# Supporting Information for

# Manganese(III)-mediated direct $C_{sp2}$ -H radical trifluoromethylation of coumarins with sodium trifluoromethanesulfinate

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#### **General information**

All reactions were performed in air. Solvents were dried by the standard procedures. <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were determined in CDCl<sub>3</sub> or DMSO- $d_6$  on a Varian-Inova 300MHz or 400 MHz spectrometer and chemical shifts were reported in ppm from internal TMS( $\delta$ ). High resolution mass spectra were recorded on a MicroMass-TOF machine (EI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted. Manganese triacetate, <sup>1</sup> coumarins, <sup>2a-d</sup> quinolinone-2, <sup>2e</sup> and pyrimidinones <sup>2f</sup> were prepared according to the reported procedures.

### References

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#### Typical procedure for the preparation of 3-(trifluoromethyl)-2H-chromen-2-one

To a solution of acetic acid (10 mL), coumarin (0.5 mmol) and sodium trifluoromethanesulfinate (1.5 mmol) was slowly added  $Mn(OAc)_3$  (2.0 mmol) at room temperature for 24h, the acetic acid was removed under vacuum. To the residue was added water (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc = 50:1) to give 3-(trifluoromethyl)-2H-chromen- 2-one.

#### Preparation of coumarins (1c, 1d, 1e, 1f, 1g, 1h, 1j, 1k)<sup>2a</sup>



# Typical procedure for the preparation of coumarins (1c, 1d, 1e, 1f, 1g, 1h, 1j, 1k)

To a solution of phenol derivative (10 mmol) in methanesulfonic acid (20 mL) was added propiolic acid (12 mmol) at room temperature. After stirring at 80-90°C under N<sub>2</sub> atmosphere for 4h, the solution was diluted with 50 mL de-ionized water and extracted with ethyl acetate (20 mL  $\times$  3). The ethyl acetate layer was washed with saturated Na<sub>2</sub>CO<sub>3</sub> (10 mL  $\times$  3), saturated NaCl, dried over MgSO<sub>4</sub> and concentrated to give a gray solid.

#### Preparation of coumarins (11, 1m, 1n, 1o)<sup>2b</sup>



#### Typical procedure for the preparation of coumarins (11, 1m, 1n, 1o)

The phenol derivative (10 mmol) was dissolved in 75% sulphuric acid (15 mL) and heated to 70-80°C, then, ethyl acetoacetate (12 mmol) was added portionwise over a period of 15 minutes. The orange mixture was poured on to crushed ice and the resultant off-white precipitate was collected, dried and recrystallized from petroleum ether to afford the pure coumarin.

#### Preparation of coumarin (1q)<sup>2c</sup>



#### Typical procedure for the preparation of coumarin (1q)

To a mixture of 2-hydroxybenzophenone (300 mg, 1.51 mmol) and acetic anhydride (0.28 mL, 3.02 mmol) in acetonitrile (5 mL) was added DBU (0.67 mL, 4.54 mmol) and the reaction mixture was allowed to stir for 8 h at room temperature. The solvent was removed in vacuo and the residue was taken up with ethyl acetate (10 mL). The organic layer was washed with water, dried over anhydrous sodium sulfate, and then concentrated to dryness. The crude was purified by column chromatography on silica gel (hexane/EtOAc = 10/1) to afford 289 mg (86% yield) of **16a** as a solid.

#### Preparation of coumarin (1p)<sup>2d</sup>



# Typical procedure for the preparation of coumarin (1p)

4-Methoxycoumarin was prepared by heating 4-hydroxycoumarin with methanolic hydrogen chloride and purified by several crystallizations from small amounts of methanol.

#### Preparation of quinolinone-2 (4a, 4b)<sup>2e</sup>



#### Typical procedure for the preparation of 2-quinolinone (4a, 4b)

AlCl<sub>3</sub> (24 mmol) was added portionwise to a suspension of amide (4 mmol) in chlorobenzene (30 mL) at  $0^{\circ}$ C. The reaction mixture was gradually warmed to 120°C and then stirred for 2h. After the mixture had been poured into ice-water (100 mL), the resulting precipitate was collected. The crude was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH = 20/1) to afford product as a solid.

