Supporting Information

A practical one-pot synthesis of coumarins in aqueous sodium bicarbonate via intramolecular Wittig reaction at room temperature

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Table of Contents

<table>
<thead>
<tr>
<th>Sr.No.</th>
<th>Description</th>
<th>Page No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General Information ..............................................</td>
<td>S2</td>
</tr>
<tr>
<td>2</td>
<td>Experimental procedure and spectral data of compounds .......</td>
<td>S2 – S8</td>
</tr>
<tr>
<td>3</td>
<td>References ...................................................................</td>
<td>S9</td>
</tr>
<tr>
<td>2</td>
<td>$^1$H NMR and $^{13}$C NMR Spectra of representative compounds</td>
<td>S10 - S19</td>
</tr>
</tbody>
</table>
**General Information**

All reagents were of analytical grade and were used directly. Thin-layer chromatography (TLC) was performed on silica gel plates (60 F254; Merck). Column chromatography was performed using silica gel (60–120 mesh size; Merck). Melting points were determined in open capillaries and are uncorrected. The IR spectra were recorded on Nicolet Impact 410 FT IR spectrophotometer using KBr pellets. $^1$H and $^{13}$C NMR were recorded on Bruker 300-MHz and 400-MHz FT NMR spectrometer in CDCl$_3$ and DMSO-d$_6$ by using TMS as internal standard.

**Experimental Section:**

**General Procedure for the synthesis of 2-formylphenyl 2-bromoacetates (2a-h):**

A modification of a literature method$^1$ was used. Salicylaldehyde (1 equiv) was added dropwise during 15 min at 0 °C to a suspension of sodium hydride (1.1 equiv) in THF (4 mL per 1 mmol of salicylaldehyde). The resulting pale yellow, viscous slurry was stirred for 2 h, and the 2-bromoacetyl bromide (1.2 equiv) was added dropwise over 10 min at 0 °C. After 25 min, the resulting white suspension of NaBr was removed by filtration; the solvent was evaporated, and the residue was quenched with saturated NH$_4$Cl (10 mL) solution and then extracted with ethyl acetate (2 x 10mL), the combined organic extracts were washed with H$_2$O (20 mL), brine (20 mL) and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure to afford the 2-formylphenyl 2-bromoacetates (2a-h) with 80-90% yield with sufficient purity for the next step reaction.

**2-formylphenyl 2-bromoacetate (2a)**

![Chemical Structure](image)

Yield: 85%; colorless oil; IR (KBr): 1765, 1702, 1276, 1254, 1196, 1118 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.12 (s, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.65 (m, 1H), 7.44 (t, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 4.18 (s, 2H); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 188.9, 165.5, 150.6, 135.4, 131.9, 127.6, 126.9, 122.9, 25.2;
4-chloro-2-formylphenyl 2-bromoacetate (2b)

\[
\begin{array}{c}
\text{Cl} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 83%; low melting solid; IR (KBr): 1767, 1705, 1278, 1257, 1200, 1119, 810 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.10 (s, 1H), 7.79 (d, \(J = 8.0\) Hz, 1H), 7.54 (dd, 1H), 7.12 (d, \(J = 8.0\) Hz, 1H), 4.08 (s, 2H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 188.9, 165.5, 150.6, 135.4, 131.8, 130.5, 123.1, 25.2;

4-bromo-2-formylphenyl 2-bromoacetate (2c)

\[
\begin{array}{c}
\text{Br} \\
\text{H} \\
\text{O} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 83%; low melting solid; IR (KBr): 1763, 1696, 1278, 1257, 1200, 1119, 640 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.10 (s, 1H), 8.01 (d, \(J = 8.0\) Hz, 1H), 7.72 (dd, 1H), 7.14 (d, \(J = 8.0\) Hz, 1H), 4.10 (s, 2H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 188.9, 165.5, 150.6, 139.4, 134.5, 124.2, 120.1, 25.2;

2-formyl-4-methylphenyl 2-bromoacetate (2d)

\[
\begin{array}{c}
\text{H} \\
\text{O} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 88%; colorless oil; IR (KBr): 1761, 1698, 1278, 1257, 1200, 1119, 640 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.10 (s, 1H), 7.82 (d, \(J = 8.0\) Hz, 1H), 7.42 (dd, 1H), 7.14 (d, \(J = 8.0\) Hz, 1H), 4.10 (s, 1H), 2.4 (s, 3H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 188.9, 165.5, 150.6, 135.4, 135.2, 134.5, 130.2, 121.3, 25.2, 24.1;
2-formyl-4-methoxyphenyl 2-bromoacetate (2e)

\[
\begin{array}{c}
\text{O} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 90%; colorless oil; IR (KBr): 1760, 1696, 1278, 1257, 1200, 1119, 640 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 10.10 (s, 1H), 7.42 (d, \(J = 8.0\) Hz, 1H), 7.22 (dd, 1H), 7.04 (d, \(J = 8.0\) Hz, 1H), 4.10 (s, 2H), 3.9 (s, 3H); \(^1^3\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 188.9, 165.5, 159.6, 146.4, 136.2, 124.5, 121.2, 115.3, 25.2, 60.5;

5-(dimethylamino)-2-formylphenyl 2-bromoacetate (2f)

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 84%; low melting solid; IR (KBr): 1660, 1690, 1278, 1257, 1200, 1119, 640 cm\(^{-1}\). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 9.7 (s, 1H), 7.52 (d, \(J = 8.8\) Hz, 1H), 6.48 (dd, 1H), 6.22 (s, 1H), 4.10 (s, 2H), 2.9 (s, 6H); \(^1^3\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 189.5, 166.5, 157.9, 155.4, 133.2, 125.2, 112.8, 106.1, 40.2, 25.2;

5-(diethylamino)-2-formylphenyl 2-bromoacetate (2g)

\[
\begin{array}{c}
\text{N} \\
\text{O} \\
\text{Br}
\end{array}
\]

Yield: 85%; low melting solid; IR (KBr): 1660, 1690, 1278, 1257, 1200, 1119, 640 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.64 (s, 1H), 7.54 (d, \(J = 8.8\) Hz, 1H), 6.48 (dd, \(J = 9.0\) Hz, 2.4 Hz, 1H), 6.22 (d, \(J = 2.4\) Hz, 1H), 4.12 (s, 2H), 3.4 (q, 4H), 1.15 (t, 6H); \(^1^3\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 189.5, 166.5, 157.9, 155.4, 133.2, 125.2, 112.8, 106.1, 44.2, 25.2, 13.1;
**1-formyl naphthalen-2-yl 2-bromoacetate (2h)**

Yield: 82%; low melting solid; IR (KBr): 1775, 1702, 1278, 1257, 1200, 1119 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 10.71 (s, 1H), 9.01 (d, \(J = 8.4\) Hz, 1H), 8.05 (d, \(J = 8.8\) Hz, 1H), 7.82 (d, \(J = 8.0\) Hz, 1H), 7.61 (t, \(J = 7.2\) Hz, 1H), 7.50 (t, \(J = 7.2\) Hz, 1H), 7.22 (dd, \(J = 8.8\) Hz, 3.2 Hz, 1H), 4.11 (s, 2H); \(^1^3\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 191.0, 167.5, 158.9, 136.4, 131.2, 130.2, 129.6, 128.2, 127.4, 126.4, 124.4, 120.4, 25.2;

**General Procedure for the Preparation of Coumarins (4a-h):**

A mixture of 2-formylphenyl 2-bromoacetates (2a-h, 2 mmol) and triphenylphosphine (2 mmol) in ethylacetate (5 mL) was stirred at 60 °C for 2 h. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2:8). The mixture was cooled to room temperature and the separated solid Wittig salt was filtered and washed with cold ethyl acetate (2 mL). The obtained Wittig salt (3a-h) was taken in saturated aqueous NaHCO\(_3\) (5 mL) and stirred vigorously for 30 min at room temperature. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2:8). After completion of the reaction, the crude reaction mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layer was washed with H\(_2\)O (10 mL), and dried over Na\(_2\)SO\(_4\). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica (60–120, eluent: EtOAc–hexane, 2:8) to afford pure products 4a-h with 65–75% yield. The physical data (mp, NMR) of all the known compounds were found to be identical with those reported in the literature.
2H-chromen-2-one (4a)

Yield: 70%; White solid; mp: 68-69 °C; IR (KBr): 1696, 1602, 1383, 1237, 1067, 985, 856, 758, 572, 525, 426 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70 (d, J = 9.6 Hz, 1H), 7.56-7.48 (m, 2H), 7.35-7.26 (m, 2H), 6.42 (d, J = 9.6 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃) δ 161.2, 154.4, 143.9, 132.3, 128.3, 124.8, 119.2, 117.3, 117.1;

6-chloro-2H-chromen-2-one (4b)

Yield: 68%; mp 152–153 °C; IR (KBr): 1699, 1602, 1383, 1237, 1067, 950, 895, 830, 820, 730, 590, 530, 500 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 9.6Hz, 1H), 7.41-7.43 (m, 2H), 7.21 (d, J = 7.0 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃) δ 159.5, 151.9, 141.7, 131.3, 129.2, 126.6, 119.3, 117.8, 117.3;

6-bromo-2H-chromen-2-one (4c)

Yield: 68%; mp 162–164 °C; IR (KBr): 1690, 1600, 1383, 1237, 1067, 950, 895, 830, 730, 620, 590, 530, 500 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.57 (m, 3H), 7.15 (d, J=7.0 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃) δ 159.9, 152.9, 142.1, 134.6, 130.2, 120.3, 118.6, 117.8, 116.9;

6-methyl-2H-chromen-2-one (4d)

Yield: 72%; colorless solid; mp: 73-75 °C; IR (KBr): 1717, 1684, 1575, 1380, 1262, 1189, 1167, 1105, 911, 841, 820, 813 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 7.69 (d, J = 9.3 Hz, 1H), 7.40-7.20 (m, 3H), 6.43 (d, J = 9.3 Hz, 1H), 2.43 (s, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 161.0, 152.0, 143.4, 134.1, 132.8, 127.6, 118.5, 116.5, 116.4, 20.7;
6-methoxy-2H-chromen-2-one (4e)

Yield: 75%; colorless solid; mp: 100-102 °C; IR (KBr): 1705, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.64 (d, \(J = 9.6\) Hz, 1H), 7.22 (d, \(J = 9.0\) Hz, 1H), 7.07 (dd, \(J = 9.0, 2.7\) Hz, 1H), 6.89 (d, \(J = 2.7\) Hz, 1H), 6.35 (d, \(J = 9.9\) Hz, 1H), 3.82 (s, 3H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 160.9, 155.9, 148.3, 143.2, 119.4, 119.0, 117.7, 116.9, 109.9, 55.7;

7-(dimethylamino)-2H-chromen-2-one (4f)

Yield: 72%; purple powder; mp: 161-162 °C; IR (KBr): 1685, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 7.54 (d, \(J = 9.3\) Hz, 1H), 7.25 (d, \(J = 2.8\) Hz, 1H), 6.61 (dd, \(J = 8.7\) Hz, 2.3 Hz, 1H), 6.49 (d, \(J = 2.2\) Hz, 1H), 6.06 (d, \(J = 9.3\) Hz, 1H), 3.82 (s, 3H), 2.9 (s 6H); \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 162.1, 156.3, 152.9, 143.7, 128.5, 109.8, 109.0, 108.8, 98.1, 40.2;

7-(diethylamino)-2H-chromen-2-one (4g)

Yield: 72%; yellowish powder; mp: 93-95 °C; IR (KBr): 1680, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.45 (d, \(J = 9.2\) Hz, 1H), 7.13 (d, \(J = 2.4\) Hz, 1H), 6.48 (d, \(J = 8.8\) Hz, 1H), 6.42 (d, \(J = 2.0\) Hz, 1H), 5.95 (d, \(J = 9.2\) Hz, 1H), 3.33 (q, \(J = 14.2\) Hz, 4H), 1.14 (t, \(J = 6.8\) Hz, 6H); \(^{13}\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) 162.3, 156.7, 150.7, 143.7, 128.7, 109.1, 108.6, 108.3, 97.5, 44.7, 12.4;
3H-benzo[f]chromen-3-one (4h)$^8$

Yield: 70%; yellowish powder; mp: 117-119 °C; IR (KBr): 1705, 1278, 1257, 1200, 1119 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.47 (d, $J = 9.7$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 9.0$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.71-7.66 (m, 1H), 7.59-7.54 (m, 1H), 7.44 (d, $J = 9.2$ Hz, 1H), 6.56 (d, $J = 9.8$ Hz, 1H); $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ 160.9, 153.9, 139.1, 133.1, 130.3, 129.0, 128.3, 126.1, 121.3, 117.1, 115.6, 113.0;
References

NMR Data: