

# Ball-milling and piezoelectric materials enabled radical trifluoromethylation of enamides and acrylamides

## Supporting Information

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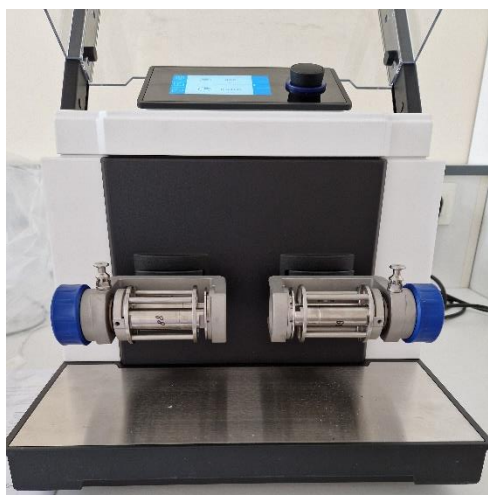
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## 1. General information

Mechanochemical reactions were conducted using a RETSCH® MIXER MILL MM 400. All reactions were performed with 7.5 mm stainless steel balls and 5 ml steel jars. Reaction mixtures were decanted in an Eppendorf™ Centrifuge 5804 R using 15 mL Eppendorf tube from Nest. Column chromatographies were completed on Biotage® Isolera™ Systems using silica gel 60 M (40-63  $\mu\text{m}$ ) obtained from Macherey-Nagel or Merck PTLC on silica gel 60 F254, 2 mm. A 25 g and 40 g puriFlash® Columns from Intershim were used to complete the purification. Analytical thin-layer chromatography was conducted on 0.20 mm pre-coated silica gel 60 aluminum plates with F-254 indicator (Alugram® Xtra SIL G/UV<sub>254</sub>) from Macherey-Nagel and visualized by UV light 254 nm and/or chemical staining with a  $\text{KMnO}_4$  solution.

$^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (101 MHz), and  $^{19}\text{F}$  (377 MHz) NMR spectra were recorded on a Bruker DXP 400 MHz spectrometer in  $\text{CDCl}_3$  unless otherwise noted. Chemical shifts ( $\delta$ ) are quoted in ppm relative to the residual solvent peak of  $\text{CDCl}_3$  ( $^1\text{H}$ :  $\delta_{\text{H}} = 7.26$  ppm and  $^{13}\text{C}$ :  $\delta_{\text{C}} = 77.16$  ppm) or to the peak of an internal standard tetramethylsilane ( $^1\text{H}$ :  $\delta_{\text{H}} = 0.00$  ppm) and relative to the internal standard  $\text{CFCl}_3$  ( $^{19}\text{F}$ :  $\delta_{\text{F}} = 0.0$  ppm). High resolution mass (HRMS) was carried out on a Waters LCP Premier XR spectrometer with a TOF analyzer.



**Figure S1.** Retsch MM400 vibrational ball mill



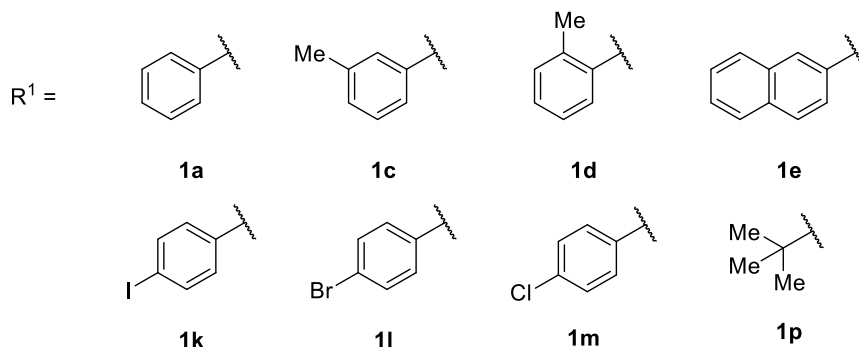
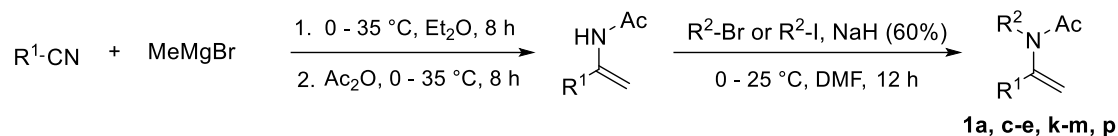
**Figure S2.** 5 mL jars and 7 mm balls

## 2. Materials

Anhydrous acetonitrile (MeCN) and Acetone were purchased from Acros Organics (Solvents Extra Dry Over Molecular Sieve, AcroSeal®), DCM was distilled over  $\text{CaH}_2$  before use, Toluene was distilled over Na before use. 2-Iodobenzoic acid, barium titanate (tetragonal powder,  $<3 \mu\text{m}$  particle size, 99%, product No. 208108), NaH (60% in min. oil), potassium acetate, sodium acetate, sodium hydrogencarbonate, potassium carbonate, hydroxylamine hydrochloride, trichloroisocyanuric acid, triethylamine, trifluoromethylbenzene, trimethyl(trifluoromethyl)silane, methacryloyl chloride, EDC, EDC hydrochloride, DMAP, acetic anhydride, benzyl bromide, pyridine, were purchased from Fisher Scientific, Sigma Aldrich, VWR and Fluka and used without additional purification.

### 3. General procedures of compounds synthesis

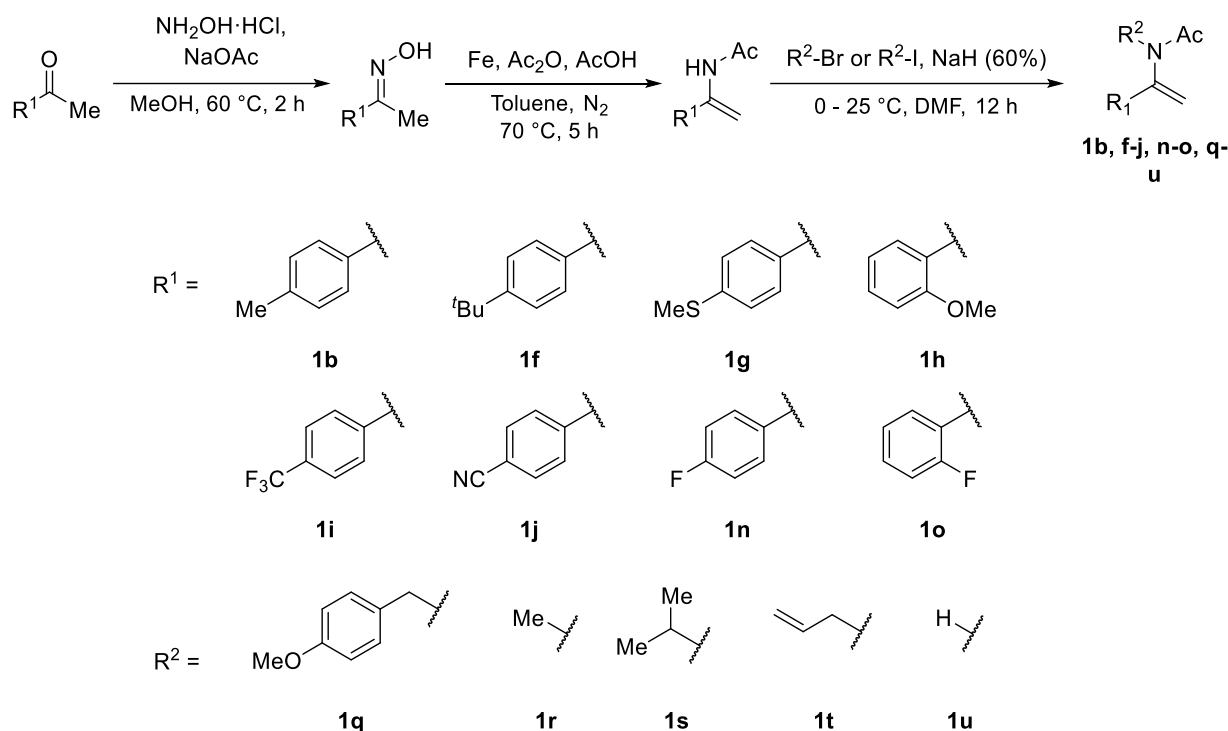
#### a. General procedure A for synthesis of enamides **1a, c-e, k-m, p**



Literature described procedure was used<sup>1</sup>: (a) To a stirred solution of methylmagnesium bromide (17.0 mmol, 3.0 mol/L diethyl ether, 6.0 mL, 1.0 equiv.) in diethyl ether (50 mL, 0.34 M) at 0 °C a solution of the corresponding benzonitrile (17.0 mmol, 1.0 equiv.) in diethyl ether (20 mL, 0.85 M) was added dropwise during a period of 30 minutes. After complete addition the solution was refluxed for eight hours. After refluxing the reaction mixture was cooled to 0 °C, and a solution of acetic anhydride (17.0 mmol, 1.0 equiv.) in diethyl ether (20 mL, 0.85 M) was added carefully over 30 minutes. The reaction mixture was refluxed for eight hours. To the resulting suspension, methanol was added at room temperature whilst stirring until all precipitates were dissolved (approximately 50 mL). The homogeneous solution was mixed with water/ethyl acetate (1:1, 100 mL). After phase separation the aqueous layer was extracted three times with ethyl acetate (50 mL). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product.

(b) 10 mmol (1.0 equiv.) of the *N*-acyl enamides was dissolved in 30 mL (0.33 M) dry DMF in a dry two-necked round-bottom flask under nitrogen. The solution was cooled to 0 °C and 15 mmol sodium hydride (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added in portions. The resulting suspension was stirred at the same temperature for 10 min. Then, 20 mmol (3.42 g, 2.0 equiv.) of benzyl bromide was added dropwise and the final solution was continued to stir overnight at room temperature. Upon completion, reaction was quenched by adding 10 mL water at 0 °C. The organic layer was extracted with ethyl acetate (2x40 mL). The combined organic layer was concentrated under reduced pressure and the crude product was purified by column chromatography over silica gel to give the pure product.

## b. General procedure B for synthesis of enamides **1b, f-j, n-o, q-u**

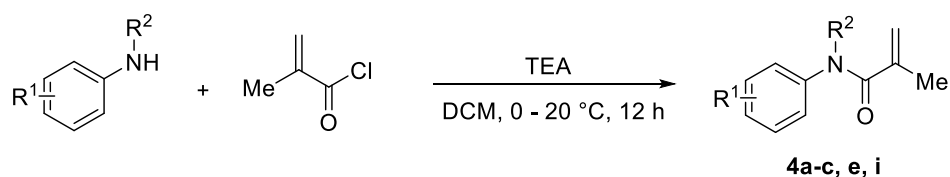


Literature-described procedure was used<sup>1</sup>: (a) A mixture of ketone (10 mmol, 1.0 equiv.), NaOAc (984 mg, 12 mmol, 1.2 equiv.) and hydroxylamine hydrochloride (834 mg, 12 mmol, 1.2 equiv.) in methanol (5 mL, 2.0 M) was stirred for 2 h at 60 °C. After cooling down to room temperature, the water was added, and then the mixture extracted with ethyl acetate (2×50 mL). The organic layer was collected, dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo to afford the crude ketoxime. Compound used without further purification in the next step.

(b) Crude ketoxime was dissolved in anhydrous toluene (20 mL) under Ar, followed by acetic anhydride (3.06 g, 30 mmol, 3.0 equiv.), acetic acid (1.80 g, 30 mmol, 3.0 equiv.) and iron powder (1.12 g, 20 mmol, 2.0 equiv.). Resulting suspension heated at 70 °C overnight. After cooling to room temperature, EtOAc (100 mL) was added and the mixture was filtered through a short pad of celite. The filtrate was evaporated to get the crude enamide, which was purified by silica gel column chromatography.

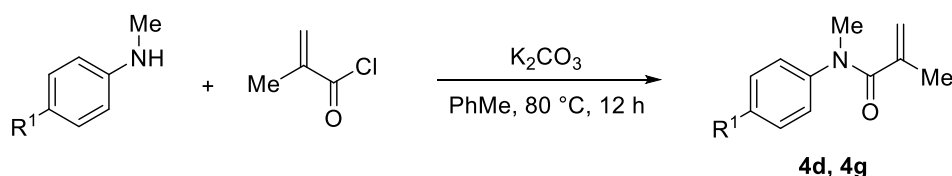
(c) *N*-acyl enamide (1.0 equiv.) was dissolved in dry DMF (0.33 M) under Ar, and the resulting solution was cooled on an ice-water bath. NaH (60% dispersion in mineral oil, 1.5 equiv.) was added portionwise and the reaction mixture was stirred for an additional 10 min. Then benzyl bromide (2.0 equiv.) was added dropwise and the final solution stirred overnight at room temperature. The reaction was re-cooled on an ice-water bath and quenched by addition of 10 mL water. The organic layer was extracted with EtOAc (2×70 mL), organic extract dried over anhydrous MgSO<sub>4</sub> and evaporated in vacuo to afford the crude product. Compound was purified by column chromatography over silica gel to give the pure product.

### c. General procedure C for synthesis of acrylamides 4a-c, e, i



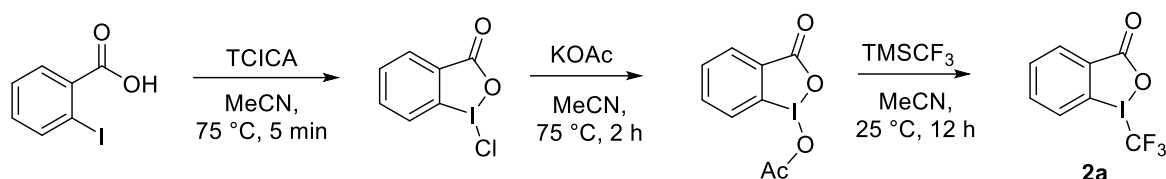
The variation of literature-described procedure was used<sup>2</sup>. Corresponding *N*-methylaniline (13.8 mmol, 1 equiv.) was dissolved in anhydrous DCM (50 mL) together with TEA (27.7 mmol, 2 equiv.). Reaction mixture closed under the Ar atmosphere and cooled on an ice-water bath. Methacryloyl chloride (18 mmol, 1.5 equiv.) was carefully added dropwise, and reaction allowed to warm up to room temperature overnight. Upon completion, the reaction mixture was diluted with water (40 mL) and transferred to a separatory funnel. DCM layer were separated, washed with brine (50 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The resulting dried organic phases were evaporated in vacuo to obtain crude product. The product was purified by silica gel column chromatography, using gradient from 5 to 25% EtOAc in petroleum ether to obtain pure product.

### d. General procedure D for synthesis of acrylamides 4d, 4g



The variation of literature-described procedure was used<sup>2</sup>. Aniline derivative (5.91 mmol, 1 equiv.) was dissolved in anhydrous toluene (30 mL) and K<sub>2</sub>CO<sub>3</sub> (8.86 mmol, 1.5 equiv.) was added in one portion. Reaction mixture was closed under Ar atmosphere and methacryloyl chloride (8.86 mmol, 1.5 equiv.) was carefully added dropwise at room temperature. The resulting suspension was heated at 80 °C overnight. Upon completion, the reaction mixture was cooled down to room temperature, diluted with water (40 mL), EtOAc (60 mL) and transferred to a separatory funnel. The organic layer was separated, washed with brine (40 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The resulting dried organic phase was evaporated in vacuo to obtain crude product. The desired compound was purified by silica gel column chromatography, using gradient from 5 to 25% EtOAc in petroleum ether to obtain pure product.

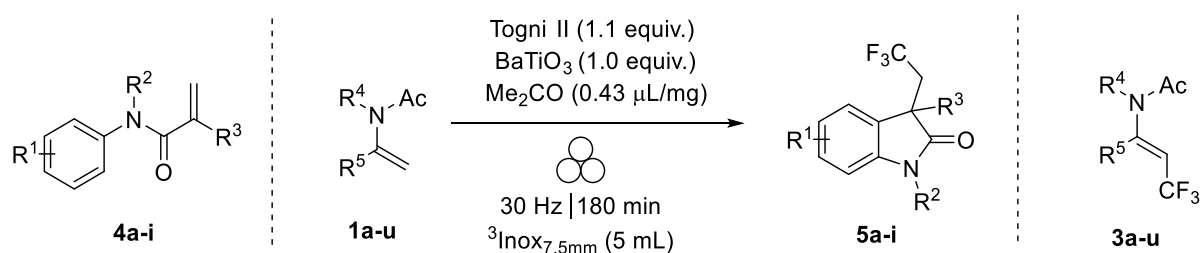
### e. Preparation of Togni II reagent from 2-Iodobenzoic Acid



Literature described procedure was used<sup>3</sup>. 2-Iodobenzoic acid (5.00 g, 20.2 mmol, 1 equiv.) was suspended in MeCN (80 mL) under Ar, and then warmed up to 75 °C. Upon warming up, the solution gradually became clean. Trichloroisocyanuric (1.58 g, 6.79 mmol, 0.34 equiv.) acid solution in MeCN (10.8 mL) was added in the course of 5 min and white precipitate formed. Then, the resulting mixture was allowed to cool down to room temperature, and anhydrous potassium acetate (3.96 g, 40.3 mmol) was added thereto. The reaction mixture was heated up again to 75 °C for 2 h. Finally, the reaction solution was let cooled down to ambient temperature and trimethyl(trifluoromethyl)silane (4.17 mL, 28.2 mmol, 1.4 equiv.) was added in one portion and the resulting white sticky suspension stirred for an additional 12 h.

Dry MeCN (50 mL) was added and reaction mixture was warmed up to 85 °C. Hot reaction mixture solution was filtered over a short (2 cm) pad of celite and warm MeCN was used for trituration (2×20 mL). Resulting solution was evaporated in vacuo to dryness. The crude material was trituated with a minimal amount of MeCN (10 mL) at room temperature, and the formed precipitate was filtered to obtain product as white solid. To remove the minor impurity of 2-Iodobenzoic acid, the obtained powder was re-suspended in DCM (200 mL), the suspension was filtered and undissolved material was washed with DCM (2×20 mL). Remaining precipitate was discarded. DCM washings were combined and evaporated in vacuo to obtain essentially clean product as an off-white powder (4.61 g, 72%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (d, *J* = 7.5 Hz, 1H), 7.80 – 7.72 (m, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.1, 135.8, 133.8, 132.0, 127.4 (d, *J* = 3.1 Hz), 114.9, 109.0, 105.3. <sup>19</sup>F NMR (377 MHz, CDCl<sub>3</sub>) δ -33.80 (s, 3F). The analytical data were consistent with the literature<sup>3</sup>.

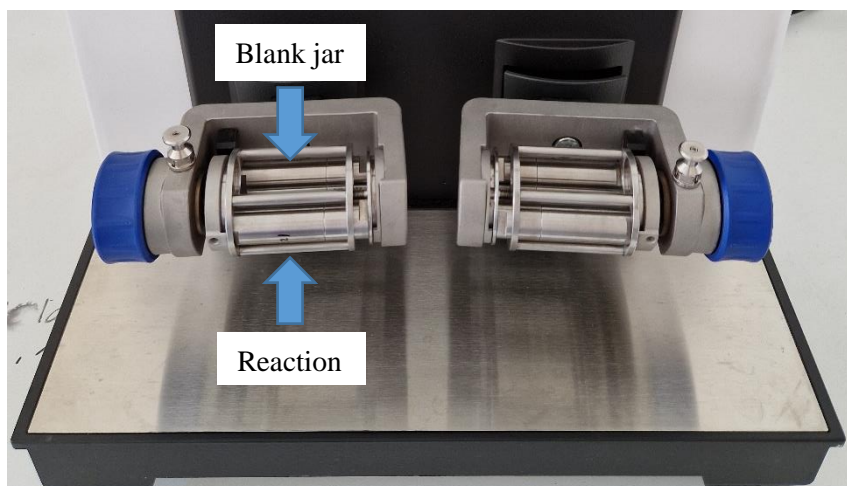
### f. General procedure E for mechanochemical trifluoromethylation



Three stainless-steel balls (7.5 mm) were added to the stainless-steel jar (5 mL) prior to addition of starting material and reagents. Then corresponding enamide or acrylamide (1 equiv.) was added to the jar, followed by <3 μm BaTiO<sub>3</sub> (1.0 equiv.) and Togni II reagent (1.1 equiv.). Acetone (0.43 μL/mg) was added to the reactants and the jar was immediately closed under air.

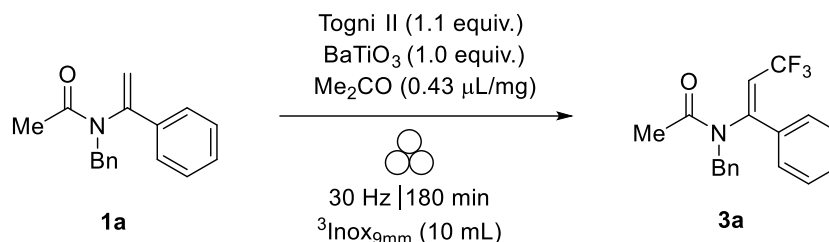
Reaction vessel placed on vibrational ball mill for 3 h at 30 Hz frequency (*NB: reaction must be performed exclusively in front position of the jar cassette to ensure high yield, see Figure S3*). After the time indicated, the jar was opened, the reaction mixture was dissolved in EtOAc (4 mL) and the suspension was transferred to a 15 mL Eppendorf tube. The jar and balls were rinsed with EtOAc twice again (2×4 mL) to ensure complete transfer of the material to the Eppendorf tube. Then suspension was placed for 5 min at 8500 rpm on the centrifuge. The supernatant was separated from the solid and fresh

EtOAc (12 mL) was added to the remaining solid. The mixture was then re-suspended again and placed on centrifuge again. Resulting supernatant joined with the first one, and the Eppendorf tube were carefully washed with EtOAc (2×5 mL). Then EtOAc extract was washed with saturated aqueous NaHCO<sub>3</sub> solution (2×20 mL) and brine (30 mL). The resulting aqueous layers were collected together and re-extracted with EtOAc (20 mL). The organic layers were combined together, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in *vacuo*. The product was purified by silica gel column chromatography, using gradient from 5 to 25% EtOAc in PE to obtain pure product.

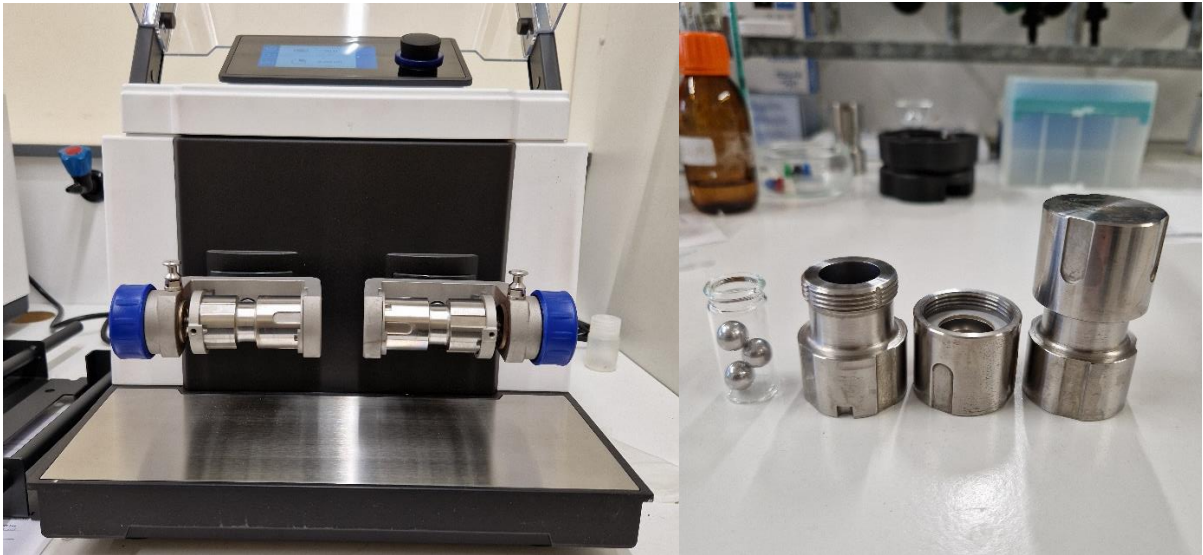


**Figure S3.** Position of the reaction mixture jar in the jar cassette

### g. Mechanochemical trifluoromethylation scale-up procedure



The scale-up procedure was performed using **General procedure E**, utilizing three stainless-steel balls (9 mm) in the 10 mL stainless-steel jar (*see Figure S4, second jar was empty and added for a counterbalance*). **(E)-N-Benzyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3a)** was synthesized from **1a** (503 mg, 2 mmol) and Togni II reagent (696 mg, 2.2 mmol). Compound **3a** obtained as a yellow oil (269 mg, 42% isolated yield) together with unreacted **1a** (181 mg). Yield of **3a** 66% (based on recovered starting material).

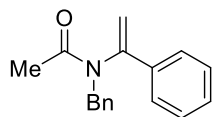


**Figure S4. Scale-up setup (left) with 10 mL stainless-steel jars and 9 mm balls (right).**

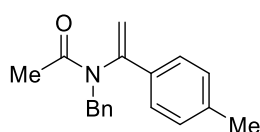


## 4. Starting materials characterization

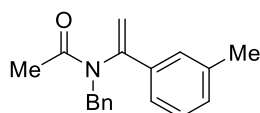
### 4.1 Enamides 1a-u



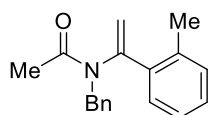
**N-Benzyl-N-(1-phenylvinyl)acetamide (1a)** was synthesized from benzonitrile (1.75 mL, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1a** was obtained as a yellow oil (1.30 g, 86% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (s, 5H), 7.20 – 7.06 (m, 5H), 5.49 (s, 1H), 4.75 (s, 1H), 4.53 (s, 2H), 1.98 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



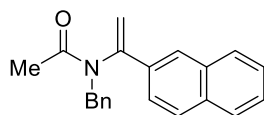
**N-Benzyl-N-(1-(p-tolyl)vinyl)acetamide (1b)** was synthesized from 4-methylacetophenone (1.07 mL, 8.00 mmol), sodium acetate (788 mg, 9.60 mmol) and hydroxylamine hydrochloride (667 mg, 9.60 mmol) following **General procedure B**. **1b** was obtained as a yellow oil (1.10 g, 94% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.16 (m, 9H), 5.56 (s, 1H), 4.82 (s, 1H), 4.66 (s, 2H), 2.37 (s, 3H), 2.10 (s, 3H). The analytical data were consistent with the literature.<sup>5</sup>



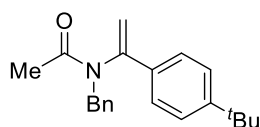
**N-Benzyl-N-(1-(m-tolyl)vinyl)acetamide (1c)** was synthesized from 3-methylbenzonitrile (2.04 mL, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1c** was obtained as a yellow oil (685 mg, 23% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.11 (m, 9H), 5.59 (s, 1H), 4.86 (s, 1H), 4.65 (s, 2H), 2.36 (s, 3H), 2.09 (s, 3H). The analytical data were consistent with the literature.<sup>1</sup>



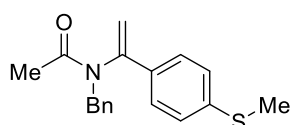
**N-Benzyl-N-(1-(o-tolyl)vinyl)acetamide (1d)** was synthesized from 2-methylbenzonitrile (2.01 mL, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1d** was obtained as a yellow oil (680 mg, 23% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 – 6.99 (m, 9H), 5.08 (s, 1H), 5.04 (s, 1H), 4.45 (s, 2H), 2.20 (s, 3H), 2.18 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



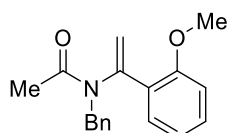
**N-Benzyl-N-(1-(naphthalen-2-yl)vinyl)acetamide (1e)** was synthesized from naphthalene-2-carbonitrile (2.60 g, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1e** was obtained as a white-yellow solid (444 mg, 18% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87 – 7.77 (m, 3H), 7.74 (s, 1H), 7.56 – 7.46 (m, 3H), 7.35 (d,  $J = 4.8$  Hz, 2H), 7.24 (s, 3H), 5.75 (s, 1H), 4.97 (s, 1H), 4.73 (s, 2H), 2.12 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



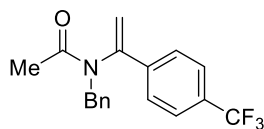
**N-Benzyl-N-(1-(4-(tert-butyl)phenyl)vinyl)acetamide (1f)** was synthesized from 4'-tert-butylacetophenone (1.83 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1f** was obtained as a yellow oil (1.25 g, 46% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.19 (m, 9H), 5.58 (s, 1H), 4.81 (s, 1H), 4.65 (s, 2H), 2.10 (s, 3H), 1.34 (s, 9H). The analytical data were consistent with the literature.<sup>1</sup>



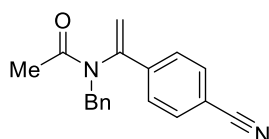
**N-Benzyl-N-(1-(4-(methylthio)phenyl)vinyl)acetamide (1g)** was synthesized from 4'-(methylthio)acetophenone (1.66 g, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1g** was obtained as a pale-yellow oil (446 mg, 23% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 – 7.20 (m, 9H), 5.58 (s, 1H), 4.84 (s, 1H), 4.65 (s, 2H), 2.51 (s, 3H), 2.09 (s, 3H). The analytical data were consistent with the literature.<sup>1,6</sup>



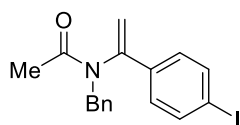
**N-Benzyl-N-(1-(2-methoxyphenyl)vinyl)acetamide (1h)** was synthesized from 2'-methoxyacetophenone (1.38 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1h** was obtained as a yellow oil (1.85 g, 54% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 – 7.18 (m, 7H), 7.03 – 6.92 (m, 2H), 5.57 (s, 1H), 5.07 (s, 1H), 4.60 (s, 2H), 3.85 (s, 3H), 2.28 (s, 3H). The analytical data were consistent with the literature.<sup>5</sup>



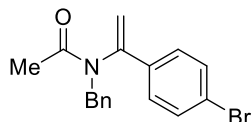
**N-Benzyl-N-(1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (1i)** was synthesized from 4-(trifluoromethyl)acetophenone (1.88 g, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1i** was obtained as a pale-yellow oil (1.05 g, 57% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.2$  Hz, 2H), 7.50 (d,  $J = 8.2$  Hz, 2H), 7.32 – 7.19 (m, 5H), 5.74 (s, 1H), 5.04 (s, 1H), 4.68 (s, 2H), 2.09 (s, 3H). The analytical data were consistent with the literature.<sup>7</sup>



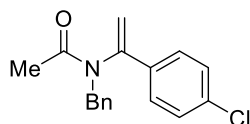
**N-Benzyl-N-(1-(4-cyanophenyl)vinyl)acetamide (1j)** was synthesized from 4-acetylbenzotrile (1.16 g, 8.00 mmol), sodium acetate (788 mg, 9.60 mmol) and hydroxylamine hydrochloride (667 mg, 9.60 mmol) following **General procedure B**. **1j** was obtained as a yellow oil (727 mg, 95% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.5$  Hz, 2H), 7.47 (d,  $J = 8.5$  Hz, 2H), 7.31 – 7.19 (m, 5H), 5.76 (s, 1H), 5.09 (s, 1H), 4.66 (s, 2H), 2.06 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



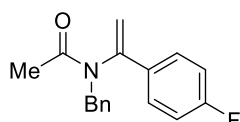
**N-Benzyl-N-(1-(4-iodophenyl)vinyl)acetamide (1k)** was synthesized from 4-iodobenzotrile (3.89 g, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1k** was obtained as a yellow oil (1.47 g, 49% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (d,  $J = 8.4$  Hz, 2H), 7.32 – 7.19 (m, 5H), 7.10 (d,  $J = 8.4$  Hz, 2H), 5.62 (s, 1H), 4.91 (s, 1H), 4.64 (s, 2H), 2.07 (s, 3H). The analytical data were consistent with the literature.<sup>1,6</sup>



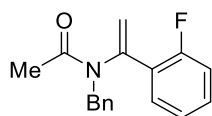
**N-Benzyl-N-(1-(4-bromophenyl)vinyl)acetamide (1l)** was synthesized from 4-bromobenzotrile (3.09 g, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1l** was obtained as a pale-yellow oil (758 mg, 14% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 8.6$  Hz, 2H), 7.33 – 7.20 (m, 7H), 5.63 (s, 1H), 4.93 (s, 1H), 4.66 (s, 2H), 2.09 (s, 3H). The analytical data were consistent with the literature.<sup>7</sup>



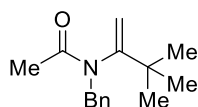
**N-Benzyl-N-(1-(4-chlorophenyl)vinyl)acetamide (1m)** was synthesized from 4-chlorobenzonitrile (2.34 g, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1m** was obtained as a pale-yellow oil (1.06 g, 22% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 – 7.15 (m, 9H), 5.55 (s, 1H), 4.86 (s, 1H), 4.59 (s, 2H), 2.03 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



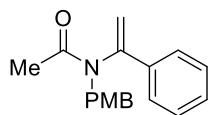
**N-Benzyl-N-(1-(4-fluorophenyl)vinyl)acetamide (1n)** was synthesized from 4'-fluoroacetophenone (1.21 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1n** was obtained as a pale-yellow oil (520 mg, 29% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41 – 7.33 (m, 2H), 7.32 – 7.21 (m, 5H), 7.08 (t,  $J = 8.6$  Hz, 2H), 5.56 (s, 1H), 4.89 (s, 1H), 4.66 (s, 2H), 2.11 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



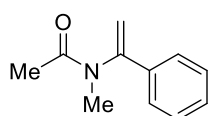
**N-Benzyl-N-(1-(2-fluorophenyl)vinyl)acetamide (1o)** was synthesized from 2'-fluoroacetophenone (1.21 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B**. **1o** was obtained as a yellow oil (895 mg, 29% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 – 7.06 (m, 9H), 5.67 (s, 1H), 5.12 (d,  $J = 1.7$  Hz, 1H), 4.62 (s, 2H), 2.16 (s, 3H). The analytical data were consistent with the literature.<sup>1</sup>



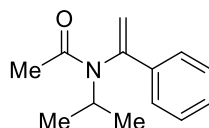
**N-Benzyl-N-(3,3-dimethylbut-1-en-2-yl)acetamide (1p)** was synthesized from pivalonitrile (1.41 g, 17.0 mmol) and methylmagnesium bromide (6.00 mL, 17.0 mmol) following **General procedure A**. **1p** was obtained as a white solid (317 mg, 9% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.28 – 7.17 (m, 5H), 5.47 (d,  $J = 14.4$  Hz, 1H), 5.14 (s, 1H), 4.55 (s, 1H), 3.84 (d,  $J = 14.4$  Hz, 1H), 2.04 (s, 3H), 1.19 (s, 9H). The analytical data were consistent with the literature.<sup>8</sup>



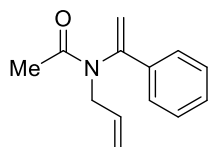
**N-(4-Methoxybenzyl)-N-(1-phenylvinyl)acetamide (1q)** was synthesized from acetophenone (7.78 mL, 66.6 mmol), sodium acetate (6.55 g, 79.9 mmol) and hydroxylamine hydrochloride (5.55 g, 79.9 mmol) following **General procedure B** with a modification brought to the last step (c), benzyl bromide was replaced by 1-chloromethyl-4-methoxybenzene. **1q** was obtained as a yellow oil (673 mg, 77% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.28 (m, 5H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 5.62 (s, 1H), 4.85 (s, 1H), 4.59 (s, 2H), 3.77 (s, 3H), 2.08 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.7, 159.0, 146.5, 135.6, 130.5, 129.9, 129.2, 129.0, 125.9, 114.6, 113.7, 55.3, 49.3, 22.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>2</sub>: 282.1494, Found: 282.1488 (Δ = -2.1 ppm).



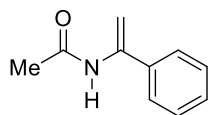
**N-Methyl-N-(1-phenylvinyl)acetamide (1r)** was synthesized from acetophenone (1.17 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B** with a modification brought to the last step (c), benzyl bromide was replaced by methyl iodide. **1r** was obtained as an orange-yellow oil (227 mg, 89% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.31 – 7.12 (m, 5H), 5.55 (s, 1H), 5.09 (s, 1H), 2.95 (s, 3H), 1.89 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>



**N-Isopropyl-N-(1-phenylvinyl)acetamide (1s)** was synthesized from acetophenone (1.17 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B** with a modification brought to the last step (c), benzyl bromide was replaced by 2-iodopropane. **1s** was obtained as a yellowish oil (161 mg, 36% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47 (d, *J* = 6.6 Hz, 2H), 7.41 – 7.27 (m, 3H), 5.86 (s, 1H), 5.18 (s, 1H), 4.71 (hept, *J* = 6.7 Hz 1H), 2.02 (s, 3H), 1.09 (s, 6H). The analytical data were consistent with the literature.<sup>4</sup>

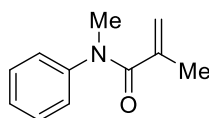


**N-Allyl-N-(1-phenylvinyl)acetamide (1t)** was synthesized from acetophenone (1.17 mL, 10.0 mmol), sodium acetate (984 mg, 12 mmol) and hydroxylamine hydrochloride (834 mg, 12 mmol) following **General procedure B** with a modification brought to the last step (c), benzyl bromide was replaced by allyl bromide. **1t** was obtained as a yellow oil (532 mg, 85% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.50 – 7.28 (m, 5H), 5.86 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.72 (s, 1H), 5.18 (s, 1H), 5.09 (dd, *J* = 18.1, 13.7 Hz, 2H), 4.08 (d, *J* = 6.4 Hz, 2H), 2.05 (s, 3H). The analytical data were consistent with the literature.<sup>4</sup>

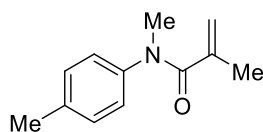


**N-(1-Phenylvinyl)acetamide (1u)** was synthesized from acetophenone (2.0 mL, 17.1 mmol), sodium acetate (1.69 g, 20.6 mmol) and hydroxylamine hydrochloride (1.43 g, 20.6 mmol) following **General procedure B** without the last step (c). **1u** was obtained as a pale-yellow powder (1.88 g, 68% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40 – 7.16 (m, 5H), 6.97 (s, 1H), 5.74 (s, 1H), 4.99 (s, 1H), 2.00 (s, 3H). The analytical data were consistent with the literature.<sup>9</sup>

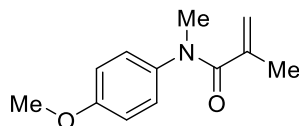
## 4.2 Acrylamides 4a-i



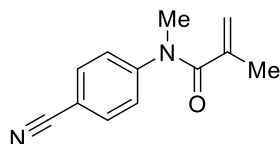
**N-Methyl-N-phenylmethacrylamide (4a)** was synthesized from *N*-methylaniline (1.5 mL, 13.8 mmol) and methacryloyl chloride (1.74 mL, 18 mmol) following **General procedure C**. **4a** was obtained as a white-yellow crystals (1.63 g, 67% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (t,  $J = 7.6$  Hz, 2H), 7.27 (t,  $J = 7.4$  Hz, 1H), 7.15 (d,  $J = 7.3$  Hz, 2H), 5.05 (s, 1H), 5.00 (s, 1H), 3.37 (s, 3H), 1.78 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



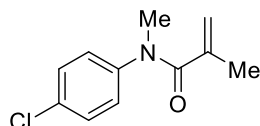
**N-Methyl-N-(p-tolyl)methacrylamide (4b)** was synthesized from *N*-methyl-*p*-toluidine (650  $\mu\text{L}$ , 5.14 mmol) and methacryloyl chloride (746  $\mu\text{L}$ , 7.71 mmol) following **General procedure C**. **4b** was obtained as a yellowish oil (1.63 g, 67% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.14 (d,  $J = 8.2$  Hz, 2H), 7.01 (d,  $J = 8.3$  Hz, 2H), 5.02 (s, 1H), 4.98 (s, 1H), 3.32 (s, 3H), 2.35 (s, 3H), 1.75 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



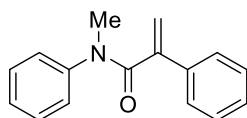
**N-(4-Methoxyphenyl)-N-methylmethacrylamide (4c)** was synthesized from 4-methoxy-*N*-methylbenzenamine (748 mg, 5.45 mmol) and methacryloyl chloride (799  $\mu\text{L}$ , 8.18 mmol) following **General procedure C**. **4c** was obtained as a light brown oil (981 mg, 88% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.05 (d,  $J = 8.9$  Hz, 2H), 6.85 (d,  $J = 8.9$  Hz, 2H), 5.02 (s, 1H), 4.99 (s, 1H), 3.81 (s, 3H), 3.30 (s, 3H), 1.74 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



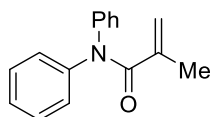
**N-(4-Cyanophenyl)-N-methylmethacrylamide (4d)** was synthesized from 4-(methylamino)benzotrile (700 mg, 5.3 mmol) and methacryloyl chloride (769  $\mu\text{L}$ , 7.94 mmol) following **General procedure D**. **4d** was obtained as a white solid (698 mg, 66% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.6$  Hz, 2H), 7.27 (d,  $J = 8.6$  Hz, 2H), 5.15 (s, 1H), 5.00 (s, 1H), 3.39 (s, 3H), 1.85 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



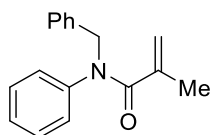
**N-(4-Chlorophenyl)-N-methylmethacrylamide (4e)** was synthesized from 4-chloro-*N*-methylbenzenamine (600  $\mu\text{L}$ , 4.94 mmol) and methacryloyl chloride (718  $\mu\text{L}$ , 7.42 mmol) following **General procedure C**. **4e** was obtained as a white solid (1.0 g, 96% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 8.6$  Hz, 2H), 7.07 (d,  $J = 8.6$  Hz, 2H), 5.07 (s, 1H), 4.98 (s, 1H), 3.32 (s, 3H), 1.77 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



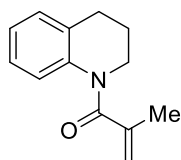
**N-Methyl-N,2-diphenylacrylamide (4f)** *N*-methylaniline (708  $\mu\text{L}$ , 6.53 mmol) and  $\alpha$ -phenylacrylic acid (1.26 g, 7.09 mmol) were combined in anhydrous DCM (30 mL) together with catalytic DMAP (160 mg, 1.31 mmol), and reaction mixture cooled on an ice-water bath. EDC (1.5 mL, 8.49 mmol) was added dropwise, and the reaction stirred overnight at room temperature. Then reaction mixture diluted with water (100 mL), organic layer separated, washed with brine (2 $\times$ 50 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuo. Compound purified by silica gel column chromatography using gradient from 5 to 20% EtOAc in petroleum ether to obtain product **4f** as a yellowish oil (1.19 g, 77% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.06 (m, 8H), 7.04 – 6.78 (m, 2H), 5.47 (s, 1H), 5.36 (s, 1H), 3.39 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



**N,N-Diphenylmethacrylamide (4g)** was synthesized from diphenylamine (1 g, 5.91 mmol) and methacryloyl chloride (858  $\mu\text{L}$ , 8.86 mmol) following **General procedure D**. **4g** was obtained as a white solid (1.01 g, 72% yield).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (t,  $J = 7.7$  Hz, 4H), 7.23 (t,  $J = 7.4$  Hz, 2H), 7.17 (d,  $J = 7.4$  Hz, 4H), 5.24 (s, 1H), 5.18 (s, 1H), 1.84 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.



**N-Benzyl-N-phenylmethacrylamide (4h)** *N*-benzylaniline (1 g, 5.46 mmol) and methacrylic acid (602  $\mu$ L, 7.09 mmol) were combined in pyridine (15 mL) and reaction mixture cooled on an ice-water bath. EDC hydrochloride (1.36 g, 7.09 mmol) was added in one portion, and the reaction stirred overnight at room temperature. Then reaction mixture diluted with EtOAc (50 mL) and water (100 mL). Organic layer separated, and washed successively with 1 M HCl (3 $\times$ 20 mL), brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuo. Compound purified by silica gel column chromatography using gradient from 5 to 20% EtOAc in petroleum ether to obtain product **4h** as a white beige solid (1.00 g, 73% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.35 – 7.12 (m, 8H), 7.02 – 6.91 (m, 2H), 5.03 (s, 1H), 5.01 (s, 1H), 4.97 (s, 2H), 1.78 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.

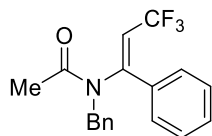


**1-(3,4-Dihydroquinolin-1(2H)-yl)-2-methylprop-2-en-1-one (4i)** was synthesized from 1,2,3,4-tetrahydroquinoline (700  $\mu$ L, 5.57 mmol) and methacryloyl chloride (816  $\mu$ L, 8.36 mmol) following **General procedure C**. **4i** was obtained as a white yellow solid (1.06 g, 95% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.20 (d, *J* = 7.4 Hz, 1H), 7.16 – 6.99 (m, 3H), 5.18 (s, 1H), 5.14 (s, 1H), 3.80 (t, *J* = 6.5 Hz, 2H), 2.77 (t, *J* = 6.7 Hz, 2H), 1.99 (p, *J* = 6.6 Hz, 2H), 1.87 (s, 3H). The analytical data were consistent with the literature<sup>2</sup>.

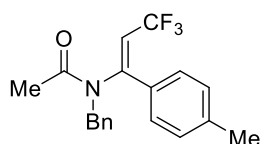


## 5. Products characterization

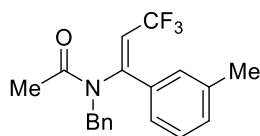
### 5.1 Trifluoromethylated enamides 3a-u



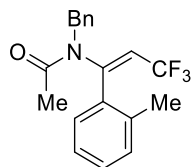
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3a)** was synthesized from **1a** (126 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3a** was obtained as a yellow oil (106 mg, 66% yield).  $R_f$  (in PE/EtOAc = 6:1): 0.55.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (dt,  $J = 20.6, 7.1$  Hz, 3H), 7.35 – 7.21 (m, 5H), 7.14 (d,  $J = 6.0$  Hz, 2H), 5.44 (q,  $J = 8.2$  Hz, 1H), 4.50 (s, 2H), 2.23 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 149.9 (q,  $J = 5.9$  Hz), 136.6, 132.9, 130.8, 129.0 (q,  $J = 2.1$  Hz), 128.8, 128.7, 128.7, 127.8, 122.2 (q,  $J = 270.2$  Hz), 116.9 (q,  $J = 35.1$  Hz), 49.6, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.78 (d,  $J = 8.3$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NO}$ : 319.11840, Found: 319.11890 ( $\Delta = 1.56$  ppm). The analytical data were consistent with the literature.<sup>10</sup>



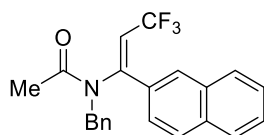
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl)acetamide (3b)** was synthesized from **1b** (133 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3b** was obtained as a yellow oil (124 mg, 74% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.69.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.17 (m, 9H), 5.44 (q,  $J = 8.2$  Hz, 1H), 4.55 (s, 2H), 2.43 (s, 3H), 2.27 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 150.0 (q,  $J = 5.9$  Hz), 141.3, 136.7, 130.0, 129.5, 128.9 (q,  $J = 2.1$  Hz), 128.8, 128.6, 127.7, 122.3 (q,  $J = 270.3$  Hz), 116.4 (q,  $J = 35.0$  Hz), 49.6, 22.6, 21.5.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.37 (d,  $J = 8.0$  Hz). **HRMS** (ESI)  $m/z$ : [M+H]<sup>+</sup> Calcd for  $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NO}$ : 334.14133, Found: 334.1413 ( $\Delta = 0.04$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



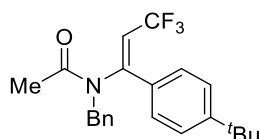
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(m-tolyl)prop-1-en-1-yl)acetamide (3c)** was synthesized from **1c** (186 mg, 0.70 mmol) and Togni II reagent (243 mg, 0.77 mmol) following **General procedure E**. **3c** was obtained as a yellow oil (116 mg, 50% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.59.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.20 (m, 5H), 7.15 (d,  $J = 6.0$  Hz, 3H), 7.08 (s, 1H), 5.42 (d,  $J = 8.2$  Hz, 1H), 4.50 (s, 2H), 2.35 (s, 3H), 2.23 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 150.1 (q,  $J = 5.9$  Hz), 138.6, 132.9, 131.6, 129.3 (q,  $J = 1.8$  Hz), 128.8, 128.6, 128.6, 127.7, 126.4 (q,  $J = 2.0$  Hz), 122.3 (q,  $J = 270.3$  Hz), 116.7 (q,  $J = 34.9$  Hz), 49.6, 22.7, 21.4.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.76 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}$ : 333.13405, Found: 333.13483 ( $\Delta = 2.34$  ppm).



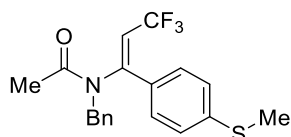
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(*o*-tolyl)prop-1-en-1-yl)acetamide (3d)** was synthesized from **1d** (152 mg, 0.57 mmol) and Togni II reagent (199 mg, 0.63 mmol) following **General procedure E**. **3d** was obtained as a yellow oil (88.0 mg, 46% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.68.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.34 (m, 6H), 7.26 (d,  $J = 16.4$  Hz, 3H), 5.86 (q,  $J = 7.8$  Hz, 1H), 4.67 (s, 2H), 2.57 (s, 3H), 2.39 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 149.7 (q,  $J = 5.5$  Hz), 137.0, 136.8, 132.2, 130.8, 130.8, 130.3, 128.6, 127.7, 127.5, 125.8, 122.5 (q,  $J = 269.9$  Hz), 115.2 (q,  $J = 34.3$  Hz), 49.2, 23.2, 19.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.75 (d,  $J = 7.8$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}$ : 333.13405, Found: 333.13483 ( $\Delta = 2.33$  ppm).



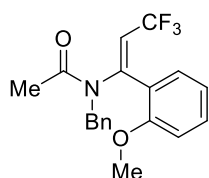
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(naphthalen-1-yl)prop-1-en-1-yl)acetamide (3e)** was synthesized from **1e** (151 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3e** was obtained as a colorless oil (48.0 mg, 26% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.64.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 – 7.75 (m, 4H), 7.54 (tt,  $J = 6.9, 5.2$  Hz, 2H), 7.36 (d,  $J = 8.5$  Hz, 1H), 7.25 (dd,  $J = 15.2, 8.1$  Hz, 3H), 7.17 – 7.10 (m, 2H), 5.52 (q,  $J = 8.2$  Hz, 1H), 4.53 (s, 2H), 2.28 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 150.0 (q,  $J = 6.0$  Hz), 136.7, 134.3, 132.8, 130.3, 129.6 (q,  $J = 2.1$  Hz), 128.8, 128.8, 128.7, 128.7, 127.9, 127.9, 127.9, 127.1, 125.4 (q,  $J = 1.8$  Hz), 122.4 (q,  $J = 270.2$  Hz), 117.2 (q,  $J = 35.0$  Hz), 49.9, 22.8.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.68 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{22}\text{H}_{18}\text{F}_3\text{NO}$ : 369.13405, Found: 369.13380 ( $\Delta = -0.67$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



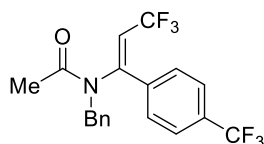
**(E)-N-Benzyl-N-(1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3f)** was synthesized from **1f** (154 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3f** was obtained as a yellow oil (151 mg, 80% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.77.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 8.5$  Hz, 2H), 7.19 (d,  $J = 7.8$  Hz, 5H), 7.08 (d,  $J = 6.0$  Hz, 2H), 5.32 (q,  $J = 8.3$  Hz, 1H), 4.44 (s, 2H), 2.14 (s, 3H), 1.26 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 154.3, 149.9 (q,  $J = 6.1$  Hz), 136.8, 129.9, 128.9, 128.8, 128.6, 127.7, 125.7, 122.3 (q,  $J = 270.3$  Hz), 116.5 (q,  $J = 35.0$  Hz), 49.7, 35.0, 31.2, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.79 (d,  $J = 8.4$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{22}\text{H}_{24}\text{F}_3\text{NO}$ : 375.18100, Found: 375.18159 ( $\Delta = 1.58$  ppm).



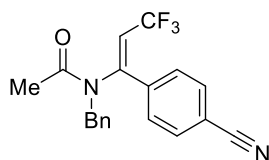
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-(methylthio)phenyl)prop-1-en-1-yl)acetamide (3g)** was synthesized from **1g** (123 mg, 0.41 mmol) and Togni II reagent (144 mg, 0.46 mmol) following **General procedure E**. **3g** was obtained as a yellow oil (108 mg, 71% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.41.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 – 7.24 (m, 7H), 7.17 (dd,  $J = 7.8, 1.8$  Hz, 2H), 5.43 (q,  $J = 8.1$  Hz, 1H), 4.55 (s, 2H), 2.52 (s, 3H), 2.24 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.1, 149.4 (q,  $J = 5.9$  Hz), 142.9, 136.6, 129.3 (q,  $J = 2.0$  Hz), 128.9, 128.7, 128.6, 127.7, 125.6, 122.3 (q,  $J = 270.2$  Hz), 116.3 (q,  $J = 34.9$  Hz), 49.7, 22.6, 14.9.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.75 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NOS}$ : 365.10612, Found: 365.10673 ( $\Delta = 1.68$  ppm).



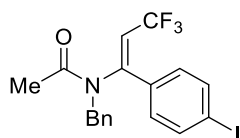
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(2-methoxyphenyl)prop-1-en-1-yl)acetamide (3h)** was synthesized from **1h** (141 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3h** was obtained as a yellow oil (132 mg, 76% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.50.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.38 (m, 1H), 7.31 – 7.20 (m, 3H), 7.15 – 7.09 (m, 3H), 6.98 (t,  $J = 8.1$  Hz, 1H), 6.89 (d,  $J = 8.4$  Hz, 1H), 5.57 (q,  $J = 7.8$  Hz, 1H), 4.51 (s, 2H), 3.78 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 157.4, 148.0 (q,  $J = 5.9$  Hz), 137.2, 132.0, 131.9 (q,  $J = 2.2$  Hz), 128.4, 128.3, 127.3, 122.3 (q,  $J = 269.9$  Hz), 121.5, 120.3, 117.5 (q,  $J = 34.3$  Hz), 110.9, 55.4, 48.8, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.45 (d,  $J = 7.8$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}_2$ : 349.12896, Found: 349.13038 ( $\Delta = 4.07$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



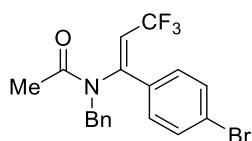
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)acetamide (3i)** was synthesized from **1i** (160 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3i** was obtained as a yellow oil (170 mg, 88% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.88.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 8.2$  Hz, 2H), 7.40 (d,  $J = 8.1$  Hz, 2H), 7.32 – 7.20 (m, 3H), 7.10 (d,  $J = 7.9$  Hz, 2H), 5.55 (q,  $J = 8.0$  Hz, 1H), 4.50 (s, 2H), 2.23 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 148.6 (q,  $J = 5.6$  Hz), 136.7, 136.3, 132.7 (q,  $J = 33.1$  Hz), 129.4 (q,  $J = 2.1$  Hz), 128.9, 128.6, 128.0, 125.8 (q,  $J = 3.8$  Hz), 122.3 (q,  $J = 271.3$  Hz), 122.0 (q,  $J = 270.5$  Hz), 118.3 (q,  $J = 35.2$  Hz), 49.9, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.81 (d,  $J = 8.1$  Hz), -63.89. **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{15}\text{F}_6\text{NO}$ : 387.10578, Found: 387.10721 ( $\Delta = 3.69$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



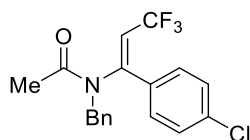
**(E)-N-Benzyl-N-(1-(4-cyanophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3j)** was synthesized from **1j** (138 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3j** was obtained as a yellow oil (102 mg, 59% yield).  $R_f$  (in PE/EtOAc = 3:2): 0.75.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.1$  Hz, 2H), 7.40 (d,  $J = 8.2$  Hz, 2H), 7.29 (d,  $J = 7.0$  Hz, 3H), 7.14 – 7.07 (m, 2H), 5.62 (q,  $J = 8.0$  Hz, 1H), 4.54 (s, 2H), 2.24 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.9, 148.2 (q,  $J = 5.8$  Hz), 137.7, 136.0, 132.4, 129.6 (q,  $J = 2.1$  Hz), 128.9, 128.4, 128.1, 123.2 (q,  $J = 270.2$  Hz), 118.4 (q,  $J = 35.7$  Hz), 117.9, 114.5, 50.2, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.32 (d,  $J = 7.8$  Hz). **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{16}\text{F}_3\text{N}_2\text{O}$ : 345.12092, Found: 345.1208 ( $\Delta = -0.24$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



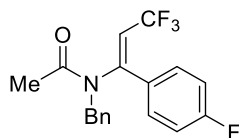
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-iodophenyl)prop-1-en-1-yl)acetamide (3k)** was synthesized from **1k** (189 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3k** was obtained as a yellow oil (155 mg, 70% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.55.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.5$  Hz, 2H), 7.33 – 7.19 (m, 3H), 7.11 (d,  $J = 5.6$  Hz, 2H), 7.02 (d,  $J = 8.5$  Hz, 2H), 5.47 (d,  $J = 8.1$  Hz, 1H), 4.51 (s, 2H), 2.21 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 149.0 (q,  $J = 5.9$  Hz), 138.0, 136.4, 132.5, 130.5 (q,  $J = 1.9$  Hz), 128.7, 128.6, 127.9, 122.1 (q,  $J = 270.4$  Hz), 117.3 (q,  $J = 35.0$  Hz), 97.5, 49.7, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.79 (d,  $J = 8.2$  Hz). **HRMS** (EI<sup>+</sup>)  $m/z$ :  $[\text{M}]$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{INO}$ : 445.01504, Found: 445.01568 ( $\Delta = 1.43$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



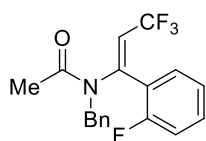
**(E)-N-Benzyl-N-(1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3l)** was synthesized from **1l** (165 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3l** was obtained as a yellow oil (155 mg, 78% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.77.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.5$  Hz, 2H), 7.32 – 7.21 (m, 3H), 7.16 (d,  $J = 8.5$  Hz, 2H), 7.11 (d,  $J = 7.5$  Hz, 2H), 5.47 (q,  $J = 8.1$  Hz, 1H), 4.50 (s, 2H), 2.21 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 148.9 (q,  $J = 5.8$  Hz), 136.4, 132.1, 131.9, 130.5 (q,  $J = 2.0$  Hz), 128.8, 128.7, 127.9, 125.4, 122.1 (q,  $J = 270.3$  Hz), 117.4 (q,  $J = 35.1$  Hz), 49.8, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.80 (d,  $J = 8.0$  Hz). **HRMS** (EI<sup>+</sup>)  $m/z$ :  $[\text{M}]$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{BrF}_3\text{NO}$ : 397.02891, Found: 397.02988 ( $\Delta = 2.43$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



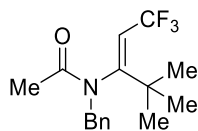
**(E)-N-Benzyl-N-(1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3m)** was synthesized from **1m** (143 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3m** was obtained as a yellow oil (133 mg, 75% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.68.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (d,  $J = 8.6$  Hz, 2H), 7.31 – 7.20 (m, 5H), 7.12 (d,  $J = 8.0$  Hz, 2H), 5.47 (q,  $J = 8.1$  Hz, 1H), 4.51 (s, 2H), 2.22 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 148.8 (q,  $J = 5.9$  Hz), 137.1, 136.4, 131.4, 130.3 (q,  $J = 1.8$  Hz), 129.1, 128.7, 128.7, 127.9, 122.1 (q,  $J = 270.3$  Hz), 117.3 (q,  $J = 35.0$  Hz), 49.7, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.81 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{18}\text{H}_{15}\text{ClF}_3\text{NO}$ : 353.07943, Found: 353.07816 ( $\Delta = -3.58$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



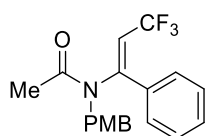
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-fluorophenyl)prop-1-en-1-yl)acetamide (3n)** was synthesized from **1n** (135 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3n** was obtained as a yellow oil (104 mg, 62% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.65.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.21 (m, 5H), 7.15 – 7.04 (m, 4H), 5.45 (q,  $J = 8.1$  Hz, 1H), 4.51 (s, 2H), 2.22 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 164.1 (d,  $J = 252.1$  Hz), 148.9 (q,  $J = 5.9$  Hz), 136.5, 131.1 (dd,  $J = 8.7, 1.9$  Hz), 129.0 (d,  $J = 3.5$  Hz), 128.7, 128.7, 127.9, 122.2 (q,  $J = 270.2$  Hz), 117.0 (q,  $J = 35.0$  Hz), 116.0 (d,  $J = 22.0$  Hz), 49.7, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.83 (d,  $J = 8.2$  Hz), -109.53. **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{NO}$ : 337.10898, Found: 337.10922 ( $\Delta = 0.72$  ppm). The analytical data were consistent with the literature.<sup>11</sup>



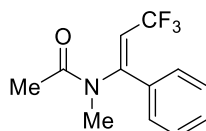
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(2-fluorophenyl)prop-1-en-1-yl)acetamide (3o)** was synthesized from **1o** (135 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3o** was obtained as a yellow oil (77.0 mg, 46% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.55.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.37 (m, 1H), 7.31 – 7.22 (m, 3H), 7.20 – 7.06 (m, 5H), 5.61 (q,  $J = 7.7$  Hz, 1H), 4.52 (s, 2H), 2.30 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 160.2 (d,  $J = 250.0$  Hz), 144.5 (q,  $J = 5.9$  Hz), 136.6, 132.6 (d,  $J = 8.5$  Hz), 131.5 (p,  $J = 1.9$  Hz), 128.7, 128.4, 127.7, 124.3 (d,  $J = 3.7$  Hz), 121.9 (q,  $J = 270.3$  Hz), 120.9 (d,  $J = 13.7$  Hz), 118.9 (q,  $J = 34.6$  Hz), 116.2 (d,  $J = 21.5$  Hz), 49.3, 22.6 (d,  $J = 2.4$  Hz).  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -59.15 (d,  $J = 7.5$  Hz), -113.95. **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_4\text{NO}$ : 337.10898, Found: 337.10933 ( $\Delta = 1.06$  ppm).



