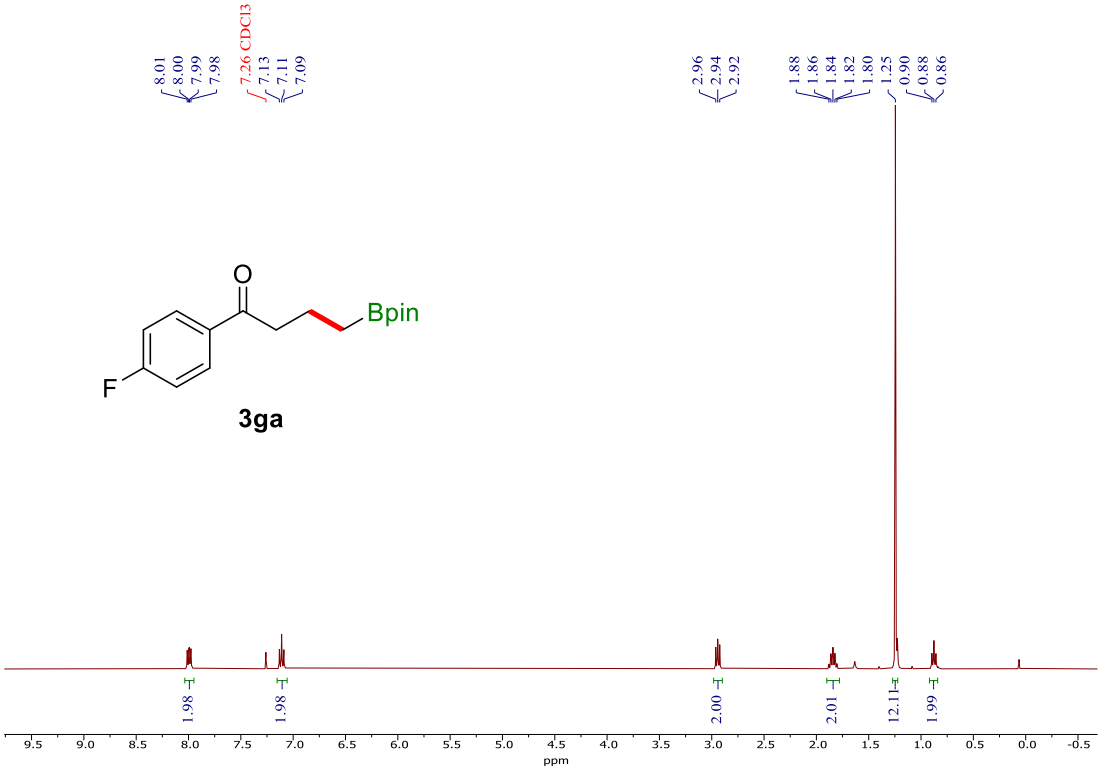
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



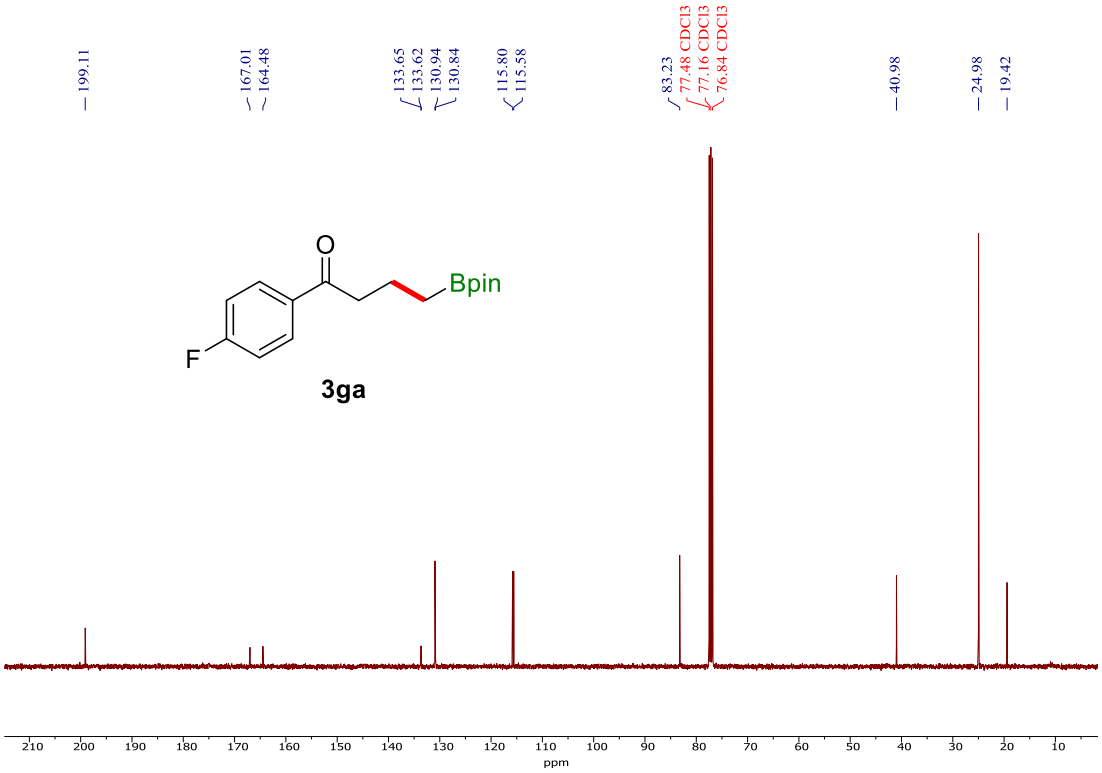
^{11}B NMR (128 MHz, $CDCl_3$) of **3fa**



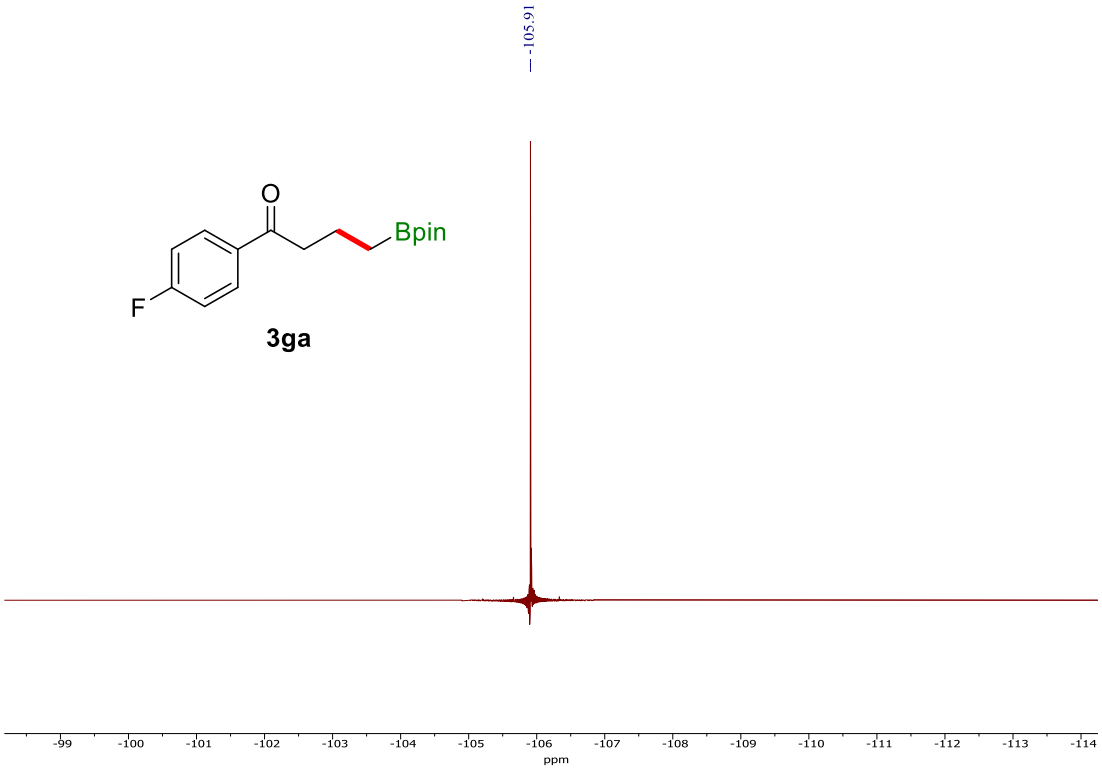
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga** (*see procedure*)



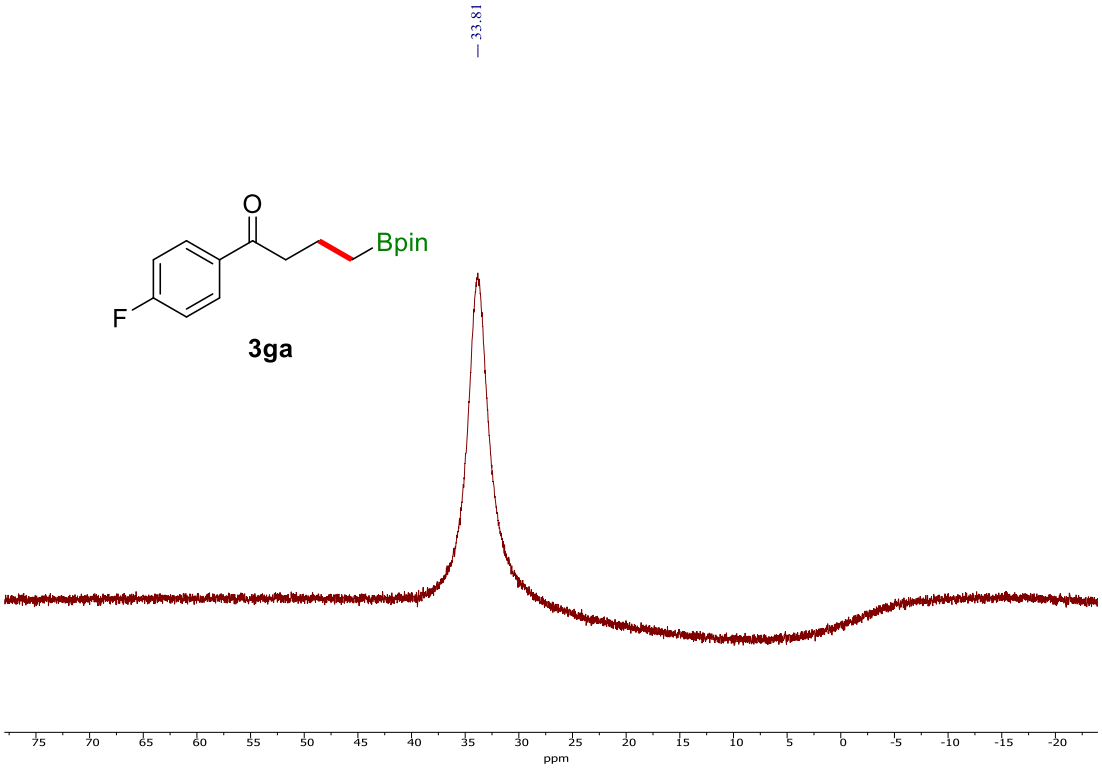
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



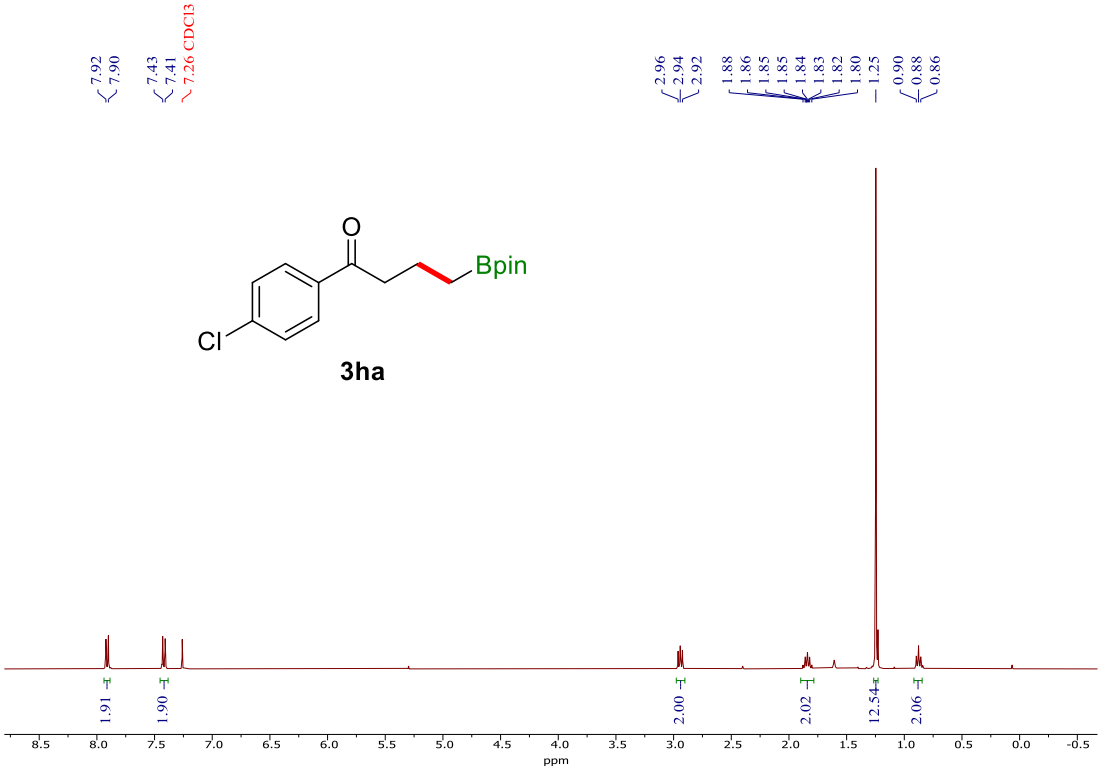
19F NMR (376 MHz, CDCl3) of **3ga**



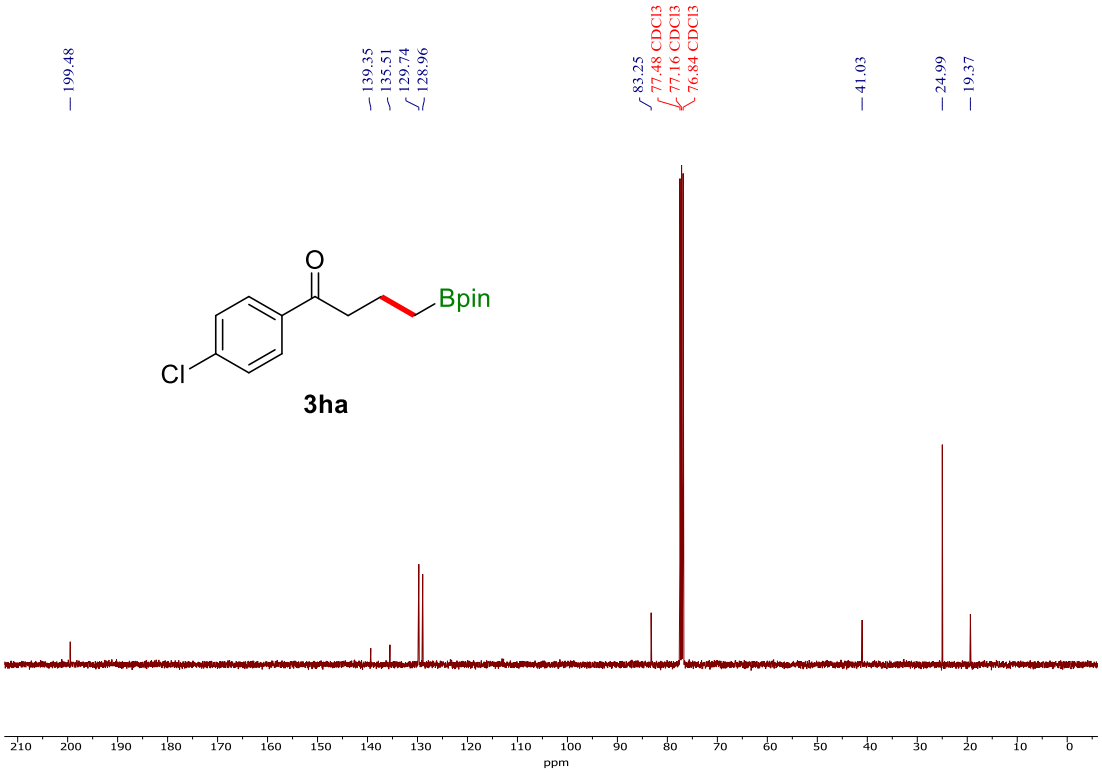
^{11}B NMR (128 MHz, $CDCl_3$) of **3ga**



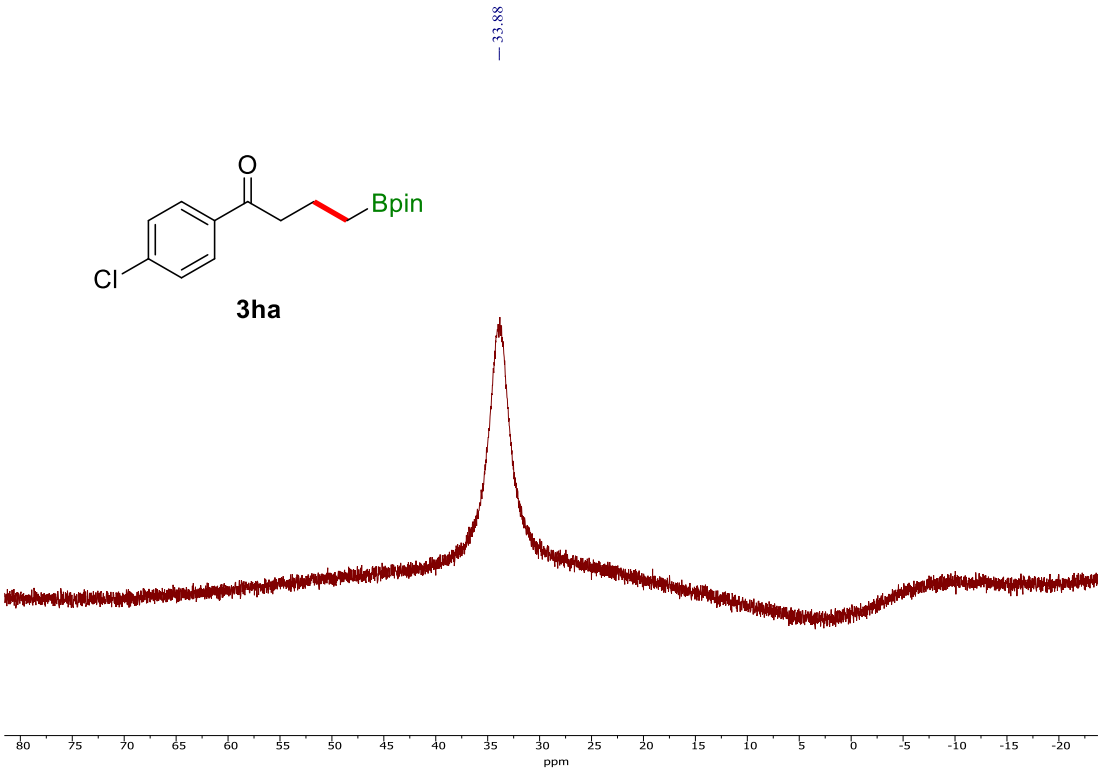
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha** (*see procedure*)



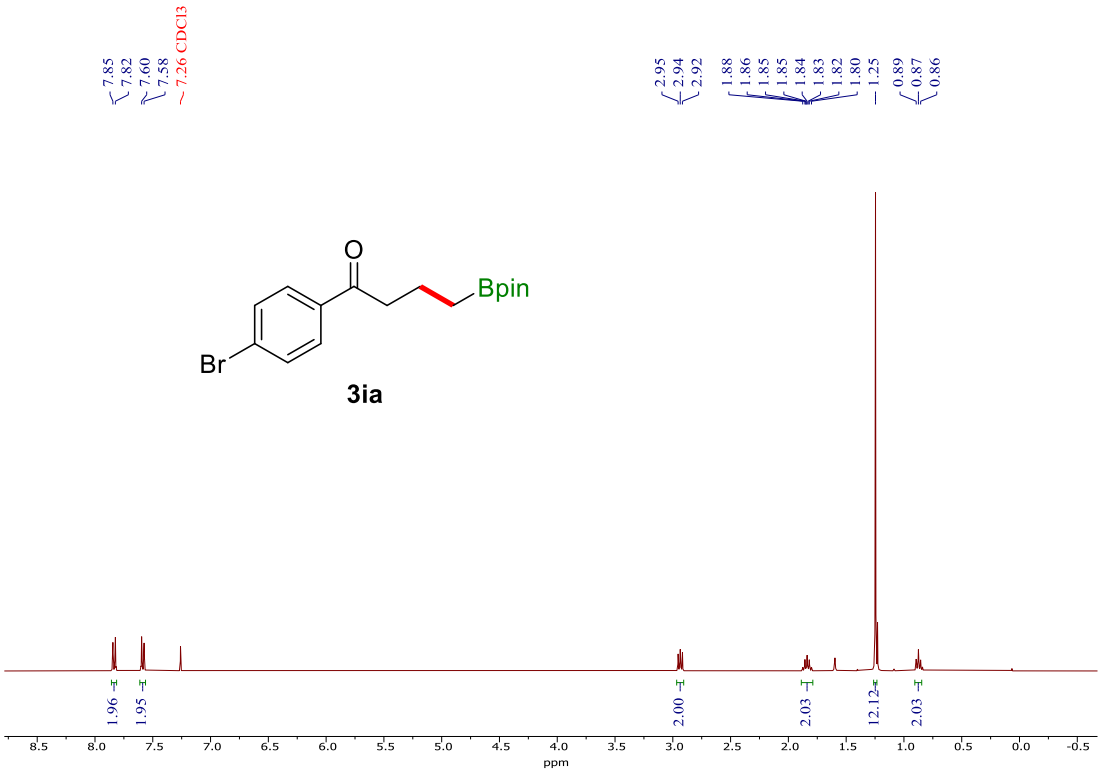
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



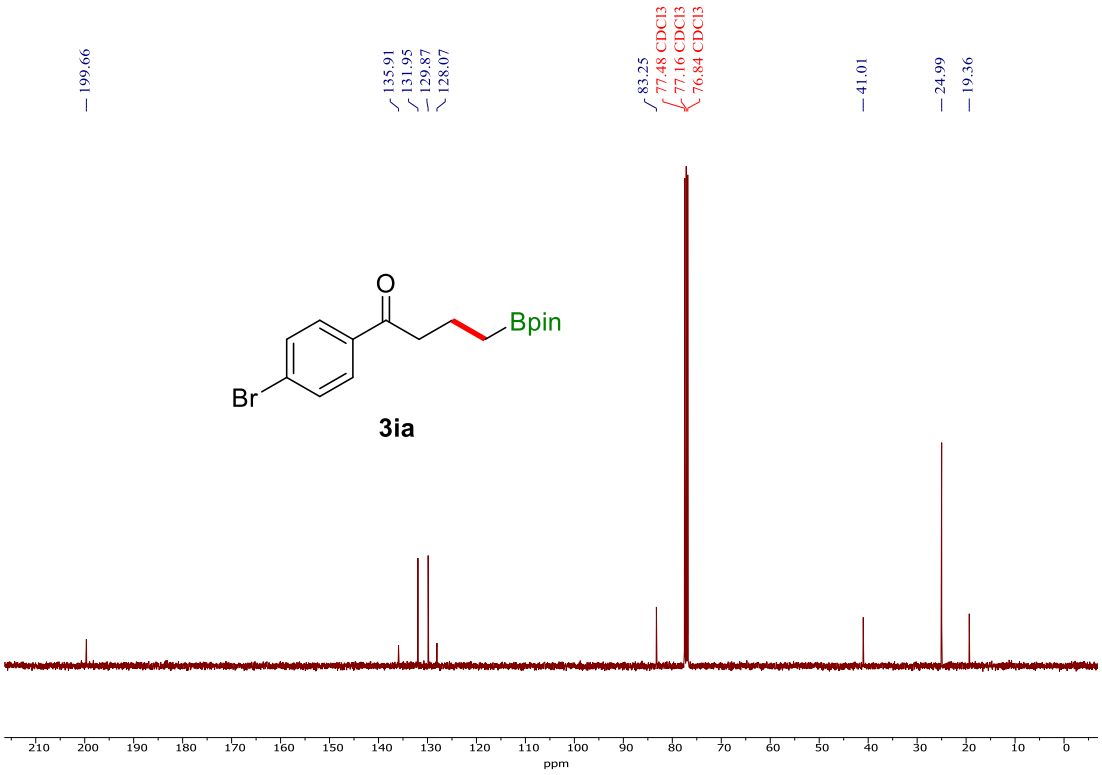
^{11}B NMR (128 MHz, $CDCl_3$) of **3ha**



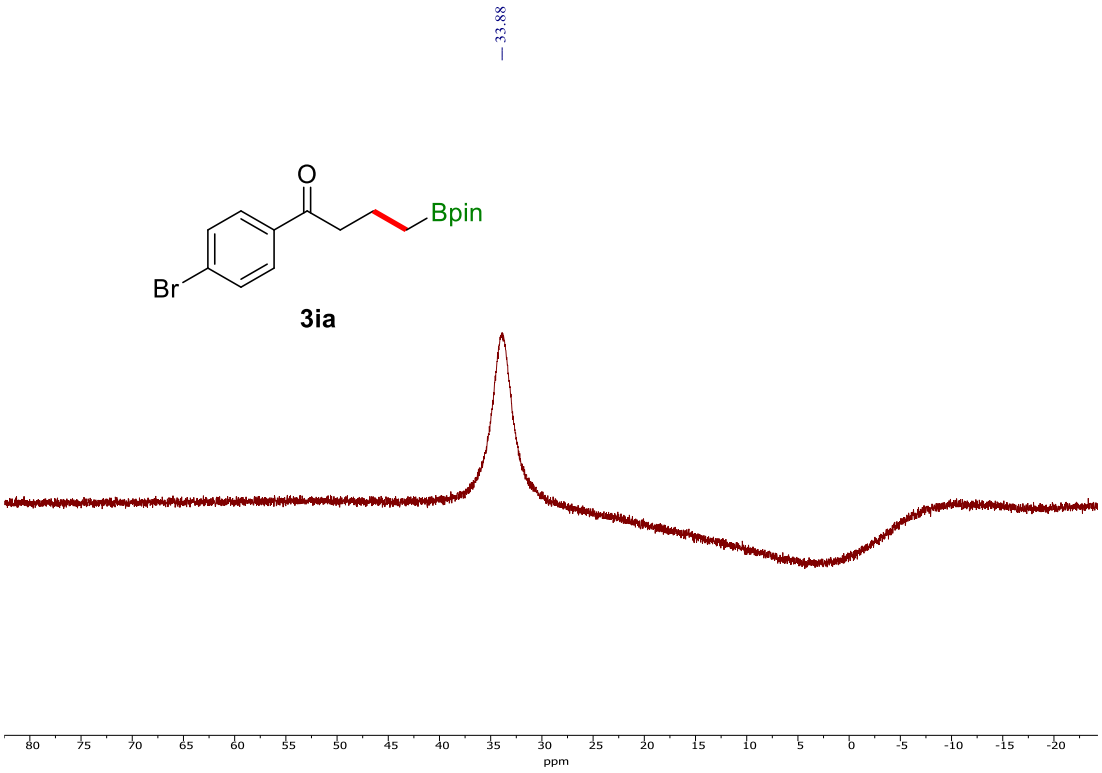
^{1}H NMR (400 MHz, $CDCl_3$) of **3ia** (*see procedure*)



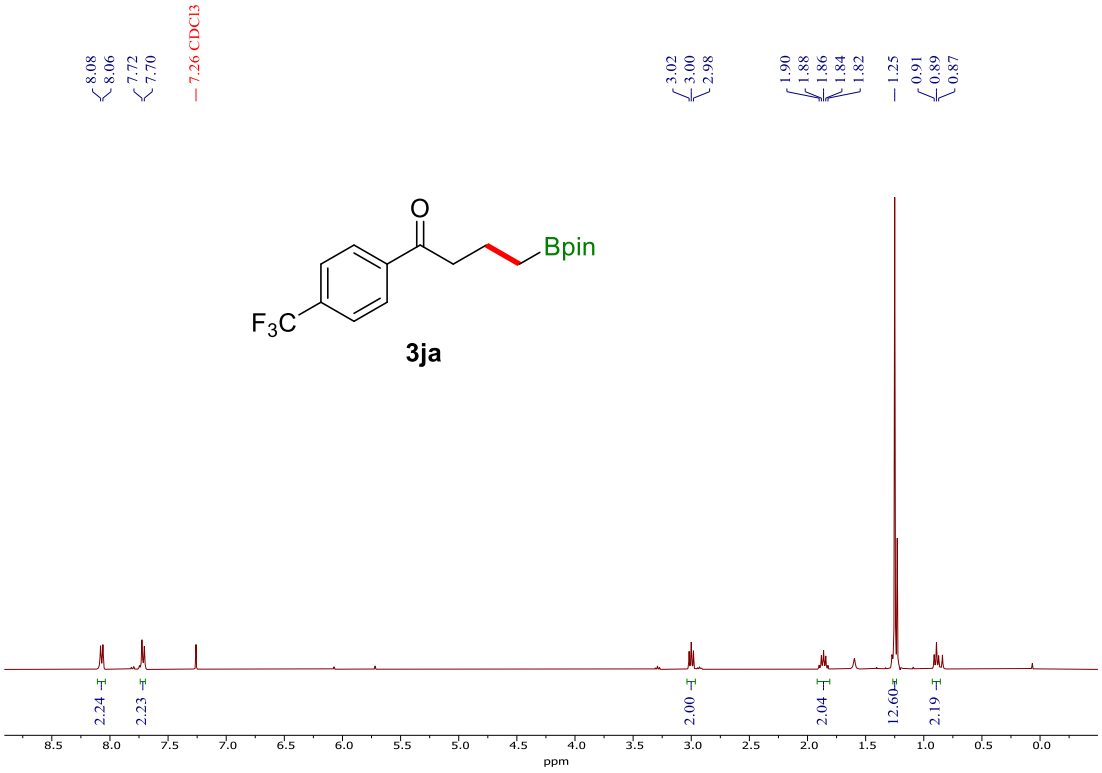
^{13}C NMR (101 MHz, $CDCl_3$) of **3ia**



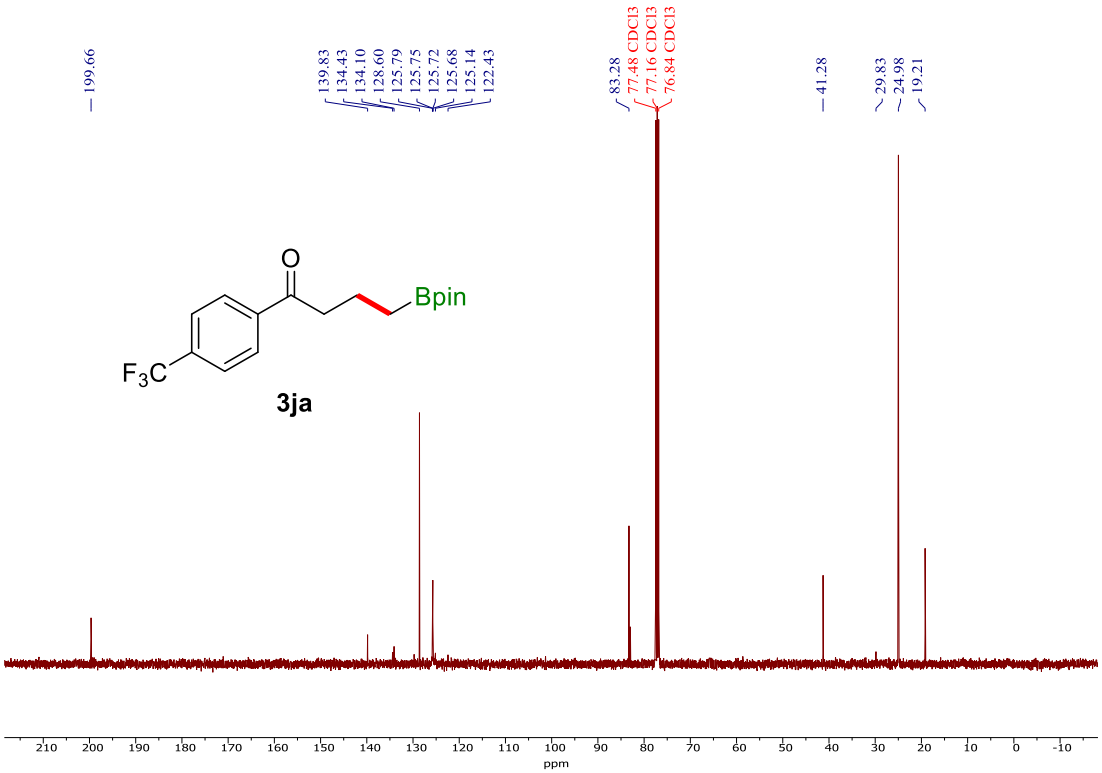
^{11}B NMR (128 MHz, $CDCl_3$) of **3ia**



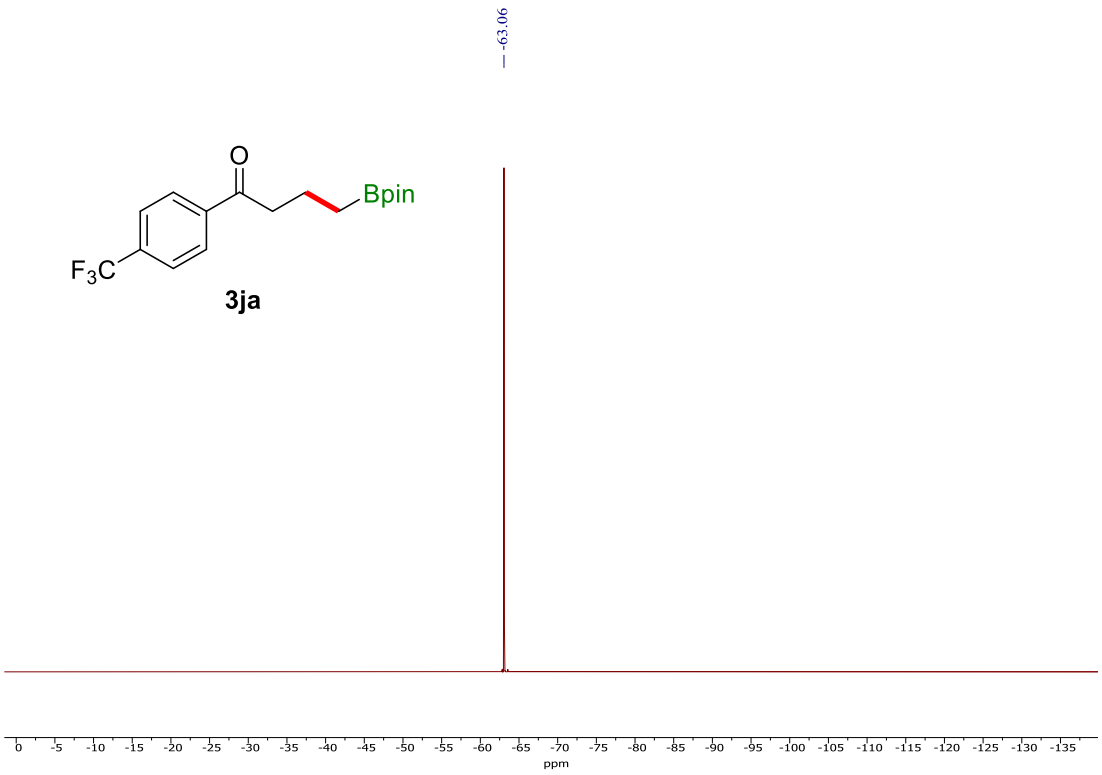
^{1}H NMR (400 MHz, $CDCl_3$) of **3ja** (*see procedure*)



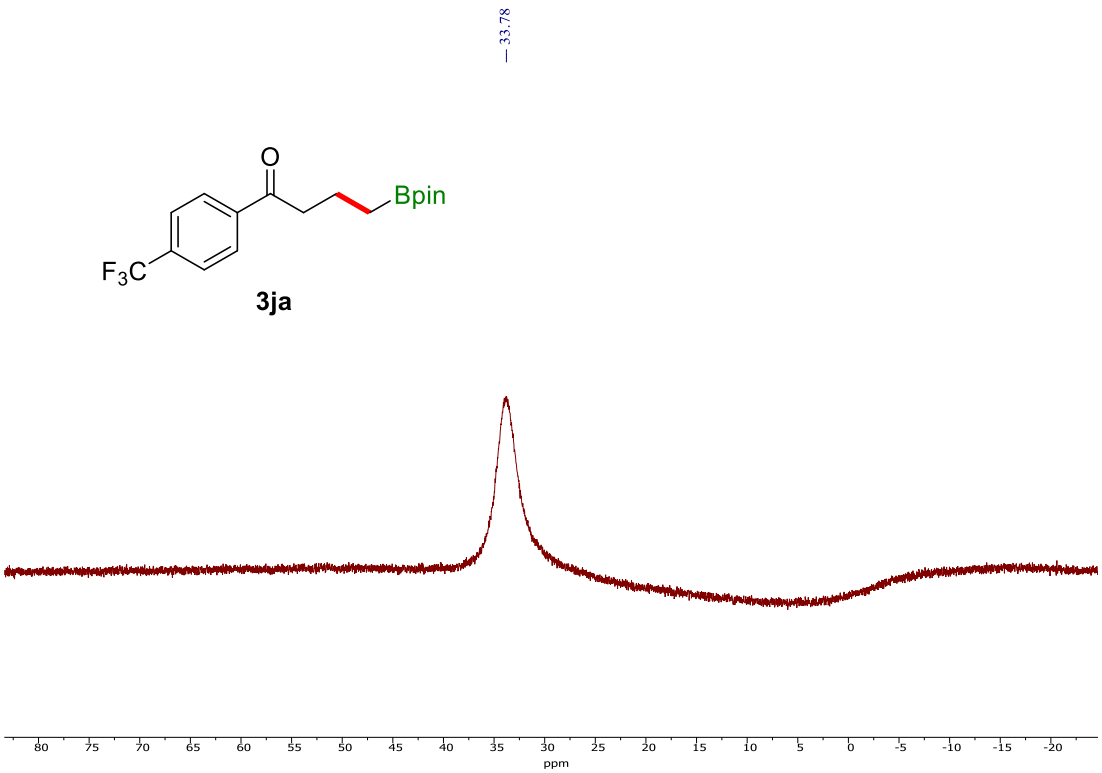
^{13}C NMR (101 MHz, $CDCl_3$) of **3ja**



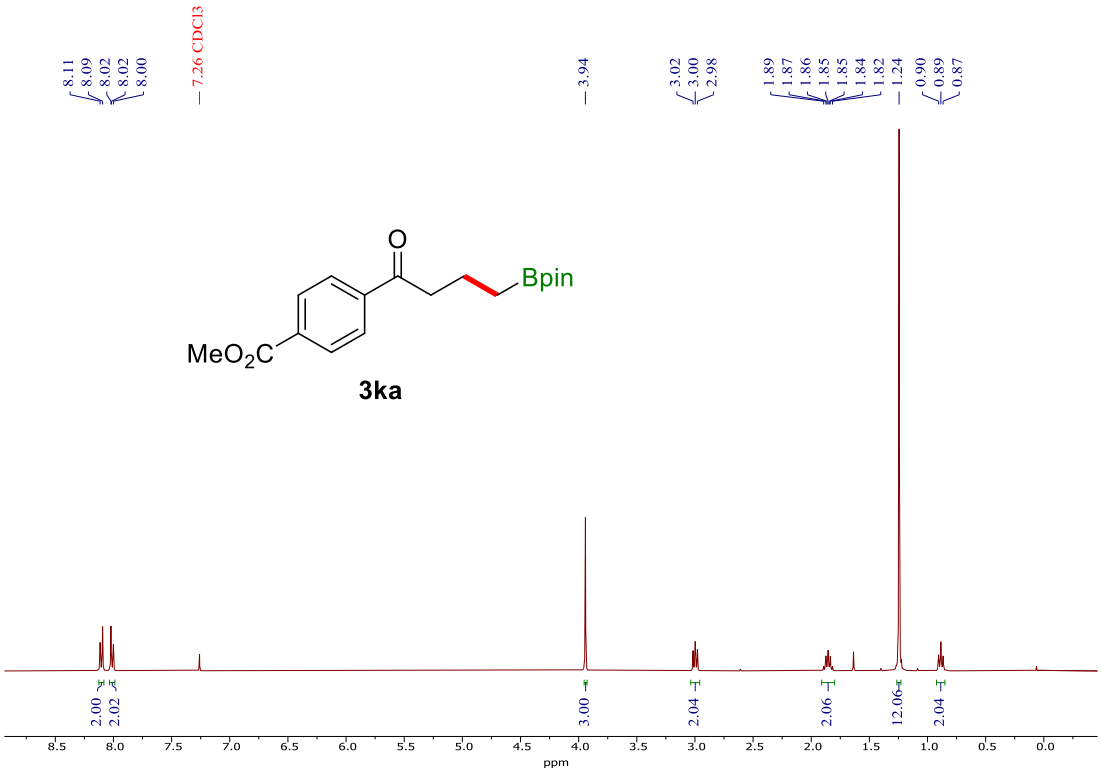
^{19}F NMR (376 MHz, CDCl3) of **3ja**



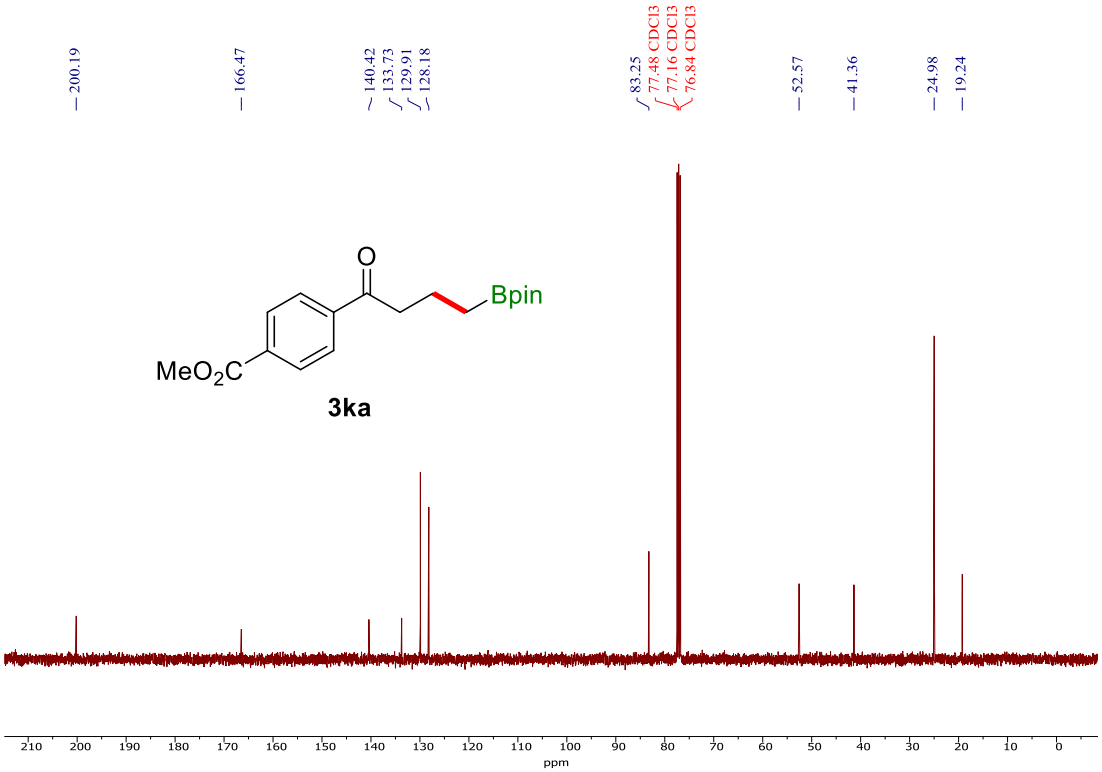
^{11}B NMR (128 MHz, $CDCl_3$) of **3ja**



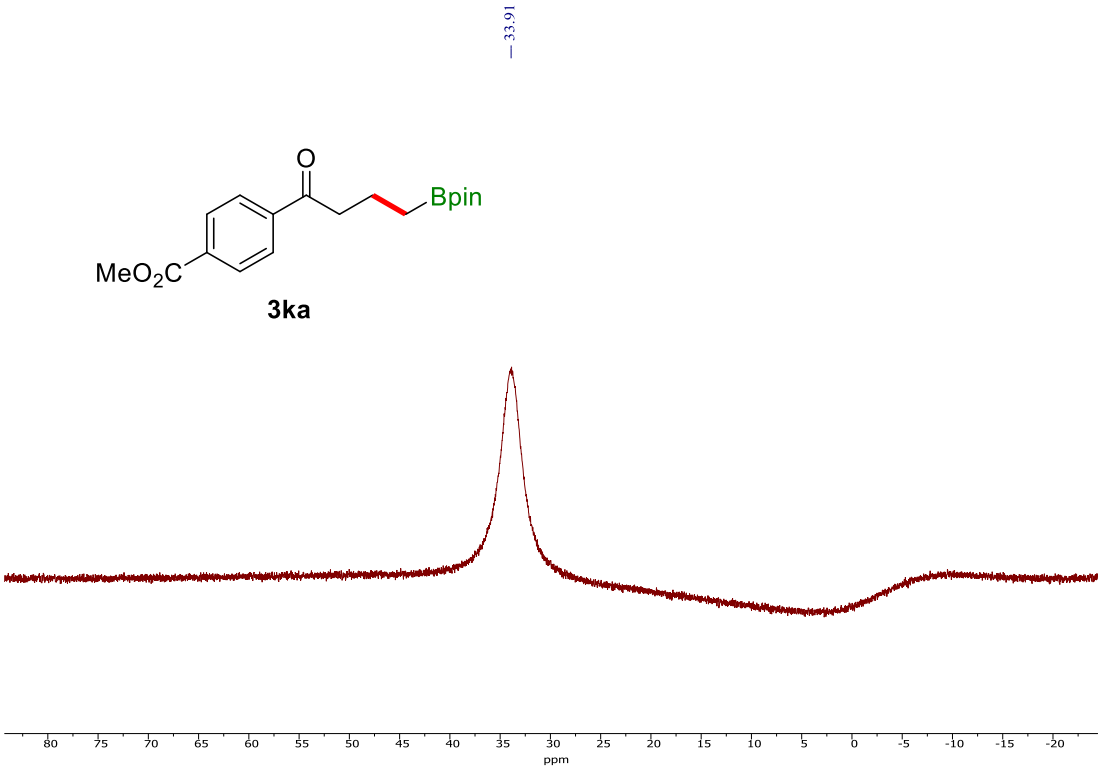
^{1}H NMR (400 MHz, $CDCl_3$) of **3ka** (*see procedure*)



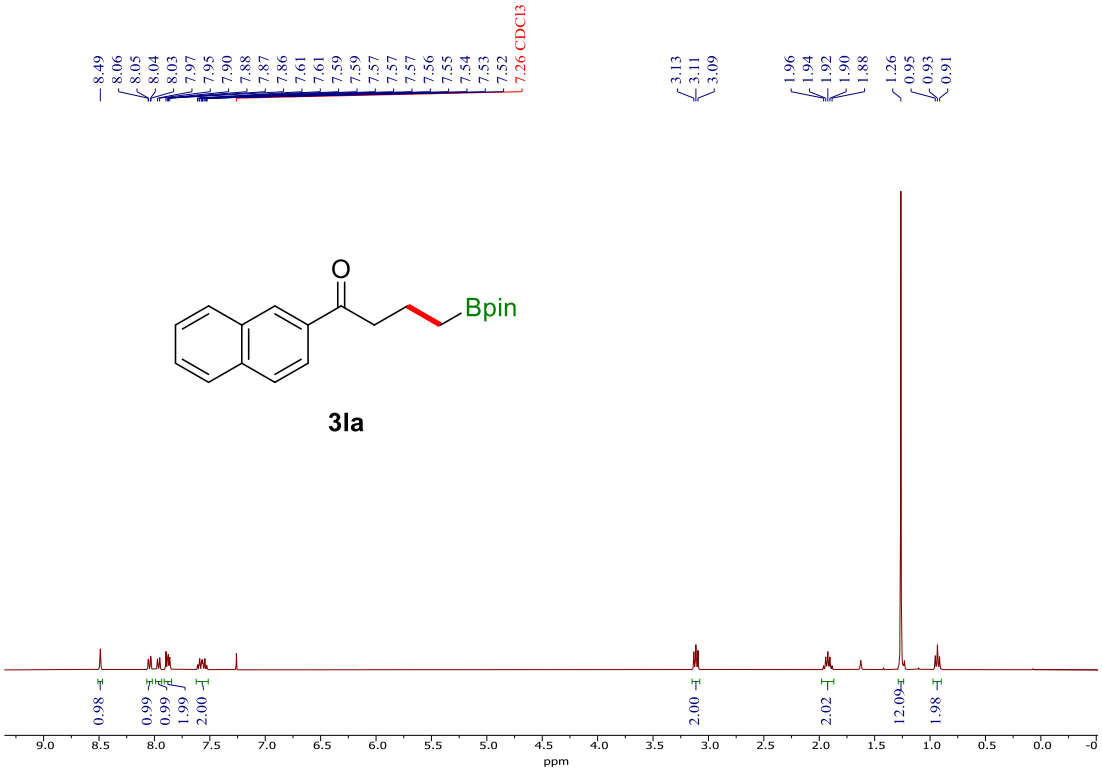
^{13}C NMR (101 MHz, $CDCl_3$) of **3ka**



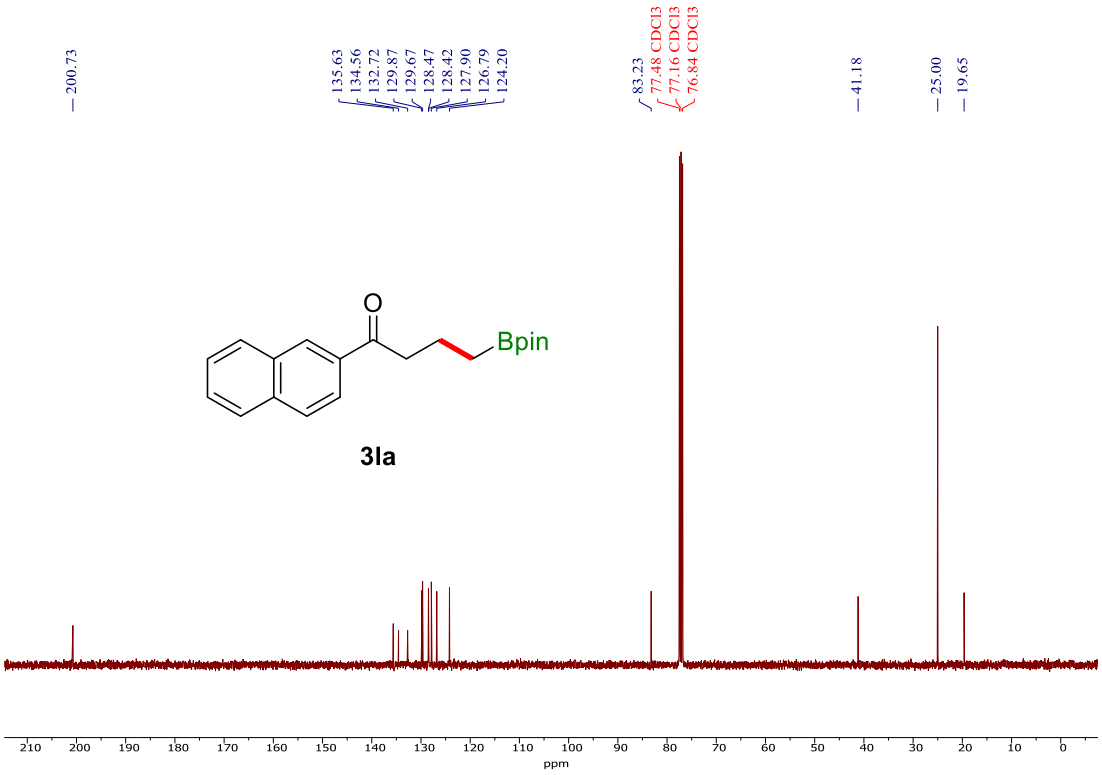
^{11}B NMR (128 MHz, $CDCl_3$) of **3ka**



