

Supporting Information

Catalyst-Free Electrochemical Trifluoromethylation of Coumarins

Using CF₃SO₂NHNHBoc as the CF₃ Source

Nannan Cen,^a Han Wang,^a Yicheng Zhou,^a Ruoqu Gong,^a

Dandan Sui,^a Wenbo Chen,^{*ab}

^aShanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai University of Electric Power, Shanghai 200090, China

^bCAS Key Laboratory of Energy Regulation Materials, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

E-mail address: wenbochen@shiep.edu.cn

1. General Information

All reagents unless otherwise noted were obtained from commercial sources and used without further purification. Electrochemical reactions were conducted using an HY3005MT potentiostat in constant current mode. Electrochemical reactions were performed under air using an undivided micro sealed cell (10 mL). Platinum electrodes (1 cm × 1 cm × 0.02 cm), graphite rod electrodes (φ6 mm) and reticulated vitreous carbon (100 PPI) are commercially available from Shanghai Chuxi Industrial Co., Ltd. All these reactions were monitored by TLC with silica gel GF254 precoated plates. The products were isolated by column chromatography on silica gel (300–400 mesh size). Cyclic voltammograms were recorded on a CHI 660E potentiostat. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on INOVA 400 instruments with the operating frequency of 400 MHz, 101 MHz and 376 MHz, respectively. Chemical shifts for ¹H NMR were reported in ppm relative to TMS. All ¹³C NMR spectra were reported in ppm relative to deuterated chloroform (77.00 ppm). The following abbreviations are used to set multiplicities: s= singlet, d= doublet, t= triplet, dd= doublet of doublets, q= quartet, m= multiplet. Coupling constants (J) were reported in Hertz (Hz).

2. Preparation procedure of CF₃SO₂NHNHBoc

A solution of triflic anhydride (1equiv, 40 mmol, 6.73 mL,) in dichloromethane (20 mL) was added dropwise to a mixture of NH₂NHBoc (1equiv, 40.0 mmol, 5.29 g) and triethylamine (1.1 equiv, 44 mmol, 6.12 mL) in dichloromethane (200 mL) under nitrogen at -78 °C. The mixture was allowed to warm to room temperature and stirred for 2 h, then washed twice with water, once with 5% aqueous hydrochloric acid, and once with water, dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuo. The residue was purified by silica gel column chromatography, eluting with ethyl acetate/petroleum ether (5:1), to give the CF₃SO₂NHNHBoc (6.31 g, 60%).

3. General Procedure for the Electrolysis

Coumarin derivatives (0.4 mmol, 1 equiv), CF₃SO₂NHNHBoc **1** (1.2 mmol, 3 equiv), ⁿBu₄NOAc (0.8 mmol, 2 equiv) and MeCN/H₂O (v/v = 8/1, 5 mL) were added to an undivided cell (10 mL) with a stir bar. The cell was equipped with a graphite rod (φ6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.02 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 60 °C (oil bath temperature). When the reaction was finished, the mixture was diluted with water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel.

4. Experimental devices

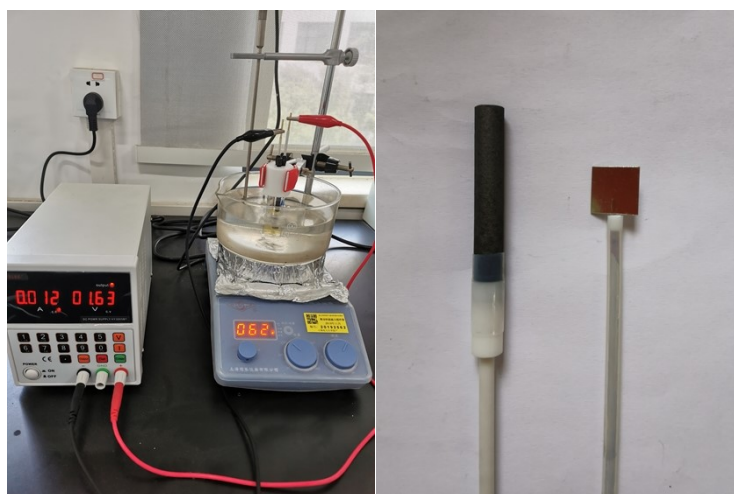
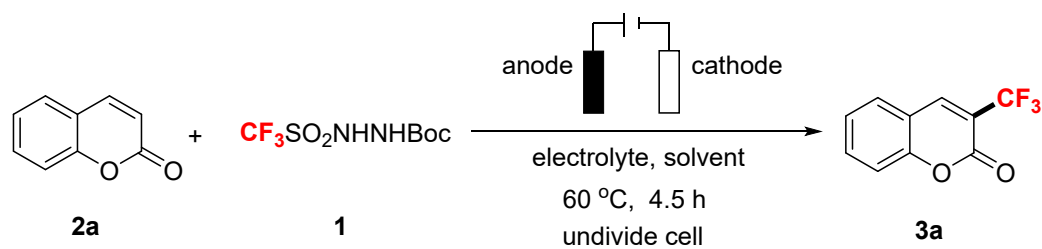


