

## Contents

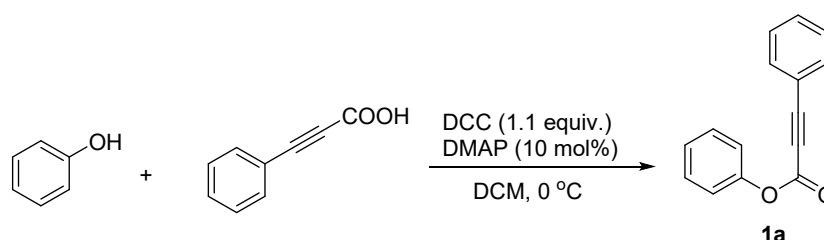
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## 1. General Information

Unless otherwise indicated, Commercial substrates, solvents and reagents were not further purified. The reactions process were monitored by TLC and visualized by UV light (254 nm and 365 nm). Column chromatography was performed using silica gel (300-400 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  400 (or 600) and 100 (or 150) MHz respectively, and both are reported in units of parts per million (ppm) downfield from tetramethylsilan ( $\text{SiMe}_4$ ,  $\delta = 0.0$  ppm). The chemical shift of NMR relative to solvent signal is reported that  $\text{CDCl}_3$  ( $\delta = 7.26$  ppm for  $^1\text{H}$  NMR and  $\delta = 77.00$  ppm for  $^{13}\text{C}$  NMR), High resolution mass spectrometry (HRMS) data were recorded by a Thermo Finnigan LCQ-Advantage spectrometer.

## 2. Experimental procedures

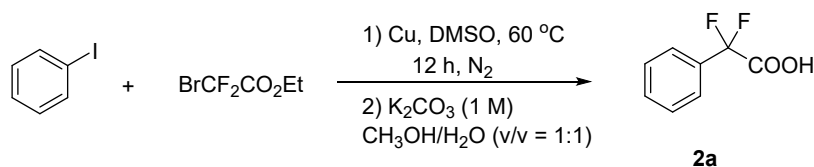
### 2.1 General Procedure for preparation of **1**<sup>1</sup>



Scheme 2-1

To a 50 mL round-bottom flask were added phenol (11 mmol, 1.1 g), 3-phenylpropionic acid (10 mmol, 1.5 g) and 20 mL of dichloromethane solution at room temperature, followed by dicyclohexylcarbodiimide (DCC, 11 mmol, 2.3 g) and 4-dimethylaminopyridine (DMAP, 1 mmol, 122.2 mg), respectively. and stirred at 0 °C for 1h, followed by 4 h at room temperature.. The reaction was quenched with water and extracted with ethyl acetate. The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 50:1, v/v) to obtain a white solid phenyl 3-phenylpropiolate **1a** in 88% yield after vacuum drying (Scheme 2-1). Other substituted phenylpropiolate compounds were prepared by the same method described above.

### 2.2 General Procedure for preparation of **2**<sup>2</sup>



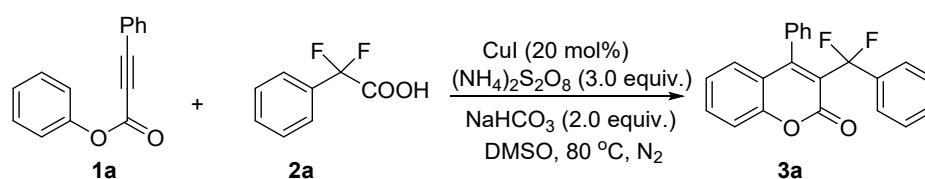
Scheme 2-2

In a 50 mL round bottom flask under air, iodobenzene (10 mmol, 2.1 g) and ethyl bromodifluoroacetate (10 mmol, 1.3 mL) were added to a suspension of copper powder (26 mmol, 1.7 g) in dimethyl sulfoxide (26 mL, 0.4 M). The reaction mixture was stirred

magnetically at 60 °C for 12 h. After the reaction was completed and cooled to room temperature, the remaining copper powder in the reaction solution was removed by filtration, and then the filtrate was poured into 100 mL of water, at which time a large amount of white flocculent material was produced. The filtrate was extracted with ethyl acetate (3×50 mL) and the combined organic phases were washed with water (3×50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated by rotary evaporator. The product was used for next step without further purification

In a 50 mL round bottom flask, The crude product obtained was added to a mixture of methanol (30 mL) and 1 M K<sub>2</sub>CO<sub>3</sub> aq. (30 mL) and stirred at room temperature for 2 h. Then 1 M HCl was added dropwise to the bottle under ice bath conditions and acidified to pH = 1. After removing a large amount of methanol by distillation under reduced pressure, the aqueous phase was extracted with ethyl acetate (3 × 50 mL) and the combined organic phases were washed with saturated brine (2 × 50 mL), washed with water (2 × 15 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuum. The resulting crude product was purified by fast silica gel column chromatography (*n*-hexane/ethyl acetate = 5:1, v/v) to give a white solid *α,α*-difluorophenylacetic acid in 63% yield after vacuum drying (Scheme 2-2). Other substituted *α,α*-difluoroarylacetic acid compounds were prepared by the same method described above.

### 2.3 General Procedure for preparation of 3-difluoroarylmethylated coumarins 3



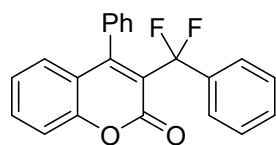
Scheme 2-3

A mixture of phenyl 3-phenylpropiolate **1a** (0.5 mmol, 111.1 mg), *α,α*-difluorophenylacetic acid **2a** (0.75 mmol, 129.1 mg), CuI (0.1 mmol, 18.9 mg), (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (1.5 mmol, 228.2 mg), and NaHCO<sub>3</sub> (1 mmol, 84.0 mg) in 3 mL of DMSO under N<sub>2</sub> atmosphere In a 10 mL Schlenk tube was stirred at 80 °C for 3 h. Then the reaction mixture was quenched with water, the aqueous layer was extracted with ethyl acetate (3 × 30 mL), The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated by rotary evaporator and the crude product obtained was purified by silica gel column chromatography (*n*-hexane/ethyl acetate = 30:1, v/v) to give the target product **3a** (Scheme 2-3) as a white solid in 60% yield after vacuum drying. The other substituted target products **3b-v** were prepared by referring to the above method.

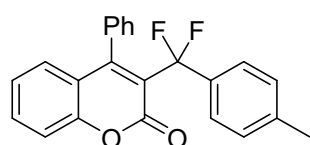
[1] T. Kitamura, K. Otsubo, *J. Org. Chem.*, 2012, **77**, 2978-2982.

[2] F. Chen, A. S. K. Hashmi, *Org. Lett.*, 2016, **18**, 2880-2882

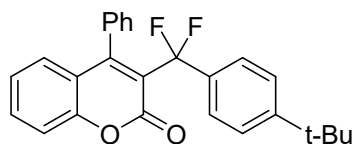
### 3. Characterization data of compounds 3



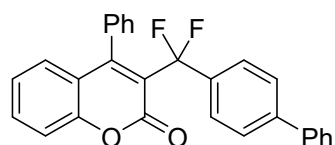
**3-[difluoro(phenyl)methyl]-4-phenyl-2H-chromen-2-one (3a):** White solid (104 mg, 60%); m.p. 142-144 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.52 (m, 3H), 7.53 – 7.46 (m, 3H), 7.41 – 7.32 (m, 4H), 7.32 – 7.25 (m, 2H), 7.15 (t,  $J = 7.8$  Hz, 1H), 6.92 (d,  $J = 8.2$  Hz, 1H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.7 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5 (t,  $J = 3.0$  Hz), 154.1, 153.1, 136.(t,  $J = 27.0$  Hz), 134.3, 132.9, 130.0 (t,  $J = 2.0$  Hz), 128.8, 128.5, 128.2, 128.1, 127.4 (t,  $J = 2.6$  Hz), 125.5 (t,  $J = 5.0$  Hz), 124.3, 121.1 (t,  $J = 26.6$  Hz), 120.5, 119.1 (t,  $J = 245.0$  Hz), 116.5; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  349.1035, mass found 349.1036.



**3-[difluoro(*p*-tolyl)methyl]-4-phenyl-2H-chromen-2-one (3b):** White solid (104 mg, 58%); m.p. 114-116 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56 – 7.51 (m, 1H), 7.50 – 7.42 (m, 5H), 7.34 (d,  $J = 8.2$  Hz, 1H), 7.29 – 7.25 (m, 2H), 7.18 (d,  $J = 8.2$  Hz, 2H), 7.16 – 7.11 (m, 1H), 6.91 (dd,  $J = 8.2, 1.6$  Hz, 1H), 2.34 (s, 3H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.0 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5 (t,  $J = 3.0$  Hz), 153.8 (t,  $J = 2.0$  Hz), 153.0, 140.0 (t,  $J = 2.0$  Hz), 134.3, 133.7 (t,  $J = 27.0$  Hz), 132.8, 128.8, 128.8, 128.4, 128.0, 127.3 (t,  $J = 2.6$  Hz), 125.4 (t,  $J = 5.0$  Hz), 124.3, 121.1 (t,  $J = 26.0$  Hz), 120.5, 119.2 (t,  $J = 245.6$  Hz), 116.4, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{23}\text{H}_{17}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  363.1191, mass found 363.1186.

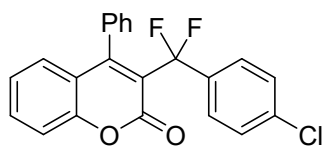


**3-[[4-(*tert*-butyl)phenyl]difluoromethyl]-4-phenyl-2H-chromen-2-one (3c):** Yellow solid (139 mg, 69%); m.p. 99-101 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 – 7.45 (m, 6H), 7.38 (d,  $J = 8.2$  Hz, 2H), 7.32 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.30 – 7.25 (m, 2H), 7.14 – 7.10 (m, 1H), 6.90 (dd,  $J = 8.2, 1.6$  Hz, 1H), 1.29 (s, 9H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.2 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.4 (t,  $J = 3.0$  Hz), 153.7 (t,  $J = 2.0$  Hz), 153.0, 152.9 (t,  $J = 2.0$  Hz), 134.4, 133.6 (t,  $J = 6.6$  Hz), 132.7, 128.8, 128.4, 128.0, 127.4 (t,  $J = 2.6$  Hz), 125.3 (t,  $J = 5.6$  Hz), 125.1, 124.3, 121.2 (t,  $J = 6.0$  Hz), 120.5, 119.2 (t,  $J = 245.0$  Hz), 116.4, 34.6, 31.1; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{26}\text{H}_{23}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  405.1661, mass found 405.1661.

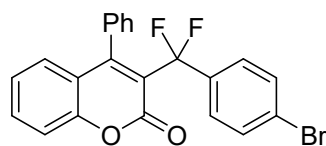


**3-[(1,1'-biphenyl)-4-yl]difluoromethyl]-4-phenyl-2H-chromen-2-one (3d):** Light yellow solid (131 mg, 62%); m.p. 169-171 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (d,  $J = 8.2$  Hz, 2H), 7.60 – 7.54 (m, 3H), 7.57 – 7.50 (m, 2H), 7.52 – 7.46 (m, 3H), 7.42 (t,  $J = 7.8$  Hz, 2H), 7.38 – 7.32 (m, 2H), 7.31 – 7.26 (m, 2H), 7.16 – 7.11 (m, 1H), 6.92 (dd,  $J = 8.2, 1.6$  Hz, 1H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.5 (s, 2F);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5, 154.1, 153.2, 142.8, 140.3, 135.5 (t,  $J = 12.0$  Hz), 134.4, 132.9, 128.8, 128.8, 128.5, 128.1, 127.7, 127.5 (t,  $J = 2.2$  Hz), 127.2, 126.9, 126.1 (t,  $J = 5.2$

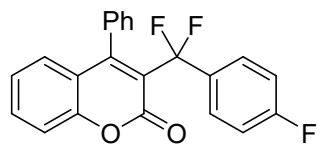
Hz), 124.3, 121.1 (t,  $J = 25.6$  Hz), 120.6, 119.2 (t,  $J = 245.2$  Hz), 116.5; **HRMS** (ESI) :  $m/z$  calcd for  $C_{28}H_{19}F_2O_2$   $[M+H]^+$  425.1348, mass found 425.1342.



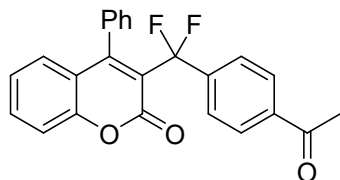
**3-[(4-chlorophenyl)difluoromethyl]-4-phenyl-2H-chromen-2-one (3e):** White solid (89 mg, 47%); m.p. 113-115 °C; **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ )  $\delta$  7.60 – 7.51 (m, 1H), 7.52 – 7.49 (m, 5H), 7.39 – 7.30 (m, 3H), 7.26 (dd,  $J = 6.6, 2.8$  Hz, 2H), 7.20 – 7.11 (m, 1H), 6.92 (dd,  $J = 8.0, 1.6$  Hz, 1H); **<sup>19</sup>F NMR** (376 MHz,  $CDCl_3$ )  $\delta$  -84.9 (s, 2F); **<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ )  $\delta$  157.5 (t,  $J = 3.0$  Hz), 154.4, 153.0, 136.0 (t,  $J = 2.6$  Hz), 135.1 (t,  $J = 7.6$  Hz), 134.1, 133.1, 128.8, 128.6, 128.4, 128.1, 127.3 (t,  $J = 2.4$  Hz), 127.1 (t,  $J = 5.6$  Hz), 124.4, 120.5 (t,  $J = 26.4$  Hz), 120.3, 118.6 (t,  $J = 245.6$  Hz), 116.5; **HRMS** (ESI) :  $m/z$  calcd for  $C_{22}H_{14}ClF_2O_2$   $[M+H]^+$  383.0645, mass found 383.0640.



**3-[(4-bromophenyl)difluoromethyl]-4-phenyl-2H-chromen-2-one (3f):** Light yellow solid (95 mg, 45%); m.p. 108-110 °C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.56 – 7.53 (m, 1H), 7.50 – 7.48 (m, 5H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.34 (dd,  $J = 8.4, 1.2$  Hz, 1H), 7.26 – 7.24 (m, 2H), 7.16 – 7.13 (m, 1H), 6.91 (dd,  $J = 8.2, 1.6$  Hz, 1H); **<sup>19</sup>F NMR** (565 MHz,  $CDCl_3$ )  $\delta$  -85.1 (s, 2F); **<sup>13</sup>C NMR** (150 MHz,  $CDCl_3$ )  $\delta$  157.4 (t,  $J = 3.0$  Hz), 154.4, 153.1, 137.3, 135.7 (t,  $J = 27.8$  Hz), 134.2, 133.0, 131.3, 128.8, 128.6, 128.2, 127.4 (t,  $J = 4.6$  Hz), 124.4, 124.4 (t,  $J = 22.4$  Hz), 120.6 (t,  $J = 25.6$  Hz), 120.4, 118.7 (t,  $J = 246.0$  Hz), 116.5; **HRMS** (ESI) :  $m/z$  calcd for  $C_{22}H_{14}BrF_2O_2$   $[M+H]^+$  427.0140, mass found 427.0147.

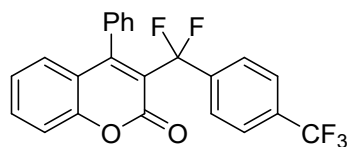


**3-[difluoro(4-fluorophenyl)methyl]-4-phenyl-2H-chromen-2-one (3g):** Light yellow solid (93 mg, 48%); m.p. 95-97°C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.58 – 7.52 (m, 3H), 7.54 – 7.47 (m, 3H), 7.35 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.28 – 7.23 (m, 2H), 7.16-7.13 (m, 1H), 7.04 (t,  $J = 8.6$  Hz, 2H), 6.91 (dd,  $J = 8.2, 1.6$  Hz, 1H); **<sup>19</sup>F NMR** (565 MHz,  $CDCl_3$ )  $\delta$  -83.9(d, 2F), -110.8, -110.9 (m, 1F); **<sup>13</sup>C NMR** (150 MHz,  $CDCl_3$ )  $\delta$  164.3, 162.7, 157.5 (t,  $J = 3.8$  Hz), 154.2 (t,  $J = 2.2$  Hz), 153.1, 134.3, 133.0, 132.7 (td,  $J = 27.0, 3.0$  Hz), 128.8, 128.6, 128.2, 127.8 (td,  $J = 19.6, 9.0, 1.6$  Hz), 127.4 (t,  $J = 3.0$  Hz), 124.4, 120.9 (t,  $J = 25.6$  Hz), 120.5, 118.7 (t,  $J = 246.0$  Hz), 116.5, 115.2, 115.1; **HRMS** (ESI) :  $m/z$  calcd for  $C_{22}H_{13}F_3NaO_2$   $[M+Na]^+$  389.0760, mass found 389.0761.

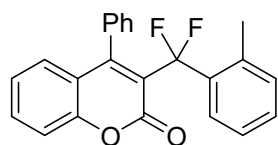


**3-[(4-acetylphenyl)difluoromethyl]-4-phenyl-2H-chromen-2-one (3h):** White solid (99 mg, 51%); m.p. 118-120 °C; **<sup>1</sup>H NMR** (600 MHz,  $CDCl_3$ )  $\delta$  7.88 (d,  $J = 8.2$  Hz, 2H), 7.58 (d,  $J = 8.2$  Hz, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.43 (m, 3H), 7.28 (d,  $J = 8.2$  Hz, 1H), 7.24 – 7.19 (m, 2H), 7.09 (t,  $J = 7.6$  Hz, 1H), 6.86 (dd,  $J = 8.2, 1.6$  Hz, 1H), 2.52 (s, 3H); **<sup>19</sup>F NMR** (376 MHz,  $CDCl_3$ )  $\delta$  -85.9 (s, 2F); **<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ )  $\delta$  197.4, 157.5 (t,  $J = 3.0$  Hz), 154.7 (t,  $J = 2.0$  Hz), 153.1, 140.9 (t,  $J = 27.0$  Hz), 138.1, 134.1, 133.1, 128.9, 128.7, 128.2, 128.1, 127.4 (t,  $J = 3.0$  Hz),

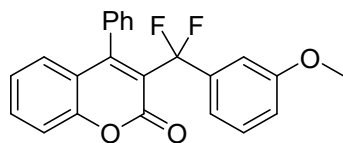
125.9 (t,  $J = 5.0$  Hz), 124.5, 120.4 (t,  $J = 25.6$  Hz), 118.6 (t,  $J = 246.0$  Hz), 116.6, 116.5, 26.7;  
**HRMS** (ESI) :  $m/z$  calcd for  $C_{24}H_{16}F_2NaO_3$   $[M+Na]^+$  413.0960, mass found 413.0963.  
**( $^1H$  NMR of 3h was detected at 600 MHz)**



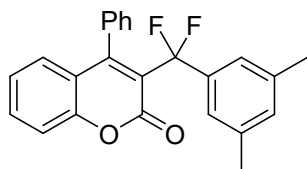
**3-[difluoro(4-(trifluoromethyl)phenyl)methyl]-4-phenyl-2H-chromen-2-one (3i)** : Yellow solid (64 mg, 31%); m.p. 107-109 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.55 (dd,  $J = 7.2, 2.4$  Hz, 2H), 7.52 – 7.48 (m, 3H), 7.43 – 7.33 (m, 3H), 7.30 – 7.23 (m, 2H), 7.06 (dd,  $J = 8.6, 2.4$  Hz, 1H), 6.96 – 6.81 (m, 2H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -62.8 (s, F), -85.8 (s, 2F);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  166.3, 163.8, 157.3 (t,  $J = 3.6$  Hz), 154.3 (d,  $J = 13.0$  Hz), 153.7, 136.5 (t,  $J = 26.6$  Hz), 134.2, 130.9 (d,  $J = 10.0$  Hz), 130.1 (t,  $J = 2.0$  Hz), 128.7, 128.3, 128.2, 127.4 (t,  $J = 2.6$  Hz), 125.6 (t,  $J = 5.6$  Hz), 120.1 (td,  $J = 26.6, 2.8$  Hz), 119.1 (t,  $J = 245.0$  Hz), 117.4 (d,  $J = 3.0$  Hz), 112.6 (d,  $J = 22.0$  Hz), 104.0 (d,  $J = 25.0$  Hz); **HRMS** (ESI) :  $m/z$  calcd for  $C_{23}H_{13}F_5NaO_2$   $[M+Na]^+$  439.0728, mass found 439.0730.



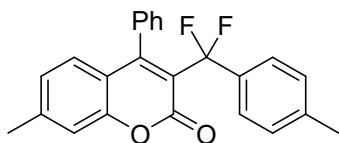
**3-[difluoro(o-tolyl)methyl]-4-phenyl-2H-chromen-2-one (3j)**: White solid (83 mg, 46%); m.p. 143-145 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.57 – 7.54 (m, 1H), 7.46 – 7.40 (m, 4H), 7.37 (dd,  $J = 8.2, 1.0$  Hz, 1H), 7.25 – 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 7.19 – 7.10 (m, 3H), 6.98 (dd,  $J = 8.2, 1.6$  Hz, 1H), 2.36 (s, 3H);  $^{19}F$  NMR (565 MHz,  $CDCl_3$ )  $\delta$  -82.4 (s, 2F);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  157.6 (t,  $J = 3.0$  Hz), 154.6 (t,  $J = 2.2$  Hz), 153.4, 135.7, 134.5 (t,  $J = 24.0$  Hz), 134.3, 132.9, 131.8, 129.8, 128.8, 128.5, 128.1, 127.5 (t,  $J = 2.2$  Hz), 127.0 (t,  $J = 6.8$  Hz), 125.3, 124.3, 121.0 (t,  $J = 10.6$  Hz), 120.4, 120.3 (t,  $J = 244.6$  Hz), 116.6, 20.2 (t,  $J = 2.2$  Hz); **HRMS** (ESI) :  $m/z$  calcd for  $C_{23}H_{17}F_2O_2$   $[M+H]^+$  363.1191, mass found 363.1201.



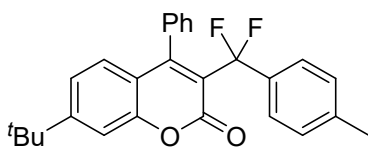
**3-[difluoro(3-methoxyphenyl)methyl]-4-phenyl-2H-chromen-2-one (3k)**: White solid (119 mg, 63%); m.p. 127-129 °C;  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.55 – 7.53 (m, 1H), 7.50 – 7.47 (m, 3H), 7.34 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.29 – 7.26 (m, 3H), 7.15 – 7.13 (m, 1H), 7.12 – 7.11 (m, 2H), 6.93 – 6.90 (m, 2H), 3.83 (s, 3H);  $^{19}F$  NMR (565 MHz,  $CDCl_3$ )  $\delta$  -84.6 (s, 2F);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  159.3, 157.5 (t,  $J = 3.0$  Hz), 154.1 (t,  $J = 1.6$  Hz), 153.1, 138.0 (t,  $J = 26.6$  Hz), 134.3, 132.9, 129.3, 128.8, 128.5, 128.1, 127.5 (t,  $J = 2.6$  Hz), 124.3, 121.0 (t,  $J = 26.0$  Hz), 120.5, 118.9 (t,  $J = 241.5$  Hz), 117.8 (t,  $J = 5.6$  Hz), 116.5, 115.8 (t,  $J = 1.6$  Hz), 111.1 (t,  $J = 5.6$  Hz), 55.3; **HRMS** (ESI) :  $m/z$  calcd for  $C_{23}H_{17}F_2O_3$   $[M+H]^+$  379.1140, mass found 379.1142.  
**( $^{13}C$  NMR of 3k was detected at 400 MHz)**



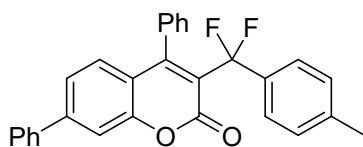
**3-[(3,5-dimethylphenyl)difluoromethyl]-4-phenyl-2H-chromen-2-one (3l):** Light yellow solid (95 mg, 51%); m.p. 91-93 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.60 – 7.56 (m, 1H), 7.52 (dd,  $J = 5.0, 1.6$  Hz, 3H), 7.39 (dd,  $J = 8.2, 1.2$  Hz, 1H), 7.34 – 7.26 (m, 2H), 7.21 – 7.16 (m, 3H), 7.05 (s, 1H), 6.96 (dd,  $J = 8.1, 1.6$  Hz, 1H), 2.35 (s, 6H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.0 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.5 (t,  $J = 3.0$  Hz), 153.9 (t,  $J = 2.0$  Hz), 153.1, 137.8, 136.4 (t,  $J = 8.6$  Hz), 134.3, 132.8, 131.6 (t,  $J = 2.0$  Hz), 128.7, 128.4, 128.0, 127.5 (t,  $J = 2.6$  Hz), 124.3, 123.1 (t,  $J = 5.6$  Hz), 121.2 (t,  $J = 26.0$  Hz), 120.5, 119.2 (t,  $J = 244.6$  Hz), 116.4, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{24}\text{H}_{19}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  377.1348, mass found 377.1356.



**3-[difluoro(*p*-tolyl)methyl]-7-methyl-4-phenyl-2H-chromen-2-one (3n):** White solid (67 mg, 37%); m.p. 138-140 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 – 7.46 (m, 3H), 7.44 (d,  $J = 8.0$  Hz, 2H), 7.26 – 7.24 (m, 2H), 7.21 – 7.13 (m, 3H), 6.95 (dd,  $J = 8.2, 1.6$  Hz, 1H), 6.78 (d,  $J = 8.2$  Hz, 1H), 2.42 (s, 3H), 2.34 (s, 3H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -83.9 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9 (t,  $J = 3.0$  Hz), 153.9 (t,  $J = 1.6$  Hz), 153.1, 144.4, 139.9 (t,  $J = 1.6$  Hz), 134.6, 133.8 (t,  $J = 27.0$  Hz), 128.8, 128.5, 128.3, 128.0, 127.3 (t,  $J = 2.6$  Hz), 125.6, 125.4 (t,  $J = 5.0$  Hz), 119.9 (t,  $J = 26.0$  Hz), 119.3 (t,  $J = 244.0$  Hz), 118.1, 116.5, 21.6, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{24}\text{H}_{19}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  377.1348, mass found 377.1348.

