Supporting Information

Visible Light Promoted Synthesis of Dihydropyrano[2,3-c]chromenes via a Multicomponent-Tandem Strategy under Solvent and Catalyst Free Conditions

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##Equal Contribution

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**Experimental**

**General Remarks**

All chemicals were reagent grade and purchased from Aldrich, Alfa Aesar, Merck, Spectrochem and Qualigens and were used without further purification. The reactions were monitored using pre-coated Aluminium TLC plates of silica gel G/UV-254 of 0.25 mm thickness (Merck 60 F-254). Column chromatography was performed using silica gel (60-120) and (100-200). NMR spectra were recorded on a Bruker Avance-II 400FT spectrometer at 400 MHz ($^1$H) and 100 MHz ($^{13}$C) in DMSO or CDCl$_3$ using TMS as an internal reference. Mass spectra (ESIMS) were obtained on a Waters UPLC-TQD mass spectrometer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrometer while UV spectra were obtained using a Varian Cary 300 UV-Vis spectrophotometer. Elemental analyses were carried out in a Thermo Scientific (FLASH 2000) CHN Elemental Analyser. Melting points were determined by open glass capillary method and were uncorrected.
General Experimental Procedure:
To a 50 mL round bottom flask were added the respective benzaldehyde (1, 5-21) (1 mmol) and malononitrile (2) (1.2 mmol) or ethyl 2-cyanoacetate (22) under visible light irradiation using a household 20W CFL with stirring. After formation of the intermediate (Knoevenagel product), (TLC control), 4-hydroxy coumarin (3) (1 mmol) or cyclic CH-acids 43-45 were added to the reaction mixture, followed by the addition of a few drops of ethanol in order to get the reaction mixture in form of a paste, and the resulting mixture was stirred till completion of the reaction (TLC control). The reaction was quenched with water resulting in the formation of a solid precipitate which was filtered and dried to obtain the crude product. The crude product was recrystallized from hot methanol to obtain the desired pure compounds (23-42, 46-48). However in a few instances required purity could not be achieved through recrystallization, necessitating purification by column chromatography over silica gel.

Compound 4

![Chemical Structure]

Pale yellow solid; Mp: 258-261°C; IR (KBr): 3347, 2745, 1730, 1159 cm⁻¹; ¹H NMR (DMSO-d₆) (δ, ppm): 4.67 (1H, s), 7.41-7.45 (2H, m), 7.49-7.50 (2H, m), 7.56-7.59 (2H, m), 7.68-7.72 (1H, m), 7.94 (1H, dd, J=7.9 & 1.3 Hz), 8.16 -8.21 (2H, m) ppm; ¹³C NMR (DMSO-d₆) (δ, ppm): 36.8, 56.6, 102.7, 112.7, 116.4, 118.7, 122.6, 123.5, 124.5, 129.0, 132.9, 146.5, 150.5, 152.2, 153.9, 158.1, 159.4; MS (ESI):m/z 361; found 362 [M+H]⁺; Anal. calcd for C₁₉H₁₁N₃O₅: C 63.16, H 3.07, N 11.63; found C 63.19 H 3.02, N 11.67 %.
**Compound 26**

![Chemical Structure of Compound 26](image)

White solid; Mp: 254-255 °C; IR (KBr): 3390, 2363, 1730, 1171 cm\(^{-1}\); \(^1\)H NMR (DMSO-\(d_6\)) (\(\delta\), ppm): 2.27 (3H, s); 4.41 (1H, s); 7.10 (2H, d, \(J = 8.1\) Hz); 7.15 (2H, d, \(J = 8.1\) Hz); 7.3 (2H, s); 7.38-7.46 (2H, m); 7.64-7.68 (1H, m); 7.92 (dd, 1H, \(J = 7.8\) & \(J = 1.2\) Hz); \(^{13}\)C NMR (DMSO-\(d_6\)) (\(\delta\), ppm): 20.6, 36.5, 58.0, 104.1, 112.9, 116.3, 119.1, 122.4, 124.4, 127.4, 128.9, 132.6, 136.1, 140.2, 152.0, 153.2, 157.9, 159.4; MS (ESI): m/z 330; found 331 [M+H]^+; Anal. calcd for C\(_{20}\)H\(_{14}\)N\(_2\)O\(_3\): C, 72.72; H, 4.27; N, 8.48; found: C, 72.69; H, 4.23; N 8.46 %.

