
The radical-radical cross-coupling of alkyl carboxylic acids and organoborons

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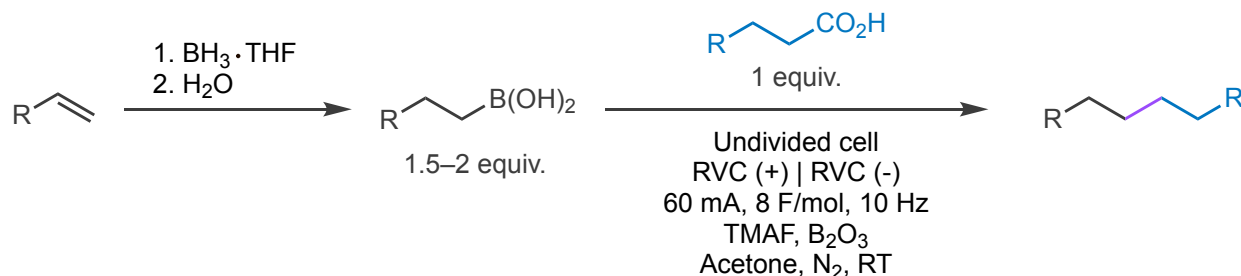
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Materials and Methods

All procedures were carried out using standard Schlenk or glovebox techniques under nitrogen atmosphere unless otherwise stated. Tetrahydrofuran (THF) and toluene were obtained by passing the degassed solvents (via argon purge) through an activated alumina column and stored over 4Å molecular sieves. Acetone was purchased from ThermoFisher Scientific as Extra Dry, AcroSeal™ (cat. 326800010) or HPLC grade (cat. 022928) and stored in the glovebox upon receipt. Methanol (anhydrous) was obtained from Sigma-Aldrich (cat. 322415). Reagents were purchased from Ambeed and Sigma-Aldrich, stored in the glovebox, and used without further purification unless otherwise stated. Electrolysis was performed on IKA ElectraSyn 2.0 using Reticulated Vitreous Carbon (RVC) electrodes purchased as foam panels (6" x 6", 100ppi, 0.5" thickness) from Duocel. Reactions were monitored by gas chromatography–mass spectrometry (GCMS), recorded on TRACE 1610–ISQ 7610 by ThermoFisher Scientific. Yields are reported according to chromatographically isolated and spectroscopically characterized products unless otherwise noted. Crude products were purified by column chromatography on a Biotage Selekt using Biotage Sfar silica (Duo 60 µm, FSRD-0445). NMR spectra were recorded on Bruker Avance III HD 500 MHz spectrometer. Deuterated chloroform was purchased from Cambridge Isotope Laboratories Inc. ¹H and ¹³C chemical shifts are reported in ppm relative to tetramethylsilane and referenced using residual undeuterated solvent (CHCl₃ at 7.26 ppm for ¹H NMR, 77.23 ppm for ¹³C NMR). High resolution mass spectra (HRMS) were recorded on Agilent 6545 LC-QTOF mass spectrometer via electrospray or electron impact ionization (ESI or EI) time of flight (TOF) experiments. Cyclic Voltammetry (CV) studies were conducted on a Biologic SP-50e potentiostat/galvanostat. Glassy carbon (3 mm dia.) and platinum (2 mm dia.) working electrodes and the non-aqueous Ag/Ag⁺ reference electrode were purchased from CH Instruments and SYC Technologies, Inc. Carbon fiber (rod, 5 mm diameter) was purchased from Amazon as the counter electrode.

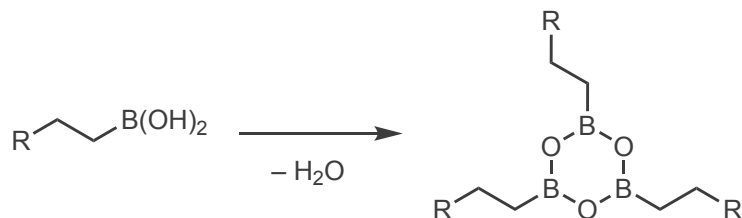
Procedures for electrochemical coupling reactions

General Procedure A: One-pot alkene hydroboration and cross-coupling with carboxylic acids



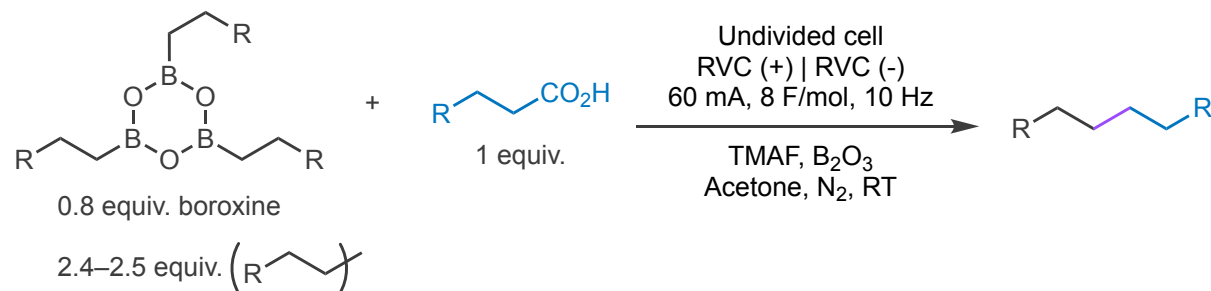
The alkylboronic acids were prepared in a similar manner to the reported procedure¹. In an oven-dried flask (100 mL) was charged a solution of $\text{BH}_3 \cdot \text{THF}$ (10 mL, 10 mmol, 1 M solution in THF), to which alkene (5 mmol) in THF (1 mL) was added dropwise at 0 °C. The mixture was stirred for 2 h at room temperature, followed by slow addition of H_2O (1 mL) and stirring for an additional 3 h at room temperature. After reaction completion, the crude mixture was concentrated *in vacuo*, diluted with ethyl acetate (20 mL), washed with saturated aqueous sodium bicarbonate (10 mL) and brine (10 mL). The organic layer was dried over sodium sulfate, filtered and concentrated *in vacuo* to afford the desired boronic acid as a thick oil. Toluene (40 mL) was added to the oil, and the mixture was concentrated *in vacuo* to remove residual water. The boronic acid was dried under high vacuum overnight and brought into the glovebox under N_2 atmosphere. Inside the glovebox, an ElectraSyn vial (5 mL) with a stir bar (10 mm) was charged the boronic acid (0.9–1 mmol, 1.5–2 equiv.), carboxylic acid (0.5–0.6 mmol, 1 equiv.), boron oxide (1 mmol, 70 mg), anhydrous tetramethyl ammonium fluoride (2.5 mmol, 233 mg) and acetone (4 mL). The ElectraSyn cap was equipped with two RVC electrodes (width: 8 mm, length: 50 mm, thickness: 2 mm) and connected to the ElectraSyn vial. The fully assembled vial of reaction mixture was electrolyzed under AP conditions outside the glovebox (constant current: 60 mA, frequency: 50 ms (10 Hz), charge: 8 F/mol for 1.5 mmol of total substrate amount). Following reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel and concentrated *in vacuo*. The crude material was purified by column chromatography to afford the desired product.

General Procedure B: Cross-coupling of boroxines with carboxylic acids



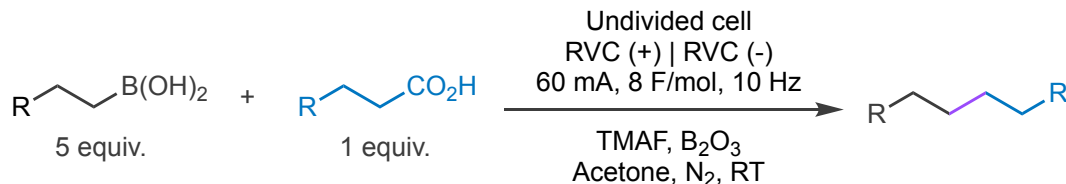
Alkylboronic acid was suspended in anhydrous toluene (10 mL per 1 mmol of material) and concentrated *in vacuo* at 50 °C to azeotropically remove hydrate water². The residue was dried under high vacuum at 50 °C for 2 hours. The dry residue was then dissolved in hot ethyl acetate (minimal volume), and hexane was added dropwise until the solution turned slightly cloudy. The mixture was allowed to cool slowly to room temperature, then stored at 0 °C for 1 h to induce

crystallization³. The resulting solid was collected by vacuum filtration, washed with cold hexanes, and dried under high vacuum overnight to afford boroxine.



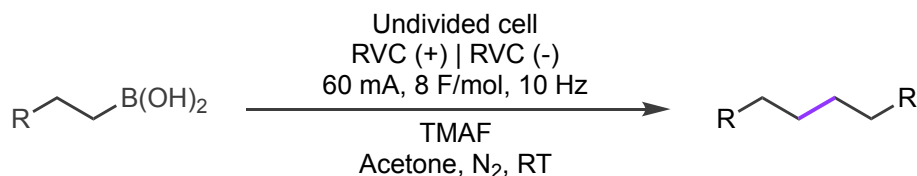
Inside a glovebox under N_2 atmosphere, in an ElectraSyn vial (5 mL) with a stir bar (10 mm) was charged the carboxylic acid (0.5 mmol), boroxine (0.4 mmol), boron oxide (1 mmol, 70 mg), anhydrous tetramethyl ammonium fluoride (2.5 mmol, 233 mg) and acetone (4 mL). The ElectraSyn cap was equipped with two RVC electrodes (width: 8 mm, length: 50 mm, thickness: 2 mm) and connected to the ElectraSyn vial. The fully assembled electrochemical reaction mixture was brought outside of the glovebox and electrolyzed under AP conditions (constant current: 60 mA, frequency: 50 ms (10 Hz), charge: 8 F/mol for 1.2 mmol of total substrate amount). Following reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel and concentrated *in vacuo*. The crude material was purified by column chromatography to afford the desired product.

General Procedure C: Cross-coupling of commercial boronic acids with carboxylic acids



Inside the glovebox, an ElectraSyn vial (5 mL) with a stir bar (10 mm) was charged the boronic acid (1 mmol, 5 equiv.), carboxylic acid (0.2 mmol, 1 equiv.), boron oxide (1 mmol, 70 mg), anhydrous tetramethyl ammonium fluoride (1.5 mmol, 140 mg) and acetone (4 mL). The ElectraSyn cap was equipped with two RVC electrodes (width: 8 mm, length: 50 mm, thickness: 2 mm) and connected to the ElectraSyn vial. The fully assembled vial of reaction mixture was electrolyzed under AP conditions outside the glovebox (constant current: 60 mA, frequency: 50 ms (10 Hz), charge: 8 F/mol for 1.5 mmol of total substrate amount). Following reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel and concentrated *in vacuo*. The crude material was purified by column chromatography to afford the desired product.

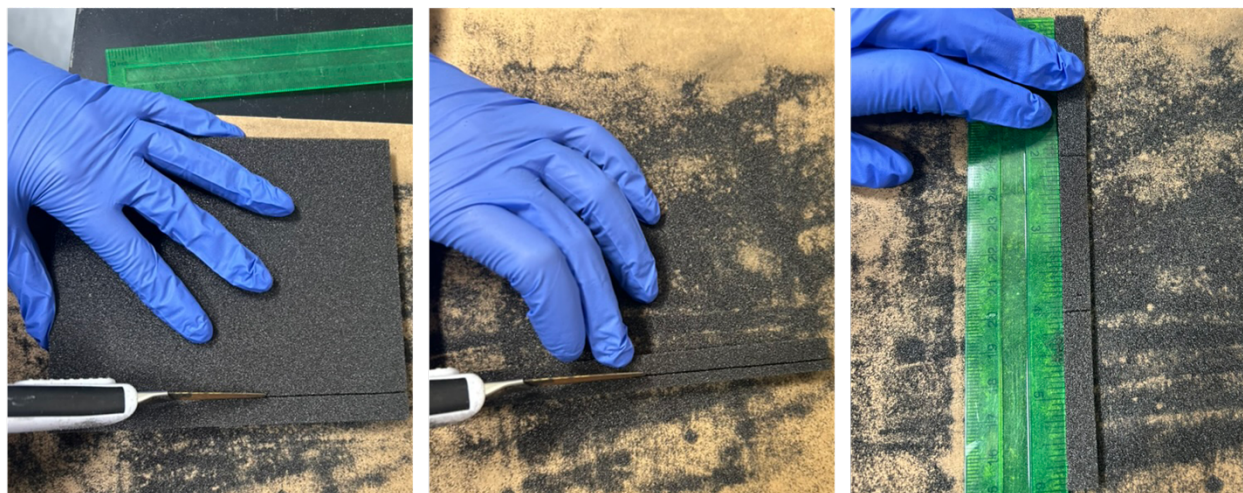
General Procedure D: Boronic acid homocoupling



Inside a glovebox under N₂ atmosphere, in an ElectraSyn vial (5 mL) with a stir bar (10 mm) was charged the boronic acid (1 mmol), anhydrous tetramethyl ammonium fluoride (1.5 mmol, 140 mg) and acetone (4 mL). The ElectraSyn cap was equipped with two RVC electrodes (width: 8 mm, length: 50 mm, thickness: 2 mm) and connected to the ElectraSyn vial. The fully assembled vial of reaction mixture was brought outside of the glovebox and electrolyzed under AP conditions (constant current: 60 mA, frequency: 50 ms (10 Hz), charge: 8 F/mol for 1 mmol of total substrate amount). Following reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel and concentrated *in vacuo*. The crude material was purified by column chromatography to afford the desired product. This procedure was used for both commercially available and laboratory-synthesized (see **General Procedure D-1 & D-2**) boronic acids.

Graphical guide for reaction setup

1. Preparation of RVC electrodes



(Left) A strip (8 mm wide) was cut from the RVC foam panel (6" x 6", 100ppi, 0.5" thickness) purchased from Duocel. **(Middle)** The strip was flipped with the side (12 mm width) facing up and cut into 3 strips (4 mm width). **(Right)** The strip was flipped with the side (8 mm wide) facing up and cut into 3 pieces (50 mm length).

2. Assembly of the ElectraSyn vial cap with electrodes



(Left) The previously cut strip (8 mm width, 50 mm length, 4 mm thickness) was threaded through an electrode holder. During this process, RVC residues flaked off to reduce the thickness of the electrode from 4 mm to 2 mm. **(Middle)** Each individual electrode with holder was inserted into the anode/cathode on the ElectraSyn vial cap and fixed in place without falling off. **(Right)** The cap was furnished with two RVC electrodes. The remaining loose RVC residues were blown off with a stream of N_2 .

3. Electrolysis



(Left) Following General Procedures, in the ElectraSyn vial was charged the reagents and solvent inside the glovebox. The cap equipped with RVC electrodes were screwed tightly on the vial and brought outside of the glovebox. **(Middle)** Turn on ElectraSyn, select “New Experiments” > “Rapid Alternating Polarity” > “Constant Current” > dial “60.0 mA” > No reference electrodes > “Total Charge” > “# mmols substrate: 1.20” (depending on the procedure) > “# of equiv. of electrons (F/mol): 8.0” > dial “50 ms (10.000 Hz)”. **(Right)** Crude mixture after reaction completion.

4. Comparison of electrode before and after reaction



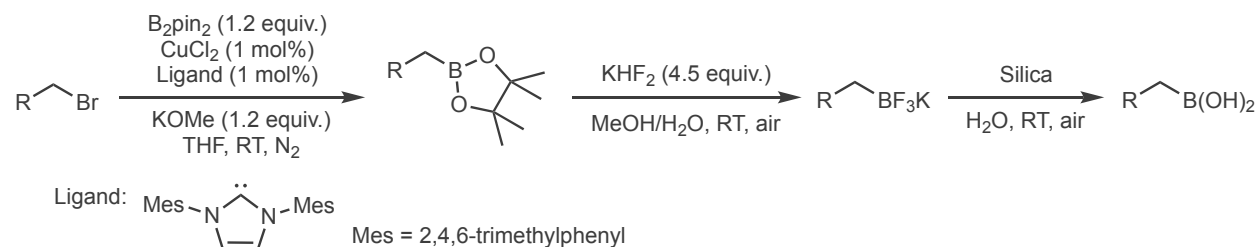
Procedure: One of the RVC electrodes was weighed before electrolysis. After electrolysis, the same electrode was washed with acetone, dried, and weighed again. **(Left)** Before: 46.7 mg. **(Right)** After: 54.2 mg. Weight change: 7.5 mg.

Procedure for drying tetramethylammonium fluoride tetrahydrate (TMAF·4H₂O)

Anhydrous TMAF was prepared in a similar manner to the reported procedure⁴. To an oven-dried flask (250 mL) was added tetramethylammonium fluoride tetrahydrate (20 g) and isopropyl alcohol (150 mL). The mixture was concentrated *in vacuo* at 45° C to near dryness. This was repeated 5 times. Toluene (100 mL) was then added to the material, and the mixture was concentrated *in vacuo* at 45° C. This was repeated 5 times until the weight of the solid material remained stable (approximately 11 g). The white powder was dried under high vacuum overnight and stored in the glovebox.

General procedures for non-commercially available boronic acids for homocoupling

General Procedure D-1: Starting from alkyl bromides

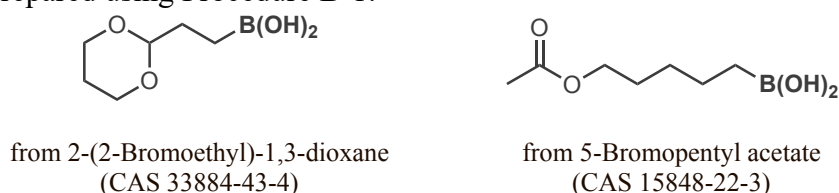


Step 1: Alkylboronate esters were prepared following the reported procedure⁵. Inside the glovebox under N₂ atmosphere, in a 25 mL Scintillation vial with a stir bar was charged CuCl₂ (1 mol%, 0.01 mmol, 1 mg), the ligand (0.01 mmol, 3 mg, 1 mol%) and THF (2 mL). The mixture was stirred for 10 min, followed by addition of bis(pinacolato)diboron (1.2 mmol, 305 mg, 1.2 equiv.) and KOMe (1.2 mmol, 84 mg, 1.2 equiv.). After stirring for an additional 10 min, the alkyl bromide (1 mmol) was added. The reaction mixture was stirred for 1 h at room temperature and monitored by GCMS. The crude mixture was diluted with diethyl ether (6 mL) and filtered through a plug of celite, which was washed with a generous amount of ether. The solvents were removed *in vacuo* and diluted with DCM (50 mL). The mixture was filtered through a plug of silica and concentrated *in vacuo* to afford a light yellow oil.

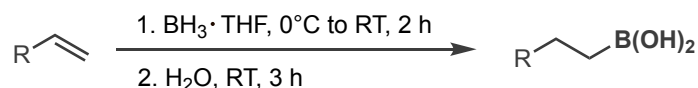
Step 2: Potassium alkyltrifluoroborate salts were prepared following the reported procedure⁶. To a 25 mL Scintillation vial with a stir bar and the boronate ester from the previous step was added methanol (5 mL) followed by dropwise addition of KHF₂ (1 mL, 4.5 M, 4.5 mmol, 4.5 equiv.). The reaction mixture was stirred for 1 h at room temperature. After reaction completion, the reaction was concentrated *in vacuo* to near dryness. The residue was re-dissolved in a 1:1 MeOH/H₂O mixture and concentrated *in vacuo*. The methanol/water azeotrope was repeated 5 times to remove pinacol until the resulting material appeared a fine white solid powder. The solid was diluted with acetone (20 mL) and filtered. The remaining salts were washed with more acetone (5 mL). The filtrate was concentrated *in vacuo* to give the desired trifluoroborate salt.

Step 3: Alkylboronic acids were prepared following the reported procedure⁷. In an 8 mL glass vial with a stir bar was charged the trifluoroborate salt from the previous step and water (3 mL) and silica (300 mg). The reaction mixture was stirred for 2 h and monitored by ¹¹B NMR. Following reaction completion, the mixture was diluted with a 1:1 ethyl acetate/diethyl ether mixture and filtered through a plug of celite. The organic layer was collected, and the aqueous phase was extracted with ethyl acetate/diethyl ether. The combined organic layer was dried over Na₂SO₄ and concentrated *in vacuo* to afford the desired boronic acid, which was used in the subsequent electrochemical homocoupling reaction without further purification.

Boronic acids prepared using Procedure B-1:

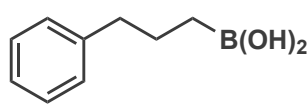


General Procedure D-2: Starting from terminal alkenes

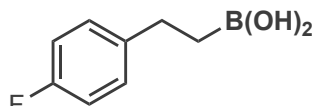


The alkylboronic acids were prepared in a similar manner to the reported procedure¹. In an oven-dried flask (100 mL) was charged a solution of $\text{BH}_3 \cdot \text{THF}$ (10 mL, 10 mmol, 1 M solution in THF), to which alkene (5 mmol) in THF (1 mL) was added dropwise at 0°C . The mixture was stirred for 2 h at room temperature, followed by slow addition of H_2O (1 mL) and stirring for an additional 3 h at room temperature. After reaction completion, the crude mixture was concentrated *in vacuo*, diluted with ethyl acetate (20 mL), washed with saturated aqueous sodium bicarbonate (10 mL) and brine (10 mL). The organic layer was dried over sodium sulfate, filtered and concentrated *in vacuo* to afford the desired boronic acid as a thick oil. Toluene (40 mL) was added to the oil, and the mixture was concentrated *in vacuo* to remove residual water. The boronic acid was dried under high vacuum overnight and stored in the glovebox. The boronic acids prepared using this procedure were used in the subsequent electrochemical homocoupling reaction without further purification.

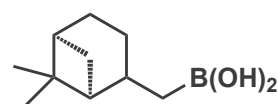
Boronic acids prepared using Procedure B-2:



from Allylbenzene
(CAS 300-57-2)



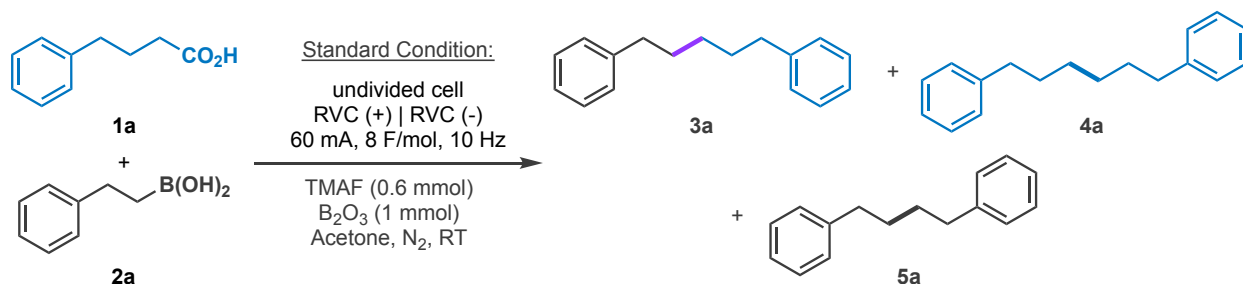
from 4-Fluorostyrene
(CAS 405-99-2)



from (-)- β -Pinene
(CAS 18172-67-3)

Effect of reaction parameters

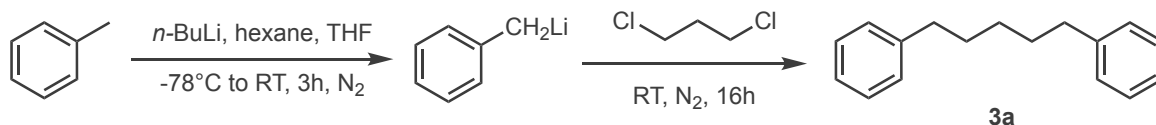
Procedure for optimization of reaction parameters



Following **General Procedure A**, 4-phenylbutyric acid (**1a**, CAS 1821-12-1) and phenethylboronic acid (**2a**, CAS 34420-17-2) on a 1.2 mmol total substrate (**1a** + **2a**) scale were electrolyzed with variations from the standard condition described in the following tables. After reaction completion, the electrodes were washed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel and analyzed by GCMS. The

yields of **3a**, **4a** and **5a** were determined from authentic samples using *n*-hexadecane as internal standard. Compound **3a**, **4a** and **5a** were synthesized according to the following procedures.

Compound 3a

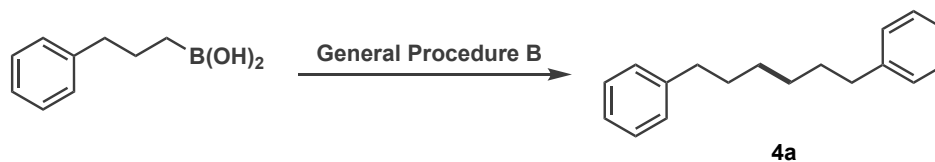


Compound **3a** was synthesized following the reported procedure⁸. To an oven-dried 100 mL round-bottom flask with a stir bar under N_2 was added toluene (10 mL) and THF (10 mL) at room temperature and cooled down to -78°C , followed by dropwise addition of *n*-Butyllithium (8 mL, 20 mmol, 2.5 M in hexane). The mixture was warmed to room temperature. After stirring for 3 h, 1,3-Dichloropropane (10 mmol, 1.1 g) was added. The suspension was stirred at room temperature for 16 h and monitored by GCMS. After completion, the reaction was quenched with water and extracted with ethyl acetate (3×20 mL). The organic layer was washed with brine (3×10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in hexane (40 mL), filtered through a plug of silica and concentrated *in vacuo* to give the titled compound (1.6 g, 72%).

^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.24 (m, 4H), 7.17 (td, $J = 6.5, 1.6$ Hz, 6H), 2.60 (t, $J = 7.7$ Hz, 4H), 1.65 (tt, $J = 9.2, 6.9$ Hz, 4H), 1.44 – 1.34 (m, 2H).

The spectroscopic data matched the literature⁸.

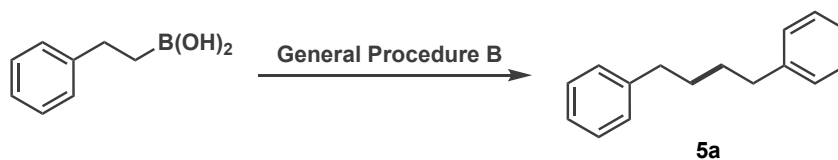
Compound 4a



Compound **4a** was prepared following **General Procedure B** on a 1 mmol scale from *boronic acid* (164 mg) synthesized from allylbenzene (CAS 300-57-2, purchased from Ambeed) following **General Procedure B-2**. Purification by flash column chromatography (hexanes) gave the titled compound (85 mg, 71%).

¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.17 (m, 4H), 7.13 – 7.07 (m, 6H), 2.55 – 2.49 (m, 4H), 1.54 (tdd, J = 9.0, 7.3, 5.5 Hz, 4H), 1.32 – 1.26 (m, 4H).
The spectroscopic data matched the literature⁹.

Compound 5a

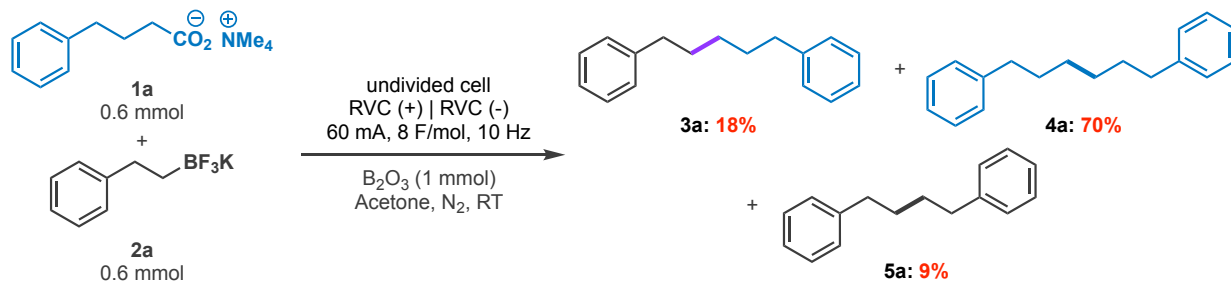


Compound **4a** was prepared following **General Procedure B** on a 1 mmol scale from phenethylboronic acid (150 mg, CAS 34420-17-2, purchased from Ambeed). Purification by flash column chromatography (hexanes) gave the titled compound (78 mg, 75%).

¹H NMR (500 MHz, CDCl₃) δ 7.28 – 7.23 (m, 4H), 7.16 (ddd, J = 7.7, 5.5, 1.7 Hz, 6H), 2.62 (dq, J = 7.7, 4.0 Hz, 4H), 1.69 – 1.63 (m, 4H).
The spectroscopic data matched the literature⁹.

Figure 1. Effect of pre-activation of one or both coupling partners

A. Both coupling partners are pre-activated



B. Only the organoboron reagent is pre-activated

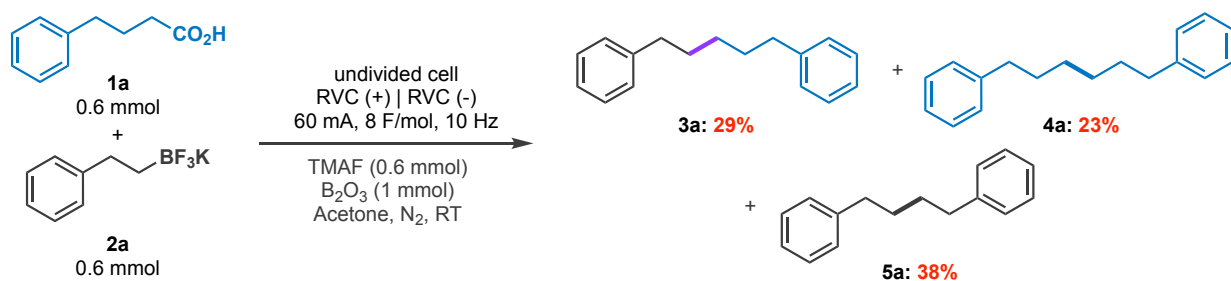
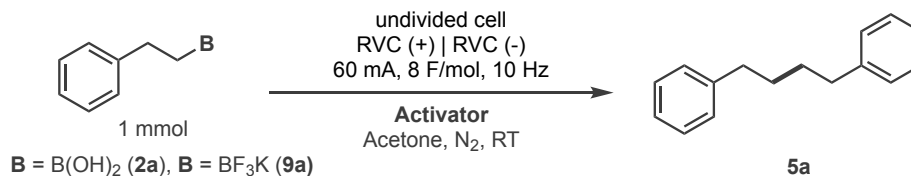
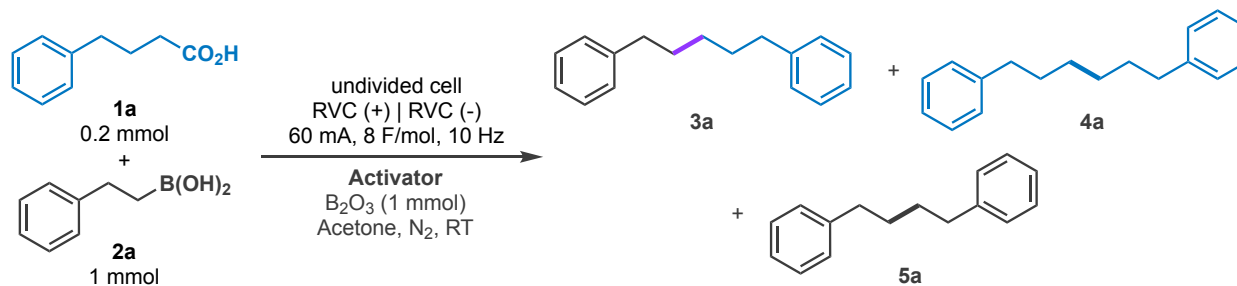


Table 1. Effect of activators and TMAF equivalence**A. Homocoupling of organoboron reagents**

Entry	Conditions	GC yield (%)
		5a
1	9a , TBABF ₄ (0.5 eq.)	22
2	9a , TMABF ₄ (0.5 eq.)	30
3	9a , TMAPF ₆ (0.5 eq.)	26
4	9a , TMAOH·5H ₂ O (0.5 eq.)	5
5	9a , CsF (1 eq.), 18-Crown-6 (1 eq.)	47
6	9a , CsF (1 eq.), HFIP (10 eq.)	50
7	9a , TMAF (anhydrous, 1 eq.)	52
8	2a , TMAF (anhydrous, 1 eq.)	65
9	2a , TMAF (anhydrous, 1.5 eq.)	82
10	2a , TMAF·4H ₂ O (1.5 eq.)	26

B. Cross-coupling of carboxylic acid and boronic acid

Entry	Conditions	GC yield (%)		
		3a	4a	5a
1	TMAOH (1.5 eq.)	0	0	0
2	TMAOH (10 mol%)	0	10	0
3 (std)	TMAF (1.25 eq.)	58	13	21
4	TMAF (2 eq.)	29	7	62
5	TMAF (3 eq.)	18	3	78

Figure 2. Cross-coupling using carboxylic acids in excess

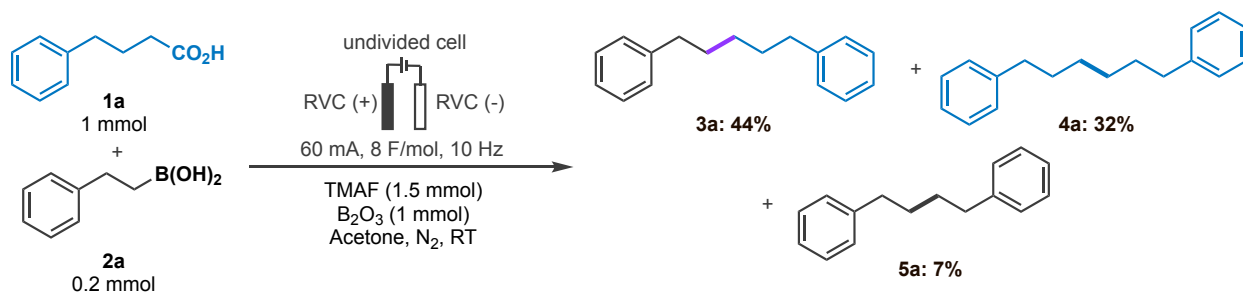
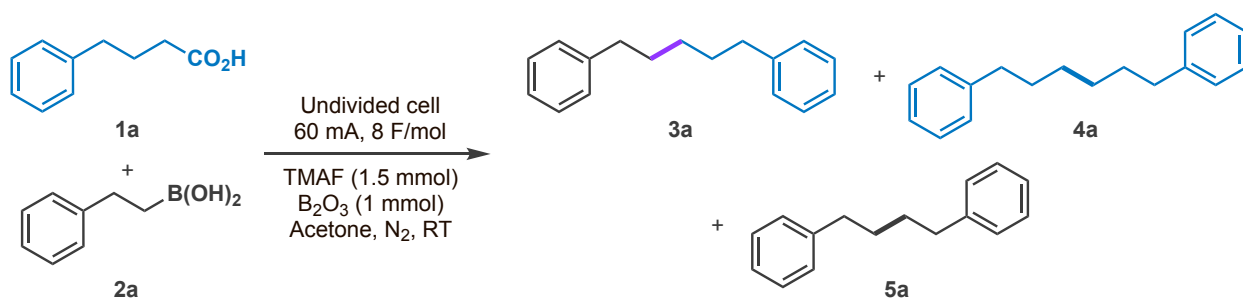
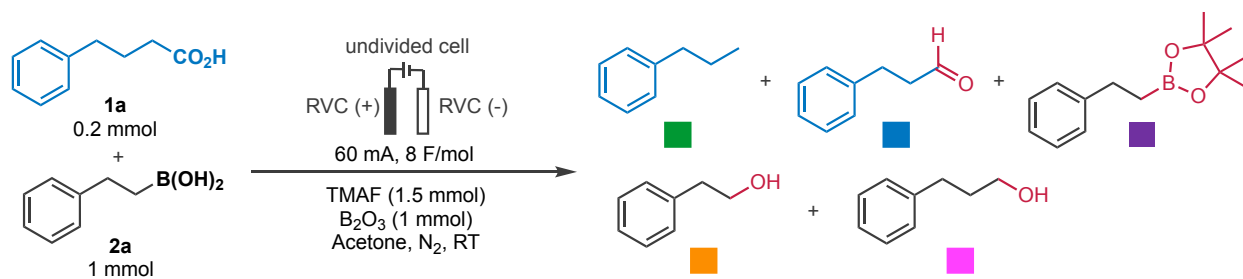


Table 2. Effect of AP vs. DC and electrode materials

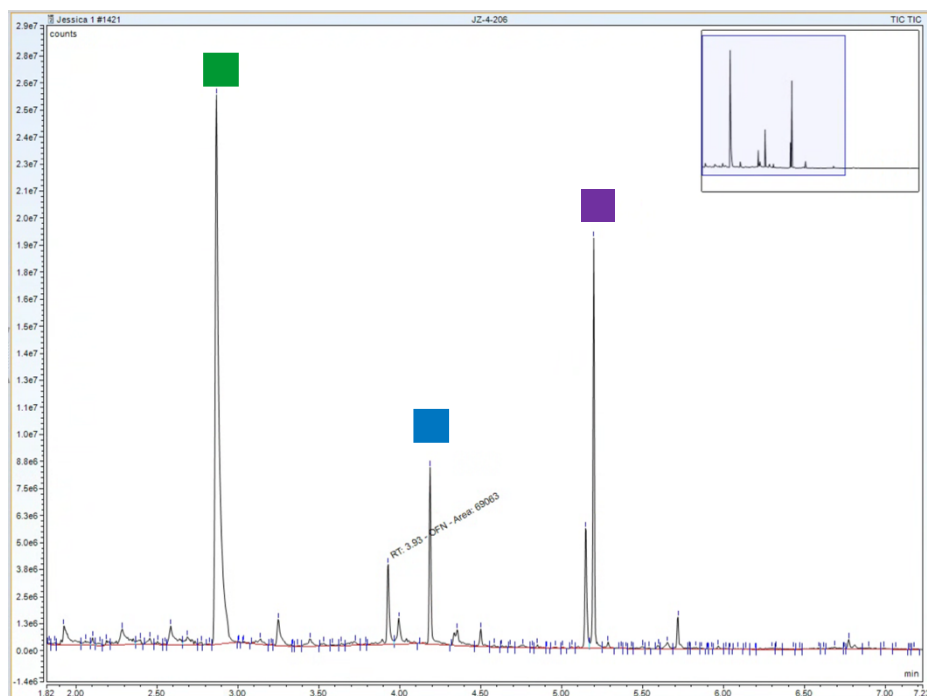


Entry	Conditions	GC yield (%)		
		3a	4a	5a
1 (std)	1a (0.2 mmol), 2a (1 mmol), 10 Hz, RVC(+)/RVC(-)	58	13	21
2	Entry 1, DC	0	0	0
3	Entry 1, Pt(+)/Pt(-)	0	0	0
4	Entry 3, Pt(+)/Pt(-), DC	0	0	0

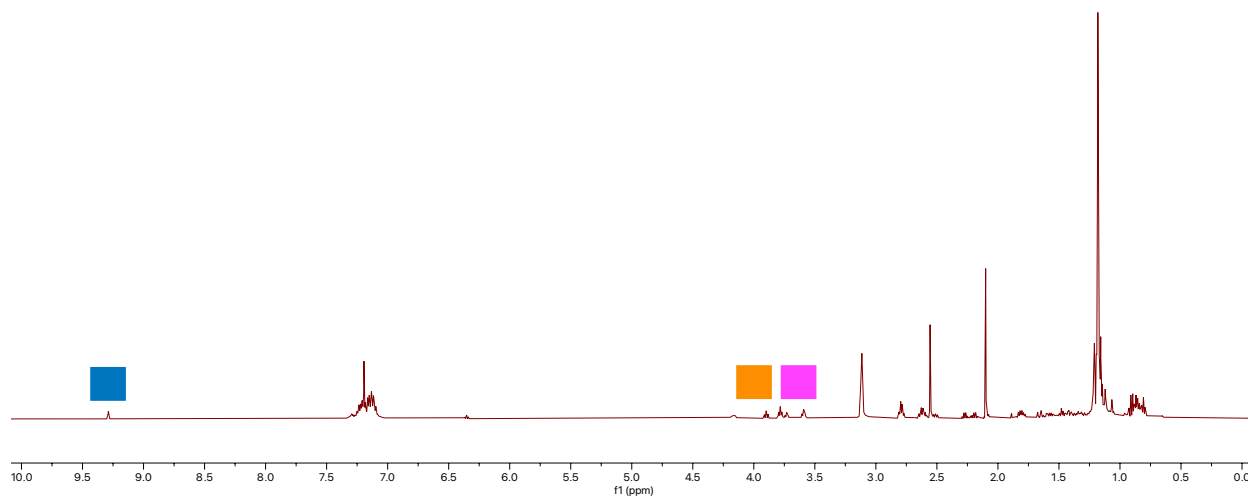
Figure 3. Cross-coupling under direct/constant current electrolysis



GC traces of crude reaction mixture:



¹H NMR of crude reaction mixture (in *d*-chloroform):



Expansion (1.8–7.4 ppm) of the crude ^1H NMR compared to authentic samples of phenethyl and phenpropyl alcohol:

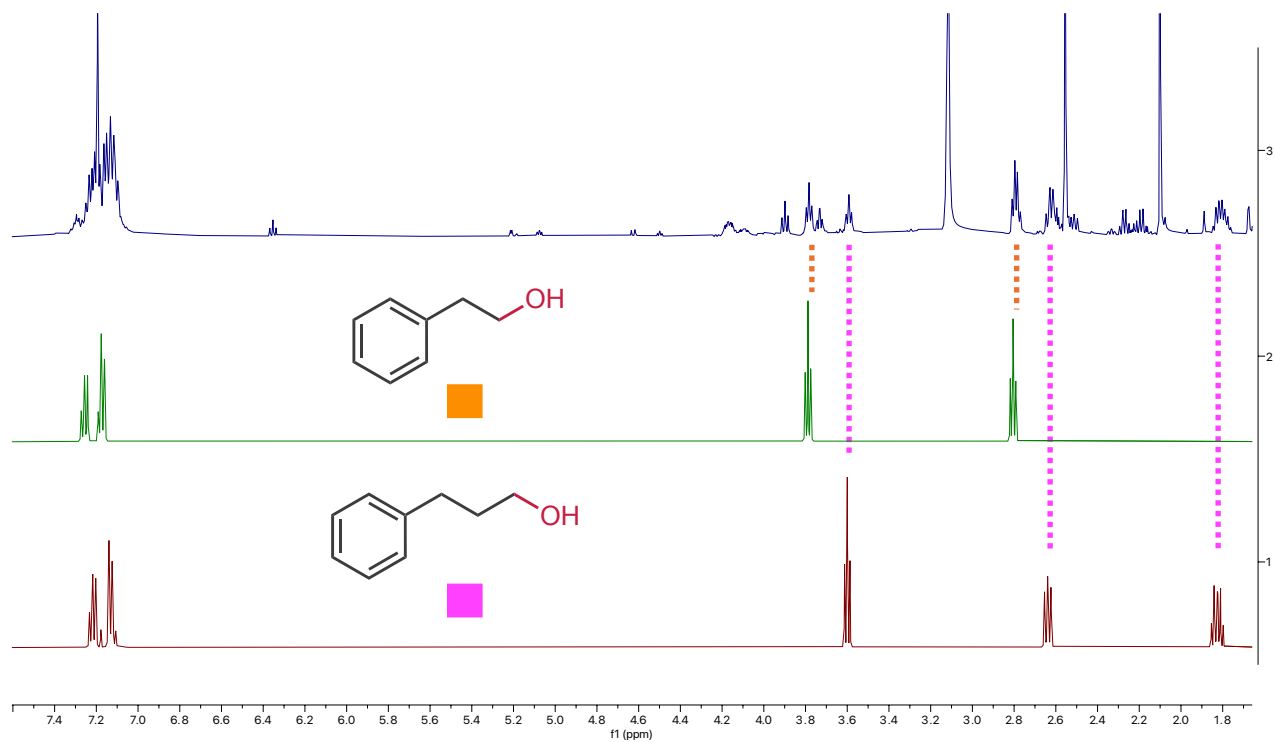
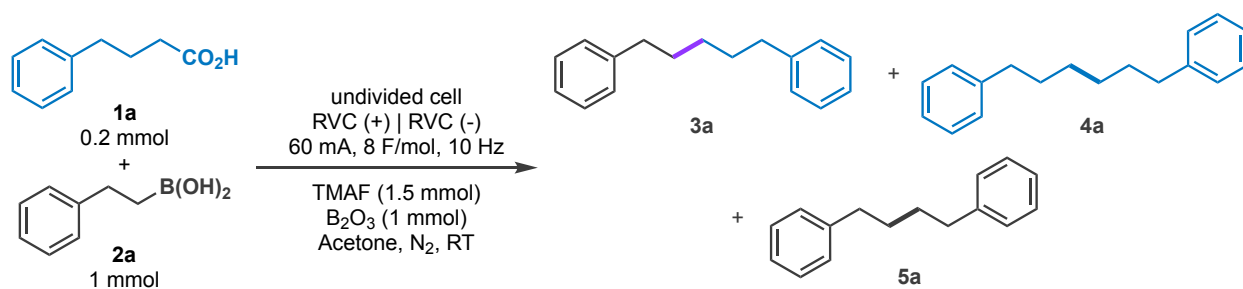
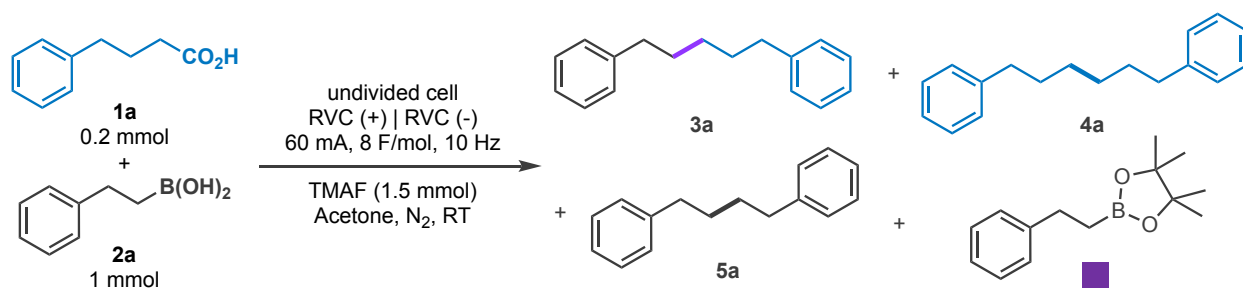


Table 3. Effect of other electrochemical parameters



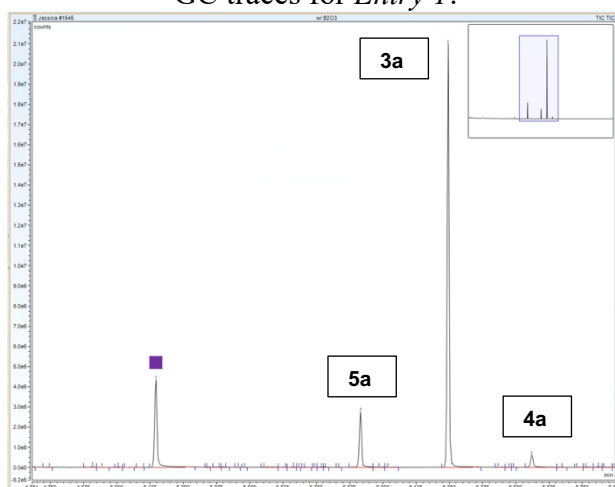
Entry	Conditions	GC yield (%)		
		3a	4a	5a
1 (std)	60 mA, 8 F/mol, 10 Hz	58	13	21
2	60 mA, 8 F/mol, DC	2	0	0
3	60 mA, 8 F/mol, 5 Hz	32	11	52
4	60 mA, 8 F/mol, 20 Hz	54	10	24
5	30 mA, 8 F/mol, 10 Hz	22	9	11
6	60 mA, 1 F/mol, 10 Hz	7	2	4
7	60 mA, 2 F/mol, 10 Hz	16	6	10
8	60 mA, 4 F/mol, 10 Hz	25	9	16
9	60 mA, 16 F/mol, 10 Hz	55	15	64

Table 4. Effect of B₂O₃

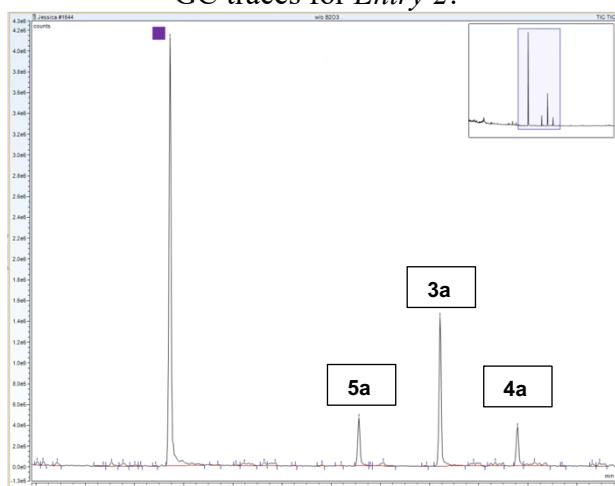


Entry	Conditions	GC yield (%)		
		3a	4a	5a
1 (std)	B ₂ O ₃ (1 mmol)	58	13	21
2	—	37	16	18

GC traces for *Entry 1*:



GC traces for *Entry 2*:



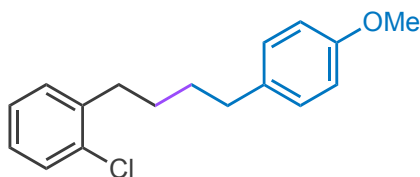
Challenging carboxylic acids:

Chemical structures of 12 different 3-phenylpropanoic acid derivatives:

- 3-(acetamido)propanoic acid
- 3-(benzoylamino)propanoic acid
- 3-(pinacolatoboryl)propanoic acid
- 3-(10-hydroxyundec-1-en-1-yl)propanoic acid
- 3-(4-hydroxyphenyl)propanoic acid
- 3-(4-(pinacolatoboryl)phenyl)propanoic acid
- 3-(2-furyl)propanoic acid
- 3-(1-tert-butoxycarbonylpyrrolidin-2-yl)propanoic acid
- 3-(4-cyanophenyl)propanoic acid
- 3-(4-nitrophenyl)propanoic acid
- 3-(2-thienyl)propanoic acid
- 3-(3-pyridyl)propanoic acid

Experimental procedures and characterization data for one-pot hydroboration of alkenes and cross-coupling with carboxylic acid

Compound 3b



3b

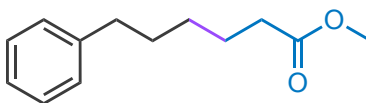
Following **General Procedure A** on a 1.5 mmol scale from 3-(4-methoxyphenyl)propionic acid (CAS 1929-29-9, 0.5 mmol, 90 mg, 1 equiv.) and boronic acid (1 mmol, 184 mg, 2 equiv.) synthesized from 2-chlorostyrene (CAS 2039-87-4, purchased from Ambeed). Purification by flash column chromatography (hexanes) gave the titled compound (71 mg, 52%).

¹H NMR (500 MHz, CDCl₃) δ 7.25 (dd, J = 7.7, 1.4 Hz, 1H), 7.13 – 7.05 (m, 3H), 7.04 – 6.99 (m, 2H), 6.77 – 6.72 (m, 2H), 3.71 (s, 3H), 2.70 – 2.64 (m, 2H), 2.54 – 2.49 (m, 2H), 1.58 (p, J = 3.8 Hz, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 156.64, 139.10, 133.58, 132.87, 129.32, 128.39, 128.24, 126.11, 125.63, 112.67, 54.22, 33.79, 32.40, 30.36, 28.29.

HRMS (EI-TOF) calc'd for C₁₇H₁₉ClO [M]⁺: 274.1150, found: 274.1150.

Compound 3c

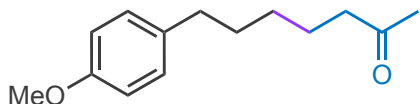


3c

Following **General Procedure A** on a 1.5 mmol scale from monomethyl succinate (CAS 3878-55-5, 0.6 mmol, 79 mg, 1 equiv.) and boronic acid (0.9 mmol, 147 mg, 1.5 equiv.) synthesized from allylbenzene (CAS 300-57-2, purchased from Ambeed). Purification by flash column chromatography (60:40 hexanes:DCM) gave the titled compound (58 mg, 47%).

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.23 (m, 2H), 7.17 (td, J = 6.2, 1.6 Hz, 3H), 3.66 (s, 3H), 2.64 – 2.57 (m, 2H), 2.30 (t, J = 7.5 Hz, 2H), 1.65 (dp, J = 11.9, 7.6 Hz, 4H), 1.41 – 1.31 (m, 2H). The spectroscopic data matched the literature¹⁰.

Compound 3d



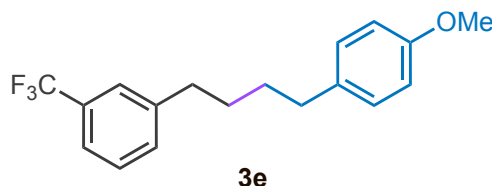
3d

Following **General Procedure A** on a 1.5 mmol scale from levulinic acid (CAS 123-76-2, 0.5 mmol, 58 mg, 1 equiv.) and boronic acid (1 mmol, 194 mg, 2 equiv.) synthesized from estragole (CAS 140-67-0, purchased from Ambeed). Purification by flash column chromatography (60:40 hexanes:DCM) gave the titled compound (68 mg, 62%).

¹H NMR (500 MHz, CDCl₃) δ 7.10 – 7.06 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 2.55 (q, J = 7.3 Hz, 2H), 2.42 (dt, J = 11.7, 7.1 Hz, 2H), 2.12 (d, J = 2.2 Hz, 3H), 1.59 (td, J = 7.7, 2.3 Hz, 2H), 1.34 – 1.28 (m, 2H), 1.27 – 1.20 (m, 2H).

The spectroscopic data matched the literature¹¹.

Compound 3e



Following **General Procedure A** on a 1.5 mmol scale from 3-(4-methoxyphenyl)propionic acid (CAS 1929-29-9, 0.6 mmol, 108 mg, 1 equiv.) and boronic acid (0.9 mmol, 196 mg, 1.5 equiv.) synthesized from 3-(trifluoromethyl)styrene (CAS 402-24-4, purchased from Ambeed). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (102 mg, 55%).

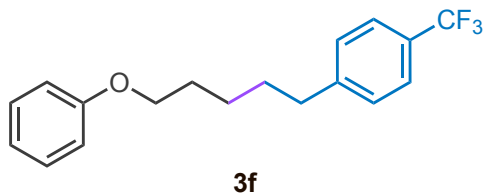
¹H NMR (500 MHz, CDCl₃) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.10 – 7.05 (m, 2H), 6.84 – 6.80 (m, 2H), 3.78 (s, 3H), 2.68 (t, J = 7.2 Hz, 2H), 2.58 (t, J = 7.0 Hz, 2H), 1.70 – 1.60 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 157.75, 143.44, 134.40, 131.82 (q, J = 1.4 Hz), 130.57 (q, J = 31.9 Hz), 129.26, 128.65, 125.07 (q, J = 3.8 Hz), 124.31 (q, J = 272.2 Hz), 122.59 (q, J = 3.9 Hz), 113.75, 55.26, 35.62, 34.79, 31.19, 30.76.

¹⁹F NMR (470 MHz, CDCl₃) δ -62.53.

HRMS (EI-TOF) calc'd for C₁₈H₁₉F₃O [M]⁺: 308.1388, found: 308.1388.

Compound 3f



Following **General Procedure A** on a 1.5 mmol scale from 4-(trifluoromethyl)hydrocinnamic acid (CAS 53473-36-2, 0.5 mmol, 109 mg, 1 equiv.) and boronic acid (1 mmol, 180 mg, 2 equiv.) synthesized from (allyloxy)benzene (CAS 1746-13-0, purchased from Ambeed). Purification by flash column chromatography (90:10 hexanes:DCM) gave the titled compound (69 mg, 45%).

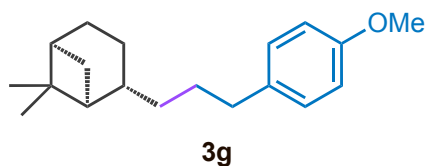
¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 2H), 7.29 – 7.21 (m, 4H), 6.97 – 6.85 (m, 3H), 3.95 (t, J = 6.4 Hz, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.81 (dq, J = 8.1, 6.5 Hz, 2H), 1.71 (tt, J = 9.2, 6.9 Hz, 2H), 1.56 – 1.51 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 159.03, 146.62 (d, J = 1.4 Hz), 129.45, 128.70 (d, J = 2.1 Hz), 128.12 (d, J = 32.3 Hz), 125.26 (d, J = 3.8 Hz), 125.20 (d, J = 3.9 Hz), 120.58, 114.48, 67.60, 35.70, 30.94, 29.12, 25.72.

¹⁹F NMR (470 MHz, CDCl₃) δ -62.26.

HRMS (EI-TOF) calc'd for C₁₈H₁₉F₃O [M]⁺: 308.1409, found: 308.1409.

Compound 3g



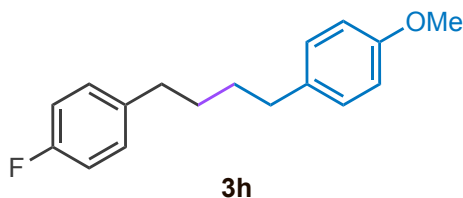
Following **General Procedure A** on a 1.5 mmol scale from 3-(4-methoxyphenyl)propionic acid (CAS 1929-29-9, 0.5 mmol, 90 mg, 1 equiv.) and boronic acid (1 mmol, 182 mg, 2 equiv.) synthesized from (-)- β -pinene (CAS 18172-67-3, purchased from Combi-Blocks). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (82 mg, 60%).

^1H NMR (500 MHz, CDCl_3) δ 7.03 – 6.99 (m, 2H), 6.76 – 6.73 (m, 2H), 3.71 (s, 3H), 2.44 (t, J = 7.7 Hz, 2H), 2.28 – 2.19 (m, 1H), 1.94 – 1.70 (m, 6H), 1.54 – 1.42 (m, 2H), 1.37 – 1.30 (m, 3H), 1.09 (s, 3H), 0.90 (s, 3H), 0.78 (d, J = 9.5 Hz, 1H).

^{13}C NMR (126 MHz, CDCl_3) δ 156.55, 134.06, 128.18, 112.61, 54.22, 45.39, 40.58, 40.42, 37.69, 36.34, 34.21, 32.76, 29.20, 27.24, 25.53, 22.27, 21.53.

HRMS (EI-TOF) calc'd for $\text{C}_{19}\text{H}_{28}\text{O}$ $[\text{M}]^+$: 272.2165, found: 272.2165.

Compound 3h

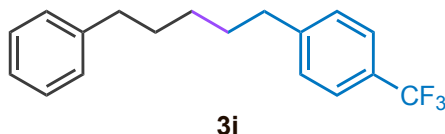


Following **General Procedure A** on a 1.5 mmol scale from 3-(4-methoxyphenyl)propionic acid (CAS 1929-29-9, 0.5 mmol, 90 mg, 1 equiv.) and boronic acid (1 mmol, 168 mg, 2 equiv.) synthesized from 4-fluorostyrene (CAS 405-99-2, purchased from Ambeed). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (72 mg, 56%).

^1H NMR (500 MHz, CDCl_3) δ 7.12 – 7.04 (m, 4H), 6.96 – 6.91 (m, 2H), 6.84 – 6.78 (m, 2H), 3.77 (s, 3H), 2.57 (qd, J = 6.8, 3.8 Hz, 4H), 1.61 (p, J = 3.7 Hz, 4H).

The spectroscopic data matched the literature¹².

Compound 3i



Following **General Procedure A** on a 1.5 mmol scale from 4-(trifluoromethyl)hydrocinnamic acid (CAS 53473-36-2, 0.5 mmol, 109 mg, 1 equiv.) and boronic acid (1 mmol, 164 mg, 2 equiv.) synthesized from allylbenzene (CAS 300-57-2, purchased from Ambeed). Purification by flash column chromatography (hexanes) gave the titled compound (85 mg, 58%).

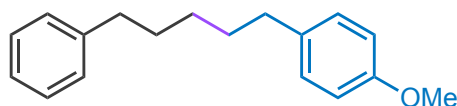
^1H NMR (500 MHz, CDCl_3) δ 7.45 (dd, J = 8.2, 3.2 Hz, 2H), 7.21 – 7.17 (m, 4H), 7.13 – 7.06 (m, 3H), 2.63 – 2.50 (m, 4H), 1.62 – 1.54 (m, 4H), 1.35 – 1.27 (m, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 145.80, 145.31, 141.81, 141.56, 127.64 (d, J = 1.1 Hz), 127.36 (d, J = 1.4 Hz), 127.25, 127.20, 124.65, 124.55, 124.18 (dt, J = 11.1, 3.8 Hz), 122.30, 34.86 (d, J = 16.0 Hz), 34.60 (d, J = 15.2 Hz), 30.31 (d, J = 18.0 Hz), 29.81 (d, J = 53.2 Hz), 27.94 (d, J = 46.0 Hz).

^{19}F NMR (470 MHz, CDCl_3) δ -62.35.

HRMS (EI-TOF) calc'd for $\text{C}_{18}\text{H}_{19}\text{F}_3$ $[\text{M}]^+$: 292.1462, found: 292.1462.

Compound 3j



3j

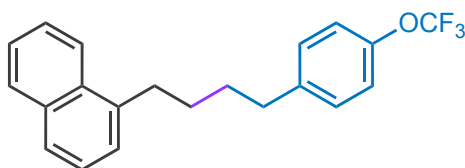
Following **General Procedure A** on a 1.5 mmol scale from 3-(4-methoxyphenyl)propionic acid (CAS 1929-29-9, 0.5 mmol, 90 mg, 1 equiv.) and boronic acid (1 mmol, 164 mg, 2 equiv.) synthesized from allylbenzene (CAS 300-57-2, purchased from Ambeed). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (67 mg, 53%).

¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.16 (m, 2H), 7.12 – 7.07 (m, 3H), 7.03 – 6.98 (m, 2H), 6.77 – 6.72 (m, 2H), 3.71 (s, 3H), 2.55 – 2.50 (m, 2H), 2.49 – 2.44 (m, 2H), 1.61 – 1.50 (m, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 156.60, 141.77, 133.85, 128.21, 127.37, 127.21, 124.57, 112.64, 54.22, 34.88, 33.91, 30.59, 30.37, 27.88.

HRMS (EI-TOF) calc'd for C₁₈H₂₂O [M]⁺: 254.1695, found: 254.1695.

Compound 3k



3k

Following **General Procedure A** on a 1.5 mmol scale from 3-(4-trifluoromethoxy)propionic acid (CAS 886499-74-7, 0.5 mmol, 117 mg, 1 equiv.) and boronic acid (1 mmol, 200 mg, 2 equiv.) synthesized from 1-vinylnaphthalene (CAS 826-74-4, purchased from Ambeed). Purification by flash column chromatography (95:5 hexanes:DCM) gave the titled compound (100 mg, 59%).

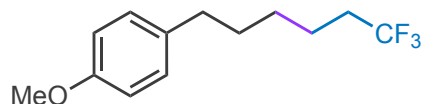
¹H NMR (500 MHz, CDCl₃) δ 8.05 – 8.02 (m, 1H), 7.91 – 7.86 (m, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.51 (pd, *J* = 6.8, 1.6 Hz, 2H), 7.42 (dd, *J* = 8.2, 7.0 Hz, 1H), 7.33 (d, *J* = 6.9 Hz, 1H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.13 (t, *J* = 7.4 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 1.88 – 1.75 (m, 4H).

¹⁹F NMR (470 MHz, CDCl₃) δ -57.91.

¹³C NMR (126 MHz, CDCl₃) δ 147.32 (d, *J* = 2.1 Hz), 141.22, 138.45, 133.92, 131.85, 129.60, 128.81, 126.59, 125.95, 125.71, 125.53, 125.44, 123.79, 123.61, 121.57, 120.87, 119.53, 117.49, 35.13, 32.92, 31.40, 30.27.

HRMS (EI-TOF) calc'd for C₂₁H₁₉F₃O [M]⁺: 344.1399, found: 344.1399.

Compound 3l



3l

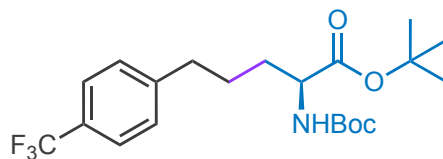
Following **General Procedure A** on a 1.5 mmol scale from 4,4,4-trifluorobutyric acid (CAS 406-93-9, 0.6 mmol, 85 mg, 1 equiv.) and boronic acid (0.9 mmol, 175 mg, 1.5 equiv.) synthesized from allylanisole (CAS 140-67-0, purchased from Ambeed). Purification by flash column chromatography (90:10 hexanes:DCM) gave the titled compound (74 mg, 50%).

¹H NMR (500 MHz, CDCl₃) δ 7.01 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.72 (s, 3H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.58 – 1.48 (m, 4H), 1.32 (q, *J* = 8.0 Hz, 2H).

¹⁹F NMR (470 MHz, CDCl₃) δ -66.43.

The spectroscopic data matched the literature¹³.

Compound 3m



3m

Following **General Procedure A** on a 1.5 mmol scale from Boc-Asp-OtBu (CAS 34582-32-6, 0.5 mmol, 145 mg, 1 equiv.) and boronic acid (1 mmol, 218 mg, 2 equiv.) synthesized from 1-(trifluoromethyl)-4-vinylbenzene (CAS 402-50-6, purchased from Ambeed). Purification by flash column chromatography (95:5 hexanes:ethyl acetate) gave the titled compound (92 mg, 44%).

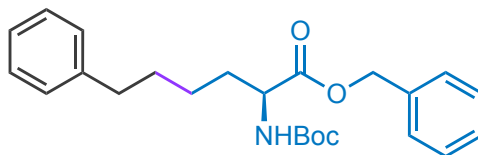
¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.4 Hz, 2H), 4.96 (d, *J* = 8.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 2.72 – 2.54 (m, 2H), 1.70 – 1.52 (m, 4H), 1.36 (s, 18H).

¹⁹F NMR (470 MHz, CDCl₃) δ -62.34.

¹³C NMR (126 MHz, CDCl₃) δ 171.82, 155.38, 146.02, 128.72, 128.41, 128.15, 127.58, 125.42, 125.31, 125.28, 125.25, 125.23, 123.26, 121.10, 81.90, 79.70, 53.55, 35.09, 32.35, 28.33, 27.98, 26.60.

HRMS (ESI-TOF) calc'd for C₂₁H₃₀F₃NO₄ [M+Na]⁺: 440.2035, found: 440.2035

Compound 3n



3n

Following **General Procedure A** on a 1.5 mmol scale from Boc-Glu-OBzl (CAS 30924-93-7, 0.5 mmol, 169 mg, 1 equiv.) and boronic acid (1 mmol, 150 mg, 2 equiv.) synthesized from styrene (CAS 100-42-5, purchased from Oakwood Chemical). Purification by flash column chromatography (90:10 hexanes:ethyl acetate) gave the titled compound (81 mg, 41%).

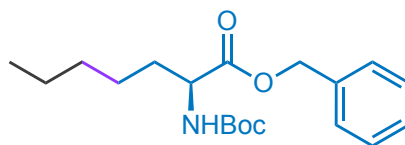
¹H NMR (500 MHz, CDCl₃) δ 7.35 (pd, *J* = 6.4, 2.2 Hz, 5H), 7.30 – 7.27 (m, 1H), 7.23 – 7.10 (m, 4H), 5.23 – 5.09 (m, 2H), 4.98 (d, *J* = 8.6 Hz, 1H), 4.38 – 4.29 (m, 1H), 2.55 (td, *J* = 7.8, 2.8 Hz, 2H), 1.87 – 1.78 (m, 1H), 1.69 – 1.57 (m, 3H), 1.43 (s, 9H), 1.38 – 1.34 (m, 1H), 1.30 – 1.21 (m, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 167.47, 150.04, 136.92, 130.16, 123.29, 123.24, 123.11, 123.06, 123.00, 120.44, 74.54, 61.65, 48.17, 30.34, 27.30, 25.66, 23.03, 19.56.

HRMS (ESI-TOF) calc'd for C₂₄H₃₁NO₄ [M+Na]⁺: 420.2158, found: 420.2158.

Experimental procedures and characterization data for the cross-coupling of boroxines and commercial boronic acids with carboxylic acids

Compound 3o



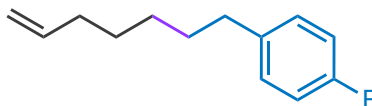
3o

Following **General Procedure B** on a 1.5 mmol scale from Boc-Glu-OBzl (CAS 30924-93-7, 0.5 mmol, 169 mg, 1 equiv.) and boroxine (0.42 mmol, 88 mg, 0.8 equiv.; 1.26 mmol, 2.5 equiv. propyl unit) from propylboronic acid (CAS 17745-45-8). Both substrates were purchased from Ambeed. Purification by flash column chromatography (90:10 hexanes:ethyl acetate) gave the titled compound (67 mg, 40%).

¹H NMR (500 MHz, CDCl₃) δ 7.34 (m, 5H), 5.24 – 5.09 (m, 2H), 4.99 (d, J = 8.5 Hz, 1H), 4.33 (q, J = 7.3 Hz, 1H), 1.79 (dd, J = 12.5, 6.4 Hz, 1H), 1.64 (dd, J = 10.8, 3.2 Hz, 1H), 1.44 (s, 9H), 1.29 – 1.23 (m, 6H), 0.87 – 0.83 (m, 3H).

The spectroscopic data matched the literature¹⁴.

Compound 3p



3p

Following **General Procedure B** on a 1.5 mmol scale from 3-(4-fluorophenyl)propionic acid (CAS 459-31-4, 0.5 mmol, 85 mg, 1 equiv.) and boroxine (0.4 mmol, 114 mg, 0.8 equiv.; 1.18 mmol, 2.4 equiv. pent-4-en-1-yl unit) from pent-4-en-1-ylboronic acid (CAS 886747-03-1). Both substrates were purchased from Ambeed. Purification by flash column chromatography (hexanes) gave the titled compound (44 mg, 46%).

¹H NMR (500 MHz, CDCl₃) δ 7.11 (ddd, J = 8.7, 5.4, 2.6 Hz, 2H), 6.99 – 6.91 (m, 2H), 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.03 – 4.90 (m, 2H), 2.60 – 2.54 (m, 2H), 2.08 – 2.00 (m, 2H), 1.63 – 1.56 (m, 2H), 1.44 – 1.38 (m, 2H), 1.37 – 1.31 (m, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 162.12, 160.19, 139.01, 138.35, 129.67, 115.01, 114.84, 114.30, 35.07, 33.70, 31.46, 28.76, 28.67.

¹⁹F NMR (470 MHz, CDCl₃) δ -114.37 (ddd, J = 14.1, 8.8, 5.3 Hz).

HRMS (EI-TOF) calc'd for C₁₃H₁₇F [M]⁺: 192.1332, found: 192.1332.

Compound 3q

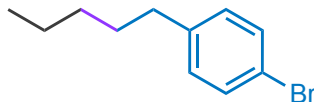


3q

Following **General Procedure B** on a 1.5 mmol scale from 10-undecenoic acid (CAS 112-38-9, 0.5 mmol, 93 mg, 1 equiv.) and boroxine (0.42 mmol, 88 mg, 0.8 equiv.; 1.26 mmol, 2.5 equiv. propyl unit) from propylboronic acid (CAS 17745-45-8). Both substrates were purchased from Ambeed. Purification by flash column chromatography (hexanes) gave the titled compound (45 mg, 49%).

¹H NMR (500 MHz, CDCl₃) δ 5.85 – 5.78 (m, 1H), 4.99 (dq, *J* = 17.2, 1.8 Hz, 1H), 4.93 (ddt, *J* = 10.2, 2.3, 1.3 Hz, 1H), 2.07 – 2.01 (m, 2H), 1.31 – 1.24 (m, 18H), 0.88 (t, *J* = 6.9 Hz, 3H). The spectroscopic data matched the literature¹⁵.

Compound 3r



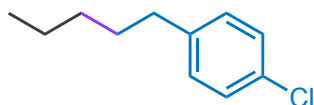
3r

Following **General Procedure B** on a 1.5 mmol scale from 3-(4-bromophenyl)propionic acid (CAS 1643-30-7, 0.5 mmol, 115 mg, 1 equiv.) and boroxine (0.42 mmol, 88 mg, 0.8 equiv.; 1.26 mmol, 2.5 equiv. propyl unit) from propylboronic acid (CAS 17745-45-8). Both substrates were purchased from Ambeed. Purification by flash column chromatography (95:5 hexanes:DCM) gave the titled compound (47 mg, 41%).

¹H NMR (500 MHz, CDCl₃) δ 7.41 – 7.35 (m, 2H), 7.08 – 7.00 (m, 2H), 2.58 – 2.51 (m, 2H), 1.58 (ddd, *J* = 14.8, 8.4, 6.6 Hz, 2H), 1.36 – 1.26 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H).

The spectroscopic data matched the literature¹⁶.

Compound 3s



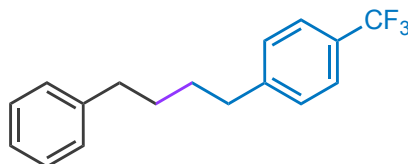
3s

Following **General Procedure B** on a 1.5 mmol scale from 3-(4-chlorophenyl)propionic acid (CAS 2019-34-3, 0.5 mmol, 93 mg, 1 equiv.) and boroxine (0.42 mmol, 88 mg, 0.8 equiv.; 1.26 mmol, 2.5 equiv. propyl unit) from propylboronic acid (CAS 17745-45-8). Both substrates were purchased from Ambeed. Purification by flash column chromatography (hexanes) gave the titled compound (55 mg, 60%).

¹H NMR (500 MHz, CDCl₃) δ 7.25 – 7.19 (m, 2H), 7.12 – 7.07 (m, 2H), 2.59 – 2.53 (m, 2H), 1.58 (p, *J* = 7.5 Hz, 2H), 1.36 – 1.26 (m, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

The spectroscopic data matched the literature¹⁷.

Compound 3t



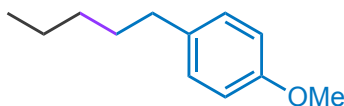
3t

Following **General Procedure C** on a 1.2 mmol scale from 4-(Trifluoromethyl)hydrocinnamic acid (CAS 53473-36-2, 0.2 mmol, 44 mg, 1 equiv.) and Phenethylboronic acid (CAS 34420-17-2, 1 mmol, 150 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (Hexanes) gave the titled compound (32 mg, 57%).

¹H NMR (500 MHz, CDCl₃) δ 7.52 (dd, *J* = 8.1, 4.3 Hz, 1H), 7.30 – 7.23 (m, 4H), 7.21 – 7.13 (m, 4H), 2.72 – 2.62 (m, 4H), 1.67 (dq, *J* = 7.4, 3.3 Hz, 4H).

The spectroscopic data matched the literature¹⁸.

Compound 3u



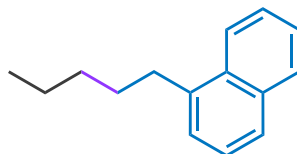
3u

Following **General Procedure C** on a 1.2 mmol scale from 3-(4-Methoxyphenyl)propionic acid (CAS 1929-29-9, 0.2 mmol, 36 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (50:50 Hexanes:DCM) gave the titled compound (24 mg, 67%).

¹H NMR (500 MHz, CDCl₃) δ 7.04–7.00 (m, 2H), 6.77–6.73 (m, 2H), 3.71 (s, 3H), 2.50–2.43 (m, 2H), 1.55–1.48 (m, 2H), 1.30–1.19 (m, 4H), 0.82 (t, J = 6.9 Hz, 3H).

The spectroscopic data matched the literature.¹⁹

Compound 3v



3v

Following **General Procedure C** on a 1.2 mmol scale from 1-Naphthalenepropanoic acid (CAS 3243-42-3, 0.2 mmol, 40 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (Hexanes) gave the titled compound (23 mg, 59%).

¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, J = 8.2 Hz, 1H), 7.77 (dd, J = 8.0, 1.6 Hz, 1H), 7.62 (d, J = 8.2 Hz, 1H), 7.40 (dddd, J = 19.3, 7.9, 6.8, 1.4 Hz, 2H), 7.31 (dd, J = 8.3, 7.0 Hz, 1H), 7.24 (d, J = 6.9 Hz, 1H), 3.01 – 2.96 (m, 2H), 1.68 (p, J = 7.5 Hz, 2H), 1.37 – 1.28 (m, 4H), 0.84 (t, J = 6.9 Hz, 3H).

The spectroscopic data matched the literature.²⁰

Compound 3w



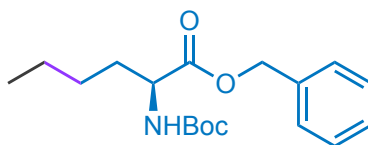
3w

Following **General Procedure C** on a 1.2 mmol scale from 4-(*p*-tolyl)butanoic acid (CAS 4521-22-6, 0.2 mmol, 36 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (Hexanes) gave the titled compound (23 mg, 65%).

¹H NMR (500 MHz, CDCl₃) δ 7.03 – 6.94 (m, 4H), 2.51 – 2.44 (m, 2H), 2.23 (s, 3H), 1.54 – 1.47 (m, 2H), 1.30 – 1.15 (m, 6H), 0.82 – 0.78 (m, 3H).

The spectroscopic data matched the literature.²¹

Compound 3x



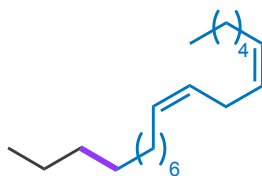
3x

Following **General Procedure C** on a 1.2 mmol scale from Boc-Glu-OBzl (CAS 30924-93-7, 0.2 mmol, 67 mg, 1 equiv.) and Ethylboronic acid (CAS 4433-63-0, 1 mmol, 74 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (90:10 Hexanes:Ethyl acetate) gave the titled compound (24 mg, 38%).

¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.33 (m, 5H), 5.24 – 5.10 (m, 2H), 4.99 (d, J = 8.4 Hz, 1H), 4.33 (q, J = 7.4 Hz, 1H), 1.79 (d, J = 13.1 Hz, 1H), 1.63 (td, J = 10.6, 4.7 Hz, 1H), 1.44 (s, 9H), 1.29 (m, 4H), 0.85 (t, J = 6.9 Hz, 3H).

The spectroscopic data matched the literature.²²

Compound 3y



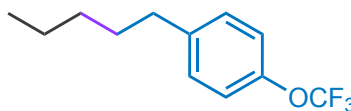
3y

Following **General Procedure C** on a 1.2 mmol scale from Linoleic acid (CAS 60-33-3, 0.2 mmol, 56 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (Hexanes) gave the titled compound (31 mg, 55%).

¹H NMR (500 MHz, CDCl₃) δ 5.42 – 5.30 (m, 4H), 2.78 (t, J = 6.8 Hz, 2H), 2.05 (q, J = 7.0 Hz, 4H), 1.38 – 1.23 (m, 22H), 0.89 (td, J = 6.8, 4.7 Hz, 6H).

The spectroscopic data matched the literature.²³

Compound 3z



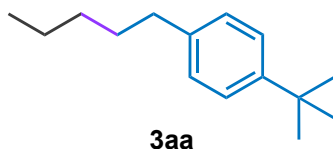
3z

Following **General Procedure C** on a 1.2 mmol scale from 3-(4-(Trifluoromethoxy)phenyl)propanoic acid (CAS 886499-74-7, 0.2 mmol, 47 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (70:30 Hexanes:DCM) gave the titled compound (26 mg, 56%).

¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.08 (m, 2H), 7.06 – 7.02 (m, 2H), 2.58 – 2.50 (m, 2H), 1.59 – 1.51 (m, 2H), 1.25 (ddd, J = 8.7, 7.2, 4.9 Hz, 2H), 0.82 (t, J = 6.9 Hz, 2H), 0.01 (s, 3H).

The spectroscopic data matched the literature.¹⁷

Compound 3aa



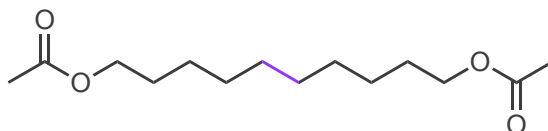
Following **General Procedure C** on a 1.2 mmol scale from 3-(4-(*tert*-Butyl)phenyl)propionic acid (CAS 1208-64-6, 0.2 mmol, 41 mg, 1 equiv.) and Propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. Purification by flash column chromatography (Hexanes) gave the titled compound (25 mg, 62%).

¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.20 (m, 2H), 7.06 – 7.01 (m, 2H), 2.51 – 2.46 (m, 2H), 1.57 – 1.49 (m, 2H), 1.28 – 1.24 (m, 4H), 1.23 (s, 9H), 0.84 – 0.79 (m, 3H).

The spectroscopic data matched the literature.¹⁹

Experimental procedures and characterization data for boronic acid homocoupling

Compound 5b



5b

Following **General Procedure C** on a 1 mmol scale from *boronic acid* (174 mg) synthesized from 5-bromopentyl acetate (CAS 15848-22-3, purchased from Ambeed) following **General Procedure C-1**. Purification by flash column chromatography (90:10 hexanes:ethyl acetate) gave the titled compound (94 mg, 73%).

¹H NMR (500 MHz, CDCl₃) δ 4.05 (t, J = 6.8 Hz, 4H), 2.05 (s, 6H), 1.62 (p, J = 6.7 Hz, 4H), 1.36 – 1.28 (m, 12H).

The spectroscopic data matched the literature²⁴.

Compound 5c



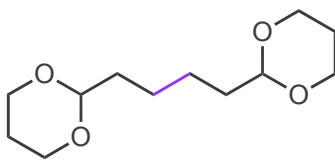
5c

Following **General Procedure C** on a 1 mmol scale from pent-4-en-1-ylboronic acid (114 mg, CAS 886747-03-1, purchased from Ambeed). Purification by flash column chromatography (hexanes) gave the titled compound (62 mg, 90%).

¹H NMR (500 MHz, CDCl₃) δ 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 2H), 4.99 (dq, J = 17.1, 1.8 Hz, 2H), 4.93 (ddt, J = 10.1, 2.4, 1.3 Hz, 2H), 2.07 – 2.01 (m, 4H), 1.38 (ddt, J = 13.7, 6.8, 4.0 Hz, 4H), 1.33 – 1.28 (m, 4H).

The spectroscopic data matched the literature²⁵.

Compound 5d



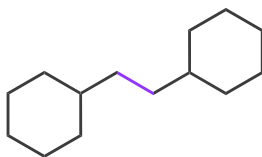
5d

Following **General Procedure C** on a 1 mmol scale from *boronic acid* (160 mg) synthesized from 2-(2-bromoethyl)-1,3-dioxane (CAS 33884-43-4, purchased from Ambeed) following **General Procedure C-1**. Purification by flash column chromatography (90:10 hexanes:ethyl acetate) gave the titled compound (52 mg, 45%).

¹H NMR (500 MHz, CDCl₃) δ 4.51 (t, J = 5.2 Hz, 2H), 4.09 (dd, J = 10.4, 5.0, 4H), 3.78 – 3.72 (m, 4H), 2.07 (dtt, J = 13.5, 12.5, 5.0 Hz, 2H), 1.43 – 1.36 (m, 4H), 1.33 (dtt, J = 13.4, 2.6, 1.4 Hz, 2H), 1.24 – 1.19 (m, 4H).

The spectroscopic data matched the literature²⁶.

Compound 5e



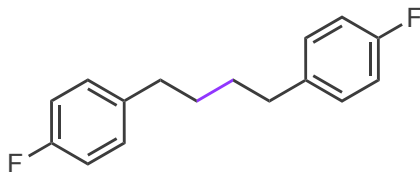
5e

Following **General Procedure C** on a 1 mmol scale from (cyclohexylmethyl)boronic acid (142 mg, CAS 27762-64-7, purchased from Ambeed). Purification by flash column chromatography (hexanes) gave the titled compound (85 mg, 87%).

¹H NMR (500 MHz, CDCl₃) δ 1.73 – 1.58 (m, 10H), 1.27 – 1.07 (m, 12H), 0.85 (m, 4H).

The spectroscopic data matched the literature⁹.

Compound 5f



5f

Following **General Procedure C** on a 1 mmol scale from *boronic acid* (168 mg) synthesized from 4-fluorostyrene (CAS 405-99-2, purchased from Ambeed) following **General Procedure C-2**. Purification by flash column chromatography (hexanes) gave the titled compound (105 mg, 85%).

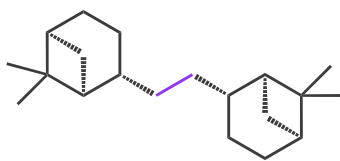
¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.07 (m, 4H), 6.98 – 6.91 (m, 4H), 2.60 (dq, J = 7.0, 3.8 Hz, 4H), 1.64 – 1.59 (m, 4H).

¹³C NMR (126 MHz, CDCl₃) δ 162.17, 160.24, 138.01 (d, J = 3.2 Hz), 129.66 (d, J = 7.7 Hz), 115.08, 114.91, 34.94, 31.04.

¹⁹F NMR (470 MHz, CDCl₃) δ -117.99 (ddd, J = 14.6, 8.7, 5.2 Hz).

HRMS (EI-TOF) calc'd for C₁₆H₁₆F₂ [M]⁺: 246.1243, found: 246.1243

Compound 5g



5g

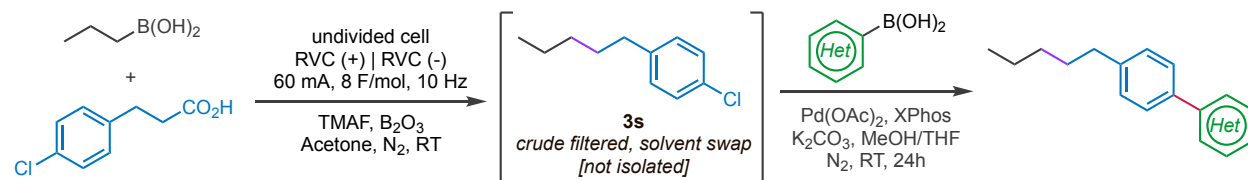
Following **General Procedure C** on a 1 mmol scale from *boronic acid* (182 mg) synthesized from (-)- β -pinene (CAS 18172-67-3, purchased from Combi-Blocks) following **General Procedure C-2**. Purification by flash column chromatography (hexanes) gave the titled compound (126 mg, 92%).

^1H NMR (500 MHz, CDCl_3) δ 2.34 – 2.26 (m, 2H), 1.96 – 1.78 (m, 12H), 1.42 (dtt, J = 10.8, 7.7, 3.9 Hz, 2H), 1.35 – 1.31 (m, 4H), 1.17 (s, 6H), 0.99 (s, 6H), 0.85 (d, J = 9.5 Hz, 2H).

The spectroscopic data matched the literature²⁷.

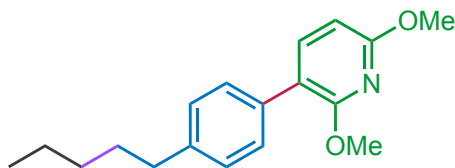
Experimental procedures and characterization data of the further functionalization of 1-Chloro-4-pentylbenzene in tandem with carboxylic acid–boronic acid cross-coupling

Procedure C-1: Suzuki-Miyaura coupling in tandem with electrolysis



Following **General Procedure C** on a 1.2 mmol scale from 3-(4-chlorophenyl)propionic acid (CAS 2019-34-3, 0.2 mmol, 37 mg, 1 equiv.) and propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. After reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel, concentrated *in vacuo* and brought into the glovebox. Inside the glovebox, the crude mixture containing 1-Chloro-4-pentylbenzene was diluted with MeOH (2 mL) and THF (1 mL) and transferred to an 8 mL vial equipped with a stir bar. Heteroaryl boronic acid (0.3 mmol, 1.5 equiv.), palladium(II) acetate (0.002 mmol, 0.5 mg, 1 mol%), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (Xphos, 0.004 mmol, 2 mg, 2 mol%), K_2CO_3 (0.4 mmol, 55 mg, 2 equiv.) were added to the mixture and stirred at room temperature under N_2 for 24 h. After reaction completion, the crude mixture was filtered through a fritted funnel, concentrated *in vacuo* and purified by column chromatography to afford the desired product. Yields were calculated over two steps based on the starting carboxylic acid as the limiting reagent.

Compound 10a



10a

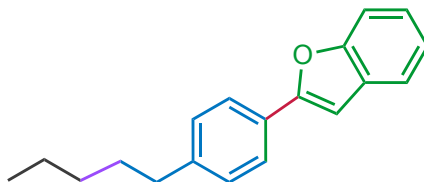
Following **Procedure C-1** from 2,6-dimethoxypyridine-3-boronic acid (CAS 221006-70-8, 0.3 mmol, 55 mg, 1.5 equiv., purchased from Ambeed). Purification by flash column chromatography (80:20 DCM:hexanes) gave the titled compound (31 mg, 55% over two steps).

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 1H), 7.38 – 7.32 (m, 2H), 7.15 – 7.10 (m, 2H), 6.29 (d, J = 8.0 Hz, 1H), 3.87 (d, J = 4.2 Hz, 6H), 2.57 – 2.50 (m, 2H), 1.61 – 1.51 (m, 2H), 1.27 (td, J = 6.3, 2.8 Hz, 4H), 0.82 (td, J = 6.1, 3.1 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 160.95, 158.25, 140.47, 140.34, 133.09, 127.74, 127.21, 114.70, 99.93, 52.52, 52.35, 34.63, 30.59, 30.12, 21.55, 13.02.

HRMS (ESI-TOF) calc'd for C₁₈H₂₃NO₂ [M+H]⁺: 286.1816, found: 286.1816

Compound 10b



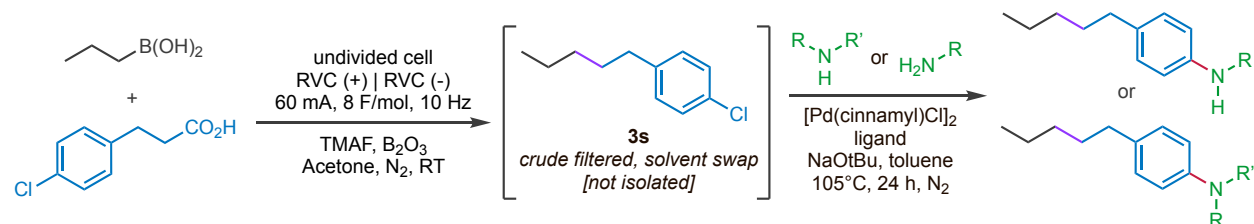
10b

Following **Procedure C-1** from benzofuran-2-ylboronic acid (CAS 98437-24-2, 0.3 mmol, 49 mg, 1.5 equiv., purchased from Ambeed). Purification by flash column chromatography (50:50 DCM:hexanes) gave the titled compound (30 mg, 56% over two steps).

¹H NMR (500 MHz, CDCl₃) δ 7.72 – 7.66 (m, 2H), 7.48 (dd, J = 7.4, 1.5 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.19 – 7.11 (m, 4H), 6.90 – 6.86 (m, 1H), 2.59 – 2.53 (m, 2H), 1.61 – 1.52 (m, 2H), 1.32 – 1.21 (m, J = 2.6, 2.2 Hz, 4H), 0.86 – 0.79 (m, 3H).

The spectroscopic data matched the literature²⁸.

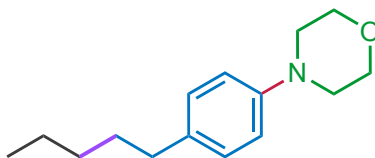
Procedure C-2: Buchwald-Hartwig amination in tandem with electrolysis



Following **General Procedure C** on a 1.2 mmol scale from 3-(4-chlorophenyl)propionic acid (CAS 2019-34-3, 0.2 mmol, 37 mg, 1 equiv.) and propylboronic acid (CAS 17745-45-8, 1 mmol, 88 mg, 5 equiv.). Both substrates were purchased from Ambeed. After reaction completion, the ElectraSyn vial cap was removed, and the electrodes were rinsed with acetone, which was combined with the crude product mixture. The mixture was filtered through a fritted funnel, concentrated *in vacuo* and brought into the glovebox. The subsequent amination was conducted

following the reported procedure²⁹. Inside the glovebox, the crude mixture containing 1-chloro-4-pentylbenzene was diluted with toluene (0.4 mL) and transferred to an 8 mL vial equipped with a stir bar. Primary or secondary amines (0.24 mmol, 1.2 equiv.), bis[cinnamyl palladium(II) chloride] (0.0004 mmol, 0.2 mg, 0.2 mol%, CAS 12131-44-1, purchased from Ambeed), ligand [2-(N,N-dimethylamino)phenyl]di-*tert*-butylphosphine (0.0008 mmol, 0.2 mg, 0.4 mol%, CAS 415941-58-1, purchased from Ambeed), NaOtBu (0.28 mmol, 27 mg, 1.4 equiv.) were added to the mixture and stirred at 105° C under N₂ for 24 h. After reaction completion, the crude mixture was filtered through a fritted funnel, concentrated *in vacuo* and purified by column chromatography to afford the desired product. Yields were calculated over two steps based on the starting carboxylic acid as the limiting reagent.

Compound 10c



10c

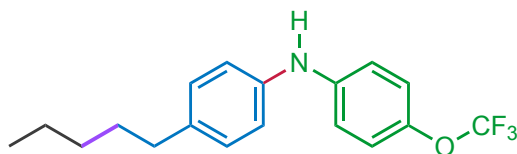
Following **Procedure C-2** from morpholine (CAS 110-91-8, 0.24 mmol, 21 mg, 1.4 equiv., purchased from Sigma Alrich). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (28 mg, 61% over two steps).

¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.06 (m, 2H), 6.87 – 6.81 (m, 2H), 3.90 – 3.82 (m, 4H), 3.14 – 3.09 (m, 4H), 2.56 – 2.49 (m, 2H), 1.58 (p, *J* = 7.2 Hz, 2H), 1.32 (qq, *J* = 7.4, 3.0 Hz, 4H), 0.88 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 149.31, 134.74, 129.08, 115.89, 67.03, 49.84, 35.00, 31.53, 31.35, 22.59, 14.08.

HRMS (ESI-TOF) calc'd for C₁₅H₂₃NO [M+H]⁺: 234.1866, found: 234.1866.

Compound 10d



10d

Following **Procedure C-2** from 3-(trifluoromethoxy)aniline (CAS 1535-73-5, 0.24 mmol, 43 mg, 1.4 equiv., purchased from Ambeed). Purification by flash column chromatography (50:50 hexanes:DCM) gave the titled compound (34 mg, 52% over two steps).

¹H NMR (500 MHz, CDCl₃) δ 7.05 – 6.98 (m, 4H), 6.95 – 6.87 (m, 4H), 5.55 (s, 1H), 2.52 – 2.45 (m, 2H), 1.57 – 1.49 (m, 2H), 1.30 – 1.21 (m, 4H), 0.83 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 141.93, 141.27 (d, *J* = 2.1 Hz), 138.89, 135.88, 128.31, 121.30, 120.63, 118.23, 116.17, 34.22, 30.48, 30.30, 21.54, 13.03.

¹⁹F NMR (470 MHz, CDCl₃) δ -58.34.

HRMS (ESI-TOF) calc'd for C₁₈H₂₀F₃NO [M+H]⁺: 324.1584, found: 324.1584.

Mechanistic studies

Procedures for NMR titration studies of phenethylboronic acid with varied equiv. of TMAF:

The five stock solutions in acetone (4 mL each) were prepared inside the glovebox:

#1: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.1 mmol, 9 mg, 0.5 equiv.)

#2: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.2 mmol, 19 mg, 1 equiv.)

#3: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.4 mmol, 37 mg, 2 equiv.)

#4: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.6 mmol, 56 mg, 3 equiv.)

#5: Potassium phenethyltrifluoroborate (0.2 mmol, 42 mg)

NMR samples (0.7 mL/tube) of the stock solutions were prepared. ^{11}B and ^{19}F NMR spectra were acquired and shown in the main text [^{19}F NMR, Figure 2D-(b)] and Figure S2 (^{11}B NMR) below.

Figure 5. ^{11}B NMR of TMAF titration of phenethylboronic acid

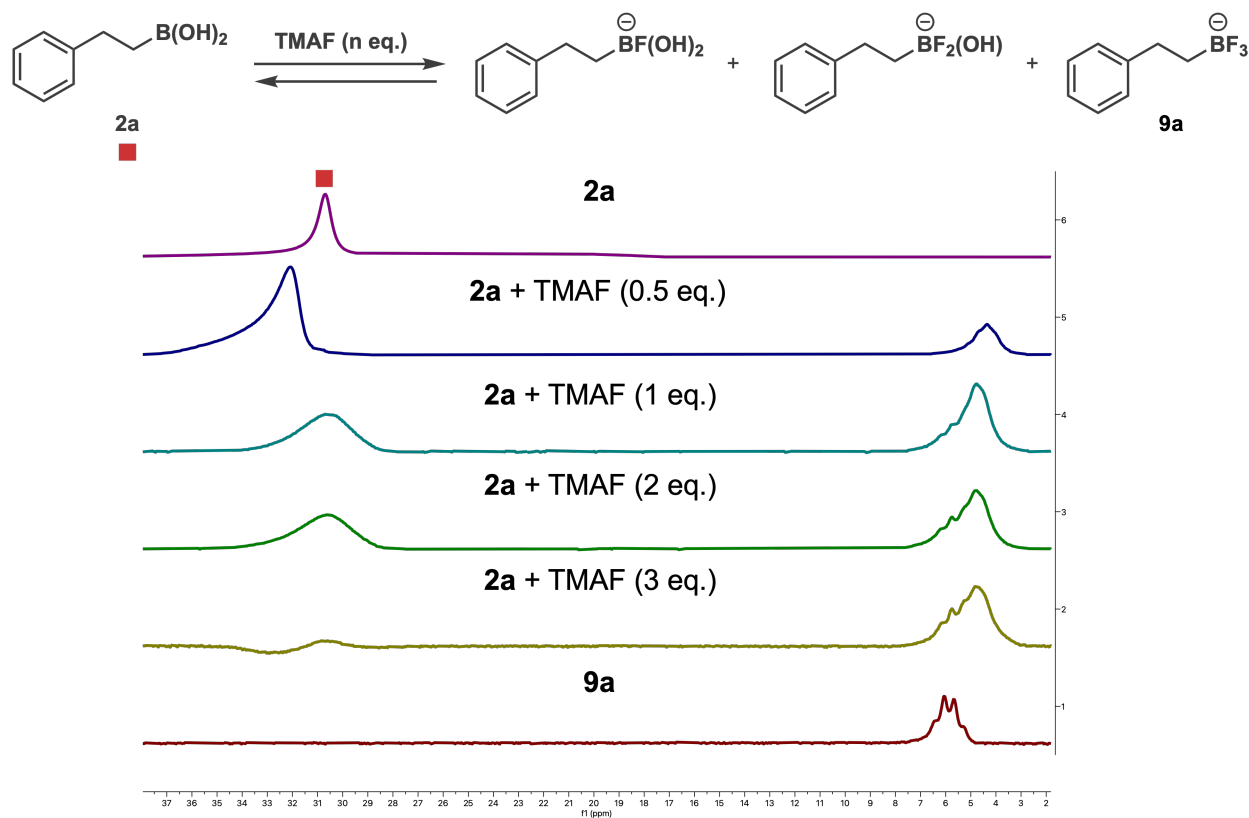
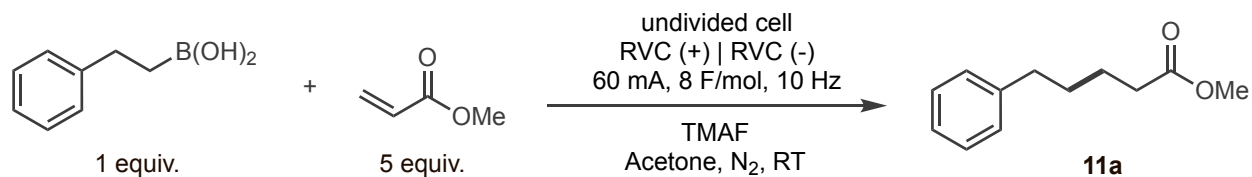


Figure 6. Experimental procedure for radical trap by methyl acrylate

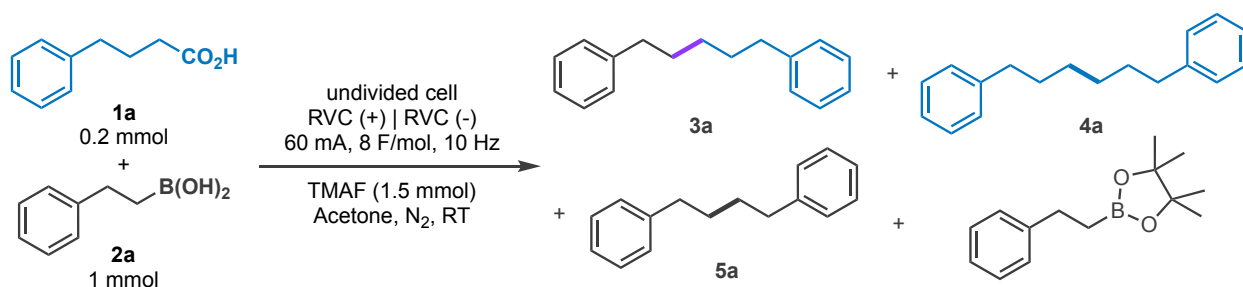


Following **General Procedure B** from phenethylboronic acid (1 mmol, 150 mg, 1 equiv., CAS 34420-17-2, purchased from Ambeed) and methyl acrylate (5 mmol, 430 mg, 5 equiv., CAS 96-33-3, purchased from ThermoFisher Scientific). Purification by flash column chromatography (70:30 hexanes:DCM) gave the titled compound (23 mg, 12%).

¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.24 (m, 2H), 7.21 – 7.14 (m, 3H), 3.66 (s, 3H), 2.63 (dd, J = 8.4, 6.0 Hz, 2H), 2.37 – 2.29 (m, 2H), 1.73 – 1.60 (m, 4H).

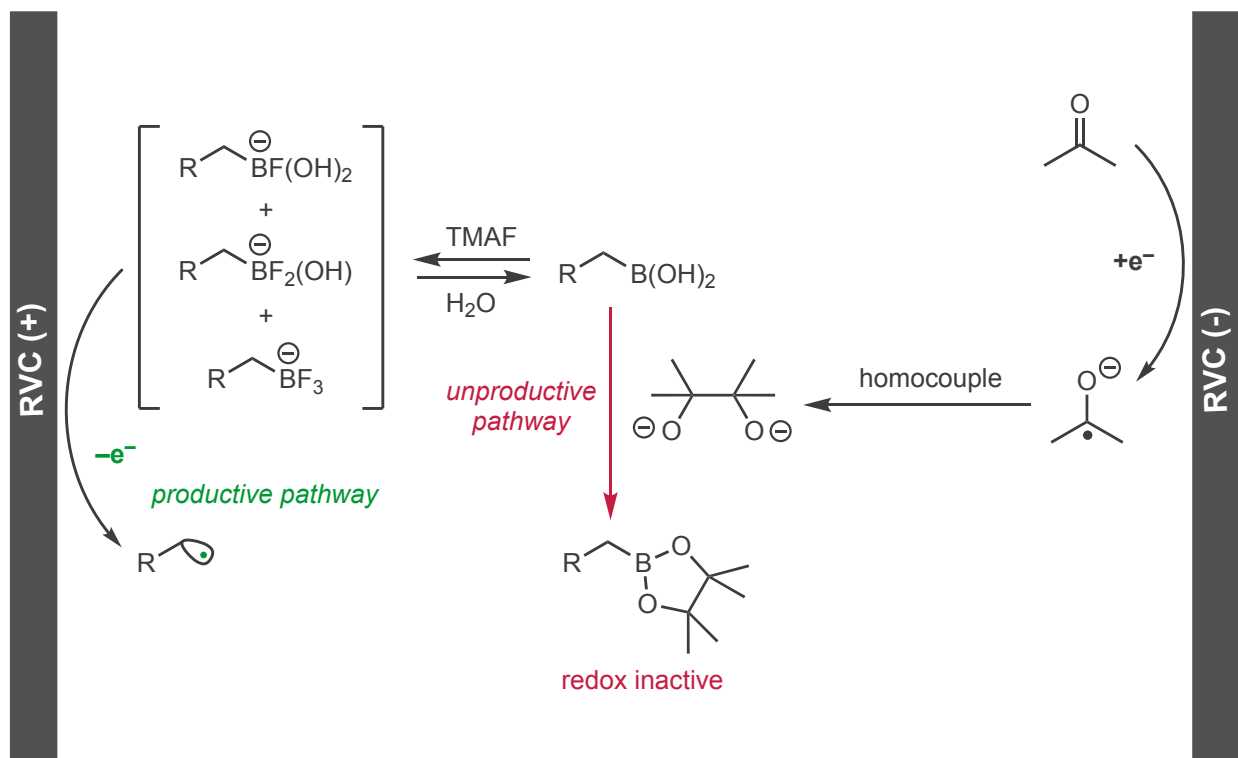
The spectroscopic data matched the literature³⁰.

Table 5. Effect of water



Entry	Conditions	GC yield (%)		
		3a	4a	5a
1 (std)	B ₂ O ₃ (1 mmol)	58	13	21
2	no B ₂ O ₃ , 0.5 mL H ₂ O (added to 4 mL acetone)	5	62	2

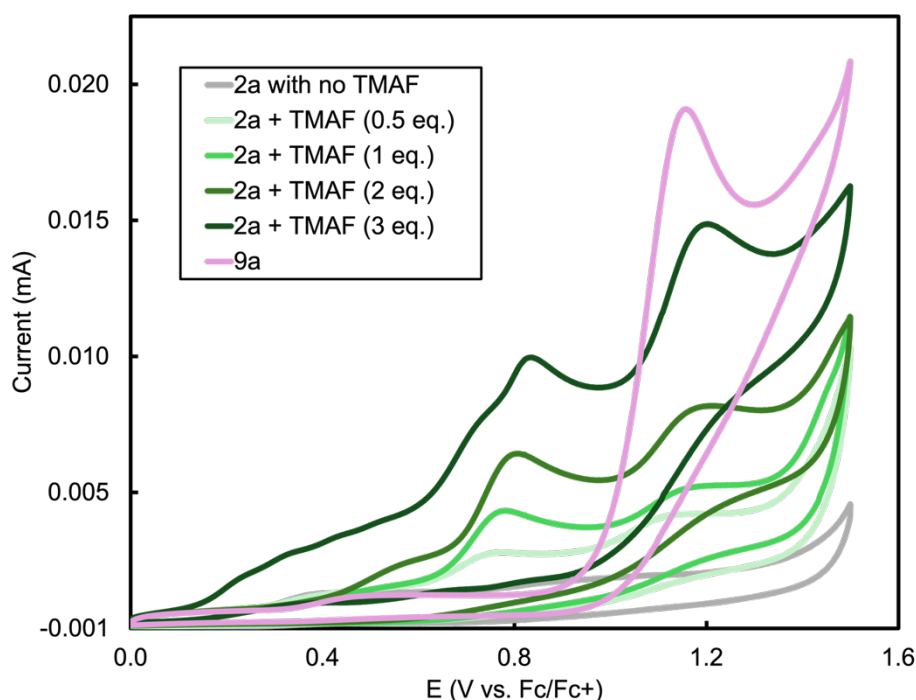
Figure 7. Proposed mechanism for *in-situ* Bpin formation



Cyclic Voltammetry studies

General procedure: Cyclic voltammograms were acquired on Biologic SP-50e in 0.1 M TBAPF₆ in acetone at a scan rate of 100 mV/s. Glassy carbon (3 mm dia.) or platinum (2 mm dia.) was used as the working electrode. A non-aqueous Ag/Ag⁺ was used as the reference electrode. Both working and reference electrodes were purchased from SYC Technologies, Inc. Carbon fiber (rod, 5 mm dia.) was used as the counter electrode (purchased from Amazon). Tetrabutylammonium hexafluorophosphate (TBAPF₆, purchased from Ambeed) was used as the electrolyte (0.1 M) and was recrystallized in ethanol and dried under vacuum overnight at 130 °C prior to the CV studies. Cyclic voltammograms of a blank electrolyte solution (0.1 M TBAPF₆ in acetone) and a ferrocene reference solution (2 mM) were taken first. The analyte solutions (2 mM) were bubbled with N₂ for 5 min prior to analysis.

Figure 8. Cyclic Voltammogram of phenethylboronic acid in the presence of TMAF



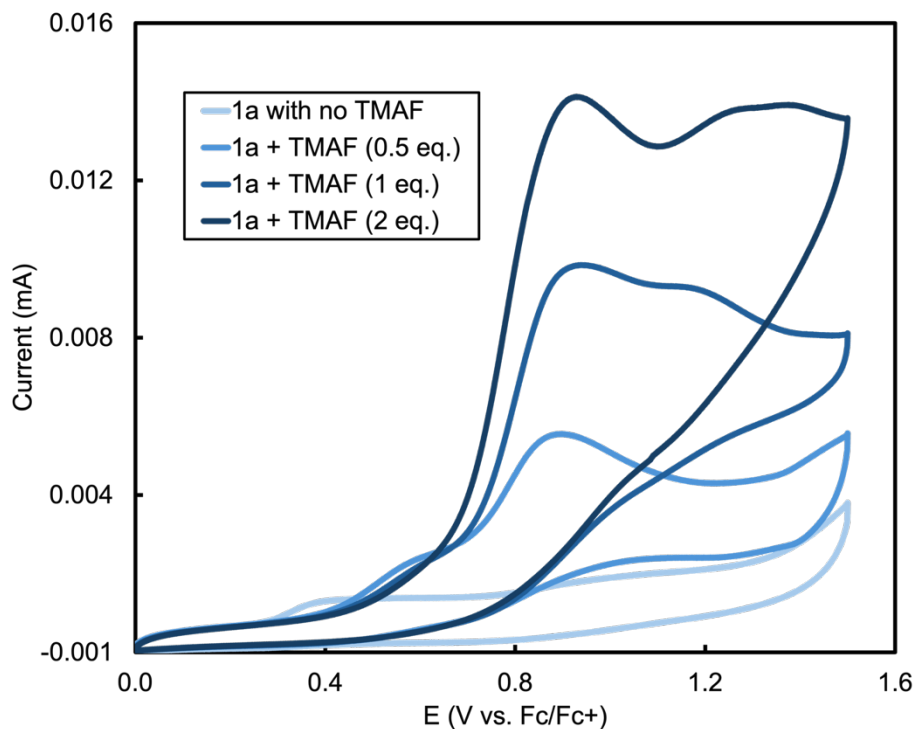
The six analyte stock solutions in acetone (10 mL each) were prepared inside the glovebox:

- #1: Phenethylboronic acid (0.2 mmol, 30 mg)
- #2: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.1 mmol, 9 mg, 0.5 equiv.)
- #3: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.2 mmol, 19 mg, 1 equiv.)
- #4: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.4 mmol, 37 mg, 2 equiv.)
- #5: Phenethylboronic acid (0.2 mmol, 30 mg, 1 equiv.) + TMAF (0.6 mmol, 56 mg, 3 equiv.)
- #6: Potassium phenethyltrifluoroborate (0.2 mmol, 42 mg)

For CV studies of each sample, an aliquot (500 μ L) from the stock solution was injected into a blank solution of TBAPF₆ (194 mg, 0.1 M) in acetone (5 mL).

Working electrode: Glassy carbon; Counter electrode: carbon fiber; Reference electrode: Ag/Ag⁺
A total of 3 scans were taken for each sample. The 2nd scans were stacked and shown.

Figure 9. Cyclic voltammogram of 4-phenylbutyric acid in the presence of TMAF



The four analyte stock solutions in acetone (10 mL each) were prepared inside the glovebox:

#1: 4-Phenylbutyric acid (0.2 mmol, 32 mg)

#2: 4-Phenylbutyric acid (0.2 mmol, 32 mg, 1 equiv.) + TMAF (0.1 mmol, 9 mg, 0.5 equiv.)

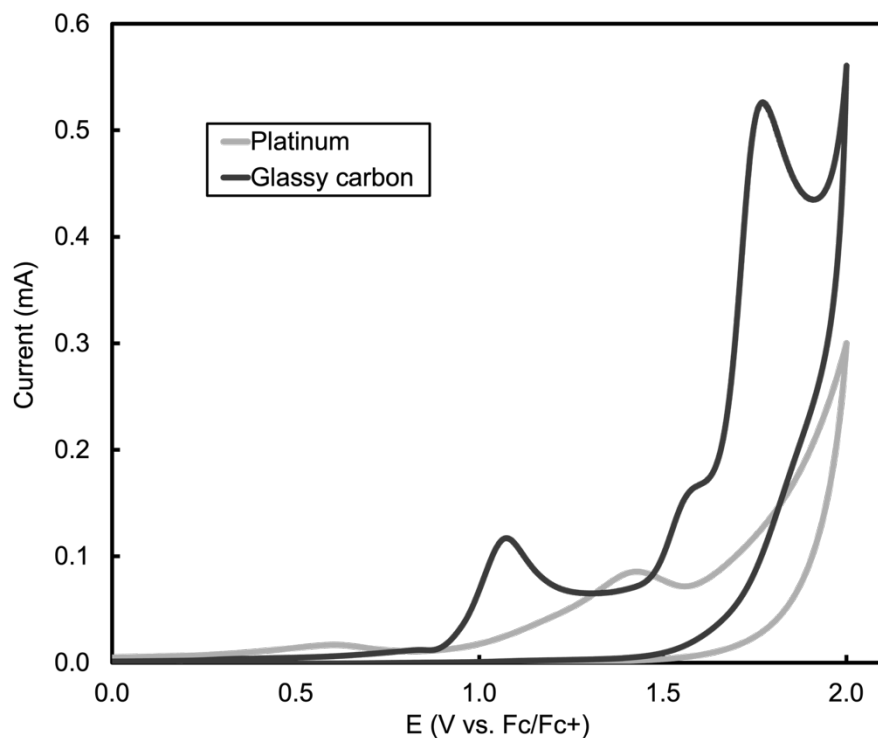
#3: 4-Phenylbutyric acid (0.2 mmol, 32 mg, 1 equiv.) + TMAF (0.2 mmol, 19 mg, 1 equiv.)

#4: 4-Phenylbutyric acid (0.2 mmol, 32 mg, 1 equiv.) + TMAF (0.4 mmol, 37 mg, 2 equiv.)

For CV studies of each sample, an aliquot (500 μ L) from the stock solution was injected into a blank solution of TBAPF₆ (194 mg, 0.1 M) in acetone (5 mL).

Working electrode: Glassy carbon; Counter electrode: carbon fiber; Reference electrode: Ag/Ag⁺
A total of 3 scans were taken for each sample. The 2nd scans were stacked and shown.

Figure 10. Comparison of platinum and glassy carbon electrodes on the oxidation of phenethyl BF_3K



An aliquot (500 μL) from the stock solution of Potassium phenethyltrifluoroborate (0.2 mmol, 42 mg) in acetone (10 mL) was injected a blank solution of TBAPF_6 (194 mg, 0.1 M) in acetone (5 mL). Cyclic Voltammograms with platinum and glassy carbon working electrodes were acquired on the sample. A total of 3 scans were taken in each analysis. The 2nd scans were shown. Counter electrode: carbon fiber; Reference electrode: Ag/Ag^+ .

Figure 11. Passivation study of phenethyl BF_3K on glassy carbon electrode

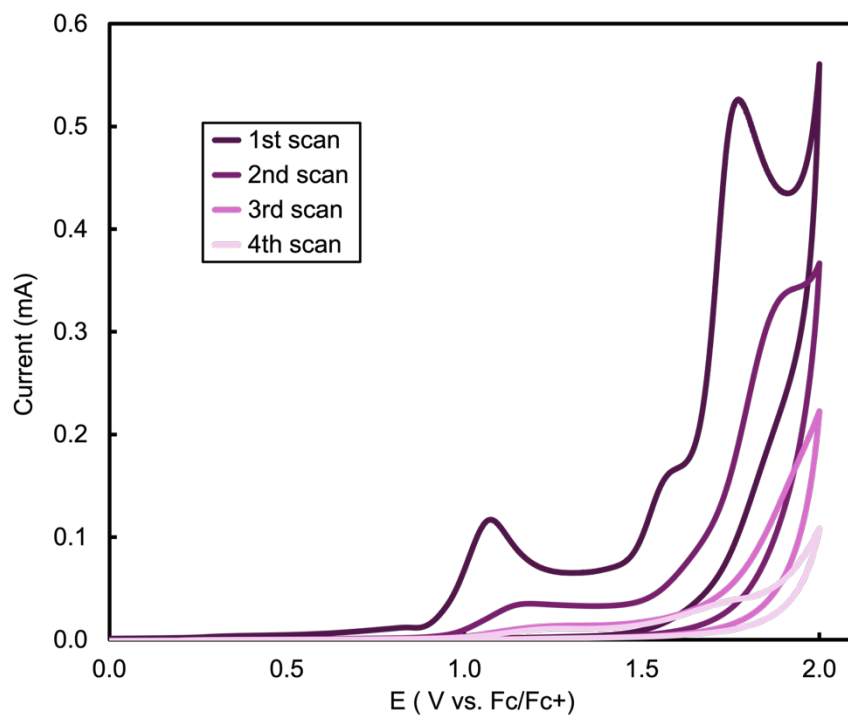
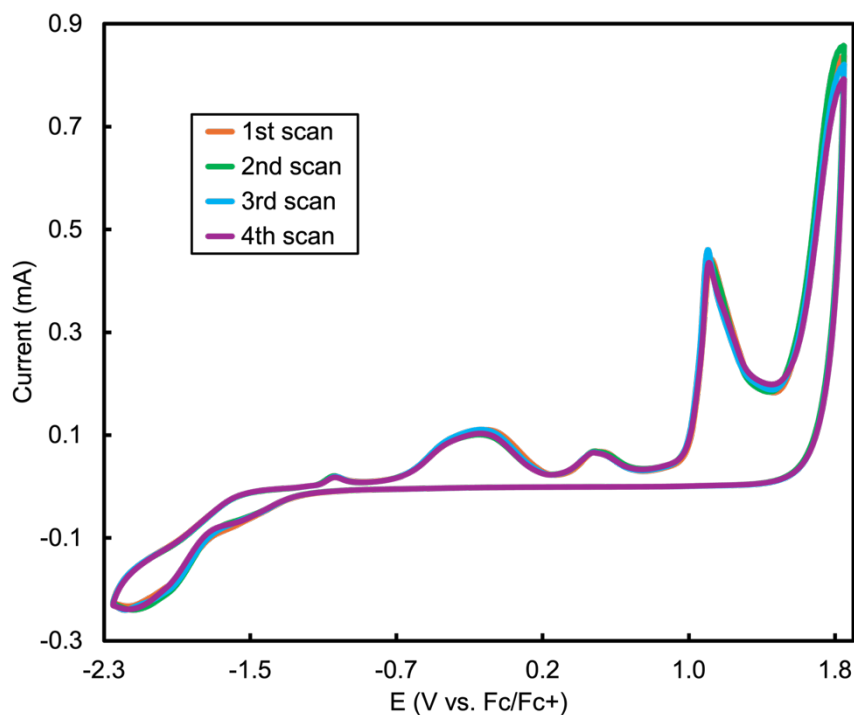


Figure 12. Reduction sweep of phenethyl BF_3K on glassy carbon electrode



An aliquot (500 μL) from the stock solution of Potassium phenethyltrifluoroborate (0.2 mmol, 42 mg) in acetone (10 mL) was injected a blank solution of TBAPF_6 (194 mg, 0.1 M) in acetone (5 mL). Counter: carbon fiber; Reference: Ag/Ag^+ . The first 4 consecutive scans are shown.

Table 6: ICP-MS experiments for trace transition metal detection

Reaction mixture	Metal concentration in reaction mixture (ppb)									
	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pd	Ag	Pt
Before	20.352	5.303	352.939	7.822	10.665	18.985	127.545	0.488	23.285	0.194
After	0.818	1.044	202.780	0.289	1.837	60.367	741.917	0.669	1.444	0.299

Or if converted to ppm:

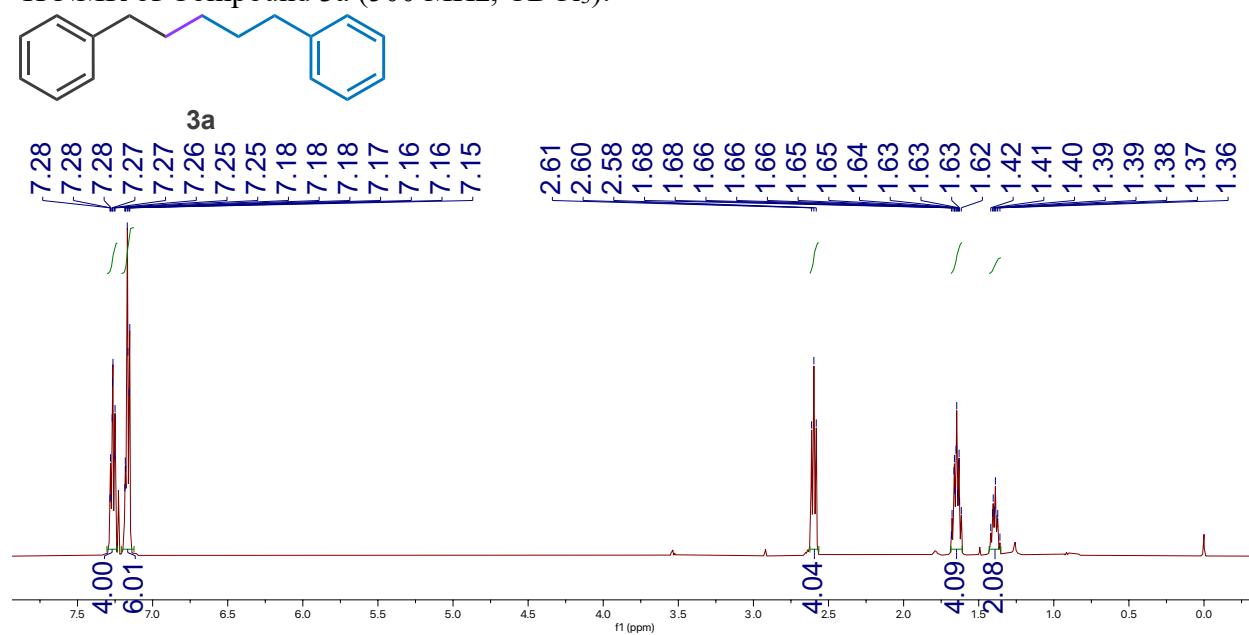
Reaction mixture	Metal concentration in reaction mixture (ppm)									
	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pd	Ag	Pt
Before	0.0204	5.303 E-3	0.353	7.822 E-3	0.0107	0.0190	0.128	0.488 E-3	0.0233	0.194 E-3
After	0.818 E-3	1.044 E-3	0.203	0.289 E-3	1.837 E-3	0.0604	0.742	0.669 E-3	1.444 E-3	0.299 E-3

Sample preparation:

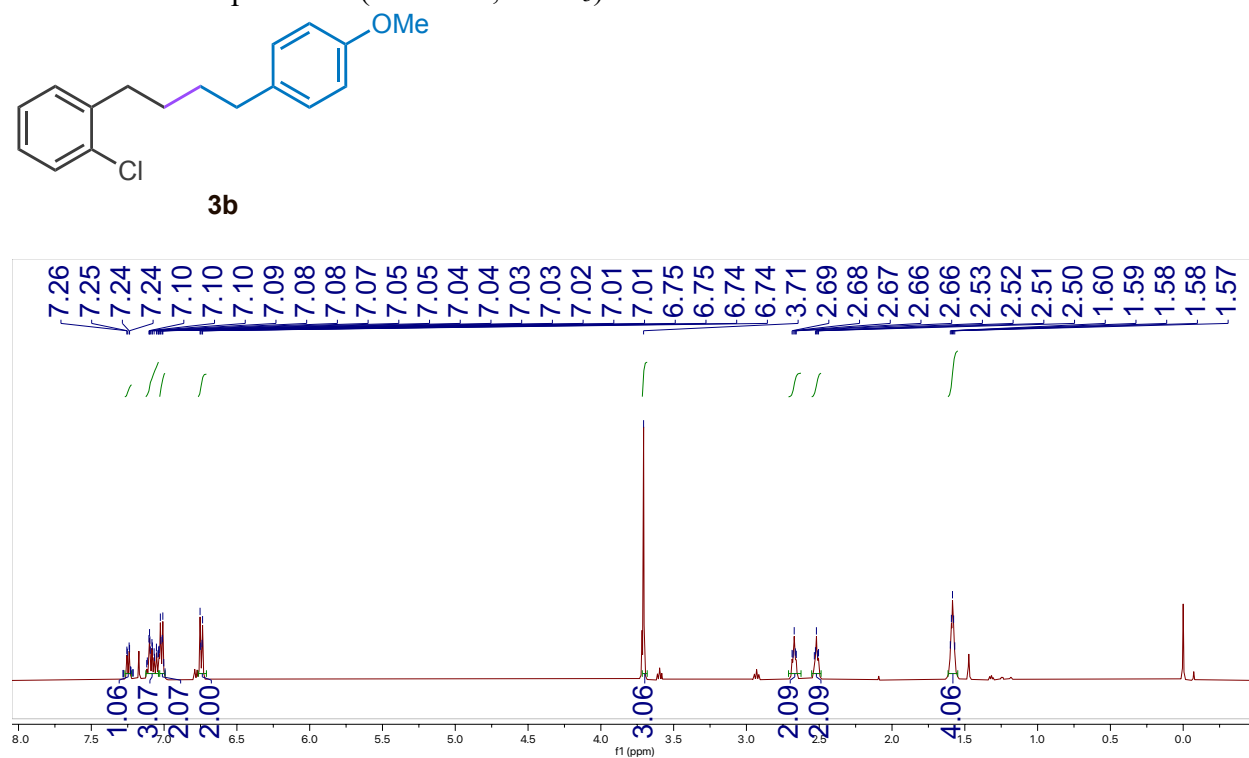
1. Added reaction mixture in acetone (5 mL) to a pre-weighed metal-free tube
2. Evaporated acetone with gentle heat and air
3. Added HNO₃ (500 µL), HCl (500 µL) and H₂O₂ (250 µL) and heated to digest the residue
4. Diluted to 10 mL with MP H₂O and weighed
5. Filtered supernatant for ICP-MS analysis

NMR Spectra

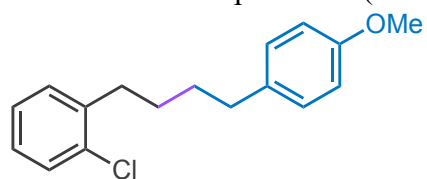
^1H NMR of Compound 3a (500 MHz, CDCl_3):



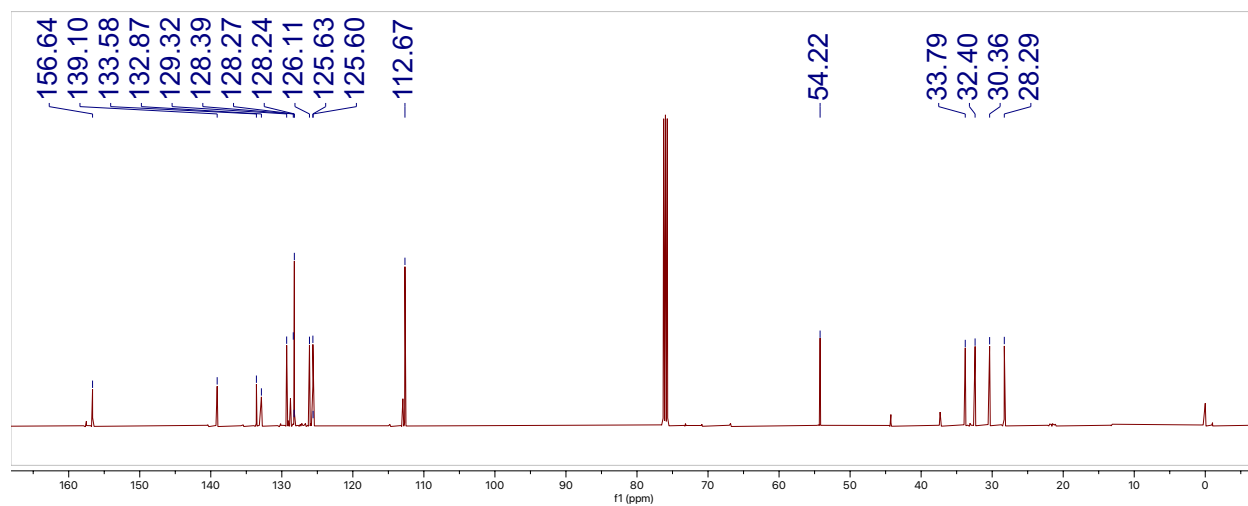
^1H NMR of Compound 3b (500 MHz, CDCl_3):



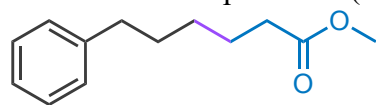
^{13}C NMR of Compound 3b (126 MHz, CDCl_3):



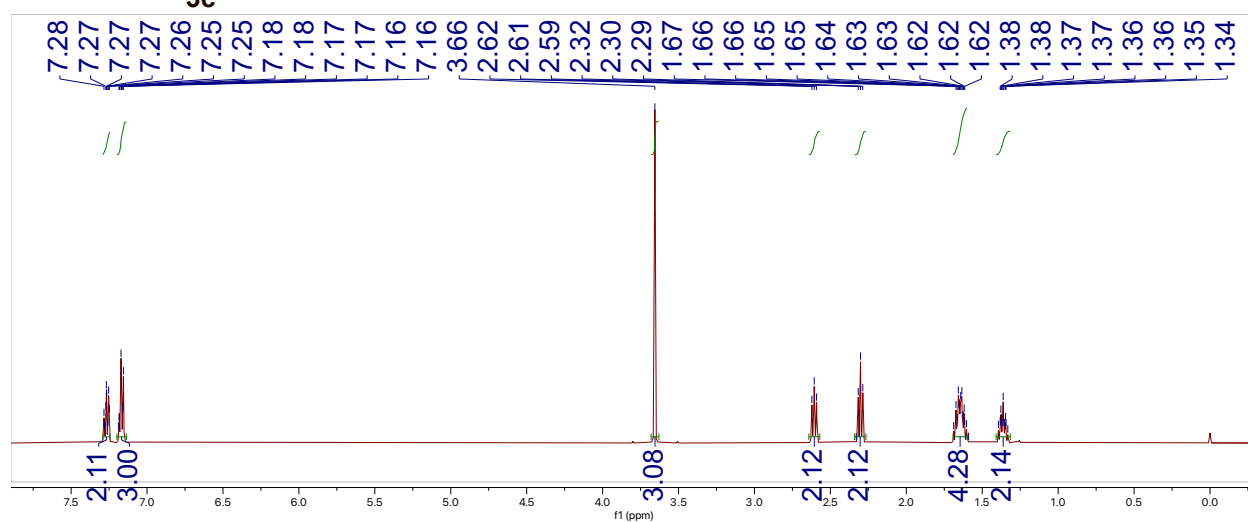
3b



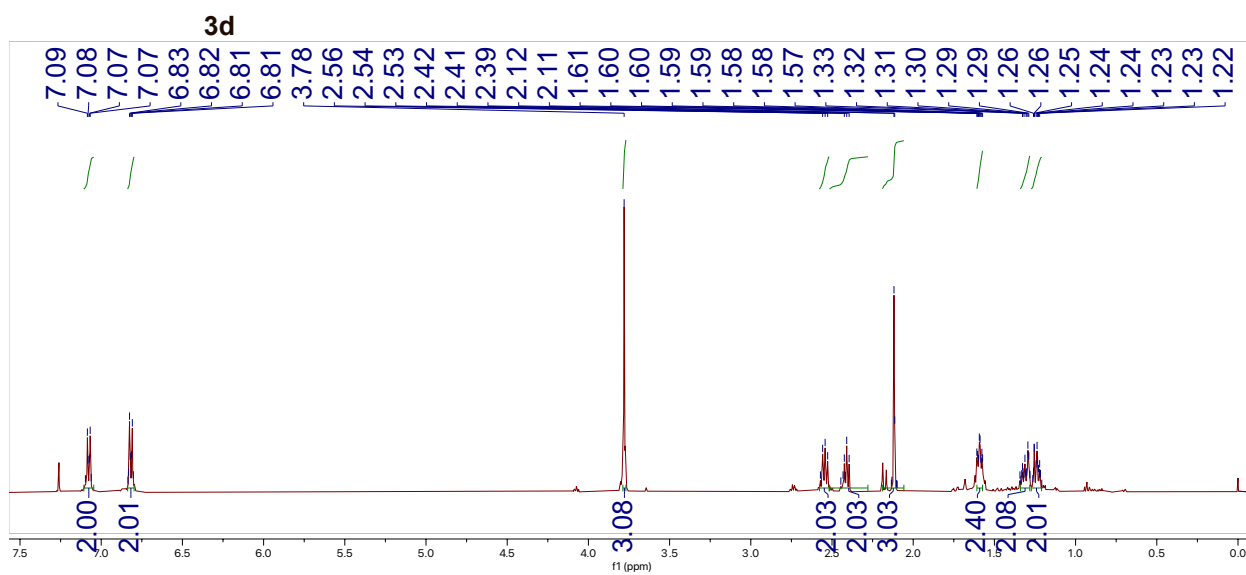
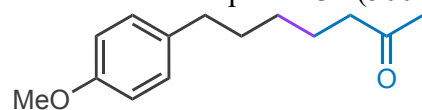
^1H NMR of Compound 3c (500 MHz, CDCl_3):



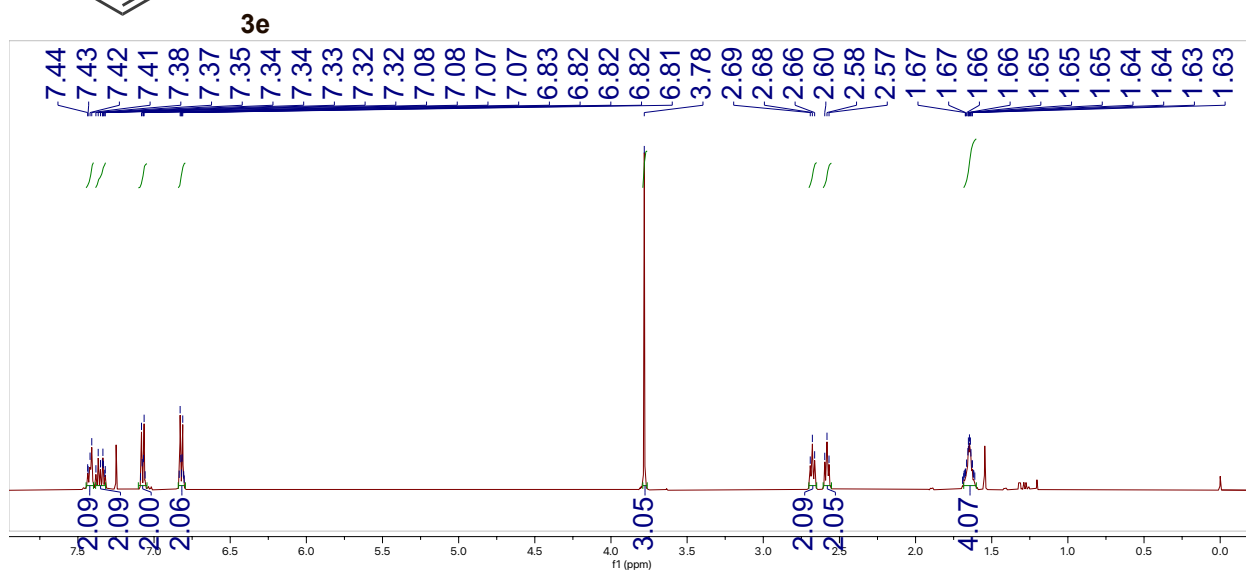
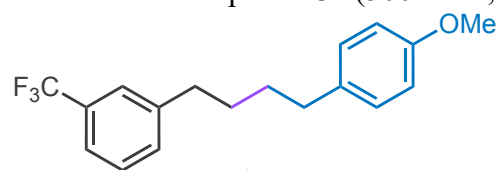
3c



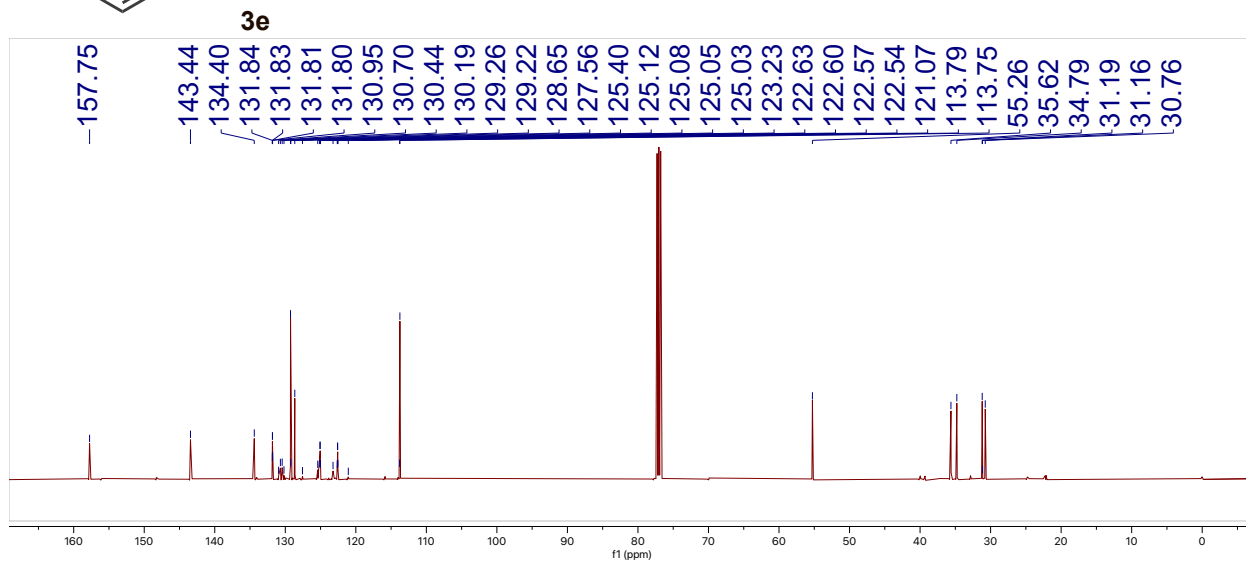
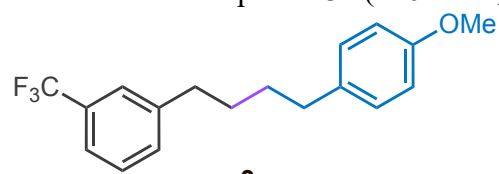
^1H NMR of Compound 3d (500 MHz, CDCl_3):