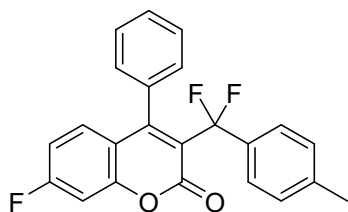


**7-(*tert*-butyl)-3-[difluoro(*p*-tolyl)methyl]-4-phenyl-2H-chromen-2-one (3o):** White solid (110 mg, 53%); m.p. 145-147 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.47 – 7.46 (m, 3H), 7.43 (d,  $J = 8.2$  Hz, 2H), 7.35 (d,  $J = 1.8$  Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25-7.24 (m, 1H), 7.22 – 7.13 (m, 3H), 6.83 (d,  $J = 8.6$  Hz, 1H), 2.34 (s, 3H), 1.32 (s, 9H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -83.8 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9 (t,  $J = 3.0$  Hz), 157.5, 153.8 (t,  $J = 2.0$  Hz), 153.2, 139.9, 134.7, 134.0 (t,  $J = 27.0$  Hz), 128.8, 128.3, 128.3, 128.0, 127.4 (t,  $J = 25.0$  Hz), 125.4 (t,  $J = 5.6$  Hz), 121.9, 120.2 (t,  $J = 26.0$  Hz), 119.3 (t,  $J = 244.6$  Hz), 118.1, 113.2, 35.2, 30.9, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{27}\text{H}_{25}\text{F}_2\text{O}_2$   $[\text{M}+\text{H}]^+$  419.1817, mass found 419.1823.

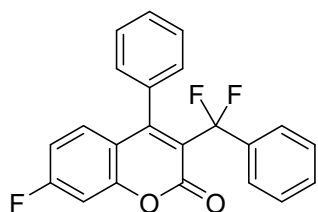


**3-[difluoro(*p*-tolyl)methyl]-4,7-diphenyl-2H-chromen-2-one (3p):** White solid (100 mg, 46%); m.p. 157-159 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.59 (d,  $J = 7.8$  Hz, 2H), 7.56 (s, 1H), 7.49 (t,  $J = 6.6$  Hz, 4H), 7.46 (d,  $J = 8.2$  Hz, 3H), 7.42 (d,  $J = 7.2$  Hz, 1H), 7.37 (d,  $J = 8.6$  Hz, 1H), 7.30 (d,  $J = 6.6$  Hz, 2H), 7.18 (d,  $J = 7.8$  Hz, 2H), 6.96 (d,  $J = 8.6$  Hz, 1H), 2.35 (s, 3H);  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.0 (s, 2F);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7 (t,  $J = 3.0$  Hz), 153.7, 153.5, 145.9, 140.0, 138.7, 134.5, 133.9 (t,  $J = 27.0$  Hz), 129.2, 129.1, 128.8, 128.8, 128.5, 128.1, 127.5, 127.2, 125.5 (t,  $J = 5.2$  Hz),

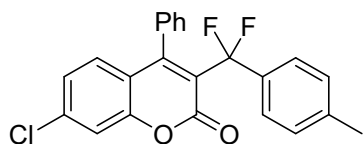
123.1, 120.8 (t,  $J = 26.2$  Hz), 119.5, 119.3 (t,  $J = 244.6$  Hz), 114.5, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $C_{29}H_{20}F_2NaO_2 [M+Na]^+$  461.1324, mass found 461.1318.



**3-[difluoro(*p*-tolyl)methyl]-7-fluoro-4-phenyl-2*H*-chromen-2-one (3q)**: White solid (102 mg, 54%); m.p. 134-136 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51 – 7.47 (m, 3H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.28 – 7.26 (m, 1H), 7.25 – 7.24 (m, 1H), 7.18 (d,  $J = 8.0$  Hz, 2H), 7.06 (dd,  $J = 8.6, 2.2$  Hz, 1H), 6.95 – 6.82 (m, 2H), 2.35 (s, 3H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -84.1(s, 2F), -103.4(s, F);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  164.9(d,  $J = 254.0$  Hz), 157.2 (t,  $J = 3.6$  Hz), 154.2 (d,  $J = 13.0$  Hz), 153.4, 140.1 (t,  $J = 2.0$  Hz), 134.1, 133.5 (t,  $J = 26.4$  Hz), 130.8 (d,  $J = 10.0$  Hz), 128.8, 128.6, 128.2, 127.3 (t,  $J = 2.6$  Hz), 125.4 (t,  $J = 5.6$  Hz), 120.1 (td,  $J = 26.6, 3.0$  Hz), 119.1 (t,  $J = 245.0$  Hz), 117.3 (d,  $J = 2.0$  Hz), 112.5 (d,  $J = 23.0$  Hz), 104.0 (d,  $J = 26.0$  Hz), 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $C_{23}H_{16}F_3O_2 [M+H]^+$  381.1097, mass found 381.1099.



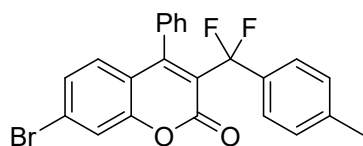
**3-[difluoro(phenyl)methyl]-7-fluoro-4-phenyl-2*H*-chromen-2-one (3r)**: White solid (130 mg, 71%); m.p. 124-126 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.71 – 7.61 (m, 4H), 7.61 – 7.52 (m, 1H), 7.53 – 7.50 (m, 3H), 7.35 (d,  $J = 8.2$  Hz, 1H), 7.33 – 7.25 (m, 2H), 7.16 (t,  $J = 7.6$  Hz, 1H), 6.93 (dd,  $J = 8.2, 1.6$ Hz, 1H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -84.8 (s, 2F), -103.4 (s, F);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  157.6 (t,  $J = 3.6$  Hz), 154.9 (t,  $J = 2.0$  Hz), 153.2, 140.3 (t,  $J = 27.6$  Hz), 134.1, 133.3, 132.0 (q,  $J = 33.0$  Hz), 129.0, 128.8, 128.3, 127.4 (t,  $J = 2.6$  Hz), 126.2 (t,  $J = 5.6$  Hz), 125.3 (q,  $J = 4.0$  Hz), 124.6, 120.4, 120.4 (t,  $J = 26.0$ Hz), 118.5 (t,  $J = 246.0$ Hz), 116.6; **HRMS** (ESI) :  $m/z$  calcd for  $C_{22}H_{14}F_3O_2 [M+H]^+$  367.0940, mass found 367.0940.



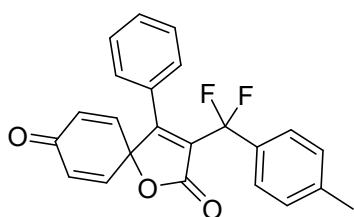
**7-chloro-3-[difluoro(*p*-tolyl)methyl]-4-phenyl-2*H*-chromen-2-one (3s)**: Light yellow solid (85 mg, 43%); m.p. 161-163 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51 – 7.47 (m, 3H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.35 (d,  $J = 2.0$  Hz, 1H), 7.26 – 7.23 (m, 2H), 7.18 (d,  $J = 8.0$  Hz, 2H), 7.10 (dd,  $J = 8.6, 2.0$  Hz, 1H), 6.83 (d,  $J = 8.6$  Hz, 1H), 2.35 (s, 3H);  $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -84.3 (s, 2F);  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  156.9 (t,  $J = 3.0$  Hz), 153.3, 153.2, 140.1, 138.8, 134.0, 133.6 (t,  $J = 26.2$  Hz), 129.7, 128.8, 128.6, 128.2, 127.3 (t,  $J = 2.2$  Hz), 125.4 (t,  $J = 5.2$  Hz), 124.9, 121.2 (t,  $J = 26.2$  Hz), 119.2, 119.1 (t,  $J = 244.6$  Hz), 116.6, 21.2; **HRMS** (ESI) :  $m/z$  calcd for  $C_{23}H_{15}ClF_2NaO_2 [M+Na]^+$  419.0621, mass found 419.0626.

( $^1H$  NMR and  $^{19}F$  NMR: 400Hz,  $^{13}C$  NMR: 600Hz)





**7-bromo-3-[difluoro(*p*-tolyl)methyl]-4-phenyl-2H-chromen-2-one (3t):** Yellow solid (99 mg, 45%); m.p. 148-150 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (d,  $J = 2.0$  Hz, 1H), 7.50 (d,  $J = 1.6$  Hz, 1H), 7.49 (d,  $J = 2.2$  Hz, 2H), 7.43 (d,  $J = 8.0$  Hz, 2H), 7.27 – 7.23 (m, 3H), 7.18 (d,  $J = 8.0$  Hz, 2H), 6.76 (d,  $J = 8.6$  Hz, 1H), 2.35 (s, 3H);  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -84.3 (s, 2F);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  156.9 (t,  $J = 3.0$  Hz), 153.2 (t,  $J = 2.0$  Hz), 153.1, 140.1 (t,  $J = 1.6$  Hz), 133.9, 133.4 (t,  $J = 26.6$  Hz), 129.8, 128.8, 128.6, 128.2, 127.8, 127.3 (t,  $J = 3.0$  Hz), 127.0, 125.4 (t,  $J = 5.6$  Hz), 121.3 (t,  $J = 27.0$  Hz), 119.9, 119.6, 119.1 (t,  $J = 245.0$  Hz), 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{23}\text{H}_{15}\text{BrF}_2\text{NaO}_2$   $[\text{M}+\text{Na}]^+$  463.0116, mass found 463.0119.

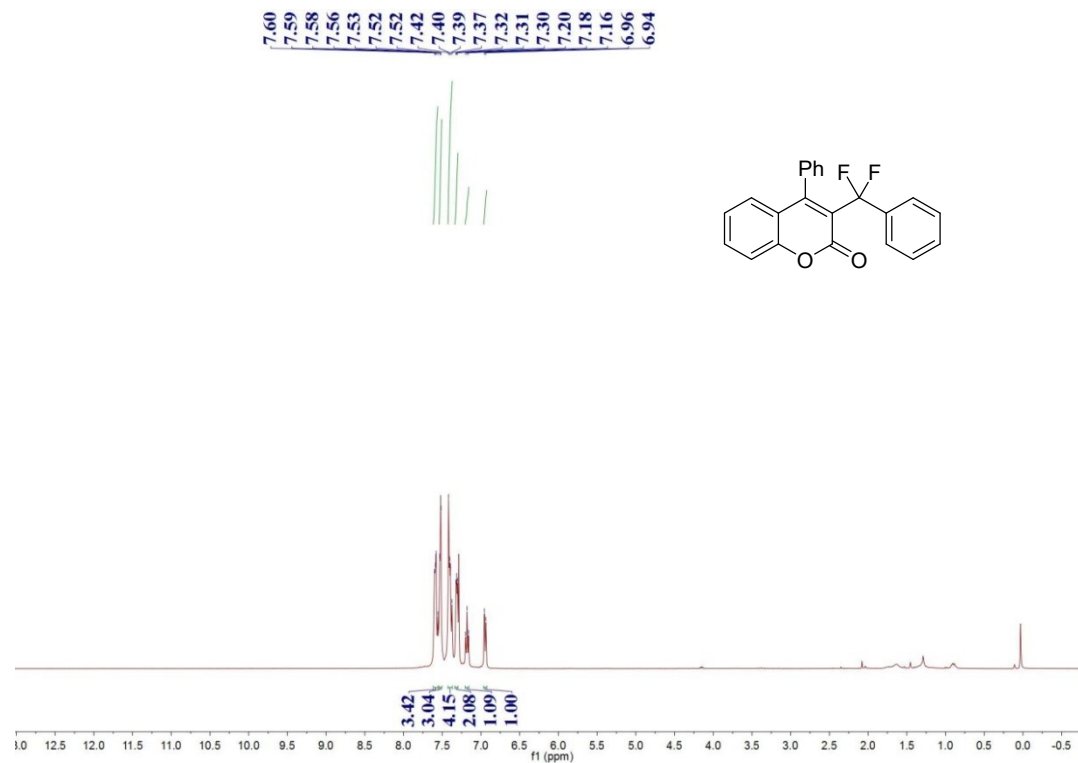


**3-[difluoro(*p*-tolyl)methyl]-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (3v):** White solid (80 mg, 40%); m.p. 231-233 °C;  $^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.2$  Hz, 3H), 7.38 – 7.35 (m, 2H), 7.23 (d,  $J = 7.8$  Hz, 2H), 7.09 (d,  $J = 7.0$  Hz, 2H), 6.64 (d,  $J = 10.2$  Hz, 2H), 6.34 (d,  $J = 10.2$  Hz, 2H), 2.40 (s, 3H);  $^{19}\text{F NMR}$  (565 MHz,  $\text{CDCl}_3$ )  $\delta$  -90.8 (s, 2F);  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  183.2, 166.7 (t,  $J = 3.0$  Hz), 164.3 (t,  $J = 2.2$  Hz), 141.1, 140.9, 132.4, 132.0 (t,  $J = 27.0$  Hz), 130.1, 129.3, 128.4, 128.1, 127.9, 127.4, 125.2 (t,  $J = 6.0$  Hz), 117.0 (t,  $J = 243.8$  Hz), 82.3, 21.3; **HRMS** (ESI) :  $m/z$  calcd for  $\text{C}_{23}\text{H}_{16}\text{F}_2\text{NaO}_3$   $[\text{M}+\text{Na}]^+$  401.0960, mass found 401.0960.

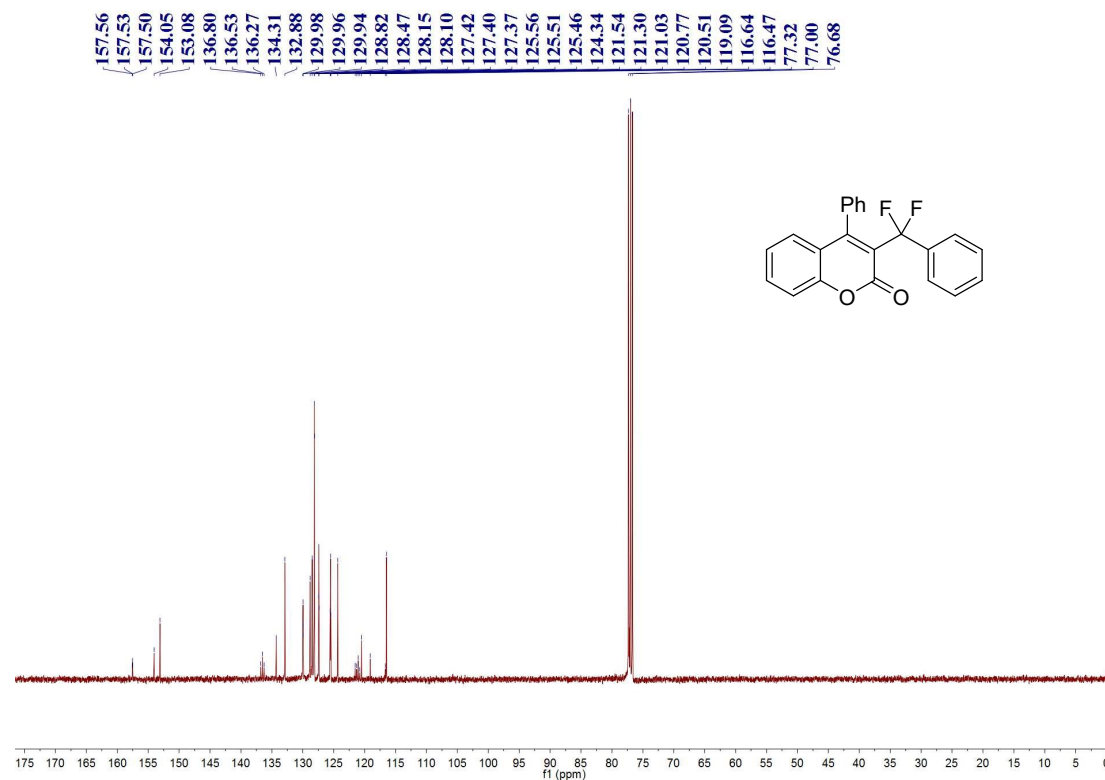
#### 4. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of compounds 3

##### 3-(difluoro(phenyl)methyl)-4-phenyl-2H-chromen-2-one (3a):

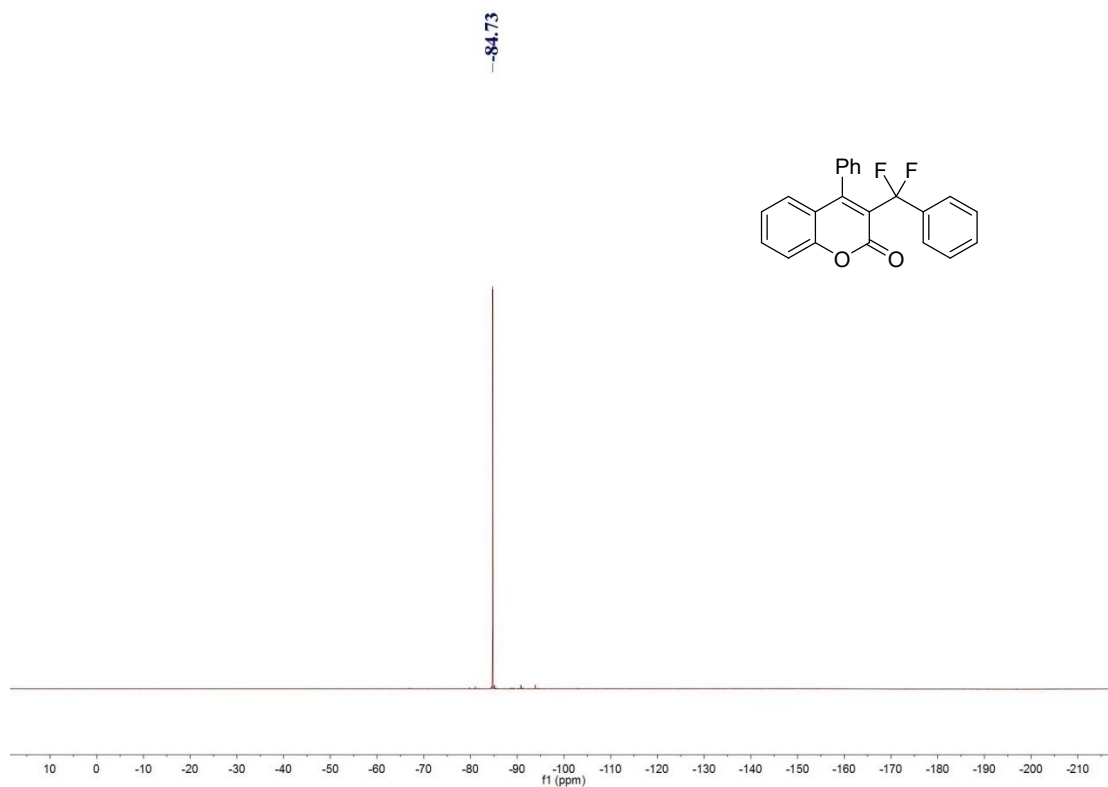
$^1\text{H}$  NMR of 3a in  $\text{CDCl}_3$



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

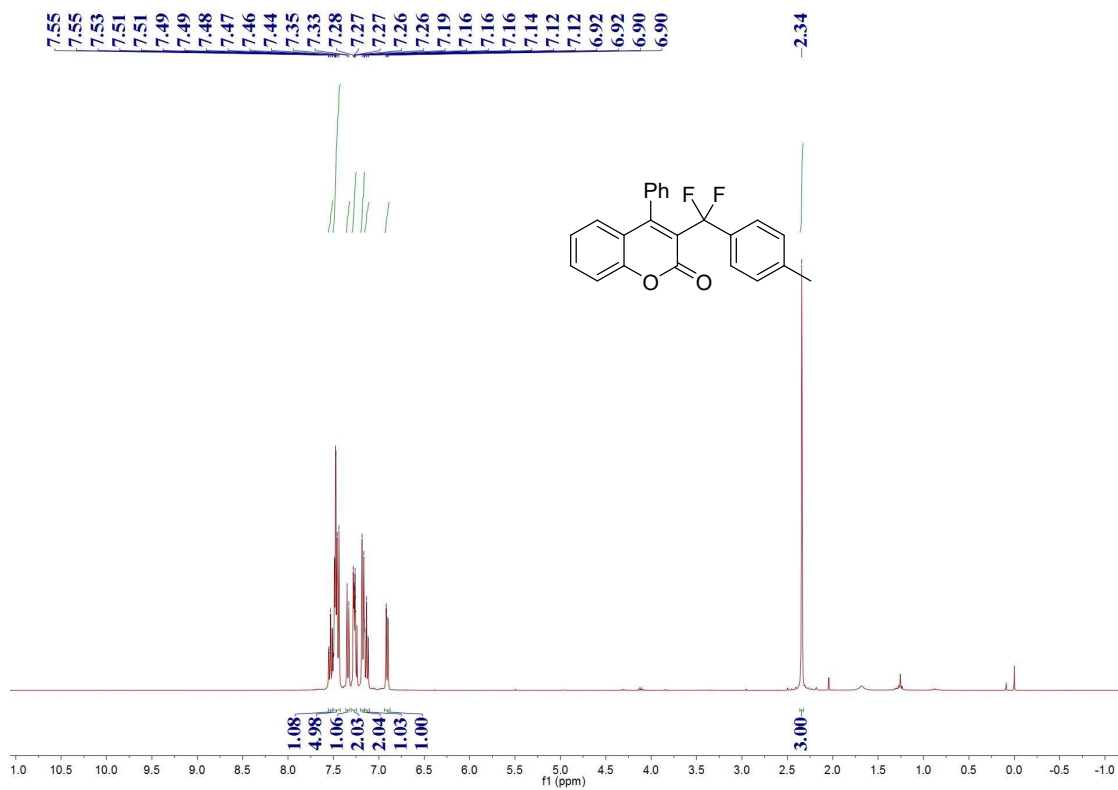


$^{19}\text{F}$  NMR of **3a** in  $\text{CDCl}_3$

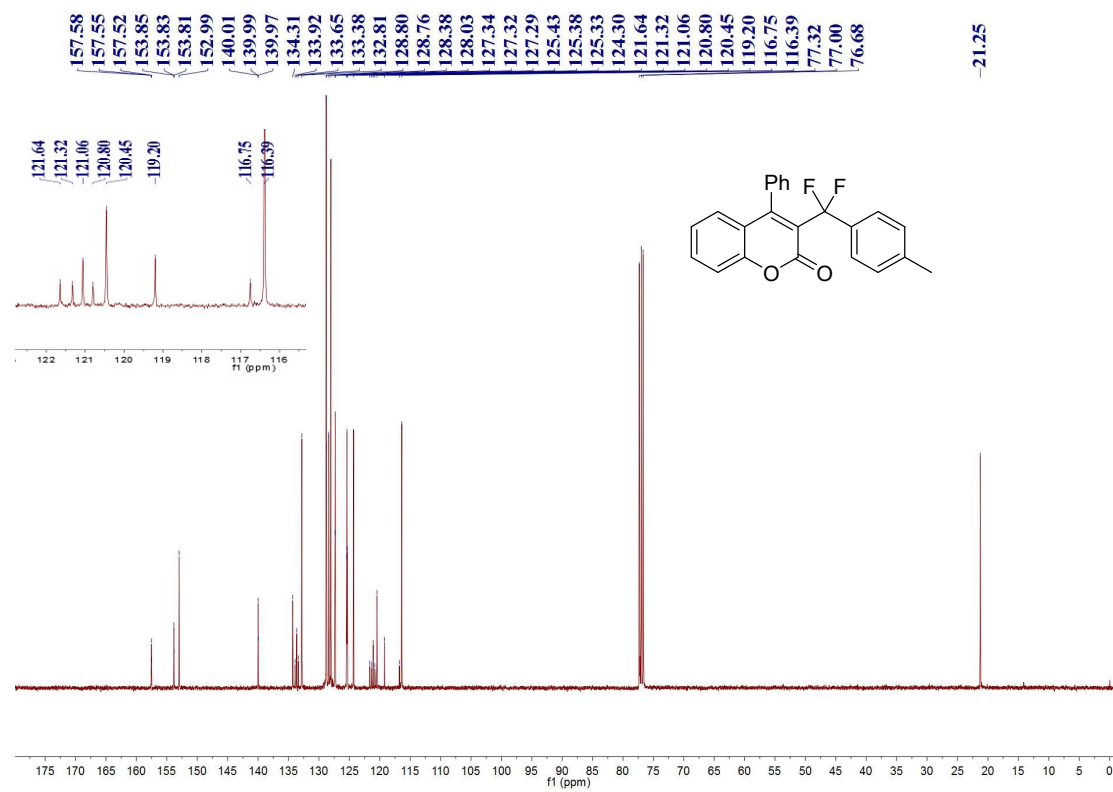


**3-(difluoro(p-tolyl)methyl)-4-phenyl-2H-chromen-2-one (3b):**

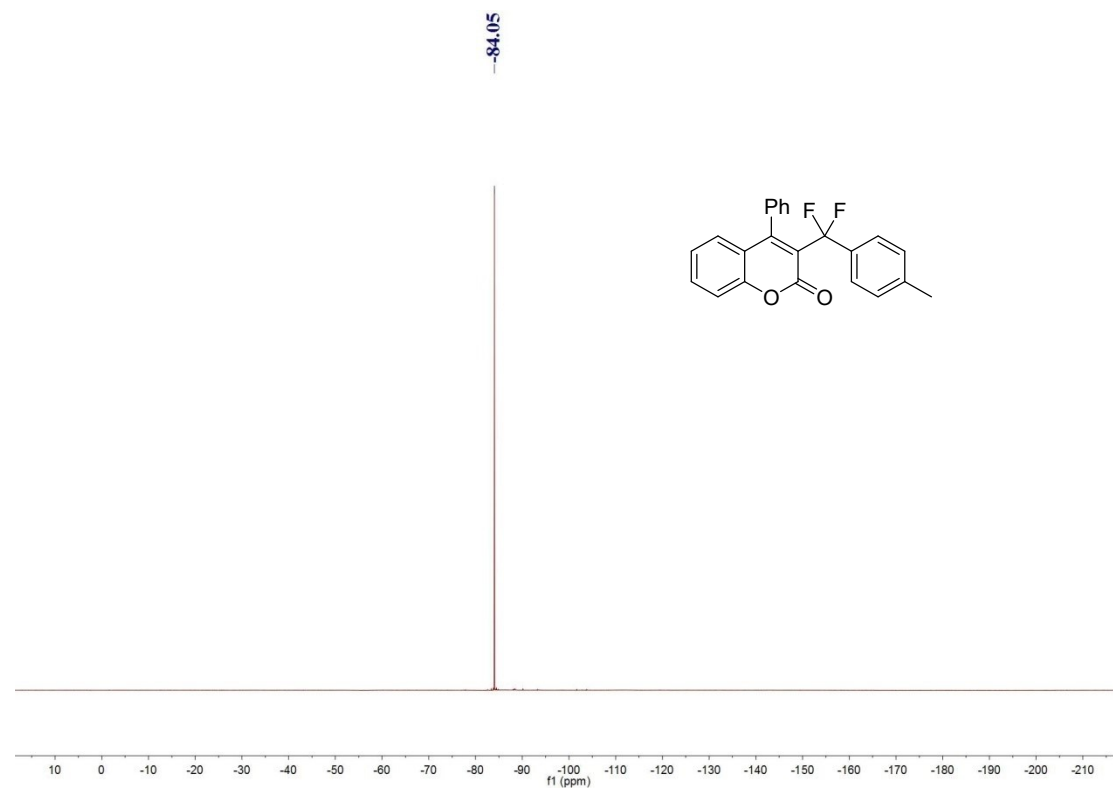
$^1\text{H}$  NMR of **3b** in  $\text{CDCl}_3$



