Semi-heterogeneous photocatalytic fluoroalkylation-distal functionalization of unactivated alkenes with R_FSO_2Na under air atmosphere

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1. General information

All reactions were carried out using oven-dried glassware and magnetic stirring under air atmosphere unless otherwise stated. All chemical were obtained from commercial supplier and were used without further purification unless otherwise stated. Analytical thin layer chromatography was carried out using silica gel GF254, visualized under UV light (at 254 nm). ^{1}H NMR data of compunds **3a**-**3d**, **3f**-**3o**, **3q**-**3t**, **3v**, **4a**, **4c** and **4e** were recorded on Brucker 500 (500 MHz). ^{1}H NMR data of compunds **3e**, **3p**, **3u**, **4b**, **4d**, **4f**-**4j**, **5a**-**5i** were record on Brucker 400 (400 MHz). ^{13}C NMR data of compunds **3a**-**3d**, **3f**-**3o**, **3q**-**3t**, **3v**, **4a** and **4e** were record on Brucker 500 (126 MHz). ^{13}C NMR data of compunds **3e**, **3t**, **4b**-**4d**, **4f**-**4j**, **5a**-**5i** were record on Brucker 400 (101 MHz). ^{19}F NMR spectra were recorded on Bruker 400 (377 MHz). All the NMR spectra were processed in MestReNova software. Chemical shifts are quoted in parts per million (ppm) relative to the residual solvent peak for $CDCl_3$. The following abbreviations have been used: δ (chemical shift), J (coupling constant expressed in hertz), s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet) and m (multiplet). High Resolution Mass Spectra were obtained on Thermo fisher Q Exactive mass spectrometer (ESI) from the Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Transmission electron microscopy (TEM) image was obtained on a Talos F200S transmission electron microscope (Thermo Inc., America). XRD patterns of the samples were recorded using X' Pert Pro X-ray diffractometer (Philips) with Co Kα radiation (λ = 1.79 Å). Fourier Transform Infrared (FTIR) spectra from 4000 to 400 cm^{-1} were recorded in KBr discs on a Nicolet IS10 FTIR spectrometer (Thermo Inc., America). X-ray photoelectron spectroscopy (XPS) was performed with a ESCALAB250Xi electron spectrometer (Thermo Inc., America) using monochromatic Al Ka radiation. Photocurrent performance was performed with a Zahner Ennium electrochemical workstation. Diffuse reflectance spectroscopy (DRS) was performed on a TU-1901 UV-visible system. Photoluminescence spectras and lifetimes were recorded on an Edinburg Instruments FLS1000 spectrofluorometer at room temperature with a 450 W Xenon lamp and a 375 nm nanosecond Pulsed Diode laser (EPL),

respectively. The Electron Spin Resonance (ESR) spectrum was recorded on a Bruker A300. Irradiance of the LED modules was measured using CEL-NP2000 Optical Power and Energy Meter equipped. The light-promoted reactions were carried out by using standard blue LEDs with 28 blue LED beads (EPISTAR, 1 W LED beads and wavelength 460 ± 5 nm)

2. Preparation of tertiary alcohol

The starting meterials **1** were prepared according to literature procedures.[1]

3. Preparation of R_F radical precursor

The starting meterials **2b** were prepared according to literature procedures.[2]

4. Preparation of carbon nitride catalysts

Synthesis of bulk g-C_3N_4: bulk g-C_3N_4 was synthesized by polymerization of melamine (12 g) at 823 K with a heating rate of 2.3 K/min under air atmosphere for 4 h.[3] The obtained product was ground to a powder and denoted as bulk g-C_3N_4 (8 g).

Synthesis of CN-K[4,6]: CN-K was prepared directly from melamine, NH_4Cl and KCl. Typically, 1 g of melamine was thoroughly grinded with NH_4Cl (3 g) and KCl (10 g). The resultant mixture was heated to 823 K at a rate of 2.3 K/min and kept at this temperature for 4 h with N_2 flow rate of 90 mL/min. After it was naturally cooled down to the room temperature, the solid mixture was thoroughly washed with DI water (3 × 10 mL) to remove the metal salts. Finally the resulting yellow material CN-K (190 mg) was obtained after drying at 60 °C under vacuum for overnight.

5. Characterization of Carbon Nitride Catalysts

5.1 Fourier transform infrared (FTIR)

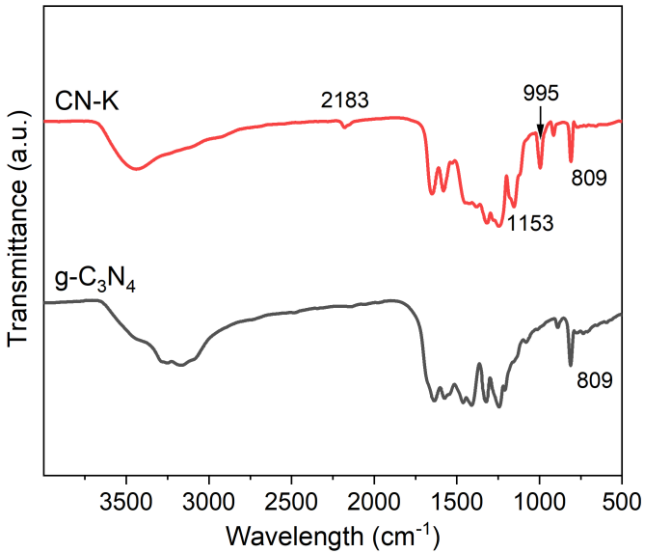


Fig. S1. FTIR spectra of bulk g-C_3N_4 and CN-K.

In the FTIR spectra of bulk g-C_3N_4 and CN-K (Fig. S1), the peak at 809 cm^{-1} corresponds to the out of plane bending of the heptazine rings and the absorption in the region of 1100−1600 cm^{-1} can be attributed to graphite the N−C=N stretching vibrations of the layer heterocycle. Compared to bulk g-C_3N_4, the typical C−N vibration signals in CN-K emerges at 995 cm^{-1} and the peak at 1153 cm^{-1} could be attributed to vibration of the −N−H structure. In addition, CN-K presents a new signal at 2183 cm^{-1}, which may be due to the stretching vibration of the −C≡N structure.[4]

5.2 The X-ray photoelectron spectroscopy (XPS)

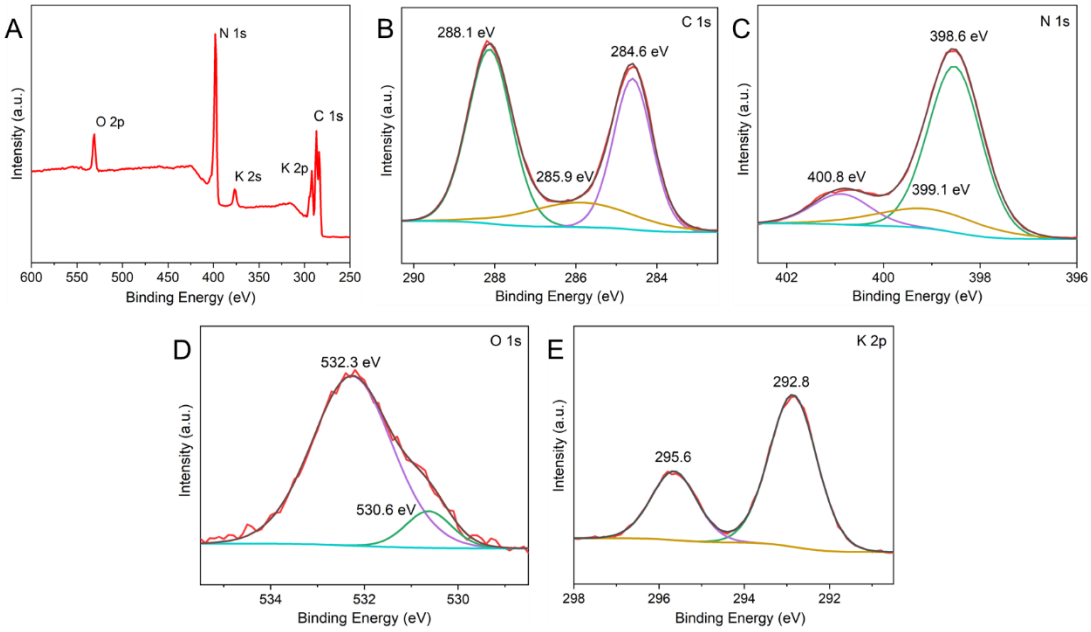


Fig. S2. XPS spectra for CN-K (A); High-resolution C 1s XPS spectra for CN-K (B); N 1s XPS spectra for CN-K (C); O 1s high-resolution XPS spectra for CN-K (D); and K 2p XPS spectra for CN-K (E).

The elemental composition and chemical states of the CN-K were measured by X-ray photoelectron spectroscopy (XPS, Fig. S2). It was found that four elements (C, N, O and K) in the CN-K. The three main peaks of the C 1s spectrum are at 288.1, 285.9, 284.6 eV, corresponding to aromatic cycles (N−C=N), C≡N on the edges of heptazine units and adventitious carbon species, respectively. In N 1s XPS spectra, the peaks at 398.6, 399.1, 400.8 eV are attributed to sp^2 hybridized nitrogen (N−C=N), tertiary nitrogen (N−$(C)_3$) groups and −NHx groups, respectively.[5] In O 1s XPS spectra, the peaks at 530.6 and 532.3 eV correspond to oxygen in the CO_2 and H_2O adsorbed on the material surface. Two characteristic peaks are at 295.6 and 292.8 eV are attributed to K $2p^{1/2}$ and K $2p^{3/2}$, respectively. Based on the above results, the K^+ have been successfully doped into the bulk g-C_3N_4 without destroying its the basic structure.

5.3 X-ray diffraction (XRD)

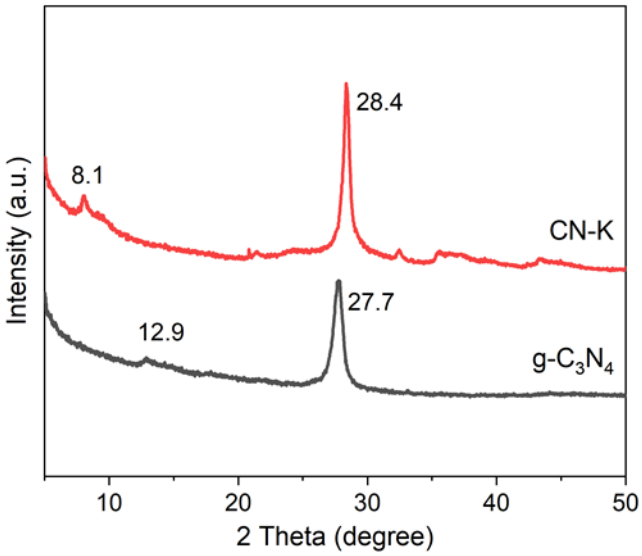


Fig. S3. XRD patterns of bulk g-C_3N_4 and CN-K.

The XRD pattern evidenced structural changes among bulk g-C_3N_4 and CN-K (Fig. S3). As shown in bulk g-C_3N_4, the typical diffraction patterns of interlayer stacking at about 27.7° (002) and in-plane stacking at about 12.9° (100). CN-K shows different XRD features with one main peak centered at 28.4° is assigned to the (002) crystal facet, which is about 0.7° shift to higher angle compared with bulk g-C_3N_4, suggesting a decreased interlayer distance. While one newborn peak at 8.1° presented, this peak could be assigned to the intrinsic (110) crystal facet of CN-K.[6] The variation of these distances may be due to the addition of K^+, which causes the variation of intramolecular force.

5.4 Scanning electron microscope (SEM) and transmission electron microscopy (TEM)

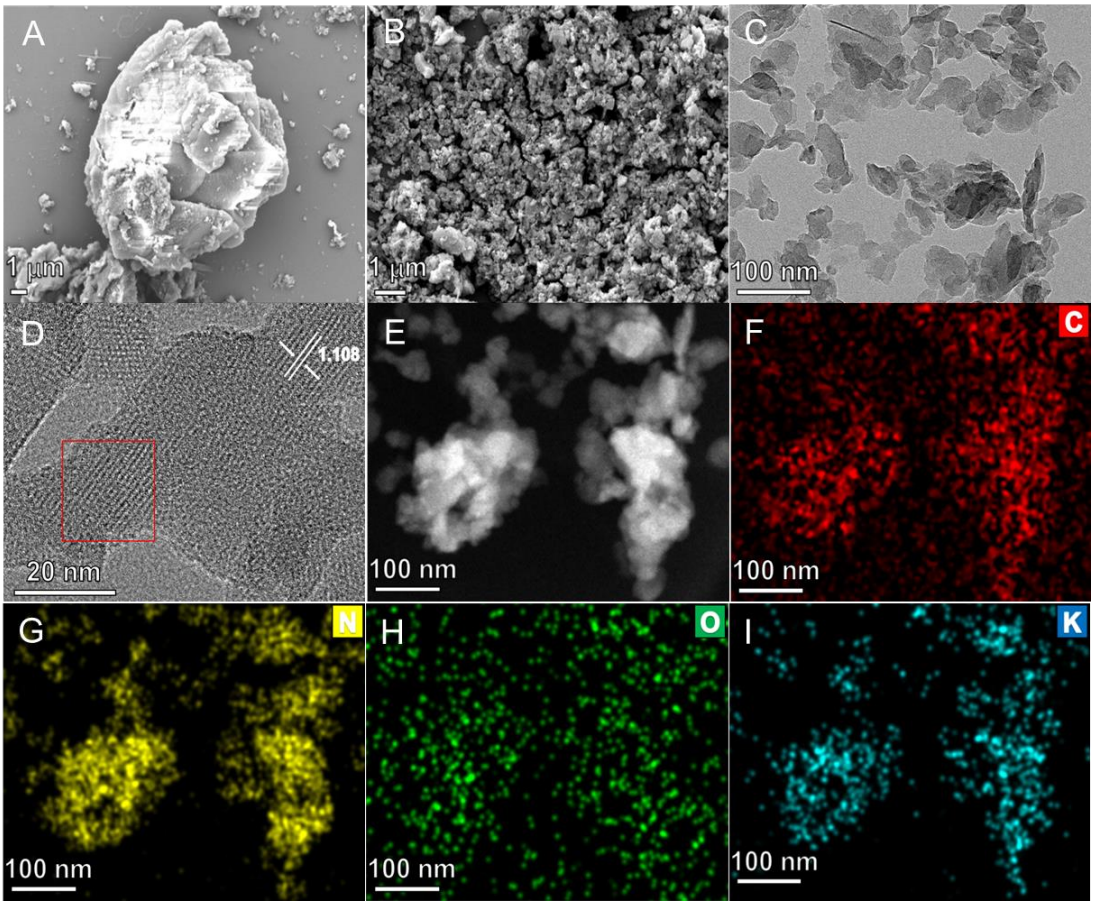


Fig. S4. SEM images of bulk g-C_3N_4 (A) and CN-K (B); TEM image of CN-K (C) and HR-TEM image of CN-K (D). The corresponding elemental mapping of CN-K (E-I). The colors of red, yellow, green and blue represent the elemental components of C, N, O, and K, respectively.

To demonstrate that the addition of KCl and NH_4Cl effectively change the morphology and microstructure of material. Bulk g-C_3N_4 and CN-K were characterized by SEM and TEM (Fig. S4). It is obvious that CN-K modified by KCl and NH_4Cl has smaller and uniform nanosheets compared with bulk g-C_3N_4. The obvious lattice fringes and a (110) in-plane spacing of 1.108 nm can be seen in the HR-TEM image of CN-K. The elemental distribution is investigated by EDX spectroscopy. The corresponding C, N, O, and K elements are evenly dispersed in the region.[7]

5.5 Photoluminescence (PL) spectra

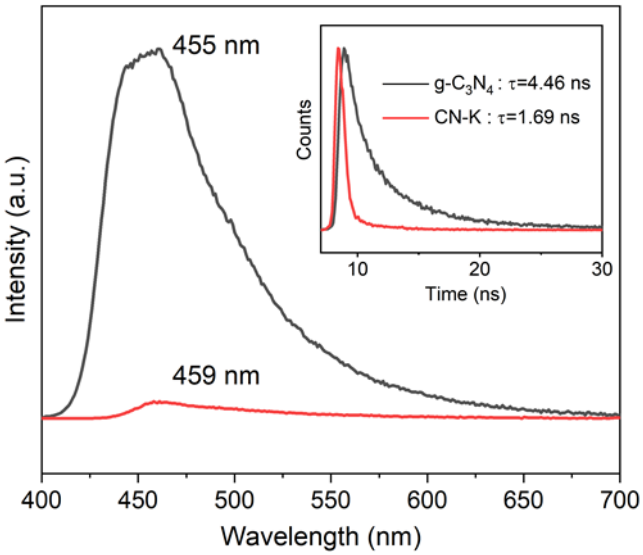


Fig. S5. photoluminescence (PL) spectra under 370 nm excitation of bulk g-C_3N_4 and CN-K (inset: fluorescent decay spectra).

The fluorescence emission peaks of bulk g-C_3N_4 and CN-K are 455 nm and 459 nm, respectively (Fig. S5). In CN-K, the fluorescence intensity decreased compared with bulk g-C_3N_4, which indicates that modified CN-K facilitates charge transfer and inhibits the recombination of photogenerated electrons and holes. Similarly, the fluorescence lifetime also reduced. CN-K presents faster PL decay with an average lifetime of 1.69 ns than that of bulk g-C_3N_4 (4.46 ns).[8]

5.6 Transient photocurrent responses of bulk g-C_3N_4 and CN-K

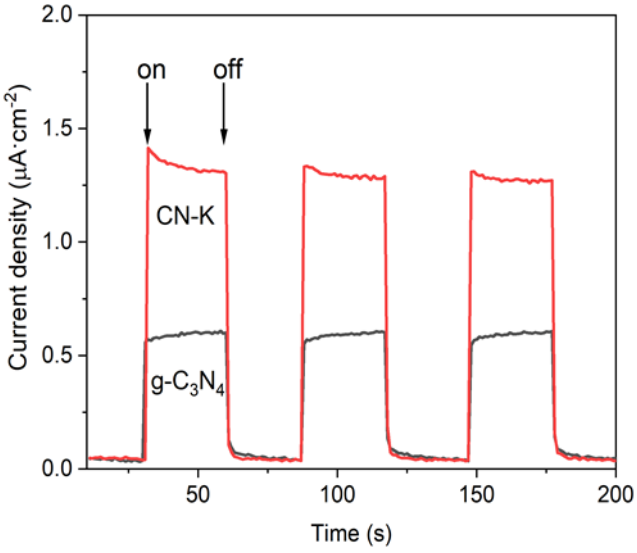


Fig. S6. Transient photocurrent responses of bulk g-C_3N_4 and CN-K.

The photocurrent test is performed during repeat light irradiation cycles. The photocurrent response of CN-K is obviously stronger than that of bulk g-C_3N_4 (Fig. S6), which reveals that CN-K achieves more photogenerated electron-hole separation.

5.7 Band gap characterization

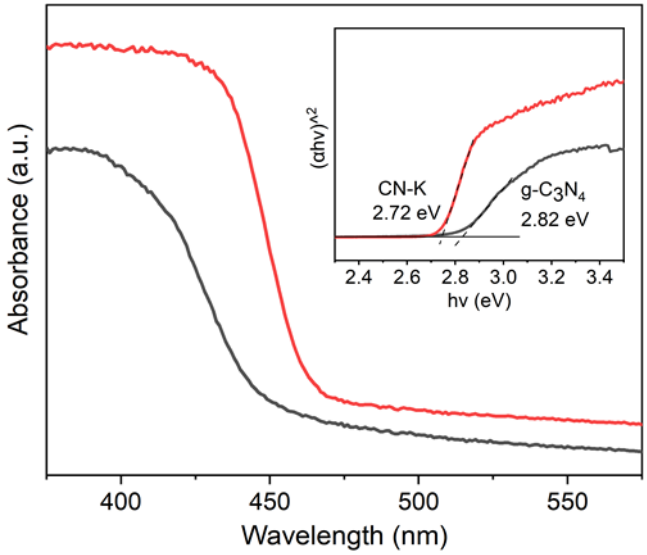


Fig. S7. DRUV-vis spectra (inset: Tauc plots of bulk g-C_3N_4 and CN-K).

It can be seen from the figure (Fig. S7) that the light absorption edge of CN-K exhibits a red shift. The band gaps of bulk g-C_3N_4 and CN-K are determined by the Tauc-Plot method. Compared with the bulk g-C_3N_4 (Eg = 2.82 eV), the band gap of CN-K (Eg = 2.72 eV) is reduced by 0.1 eV.[9]

5.8 Mott Schottky analysis of bulk g-C_3N_4 and CN-K

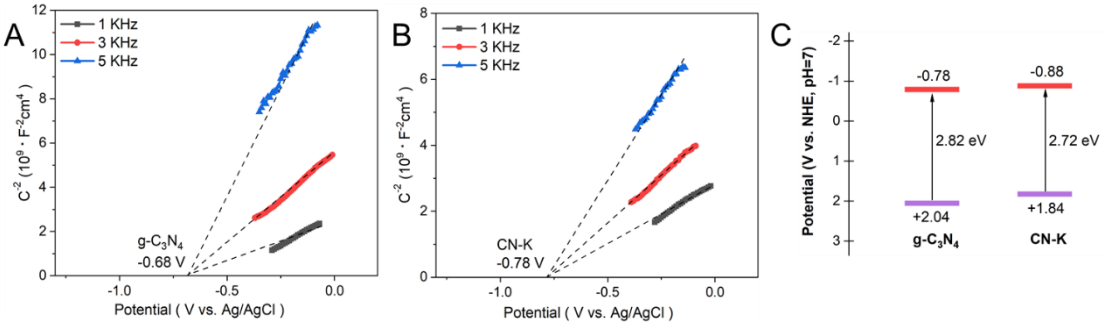


Fig. S8. Mott-Schottky plots of bulk g-C_3N_4 (A) and CN-K (B) recorded at 1, 3 and 5 KHz and schematic illustration of band structure (C).

The figures show the typical Mott-Schottky curves of bulk g-C_3N_4 and CN-K under the three-electrode systems (Fig. S8) and the slope of the curves is positive, which means

that this series of materials are n-type semiconductors. The intercept of the curves on the abscissa are the flat band potential of the samples and its values (vs. Ag/AgCl) are -0.68 and -0.78 of bulk g-C_3N_4 and CN-K, respectively. According to the band gap measured by UV-Vis DR spectroscopy, the valence band of the samples can be calculated. The schematic diagram of the energy band structure drawn from the above data can clearly see the changes in the conduction band and valence band of these series of materials.[10]

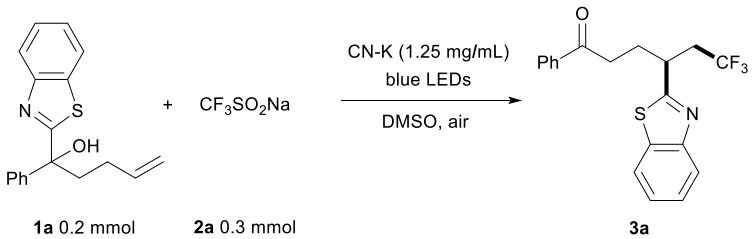
6. Screening of different stoichiometry of reactants

1a **2a** **3a**

entry[a]	amount of **1a**	amount of **2a**	yield[b] (%)
1	1 equiv	1 equiv	49
2	1 equiv	1.5 equiv	82
3	1 equiv	2 equiv	82

[a]Reaction conditions: **1a**, CF_3SO_2Na (**2a**), DMSO (4 mL), CN-K (1.25 mg/mL), 2*24 W blue LEDs (460 ± 5 nm) without extra heating (at 30–35 °C), air, 24 h. [b]Yield determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

7. General procedure



1a 0.2 mmol **2a** 0.3 mmol **3a**

To a 10 mL oven-dried tube equipped with a magnetic stir bar was added **1** (0.2 mmol), **2** (0.3 mmol) and CN-K (5 mg). Then, DMSO (4 mL) were added via syringe. The open flask tube was irradiated by two blue LEDs (460 ± 5 nm) and the reaction mixture was

stirred without extra heating (at 30 – 35 ºC) for the indicated time. In each case, the blue LEDs was placed 4 cm from the 10 mL reaction tube (Fig. S9). After complete consumption of the starting material (followed by TLC), the mixture was filtered to remove the CN-K. The reaction mixture was diluted with ethyl acetate (10 mL), transferred to a 60 mL separatory funnel and washed with water (3 × 4 mL). After removal of solvent, the crude product was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate 5:1~20:1). The final product was characterized by ^{1}H-NMR, ^{13}C-NMR, ^{19}F-NMR and HRMS (ESI). The light-promoted reactions were carried out by using a standard blue LEDs with 28 blue LED beads (EPISTAR, 1 W LED beads and wavelength 460 ± 5 nm). The distance from the blue LEDs to the reaction tube was 4 cm (18.9 mW/cm^2 determined by power meter).

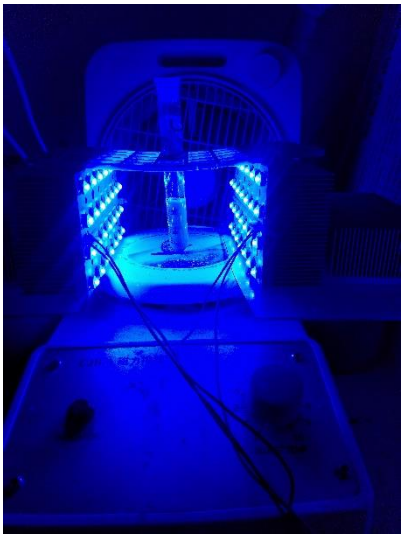
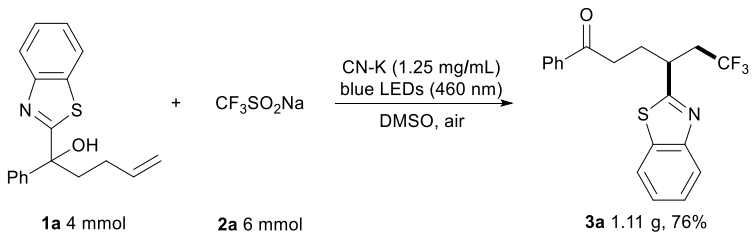


Fig. S9. Experimental setup

8. Gram-scale experiment



1a 4 mmol **2a** 6 mmol **3a** 1.11 g, 76%

To a 200 mL oven-dried tube equipped with a magnetic stir bar was added **1a** (4 mmol), **2a** (6 mmol) and CN-K (100 mg). Then, DMSO (80 mL) was added via syringe. The open flask tube was irradiated by four blue LEDs boards (460 ± 5 nm) and the reaction

mixture was stirred without extra heating (at 30 – 35 °C) for 48 h. After complete consumption of the starting material (followed by TLC), the mixture was filtered to remove the CN-K. The reaction mixture was diluted with ethyl acetate (150 mL), transferred to a 500 mL separatory funnel and washed with water (3 × 40 mL), then dried over anhydrous Na_2SO_4, filtered. After removal of solvent, the crude product was purified via silica gel flash column chromatography (petroleum ether /ethyl acetate: 10/1) to give the final product **3a (**1.11 g, 76%).

9. Catalyst Recycling

To a 10 mL oven-dried tube equipped with a magnetic stir bar was added **1a** (0.2 mmol), **2a** (0.3 mmol) and CN-K (5 mg). Then, DMSO (4 mL) was added via syringe. The open flask tube was irradiated by two blue LEDs (460 ± 5 nm) and the reaction mixture was stirred without extra heating (at 30 – 35 °C) for 24 h. After completion, the reaction mixture was centrifuged to separate CN-K and the liquid mixture. Then the liquid mixture was transferred to a separatory funnel, diluted with ethyl acetate (10 mL), and washed with water (3 × 4 mL). After evaporated of solvent, the crude product was purified via silica gel flash column chromatography to afford the desired products. The catalyst CN-K was washed with EA (3 × 5 mL) and DI water (5 × 8 mL). Finally, the revovered CN-K powders were dried at 343 K under vacuum for overnight and reused in the subsequent reaction.

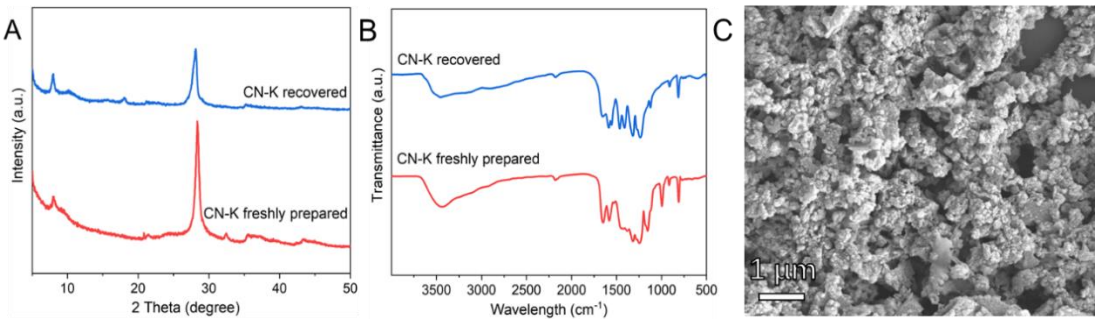


Fig. S10. XRD patterns (A) and FTIR spectra (B) of CN-K freshly prepared and recovered; (C) SEM images of CN-K recovered.

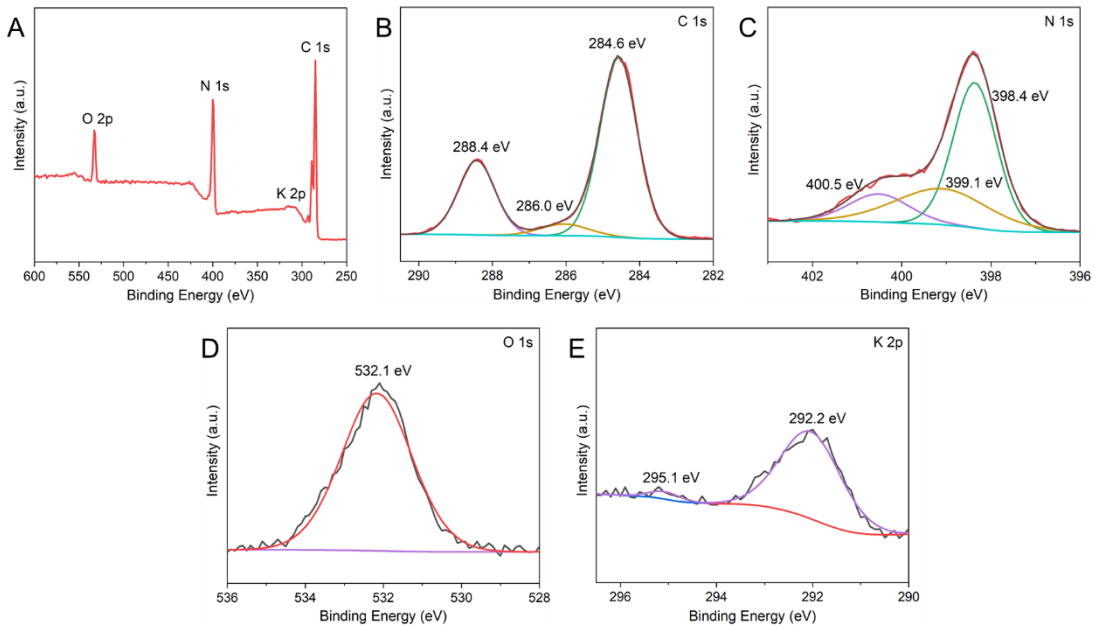
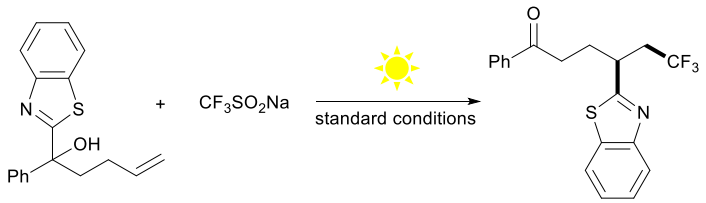


Fig. S11. CN-K recovered characterization (A) XPS spectra; (B) C 1s high-resolution XPS spectra; (C) N 1s high-resolution XPS spectra; (D) O 1s high-resolution XPS spectra; (E) K 2p high-resolution XPS spectra.

In order to further prove the stability of CN-K, we characterized the recovered CN-K (Fig. S10). The recovered CN-K displayed unchanged XRD diffraction pattern, spectroscopic features and morphology. At the same time, X-ray photoelectron spectroscopy (Fig. S11) also showed that the recovered CN-K maintained its original structure.

10. Sunlight driven experiment



1a 0.2 mmol **2a** 0.3 mmol **3a**

To a 10 mL oven-dried tube equipped with a magnetic stir bar was added **1a** (0.2 mmol), **2a** (0.3mmol), CN-K (5 mg) and DMSO (4 mL). Then, the open flask tube was placed under sun light for 3 days (from 9:00 to 17:00, 3 × 8 h). The temperature was maintained between 36 – 45 ºC. No additional temperature control was required (Fig. S12). After complete consumption of the starting material (followed by TLC), the mixture was

centrifuged to remove the CN-K. The reaction mixture was diluted with ethyl acetate (10 mL), transferred to a 60 mL separatory funnel, and washed with water (3 × 4 mL). The combined liquid mixture was evapored and the crude product was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate 10:1) to give the final product **3a** (54.5 mg, 75% yield).

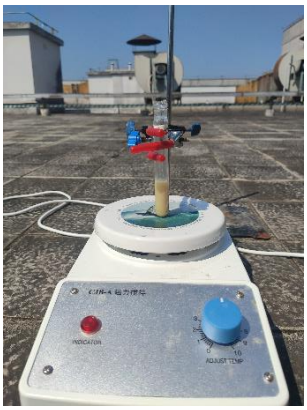
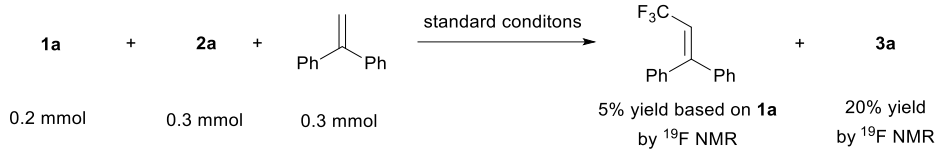


Fig. S12. Sunlight driven experimental setup

11. Radical trapping experiment



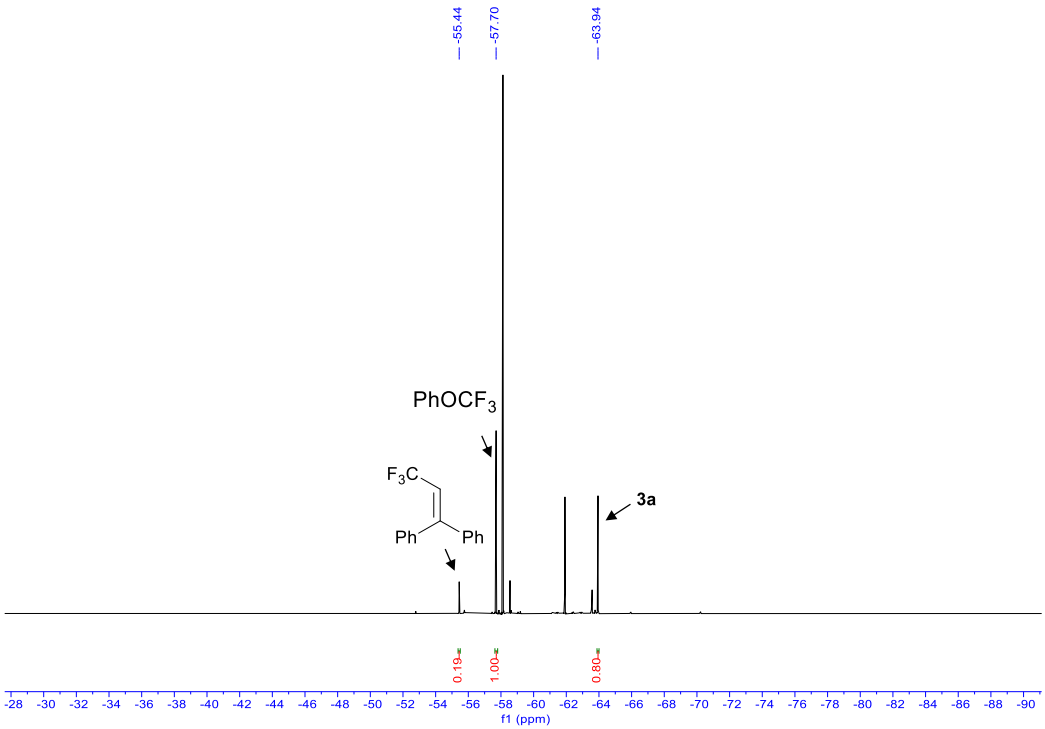


Fig. S13. ^{19}F NMR spectra of the adduct 1,1-diphenylethylene-CF_3.

To a 10 mL oven-dried tube equipped with a magnetic stir bar was added **1a** (0.2 mmol), **2a** (0.3mmol), CN-K (5 mg), DMSO (4 mL) and 1,1-diphenylethylene (0.3 mmol). Then, the open flask tube was irradiated by two blue LEDs (460 ± 5 nm) and the reaction mixture was stirred without extra heating (at 30 – 35 ºC) for 24 h. After completion, the reaction mixture was centrifuged to separate CN-K and the liquid mixture. The reaction mixture was diluted with ethyl acetate (10 mL), transferred to a 60 mL separatory funnel, and washed with water (3 × 4 mL). After evaporated of solvent, the crude reaction mixture was then purified by flash column chromatography to afford the crude product. $PhOCF_3$ (internal standard, 0.05 mmol) and $CDCl_3$ was added. Yield was calculated based on ^{19}F NMR analysis of the crude product.

12. The light on-off experiments

The light on-off experiments were carried out under the standard reaction conditions using a mixture of **1a** (1 mmol), **2a** (1.5 mmol), CN-K (50 mg) and DMSO (40 mL). After being irradiated for 2 h, an aliquot (1 mL) from the reaction mixture was transferred into a 60 mL separatory funnel, diluted with ethyl acetate (5 mL), and washed with water (3 × 2 mL). After evaporated of solvent, the crude reaction mixture was then purified by flash column chromatography to afford the crude product. The yield of product **3a** was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. All of the following yields were analyzed in the identical way after 2 h light on or off.

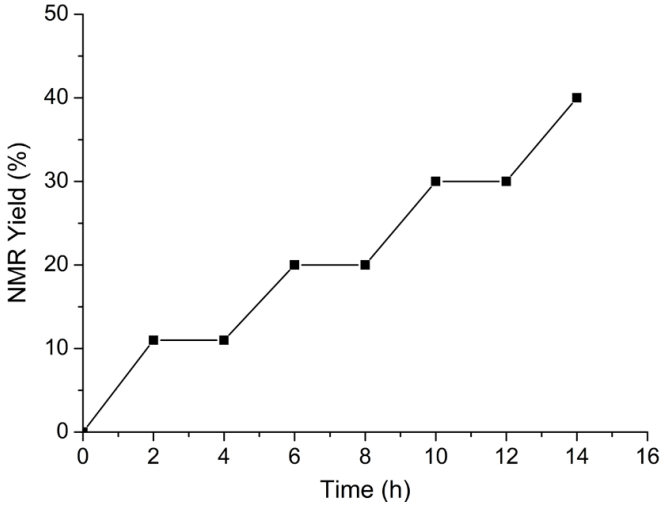


Fig. S14. The light on-off experiments

13. Quantum yield determination

To an oven-dried tube equipped with a magnetic stir bar was added **1a** (0.2 mmol), **2a** (0.3 mmol), CN-K (5 mg) and DMSO (4 mL). The front of the reactor was covered with a black screen, and the reaction mixture was vigorously stirred under blue light irradiation (460 – 465 nm, 19 mW·cm^{-2}). Light was delivered to the reaction mixture through the rectangular hole (3×1.3 cm^2) in the black screen for indicated time. Temperature of the reaction mixture was maintained at 30 °C. After irradation, the reaction mixture was centrifuged, diluted with ethyl acetate (10 mL), transferred to a separatory funnel, and washed with water (3 × 4 mL). The combined liquid mixture was evapored and the yield of product formed was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The quantum yield is calculated using the following equation:

$$\Phi = \frac{Ne}{Np} \times 100\% = \frac{M \times N_A}{\frac{E_{total}}{E_{photon}}}$$

$$\Phi = \frac{M \times N_A}{\frac{S \times P \times t}{h \times \frac{c}{\lambda}}} = \frac{M \times N_A \times h \times c}{S \times P \times t \times \lambda}$$

Where, Φ is quantum yield, Ne is the amount of reaction electrons, Np is the incident photons, M is the amount of **3a** molecules (mol), N_A is Avogadro constant (6.022×10^{23}/mol), h is the Planck constant (6.626×10^{-34} J·S), c is the speed of light (3×10^8 m/s), S is the irradiation area (cm^2), P is the intensity of irradiation light (W/cm^2), t is the photoreaction time (s), λ is the wavelength of the monochromatic light (m).