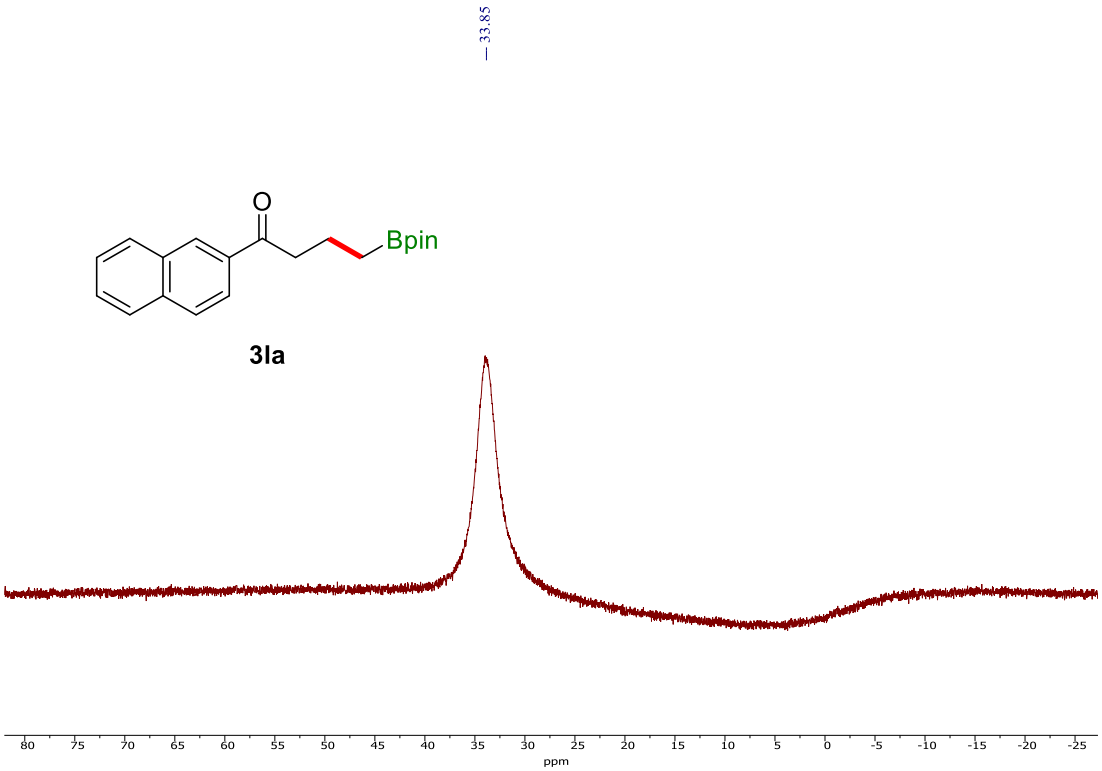
^{1}H NMR (400 MHz, $CDCl_3$) of **3la** (*see procedure*)



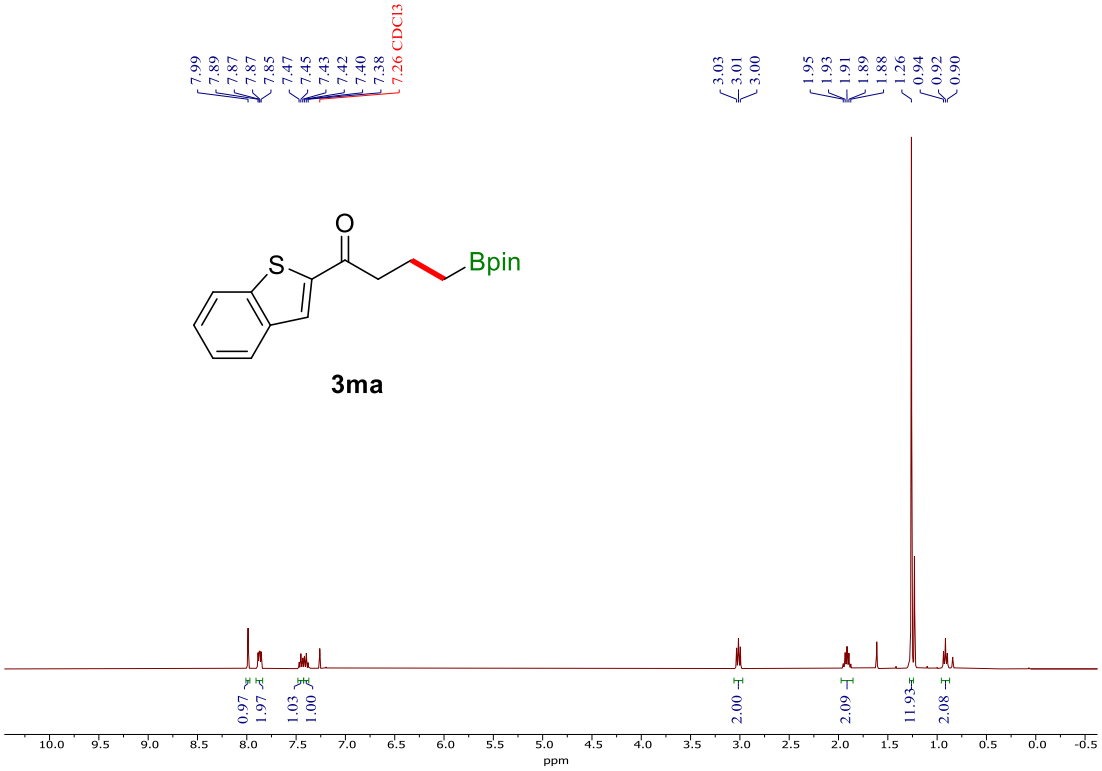
^{13}C NMR (101 MHz, $CDCl_3$) of **3la**



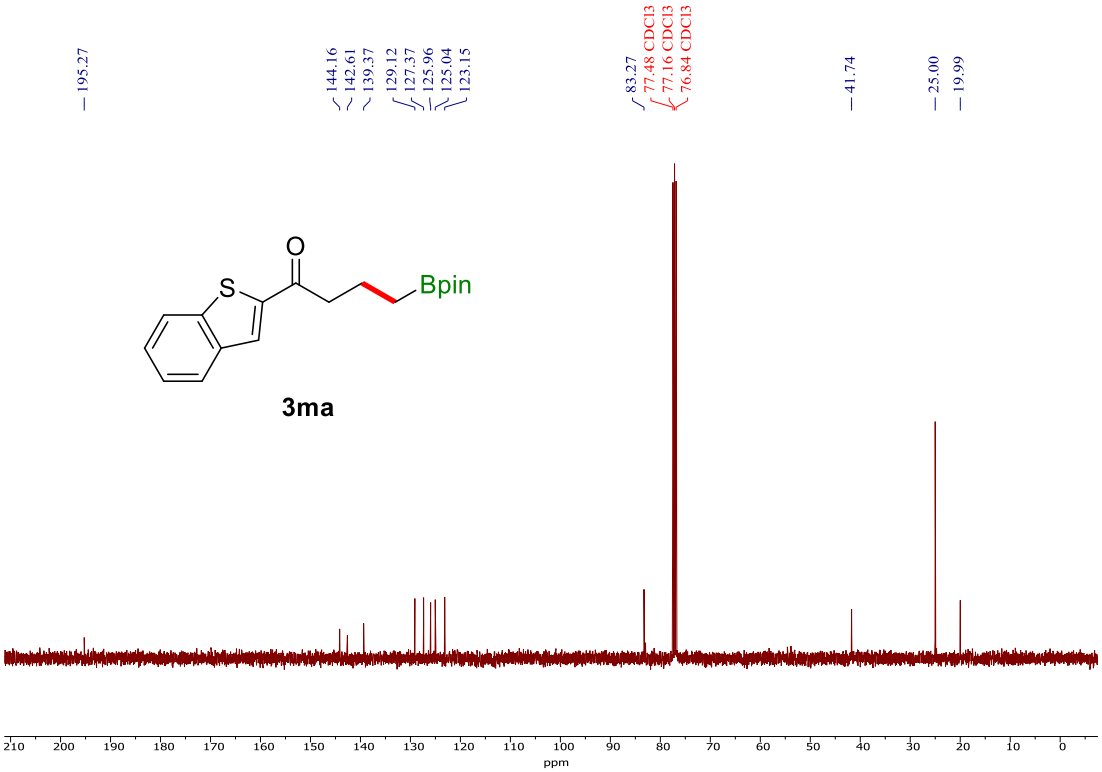
^{11}B NMR (128 MHz, $CDCl_3$) of **3la**



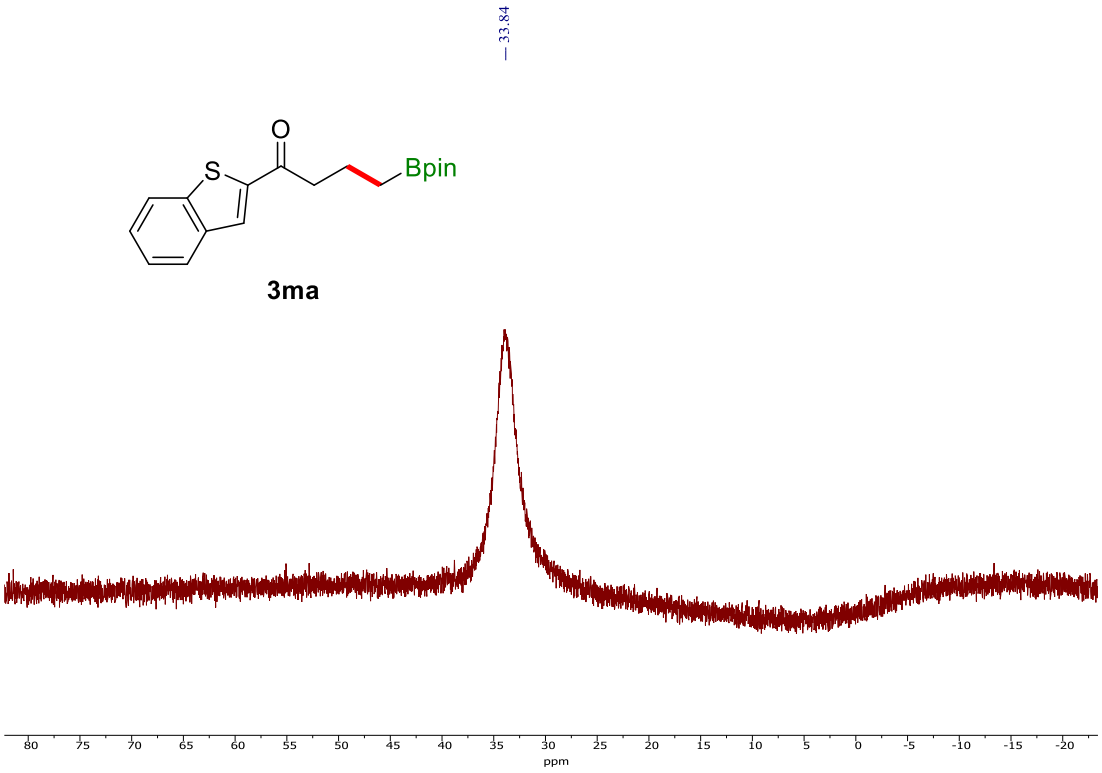
^{1}H NMR (400 MHz, $CDCl_3$) of **3ma** (*see procedure*)



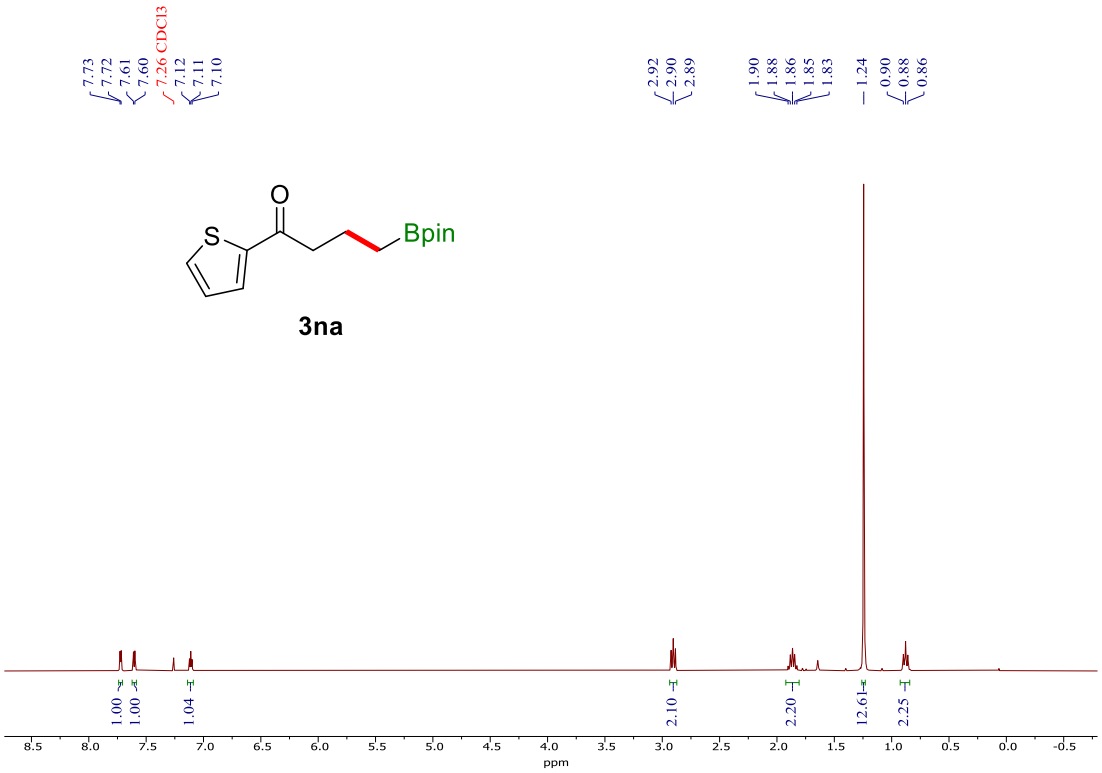
^{13}C NMR (101 MHz, $CDCl_3$) of **3ma**



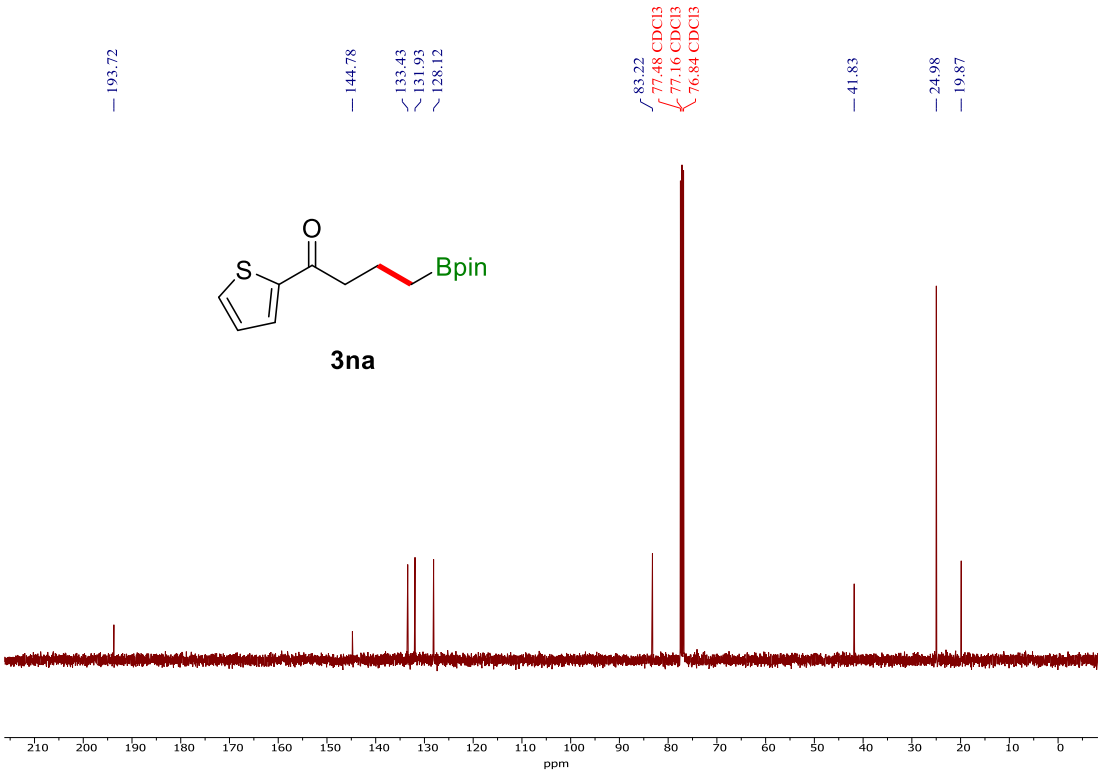
^{11}B NMR (128 MHz, $CDCl_3$) of **3ma**



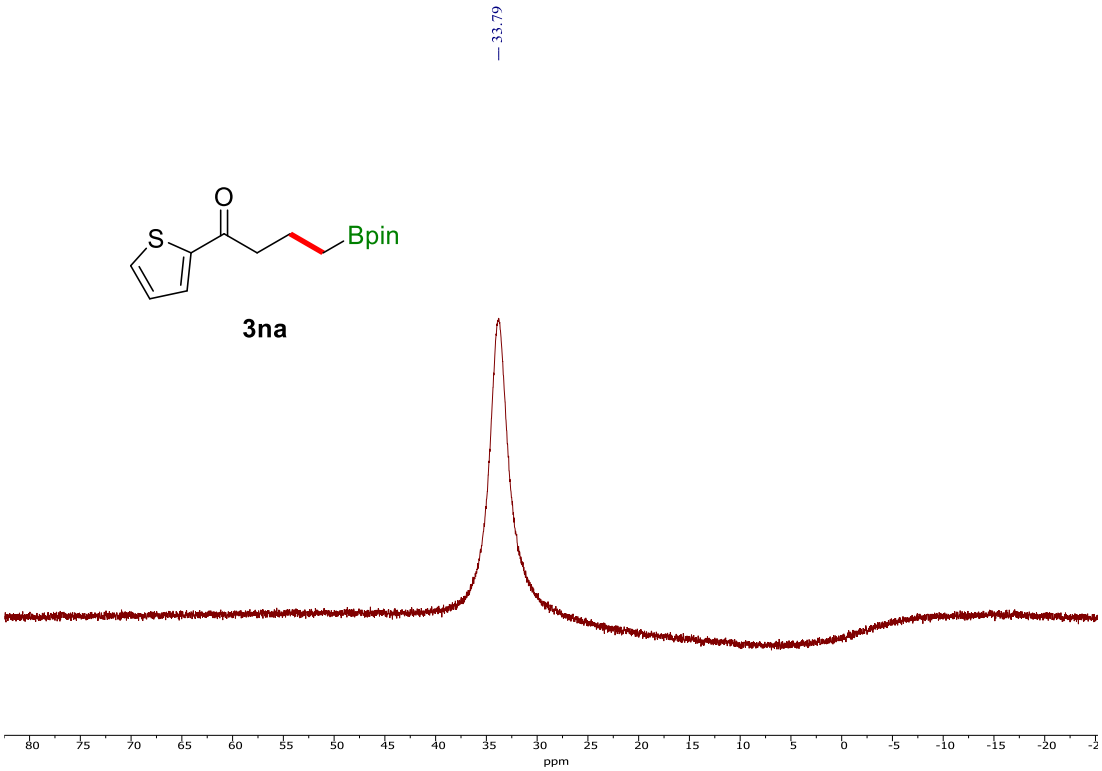
^{1}H NMR (400 MHz, $CDCl_3$) of **3na** (*see procedure*)



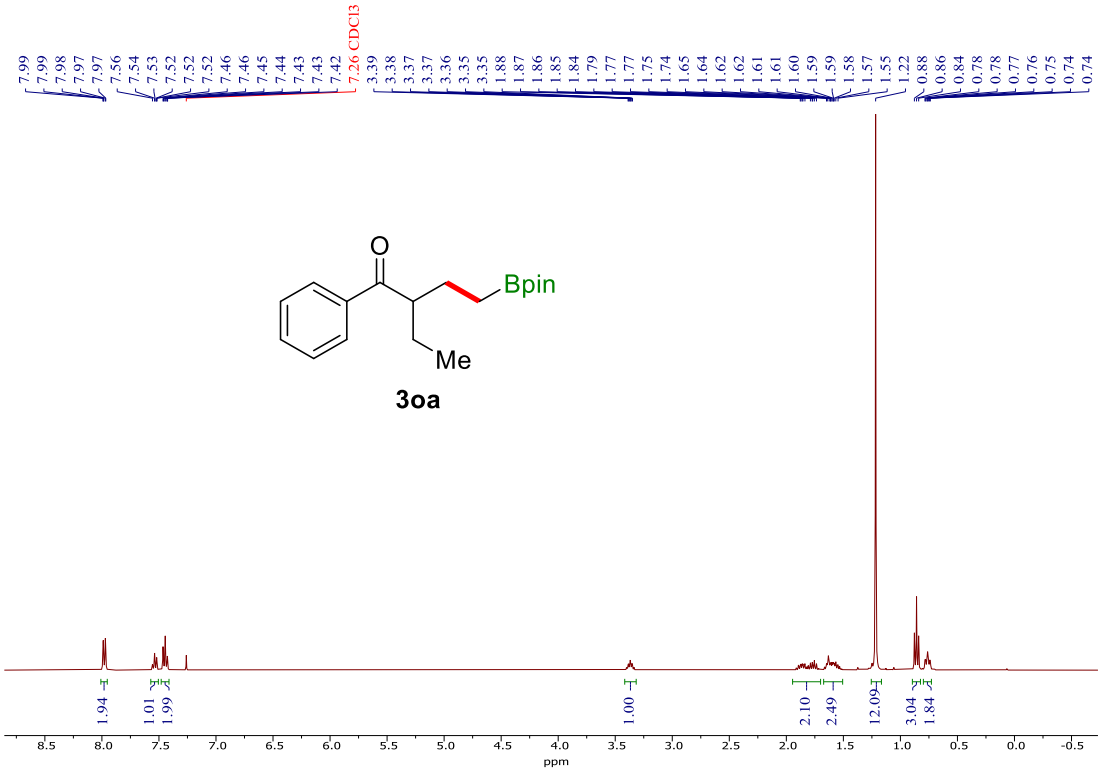
^{13}C NMR (101 MHz, $CDCl_3$) of **3na**



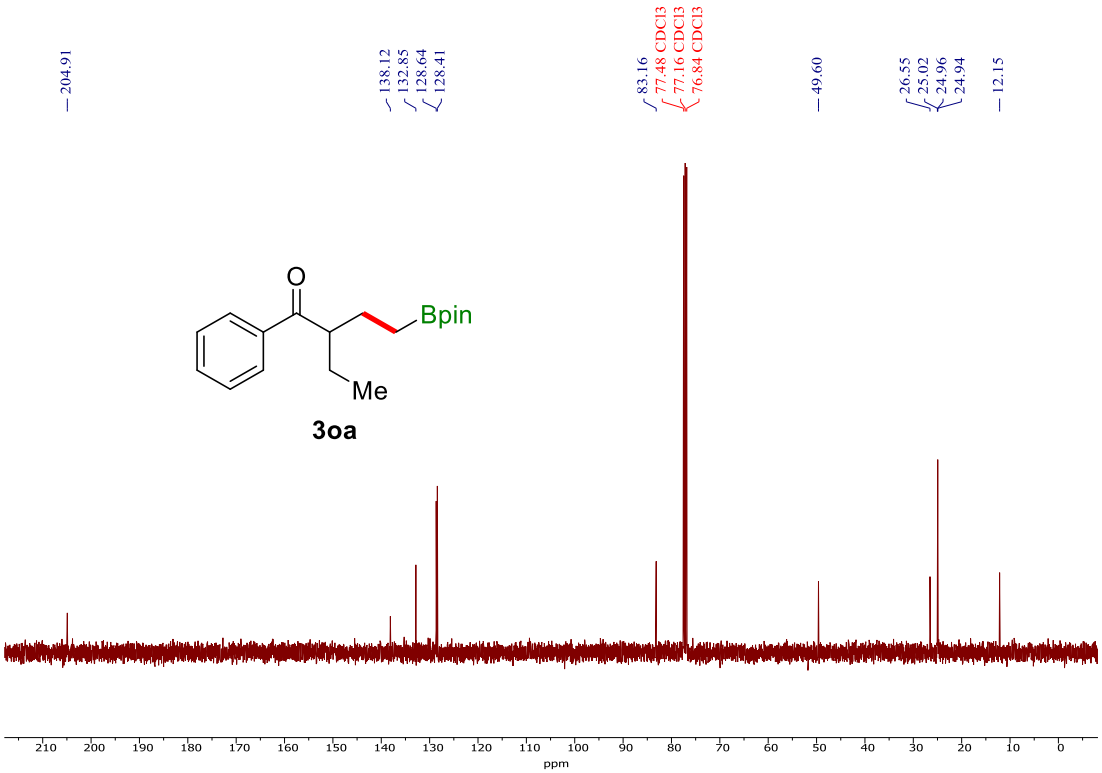
^{11}B NMR (128 MHz, $CDCl_3$) of **3na**



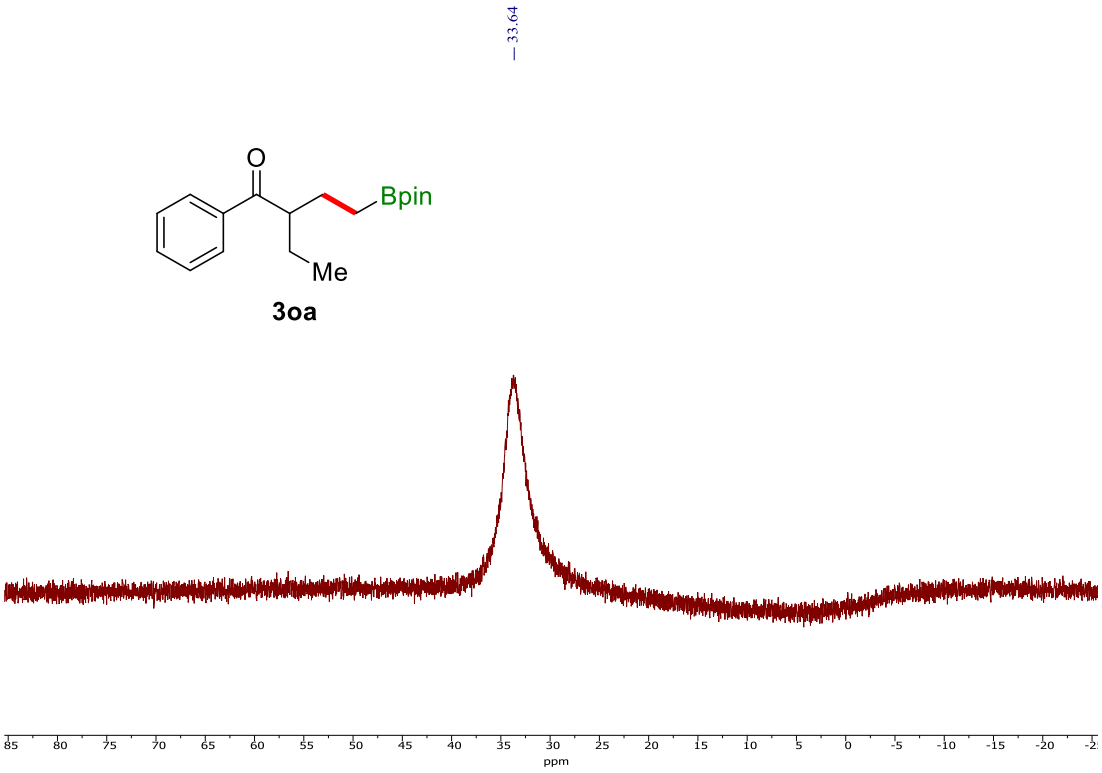
^{1}H NMR (400 MHz, $CDCl_3$) of **3oa** (*see procedure*)



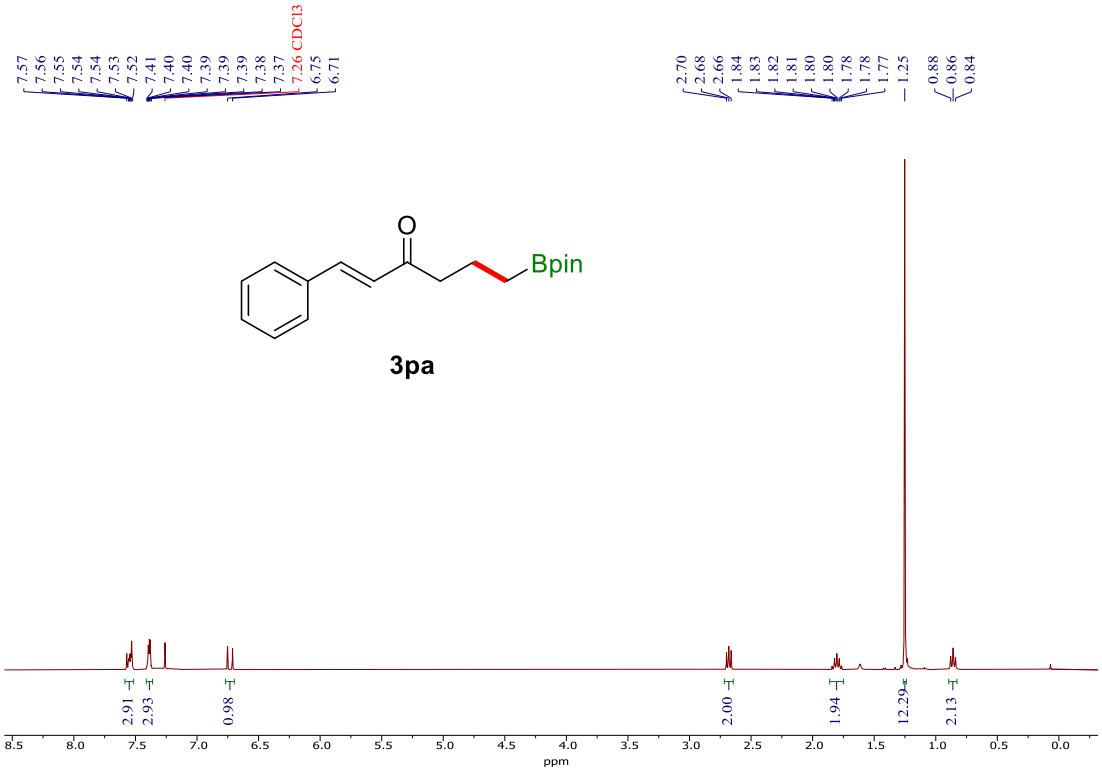
^{13}C NMR (101 MHz, $CDCl_3$) of **3oa**



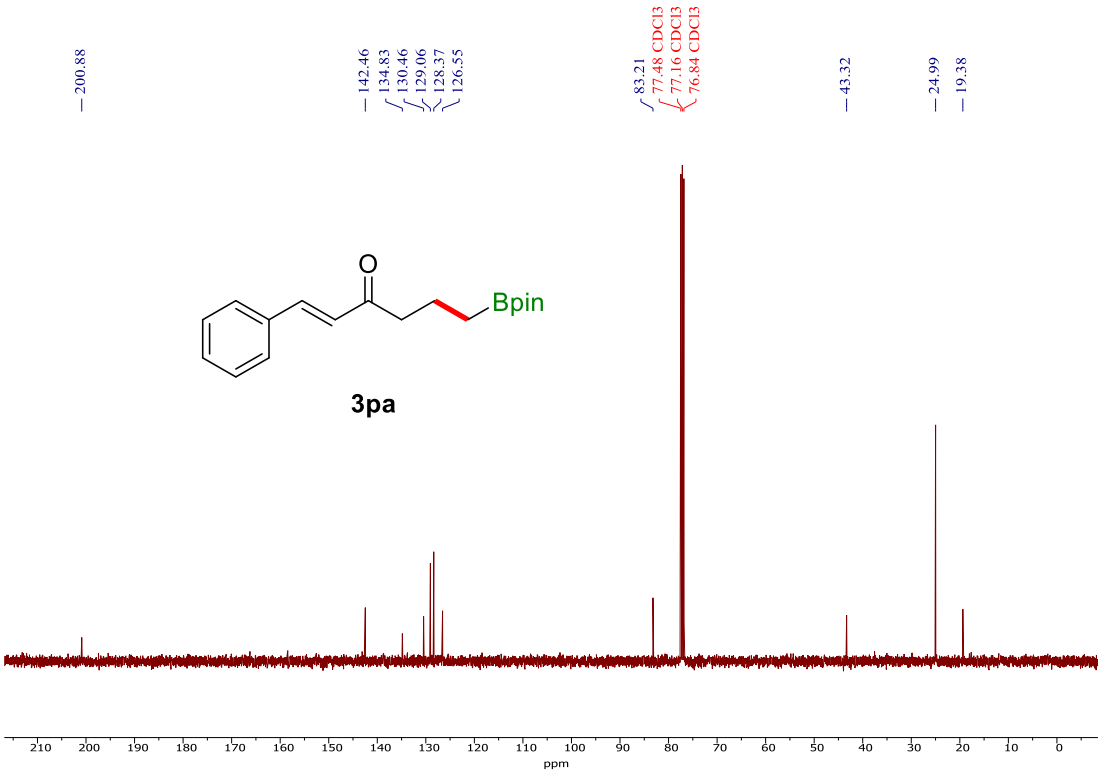
^{11}B NMR (128 MHz, $CDCl_3$) of **3oa**



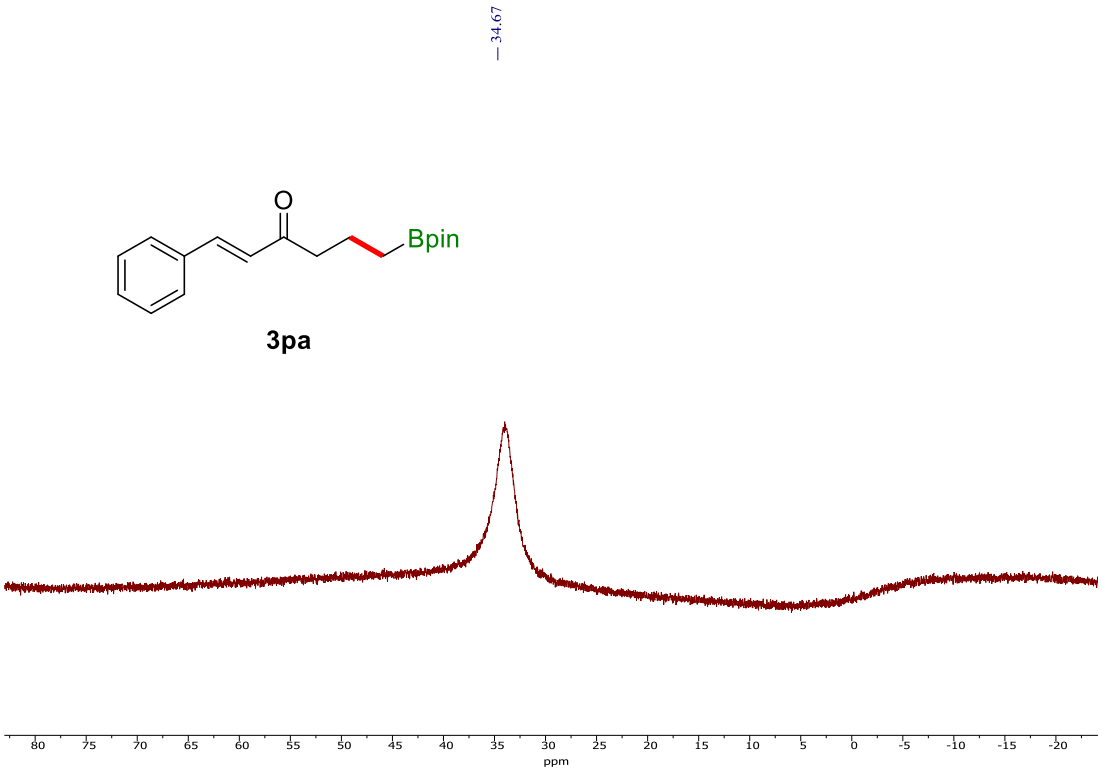
^{1}H NMR (400 MHz, $CDCl_3$) of **3pa** (*see procedure*)



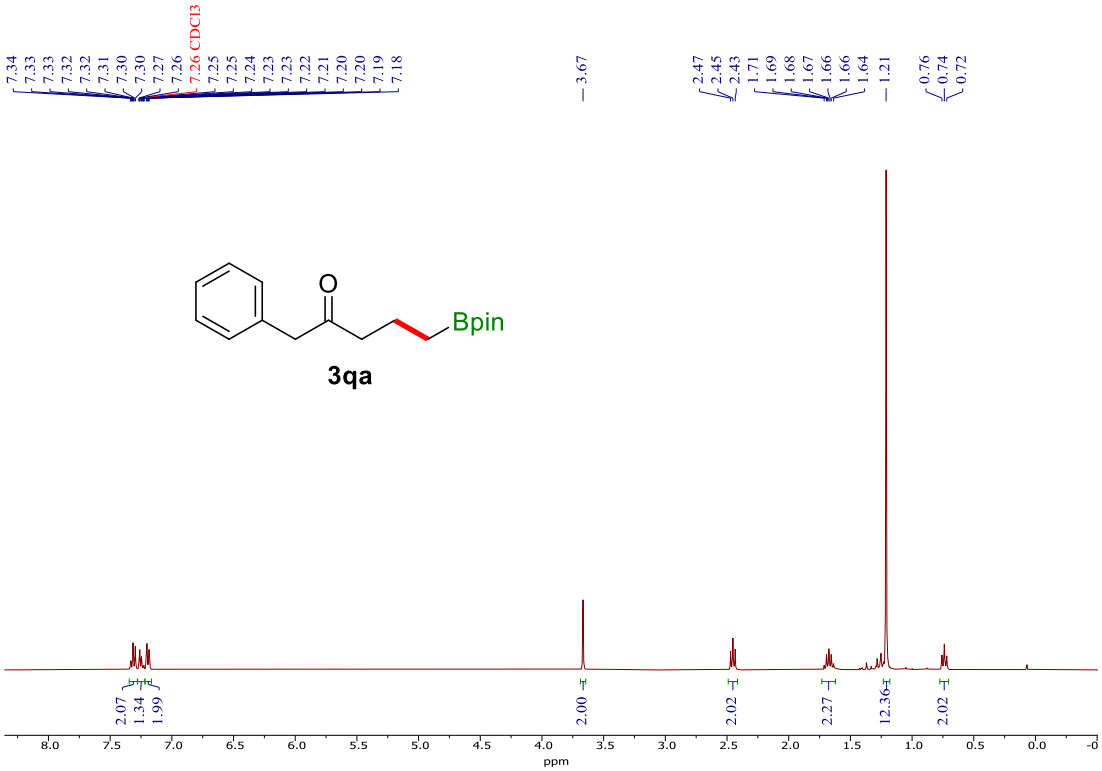
^{13}C NMR (101 MHz, $CDCl_3$) of **3pa**



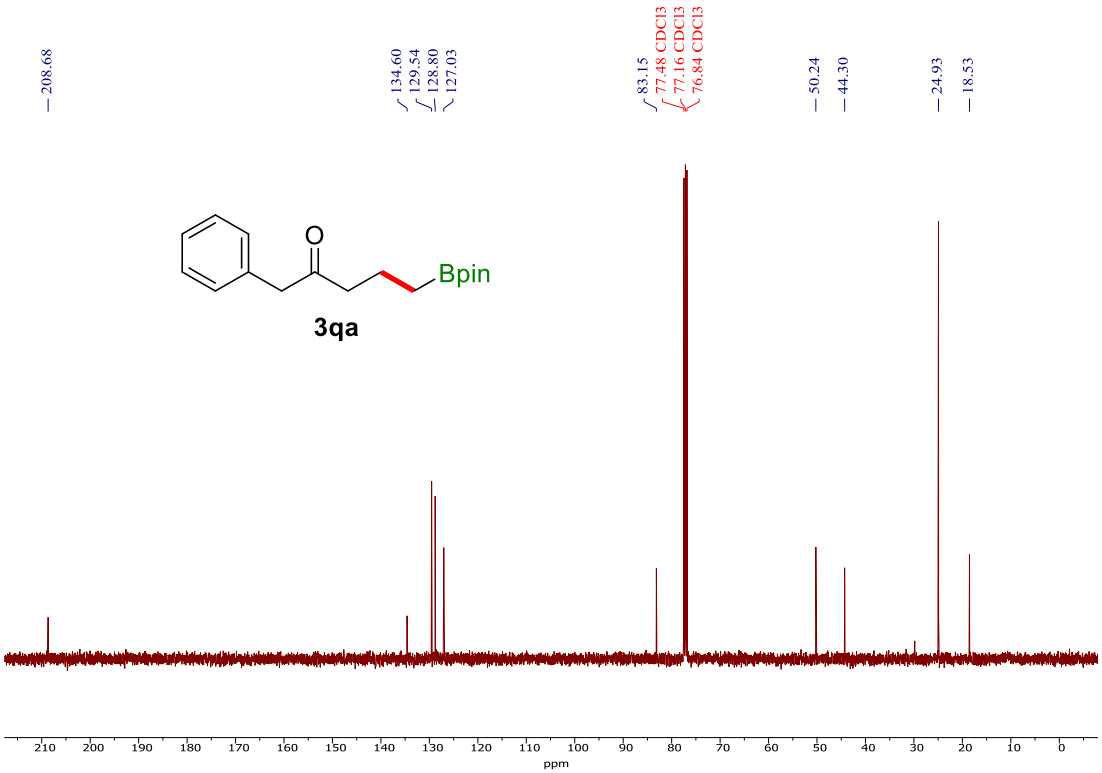
^{11}B NMR (128 MHz, $CDCl_3$) of **3pa**



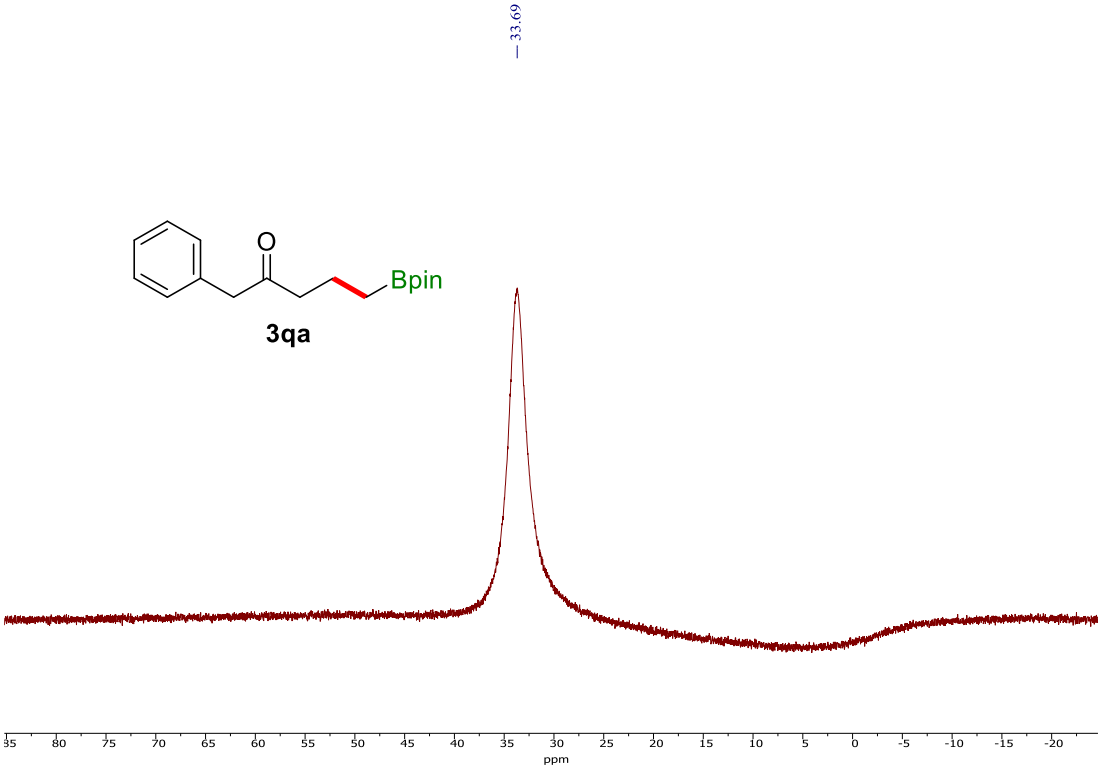
^{1}H NMR (400 MHz, $CDCl_3$) of **3qa** (*see procedure*)



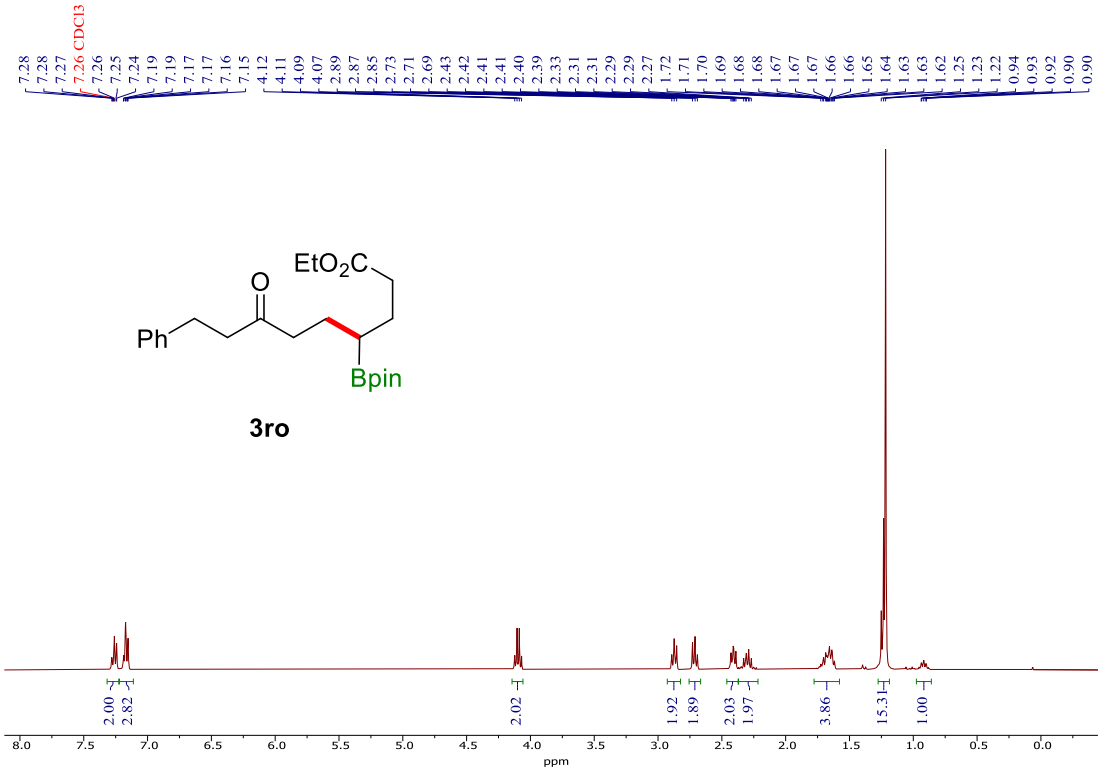
^{13}C NMR (101 MHz, $CDCl_3$) of **3qa**



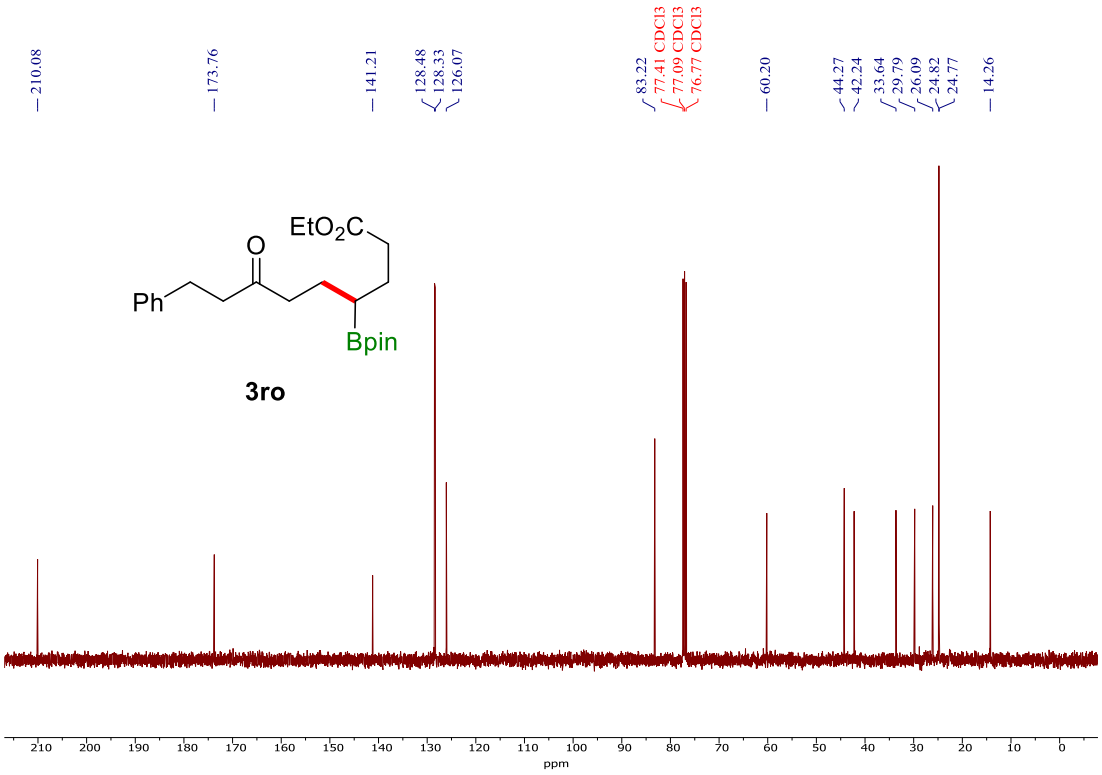
^{11}B NMR (128 MHz, $CDCl_3$) of **3qa**



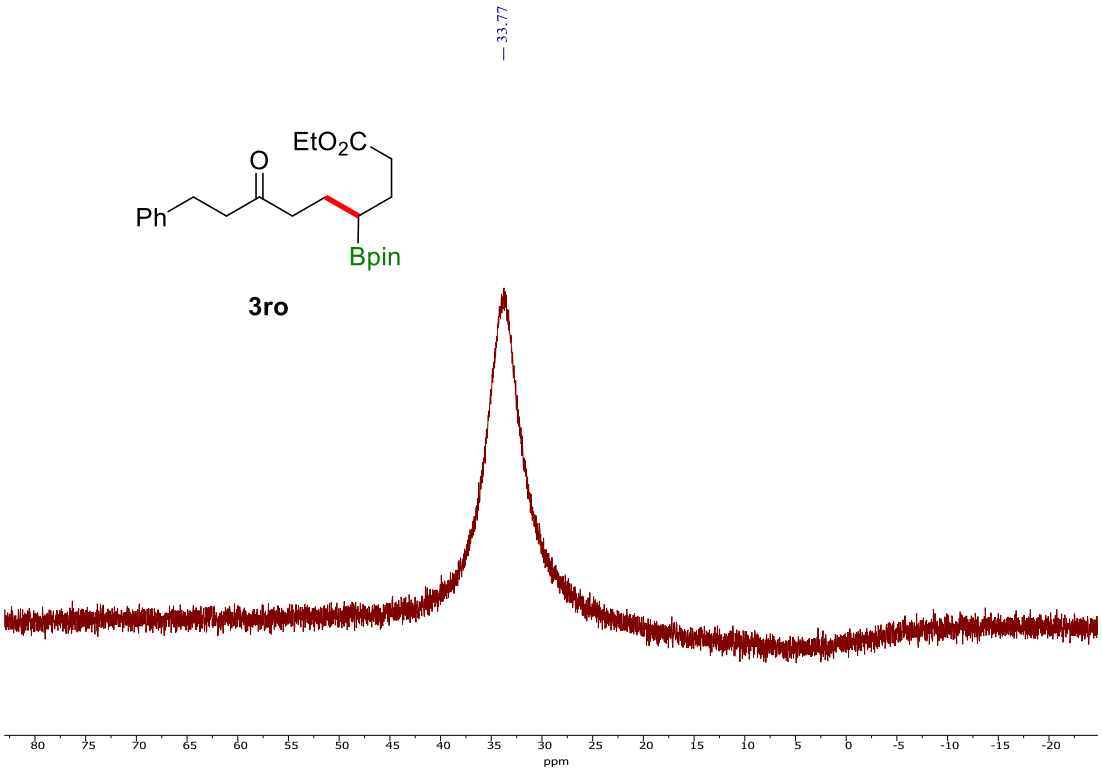
^{1}H NMR (400 MHz, $CDCl_3$) of **3ro** (*see procedure*)



