

# Synthesis of 4-(trifluoromethyl) coumarins using nano sulfated-titania as solid acid catalyst under solvent-free conditions

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## 7-Hydroxy-4-trifluoromethyl-coumarin (**3a**)

Light yellow solid; m.p. 178-180°C; <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 9.95-10.15 (brs, 1H, -OH), 7.54 (d, *J* = 8.84 Hz, 1H, Ar-H), 6.86 (d, *J* = 8.84 Hz, 1H, Ar-H), 6.80 (s, 1H, Ar-H), 6.714 (s, 1H, -CH=); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 162.09, 158.73, 155.78, 140.44; 139.93; 139.42; 138.91" (-C-CF<sub>3</sub>, *J* = 32.05 Hz), 125.98, (128.20, 123.82, 119.44, 115.06) (-CF<sub>3</sub>, *J* = 275.62 Hz) 113.92, 111.73, 105.05, 102.99; Anal. Calcd. For C<sub>10</sub>H<sub>5</sub>F<sub>3</sub>O<sub>3</sub>: C, 53.11; H, 2.32 %. Found: C, 53.31; H, 2.40; IR (KBr): ν 3425, 1720, 1604 cm<sup>-1</sup>.

## 8-Hydroxy-4-trifluoromethyl-coumarin (**3b**)

Yellow solid; 275°C; <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 10.47-10.63 (brs, 1H, -OH), 7.15-7.22 (m, 2H, Ar-H), 7.04-7.09 (m, 1H, Ar-H), 6.94 (s, 1H, -CH=); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 158.16, 145.27, 142.53, (140.39, 139.87, 139.36, 138.85) (-C-CF<sub>3</sub>, *J* = 32.08 Hz), 125.03, (128.12, 123.74, 119.36, 114.98) (-CF<sub>3</sub>, *J* = 275.46 Hz) 119.15, 116.93, 114.29, 113.81; Anal. Calcd. For C<sub>10</sub>H<sub>5</sub>F<sub>3</sub>O<sub>3</sub>: C, 52.81; H, 2.23 %. Found: C, 53.31; H, 2.40; IR (KBr): ν 3405, 1726, 1607 cm<sup>-1</sup>.

## 6-Hydroxy-4-trifluoromethyl-coumarin (**3c**)

Yellow solid; m.p. 208-210°C; <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 10.04 (s, 1H, -OH), 7.37 (d, *J* = 9.00 Hz, 1H, Ar-H), 7.15 (dd, *J* = 9.00, 2.70 Hz, 1H, Ar-H), 7.01 (t, *J* = 2.20 Hz, 1H, Ar-H), 6.96 (s, 1H, -CH=); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 158.51, 154.08, 146.99, 139.73;

139.22; 138.71; 138.20" ( $-\underline{\text{C}}\text{-CF}_3$ ,  $J = 31.94$  Hz), (128.14, 123.76, 119.39, 115.11) ( $-\underline{\text{C}}\text{F}_3$ ,  $J = 275.18$  Hz), 121.23, 118.40, 117.15, 113.32, 108.62; Anal. Calcd. For  $\text{C}_{10}\text{H}_5\text{F}_3\text{O}_3$ : C, 52.19; H, 2.19 %. Found: C, 53.31; H, 2.40; IR (KBr):  $\nu$  3412, 1720, 1611  $\text{cm}^{-1}$ .

*5,7-Dihydroxy-4-trifluoromethyl-coumarin (3d)*

Yellow solid; m.p. 249-251°C (lit.[27] 250-252 °C);  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  10.25-10.84 (brs, 2H,  $-\text{OH}$ ), 6.48 (s, 1H,  $-\underline{\text{C}}\text{H}=\text{)$ , 6.24-6.29 (m, 2H, Ar- $\underline{\text{H}}$ );  $^{13}\text{C}$  NMR (62.9 MHz, DMSO- $d_6$ ):  $\delta$  162.30, 159.03, 156.91, 155.79, "140.25; 139.73; 139.20; 138.67" ( $-\underline{\text{C}}\text{-CF}_3$ ,  $J = 33.05$  Hz), "128.23; 123.87; 119.49; 116.11" ( $-\underline{\text{C}}\text{F}_3$ ,  $J = 275.06$  Hz), 110.53, 99.46, 96.24, 95.143; Anal. Calcd. For  $\text{C}_{10}\text{H}_5\text{F}_3\text{O}_4$ : C, 48.80; H, 2.05 %. Found: C, 47.36; H, 2.15; IR (KBr):  $\nu$  3417, 1724, 1601  $\text{cm}^{-1}$ .

*7,8-Dihydroxy-4-trifluoromethyl-coumarin (3e)*

Yellow solid; m.p. 213-215°C;  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  10.54 (s, 1H,  $-\text{OH}$ ), 9.60 (s, 1H,  $-\text{OH}$ ), 7.20 (d,  $J = 8.82$  Hz, 1H, Ar- $\underline{\text{H}}$ ), 7.05 (d,  $J = 8.82$  Hz, 1H, Ar- $\underline{\text{H}}$ ), 6.76 (s, 1H,  $-\underline{\text{C}}\text{H}=\text{)$ ,  $^{13}\text{C}$  NMR (62.9 MHz, DMSO- $d_6$ ):  $\delta$  158.76, 150.47, 143.98, "140.90; 140.40; 139.90; 139.40" ( $-\underline{\text{C}}\text{-CF}_3$ ,  $J = 31.45$  Hz) 132.85, "128.28; 123.90; 119.52; 115.14" ( $-\underline{\text{C}}\text{F}_3$ ,  $J = 275.50$  Hz), 115.18, 113.04, 111.66, 105.90; Anal. Calcd. For  $\text{C}_{10}\text{H}_5\text{F}_3\text{O}_4$ : C, 48.80; H, 2.05 %. Found: C, 48.28; H, 2.12; IR (KBr):  $\nu$  3349, 1720, 1604  $\text{cm}^{-1}$ .