#### Preparation of pyrimidinones (4c, 4d, 4e)<sup>2f</sup>



# Typical procedure for the preparation of pyrimidinones (4c, 4d, 4e)

Four eq of NaH, as a 60% mineral oil dispersion, were placed in a round bottom flask under  $N_2$  and washed with hexanes (3 x 50 mL), then toluene (150 mL) and 5 eq of the dialkyl carbonate were added. To the resulting suspension, 1 eq of acetophenone was slowly added over 1 hr with stirring at r.t. The solution was then stirred at reflux overnight. The resulting mixture was cooled to rt. and glacial acetic acid (35 mL) was added and this was followed by dilution with a solution of of conc. HCl (20 mL) in ice water (150 mL). The aqueous solution was extracted with ethyl acetate (3 x 75mL). The organic layers were neutralized by extraction with sat. NaHCO<sub>3</sub> and dried over sodium sulfate. The volatiles were then removed under reduced pressure. The crude oil was purified by Kugelrohr distillation.

Followed by adding sodium ethoxide (5 mmol), ethyl benzoylacetate (5 mmol) and acetamidine hydrochloride (5 mmol), refluxing for 24 hours. TLC tracking after the reaction, adding proper amount of water, extraction by ethyl acetate. Hydrochloric acid (6M) to regulate pH=6, get the suspension, filtration, drying to obtain the product.

### 3-(Trifluoromethyl)-2H-chromen-2-one (3a)

 $CF_3$ 

White powder; mp 130-131°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.17 (s, 1H, C<sub>4</sub>-H), 7.69 (t, J = 7.8 Hz, 1H, ArH), 7.63 (d, J = 7.8 Hz, 1H, ArH), 7.42-7.37 (m, 2H, ArH), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  155.9, 154.6, 143.4 (q, J = 4.8 Hz), 134.4, 129.5, 125.3, 121.3 (q, J = 272.1 Hz), 117.6 (q, J = 33.2 Hz), 116.7, 115.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz)  $\delta$  -66.2 (s, 3F). ESI-HRMS: Anal. Calcd for C<sub>10</sub>H<sub>3</sub>F<sub>3</sub> NaO<sub>2</sub> 237.0140 [(M+Na)<sup>+</sup>], found 237.0141 [(M+Na)<sup>+</sup>].

#### 6-Methyl-3-(trifluoromethyl)-2H-chromen-2-one (3b)

White powder; mp 141-142°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz ):  $\delta$  8.09 (s, 1H, C<sub>4</sub>-H), 7.48 (d, *J* = 8.6 Hz, 1H, ArH), 7.39 (s, 1H, ArH), 7.29 (d, *J* = 8.6 Hz, 1H, ArH), 2.44 (s, 3H, 6-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.2, 152.8, 143.3 (q, *J* = 4.8 Hz), 135.5, 135.2, 129.1, 121.4 (q, *J* = 272.0 Hz), 117.5 (q, *J* = 33.1 Hz), 116.8, 116.5, 20.7. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  - 65.9(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>11</sub>H<sub>7</sub>O<sub>2</sub>F<sub>3</sub> 228.0398 (M<sup>+</sup>), found 228.0399 (M<sup>+</sup>).

# 7-Methyl-3-(trifluoromethyl)-2H-chromen-2-one (3c)



White powder; mp 120-121 °C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.11 (s, 1H, C<sub>4</sub>-H), 7.49 (d, J = 7.9 Hz, 1H, ArH), 7.19 (d, J = 7.4 Hz, 2H, ArH), 2.50 (s, 3H, 7-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.2, 154.8, 146.4, 143.2 (q, J = 4.9 Hz), 129.1, 126.5, 121.5 (q, J = 271.8 Hz), 117.5, 116.4 (q, J = 33.2 Hz), 114.4, 22.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.0(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>11</sub>H<sub>8</sub>F<sub>3</sub>O<sub>2</sub> 229.0471 [(M+H)<sup>+</sup>], found 229.0469 [(M+H)<sup>+</sup>].