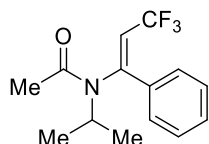
**(E)-N-Benzyl-N-(1,1,1-trifluoro-4,4-dimethylpent-2-en-3-yl)acetamide (3p)** was synthesized from **1p** (116 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3p** was obtained as a yellow oil (23.0 mg, 15% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.62.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 – 7.16 (m, 5H), 5.76 (q,  $J = 7.8$  Hz, 1H), 4.97 (d,  $J = 15.2$  Hz, 1H), 4.29 (d,  $J = 15.2$  Hz, 1H), 2.02 (s, 3H), 1.10 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 161.3, 137.3, 128.9, 128.4, 127.5, 122.3 (q,  $J = 271.0$  Hz), 116.2 (q,  $J = 34.0$  Hz), 54.0, 38.5, 30.3, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  - 60.95 (d,  $J = 8.1$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{16}\text{H}_{20}\text{F}_3\text{NO}$ : 299.14970, Found: 299.14944 ( $\Delta = -0.86$  ppm).



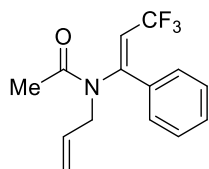
**(E)-N-(4-Methoxybenzyl)-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3q)** was synthesized from **1q** (141 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3q** was obtained as a yellowish oil (97 mg, 56% yield).  $R_f$  (in PE/EA = 2:1): 0.43.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.38 (m, 3H), 7.34 (d,  $J = 7.2$  Hz, 2H), 7.09 (d,  $J = 8.6$  Hz, 2H), 6.82 (d,  $J = 8.7$  Hz, 2H), 5.43 (q,  $J = 8.2$  Hz, 1H), 4.46 (s, 2H), 3.79 (s, 3H), 2.24 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 159.2, 149.9 (q,  $J = 5.9$  Hz), 133.1, 130.9, 130.2, 129.0, 128.9, 128.8, 122.3 (q,  $J = 270.2$  Hz), 117.0 (q,  $J = 35.0$  Hz), 114.0, 55.3, 49.0, 22.7.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.89 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NO}_2$ : 350.13624, Found: 350.1362 ( $\Delta = -0.23$  ppm).



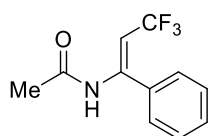
**(E)-N-Methyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3r)** was synthesized from **1r** (87.6 mg, 0.50 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3r** was obtained as a yellow oil (44 mg, 36% yield).  $R_f$  (in PE/EtOAc = 4:1): 0.29.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 – 7.33 (m, 5H), 5.71 (q,  $J = 8.1$  Hz, 1H), 2.96 (s, 3H), 2.16 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 151.8 (q,  $J = 6.1$  Hz), 133.2, 130.8, 128.8, 128.8, 122.6 (q,  $J = 269.9$  Hz), 114.8 (q,  $J = 35.2$  Hz), 35.4, 22.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.58 (d,  $J = 8.2$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{12}\text{H}_{12}\text{F}_3\text{NO}$ : 243.08710, Found: 243.08720 ( $\Delta = 0.42$  ppm). The analytical data were consistent with the literature.<sup>10</sup>



**(E)-N-Isopropyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3s)** was synthesized from **1s** (102 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3s** was obtained as a yellow oil (87 mg, 64% yield).  $R_f$  (in PE/EA = 2:1): 0.41.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.31 (m, 5H), 5.69 (q,  $J = 8.3$  Hz, 1H), 4.44 (hept,  $J = 6.9$  Hz, 1H), 2.19 (s, 3H), 1.03 (d,  $J = 6.9$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.6, 149.6 (q,  $J = 6.0$  Hz), 134.7, 130.8, 129.2, 129.1, 128.5, 122.3 (q,  $J = 270.6$  Hz), 118.3 (q,  $J = 34.9$  Hz), 48.8, 23.6, 20.6.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -56.12 (d,  $J = 8.3$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NO}$ : 272.12568, Found: 272.1257 ( $\Delta = 0.21$  ppm). The analytical data were consistent with the literature.<sup>10</sup>

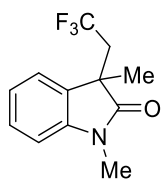


**(E)-N-Allyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3t)** was synthesized from **1t** (101 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **3t** was obtained as a yellowish oil (34 mg, 25% yield).  $R_f$  (in PE/EA = 2:1): 0.49.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.29 (m, 5H), 5.86 – 5.61 (m, 2H), 5.15 (dd,  $J = 10.2, 1.1$  Hz, 1H), 5.02 (dd,  $J = 17.1, 1.3$  Hz, 1H), 3.96 (d,  $J = 6.3$  Hz, 2H), 2.19 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 150.3 (q,  $J = 5.9$  Hz), 133.3, 132.4, 130.8, 128.9, 128.7, 122.4 (q,  $J = 270.2$  Hz), 118.6, 116.1 (q,  $J = 35.0$  Hz), 49.5, 22.8.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -55.69 (d,  $J = 8.0$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NO}$ : 270.11003, Found: 270.1100 ( $\Delta = -0.16$  ppm). The analytical data were consistent with the literature.<sup>10</sup>

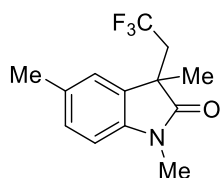


**(E)-N-(3,3,3-Trifluoro-1-phenylprop-1-en-1-yl)acetamide (3u)** was synthesized from **1u** (80.6 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. Compound was additionally re-crystallized from PE/EtOAc 9:1 to obtain **3u** as a white solid (36 mg, 31% yield).  $R_f$  (in PE/EA = 2:1): 0.31.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.39 (m, 3H), 7.38 – 7.32 (m, 2H), 7.08 (q,  $J = 8.3$  Hz, 1H), 6.57 (br. s, 1H), 2.11 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  169.3, 143.9 (q,  $J = 6.0$  Hz), 135.0, 129.9, 128.8, 128.3, 124.4 (q,  $J = 268.6$  Hz), 103.1 (q,  $J = 34.9$  Hz), 24.9.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -53.30 (d,  $J = 8.3$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{11}\text{H}_{11}\text{F}_3\text{NO}$ : 230.07873, Found: 230.0786 ( $\Delta = -0.41$  ppm). The analytical data were consistent with the literature.<sup>12</sup>

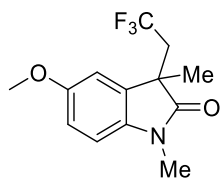
## 5.2 Oxindoles 5a-i



**1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5a)** was synthesized from **4a** (140 mg, 0.8 mmol) and Togni II reagent (278 mg, 0.88 mmol) following **General procedure E**. **5a** was obtained as a yellowish oil (116 mg, 60% yield).  $R_f$  (in PE/EA = 2:1): 0.46.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (td,  $J = 7.7, 1.2$  Hz, 1H), 7.26 (d,  $J = 7.3$  Hz, 1H), 7.09 (td,  $J = 7.6, 0.9$  Hz, 1H), 6.88 (d,  $J = 7.8$  Hz, 1H), 3.23 (s, 3H), 2.82 (dq,  $J = 15.2, 10.7$  Hz, 1H), 2.65 (dq,  $J = 15.2, 10.5$  Hz, 1H), 1.40 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 131.1, 128.6, 125.4 (q,  $J = 278.1$  Hz), 123.7, 122.8, 108.6, 44.5 (q,  $J = 1.9$  Hz), 40.8 (q,  $J = 28.3$  Hz), 26.5, 25.1.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.95. **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{12}\text{H}_{12}\text{F}_3\text{NO}$ : 243.08710, Found: 243.08789 ( $\Delta = 3.28$  ppm). The analytical data were consistent with the literature<sup>13</sup>.



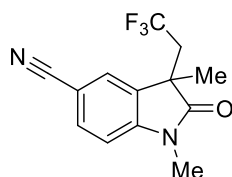
**1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5b)** was synthesized from **4b** (95 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5b** was obtained as a white solid (62 mg, 48% yield).  $R_f$  (in PE/EA = 2:1): 0.49.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (d,  $J = 7.9$  Hz, 1H), 7.07 (s, 1H), 6.76 (d,  $J = 7.9$  Hz, 1H), 3.20 (s, 3H), 2.80 (dq,  $J = 15.1, 10.8$  Hz, 1H), 2.62 (dq,  $J = 15.1, 10.5$  Hz, 1H), 2.34 (s, 3H), 1.38 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.5, 140.6, 132.3, 131.2, 128.9, 125.4 (q,  $J = 278.3$  Hz), 124.4, 108.3, 44.5 (q,  $J = 2.0$  Hz), 40.7 (q,  $J = 28.2$  Hz), 26.5, 25.1, 21.2.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.89 (t,  $J = 10.8$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NO}$ : 257.10275, Found: 257.10289 ( $\Delta = 0.53$  ppm). The analytical data were consistent with the literature<sup>13</sup>.



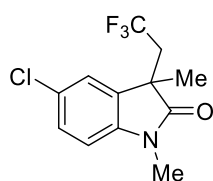
**5-Methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5c)** was synthesized from **4c** (103 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5c** was obtained as a white solid (49 mg, 36% yield).  $R_f$  (in PE/EA = 2:1): 0.35.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.88 (d,  $J = 2.3$  Hz, 1H), 6.83 (dd,  $J = 8.4, 2.5$  Hz, 1H), 6.78 (d,  $J = 8.4$  Hz, 1H), 3.80 (s, 3H), 3.21 (s, 3H), 2.81 (dq,  $J = 15.2, 10.7$  Hz, 1H), 2.62 (dq,  $J = 15.2, 10.5$  Hz, 1H), 1.40 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.2, 156.2, 136.5, 132.5, 125.4 (q,  $J = 278.3$  Hz), 112.7, 111.4, 108.8, 55.9, 44.9 (q,  $J = 2.1$  Hz), 40.7 (q,  $J = 28.3$  Hz), 26.6, 25.1.  $^{19}\text{F NMR}$  (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.86 (t,  $J = 10.6$  Hz).



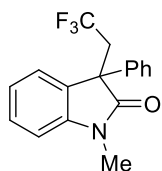
**HRMS** (EI<sup>+</sup>) m/z: [M] Calcd for C<sub>13</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>2</sub>: 274.10494, Found: 274.1049 ( $\Delta$  = -0.31 ppm). The analytical data were consistent with the literature<sup>13</sup>.



**1,3-Dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (5d)** was synthesized from **4d** (100 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5d** was obtained as a white solid (89 mg, 66% yield). *R<sub>f</sub>* (in PE/EA = 2:1): 0.28. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.51 (d, *J* = 1.1 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 3.26 (s, 3H), 2.85 (dq, *J* = 15.3, 10.6 Hz, 1H), 2.67 (dq, *J* = 15.3, 10.3 Hz, 1H), 1.42 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  178.2, 146.9, 134.0, 132.1, 127.1, 125.0 (q, *J* = 278.2 Hz), 119.1, 109.1, 106.1, 44.3 (q, *J* = 2.0 Hz), 40.7 (q, *J* = 28.6 Hz), 26.8, 25.0. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  -62.02 (t, *J* = 10.4 Hz). **HRMS** (EI<sup>+</sup>) m/z: [M] Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O: 268.08235, Found: 268.08193 ( $\Delta$  = -1.55 ppm). The analytical data were consistent with the literature<sup>14</sup>.

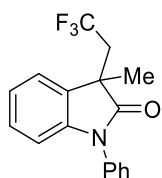


**5-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5e)** was synthesized from **4e** (105 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5e** was obtained as a white solid (91 mg, 66% yield). *R<sub>f</sub>* (in PE/EA = 2:1): 0.46. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.23 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 3.21 (s, 3H), 2.82 (dq, *J* = 15.2, 10.7 Hz, 1H), 2.62 (dq, *J* = 15.2, 10.4 Hz, 1H), 1.39 (s, 3H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)  $\delta$  178.0, 141.6, 132.8, 128.7, 128.2, 125.2 (q, *J* = 278.2 Hz), 124.2, 109.5, 44.7 (q, *J* = 2.0 Hz), 40.7 (q, *J* = 28.4 Hz), 26.7, 25.0. **<sup>19</sup>F NMR** (377 MHz, CDCl<sub>3</sub>)  $\delta$  -61.96 (t, *J* = 10.5 Hz). **HRMS** (EI<sup>+</sup>) m/z: [M] Calcd for C<sub>12</sub>H<sub>11</sub><sup>35</sup>ClF<sub>3</sub>N<sub>2</sub>O: 277.04813, Found: 277.04828 ( $\Delta$  = 0.57 ppm), Calcd for C<sub>12</sub>H<sub>11</sub><sup>37</sup>ClF<sub>3</sub>N<sub>2</sub>O: 279.04518, Found: 279.04559 ( $\Delta$  = 1.47 ppm). The analytical data were consistent with the literature<sup>13</sup>.

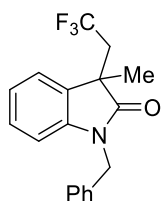


**1-Methyl-3-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5f)** was synthesized from **4f** (190 mg, 0.8 mmol) and Togni II reagent (278 mg, 0.88 mmol) following **General procedure E**. **4f** was obtained as a white solid (113 mg, 46% yield). *R<sub>f</sub>* (in PE/EA = 2:1): 0.59. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (td, *J* = 7.8, 1.2 Hz, 1H), 7.37 – 7.23 (m, 6H), 7.17 (td, *J* = 7.6, 0.8 Hz, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 3.44 (dq, *J* = 15.1, 10.5 Hz, 1H), 3.23 (s, 3H), 3.06 (dq, *J* = 15.1, 10.2 Hz, 1H). **<sup>13</sup>C NMR** (101 MHz, CDCl<sub>3</sub>)

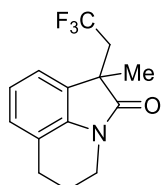
$\delta$  176.8, 143.9, 138.8, 129.2, 129.0, 128.9, 128.1, 126.6, 126.2, 125.2 (q,  $J = 278.7$  Hz), 122.7, 108.9, 52.1 (q,  $J = 2.0$  Hz), 41.0 (q,  $J = 28.1$  Hz), 26.8.  **$^{19}\text{F}$  NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.16 (t,  $J = 10.4$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NO}$ : 305.10275, Found: 305.10342 ( $\Delta = 2.19$  ppm). The analytical data were consistent with the literature<sup>13</sup>.



**3-Methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5g)** was synthesized from **4g** (119 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5g** was obtained as a white solid (108 mg, 71% yield).  $R_f$  (in PE/EA = 2:1): 0.58.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 – 7.48 (m, 2H), 7.47 – 7.36 (m, 3H), 7.33 (d,  $J = 7.4$  Hz, 1H), 7.28 – 7.20 (m, 1H), 7.13 (td,  $J = 7.5$ , 0.8 Hz, 1H), 6.84 (d,  $J = 7.9$  Hz, 1H), 2.97 (dq,  $J = 15.1$ , 10.7 Hz, 1H), 2.73 (dq,  $J = 15.1$ , 10.4 Hz, 1H), 1.54 (s, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.1, 143.1, 134.5, 130.8, 129.8, 128.6, 128.4, 126.7, 125.4 (q,  $J = 278.3$  Hz), 123.9, 123.2, 109.9, 44.6 (q,  $J = 1.9$  Hz), 41.2 (q,  $J = 28.2$  Hz), 25.6.  **$^{19}\text{F}$  NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.87 (t,  $J = 10.5$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NO}$ : 305.10275, Found: 305.10316 ( $\Delta = 1.34$  ppm). The analytical data were consistent with the literature<sup>13</sup>.



**1-Benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5h)** was synthesized from **4h** (201 mg, 0.8 mmol) and Togni II reagent (278 mg, 0.88 mmol) following **General procedure E**. **5h** was obtained as a white solid (135 mg, 53% yield).  $R_f$  (in PE/EA = 2:1): 0.59.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 – 7.23 (m, 6H), 7.19 (td,  $J = 7.8$ , 1.2 Hz, 1H), 7.06 (td,  $J = 7.6$ , 0.8 Hz, 1H), 6.76 (d,  $J = 7.8$  Hz, 1H), 4.94 (dd,  $J = 36.3$ , 15.7 Hz, 2H), 2.92 (dq,  $J = 15.1$ , 10.7 Hz, 1H), 2.71 (dq,  $J = 15.1$ , 10.5 Hz, 1H), 1.47 (s, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  178.7, 142.1, 135.8, 131.1, 128.9, 128.5, 127.8, 127.4, 125.4 (q,  $J = 278.2$  Hz), 123.7, 122.8, 109.7, 44.6 (q,  $J = 2.0$  Hz), 44.1, 40.6 (q,  $J = 28.3$  Hz), 25.8.  **$^{19}\text{F}$  NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.71 (t,  $J = 10.7$  Hz). **HRMS** ( $\text{EI}^+$ )  $m/z$ : [M] Calcd for  $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NO}$ : 319.11840, Found: 319.11957 ( $\Delta = 3.66$  ppm). The analytical data were consistent with the literature<sup>13</sup>.



**1-Methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (5i)** was synthesized from **4i** (101 mg, 0.5 mmol) and Togni II reagent (174 mg, 0.55 mmol) following **General procedure E**. **5i** was obtained as a yellowish oil (89 mg, 66% yield).  $R_f$  (in PE/EA = 2:1): 0.39.  **$^1\text{H}$  NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.10 (d,  $J = 7.4$  Hz, 1H), 7.05 (d,  $J = 7.6$  Hz, 1H), 6.97 (t,  $J = 7.5$  Hz, 1H),

3.78 – 3.66 (m, 2H), 2.87 – 2.70 (m, 3H), 2.64 (dq,  $J = 15.2, 10.6$  Hz, 1H), 2.11 – 1.90 (m, 2H), 1.41 (s, 3H).  **$^{13}\text{C}$  NMR** (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.5, 138.8, 129.8, 127.4, 125.5 (q,  $J = 278.1$  Hz), 122.2, 121.6 (d,  $J = 1.3$  Hz), 120.6, 45.8 (q,  $J = 2.0$  Hz), 40.6 (q,  $J = 28.2$  Hz), 39.2, 24.7, 24.6, 21.3.  **$^{19}\text{F}$  NMR** (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.81 (t,  $J = 10.8$  Hz). **HRMS** (EI<sup>+</sup>)  $m/z$ : [M] Calcd for  $\text{C}_{14}\text{H}_{14}\text{F}_3\text{NO}$ : 269.10275, Found: 269.10204 ( $\Delta = -2.64$  ppm). The analytical data were consistent with the literature<sup>14</sup>.

## 6. List of references

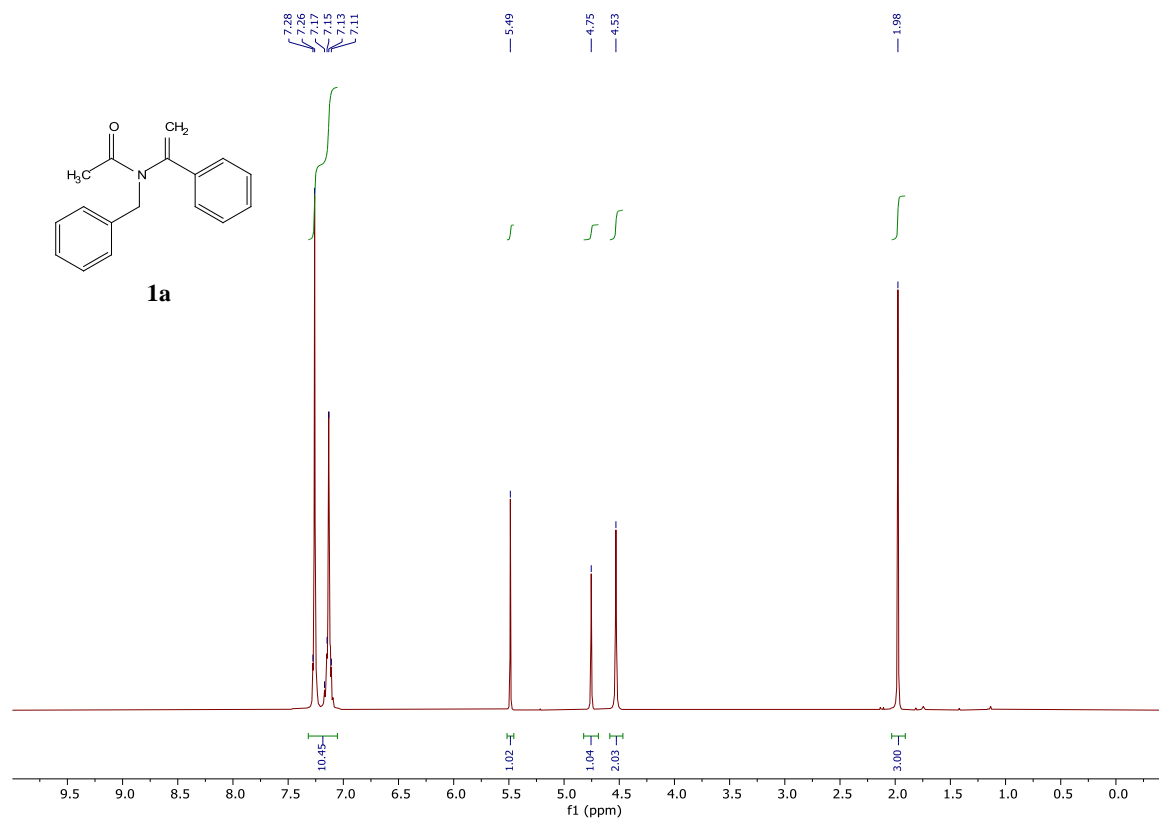
- 1 S. Luan, T. Castanheiro and T. Poisson, *Green Chem.*, 2024, **26**, 3429–3434.
- 2 M. Zhang, X. Ding, A. Lu, J. Kang, Y. Gao, Z. Wang, H. Li and Q. Wang, *Org. Chem. Front.*, 2021, **8**, 961–967.
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- 6 X.-Y. Lu, J.-C. Wang, X.-M. Sun, M.-T. Gao, W.-J. Ying, M.-Y. Ge, Z.-H. Wei, Z. Liu and X.-K. Chen, *J. Org. Chem.*, 2023, **88**, 513–524.
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- 11 F. Zhang, X. Zhao, J. Zhang, L. Zhao, L. Li, J. Yang, H. Li and H. Luo, *Adv. Synth. Catal.*, 2022, **364**, 4036–4042.
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- 13 P. Xu, J. Xie, Q. Xue, C. Pan, Y. Cheng and C. Zhu, *Chem. – Eur. J.*, 2013, **19**, 14039–14042.
- 14 J. Guo, C. Xu, L. Wang, W. Huang and M. Wang, *Org. Biomol. Chem.*, 2019, **17**, 4593–4599.

## 7. NMR spectra

### 7.1 Starting materials 1a-u, 4a-i

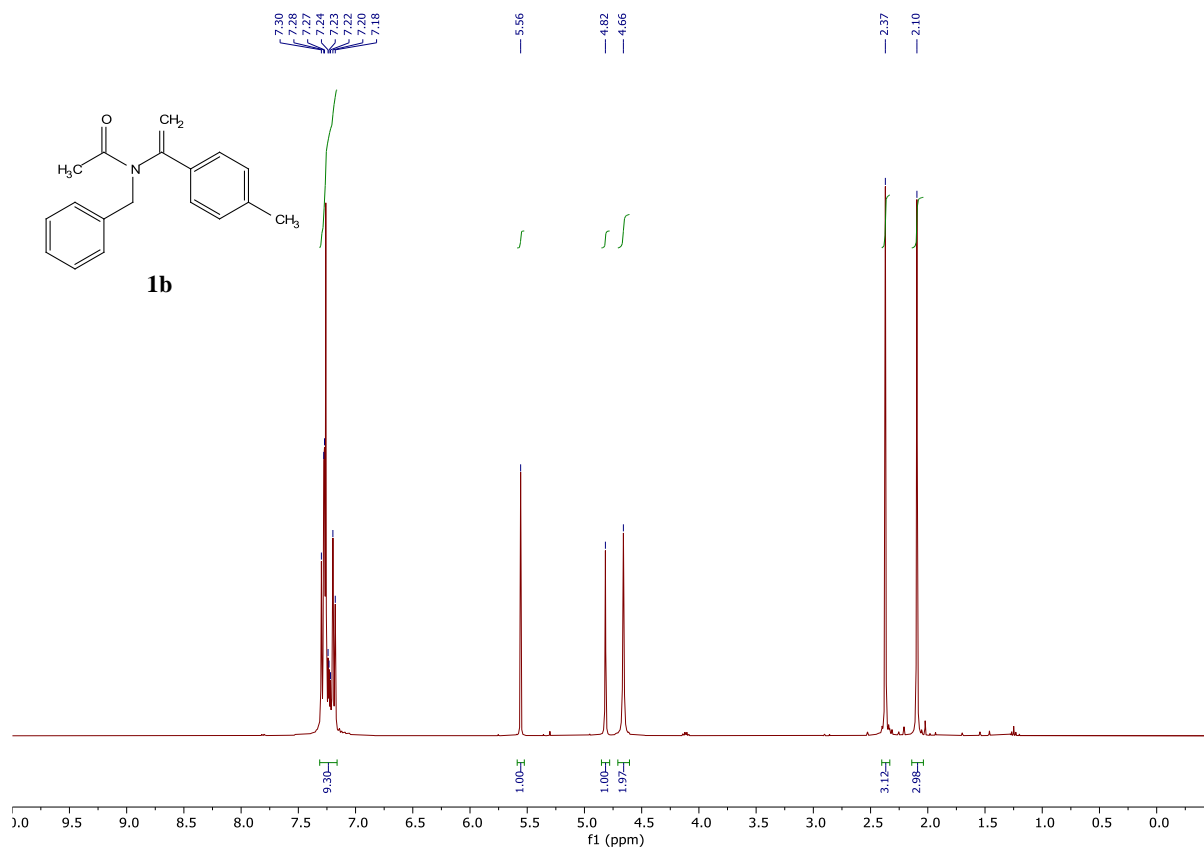
#### *N*-Benzyl-*N*-(1-phenylvinyl)acetamide (1a)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



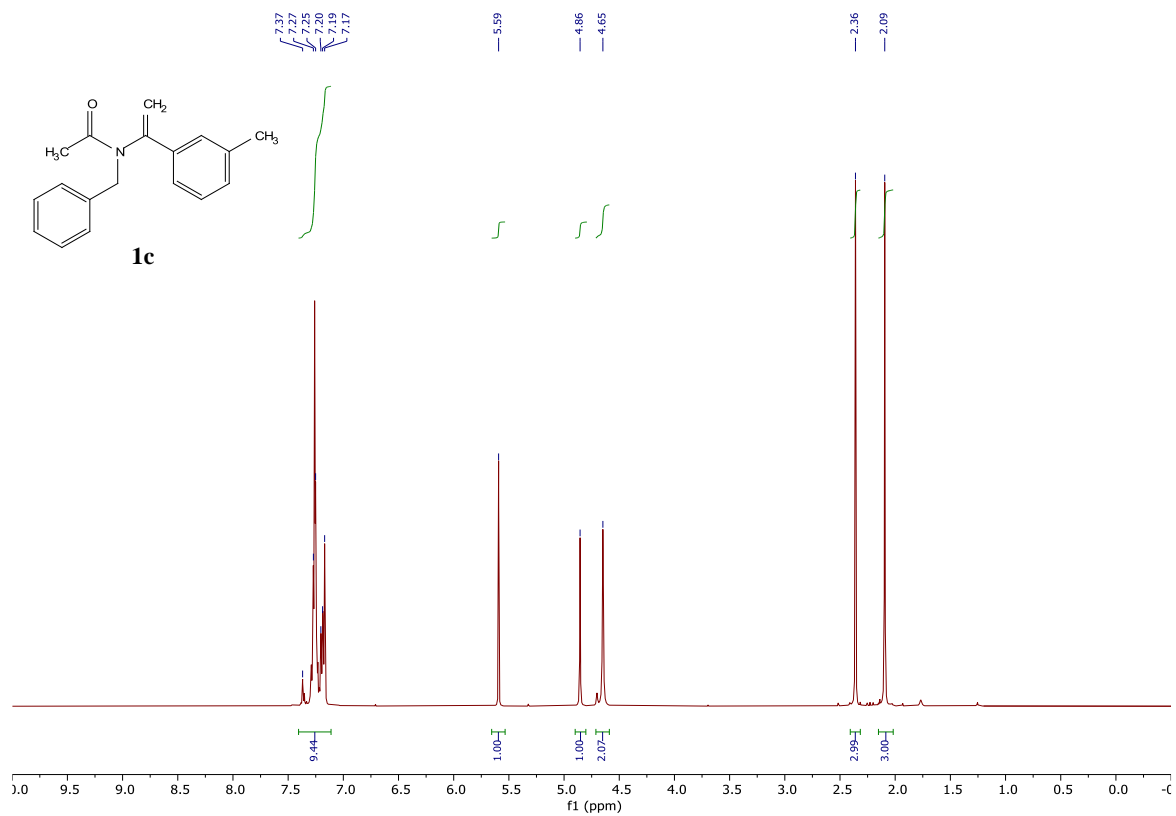
# ***N*-Benzyl-*N*-(1-(*p*-tolyl)vinyl)acetamide (**1b**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



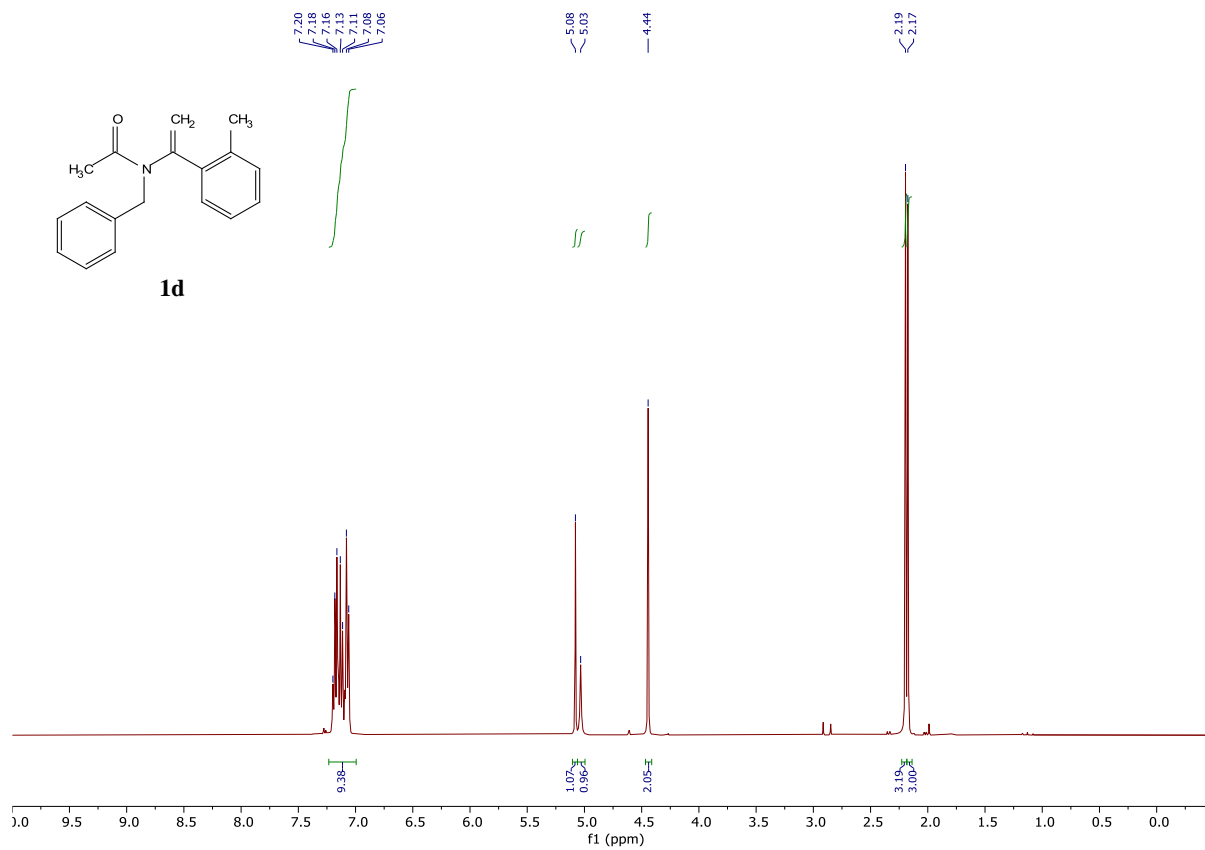
# ***N*-Benzyl-*N*-(1-(*m*-tolyl)vinyl)acetamide (**1c**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



# ***N*-Benzyl-*N*-(1-(*o*-tolyl)vinyl)acetamide (**1d**)**

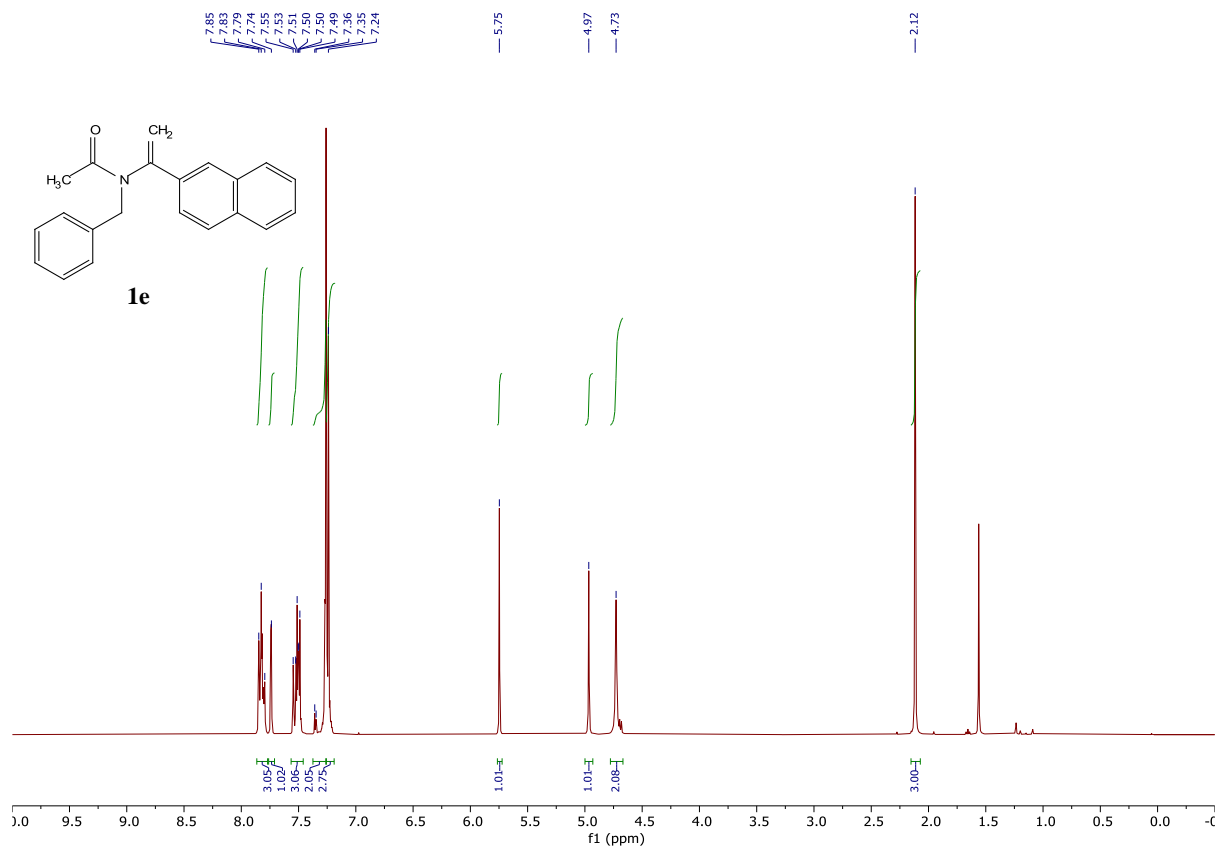
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





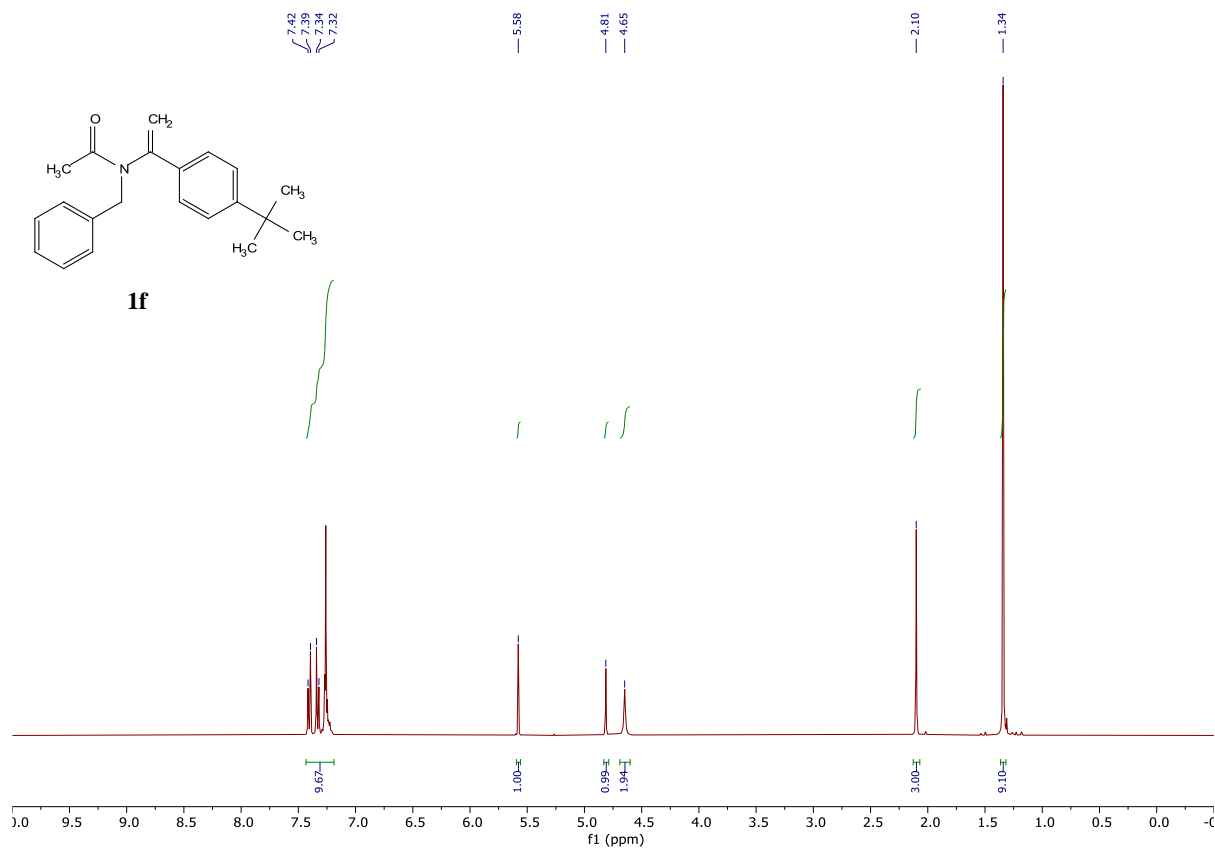
# *N*-Benzyl-*N*-(1-(naphthalen-2-yl)vinyl)acetamide (**1e**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



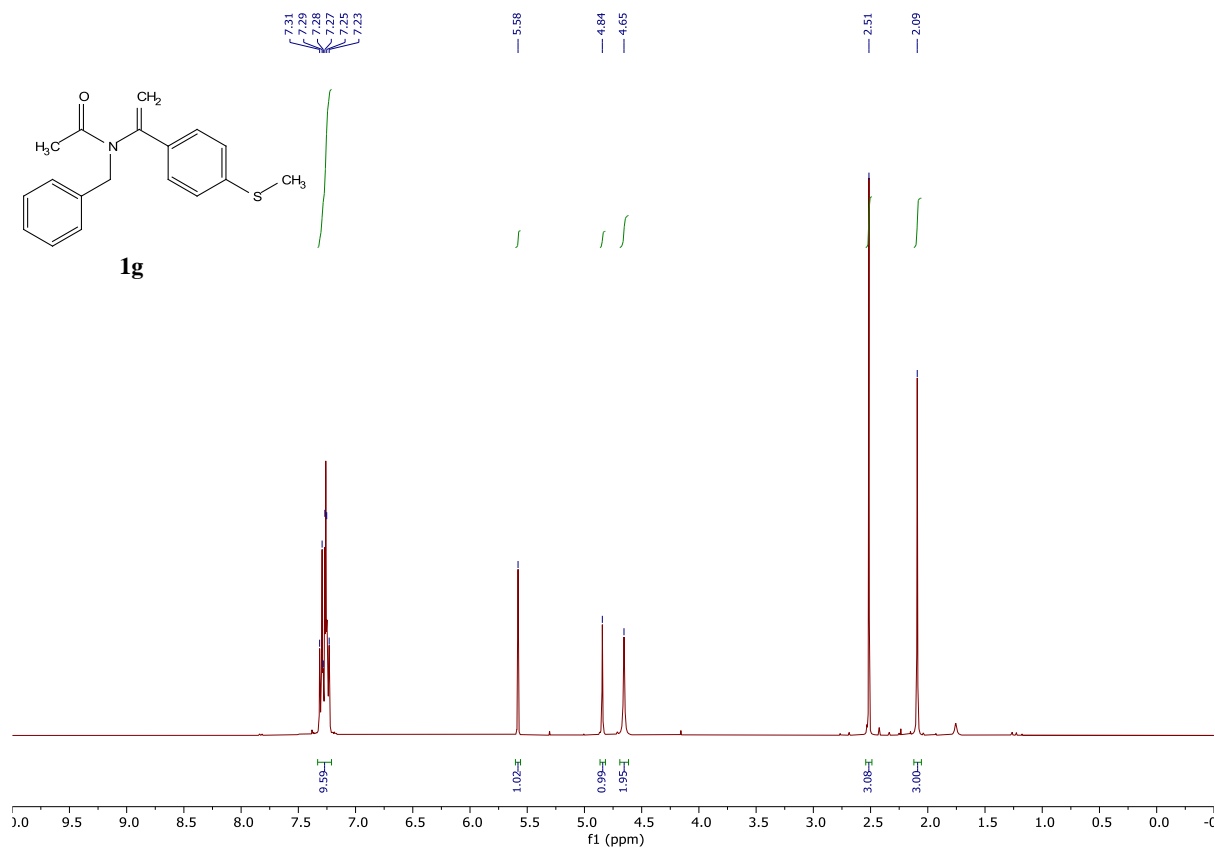
***N*-Benzyl-*N*-(1-(4-(*tert*-butyl)phenyl)vinyl)acetamide (**1f**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



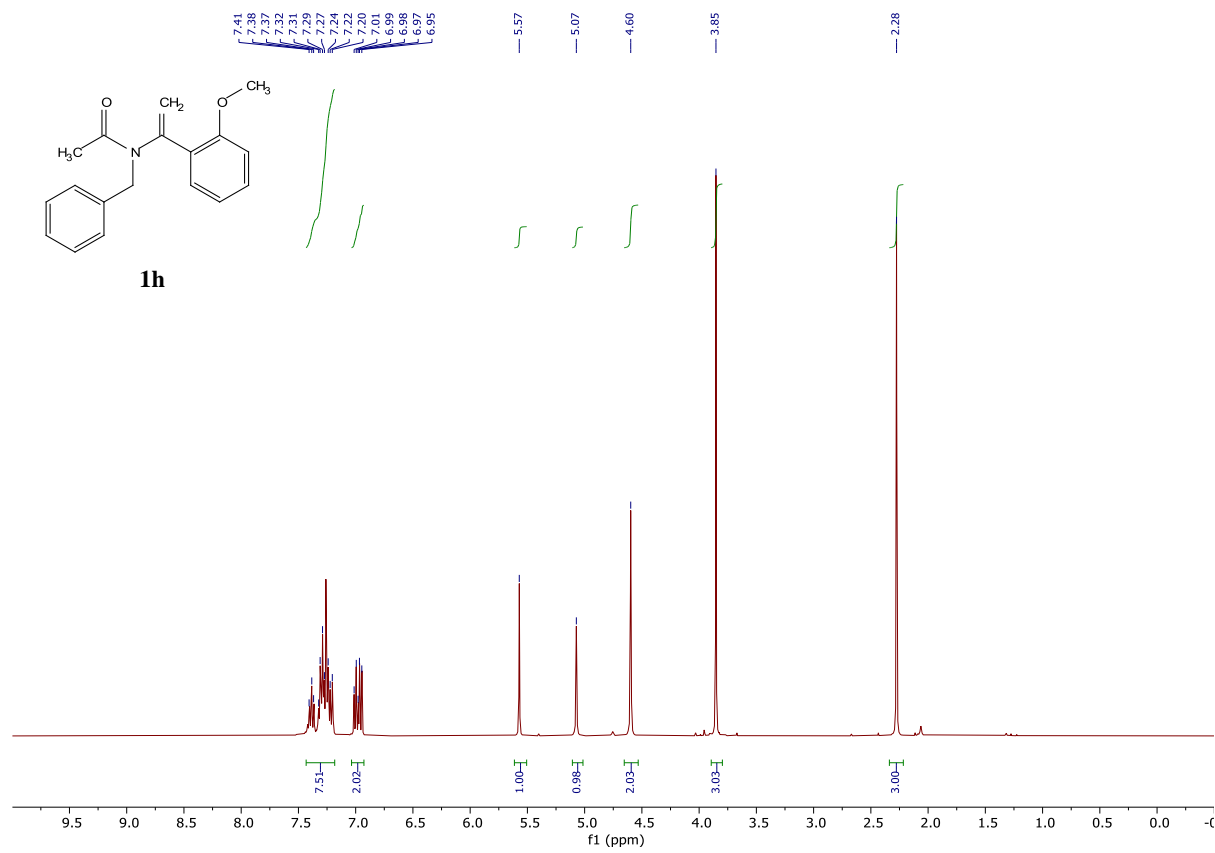
# ***N*-Benzyl-*N*-(1-(4-(methylthio)phenyl)vinyl)acetamide (**1g**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



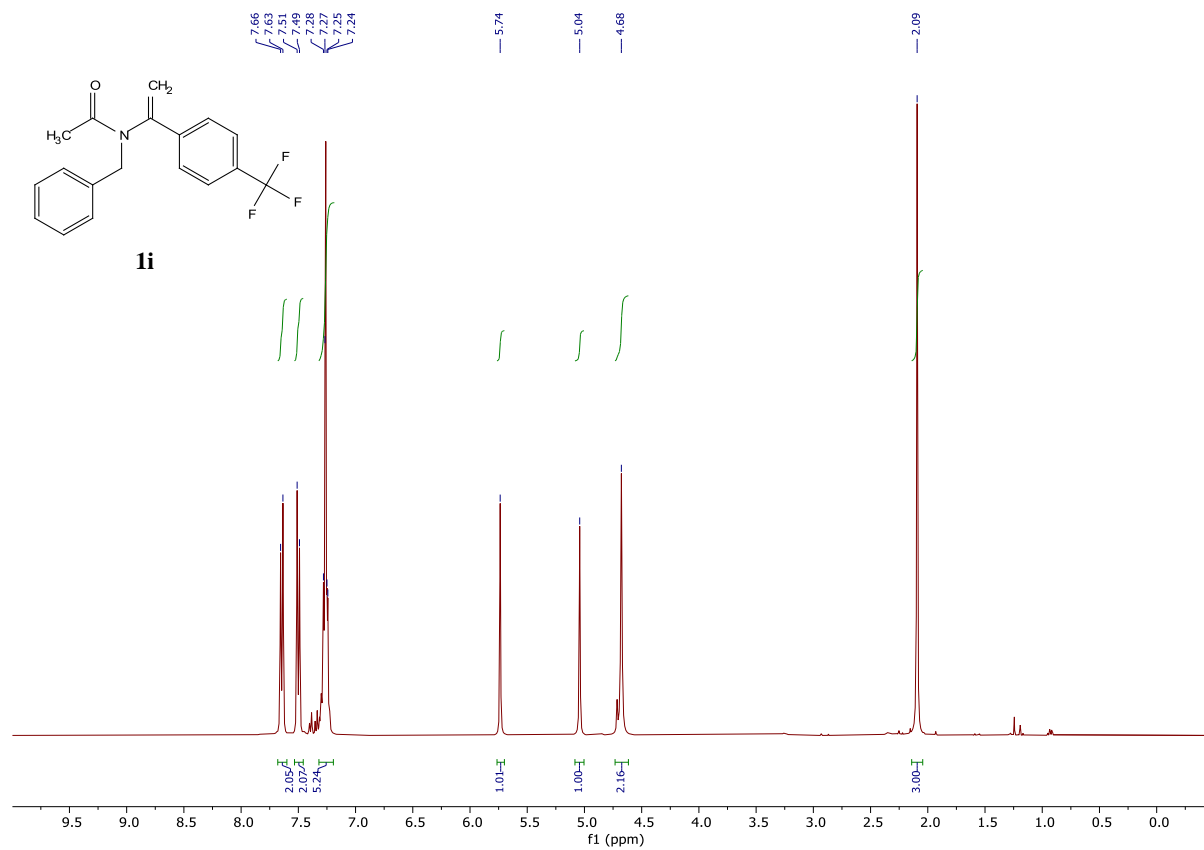
# *N*-Benzyl-*N*-(1-(2-methoxyphenyl)vinyl)acetamide (**1h**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



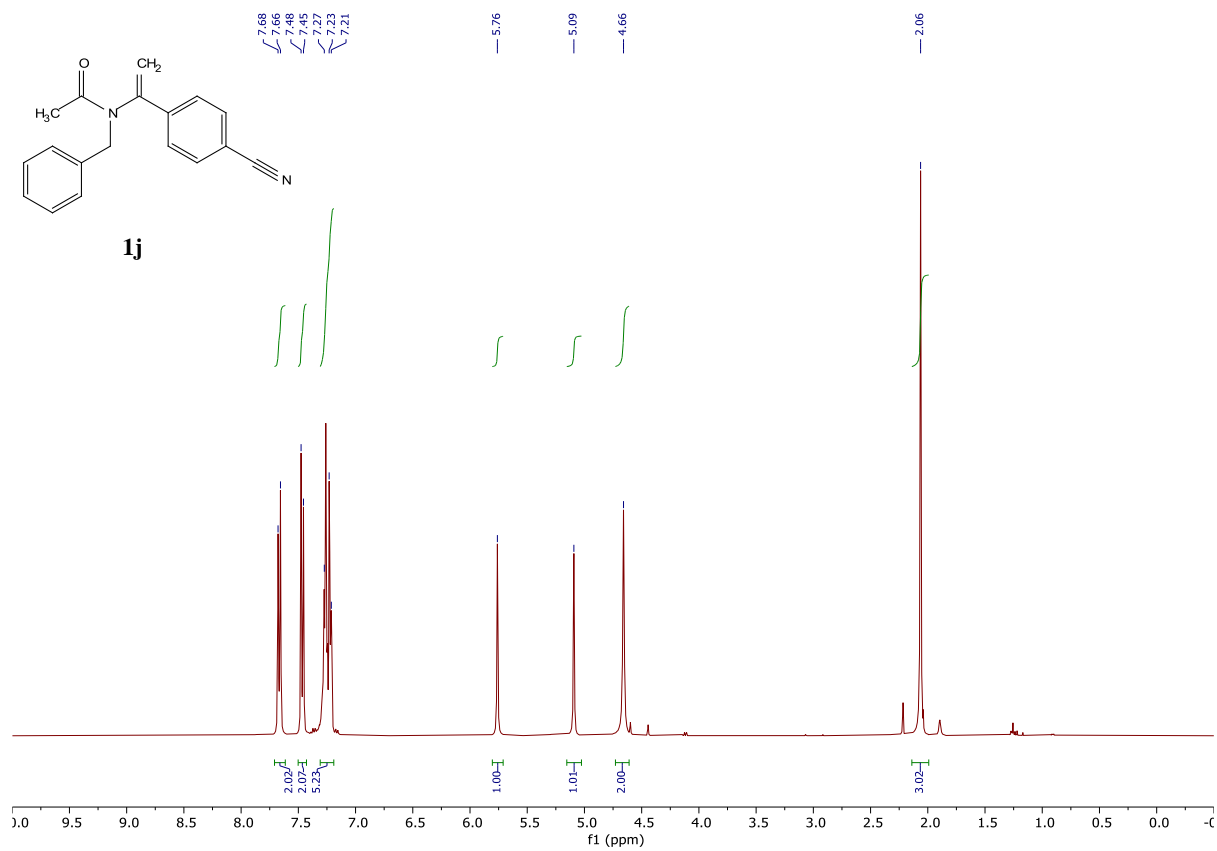
# *N*-Benzyl-*N*-(1-(4-(trifluoromethyl)phenyl)vinyl)acetamide (**1i**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



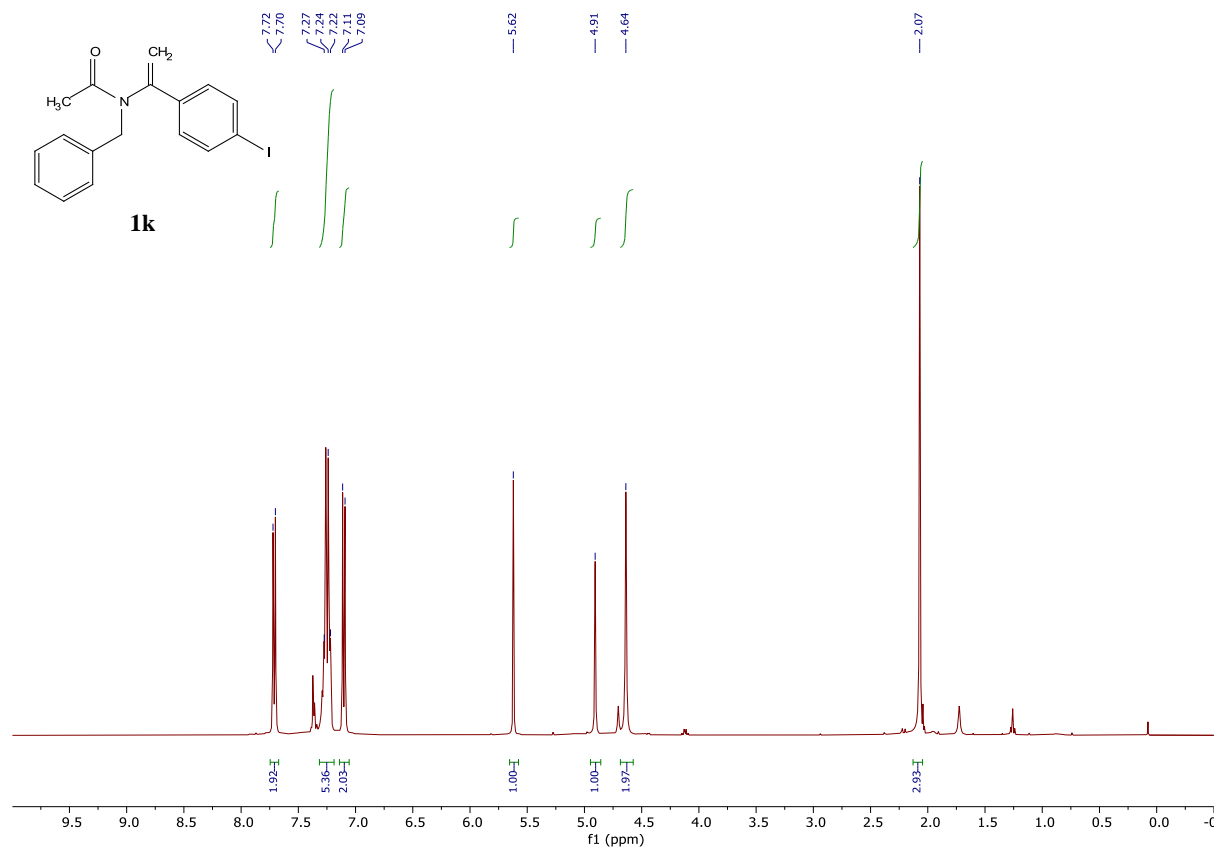
# ***N*-Benzyl-*N*-(1-(4-cyanophenyl)vinyl)acetamide (**1j**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



