

**Supporting Information**  
**For**  
**Radical Trifluoromethylation of Vinyl Azides via Organic**  
**Photoredox Catalysis for the Synthesis of  $\alpha$ -**  
**Trifluoromethylated Ketones**

Hai-Tao Qin,<sup>†, #</sup> Shu-Wei Wu,<sup>†, #</sup> Jia-Li Liu<sup>†</sup> and Feng Liu<sup>\*, †, §</sup>

<sup>†</sup>Jiangsu Key Laboratory of Translational Research and Therapy for Neuro-Psycho-Diseases and Department of Medicinal Chemistry, College of Pharmaceutical Sciences, Soochow University, 199 Ren-Ai Road, Suzhou, Jiangsu 215123, People's Republic of China

<sup>§</sup>Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, People's Republic of China

<sup>#</sup>These authors contributed equally to this work.

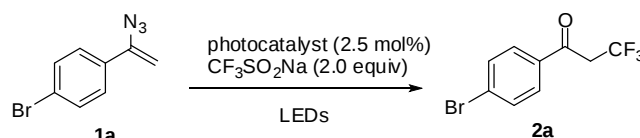
**Table of Contents**

|                                  |         |
|----------------------------------|---------|
| General remarks                  | S2      |
| Screening of solvents            | S2      |
| Synthesis of vinyl azides        | S2      |
| Typical experimental procedure   | S3      |
| References for known products    | S4      |
| Characterization of the products | S4-S10  |
| NMR Spectra for the products     | S11-S45 |

## 1. General remarks

$^1\text{H}$  NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for  $^{13}\text{C}$  NMR, 376 or 564 MHz for  $^{19}\text{F}$  NMR) agilent NMR spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm,  $\delta$  scale) downfield from TMS at 0.00 ppm and referenced to the  $\text{CDCl}_3$  at 7.26 ppm (for  $^1\text{H}$  NMR) or 77.16 ppm (for  $^{13}\text{C}$  NMR). HRMS was recorded on a GCT Premier<sup>TM</sup> (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000 FT-IR,  $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ . Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates were readily prepared from phenylethylenes or alkynes (*Org. Lett.* **2016**, *18*, 3642; *Angew. Chem., Int. Ed.* **2014**, *53*, 4390; *Org. Lett.* **2014**, *16*, 3668).

## 2. Screening of solvents

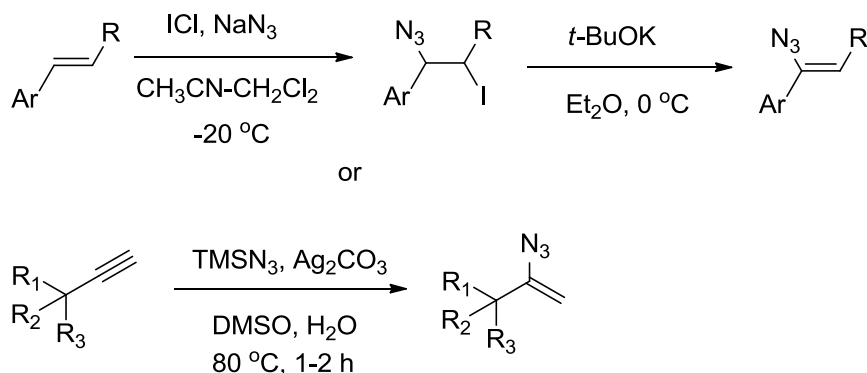


| entry <sup>a</sup> | LEDs         | catalyst                   | solvent                | yield (%) <sup>b</sup> |
|--------------------|--------------|----------------------------|------------------------|------------------------|
| 1                  | White        | Mes-Acr <sup>+</sup>       | $\text{CH}_3\text{CN}$ | 61                     |
| 2                  | White        | Mes-Acr <sup>+</sup>       | DMF                    | 44                     |
| 3                  | White        | Mes-Acr <sup>+</sup>       | DMSO                   | 21                     |
| 4                  | White        | Mes-Acr <sup>+</sup>       | DCE                    | 20                     |
| 5                  | White        | Mes-Acr <sup>+</sup>       | ethyl acetate          | 48                     |
| 6                  | White        | Mes-Acr <sup>+</sup>       | acetone                | 63                     |
| 7                  | <b>White</b> | <b>Mes-Acr<sup>+</sup></b> | <b>1,4-dioxane</b>     | <b>65</b>              |
| 8                  | White        | Mes-Acr <sup>+</sup>       | $\text{CH}_3\text{OH}$ | 20                     |
| 9                  | White        | Mes-Acr <sup>+</sup>       | HFIP                   | <5                     |
| 10                 | White        | Mes-Acr <sup>+</sup>       | THF                    | 65                     |
| 11                 | White        | Mes-Acr <sup>+</sup>       | $\text{PhCH}_3$        | 25                     |
| 12                 | White        | Mes-Acr <sup>+</sup>       | $\text{PhCl}$          | 37                     |

<sup>a</sup>1a (0.20 mmol), catalyst (2.5 mol%),  $\text{CF}_3\text{SO}_2\text{Na}$  (0.40 mmol), solvent (2 mL), Argon balloon, 5 W LEDs, 36-60 h. <sup>b</sup>Isolated yield.

## 3. Synthesis of vinyl azides

Synthetic Scheme:



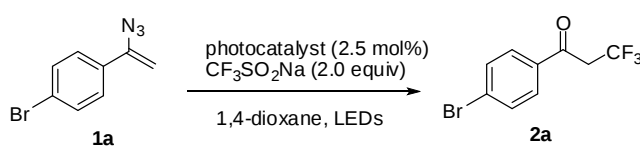
#### Typical synthetic procedures:

1: To a suspension of NaN<sub>3</sub> (3.9 g, 60 mmol) in acetonitrile (18 mL) was added dropwise a solution of iodine monochloride (5.8 g, 36 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at –20 °C, and the mixture was stirred at the same temperature. After 30 min, a solution of 4-vinylbiphenyl (4.3 g, 24 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, and the organic materials were extracted two times with Et<sub>2</sub>O. The combined extracts were washed with brine and dried over MgSO<sub>4</sub>. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.

To a solution of the obtained compounds above in Et<sub>2</sub>O (60 mL) was added *t*-BuOK (3.2 g, 28.8 mmol) at 0 °C, and the mixture was stirred for 1.5 h at the same temperature. The reaction mixture was filtered through celite and the solvent was removed *in vacuo*. The resulting crude materials were purified by flash column chromatography (silica gel; hexane) to give 4-(1-azidovinyl)biphenyl (**1a**) (4.5 g, 84% yield) as a white solid.

2: To a solution of (prop-2-yn-1-yloxy) benzene (660 mg, 5 mmol), TMSN<sub>3</sub> (1.15 g, 10 mmol) and H<sub>2</sub>O (0.18 mL, 10 mmol) in DMSO (8 mL) at 80 °C, Ag<sub>2</sub>CO<sub>3</sub> (138 mg, 0.5 mmol) was added. The mixture was then stirred for 1-2 h until substrate (prop-2-yn-1-yloxy) benzene consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 × 30 mL). The organic layer was washed with brine (3 × 40 mL), dried over MgSO<sub>4</sub> and concentrated. The resulting crude materials were purified by flash column chromatography (silica gel; hexane) to give (2-azidoallyloxy)benzene (**1s**) (717 mg, 82% yield) as a yellow oil.

#### 4. Typical experimental procedure

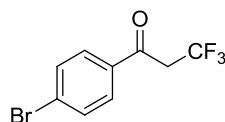


To a suspension of CF<sub>3</sub>SO<sub>2</sub>Na (62.4 mg, 0.4 mmol) and *N*-Methyl-9-mesityl acridinium perchlorate (2 mg, 0.005 mmol) in 1,4-dioxane (2 mL) was added vinyl azide **1a** (44.2 mg, 0.2 mmol) at rt. The resulting mixture was stirred upon 5W blue LEDs irradiation under argon balloon. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **2a** as a white solid (38.3 mg, 72% yield).

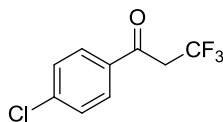
## 5. References for known products

| Entry | Reference                                                                        | Compound                                                              |
|-------|----------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| 1     | Maji, A.; Hazra, A. <i>Org. Lett.</i> , <b>2014</b> , 16, 4524.                  | <b>2a</b> , <b>2c</b> , <b>2d</b> , <b>2e</b> , <b>2k</b> , <b>2q</b> |
| 2     | Deb, A.; Manna, S. <i>Angew. Chem. Int. Ed.</i> , <b>2013</b> , 37, 9747.        | <b>2b</b> , <b>2l</b> , <b>2n</b> , <b>2p</b>                         |
| 3     | Zhang, C.-P.; Wang, Z.-L. <i>Chem. Commun.</i> , <b>2011</b> , 47, 6632.         | <b>2f</b>                                                             |
| 4     | Novak, P.; Lishchynskyi, A. <i>J. Am. Chem. Soc.</i> , <b>2012</b> , 134, 16167. | <b>2m</b> , <b>2j</b>                                                 |
| 5     | Li, L.; Chen, Q.-Y. <i>J. Org. Chem.</i> , <b>2014</b> , 79, 5145.               | <b>2o</b>                                                             |
| 6     | He, Z.-B.; Zhang, R. <i>Chem. Sci.</i> , <b>2013</b> , 4, 3478.                  | <b>2r</b>                                                             |
| 7     | Lerch, M.-M.; Morandi, B. <i>Angew. Chem. Int. Ed.</i> , <b>2014</b> , 33, 8654. | <b>2s</b>                                                             |
| 8     | Miura, K.; Taniguchi, M. <i>Tetrahedron</i> , <b>1990</b> , 31, 6391.            | <b>2v</b>                                                             |
| 9     | Sun, X.-Y.; Yu, S.-Y. <i>Chem. Commun.</i> , <b>2016</b> , 52, 10898.            | <b>7</b>                                                              |

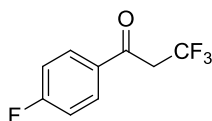
## 6. Characterization of the products



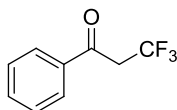
**1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-one (2a):** White solid; m.p. 65-67 °C; 72% (38.3 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 3.76 (q, *J* = 9.9 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 188.9, 134.6, 132.5, 129.9, 129.8, 123.9 (q, *J* = 277.1 Hz), 42.3 (q, *J* = 28.5 Hz); <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -62.04 (t, *J* = 9.9 Hz, 3F).



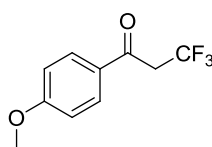
**1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-one (2b):** Light yellow oil; 66% (29.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J$  = 8.4 Hz, 2H), 7.49 (d,  $J$  = 8.4 Hz, 2H), 3.77 (q,  $J$  = 9.9 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  188.7, 141.05, 134.3, 129.9, 129.5, 124.0 (q,  $J$  = 277.0 Hz), 42.3 (q,  $J$  = 28.5 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.03 (t,  $J$  = 9.9 Hz, 3F).



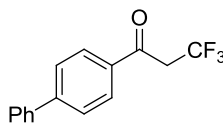
**3,3,3-Trifluoro-1-(4-fluorophenyl)propan-1-one (2c):** Colorless oil; 67% (27.6 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 – 7.91 (m, 2H), 7.23 – 7.13 (m, 2H), 3.77 (q,  $J$  = 9.9 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  188.3, 166.5 (d,  $J$  = 257.1 Hz), 132.4, 131.3 (d,  $J$  = 9.6 Hz), 124.0 (q,  $J$  = 277.0 Hz), 116.4 (d,  $J$  = 22.1 Hz), 42.3 (q,  $J$  = 28.4 Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.00 (t,  $J$  = 9.9 Hz, 3F), -100.26 – -109.04 (m, 1F).



**3,3,3-Trifluoro-1-phenylpropan-1-one (2d):** Colorless oil; 59% (22.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 7.7 Hz, 2H), 7.64 (t,  $J$  = 7.3 Hz, 1H), 7.51 (t,  $J$  = 7.6 Hz, 2H), 3.80 (q,  $J$  = 10.0 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  189.8, 136.0, 134.3, 129.1, 128.5, 124.1 (q,  $J$  = 276.9 Hz), 42.2 (q,  $J$  = 28.2 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -58.13 (t,  $J$  = 10.0 Hz, 3F).

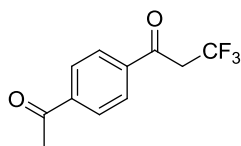


**3,3,3-Trifluoro-1-(4-methoxyphenyl)propan-1-one (2e):** White solid; m.p. 47-49 °C; 64% (27.9 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J$  = 8.7 Hz, 2H), 6.97 (d,  $J$  = 8.7 Hz, 2H), 3.89 (s, 3H), 3.74 (q,  $J$  = 10.1 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  188.1, 164.3, 130.8, 128.9, 124.1 (q,  $J$  = 277.0 Hz), 114.1, 55.6, 41.8 (q,  $J$  = 28.0 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.99 (t,  $J$  = 10.1 Hz, 3F).

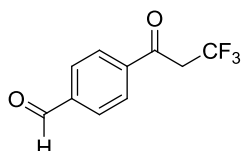


**1-(Biphenyl-4-yl)-3,3,3-trifluoropropan-1-one (2f):** White solid; m.p. 126-128 °C; 46% (24.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J$  = 8.1 Hz, 2H), 7.73 (d,  $J$  = 8.1 Hz, 2H), 7.64 (d,  $J$  = 7.4 Hz, 2H), 7.49 (t,  $J$  = 7.3 Hz, 2H), 7.46 – 7.40 (m, 1H),

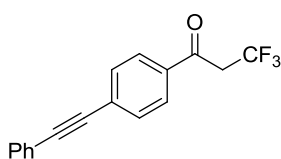
3.83 (q,  $J = 10.0$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  189.4, 147.1, 139.6, 134.6, 129.2, 129.1, 128.7, 127.7, 127.5, 124.2 (q,  $J = 277.3$  Hz), 42.3 (q,  $J = 28.2$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.97 (t,  $J = 10.1$  Hz, 3F).



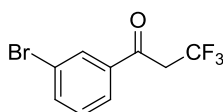
**1-(4-Acetylphenyl)-3,3,3-trifluoropropan-1-one (2g):** White solid; m.p. 113-115 °C; 69% (31.7 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.3$  Hz, 2H), 8.02 (d,  $J = 8.3$  Hz, 2H), 3.83 (q,  $J = 9.8$  Hz, 2H), 2.66 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 189.4, 141.1, 138.9, 128.9, 128.8, 123.9 (q,  $J = 277.0$  Hz), 42.7 (q,  $J = 28.6$  Hz), 27.1;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.06 (t,  $J = 9.9$  Hz, 3F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2921, 1680, 1272, 1018, 643; HRMS(CI) calcd  $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}_2$   $[\text{M} + \text{H}]^+$ : 231.0633, found: 231.0632.



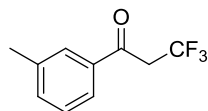
**4-(3,3,3-Trifluoropropanoyl)benzaldehyde (2h):** White solid; m.p. 89-91 °C; 77% (33.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.12 (s, 1H), 8.09 (d,  $J = 8.1$  Hz, 2H), 8.02 (d,  $J = 8.1$  Hz, 2H), 3.85 (q,  $J = 9.8$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.4, 189.4, 139.9, 139.8, 130.1, 129.0, 123.9 (q,  $J = 277.1$  Hz), 42.7 (q,  $J = 28.6$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.06 (t,  $J = 9.8$  Hz, 3F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2949, 2850, 1688, 1370, 800; HRMS(CI) calcd  $\text{C}_{10}\text{H}_8\text{F}_3\text{O}_2$   $[\text{M} + \text{H}]^+$ : 217.0476, found: 217.0479.



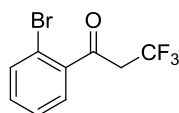
**3,3,3-Trifluoro-1-(4-(phenylethynyl)phenyl)propan-1-one (2i):** White solid; m.p. 140 -142 °C; 54% (31.1 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92 (d,  $J = 8.1$  Hz, 2H), 7.65 (d,  $J = 8.1$  Hz, 2H), 7.61 – 7.52 (m, 2H), 7.43 – 7.33 (m, 3H), 3.80 (q,  $J = 9.9$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  189.0, 134.9, 132.1, 131.9, 129.6, 129.2, 128.6, 128.5, 124.1 (q,  $J = 277.1$  Hz), 122.5, 93.9, 88.4, 42.3 (q,  $J = 28.4$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.01 (t,  $J = 9.9$  Hz, 3F); FT-IR (thin film, KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 2921, 2217, 1687, 1123, 848; HRMS(CI) calcd  $\text{C}_{17}\text{H}_{12}\text{F}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 289.0840, found: 289.0846.



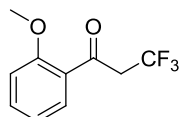
**1-(3-Bromophenyl)-3,3,3-trifluoropropan-1-one (2j):** Colorless oil; 67% (35.5 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (s, 1H), 7.85 (d,  $J = 7.8$  Hz, 1H), 7.76 (d,  $J = 7.8$  Hz, 1H), 7.40 (t,  $J = 7.9$  Hz, 1H), 3.78 (q,  $J = 9.8$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  188.5, 137.6, 137.2, 131.5, 130.6, 127.0, 123.9 (q,  $J = 277.1$  Hz), 123.5, 42.4 (q,  $J = 28.6$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.06 (t,  $J = 9.8$  Hz, 3F).



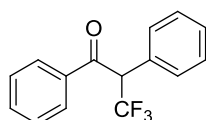
**3,3,3-Trifluoro-1-m-tolylpropan-1-one (2k):** Colorless oil; 65% (26.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (s, 1H), 7.72 (d,  $J = 7.9$  Hz, 1H), 7.45 (d,  $J = 7.4$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 1H), 3.78 (q,  $J = 10.0$  Hz, 2H), 2.43 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.0, 139.0, 136.0, 135.1, 129.0, 128.9, 125.7, 124.2 (q,  $J = 277.0$  Hz), 42.3 (q,  $J = 28.1$  Hz), 21.5;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.08 (t,  $J = 10.1$  Hz, 3F).



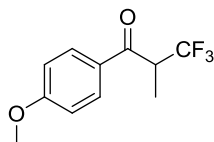
**1-(2-Bromophenyl)-3,3,3-trifluoropropan-1-one (2l):** Colorless oil; 68% (36.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.8$  Hz, 1H), 7.51 – 7.32 (m, 3H), 3.84 (q,  $J = 10.0$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  193.4, 140.1, 134.1, 132.8, 129.3, 127.9, 123.6 (q,  $J = 277.6$  Hz), 119.0, 45.9 (q,  $J = 28.4$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.17 (t,  $J = 10.0$  Hz, 3F).



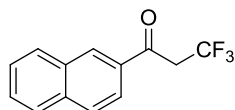
**3,3,3-Trifluoro-1-(2-methoxyphenyl)propan-1-one (2m):** Colorless oil; 67% (29.2 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (dd,  $J = 7.8, 1.8$  Hz, 1H), 7.57 – 7.49 (m, 1H), 7.08 – 7.01 (m, 1H), 6.99 (d,  $J = 8.4$  Hz, 1H), 3.94 (s, 3H), 3.88 (q,  $J = 10.3$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.1, 159.1, 135.1, 131.0, 126.6, 124.4 (q,  $J = 276.9$  Hz), 121.1, 111.8, 55.7, 47.0 (q,  $J = 27.4$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.60 (t,  $J = 10.3$  Hz, 3F).



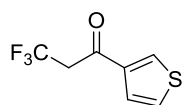
**3,3,3-Trifluoro-1,2-diphenylpropan-1-one (2n):** Colorless oil; 65% (34.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 7.7$  Hz, 2H), 7.53 (t,  $J = 7.3$  Hz, 1H), 7.49 – 7.32 (m, 7H), 5.29 (q,  $J = 8.2$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  191.2, 135.5, 133.9, 130.0, 129.8, 129.4, 129.3, 129.0, 128.9, 124.4 (q,  $J = 280.3$  Hz), 56.7 (q,  $J = 26.6$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -66.55 (d,  $J = 8.2$  Hz, 3F).



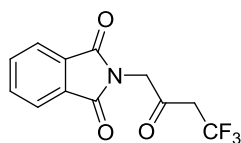
**3,3,3-Trifluoro-1-(4-methoxyphenyl)-2-methylpropan-1-one (2o):** Colorless oil; 59% (22.2 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 8.7 Hz, 2H), 6.97 (d,  $J$  = 8.7 Hz, 2H), 4.32 – 4.06 (m, 1H), 3.89 (s, 3H), 1.46 (d,  $J$  = 7.1 Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 164.4, 131.2, 128.8, 125.6 (q,  $J$  = 280.2 Hz), 114.2, 55.72, 44.0 (q,  $J$  = 26.3 Hz), 11.9;  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -65.76 (d,  $J$  = 8.2 Hz, 3F).



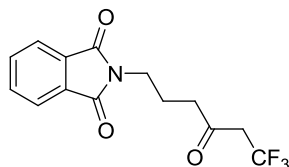
**3,3,3-Trifluoro-1-(naphthalen-2-yl)propan-1-one (2p):** White solid; m.p. 87 -89 °C; 70% (33.3 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (s, 1H), 8.00 (t,  $J$  = 9.4 Hz, 2H), 7.96 – 7.87 (m, 2H), 7.66 (t,  $J$  = 7.3 Hz, 1H), 7.60 (t,  $J$  = 7.4 Hz, 1H), 3.94 (q,  $J$  = 10.0 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  189.8, 136.1, 133.4, 132.5, 130.7, 129.9, 129.4, 129.1, 128.0, 127.4, 124.2 (q,  $J$  = 277.7 Hz), 123.6, 42.4 (q,  $J$  = 28.2 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.92 (t,  $J$  = 9.9 Hz, 3F).



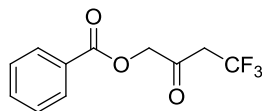
**3,3,3-Trifluoro-1-(thiophen-3-yl)propan-1-one (2q):** light yellow oil; 62% (24.1 mg);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (s, 1H), 7.56 (d,  $J$  = 5.0 Hz, 1H), 7.43 – 7.33 (m, 1H), 3.69 (q,  $J$  = 10.1 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  183.7, 141.4, 133.7, 127.3, 127.0, 123.9 (q,  $J$  = 277.0 Hz), 43.6 (q,  $J$  = 28.3 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.00 (t,  $J$  = 10.1 Hz, 3F).



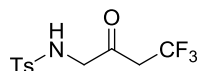
**2-(4,4,4-Trifluoro-2-oxobutyl)isoindoline-1,3-dione (2r):** White solid; m.p. 160-162 °C; 69% (37.4 mg);  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J$  = 5.4, 3.1 Hz, 2H), 7.75 (dd,  $J$  = 5.5, 3.0 Hz, 2H), 4.59 (s, 2H), 3.40 (q,  $J$  = 10.2 Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3, 167.4, 134.5, 132.0, 123.9, 123.4 (q,  $J$  = 277.1 Hz), 46.9, 44.4 (q,  $J$  = 29.6 Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.01 (t,  $J$  = 10.2 Hz, 3F).



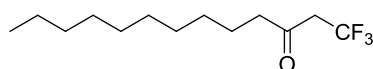
**2-(6,6,6-Trifluoro-4-oxohexyl)isoindoline-1,3-dione (2s):** White solid; m.p. 100-102 °C; 67% (40.1 mg); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.83 (dd, *J* = 5.3, 3.0 Hz, 2H), 7.72 (dd, *J* = 5.4, 3.0 Hz, 2H), 3.71 (t, *J* = 6.5 Hz, 2H), 3.25 (q, *J* = 10.5 Hz, 2H), 2.59 (t, *J* = 6.9 Hz, 2H), 1.99 (p, *J* = 6.7 Hz, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 199.0, 168.6, 134.2, 132.1, 123.7 (q, *J* = 276.9 Hz), 123.4, 46.4 (q, *J* = 28.3 Hz), 40.4, 36.9, 22.3; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -62.50 (t, *J* = 10.4 Hz, 3F).



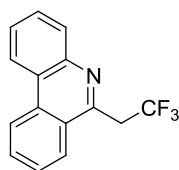
**4,4,4-Trifluoro-2-oxobutyl benzoate (2t):** White solid; m.p. 98-100 °C; 71% (34.9 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 – 8.00 (m, 2H), 7.74 – 7.54 (m, 1H), 7.54 – 7.42 (m, 2H), 4.96 (s, 2H), 3.38 (q, *J* = 10.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, overlapping peaks) δ 194.0, 165.8, 133.9, 130.1, 128.8, 123.5 (q, *J* = 277.1 Hz), 68.4 (q, *J* = 2.4 Hz), 43.5 (q, *J* = 29.3 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.00 (t, *J* = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 2924, 1742, 1413, 1159, 686; HRMS(CI) calcd C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>O<sub>3</sub> [M + H]<sup>+</sup>: 247.0582, found: 247.0589.



**4-Methyl-N-(4,4,4-trifluoro-2-oxobutyl)benzenesulfonamide (2u):** White solid; m.p. 157-159 °C; 63% (37.2 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 5.24 (brs, 1H), 3.94 (d, *J* = 4.9 Hz, 2H), 3.24 (q, *J* = 10.1 Hz, 2H), 2.43 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 194.3, 144.4, 135.9, 130.1, 127.3, 123.1 (q, *J* = 276.9 Hz), 52.3, 44.2 (q, *J* = 29.7 Hz), 21.7; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -58.87 – -65.52 (m, 3F); FT-IR (thin film, KBr): ν (cm<sup>-1</sup>) 3285, 1736, 1307, 1037, 677; HRMS(CI) calcd C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>NO<sub>3</sub>S [M + H]<sup>+</sup>: 296.0568, found: 296.0574.



**1,1,1-Trifluorotridecan-3-one (2v):** White solid; m.p. 44-46 °C; 66% (33.3 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.20 (q, *J* = 10.5 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 1.65 – 1.52 (m, 2H), 1.30 – 1.22 (m, 14H), 0.87 (t, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 200.4, 123.8 (q, *J* = 276.9 Hz), 46.3 (q, *J* = 28.1 Hz), 43.7, 32.0, 29.7, 29.6, 29.5, 29.4, 29.1, 23.3, 22.8, 14.2; <sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>) δ -62.47 (t, *J* = 10.5 Hz, 3F).

