DDQ-MEDIATED TANDEM SYNTHESIS OF FUNCTIONALIZED PYRANOCOUMARINS FROM 4-HYDROXYCOUMARINS AND 1,3-DIARYLALLYLIC COMPOUNDS

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Abstract - A simple and efficient DDQ-mediated oxidative cross-coupling between 4-hydroxycoumarin and 1,3-diarylallylic compounds was developed. The reaction furnished functionalized pyranocoumarins in a single step without using any metal catalyst. The tandem process involves an intermolecular C–C bond formation and an intramolecular C–O bond formation through double oxidative C–H activation.

There has been great development of various transition-metal-catalyzed coupling reactions in organic synthesis and related disciplines. On the other hand, with the prevalence of “atom economy” and “green chemistry”, the direct formations of carbon-carbon bonds or carbon-heteroatom bonds from C-H bonds by cross-coupling reactions have attracted great attention recently.

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is a well-known powerful oxidant in organic chemistry, particularly useful for dehydrogenation to form aromatic compounds, oxidizes activated methylene and hydroxy groups to carbonyl compounds. In recent years, there has been enormous interest in developing DDQ-mediated direct oxidative cross-coupling by C-H activation without using any metal catalyst.

Coumarin and its derivatives are one of the important classes of heterocyclic compounds and are known to possess a wide range of biological activities such as anti-HIV, antimalarial, antibacterial, and cytotoxic. Among the various coumarin derivatives, functionalized pyranocoumarin represents a significant class of compounds as biologically active compounds. As a part of our continuing program on development of
tandem synthesis of heterocycles, we herein reported a tandem approach to functionalized pyranocoumarins from 1,3-diarylallylic compounds and 4-hydroxycoumarin via the DDQ-mediated double oxidative C-H activation.

We initially examined the reaction of 4-hydroxycoumarin (1a) with 1,3-diphenyl-1-propene (2a) in the presence of DDQ (2.0 equiv) using CH₂Cl₂ as a solvent (Table 1, entry 1). After reacting under ambient conditions for 1 h, the resulting mixture was filtered to separate a black solid, consisting mainly of hydroquinone (DDQH₂). The filtrate was concentrated and purified by chromatography on a silica gel column to give pyranocoumarin 3a with 52% yield. The structure of compound 3a was unambiguously confirmed by single-crystal X-ray analysis (Figure 1). Furthermore, we found that the desired product 3a could be obtained in 68% yield with 4 Å MS as an additive (Table 1, entry 2). In order to slow the reaction, we then set the reaction temperature to 0 °C and this reaction was completed for 3 h. However, the yield reduced obviously (Table 1, entry 3). When the reaction temperature was increased to reflux, the yield resulted in a slight decrease (Table 1, entry 4). Then various solvents were screened. The reaction could proceed in CICH₂CH₂Cl with good efficiency (Table 1, entry 5). When MeCN and PhMe were used as solvents, the yield was remarkably diminished (Table 1, entries 6 and 7). No desired product was detected when CHCl₃, MeNO₂ or THF were used as solvents (Table 1, entries 8, 9 and 10). Switching the ratio of substrates 1a/2a decreased the yield (Table 1, entry 11). The influence of the amount of DDQ was also evaluated and both increase and decrease the amount of DDQ reduced the yield (Table 1, entries 13 and 14). No product was detected in the absence of DDQ (Table 1, entry 15). Thus, the most suitable reaction conditions for the formation of 3a were established (Table 1, entry 2).