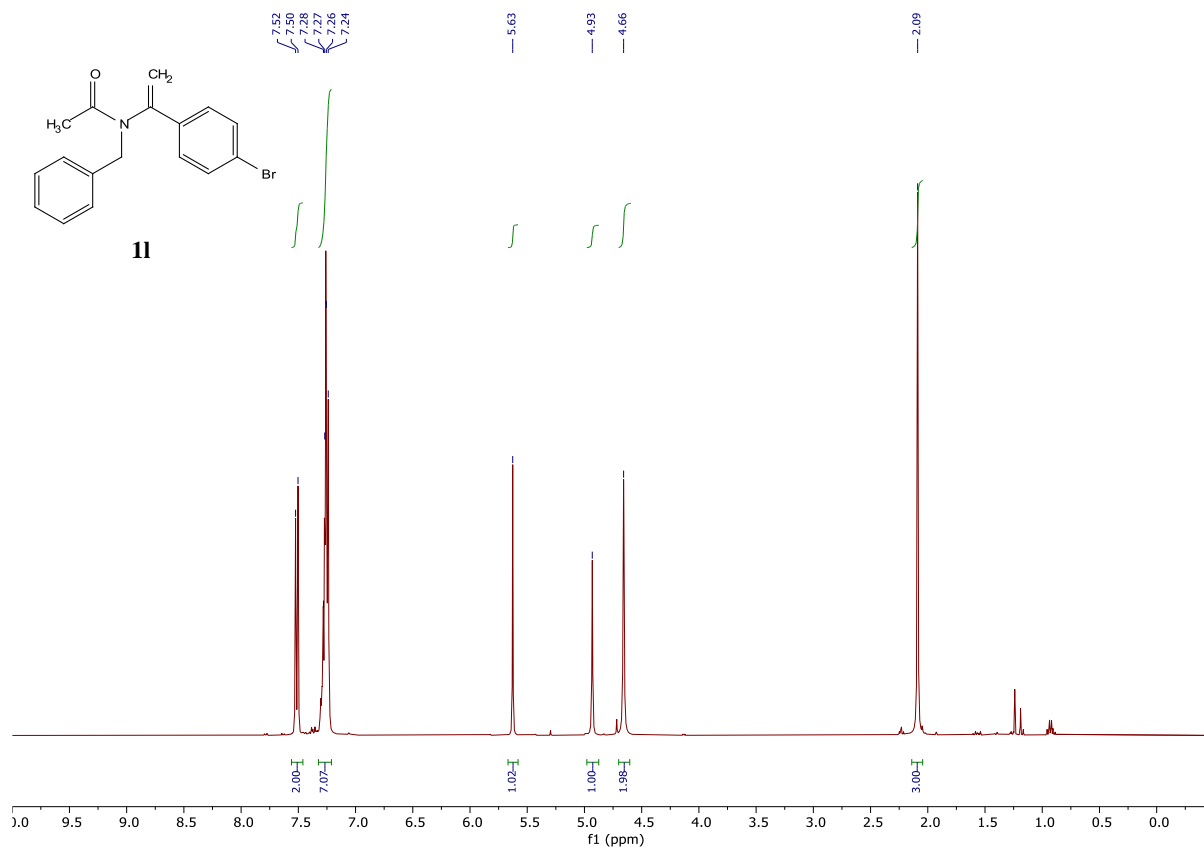
# ***N*-Benzyl-*N*-(1-(4-iodophenyl)vinyl)acetamide (**1k**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



# ***N*-Benzyl-*N*-(1-(4-bromophenyl)vinyl)acetamide (**11**)**

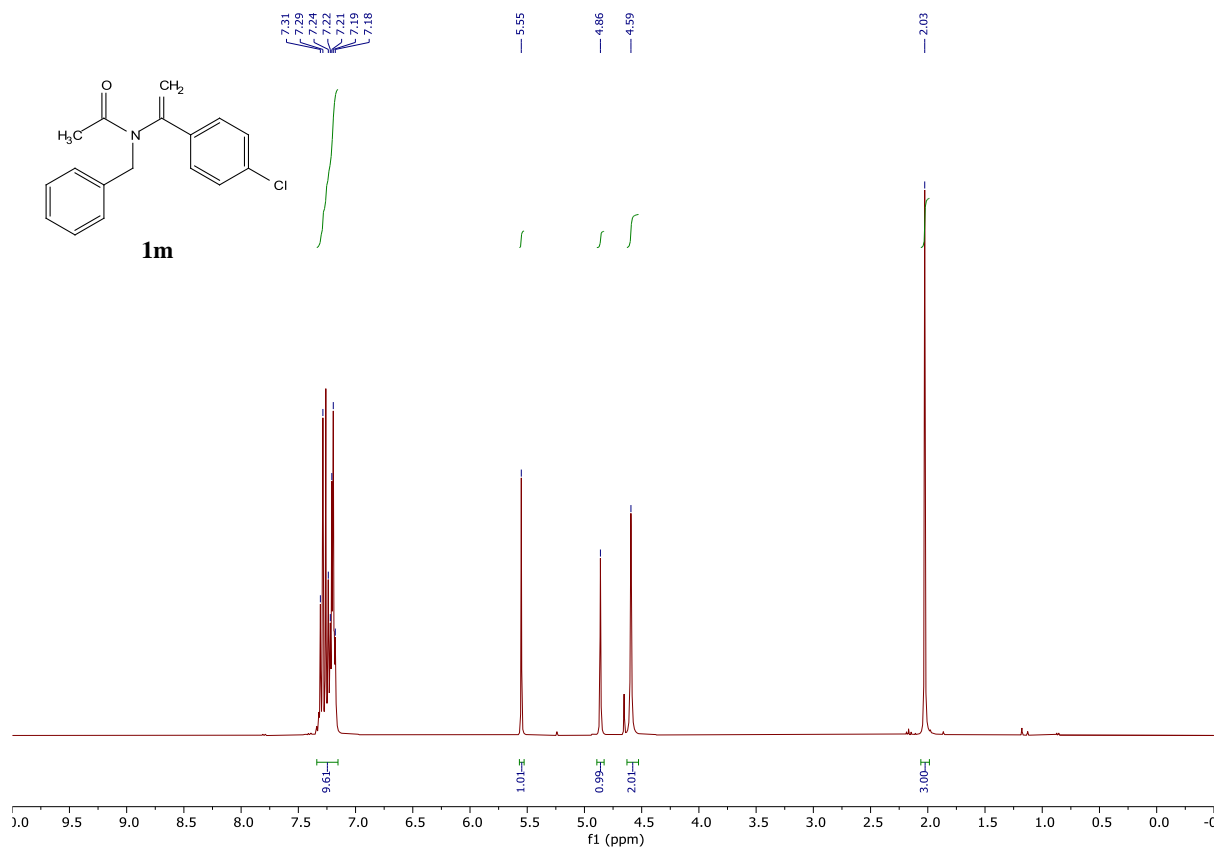
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





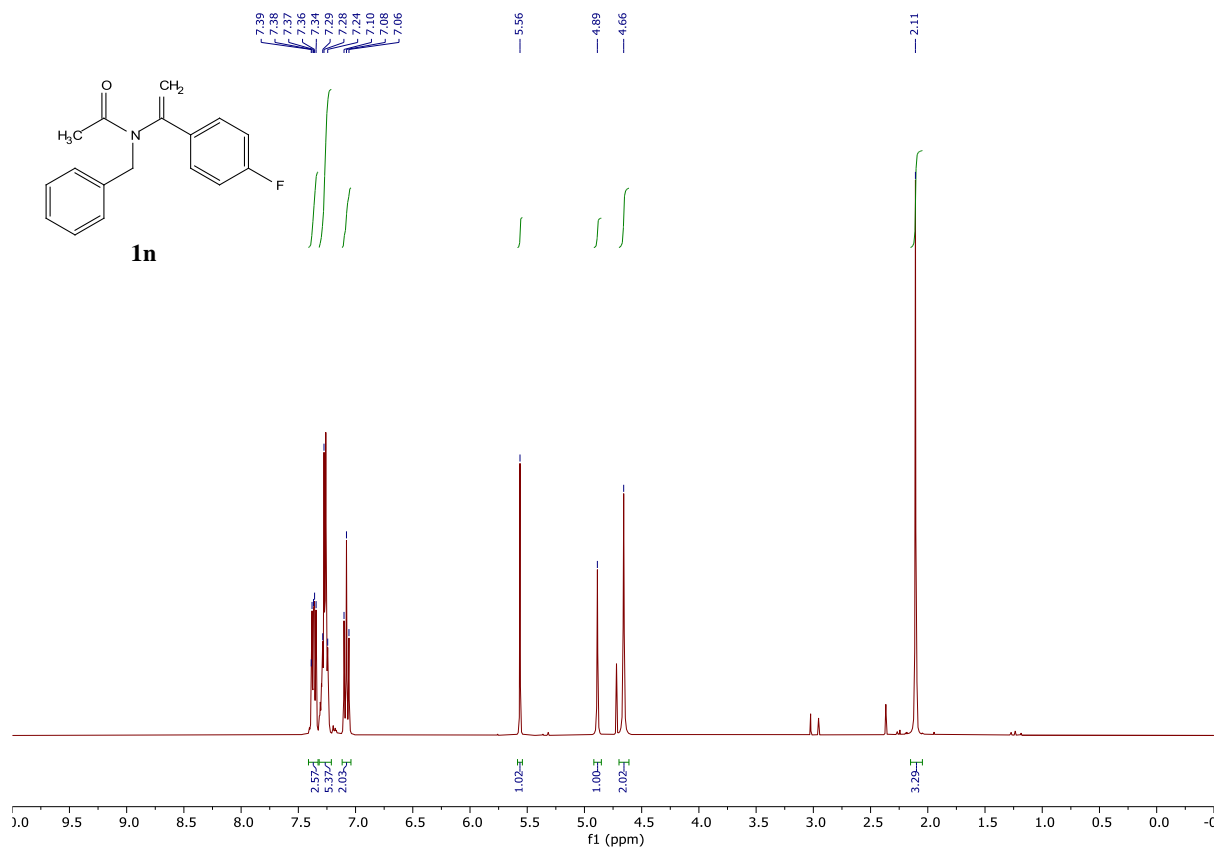
# ***N*-Benzyl-*N*-(1-(4-chlorophenyl)vinyl)acetamide (**1m**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



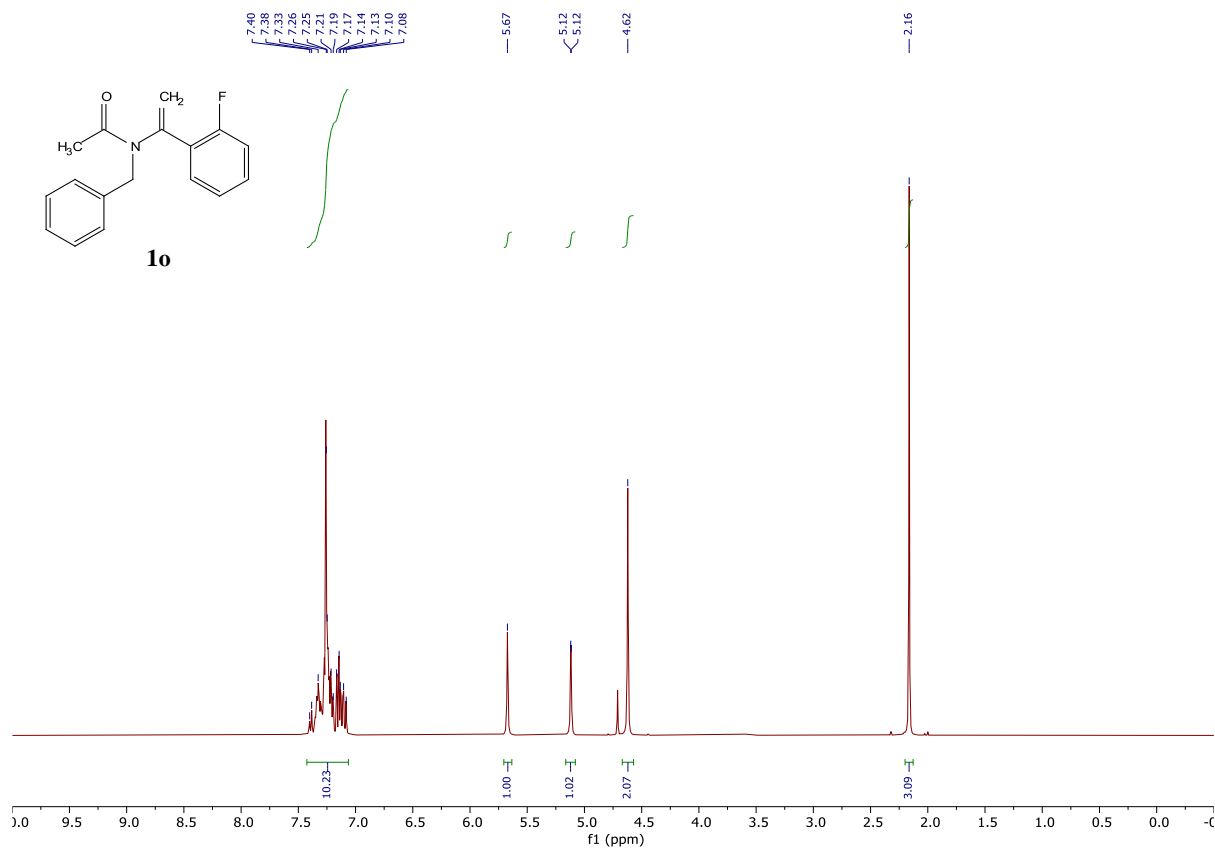
# ***N*-Benzyl-*N*-(1-(4-fluorophenyl)vinyl)acetamide (**1n**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



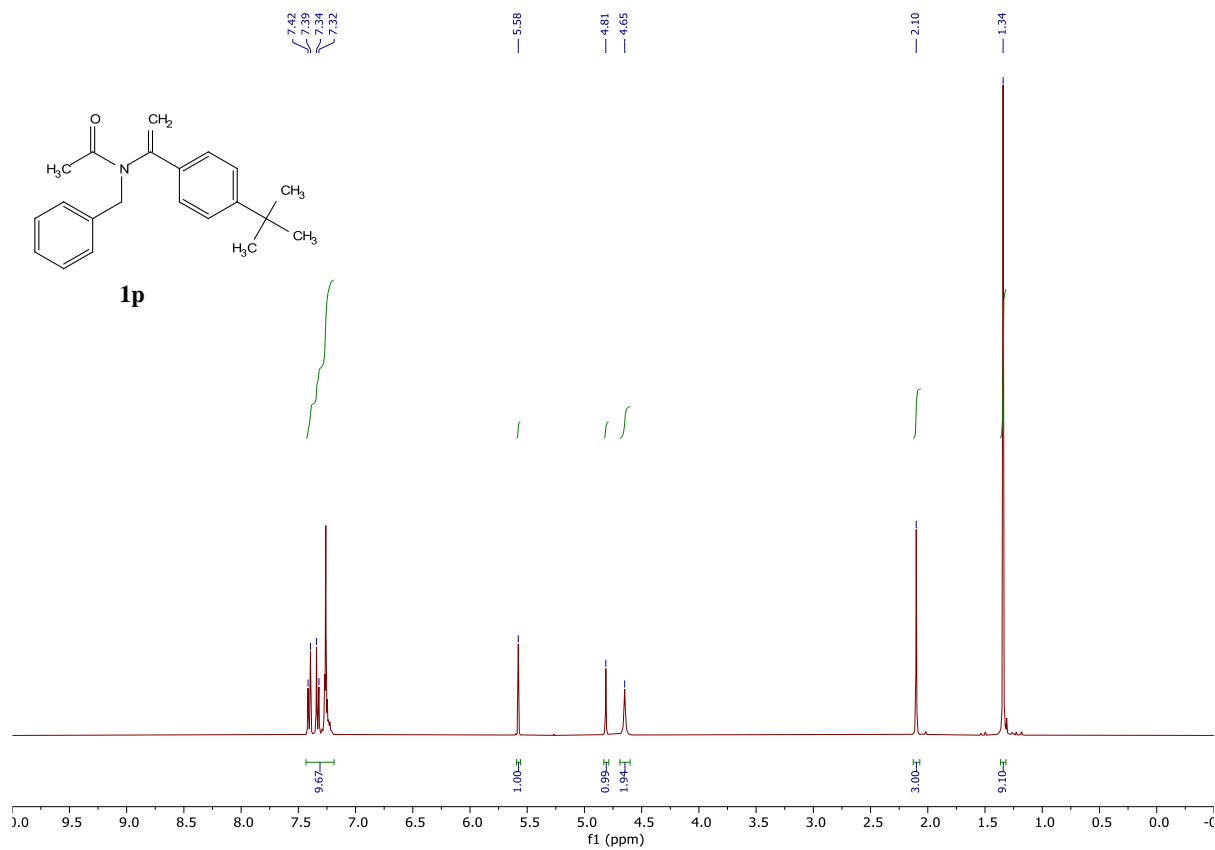
# *N*-Benzyl-*N*-(1-(2-fluorophenyl)vinyl)acetamide (**10**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



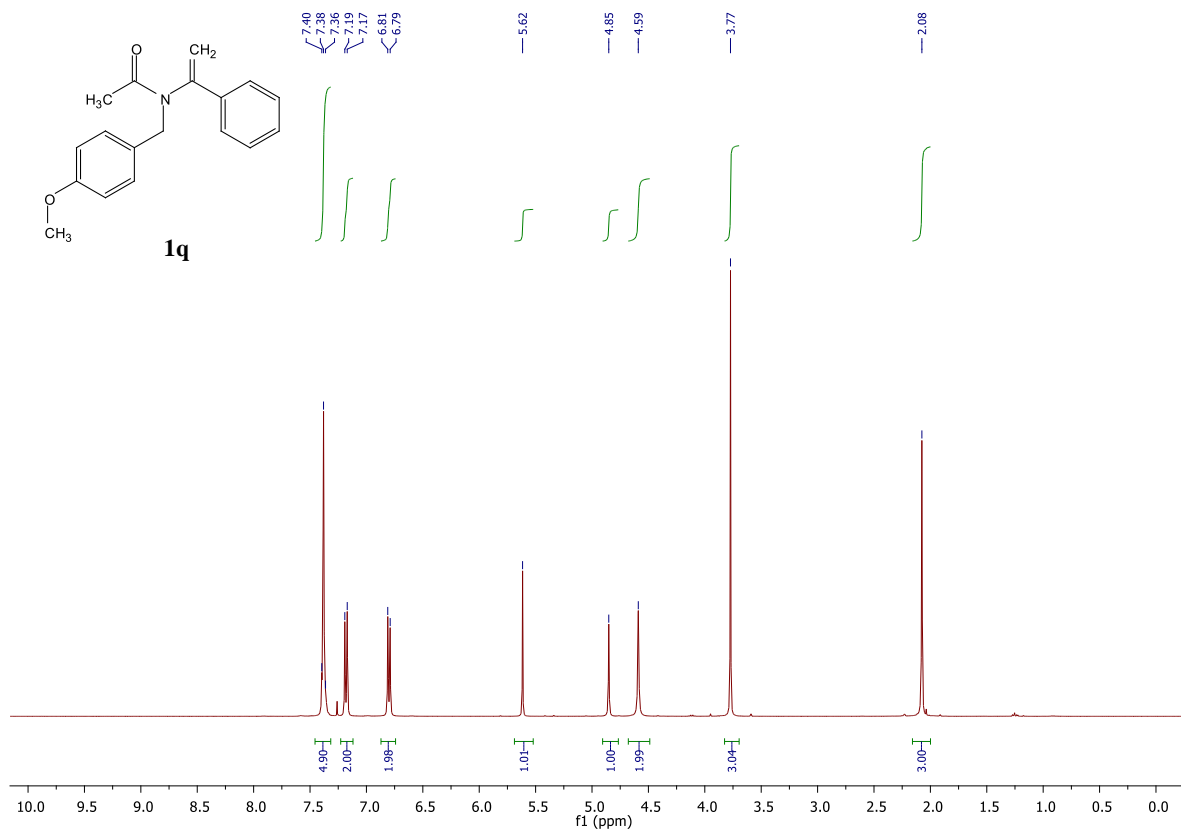
# ***N*-Benzyl-*N*-(1-(4-(*tert*-butyl)phenyl)vinyl)acetamide (**1p**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

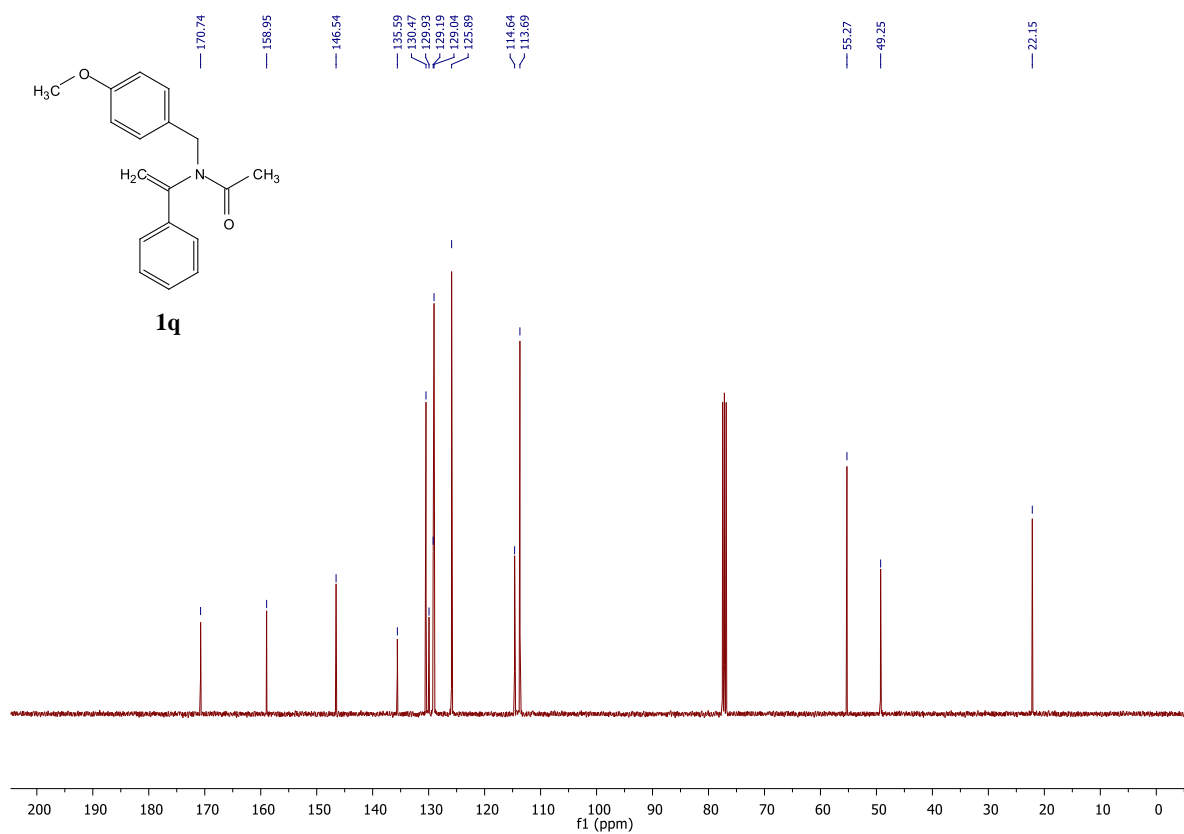


***N*-(4-Methoxybenzyl)-*N*-(1-phenylvinyl)acetamide (**1q**)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

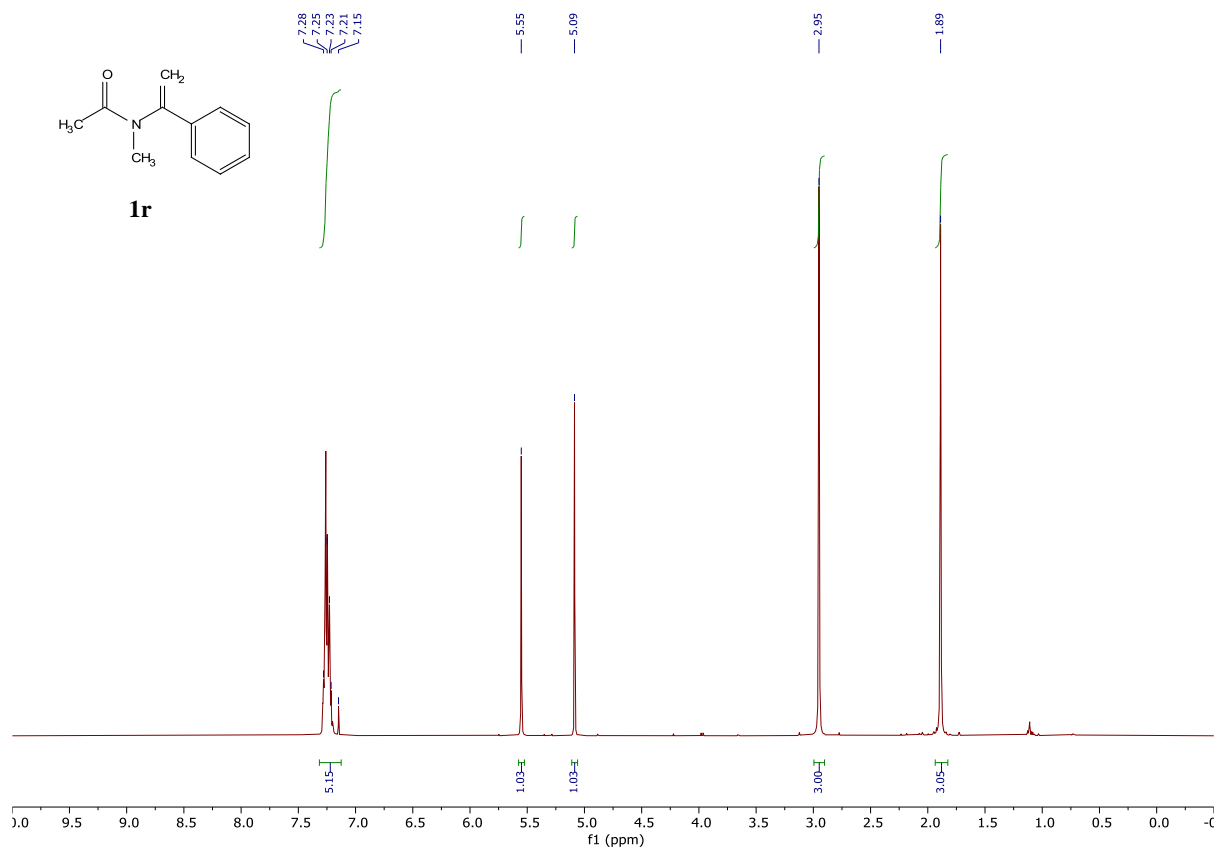


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



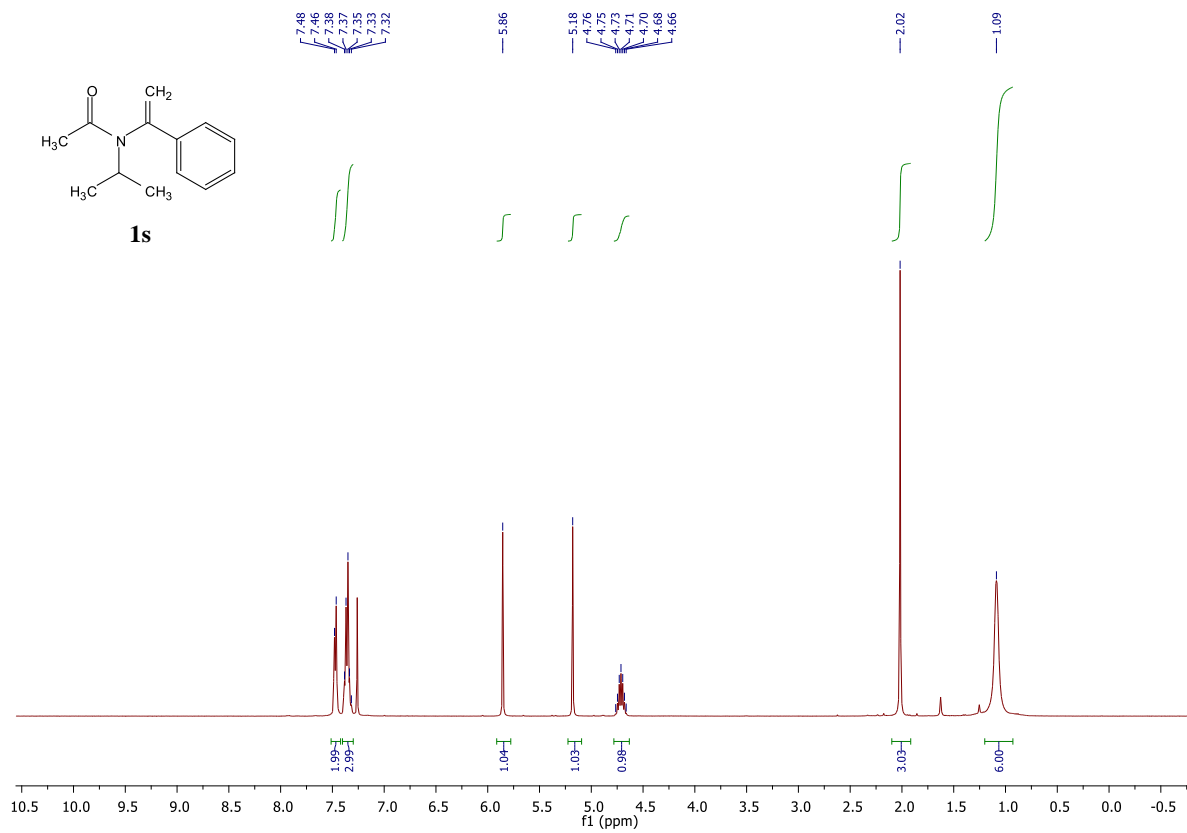
# *N*-Methyl-*N*-(1-phenylvinyl)acetamide (**1r**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



# *N*-Isopropyl-*N*-(1-phenylvinyl)acetamide (**1s**)

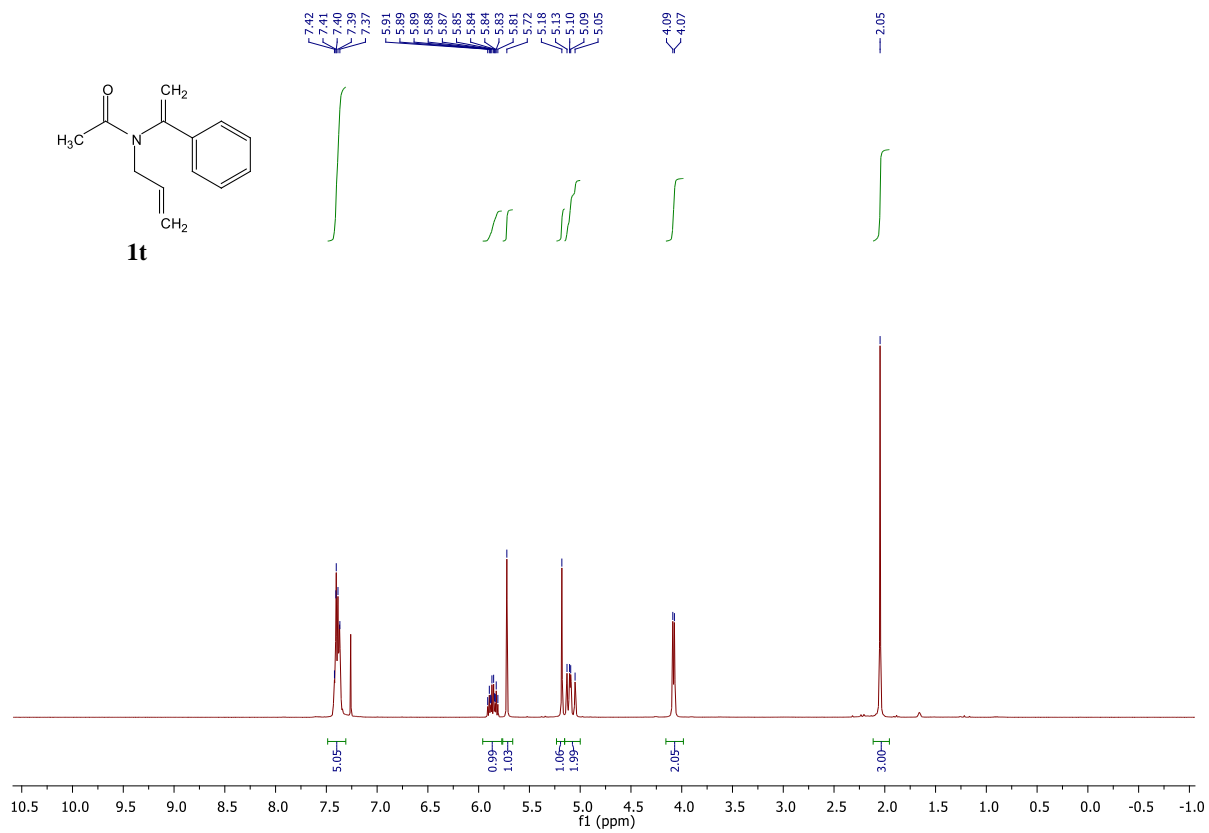
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





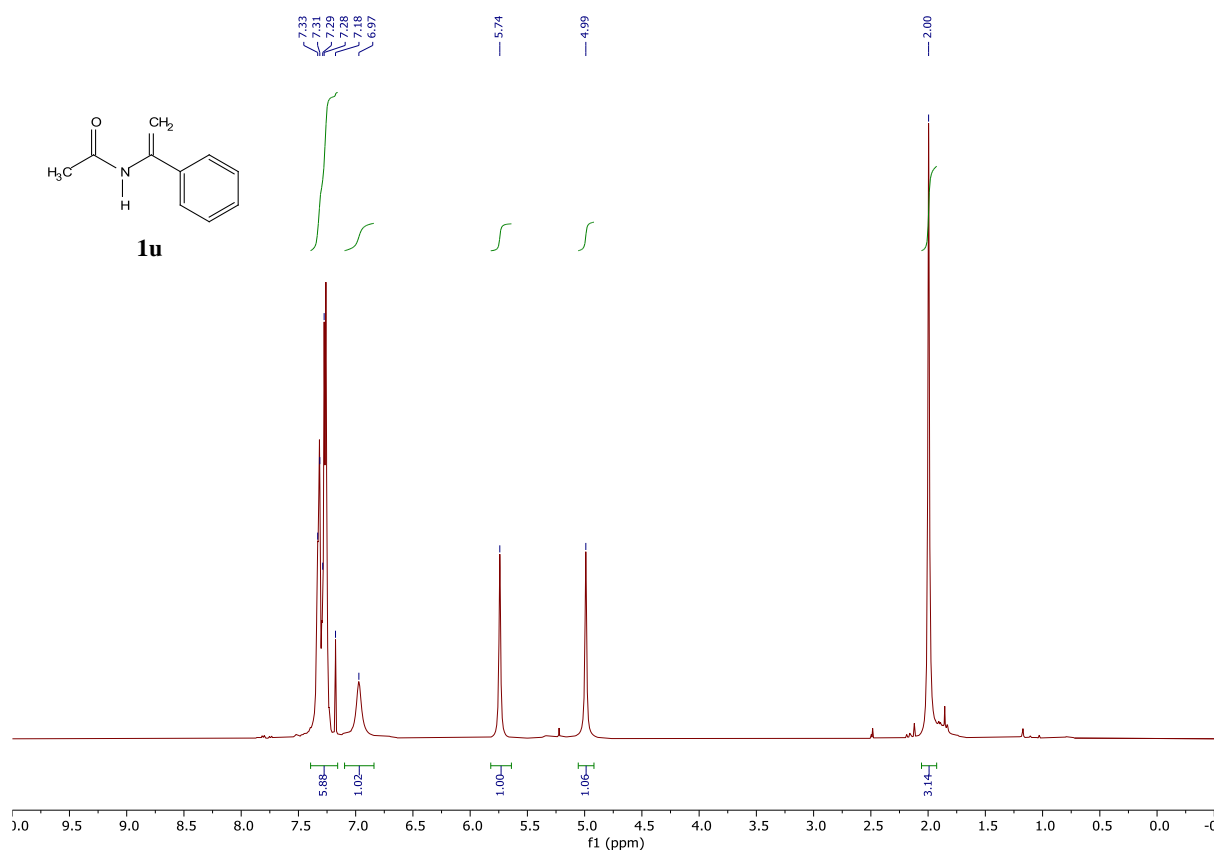
# *N*-Allyl-*N*-(1-phenylvinyl)acetamide (**1t**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



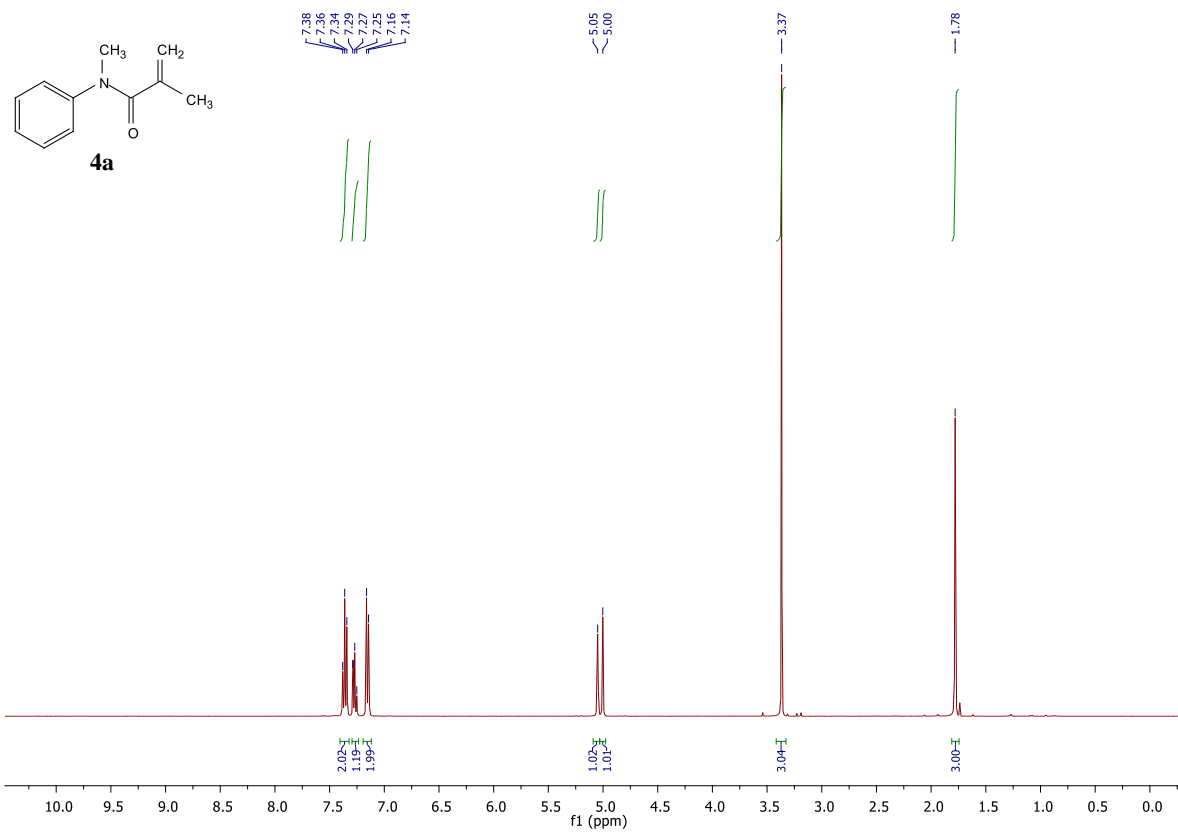
# *N*-(1-Phenylvinyl)acetamide (**1u**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



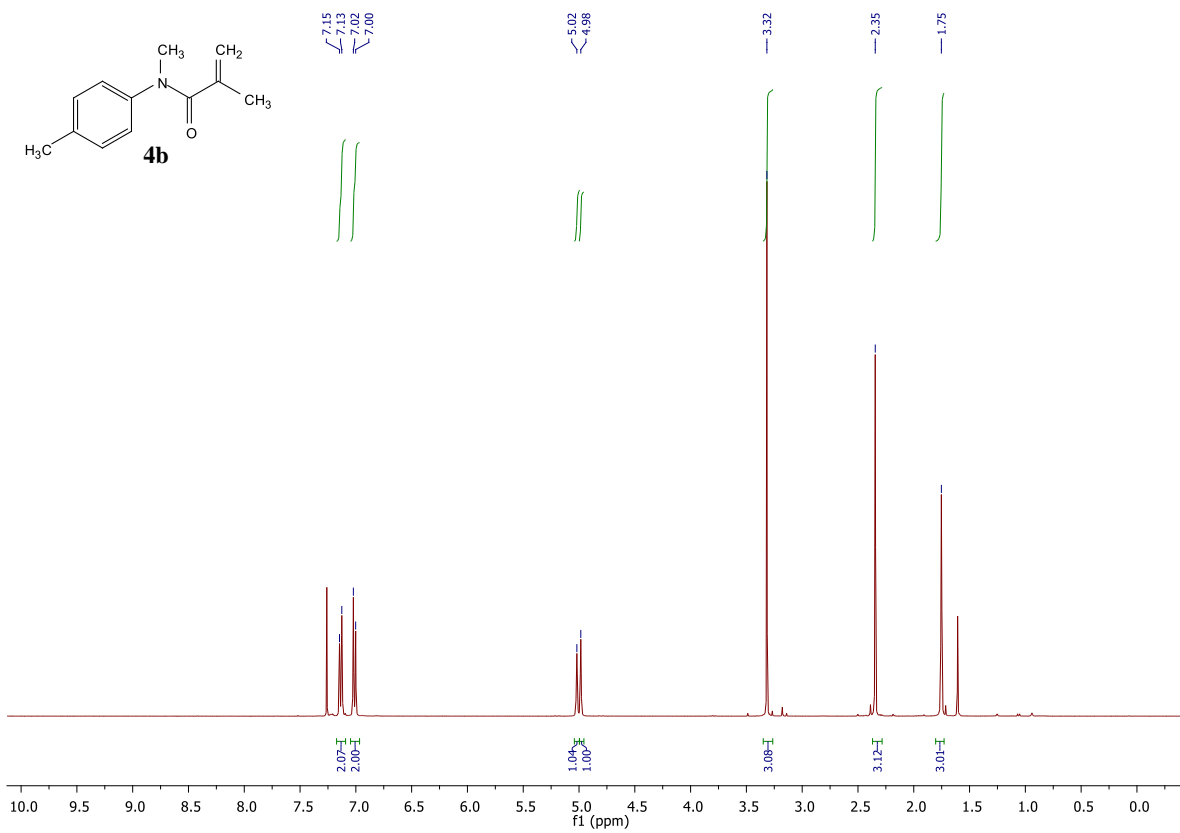
# ***N*-Methyl-*N*-phenylmethacrylamide (4a)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



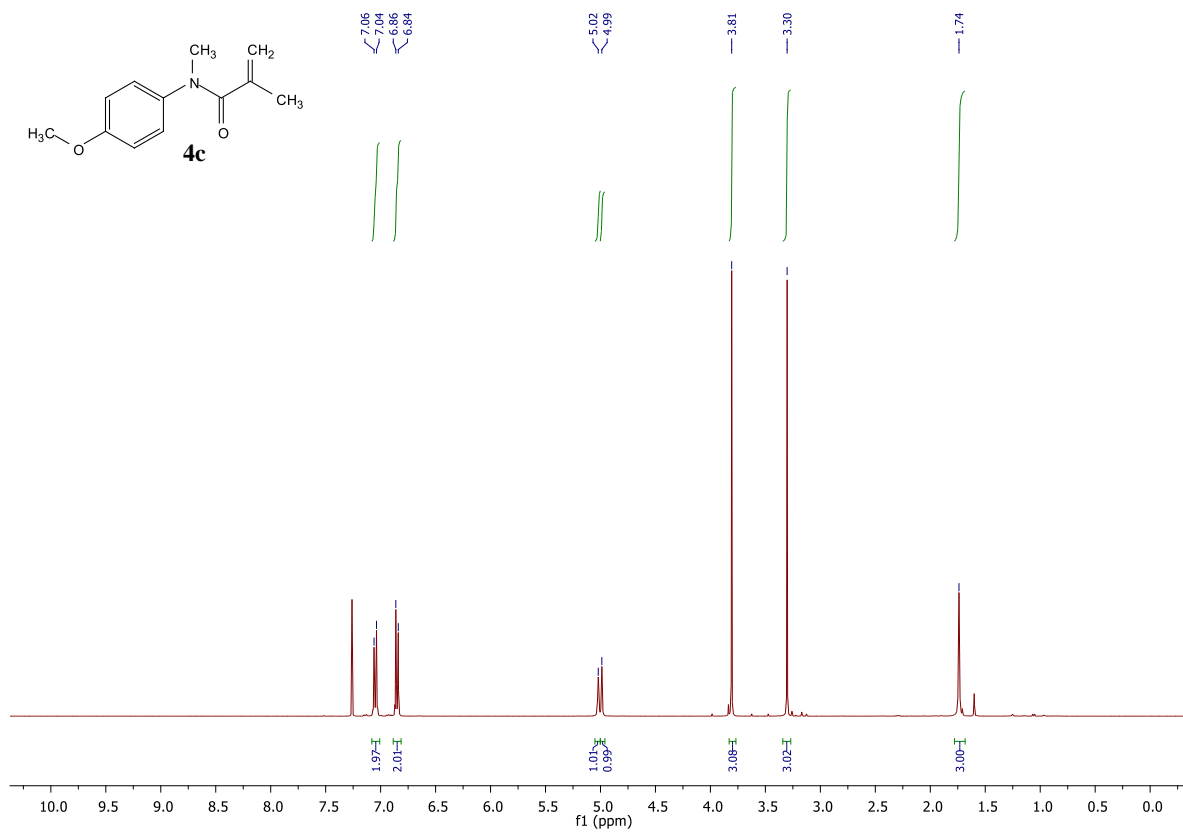
# ***N*-Methyl-*N*-(*p*-tolyl)methacrylamide (4b)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



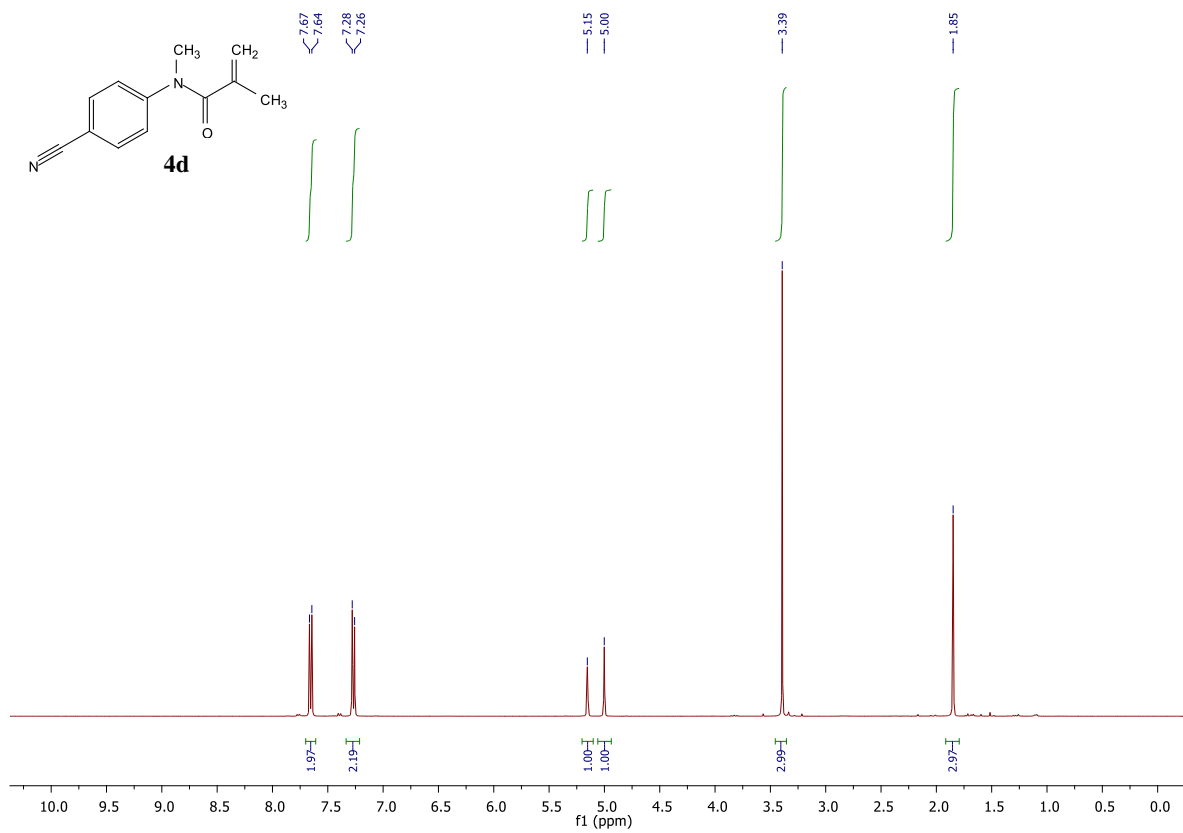
# *N*-(4-Methoxyphenyl)-*N*-methylmethacrylamide (**4c**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



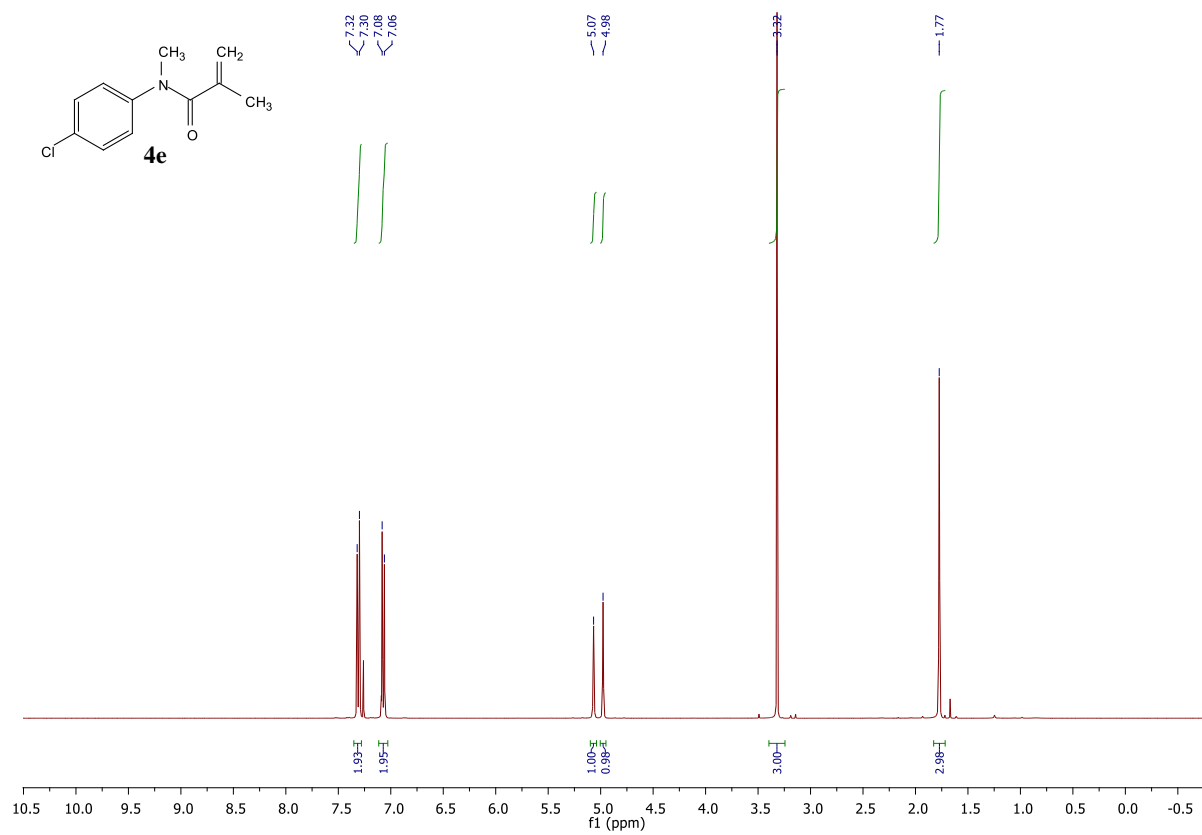
# *N*-(4-Cyanophenyl)-*N*-methylmethacrylamide (**4d**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



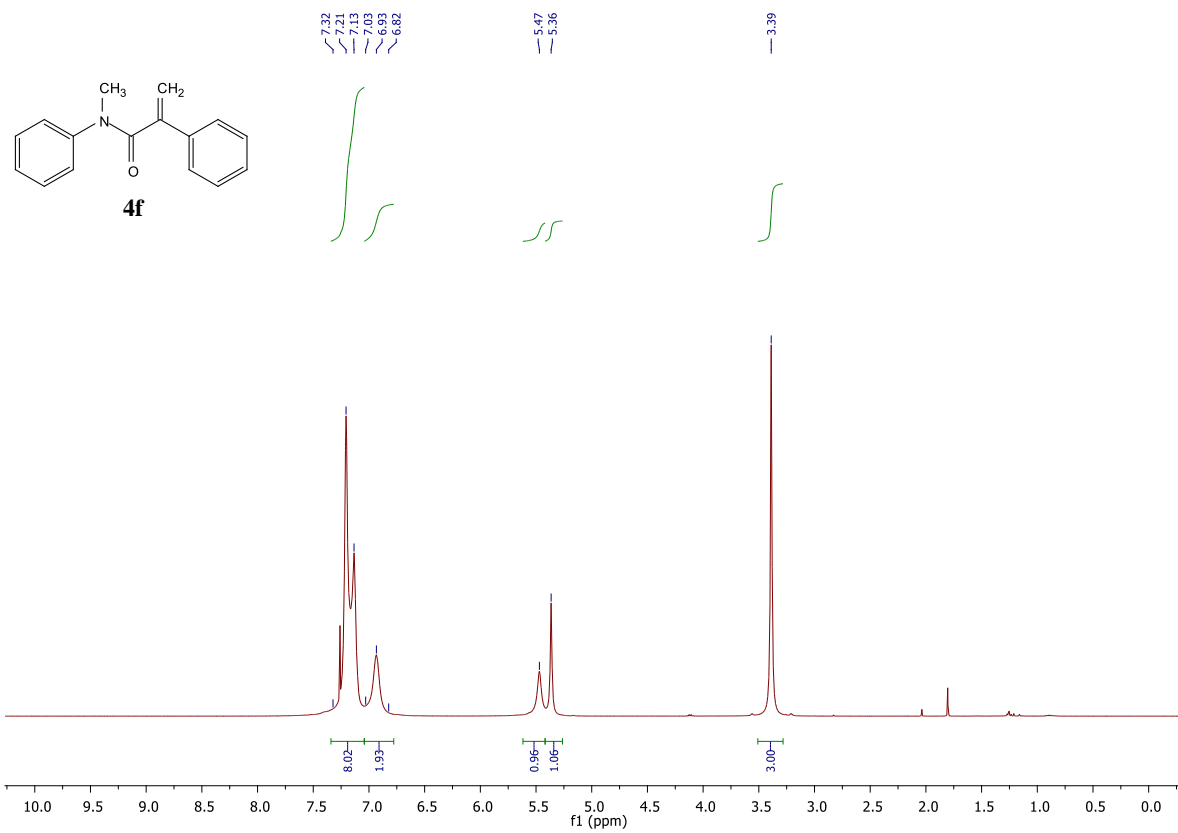
# *N*-(4-Chlorophenyl)-*N*-methylmethacrylamide (**4e**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



# ***N*-Methyl-*N*,2-diphenylacrylamide (4f)**

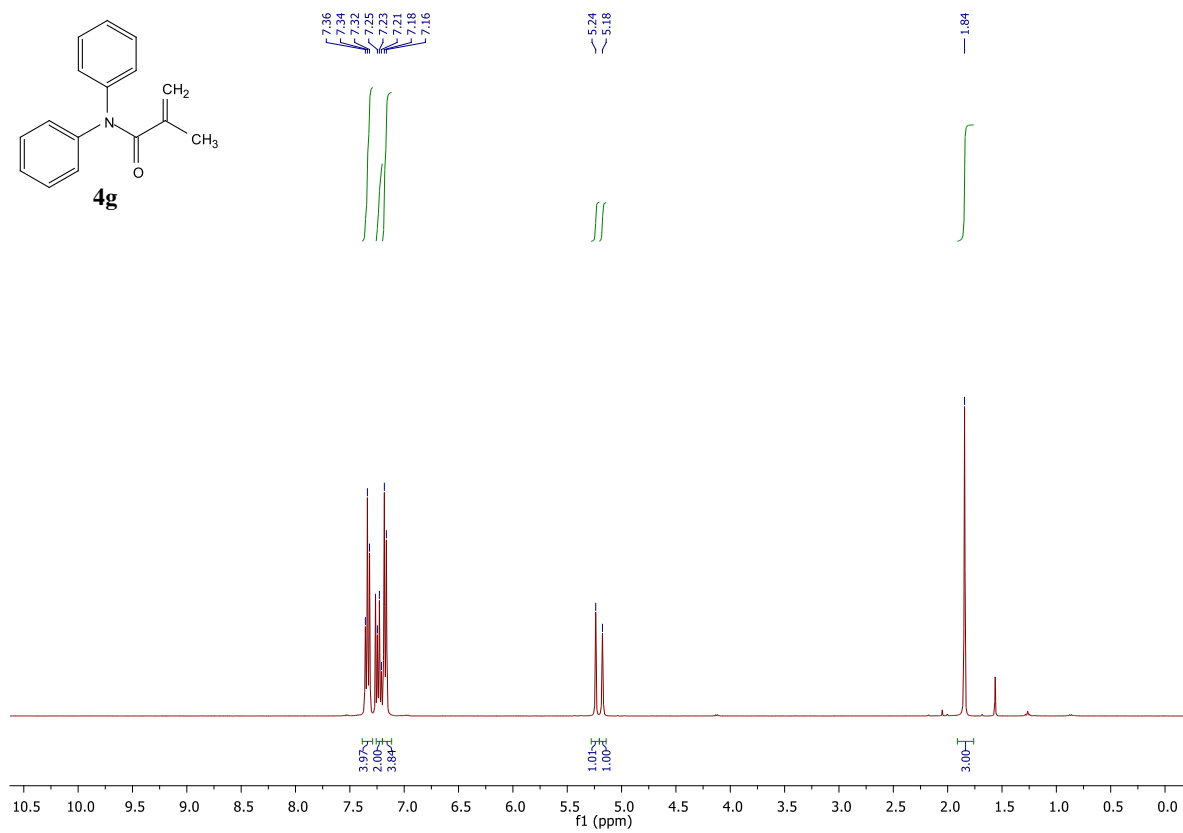
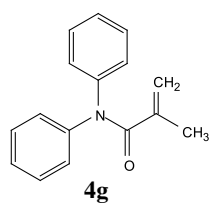
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)





