Supporting Information

Visible-light-induced 1,3-difunctionalization of allylboronic esters enabled by 1,2-boron shift

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Table of Contents

1. General Information

All chemical reagents were obtained commercially and used without further purification. The progress of reactions was monitored using Thin Layer Chromatography (TLC) under UV light at wavelengths of 254 nm and 365 nm. Products were purified via column chromatography on silica gel with a mesh size of 200-300. All ^{1}H, ^{13}C, ^{19}F and ^{11}B NMR spectra were recorded on a Bruker Avance spectrometer operating at either 600 MHz or 400 MHz. Proton chemical shifts (δ) are reported in parts per million (ppm), referencing tetramethylsilane as an internal standard. NMR spectra were recorded in $CDCl_3$ at room temperature (20 ± 3 °C). High-resolution mass spectrometry (HRMS) was conducted using an Agilent Infinity II Q-TOF 6546 mass spectrometer with electrospray ionization (ESI). Allylboronic esters and enol triflates were prepared according to the reported literatures.[1]

2. Experimental Procedures

2.1 Emission spectrum of photoreactor lamp

The photochemical reaction was carried out under visible light irradiation by a blue LED at room temperature. RLH-18 8-position Photo Reaction System manufactured by Beijing Roger Tech Ltd. was used in this system. Eight 10 W blue LEDs were equipped in this Photo reactor. The blue LED's energy peak wavelength is 430 nm, peak width at half-height is 18.4 nm, lirradiance@10 W is 237.57 mW/cm^2. The reaction vessel is a borosilicate glass tube with 1.5 cm from the lamp, and no filter is applied.

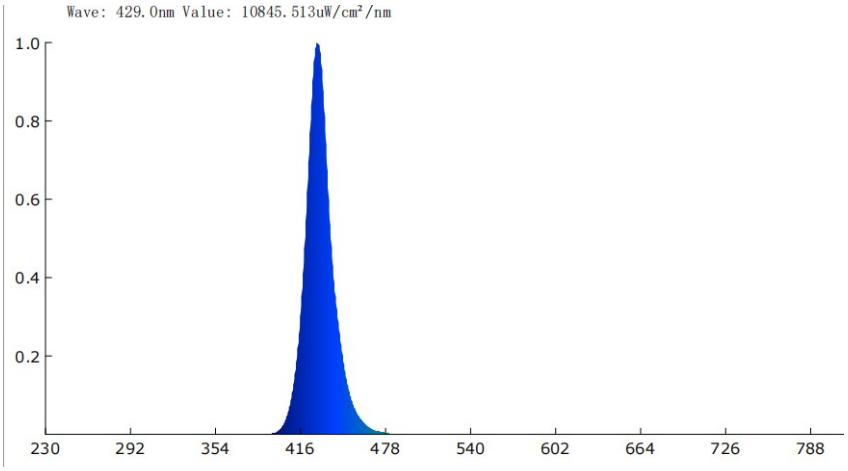


Figure S1. The emission spectrum of our lamp (blue LED)

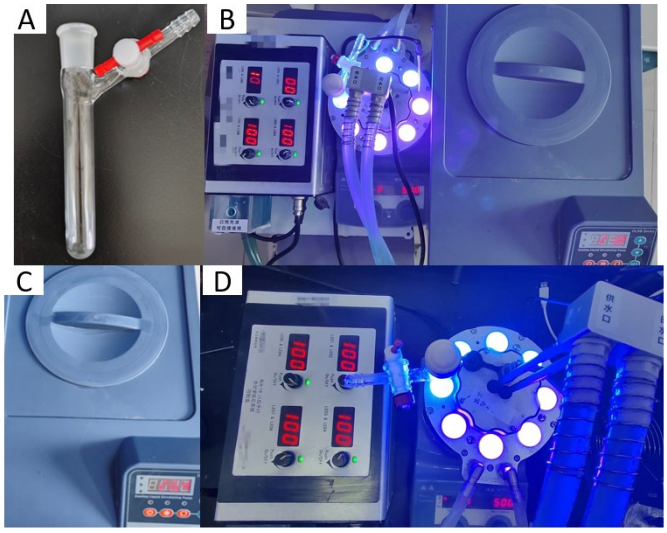
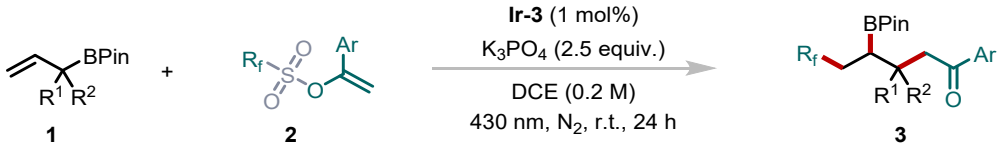


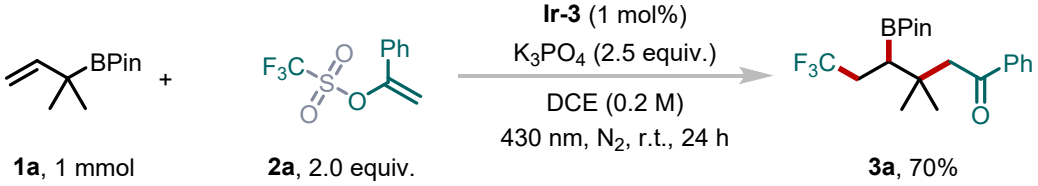
Figure S2. A: Schlenk tube; **B:** Total reaction system; **C**: Cooling water circuit; **D**: Photoreactor

2.2 General experimental procedures for the desired product



A mixture of allylboronic ester **1** (0.2 mmol), vinyl triflate **2** (0.4 mmol, 2.0 equiv.), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.002 mmol, 1 mol%), K_3PO_4 (0.5 mmol, 2.5 equiv.), and DCE (1.0 mL) was sequentially added to a 25 mL Schlenk tube. The reaction mixtures were degassed with N_2 and then irradiated with a 10 W blue LED (430 nm) at room temperature under N_2 atmosphere for 24 hours. After this period, the reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude products were purified by silica gel chromatography, using petroleum ether/ethyl acetate (200:1) as the eluting solvent, to yield the desired products **3**.

2.3 Scale-up synthesis



A mixture of allylboronic ester **1a** (1 mmol), 1-phenyl vinyl trifluoromethanesulfonate **2a** (2 mmol, 2.0 equiv.), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.01 mmol, 1 mol%), K_3PO_4 (2.5 mmol, 2.5 equiv.), and DCE (5.0 mL) was sequentially added to a 25 mL Schlenk

tube. The reaction vessel was then irradiated with 10 W blue LED (430 nm) at room temperature under N_2 atmosphere for 24 hours. Afterward, the reaction was quenched with H_2O, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product were purified by silica gel chromatography using petroleum ether/ethyl acetate as the eluting solvent, yielding the desired product **3a** (269 mg, 70%).

2.4 Procedure for emission quenching experiments

Emission intensities were recorded using an F-4600 FL Spectrophotometer. The solutions were irradiated at 392 nm (Maximum absorption wavelength of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] and fluorescence was measured from 350 nm to 750 nm. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] with different concentrations of **2a** in degassed anhydrous solvent in 10 mm path length quartz cuvette was collected.

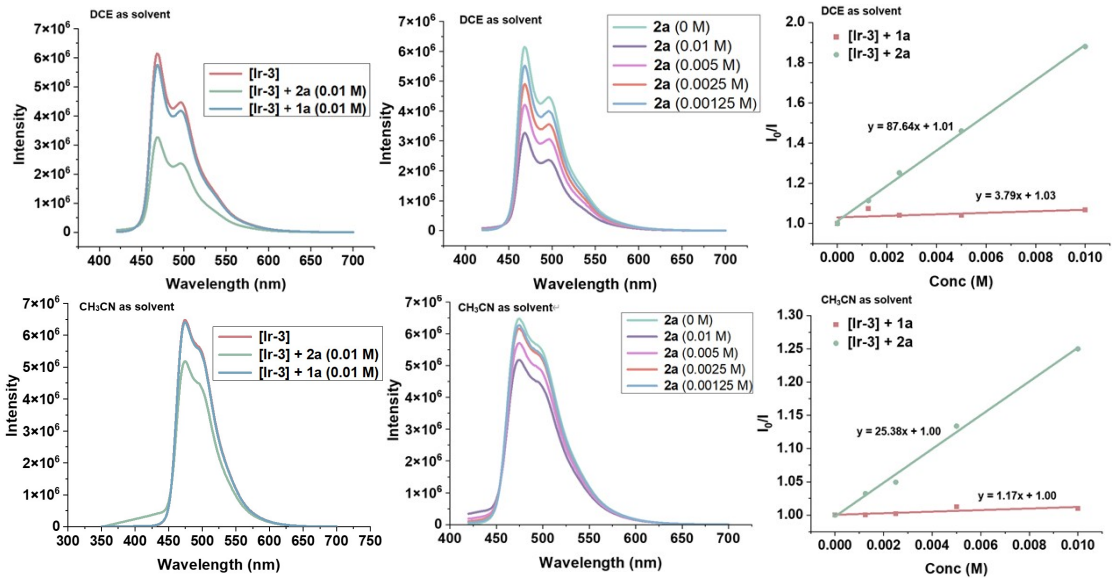


Figure S3. Luminescence quenching experiments

2.5 Cyclic voltammetry experiment

Cyclic voltammetry was performed on the CHI-660E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). Cyclic voltammograms of 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) and 1-phenyl vinyl trifluoromethanesulfonate (**2a**) in CH_3CN using glassy carbon disk electrode as working electrode, Pt wire as the counter electrode, and silver chloride electrode (Ag/AgCl) as reference electrode at 100 mV/s scan rate.

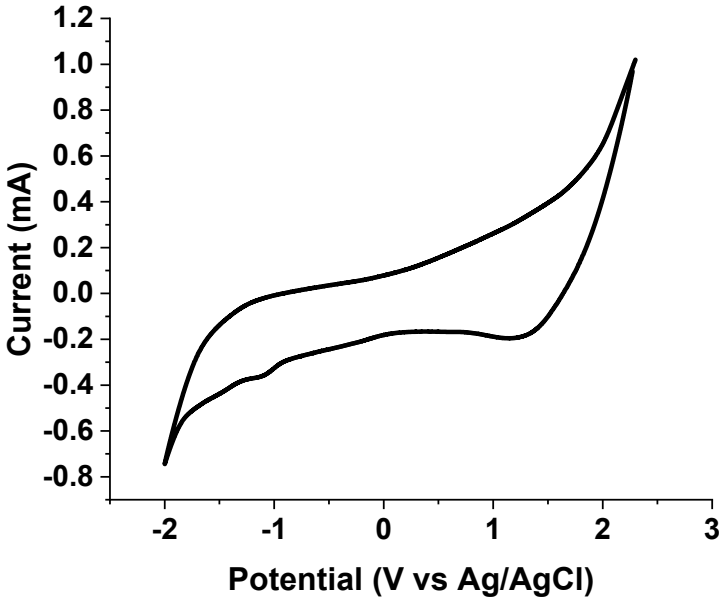
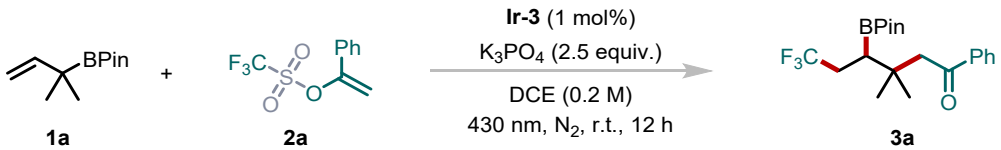


Figure S4. Cyclic voltammetry experiment of **2a**

2.6 Light on-off experiment

Reaction mixtures in a 25 mL reaction vessel were charged with allylboronic esters (**1a**) (0.2 mmol), 1-phenyl vinyl trifluoromethanesulfonate (**2a**) (0.4 mmol, 2.0 equiv.), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.002 mmol, 1 mol%), K_3PO_4 (0.5 mmol, 2.5 equiv.) and DCE (1.0 mL). The reaction mixtures were degassed by N_2, and then irradiated with 10 W blue LED. After 2 h, the lamps were turned off, and one vial was removed from the irradiation setup. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. The organic extracts were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The yield of the product was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as the internal standard. The remaining mixture was stirred in the absence of light for an additional 2 h. Then remove one of the tubes. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2. ^{1}H NMR analysis was performed every 2 h until the reaction time reached 12 h.



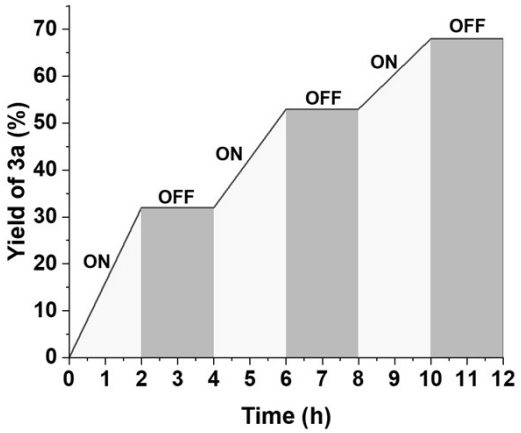


Figure S5 Light on-off experiments

2.7 Measurement of quantum yield

(a) Determination of the light intensity at 436 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry[2]. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30.0 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50.0 mg of phenanthroline and 11.25 g of sodium acetate in 50.0 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 436 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate with the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1:

$$mol\ Fe^{2+} = \frac{V * \Delta A}{L * \varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after the addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, L is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

$$photon\ flux = \frac{mol\ Fe^{2+}}{\varphi * t * f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ = 436 nm (0.998, vide infra). The photon flux was calculated to be 3.22 x 10^{-9} einstein s^{-1}.

Sample calculation:

$$\text{mol } Fe^{2+} = \frac{0.00235\ L\ *\ (2.7653 - 1.3853)}{1.0000\ cm\ *\ 11100\ L\ mol^{-1} cm^{-1}} = 2.92 * 10^{-7}\ mol$$

$$\text{photon flux} = \frac{2.92\ *\ 10^{-7}\ mol}{1.01\ *\ 90\ *\ 0.998} = 3.22 * 10^{-9}$$

(b) Determination of the quantum yield

A cuvette was pumped into the glovebox. A mixture of **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv.), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (0.002 mmol, 1 mol%) and K_3PO_4 (0.5 mmol, 2.5 equiv.) were dissolved in DCE (1.0 mL) under N_2 atmosphere. The sample was stirred and irradiated (λ = 436 nm) at room temperature for 1 h. After irradiation, the yield of product formed was determined by ^{1}H NMR. The quantum yield was determined using eq 3

$$\varphi = \frac{mol\ product}{flux * t * f} \quad (3)$$

$$f = 1 - 10^{-A} \quad (4)$$

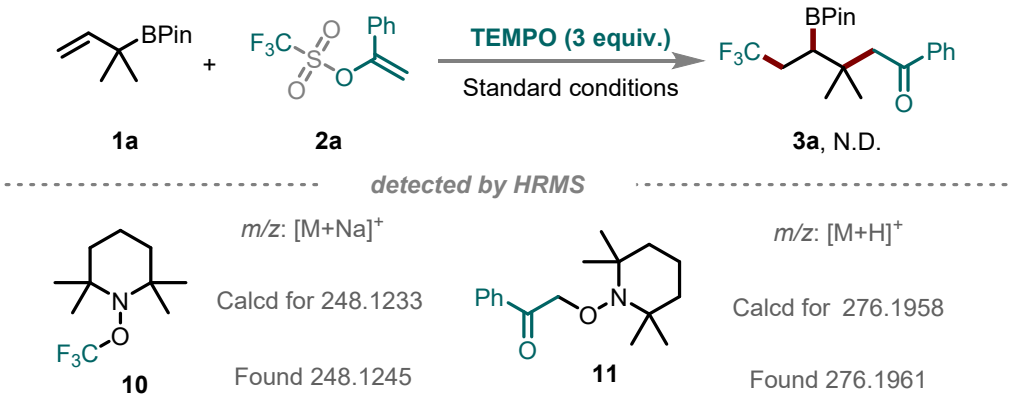
Sample calculation:

$$\varphi = \frac{1 *\ 10^{-5}\ mol}{3.22 *\ 10^{-9}\ einstein\ s^{-1} * 3600\ s * 0.999} = 0.86$$

Thus, 0.86 equivalent of product was formed for every photon absorbed by the photocatalyst, ruling out the possibility of chain propagation process.

2.8 Control experiments

The treatment of model reaction with 3.0 equivalent of radical scavengers such as 2,2,6,6-tetramethylpiperidinyl-1-oxide (TEMPO) or 1,1-Diphenylethylene failed to access the desired product efficiently, indicating the possible involvement of radical pathway in this transformation. Furthermore, compounds **10** - **13** were successfully detected by high-resolution mass spectrometry (HRMS), implying the existence of CF_3 radical and α-carbonyl radical (Figure S6 - 9).



Scheme S1 The trapping experiment of TEMPO

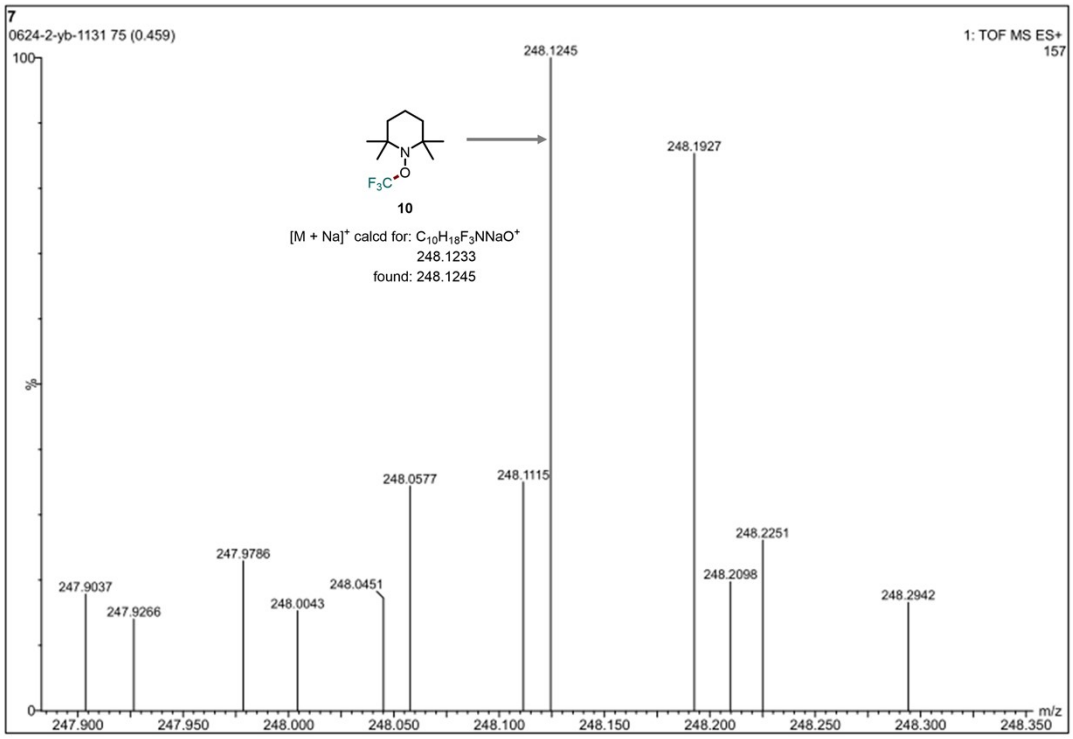


Figure S6. The HRMS analysis of compound **10**

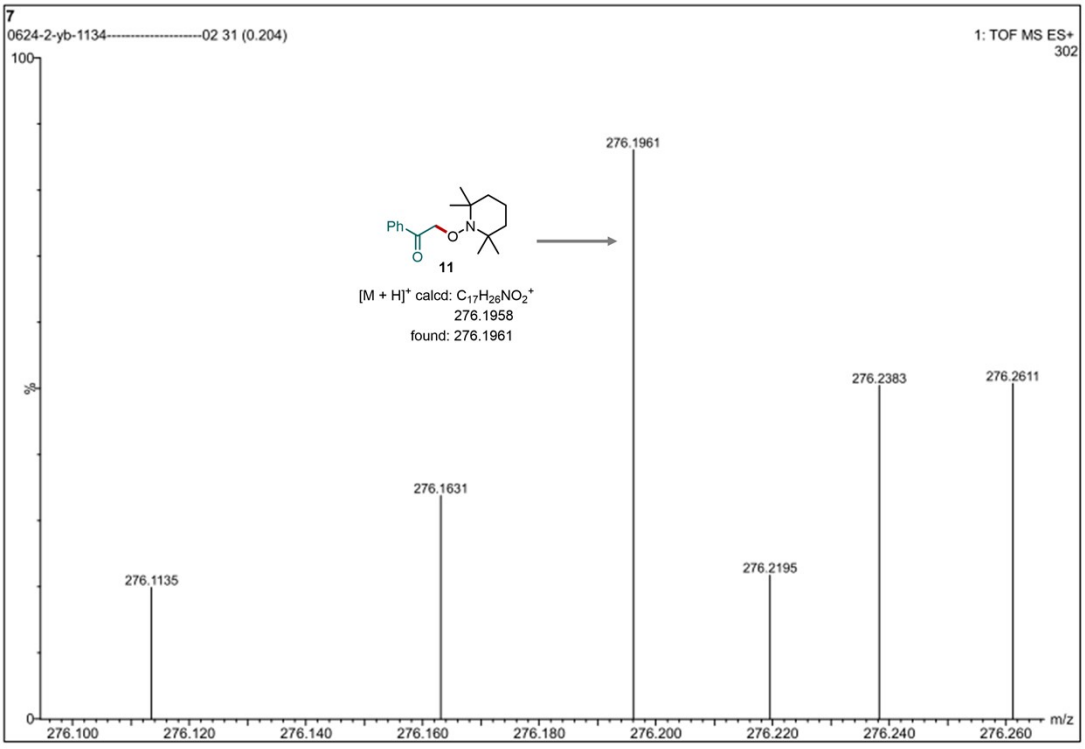
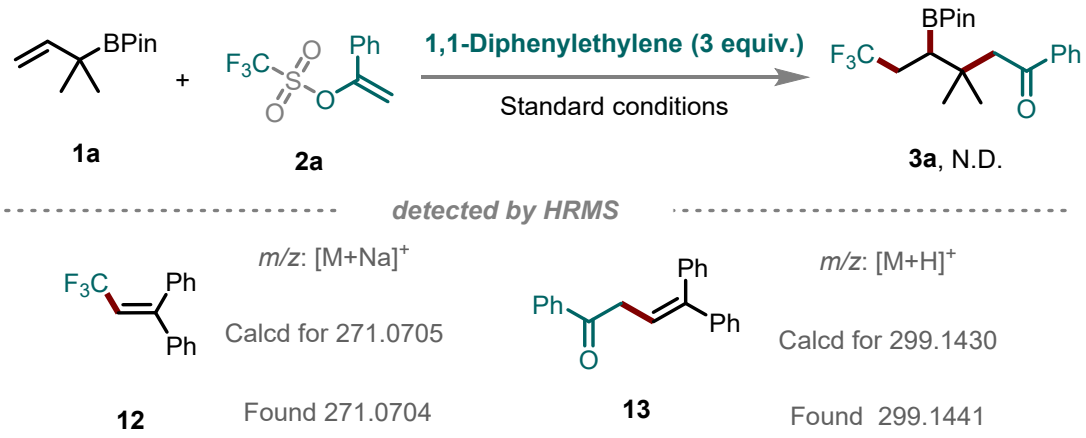


Figure S7. The HRMS analysis of compound **11**



Scheme S2 The trapping experiment of 1,1-diphenylethylene

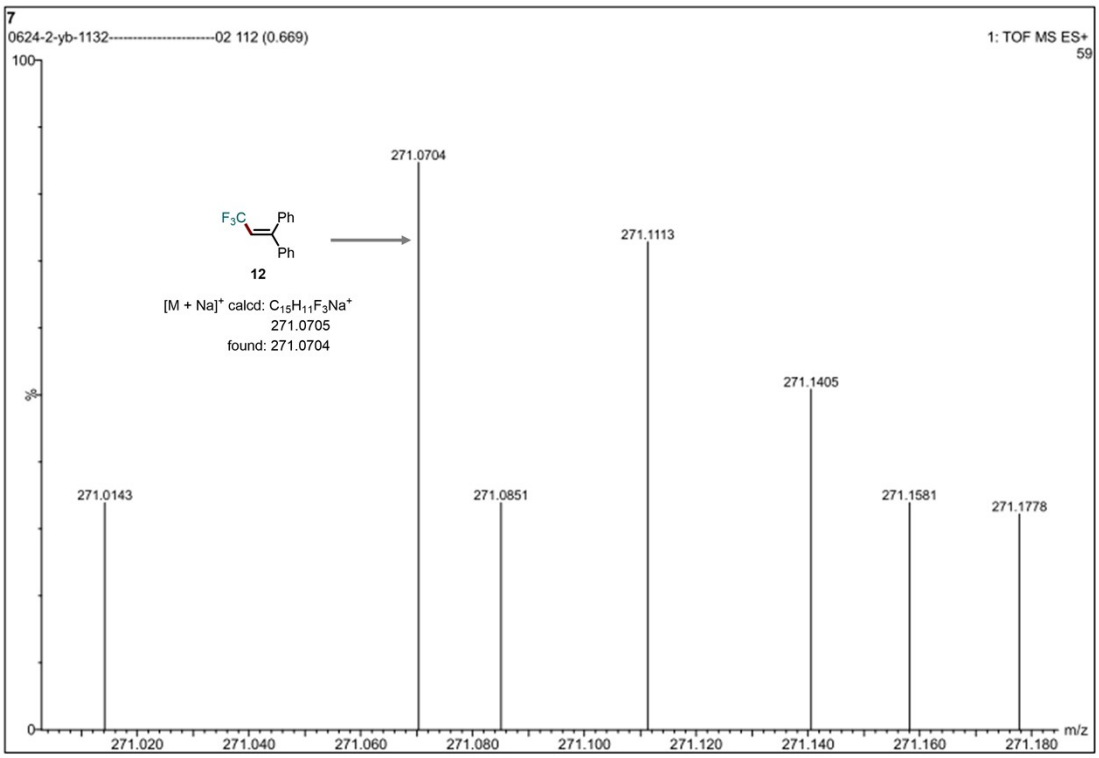


Figure S8. The HRMS analysis of compound **12**

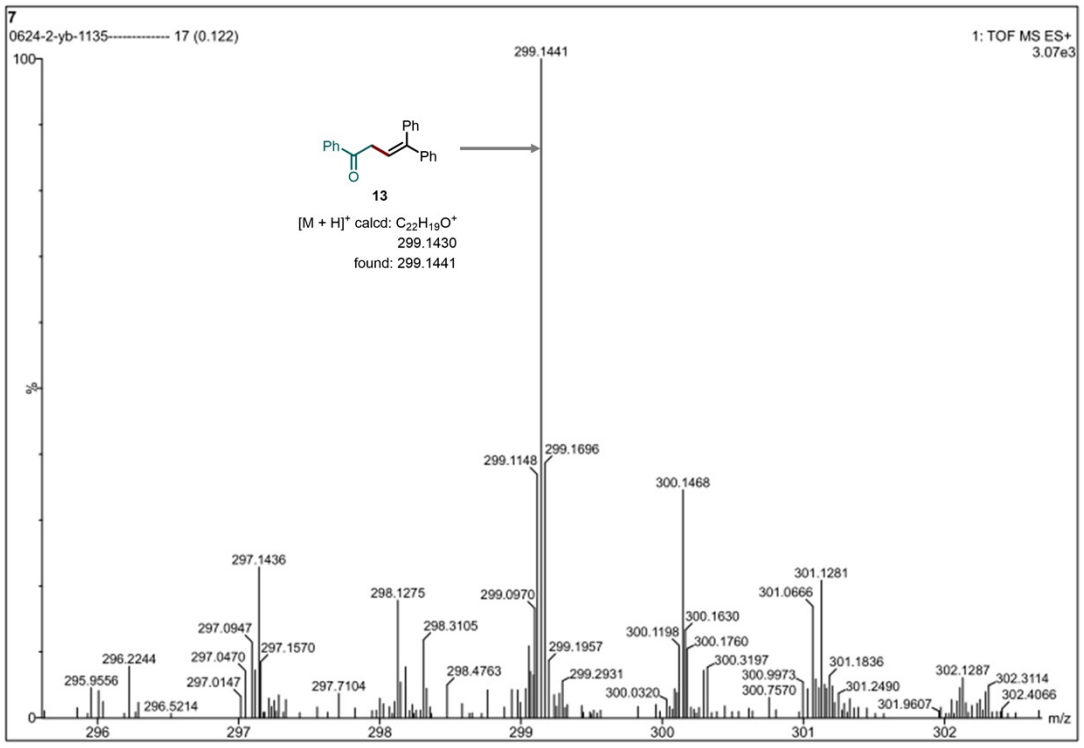
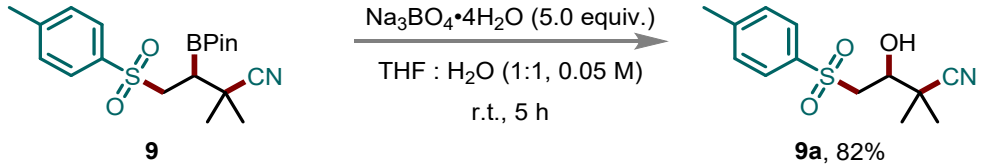


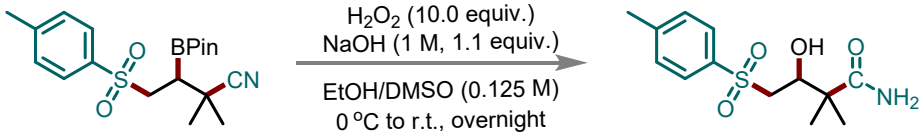
Figure S9. The HRMS analysis of compound **13**

2.9 Synthetic transformation of compound 9



9 **9a**, 82%

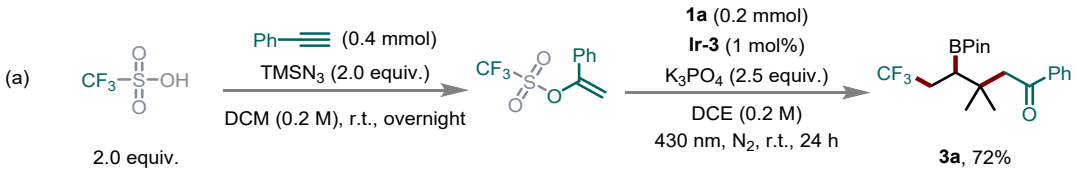
To a 25 mL round-bottomed flask equipped with a magnetic stir bar, compound **9** (0.2 mmol, 1.0 equiv.), sodium perborate tetrahydrate (1.0 mmol, 5.0 equiv.), and a 1:1 (v/v) mixture of THF and H_2O (4 mL) were added. The reaction mixture was stirred for 5 hours at room temperature. The reaction was then quenched with a saturated solution of sodium bicarbonate and extracted with ethyl acetate. The organic extracts were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (PE:EA = 5:1), yielding product **9a** in 82% yield.



9 **9b**, 85%

To a 25 mL round-bottomed flask equipped with a magnetic stir bar, compound **9** (0.2 mmol, 1.0 equiv.), a 7:1 (v/v) mixture of EtOH and DMSO (1.6 mL), and a hydrogen peroxide solution (30% in H_2O, 204.0 μL, 10.0 equiv.) were added. The mixture was cooled to 0 °C, and then 1.0 M NaOH solution was added gradually while stirring at room temperature for 20 hours. Once the reaction was completed, 0.4 mL of a saturated $Na_2S_2O_3$ solution was added, and the mixture was stirred for 1 hour. The solution was then extracted with ethyl acetate, and the organic extracts were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (DCM:MeOH = 20:1), yielding product **9b** in 85% yield.

2.10 One-pot synthesis

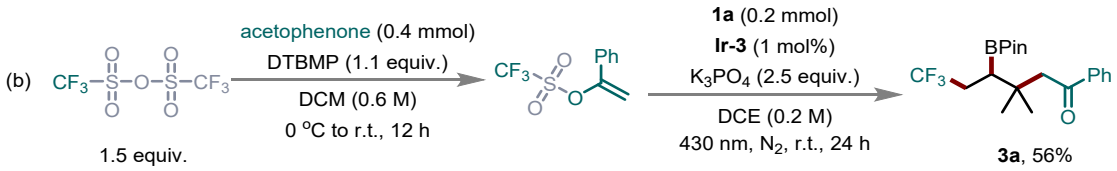


3a, 72%

(a): To a 25 mL round-bottomed flask equipped with a magnetic stir bar, phenylacetylene (0.4 mmol, 1.0 equiv.) and DCM (2.0 mL, 0.2 M) were added.

Trifluoromethanesulfonic acid (0.8 mmol, 2.0 equiv.) and $TMSN_3$ (0.8 mmol, 2.0 equiv.) were slowly added. The reaction mixture was stirred for 5 minutes at room temperature. The reaction was then quenched with petroleum ether and filtered through silica gel to remove insoluble substances. The filtrate was concentrated by rotary evaporation and used directly for the next step.

A mixture of allylboronic ester **1a** (0.2 mmol), 1-phenyl vinyl trifluoromethanesulfonate **2a**, $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (0.002 mmol, 1 mol%), K_3PO_4 (0.5 mmol, 2.5 equiv.), and DCE (1.0 mL) was added sequentially to a 25 mL Schlenk tube. The reaction mixture was then irradiated with a 10 W blue LED (430 nm) at room temperature under a nitrogen atmosphere for 24 hours. After completion, the reaction was quenched with water, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to yield product **3a** in 72% yield.



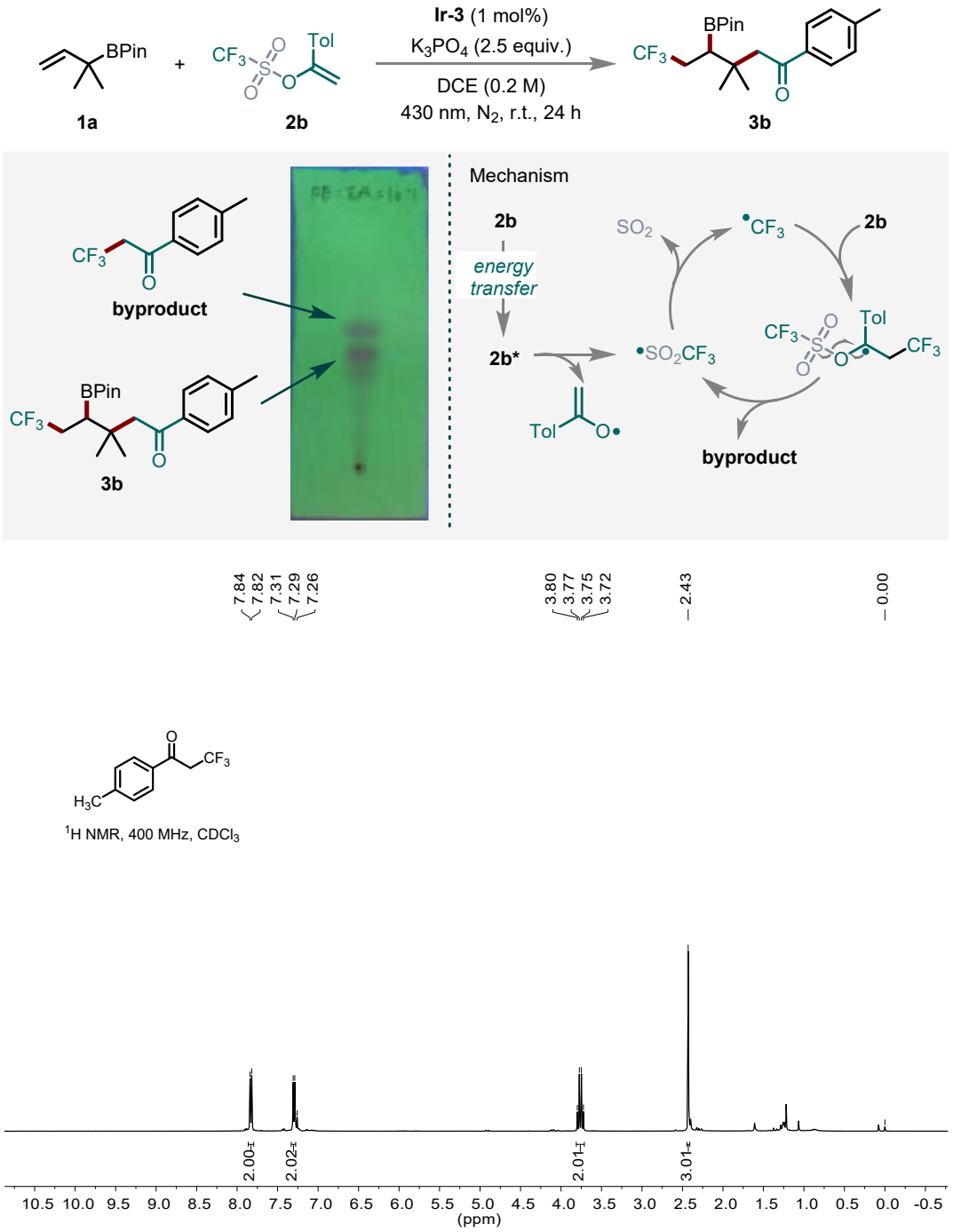
(b): To a 25 mL round-bottomed flask equipped with a magnetic stir bar, acetophenone (0.4 mmol, 1.0 equiv.), dibutylmethylpyridine (DTBMP, 1.1 equiv.), and DCM (0.6 mL, 0.6 M) were added. The reaction solution was cooled to 0 °C, and Trifluoromethanesulfonic anhydride was added slowly. The reaction mixture was then stirred at room temperature for 12 hours. After completion, the reaction was quenched with petroleum ether and filtered to remove insoluble substances. The filtrate was concentrated by rotary evaporation and used directly for the next step.

A mixture of allylboronic ester **1a** (0.2 mmol), 1-phenyl vinyl trifluoromethanesulfonate **2a**, $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (0.002 mmol, 1 mol%), K_3PO_4 (0.5 mmol, 2.5 equiv.), and DCE (1.0 mL) was added sequentially to a 25 mL Schlenk tube. The reaction mixture was then irradiated with a 10 W blue LED (430 nm) at room temperature under a nitrogen atmosphere for 24 hours. Afterward, the reaction was quenched with water, and the mixture was extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The

crude product was purified by silica gel chromatography to yielding product **3a** in 56% yield.

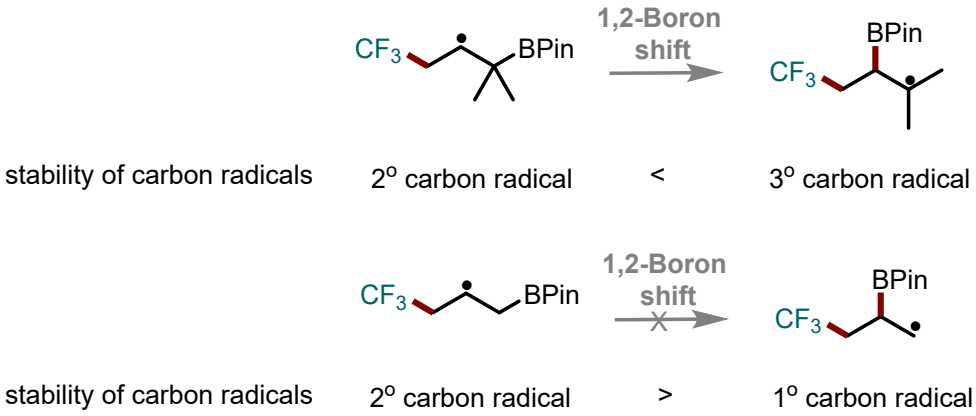
2.11 The fate of 2a

The use of 2 equiv. of **2a** ensured a high yield, as vinyl triflates are unstable and can lead to the formation of the byproduct β-CF_3 ketone (which can be detected by TLC).