#### 7-Methoxy-3-(trifluoromethyl)-2H-chromen-2-one (3d)



White powder; mp 131-132°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.08 (s, 1H, C<sub>4</sub>-H), 7.50 (d, J = 8.7 Hz, 1H, ArH), 6.92 (d, J = 8.7 Hz, 1H, ArH), 6.85 (s, 1H, ArH), 3.91 (s, 3H, 7-OCH<sub>3</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  164.9, 156.8, 156.4, 143.2 (q, J = 4.7 Hz), 130.5, 121.7 (q, J = 271.3 Hz), 113.8, 113.8 (q, J = 33.2 Hz), 110.3, 100.7, 56.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  - 65.7(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>11</sub>H<sub>7</sub>O<sub>3</sub>F<sub>3</sub> 244.0347 (M<sup>+</sup>), found 244.0350 (M<sup>+</sup>).

#### 2-Oxo-3-(trifluoromethyl)-2H-chromen-7-yl acetate (3e)

CF3

White powder; mp 172-174°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.14 (s, 1H, C<sub>4</sub>-H), 7.62 (d, *J* = 8.5 Hz, 1H, ArH), 7.20 (s, 1H, ArH), 7.16 (d, *J* = 8.5 Hz, 1H, ArH), 2.34 (s, 3H), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  168.3, 155.5, 155.4, 155.2, 142.7 (q, *J* = 4.8 Hz), 130.3, 124.9 (q, *J* = 271.9 Hz), 119.3, 117.0 (q, *J* = 33.3 Hz), 114.4, 100.5, 21.1. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  - 66.2(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>12</sub>H<sub>11</sub>F<sub>3</sub>NO<sub>4</sub> 290.0635 [(M+NH<sub>4</sub>)<sup>+</sup>], found 290.0632 [(M+NH<sub>4</sub>)<sup>+</sup>].

#### 8-Methyl-3-(trifluoromethyl)-2H-chromen-2-one (3f)

White powder; mp 148-149°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.14 (s, 1H, C<sub>4</sub>-H), 7.53 (d, J = 7.4 Hz, 1H, ArH), 7.45 (d, J = 7.4 Hz, 1H, ArH), 7.28 (m, 1H, ArH), 2.48 (s, 3H, 8-CH<sub>3</sub>) . <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.1, 153.0, 143.6 (q, J = 4.7 Hz), 135.7, 127.1, 126.7, 124.8, 121.4 (q, J = 272.0 Hz), 117.3 (q, J = 33.2 Hz), 116.5, 15.4. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.1(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>F<sub>3</sub> 229.0471 [(M+H)<sup>+</sup>], found 229.0472 [(M+H)<sup>+</sup>].

#### 5,8-Dimethyl-3-(trifluoromethyl)-2H-chromen-2-one (3g)



White powder; mp 134-135°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.33 (s, 1H, C<sub>4</sub>-H), 7.39 (d, J = 7.5 Hz, 1H, ArH), 7.08 (d, J = 7.5 Hz, 1H, ArH), 2.55 (s, 3H, 5-CH<sub>3</sub>), 2.43 (s, 3H, 8-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.0, 153.6, 140.5 (q, J = 4.8 Hz), 135.5, 135.3, 126.0, 124.2, 121.6 (q, J = 272.0 Hz), 116.3 (q, J = 33.0 Hz), 115.5, 18.1, 15.3. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -65.9(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub> 242.0555 (M<sup>+</sup>), found 242.0559 (M<sup>+</sup>).

#### 7-Chloro-3-(trifluoromethyl)-2H-chromen-2-one (3h)



White powder; mp 104-105°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.12 (s, 1H, C<sub>4</sub>-H), 7.56 (d, J = 8.4 Hz, 1H, ArH), 7.42 (s, 1H, ArH), 7.36 (d, J = 8.4 Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  150.4, 150.1, 137.7 (q, J = 4.7 Hz), 136.0, 125.5, 121.3, 116.4 (q, J = 272.1 Hz), 113.3 (q, J = 33.9 Hz), 112.6, 100.6. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.3(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>10</sub>H<sub>4</sub>F<sub>3</sub>NaO<sub>2</sub>Cl 270.9744 [(M+Na)<sup>+</sup>], found 270.9744 [(M+Na)<sup>+</sup>].

#### 6-Nitro-3-(trifluoromethyl)-2H-chromen-2-one (3i)

Yellow powder; mp 190-192°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz): δ 8.58 (s, 1H, ArH), 8.54 (d, *J* = 9.1 Hz, 1H, ArH), 8.26 (s, 1H, C<sub>4</sub>-H), 7.56 (d, *J* = 9.1 Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz): δ 157.8, 154.1, 144.4, 142.1 (q, *J* = 4.7 Hz), 128.8, 125.2, 120.7 (q,

J = 273.2 Hz), 120.0 (q, J = 34.7 Hz), 118.4, 116.8. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.6(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>10</sub>H<sub>4</sub>O<sub>4</sub>NF<sub>3</sub> 259.0092 (M<sup>+</sup>), found 259.0090 (M<sup>+</sup>).

8-Chloro-3-(trifluoromethyl)-2H-chromen-2-one (3j)

White powder; mp 82-83 °C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.17 (s, 1H, C<sub>4</sub>-H), 7.74 (d, *J* = 8.0 Hz, 1H, ArH), 7.56 (d, *J* = 7.6 Hz, 1H, ArH), 7.34 (t, *J* = 7.9 Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  154.7, 150.3, 143.0 (q, *J* = 4.9 Hz), 134.7, 128.0, 125.5, 122.1, 121.1 (q, *J* = 272.3 Hz), 118.5 (q, *J* = 33.6 Hz), 117.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.3(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>10</sub>H<sub>4</sub>O<sub>2</sub>F<sub>3</sub>Cl 247.9852 (M<sup>+</sup>), found 247.9842 (M<sup>+</sup>).

### 6,8-Dichloro-3-(trifluoromethyl)-2H-chromen-2-one (3k)



White powder; mp 123-124 °C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  8.10 (s, 1H, C<sub>4</sub>-H), 7.75 (d, *J* = 2.3 Hz, 1H, ArH), 7.55 (d, *J* = 2.3 Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  154.0, 149.0, 141.8 (q, *J* = 4.9 Hz), 134.2, 130.5, 127.1, 123.2, 121.0 (q, *J* = 279.7 Hz), 119.7 (q, *J* = 33.9 Hz), 118.5. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -66.4(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>10</sub>H<sub>3</sub>O<sub>2</sub>F<sub>3</sub>Cl<sub>2</sub> 281.9462 (M<sup>+</sup>), found 281.9456 (M<sup>+</sup>).

#### 4,6-Dimethyl-3-(trifluoromethyl)-2H-chromen-2-one (3l)



White powder; mp 158-159°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.58 (s, 1H, ArH), 7.45 (d, J = 8.4 Hz, 1H, ArH), 7.25 (d, J = 8.4 Hz, 1H, ArH), 2.67 (s, 3H, 4-CH<sub>3</sub>), 2.46 (s, 3H, 6-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.0, 154.9, 151.1, 135.0, 134.6, 125.6, 122.8 (q, J = 275.3 Hz), 118.6, 116.8, 115.1 (q, J = 30.2 Hz), 21.1, 15.6 (q, J = 3.9 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -56.7(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub> 242.0555 (M<sup>+</sup>), found 242.0551 (M<sup>+</sup>).

#### 7-Methoxy-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (3m)



White powder; mp 140-141°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.70 (d, J = 9.0 Hz, 1H, ArH), 6.92(d, J = 9.0 Hz, 1H, ArH), 6.80 (s, 1H, ArH), 3.90 (s, 3H, 7-OCH<sub>3</sub>), 2.63 (s, 3H, 4-CH<sub>3</sub>), <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  164.4, 156.4, 156.1, 127.1, 123.1 (q, J =

274.8 Hz), 113.4, 112.4, 120.0 (q, J = 30.3 Hz), 100.4, 56.0, 15.7 (q, J = 3.7 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz): δ - 56.4(s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>12</sub>H<sub>9</sub>O<sub>3</sub>F<sub>3</sub> 258.0504 (M<sup>+</sup>), found 258.0501 (M<sup>+</sup>).