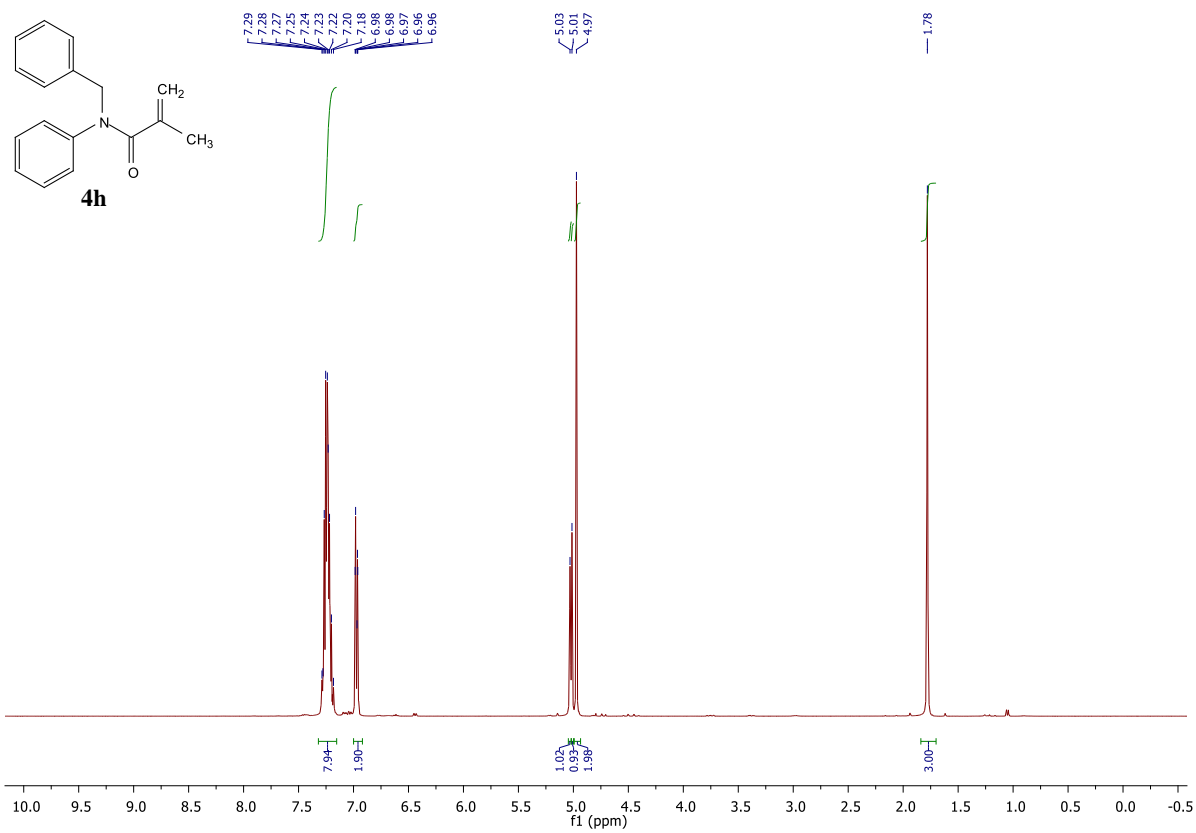
# *N,N*-Diphenylmethacrylamide (4g)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



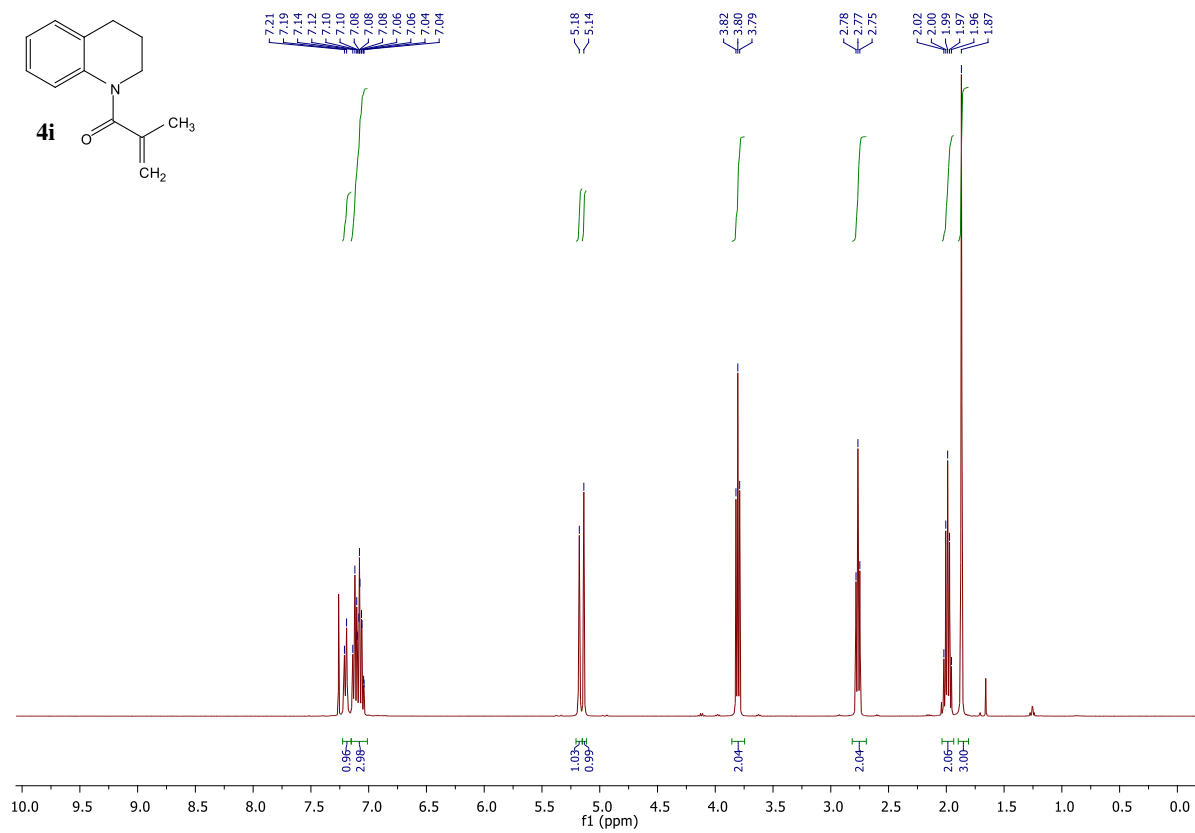
# ***N*-Benzyl-*N*-phenylmethacrylamide (4h)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



# 1-(3,4-Dihydroquinolin-1(2H)-yl)-2-methylprop-2-en-1-one (4i)

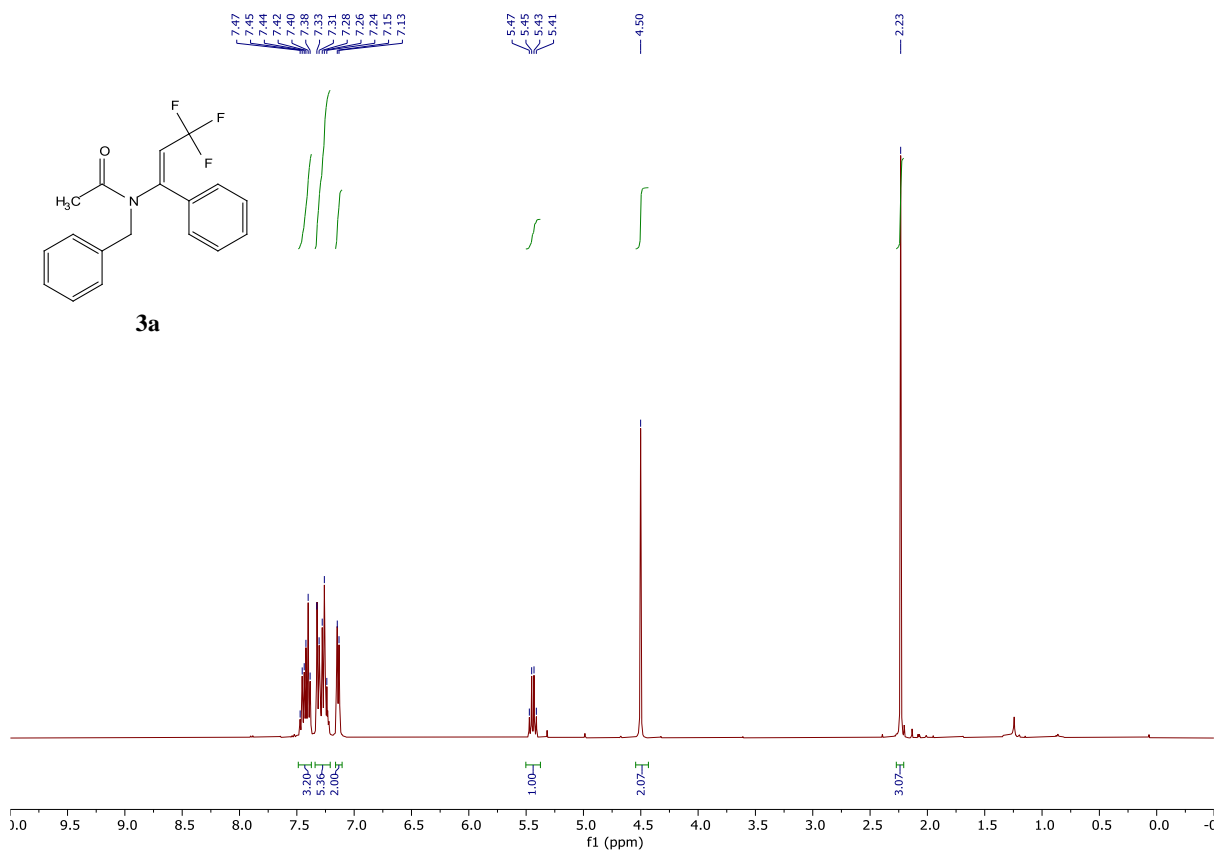
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



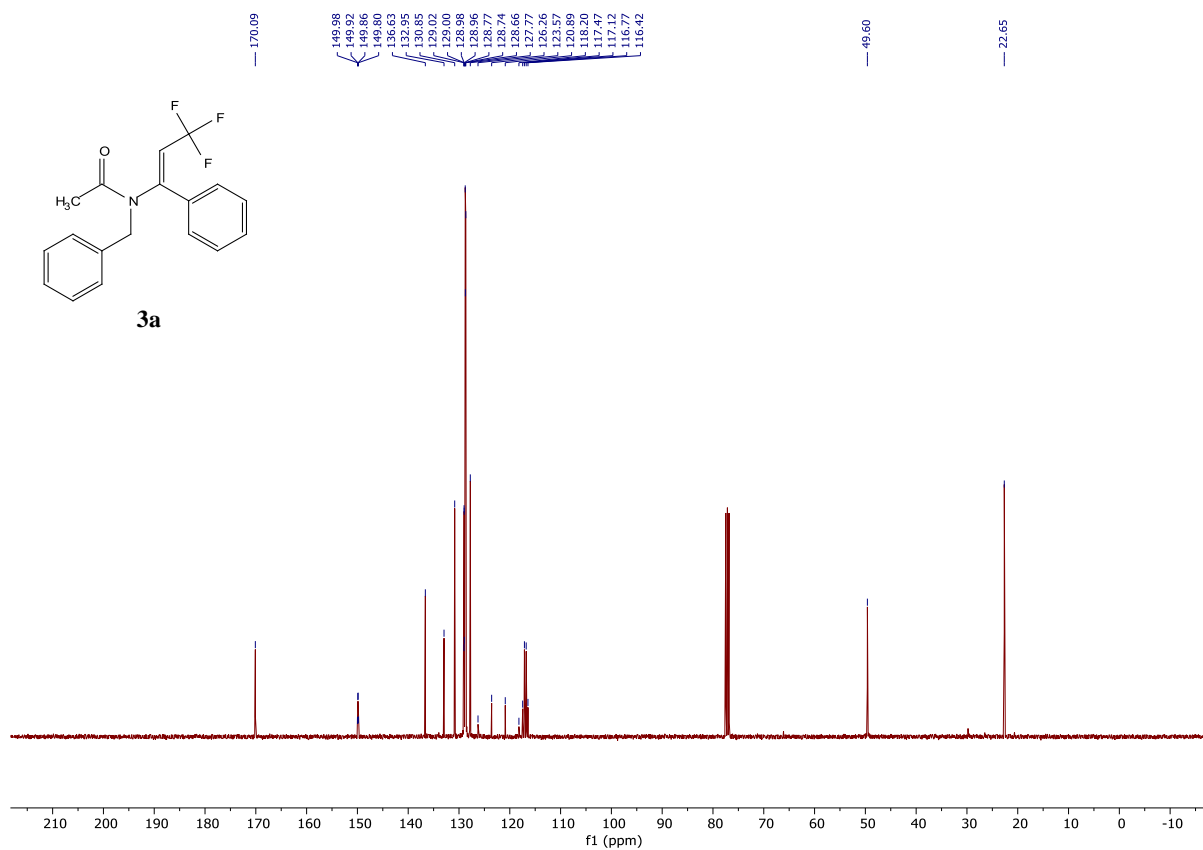
## 7.2 Products 3a-u, 5a-i

### (*E*)-*N*-Benzyl-*N*-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3a)

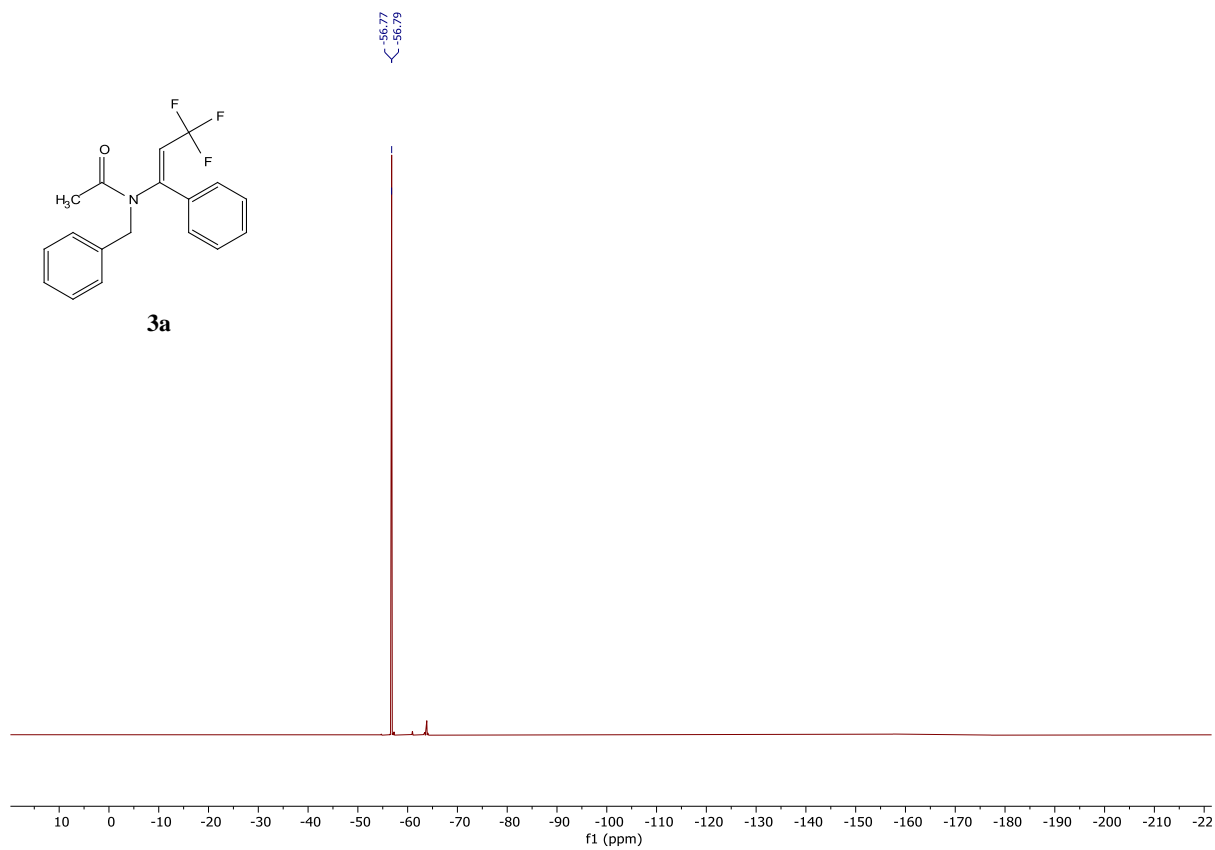
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

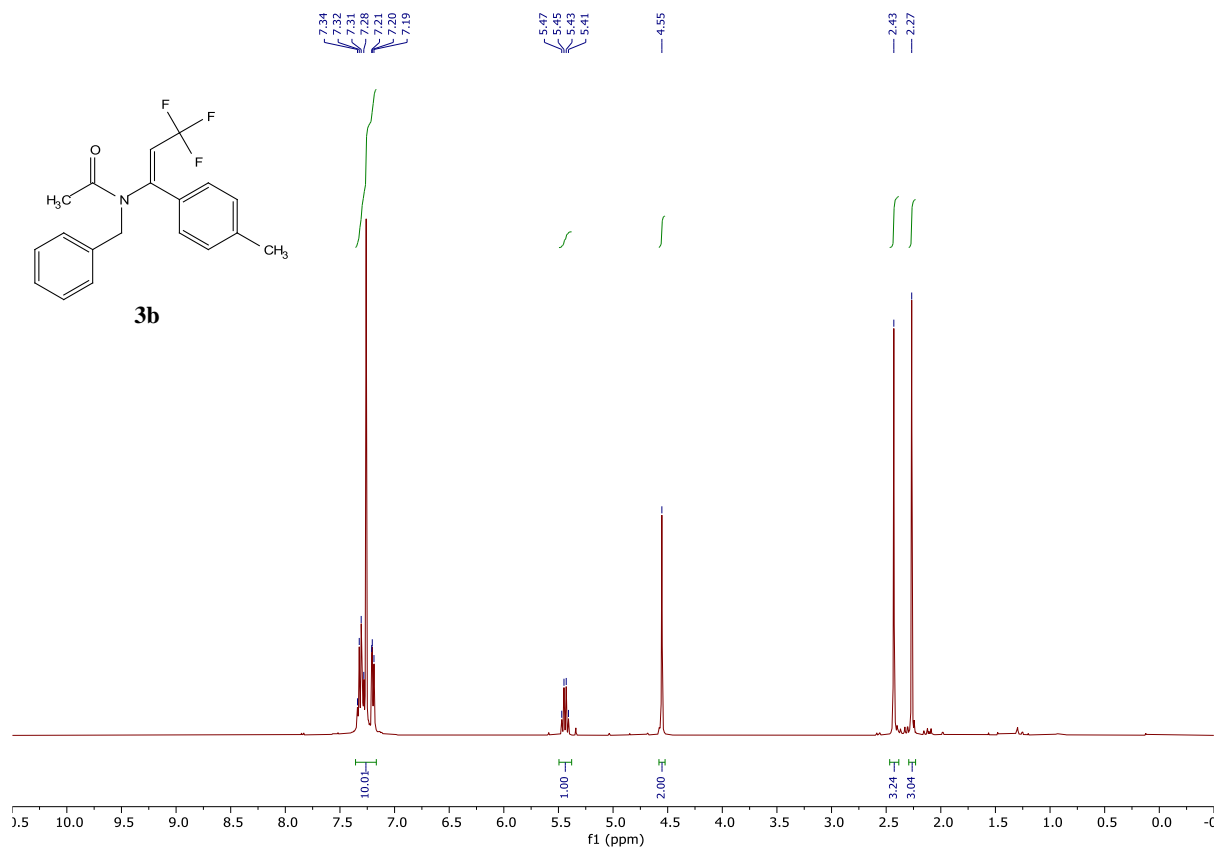


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

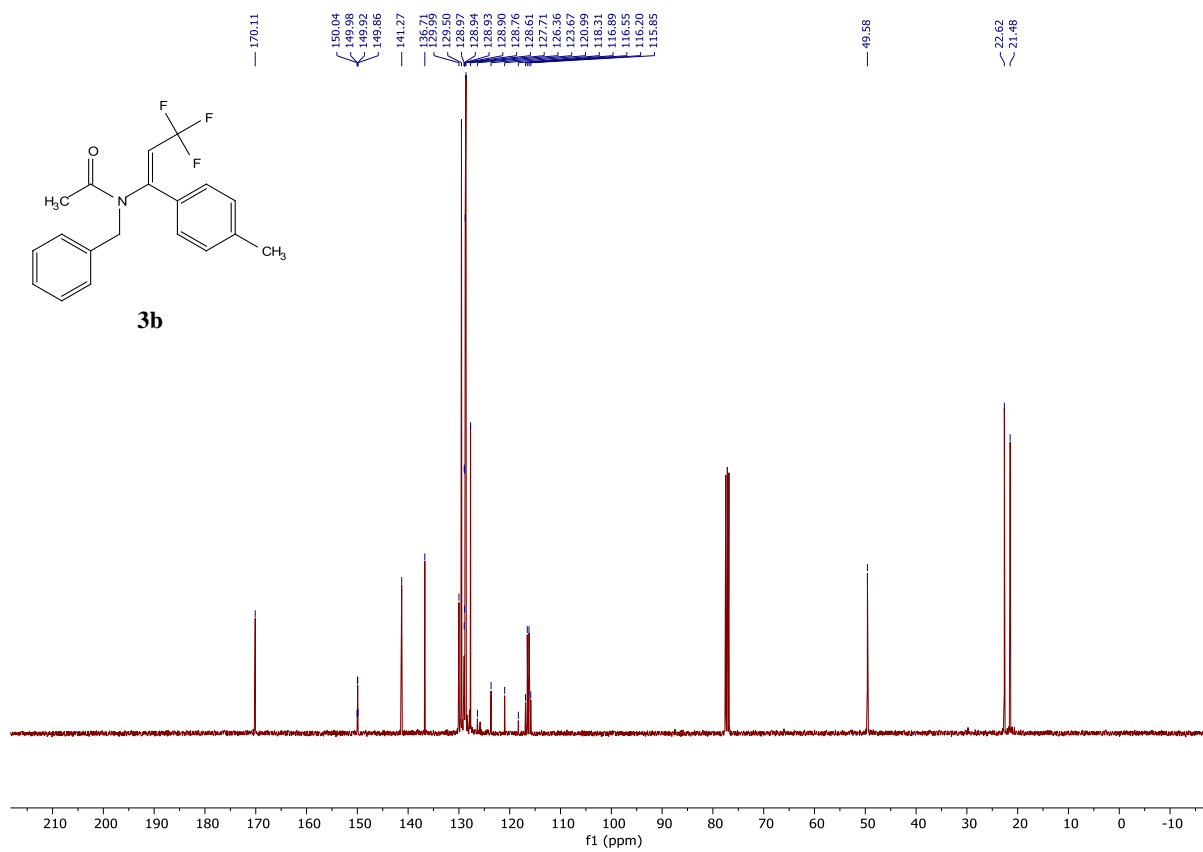


**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(p-tolyl)prop-1-en-1-yl)acetamide (3b)**

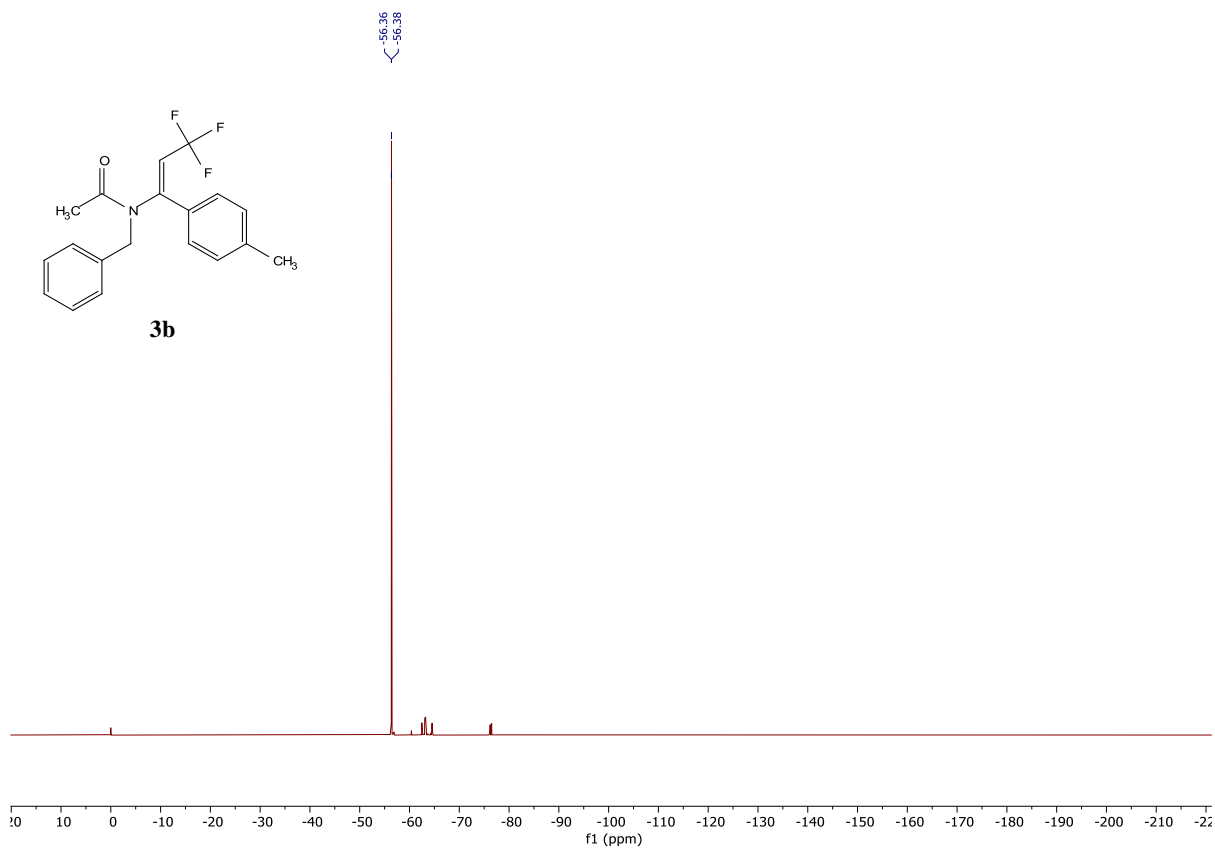
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

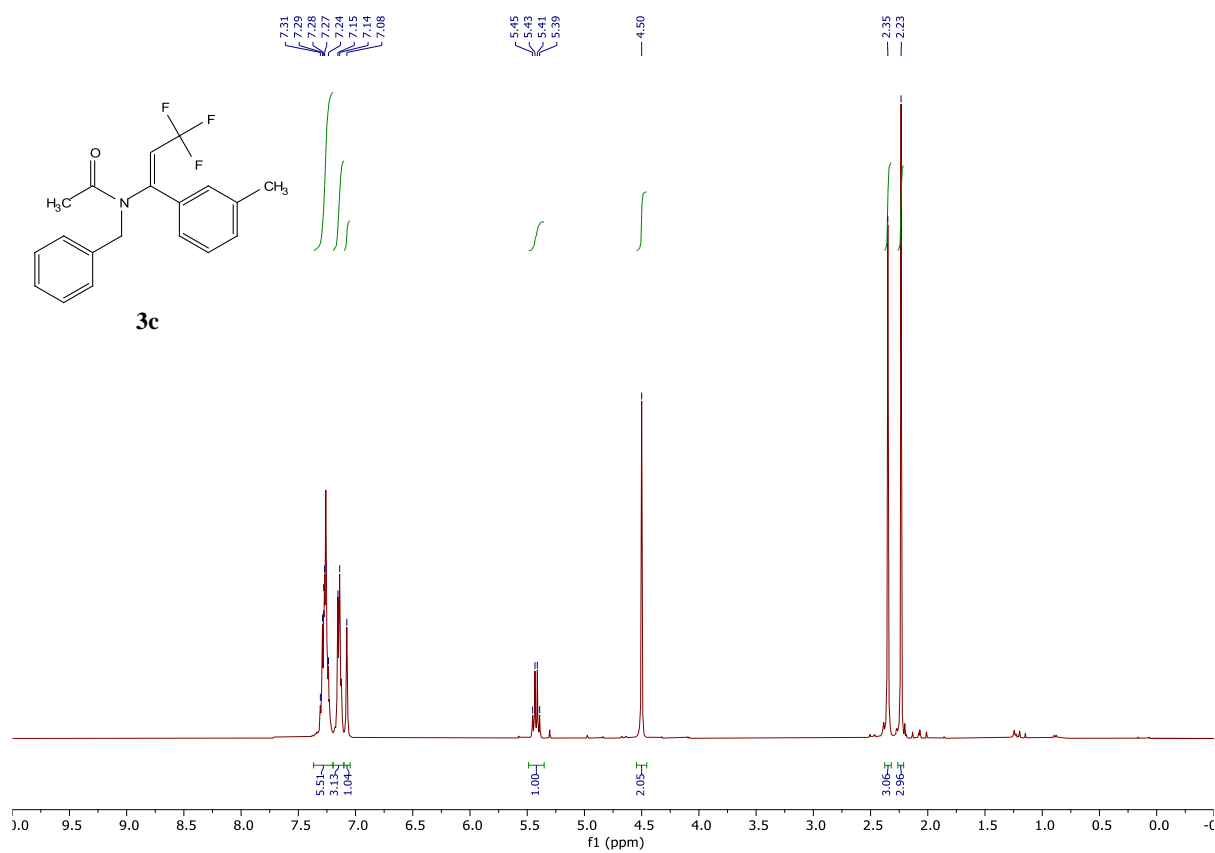


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



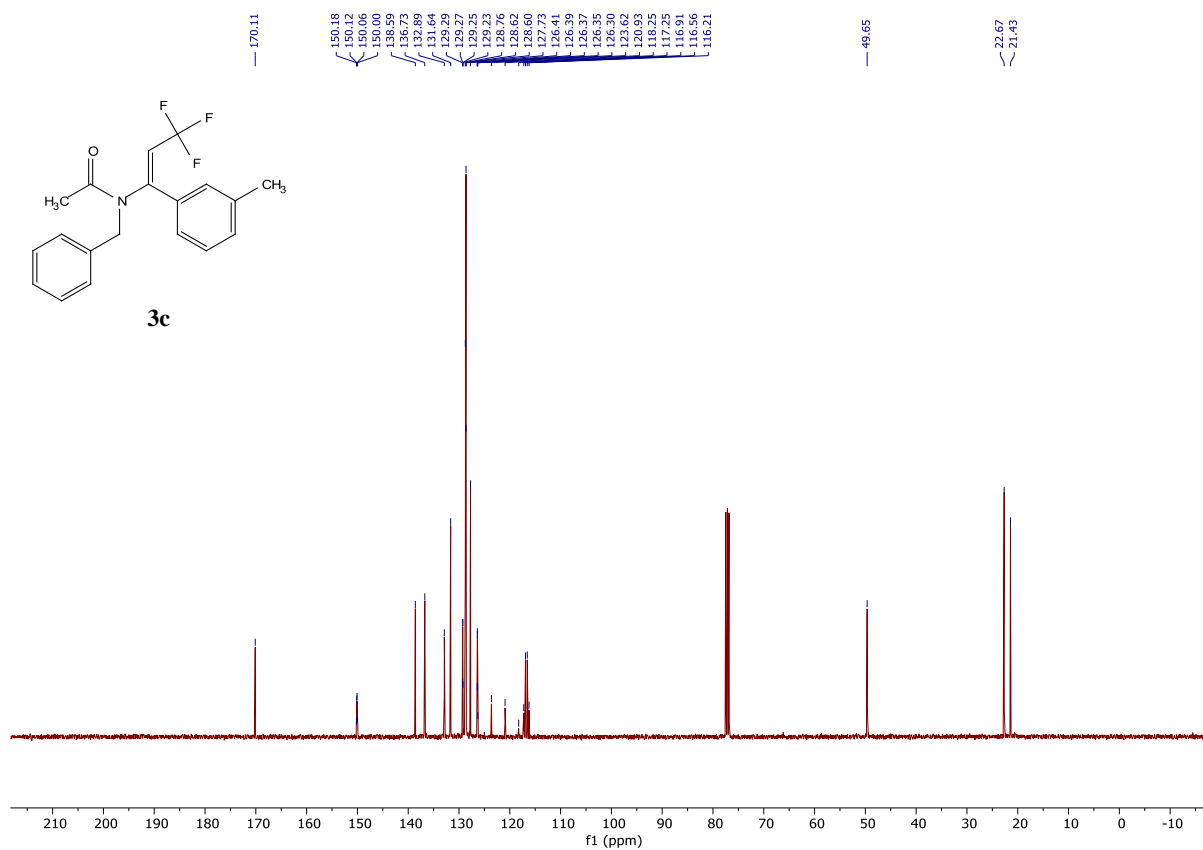
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(*m*-tolyl)prop-1-en-1-yl)acetamide (3c)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

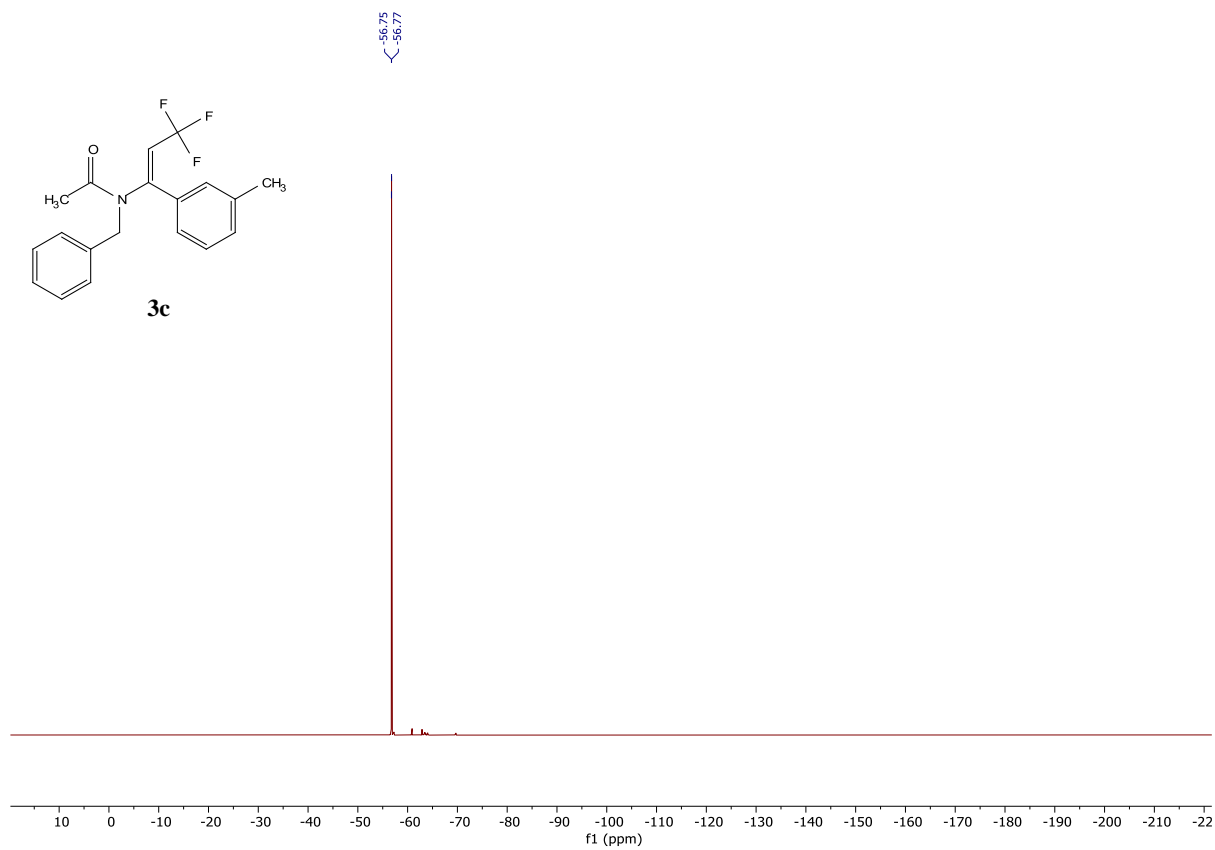




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

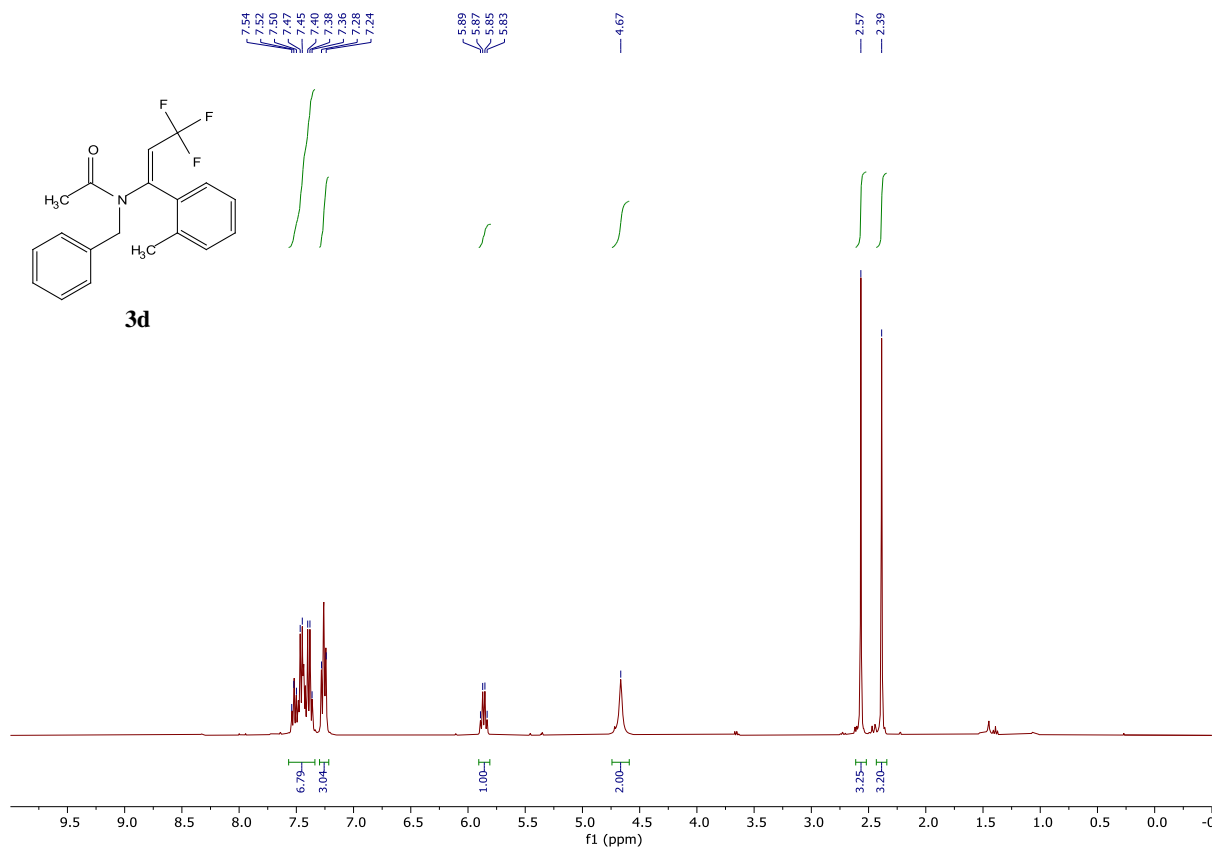


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

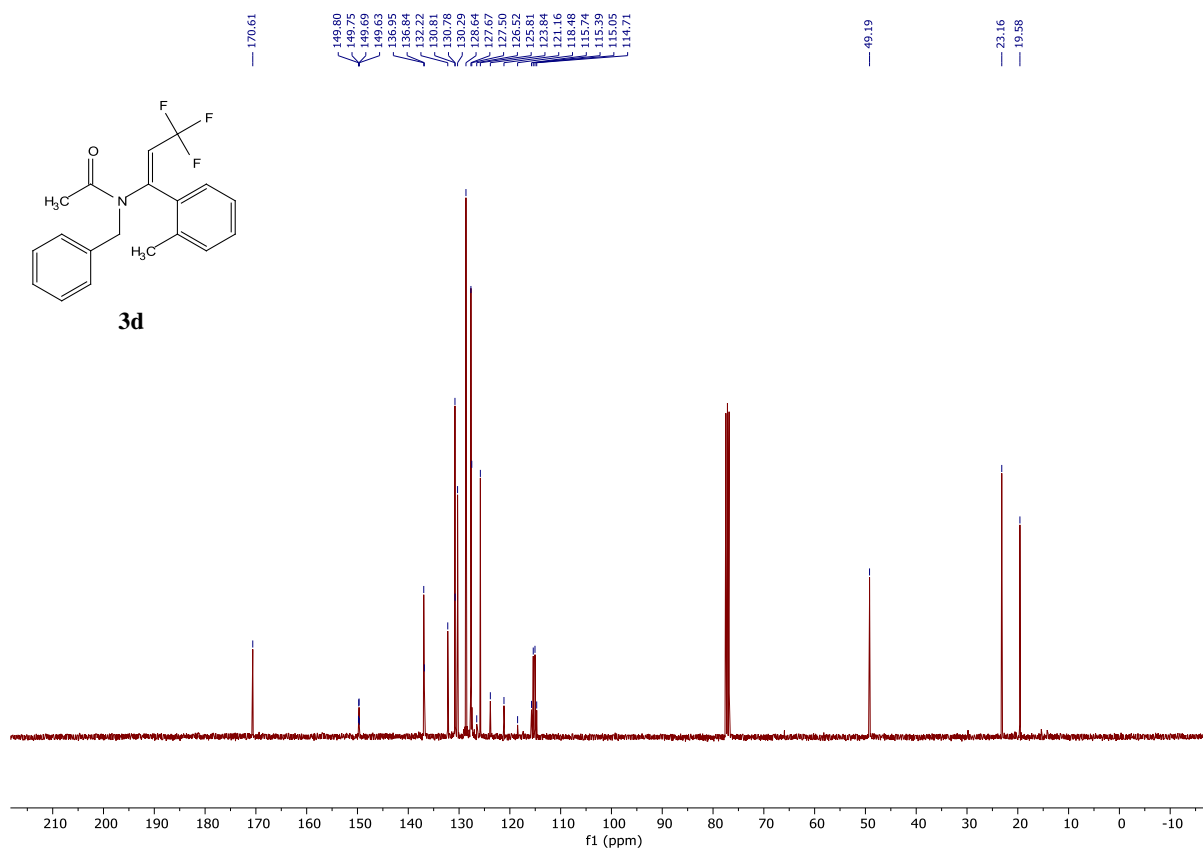


**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(o-tolyl)prop-1-en-1-yl)acetamide (3d)**

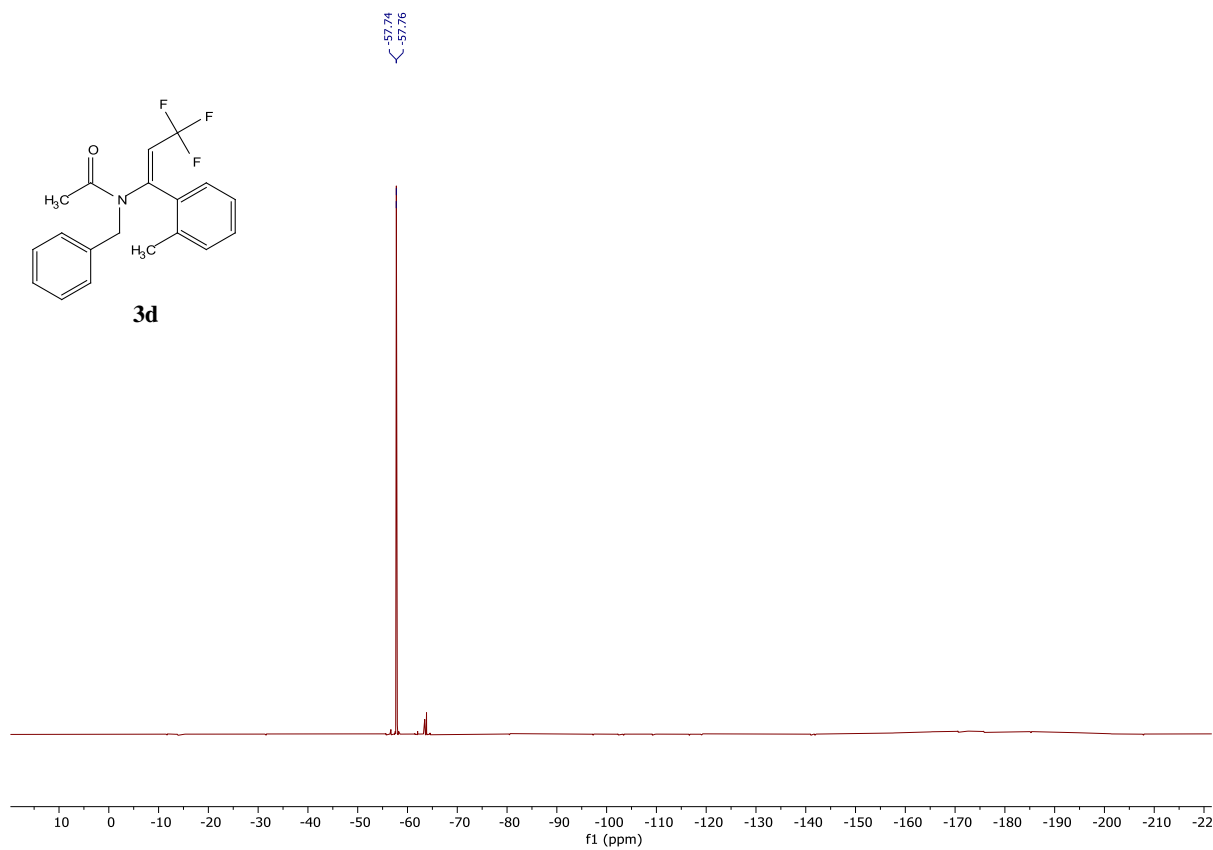
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

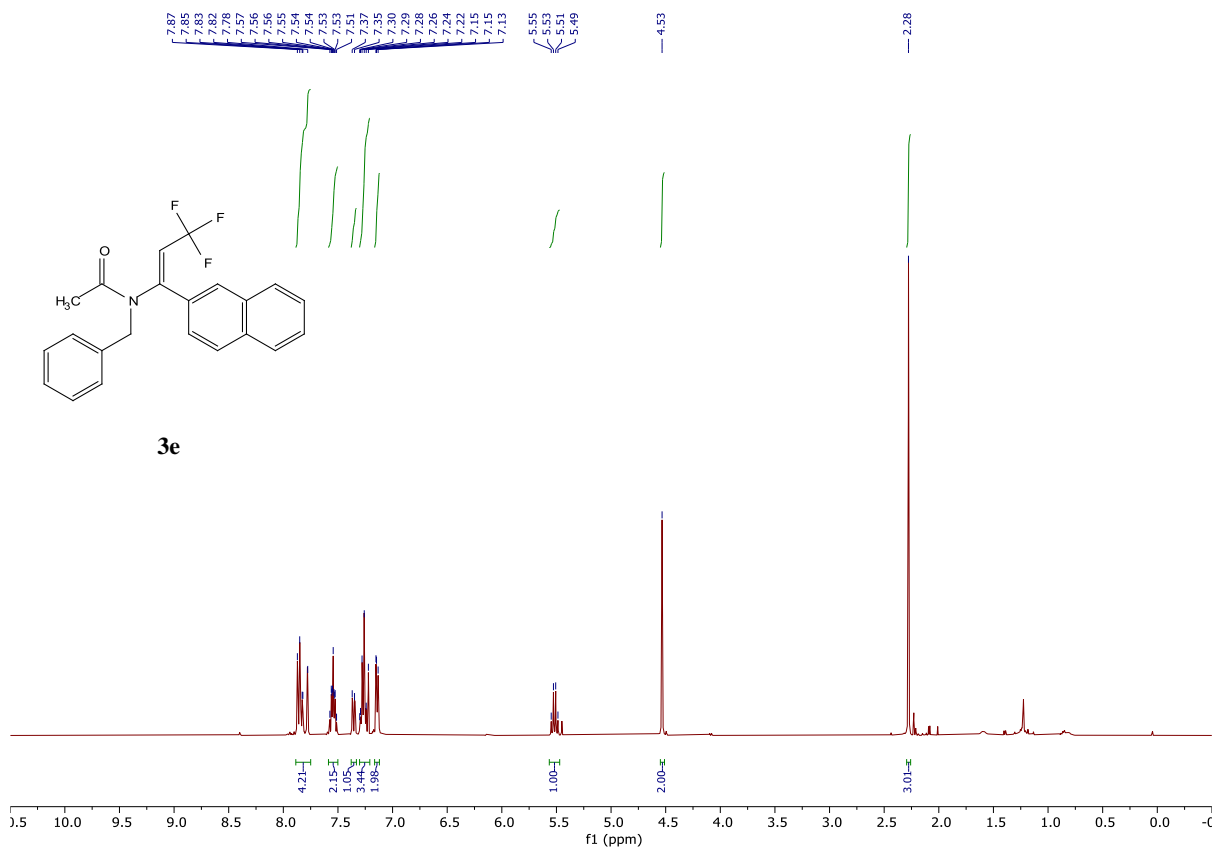


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

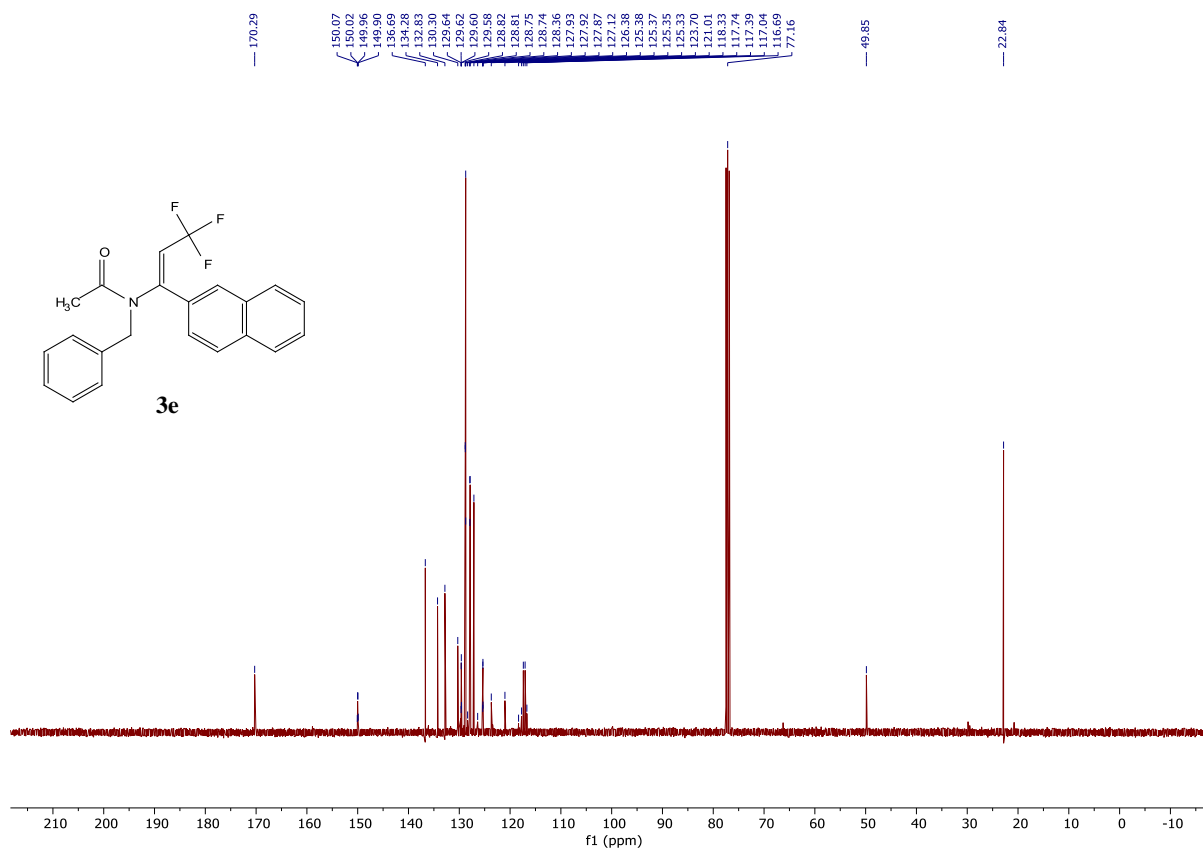


**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(naphthalen-2-yl)prop-1-en-1-yl)acetamide (3e)**

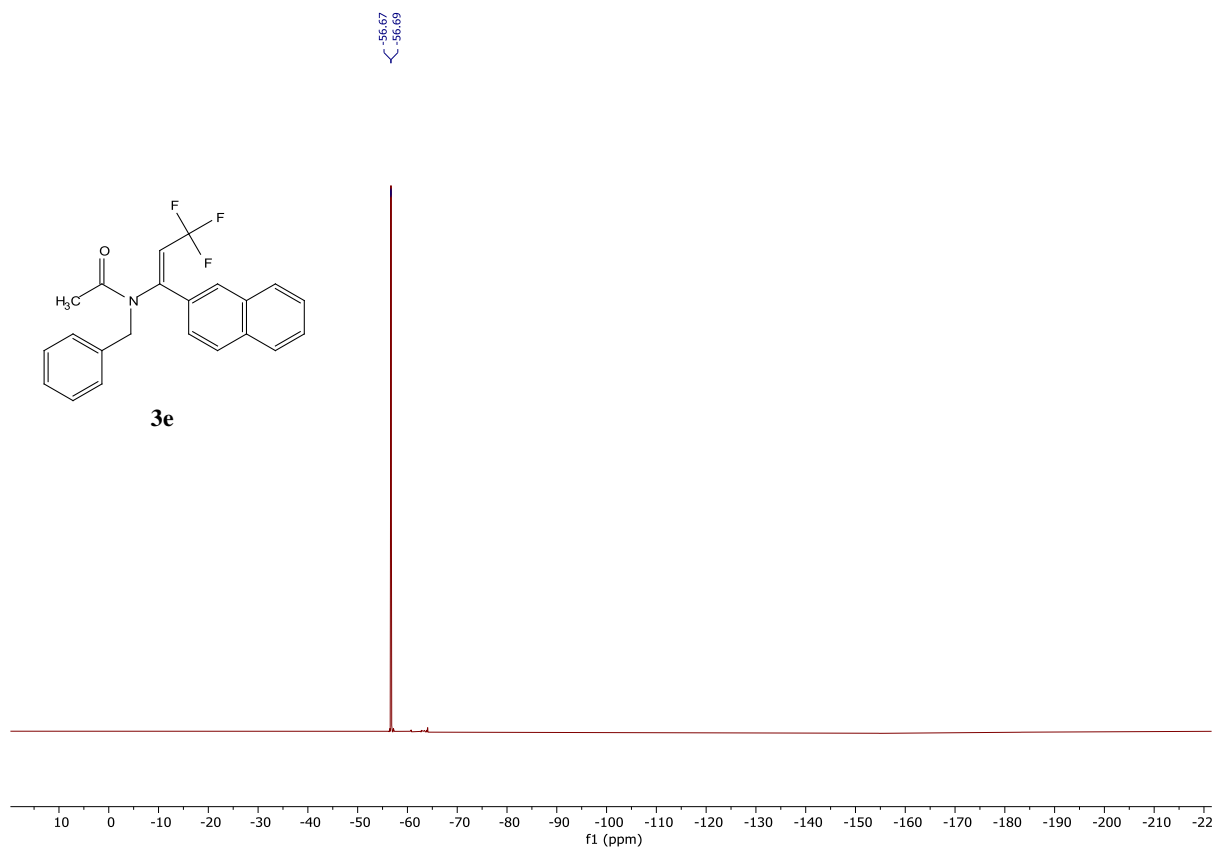
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

