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Versatile One-Pot Synthesis of 3-Alkenylcoumarins

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Dedicated to Professor W. Pfleiderer on the occasion of his 80th birthday

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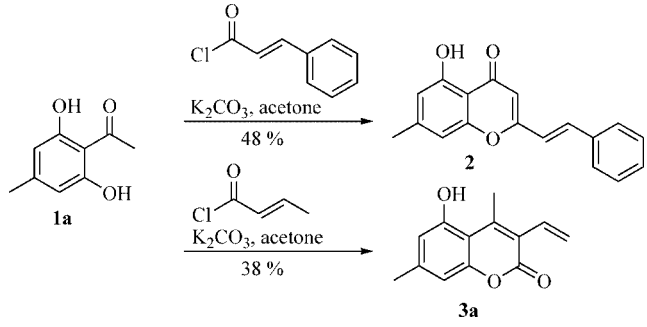
A variety of 2-acyl-, 2-aroyl- and 2-formyl-substituted phenols are converted in a one-pot reaction with α,β-unsaturated carboxylic acid chlorides into the corresponding 3-alkenylcoumarins. Especially the labile 3-vinylcoumarins are readily available by the simple to perform protocol. If longer alkenyl chains are involved in position 3, small molecules with excellent organo gelating properties are established. The mode of action for such aggregates is confirmed by X-ray analysis of an analogue.

Introduction

Coumarins are common motifs in a variety of naturally occurring products and represent the core structure of several top-selling drugs like warfarin.[1] Recently, coumarins have found wide applications in the labelling[2] and caging[3] of biomolecules. Because of the utmost significance of this heterocyclic system many strategies for the synthesis of a variety of substituted coumarins have been elaborated.[4] Examples of 3-alkenyl- and 3-vinylcoumarins in particular are scarce since they are considered as labile intermediates. Early reports describe these compounds as by-products.[5] For the preparation of 3-vinylcoumarins a multi-step sequence was developed including an in situ formation of the substituent in position 3. The vinyl moiety is usually trapped in situ by a Diels–Alder reaction with electron-poor dienophiles.[6] Further investigations of the photochemistry of the pyrone double bond confirmed its reactivity in [2+2]-cycloadditions.[7] Since only a limited number of 3-vinylcoumarins is known the reactions of these compounds were treated theoretically.[8] Resonance-stabilized derivatives have been synthesized by palladium-catalyzed reactions and were only characterized by fluorescence spectroscopy.[9]

Results and Discussion

In the course of natural product synthesis we were prompted to synthesize chromenone derivatives which exhibit alkenyl moieties in position 2. Starting from 2-acetylorcinol[10] (**1a**) we accomplished the styryl derivative **2** following a known protocol.[11] Upon switching from cinnamoyl chloride to crotonyl chloride chromenones were no longer obtained, but 3-vinylcoumarin **3a** was exclusively formed (Scheme 1).



Scheme 1. Serendipitous formation of 3-vinylcoumarins.

In contrast to earlier reports,[6,7] compounds like **3a** turned out to be rather stable and could be isolated as colourless crystals. Suitable crystals for X-ray analysis were obtained by slow evaporation and allowed structural confirmation (Figure 1).

The asymmetric unit of crystalline **3a** contains two independent molecules of coumarin possessing planar heterocyclic moieties as expected. The essential difference between the two molecules A and B is based on the orientation of the vinyl groups. One of the coumarin fragments is totally planar with the attached vinyl group facing the carbonyl substituent in position 2. In molecule B, the vinyl group is twisted out of the plane by 50° towards the methyl substituent in position 4. This provides close packing and orienta-