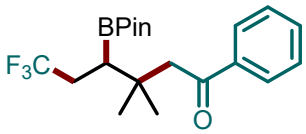
2.12 The explanation for the necessity of gem-dialkyl group

The migration step is driven by the formation of a more stable tertiary carbon-centered radical from a secondary carbon-centered radical. The gem-dialkyl substitution plays a vital role in stabilizing the radical intermediate, which is key to promoting the reaction. Without these alkyl groups, the 1,2-boron migration would lead to the formation of a primary radical, which is significantly less stable and would hinder the reaction.



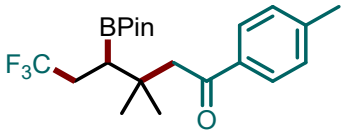
3. Characterization Data for Products

6,6,6-trifluoro-3,3-dimethyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3a)



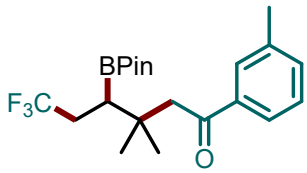
Colorless liquid (52.7 mg, 69%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 3.13 (d, *J* = 14.9 Hz, 1H), 2.79 (d, *J* = 14.9 Hz, 1H), 2.40 – 2.30 (m, 1H), 2.26 – 2.18 (m, 1H), 1.46 (d, *J* = 11.9 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.6, 138.5, 132.8, 128.5, 128.1, 127.8 (q, *J* = 276.54 Hz), 83.7, 47.1, 35.1, 31.5 (q, *J* = 27.77 Hz), 26.9, 26.6, 24.9, 24.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.04; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.57; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{29}BF_3O_3^+$ 385.2156; found, 385.2164.

6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(p-tolyl)hexan-1-one (3b)



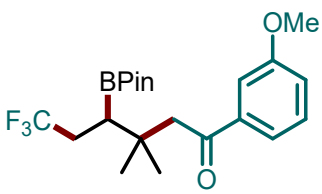
Colorless liquid (53.7 mg, 67%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.23 Hz, 2H), 7.24 (d, *J* = 8.03 Hz, 2H), 2.93 (dd, *J* = 142.60, 14.70 Hz, 2H), 2.40 (s, 3H), 2.37 – 2.19 (m, 2H), 1.46 – 1.43 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.10 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.4, 143.5, 136.1, 127.8 (q, *J* = 277.75 Hz), 129.2, 128.3, 83.7, 46.9, 35.1, 31.6 (q, *J* = 27.97 Hz), 26.9, 26.7, 24.94, 24.92, 21.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.02; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.01; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{31}BF_3O_3^+$ 399.2313; found, 399.2322.

6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(m-tolyl)hexan-1-one (3c)



Colorless liquid (54.7 mg, 69%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.72 (m, 2H), 7.37 – 7.31 (m, 2H), 3.11 (d, *J* = 14.87 Hz, 1H), 2.78 (d, *J* = 14.87 Hz, 1H), 2.41 (s, 3H), 2.37 – 2.16 (m, 2H), 1.46 (dd, *J* = 12.11, 1.60 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.0, 138.6, 138.3, 133.5, 128.6, 128.3, 127.8 (q, *J* = 276.54 Hz), 125.4, 83.7, 47.2, 31.6 (q, *J* = 27.82 Hz), 26.8, 26.7, 25.0, 24.9, 21.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.03; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.29; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{31}BF_3O_3^+$ 399.2313; found, 399.2327.

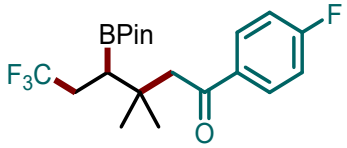
6,6,6-trifluoro-1-(3-methoxyphenyl)-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3d)



Colorless liquid (43.1 mg, 52%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 – 7.47 (m, 2H), 7.35 (t, *J* = 7.92 Hz, 1H), 7.09 (dd, *J* = 8.18, 2.40 Hz, 1H), 3.85 (s, 3H), 3.11 (d, *J*

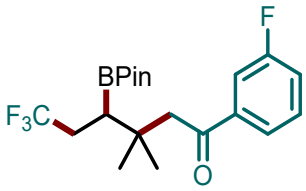
= 14.97 Hz, 1H), 2.78 (d, *J* = 14.99 Hz, 1H), 2.42 – 2.15 (m, 2H), 1.47 (d, *J* = 11.61 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.5, 159.8, 139.9, 129.4, 127.8 (q, *J* = 276.49 Hz), 120.8, 119.2, 112.4, 83.7, 55.4, 47.3, 35.1, 31.6 (q, *J* = 27.95 Hz), 26.9, 26.6, 24.93, 24.88. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.03; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.89; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{31}BF_3O_4^+$ 415.2262; found, 415.2274;

6,6,6-trifluoro-1-(4-fluorophenyl)-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3e)



Colorless liquid (60.2 mg, 75%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.91 (m, 2H), 7.16 – 7.07 (m, 2H), 3.11 (d, *J* = 15.01 Hz, 1H), 2.76 (d, *J* = 15.01 Hz, 1H), 2.42 – 2.14 (m, 2H), 1.49 – 1.46 (m, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.0, 165.6 (d, *J* = 254.40 Hz), 134.9 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 9.22 Hz), 127.7 (q, *J* = 276.44 Hz), 115.5 (d, *J* = 21.82 Hz), 83.7, 47.1, 35.1, 31.5 (q, *J* = 27.88 Hz), 26.9, 26.6, 24.91, 24.88; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.06 (s, 3F), -105.86 (s, 1F); ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.66; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}BF_4O_3^+$ 403.2062; found, 403.2065.

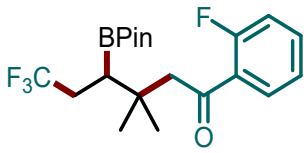
6,6,6-trifluoro-1-(3-fluorophenyl)-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3f)



Colorless liquid (62.3 mg, 77%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.71 (m, 1H), 7.65 – 7.61 (m, 1H), 7.46 - 7.40 (m, 1H), 7.30 – 7.22 (m, 1H), 3.13 (d, *J* = 15.14 Hz, 1H), 2.76 (d, *J* = 15.14 Hz, 1H), 2.42 – 2.14 (m, 2H), 1.49 – 1.46 (m, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4 (d, *J* = 1.9 Hz), 162.8 (d, *J* = 247.66 Hz), 140.6 (d, *J* = 5.93 Hz), 130.1 (d, *J* = 7.63 Hz), 127.7 (q, *J* = 276.50 Hz), 123.8 (d, *J* = 3.0 Hz), 119.8 (d, *J* = 21.50 Hz), 114.9 (d, *J* = 22.31 Hz), 83.8, 47.3, 35.1, 31.5 (q, *J* = 27.95 Hz), 26.8, 26.7, 24.90, 24.87; ^{19}F NMR (376 MHz,

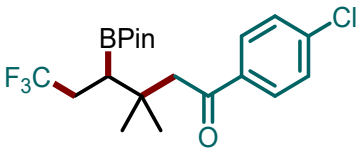
Chloroform-*d*) δ -65.07 (s, 3F), -112.03 (s, 1F); ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.89; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}BF_4O_3^+$ 403.2062; found, 403.2073.

6,6,6-trifluoro-1-(2-fluorophenyl)-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3g)



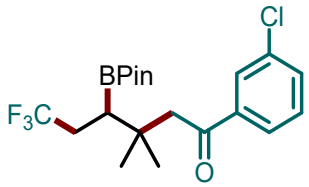
Colorless liquid (64.8 mg, 81%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (td, *J* = 7.64, 1.82 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.21 (td, *J* = 7.77, 0.98 Hz, 1H), 7.13 – 7.08 (m, 1H), 3.08 (dd, *J* = 16.06, 1.98 Hz, 1H), 2.90 (dd, *J* = 16.06, 2.11 Hz, 1H), 2.41 – 2.12 (m, 2H), 1.52 – 1.49 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H), 1.14 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2 (d, *J* = 4.06 Hz), 161.2 (d, *J* = 252.93 Hz), 134.0 (d, *J* = 8.96 Hz), 130.5 (d, *J* = 2.70 Hz), 127.8 (q, *J* = 276.47 Hz), 127.7 (d, *J* = 13.29 Hz), 124.4 (d, *J* = 3.36 Hz), 116.5 (d, *J* = 24.04 Hz), 83.6, 52.8 (d, *J* = 6.58 Hz), 35.2, 31.5 (q, *J* = 27.74 Hz), 26.7, 26.5, 24.9, 24.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.13 (s, 3F), -109.62 (s, 1F); ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.83; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}BF_4O_3^+$ 403.2062; found, 403.2070.

1-(4-chlorophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3h)



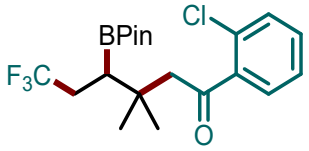
Colorless liquid (67.5 mg, 81%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.87 (m, 2H), 7.43 – 7.40 (m, 2H), 3.11 (d, *J* = 15.06 Hz, 1H), 2.75 (d, *J* = 15.06 Hz, 1H), 2.42 – 2.14 (m, 2H), 1.49 – 1.45 (m, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.102 (s, 3H), 1.098 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 139.2, 136.8, 129.5, 128.8, 127.8 (q, *J* = 276.50 Hz), 83.7, 47.1, 35.1, 31.5 (q, *J* = 27.89 Hz), 26.8, 26.6, 24.92, 24.89; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.89; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}BClF_3O_3^+$ 419.1767; found, 419.1782.

1-(3-chlorophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3i)



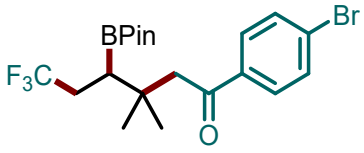
Colorless liquid (67.8 mg, 81%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 1.73 Hz, 1H), 7.81 (d, *J* = 7.80 Hz, 1H), 7.53 – 7.51 (m, 1H), 7.39 (t, *J* = 7.87 Hz, 1H), 3.12 (d, *J* = 15.16 Hz, 1H), 2.76 (d, *J* = 15.16 Hz, 1H), 2.54 – 2.00 (m, 2H), 1.47 (d, *J* = 10.80 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.109 (s, 3H), 1.101 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 140.1, 134.8, 132.7, 129.8, 128.2, 127.7 (q, *J* = 276.33 Hz), 126.2, 83.8, 47.3, 35.1, 31.5 (q, *J* = 27.97 Hz), 26.8, 26.7, 24.93, 24.87; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.06; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.90; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}BClF_3NaO_3^+$ 441.1586; found, 441.1595.

1-(2-chlorophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3j)



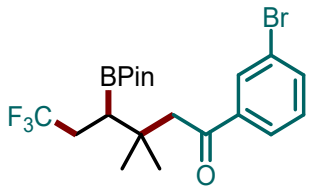
Colorless liquid (53.7 mg, 64%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.28 (m, 4H), 3.05 (d, *J* = 15.81 Hz, 1H), 2.88 (d, *J* = 15.81 Hz, 1H), 2.39 – 2.10 (m, 2H), 1.42 (d, *J* = 10.75 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.14 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.8, 141.1, 131.3, 130.40, 130.35, 128.6, 127.7 (q, *J* = 276.43 Hz), 126.9, 83.7, 52.3, 35.4, 31.5 (q, *J* = 27.93 Hz), 26.7, 26.5, 24.9, 24.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.07; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.88; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}BClF_3NaO_3^+$ 441.1586; found, 441.1594.

1-(4-bromophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3k)



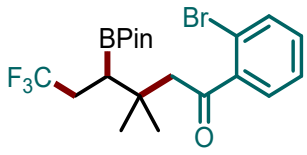
Colorless liquid (75.8 mg, 82%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.79 (m, 2H), 7.60 – 7.57 (m, 2H), 3.10 (d, *J* = 15.06 Hz, 1H), 2.74 (d, *J* = 15.06 Hz, 1H), 2.39 – 2.14 (m, 2H), 1.48 – 1.45 (m, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.099 (s, 3H) , 1.095 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.6, 137.2, 131.8, 129.7, 128.0, 127.7 (q, *J* = 276.74 Hz), 83.7, 47.1, 35.1, 31.5 (q, *J* = 28.00 Hz), 26.8, 26.7, 24.93, 24.90; ^{9}F NMR (376 MHz, Chloroform-*d*) δ -65.04; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.86; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}B^{79}BrF_3O_3^+$ 463.1261; found, 463.1273; $[M + H]^+$ calcd for $C_{20}H_{28}B^{81}BrF_3O_3^+$ 465.1241; found, 465.1179.

1-(3-bromophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3l)



Colorless liquid (71.2 mg, 77%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (t, *J* = 1.62 Hz, 1H), 7.86 (d, *J* = 7.83 Hz, 1H), 7.68 – 7.66 (m, 1H), 7.33 (t, *J* = 7.87 Hz, 1H), 3.11 (d, *J* = 15.19 Hz, 1H), 2.75 (d, *J* = 15.19 Hz, 1H), 2.42 – 2.14 (m, 2H), 1.47 (d, *J* = 10.92 Hz, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.11 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2, 140.3, 135.6, 131.2, 130.1, 127.7 (q, *J* = 276.39 Hz), 126.6, 122.9, 83.8, 47.3, 35.1, 31.5 (q, *J* = 27.91 Hz), 26.8, 26.7, 25.0, 24.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.77; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{20}H_{27}B^{79}BrF_3NaO_3^+$ 485.1081; found, 485.1090; $[M + Na]^+$ calcd for $C_{20}H_{27}B^{81}BrF_3NaO_3^+$ 487.1060; found, 487.1074.

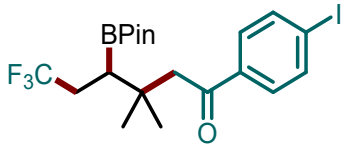
1-(2-bromophenyl)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3m)



Colorless liquid (49.9 mg, 54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, *J* = 7.75 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.29 – 7.24 (m, 1H), 3.04 (d, *J* = 15.98 Hz, 1H), 2.86 (d, *J* = 15.99 Hz, 1H), 2.39 – 2.11 (m, 2H), 1.44 – 1.41 (m, 1H), 1.234 (s, 6H), 1.229 (s, 6H), 1.15 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.4,

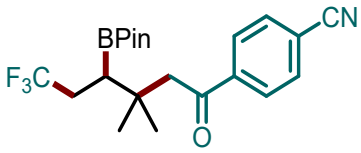
143.1, 133.6, 131.2, 128.3, 127.7 (q, J = 276.70 Hz), 127.3, 118.4, 83.7, 52.1, 35.4, 31.5 (q, J = 27.81 Hz), 26.6, 26.4, 24.9, 24.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.95; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}B^{79}BrF_3O_3^+$ 463.1261; found, 463.1274; $[M + H]^+$ calcd for $C_{20}H_{28}B^{81}BrF_3O_3^+$ 465.1241; found, 465.1167.

6,6,6-trifluoro-1-(4-iodophenyl)-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3n)



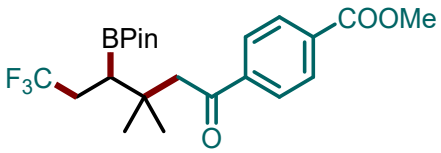
Colorless liquid (75.3 mg, 74%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, J = 8.47 Hz, 2H), 7.65 (d, J = 8.47 Hz, 2H), 2.91 (dd, J = 142.40, 15.05 Hz, 2H), 2.42 – 2.19 (m, 2H), 1.46 (d, J = 11.71 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.9, 137.78, 137.75, 129.6, 127.7 (q, J = 276.74 Hz), 100.7, 83.7, 47.0, 35.1, 31.5 (q, J = 27.88 Hz), 26.8, 26.7, 24.94, 24.91, ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.02; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.03; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{28}BF_3IO_3^+$ 511.1123; found, 511.1127.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)benzonitrile (3o)



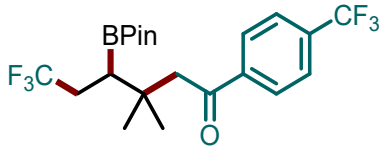
Colorless liquid (56.9 mg, 70%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, J = 8.17 Hz, 2H), 7.77 (d, J = 8.11 Hz, 2H), 3.15 (d, J = 15.55 Hz, 1H), 2.82 (d, J = 15.55 Hz, 1H), 2.43 – 2.13 (m, 2H), 1.51 (d, J = 11.71 Hz, 1H), 1.25 (s, 6H), 1.21 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2, 141.4, 132.4, 128.4, 127.7 (q, J = 276.53 Hz), 118.0, 116.1, 83.8, 47.7, 35.1, 31.5 (q, J = 28.31 Hz), 26.9, 26.6, 24.91, 24.85. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.09; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.95; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{27}BF_3NNaO_3^+$ 432.1928; found, 432.1945.

methyl 4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)benzoate (3p)



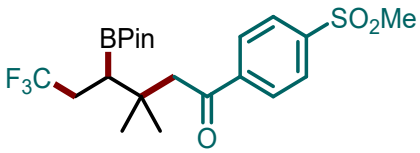
Colorless liquid (72.5 mg, 82%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 50.66, 8.30 Hz, 4H), 3.95 (s, 3H), 2.99 (dd, *J* = 143.64, 15.24 Hz, 2H), 2.43 – 2.15 (m, 2H), 1.49 (d, *J* = 11.46 Hz, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 166.2, 141.8, 133.6, 129.7, 128.0, 127.7 (q, *J* = 277.75 Hz), 83.7, 52.4, 47.6, 35.1, 31.5 (q, *J* = 27.77 Hz), 26.8, 26.7, 24.93, 24.87; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.08; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 32.42; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}BF_3NaO_5^+$ 465.2031; found, 465.2033.

6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)hexan-1-one (3q)



Colorless liquid (57.3 mg, 63%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.1 Hz, 2H), 3.16 (d, *J* = 15.3 Hz, 1H), 2.82 (d, *J* = 15.3 Hz, 1H), 2.411 – 2.31 (m, 1H), 2.25 – 2.17 (M, 1H), 1.50 (d, *J* = 11.9 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.12 (s, 3H), 1.11 (s, 3H).; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.11 (s, 3F), -65.11 (s, 3F); ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.24; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{28}BF_6O_3^+$ 453.2030; found, 453.2029.

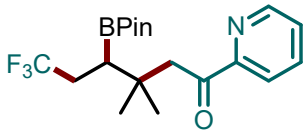
6,6,6-trifluoro-3,3-dimethyl-1-(4-(methylsulfonyl)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3r)



Colorless liquid (41.6 mg, 45%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 – 7.96 (m, 4H), 3.08 (s, 3H), 3.00 (dd, *J* = 136.72, 15.44 Hz, 2H), 2.42 – 2.13 (m, 2H), 1.51 – 1.48

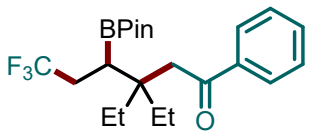
(m, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.12 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.4, 143.9, 142.5, 128.9, 127.70, 127.66 (q, *J* = 276.7 Hz), 83.8, 47.9, 44.3, 35.2, 31.5 (q, *J* = 27.9 Hz), 26.9, 26.7, 24.94, 24.87; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.10; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.47; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{30}BF_3NaO_5S^+$ 485.1751; found, 485.1758.

6,6,6-trifluoro-3,3-dimethyl-1-(pyridin-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3s)



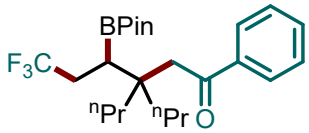
Colorless liquid (73.1 mg, 95%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 4.5 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.45 – 7.43 (m, 1H), 3.30 – 3.21 (m, 2H), 2.41 – 2.27 (m, 2H), 1.49 (d, *J* = 11.7 Hz, 1H), 1.24 (s, 6H), 1.21 (s, 6H), 1.12 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 201.3, 154.4, 148.6, 136.8, 127.9 (q, *J* = 277.84 Hz), 126.8, 121.7, 83.6, 45.8, 35.3, 31.6 (q, *J* = 27.8 Hz), 27.2, 26.6, 25.0, 24.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.04; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.54; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{28}BF_3NO_3^+$ 386.2109; found, 386.2117.

3,3-diethyl-6,6,6-trifluoro-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3t)



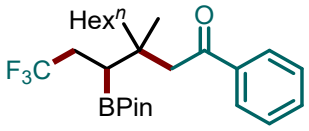
Colorless liquid (38.0 mg, 46%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.95 (m, 2H), 7.56 – 7.52 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.06 (d, *J* = 16.3 Hz, 1H), 2.93 (d, *J* = 16.3 Hz, 1H), 2.40 – 2.14 (m, 1H), 1.71 – 1.56 (m, 5H), 1.25 (s, 6H), 1.23 (s, 6H), 0.82 (q, *J* = 7.4 Hz, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.0, 138.7, 132.6, 128.4, 128.0, 127.9 (q, *J* = 277.1 Hz), 83.6, 42.9, 41.4, 31.2 (q, *J* = 27.4 Hz), 29.5, 28.3, 25.1, 24.8, 8.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.08; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.78; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{32}BF_3O_3Na^+$ 435.2289; found, 435.2297.

6,6,6-trifluoro-1-phenyl-3,3-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-one (3u)



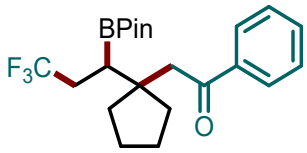
Colorless liquid (26.7 mg, 30%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 3.10 – 2.92 (m, 2H), 2.39 – 2.19 (m, 2H), 1.63 – 1.39 (m, 5H), 1.26 (s, 10H), 1.24 (s, 6H), 0.87 – 0.78 (m, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.1, 138.7, 132.6, 128.4, 128.0, 127.9 (q, *J* = 277.8 Hz), 83.6, 43.8, 41.2, 40.3, 39.1, 31.3 (q, *J* = 27.5 Hz), 25.1, 24.8, 17.23, 17.18, 14.8, 14.7; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.09; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.71; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{24}H_{36}BF_3O_3Na^+$ 463.2602; found, 463.2603.

3-methyl-1-phenyl-3-(3,3,3-trifluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)nonan-1-one (3v)



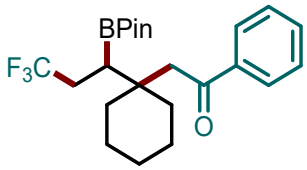
Colorless liquid (20 mg, 22%, dr = 1:1); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.92 (m, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.18 (d, *J* = 15.2 Hz, 1H), 2.78 (dd, *J* = 15.4, 3.4 Hz, 1H), 2.41 – 2.25 (m, 1H), 2.22 – 2.10 (m, 1H), 1.62 – 1.52 (m, 2H), 1.51 – 1.41 (m, 2H), 1.28 – 1.23 (m, 18H), 1.08 (d, *J* = 4.7 Hz, 3H), 0.88 – 0.82 (m, 4H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 200.2, 199.9, 147.1, 138.8, 138.7, 132.7, 128.4, 128.03, 128.00, 127.9 (q, *J* = 277.8 Hz), 124.5, 124.0, 83.66, 83.65, 45.2, 44.8, 38.8, 38.4, 37.92, 37.89, 34.9, 34.5, 31.8, 31.7, 31.4, 31.2 (q, *J* = 27.3 Hz), 30.2, 29.9, 29.8, 29.7, 24.97, 24.94, 24.89, 24.6, 24.1, 23.6, 23.5, 22.6, 14.04, 14.03; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.98; -64.90; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.55; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{25}BF_3O_3Na^+$ 392.1741; found, 392.1752.

1-phenyl-2-(1-(3,3,3-trifluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)cyclopentyl)ethan-1-one(3w)



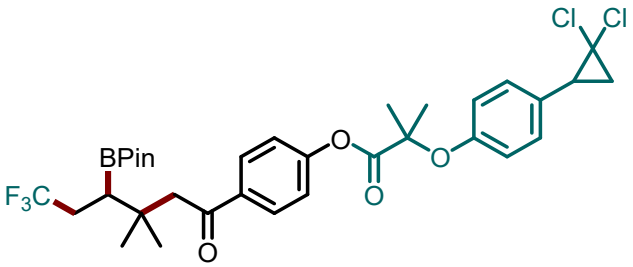
Colorless liquid (44.2 mg, 54%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.95 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.07 (dd, *J* = 136.6, 15.5 Hz, 2H), 2.45 – 2.13 (m, 3H), 1.83 – 1.80 (m, 1H), 1.69 – 1.58 (m, 8H), 1.26 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.3, 138.5, 132.8, 128.5, 128.1, 127.7 (q, *J* = 276.1 Hz), 83.6, 46.3, 44.4, 37.4, 36.3, 32.8 (q, *J* = 27.5 Hz), 25.2, 25.0, 24.8, 24.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.20; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.39; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{22}H_{30}BF_3O_3Na^+$ 433.2132; found, 433.2136.

1-phenyl-2-(1-(3,3,3-trifluoro-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)cyclohexyl)ethan-1-one (3x)



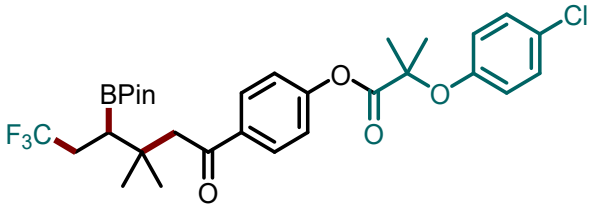
Colorless liquid (48.4 mg, 57%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.98 (m, 2H), 7.57 – 7.53 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 3.32 (d, *J* = 14.5 Hz, 1H), 2.69 (d, *J* = 14.5 Hz, 1H), 2.36 – 2.12 (m, 2H), 1.93 (d, *J* = 11.2 Hz, 1H), 1.77 – 1.70 (m, 1H), 1.65 – 1.38 (m, 9H), 1.29 (s, 6H), 1.24 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.6, 138.9, 132.8, 128.4, 128.3, 127.9 (q, *J* = 277.8 Hz), 83.6, 43.2, 38.6, 35.9, 32.9, 31.1 (q, *J* = 27.9 Hz), 25.6, 25.1, 24.8, 21.42, 21.38; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.97; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 35.23; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{32}BF_3O_3Na^+$ 447.2289; found, 447.2296.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl 2-(4-(2,2-dichlorocyclopropyl)phenoxy)-2-methylpropanoate (3y)



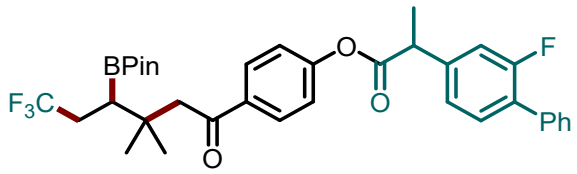
Colorless liquid (84.6 mg, 63%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.39 Hz, 2H), 7.17 (d, *J* = 8.26 Hz, 2H), 7.05 (d, *J* = 8.37 Hz, 2H), 6.93 (d, *J* = 8.32 Hz, 2H), 3.10 (d, *J* = 15.10 Hz, 1H), 2.89 – 2.84 (m, 1H), 2.76 (d, *J* = 15.10 Hz, 1H), 2.42 – 2.15 (m, 2H), 1.96 (dd, *J* = 10.55, 7.55 Hz, 1H), 1.81 (d, *J* = 8.06 Hz, 1H), 1.77 (s, 6H), 1.46 (d, *J* = 11.84 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.3, 172.4, 154.9, 154.0, 136.4, 129.9, 129.8, 128.7, 127.7 (q, *J* = 277.75 Hz) 121.4, 118.6, 83.7, 79.3, 60.8, 47.2, 35.1, 34.8, 31.5 (q, *J* = 28.15 Hz), 26.8, 26.7, 25.8, 25.5, 25.4, 25.0, 24.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.00; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 32.29; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{33}H_{40}BCl_2F_3O_6Na^+$ 693.2139; found, 693.2153.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl 2-(4-chlorophenoxy)-2-methylpropanoate (3z)



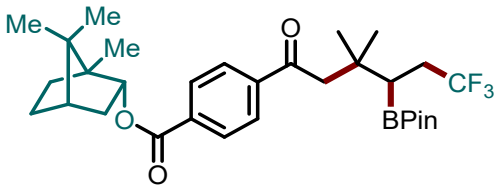
Colorless liquid (72.5 mg, 61%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.72 Hz, 2H), 7.25 (d, *J* = 8.95 Hz, 2H), 7.10 (d, *J* = 8.71 Hz, 2H), 6.90 (d, *J* = 8.94 Hz, 2H), 2.94 (dd, *J* = 141.06, 15.12 Hz, 2H), 2.42 – 2.15 (m, 2H), 1.74 (s, 6H), 1.48 – 1.46 (m, 1H), 1.25 (s, 6H), 1.23 (s, 6H), 1.11 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.2, 172.2, 153.9, 136.4, 129.8, 129.3, 127.75 (q, *J* = 277.75 Hz), 127.72, 121.3, 120.6, 83.7, 79.6, 47.1, 35.1, 31.5 (q, *J* = 27.8 Hz), 26.8, 26.7, 25.3, 24.94, 24.90; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.01; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.19; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{30}H_{37}BClF_3O_6Na^+$ 619.2216; found, 619.2231.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (3aa)



Colorless liquid (84.8 mg, 68%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.94 (m, 2H), 7.57 – 7.55 (m, 2H), 7.48 – 7.43 (m, 3H), 7.40 – 7.35 (m, 1H), 7.26 – 7.20 (m, 2H), 7.16 – 7.12 (m, 2H), 4.01 (q, *J* = 7.12 Hz, 1H), 2.93 (dd, *J* = 142.69, 15.04 Hz, 2H), 2.39 – 2.14 (m, 2H), 1.67 (d, *J* = 7.16 Hz, 3H), 1.47 – 1.43 (m, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.09 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 172.0, 159.8 (d, *J* = 248.75 Hz), 154.2, 140.9 (d, *J* = 7.60 Hz), 136.2, 135.30, 135.29, 131.1 (d, *J* = 3.97 Hz), 129.0, 128.9, 128.5, 128.3 (d, *J* = 13.48 Hz), 127.8, 127.7 (q, *J* = 277.75), 121.44, 115.3 (d, *J* = 23.77 Hz), 83.7, 47.1, 45.2, 35.1, 31.5 (q, *J* = 28.28 Hz), 26.8, 26.7, 25.0, 24.9, 18.4; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.02 (s, 3F), -117.07 (s, 1F); ^{11}B NMR (193 MHz, Chloroform-*d*) δ 32.28; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{35}H_{39}BF_4O_5Na^+$ 649.2719; found, 649.2731.

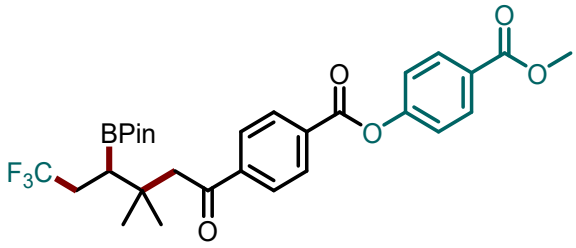
(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-((R)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)benzoate (3ab)



Colorless liquid (102.4 mg, 91%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 8.25 Hz, 2H), 8.00 (d, *J* = 8.37 Hz, 2H), 5.15 – 5.13 (m, 1H), 3.00 (dd, *J* = 137.64, 15.16 Hz, 2H), 2.52 – 2.46 (m, 1H), 2.40 – 2.32 (m, 1H), 2.24 – 2.18 (m, 1H), 2.16 – 2.09 (m, 1H), 1.86 -1.78 (m, 1H), 1.77 – 1.75 (m, 1H), 1.49 (d, *J* = 12.14 Hz, 2H), 1.42 (d, *J* = 2.78 Hz, 2H), 1.29 (d, *J* = 2.94 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 5H), 1.16 – 1.14 (m, 1H), 1.12 (s, 3H), 1.11 (s, 3H), 0.98 (s, 3H), 0.93 (s, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 166.0, 141.6, 134.4, 129.7, 128.0, 127.7 (q, *J* = 277.75 Hz), 83.8, 81.2, 49.1, 47.9, 47.6, 45.0, 36.9, 35.2, 31.5 (q, *J* = 28.01 Hz), 28.1, 27.4, 26.8, 26.7, 24.93, 24.89, 19.7, 18.9, 13.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05; ^{11}B

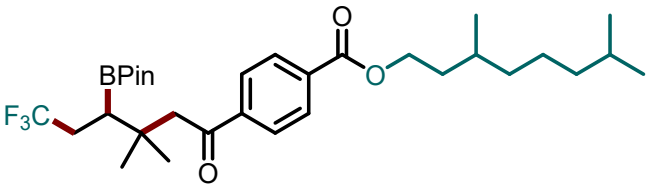
NMR (193 MHz, Chloroform-*d*) δ 33.59; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{44}BF_3O_5Na^+$ 587.3126; found, 587.3135.

Methyl (4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl) terephthalate (3ac)



Colorless liquid (74.6 mg, 66%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 8.44 Hz, 2H), 8.14 (d, *J* = 8.72 Hz, 2H), 8.06 (d, *J* = 8.46 Hz, 2H), 7.33 (d, *J* = 8.72 Hz, 2H), 3.93 (s, 3H), 3.03 (dd, *J* = 139.17, 15.35 Hz, 2H), 2.45 – 2.16 (m, 2H), 1.52 (d, *J* = 10.85 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.14 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.0, 166.2, 163.8, 154.3, 142.4, 132.5, 131.3, 130.4, 128.2, 128.0. 127.7 (q, *J* = 276.48 Hz), 121.6, 83.8, 52.2, 47.8, 35.2, 31.5 (q, *J* = 27.99 Hz), 26.8, 26.7, 24.93, 24.88; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.05; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.53; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{29}H_{34}BF_3O_7Na^+$ 585.2242; found, 585.2245.

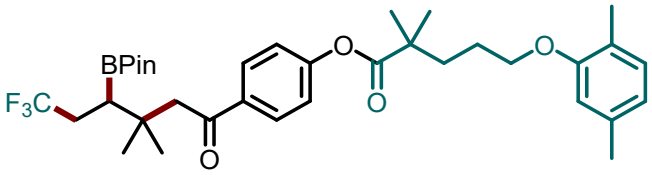
3,7-dimethyloctyl 4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)benzoatev (3ad)



Colorless liquid (82.8 mg, 73%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, *J* = 49.3, 8.4 Hz, 4H), 4.44 – 4.34 (m, 2H), 2.99 (dd, *J* = 142.5, 15.2 Hz, 1H), 2.43 – 2.15 (m, 2H), 1.86 – 1.79 (m, 1H), 1.68 – 1.42 (m, 5H), 1.42 (s, 1H), 1.29 (s, 1H), 1.25 (s, 6H), 1.22 (s, 6H), 1.18 – 1.15 (m, 3H), 1.12 (s, 3H), 1.10 (s, 3H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.88 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 165.8, 141.7, 134.0, 129.7, 128.0, 127.7 (q, *J* = 276.35 Hz), 83.7, 64.1, 47.6, 39.2, 37.1, 35.5, 35.1, 31.5 (q, *J* = 27.95 Hz), 30.0, 27.9, 26.8, 26.7, 24.93, 24.88, 24.6, 22.7, 22.6, 19.6; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.07; ^{11}B NMR (193 MHz, Chloroform-*d*) δ

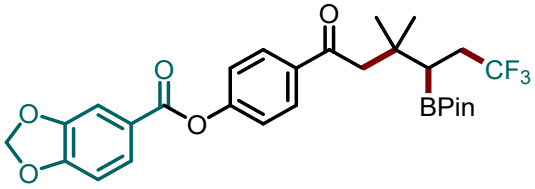
33.24; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{48}BF_3O_5Na^+$ 591.3439; found, 591.3444.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl 5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoate (3ae)



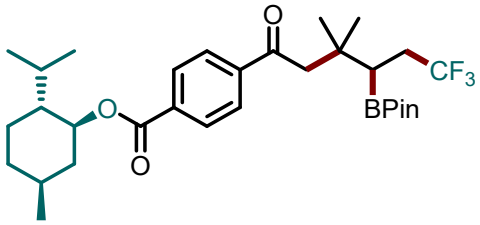
Colorless liquid (54.0 mg, 43%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.74 Hz, 2H), 7.11 (d, *J* = 8.73 Hz, 2H), 7.00 (d, *J* = 7.48 Hz, 1H), 6.67 (d, *J* = 7.49 Hz, 1H), 6.62 (s, 1H), 3.99 (t, *J* = 5.30 Hz, 2H), 2.94 (dd, *J* = 144.18, 15.01 Hz, 2H), 2.39 – 2.17 (m, 8H), 1.91 – 1.87 (m, 4H), 1.48 – 1.44 (m, 1H), 1.38 (s, 6H), 1.26 (s, 6H), 1.23 (s, 6H), 1.10 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 175.8, 156.8, 154.6, 136.5, 135.9, 130.4, 129.7, 127.8 (q, *J* = 277.75 Hz) 123.6, 121.6, 120.8, 111.9, 83.7, 67.7, 47.1, 42.6, 37.1, 35.1, 31.6 (q, *J* = 27.94 Hz), 26.8, 26.7, 25.3, 25.1, 25.0, 24.9, 21.4, 15.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.03; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.75; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{35}H_{48}BF_3O_6Na^+$ 655.3388; found, 655.3400.

4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl benzo[d][1,3]dioxole-5-carboxylate (3af)



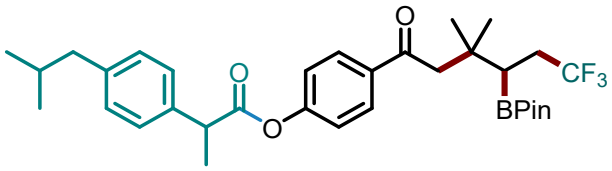
Colorless liquid (30 mg, 27%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.01 (m, 2H), 7.82 (dd, *J* = 8.21, 1.71 Hz, 1H), 7.60 (d, *J* = 1.65 Hz, 1H), 7.31 – 7.28 (m, 2H), 6.91 (d, *J* = 8.21 Hz, 1H), 6.09 (s, 2H), 2.97 (dd, *J* = 146.28, 15.03 Hz, 2H), 2.43 – 2.16 (m, 2H), 1.49 – 1.46 (m, 1H), 1.26 (s, 6H), 1.24 (s, 6H), 1.12 (s, 6H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 163.9, 154.5, 152.5, 148.0, 136.0, 129.8, 127.8 (q, *J* = 277.75 Hz), 126.4, 122.9, 121.8, 109.9, 108.2, 102.1, 83.7, 47.1, 35.1, 31.6 (q, *J* = 27.97 Hz), 26.8, 26.7, 25.0, 24.9; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.02; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{28}H_{32}BF_3O_7Na^+$ 571.2085; found, 571.2095.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-(6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)benzoate (3ag)



Colorless liquid (52.1 mg, 46%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.23 Hz, 2H), 7.98 (d, *J* = 8.28 Hz, 2H), 4.96 (td, *J* = 10.85, 4.32 Hz, 1H), 2.99 (dd, *J* = 140.99, 15.12 Hz, 2H), 2.43 – 2.12 (m, 3H), 1.98 – 1.91 (m, 1H), 1.74 (d, *J* = 11.92 Hz, 3H), 1.61 – 1.55 (m, 2H), 1.48 (d, *J* = 11.77 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.16 (d, *J* = 4.09 Hz, 1H), 1.14 (s, 1H), 1.11 (d, *J* = 3.89 Hz, 6H), 0.97 – 0.89 (m, 6H), 0.80 (d, *J* = 6.92 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 165.3, 141.6, 134.3, 129.7, 128.0, 127.7 (q, *J* = 277.75 Hz), 83.7, 75.5, 47.68, 47.66, 47.2, 40.9, 35.2, 34.3, 31.52 (q, *J* = 27.70 Hz), 31.45, 26.83, 26.80, 26.7, 26.6, 24.93, 24.88, 23.7, 22.0, 20.7, 16.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.06; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 33.33; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{31}H_{46}BF_3O_5Na^+$ 589.3283; found, 589.3295.