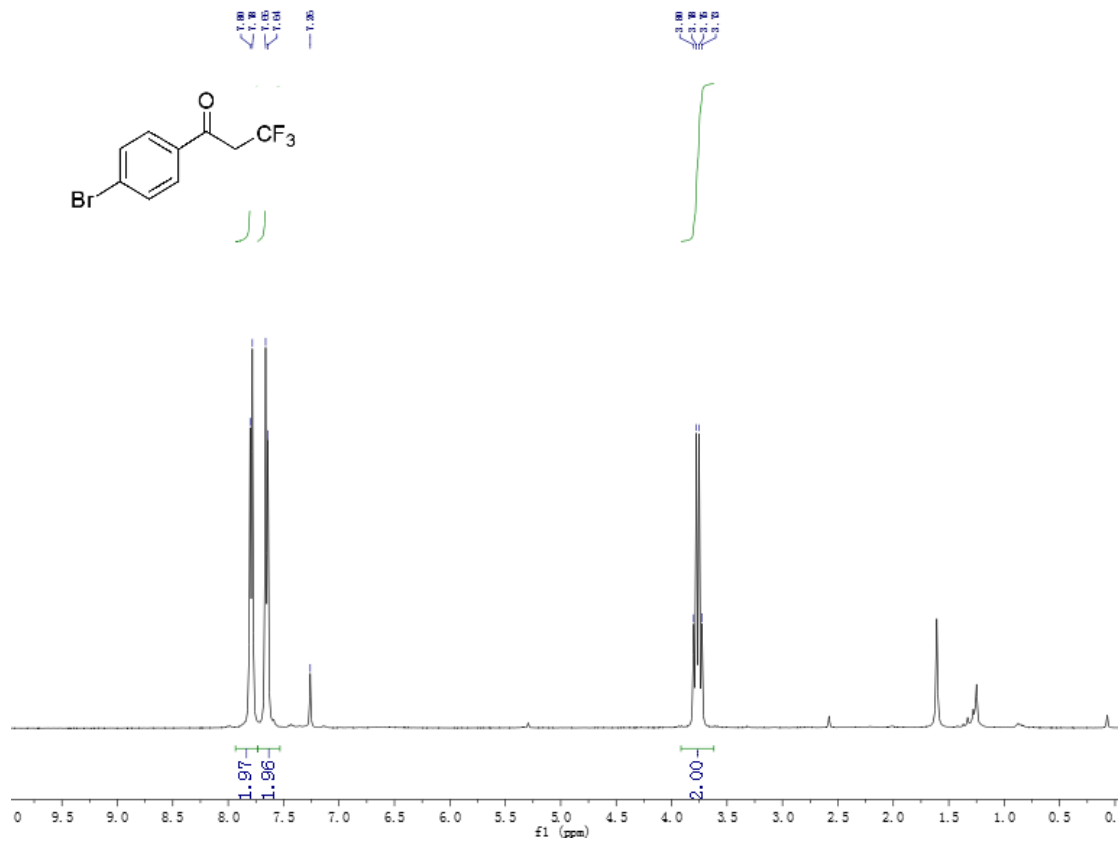


**6-(2,2,2-Trifluoroethyl)phenanthridine (7):** Yellow solid; m.p. 99-101 °C; 74% (38.6 mg); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.59 (d, *J* = 8.0 Hz, 1H),

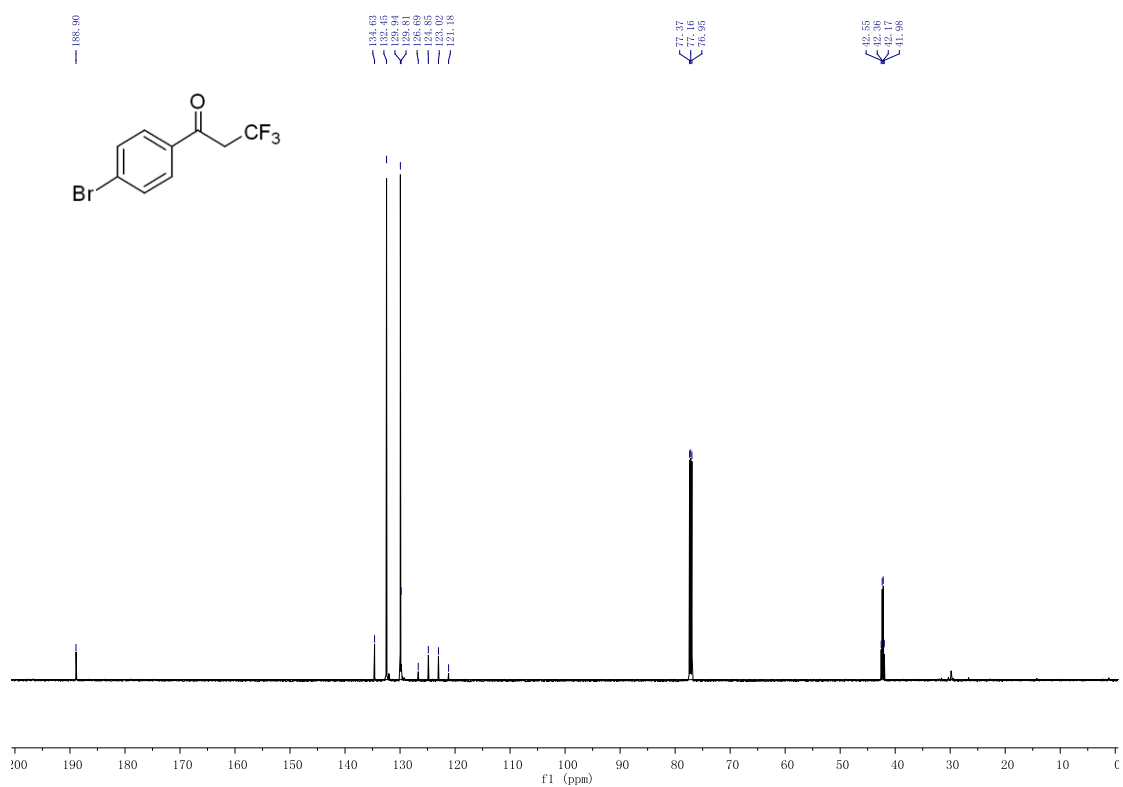
8.21 (t,  $J = 9.0$  Hz, 2H), 7.89 (t,  $J = 7.6$  Hz, 1H), 7.84 – 7.62 (m, 3H), 4.22 (q,  $J = 10.3$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  151.3, 143.6, 133.4, 131.0, 130.3, 129.1, 127.8, 127.7, 126.4, 125.8 (q,  $J = 278.1$  Hz), 125.7, 124.2, 122.7, 122.1, 40.7 (q,  $J = 29.2$  Hz);  $^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.54 (t,  $J = 10.4$  Hz, 3F).

## NMR Spectra for the products

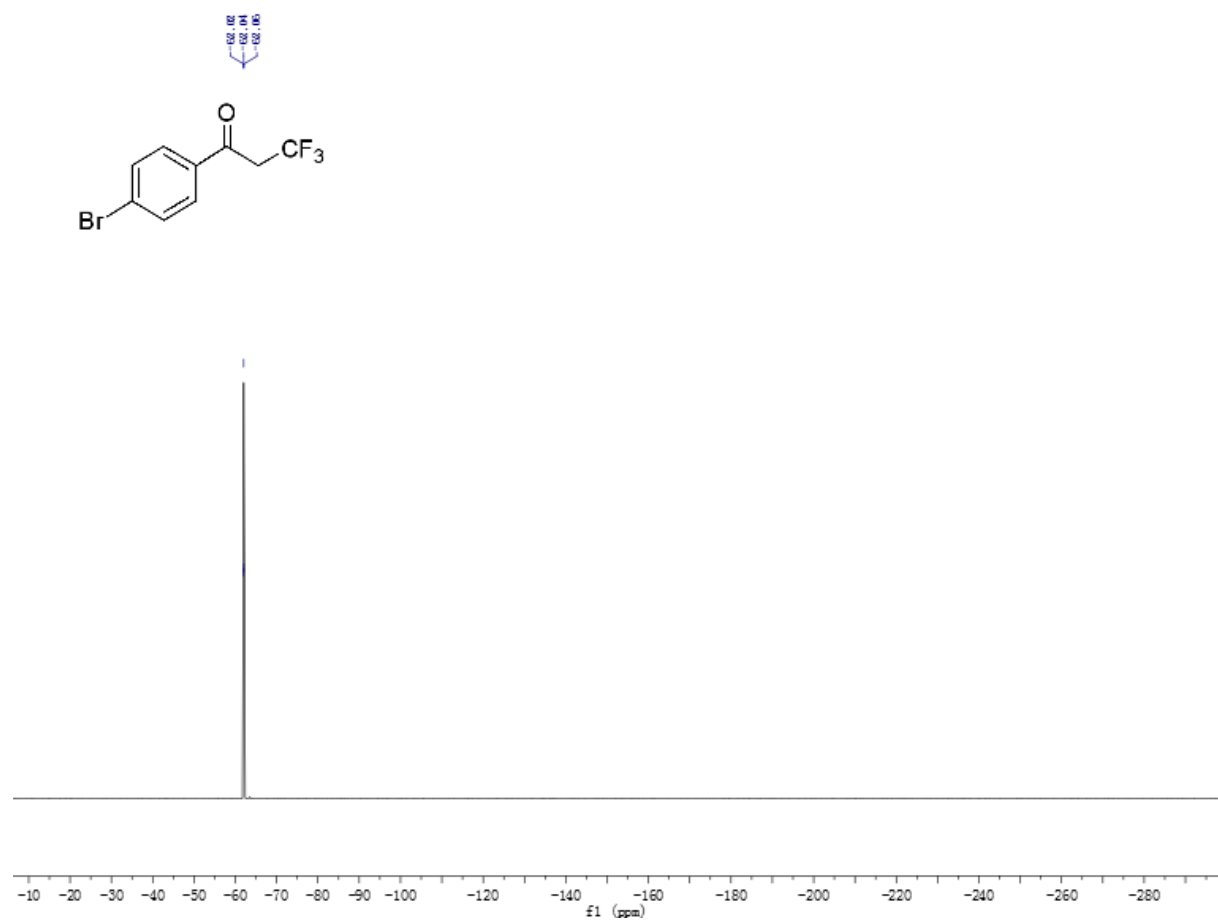
### $^1\text{H}$ NMR of **2a**



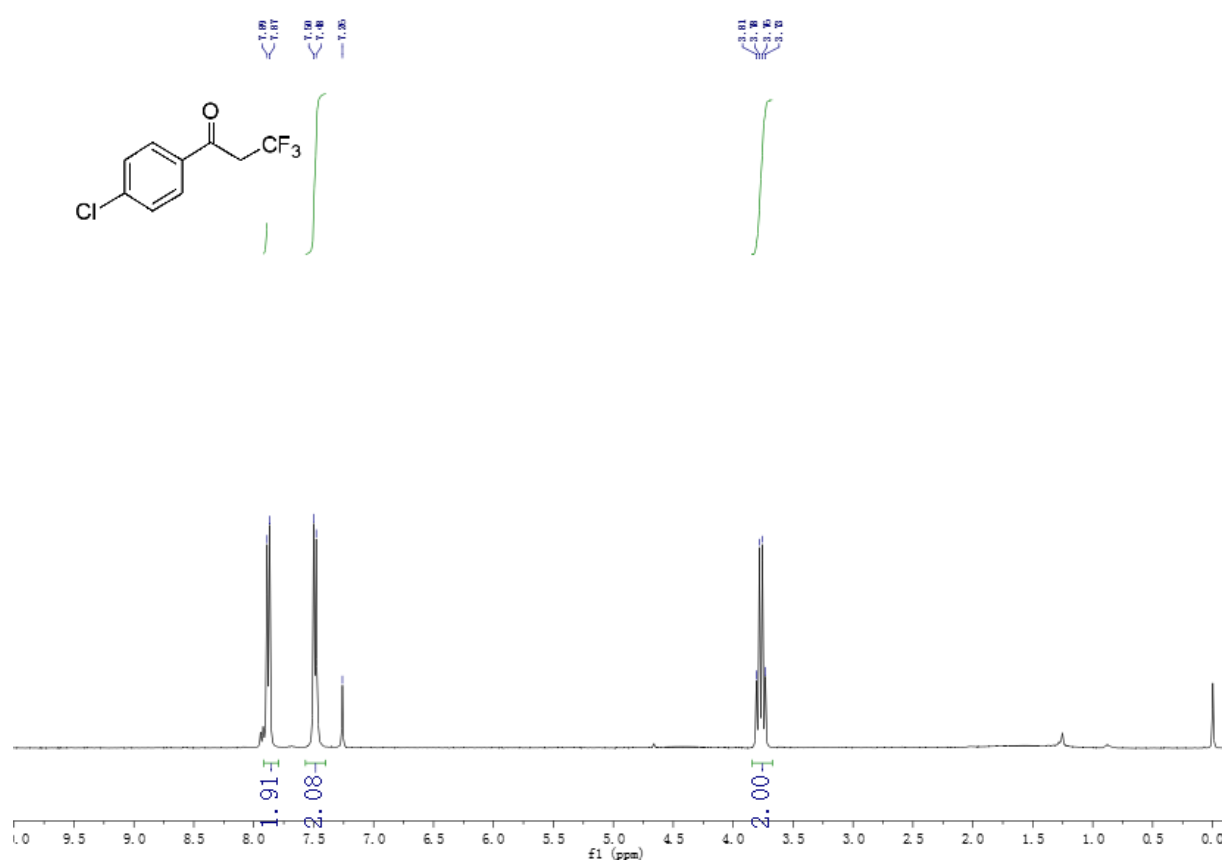
### $^{13}\text{C}$ NMR of **2a**



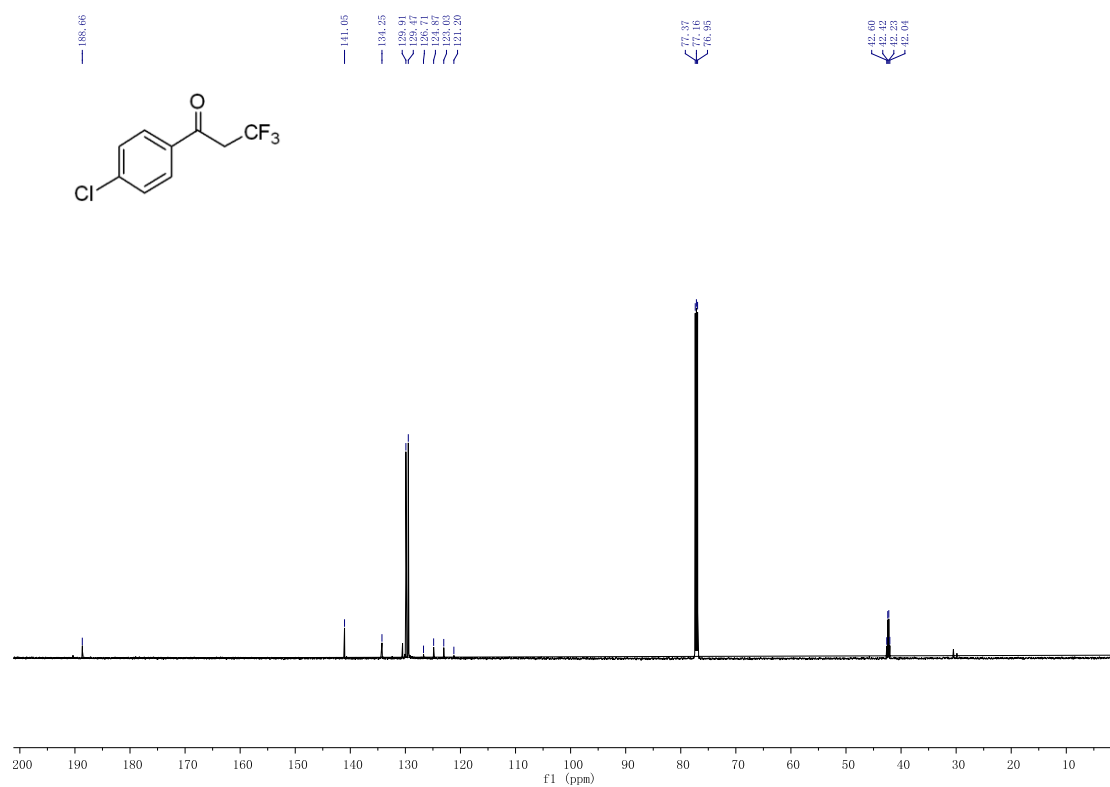
<sup>19</sup>F NMR of 2a



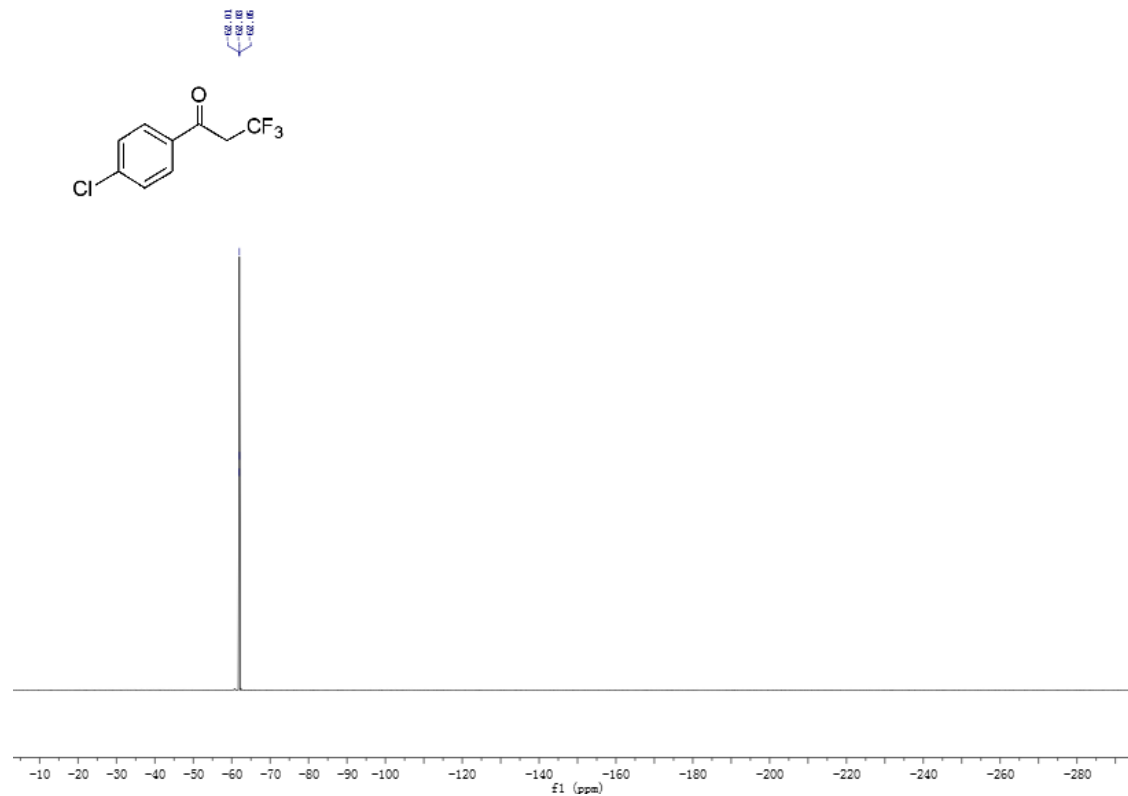
<sup>1</sup>H NMR of 2b



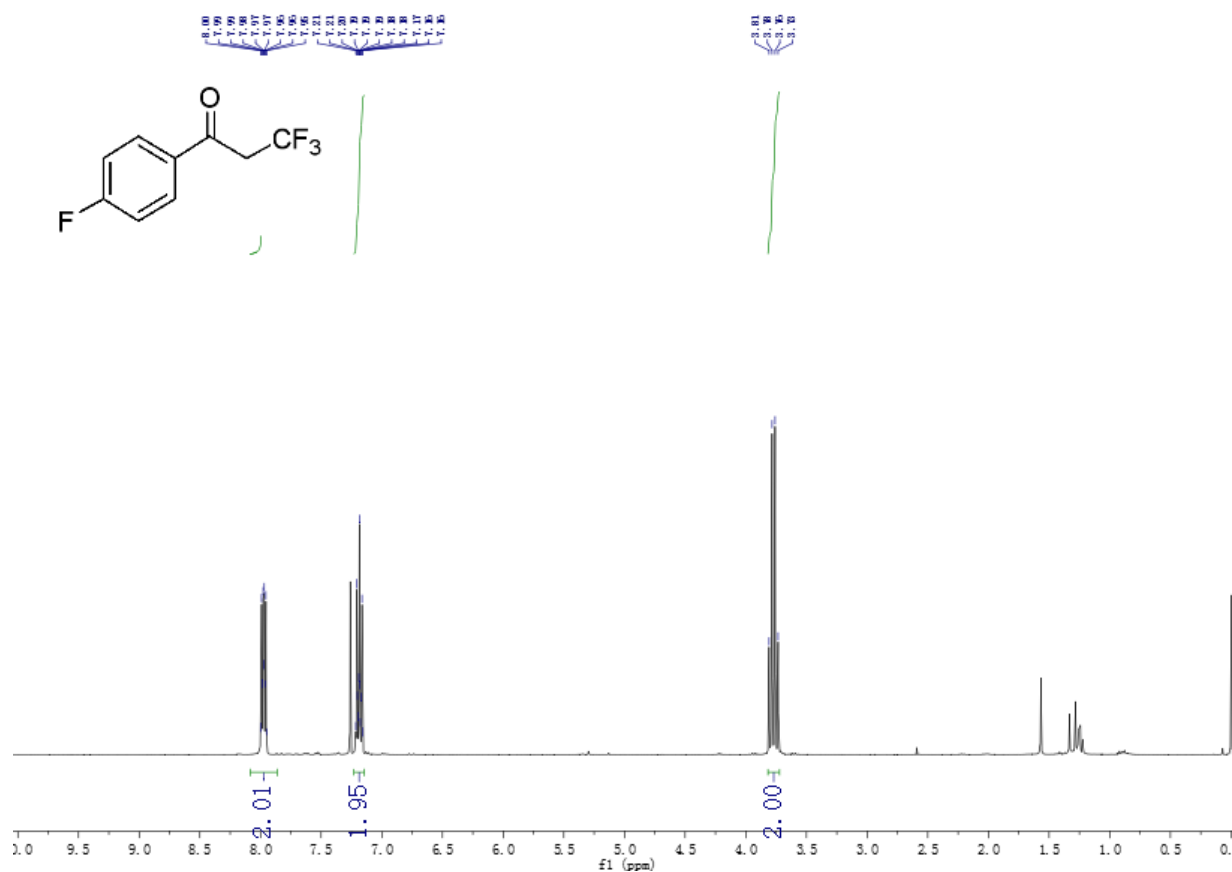
# <sup>13</sup>C NMR of 2b



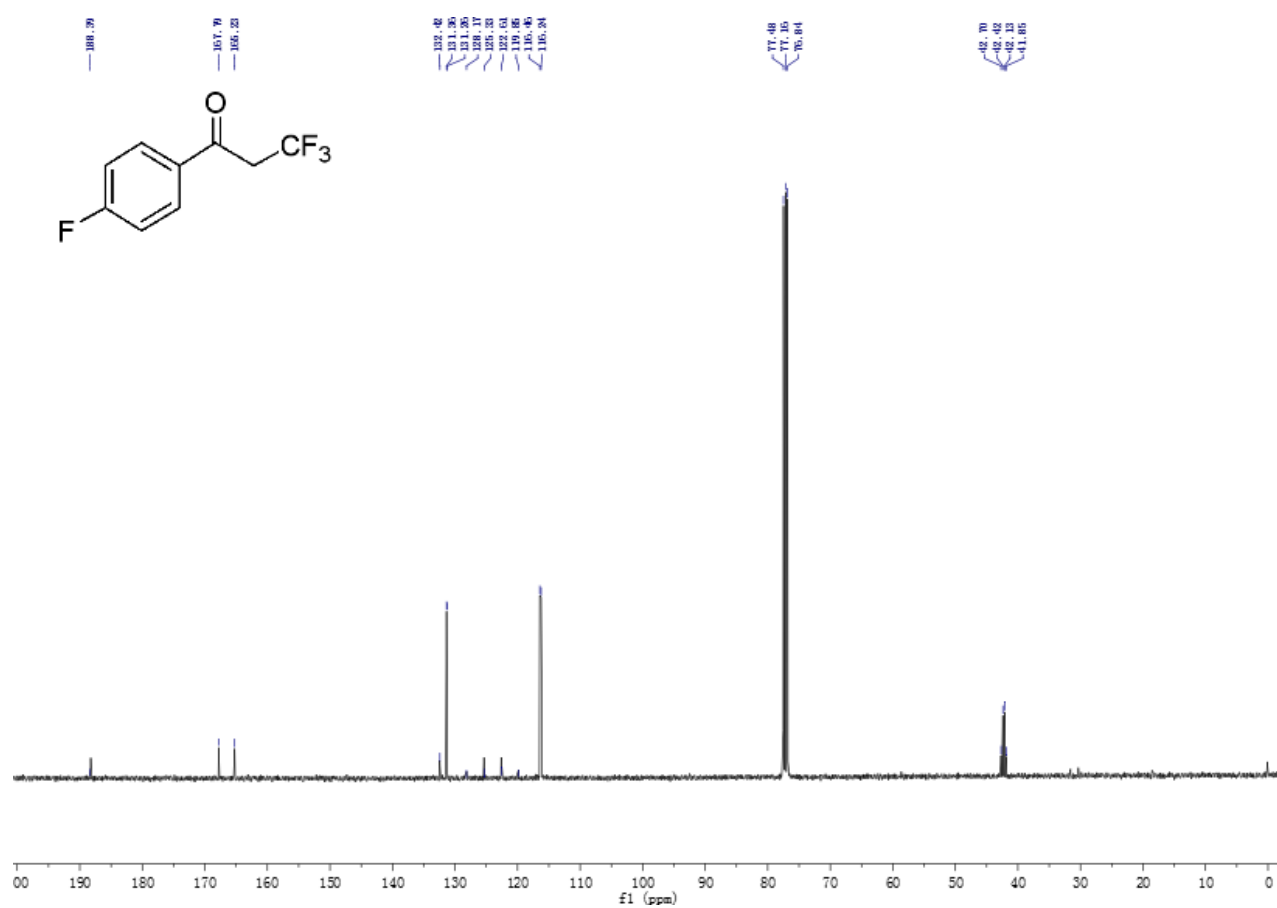
# <sup>19</sup>F NMR of 2b



<sup>1</sup>H NMR of 2c



<sup>13</sup>C NMR of 2c



CC(F)(F)FCC(=O)c1ccc(F)cc1

Chemical structure: 2-(4-fluorophenyl)propan-1-one

<sup>13</sup>C NMR spectrum (ppm):

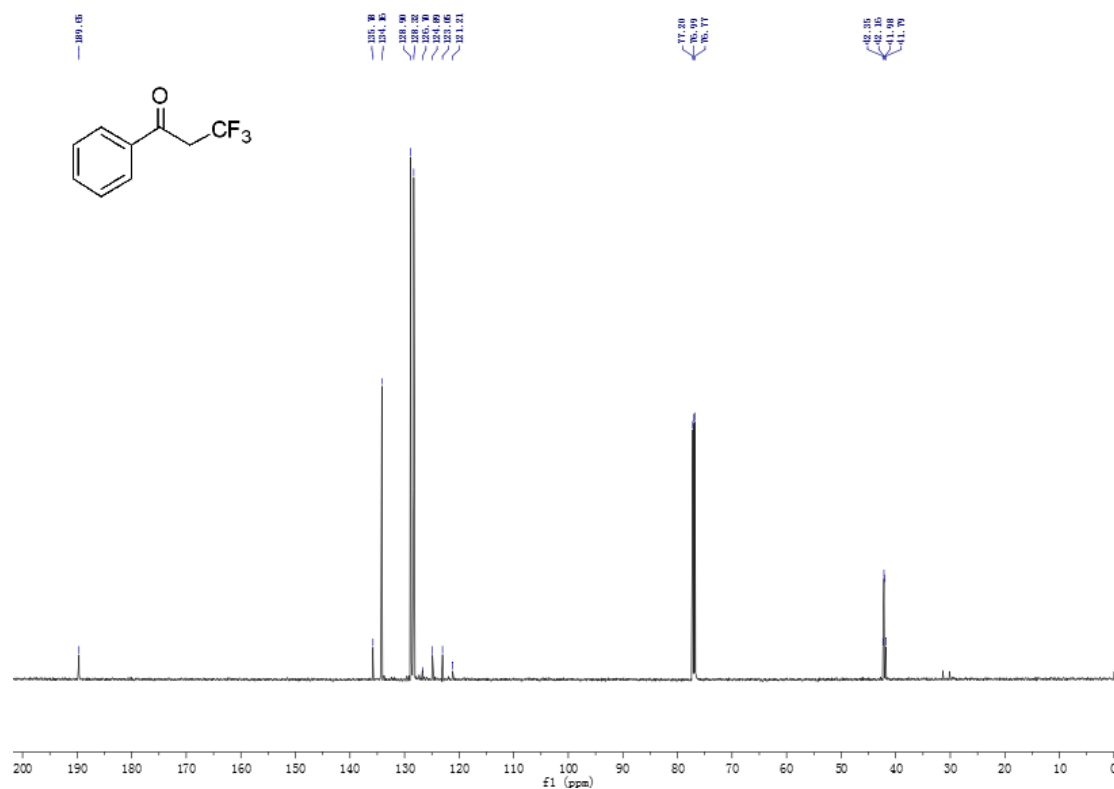
- 61.97
- 62.00
- 62.03
- 102.81
- 102.83
- 102.85
- 102.86
- 102.88
- 102.90
- 102.92
- 102.94
- 102.96
- 102.98
- 102.99

f1 (ppm)