**Compound 29**

![Chemical Structure of Compound 29](image)

White solid; Mp: 257-259 °C; IR (KBr): 3367, 2375, 1707, 1526 cm\(^{-1}\); \(^1\)H NMR (DMSO-\(d_6\)) (\(\delta\), ppm): 4.98 (1H, s); 7.31-7.37 (2H, m); 7.42-7.51 (5H, m); 7.68-7.73 (1H, m); 7.91 (dd, 2H, \(J = 7.88\) & 1.5 Hz); \(^{13}\)C NMR (DMSO-\(d_6\)) (\(\delta\), ppm): 33.9, 55.9, 102.4, 112.7,
116.4, 118.5, 122.5, 124.5, 127.6, 128.8, 131.8, 132.4, 132.9, 133.3, 139.2, 152.2, 154.1, 158.1, 159.2; MS (ESI): m/z 384; found 385 [M+H]^+; Anal. calcd for C_{19}H_{10}Cl_2N_2O_3: C 59.24, H 2.62, N 7.27; found C 59.29, H 2.66, N 7.27 %.

**Compound 34**

White solid; Mp: 262-266 °C; IR (KBr): 3428, 2340, 1723, 1580, 1182 cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) (δ, ppm): 4.34 (1H, s); 6.72 (2H, s); 7.07 (2H, s); 7.34-7.43 (4H, m); 7.66 (1H, s); 7.88 (1H, s); 9.38 (1H, s); \(^1^3\)C NMR (DMSO-d\(_6\)) (δ, ppm): 36.13, 58.4, 104.4, 112.9, 115.1, 116.4, 119.3, 122.3, 124.5, 128.6, 132.7, 133.6, 152.0, 152.9, 156.4, 157.8, 159.4; MS (ESI): m/z 332; found 333 [M+H]^+; Anal. calcd for C_{19}H_{12}N_2O_4: C, 68.67; H, 3.64; N, 8.43; found C, 68.72; H, 3.56; N, 8.44 %.

**Compound 40**

![Diagram of Compound 40](image)
Yellow solid; Mp: 241-244 °C; IR (KBr); 3324, 2327, 1729, 1166 cm⁻¹; ¹H NMR (DMSO-d₆) (δ, ppm): 1.12 (3H, t); 4.00 (2H, q); 4.86 (1H, s); 7.38 (1H, d, J = 7.8 Hz); 7.43-7.46 (1H, m); 7.53 (2H, d, J = 8.7 Hz); 7.64-7.68 (1H, m); 7.92 (2H, brs); 8.00 (1H, dd, J = 7.9 & 1.3 Hz); 8.10 (d, 2H, J = 8.7 Hz) ¹³C NMR (DMSO-d₆) (δ, ppm): 14.0, 35.5, 59.0, 75.8, 105.4, 112.9, 116.3, 122.5, 122.9, 124.4, 129.3, 132.6, 145.9, 152.2, 152.4, 153.4, 158.5, 159.7, 167.2.; MS (ESI): m/z 408; found: 409 [M+H]⁺, Anal. calcd for C₂₁H₁₆N₂O₇: C, 61.77; H, 3.95; N, 6.85; found: C, 61.80; H, 3.98; N, 6.90 %.

**Compound 46**

![Compound 46](image)

White solid; Mp: 241-243 °C; IR (KBr): 3390, 2363, 1730, 1171 cm⁻¹; ¹H NMR (DMSO-d₆) (δ, ppm): 1.93-1.99 (2H, m); 2.26-2.32 (2H, m); 2.64-2.65 (2H, m); 4.36 (1H, s); 7.13 (2H, s); 7.45 (d, 2H, J = 8.5 Hz); 8.15 (d, 2H, J = 8.4 Hz); ¹³C NMR (DMSO-d₆) (δ, ppm): 19.7, 26.5, 35.5, 36.1, 56.8, 112.8, 119.2, 123.3, 128.4, 146.1, 152.0, 158.5, 164.7, 195.5; MS (ESI): m/z 311; found: 312 [M+H]⁺, Anal. calcd for C₁₆H₁₃N₃O₄: C 61.73, H 4.21, N 13.50; found: C 61.74, H 4.27, N 13.57 %.

**Compound 47**
White solid; Mp: 212-215 °C; IR (KBr): 3359, 2305, 1673, 1163 cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) (δ, ppm): 0.99 (3H, s); 1.08 (3H, s); 2.12 (2H, d, \(J = 16.1\) Hz); 2.23 (2H, d, \(J = 16.1\) Hz); 2.48 (2H, s); 4.22 (1H, s); 6.82 (2H, brs); 7.17 (d, 2H, \(J = 8.4\) Hz); 7.26 (d, 2H, \(J = 8.4\) Hz); \(^{13}\)C NMR (DMSO-d\(_6\)) (δ, ppm): 26.9, 28.3, 31.7, 35.1, 49.9, 57.7, 112.4, 119.4, 128.1, 128.9, 131.2, 143.5, 158.4, 162.3, 195.3; MS (ESI): m/z 328; found 329 [M+H]^+; Anal. calcd for C\(_{18}\)H\(_{17}\)N\(_2\)O\(_2\): C, 65.75; H, 5.21; N, 8.52; found: C, 65.70; H, 5.25; N, 8.55 %.

**Compound 48**

White solid; Mp: 237-240°C; IR (KBr): 3355, 2332, 1623, 1342 cm\(^{-1}\); \(^1\)H NMR (DMSO-d\(_6\)) (δ, ppm): 4.43 (1H, s); 7.23 (2H, s); 7.52 (2H, d, \(J = 7.5\) Hz); 8.16 (2H, d, \(J = 7.4\) Hz); 11.11 (1H, s); 12.15 (1H, brs); \(^{13}\)C NMR (DMSO-d\(_6\)) (δ, ppm): 35.6, 57.3, 87.4, 118.7,
123.3, 128.6, 146.3, 149.4, 151.5, 152.5, 157.7, 162.4; MS (ESI): m/z 327; found: 328 [M+H]^+, Anal. calcd for C_{14}H_{9}N_{5}O_{5}: C, 51.38; H 2.77; N, 21.40; found C, 51.40; H, 2.76; N, 21.47 %.

**Intermediate I**

Pale Yellow solid; Mp: 104-106°C; IR (KBr): 3371, 2302,1742,1391 cm⁻¹; ¹H NMR (CDCl₃) (δ, ppm): 7.90 (1H, s); 8.09 (2H, d, J = 8.9 Hz); 8.41 (2H, d, J = 8.8 Hz); ¹³C NMR (CDCl₃) (δ, ppm): 87.5, 111.6, 112.6, 124.6, 131.3, 135.8, 150.3, 156.8; MS (ESI): m/z 199; found: 200 [M+H]^+, Anal. calcd for C_{10}H_{5}N_{3}O_{2}: C, 60.31; H, 2.53; N, 21.10; found: C, 60.24; H, 2.59; N, 21.11 %.
$^{1}$H NMR spectrum of compound 4 and its expansion
$^{13}$C NMR spectrum of compound 4
$^1$H NMR spectrum of compound 26 and its expansion
$^{13}$C NMR spectrum of compound 26
$^1$H NMR spectrum of compound 29 and its expansion
$^{13}$C NMR spectrum of compound 29
$^1$H NMR spectrum of compound 34
$^{13}$C NMR spectrum of compound 34
$^1$H NMR spectrum of compound 40 and its expansion
$^{13}$C NMR spectrum of compound 40
$^1$H NMR spectrum of compound 46 and its expansion
$^{13}$C NMR spectrum of compound 46
H NMR spectrum of compound 47
$^{13}$C NMR spectrum of compound 47
$^1$H NMR spectrum of compound 48
$^{13}$C NMR spectrum of compound 48
$^1$H NMR spectrum of Intermediate I
$^{13}$C NMR spectrum of Intermediate I
UV spectrum of 4-Nitrobenzaldehyde (1) in (Solvent: methanol; Conc. 1.0 x 10^{-4} mol/L)

UV spectrum of 4-Hydroxy coumarin (3) in (Solvent: ethanol; Conc. 1.0 x 10^{-4} mol/L)
UV spectrum of 4-Tolualdehyde (8) (Solvent: ethanol; Conc. $2.5 \times 10^{-5}$ mol/L)

UV spectrum of 4-Chlorobenzaldehyde (15) (Solvent: methanol; Conc. $1.25 \times 10^{-4}$ mol/L)
UV spectrum of Dimedone (44) in methanol (Conc. 5.0 x 10^{-5} mol/L)

UV spectrum of Barbituric acid (45) in water (Conc. 1.25 x 10^{-4} mol/L)
Table S1. Melting point chart for the remaining dihydropyrano[2,3-c]chromenes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dihydropyrano[2,3-c]chromene</th>
<th>M.P. (°C) Observed</th>
<th>M.P. (°C) Reported</th>
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<tr>
<td>1</td>
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<td>269-272</td>
<td>268-270 \textsuperscript{21b}</td>
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<td>255-257</td>
<td>258-259 \textsuperscript{19}</td>
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<td>247-250</td>
<td>246-248 \textsuperscript{21b}</td>
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<td>4</td>
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<td>246-248&lt;sup&gt;9&lt;/sup&gt;</td>
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<td>263-266</td>
<td>266-267 $^{24}$</td>
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<td>8</td>
<td>[\text{![Image of compound 32]}]</td>
<td>265-267</td>
<td>266-268 $^{23}$</td>
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<td>250-254</td>
<td>252–255 $^{21b}$</td>
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<td>10</td>
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<td>246-248</td>
<td>247-249 $^9$</td>
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| 11| ![Image](image1)
|     |     |     |     |     |
| 12| ![Image](image2)
|     |     |     |     |     |
| 13| ![Image](image3)
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<td>189-190</td>
<td>191-192&lt;sup&gt;23&lt;/sup&gt;</td>
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**References**