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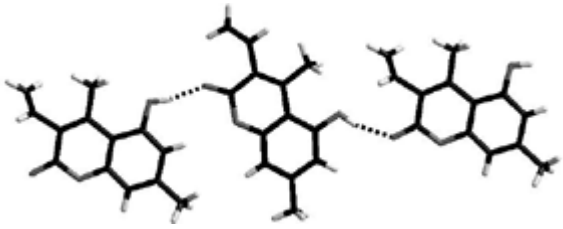
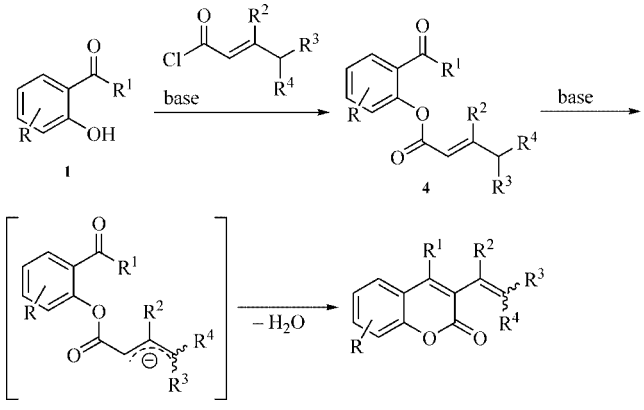


Figure 1. A fragment of crystal packing and hydrogen bonding scheme showing different orientations of the vinyl substituents in independent coumarin molecules A and B of **3a**. Hydrogen bonds are indicated.

tion favourable for strong intermolecular C=O···HO hydrogen bonds (Figure 1). As a result, the crystal packing consists of infinite hydrogen-bonded planar ribbons parallel to each other with an interplanar distance being equal to 3.4 Å, indicating π···π stacking interactions. All vinyl groups point to the same side of the particular aggregate.

The illustrated conversion to the 3-alkenylcoumarin can be described as an isomerizative version of the Kostanecki–Robinson reaction.

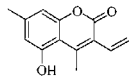
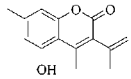
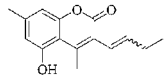
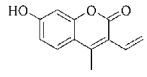
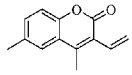
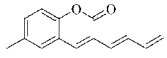
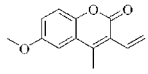
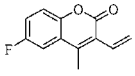
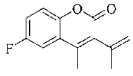
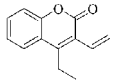
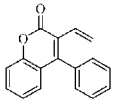
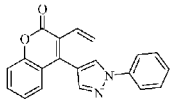
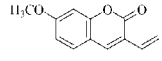
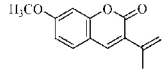
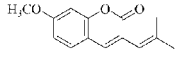
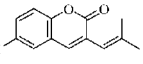
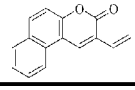
The initial step of the domino reaction[12] involves the acylation of the phenolic hydroxy group. The intermediate ester **4** can be detected and in some cases isolated after short reaction times. The next steps consist of a γ-deprotonation and α-attack onto the carbonyl moiety in order to construct the six-membered heterocycle (Scheme 2). Consequently, this reaction pathway was not possible for the cinnamate and chromenone **2** was formed. In order to elucidate the scope of the one-pot sequence which was found by serendipity, we subjected a variety of phenolic substrates with different carbonyl moieties in position **2** to a selection of α,β-unsaturated acid chlorides. Alteration of the base mainly resulted in the formation of the corresponding ester **4** (Hünig's base, DBU and sodium hydride were explored). γ-Deprotonation is easily accomplished by the use of potassium carbonate and furnishes the coumarin derivative in satisfying yield. In general, the transformation seems to be rather slow. The time-consuming step is attributed to the condensation reaction which requires several hours up to a few days for good conversions. 2-Acetylorcinol (**1a**) was



Scheme 2. Plausible mechanism for the formation of 2-alkenylcoumarins.

treated with crotonyl chloride furnishing **3a** as sole product (entry 1). The yield for the 3-alkenylcoumarin derivative was increased when 3-methyl-2-butenoyl chloride was applied providing the coumarin with a 2-propenyl substituent in position **3** (entry 2). Subjecting **1a** to a long-chain α,β-unsaturated acyl chloride afforded an isomeric mixture of

Table 1. Survey of substrates subjected in the isomerizing Kostanecki–Robinson reaction.