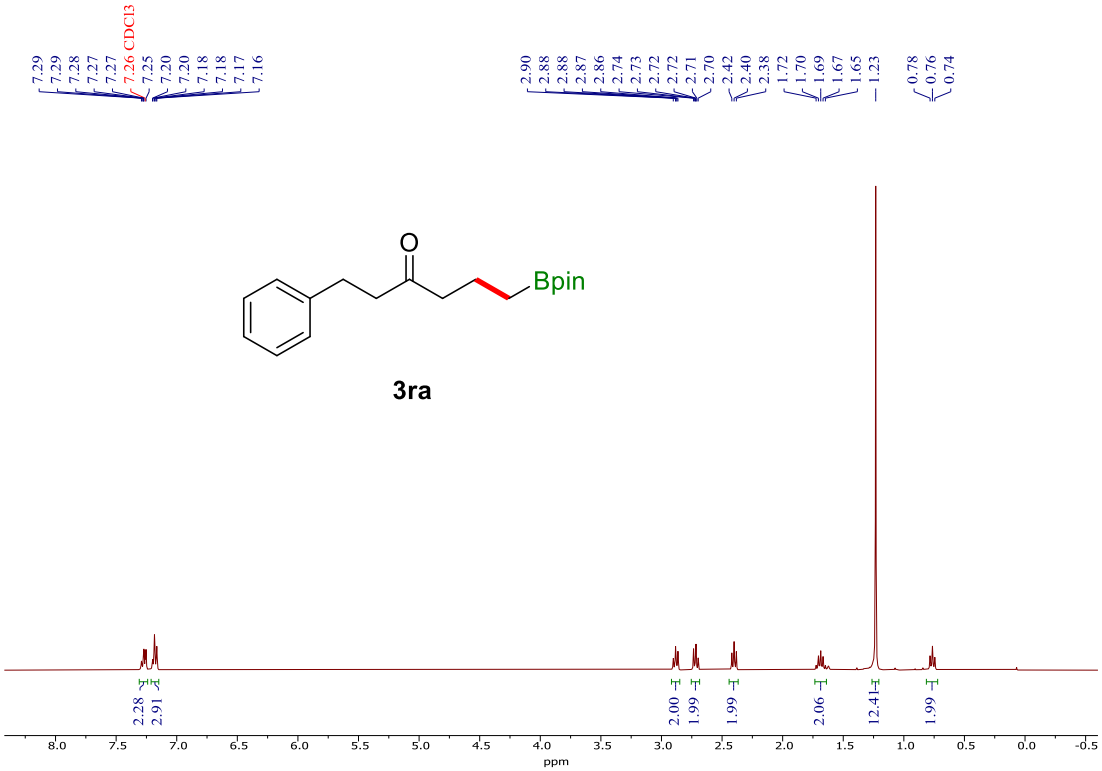
^{13}C NMR (101 MHz, $CDCl_3$) of **3ro**



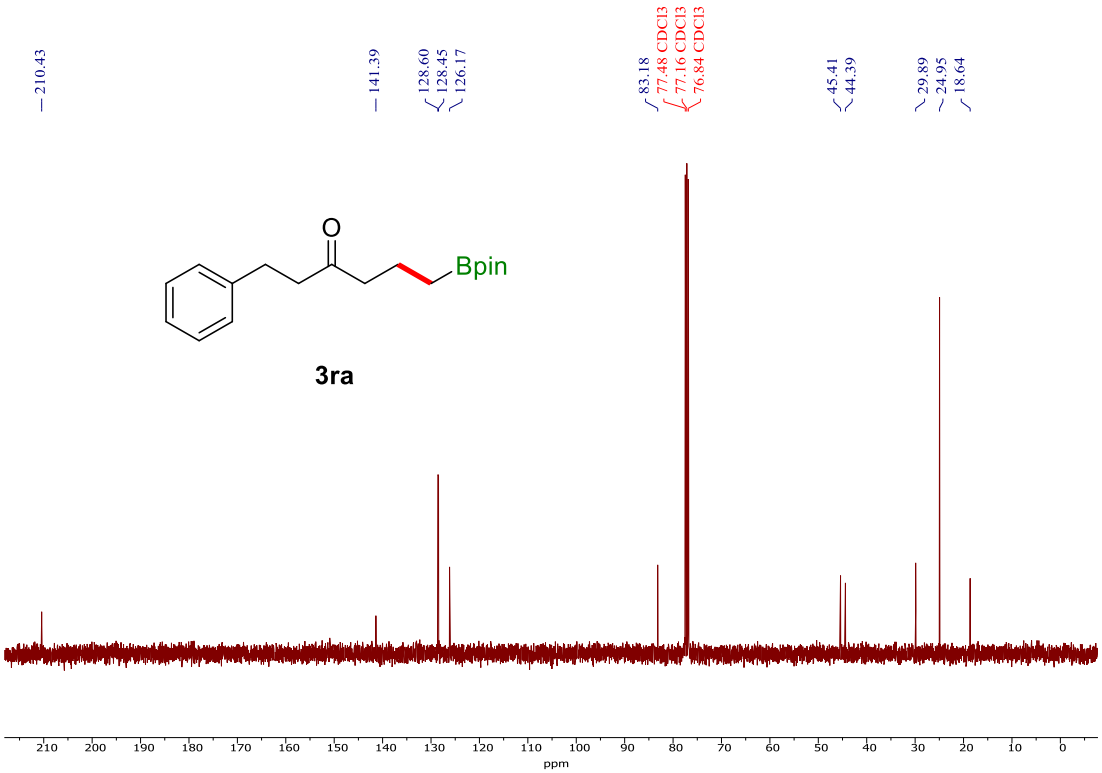
^{11}B NMR (128 MHz, $CDCl_3$) of **3ro**



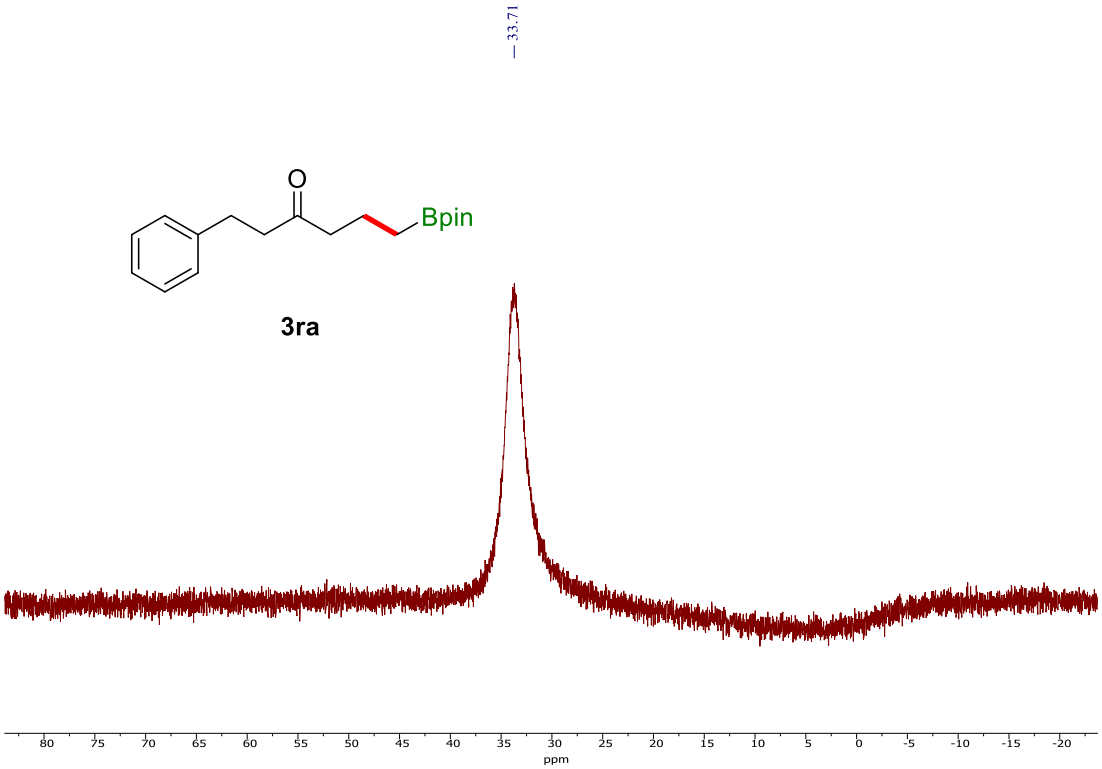
^{1}H NMR (400 MHz, $CDCl_3$) of **3ra** (*see procedure*)



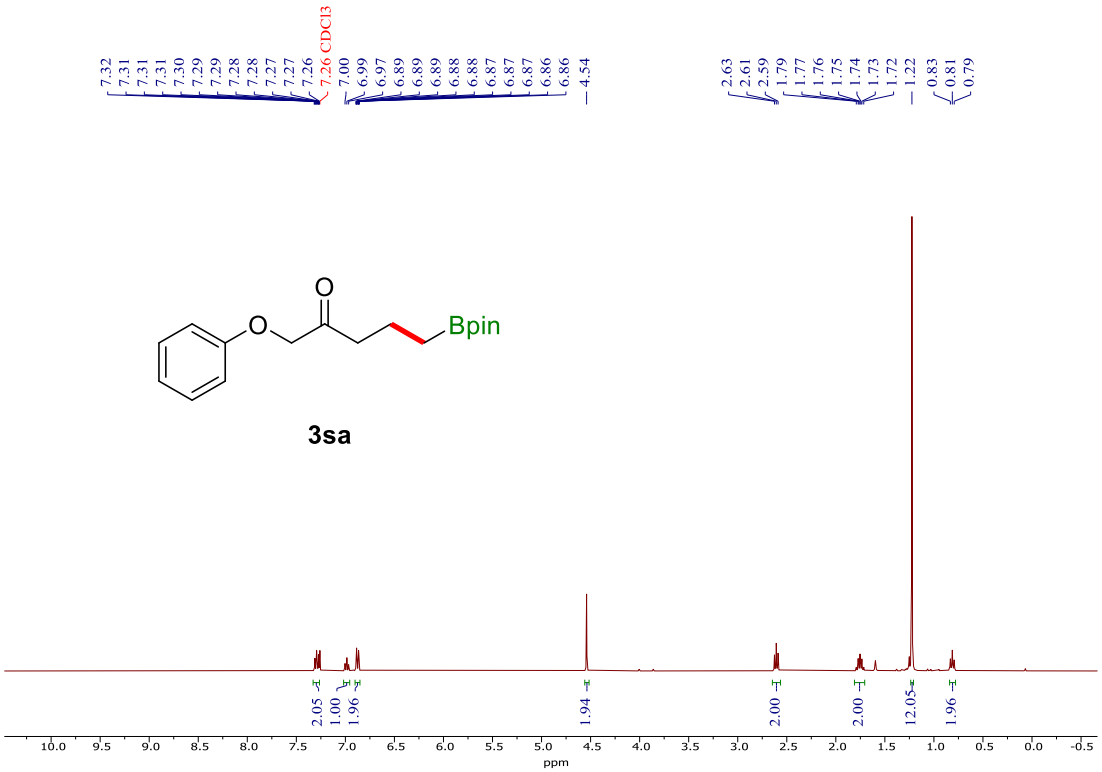
^{13}C NMR (101 MHz, $CDCl_3$) of **3ra**



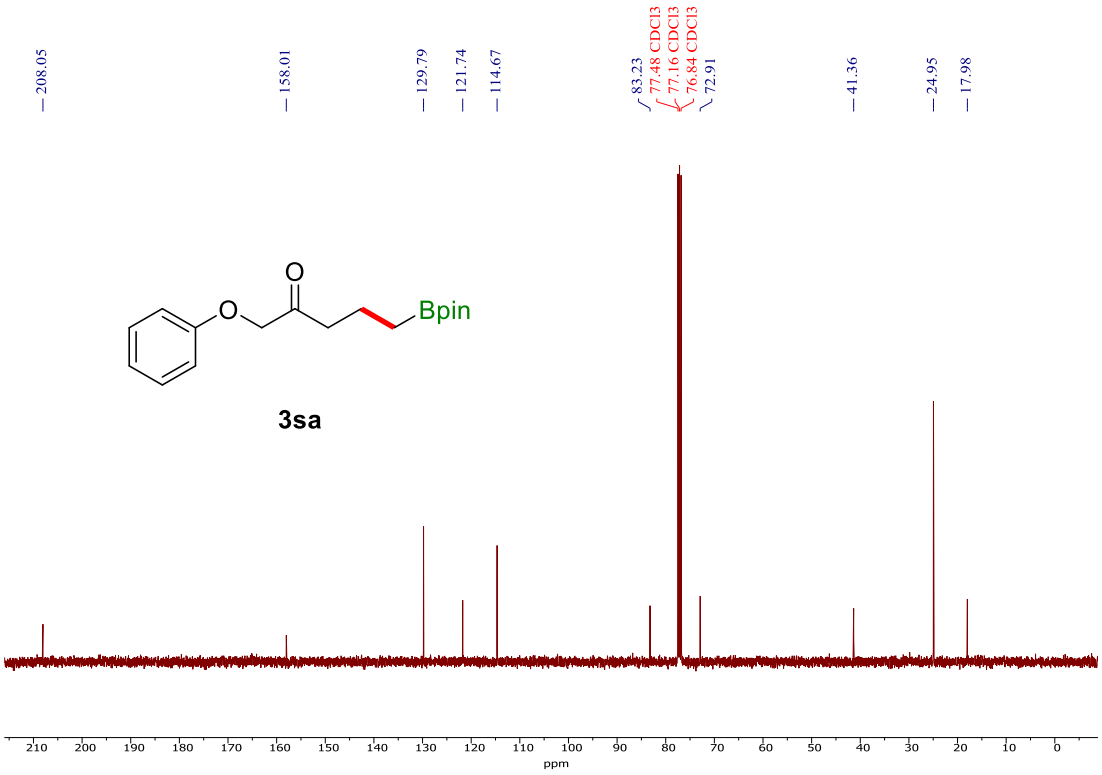
^{11}B NMR (128 MHz, $CDCl_3$) of **3ra**



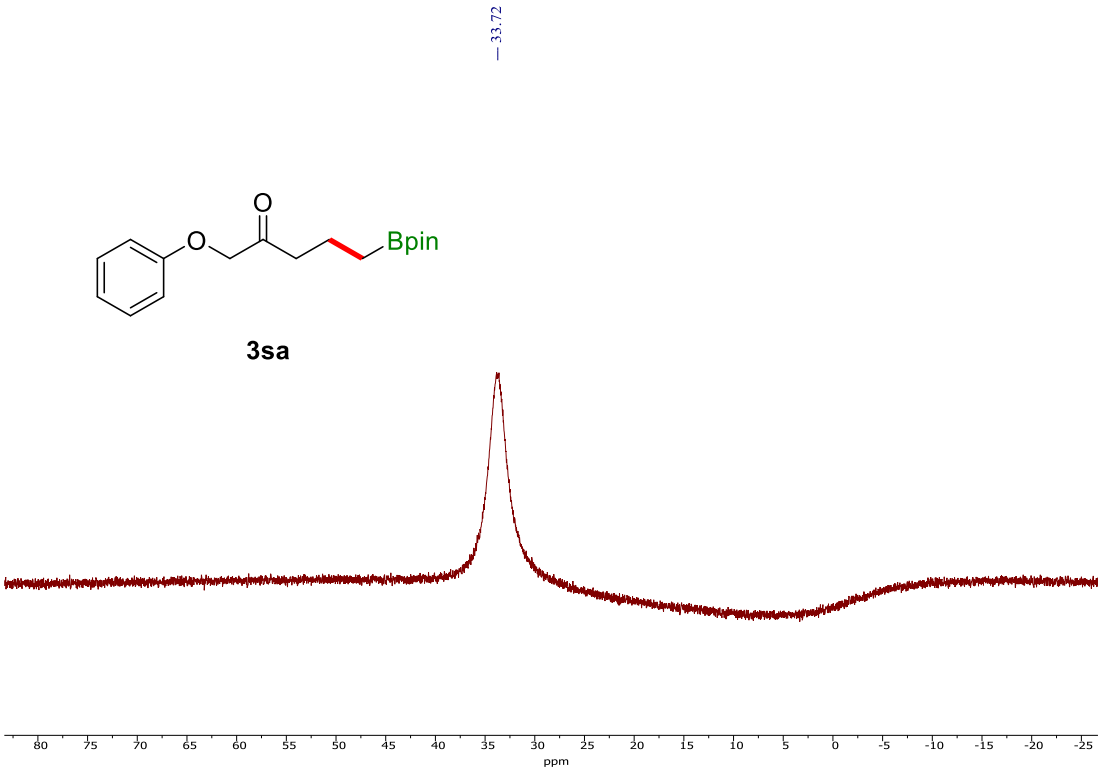
^{1}H NMR (400 MHz, $CDCl_3$) of **3sa** (*see procedure*)



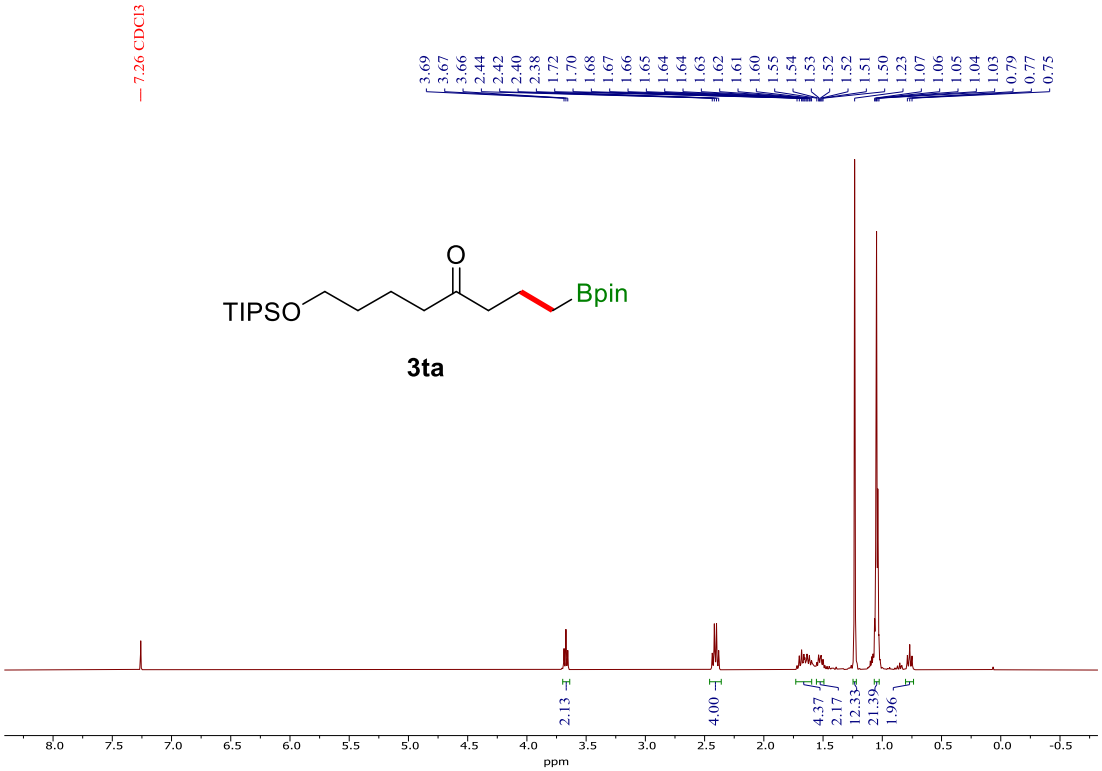
^{13}C NMR (101 MHz, $CDCl_3$) of **3sa**



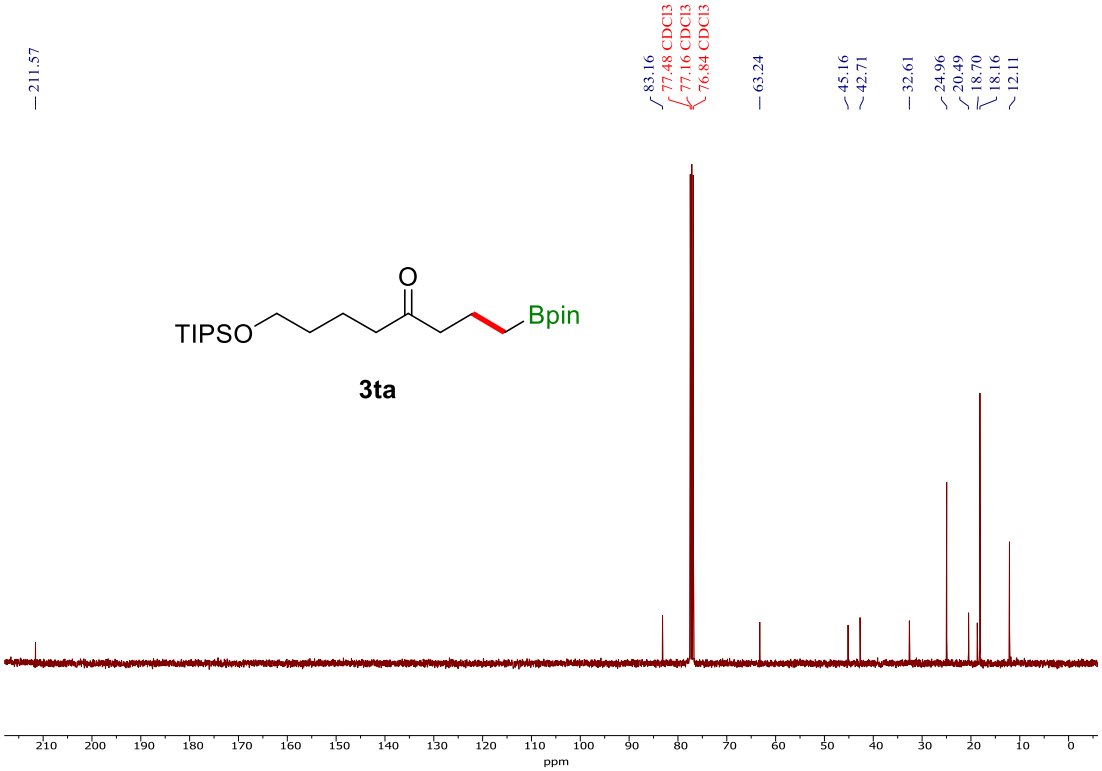
^{11}B NMR (128 MHz, $CDCl_3$) of **3sa**



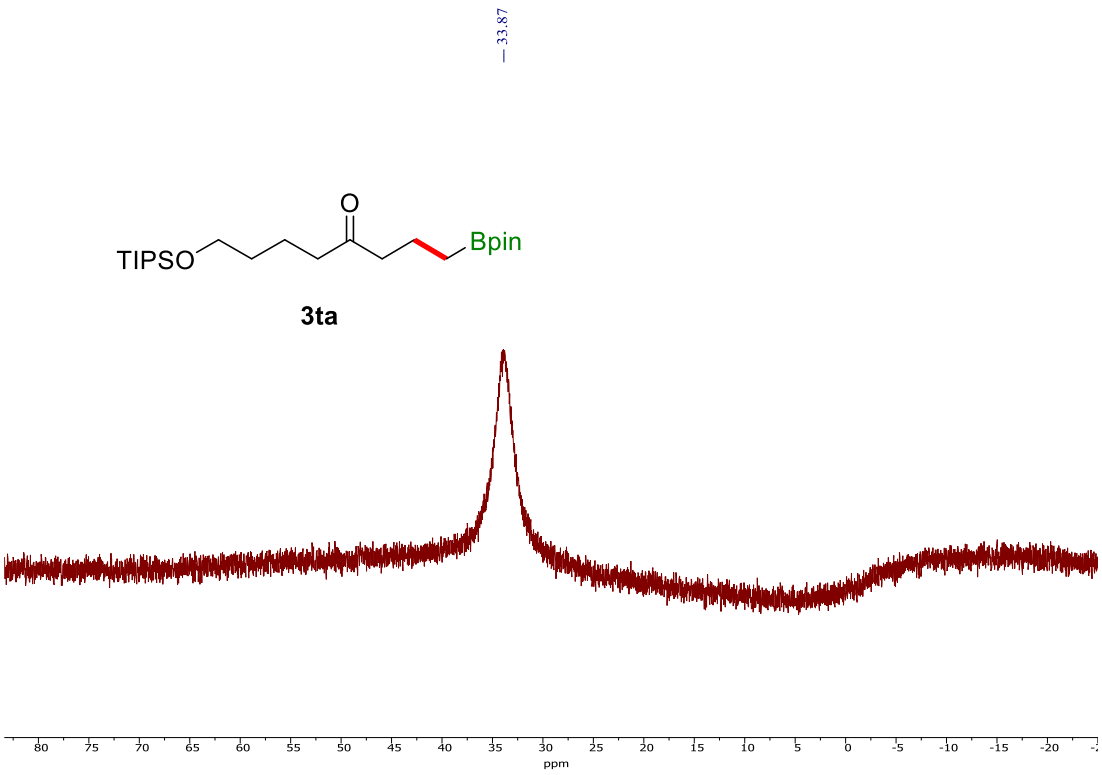
^{1}H NMR (400 MHz, $CDCl_3$) of **3ta** (*see procedure*)



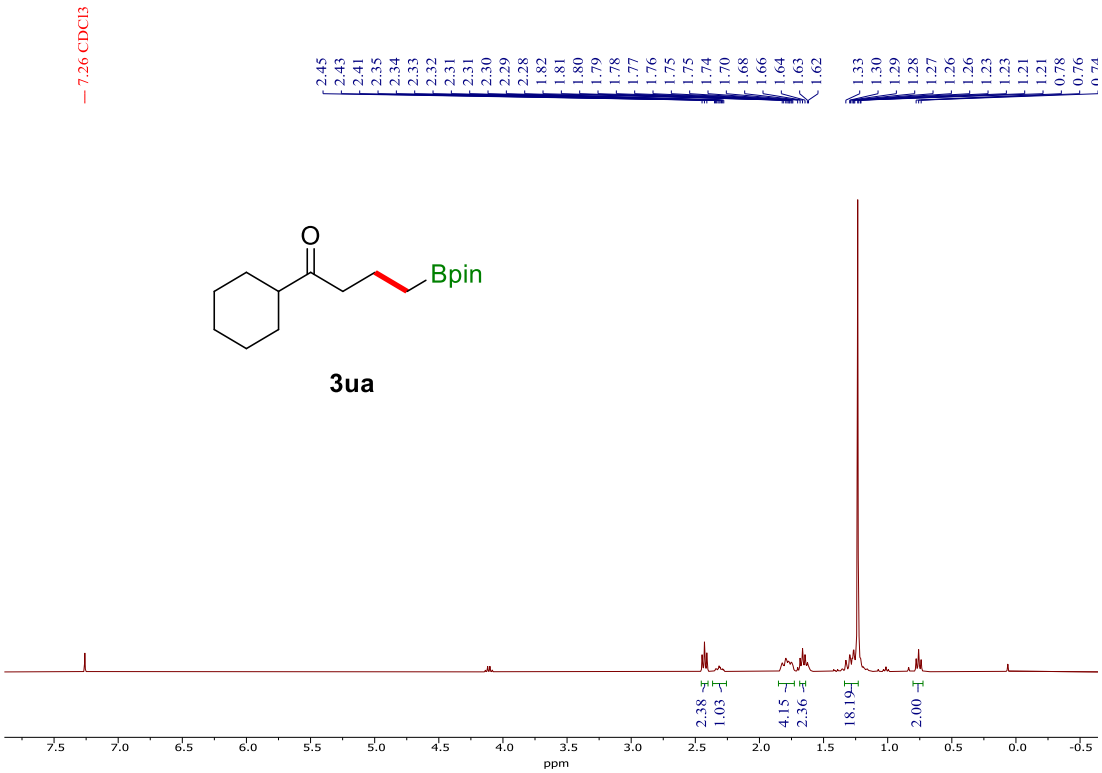
^{13}C NMR (101 MHz, $CDCl_3$) of **3ta**



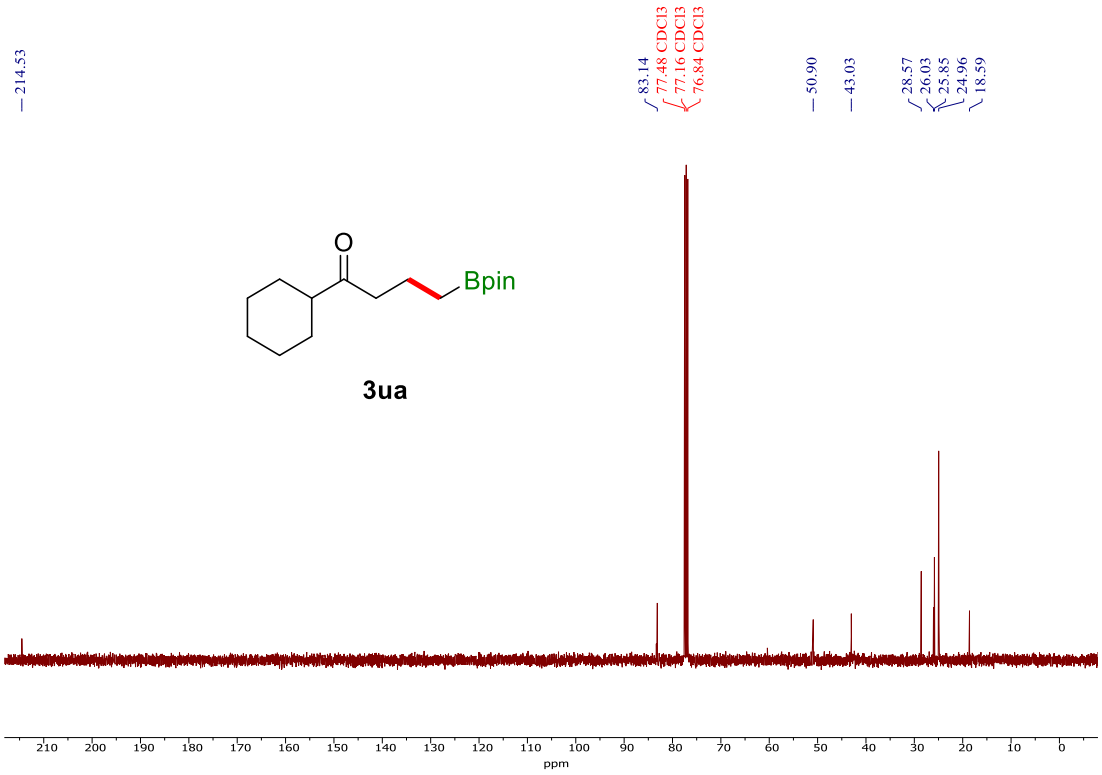
^{11}B NMR (128 MHz, $CDCl_3$) of **3ta**



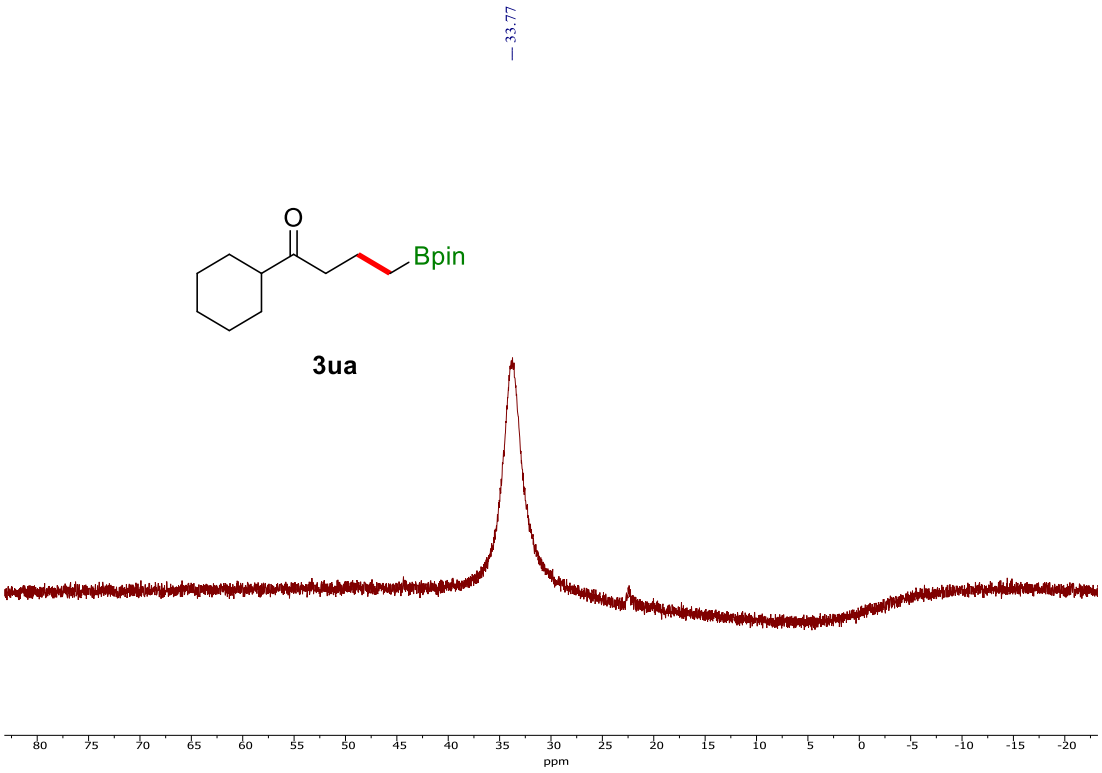
^{1}H NMR (400 MHz, $CDCl_3$) of **3ua** (*see procedure*)



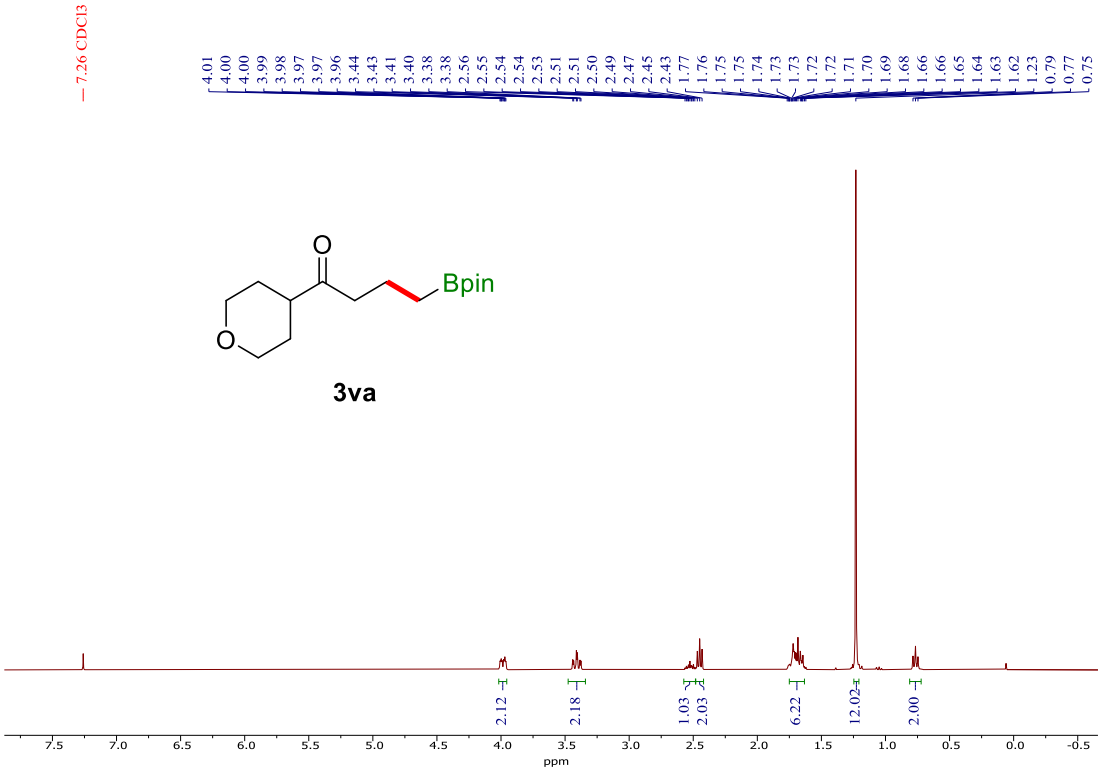
^{13}C NMR (101 MHz, $CDCl_3$) of **3ua**



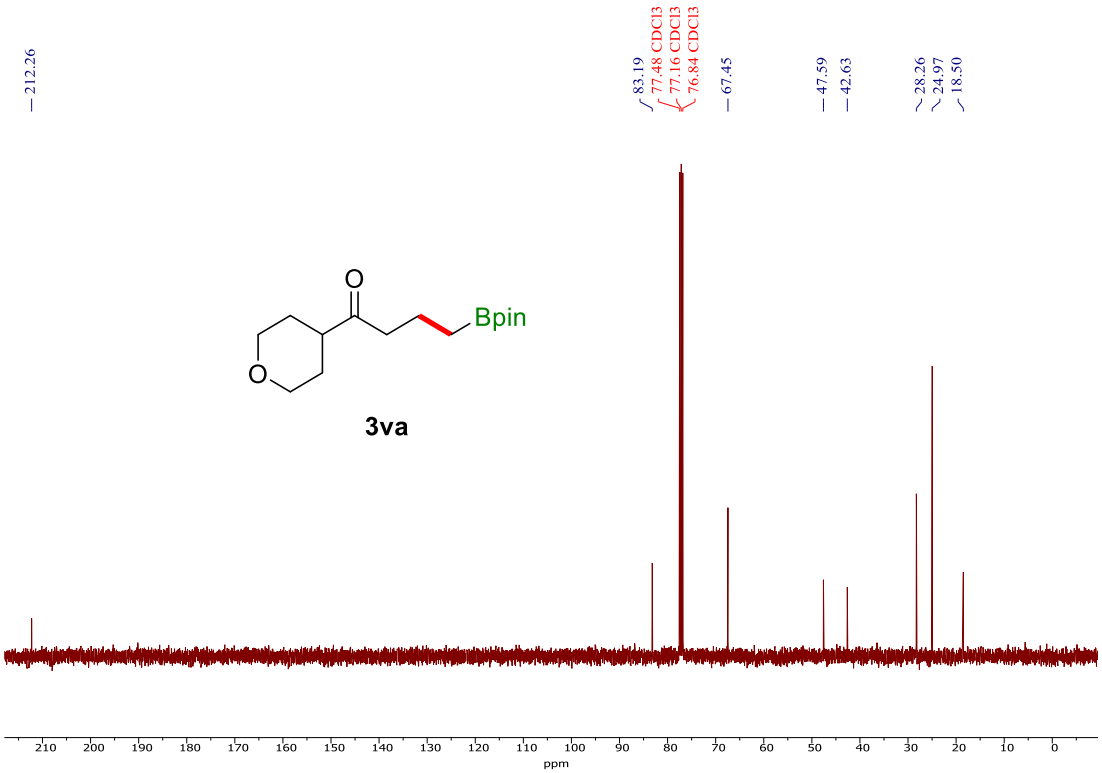
^{11}B NMR (128 MHz, $CDCl_3$) of **3ua**



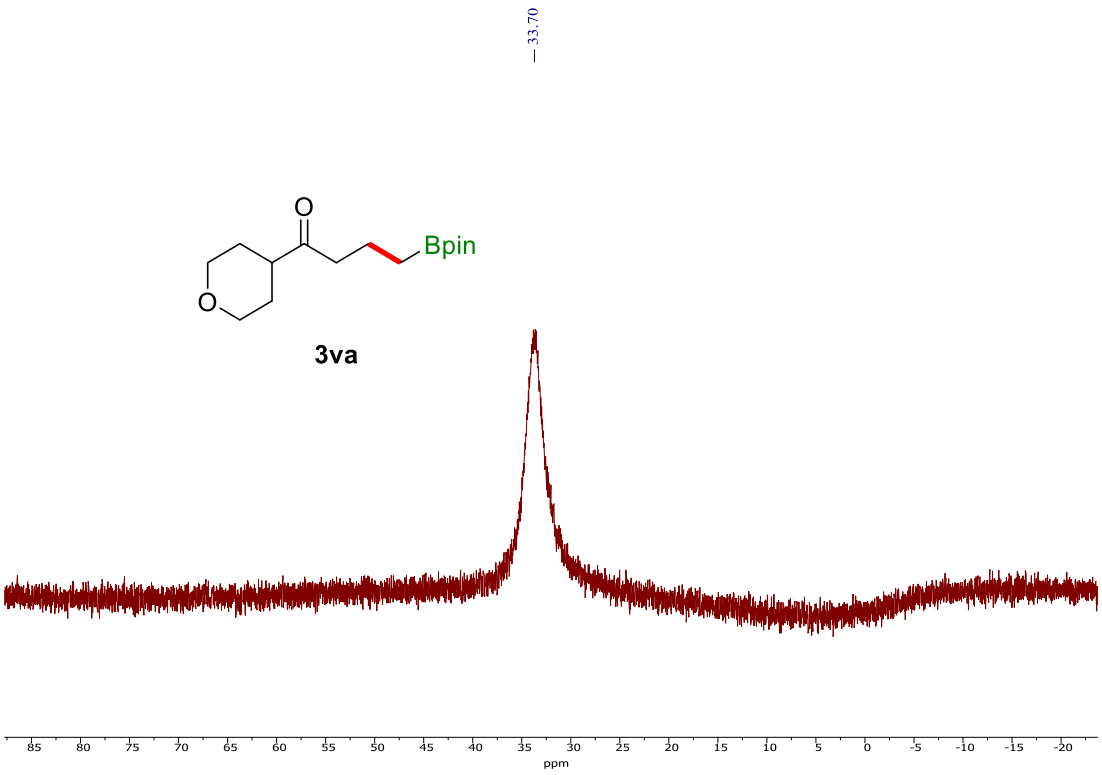
^{1}H NMR (400 MHz, $CDCl_3$) of **3va** (*see procedure*)



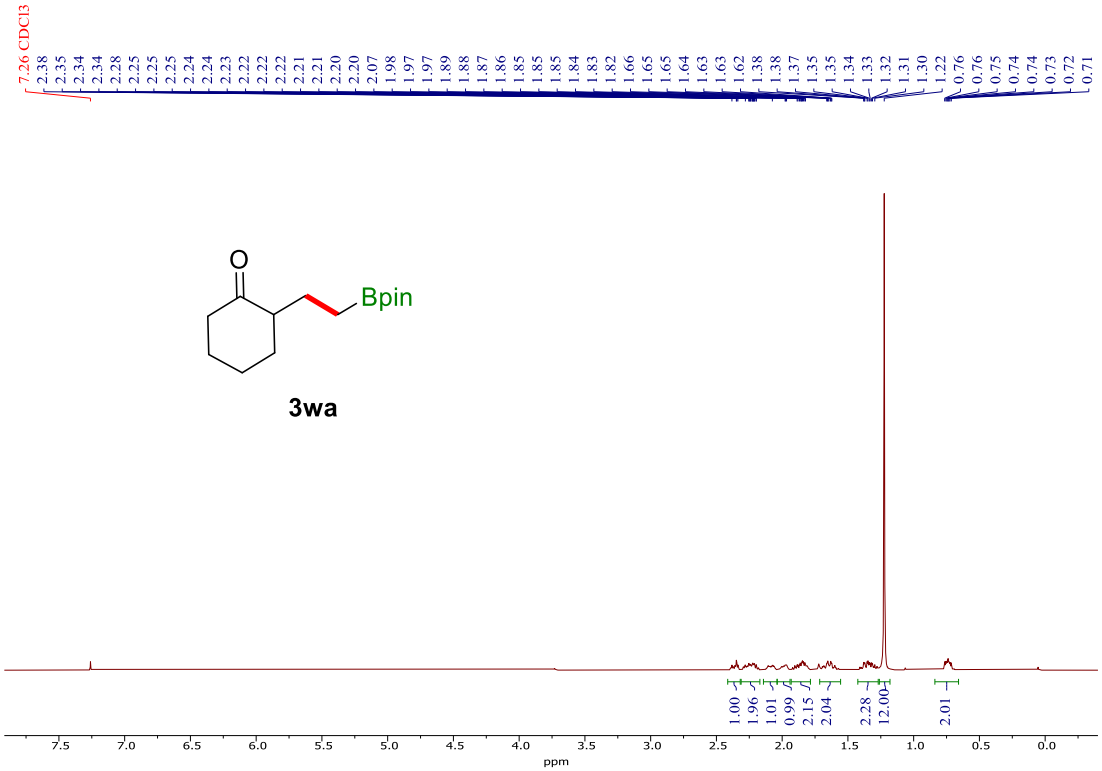
^{13}C NMR (101 MHz, $CDCl_3$) of **3va**



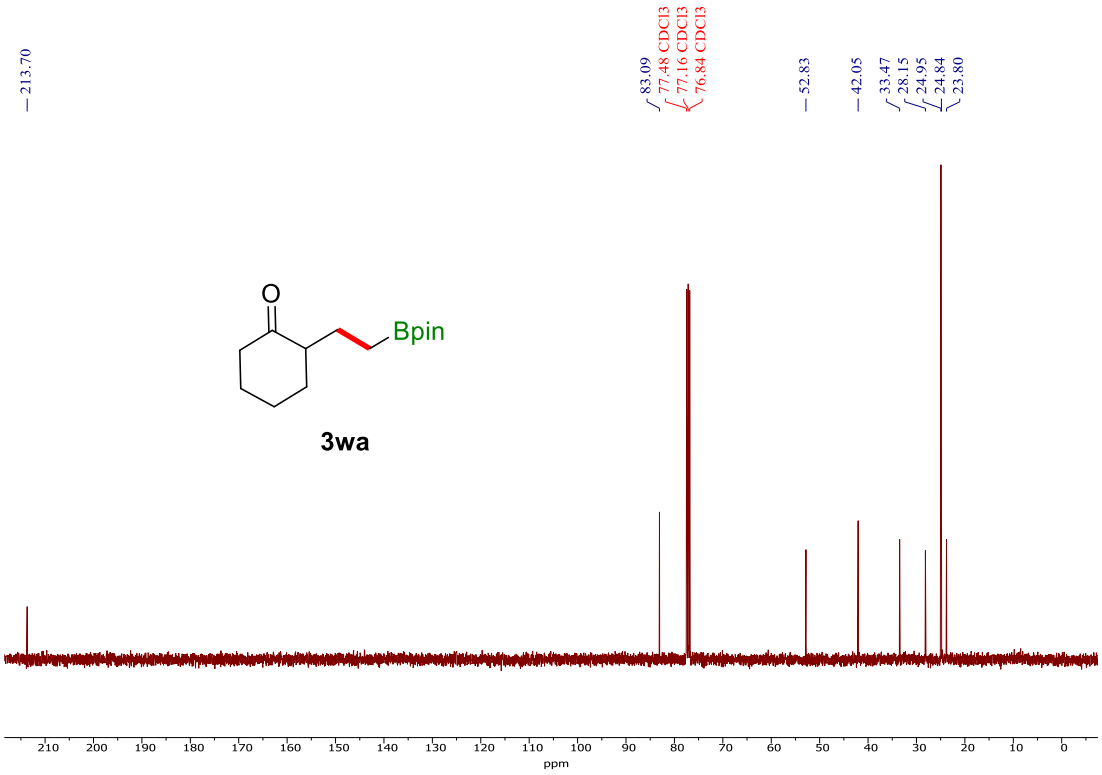
^{11}B NMR (128 MHz, $CDCl_3$) of **3va**



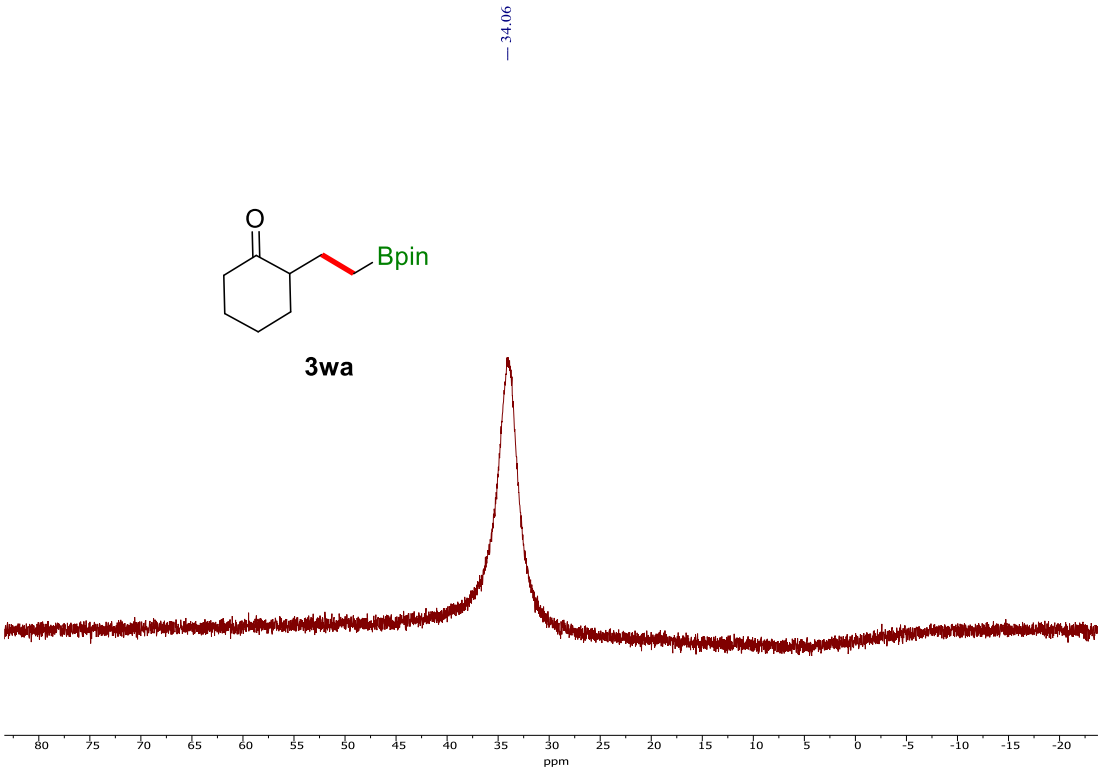
^{1}H NMR (400 MHz, $CDCl_3$) of **3wa** (*see procedure*)