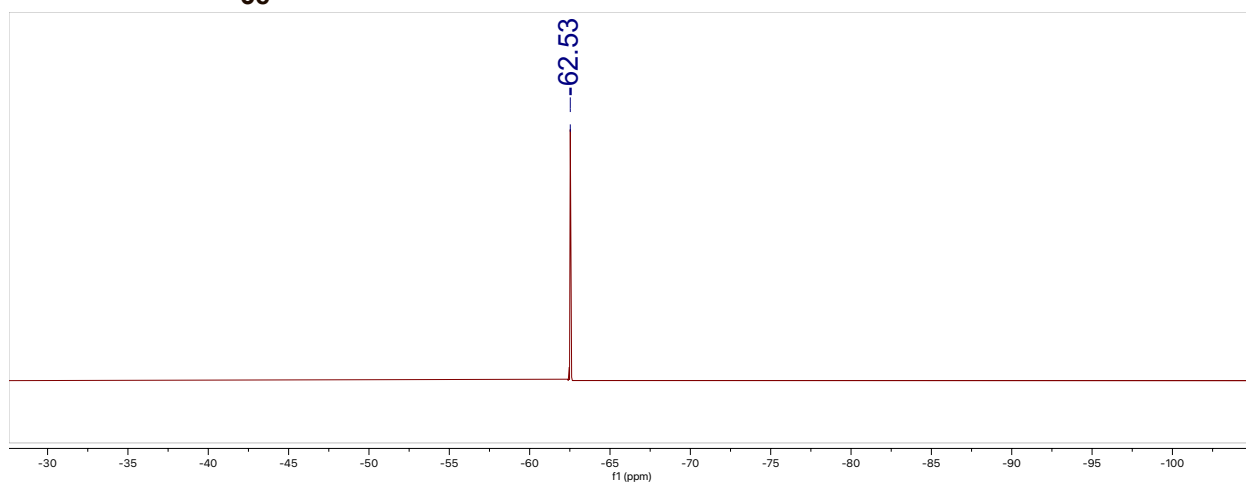
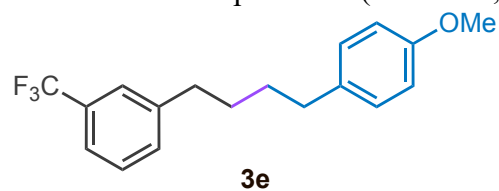
^1H NMR of Compound 3e (500 MHz, CDCl_3):



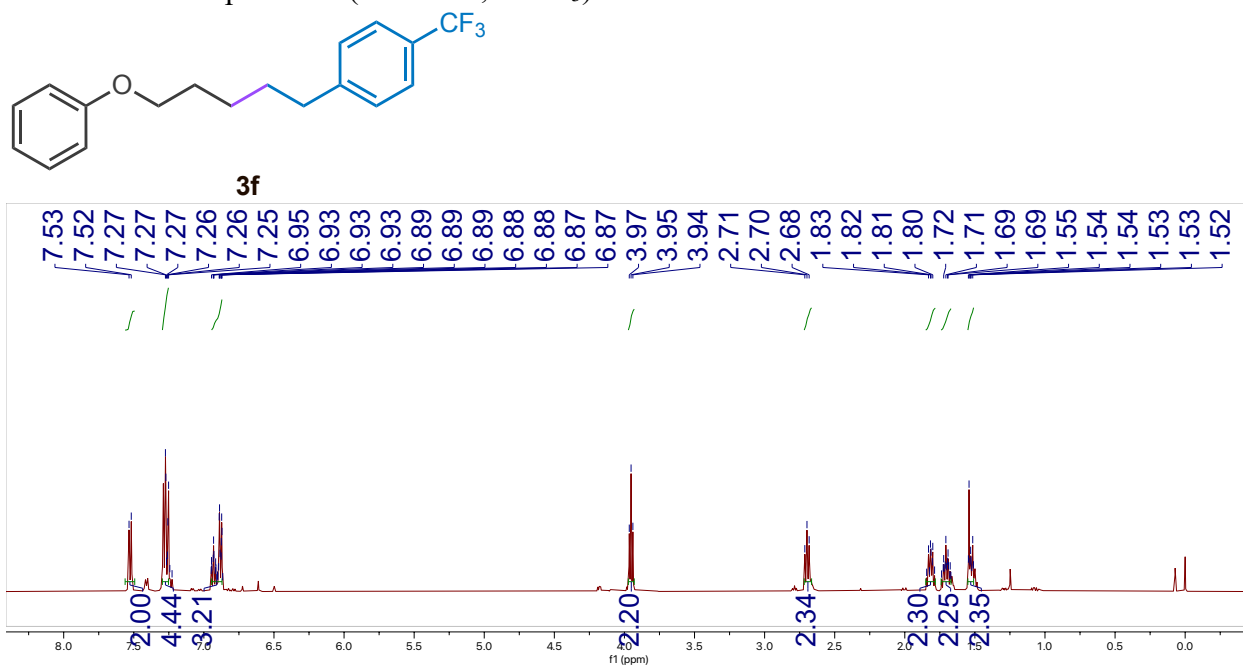
^{13}C NMR of Compound 3e (126 MHz, CDCl_3):



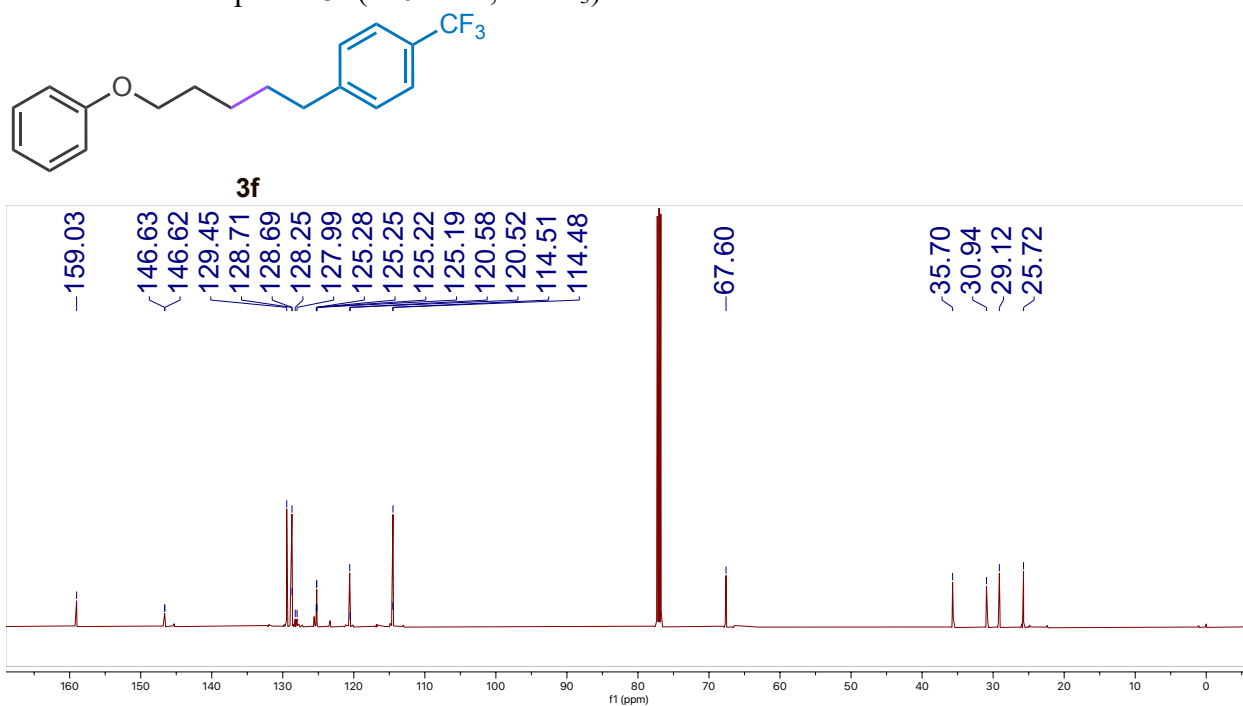
^{19}F NMR of Compound 3e (470 MHz, CDCl_3):



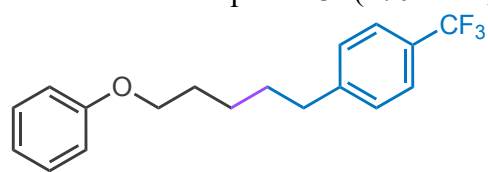
^1H NMR of Compound 3f (500 MHz, CDCl_3):



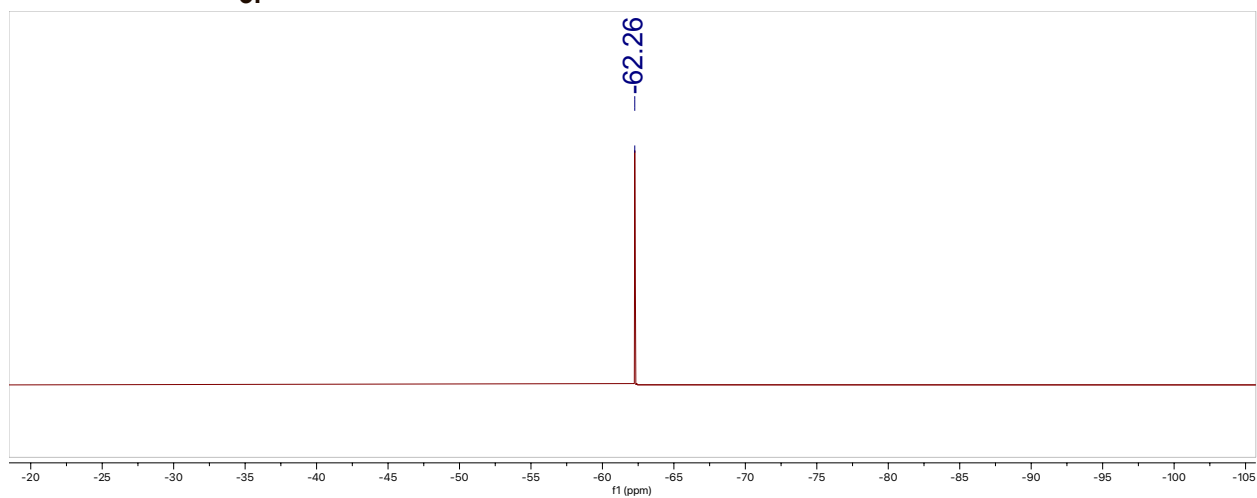
^{13}C NMR of Compound 3f (126 MHz, CDCl_3):



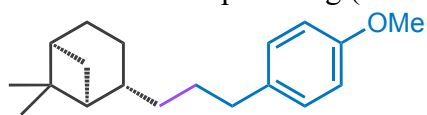
^{19}F NMR of Compound 3f (470 MHz, CDCl_3):



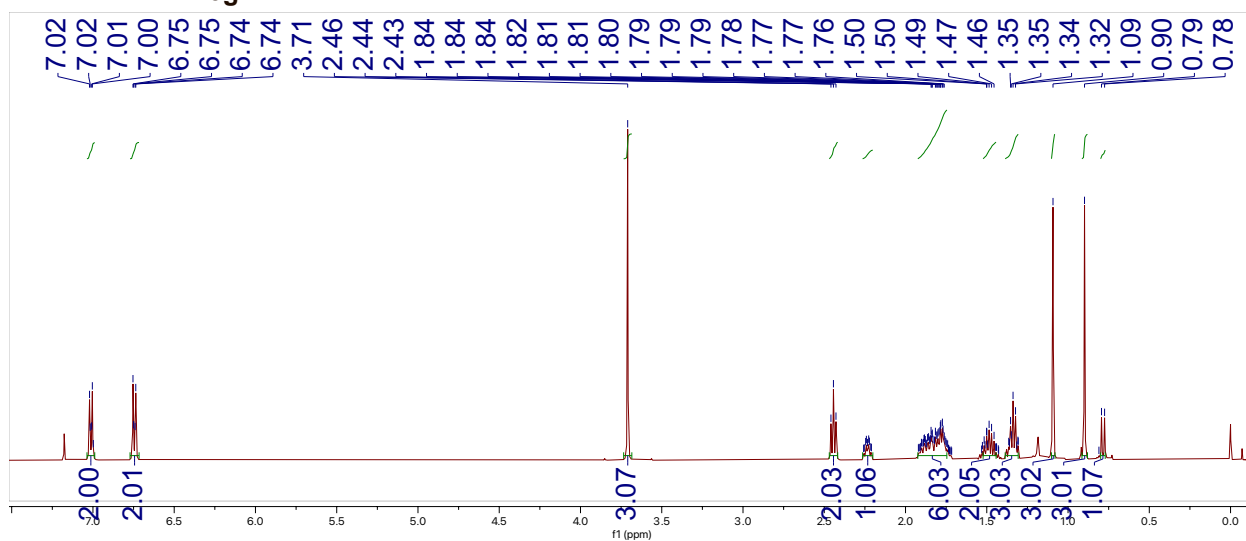
3f



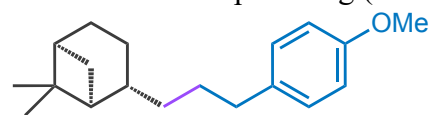
^1H NMR of Compound 3g (500 MHz, CDCl_3):



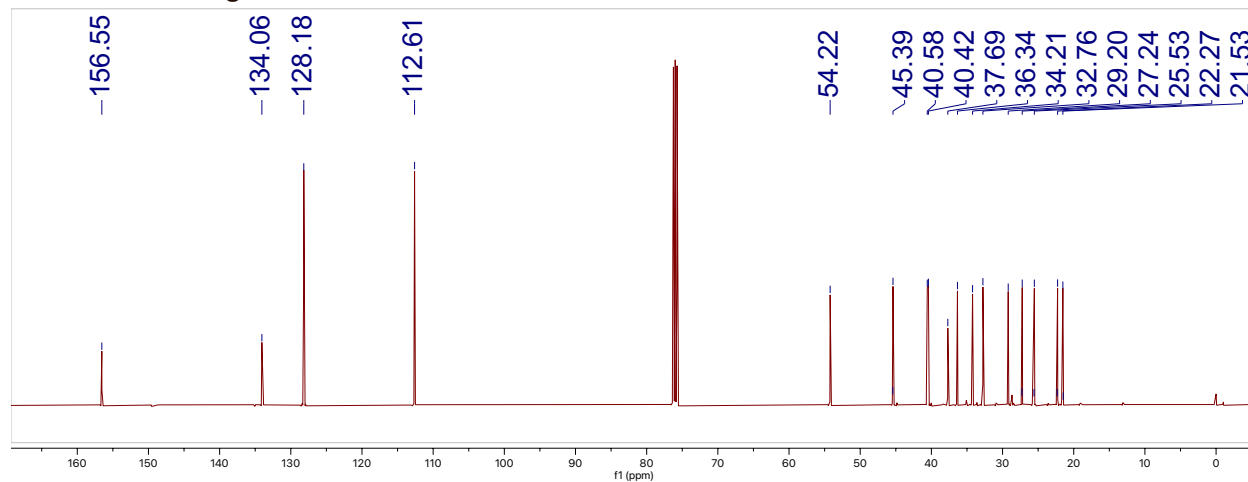
3g



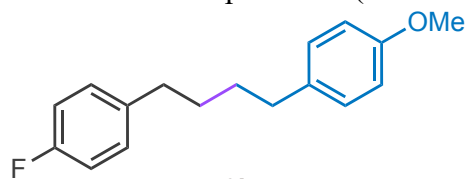
^{13}C NMR of Compound 3g (126 MHz, CDCl_3):



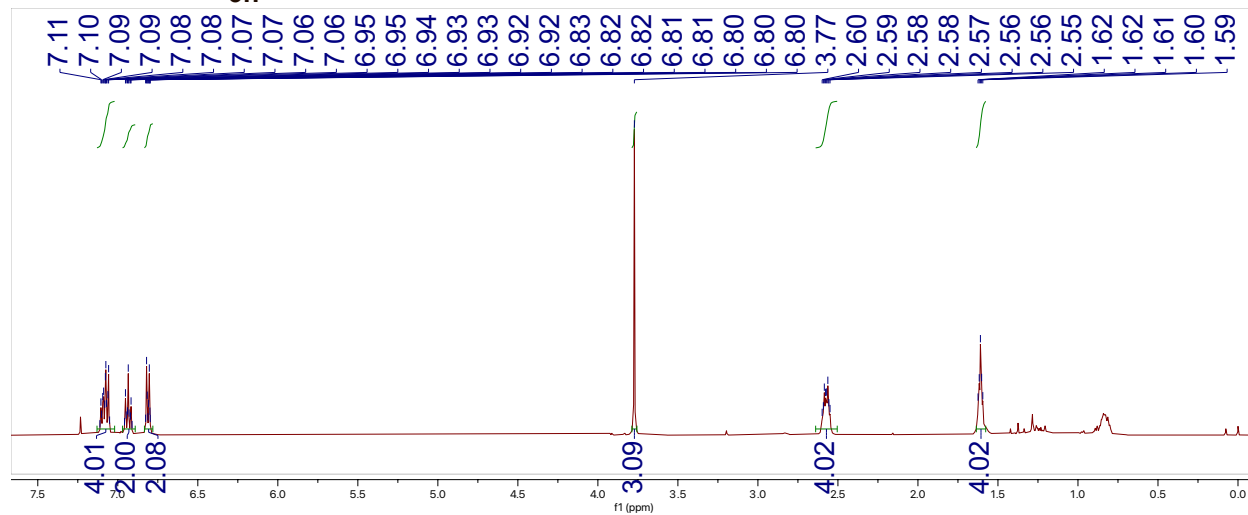
3g



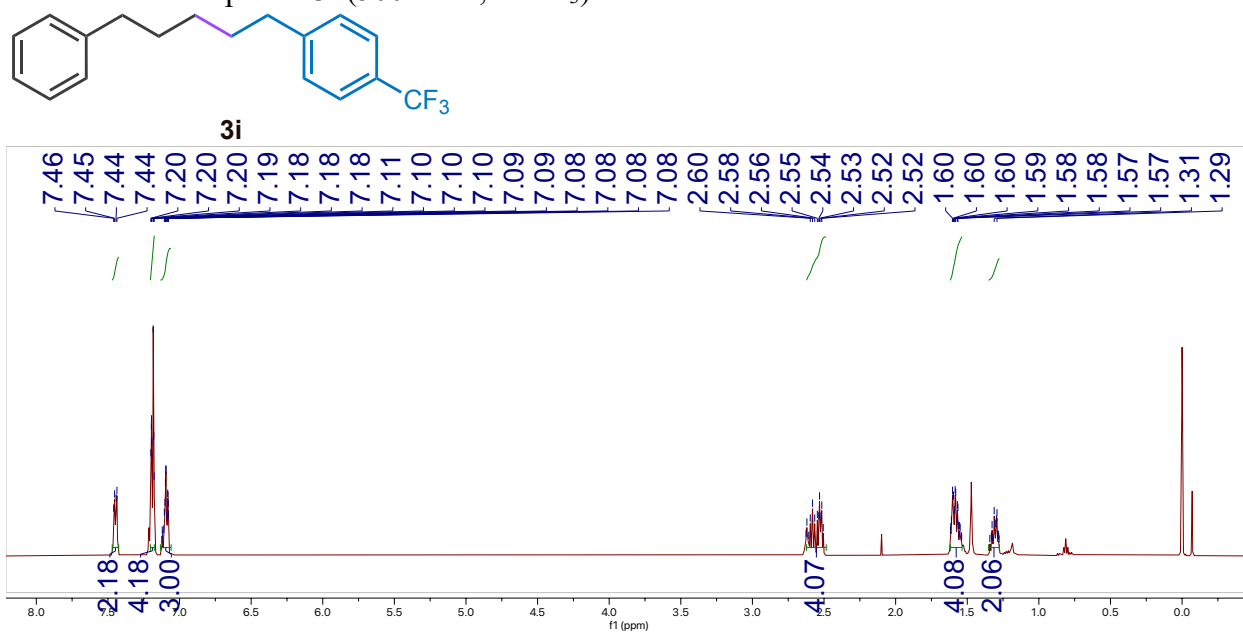
^1H NMR of Compound 3h (500 MHz, CDCl_3):



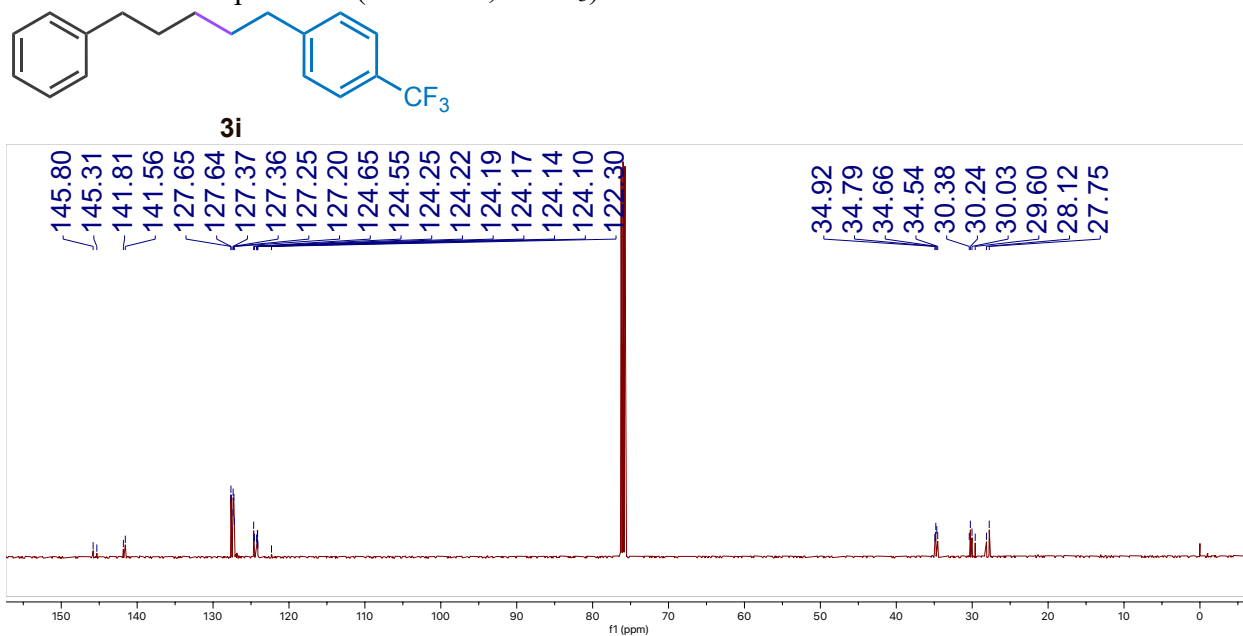
3h



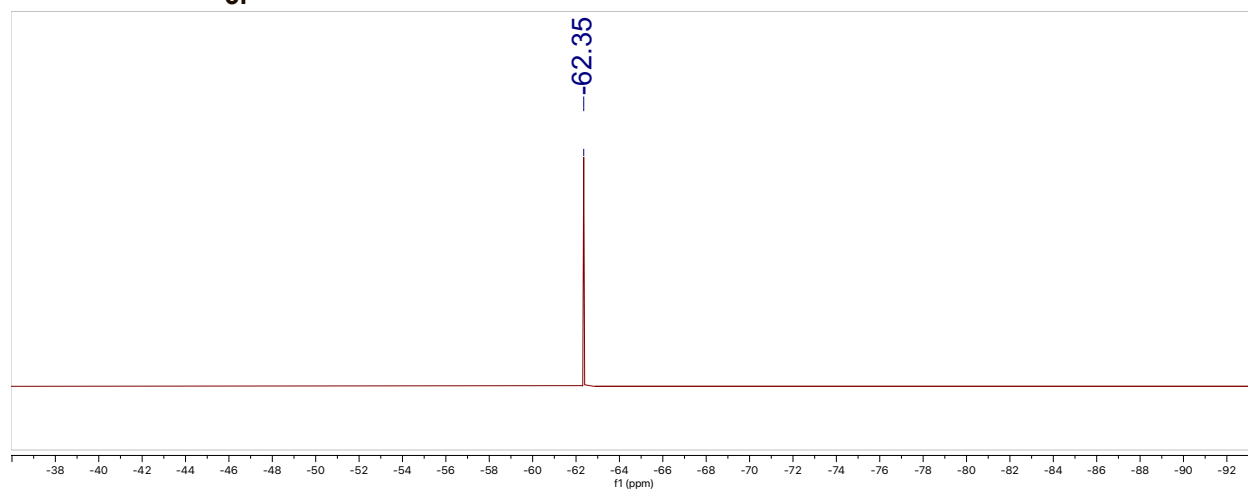
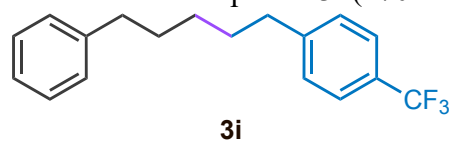
^1H NMR of Compound 3i (500 MHz, CDCl_3):



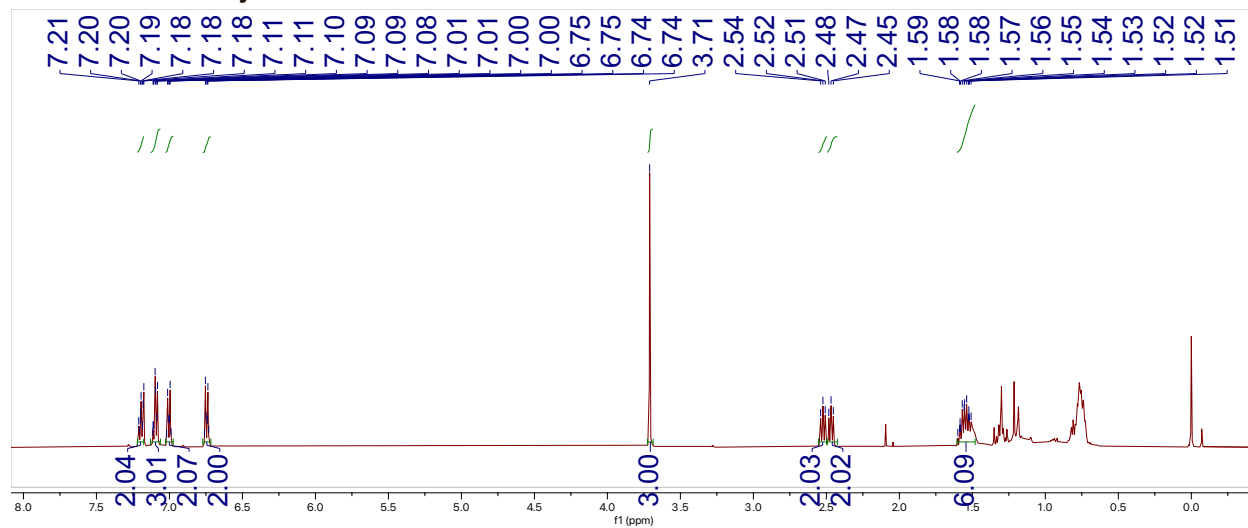
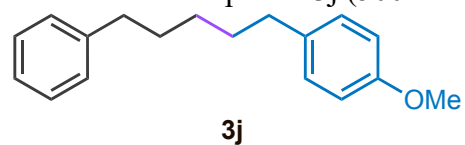
^{13}C NMR of Compound 3i (126 MHz, CDCl_3):



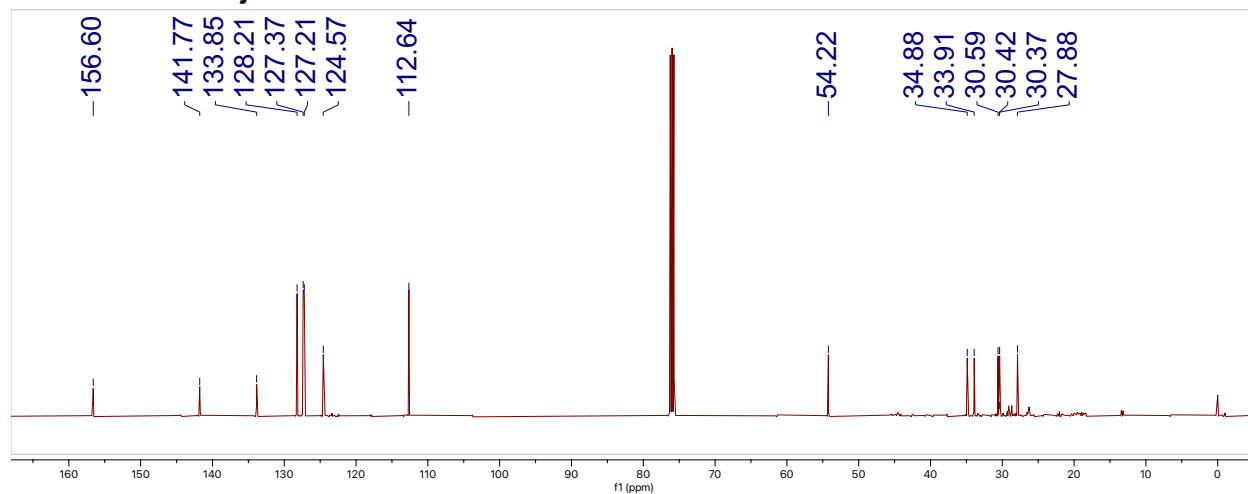
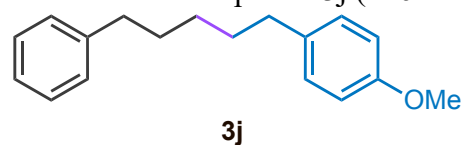
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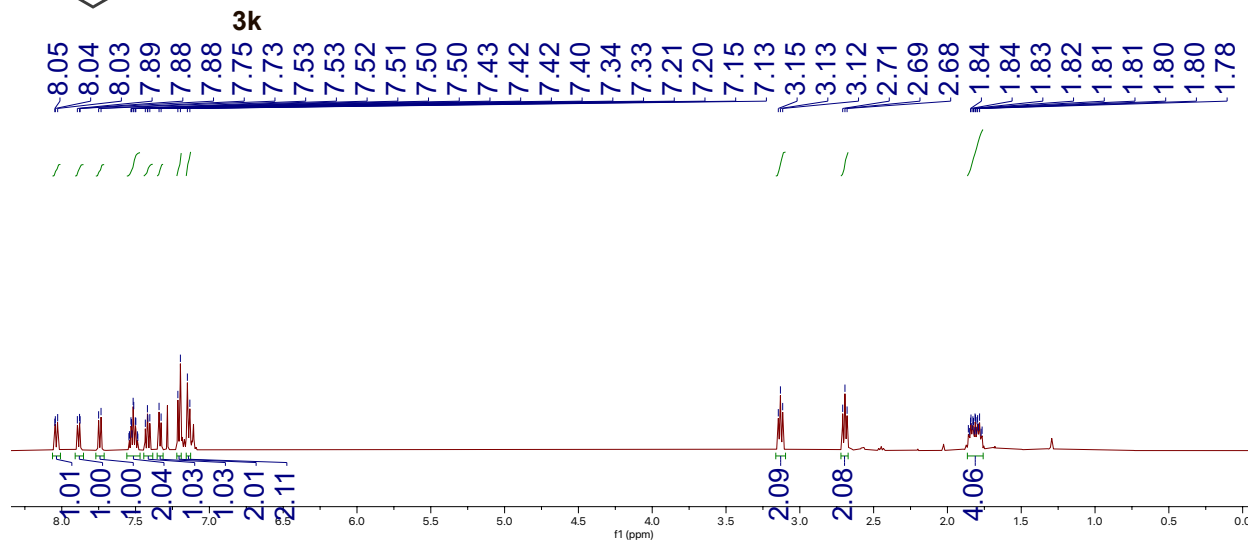
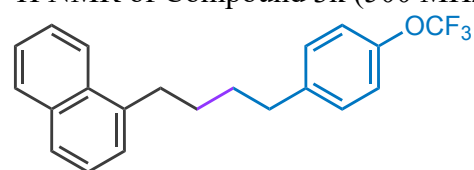
^1H NMR of Compound 3j (500 MHz, CDCl_3):



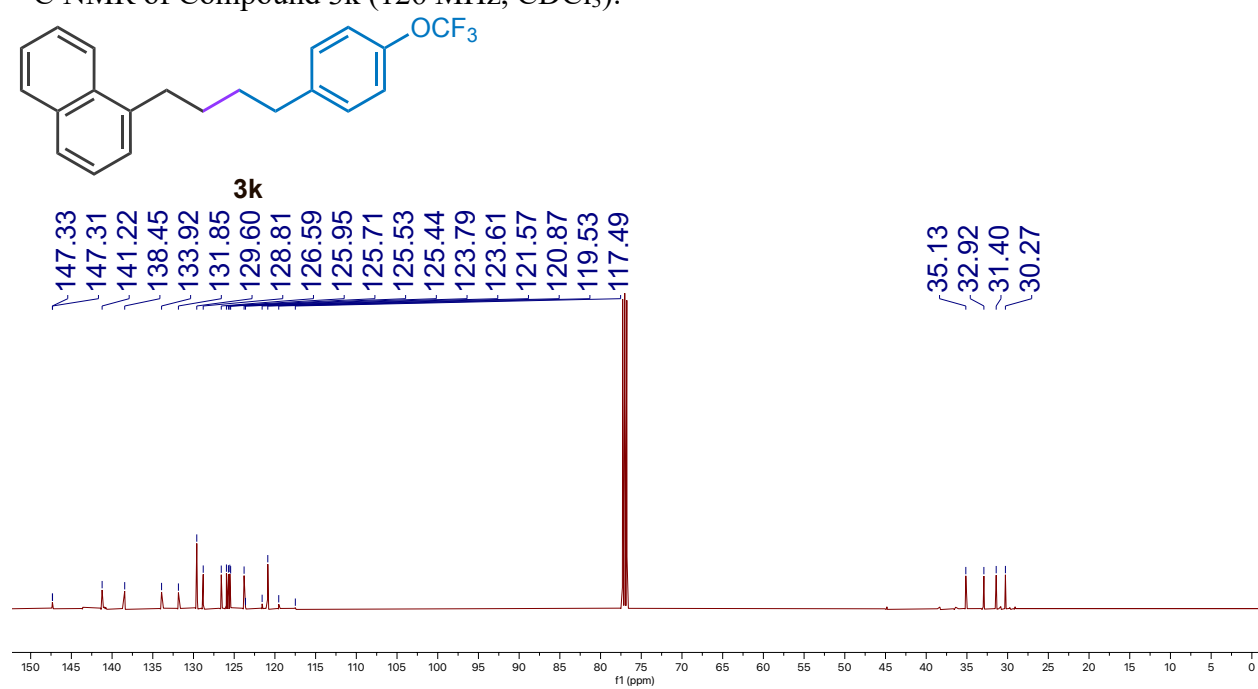
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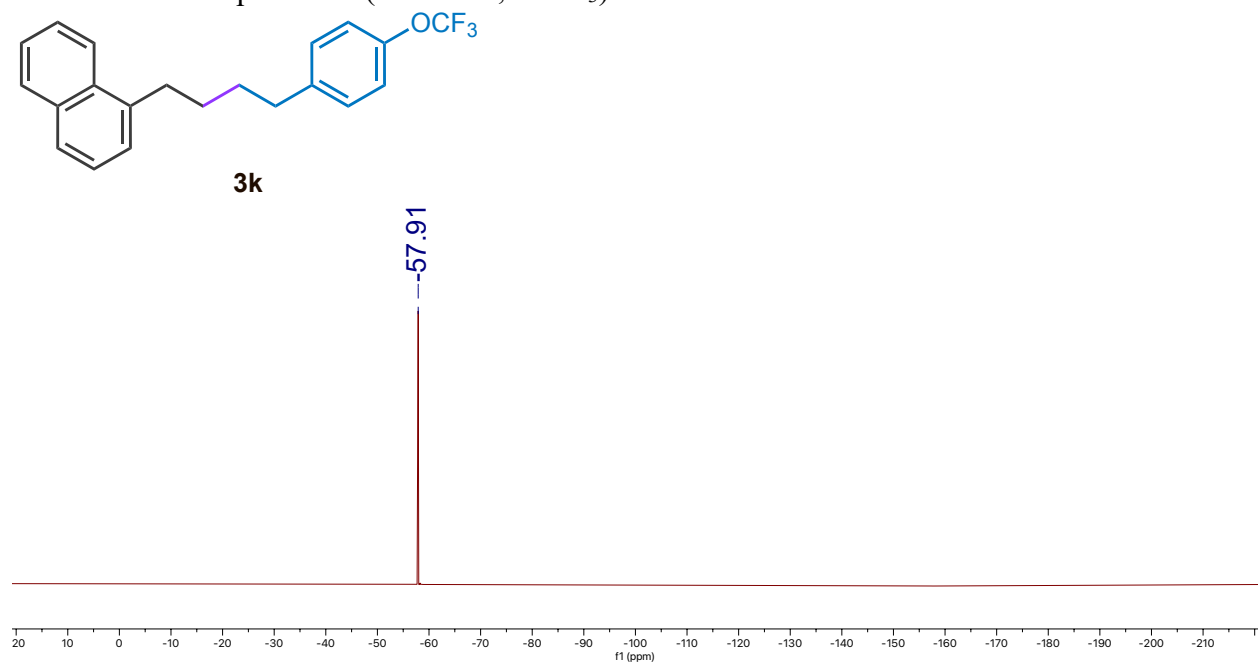
^1H NMR of Compound 3k (500 MHz, CDCl_3):