Entry	Product		Conditions[a]	Yield %
1		**3a**	2 d	38
2		**3b**	12 h	78
3		**3c**	12 h	58[b]
4		**3d**	12 h	62
5		**3e**	12 h	87
6		**3f**	16 h, DBU as base	95
7		**3g**	12 h	60
8		**3h**	2.5 d	64
9		**3i**	22 h	81
10		**3j**	12 h	79
11		**3k**	6 d	50
12		**3l**	2.5 d	59
13		**3m**	12 h	97[5b]
14		**3n**	12 h	94
15		**3o**	12 h	89
16		**3p**	5 d	38
17		**3q**	12 h	72

[a] All reactions were carried out with 1.25 equiv. of acyl chloride and 3.0 equiv. K_2CO_3 in acetone under reflux conditions. [b] Both isomers are found, *E*:*Z* = 1.8:1.

3-alkenylcoumarins. Since the γ-deprotonation is not selectively performed, the subsequent steps result in an olefinic mixture. **3c** is obtained in an *E*:*Z* ratio of 1.8:1. Most interestingly, the longer side chain exhibits very pronounced properties as an organogelator[13] and causes a lower yield due to the problems during purification. 0.02 M solutions of **3c** in a mixture of *tert*-butyl methyl ether/cyclohexane (1:3) form a transparent organogel which liquifies upon heating to 50 °C (Table 1).

The gelating properties are attributed to aggregates by hydrogen bonding. An arrangement which results in infinite ribbons similar to the one found in the X-ray analysis of **3a** can be anticipated. Noteworthy, **3c** represents an unusual simple and small molecule as organogelator.[13]

Acetophenones with multiple hydroxy groups yield the vinylcoumarin system directly (entry 4). If this unprotected 4-hydroxy group is replaced by a methyl group the yield is significantly increased. The transformation can be extended to the corresponding 1,3-butadienyl-substituted coumarins by employing sorbyl chloride.[14] In this particular conversion DBU is the base of choice providing the product almost quantitatively and isomerically pure in relatively short reaction times (entry 6). A variety of differently substituted acetophenones was tested. The electron-rich substrate **1d** is successfully converted within 12 h, whereas the electron-deficient congener **1e** requires significantly prolonged reaction times and additional acyl chloride (entries 7 and 8). The situation is ameliorated upon using 3-methyl-2-butenoyl chloride. The fluorinated coumarin **3h** is isolated in 89% yield. Other alkyl aryl ketones can also be converted into vinylcoumarins in good yield (entry 10). Due to the low carbonyl activity these compounds require prolonged reaction times of several days (entries 11 and 12). Even complex heterocyclic substrates are compatible with this one-pot sequence. Salicylic aldehydes are also useful substrates for this transformation allowing the construction of a variety of 3-alkenylcoumarins in very good to excellent yield (entries 13–15). Even synthetically valuable iodo moieties are tolerated in this protocol yielding the corresponding iodinated heterocycle. In this reaction sequence, 2-hydroxy-1-naphthaldehyde (**1k**) furnishes 3-vinylbenzo[*f*]coumarin (**3q**) in good yield.

Conclusions

In conclusion, a versatile and reliable strategy to 3-alkenylcoumarins was established. This domino reaction consists of an *O*-acylation with a subsequent isomerizative condensation reaction. The one-pot protocol is easily performed and provides synthetic intermediates which have been described before as in-situ-generated species! Since the substitution pattern of naturally occurring 3-alkenylcoumarins[15] is easily constructed, the synthesis of the natural products phebaclavin G and H will be reported in due course. Moreover, vinyl and alkenyl moieties exhibit a unique reactivity which can be exploited in powerful synthetic operations like olefin metathesis[16] or stereoselective transformations.[17]

