Supplementary Material

Preparation of tetrahydro-1H-xanthen-1-one and chromen-1-one derivatives via a Morita-Baylis-Hillman/oxa-Michael/elimination cascade

Manoel T. Rodrigues Jr.,a Hugo Santos, ª Lucas A. Zeoly,a Deborah A. Simoni, b Albert Moyano,c and Fernando Coelho* a

ª Laboratory of Synthesis of Natural Products and Drugs, and b Laboratory of Crystallography, Institute of Chemistry, University of Campinas, UNICAMP, P.O. Box 6154, 13083-970, Campinas, SP, Brazil
 c Secció de Química Orgànica, Departament de Química Inorgànica i Orgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Catalonia, Spain
 E-mail: facoelho@unicamp.br

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X-Ray Crystallographic Data for Compound 4c

Crystal structure of (2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one (4c) (Figure S44) was determined by single crystal X-ray diffraction analysis using a crystal that had been obtained by slow evaporation of a ethyl acetate/chloroform mixture (1:1 v/v) of 4c. Data collection was performed on a Bruker APEX II DUO area diffractometer, at low temperature (150 K, CRYOSTREAM 700 - Oxford Cryosystem), based on a strategy combining omega and phi scans, with 0.5° width and 10 s of acquisition time per frame, operating with a Mo fine-focus sealed tube source of radiation (Kα λ = 0.71073 Å).

Cell refinement and data reduction were done using SAINT³ and multi-scan absorption correction was applied using SADABS-2014/5³. Solution structure was obtained by primary atom site location by structure-invariant direct methods SHELXS97². SHELXL2014/7³ was chosen to perform structure refinement using least squares methods against $F^2$ and hydrogen atoms were placed during the refinement, with their location inferred from neighbouring sites. All non-hydrogen atoms were refined anisotropically, while H-atom parameters were not refined. 311 parameters were refined (0 restraints), $R(F^2 > 2 \sigma(F^2)) = 0.033$, $wR(F^2) = 0.079$, $S = 1.02$, with maximum and minimum residual electron density of 0.65 e Å⁻³ and -0.47 e Å⁻³, respectively. Details about the analyzed crystal and data collection are presented in Table S1 and Table S2, respectively.
**Figure S44.** The molecular structure of (2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one (4c) with 50% probability displacement ellipsoids.
Table S1. Selected crystallographic data for (2E)-2-[(2-hydroxy-3-methoxyphenyl)methylidene]-5-methoxy-1H,2H,3H,3aH-cyclopenta[b]chromen-1-one (4c) crystal

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| C$_{21}$H$_{18}$O$_5$·2(CHCl$_3$)             | Z = 2                        |
| Mr = 589.09                                    |                              |
| Triclinic, P1                                  | $D_x$ = 1.536 Mg m$^{-3}$    |
| $a$ = 8.8569 (8) Å                             | Mo Kα radiation, $\lambda$ = 0.71073 Å |
| $b$ = 10.8992 (11) Å                          | Cell parameters from 134 reflections |
| $c$ = 14.8123 (14) Å                          | $\theta$ = 3.2–24.4°        |
| $\alpha$ = 71.700 (2)$^\circ$                 | $\mu$ = 0.71 mm$^{-1}$      |
| $\beta$ = 79.556 (2)$^\circ$                  | $T$ = 150 K                  |
| $\gamma$ = 70.333 (2)$^\circ$                 | Block, yellow               |
| $V$ = 1273.8 (2) Å³                            | 0.22 × 0.12 × 0.08 mm       |

Table S2. Selected crystallographic data for data collection

| Property                                      | Value                        |
|-----------------------------------------------|------------------------------|
| Absorption correction: multi-scan             | $R_{int}$ = 0.037            |
| $T_{\text{min}}$ = 0.684, $T_{\text{max}}$ = 0.745 | $\theta_{\text{max}}$ = 26.8$^\circ$, $\theta_{\text{min}}$ = 1.5$^\circ$ |
| 35447 measured reflections                    | $h = -11 \rightarrow 11$    |
| 5395 independent reflections                  | $k = -13 \rightarrow 13$    |
| 4302 reflections with $l > 2\sigma(l)$        | $l = -18 \rightarrow 18$    |

References

1. Bruker (2010). APEX2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. (2008). Acta Cryst. A64, 112–122.
3. Sheldrick, G. M. (2015). Acta Cryst. C71, 3-8.