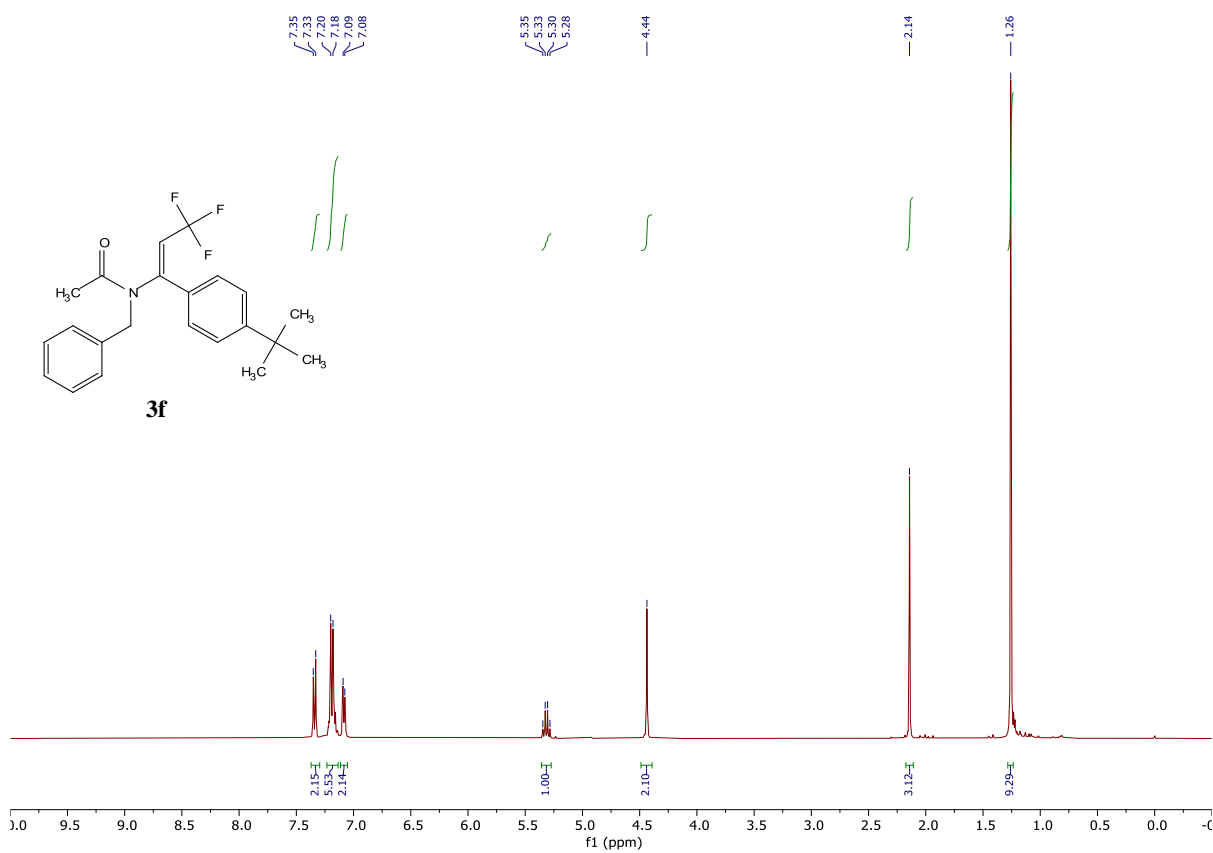


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

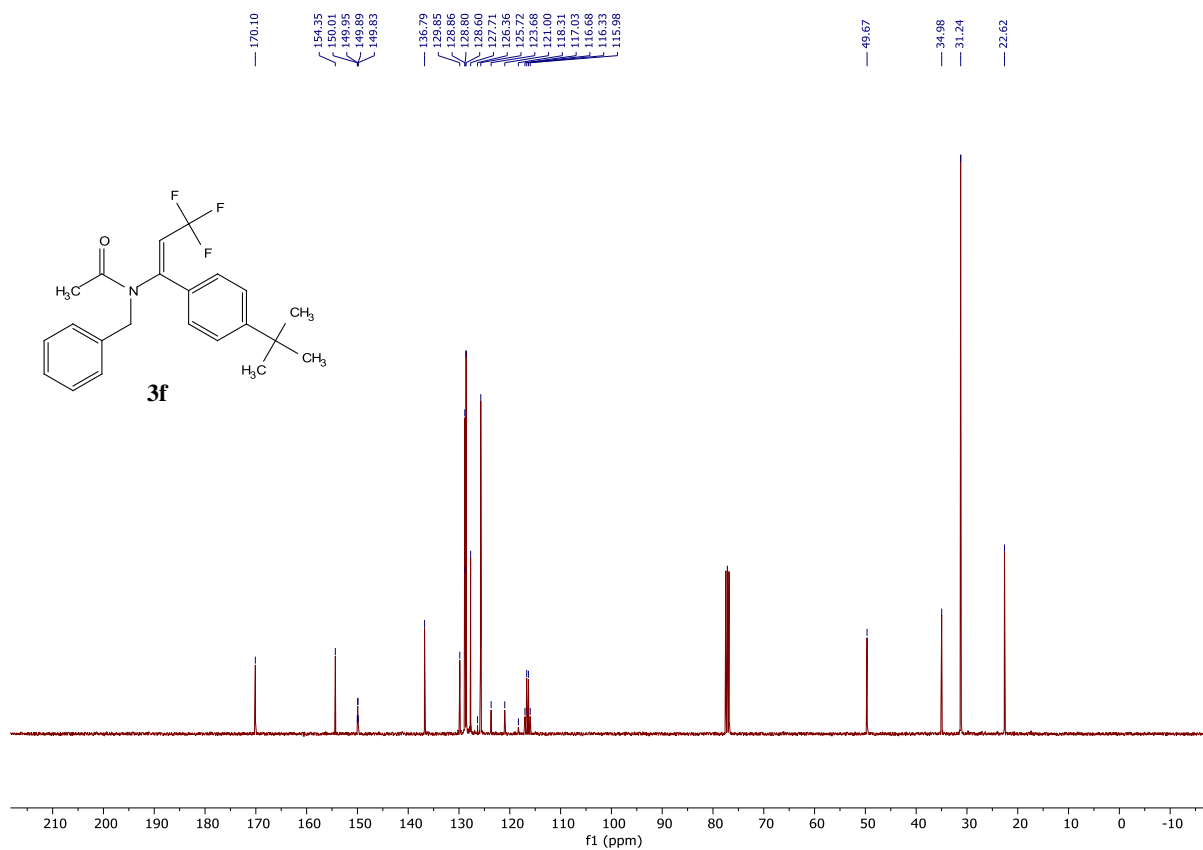


**(E)-N-Benzyl-N-(1-(4-(*tert*-butyl)phenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3f)**

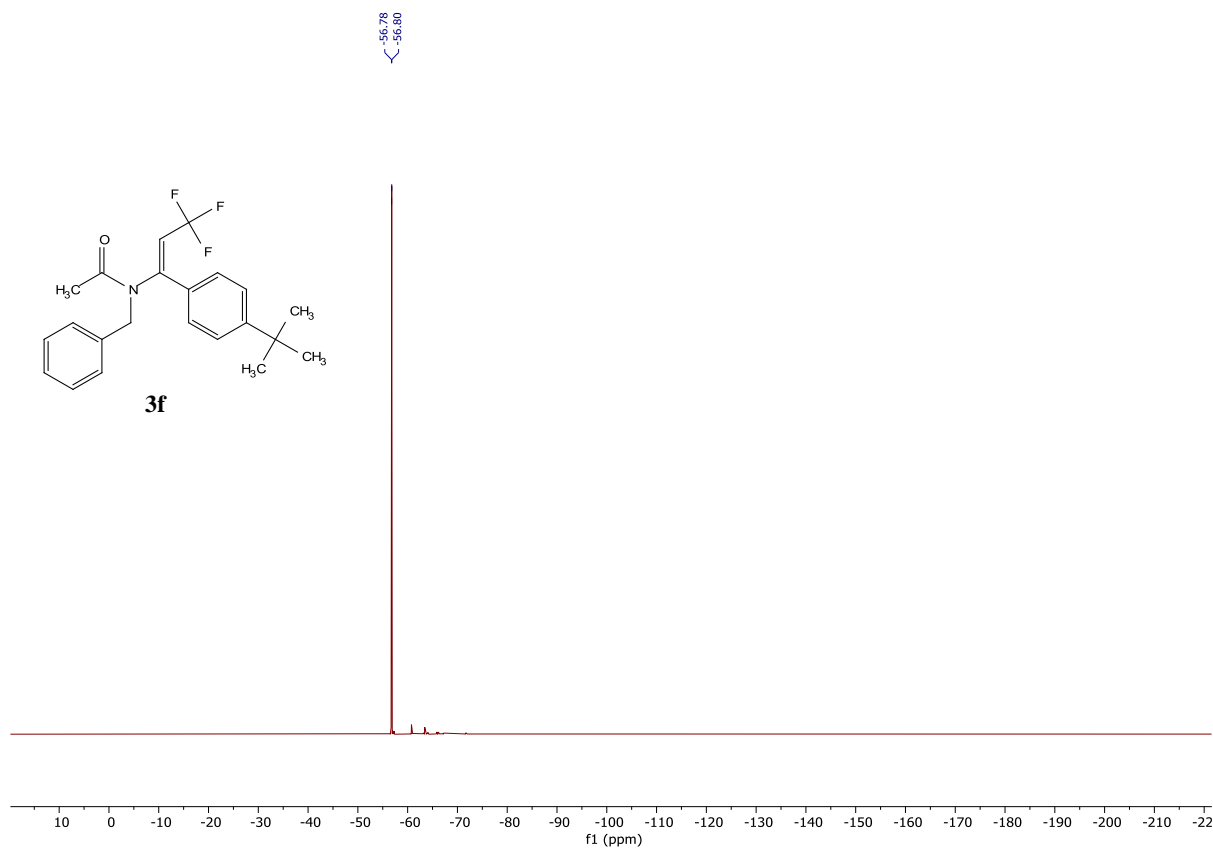
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

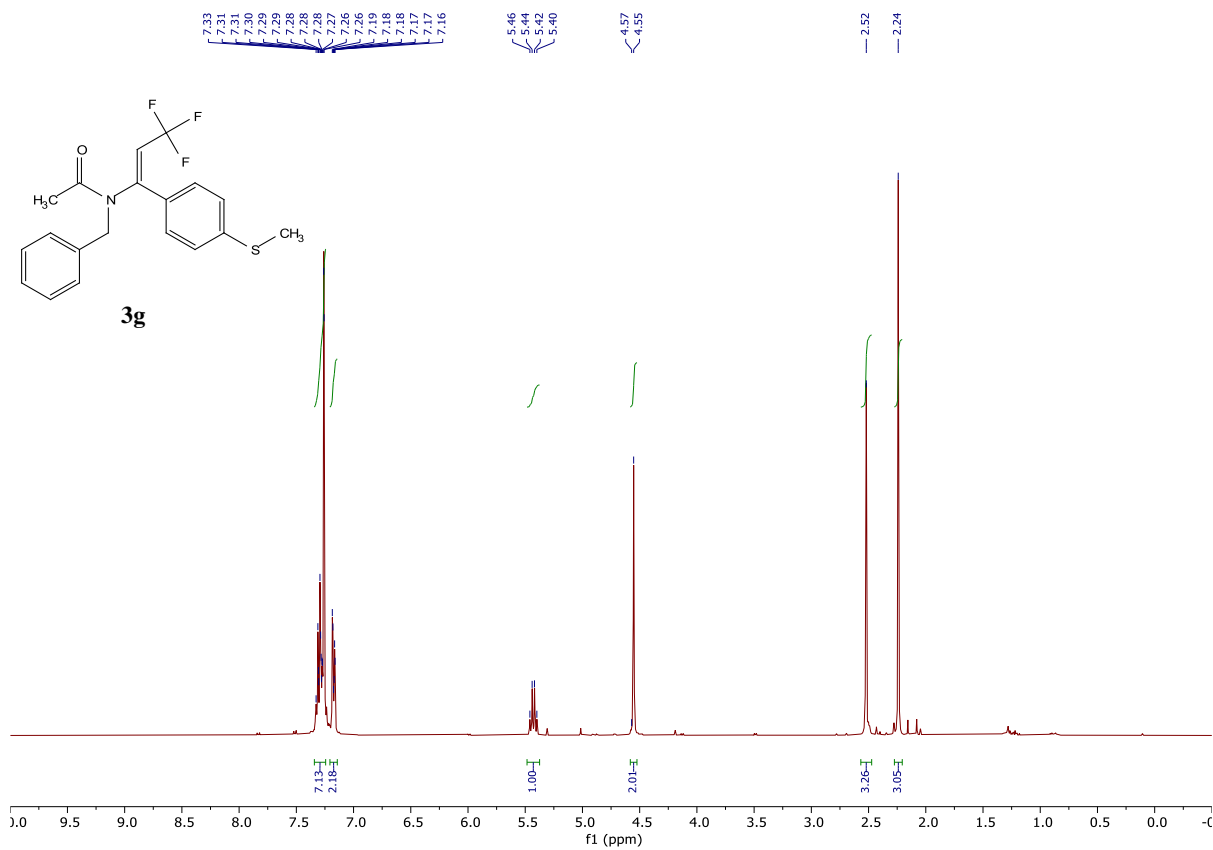


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



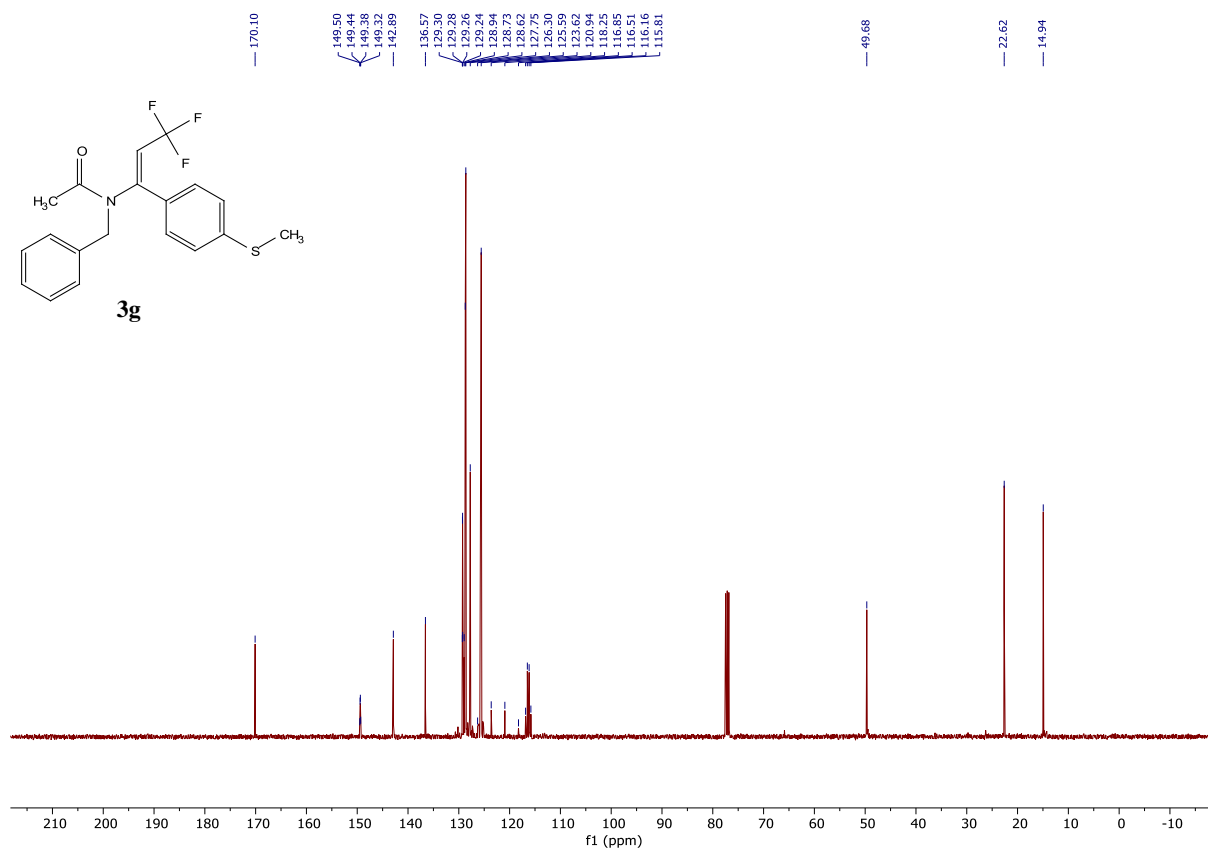
**(E)-N-benzyl-N-(3,3,3-trifluoro-1-(4-(methylthio)phenyl)prop-1-en-1-yl)acetamide (3g)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

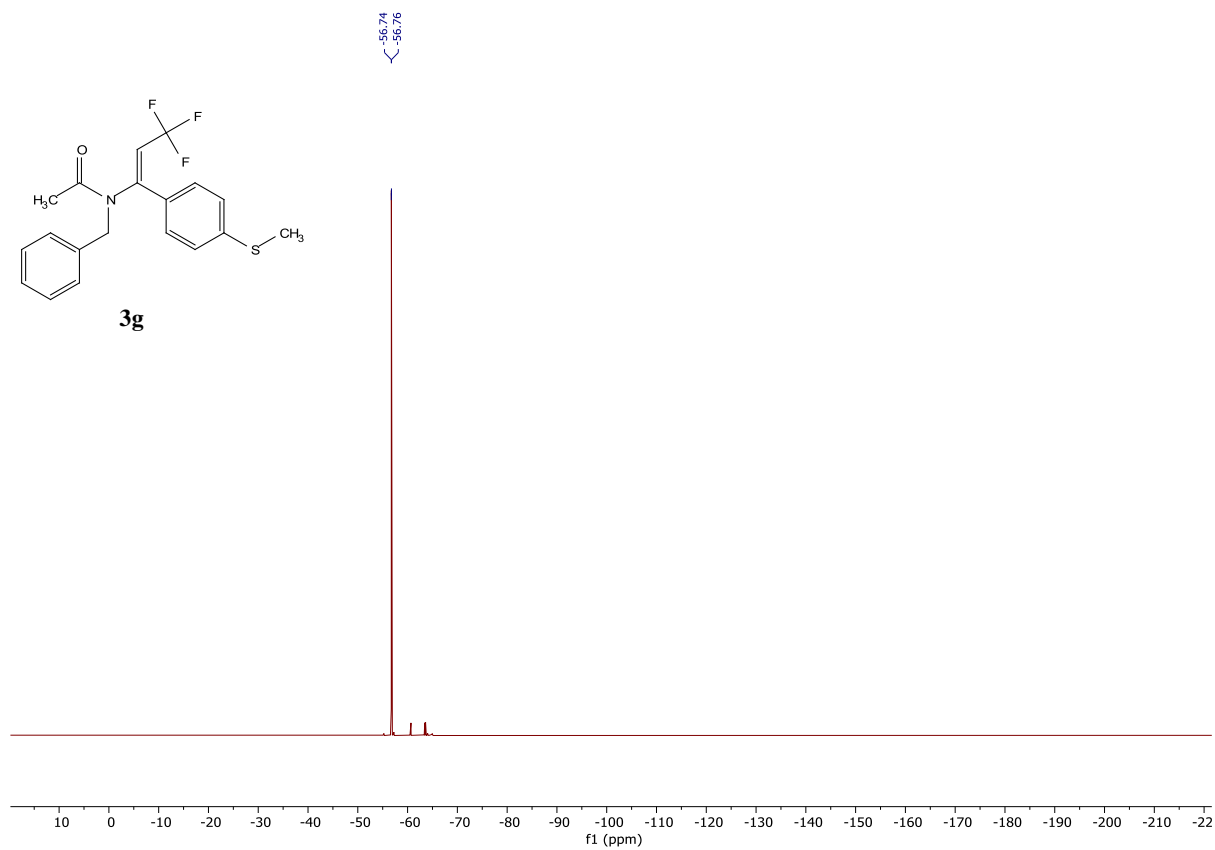




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

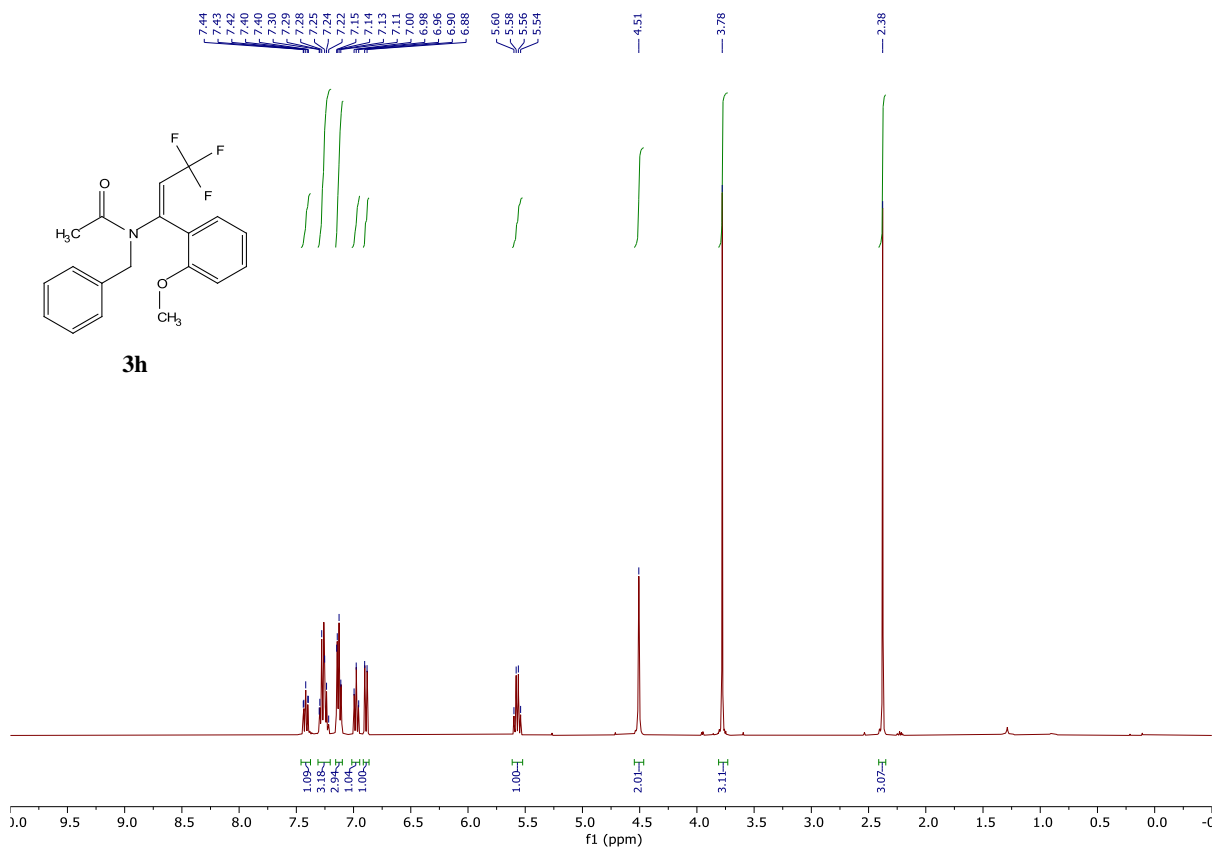


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

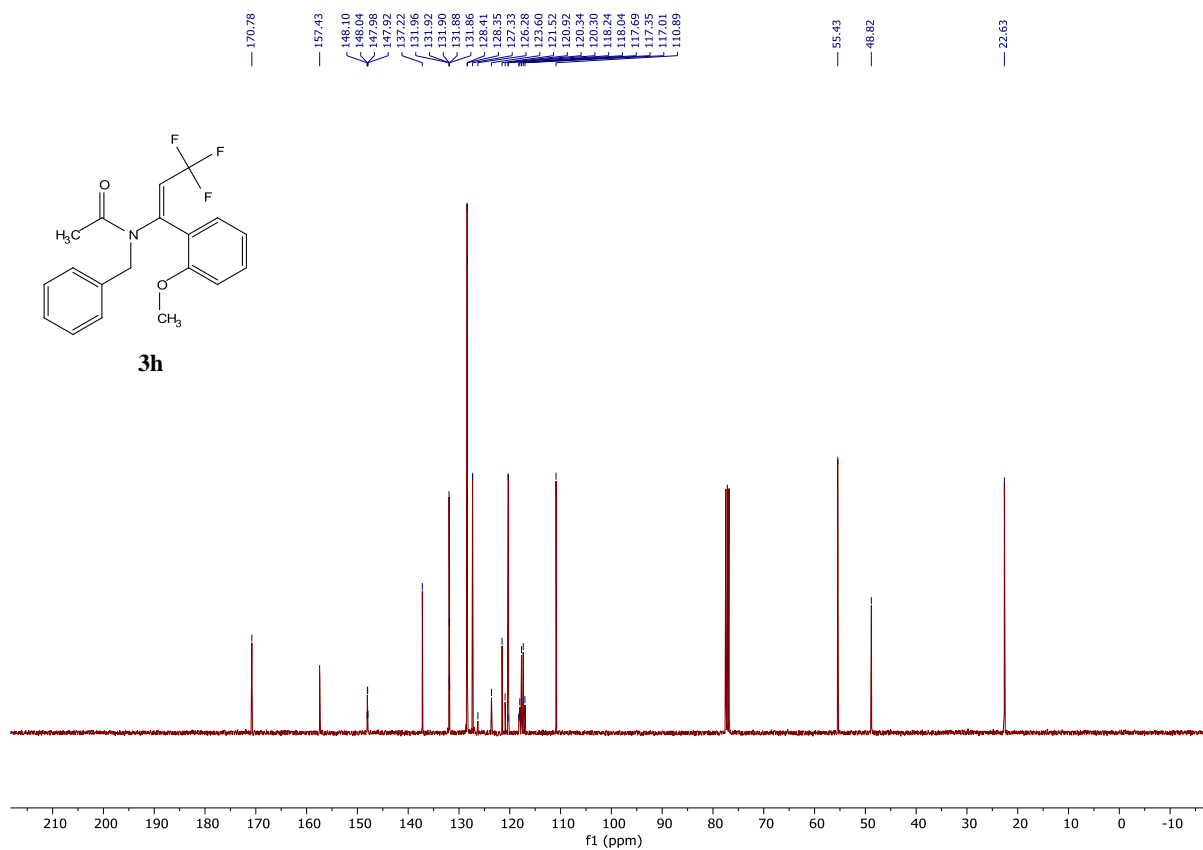


**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(2-methoxyphenyl)prop-1-en-1-yl)acetamide (3h)**

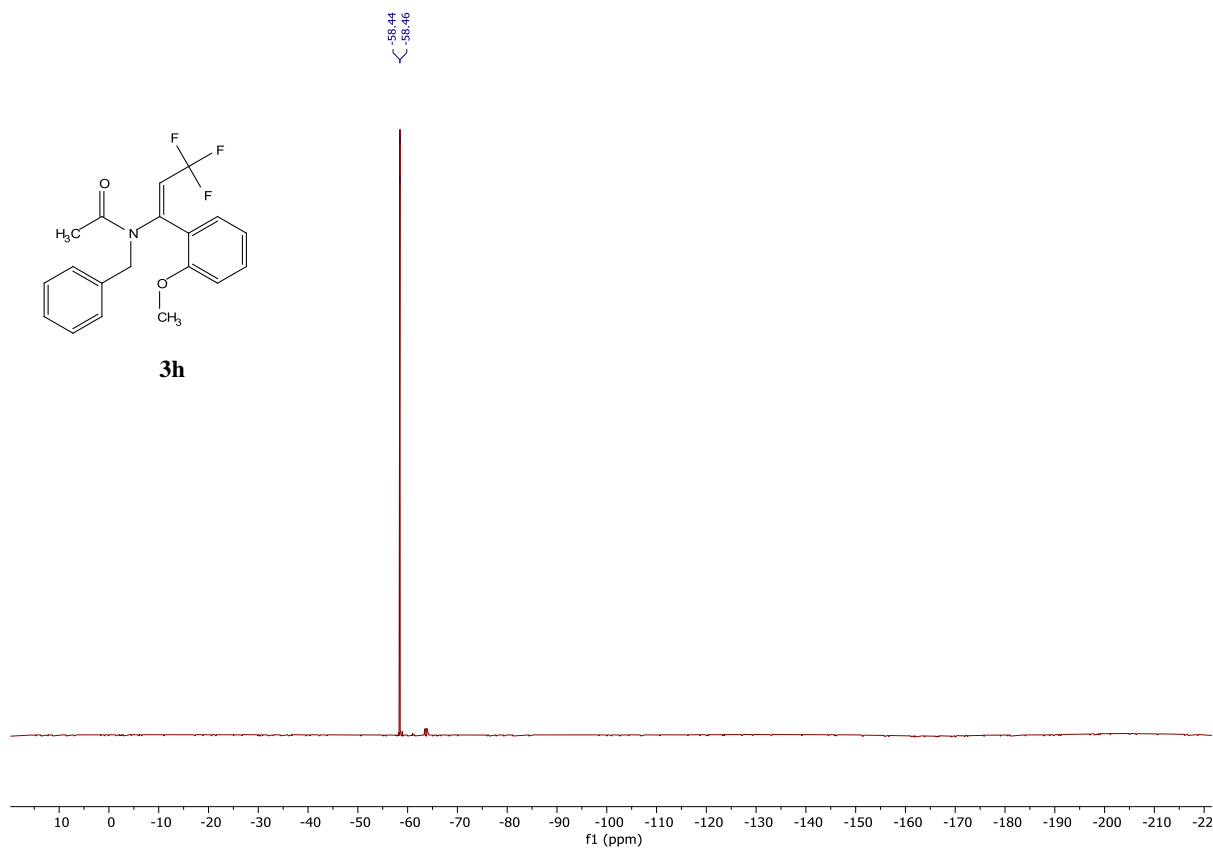
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

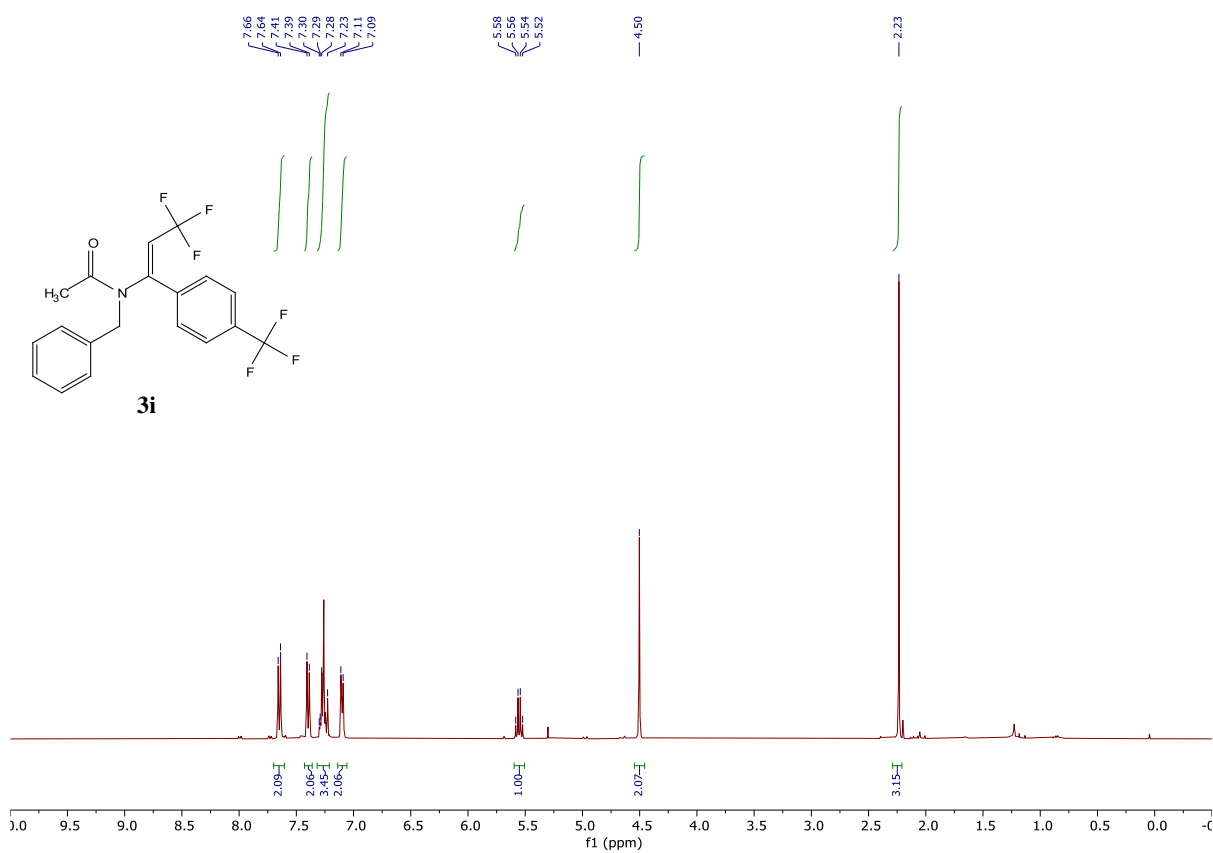


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

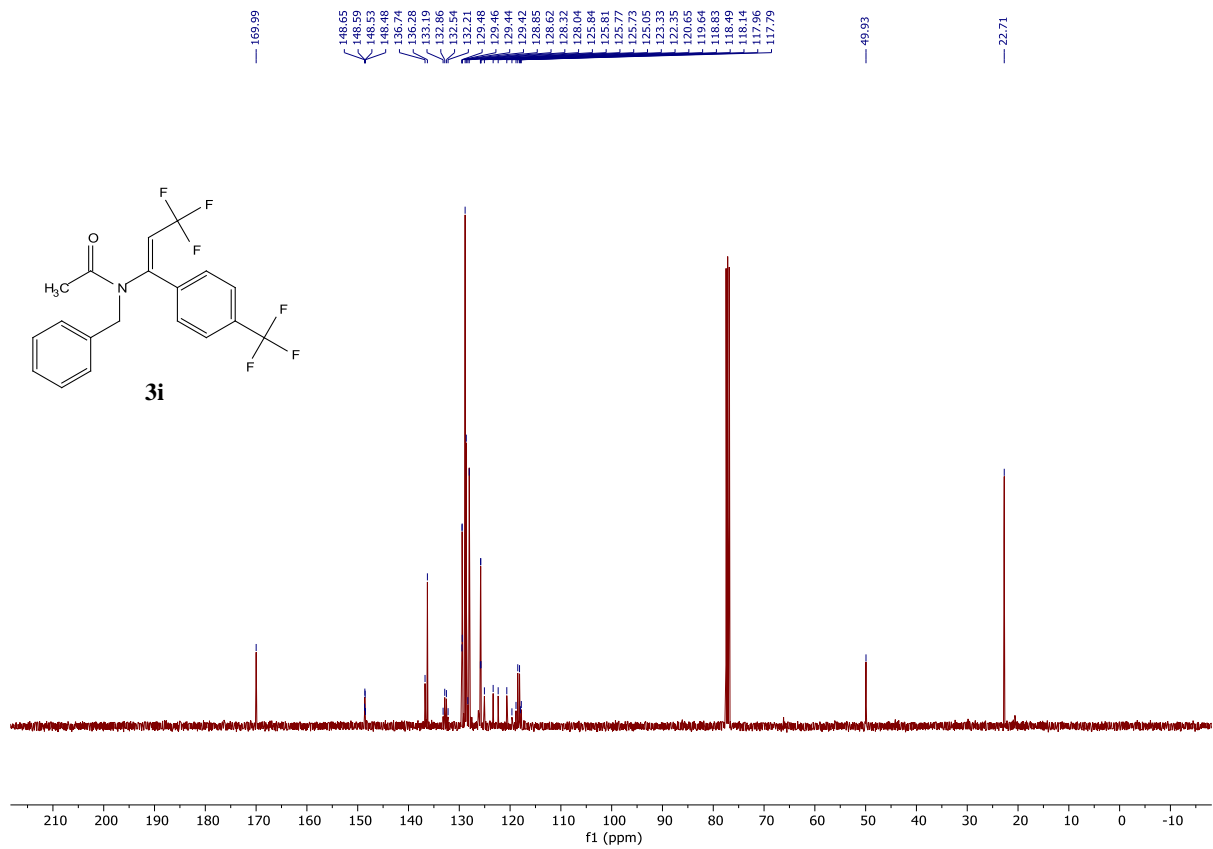


**(E)-N-benzyl-N-(3,3,3-trifluoro-1-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)acetamide (3i)**

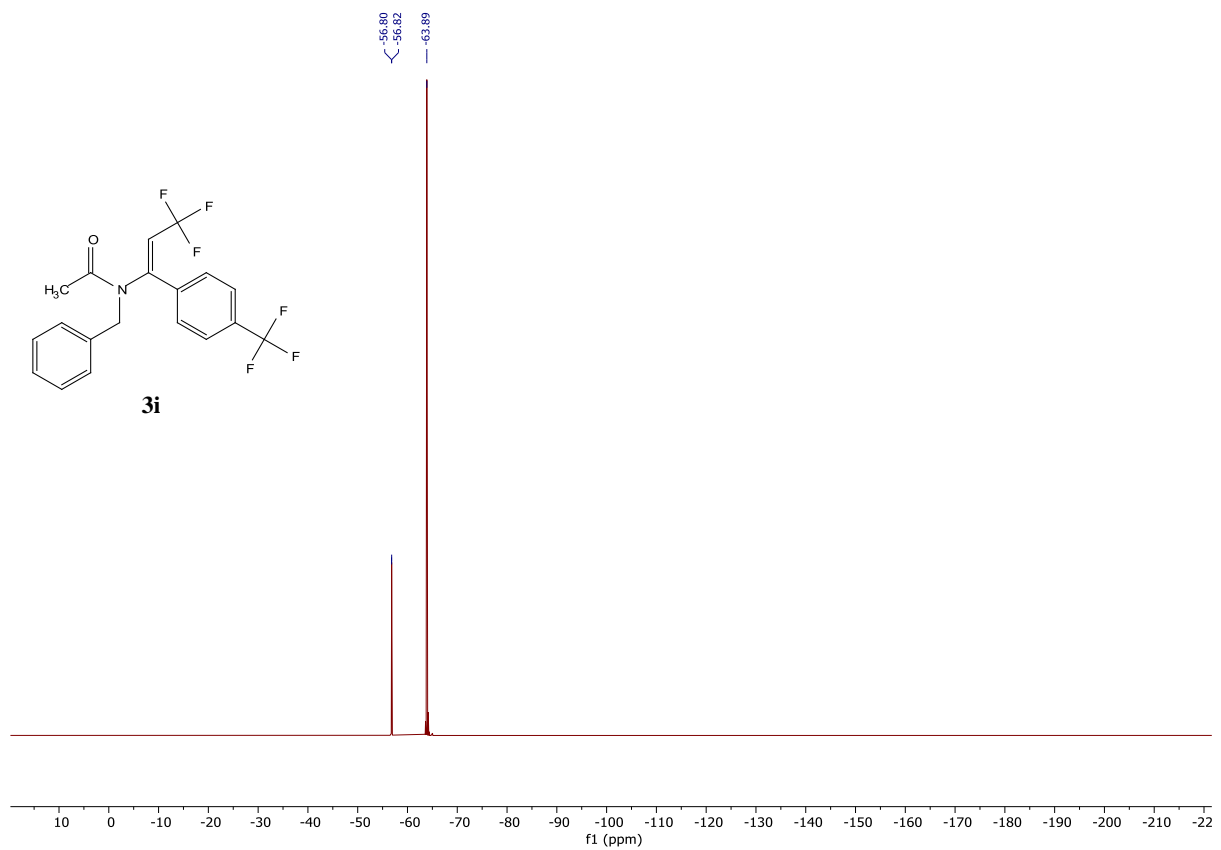
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

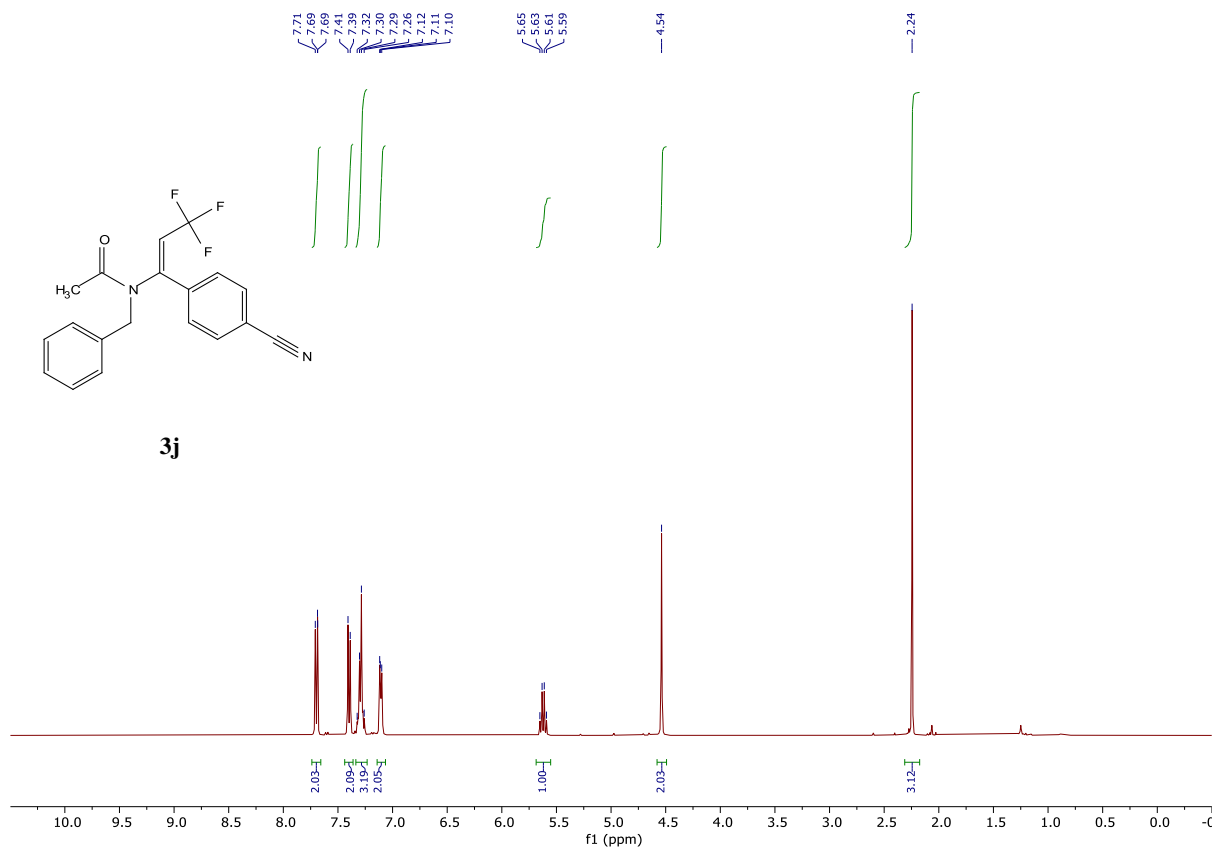


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

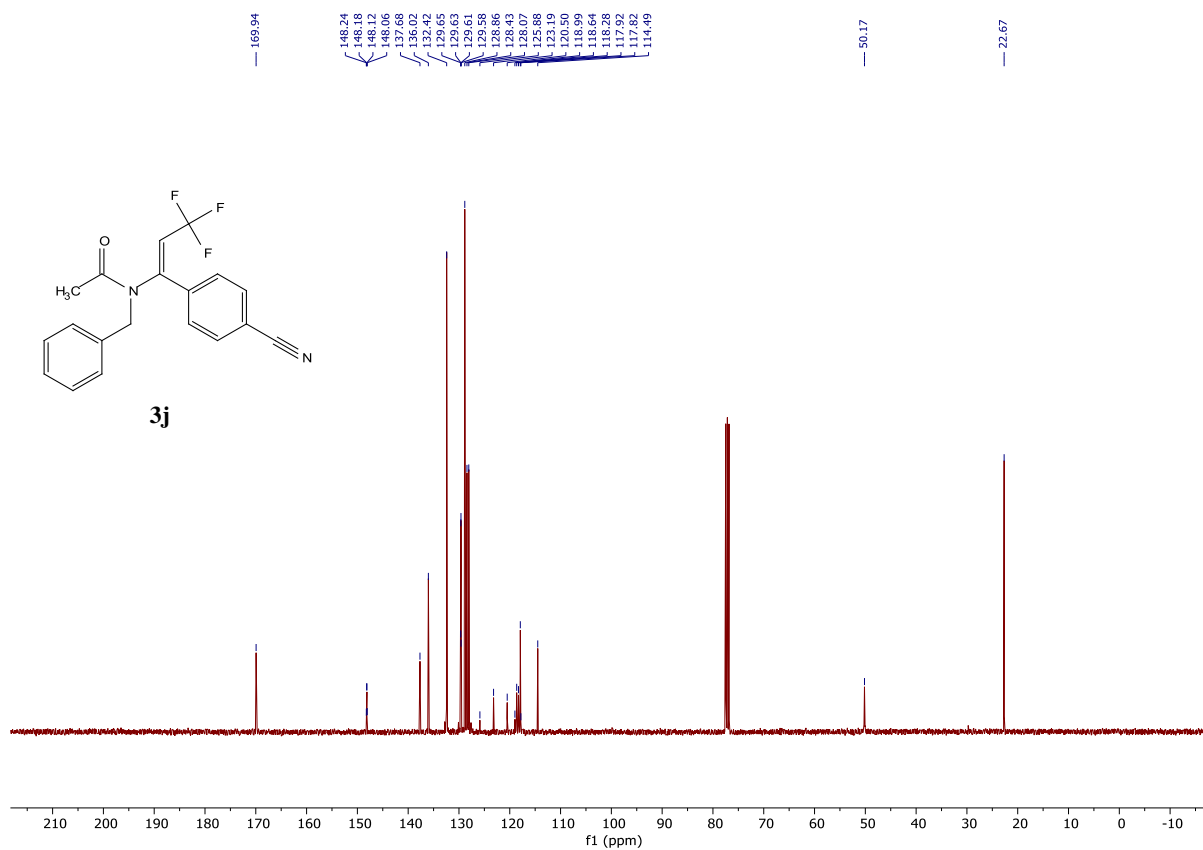


**(E)-N-Benzyl-N-(1-(4-cyanophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3j)**

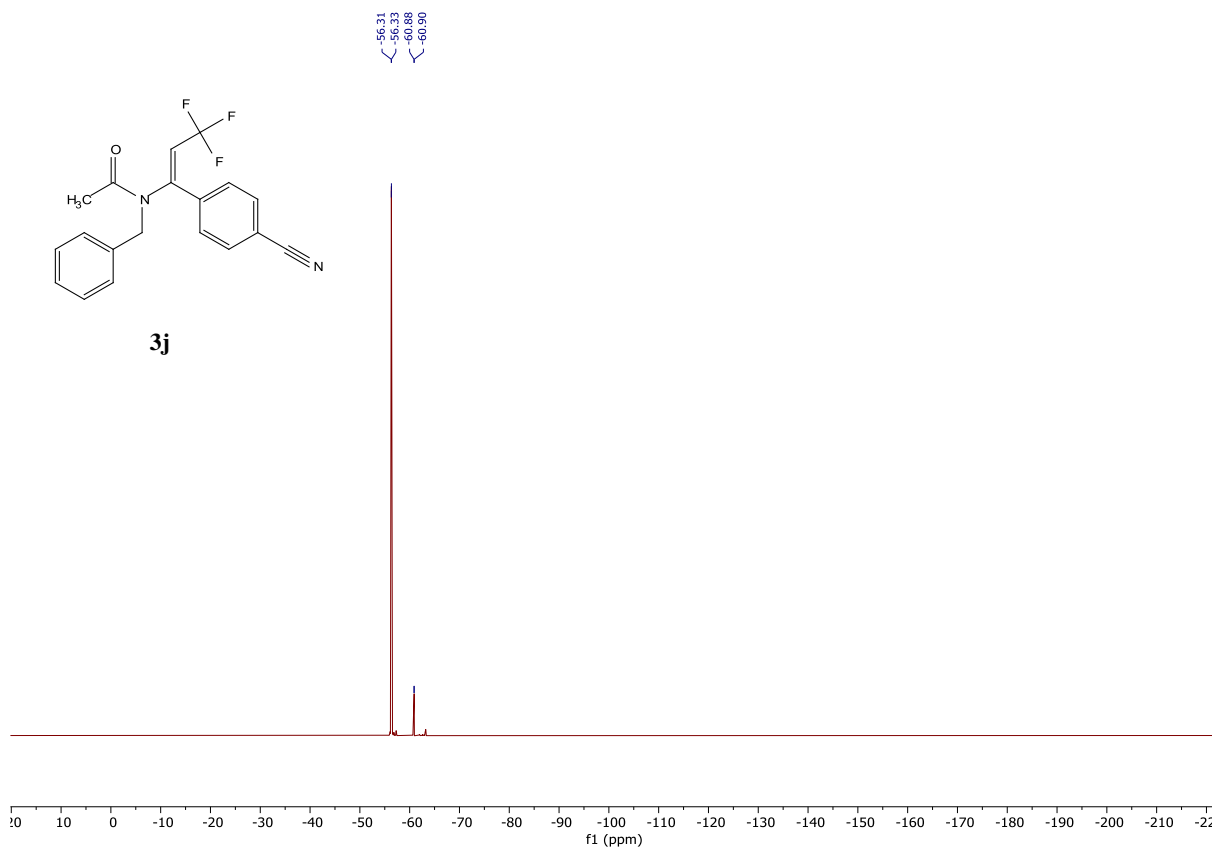
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

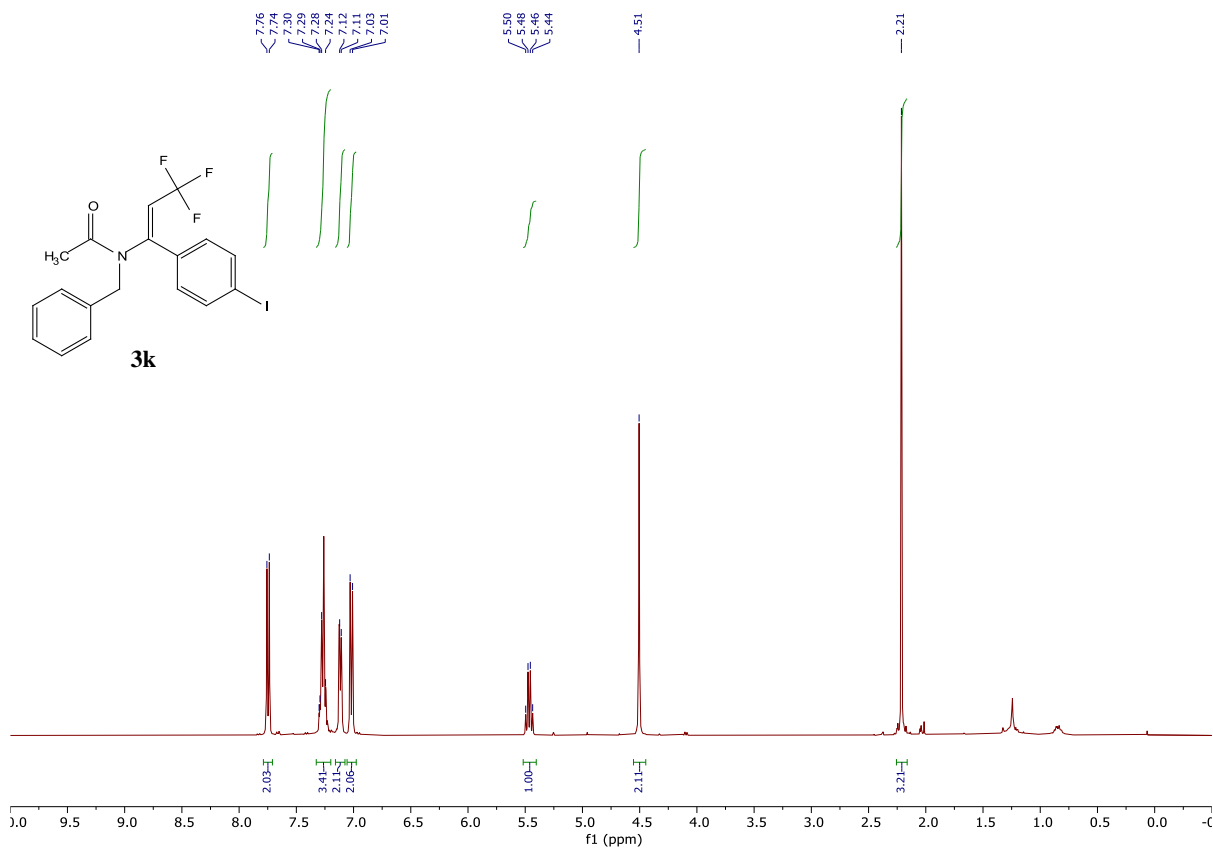


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



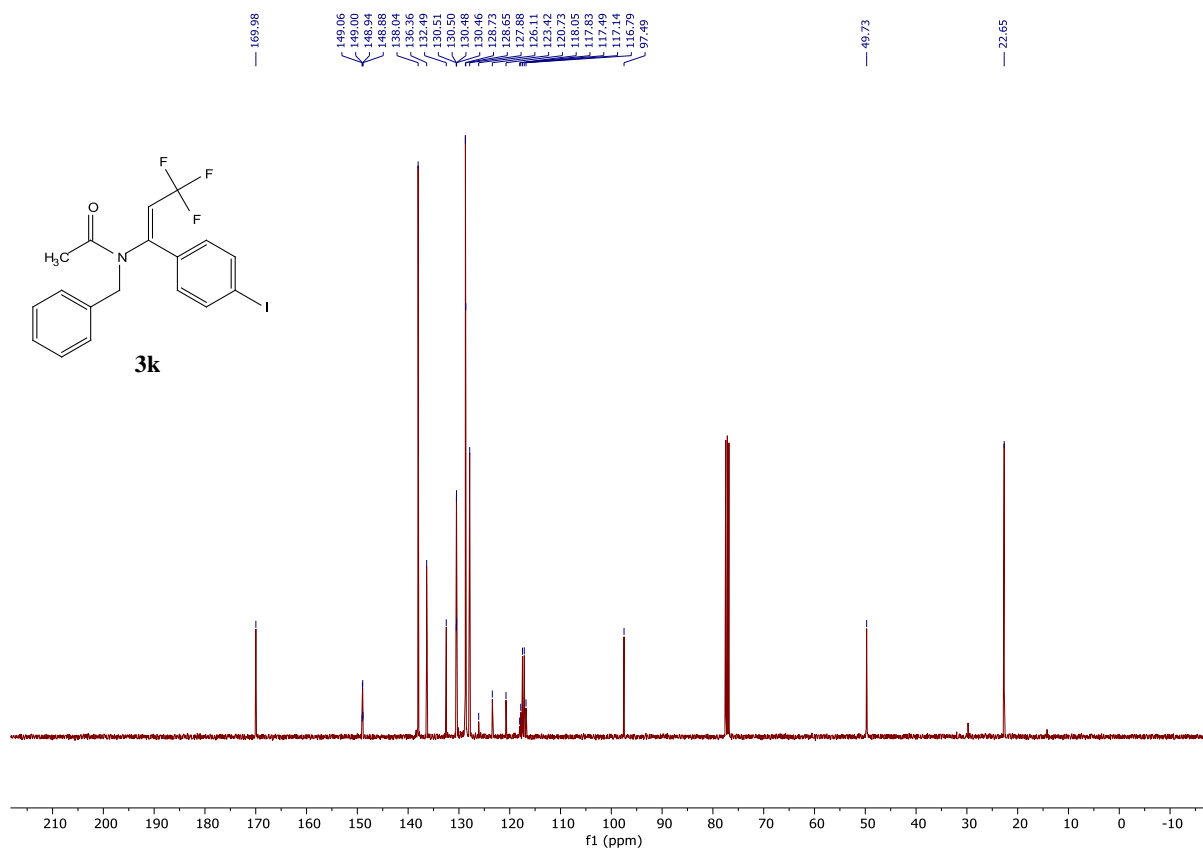
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-iodophenyl)prop-1-en-1-yl)acetamide (3k)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