Figure 1. Electrolysis experiment and electrodes material

5. Optimization Studies

Table1. Optimization of Reaction Conditions^[a]

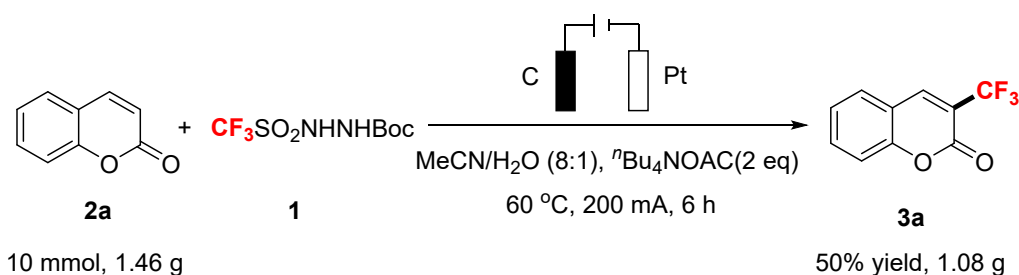


Entry	Anode-Cathode	Electrolyte	Solvent	Constant current	Yield (%) ^b
1	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN	12 mA	28
2	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (1:4)	12 mA	19
3	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (4:1)	12 mA	55
4	C-Pt	<i>n</i>Bu₄NOAc	CH₃CN/H₂O (8:1)	12 mA	64
5	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (10:1)	12 mA	56
6	C-Pt	<i>n</i> Bu ₄ NOAc	DMSO	12 mA	0
7 ^c	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	42
8 ^d	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	35
9	C-Pt	<i>n</i> Bu ₄ NClO ₄	CH ₃ CN/H ₂ O (8:1)	12 mA	43
10	C-Pt	Et ₄ NClO ₄	CH ₃ CN/H ₂ O (8:1)	12 mA	51
11	C-Pt	<i>n</i> Bu ₄ NPF ₆	CH ₃ CN/H ₂ O (8:1)	12 mA	38
12	C-Pt	<i>n</i> Bu ₄ NI	CH ₃ CN/H ₂ O (8:1)	12 mA	0
13	C-Pt	Et ₄ NOTs	CH ₃ CN/H ₂ O (8:1)	12 mA	0
14	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	10 mA	48
15	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	20 mA	42
16 ^e	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	54
17 ^f	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	56
18	Pt-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	20
19	RVC-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	40

20	Pt-C	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	15
21 ^g	C-Pt	<i>n</i> Bu ₄ NOAc	CH ₃ CN/H ₂ O (8:1)	12 mA	0

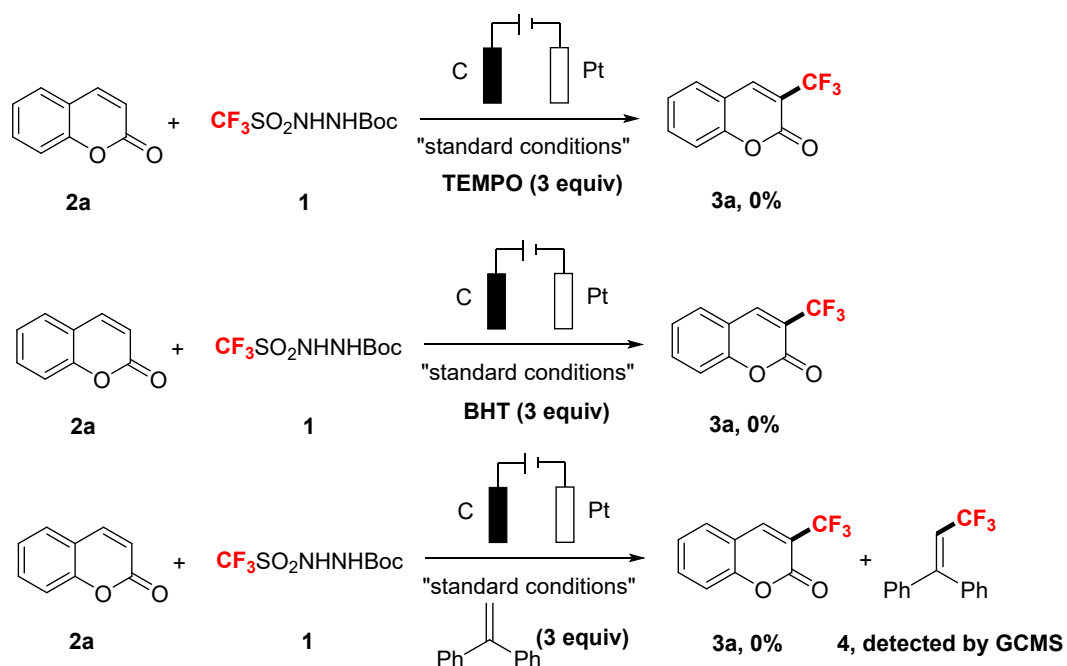
^aReaction conditions: graphite rod (ϕ 6 mm) anode, Pt plate (10 mm × 10 mm) cathode, **1a** (0.2 mmol), **2a** (0.6 mmol), electrolyte *n*Bu₄NOAc (2 equiv), constant current (12 mA), Solvent (5 mL) in an undivided cell, air, 60 °C, 4.5 h. ^bIsolated yield. ^cTemperature is 40 °C. ^dTemperature is 80 °C. ^eSolvent (3 mL) in an undivided cell. ^fSolvent (10 mL) in an undivided cell. ^gNo electricity.

