Supporting information

Annulation of β-naphthols and 1,4-hydroxycoumarins with vinylsulfonium salts: Synthesis of dihydrofuran derivatives

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1. General Information

$^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker AVANCE 400 or 500 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual deuterium in the NMR solvent (CDCl$_3$: δ 7.26; $d$-DMSO: δ 2.50). Chemical shifts of carbon are referenced to the carbon resonances of the solvent (CDCl$_3$: δ 77.16 ppm; $d$-DMSO: δ 39.52 ppm). Peaks are labeled as singlet (s), doublet (d), triplet (t), quartet (q) and multiplet (m). Infrared data were recorded on a Nicolet 6700-Contium spectrometer. Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their $^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra were provided.
2. Optimization of reaction conditions

Table 1. Optimization of the conditions for the reaction of 4-hydroxycoumarin (5a) and sufonium salt (1a)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>K$_2$CO$_3$</td>
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<tr>
<td>2</td>
<td>acetone</td>
<td>K$_2$CO$_3$</td>
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<td>59</td>
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<td>DMSO</td>
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<tr>
<td>5</td>
<td>1,4-dioxane</td>
<td>K$_2$CO$_3$</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>DBU</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>1,4-dioxane</td>
<td>DBU</td>
<td>67</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>DBU</td>
<td>53</td>
</tr>
<tr>
<td>9c</td>
<td>1,4-dioxane</td>
<td>DBU</td>
<td>83</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 1a (0.3 mmol), 5a (0.2 mmol), base (0.6 mmol), solvent (4.0 mL), under an argon atmosphere at 0 °C, 24 h. $^b$ Isolated Yields. $^c$ The reaction was carried out at room temperature.
3. Experiment procedures and characterization data

3.1 Synthesis and characterization data of the starting materials

(2-Bromoethyl)diphenylsulfonium trifluoromethanesulfonate (1a)\(^1\)

\[
\begin{align*}
\text{Br} & \quad \text{OH} \quad \text{F}_3\text{SO}_3\text{S}\text{CF}_3 \\
\text{DCM, } -20 \, ^\circ\text{C to r.t.} & \quad \text{Br} \quad \text{O} \quad \text{O} \quad \text{S}\text{CF}_3 \\
\text{pyridine} & \quad \text{toluene, } 100 \, ^\circ\text{C} \\
S1 & \quad S2 \\
\end{align*}
\]

To a solution of pyridine (2.9 g, 36.8 mmol) in anhydrous DCM (35.0 mL) was added trifluoromethanesulfonic anhydride (10.0 g, 35.4 mmol) dropwise at -20 °C. After stirring for 5 min, 2-bromoethanol S1 (4.2 g, 33.6 mmol) was added dropwise and the reaction was stirred at room temperature for 10 min. The resulting suspension was filtered. The filtrate was concentrated (using a rotary evaporator, keeping the water bath temperature below 20 °C). Then petroleum ether (30.0 mL) was added while stirring. The petroleum ether layer was separated and evaporated under vacuum to afford 2-bromoethyl trifluoromethanesulfonate S2 (4.2 g, 49% yield) as pale brown liquid, which was used in the next step without further purification.

To a solution of 2-bromoethyl trifluoromethanesulfonate S2 (3.3 g, 12.8 mmol) in anhydrous toluene was added diphenyl sulfide (2.9 g, 15.6 mmol) at room temperature. Then the mixture was stirred at 100 °C overnight under an argon atmosphere. After being cooled down to room temperature, Et\(_2\)O (30.0 mL) was added to precipitate the product 1a. The precipitation was filtrated, washed with Et\(_2\)O and dried under vacuum. 1a (4.5 g, 86% yield) was obtained as a white solid. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 8.16–8.11 (m, 4H), 7.86–7.79 (m, 2H), 7.79–7.73 (m, 4H), 5.00–4.92 (m, 2H), 3.85–3.77 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, DMSO) \(\delta\) -77.71 ppm. \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 134.4, 131.2, 130.9, 124.8, 45.4, 24.9 ppm. The data are consistent with that reported in the literature.\(^1\)

\((E)\)-diphenyl(styryl)sulfonium trifluoromethanesulfonate (7a)\(^2\)
A solution of phenyl sulfoxide S3 (2.2 g, 11.0 mmol) in anhydrous DCM (200.0 mL) was cooled down to -78 °C. Trifluoromethanesulfonic anhydride (2.8 g, 10.0 mmol) was slowly added to the solution while stirring. After 30 min, a solution of styrene S4 (1.0 g, 10.0 mmol) in anhydrous DCM (25.0 mL) was slowly added and the mixture was stirred overnight. The solvent was removed and the crude product was purified by column chromatography (DCM/MeOH = 10:1) to give 7a (2.2 g, 49% yield) as a white solid. 

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3) \delta 7.96–7.75 \text{ (m, 8H), 7.69–7.60 (m, 6H), 7.46–7.36 (m, 3H)} \text{ ppm.} \]

\[ ^{19}F \text{ NMR (376 MHz, CDCl}_3) \delta -78.16 \text{ ppm.} \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 153.5, 134.4, 132.8, 132.2, 131.6, 130.6, 129.8, 129.4, 127.4, 121.0 (q, ^{1}J_{CF} = 320.4 \text{ Hz), 110.0 ppm.} \]

The data are consistent with that reported in the literature.\(^2\)

\[(E)\text{-Diphenyl-β-(trifluoromethyl)vinylsulfonium trifluoromethanesulfonate (7b)}\]^3

To a mixture of KOH (544.3 mg, 9.7 mmol) in EtOH (10.0 mL) were added thiophenol S6 (892.5 mg, 8.1 mmol) and 3,3,3-trifluoro-2-bromoprop-1-ene S5 (1.7 g, 9.7 mmol) at 0 °C. The mixture was gradually warmed to room temperature and stirred overnight. The reaction was quenched with saturated aqueous NH\(_4\)Cl (10 mL) and the water layer was extracted with hexane (10 mL \(\times 2\)). The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under vacuum. The resulting residue was purified by column chromatography (petroleum ether as eluent) to give (E)-phenyl β-(trifluoromethyl)vinyl sulfide S7 (785.9 mg, 48% yield) as colorless liquid.