Experiment: output power at 1 cm distance from the light source 19 mW/cm^2 (measured by TBQ-5 photosynthetic active radiation meter, TRM-SCY), the irradiation area was 3.9 cm^2. The product yield were 28% after 21 h (75600 s)

Quantum yield calculation:

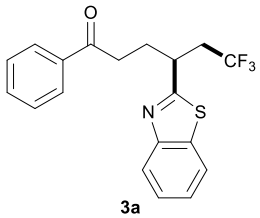
$$\Phi = \frac{M \times N_A \times h \times c}{S \times P \times t \times \lambda} = 0.0026$$

14. ESR experiment

In ESR experiment, **1a** (0.2 mmol), **2a** (0.3 mmol) and 5 mg CN-K were added in 4 mL of DMSO together with the addition of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, 0.4 mmol) under black environment or visible light irradation (λ: 450 – 465 nm) for 10 min, the g-factors is 2.01.

15. Characterization of the products

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (3a)



3a

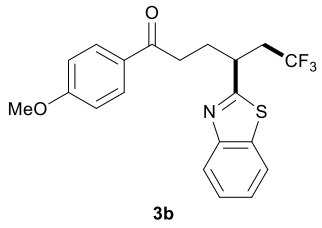
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3a** as a yellow solid (59.5 mg, 81% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 7.4 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 3H), 7.56 – 7.45 (m, 2H), 7.44 – 7.34 (m, 3H), 3.74 – 3.64 (m, 1H), 3.05 – 2.87 (m, 3H), 2.71 – 2.58 (m, 1H), 2.47 – 2.27 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.85, 170.84, 152.39, 136.59, 134.70, 133.81, 128.62, 127.99, 126.26, 126.14 (q, *J* = 277.5 Hz), 125.28, 123.03, 121.76, 39.37 (q, *J* = 28.3 Hz), 37.99 (q, *J* = 2.1 Hz), 34.74, 31.16.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.01(s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(4-methoxyphenyl)hexan-1-one (3b)



3b

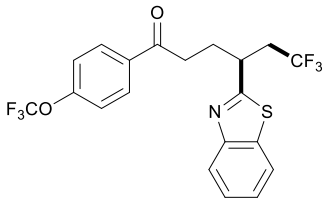
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(4-methoxyphenyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 5/1) provided the desired compound **3b** as a yellow solid (59.0 mg, 75% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.6 Hz, 1H), 7.85 (t, *J* = 8.7 Hz, 3H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.2 Hz, 2H), 3.83 (s, 3H), 3.71 – 3.63 (m, 1H), 3.02 – 2.86 (m, 3H), 2.71 – 2.55 (m, 1H), 2.46 – 2.25 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.16, 171.16, 162.53, 152.54, 133.28, 129.22, 128.66, 125.17, 125.10 (q, *J* = 277.3 Hz), 124.19, 121.96, 120.70, 112.68, 54.42, 38.32 (q, *J* = 28.7 Hz), 37.00 (q, *J* = 2.9 Hz), 33.87, 29.97.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.06 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(4-(trifluoromethoxy)phenyl)hexan-1-one (3c)



3c

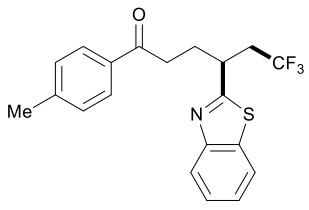
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(4-(trifluoromethoxy)phenyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3c** as a yellow oil (66.2 mg, 74% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.73 – 3.65 (m, 1H), 3.07 – 2.86 (m, 3H), 2.70 – 2.57 (m, 1H), 2.48 – 2.28 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.10, 171.89, 153.07, 152.69 (q, *J* = 1.3 Hz), 134.79, 134.67, 130.02, 126.31, 126.11 (q, *J* = 277.4 Hz), 125.34, 123.03, 121.77, 120.39, 120.28 (q, *J* = 258.9 Hz), 39.36 (q, *J* = 28.4 Hz), 37.92 (q, *J* = 2.7 Hz), 35.30, 29.86.

^{19}F NMR (377 MHz, $CDCl_3$): δ -57.66 (s), -64.08 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(*p*-tolyl)hexan-1-one (3d)



3d

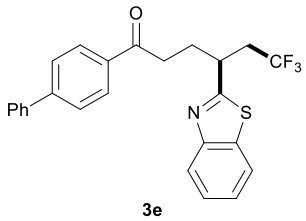
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(*p*-tolyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3d** as a yellow solid (50.5 mg, 67% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 10.0 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 2H), 3.74 – 3.63 (m, 1H), 3.04 – 2.86 (m, 3H), 2.71 – 2.57 (m, 1H), 2.42 – 2.28 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.33, 172.16, 153.11, 144.05, 134.71, 134.15, 129.29, 128.11, 126.23, 126.14 (q, *J* = 277.3 Hz), 125.24, 123.03, 121.75, 39.37 (q, *J* = 28.1 Hz), 38.02 (q, *J* = 2.0 Hz), 35.18, 30.13, 21.64.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.08 (s).

1-([1,1'-biphenyl]-4-yl)-4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluorohexan-1-one (3e)



3e

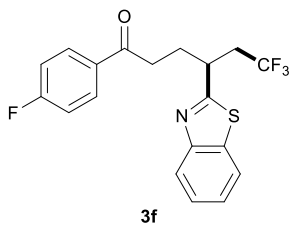
Prepared following the general procedure starting from 1-([1,1'-biphenyl]-4-yl)-1-(benzo[*d*]thiazol-2-yl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3e** as a yellow solid (43.9 mg, 50% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.55 (m, 4H), 7.51 – 7.35 (m, 5H), 3.75 – 3.65 (m, 1H), 3.06 – 2.87 (m, 3H), 2.74 – 2.57 (m, 1H), 2.51 – 2.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.27, 172.11, 153.10, 145.89, 139.79, 135.26, 134.70, 128.97, 128.59, 128.28, 127.26, 127.24, 126.26, 126.14 (q, *J* = 276.1 Hz), 125.28, 123.03, 121.77, 39.38 (q, *J* = 28.6 Hz), 38.00 (q, *J* = 2.2 Hz), 35.33, 30.08.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.02 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(4-fluorophenyl)hexan-1-one (3f)



3f

Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(4-fluorophenyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl

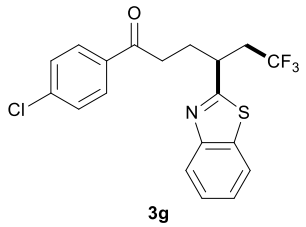
acetate: 10/1) provided the desired compound **3f** as a yellow solid (49.5mg, 65% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.92 – 7.83 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 3.73 – 3.63 (m, 1H), 3.00 – 2.84 (m, 3H), 2.70 – 2.57 (m, 1H), 2.38 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.99, 170.93, 164.76 (d, *J* = 254.9 Hz), 152.03, 133.63, 131.98 (d, *J* = 3.0 Hz), 129.58 (d, *J* = 9.4 Hz), 125.24, 125.06 (q, *J* = 277.4 Hz), 124.26, 121.98, 120.71, 114.66 (d, *J* = 21.9 Hz), 38.32 (q, *J* = 28.4 Hz), 36.90 (q, *J* = 3.0 Hz), 34.14, 28.90.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.07 (s), -106.02 (s).

4-(benzo[*d*]thiazol-2-yl)-1-(4-chlorophenyl)-6,6,6-trifluorohexan-1-one (3g)



3g

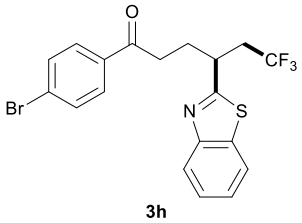
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(4-chlorophenyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3g** as a white solid (39.7 mg, 50% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.45 – 7.30 (m, 3H), 3.78 – 3.59 (m, 1H), 3.02 – 2.87 (m, 3H), 2.70 – 2.55 (m, 1H), 2.47 – 2.27 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.44, 171.92, 153.08, 140.54, 134.89, 134.67, 129.41, 128.93, 126.31, 126.11 (q, *J* = 277.3 Hz), 125.33, 123.04, 121.77, 39.37 (q, *J* = 28.3 Hz), 37.93 (q, *J* = 2.8 Hz), 35.26, 29.89.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.06 (s).

4-(benzo[*d*]thiazol-2-yl)-1-(4-bromophenyl)-6,6,6-trifluorohexan-1-one (3h)



3h

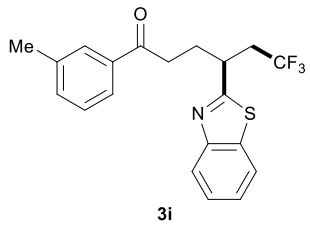
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(4-bromophenyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C. for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3h** as a white solid (54.7mg, 62% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 6.5 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.78 – 3.53 (m, 1H), 3.02 – 2.86 (m, 3H), 2.70 – 2.56 (m, 1H), 2.50 – 2.25 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 197.63, 171.90, 153.08, 135.29, 134.66, 131.93, 129.51, 128.43, 126.31, 126.10 (q, *J* = 277.4 Hz), 125.34, 123.04, 121.77, 39.38 (q, *J* = 28.4 Hz), 37.92 (q, *J* = 2.9 Hz), 35.25, 29.87.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.12 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(*m*-tolyl)hexan-1-one (3i)



3i

Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(*m*-tolyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3i** as a yellow solid (61.8 mg, 82% yield). Data are consistent with those reported in the literature.[1a]

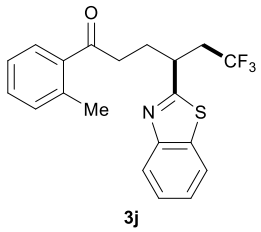
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 10.0 Hz, 1H), 7.86 (d, *J* = 9.7 Hz, 1H), 7.64 (d, *J* = 10.9 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.74 – 3.63 (m, 1H), 3.12 – 2.85 (m, 3H), 2.71 – 2.57 (m, 1H), 2.44 – 2.30 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.91, 172.15, 153.12, 138.43, 136.65, 134.73, 133.99, 128.51, 128.49, 126.25, 126.16 (q, *J* = 277.6 Hz),125.26, 125.22, 123.03,

121.76, 39.36 (q, *J* = 28.4 Hz), 37.99 (q, *J* = 2.3 Hz), 35.35, 30.12, 21.32.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.12 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(*o*-tolyl)hexan-1-one (3j)



3j

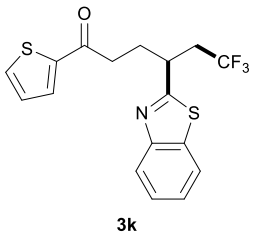
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(*o*-tolyl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3j** as a yellow solid (61.1 mg, 81% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.23 – 7.15 (m, 2H), 3.70 – 3.64 (m, 1H), 3.01 – 2.86 (m, 3H), 2.70 – 2.57 (m, 1H), 2.45 (s, 3H), 2.42 – 2.22 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 201.85, 172.05, 153.11, 138.22, 137.43, 134.68, 132.04, 131.47, 128.46, 126.26, 126.15 (q, *J* = 277.5 Hz), 125.71, 125.27, 123.03, 121.76, 39.35 (q, *J* = 28.3 Hz), 38.07, 37.95 (q, *J* = 2.7 Hz), 30.17, 21.36.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.12 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-1-(thiophen-2-yl)hexan-1-one (3k)



3k

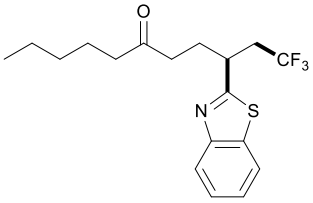
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-(thiophen-2-yl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3k** as a yellow solid (36.9 mg, 50% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.75 (s, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.23 (m, 1H), 3.68 – 3.58 (m, 1H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.90 – 2.74 (m, 1H), 2.67 – 2.51 (m, 1H), 2.42 – 2.18 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 191.57, 171.90, 153.06, 143.79, 134.68, 133.76, 131.96, 128.08, 126.25, 126.08 (q, *J* = 277.5 Hz), 125.27, 123.00, 121.75, 39.29 (q, *J* = 28.4 Hz), 37.93 (q, *J* = 2.8 Hz), 35.93, 30.14.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.07 (s).

3-(benzo[*d*]thiazol-2-yl)-1,1,1-trifluoroundecan-6-one (3l)



3l

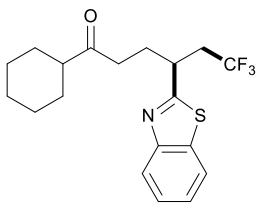
Prepared following the general procedure starting from 5-(benzo[*d*]thiazol-2-yl)dec-1-en-5-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3l** as a yellow oil (29.3 mg, 41% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 5.4 Hz, 1H), 7.87 (d, *J* = 11.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 3.61 – 3.52 (m, 1H), 2.98 – 2.81 (m, 1H), 2.64 – 2.50 (m, 1H), 2.42 – 2.37 (m, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.29 – 2.07 (m, 2H), 1.54 – 1.44 (m, 2H), 1.29 – 1.75 (m, 4H), 0.88 – 0.82 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 209.65, 172.06, 153.07, 134.67, 126.25, 126.11 (q, *J* = 277.3 Hz), 125.26, 123.00, 121.73, 42.91, 39.23 (q, *J* = 28.6 Hz), 39.20, 37.82 (q, *J* = 2.8 Hz), 31.34, 29.56, 23.44, 22.41, 13.89.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.15 (s).

4-(benzo[*d*]thiazol-2-yl)-1-cyclohexyl-6,6,6-trifluorohexan-1-one (3m)



3m

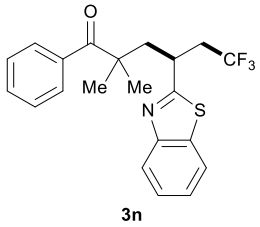
Prepared following the general procedure starting from 5-(benzo[*d*]thiazol-2-yl)dec-1-en-5-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3m** as a yellow oil (25.8 mg, 35% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 3.60 – 3.51 (m, 1H), 2.97 – 2.83 (m, 1H), 2.65 – 2.46 (m, 1H), 2.43 (t, J = 7.4 Hz, 2H), 2.26 – 2.19 (m, 2H), 2.15 – 2.06 (m, 1H), 1.76 – 1.69 (m, 4H), 1.63 – 1.58 (m, 1H), 1.28 – 1.13 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 212.58, 172.16, 153.08, 134.68, 126.23, 126.12 (q, *J* = 277.1 Hz), 125.23, 123.00, 121.75, 50.83, 39.29 (q, *J* = 28.3 Hz), 37.85 (q, *J* = 2.8 Hz), 37.15, 29.56, 28.52, 28.41, 25.77, 25.62, 25.57.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.14 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-2,2-dimethyl-1-phenylhexan-1-one (3n)



3n

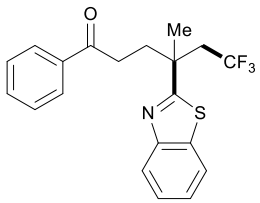
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-2,2-dimethyl-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3n** as a yellow oil (39.1 mg, 50% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.36 – 7.28 (m, 3H), 3.64 – 3.57 (m, 1H), 2.83 – 2.74 (m, 1H), 2.73 – 2.66 (m, 1H), 2.69 – 2.49 (m, 1H), 2.35 – 2.25 (m, 1H), 1.37 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 207.35, 172.94, 152.87, 137.99, 134.78, 131.17, 128.03, 127.95, 126.06, 125.89 (q, *J* = 277.1 Hz), 125.14, 122.91, 121.67, 47.80, 46.23, 41.08 (q, *J* = 28.0 Hz), 35.75 (q, *J* = 2.7 Hz), 26.84, 26.52.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.97 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-4-methyl-1-phenylhexan-1-one (3o)



3o

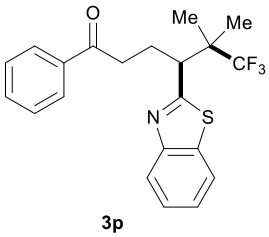
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-4-methyl-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3o** as a yellow solid (47.5 mg, 63% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.44 (m, 2H), 7.43 – 7.35 (m, 3H), 3.14 – 3.01 (m, 1H), 3.00 – 2.82 (m, 2H), 2.82 – 2.68 (m, 1H), 2.51 – 2.41 (m, 1H), 2.34 – 2.24 (m, 1H), 1.74 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.88, 176.78, 152.96, 136.61, 134.92, 133.17, 128.59, 128.04, 126.23 (q, *J* = 277.3 Hz), 126.15, 125.16, 123.10, 121.68, 43.73 (q, *J* = 27.1 Hz), 41.71 (q, *J* = 1.8 Hz), 36.87, 33.37, 24.65.

^{19}F NMR (377 MHz, $CDCl_3$): δ -59.44 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6,6-trifluoro-5,5-dimethyl-1-phenylhexan-1-one (3p)



3p

Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-5-methyl-1-phenylhex-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 30 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 20/1) provided the desired compound **3p** as a yellow oil (15.6 mg, 20% yield). Data are consistent with those reported in the literature.[1a]

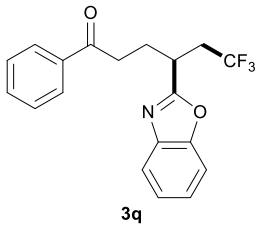
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.83 – 7.67 (m, 2H), 7.53 – 7.43 (m, 2H), 7.40 – 7.32 (m, 3H), 3.38 – 3.30 (m, 1H), 3.23 – 3.13 (m, 1H), 3.11 – 3.01 (m, 1H), 2.14 – 2.02 (m, 1H), 2.00 – 1.90 (m, 3H), 1.64 – 1.60 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.97, 180.04, 153.04, 136.43, 134.58, 133.10, 128.55, 128.40 (q, *J* = 283.0 Hz), 127.91, 126.09, 124.94, 122.84, 121.63, 50.40 (q, *J*

= 23.2 Hz), 43.54, 38.08 (d, *J* = 1.0 Hz), 27.36 (d, *J* = 3.0 Hz), 25.06 (d, *J* = 1.0 Hz), 21.22 (q, *J* = 3.0 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): -62.05(s).

4-(benzo[*d*]oxazol-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (3q)



3q

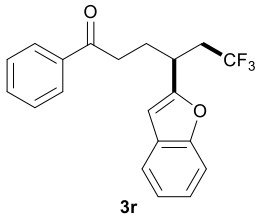
Prepared following the general procedure starting from 1-(benzo[*d*]oxazol-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3q** as a yellow solid (56.9 mg, 82% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.72 – 7.66 (m, 1H), 7.56 – 7.48 (m, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 3.63 – 3.50 (m, 1H), 3.10 – 2.84 (m, 3H), 2.69 – 2.55 (m, 1H), 2.43 – 2.30 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.39, 166.35, 150.75, 140.93, 136.55, 133.27, 128.62, 127.99, 126.01 (q, *J* = 277.2 Hz), 125.13, 124.51, 120.01, 110.68, 37.43 (q, *J* = 29.0 Hz), 35.31, 33.64 (q, *J* = 2.9 Hz), 27.79.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.76 (s).

4-(benzofuran-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (3r)



3r

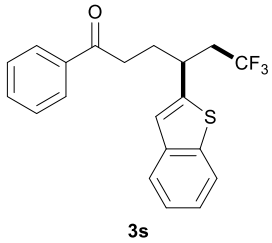
Prepared following the general procedure starting from 1-(benzofuran-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3r** as a yellow solid (50.5 mg, 73% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.35 (m, 3H), 7.27 – 7.15 (m, 2H), 6.49 (s, 1H), 3.40 – 3.30 (m, 1H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.80 – 2.66 (m, 1H), 2.57 – 2.42 (m, 1H), 2.34 – 2.14 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.04, 157.36, 154.87, 136.68, 133.22, 128.63, 128.29, 127.99, 126.28 (q, *J* = 277.2 Hz), 123.95, 122.85, 120.81, 111.12, 104.08, 38.17 (q, *J* = 28.0 Hz), 35.62, 33.22 (q, *J* = 2.8 Hz), 27.93.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.31 (s).

4-(benzo[*b*]thiophen-2-yl)-6,6,6-trifluoro-1-phenylhexan-1-one (3s)



3s

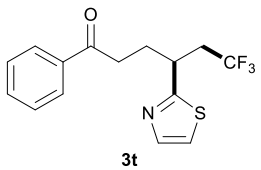
Prepared following the general procedure starting from 1-(benzo[*b*]thiophen-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3s** as a white solid (36.9 mg, 51% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, *J* = 7.7 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.26 (m, 2H), 7.09 (s, 1H), 3.57 – 3.57 (m, 1H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.67 – 2.51 (m, 2H), 2.42 – 2.34 (m, 1H), 2.10 – 2.00 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.15, 146.79, 139.58, 139.16, 136.67, 133.29, 133.21, 128.61, 128.00, 126.17 (q, *J* = 277.7 Hz), 124.48, 124.22, 123.33, 122.49, 122.06, 111.11, 41.59 (q, *J* = 27.5 Hz), 35.78, 35.66 (q, *J* = 2.8 Hz), 31.09.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.89 (s).

6,6,6-trifluoro-1-phenyl-4-(thiazol-2-yl)hexan-1-one (3t)



3t

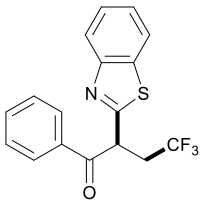
Prepared following the general procedure starting from 1-phenyl-1-(thiazol-2-yl)pent-4-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3t** as a white solid (36.9 mg, 59% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.76 – 7.72 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.25 (s, 1H), 3.66 – 3.59 (m, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.88 – 2.78 (m, 1H), 2.65 – 2.51 (m, 1H), 2.40 – 2.19 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.78, 171.16, 142.77, 136.65, 133.22, 128.63, 127.96, 126.17 (q, *J* = 277.6 Hz), 118.58, 39.64 (q, *J* = 28.3 Hz), 36.94 (q, *J* = 2.8 Hz), 35.27, 30.30.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.11 (s).

2-(benzo[*d*]thiazol-2-yl)-4,4,4-trifluoro-1-phenylbutan-1-one (3u)



3u

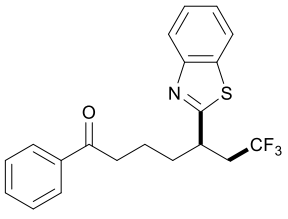
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylprop-2-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 20/1) provided the desired compound **3u** as a yellow oil (36.2 mg, 54% yield). Data are consistent with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.8 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.69 – 5.50 (m, 1H), 3.55 – 3.28 (m, 1H), 3.04 – 2.89 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.93, 165.65, 152.72, 135.46, 135.03, 134.20, 129.20, 128.96, 126.43, 125.91 (q, *J* = 277.4 Hz), 125.67, 123.42, 121.70, 46.32 (q, *J* = 2.6 Hz), 36.47 (q, *J* = 29.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.62 (s).

5-(benzo[*d*]thiazol-2-yl)-7,7,7-trifluoro-1-phenylheptan-1-one (3v)



3v

Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylhex-5-en-1-ol (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **3v** as a yellow solid (48.3 mg, 64% yield). Data are

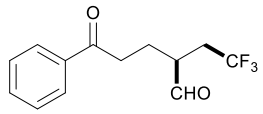
consistent with those reported in the literature.[1a]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.90 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.04 – 2.84 (m, 3H), 2.64 – 2.55 (m, 1H), 2.08 – 1.93 (m, 2H), 1.84 – 1.73 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 199.39, 172.55, 153.08, 136.82, 134.70, 133.10, 128.62, 127.99, 126.25 (q, *J* = 277.4 Hz), 126.17, 125.15, 122.97, 121.70, 39.00 (q, *J* = 28.4 Hz), 38.74 (q, *J* = 2.7 Hz), 37.88, 35.41, 21.33.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.08 (s).

5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanal (4a)



4a

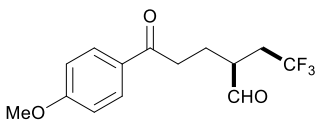
Prepared following the general procedure starting from 2-hydroxy-2-phenylhex-5-enal (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 20 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4a** as a colorless oil (36.1 mg, 70% yield). Data are consistent with those reported in the literature.[1b]

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.13 – 2.99 (m, 2H), 2.86 – 2.78 (m, 1H), 2.78 – 2.64 (m, 1H), 2.27 – 2.17 (m, 2H), 2.11 – 2.05 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.54, 198.42, 136.48, 133.46, 128.75, 127.99, 126.34 (q, *J* = 276.8 Hz), 45.01 (q, *J* = 2.1 Hz), 34.78, 32.58 (q, *J* = 29.4 Hz), 22.79.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.22 (s).

5-(4-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal (4b)



4b

Prepared following the general procedure starting from 2-hydroxy-2-(4-methoxyphenyl)hex-5-enal (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 20 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4b** as a yellow oil (24.2 mg, 42% yield).

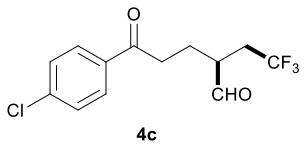
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s,1H), 7.99 – 7.79 (m, 2H), 6.97 – 6.91 (m, 2H), 3.87 (s, 3H), 3.07 – 2.95 (m, 2H), 2.85 – 2.68 (m, 2H), 2.28 – 2.15 (m, 2H), 2.10 – 2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.65, 196.91, 163.75, 130.27, 129.53, 126.35 (q, *J* = 276.7 Hz), 113.41, 55.51, 45.03 (q, *J* = 2.1 Hz), 34.34, 32.50 (q, *J* = 29.3 Hz), 22.92.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.23 (s).

HRMS (ESI) m/z calcd. For $C_{13}H_{12}ClF_3O_2$ $[M+H]^+$ 293.0551, found 291.0403.

5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal (4c)



4c

Prepared following the general procedure starting from 2-(4-chlorophenyl)-2-hydroxyhex-5-enal (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 20 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4c** as a colorless oil (38.6mg, 66% yield).

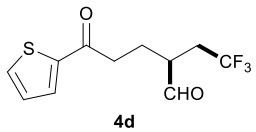
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 3.10-2.95 (m, 2H), 2.84 – 2.68 (m, 2H), 2.27 – 2.12 (m, 2H), 2.12-2.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.52, 197.20, 139.95, 134.71, 129.39, 129.06, 126.29 (d, *J* = 276.7 Hz), 122.14, 44.93 (q, *J* = 2.1 Hz), 34.76, 32.59 (q, *J* = 29.3 Hz), 22.63.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.20 (s).

HRMS (ESI) m/z calcd. For $C_{14}H_{15}F_3O_3$ $[M – H]^+$ 289.1046, found 289.1042.

5-oxo-5-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl)pentanal (4d)



4d

Prepared following the general procedure starting from 2-hydroxy-2-(thiophen-2-yl)hex-5-enal (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 20 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4d** as a brown oil (16.9 mg, 32% yield).

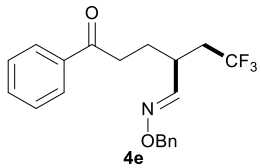
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.70 (s, 1H), 7.73 – 7.68 (m, 1H), 7.67 – 7.63 m, 1H), 7.16 – 7.10 (m, 1H), 3.04 – 2.89 (m, 2H), 2.81 – 2.66 (m, 2H), 2.27 – 2.15 (m, 2H), 2.11-2.00 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.48, 191.30, 143.58, 134.06, 132.09, 128.26, 126.30 (q, *J* = 276.8 Hz), 44.93 (q, *J* = 2.2 Hz), 35.43, 32.53 (q, *J* = 29.3 Hz), 22.91.

^{19}F NMR (377 MHz, $CDCl_3$): δ -64.18 (s).

HRMS (ESI) m/z calcd. For $C_{11}H_{11}F_3O_2S$ $[M+H]^+$ 265.0505, found 265.0500

(*E*)-5-oxo-5-phenyl-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4e)



4e

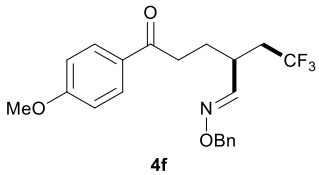
Prepared following the general procedure starting from (*E*)-2-hydroxy-2-phenylhex-5-enal O-benzyl oxime (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4e** as a white solid (63.2 mg, 87% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.26 (m, 6H), 5.08 – 4.99 (m, 2H), 2.96 – 2.90 (m, 2H), 2.80 – 2.69 (m, 1H), 2.54 – 2.14 (m, 2H), 2.04 (m 1H), 1.98 – 1.82 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 198.90, 151.21, 137.62, 136.75, 133.20, 128.63, 128.39, 128.16, 128.03, 127.86, 126.25 (q, *J* = 277.5 Hz), 75.84 37.02 (q, *J* = 28.0 Hz), 35.24, 34.00 (q, *J* = 2.5 Hz). 24.17.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.59 (s).

(*E*)-5-(4-methoxyphenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4f)



4f

Prepared following the general procedure starting from (*E*)-2-hydroxy-2-(4-methoxyphenyl)hex-5-enal O-benzyl oxime (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1)

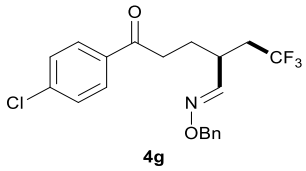
provided the desired compound **4f** as a white solid (34.6 mg, 44% yield). Data are consistent with those reported in the literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.36 – 7.26 (m, 6H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.04 (s, 2H), 3.87 (s, 3H), 2.98 – 2.84 (m, 2H), 2.77 – 2.61 (m, 1H), 2.43 – 2.34 (m, 2H), 2.06 – 1.97 (m, 1H), 1.95 – 1.84 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.05, 163.55, 151.30, 137.61, 130.29, 129.82, 128.38, 128.14, 127.83, 126.26 (q, *J* = 277.2 Hz), 113.73, 75.80, 55.48, 36.98 (q, *J* = 28.2 Hz), 34.02 (q, *J* = 2.5 Hz), 26.69.

^{19}F NMR (377 MHz, CDCl3): δ -63.57 (s).

(*E*)-5-(4-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4g)



4g

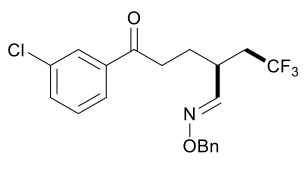
Prepared following the general procedure starting from (*E*)-2-(4-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4g** as a white solid (58.8 mg, 74% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.73 (m, 2H), 7.45–7.37 (m, 2H), 7.37 – 7.18 (m, 6H), 5.06 – 4.99 (m, 2H), 2.96 – 2.82 (m, 2H), 2.79 – 2.69 (m, 1H), 2.45 – 2.24 (m, 2H), 2.06 – 1.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 197.64, 150.75, 139.63, 137.60, 134.98, 129.43, 128.92, 128.39, 128.14, 127.87, 126.19 (q, *J* = 277.4 Hz), 74.98, 37.04 (q, *J* = 28.2 Hz), 35.19, 33.94 (q, *J* = 2.6 Hz), 26.79.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.59 (s).

***(E)*-5-(3-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4h)**



4h

Prepared following the general procedure starting from (*E*)-2-(3-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h.

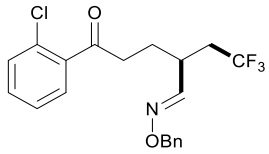
Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4h** as a white solid (50.8 mg, 64% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.24 (m, 7H), 5.06 – 4.98 (m, 1H), 2.92 – 2.83 (m, 2H), 2.79 – 2.66 (m, 1H), 2.42 – 2.22 (m, 2H), 2.05 – 1.86 (m, 2H).

^{13}C NMR (101 MHz, CDCl3): δ 197.60, 151.11, 138.21, 137.56, 134.96, 133.13, 129.99, 128.39, 128.17, 128.12, 127.91, 126.23 (q, *J* = 277.4 Hz), 126.12, 37.03 (q, *J* = 28.2 Hz), 35.33, 33.91 (q, *J* = 2.5 Hz), 26.25.

.**^{19}F NMR** (377 MHz, $CDCl_3$): δ -83.52 (s).

***(E)*-5-(2-chlorophenyl)-5-oxo-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4i)**



4i

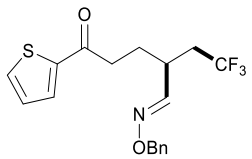
Prepared following the general procedure starting from (*E*)-2-(2-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (0.2 mmol) and CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4i** as a white solid (50.0 mg, 63% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.34 (m, 3H), 7.34 – 7.26 (m, 6H), 7.24 – 7.20 (m, 1H), 5.09 – 4.99 (m, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.80 – 2.69 (m, 1H), 2.42 – 2.19 (m, 2H), 2.06 – 1.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.01, 150.99, 139.16, 137.48, 131.80, 130.87, 130.60, 128.90, 128.37, 128.17, 127.87, 126.96, 126.22 (q, *J* = 277.8 Hz), 75.89, 39.25, 36.84 (q, *J* = 28.3 Hz), 33.82 (q, *J* = 2.5 Hz), 26.49.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.59 (s).

(*E*)-5-oxo-5-(thiophen-2-yl)-2-(2,2,2-trifluoroethyl)pentanal O-benzyl oxime (4j)



4j

Prepared following the general procedure starting from (*E*)-2-(2-chlorophenyl)-2-hydroxyhex-5-enal O-benzyl oxime (0.2 mmol), CF_3SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO

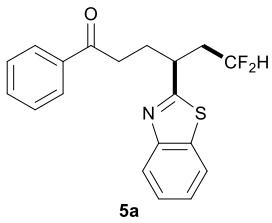
(4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **4j** as a white solid (27.3 mg, 37% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.56 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.37 – 7.26 (m, 6H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 5.07 – 4.99 (m, 2H), 2.93 – 2.83 (m, 2H), 2.78 – 2.67 (m, 1H), 2.42 – 2.23 (m, 2H), 2.09 – 2.00 (m, 1H), 1.96 – 1.83 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.81, 151.05, 143.94, 137.58, 133.72, 131.97, 128.40, 128.16, 128.10, 127.87, 126.21 (q, *J* = 277.3 Hz), 75.84, 36.94 (q, *J* = 28.3 Hz), 35.88, 33.96 (q, *J* = 2.5 Hz), 24.86.

^{19}F NMR (377 MHz, $CDCl_3$): δ -63.57 (s).

4-(benzo[*d*]thiazol-2-yl)-6,6-difluoro-1-phenylhexan-1-one (5a)



5a

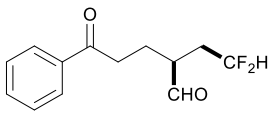
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and HCF_2SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5a** as a white solid (48.3 mg, 70% yield). Data are consistent with those reported in the literature.1[d]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.96 (m, 1H), 7.91 – 7.82 (m, 3H), 7.55 – 7.45 (m, 2H), 7.43 – 7.35 (m, 3H), 5.89 (tdd, *J* = 56.5, 6.0, 3.5 Hz, 1H), 3.61 – 3.50 (m, 1H), 3.07 – 2.95 (m, 2H), 2.66 – 2.49 (m, 1H), 2.45 – 2.25 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.81, 172.77, 153.08, 136.59, 134.66, 133.19, 128.59, 127.97, 126.22, 125.23, 122.98, 121.73, 115.84 (t, *J* = 239.5 Hz), 39.70 (t, *J* = 21.8 Hz), 38.48 (dd, *J* = 7.0, 4.2 Hz), 35.47, 30.08.

^{19}F NMR (377 MHz, $CDCl_3$): δ -113.35 – -118.08 (m).

2-(2,2-difluoroethyl)-5-oxo-5-phenylpentanal (5b)



5b

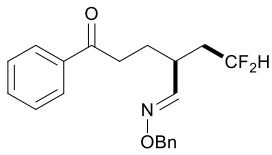
Prepared following the general procedure starting from 2-hydroxy-2-phenylhex-5-enal (0.2 mmol) and HCF_2SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5b** as a white solid (19.2 mg, 40% yield). Data are consistent with those reported in the literature.[1b]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.71 – 9.68 (m, 1H), 8.14 – 7.80 (m, 2H), 7.67 – 7.54 (m, 1H), 7.52 – 7.43 (m, 2H), 6.19 – 5.80 (m, 1H), 3.21 – 2.90 (m, 2H), 2.86 – 2.61 (m, 1H), 2.50 – 2.13 (m, 2H), 2.11 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 202.68, 199.40, 136.51, 132.48, 129.61, 128.04, 115.68 (t, *J* = 239.5 Hz), 45.20 (t, *J* = 4.4 Hz), 35.08, 33.08 (t, *J* = 21.9 Hz), 23.28.

^{19}F NMR (377 MHz, $CDCl_3$): δ -112.43 – -117.56 (m).

(*E*)-2-(2,2-difluoroethyl)-5-oxo-5-phenylpentanal O-benzyl oxime (5c)



5c

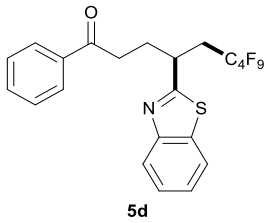
Prepared following the general procedure starting from (*E*)-2-hydroxy-2-phenylhex-5-enal O-benzyl oxime (0.2 mmol) and HCF_2SO_2Na (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5c** as a white solid (46.3mg,67% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.0 Hz, 2H), 7.63 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.26 (m, 6H), 5.84 (tdd, J = 56.5, 5.6, 3.8 Hz, 1H), 5.06 – 5.00 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.67 – 2.55 (m, 1H), 2.12 – 1.85 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 199.02, 151.98, 137.58, 136.74, 133.18, 128.63, 128.41, 128.24, 128.02, 127.91, 116.03 (t, *J* = 239.2 Hz), 75.81, 37.11 (t, *J* = 21.4 Hz), 35.35, 34.27 (dd, *J* = 6.4, 4.4 Hz), 26.75.

^{19}F NMR (377 MHz, $CDCl_3$): δ -113.74 – -117.40 (m).

4-(benzo[*d*]thiazol-2-yl)-9,9,9,9,9,9,9,9,9-nonafluoro-1-phenyl-9λ^{12}-nona-6,8-diyn-1-one (5d)



5d

Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and $C_4F_9SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5d** as a white solid (75.9 mg, 74% yield). mp = 78 – 80 °C.

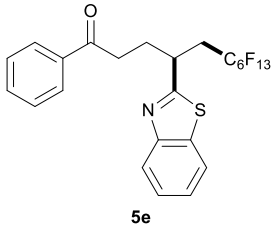
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.86 (d, *J* = 7.1 Hz, 3H), 7.63 – 7.43 (m, 2H), 7.43 – 7.35 (m, 3H), 3.87 – 3.75 (m, 1H), 3.21 – 2.80 (m, 3H), 2.80 – 2.51 (m, 1H), 2.49 – 2.30 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.61, 172.31, 153.10, 136.57, 134.68, 133.29, 128.59, 127.97, 126.24, 125.27, 123.04, 121.74, 128.58 – 105.62 (m), 36.58, 36.29, 36.08 (t, *J* = 21.3 Hz), 30.65.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.96 – -81.13 (m), -112.76 – -112.96 (m), -124.19 – -124.48 (m), -125.79 – -126.02 (m).

HRMS (ESI) m/z calcd. For $C_{22}H_{16}F_9NOS$ $[M+H]^+$ 514.0882, found 514.0887.