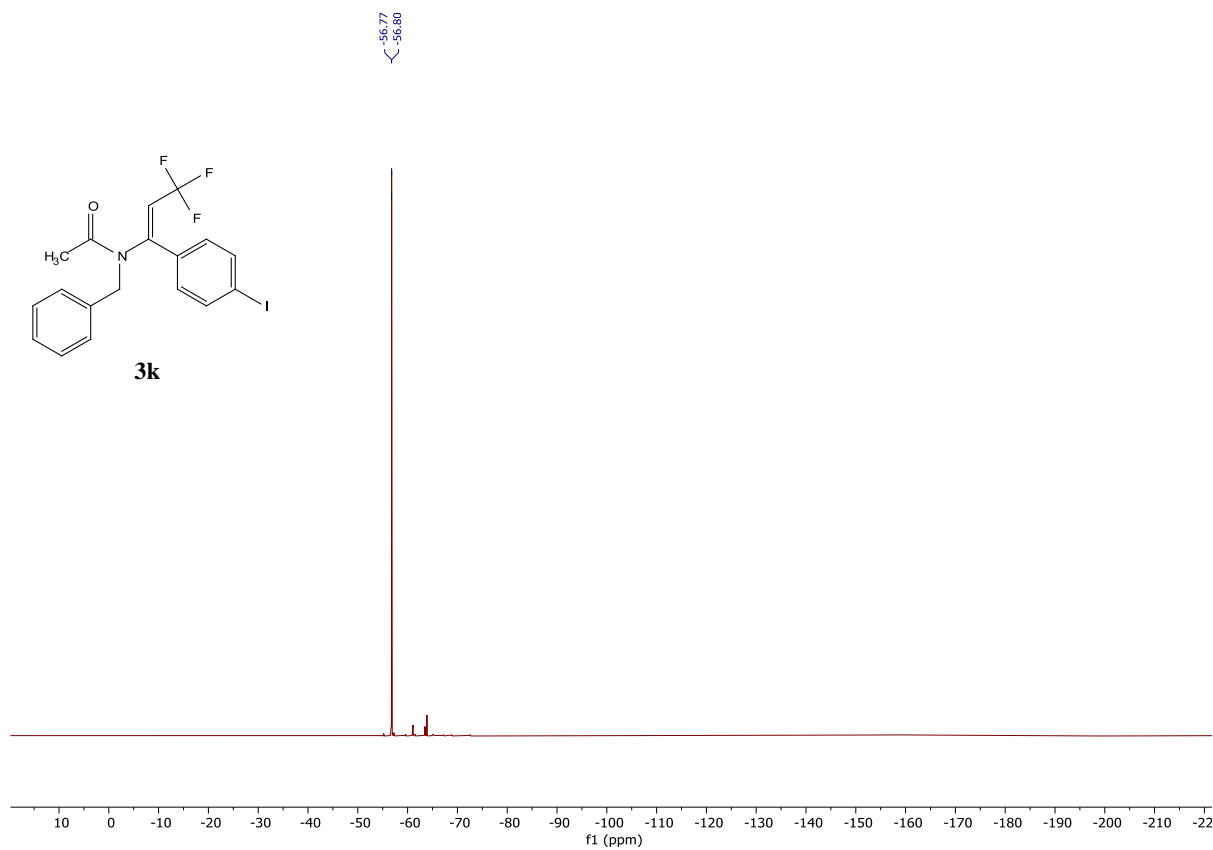




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

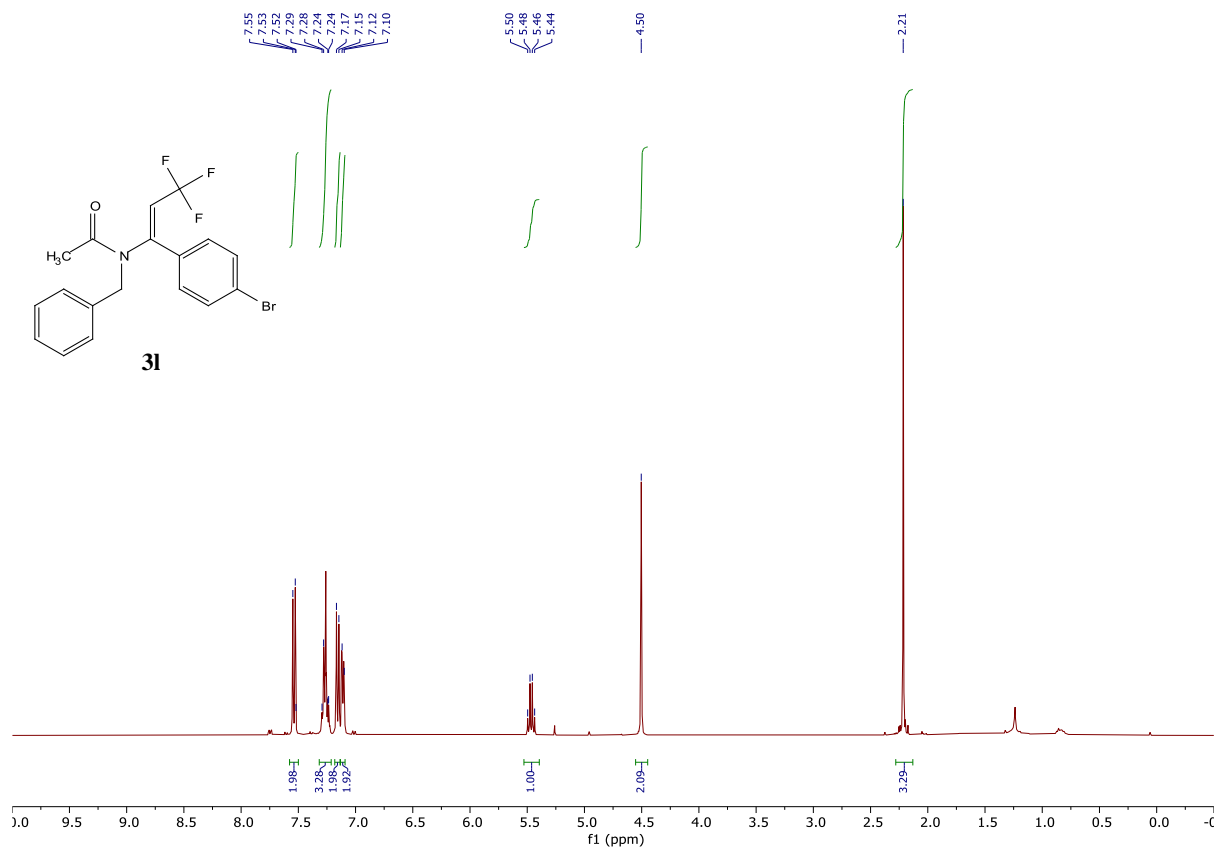


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

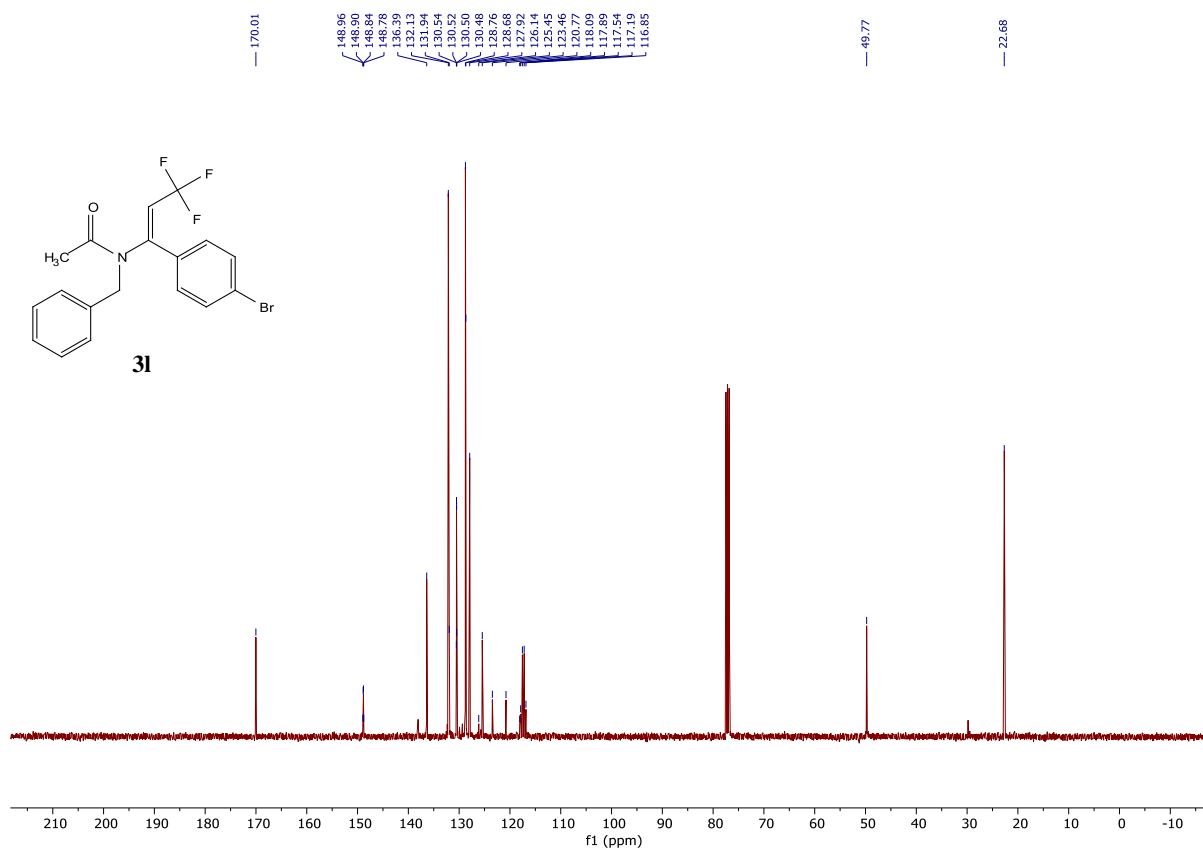


**(E)-N-Benzyl-N-(1-(4-bromophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (31)**

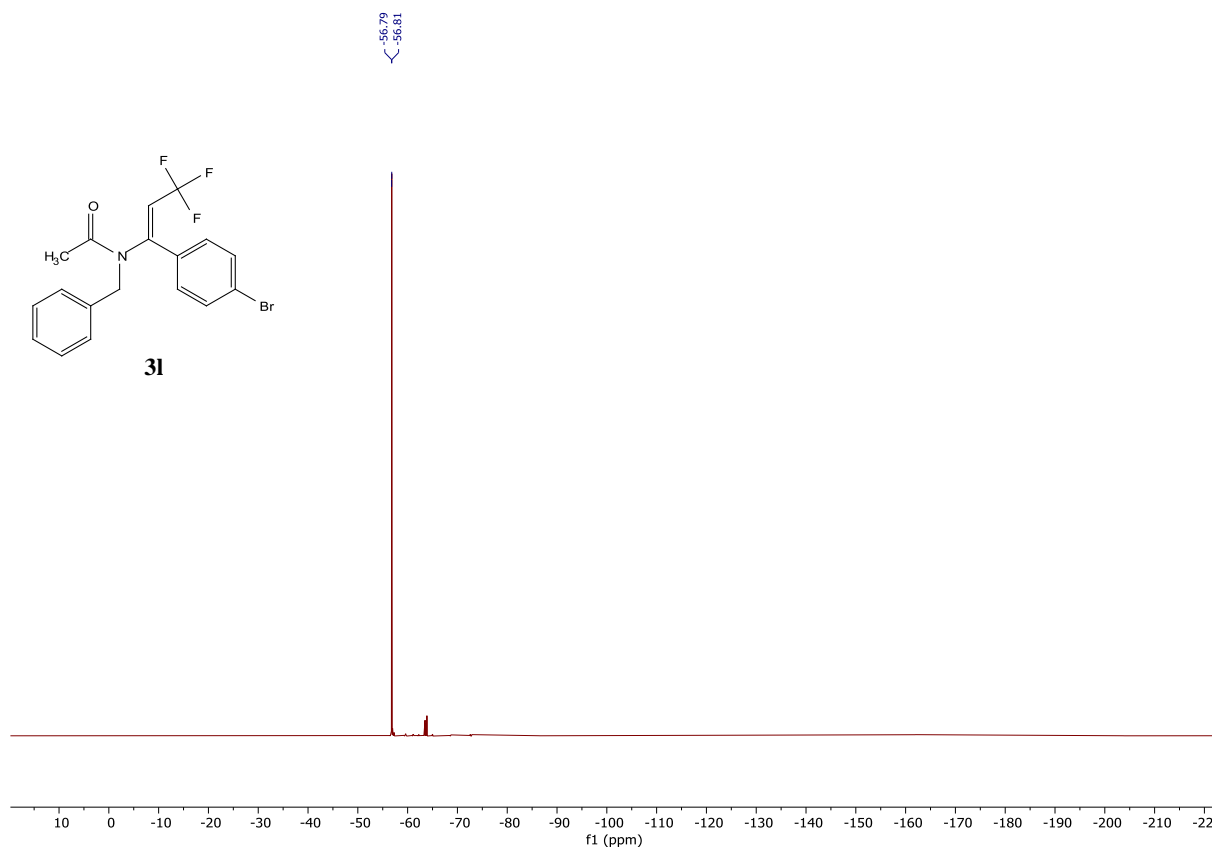
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

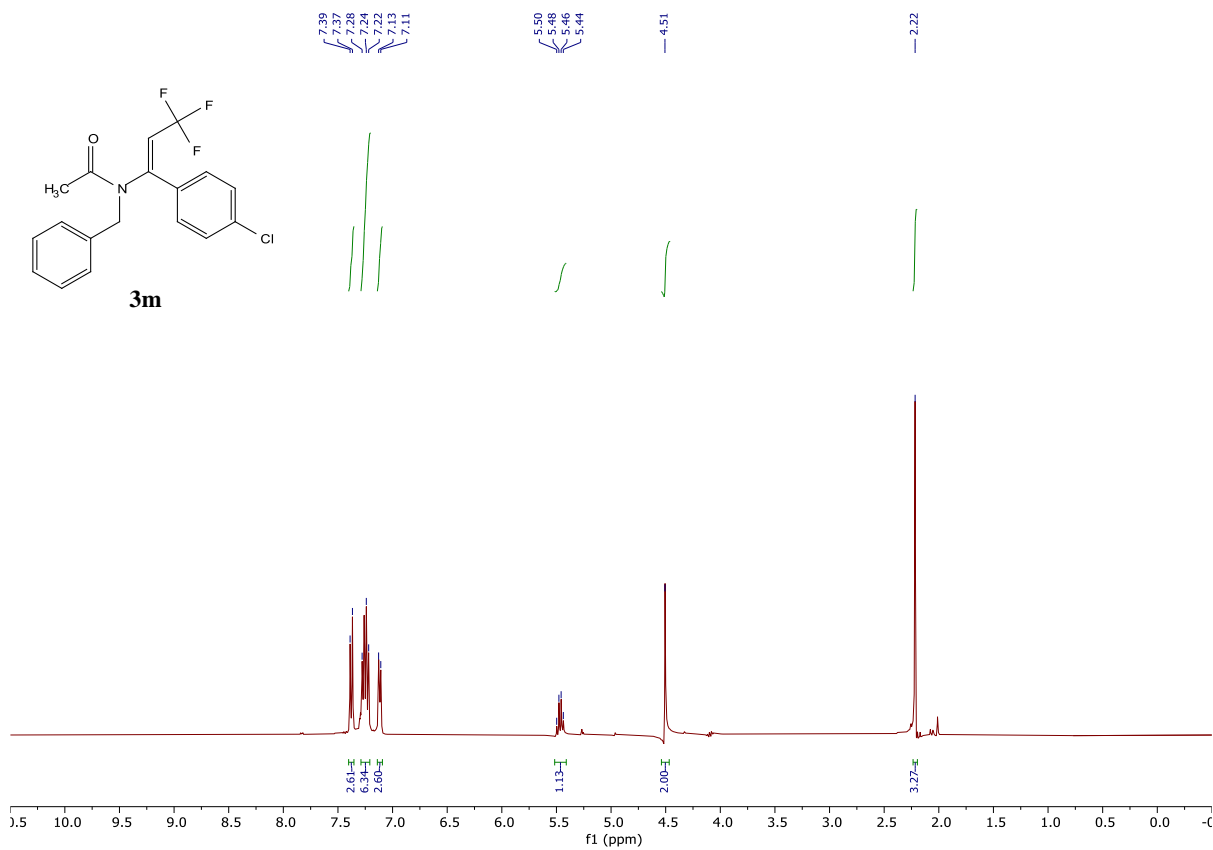


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

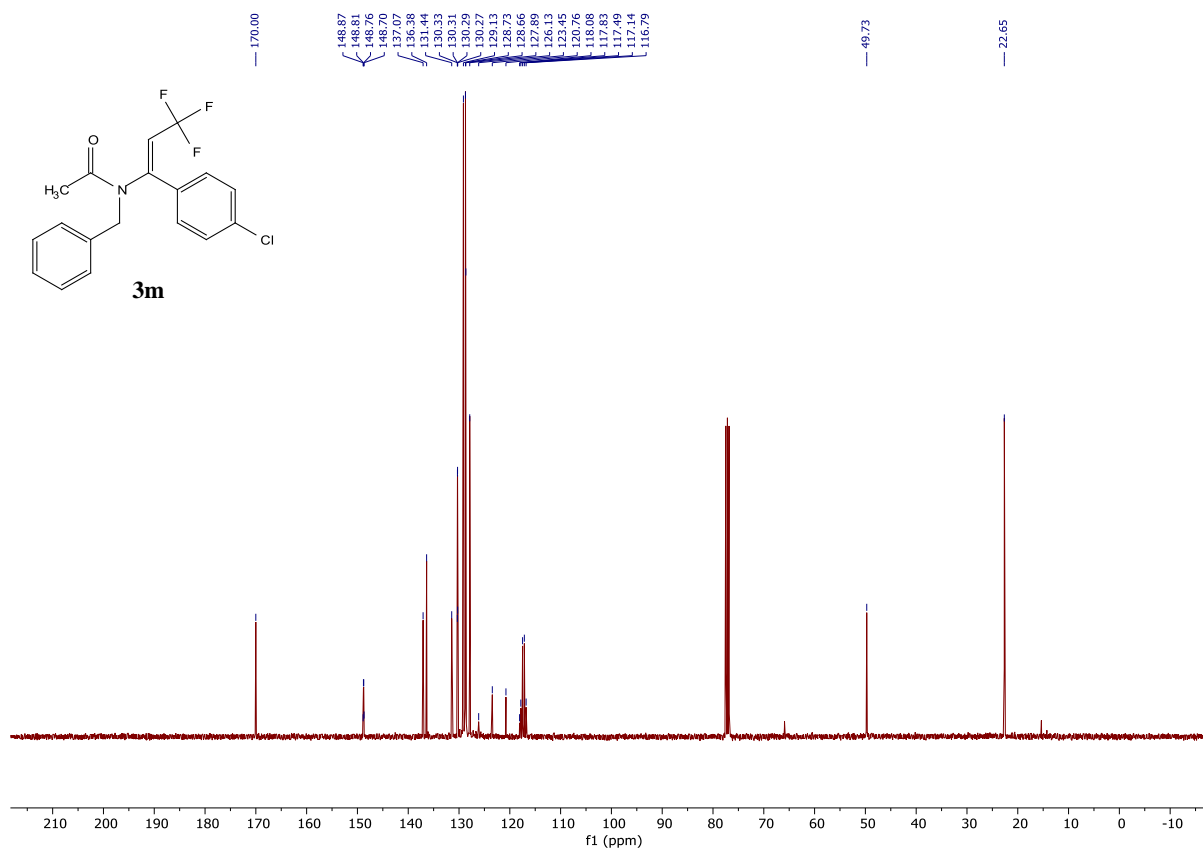


**(E)-N-Benzyl-N-(1-(4-chlorophenyl)-3,3,3-trifluoroprop-1-en-1-yl)acetamide (3m)**

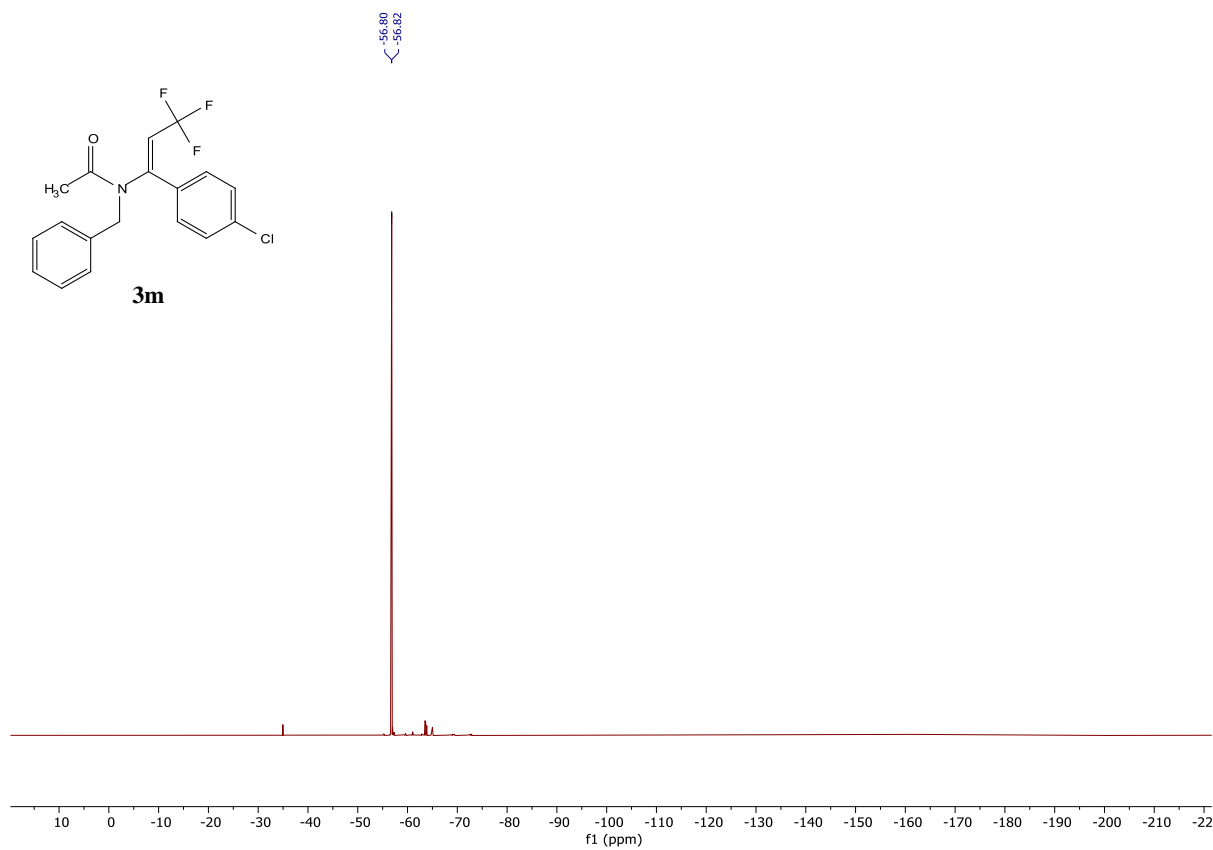
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

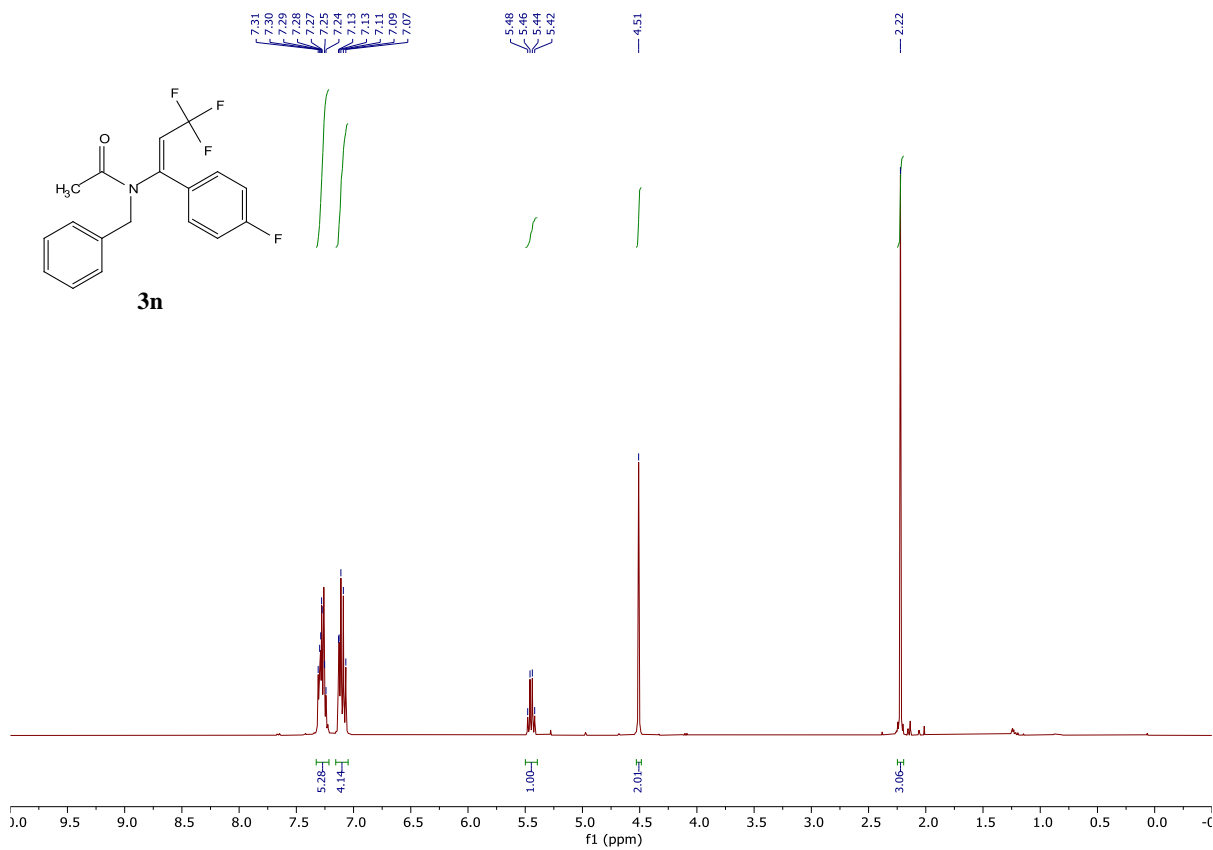


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

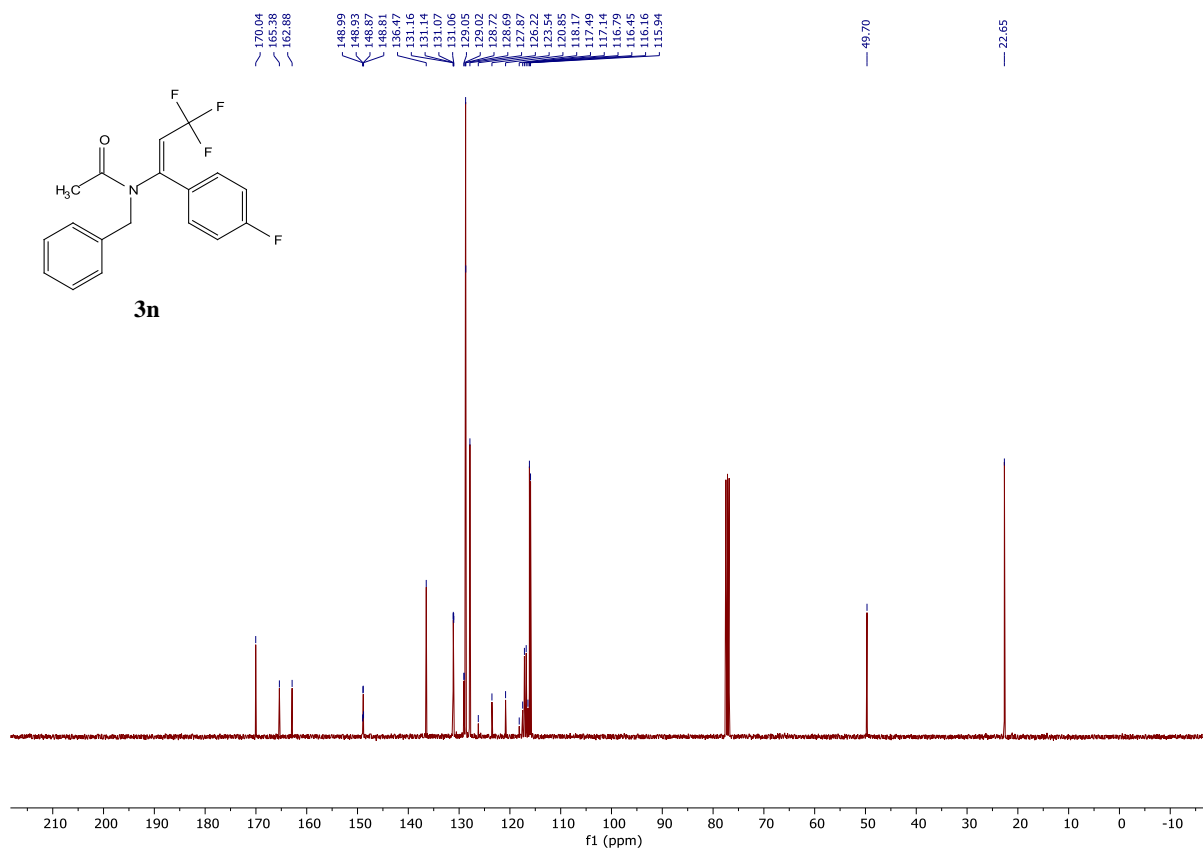


**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(4-fluorophenyl)prop-1-en-1-yl)acetamide (3n)**

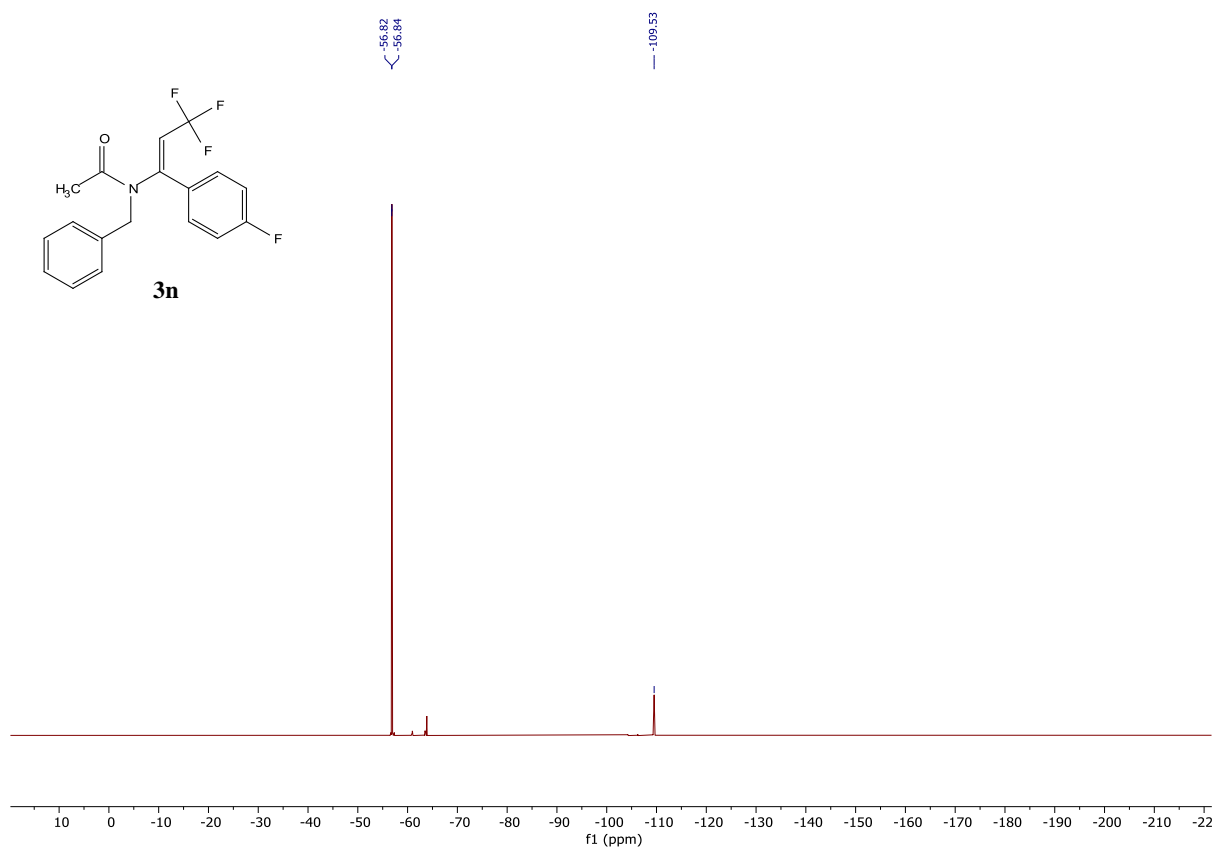
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

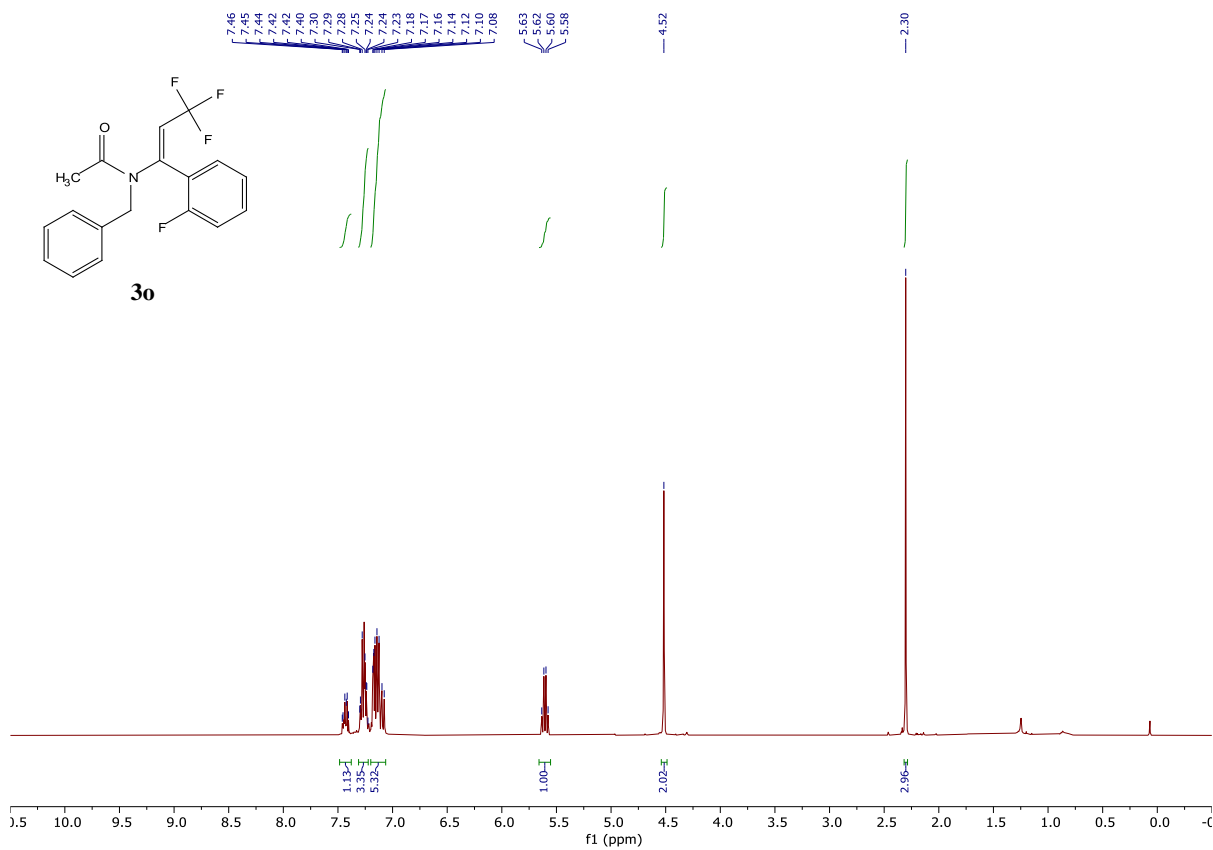


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



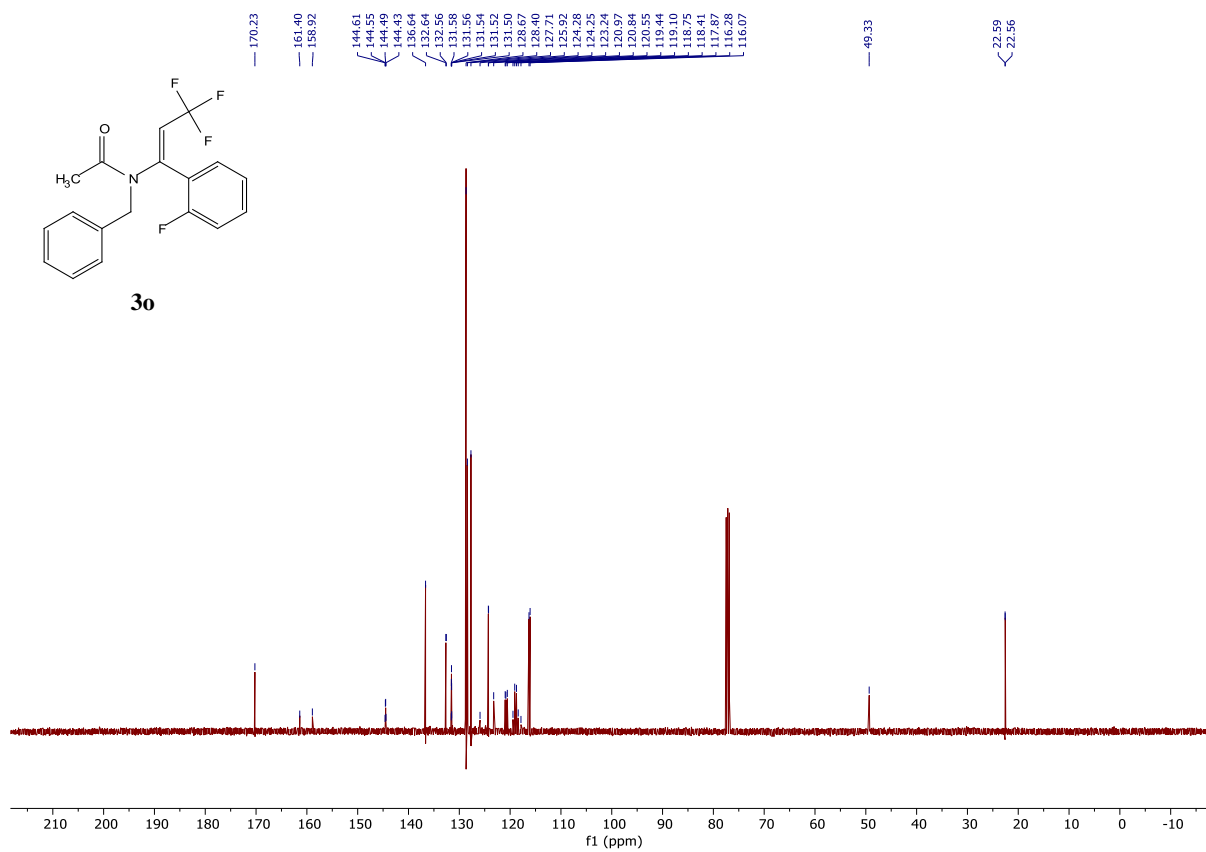
**(E)-N-Benzyl-N-(3,3,3-trifluoro-1-(2-fluorophenyl)prop-1-en-1-yl)acetamide (3o)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

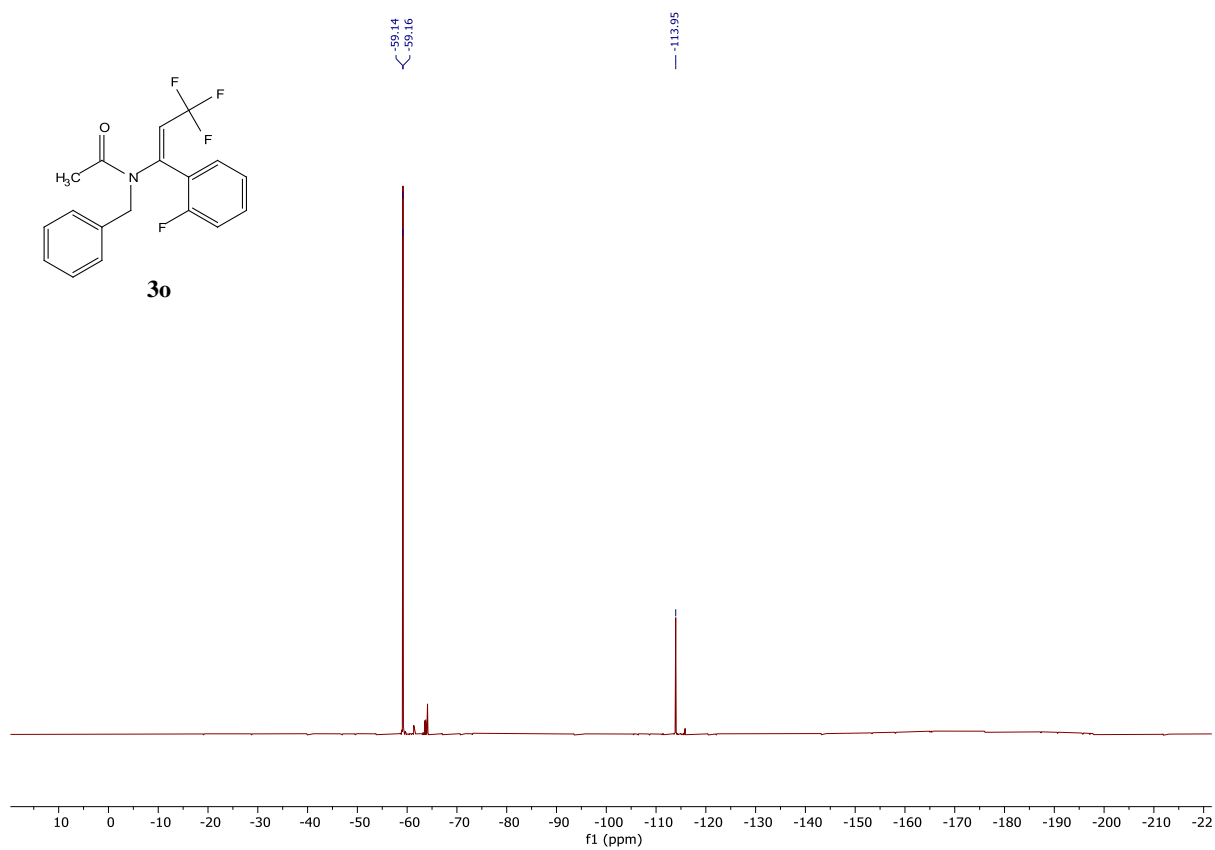




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

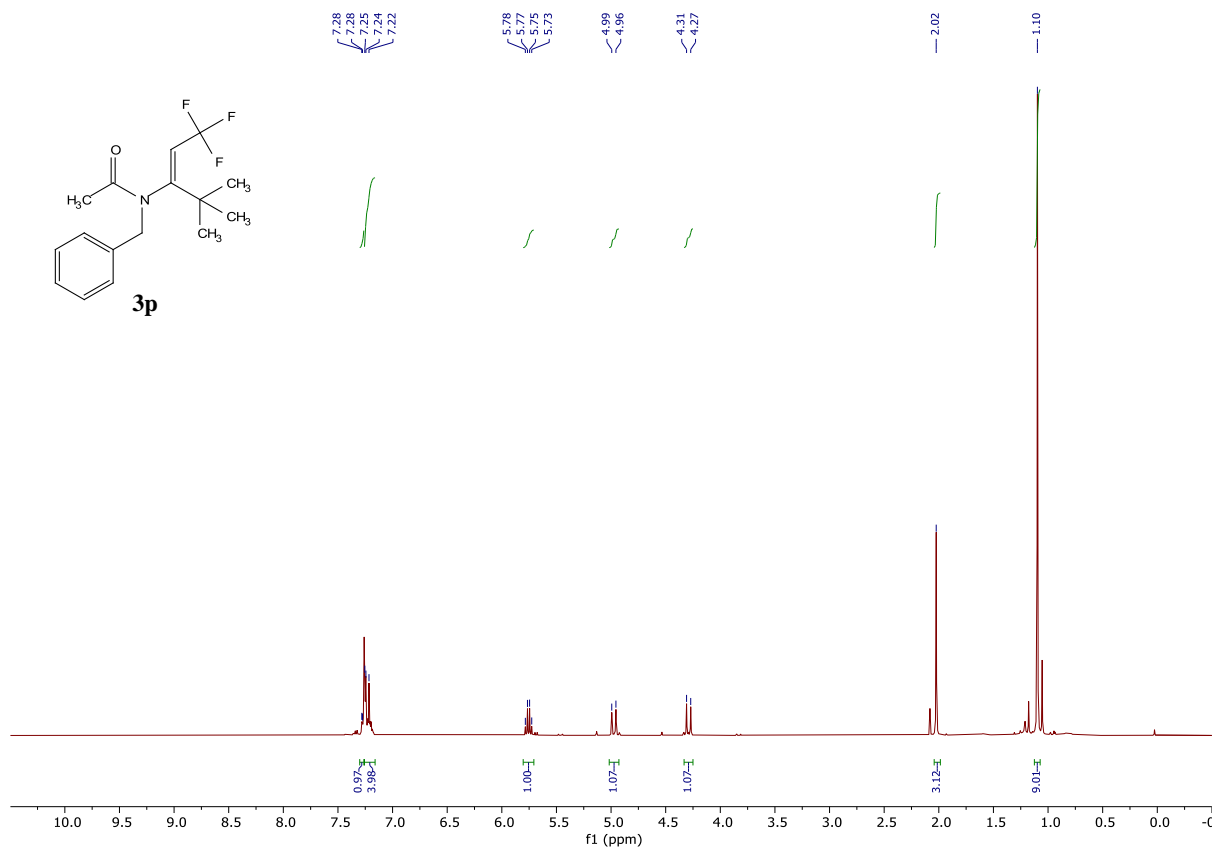


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

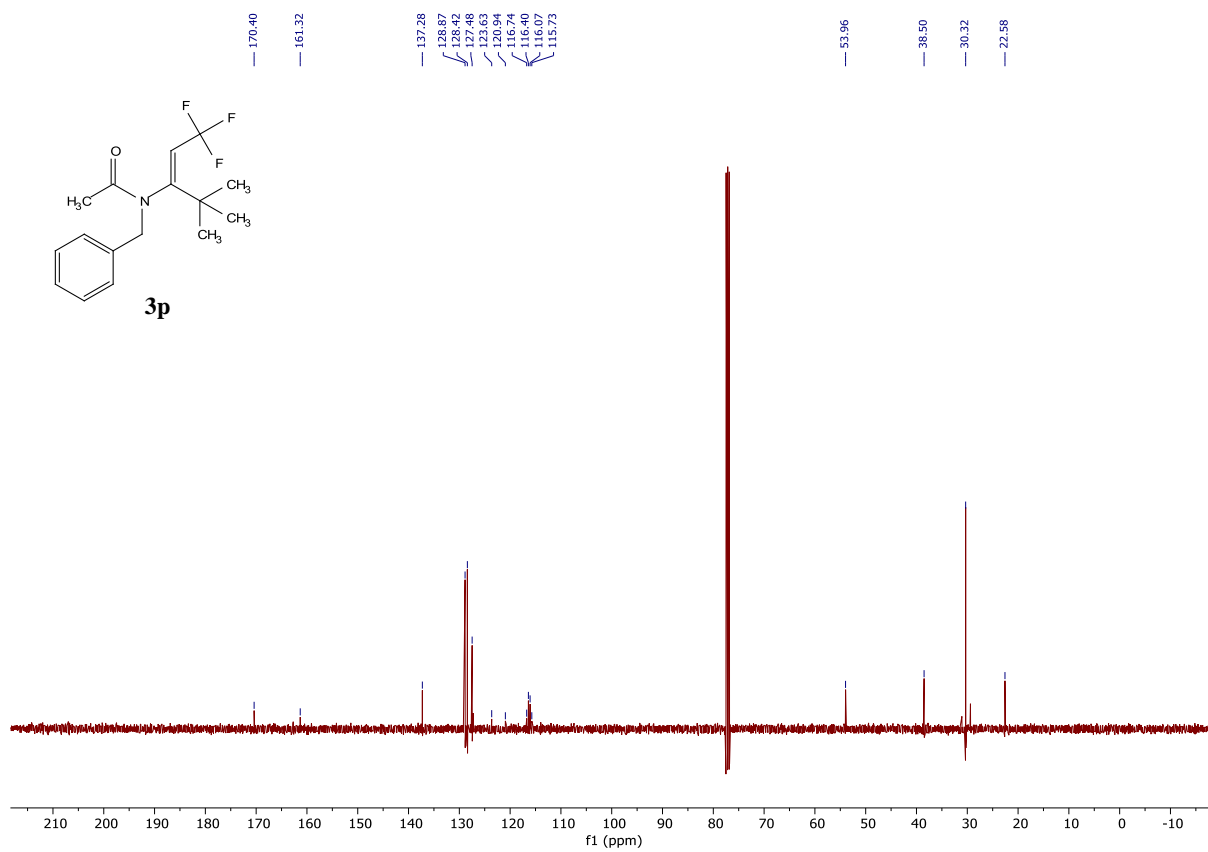


**(E)-N-Benzyl-N-(1,1,1-trifluoro-4,4-dimethylpent-2-en-3-yl)acetamide (3p)**

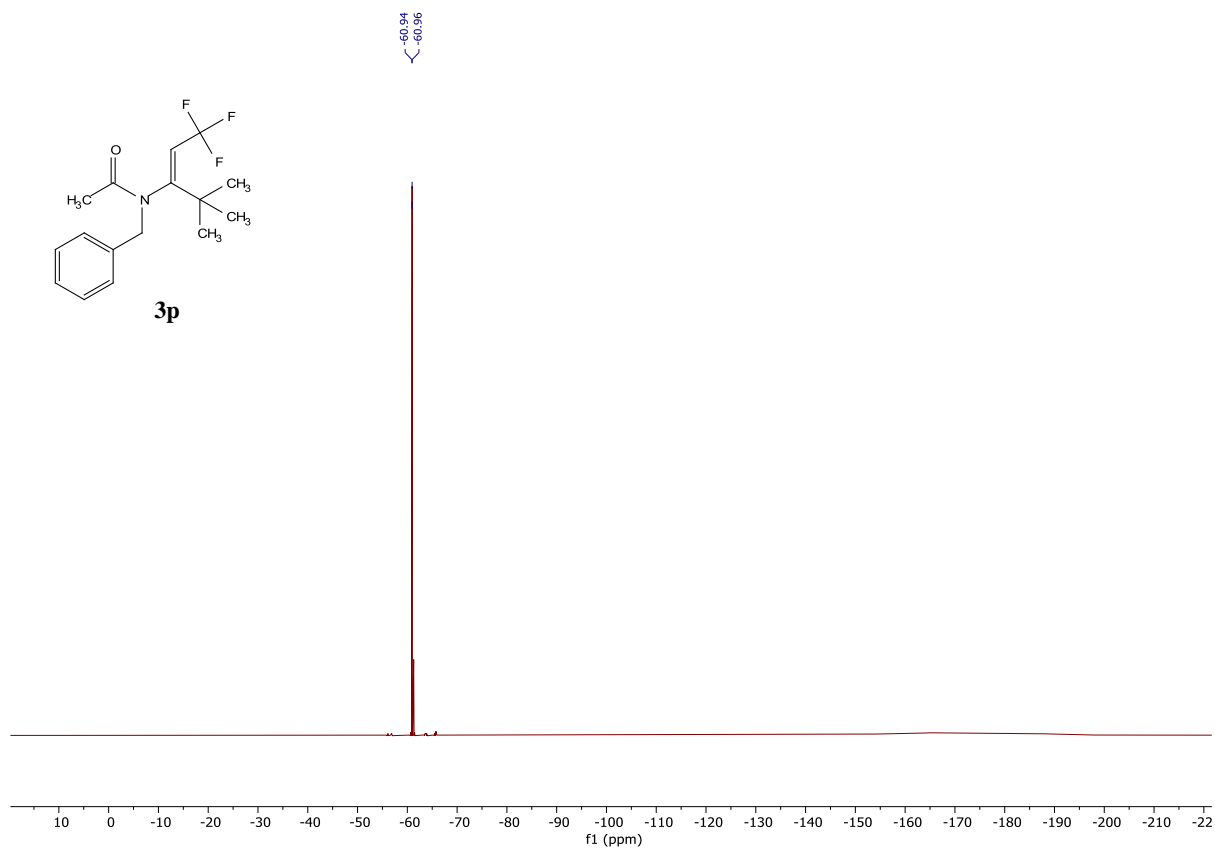
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

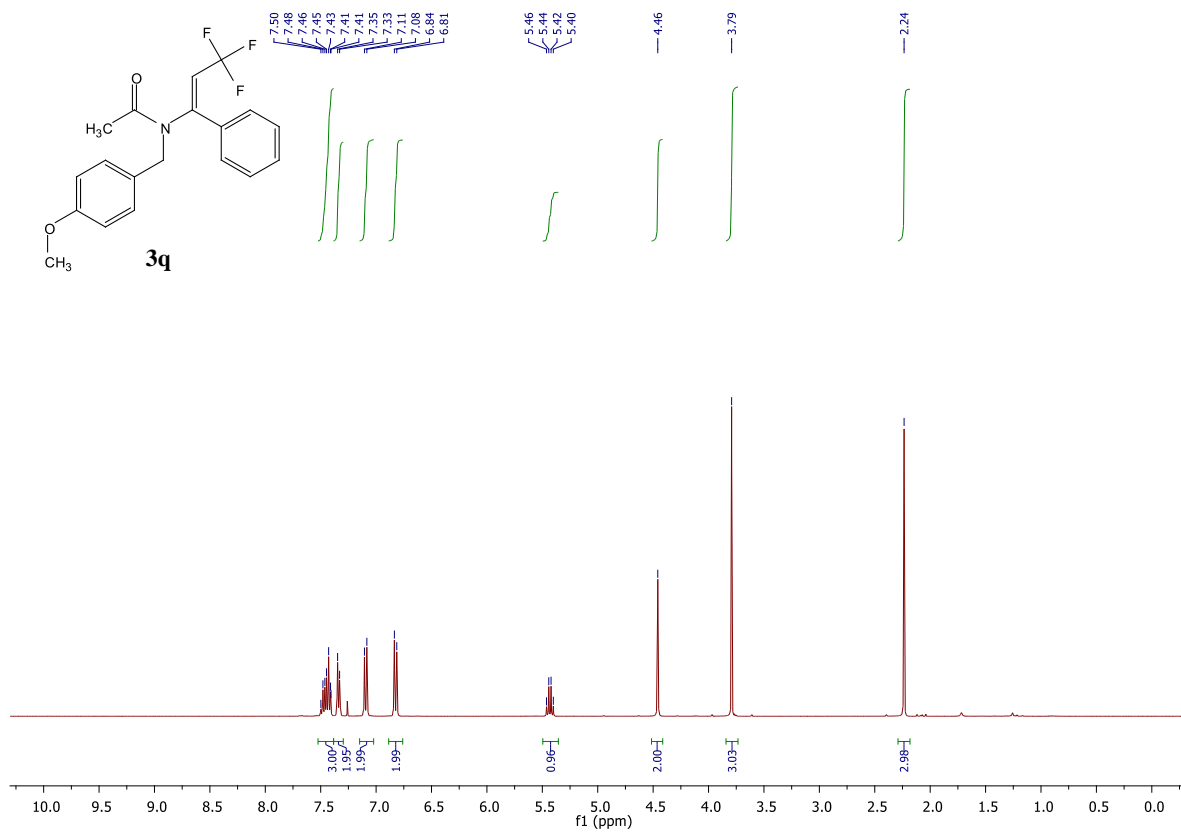


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

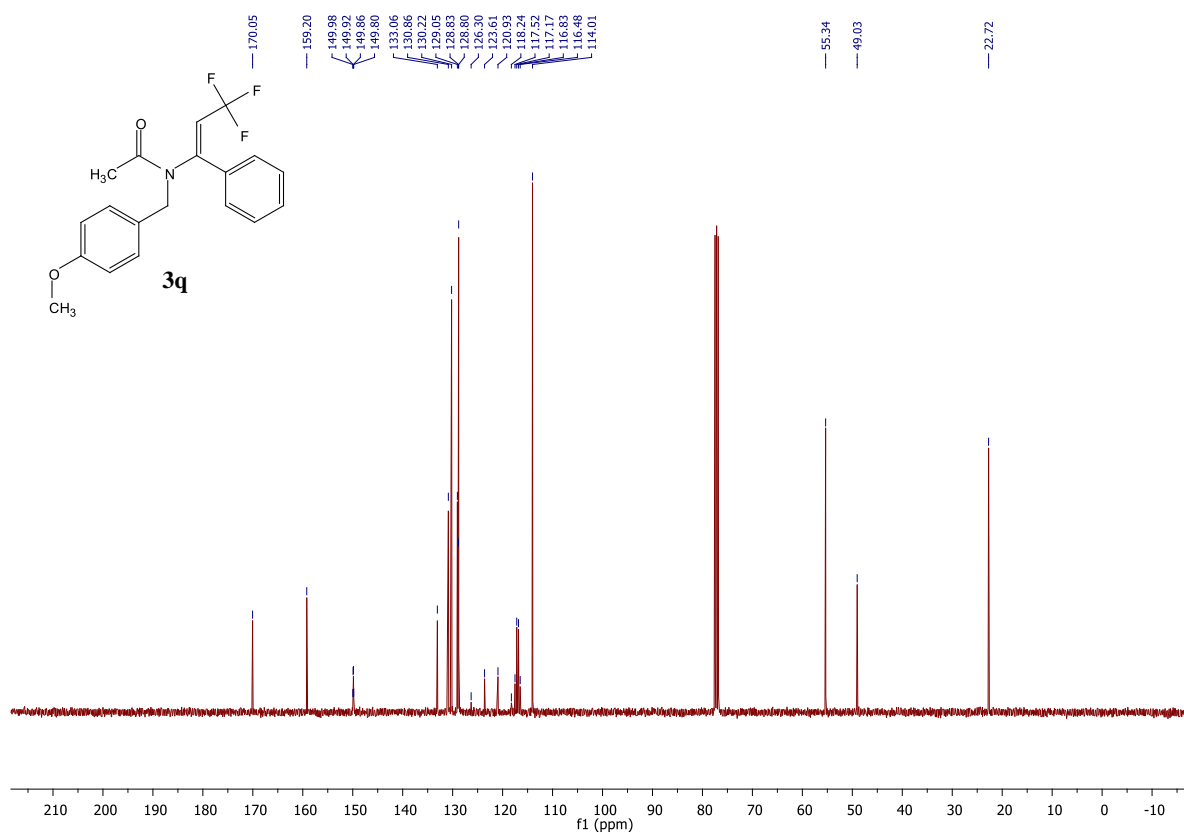


**(E)-N-(4-Methoxybenzyl)-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3q)**

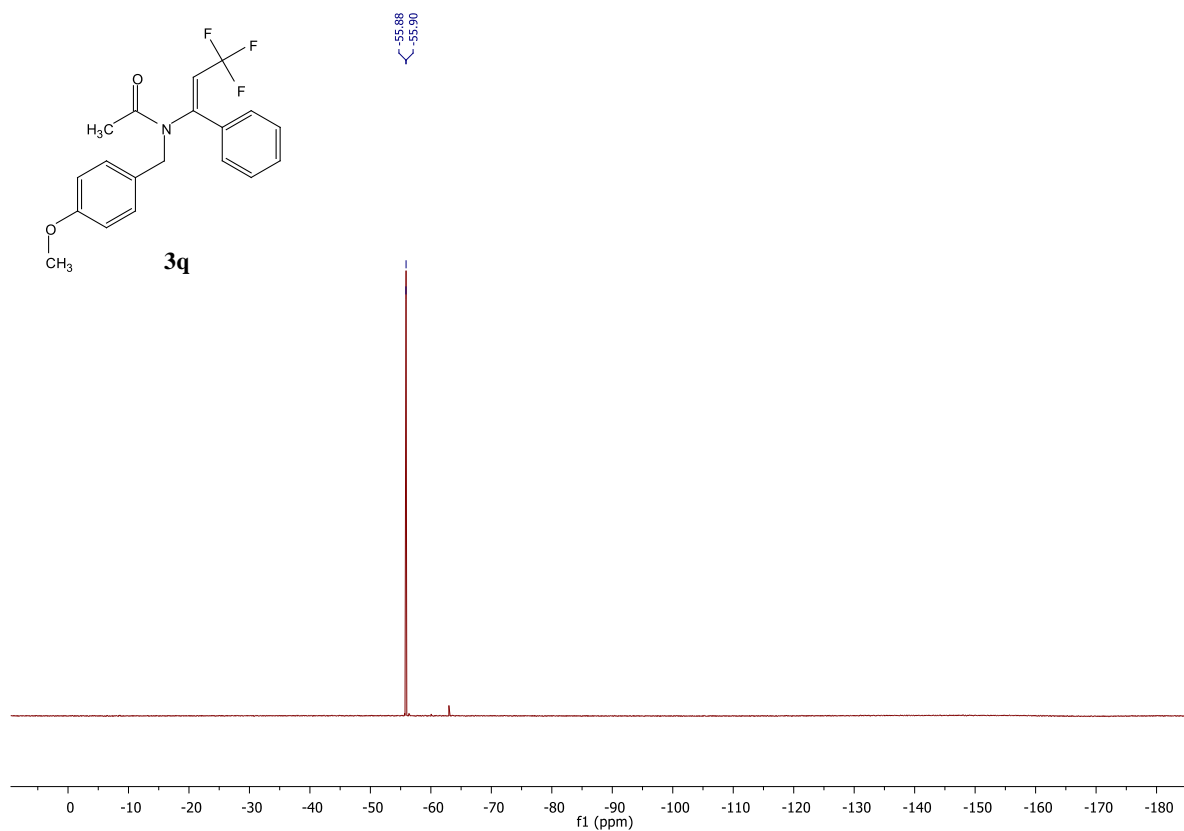
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