6. Gram-Scale Experiment

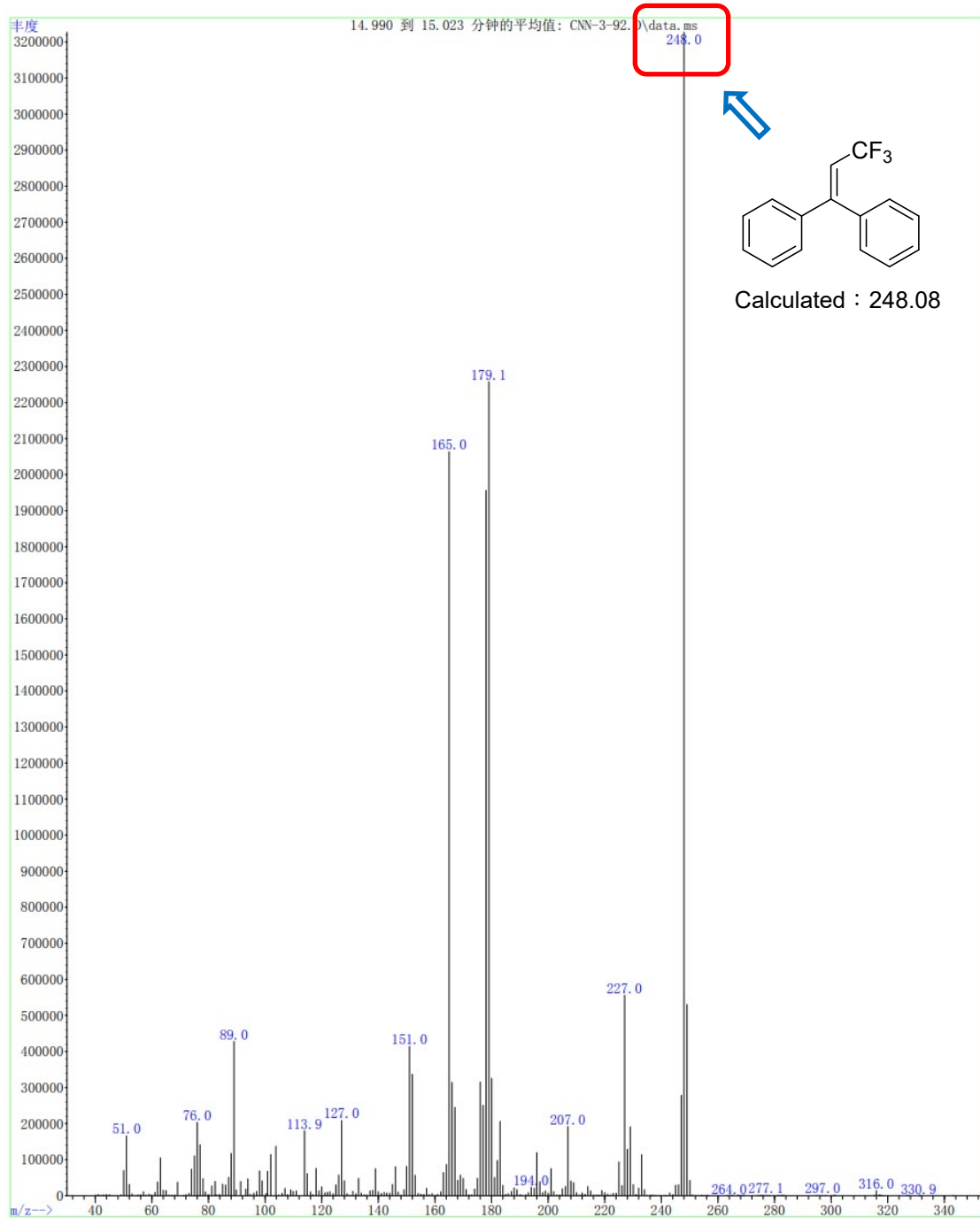


To an undivided cell (250 mL) were sequentially added the coumarins **2a** (10 mmol, 1.46 g), CF₃SO₂NHNHBoc **1** (30 mmol, 7.93 g), *n*Bu₄NOAc (1 mmol) and CH₃CN/H₂O (v/v = 8/1, 125 mL). The cell was equipped with a graphite (ϕ6 mm) as the anode and platinum plate (1 cm × 1 cm × 0.02 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 200 mA at 60 °C for 6 h. When the reaction was finished, the mixture was diluted with water and extracted with EtOAc. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to provide the desired product **3a** (50% yield, 1.08 g).

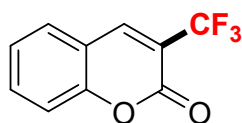
7. Free Radical-Trapping Experiment



To an undivided cell (10 mL) were sequentially added the coumarins **2a** (0.2 mmol), $\text{CF}_3\text{SO}_2\text{NHNHBoc}$ **1** (0.6 mmol, 3 equiv), $n\text{Bu}_4\text{NOAc}$ (0.4 mmol, 2 equiv), radical-trapping reagent (TEMPO, BHT or 1,1-Diphenylethylene) (0.6 mmol, 3 equiv), and $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (v/v = 8/1, 5 mL). The cell was equipped with a graphite rod ($\phi 6$ mm) as the anode and platinum plate (1 cm \times 1 cm \times 0.02 cm) as the cathode and connected to a DC regulated power supply. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at 60 °C (oil bath temperature). The trapping product **4** was detected by GCMS, indicating this electrochemical transformation might go through a free radical process.