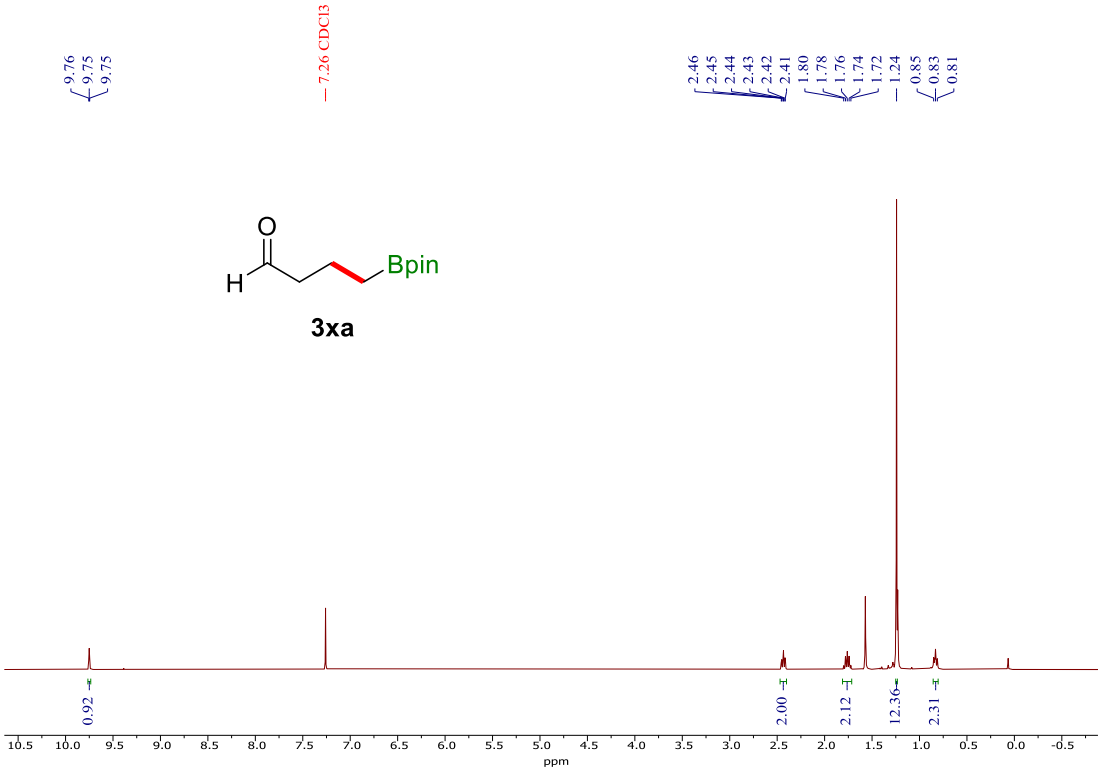
^{13}C NMR (101 MHz, $CDCl_3$) of **3wa**



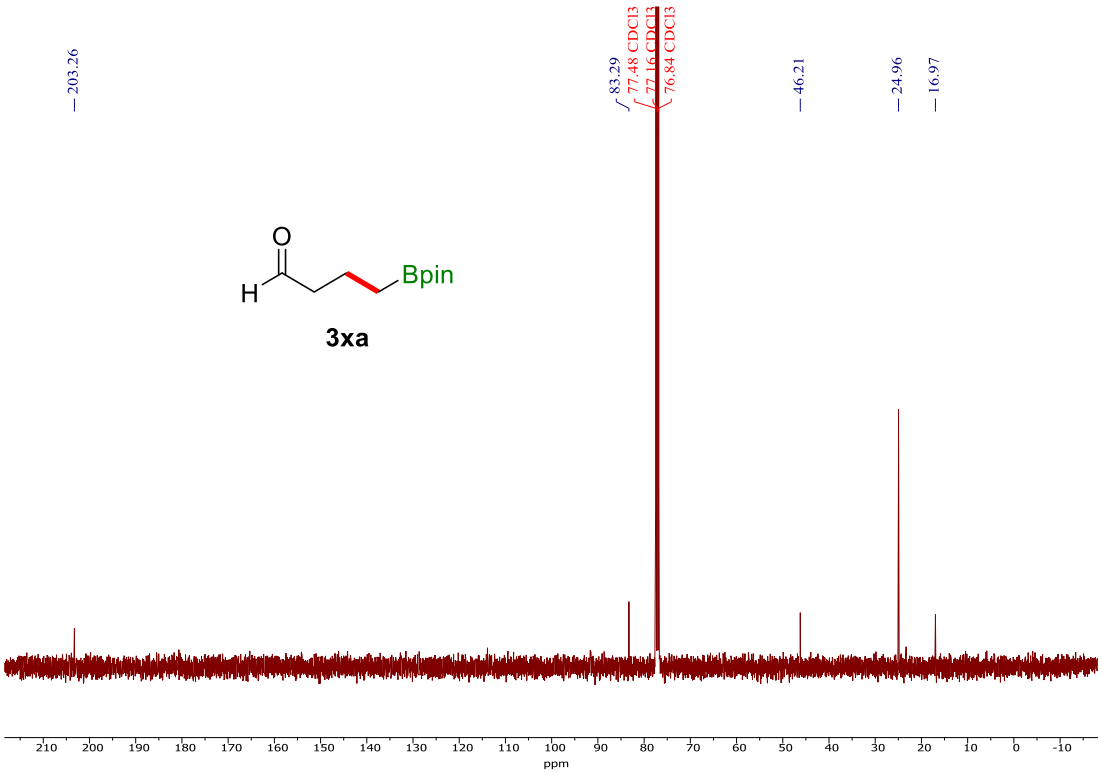
^{11}B NMR (128 MHz, $CDCl_3$) of **3wa**



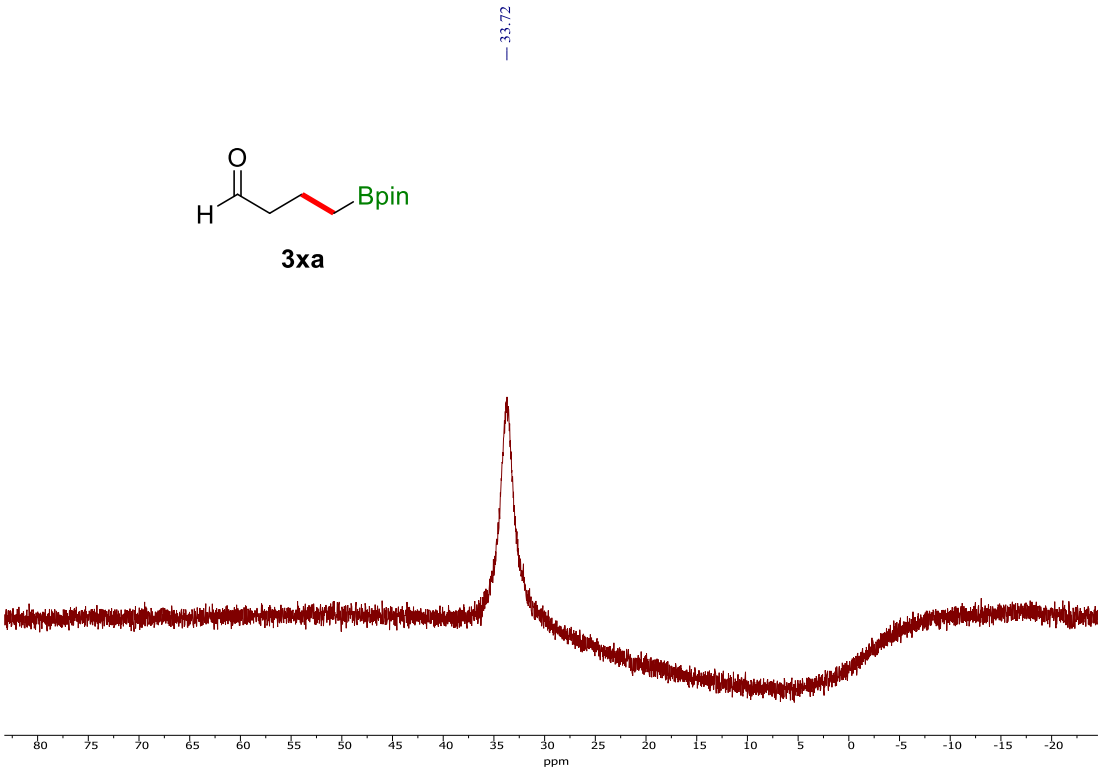
^{1}H NMR (400 MHz, $CDCl_3$) of **3xa** (*see procedure*)



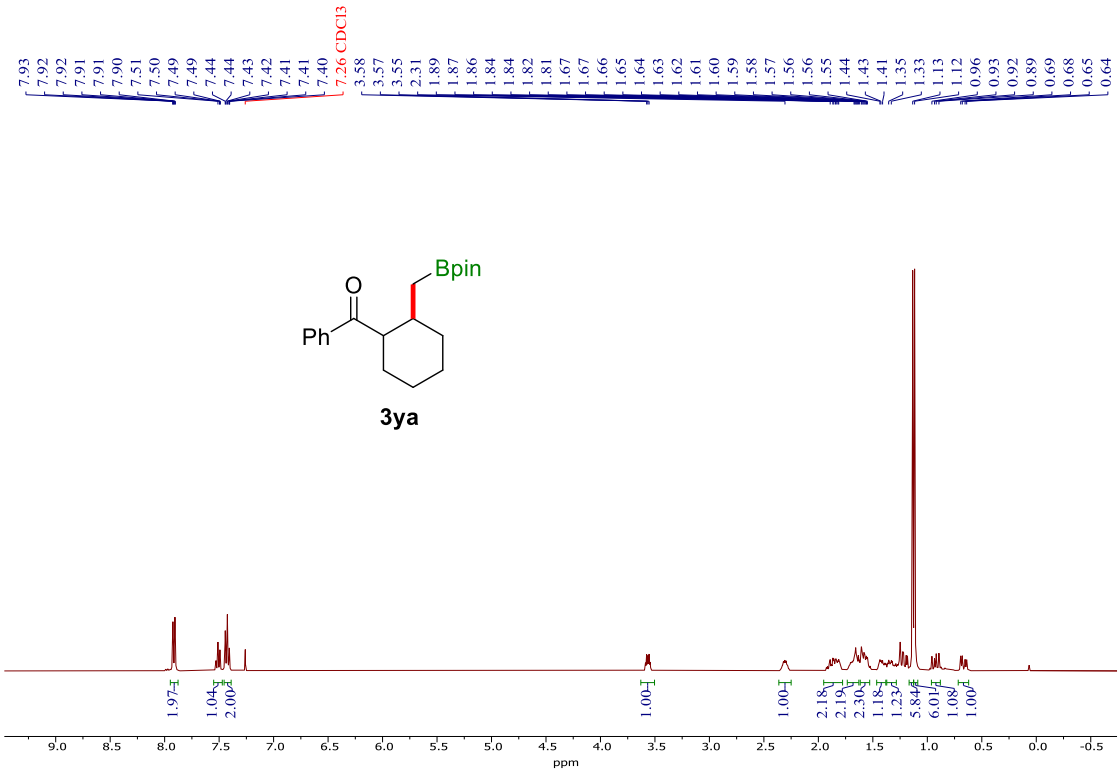
^{13}C NMR (101 MHz, $CDCl_3$) of **3xa**



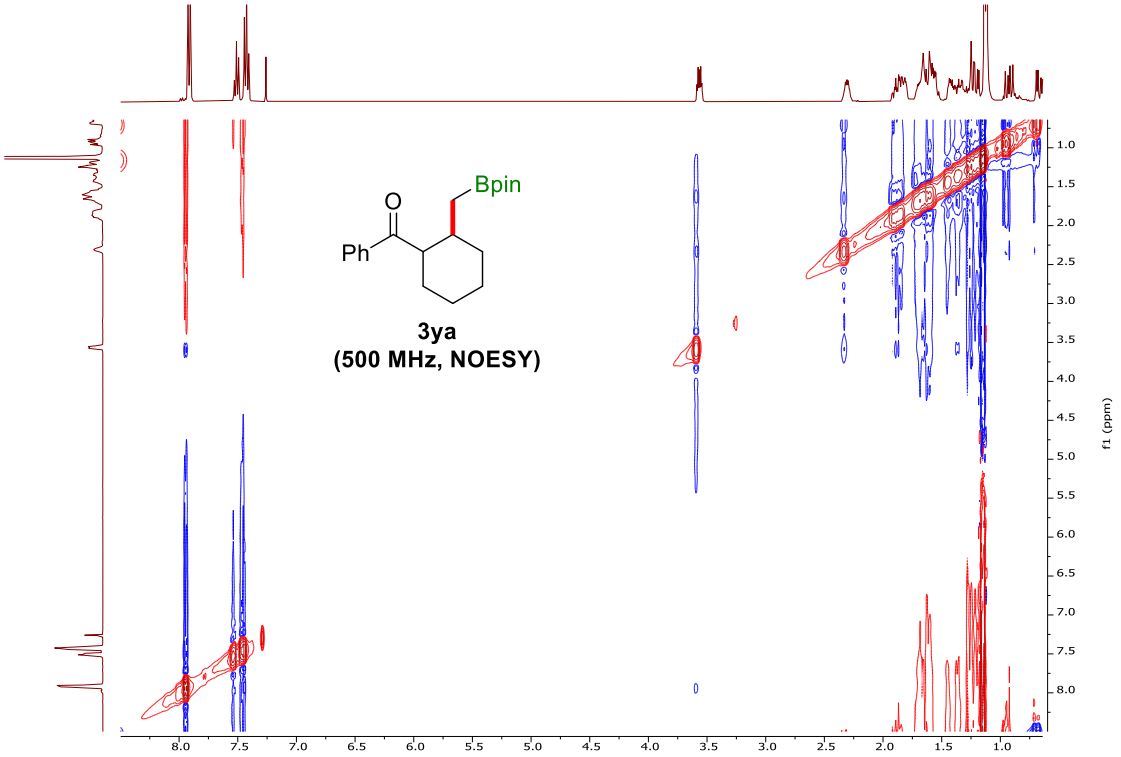
^{11}B NMR (128 MHz, $CDCl_3$) of **3xa**



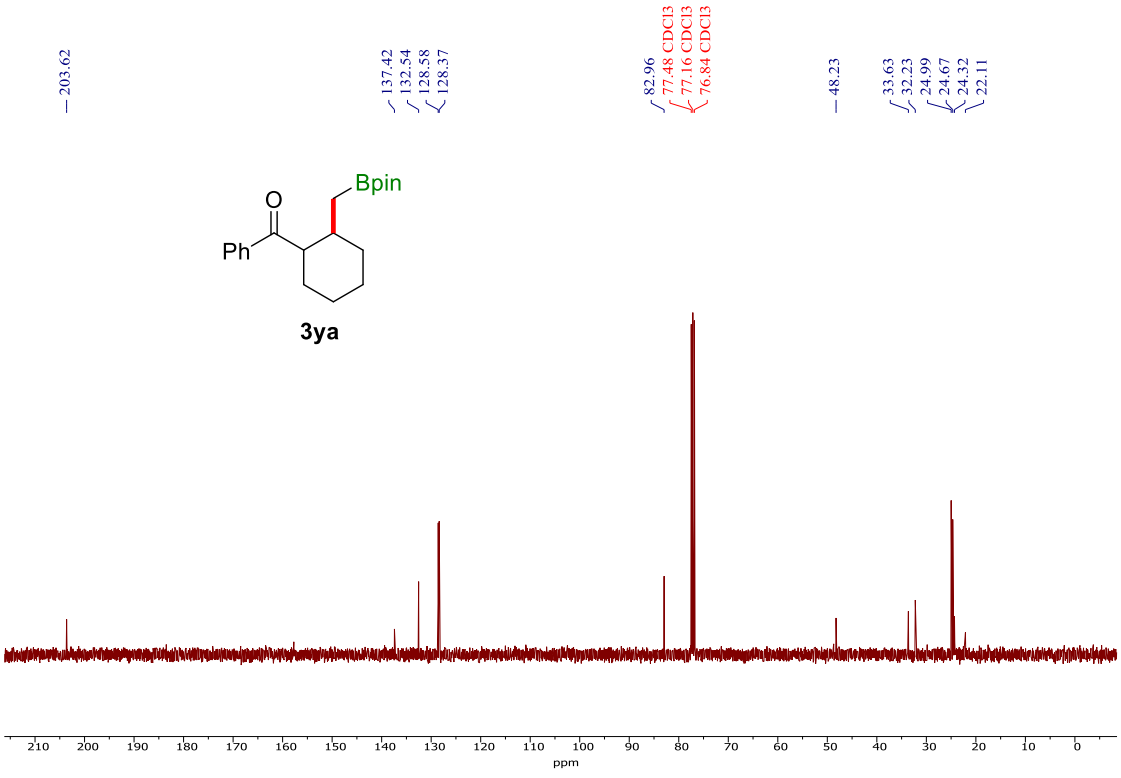
^{1}H NMR (400 MHz, $CDCl_3$) of **3ya** (*see procedure*)



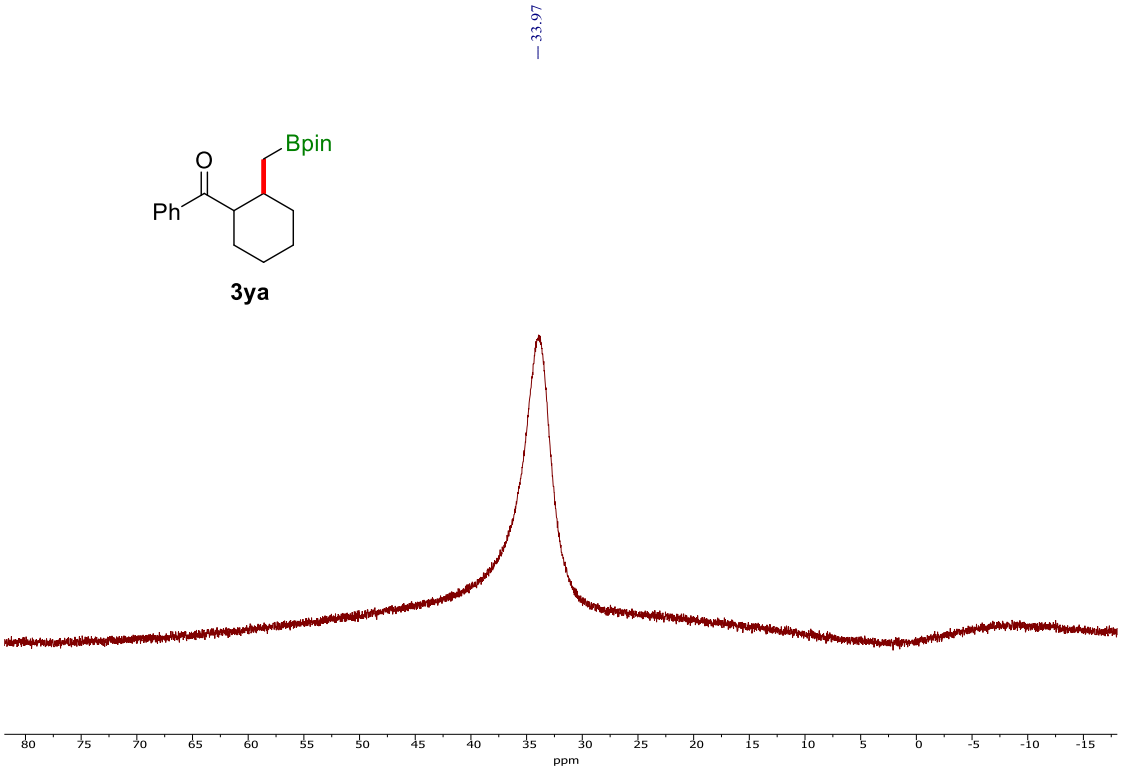
NOESY (400 MHz, $CDCl_3$) of **3ya**



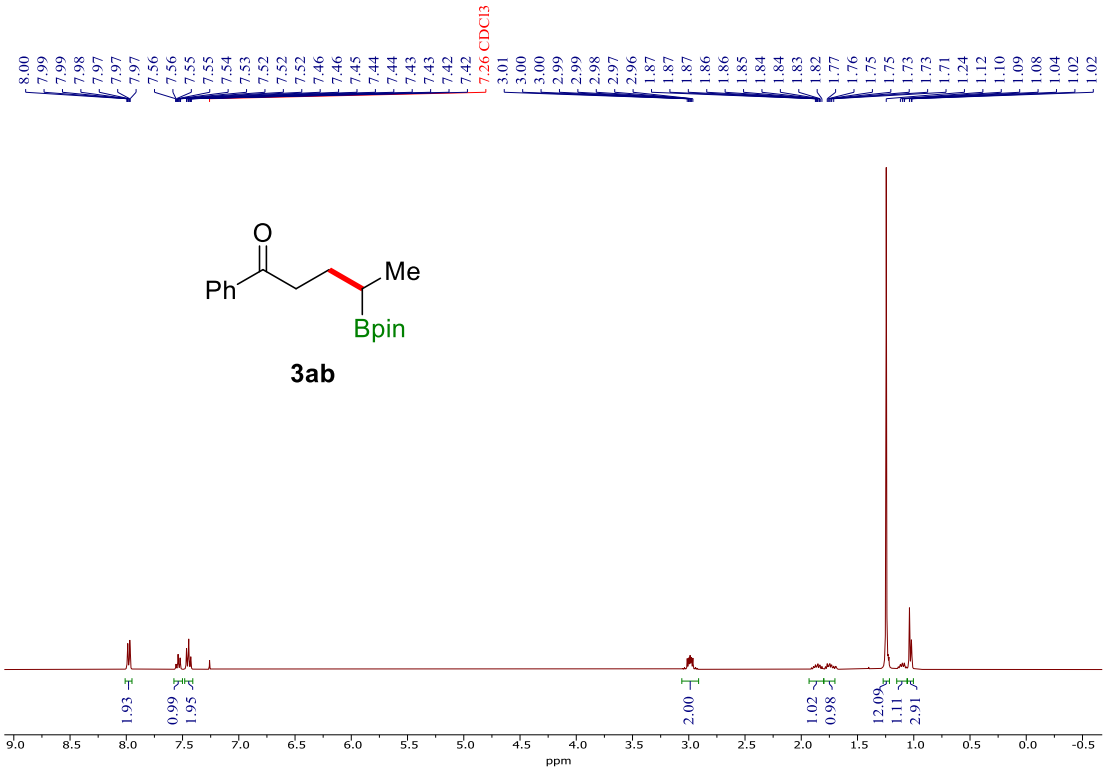
^{13}C NMR (101 MHz, $CDCl_3$) of **3ya**



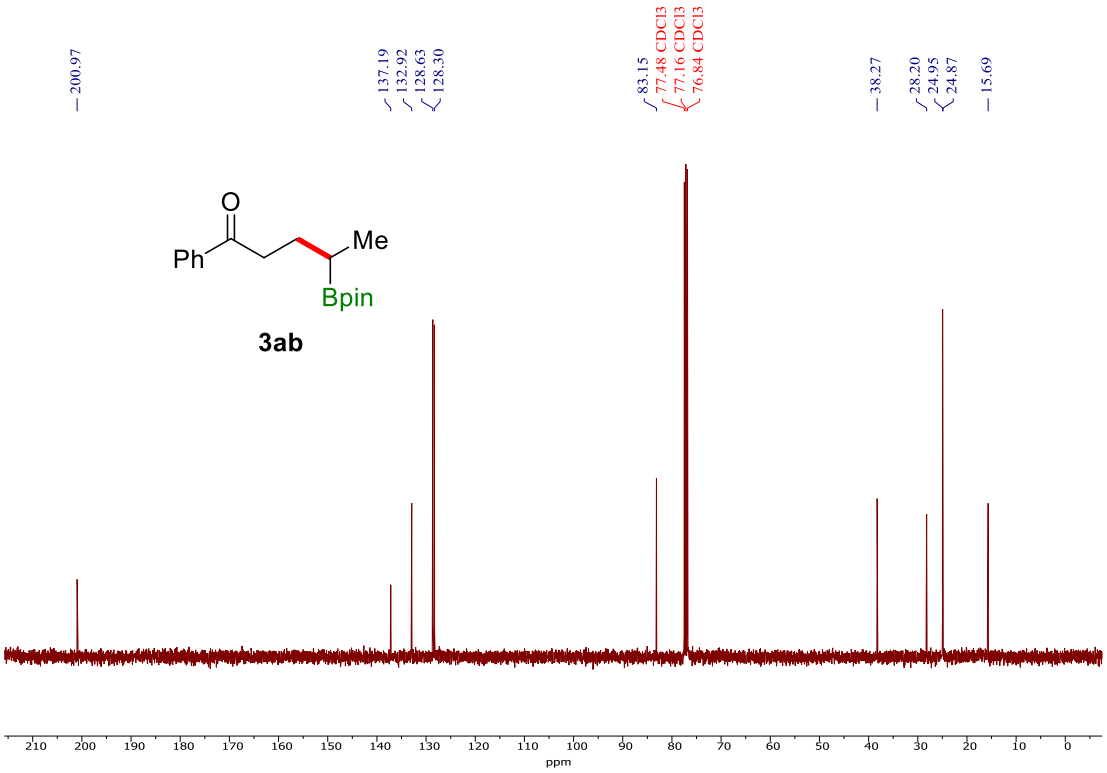
^{11}B NMR (128 MHz, $CDCl_3$) of **3ya**



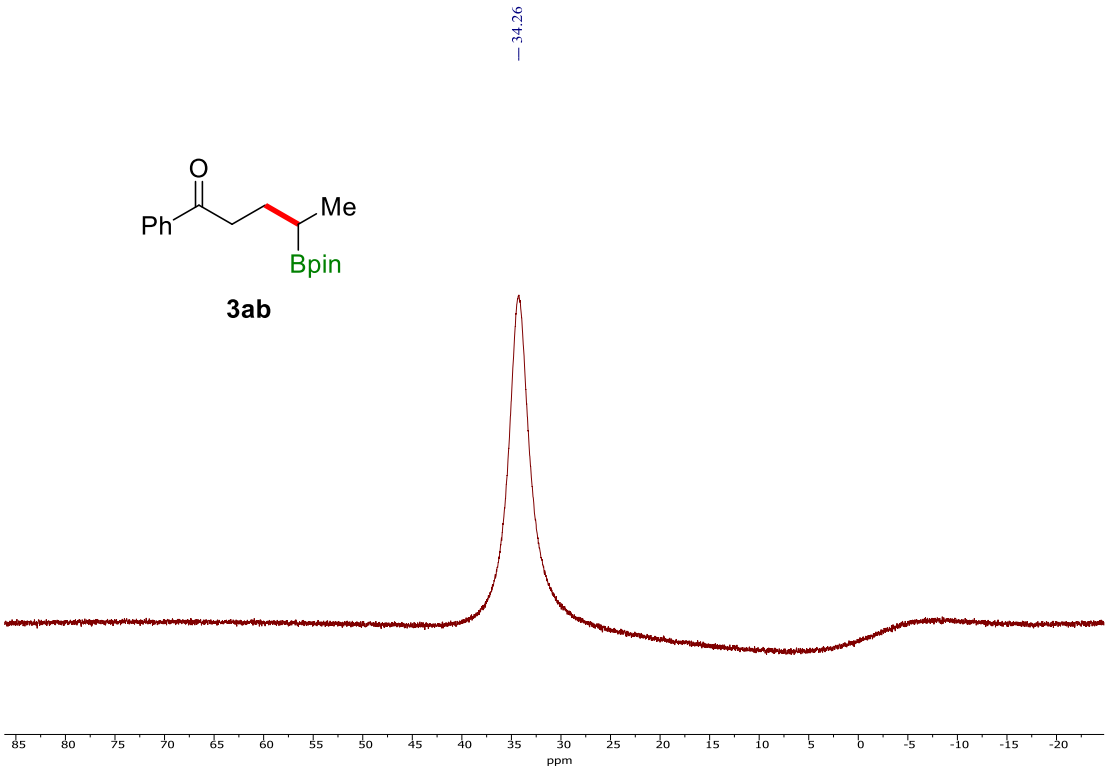
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab** (*see procedure*)



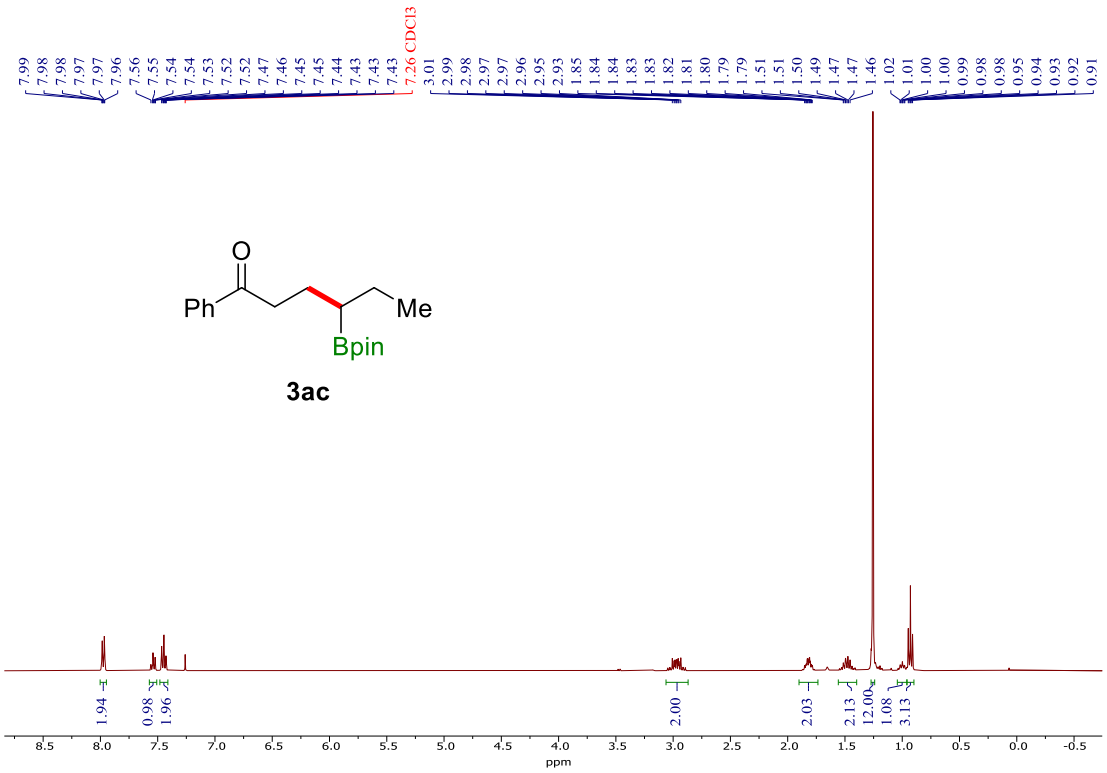
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



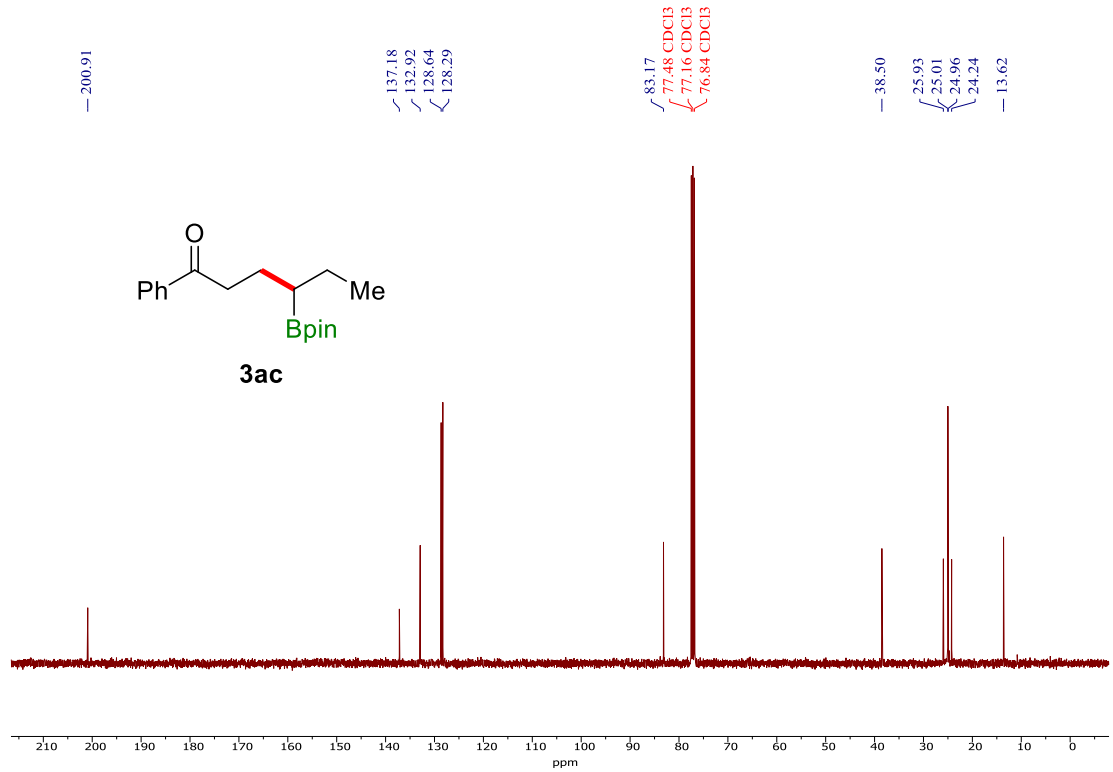
^{11}B NMR (128 MHz, $CDCl_3$) of **3ab**



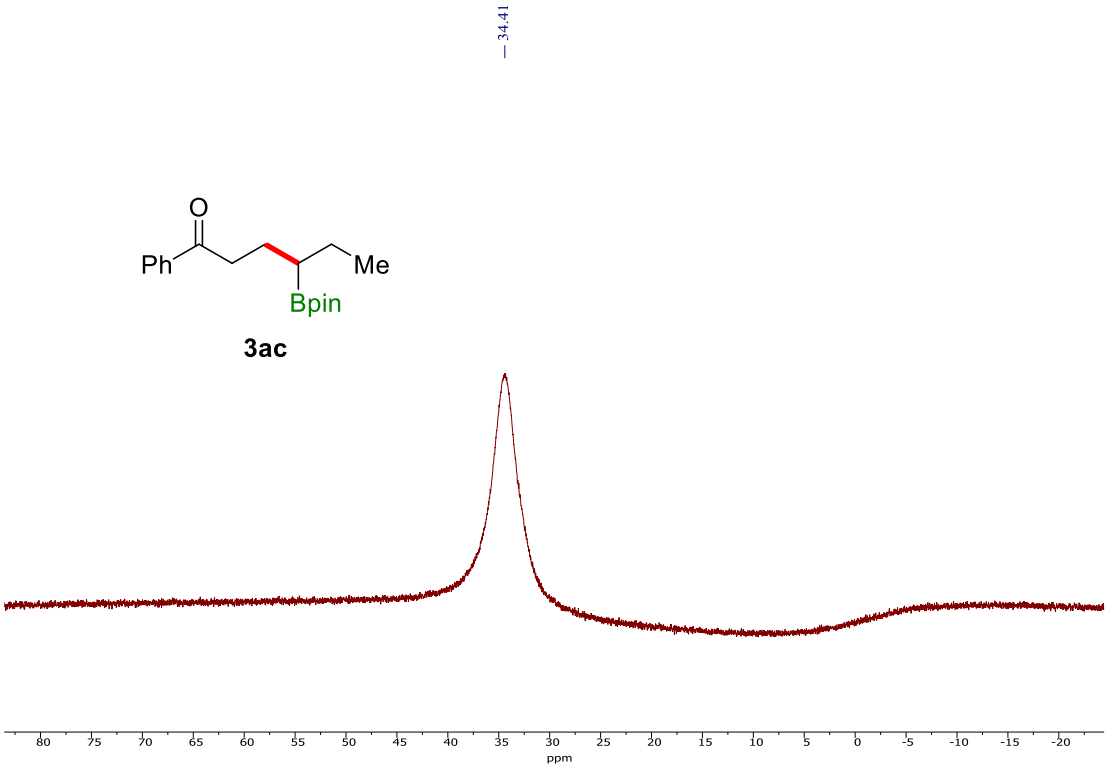
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac** (*see procedure*)



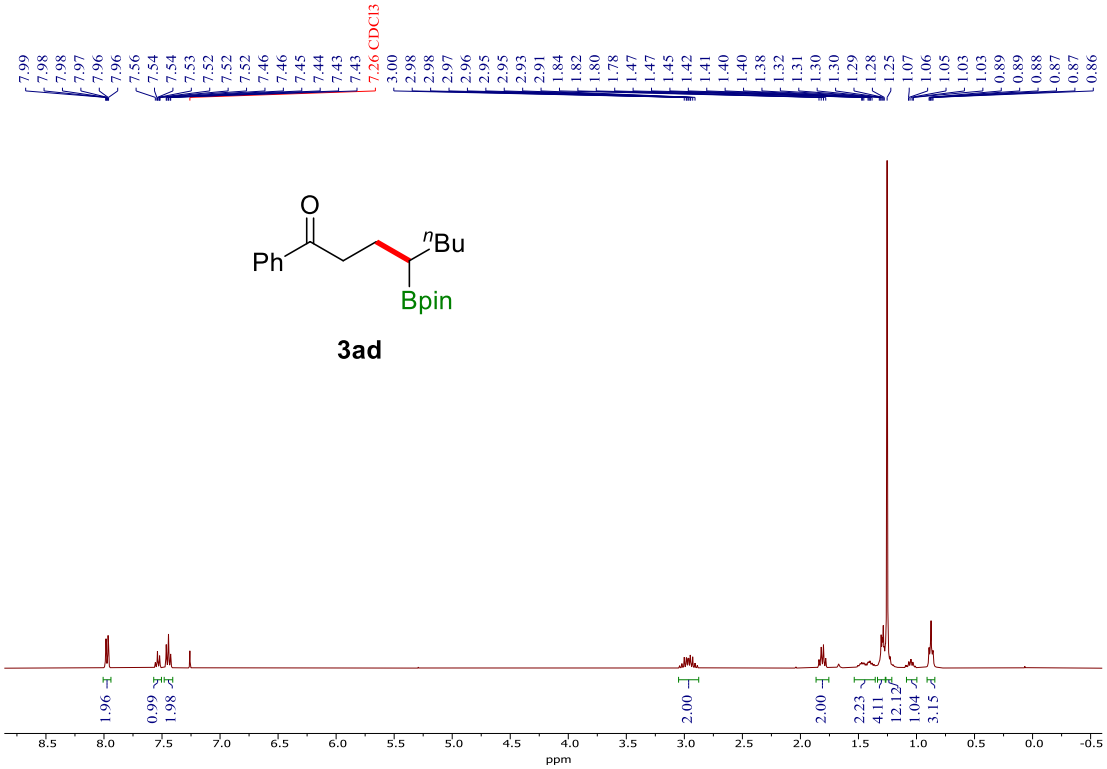
^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



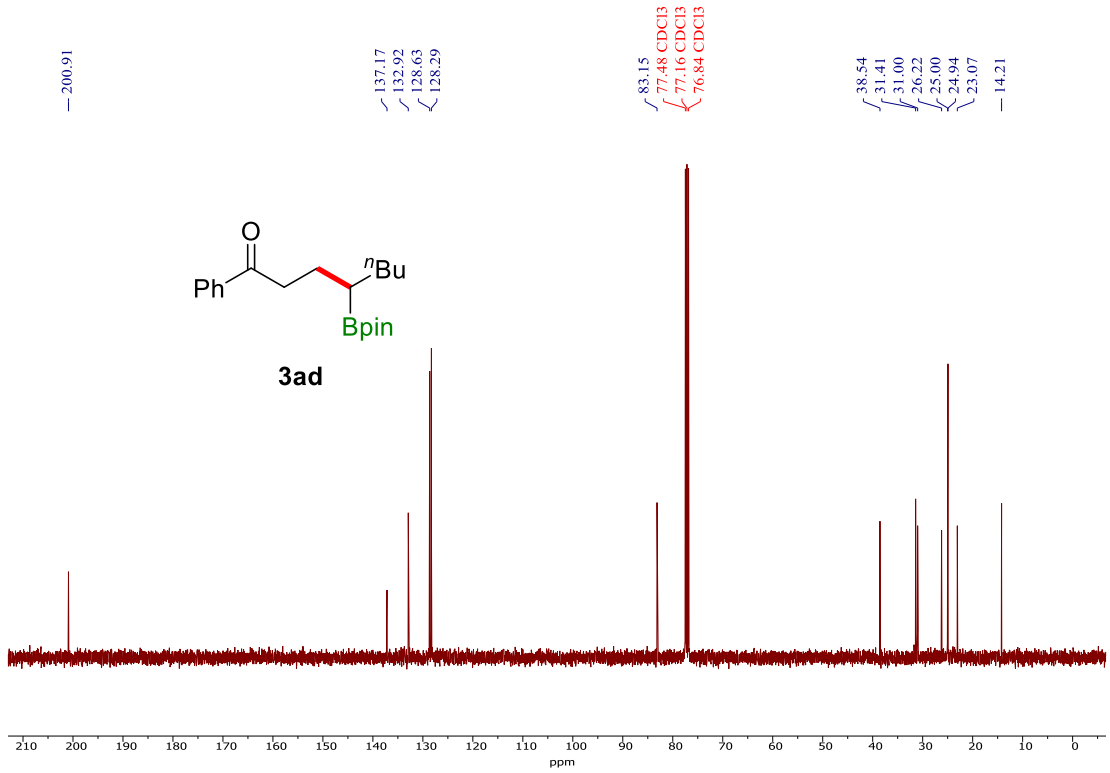
^{11}B NMR (128 MHz, $CDCl_3$) of **3ac**



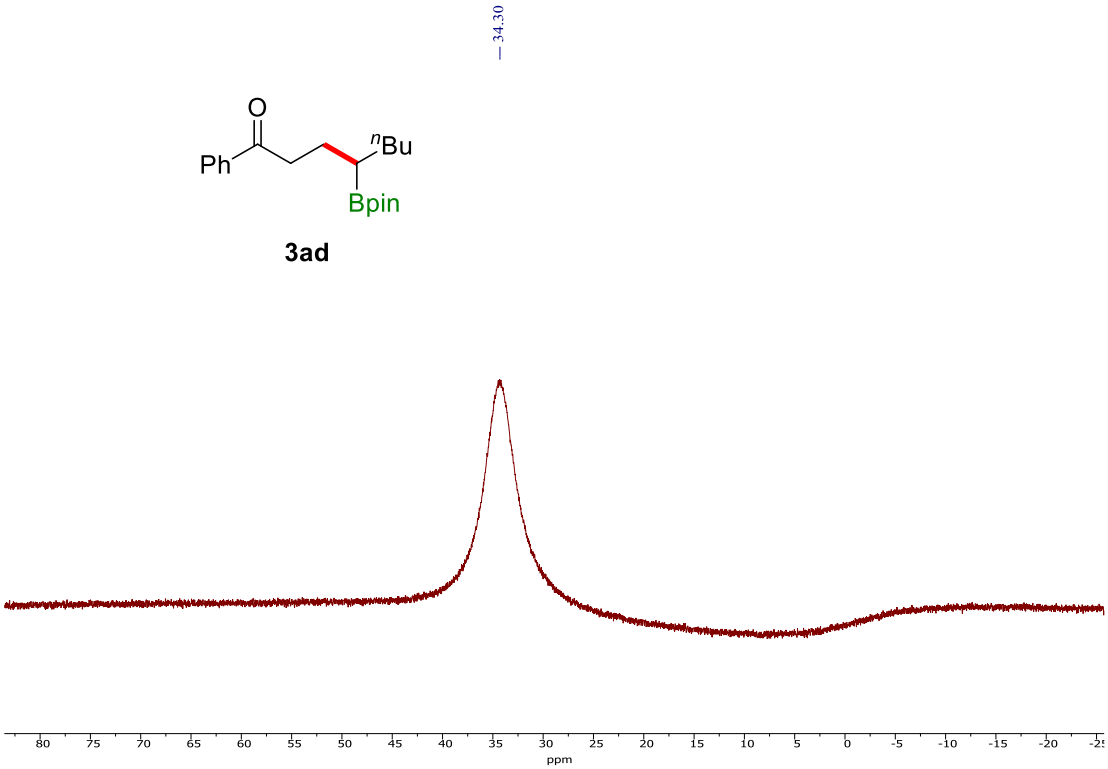
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad** (*see procedure*)



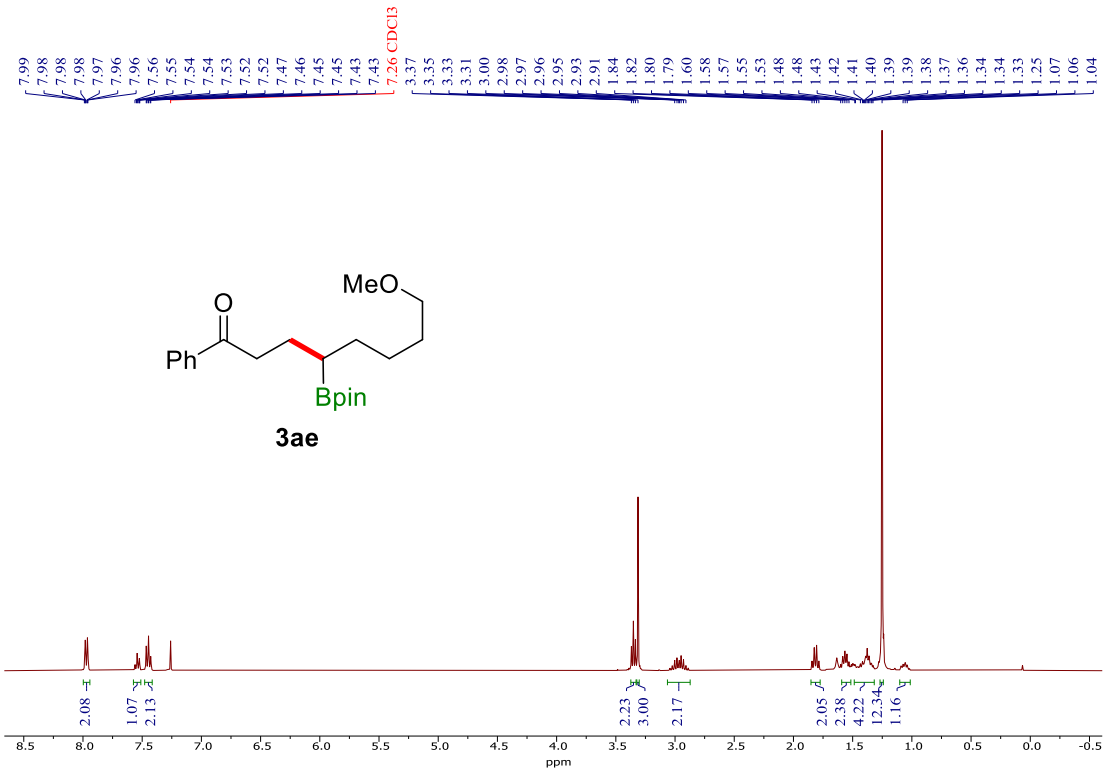
^{13}C NMR (101 MHz, $CDCl_3$) of **3ad**



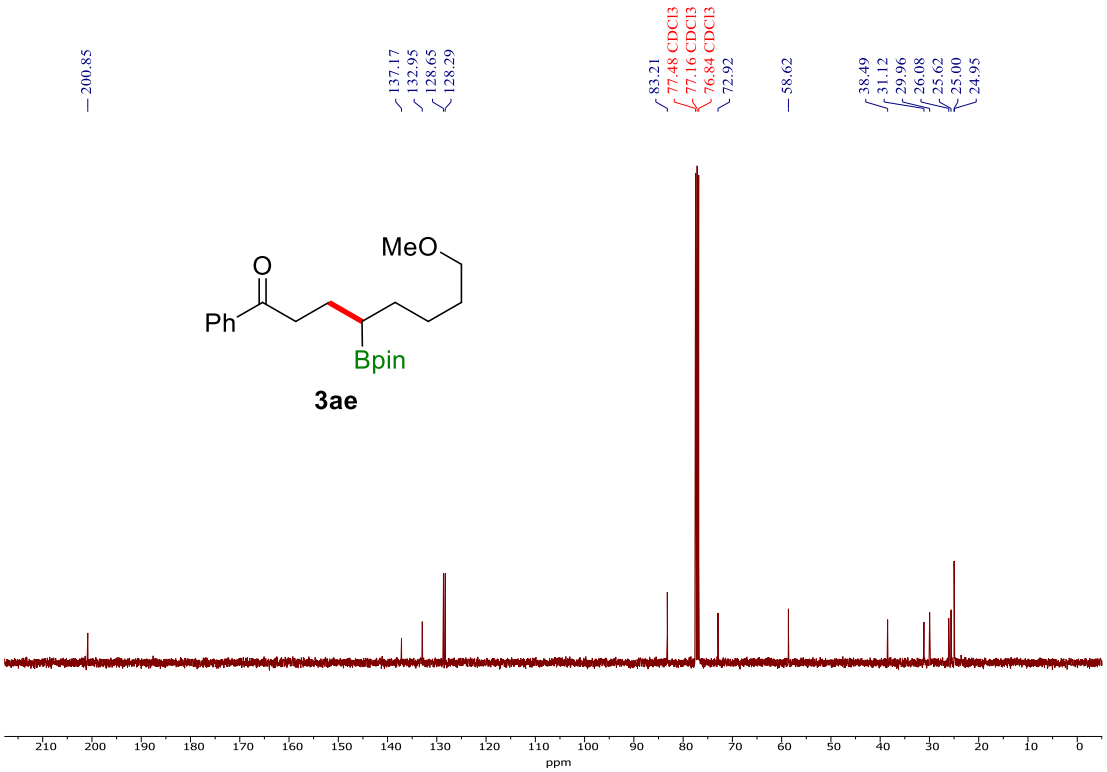
^{11}B NMR (128 MHz, $CDCl_3$) of **3ad**



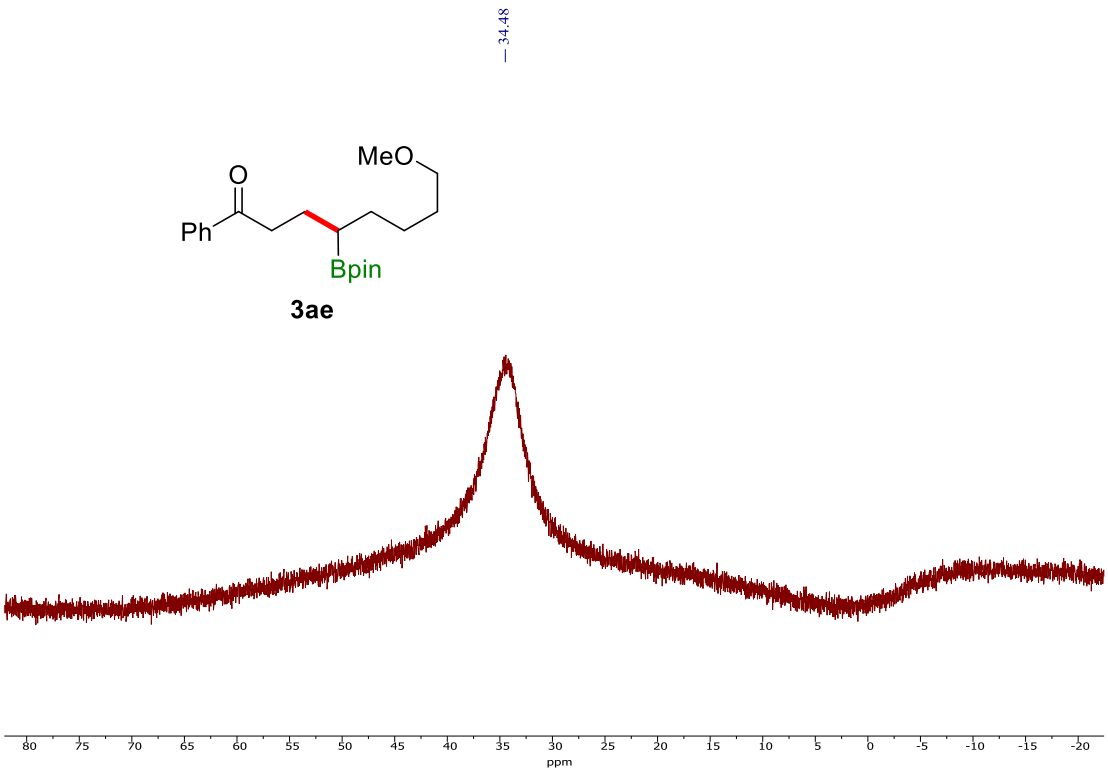
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae** (*see procedure*)