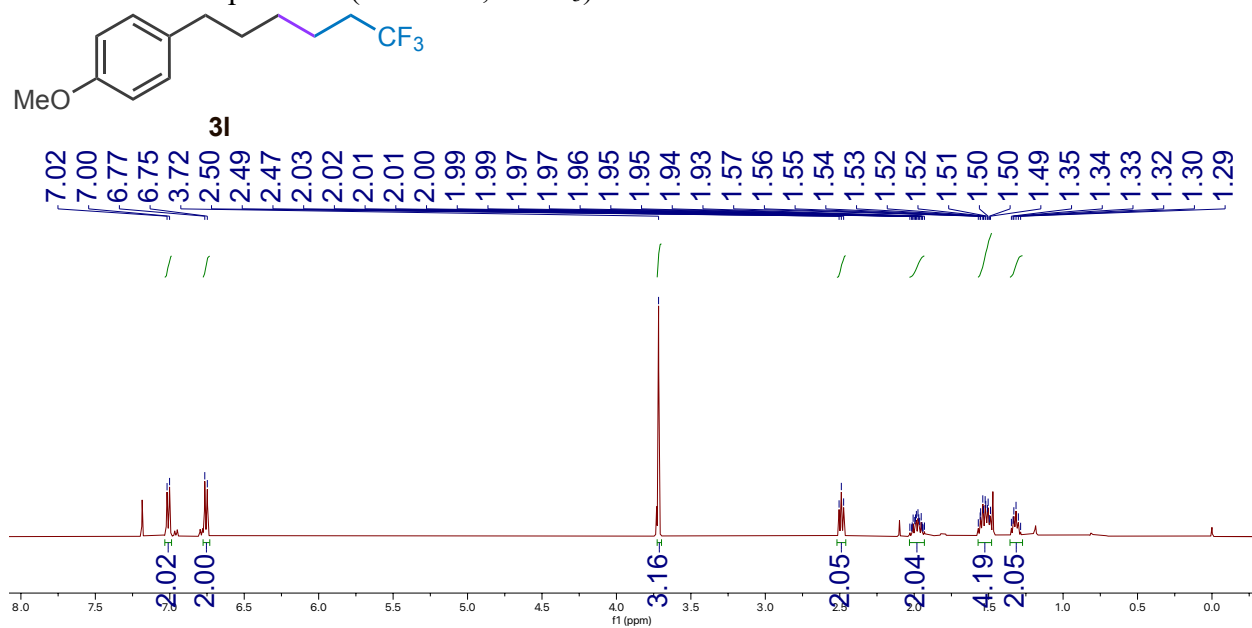
^{13}C NMR of Compound 3k (126 MHz, CDCl_3):



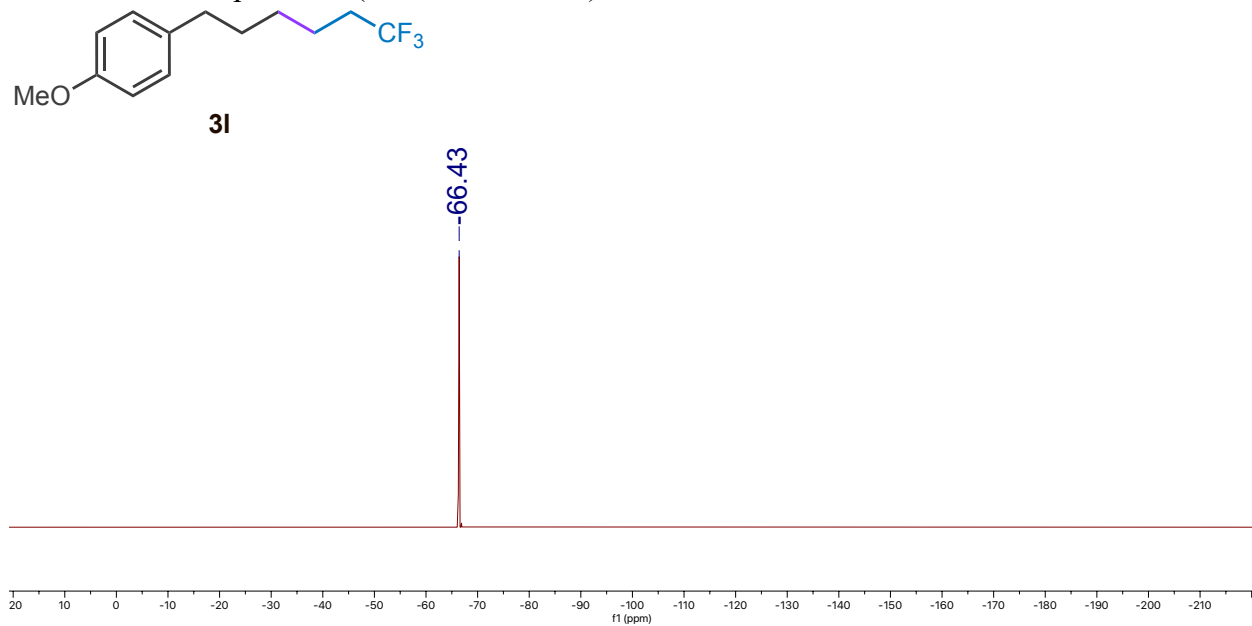
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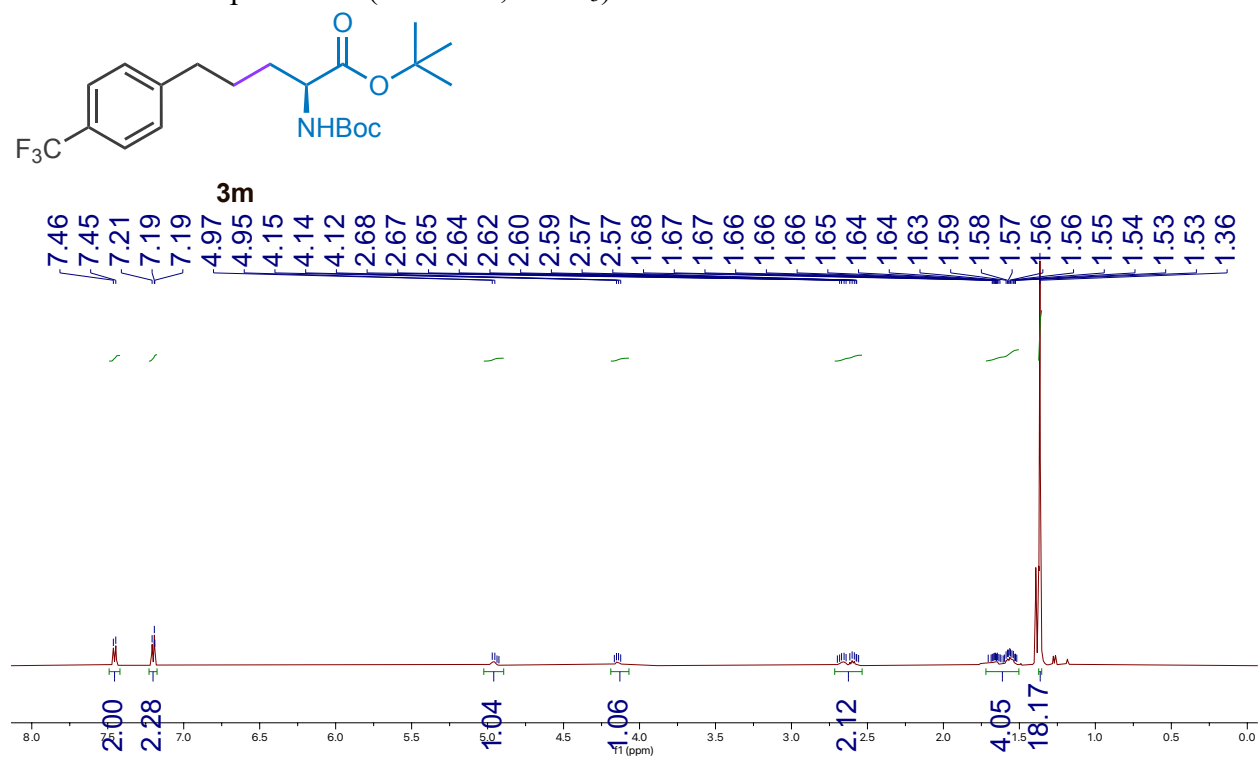
^1H NMR of Compound 31 (500 MHz, CDCl_3):



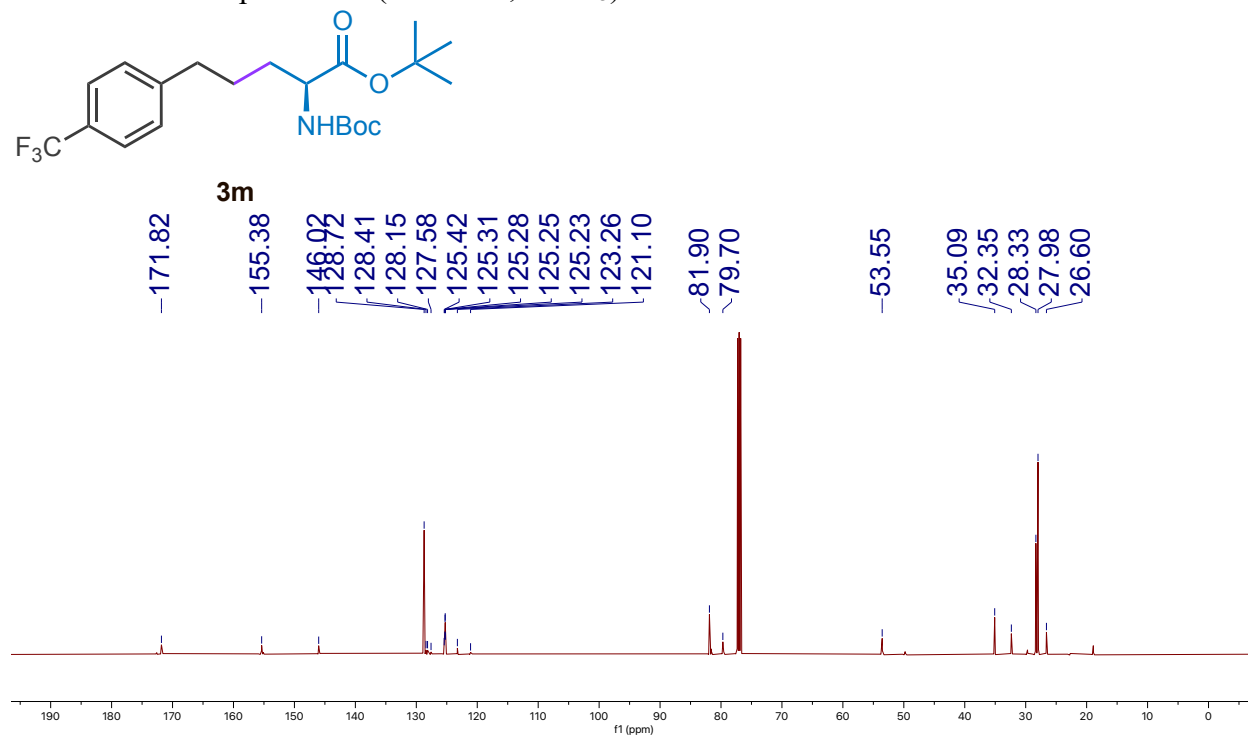
^{19}F NMR of Compound 31 (470 MHz, CDCl_3):



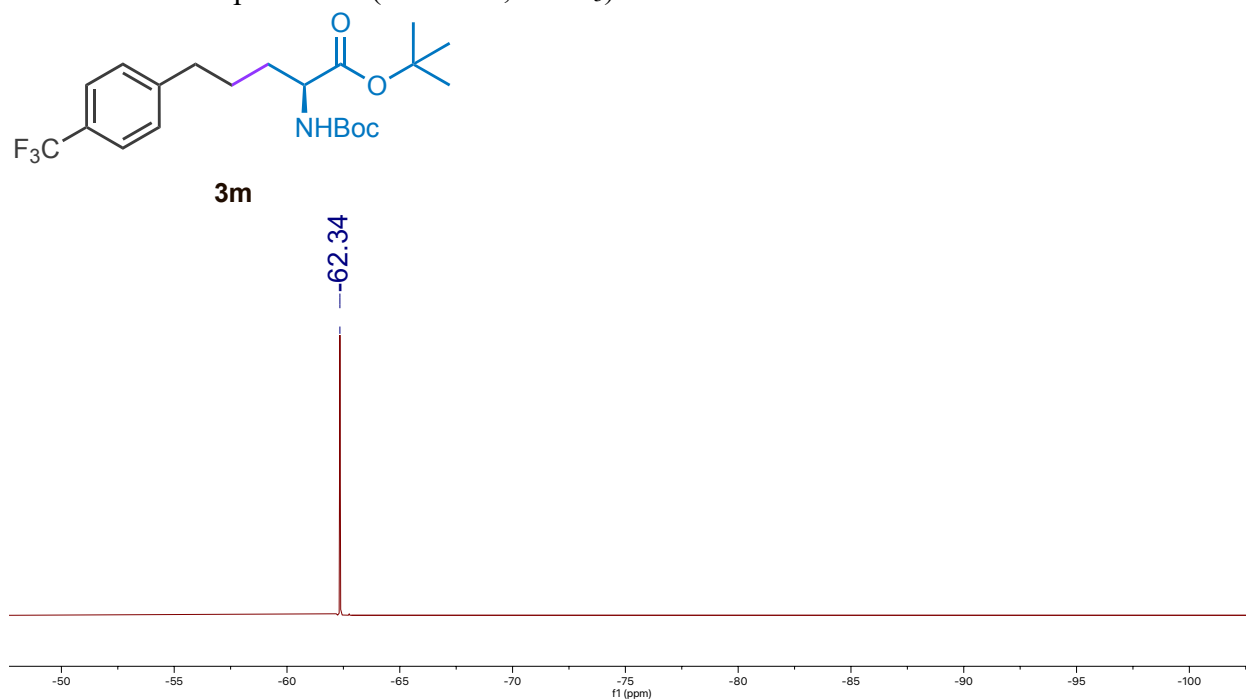
^1H NMR of Compound 3m (500 MHz, CDCl_3):



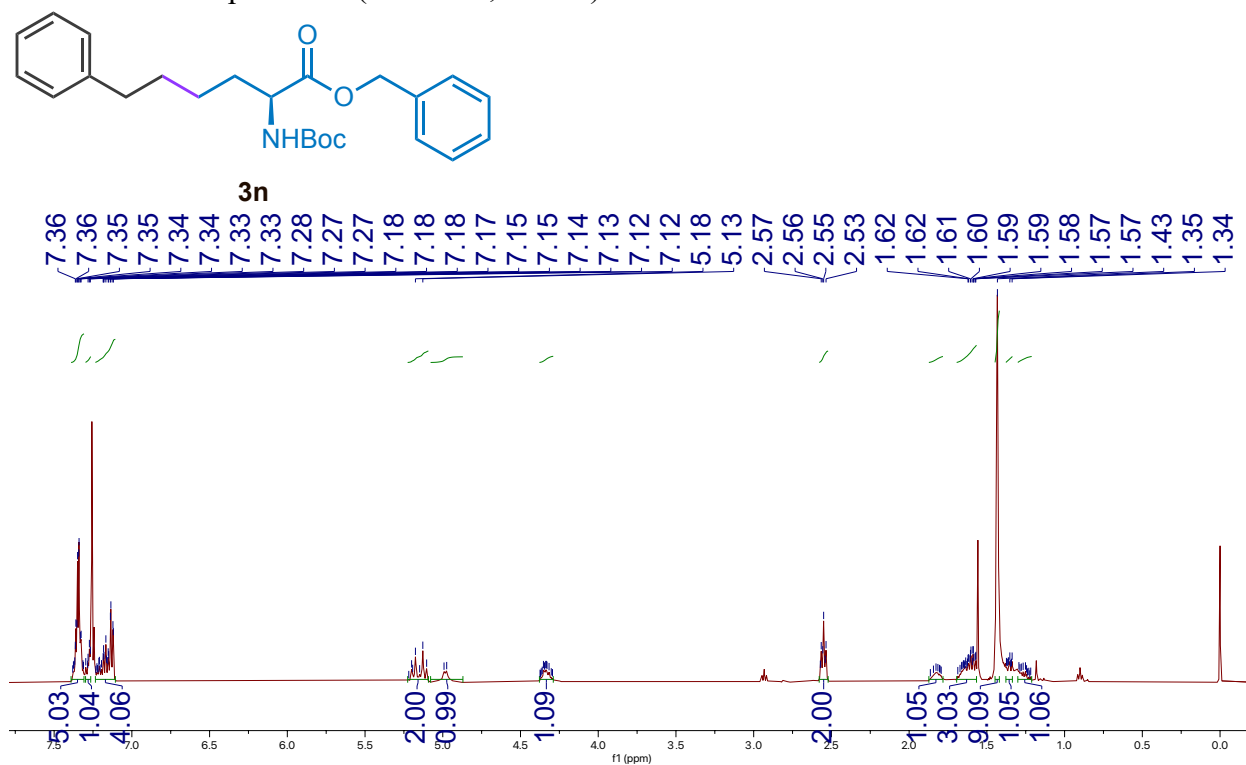
^{13}C NMR of Compound 3m (126 MHz, CDCl_3):



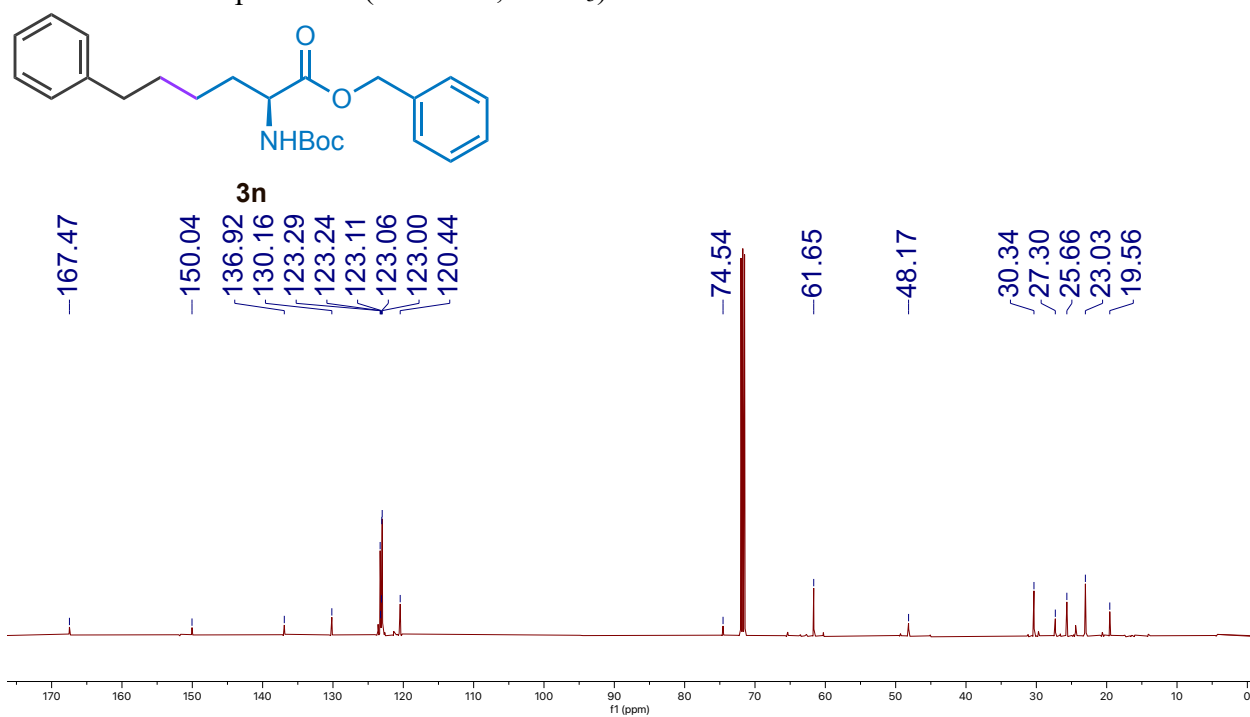
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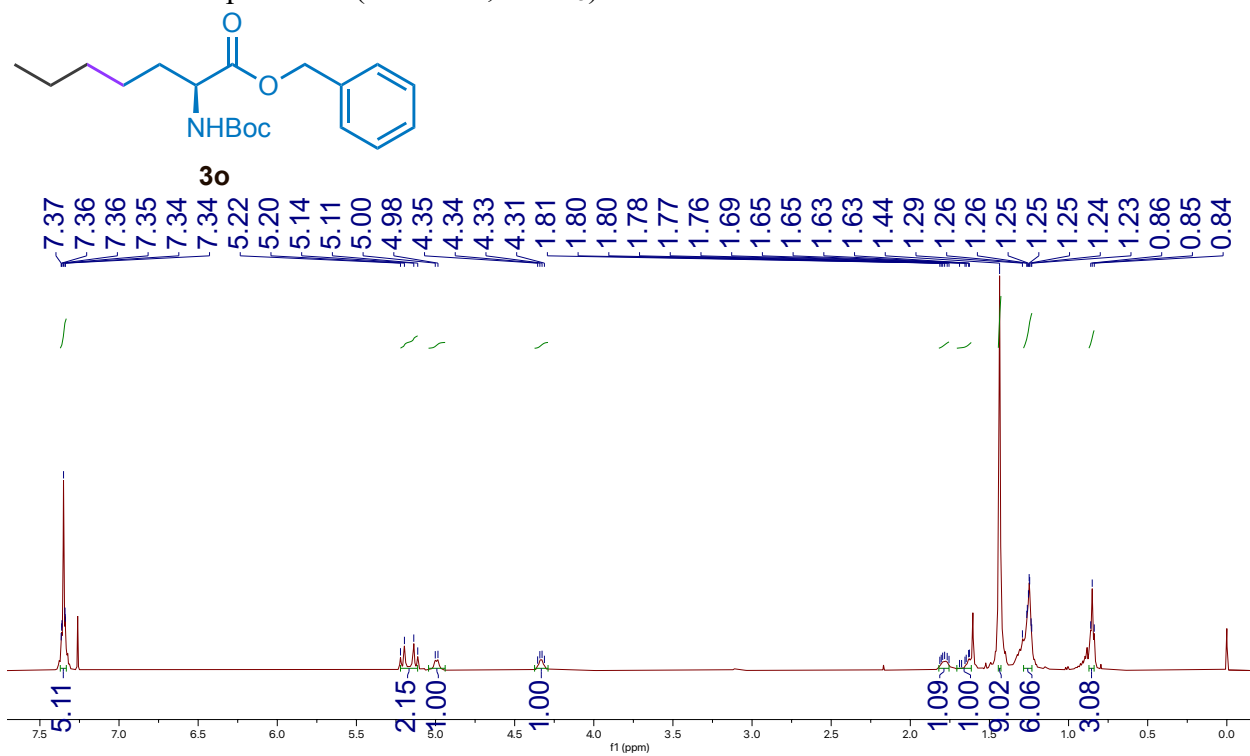
^1H NMR of Compound 3n (500 MHz, CDCl_3):



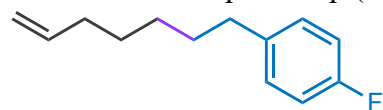
^{13}C NMR of Compound 3n (126 MHz, CDCl_3):



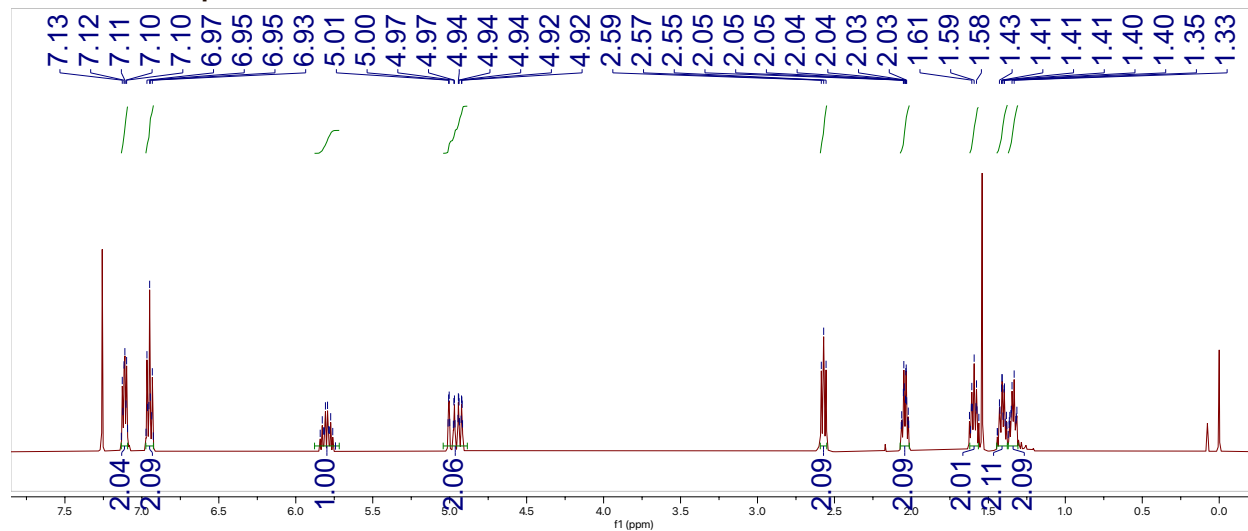
^1H NMR of Compound 3o (500 MHz, CDCl_3):



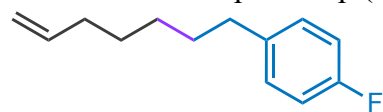
^1H NMR of Compound 3p (500 MHz, CDCl_3):



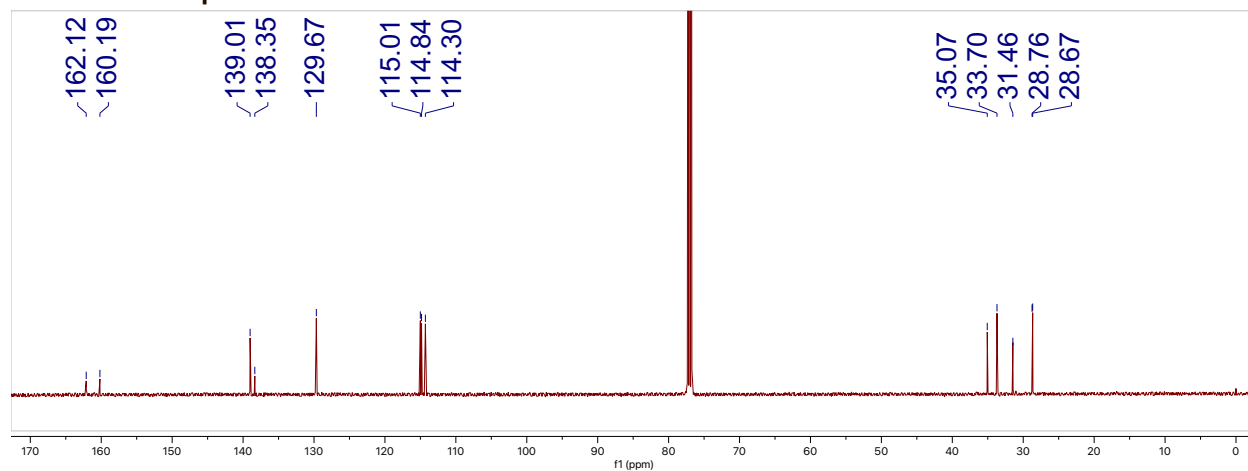
3p



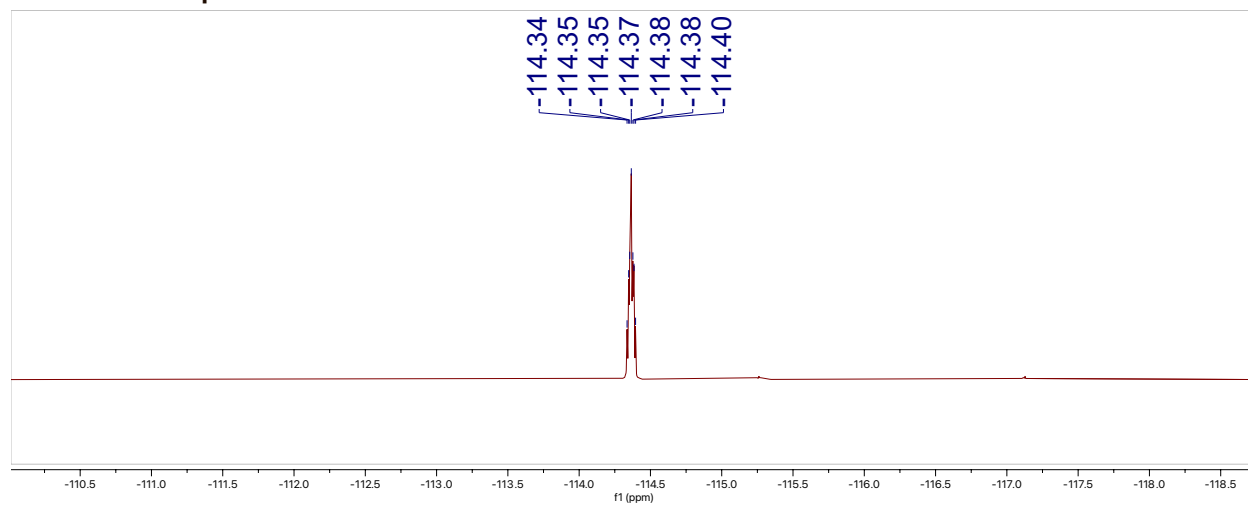
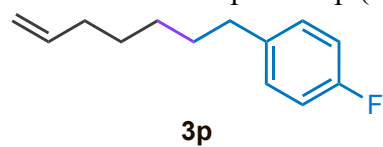
^{13}C NMR of Compound 3p (126 MHz, CDCl_3):



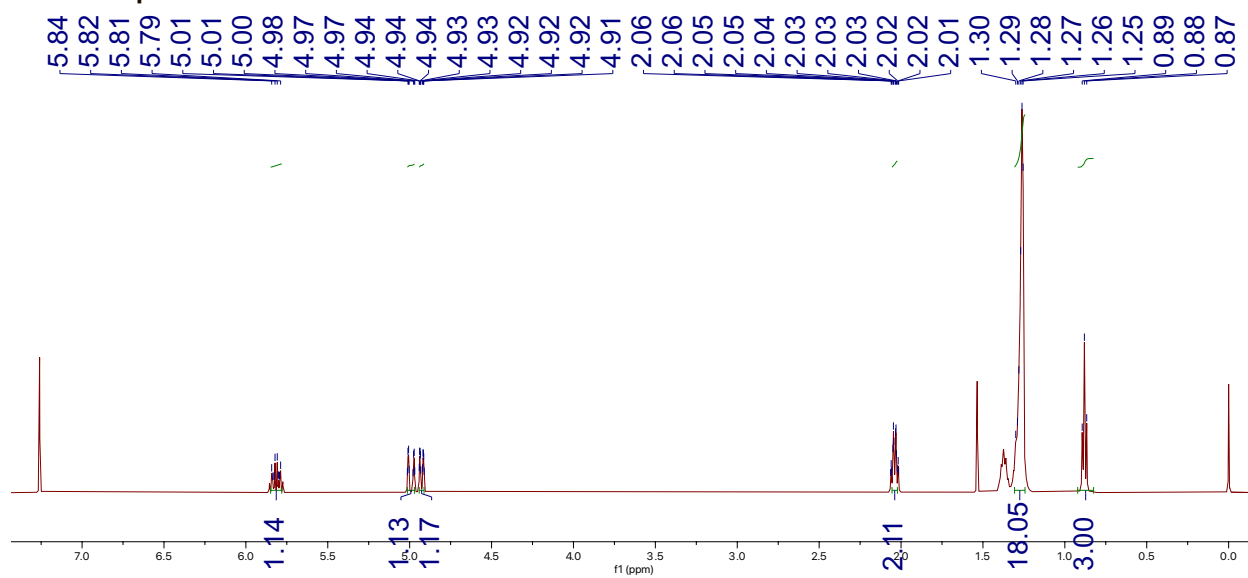
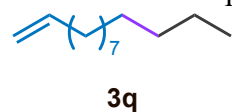
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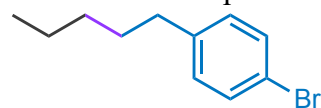
^{19}F NMR of Compound 3p (470 MHz, CDCl_3):