4-(benzo[*d*]thiazol-2-yl)-11,11,11,11,11,11,11,11,11,11,11,11,11,11-tridecafluoro-1-phenyl-11λ^{16}-undeca-6,8,10-triyn-1-one (5e)



5e

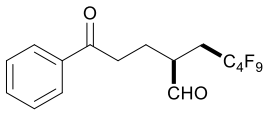
Prepared following the general procedure starting from 1-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-ol (0.2 mmol) and $C_6F_{13}SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 °C for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5e** as a white solid (83.4 mg, 68% yield). Data are consistent with those reported in the literature.[1a]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 3H), 7.55 – 7.44(m, 2H), 7.43 – 7.33 (m, 3H), 3.88 – 3.73 (m, 1H), 3.17 – 2.82 (m, 3H), 2.70 – 2.50 (m, 1H), 2.52 – 2.22 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.61, 172.32, 153.10, 136.57, 134.68, 133.22, 128.59, 127.97, 126.24, 125.26, 123.03, 121.74,128.50 – 107.52 (m), 36.61, 36.18 (t, *J* = 21.2 Hz), 35.31, 30.64.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.77 – -80.86 (m), -112.55 – -112.73 (m), -121.71 – 121.76 (m), -122.74 – 123.00 (m), -123.19 – -123.98 (m), -126.10 – -126.21 (m).

7,7,7,7,7,7,7,7,7-nonafluoro-2-(3-oxo-3-phenylpropyl)-7λ^{12}-hepta-4,6-diynal (5f)



5f

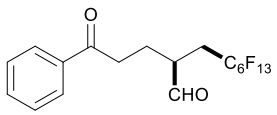
Prepared following the general procedure starting from 2-hydroxy-2-phenylhex-5-enal (0.2 mmol) and $C_4F_9SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5f** as a colorless oil (43.3 mg, 53% yield). Data are consistent with those reported in the literature.[1b]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (s, 1H), 7.99 – 7.91 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 – 7.44 (m, 2H), 3.22 – 2.99 (m, 2H), 2.99 – 2.87 (m, 1H), 2.78 – 2.69 (m, 1H), 2.30 – 2.19 (m, 2H), 2.19 – 2.00 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.43, 198.34, 136.42, 133.48, 128.75, 127.97,130.78 – 108.72 (m), 43.66, 34.76, 29.37 (t, *J* = 21.8 Hz), 23.30

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.95 – - 81.16 (m), -112.16 – -112.39 (m), -121.40 – -125.45 (m), -125.82 – -125.98 (m).

9,9,9,9,9,9,9,9,9,9,9,9,9-tridecafluoro-2-(3-oxo-3-phenylpropyl)-9λ^{16}-nona-4,6,8-triynal (5g)



5g

Prepared following the general procedure starting from 2-hydroxy-2-phenylhex-5-enal (0.2 mmol) and $C_6F_{13}SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5g** as a yellow solid (47.8 mg, 47% yield). mp = 54 – 56 ºC.

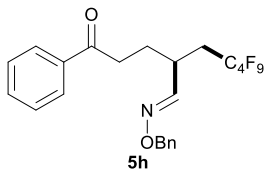
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 3.14 – 3.02 (m, 2H), 3.01 – 2.89 (m, 1H), 2.84 – 2.71 (m, 1H), 2.27 – 1.81 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 200.44, 198.35, 136.42, 133.47, 128.73, 127.96, 121.09 – 107.16 (m), 43.67, 34.76, 29.46 (t, *J* = 21.9 Hz), 23.30.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.76 – -80.93 (m), -111.99 – -112.13 (m), -121.68 – 121.98 (m), -122.69 – 123.07 (m), -123.12 – -123.85 (m), -126.05 – -126.34 (m).

HRMS (ESI) m/z calcd. For $C_{18}H_{13}F_{13}O_2$ $[M+H]^+$ 509.0781, found 509.0786.

(*E*)-7,7,7,7,7,7,7,7,7-nonafluoro-2-(3-oxo-3-phenylpropyl)-7λ^{12}-hepta-4,6-diynal O-benzyl oxime (5h)



5h

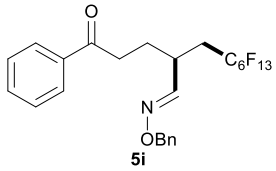
Prepared following the general procedure starting from (*E*)-2-hydroxy-2-phenylhex-5-enal O-benzyl oxime (0.2 mmol) and $C_4F_9SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5h** as a colorless oil (84.2 mg, 82% yield). Data are consistent with those reported in the literature.[1c]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.33 – 7.20 (m, 4H), 5.09 – 4.97 (m, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.90 – 2.81 (m, 1H), 2.55 – 2.12 (m, 2H), 2.12 – 1.83 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.85, 151.39, 137.59, 136.69, 133.20, 128.62, 128.37, 128.16, 128.02, 127.85, 120.33 – 110.58 (m), 75.82, 35.24, 33.71 (t, *J* = 21.2 Hz), 32.83, 27.08.

^{19}F NMR (377 MHz, CDCl3): δ -80.96 – -81.16 (m), -111.05 – -114.15 (m), -124.33 – -124.61 (m), -125.84 – -126.03 (m).

(*E*)-9,9,9,9,9,9,9,9,9,9,9,9,9-tridecafluoro-2-(3-oxo-3-phenylpropyl)-9λ^{16}-nona-4,6,8-triynal O-benzyl oxime (5i)



5i

Prepared following the general procedure starting from (*E*)-2-hydroxy-2-phenylhex-5-enal O-benzyl oxime (0.2 mmol) and $C_6F_{13}SO_2Na$ (0.3 mmol) using 5 mg of CN-K as catalyst in DMSO (4 mL) at 30 – 35 ºC for 24 h. Purification by flash column chromatography (petroleum ether/ethyl acetate: 10/1) provided the desired compound **5i** as a white solid (98.1 mg, 80% yield). mp = 70 – 72 ºC.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.33 – 7.19 (m, 4H), 5.12 – 4.95 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.90 – 2.79 (m, 1H), 2.62 – 2.13 (m, 2H), 2.13 – 1.88 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 198.84, 151.41, 137.60, 136.69, 133.18, 128.61, 128.36, 128.16, 128.02, 127.84, 120.61 –108.67 (m), 75.62, 35.24, 33.80 (t, *J* = 21.3 Hz), 32.86, 27.08.

^{19}F NMR (377 MHz, $CDCl_3$): δ -80.80 – -80.91 (m), -110.24 – -114.90 (m), -121.66 – -121.97 (m), -122.76 – -123.03(m), -123.38 – -123.62(m), -125.27 – -126.67 (m).

HRMS (ESI) m/z calcd. For $C_{25}H_{20}F_{13}NO_2$ $[M+H]^+$ 614.1359, found 614.1357.

16. References

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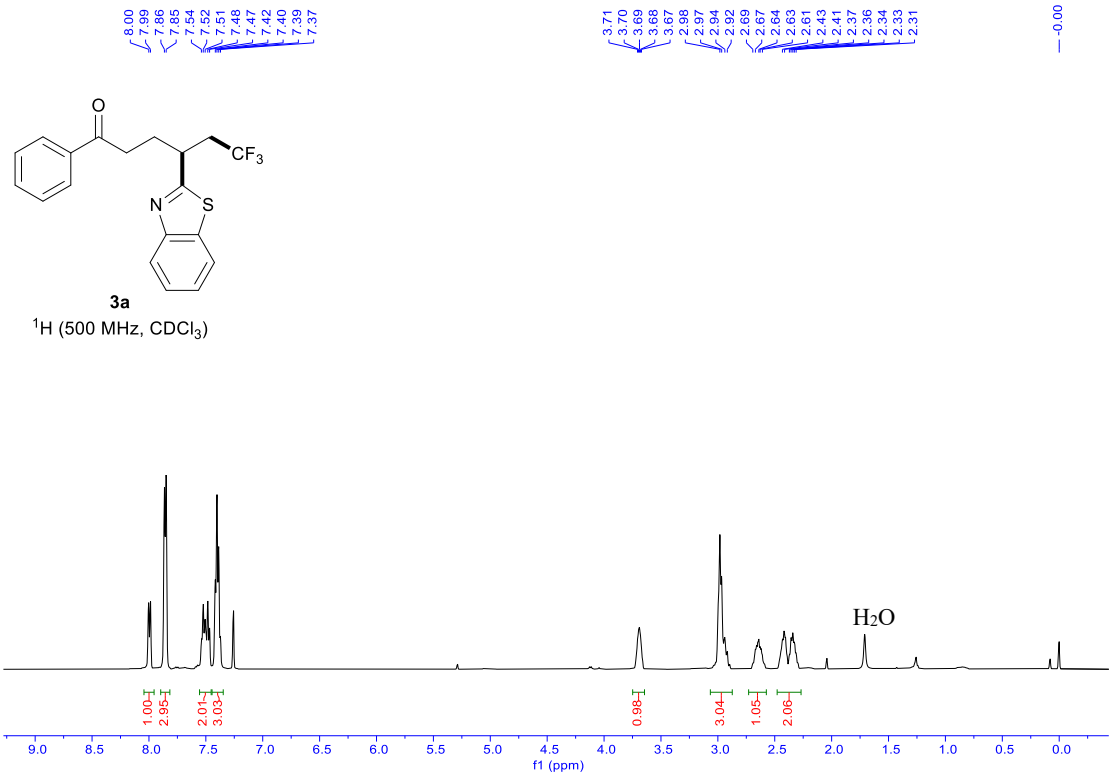
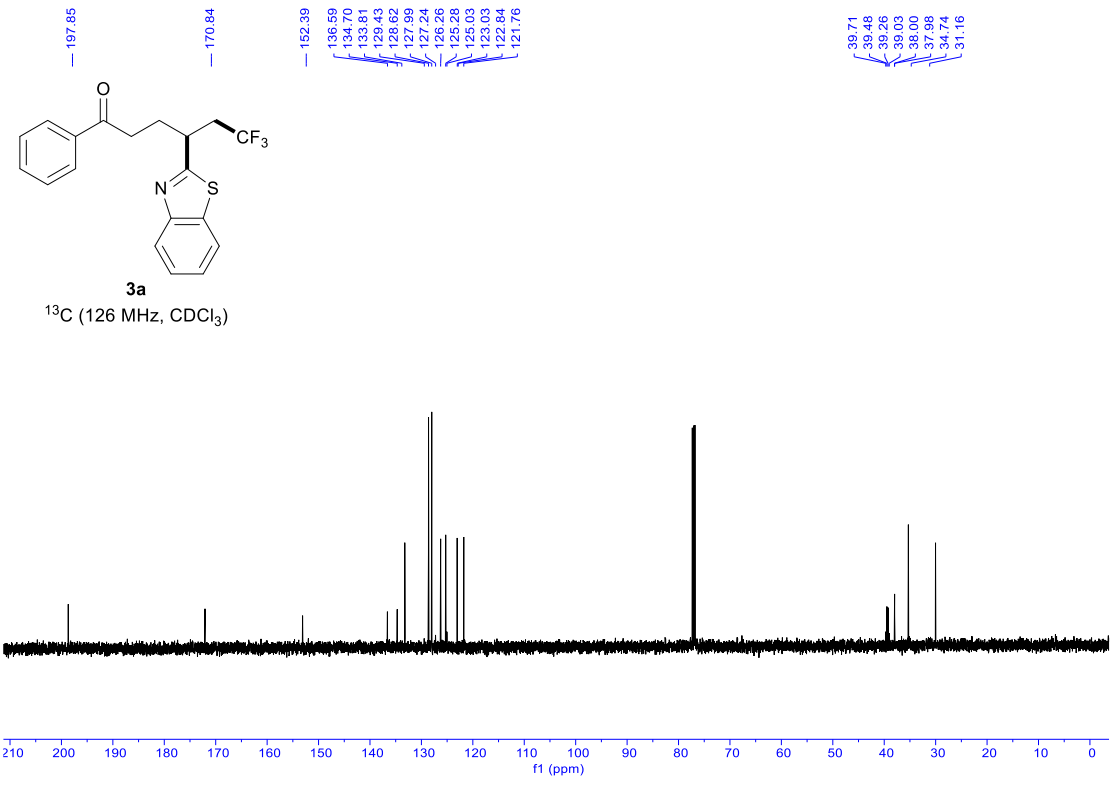
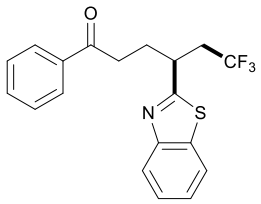
17. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra of products

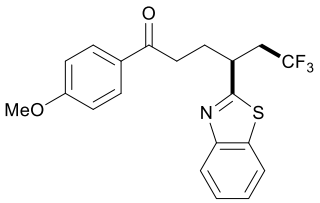






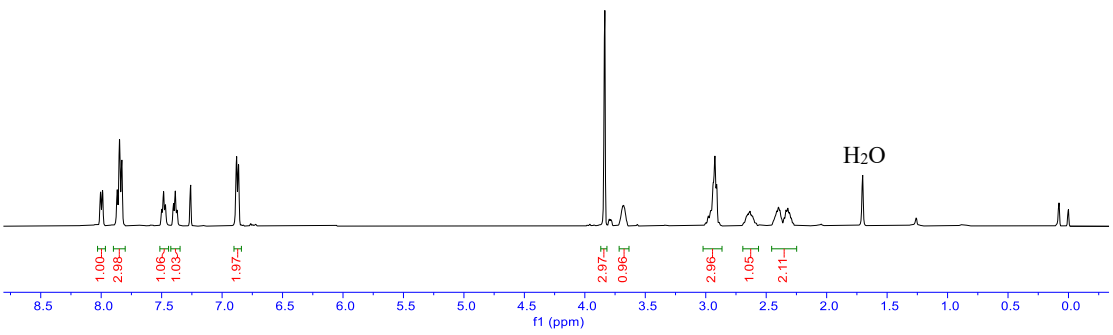
3a

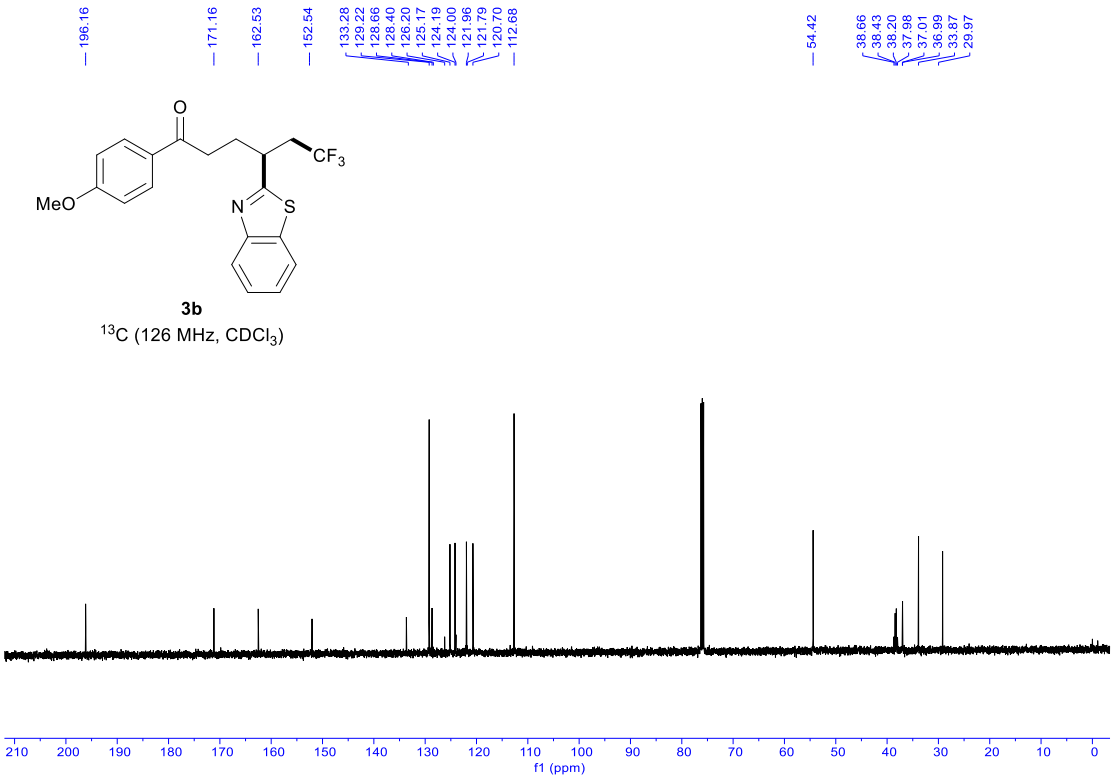
^{19}F (377 MHz, $CDCl_3$)



3b

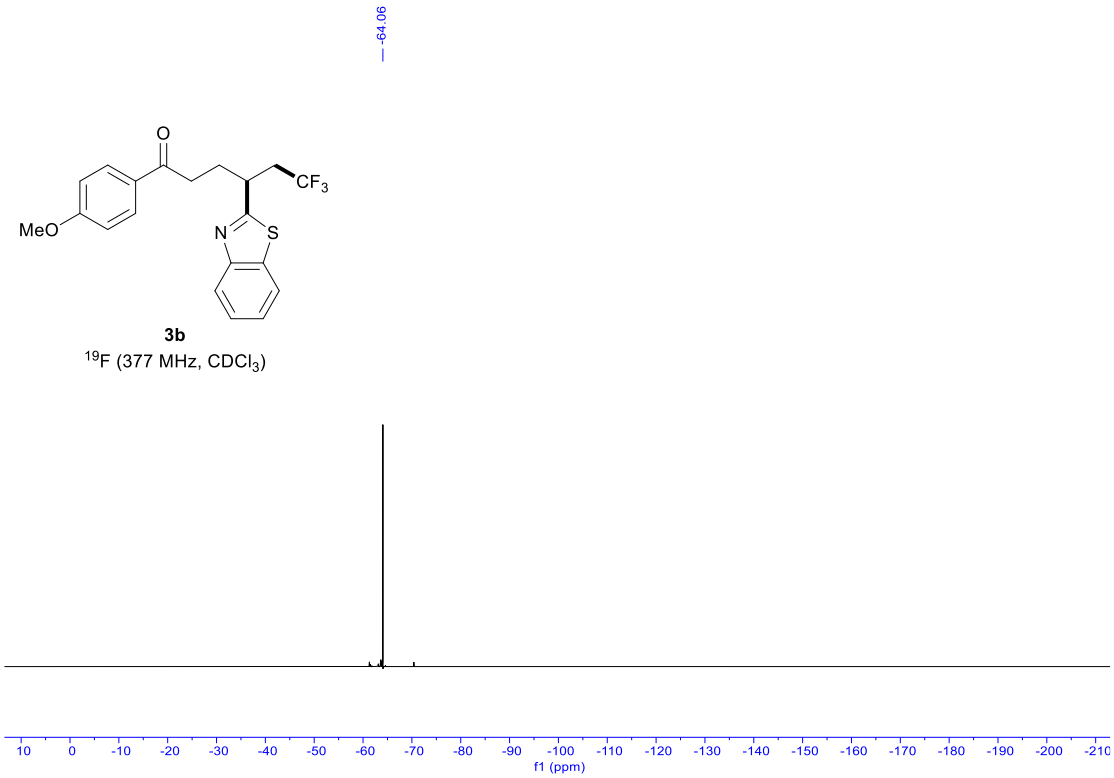
^{1}H (500 MHz, $CDCl_3$)





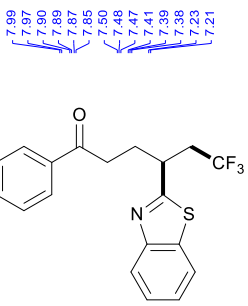
3b

^{13}C (126 MHz, $CDCl_3$)



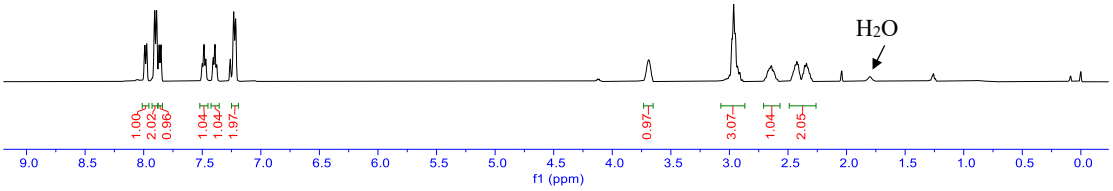
3b

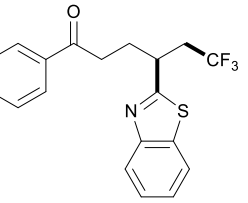
^{19}F (377 MHz, $CDCl_3$)



3c

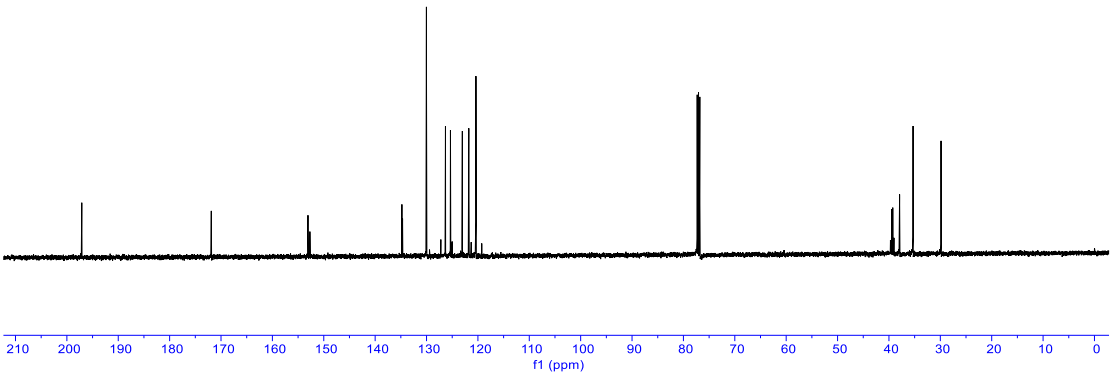
^{1}H (500 MHz, $CDCl_3$)

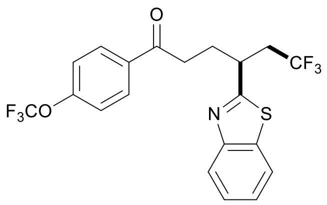




3c

^{13}C (126 MHz, $CDCl_3$)





3c

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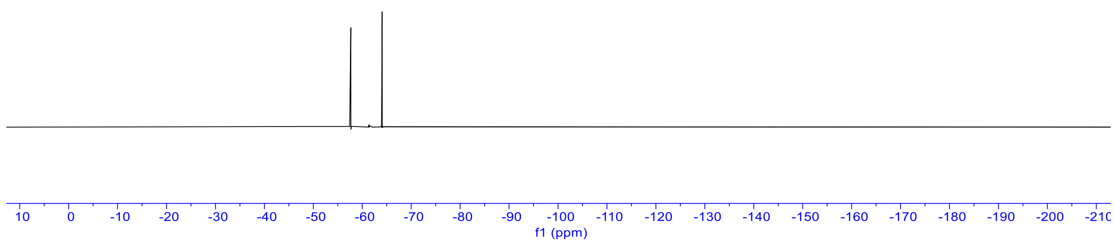
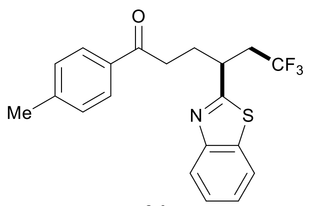
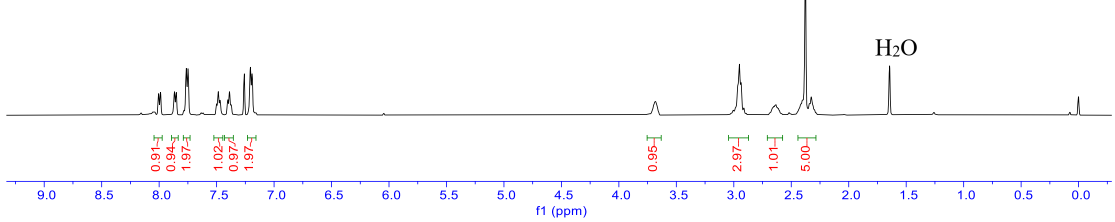
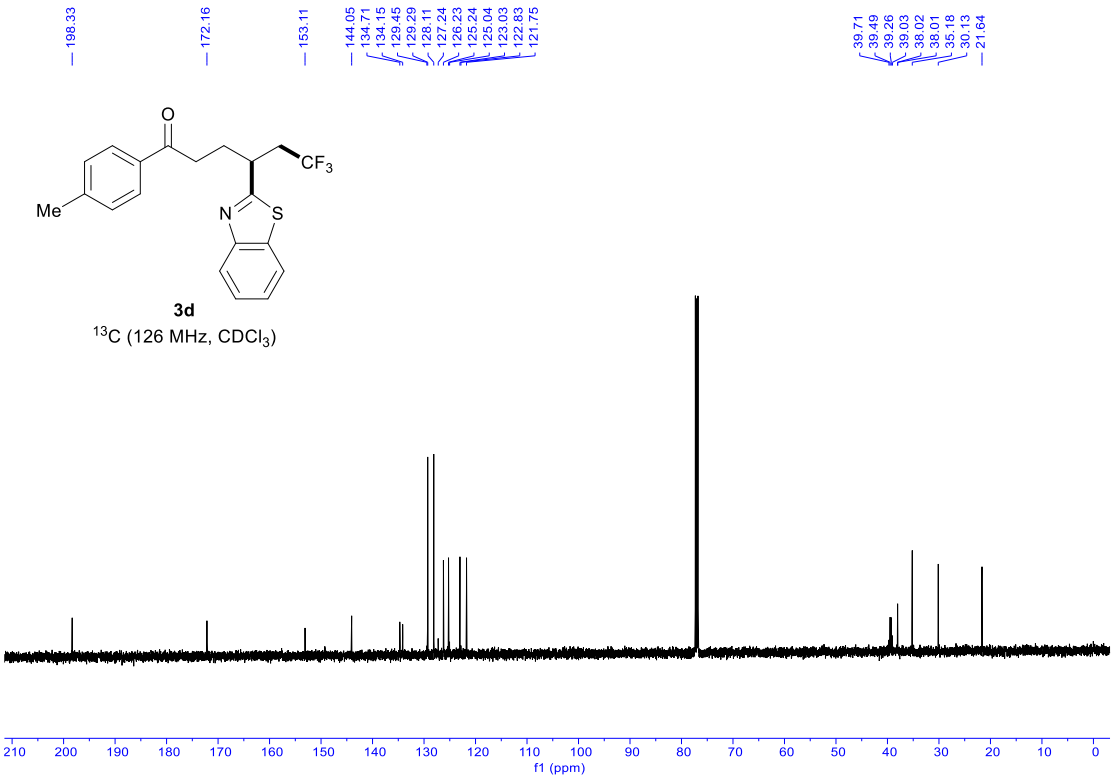




3d

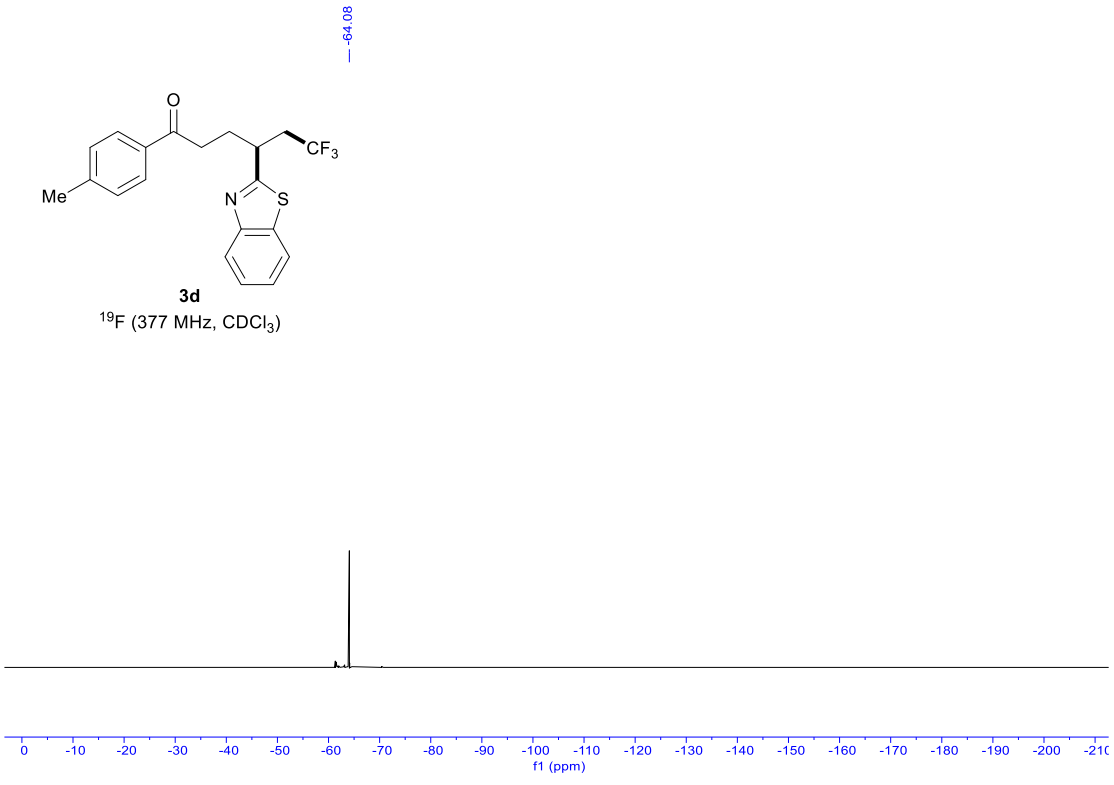
^{1}H (500 MHz, $CDCl_3$)





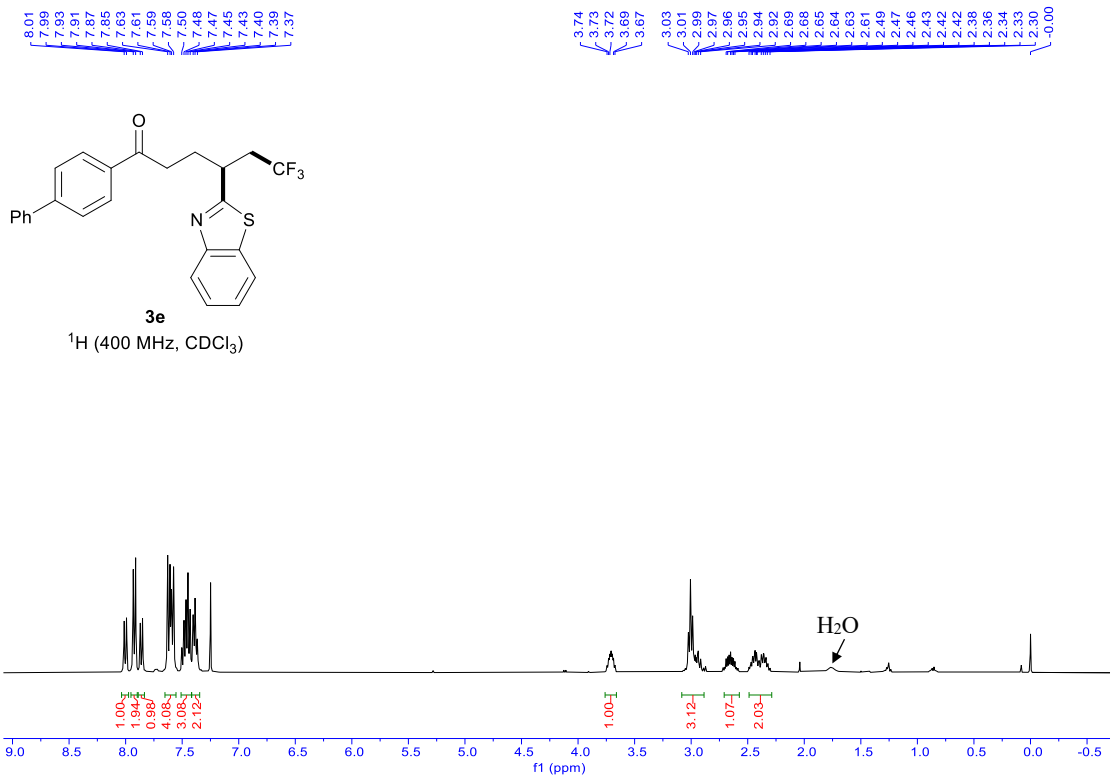
3d

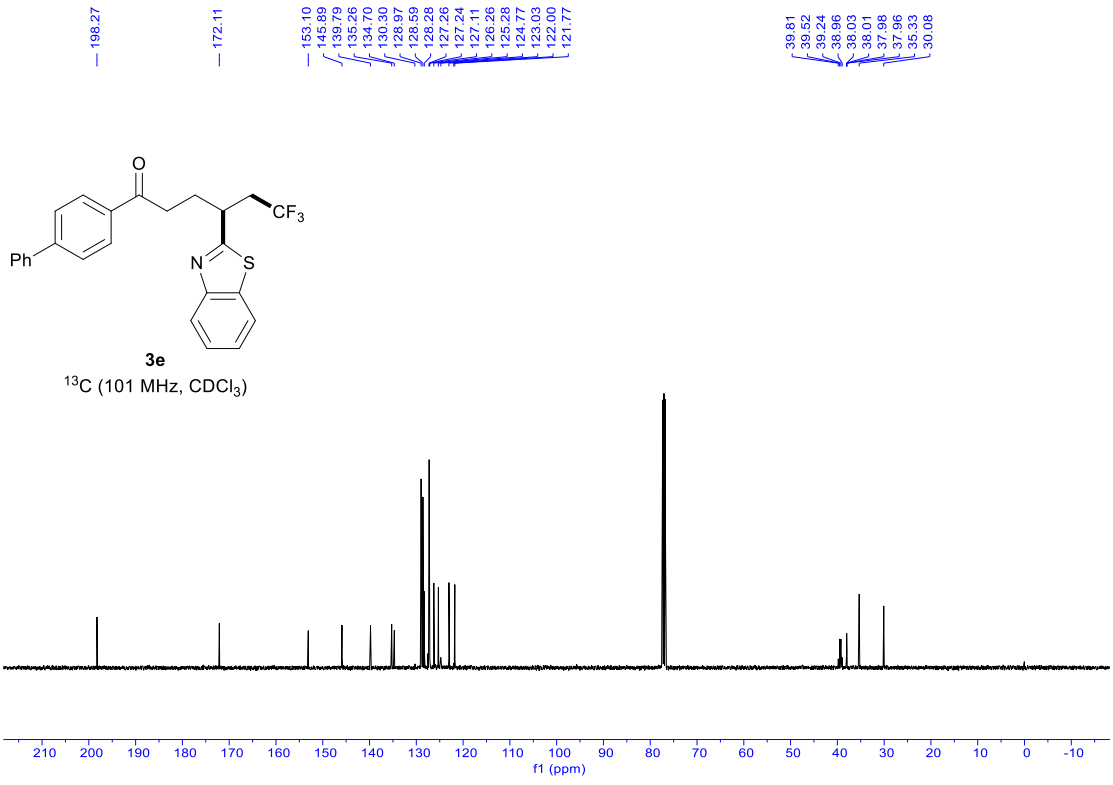
^{13}C (126 MHz, $CDCl_3$)



3d

^{19}F (377 MHz, $CDCl_3$)


8.01
7.99
7.93
7.91
7.87
7.85
7.63
7.61
7.59
7.58
7.50
7.48
7.47
7.45
7.43
7.40
7.39
7.37
3.74
3.73
3.72
3.69
3.67
3.03
3.01
2.99
2.97
2.96
2.95
2.94
2.92
2.69
2.68
2.65
2.64
2.63
2.61
2.49
2.47
2.46
2.43
2.42
2.42
2.38
2.36
2.34
2.33
2.30
-0.00
O
CF3
Ph
N
S
3e
1H (400 MHz, CDCl3)
H2O
1.00
1.94
0.98
4.08
3.08
2.12
1.00
3.12
1.07
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


198.27
172.11
153.10
145.89
139.79
135.26
134.70
130.30
128.97
128.59
128.28
127.26
127.24
127.11
126.26
125.28
124.77
123.03
122.00
121.77
39.81
39.52
39.24
38.96
38.03
38.01
37.98
37.96
35.33
30.08
O
CF3
Ph
N
S
3e
13C (101 MHz, CDCl3)
210
200
190
180
170
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150
140
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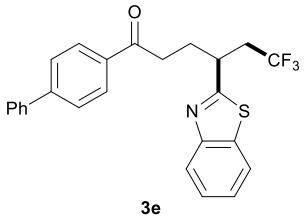
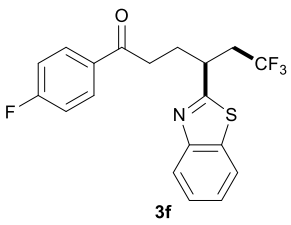
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



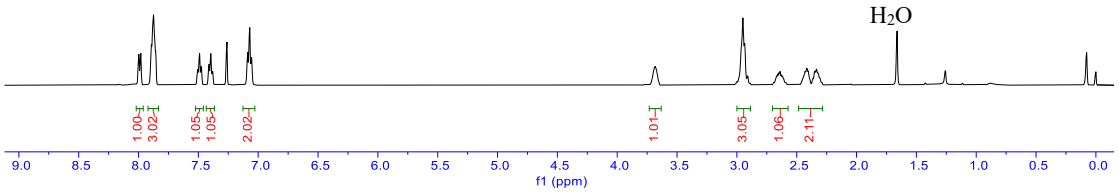
3e

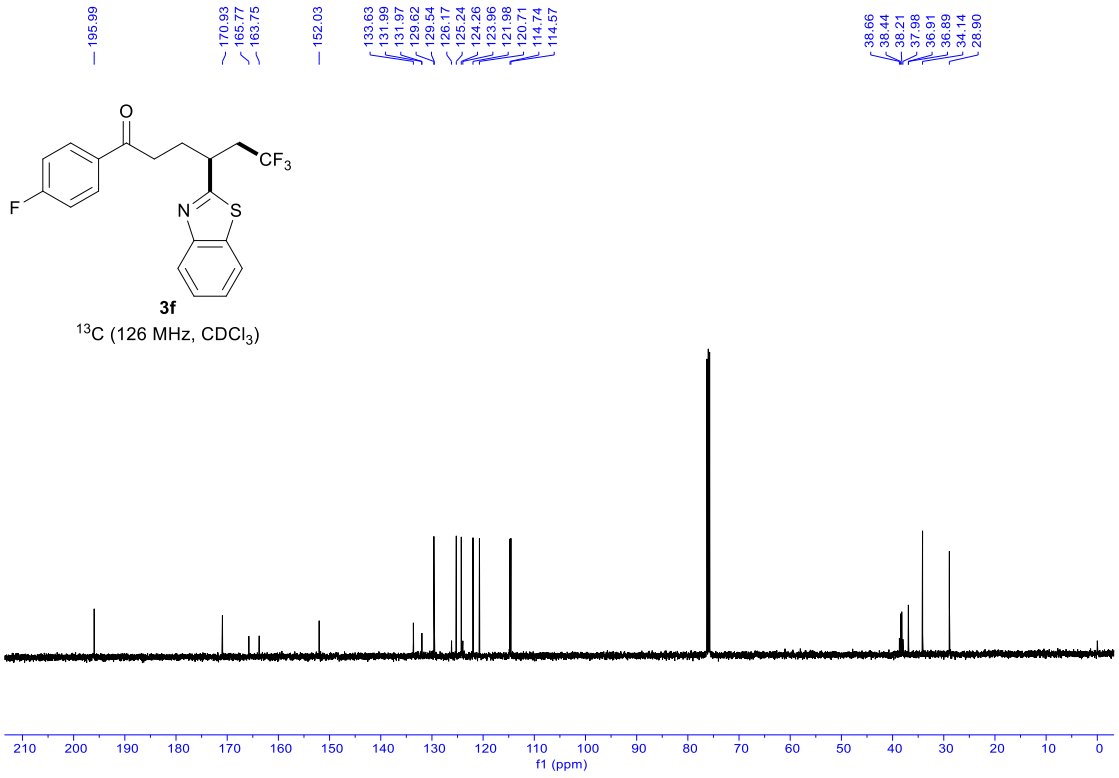
^{19}F (377 MHz, $CDCl_3$)