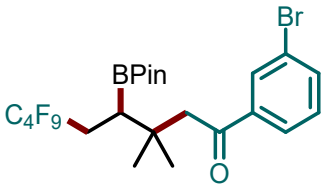
4-((R)-6,6,6-trifluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexanoyl)phenyl 2-(4-isobutylphenyl)propanoate (3ah)



Colorless liquid (50.2 mg, 43%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.96 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.11 – 7.07 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 1H), 2.92 (dd, *J* = 142.2, 15.0 Hz, 2H), 2.47 (d, *J* = 7.2 Hz, 2H), 2.38 – 2.13 (m, 2H), 1.92 – 1.82 (m, 1H), 1.61 (d, *J* = 7.2 Hz, 3H), 1.45 (dd, *J* = 12.0, 1.6 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.09 (s, 6H), 0.92 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.4, 172.7, 154.4, 141.0, 136.9, 136.0, 129.7, 129.6, 127.8 (q, *J* = 277.75 Hz), 127.2, 121.5, 83.7, 47.1, 45.3, 45.1, 35.1, 31.5 (q, *J* = 28.1, 27.0 Hz), 30.2, 26.8, 26.7, 24.94, 24.91, 22.4, 18.5; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -65.03; ^{11}B

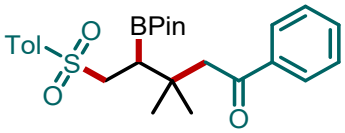
NMR (193 MHz, Chloroform-*d*) δ 32.25; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{33}H_{44}BF_3O_5Na^+$ 611.3126; found, 611.3131.

1-(3-bromophenyl)-7,7,8,8,9,9,10,10,10-nonafluoro-3,3-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)decan-1-one (5)



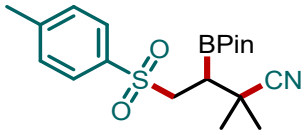
Yellow liquid (115 mg, 92%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.9 Hz, 1H), 2.94 (dd, *J* = 208.0, 15.2 Hz, 2H), 2.44 – 2.10 (m, 2H), 1.57 (d, *J* = 11.4 Hz, 1H), 1.26 (s, 6H), 1.23 (s, 6H), 1.12 (s, 3H), 1.11 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 198.2, 140.3, 135.6, 131.2, 130.1, 126.6, 122.9, 120.5 – 108.7 (m, $CF_2CF_2CF_2CF_3$), 83.8, 47.4, 35.2, 28.3 (t, *J* = 21.6 Hz), 26.70, 26.67, 24.87, 24.84; ^{19}F NMR (565 MHz, Chloroform-*d*) δ -81.06 (t, *J* = 9.5 Hz, 3F), -111.86 – -114.30 (m, 2F), -124.51– -124.50 (m, 2F), -125.90 – -125.94 (m, 2F); ^{11}B NMR (193 MHz, Chloroform-*d*) δ 32.95; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{23}H_{27}B^{79}BrF_9O_3Na^+$ 635.0985; found, 635.1005.

3,3-dimethyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-tosylpentan-1-one (7)



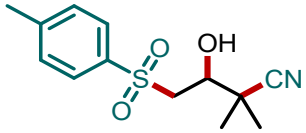
Colorless liquid (41.4 mg, 44%); ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 3.47 – 3.42 (m, 1H), 3.16 (d, *J* = 13.7 Hz, 1H), 2.99 (d, *J* = 15.3 Hz, 1H), 2.71 (d, *J* = 15.3 Hz, 1H), 2.44 (s, 3H), 1.53 (d, *J* = 11.7 Hz, 1H), 1.31 (s, 6H), 1.29 (s, 6H), 1.00 (s, 3H), 0.99 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.2, 144.4, 138.3, 136.2, 132.8, 129.8, 128.5, 128.3, 128.1, 84.0, 55.1, 47.8, 35.3, 26.7, 26.6, 25.2, 25.1, 21.7; ^{11}B NMR (193 MHz, Chloroform-*d*) δ 32.31; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{26}H_{35}BNO_5SNa^+$ 493.2190; found, 493.2202.

2,2-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-tosylbutanenitrile (9)



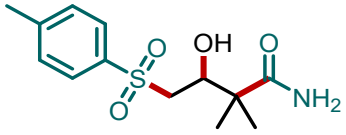
White solid (55.0 mg, 73%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.58 – 3.51 (m, 1H), 3.27 (dd, *J* = 13.6, 1.8 Hz, 1H), 2.45 (s, 3H), 1.58 (dd, *J* = 12.3, 1.7 Hz, 1H), 1.36 (s, 3H), 1.33 (s, 12H), 1.31 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 135.7, 130.0, 128.2, 123.9, 84.7, 55.8, 33.9, 27.1, 25.1, 25.0, 24.6, 21.7; ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.89; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{28}BNO_5Na^+$ 400.1724; found, 400.1737.

3-hydroxy-2,2-dimethyl-4-tosylbutanenitrile (9a)



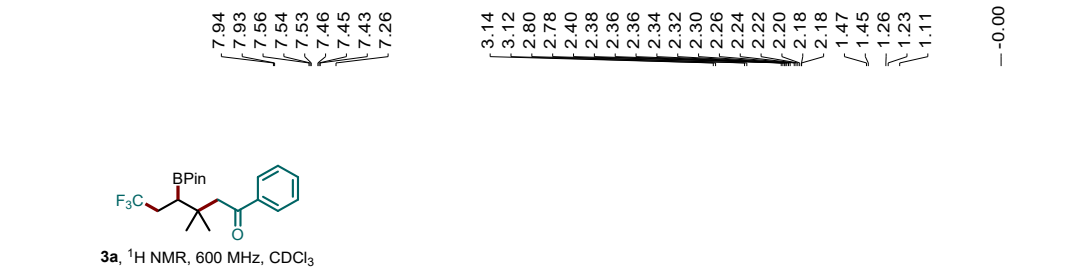
Colorless liquid (47.6 mg, 82%); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 4.05 (d, *J* = 9.9 Hz, 1H), 3.84 (s, 1H), 3.41 – 3.38 (m, 1H), 3.29 (dd, *J* = 14.0, 10.0 Hz, 1H), 2.47 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.5, 136.0, 130.2, 127.9, 122.4, 70.4, 58.9, 37.6, 23.3, 21.6; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{17}NO_3SNa^+$ 290.0821; found, 290.0826.

3-hydroxy-2,2-dimethyl-4-tosylbutanamide (9b)

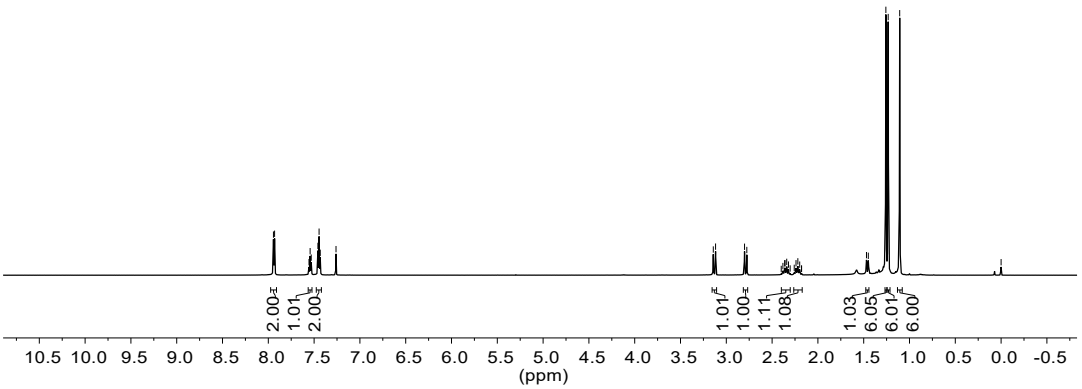


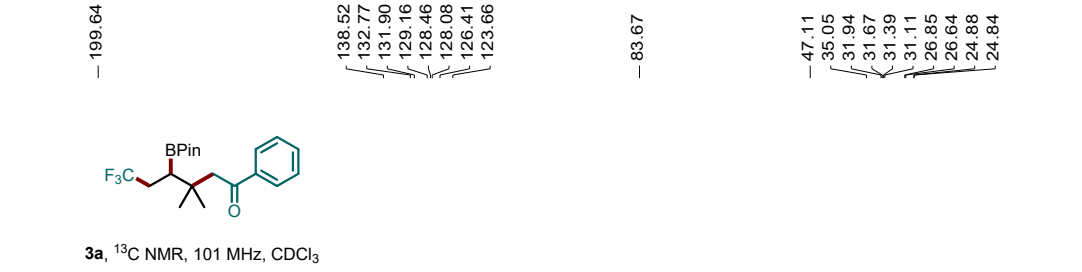
White solid (52.4 mg, 85%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.06 (s, 1H), 6.91 (s, 1H), 5.20 (d, *J* = 6.2 Hz, 1H), 4.06 – 4.03 (m, 1H), 3.28 (dd, *J* = 14.6, 9.6 Hz, 1H), 3.18 (d, *J* = 14.6 Hz, 1H), 2.40 (s, 3H), 1.00 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.3, 144.3, 138.3, 130.0, 128.2, 70.9, 59.9, 46.8, 22.5, 21.5, 20.9; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{19}NO_4SNa^+$ 308.0927; found, 308.0932.