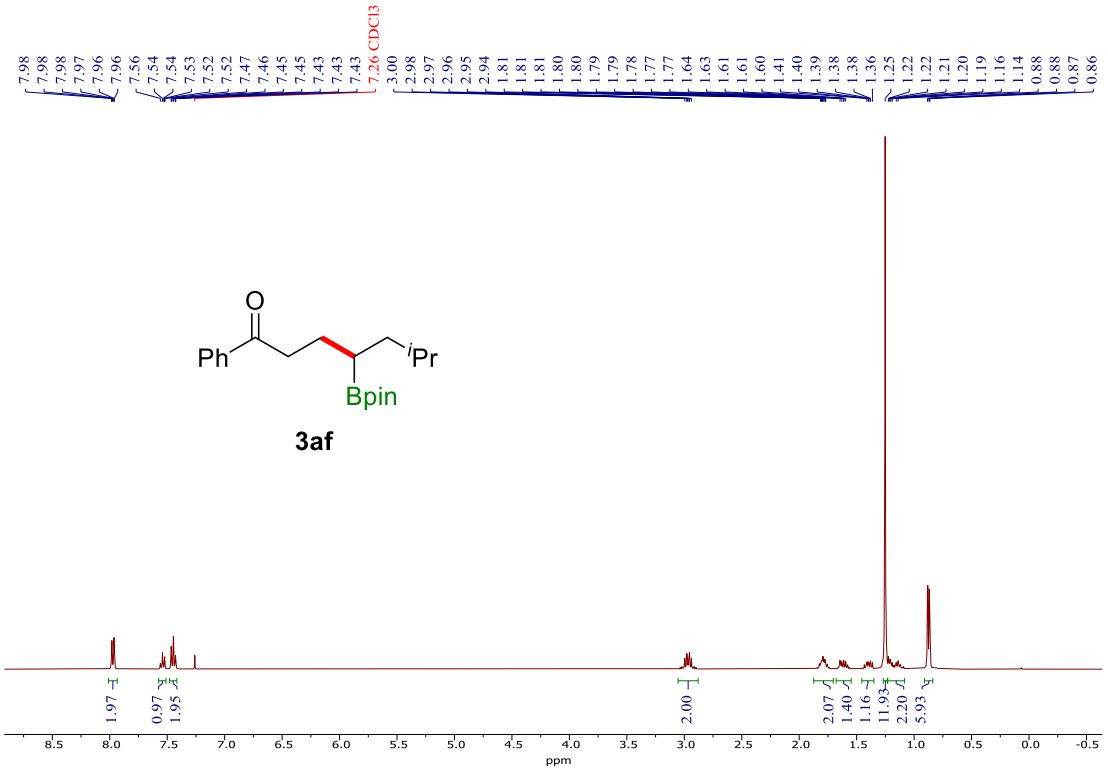
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



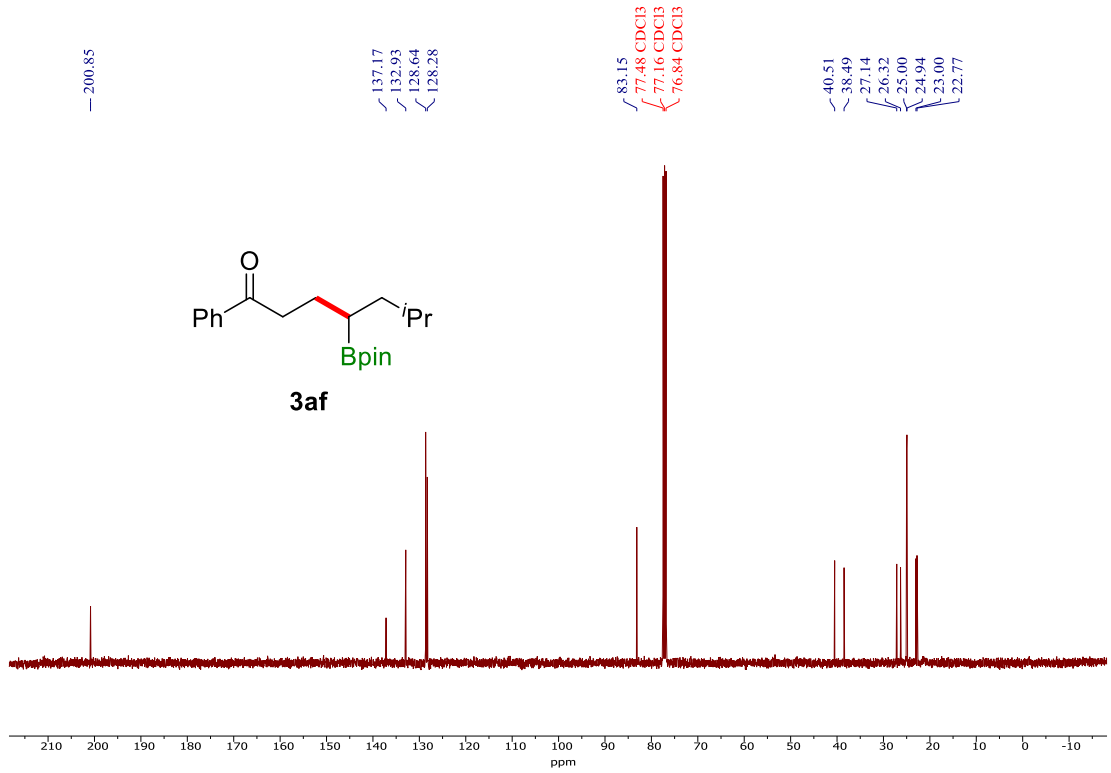
^{11}B NMR (128 MHz, $CDCl_3$) of **3ae**



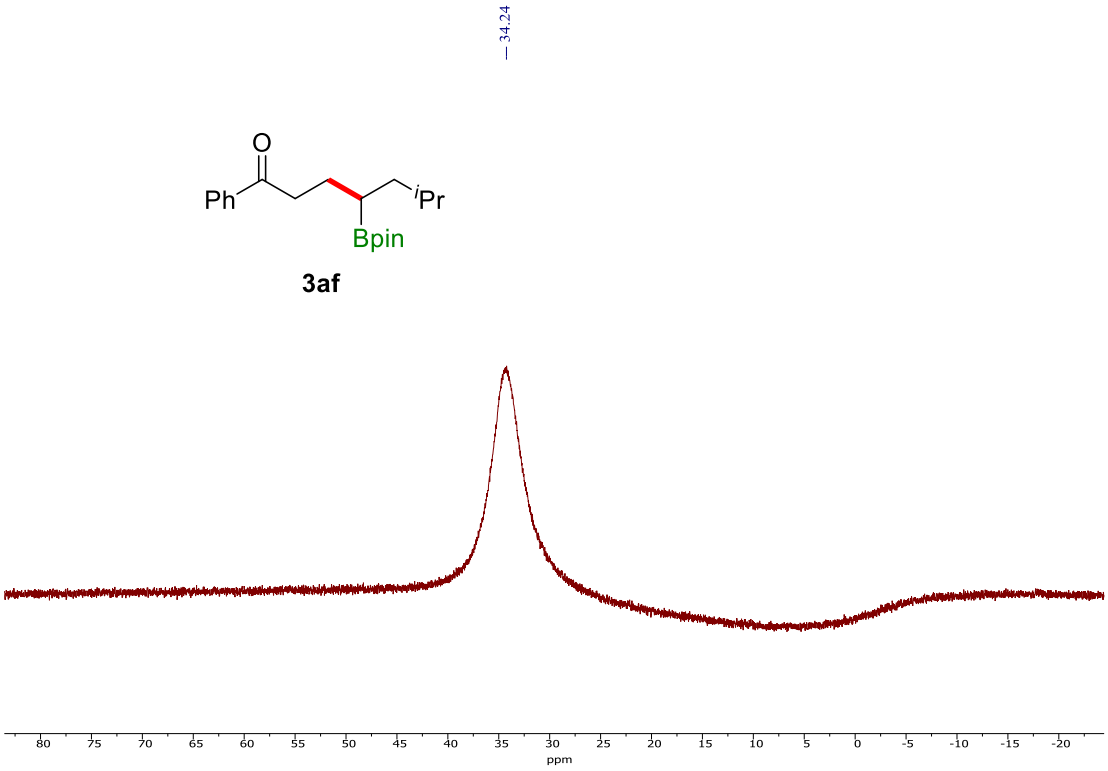
^{1}H NMR (400 MHz, $CDCl_3$) of **3af** (*see procedure*)



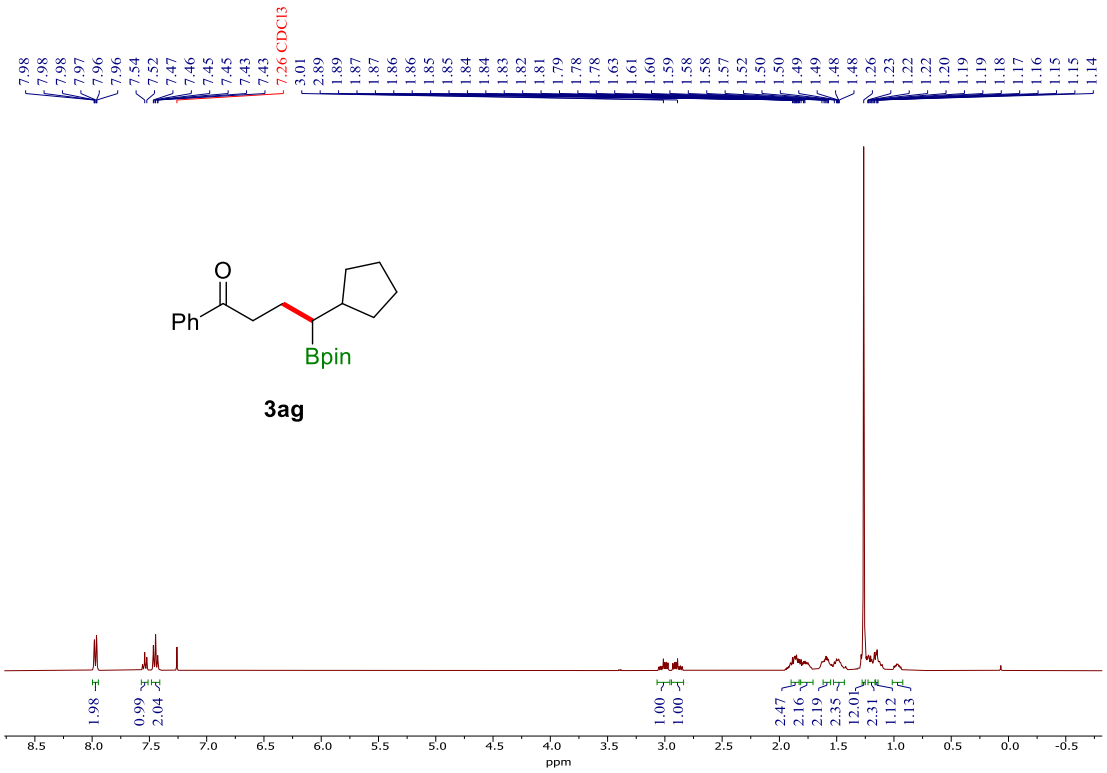
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



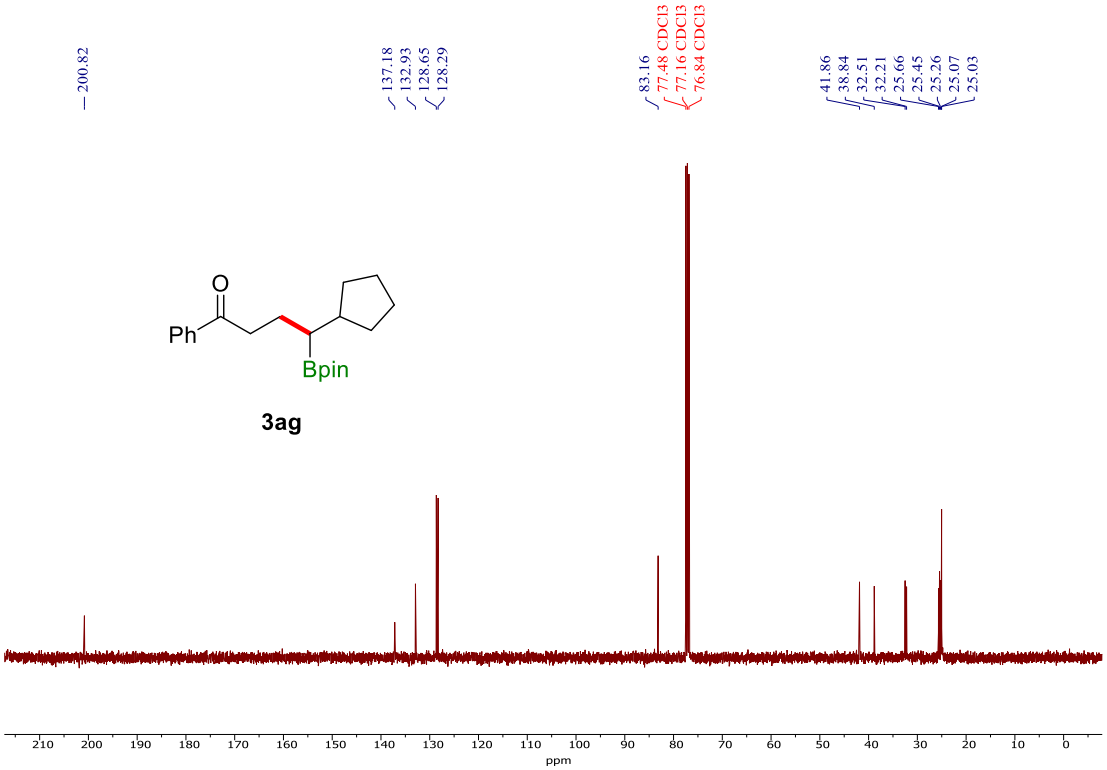
^{11}B NMR (128 MHz, $CDCl_3$) of **3af**



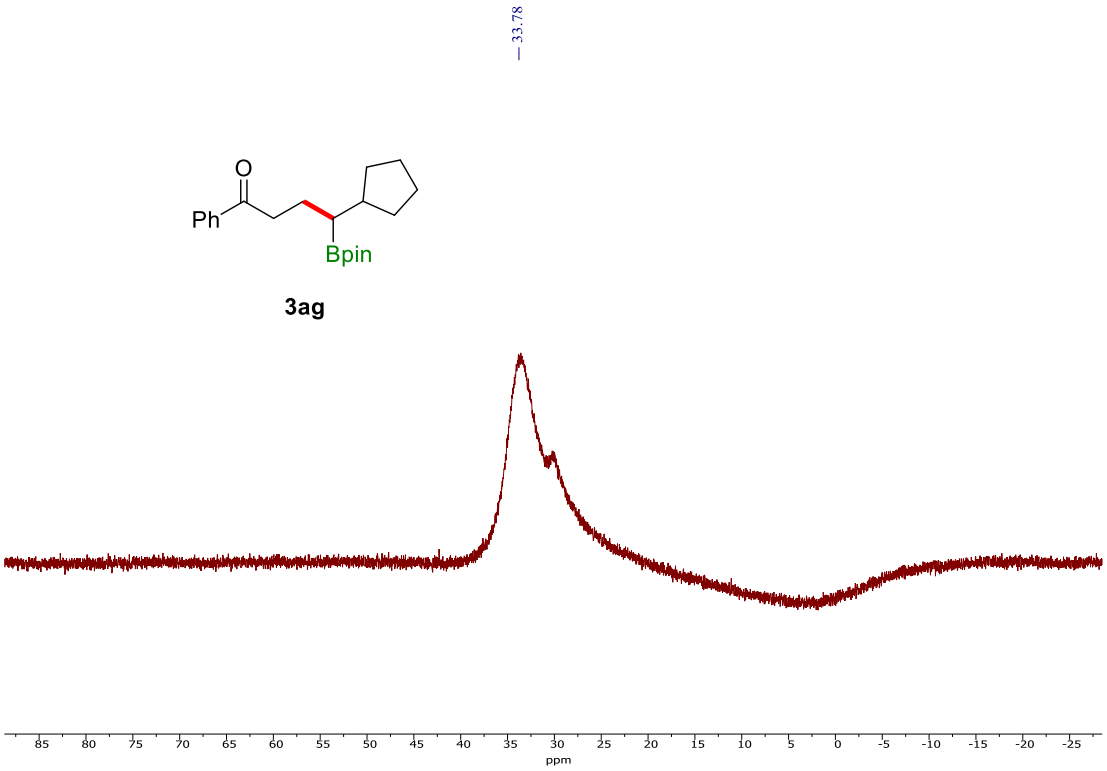
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag** (*see procedure*)



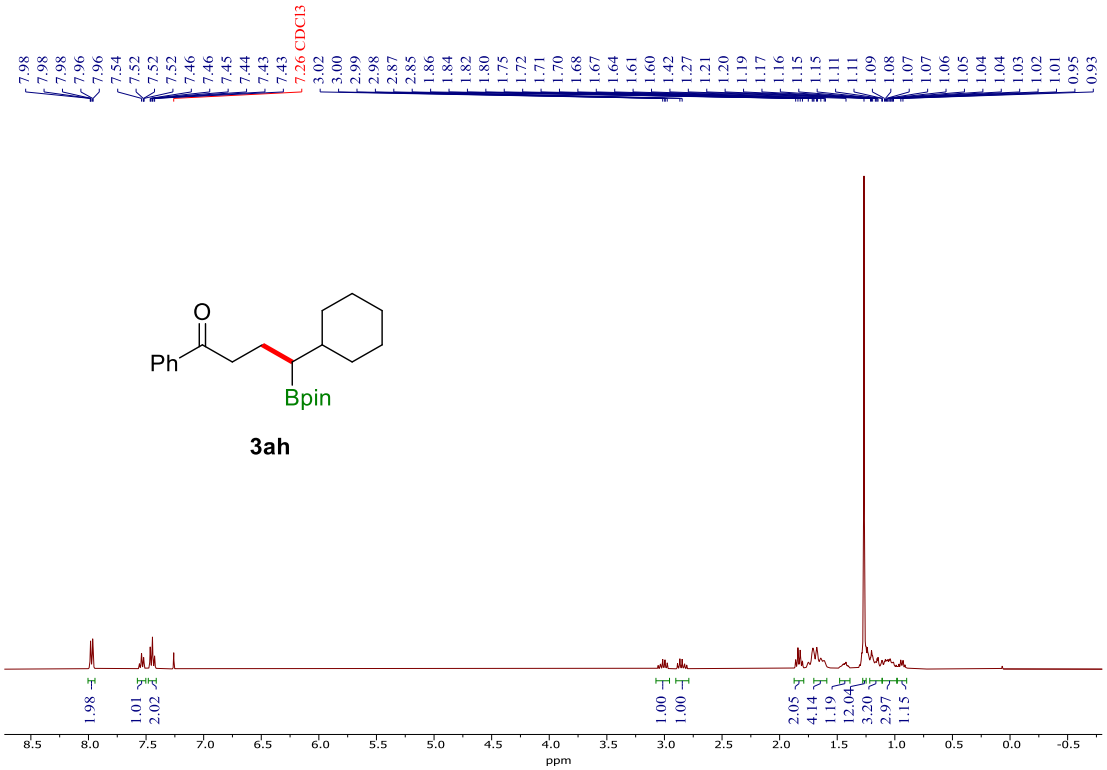
^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



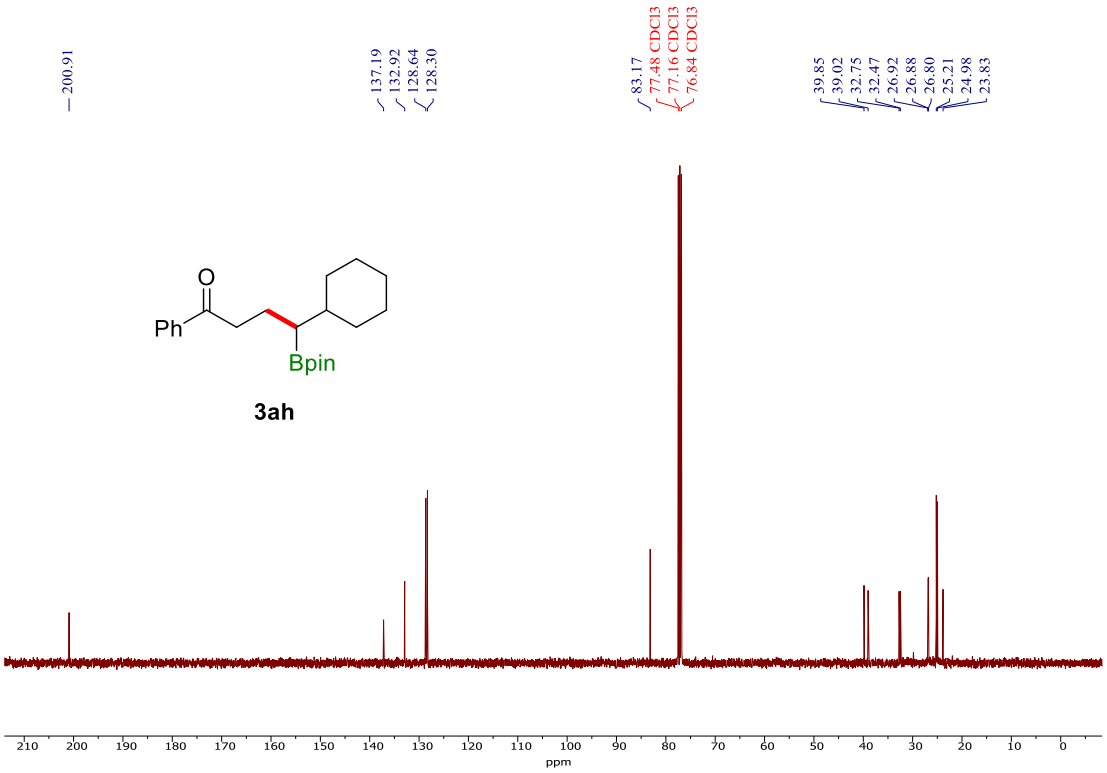
^{11}B NMR (128 MHz, $CDCl_3$) of **3ag**



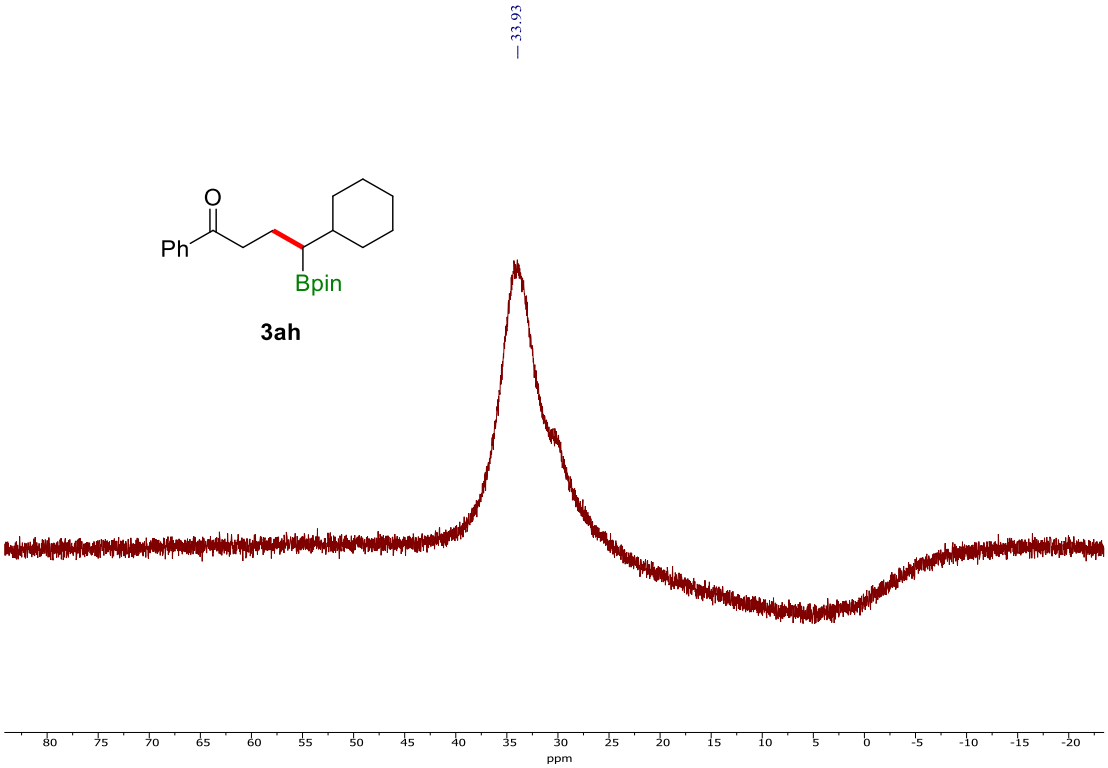
^{1}H NMR (400 MHz, $CDCl_3$) of **3ah** (*see procedure*)



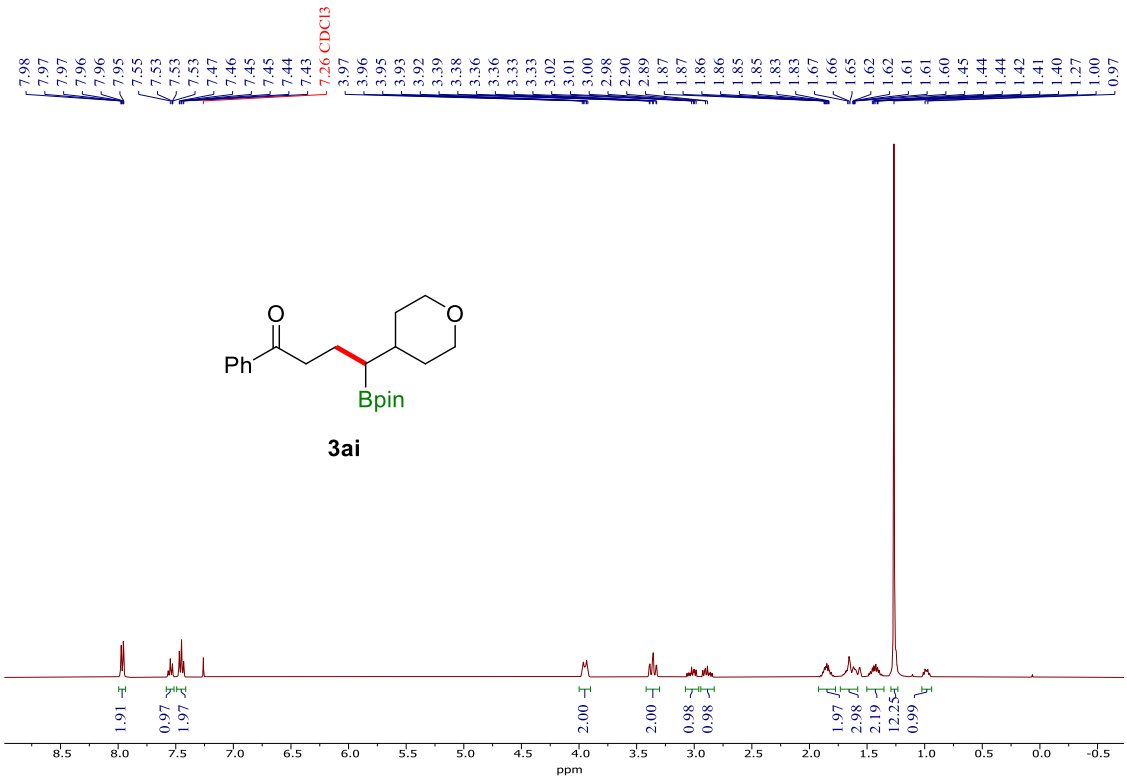
^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**



^{11}B NMR (128 MHz, $CDCl_3$) of **3ah**

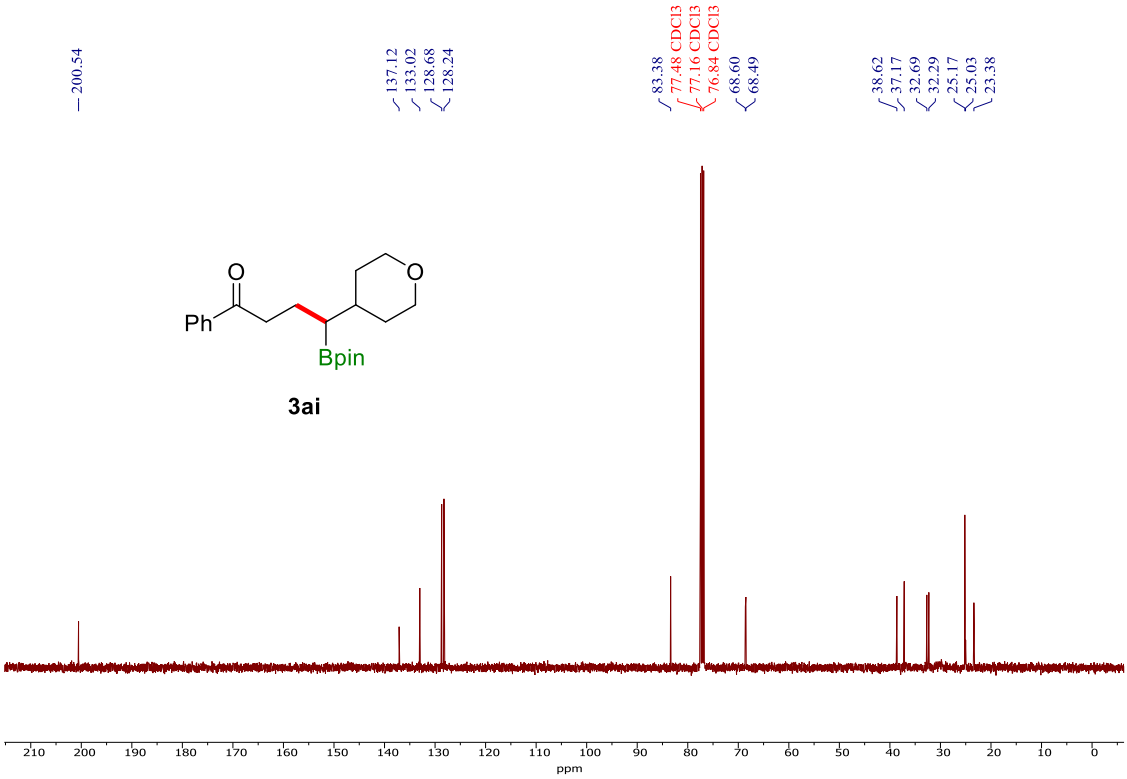


^{1}H NMR (400 MHz, $CDCl_3$) of **3ai** (*see procedure*)



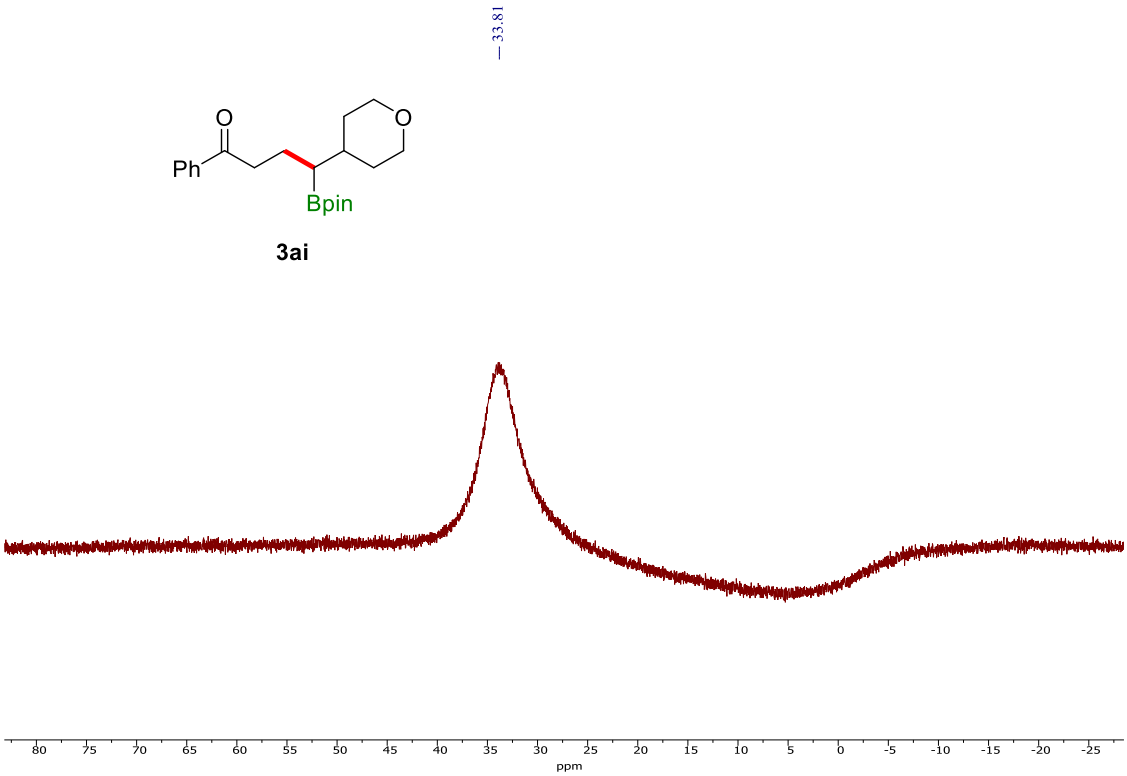
3ai

^{13}C NMR (101 MHz, $CDCl_3$) of **3ai**

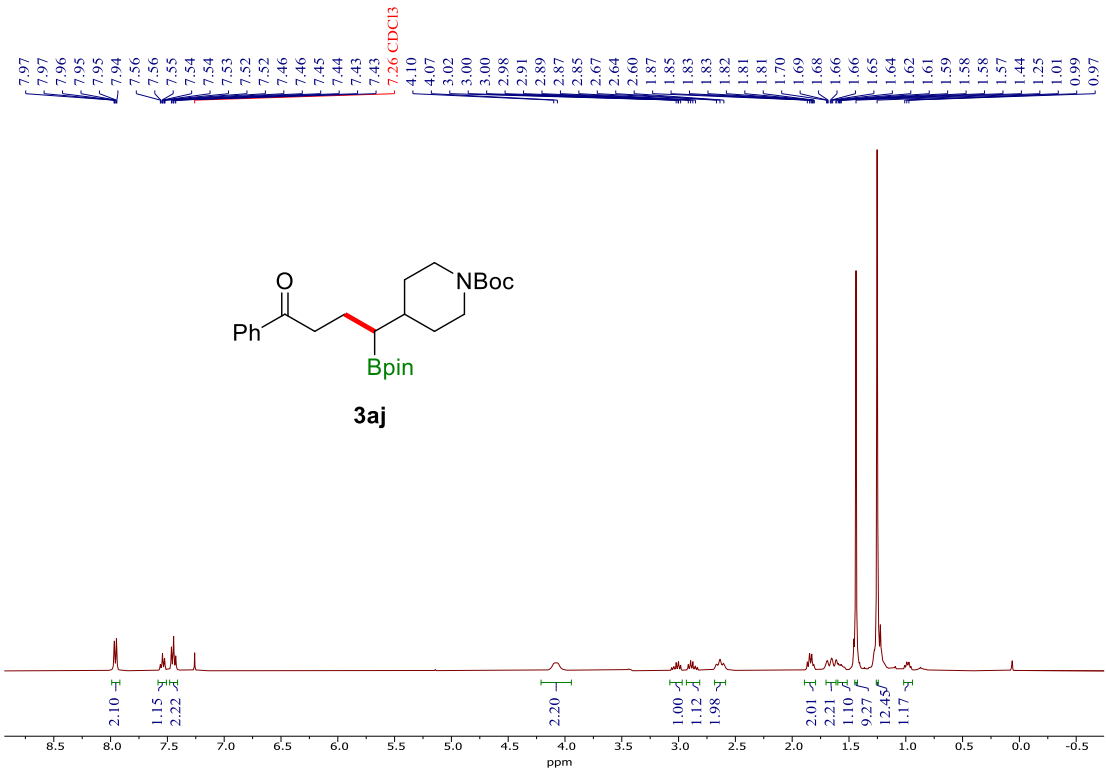


3ai

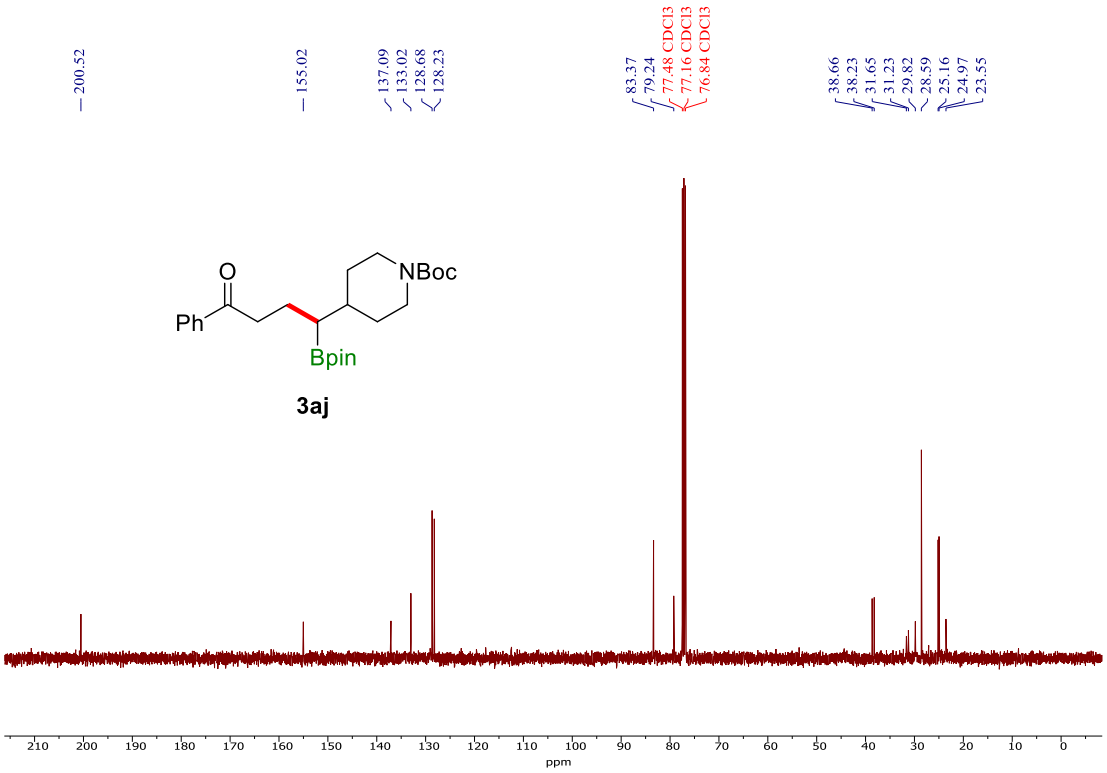
^{11}B NMR (128 MHz, $CDCl_3$) of **3ai**



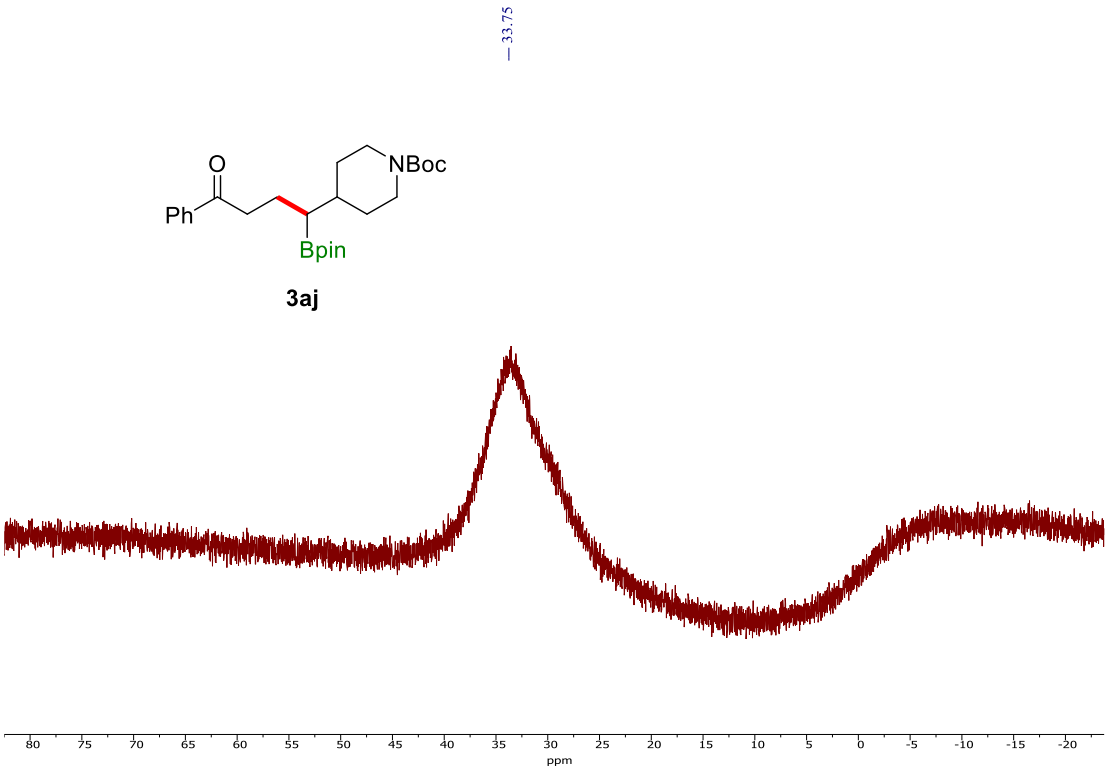
^{1}H NMR (400 MHz, $CDCl_3$) of **3aj** (*see procedure*)



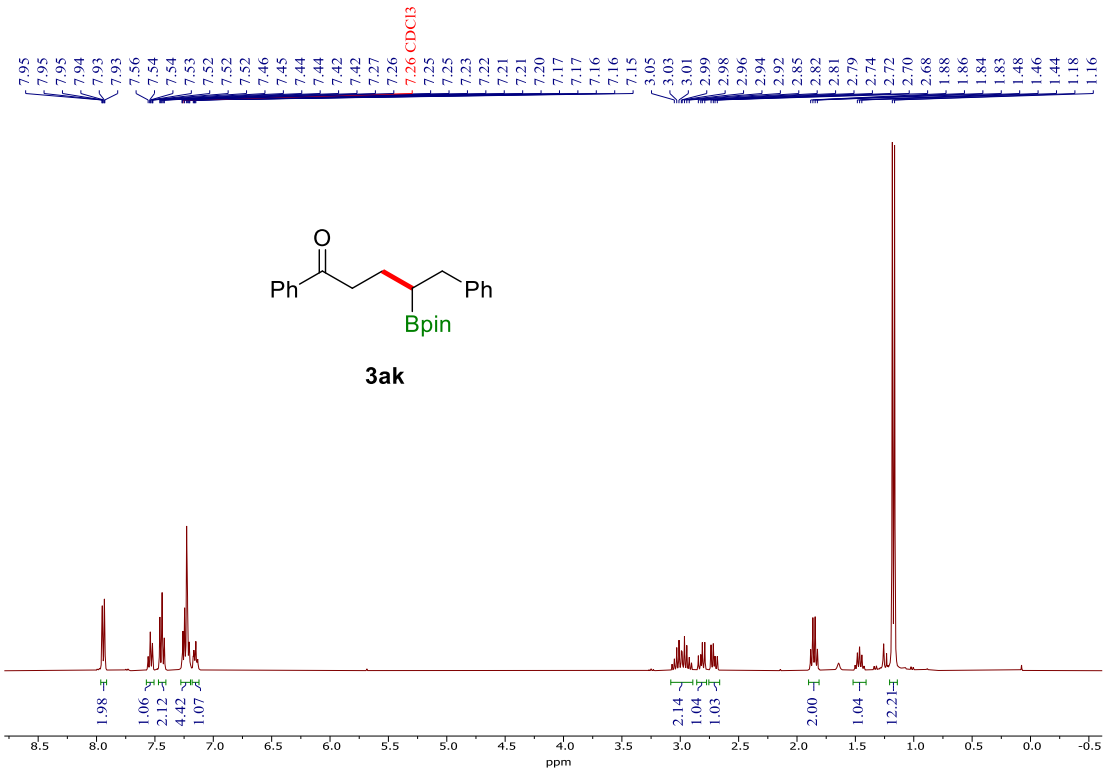
^{13}C NMR (101 MHz, $CDCl_3$) of **3aj**



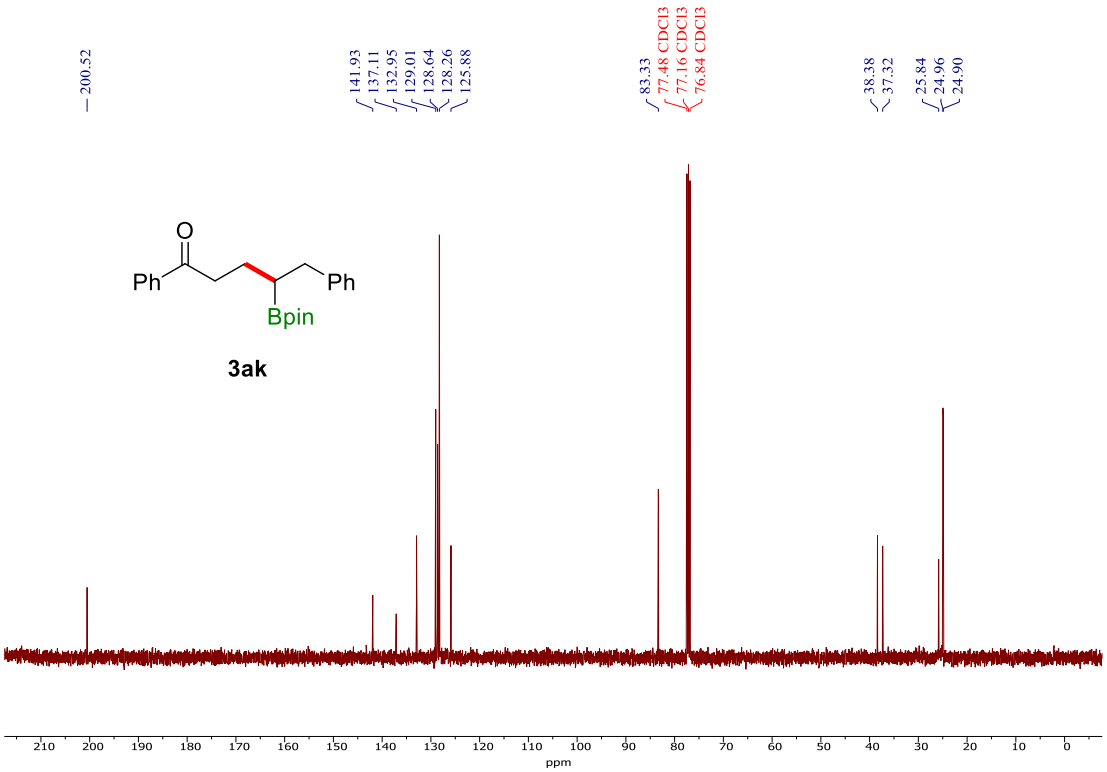
^{11}B NMR (128 MHz, $CDCl_3$) of **3aj**



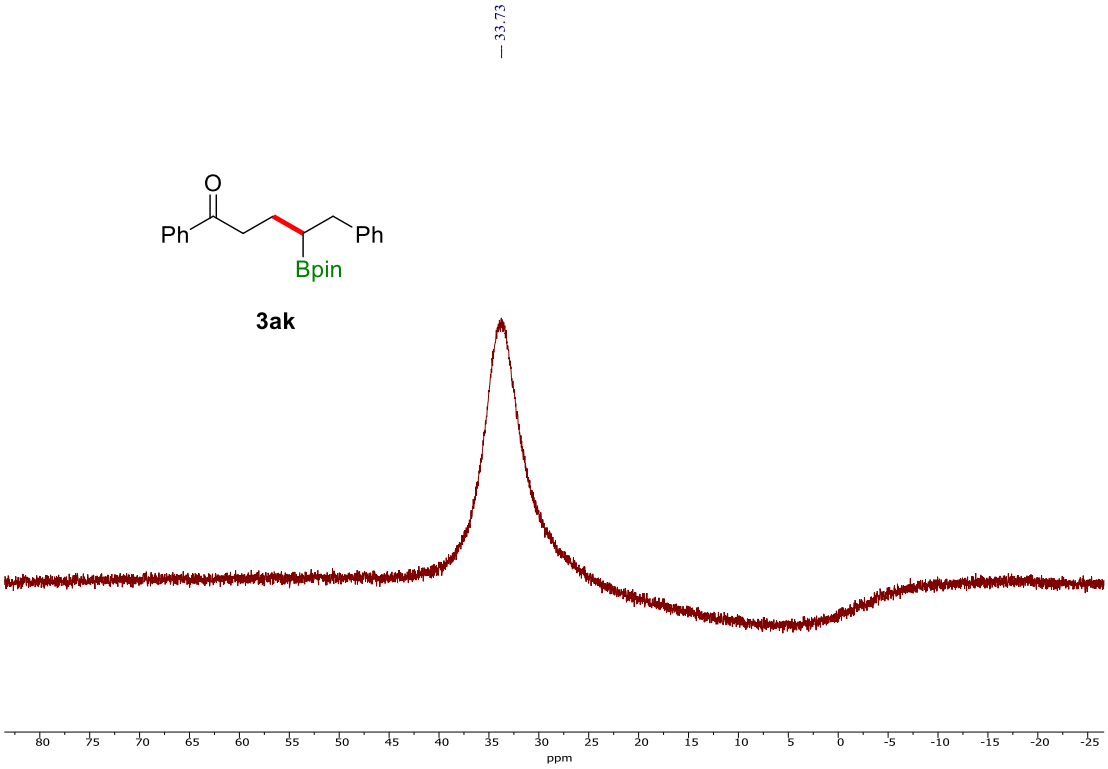
^{1}H NMR (400 MHz, $CDCl_3$) of **3ak** (*see procedure*)



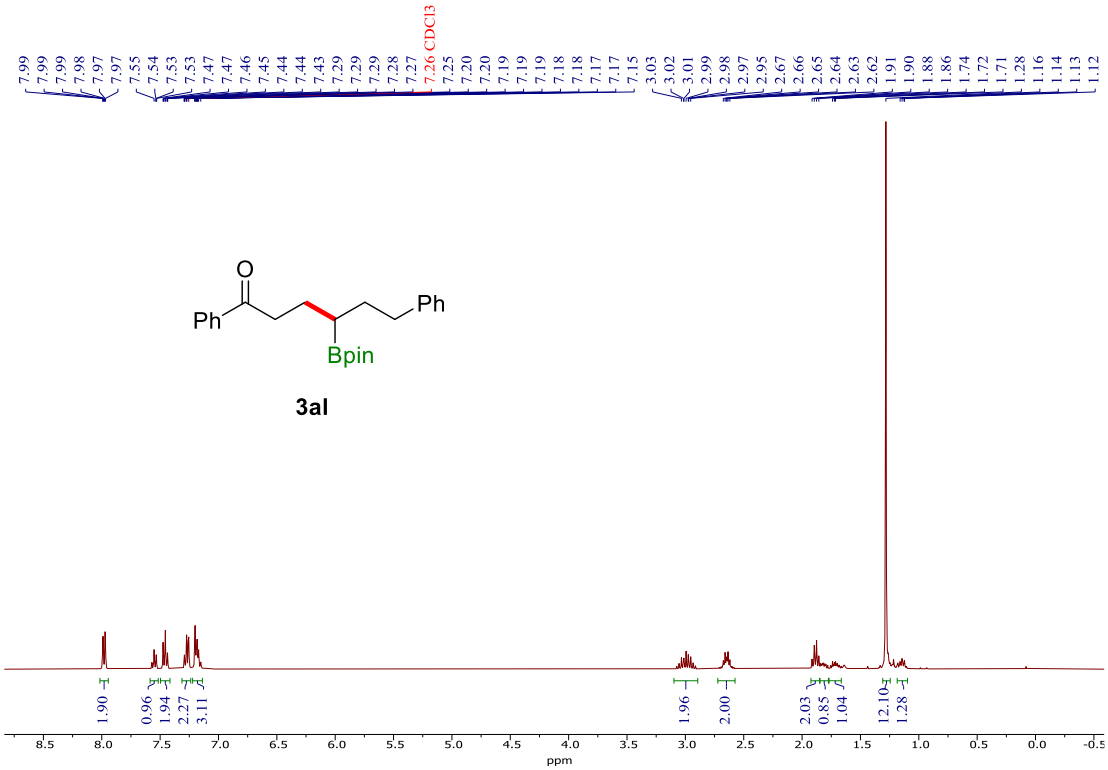
^{13}C NMR (101 MHz, $CDCl_3$) of **3ak**