Experimental Section

General Comments: All reagents were used in analytical grades. Solvents were desiccated if necessary by standard methods. Melting points were determined with a Melting Point Apparatus SMP3 (Stuart Scientific, Watford Herts, UK) and were uncorrected. Microanalysis was performed with a Vario EL III (Elementar-Analysensysteme, Hanau, Germany). NMR spectra were recorded with a Bruker ARX 300, (Analytische Messtechnik, Karlsruhe, Germany) by calibration on $CHCl_3$ with δ = 7.26 ppm or [D_6]DMSO with 2.50 ppm for ^{1}H NMR spectroscopy. Mass spectra were obtained on a MAT8200 (Finnigan, Bremen, Germany) employing EI or on a MS50 (Kratos, Manchester, England) or MAT95XL (Finnigan, Bremen, Germany) employing HRMS. GC Mass Spectra were obtained on a MS-50 (A.E.I., Manchester, GB) employing EI. Column chromatography was performed on silica gel (particle size 63–200 μm, Merck, Darmstadt, Germany) using mixtures of cyclohexane with ethyl acetate as eluents.

General Procedure: At room temperature 2.0 mmol of the corresponding (2-hydroxyphenyl)carbonyl derivative **1** is dissolved in acetone (10.0 mL). Then 6.0 mmol of potassium carbonate and 2.5 mmol of the α,β-unsaturated acyl chloride are added and the reaction mixture is stirred for the given time (see Table 1) under reflux conditions. After the reaction is finished, the suspension is poured onto ice (20 mL), acidified to pH = 4 with citric acid and subsequently the aqueous layer is extracted with ethyl acetate (3 × 20 mL). The combined organic fractions are washed with H_2O and brine, dried with magnesium sulfate and concentrated under reduced pressure. Purification of the resulting coumarin derivative **3** is achieved via column chromatography with cyclohexane/ethyl acetate as eluents.

5-Hydroxy-4,7-dimethyl-3-vinylcoumarin (3a): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 75:25, then 50:50) as yellow crystals in 166 mg (38%) yield. R_f = 0.27 (cyclohexane/EtOAc, 9:1); m.p. 192 °C. ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C): δ = 2.24 (s, 3 H, CH_3), 2.63 (s, 3 H, CH_3), 5.53 [dd, 1 H, ^2J(H,H) = 2.3 Hz, ^3J(*cis*H,H) = 11.7 Hz, HC=CH_2], 5.89 [dd, 1 H, ^2J(H,H) = 2.3 Hz, ^3J(*trans*H,H) = 17.6 Hz, HC=CH_2], 6.55 (br., 1 H, Ar-H), 6.62 [dd, 1 H, ^3J(*cis*H,H) = 11.7 Hz, ^3J(*trans*H,H) = 17.6 Hz, *H*C=CH_2], 10.54 (s, 1 H, O*H*) ppm. ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 20.5 (CH_3), 22.0 (CH_3), 108.0 (C_{quat}), 108.3 (CH), 113.2 (CH), 119.9 [*C*C(O)O], 122.2 (HC=CH_2), 130.4 (H*C*=*C*H_2), 143.2 (C_{quat}), 150.5 (C_{quat}), 154.0 (C_{quat}), 157.5 (*C*OH), 159.8 [*C*(O)O]. MS (70 eV, EI): *m*/*z* (%) = 216 (100) [M]$^{+\cdot}$, 188 (24) [M – CO]$^{+\cdot}$, 151 (56) [$C_8H_7O_3$]$^+$. HRMS (EI): *m*/*z* [M – H]$^{+\cdot}$ calcd. for $C_{13}H_{12}O_3$: 215.0714, found 215.0710; elemental analysis calcd. for $C_{13}H_{12}O_3$: C 72.21, H 5.59; found C 71.33, H 5.50.

X-ray Crystal Data for 3a: Formula $C_{13}H_{12}O_3$, *M* = 216.23, colourless crystal, 0.35 × 0.30 × 0.10 mm, *a* = 9.080(1), *b* = 10.012(1), *c* = 13.130(1) Å, *α* = 105.97(1), *β* = 96.07(1), *γ* = 109.21(1), *V* = 1058.0(2) Å^3, ρ_{calc} = 1.357 g cm^{-3}, *μ* = 0.790 mm^{-1}, empirical absorption correction (0.770 ≤ *T* ≤ 0.925), *Z* = 4, triclinic, space group $P\bar{1}$ (No. 2), *λ* = 1.54178 Å, *T* = 223 K, ω and φ scans, 8825 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 3589 independent (R_{int} = 0.033) and 3238 observed reflections [*I* ≥ 2 σ(*I*)], 301 refined parameters, *R* = 0.057, *wR*^{2} = 0.152, max. residual electron density 0.79 (–0.33) e Å^{-3}, hydrogen atoms were calculated and refined as riding atoms, except for O–H which were located from the difference Fourier map and refined isotropically.

Data set for **3a** was collected with Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius

B.V., 1998), data reduction Denzo-SMN,[18] absorption correction Denzo,[19] structure solution SHELXS-97,[20] structure refinement by full-matrix least-squares against F^2 using SHELXL-97.

CCDC-653823 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5-Hydroxy-4,7-dimethyl-3-(propen-2-yl)coumarin (3b): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 75:25) as light yellow crystals in 360 mg (78%) yield. R_f = 0.26 (cyclohexane/EtOAc, 75:25); m.p. 231 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.89 (s, 3 H, CH_3), 2.27 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 4.84 (s, 1 H, HC=CH_2), 5.28 (s, 1 H, HC=CH_2), 6.57 (s, 1 H, Ar-H), 6.58 (s, 1 H, Ar-H), 10.45 (s, 1 H, O*H*) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 15.3 (CH$_3$), 21.1 (CH$_3$), 22.2 (CH$_3$), 106.6 (C$_{quat}$), 107.3 (CH), 112.0 (CH), 117.2 (C=CH$_2$), 125.2 [*C*C(O)O], 139.9 (C$_{quat}$), 141.8 (*C*=*C*H$_2$), 148.2 (C$_{quat}$), 153.4 (C$_{quat}$), 156.4 (*C*OH), 158.7 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 230 (100) [M]$^{\cdot+}$, 251 (24) [M – CH$_3$]$^{\cdot+}$, 202 (12) [M – CO]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for C$_{14}$H$_{14}$O$_3$: 229.0870, found 229.0869.

3-[(*E*)-Buten-1-yl]-5-hydroxy-4,7-dimethylcoumarin (3c): This compound was prepared according to the general procedure using 2,6-dihydroxy-4-methylacetophenone (0.50 g, 3.0 mmol), 10 mL acetone, potassium carbonate (1.25 g, 9.0 mmol) and (*E*)-hexenoyl chloride[21] (0.60 g, 4.5 mmol). **3c** was obtained after column chromatography (cyclohexane/methyl *tert*-butyl ether, 80:20, then 50:50) as yellow crystals in 425 mg (58%) yield. (*E*)- and (*Z*)-Isomer were not separated, ratio *E*:*Z* = 1.8:1. NMR spectroscopic data refer to the (*E*)-isomer. R_f = 0.28 (cyclohexane/EtOAc, 75:25). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.99 (t, 3 H, CH_3), 1.95 [quin, 2 H, ^3J(H,H) = 7.2 Hz, CH_2], 2.33 (s, 3 H, CH_3), 2.59 (s, 3 H, CH_3), 5.88 [dt, 1 H, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 11.2 Hz, HC=C$H_{(E)}$], 6.12 [d, 1 H, ^3J(H,H) = 11.2 Hz, C*H* = CH], 6.53 (s, 1 H, Ar-H), 6.70 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 13.6 (CH$_3$), 21.2 (CH$_3$), 23.2 (CH$_3$), 27.3 (*C*H$_2$CH$_3$), 108.1 (C$_{quat}$), 110.0 (CH), 113.0 (CH), 120.9 [*C*C(O)O], 121.6 (H*C*=*C*H), 139.0 (HC=CH), 142.5 (C$_{quat}$), 150.3 (C$_{quat}$), 154.3 (C$_{quat}$), 154.9 (*C*OH), 161.7 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 244 (100) [M]$^{\cdot+}$, 229 (82) [M – CH$_3$]$^{\cdot+}$, 215 (83) [M – C$_2$H$_5$]$^{\cdot+}$, 201 (37) [M – C$_2$H$_3$O]$^{\cdot+}$, 151 (18) [C$_8$H$_7$O$_3$]$^+$. HRMS (EI): *m*/*z* [M]$^{\cdot+}$ calcd. for C$_{15}$H$_{16}$O$_3$: 244.1099, found 244.1104.