4. NMR Spectra

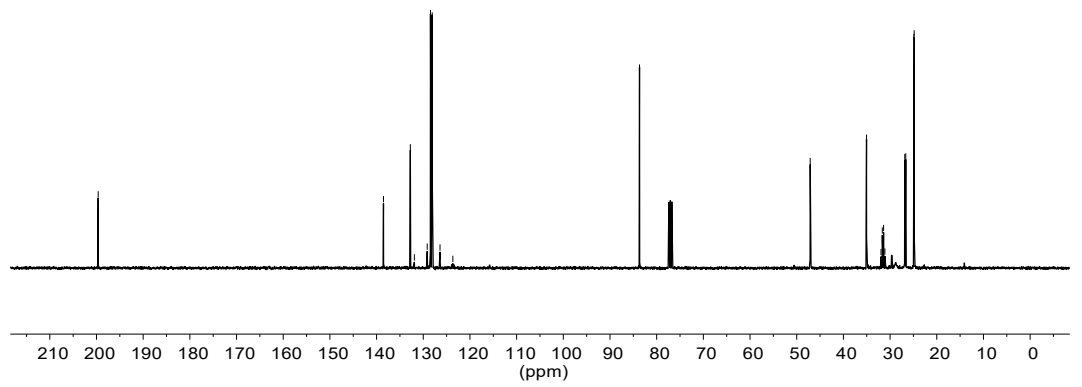


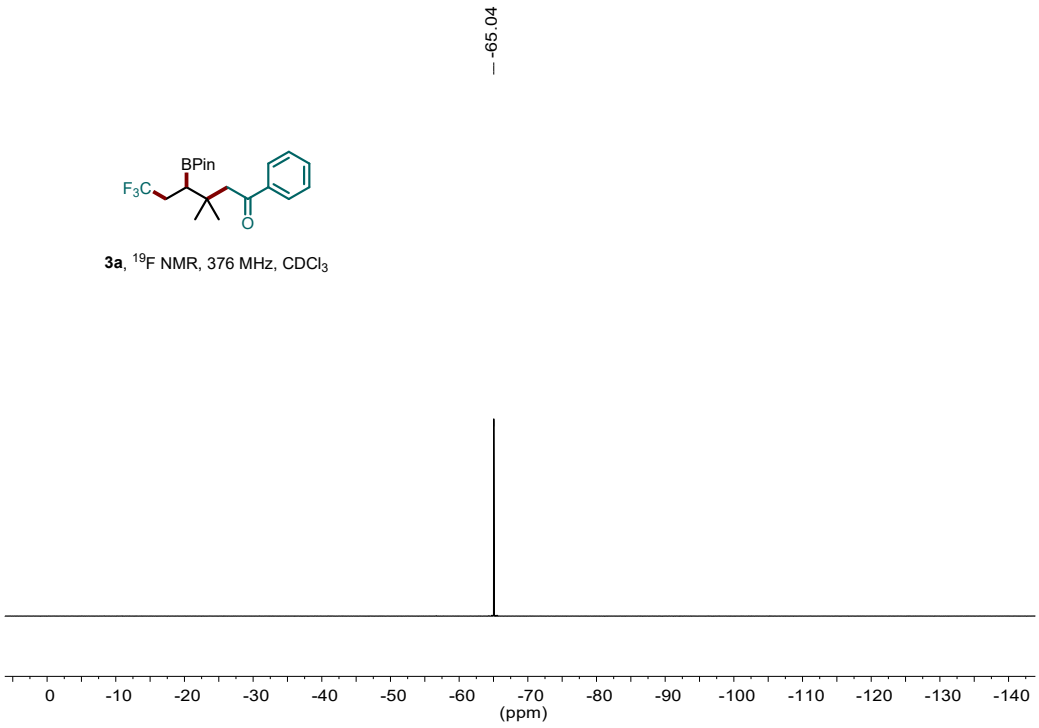
3a, ^{1}H NMR, 600 MHz, $CDCl_3$



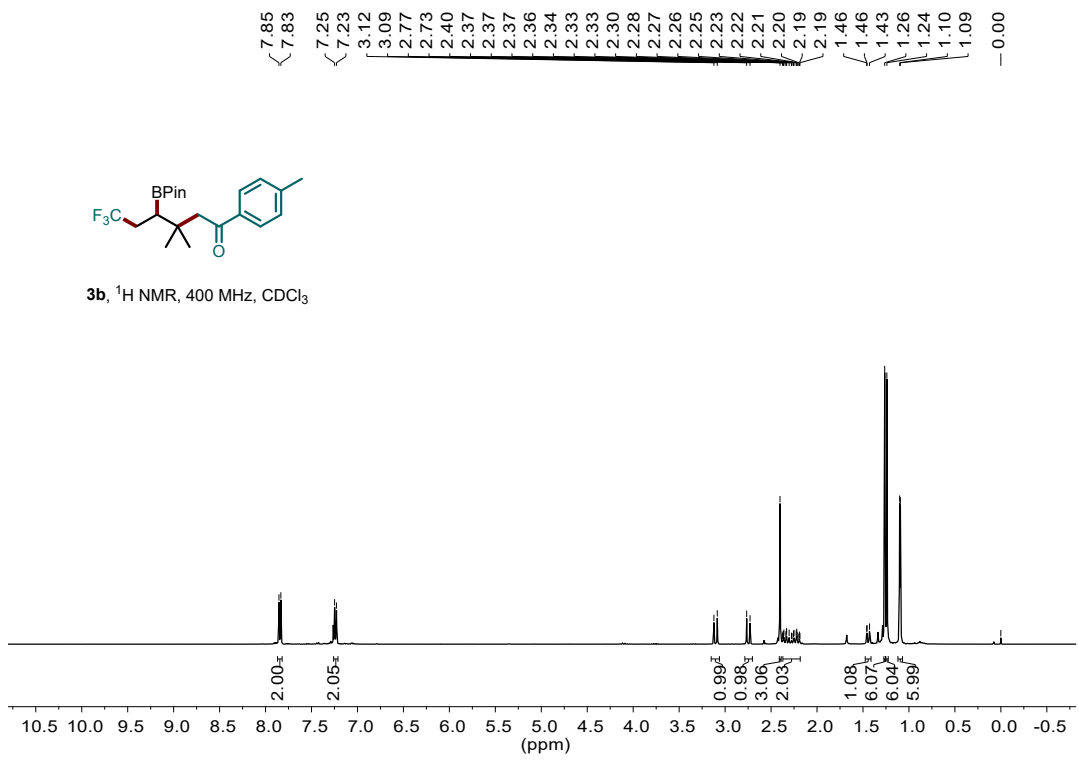


3a, ^{13}C NMR, 101 MHz, $CDCl_3$

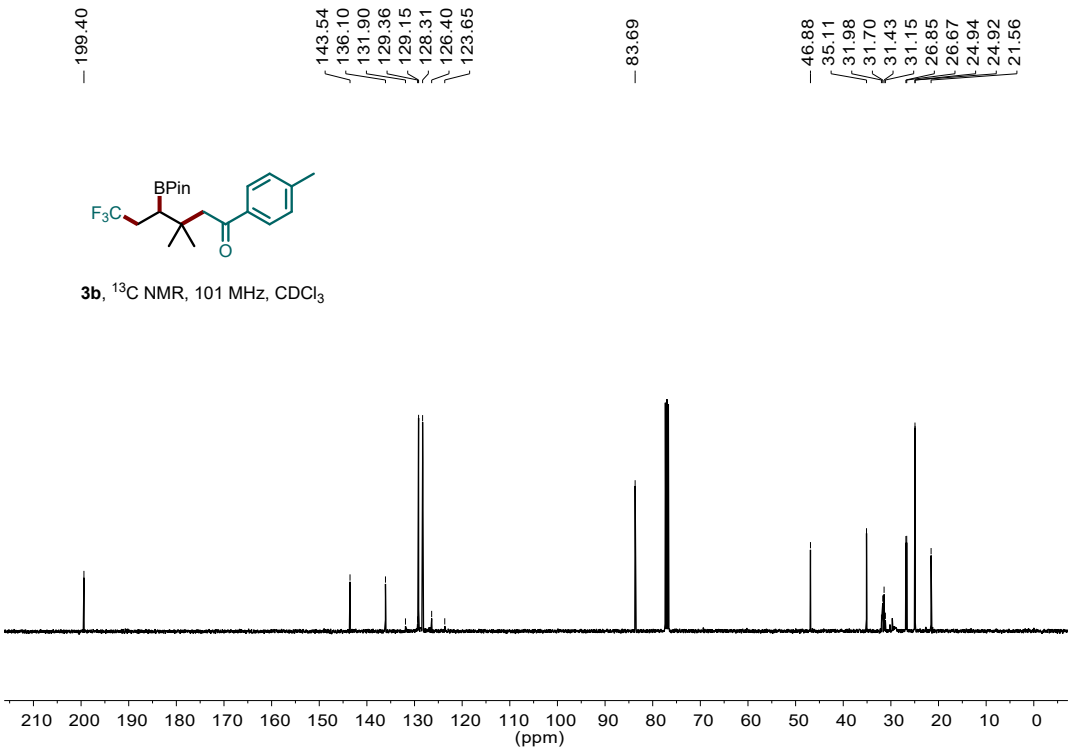




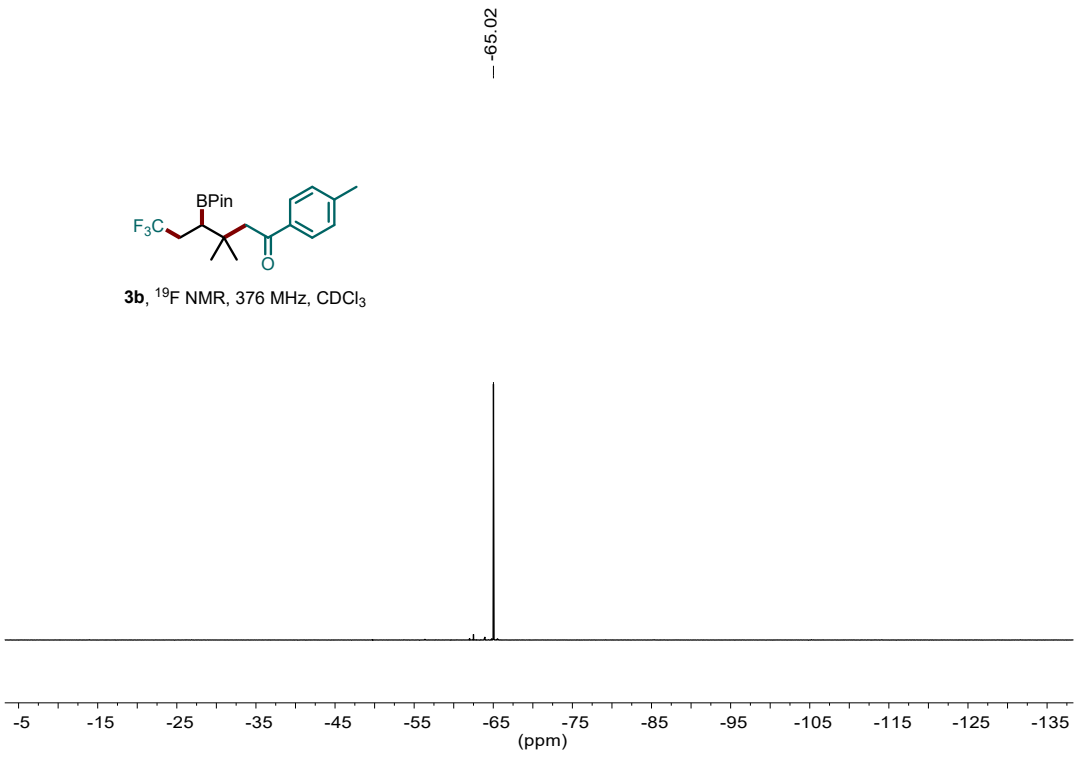
3a, ^{19}F NMR, 376 MHz, $CDCl_3$



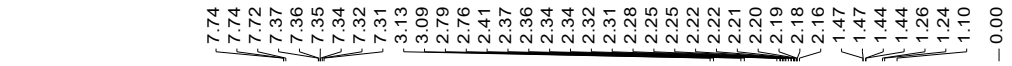
3b, ^{1}H NMR, 400 MHz, $CDCl_3$

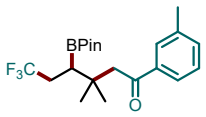


3b, ^{13}C NMR, 101 MHz, $CDCl_3$

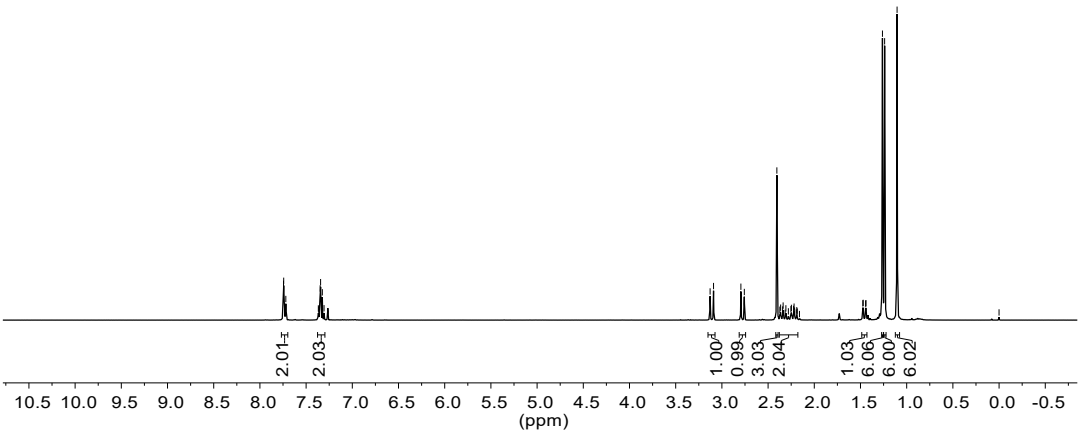


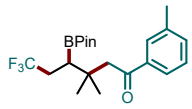
3b, ^{19}F NMR, 376 MHz, $CDCl_3$



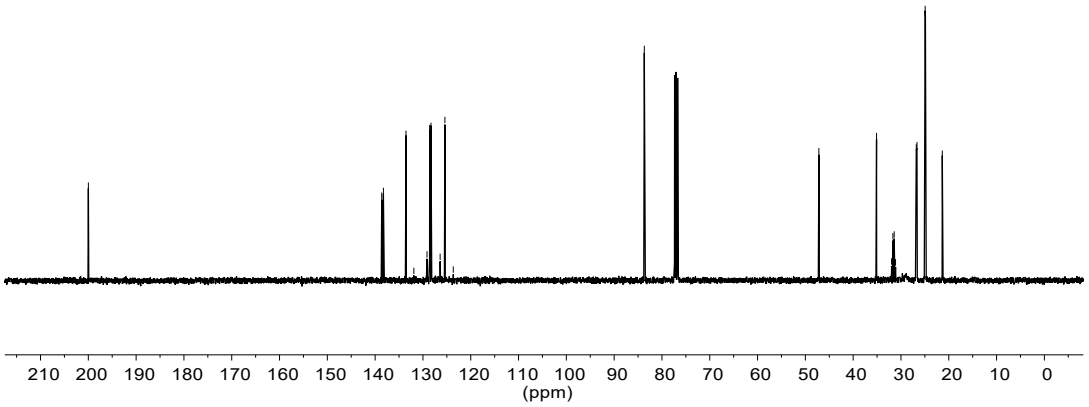


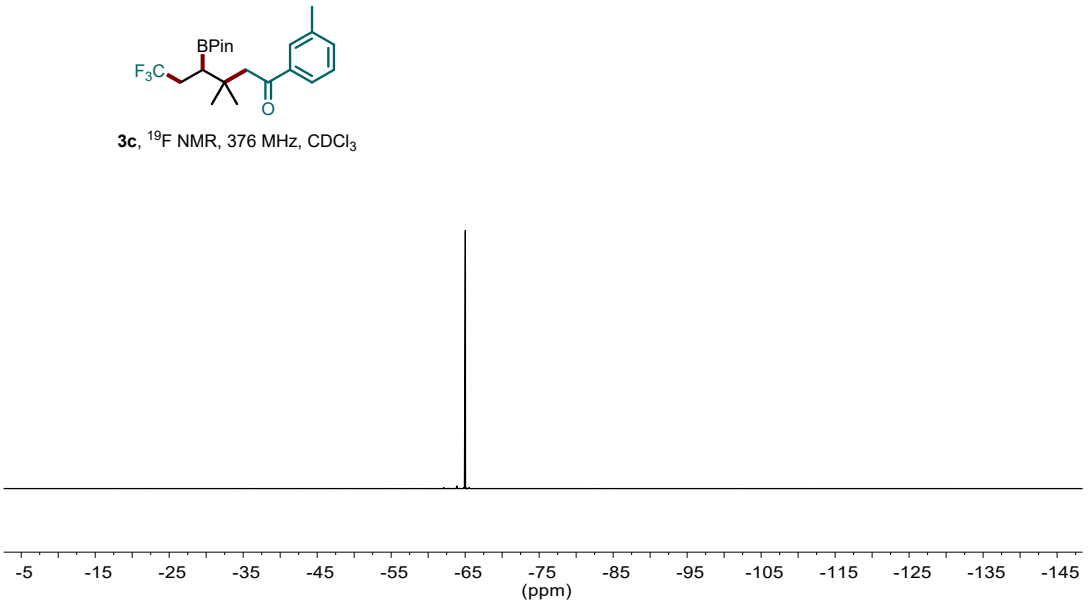
3c, ^{1}H NMR, 400 MHz, $CDCl_3$



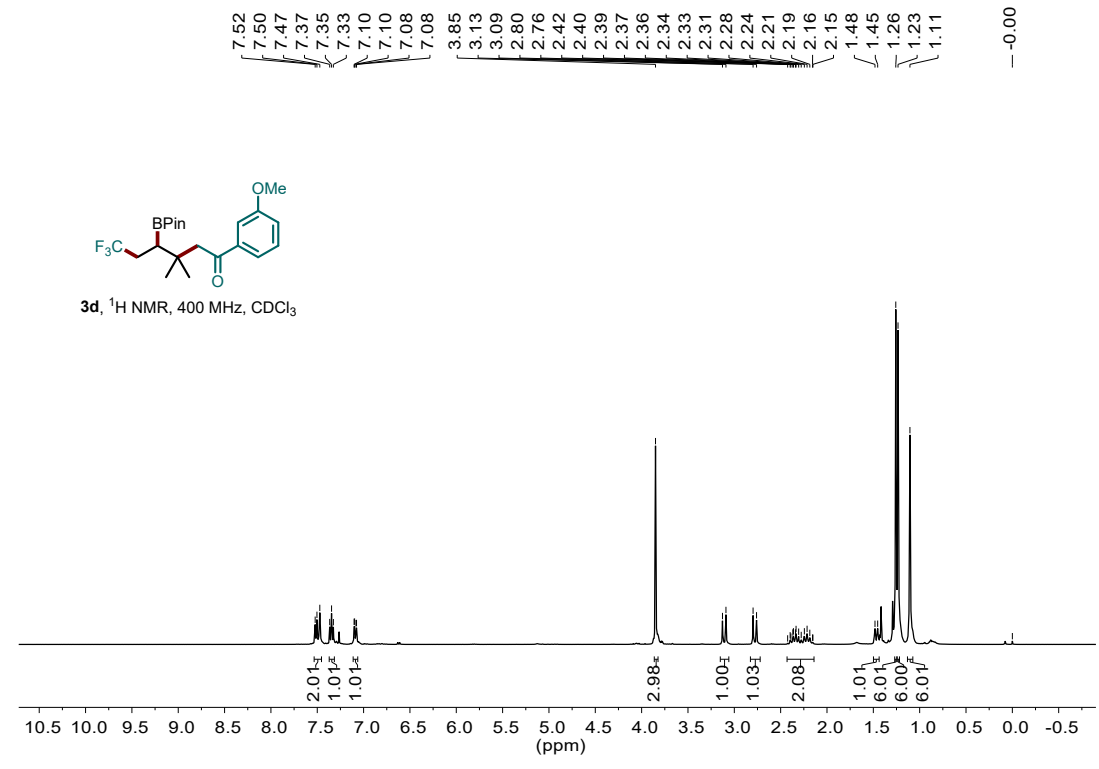


3c, ^{13}C NMR, 101 MHz, $CDCl_3$

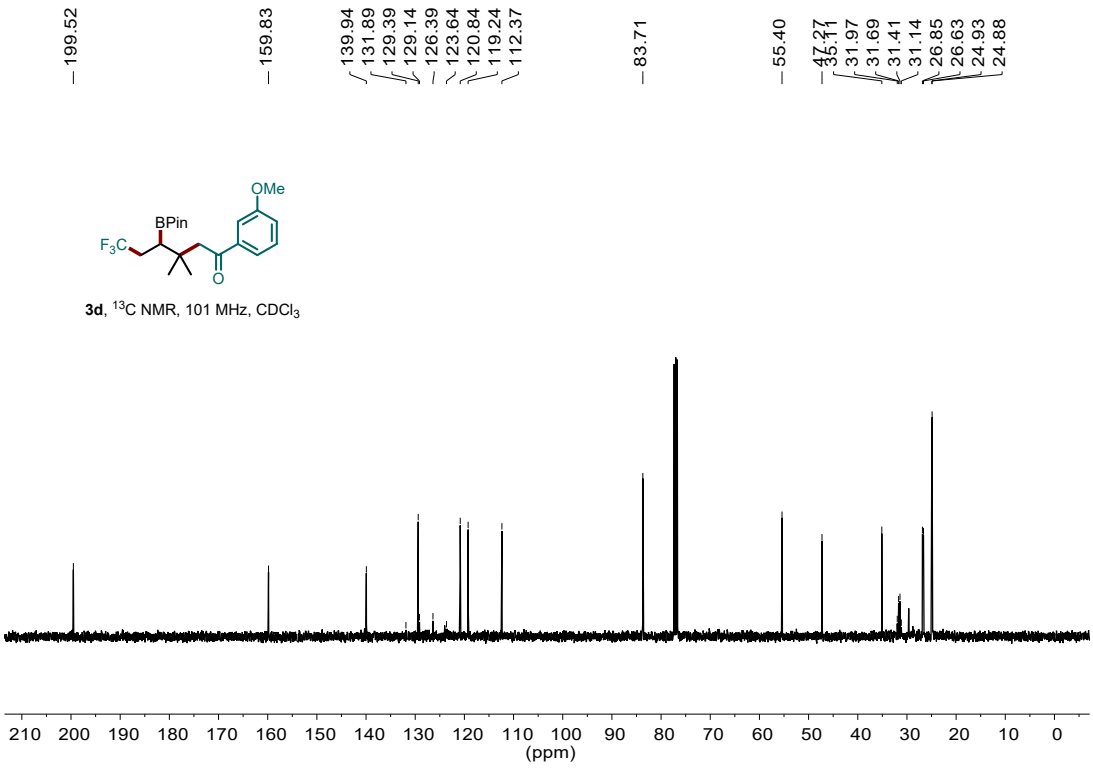




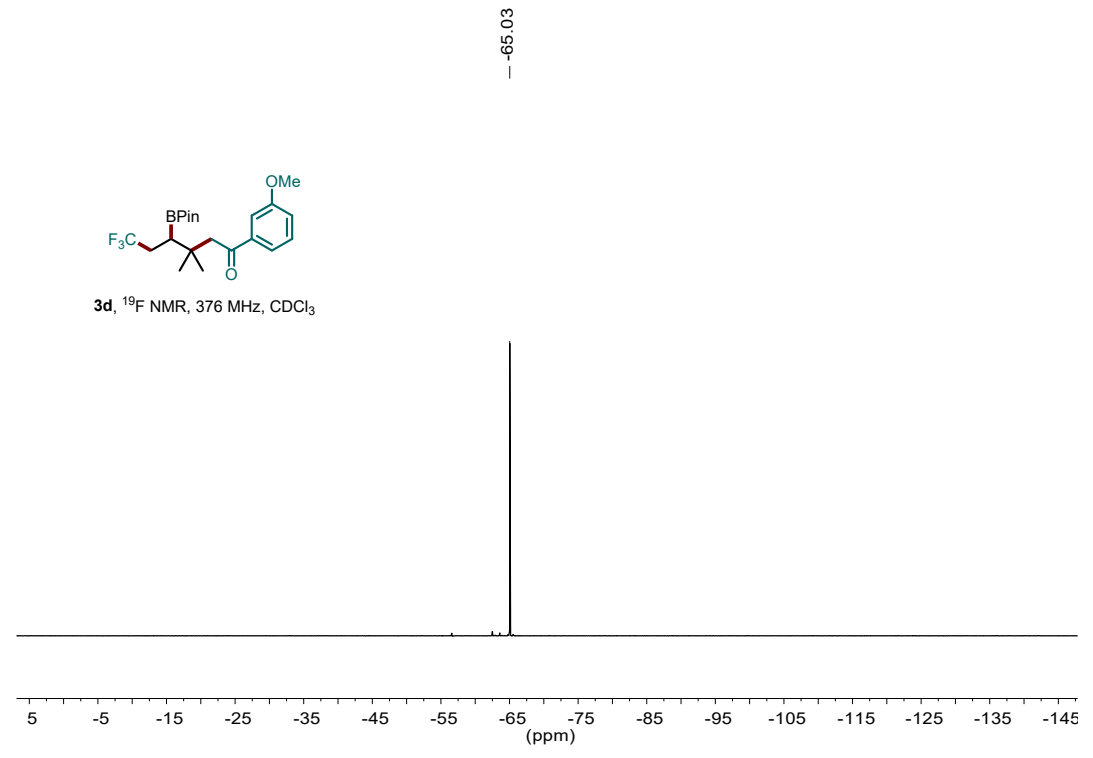
3c, ^{19}F NMR, 376 MHz, $CDCl_3$



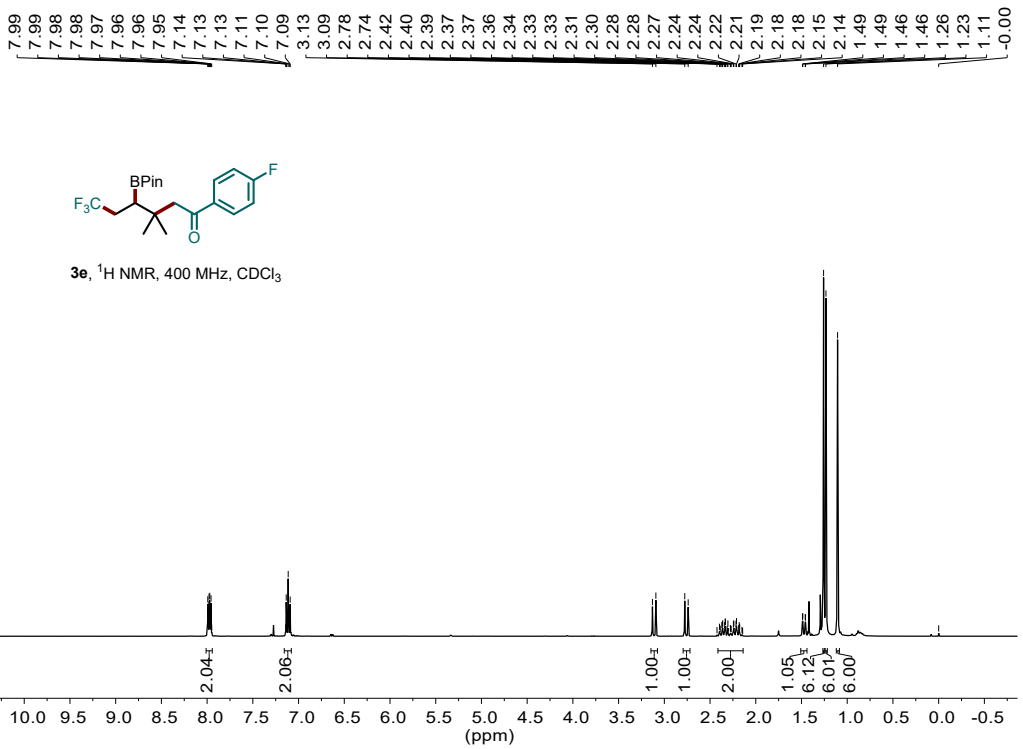
3d, ^{1}H NMR, 400 MHz, $CDCl_3$



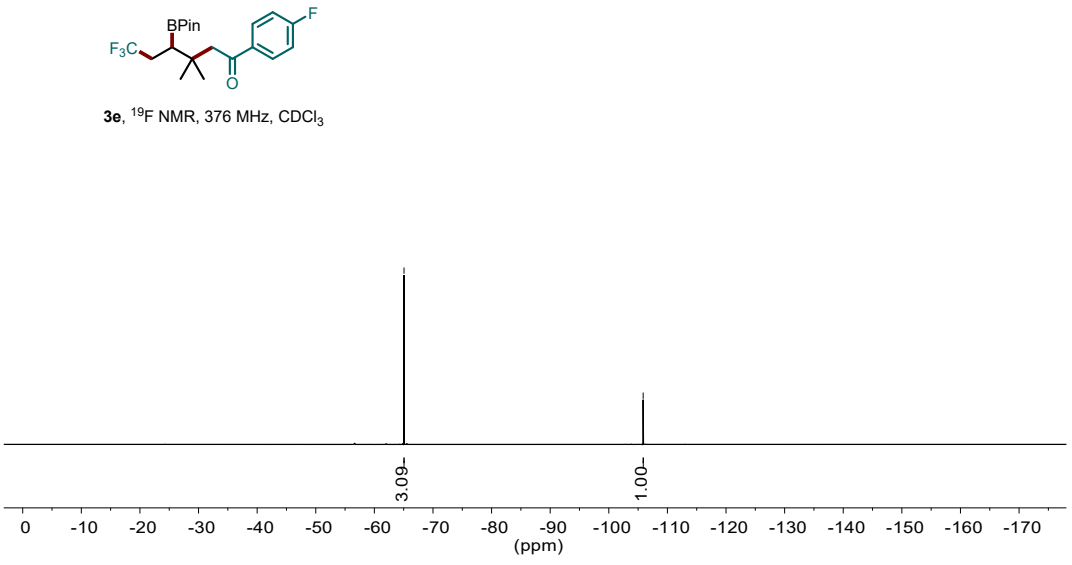
3d, ^{13}C NMR, 101 MHz, $CDCl_3$



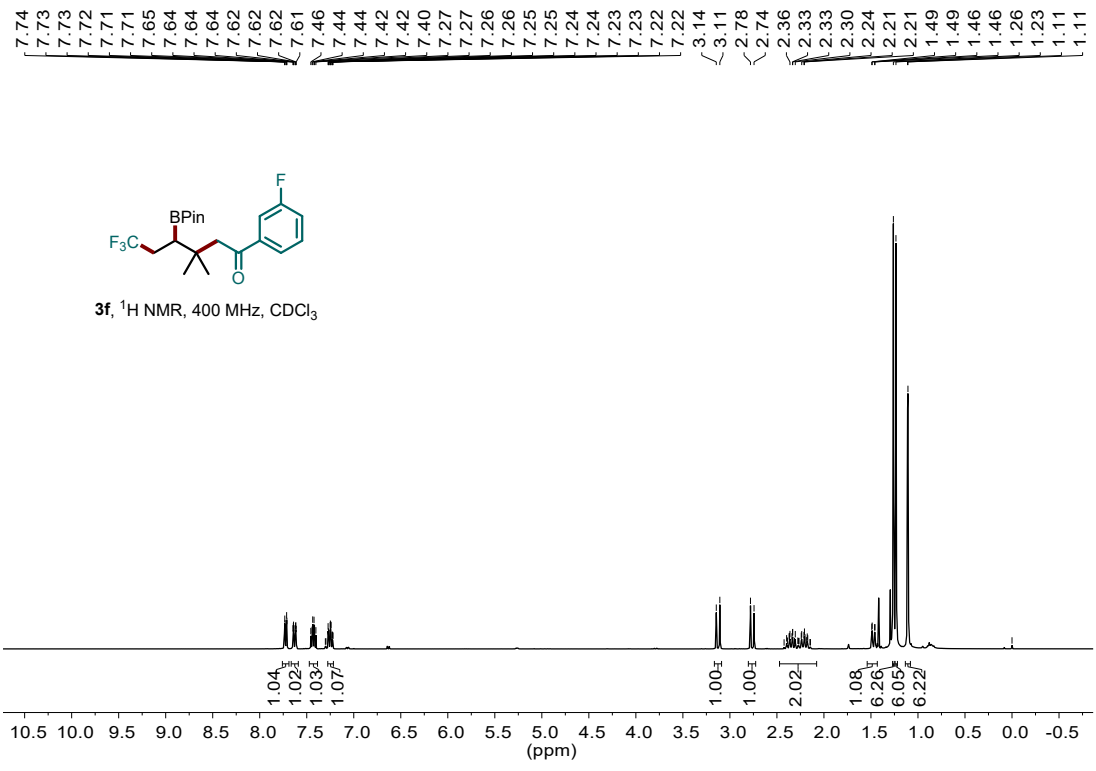
3d, ^{19}F NMR, 376 MHz, $CDCl_3$



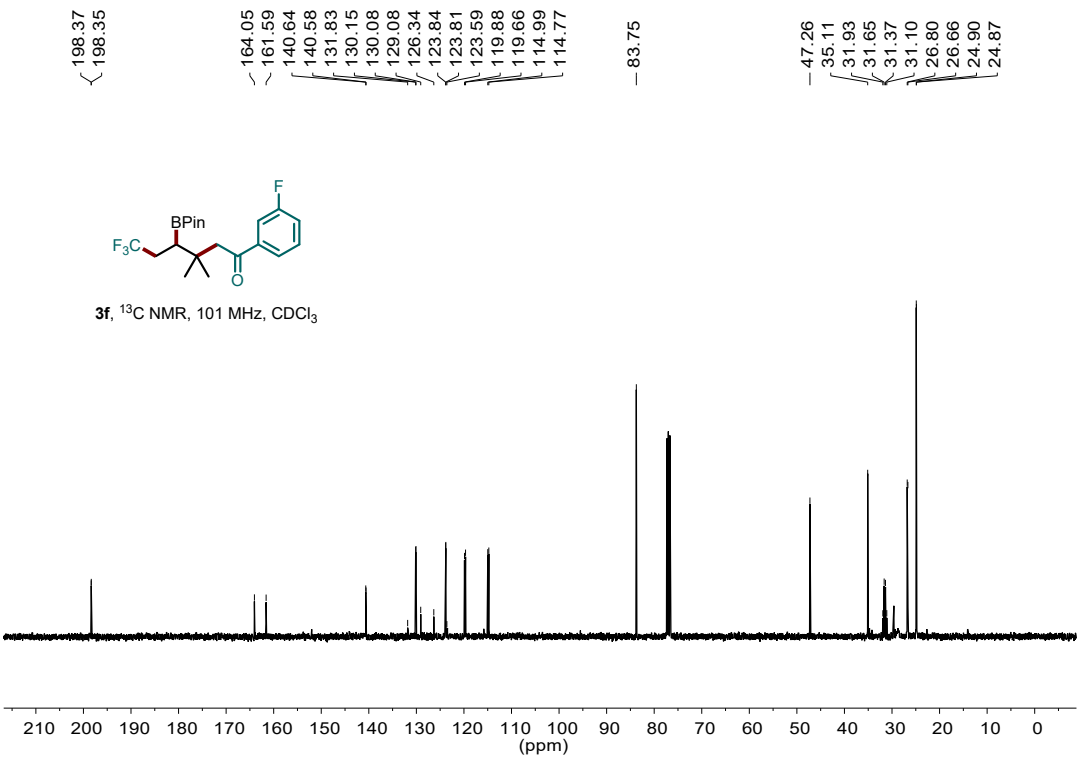
3e, ^{1}H NMR, 400 MHz, $CDCl_3$



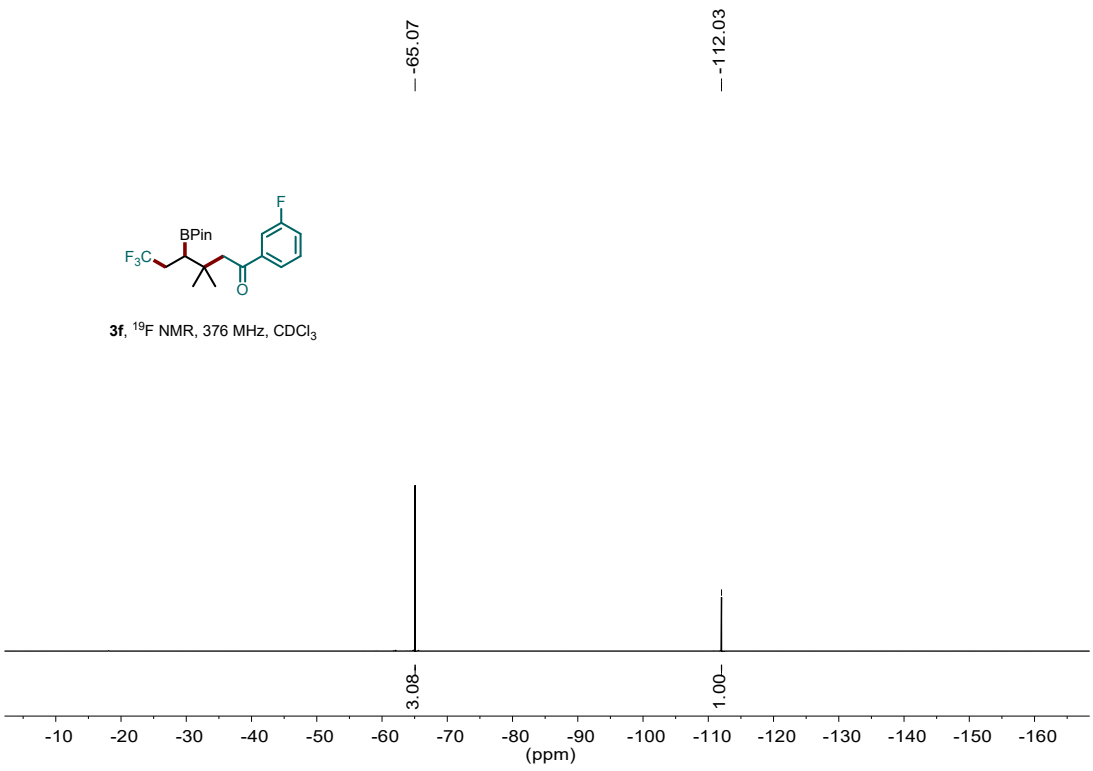
3e, ^{19}F NMR, 376 MHz, $CDCl_3$



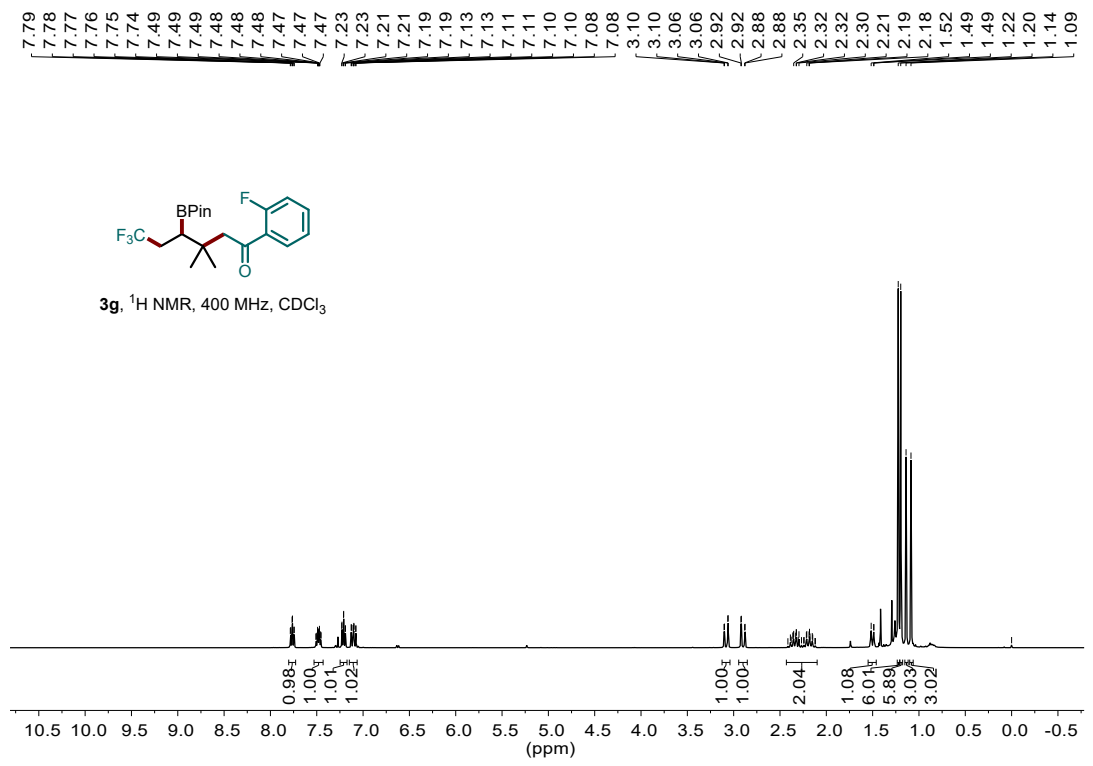
3f, ^{1}H NMR, 400 MHz, $CDCl_3$



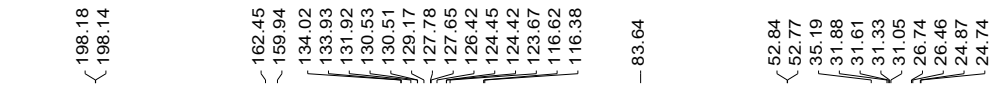
3f, ^{13}C NMR, 101 MHz, $CDCl_3$

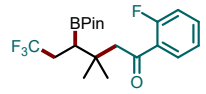


3f, ^{19}F NMR, 376 MHz, $CDCl_3$

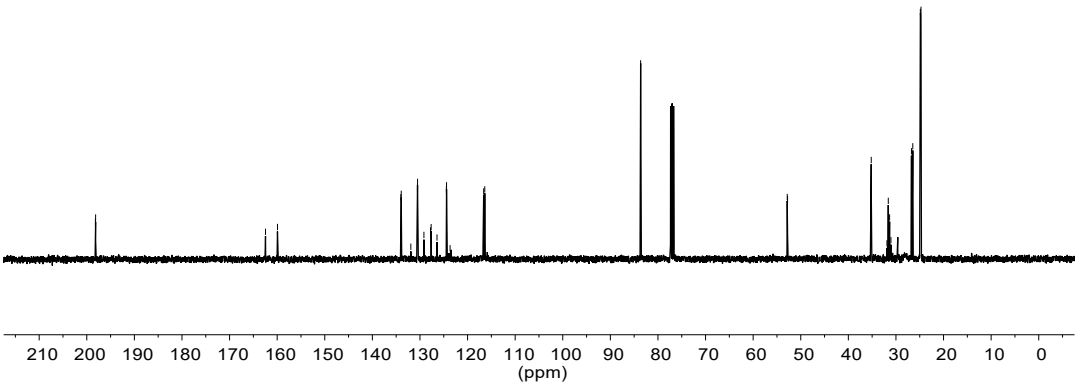


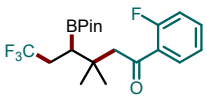
3g, ^{1}H NMR, 400 MHz, $CDCl_3$



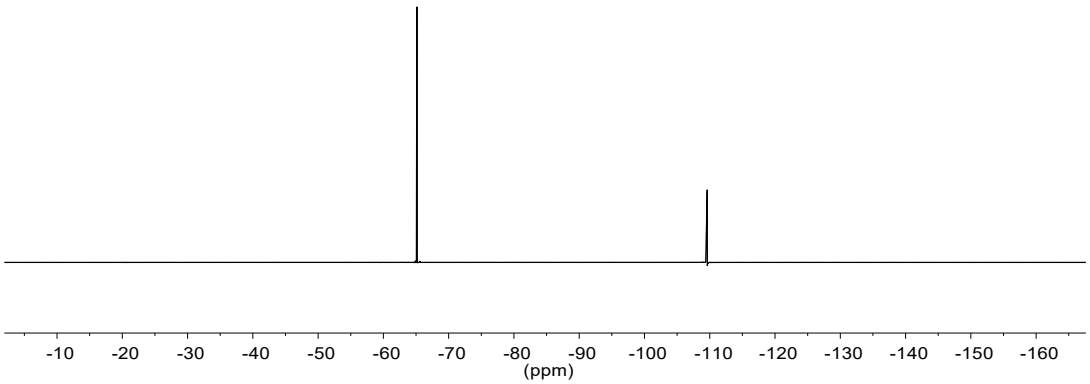


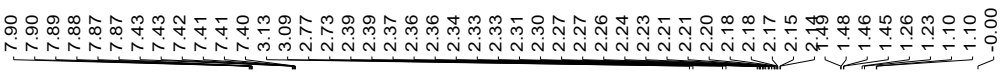
3g, ^{13}C NMR, 101 MHz, $CDCl_3$

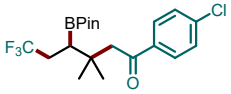




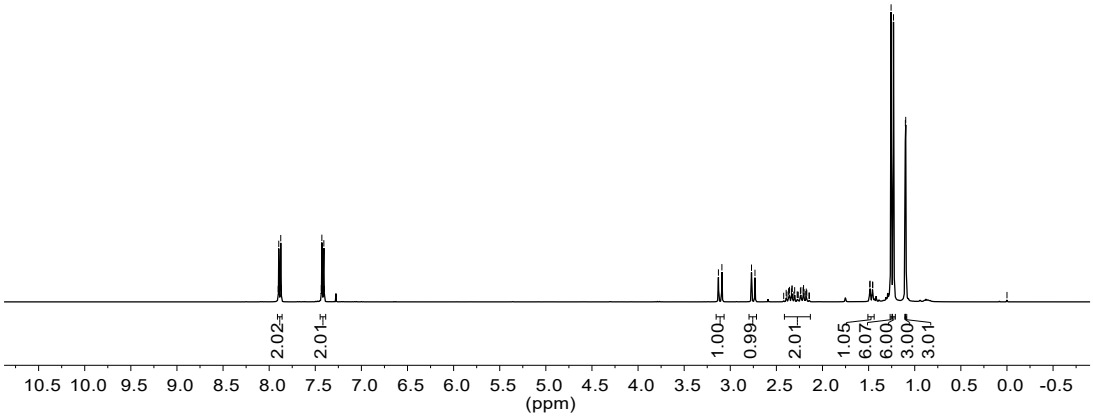
3g, ^{19}F NMR, 376 MHz, $CDCl_3$

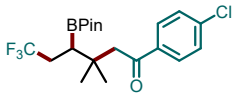




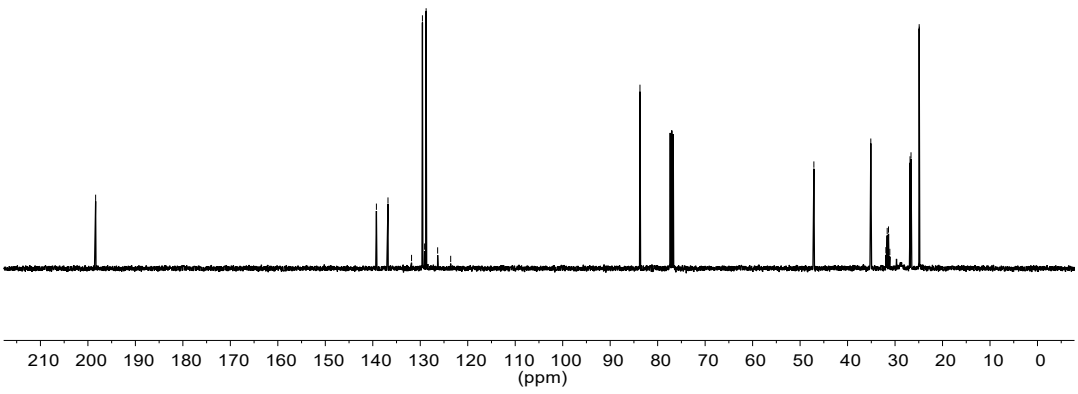


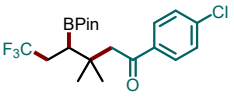
3h, ^{1}H NMR, 400 MHz, $CDCl_3$



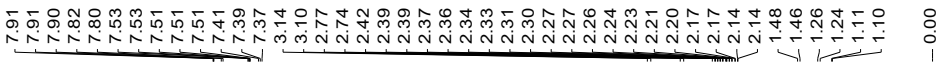


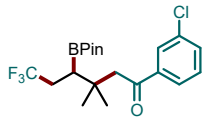
3h, ^{13}C NMR, 101 MHz, $CDCl_3$



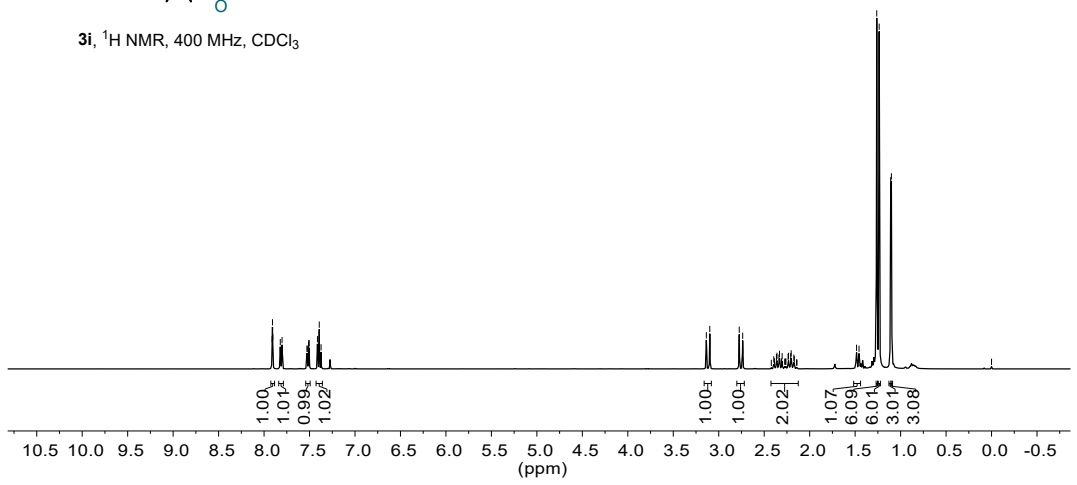


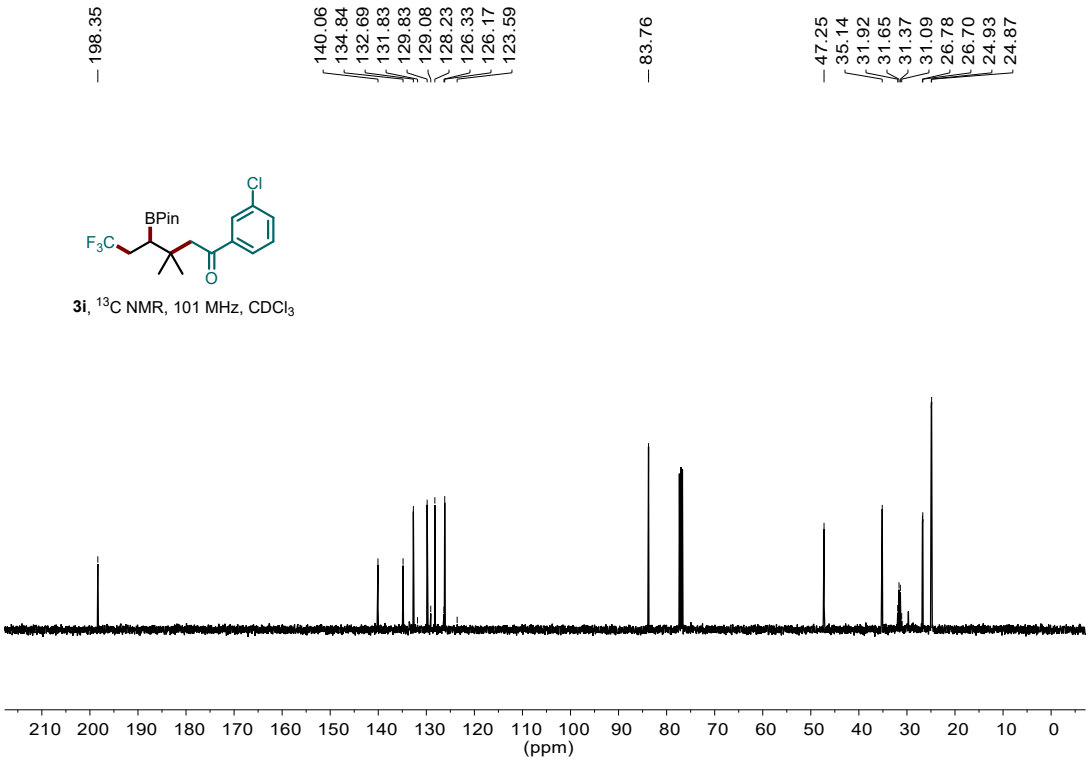
3h, ^{19}F NMR, 376 MHz, $CDCl_3$