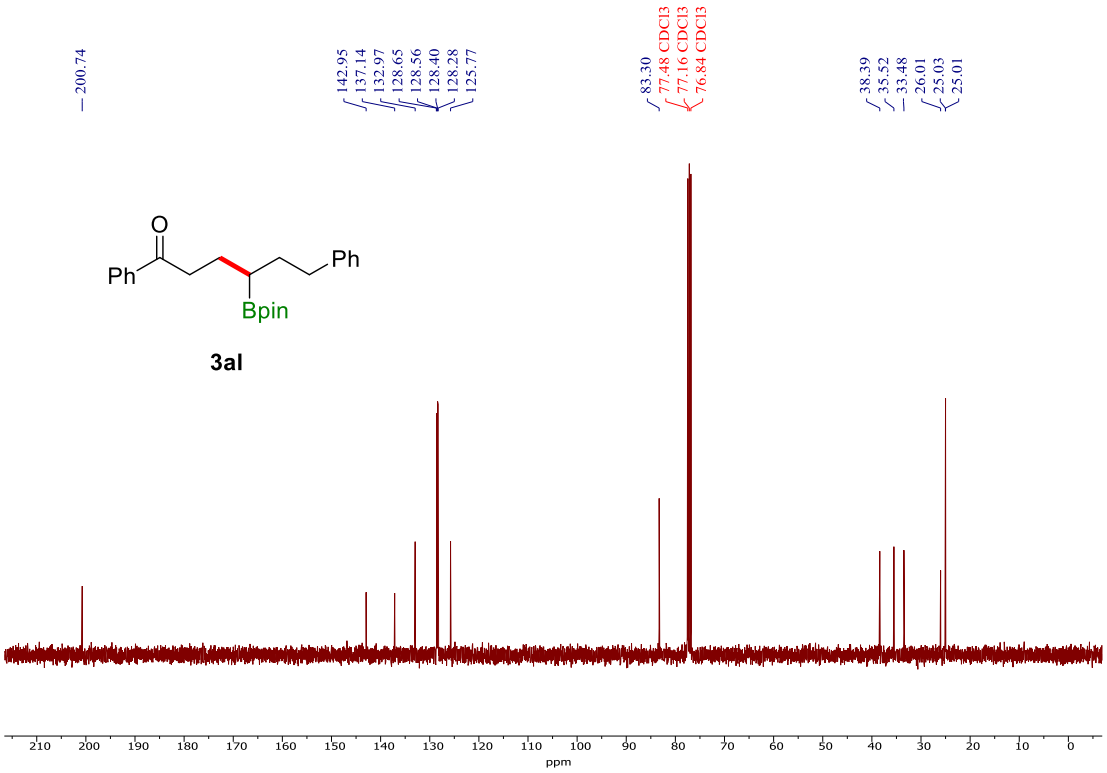
^{11}B NMR (128 MHz, $CDCl_3$) of **3ak**



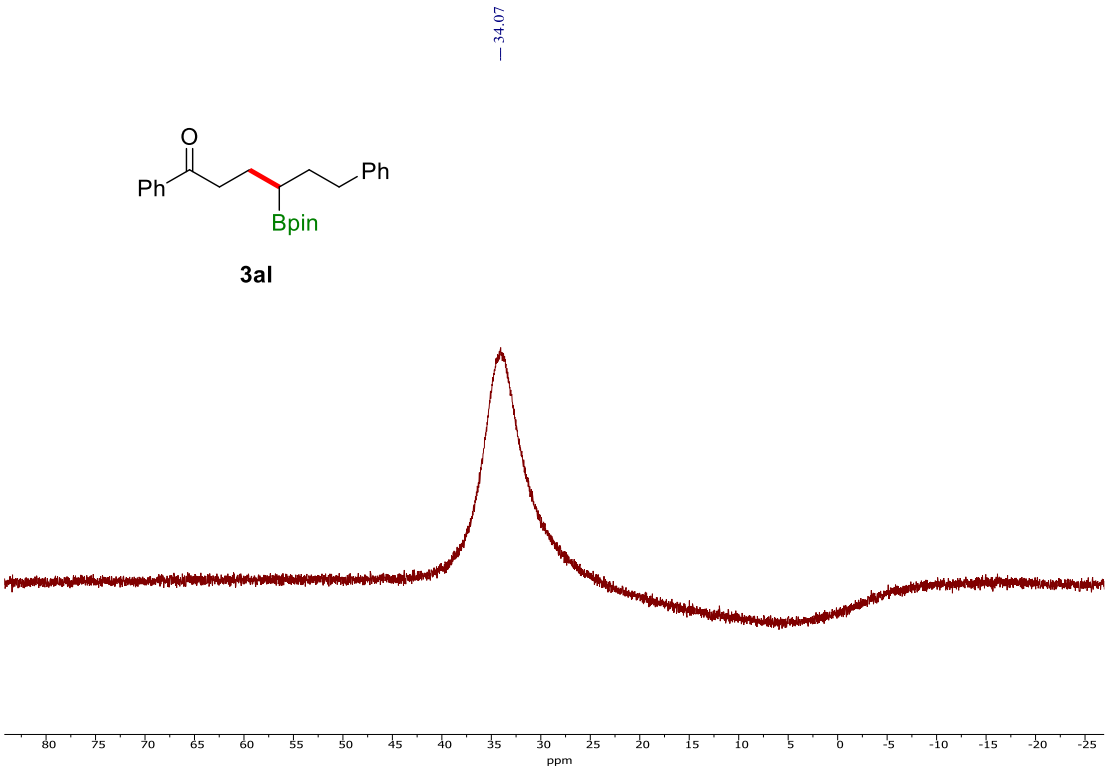
^{1}H NMR (400 MHz, $CDCl_3$) of **3al** (*see procedure*)



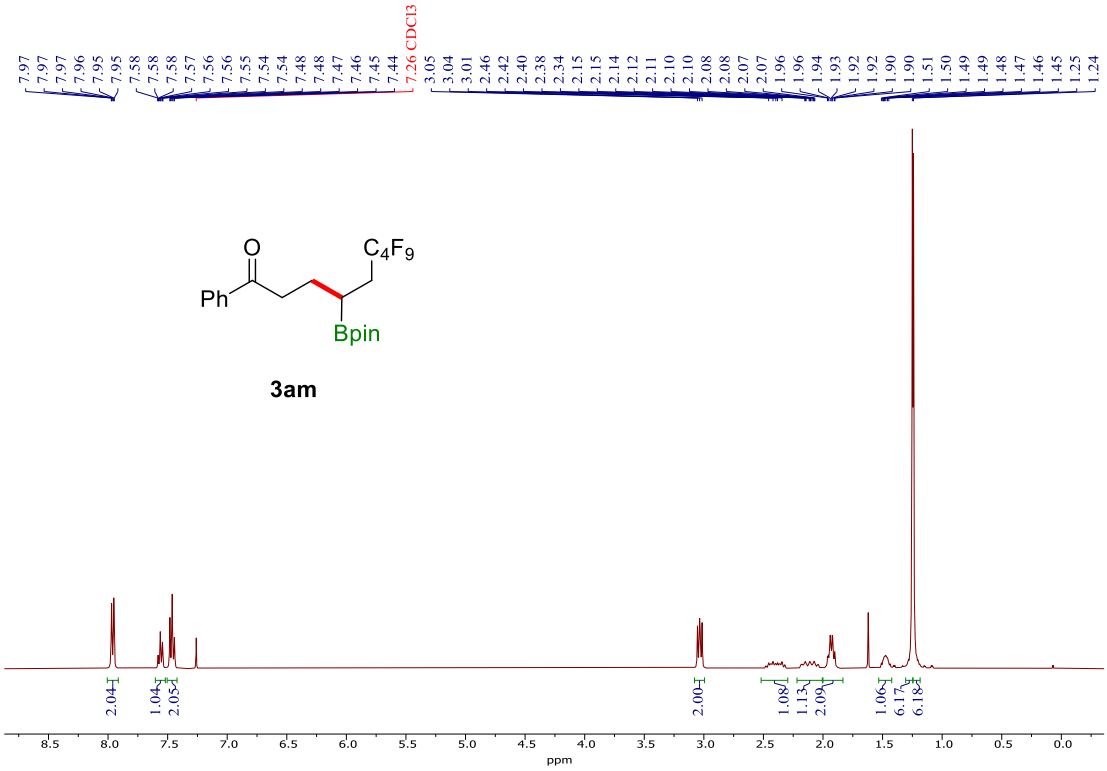
^{13}C NMR (101 MHz, $CDCl_3$) of **3al**



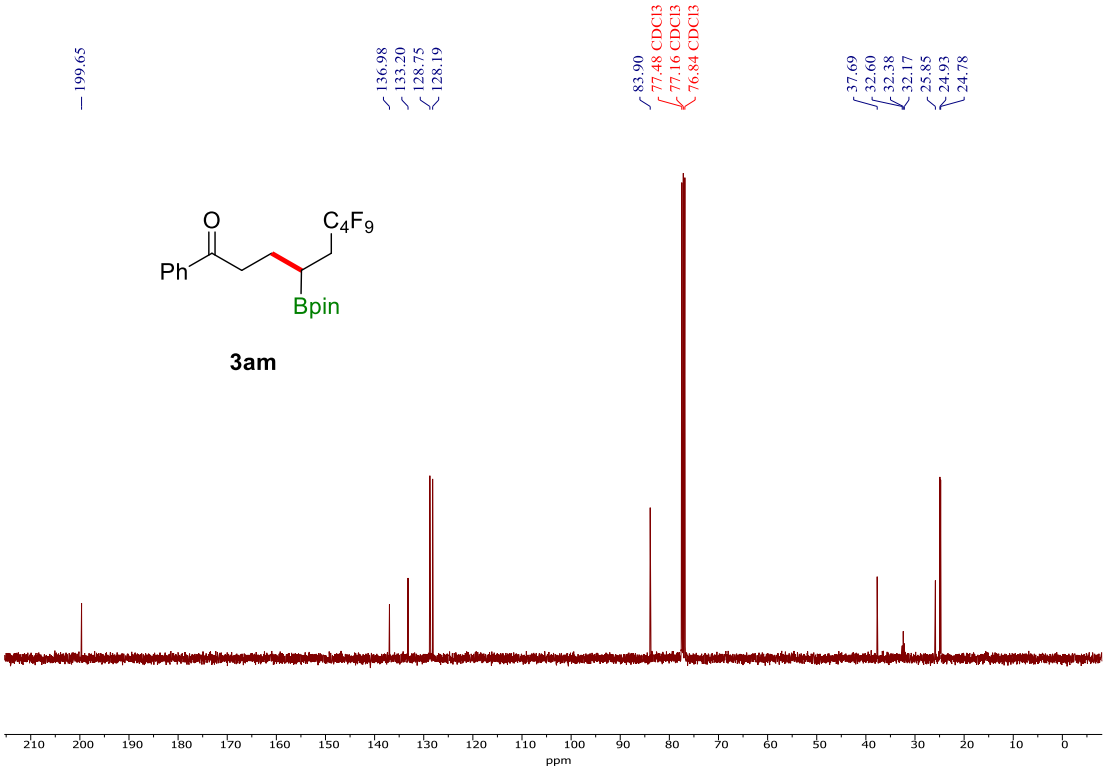
^{11}B NMR (128 MHz, $CDCl_3$) of **3al**



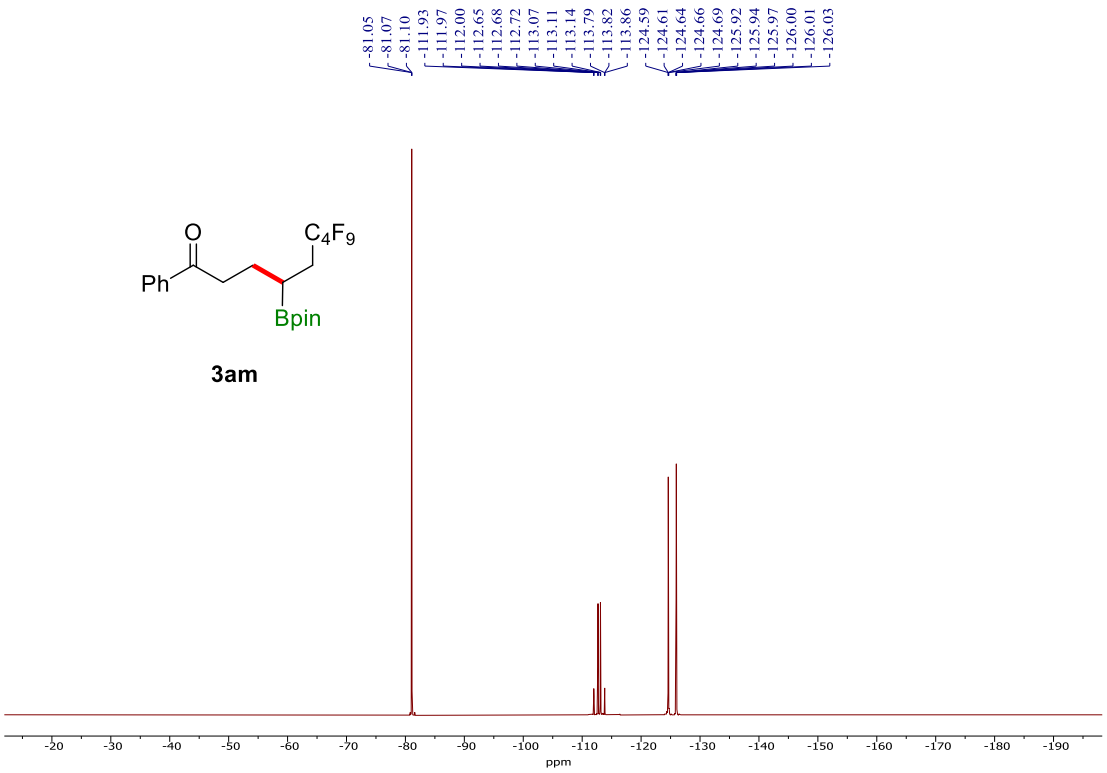
^{1}H NMR (400 MHz, $CDCl_3$) of **3am** (*see procedure*)



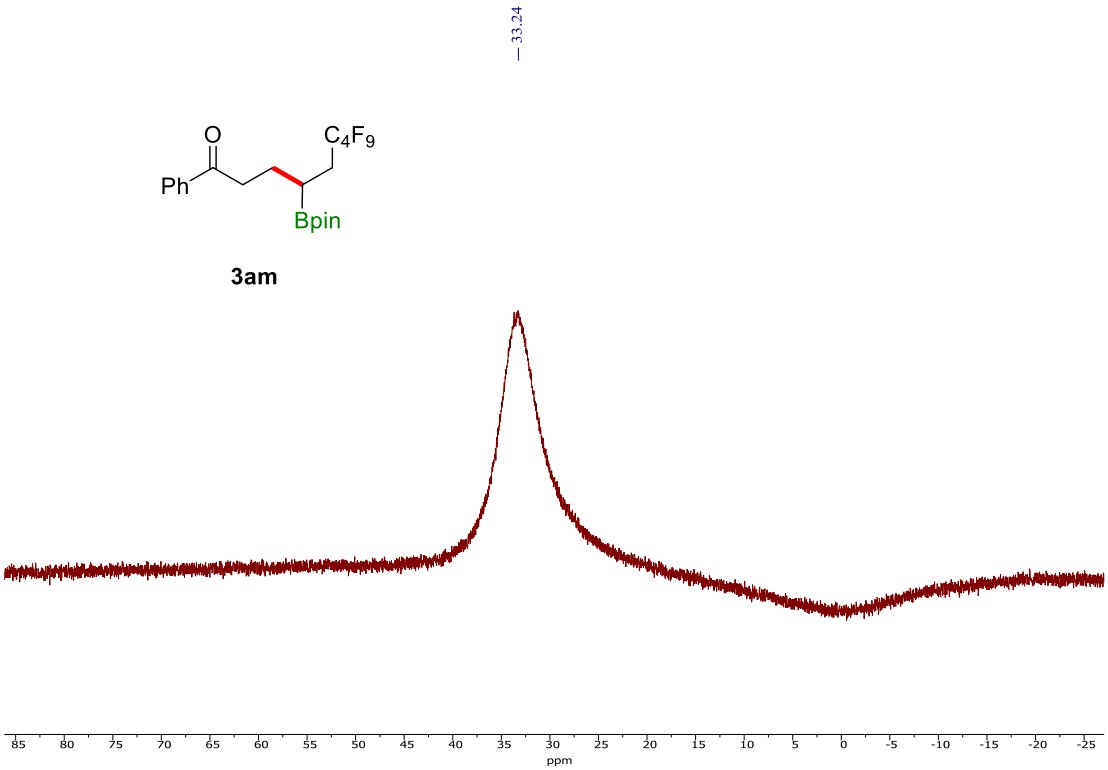
^{13}C NMR (101 MHz, $CDCl_3$) of **3am**



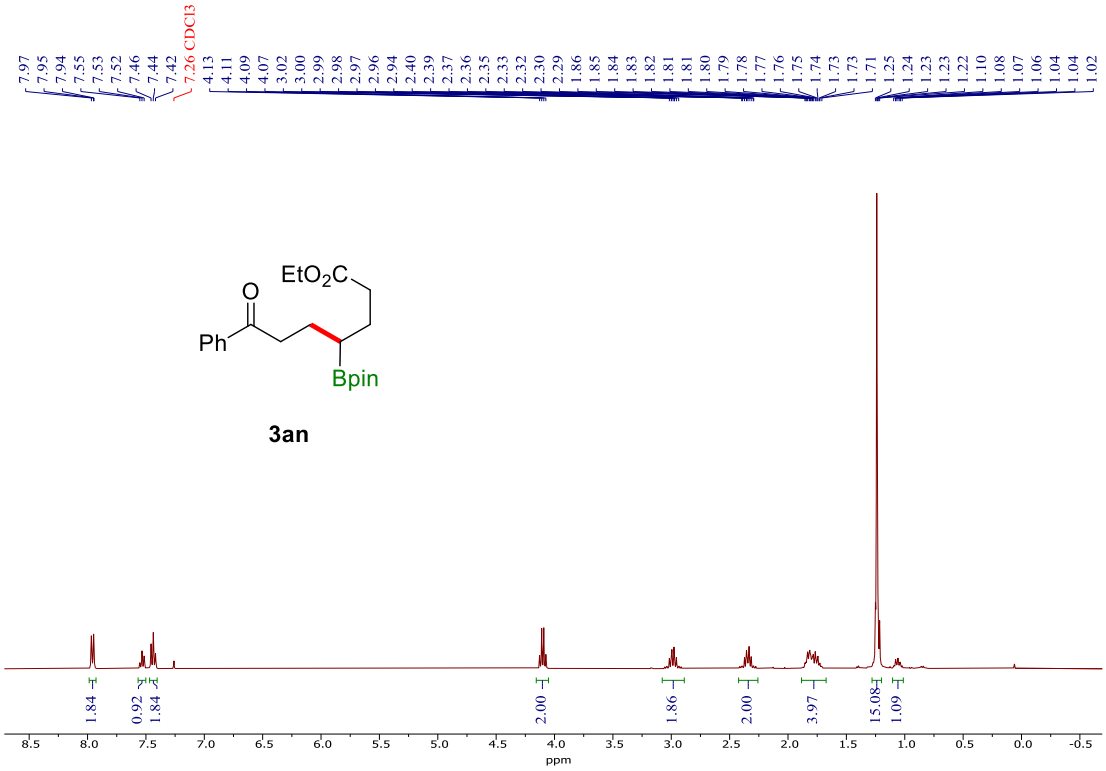
^{19}F NMR (377 MHz, $CDCl_3$) of **3am**



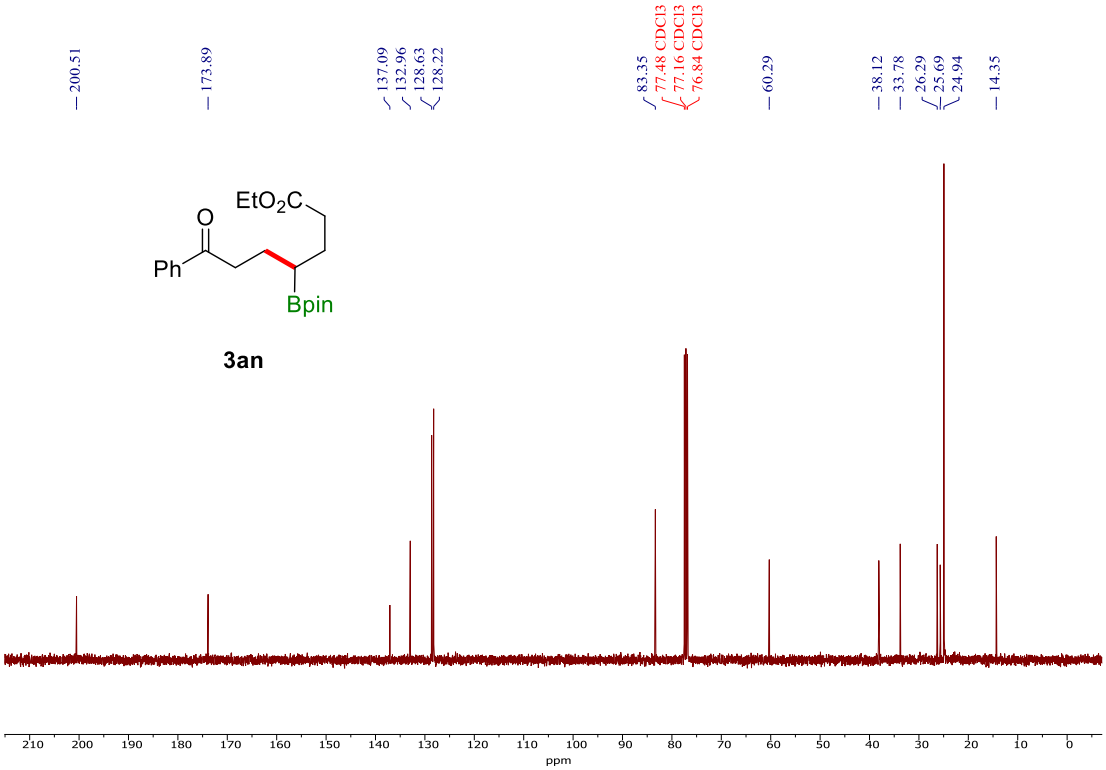
^{11}B NMR (128 MHz, $CDCl_3$) of **3am**



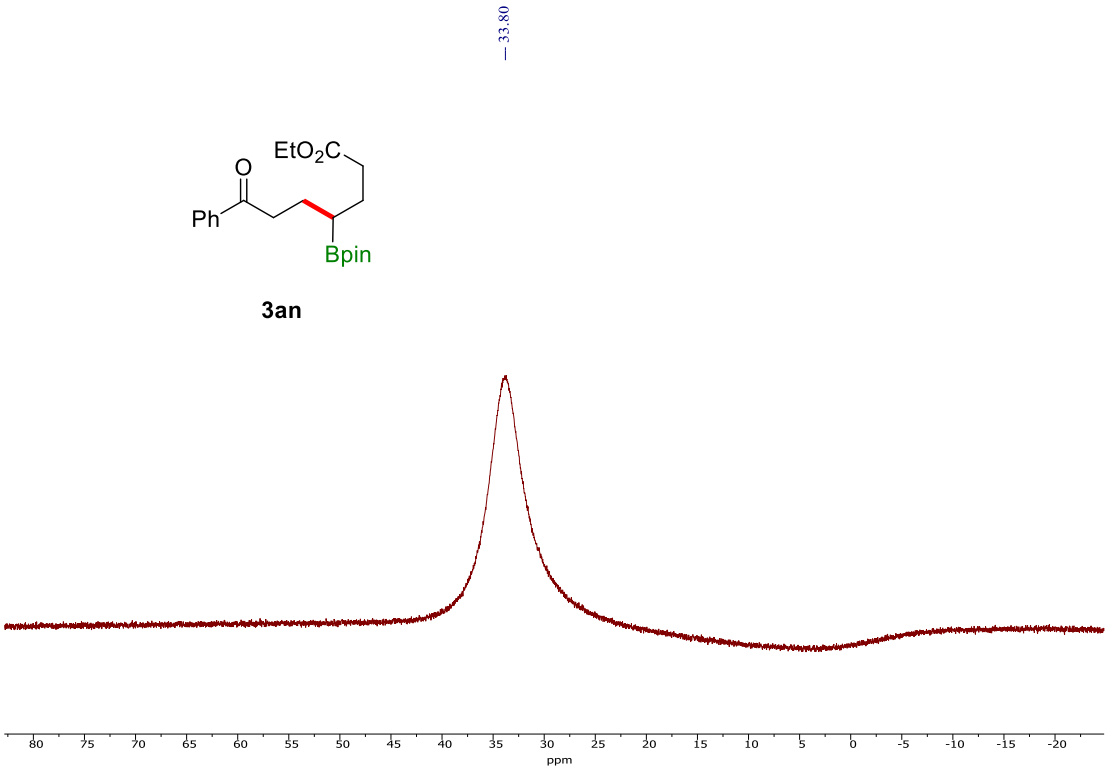
^{1}H NMR (400 MHz, $CDCl_3$) of **3an** (*see procedure*)



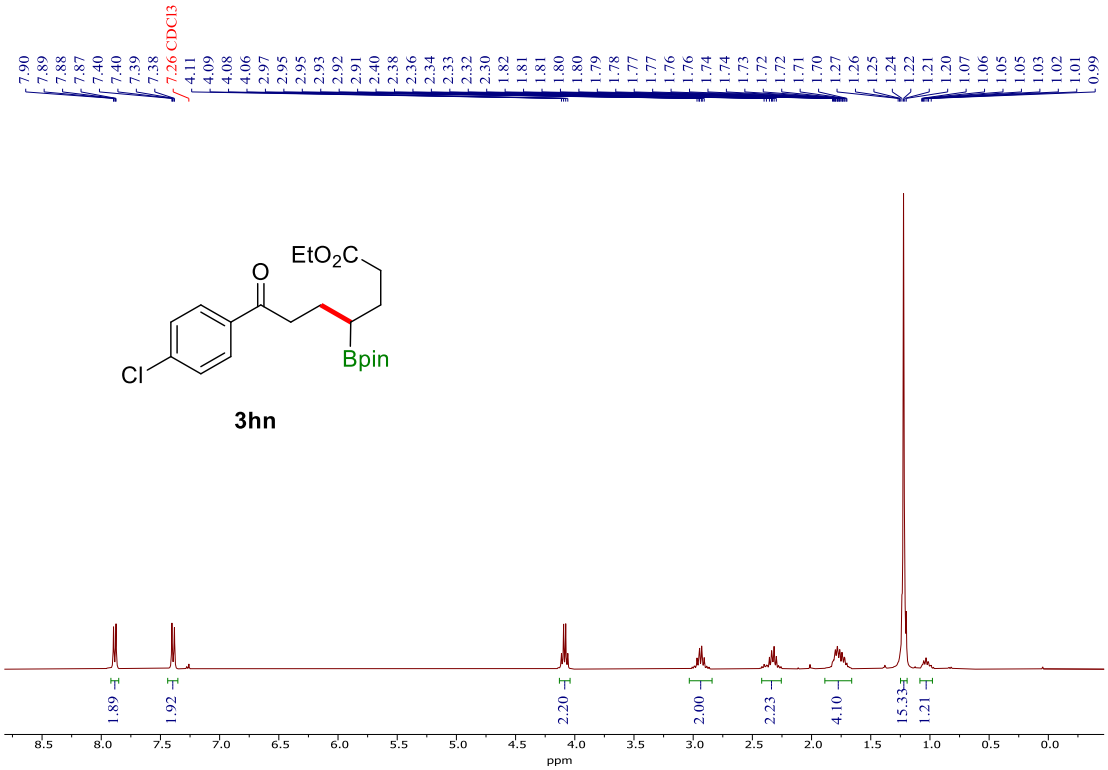
^{13}C NMR (101 MHz, $CDCl_3$) of **3an**



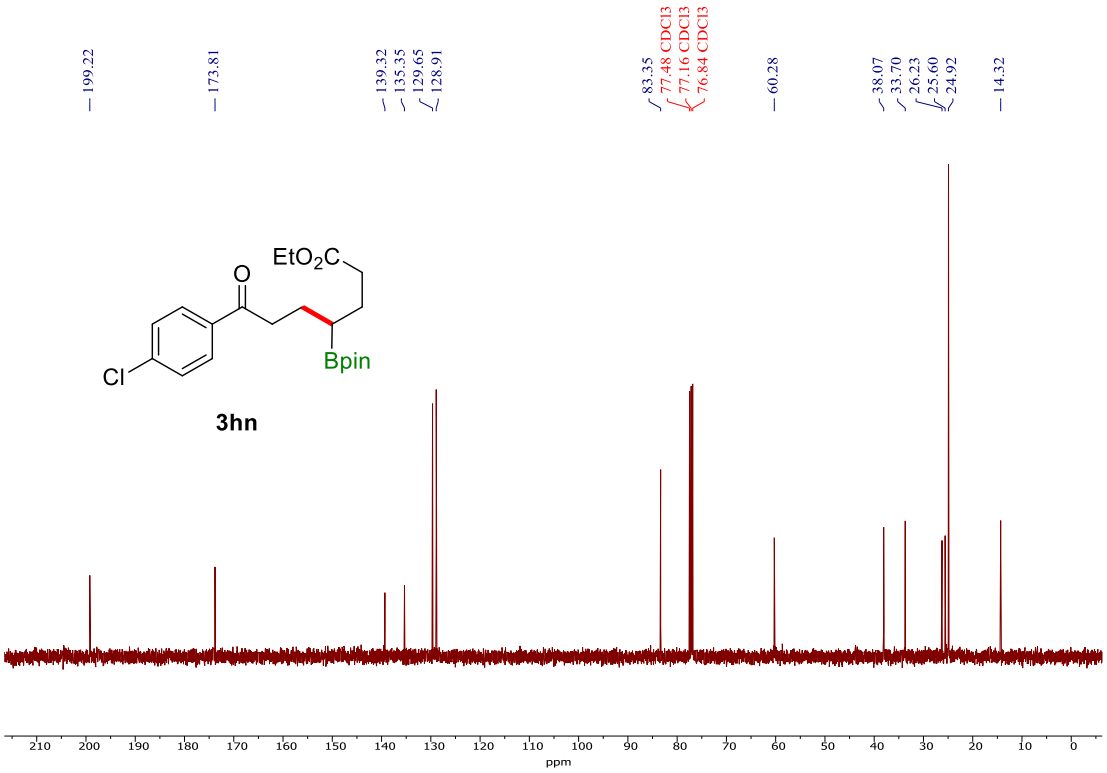
^{11}B NMR (128 MHz, $CDCl_3$) of **3an**



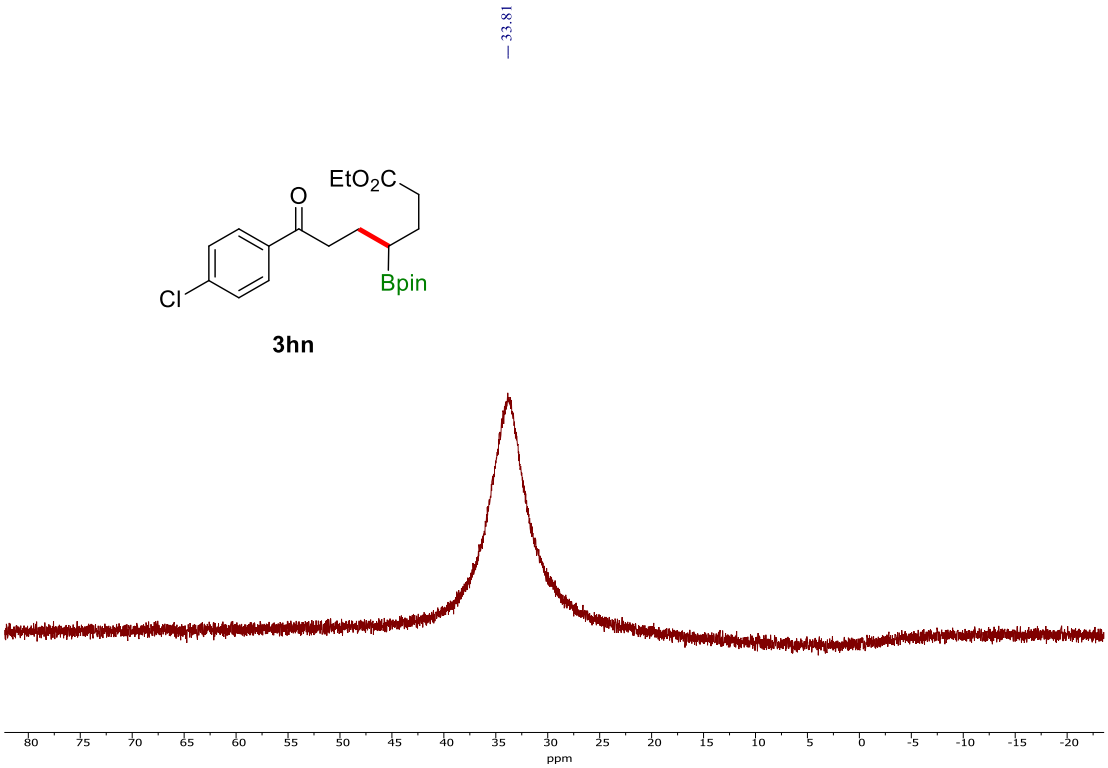
^{1}H NMR (400 MHz, $CDCl_3$) of **3hn** (*see procedure*)



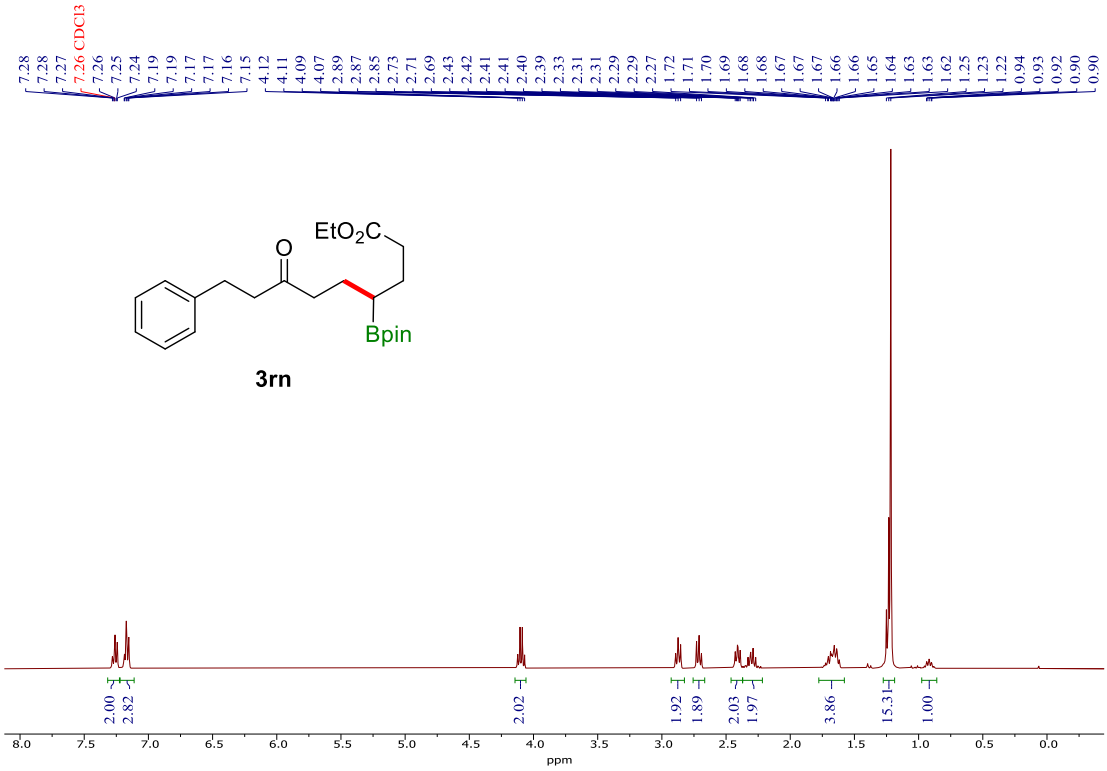
^{13}C NMR (101 MHz, $CDCl_3$) of **3hn**



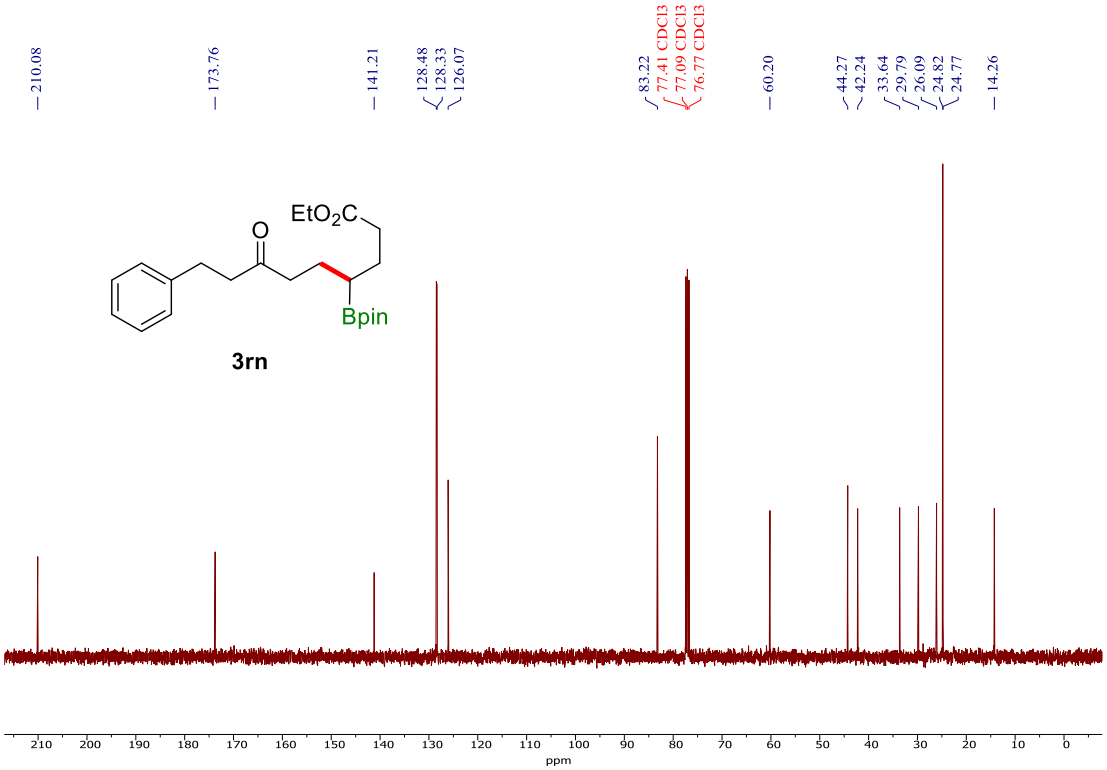
^{11}B NMR (128 MHz, $CDCl_3$) of **3hn**



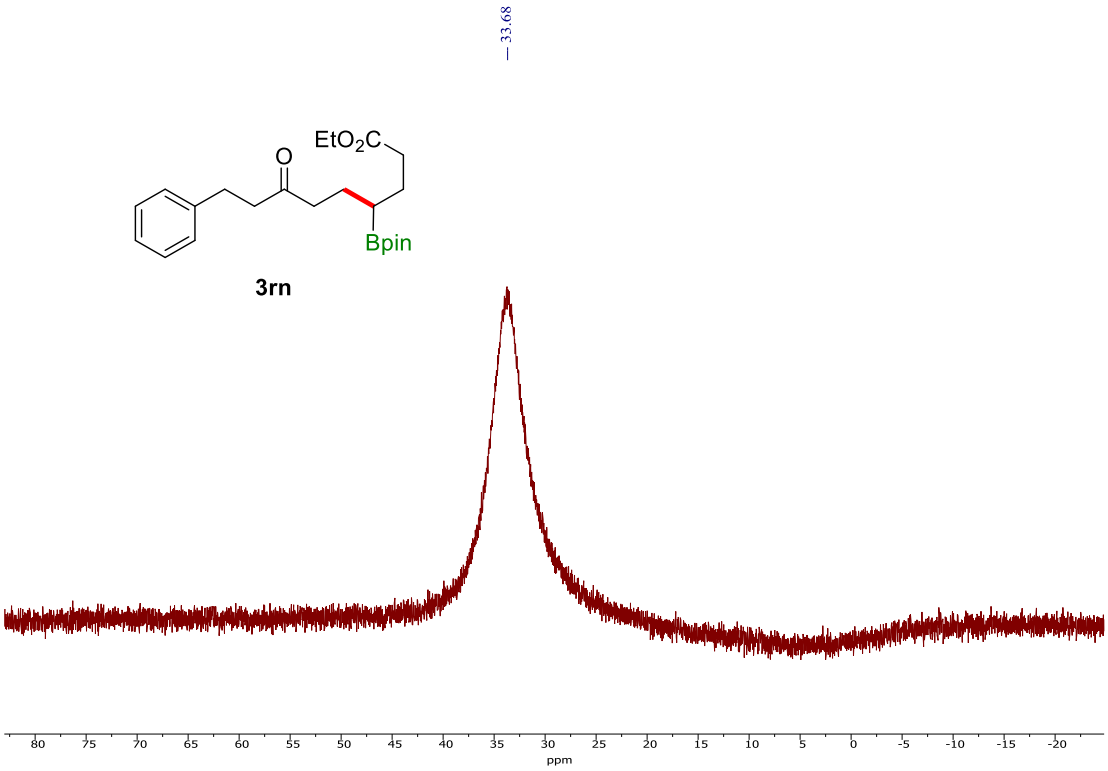
^{1}H NMR (400 MHz, $CDCl_3$) of **3rn** (*see procedure*)



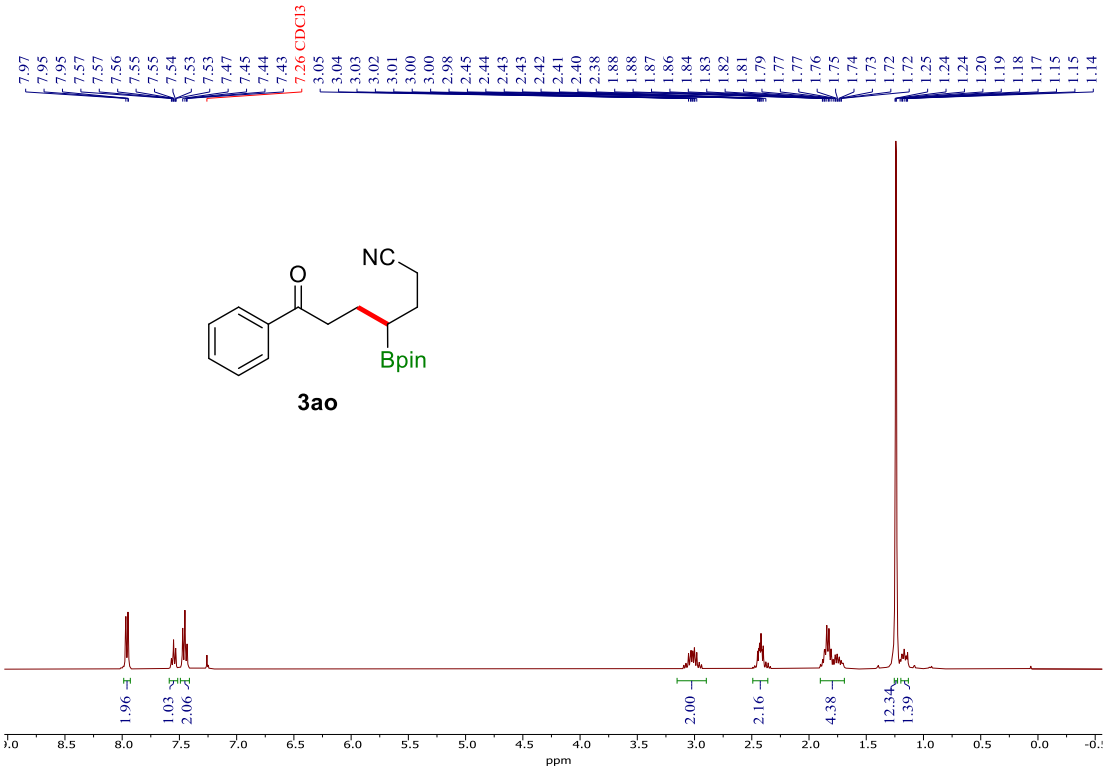
^{13}C NMR (101 MHz, $CDCl_3$) of **3rn**



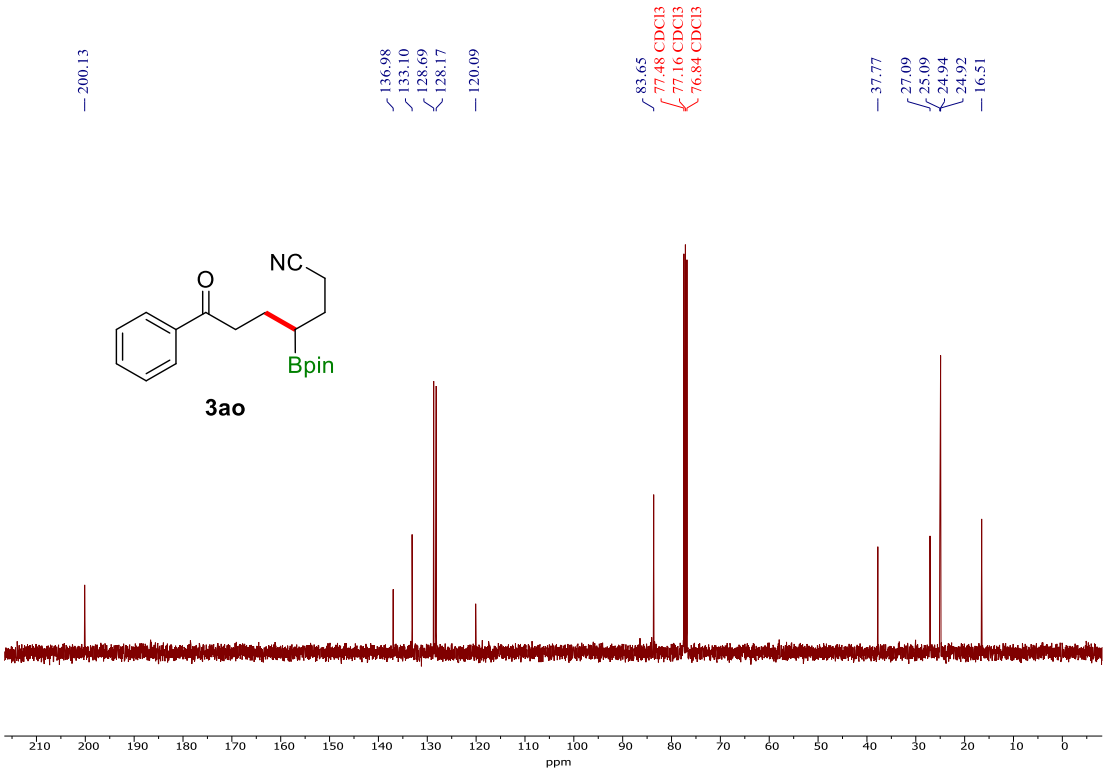
^{11}B NMR (128 MHz, $CDCl_3$) of **3rn**



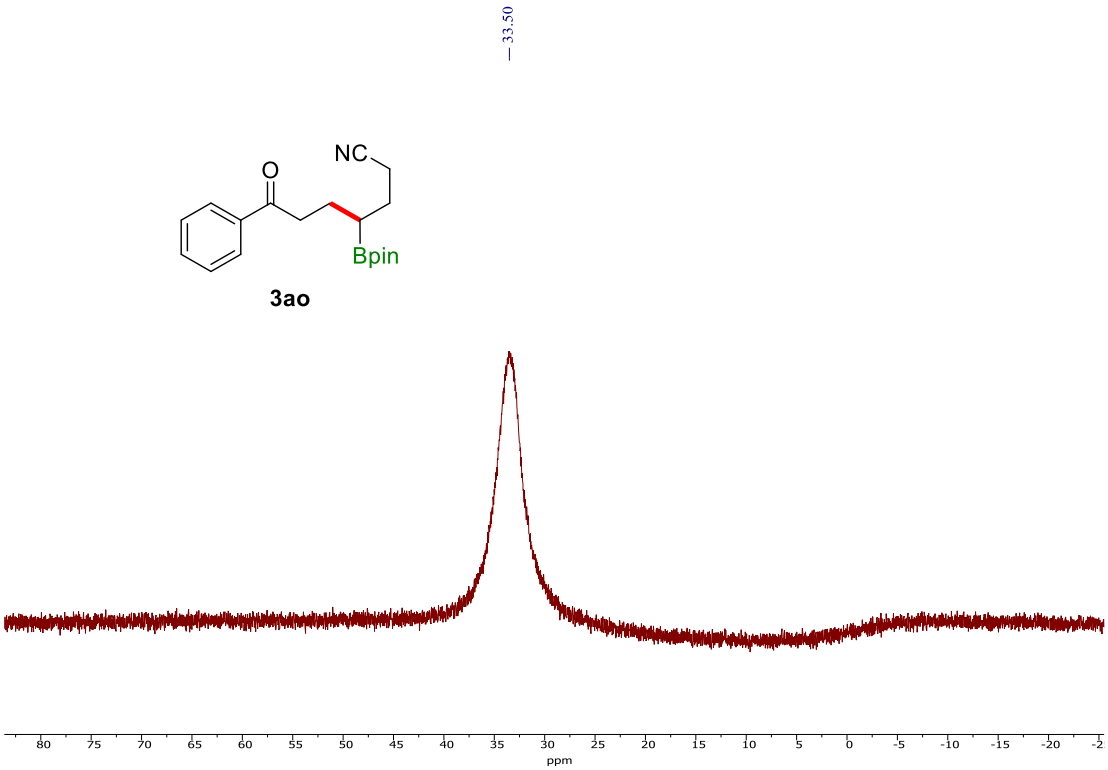
^{1}H NMR (400 MHz, $CDCl_3$) of **3ao** (*see procedure*)



