

## Supporting Information

### Visible-Light-Induced Mesoporous Graphitic Carbon Nitride-Catalyzed Trifluoromethylation and Perfluoroalkylation of 4-Aminocoumarins

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## 1. General Information

Unless otherwise specified, all reagents and solvents were obtained from commercial suppliers and used without further purification.  $^1\text{H}$  NMR spectra were recorded at 400 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz by using a Bruker Avance 400 spectrometer in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  with TMS as internal standard. The chemical shifts ( $\delta$ ) were expressed in ppm and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Bruker Tensor II Fourier infrared spectrometer (Bremen, Germany) was used to analyze the functional group of catalyst. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder diffractometer. The absorption spectrum was recorded using a Hitachi UV-2910 UV spectrophotometer (Tokyo, Japan). High-resolution mass spectral (HRMS) analysis was performed on a Bruker micr OTOF-Q II instrument using ESI techniques. TLC analysis was performed using precoated glass plates. Column chromatography was performed on silica gel (200-300 mesh). 4-anilinocoumarins were prepared according to literature.<sup>1</sup>

### The Light Source and the Material of the Irradiation Vessel

Manufacturer: Beijing Rogertech Ltd.

Model: RLH-18

Broadband source:  $\lambda = 455\text{ nm}$

Material of the irradiation vessel: quartz tube

Not use any filters

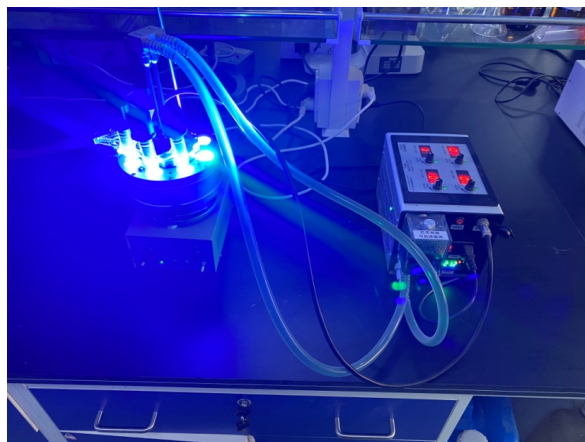
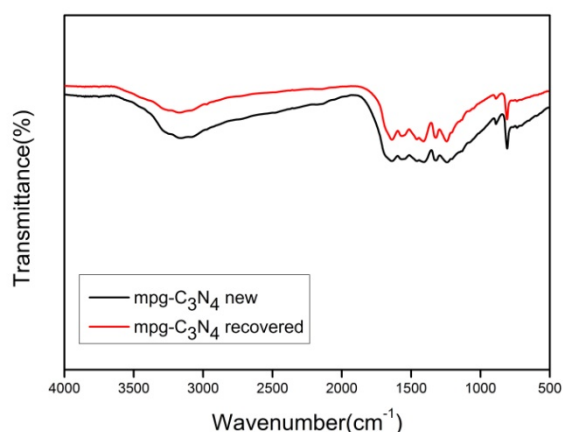


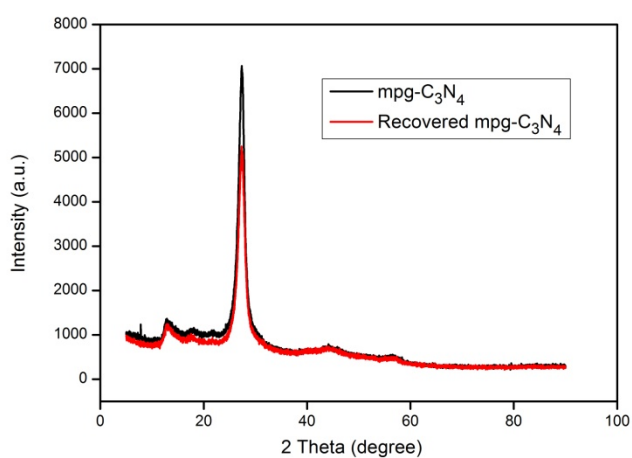
Figure S1 (Photographed by author Ningbo Li)

## 2. Experimental Section

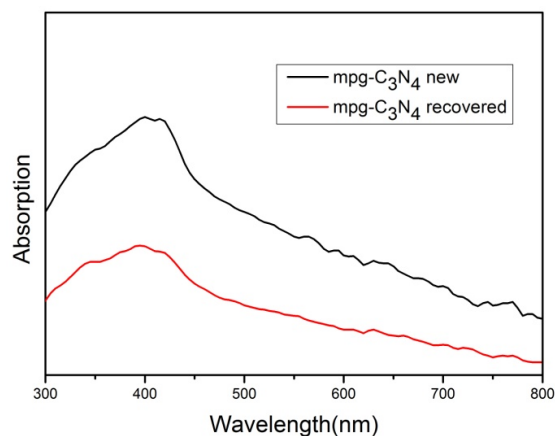
**2.1 Catalyst mpg-C<sub>3</sub>N<sub>4</sub> synthesis:** mpg-C<sub>3</sub>N<sub>4</sub> was synthesized according to the following literature<sup>2</sup>. A mixture of cyanamide (3.00 g) and colloidal silica aqueous solution (Ludox HS-40, 40 wt. %, 7.50 g) was stirred in a glass vial at room temperature for about 15 minutes until cyanamide was dissolved completely. Water was slowly evaporated upon stirring the mixture overnight at 60 °C. Magnetic stirring bar was removed and the white solid was transferred into a porcelain crucible and calcinated at 550 °C for 4 h under flow of nitrogen in a muffle oven. The oven was allowed to cool to room temperature, the content from the crucible was transferred into a polypropylene bottle, NH<sub>4</sub>HF<sub>2</sub> (12.0 g), and water (50 mL) were added. The mixture was then stirred at room temperature for 24 h. Solid was separated by filtration and washed thoroughly with water, ethanol, and dried overnight in a vacuum drying oven (50 °C). Yield: 1.75 g. All analytical data (FTIR, XRD, UV/Vis, SEM, etc., see Figure S2-S5) are in full agreement with those published in the literature.<sup>2-4</sup>



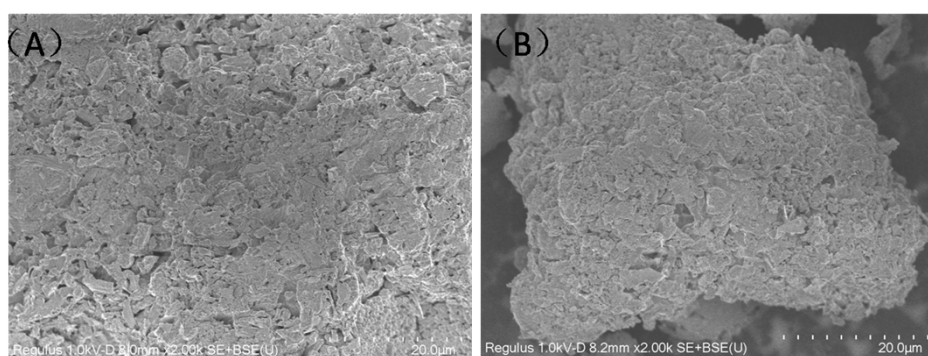
**Figure S2.** FTIR spectra of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction



**Figure S3.** XRD spectra of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction



**Figure S4.** UV-vis absorption spectra of mpg-C<sub>3</sub>N<sub>4</sub> before and after the photocatalytic reaction

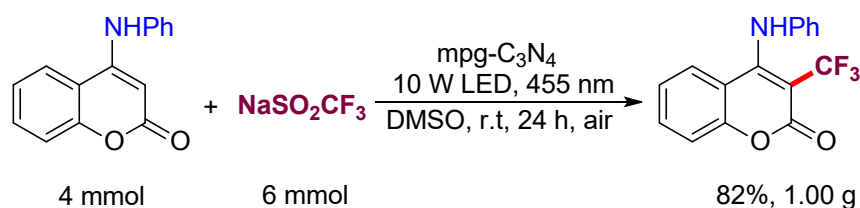


**Figure S5.** (A) SEM image of the fresh catalyst; (B) SEM image of recycled catalyst

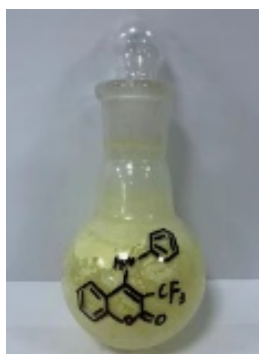
## 2.2 Typical Procedure for Trifluoromethylation of 4-Anilincoumarins:

To a solution of 4-anilincoumarins **1** (0.2 mmol) in DMSO (1 mL) was added CF<sub>3</sub>SO<sub>2</sub>Na **2** (0.3 mmol) and mpg-C<sub>3</sub>N<sub>4</sub> (15 mg). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 10 W LED (455 nm) for about 24 h. Upon the completion of reaction as monitored by TLC, the reaction mixture was transferred to a centrifuge tube (3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged (time approx. 10 minutes) until the mpg-C<sub>3</sub>N<sub>4</sub> precipitates. The supernatant liquid was then collected in a separating funnel, and the solid in the centrifuge tube was washed three times using approx. 10 mL ethyl acetate and collected in the same separating funnel. Then, approx. 15 mL of brine solution was added, shaken, and the organic layer was collected. The water layer was extracted again with ethyl acetate (3 × 10 mL). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent (PE/EA = 5/1-3/1) to give the desired products **3**.

### 2.3 Procedure for gram-scale synthesis of 3a



To a solution of 4-anilincoumarin **1a** (4 mmol) in DMSO (15 mL) was added  $\text{CF}_3\text{SO}_2\text{Na}$  **2** (6 mmol) and mpg- $\text{C}_3\text{N}_4$  (0.35 g). The reaction mixture was open to the air and stirred at room temperature under the irradiation of 10 W LED (455 nm) for about 24 h. After completion of the reaction, the catalyst was filtered and washed with ethyl acetate (15 mL) three times. Then filtrate was quenched with brine (50 mL) and extracted three times with ethyl acetate (15 mL). The combined organic extracts were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (PE/EA = 4/1) afforded the desired products **3aa** (1.00 g, 82% yield).



**Figure S6.** Photograph of gram-scale synthesis of **3aa**

### 2.4 Recycling Experiment

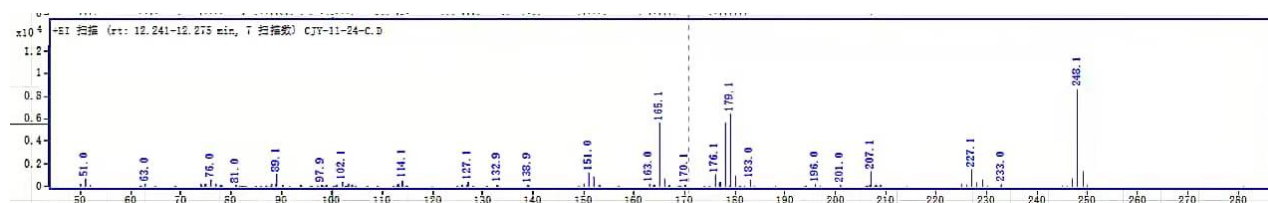
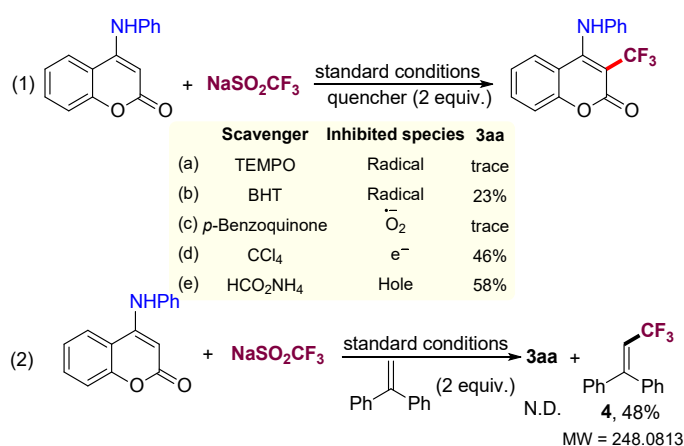
The mixture of 4-anilincoumarins **1a** (0.2 mmol), sodium trifluoromethanesulfonate **2** (0.3 mmol), mpg- $\text{C}_3\text{N}_4$  (15.0 mg) and DMSO (1.0 mL) were sequentially added to an oven-dried reaction tube. After that, the reaction mixture was stirred under the irradiation of an 10 W blue LED strip at room temperature for 24 h. After completion, the reaction mixture was transferred to a centrifuge tube (3 mL of ethyl acetate was used in order to transfer the reaction mixture completely), and the mixture was centrifuged (time approx. 10 minutes) until the mpg- $\text{C}_3\text{N}_4$  precipitates. The residual solid catalyst was washed with deionized water and ethyl acetate for three times respectively, dried at 60 °C under vacuum for overnight and directly reused in the next runs.



**Figure S7.** Catalyst mpg-C<sub>3</sub>N<sub>4</sub> centrifugal photograph

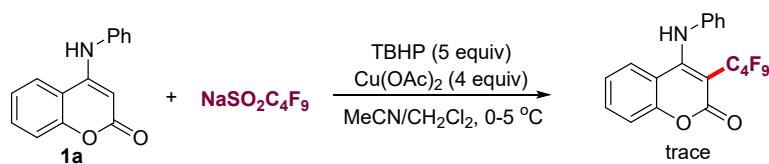
## 2.5. Active species trapping experiments

To get insight into the contribution of different active species to the reaction, radical trapping and active species trapping experiments were performed. The commonly used scavengers 2,2,6,6-tetramethylpiperidinoxy (TEMPO), 2,6-di-tert-butyl-4-methylphenol (BHT), *p*-benzoquinone (BQ), CCl<sub>4</sub>, and ammonium hydrogen carbonate (HCO<sub>2</sub>NH<sub>4</sub>) were used in the model reaction, respectively. In a typical experiment: 4-anilinocoumarins **1a** (0.2 mmol), sodium trifluoromethanesulfonate **2** (0.3 mmol), mpg-C<sub>3</sub>N<sub>4</sub> (15.0 mg), quencher and DMSO (1.0 mL) were sequentially added to an oven-dried reaction tube. After that, the reaction mixture was stirred under the irradiation of an 10 W blue LED strip at room temperature for 24 h. When each round of the reactions was completed, one equivalent of 1,3,5-trimethoxybenzene was added and the mixture was stirred for 10 min. The catalyst was separated by centrifugation and the supernatant liquid phase was analyzed by <sup>1</sup>H NMR. The results were presented in following scheme.



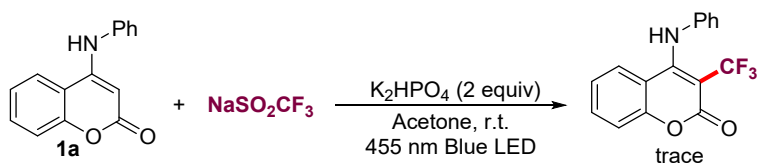
**Figure S8.** Control experiments and Ms of adduct **4**

## 2.6 Control experiments comparing with previous reports



Reaction conditions: **1a** (0.15 mmol), NaSO<sub>2</sub>C<sub>4</sub>F<sub>9</sub> (0.45 mmol), Cu(OAc)<sub>2</sub> (4 equiv, 0.6 mmol), TBHP (5 equiv, 0.75 mmol), MeCN/CH<sub>2</sub>Cl<sub>2</sub> = 1.5 mL : 1.5 mL, 0-5 °C, N<sub>2</sub>, 24 h

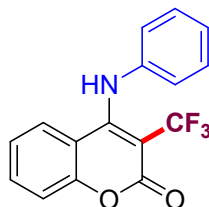
When 4-anilincoumarin **1a** was employed as a substrate in the reported reaction system (*J. Fluorine Chem.* **2017**, *197*, 42-48), only a trace amount of the desired product was detected by TLC. It is probably due to the coordination between the excess amount of Cu(II) salts and the sensitive amino groups thus poisoning the reaction.



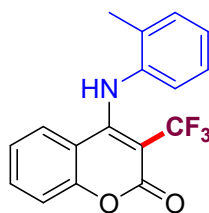
Reaction conditions: **1a** (0.2 mmol), NaSO<sub>2</sub>CF<sub>3</sub> (0.6 mmol), K<sub>2</sub>HPO<sub>4</sub> (2 equiv, 0.4 mmol), acetone (2 mL), r.t., N<sub>2</sub>, 12 h

When 4-anilincoumarin **1a** was employed as a substrate in the irradiation of 455 nm blue LED rather than the high-power Xenon lamp. Compared with the reported photocatalytic reaction system (*J. Fluorine Chem.* **2018**, *214*, 42-47), only a trace amount of the desired product was detected by TLC. It suggests that a high-power Xenon lamp as a light source is very critical in the previous system.

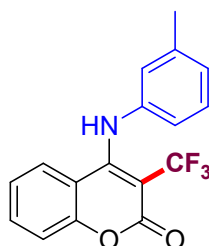
## 3. Characterization data of products



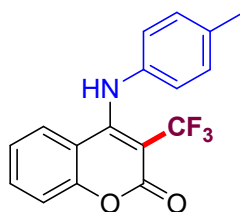
**4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3aa):** Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.41 (t, *J* = 6.2 Hz, 2H), 7.28-7.20 (m, 4H), 7.15 (t, *J* = 6.0 Hz, 1H), 7.01 (d, *J* = 4.0 Hz, 2H), 6.88 (t, *J* = 6.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.7, 152.6 (d, *J* = 43.1 Hz), 140.1, 132.5, 128.8, 126.5, 125.1, 122.3 (d, *J* = 10.4 Hz), 116.6, 113.1, 96.1 (q, *J* = 23.2 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -55.82 (d, *J* = 4.5 Hz); HRMS: calcd for C<sub>16</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 306.0742, found 306.0748.



**4-(o-tolylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ab):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (t,  $J = 6.0$  Hz, 1H), 7.25-7.20 (m, 2H), 7.14 (t,  $J = 5.8$  Hz, 2H), 7.08-7.02 (m, 2H), 6.85 (d,  $J = 7.6$  Hz, 2H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.7, 154.2 (d,  $J = 42.4$  Hz), 139.4, 133.5, 131.8 (d,  $J = 41.6$  Hz), 127.2 (d,  $J = 25.6$  Hz), 126.9, 125.0, 123.4, 117.7, 113.9, 95.4 (q,  $J = 23.1$  Hz), 18.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.44; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0903



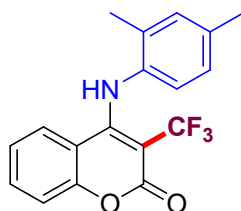
**5-(m-tolylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ac):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (d,  $J = 6.0$  Hz, 1H), 7.33 (s, 1H), 7.26-7.20 (m, 2H), 7.14 (t,  $J = 6.2$  Hz, 1H), 6.97 (d,  $J = 6.0$  Hz, 1H), 6.88 (t,  $J = 6.0$  Hz, 1H), 6.84 (s, 1H), 6.78 (d,  $J = 6.4$  Hz, 1H), 2.24 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.6, 153.6 (d,  $J = 39.1$  Hz), 140.4 (d,  $J = 88.9$  Hz), 133.5, 129.5, 127.6, 125.4, 123.6 (d,  $J = 59.0$  Hz), 120.4, 117.5, 113.9, 96.7 (q,  $J = 23.2$  Hz), 21.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.76; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0902.



**4-(p-tolylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ad):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (t,  $J = 6.0$  Hz, 1H), 7.32 (s, 1H), 7.22 (d,  $J = 6.4$  Hz, 2H), 7.08 (d,  $J = 6.0$  Hz, 2H), 6.91-6.86 (m, 3H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.7, 153.8 (d,  $J = 29.8$  Hz), 138.4, 136.3, 133.4, 130.5, 127.7, 123.3 (d,  $J = 23.1$  Hz), 18.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.44; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0903

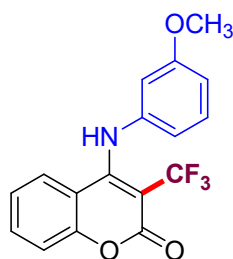


= 29.5 Hz), 123.2, 117.6, 113.9, 96.3 (q,  $J = 23.0$  Hz), 29.7, 21.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.65 (d,  $J = 4.9$  Hz); HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0904.

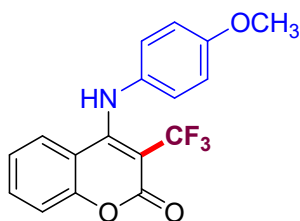


**4-((2,4-dimethylphenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3ae):**

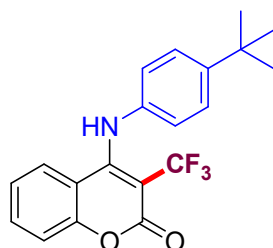
Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (t,  $J = 6.2$  Hz, 1H), 7.21 (t,  $J = 6.2$  Hz, 1H), 7.13 (d,  $J = 3.6$  Hz, 1H), 7.04 (d,  $J = 5.6$  Hz, 2H), 6.89-6.82 (m, 2H), 6.77 (d,  $J = 6.4$  Hz, 1H), 2.27 (s, 3H), 2.23 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.7, 154.1 (d,  $J = 55.5$  Hz), 136.9 (d,  $J = 60.3$  Hz), 133.4, 132.2, 128.0, 126.9, 125.2, 123.3, 117.7, 94.5 (q,  $J = 23.0$  Hz), 21.0, 17.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.30 (d,  $J = 4.9$  Hz); HRMS: calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  334.1055, found 334.1059.



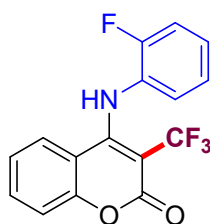
**4-((4-methoxyphenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3af):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.43 (t,  $J = 6.2$  Hz, 1H), 7.29-7.23 (m, 3H), 7.19-7.15 (m, 1H), 6.91 (t,  $J = 6.2$  Hz, 1H), 6.70 (d,  $J = 6.8$  Hz, 1H), 6.55 (d,  $J = 8.0$  Hz, 2H), 3.70 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.7, 152.5 (d,  $J = 48.2$  Hz), 141.1, 132.6, 129.6, 126.6, 122.3, 116.6, 114.5, 112.8, 110.5, 108.0, 94.5 (q,  $J = 23.0$  Hz), 54.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.78; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_3$   $[\text{M}+\text{H}]^+$  336.0848, found 336.0853.



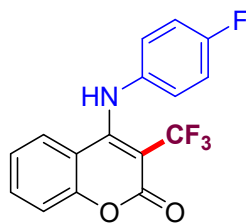
**4-((4-methoxyphenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3ag):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.40 (t,  $J = 6.2$  Hz, 1H), 7.33 (s, 1 H), 7.23-7.18 (m, 2H), 6.98 (d,  $J = 6.8$  Hz, 2H), 6.88-6.76 (m, 3H), 3.76 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.2, 153.9 (d,  $J = 19.7$  Hz), 133.5 (d,  $J = 41.8$  Hz), 127.6, 125.5, 123.2, 117.7, 115.1, 113.7, 95.4 (q,  $J = 23.1$  Hz), 55.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.46 (d,  $J = 4.9$  Hz); HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_3$   $[\text{M}+\text{H}]^+$  336.0848, found 336.0852.



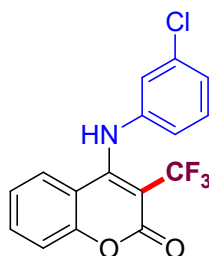
**4-((4-(tert-butyl)phenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3ah):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.41 (t,  $J = 5.6$  Hz, 1H), 7.34 (d,  $J = 6.0$  Hz, 1H), 7.29-7.21 (m, 4 H), 6.94 (d,  $J = 6.4$  Hz, 2H), 6.88 (t,  $J = 6.2$  Hz, 1H), 1.25 (s, 9H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.7, 153.7 (d,  $J = 28.5$  Hz), 149.6, 138.3, 133.4, 127.7, 126.7, 125.5, 123.1 (d,  $J = 19.5$  Hz), 117.6, 113.9, 96.5 (q,  $J = 22.9$  Hz), 34.6, 31.3;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.65 (d,  $J = 4.9$  Hz); HRMS: calcd for  $\text{C}_{20}\text{H}_{19}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  362.1368, found 362.1373.



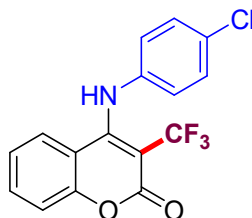
**4-((2-fluorophenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3ai):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (t,  $J = 6.2$  Hz, 1H), 7.27 (t,  $J = 5.6$  Hz, 2H), 7.14-7.10 (m, 3H), 7.02 (t,  $J = 5.8$  Hz, 1H), 6.95 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.9 (d,  $J = 124.9$  Hz), 154.2, 153.5 (d,  $J = 33.1$  Hz), 133.8, 129.1 (d,  $J = 9.3$  Hz), 127.1 (d,  $J = 5.9$  Hz), 126.3, 124.9 (d,  $J = 3.1$  Hz), 124.6 (d,  $J = 47.5$  Hz), 123.6, 117.8, 116.7 (d,  $J = 15.2$  Hz), 114.0, 98.3 (q,  $J = 23.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -56.00 (d,  $J = 4.1$  Hz), -125.12; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_4\text{NO}_2$   $[\text{M}+\text{H}]^+$  324.0648, found 324.0652.



**4-((4-fluorophenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3aj):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44 (s, 1H), 7.29-7.19 (m, 3 H), 7.00-6.91 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  161.7, 159.7, 157.5, 154.0, 153.5 (d,  $J = 49.6$  Hz), 137.1, 133.6, 127.4, 125.2, 123.4, 117.8, 116.9 (d,  $J = 18.4$  Hz), 113.7, 97.1 (q,  $J = 23.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.75 (d,  $J = 4.1$  Hz), -114.96; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_4\text{NO}_2$   $[\text{M}+\text{H}]^+$  324.0648, found 324.0653.

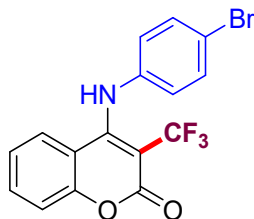


**4-((3-chlorophenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3ak):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.47 (t,  $J = 5.8$  Hz, 1H), 7.28-7.11 (m, 5 H), 7.03 (s, 1H), 6.97 (t,  $J = 5.6$  Hz, 1H), 6.85 (d,  $J = 5.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.4, 153.5 (d,  $J = 101.4$  Hz), 142.5, 135.5, 133.9, 130.8, 127.3, 125.9, 123.4 (d,  $J = 95.2$  Hz), 120.8, 117.8, 113.8, 99.0 (d,  $J = 23.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -56.09 (d,  $J = 4.1$  Hz); HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{ClF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  340.0352, found 340.0356.

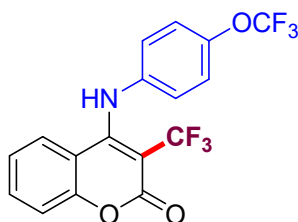


**4-((4-chlorophenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3al):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  9.53 (s, 1H), 8.09 (d,  $J = 6.4$  Hz, 1 H), 7.73 (t,  $J = 6.2$  Hz, 1H), 7.45-7.36 (m, 4H), 7.27 (d,  $J = 6.8$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 152.8 (d,  $J = 48.7$  Hz), 141.7, 134.4, 129.4, 128.8, 125.2, 124.2 (d,  $J = 18.4$  Hz), 113.7, 97.1 (q,  $J = 23.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -56.09 (d,  $J = 4.1$  Hz); HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{ClF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  340.0352, found 340.0356.

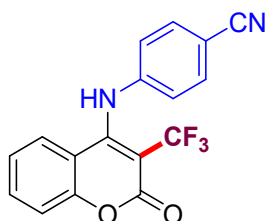
= 70.1 Hz), 117.6, 116.4, 94.9 (d,  $J = 25.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO):  $\delta$  -56.62; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{ClF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  340.0352, found 342.0357.



**4-((4-bromophenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3am):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.53 (t,  $J = 6.0$  Hz, 1H), 7.46 (d,  $J = 6.4$  Hz, 2H), 7.33-7.30 (m, 3 H), 7.03 (t,  $J = 6.4$  Hz, 1H), 6.95 (d,  $J = 6.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.4, 153.4 (d,  $J = 94.5$  Hz), 140.3, 133.8, 132.9, 127.4, 124.1 (d,  $J = 79.4$  Hz), 119.1, 117.8, 113.7, 98.5 (d,  $J = 23.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.94; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{BrF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  383.9847, found 383.9853.

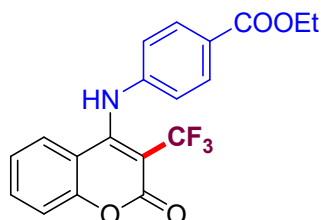


**4-((4-(trifluoromethoxy)phenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3an):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46 (t,  $J = 6.2$  Hz, 1H), 7.26 (d,  $J = 6.8$  Hz, 1 H), 7.20 (t,  $J = 6.0$  Hz, 2H), 7.13 (d,  $J = 6.8$  Hz, 2H), 7.01 (d,  $J = 7.2$  Hz, 2H), 6.95 (t,  $J = 6.2$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.3, 152.5 (d,  $J = 82.4$  Hz), 145.6, 138.8, 132.8, 126.3, 122.8 (d,  $J = 46.2$  Hz), 121.5, 116.8, 112.5, 107.2, 95.8 (q,  $J = 23.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.93, -58.11; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_6\text{NO}_3$   $[\text{M}+\text{H}]^+$  390.0565, found 390.0569

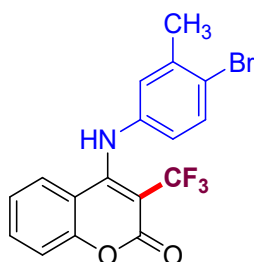


**4-((2-oxo-3-(trifluoromethyl)-2H-chromen-4-yl)amino)benzonitrile (3ao):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.54 (d,  $J = 6.8$  Hz, 3H), 7.31 (d,  $J = 6.8$  Hz, 1

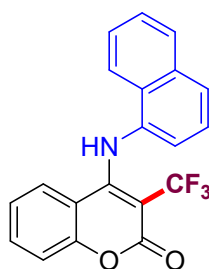
H), 7.19 (s, 1 H), 7.14 (s, 1H), 7.05-6.97 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 155.8, 152.9, 150.8, 144.5, 133.1(d, *J* = 55.6 Hz), 125.9, 123.0, 120.1, 117.0 (d, *J* = 27.9 Hz), 112.8, 107.0, 96.1 (q, *J* = 22.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -56.57; HRMS: calcd for C<sub>17</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 331.0694, found 331.0699.



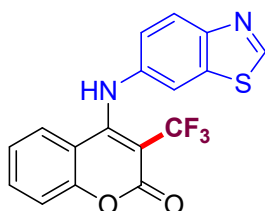
**ethyl 4-((2-oxo-3-(trifluoromethyl)-2H-chromen-4-yl)amino)benzoate (3ap):** Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.93 (d, *J* = 6.8 Hz, 2H), 7.47 (t, *J* = 6.2 Hz, 1 H), 7.27 (d, *J* = 7.2 Hz, 3H), 6.99-6.94 (m, 3H), 4.32-4.28 (m, 2H), 1.32 (t, *J* = 5.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.7, 158.0, 153.2 (d, *J* = 126.6 Hz), 145.3, 134.1, 131.3, 127.4, 123.7, 121.2, 117.8, 113.8 (d, *J* = 13.4 Hz), 100.3 (d, *J* = 23.2 Hz), 61.2, 14.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -56.27; HRMS: calcd for C<sub>19</sub>H<sub>15</sub>F<sub>3</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 378.0953, found 378.0958.



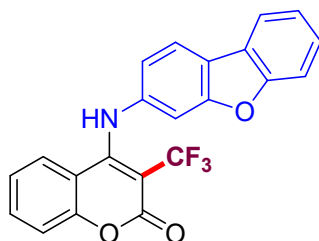
**4-((4-bromo-3-methylphenyl)amino)-3-(trifluoromethyl)-2H-chromen-2-one (3aq):** Yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.47-7.39 (m, 2H), 7.26-7.15 (m, 3H), 6.96-6.90 (m, 2H), 6.67 (d, *J* = 5.6 Hz, 1H), 2.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.4, 152.5 (d, *J* = 87.2 Hz), 139.1(d, *J* = 47.7 Hz), 132.6 (d, *J* = 22.8 Hz), 126.4, 123.9, 122.5, 120.8, 116.7, 112.8, 94.2 (q, *J* = 23.2 Hz), 22.0; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>): δ -55.89; HRMS: calcd for C<sub>17</sub>H<sub>12</sub>BrF<sub>3</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 398.0004, found 398.0010.



**4-(naphthalen-1-ylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ar):** Brown solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.46-7.38 (m, 3H), 7.26-7.19 (m, 4H), 6.96-6.78 (m, 4H), 6.67 (d,  $J = 6.4$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.5, 152.4 (d,  $J = 80.5$  Hz), 139.1 (d,  $J = 45.5$  Hz), 132.6 (d,  $J = 29.9$  Hz), 126.4, 123.9, 122.5, 120.8, 116.7, 112.7, 96.8 (q,  $J = 23.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.89; HRMS: calcd for  $\text{C}_{20}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  356.0898, found 356.0904.

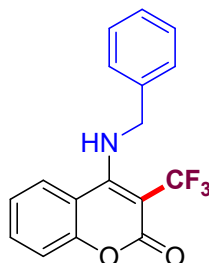


**4-(benzo[d]thiazol-6-ylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3as):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  9.71 (s, 1H), 9.33 (s, 1H), 8.13-8.05 (m, 3H), 7.73 (t,  $J = 6.2$  Hz, 1H), 7.46 (d,  $J = 6.8$  Hz, 2H), 7.36 (t,  $J = 6.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  158.5, 156.1, 152.9 (d,  $J = 25.8$  Hz), 150.6, 140.5, 134.6 (d,  $J = 44.2$  Hz), 125.4, 124.6, 123.7, 121.8, 117.7, 116.4, 115.5, 95.0 (q,  $J = 20.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO):  $\delta$  -56.58; HRMS: calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_3\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$  363.0415, found 363.0420.

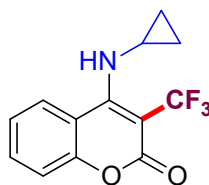


**4-(dibenzo[b,d]furan-3-ylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3at):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.85-7.80 (m, 2H), 7.48 (d,  $J = 6.8$  Hz, 2H), 7.40 (d,  $J = 4.0$  Hz, 2H), 7.31-7.18 (m, 4H), 6.99 (d,  $J = 6.8$  Hz, 1H), 6.83 (t,  $J = 6.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.6 (d,  $J = 20.9$  Hz), 152.6 (d,  $J =$

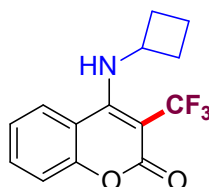
69.7 Hz), 139.2, 132.6, 126.5 (d,  $J = 9.6$  Hz), 122.3 (d,  $J = 14.5$  Hz), 121.4, 120.6, 119.6, 117.4, 116.7, 112.8, 110.8, 105.7, 96.6 (q,  $J = 23.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.71; HRMS: calcd for  $\text{C}_{22}\text{H}_{13}\text{F}_3\text{NO}_3$   $[\text{M}+\text{H}]^+$  396.0848, found 396.0853.



**4-(benzylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3au):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.62 (d,  $J = 6.4$  Hz, 1H), 7.51 (t,  $J = 6.2$  Hz, 1H), 7.34-7.24 (m, 6 H), 7.18 (t,  $J = 6.2$  Hz, 1H), 5.86 (s, 1H), 4.68 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.3, 154.7, 151.9, 135.8, 132.4, 128.3, 127.7, 126.7, 122.8 (d,  $J = 26.2$  Hz), 117.0, 113.7, 89.3 (q,  $J = 23.7$  Hz), 52.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -54.26; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0902.

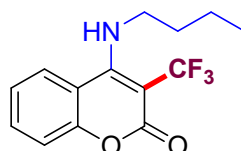


**4-(cyclopropylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3av):** Pale yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.30 (t,  $J = 6.4$  Hz, 1H), 7.53 (t,  $J = 6.2$  Hz, 1H), 7.21 (t,  $J = 6.6$  Hz, 2H), 6.17 (s, 1H), 3.12 (s, 1H), 0.99 (d,  $J = 5.2$  Hz, 2H), 0.72 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.1, 152.4, 132.5, 124.9, 122.4, 116.9, 113.2, 98.3 (q,  $J = 22.5$  Hz), 28.7, 10.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -54.76; HRMS: calcd for  $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  270.0742, found 270.0746.

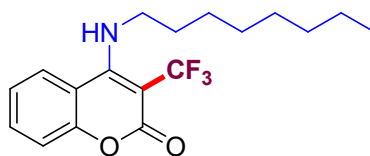


**4-(cyclobutylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3aw):** Pale yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.61 (d,  $J = 6.8$  Hz, 1H), 7.52 (t,  $J = 6.2$  Hz,

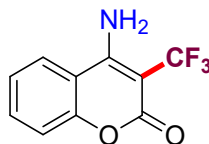
1H), 7.19-7.26 (m, 3H), 4.26-4.31 (m, 1H), 4.50 (d,  $J = 6.8$  Hz, 2H), 2.06 (t,  $J = 7.8$  Hz, 2H), 1.80-1.67 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.0, 154.5, 152.5, 132.5, 123.9, 122.5, 117.0, 113.4, 89.4 (q,  $J = 23.6$  Hz), 52.6, 32.1, 28.7, 13.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.25 (d,  $J = 3.8$  Hz); HRMS: calcd for  $\text{C}_{14}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  284.0898, found 284.0903.



**4-(butylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ax):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.71 (d,  $J = 6.4$  Hz, 1H), 7.51 (t,  $J = 6.2$  Hz, 1 H), 7.24-7.20 (m, 2H), 5.72 (s, 1H), 3.57 (d,  $J = 4.4$  Hz, 2H), 1.68-1.62 (m, 2H), 1.40-1.34 (m, 2H), 0.89 (t,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 156.1, 153.0, 133.3, 124.0, 123.6 (d,  $J = 20.5$  Hz), 117.9, 114.9, 89.3 (q,  $J = 24.6$  Hz), 49.0, 32.9, 19.7, 13.6;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -54.44; HRMS: calcd for  $\text{C}_{14}\text{H}_{15}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  286.1055, found 286.1059.



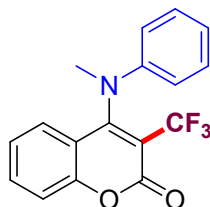
**4-(octylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ay):** Pale yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.75 (d,  $J = 6.4$  Hz, 1H), 7.48 (t,  $J = 6.2$  Hz, 1 H), 7.25-7.20 (s, 2 H), 5.87 (s, 1H), 3.58-3.53 (m, 2H), 1.69-1.63 (m, 2H), 1.30-1.17 (m, 10H), 0.78 (t,  $J = 6.0$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.7, 156.1, 152.9, 133.2, 123.8, 117.8, 115.0, 88.9 (q,  $J = 21.3$  Hz), 49.3, 31.6, 30.8, 29.0, 26.5, 22.6, 14.0;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -54.32; HRMS: calcd for  $\text{C}_{18}\text{H}_{23}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  342.1681, found 342.1685.



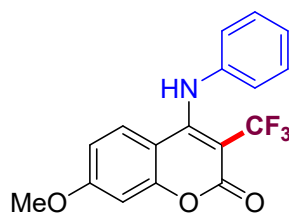
**4-(octylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3az):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  8.29 (d,  $J = 6.4$  Hz, 2H), 7.78-7.70 (m, 2 H), 7.40-



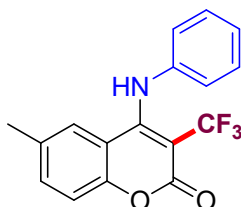
7.35 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  157.9, 154.2, 152.9, 134.5, 124.5, 117.5, 114.0, 85.2 (t,  $J = 23.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO):  $\delta$  -54.92; HRMS: calcd for  $\text{C}_{10}\text{H}_7\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  230.0429, found 230.0434.



**4-(octylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3aa')**: Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.48 (t,  $J = 6.2$  Hz, 1H), 7.29 (t,  $J = 6.6$  Hz, 2H), 7.19 (t,  $J = 6.2$  Hz, 2H), 7.04 (t,  $J = 6.0$  Hz, 1H), 6.87 (t,  $J = 5.8$  Hz, 1H), 6.70 (d,  $J = 6.4$  Hz, 2H), 3.38 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.1, 156.9, 153.2, 145.5, 132.8, 128.5, 126.3, 123.5, 119.9, 116.5, 114.7, 111.9 (q,  $J = 24.4$  Hz), 40.2;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -61.79; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0903.

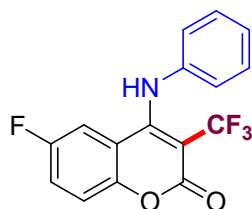


**7-methoxy-4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3ba)**: Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.27 (t,  $J = 6.2$  Hz, 3H), 7.16-7.08 (m, 2H), 7.00 (d,  $J = 6.0$  Hz, 2H), 6.66 (s, 1H), 6.43 (d,  $J = 7.2$  Hz, 1H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  162.8, 157.0, 155.1, 152.8, 140.2, 128.8, 127.9, 125.0, 122.2, 111.1, 105.7, 99.5, 93.7 (d,  $J = 23.0$  Hz), 54.8;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.25; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  336.0848, found 336.0852.

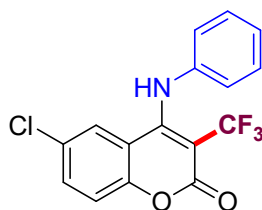


**6-methyl-4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3bb)**: Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.29 (t,  $J = 6.0$  Hz, 3H), 7.23-7.12 (m, 3H), 7.00 (d,  $J = 6.4$  Hz, 2H), 6.95 (s, 1H), 2.01 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$

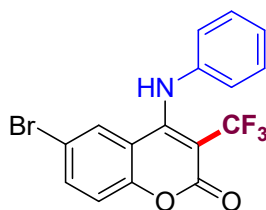
158.0, 152.8 (d,  $J = 140.7$  Hz), 141.1, 134.7, 132.9, 129.8, 127.4, 126.1, 123.3, 117.4, 113.4, 97.0 (q,  $J = 23.3$  Hz), 20.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.71; HRMS: calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  320.0898, found 320.0904.



**6-fluoro-4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3bc):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32 (t,  $J = 6.0$  Hz, 3H), 7.24-7.14 (m, 3H), 7.02 (d,  $J = 6.0$  Hz, 2H), 6.84 (d,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 156.9 (d,  $J = 80.4$  Hz), 152.7, 150.2, 140.4, 130.1, 126.7, 123.5, 121.4 (d,  $J = 19.5$  Hz), 119.3 (d,  $J = 6.7$  Hz), 113.3 (d,  $J = 21.3$  Hz), 97.9 (q,  $J = 22.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.94, -116.27; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_4\text{NO}_2$   $[\text{M}+\text{H}]^+$  324.0648, found 324.0652.

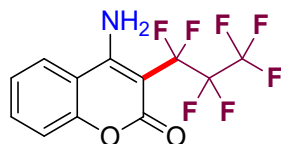


**6-chloro-4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3bd):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.44-7.38 (m, 4H), 7.31 (t,  $J = 6.0$  Hz, 1H), 7.26 (d,  $J = 5.2$  Hz, 1H), 7.19 (s, 1H), 7.09 (d,  $J = 6.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.2, 152.3 (d,  $J = 5.9$  Hz), 140.4, 133.6, 130.1, 128.8, 127.0 (d,  $J = 42.9$  Hz), 123.5, 119.1, 116.3, 114.9, 97.5 (q,  $J = 22.2$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.90; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{ClF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  340.0352, found 340.0356



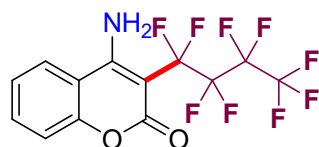
**6-bromo-4-(phenylamino)-3-(trifluoromethyl)-2H-chromen-2-one (3be):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.50 (d,  $J = 6.8$  Hz, 1H), 7.34 (t,  $J = 5.8$  Hz,

3H), 7.25 (t,  $J = 6.4$  Hz, 2H), 7.12(d,  $J = 6.8$  Hz, 1H), 7.02 (d,  $J = 6.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.1, 152.6 (d,  $J = 51.1$  Hz), 140.3, 136.4, 130.2 (d,  $J = 17.5$  Hz), 126.8, 123.6, 119.3, 115.6 (d,  $J = 61.0$  Hz), 97.5 (q,  $J = 23.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -55.89; HRMS: calcd for  $\text{C}_{16}\text{H}_{10}\text{BrF}_3\text{NO}_2$   $[\text{M}+\text{H}]^+$  383.9847, found 383.9852.