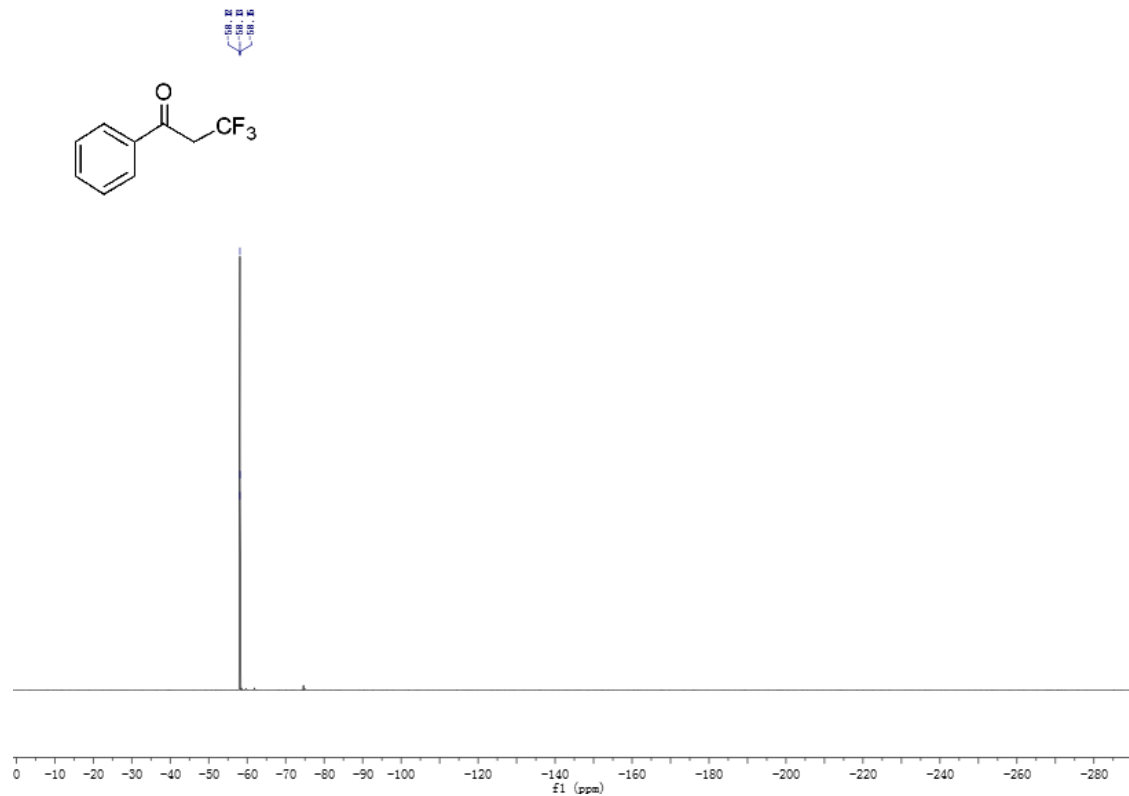
CC(=O)c1ccccc1

9.7  
 9.3

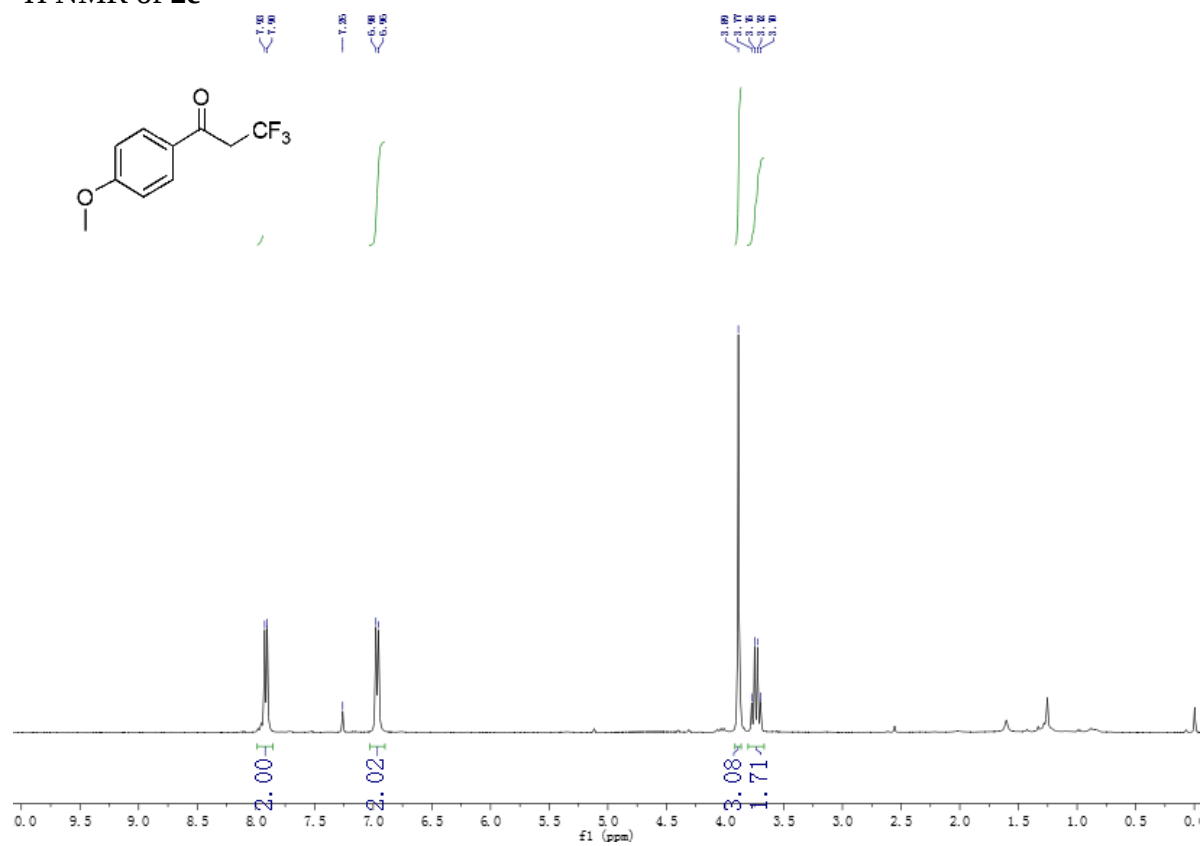
<sup>13</sup>C NMR of **2d**



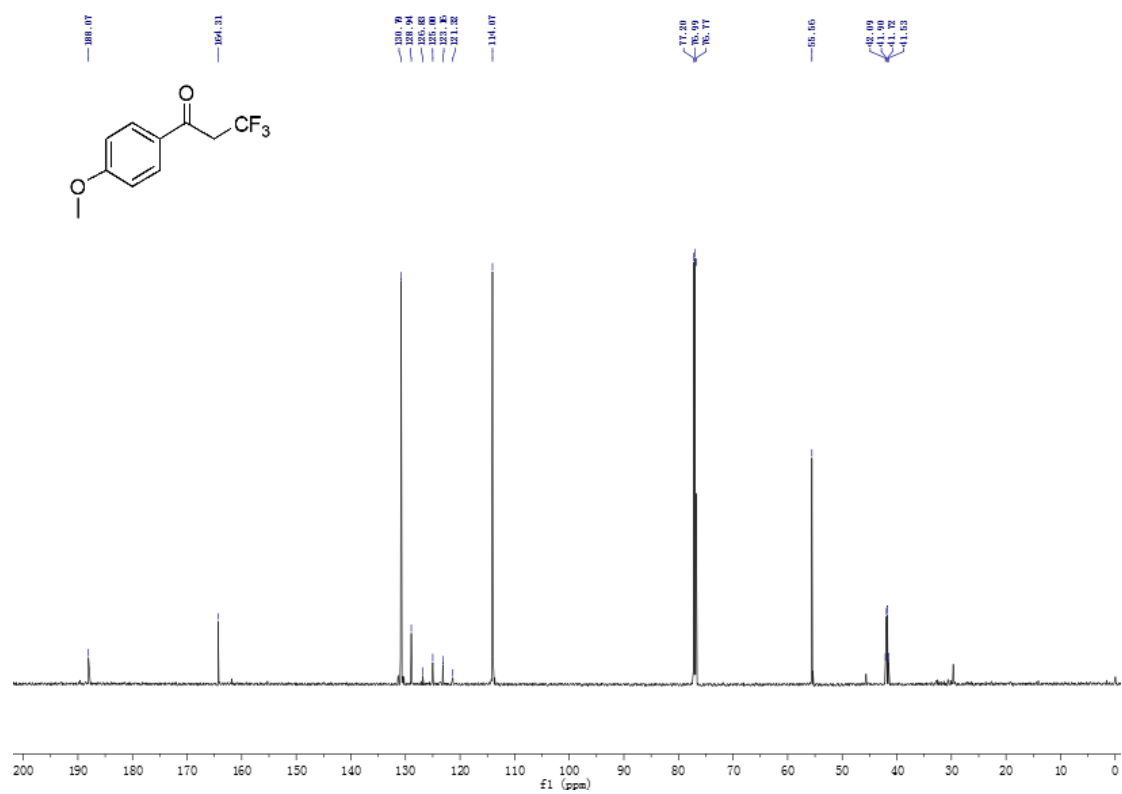
<sup>19</sup>F NMR of **2d**



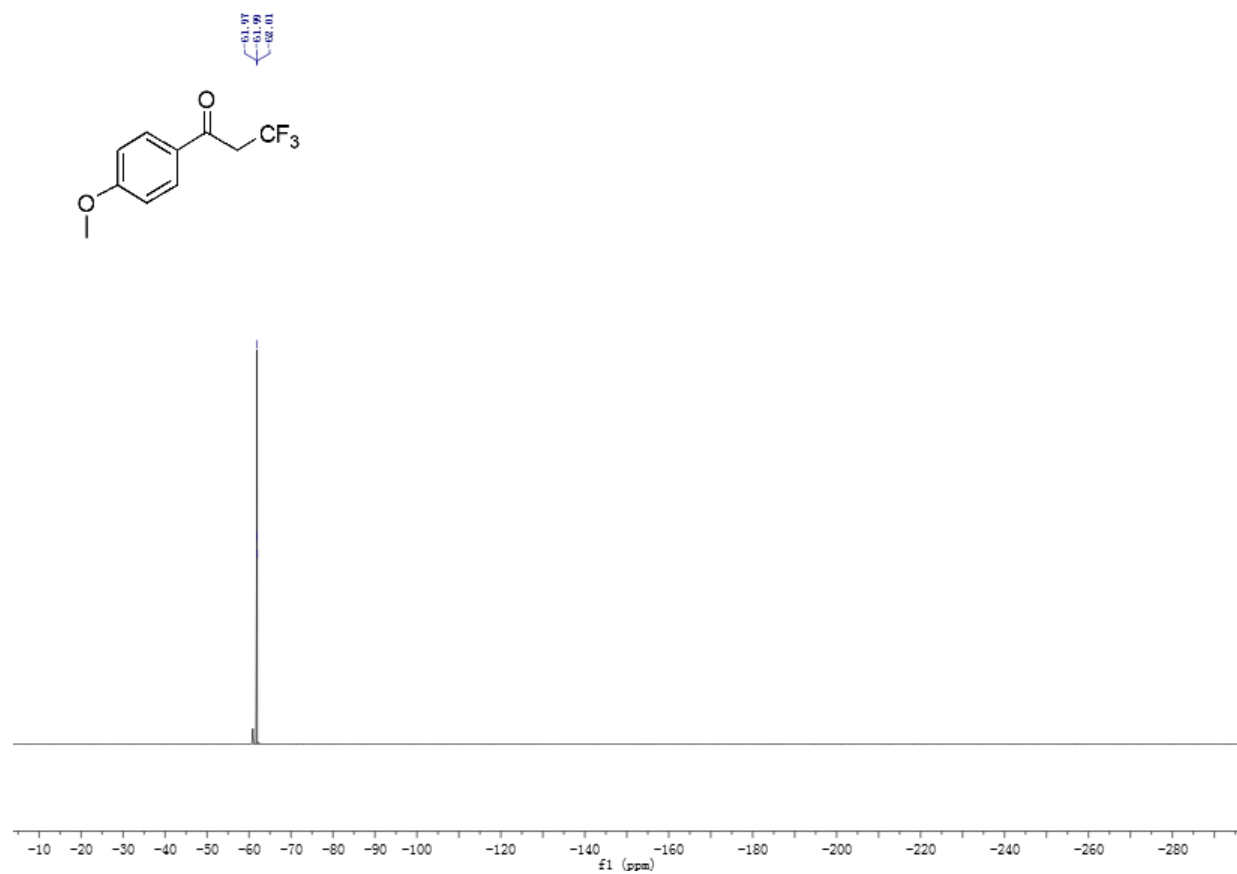
<sup>1</sup>H NMR of **2e**



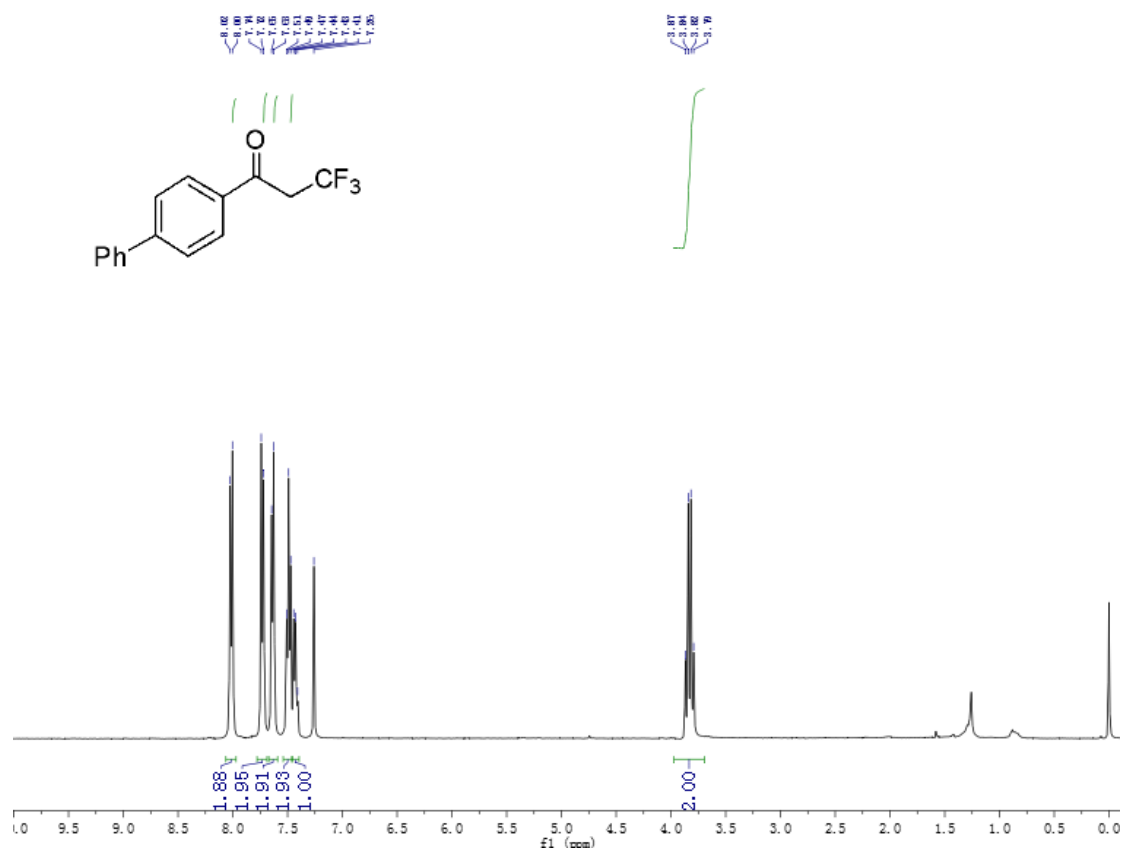
<sup>13</sup>C NMR of **2e**



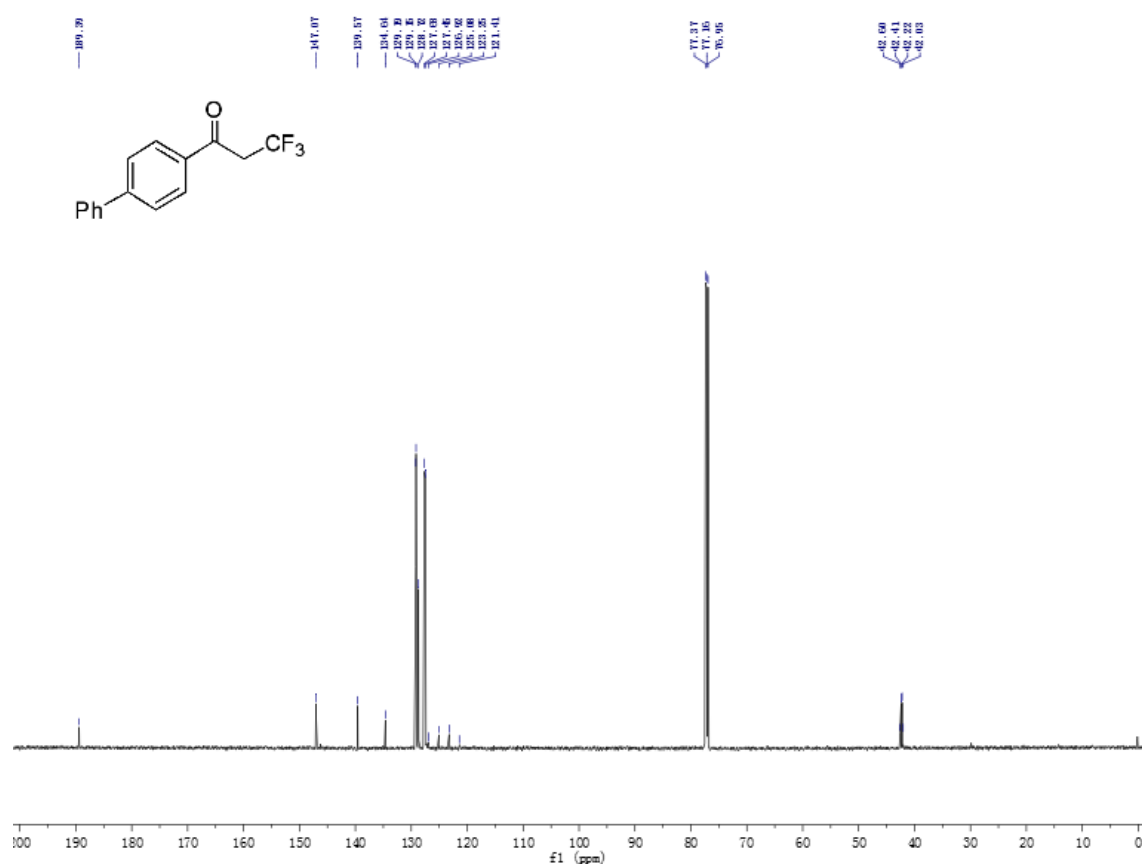
<sup>19</sup>F NMR of 2e



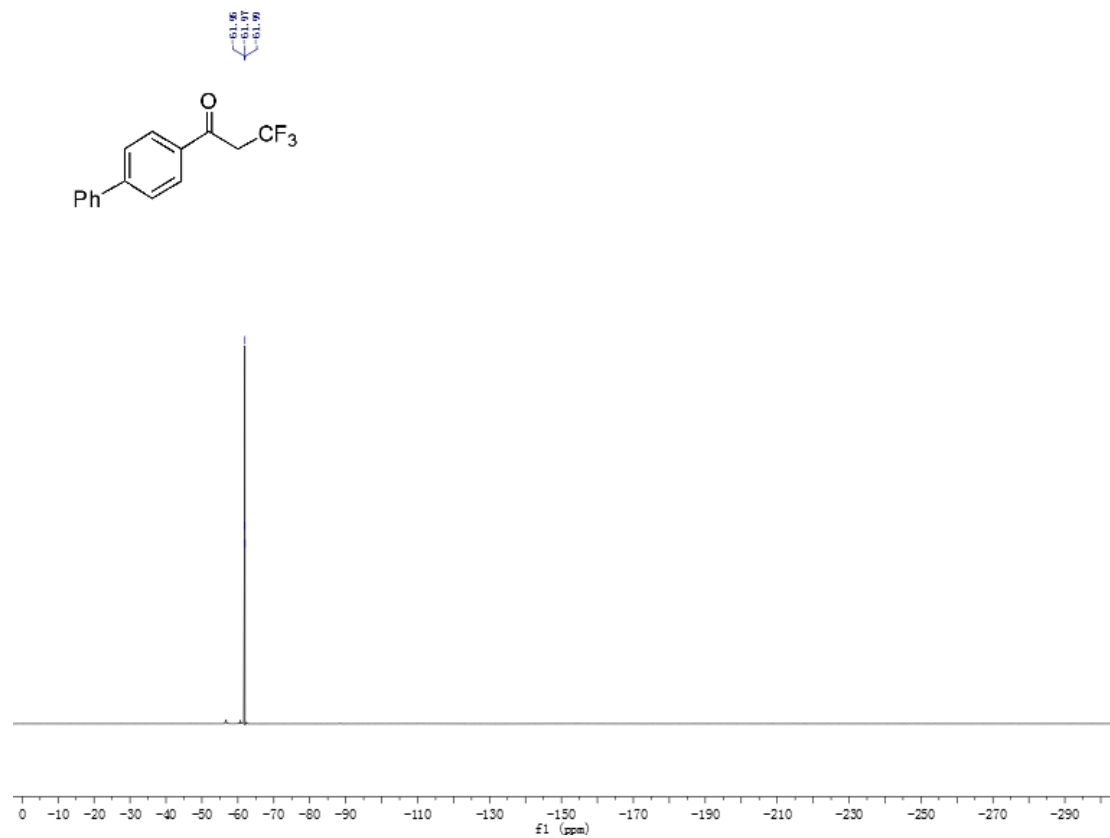
<sup>1</sup>H NMR of 2f



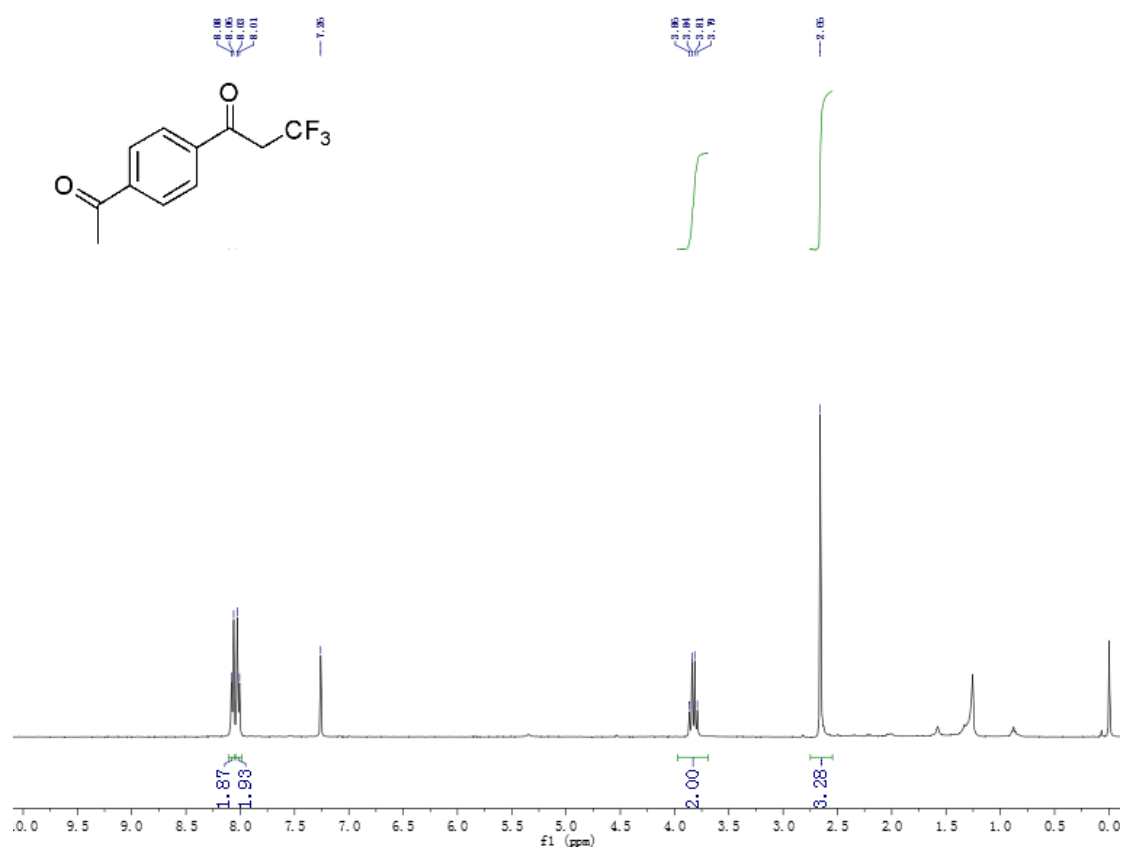
<sup>13</sup>C NMR of **2f**



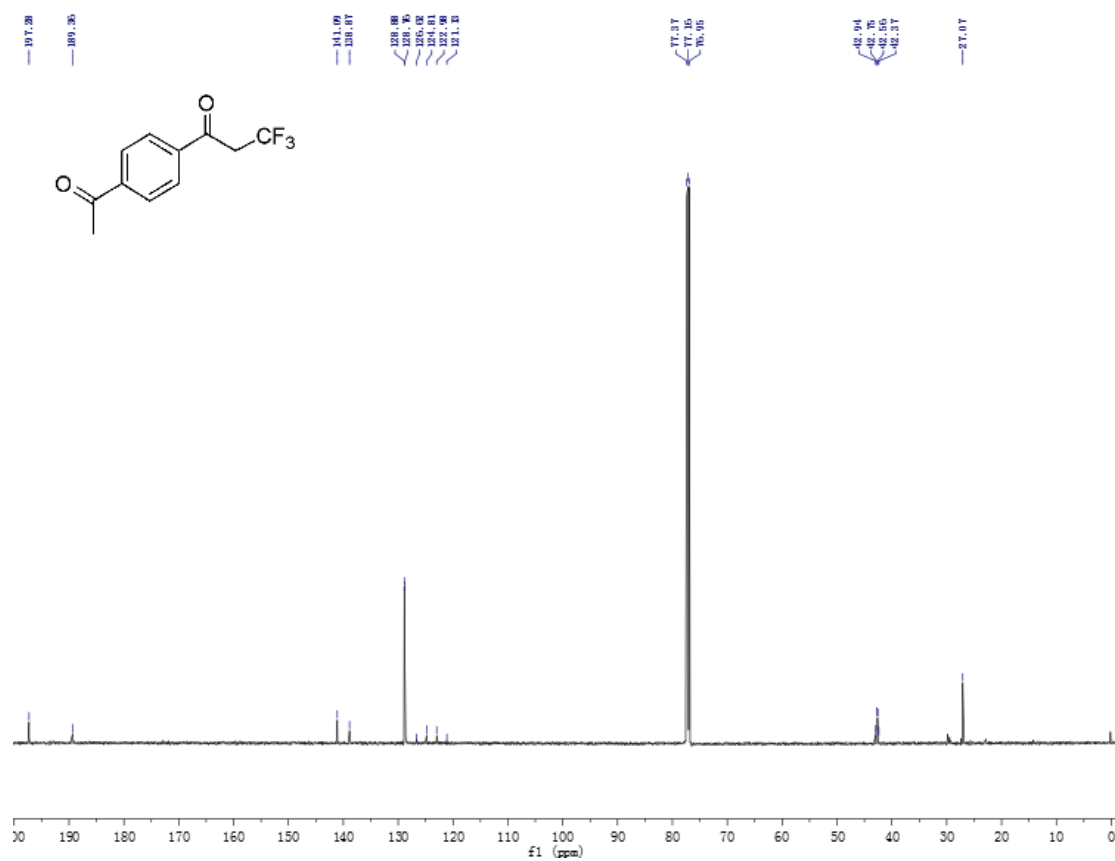
<sup>19</sup>F NMR of **2f**



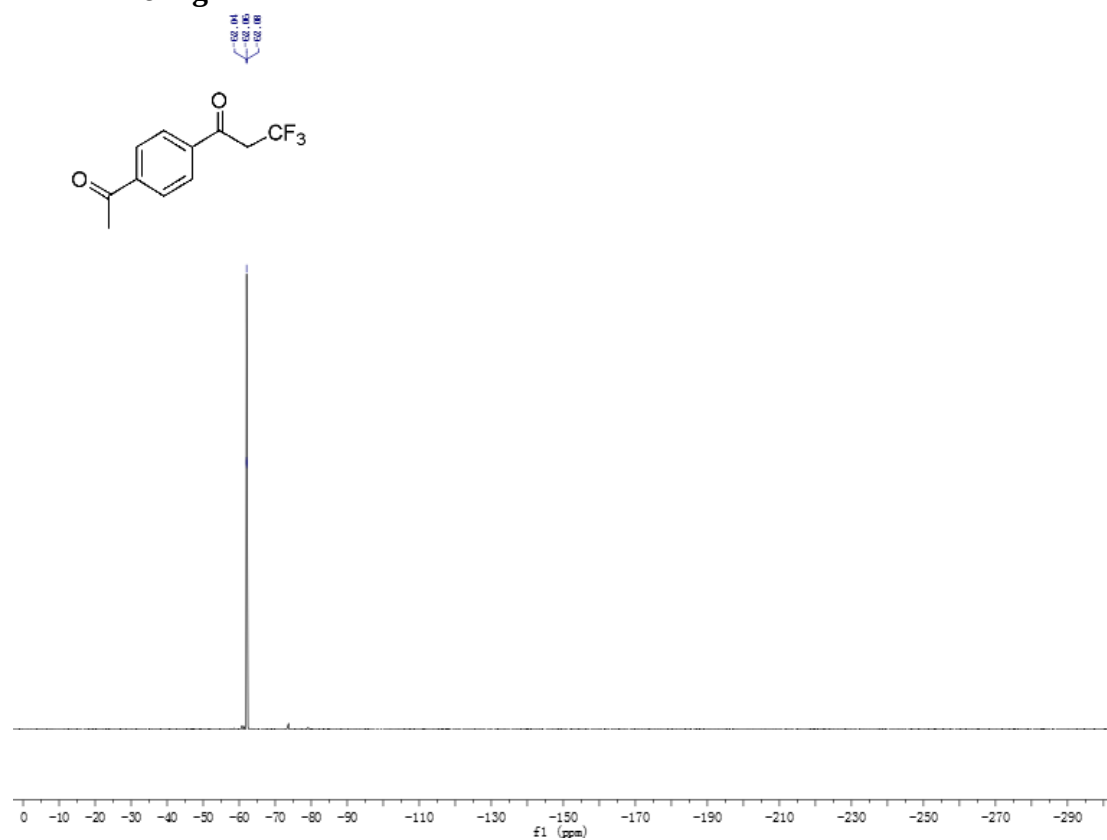
<sup>1</sup>H NMR of **2g**



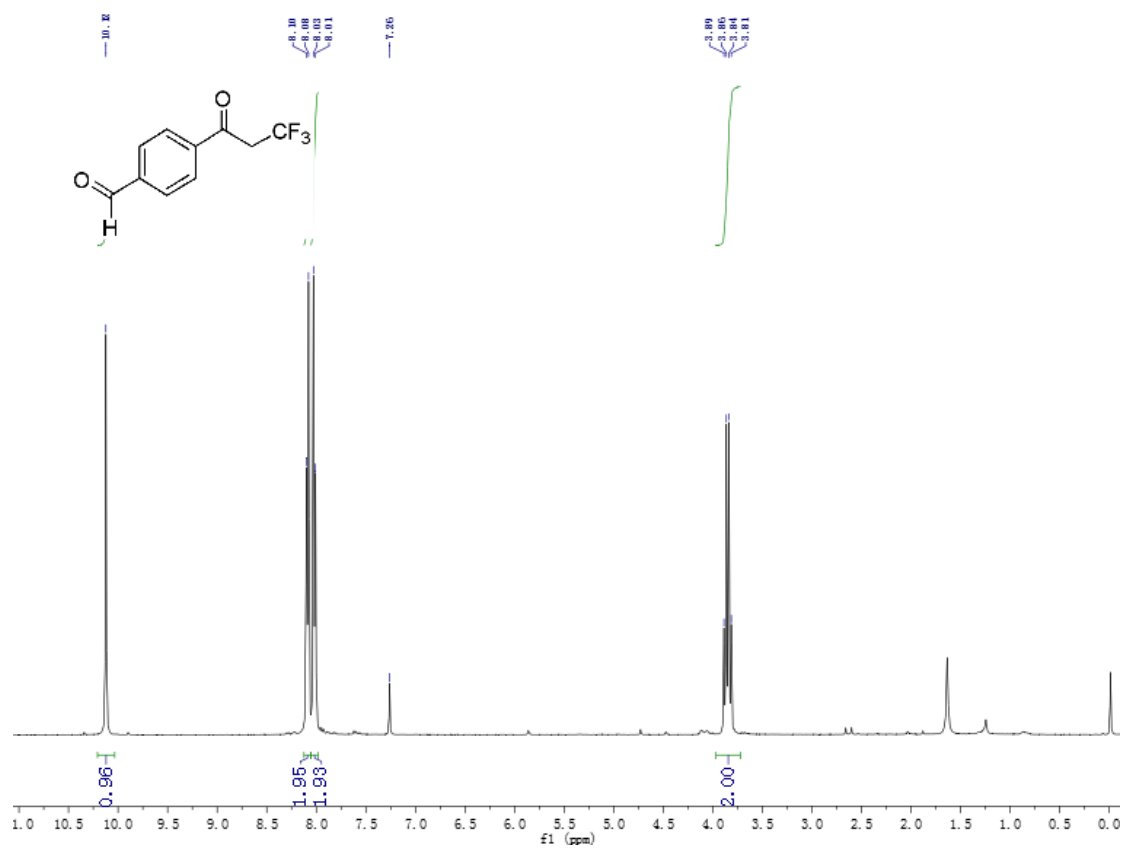
<sup>13</sup>C NMR of **2g**



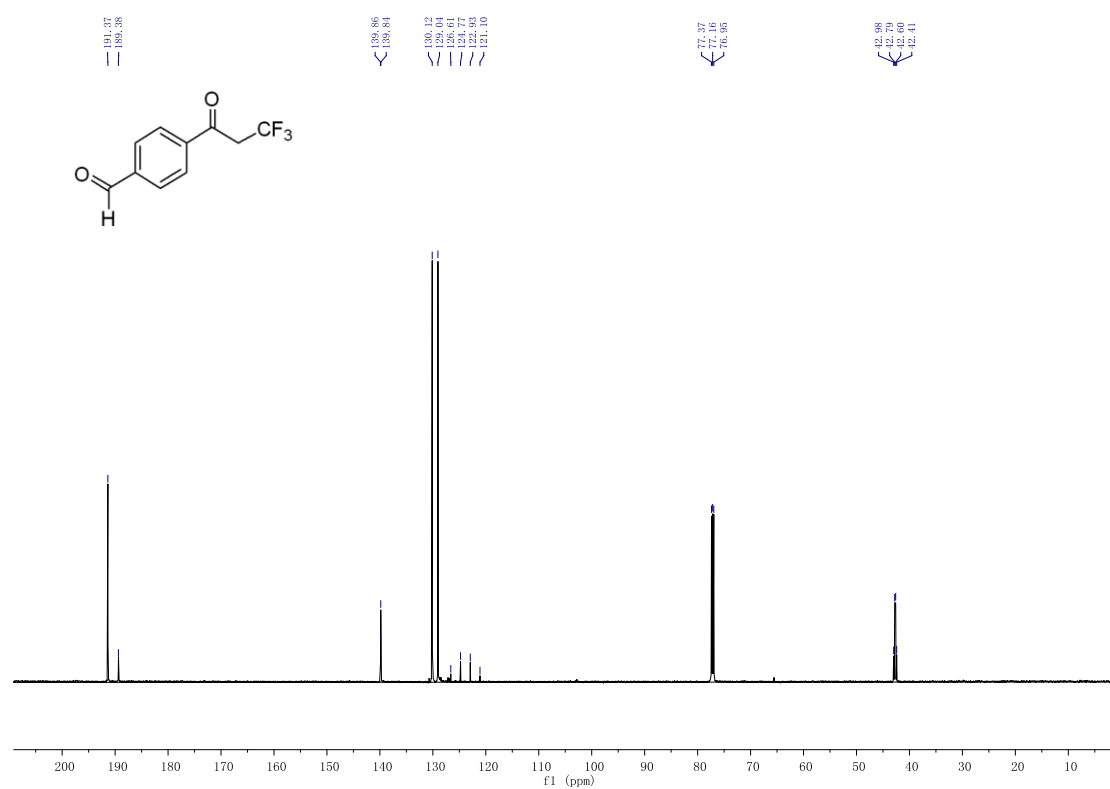
<sup>19</sup>F NMR of **2g**



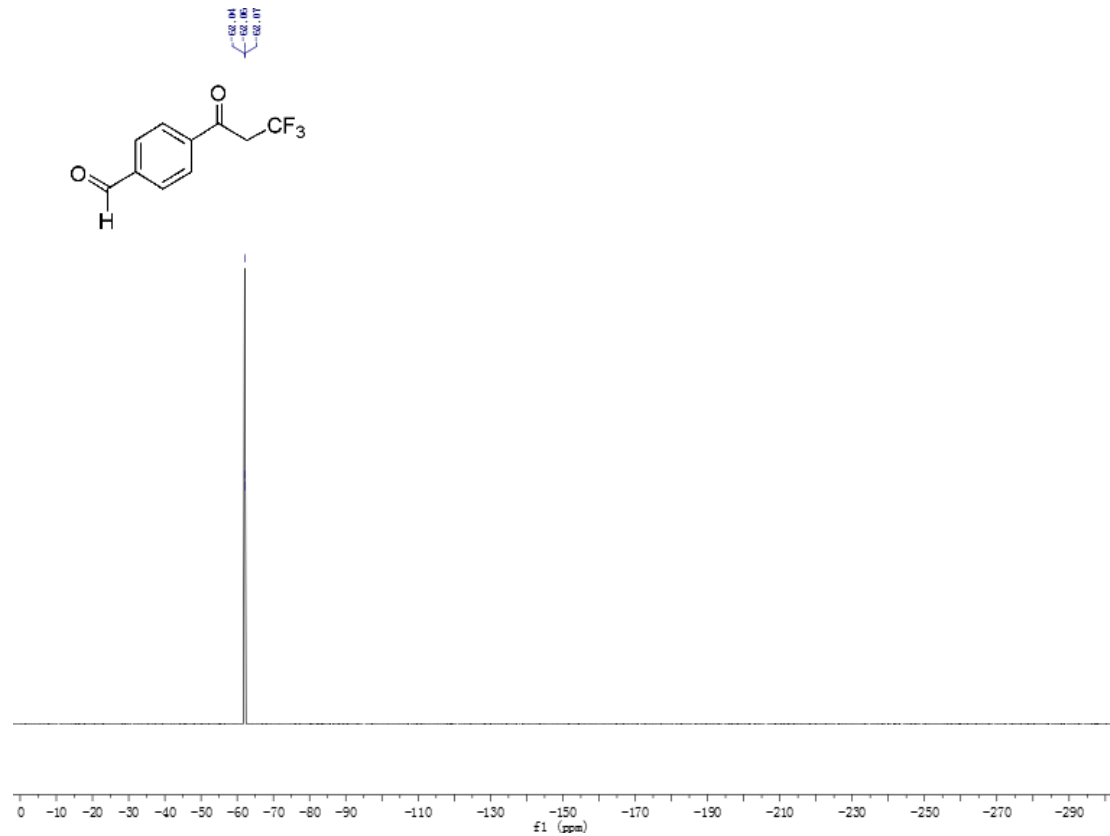
<sup>1</sup>H NMR of **2h**



# <sup>13</sup>C NMR of 2h



# <sup>19</sup>F NMR of 2h



CC(F)(F)FCC(=O)c1ccc(C#Cc2ccccc2)cc1