Table 1. Screening for the Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp.</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>52</td>
</tr>
<tr>
<td>2</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>68</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂</td>
<td>0 °C</td>
<td>48</td>
</tr>
<tr>
<td>4</td>
<td>CH₂Cl₂</td>
<td>reflux</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>ClCH₂CH₂Cl</td>
<td>rt</td>
<td>66</td>
</tr>
<tr>
<td>6</td>
<td>MeCN</td>
<td>rt</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>PhMe</td>
<td>rt</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>CHCl₃</td>
<td>rt</td>
<td>nd</td>
</tr>
<tr>
<td>9</td>
<td>MeNO₂</td>
<td>rt</td>
<td>nd</td>
</tr>
<tr>
<td>10</td>
<td>THF</td>
<td>rt</td>
<td>nd</td>
</tr>
</tbody>
</table>
The scope of the reaction was investigated with a variety of reactants under the optimized reaction conditions, and the results were presented in Table 2. 4-Hydroxycoumarins 1a-1d and 1,3-diarylallylic compounds 2a-2e underwent the oxidative cross-coupling process to generate 3a-3l in modest to good yields (48-72%). The electronic effect of the substituents on aromatic ring of substrates 1 was observed (Table 2, entries 1-3 and 5-7). The electron-donating group substituted 4-hydroxycoumarin 1b (Table 2, entries 2 and 6) gave higher yields than the electron-withdrawing group substituted substrates 1c (Table 2, entries 3 and 7). Similarly, reaction of 1,3-diarylallylic compounds 2a and 2b with 4-hydroxy-6-methyl-2-pyrone 1d allows the efficient synthesis of product 3d and 3h in moderate yields under the optimized conditions, respectively (Table 2, entries 4 and 8). The electronic effect of the substituents on the aromatic ring of 2 was examined. When the substrates 2 are bearing a halogen group, the reaction gave good yields in a rapid rate (Table 2, entries 5-8). However, the result was the opposite when an electron-donating group was introduced (Table 2, entry 9).
Table 2. Formation of functionalized pyranocoumarins\textsuperscript{a}

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
<th>2 (Ar)</th>
<th>reaction time (h)</th>
<th>product</th>
<th>yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2a(C_6H_5)</td>
<td>1</td>
<td>3a</td>
<td>68</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>2a</td>
<td>1</td>
<td>3b</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>2a</td>
<td>1</td>
<td>3c</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>2a</td>
<td>1</td>
<td>3d</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>1a</td>
<td>2b(4-BrC_6H_4)</td>
<td>0.75</td>
<td>3e</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>1b</td>
<td>2b</td>
<td>0.75</td>
<td>3f</td>
<td>72</td>
</tr>
<tr>
<td>7</td>
<td>1c</td>
<td>2b</td>
<td>0.75</td>
<td>3g</td>
<td>64</td>
</tr>
<tr>
<td>8</td>
<td>1d</td>
<td>2b</td>
<td>0.75</td>
<td>3h</td>
<td>66</td>
</tr>
<tr>
<td>9</td>
<td>1a</td>
<td>2c(4-CH_3C_6H_4)</td>
<td>1.5</td>
<td>3i</td>
<td>48</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: 2 (0.25 mmol), 1 (1.2 equiv.), DDQ (2.0 equiv.), 4 Å MS (0.25 g), CH_2Cl_2 (3 mL), rt
\textsuperscript{b} Isolated yield

To expand the scope of the substrates, we further examined the mono-substituted 1,3-diarylpropenes 2d (Scheme 1) and 2e (Scheme 2). In these cases, we obtained a mixture of two isomers 3j+3j’ (in 65% total yield), 3k+3k’ (in 57% total yield) or 3l+3l’ (in 48% total yield), respectively. The ratios of two isomers 3j+3j’, 3k+3k’ and 3l+3l’ were 4:1, 7:3, and 3:1, respectively, which were determined by \textsuperscript{1}H NMR analysis.

Scheme 1. Synthesis of 3j+3j’ and 3k+3k’
To provide further insight into the mechanism, (E)-3-(1,3-diphenylallyl)-4-hydroxy-2H-chromen-2-one 4a was conducted the oxidative coupling reaction in the presence of 1.1 equiv. DDQ under ambient conditions in CH₂Cl₂ (Scheme 3). The expected product 3a was obtained in 86% yield by an intramolecular oxidation coupling reaction promoted by DDQ. Furthermore, we found that the reaction did not proceed in the absence of DDQ (Table 1, entry 15).

According to the literatures⁷ and on the basis of our experiments, a tentative mechanism for the coupling reaction is proposed in Scheme 4. A single electron transfer from alkene 2a to DDQ generates a radical ion pair 2a-1, which further converts to the ion pair 2a-2 through hydrogen transfer from the allylic radical cation to DDQ radical anion. Then, a proton transfer from 1a to DDQH anion forms the ion pair 1a-1 and DDQH₂. The attack of the enolate anion to the allylic cation in the ion pair 1a-1 generates the intermediate 4a. A single electron transfer from 4a to DDQ generates another radical ion pair 4a-1, which is immediately converted to the ion pair 4a-2 through a hydrogen transfer. Further proton transfer from hydroxyl group to DDQH anion in the ion pair 4a-2 generates the Zwitterion 4a' and DDQH₂. The ring closing of 4a' and the subsequent 1,3 H-shift afford the desired product 3a. For the mono-substituted
1,3-diarylallylic compounds 2d and 2e, they could generate two different allylic carbocations, which led to the formation of two isomer products $3j+3j'$, $3k+3k'$ and $3l+3l'$ (Scheme 5).