To a mixture of diphenyliodonium triflate S8 (1.6 g, 3.9 mmol) and Cu powder (1.3 g, 19.3 mmol) in DCE (10.0 mL) was added (E)-phenyl β-(trifluoromethyl)vinyl sulfide

\[ F_3C=S\text{SO}^{+}Cl^{-} \]
S7 (785.9 mg, 3.8 mmol) under an argon atmosphere. The mixture was stirred at 100 °C for 5 h. After being cooled down to room temperature, the mixture was filtered through Celite and the filtrate was concentrated under vacuum. The resulting residue was purified by column chromatography (DCM/acetone = 5:2) to give 7b (643.9 mg, 38% yield) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl₃) δ 8.05–7.92 (m, 5H), 7.80–7.65 (m, 6H), 7.12–7.02 (m, 1H) ppm. $^{19}$F NMR (376 MHz, CDCl₃) δ -64.59, -78.45 ppm. $^{13}$C NMR (100 MHz, CDCl₃) δ 137.5 (q, $^2$J₇₁₇₉ = 37.4 Hz), 135.4, 132.1, 131.2, 127.2 (q, $^2$J₇₁₇₉ = 6.8 Hz), 123.8, 120.8 (q, $^1$J₇₁₇₉ = 320.1 Hz), 120.2 (q, $^1$J₇₁₇₉ = 237.4 Hz) ppm. The data are consistent with that reported in the literature.³

6-Methylnaphthalen-2-ol (2b)⁴

![Chemical reaction diagram]

To a solution of 6-bromo-2-naphthol S9 (446.1 mg, 2.0 mmol) and PdCl₂(dppf)·CH₂Cl₂ (163.3 mg, 10 mol%) in anhydrous THF (15.0 mL) was added methyl magnesium bromide (10.0 mL, 1 M in THF) with constant stirring at 0 °C. The mixture was then heated to reflux for 5 h. The mixture was cooled down to room temperature, quenched with saturated aqueous NH₄Cl (10 mL) and extracted with ethyl acetate (10 mL × 2). The combined organic layer was washed with brine and dried over anhydrous Na₂SO₄. The solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give 2b (153.3 mg, 48% yield) as a white solid. M.p.: 127.5-129.5 °C. $^1$H NMR (400 MHz, DMSO) δ 9.58 (br, 1H), 7.64 (d, $J = 8.8$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 7.53–7.51 (m, 1H), 7.22 (dd, $J = 8.4$, 1.5 Hz, 1H), 7.08–7.06 (m, 1H), 7.04 (dd, $J = 8.8$, 2.4 Hz, 1H), 2.39 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO) δ 154.6, 132.7, 131.5, 128.5, 128.3, 127.9, 126.4, 125.9, 118.5, 108.5, 21.0 ppm. The data are consistent with that reported in the literature.⁴

7-Benzynaphthalen-2-ol (2i)
2i (157.2 mg, 67% yield) was obtained as a white solid via a similar procedure for the synthesis of 2b. M.p.: 94.5-95.8 °C. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.68 (br, 1H), 7.70–7.64 (m, 2H), 7.53–7.50 (m, 1H), 7.31–7.24 (m, 4H), 7.20–7.15 (m, 1H), 7.11 (dd, \(J = 8.4, 1.6\) Hz, 1H), 7.06–7.04 (m, 1H), 7.01 (dd, \(J = 8.4, 2.4\) Hz, 1H), 4.03 (s, 2H) ppm. \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\) 155.5, 141.3, 139.0, 134.8, 129.0, 128.8, 128.4, 127.7, 126.3, 125.9, 124.9, 124.3, 117.9, 108.4, 41.4 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 3234, 3026, 2917, 1633, 1515. HRMS (ESI) calculated for C\(_{17}\)H\(_{13}\)O [M-H] \(\cdot\) 233.0972, found: 233.0976.

6-Phenynaphthalen-2-ol (2c)\(^6\)

To a solution of 6-bromo-2-naphthol S9 (334.7 mg, 1.5 mmol), Pd(PPh\(_3\))\(_4\) (86.7 mg, 5 mol %) in toluene (15.0 mL) was added a solution of NaHCO\(_3\) (378.0 mg, 4.5 mmol) in water (4.0 mL). The mixture was stirred at room temperature under an argon atmosphere. A solution of phenyl boronic acid (243.9 mg, 2.0 mmol) in ethanol (4.5 mL) was added and the mixture was stirred for 10 min. Then the reaction mixture was heated to 80 °C and stirred overnight. The mixture was cooled down to room temperature and extracted with ethyl acetate (10 mL \(\times\) 2). The combined organic layer was washed with water, brine and dried over anhydrous Na\(_2\)SO\(_4\). The solvent was removed and the residue was purified by column chromatography (petroleum ether/ethyl acetate = 10:1) to give 2c (237.9 mg, 72% yield) as a white solid. M.p.: 175.3-176.1 °C. \(^1\)H NMR (400 MHz, DMSO) \(\delta\) 9.78 (br, 1H), 8.09–8.06 (m, 1H), 7.84 (d, \(J = 8.8\) Hz, 1H), 7.79–7.69 (m, 4H), 7.51–7.45 (m, 2H), 7.38–7.33 (m, 1H), 7.15 (d, \(J = 2.0\) Hz, 1H), 7.12 (dd, \(J = 8.8, 2.4\) Hz, 1H) ppm. \(^{13}\)C NMR (100 MHz, DMSO) \(\delta\)
155.5, 140.3, 134.3, 133.8, 129.8, 128.9, 127.9, 127.0, 126.7, 126.6, 125.2, 125.1, 119.0, 108.4 ppm. The data are consistent with that reported in the literature.\textsuperscript{5}

1-(6-Hydroxynaphthalen-2-yl)ethanone (2e)\textsuperscript{6}

\begin{center}
\begin{tikzpicture}
  \node[draw] (a) {O};
  \node[draw, right of=a] (b) {OH};
  \node[below of=a] (c) {DCM, -40 °C to r.t.};
  \node[below of=b] (d) {2e};
  \node[below of=a] (e) {BBr\textsubscript{3}};
  \node[below of=b] (f) {S11};
  \node[below of=a] (g) {S12};
  \node[below of=b] (h) {S13};
  \node[below of=a] (i) {MeOH};
  \node[below of=b] (j) {70 °C, overnight};
  \node[below of=a] (k) {S12 + S13};
  \node[below of=b] (l) {2j};
  \draw[->] (a) -- (b);
  \draw[->] (a) -- (e);
  \draw[->] (a) -- (f);
  \draw[->] (a) -- (g);
  \draw[->] (a) -- (h);
  \draw[->] (a) -- (i);
  \draw[->] (a) -- (j);
  \draw[->] (a) -- (k);
  \draw[->] (a) -- (l);
\end{tikzpicture}
\end{center}

To a solution of 1-(6-methoxynaphthalen-2-yl)ethanone (600.0 mg, 3.0 mmol) in anhydrous DCM (10.0 mL) was added boron tribromide (3.8 g, 15.2 mmol) at -40 °C under an argon atmosphere. Then the mixture was allowed to stir at room temperature for 1 h. The reaction was quenched with water and saturated NaHCO\textsubscript{3}. The mixture was extracted with DCM and the solvent was removed to give the crude product which was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give 2e (156.4 mg, 28% yield) as a white solid. M.p.: 175.0-176.0 °C. \textsuperscript{1}H NMR (400 MHz, DMSO) $\delta$ 10.16 (br, 1H), 8.52 (d, $J = 0.9$ Hz, 1H), 7.99–7.94 (m, 1H), 7.87 (dd, $J = 8.6$, 1.7 Hz, 1H), 7.75 (d, $J = 8.7$ Hz, 1H), 7.20–7.14 (m, 2H), 2.64 (s, 3H) ppm. \textsuperscript{13}C NMR (100 MHz, DMSO) $\delta$ 197.3, 157.8, 137.1, 131.4, 131.4, 130.4, 126.5, 126.2, 123.9, 119.5, 108.8, 26.4 ppm. IR (thin film): $\nu$ (cm\textsuperscript{-1}) 3357, 1660, 1626, 1483, 1433. HRMS (ESI) calculated for C\textsubscript{12}H\textsubscript{10}O\textsubscript{2}Na [M+Na]$^+$: 209.0573, found: 209.0578.