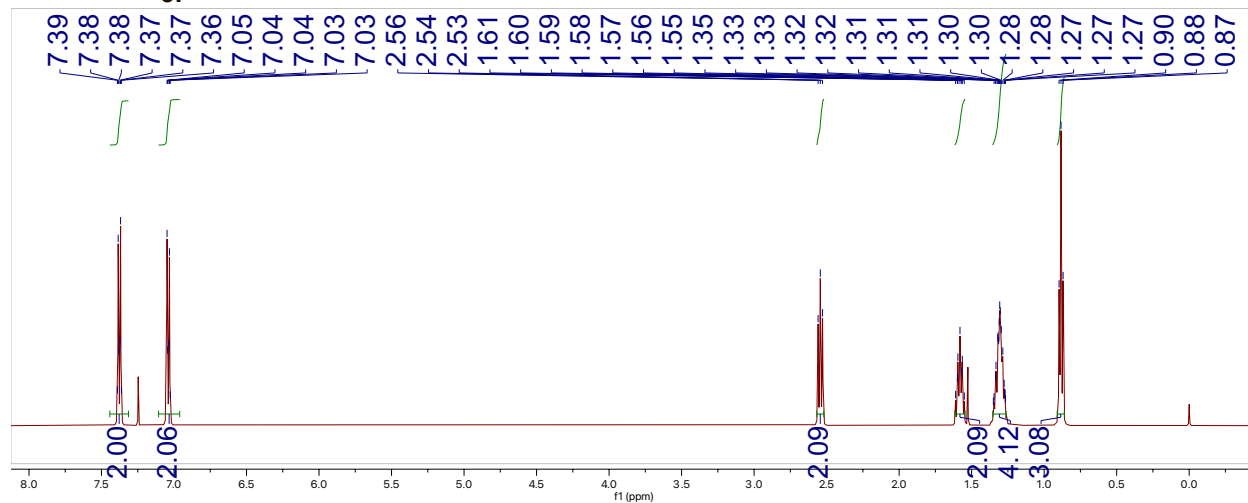
^1H NMR of Compound 3q (500 MHz, CDCl_3):



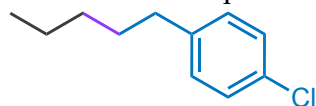
^1H NMR of Compound 3r (500 MHz, CDCl_3):



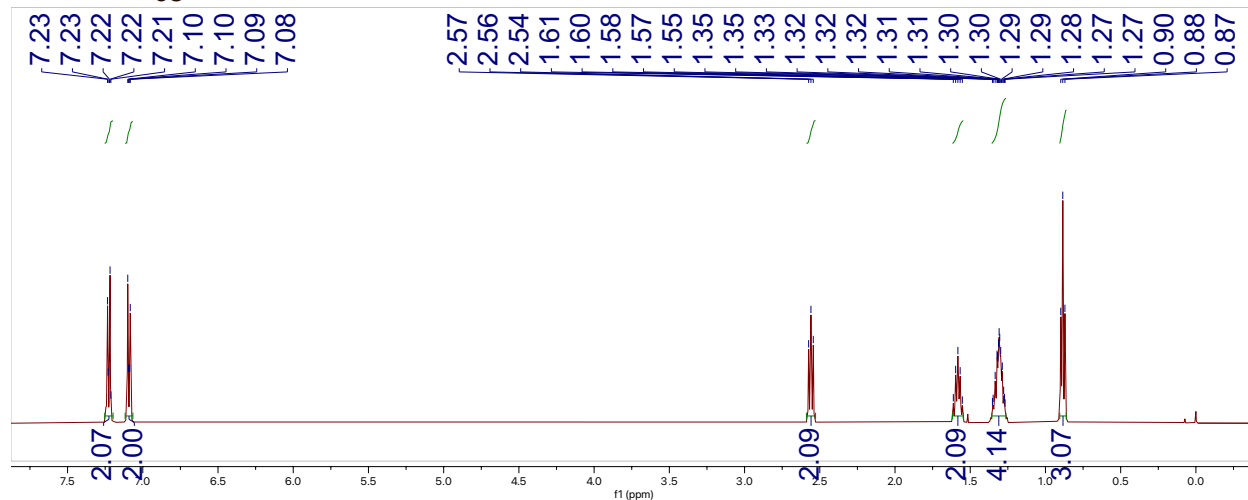
3r



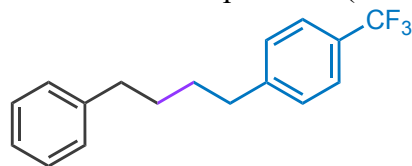
^1H NMR of Compound 3s (500 MHz, CDCl_3):



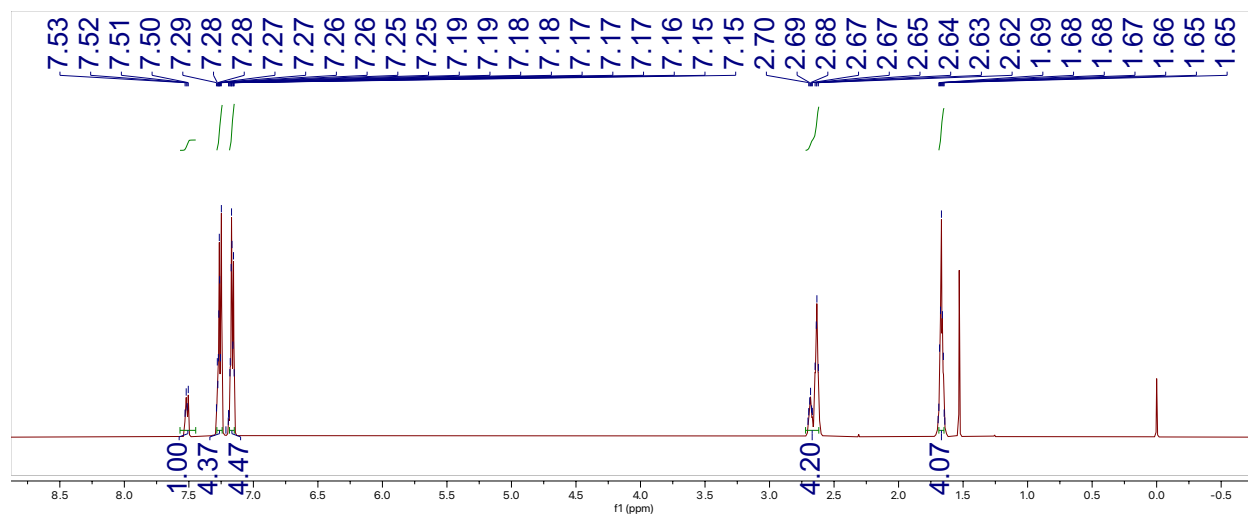
3s



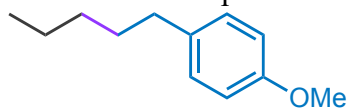
^1H NMR of Compound 3t (500 MHz, CDCl_3):



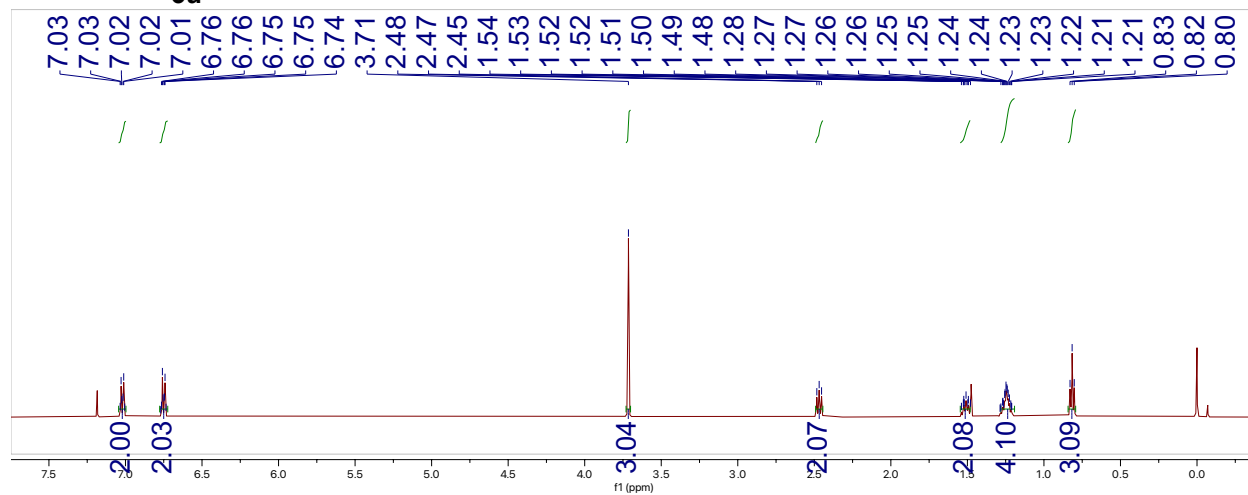
3t



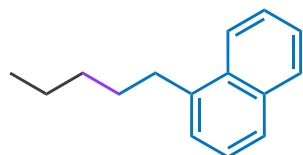
¹H NMR of Compound 3u (500 MHz, CDCl₃):



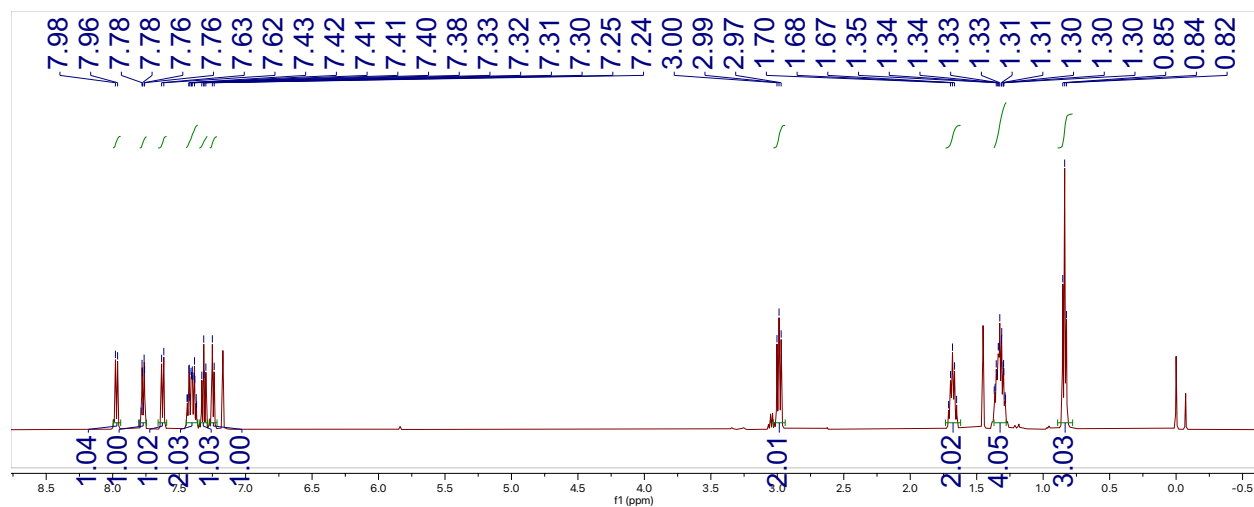
3u



¹H NMR of Compound 3v (500 MHz, CDCl₃):



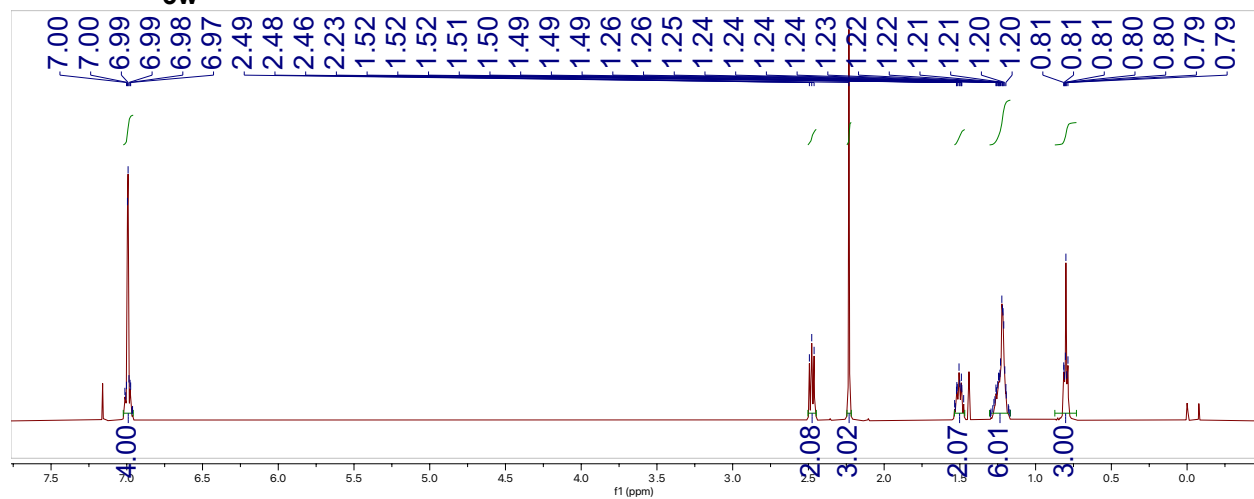
3v



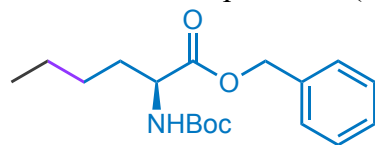
¹H NMR of Compound 3w (500 MHz, CDCl₃):



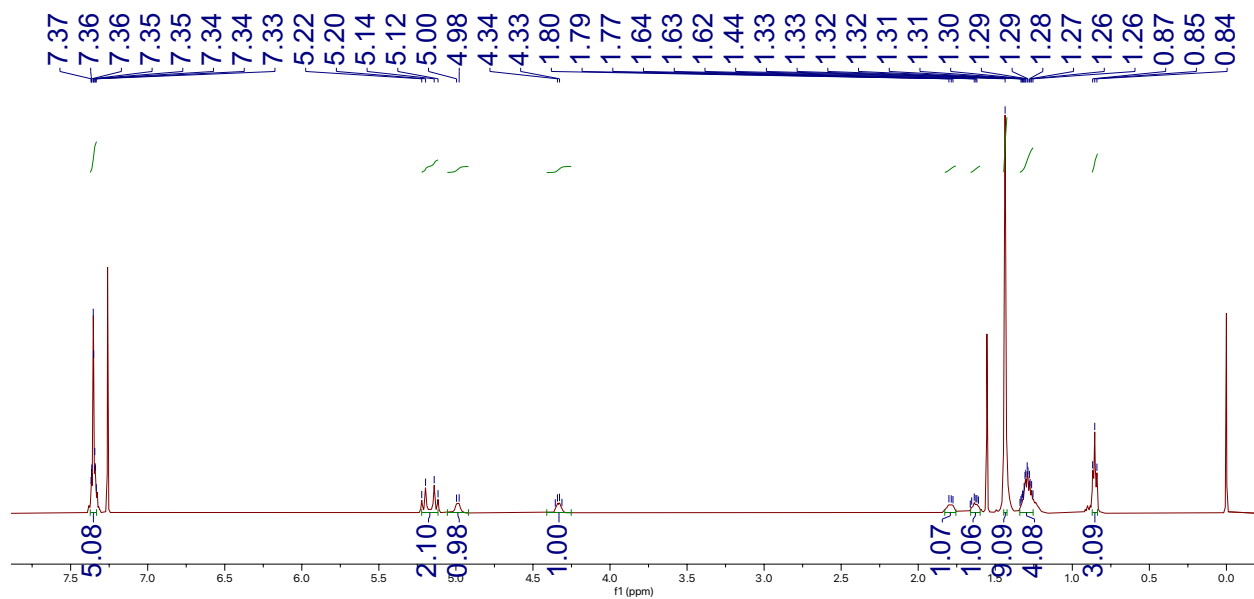
3w



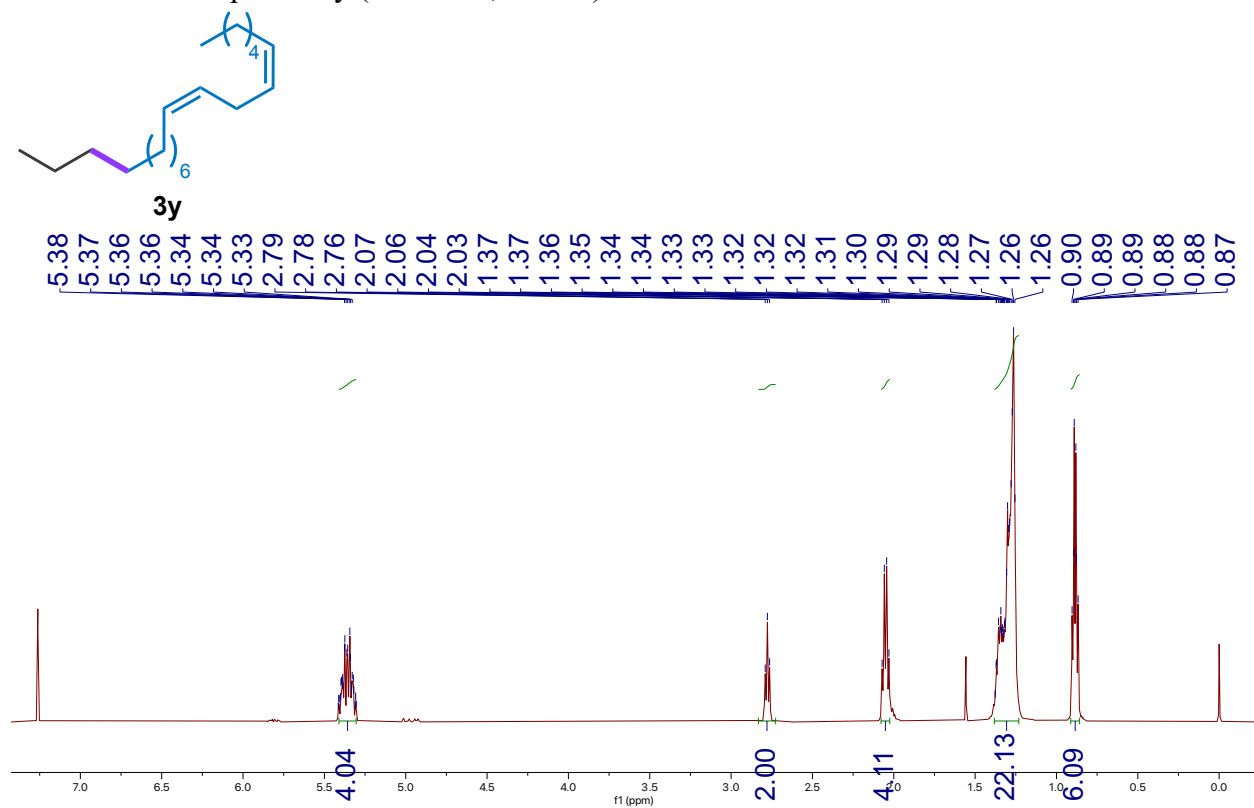
¹H NMR of Compound 3x (500 MHz, CDCl₃):



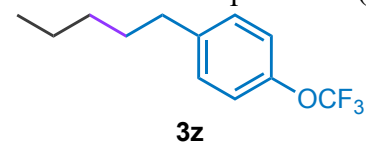
3x

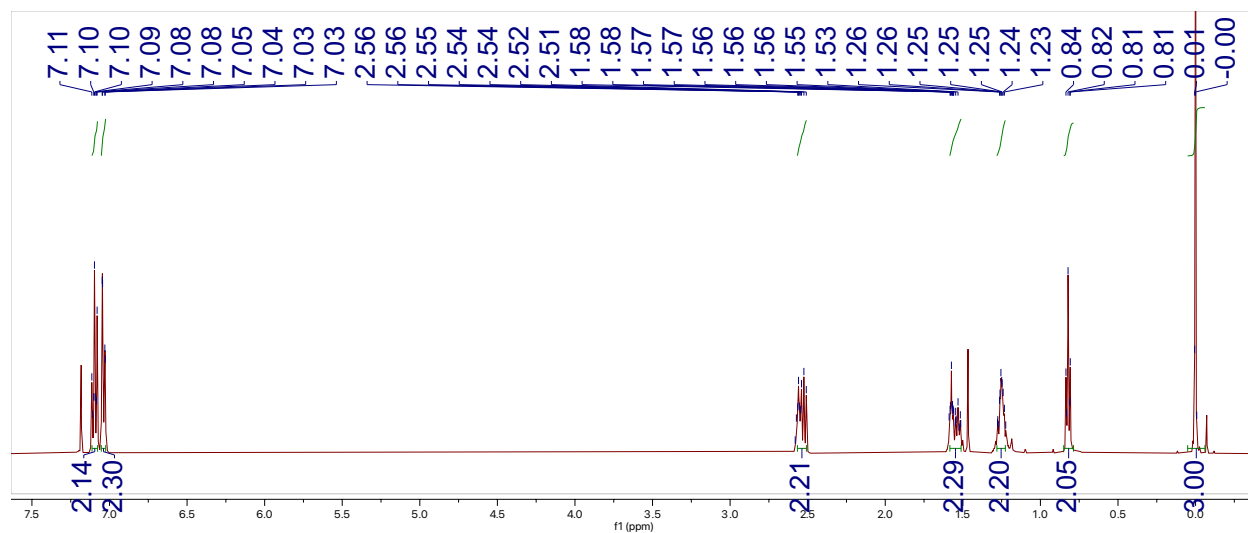


¹H NMR of Compound 3y (500 MHz, CDCl₃):

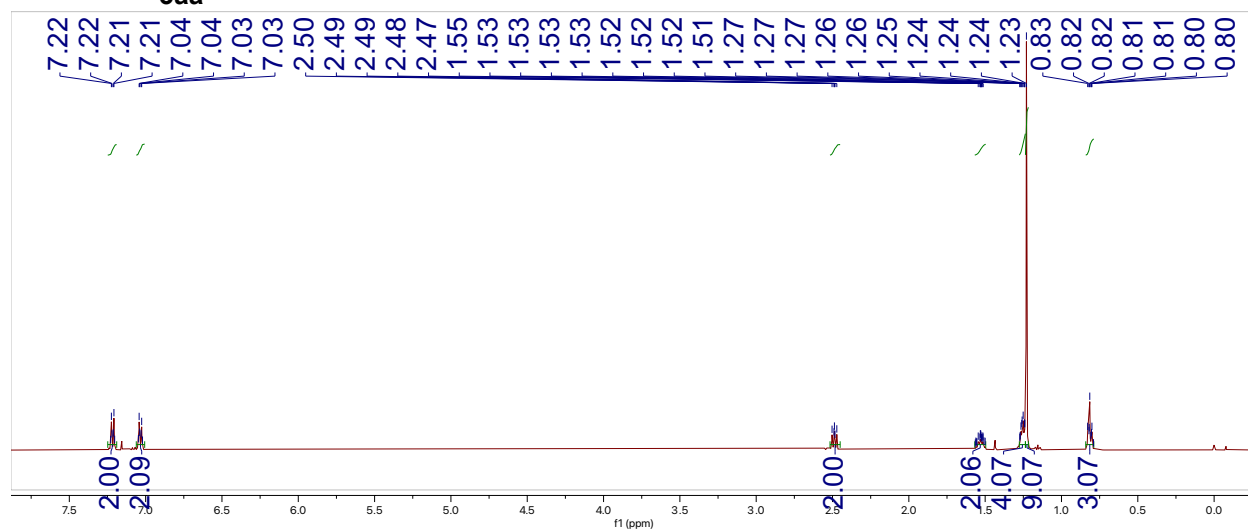
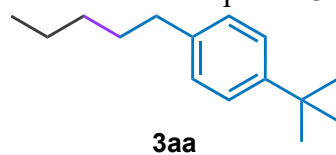


¹H NMR of Compound 3z (500 MHz, CDCl₃):

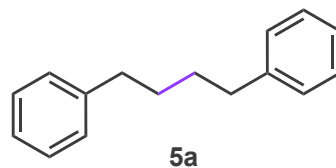


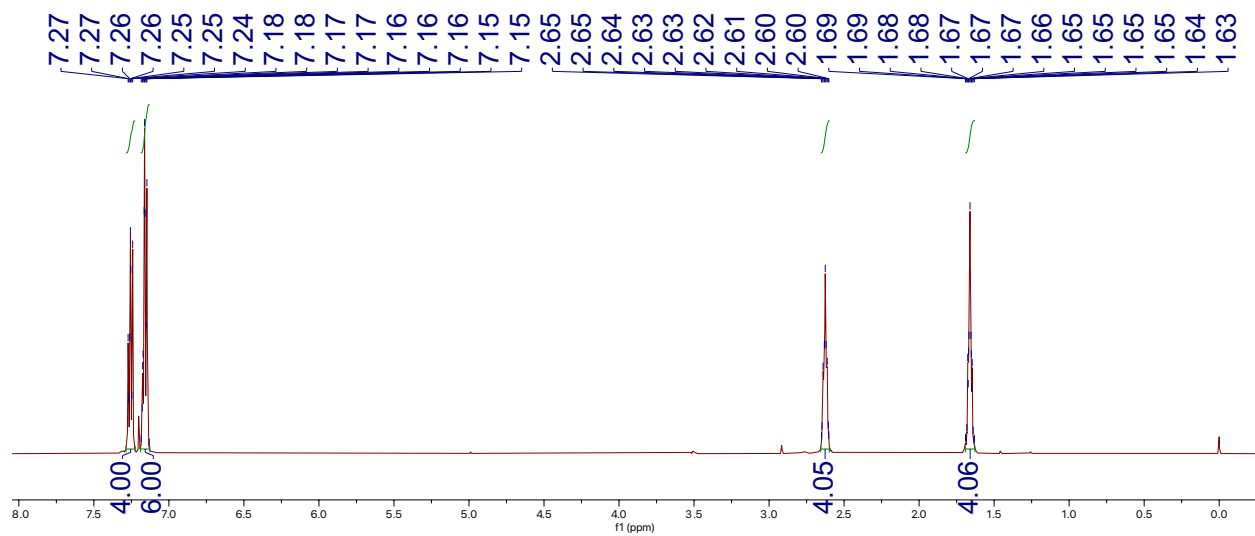


¹H NMR of Compound 3aa (500 MHz, CDCl₃):

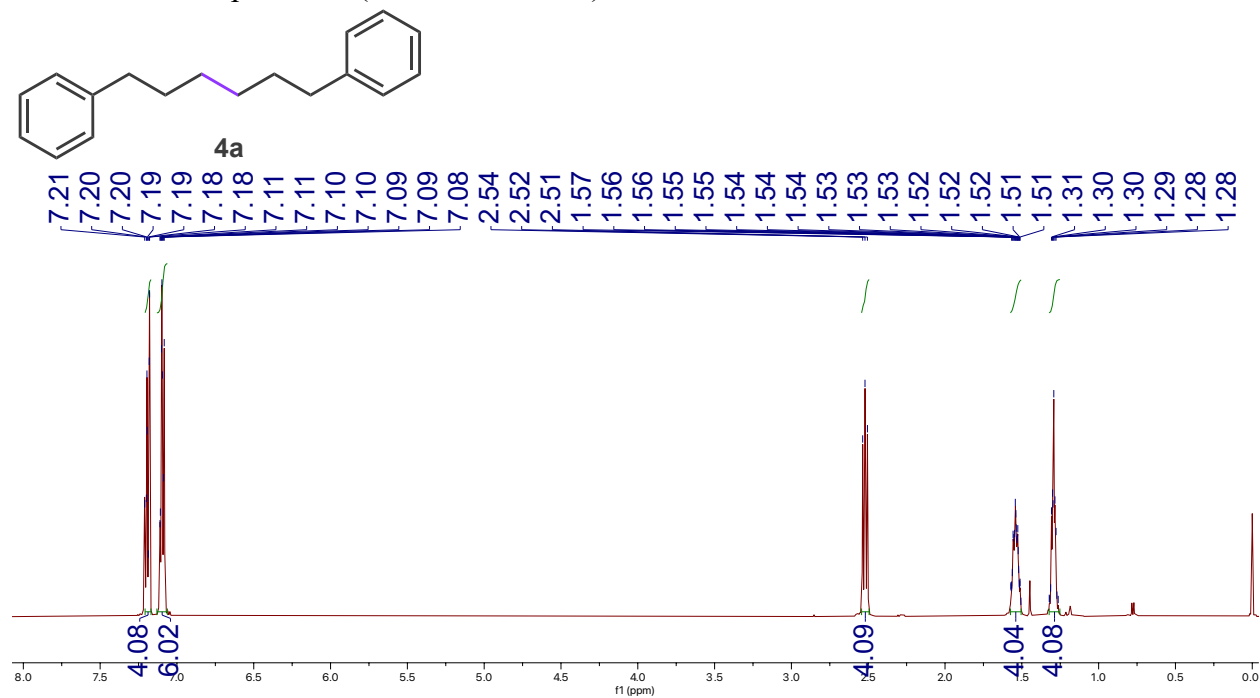


¹H NMR of Compound 5a (500 MHz, CDCl₃):

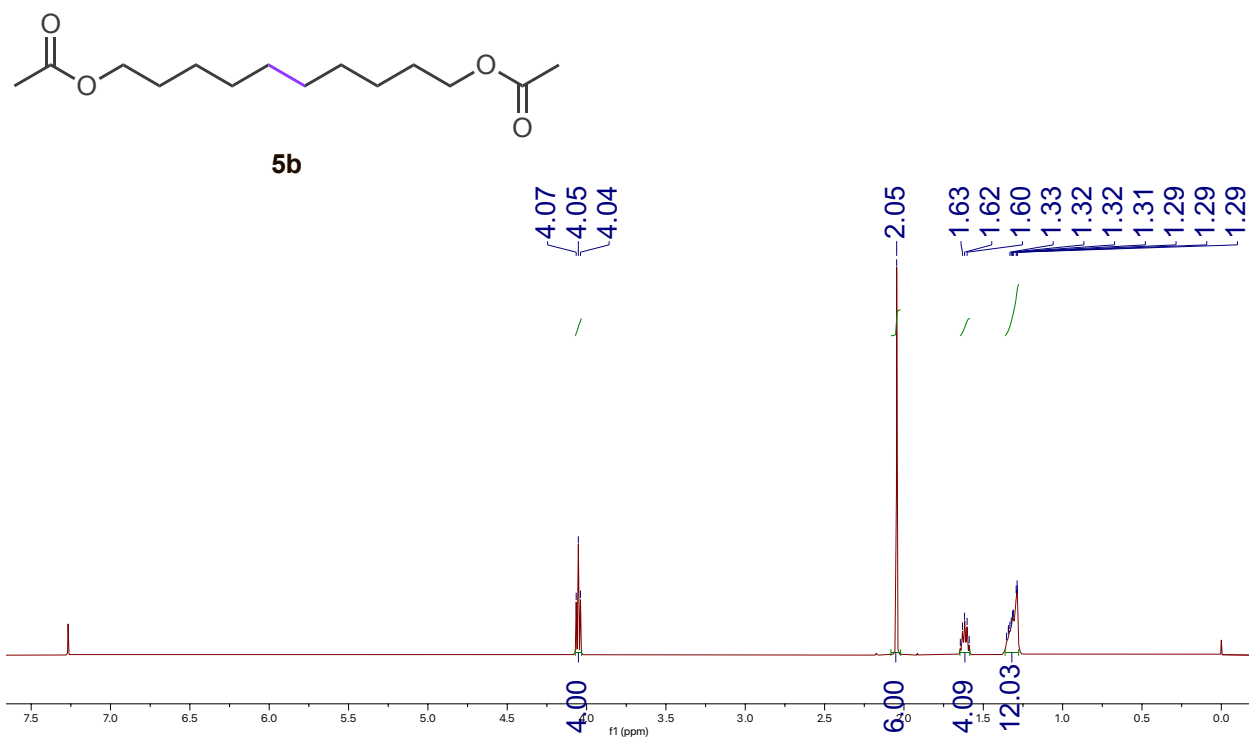




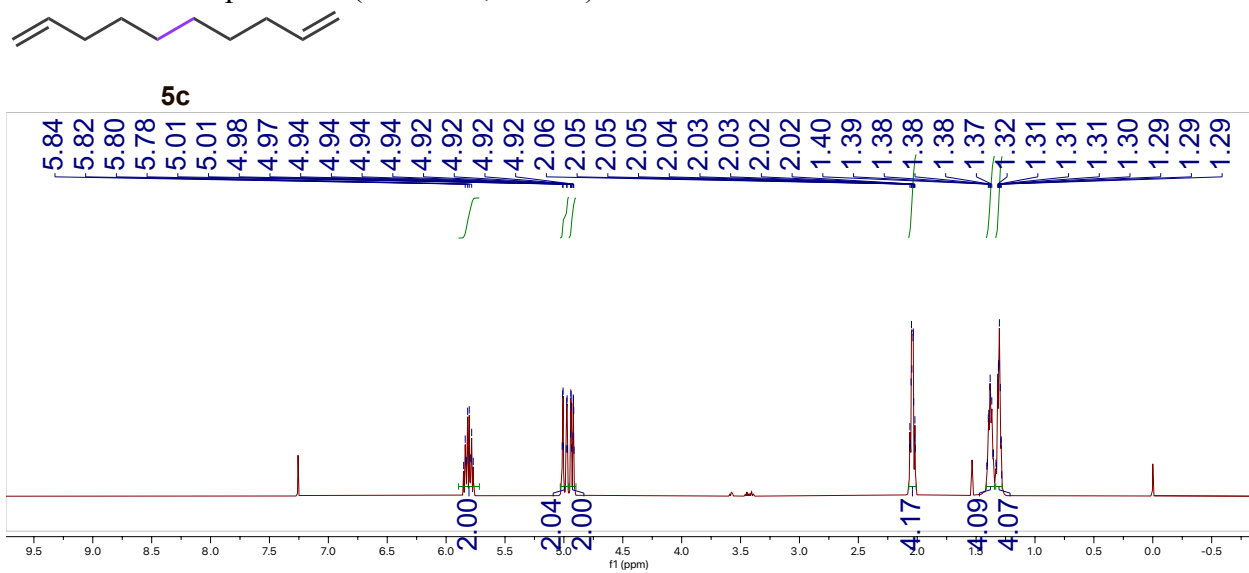
¹H NMR of Compound 4a (500 MHz, CDCl₃):



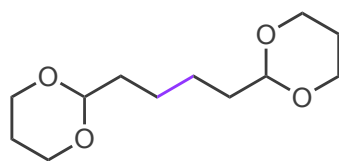
¹H NMR of Compound 5b (500 MHz, CDCl₃):