7-Hydroxy-4-methyl-3-vinylcoumarin (3d): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 75:25) as light yellow crystals in 255 mg (62%) yield. Recrystallization from CH_2Cl_2 furnished the analytically pure product. R_f = 0.18 (cyclohexane/EtOAc, 75:25); m.p. 177–179 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.43 (s, 3 H, CH_3), 5.50 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*cis* H,H) = 11.7 Hz, CH=CH_2], 6.00 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*trans* H,H) = 17.4 Hz, CH=CH_2], 6.67 [d, 1 H, ^4J(H,H) = 2.1 Hz, Ar-H], 6.71 [dd, 1 H, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2.1 Hz, Ar-H], 6.78 [dd, 1 H, ^3J(*cis* H,H) = 11.7 Hz, ^3J(*trans* H,H) = 17.4 Hz, C*H* = CH$_2$], 7.65 [d, 1 H, ^3J(H,H) = 9.0 Hz, Ar-H], 10.52 (s, 1 H, O*H*) ppm. ^{13}C NMR (75 MHz, [D$_6$]-DMSO): δ = 14.8 (CH$_3$), 101.7 (CH = *C*H$_2$), 112.3 (C$_{quat}$), 113.0 (CH), 117.1 [*C*C(O)O], 120.6 (CH), 127.2 (CH), 129.3 (*C*H = CH$_2$), 148.1 (C$_{quat}$), 153.3 (C$_{quat}$), 159.1 [*C*(O)O], 160.8 (*C*OH) ppm. MS (70 eV, EI): *m*/*z* (%) = 202 (100) [M]$^{\cdot+}$, 201(44) [M – H]$^{\cdot+}$, 174 (32) [M – C$_2$H$_4$]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^{\cdot+}$ calcd. for C$_{12}$H$_{10}$O$_3$: 201.0557, found 201.0555; elemental analysis calcd. (%) for C$_{12}$H$_{10}$O$_3$ (202.1): C 71.28, H 4.98; found C 69.25, H, 5.12.

4,6-Dimethyl-3-vinylcoumarin (3e): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as light yellow crystals in 350 mg (87%) yield. R_f = 0.20 (cyclohexane/EtOAc, 9:1); m.p. 103 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.42 (s, 3 H, CH_3), 2.50 (s, 3 H, CH_3), 5.65 [dd, 1 H, ^2J(H,H) = 2.0 Hz, ^3J(*cis* H,H) = 12.0 Hz, HC=CH_2], 6.02 [dd, 1 H, ^2J(H,H) = 2.0 Hz, ^3J(*trans* H,H) = 17.6 Hz, HC=CH_2], 6.72 [dd, 1 H, ^3J(*cis* H,H) = 12.0 Hz, ^3J(*trans* H,H) = 17.6 Hz, *H*C=CH$_2$], 7.18 [d, 1 H, ^3J(H,H) = 8.0 Hz, Ar-H], 7.28 [dd, 1 H, ^3J(H,H) = 8.0 Hz, Ar-H], 7.43 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 15.3 (CH$_3$), 21.1 (CH$_3$), 116.4 (CH = *C*H$_2$), 120.2 (C$_{quat}$), 122.6 (CH), 122.8 (CH), 124.9 [*C*C(O)O], 129.2 (C$_{quat}$), 132.1 (CH), 133.7 (*C*H = CH$_2$), 146.4 (C$_{quat}$), 150.2 (C$_{quat}$), 160.2 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 200 (100) [M]$^{\cdot+}$, 199 (68) [M – H]$^{\cdot+}$, 171 (24) [M – CO]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for C$_{13}$H$_{12}$O$_2$: 199.0765, found 199.0762; elemental analysis calcd. (%) for C$_{13}$H$_{12}$O$_2$ (200.1): C 77.98, H 6.04; found C 77.09, H 6.14.