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

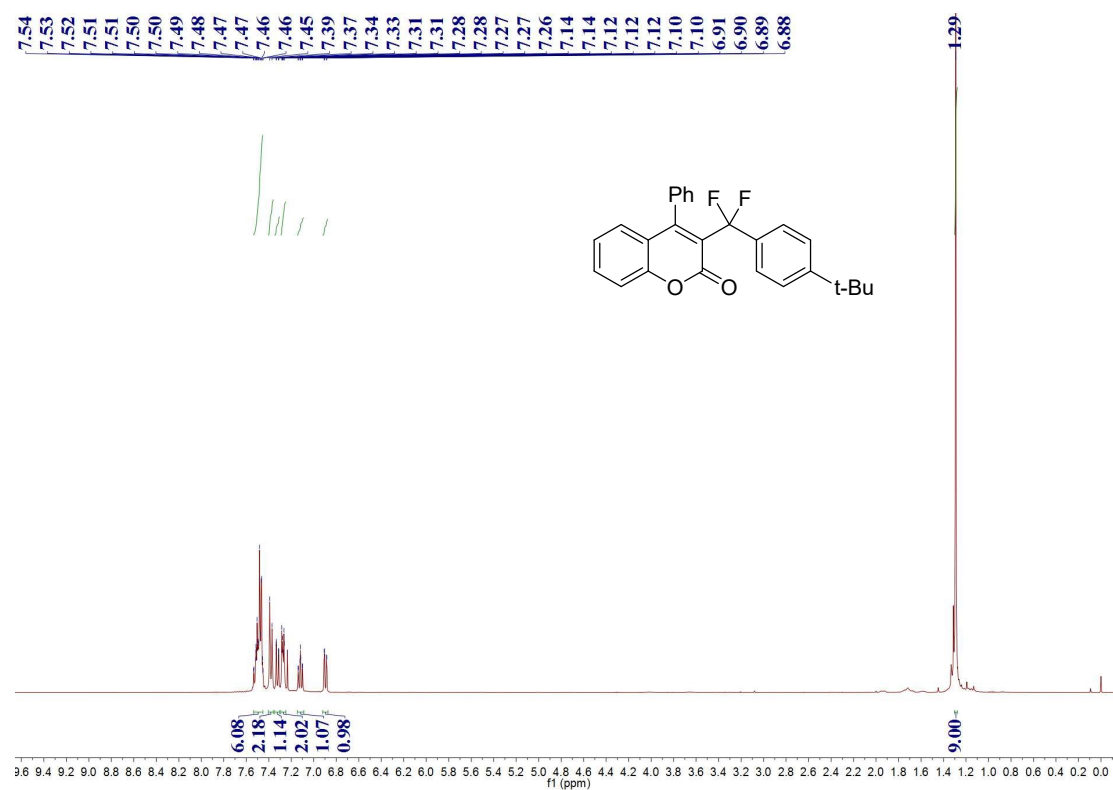


$^{19}\text{F}$  NMR of **3b** in  $\text{CDCl}_3$

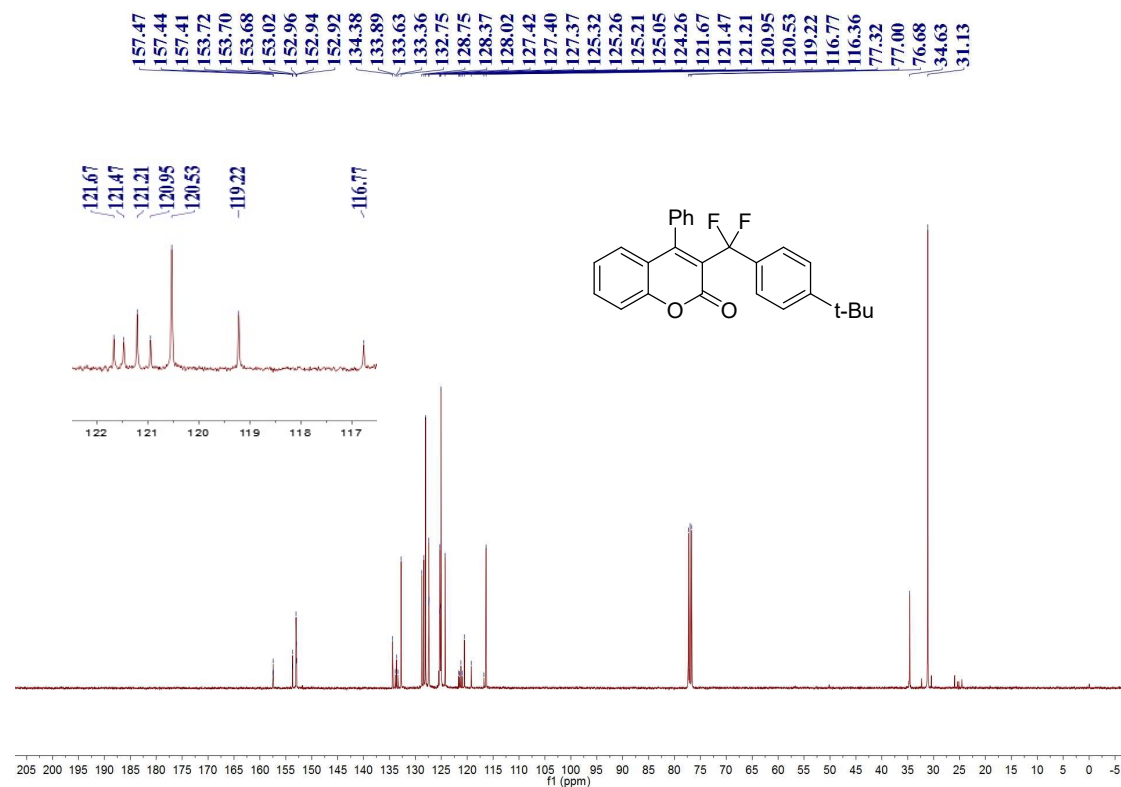


### 3-((4-(tert-butyl)phenyl)difluoromethyl)-4-phenyl-2H-chromen-2-one (3c):

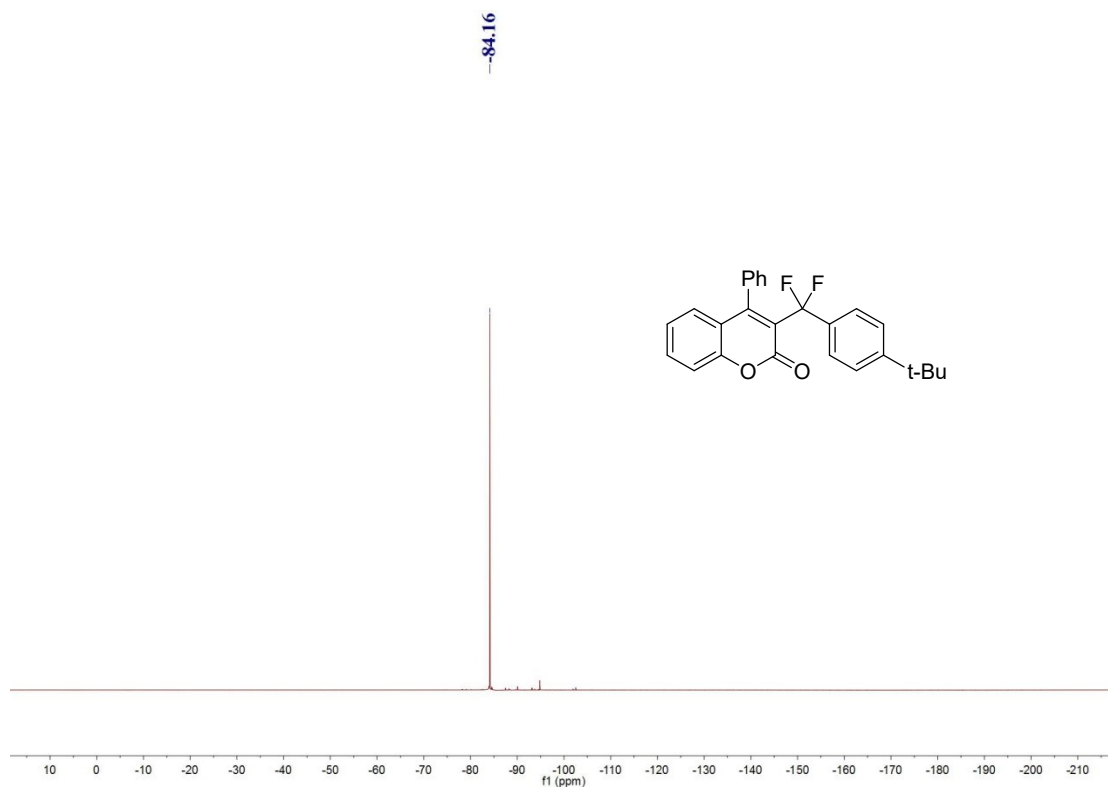
$^1\text{H}$  NMR of **3c** in  $\text{CDCl}_3$



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

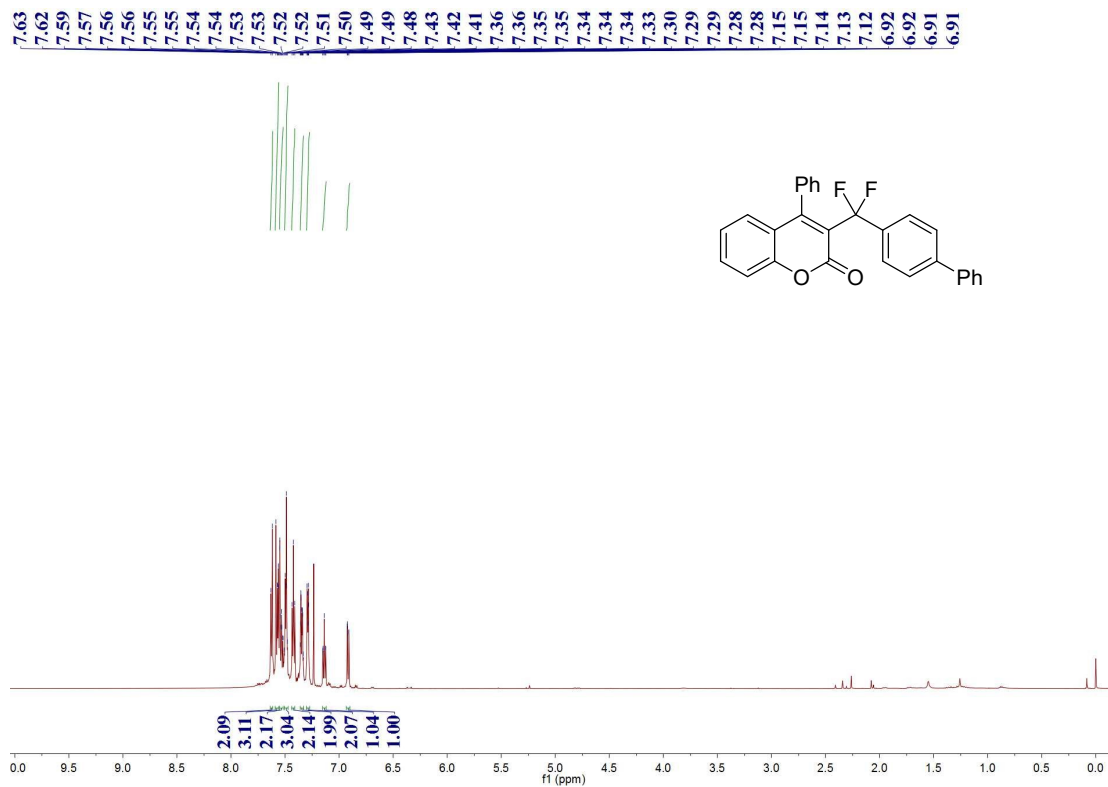


$^{19}\text{F}$  NMR of **3c** in  $\text{CDCl}_3$

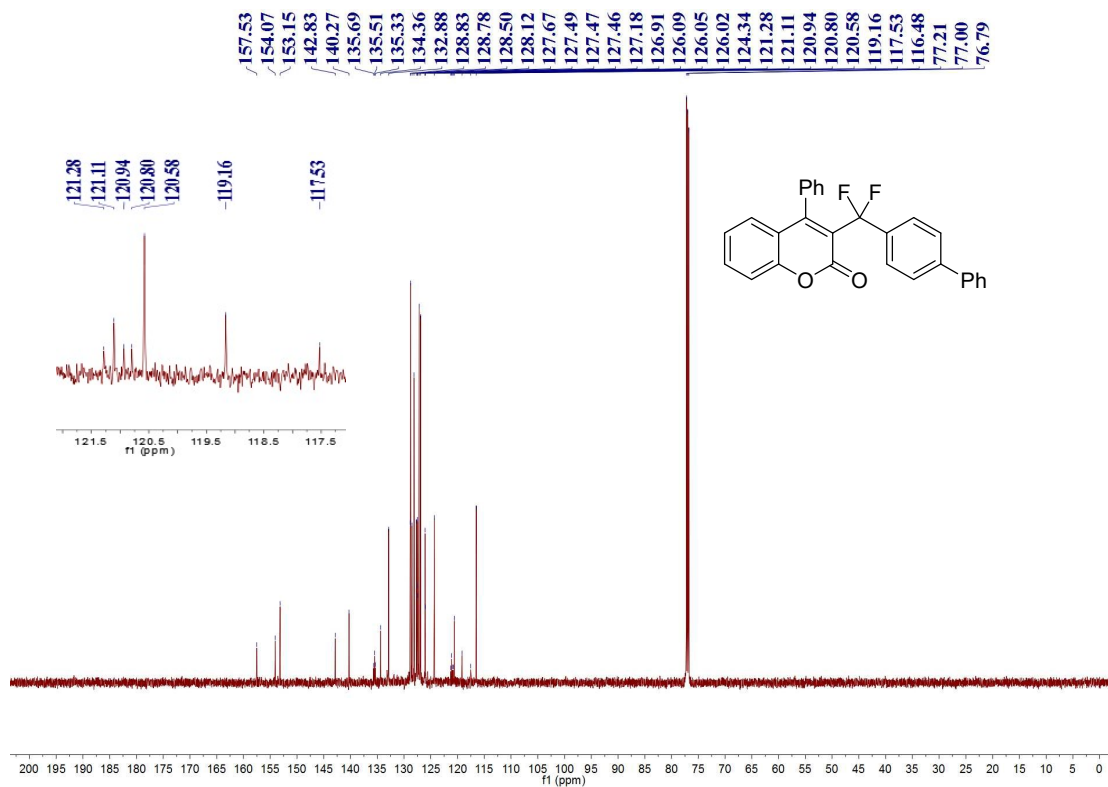


**3-([1,1'-biphenyl]-4-yl)-2,2-difluoro-4-phenyl-2H-chromen-2-one (3d):**

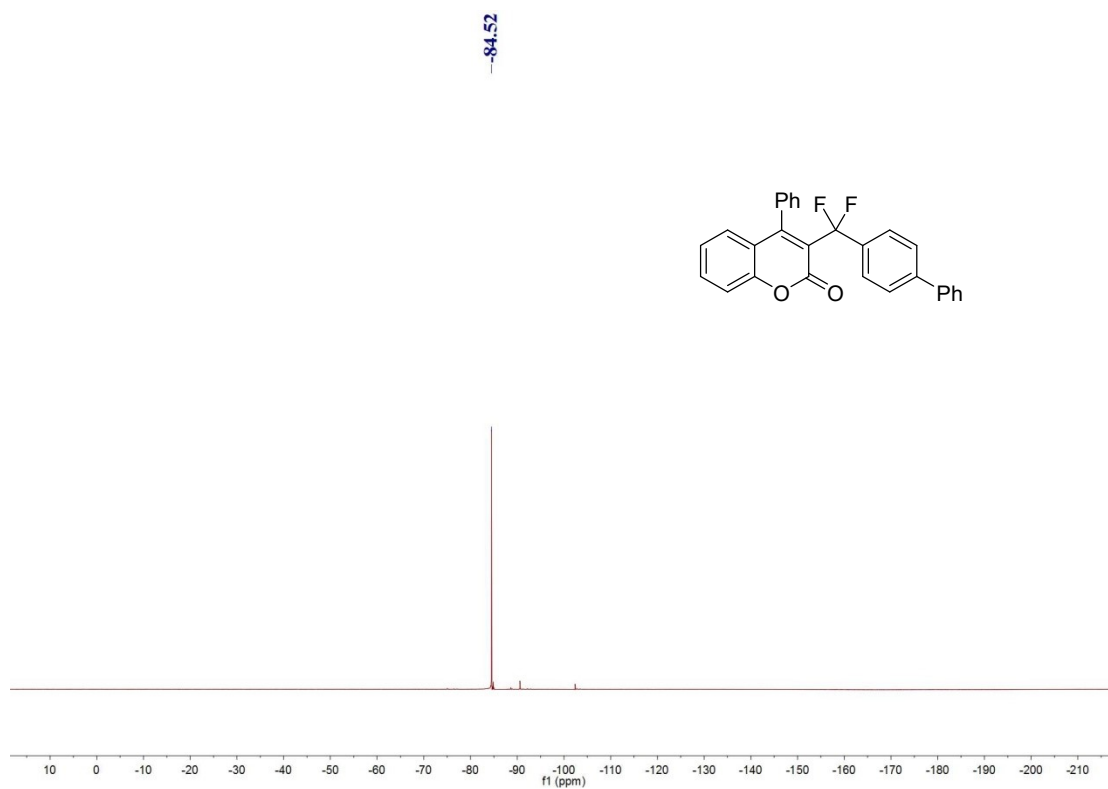
$^1\text{H}$  NMR of **3d** in  $\text{CDCl}_3$