2-(7-Hydroxynaphthalen-1-yl)isoindoline-1,3-dione (2j)

A mixture of 8-aminonaphthalen-2-ol S\textsubscript{12} (477.5 mg, 3.0 mmol) and phthalic anhydride S\textsubscript{13} (615.7 mg, 3.6 mmol) in methanol (25.0 mL) was stirred at 70 °C overnight. After completion, the solvent was removed to give the crude product which
was purified by column chromatography (petroleum ether/ethyl acetate = 5:2) to give 2j (224.4 mg, 30% yield) as a yellow solid. M.p.: 204.6–207.1 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.80 (br, 1H), 8.08–8.02 (m, 2H), 8.00–7.94 (m, 3H), 7.92 (d, $J$ = 8.9 Hz, 1H), 7.57–7.53 (m, 1H), 7.45–7.38 (m, 1H), 7.15 (dd, $J$ = 8.8, 2.3 Hz, 1H), 6.85 (d, $J$ = 2.1 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO) $\delta$ 167.5, 156.4, 134.9, 131.8, 131.6, 130.2, 129.2, 128.5, 127.7, 126.7, 123.6, 122.1, 119.2, 103.5 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 3306, 1076, 1631, 1511, 1607, 1382. HRMS (ESI) calculated for C$_{18}$H$_{10}$NO$_3$ [M-H]: 288.0666, found: 288.0657.

8-(Benzylamino)naphthalen-2-ol (2k)

![Chemical structure of 8-(Benzylamino)naphthalen-2-ol (2k)]

To a mixture of 8-aminonaphthalen-2-ol S12 (795.9 mg, 5.0 mmol) and NaHCO$_3$ (1.3 g, 15.5 mmol) in THF (20.0 mL) was added benzyl bromide (940.5 mg, 5.5 mmol) at 0 °C under an argon atmosphere. The mixture was allowed to stir at room temperature overnight. After completion, the solvent was removed to give the residue which was purified by column chromatography (petroleum ether/ethyl acetate = 5:1) to give 2k (560.1 mg, 45% yield) as a white solid. M.p.: 125.4–126.8 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 9.45 (br, 1H), 7.60 (d, $J$ = 8.8 Hz, 1H), 7.44 (d, $J$ = 2.0 Hz, 1H), 7.42–7.37 (m, 2H), 7.33–7.27 (m, 2H), 7.23–7.17 (m, 1H), 7.05 (dd, $J$ = 8.8, 2.4 Hz, 1H), 7.00–6.90 (m, 2H), 6.46–6.40 (m, 1H), 6.30–6.26 (m, 1H), 4.48–4.42 (m, 2H) ppm. $^{13}$C NMR (100 MHz, DMSO) $\delta$ 154.2, 142.3, 140.3, 129.4, 128.4, 128.2, 126.9, 126.4, 124.7, 123.1, 117.7, 115.8, 103.9, 103.9, 46.6 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 3439, 3026, 1623, 1485, 1438, 1345, 1223, 821. HRMS (ESI) calculated for C$_{17}$H$_{16}$NO [M+H]$: 250.1226$, found: 250.1225.

4-Hydroxy-6-methyl-2H-chromen-2-one (5b)
To a solution of 5-methyl-1-(2-hydroxyphenyl)ethanone \( \textbf{S14} \) (1.5 g, 10.0 mmol) and diethyl carbonate \( \textbf{S15} \) (1.8 g, 15.0 mmol) in DMSO (15.0 mL) was added NaH (60%, 1.2 g, 50.0 mmol) in portions while stirring at 0 °C. Then the mixture was allowed to stir at 100 °C for 2 h. After completion, the mixture was cooled down to room temperature. Water (30.0 mL) was added and the solution was acidified to \( \text{pH} = 6-7 \) by adding saturated aqueous \( \text{NH}_4\text{Cl} \). The water layer was extracted with ethyl acetate. The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and the solvent was removed under vacuum. The residue was purified by recrystallization with 70% EtOH (aq.) to afford \( \textbf{5b} \) (423.6 mg, 24% yield) as a pale brown solid. **M.p.**: 260.9-262.3 °C. **\( ^1\text{H NMR} \)** (400 MHz, DMSO) \( \delta \) 12.46 (br, 1H), 7.61 (d, \( J = 1.1 \) Hz, 1H), 7.45 (dd, \( J = 8.4, 1.9 \) Hz, 1H), 7.26 (d, \( J = 8.4 \) Hz, 1H), 5.58 (s, 1H), 2.37 (s, 3H) ppm. **\( ^{13}\text{C NMR} \)** (100 MHz, DMSO) \( \delta \) 165.7, 162.1, 151.7, 133.5, 133.1, 122.8, 116.2, 115.5, 90.9, 20.3 ppm. **IR (thin film)**: \( \nu (\text{cm}^{-1}) \) 3082, 2929, 2734, 2604, 1687, 1634, 1606. **HRMS (ESI)** calculated for \( \text{C}_{10}\text{H}_8\text{O}_3\text{Na} [\text{M}+\text{Na}]^+ \): 199.0366, found: 199.0362.

6-Fluoro-4-hydroxy-2\( \text{H} \)-chromen-2-one (\( \textbf{5c} \))

\[ \begin{array}{c}
\text{F} \\
\text{OH} \\
\text{O}
\end{array} \]

\( \textbf{5c} \) (340.2 mg, 29% yield) was obtained as a white solid following the similar procedure for the synthesis of \( \textbf{5b} \). **M.p.**: 247.0-248.0 °C. **\( ^1\text{H NMR} \)** (400 MHz, DMSO) \( \delta \) 12.75 (br, 1H), 7.54–7.47 (m, 2H), 7.45–7.40 (m, 1H), 5.67 (s, 1H) ppm. **\( ^{19}\text{F NMR} \)** (376 MHz, DMSO) \( \delta \) -118.07 ppm. **\( ^{13}\text{C NMR} \)** (100 MHz, DMSO) \( \delta \) 164.8 (d, \( ^4\text{J}_{\text{CF}} = 2.5 \) Hz), 161.6, 157.9 (d, \( ^1\text{J}_{\text{CF}} = 240.8 \) Hz), 149.8 (d, \( ^4\text{J}_{\text{CF}} = 1.6 \) Hz), 119.9 (d, \( ^2\text{J}_{\text{CF}} = 24.5 \) Hz), 118.5 (d, \( ^3\text{J}_{\text{CF}} = 8.5 \) Hz), 117.0 (d, \( ^3\text{J}_{\text{CF}} = 9.0 \) Hz), 108.6 (d, \( ^2\text{J}_{\text{CF}} = 25.1 \) Hz), 91.6 ppm. **IR (thin film)**: \( \nu (\text{cm}^{-1}) \) 3088, 2962, 1703, 1617, 1574, 1309. **HRMS (ESI)** calculated for \( \text{C}_{9}\text{H}_5\text{FO}_3\text{Na} [\text{M}+\text{Na}]^+ \): 203.0115, found: 203.0121.
4-Hydroxy-7-methoxy-2H-chromen-2-one (5e)