Scheme 4. Tentative mechanism for the tandem reaction

Scheme 5. Formation of two isomer products $3j+3j'$, $3k+3k'$ and $3l+3l'$
In conclusion, we have demonstrated a DDQ-mediated oxidative cross-coupling reaction between 4-hydroxycoumarin and 1,3-diarylallylic compounds, which furnished biologically interesting pyranocoumarins under ambient conditions without using any metal catalyst. The process involves a direct intermolecular C-C bond formation and an intramolecular C-O bond formation. It is the first example for the DDQ-mediated tandem double oxidative C-H activation and further application of this method is under investigation.

**EXPERIMENTAL**

Column chromatography was carried out on silica gel (300-400 mesh) with mixed solvents (petroleum-EtOAc). CH₂Cl₂ was distilled from CaH₂. Infrared spectra was obtained on a FTIR spectrometer. NMR spectra was recorded for ¹H NMR at 400 MHz, for ¹³C NMR at 100 MHz at 293 K unless otherwise noted. Chemical shifts are reported relative to residue peaks of the solvents either CDCl₃ (7.26 ppm for ¹H and 77.27 ppm for ¹³C) or DMSO-­d₆ (2.50 ppm for ¹H and 40.00 ppm for ¹³C). Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant, J (Hz) and integration. Low-resolution MS and HRMS were obtained using ESI ionization.

**Starting Materials.** ¹b and ¹c were prepared according to the literature.¹² The diarylallylic compounds were prepared according to the literature.¹³ ⁴a was prepared according to the literature.¹⁴

**General Procedure for the Synthesis of 3**

A 10 mL round-bottom flask was charged with 4-hydroxycoumarin (¹) (1.2 equiv.), 1,3-diphenyl-1-propene (²) (0.25 mmol) and 4 Å MS (0.25 g) in 3 mL of CH₂Cl₂. Then DDQ (2.0 equiv.) was added in portions during 15 min. The reaction mixture was stirred for the corresponding time, and then filtered through a Celite plug. Purification was done by column chromatography on silica gel with petroleum and EtOAc (10:1) as the eluent to give the pure product ³.

**2,4-Diphenylpyrano[3,2-c]chromen-5(4H)-one (³a)**: A white solid; mp 168-169 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, J₁ = 1.6 Hz, J₂ = 8.0 Hz, 1 H), 7.73 (d, J = 7.2 Hz, 2 H), 7.56 (m, 1 H), 7.47-7.30 (m, 9 H), 7.23 (m, 1 H), 5.84 (d, J = 4.8 Hz, 1 H), 4.70 (d, J = 4.8 Hz, 1 H), ppm; ¹³C NMR (100 MHz, CDCl₃) δ 161.42, 155.69, 152.69, 146.82, 143.49, 132.56, 131.96, 129.21, 128.63, 128.59, 128.43, 127.19, 124.61, 124.12, 122.63, 116.78, 114.50, 103.69, 103.62, 36.57 ppm; IR (KBr) ν 3026, 2918, 1720, 1632, 1610, 1492, 1387, 1270, 1169, 1012, 765, 692 cm⁻¹; MS (ESI) m/z 374.8 ([M+Na⁺]); HRMS (ESI) calcd for C₂₄H₁₆O₃ ([M+Na⁺]), 375.0992; found, 375.0986.