Chemical structure: CC(F)(F)FCC(=O)c1ccc(C#Cc2ccccc2)cc1

<sup>1</sup>H NMR spectrum (ppm):

- 7.2 - 8.0 ppm (aromatic signals, integration: 2.00, 2.01, 2.96)
- 3.3 ppm (alkyne, integration: 2.00)
- 2.6 ppm (methylene, integration: 2.00)
- 1.1 ppm (ethyl, integration: 3.00)

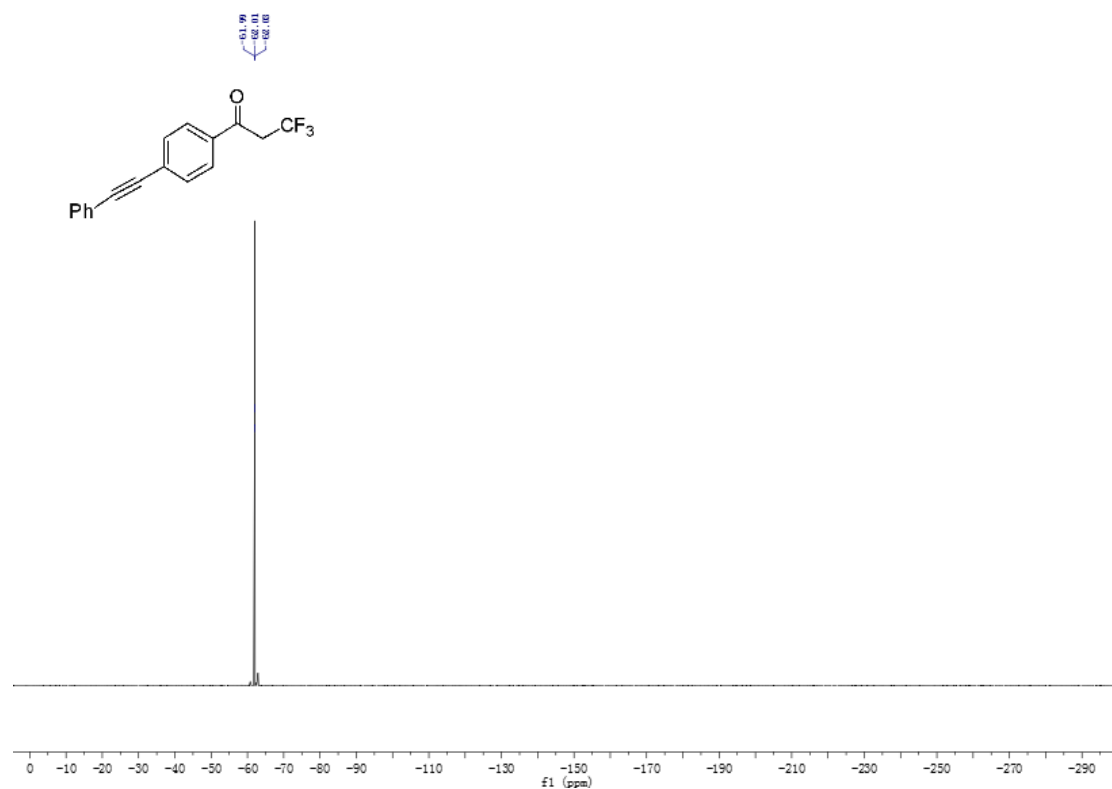
Chemical structure: CC(F)(F)FCC(=O)c1ccc(C#Cc2ccccc2)cc1

<sup>13</sup>C NMR spectrum (ppm):

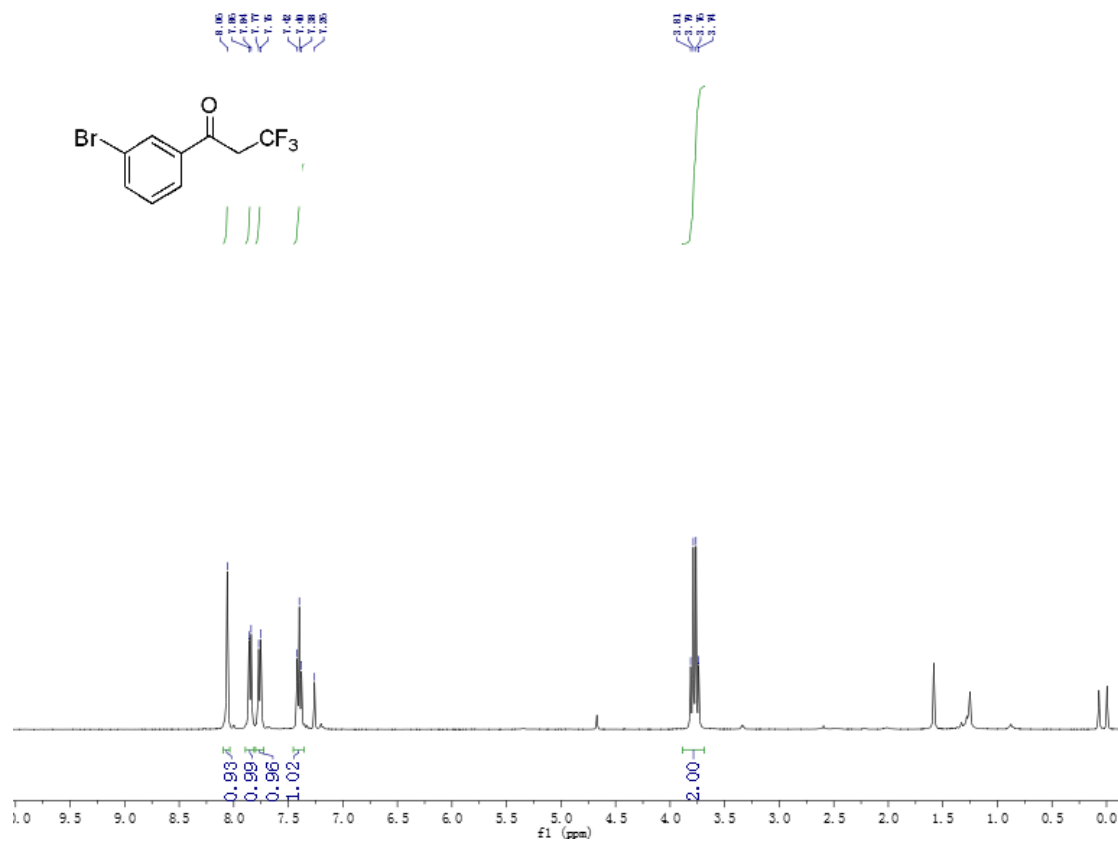
- 193.25
- 134.85
- 132.30
- 131.94
- 129.04
- 128.04
- 128.47
- 128.20
- 127.93
- 122.50
- 122.54
- 119.94
- 93.88
- 88.40
- 77.48
- 77.16
- 76.84
- 42.70
- 42.42
- 42.13
- 41.85

Figure 1 shows the <sup>13</sup>C NMR spectrum of compound 1. The chemical structure of compound 1 is shown above the spectrum. The spectrum displays peaks corresponding to the carbon atoms in the molecule, with the following chemical shifts (ppm) labeled: 193.25, 134.85, 132.30, 131.94, 129.04, 128.04, 128.47, 128.20, 127.93, 122.50, 122.54, 119.94, 93.88, 88.40, 77.48, 77.16, 76.84, 42.70, 42.42, 42.13, and 41.85.