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

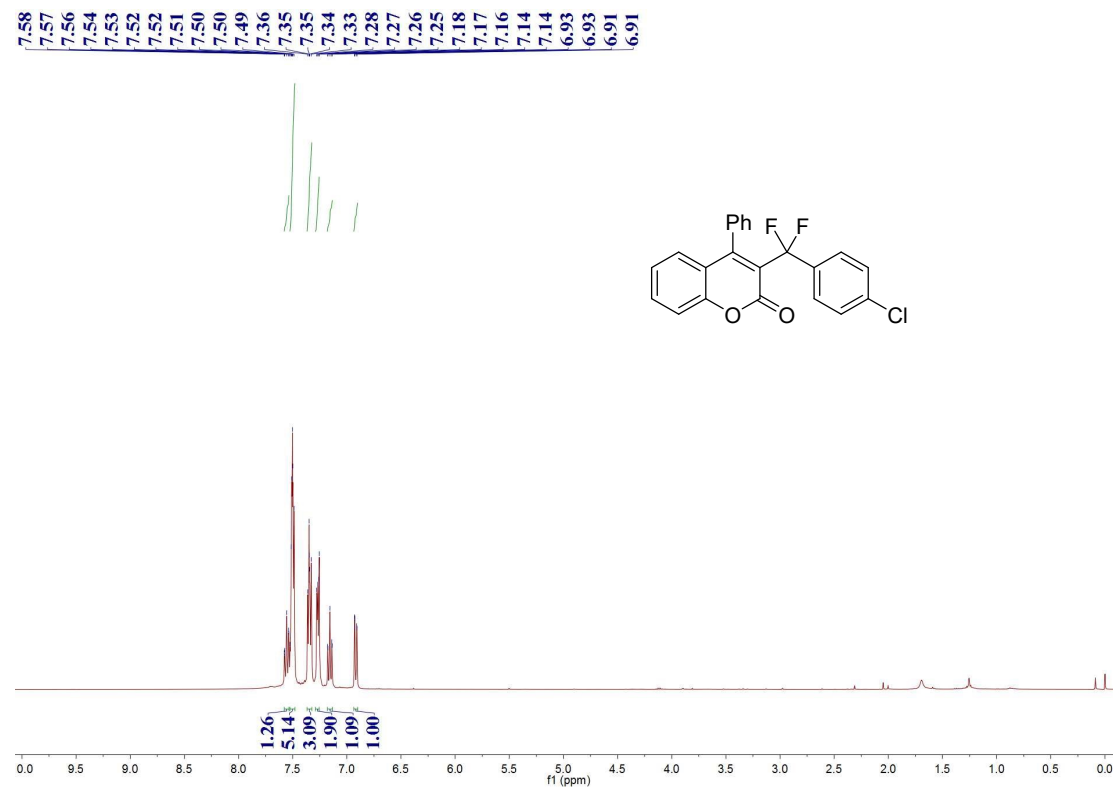


$^{19}\text{F}$  NMR of **3d** in  $\text{CDCl}_3$

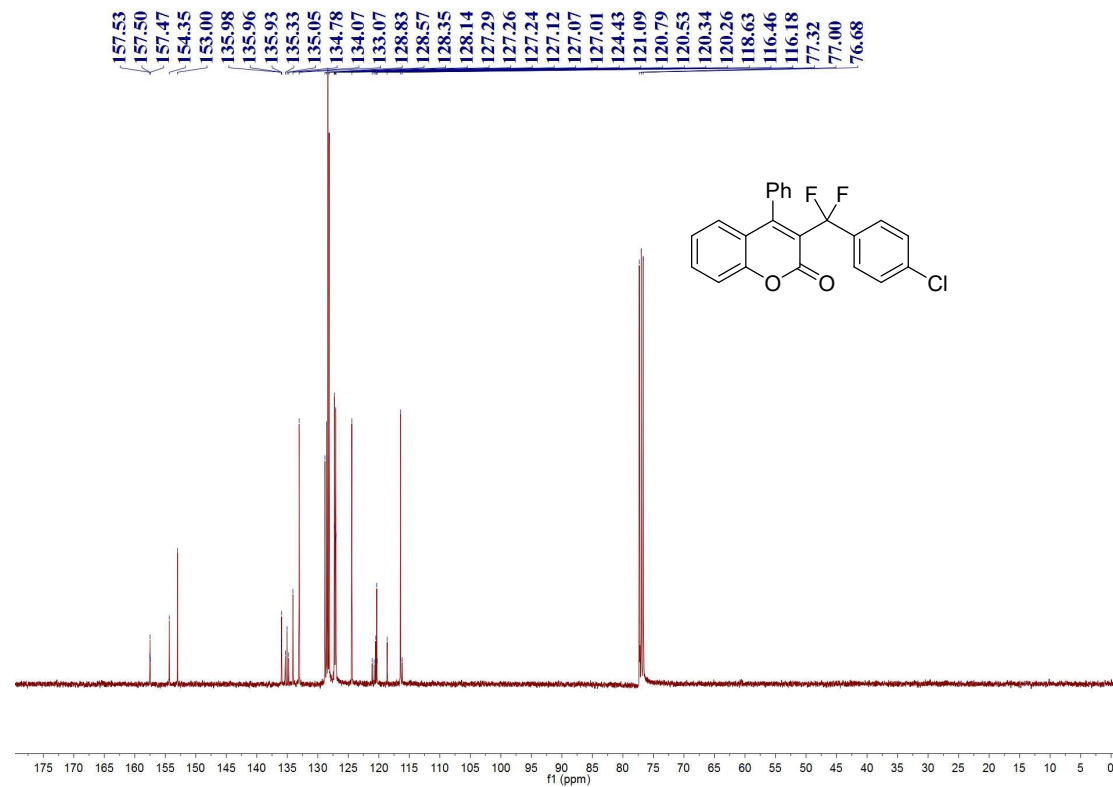


**3-((4-chlorophenyl)difluoromethyl)-4-phenyl-2H-chromen-2-one (3e):**

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

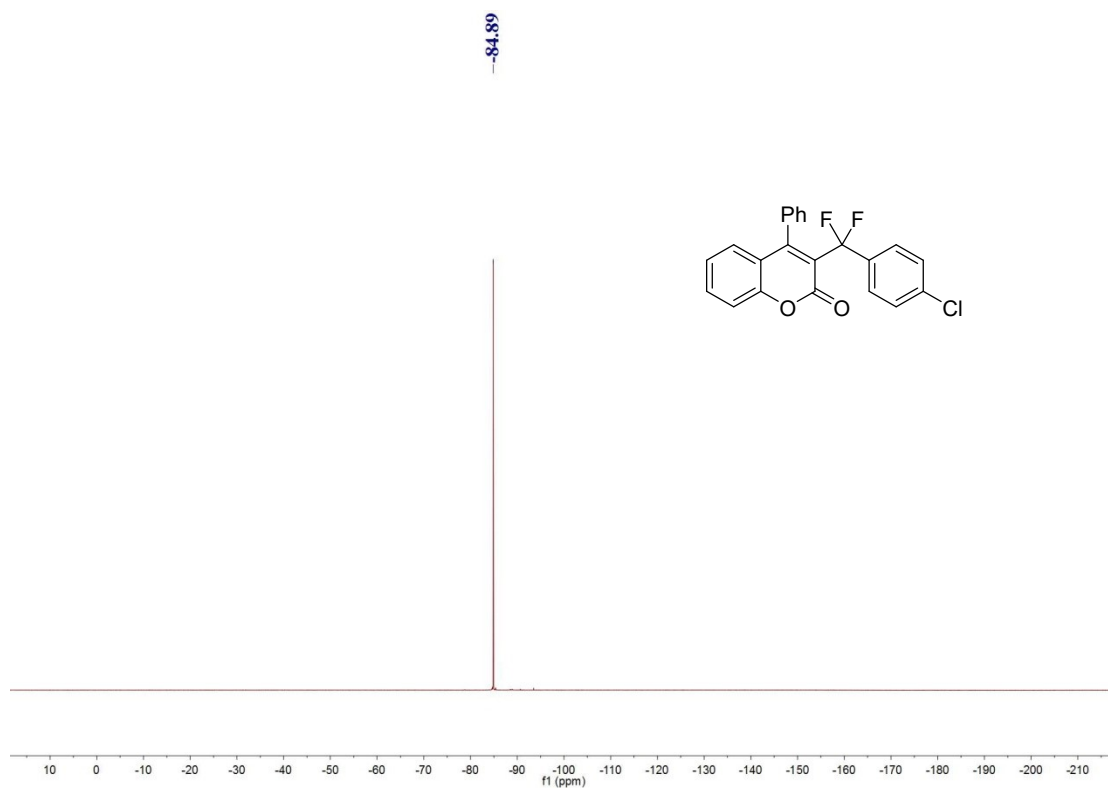


<sup>13</sup>C NMR of **3e** in CDCl<sub>3</sub>



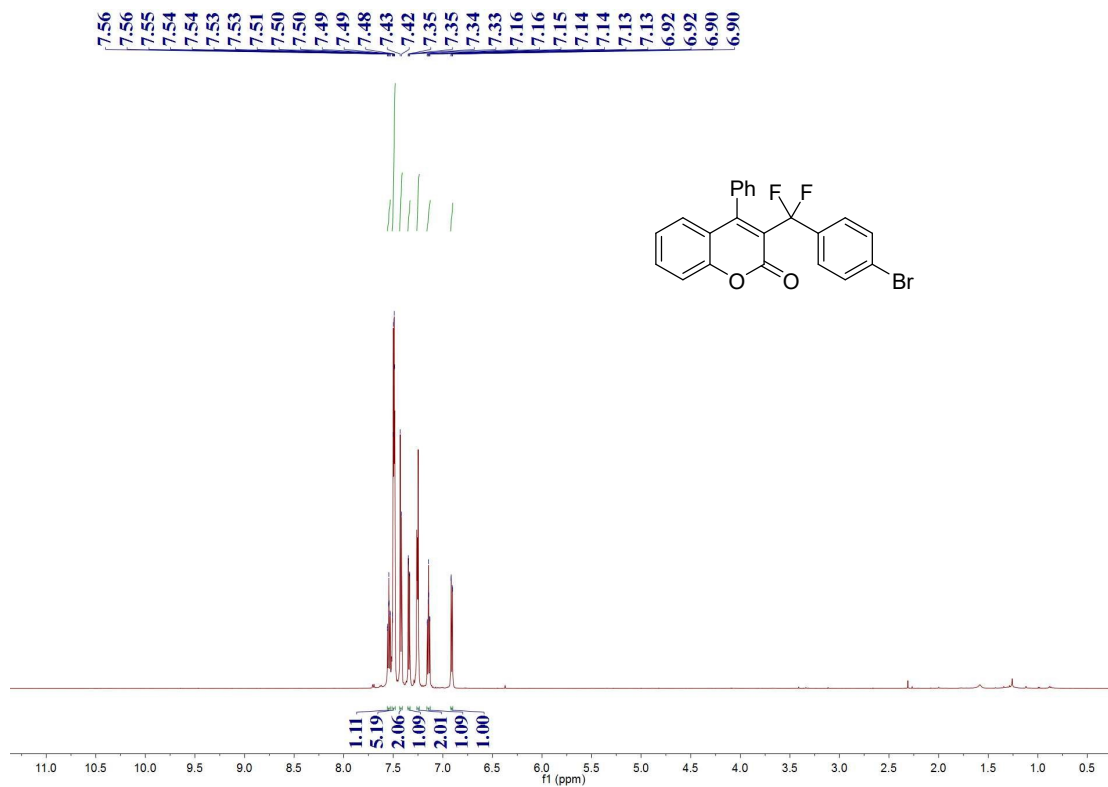


$^{19}\text{F}$  NMR of **3e** in  $\text{CDCl}_3$

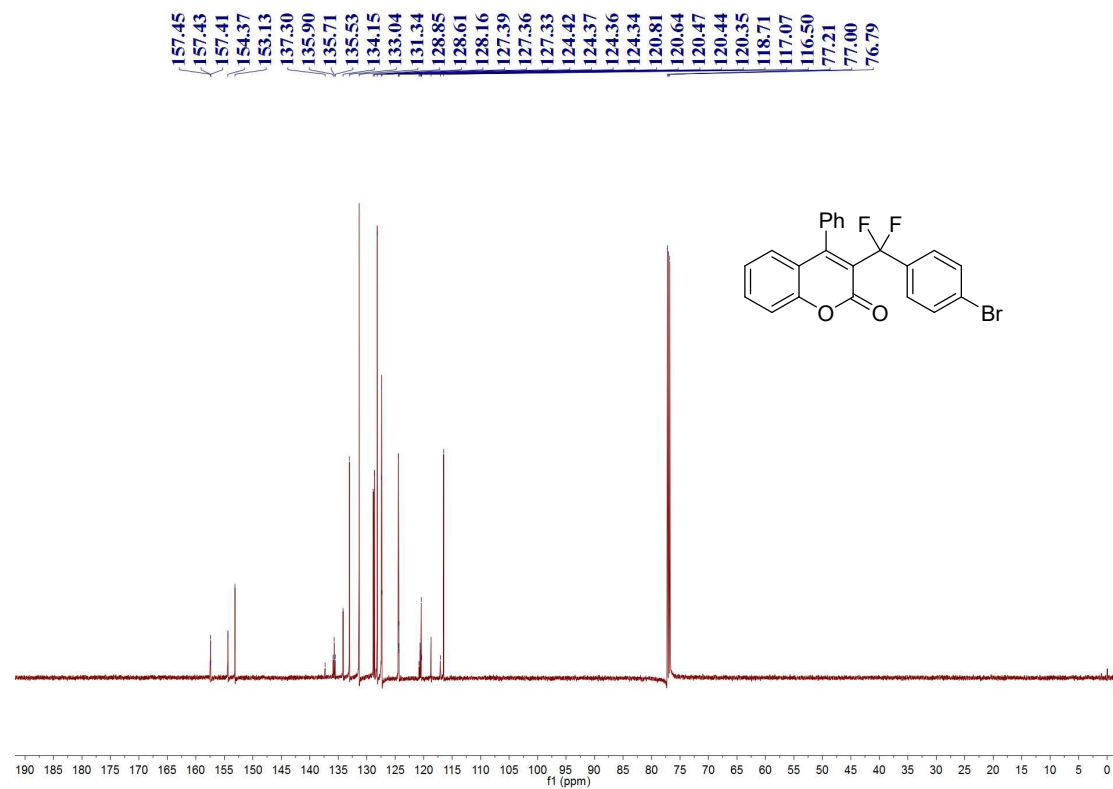


**3-((4-bromophenyl)difluoromethyl)-4-phenyl-2H-chromen-2-one (3f)**

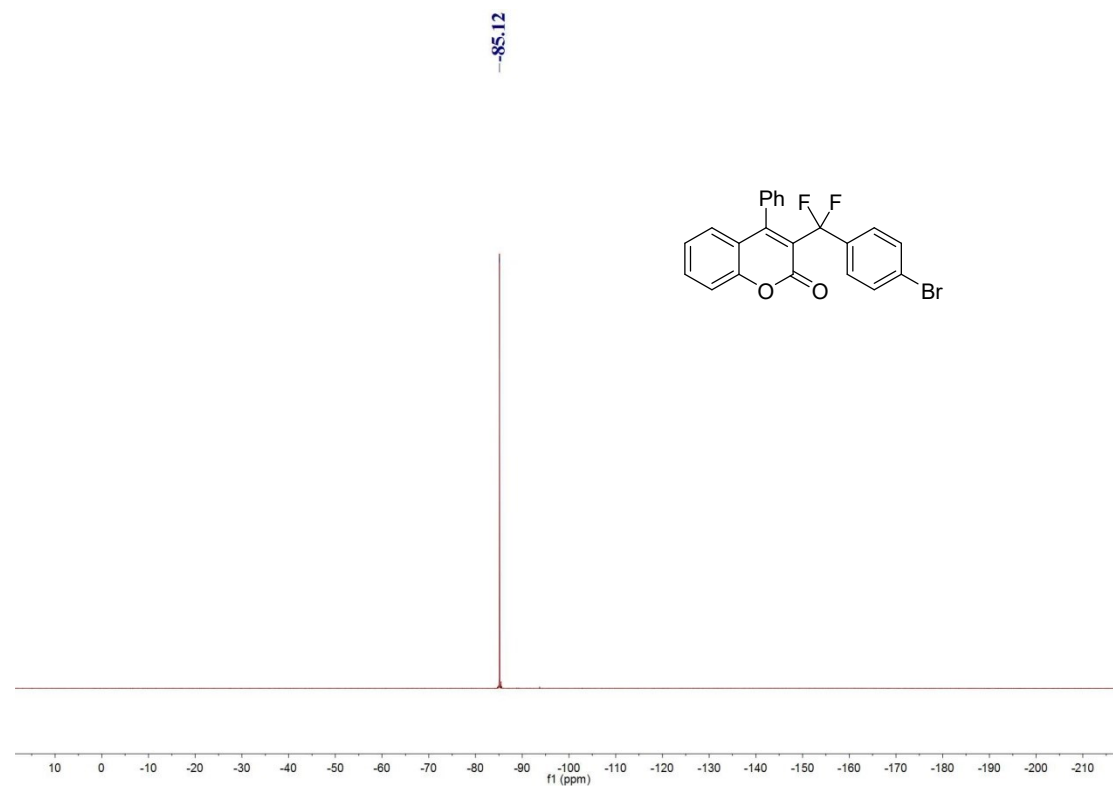
$^1\text{H}$  NMR of **3f** in  $\text{CDCl}_3$



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

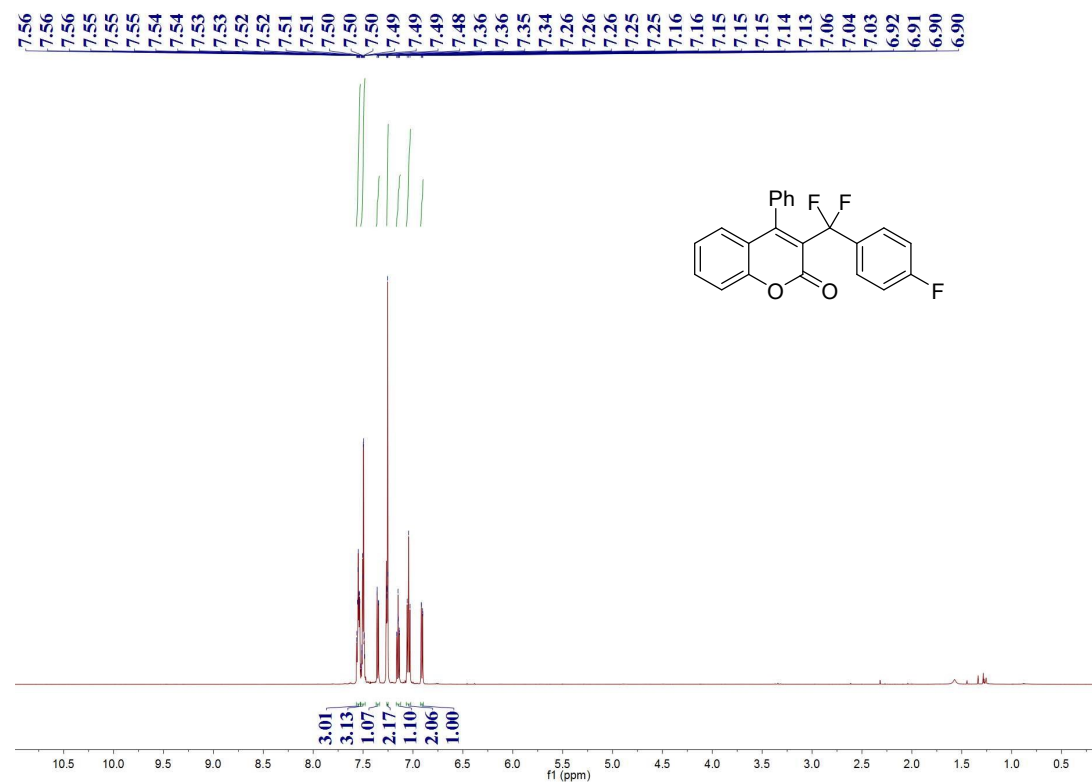


$^{19}\text{F}$  NMR of **3f** in  $\text{CDCl}_3$

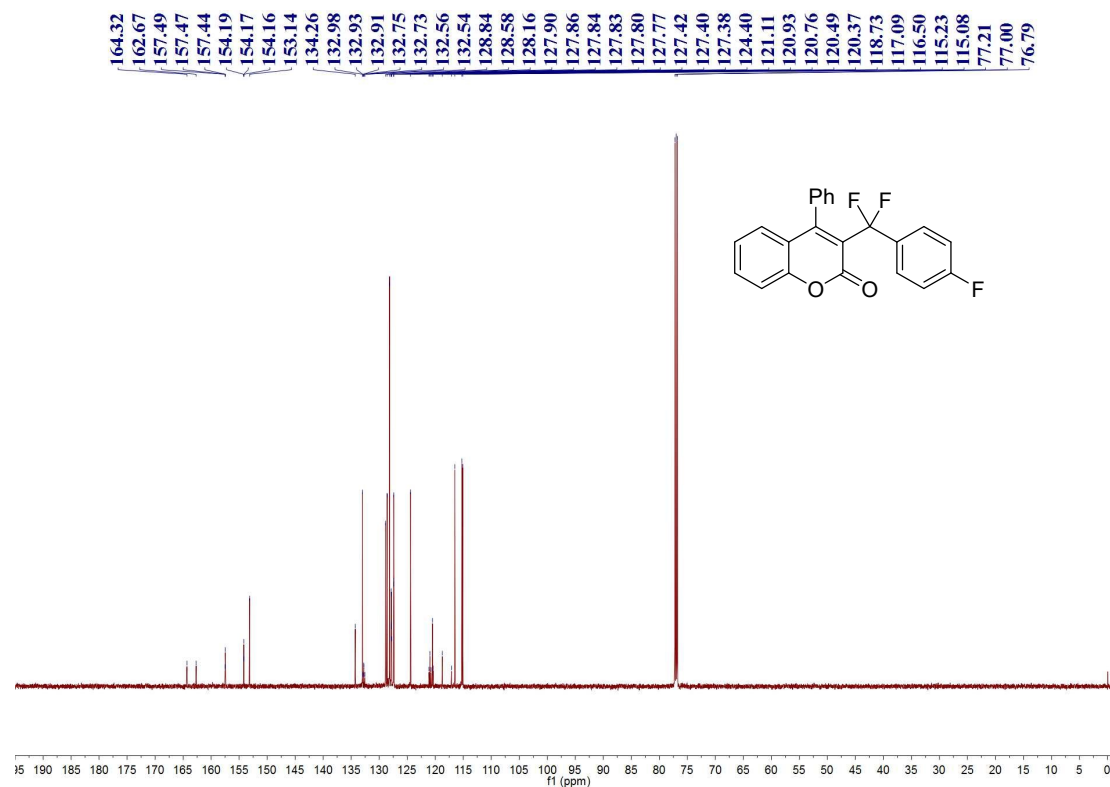


### 3-(difluoro(4-fluorophenyl)methyl)-4-phenyl-2H-chromen-2-one (3g):

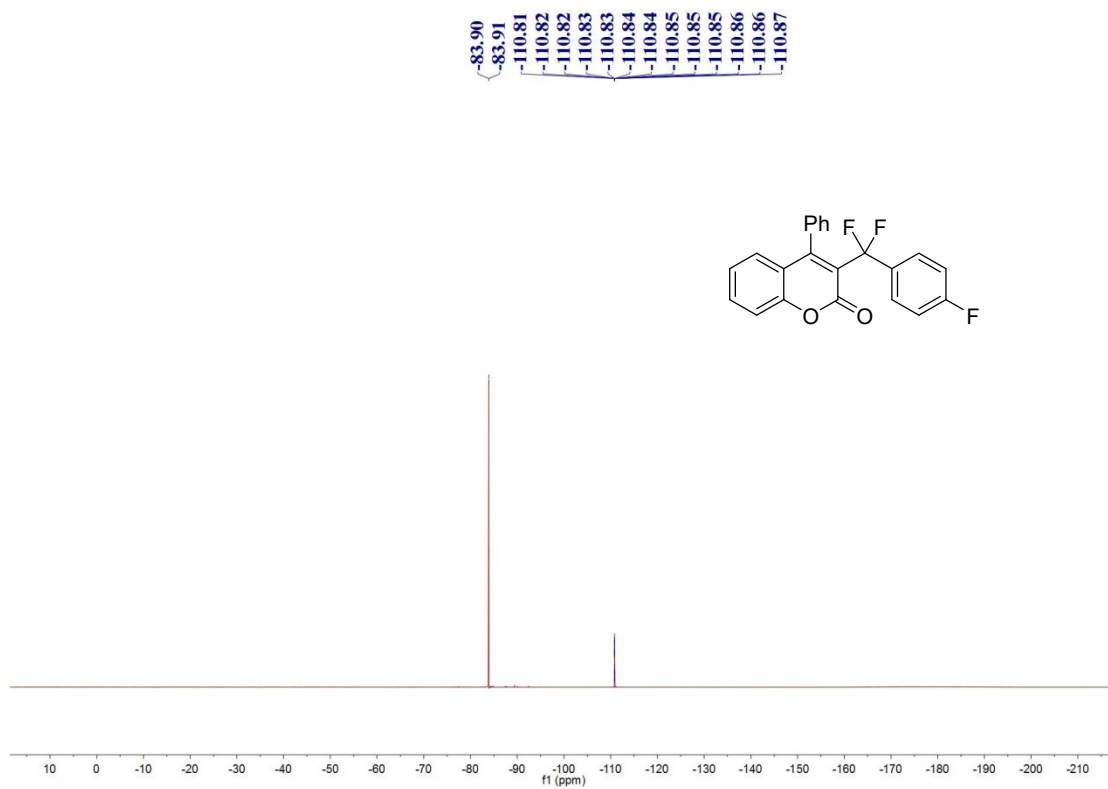
<sup>1</sup>H NMR of 3g in CDCl<sub>3</sub>



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

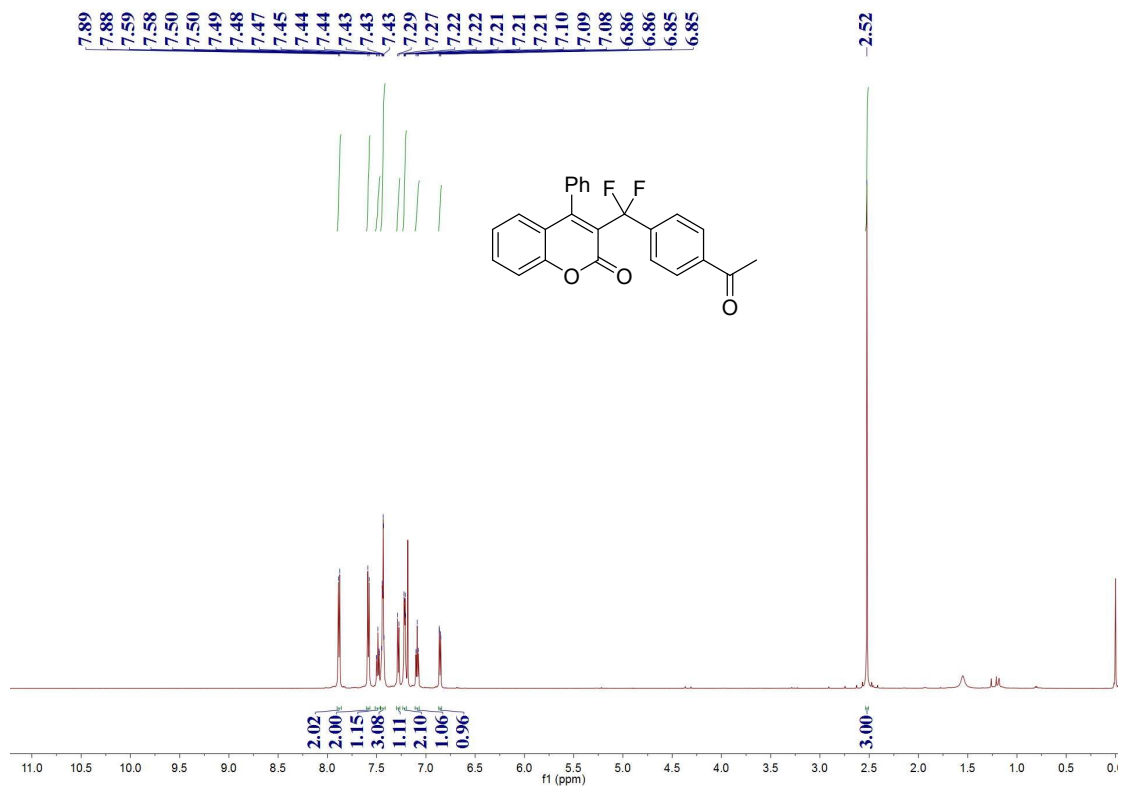


$^{19}\text{F}$  NMR of **3g** in  $\text{CDCl}_3$

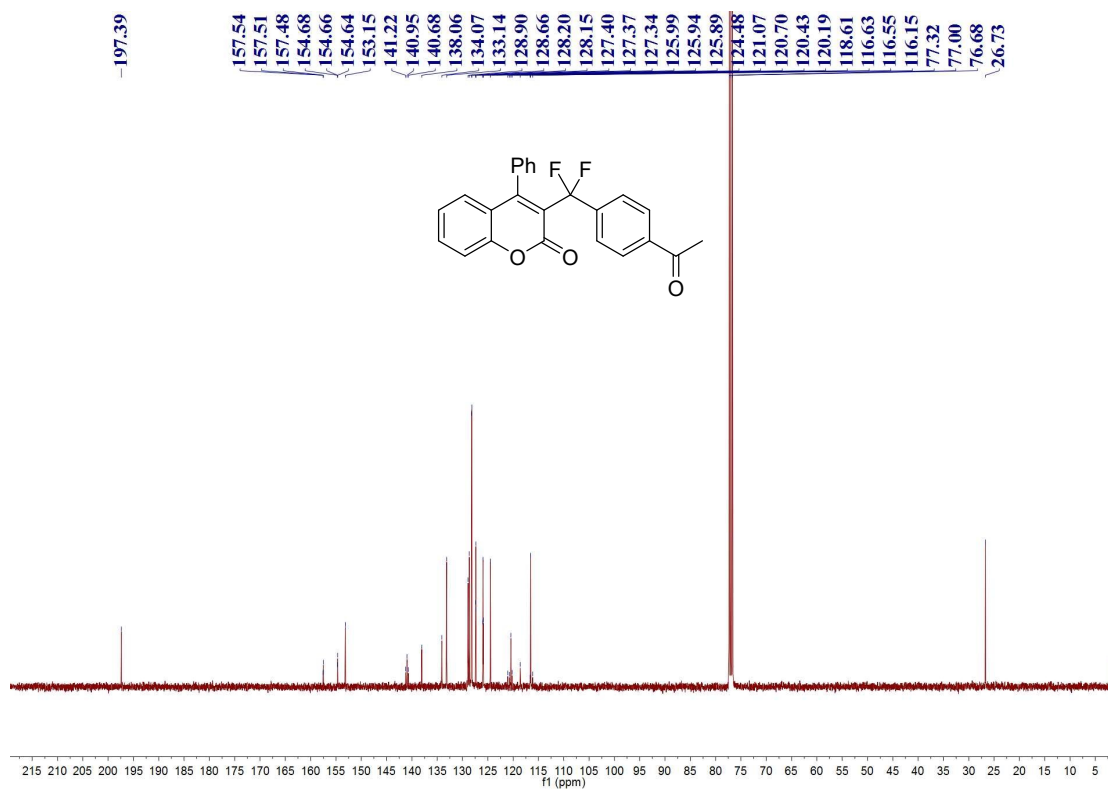


**3-((4-acetylphenyl)difluoromethyl)-4-phenyl-2H-chromen-2-one (3h)**

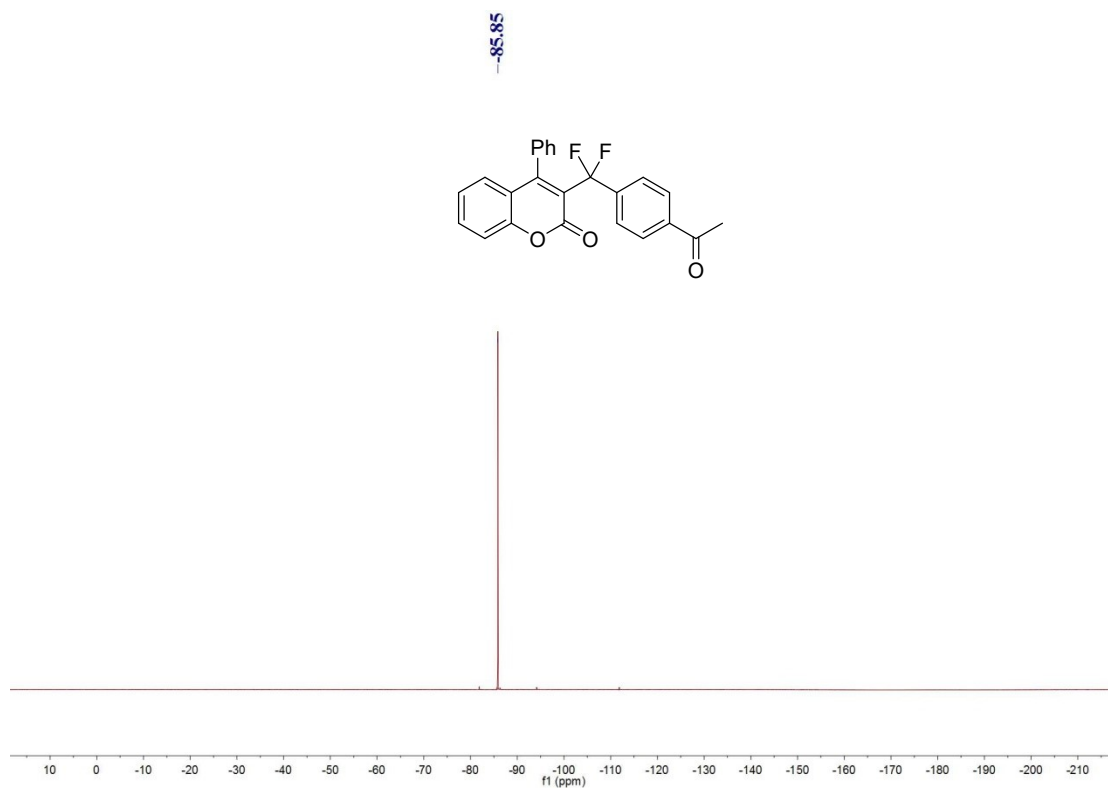
$^1\text{H}$  NMR of **3h** in  $\text{CDCl}_3$



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

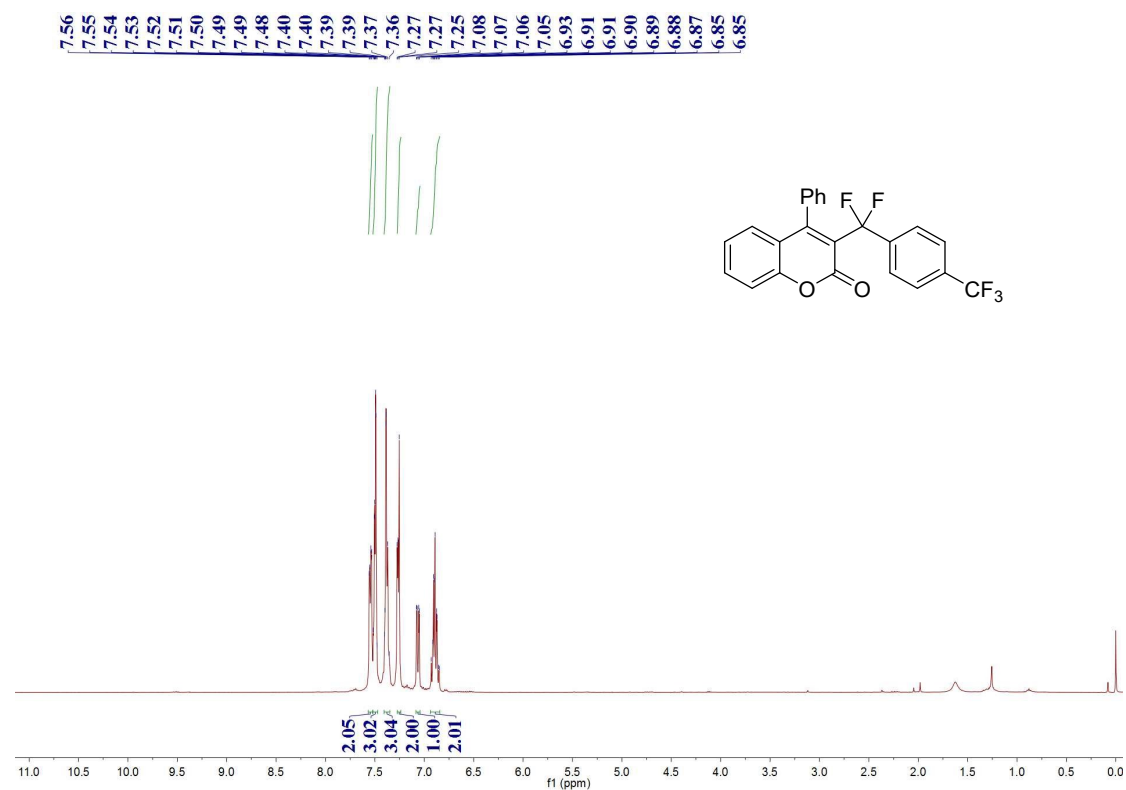


<sup>19</sup>F NMR of **3h** in CDCl<sub>3</sub>

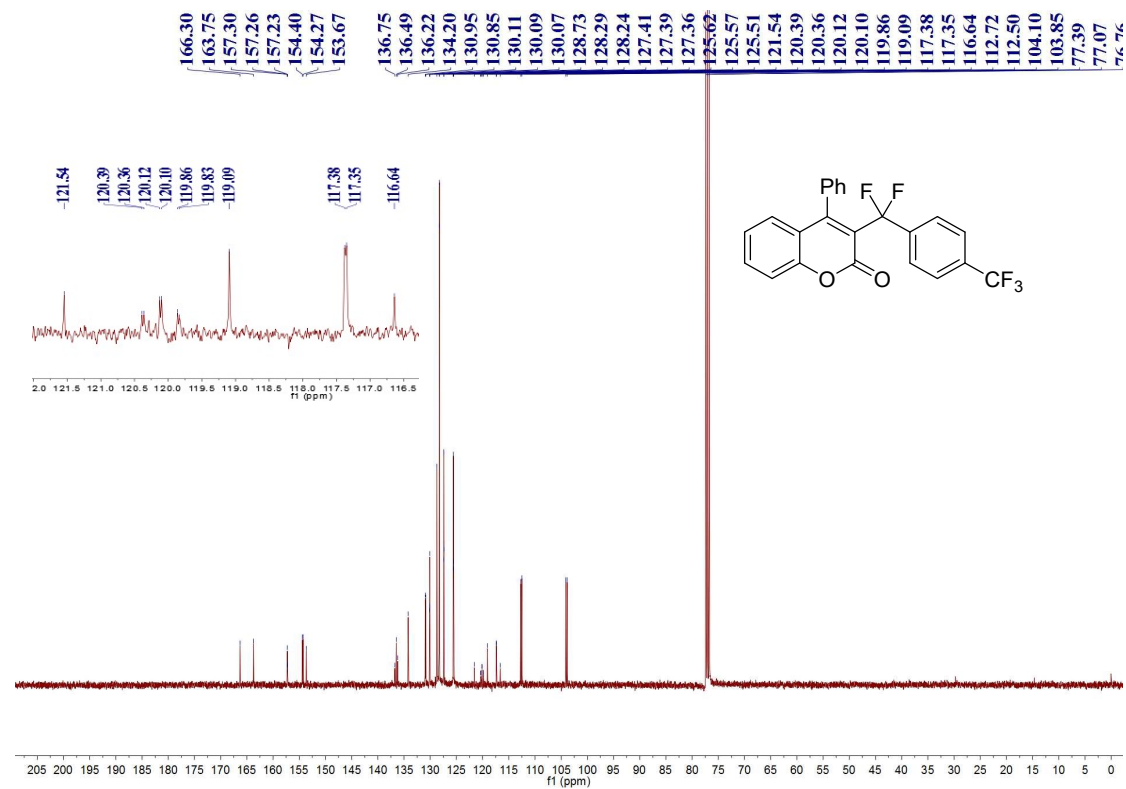


### 3-(difluoro(4-(trifluoromethyl)phenyl)methyl)-4-phenyl-2H-chromen-2-one (3i)

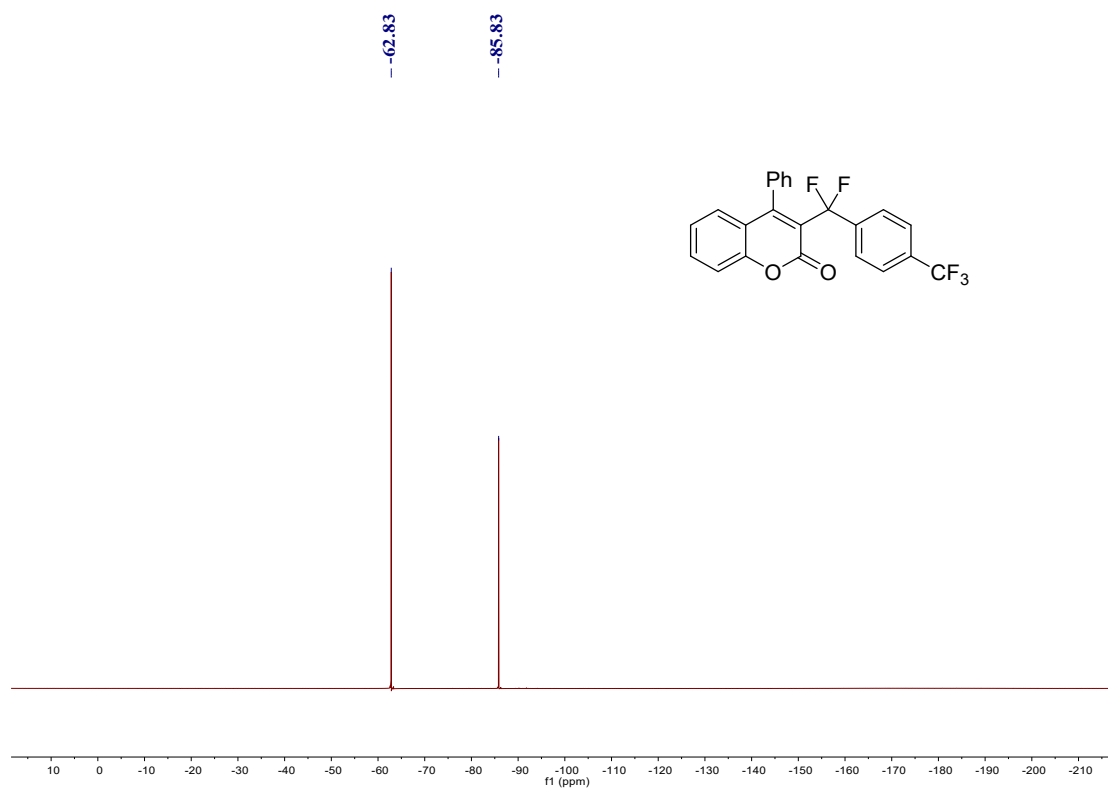
<sup>1</sup>H NMR of **3i** in CDCl<sub>3</sub>



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

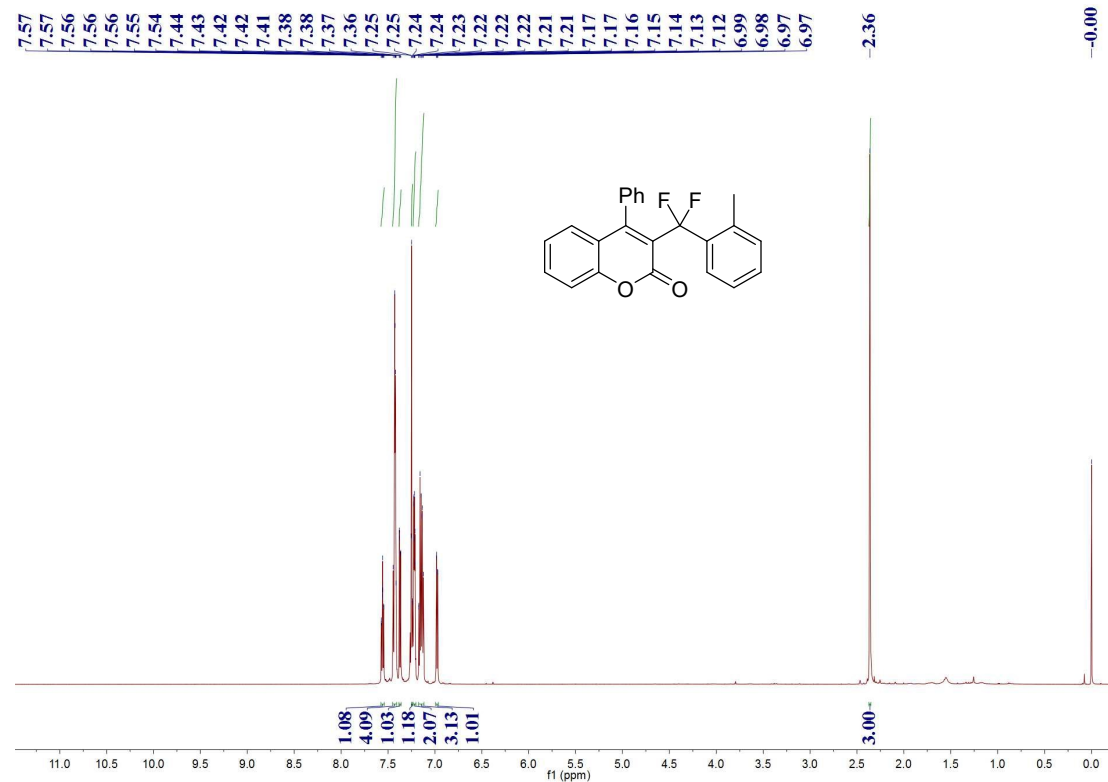


$^{19}\text{F}$  NMR of **3i** in  $\text{CDCl}_3$

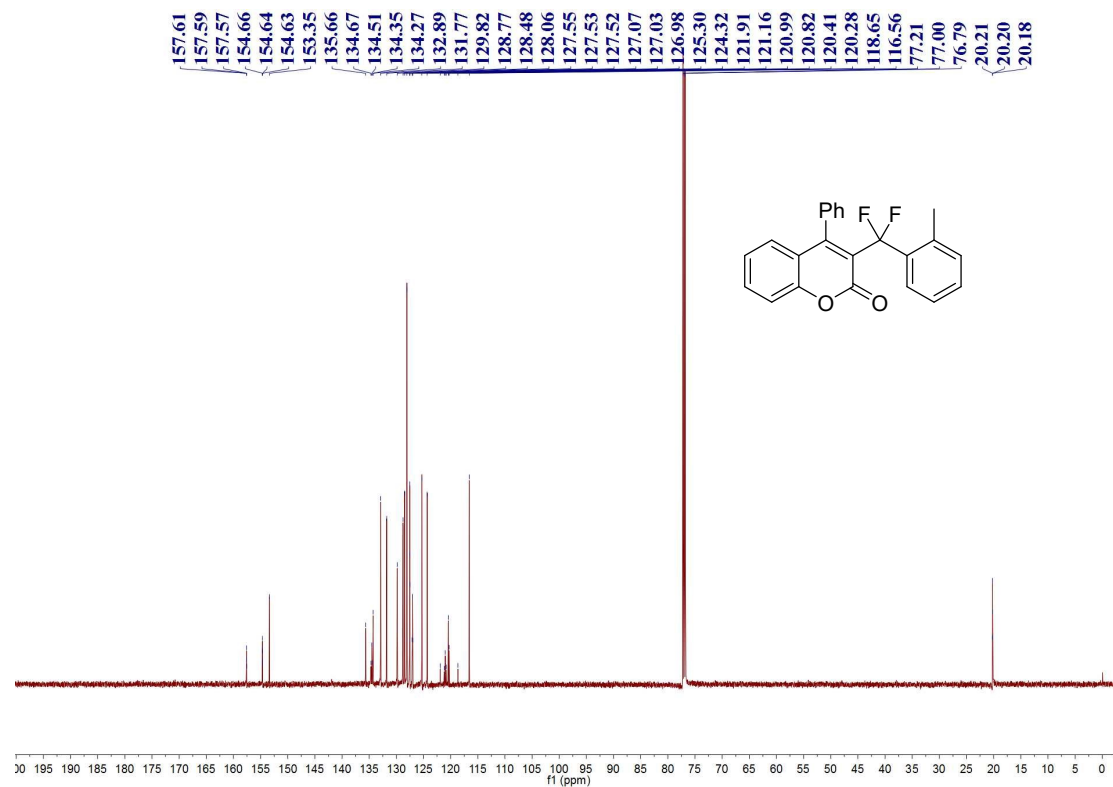


**3-(difluoro(o-tolyl)methyl)-4-phenyl-2H-chromen-2-one (3j):**

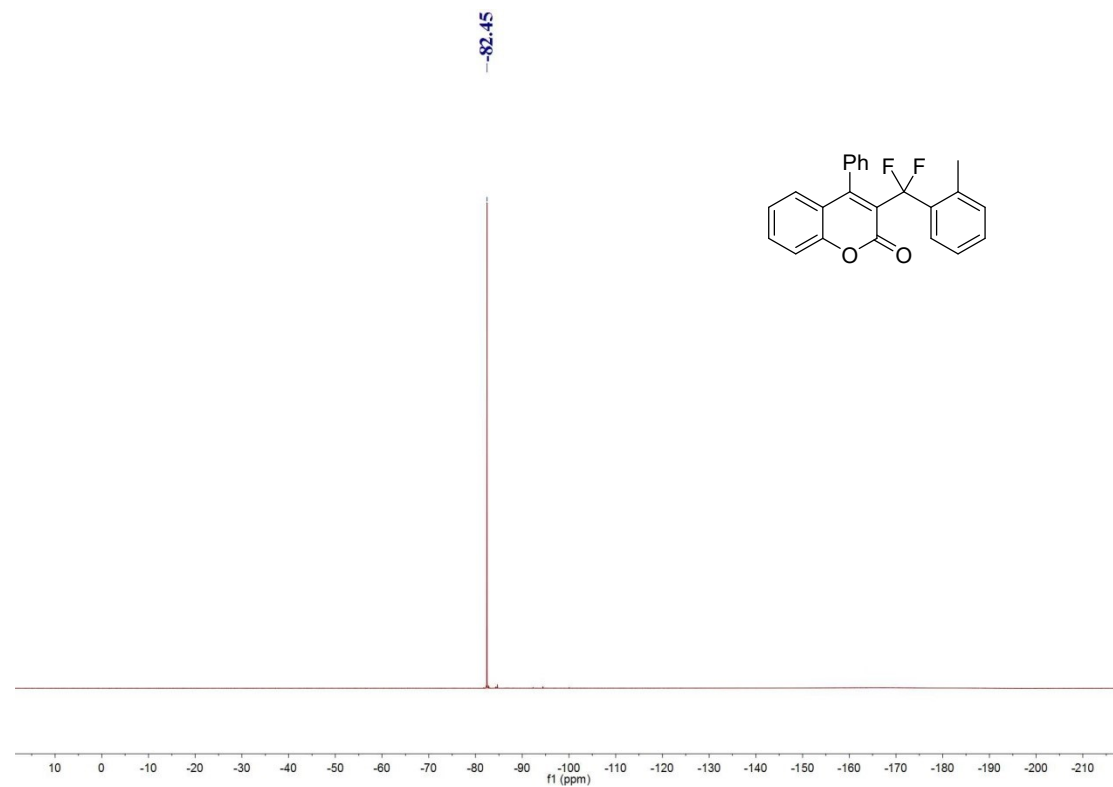
$^1\text{H}$  NMR of **3j** in  $\text{CDCl}_3$



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



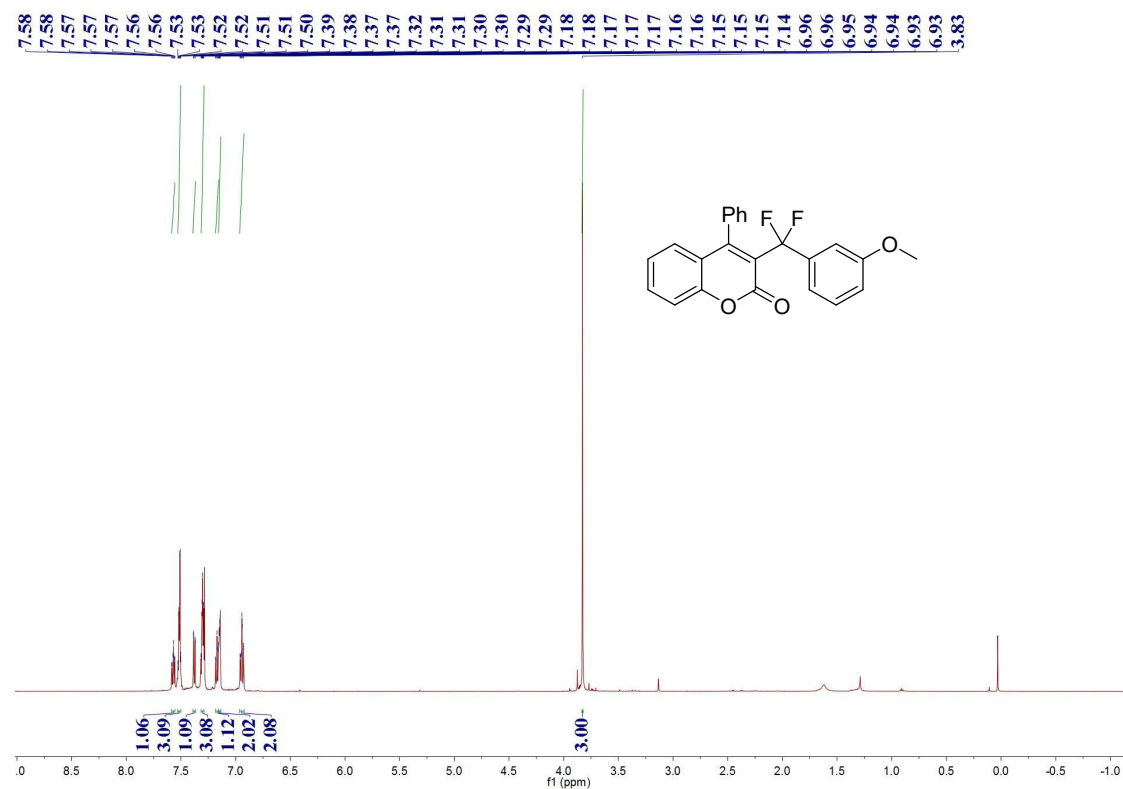
$^{19}\text{F}$  NMR of **3j** in  $\text{CDCl}_3$



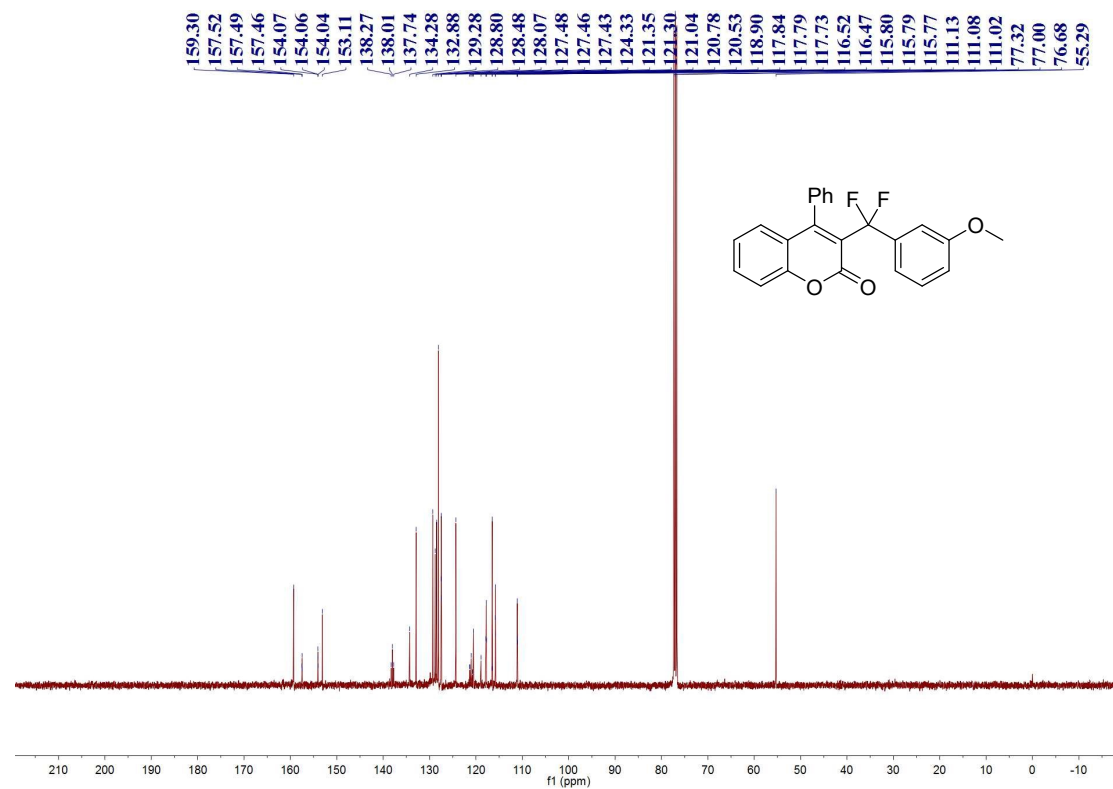


**3-(difluoro(3-methoxyphenyl)methyl)-4-phenyl-2H-chromen-2-one (3k):**

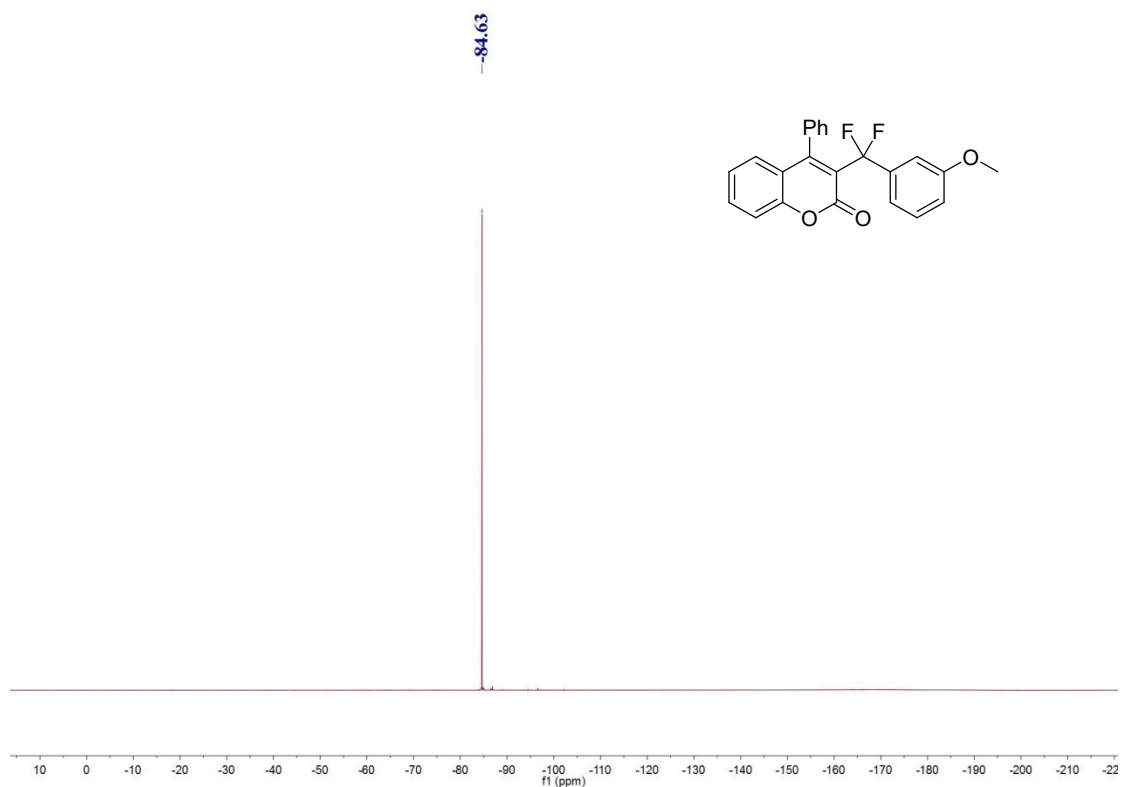
<sup>1</sup>H NMR of **3k** in CDCl<sub>3</sub>