3f

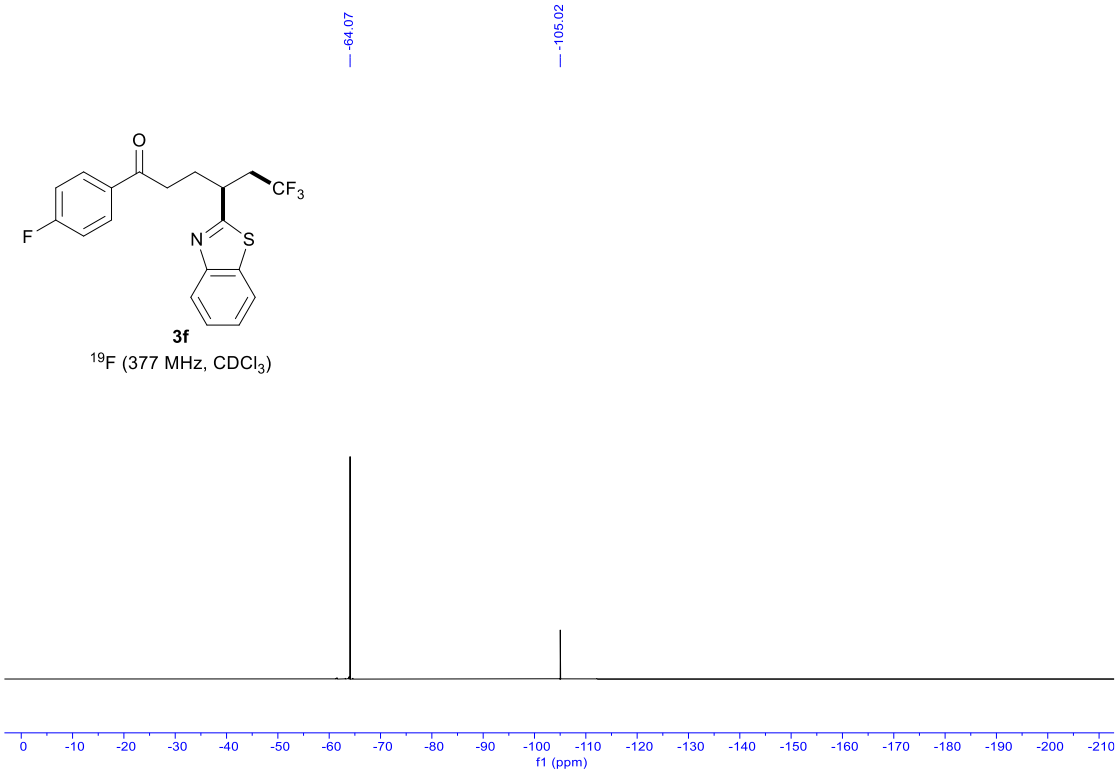
^{1}H (500 Mz, $CDCl_3$)





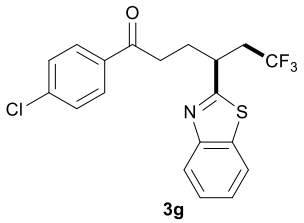
3f

^{13}C (126 MHz, $CDCl_3$)



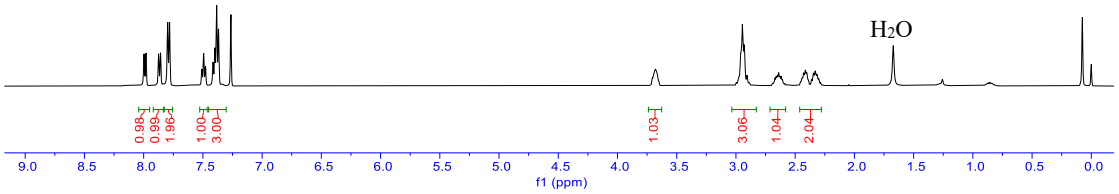
3f

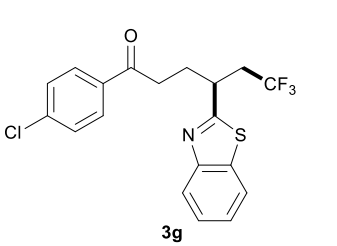
^{19}F (377 MHz, $CDCl_3$)



3g

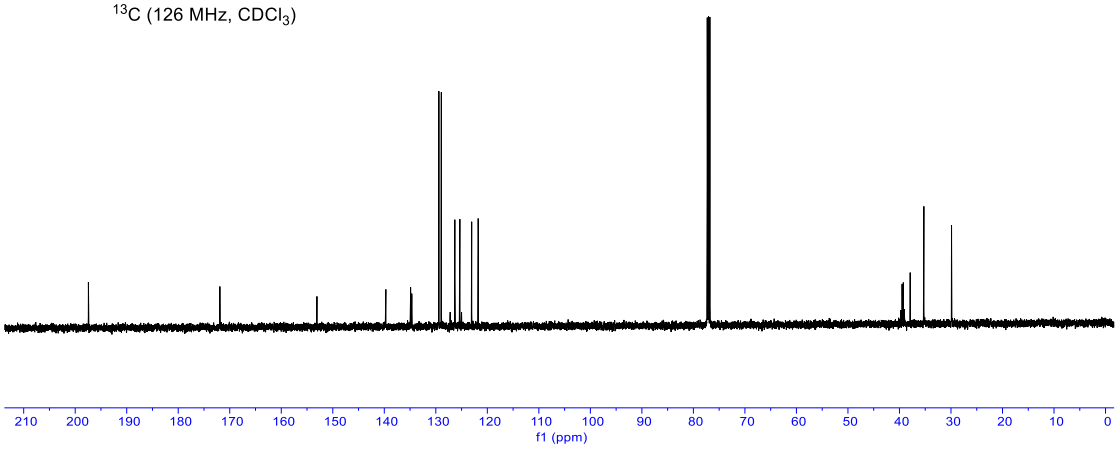
^{1}H (500 Mz, $CDCl_3$)

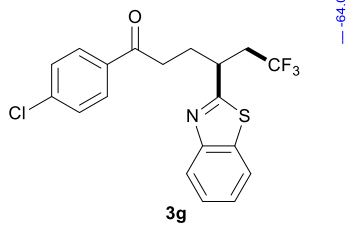




3g

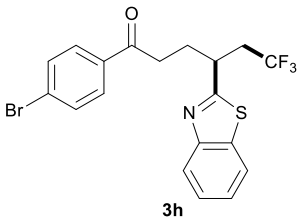
^{13}C (126 MHz, $CDCl_3$)





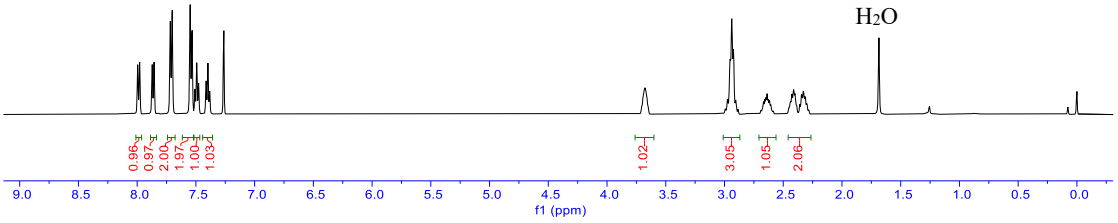
3g

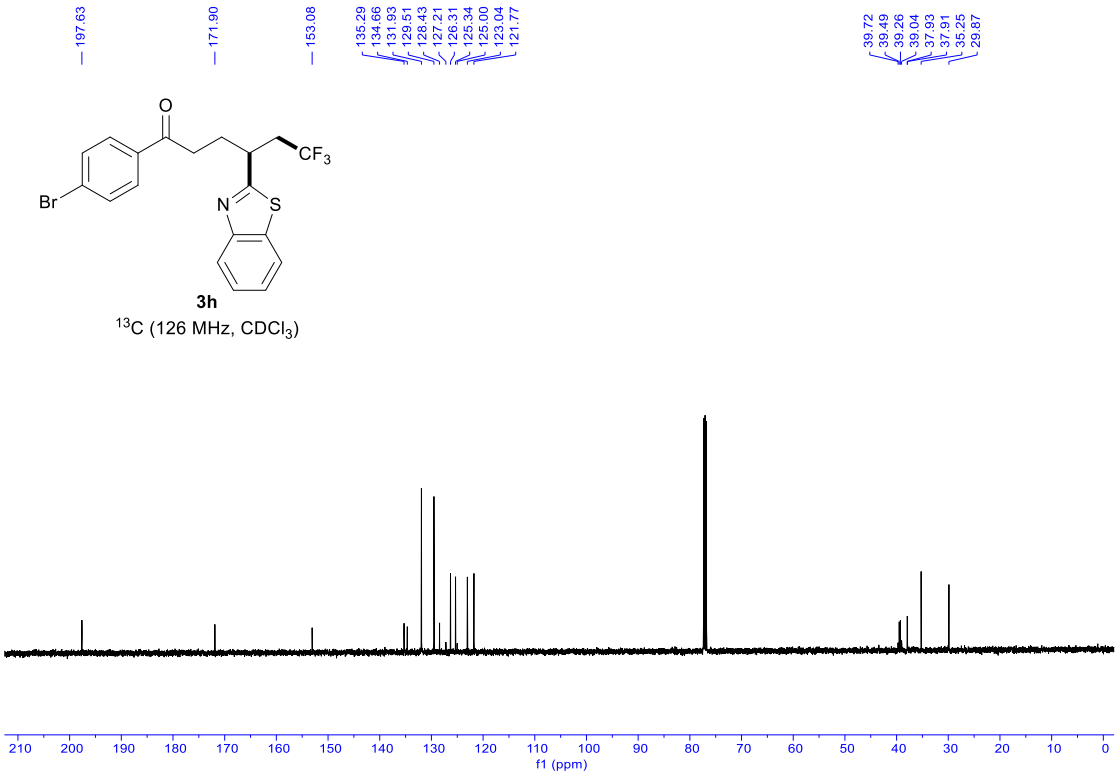
^{19}F (377 MHz, $CDCl_3$)



3h

^{1}H (500 Mz, $CDCl_3$)

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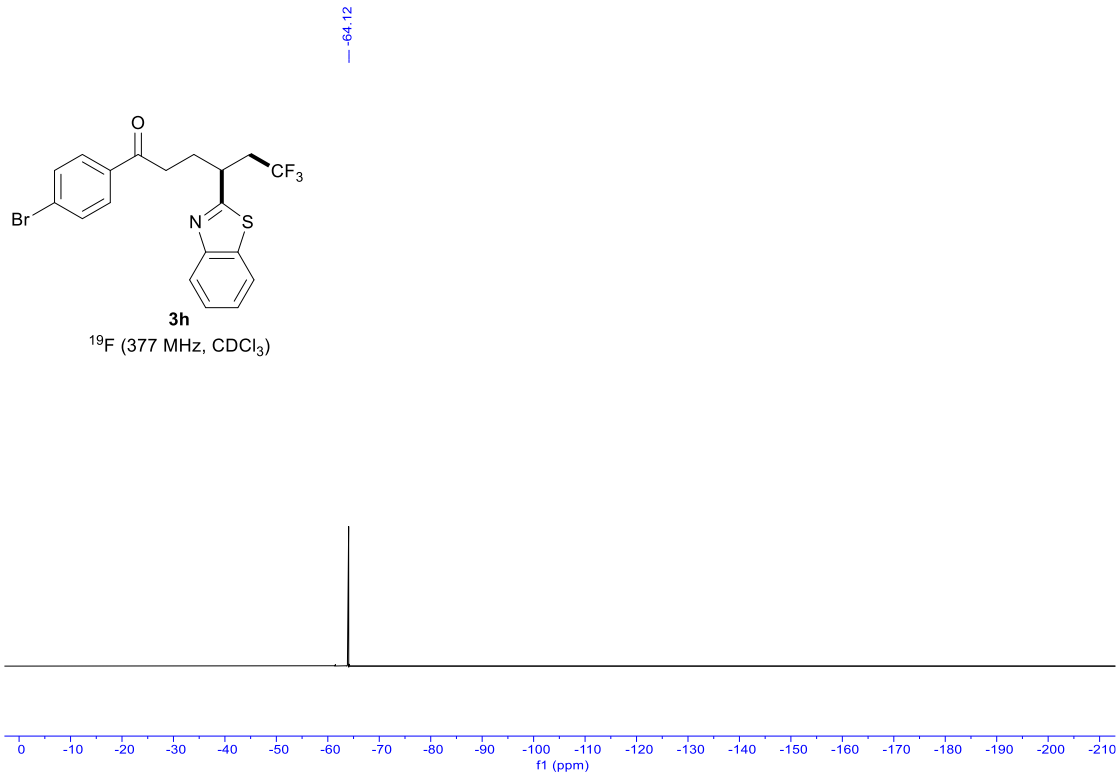
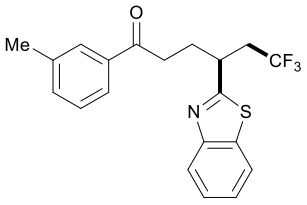
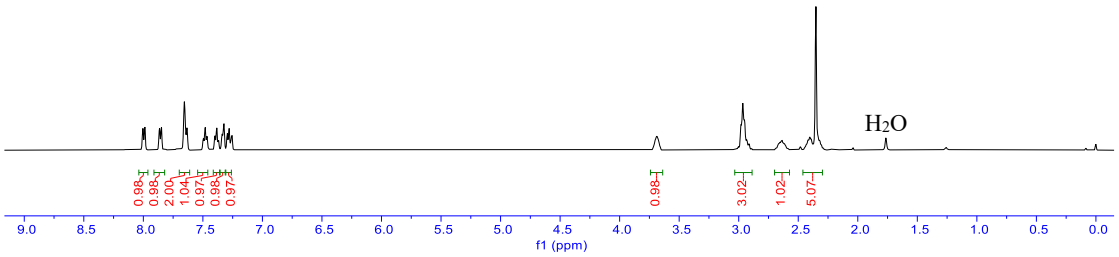
134.66
131.93
129.51
128.43
127.21
126.31
125.34
125.00
123.04
121.77
39.72
39.49
39.26
39.04
37.93
37.91
35.25
29.87
O
CF3
Br
N
S
3h
13C (126 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

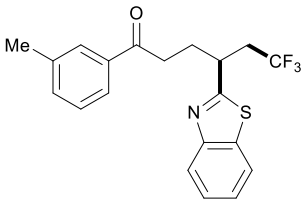

-64.12
O
CF3
Br
N
S
3h
19F (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



3i

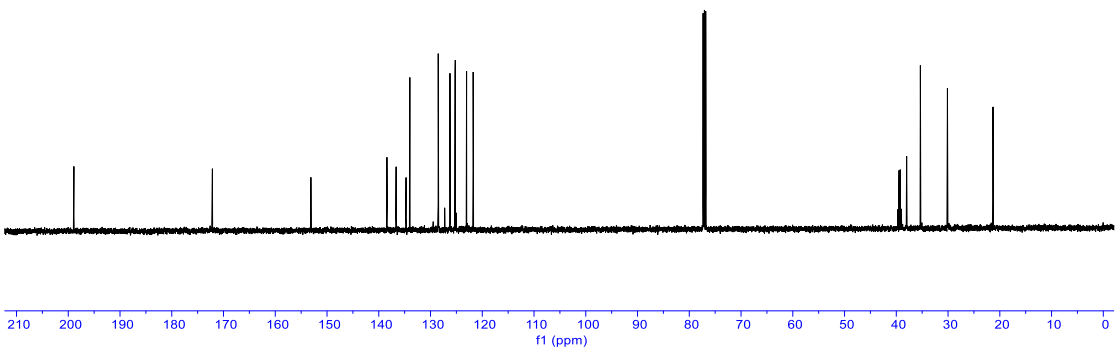
^{1}H (500 MHz, $CDCl_3$)

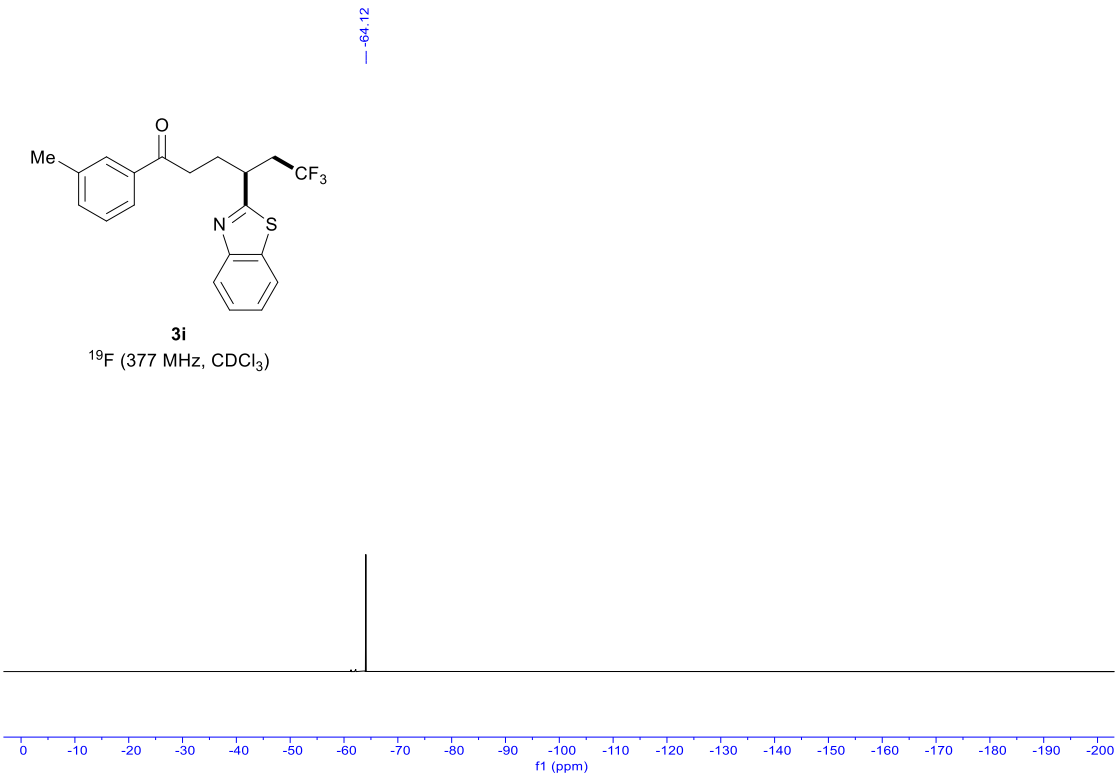




3i

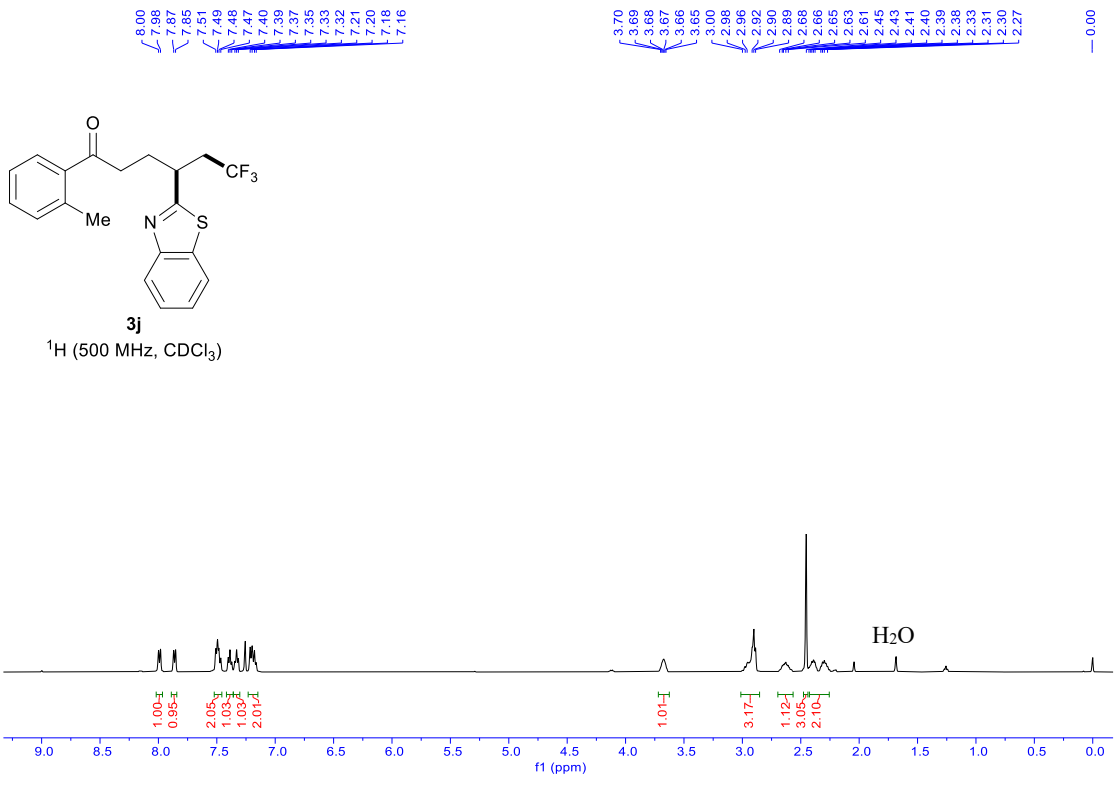
^{13}C (126 MHz, $CDCl_3$)





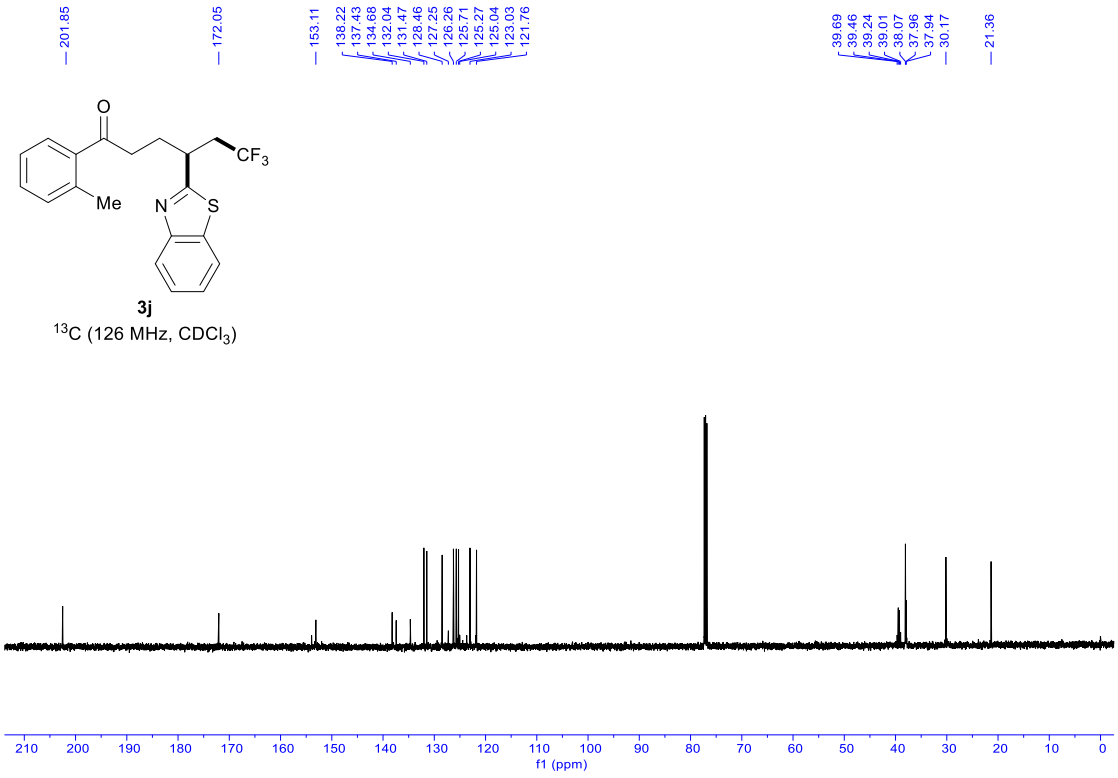
3i

^{19}F (377 MHz, $CDCl_3$)



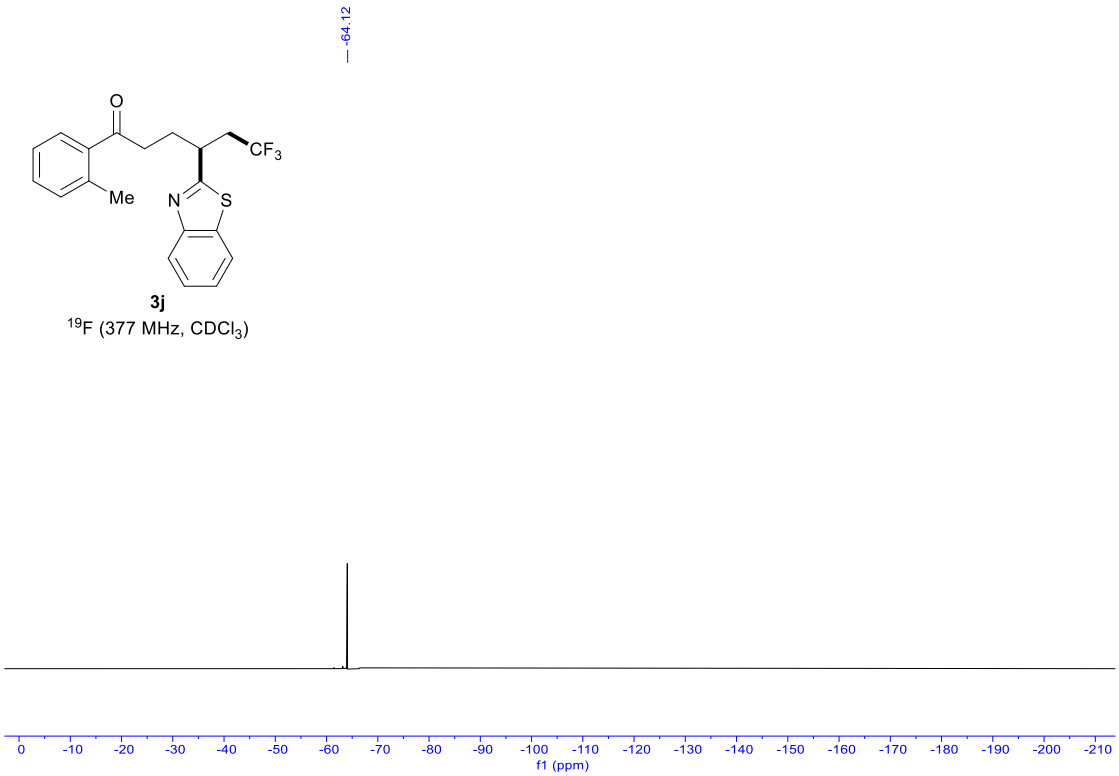
3j

^{1}H (500 MHz, $CDCl_3$)



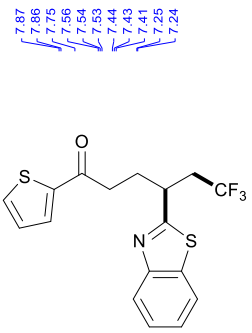
3j

^{13}C (126 MHz, $CDCl_3$)



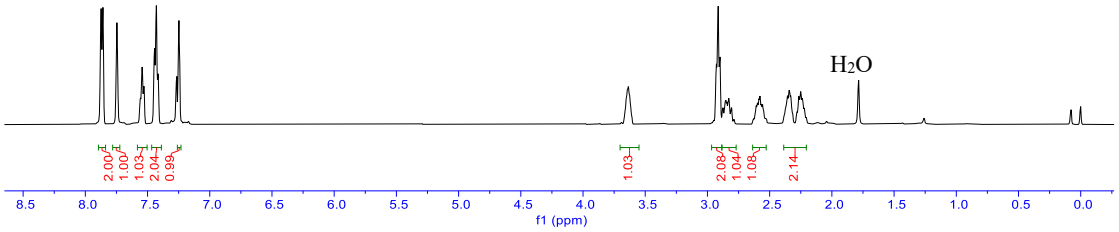
3j

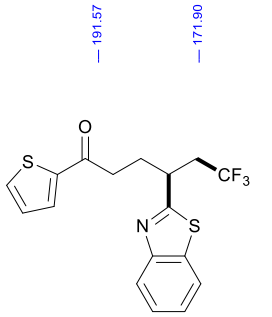
^{19}F (377 MHz, $CDCl_3$)



3k

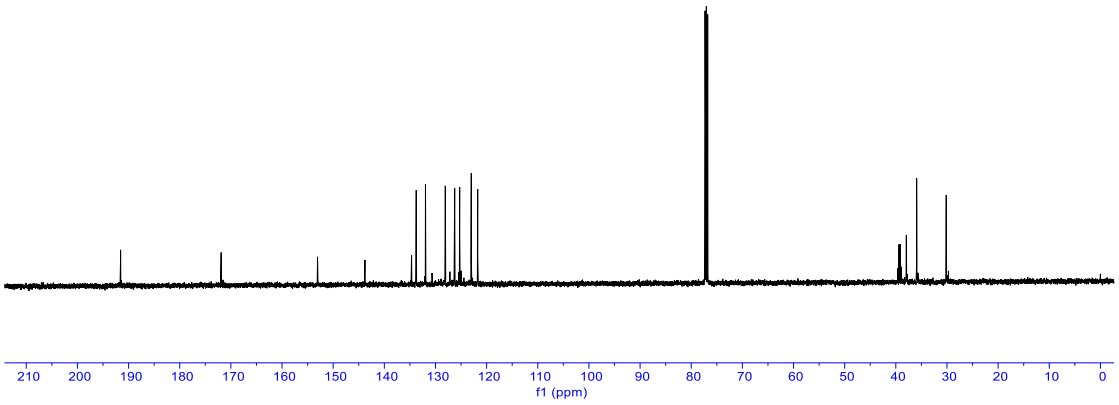
^{1}H (500 MHz, $CDCl_3$)

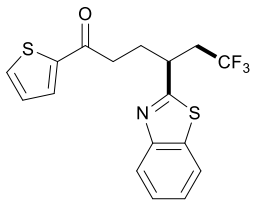




3k

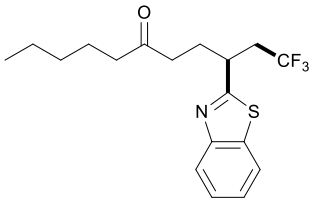
^{13}C (126 MHz, $CDCl_3$)





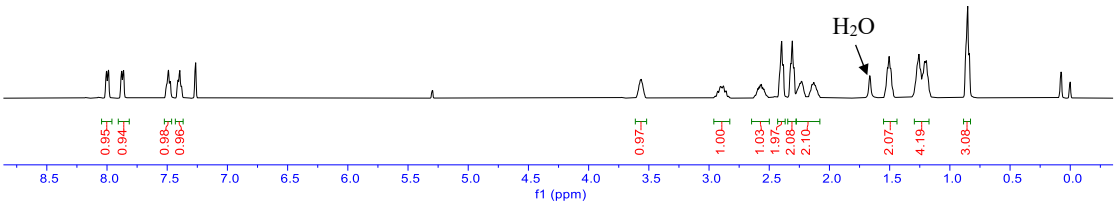
3k

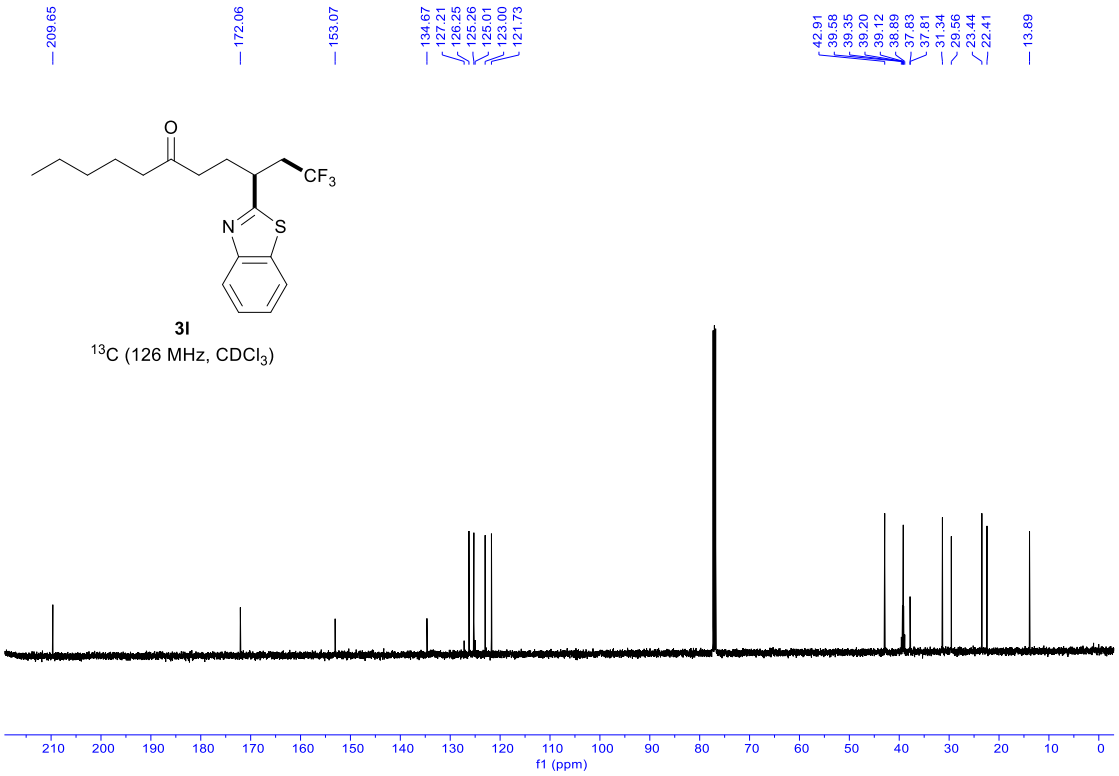
^{19}F (377 MHz, $CDCl_3$)



3l

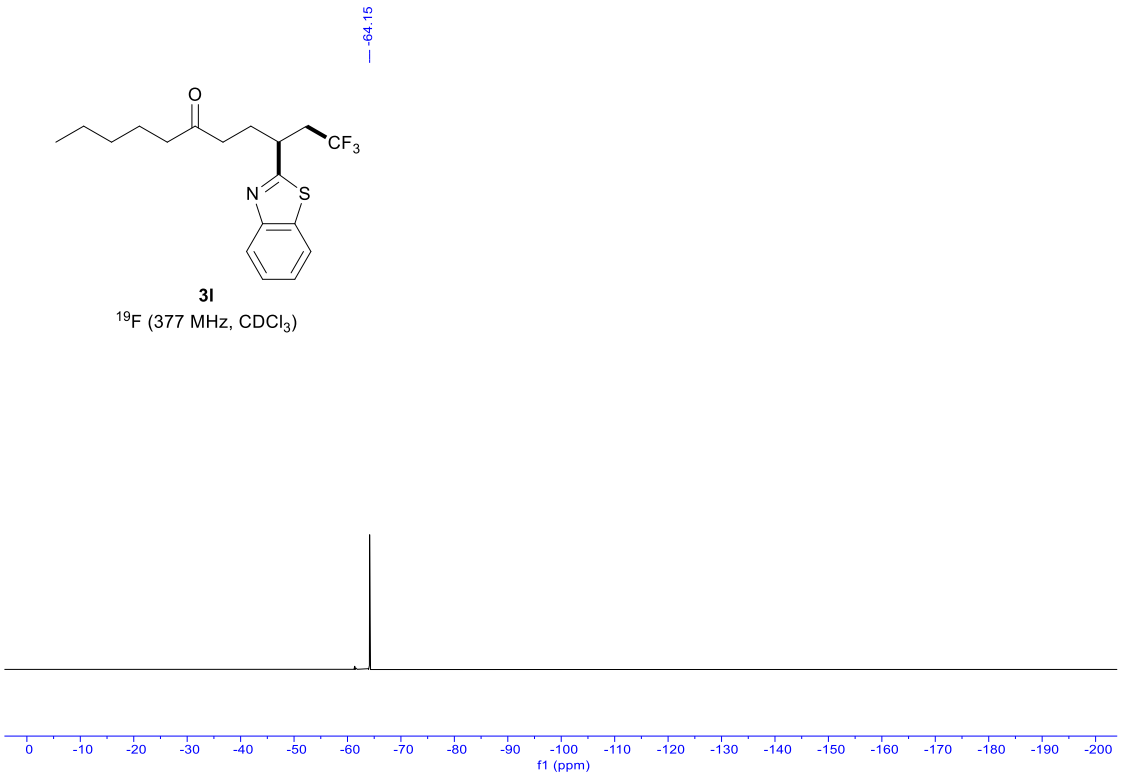
^{1}H (500 MHz, $CDCl_3$)





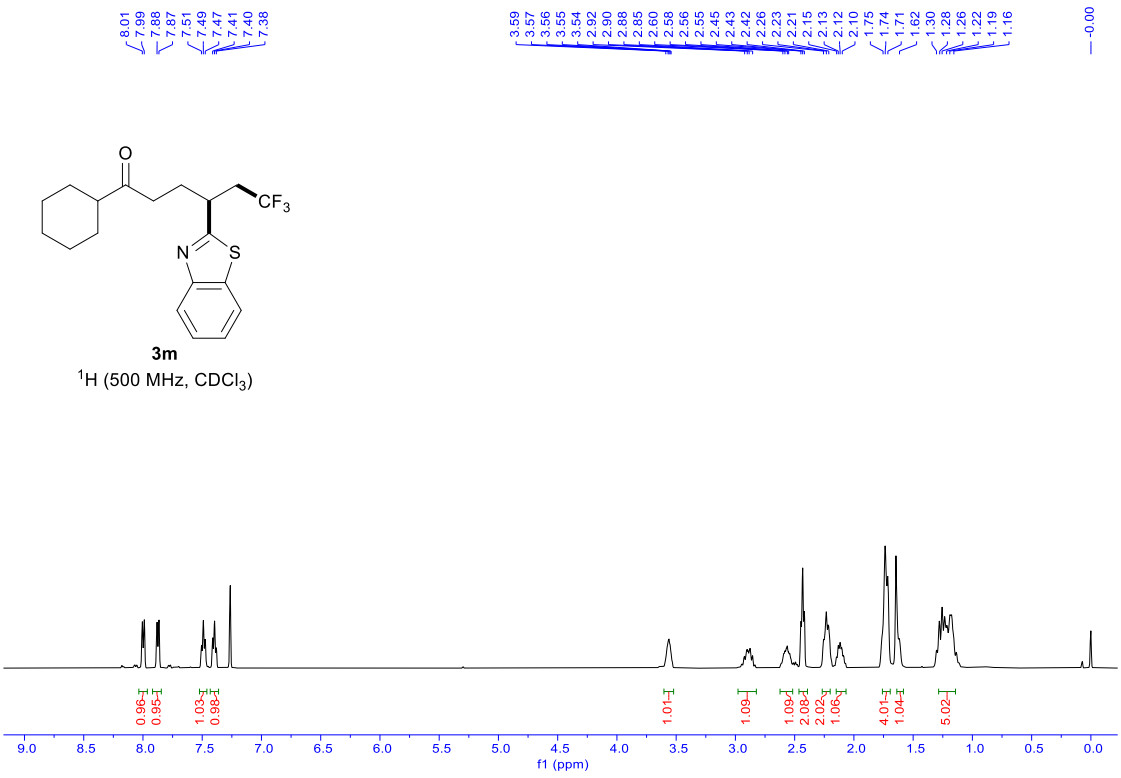
3l

^{13}C (126 MHz, $CDCl_3$)