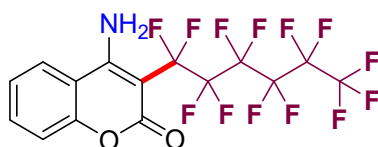


**4-amino-3-(perfluoropropyl)-2H-chromen-2-one (3ca):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  8.35 (d,  $J = 6.4$  Hz, 1H), 8.29 (s, 1H), 7.13 (t,  $J = 6.2$  Hz, 2H), 7.42-7.36 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  157.7, 155.7, 153.0, 134.6, 124.6, 117.4, 113.9, 82.4 (t,  $J = 18.0$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO):  $\delta$  -79.91, -104.91, -125.77; HRMS: calcd for  $\text{C}_{12}\text{H}_7\text{F}_7\text{NO}_2$   $[\text{M}+\text{H}]^+$  330.0365, found 330.0369.

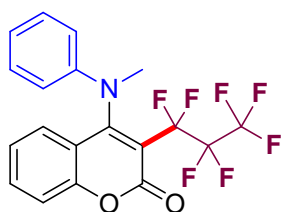
Crystal data for **3ca**:  $\text{C}_{12}\text{H}_6\text{F}_7\text{NO}_2$ ;  $M_r = 329.18$ , Triclinic, space group  $P -1$ ,  $a = 7.2140(12)$  Å,  $b = 7.4875(12)$  Å,  $c = 11.7137(18)$  Å;  $V = 616.20(17)$  Å<sup>3</sup>;  $T = 273.15$  K;  $Z = 4$ ; Reflections collected/unique, 12962/2850,  $R_{\text{int}} = 0.0439$ ,  $R_1 = 0.0604$ ,  $wR_2 = 0.1639$ ;  $GOF = 1.021$ ; CCDC-2175980 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



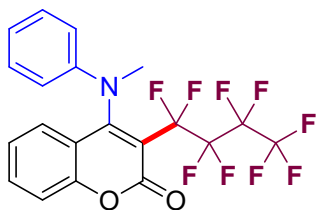
**4-amino-3-(perfluorobutyl)-2H-chromen-2-one (3cb):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  8.35 (d,  $J = 6.8$  Hz, 1H), 8.29 (s, 1 H), 7.73 (t,  $J = 6.2$  Hz, 2H), 7.42-7.37 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  157.8, 155.8, 153.0, 134.6, 124.6, 117.4, 113.9, 82.6 (t,  $J = 17.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO):  $\delta$  -80.56, -104.25, -122.24, -125.87; HRMS: calcd for  $\text{C}_{13}\text{H}_7\text{F}_9\text{NO}_2$   $[\text{M}+\text{H}]^+$  380.0333, found 380.0338.



**4-amino-3-(perfluorohexyl)-2H-chromen-2-one (3cc):** Yellow solid,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  8.36 (d,  $J = 6.4$  Hz, 1H), 8.29 (s, 1 H), 7.73 (t,  $J = 6.2$  Hz, 2H), 7.42-7.37(m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  157.7, 155.8, 153.0, 134.5, 124.4, 117.3, 113.9, 82.6 (t,  $J = 17.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO)  $\delta$  -80.74, -104.10, -121.59, -121.94, -122.7, -126.17; HRMS: calcd for  $\text{C}_{15}\text{H}_7\text{F}_{13}\text{NO}_2$   $[\text{M}+\text{H}]^+$  480.0269, found 480.0275

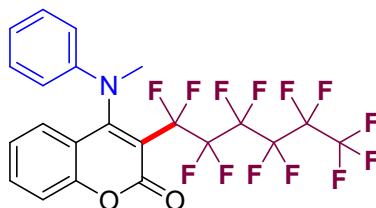


**4-(methyl(phenyl)amino)-3-(perfluoropropyl)-2H-chromen-2-one (3cd):** Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  7.74 (t,  $J = 6.0$  Hz, 1H), 7.55 (d,  $J = 6.8$  Hz, 1 H), 7.30-7.19 (m, 4H), 6.80 (t,  $J = 5.8$  Hz, 3H), 3.34-3.30 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  162.0, 157.8, 155.0, 147.8, 135.2, 129.6, 127.5, 125.3, 119.1, 118.0, 117.6, 115.5, 115.2 (d,  $J = 19.5$  Hz), 115.0, 113.8;  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO)  $\delta$  -80.14, -106.81, -121.79; HRMS: calcd for  $\text{C}_{19}\text{H}_{13}\text{F}_7\text{NO}_2$   $[\text{M}+\text{H}]^+$  420.0835, found 420.0842.



**4-(methyl(phenyl)amino)-3-(perfluorobutyl)-2H-chromen-2-one (3ce):** Yellow oil,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO):  $\delta$  7.74 (t,  $J = 6.0$  Hz, 1H), 7.55 (d,  $J = 6.4$  Hz, 1H), 7.29-7.19 (m, 4 H), 6.80 (t,  $J = 5.8$  Hz, 3H), 3.55-3.30 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO):  $\delta$  162.1, 157.7, 155.1, 147.8, 135.2, 129.5, 127.5, 125.3, 119.1, 117.9, 117.6, 115.5, 115.2 (d,  $J = 16.4$  Hz), 113.7;  $^{19}\text{F}$  NMR (376 MHz,  $d_6$ -DMSO)  $\delta$  -80.37,

-106.64, -118.75, -125.97; HRMS: calcd for C<sub>20</sub>H<sub>13</sub>F<sub>9</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 470.0803, found 470.0808.



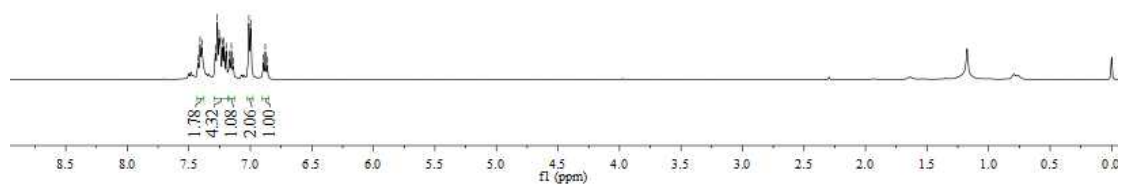
**4-(methyl(phenyl)amino)-3-(perfluorohexyl)-2H-chromen-2-one (3cf):** Yellow oil, <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO): δ 7.74 (t, *J* = 6.2 Hz, 1H), 7.55 (d, *J* = 6.8 Hz, 1H), 7.30-7.23 (m, 4 H), 6.79 (t, *J* = 5.8 Hz, 3H), 3.29 (s, 3H); <sup>13</sup>C NMR (100 MHz, *d*<sub>6</sub>-DMSO): δ 162.1, 157.7, 155.1, 147.8, 135.2, 129.5, 127.5, 125.3, 119.1, 118.0, 117.6 (d, *J* = 39.9 Hz), 115.3 (d, *J* = 15.7 Hz), 113.7; <sup>19</sup>F NMR (376 MHz, *d*<sub>6</sub>-DMSO) δ -80.41, -106.32, -117.80, -121.93, -122.49, -125.93; HRMS: calcd for C<sub>22</sub>H<sub>13</sub>F<sub>13</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 570.0739, found 570.0746.

#### 4. References

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- [4] V. W. H. Lau, I. Moudrakovski, T. Botari, S. Weinberger, M. B. Mesch, V. Duppel, J. Senker, V. Blum and B. V. Lotsch, *Nat. Commun.*, 2016, 7, 12165.

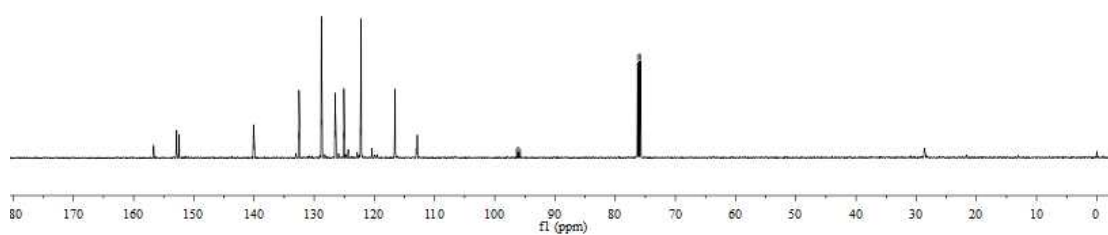
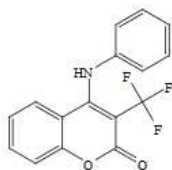
## 5. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of products

7.425  
7.409  
7.394  
7.283  
7.268  
7.253  
7.243  
7.226  
7.213  
7.196  
7.169  
7.154  
7.139  
7.012  
6.997  
6.894  
6.879  
6.863



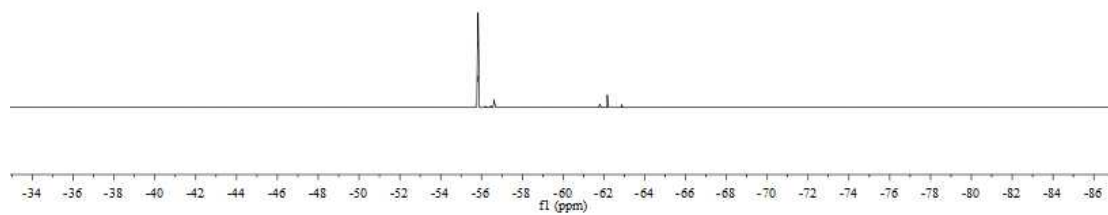
$^1\text{H}$  NMR of **3aa** in  $\text{CDCl}_3$

156.685  
 152.856  
 152.425  
 140.092  
 132.531  
 128.822  
 126.547  
 125.084  
 122.305  
 122.201  
 116.560  
 113.079  
 96.423  
 96.205  
 95.973  
 95.740  
 76.285  
 76.031  
 75.777

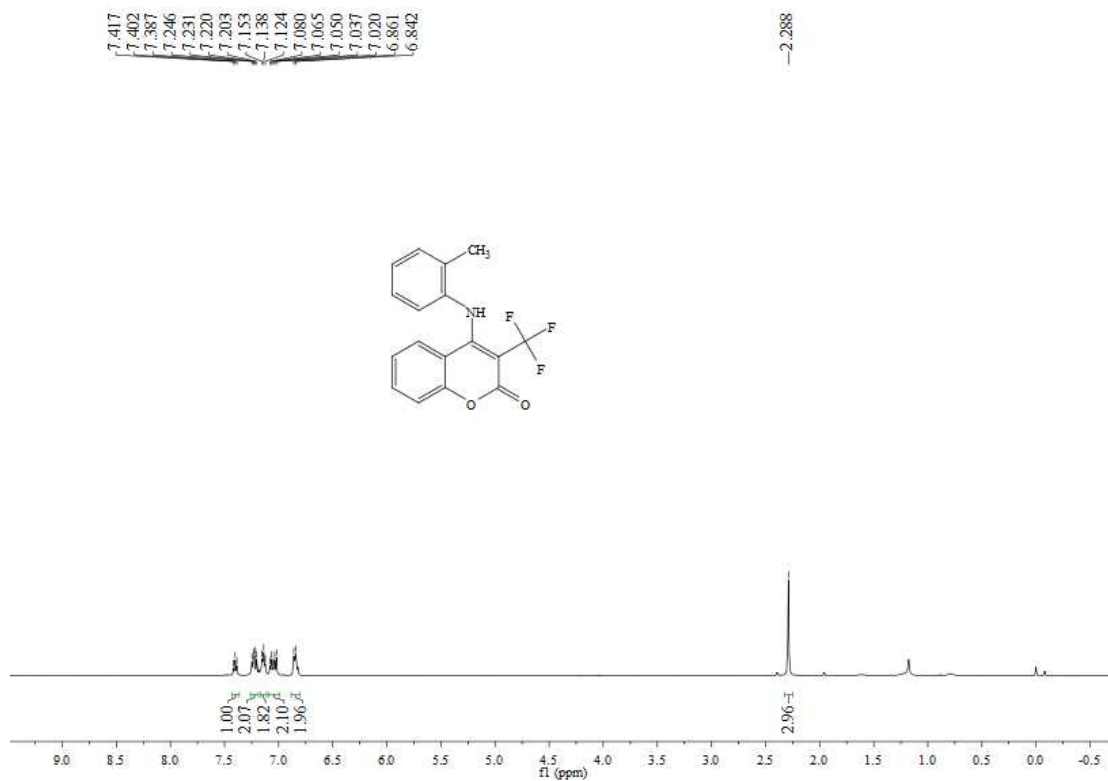


$^{13}\text{C}$  NMR of **3aa** in  $\text{CDCl}_3$

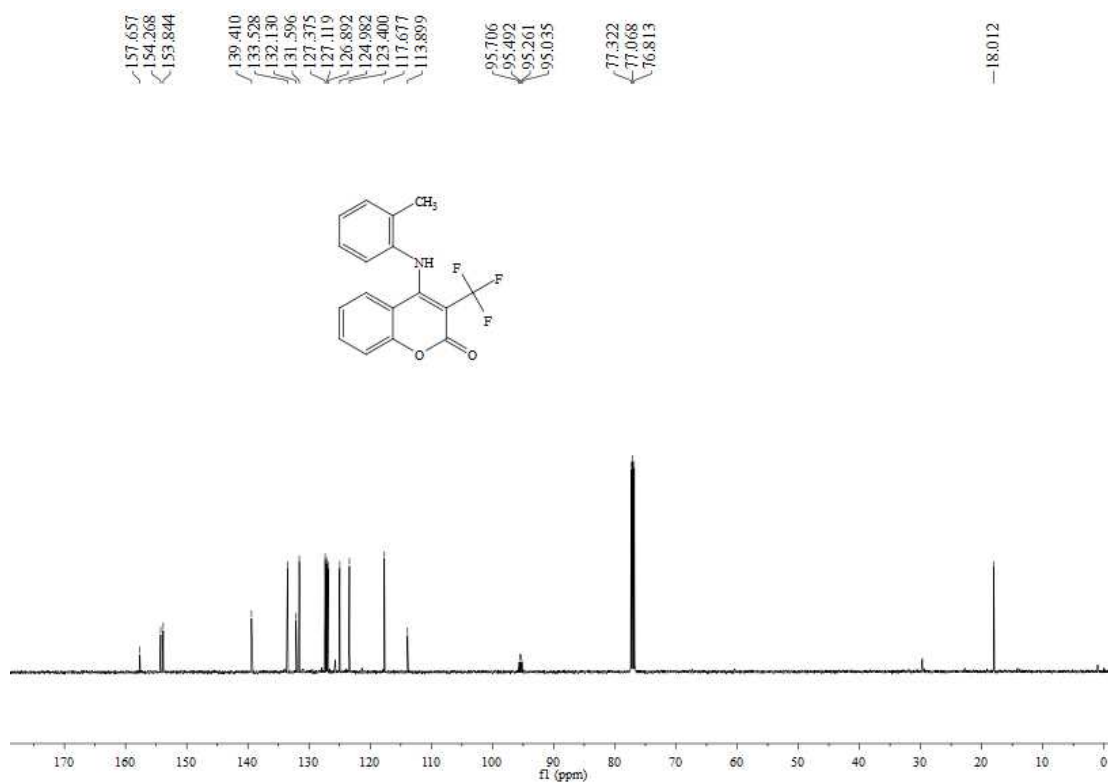
55.818  
 55.830



$^{19}\text{F}$  NMR of **3aa** in  $\text{CDCl}_3$

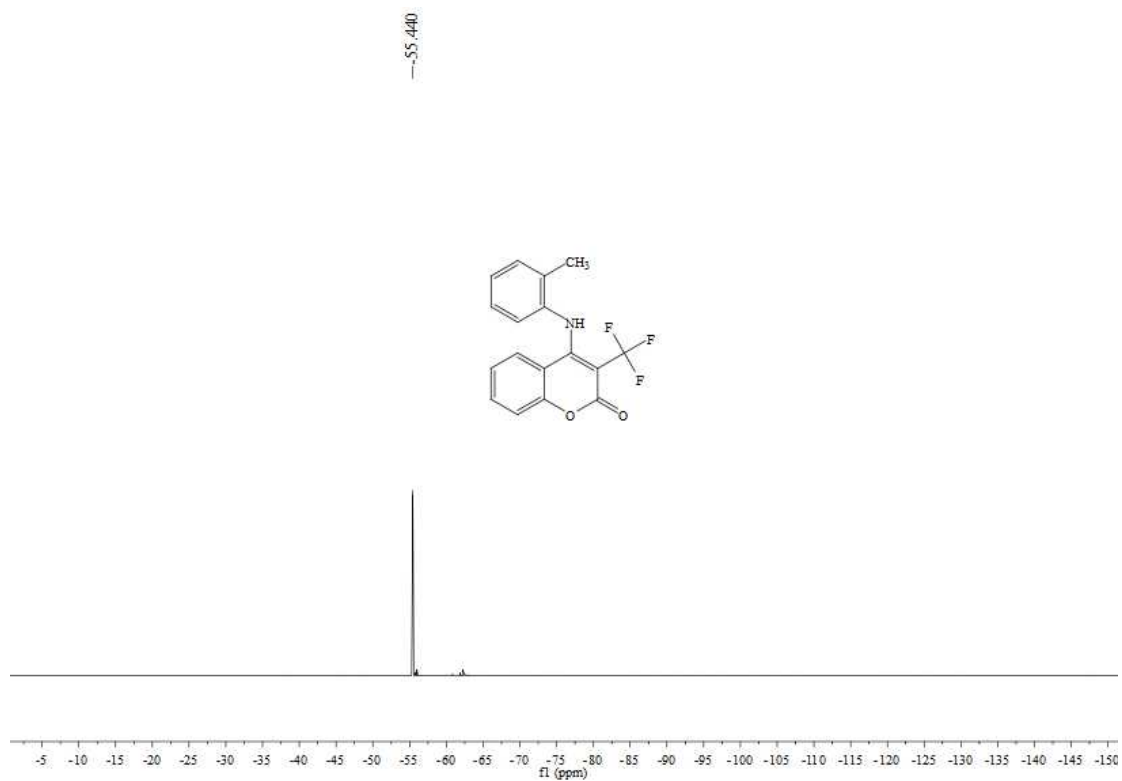


$^1\text{H}$  NMR of **3ab** in  $\text{CDCl}_3$

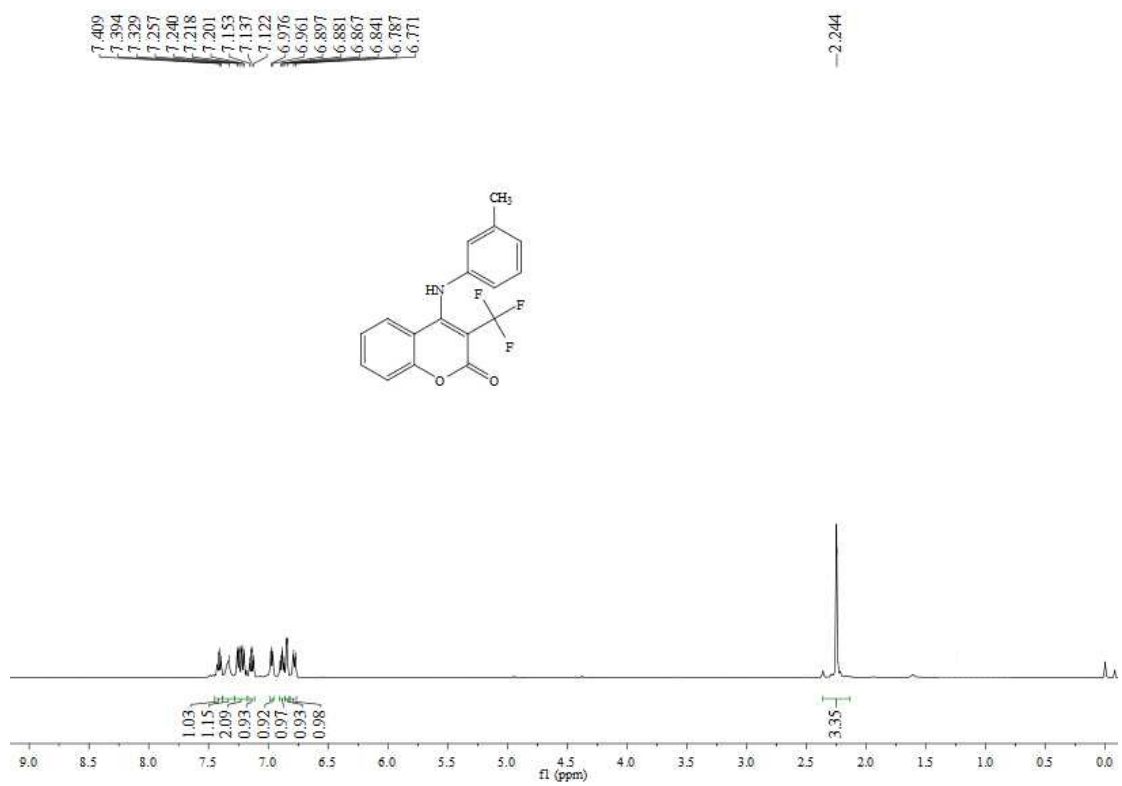


$^{13}\text{C}$  NMR of **3ab** in  $\text{CDCl}_3$

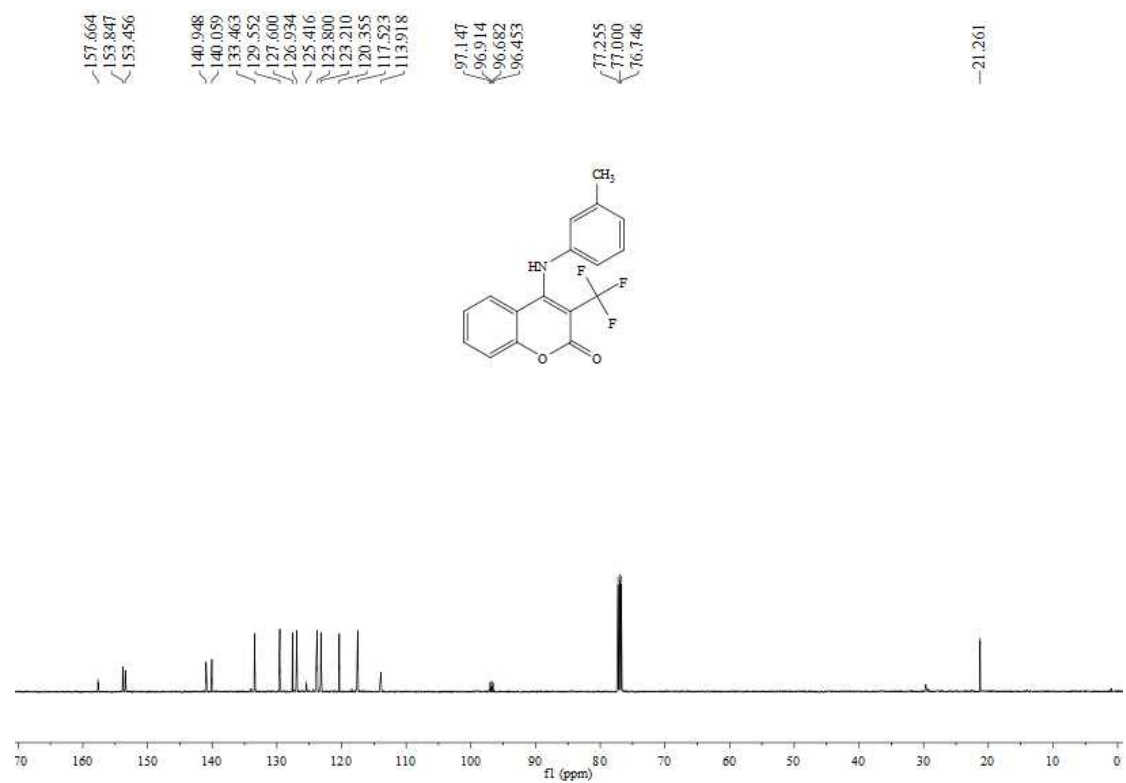




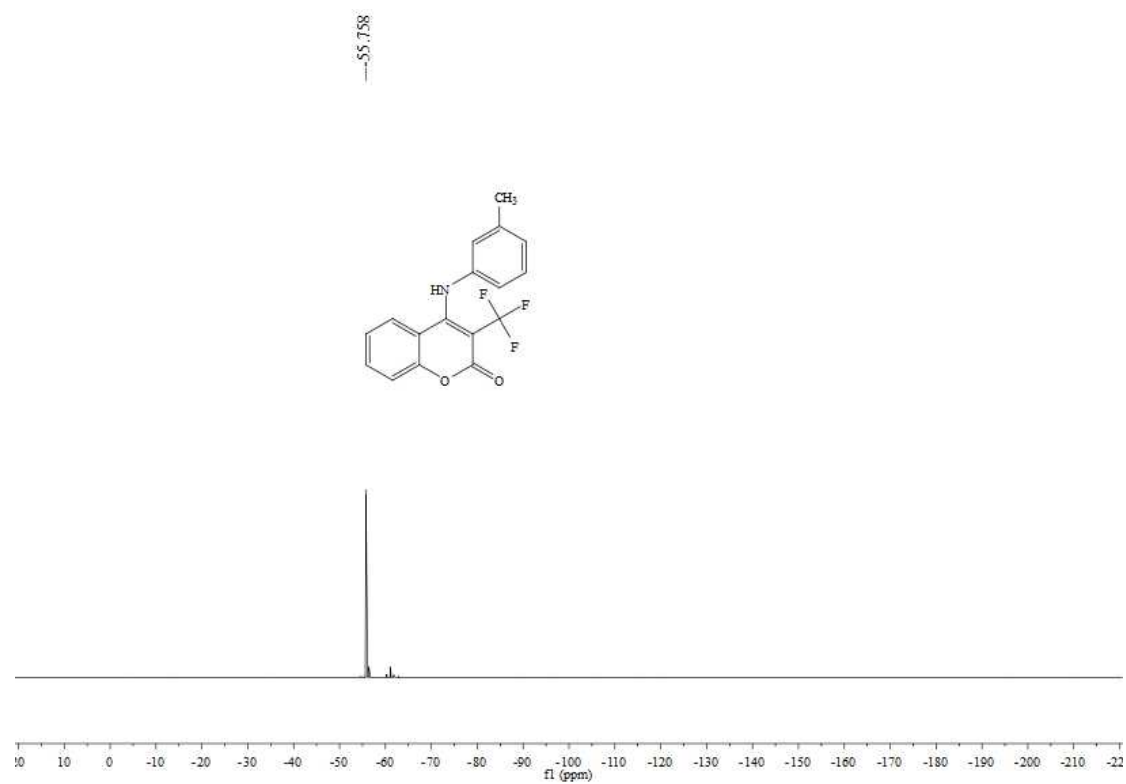
$^{19}\text{F}$  NMR of **3ab** in  $\text{CDCl}_3$



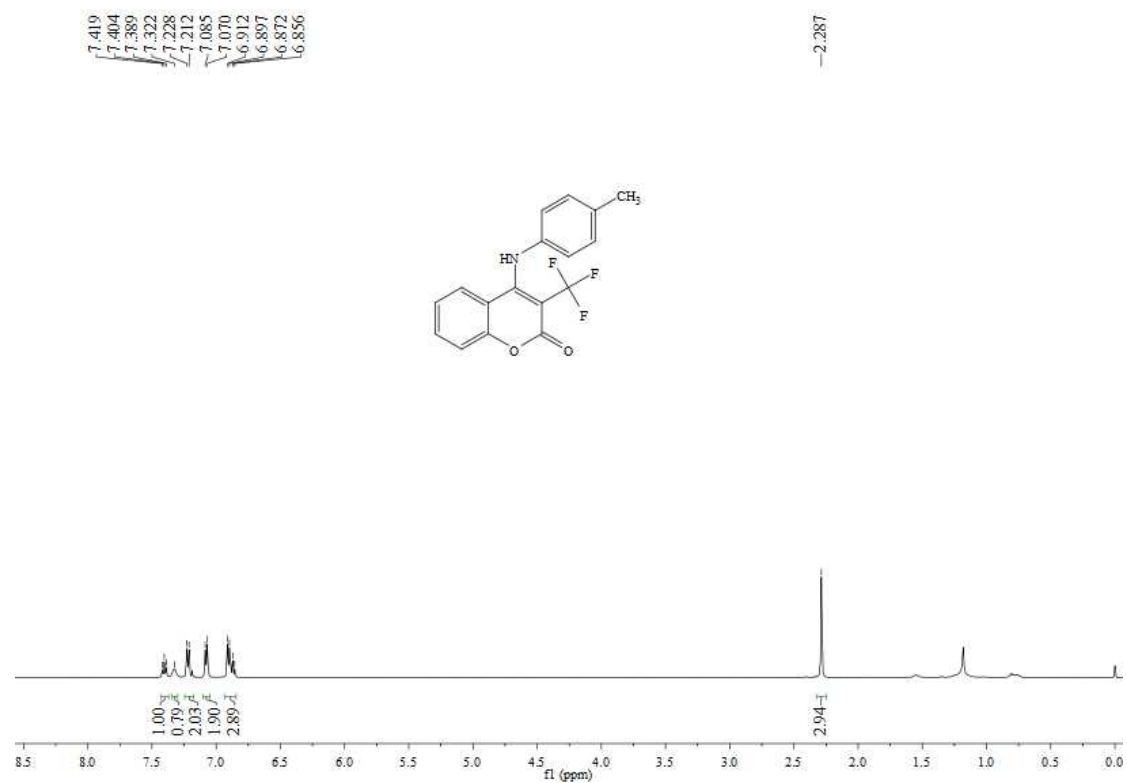
$^1\text{H}$  NMR of **3ac** in  $\text{CDCl}_3$



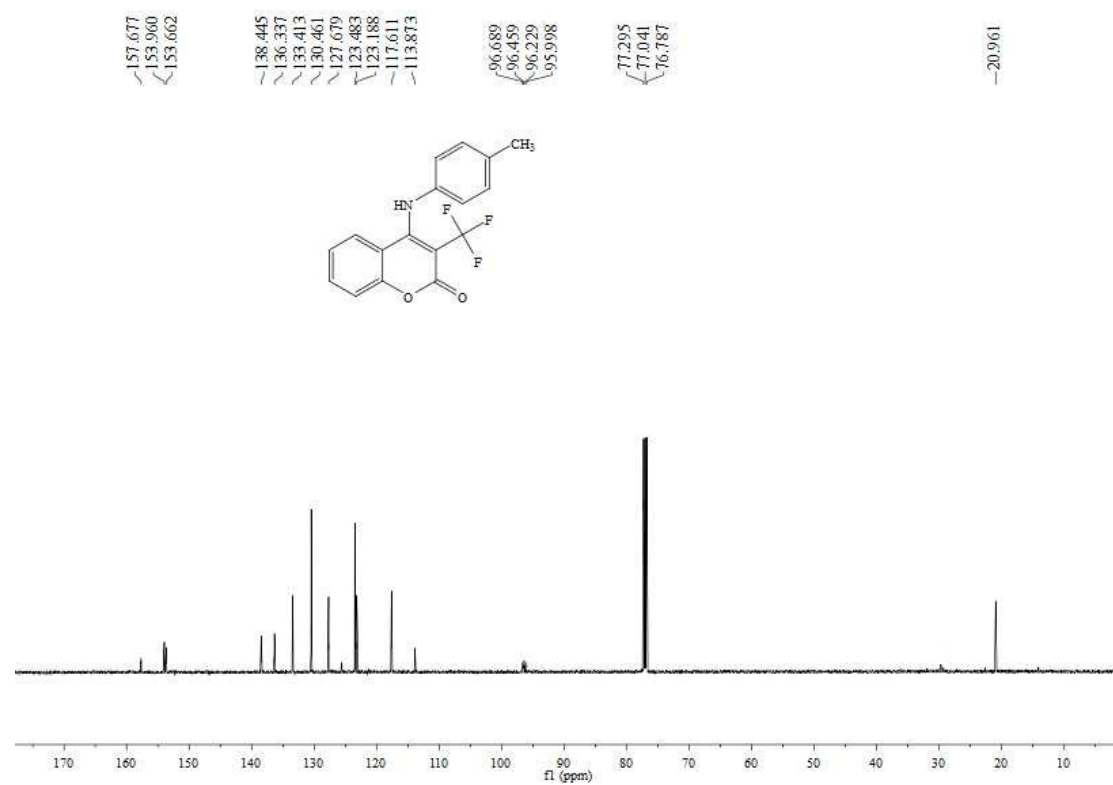
$^{13}\text{C}$  NMR of **3ac** in  $\text{CDCl}_3$



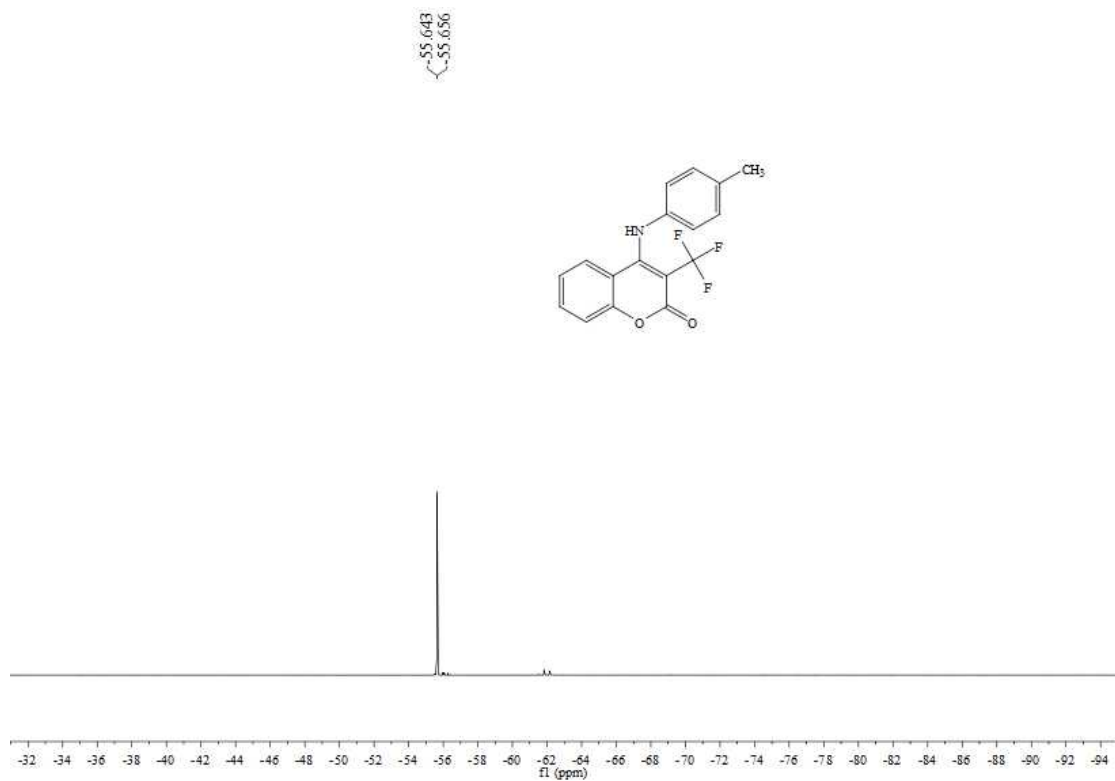
$^{19}\text{F}$  NMR of **3ac** in  $\text{CDCl}_3$



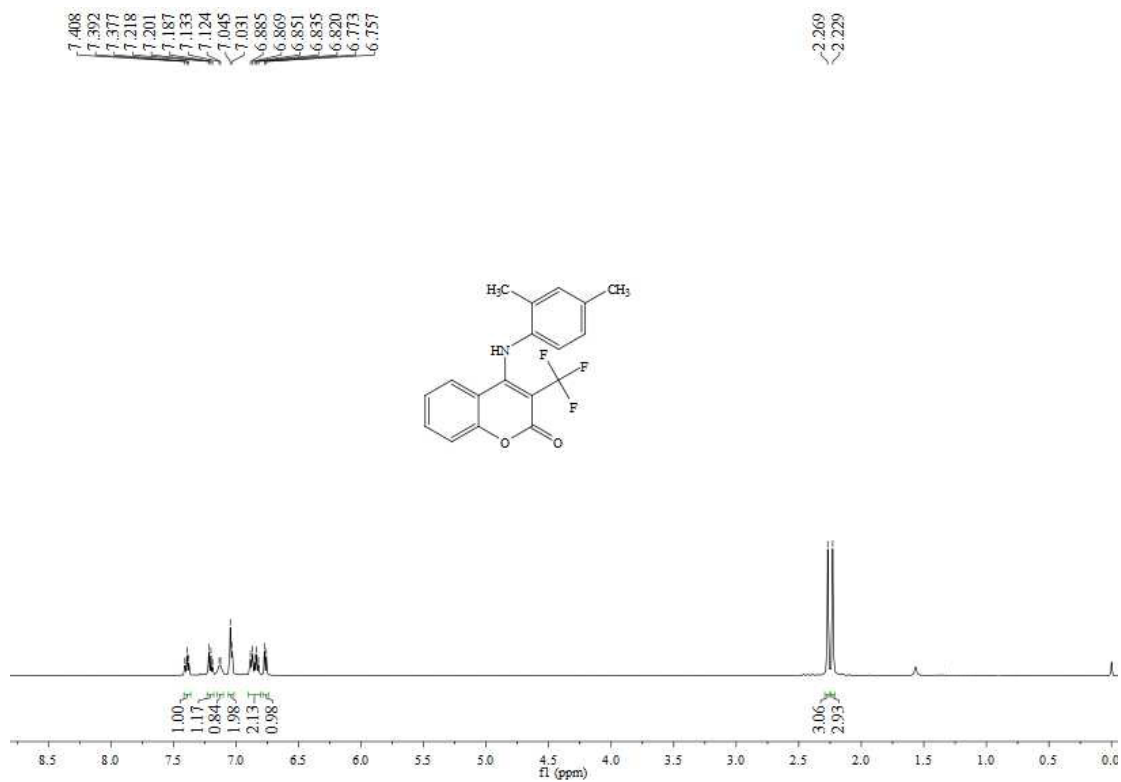
<sup>1</sup>H NMR of **3ad** in CDCl<sub>3</sub>



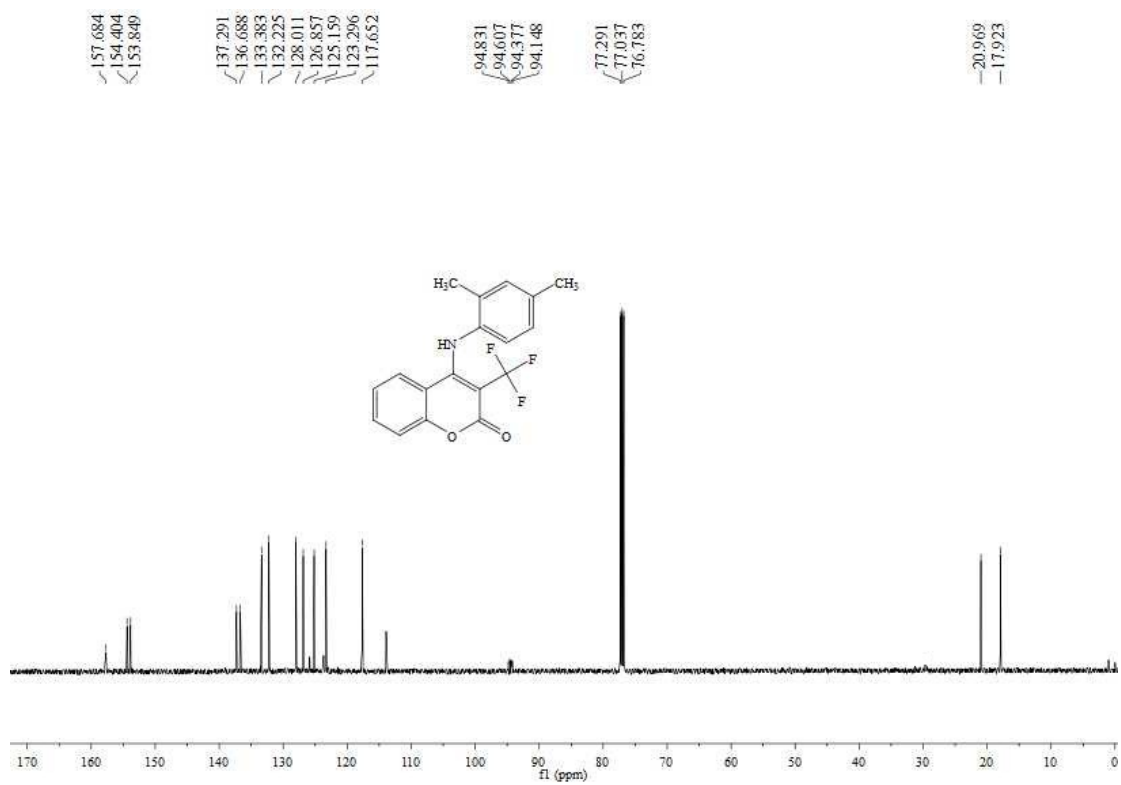
<sup>13</sup>C NMR of **3ad** in CDCl<sub>3</sub>



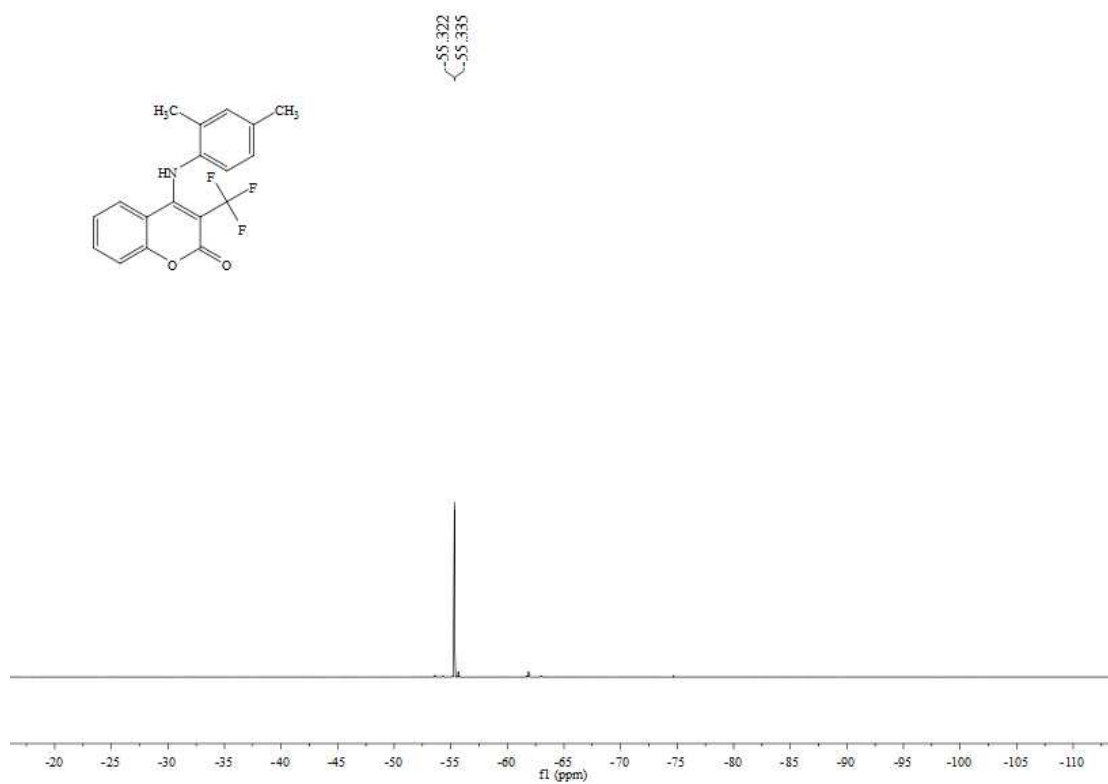
$^{19}\text{F}$  NMR of **3ad** in  $\text{CDCl}_3$