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

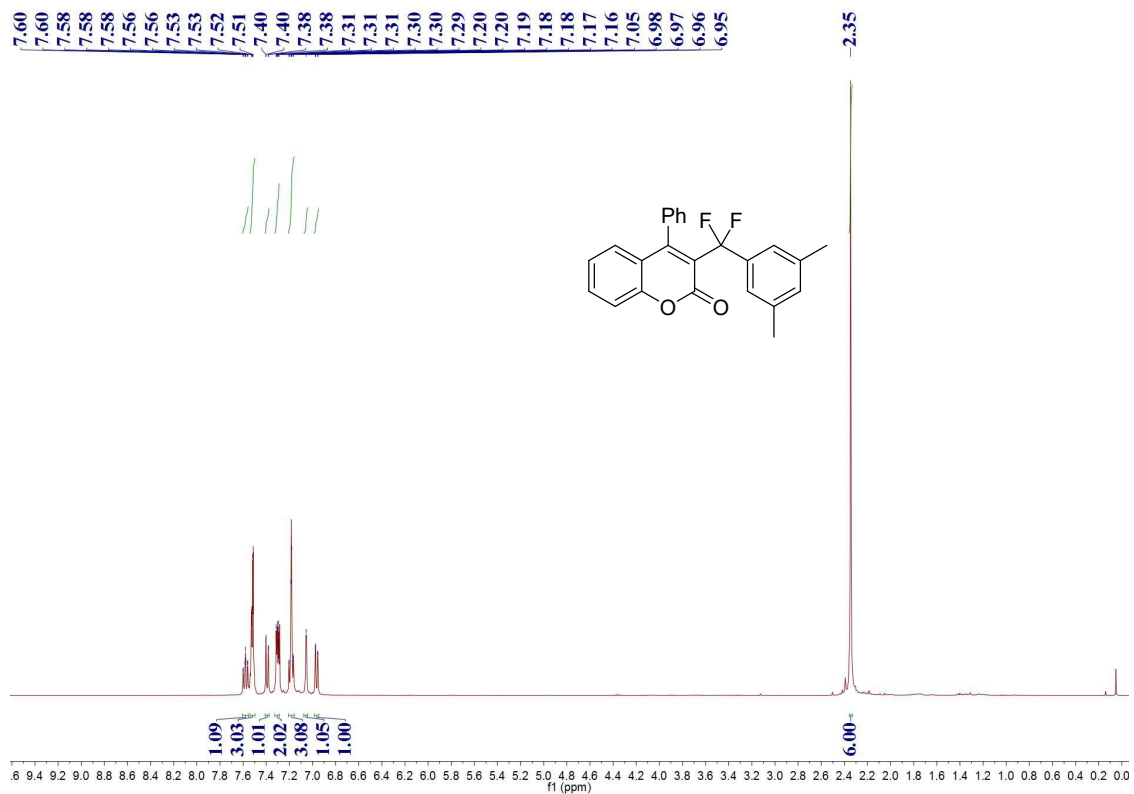


$^{19}\text{F}$  NMR of **3k** in  $\text{CDCl}_3$

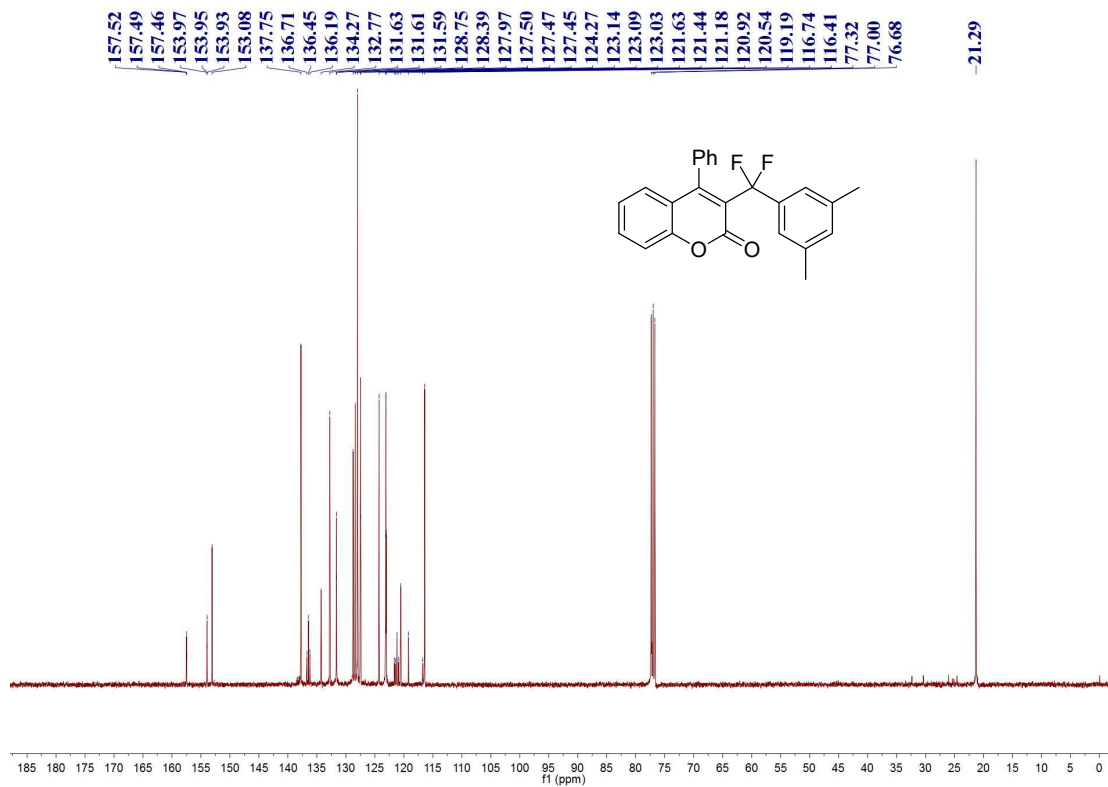


**3-((3,5-dimethylphenyl)difluoromethyl)-4-phenyl-2H-chromen-2-one (3l):**

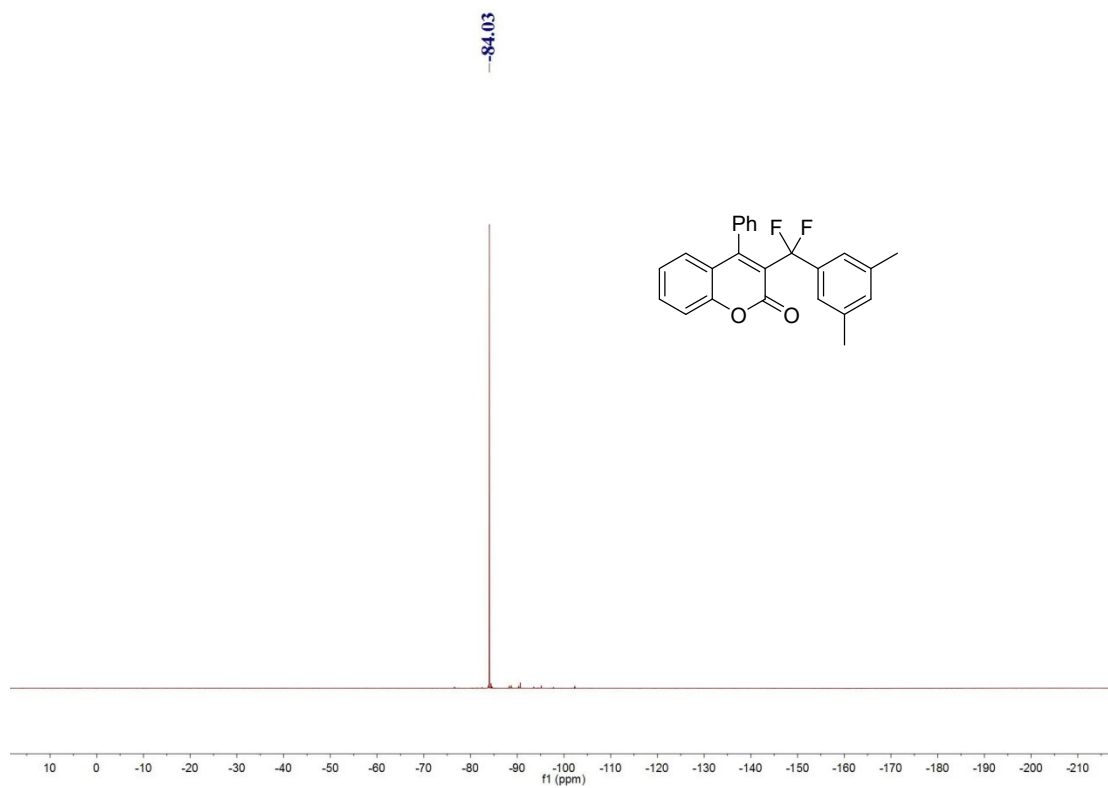
$^1\text{H}$  NMR of **3l** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR of **31** in  $\text{CDCl}_3$

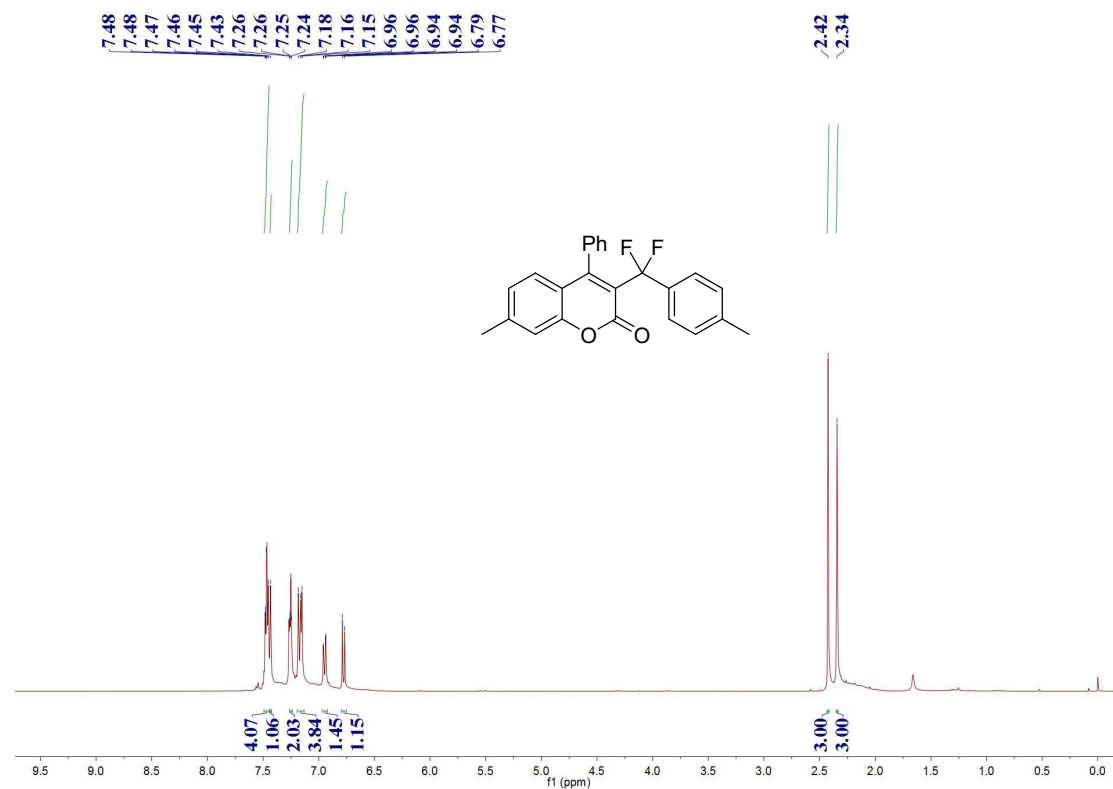


$^{19}\text{F}$  NMR of **31** in  $\text{CDCl}_3$

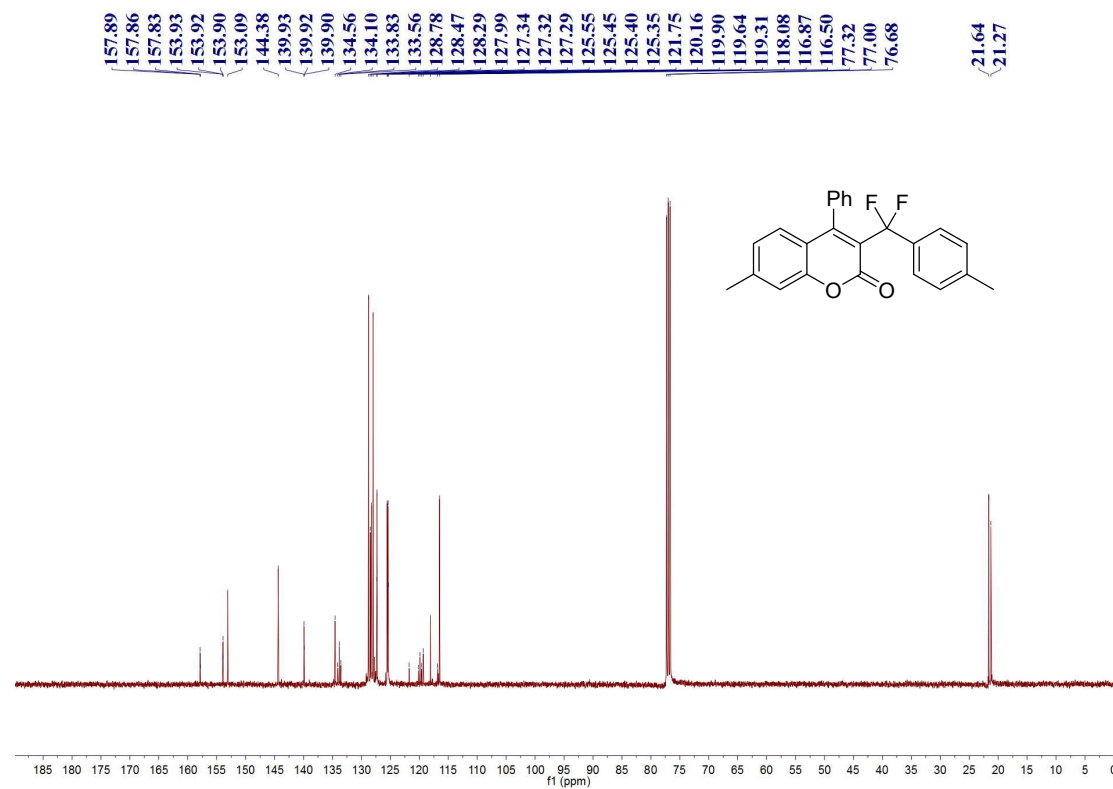


### 3-(difluoro(p-tolyl)methyl)-7-methyl-4-phenyl-2H-chromen-2-one (3n):

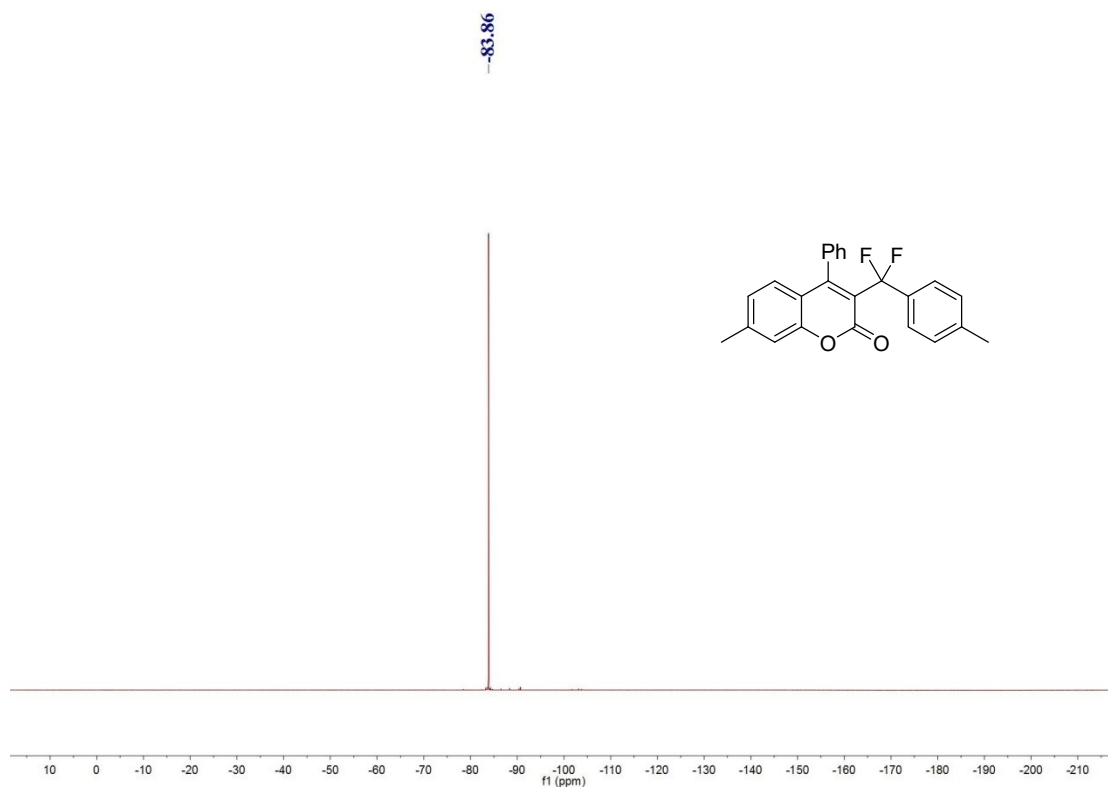
<sup>1</sup>H NMR of **3n** in CDCl<sub>3</sub>



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

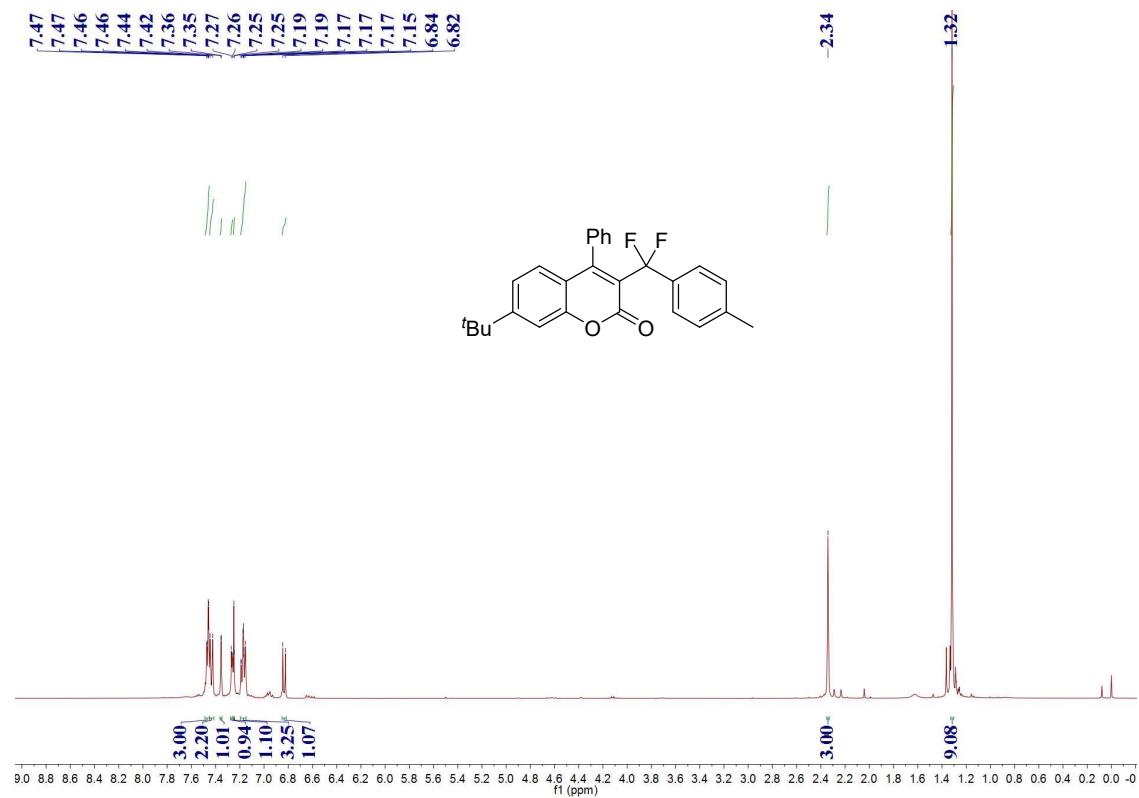


$^{19}\text{F}$  NMR of **3n** in  $\text{CDCl}_3$

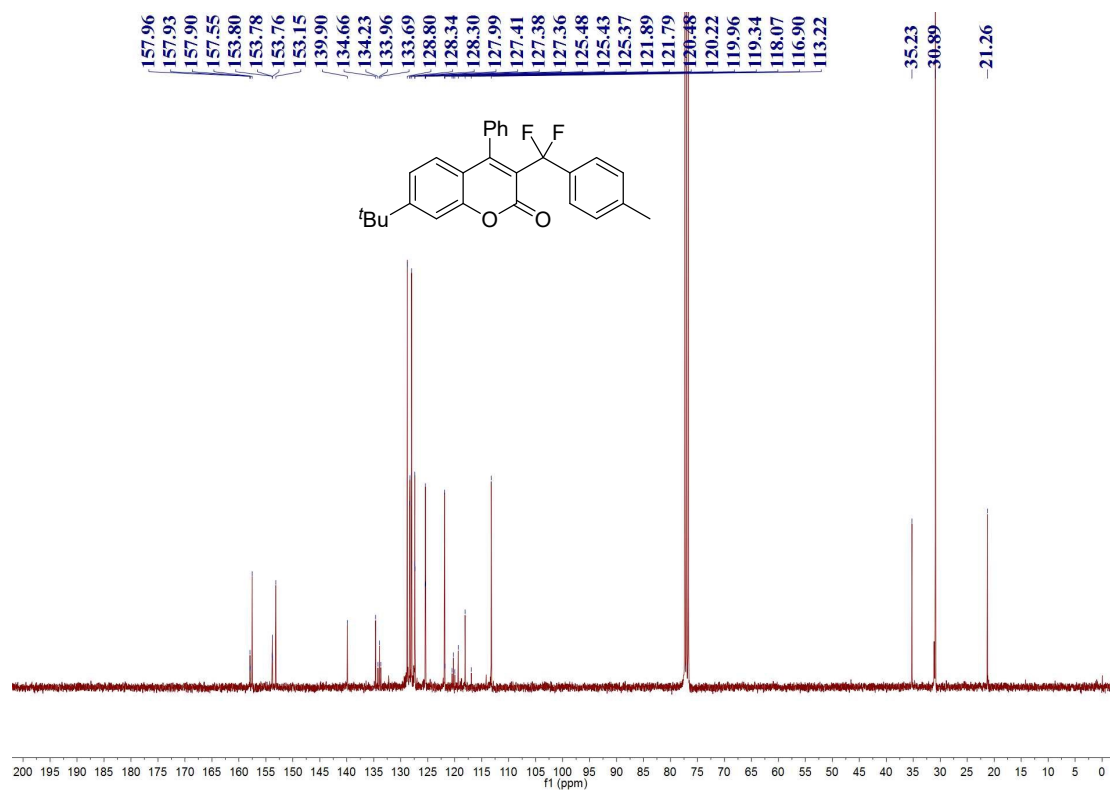


7-(tert-butyl)-3-(difluoro(p-tolyl)methyl)-4-phenyl-2H-chromen-2-one (**3o**):

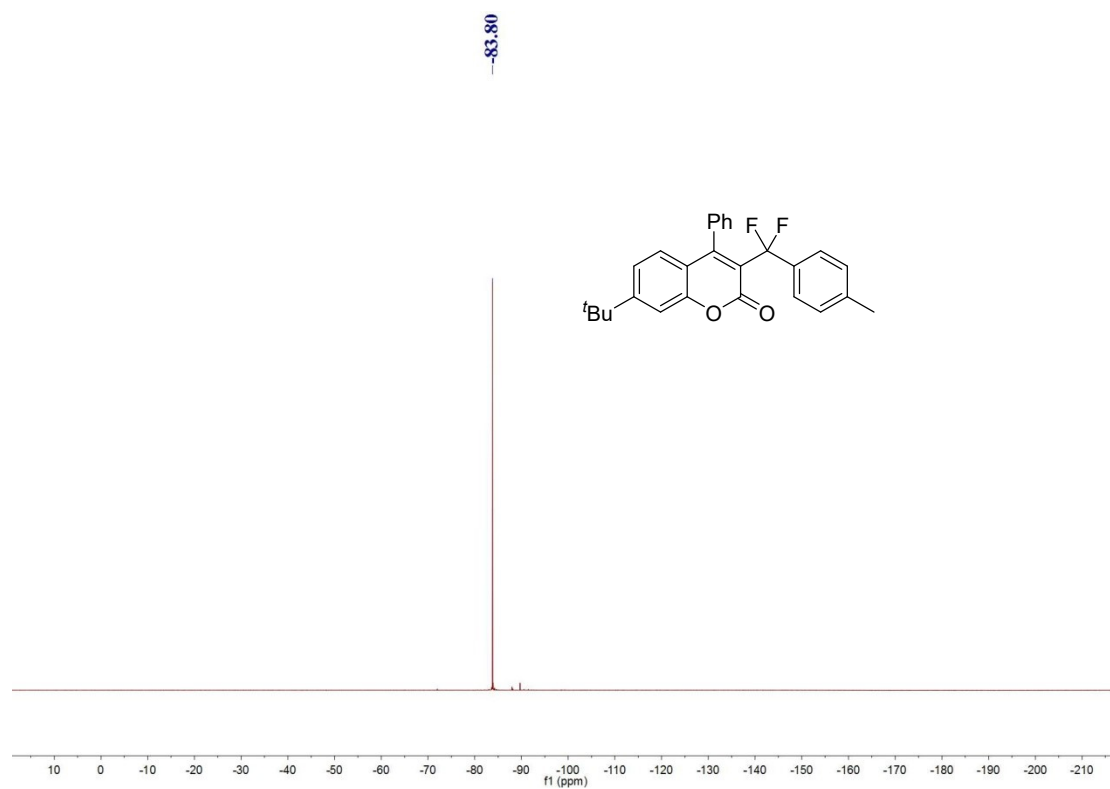
$^1\text{H}$  NMR of **3o** in  $\text{CDCl}_3$