4-Methyl-2-oxo-3-(trifluoromethyl)-2H-chromen-7-yl acetate (3n)

CF<sub>3</sub>

White powder; mp 134-135°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.81 (d, J = 9.4 Hz, 1H, ArH), 7.17-7.15 (m, 2H, ArH), 2.67 (d, J = 2.0 Hz, 3H, 4-CH<sub>3</sub>), 2.35 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  168.3, 155.5, 154.7, 154.5, 153.7, 127.0, 122.7 (q, J = 275.2 Hz), 118.8, 116.7, 114.7 (q, J = 29.6 Hz), 110.3, 21.1, 15.8 (q, J = 4.0 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  - 56.8(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>13</sub>H<sub>10</sub>F<sub>3</sub>O<sub>4</sub> 287.0526 [(M+H)<sup>+</sup>], found 287.0521 [(M+H)<sup>+</sup>].

# 7-Chloro-4-methyl-3-(trifluoromethyl)-2H-chromen-2-one (30)



White powder; mp 112-113°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.74 (d, *J* = 8.5 Hz, 1H, ArH), 7.47-7.29 (m, 2H, ArH), 2.67 (q, *J* = 2.1 Hz, 3H, 4-CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  155.4, 154.6, 153.5, 140.4, 127.2, 125.8, 122.8 (q, *J* = 275.4 Hz), 117.9, 117.5, 115.6 (q, *J* = 30.6 Hz), 21.1, 16.0 (q, *J* = 4.0 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -56.9(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>11</sub>H<sub>7</sub>F<sub>3</sub>O<sub>2</sub>Cl 263.0081 [(M+H) <sup>+</sup>], found 263.0080 [(M+H) <sup>+</sup>].

# 4-Methoxy-3-(trifluoromethyl)-2H-chromen-2-one (3p)



White powder; mp 67-68°C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.84 (d, J = 8.2 Hz, 1H, ArH), 7.67 (t, J = 7.8 Hz, 1H, ArH), 7.44-7.31 (m, 2H, ArH), 4.18 (s, 3H, 4-OCH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  169.6, 157.8, 153.7, 134.6, 127.3, 121.8 (q, J = 273.5 Hz), 117.1, 116.1, 105.7 (q, J = 31.9 Hz), 64.7 (d, J = 2.8 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -58.8 (s, 3F). ESI-HRMS: Anal. Calcd for C<sub>11</sub>H<sub>8</sub>F<sub>3</sub>O<sub>3</sub> 245.0420 [(M+H)<sup>+</sup>], found 245.0417 [(M+H)<sup>+</sup>].

# 4-Phenyl-3-(trifluoromethyl)-2H-chromen-2-one (3q)

CF<sub>3</sub>

#### White powder; mp 138-139 °C;

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz):  $\delta$  7.64 (t, *J* = 8.4 Hz, 1H, ArH), 7.51-7.53 (m, 3H, ArH), 7.40 (d, *J* = 7.9 Hz, 1H, ArH), 7.25 (dd, *J* = 5.8, 3.6 Hz, 2H, ArH), 7.19 (t, *J* = 7.7 Hz, 1H, ArH), 7.00 (d, *J* = 7.3 Hz, 1H, ArH). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75MHz):  $\delta$  156.9, 156.3, 153.4, 134.1, 132.8, 129.3, 128.5, 127.3, 127.2, 124.8, 121.9 (q, *J* = 275.2 Hz), 119.4, 116.8, 114.8 (q, *J* = 30.1 Hz). <sup>19</sup>F NMR (CDCl<sub>3</sub>, 283MHz):  $\delta$  -57.5(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>16</sub>H<sub>10</sub>F<sub>3</sub>O<sub>2</sub> 291.0627 [(M+H)<sup>+</sup>], found 291.0624 [(M+H)<sup>+</sup>].

#### 3-(Trifluoromethyl)quinolin-2(1H)-one (5a)

White powder; mp 213-215 °C;

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz): δ 12.31(s, 1H, NH), 8.56 (s, 1H, C<sub>4</sub>-H), 7.86 (d, J = 6.8 Hz, 1H, ArH), 7.65 (d, J = 7.2 Hz, 1H, ArH), 7.26-7.38 (m, 2H, ArH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75MHz): δ 158.1, 141.2 (q, J = 5.3 Hz), 140.5, 133.6, 130.2, 123.2 (q, J = 271.7 Hz), 123.1, 120.1 (q, J = 30.0 Hz), 117.4, 115.7. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 283MHz): δ -64.1(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>NO 214.0474 [(M+H)<sup>+</sup>], found 214.0471 [(M+H)<sup>+</sup>].