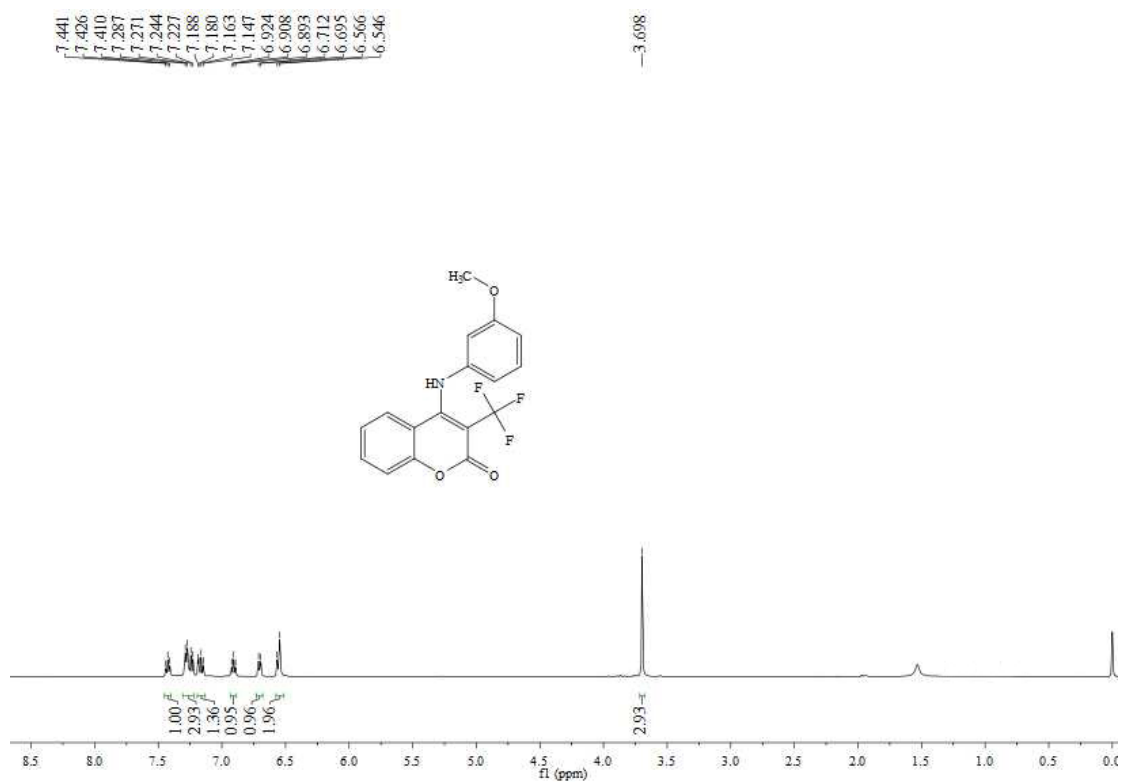
$^1\text{H}$  NMR of **3ae** in  $\text{CDCl}_3$



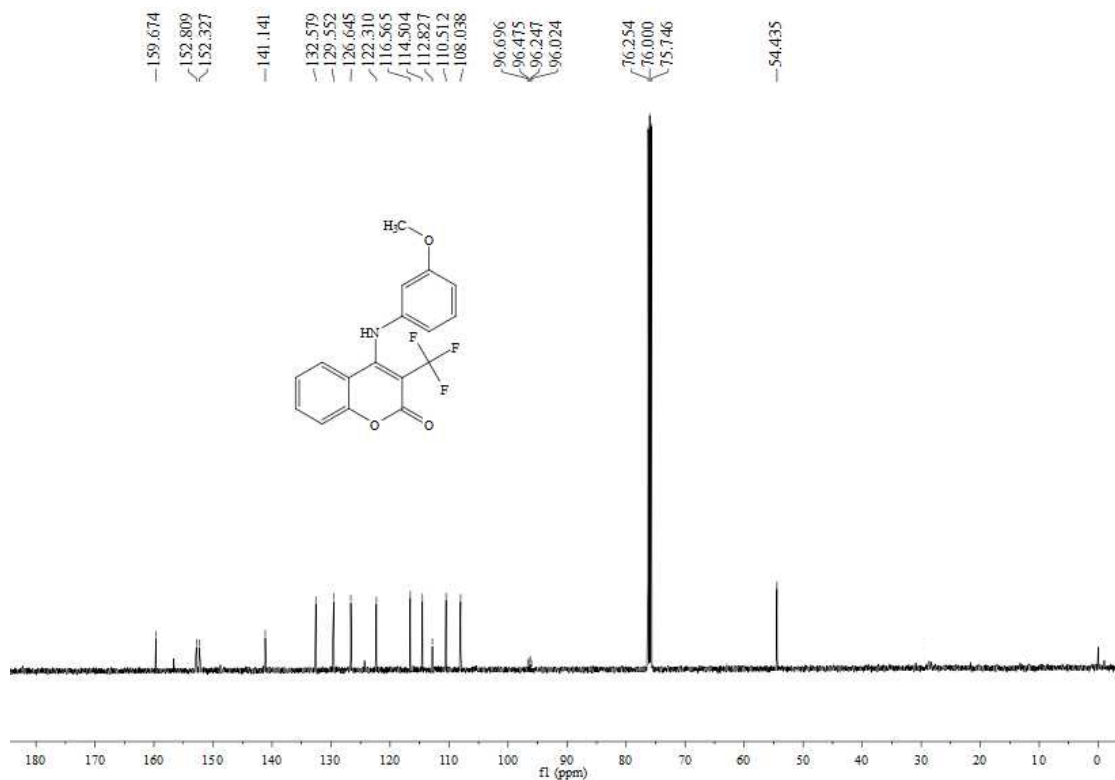
$^{13}\text{C}$  NMR of **3ae** in  $\text{CDCl}_3$



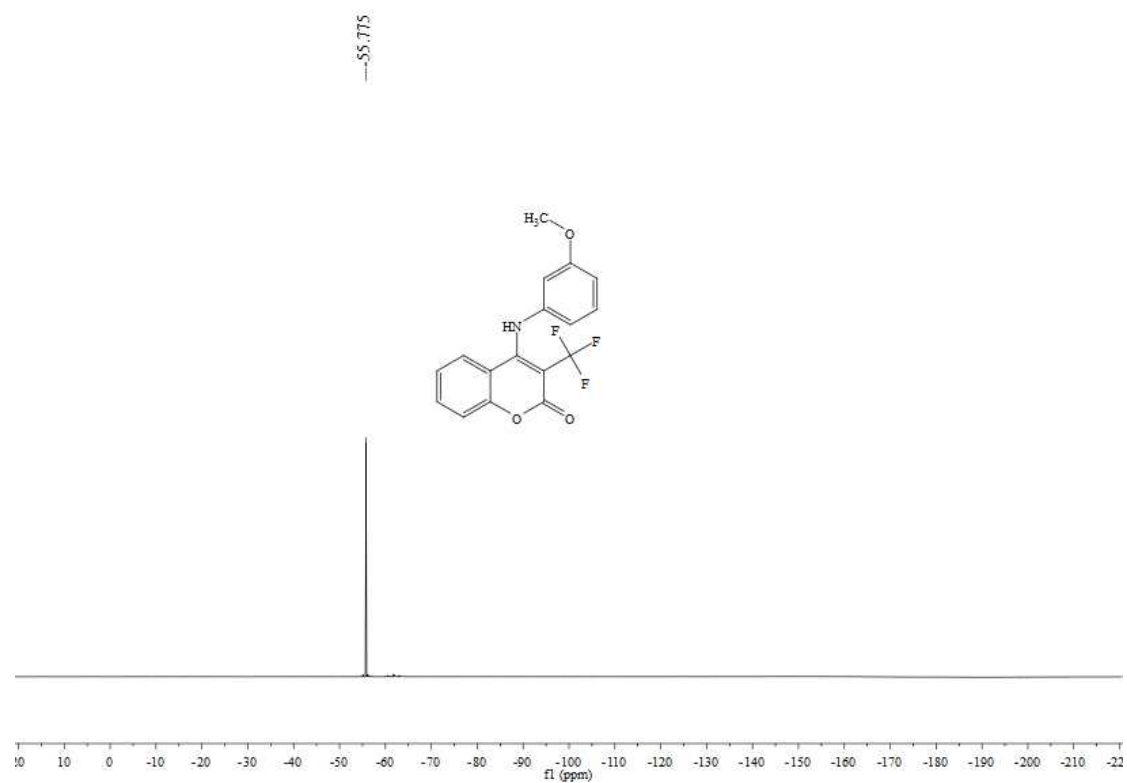
$^{19}\text{F}$  NMR of **3ae** in  $\text{CDCl}_3$



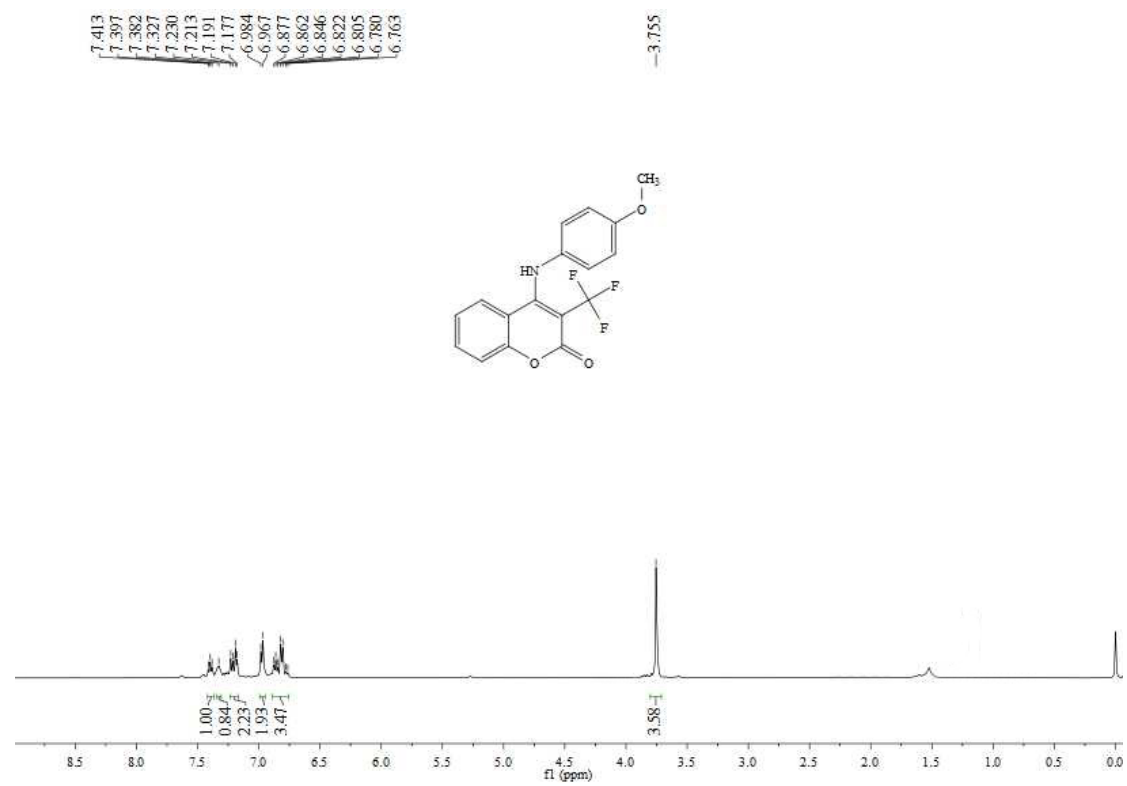
$^1\text{H}$  NMR of **3af** in  $\text{CDCl}_3$



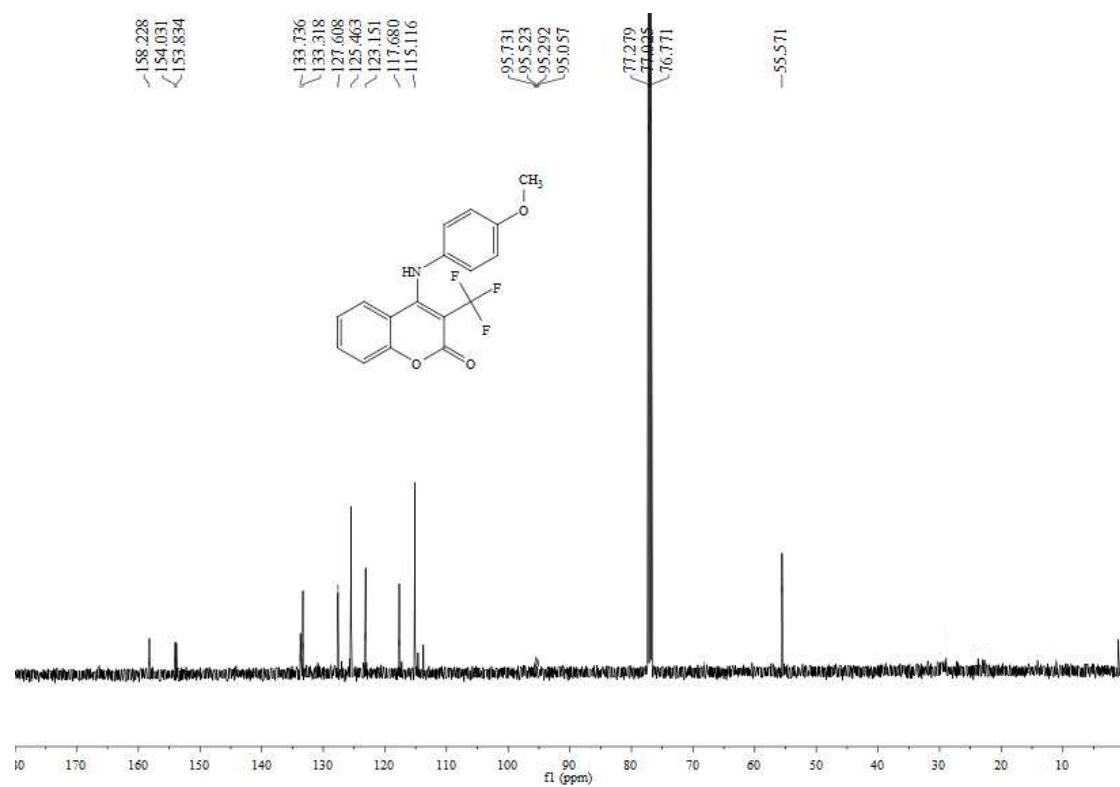
$^{13}\text{C}$  NMR of **3af** in  $\text{CDCl}_3$



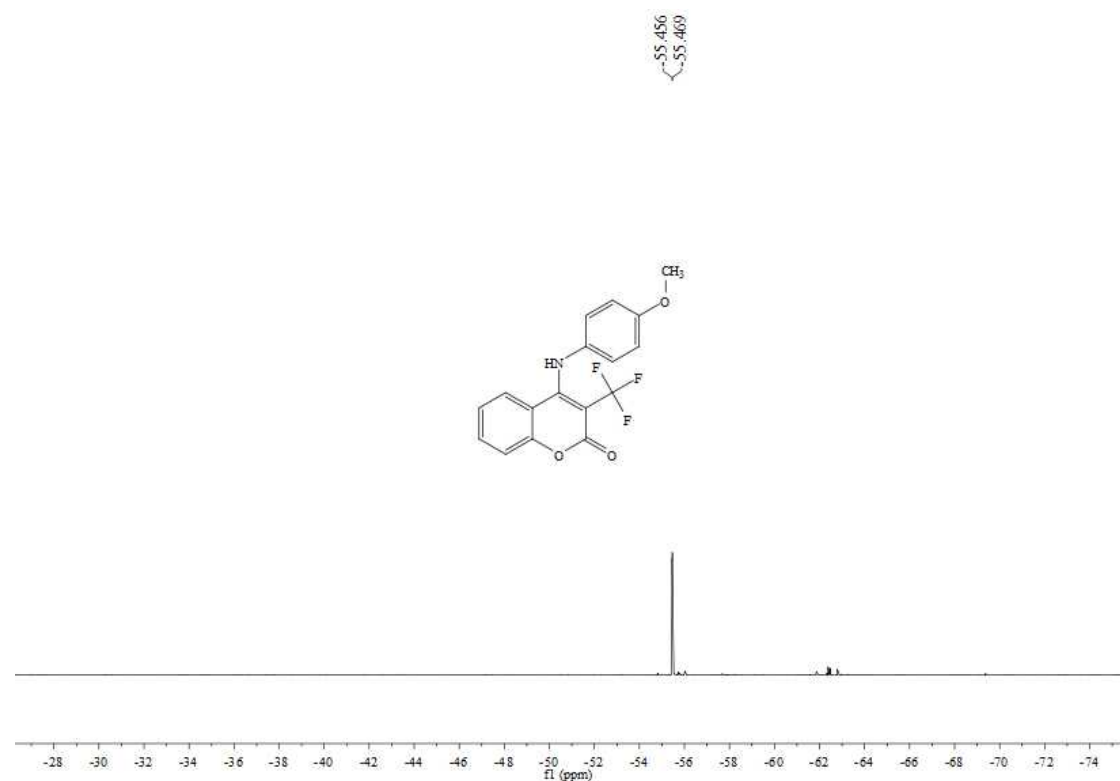
$^{19}\text{F}$  NMR of **3af** in  $\text{CDCl}_3$



$^1\text{H}$  NMR of **3ag** in  $\text{CDCl}_3$

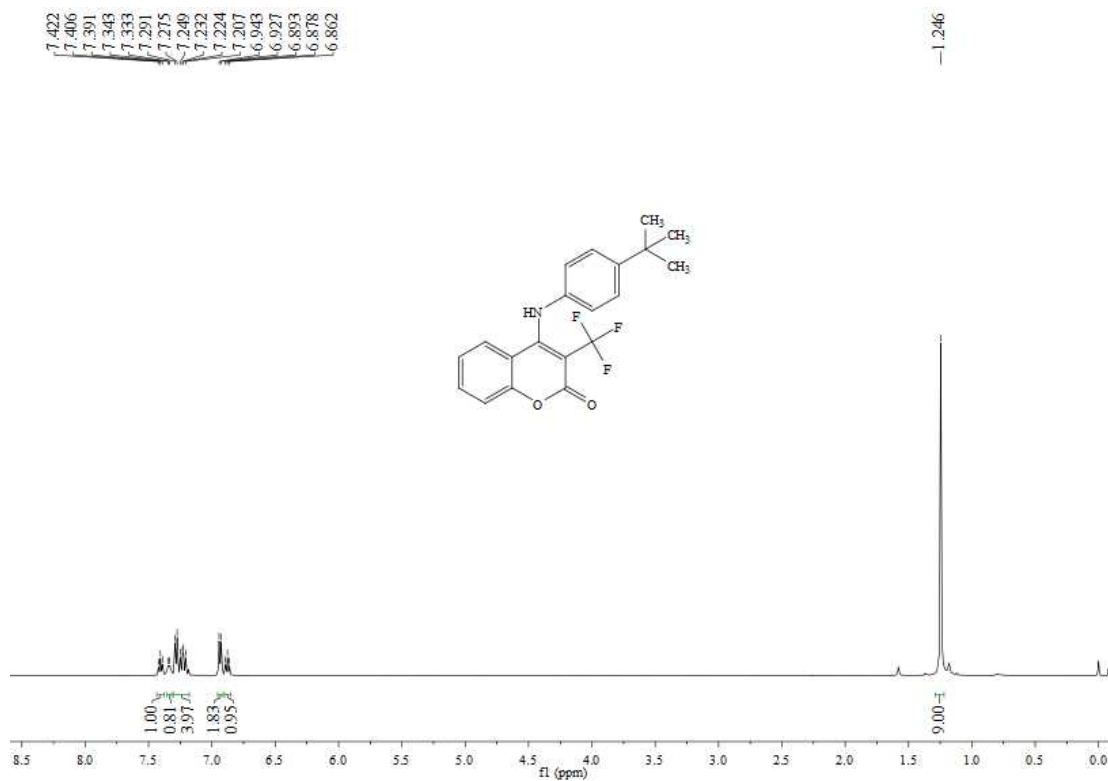


<sup>13</sup>C NMR of **3ag** in CDCl<sub>3</sub>

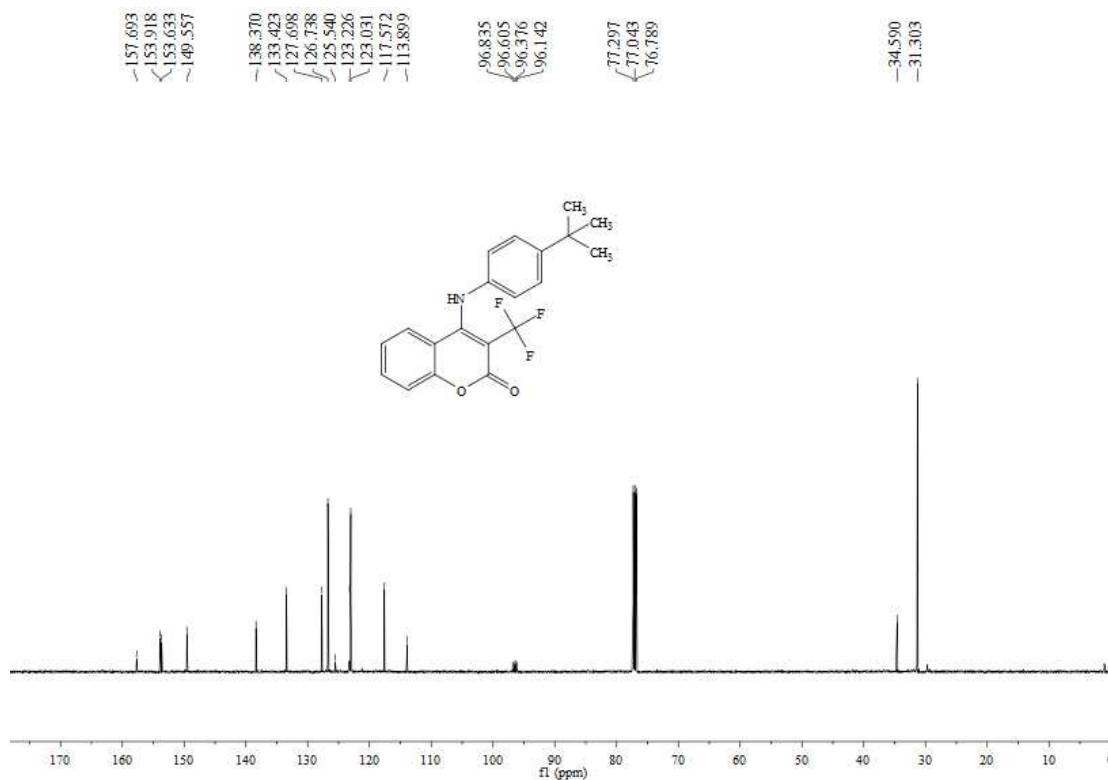


<sup>19</sup>F NMR of **3ag** in CDCl<sub>3</sub>

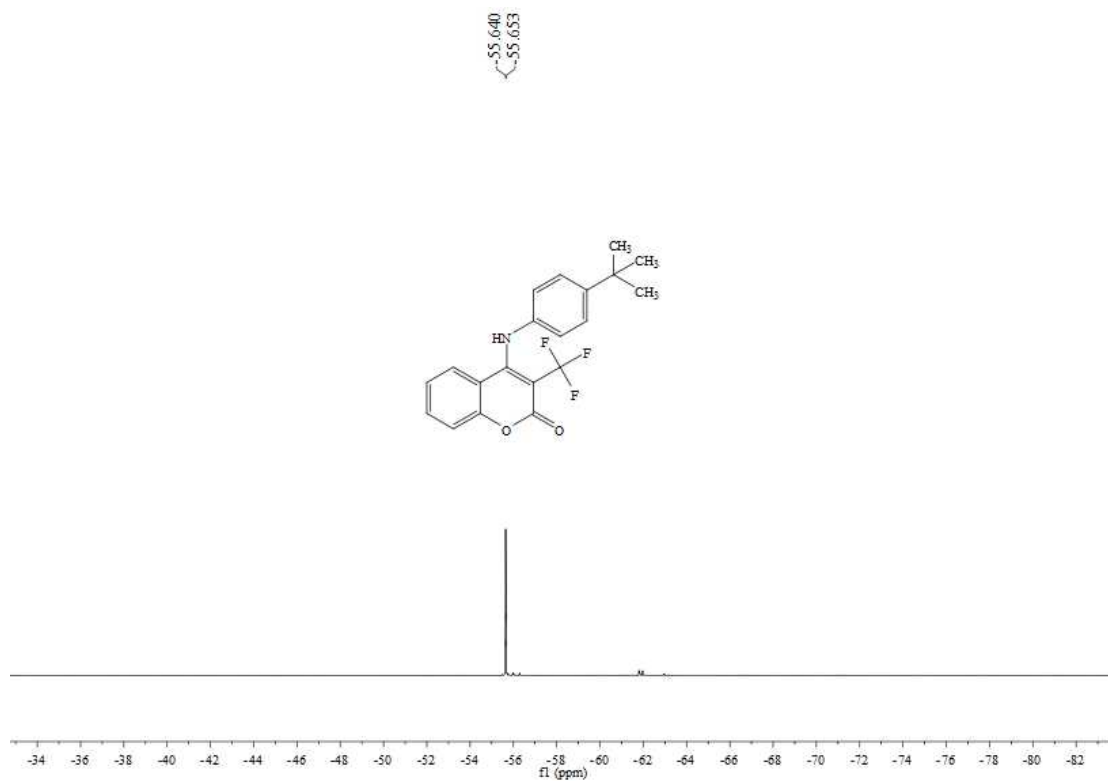




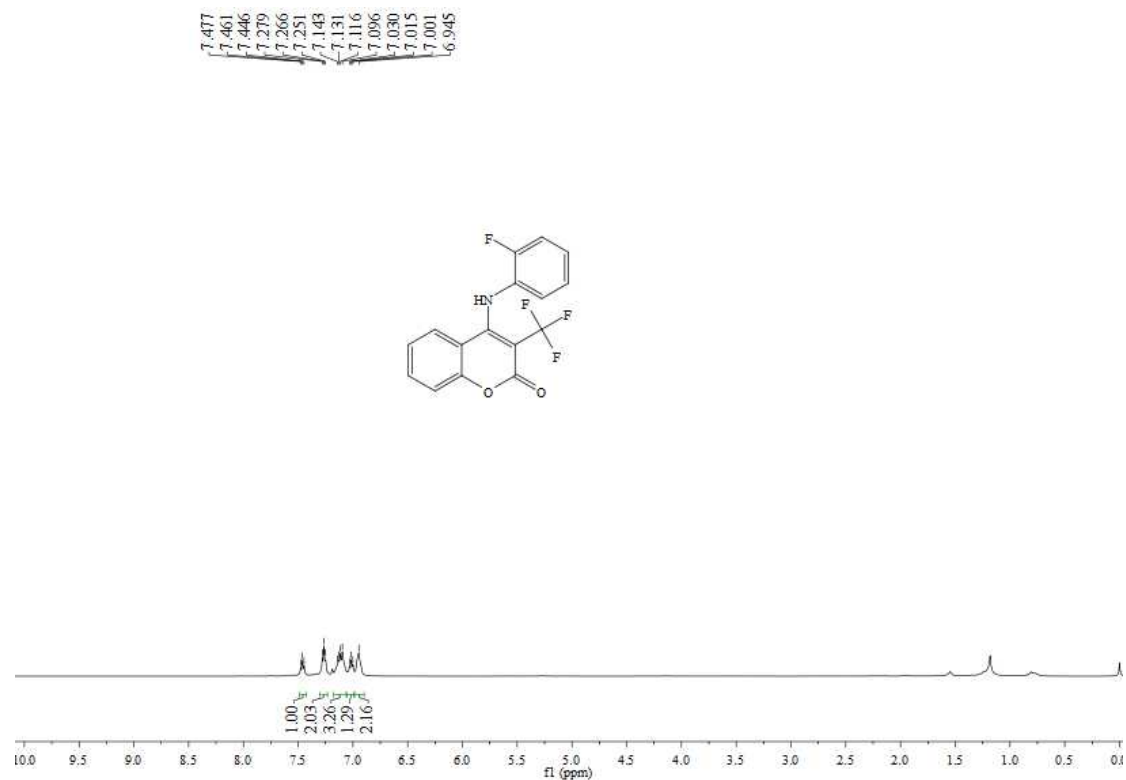
<sup>1</sup>H NMR of **3ah** in CDCl<sub>3</sub>



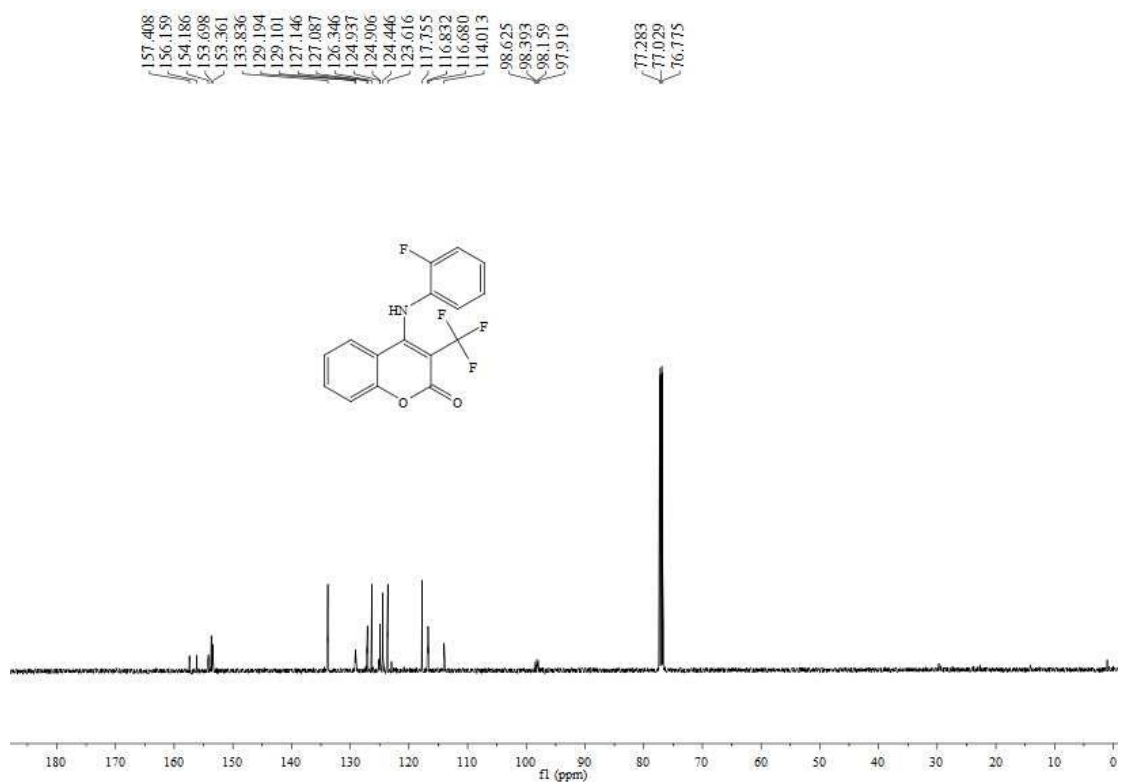
<sup>13</sup>C NMR of **3ah** in CDCl<sub>3</sub>



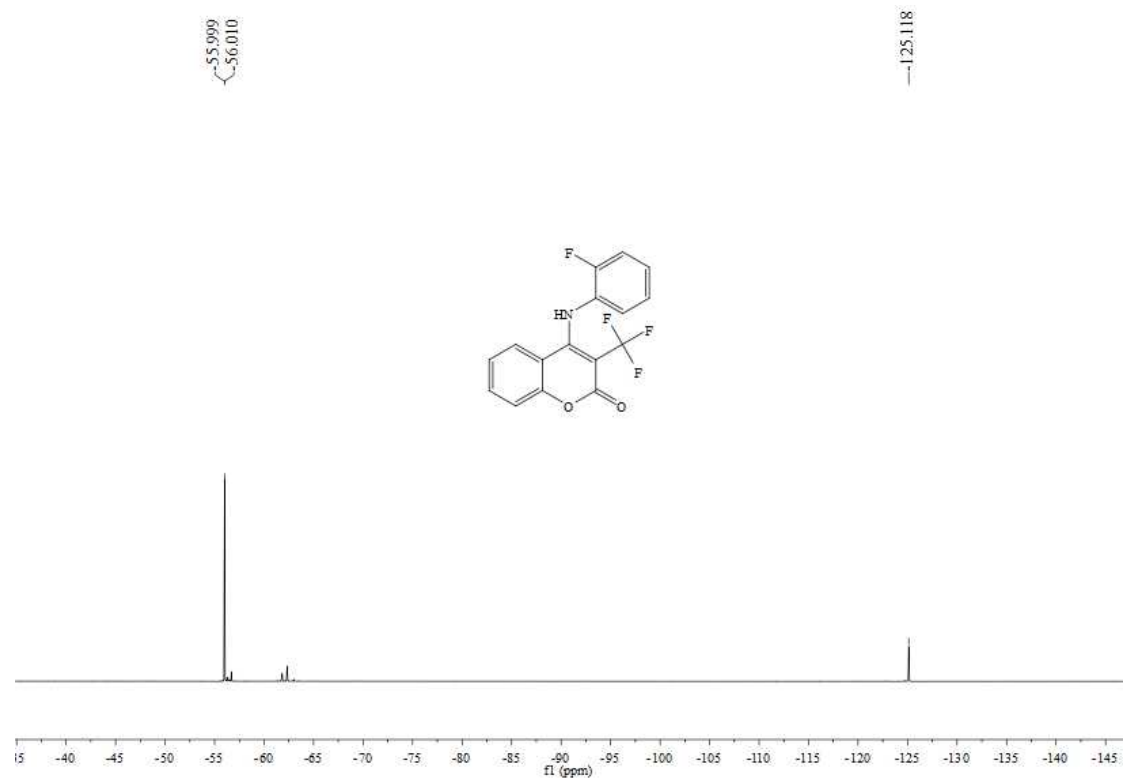
$^{19}\text{F}$  NMR of **3ah** in  $\text{CDCl}_3$



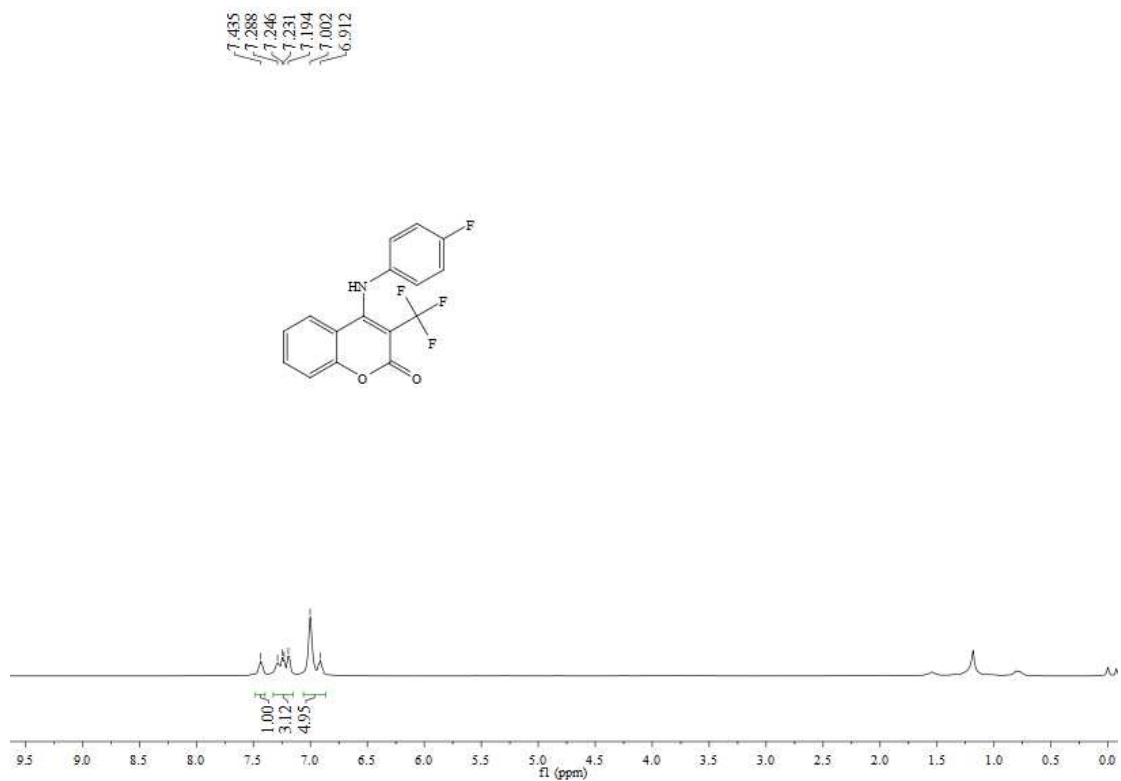
$^1\text{H}$  NMR of **3ai** in  $\text{CDCl}_3$



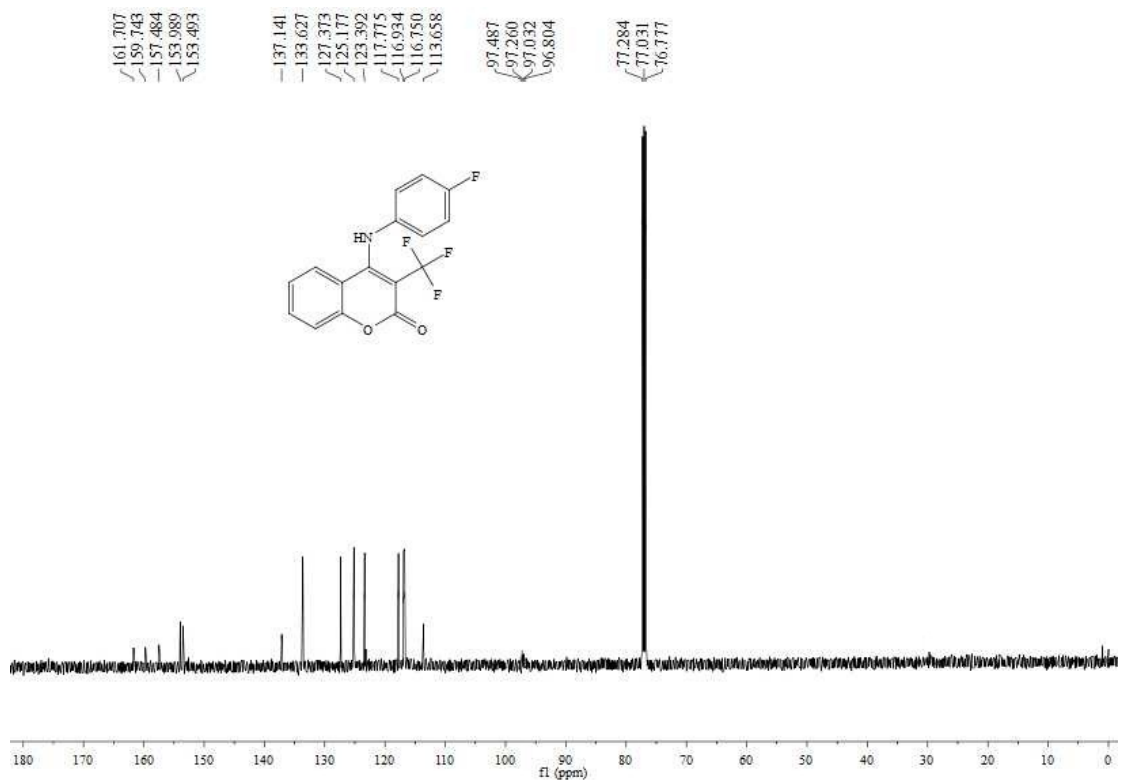
$^{13}\text{C}$  NMR of **3ai** in  $\text{CDCl}_3$



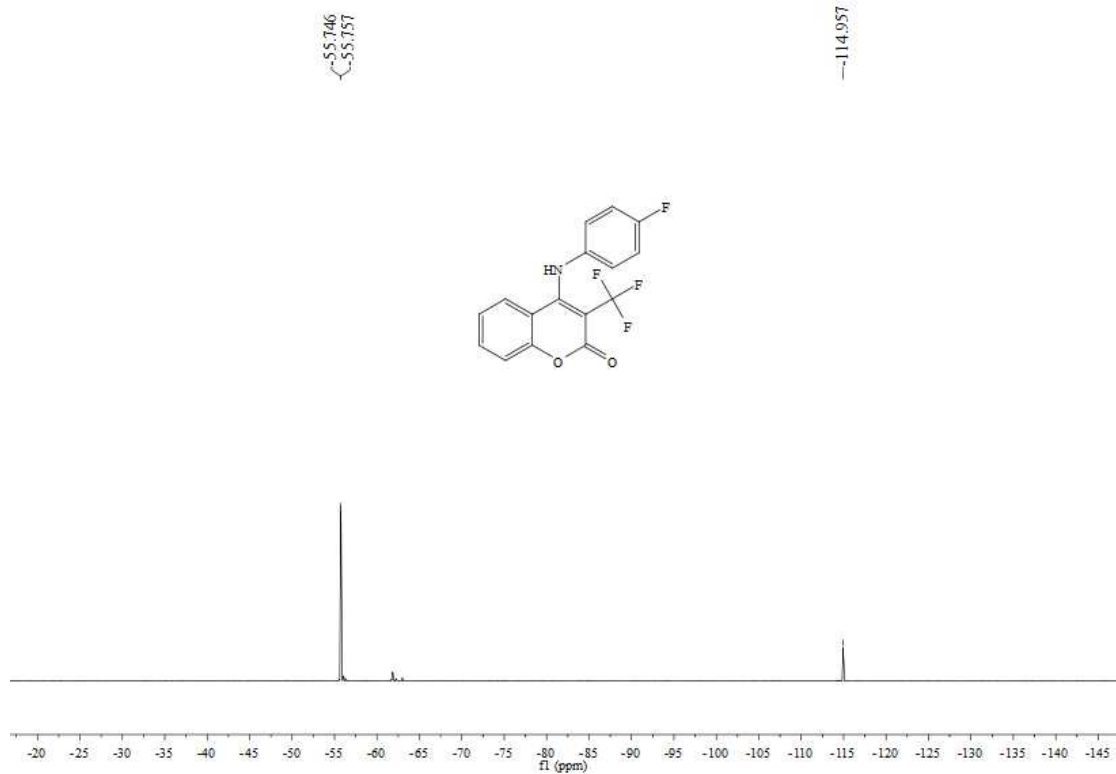
$^{19}\text{F}$  NMR of **3ai** in  $\text{CDCl}_3$



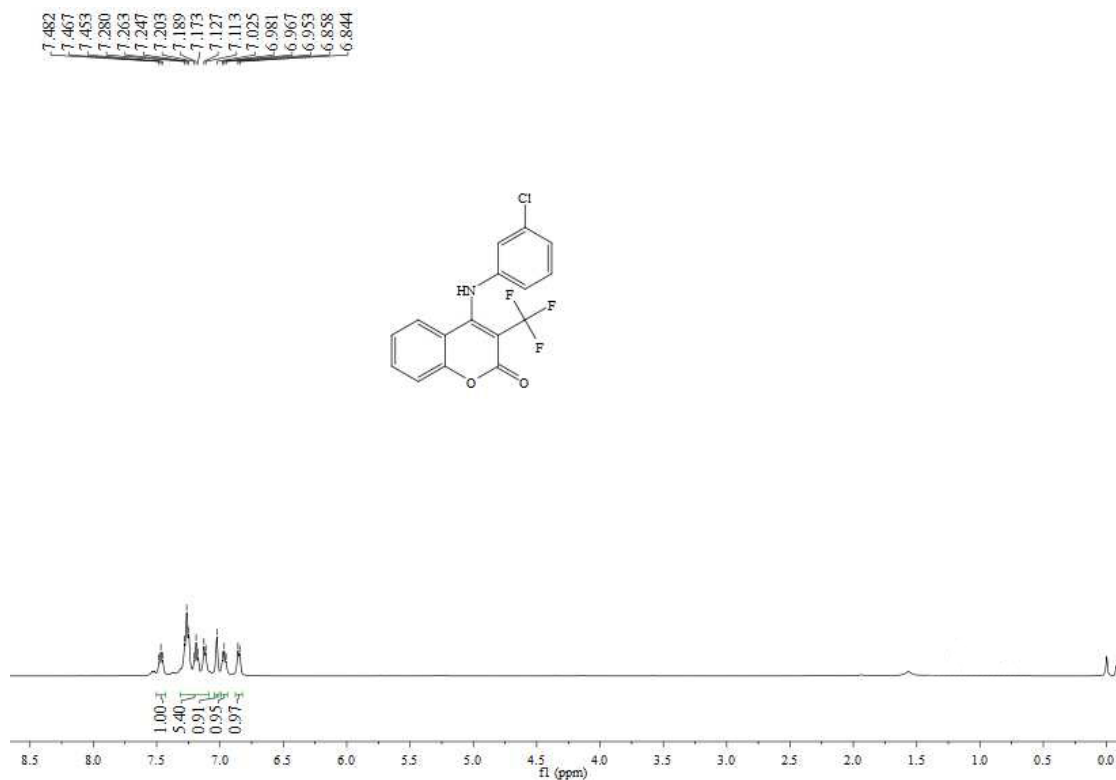
$^1\text{H}$  NMR of **3aj** in  $\text{CDCl}_3$



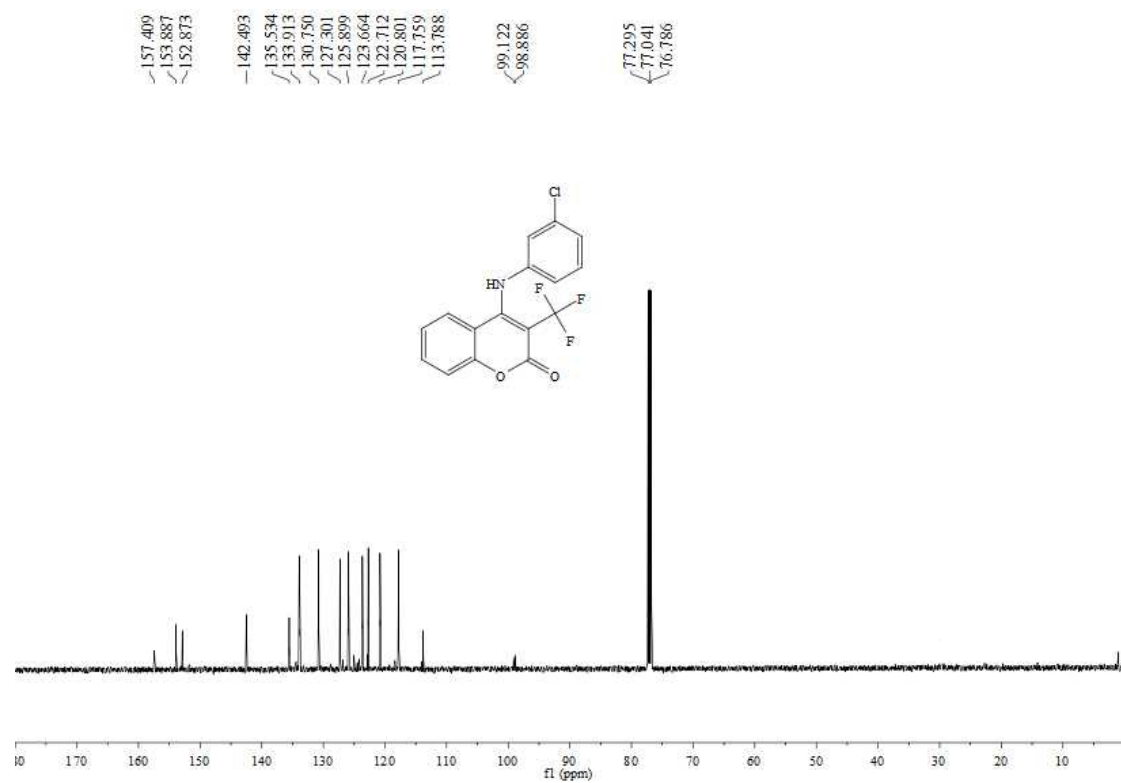
$^{13}\text{C}$  NMR of **3aj** in  $\text{CDCl}_3$



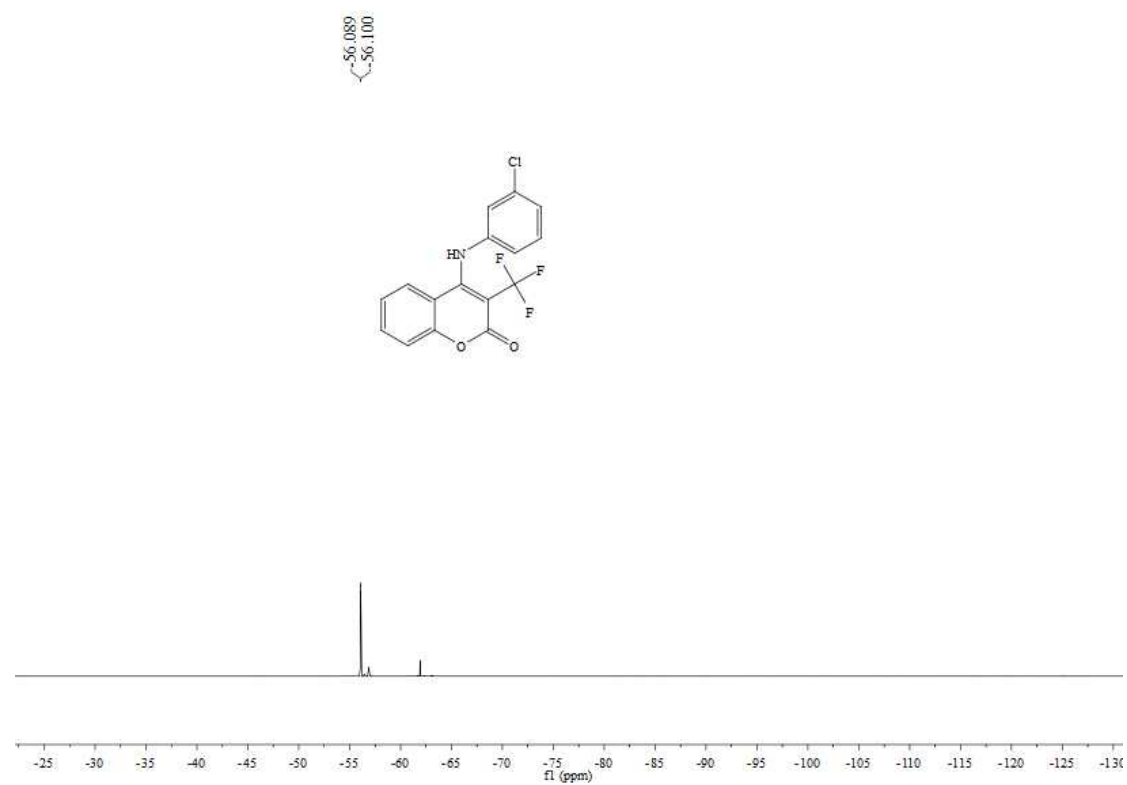
$^{19}\text{F}$  NMR of **3aj** in  $\text{CDCl}_3$



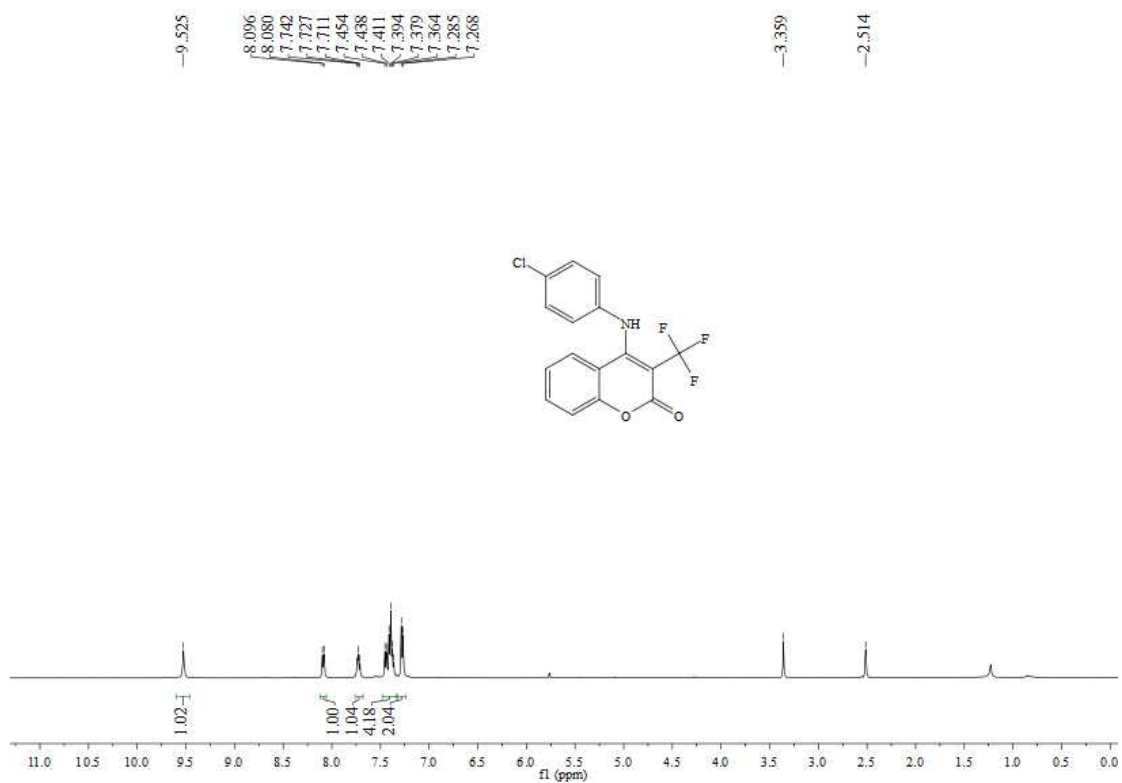
$^1\text{H}$  NMR of **3ak** in  $\text{CDCl}_3$



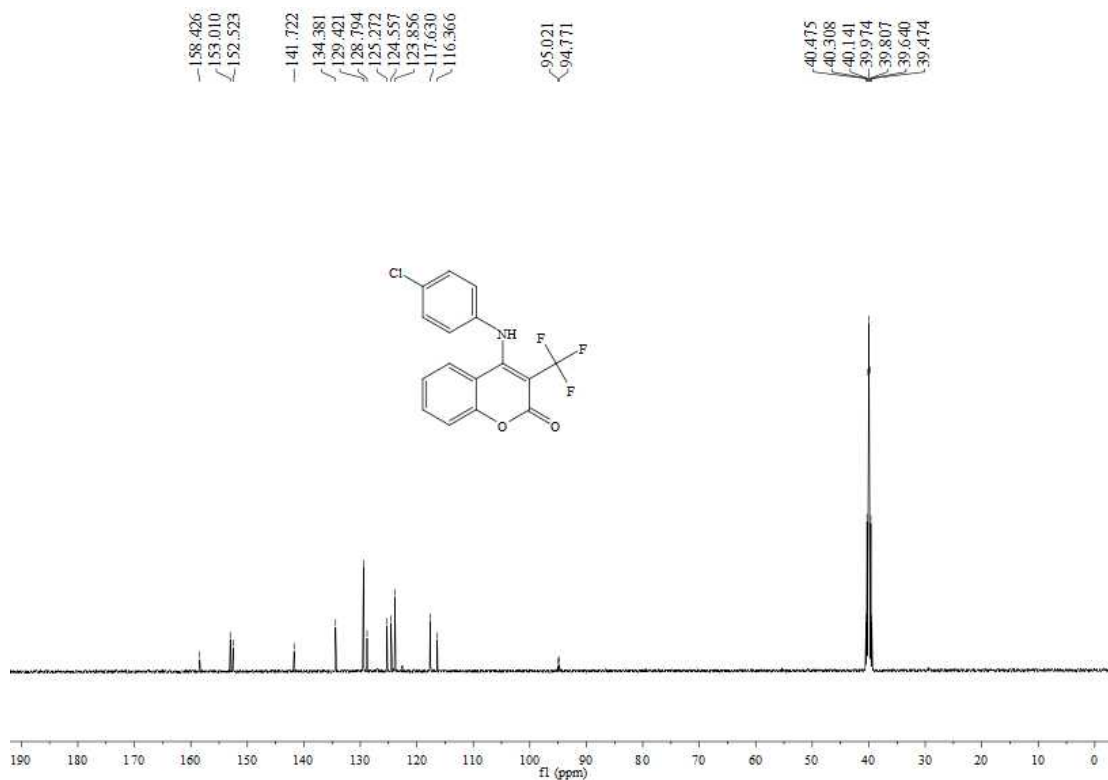
<sup>13</sup>C NMR of **3ak** in CDCl<sub>3</sub>



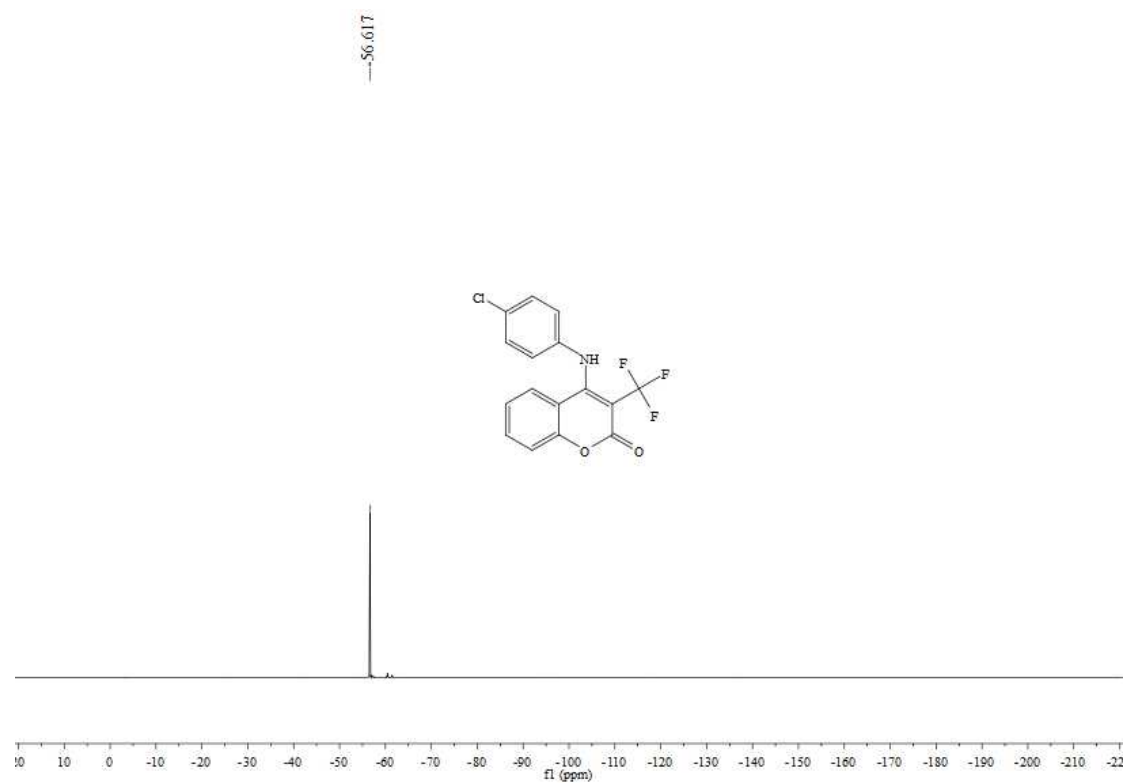
<sup>19</sup>F NMR of **3ak** in CDCl<sub>3</sub>



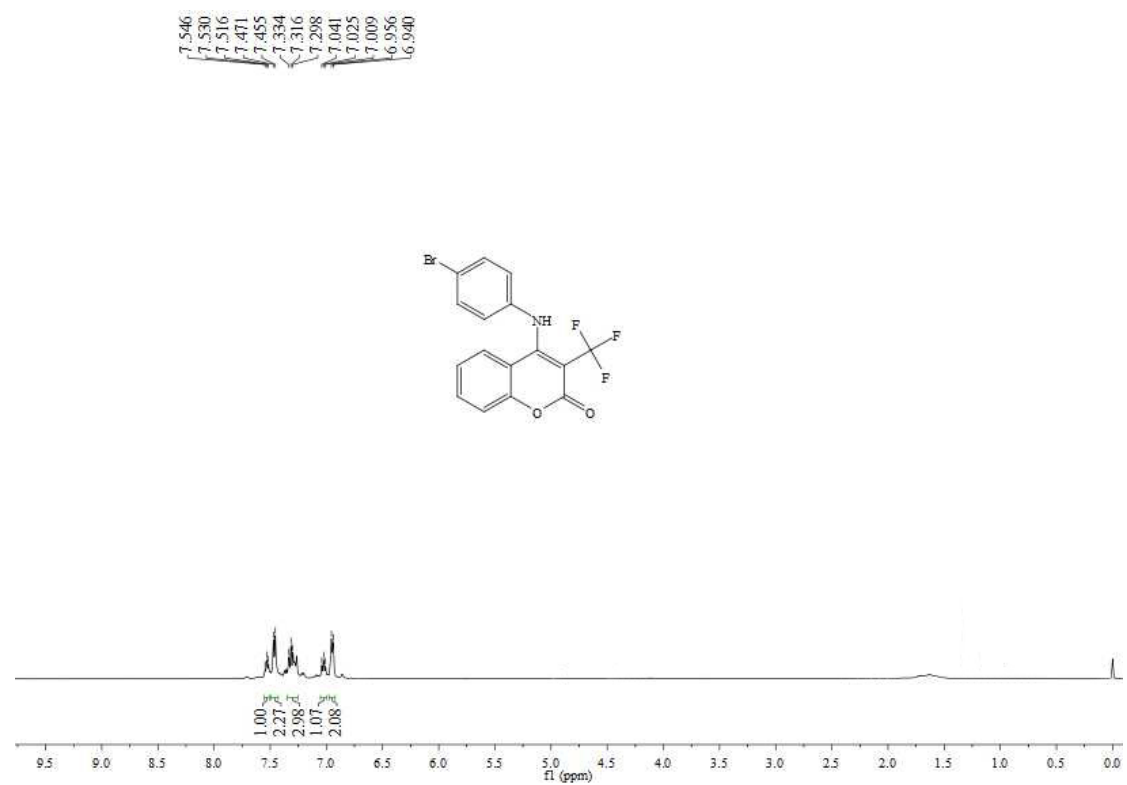
<sup>1</sup>H NMR of **3al** in *d*<sub>6</sub>-DMSO



<sup>13</sup>C NMR of **3al** in *d*<sub>6</sub>-DMSO

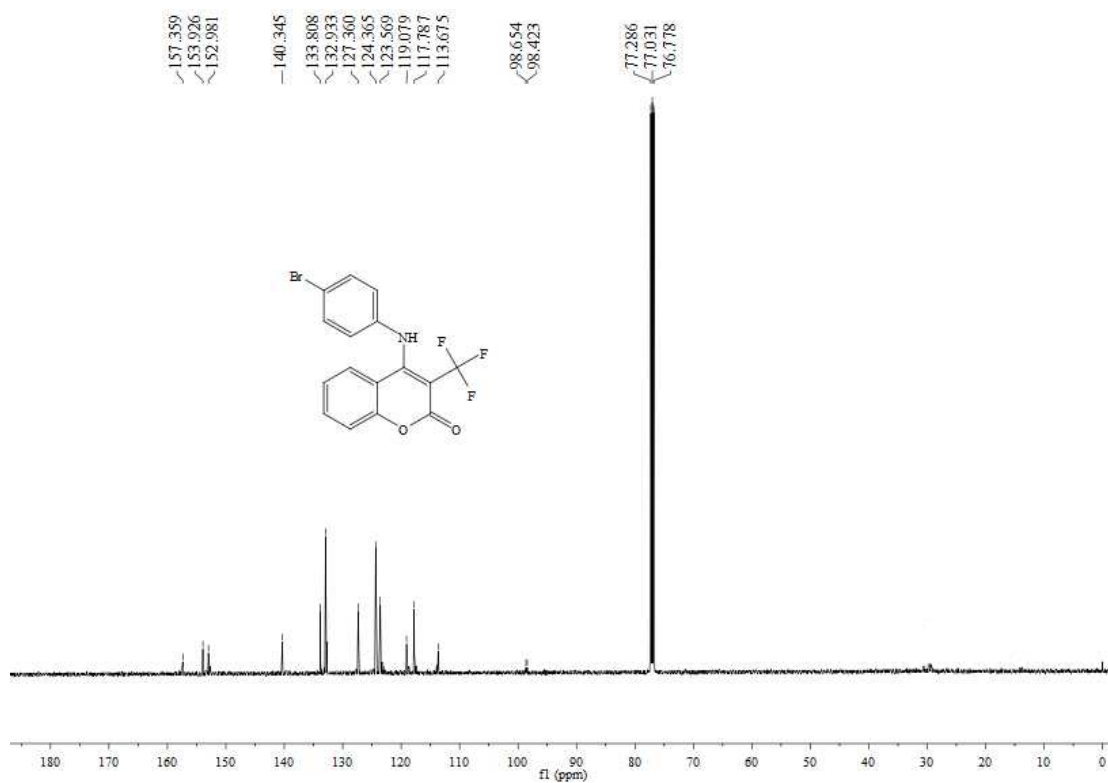


$^{19}\text{F}$  NMR of **3al** in  $d_6$ -DMSO

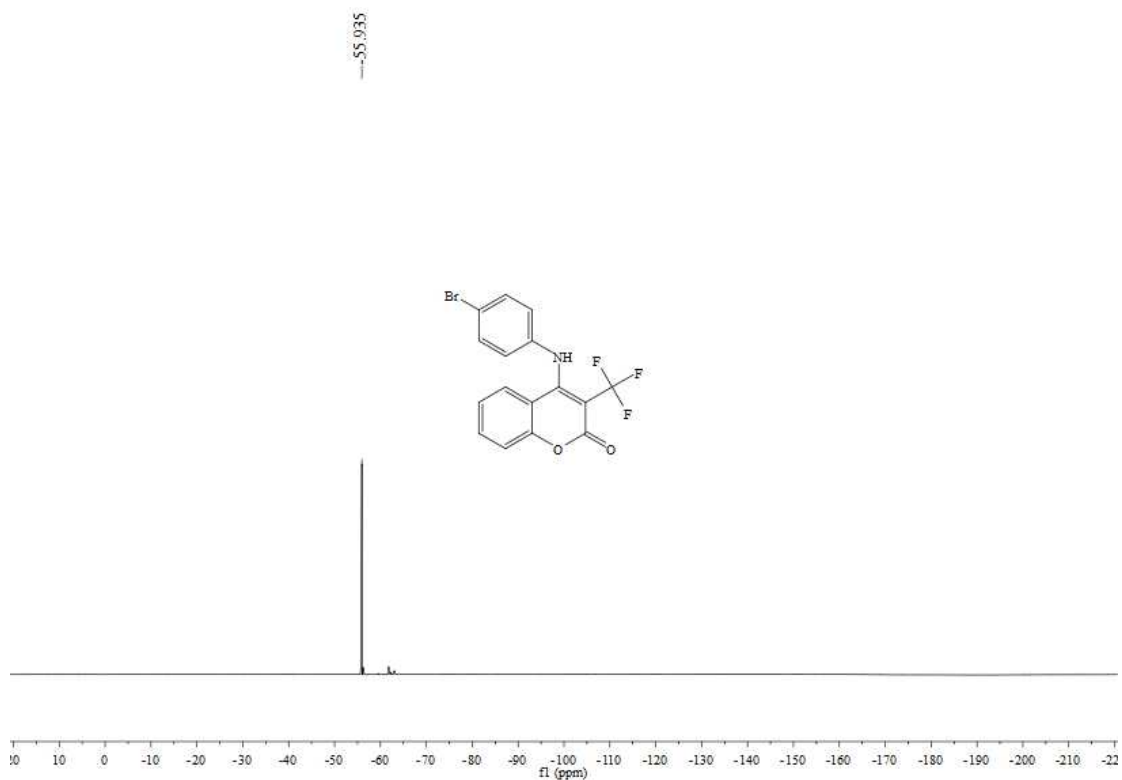


$^1\text{H}$  NMR of **3am** in  $\text{CDCl}_3$

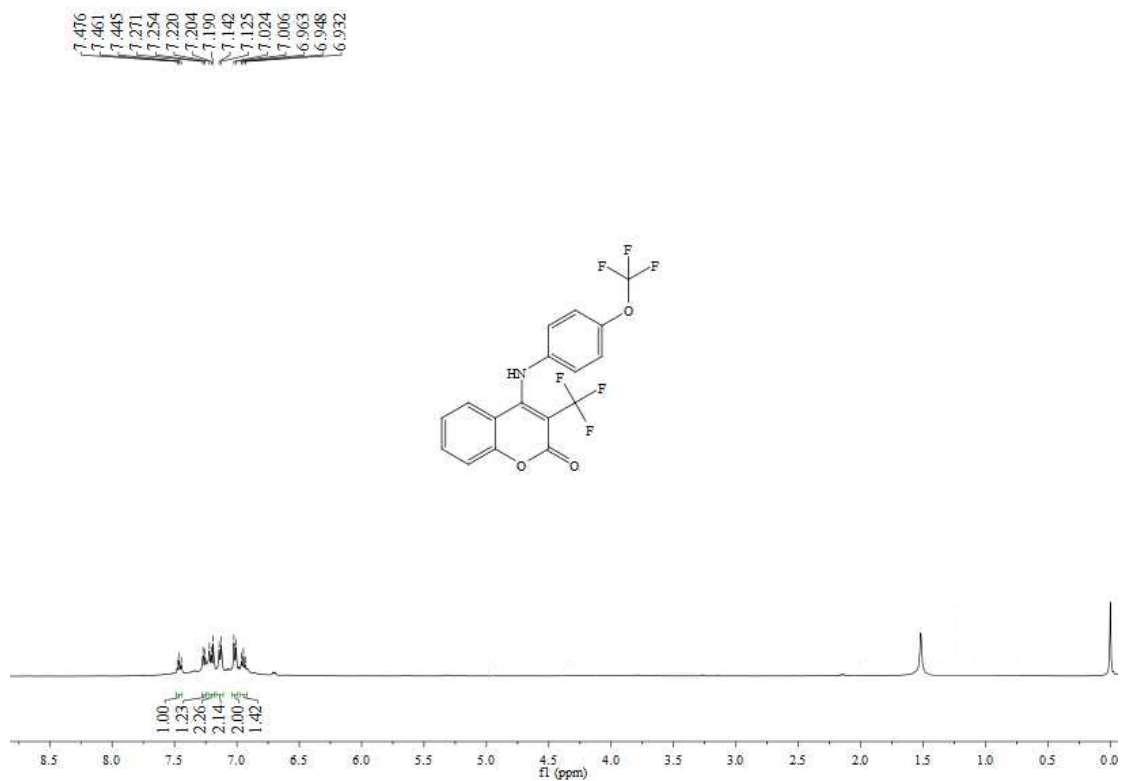




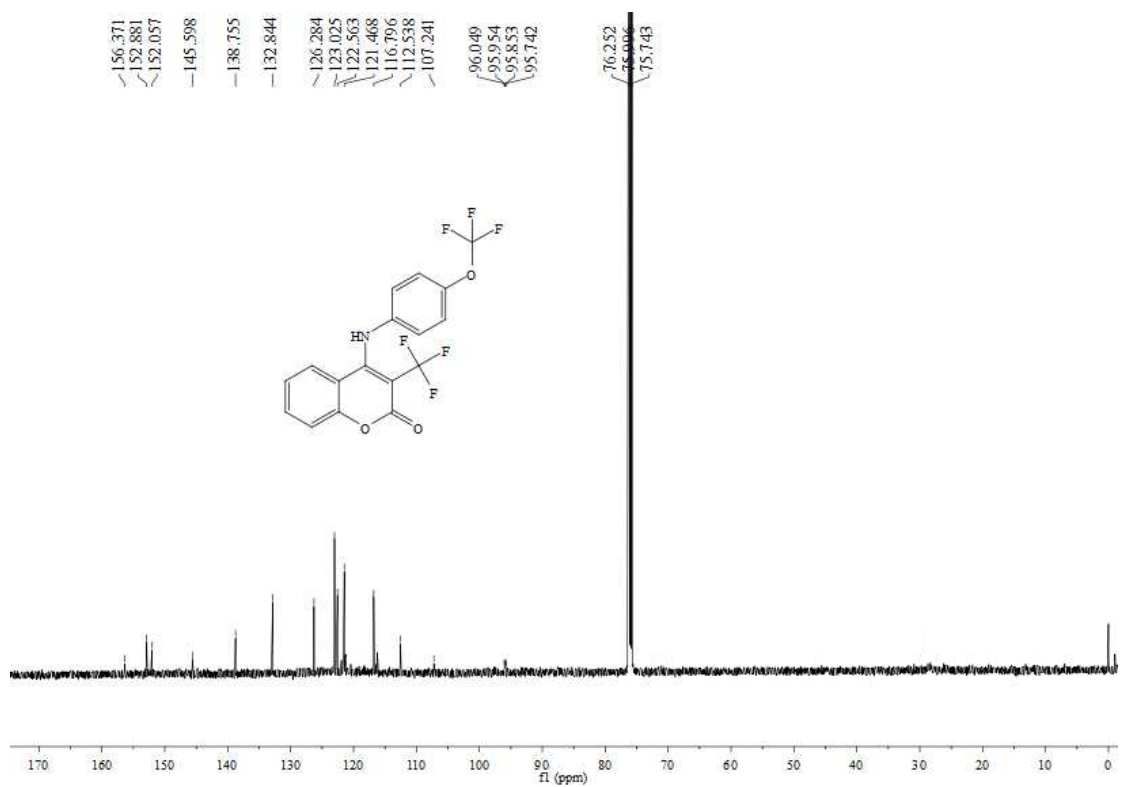
<sup>13</sup>C NMR of **3ak** in CDCl<sub>3</sub>



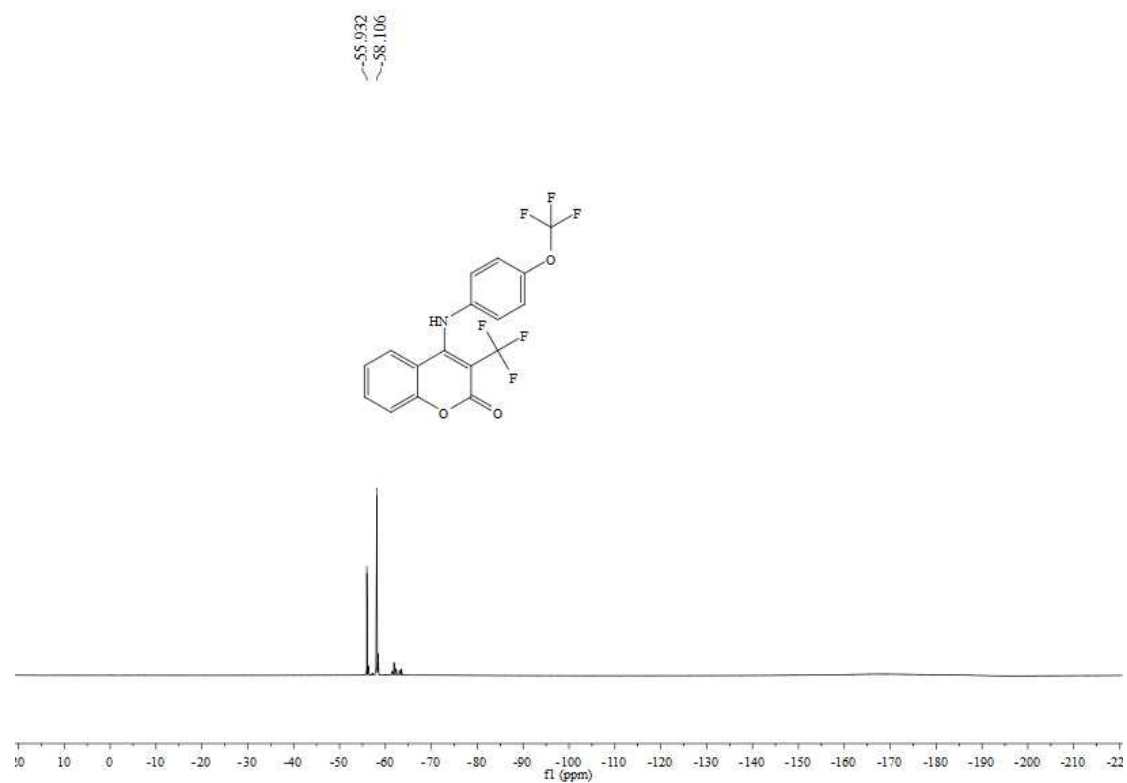
<sup>19</sup>F NMR of **3am** in CDCl<sub>3</sub>



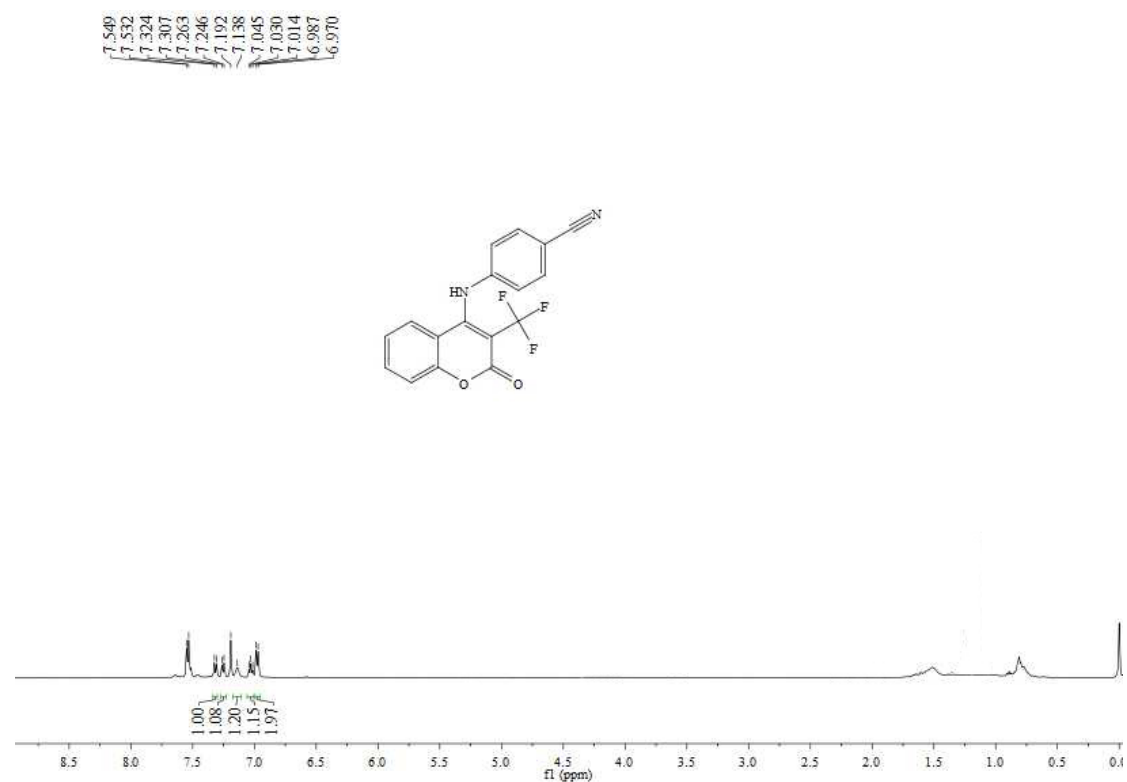
$^1\text{H}$  NMR of **3an** in  $\text{CDCl}_3$



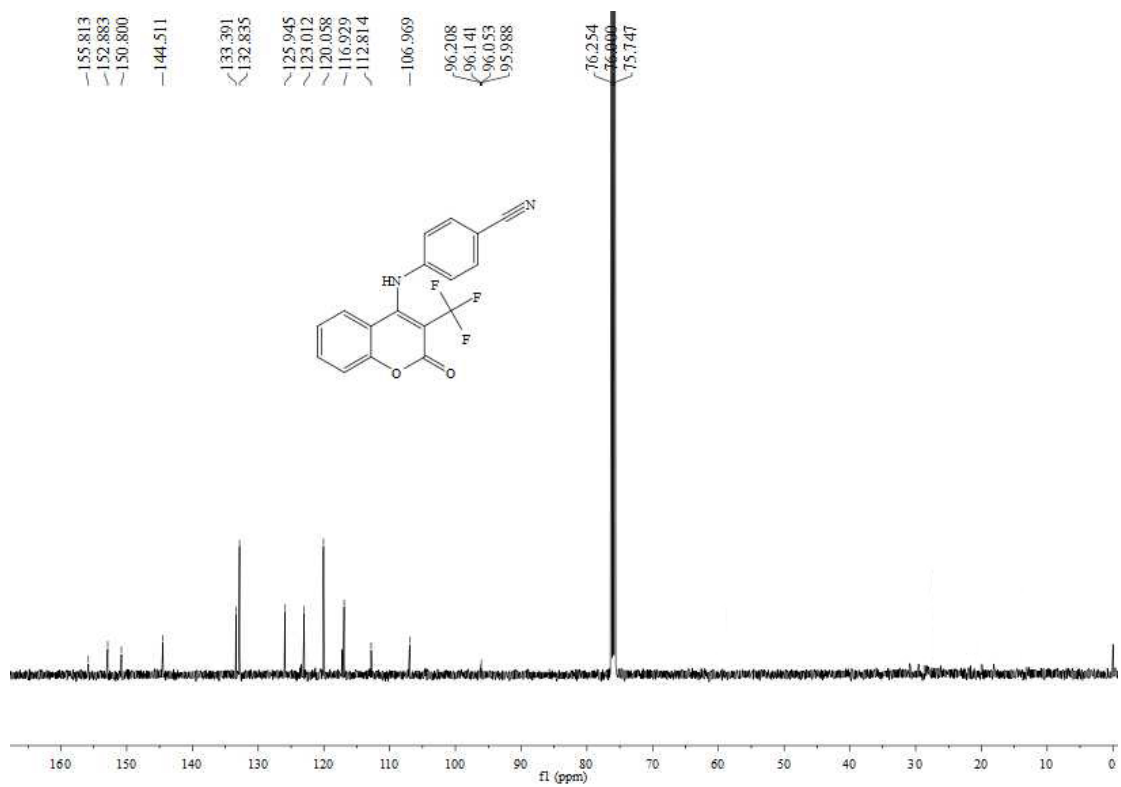
$^{13}\text{C}$  NMR of **3an** in  $\text{CDCl}_3$



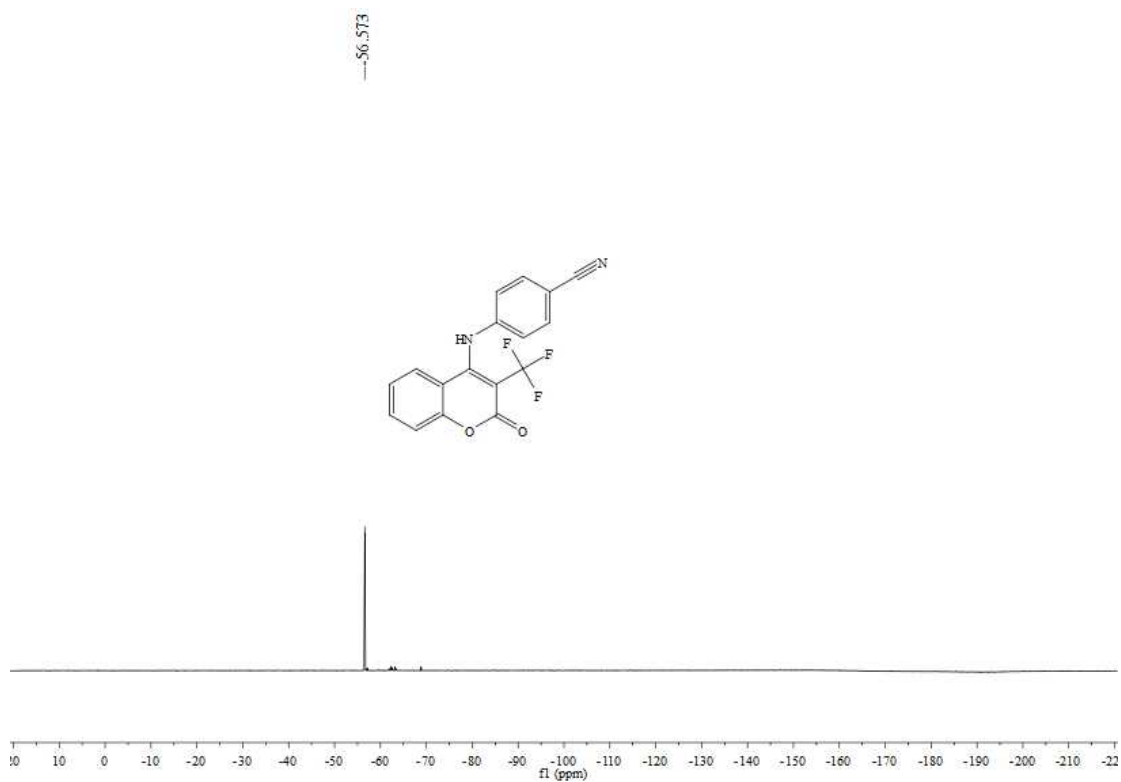
$^{19}\text{F}$  NMR of **3an** in  $\text{CDCl}_3$



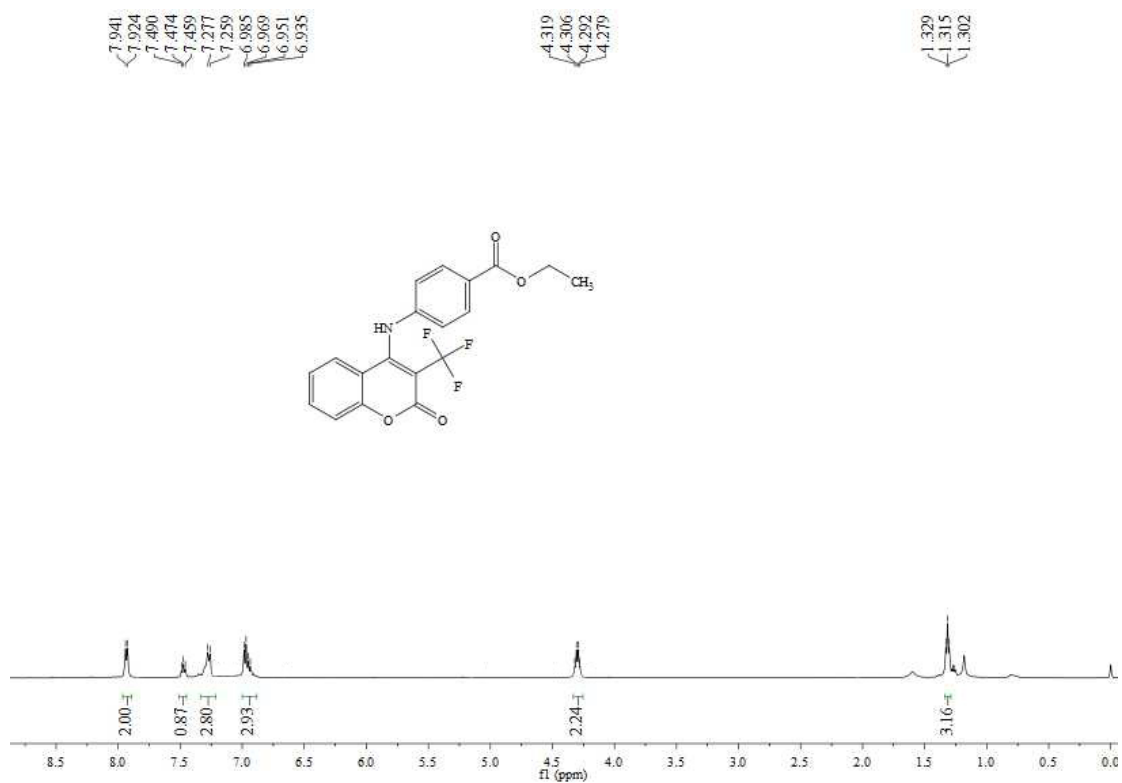
$^1\text{H}$  NMR of **3ao** in  $\text{CDCl}_3$



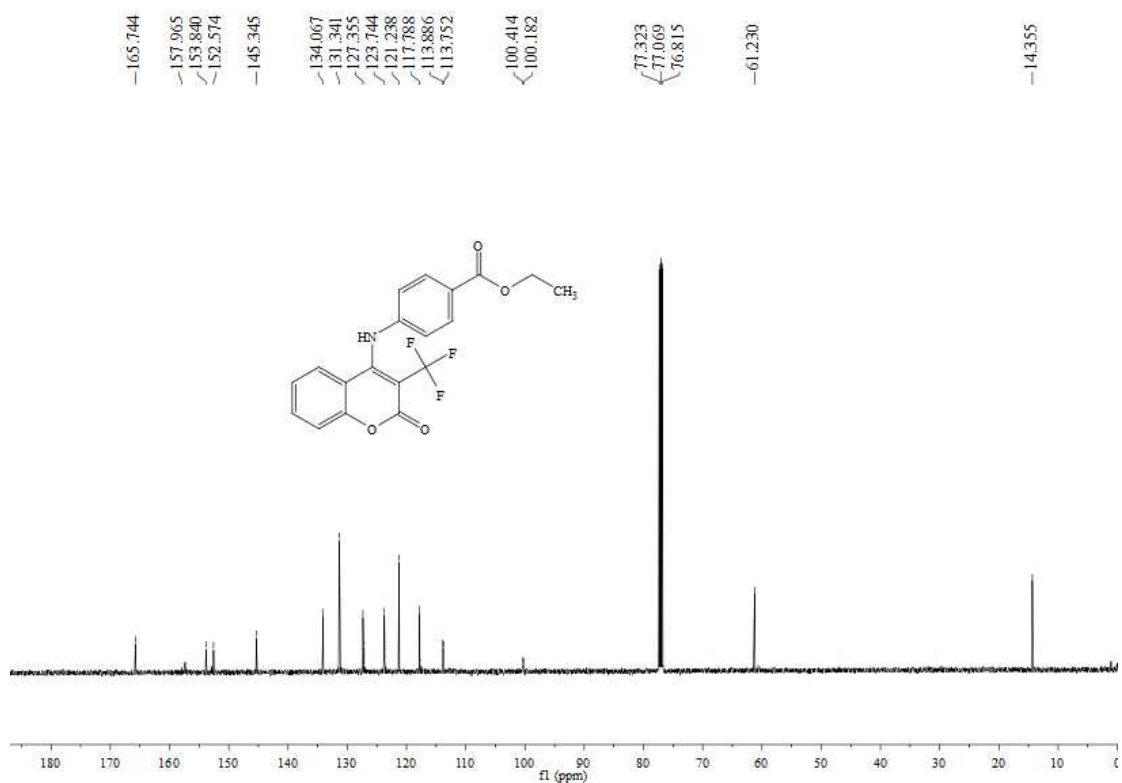
<sup>13</sup>C NMR of **3ao** in CDCl<sub>3</sub>



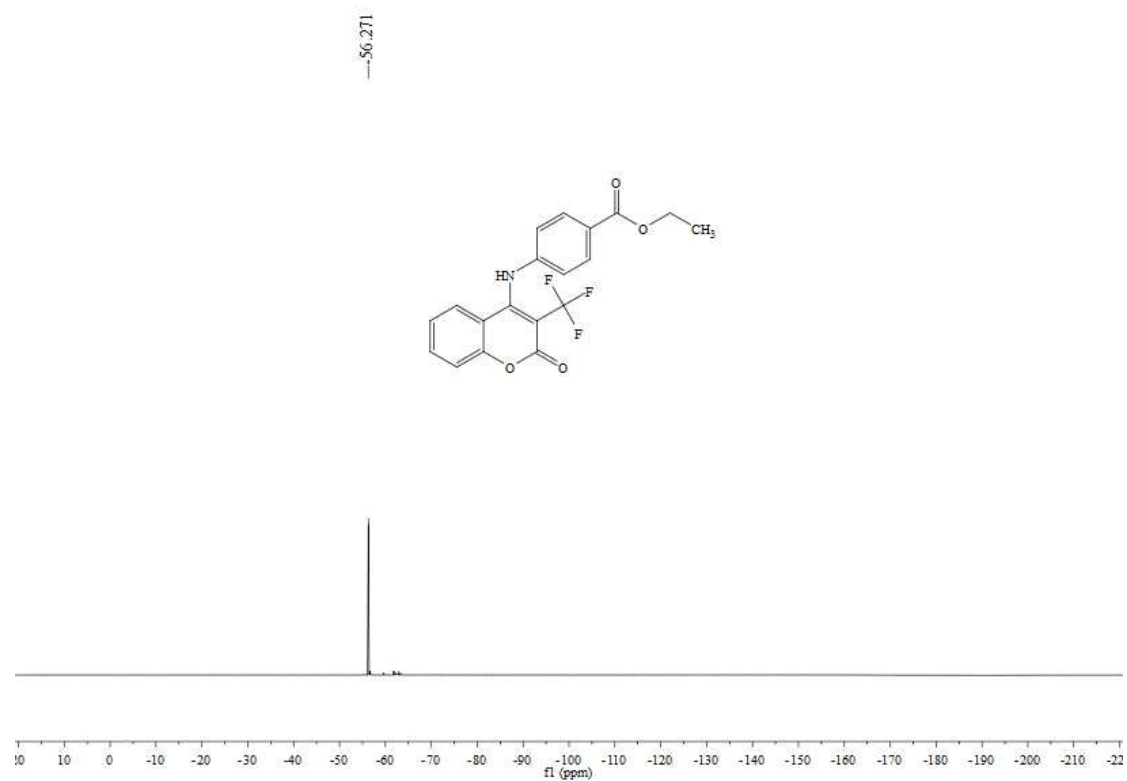
<sup>19</sup>F NMR of **3ao** in CDCl<sub>3</sub>



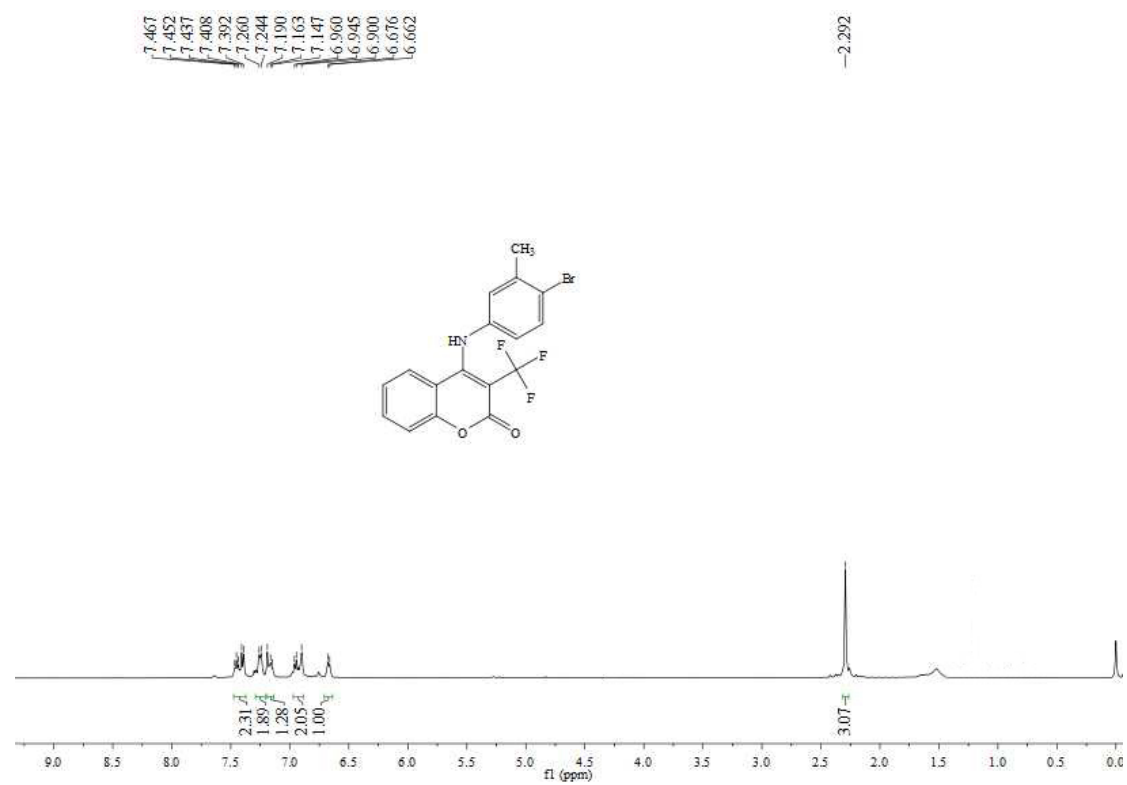
$^1\text{H}$  NMR of **3ap** in  $\text{CDCl}_3$



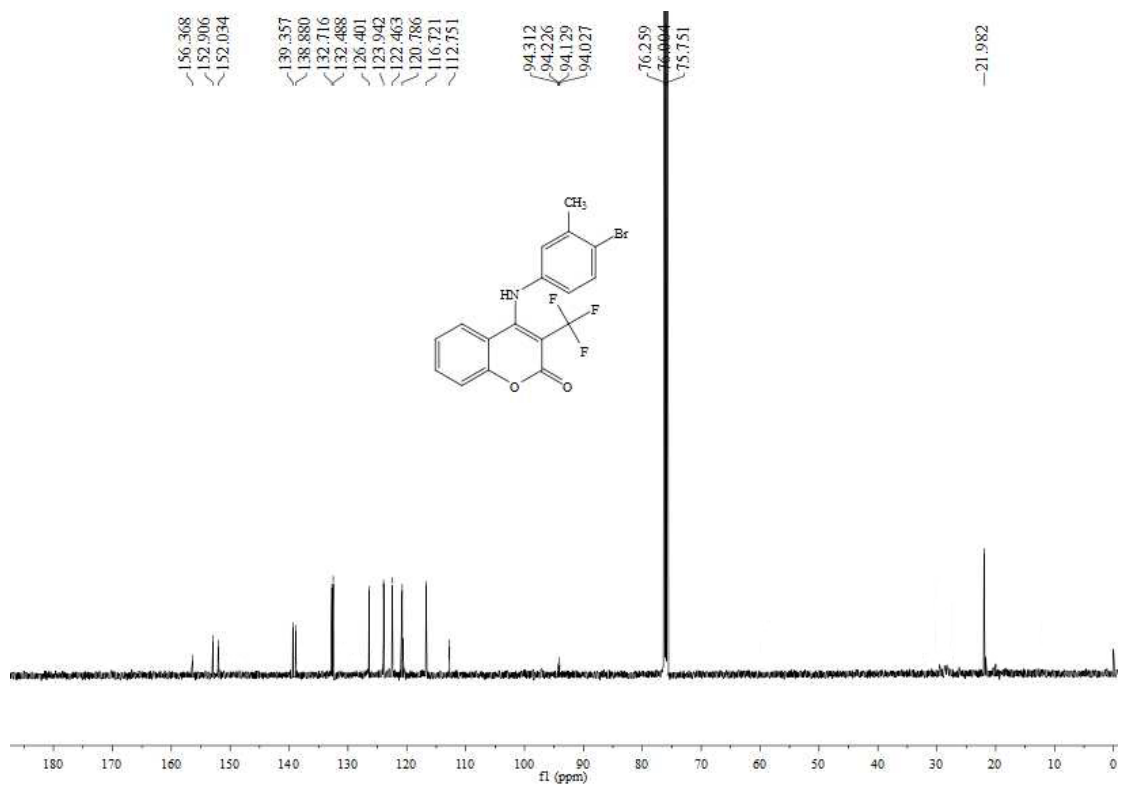
$^{13}\text{C}$  NMR of **3ap** in  $\text{CDCl}_3$



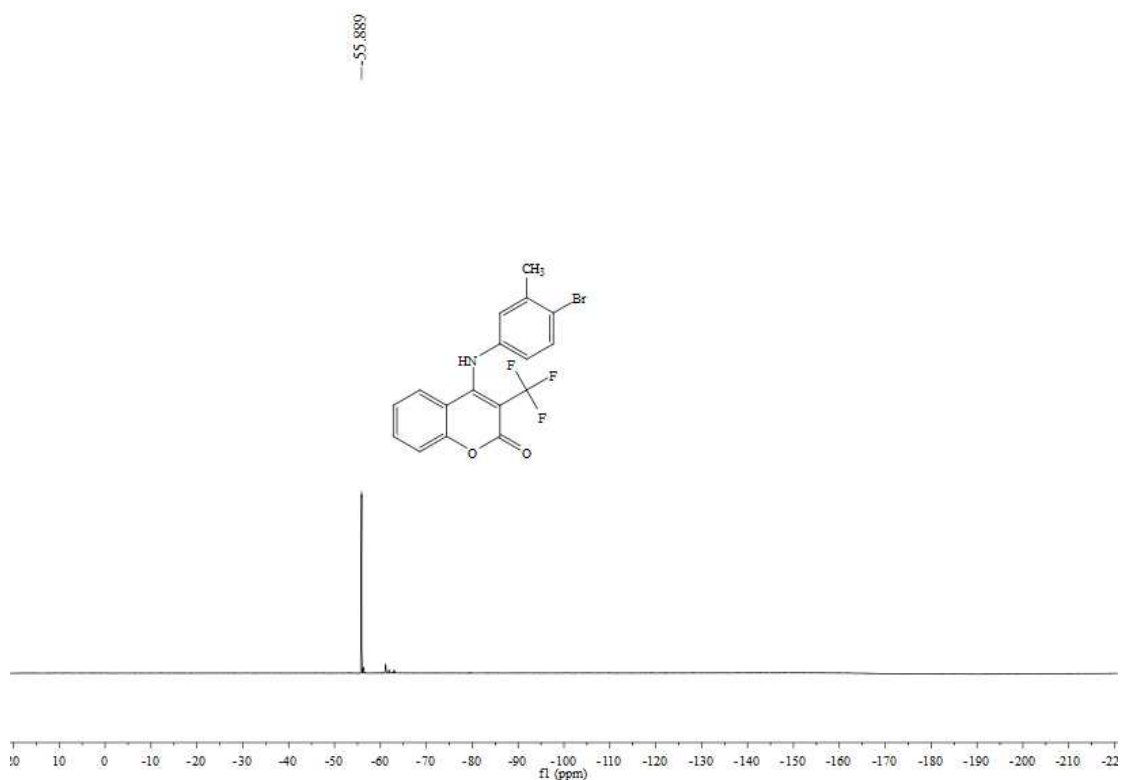
$^{19}\text{F}$  NMR of **3ap** in  $\text{CDCl}_3$



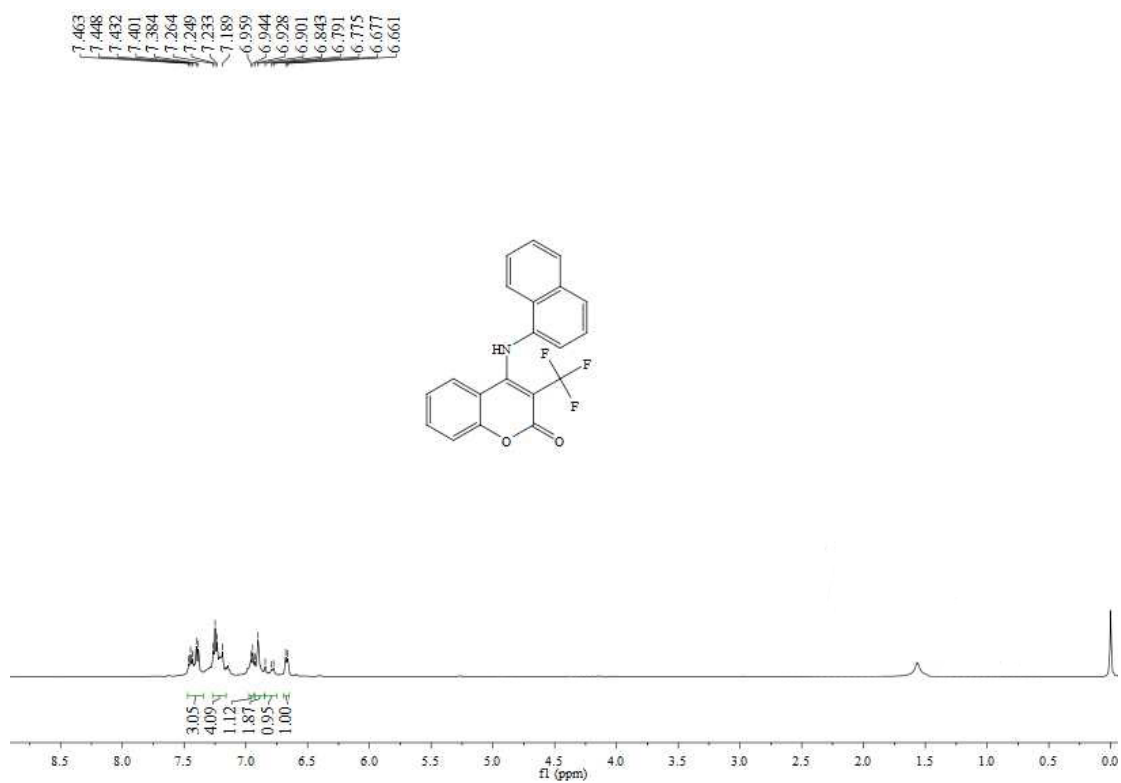
$^1\text{H}$  NMR of **3aq** in  $\text{CDCl}_3$



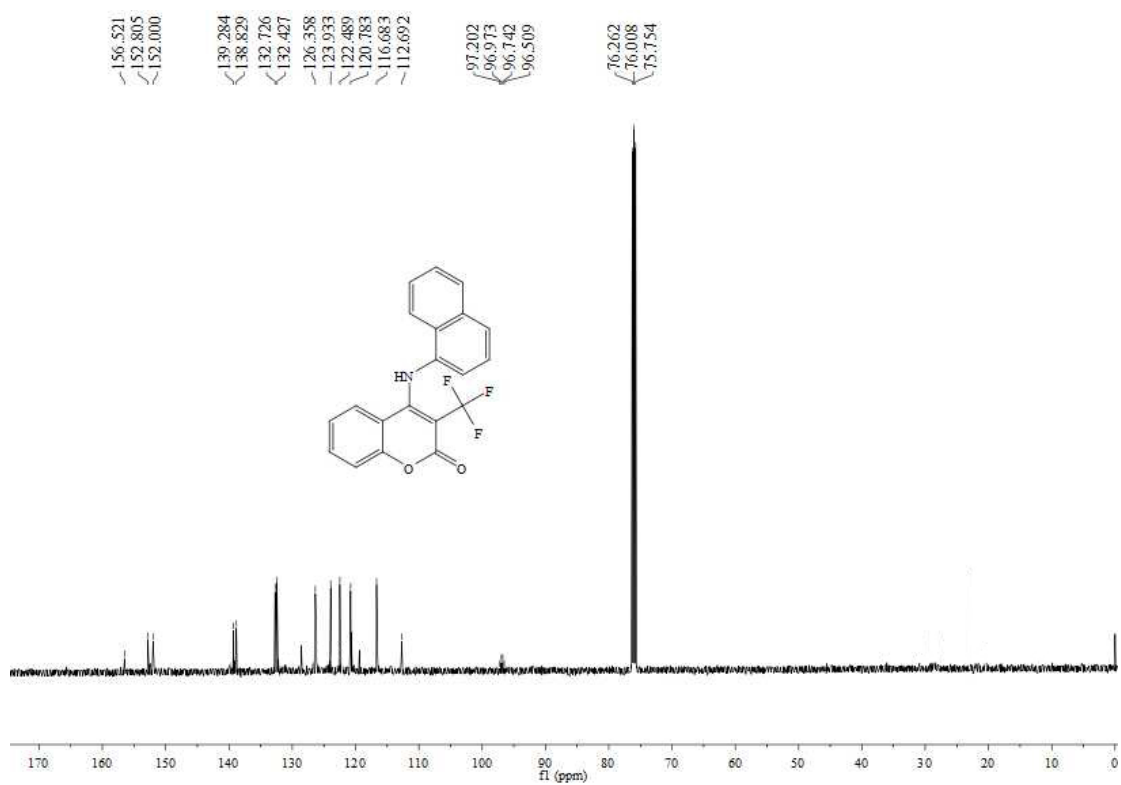
**<sup>13</sup>C NMR of 3aq in CDCl<sub>3</sub>**



**<sup>19</sup>F NMR of 3aq in CDCl<sub>3</sub>**

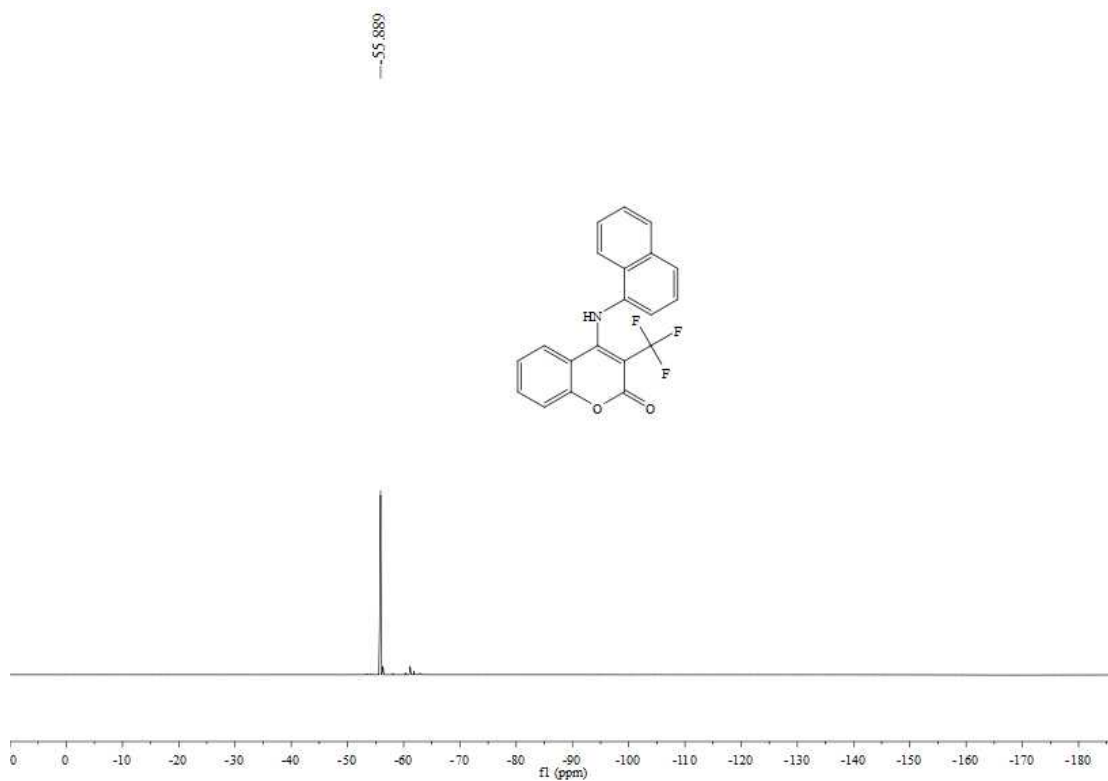


$^1\text{H}$  NMR of **3ar** in  $\text{CDCl}_3$

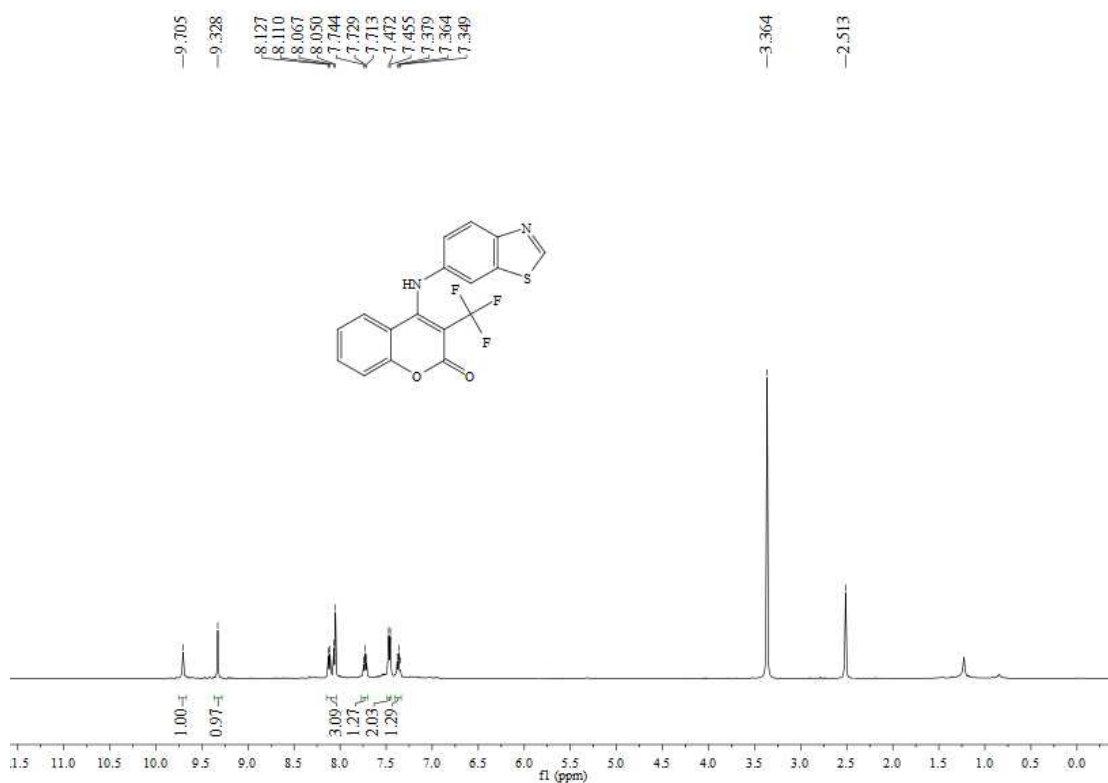


$^{13}\text{C}$  NMR of **3ar** in  $\text{CDCl}_3$

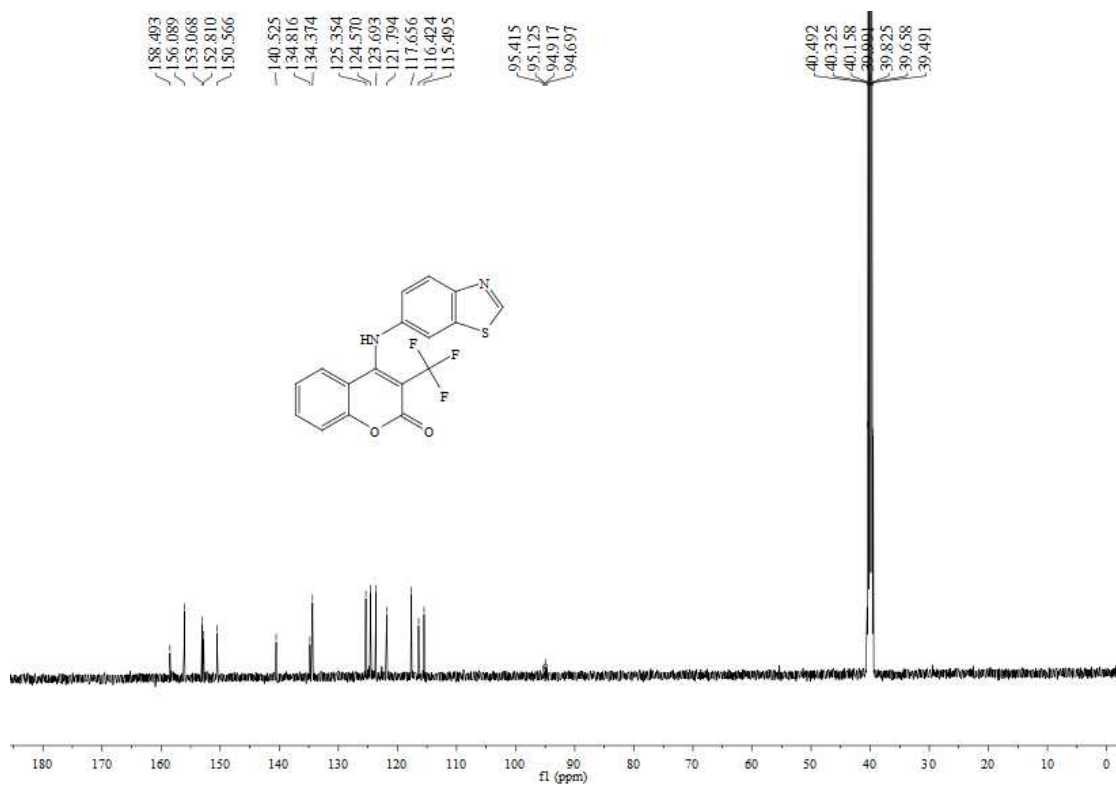




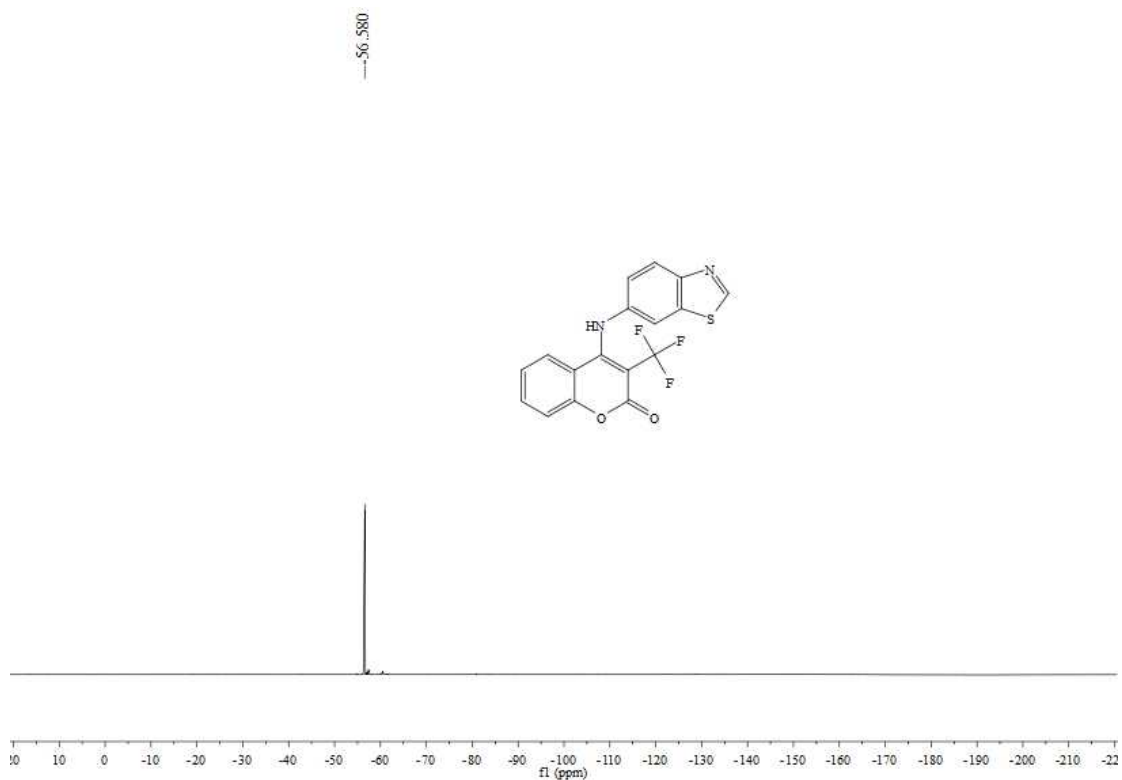
**<sup>19</sup>F NMR of 3ar in CDCl<sub>3</sub>**



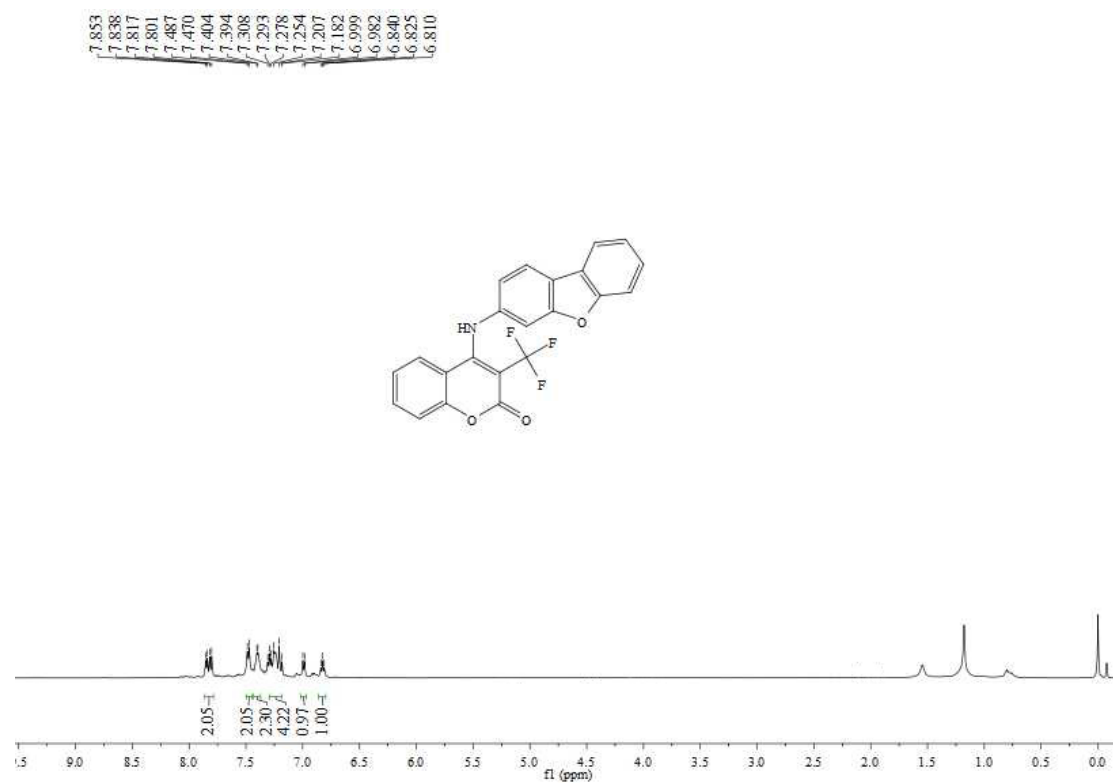
**<sup>1</sup>H NMR of 3as in d<sub>6</sub>-DMSO**



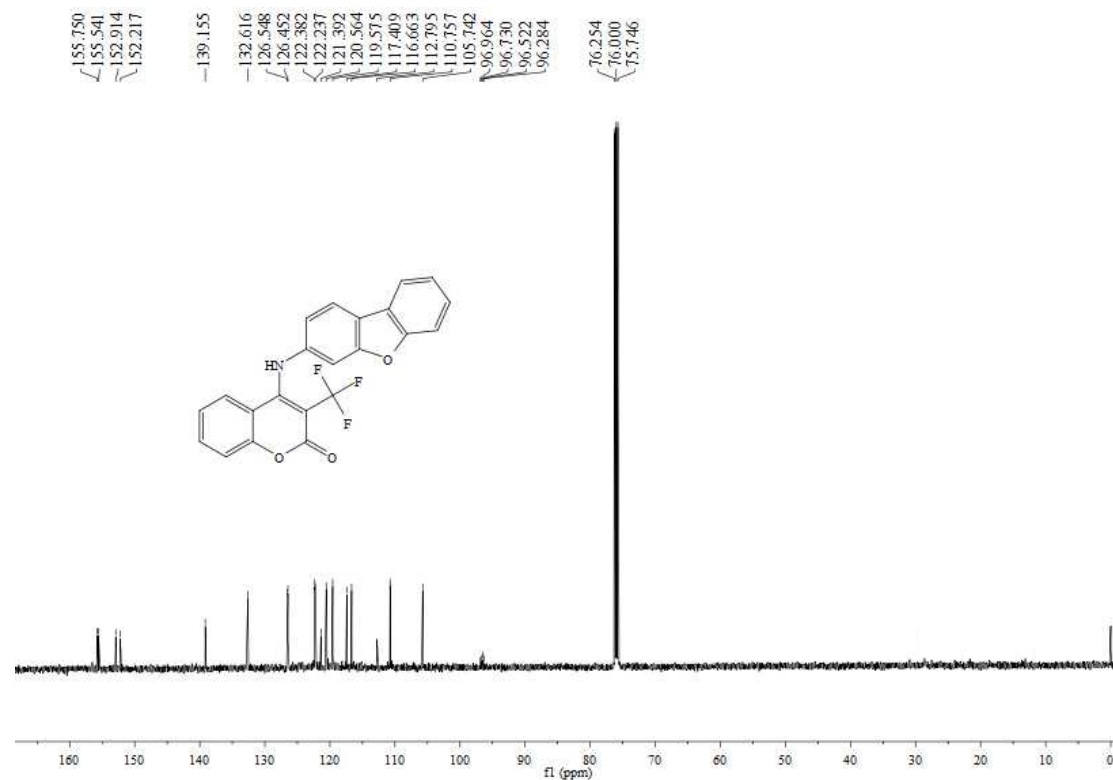
<sup>13</sup>C NMR of **3as** in *d*<sub>6</sub>-DMSO



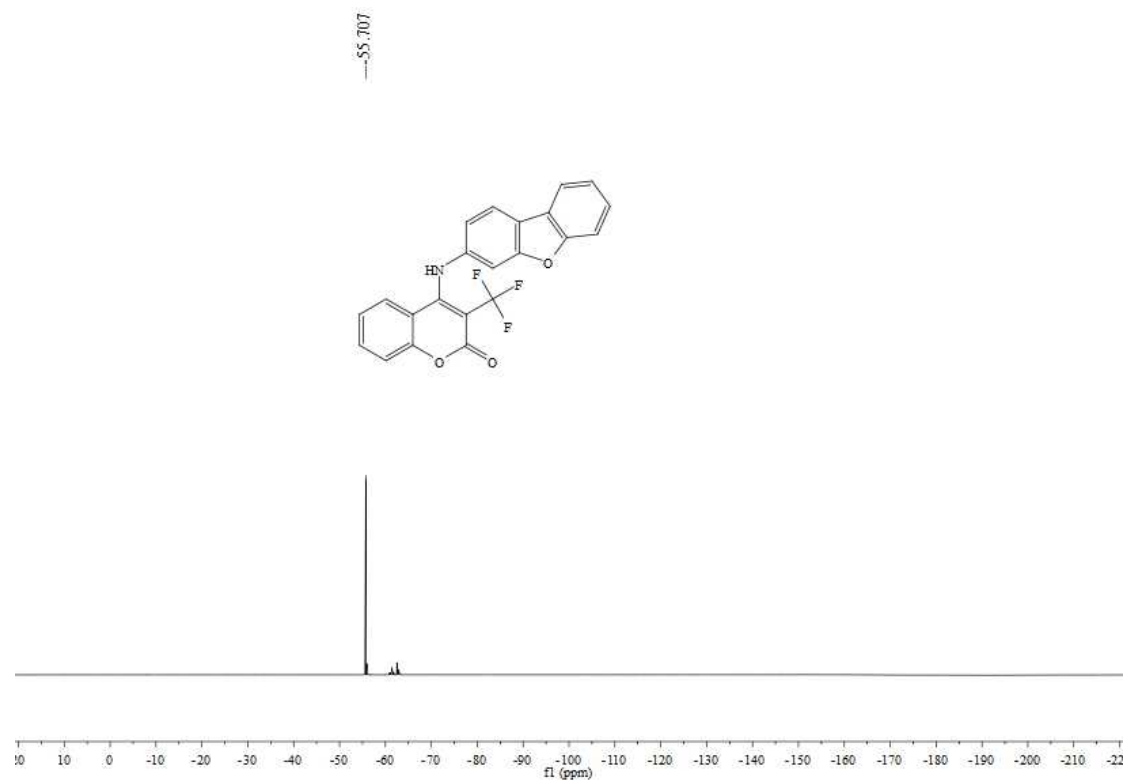
<sup>19</sup>F NMR of **3as** in *d*<sub>6</sub>-DMSO



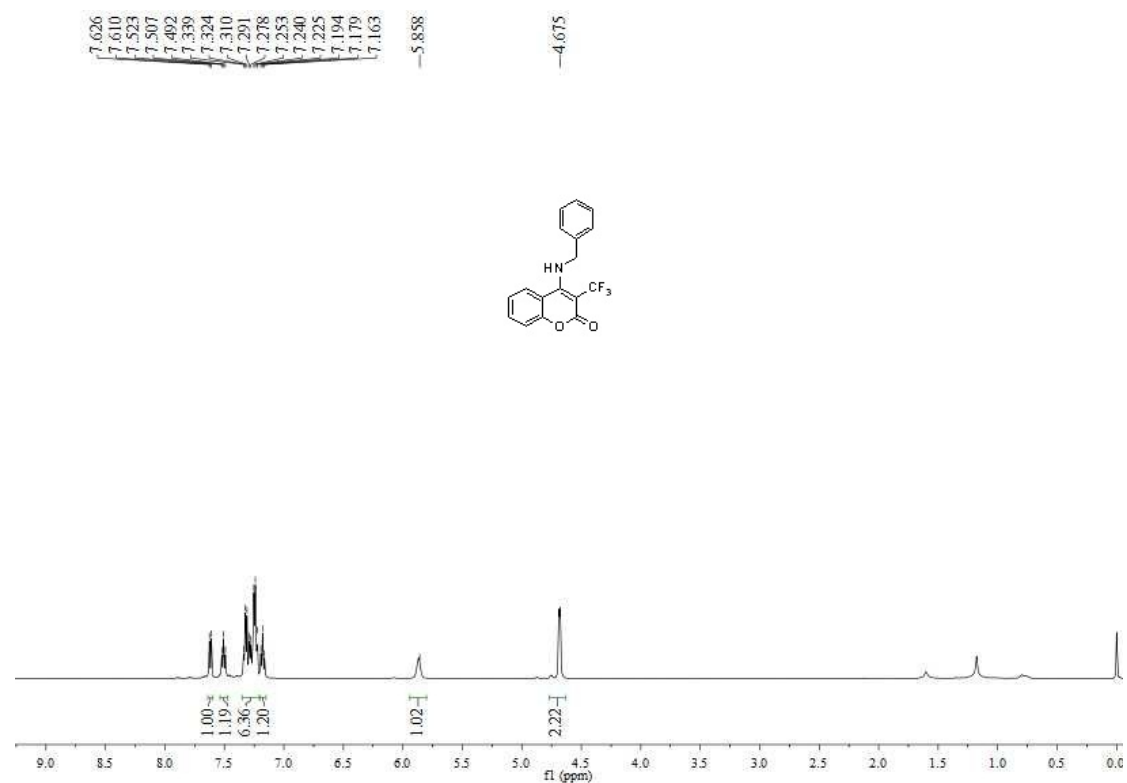
$^1\text{H}$  NMR of **3at** in  $d_6$ -DMSO