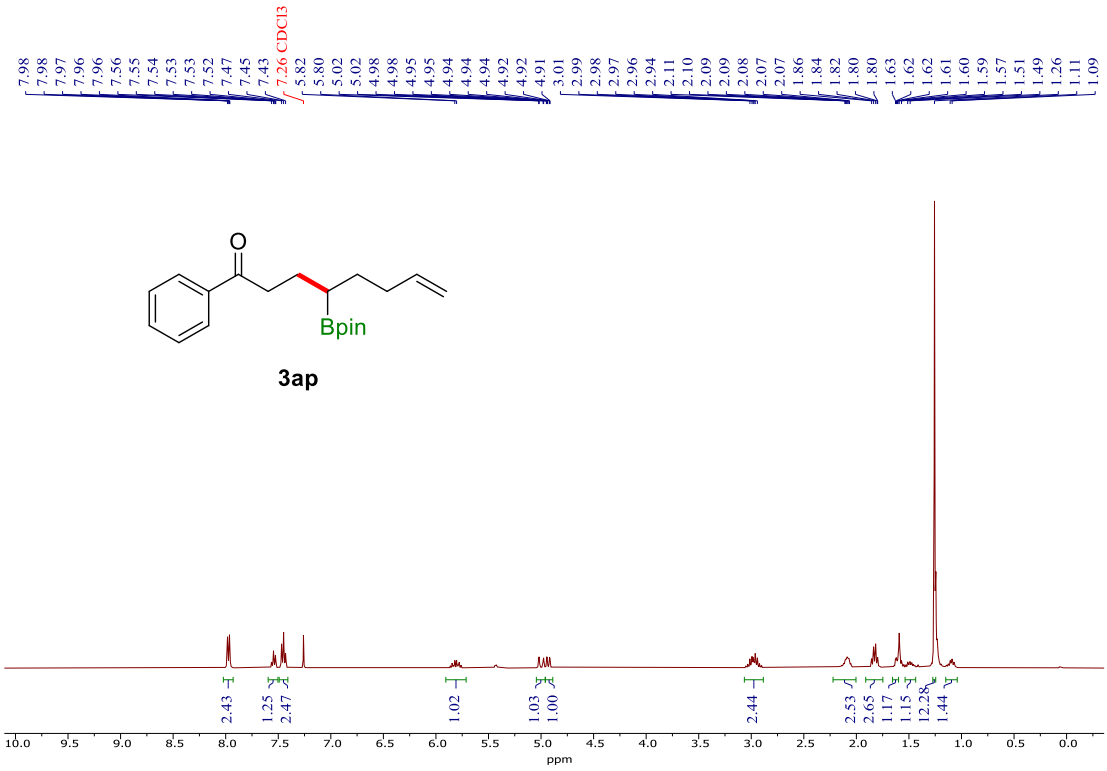
^{13}C NMR (101 MHz, $CDCl_3$) of **3ao**



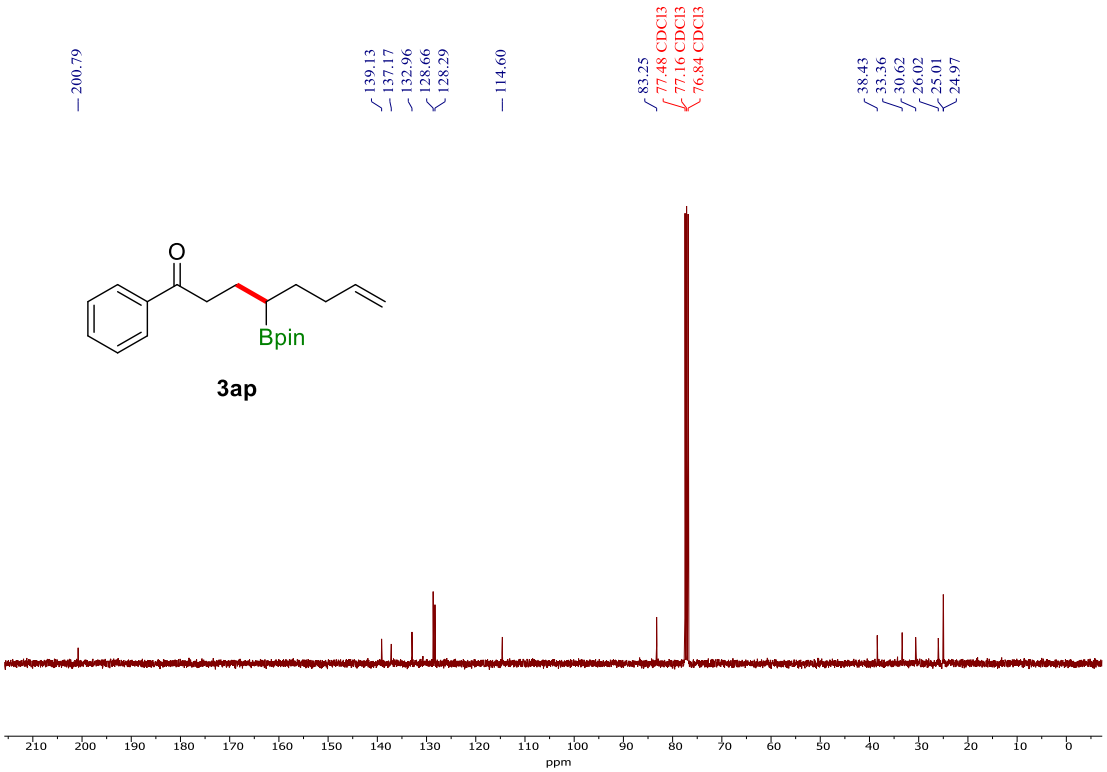
^{11}B NMR (128 MHz, $CDCl_3$) of **3ao**



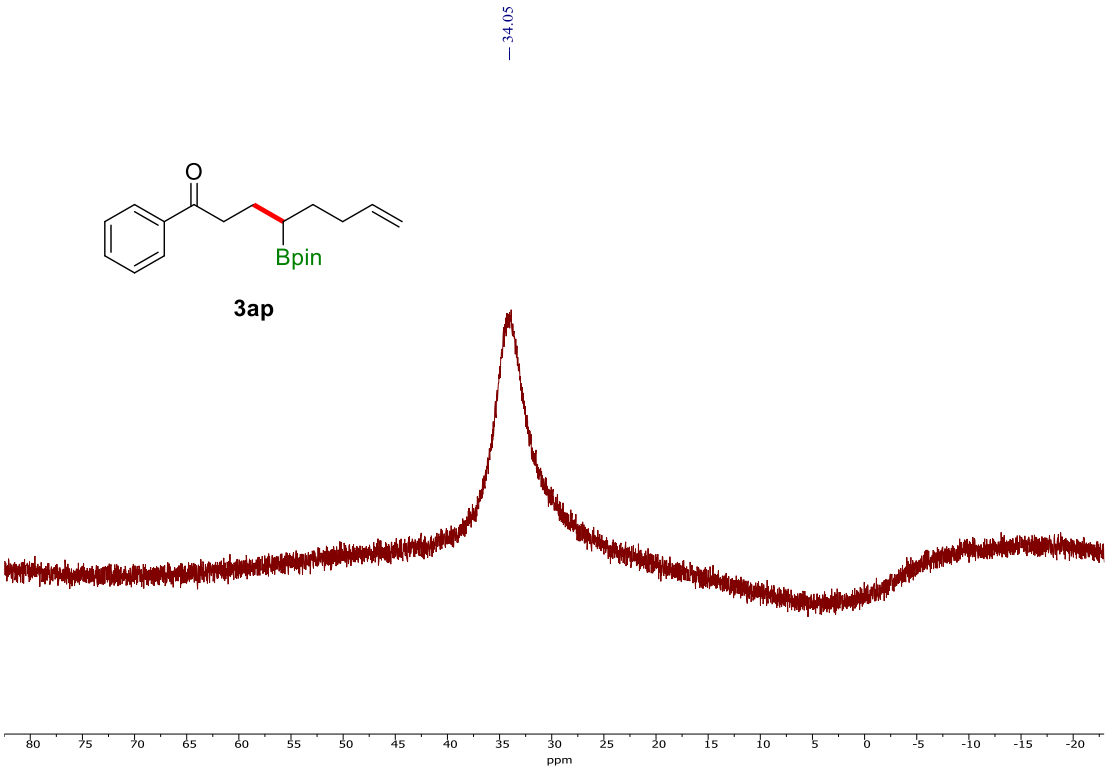
^{1}H NMR (400 MHz, $CDCl_3$) of **3ap** (*see procedure*)



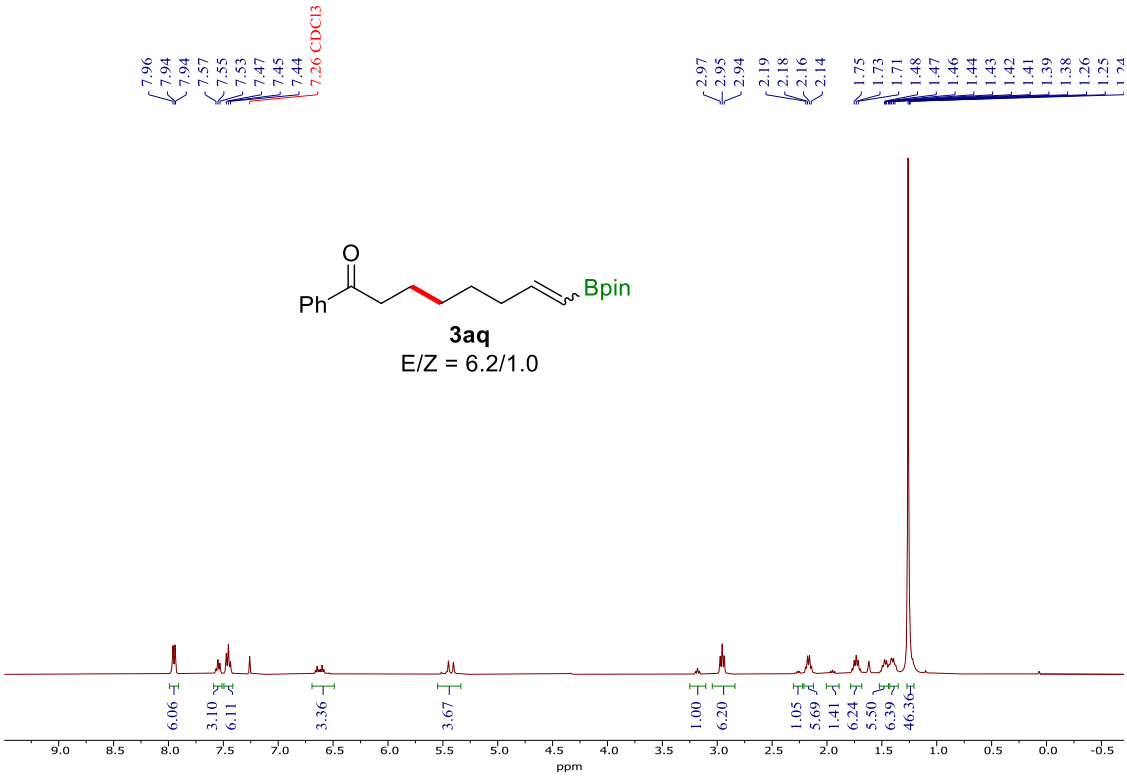
^{13}C NMR (101 MHz, $CDCl_3$) of **3ap**



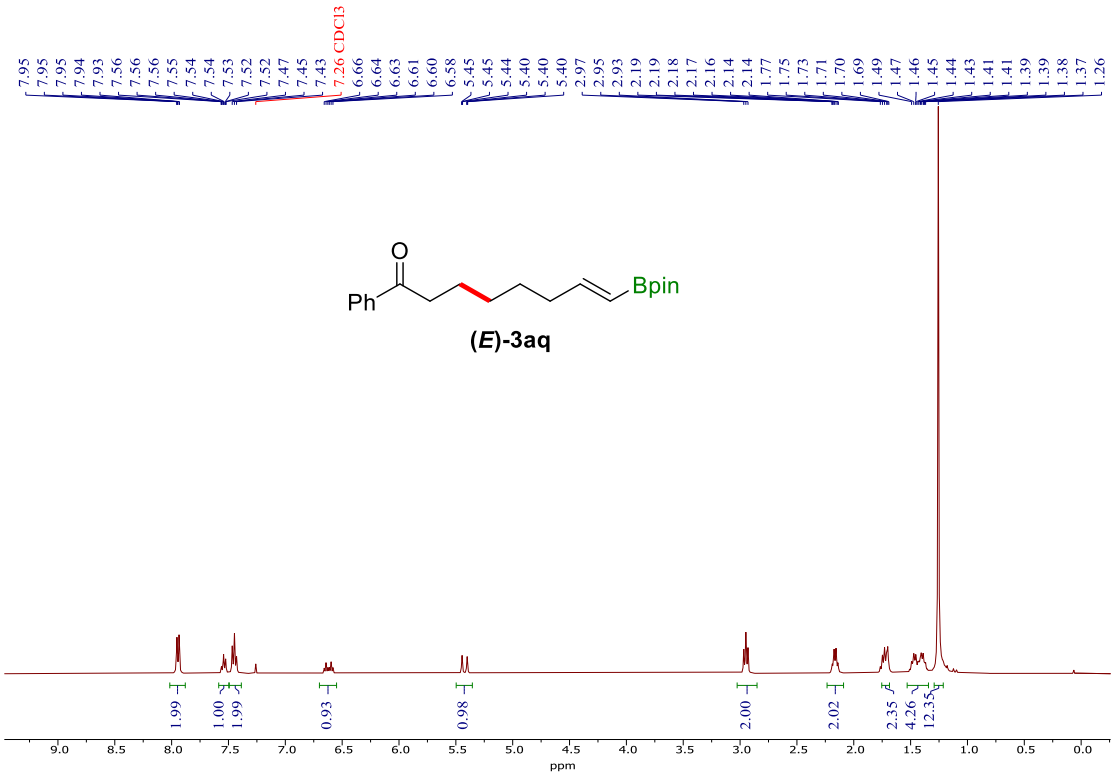
^{11}B NMR (128 MHz, $CDCl_3$) of **3ap**



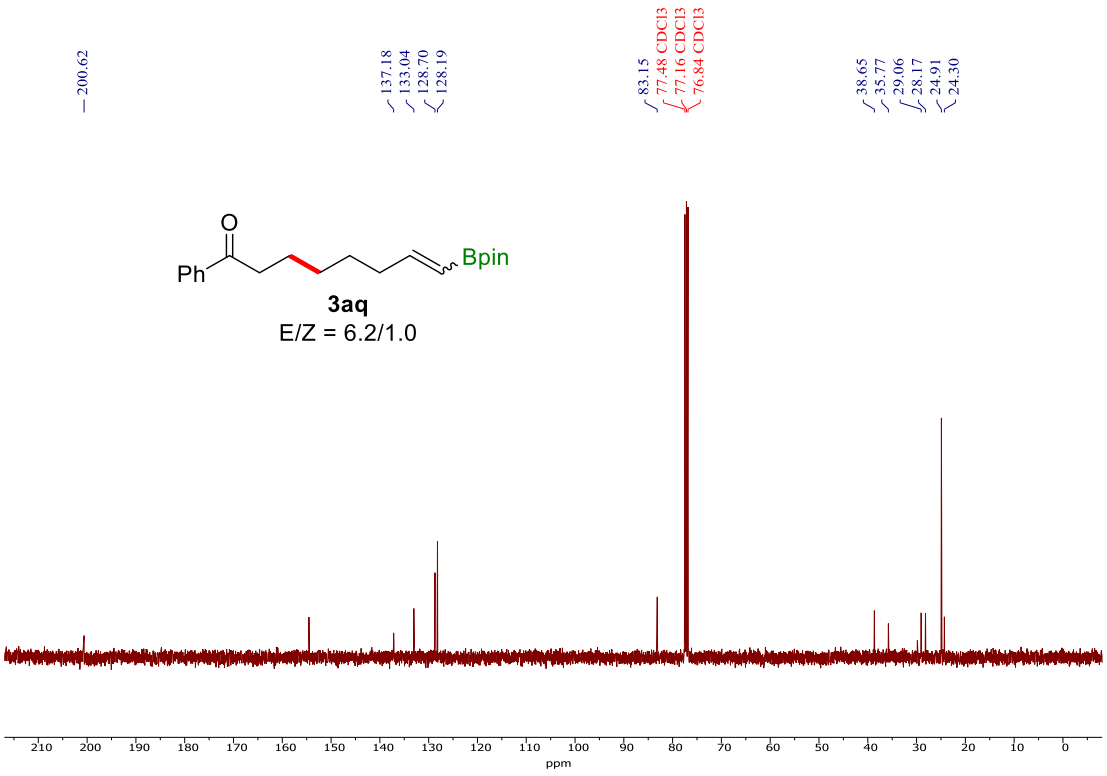
^{1}H NMR (400 MHz, $CDCl_3$) of **3aq**



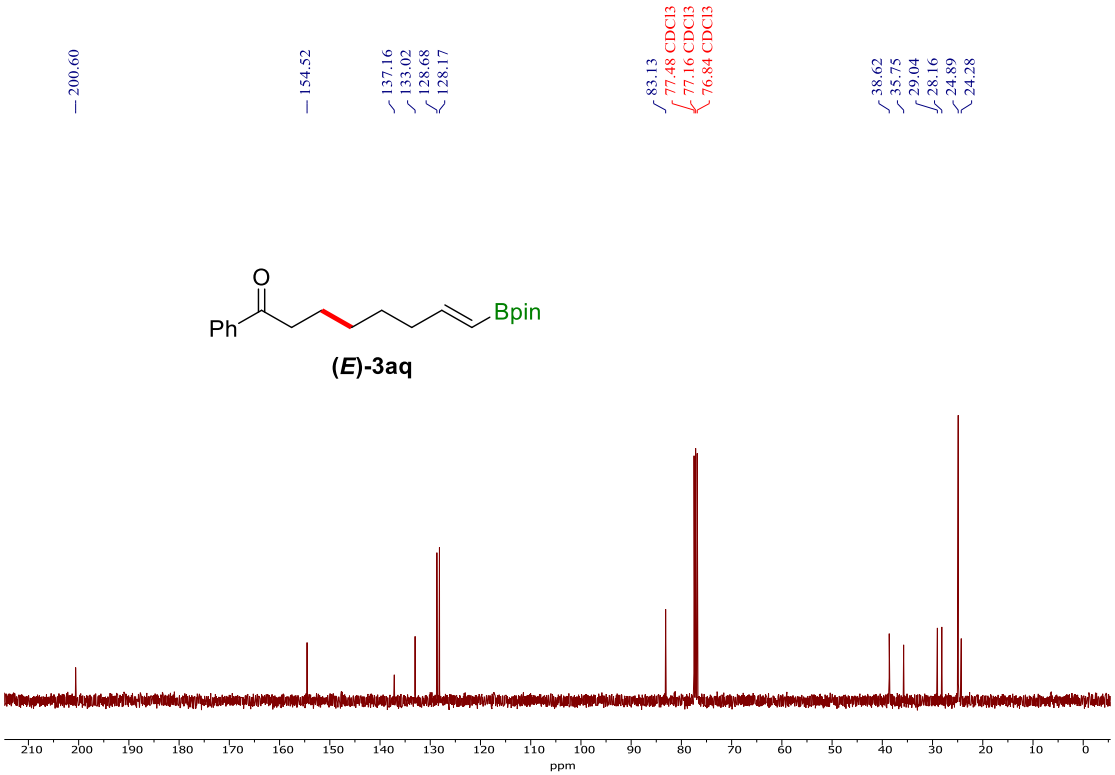
^{1}H NMR (400 MHz, $CDCl_3$) of **(*E*)-3aq** (*see procedure*)



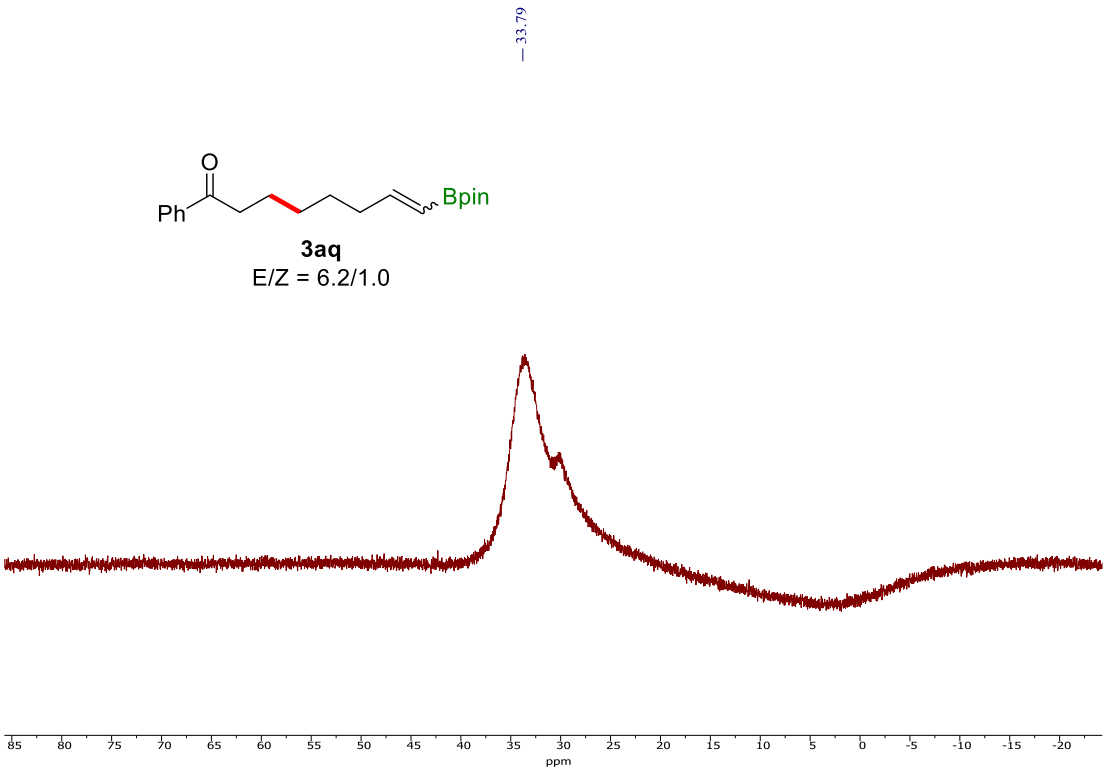
^{13}C NMR (101 MHz, $CDCl_3$) of **3aq**



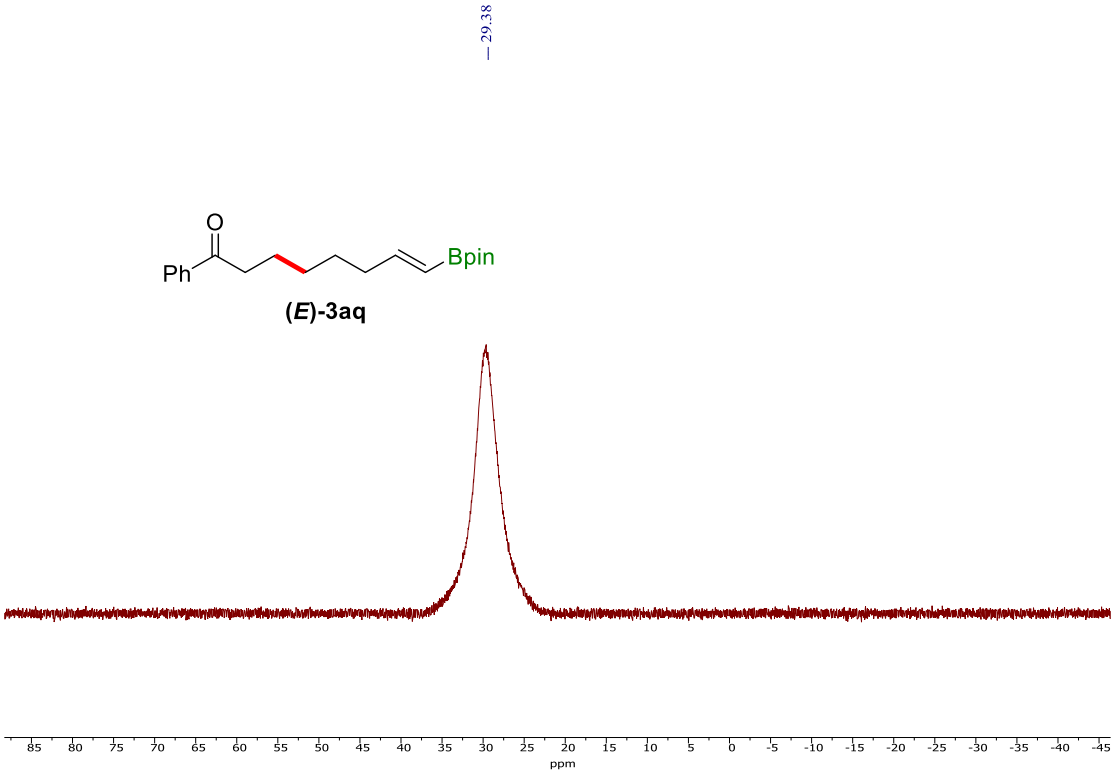
^{13}C NMR (101 MHz, $CDCl_3$) of **(*E*)-3aq**



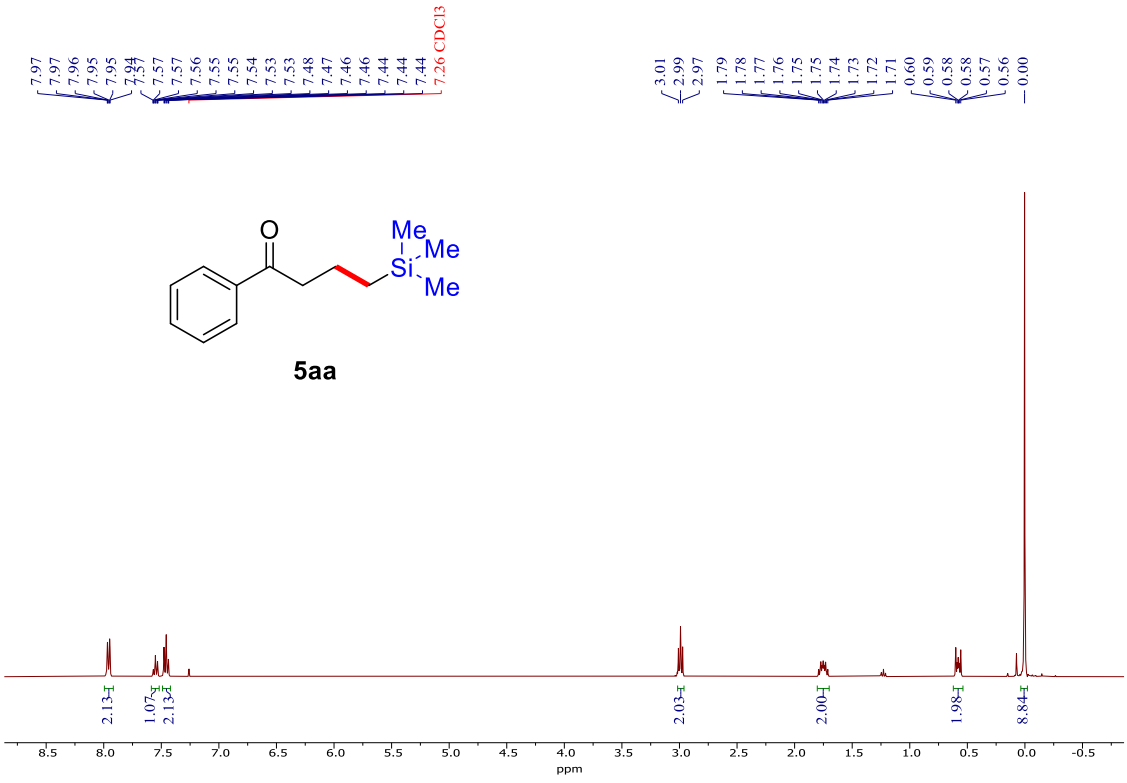
^{11}B NMR (128 MHz, $CDCl_3$) of **3aq**



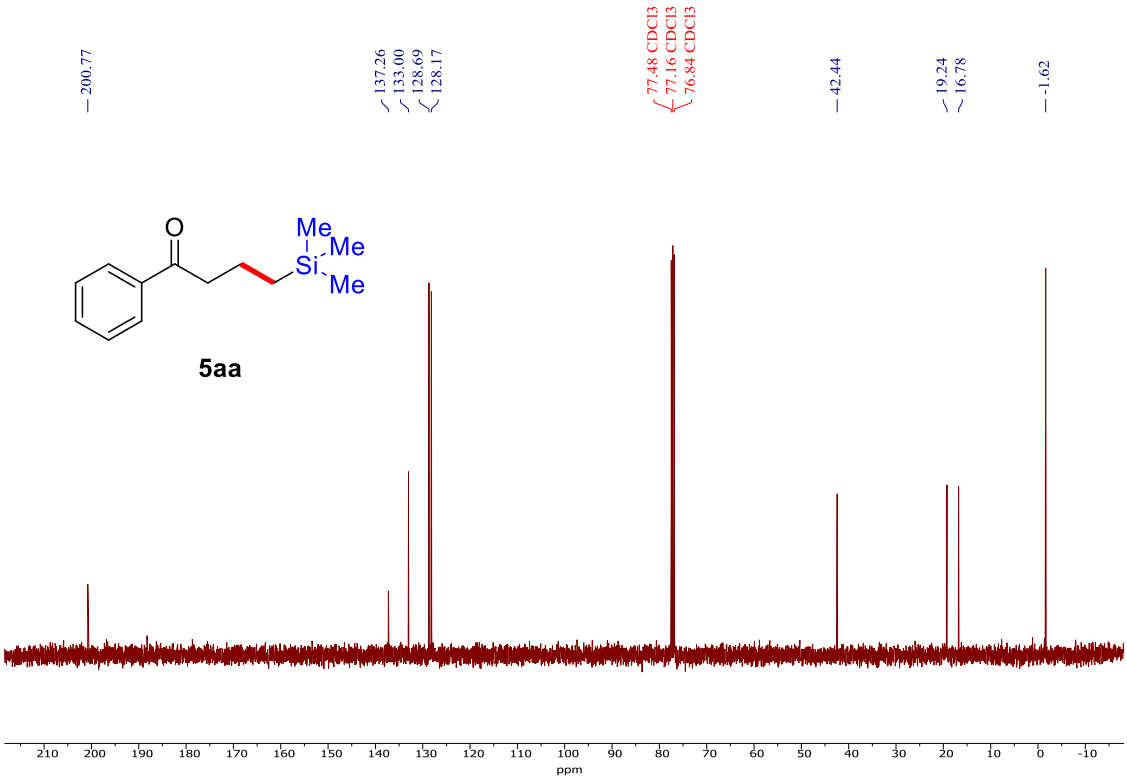
^{11}B NMR (128 MHz, $CDCl_3$) of **(*E*)-3aq**



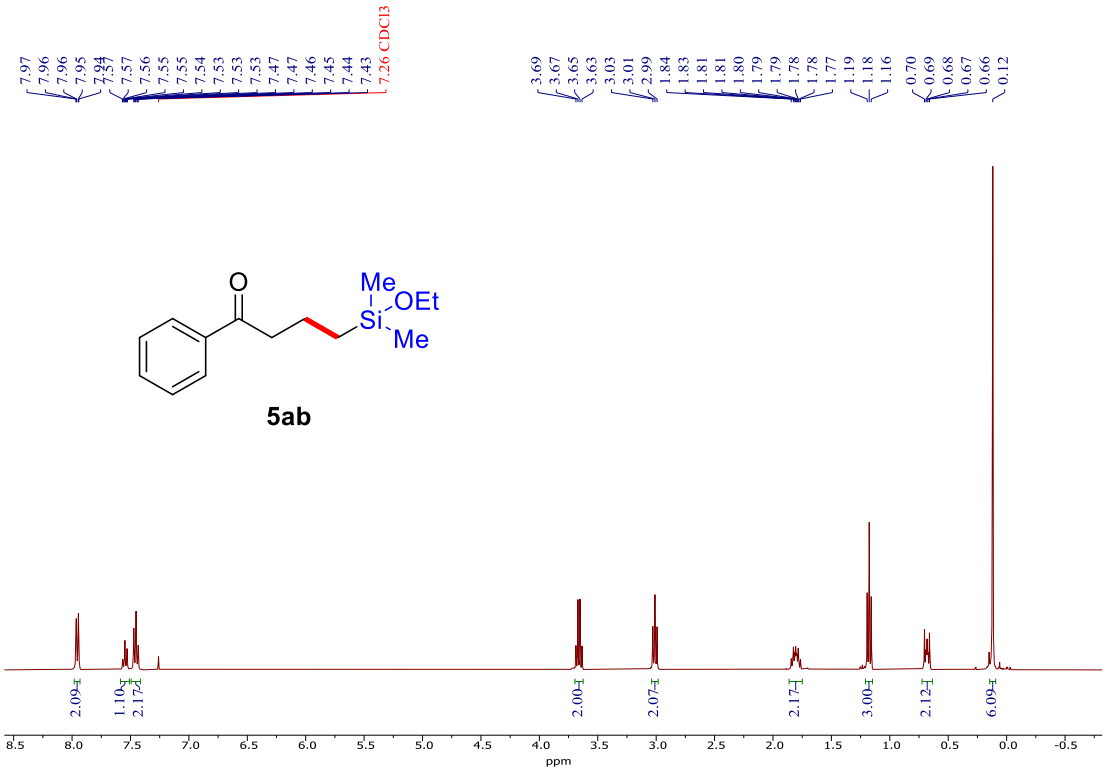
^{1}H NMR (400 MHz, $CDCl_3$) of **5aa** (*see procedure*)



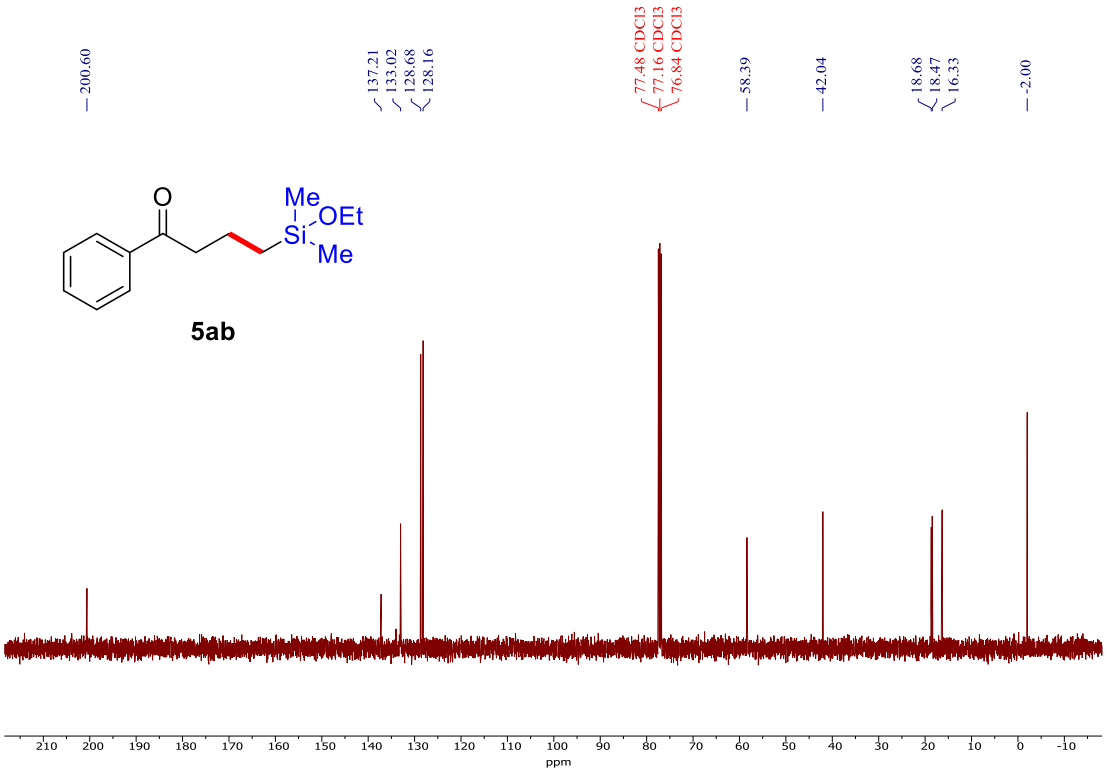
^{13}C NMR (101 MHz, $CDCl_3$) of **5aa**



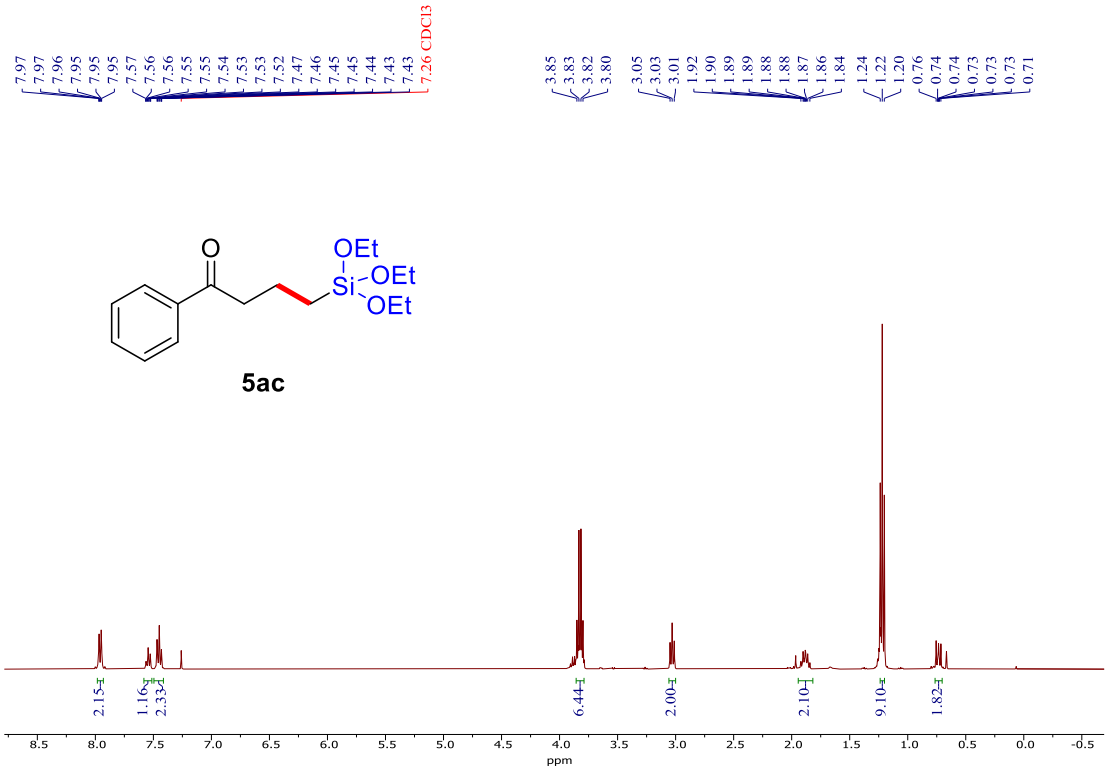
^{1}H NMR (400 MHz, $CDCl_3$) of **5ab** (*see procedure*)



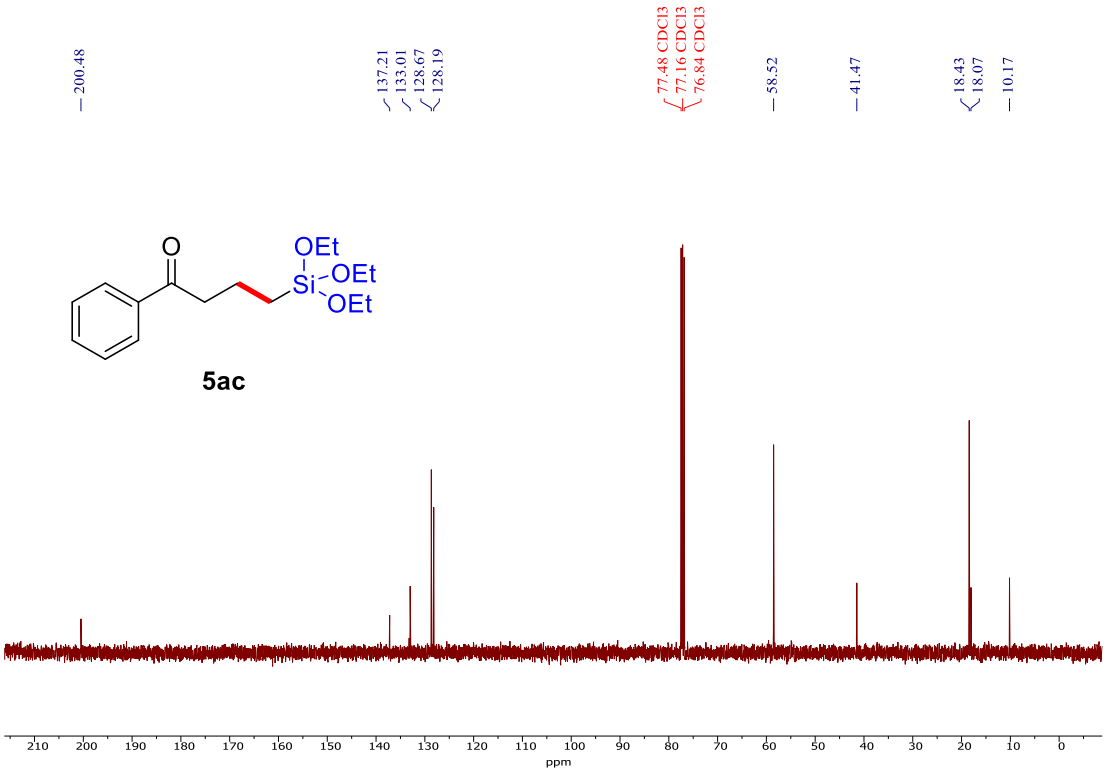
^{13}C NMR (101 MHz, $CDCl_3$) of **5ab**



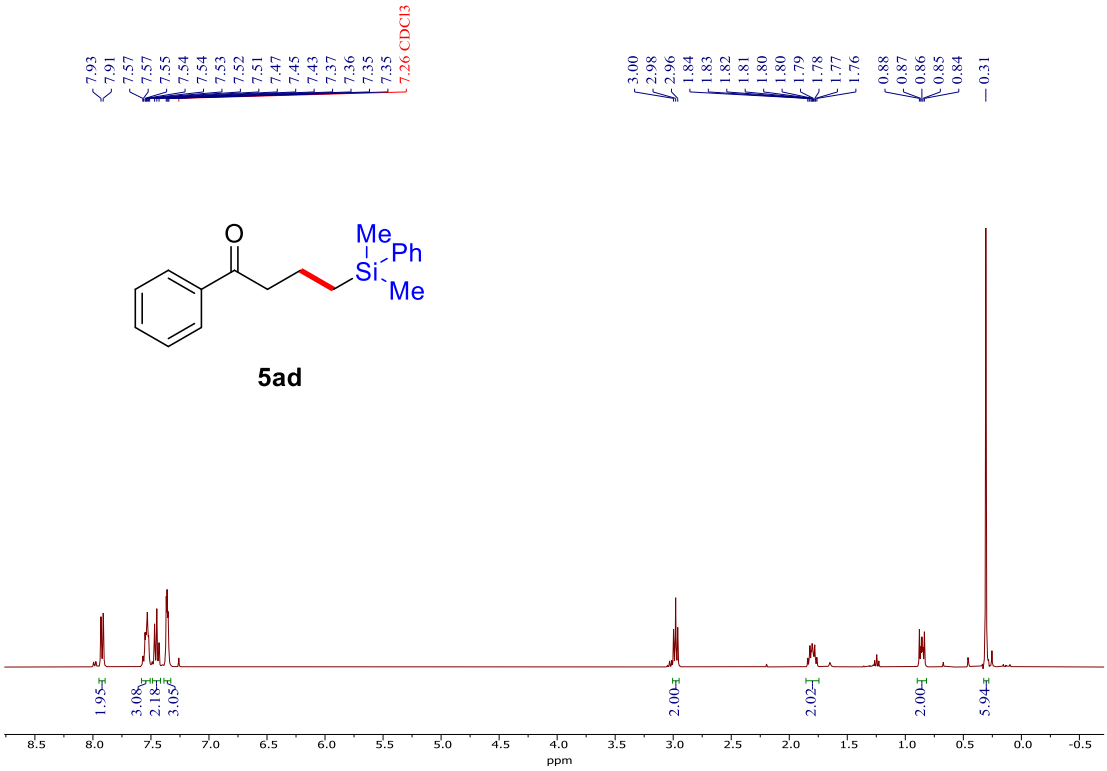
^{1}H NMR (400 MHz, $CDCl_3$) of **5ac** (*see procedure*)



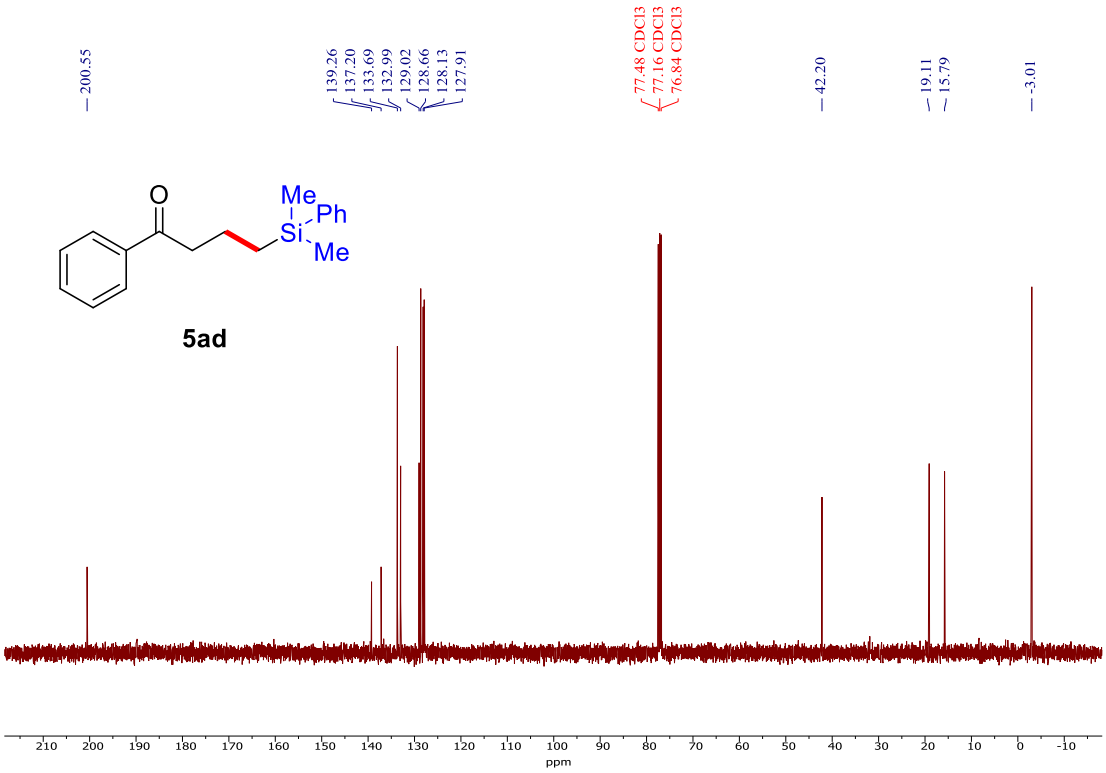
^{13}C NMR (101 MHz, $CDCl_3$) of **5ac**



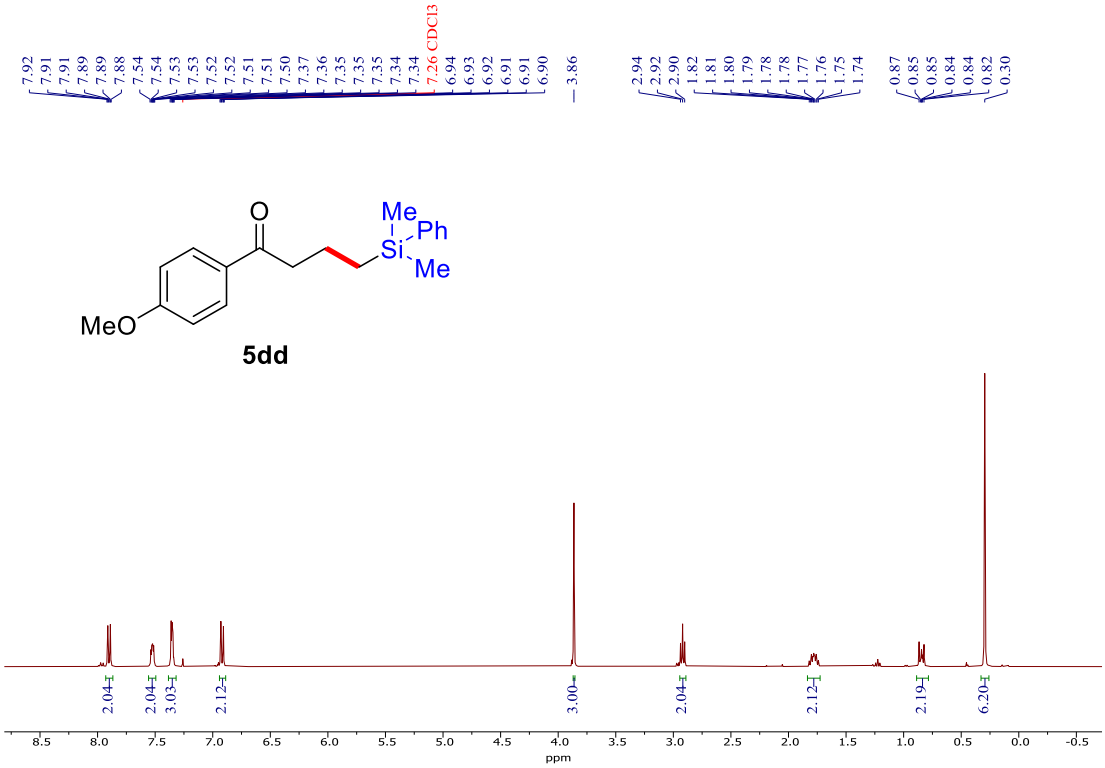
^{1}H NMR (400 MHz, $CDCl_3$) of **5ad** (*see procedure*)



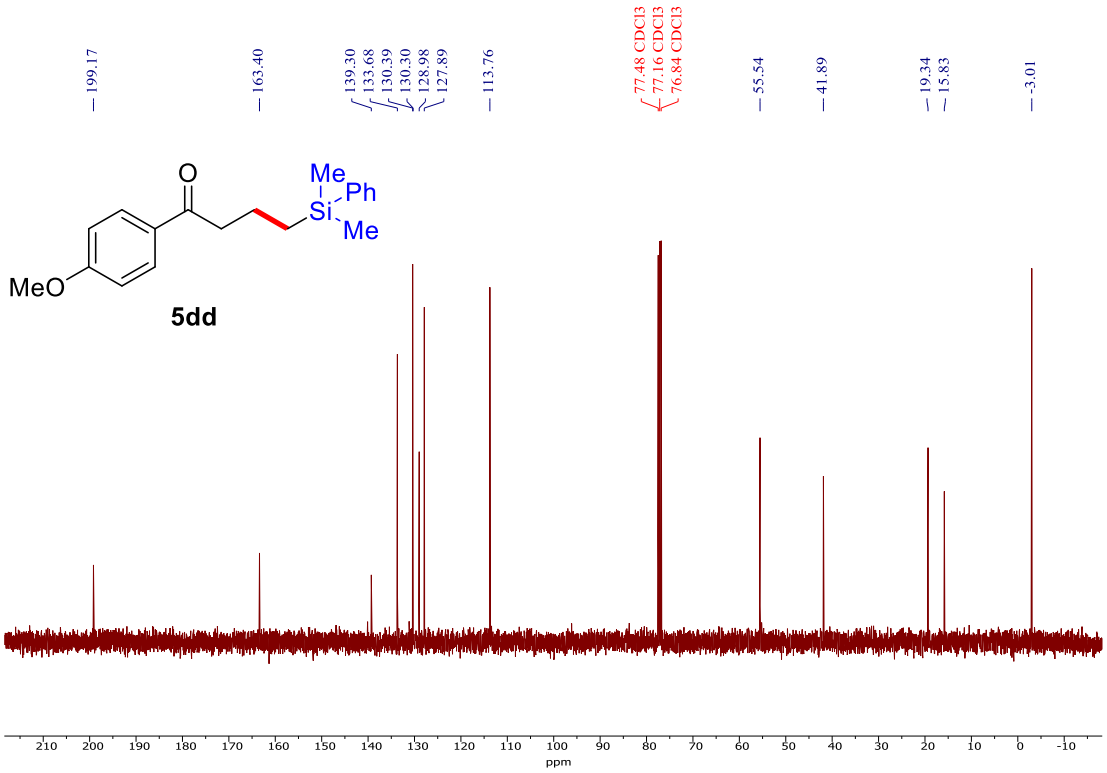
^{13}C NMR (101 MHz, $CDCl_3$) of **5ad**