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

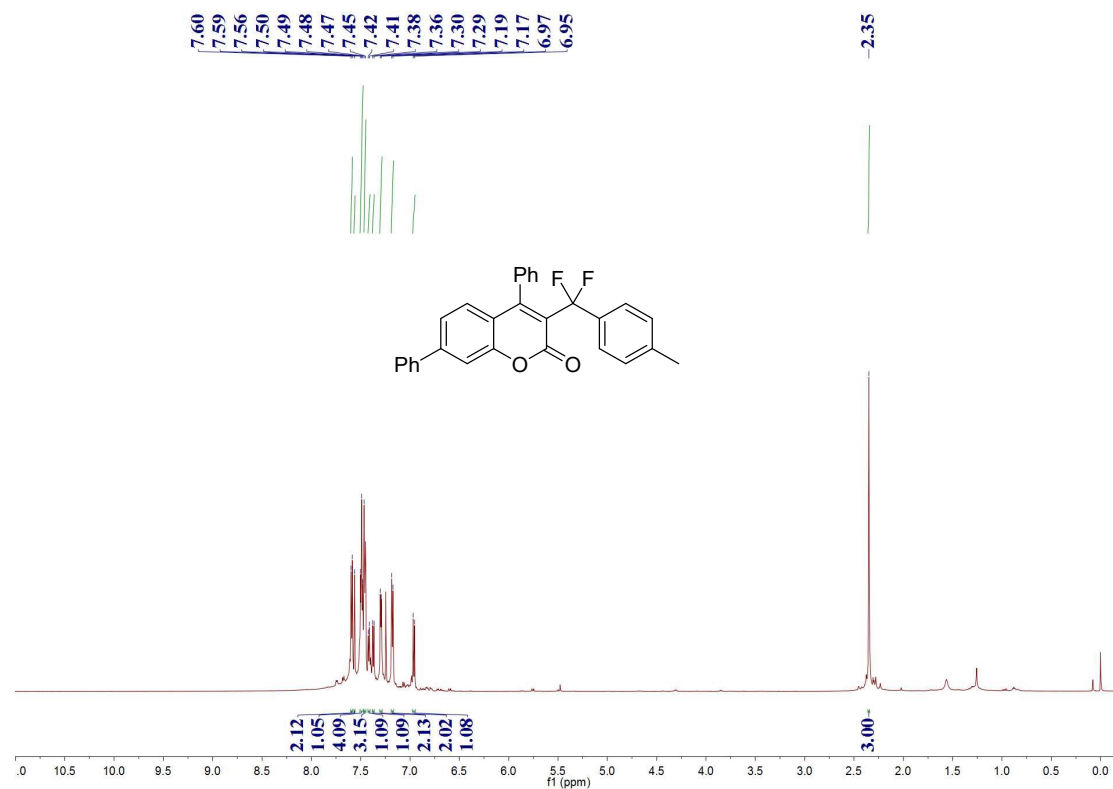


$^{19}\text{F}$  NMR of **3o** in  $\text{CDCl}_3$

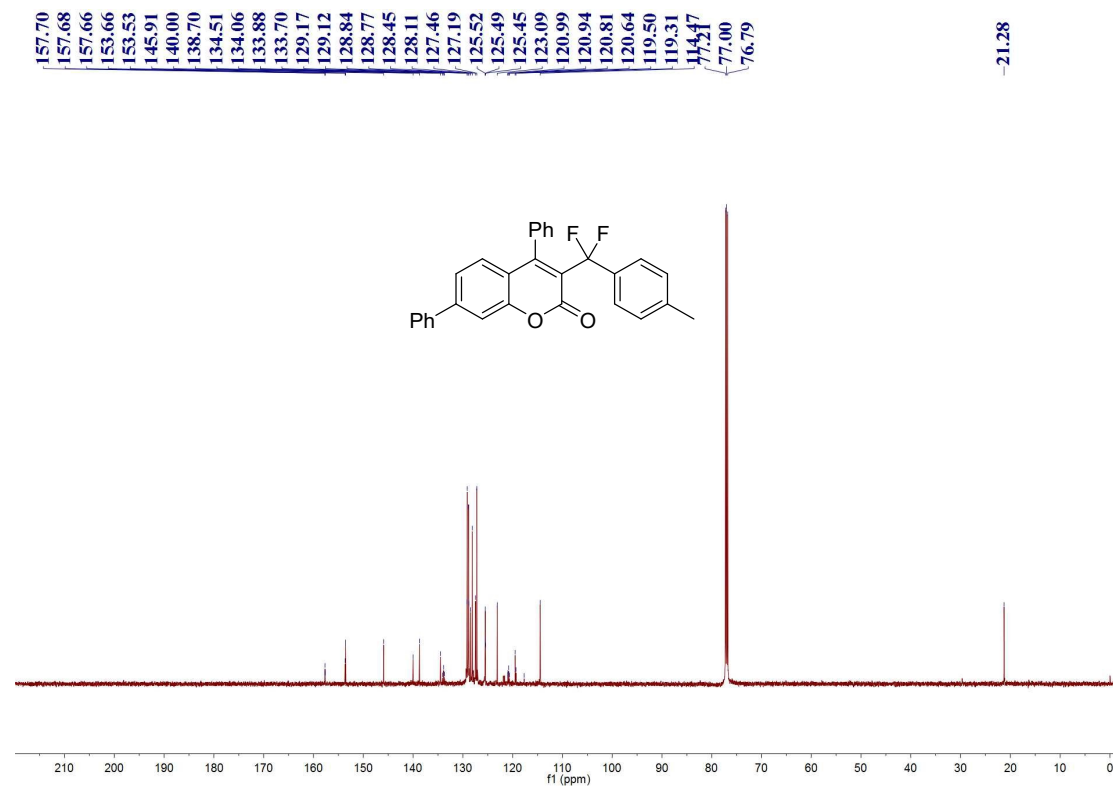


**3-(difluoro(p-tolyl)methyl)-4,7-diphenyl-2H-chromen-2-one (3p):**

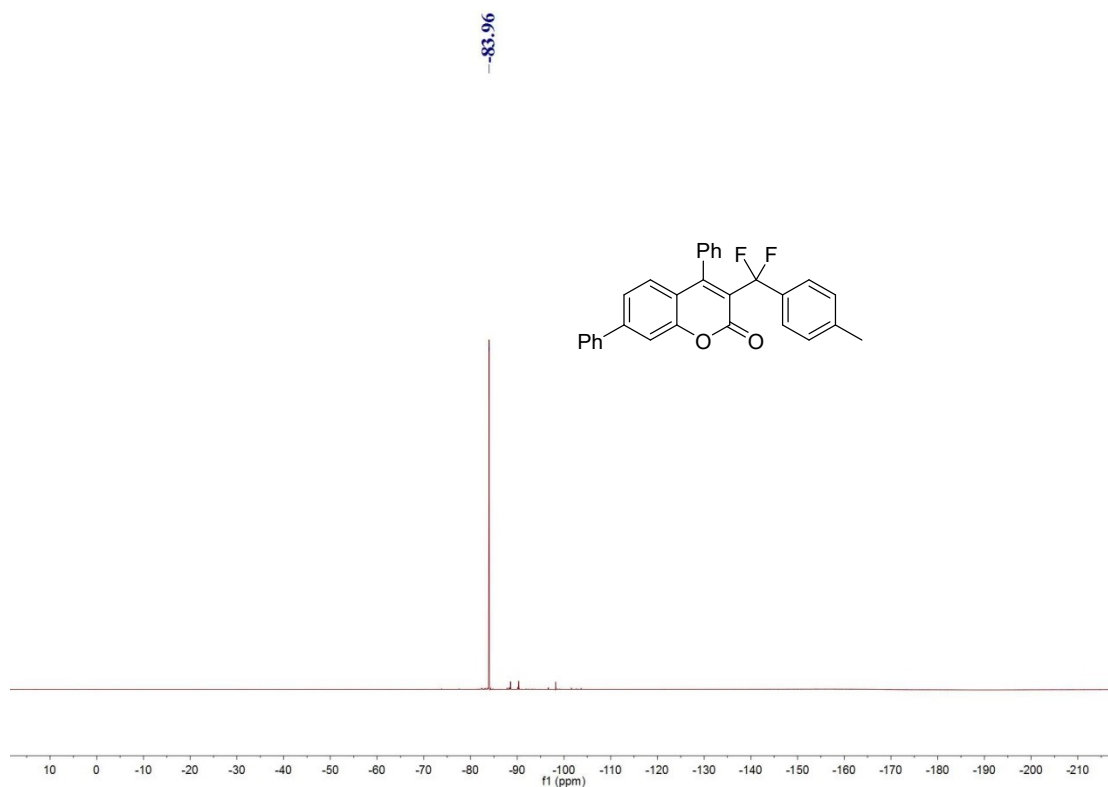
<sup>1</sup>H NMR of **3p** in CDCl<sub>3</sub>



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

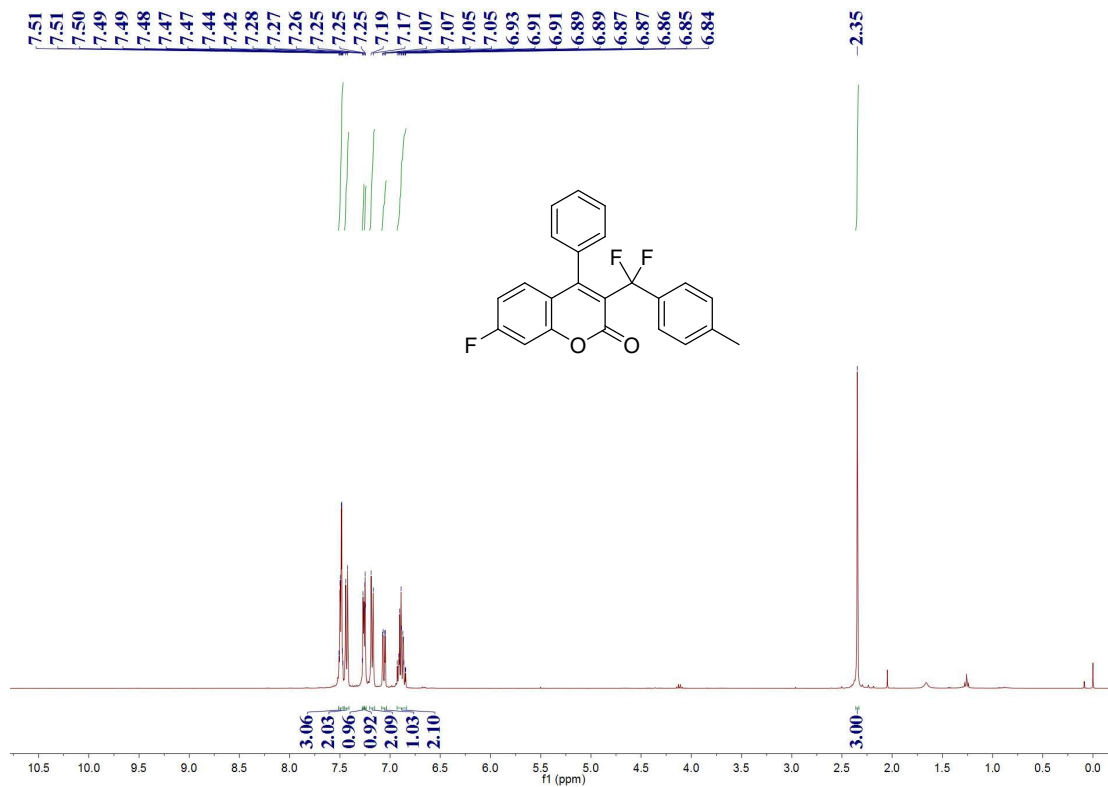


$^{19}\text{F}$  NMR of **3p** in  $\text{CDCl}_3$



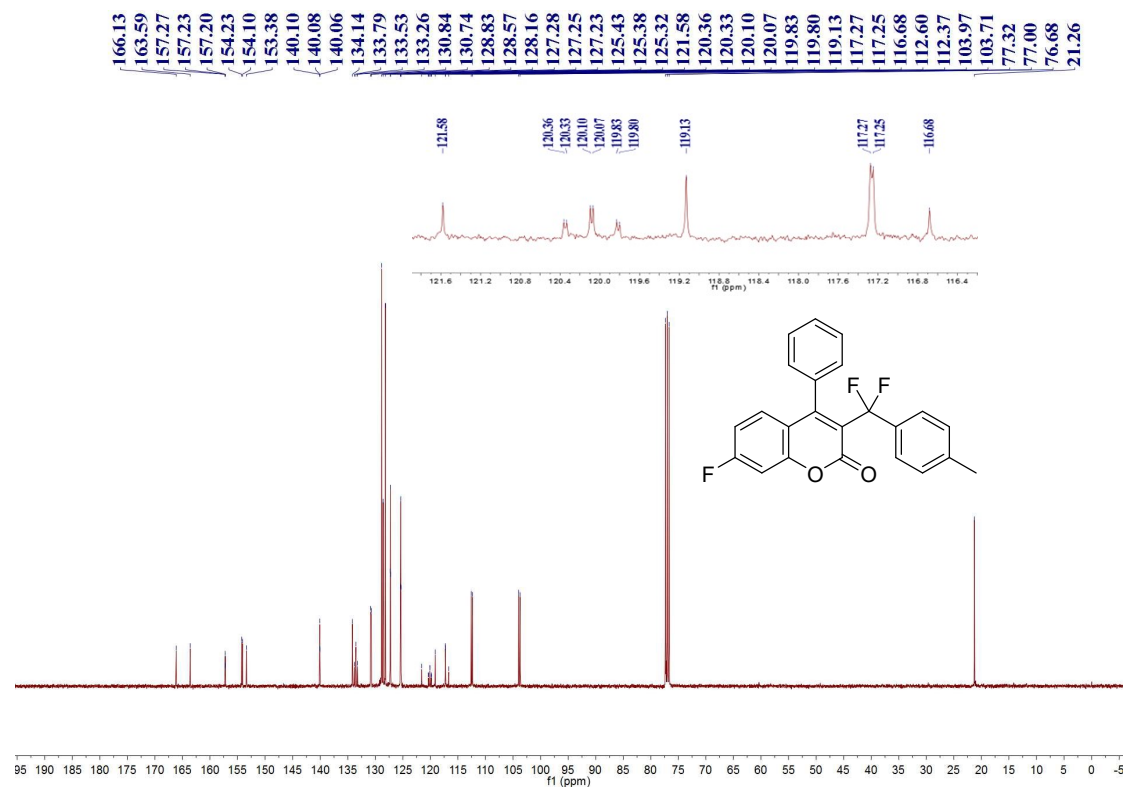
**3-(difluoro(p-tolyl)methyl)-7-fluoro-4-phenyl-2H-chromen-2-one (3q):**

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





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

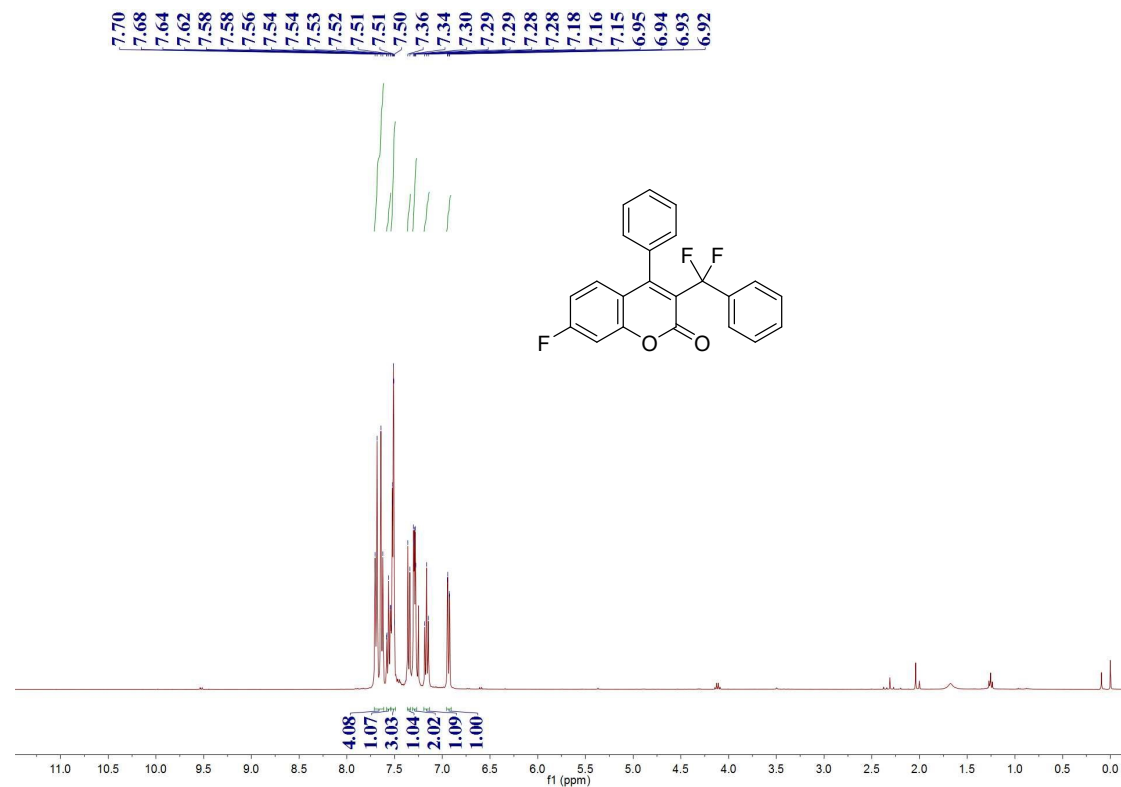


<sup>19</sup>F NMR of **3q** in CDCl<sub>3</sub>

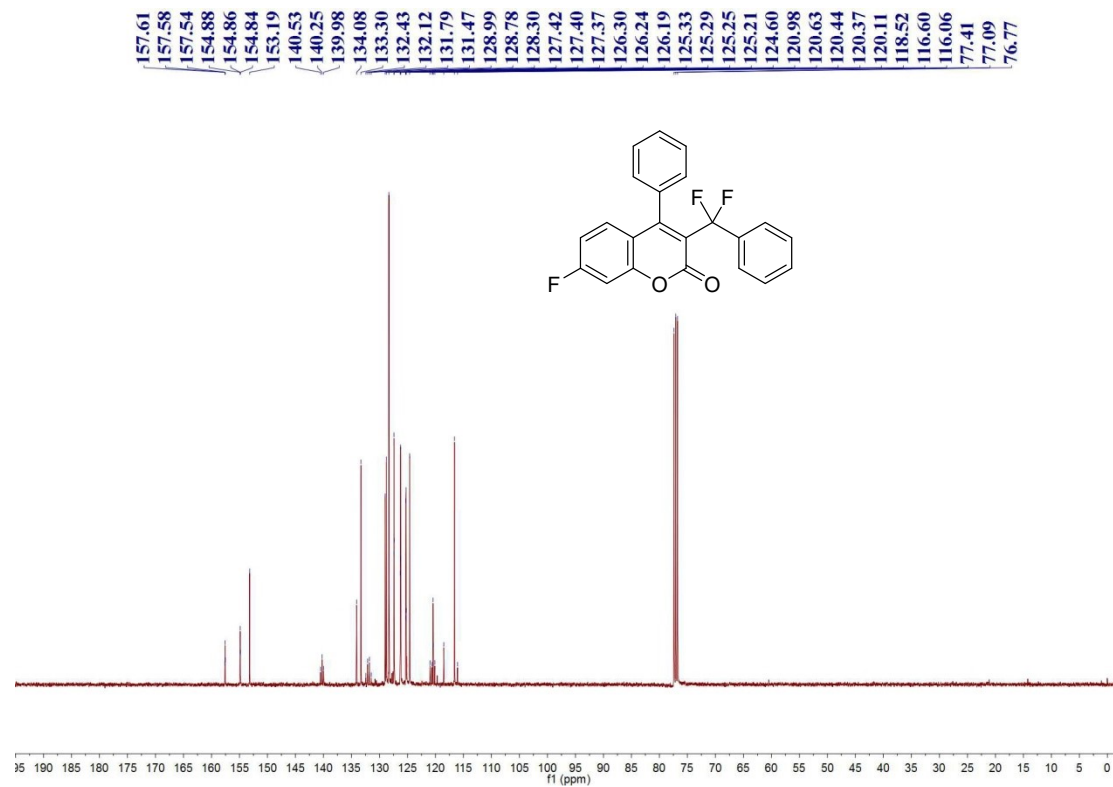


### 3-(difluoro(phenyl)methyl)-7-fluoro-4-phenyl-2H-chromen-2-one(3r):

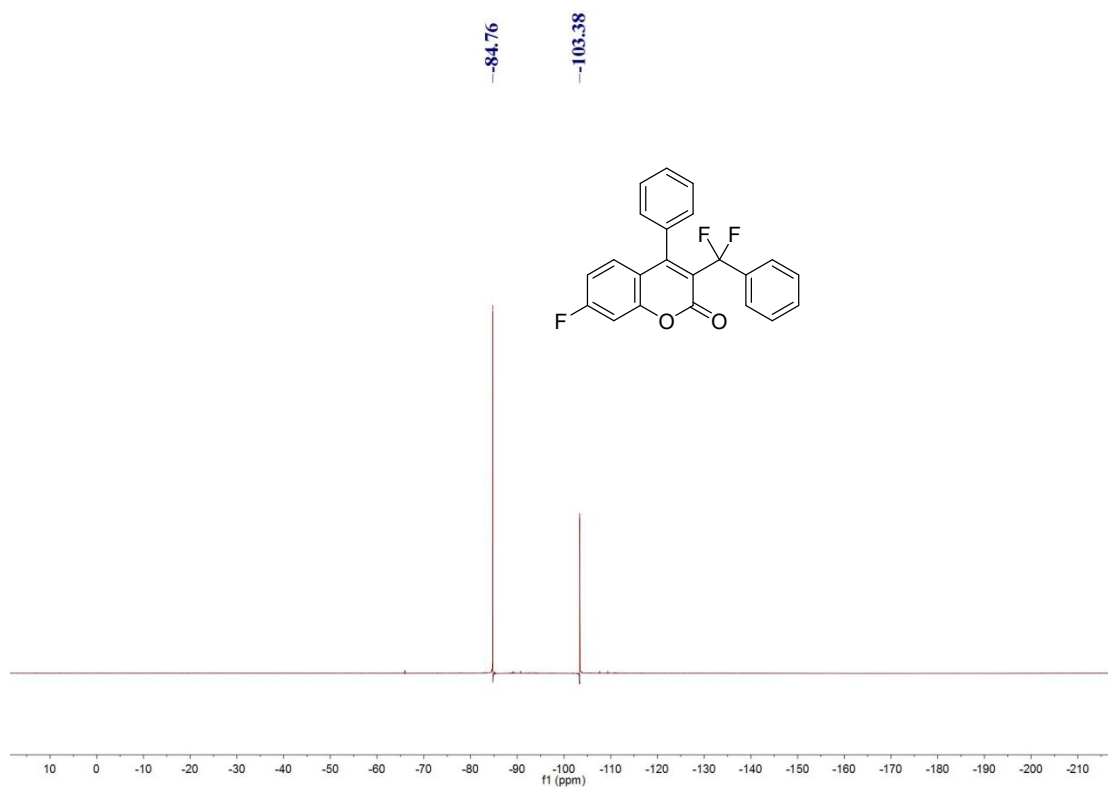
$^1\text{H}$  NMR of **3r** in  $\text{CDCl}_3$



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

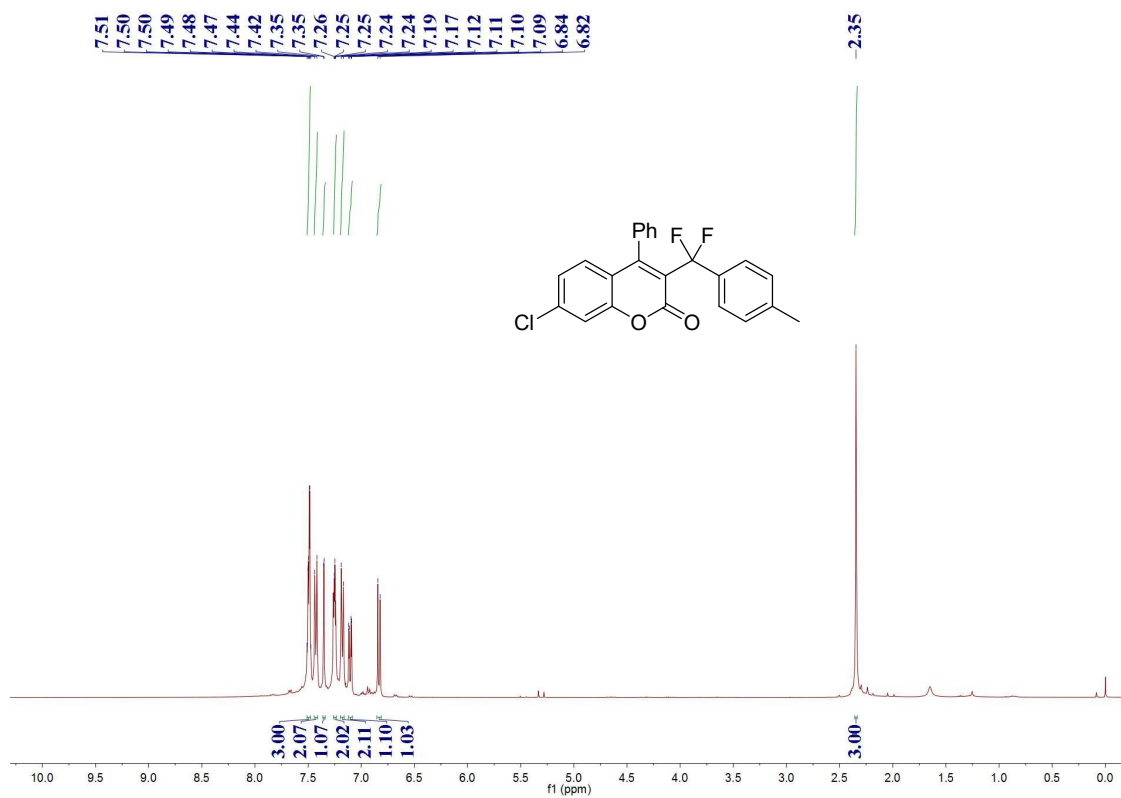


$^{19}\text{F}$  NMR of **3r** in  $\text{CDCl}_3$



**7-chloro-3-(difluoro(p-tolyl)methyl)-4-phenyl-2H-chromen-2-one (3s):**

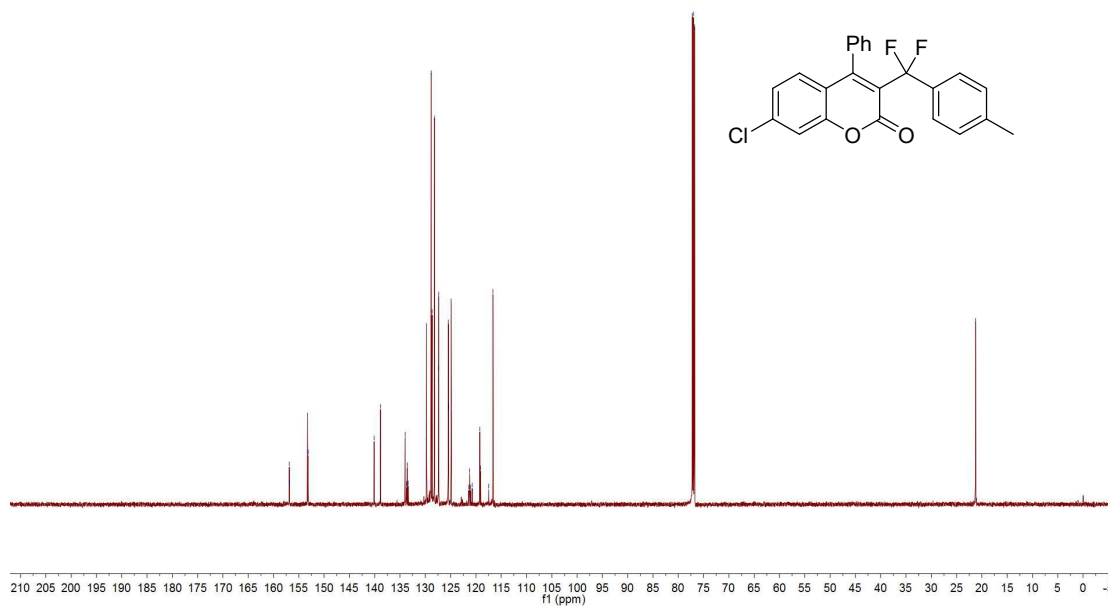
$^1\text{H}$  NMR of **3s** in  $\text{CDCl}_3$