3-(Buta-1,3-dienyl)-4,6-dimethylcoumarin (3f): For the synthesis of **3f** the general protocol was altered: 2-hydroxy-5-methylacetophenone (150 mg, 1.0 mmol), 5.0 mL acetone, potassium carbonate (0.415 g, 6.0 mmol) and sorbyl chloride[22] (163 mg, 2.5 mmol) were used. The reaction mixture was stirred under reflux conditions for 14 h. Subsequently, 1,8-diazabicyclo[5.4.0]undec-7-ene (183 mg, 1.2 mmol) was added and the mixture was heated to reflux for additional 4 h. **3f** was obtained after column chromatography (cyclohexane/ethyl acetate, 95:5) as yellow crystals in 214 mg (95%) yield. R_f = 0.11 (cyclohexane/EtOAc, 95:5); m.p. 101–103 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.34 (s, 3 H, CH_3), 2.42 (s, 3 H, CH_3), 5.18 [d, 1 H, ^3J(*cis* H,H) = 10.8 Hz, HC=CH_2], 5.35 [d, 1 H, ^3J(*trans* H,H) = 16.8 Hz, HC=CH_2], 6.43 [td, 1 H, ^3J(*cis* H,H) = 10.8 Hz, ^3J(*trans* H,H) = 16.8 Hz, HCC*H* = CH$_2$], 6.53 [d, 1 H, ^3J(H,H) = 15.6 Hz, *H*C=CH], 7.10 [d, 1 H, ^3J(H,H) = 8.4 Hz, Ar-H], 7.19 [d, 1 H, ^3J(H,H) = 8.4 Hz, Ar-H], 7.25 [dd, 1 H, ^3J(H,H) = 10.8 Hz, ^3J(H,H) = 15.6 Hz, HC=C*H*], 7.35 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 15.1 (CH$_3$), 21.1 (CH$_3$), 116.3 (HC=CH$_2$), 119.7 (CH), 120.3 [*C*C(O)O], 121.7 (C$_{quat}$), 124.7 (H*C*CH=CH$_2$), 124.9 (HC*C*H = CH$_2$), 132.1 (CH), 131.9 (CH), 133.7 (C$_{quat}$), 137.5 (CH), 137.8 (HC=CH$_2$), 145.8 (C$_{quat}$), 150.0 (C$_{quat}$), 159.8 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 226 (100) [M]$^{\cdot+}$, 211 (26) [M – CH$_3$]$^{\cdot+}$, 197 (20) [M – C$_2$H$_5$]$^{\cdot+}$, 183 (36) [M – C$_2$H$_3$O]$^{\cdot+}$. HRMS (EI): *m*/*z* [M]$^+$ calcd. for C$_{15}$H$_{14}$O$_2$: 226.0994, found 226.0989; elemental analysis calcd. (%) for C$_{15}$H$_{14}$O$_2$ (226.1): C 79.26, H 6.24; found C 78.48, H 6.22.