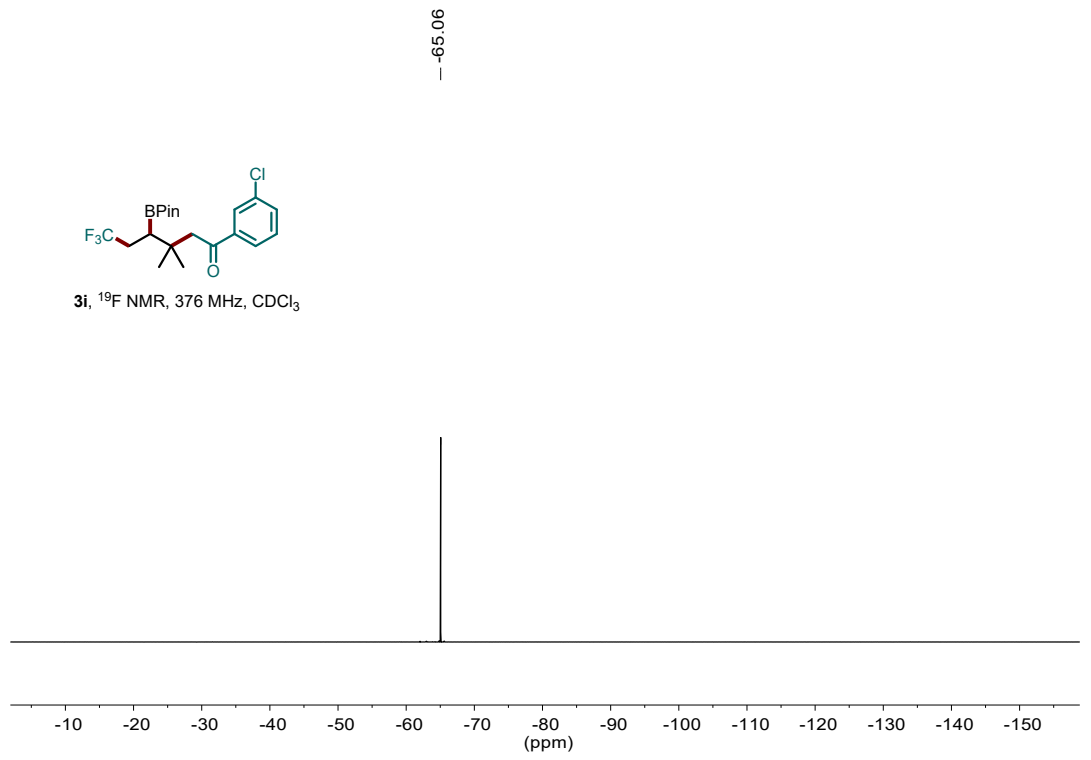


3i, ^{1}H NMR, 400 MHz, $CDCl_3$

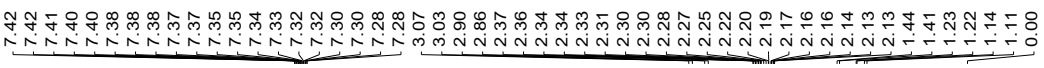


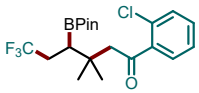


3i, ^{13}C NMR, 101 MHz, $CDCl_3$

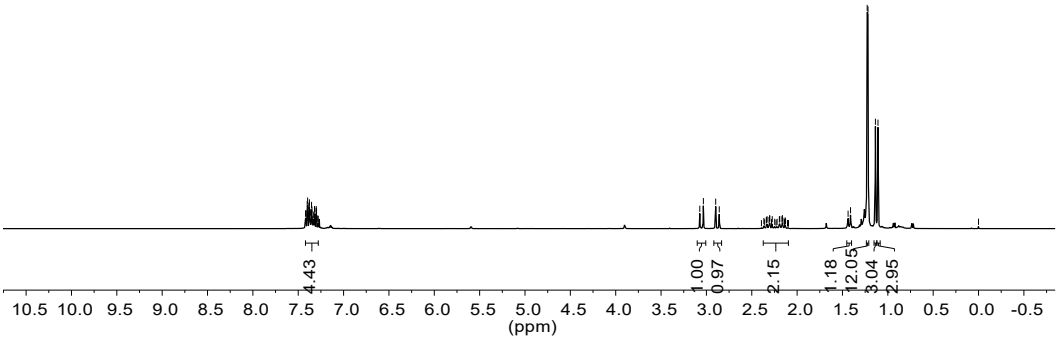


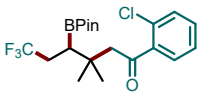
3i, ^{19}F NMR, 376 MHz, $CDCl_3$



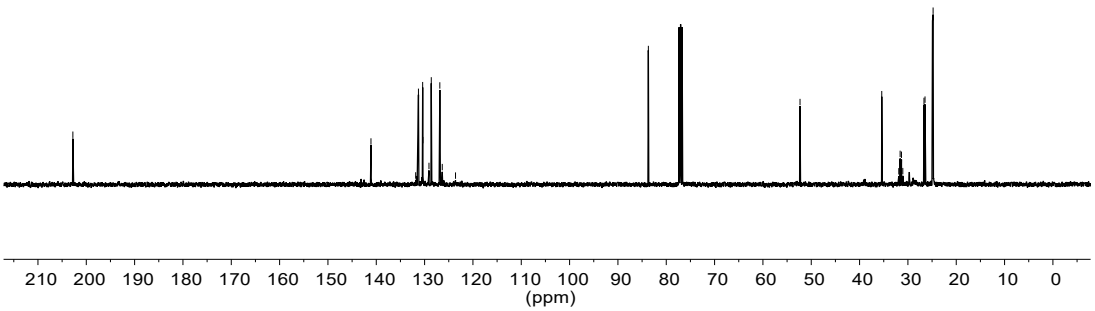


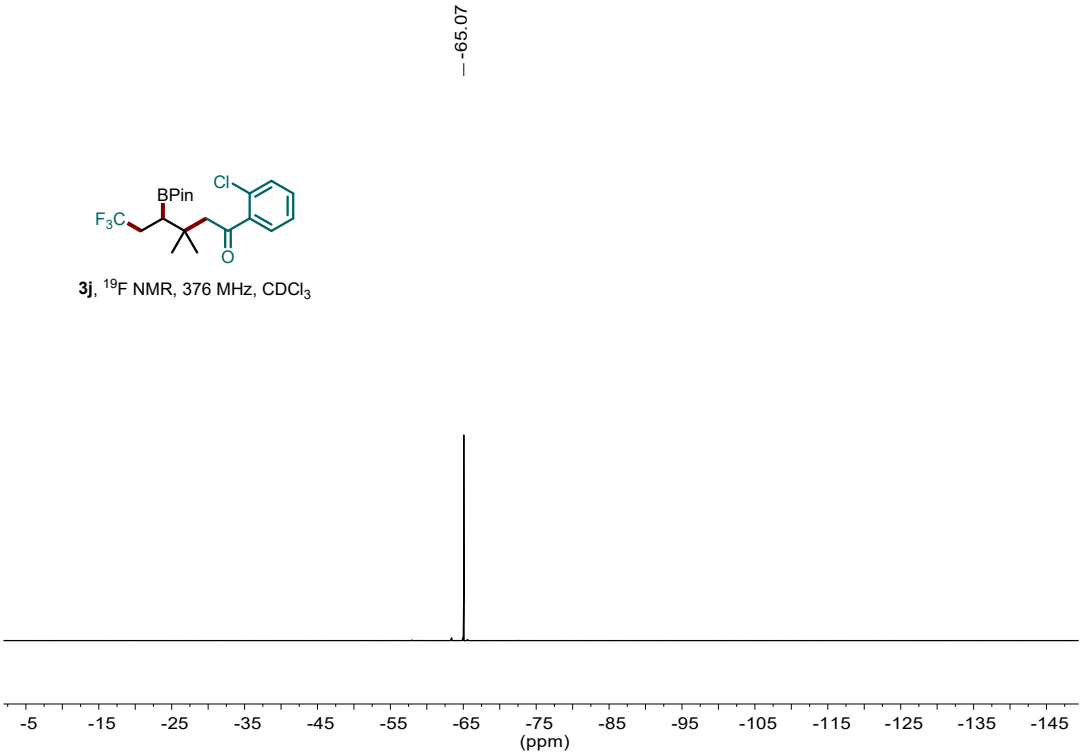
3j, ^{1}H NMR, 400 MHz, $CDCl_3$



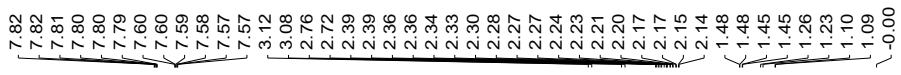


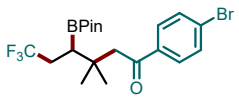
3j, ^{13}C NMR, 101 MHz, $CDCl_3$



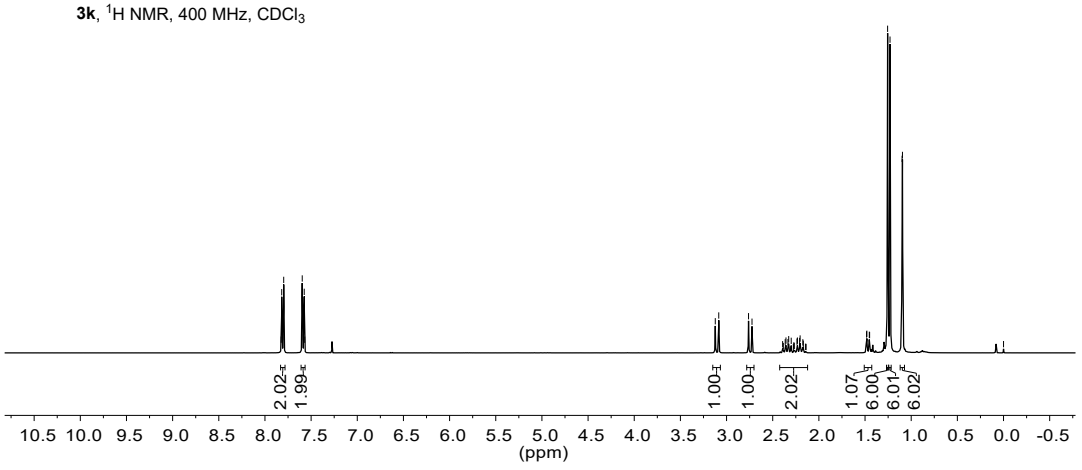


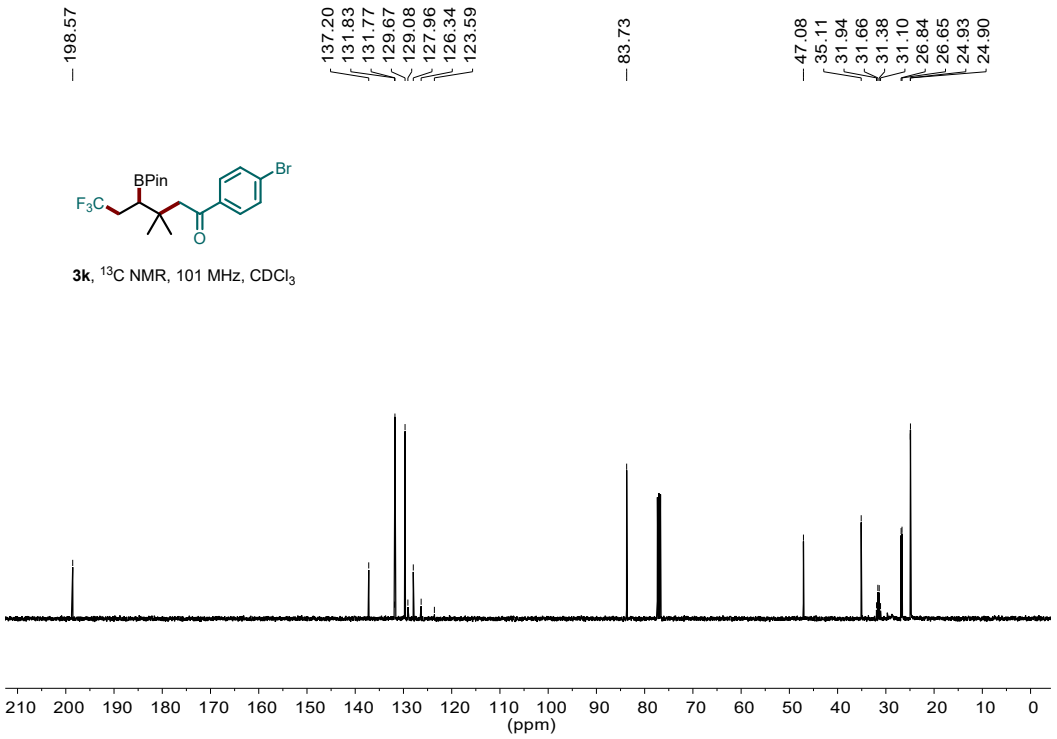
3j, ^{19}F NMR, 376 MHz, $CDCl_3$



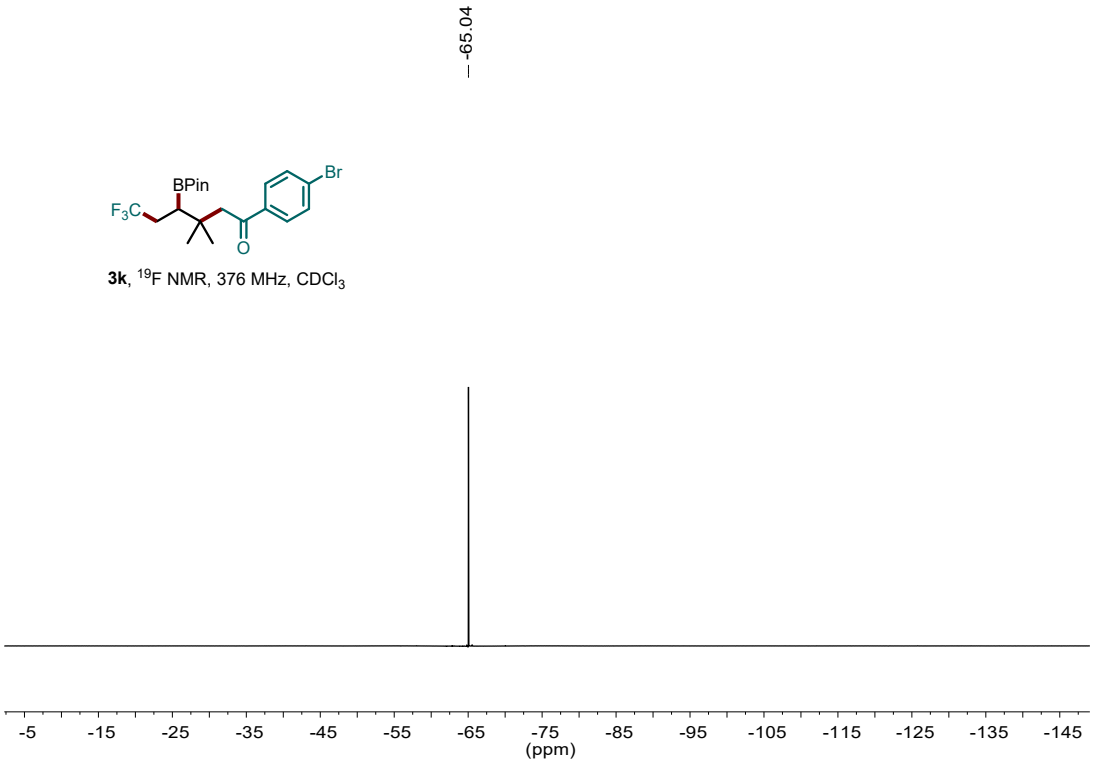


3k, ^{1}H NMR, 400 MHz, $CDCl_3$

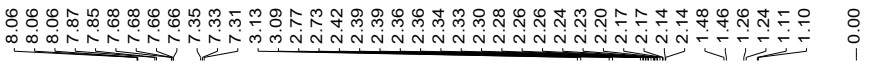


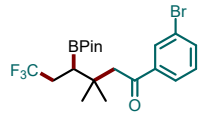


3k, ^{13}C NMR, 101 MHz, $CDCl_3$

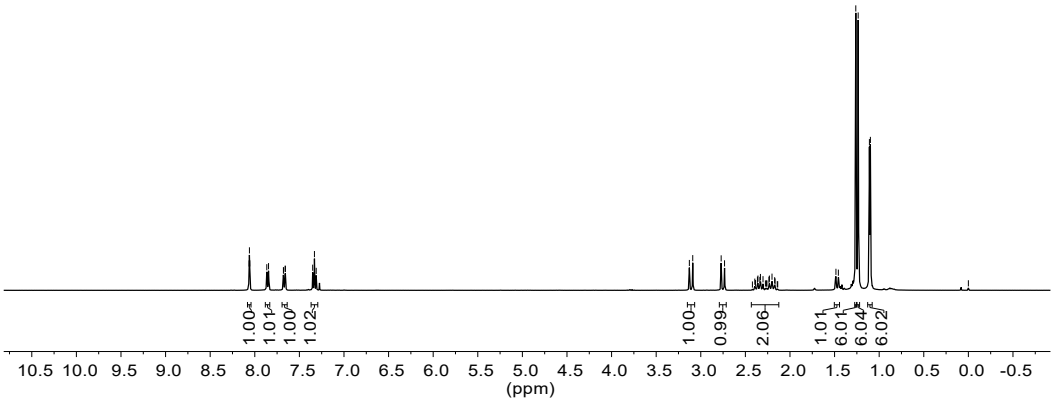


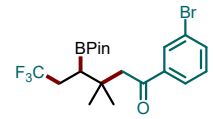
3k, ^{19}F NMR, 376 MHz, $CDCl_3$



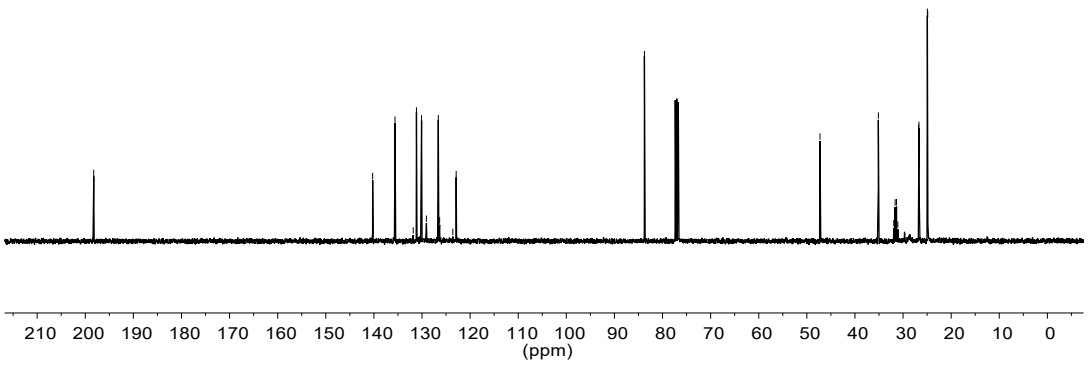


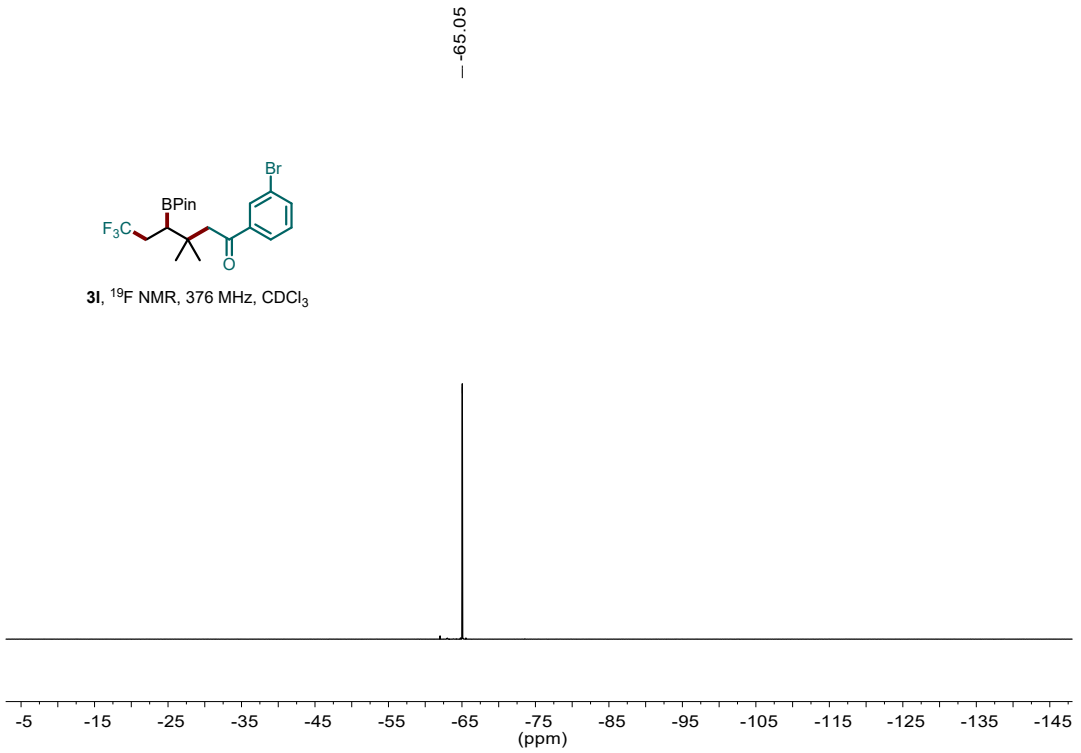
3l, ^{1}H NMR, 400 MHz, $CDCl_3$



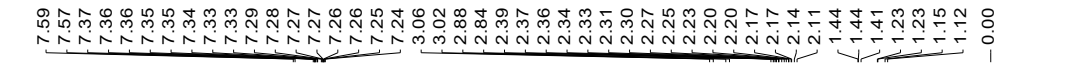


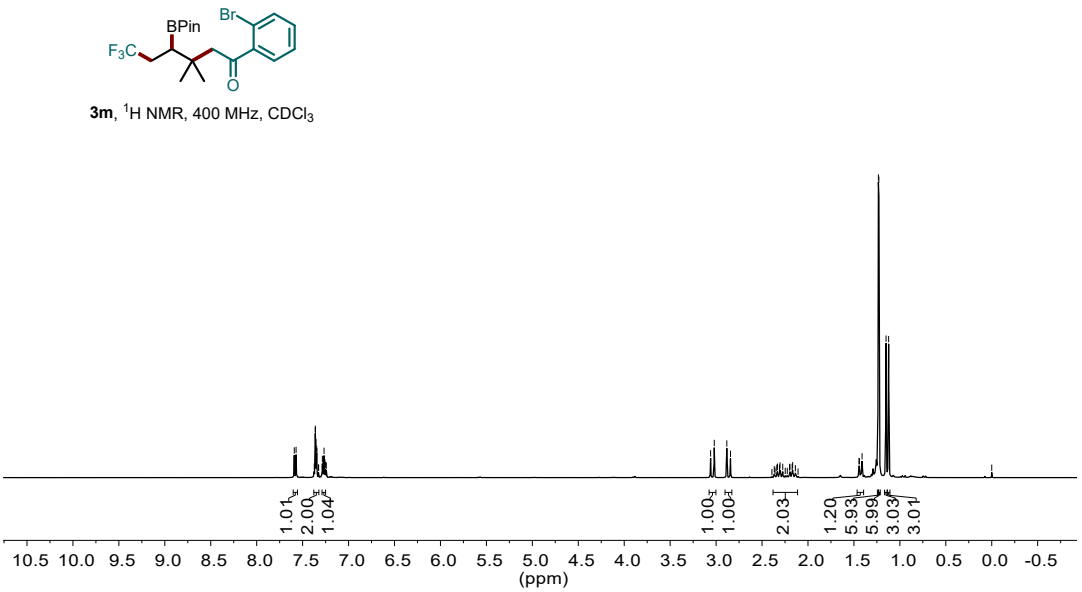
3l, ^{13}C NMR, 101 MHz, $CDCl_3$



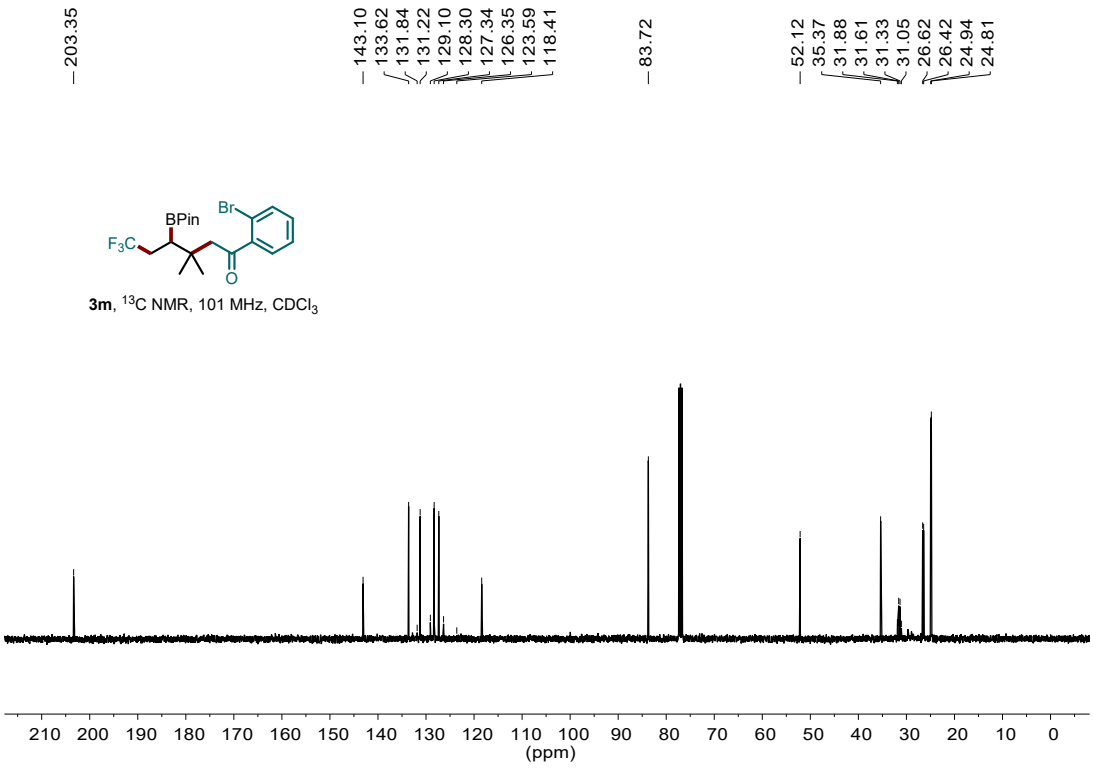


3l, ^{19}F NMR, 376 MHz, $CDCl_3$

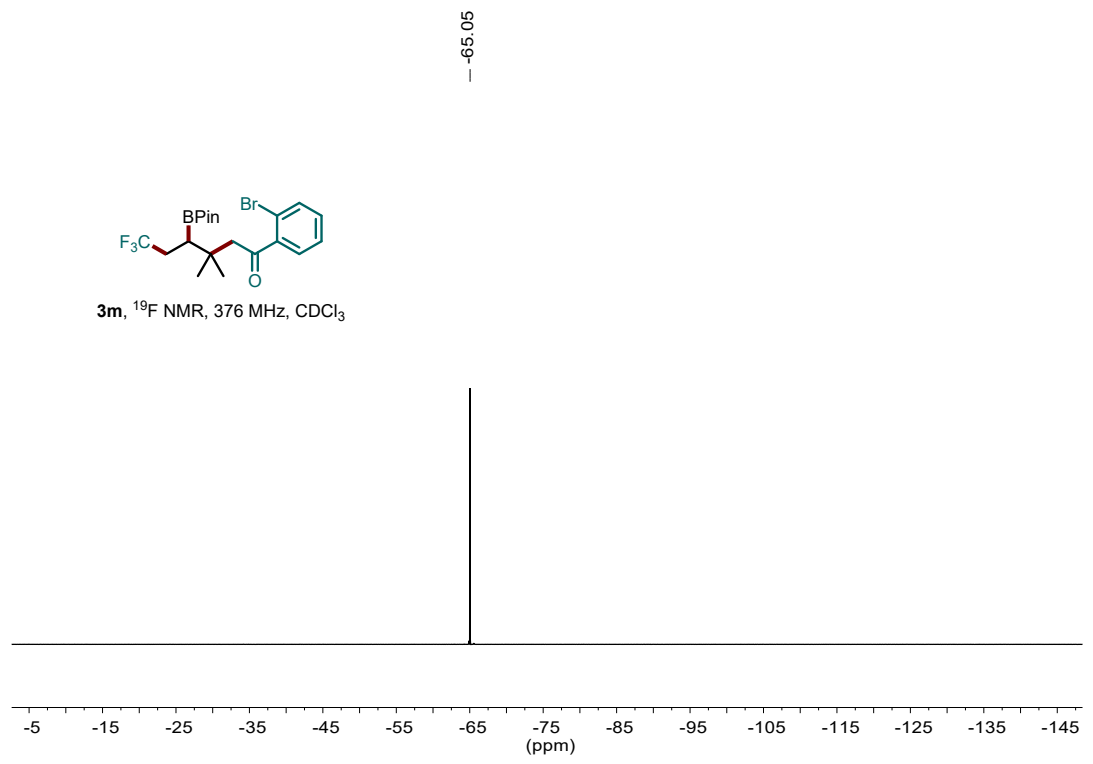




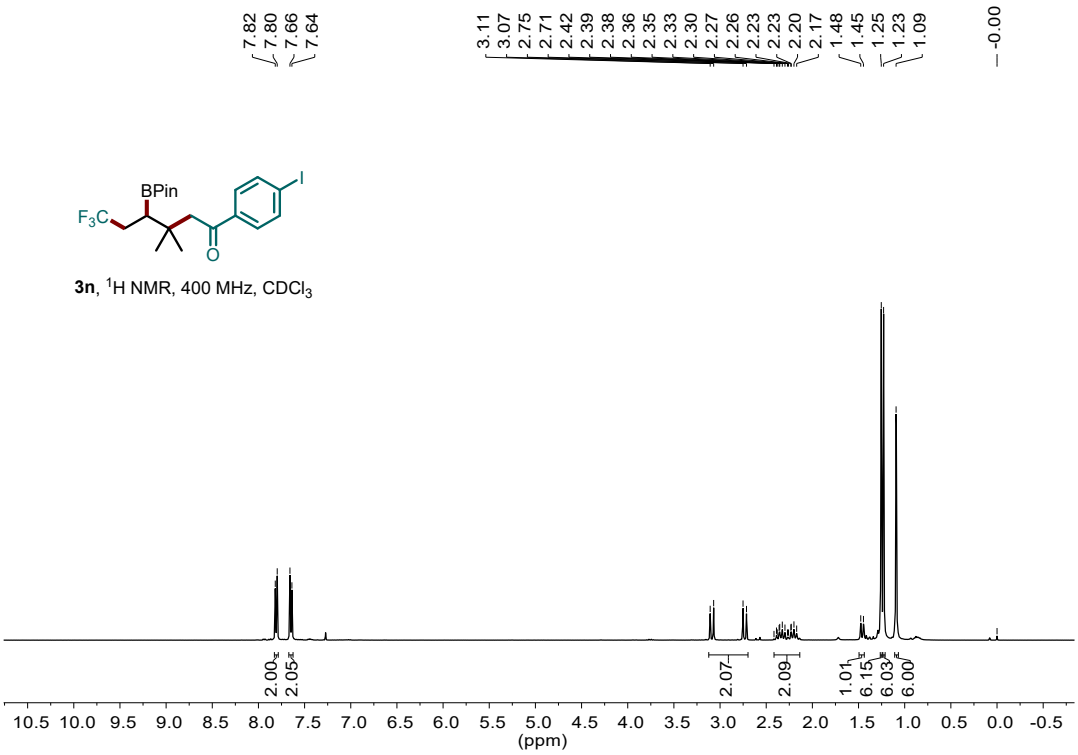
3m, ^{1}H NMR, 400 MHz, $CDCl_3$



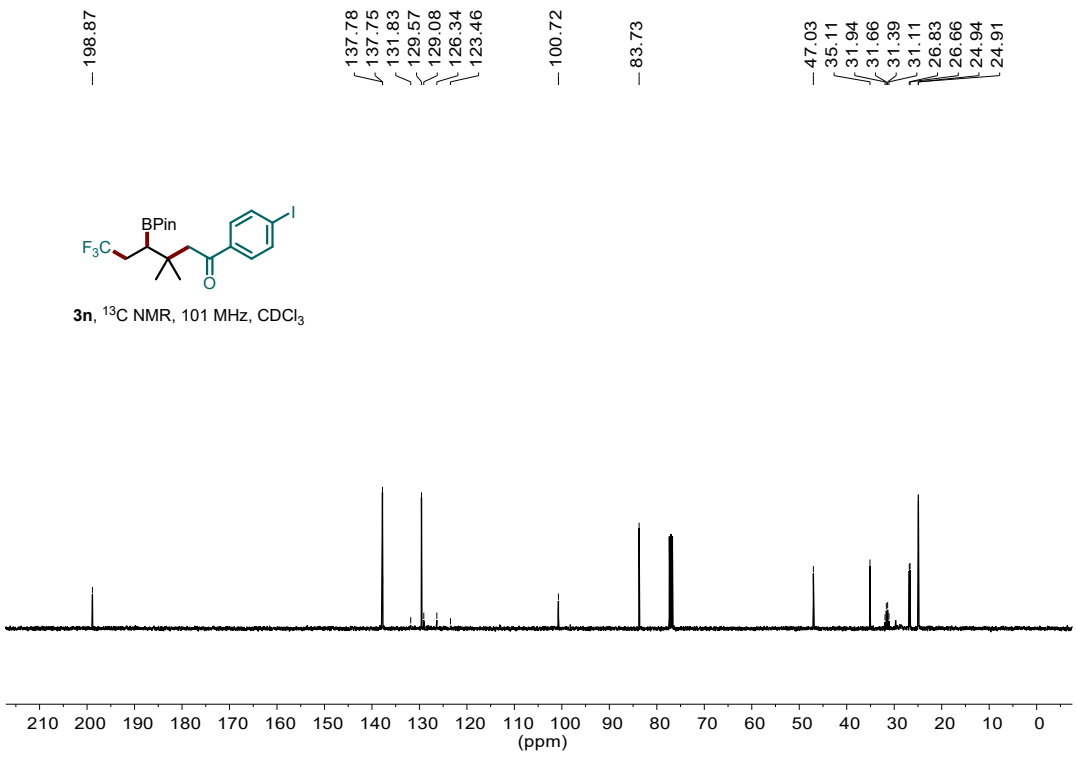
3m, ^{13}C NMR, 101 MHz, $CDCl_3$



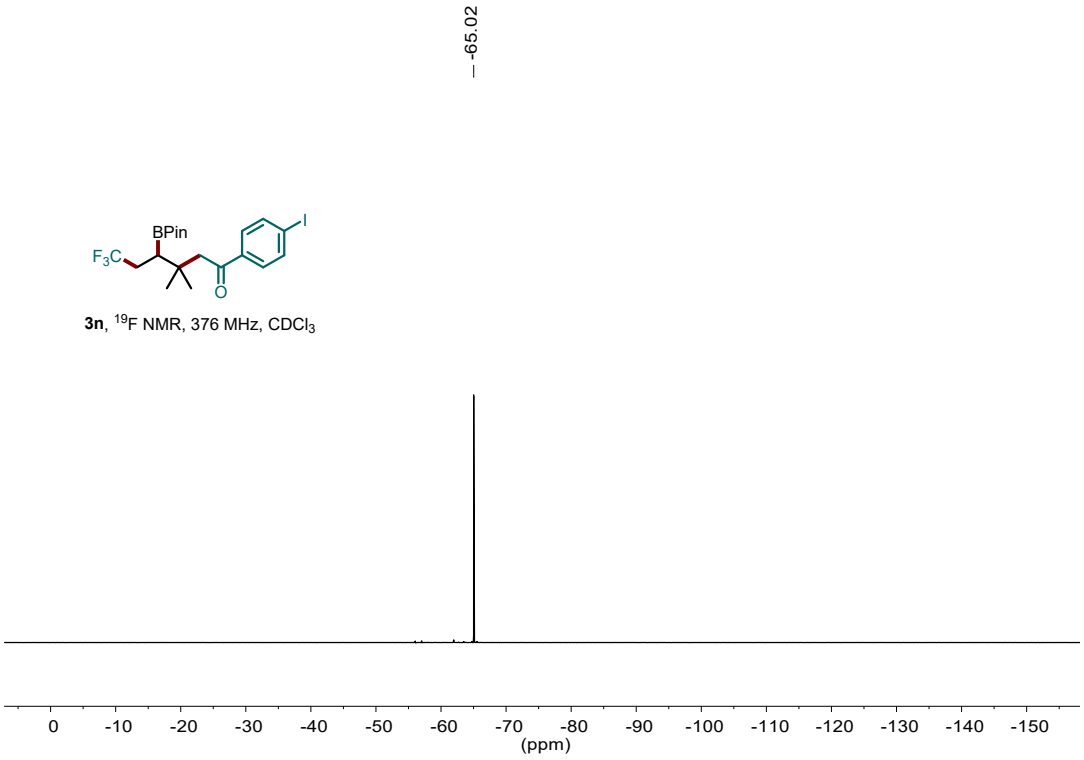
3m, ^{19}F NMR, 376 MHz, $CDCl_3$



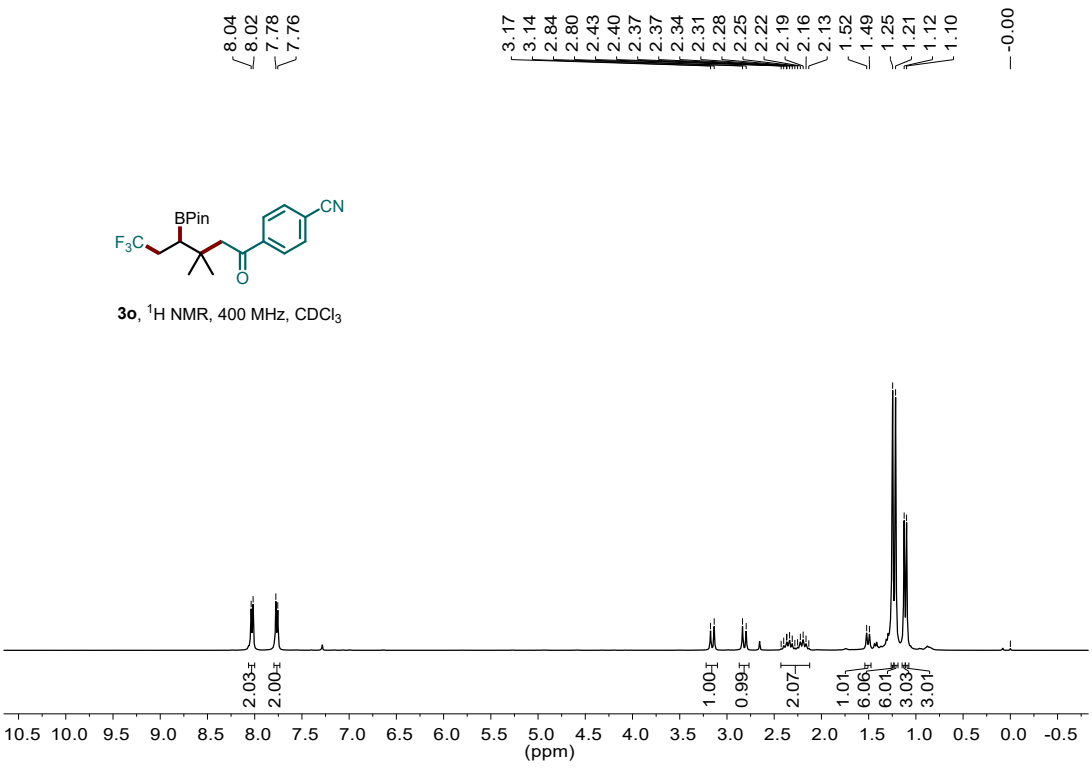
3n, ^{1}H NMR, 400 MHz, $CDCl_3$



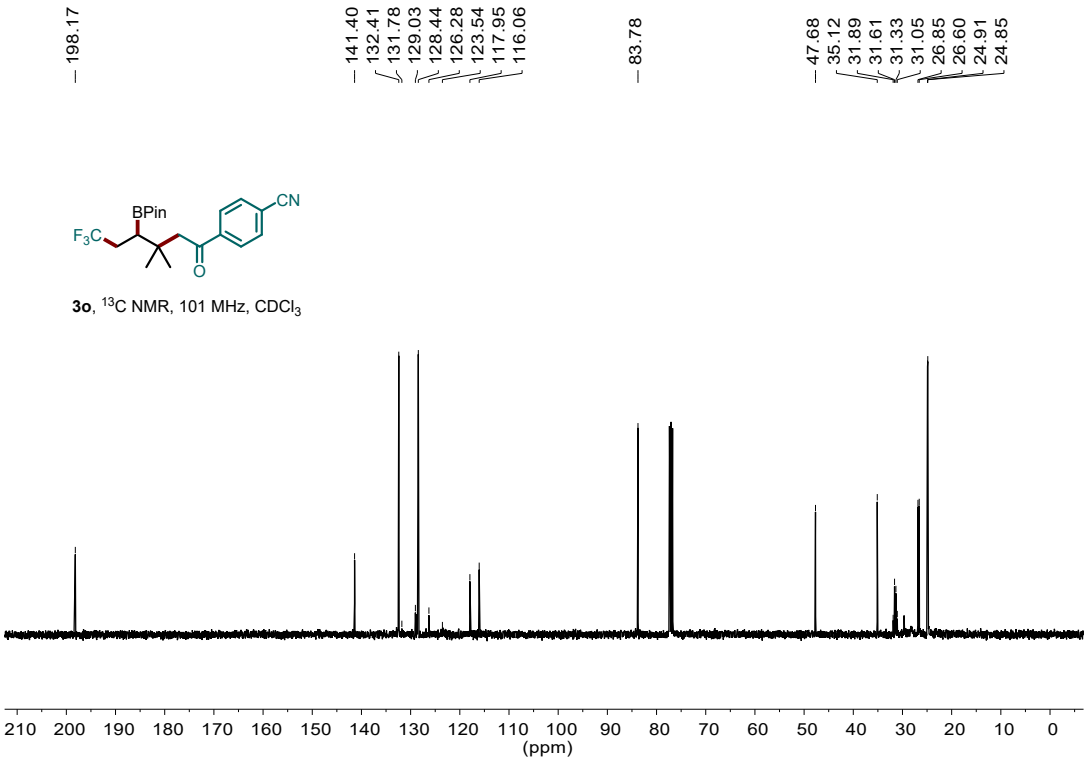
3n, ^{13}C NMR, 101 MHz, $CDCl_3$



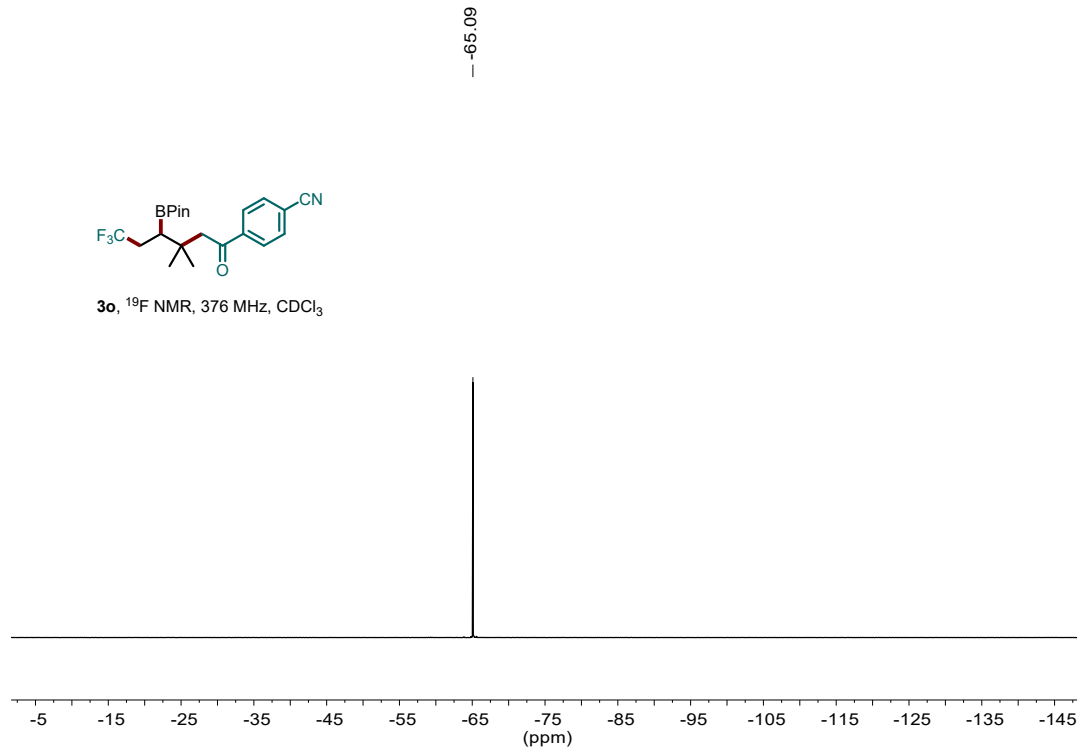
3n, ^{19}F NMR, 376 MHz, $CDCl_3$



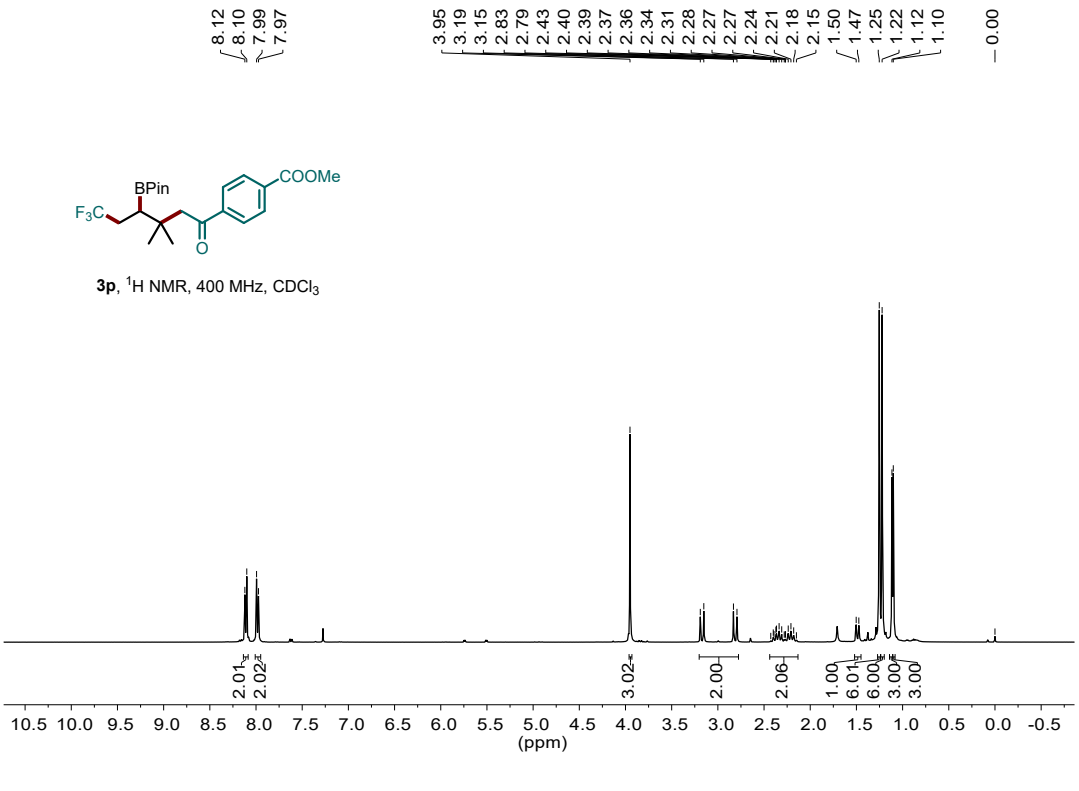
3o, ^{1}H NMR, 400 MHz, $CDCl_3$



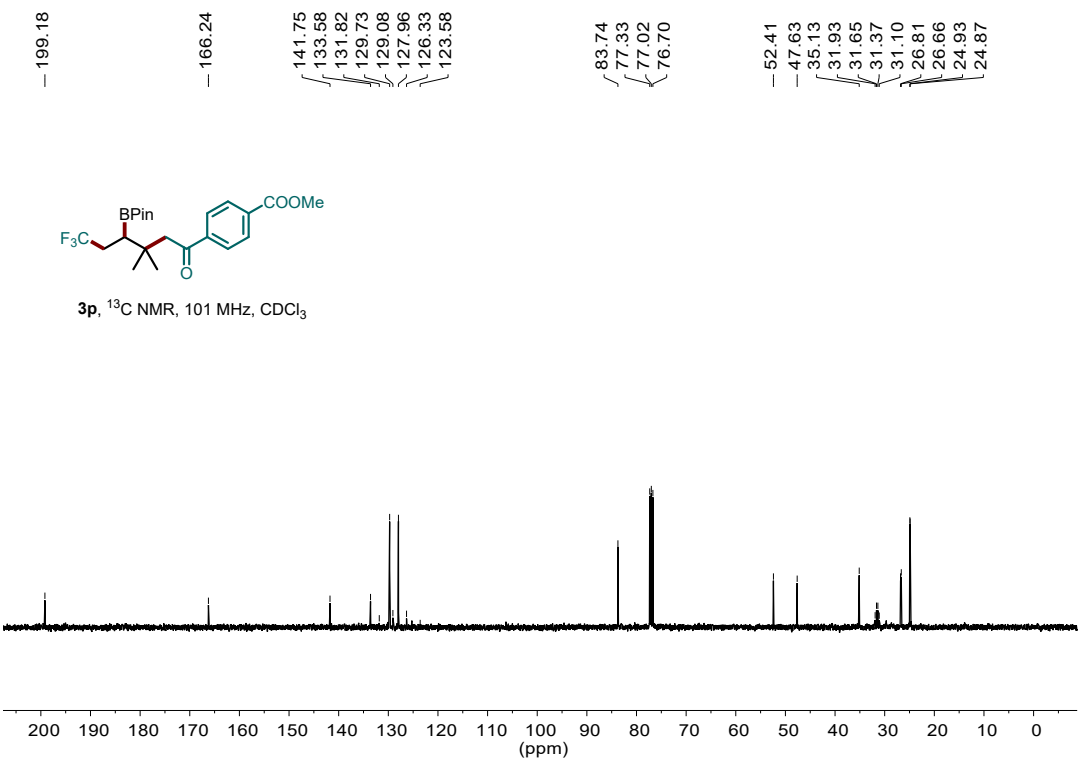
3o, ^{13}C NMR, 101 MHz, $CDCl_3$



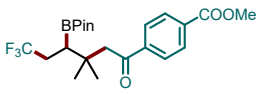
3o, ^{19}F NMR, 376 MHz, $CDCl_3$



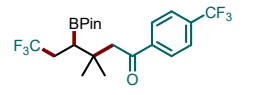
3p, ^{1}H NMR, 400 MHz, $CDCl_3$



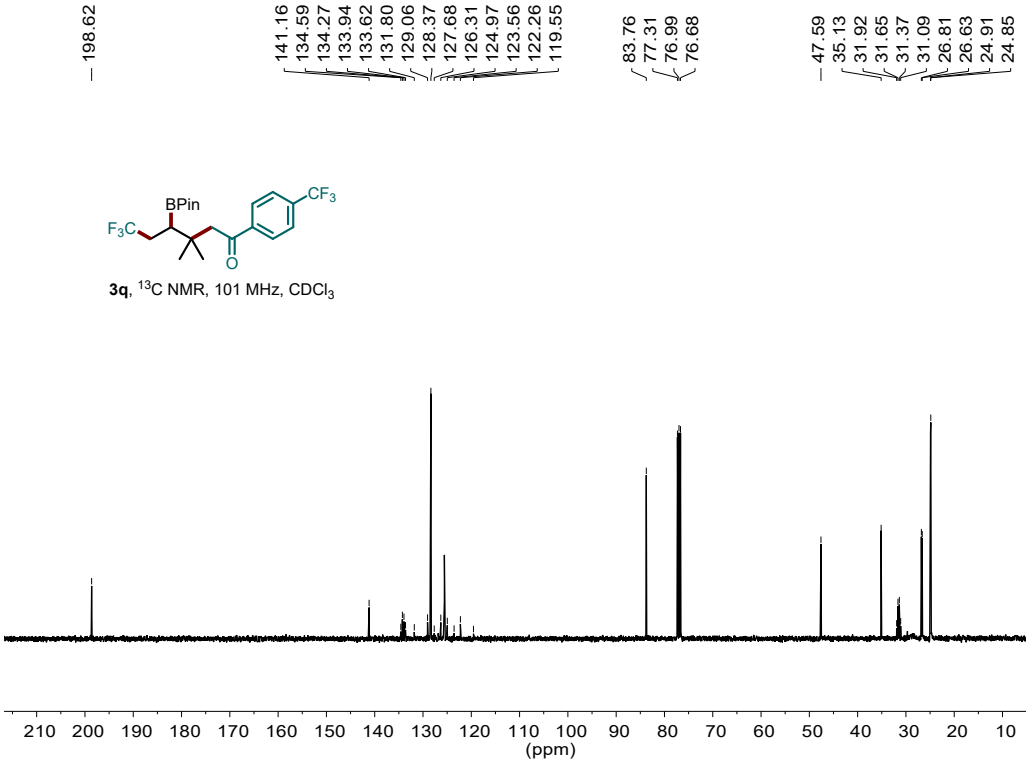
3p, ^{13}C NMR, 101 MHz, $CDCl_3$



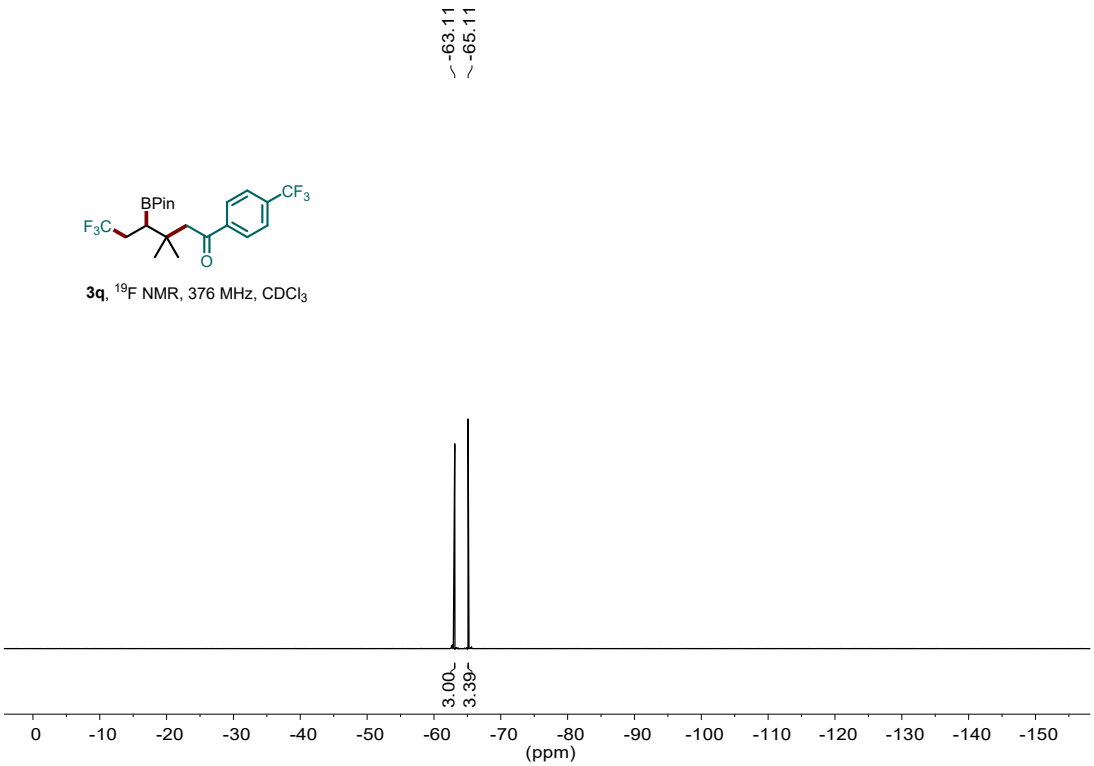
3p, ^{19}F NMR, 376 MHz, $CDCl_3$



