Supporting Information for

Synthesis of 4-trifluoromethyl 2-pyrones and pyridones through
Brønsted base catalyzed Pechmann type reaction with cyclic
1,3-diones

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Procedure for gram scale reaction for synthesis of 4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3a)

\[
\begin{align*}
&\text{1a} \quad \text{10 mmol, 1.12 g, 1.0 equiv} \\
&\text{2} \quad \text{2.76 g, 1.5 equiv} \\
&\text{2-DMAP (20 mmol\%)} \\
&\text{DCE, 120 °C, 20 h} \\
&\text{3a} \quad \text{1.30 g, 56\% yield}
\end{align*}
\]

In a glove box filled with nitrogen, to an oven-dried 25 mL pressure tube equipped with a stir bar were added 1,3-cyclohexanedicarboxaldehyde (10 mmol, 1.12 g, 1.0 equiv), ethyl 4,4,4-trifluoroacetetoacetate (15 mmol, 2.76 g, 1.50 equiv), 2-dimethylaminopyridine (2 mmol, 0.24 g, 0.20 equiv), and 1,2-bichloroethane (10 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 120 °C for 20 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, washed with saturated ammonium chloride solution (3 × 60 mL) and water (60 mL), dried over MgSO₄, and filtered. The residue obtained was purified by flash column chromatography over silica gel with n-pentane/dichloromethane (1:1) to give 1.30 g of product 3a (56% yield).
Procedure for the synthesis of compound 5

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added 4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione 3a (47 mg, 0.20 mmol, 1.0 equiv), dimethyl acetylenedicarboxylate (142 mg, 1.0 mmol, 5.0 equiv), and xylene (0.20 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 200 °C for 72 h. The reaction mixture was cooled to room temperature and was filtered through a layer of Celite, eluted with dichloromethane. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane/dichloromethane to give product 5 (48 mg, 0.14 mol, 72% yield).
Procedure for the synthesis of compound 6

Under atmospheric conditions, a scintillation vial equipped with a stir bar were added 4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione 3a (47 mg, 0.20 mmol, 1.0 equiv), p-toluidine (26 mg, 0.24 mmol, 1.2 equiv), and C₂H₅OH (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at room temperature for 24 h. The reaction mixture was filtered through a layer of Celite, eluted with dichloromethane. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane/dichloromethane to give product 6 (51 mg, 0.16 mmol, 80% yield).
Mechanism exploratory experiments

(1).

\[ \text{1a} + \text{2} \xrightarrow{2-\text{DMAP} (20 \text{mmol\%})} \text{DCE, 60°C} \] 

HRMS (ESI) detected

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added 1,3-cyclohexanedione (33.6 mg, 0.30 mmol, 1.0 equiv), ethyl 4,4,4-trifluoroacetooacetate (82.8 mg, 0.45 mmol, 1.5 equiv), 2-dimethylaminopyridine (7.3 mg, 0.060 mmol, 0.20 equiv), and 1,2-bichloroethane (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 60 °C in oil bath for 10 h. The reaction mixture was cooled to room temperature, and then 10\(\mu\)L (trifluoromethoxy)benzene was added as an internal standard. The filtrate was analyzed by \(^{19}\text{F}\) NMR and HRMS (ESI). The yield of the intermediate I was calculated to be 99\%.
The reaction mixture was further stirred at 120 °C in oil bath for 10 h, and was cooled to room temperature. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by \(^{19}\)F NMR and GC-MS. The yield of the 3a was calculated to be 70%.
In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added 4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione 3a (23.2 mg, 0.10 mmol, 1.0 equiv), NH₄OAc (23.1 mg, 0.30 mmol, 3.0 equiv), and 1,2-bichloroethane (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 140 °C in oil bath for 10 h. The reaction mixture was cooled to room temperature, and then 10 µL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by ¹⁹F NMR and GC-MS. The yield of the 4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione 4a was calculated to be 76%.
Under nitrogen atmospheric conditions, a scintillation vial equipped with a stir bar were added 1,3-cyclohexanedione (224 mg, 2.0 mmol, 1.0 equiv), NH$_4$OAc (154 mg, 2.0 mmol, 1.0 equiv), and dry toluene (6.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 130 °C for 8 h. The reaction mixture was cooled to room temperature for two hours. The upper layer of toluene solution was separated and the lower layer was extracted with ethyl acetate, and dried. The solvent was removed by rotary evaporation and the resulting crude product was recrystallized by ethyl acetate to give 3-iminocyclohexanone 5.