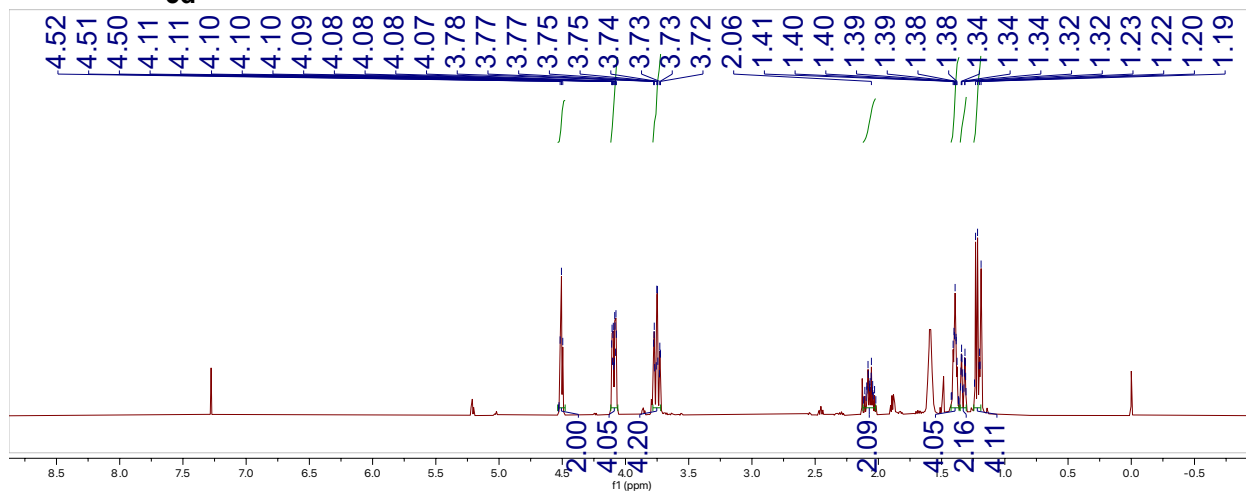
^1H NMR of Compound 5c (500 MHz, CDCl_3):



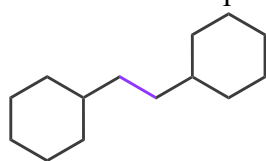
^1H NMR of Compound 5d (500 MHz, CDCl_3):



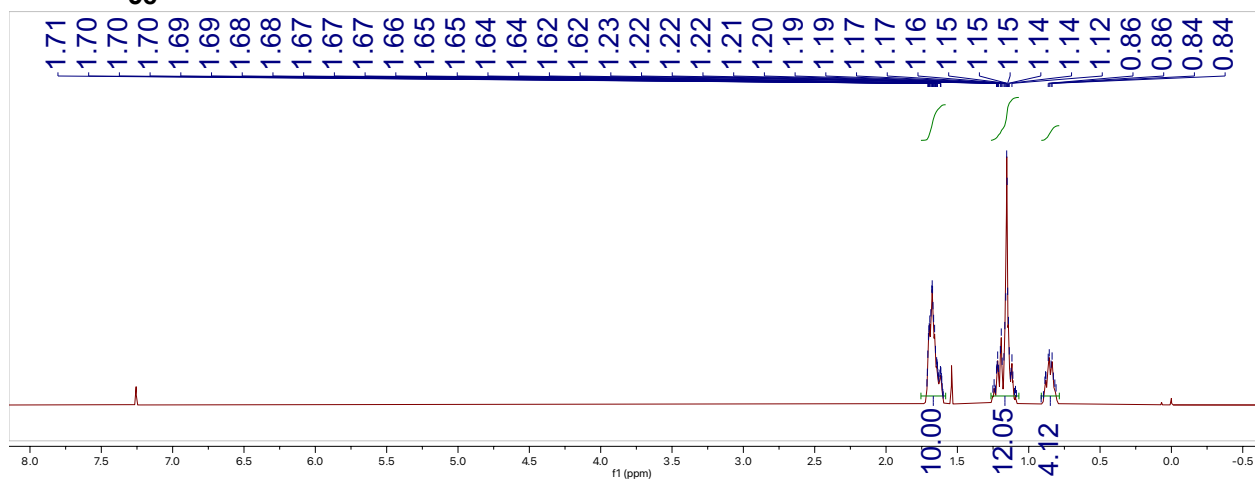
5d



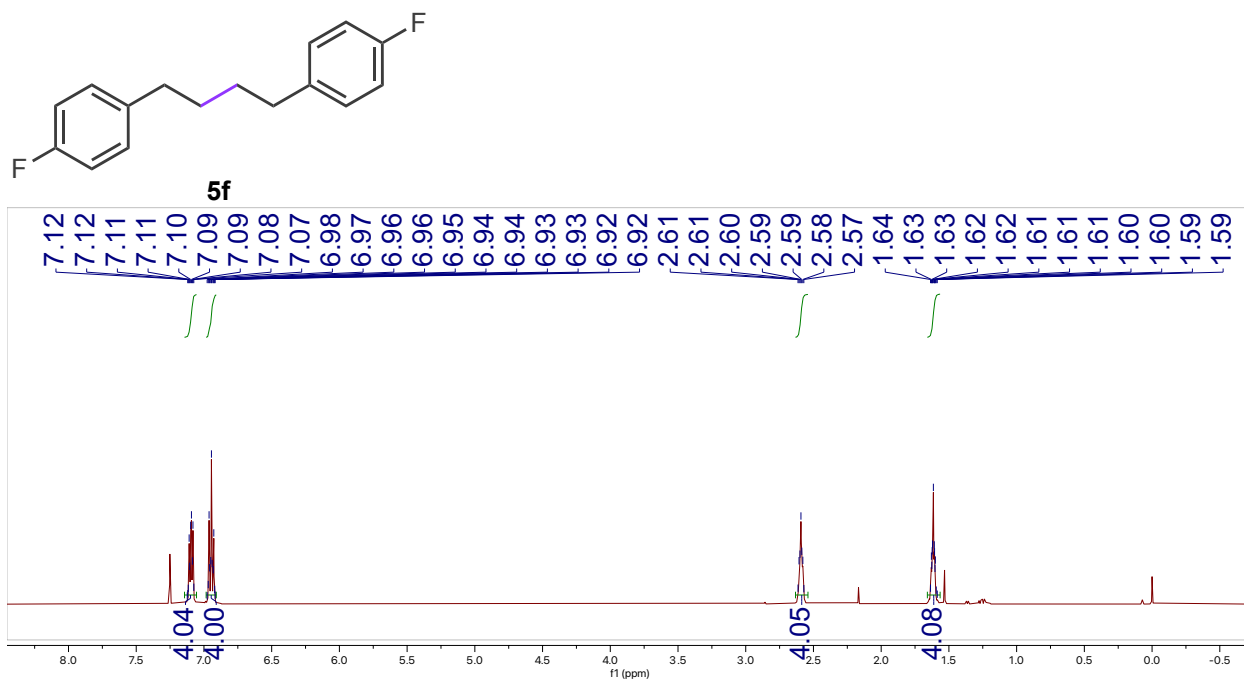
¹H NMR of Compound 5e (500 MHz, CDCl₃):



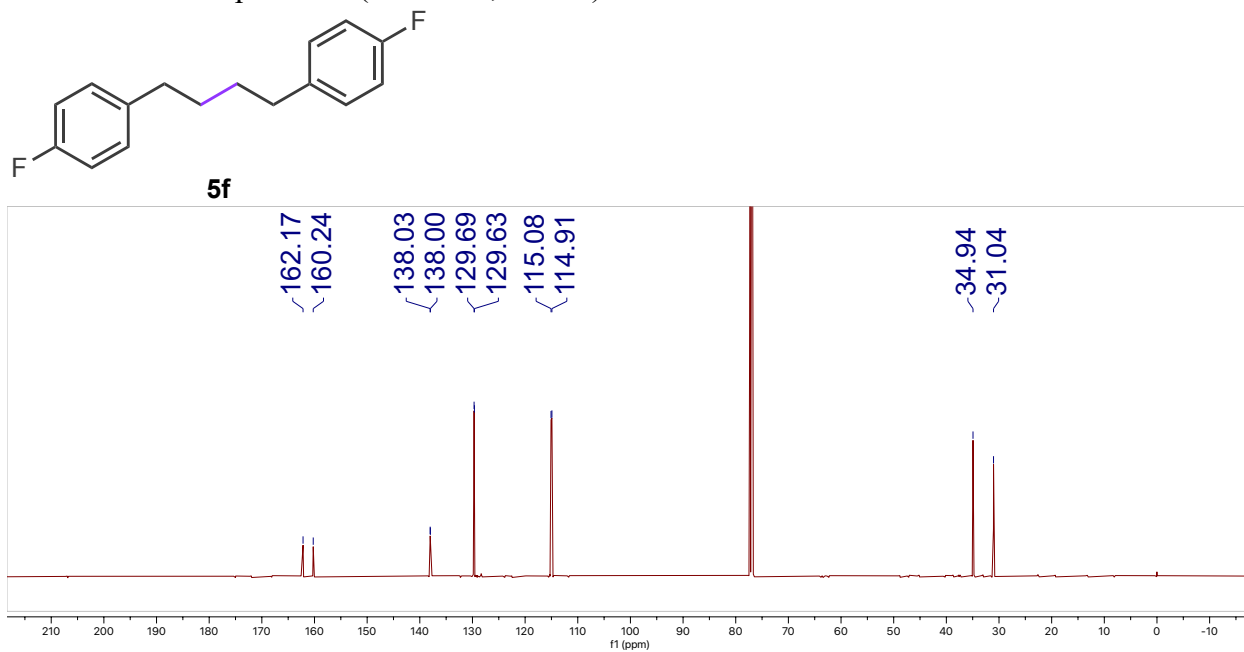
5e



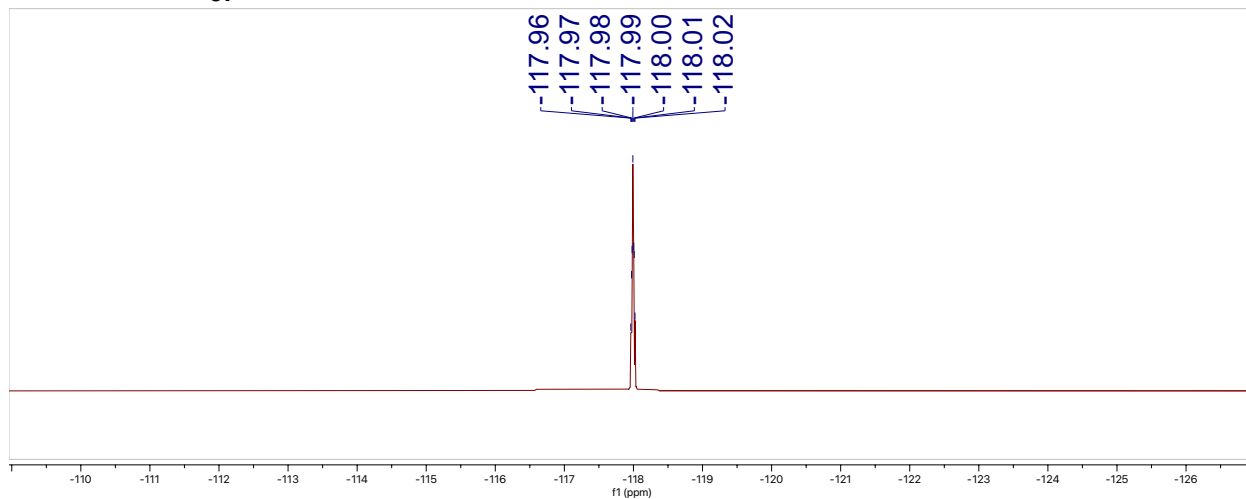
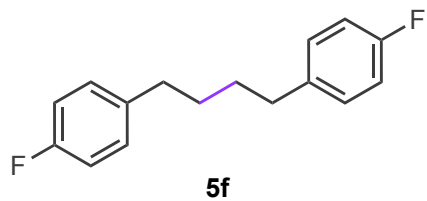
¹H NMR of Compound 5f (500 MHz, CDCl₃):



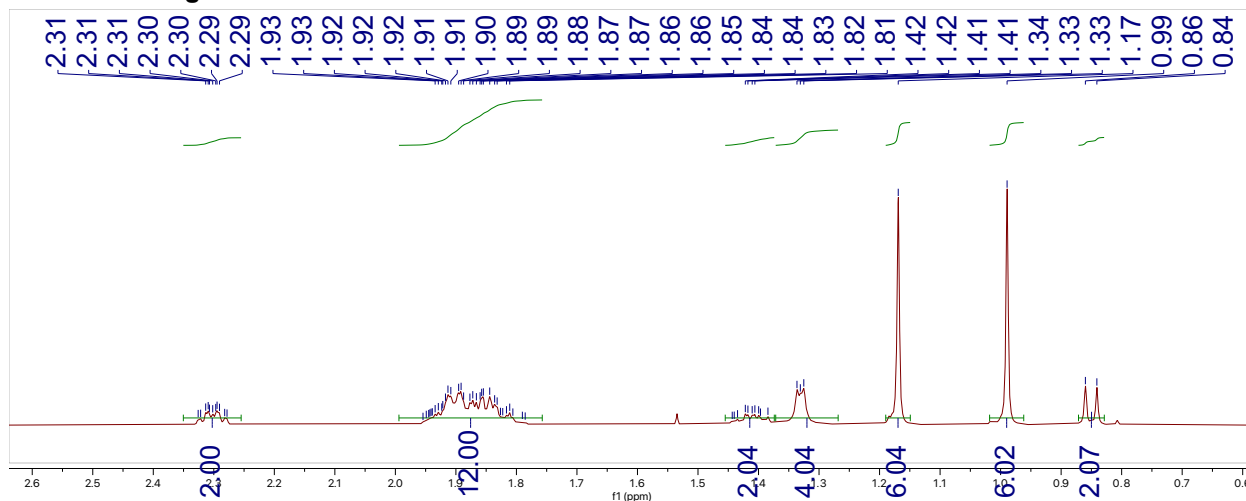
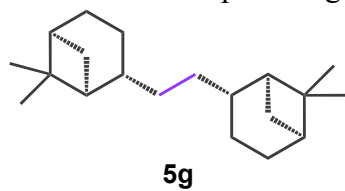
¹³C NMR of Compound 5f (126 MHz, CDCl₃):



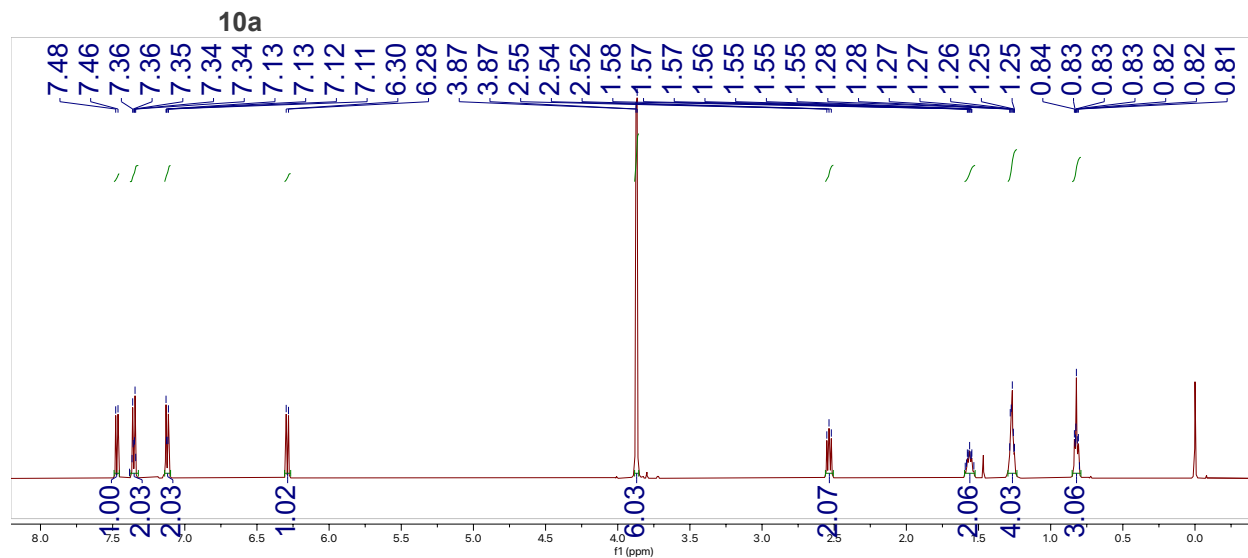
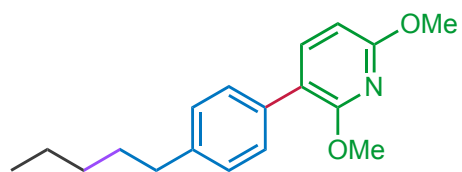
¹⁹F NMR of Compound 5f (470 MHz, CDCl₃):



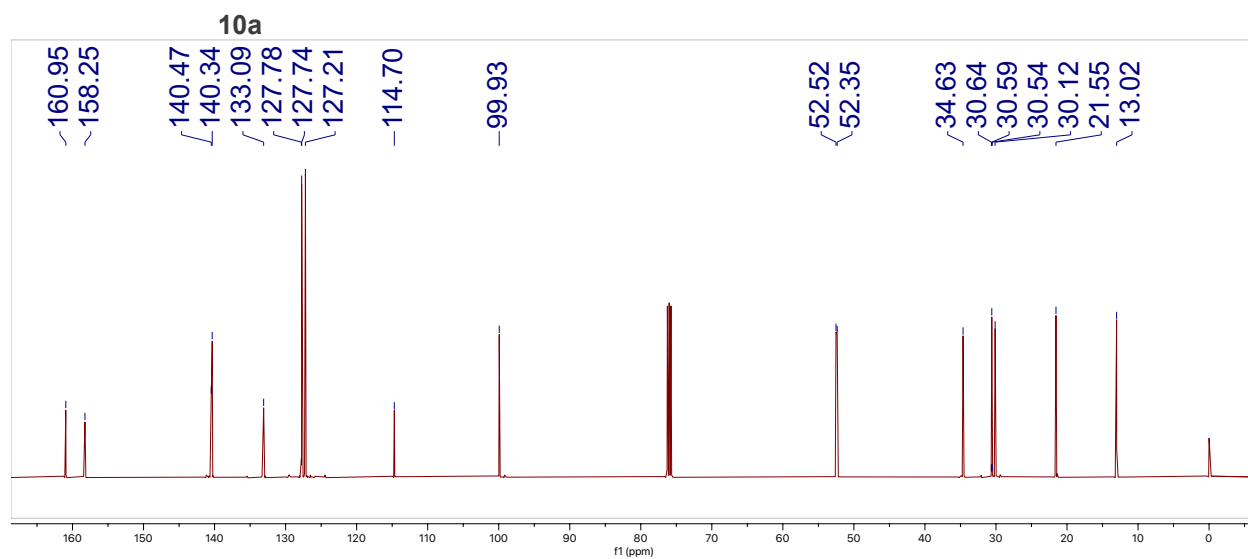
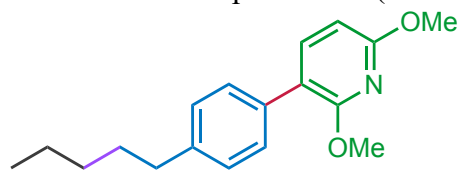
¹H NMR of Compound **5g** (500 MHz, CDCl₃):



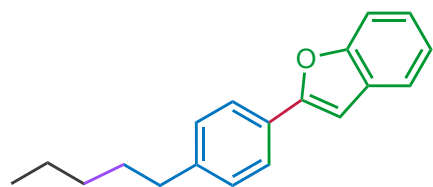
¹H NMR of Compound **10a** (500 MHz, CDCl₃):



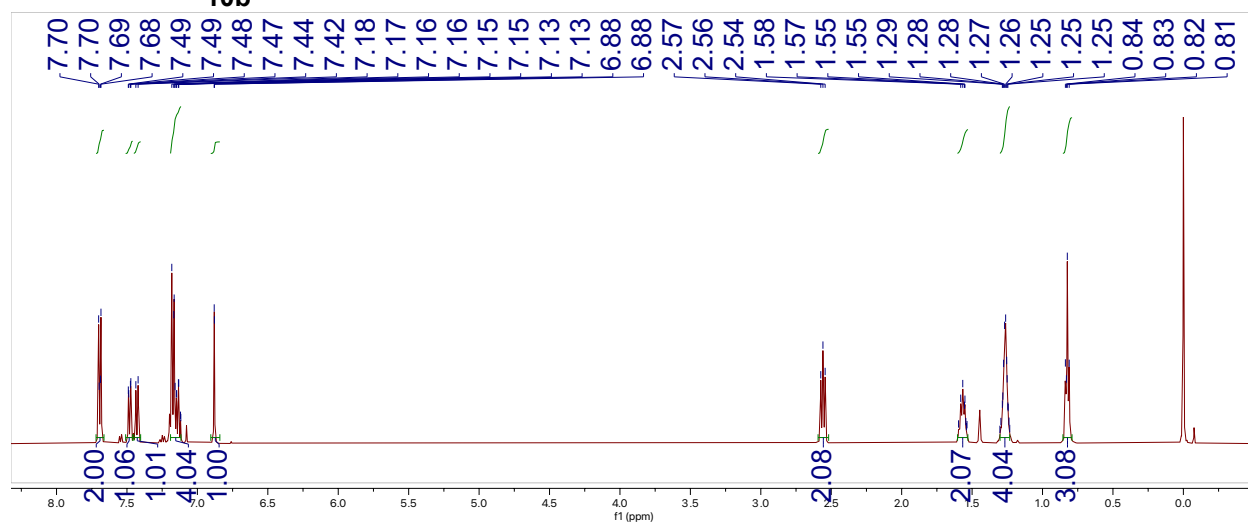
¹³C NMR of Compound 10a (126 MHz, CDCl₃):



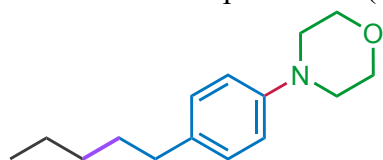
¹H NMR of Compound 10b (500 MHz, CDCl₃):



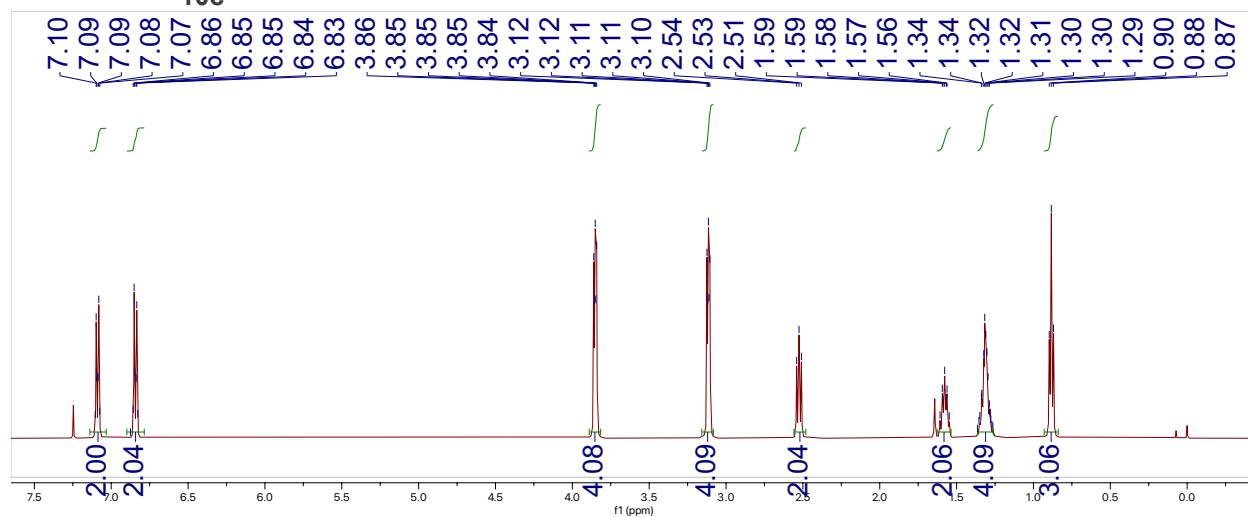
10b



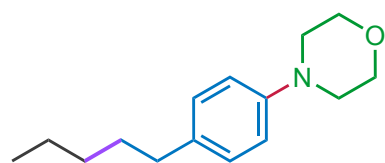
^1H NMR of Compound 10c (500 MHz, CDCl_3):



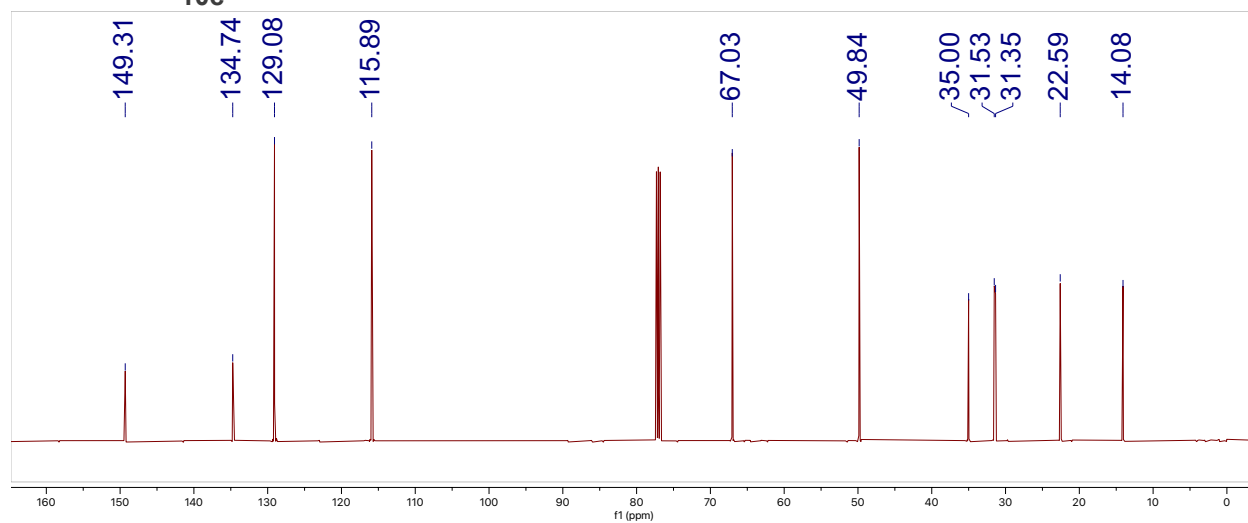
10c



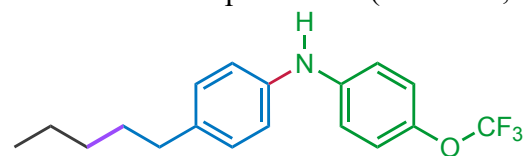
^{13}C NMR of Compound 10c (126 MHz, CDCl_3):



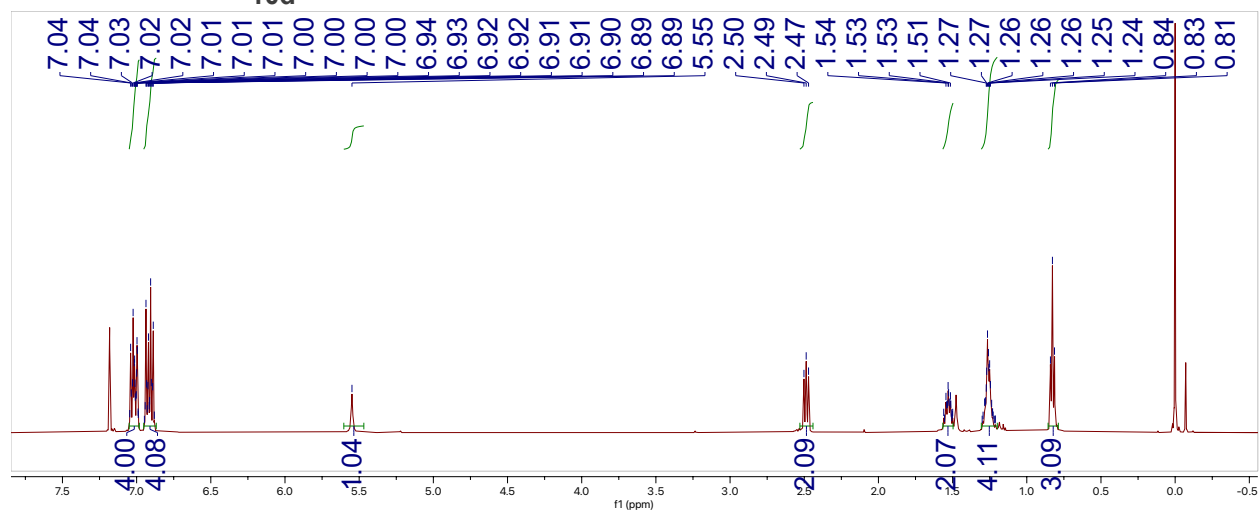
10c



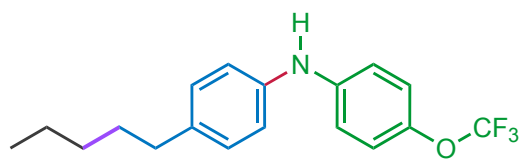
¹H NMR of Compound 10d (500 MHz, CDCl₃):



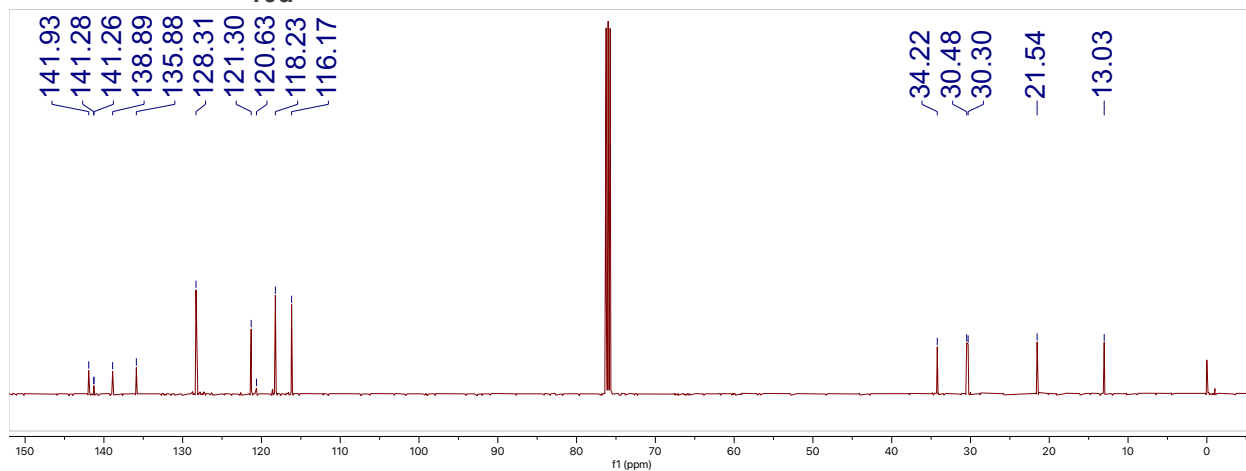
10d



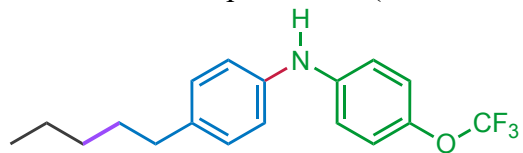
¹³C NMR of Compound 10d (126 MHz, CDCl₃):



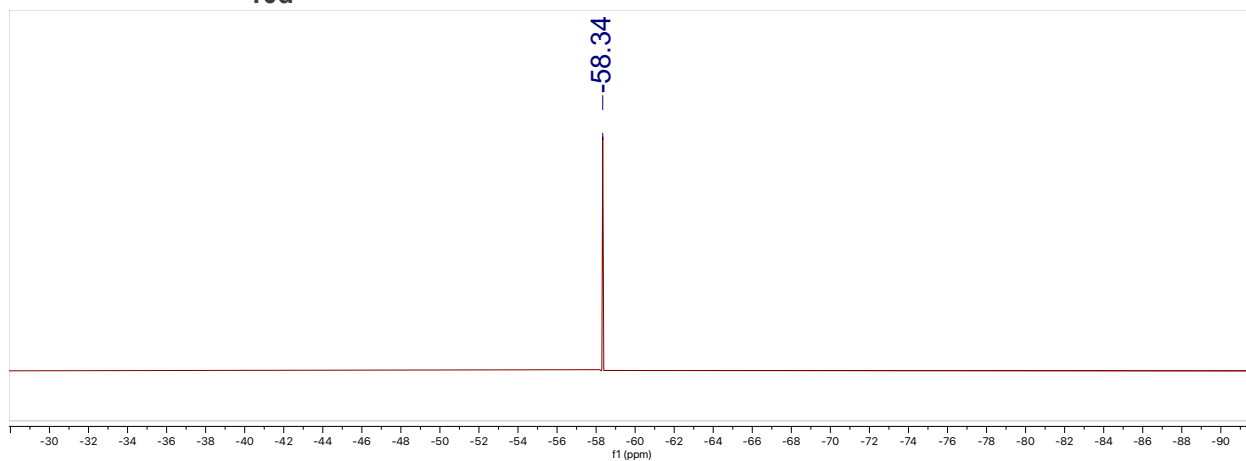
10d



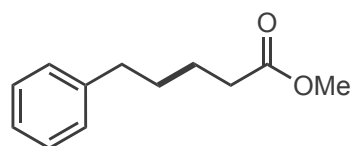
¹⁹F NMR of Compound 10d (470 MHz, CDCl₃):



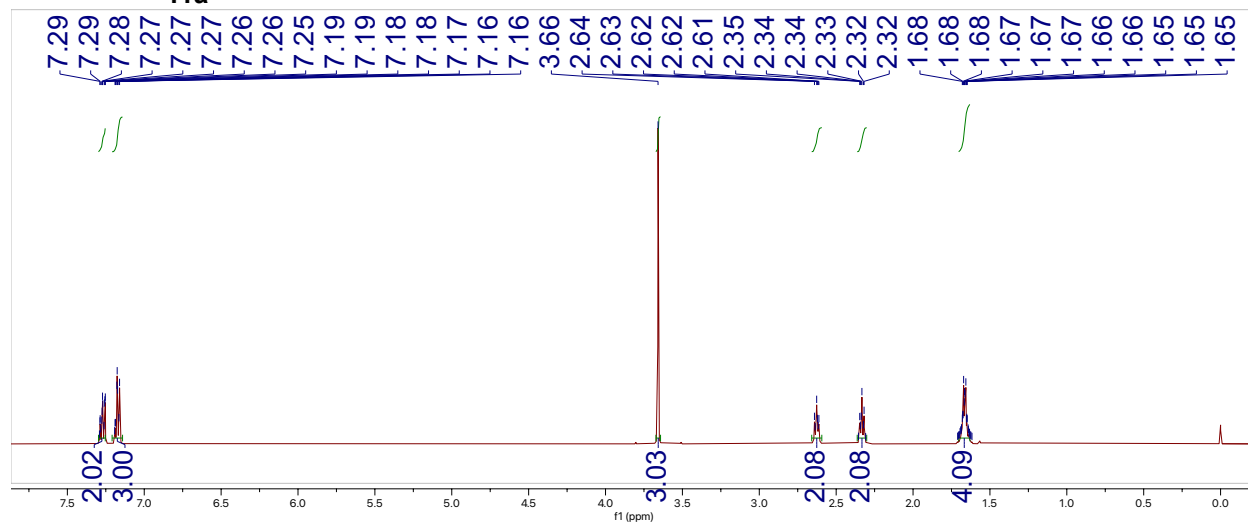
10d



¹H NMR of Compound 11a (500 MHz, CDCl₃):



11a



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