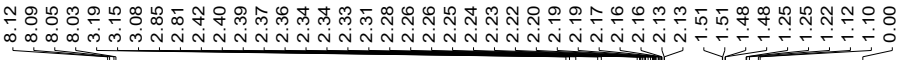
3q, ^{1}H NMR, 600 MHz, $CDCl_3$

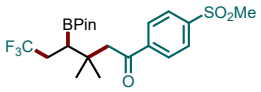


3q, ^{13}C NMR, 101 MHz, $CDCl_3$

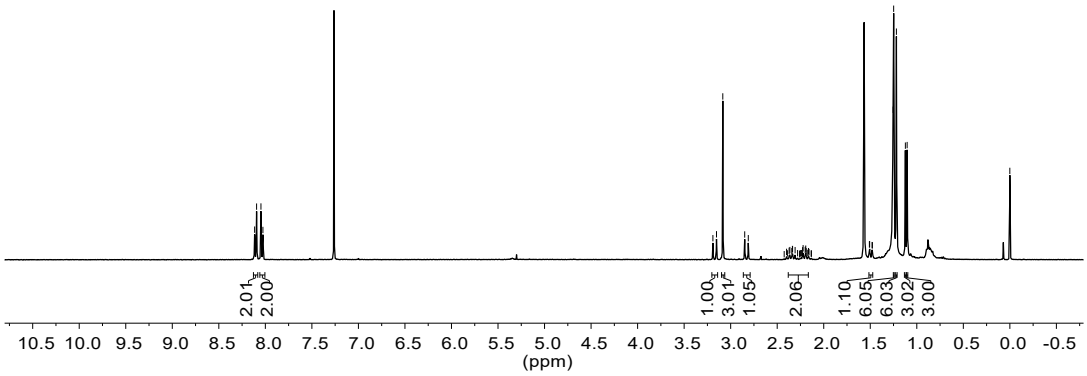


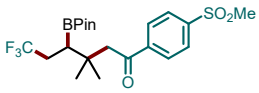
3q, ^{19}F NMR, 376 MHz, $CDCl_3$



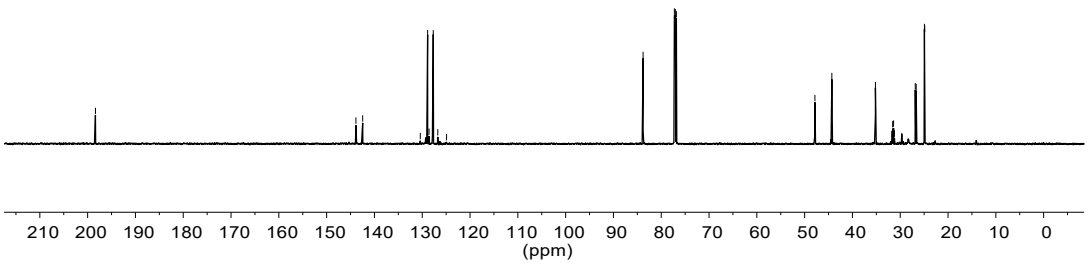


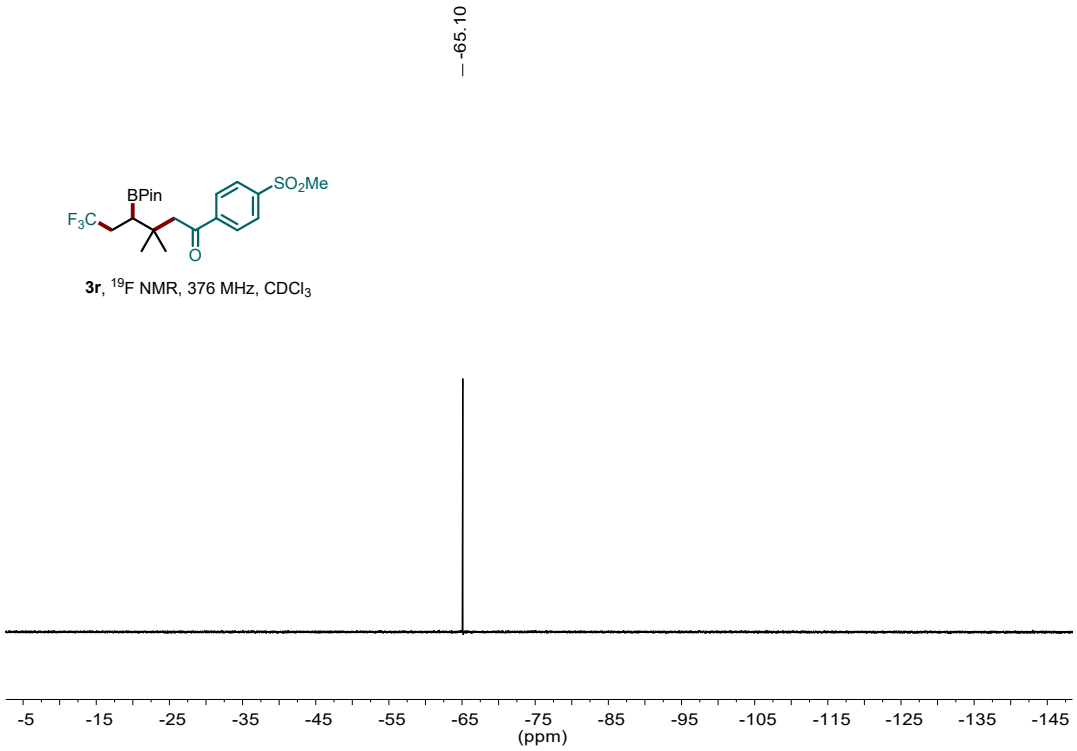
3r, ^{1}H NMR, 400 MHz, $CDCl_3$



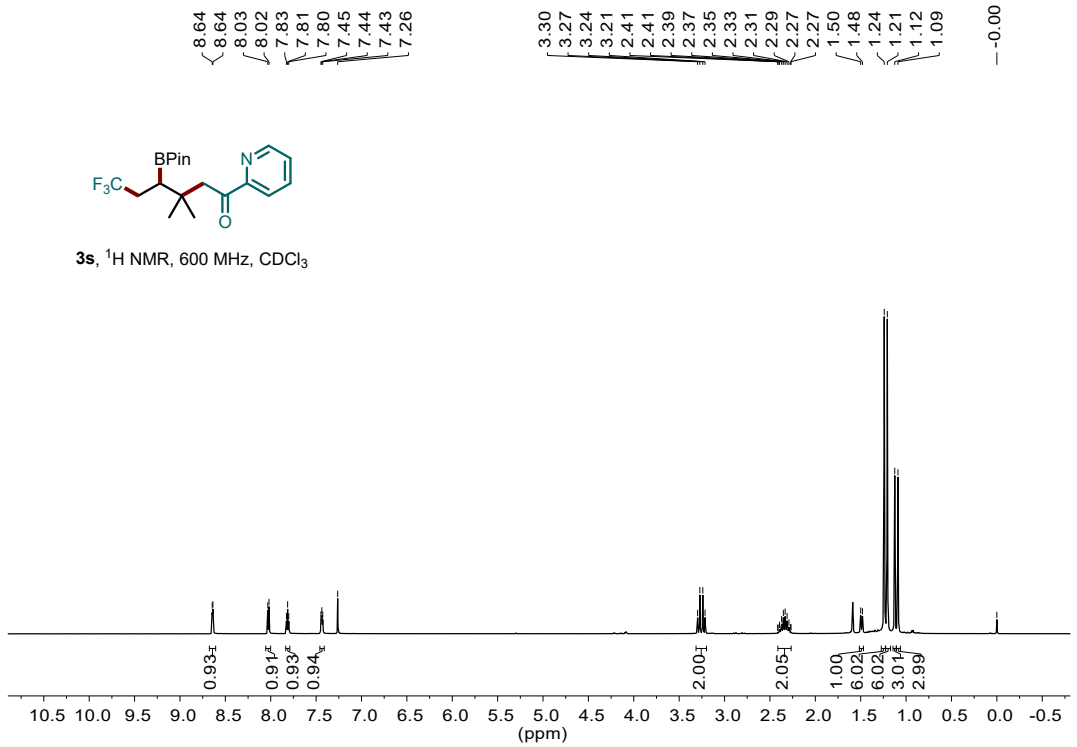


3r, ^{13}C NMR, 101 MHz, $CDCl_3$

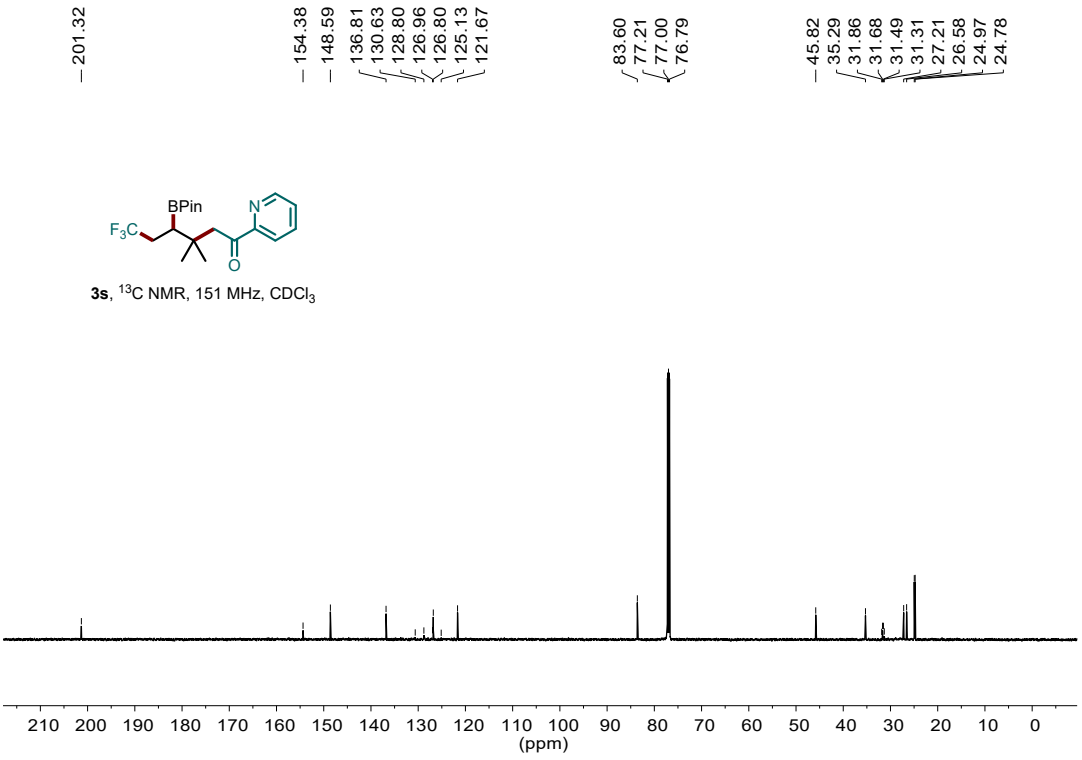




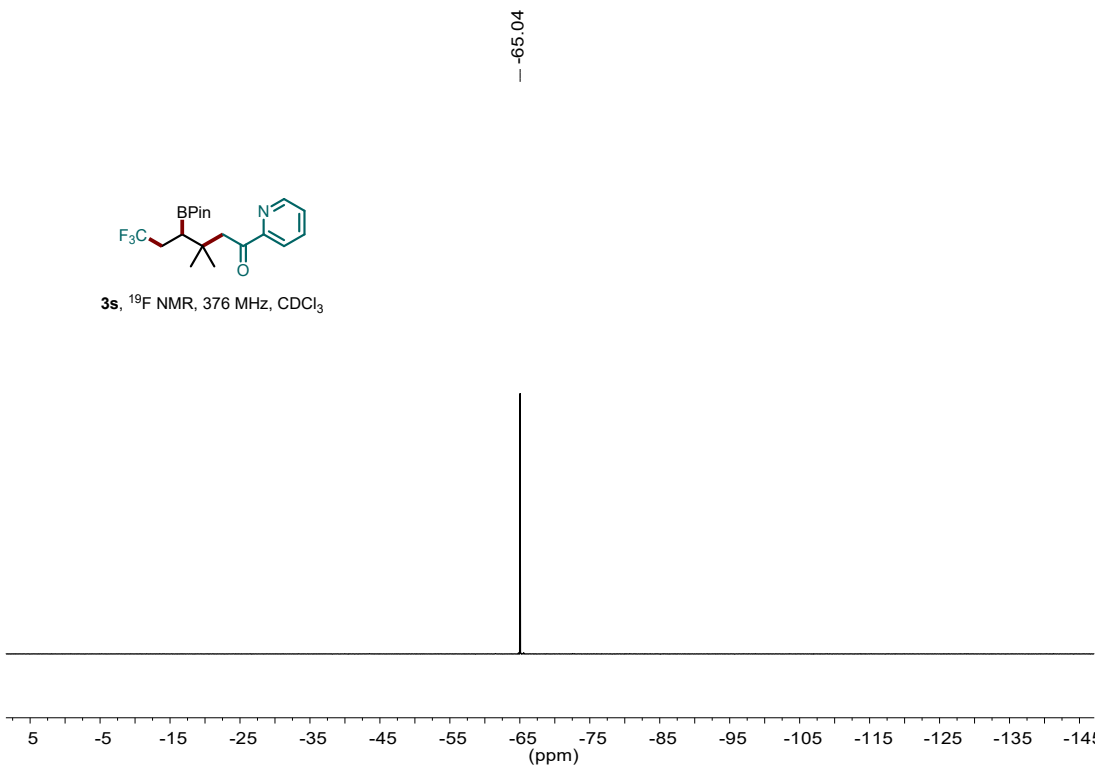
3r, ^{19}F NMR, 376 MHz, $CDCl_3$



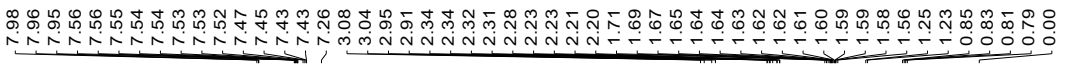
3s, ^{1}H NMR, 600 MHz, $CDCl_3$

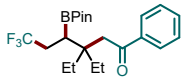


3s, ^{13}C NMR, 151 MHz, $CDCl_3$

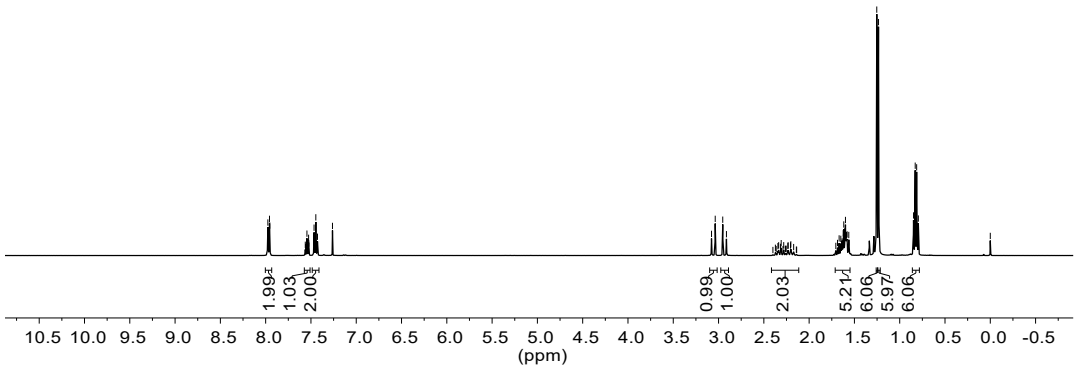


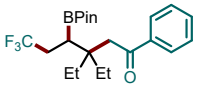
3s, ^{19}F NMR, 376 MHz, $CDCl_3$



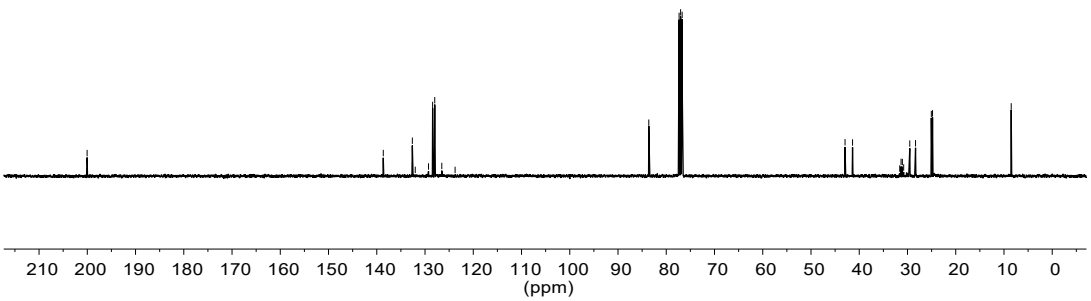


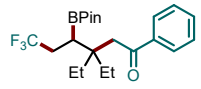
3t, ^{1}H NMR, 400 Hz, $CDCl_3$



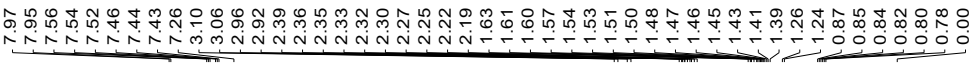


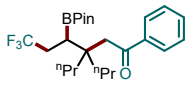
3t, ^{13}C NMR, 101 Hz, $CDCl_3$



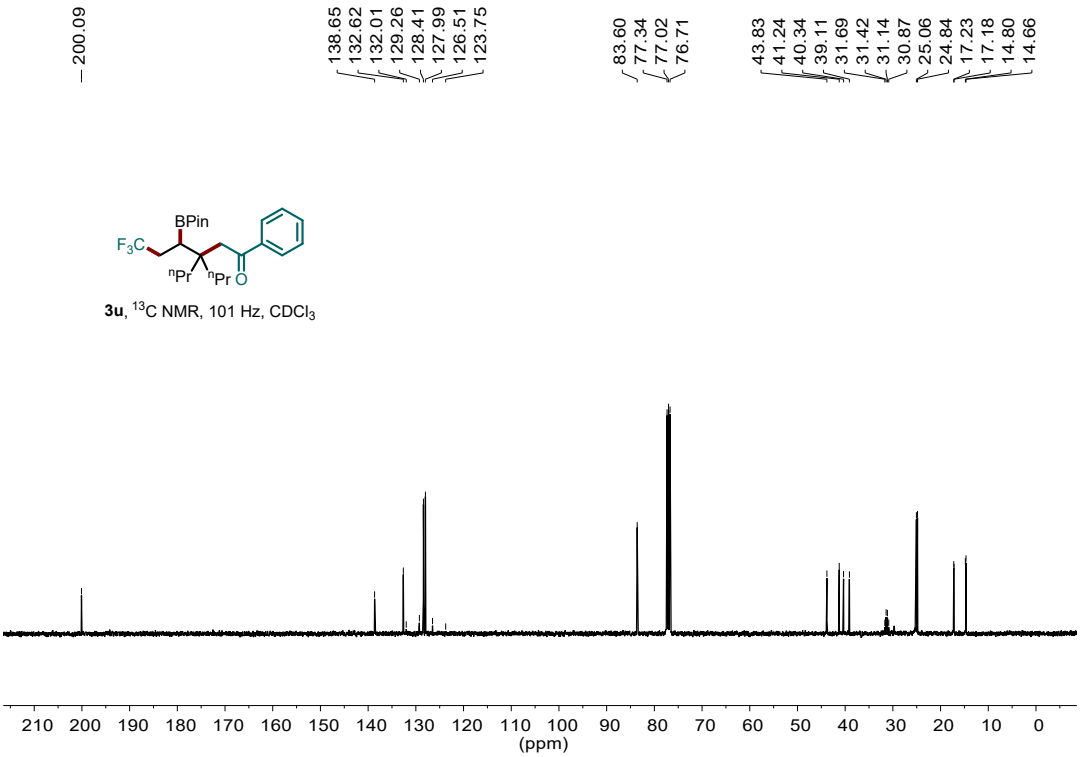


3t, ^{19}F NMR,376 Hz, $CDCl_3$

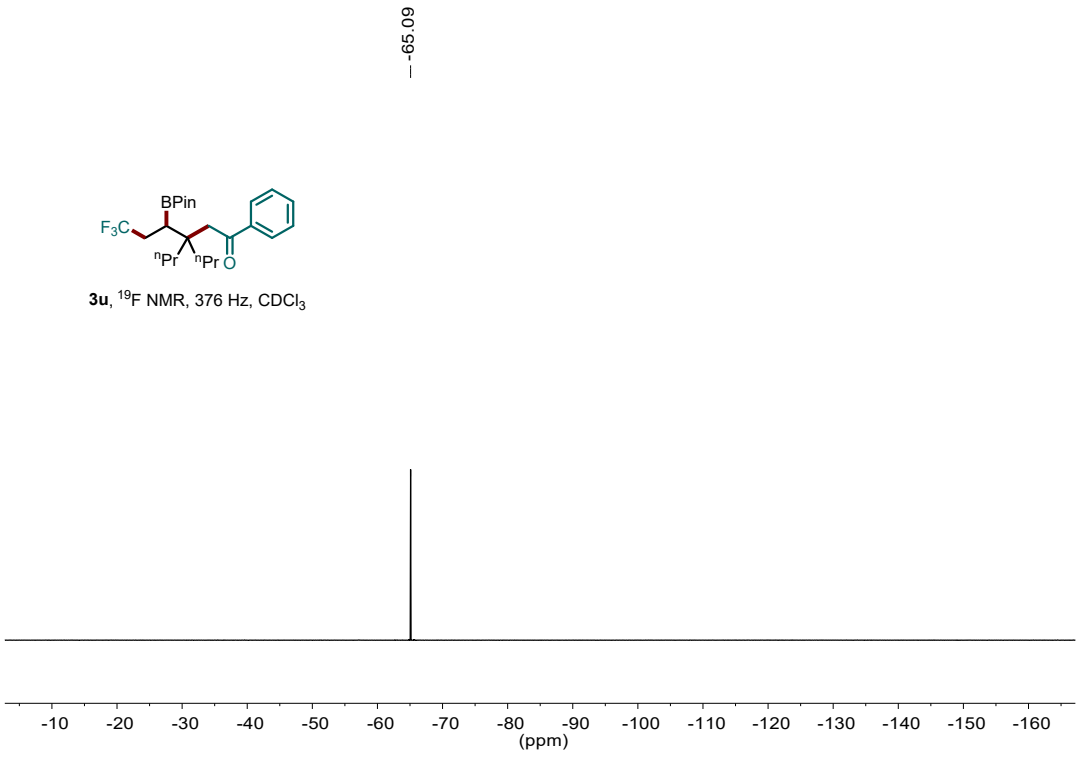




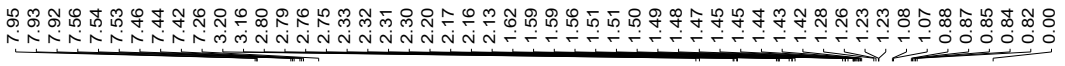
3u, ^{1}H NMR, 400 Hz, $CDCl_3$

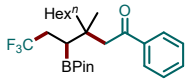


3u, ^{13}C NMR, 101 Hz, $CDCl_3$

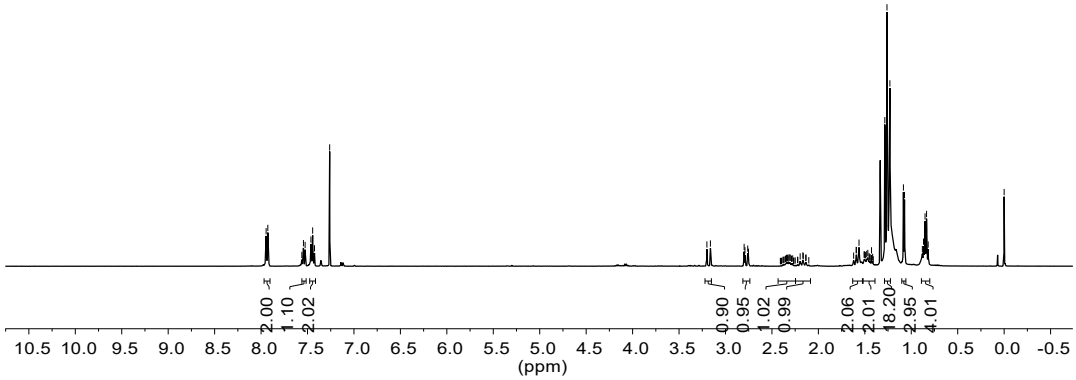


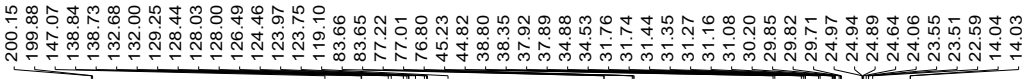
3u, ^{19}F NMR, 376 Hz, $CDCl_3$

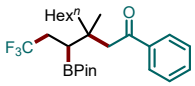




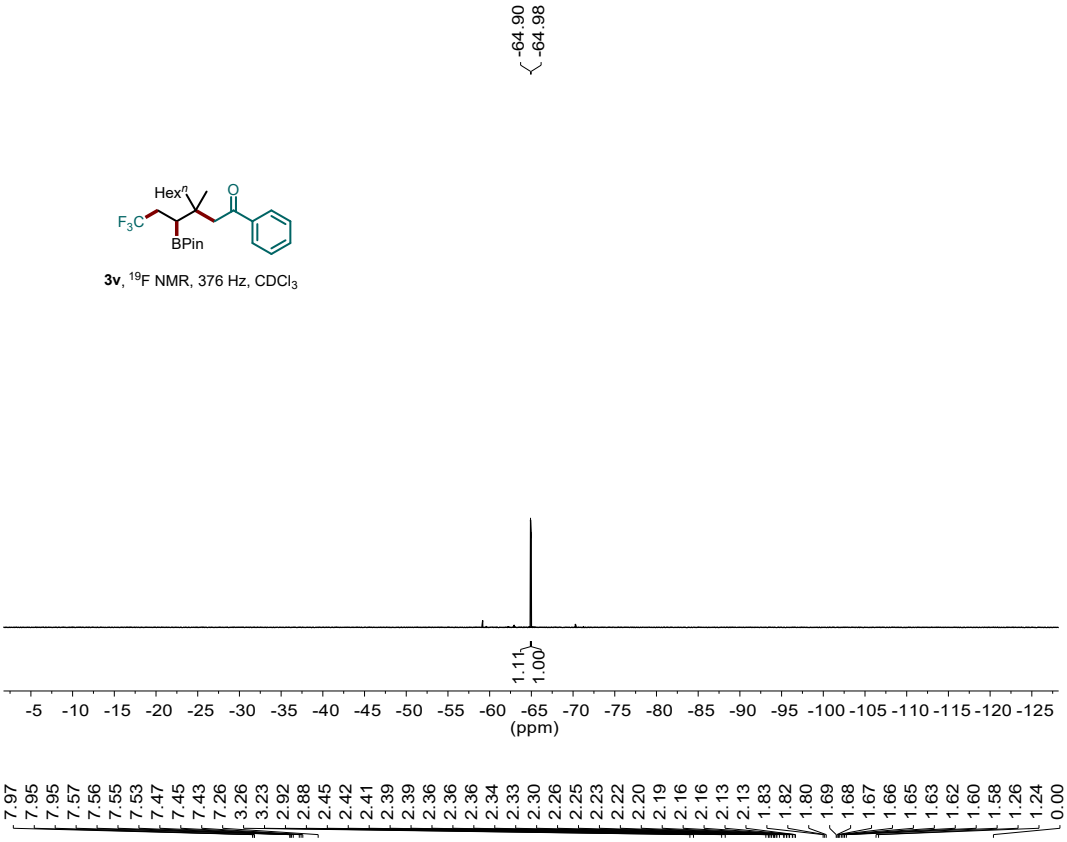
3v, ^{1}H NMR, 400 Hz, $CDCl_3$



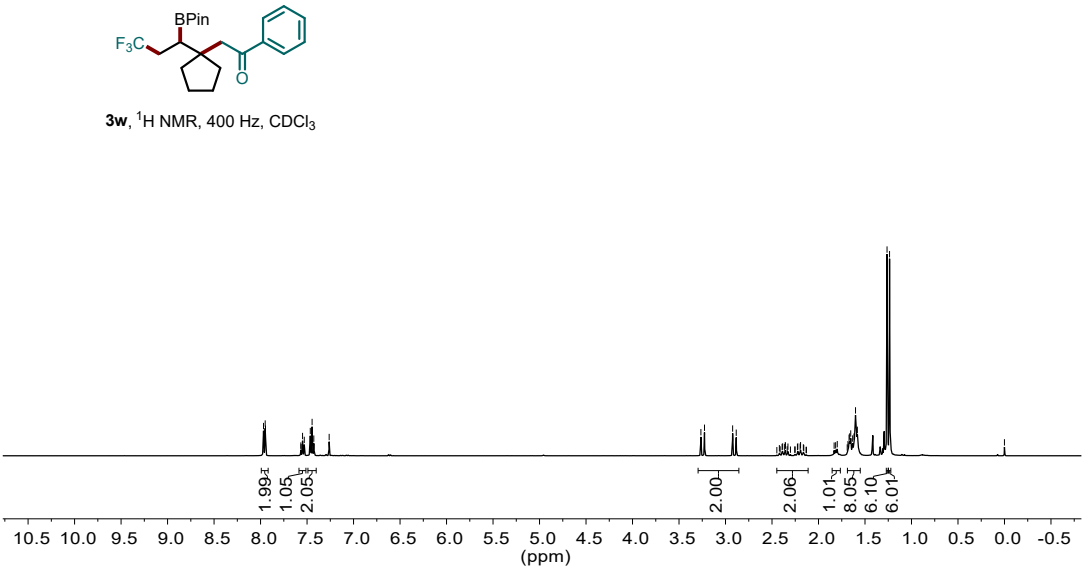




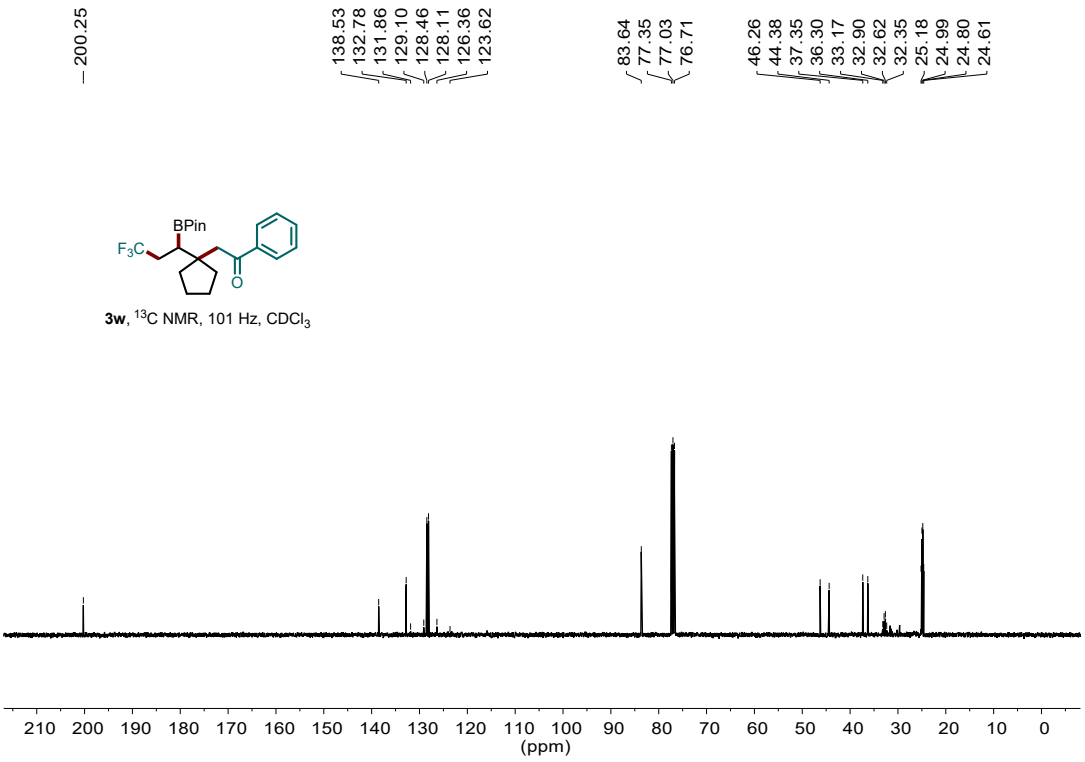
3v, ^{13}C NMR, 151 Hz, $CDCl_3$



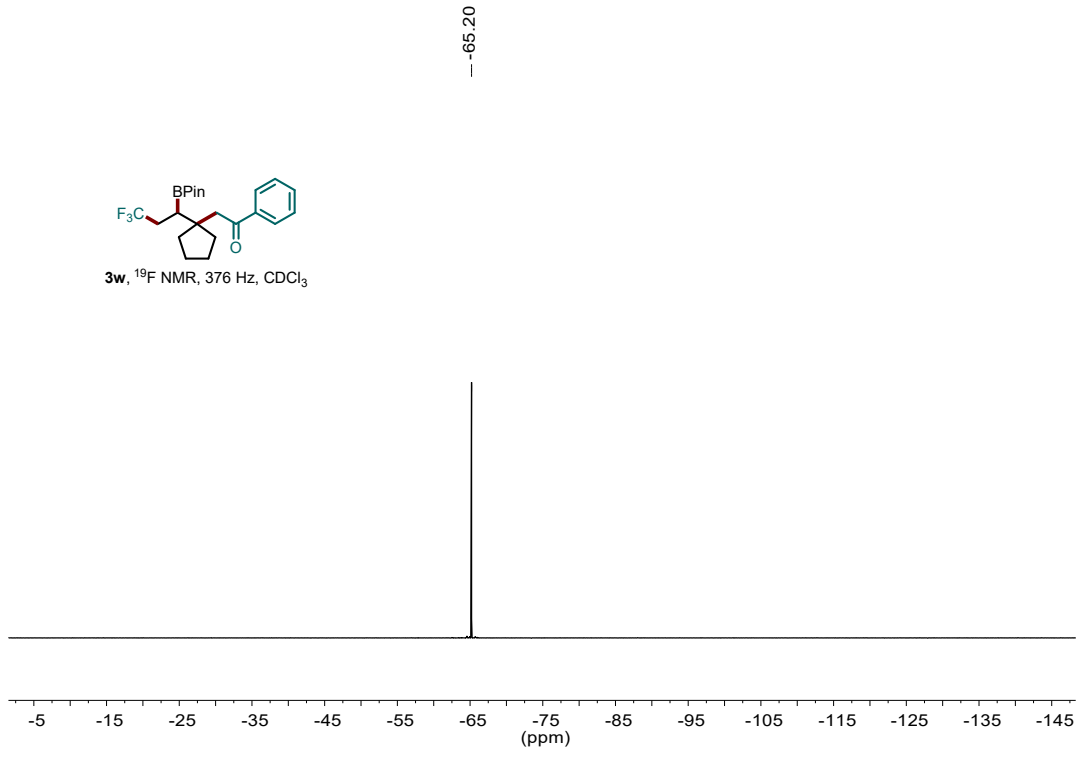
3v, ^{19}F NMR, 376 Hz, $CDCl_3$



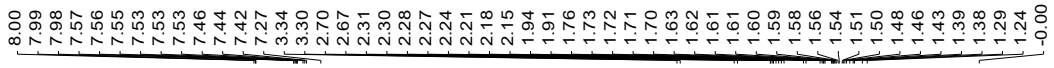
3w, ^{1}H NMR, 400 Hz, $CDCl_3$

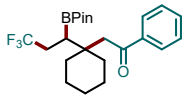


3w, ^{13}C NMR, 101 Hz, $CDCl_3$

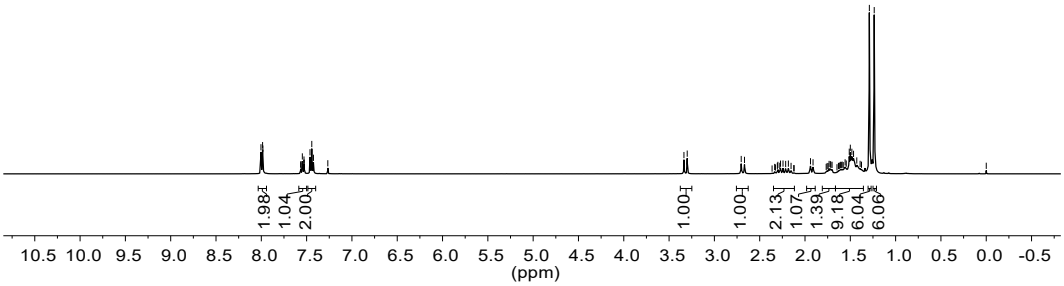


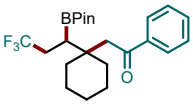
3w, ^{19}F NMR, 376 Hz, $CDCl_3$



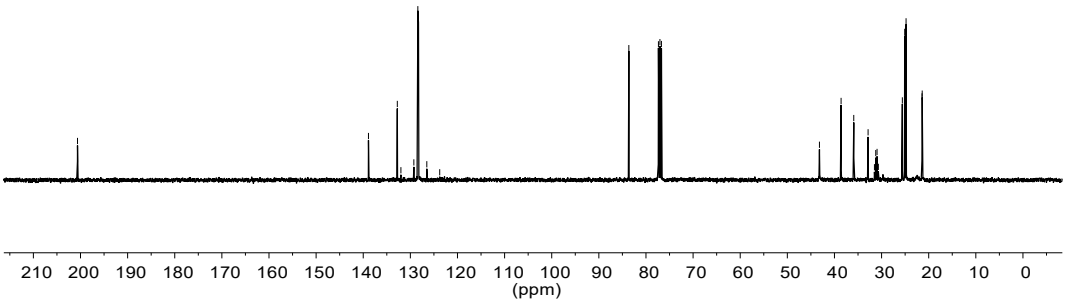


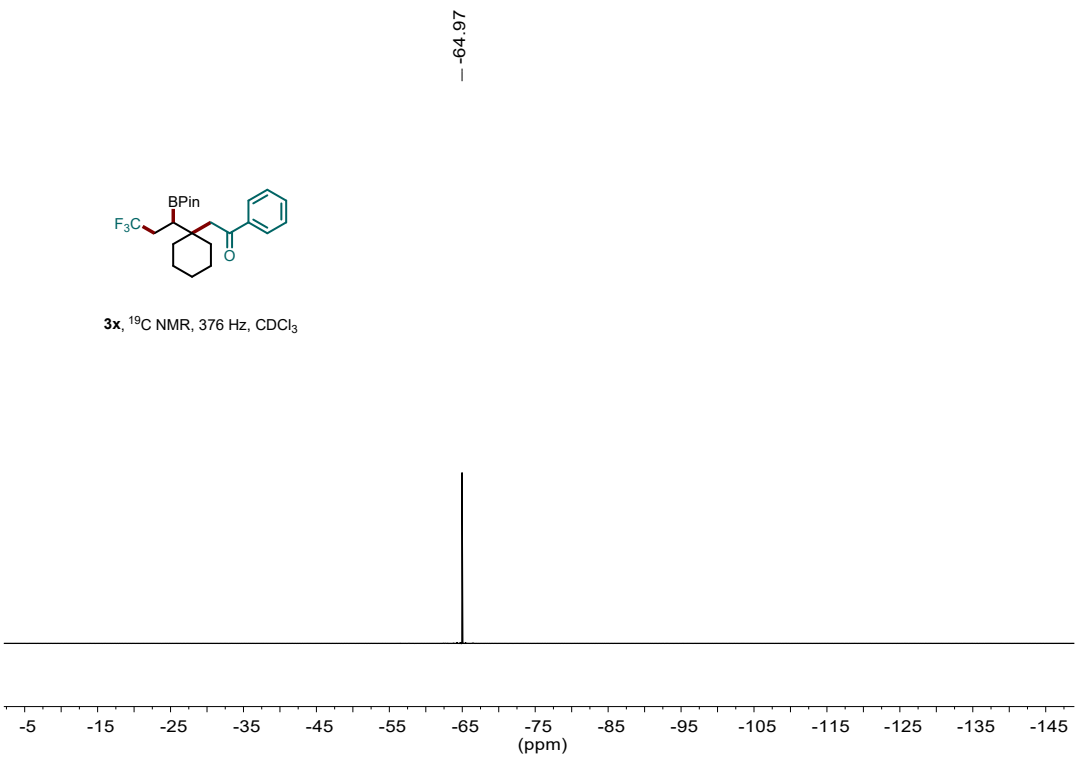
3x, ^{1}H NMR, 400 Hz, $CDCl_3$



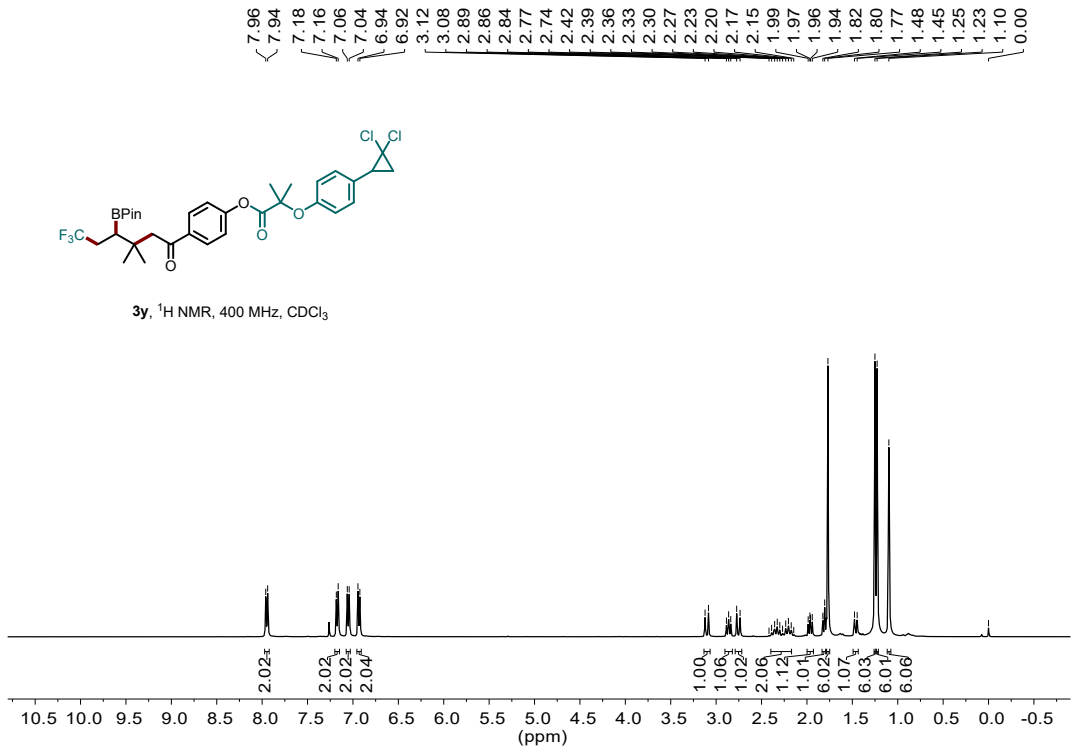


3x, ^{13}C NMR, 101 Hz, $CDCl_3$

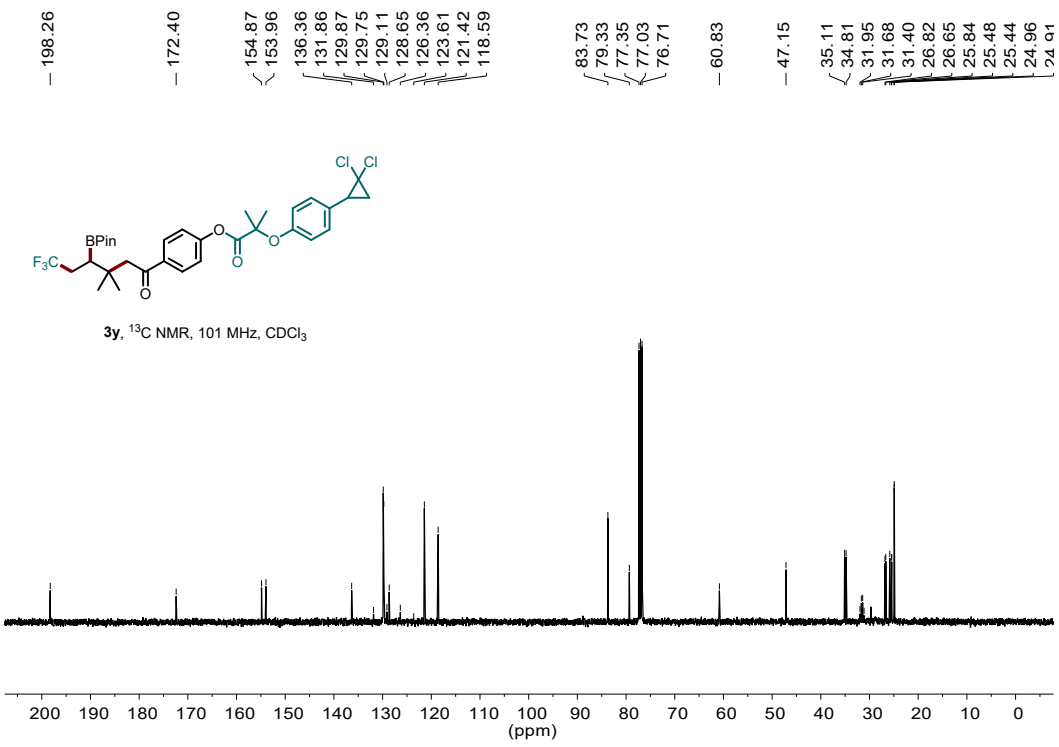