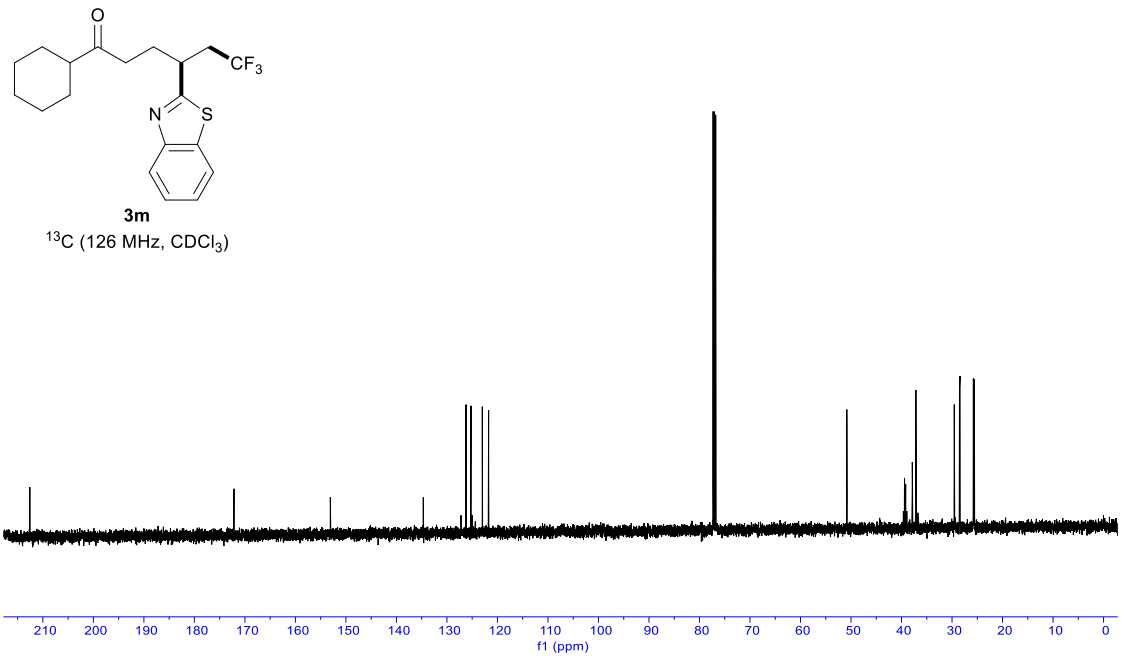
3l

^{19}F (377 MHz, $CDCl_3$)



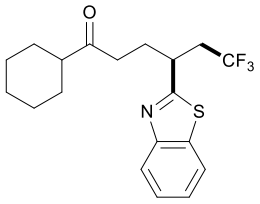
3m

^{1}H (500 MHz, $CDCl_3$)



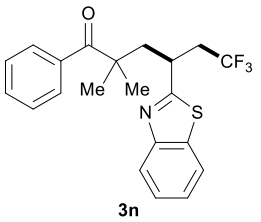
3m

^{13}C (126 MHz, $CDCl_3$)



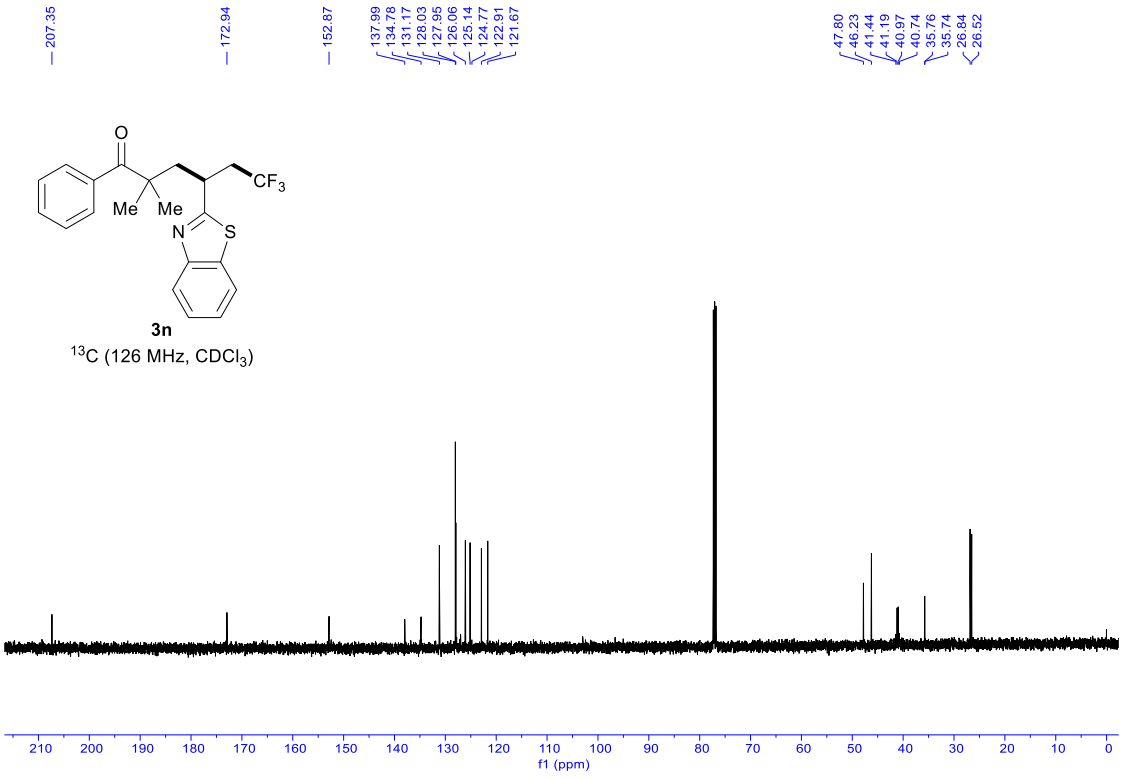
3m

^{13}F (377 MHz, $CDCl_3$)



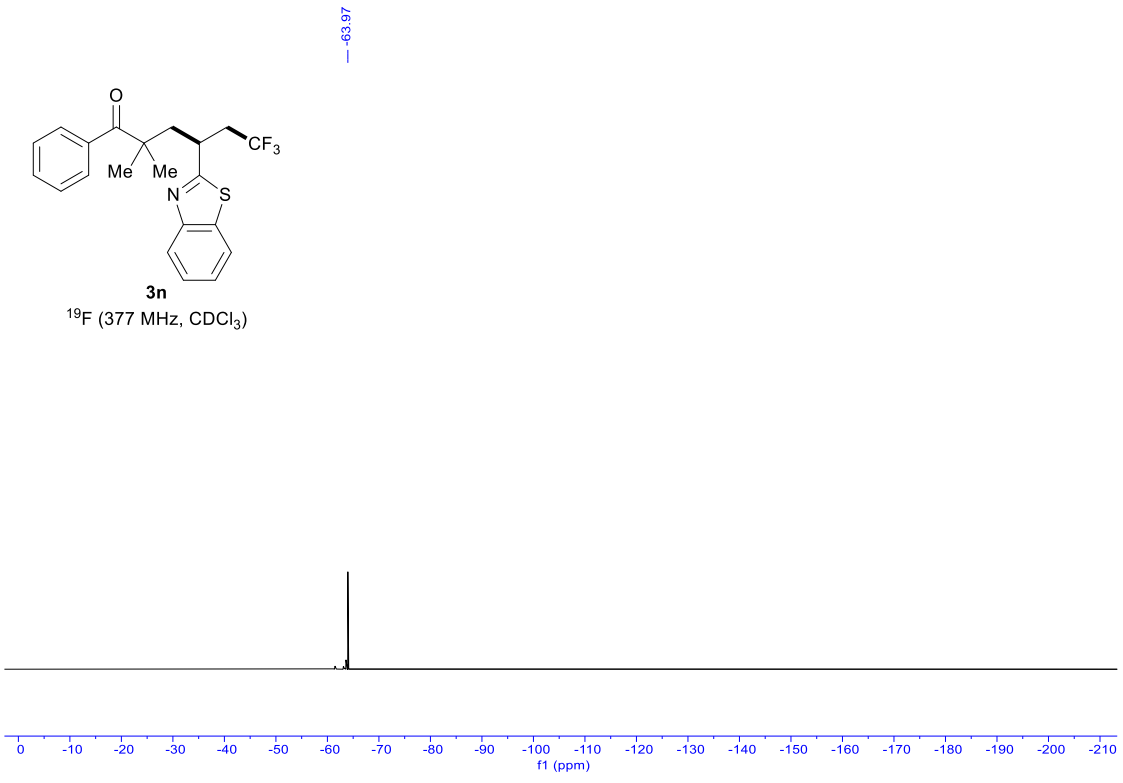
3n

^{1}H (500 MHz, $CDCl_3$)



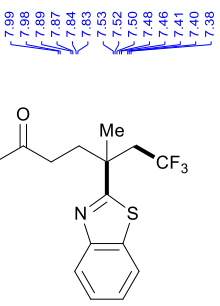
3n

^{13}C (126 MHz, $CDCl_3$)



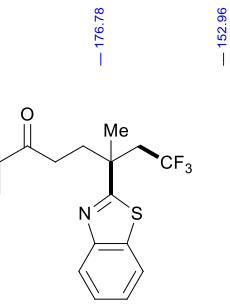
3n

^{19}F (377 MHz, $CDCl_3$)



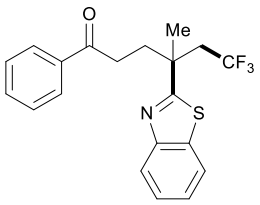
3o

^{1}H (500 MHz, $CDCl_3$)



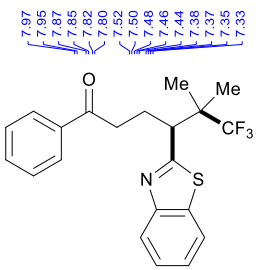
3o

^{13}C (126 MHz, $CDCl_3$)



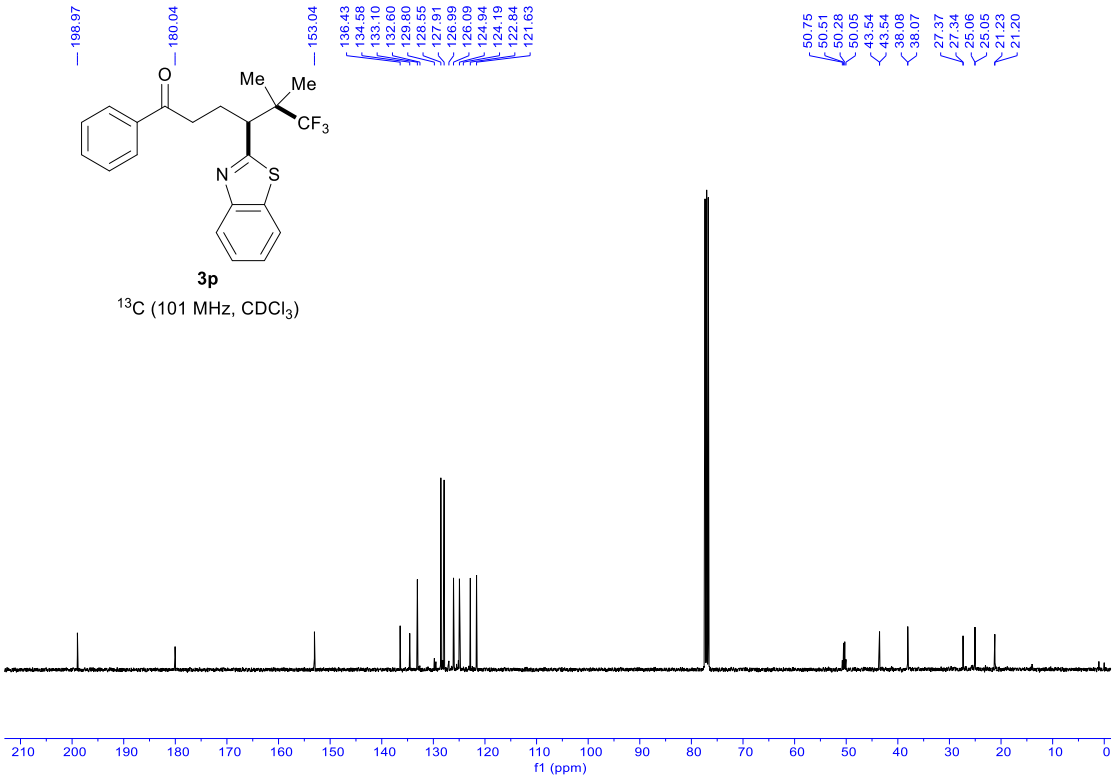
3o

^{19}F (377 MHz, $CDCl_3$)



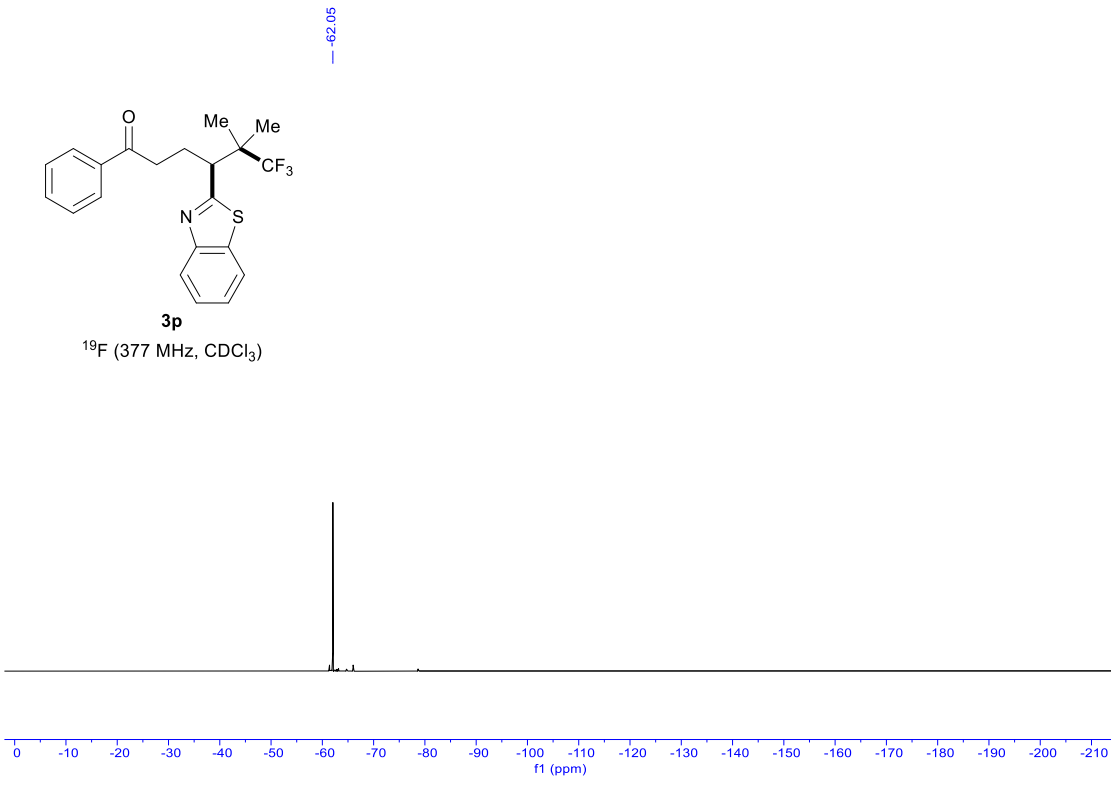
3p

^{1}H (400 MHz, $CDCl_3$)



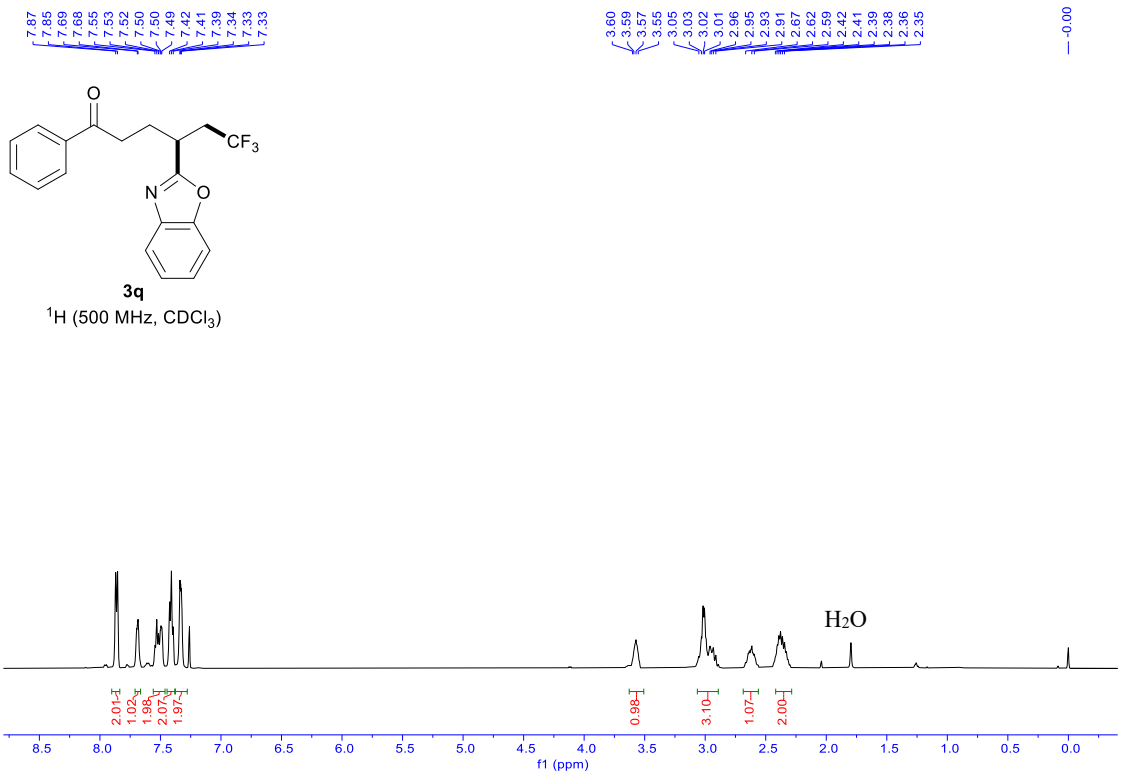
3p

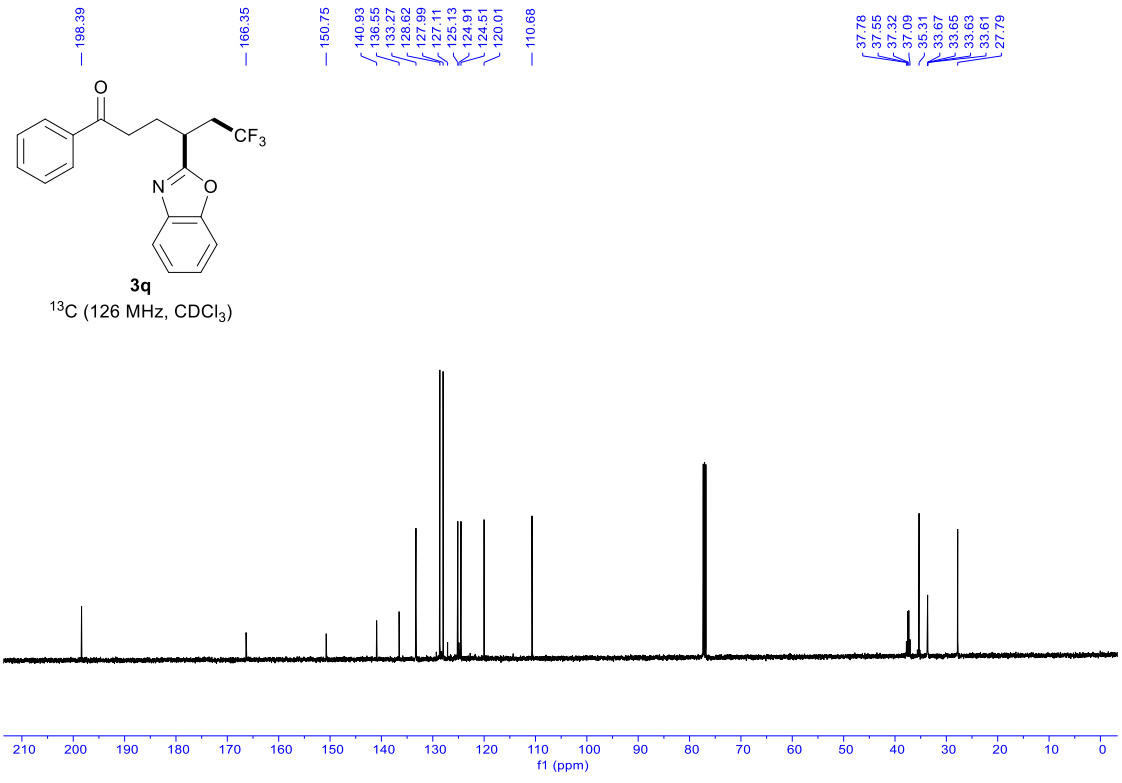
^{13}C (101 MHz, $CDCl_3$)

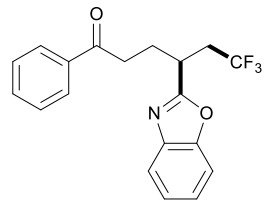


3p

^{19}F (377 MHz, $CDCl_3$)

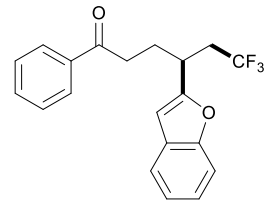

7.87
7.85
7.69
7.68
7.55
7.53
7.52
7.50
7.50
7.49
7.42
7.41
7.39
7.34
7.33
7.33
3.60
3.59
3.57
3.55
3.05
3.03
3.02
3.01
2.96
2.95
2.93
2.91
2.67
2.62
2.59
2.42
2.41
2.39
2.38
2.36
2.35
-0.00
O
CF3
N
O
3q
1H (500 MHz, CDCl3)
H2O
2.01
1.02
1.98
2.07
1.97
0.98
3.10
1.07
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.39
166.35
150.75
140.93
136.55
133.27
128.62
127.99
127.11
125.13
124.91
124.51
120.01
110.68
37.78
37.55
37.32
37.09
35.31
33.67
33.65
33.63
33.61
27.79
O
CF3
N
O
3q
13C (126 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



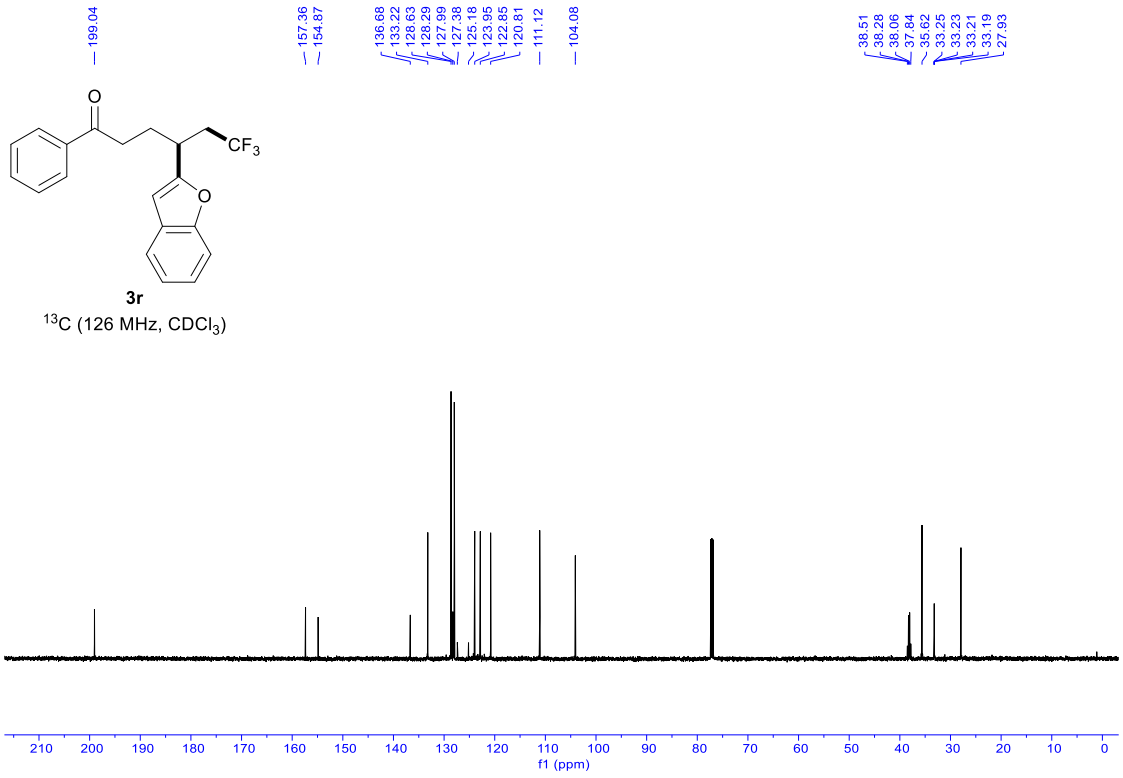
3q

^{19}F (377 MHz, $CDCl_3$)



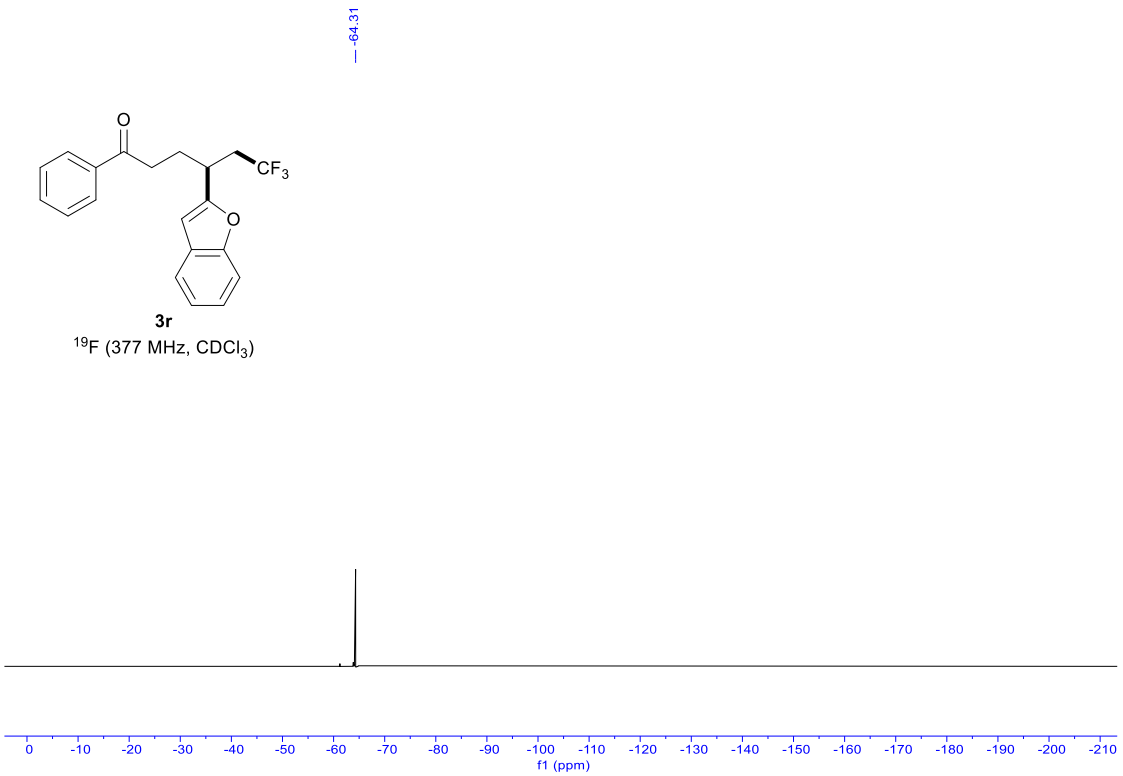
3r

^{1}H (500 MHz, $CDCl_3$)



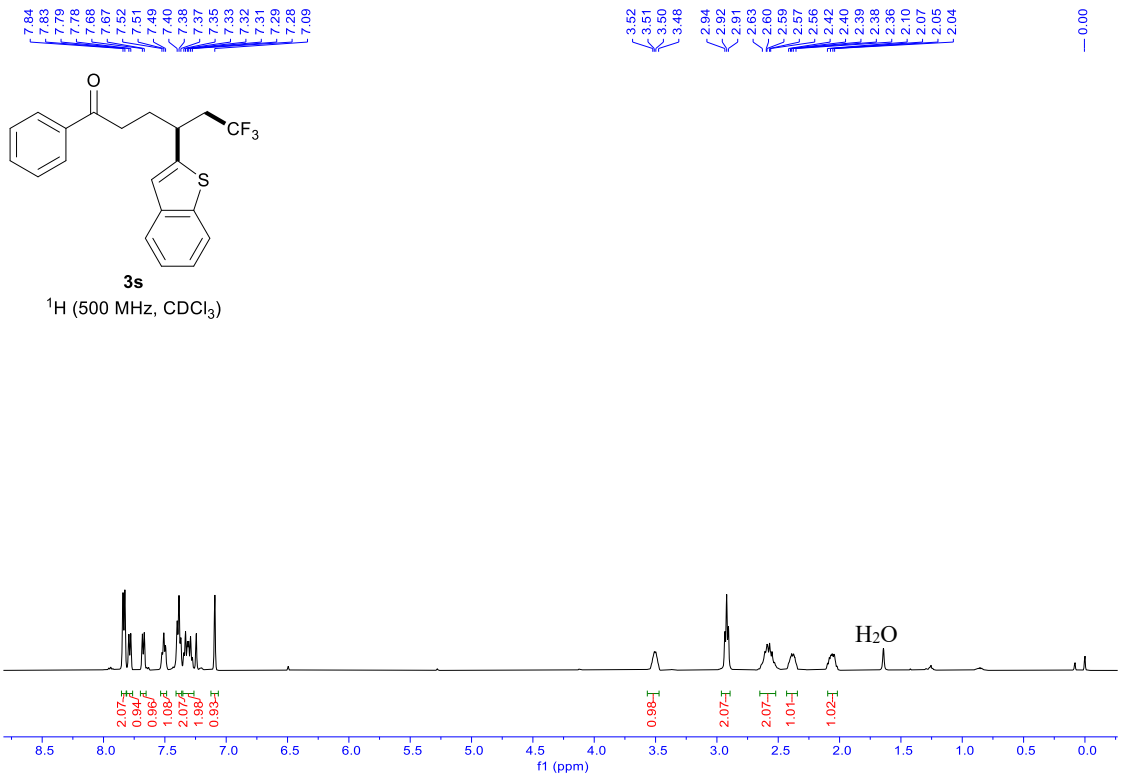
3r

^{13}C (126 MHz, $CDCl_3$)



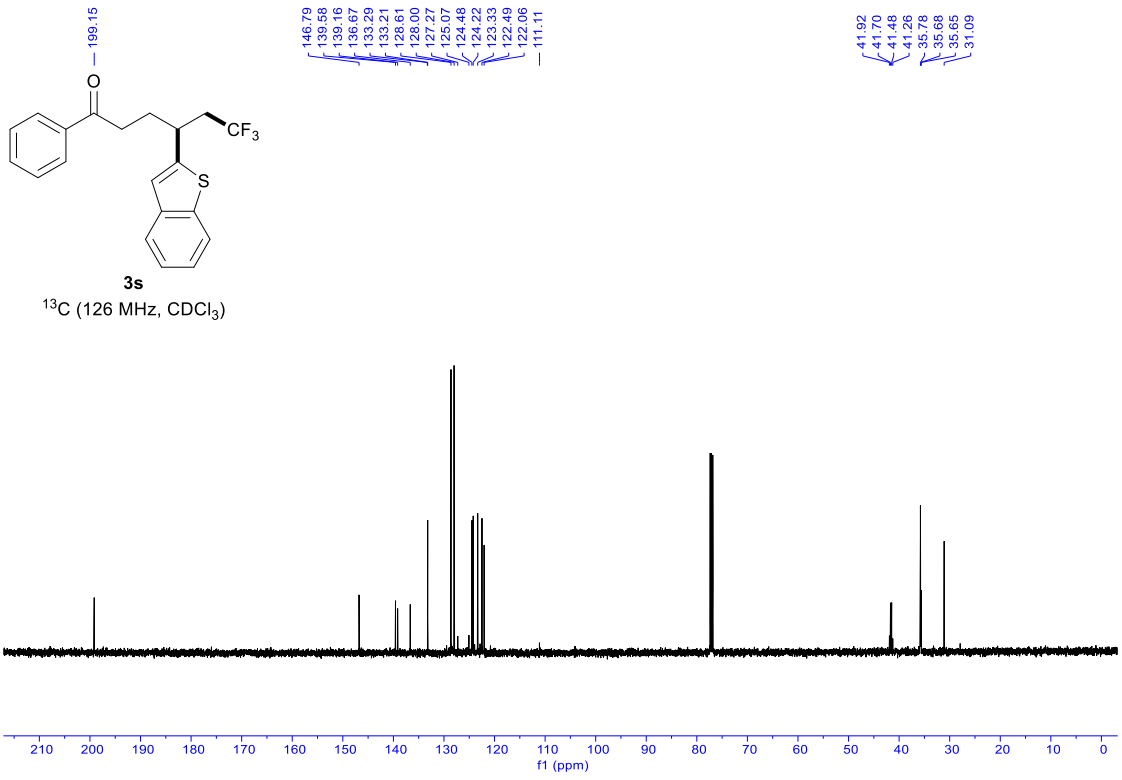
3r

^{19}F (377 MHz, $CDCl_3$)



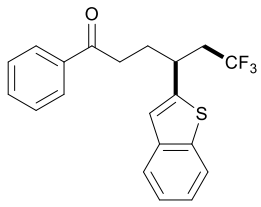
3s

^{1}H (500 MHz, $CDCl_3$)



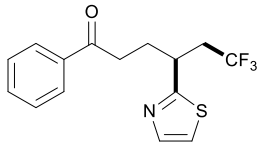
3s

^{13}C (126 MHz, $CDCl_3$)



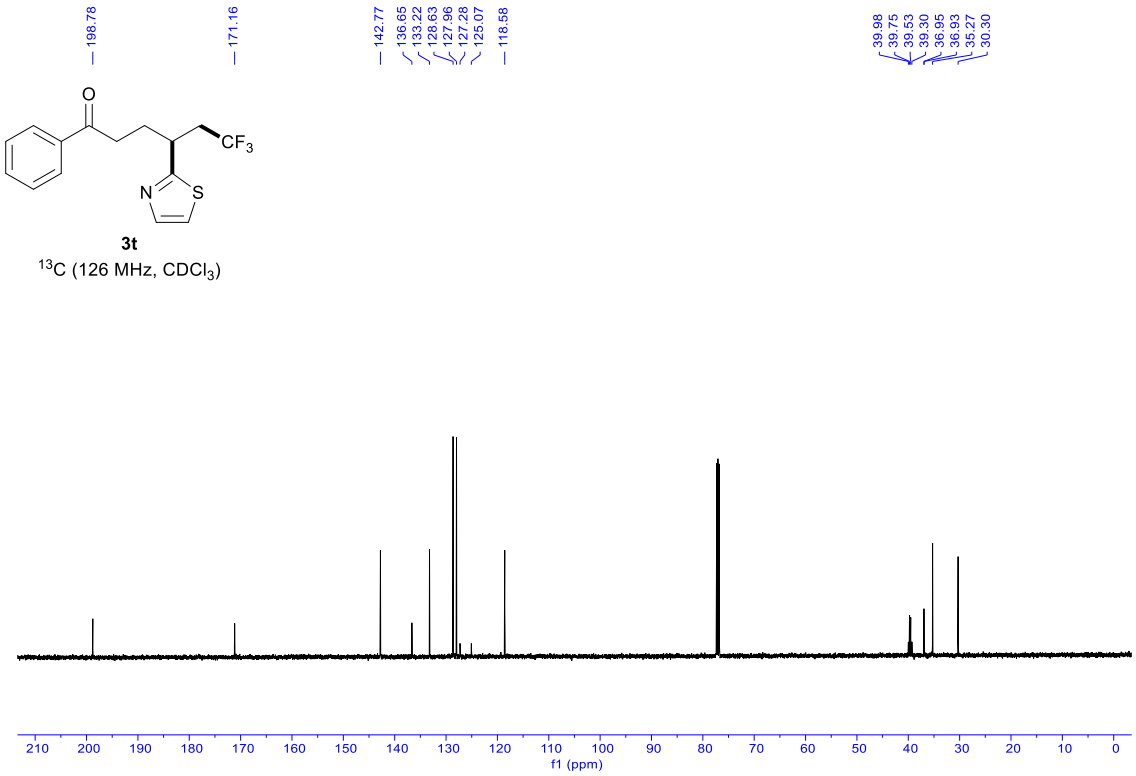
3s

^{19}F (377 MHz, $CDCl_3$)



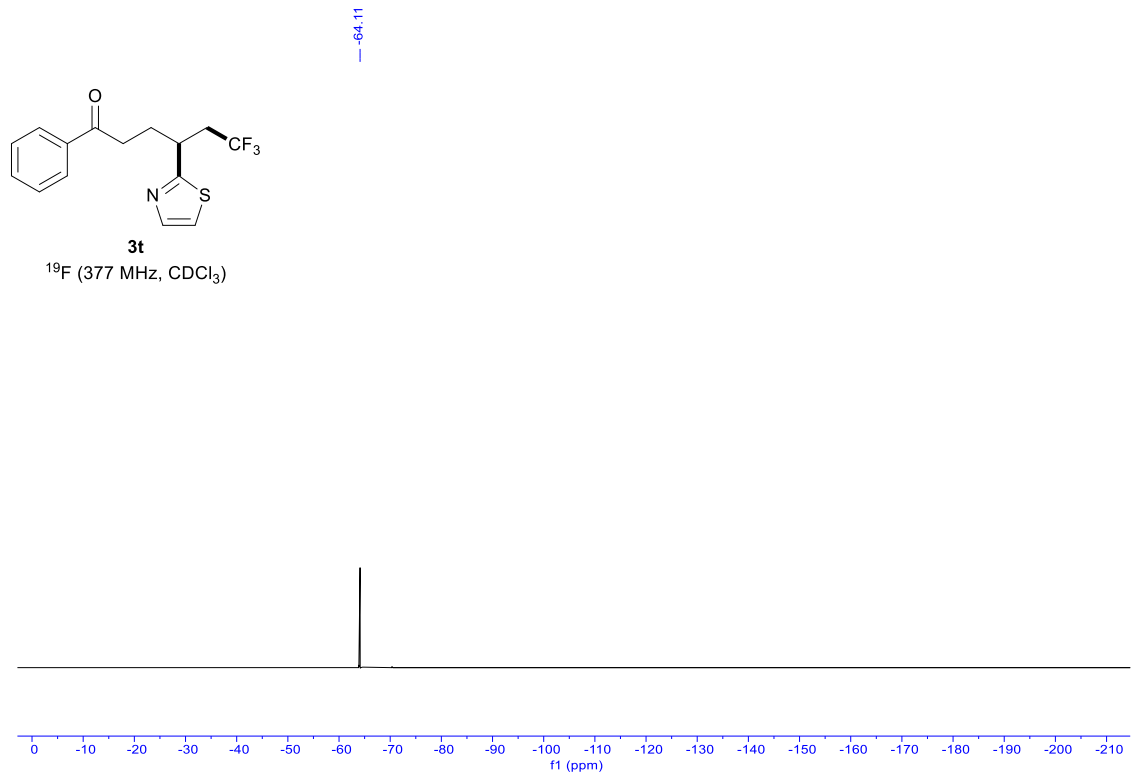
3t

^{1}H (500 MHz, $CDCl_3$)