#### 6-Bromo-3-(trifluoromethyl)quinolin-2(1H)-one (5b)



White powder; mp 230-232°C;

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz):  $\delta$  12.44 (s, 1H, NH), 8.53 (s, 1H, C<sub>4</sub>-H), 8.12 (s, 1H, ArH), 7.80 (d, *J* = 8.3 Hz, 1H, ArH), 7.31 (d, *J* = 8.6 Hz, 1H, ArH). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75MHz):  $\delta$  157.8, 140.2 (q, *J* = 5.4 Hz), 139.5, 136.0, 132.0, 122.9 (q, *J* = 264.0 Hz), 121.0 (q, *J* = 33.1 Hz), 119.0, 117.9, 114.5. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 283MHz):  $\delta$  -64.4(s, 3F). ESI-HRMS: Anal. Calcd for C<sub>10</sub>H<sub>6</sub>F<sub>3</sub>NOBr 291.9579 [(M+H)<sup>+</sup>], found 291.9575 [(M+H)<sup>+</sup>].

# 2-Methyl-6-phenyl-5-(trifluoromethyl)pyrimidin-4(3H)-one (5c)

White powder; mp 194-196 °C;

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz): δ 13.21 (s, 1H, NH), 7.44-7.47 (m, 3H, ArH), 7.38-7.41 (m, 2H, ArH), 2.37 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75MHz): δ 165.3, 162.0, 159.8, 138.6, 130.0, 128.3, 128.2, 123.8 (q, *J* = 272.9 Hz), 110.6 (q, *J* = 29.4 Hz), 21.9. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 283MHz): δ -56.6 (s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>12</sub>H<sub>9</sub>F<sub>3</sub>N<sub>2</sub>O 254.0667 (M<sup>+</sup>), found 254.0674 (M<sup>+</sup>).

#### 2-Methyl-6-(p-tolyl)-5-(trifluoromethyl)pyrimidin-4(3H)-one (5d)



White powder; mp 218-219 °C;

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz):  $\delta$  13.15 (s, 1H, NH), 7.31 (d, *J* = 8.1 Hz, 2H, ArH), 7.26 (d, *J* = 8.1 Hz, 2H, ArH), 2.36 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75MHz):  $\delta$  165.2, 161.8, 160.1, 139.8, 135.7, 128.9, 128.4, 124.0 (q, *J* = 272.9 Hz), 110.3 (q, *J* = 30.9 Hz), 21.9, 21.4. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 283MHz):  $\delta$  -56.6 (s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>13</sub>H<sub>11</sub>F<sub>3</sub>N<sub>2</sub>O 268.0823 (M<sup>+</sup>), found 268.0828 (M<sup>+</sup>).

2-Phenyl-6-(p-tolyl)-5-(trifluoromethyl)pyrimidin-4(3H)-one (5e)



White powder; mp 269-271 °C;

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400MHz): δ 13.49 (s, 1H, NH), 8.15 (d, J = 6.6 Hz, 2H, ArH), 7.43-7.64 (m, 5H, ArH), 7.30 (d, J = 7.0 Hz, 2H, ArH), 2.39 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75MHz): δ 165.2, 160.8, 158.4, 140.1, 135.8, 133.1, 131.8, 129.2, 128.9, 128.7, 124.0 (q, J = 272.9 Hz), 110.5 (q, J = 30.8 Hz), 21.4. <sup>19</sup>F NMR (DMSO-*d*<sub>6</sub>, 283MHz): δ -56.6 (s, 3F). TOF-HRMS (EI): Anal. Calcd for C<sub>18</sub>H<sub>13</sub>F<sub>3</sub>N<sub>2</sub>O 330.0980 (M<sup>+</sup>), found 330.0987 (M<sup>+</sup>).



3a















3d









S16



3f













3h











3j













31









S28















Зр









S34















5c



S38









-2000

1500

1000

500

-0

-500



5e



S41