5e (341.8 mg, 16% yield) was obtained as a pink solid following the similar procedure for the synthesis of 5b. M.p.: 252.3-253.3 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 12.31 (br, 1H), 7.71 (d, $J = 8.9$ Hz, 1H), 6.95–6.90 (m, 2H), 5.44 (s, 1H), 3.85 (s, 3H) ppm. $^{13}$C NMR (100 MHz, DMSO) $\delta$ 166.0, 163.0, 162.3, 155.4, 124.3, 111.9, 108.9, 100.5, 88.5, 55.9 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 3072, 2988, 2748, 2595, 1697, 1614. HRMS (ESI) calculated for C$_{10}$H$_8$O$_4$Na [M+Na]$^+$: 215.0315, found: 215.0325.

7-Chloro-4-hydroxy-2H-chromen-2-one (5g)

5g (300.2 mg, 15% yield) was obtained as a pink solid following the similar procedure for the synthesis of 5b. M.p.: 227.3-229.5 °C. $^1$H NMR (400 MHz, DMSO) $\delta$ 7.81 (d, $J = 8.4$ Hz, 1H), 7.55 (d, $J = 2.0$ Hz, 1H), 7.40 (dd, $J = 8.4$, 2.0 Hz, 1H), 5.59 (s, 1H) ppm. $^{13}$C NMR (100 MHz, DMSO) $\delta$ 165.2, 161.5, 154.0, 136.9, 124.8, 124.2, 116.5, 114.9, 91.0 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 3406, 3094, 2929, 1679, 1624, 1602, 777. HRMS (ESI) calculated for C$_9$H$_{5}^{35}$ClO$_3$Na [M+Na]$^+$: 218.9819, found: 218.9822. HRMS (ESI) calculated for C$_9$H$_{5}^{37}$ClO$_3$Na [M+Na]$^+$: 220.9793, found: 220.9804.

4-Hydroxy-6-nitro-2H-chromen-2-one (5d)

4-Hydroxy-6-nitro-2H-chromen-2-one (5d)
To a solution of potassium nitrate (687.5 mg, 6.8 mmol) in sulphuric acid at 0 °C was added 4-hydroxy-2H-chromen-2-one S16 (1.0 g, 6.2 mmol) in portions. After being stirred at 0 °C for 1 h, the solution was poured into cold water. The produced solid was filtered and purified by recrystallization with ethanol to give 5d (834.8 mg, 65% yield) as a pale yellow solid. **M.p.**: 237.2-238.5 °C. **1H NMR** (400 MHz, DMSO) δ 8.52 (d, J = 2.4 Hz, 1H), 8.44 (dd, J = 9.0, 2.5 Hz, 1H), 7.60 (d, J = 9.0 Hz, 1H), 5.70 (s, 1H) ppm. **13C NMR** (100 MHz, DMSO) δ 164.5, 160.8, 157.1, 143.2, 127.3, 119.1, 118.1, 116.4, 92.0 ppm. The data are consistent with that reported in the literature.7

7-(Dimethylamino)-4-hydroxy-2H-chromen-2-one (5f)8

To a mixture of malonic acid S17 (5.2 g, 49.9 mmol) and phenol (9.4 g, 100 mmol) was slowly added POCl3 (9.3 mL, 100.0 mmol) at 0 °C. Then the mixture was stirred at 110 °C until the release of HCl was ceased. The upper layer of the reaction mixture was poured into water (150.0 mL). The mixture was extracted with ethyl acetate, dried over anhydrous Na2SO4 and evaporated under vacuum. Diphenyl malonate S18 (12.3 g, 90% yield) was obtained as pale brown oil, which was used in the next step without further purification.

To a solution of diphenyl malonate S18 (1.5 g, 5.9 mmol) in toluene (20.0 mL) was added 3-N,N-dimethylaminophenol S19 (685.9 mg, 5.0 mmol). The mixture was heated to reflux and stirred for 7 h. The precipitation was filtered and recrystallized from 70% EtOH (aq.) to give 5f (719 mg, 70% yield) as a purple solid. **M.p.**: 252.3-253.6 °C. **1H NMR** (400 MHz, DMSO) δ 7.56 (d, J = 8.8 Hz, 1H), 7.72–7.65 (m, 1H), 6.51–6.45 (m, 1H), 5.28 (s, 1H), 3.00 (s, 6H) ppm. **13C NMR** (100 MHz, DMSO) δ 166.5, 162.8, 155.8, 153.4, 123.8, 108.6, 104.1, 97.9, 86.5, 39.7 ppm. The data are consistent with that reported in the literature.8
3.2 Experiment procedures and characterization data of products 3a-3l and 6a-6h

3.2.1 General procedure for the synthesis of 3a-3l

A solution of 2a (28.8 mg, 0.2 mmol), 1a (122.2 mg, 0.3 mmol) and K₂CO₃ (82.9 mg, 0.6 mmol) in MeCN (4.0 mL) was stirred at 0 °C under an argon atmosphere for 24 h. Then piperazine (17.2 mg, 0.2 mmol) was added and the reaction mixture was stirred at 60 °C for 5 h to remove the side product 4a. After being cooled down to room temperature, water (10 mL) was added. Then mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was purified by column chromatography to give the product 3a.

1,2-Dihydronaphtho[2,1-b]furan (3a)

The product 3a (31.0 mg, 91% yield) was obtained as colorless liquid following the general procedure. Rf = 0.3 (petroleum ether). ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.61 (d, J = 8.3 Hz, 1H), 7.51–7.46 (m, 1H), 7.35–7.29 (m, 1H), 7.14 (d, J = 8.7 Hz, 1H), 4.81–4.73 (m, 2H), 3.54–3.46 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 131.0, 129.3, 129.0, 128.8, 126.8, 122.9, 122.9, 118.7, 112.2, 71.9, 28.8 ppm. IR (thin film): ν (cm⁻¹) 3057, 2966, 2894, 1631, 1521, 1463, 1259, 1244. HRMS (EI) calculated for C₁₂H₁₀O [M]⁺: 170.0726, found: 170.0727.
7-Methyl-1,2-dihydronaphtho[2,1-\textit{b}]furan (3b)

The product 3b (33.9 mg, 92% yield) was obtained as a white solid following the general procedure. **M.p.:** 70.2–71.3 °C. **Rf** = 0.2 (petroleum ether). \textbf{\textit{\textsuperscript{1}H NMR}} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.61–7.58 (m, 2H), 7.52 (d, \(J = 8.4\) Hz, 1H), 7.35–7.30 (m, 1H), 7.10 (d, \(J = 8.8\) Hz, 1H), 4.78–4.72 (m, 2H), 3.51–3.44 (m, 2H), 2.49 (s, 3H) ppm. \textbf{\textit{\textsuperscript{13}C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 157.2, 132.3, 129.6, 129.1, 129.0, 128.2, 127.8, 122.7, 118.6, 112.1, 71.7, 28.8, 21.6 ppm. **IR (thin film):** \(\nu\) (cm\textsuperscript{-1}) 2967, 2894, 1602, 1479, 1356, 1243, 1160, 811. **HRMS (EI) calculated for C\textsubscript{13}H\textsubscript{12}O [M]\textsuperscript{+}: 184.0883, found: 184.0882.

7-Phenyl-1,2-dihydronaphtho[2,1-\textit{b}]furan (3c)

The product 3c (42.4 mg, 86% yield) was obtained as a white solid following the general procedure. **M.p.:** 133.1–134.6 °C. **Rf** = 0.8 (petroleum ether/ethyl acetate = 10:1). \textbf{\textit{\textsuperscript{1}H NMR}} (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.04 (d, \(J = 1.5\) Hz, 1H), 7.79–7.66 (m, 5H), 7.53–7.47 (m, 2H), 7.41–7.36 (m, 1H), 7.17 (d, \(J = 8.7\) Hz, 1H), 4.83–4.76 (m, 2H), 3.55–3.48 (m, 2H) ppm. \textbf{\textit{\textsuperscript{13}C NMR}} (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.0, 141.4, 135.7, 130.1, 129.6, 129.4, 129.0, 127.3, 127.2, 126.8, 126.5, 123.5, 118.7, 112.6, 72.0, 28.8 ppm. **IR (thin film):** \(\nu\) (cm\textsuperscript{-1}) 3062, 2956, 2890, 1601, 1496, 1241. **HRMS (EI) calculated for C\textsubscript{18}H\textsubscript{14}O [M]\textsuperscript{+}: 246.1039, found: 246.1037.

7-Bromo-1,2-dihydronaphtho[2,1-\textit{b}]furan (3d)
The product 3d (46.3 mg, 93% yield) was obtained as a white solid following the general procedure. M.p.: 63.1–64.9 °C. $R_f = 0.7$ (petroleum ether/ethyl acetate = 10:1). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 1.9$ Hz, 1H), 7.56 (d, $J = 8.8$ Hz, 1H), 7.52 (dd, $J = 8.8$, 1.9 Hz, 1H), 7.43 (d, $J = 8.8$ Hz, 1H), 7.13 (d, $J = 8.8$ Hz, 1H), 4.79–4.72 (m, 2H), 3.48–3.40 (m, 2H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 158.2, 130.7, 130.4, 130.0, 129.4, 128.2, 124.6, 119.0, 116.4, 113.2, 71.9, 28.7 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 2963, 2895, 1620, 1586, 1347, 1243, 811. HRMS (EI) calculated for C$_{12}$H$_7$BrO [M]$^+$: 247.9831, found: 247.9833. HRMS (EI) calculated for C$_{12}$H$_8$BrO [M]$^+$: 249.9816, found: 249.9814.

1-(1,2-Dihyronaphtho[2,1-b]furan-7-yl)ethanone (3e)

The product 3e (35.7 mg, 84% yield) was as a white solid obtained following the general procedure. M.p.: 101.8–103.0 °C. $R_f = 0.4$ (petroleum ether/ethyl acetate = 10:1). $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 8.42 (d, $J = 1.5$ Hz, 1H), 8.03 (dd, $J = 8.7$, 1.7 Hz, 1H), 7.79 (d, $J = 8.7$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.17 (d, $J = 8.8$ Hz, 1H), 4.85–4.76 (m, 2H), 3.54–3.46 (m, 2H), 2.69 (s, 3H) ppm. $^{13}C$ NMR (100 MHz, CDCl$_3$) $\delta$ 197.8, 160.2, 133.2, 132.0, 131.3, 131.2, 128.1, 125.0, 123.2, 119.2, 113.1, 72.3, 28.4, 26.5 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 2947, 2912, 2854, 1663, 1624, 1476, 1357, 1242, 1187. HRMS (ESI) calculated for C$_{14}$H$_{12}$O$_2$Na [M+Na]$^+$: 235.0730, found: 235.0723.

Methyl 1,2-dihyronaphtho[2,1-b]furan-7-carboxylate (3f)

The product 3f (36.1 mg, 79% yield) was obtained as a white solid following the general procedure. M.p.: 93.7–94.8 °C. $R_f = 0.5$ (petroleum ether/ethyl acetate = 10:1). $^1H$
NMR (400 MHz, CDCl3) δ 8.54 (d, J = 1.3 Hz, 1H), 8.03 (dd, J = 8.7, 1.6 Hz, 1H), 7.77 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.15 (d, J = 8.8 Hz, 1H), 4.81–4.74 (m, 2H), 3.94 (s, 3H), 3.50–3.42 (m, 2H) ppm. 

13C NMR (100 MHz, CDCl3) δ 167.5, 160.0, 133.2, 132.1, 130.9, 128.2, 126.3, 124.5, 122.9, 119.0, 113.0, 72.2, 52.2, 28.5 ppm. 

IR (thin film): ν (cm⁻¹) 2948, 2911, 2855, 1709, 1624, 1479, 1280, 1241, 1197. 


**1,2-Dihydronaphtho[2,1-b]furan-7-carbonitrile (3g)** 

The product 3g (21.1 mg, 54% yield) was obtained as a white solid following the general procedure. M.p.: 115.6–117.9 °C. Rf = 0.4 (petroleum ether/ethyl acetate = 10:1). 

1H NMR (400 MHz, CDCl3) δ 8.19–8.16 (m, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.6 Hz, 1H), 7.58 (dd, J = 8.6, 1.4 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 4.87–4.78 (m, 2H), 3.54–3.46 (m, 2H) ppm. 

13C NMR (100 MHz, CDCl3) δ 160.6, 135.0, 132.4, 130.1, 128.0, 127.3, 124.0, 119.8, 119.44, 114.0, 106.0, 72.4, 28.3 ppm. 

IR (thin film): ν (cm⁻¹) 3052, 2921, 2853, 2221, 1625, 1473, 1359, 1264, 1243, 1159. 


**8-Methoxy-1,2-dihydronaphtho[2,1-b]furan (3h)** 

The product 3h (31.2 mg, 78% yield) was obtained as a white solid following the general procedure. M.p.: 133.2–134.2 °C. Rf = 0.7 (petroleum ether/ethyl acetate = 10:1). 

1H NMR (400 MHz, CDCl3) δ 7.70 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.00–6.95 (m, 2H), 6.83 (d, J = 2.4 Hz, 1H), 4.79–4.72 (m, 2H), 3.93 (s, 3H), 3.47–3.39 (m, 2H) ppm. 

13C NMR (100 MHz, CDCl3) δ 158.6, 158.4, 132.2, 130.4, 128.8, 124.8, 117.8, 115.5, 109.6, 101.4, 71.8, 55.4, 28.8 ppm. 

IR (thin film): ν (cm⁻¹) 3010, 2965,
2022, 1629, 1516, 1472, 1244, 1224. **HRMS (EI)** calculated for C\textsubscript{13}H\textsubscript{12}O\textsubscript{2} [M]\textsuperscript{+}: 200.0832, found: 200.0831.

8-Benzyl-1,2-dihyronaphtho[2,1-b]furan (3i)

![8-Benzyl-1,2-dihyronaphtho[2,1-b]furan (3i)](image)

The product 3i (32.8 mg, 63% yield) was obtained as a white solid following the general procedure. **M.p.**: 98.1–99.3 °C. **Rf** = 0.1 (petroleum ether). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.69 (d, \(J = 8.4\) Hz, 1H), 7.60 (d, \(J = 8.7\) Hz, 1H), 7.40–7.37 (m, 1H), 7.30–7.25 (m, 2H), 7.23–7.16 (m, 3H), 7.12 (dd, \(J = 8.4, 1.5\) Hz, 1H), 7.05 (d, \(J = 8.7\) Hz, 1H), 4.75–4.67 (m, 2H), 4.11 (s, 2H), 3.45–3.37 (m, 2H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 158.0, 141.2, 139.6, 131.2, 129.1, 129.0, 128.8, 128.6, 128.0, 126.3, 124.8, 122.3, 118.4, 111.6, 72.0, 42.5, 28.8 ppm. **IR (thin film)**: \(\nu\) (cm\textsuperscript{-1}) 3039, 2965, 2924, 2904, 2847, 1633, 1601, 1512, 1453, 1245. **HRMS (EI)** calculated for C\textsubscript{19}H\textsubscript{16}O [M]\textsuperscript{+}: 260.1196, found: 260.1194.

2-(1,2-Dihyronaphtho[2,1-b]furan-9-yl)isoindoline-1,3-dione (3j)

![2-(1,2-Dihyronaphtho[2,1-b]furan-9-yl)isoindoline-1,3-dione (3j)](image)

The product 3j (44.1 mg, 70% yield) was obtained as a yellow solid following the general procedure. **M.p.**: 213.8–215.8 °C. **Rf** = 0.6 (petroleum ether/ethyl acetate/DCM = 5:1:1). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.05–7.99 (m, 2H), 7.94 (dd, \(J = 8.3, 1.2\) Hz, 1H), 7.86–7.81 (m, 2H), 7.77 (d, \(J = 8.8\) Hz, 1H), 7.41–7.36 (m, 1H), 7.34 (dd, \(J = 7.2, 1.4\) Hz, 1H), 7.15 (d, \(J = 8.8\) Hz, 1H), 4.57–4.50 (m, 2H), 3.24–3.16 (m, 2H) ppm. \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 168.2, 159.9, 134.6, 132.5, 131.4, 131.2, 130.5, 129.9, 129.2, 125.6, 124.3, 122.6, 115.2, 113.22, 71.5, 29.8 ppm. **IR (thin film)**:
N-benzyl-1,2-dihydronaphtho[2,1-b]furan-9-amine (3k)

The product 3k (33.0 mg, 60% yield) was obtained as a yellow solid following the general procedure. M.p.: 136.7–138.6 °C. Rf = 0.7 (petroleum ether/ethyl acetate = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 8.7$ Hz, 1H), 7.47–7.43 (m, 2H), 7.42–7.36 (m, 2H), 7.35–7.30 (m, 1H), 7.23–7.19 (m, 1H), 7.16–7.10 (m, 1H), 7.06 (d, $J = 8.7$ Hz, 1H), 6.58 (d, $J = 7.4$ Hz, 1H), 4.69–4.59 (m, 2H), 4.39 (s, 2H), 3.86–3.78 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.8, 143.7, 139.3, 131.1, 129.9, 128.9, 127.8, 127.5, 123.8, 123.3, 119.3, 115.8, 112.1, 106.4, 71.0, 49.3, 32.7 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 3390, 2921, 2870, 1618, 1510, 1474, 1254, 1232. HRMS (ESI) calculated for C$_{19}$H$_{18}$NO [M+H]$^+$: 276.1384, found: 276.1383.

1,2-Dihydrofuro[3,2-f]quinoline (3l)

The product 3l (21.2 mg, 62% yield) was obtained as a yellow solid following the general procedure. M.p.: 83.4–86.9 °C. Rf = 0.2 (petroleum ether/ethyl acetate = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.77–8.72 (m, 1H), 7.97–7.89 (m, 2H), 7.35–7.30 (m, 1H), 7.23–7.19 (m, 1H), 7.16–7.10 (m, 1H), 7.06 (d, $J = 8.7$ Hz, 1H), 4.84–4.79 (m, 2H), 4.35–3.42 (m, 2H) ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.0, 147.5, 144.8, 131.0, 130.5, 126.0, 121.5, 118.5, 115.8, 72.3, 28.4 ppm. IR (thin film): $\nu$ (cm$^{-1}$) 2970, 2905, 2870, 1618, 1510, 1474, 1254, 1232. HRMS (ESI) calculated for C$_{11}$H$_{10}$NO [M+H]$^+$: 172.0757, found: 172.0757.
3.2.2 General procedure for the synthesis of 6a-6h

To a solution of 5a (32.4 mg, 0.2 mmol) and 1a (122.2 mg, 0.3 mmol) in 1,4-dioxane (4.0 mL) was added DBU (91.3 mg, 0.6 mmol). The mixture was stirred at room temperature for 24 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated under vacuum. The residue was purified by column chromatography to give 6a.

2H-furo[3,2-c]chromen-4(3H)-one (6a)

The product 6a (31.2 mg, 83% yield) was obtained as a white solid following the general procedure. M.p.: 143.3–145.5 °C. Rf = 0.2 (petroleum ether/ethyl acetate = 5:1). ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.8, 1.6 Hz, 1H), 7.58–7.52 (m, 1H), 7.39–7.35 (m, 1H), 7.30–7.25 (m, 1H), 4.92–4.84 (m, 2H), 3.24–3.16 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 167.5, 160.9, 155.0, 132.5, 124.1, 122.8, 117.1, 112.7, 102.5, 74.5, 27.0 ppm. IR (thin film): ν (cm⁻¹) 2916, 1708, 1644, 1640, 1500, 1419, 1328, 1275, 1249. HRMS (ESI) calculated for C₁₁H₈O₃Na [M+Na]⁺: 211.0358, found: 211.0366.

8-Methyl-2H-furo[3,2-c]chromen-4(3H)-one (6b)
The product 6b (25.1 mg, 62% yield) was obtained as a white solid following the general procedure. M.p.: 154.1–155.7 °C. Rf = 0.4 (petroleum ether/ethyl acetate = 5:1). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.44–7.42 (m, 1H), 7.37 (dd, \(J = 8.5, 1.9\) Hz, 1H), 7.29–7.27 (m, 1H), 4.92–4.84 (m, 2H), 3.25–3.16 (m, 2H), 2.42 (s, 3H) ppm. \(^{13}\)C NMR (100 MHz, CDCl3) \(\delta\) 167.4, 161.0, 153.2, 133.8, 133.5, 122.4, 116.7, 112.4, 102.4, 74.5, 27.0, 20.9 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 2977, 2954, 2925, 2866, 1714, 1646, 1491, 1206, 1097, 1437, 1401, 1375. HRMS (ESI) calculated for C\(_{12}\)H\(_{10}\)O\(_3\)Na [M+Na]\(^+\): 225.0517, found: 225.0522.

8-Fluoro-2H-furo[3,2-c]chromen-4(3H)-one (6c)

![Fluoro-2H-furo[3,2-c]chromen-4(3H)-one (6c)](image)

The product 6c (35.9 mg, 87% yield) was obtained as a white solid following the general procedure. M.p.: 161.6–163.7 °C. Rf = 0.2 (petroleum ether/ethyl acetate = 5:1). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.40–7.25 (m, 3H), 4.96–4.87 (m, 2H), 3.28–3.19 (m, 2H) ppm. \(^{19}\)F NMR (376 MHz, DMSO) \(\delta\) -117.12 ppm. \(^{13}\)C NMR (100 MHz, CDCl3) \(\delta\) 166.7 (d, \(^4\)J\(_{CF}\) = 2.8 Hz), 160.5, 158.5 (d, \(^1\)J\(_{CF}\) = 244.6 Hz), 151.1 (d, \(^4\)J\(_{CF}\) = 2.1 Hz), 120.0 (d, \(^2\)J\(_{CF}\) = 24.6 Hz), 118.7 (d, \(^3\)J\(_{CF}\) = 8.3 Hz), 113.4 (d, \(^3\)J\(_{CF}\) = 9.3 Hz), 108.4 (d, \(^2\)J\(_{CF}\) = 25.2 Hz), 103.5, 74.7, 27.0 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 3070, 2971, 2852, 1714, 1647, 1575, 1499, 1445, 1259, 1185, 1033. HRMS (ESI) calculated for C\(_{11}\)H\(_{8}\)FO\(_3\) [M+H]\(^+\): 207.0450, found: 207.0452.

8-Nitro-2H-furo[3,2-c]chromen-4(3H)-one (6d)

![8-Nitro-2H-furo[3,2-c]chromen-4(3H)-one (6d)](image)

The product 6d (31.7 mg, 68% yield) was obtained as a pale yellow solid following the general procedure. M.p.: 189.2–191.8 °C. Rf = 0.2 (petroleum ether/ethyl acetate = 5:1). \(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 8.55 (d, \(J = 2.5\) Hz, 1H), 8.41 (dd, \(J = 9.2, 2.6\) Hz,
1H), 7.49 (d, \(J = 9.2\) Hz, 1H), 5.01–4.91 (m, 2H), 3.30–3.20 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.3, 159.1, 158.2, 143.8, 127.1, 119.3, 118.2, 113.0, 104.3, 75.1, 27.1 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 3082, 2975, 2919, 2851, 1726, 1648, 1620, 1528, 1492, 1433, 1336, 1265, 1126, 1072. HRMS (EI) calculated for C\(_{11}\)H\(_7\)NO\(_5\) [M]: 233.0320, found: 233.0324.

7-Methoxy-2H-furo[3,2-c]chromen-4(3H)-one (6e)

![7-Methoxy-2H-furo[3,2-c]chromen-4(3H)-one (6e)](image)

The product 6e (34.9 mg, 80% yield) was obtained as a white solid following the general procedure. M.p.: 144.1–146.4 °C. \(R_f\) = 0.2 (petroleum ether/ethyl acetate = 5:1). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.52–7.46 (m, 1H), 6.86–6.77 (m, 2H), 4.86–4.77 (m, 2H), 3.84 (s, 3H), 3.18–3.09 (m, 2H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 167.8, 163.4, 161.1, 156.9, 123.7, 112.4, 106.0, 100.8, 99.5, 74.5, 55.8, 26.7 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 3009, 2976, 2910, 1738, 1643, 1614, 1419, 1275, 1156, 1090. HRMS (ESI) calculated for C\(_{12}\)H\(_{10}\)O\(_4\)Na [M+Na]: 241.0459, found: 241.0471.

7-(Dimethylamino)-2H-furo[3,2-c]chromen-4(3H)-one (6f)

![7-(Dimethylamino)-2H-furo[3,2-c]chromen-4(3H)-one (6f)](image)

The product 6f (30.1 mg, 65% yield) was obtained as a pink solid following the general procedure. M.p.: 171.8–173.7 °C. \(R_f\) = 0.4 (petroleum ether/ethyl acetate = 5:2). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.41 (d, \(J = 8.8\) Hz, 1H), 6.58 (dd, \(J = 8.8, 2.3\) Hz, 1H), 6.52 (d, \(J = 2.3\) Hz, 1H), 4.83–4.73 (m, 2H), 3.15–3.06 (m, 2H), 3.03 (s, 6H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 168.3, 161.8, 157.3, 153.5, 123.3, 108.8, 101.5, 98.1, 97.1, 74.3, 40.2, 26.6 ppm. IR (thin film): \(\nu\) (cm\(^{-1}\)) 2918, 2875, 2852, 1693, 1622, 1545,
1527, 1425, 1327, 1272, 1248, 1092. HRMS (ESI) calculated for $\text{C}_{13}\text{H}_{13}\text{NO}_3\text{Na} \ [\text{M+Na}]^+$: 254.0787, found: 254.0788.

7-Chloro-2H-furo[3,2-c]chromen-4(3H)-one (6g)

![Chemical structure](image)

The product 6g (16.9 mg, 38% yield) was obtained as a white solid following the general procedure. **M.p.**: 201.6–204.1 °C. **Rf** = 0.3 (petroleum ether/ethyl acetate = 5:1). $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.55 (d, $J = 8.4$ Hz, 1H), 7.36 (d, $J = 1.8$ Hz, 1H), 7.25 (dd, $J = 7.2$, 1.8 Hz, 1H), 4.93–4.83 (m, 2H), 3.24–3.13 (m, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) δ 166.9, 160.2, 155.2, 124.7, 123.7, 117.4, 111.3, 102.5, 74.7, 26.9 ppm. **IR (thin film)**: ν (cm$^{-1}$) 3084, 2920, 2851, 1723, 1641, 1419, 1104, 1026, 741. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{7}\text{ClO}_3\text{Na} \ [\text{M+Na}]^+$: 244.9976, found: 244.9974. HRMS (ESI) calculated for $\text{C}_{11}\text{H}_{7}\text{ClO}_3\text{Na} \ [\text{M+Na}]^+$: 246.9950, found: 246.9946.

5-Methyl-2,3-dihydrofuro[3,2-c]quinolin-4(5H)-one (6h)

![Chemical structure](image)

The product 6h (13.7 mg, 34% yield) was obtained as a white solid following the general procedure. **M.p.**: 130.2–132.7 °C. **Rf** = 0.2 (petroleum ether/ethyl acetate = 5:3). $^1\text{H NMR}$ (400 MHz, CDCl$_3$) δ 7.73 (dd, $J = 7.9$, 1.4 Hz, 1H), 7.56 (ddd, $J = 8.7$, 7.3, 1.5 Hz, 1H), 7.38–7.36 (d, $J = 8.6$ Hz, 1H), 7.24–7.19 (m, 1H), 4.86–4.75 (m, 2H), 3.70 (s, 3H), 3.29–3.18 (m, 2H) ppm. $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) δ 163.1, 161.6, 140.7, 131.0, 123.1, 121.7, 114.6, 112.7, 108.5, 73.5, 29.2, 28.1 ppm. **IR (thin film)**: ν (cm$^{-1}$) 2970, 2921, 2860, 1657, 1621, 1576, 1424, 1106, 752. HRMS (ESI) calculated for $\text{C}_{12}\text{H}_{11}\text{NO}_2\text{Na} \ [\text{M+Na}]^+$: 224.0684, found: 224.0682.
3.3 Reaction of (E)-diphenyl-β-(trifluoromethyl)vinylsulfonium triflate 7b with β-naphthol 2a

The solution of 2a (28.8 mg, 0.2 mmol), K$_2$CO$_3$ (82.9 mg, 0.6 mmol) and (E)-diphenyl-β-(trifluoromethyl)vinylsulfonium triflate 7b (129.1 mg, 0.3 mmol) in MeCN (4.0 mL) was stirred at 0 °C under an argon atmosphere for 24 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under vacuum. The residue was purified by column chromatography to give (E)-2-(3,3,3-trifluoroprop-1-en-1-yl)oxy)naphthalene (8a) as a colorless liquid (11.9 mg, 25% yield). R$_f$ = 0.5 (petroleum ether/DCM = 10:1). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.88–7.81 (m, 2H), 7.81–7.76 (m, 1H), 7.54–7.43 (m, 2H), 7.42–7.39 (m, 1H), 7.30–7.26 (m, 1H), 6.91–6.87 (m, 1H), 5.14–5.03 (m, 1H) ppm. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -57.60 ppm. $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.5, 149.3 (q, J$_{CF}$ = 5.3 Hz), 134.1, 130.9, 130.4, 128.0, 127.4, 127.2, 125.5, 123.0 (q, J$_{CF}$ = 269.4 Hz), 118.4, 112.6, 99.8 (q, J$_{CF}$ = 35.3 Hz) ppm. IR (thin film): ν (cm$^{-1}$) 2924, 2853, 1678, 1630, 1598, 1248. HRMS (EI) calculated for C$_{13}$H$_9$F$_3$O [M]$^+$: 238.0600, found: 238.0601.

3.4 Reaction of (E)-diphenyl-β-(trifluoromethyl)vinylsulfonium triflate 7b with 4-hydroxycoumarin 5a

A solution of 4-hydroxycoumarin 5a (32.4 mg, 0.2 mmol), (E)-diphenyl-β-(trifluoromethyl)vinylsulfonium triflate 7b (129.1 mg, 0.3 mmol) and DBU (91.3 mg, 0.6 mmol) in 1,4-dioxane (4.0 mL) was stirred at room temperature for 16 h. Water (10 mL) was added and the mixture was extracted with ethyl acetate (10 mL × 2). The
combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and evaporated under vacuum. The residue was purified by column chromatography to give 3-(Trifluoromethyl)-2H-furo[3,2-c]chromen-4(3H)-one (8b) as a white solid (19.0 mg, 37% yield). **M.p.:** 127.9–131.2 °C. **Rf** = 0.6 (petroleum ether/ethyl acetate = 5:2). **$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.74–7.57 (m, 2H), 7.39 (d, $J$ = 8.4 Hz, 1H), 7.35–7.27 (m, 1H), 5.09–4.99 (m, 1H), 4.96–4.86 (m, 1H), 4.26–4.14 (m, 1H) ppm. **$^{19}$F NMR** (376 MHz, CDCl$_3$) $\delta$ -71.37 ppm. **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 170.2, 158.9, 155.6, 133.9, δ 125.5 (q, $^1$J$_{CF}$ = 280.4 Hz), 124.4, 123.3, 117.3, 111.8, 97.5 (q, $^3$J$_{CF}$ = 2.0 Hz), 74.1 (q, $^3$J$_{CF}$ = 3.0 Hz), 45.1 (q, $^2$J$_{CF}$ = 31.7 Hz) ppm. **IR (thin film):** $\nu$ (cm$^{-1}$) 3098, 2975, 2923, 1706, 1646, 1271. **HRMS (ESI) calculated for C$_{12}$H$_7$F$_3$O$_3$Na [M+Na]$^+$: 279.0239, found: 279.0240.

3.5 Synthesis of furans 9a and 9b

![Chemical structure of 3a and 9a](image)

To a solution of 3a (34.0 mg, 0.2 mmol) in toluene (4.0 mL) was added DDQ (49.9 mg, 0.22 mmol). The solution was heated to reflux overnight. The precipitation was filtered and the filtrate was evaporated under vacuum. The residue was purified by column chromatography to give naphtho[2,1-b]furan 9a (36.9 mg, 99% yield) as a white solid. **M.p.:** 60.4-61.5 °C. **$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.17 (d, $J$ = 8.2 Hz, 1H), 7.98 (d, $J$ = 8.1 Hz, 1H), 7.79 (d, $J$ = 1.9 Hz, 1H), 7.78–7.68 (m, 2H), 7.65–7.59 (m, 1H), 7.55–7.49 (m, 1H), 7.29 (d, $J$ = 1.9 Hz, 1H). **$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 152.6, 144.2, 130.4, 128.8, 127.9, 126.3, 125.2, 124.5, 123.5, 122.7, 112.6, 105.6. **IR (thin film):** $\nu$ (cm$^{-1}$) 3144, 3052, 2922, 2852, 1622, 1510, 810, 749. **HRMS (EI) calculated for C$_{12}$H$_7$O [M$^+$]: 168.0570, found: 168.0570.

4H-furo[3,2-c]chromen-4-one (9b)
The product **9b** (27.9 mg, 75% yield) was obtained as a pink solid via a similar procedure except DDQ (68.1 mg, 0.3 mmol) was used. **M.p.:** 96.8-98.7 °C. **1H NMR** (500 MHz, CDCl₃) δ 7.86 (d, J = 7.7 Hz, 1H), 7.66–7.62 (m, 1H), 7.54–7.48 (m, 1H), 7.45–7.41 (m, 1H), 7.37–7.31 (m, 1H), 7.01–7.98 (m, 1H). **13C NMR** (125 MHz, CDCl₃) δ 158.4, 157.8, 152.7, 144.9, 130.9, 124.7, 121.0, 117.4, 112.9, 110.8, 108.7. **IR (thin film):** ν (cm⁻¹) 3125, 3079, 1738, 1630, 1495, 753, 727. **HRMS (EI) calculated for C₁₁H₆O₃ [M]⁺:** 186.0311, found: 186.0312.
4. References

5. NMR Spectra