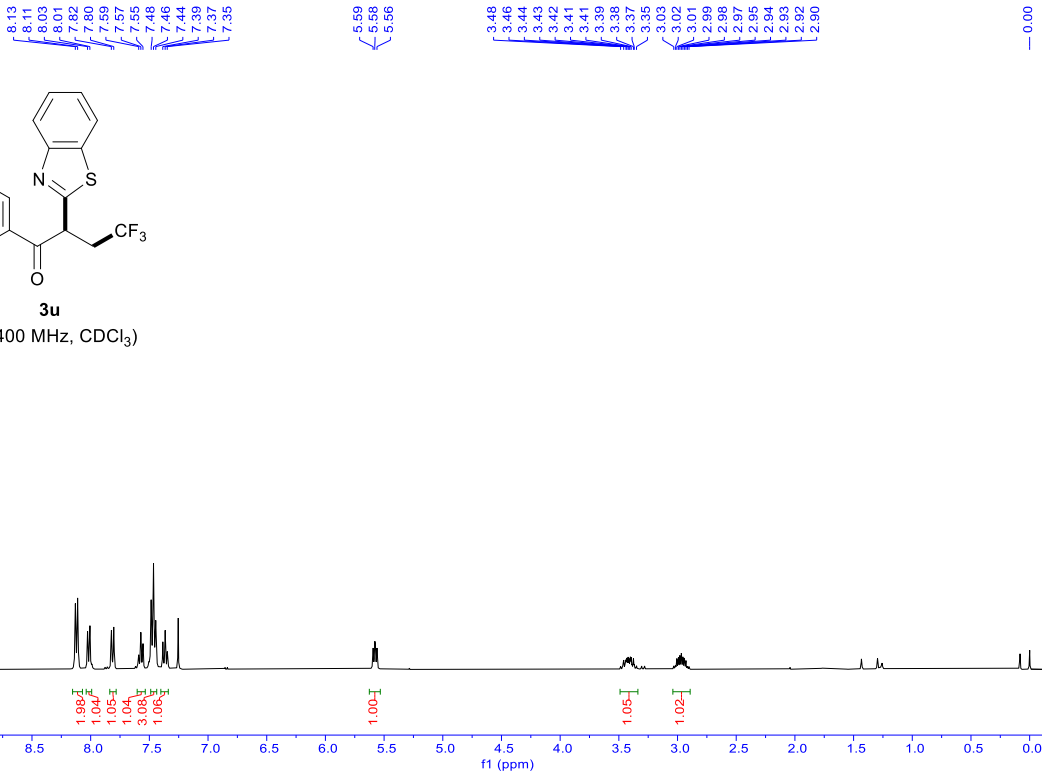
3t

^{13}C (126 MHz, $CDCl_3$)



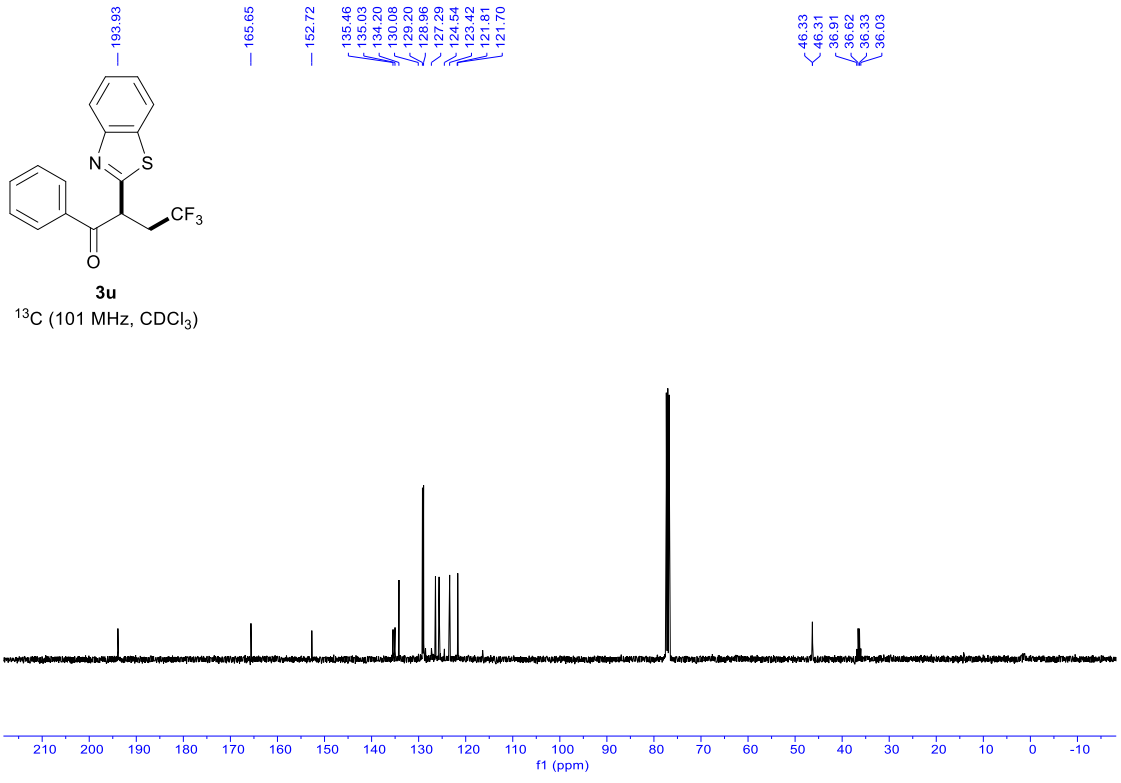
3t

^{19}F (377 MHz, $CDCl_3$)



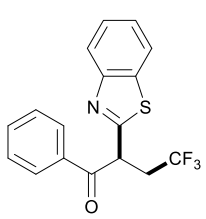
3u

^{1}H (400 MHz, $CDCl_3$)



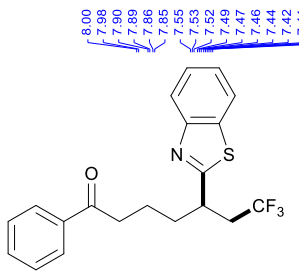
3u

^{13}C (101 MHz, $CDCl_3$)



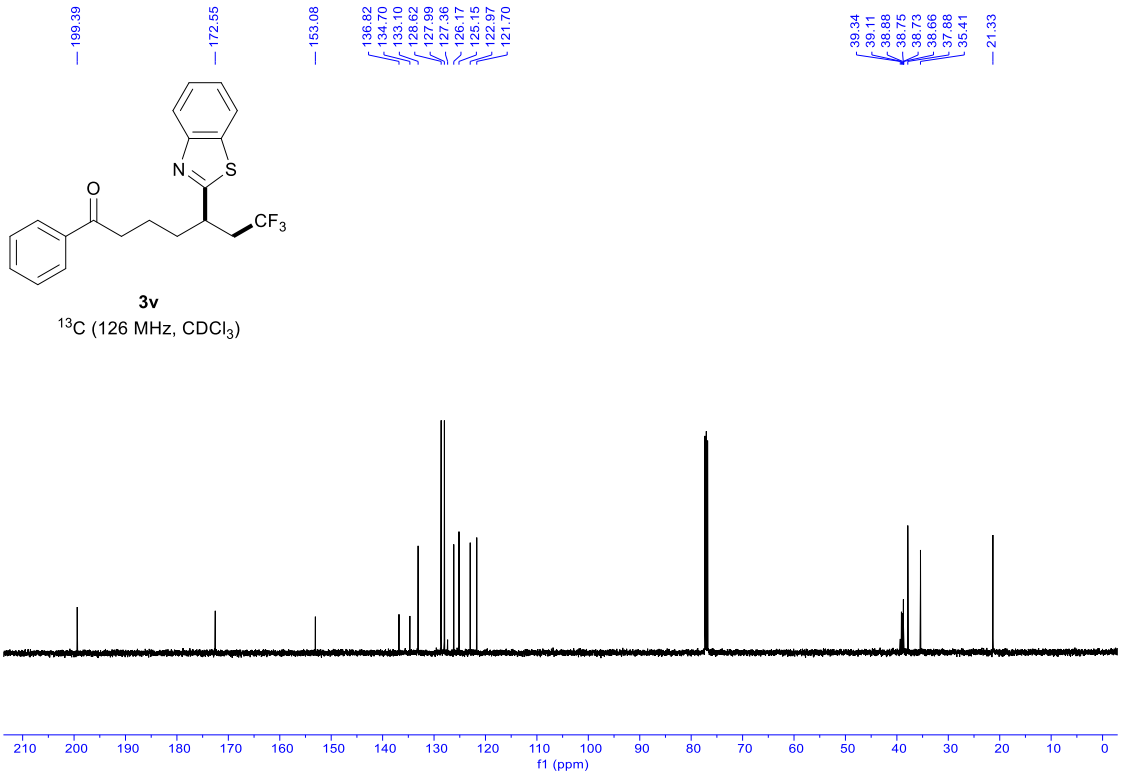
3u

^{19}F (377 MHz, $CDCl_3$)



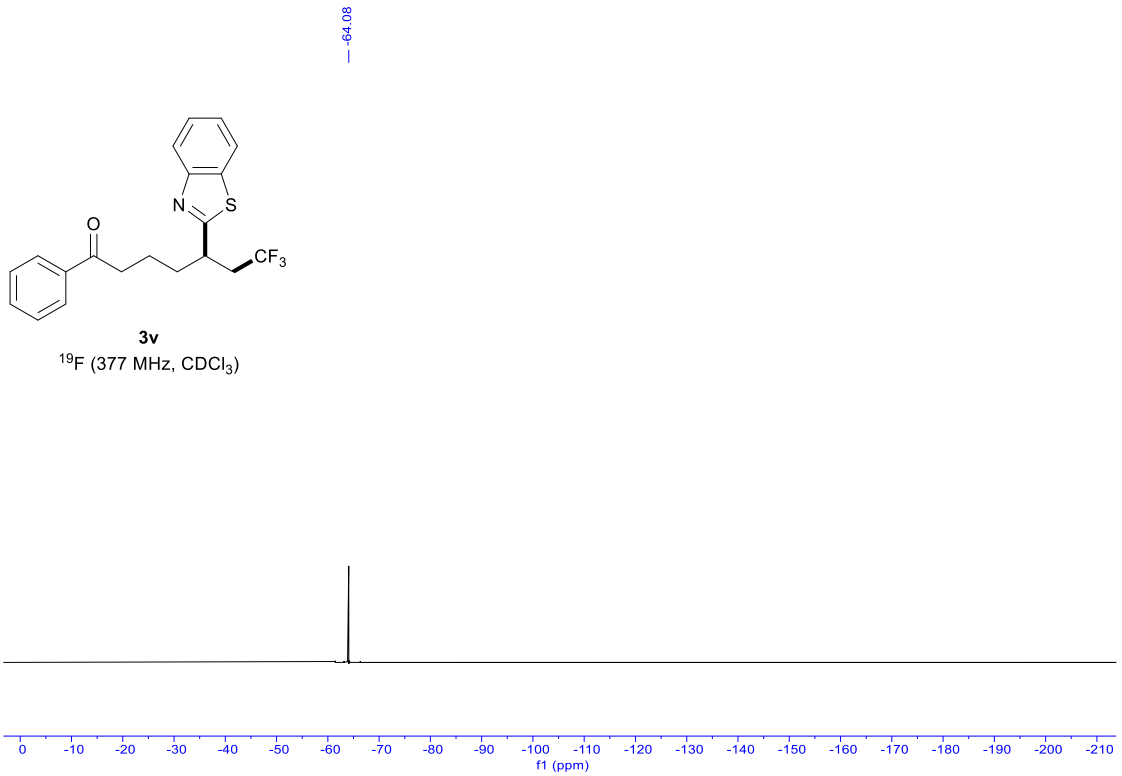
3v

^{1}H (500 MHz, $CDCl_3$)



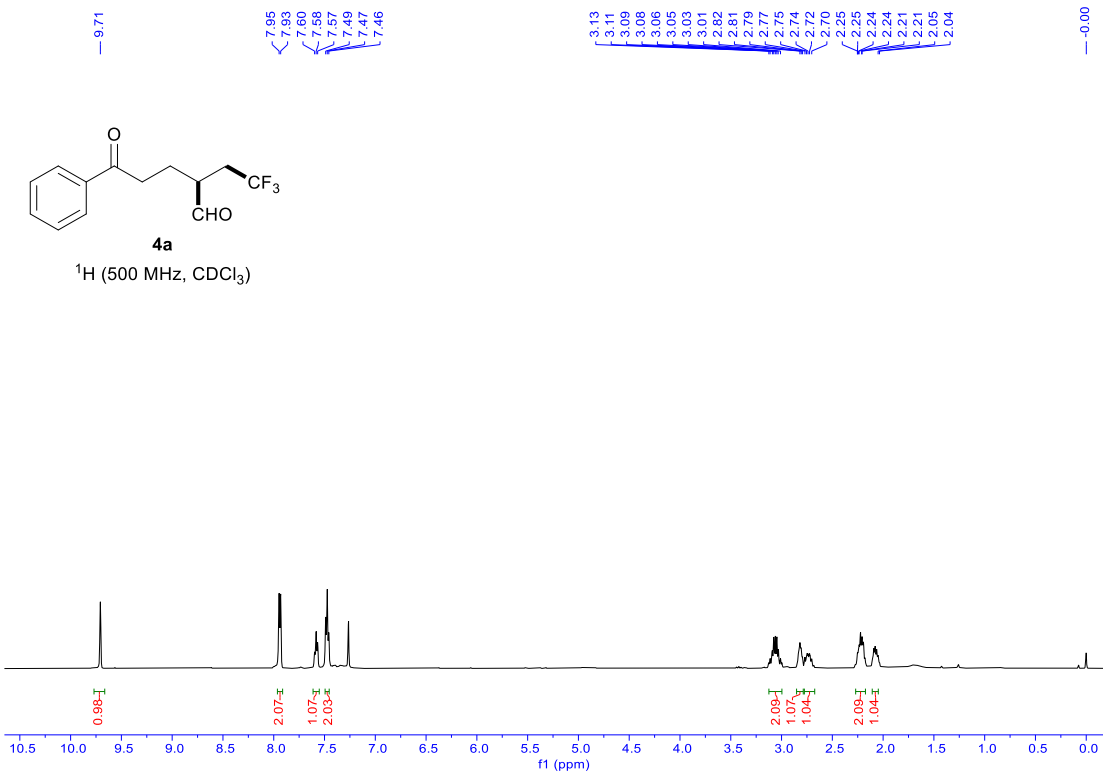
3v

^{13}C (126 MHz, $CDCl_3$)



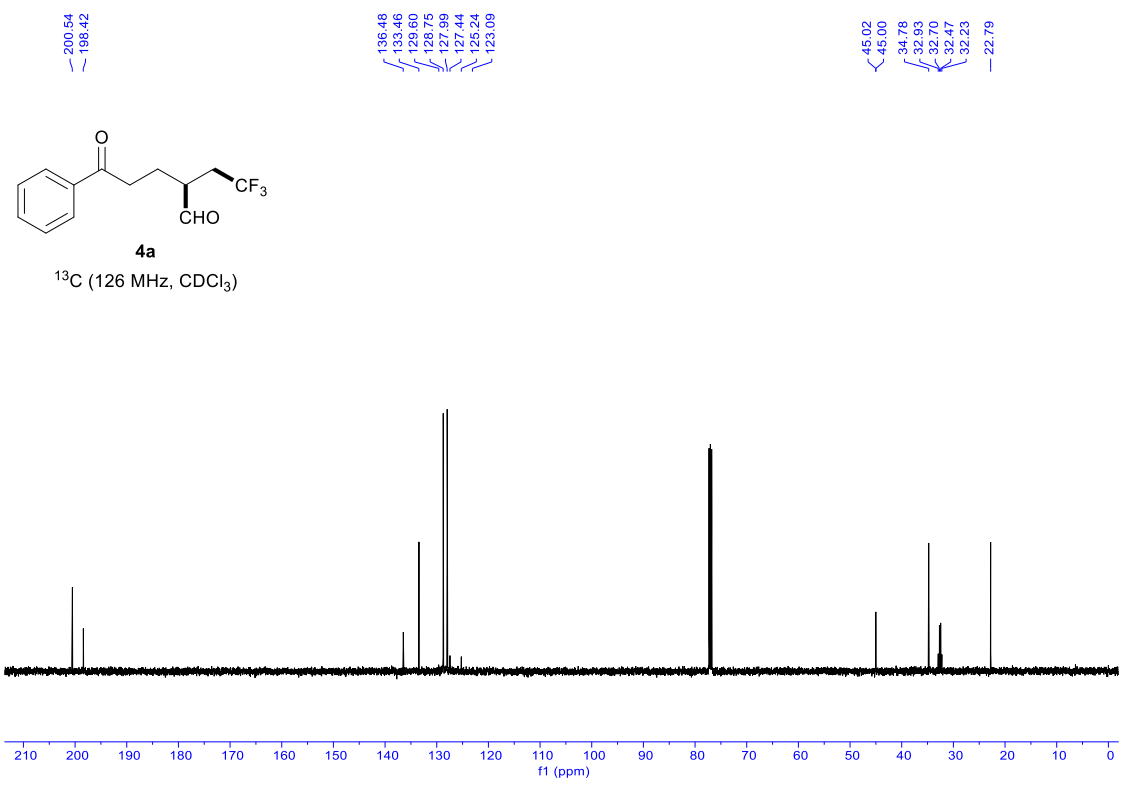
3v

^{19}F (377 MHz, $CDCl_3$)



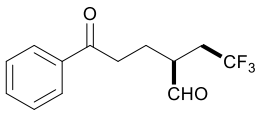
4a

^{1}H (500 MHz, $CDCl_3$)



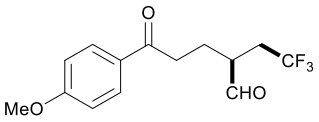
4a

^{13}C (126 MHz, $CDCl_3$)



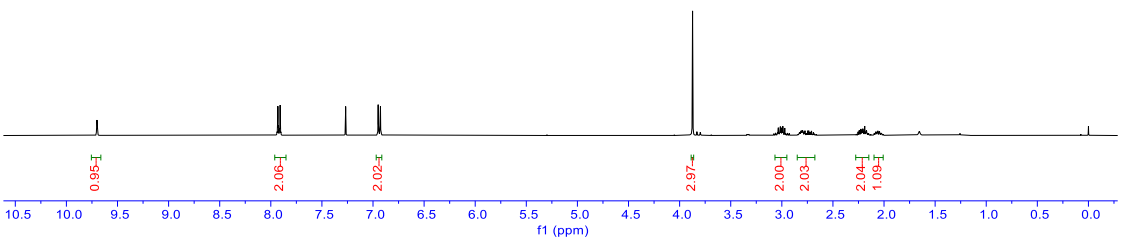
4a

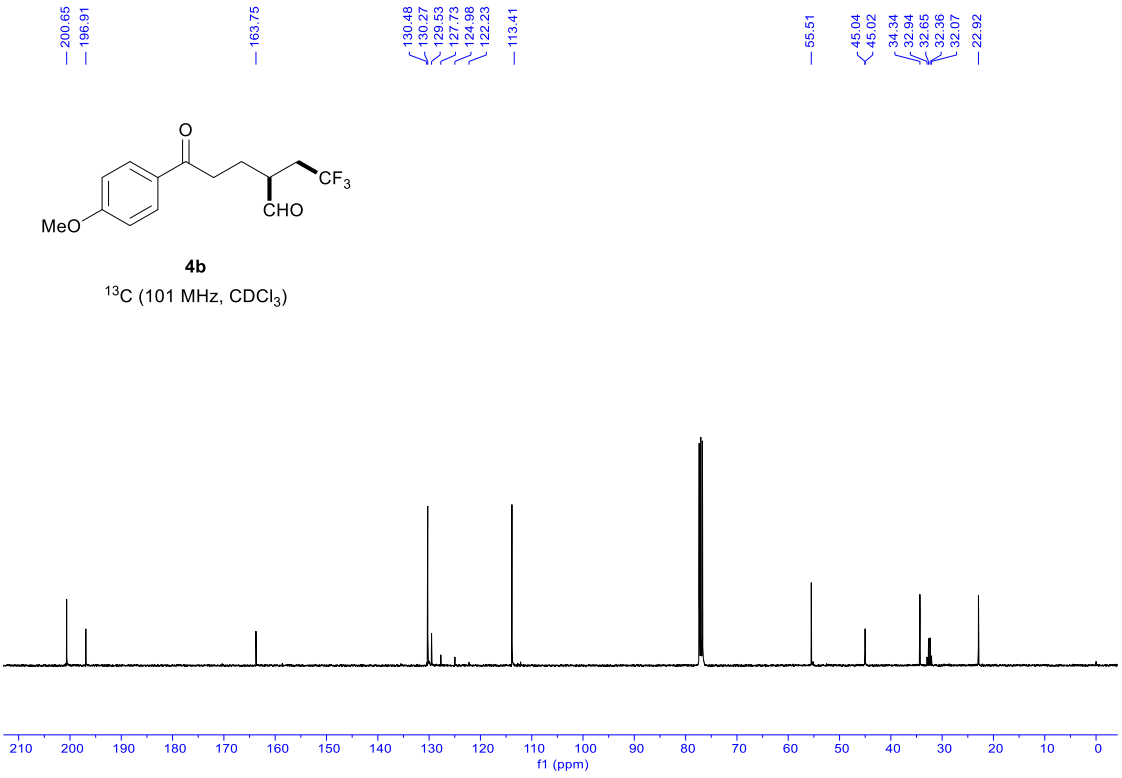
^{19}F (377 MHz, $CDCl_3$)



4b

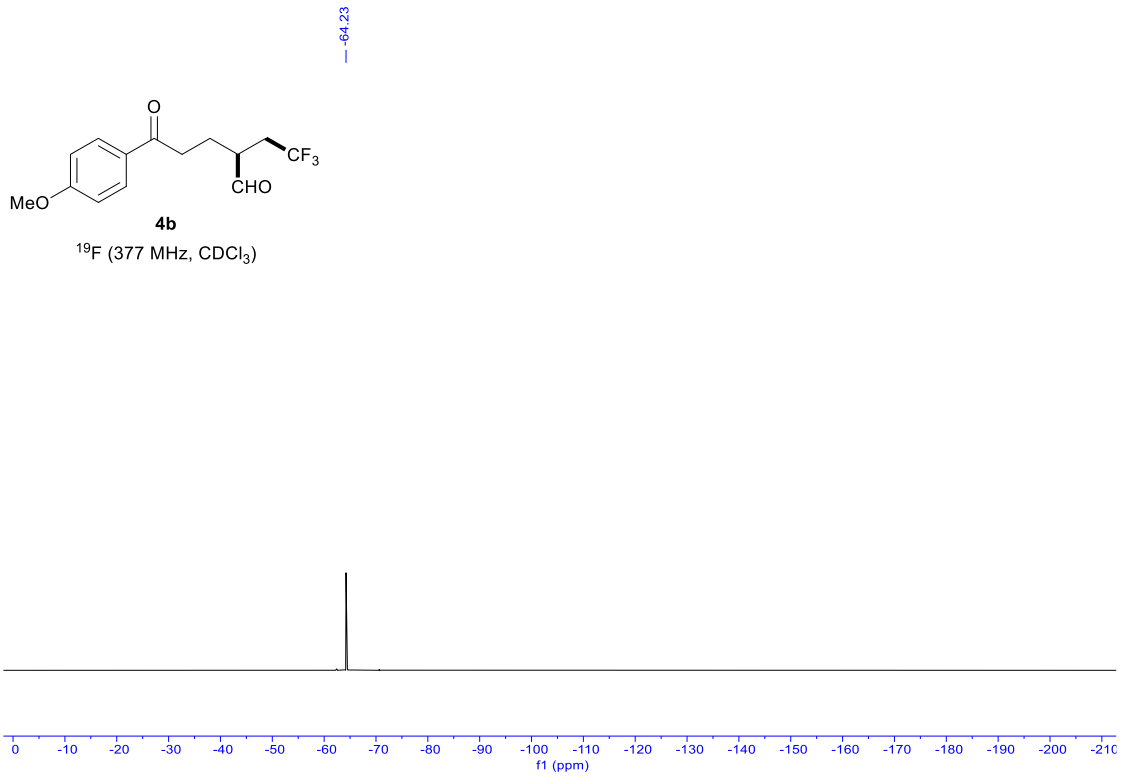
^{1}H (400 MHz, $CDCl_3$)





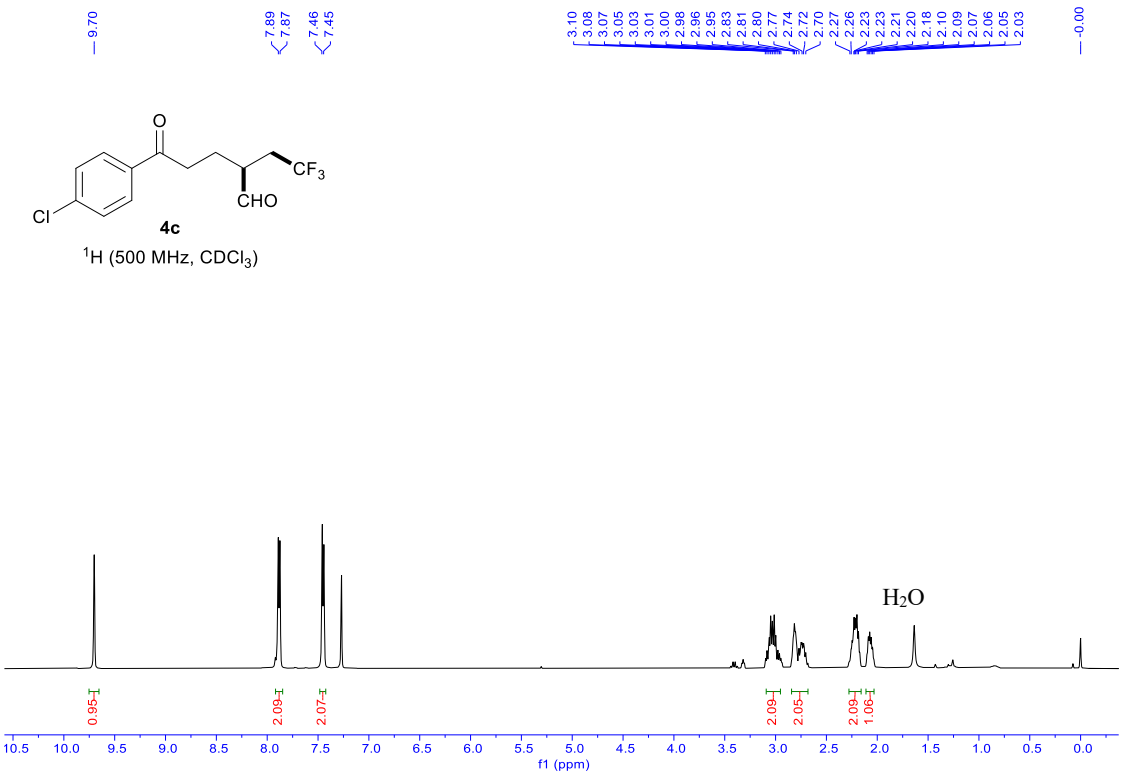
4b

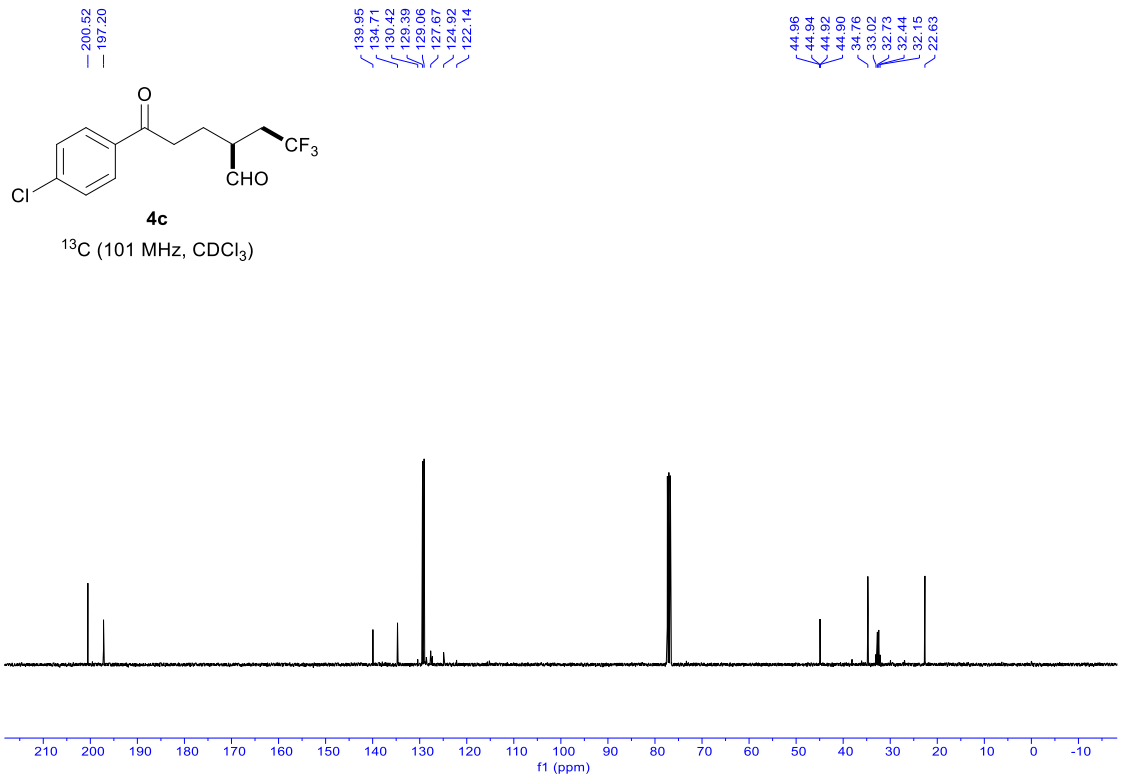
^{13}C (101 MHz, $CDCl_3$)

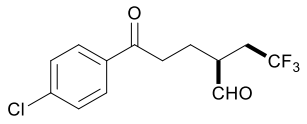


4b

^{19}F (377 MHz, $CDCl_3$)

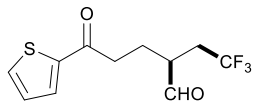

9.70
7.89
7.87
7.46
7.45
3.10
3.08
3.07
3.05
3.03
3.01
3.00
2.98
2.96
2.95
2.83
2.81
2.80
2.77
2.74
2.72
2.70
2.27
2.26
2.23
2.23
2.21
2.20
2.18
2.10
2.09
2.07
2.06
2.05
2.03
0.00
O
CF3
CHO
Cl
4c
1H (500 MHz, CDCl3)
H2O
0.95
2.09
2.07
2.09
2.05
2.09
1.06
f1 (ppm)


200.52
197.20
139.95
134.71
130.42
129.39
129.06
127.67
124.92
122.14
44.96
44.94
44.92
44.90
34.76
33.02
32.73
32.44
32.15
22.63
O
CF3
CHO
Cl
4c
13C (101 MHz, CDCl3)
f1 (ppm)



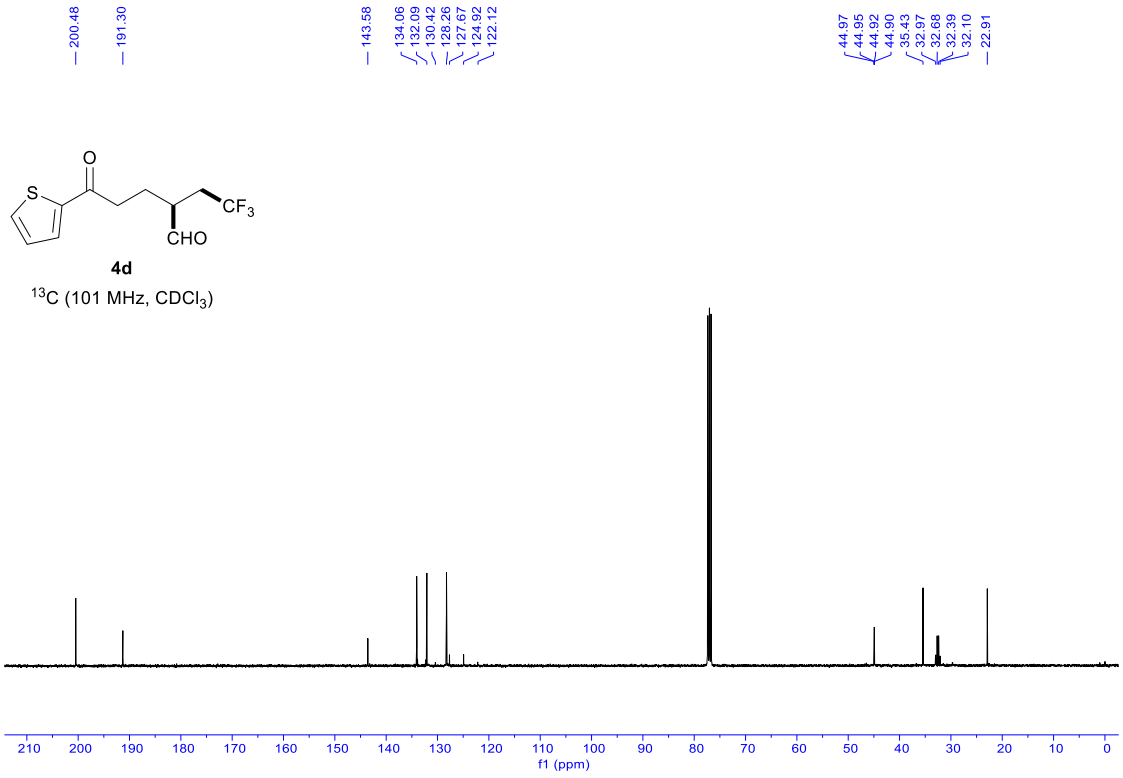
4c

^{19}F (377 MHz, $CDCl_3$)



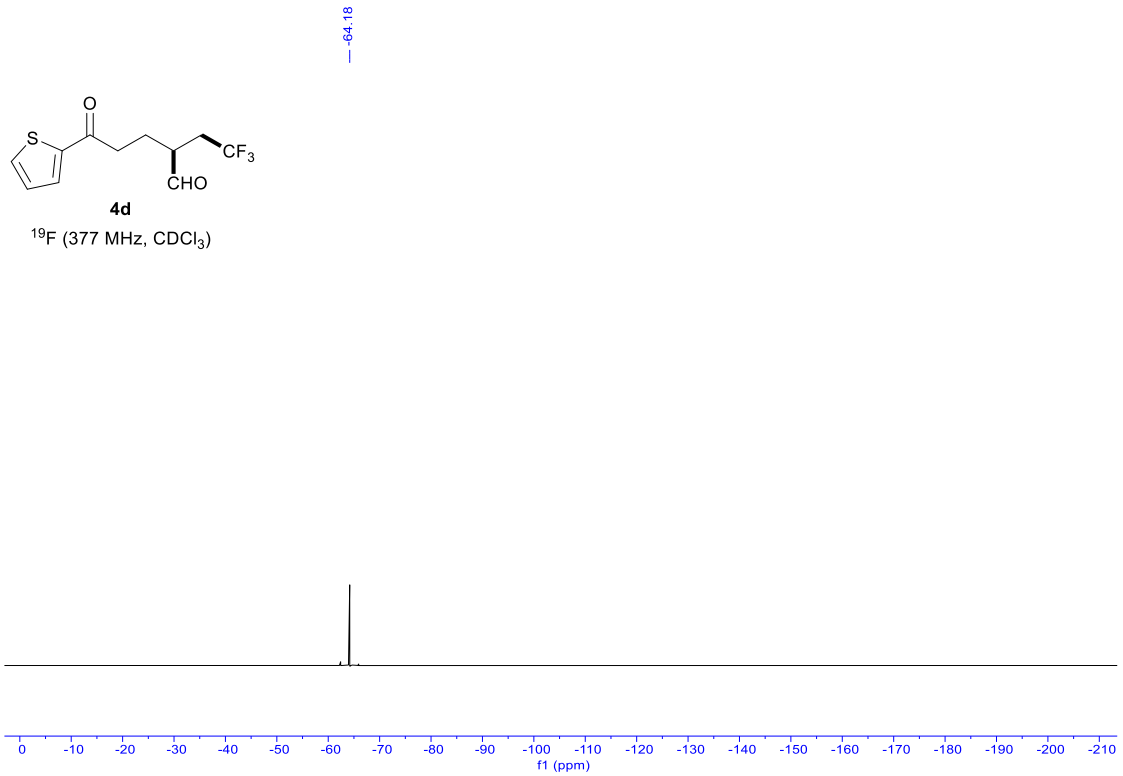
4d

^{1}H (400 MHz, $CDCl_3$)



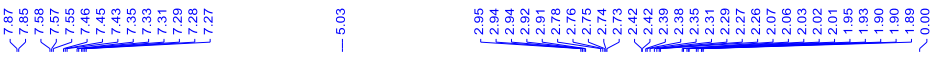
4d

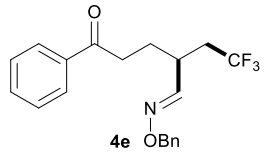
^{13}C (101 MHz, $CDCl_3$)



4d

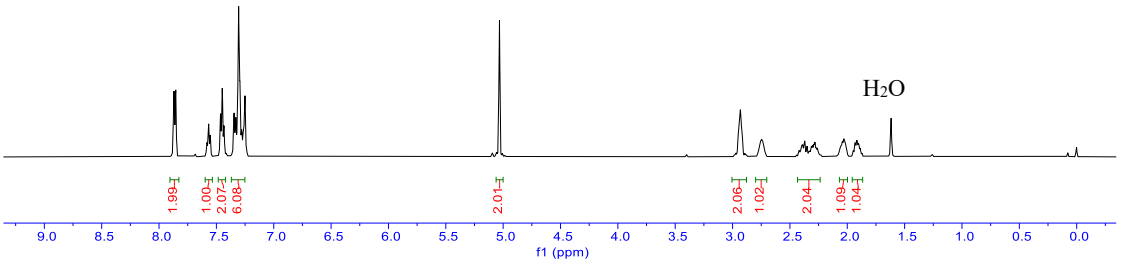
^{19}F (377 MHz, $CDCl_3$)

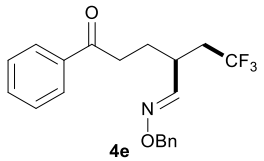




4e

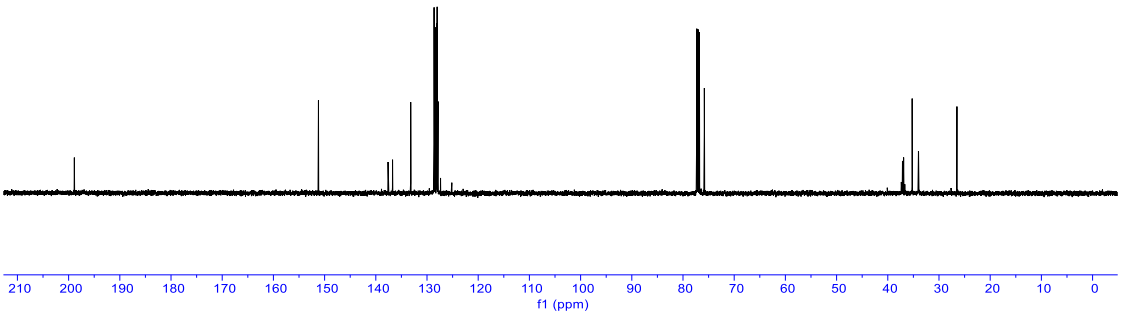
^{1}H (500 MHz, $CDCl_3$)

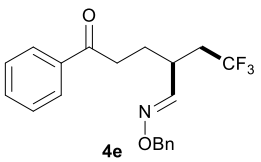




4e

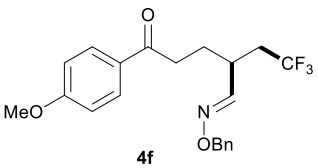
^{13}C (126 MHz, $CDCl_3$)