$^{13}\text{C}$  NMR of **3s** in  $\text{CDCl}_3$  (600Hz)

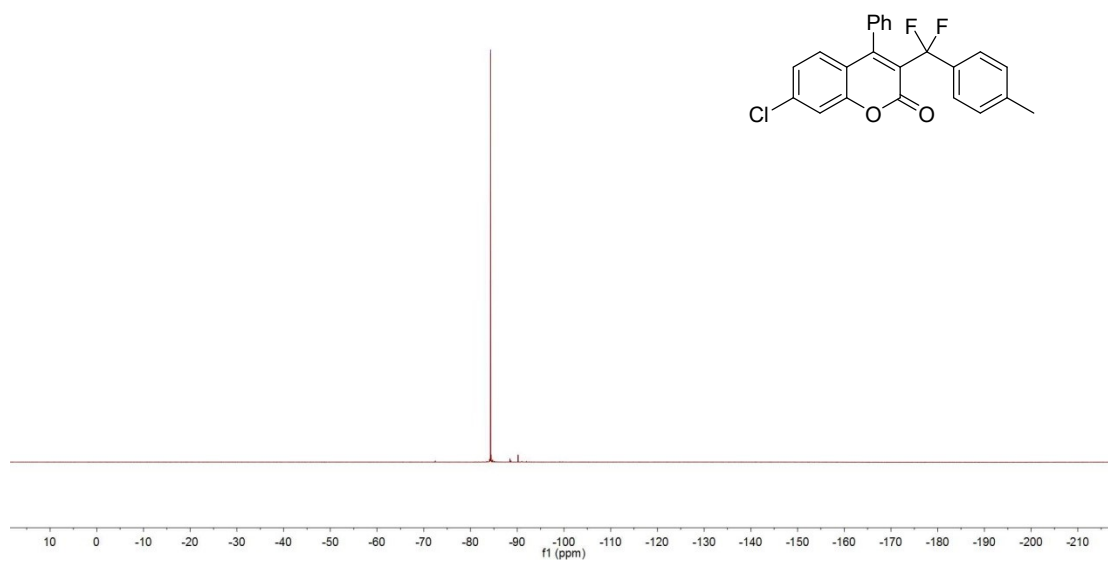
156.90  
156.88  
156.86  
153.27  
153.16  
140.10  
138.84  
133.99  
133.73  
133.56  
133.38  
129.74  
128.84  
128.64  
128.20  
127.36  
127.35  
127.33  
125.47  
125.43  
125.40  
124.90  
121.41  
121.23  
121.06  
120.72  
119.24  
119.09  
117.46  
116.62  
77.21  
77.00  
76.79

-21.25



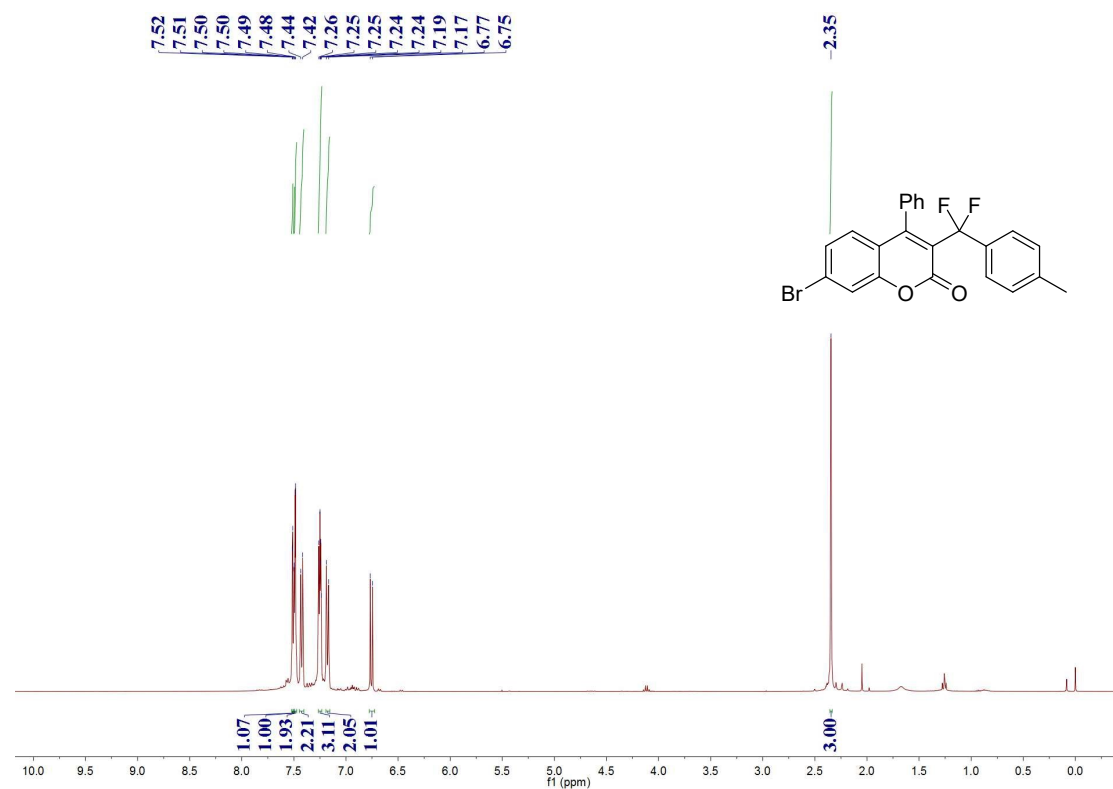
$^{19}\text{F}$  NMR of **3s** in  $\text{CDCl}_3$

-84.27

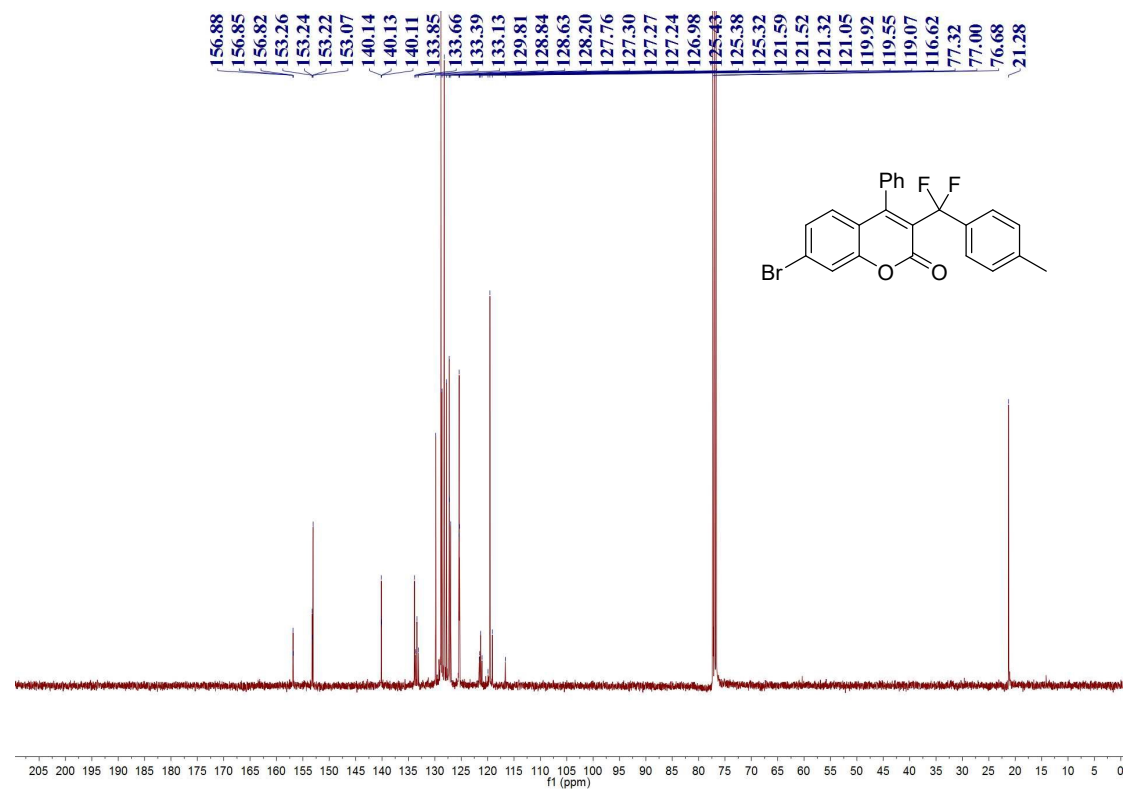


**7-bromo-3-(difluoro(p-tolyl)methyl)-4-phenyl-2H-chromen-2-one (3t):**

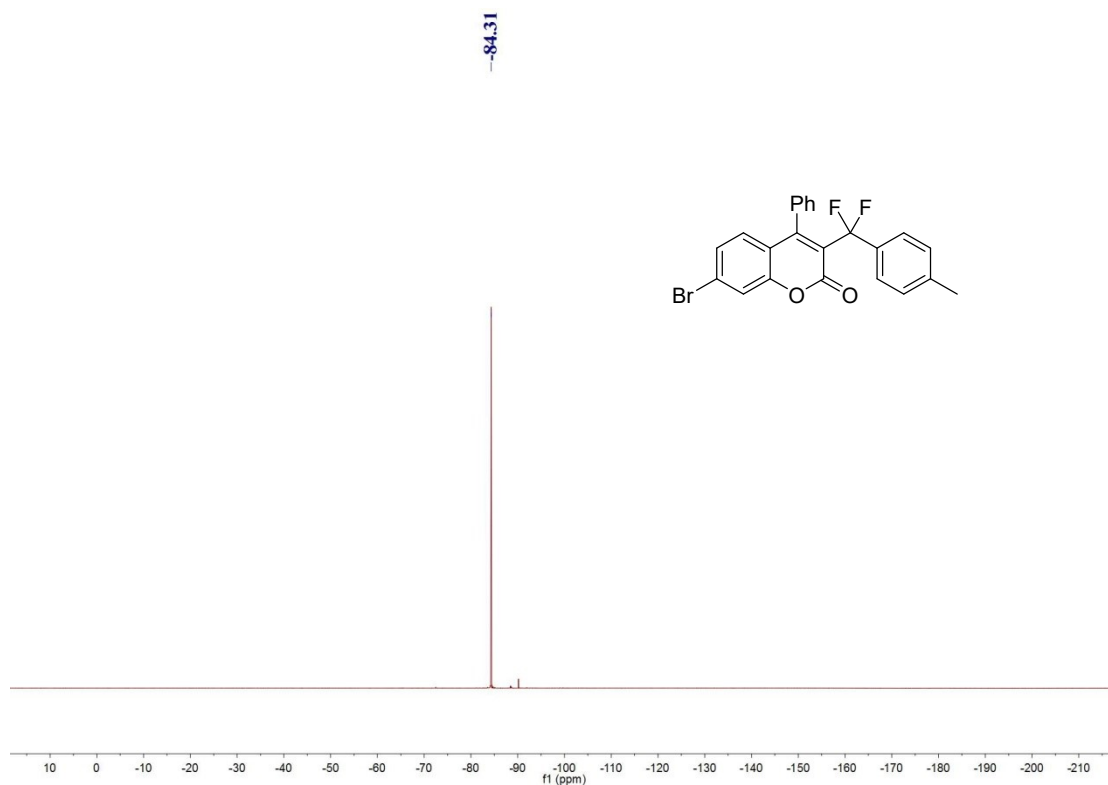
<sup>1</sup>H NMR of **3t** in CDCl<sub>3</sub>



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

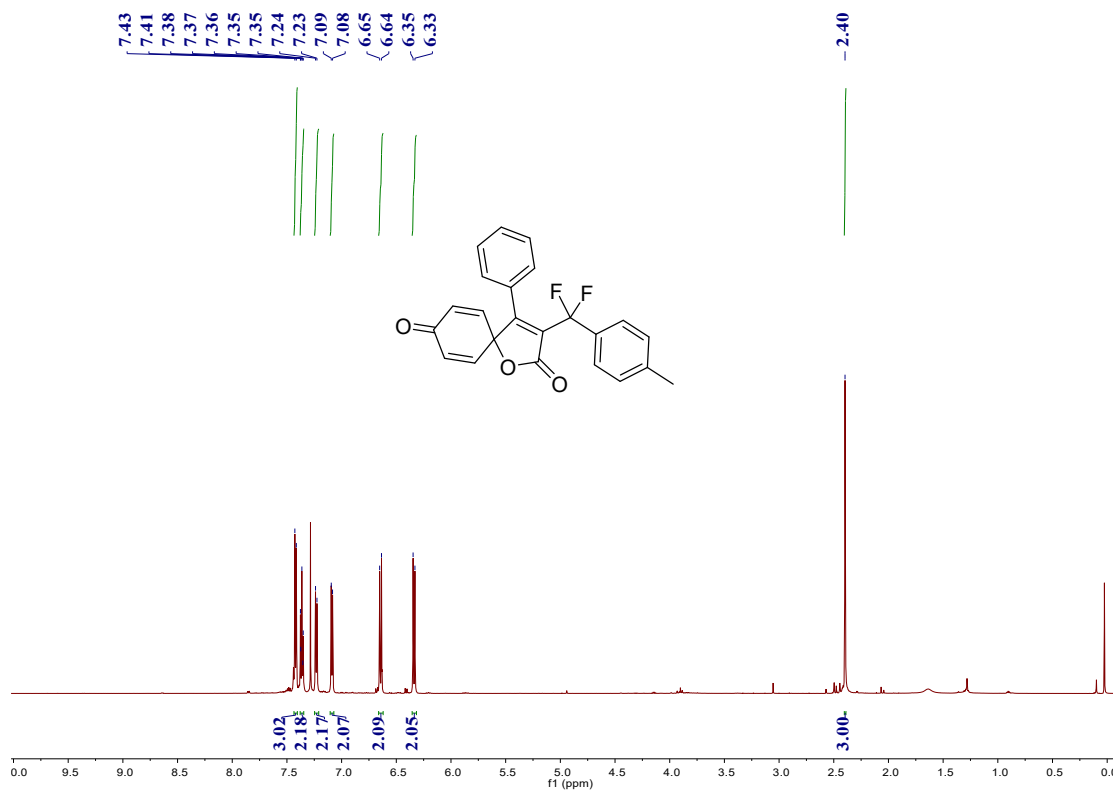


$^{19}\text{F}$  NMR of **3t** in  $\text{CDCl}_3$

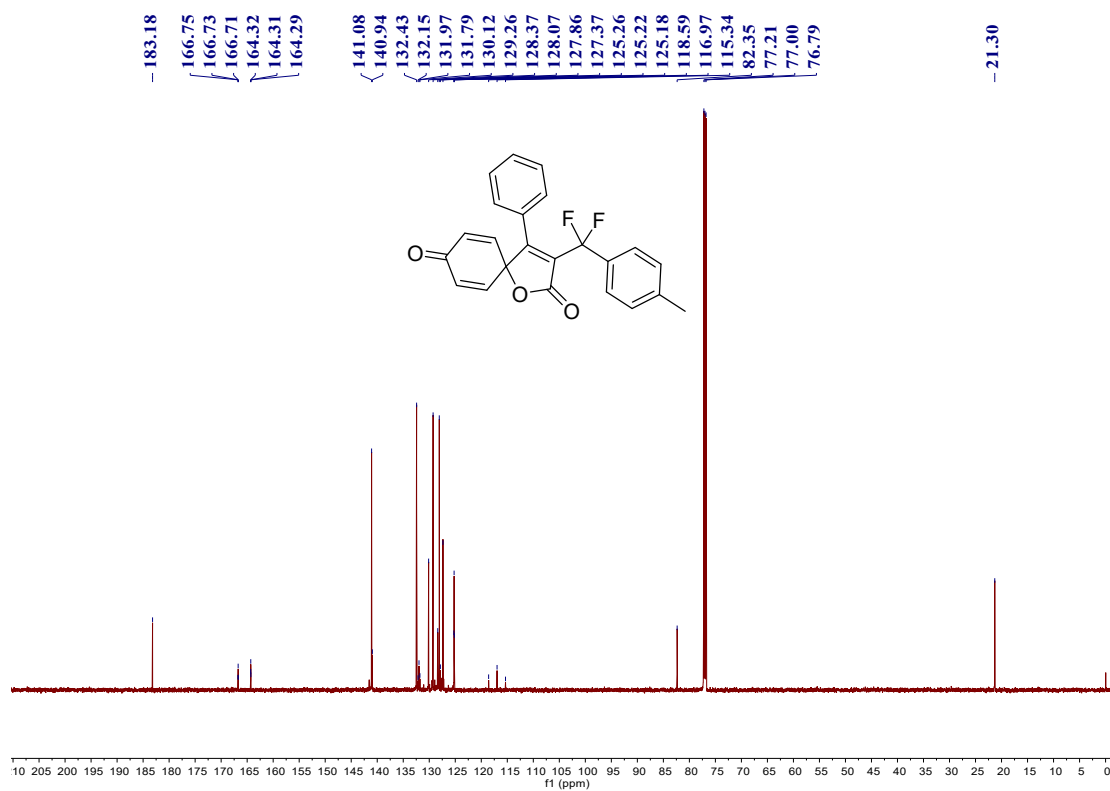


**3-(difluoro(p-tolyl)methyl)-4-phenyl-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione (3v)**

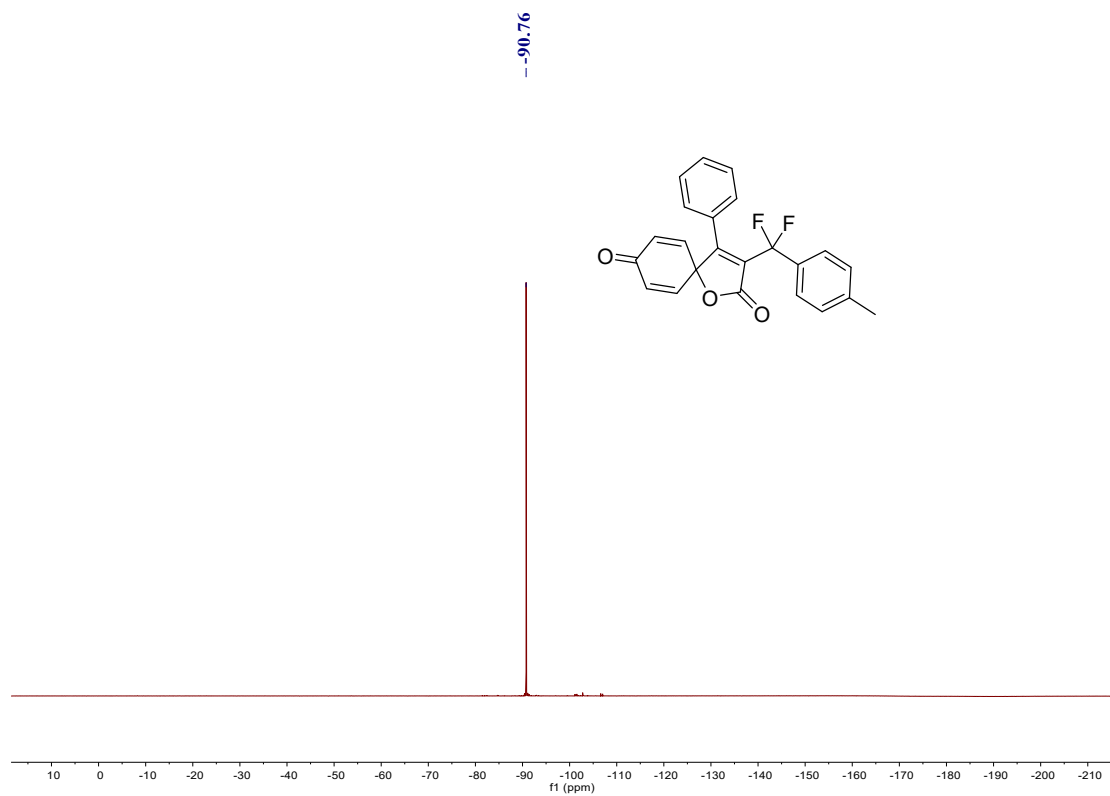
$^1\text{H}$  NMR of **3v** in  $\text{CDCl}_3$



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



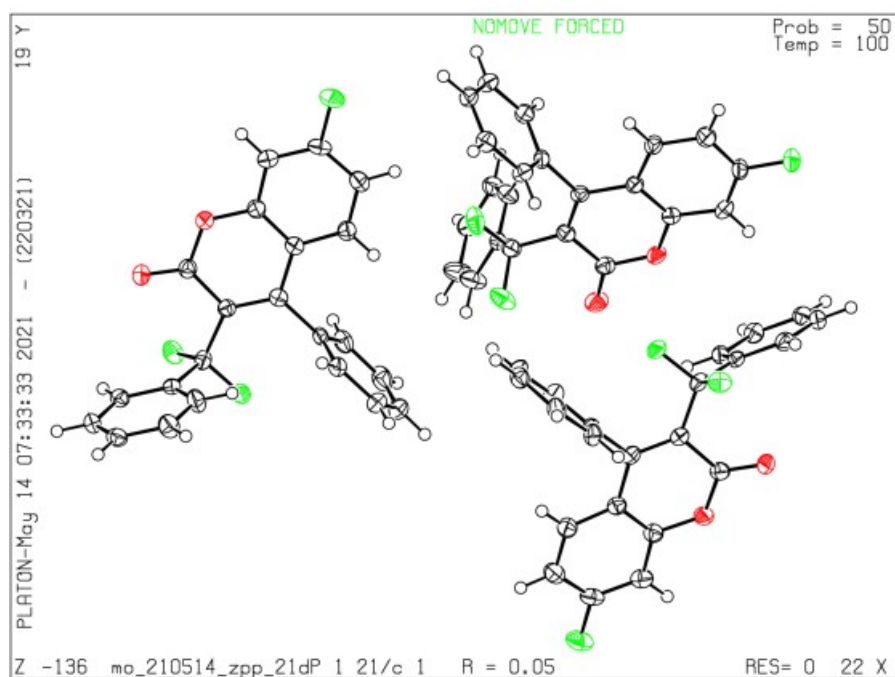
$^{19}\text{F}$  NMR of **3v** in  $\text{CDCl}_3$







## 5. X-ray structure of compound 3r.



**Table 1 Crystal data and structure refinement for 3r**

Identification code	mo_210514_ZPP_21DJ_0m
Empirical formula	C <sub>22</sub> H <sub>13</sub> F <sub>3</sub> O <sub>2</sub>
Formula weight	366.32
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	14.1040(6)
b/Å	15.1682(9)
c/Å	24.3684(12)
α/°	90
β/°	102.661(2)
γ/°	90
Volume/Å <sup>3</sup>	5086.4(4)
Z	12

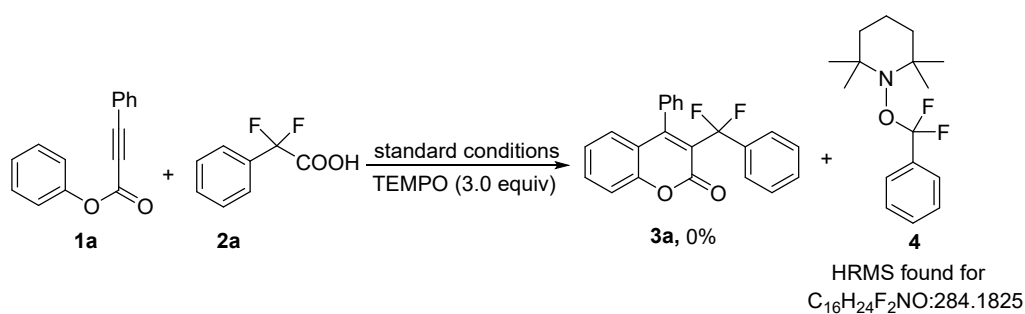
**Continue to table 1**

---

$\rho_{\text{calc}}/\text{cm}^3$	1.435
$\mu/\text{mm}^{-1}$	0.113
F(000)	2256.0
Crystal size/ $\text{mm}^3$	$0.16 \times 0.09 \times 0.08$
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^\circ$	3.996 to 54.234
Index ranges	$-16 \leq h \leq 18, -18 \leq k \leq 19, -29 \leq l \leq 31$
Reflections collected	54654
Independent reflections	11216 [ $R_{\text{int}} = 0.0787, R_{\text{sigma}} = 0.0564$ ]
Data/restraints/parameters	11216/0/730
Goodness-of-fit on $F^2$	1.031
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0479, wR_2 = 0.0954$
Final R indexes [all data]	$R_1 = 0.0856, wR_2 = 0.1133$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.22/-0.29

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## 6. HRMS data of compound 4



### Compound Spectrum SmartFormula Report

#### Analysis Info

Analysis Name D:\Data\YL\CLY-SYM\Acq000004.d  
 Method LC-MS-POS\_2MIN.m  
 Sample Name ZPP210427-1  
 Comment

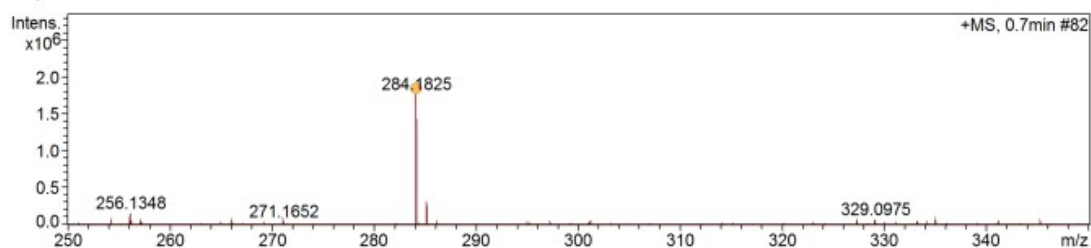
Acquisition Date 4/30/2021 3:03:07 PM

Operator Demo User  
 Instrument compact 8255754.20167

#### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	2.3 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	220 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C

#### +MS, 0.7min #82



Meas. m/z	Ion Formula	m/z	err [ppm]	mSigma
284.1825	C <sub>16</sub> H <sub>24</sub> F <sub>2</sub> NO	284.1820	-1.7	0.7