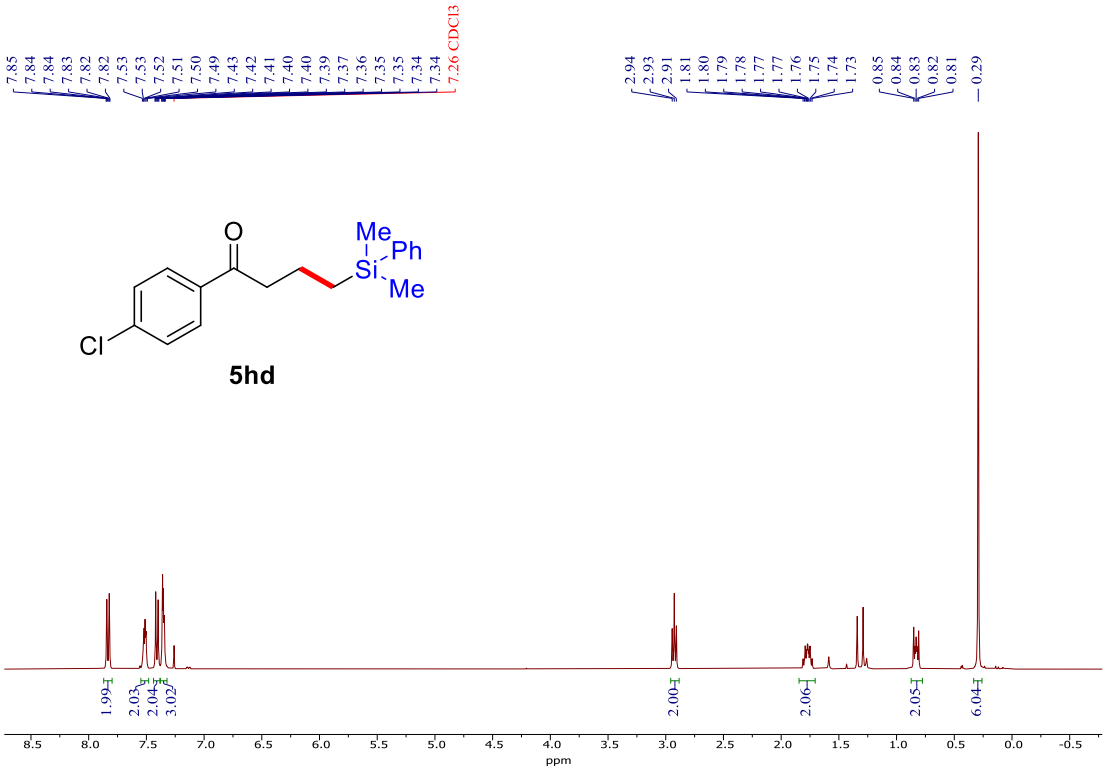
^{1}H NMR (400 MHz, $CDCl_3$) of **5dd** (*see procedure*)



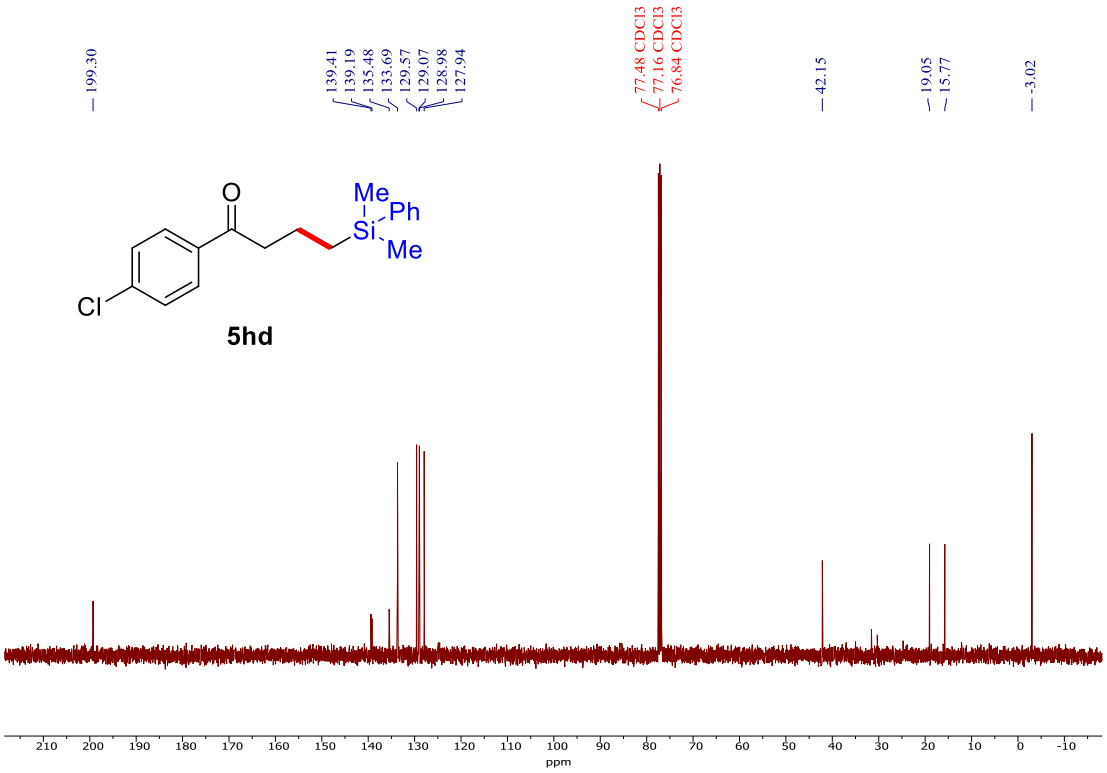
^{13}C NMR (101 MHz, $CDCl_3$) of **5dd**



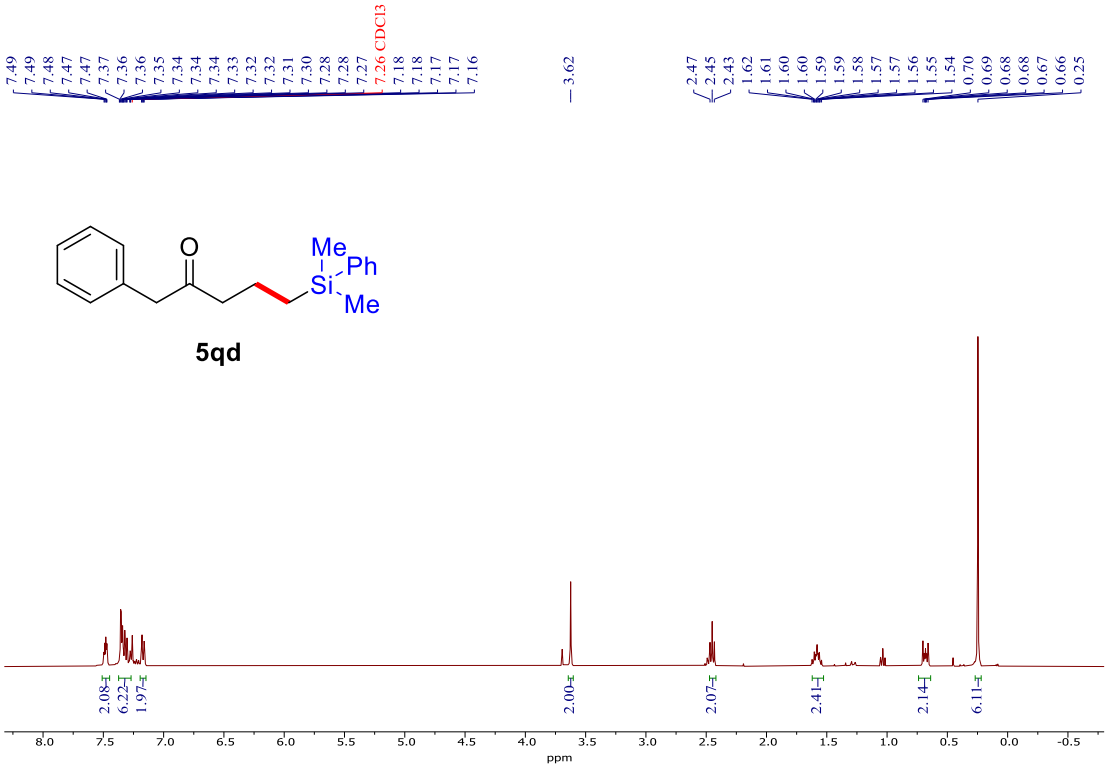
^{1}H NMR (400 MHz, $CDCl_3$) of **5hd** (*see procedure*)



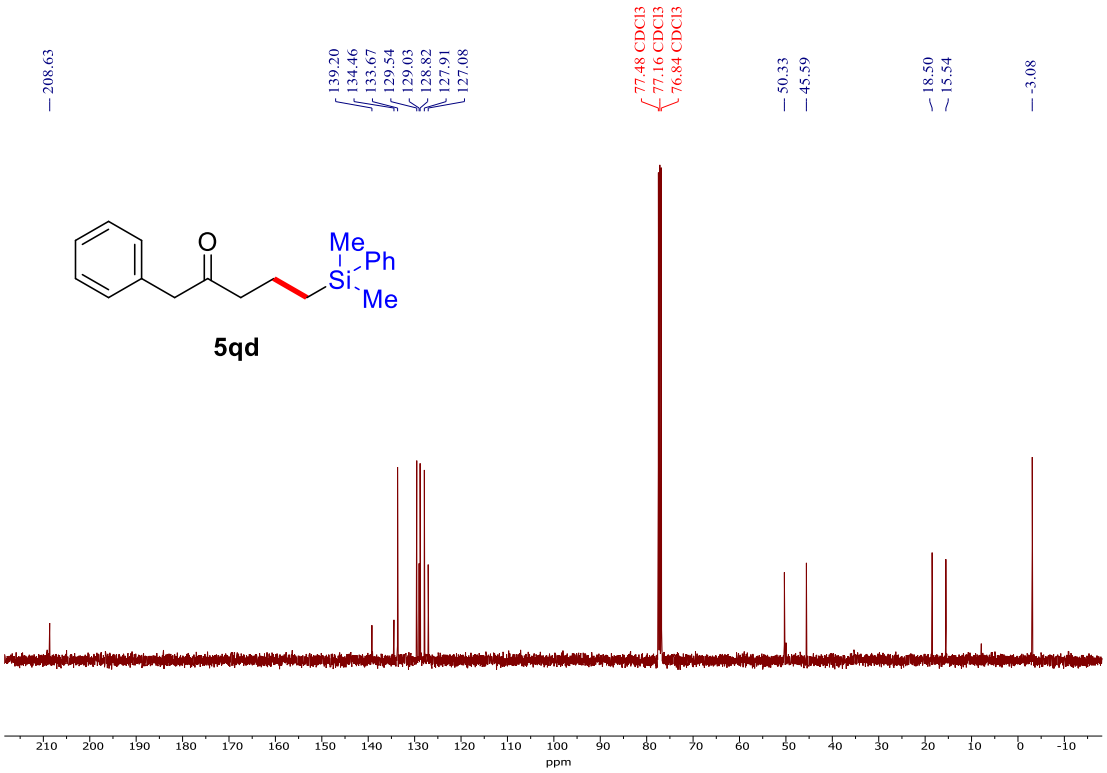
^{13}C NMR (101 MHz, $CDCl_3$) of **5hd**



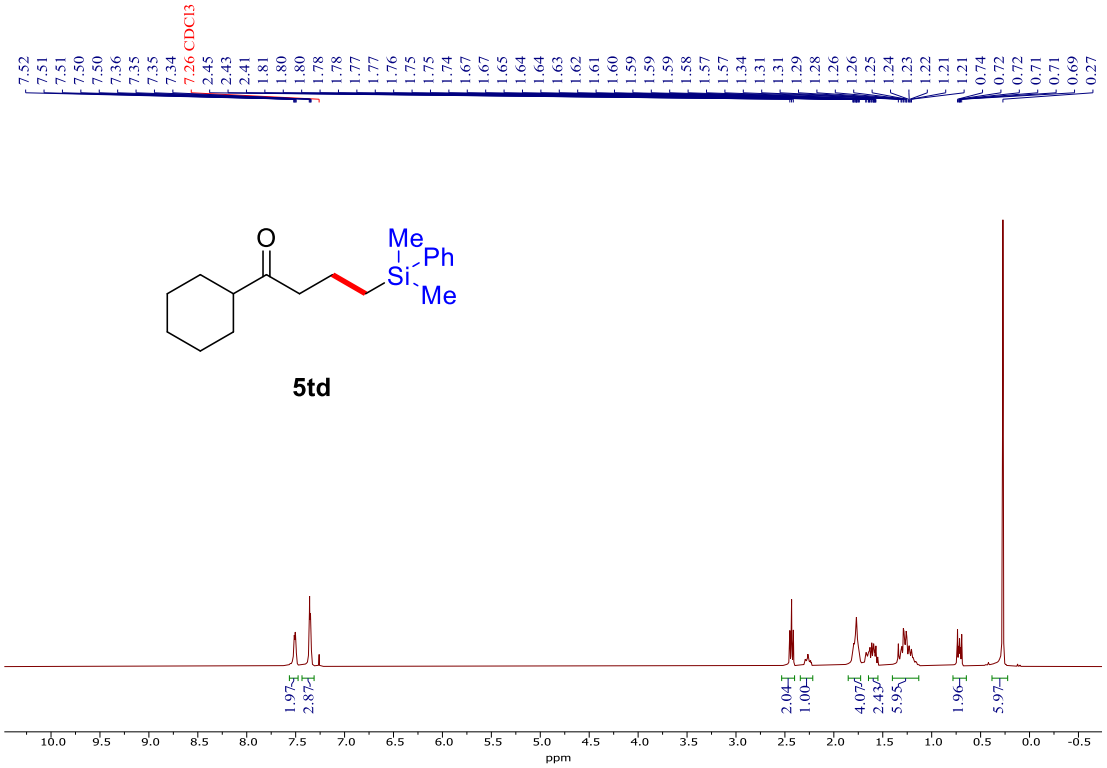
^{1}H NMR (400 MHz, $CDCl_3$) of **5qd** (*see procedure*)



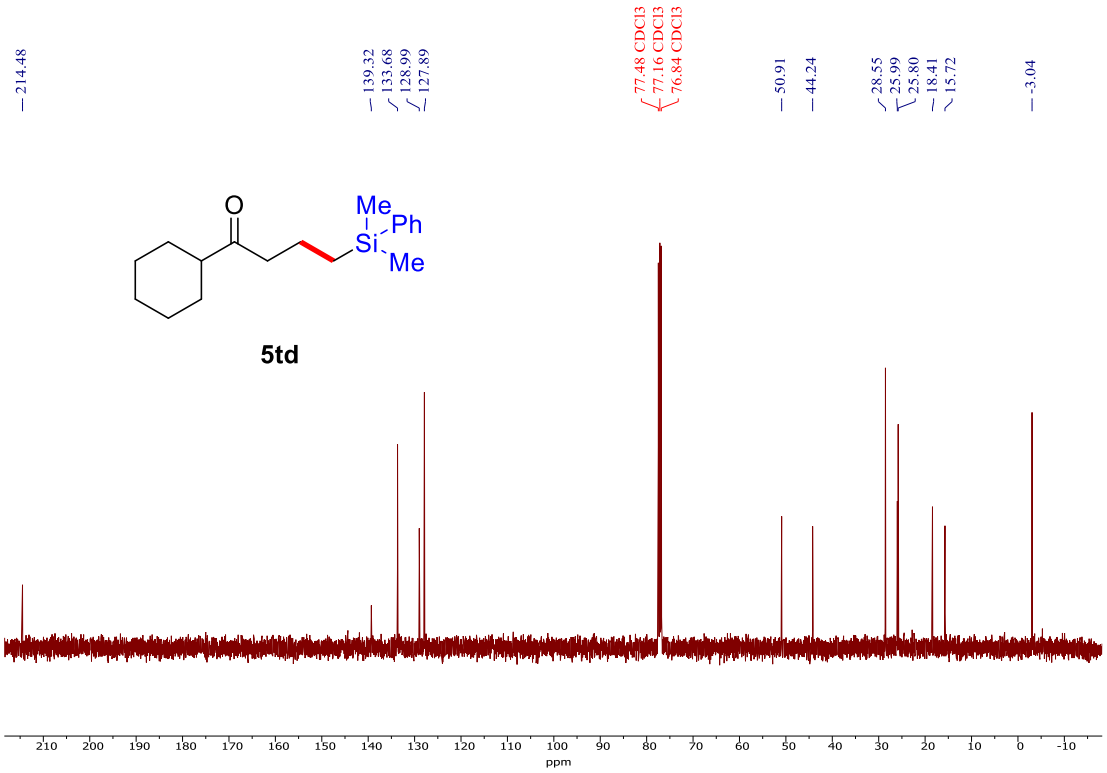
^{13}C NMR (101 MHz, $CDCl_3$) of **5qd**



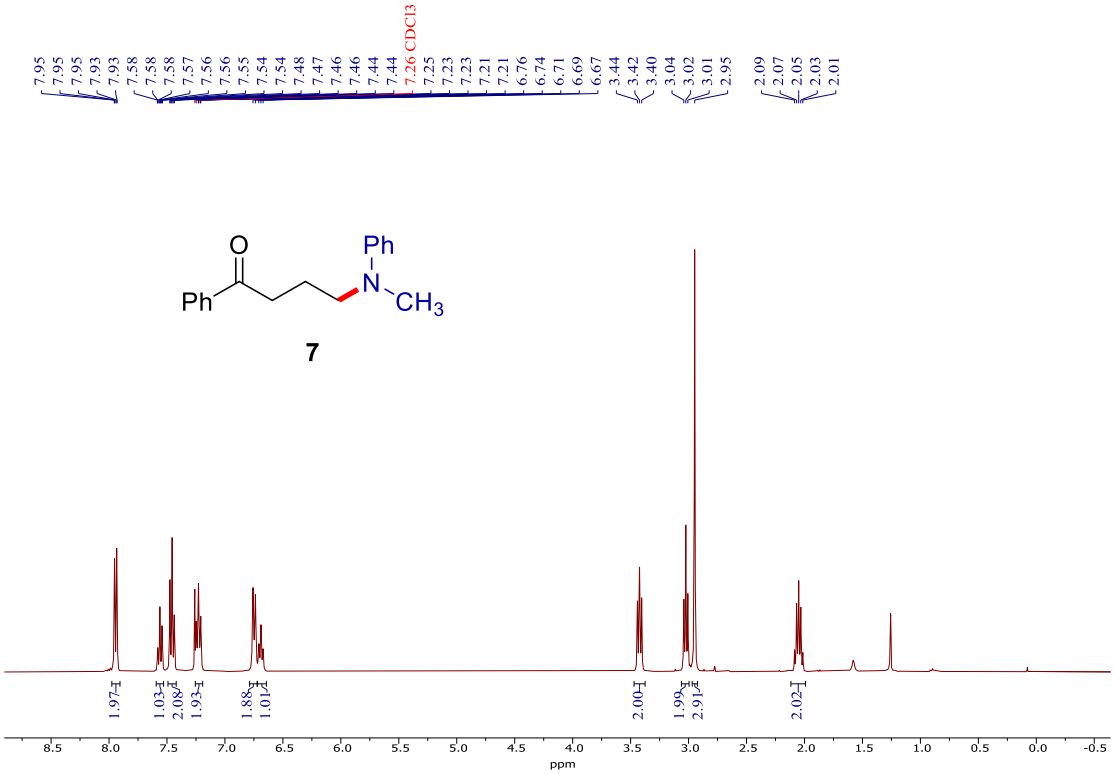
^{1}H NMR (400 MHz, $CDCl_3$) of **5td** (*see procedure*)



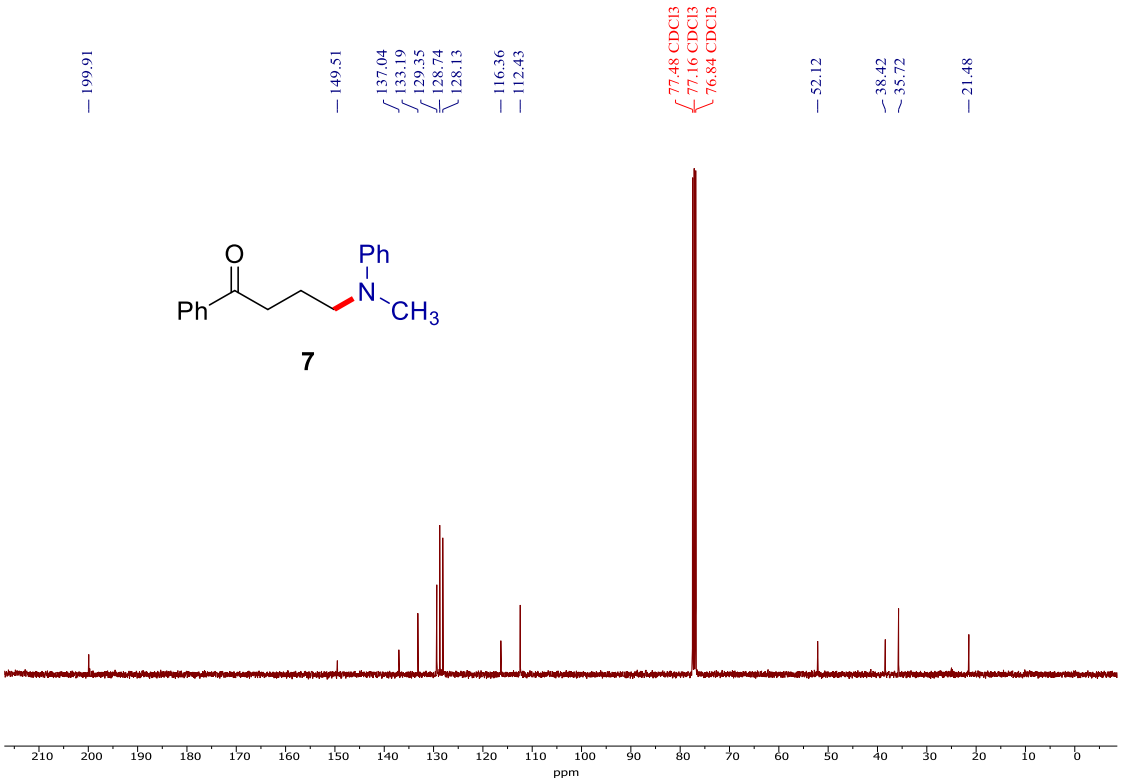
^{13}C NMR (101 MHz, $CDCl_3$) of **5td**



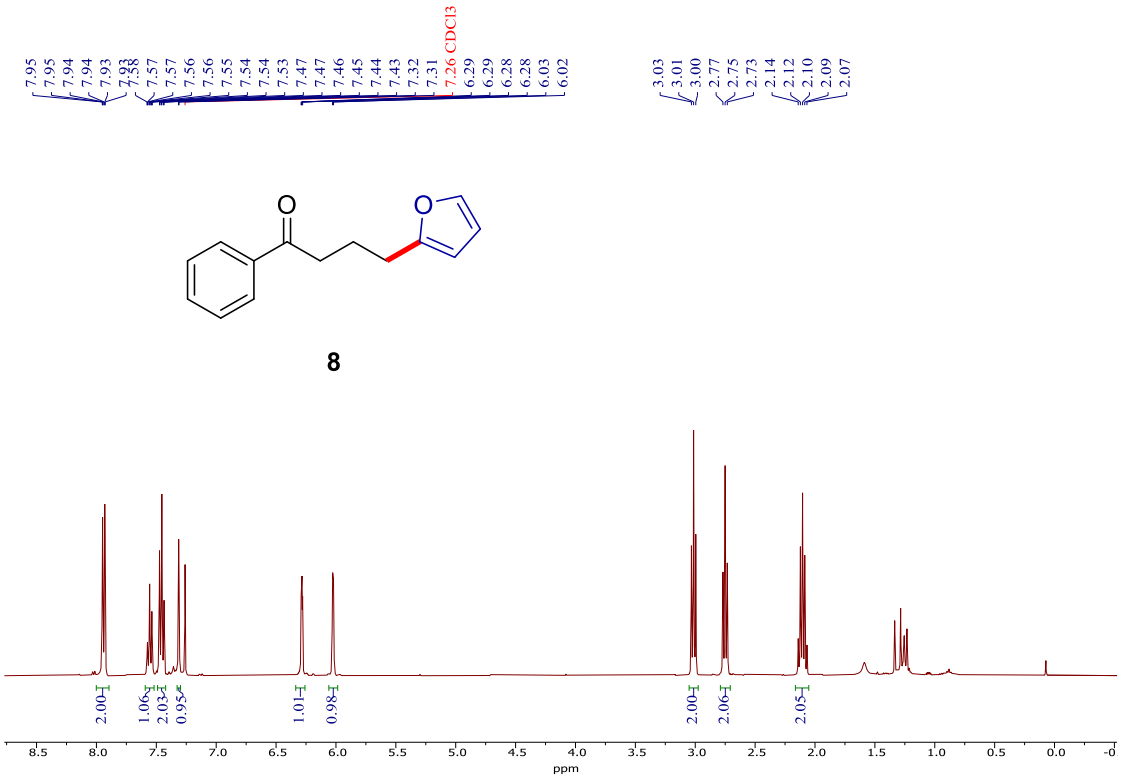
^{1}H NMR (400 MHz, $CDCl_3$) of **7** (*see procedure*)



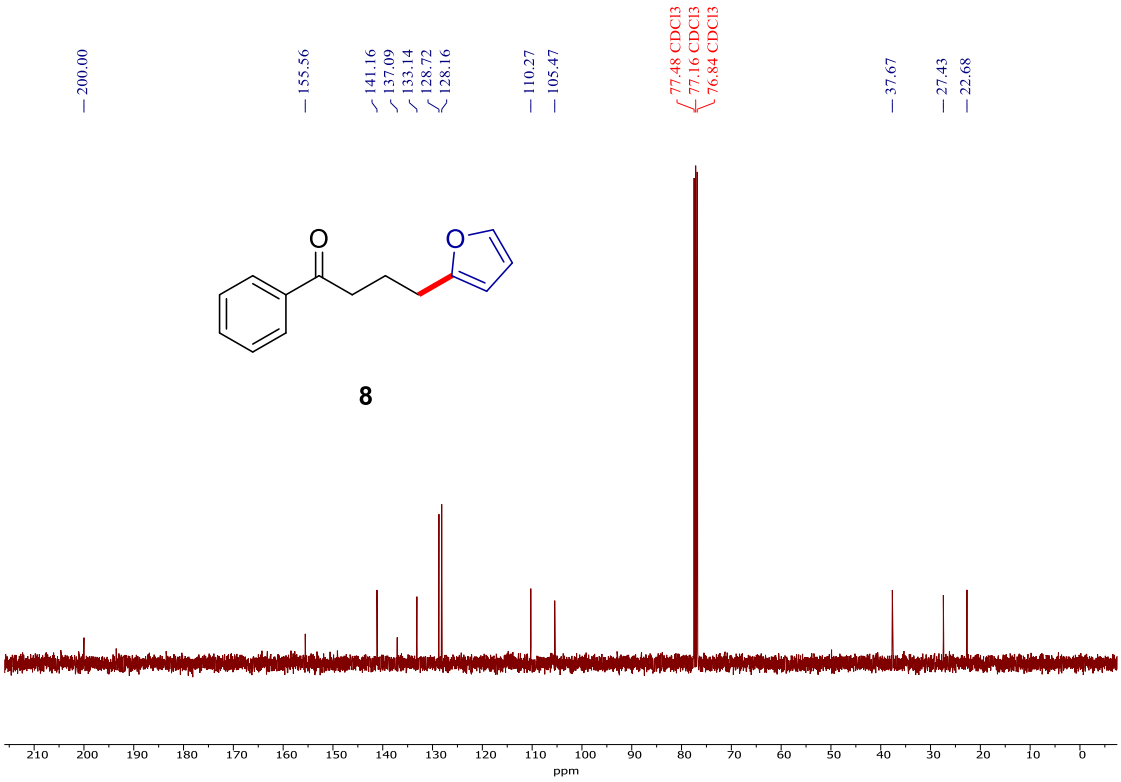
^{13}C NMR (101 MHz, $CDCl_3$) of **7**



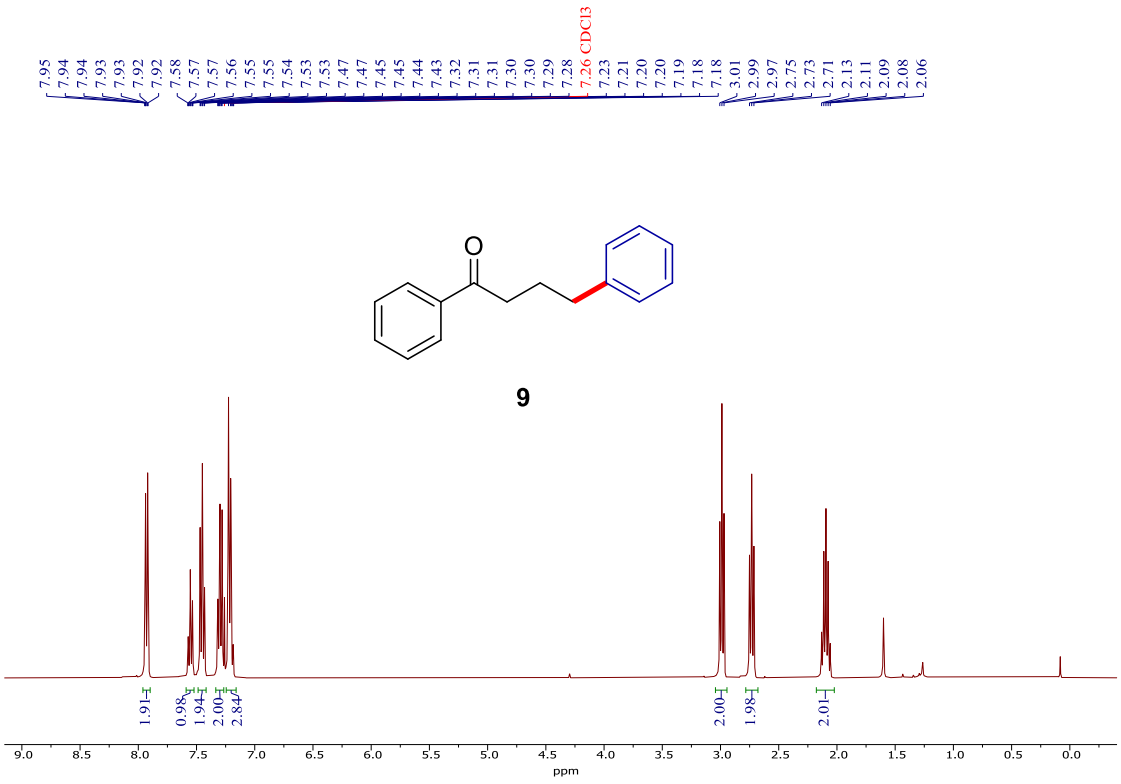
^{1}H NMR (400 MHz, $CDCl_3$) of **8** (*see procedure*)



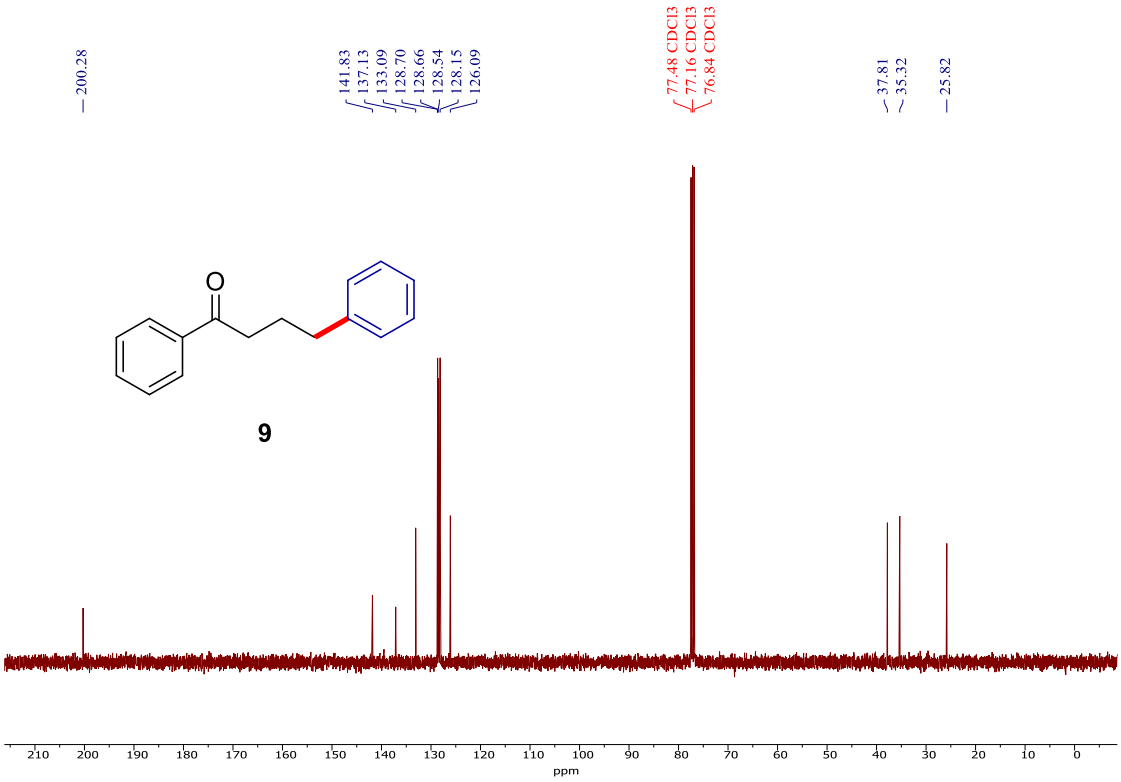
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



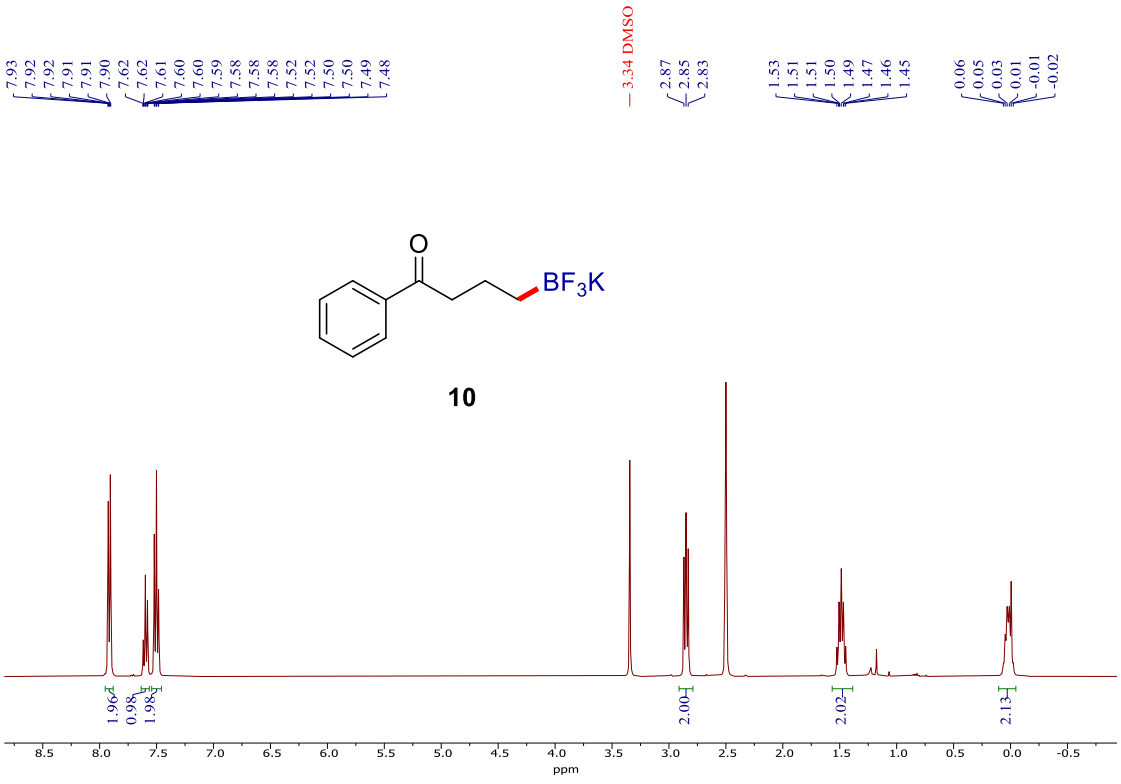
^{1}H NMR (400 MHz, $CDCl_3$) of **9** (*see procedure*)



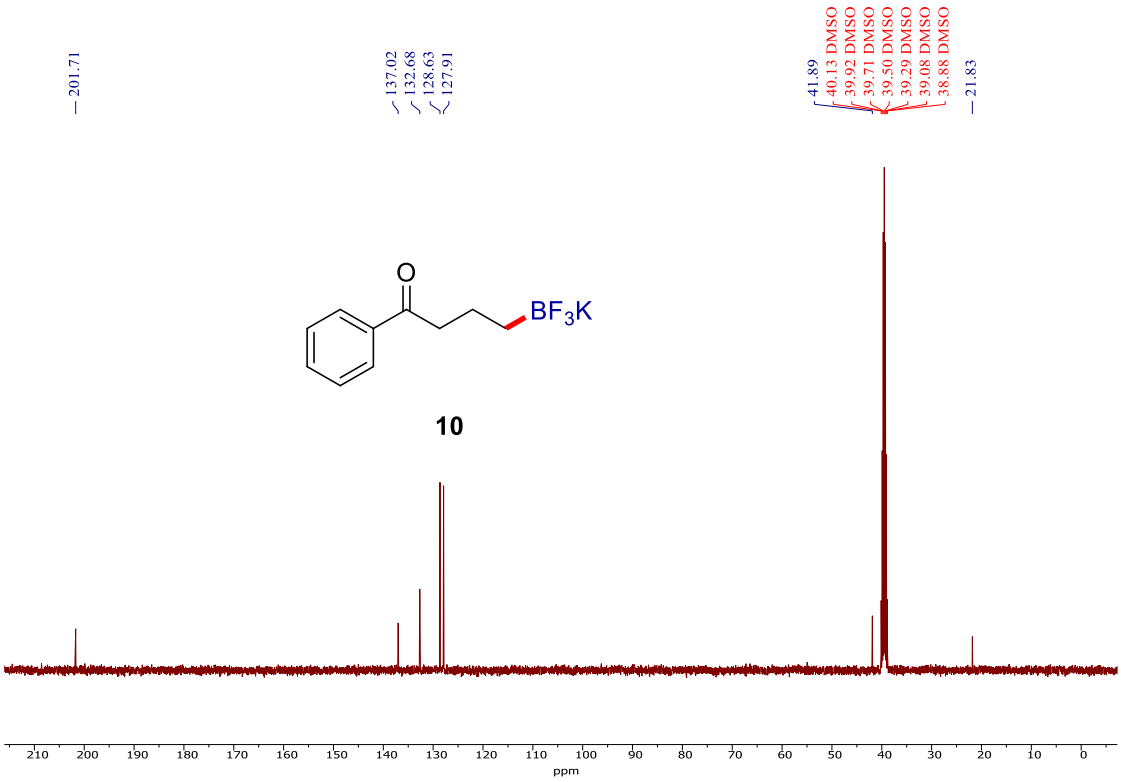
^{13}C NMR (101 MHz, $CDCl_3$) of **9**



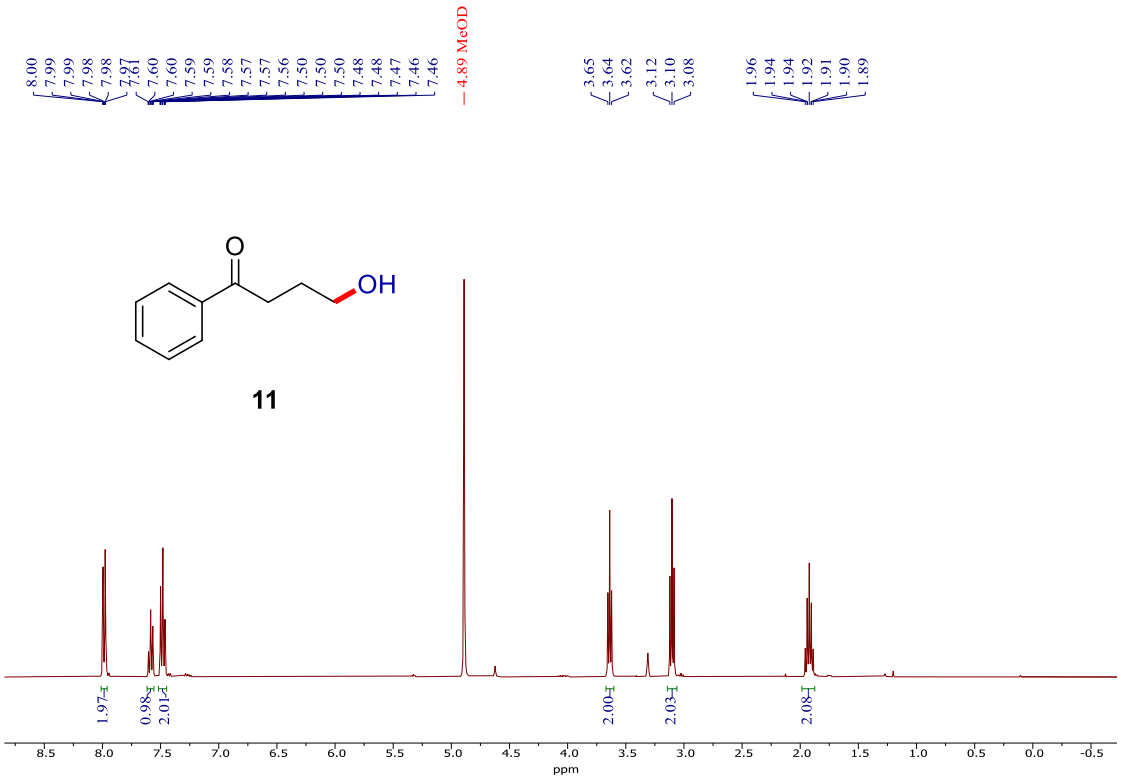
^{1}H NMR (400 MHz, d_6-DMSO) of **10** (*see procedure*)



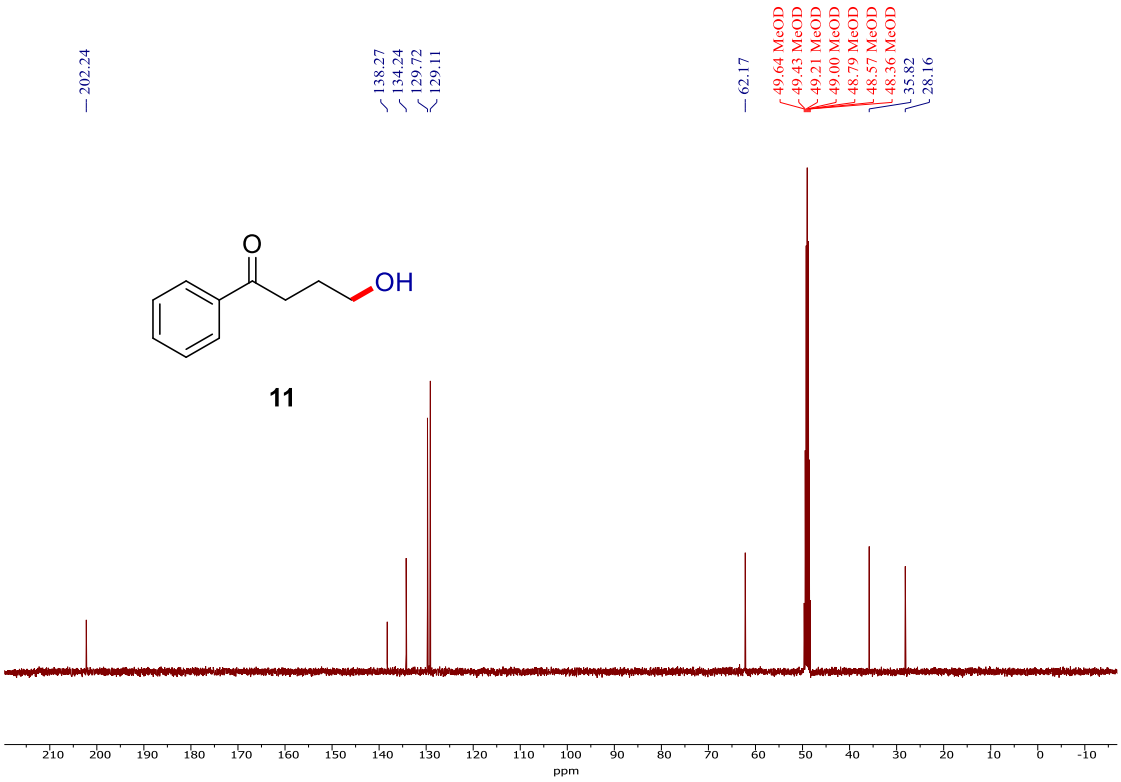
^{13}C NMR (101 MHz, d_6-DMSO) of **10**



^{1}H NMR (400 MHz, MeOD) of **11** (*see procedure*)



^{13}C NMR (101 MHz, MeOD) of **11**



6. REFERENCES

(1) Hitosugi, S.; Tanimoto, D.; Nakanishi, W.; Isobe, H. A Facile Chromatographic Method for Purification of Pinacol Boronic Esters. *Chem. Lett.* **2012**, *41*, 972-973.

(2) Zhang, X.; Cui, S.; Wei, S.; Zhao, M.; Liu, X.; Zhang, G. Nickel-Catalyzed Deaminative Alkyl–Alkyl Cross-Coupling of Katritzky Salts with Cyclopropanols: Merging C–N and C–C Bond Activation. *Org. Lett.* **2024**, *26*, 2114-2118.

(3) Jiang, J.; Liu, J.; Yang, Z.; Zheng, L.; Liu, Z.-Q. Three-Component Synthesis of Benzofuran-3(2H)-ones with Tetrasubstituted Carbon Stereocenters via Rh(III)-Catalyzed C−H/C−C Bond Activation and Cascade Annulation. *Adv. Synth. Catal.* **2022**, *364*, 2540-2545.

(4) Lou, C.; Wang, X.; Lv, L.; Li, Z. Iron-Catalyzed Ring-Opening Reactions of Cyclopropanols with Alkenes and TBHP: Synthesis of 5-Oxo Peroxides. *Org. Lett.* **2021**, *23*, 7608-7612.

(5) West, M. S.; Pia, J. E.; Rousseaux, S. A. L. Synthesis of 1- and 1,2-Substituted Cyclopropylamines from Ketone Homoenolates. *Org. Lett.* **2022**, *24*, 5869-5873.

(6) Bastick, K. A. C.; Watson, A. J. B. Pd-Catalyzed Organometallic-Free Homologation of Arylboronic Acids Enabled by Chemoselective Transmetalation. *ACS. Catal.* **2023**, *13*, 7013-7018.

(7) Lacker, C. R.; Delano, T. J.; Chen, E. P.; Kong, J.; Belyk, K. M.; Piou, T.; Reisman, S. E. Enantioselective Synthesis of N-Benzylic Heterocycles by Ni/Photoredox Dual Catalysis. *J. Am. Chem. Soc.* **2022**, *144*, 20190-20195.

(8) Wang, J.-W.; Li, Y.; Nie, W.; Chang, Z.; Yu, Z.-A.; Zhao, Y.-F.; Lu, X.; Fu, Y. Catalytic asymmetric reductive hydroalkylation of enamides and enecarbamates to chiral aliphatic amines. *Nat. Commun*. **2021**, *12*, 1313.

(9) 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* **2016**, *354*, 1265-1269.

(10) Marotta, A.; Fang, H.; Adams, C. E.; Sun Marcus, K.; Daniliuc, C. G.; Molloy, J. J. Direct Light-Enabled Access to α-Boryl Radicals: Application in the Stereodivergent Synthesis of Allyl Boronic Esters. *Angew. Chem. Int. Ed*. **2023**, *62*, e202307540.

(11) Wang, D.; Zhou, J.; Hu, Z.; Xu, T. Deoxygenative Haloboration and Enantioselective Chloroboration of Carbonyls. *J. Am. Chem. Soc.* **2022**, *144*, 22870-22876.

(12) Ho, T. D.; Lee, B. J.; Tan, C.; Utley, J. A.; Ngo, N. Q.; Hull, K. L. Efficient Synthesis of α-Haloboronic Esters via Cu-Catalyzed Atom Transfer Radical Addition. *J. Am. Chem. Soc.* **2023**, *145*, 27230-27235.

(13) Mercadante, M. A.; Kelly, C. B.; Hamlin, T. A.; Delle Chiaie, K. R.; Drago, M. D.; Duffy, K. K.; Dumas, M. T.; Fager, D. C.; Glod, B. L. C.; Hansen, K. E.; Hill, C. R.; Leising, R. M.; Lynes, C. L.; Macinnis, A. E.; Mcgohey, M. R.; Murray, S. A.; Piquette, M. C.; Roy, S. L.; Smith, R. M.; Sullivan, K. R.; Truong, B. H.; Vailonis, K. M.; Gorbatyuk, V.; Leadbeater, N. E.; Tilley, L. J. 1,3-γ-Silyl-elimination in electron-deficient cationic systems. *Chem. Sci*. **2014**, *5*, 3983-3994.

(14) Kurandina, D.; Parasram, M.; Gevorgyan, V. Visible Light-Induced Room-Temperature Heck Reaction of Functionalized Alkyl Halides with Vinyl Arenes/Heteroarenes. *Angew. Chem. Int. Ed*. **2017**, *56*, 14212-14216.

(15) Sumida, Y.; Yorimitsu, H.; Oshima, K. Nickel-Catalyzed Borylation of Aryl Cyclopropyl Ketones with Bis(pinacolato)diboron to Synthesize 4-Oxoalkylboronates. *J. Org. Chem*. **2009**, *74*, 3196-3198.

(16) Yang, J.-C.; Chen, L.; Yang, F.; Li, P.; Guo, L.-N. Copper-catalyzed borylation of cycloalkylsilyl peroxides via radical C–C bond cleavage. *Org. Chem. Front*. **2019**, *6*, 2792-2795.

(17) Sueki, S.; Kuninobu, Y. Copper-Catalyzed N- and O-Alkylation of Amines and Phenols using Alkylborane Reagents. *Org. Lett*. **2013**, *15*, 1544-1547.

(18) Piehl, P.; Amuso, R.; Alberico, E.; Junge, H.; Gabriele, B.; Neumann, H.; Beller, M. Cyclometalated Ruthenium Pincer Complexes as Catalysts for the α-Alkylation of Ketones with Alcohols. *Chem. Eur. J*. **2020**, *26*, 6050-6055.

(19) Zhang, B.; Xu, X.; Tao, L.; Lin, Z.; Zhao, W. Rhodium-Catalyzed Regiodivergent Synthesis of Alkylboronates via Deoxygenative Hydroboration of Aryl Ketones: Mechanism and Origin of Selectivities. *ACS. Catal*. **2021**, *11*, 9495-9505.

(20) Sun, Y.-W.; Tang, X.-Y.; Shi, M. A gold-catalyzed 1,2-acyloxy migration/intramolecular cyclopropanation/ring enlargement cascade: syntheses of medium-sized heterocycles. *Chem. Commun*. **2015**, *51*, 13937-13940.

(21) Yuan, Y.; Xu, J.-X.; Wu, X.-F. Cooperative Cu/Pd-catalyzed borocarbonylation of ethylene. *Chem. Commun*. **2022**, *58*, 12110-12113.

(22) Wang, X.; Liu, F.; Yan, Z.; Qiang, Q.; Huang, W.; Rong, Z.-Q. Redox-Neutral Nickel-Catalyzed Cross-Coupling Reactions of (Homo)allylic Alcohols and Aryltriflates. *ACS. Catal*. **2021**, *11*, 7319-7326.

(23) Zhao, L.-M.; Meng, Q.-Y.; Fan, X.-B.; Ye, C.; Li, X.-B.; Chen, B.; Ramamurthy, V., Tung, C.-H., Wu, L.-Z. Photocatalysis with Quantum Dots and Visible Light: Selective and Efficient Oxidation of Alcohols to Carbonyl Compounds through a Radical Relay Process in Water. *Angew. Chem. Int. Ed*. **2017**, *56*, 3020-3024.