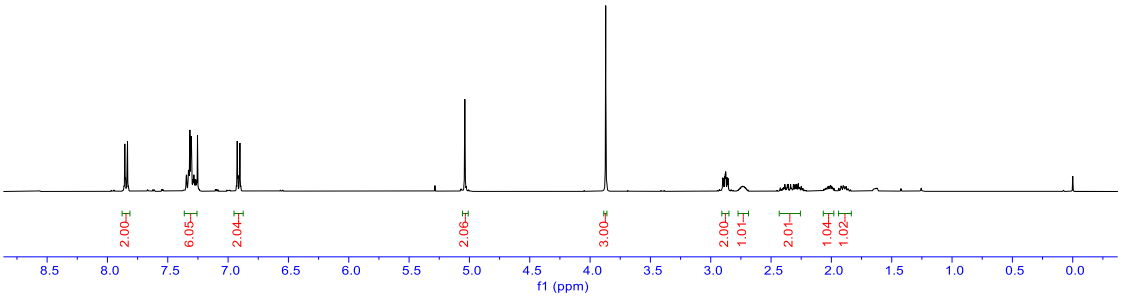
4e

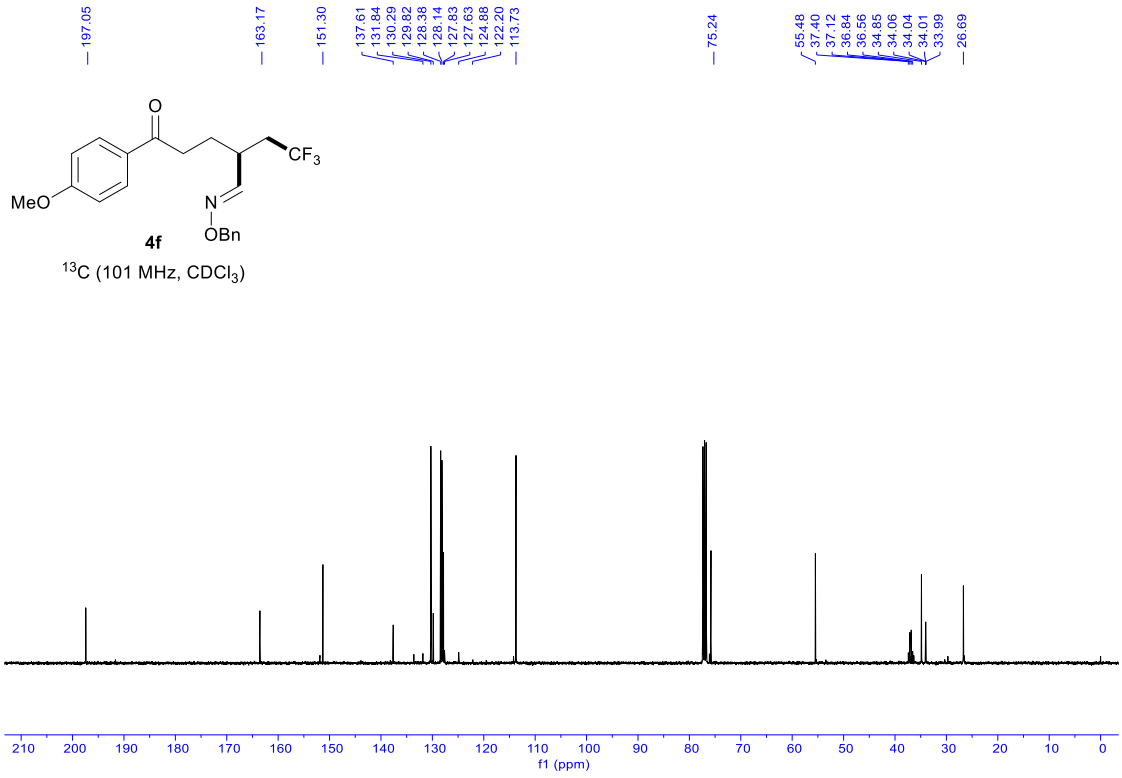
^{19}F (377 MHz, $CDCl_3$)

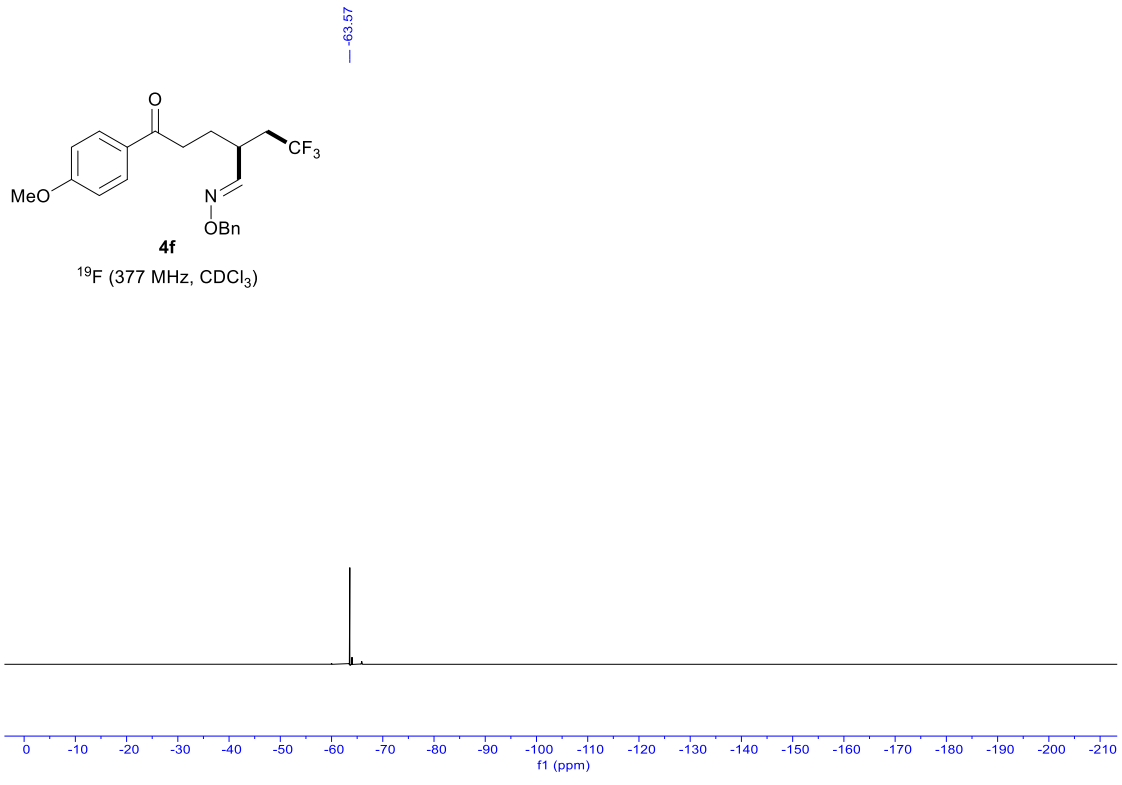


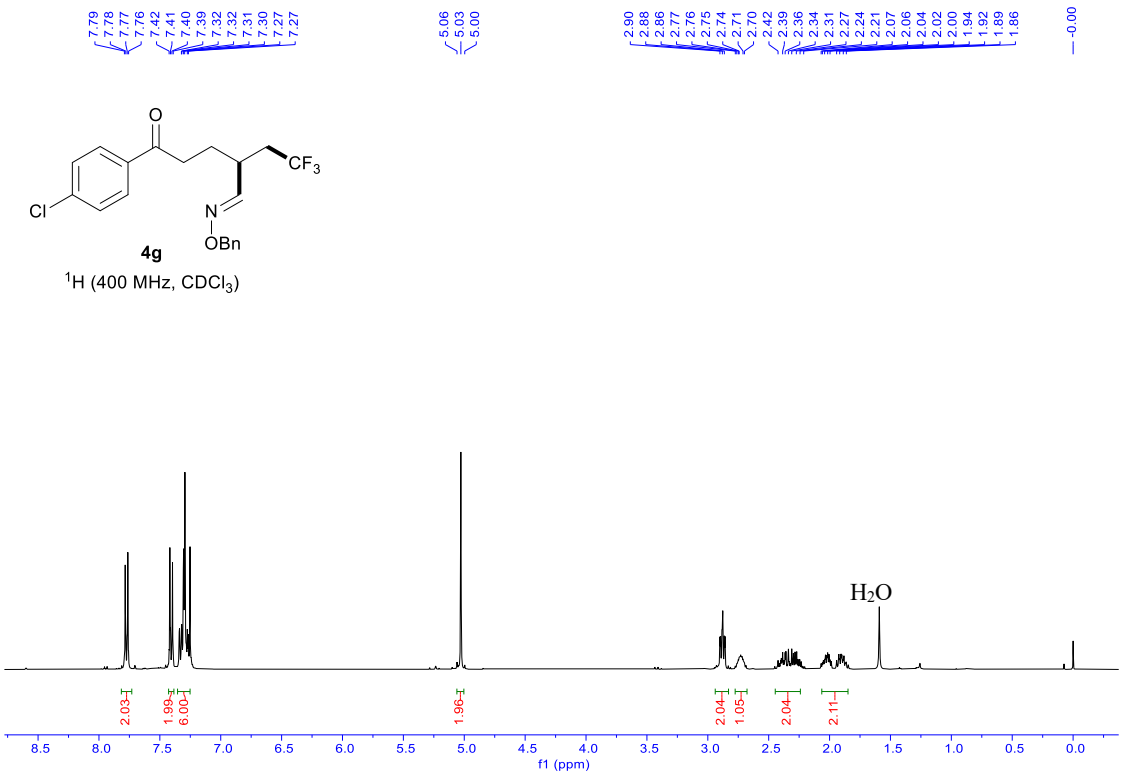
4f

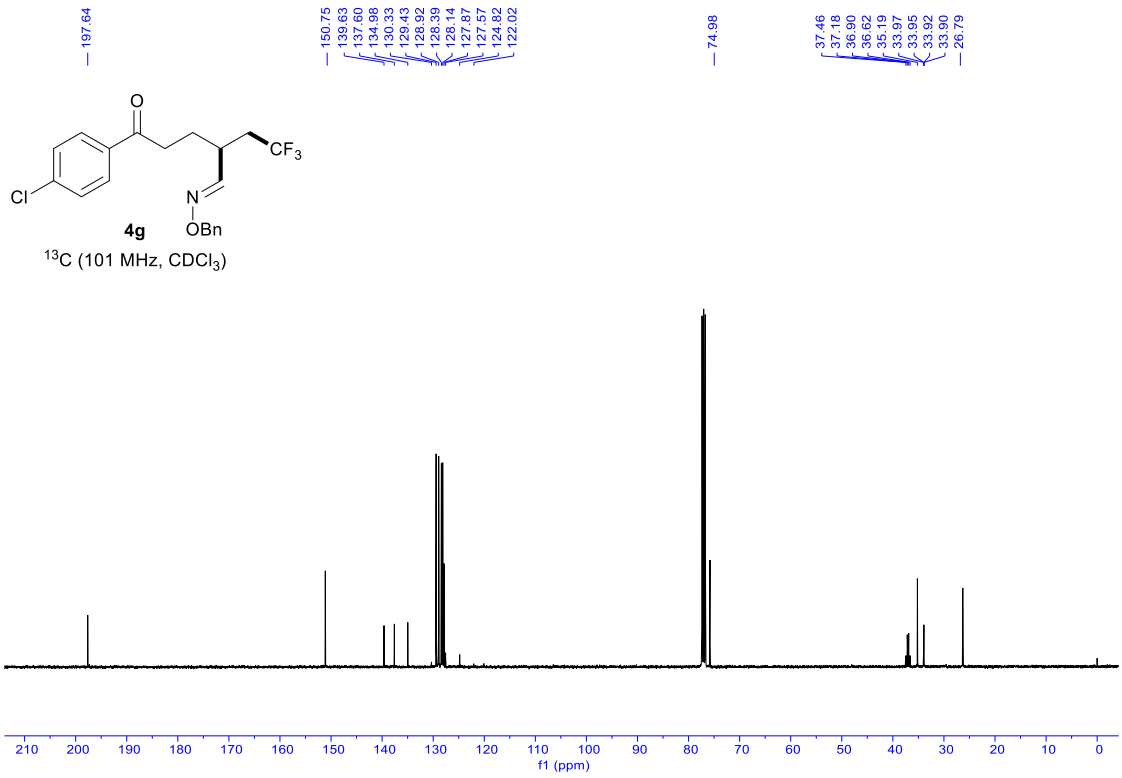
^{1}H (400 MHz, $CDCl_3$)

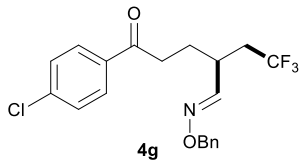



197.05
163.17
151.30
137.61
131.84
130.29
129.82
128.38
128.14
127.83
127.63
124.88
122.20
113.73
75.24
55.48
37.40
37.12
36.84
36.56
34.85
34.06
34.04
34.01
33.99
26.69
O
CF3
MeO
N
OBn
4f
13C (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.57
O
CF3
MeO
N
OBn
4f
19F (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

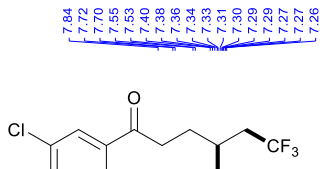

7.79
7.78
7.77
7.76
7.42
7.41
7.40
7.39
7.32
7.32
7.31
7.30
7.27
7.27
5.06
5.03
5.00
2.90
2.88
2.86
2.77
2.76
2.75
2.74
2.71
2.70
2.42
2.39
2.36
2.34
2.31
2.27
2.24
2.21
2.07
2.06
2.04
2.02
2.00
1.94
1.92
1.89
1.86
-0.00
O
CF3
Cl
N
OBn
4g
1H (400 MHz, CDCl3)
H2O
2.03
1.99
6.00
1.96
2.04
1.05
2.04
2.11
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


197.64
150.75
139.63
137.60
134.98
130.33
129.43
128.92
128.39
128.14
127.87
127.57
124.82
122.02
74.98
37.46
37.18
36.90
36.62
35.19
33.97
33.95
33.92
33.90
26.79
O
CF3
Cl
N
OBn
4g
13C (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



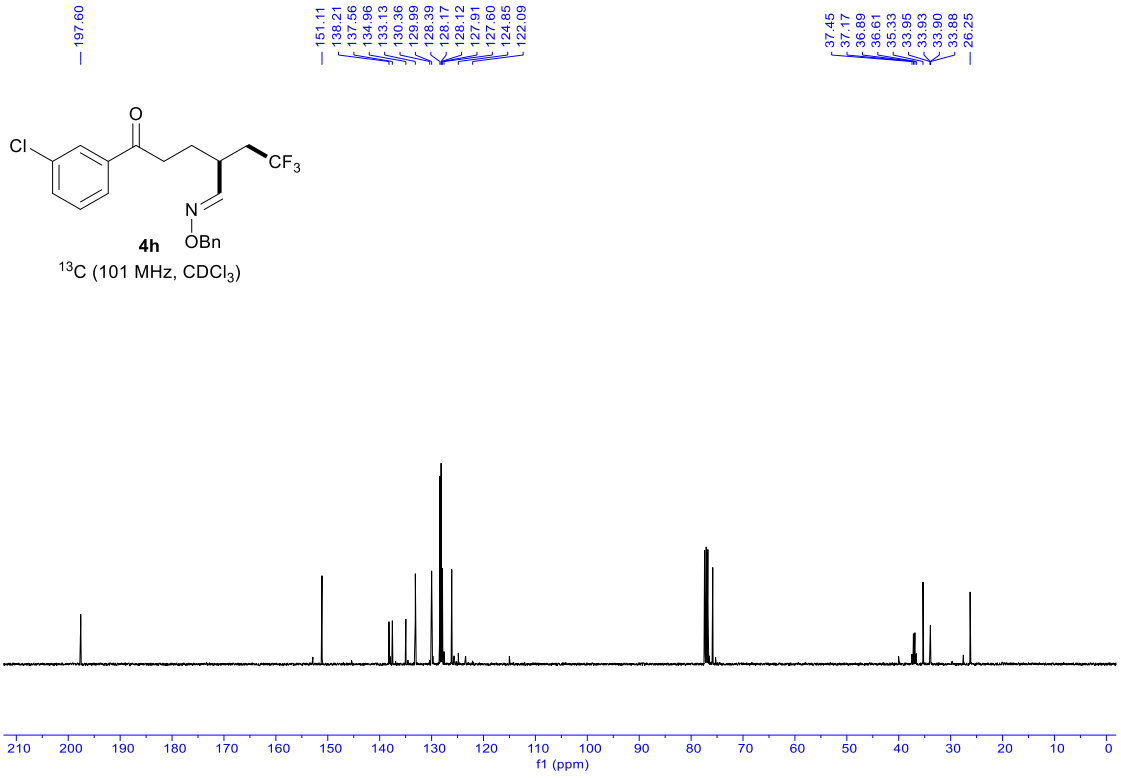
4g

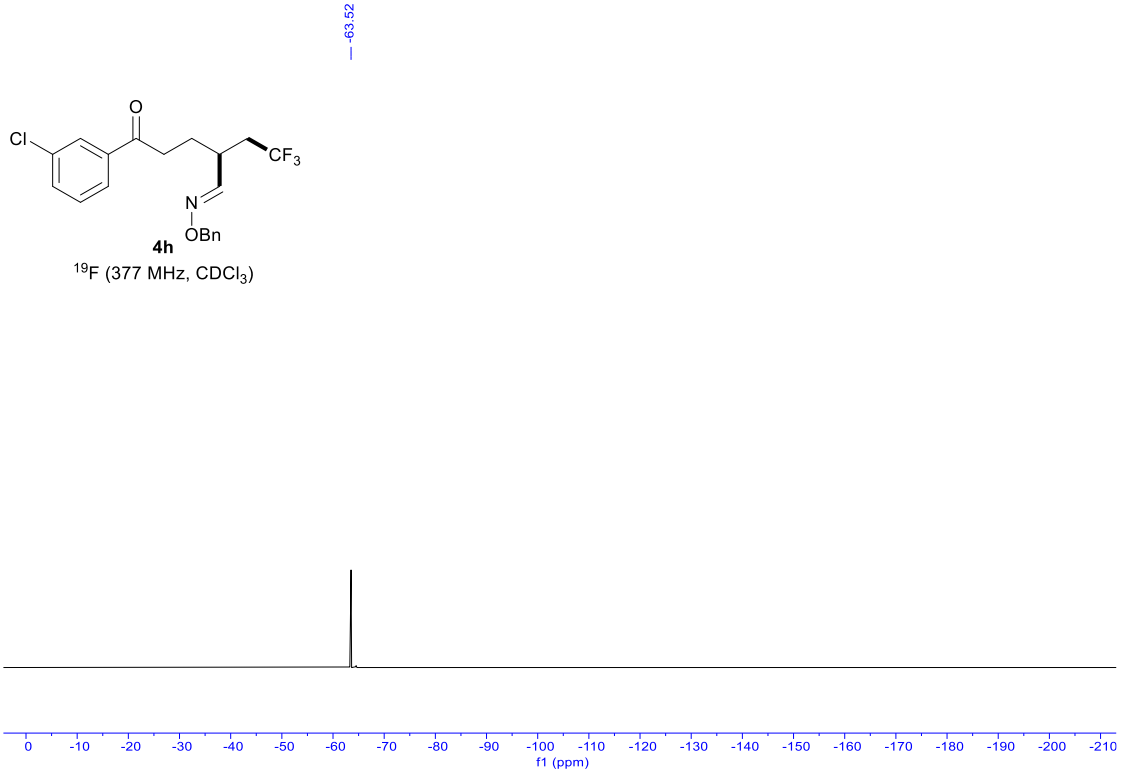
^{19}F (377 MHz, $CDCl_3$)

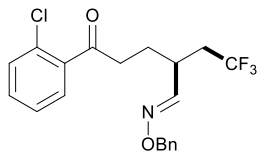


4h

^{1}H (400 MHz, $CDCl_3$)

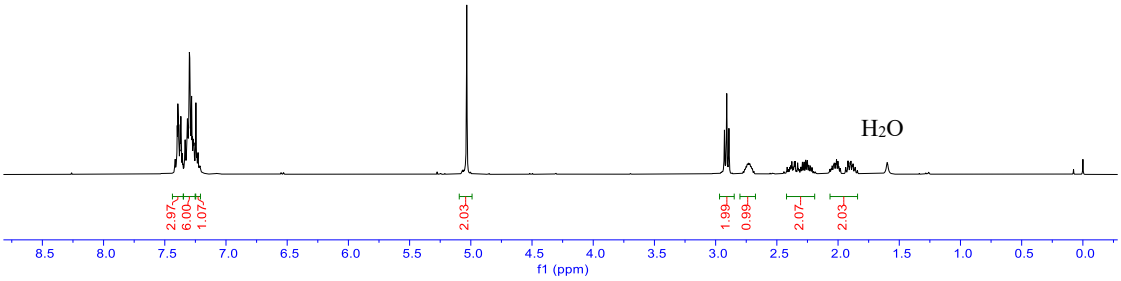

197.60
151.11
138.21
137.56
134.96
133.13
130.36
129.99
128.39
128.17
128.12
127.91
127.60
124.85
122.09
37.45
37.17
36.89
36.61
35.33
33.95
33.93
33.90
33.88
26.25
O
Cl
CF3
N
OBn
4h
13C (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

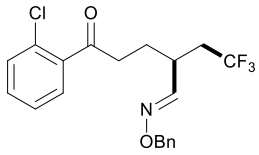

-63.52
O
Cl
CF3
N
OBn
4h
19F (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



4i

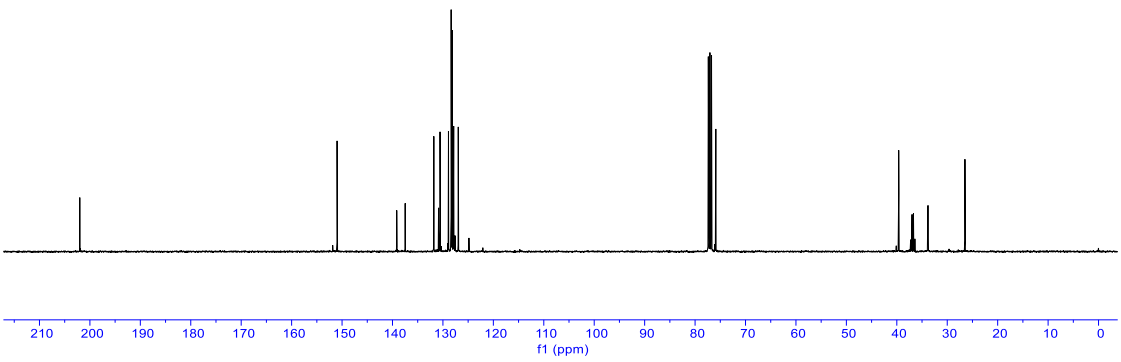
^{1}H (400 MHz, $CDCl_3$)

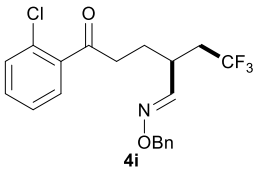




4i

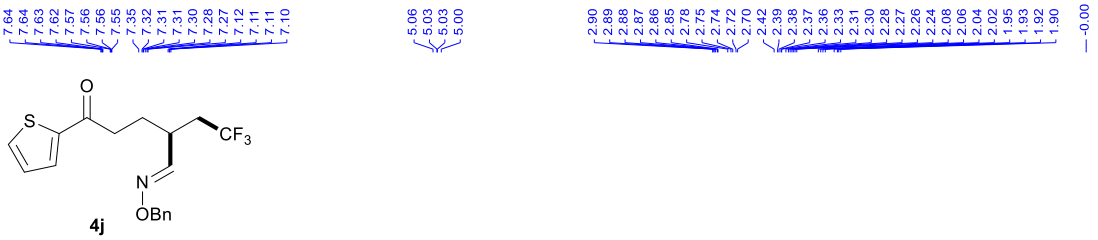
^{13}C (101 MHz, $CDCl_3$)





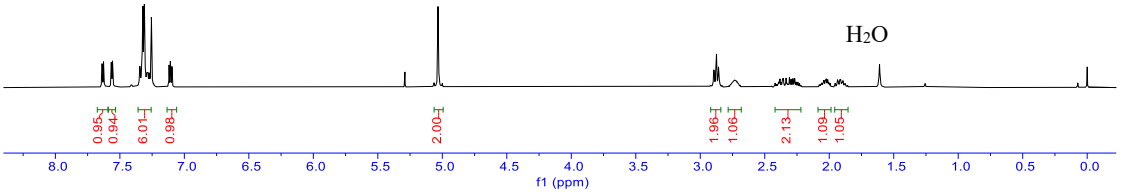
4i

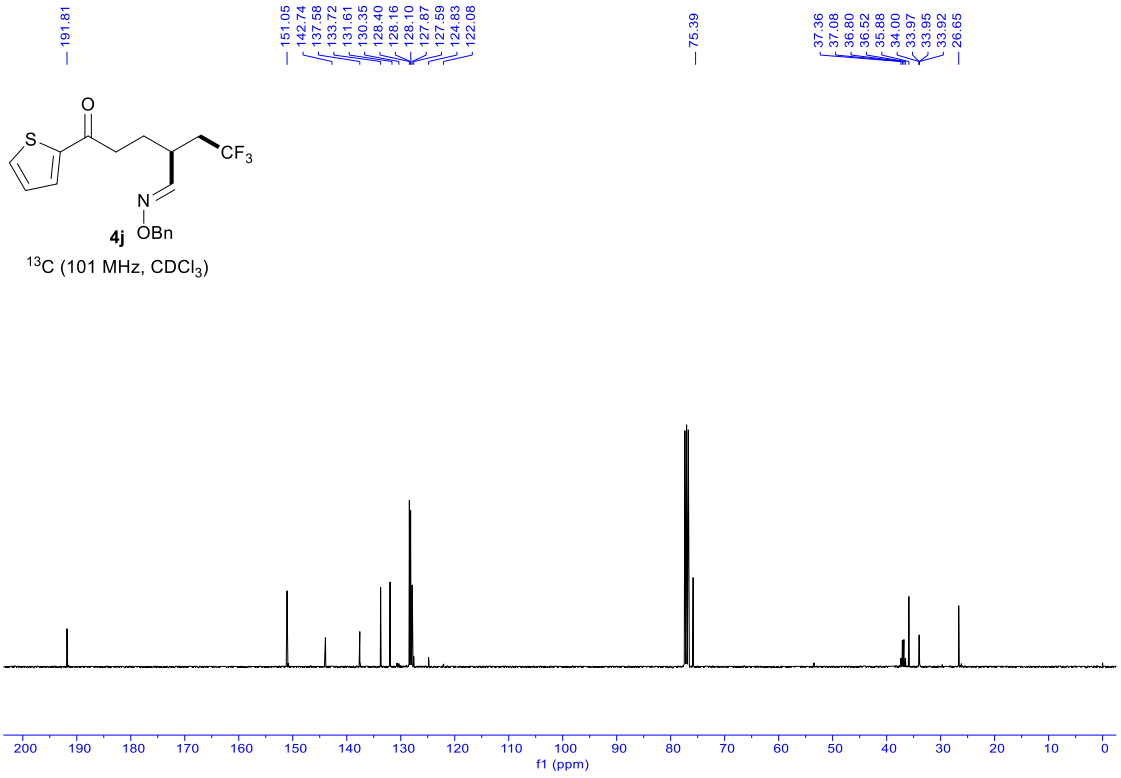
^{19}F (377 MHz, $CDCl_3$)



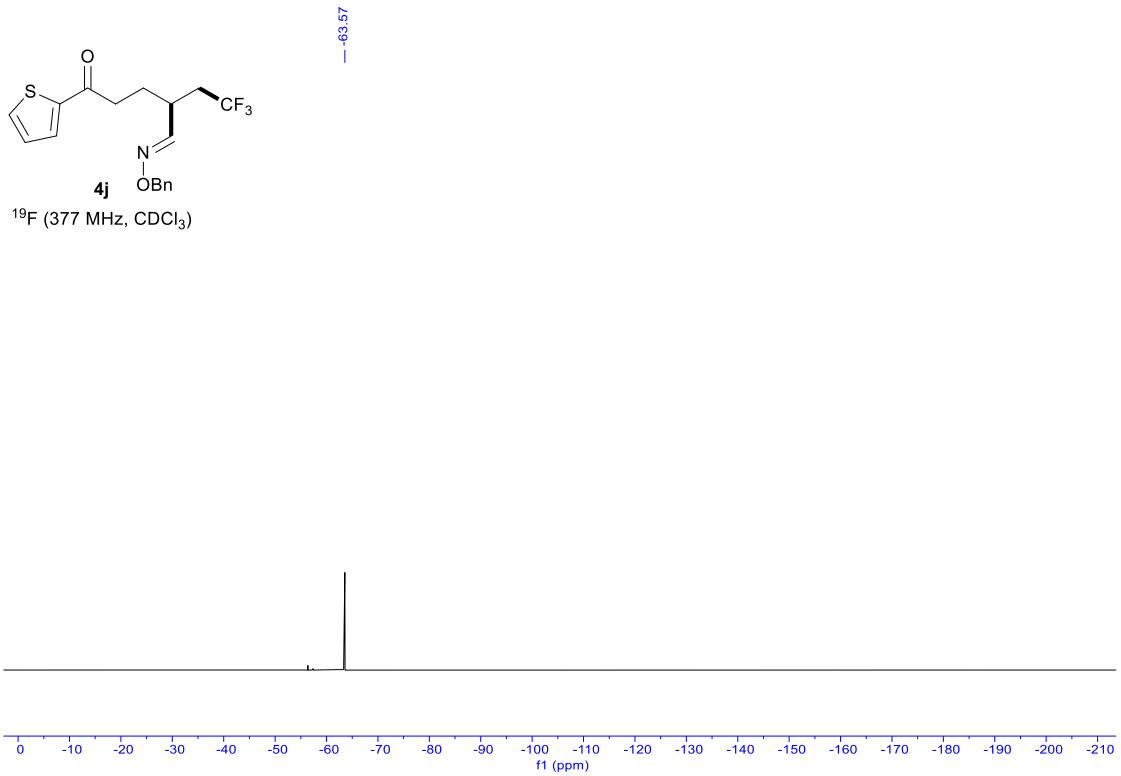
4j

^{1}H (400 MHz, $CDCl_3$)

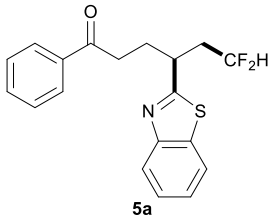




^{13}C (101 MHz, $CDCl_3$)

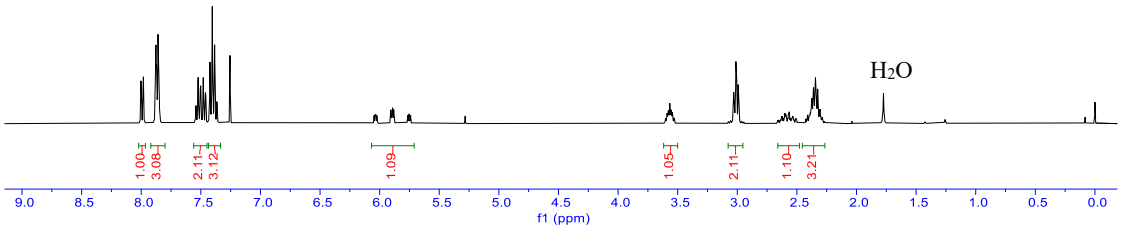


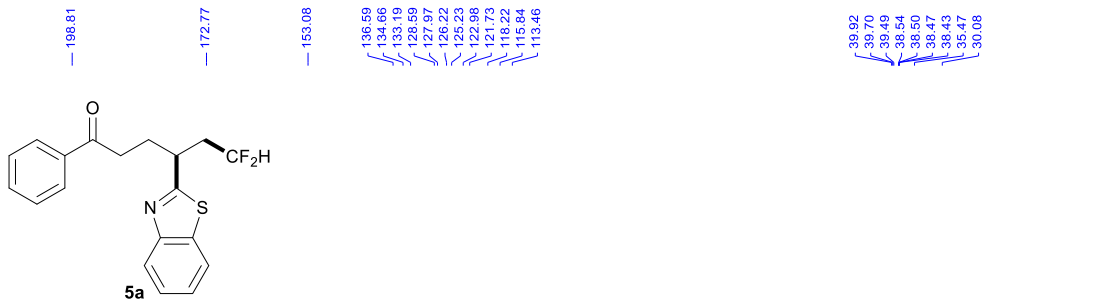
^{19}F (377 MHz, $CDCl_3$)



5a

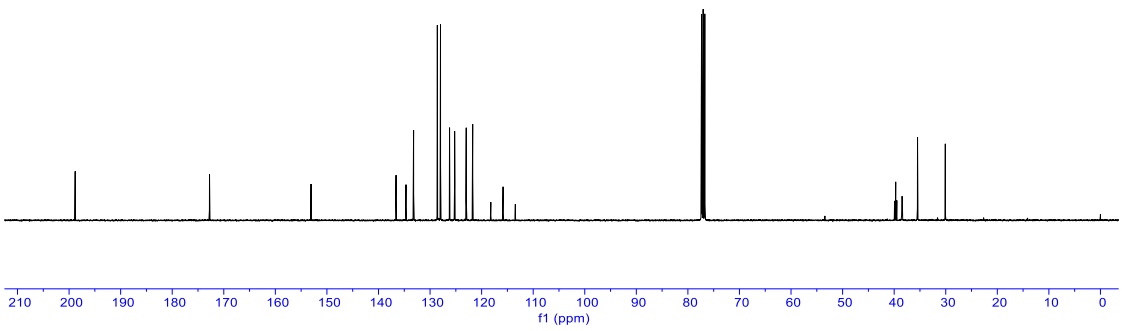
^{1}H (400 MHz, $CDCl_3$)

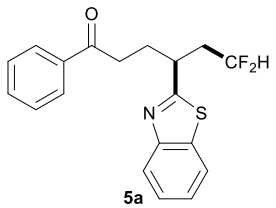




5a

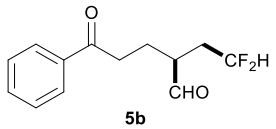
^{13}C (101 MHz, $CDCl_3$)





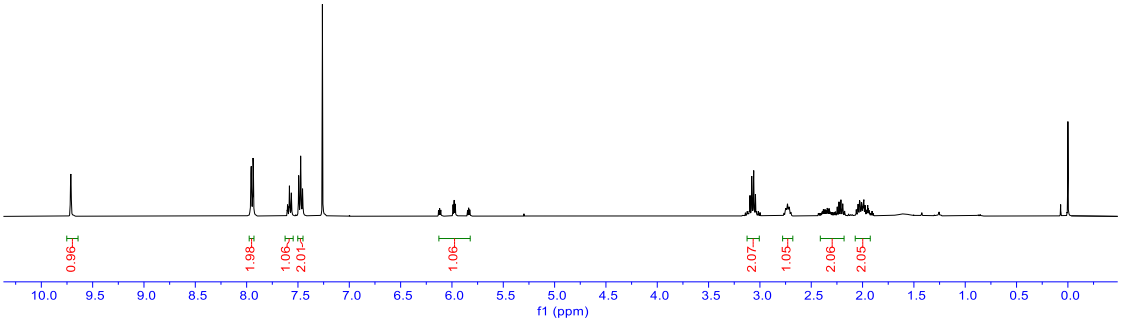
5a

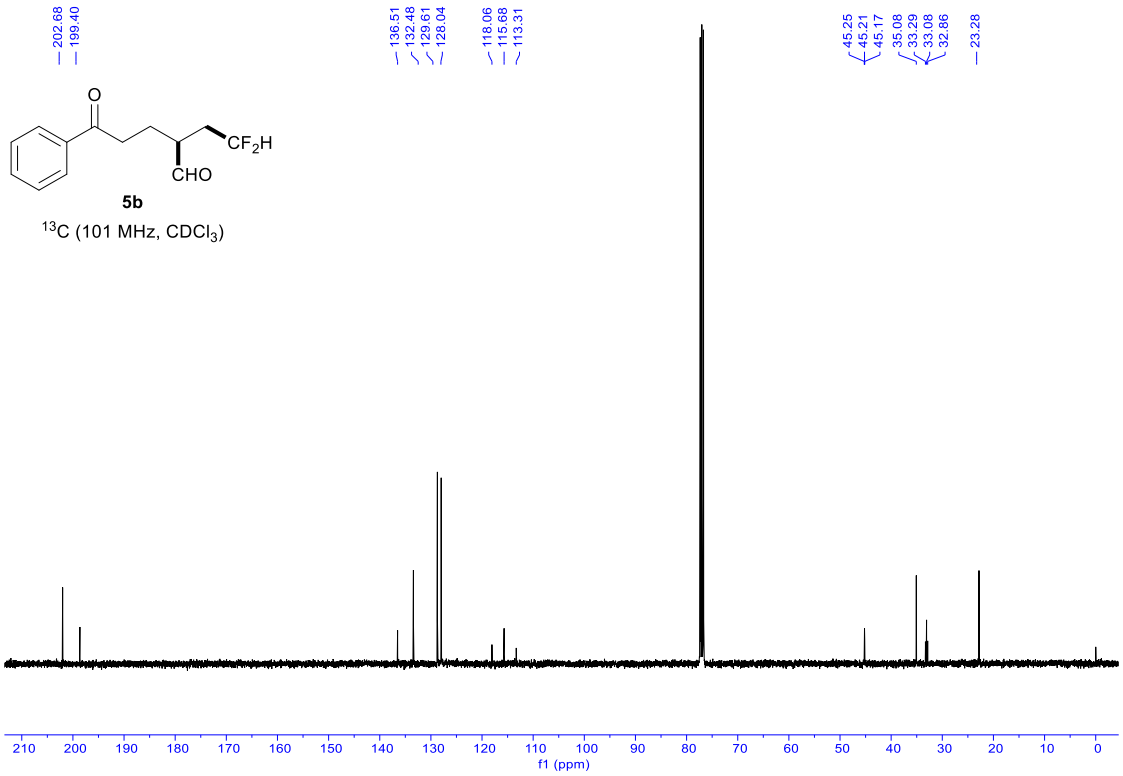
^{19}F (377 MHz, $CDCl_3$)



5b

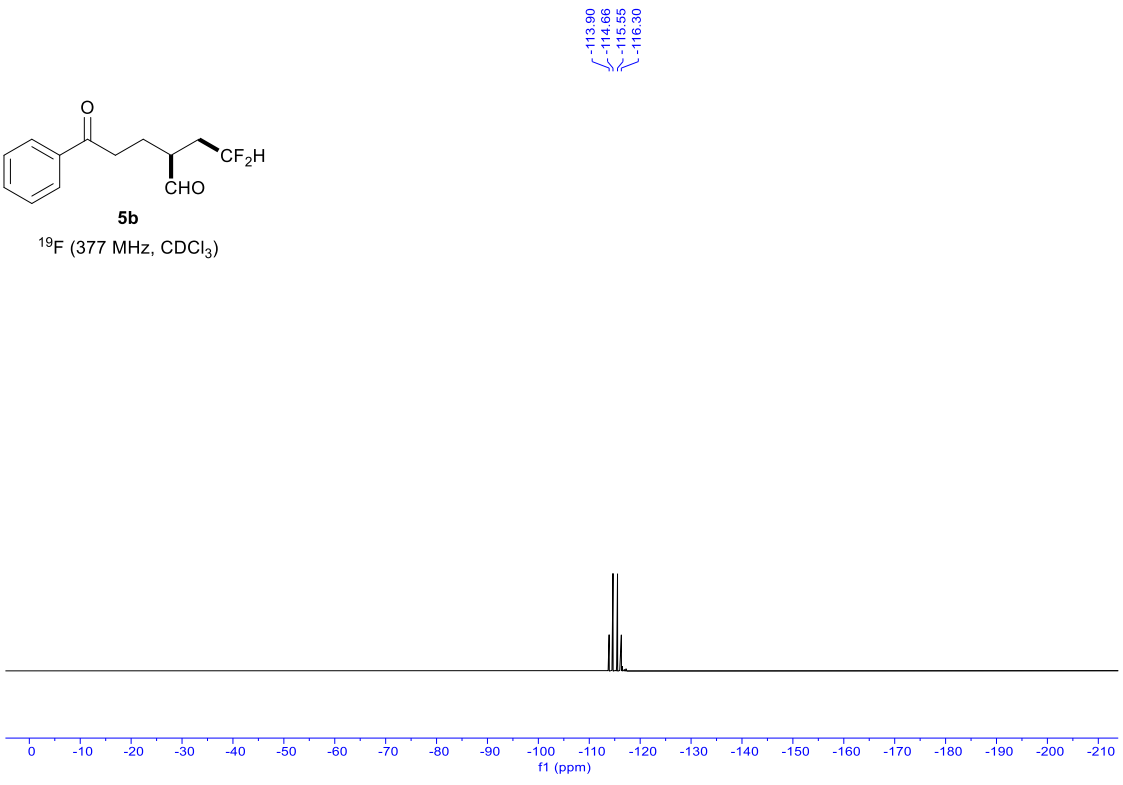
^{1}H (400 MHz, $CDCl_3$)





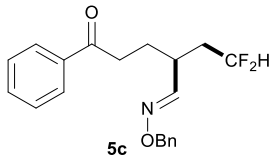
5b

^{13}C (101 MHz, $CDCl_3$)