Obtained as a reddish-brown solid in 45% yield (100 mg). M.p.: 108.6-109.2 °C. R$_f$ (dichloromethane : methanol 1:1) = 0.37. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 5.55 (br, s, 2H), 5.25 (s, 1H), 2.36 (t, $J$ = 5.3 Hz, 2H), 2.26 (t, $J$ = 5.7 Hz, 2H), 2.03 – 1.86 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 198.1 (s), 167.1 (s), 99.7 (s), 35.7 (s), 28.7 (s), 21.7 (s). IR (ATR): $\nu$ 3319, 3121, 2939, 1673, 1522, 1378, 1249, 1186, 825, 645 cm$^{-1}$. GC-MS (EI) for C$_6$H$_9$NO m/z: [M]$^+$: 111.07.

In a glove box filled with nitrogen, to an oven-dried 5 mL pressure tube equipped with a stir bar were added 3-iminocyclohexanone 5 (22.2 mg, 0.20 mmol, 1.0 equiv), ethyl 4,4,4-trifluoroacetoacetate (55.2 mg, 0.30 mmol, 1.5 equiv),
2-dimethylaminopyridine (4.9 mg, 0.04 mmol, 0.2 equiv), and 1,2-bichloroethane (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at 140 °C in oil bath for 10 h. The reaction mixture was cooled to room temperature, and then 10µL (trifluoromethoxy)benzene was added as an internal standard. The resulting mixture was filtered through a layer of Celite. The filtrate was analyzed by $^{19}$F NMR and GC-MS. The yield of the 4a was calculated to be 16%.
Under atmospheric conditions, a scintillation vial equipped with a stir bar were added a mixture containing two regioisomers 3d and 3d′ (1:3 ratio) (52 mg, 0.20 mmol, 1.0 equiv), p-toluidine (26 mg, 0.24 mmol, 1.2 equiv), and C₂H₅OH (1.0 mL). The tube was sealed with Teflon screw cap and the solution was stirred at room temperature for 24 h. The reaction mixture was filtered through a layer of Celite, eluted with dichloromethane. The solvent was removed by rotary evaporation and the resulting product was purified by column chromatography on silica gel with n-pentane/dichloromethane to give product 8 as single regioisomer (21 mg, 0.06 mmol, 30% yield).
The $^{19}$F NMR of the crude reaction mixture of the reaction of 1d with 2
Data for compounds 3–6

4-(Trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3a)

Obtained as a light yellow solid in 99% yield (70 mg). Mp: 78.2-79.5 °C. Rf (n-pentane:dichloromethane 1:2) = 0.36. ¹H NMR (400 MHz, CDCl₃): δ 6.67 (s, 1H), 2.94 (t, J = 6.2 Hz, 2H), 2.62 (t, J = 6.2 Hz, 2H), 2.23 – 2.10 (m, 2H). ¹⁹F NMR (376 MHz, CDCl₃): δ -63.6 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 190.8 (s), 176.2 (d, J = 1.3 Hz), 158.0 (s), 141.6 (q, J = 35.1 Hz), 120.8 (q, J = 275.1 Hz), 115.0 (q, J = 7.3 Hz), 111.3 (s), 38.0 (s), 29.2 (s), 19.4 (s). IR (ATR): ν 3082, 2971, 1749, 1687, 1629, 1460, 1276, 1138, 1019 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₀H₈F₃O₃ [M+H]^+: 233.0420; found: 233.0416.