*7-Methoxy-4-trifluoromethyl-coumarin (3f)*

Pink solid; m.p. 158-160°C;  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  7.61 (d,  $J = 8.88$  Hz, 1H, Ar- $\underline{\text{H}}$ ), 7.12 (s, 1H, Ar- $\underline{\text{H}}$ ), 7.05 (d,  $J = 8.44$  Hz, 1H, Ar- $\underline{\text{H}}$ ), 6.81 (s, 1H,  $-\underline{\text{C}}\text{H}=\text{)$ , 3.86 (s, 3H,  $-\text{OCH}_3$ );  $^{13}\text{C}$  NMR (62.9 MHz, DMSO- $d_6$ ):  $\delta$  163.05, 158.63, 155.80, "140.16; 139.65; 139.14; 138.63" ( $-\underline{\text{C}}\text{-CF}_3$ ,  $J = 32.01$  Hz), "128.18; 123.81; 119.43; 115.05" ( $-\underline{\text{C}}\text{F}_3$ ,  $J = 275.48$  Hz), 125.72, 113.08, 106.25, 101.56, 56.08; Anal. Calcd. For  $\text{C}_{11}\text{H}_7\text{F}_3\text{O}_3$ : C, 54.11; H, 2.89 %. Found: C, 53.92; H, 2.79; IR (KBr):  $\nu$  1716, 1605  $\text{cm}^{-1}$ .

*7-Hydroxy-4-methyl-coumarin (3g)*

White solid; m.p. 183-185°C (lit. [28] 185-187 °C); <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 10.49 (s, 1H, -OH), 7.56 (d, *J* = 8.50 Hz, 1H, Ar-H), 6.79 (d, *J* = 8.50 Hz, 2H, Ar-H), 6.67 (s, 1H, Ar-H), 6.09 (s, 1H, -CH=), 2.33 (s, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 161.06, 160.20, 154.73, 153.34, 126.40, 112.73, 111.89, 110.15, 102.07, 17.98.

*8-Hydroxy-4-methyl-coumarin (3i)*

White solid; <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 9.31-9.57 (brs, 1H, -OH), 6.98-7.22 (m, 3H, Ar-H), 6.21 (s, 1H, -CH=), 2.44 (s, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 158.52, 153.52, 144.71, 126.20, 124.06, 120.49, 118.16, 115.03, 114.24, 18.33.

*6-Hydroxy-4-methyl-coumarin (3j)*

White solid; m.p. 242-244°C (lit.[29] 242-244°C); <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 9.71 (s, 1H, -OH), 7.17-7.23 (m, 1H, Ar-H), 7.00-7.04 (m, 2H, Ar-H), 6.32 (s, 1H, -CH=), 2.34 (s, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 160.48, 158.93, 157.99, 146.65, 122.51, 120.63, 120.21, 119.67, 114.73, 23.25.

*5,7-Dihydroxy-4-methyl-coumarin (3k)*

White solid; m.p. 284-285°C (lit.[30] 283-285°C); <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 10.49 (s, 1H, -OH), 10.27 (s, 1H, -OH), 6.23 (s, 1H, Ar-H), 6.14 (s, 1H, Ar-H), 5.81 (s, 1H, -CH=), 2.45 (s, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 161.49, 160.53, 158.37, 156.93, 155.41, 109.25, 102.52, 99.49, 94.94, 23.87.

*7,8-Dihydroxy-4-methyl-coumarin (3l)*

White solid; m.p. 240-242°C (lit.[31] 241-243°C); <sup>1</sup>H NMR (250 MHz; DMSO-d<sub>6</sub>): δ 9.1-10.1 (brs, 2H, -OH), 7.07 (d, *J* = 8.50 Hz, 1H, Ar-H), 6.80 (d, *J* = 8.50 Hz, 1H, Ar-H), 6.08 (s, 1H, -CH=), 2.31 (s, 3H, -CH<sub>3</sub>); <sup>13</sup>C NMR (62.9 MHz, DMSO-d<sub>6</sub>): δ 160.64, 154.33, 149.84, 147.76, 132.59, 115.90, 113.20, 112.55, 110.62, 18.66.

*7-Methoxy-4-methyl-coumarin (3m)*

White solid; m.p. 155-158°C (lit.[27] 156-158°C);  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  7.67 (d,  $J = 8.50$  Hz, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.92 (d,  $J = 2.5$  Hz, 1H, Ar-H), 6.18 (s, 1H, -CH=), 3.83 (s, 3H, -OCH<sub>3</sub>), 2.37 (s, 3H, -CH<sub>3</sub>);  $^{13}\text{C}$  NMR (62.9 MHz, DMSO- $d_6$ ):  $\delta$  162.81, 160.59, 155.22, 153.88, 126.89, 113.54, 112.55, 111.56, 101.14, 56.35, 18.58.

*4-Methyl-coumarin (3n)*

Colorless crystals; m.p. 78-80°C (lit.[27] 83-84°C);  $^1\text{H}$  NMR (250 MHz; DMSO- $d_6$ ):  $\delta$  7.30–7.65 (m, 4H, Ar-H), 6.48 (s, 1H, -CH=), 2.62 (s, 3H, Me);  $^{13}\text{C}$  NMR (62.9 MHz, DMSO- $d_6$ ):  $\delta$  161.56, 160.70, 155.24, 153.83, 126.90, 113.24, 112.41, 110.66, 102.59, 18.48.