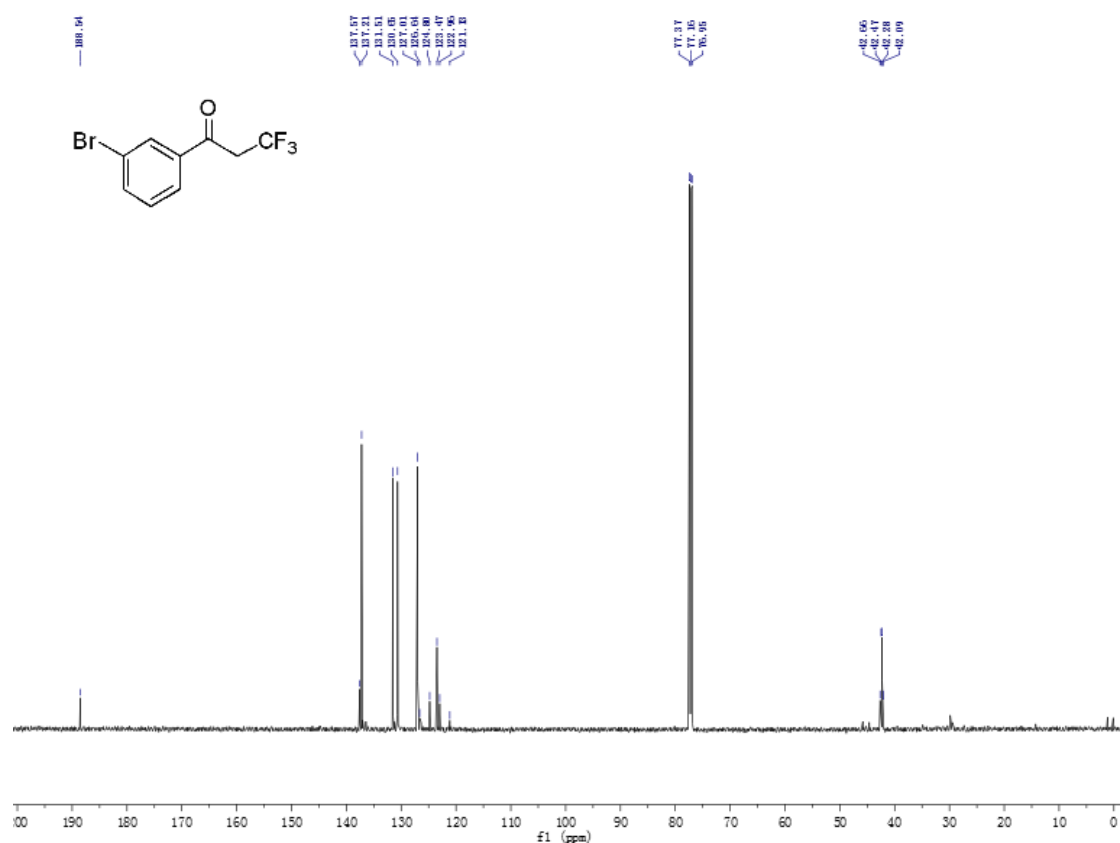
<sup>19</sup>F NMR of **2i**



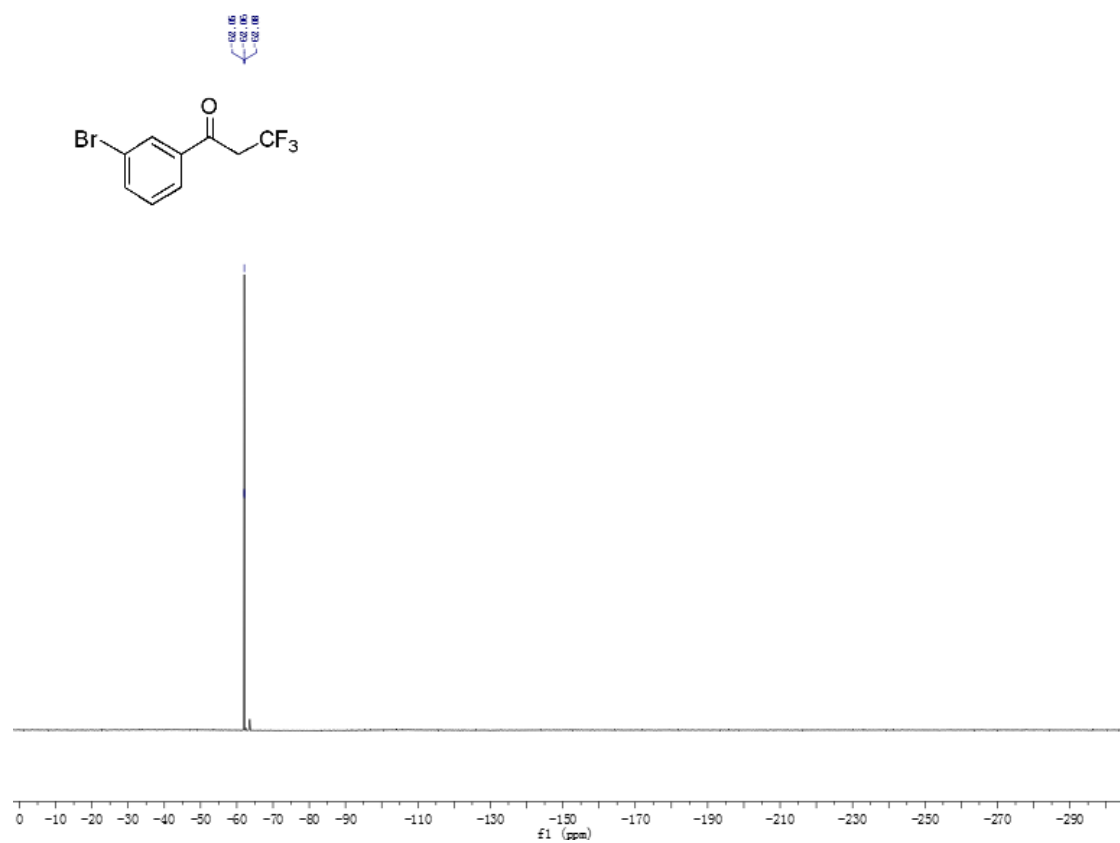
<sup>1</sup>H NMR of **2j**



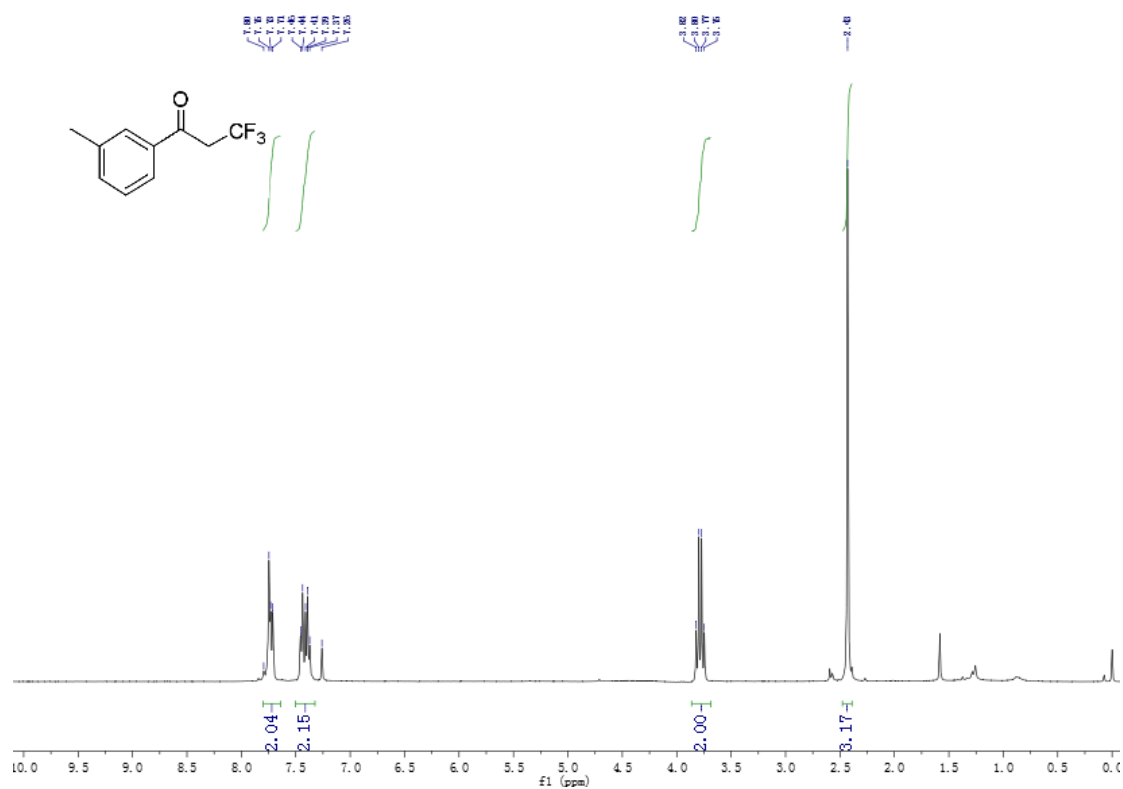
<sup>13</sup>C NMR of **2j**



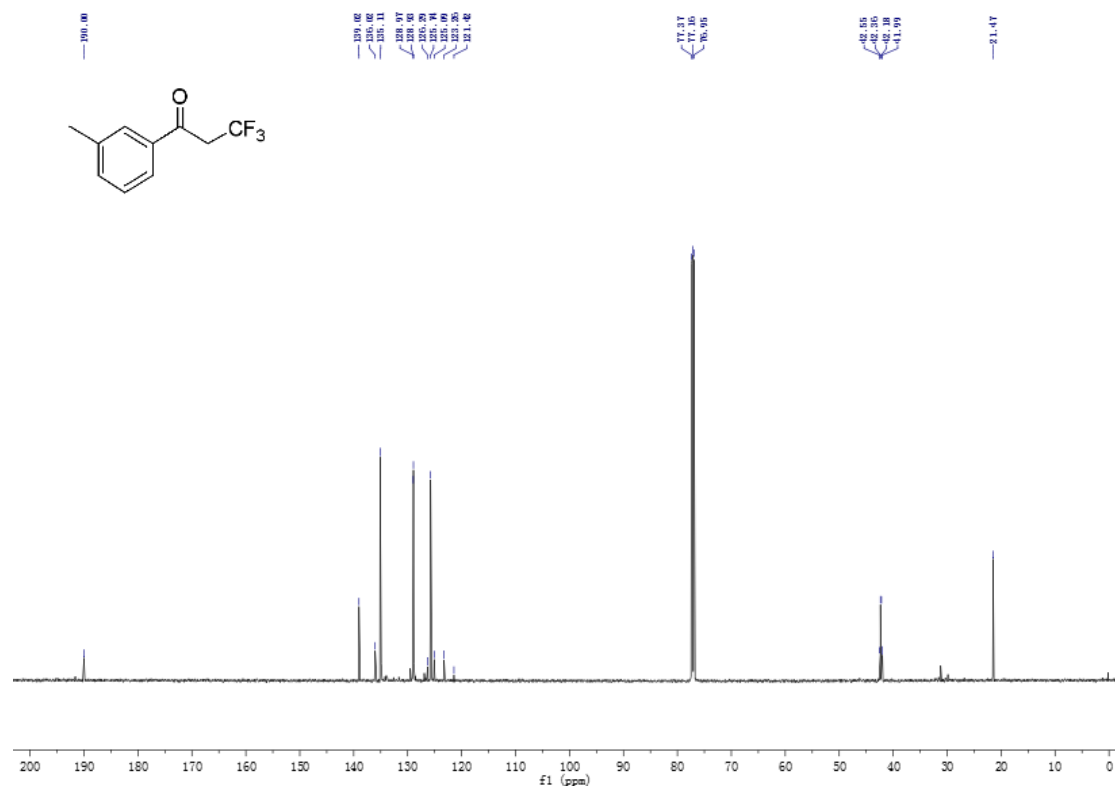
<sup>19</sup>F NMR of **2j**



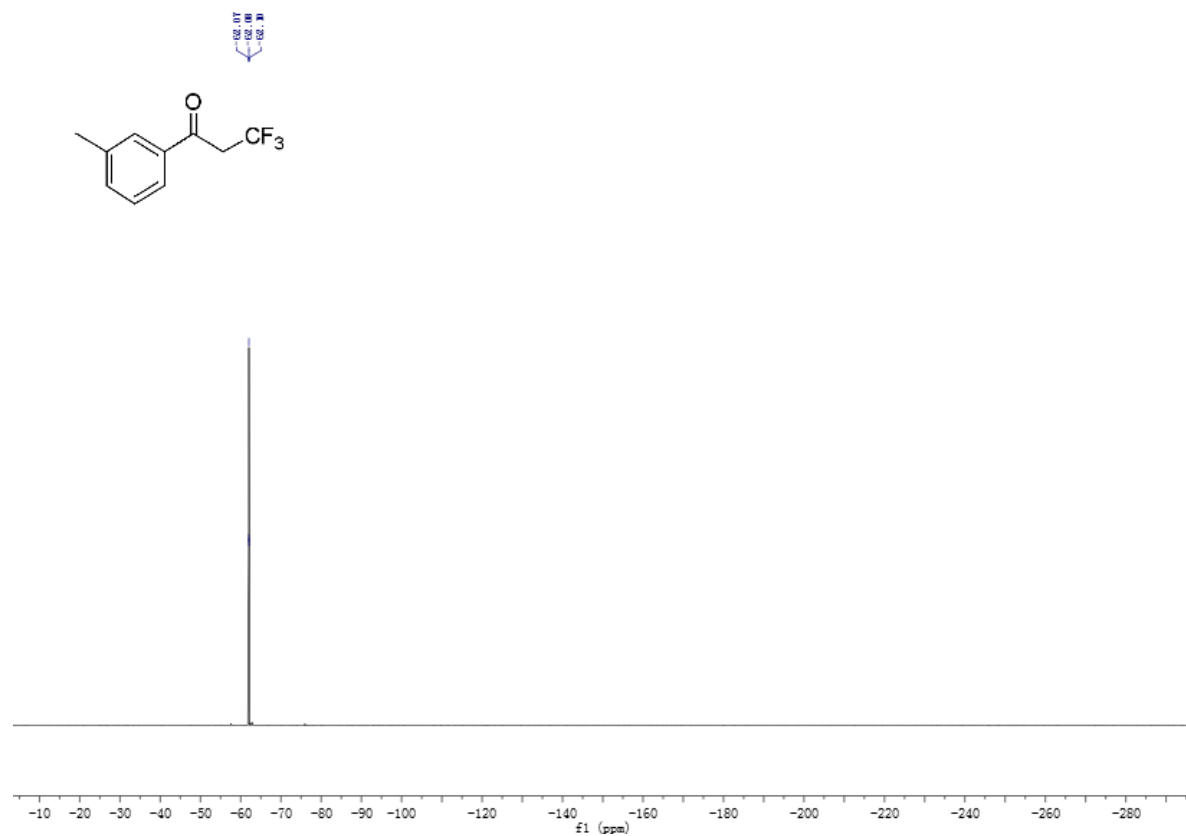
<sup>1</sup>H NMR of 2k



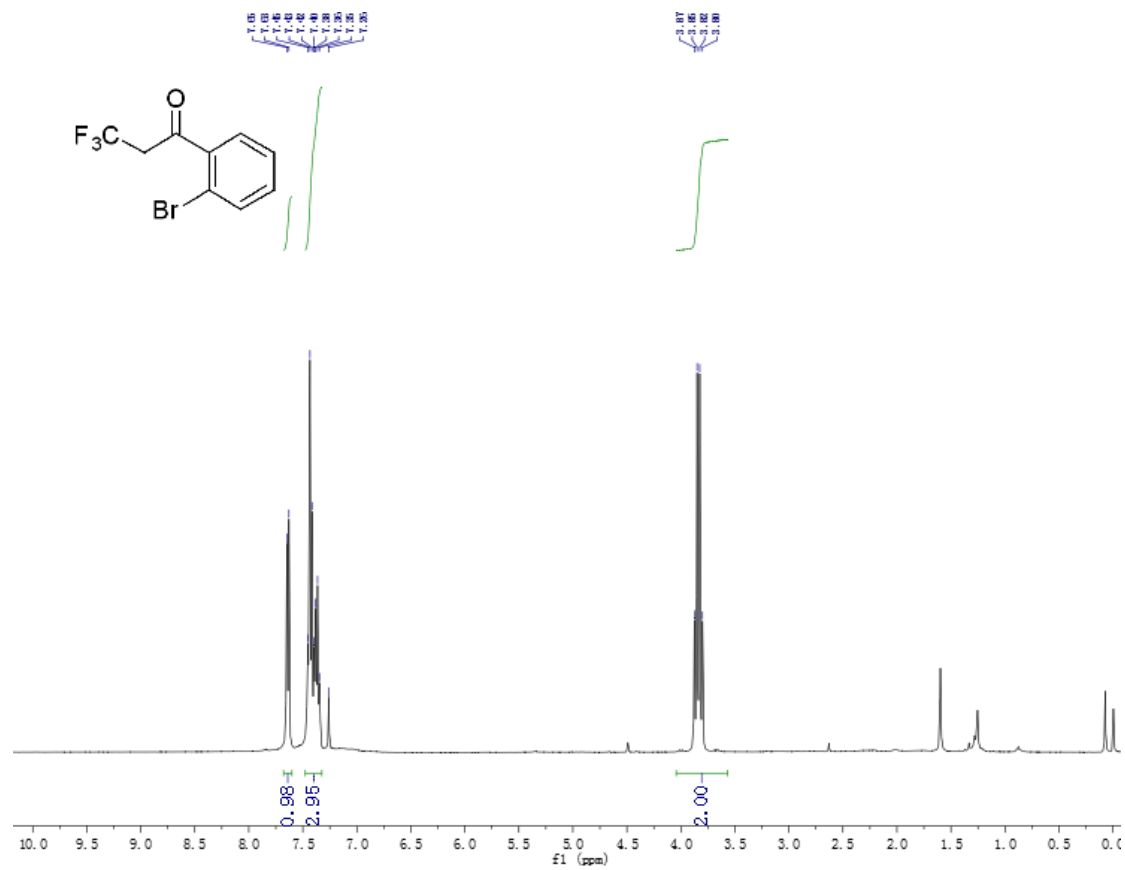
<sup>13</sup>C NMR of 2k



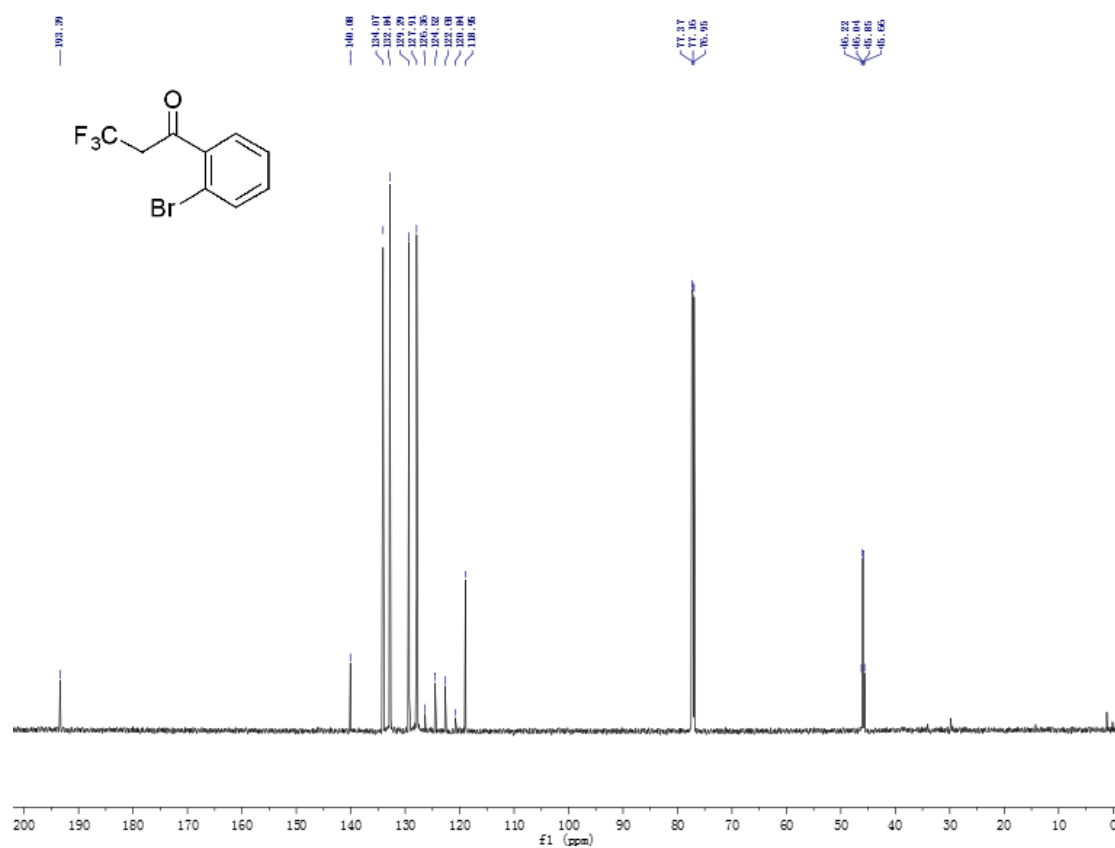
<sup>19</sup>F NMR of 2k



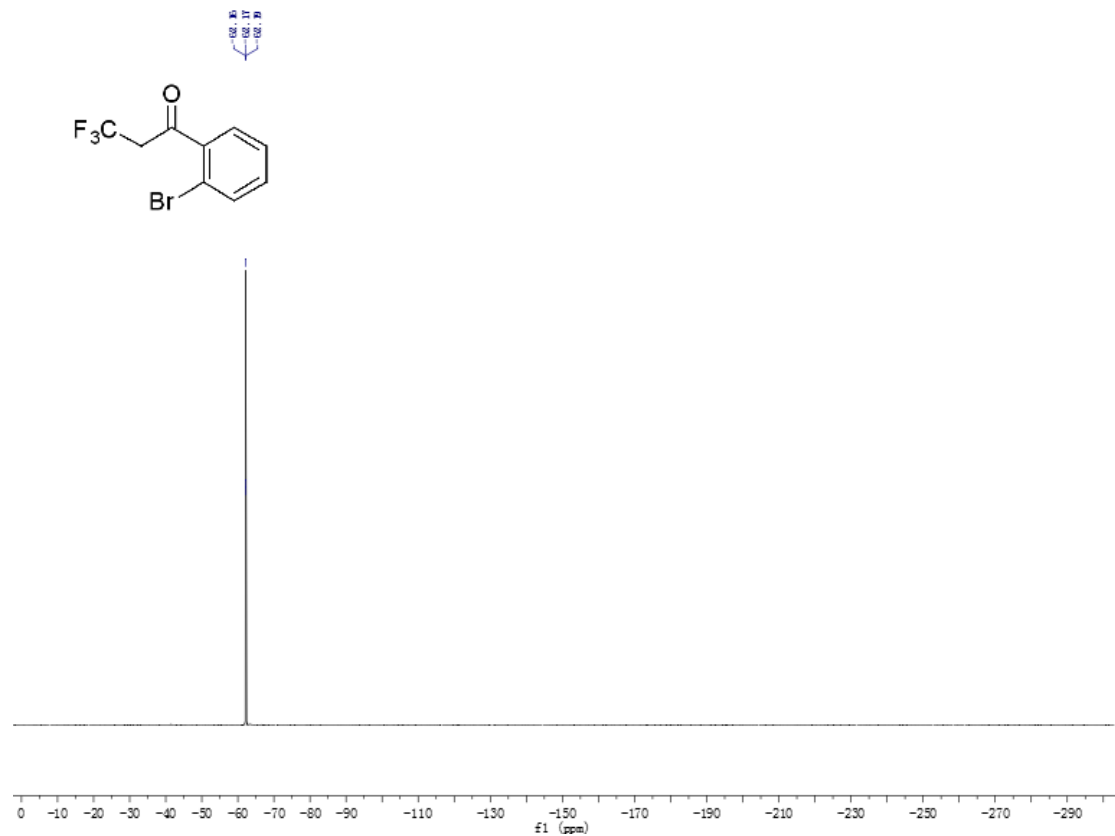
<sup>1</sup>H NMR of 2l



<sup>13</sup>C NMR of **2l**



<sup>19</sup>F NMR of **2l**



**<sup>1</sup>H NMR Spectrum (400 MHz, CDCl<sub>3</sub>) of 2-methoxy-1-(2,2,2-trifluoroethyl)benzene-1-one**

**Chemical Structure:** COc1ccccc1C(=O)CC(F)(F)F

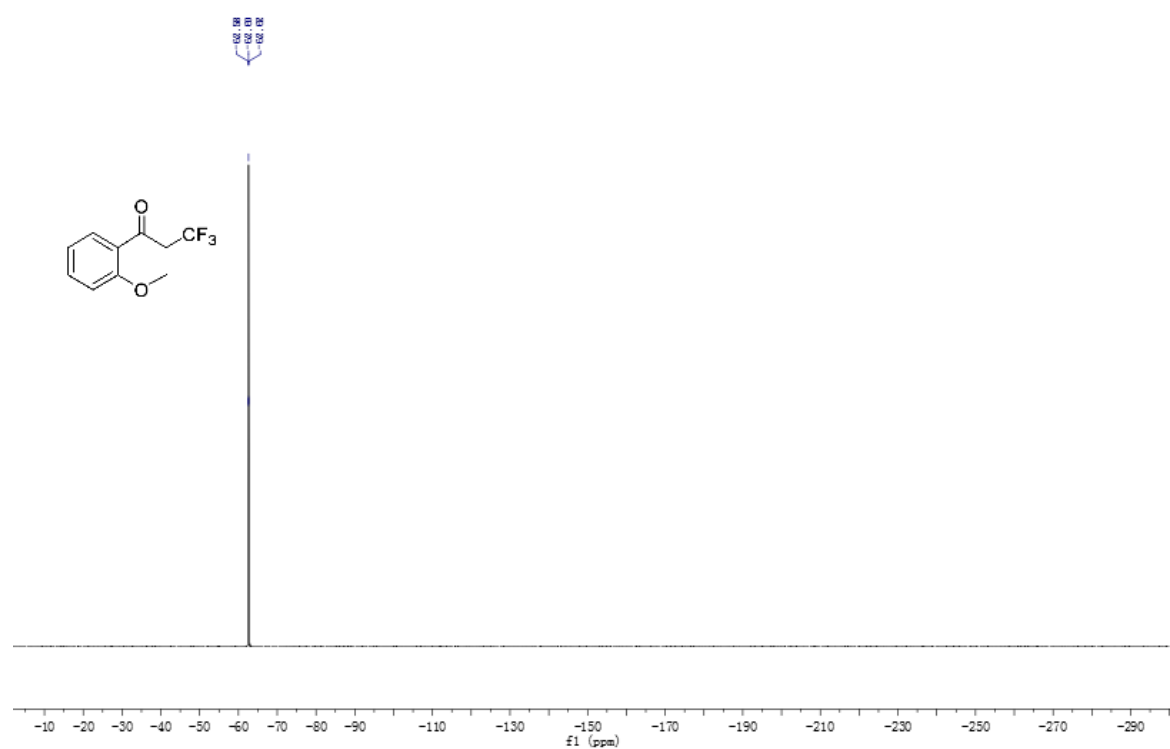
**Peak Data:**

| Chemical Shift (ppm)                   | Multiplicity                                        | Integration            |
|----------------------------------------|-----------------------------------------------------|------------------------|
| 7.75 (d), 7.65 (d), 7.55 (d), 7.45 (d) | Aromatic                                            | 0.94, 1.00, 0.93, 0.94 |
| 3.80 (s)                               | Methoxy (-OCH <sub>3</sub> )                        | 3.06                   |
| 3.90 (q)                               | Trifluoroethyl (-CH <sub>2</sub> -CF <sub>3</sub> ) | 1.96                   |

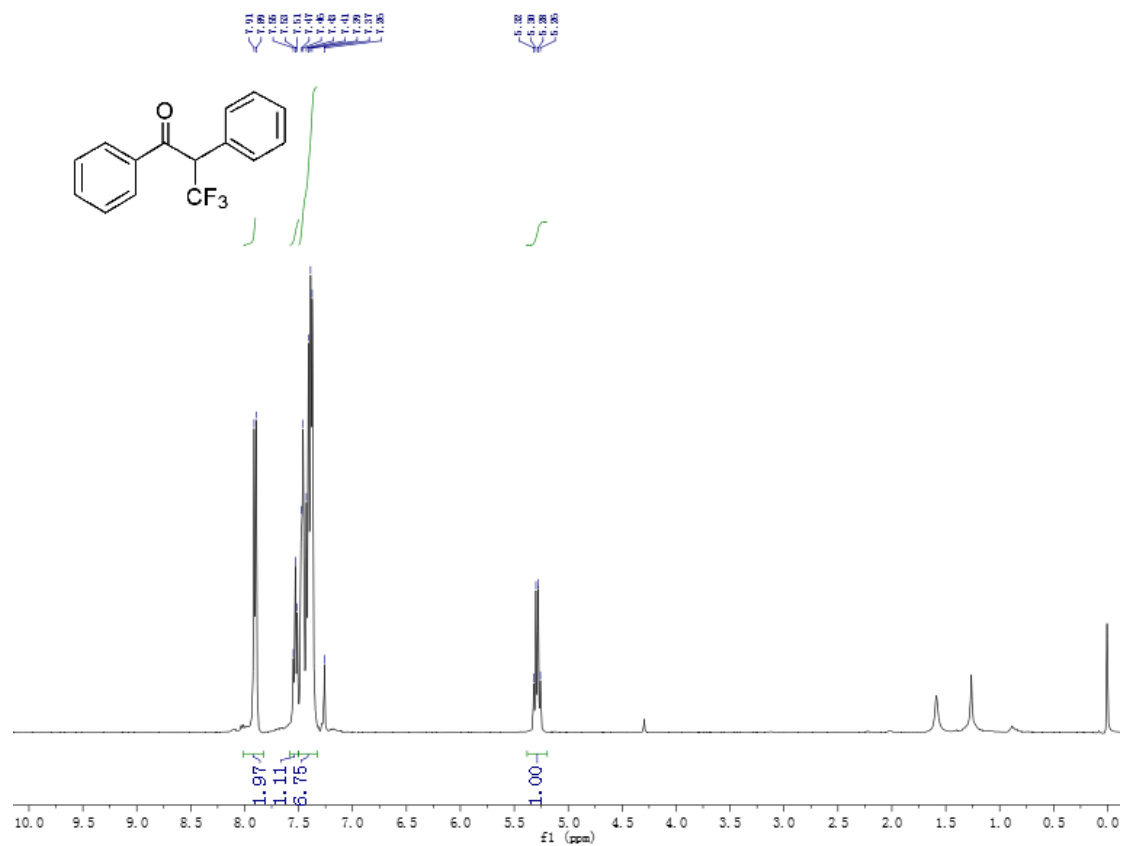
COc1ccccc1C(=O)CC(F)(F)F

13C NMR spectrum (CDCl<sub>3</sub>) of 1-(2-methoxyphenyl)propan-1-one, 2,2,2-trifluoroethyl ester. The spectrum shows peaks at 191.00, 159.05, 135.06, 134.10, 132.71, 126.65, 125.77, 125.46, 123.00, 121.34, 111.88, 77.37, 77.16, 76.95, 55.34, 47.30, 46.94, and 46.75 ppm.

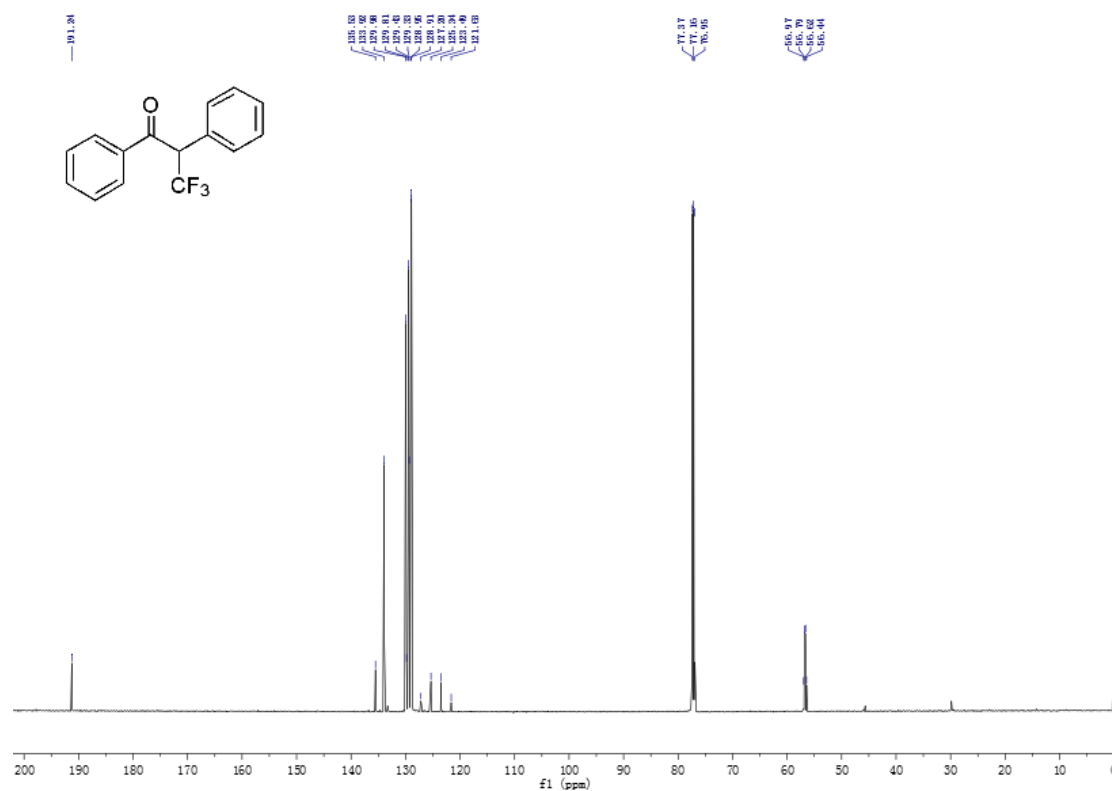
$^{19}\text{F}$  NMR of **2m**



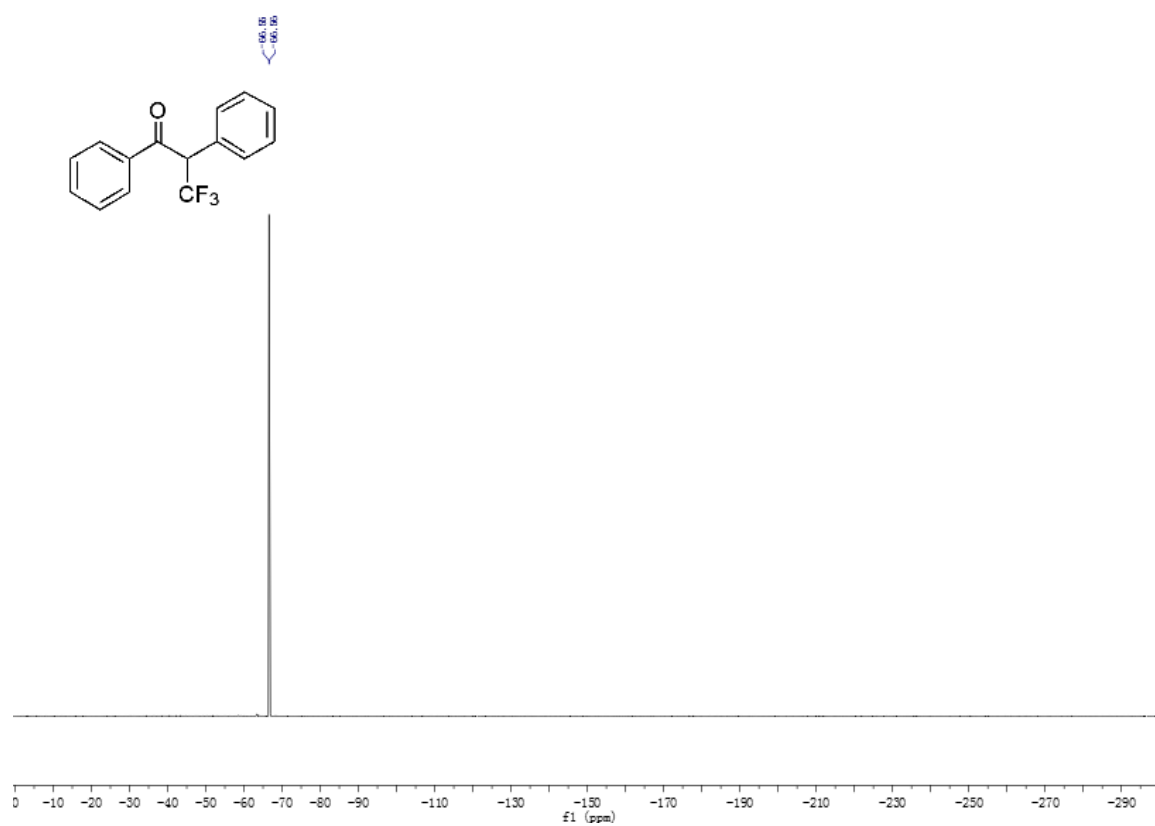
$^1\text{H}$  NMR of **2n**



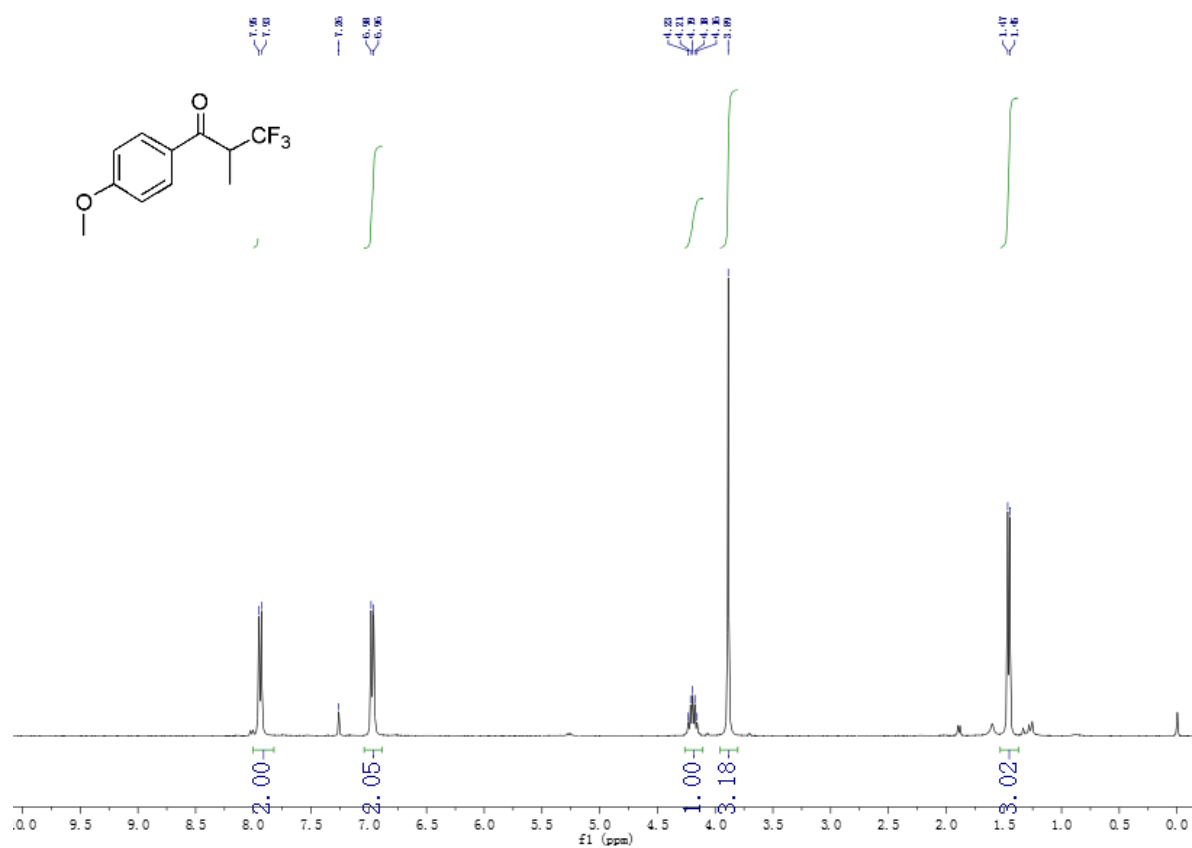
<sup>13</sup>C NMR of **2n**



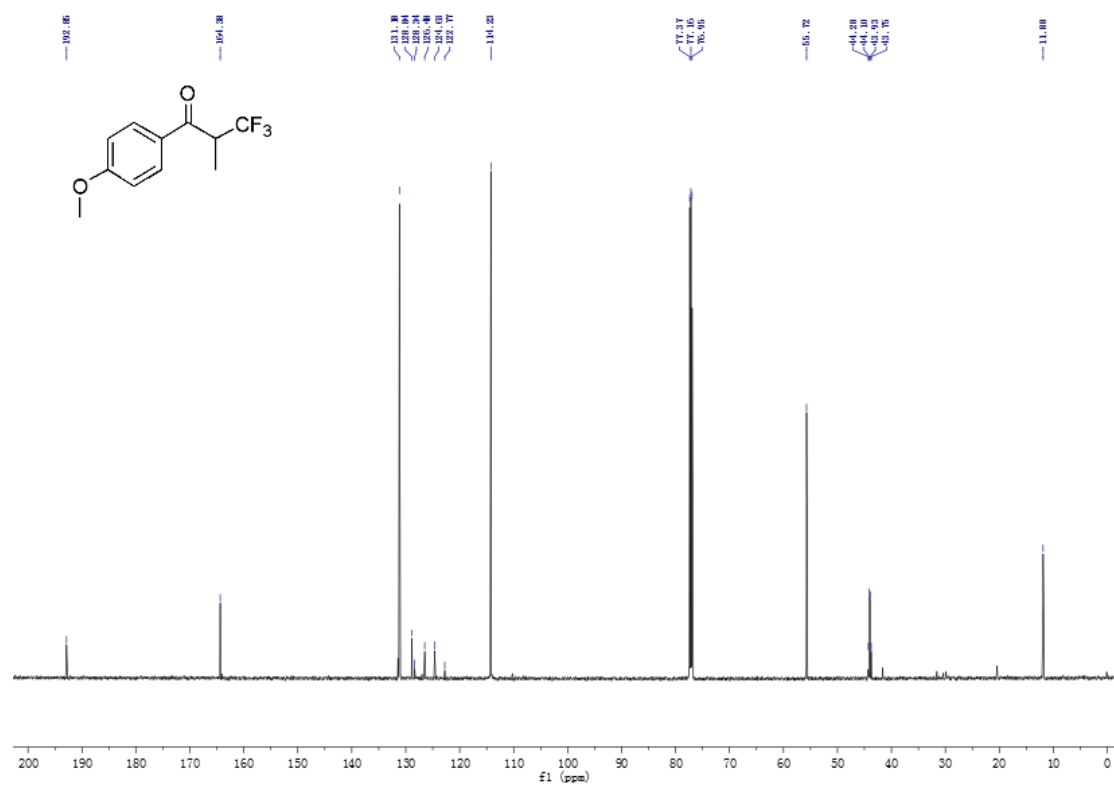
<sup>19</sup>F NMR of **2n**



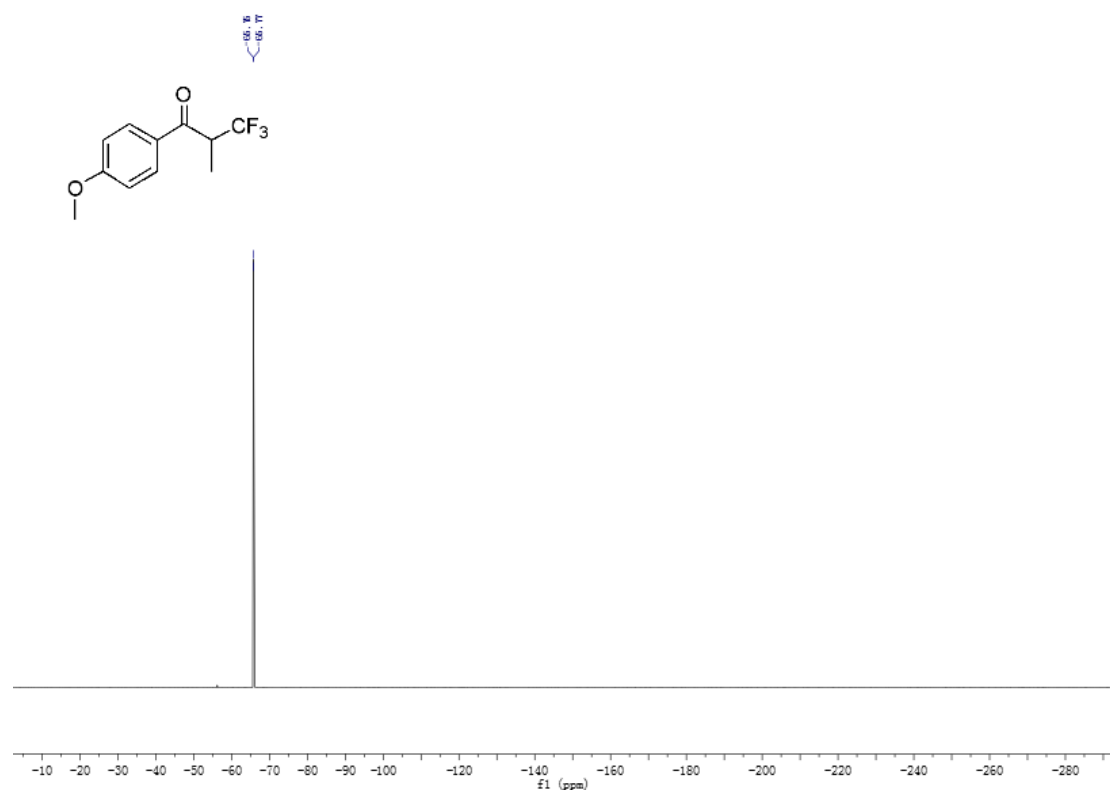
<sup>1</sup>H NMR of **2o**



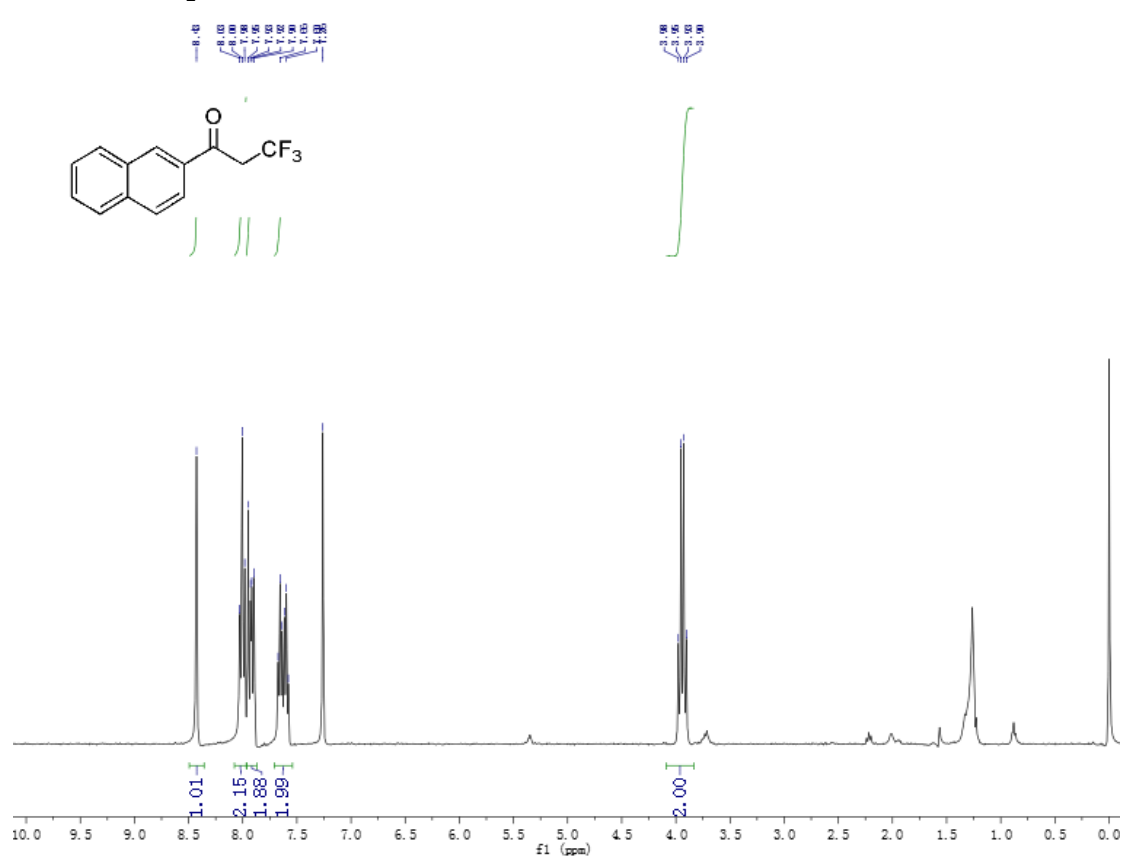
<sup>13</sup>C NMR of **2o**



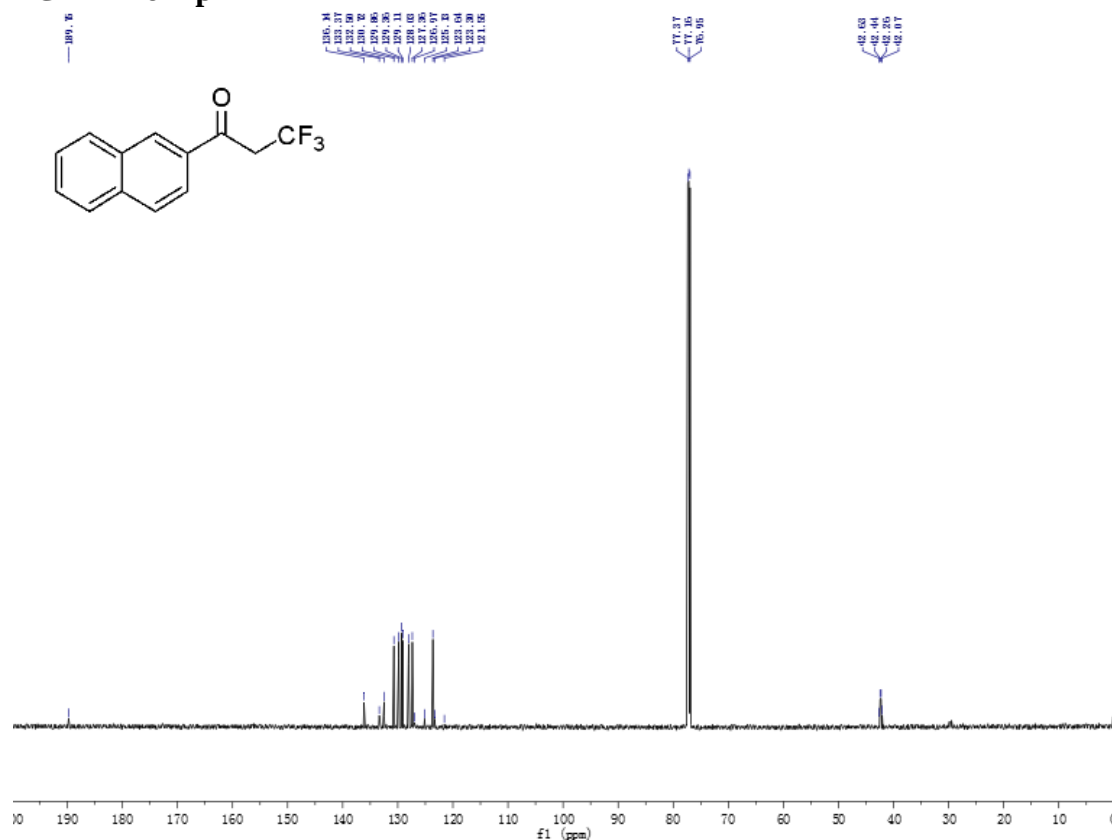
<sup>19</sup>F NMR of **2o**



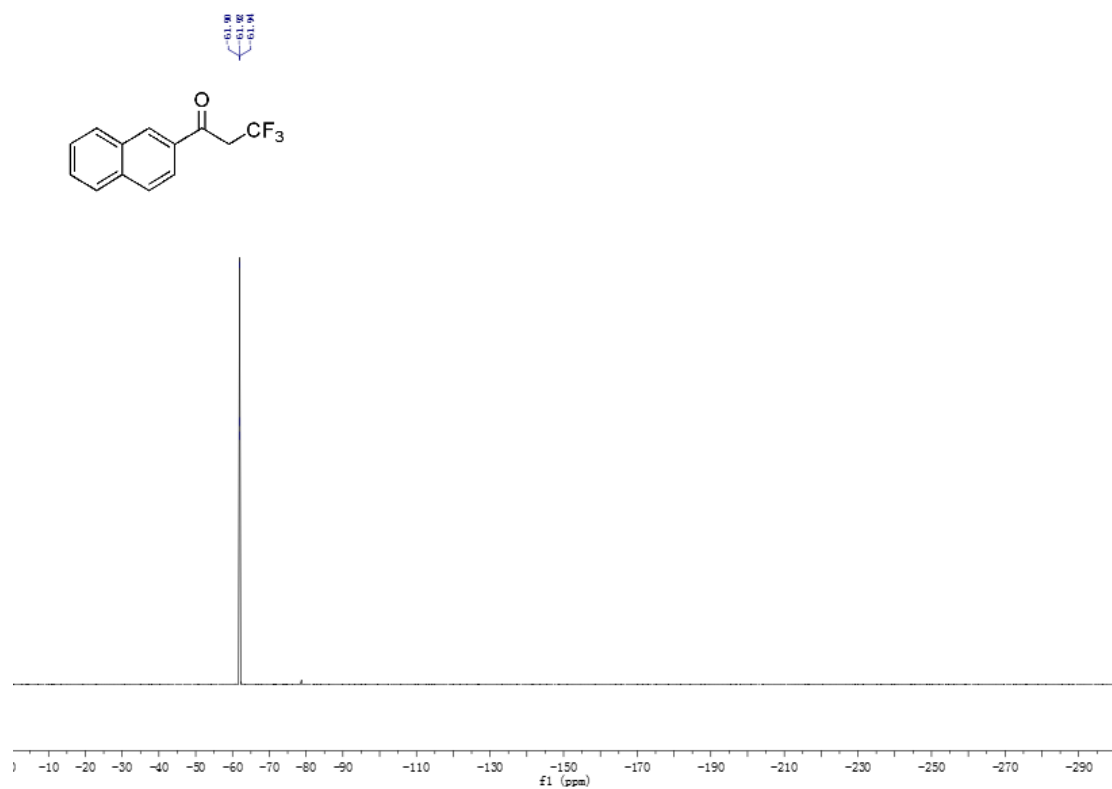
<sup>1</sup>H NMR of **2p**



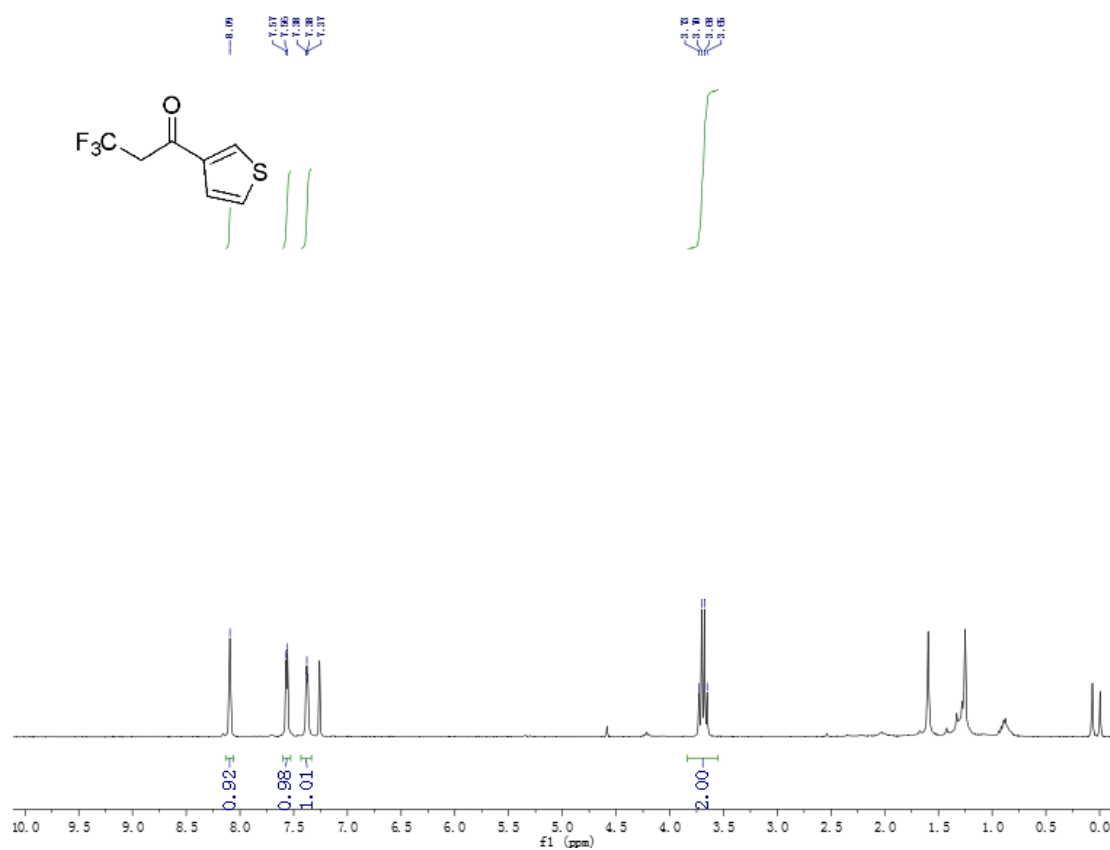
<sup>13</sup>C NMR of **2p**



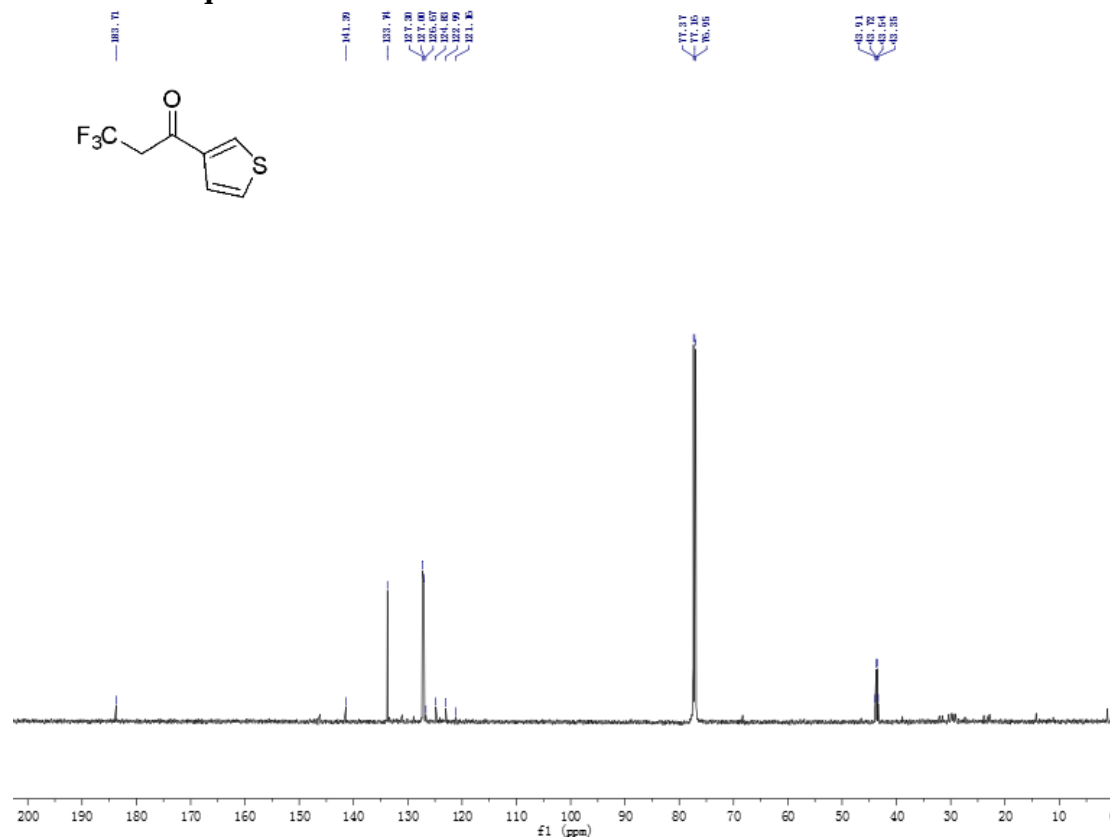
<sup>19</sup>F NMR of **2p**



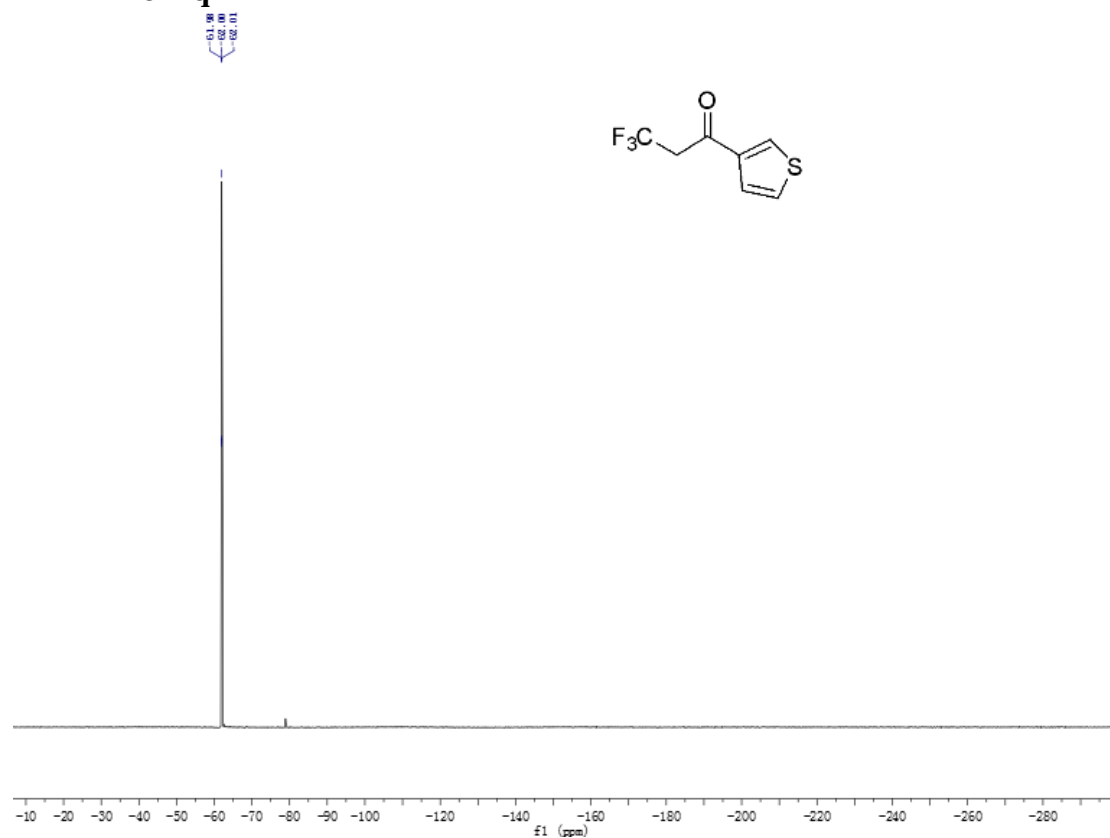
<sup>1</sup>H NMR of **2q**



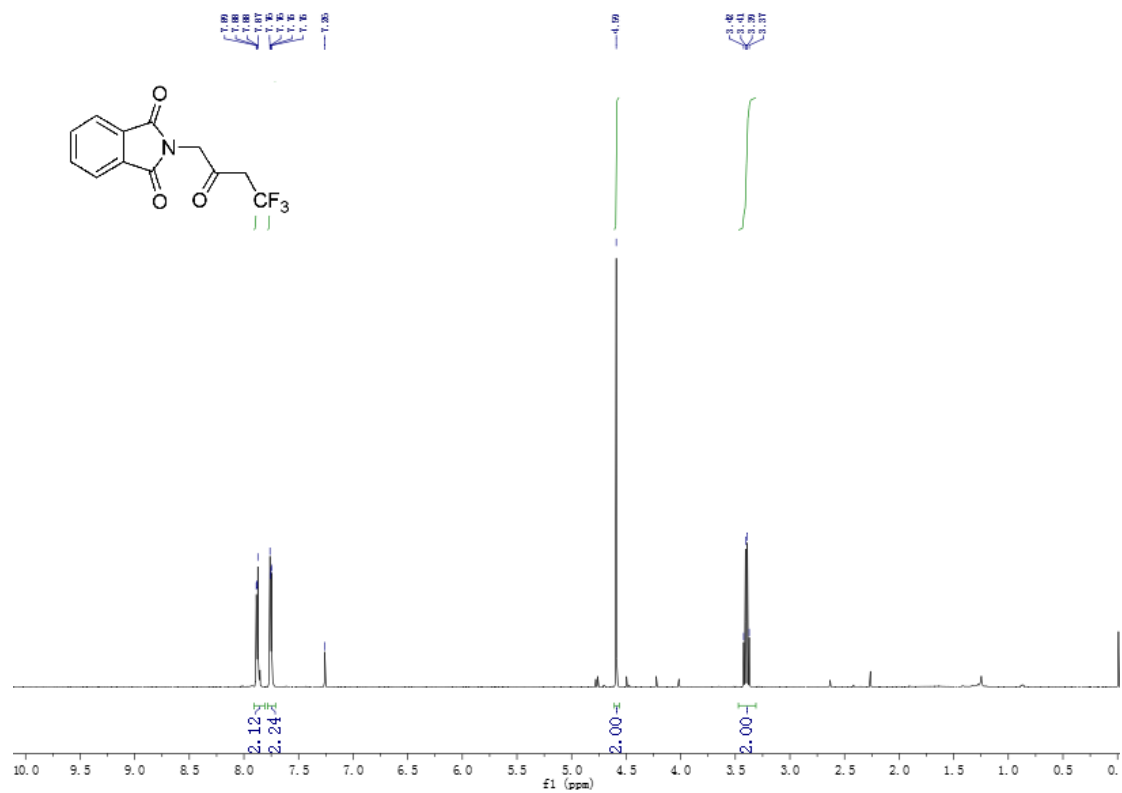
<sup>13</sup>C NMR of **2q**



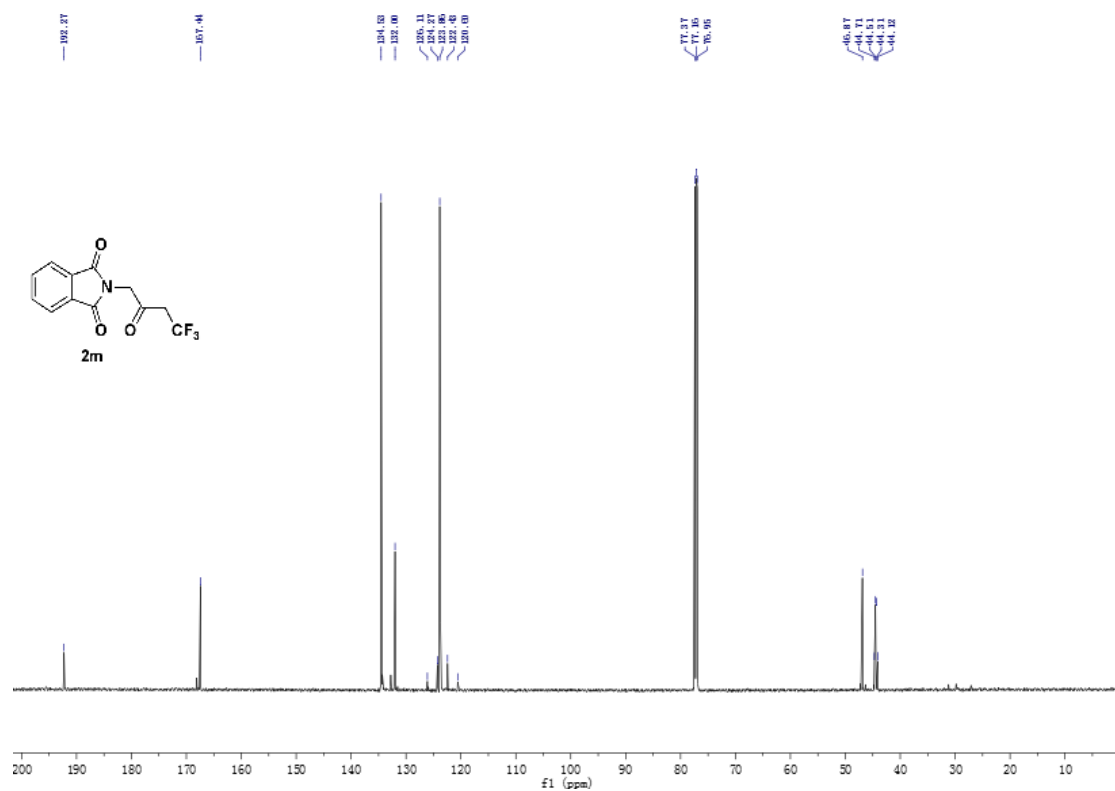
<sup>19</sup>F NMR of **2q**



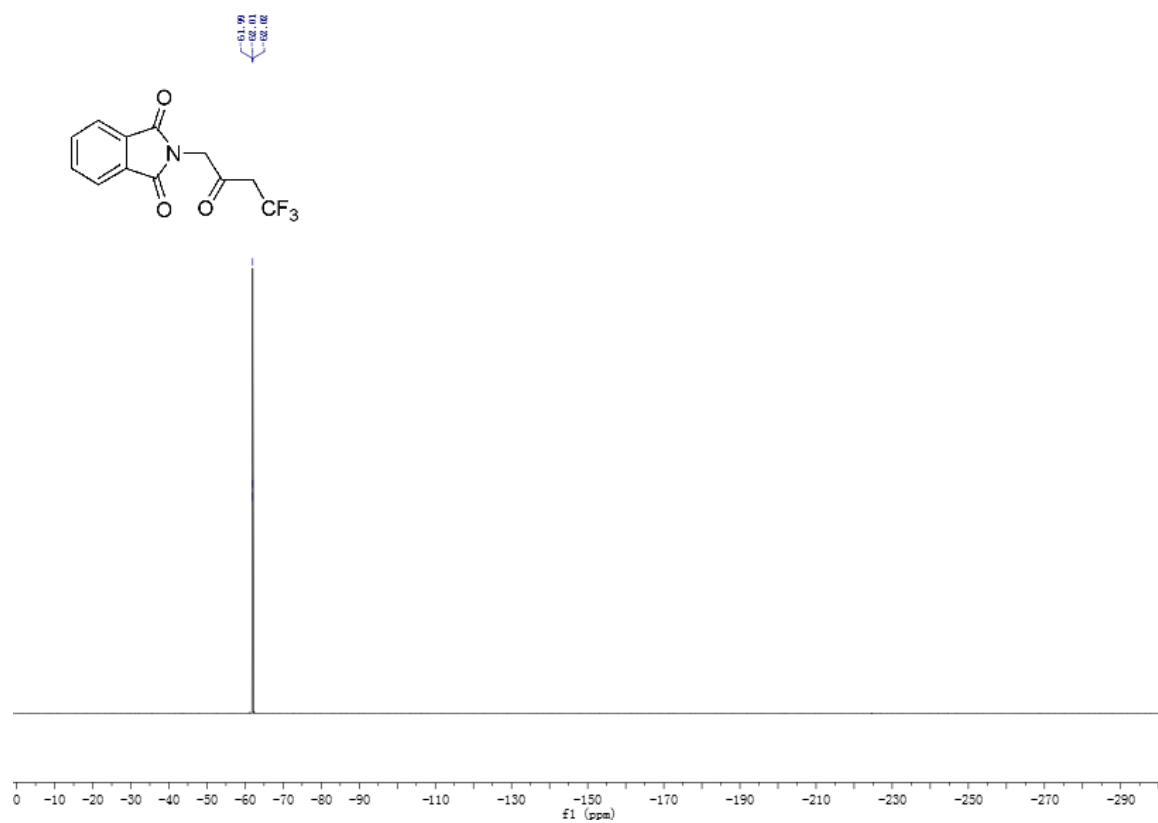
<sup>1</sup>H NMR of **2r**



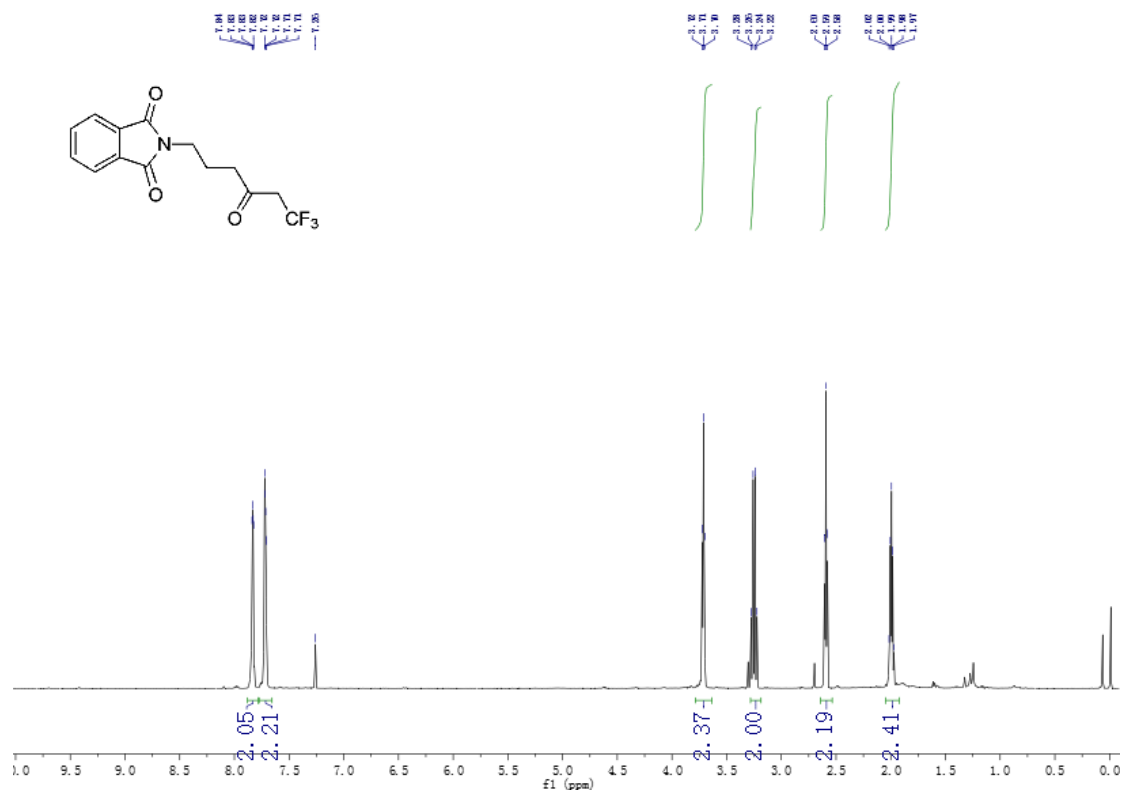
<sup>13</sup>C NMR of **2r**



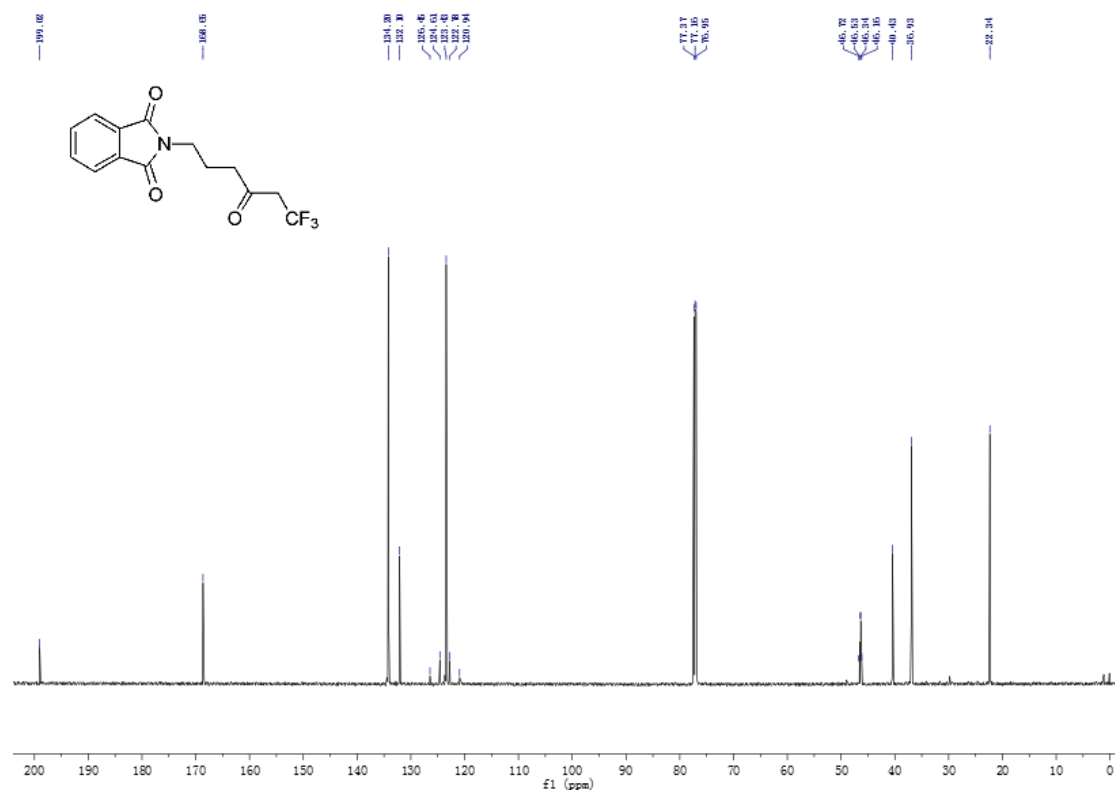
<sup>19</sup>F NMR of **2r**



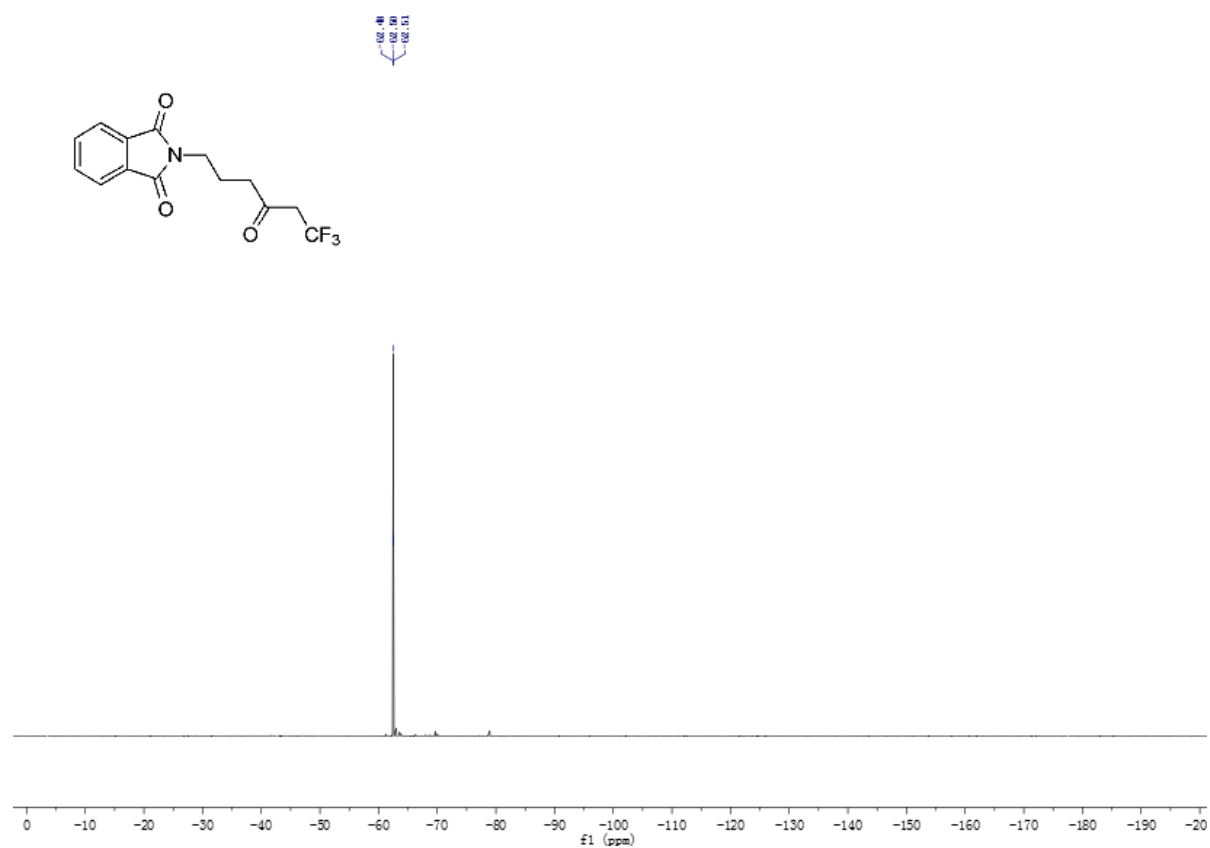
<sup>1</sup>H NMR of 2s



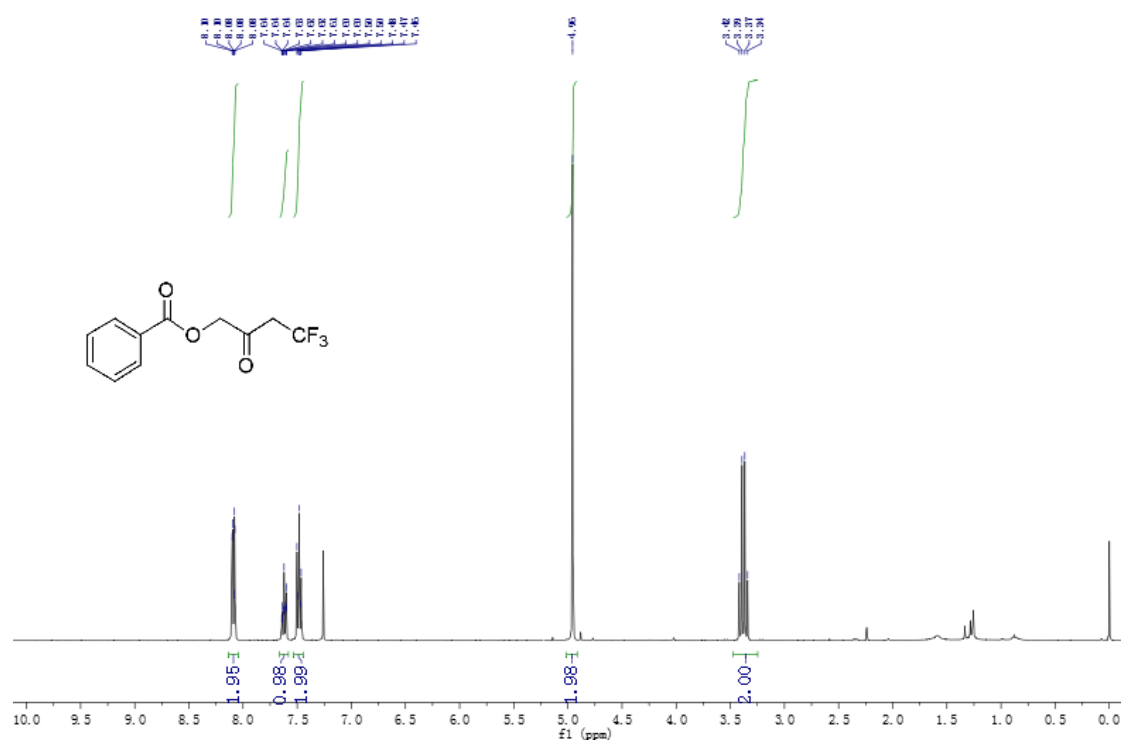
<sup>13</sup>C NMR of 2s



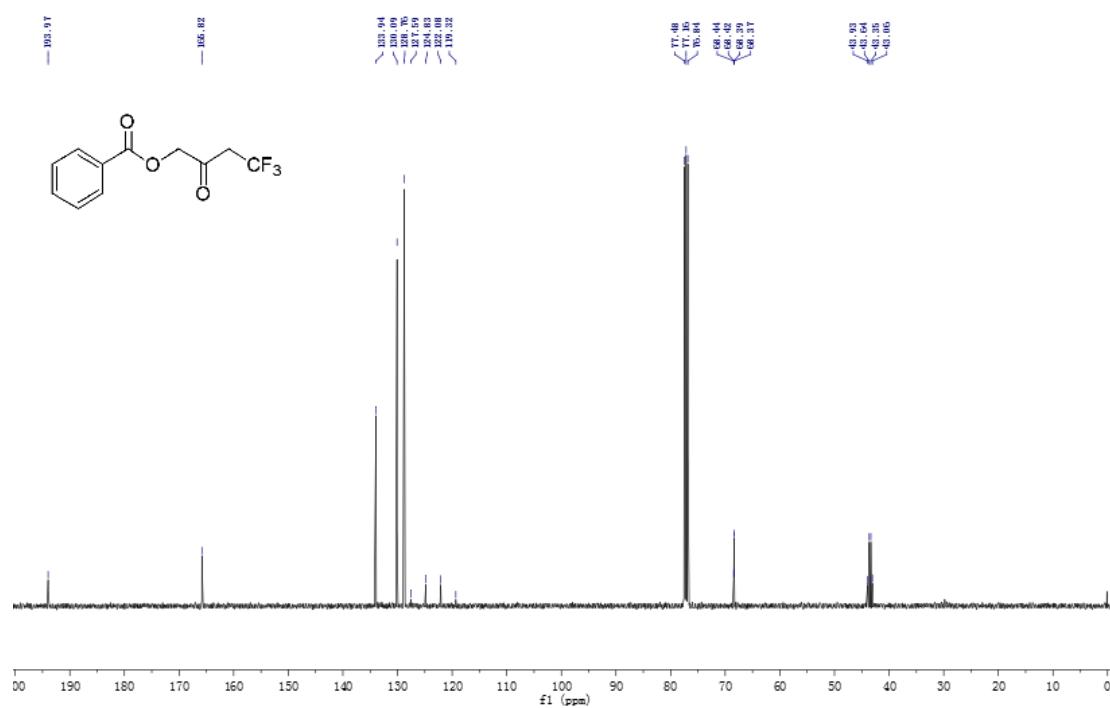
<sup>19</sup>F NMR of 2s



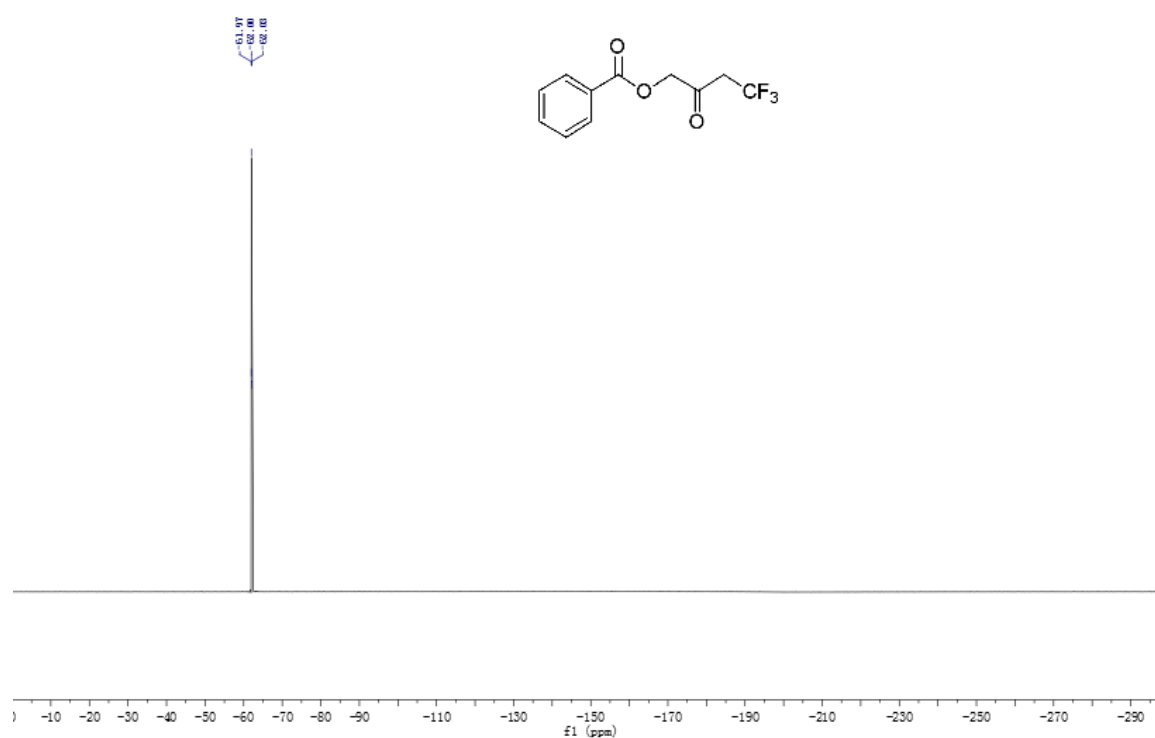
<sup>1</sup>H NMR of 2t



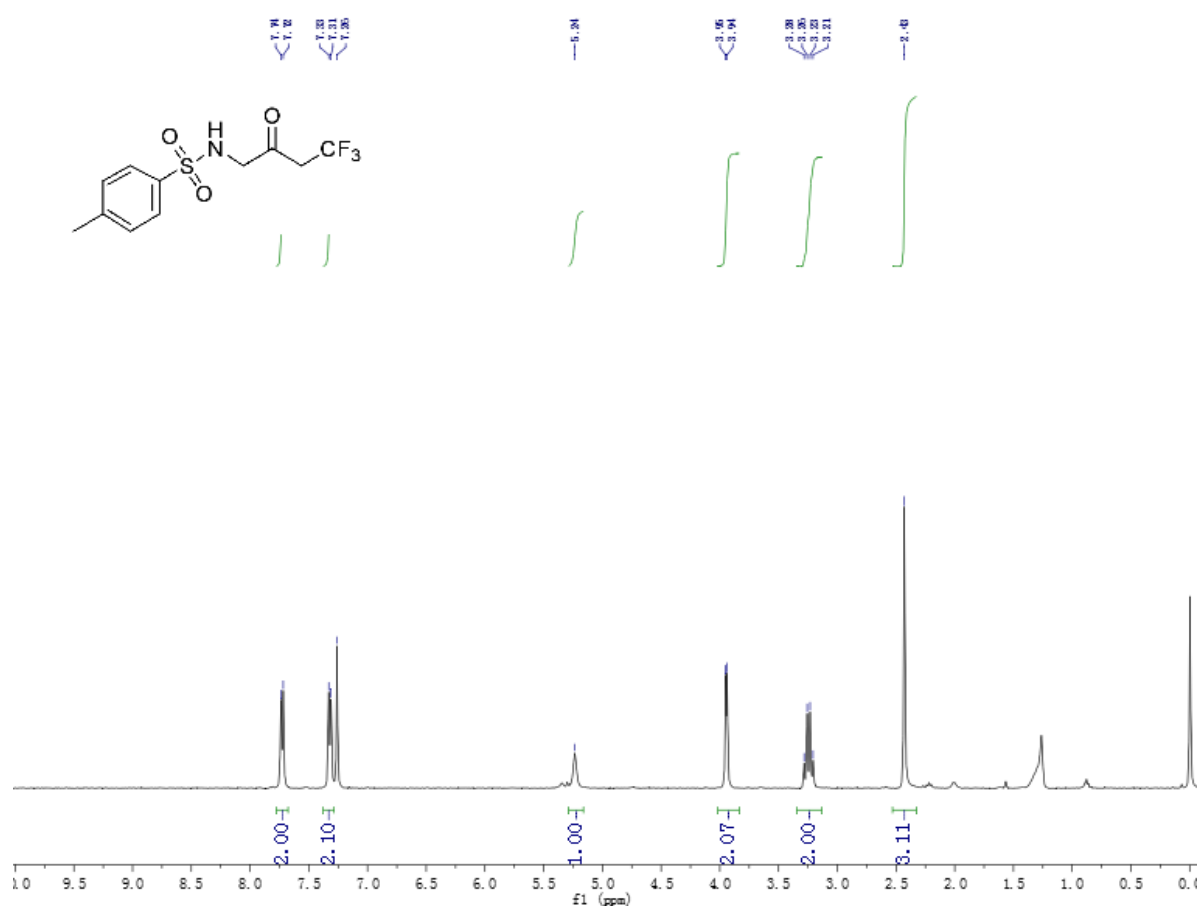
<sup>13</sup>C NMR of **2t**



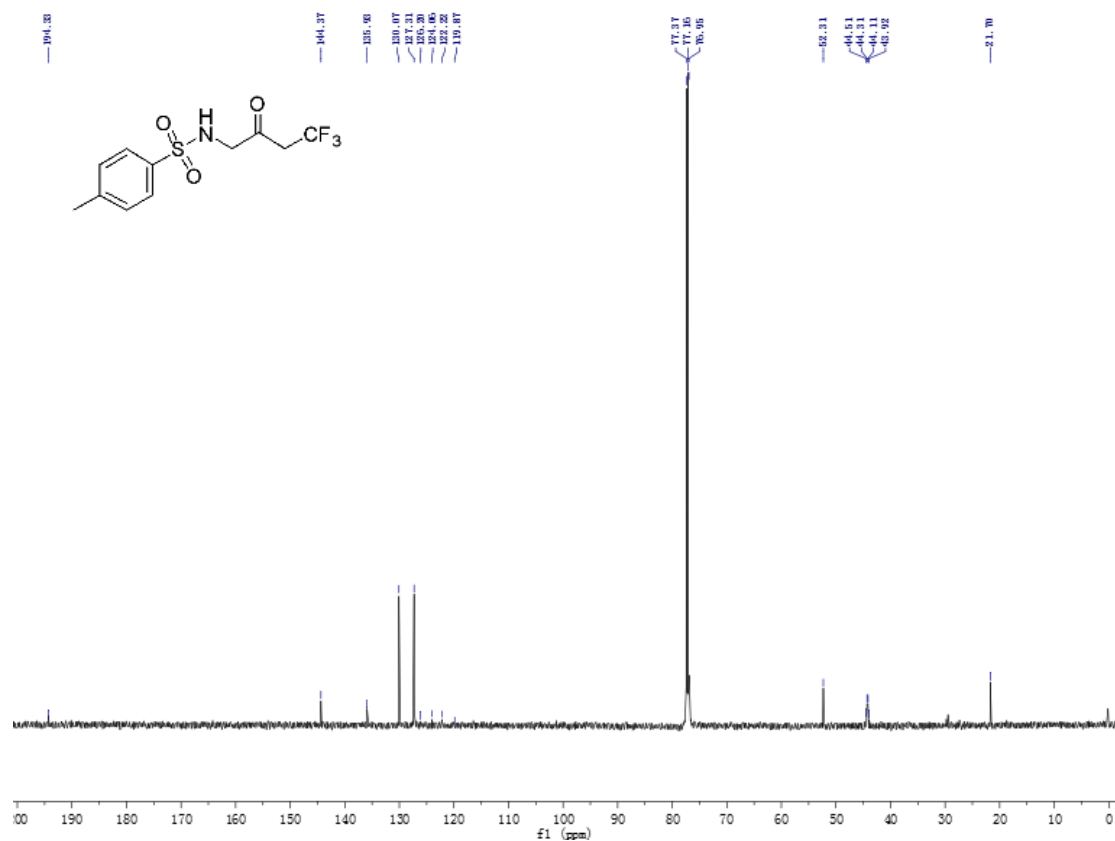
<sup>19</sup>F NMR of **2t**



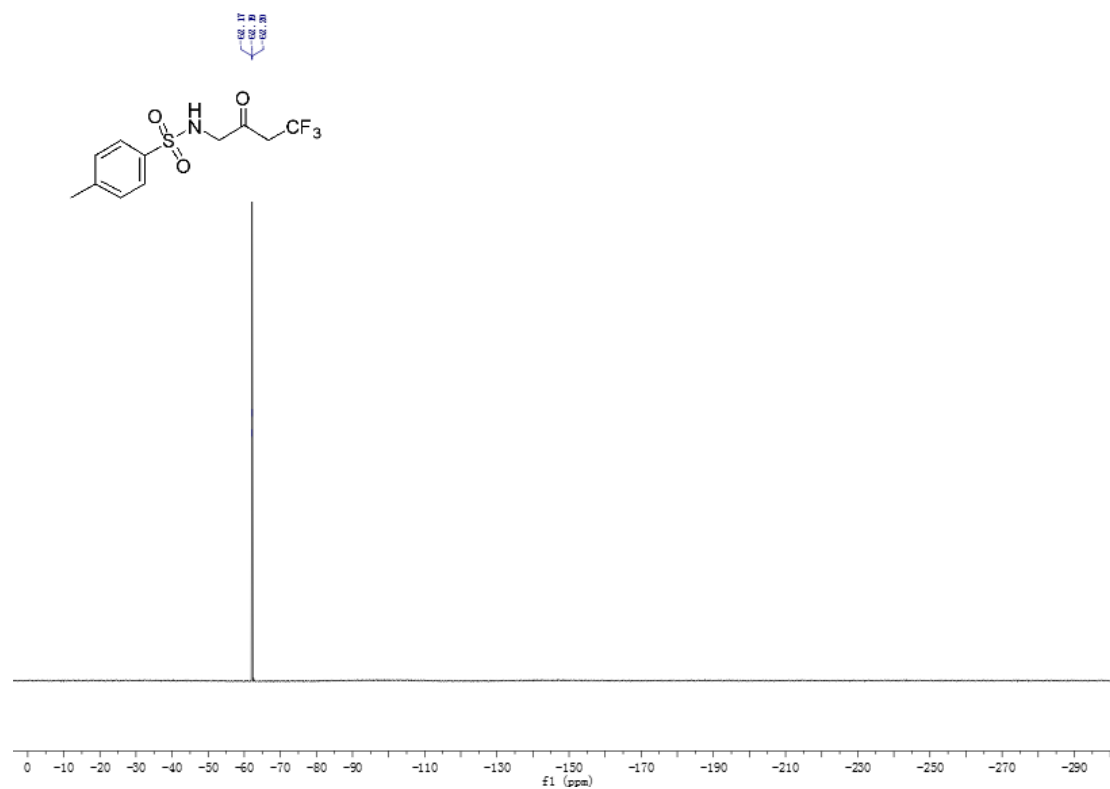
<sup>1</sup>H NMR of **2u**



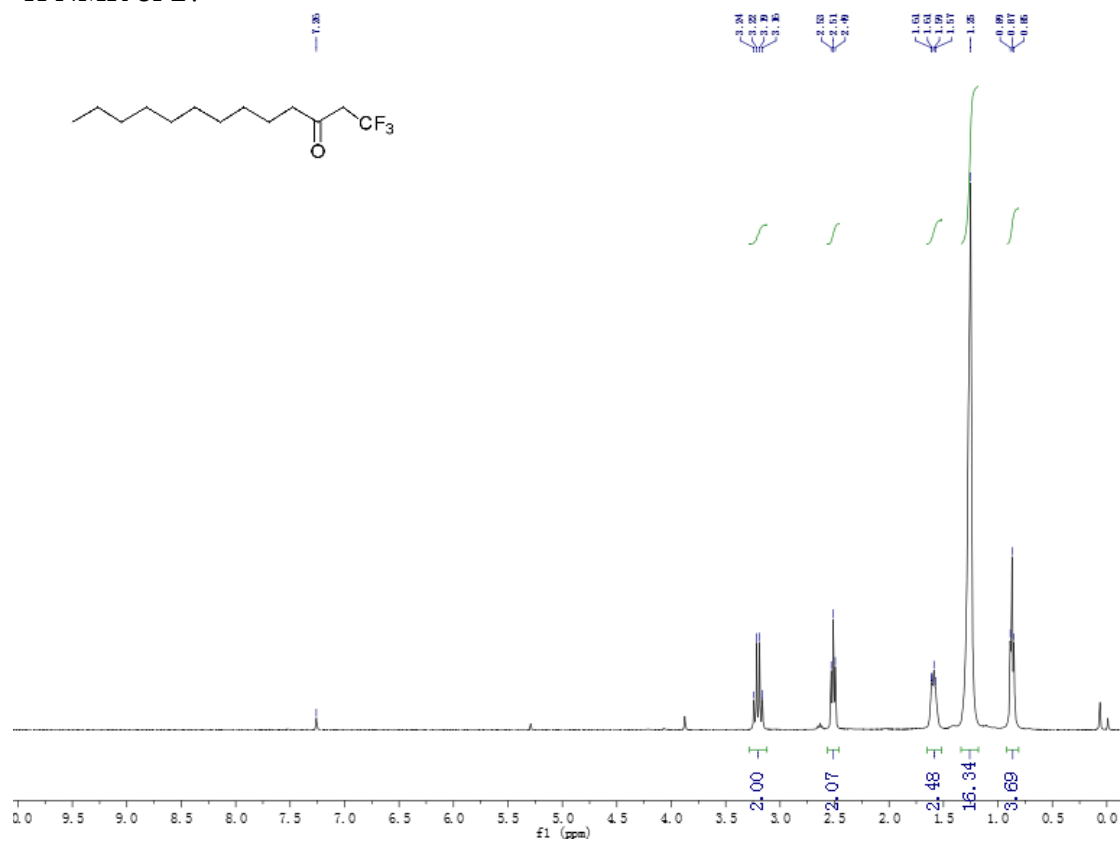
<sup>13</sup>C NMR of **2u**



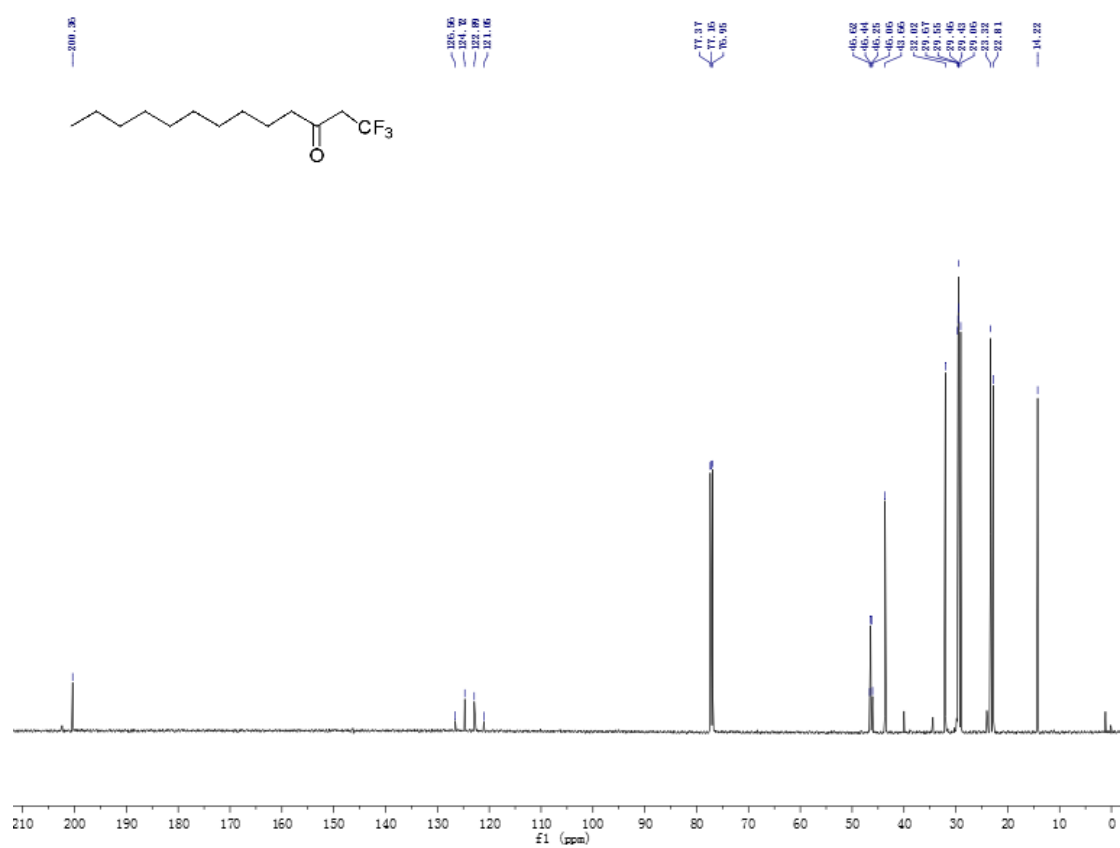
<sup>19</sup>F NMR of **2u**



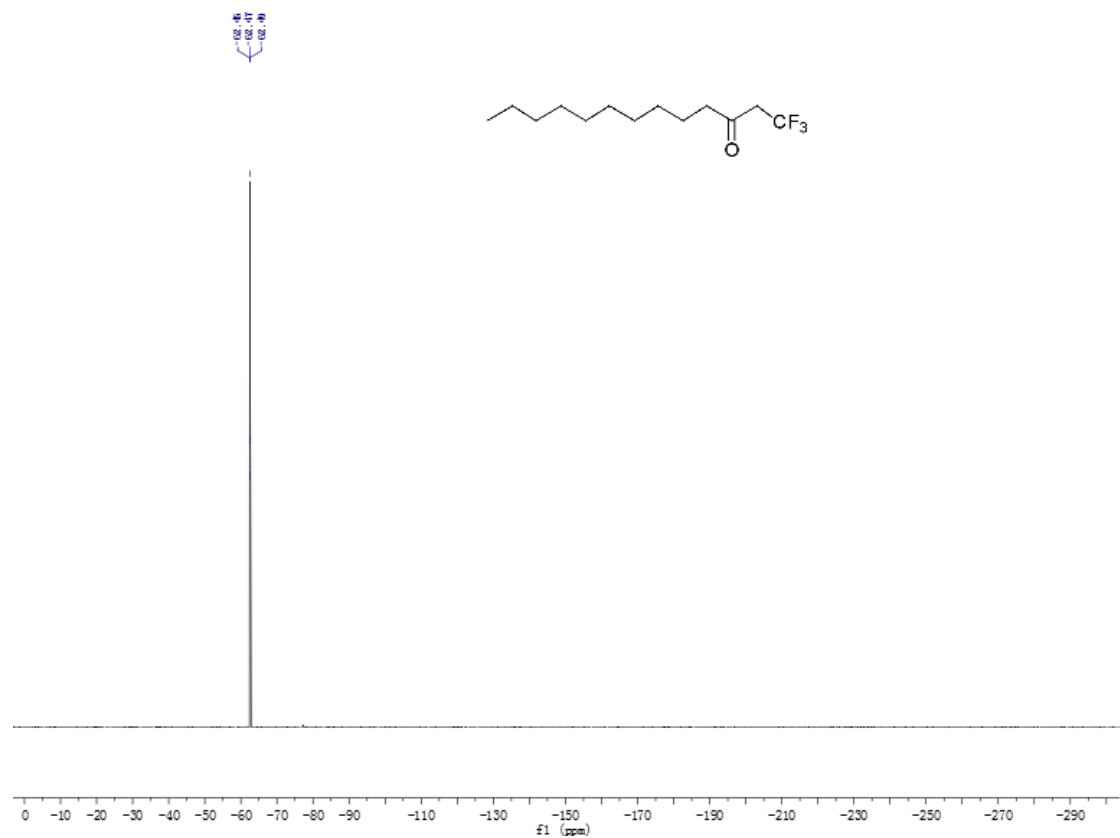
<sup>1</sup>H NMR of **2v**



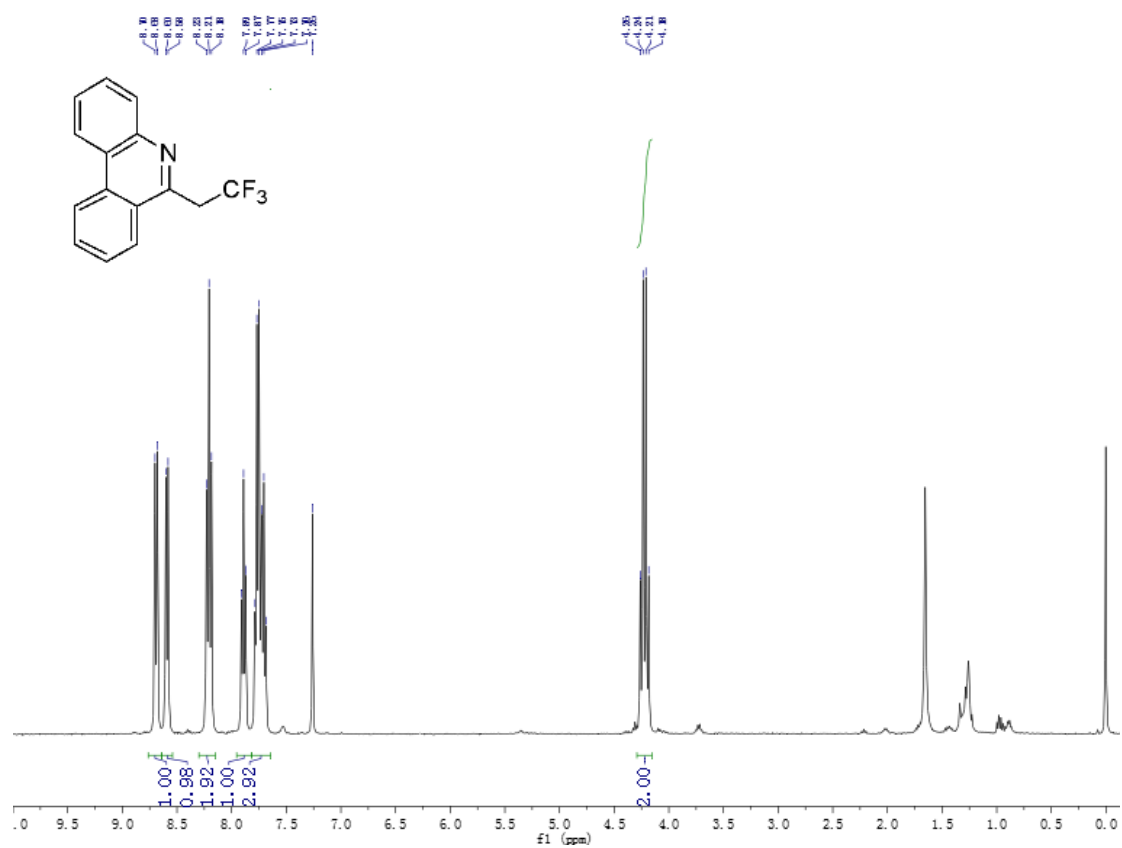
<sup>13</sup>C NMR of **2v**



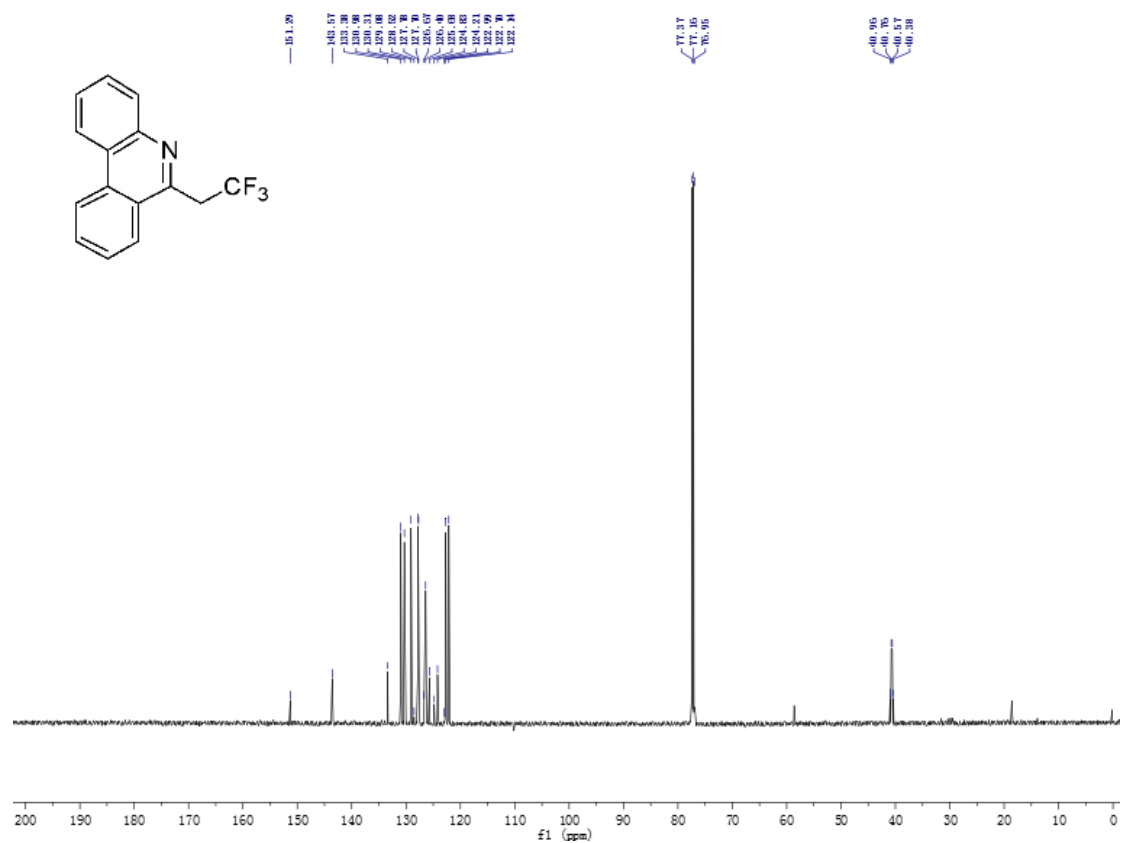
<sup>19</sup>F NMR of **2v**



<sup>1</sup>H NMR of 7



<sup>13</sup>C NMR of 7



$^{19}\text{F}$  NMR of 7