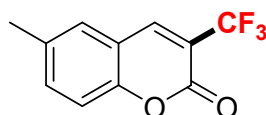


8. Characterization Data for the Trifluoromethylation Products



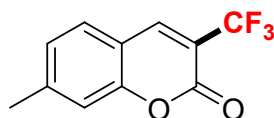
3a

3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3a)^{1, 2}. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (58.5 mg, 68%); ¹H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1H), 7.68 (m, J = 16.0 Hz, 1H), 7.62 (dd, J = 1.5, 7.7 Hz, 1H), 7.42-7.40 (m, 2H). ¹³C NMR (101 MHz, CDCl₃): δ 155.88 (s), 154.67 (s), 143.35 (q, J = 4.8 Hz), 134.45 (s), 129.49 (s), 125.29 (s), 121.36 (q, J = 272.7 Hz), 117.78 (q, J = 33.3 Hz), 117.04 (s), 116.81 (s). ¹⁹F NMR (376 MHz, CDCl₃): δ -66.24 (s, 3F).



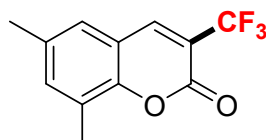
3b

6-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3b)^{1, 2}. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (54.7 mg, 60%); ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.40 (s, 1H), 7.26 (s, 1H), 2.45 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 156.03 (s), 152.79 (s), 143.27 (q, J = 5.1 Hz), 135.48 (s), 135.18 (s), 129.10 (s), 120.47 (q, J = 273.7 Hz), 117.51 (q, J = 33.3 Hz), 116.68 (s), 116.52 (s), 20.62 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -66.18 (s, 3F).



3c

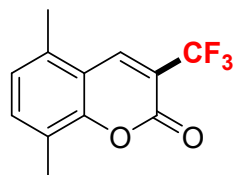
6-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3c)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (59.2 mg, 65%); ¹H NMR (CDCl₃, 400 MHz): δ 8.12 (s, 1H), 7.49 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 2.51 (s, 3H). ¹³C NMR (CDCl₃, 101 MHz): δ 156.22(s), 154.81(s), 146.43(s), 143.31 (q, J = 4.0 Hz), 129.16(s), 126.58(s), 121.6 (q, J = 272.7 Hz), 117.11(s), 116.40 (q, J = 33.3 Hz), 114.44(s), 22.08(s). ¹⁹F NMR (CDCl₃, 376 MHz): δ -66.05(s, 3F).



3d

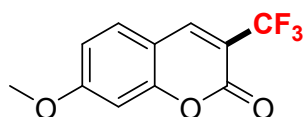
6,8-Dimethyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3d)². The product was

purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1) as a white powder (52.3 mg, 54%); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1H), 7.34 (s, 1H), 7.22 (s, 1H), 2.44 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 156.32 (s), 151.24 (s), 143.59 (q, $J = 4.8$ Hz), 136.93 (s), 134.61 (s), 126.78 (s), 126.32 (s), 121.56 (q, $J = 272.7$ Hz), 117.25 (q, $J = 38.4$ Hz), 116.37 (s), 20.64 (s), 15.30 (s); ^{19}F NMR (376 MHz, CDCl_3) δ -66.20 (s, 3F).



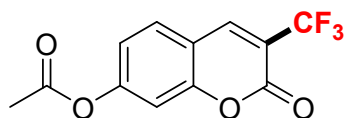
3e

5,8-Dimethyl-3-(trifluoromethyl)-2H-chromen-2-one (3e)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (38.7 mg, 40%); ^1H NMR (CDCl_3 , 400 MHz): δ 8.33 (m, 1H), 7.39 (d, $J = 7.7$ Hz, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 2.55 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (CDCl_3 , 101 MHz): δ 156.01(s), 153.62(s), 140.49 (q, $J = 4.8$ Hz), 135.48(s), 135.35(s), 126.02(s), 124.26(s), 121.67 (q, $J = 273.7$ Hz), 116.35 (q, $J = 32.3$ Hz), 115.57(s), 18.06(s), 15.25(s). ^{19}F NMR (CDCl_3 , 376 MHz): δ -65.96(s, 3F).



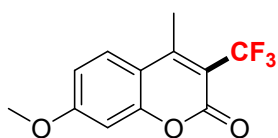
3f

7-Methoxy-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3f)^{1, 2}. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (68.3 mg, 70%); ^1H NMR (400 MHz, CDCl_3): δ 8.08 (s, 1H), 7.50 (d, $J = 8.7$ Hz, 1H), 6.93 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.86 (d, $J = 2.4$ Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 165.02 (s), 156.91 (s), 156.35 (s), 143.23 (q, $J = 4.1$ Hz), 130.54 (s), 121.78 (q, $J = 272.0$ Hz), 113.94 (q, $J = 33.3$ Hz), 113.76 (s), 110.43 (s), 100.78 (s), 56.06 (s). ^{19}F NMR (376 MHz, CDCl_3): δ -65.73 (s).



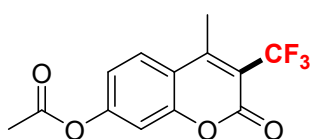
3g

7-Acetyloxy-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3g)^{1, 2}. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 10:1) as a white powder (67.5 mg, 62%); ^1H NMR (400 MHz, CDCl_3): δ 8.15 (s, 1H), 7.63 (d, $J = 8.5$ Hz, 1H), 7.21 (d, $J = 2.2$ Hz, 1H), 7.17 (dd, $J = 8.5, 2.2$ Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3): δ 168.49 (s), 155.70 (s), 155.37 (s), 155.24 (s), 142.90 (q, $J = 4.9$ Hz), 130.39 (s), 121.34 (q, $J = 272.7$ Hz), 119.43 (s), 116.99 (q, $J = 33.3$ Hz), 114.52 (s), 110.53 (s), 21.12 (s). ^{19}F NMR (376 MHz, CDCl_3): δ -66.18 (s).



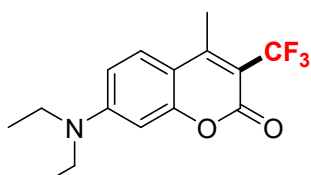
3h

7-Methoxy-4-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3h)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (72.2 mg, 70%); ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 9.1 Hz, 1H), 6.92 (dd, J = 9.1, 2.4 Hz, 1H), 6.80 (d, J = 2.5 Hz, 1H), 3.91 (s, 3H), 2.64 (dd, J = 2.0, 2.17Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.40 (s), 156.35 (s), 155.16 (s), 155.09 (d, J = 1.2 Hz), 127.16 (s), 123.18 (q, J = 274.7 Hz), 113.41 (s), 112.50 (s), 112.10 (q, J = 30.3 Hz), 100.45 (s), 55.98 (s), 15.72 (q, J = 4.1 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -56.35 (s).



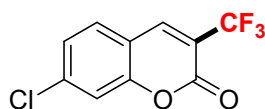
3i

7-Acetyloxy-4-Methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3i)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (82.3 mg, 72%); ¹H NMR (CDCl₃, 400 MHz): δ 7.82 (m, 1H), 7.17-7.15 (m, 2H), 2.68 (d, J = 2.0 Hz, 3H), 2.36 (s, 3H). ¹³C NMR (CDCl₃, 101MHz): δ 168.52(s), 155.75(s), 154.69(s), 154.61(s), 153.78(s), 127.01(s), 122.74 (q, J= 276.7 Hz), 118.91(s), 116.79(s), 114.81 (q, J = 31.3 Hz), 110.36(s), 21.13(s), 15.84 (q, J = 4.0 Hz). ¹⁹F NMR (CDCl₃, 376 MHz): δ -56.8(q, J = 3.8 Hz).



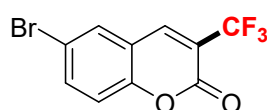
3j

7-(Diethylamino)-4-methyl-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3j)². The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (83.7 mg, 70%); ¹H NMR (CDCl₃, 400 MHz): δ 7.56 (d, J = 9.3 Hz, 1H), 6.63 (dd, J = 2.7, 9.2 Hz, 1H), 6.43 (d, J = 2.6 Hz, 1H), 3.44 (q, J = 7.1 Hz, 4H), 2.54 (q, J = 2.3 Hz, 3H), 1.22 (t, J = 7.1 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 157.40 (s), 155.95 (s), 155.08 (s), 152.05 (s), 127.20 (s), 123.85 (q, J = 274.7 Hz), 109.34 (s), 107.92 (s), 107.85 (q, J = 30.3 Hz), 96.80 (s), 44.89 (s), 15.26 (s), 12.39 (s); ¹⁹F NMR (376 MHz, CDCl₃) δ -55.52 (s).