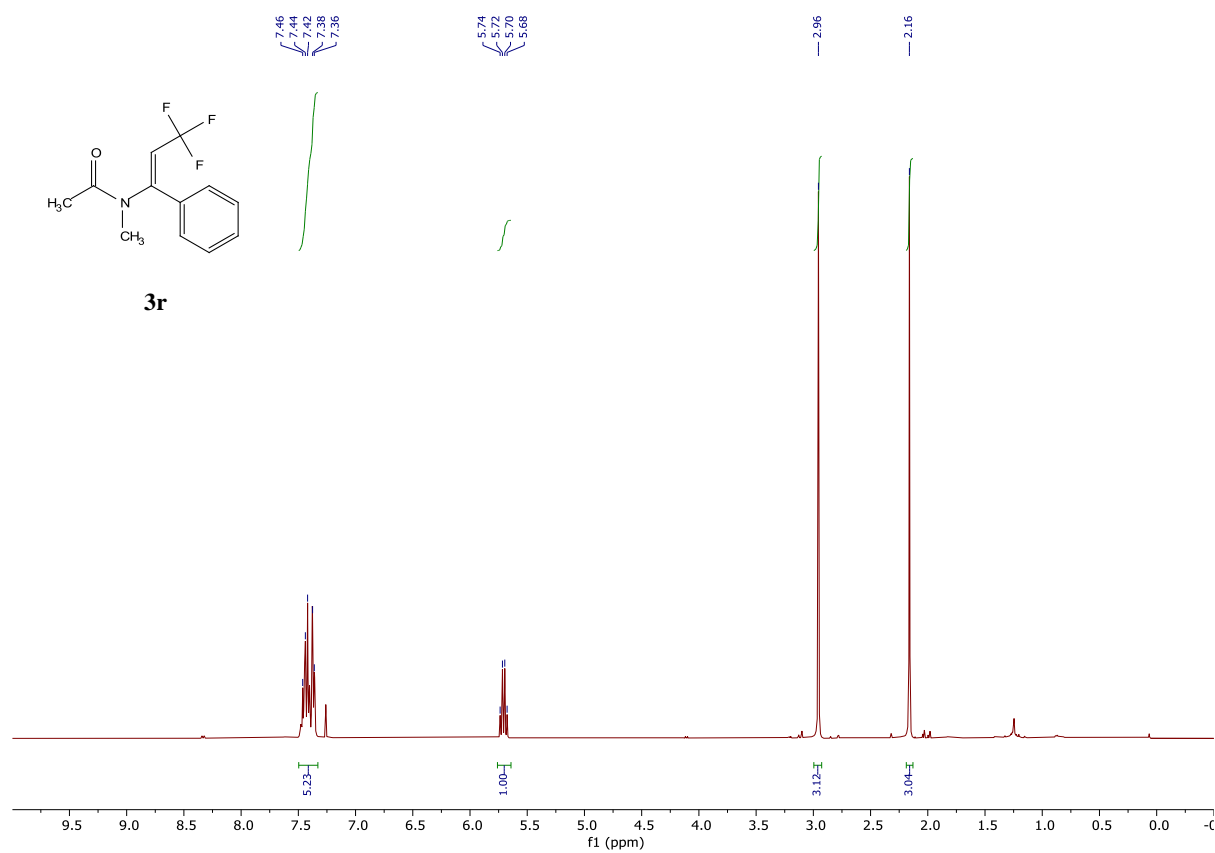


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

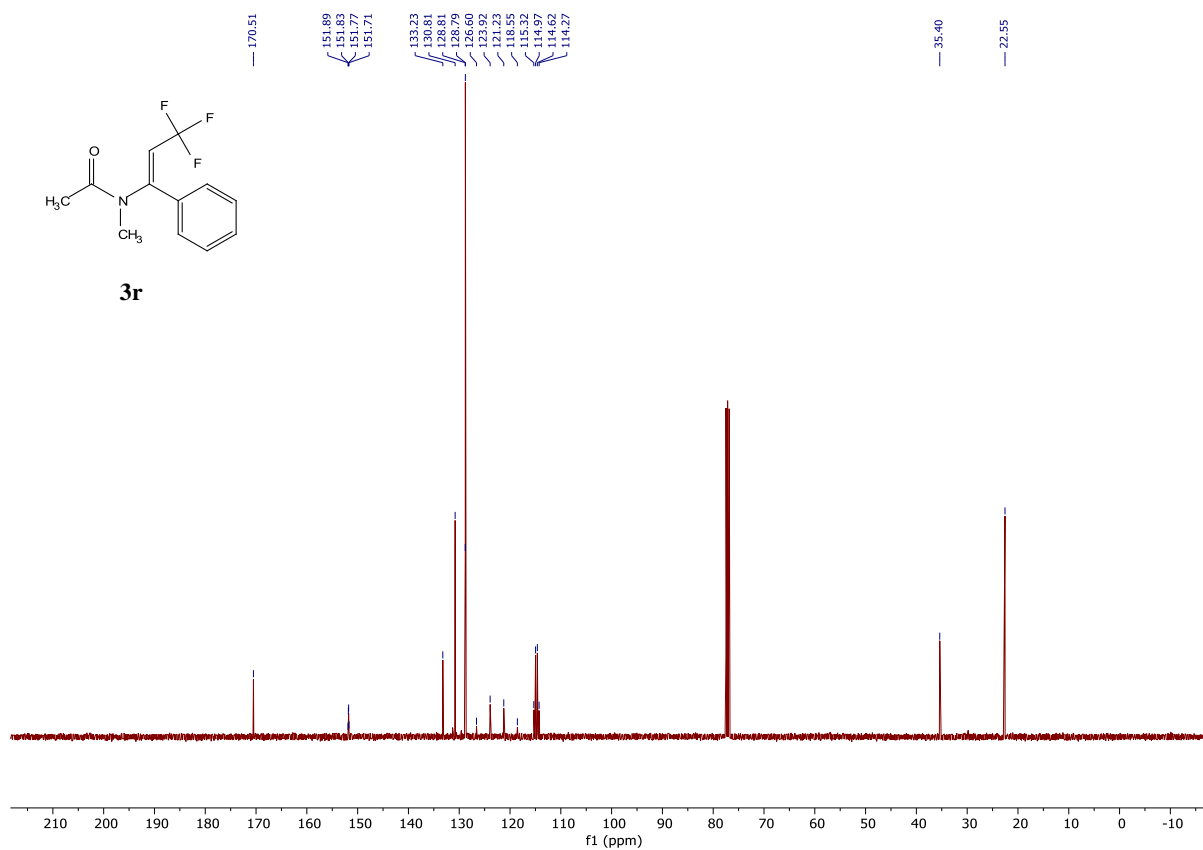


**(E)-N-Methyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3r)**

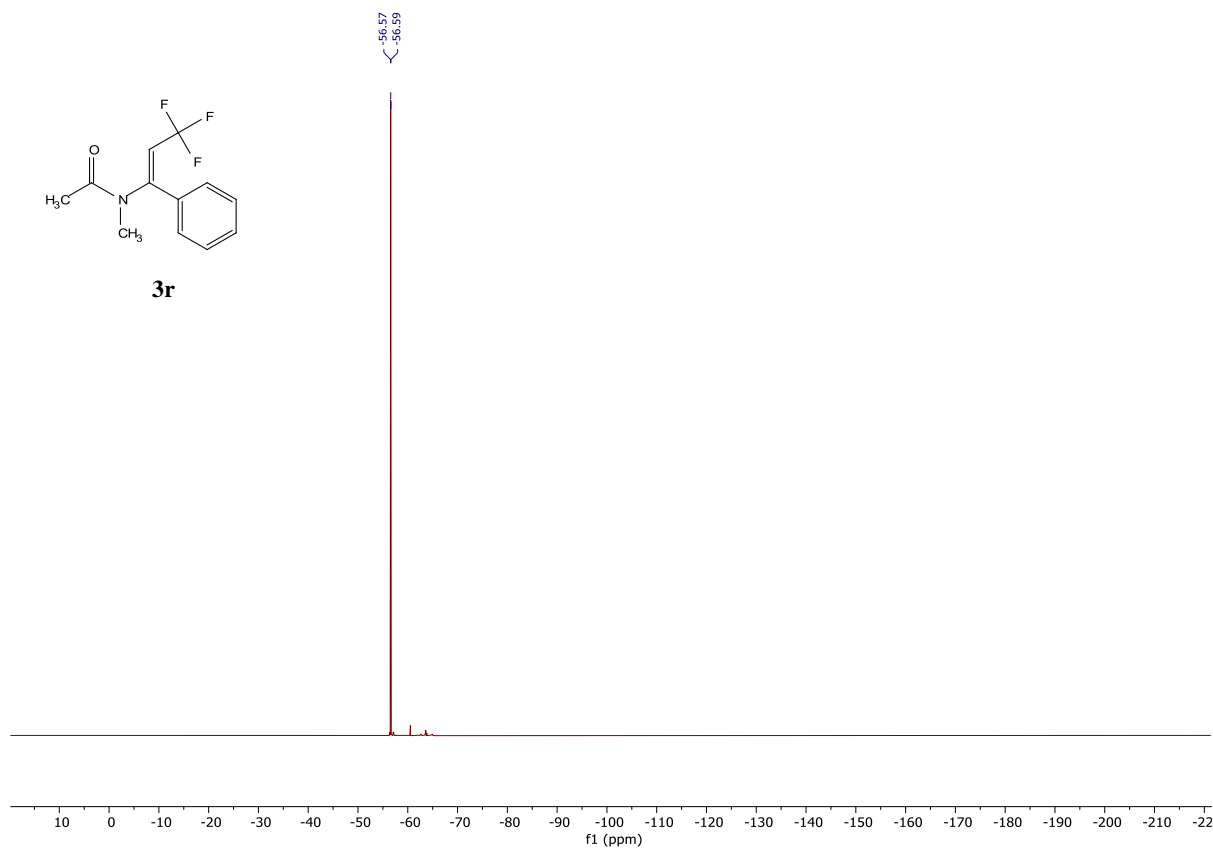
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

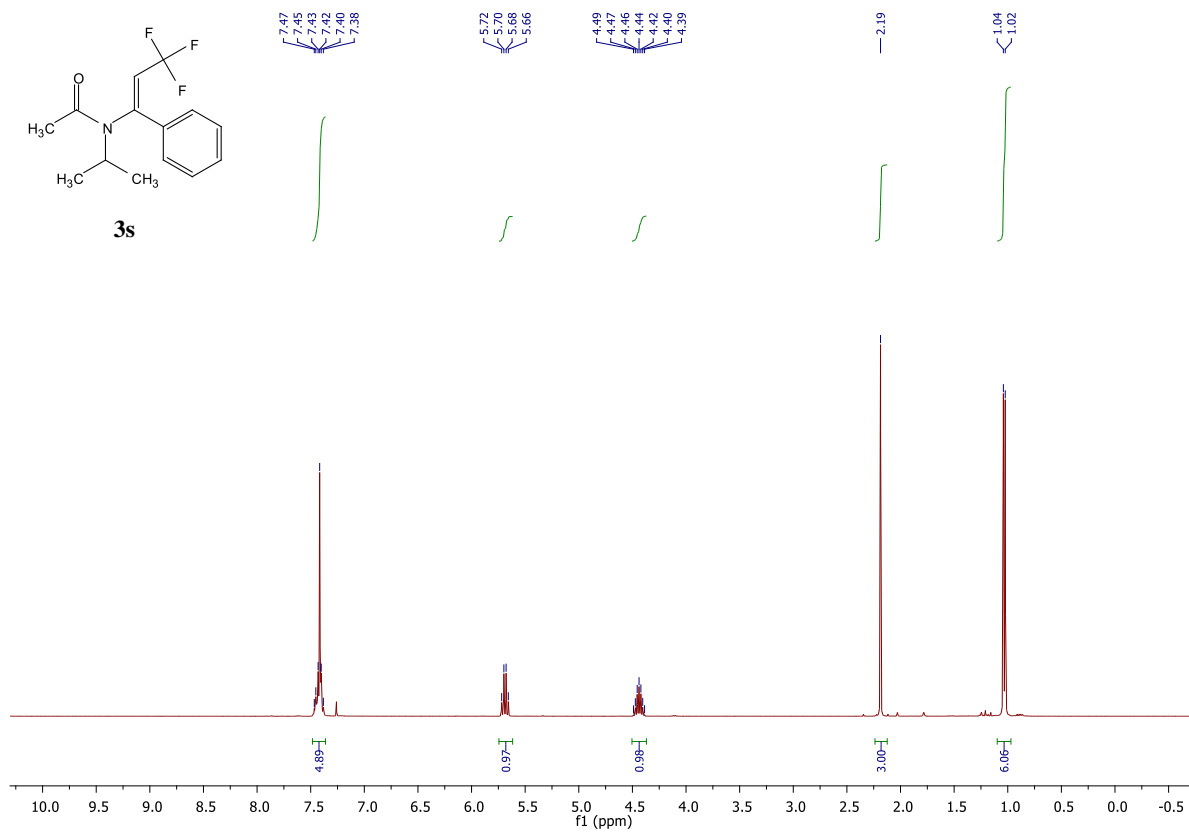


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



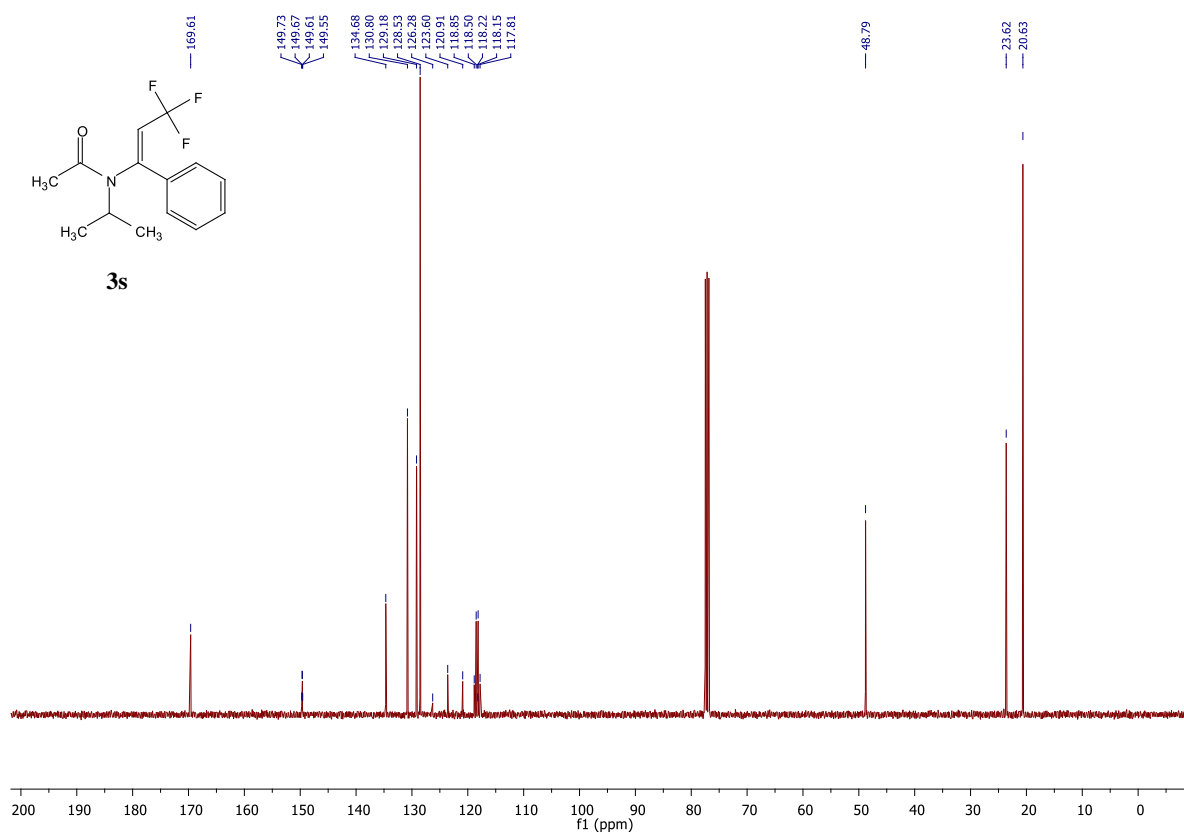
**(E)-N-Isopropyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3s)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

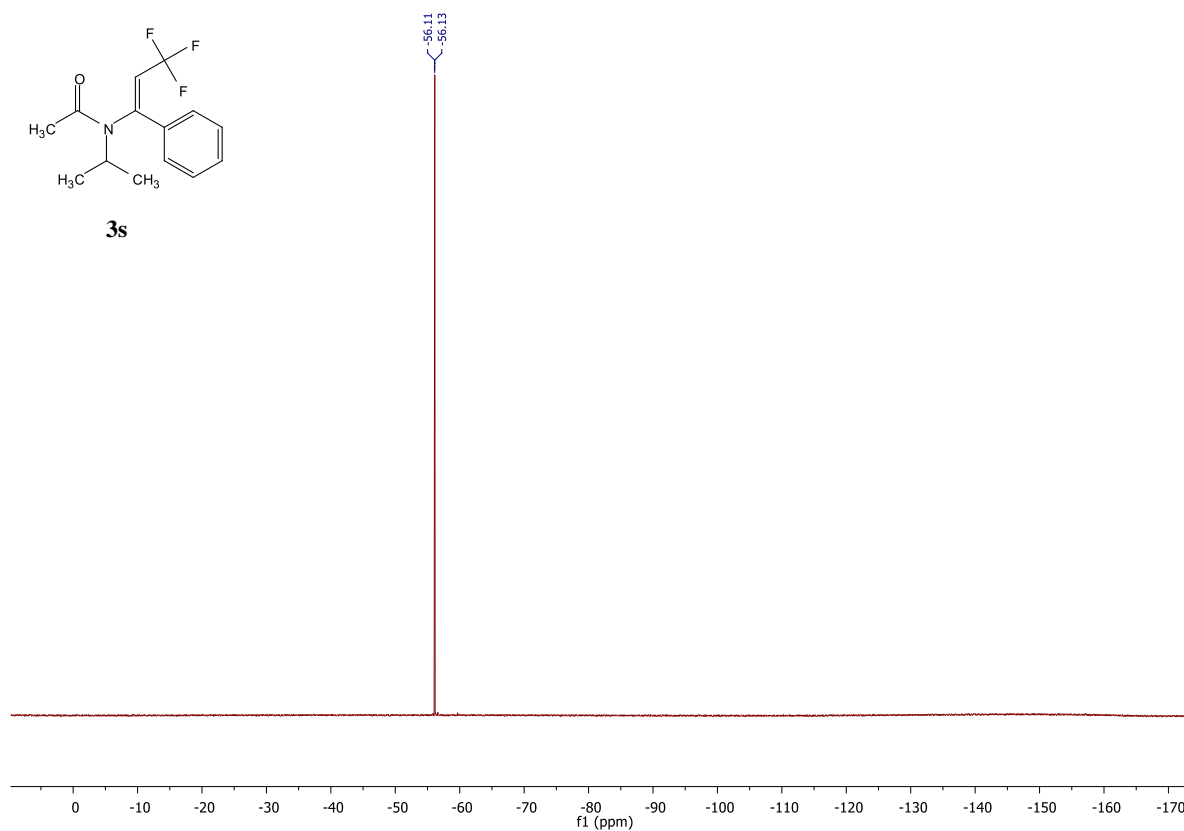




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

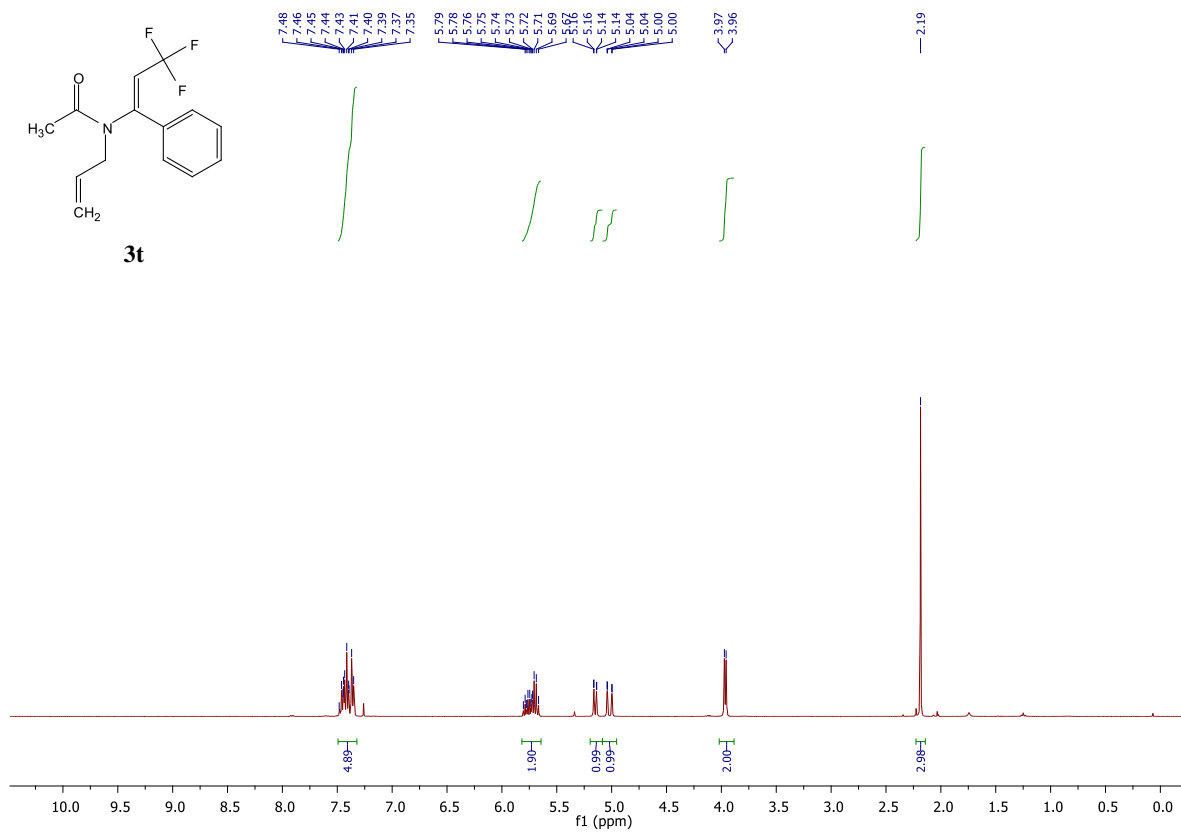


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

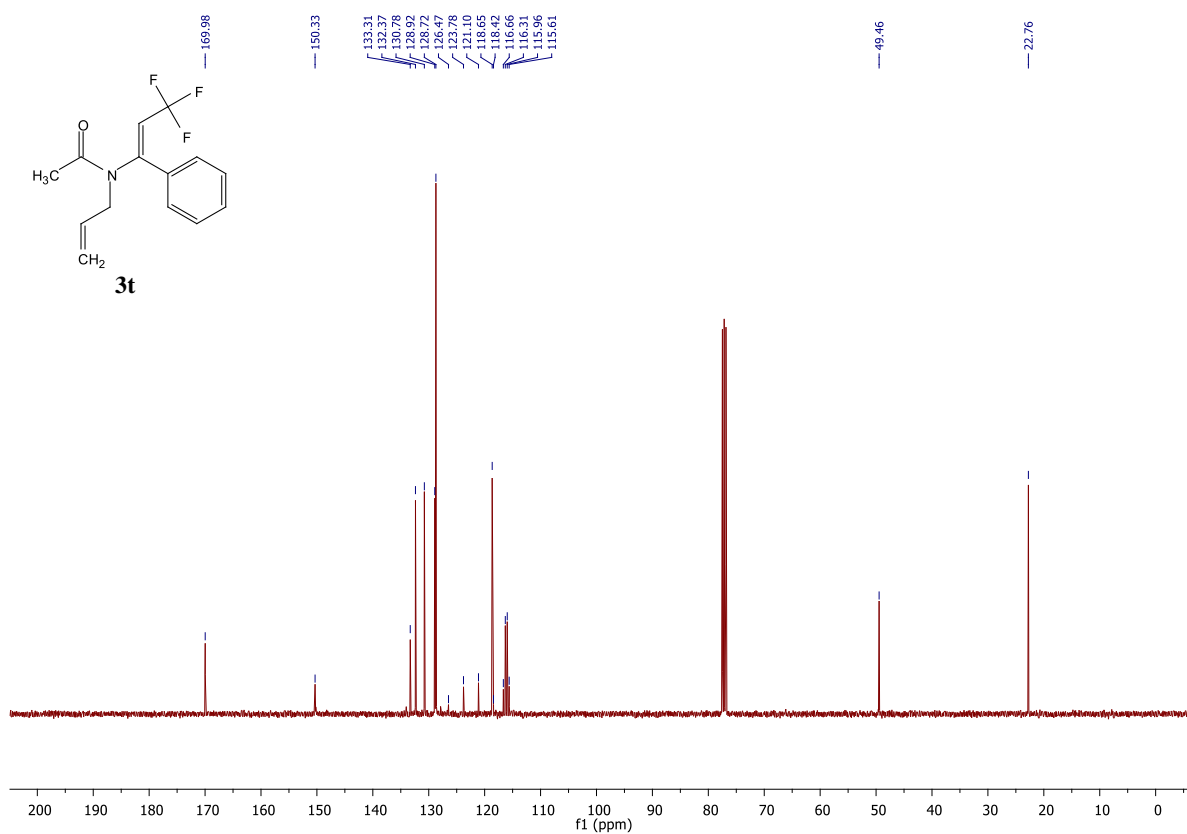


**(E)-N-Allyl-N-(3,3,3-trifluoro-1-phenylprop-1-en-1-yl)acetamide (3t)**

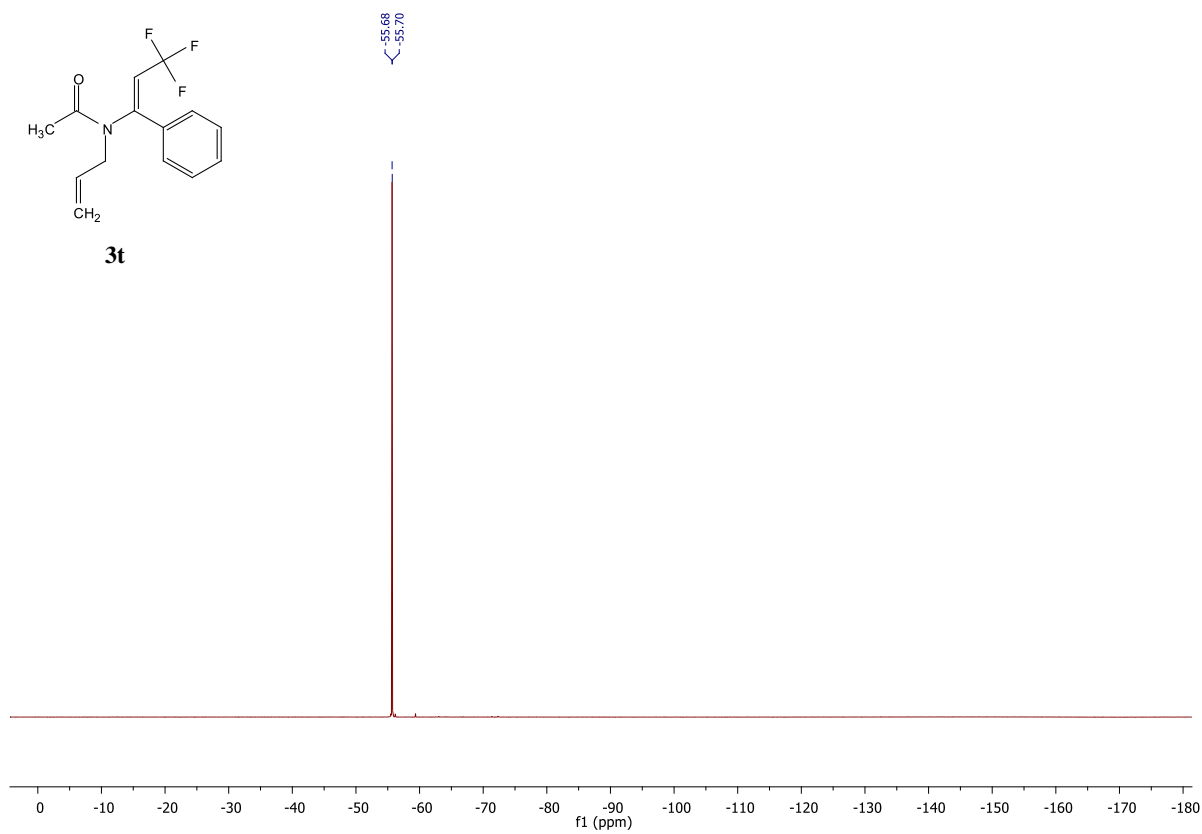
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

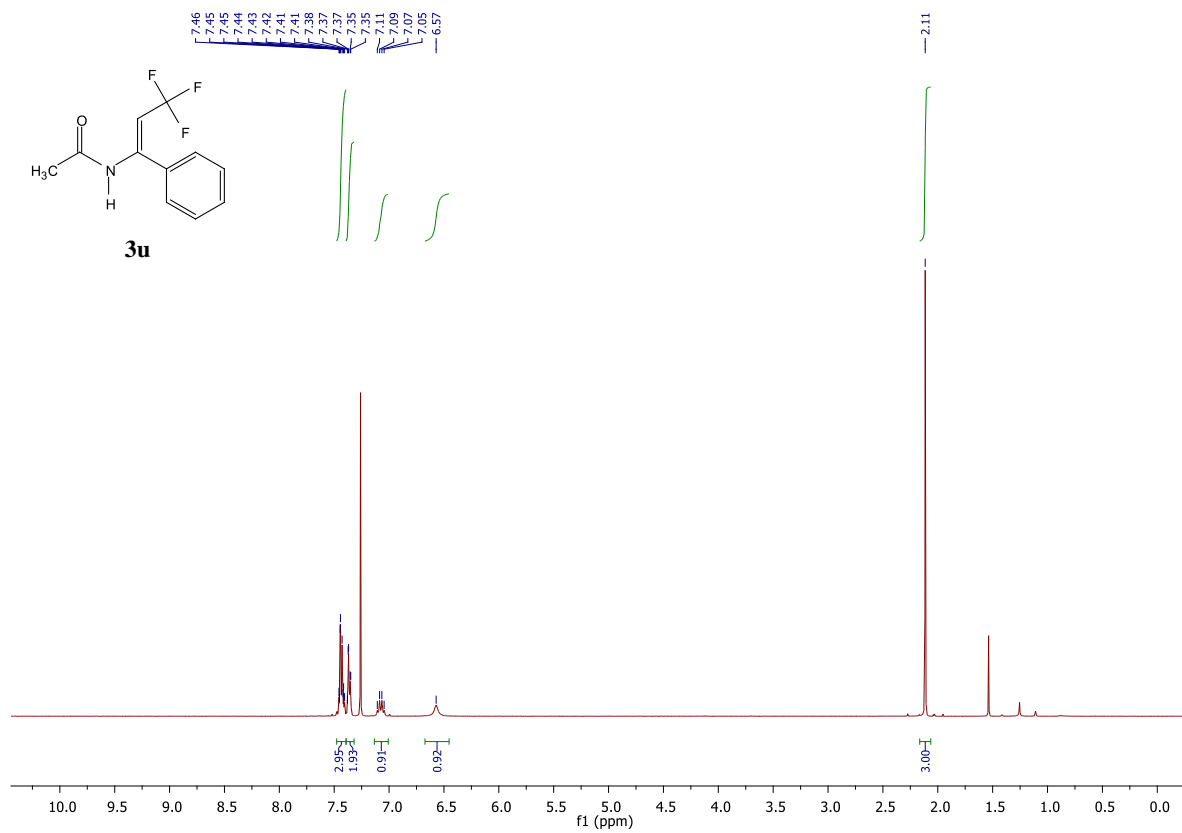


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

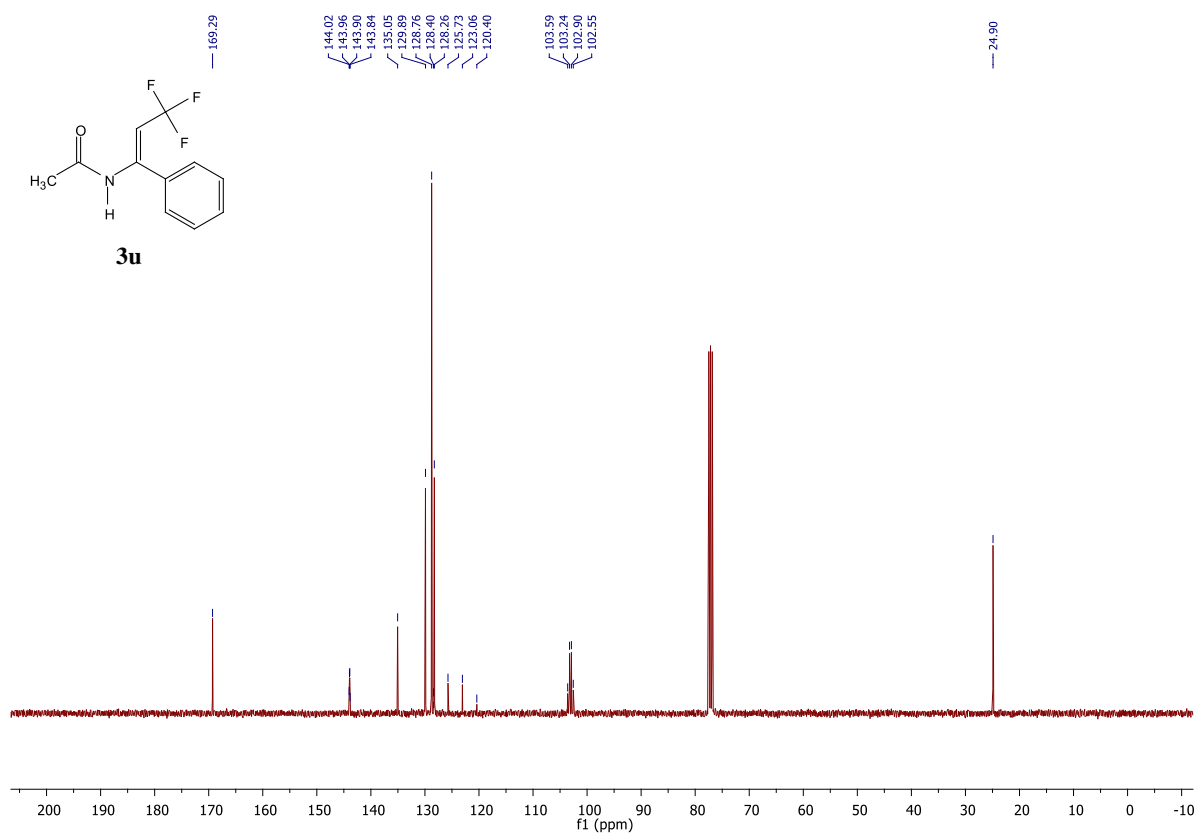


**(E)-N-(3,3,3-Trifluoro-1-phenylprop-1-en-1-yl)acetamide (3u)**

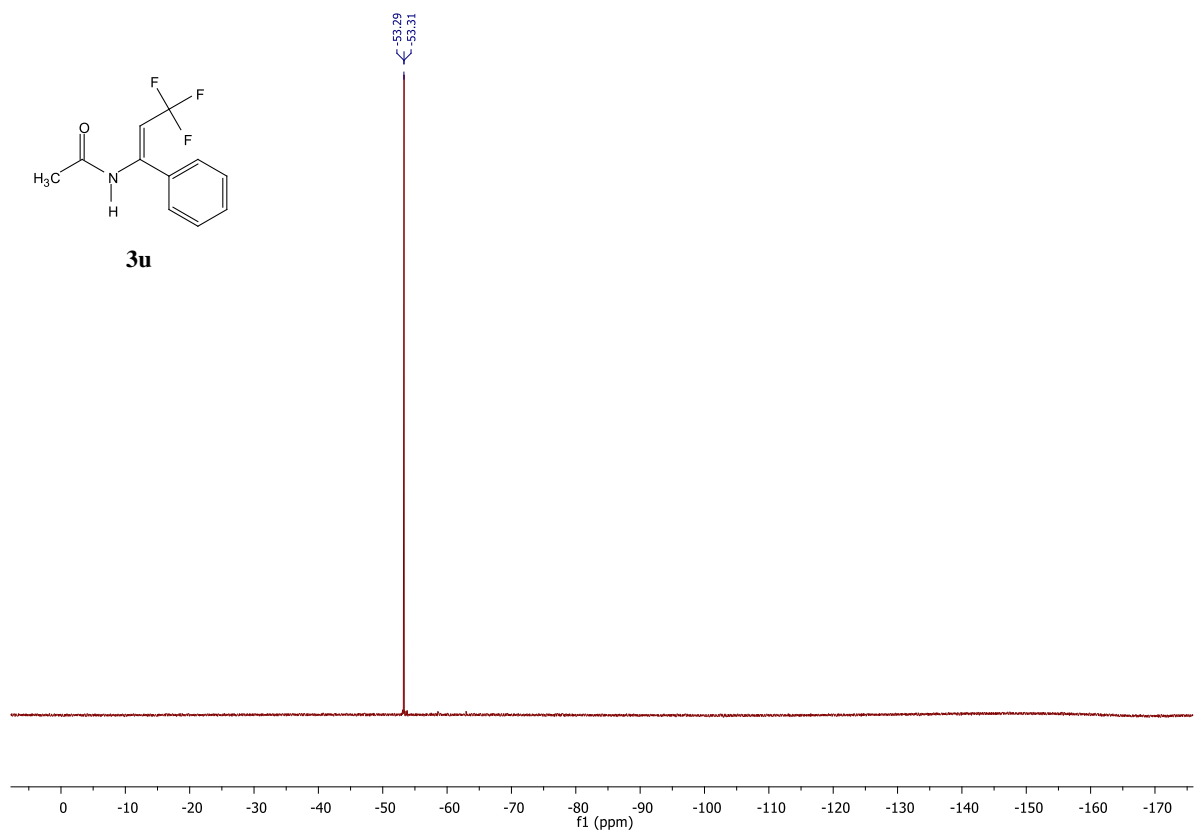
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

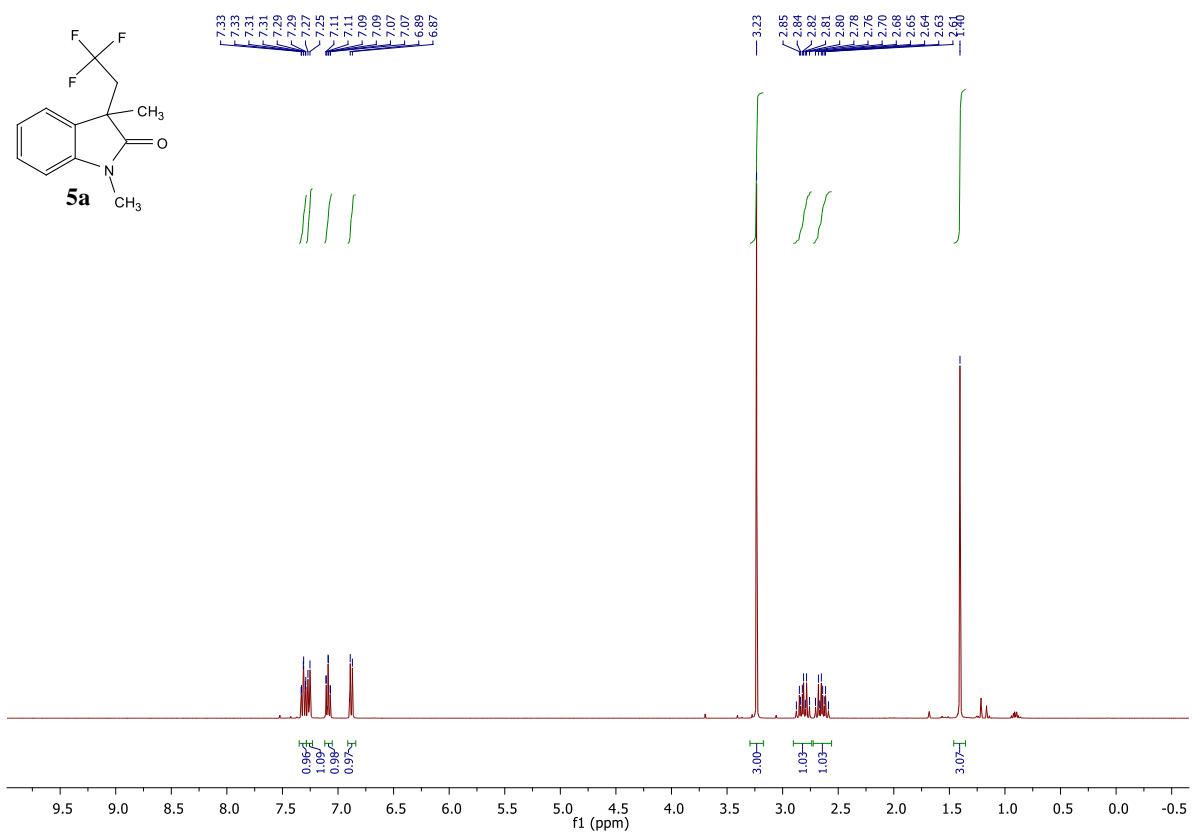


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

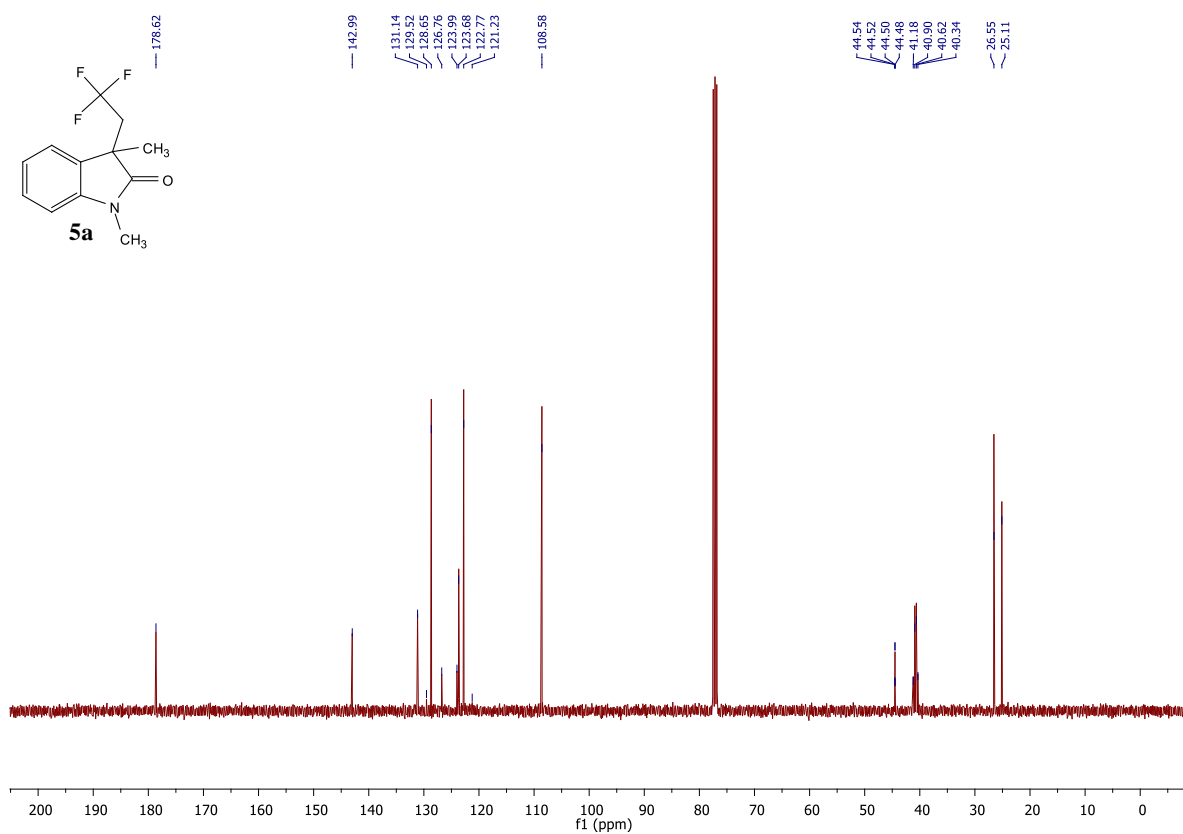


# 1,3-Dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5a)

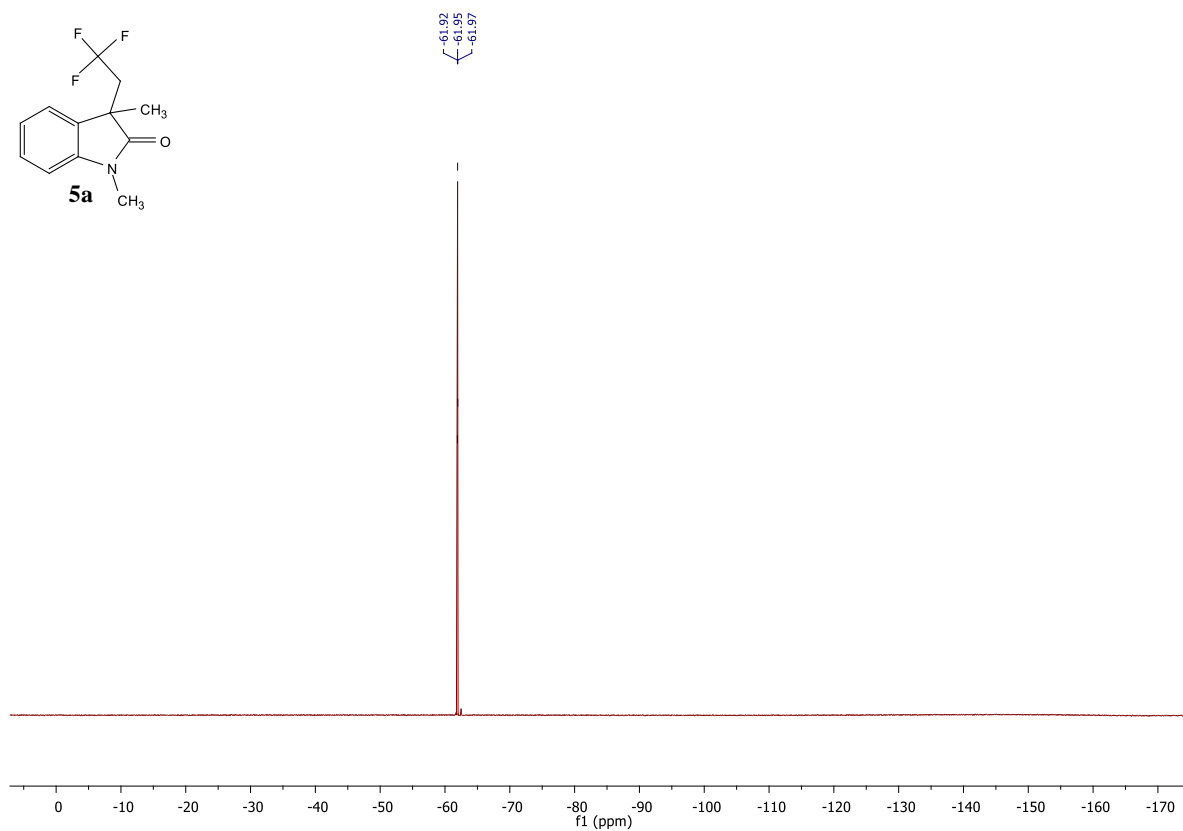
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

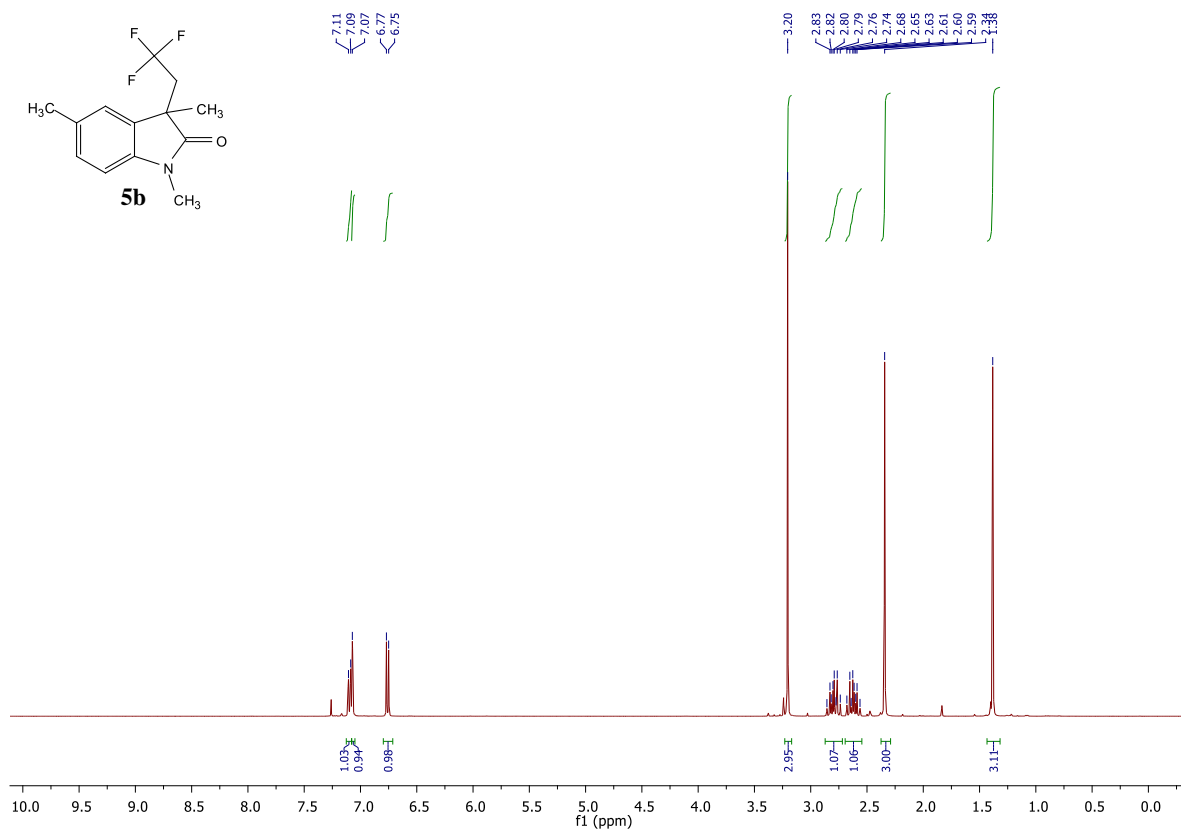


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



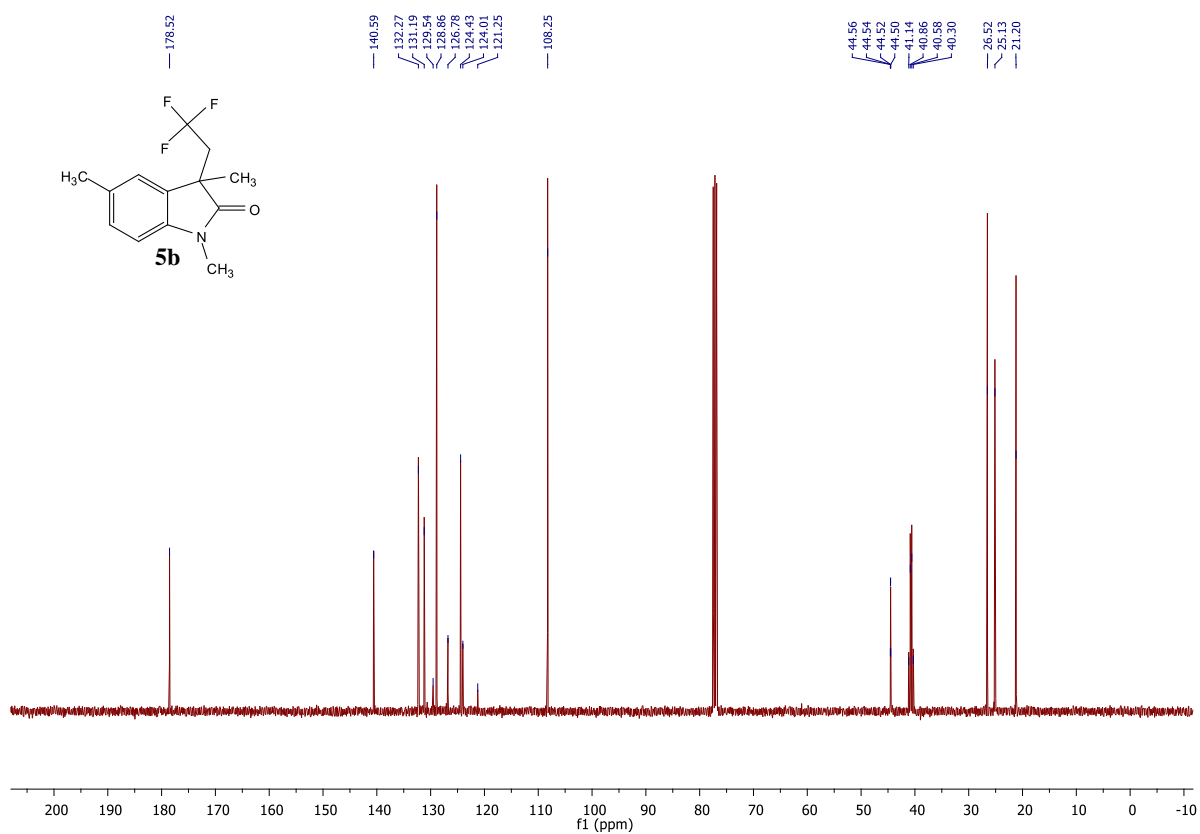
# 1,3,5-Trimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5b)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

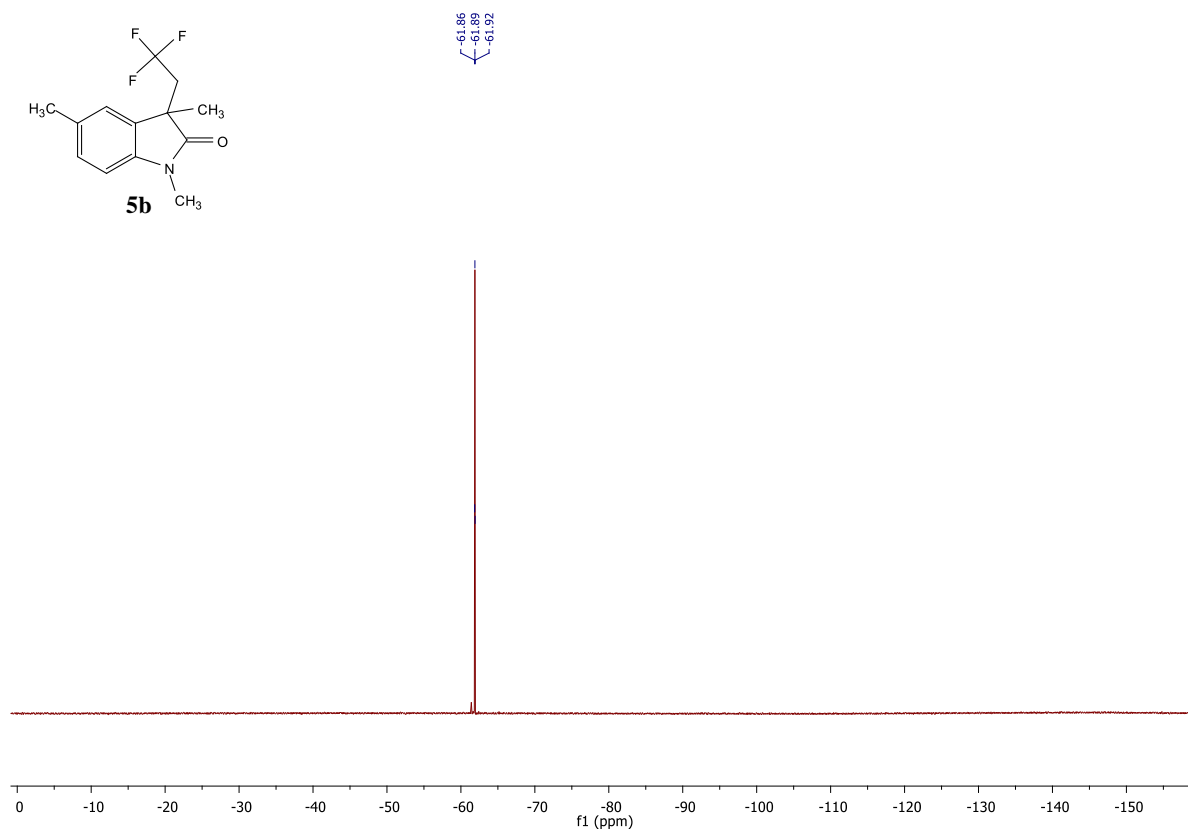




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

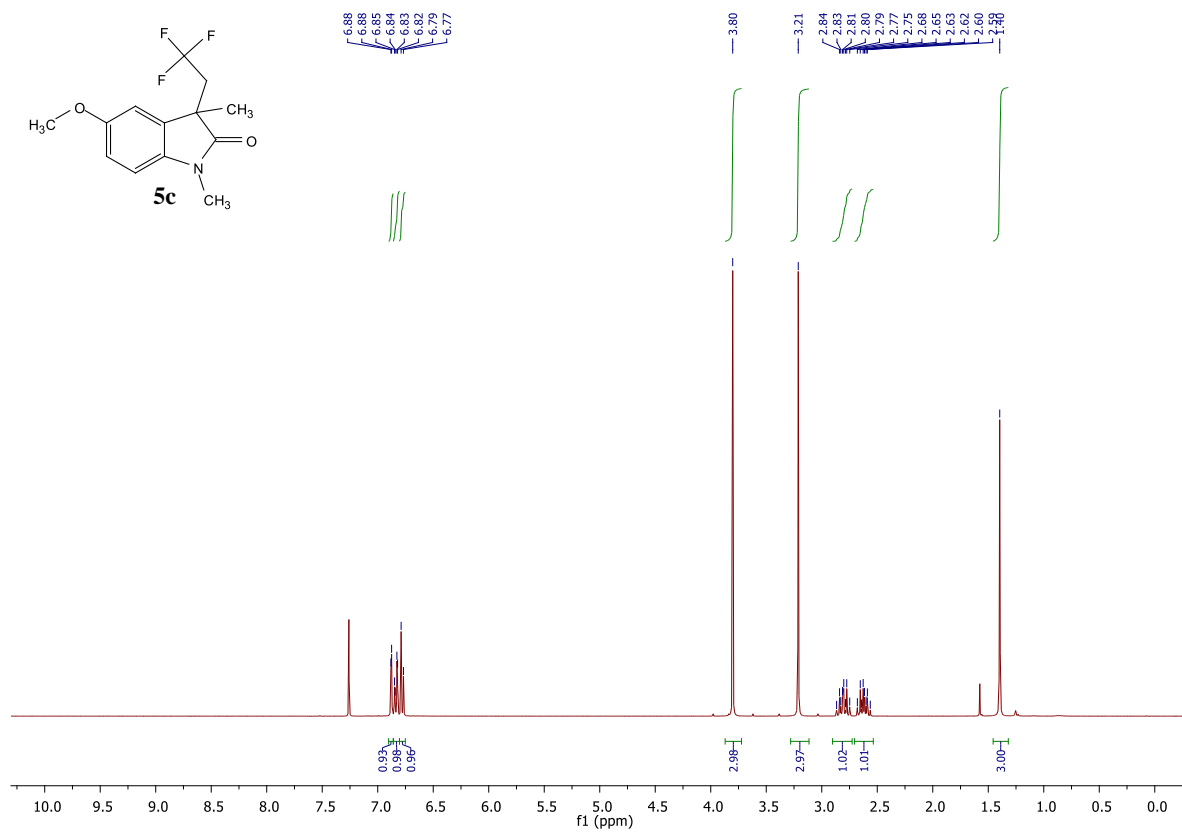


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

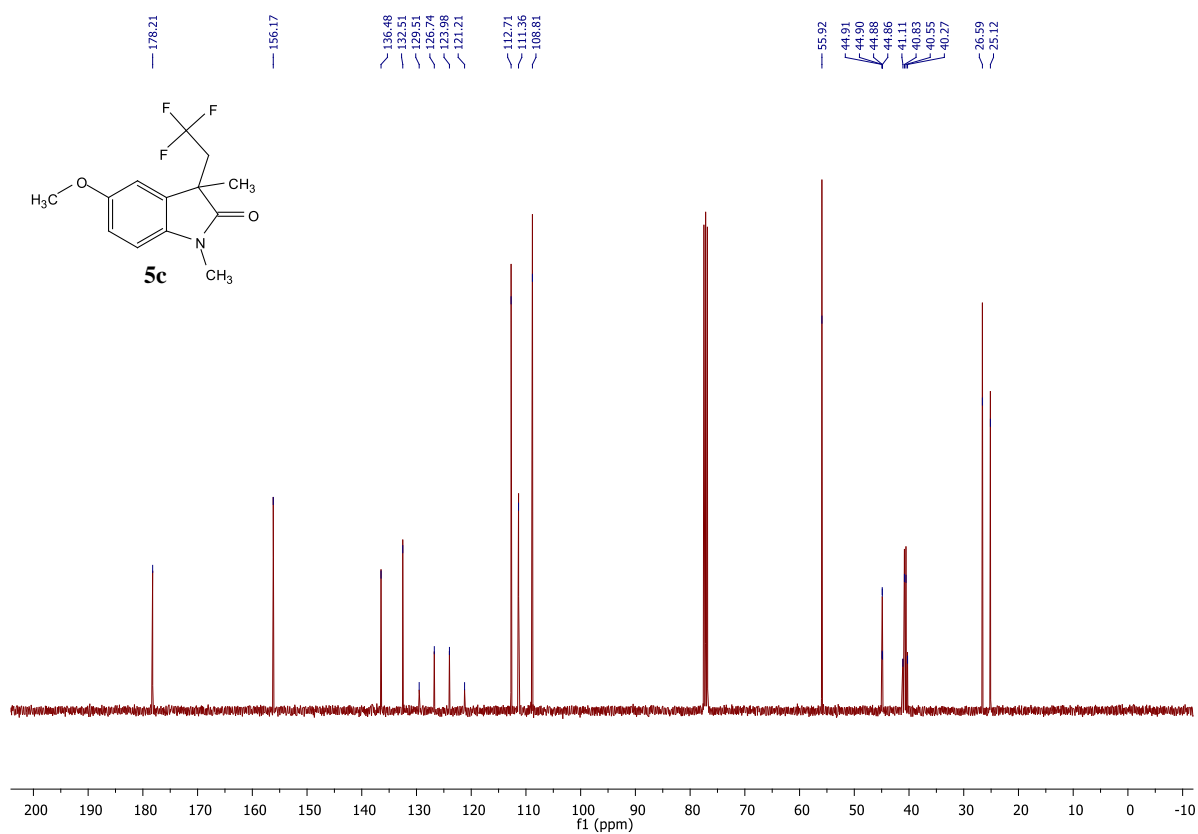


### 5-Methoxy-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5c)

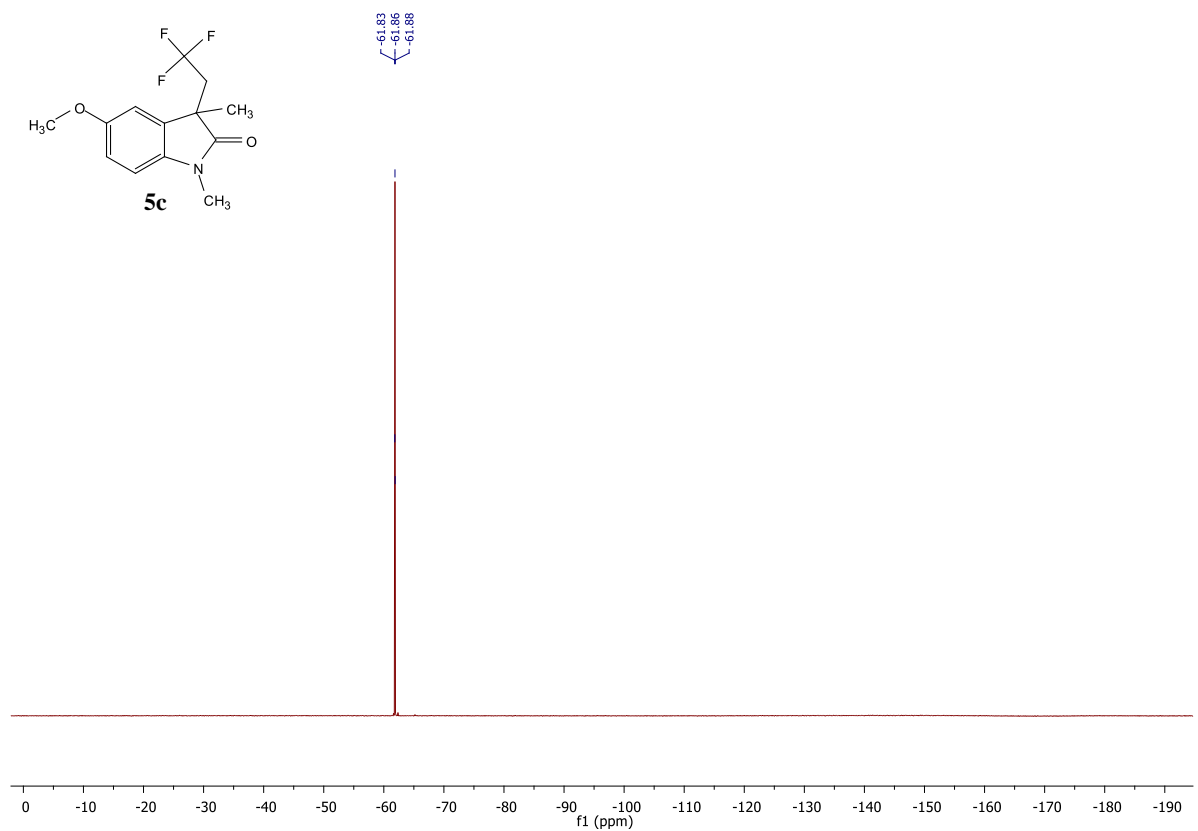
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