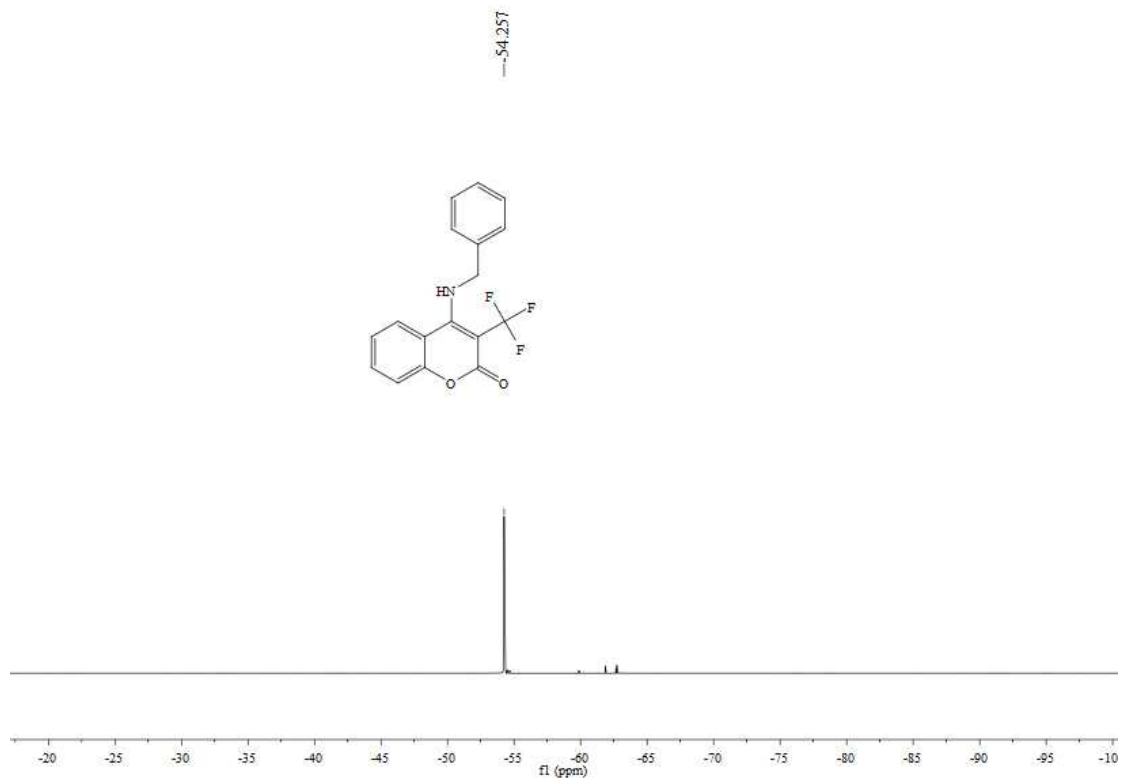
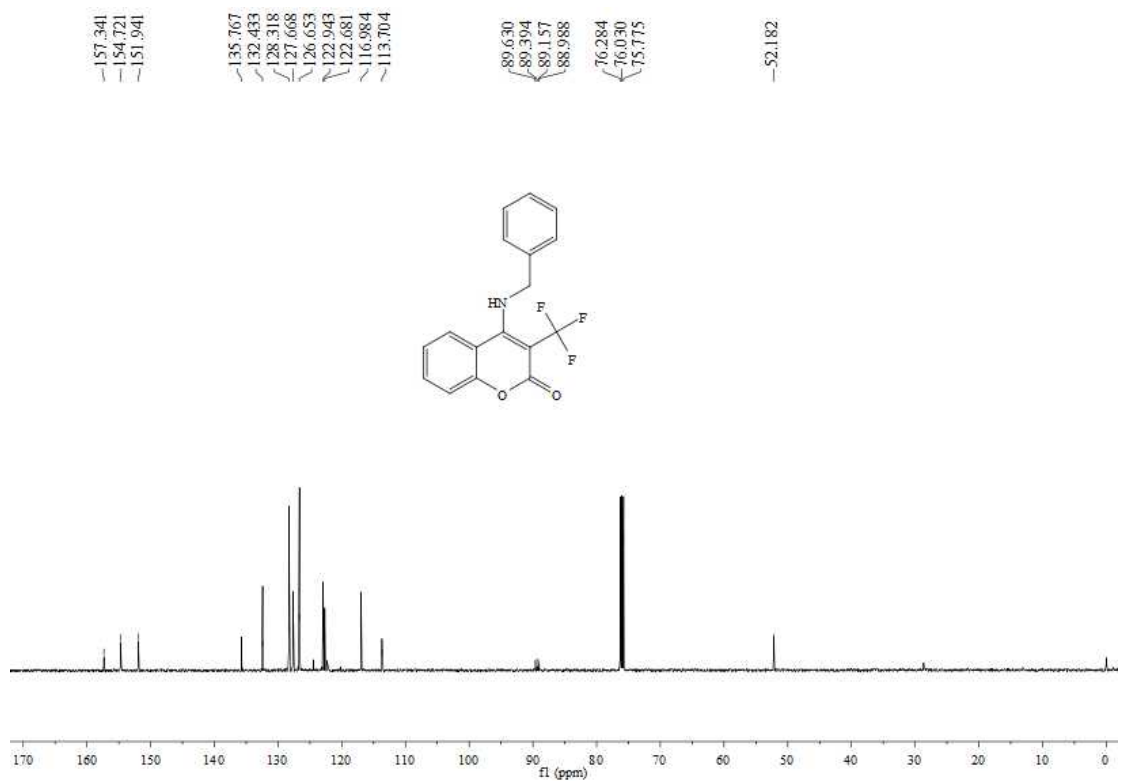
$^{13}\text{C}$  NMR of **3at** in  $d_6$ -DMSO

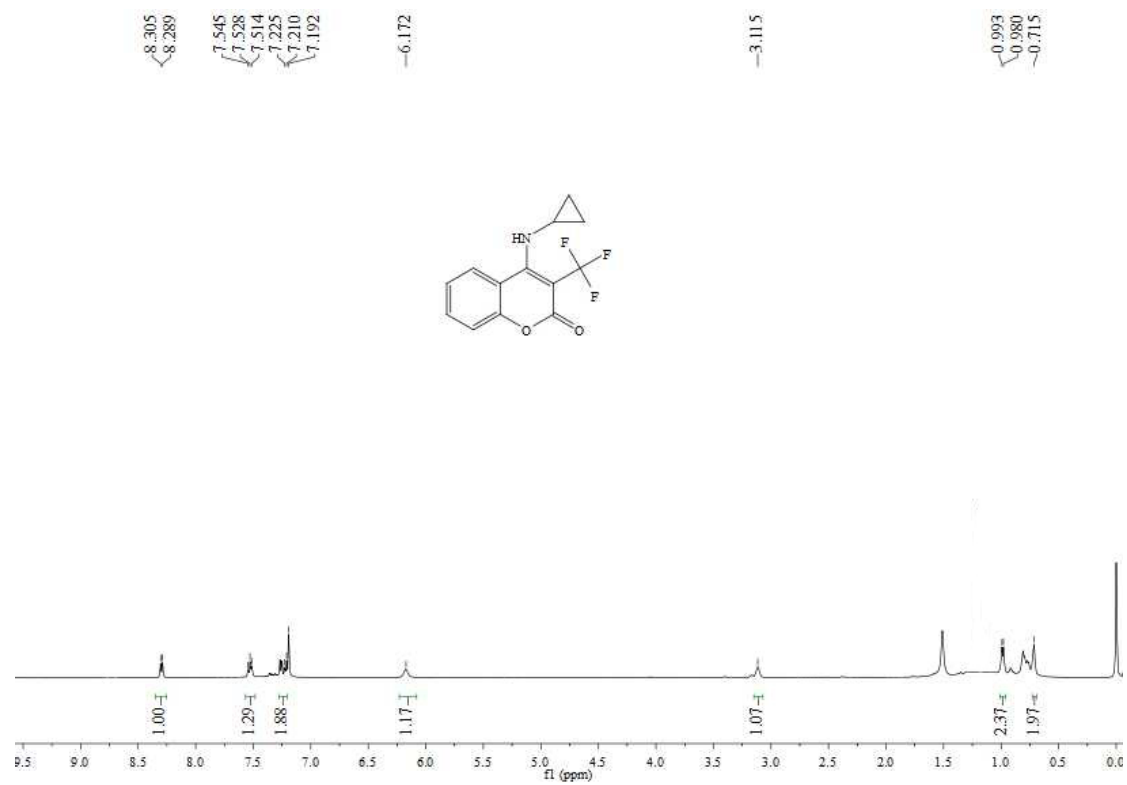


$^{19}\text{F}$  NMR of **3at** in  $d_6$ -DMSO

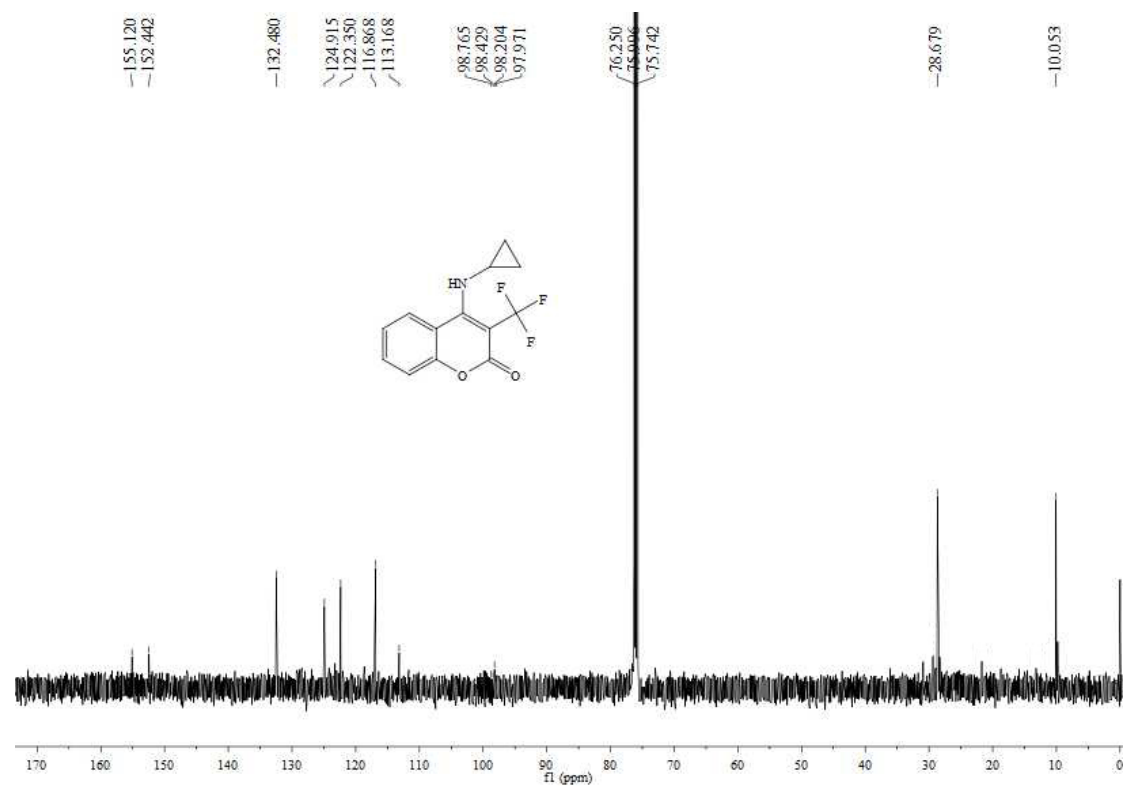


$^1\text{H}$  NMR of **3au** in  $\text{CDCl}_3$

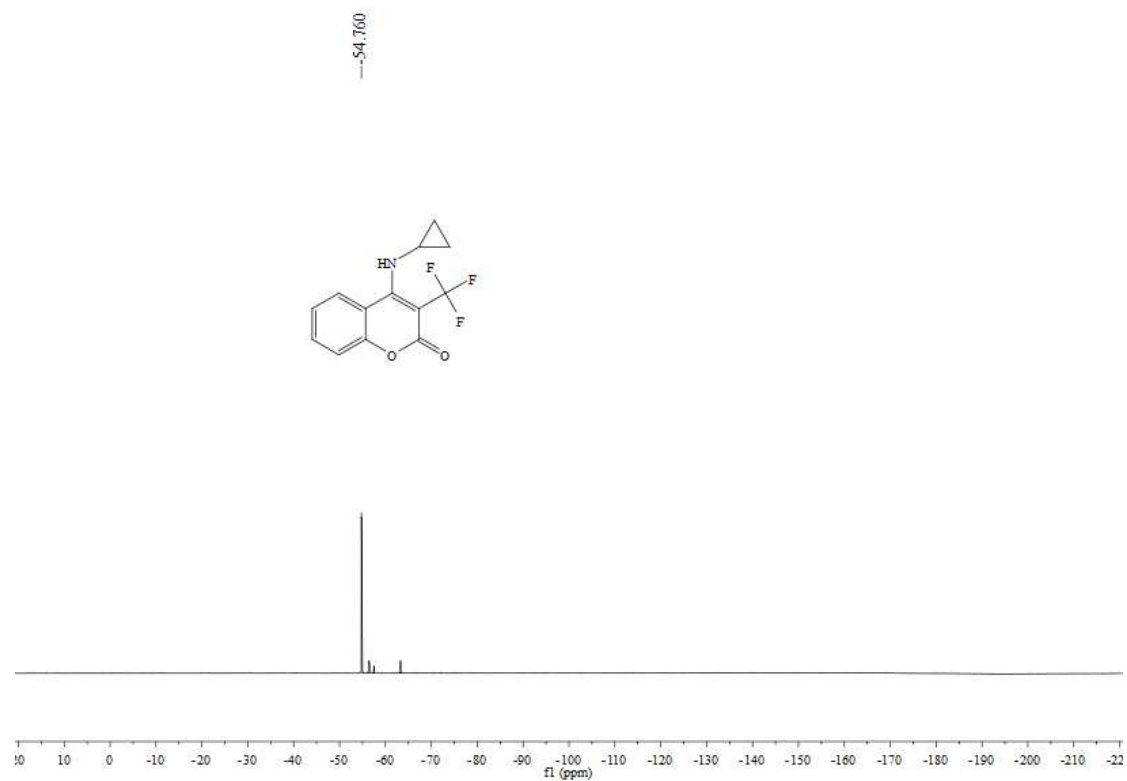




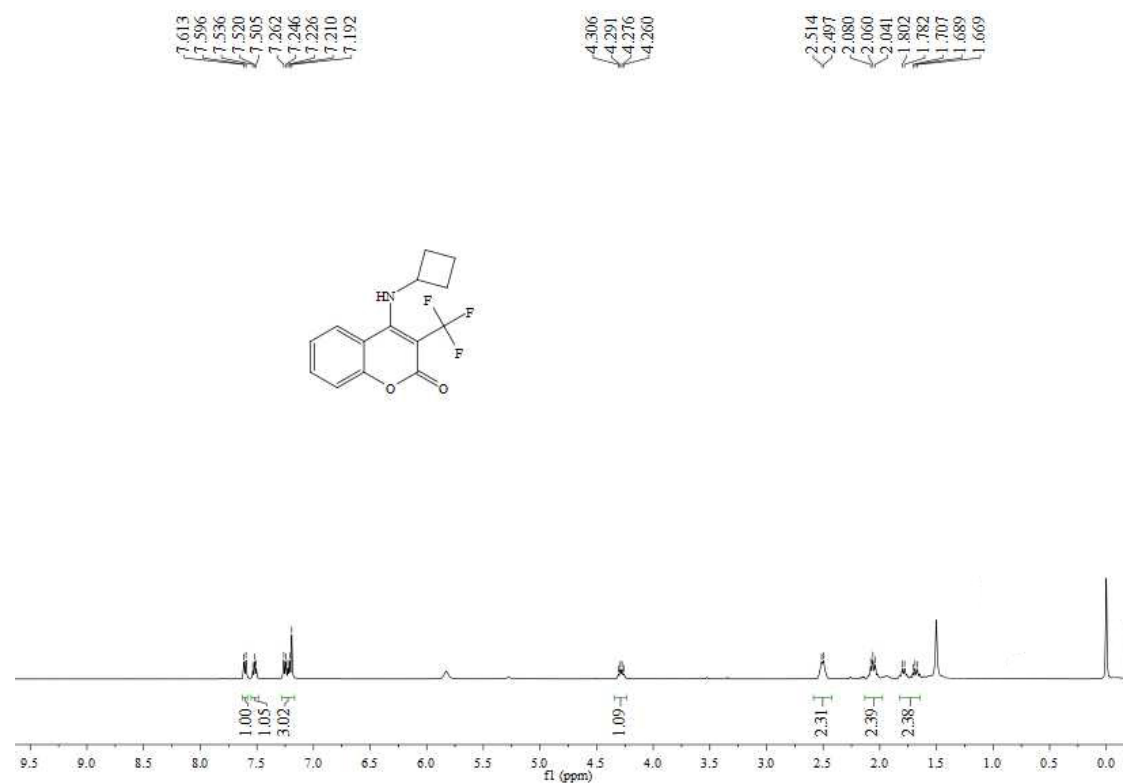
<sup>1</sup>H NMR of **3av** in CDCl<sub>3</sub>



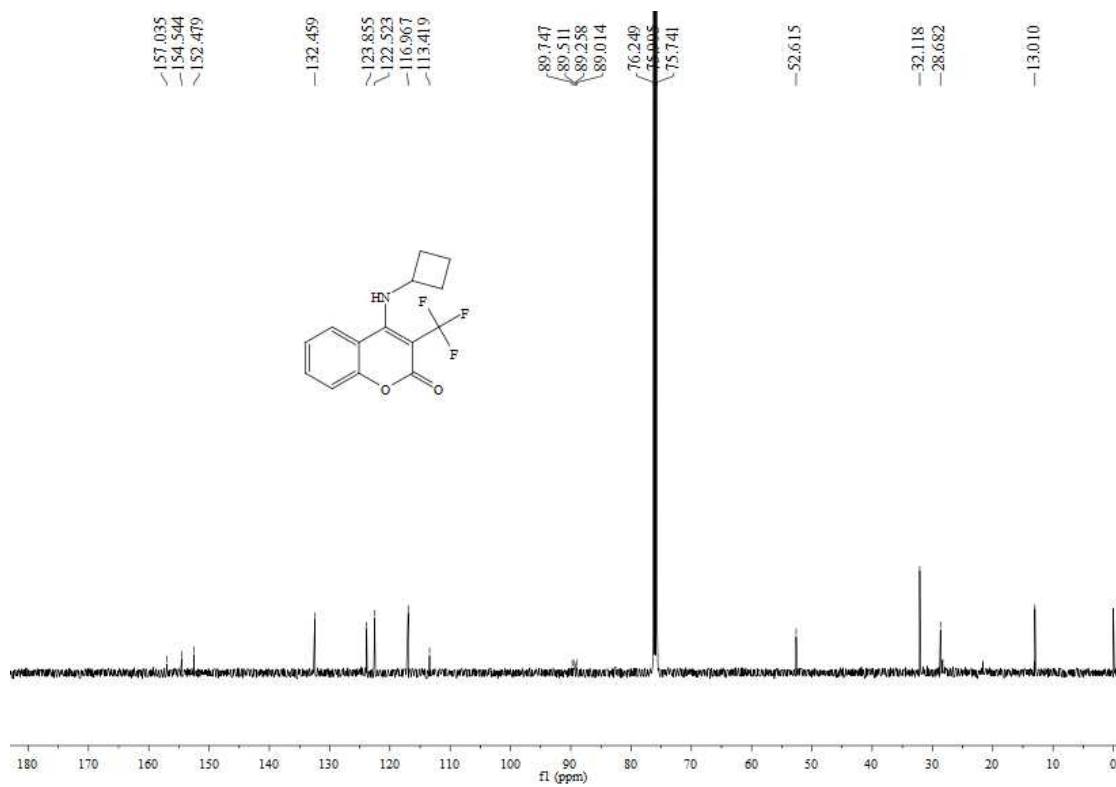
<sup>13</sup>C NMR of **3av** in CDCl<sub>3</sub>



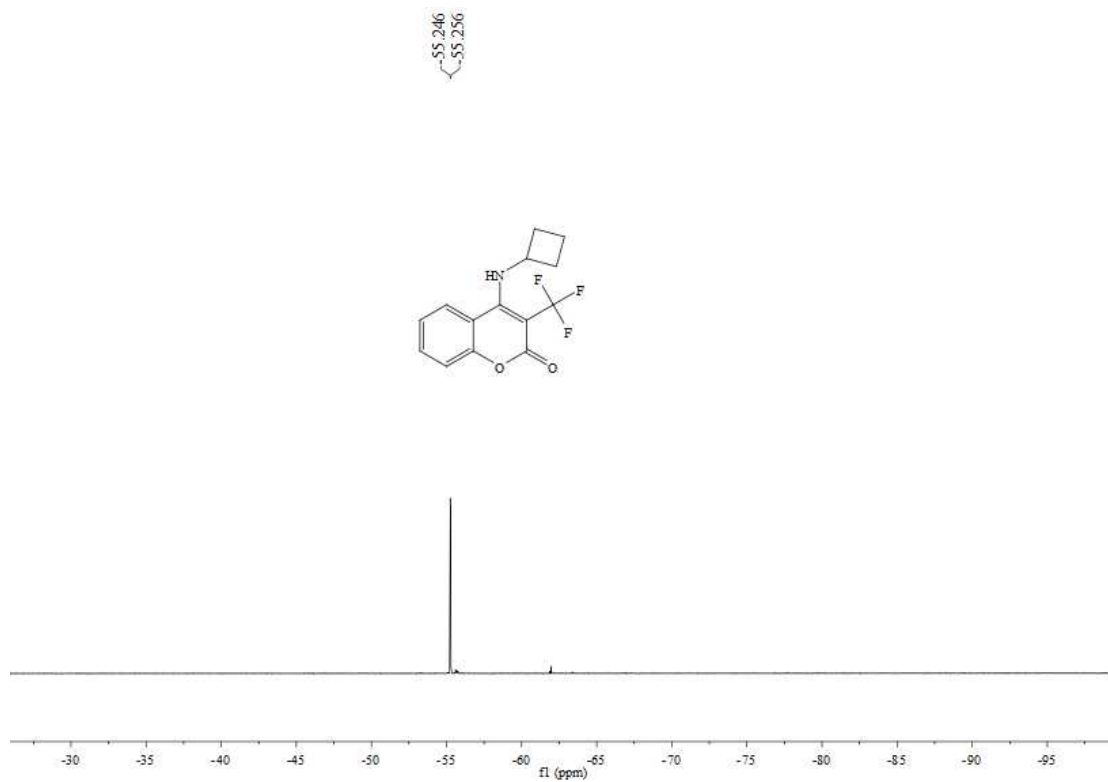
$^{19}\text{F}$  NMR of **3av** in  $\text{CDCl}_3$



$^1\text{H}$  NMR of **3aw** in  $\text{CDCl}_3$

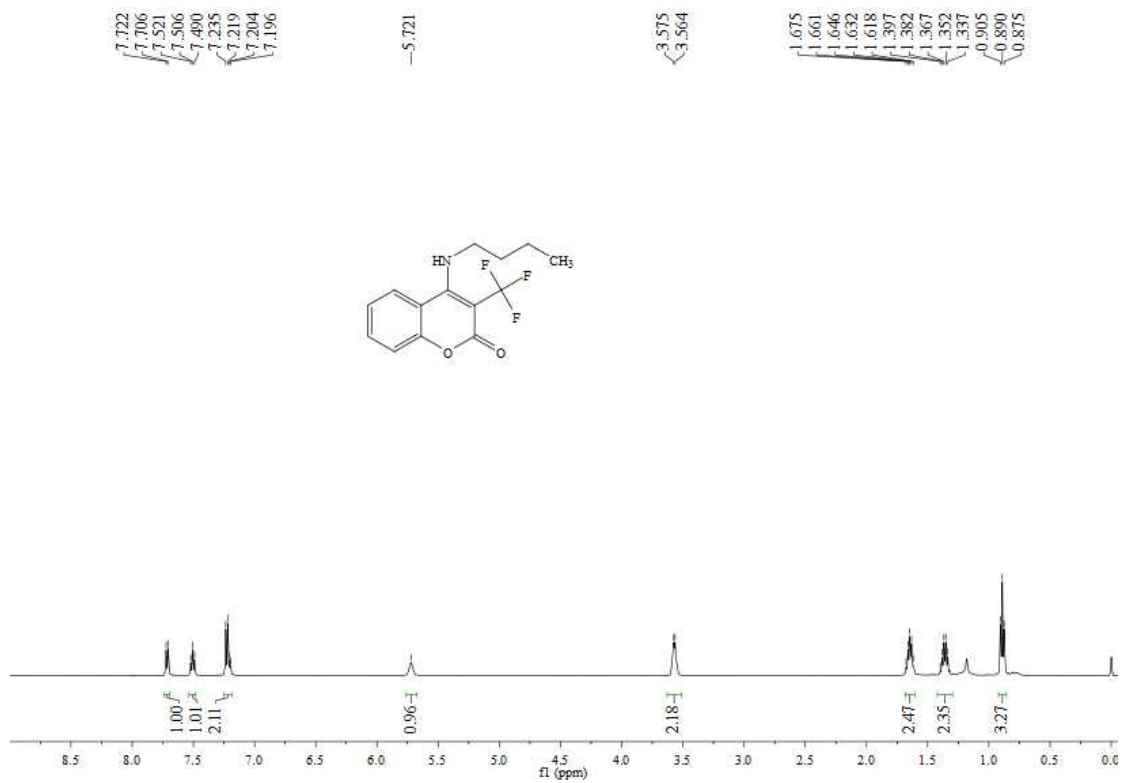


<sup>13</sup>C NMR of **3aw** in CDCl<sub>3</sub>

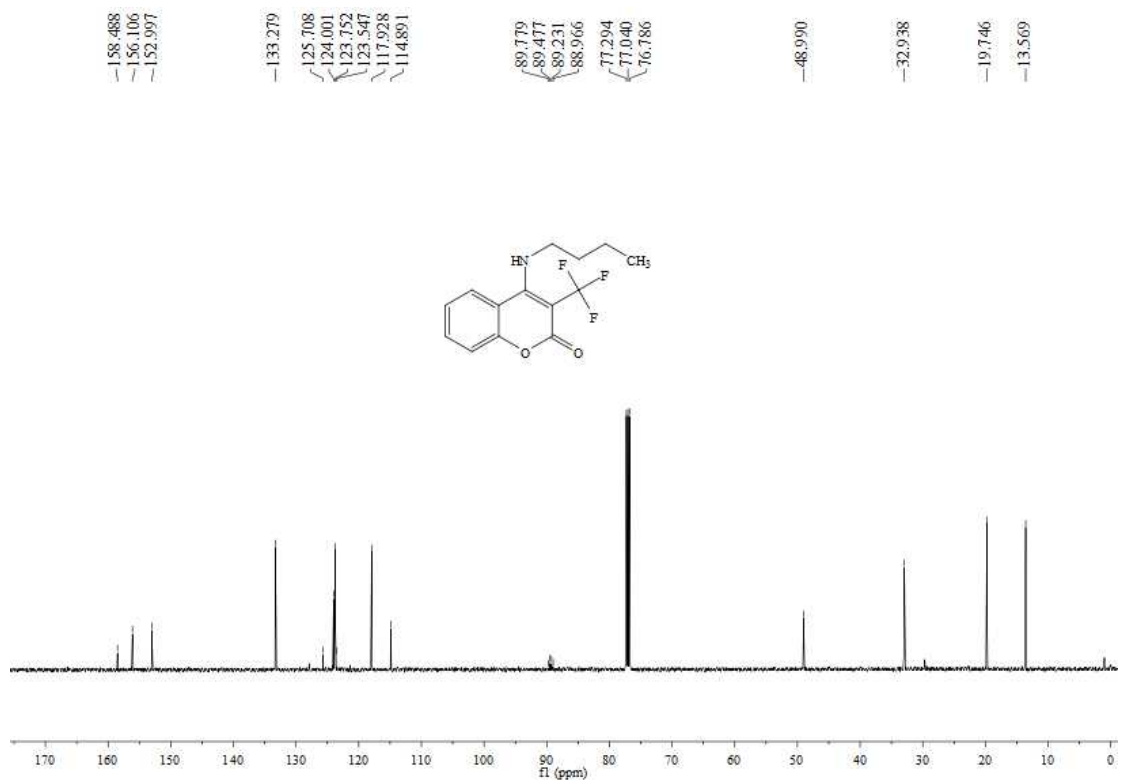


<sup>19</sup>F NMR of **3aw** in CDCl<sub>3</sub>



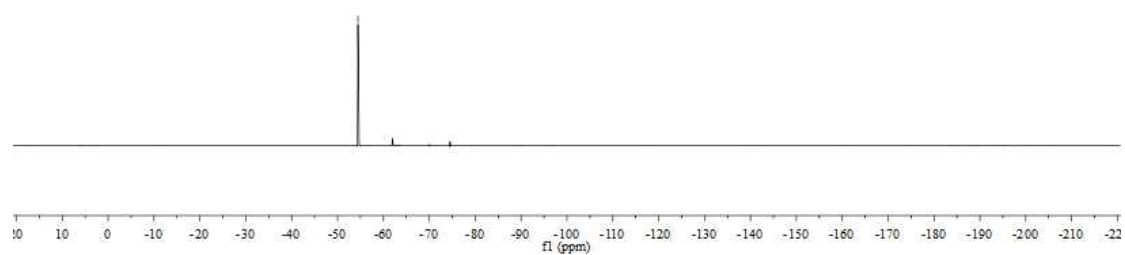
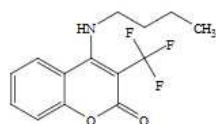


<sup>1</sup>H NMR of **3ax** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **3ax** in CDCl<sub>3</sub>

—54.441



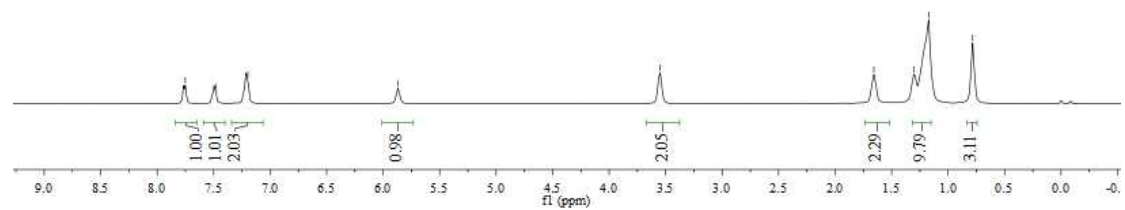
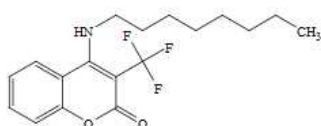
$^{19}\text{F}$  NMR of **3ax** in  $\text{CDCl}_3$

-7.751  
-7.482  
-7.197

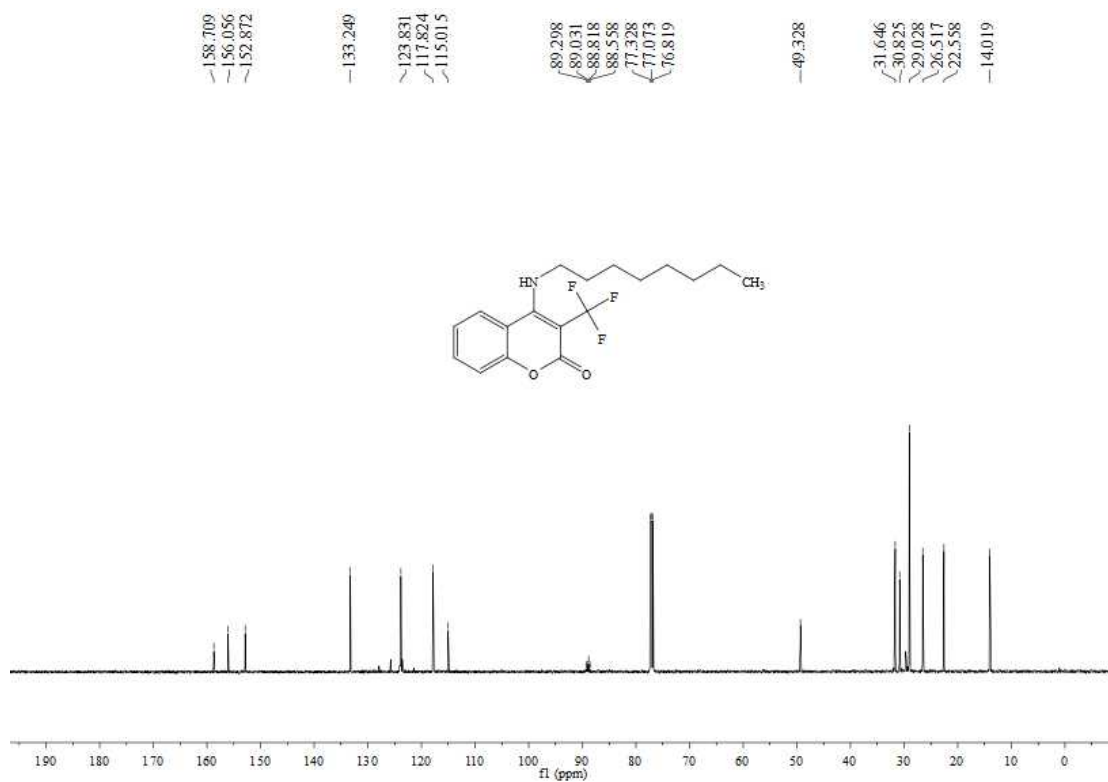
-5.869

-3.549

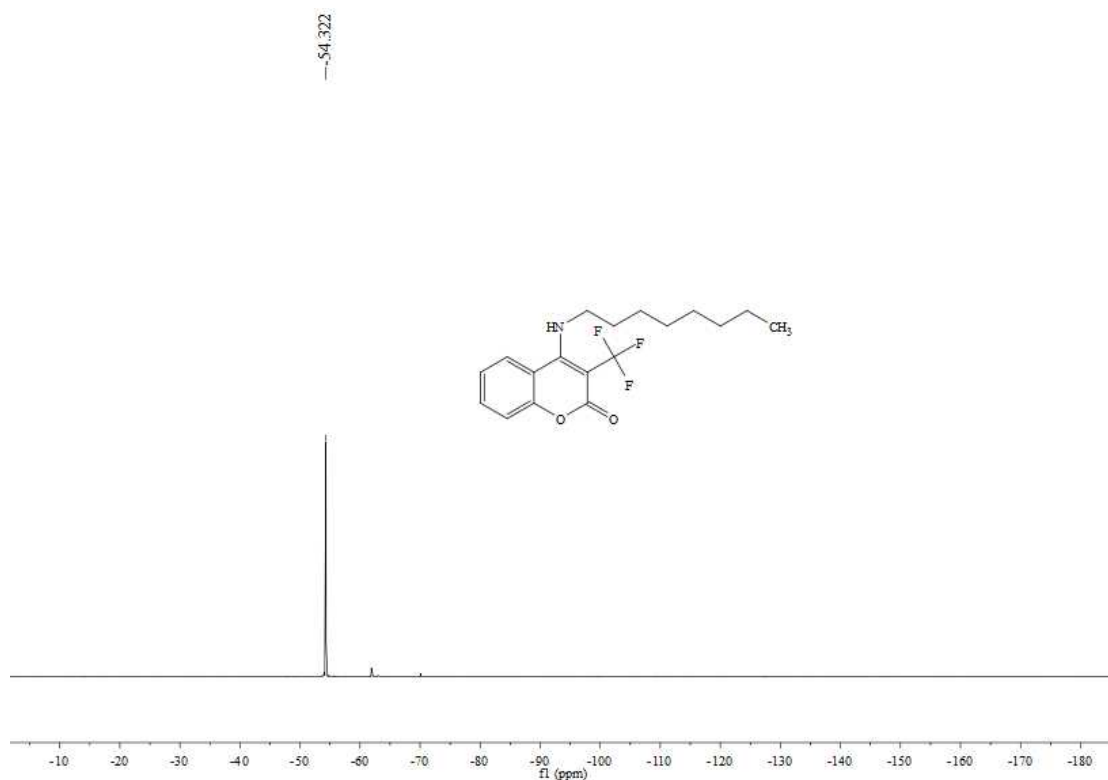
-1.657  
-1.303  
-1.173  
-0.782



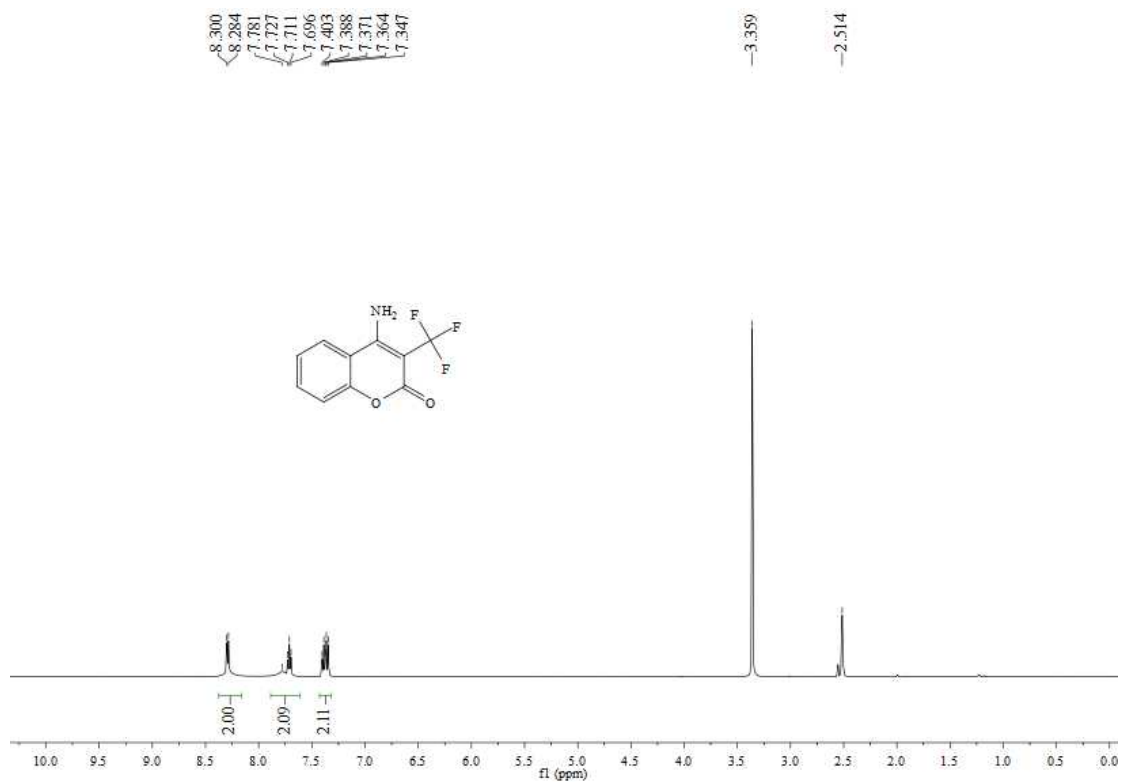
$^1\text{H}$  NMR of **3ay** in  $\text{CDCl}_3$



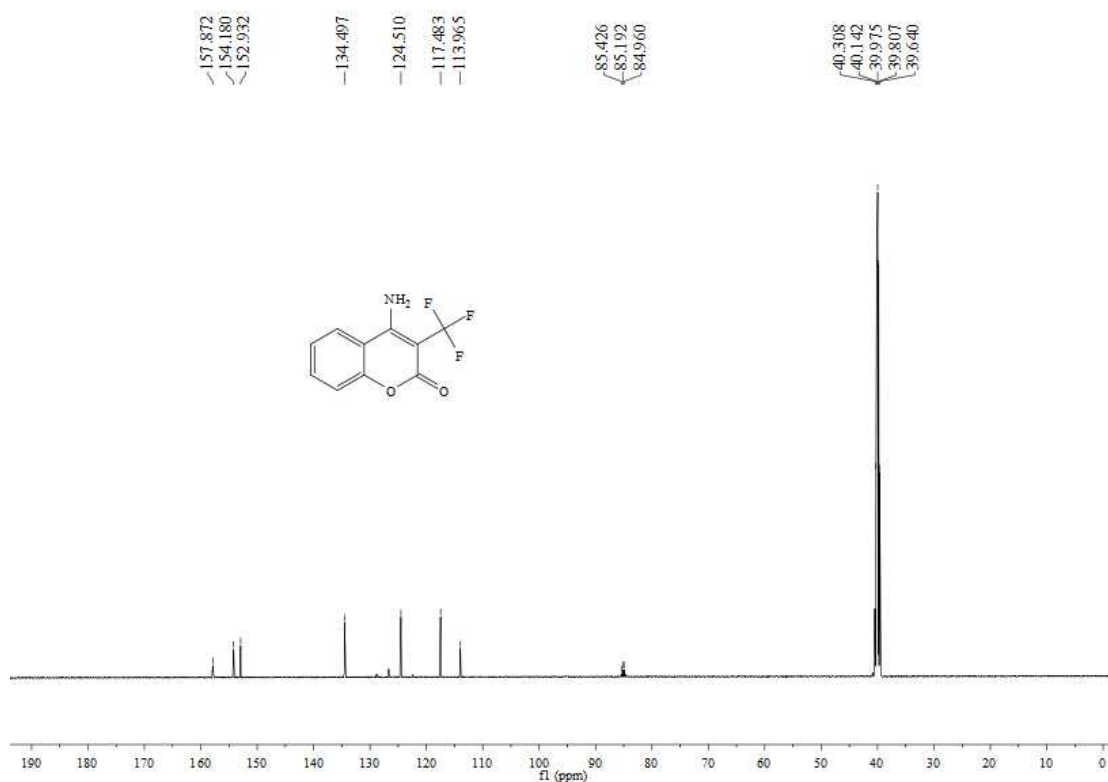
$^{13}\text{C}$  NMR of **3ay** in  $\text{CDCl}_3$



$^{19}\text{F}$  NMR of **3ay** in  $\text{CDCl}_3$

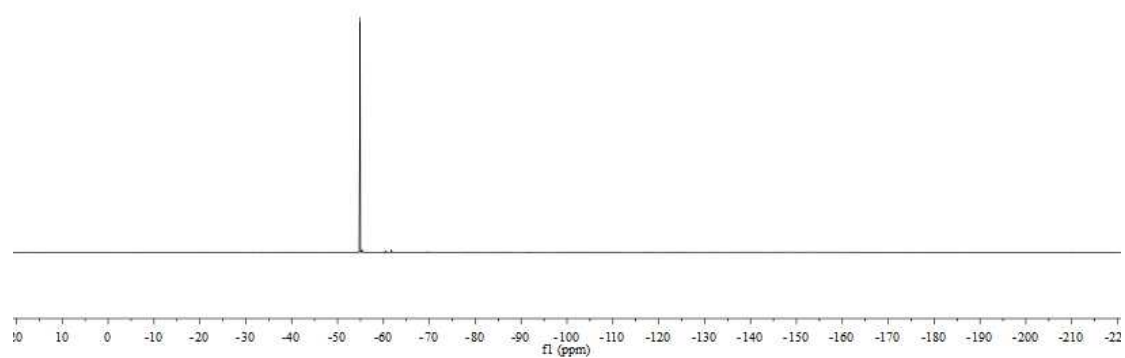
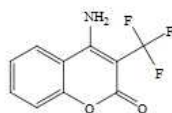


$^1\text{H NMR}$  of **3az** in  $d_6$ -DMSO



$^{13}\text{C NMR}$  of **3az** in  $d_6$ -DMSO

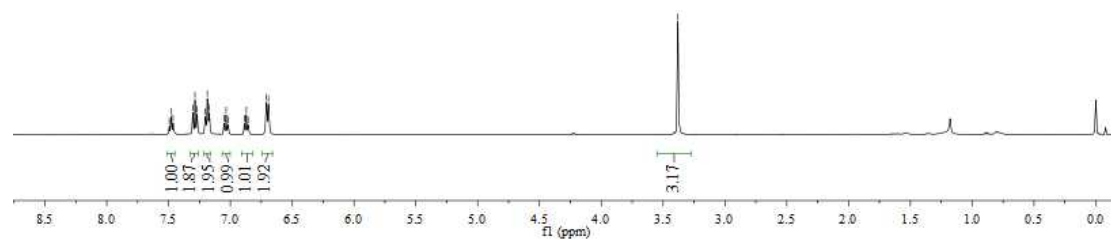
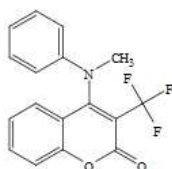
—54.915



$^{19}\text{F}$  NMR of **3az** in  $d_6$ -DMSO

7.494  
7.479  
7.463  
7.303  
7.286  
7.270  
7.202  
7.186  
7.171  
7.050  
7.035  
7.020  
6.885  
6.871  
6.856  
6.708  
6.692

—3.380

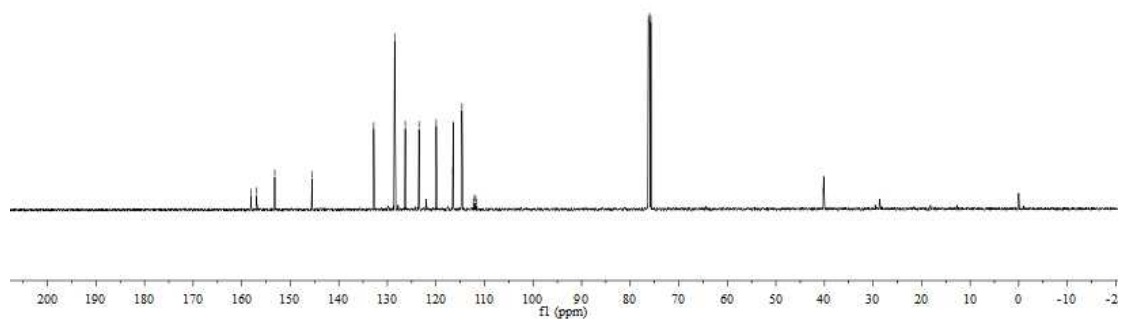
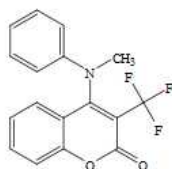


$^1\text{H}$  NMR of **3aa'** in  $\text{CDCl}_3$

158.062  
156.923  
153.195  
145.507  
132.819  
128.508  
126.370  
123.505  
119.941  
116.523  
114.654  
112.333  
111.845  
111.598

