SUPPLEMENTARY INFORMATION

An expeditious coumarin synthesis via a “pseudo-cycloaddition” between salicylaldehydes and ketene

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Contains full experimental details including characterization data for all compounds reported in the main paper

General comments. Melting points (m.p.) are uncorrected. IR values ($\nu_{\max}$) are for KBr discs and are cited in cm^{-1} . NMR spectra were recorded in CDCl_3 solution with tetramethylsilane as internal standard at either 300 MHz (δ_{H}) or 75 MHz (δ_{C}); coupling constants (J) are cited in Hz. Abbreviations employed:- IR: s (strong), b (broad); NMR: s (singlet), d (doublet), the assigned atom being italicized.

Scheme 1. The synthesis of coumarins **2** from salicylaldehydes **1** and ketene generated *in situ* from acetyl chloride and triethylamine in dichloromethane solution

General procedure for the preparation of coumarins (2). A mixture of substituted salicylaldehydes (**1a-f**) (1.0 mmol), triethylamine (3.0 mmol), and freshly distilled acetyl chloride (2.0 mmol) and molecular sieves (~ 0.25 g, 4 Å, in pellet form) in dry CH_2Cl_2

was stirred for 9 h at 10 °C. The insolubles (presumed to be triethylamine hydrochloride and molecular sieves) were filtered off on a sintered glass funnel (under water-jet suction). The filtrate was washed with ice cold water, the separated organic layer dried (Na_2SO_4) and concentrated *in vacuo* to obtain the corresponding coumarins (**2a-f**). These were purified by column chromatography on silica gel eluting with 20% ethyl acetate-hexane, and identified by m.p., and spectra as described below.

Coumarin (2a). White solid (72%), m.p. 70-73 °C (lit.^[1] 68-69 °C); ν_{max} 3058 (b, C-H), 1715 (s, CO); δ_{H} 7.26-7.72 (5 H, m, ArH + ArCH=C), 6.42 (1 H, d, J 9.5, ArC=CH).

6-Chlorocoumarin (2b). White solid (64%), m.p. 162-165 °C (lit.^[1] 164-165 °C); ν_{max} 3058 (b, C-H), 1713 (s, CO), 1177 (s); δ_{H} 7.73-7.26 (4 H, m, ArH + ArCH=C), 6.41 (1 H, d, J 9.6, ArC=CH); δ_{C} 160.72 (C=O), 153.97 (C_{Ar}), 143.40 (C_{Ar}), 131.77 (C_{Ar}), 127.81 (C_{Ar}), 124.37 (C_{Ar}), 118.76 (C_{Ar}), 116.82 (C_4), 116.62 (C_3).

6-Methylcoumarin (2c). White solid (58%), m.p. 73-75 °C (lit.^[2] 74-76 °C); ν_{max} 3080 (s, C-H), 1721 (s, CO), 1262 (s); δ_{H} 7.21-7.67 (4 H, m, ArH + ArCH=C), 6.39 (1 H, d, J 9.6, ArC=CH), 2.40 (s, 3H, CH_3); δ_{C} 161.04 (C=O), 152.11 (C_{Ar}), 143.38 (C_{Ar}), 134.08 (C_{Ar}), 132.78 (C_{Ar}), 127.63 (C_{Ar}), 118.52 (C_{Ar}), 116.54 (C_4), 116.52 (C_3), 20.68 (C_{Me}).

8-Methoxycoumarin (2d). Yellow solid (70%), m.p. 83-85 °C (lit.^[3] 86-87 °C); ν_{max} 2854 (s, C-H), 1694 (s, CO), 1603 (s), 1537 (s), 1335 (s); δ_{H} 7.35-6.43 (4 H, m, ArH + ArCH=C), 5.90 (1 H, d, J 10.8, ArC=CH), 3.40 (3 H, s, OMe); δ_{C} 160.83 (C=O), 155.66 (C_{Ar}), 153.0 (C_{Ar}), 152.93 (C_{Ar}), 125.4 (C_{Ar}), 111.22 (C_{Ar}), 106.27 (C_{Ar}), 104.8 (C_4), 98.60 (C_3), 58.3 (C_{MeO}).

6-Nitrocoumarin (2e). White solid (62%), m.p. 187-189 °C (lit.^[4] 185±2 °C); ν_{max} 3055 (b, C-H), 1694 (s, CO), 1609 (s), 1175 (s); δ_{H} 7.73-7.27 (4 H, m, ArH + ArCH=C), 6.42

(1 H, d, J 9.2, ArC=CH); δ_C 160.76 (C=O), 153.99 (C_{Ar}), 143.41 (C_{Ar}), 131.79 (C_{Ar}), 127.82 (C_{Ar}), 124.39 (C_{Ar}), 118.78 (C_{Ar}), 116.85 (C_4), 116.65 (C_3).

6-Bromocoumarin (2f). Yellow solid (67%), m.p. 162-165 °C (lit.^[5] 165-167 °C); ν_{max} 2897 (b, C-H), 1694 (s, CO), 1609 (s), 1175 (s); δ_H 7.7-6.4 (4 H, m, ArH + ArCH=C), 6.42 (1 H, d, J 9.6, ArC=CH); δ_C 160.7 (C=O), 153.99 (C_{Ar}), 143.4 (C_{Ar}), 131.7 (C_{Ar}), 127.8 (C_{Ar}), 124.3 (C_{Ar}), 118.7 (C_{Ar}), 116.8 (C_4), 116.6 (C_3).

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