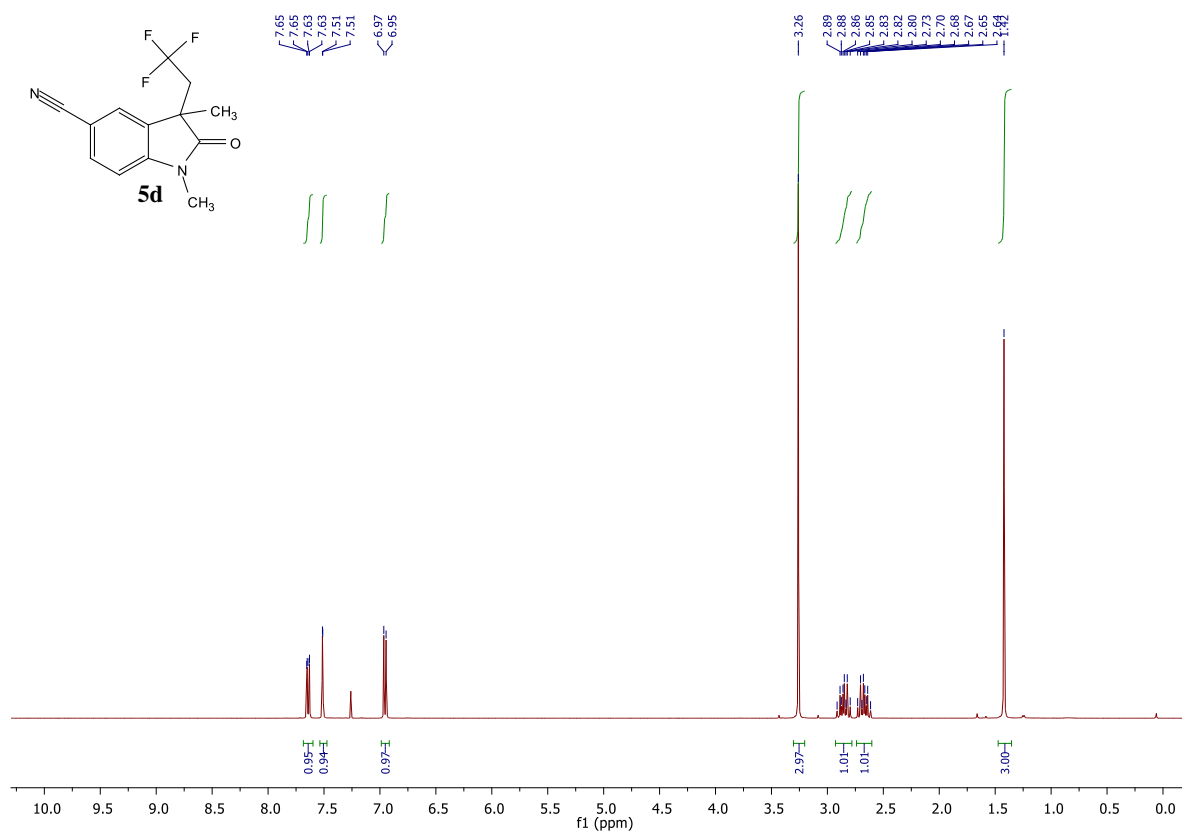


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

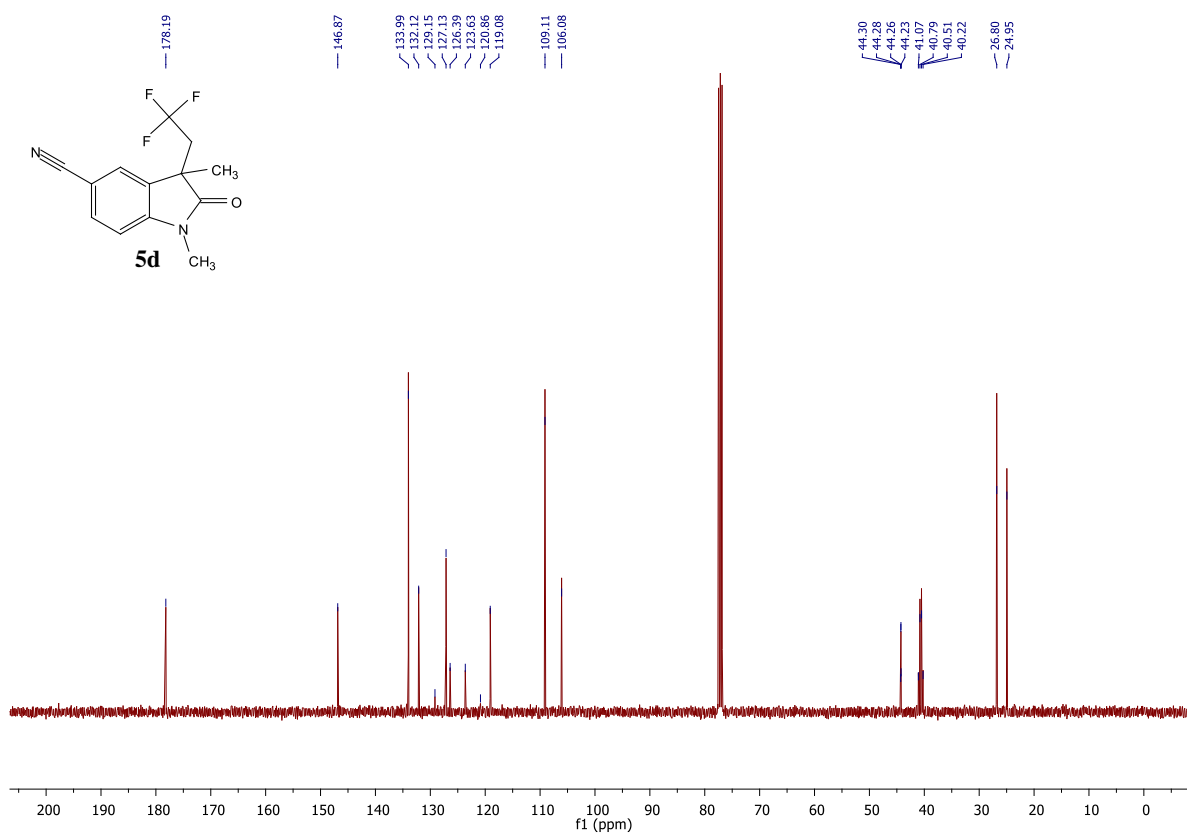


# 1,3-Dimethyl-2-oxo-3-(2,2,2-trifluoroethyl)indoline-5-carbonitrile (5d)

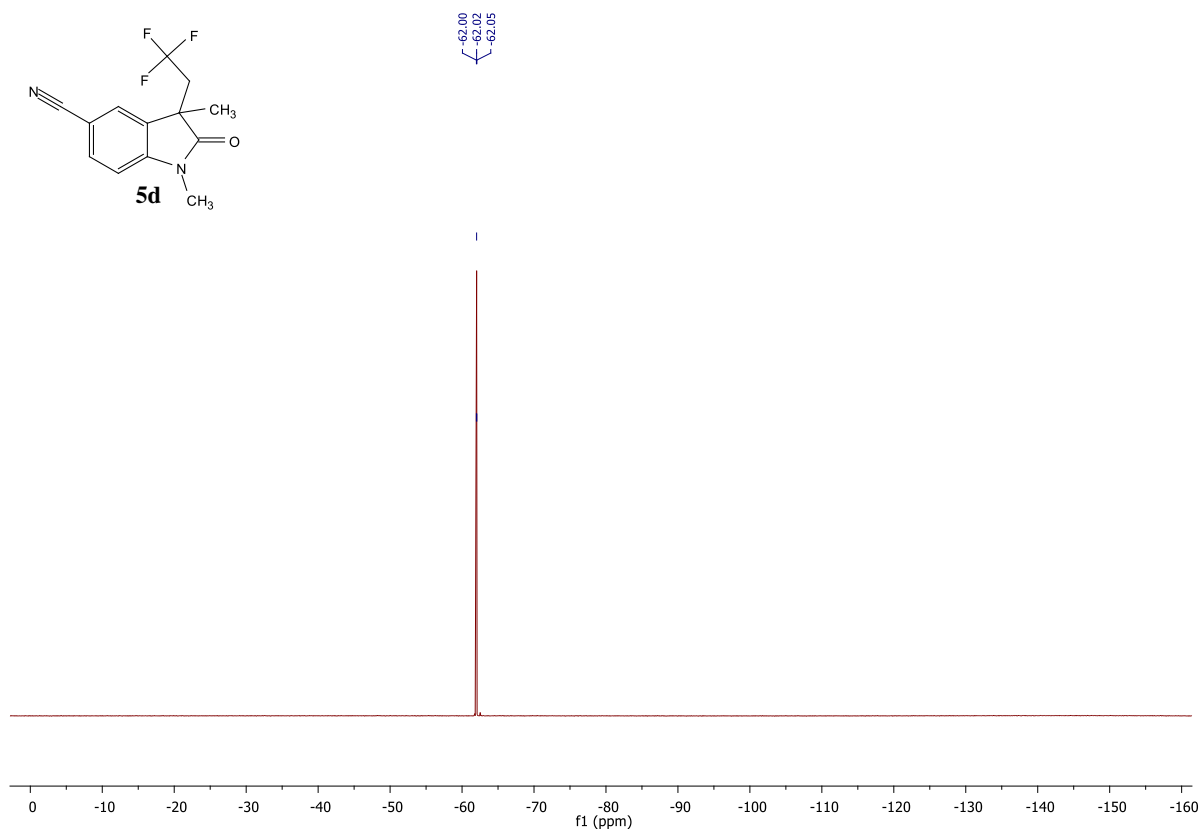
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

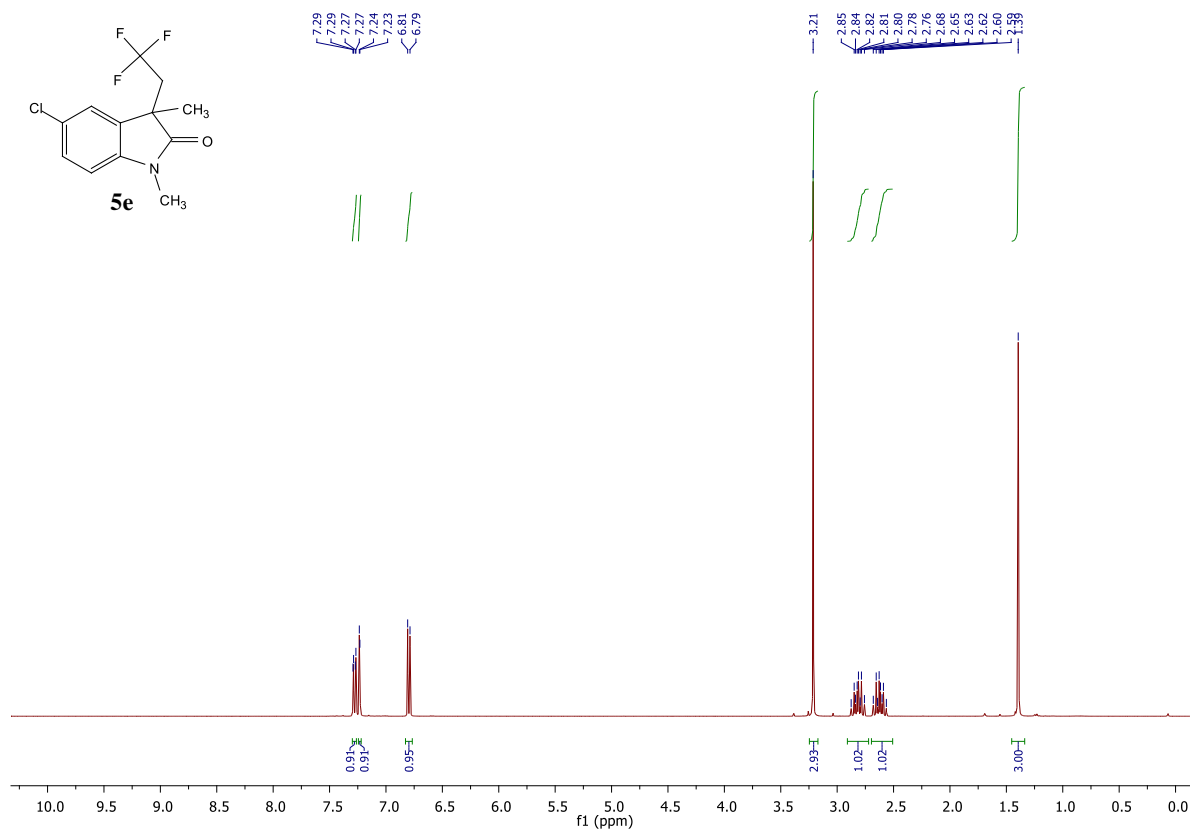


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

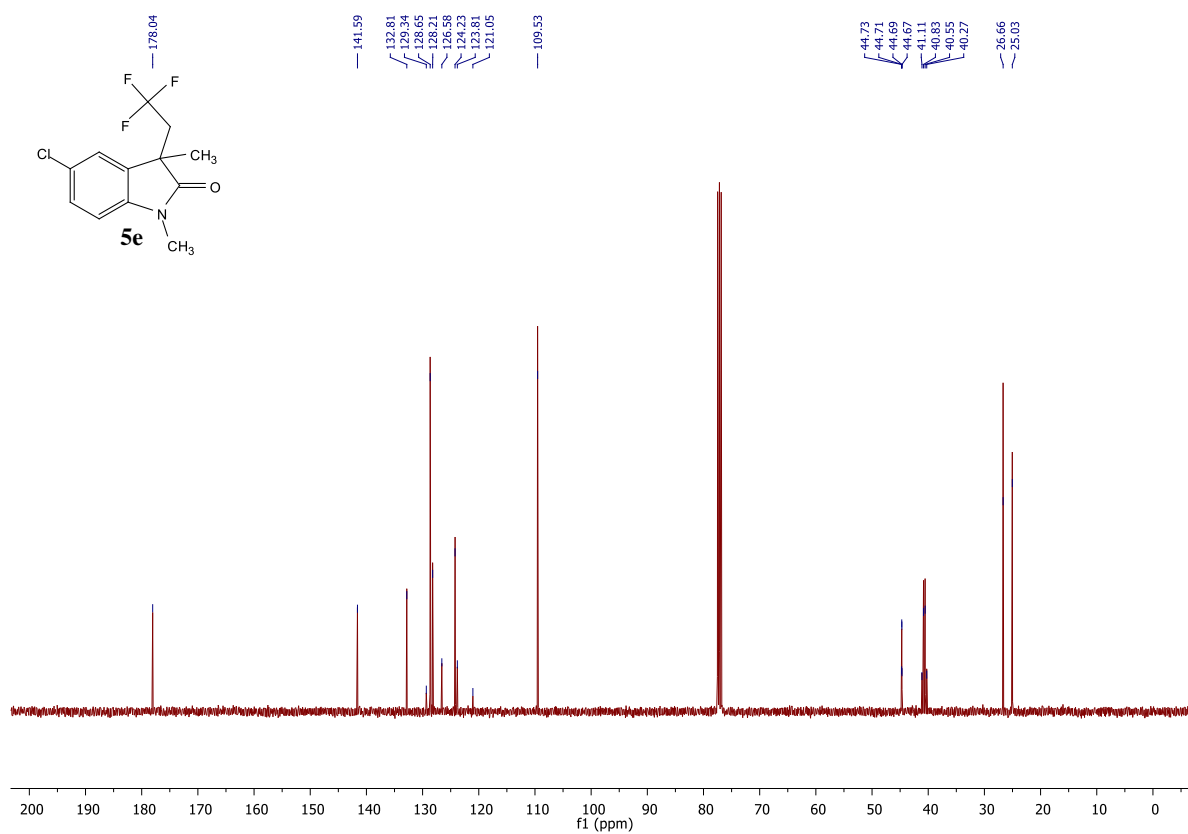


### 5-Chloro-1,3-dimethyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5e)

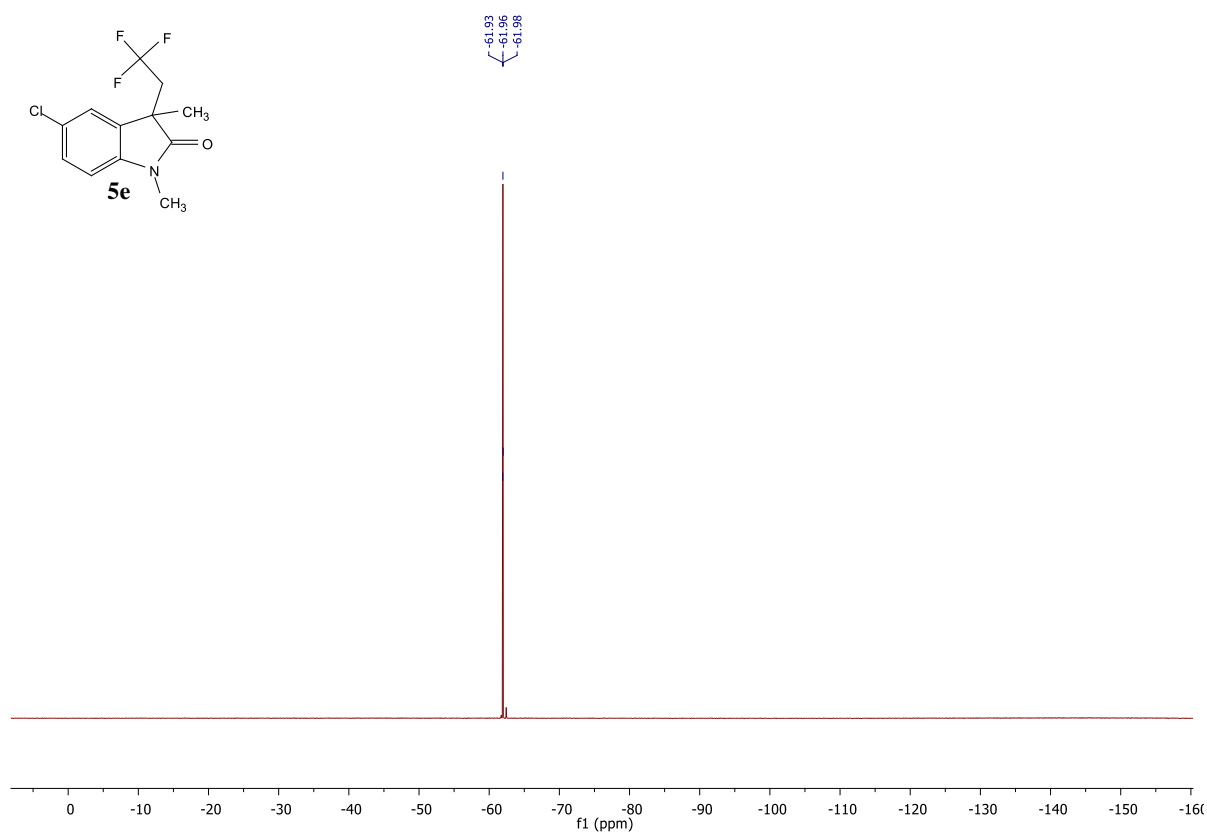
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

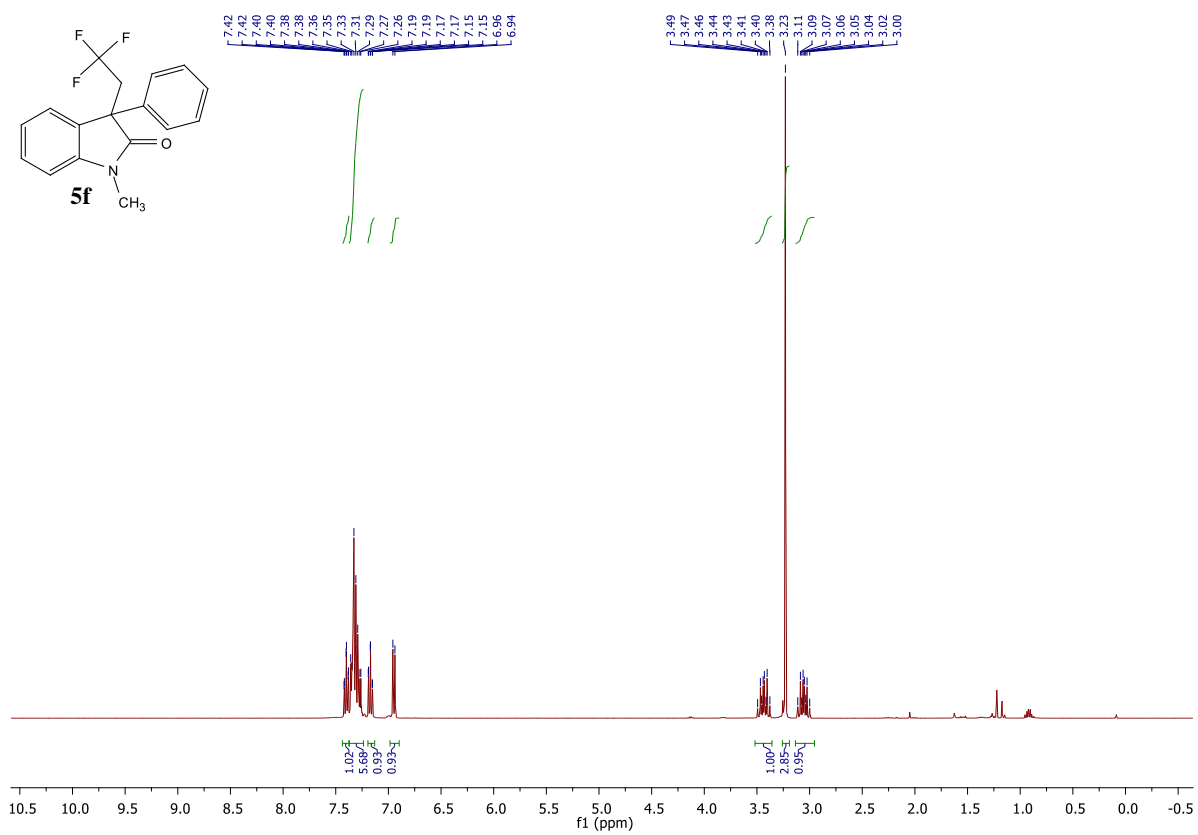


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )



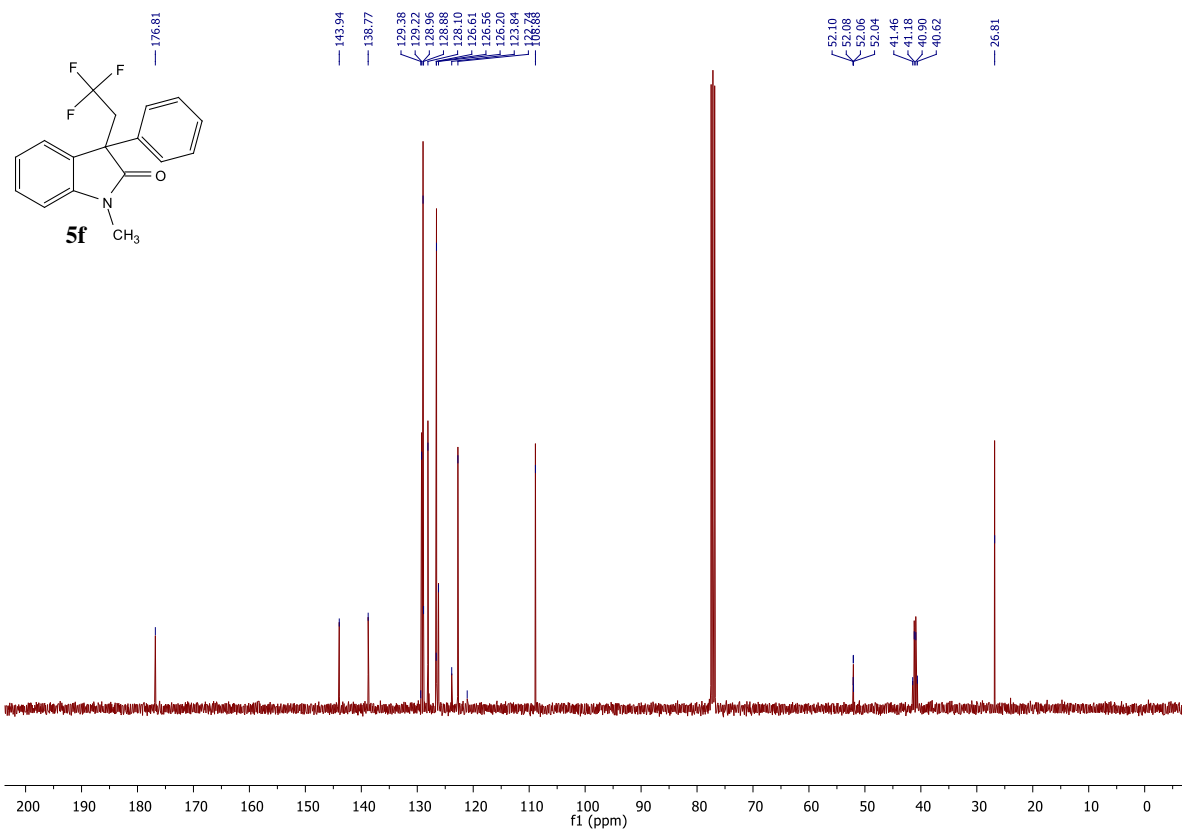
# 1-Methyl-3-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5f)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

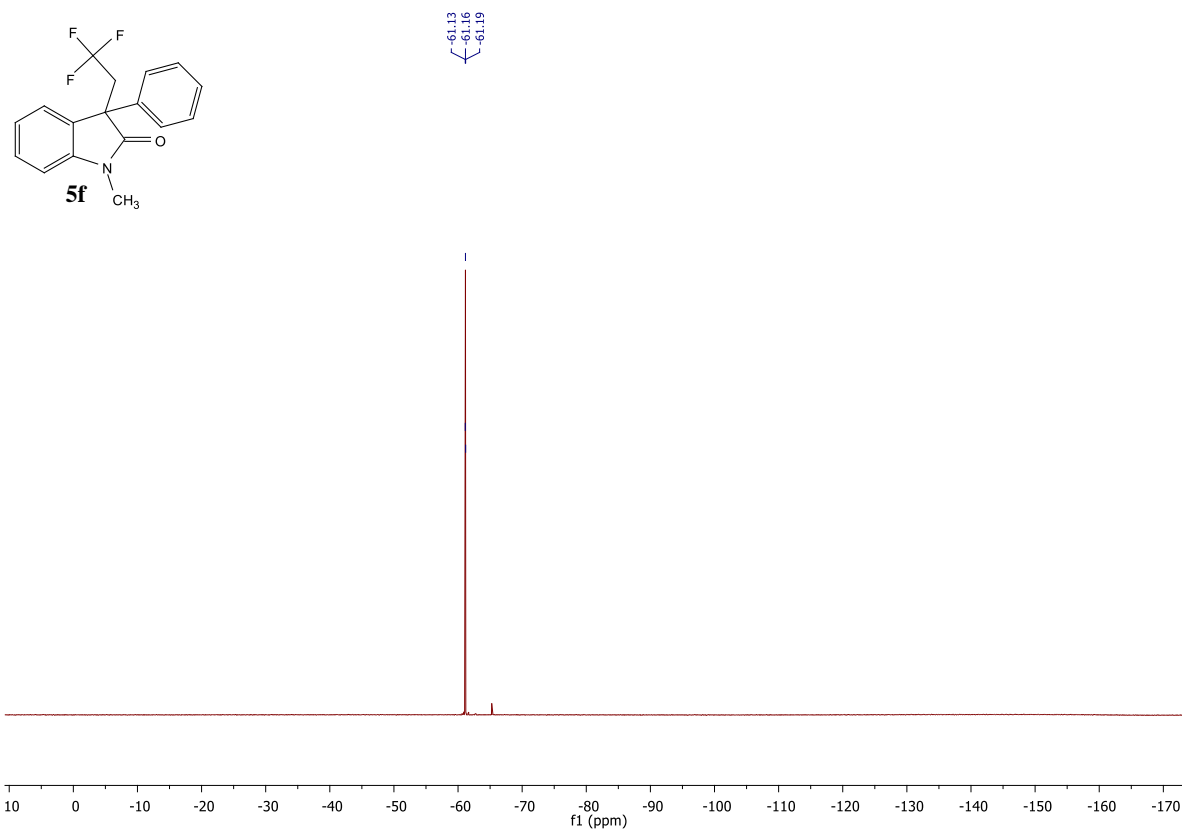




$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

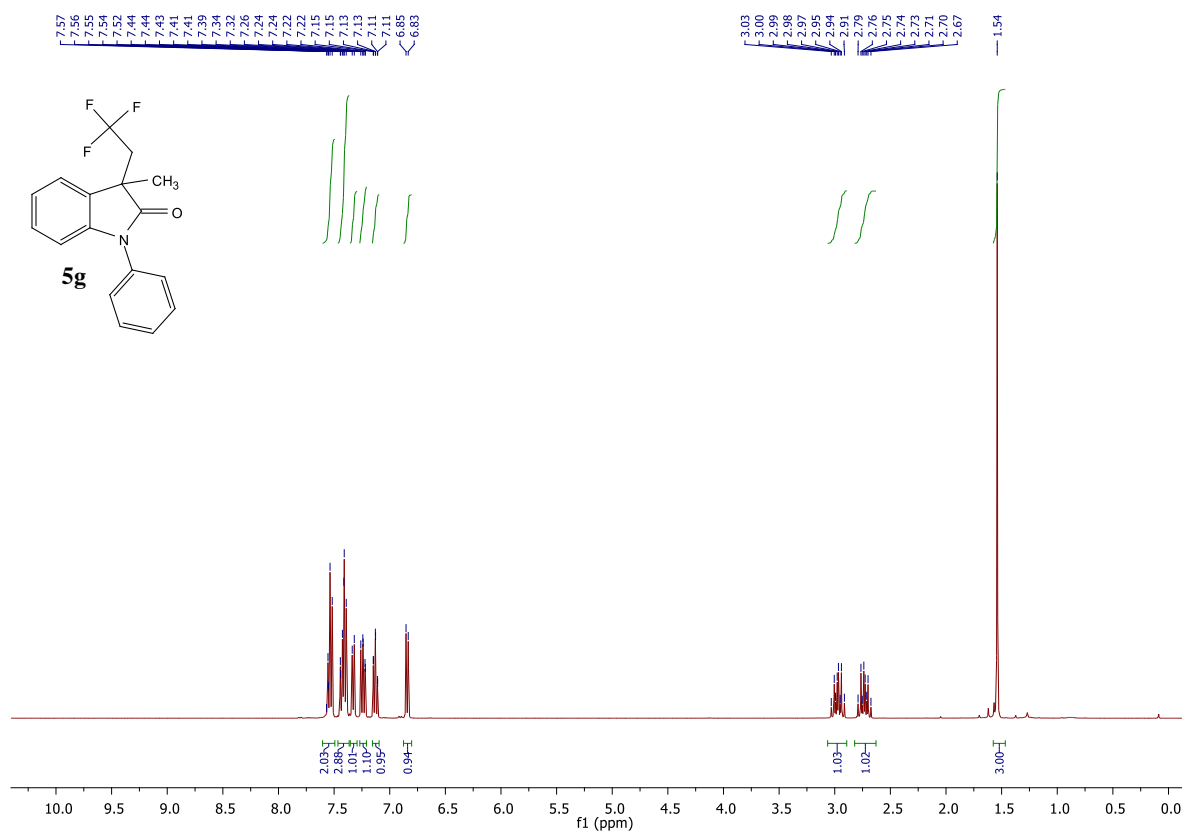


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

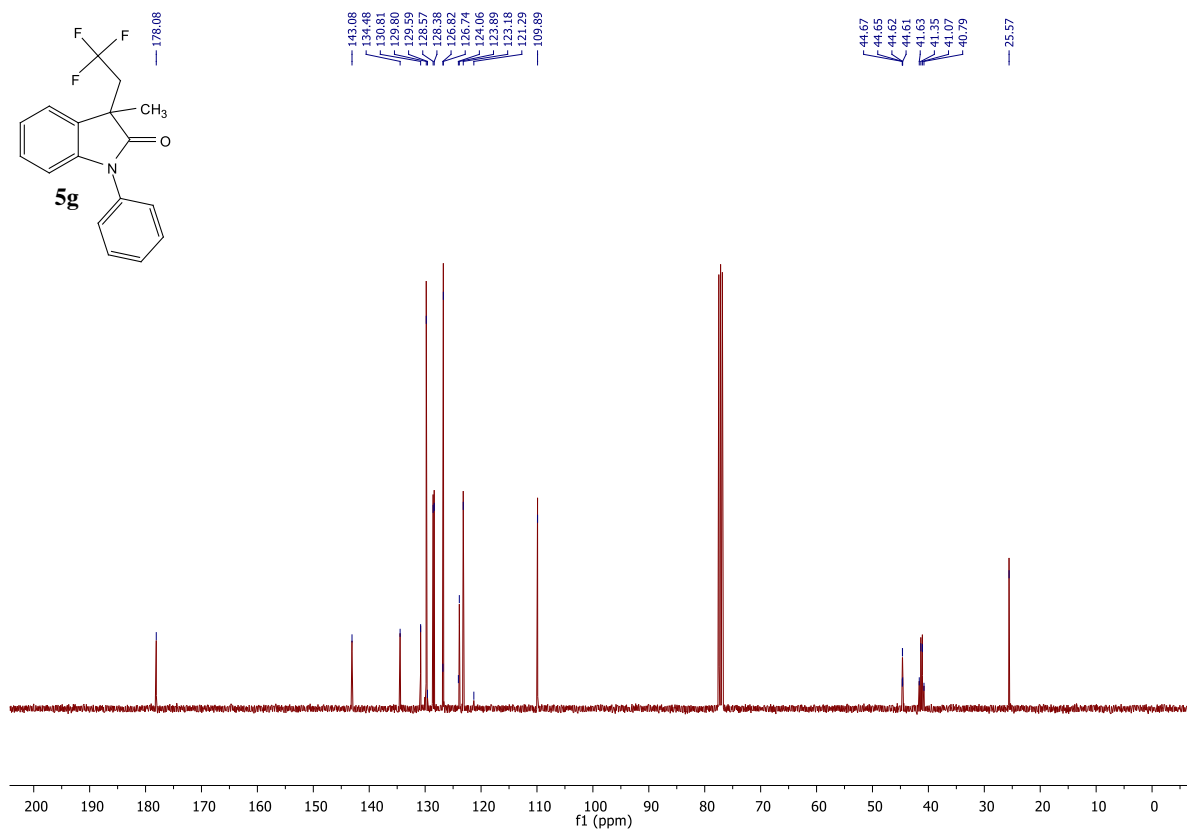
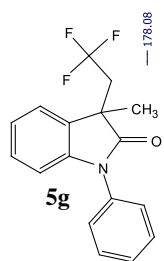


### 3-Methyl-1-phenyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5g)

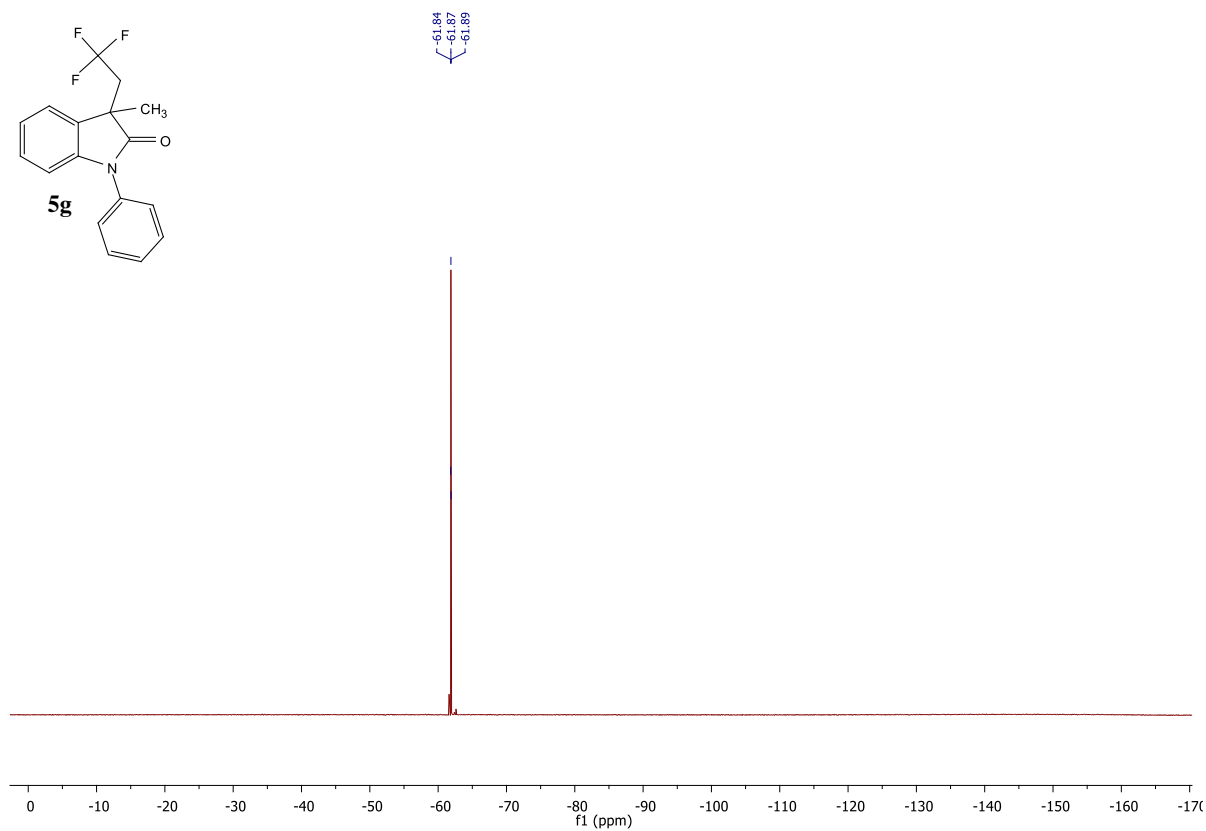
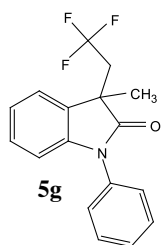
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

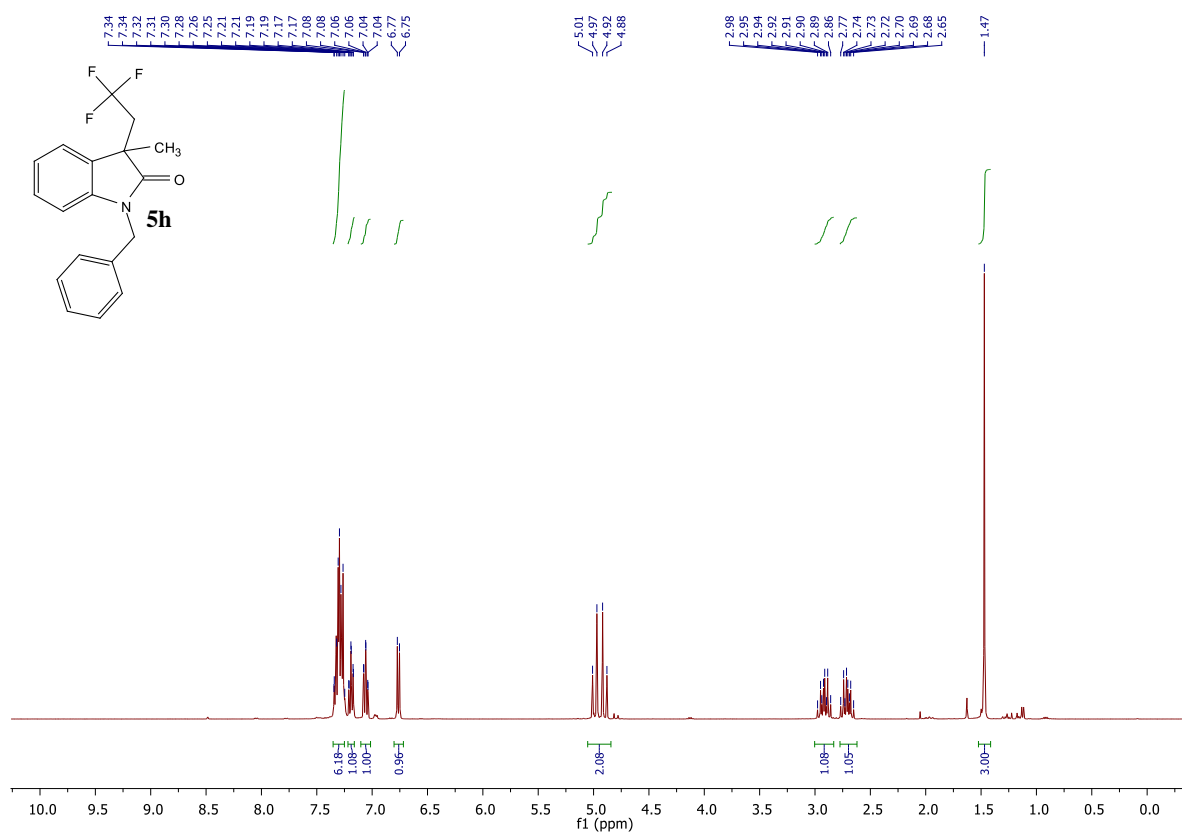


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

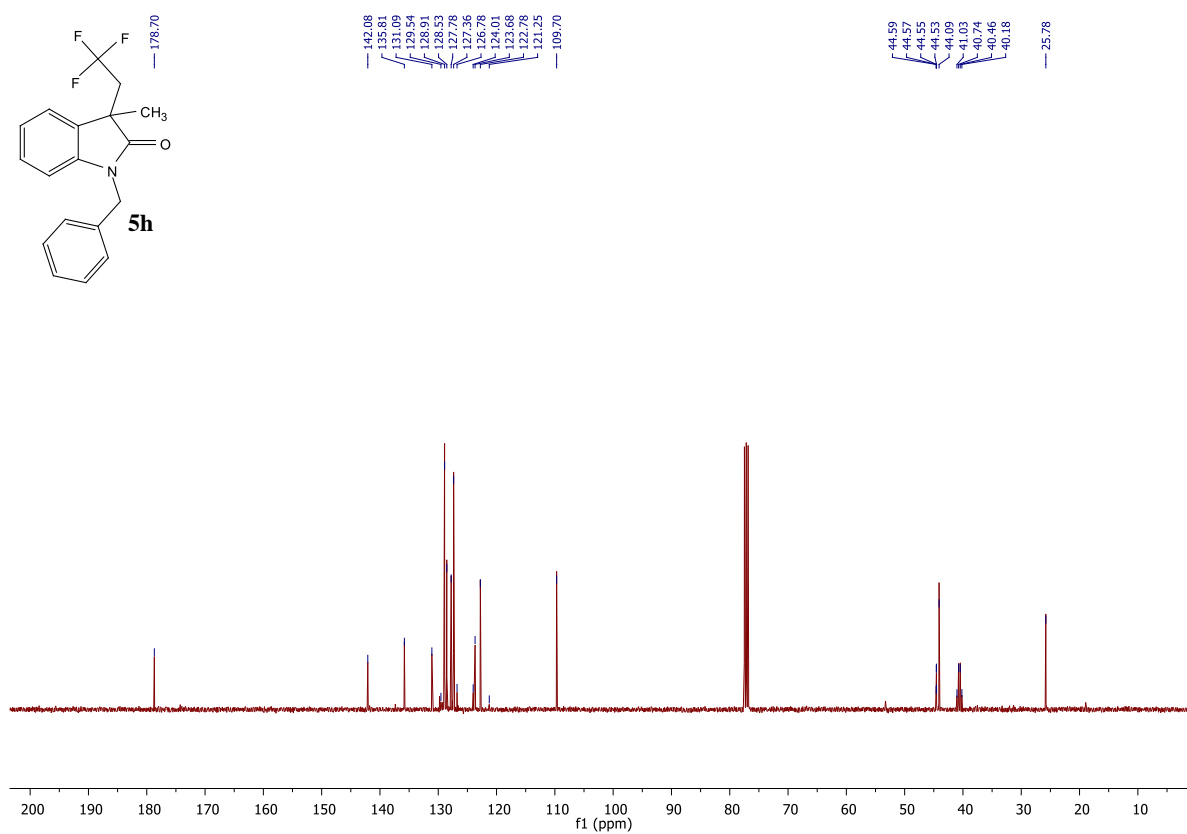
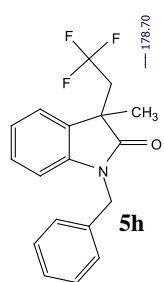


# 1-Benzyl-3-methyl-3-(2,2,2-trifluoroethyl)indolin-2-one (5h)

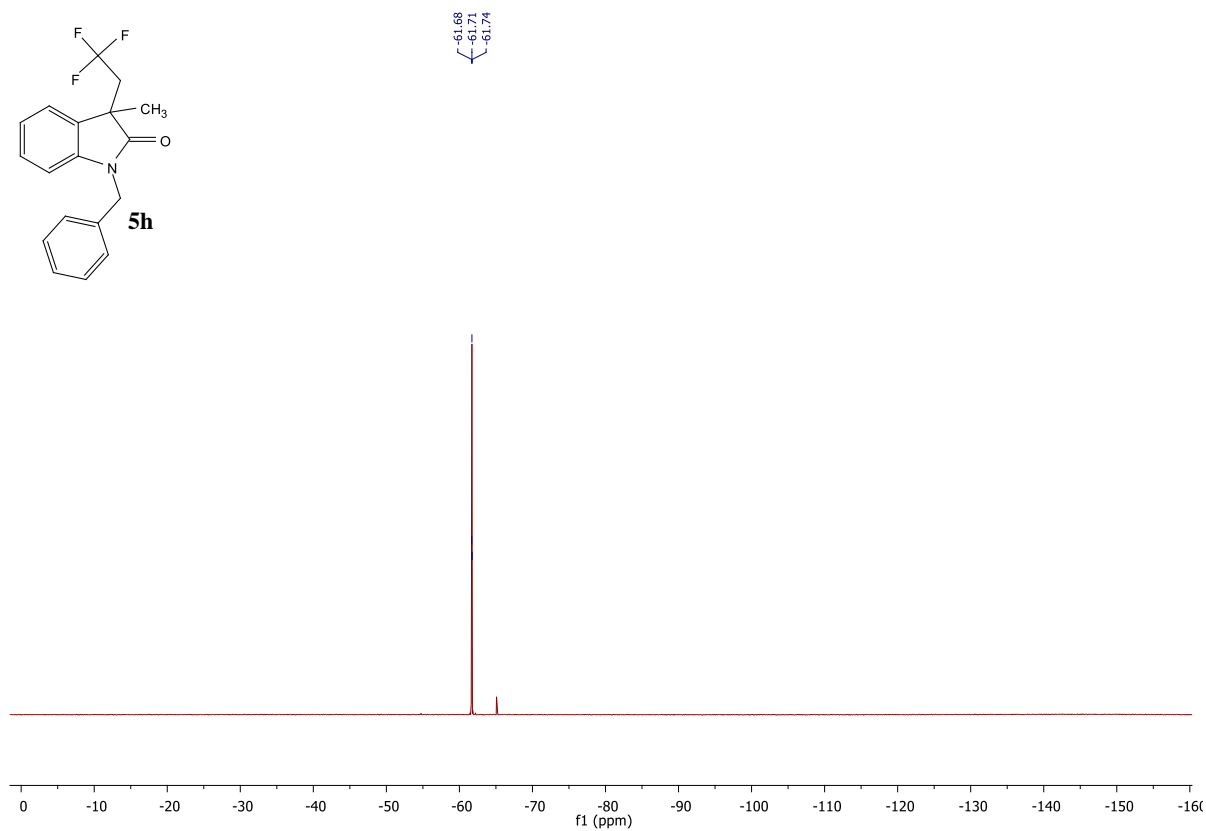
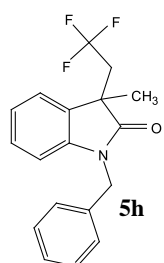
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

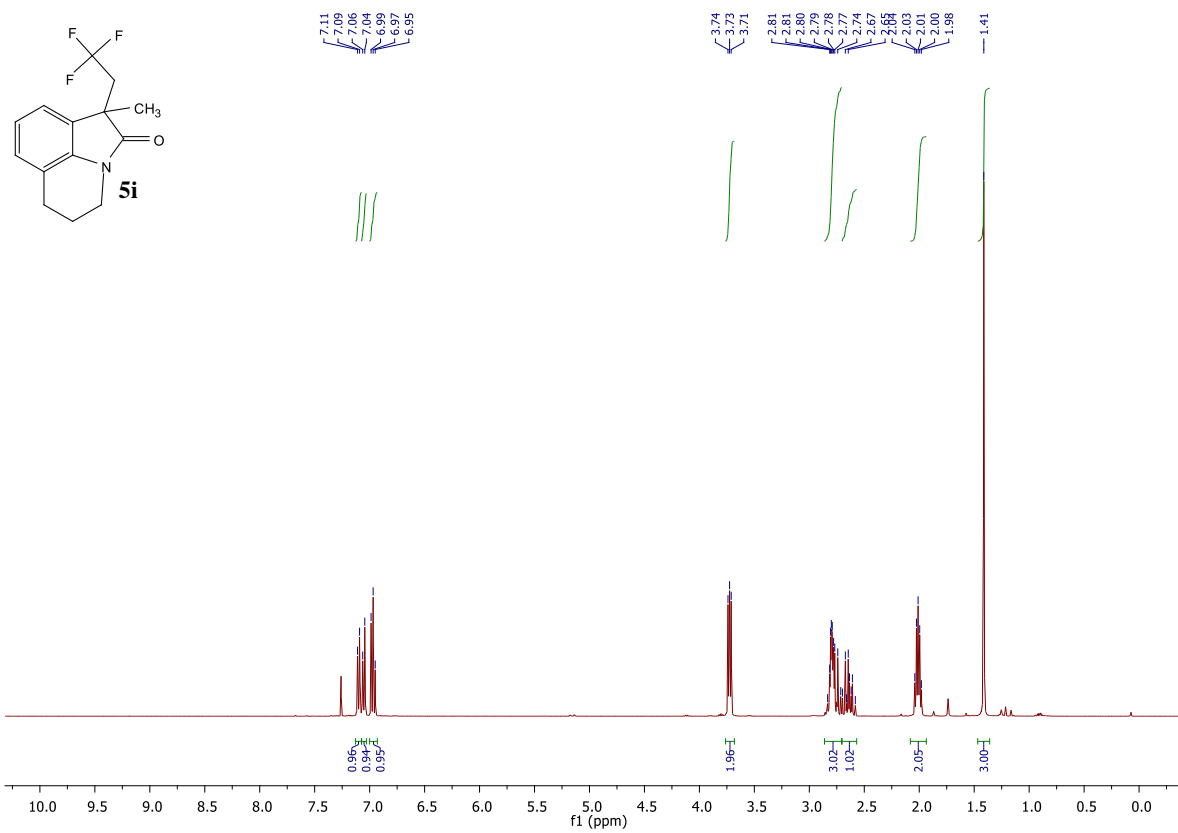


$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

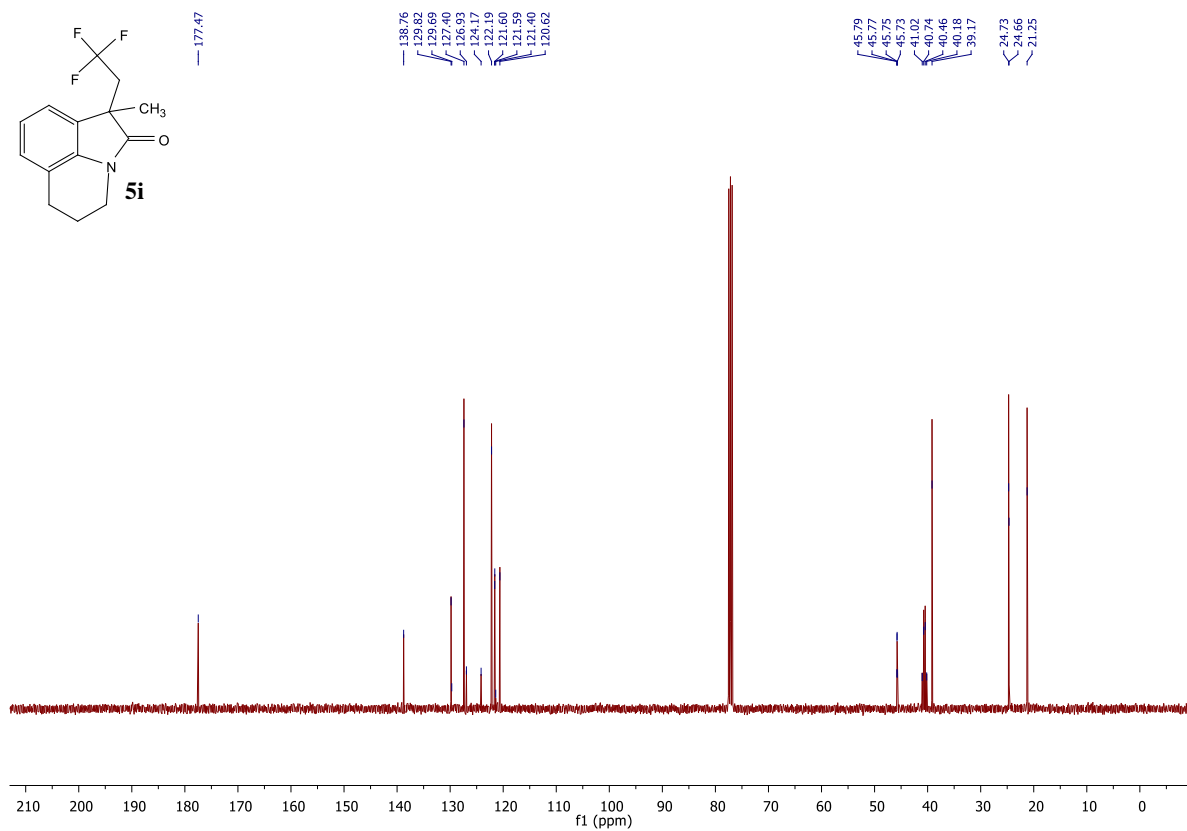
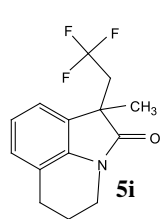


**1-Methyl-1-(2,2,2-trifluoroethyl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (5i)**

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



$^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )