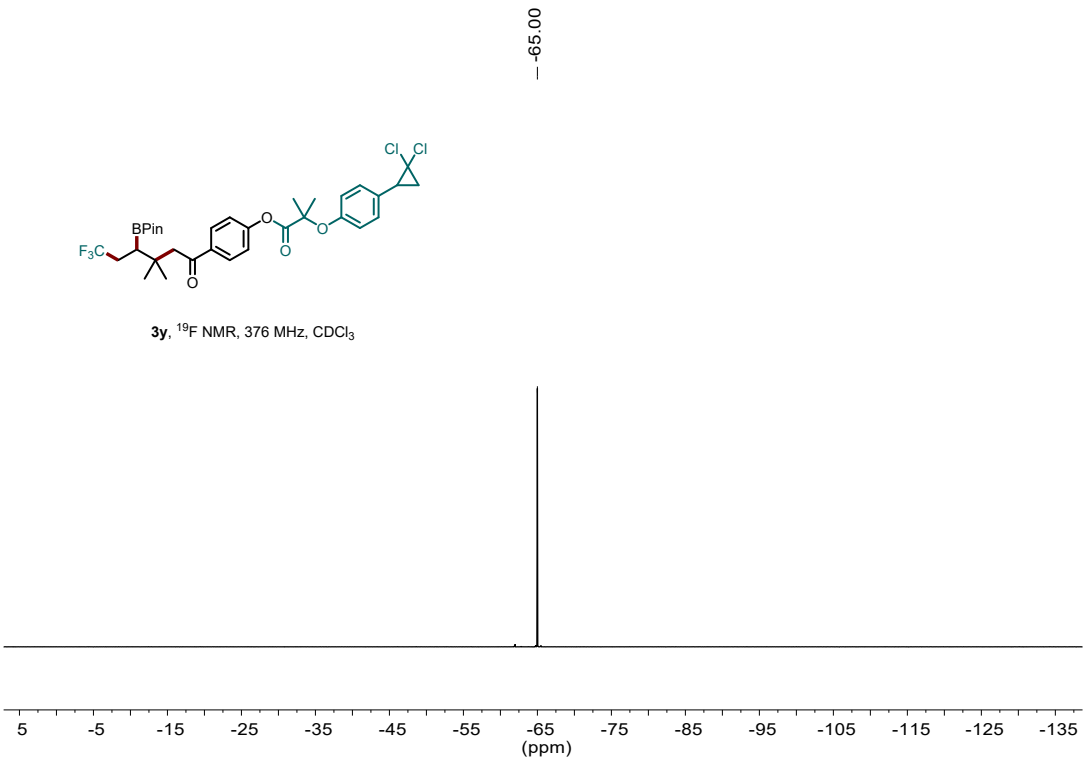
3x, ^{19}C NMR, 376 Hz, $CDCl_3$



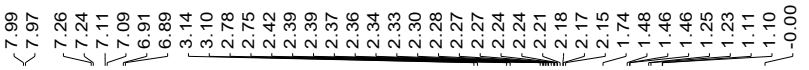
3y, ^{1}H NMR, 400 MHz, $CDCl_3$

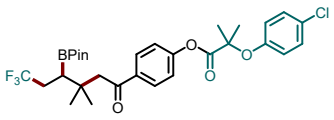


3y, ^{13}C NMR, 101 MHz, $CDCl_3$

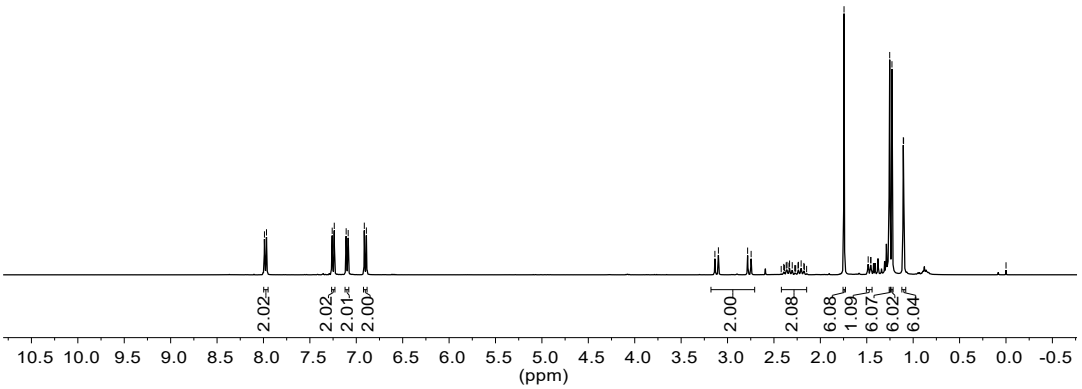


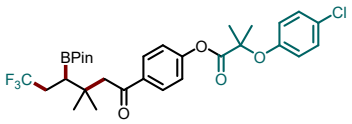
3y, ^{19}F NMR, 376 MHz, $CDCl_3$



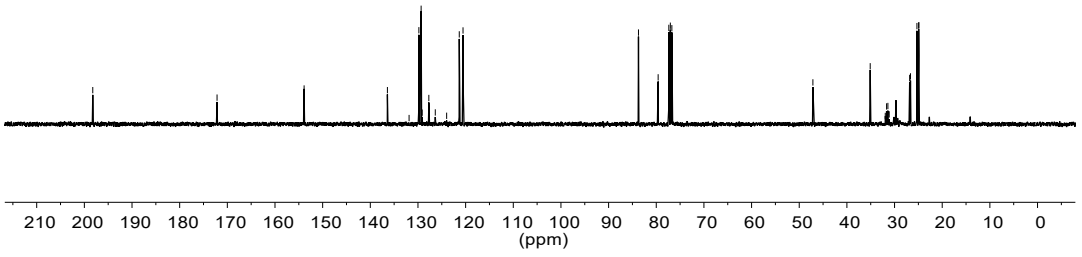


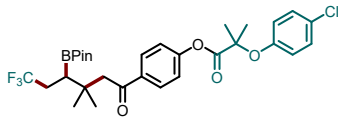
3z, ^{1}H NMR, 400 MHz, $CDCl_3$



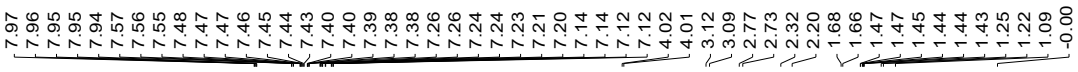


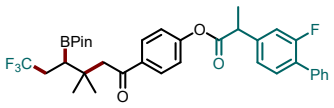
3z, ^{13}C NMR, 101 MHz, $CDCl_3$



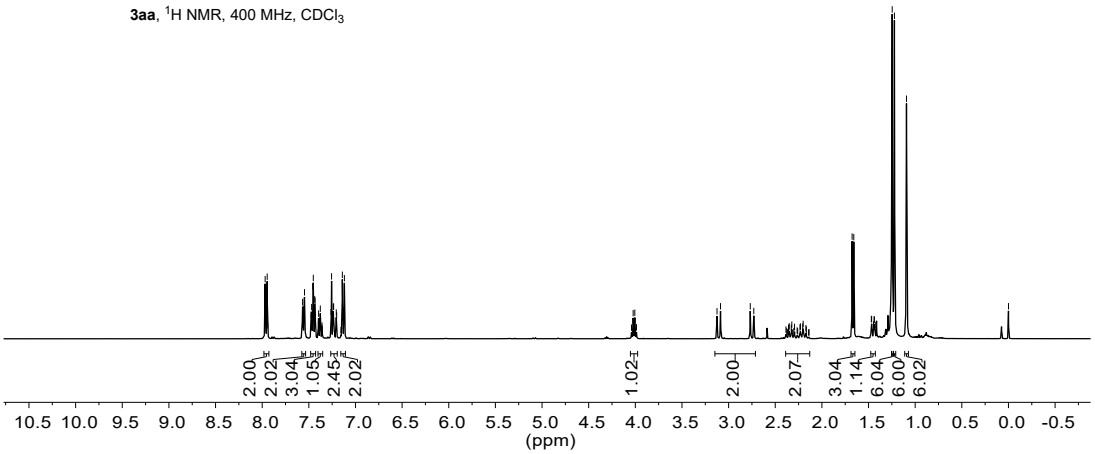


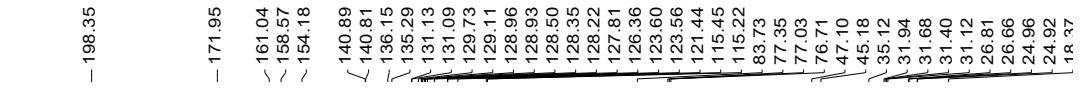
3z, ^{19}F NMR, 376 MHz, $CDCl_3$

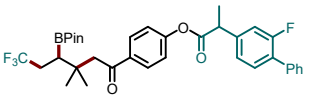




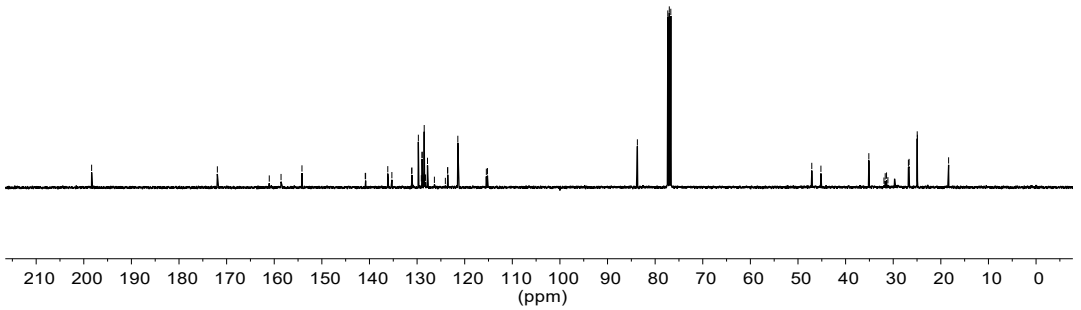
3aa, ^{1}H NMR, 400 MHz, $CDCl_3$

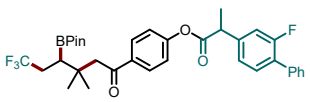




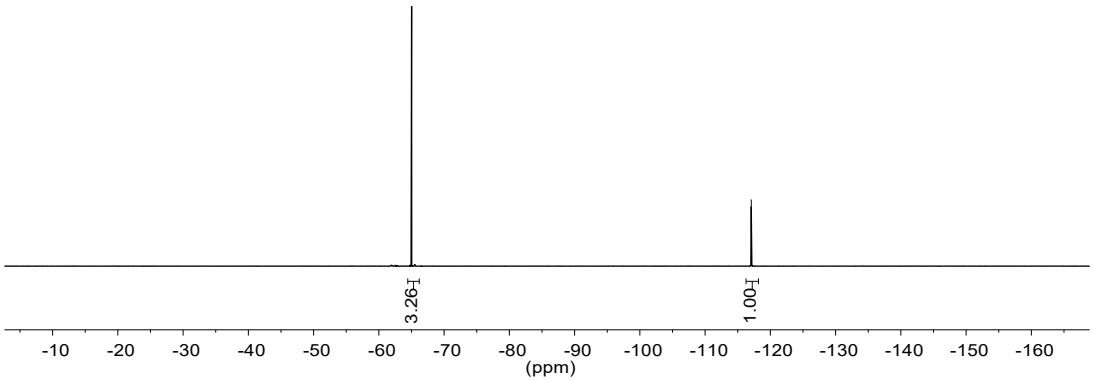


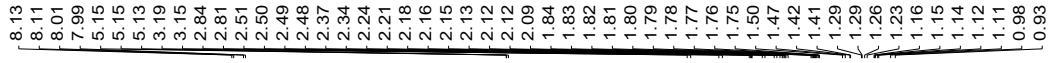
3aa, ^{13}C NMR, 101 MHz, $CDCl_3$

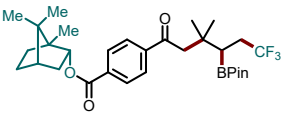




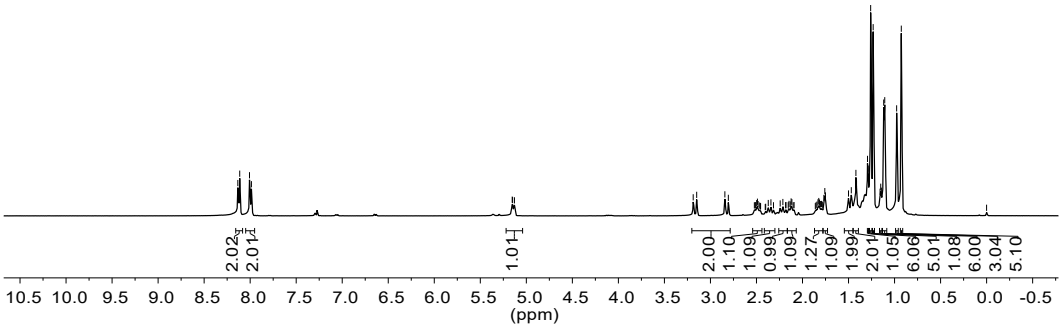
3aa, ^{19}F NMR, 376 MHz, $CDCl_3$

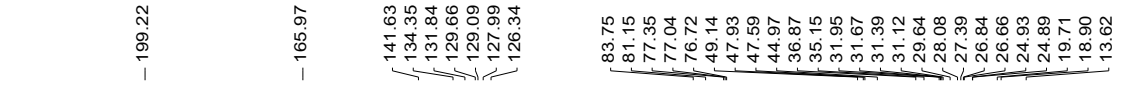


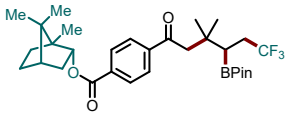




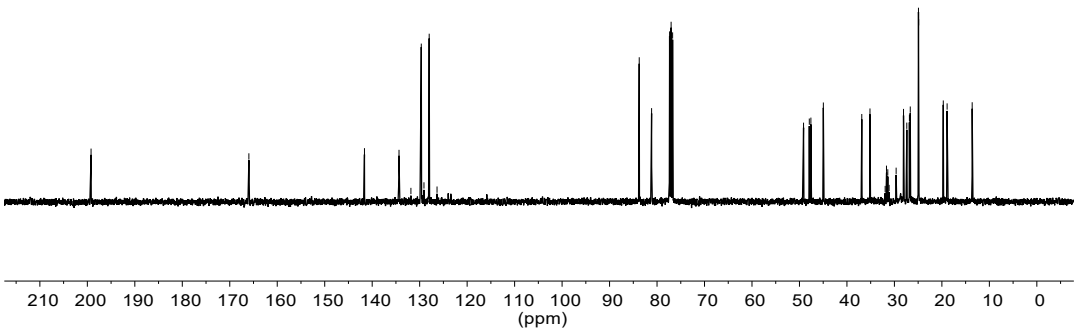
3ab, ^{1}H NMR, 400 MHz, $CDCl_3$

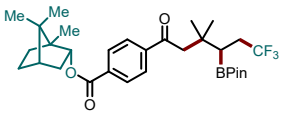




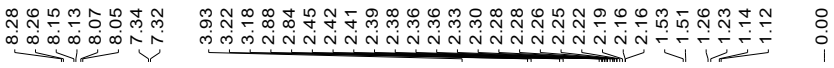


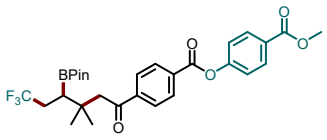
3ab, ^{13}C NMR, 101 MHz, $CDCl_3$



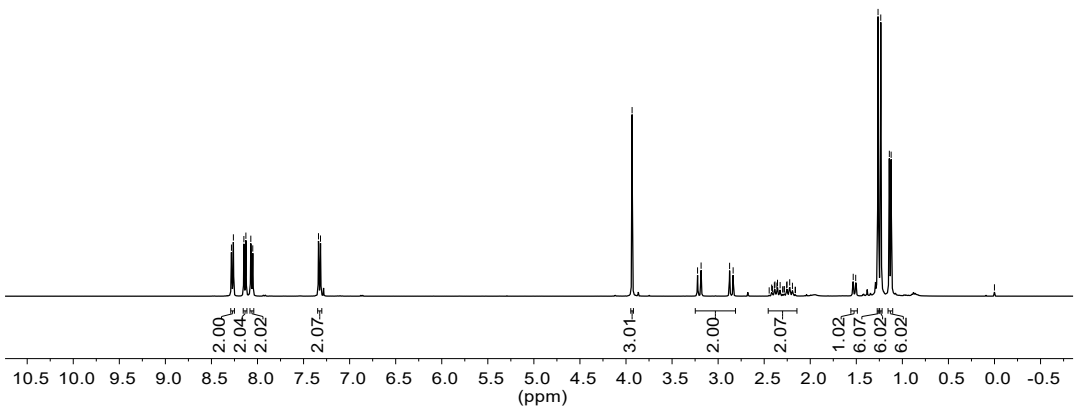


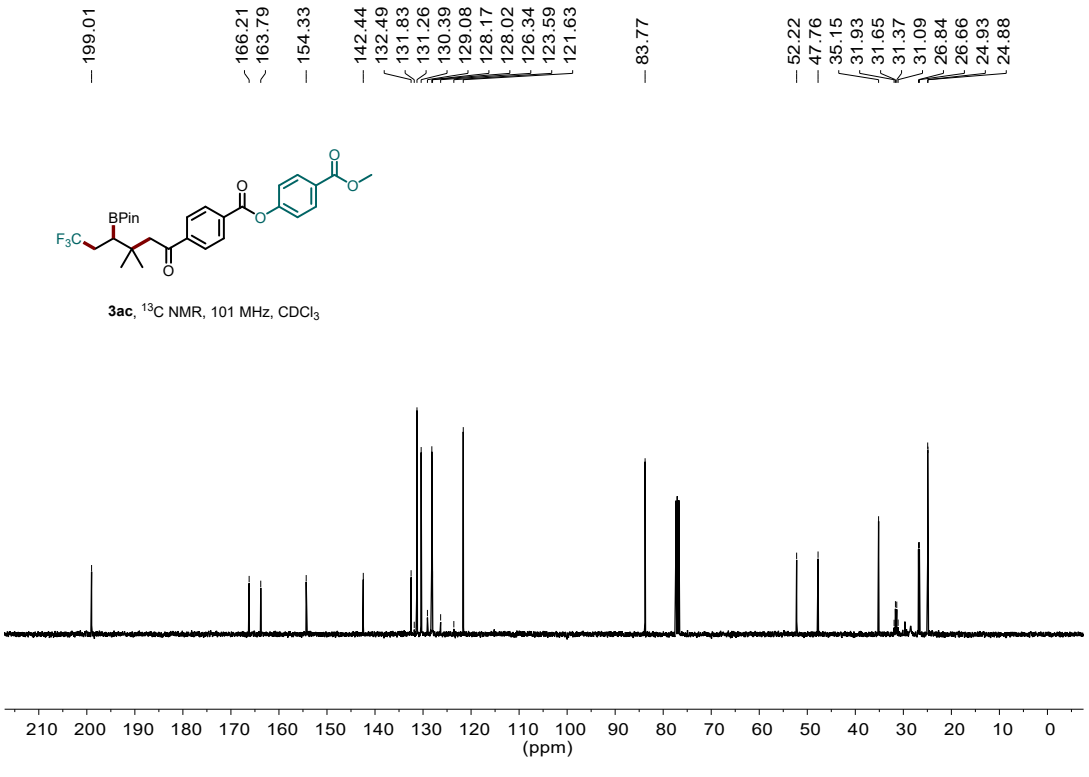
3ab, ^{19}F NMR, 376 MHz, $CDCl_3$



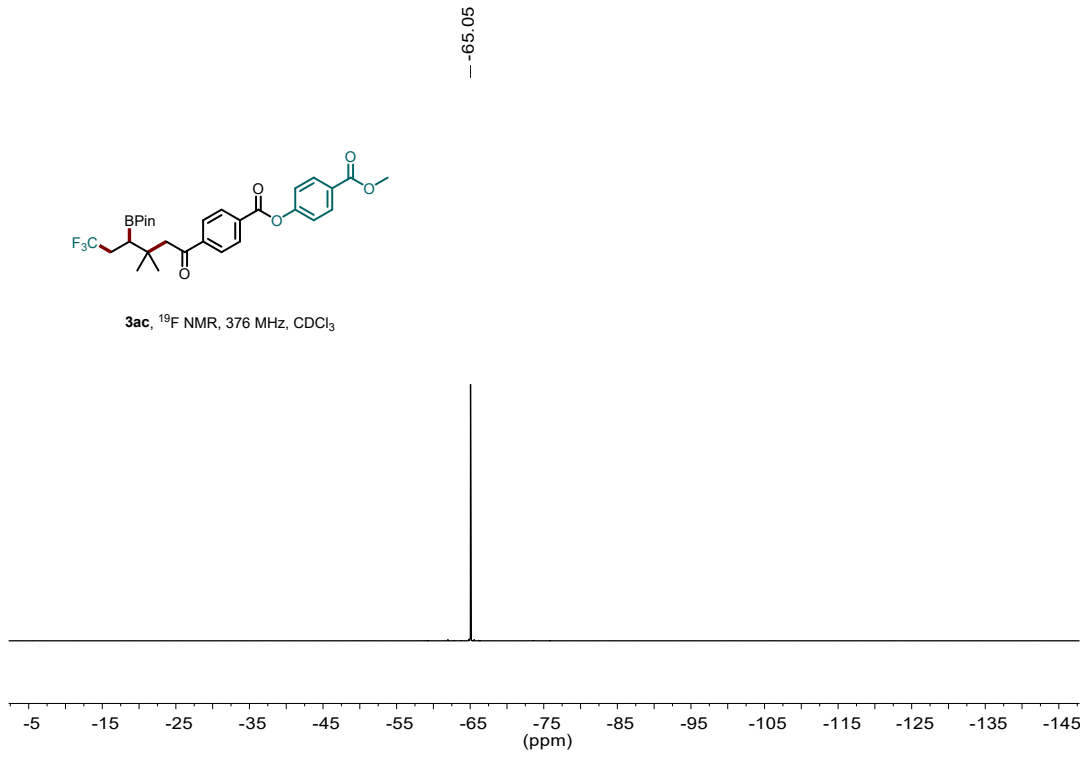


3ac, ^{1}H NMR, 400 MHz, $CDCl_3$

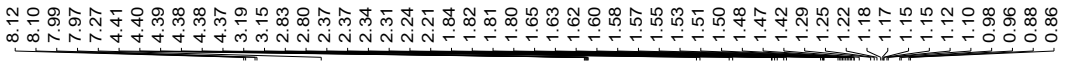


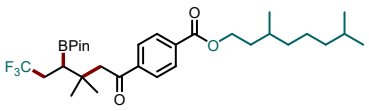


3ac, ^{13}C NMR, 101 MHz, $CDCl_3$

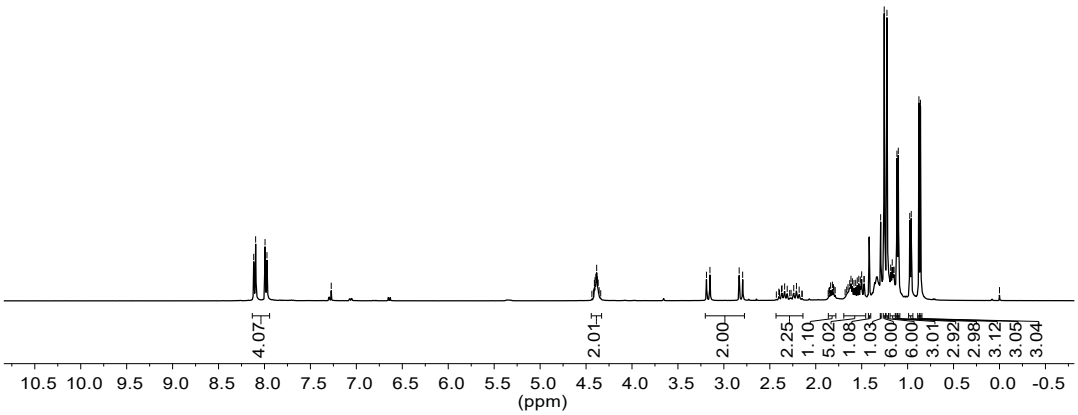


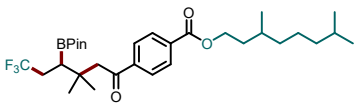
3ac, ^{19}F NMR, 376 MHz, $CDCl_3$



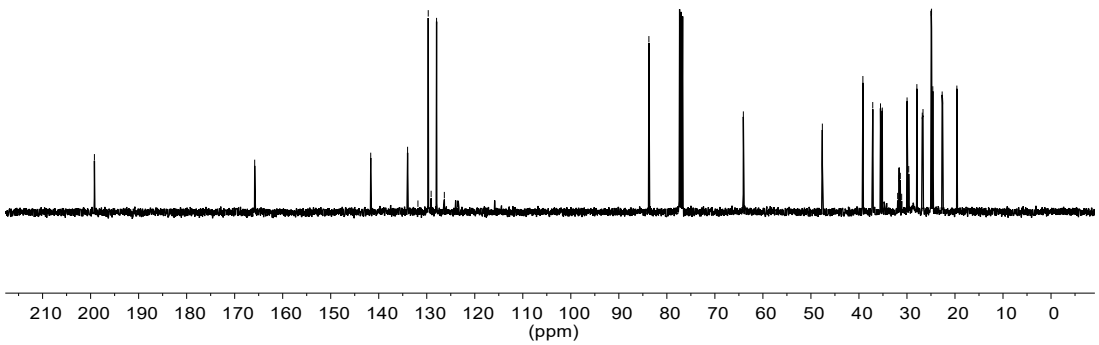


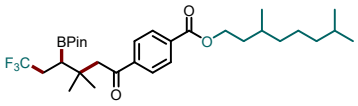
3ad, ^{1}H NMR, 400 MHz, $CDCl_3$



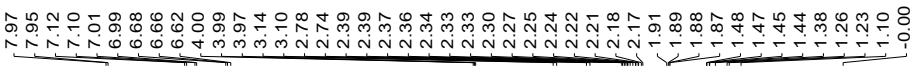


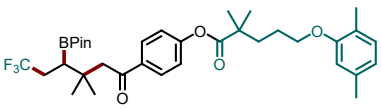
3ad, ^{13}C NMR, 101 MHz, $CDCl_3$



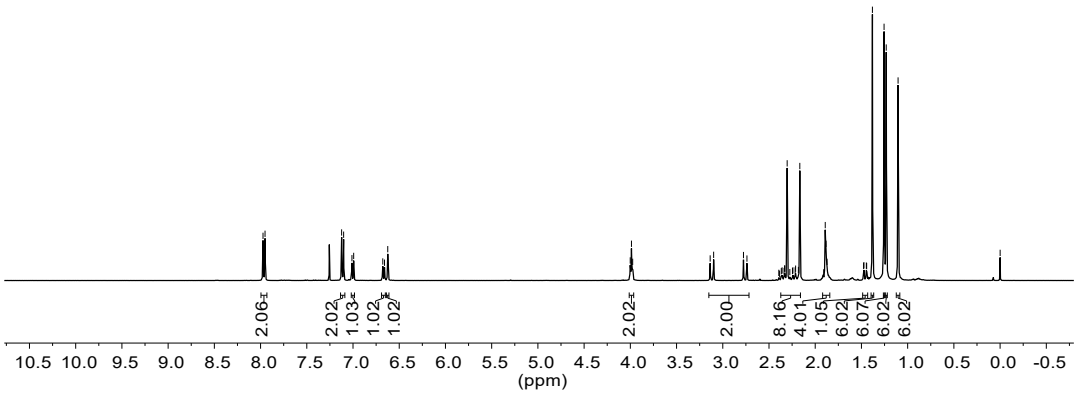


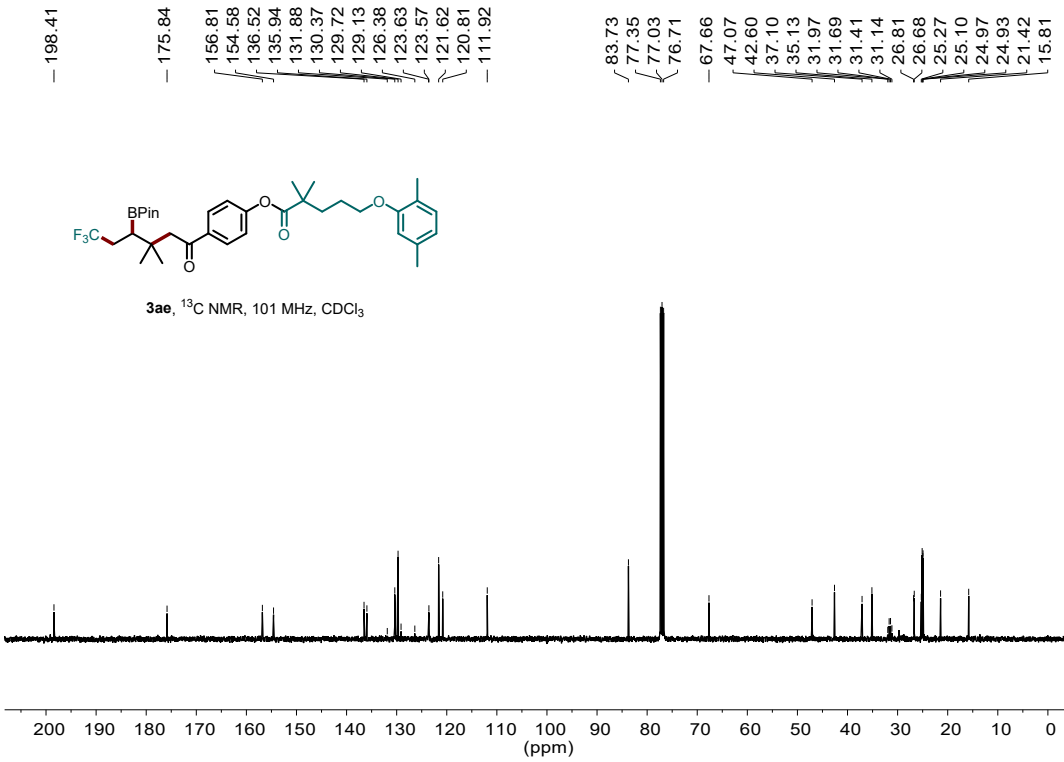
3ad, ^{19}F NMR, 376 MHz, $CDCl_3$



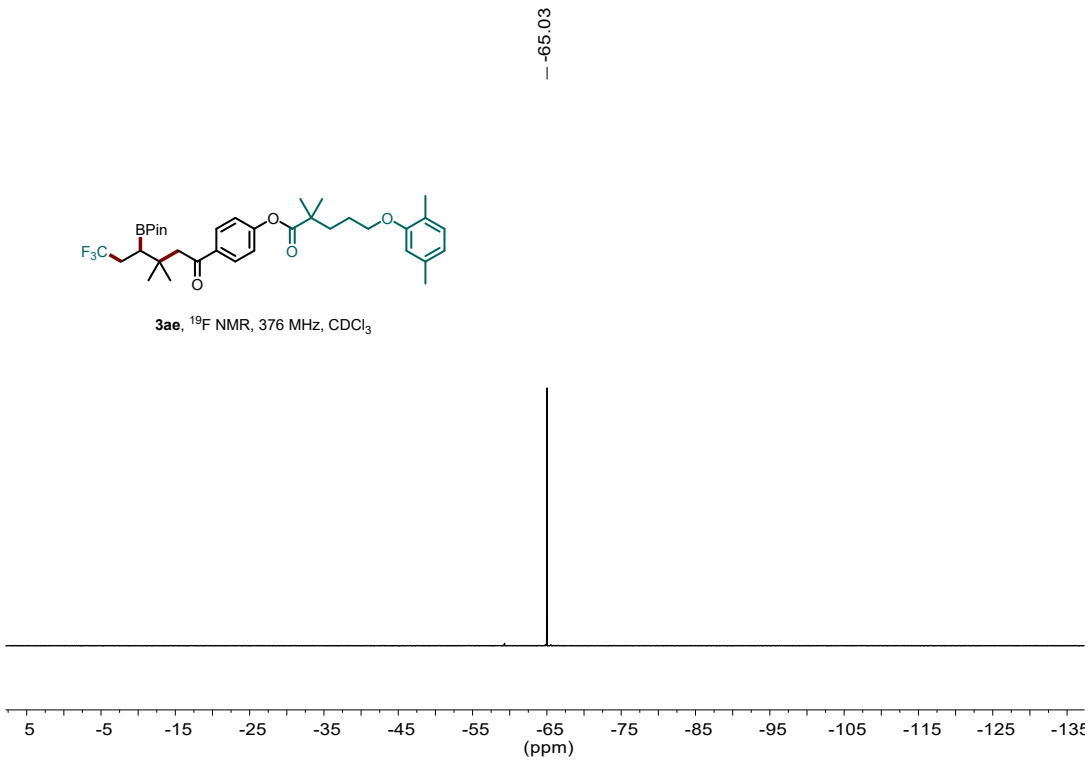


3ae, ^{1}H NMR, 400 MHz, $CDCl_3$

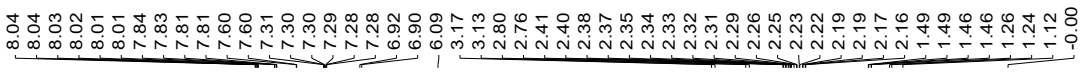


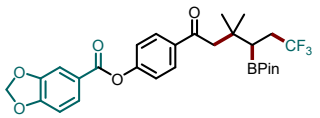


3ae, ^{13}C NMR, 101 MHz, $CDCl_3$

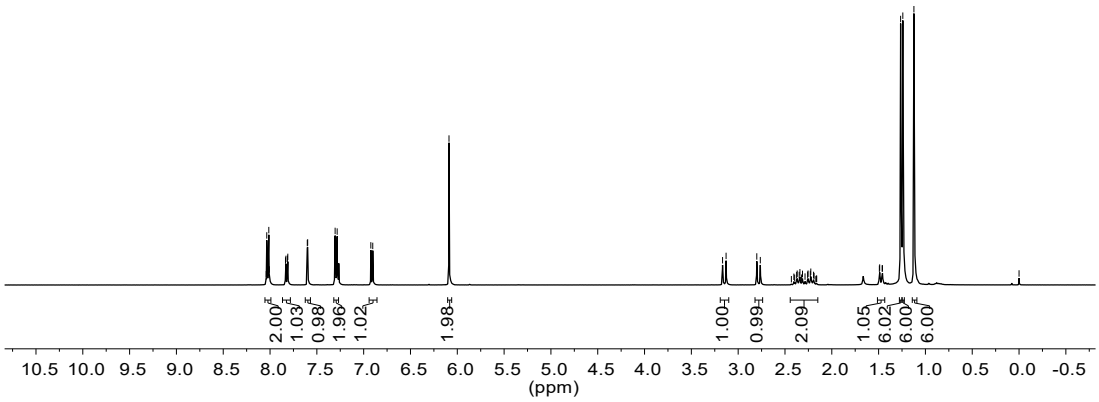


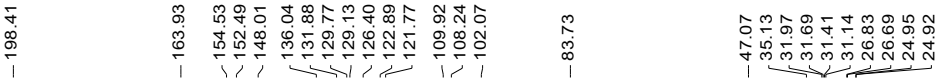
3ae, ^{19}F NMR, 376 MHz, $CDCl_3$

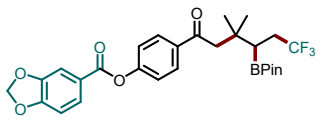




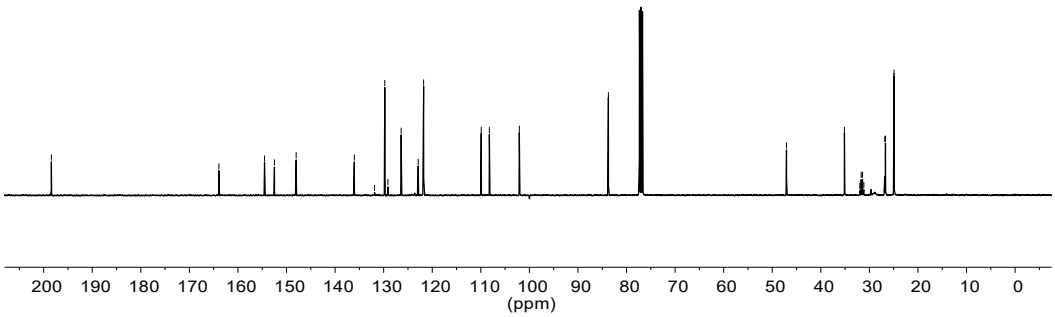
3af, ^{1}H NMR, 400 MHz, $CDCl_3$

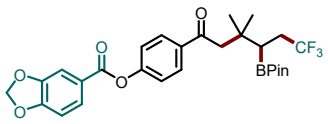




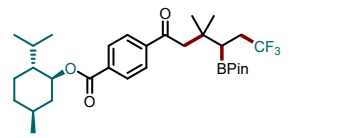


3af, ^{13}C NMR, 101 MHz, $CDCl_3$

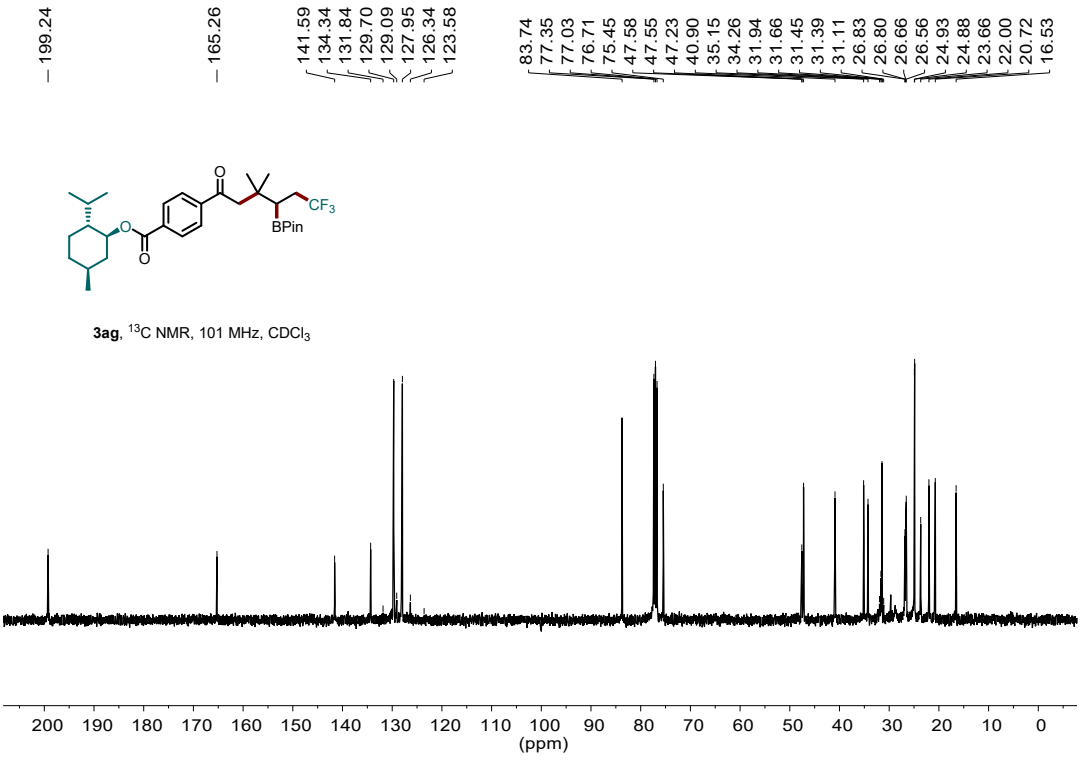




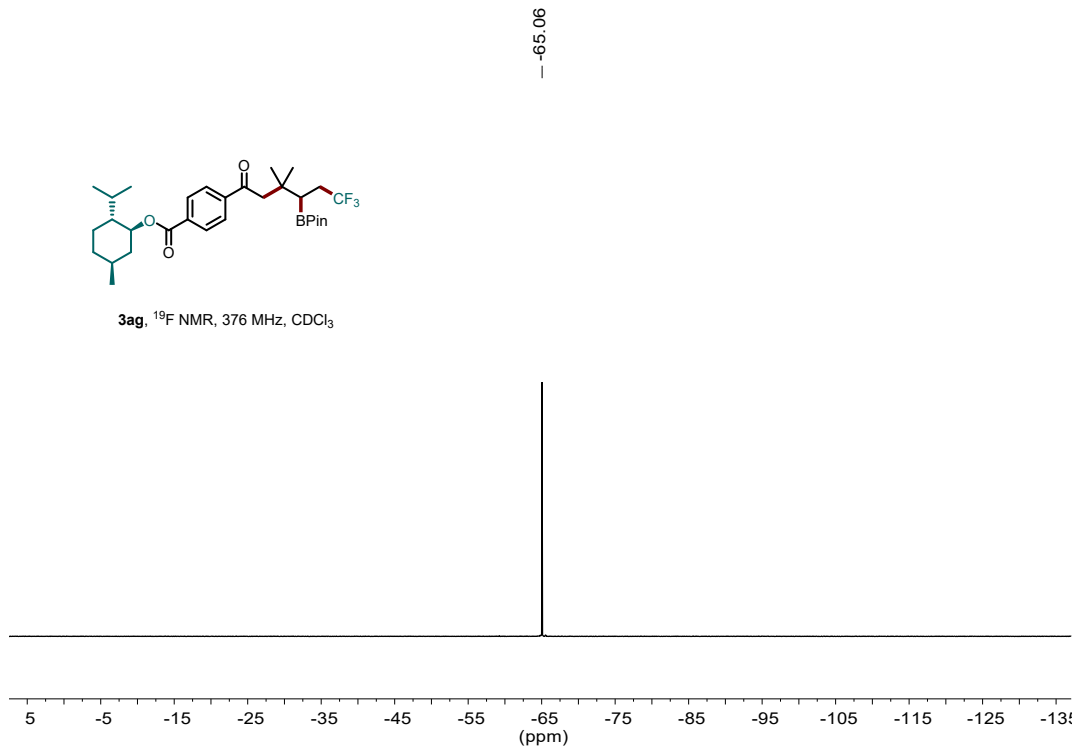
3af, ^{19}F NMR, 376 MHz, $CDCl_3$



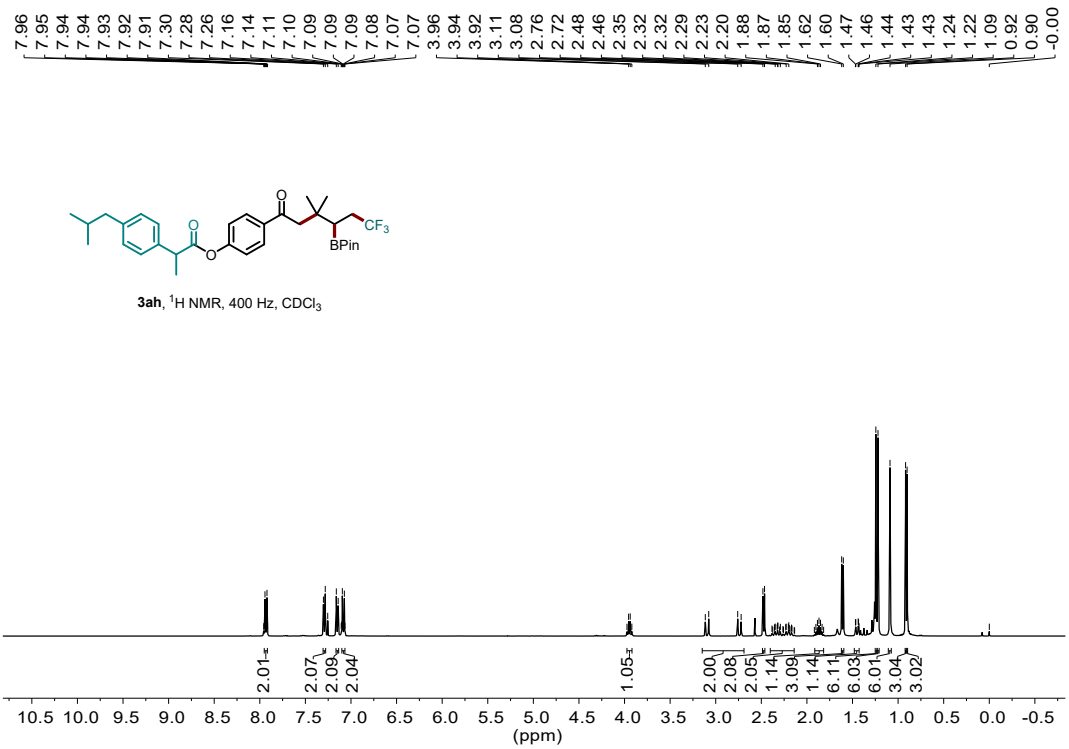
3ag, ^{1}H NMR, 400 MHz, $CDCl_3$



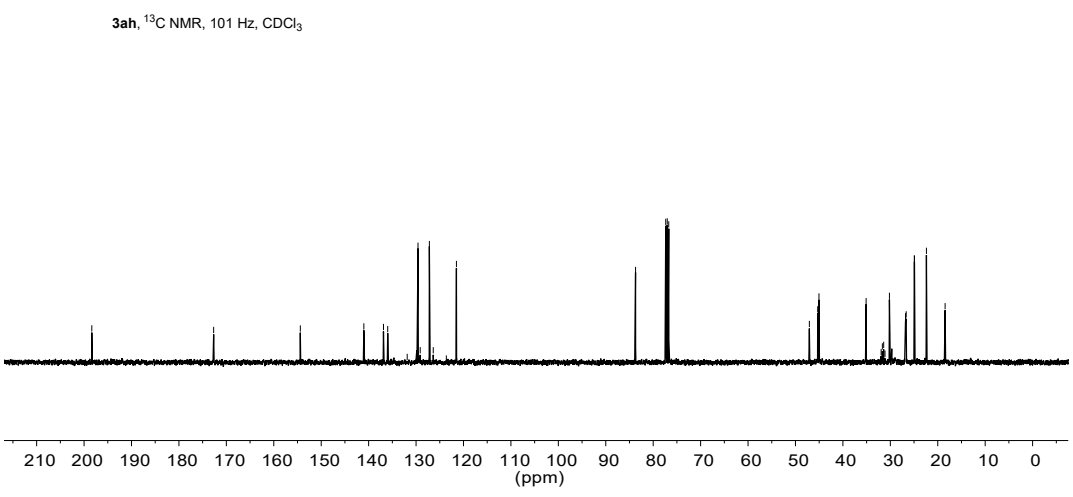
3ag, ^{13}C NMR, 101 MHz, $CDCl_3$



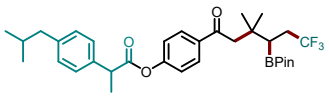
3ag, ^{19}F NMR, 376 MHz, $CDCl_3$



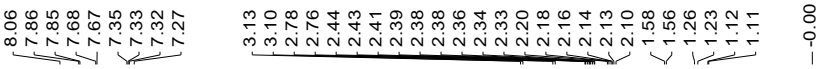
3ah, ^{1}H NMR, 400 Hz, $CDCl_3$

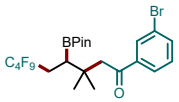


3ah, ^{13}C NMR, 101 Hz, $CDCl_3$

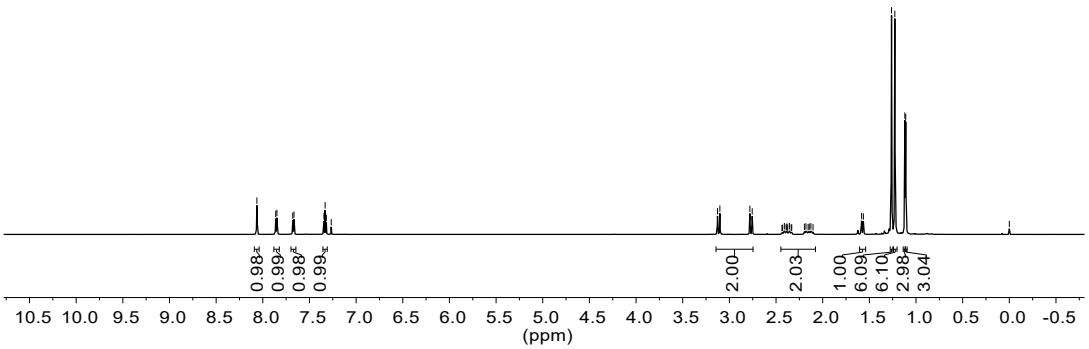


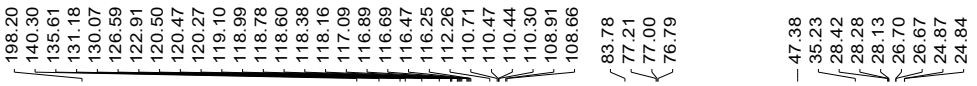
3ah, ^{19}F NMR, 376 Hz, $CDCl_3$

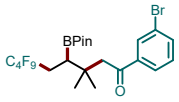




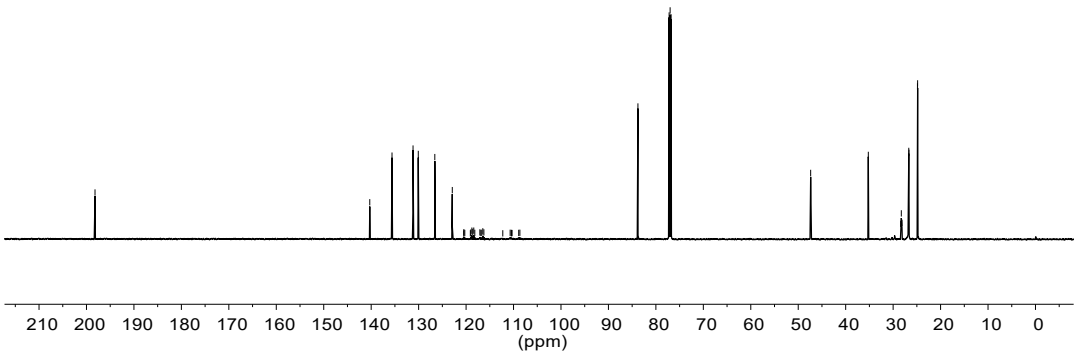
5, ^{1}H NMR, 600 Hz, $CDCl_3$

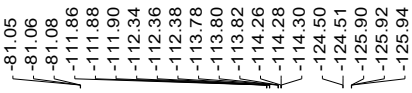


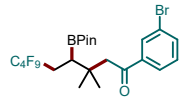




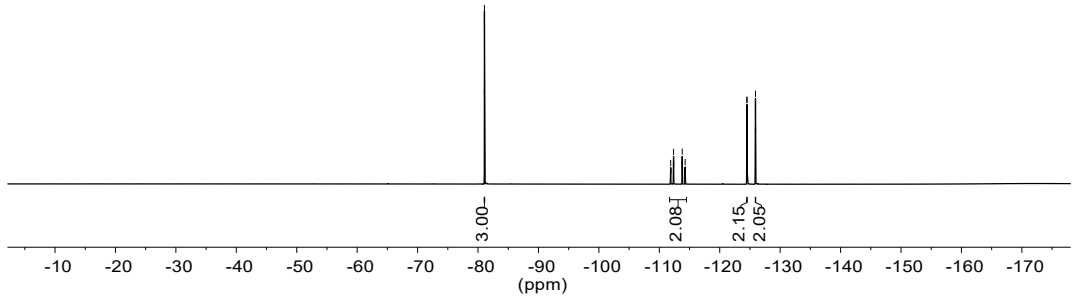
5, ^{13}C NMR, 151 Hz, $CDCl_3$

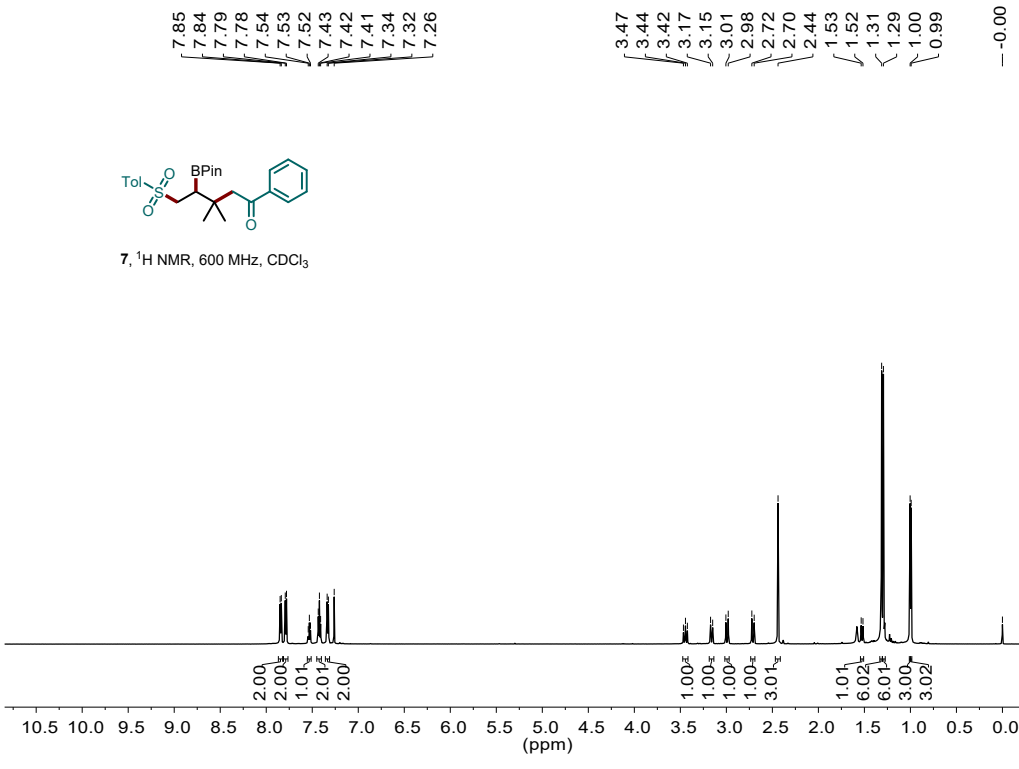




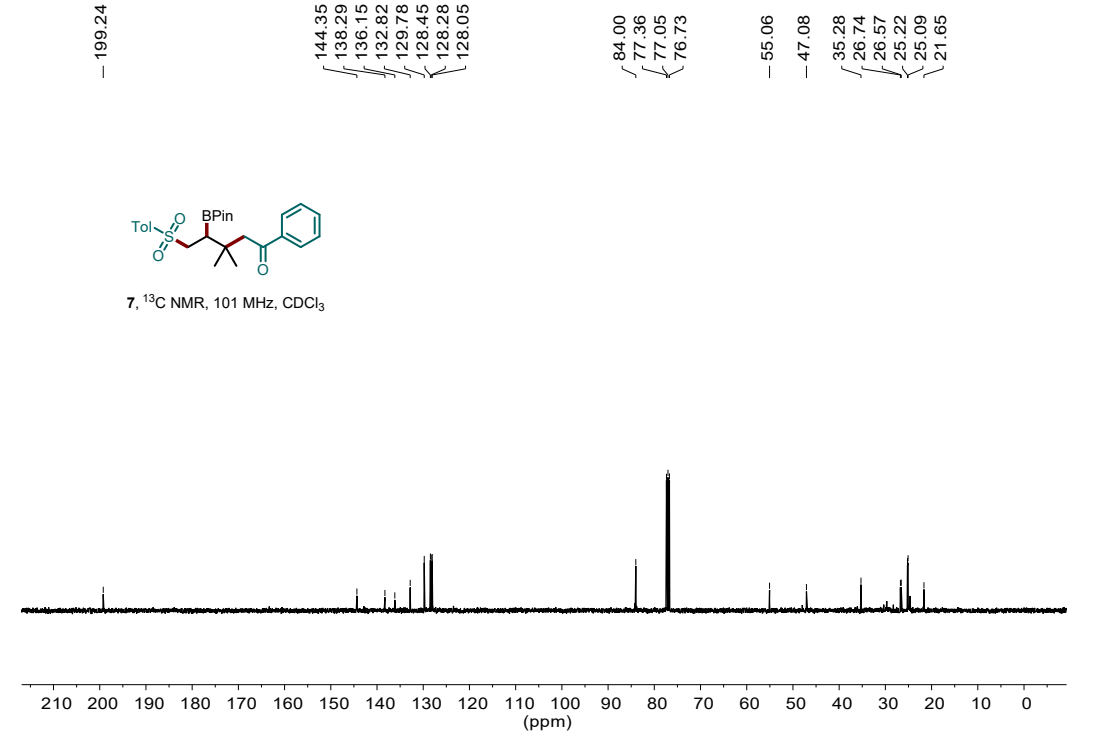


5, ^{19}F NMR, 565 Hz, $CDCl_3$

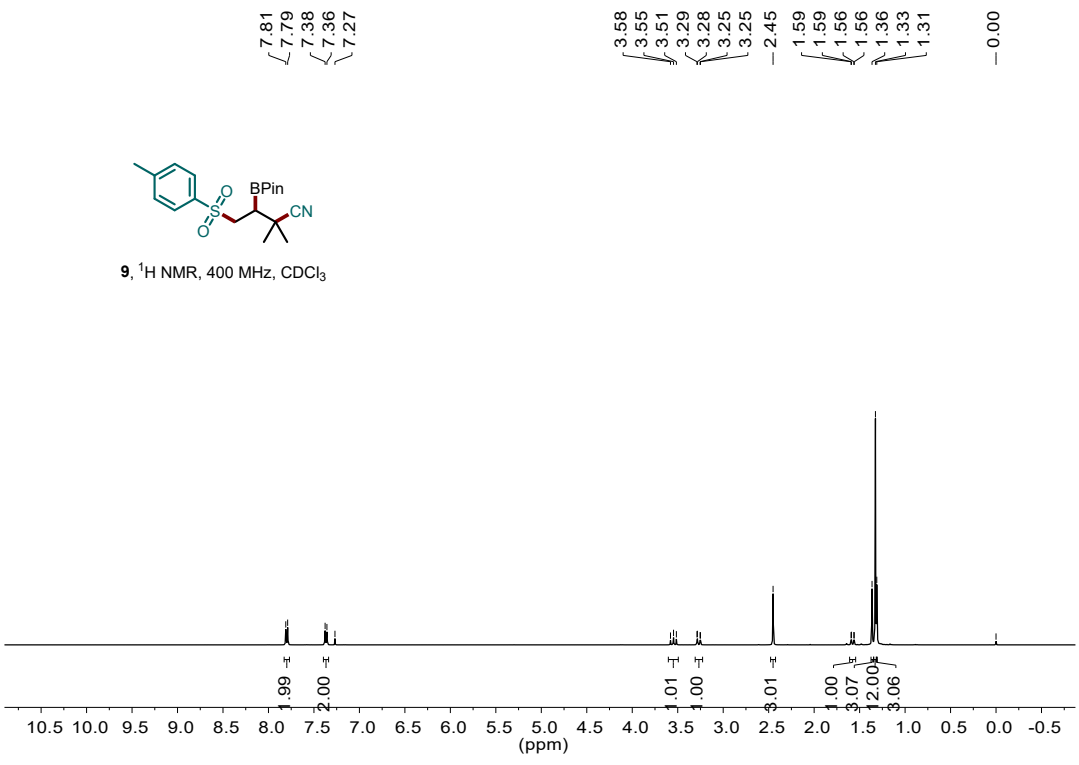




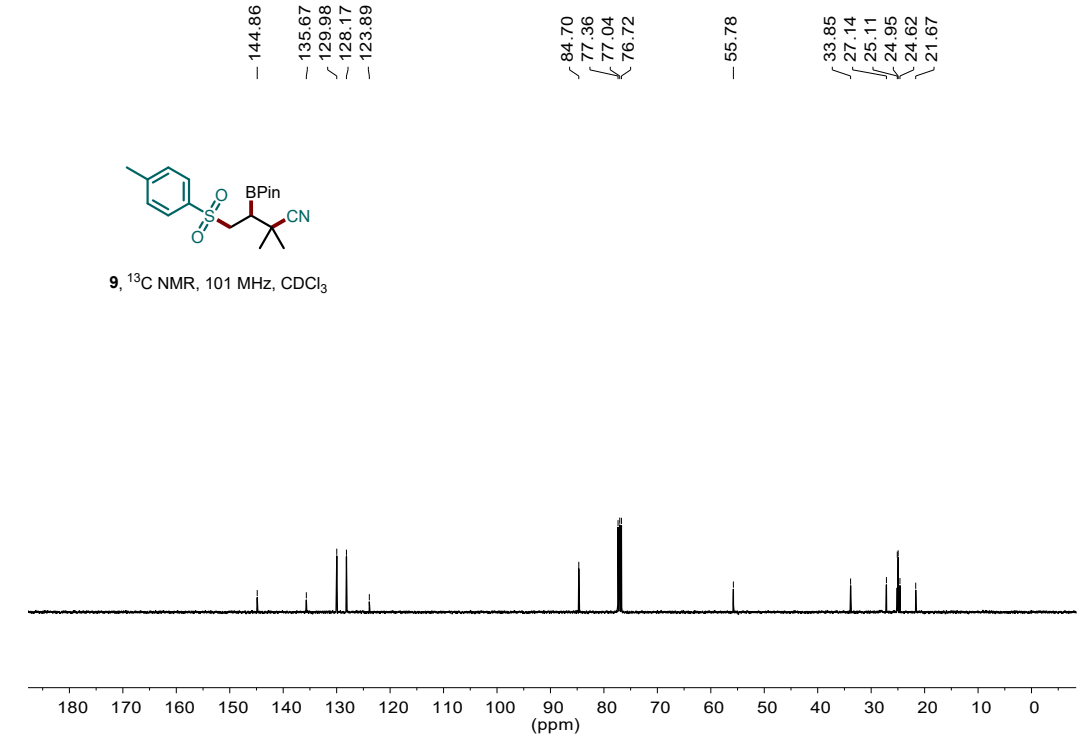
7, ^{1}H NMR, 600 MHz, $CDCl_3$



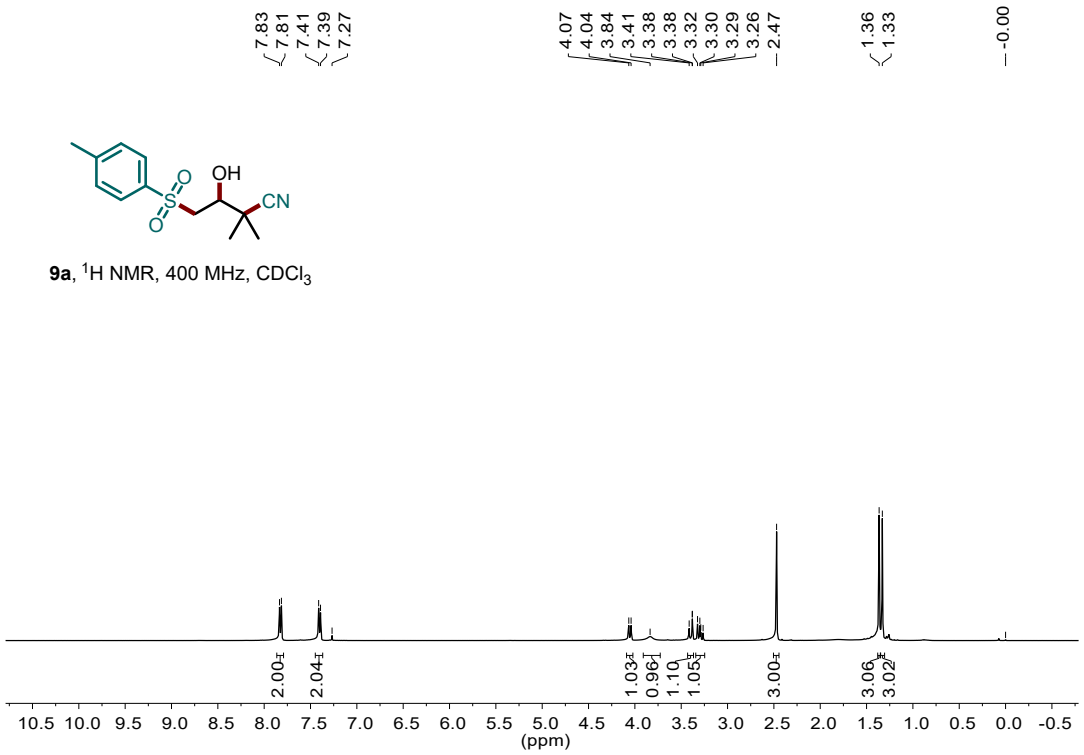
7, ^{13}C NMR, 101 MHz, $CDCl_3$



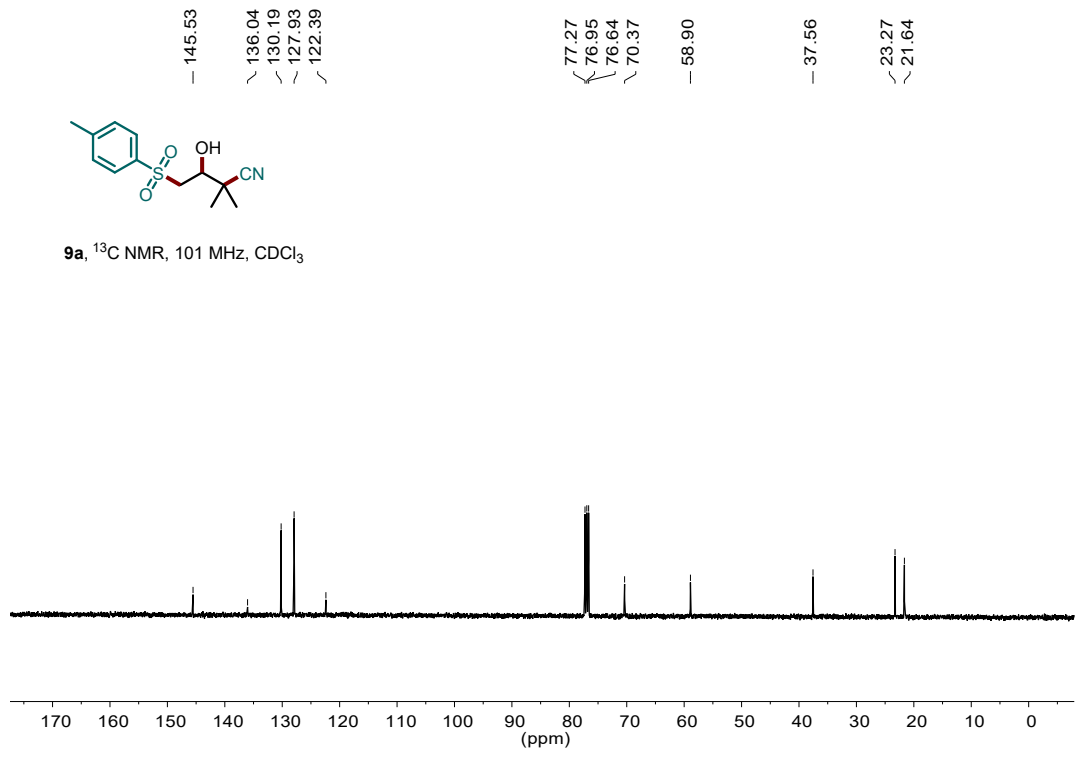
9, ^{1}H NMR, 400 MHz, $CDCl_3$



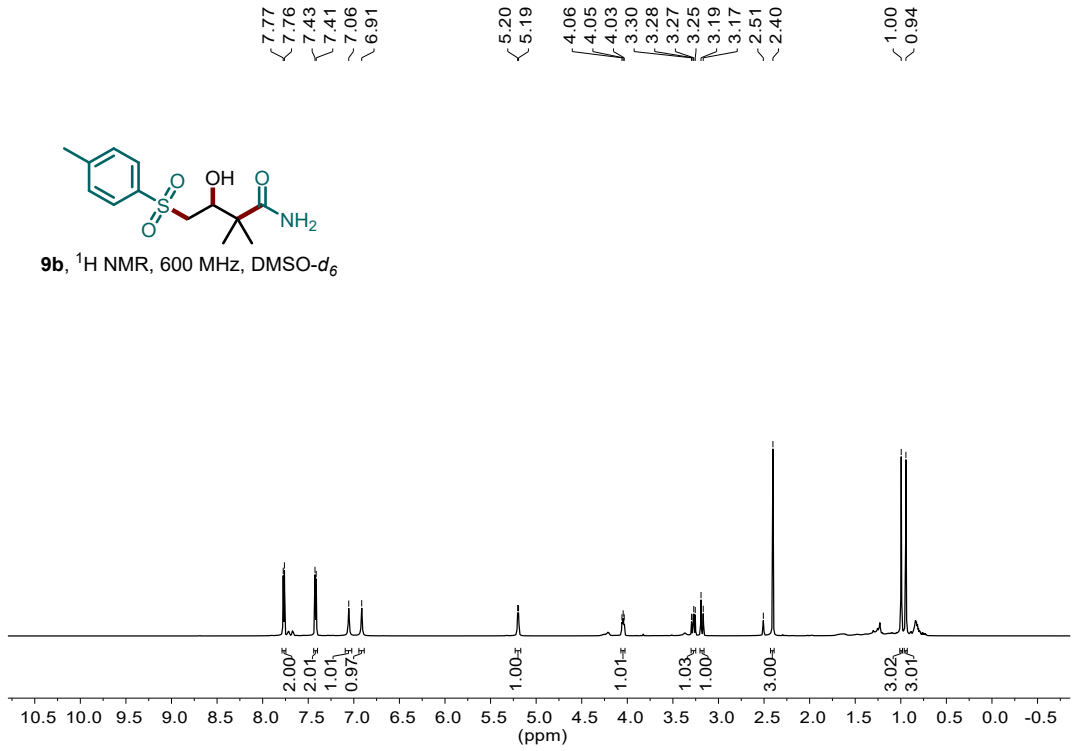
9, ^{13}C NMR, 101 MHz, $CDCl_3$



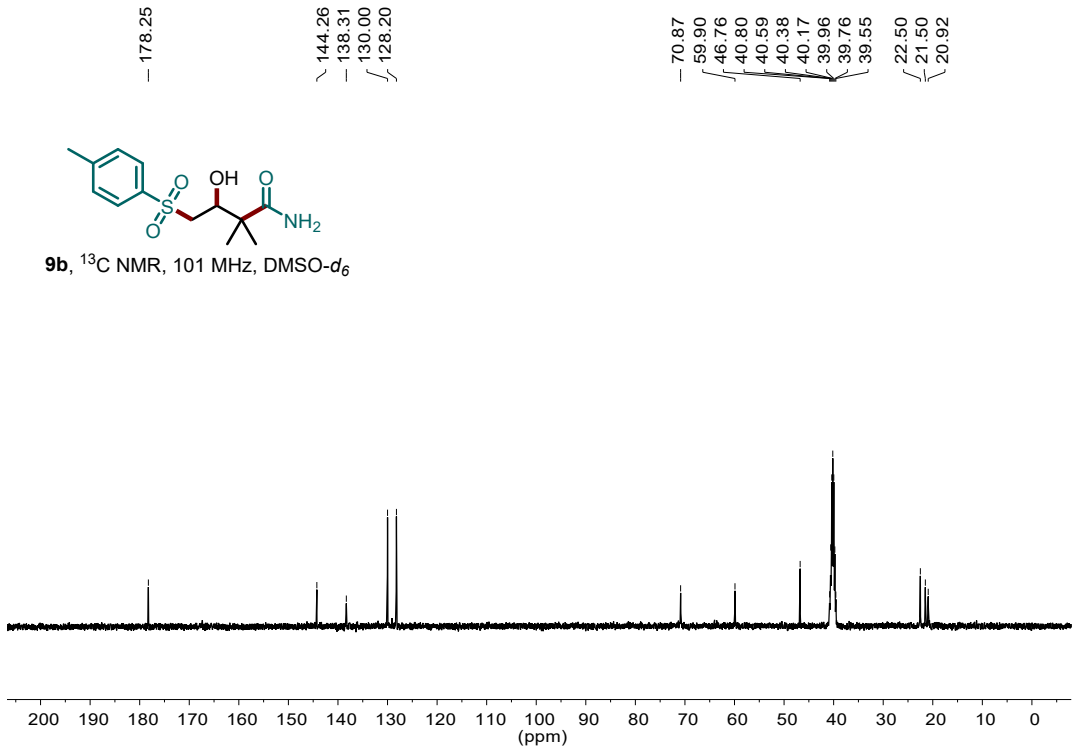
9a, ^{1}H NMR, 400 MHz, $CDCl_3$



9a, ^{13}C NMR, 101 MHz, $CDCl_3$



9b, ^{1}H NMR, 600 MHz, DMSO-d_6



9b, ^{13}C NMR, 101 MHz, DMSO-d_6

5. References

1. (a)M. J. Ardolino and J. P. Morken, *J. Am. Chem. Soc.*, 2014, **136**, 7092; (b)X. Su, H. Huang, Y. Yuan and Y. Li, *Angew. Chem. Int. Ed.*, 2017, **56**, 1338.
2. M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426.