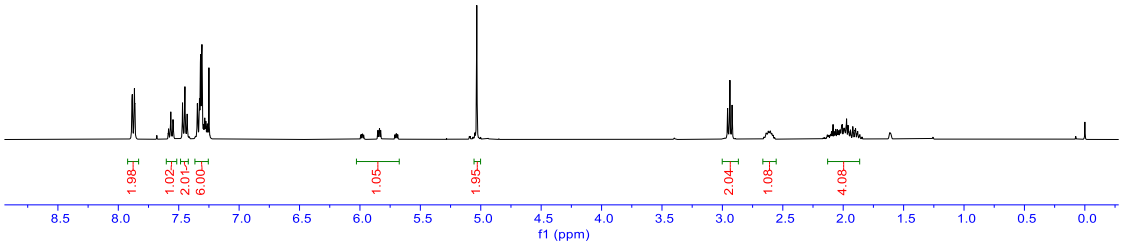
5b

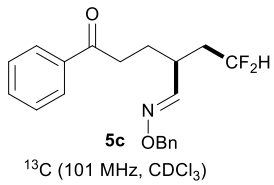
^{19}F (377 MHz, $CDCl_3$)



5c

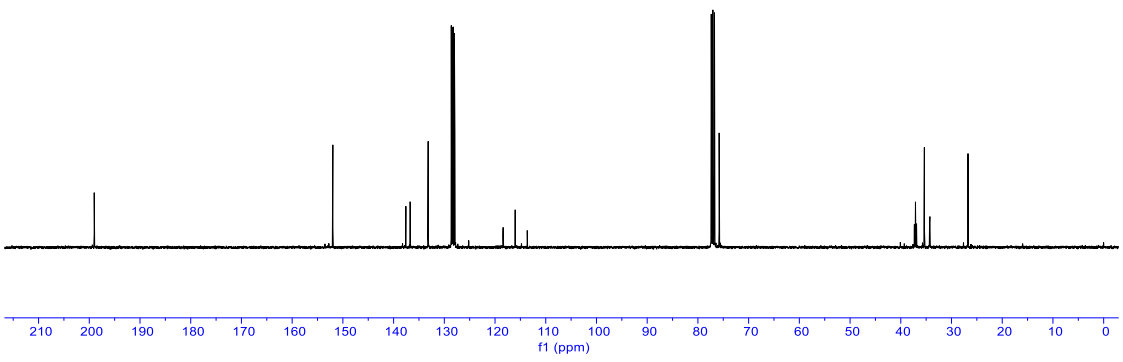
^{1}H (400 MHz, $CDCl_3$)

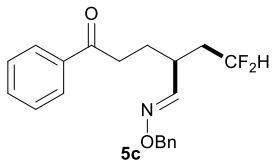




5c

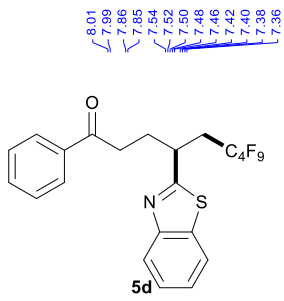
^{13}C (101 MHz, $CDCl_3$)





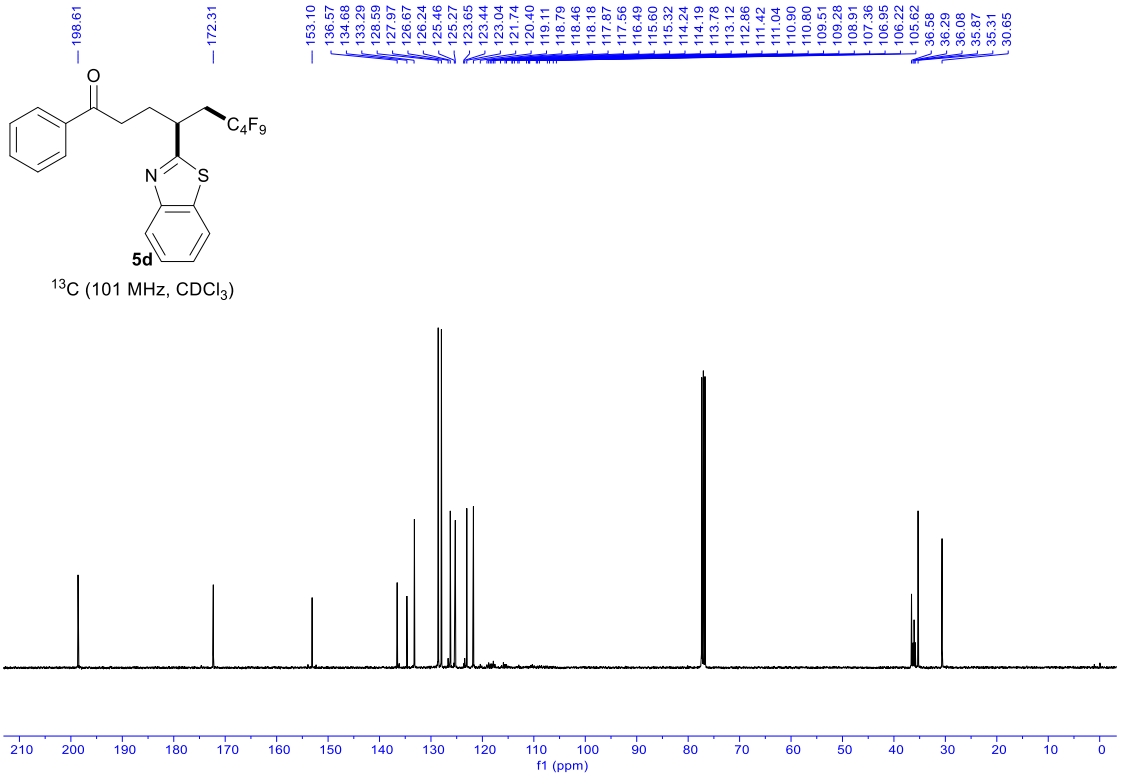
5c

^{19}F (377 MHz, $CDCl_3$)

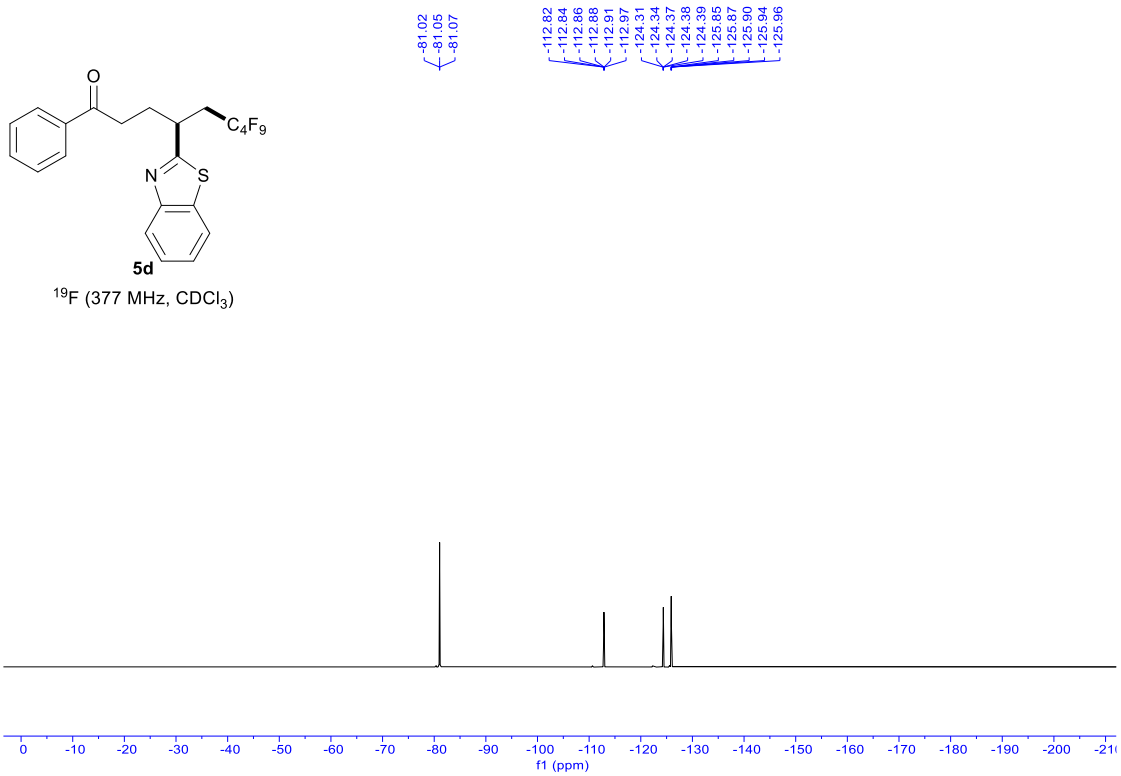


5d

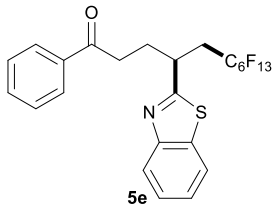
^{1}H (400 MHz, $CDCl_3$)



^{13}C (101 MHz, $CDCl_3$)

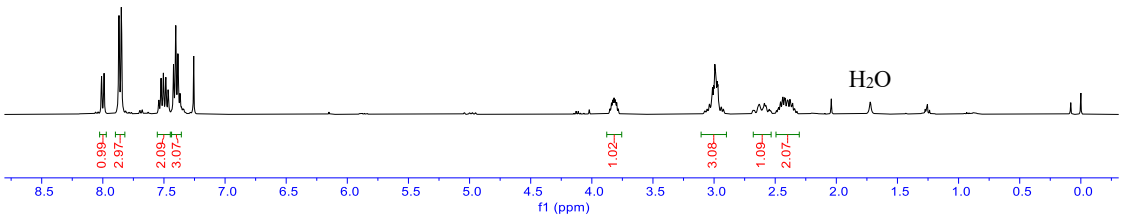


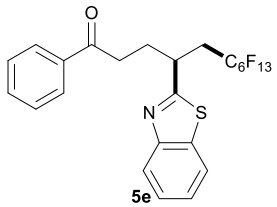
^{19}F (377 MHz, $CDCl_3$)



5e

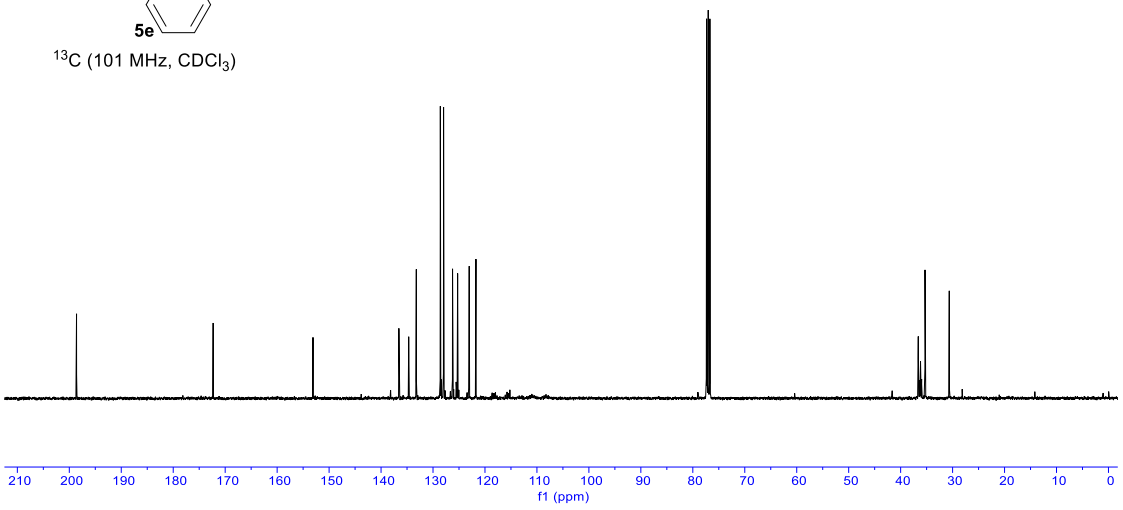
^{1}H (400 MHz, $CDCl_3$)

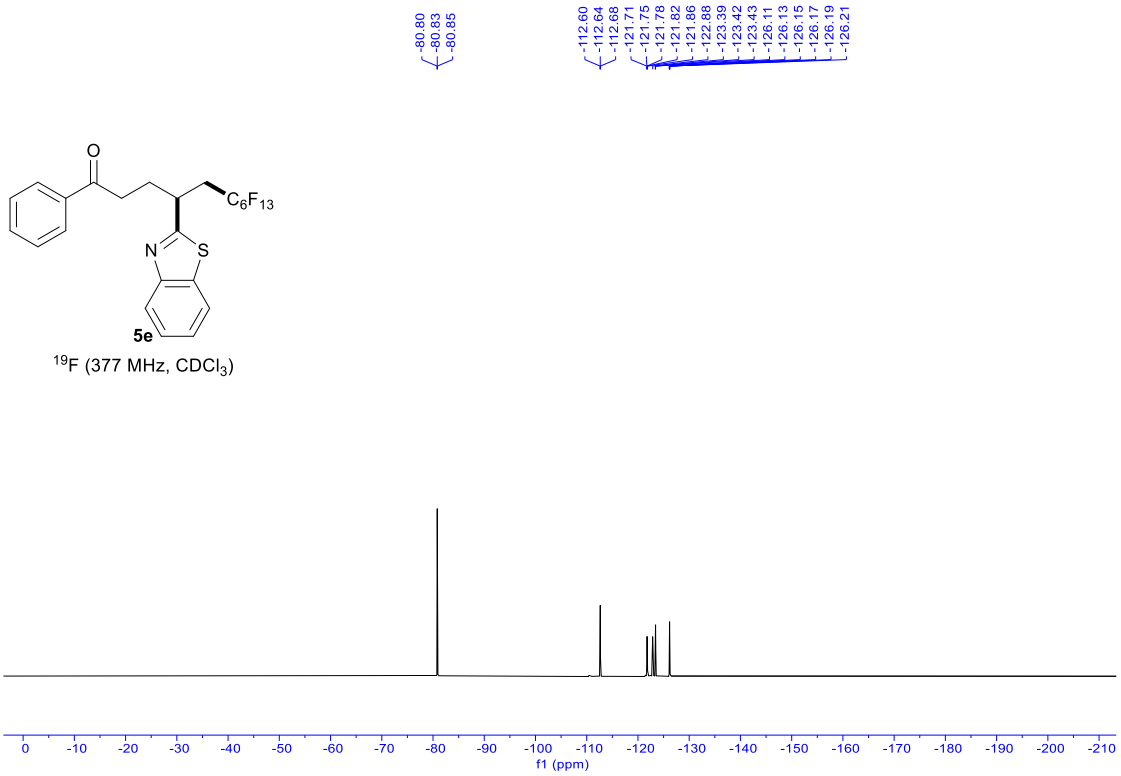


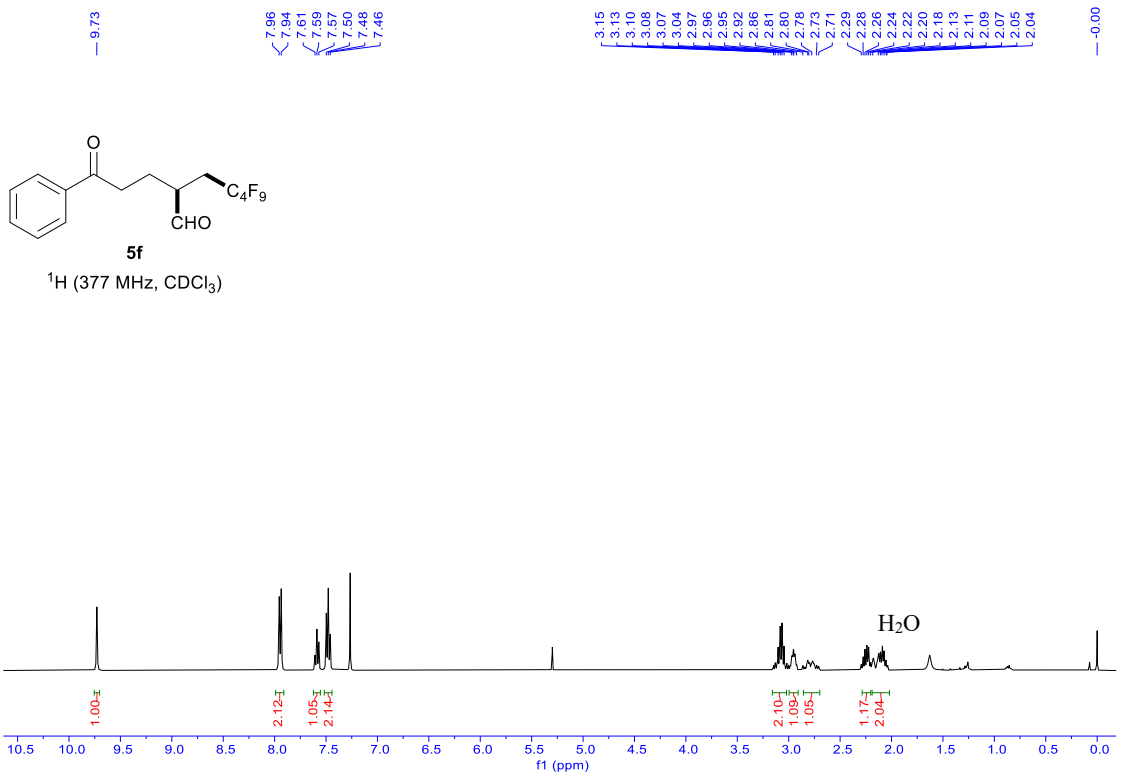


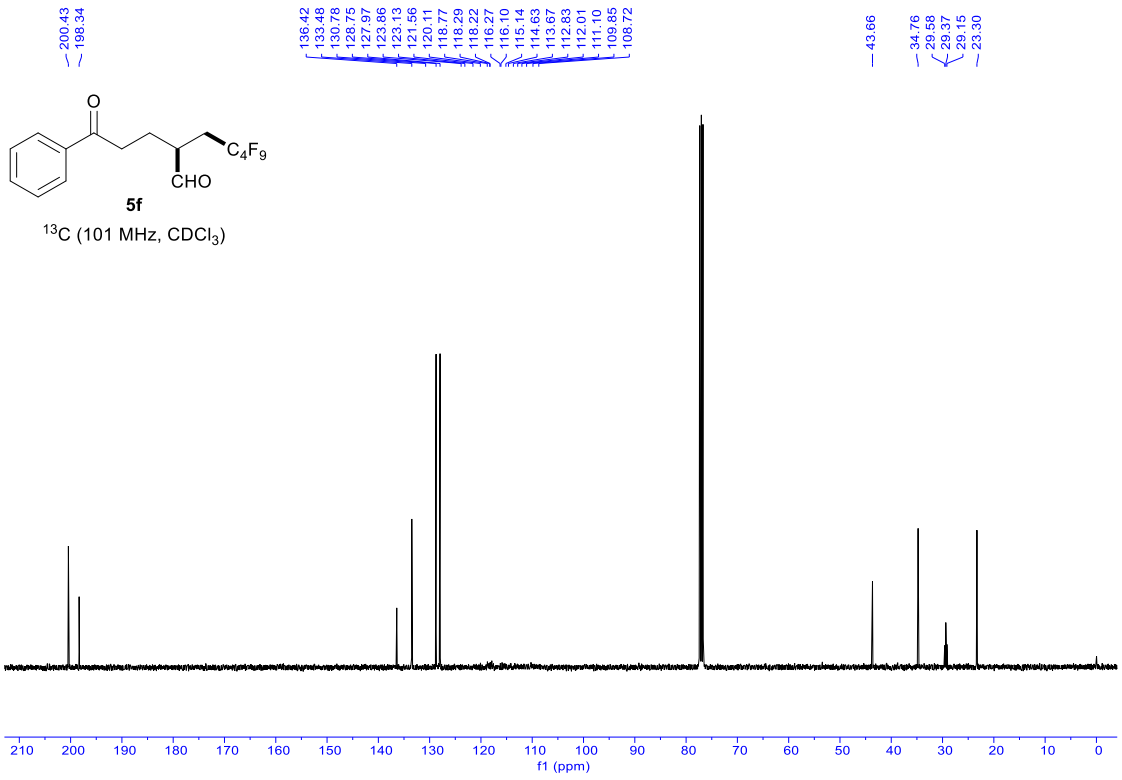
5e

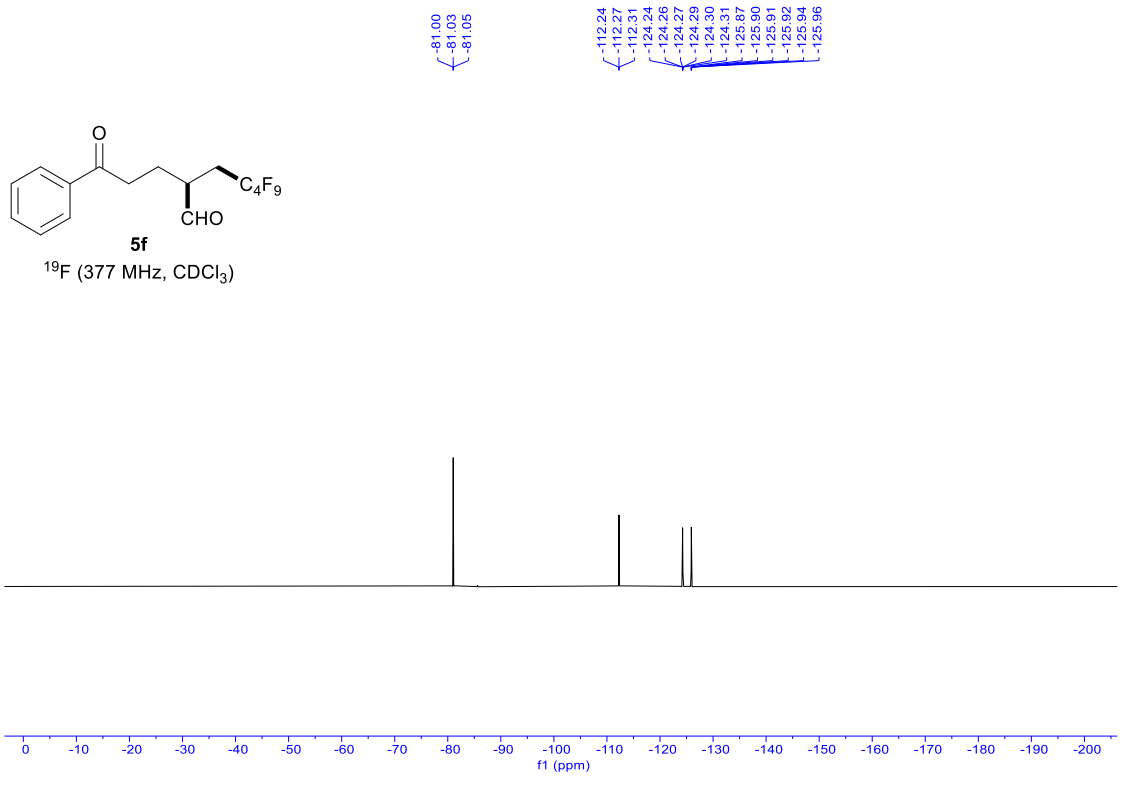
^{13}C (101 MHz, $CDCl_3$)

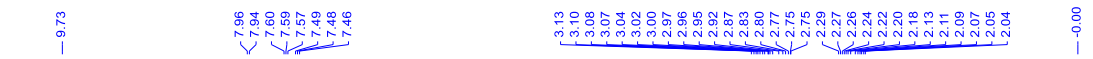


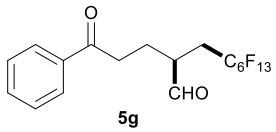

-80.80
-80.83
-80.85
-112.60
-112.64
-112.68
-121.71
-121.75
-121.78
-121.82
-121.86
-122.88
-123.39
-123.42
-123.43
-126.11
-126.13
-126.15
-126.17
-126.19
-126.21
O
C6F13
N
S
5e
19F (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


9.73
7.96
7.94
7.61
7.59
7.57
7.50
7.48
7.46
3.15
3.13
3.10
3.08
3.07
3.04
2.97
2.96
2.95
2.92
2.86
2.81
2.80
2.78
2.73
2.71
2.29
2.28
2.26
2.24
2.22
2.20
2.18
2.13
2.11
2.09
2.07
2.05
2.04
0.00
O
C4F9
CHO
5f
1H (377 MHz, CDCl3)
H2O
1.00
2.12
1.05
2.14
2.10
1.09
1.05
1.17
2.04
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


200.43
198.34
136.42
133.48
130.78
128.75
127.97
123.86
123.13
121.56
120.11
118.77
118.29
118.22
116.27
116.10
115.14
114.63
113.67
112.83
112.01
111.10
109.85
108.72
43.66
34.76
29.58
29.37
29.15
23.30
O
C4F9
CHO
5f
13C (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

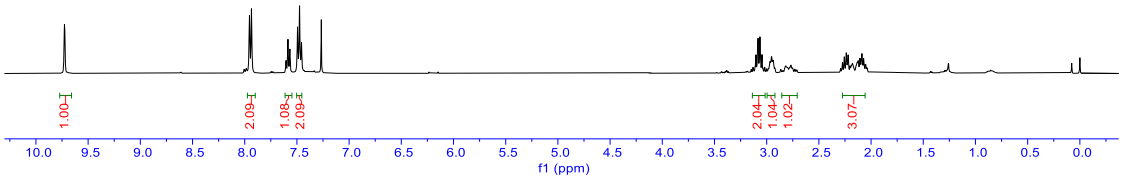

-81.00
-81.03
-81.05
-112.24
-112.27
-112.31
-124.24
-124.26
-124.27
-124.29
-124.30
-124.31
-125.87
-125.90
-125.91
-125.92
-125.94
-125.96
O
C4F9
CHO
5f
19F (377 MHz, CDCl3)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

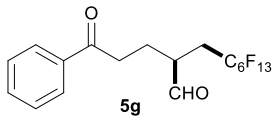




5g

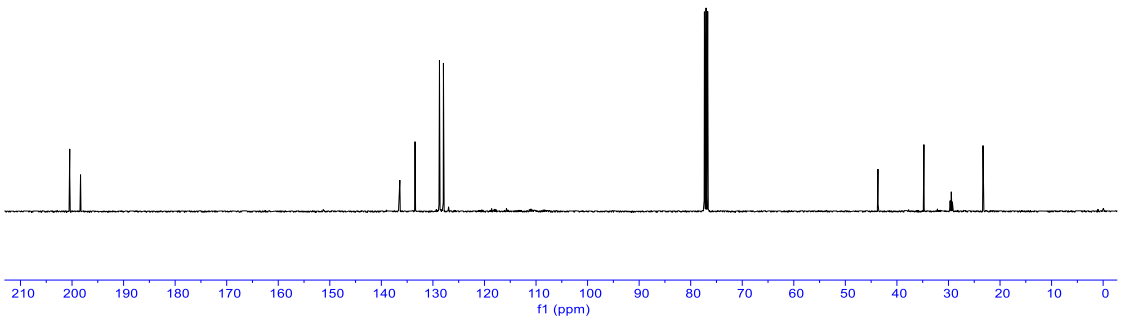
^{1}H (400 MHz, $CDCl_3$)

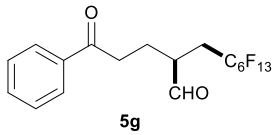




5g

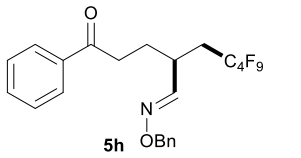
^{13}C (101 MHz, $CDCl_3$)





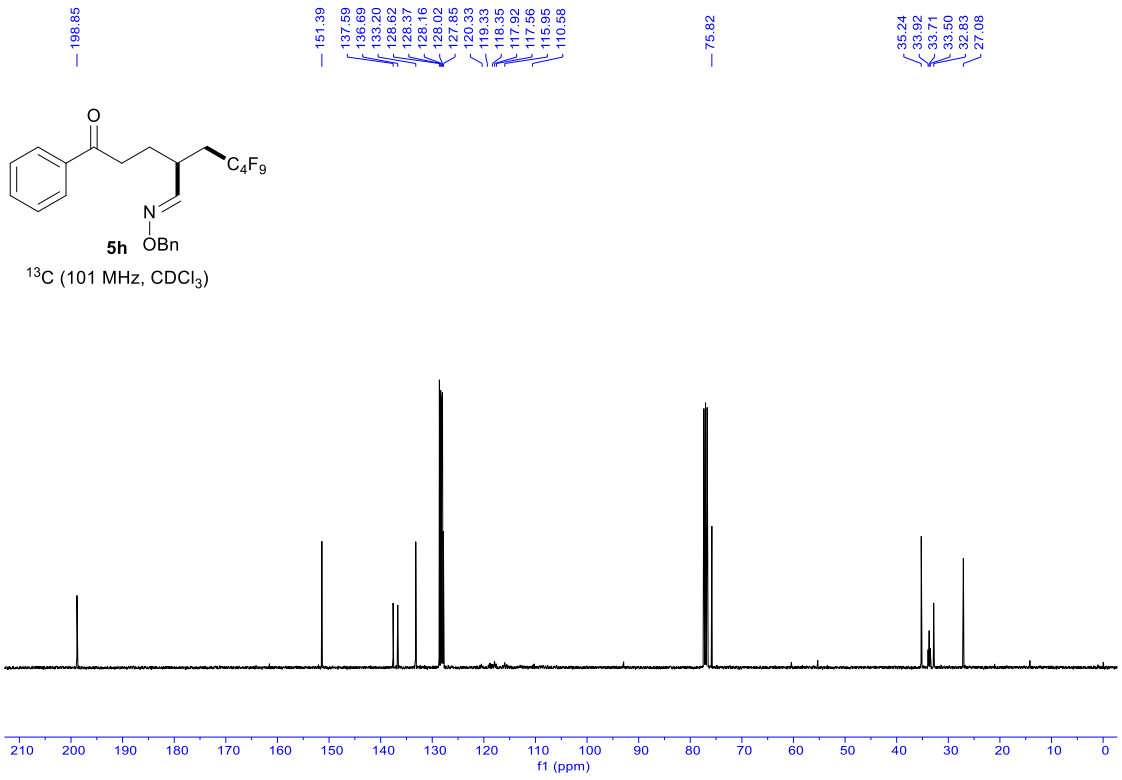
5g

^{19}F (377 MHz, $CDCl_3$)

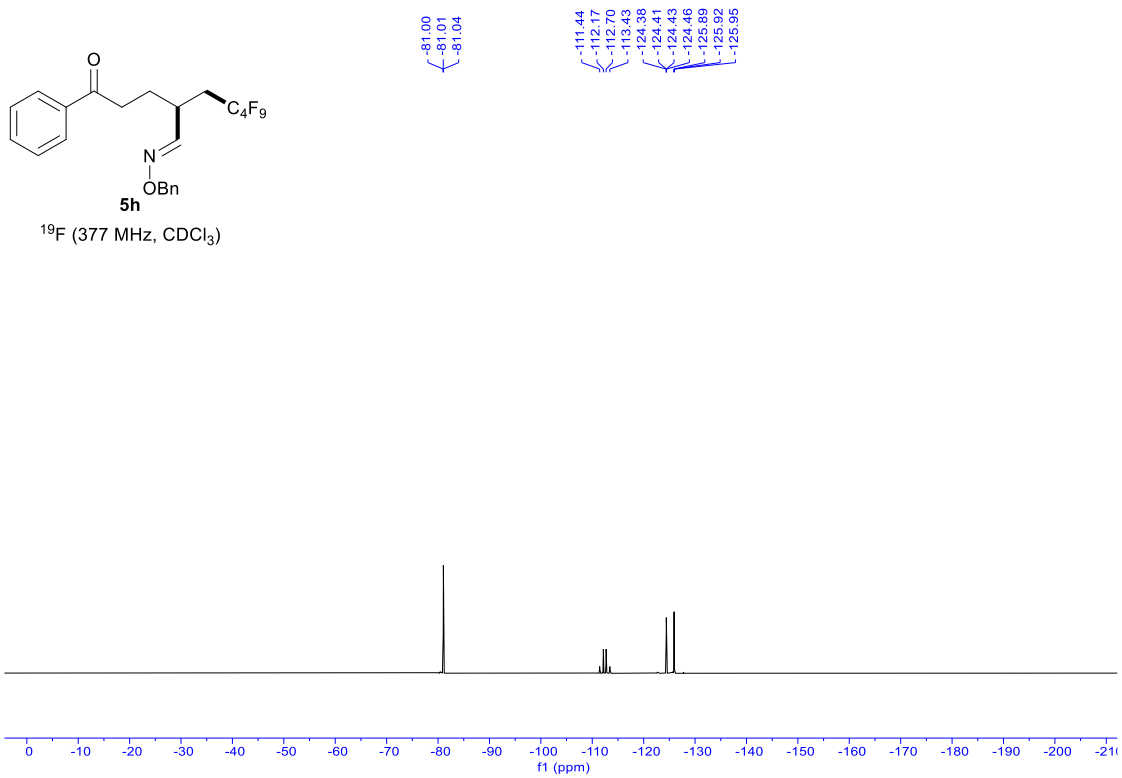


5h

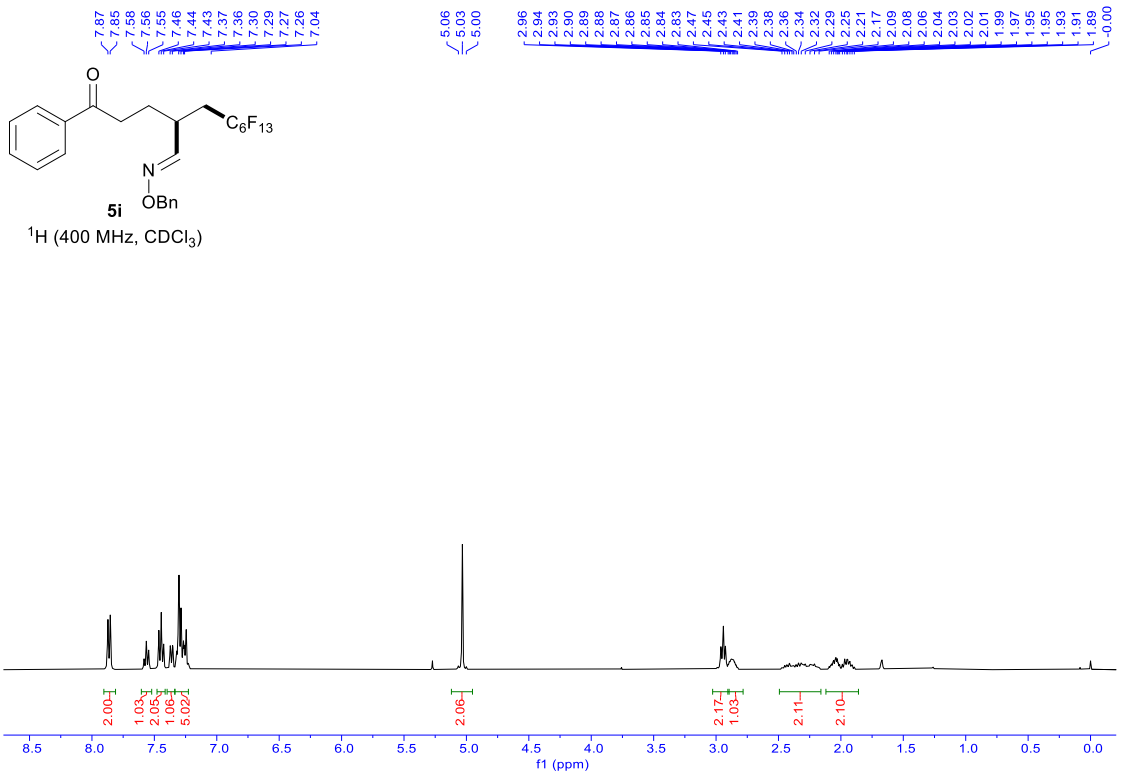
^{1}H (400 MHz, $CDCl_3$)

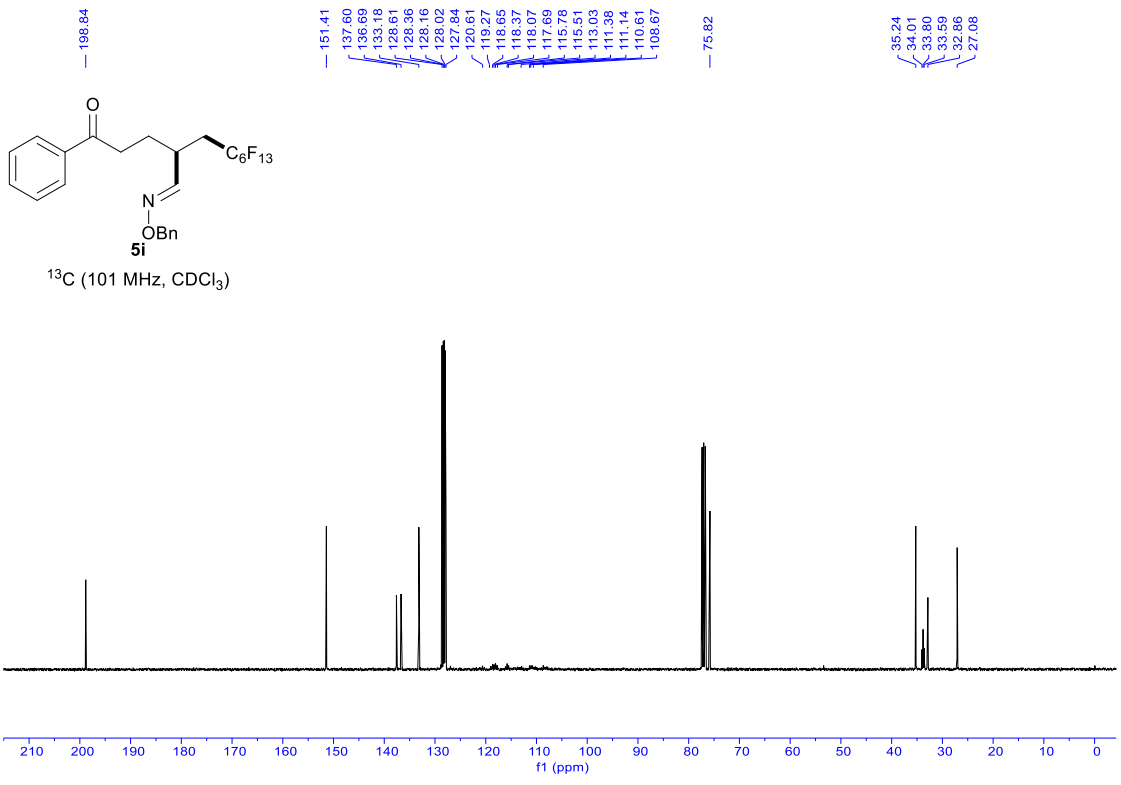


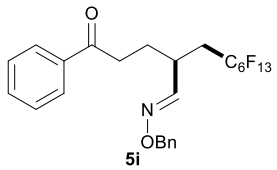
^{13}C (101 MHz, $CDCl_3$)



^{19}F (377 MHz, $CDCl_3$)


7.87
7.85
7.58
7.56
7.55
7.46
7.44
7.43
7.37
7.36
7.30
7.29
7.27
7.26
7.04
5.06
5.03
5.00
2.96
2.94
2.93
2.90
2.89
2.88
2.87
2.86
2.85
2.84
2.83
2.47
2.45
2.43
2.41
2.39
2.38
2.36
2.34
2.32
2.29
2.25
2.21
2.17
2.09
2.08
2.06
2.04
2.03
2.02
2.01
1.99
1.97
1.95
1.95
1.93
1.91
1.89
-0.00
O
C6F13
N
OBn
5i
1H (400 MHz, CDCl3)
2.00
1.03
2.05
1.06
5.02
2.06
2.17
1.03
2.11
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


198.84
151.41
137.60
136.69
133.18
128.61
128.36
128.16
128.02
127.84
120.61
119.27
118.65
118.37
118.07
117.69
115.78
115.51
113.03
111.38
111.14
110.61
108.67
75.82
35.24
34.01
33.80
33.59
32.86
27.08
O
C6F13
N
OBn
5i
13C (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



5i

^{19}F (377 MHz, $CDCl_3$)