**9-Methyl-2,4-diphenylpyrano[3,2-c]chromen-5(4H)-one (³b)**: A white solid; mp 212-213 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (s, 1 H), 7.60 (d, J = 6.4 Hz, 2 H), 7.48~7.36 (m, 9 H), 7.23 (d, J = 8.4 Hz, 1 H), 6.15 (d, J = 3.6 Hz 1 H), 5.77 (d, J = 4.4 Hz, 1 H), 2.43 (s, 3 H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ
9-Chloro-2,4-diphenylpyrano[3,2-c]chromen-5(4H)-one (3c): A light yellow solid; mp 177-178 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 2.0\) Hz, 1 H), 7.60 (d, \(J = 6.8\) Hz, 2 H), 7.53-7.46 (m, 4 H), 7.42~7.36 (m, 5 H), 7.29 (m, 1 H), 6.20 (d, \(J = 4.4\) Hz, 1 H), ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 160.06, 158.12, 151.89, 137.83, 137.58, 134.93, 132.52, 129.50, 129.47, 129.00, 127.97, 127.94, 127.59, 127.40, 122.70, 120.74, 118.07, 116.07, 116.33, 79.05 ppm; IR (KBr) \(v\) 3059, 2925, 1721, 1625, 1544, 1480, 1391, 1156, 1114, 993, 760, 699 cm\(^{-1}\); MS (ESI) m/z 409.2 ([M+Na]\(^+\)); HRMS (ESI) calcd for C\(_{24}\)H\(_{15}\)ClO\(_3\) ([M+Na]\(^+\)), 409.0602; found, 409.0594.

7-Methyl-2,4-diphenylpyrano[4,3-b]pyran-5(4H)-one (3d): A yellow oil; \(^1\)H NMR (400 MHz, CD\(_3\)SOCD\(_3\)) \(\delta\) 7.45 (d, \(J = 8.0\) Hz 2 H), 7.30~7.34 (m, 3 H), 7.25~7.18 (m, 5 H), 6.19 (s, 1 H), 6.10 (d, \(J = 4.4\) Hz, 1 H), 2.14 (s, 3 H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.64, 164.86, 159.51, 159.25, 138.86, 138.08, 133.75, 129.36, 129.19, 127.96, 127.75, 127.71, 120.11, 100.16, 99.35, 77.72, 20.01 ppm; IR (film) \(v\) 3061, 2925, 1723, 1644, 1542, 1493, 1446, 1409, 1206, 1121, 998, 155, 699 cm\(^{-1}\); MS (ESI) m/z 338.9 ([M+Na]\(^+\)); HRMS (ESI) calcd for C\(_{21}\)H\(_{16}\)O\(_3\) ([M+Na]\(^+\)), 339.0992; found, 339.0996.

2,4-Bis(4-bromophenyl)pyrano[3,2-c]chromen-5(4H)-one (3e): A white solid; mp 158-159 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 8.0\) Hz, 1 H), 7.59~7.56 (m, 3 H), 7.50 (d, \(J = 7.6\) Hz, 2 H), 7.43 (d, \(J = 8.0\) Hz, 2 H), 7.33 (d, \(J = 8.4\) Hz, 1 H), 7.28 (d, \(J = 7.6\) Hz, 1 H), 7.21 (d, \(J = 7.6\) Hz, 2 H), 6.11 (d, \(J = 4.0\) Hz, 1 H), 5.73 (d, \(J = 4.0\) Hz, 1 H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.33, 158.53, 153.56, 136.86, 136.58, 134.66, 132.98, 132.16, 131.10, 129.12, 129.06, 124.13, 123.60, 123.23, 122.07, 119.79, 116.71, 114.90, 102.34, 77.88 ppm; IR (KBr) \(v\) 3055, 1724, 1632, 1608, 1553, 1489, 1404, 1385, 1329, 1265, 1211, 1072, 1023, 999, 812, 756 cm\(^{-1}\); MS (ESI) m/z 530.2 ([M+Na]\(^+\)); HRMS (ESI) calcd for C\(_{24}\)H\(_{14}\)Br\(_2\)O\(_3\) ([M+Na]\(^+\)), 530.9202; found, 530.9205.