7-Methyl-4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione(3b)

Obtained as a white solid in 99% yield (74 mg). Mp: 131.3-133.0 °C. Rf (n-pentane:dichloromethane 1:2) = 0.44. ¹H NMR (400 MHz, CDCl₃): δ 6.64 (s, 1H), 2.05 – 2.86 (m, 1H), 2.79 – 2.56 (m, 2H), 2.51 – 2.22 (m, 2H), 1.25 – 1.05 (m, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ -63.6 (s, 3F). ¹³C NMR (101 MHz, CDCl₃): δ 190.7 (s), 175.6 (s), 158.1 (s), 141.6 (q, J = 35.1 Hz), 120.8 (q, J = 275.2 Hz), 115.0 (q, J = 7.4 Hz), 110.9 (s), 46.2 (s), 37.0 (s), 27.2 (s), 20.5 (s). IR (ATR): ν 3088, 2959, 2930, 1750, 1686, 1545, 1457, 1279, 1144, 1029 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₁H₁₀F₃O₃ [M+H]^+: 247.0577; found: 247.0571.
7,7-Dimethyl-4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3c)

Obtained as a white solid in 99% yield (78 mg). Mp: 109.8-111.6 °C. Rf (n-pentane:dichloromethane 1:2) = 0.44. 1H NMR (400 MHz, CDCl₃): δ 6.63 (s, 1H), 2.78 (s, 2H), 2.47 (s, 2H), 1.14 (s, 6H). 19F NMR (376 MHz, CDCl₃): δ -63.6 (s, 3F). 13C NMR (101 MHz, CDCl₃): δ 190.8 (s), 174.7 (s), 158.3 (s), 141.4 (q, J = 35.4 Hz), 120.8 (q, J = 275.1 Hz), 114.8 (q, J = 7.4 Hz), 110.4 (s), 51.9 (s), 42.7 (s), 31.7 (s), 27.9 (s). IR (ATR): ν 3102, 2965, 1756, 1679, 1550, 1471, 1400, 1278, 1129, 1047 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₂H₁₂F₃O₃ [M+H]^+: 261.0739; found: 261.0746.

6,6-Dimethyl-4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3d)

8,8-Dimethyl-4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3d')

Obtained as a light red solid mixture in 99% yield (78 mg) with 3d:3d' ratio 3:1. 1H NMR (400 MHz, CDCl₃) 3d + 3d': δ 6.67 (s), 6.65 (s), 2.93 (t, J = 6.0 Hz), 2.65 (t, J = 6.4 Hz), 2.32 – 2.12 (m), 2.07 – 1.88 (m), 1.45 (s), 1.21 (s). 19F NMR (376 MHz, CDCl₃) 3d': δ -63.1 (s, 3F), 3d: -63.5 (s, 3F). 13C NMR (101 MHz, CDCl₃) 3d + 3d': δ 196.1 (s), 191.0 (s), 180.9 (s), 174.0 (s), 158.2 (s), 142.3 (q, J = 35.0 Hz), 141.9 (q, J = 35.0 Hz), 120.9 (q, J = 275.1 Hz), 115.3 (q, J = 7.4 Hz), 115.1 (q, J = 7.3 Hz), 110.0 (s), 109.9 (s), 41.7 (s), 36.9 (s), 34.9 (s), 34.3 (s), 32.6 (s), 26.2 (s), 26.0 (s), 24.0 (s). IR (ATR) 3d + 3d': ν 2969, 2924, 1744, 1689, 1552, 1474, 1401, 1316, 1154, 1074, 1039 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₂H₁₂F₃O₃ [M+H]^+: 261.0733; found 3d + 3d': 261.0728, 261.0729.
**7-Phenyl-4-(trifluoromethyl)-7,8-dihydro-2H-chromene-2,5(6H)-dione (3e)**

Obtained as a light yellow solid in 99% yield (92 mg). Mp: 138.2-140.1 °C. \( R_f \) (n-pentane:dichloromethane 1:2) = 0.44. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.42 (t, \( J = 7.1 \) Hz, 2H), 7.35 (d, \( J = 7.0 \) Hz, 1H), 7.29 (d, \( J = 7.1 \) Hz, 2H), 6.71 (s, 1H), 3.65 – 3.45 (m, 1H), 3.17 (d, \( J = 7.8 \) Hz, 2H), 3.02 – 2.60 (m, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -63.5 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 190.0 (s), 175.2 (s), 157.9 (s), 141.5 (q, \( J = 35.3 \) Hz), 140.7 (s), 129.2 (s), 127.8 (s), 126.5 (s), 120.9 (q, \( J = 275.2 \) Hz), 115.3 (q, \( J = 7.4 \) Hz), 111.1 (s), 45.1 (s), 37.4 (s), 36.7 (s). IR (ATR): \( \nu \) 3111, 3037, 2919, 1755, 1683, 1547, 1499, 1398, 1267, 1134, 1055 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( \text{C}_{16}\text{H}_{12}\text{F}_{3}\text{O}_{3} \)[M+H]\(^+\): 309.0739; found: 309.0749.