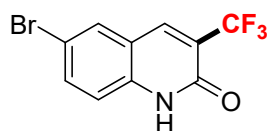
3m

7-Chloro-3-(trifluoromethyl)-2H-chromen-2-one (3m)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (64.2 mg, 65%); ¹H NMR (CDCl₃, 400 MHz): δ 8.12 (s, 1H,), 7.56 (d, J = 8.3 Hz, 1H), 7.42 (m, 1H,), 7.36 (d, J = 1.8, 8.7 Hz, 1H,). ¹³C NMR (CDCl₃, 101 MHz): δ 155.12(s), 154.91(s), 142.48 (q, J = 4.7 Hz), 140.78(s), 130.21(s), 126.02(s), 121.18(q, J = 272.7 Hz), 117.72 (q, J = 33.3 Hz), 117.45(s), 115.39(s). ¹⁹F NMR (CDCl₃, 283 MHz): δ -66.3(s, 3F).



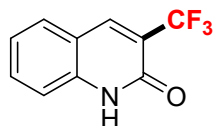
3n

6-Bromo-3-(trifluoromethyl)-2H-1-Benzopyran-2-one (3n)². The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 20:1) as a white powder (67.7 mg, 58%); ¹H NMR (400 MHz, CDCl₃): δ 8.09 (s, 1 H), 7.76 (dd, J= 7.0, 2.2 Hz, 2 H), 7.30 (d, J = 9.5 Hz, 1 H). ¹³C NMR (101 MHz, CDCl₃): δ 155.11 (s), 153.49 (s), 141.95 (q, J = 4.9 Hz), 137.17 (s), 131.61 (s), 121.06 (q, J= 270.4 Hz), 118.90 (q, J = 33.4 Hz), 118.75 (s), 118.24 (s), 117.85 (s). ¹⁹F NMR (376 MHz, CDCl₃): δ -66.34 (s).



3q

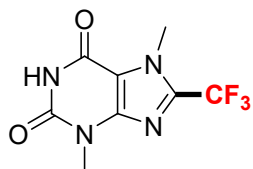
6-Bromo-3-(trifluoromethyl)-quinolin-2(1H)-one (3q)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (55.7 mg, 48%); ¹H NMR (400 MHz, DMSO-d₆): δ 12.44 (s, 1H,), 8.54 (s, 1H,), 8.14 (d, J = 2.3 Hz, 1H,), 7.81 (dd, J = 2.3, 8.8 Hz, 1H,), 7.32 (d, J = 8.8 Hz, 1H,). ¹³C NMR (101MHz, DMSO-d₆): δ 157.84(s), 140.20 (q, J = 5.4 Hz), 139.51 (s), 135.97 (s), 132.04 (s), 122.91 (q, J= 272.7 Hz), 121.43 (q, J = 30.3 Hz), 119.01 (s), 117.93 (s), 114.50 (s). ¹⁹F NMR (DMSO-d₆, 376 MHz): δ -64.44(s, 3F).



3r

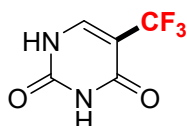
3-(Trifluoromethyl)-quinolin-2(1H)-one (3r)¹. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 40:1) as a white powder (55.4 mg, 65%); ¹H NMR (DMSO-d₆, 400 MHz): δ 12.33 (s, 1H), 8.56 (s, 1H), 7.88 (d, J =

1.4, 8.0 Hz, 1H), 7.67 (t, J = 1.4, 7.2 Hz, 1H), 7.39 (d, J = 8.3 Hz, 1H), 7.29 (t, J = 1.0, 7.6 Hz, 1H); ¹³C NMR (DMSO-d₆, 101 MHz): δ 158.08 (s), 141.20 (q, J = 5.1 Hz), 140.46 (s), 133.50 (s), 130.19 (s), 124.52 (q, J = 239.4 Hz), 123.00 (s), 120.46 (q, J = 20.2 Hz), 117.36 (s), 115.71 (s); ¹⁹F NMR (376 MHz, CDCl₃): δ -63.09 (d, J = 15.0 Hz).