2,4-Bis(4-bromophenyl)-9-methylpyrano[3,2-c]chromen-5(4H)-one (3f): A light yellow solid; mp 187-188 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (s, 1 H), 7.57 (d, \(J = 8.4\) Hz, 2 H), 7.48 (d, \(J = 8.4\) Hz, 2 H), 7.42 (d, \(J = 8.4\) Hz, 2 H), 7.36 (dd, \(J_1 = 2.0\) Hz, \(J_2 = 8.8\) Hz, 1 H), 7.21~7.18 (m, 3 H), 6.07 (d, \(J = 4.4\) Hz, 1 H), 5.69 (d, \(J = 4.4\) Hz, 1 H), 2.40 (s, 3 H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 161.38, 158.72, 151.78, 136.96, 136.67, 134.76, 134.09, 133.92, 132.16, 131.06, 129.16, 129.05, 123.57, 122.76, 122.02, 119.68, 116.48, 114.52, 102.24, 77.91, 20.90 ppm; IR (KBr) \(v\) 3064, 2922, 1724, 1630, 1556, 1489, 1402, 1200, 1118, 1072, 1010, 814, 532 cm\(^{-1}\); MS (ESI) m/z 544.8 ([M+Na]\(^+\)); HRMS (ESI) calcd for C\(_{25}\)H\(_{16}\)Br\(_2\)O\(_3\) ([M+Na]\(^+\)), 544.9358; found, 544.9345.
2,4-Bis(4-bromophenyl)-9-chloropyrano[3,2-c]chromen-5(4H)-one (3g): A light yellow solid; mp 185-186 °C; †H NMR (400 MHz, CDCl3) δ 7.77 (d, J = 2.4 Hz, 1 H), 7.57 (d, J = 8.4 Hz, 2 H), 7.50 (m, 3 H), 7.41 (d, J = 8.4 Hz, 2 H), 7.27 (s, 1 H), 7.17 (d, J = 8.4 Hz, 2 H), 6.11 (d, J = 3.6 Hz, 1 H), 5.73 (d, J = 4.4 Hz, 1 H) ppm; †3C NMR (100 MHz, CDCl3) δ 160.06, 157.96, 151.87, 136.48, 136.30, 134.37, 132.88, 132.27, 131.14, 129.72, 129.20, 129.04, 123.82, 122.63, 122.20, 120.32, 118.18, 116.03, 102.88, 77.18 ppm; IR (KBr) v 3064, 2922, 1724, 1630, 1556, 1489, 1402, 1267, 1200, 1117, 1072, 1009, 814, 772 cm⁻¹; MS (ESI) m/z 565.2 ([M+Na]+); HRMS (ESI) calcd for C24H13Br2ClO3 ([M+Na]+), 564.9032; found, 564.9065.

2,4-Bis(4-bromophenyl)-7-methylpyrano[4,3-b]pyran-5(4H)-one (3h): A white solid; mp 186-187 °C; †H NMR (400 MHz, CDCl3) δ 7.55 (d, J = 8.0 Hz, 2 H), 7.47 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.18 (d, J = 8.4 Hz, 2 H), 5.91 (m, 2 H), 5.55 (d, J = 4.4 Hz, 1 H), 2.25 (s, 3 H) ppm; †3C NMR (100 MHz, CDCl3) δ 166.40, 164.37, 159.96, 137.06, 136.39, 134.13, 132.07, 130.96, 129.21, 129.11, 123.47, 121.97, 118.55, 100.00, 99.34, 77.70, 20.29 ppm; IR (KBr) v 3097, 2924, 1718, 1641, 1541, 1487, 1406, 1205, 1007, 997, 827, 540 cm⁻¹; MS (ESI) m/z 494.9 ([M+Na]+); HRMS (ESI) calcd for C21H14Br2O3 ([M+Na]+), 494.9202; found, 494.9199.

2,4-Dip-tolylpyrano[3,2-c]chromen-5(4H)-one (3i): A yellow oil; †H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 8.0 Hz, 1 H), 7.65 (t, J = 8.0 Hz, 1 H), 7.46 (d, J = 7.6 Hz, 2 H), 7.36 (m, 2 H), 7.22 (m, 4 H), 7.13 (d, J = 7.6 Hz, 2 H), 6.31 (d, J = 5.2 Hz, 1 H), 5.88 (d, J = 4.8 Hz, 1 H), 2.31 (s, 3 H), 2.28 (s, 3 H) ppm; †3C NMR (100 MHz, CDCl3) δ 160.94, 158.03, 153.29, 138.99, 137.08, 135.54, 135.37, 134.09, 129.75, 128.65, 127.68, 124.81, 123.35, 121.11, 116.72, 115.14, 102.99, 77.81, 21.19, 21.16 ppm; IR (film) v 3028, 2924, 1731, 1614, 1573, 1493, 1398, 1327, 1266, 1177, 759 cm⁻¹; MS (ESI) m/z 403.1 ([M+Na]+); HRMS (ESI) calcd for C26H20O3 ([M+Na]+), 403.1305; found, 403.1320.

2-(4-Chlorophenyl)-4-phenylpyrano[3,2-c]chromen-5(4H)-one (3j + 3j') A white solid; mp 185-186 °C; †H NMR (400 MHz, CDCl3) δ 7.86-7.81 (m, 1 H), 7.58-7.49 (m, 3 H), 7.44-7.24 (m, 9 H), 6.14 (d, J = 4.0 Hz, 0.8 H), 6.11 (d, J = 4.8 Hz, 0.2 H), 5.74-5.72 (m, 1 H) ppm; †3C NMR (100 MHz, CDCl3) δ 161.45, 158.61, 153.57, 137.99, 137.64, 136.34, 135.26, 134.16, 133.69, 132.74, 132.70, 129.32, 129.11, 128.93, 128.88, 128.77, 128.07, 127.94, 127.92, 127.38, 127.35, 123.98, 123.29, 123.15, 120.49, 119.51, 116.64, 116.61, 115.06, 102.31, 79.69, 77.85 ppm; IR (KBr) v 3034, 2870, 1719, 1624, 1492, 1106, 1022, 986, 759 cm⁻¹; MS (ESI) m/z 409.3 ([M+Na]+); HRMS (ESI) calcd for C24H15ClO3 ([M+Na]+), 409.0602; found, 409.0598.

2-(4-Chlorophenyl)-9-methyl-4-phenylpyrano[3,2-c]chromen-5(4H)-one (3k + 3k') A white solid; mp 172-173 °C; †H NMR (400 MHz, CDCl3) (3k/3k’ = 7:3) δ 7.61-7.59 (m, 1 H), 7.55-7.49 (m, 2 H), 7.45-7.38 (m, 3 H), 7.35-7.30 (m, 4 H), 7.28-7.24 (m, 1 H), 7.20-7.18 (m, 1 H), 6.11 (d, J = 4.4 Hz, 0.69
H), 6.08 (d, J = 4.4 Hz, 0.31 H), 5.72-5.70 (m, 1 H), 2.39 (s, 3 H) ppm; 13C NMR (100 MHz, CDCl3) δ 161.52, 161.14, 158.82, 158.70, 151.77, 138.09, 137.72, 136.65, 136.41, 135.75, 135.24, 134.27, 133.86, 133.82, 133.76, 133.74, 133.64, 129.31, 129.11, 128.93, 128.76, 128.05, 127.89, 127.43, 127.35, 122.84, 122.71, 120.38, 119.41, 116.41, 116.38, 114.67, 114.65, 102.23, 78.73, 20.83 ppm; IR (KBr) v 3066, 2924, 1721, 1632, 1560, 1492, 1400, 1120, 1007, 812, 727 cm⁻¹; MS (ESI) m/z 422.9 ([M+Na]+); HRMS (ESI) calcd for C25H17ClO3 ([M+Na]+), 423.0758; found, 423.0751.

2-(2-Chlorophenyl)-9-methyl-4-phenylpyrano[3,2-c]chromen-5(4H)-one (3l + 3l') A white solid; mp 198-199 ºC; 1H NMR (400 MHz, CDCl3) (3l/3l' = 3:1) δ 7.65-7.63 (m, 2 H), 7.47-7.44 (m, 1 H), 7.36-7.29 (m, 8 H), 7.19 (d, J = 8.4 Hz, 1 H), 6.54 (d, J = 4.0 Hz, 1 H), 5.69 (d, J = 3.6 Hz, 1 H), 2.38 (s, 2.25 H), 2.36 (s, 0.75 H) ppm; 13C NMR (100 MHz, CDCl3) δ 161.42, 158.78, 151.78, 137.75, 135.67, 135.37, 133.80, 133.77, 133.57, 133.51, 133.11, 132.93, 130.29, 130.14, 129.87, 129.29, 128.94, 128.86, 127.87, 127.35, 127.24, 122.92, 122.79, 119.06, 116.36, 114.48, 102.54, 102.43, 75.39, 20.89, 20.83 ppm; IR (KBr) v 3057, 2926, 1723, 1627, 1556, 1493, 1397, 1285, 1202, 1144, 1009, 760, 698 cm⁻¹; MS (ESI) m/z 422.8 ([M+Na]+); HRMS (ESI) calcd for C25H17ClO3 ([M+Na]+), 423.0753; found, 423.0751.

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REFERENCES (AND NOTES)


11. CCDC-751023 (for 3a) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via