**4-(Trifluoromethyl)pyrano[3,4-\(b\)]pyran-2,5(6\(H\),8\(H\))-dione (3f)**

Obtained as a brown solid in 43% yield (30 mg). Mp: 119.0-120.5 °C. \( R_f \) (n-pentane:dichloromethane 1:2) = 0.36. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.75 (s, 1H), 4.73 (s, 2H), 4.32 (s, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -64.5 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 186.2 (s), 173.1 (s), 156.5 (s), 140.7 (q, \( J = 36.4 \) Hz), 120.4 (q, \( J = 275.3 \) Hz), 115.6 (q, \( J = 7.1 \) Hz), 108.9 (s), 72.3 (s), 65.2 (s). IR (ATR): \( \nu \) 3107, 2992, 2921, 1770, 1699, 1559, 1412, 1271, 1138, 1055 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( \text{C}_9\text{H}_6\text{F}_3\text{O}_4 \)[M+H]\(^+\): 235.0218; found: 235.0223.
4-(Trifluoromethyl)-6,7-dihydrocyclopenta[b]pyran-2,5-dione (3g)

Obtained as a light yellow solid powder in 84% yield (55 mg). Mp: 98.5-100.2 °C. \( R_f \) (n-pentane:dichloromethane 1:2) = 0.28. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.60 (s, 1H), 3.17 – 3.01 (m, 2H), 2.85 – 2.72 (m, 2H). \(^{19}\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -66.3 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 194.2 (s), 187.4 (s), 158.9 (s), 139.5 (q, \( J = 37.2 \) Hz), 120.1 (q, \( J = 275.1 \) Hz), 112.7 (s), 112.6 (q, \( J = 6.1 \) Hz), 34.4 (s), 26.3 (s). IR (ATR): \( \nu \) 3095, 2923, 1757, 1714, 1575, 1482, 1278, 1140, 1030 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_9\)H\(_6\)F\(_3\)O\(_3\) [M+H]\(^+\): 219.0264; found: 219.0259.
4-(Trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (4a)

Obtained as a white solid in 78% yield (54 mg). Mp: 209.5-211.2 °C. Rf (n-pentane:ethyl acetate 1:4) = 0.30. ¹H NMR (400 MHz, DMSO-d₆): δ 12.63 (br, 1H), 6.67 (s, 1H), 2.87 (t, J = 5.5 Hz, 2H), 2.48 (t, J = 6.1 Hz, 2H), 2.12 – 1.82 (m, 2H). ¹⁹F NMR (376 MHz, DMSO-d₆): δ -61.2 (s, 3F). ¹³C NMR (101 MHz, DMSO-d₆): δ 191.6 (s), 161.5 (s), 161.0 (s), 138.6 (q, J = 33.0 Hz), 122.6 (q, J = 274.6 Hz), 119.2 (q, J = 7.0 Hz), 109.3 (s), 38.6 (s), 28.2 (s), 20.5 (s). IR (ATR): ν 3447, 2987, 1749, 1698, 1557, 1477, 1407, 1279, 1165, 1025, 1007, 821 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₀H₉F₃NO₂ [M+H]^+: 232.0580; found: 232.0574.

7-Methyl-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (4b)

Obtained as a white solid powder in 91% yield (67 mg). Mp: 214.2-215.7 °C. Rf (n-pentane:ethyl acetate 1:2) = 0.40. ¹H NMR (400 MHz, DMSO-d₆): δ 12.65 (br, 1H), 6.67 (s, 1H), 2.88 (d, J = 17.9 Hz, 1H), 2.71 – 2.39 (m, 2H), 2.36 – 2.19 (m, 2H), 1.04 (d, J = 4.5 Hz, 3H). ¹⁹F NMR (376 MHz, DMSO-d₆): δ -61.2 (s, 3F). ¹³C NMR (101 MHz, DMSO-d₆): δ 191.6 (s), 161.6 (s), 160.3 (s), 138.4 (q, J = 33.0 Hz), 122.6 (q, J = 274.5 Hz), 119.1 (q, J = 7.5 Hz), 109.0 (s), 46.6 (s), 35.8 (s), 27.9 (s), 20.8 (s). IR (ATR): ν 3072, 2924, 1693, 1648, 1558, 1475, 1283, 1140, 1046, 888 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₁H₁₁F₃NO₂ [M+H]^+: 246.0736; found: 246.0731.
7,7-Dimethyl-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (4c)

Obtained as a light yellow solid powder in 82% yield (64 mg). Mp: 195.0-196.2 °C. 

$R_f$ (n-pentane:ethyl acetate 1:2) = 0.43. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 12.65 (br, 1H), 6.67 (s, 1H), 2.79 (s, 2H), 2.40 (s, 2H), 1.02 (s, 6H). $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -61.3 (s, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 191.5 (s), 161.8 (s), 159.1 (s), 138.2 (q, $J$ = 32.7 Hz), 122.6 (q, $J$ = 274.2 Hz), 119.0 (q, $J$ = 6.8 Hz), 108.5 (s), 52.1 (s), 41.3 (s), 32.2 (s), 27.8 (s). IR (ATR): $\nu$ 3079, 2945, 1689, 1655, 1605, 1477, 1284, 1124, 1041, 880 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{12}$H$_{13}$F$_3$NO$_2$ [M+H]$^+$: 260.0893; found: 260.0887.

8,8-Dimethyl-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (4d)

Obtained as a yellow solid powder in 47% yield (37 mg). Mp: 196.5-198.0 °C. 

$R_f$ (n-pentane:ethyl acetate 1:2) = 0.40. $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ 12.57 (br, 1H), 6.66 (s, 1H), 2.88 (t, $J$ = 6.0 Hz, 2H), 1.87 (t, $J$ = 6.0 Hz, 2H), 1.08 (s, 6H). $^{19}$F NMR (376 MHz, DMSO-$d_6$): $\delta$ -61.1 (s, 3F). $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ 196.8 (s), 161.6 (s), 159.2 (s), 139.1 (q, $J$ = 33.0 Hz), 122.7 (q, $J$ = 274.6 Hz), 119.5 (q, $J$ = 6.9 Hz), 108.1 (s), 41.6 (s), 33.5 (s), 24.7 (s). IR (ATR): $\nu$ 2976, 2920, 2850, 1672, 1614, 1558, 1475, 1236, 1156, 1051, 880, 842 cm$^{-1}$. HRMS (ESI) m/z: calcd. for C$_{12}$H$_{13}$F$_3$NO$_2$ [M+H]$^+$: 260.0893; found: 260.0887.
7-Phenyl-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (4e)

Obtained as a white solid in 50% yield (46 mg). Mp: 230.6-232.4 °C. 

\( R_f \) (n-pentane:ethyl acetate 1:2) = 0.59. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta \) 12.73 (br, 1H), 7.43 – 7.33 (m, 4H), 7.32 – 7.24 (m, 1H), 6.73 (s, 1H), 3.51 (t, \( J = 12.6 \) Hz, 1H), 3.27 – 3.15 (m, 1H), 3.03 (d, \( J = 17.1 \) Hz, 1H), 2.90 (t, \( J = 16.0 \) Hz, 1H), 2.64 (d, \( J = 15.1 \) Hz, 1H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \( \delta \) -61.2 (s, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \( \delta \) 190.5 (s), 161.2 (s), 159.7 (s), 142.5 (s), 138.0 (q, \( J = 33.3 \) Hz), 128.7 (s), 127.0 (s), 126.8 (s), 122.2 (q, \( J = 275.0 \) Hz), 118.9 (q, \( J = 6.8 \) Hz), 108.5 (s), 45.1 (s), 37.5 (s), 34.9 (s). IR (ATR): \( \nu \) 2921, 2850, 1659, 1604, 1560, 1478, 1269, 1148, 1123, 1016, 888 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( \text{C}_{16}\text{H}_{13}\text{F}_{3}\text{NO}_{2} \) [M+H]\(^{+}\): 308.0893; found: 308.0887.

4-(Trifluoromethyl)-6,7-dihydro-1H-cyclopenta[b]pyridine-2,5-dione (4g)

Obtained as a brown solid in 50% yield (33 mg). Mp: 191.9-193.3 °C. 

\( R_f \) (n-pentane:ethyl acetate 1:4) = 0.30. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): \( \delta \) 13.07 (br, 1H), 6.64 (s, 1H), 2.96 (t, \( J = 4.0 \) Hz, 2H), 2.58 (t, \( J = 4.0 \) Hz, 2H). \(^{19}\)F NMR (376 MHz, DMSO-\(d_6\)): \( \delta \) -63.9 (s, 3F). \(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)): \( \delta \) 196.5 (s), 172.3 (s), 163.0 (s), 135.5 (q, \( J = 34.9 \) Hz), 123.2 (q, \( J = 275.7 \) Hz), 117.8 (q, \( J = 5.6 \) Hz), 111.1 (s), 35.2 (s), 24.9 (s). IR (ATR): \( \nu \) 3217, 3068, 2921, 1668, 1571, 1505, 1490, 1256, 1120, 1038, 888, 840 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for \( \text{C}_{9}\text{H}_{7}\text{F}_{3}\text{NO}_{2} \) [M]\(^{+}\): 217.0345; found: 217.0303.
**Dimethyl**

**5-oxo-4-(trifluoromethyl)-5,6,7,8-tetrahydronaphthalene-1,2-dicarboxylate (6)**

Obtained as a yellow solid in 72% yield (48 mg). Mp: 110.0-111.5 °C. \( R_f \) (dichloromethane) = 0.67. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.34 (s, 1H), 4.01 (d, \( J = 1.0 \) Hz, 3H), 3.98 (d, \( J = 1.0 \) Hz, 3H), 2.96 (t, \( J = 5.7 \) Hz, 2H), 2.80 (t, \( J = 6.3 \) Hz, 2H), 2.19 (dt, \( J = 12.0 \) 5.6 Hz, 2H). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -59.2 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 195.9 (s), 167.8 (s), 164.2 (s), 143.4 (s), 138.8 (d, \( J = 0.9 \) Hz), 135.9 (d, \( J = 0.7 \) Hz), 130.4 (q, \( J = 33.3 \) Hz), 130.1 (s), 127.4 (q, \( J = 6.9 \) Hz), 122.7 (q, \( J = 274.2 \) Hz), 53.2 (s), 53.1 (s), 39.4 (s), 27.1 (s), 22.0 (s). IR (ATR): ν 3079, 2978, 2948, 2920, 2870, 1735, 1689, 1597, 1561, 1440, 1234, 1158, 1005, 904, 807, 751, 716, 690 cm\(^{-1}\). HRMS (ESI) m/z: calcd. for C\(_{15}\)H\(_{14}\)F\(_3\)O\(_5\) [M+H]\(^+\): 331.0793; found: 331.0774.

**1-(p-Tolyl)-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (7)**

Obtained as a white solid in 80% yield (51 mg). Mp: 175.0-176.2 °C. \( R_f \) (dichloromethane) = 0.58. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.40 (d, \( J = 7.2 \) Hz, 2H), 7.09 (d, \( J = 7.2 \) Hz, 2H), 7.04 (s, 1H), 2.63 – 2.49 (m, 4H), 2.47 (s, 3H), 2.02 (dt, \( J = 11.2 \), 5.5 Hz, 2H). \(^1^9\)F NMR (376 MHz, CDCl\(_3\)): \( \delta \) -62.1 (s, 3F). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)): \( \delta \) 191.7 (s), 161.7 (s), 159.4 (s), 140.1 (s), 139.1 (q, \( J = 33.8 \) Hz), 134.2 (s), 130.4 (q, \( J = 33.3 \) Hz), 127.4 (q, \( J = 6.9 \) Hz), 122.7 (q, \( J = 274.2 \) Hz), 53.2 (s), 53.1 (s), 39.4 (s), 27.1 (s), 22.0 (s).
131.0 (s), 127.1 (s), 122.0 (q, J = 275.2 Hz), 120.3 (q, J = 7.1 Hz), 111.8 (s), 37.9 (s), 30.3 (s), 21.3 (s), 20.7 (s). IR (ATR): ν 3005, 2957, 2920, 2849, 1727, 1705, 1549, 1458, 1360, 1265, 1129, 1085, 786 cm⁻¹. HRMS (ESI) m/z: calcd. for C₁₇H₁₅F₃NO₂ [M+H]^+: 322.1055; found: 322.1039.

6,6-Dimethyl-1-(p-tolyl)-4-(trifluoromethyl)-7,8-dihydroquinoline-2,5(1H,6H)-dione (8)

Obtained as a white solid in 30% yield (21 mg). Mp: 205.1-205.9 °C. Rf (dichloromethane) = 0.35. ¹H NMR (400 MHz, CDCl₃): δ 7.40 (d, J = 7.3 Hz, 2H), 7.10 (s, 1H), 7.07 (d, J = 7.3 Hz, 2H), 2.51 (t, J = 5.8 Hz, 2H), 2.47 (s, 3H), 1.85 (t, J = 5.6 Hz, 2H), 1.21 (s, 6H). ¹⁹F NMR (376 MHz, CDCl₃) δ -62.0 (s, 3F). ¹³C NMR (101 MHz, CDCl₃) δ 197.3 (s), 161.8 (s), 157.5 (s), 140.1 (s), 139.7 (q, J = 33.8 Hz), 134.1 (s), 131.0 (s), 127.1 (s), 122.1 (q, J = 274.9 Hz), 120.5 (q, J = 7.2 Hz), 110.6 (s), 41.0 (s), 34.0 (s), 26.8 (s), 24.2 (s), 21.3 (s). IR (ATR): ν 3046, 2982, 2926, 2869, 1665, 1520, 1429, 1413, 1279, 1258, 1138, 1106, 878, 815, 497 cm⁻¹. GC-MS (EI) for C₁₉H₁₈F₃NO₂ m/z: [M]^+: 349.50.
Obtained as an oil liquid in 98% yield (20 mg). \( R_f \) (dichloromethane : ethyl acetate = 1:2) = 0.42. \( ^1H \) NMR (400 MHz, C\textsubscript{6}D\textsubscript{6}) \( \delta \) 3.87 (d, \( J = 17.2 \) Hz, 1H), 3.75 (t, \( J = 6.7 \) Hz, 2H), 3.20 (d, \( J = 17.2 \) Hz, 1H), 1.97 (dt, \( J = 24.4 \), 4.2 Hz, 4H), 1.25 – 1.14 (m, 2H), 0.80 (t, \( J = 7.1 \) Hz, 3H). \( ^19F \) NMR (376 MHz, C\textsubscript{6}D\textsubscript{6}) \( \delta \) -81.1 (s, 3F). \( ^13C \) NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 173.5 (s), 124.9 (q, \( J = 286.3 \) Hz), 107.7 (s), 77.9 (q, \( J = 31.2 \) Hz), 61.8 (s), 36.6 (s), 19.8 (s), 13.9 (s). HRMS (ESI) m/z: calcd. for C\textsubscript{12}H\textsubscript{16}F\textsubscript{3}O\textsubscript{5} [M+H]\(^+\): 297.0944; found: 297.0933.
Crystal structure analyses

The suitable crystals of 3a (CCDC 1872006), and 4e (CCDC 1870545) were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector at -50 °C, using MoKα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs and for absorption effects with SADABS.¹ Structure solution and refinement were carried out with the SHELXTL suite of programs.¹ The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms.
ORTEP diagrams

ORTEP diagram of compound 3a. Thermal ellipsoids are drawn at 40% probability
ORTEP diagram of compound 4e-DMSO. Thermal ellipsoids are drawn at 40% probability
References

1. SHELXTL version 5.03; Bruker Analytical X-ray Systems, Madison, WI, 1997.
Copies of $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra

$^1$H NMR spectrum of 3a in CDCl$_3$

$^{19}$F NMR spectrum of 3a in CDCl$_3$
$^{13}$C NMR spectrum of 3a in CDCl$_3$

$^1$H NMR spectrum of 3b in CDCl$_3$
$^{19}\text{F NMR}$ spectrum of $3\text{b}$ in $\text{CDCl}_3$

$^{13}\text{C NMR}$ spectrum of $3\text{b}$ in $\text{CDCl}_3$
$^1$H NMR spectrum of $3c$ in CDCl$_3$

$^{19}$F NMR spectrum of $3c$ in CDCl$_3$
$^{13}$C NMR spectrum of 3c in CDCl$_3$

$^1$H NMR spectrum of 3d in CDCl$_3$
$^{19}$F NMR spectrum of 3d in CDCl$_3$

$^{13}$C NMR spectrum of 3d in CDCl$_3$
$^{1}H$ NMR spectrum of 3e in CDCl$_3$

$^{19}F$ NMR spectrum of 3e in CDCl$_3$
$^{13}$C NMR spectrum of 3e in CDCl$_3$

$^1$H NMR spectrum of 3f in CDCl$_3$
$^{19}$F NMR spectrum of 3f in CDCl$_3$

$^{13}$C NMR spectrum of 3f in CDCl$_3$
$^1$H NMR spectrum of 3g in CDCl$_3$

$^{19}$F NMR spectrum of 3g in CDCl$_3$
$^{13}$C NMR spectrum of 3g in CDCl$_3$

$^1$H NMR spectrum of 4a in DMSO-$d_6$
$^{19}$F NMR spectrum of 4a in DMSO-$d_6$ 

$^{13}$C NMR spectrum of 4a in DMSO-$d_6$
$^1$H NMR spectrum of 4b in DMSO-d$_6$

$^{19}$F NMR spectrum of 4b in DMSO-d$_6$
$^{13}$C NMR spectrum of 4b in DMSO-$d_6$

$^1$H NMR spectrum of 4c in DMSO-$d_6$
$^{19}$F NMR spectrum of 4c in DMSO-$d_6$

$^{13}$C NMR spectrum of 4c in DMSO-$d_6$
$^1$H NMR spectrum of 4d in DMSO-$d_6$

$^{19}$F NMR spectrum of 4d in DMSO-$d_6$
$^{13}\text{C}$ NMR spectrum of 4d in DMSO-$d_6$

$^1\text{H}$ NMR spectrum of 4e in DMSO-$d_6$
\( ^{19}\text{F NMR spectrum of 4e in DMSO-}d_6 \)

\( ^{13}\text{C NMR spectrum of 4e in DMSO-}d_6 \)
$^1$H NMR spectrum of 4g in DMSO-$d_6$

$^{19}$F NMR spectrum of 4g in DMSO-$d_6$
$^{13}$C NMR spectrum of 4g in DMSO-$d_6$

$^1$H NMR spectrum of 5 in CDCl$_3$
**13C NMR spectrum of 5 in CDCl₃**

![13C NMR spectrum](image)

**1H NMR spectrum of 6 in CDCl₃**

![1H NMR spectrum](image)
$^{19}$F NMR spectrum of 6 in CDCl$_3$

$^{13}$C NMR spectrum of 6 in CDCl$_3$
$^1$H NMR spectrum of 7 in CDCl$_3$

$^{19}$F NMR spectrum of 7 in CDCl$_3$
$^{13}$C NMR spectrum of 7 in CDCl$_3$

$^1$H NMR spectrum of 8 in CDCl$_3$
$^{19}$F NMR spectrum of 8 in CDCl$_3$

$^{13}$C NMR spectrum of 8 in CDCl$_3$
$^1$H NMR spectrum of intermediate (I) in C$_6$D$_6$

$^{19}$F NMR spectrum of intermediate (I) in C$_6$D$_6$
$^{13}$C NMR spectrum of intermediate (I) in C$_6$D$_6$