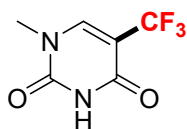
3s

8-Trifluoromethyltheobromine (3s)^{3, 4}. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 1:2) as a white powder (41.7 mg, 42%); ¹H NMR (DMSO-d₆, 400 MHz): δ 3.16 (s, J=1.7 Hz, 3H), 3.33 (s, 3H), 11.42 (s, 1H). ¹⁹F NMR (DMSO-d₆, 376 MHz): δ -61.98. ¹³C NMR (DMSO-d₆, 101 MHz): δ 154.24 (s), 150.73 (s), 147.50 (s), 140.81 (q, J = 28.3 Hz), 118.10 (q, J = 268.7 Hz), 110.07 (s), 33.85 (s), 29.30(s).



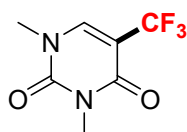
3t

Trifluorothymine (3t)⁵. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 1:2) as a white powder (34.6 mg, 48%); ¹H NMR (400 MHz, d⁶-Acetone) δ 11.06 (br, 2H), 8.04 (s, 1H). ¹⁹F NMR (376 MHz, d⁶-Acetone) δ -60.39 (s, 3F). ¹³C NMR (101 MHz, d⁶-Acetone) δ 160.32(s), 151.08(s), 144.35 (q, J = 5.1 Hz), 123.28 (q, J = 270.7 Hz), 103.12 (q, J = 32.3 Hz).



3u

1-Methyltrifluorothymine (3u)⁵. The product was purified with silica gel chromatography (Petroleum ether /Ethyl Acetate = 2:1) as a white powder (40.6 mg, 52%); ¹H NMR (400 MHz, d⁶-Acetone): δ 10.45 (br, 1H), 8.22 (q, J = 1.2 Hz, 1H), 3.46 (s, 3H). ¹⁹F NMR (376 MHz, d⁶-Acetone): δ -61.92 (s, 3F). ¹³C NMR (101 MHz, d⁶-Acetone) δ 159.96(s), 150.96(s), 148.48 (q, J = 6.1 Hz), 123.26 (q, J = 269.7 Hz), 102.08 (q, J = 32.3 Hz), 36.21 (s).



3v

1, 3-Dimethyltrifluorothymine (3v)⁵. The product was purified with silica gel

chromatography (Petroleum ether /Ethyl Acetate = 1:1) as a white powder (46.6 mg, 56%); ¹H NMR (400 MHz, d⁶-Acetone): δ 8.23 (s, 1H), 3.51 (s, 3H), 3.25 (s, 3H) ¹⁹F NMR (376 MHz, d⁶-Acetone): -62.25 (s, 3F). ¹³C NMR (101 MHz, d⁶-Acetone) δ 158.66(s), 151.00(s), 145.51 (q, J = 6.1 Hz), 122.91 (q, J = 269.7 Hz), 102.02 (q, J = 33.3 Hz), 36.75(s), 26.94(s).

9. Notes and references

1. X.-H. Cao, X. Pan, P.-J. Zhou, J.-P. Zou and O. T. Asekun, *Chem. Commun.*, 2014, **50**, 3359-3362.
2. X. Zhang, P. Huang, Y. Li and C. Duan, *Org. Biomol. Chem.*, 2015, **13**, 10917-10922.
3. Y. Qiu, A. Scheremetjew, L. H. Finger and L. Ackermann, *Chem. - Eur. J.*, 2020, **26**, 3241-3246.
4. Y. Tetsu, Y. Kyoko, U. Daisuke and T. Kenji, *Journal*, 2015.
5. Y. Huang, Y.-Y. Lei, L. Zhao, J. Gu, Q. Yao, Z. Wang, X.-F. Li, X. Zhang and C.-Y. He, *Chem. Commun.*, 2018, **54**, 13662-13665.

10. ^1H , ^{13}C and ^{19}F NMR Spectra