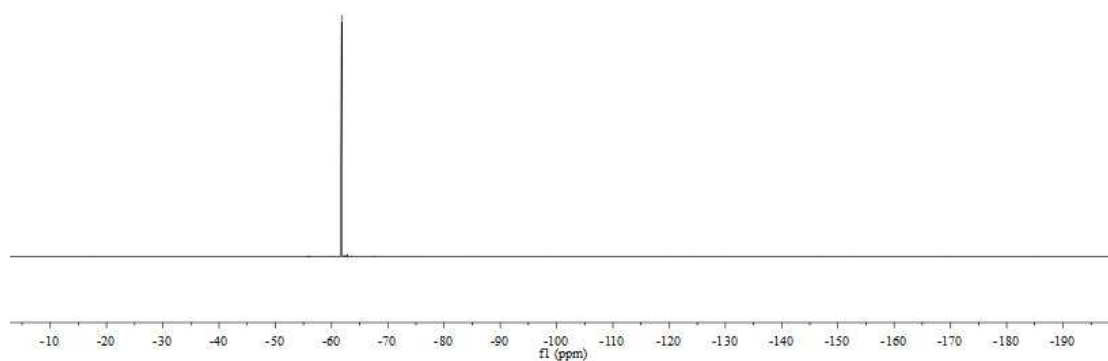
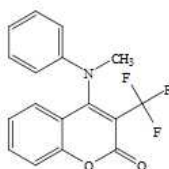
76.264  
76.010  
75.756

40.211

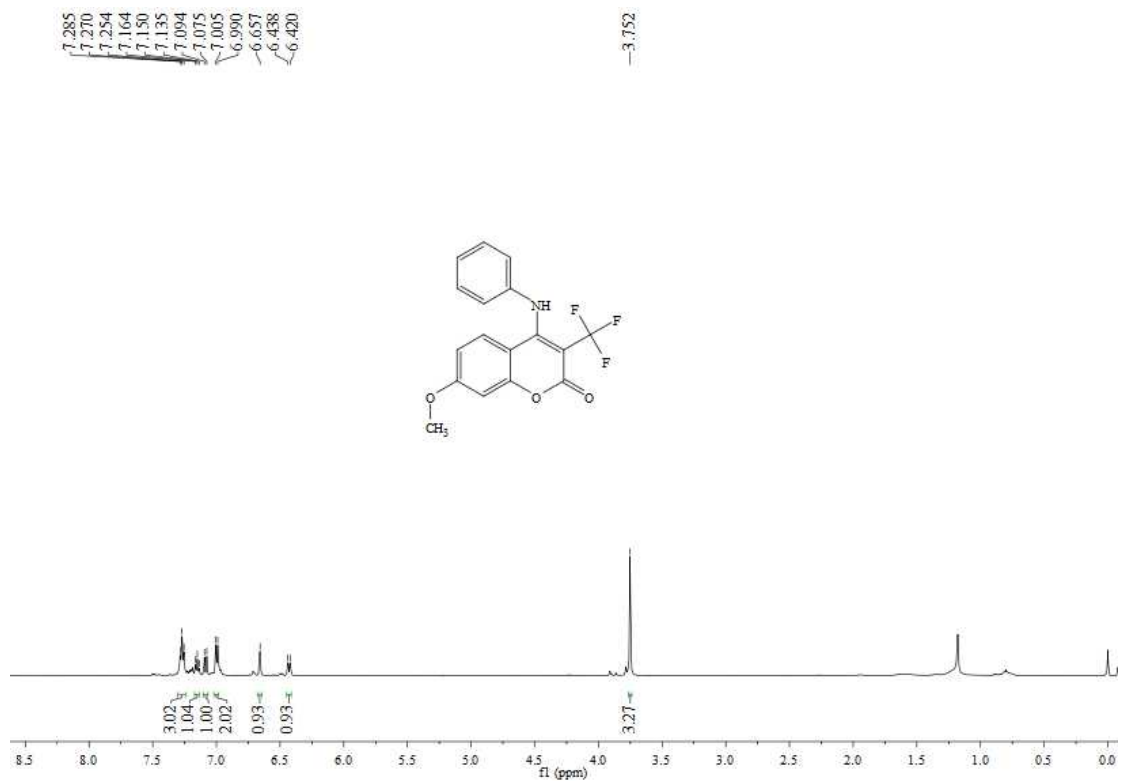


$^{13}\text{C}$  NMR of **3aa'** in  $\text{CDCl}_3$

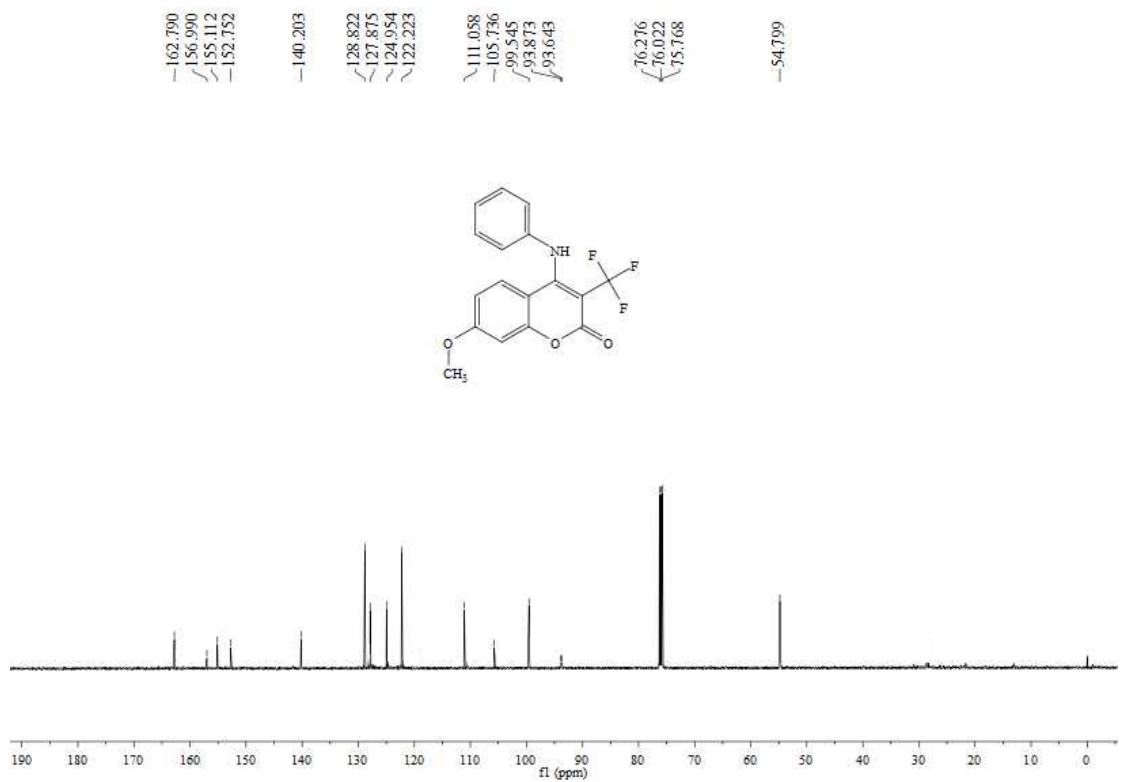
61.792



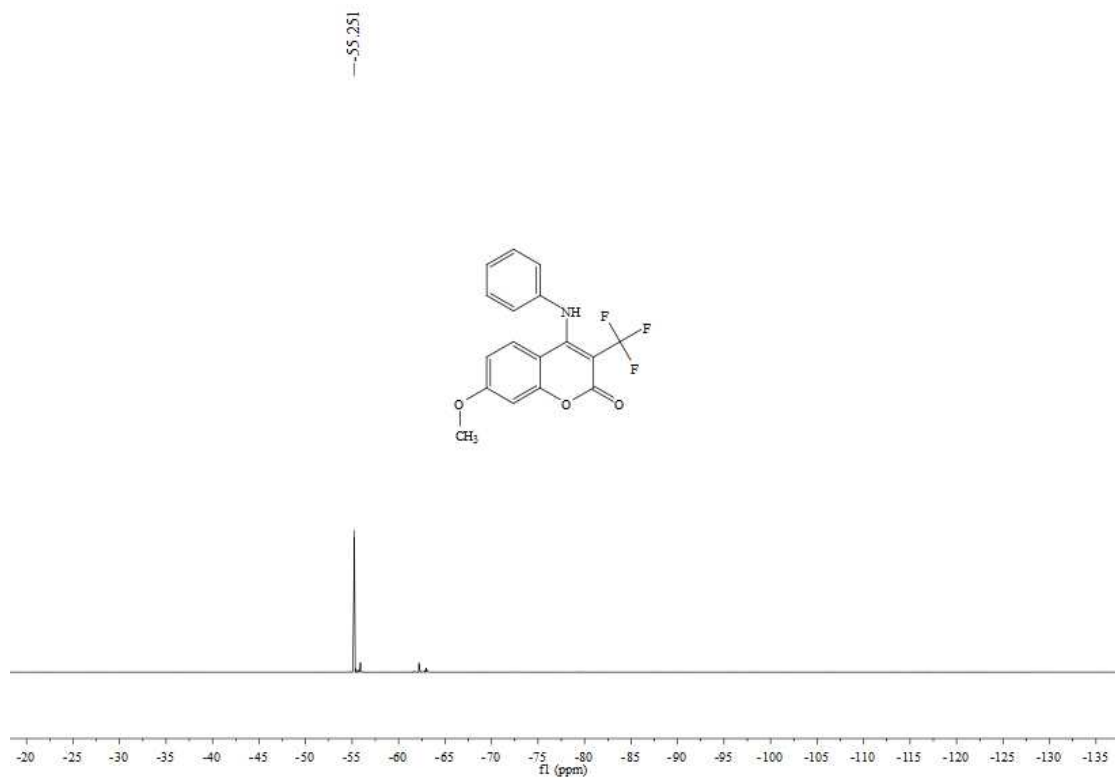
$^{19}\text{F}$  NMR of **3aa'** in  $\text{CDCl}_3$



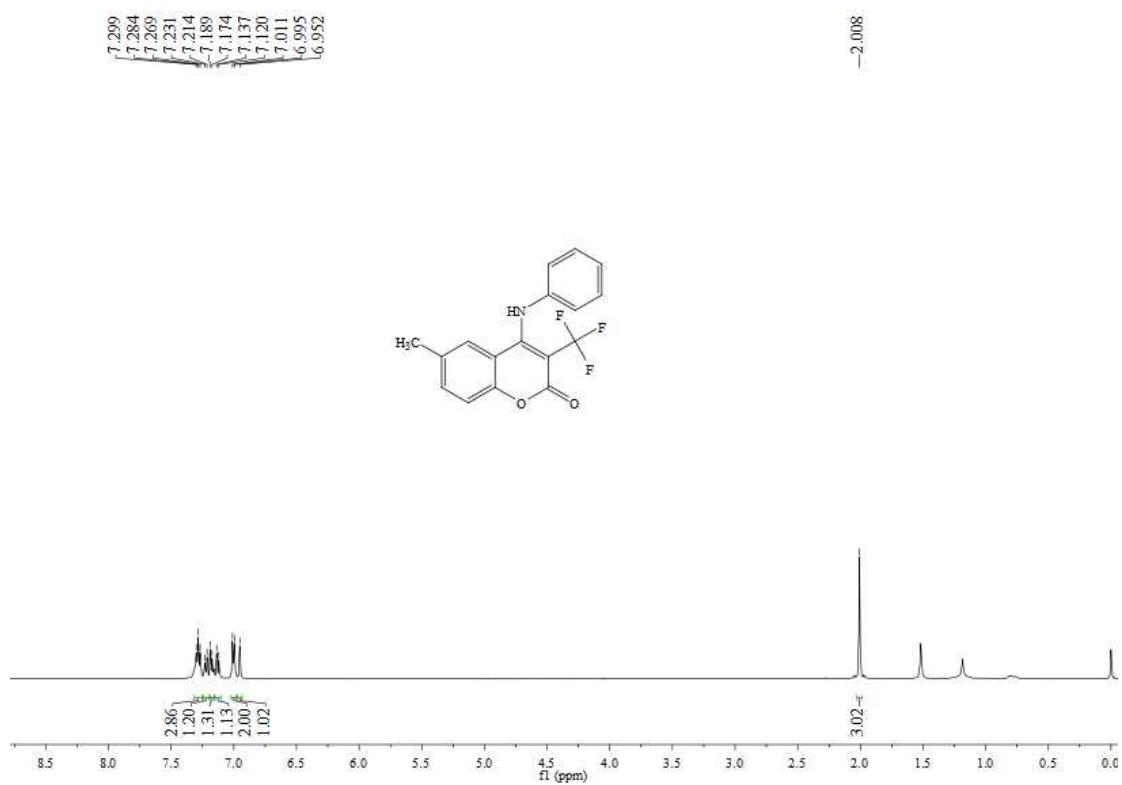
$^1\text{H}$  NMR of **3ba** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR of **3ba** in  $\text{CDCl}_3$

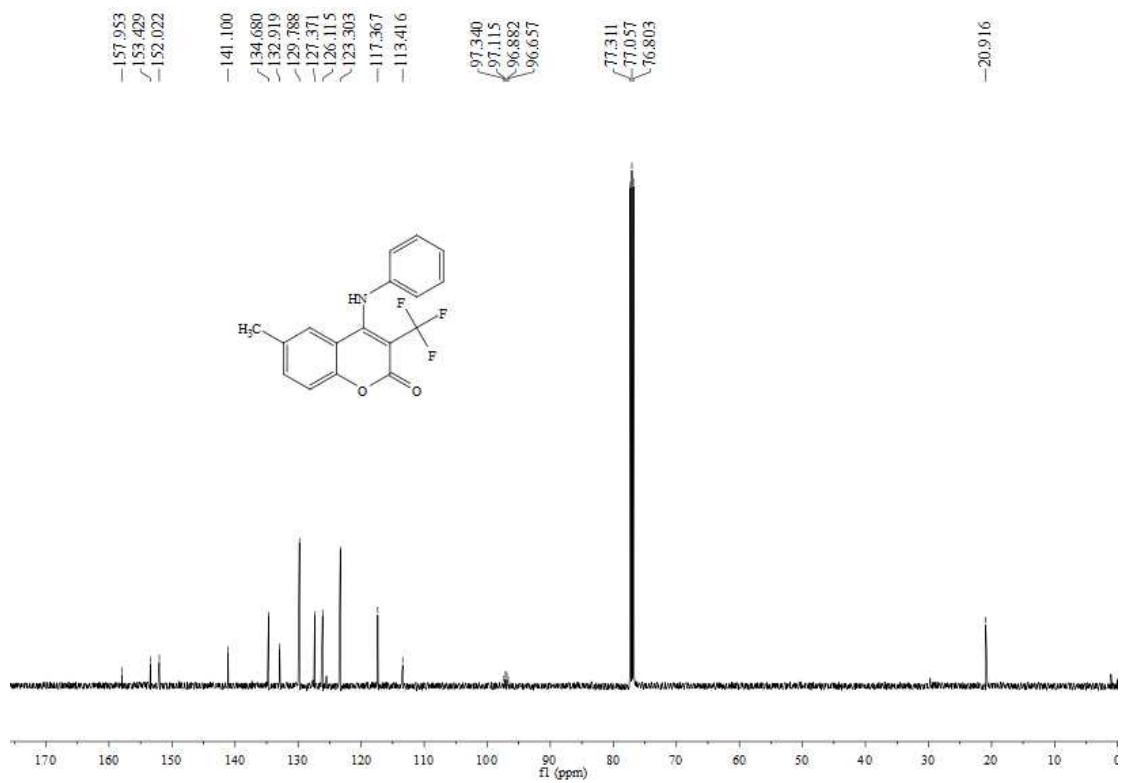


$^{19}\text{F}$  NMR of **3ba** in  $\text{CDCl}_3$

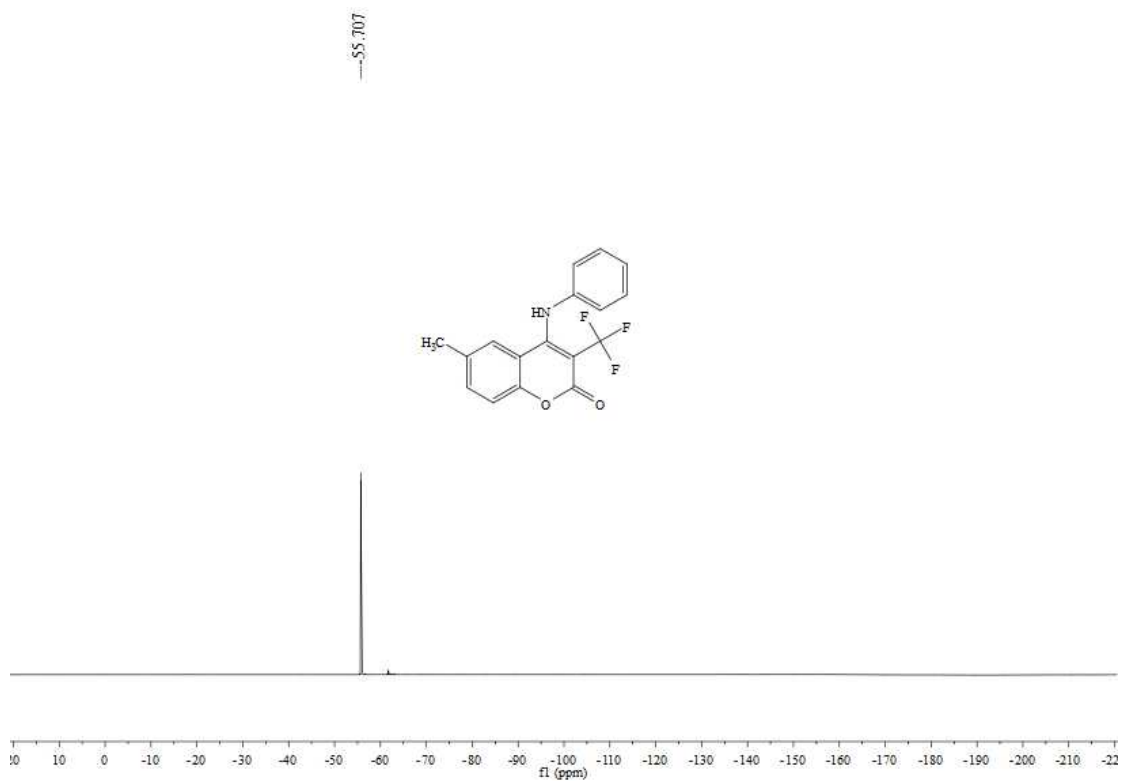


$^1\text{H}$  NMR of **3bb** in  $\text{CDCl}_3$

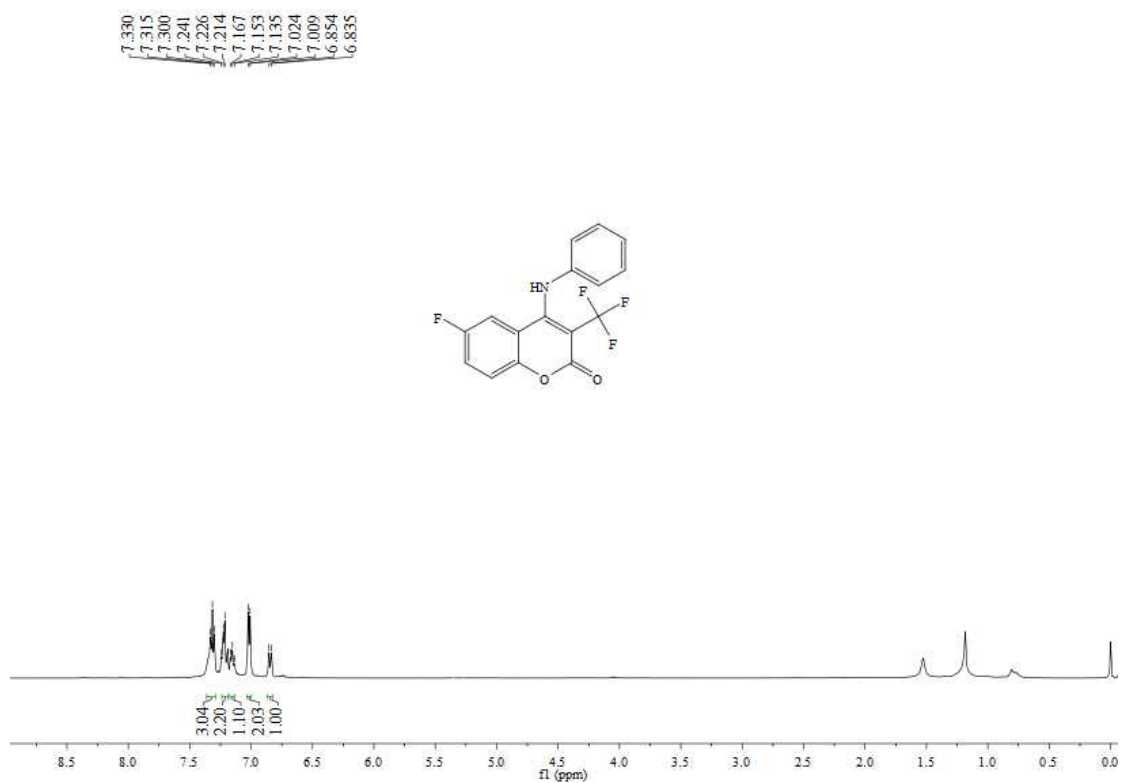




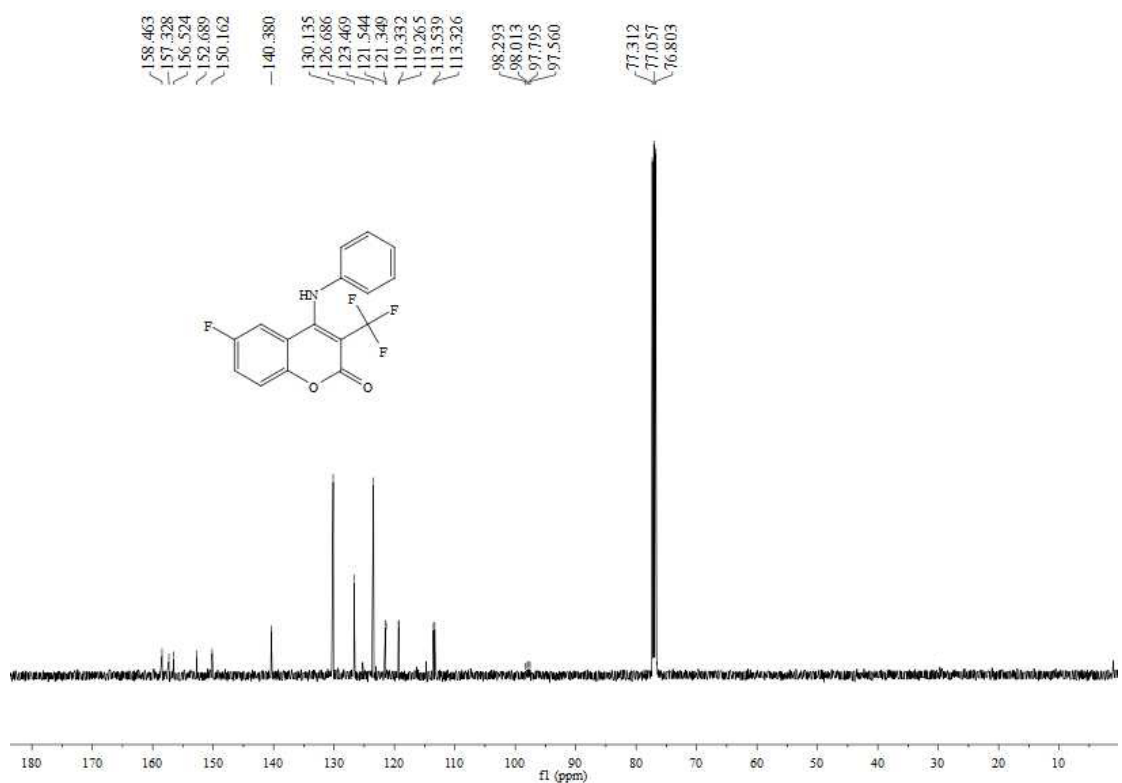
<sup>13</sup>C NMR of **3bb** in CDCl<sub>3</sub>



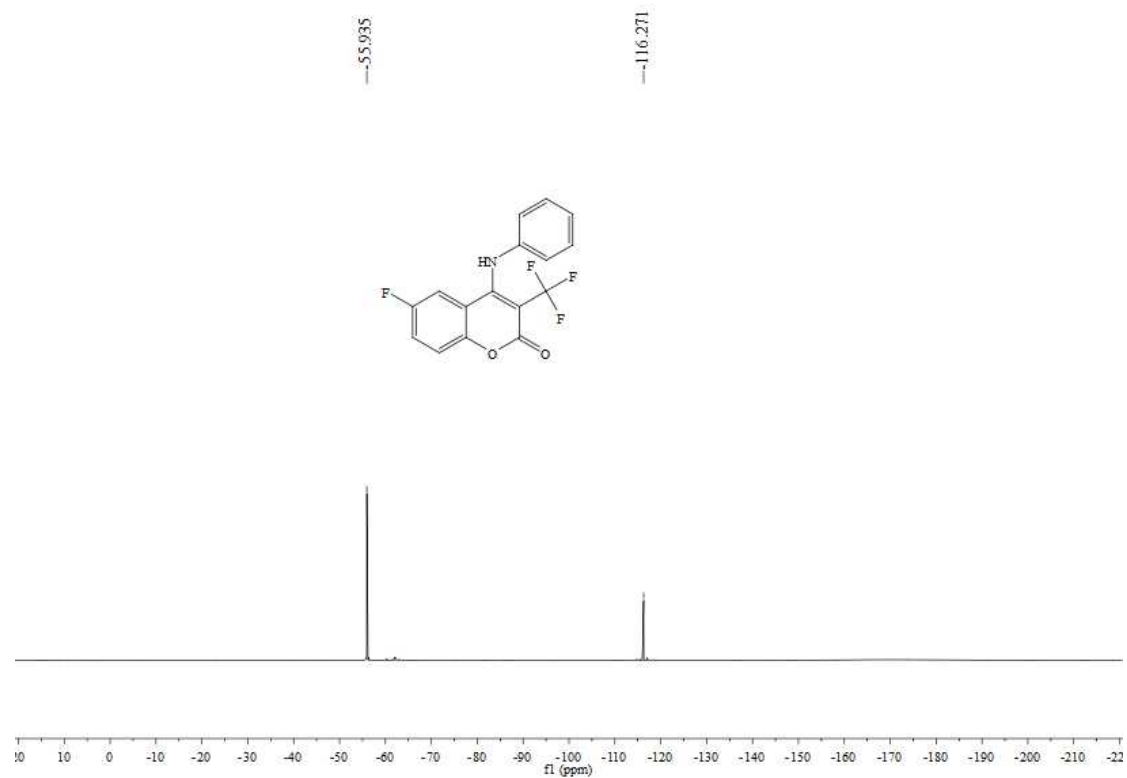
<sup>19</sup>F NMR of **3bb** in CDCl<sub>3</sub>



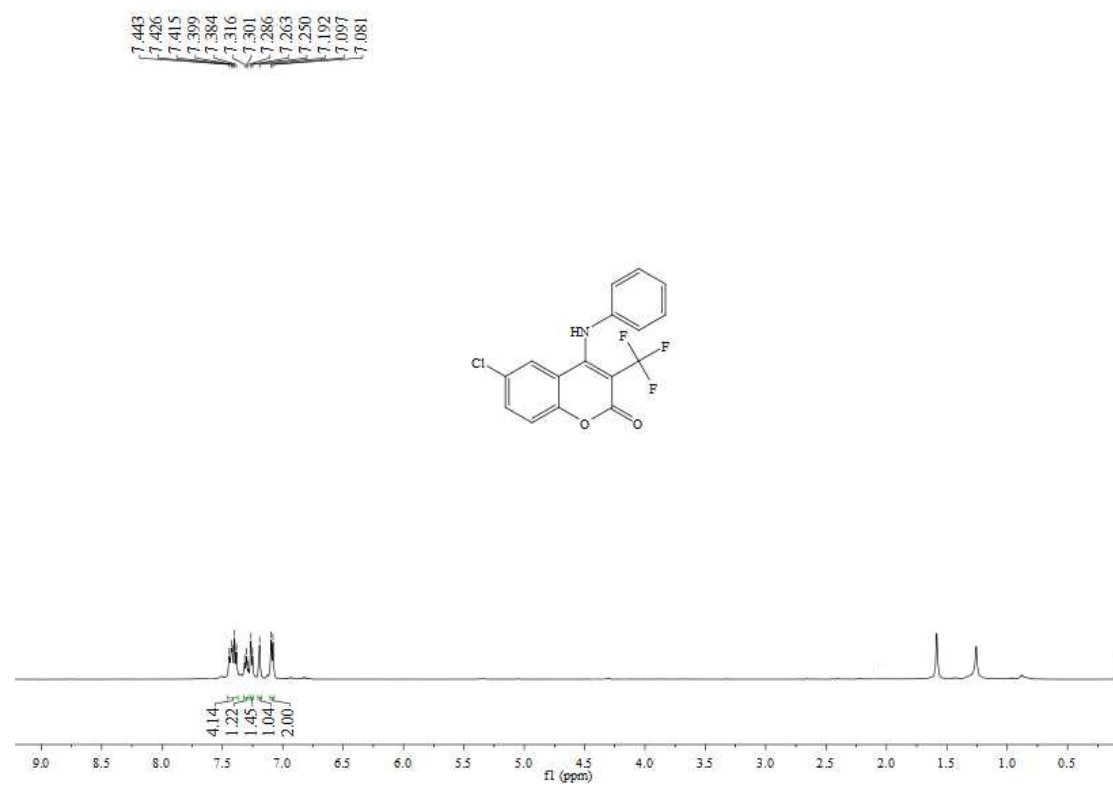
$^1\text{H}$  NMR of **3bc** in  $\text{CDCl}_3$



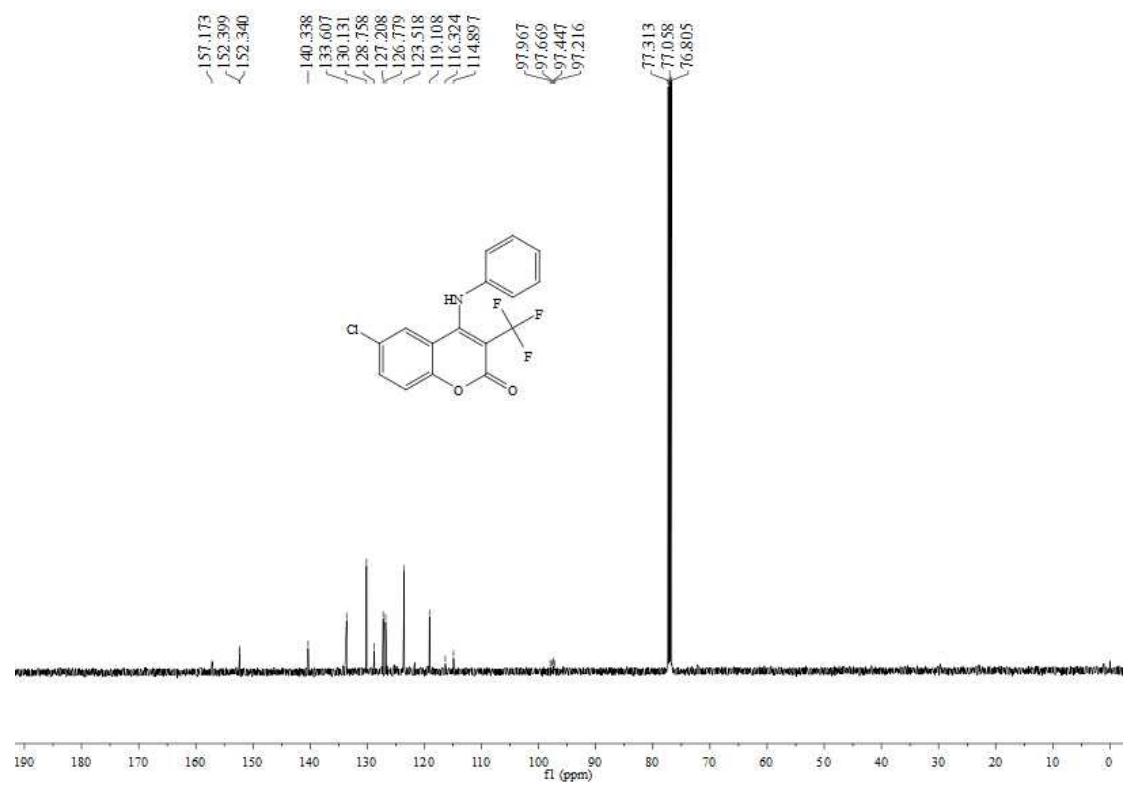
$^{13}\text{C}$  NMR of **3bc** in  $\text{CDCl}_3$



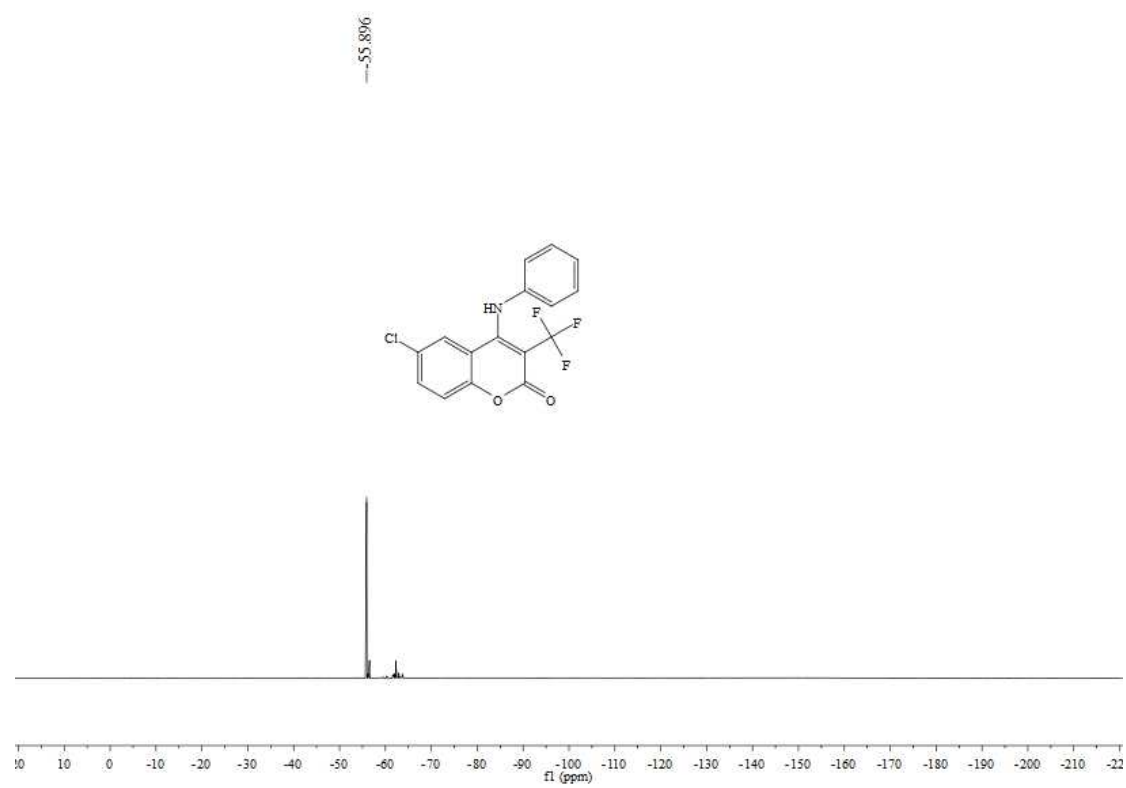
$^{19}\text{F}$  NMR of **3bc** in  $\text{CDCl}_3$



$^1\text{H}$  NMR of **3bd** in  $\text{CDCl}_3$

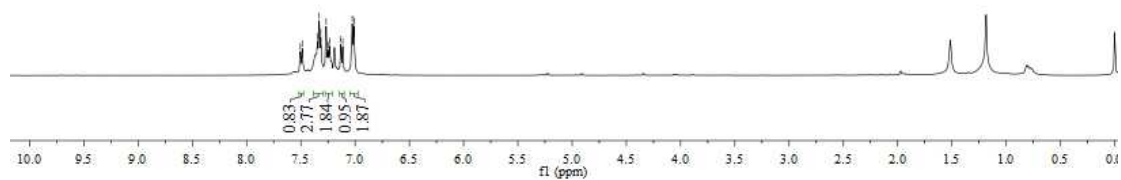
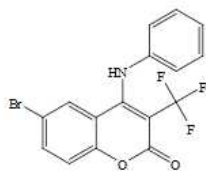


<sup>13</sup>C NMR of **3bd** in CDCl<sub>3</sub>



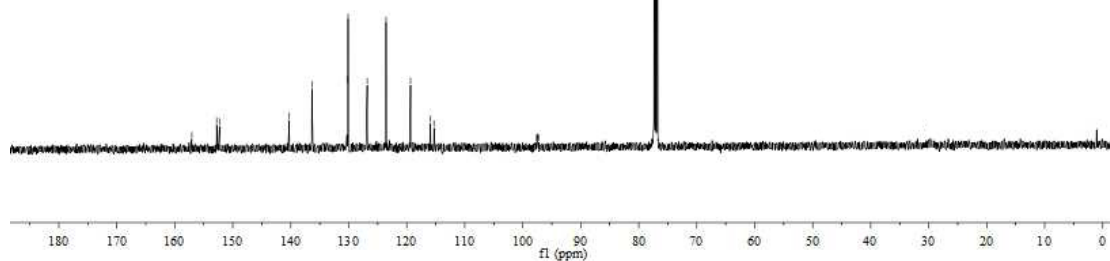
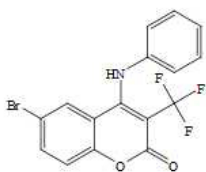
<sup>19</sup>F NMR of **3bd** in CDCl<sub>3</sub>

7.504  
7.487  
7.346  
7.331  
7.317  
7.267  
7.249  
7.235  
7.131  
7.114  
7.026  
7.011

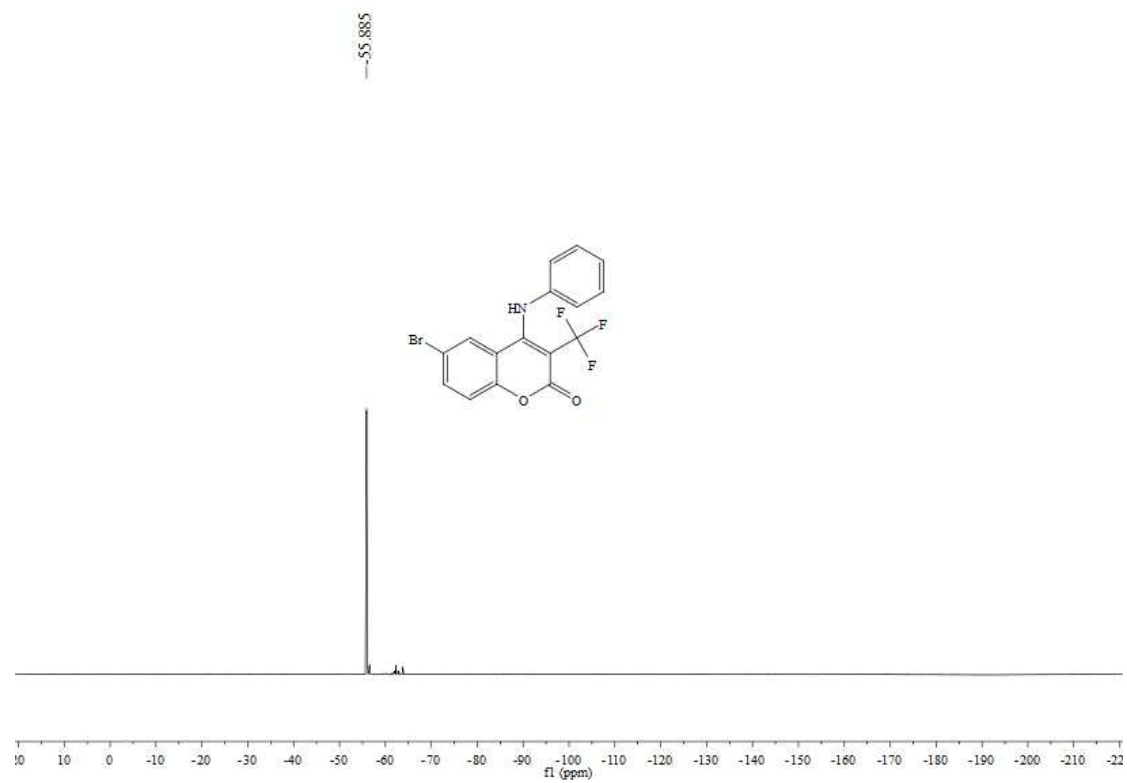


$^1\text{H}$  NMR of **3be** in  $\text{CDCl}_3$

157.067  
152.785  
152.274  
140.291  
136.360  
130.293  
130.118  
126.813  
123.567  
119.349  
115.925  
115.315  
97.617  
97.508  
97.458  
97.274  
77.316  
77.061  
76.808



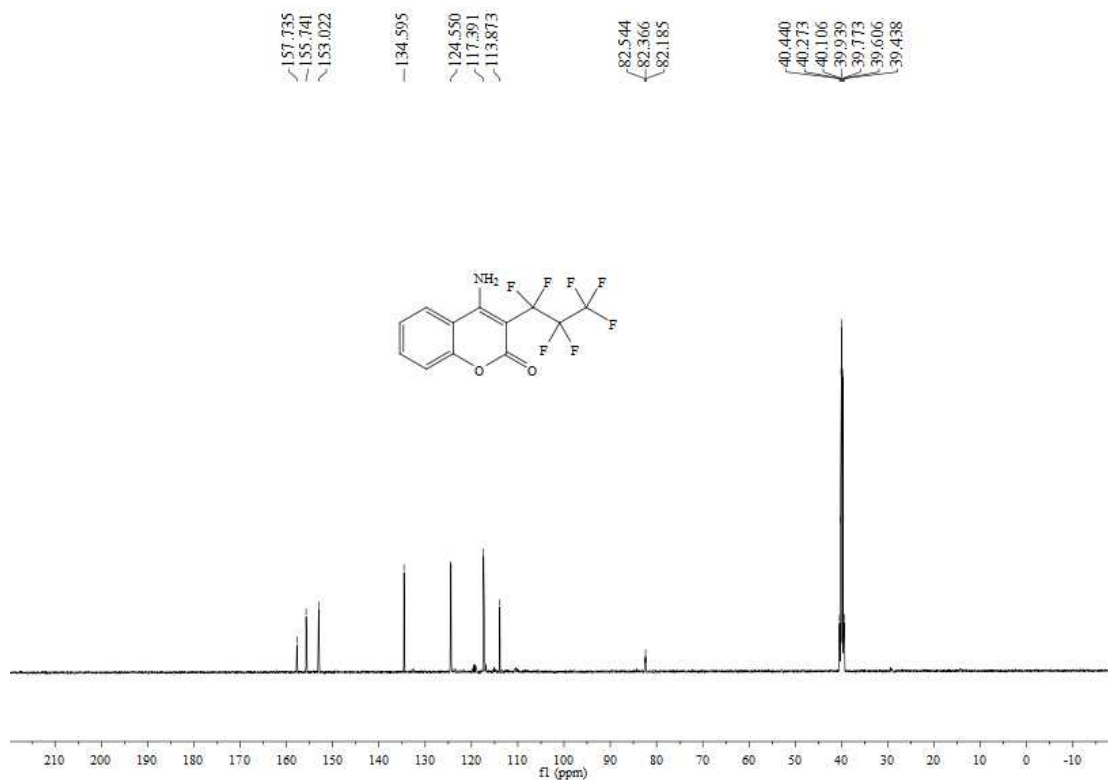
$^{13}\text{C}$  NMR of **3be** in  $\text{CDCl}_3$



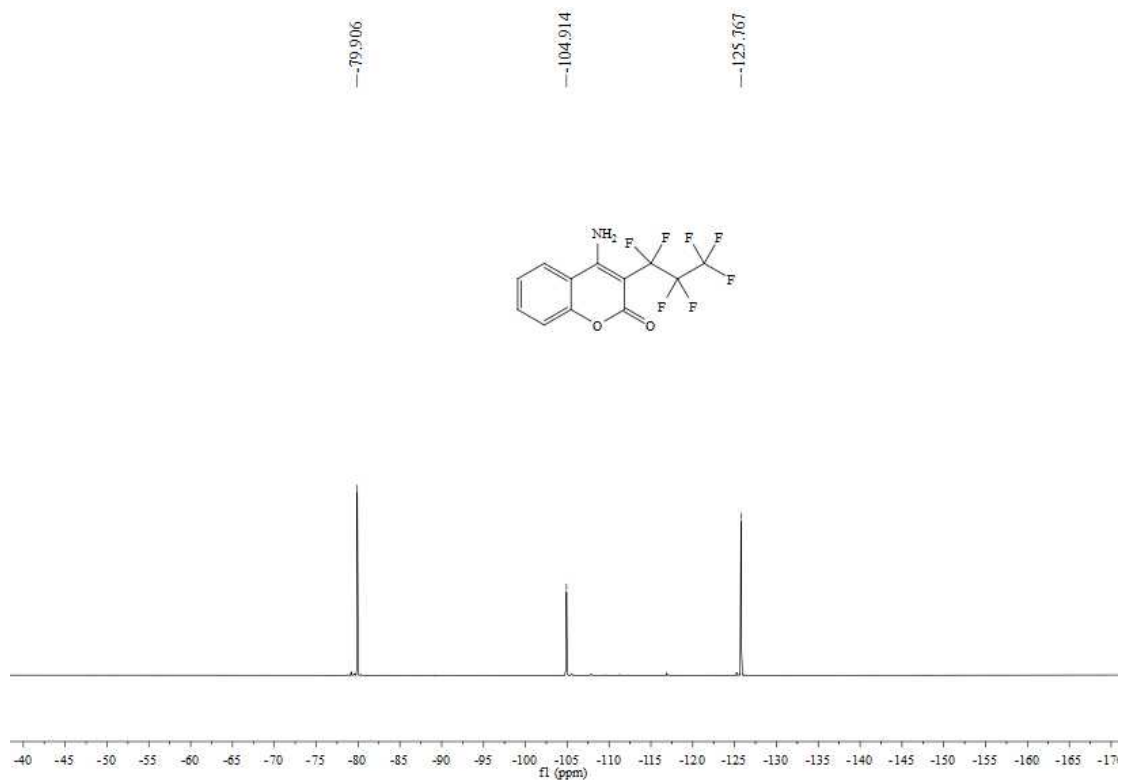
$^{19}\text{F}$  NMR of **3be** in  $\text{CDCl}_3$



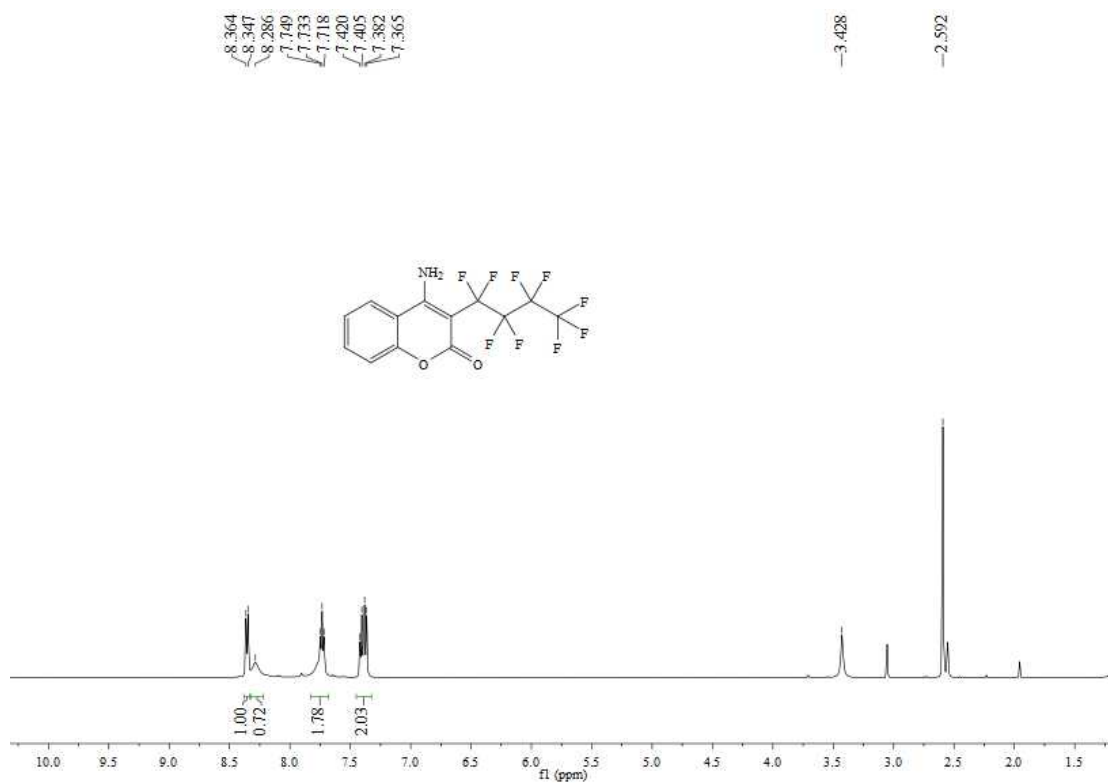
$^1\text{H}$  NMR of **3ca** in  $d_6$ -DMSO



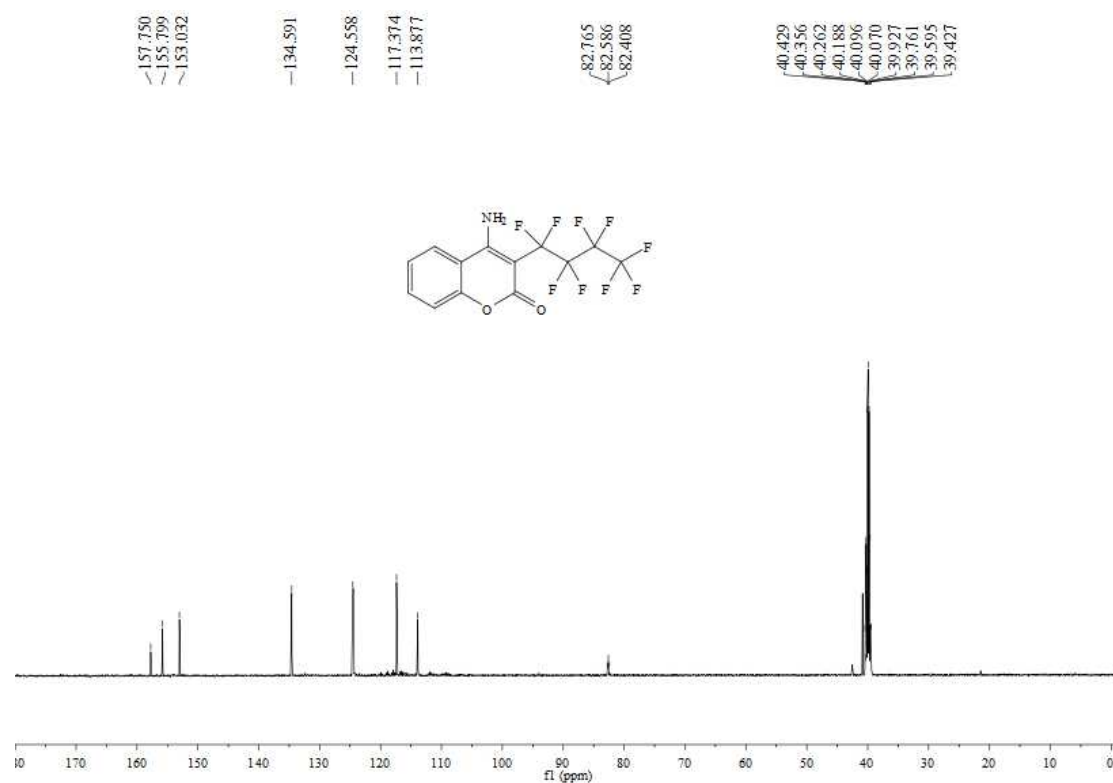
$^{13}\text{C}$  NMR of **3ca** in  $d_6$ -DMSO



$^{19}\text{F}$  NMR of **3ca** in  $d_6$ -DMSO

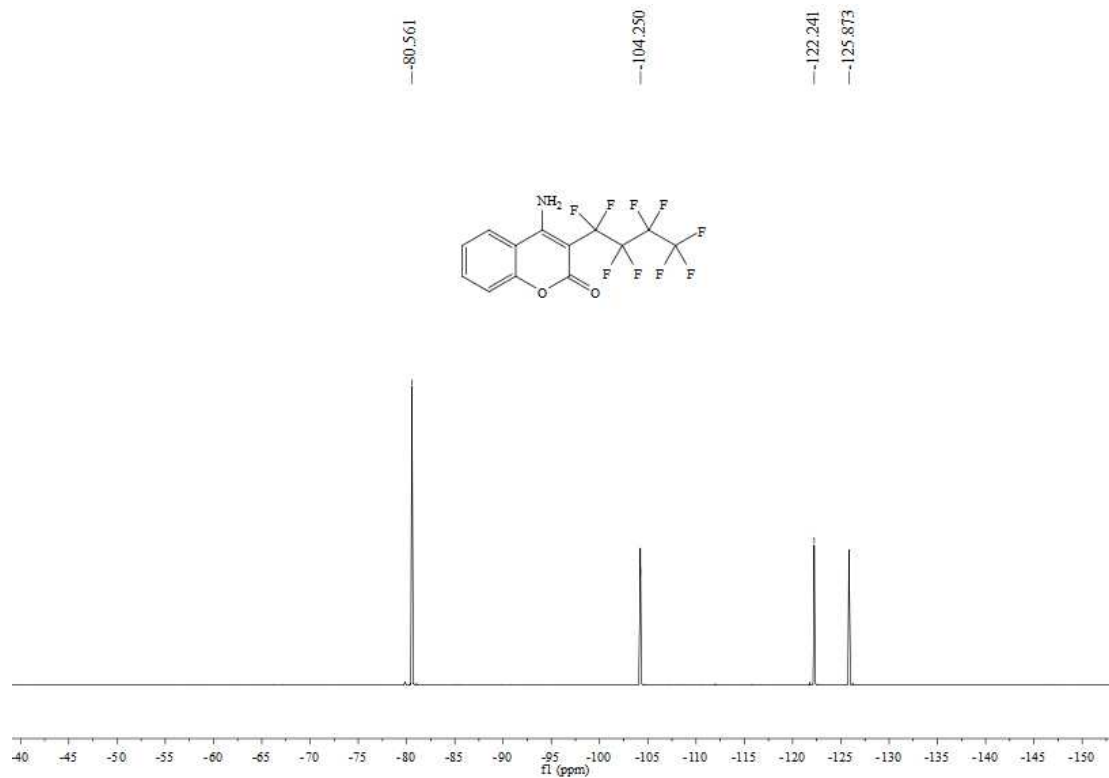


<sup>1</sup>H NMR of **3cb** in *d*<sub>6</sub>-DMSO

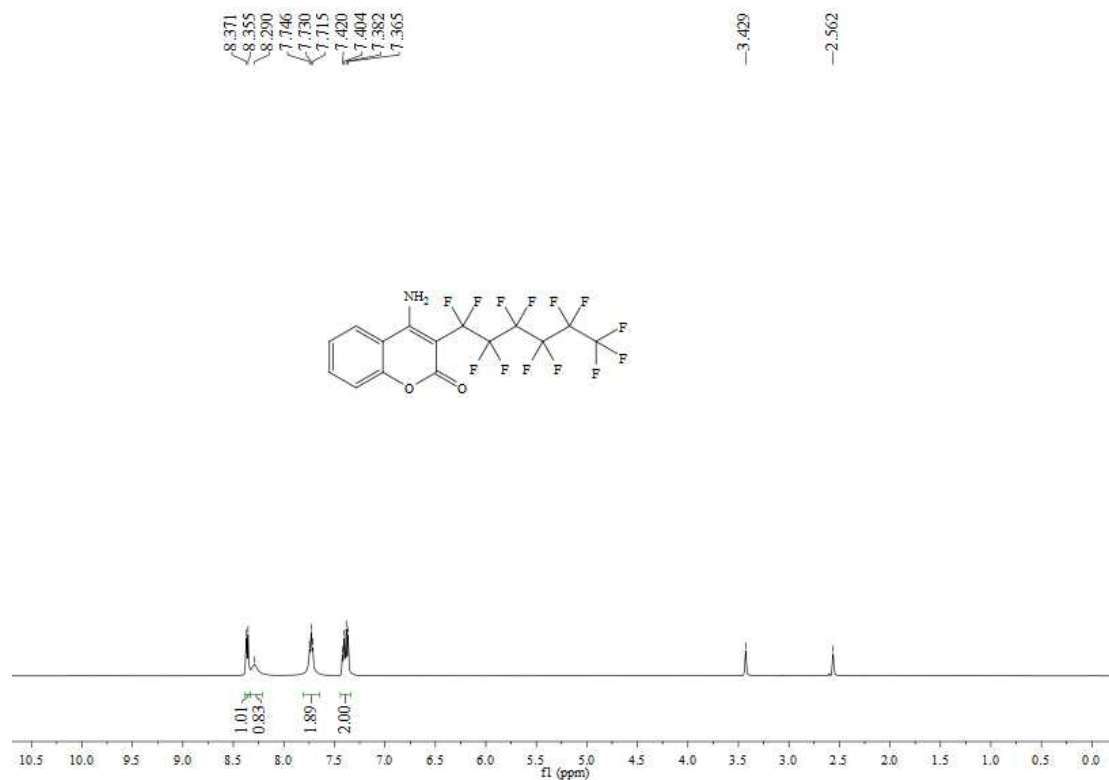


<sup>13</sup>C NMR of **3cb** in *d*<sub>6</sub>-DMSO

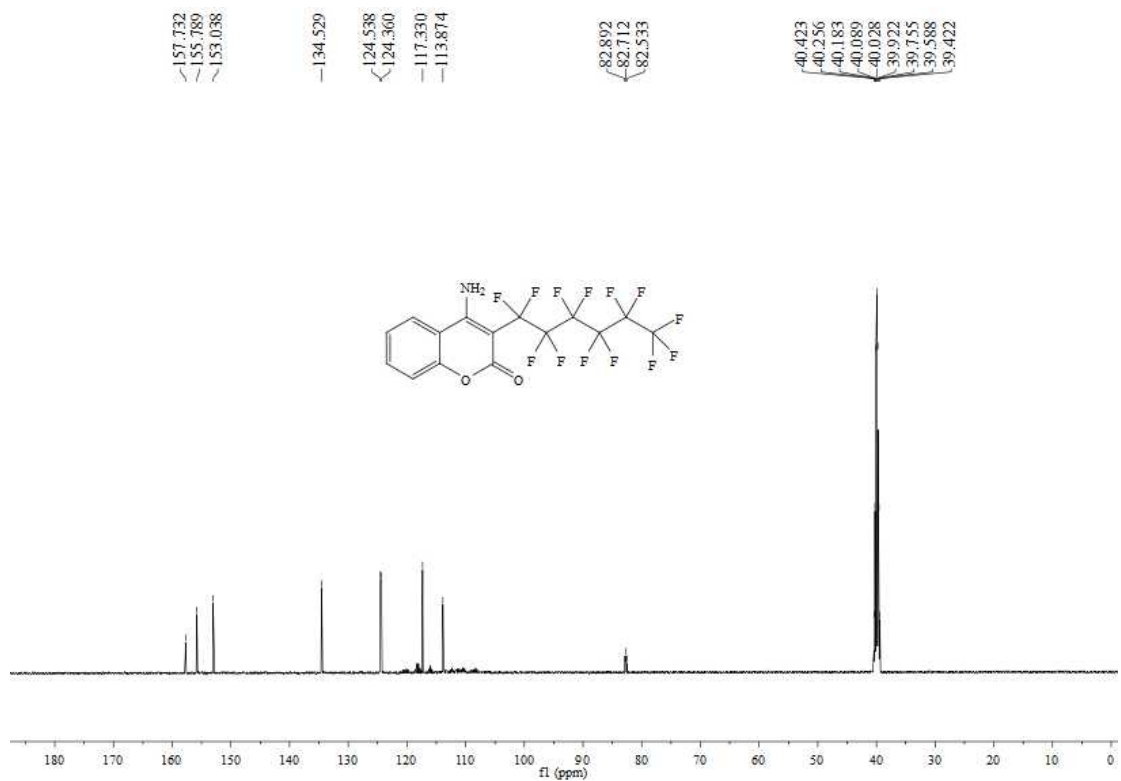




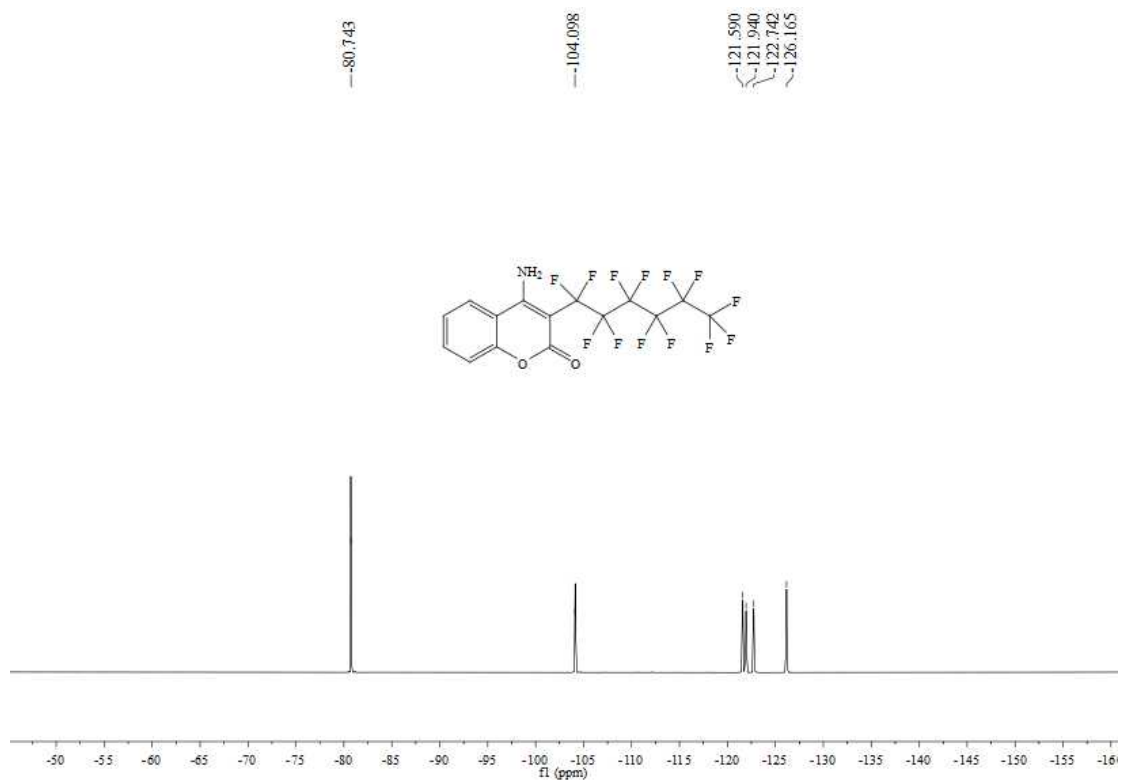
$^{19}\text{F}$  NMR of **3b** in  $d_6$ -DMSO



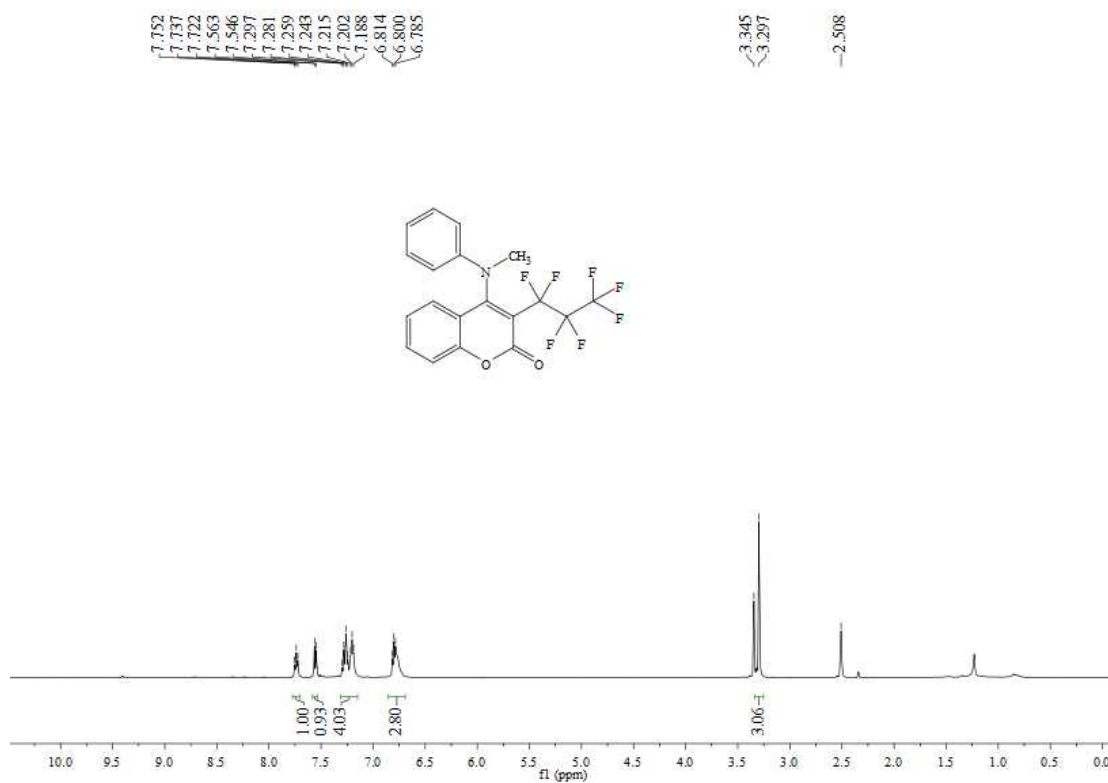
$^1\text{H}$  NMR of **3cc** in  $d_6$ -DMSO



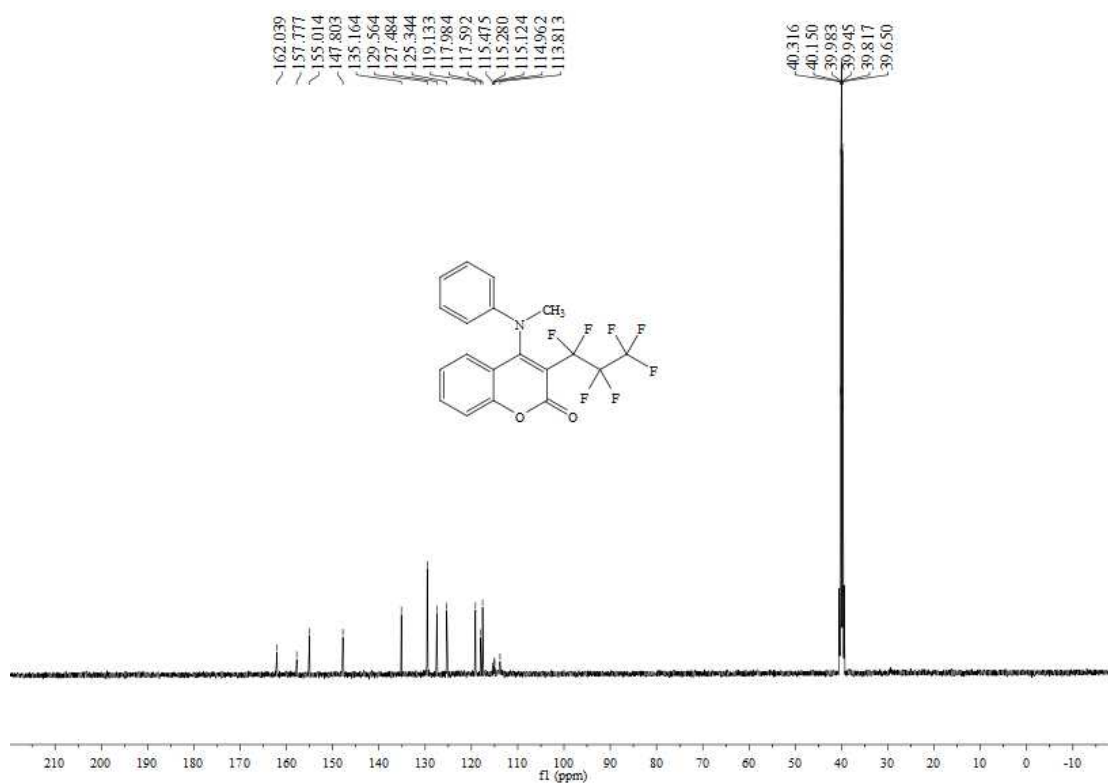
$^{13}\text{C}$  NMR of **3cc** in  $d_6$ -DMSO



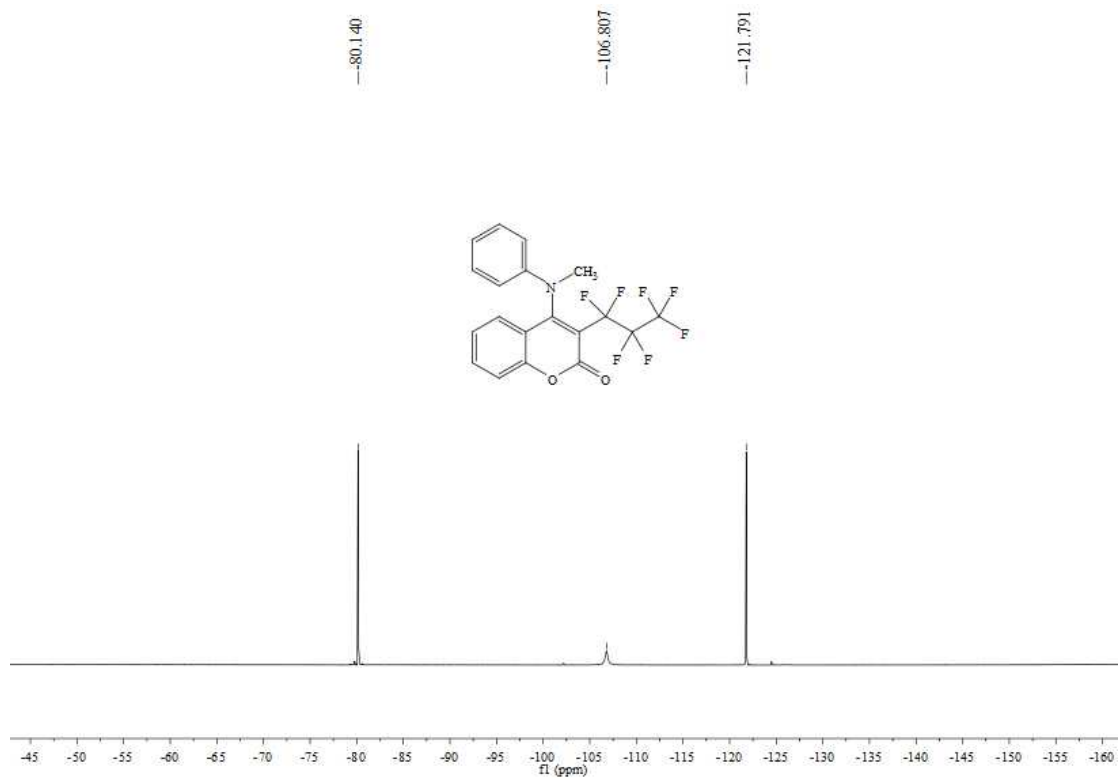
$^{19}\text{F}$  NMR of **3cc** in  $d_6$ -DMSO



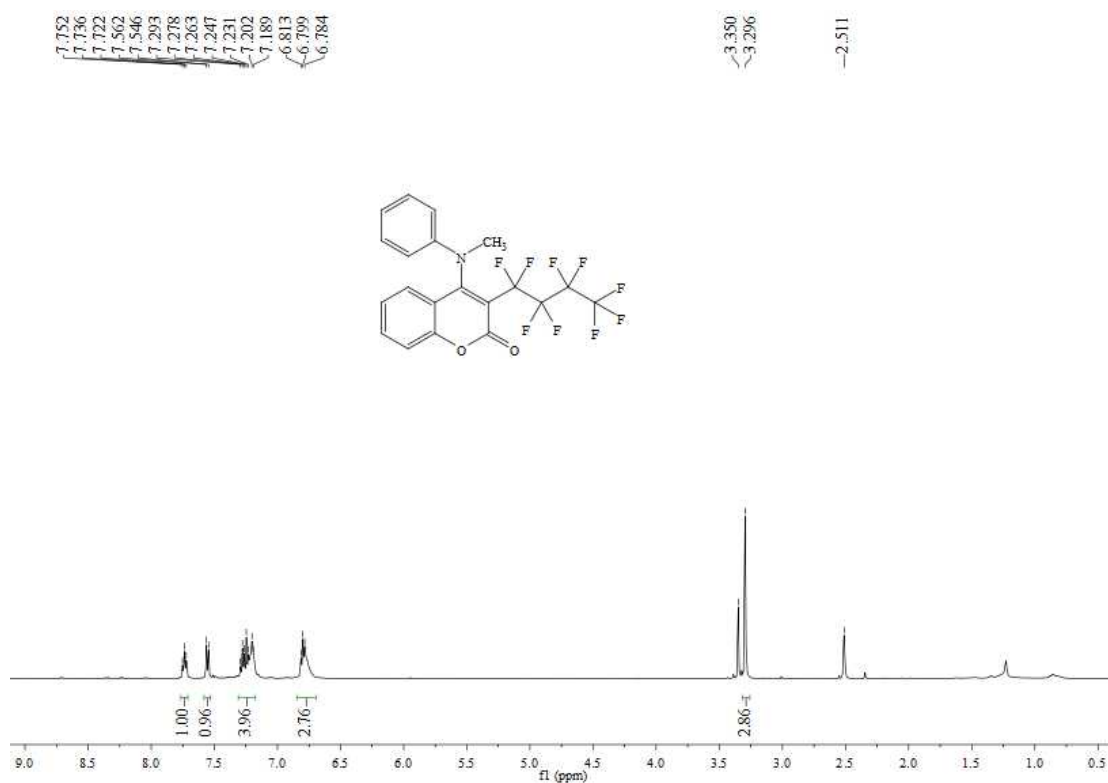
<sup>1</sup>H NMR of **3cd** in *d*<sub>6</sub>-DMSO



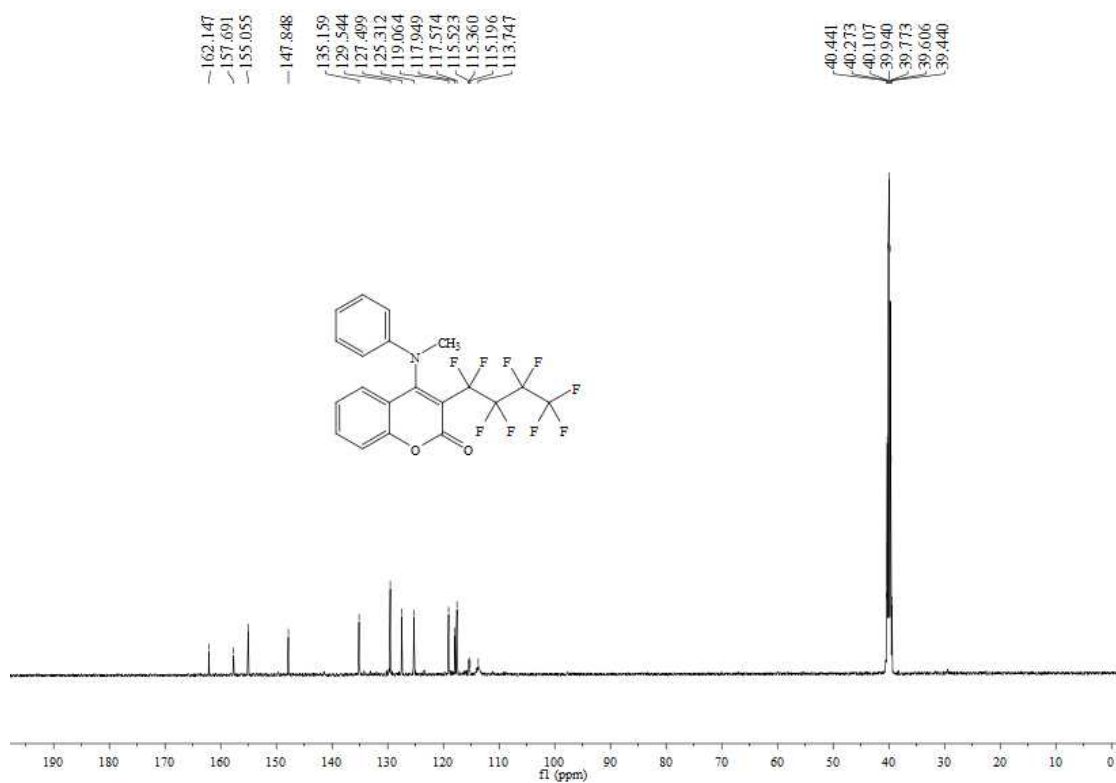
<sup>13</sup>C NMR of **3cd** in *d*<sub>6</sub>-DMSO



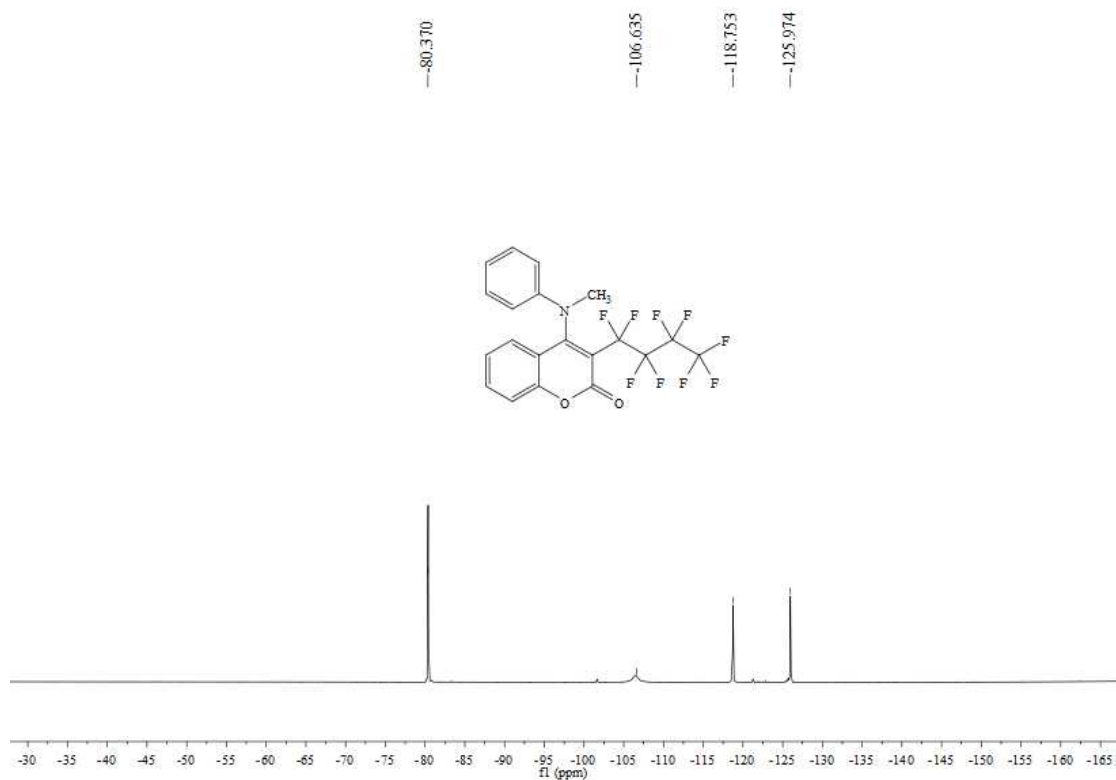
$^{19}\text{F}$  NMR of **3cd** in  $d_6$ -DMSO



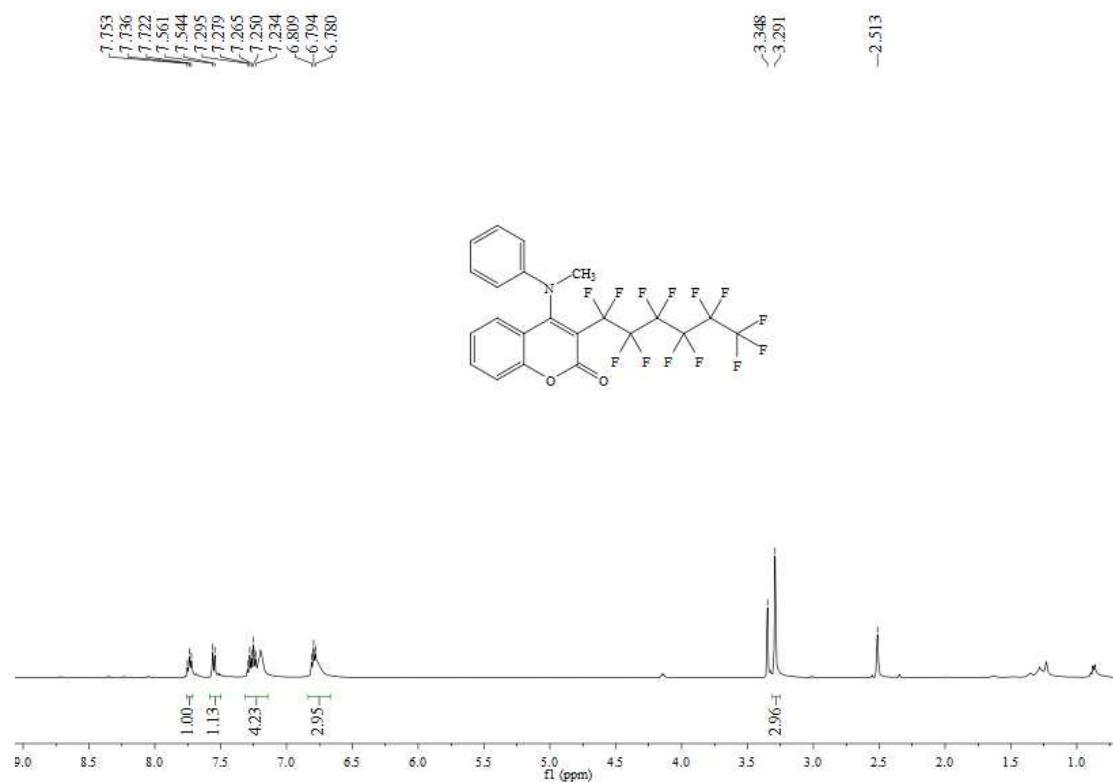
$^1\text{H}$  NMR of **3ce** in  $d_6$ -DMSO



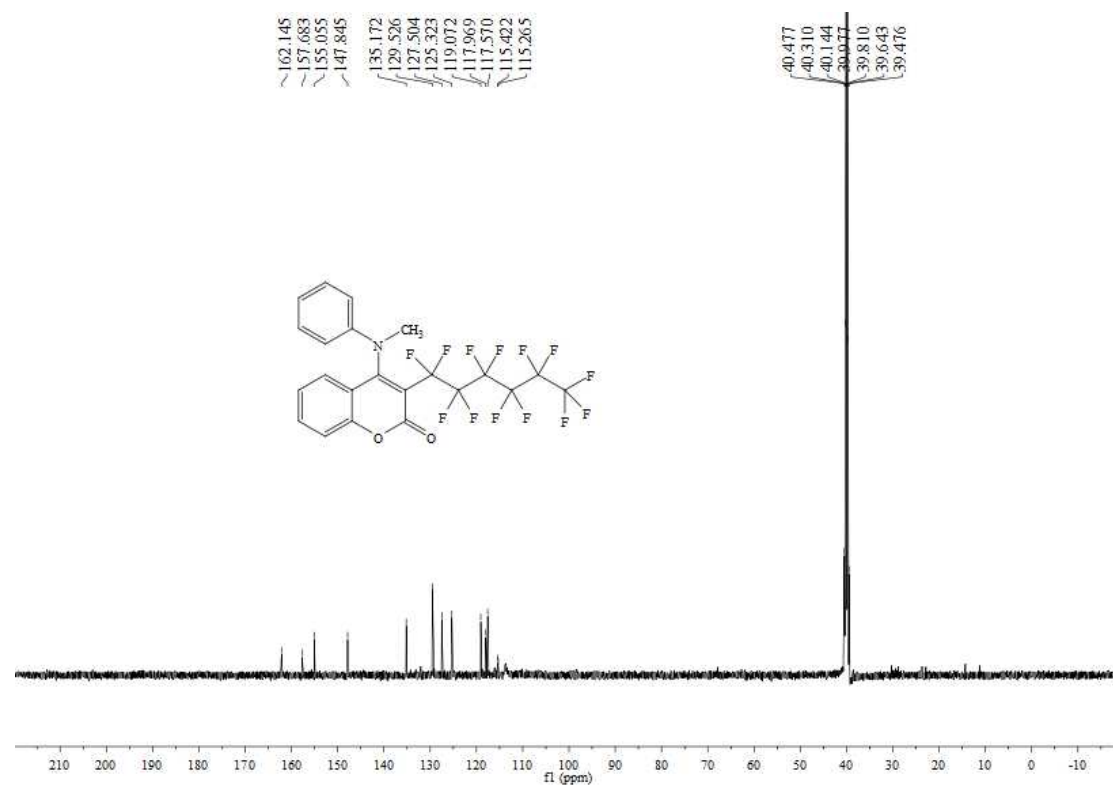
<sup>13</sup>C NMR of **3ce** in *d*<sub>6</sub>-DMSO



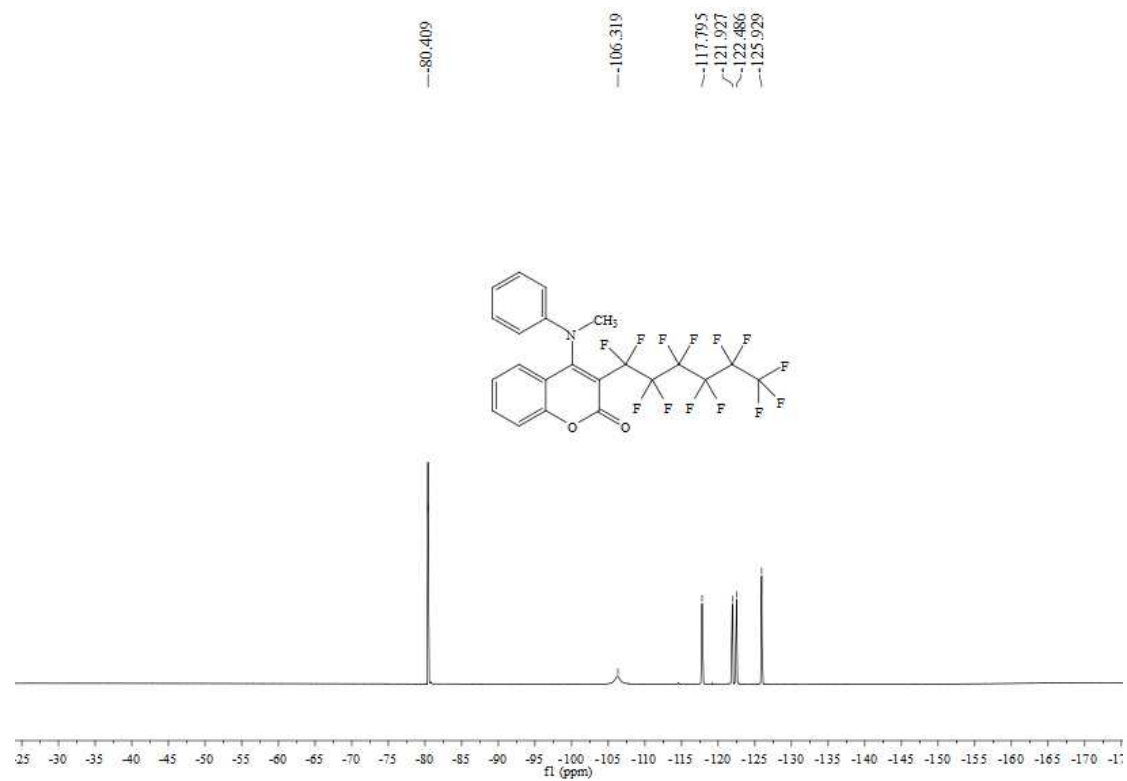
<sup>19</sup>F NMR of **3ce** in *d*<sub>6</sub>-DMSO



<sup>1</sup>H NMR of **3cf** in *d*<sub>6</sub>-DMSO



<sup>13</sup>C NMR of **3cf** in *d*<sub>6</sub>-DMSO



$^{19}\text{F}$  NMR of **3cf** in  $d_6$ -DMSO