6-Methoxy-4-methyl-3-vinylcoumarin (3g): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as light yellow crystals in 260 mg (60%) yield. R_f = 0.21 (cyclohexane/EtOAc, 9:1); m.p. 80 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 2.49 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 5.66 [dd, 1 H, ^2J(H,H) = 2.0 Hz, ^3J(*cis* H,H) = 12.0 Hz, HC=CH_2], 6.02 [dd, 1 H, ^2J(H,H) = 2.0 Hz, ^3J(*trans* H,H) = 17.6 Hz, HC=CH_2], 6.72 [dd, 1 H, ^3J(*cis* H,H) = 12.0 Hz, ^3J(*trans* H,H) = 17.6 Hz, *H*C=CH$_2$], 7.06 [d, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H], 7.08 (s, 1 H, Ar-H), 7.22 [d, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H] ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 15.4 (CH$_3$), 55.82 (O*C*H$_3$), 108.2 (HC=CH$_2$), 117.6 (C$_{quat}$), 117.7 (CH), 118.0 (CH), 121.0 [*C*C(O)O], 123.0 (C$_{quat}$), 129.2 (CH), 146.1 (H*C*=*C*H$_2$), 146.5 (C$_{quat}$), 155.9 (C$_{quat}$), 160.1 (C$_{quat}$), 160.0 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 216 (100) [M]$^{\cdot+}$, 215 (46) [M – H]$^{\cdot+}$, 188 (12) [M – CO]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for C$_{13}$H$_{12}$O$_3$: 215.0714, found 215.0706; elemental analysis calcd. (%) for C$_{13}$H$_{12}$O$_3$ (216.1): C 72.21, H 5.59; found C 71.64, H 5.51.

6-Fluoro-4-methyl-3-vinylcoumarin (3h): This compound was obtained after column chromatography (cyclohexane/ethyl acetate,

75:25) and recrystallisation from ethanol (4.0 mL) as colourless crystals in 259 mg (64%) yield. R_f = 0.59 (cyclohexane/EtOAc, 75:25); m.p. 93 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 2.47 (s, 3 H, CH_3), 5.62 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*cis* H,H) = 11.7 Hz, HC=CH_2], 6.05 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*trans* H,H) = 17.4 Hz, HC=CH_2], 6.74 [dd, 1 H, ^3J(*cis* H,H) = 11.7 Hz, ^3J(*trans* H,H) = 17.4 Hz, *H*C=CH$_2$], 7.42 [s, 1 H, ^3J(H, F) = 9.8 Hz, Ar-H], 7.45 [d, 1 H, ^3J(H,H) = 4.8 Hz, Ar-H], 7.66 [dd, 1 H, ^3J(H,F) = 8.1 Hz, ^4J(H,H) = 2.8 Hz, Ar-H] ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 15.6 (CH$_3$), 111.9 [^2J(C,F) = 24.9 Hz, CH], 118.4 [^3J(C,F) = 8.6 Hz, CH], 119.0 [^2J(C,F) = 24.4 Hz, CH], 121.6 [^3J(C,F) = 8.4 Hz, C$_{quat}$], 122.4 (C-3), 129.6 (H*C*=*C*H$_2$), 147.3 (C$_{quat}$), 148.2 (C$_{quat}$), 157.5 [^1J(C,F) = 238.6 Hz, CF], 159.0 [C(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 205/204 (14/100) [M]$^{\cdot+}$, 176/175 (14/36) [M – CO]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for $C_{12}H_9FO_2$: 203.0514, found 203.0508; elemental analysis calcd. (%) for $C_{12}H_9O_2F$ (204.1): C 70.58, H 4.44; found C 70.49, H 4.21.

6-Fluoro-4-methyl-3-(propen-2-yl)coumarin (3i): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as colourless crystals in 354 mg (81%) yield. R_f = 0.22 (cyclohexane/EtOAc, 9:1); m.p. 151 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 3 H, CH_3), 2.36 (s, 3 H, CH_3), 4.91 (s, 1 H, C=CH_2), 5.36 (s, 1 H, C=CH_2), 7.16 [dd, 1 H, ^3J(H,H) = 9.0 Hz, ^4J(H,F) = 2.7 Hz, Ar-H], 7.23 [dd, 1 H, ^3J(H,F) = 7.8 Hz, Ar-H], 7.25 [td, 1 H, ^3J(H,H) = 9.0 Hz, ^4J(H,H) = 2.7 Hz ^3J(H,F) = 8.7 Hz, Ar-H] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.9 (CH$_3$), 22.3 (CH$_3$), 110.6 [^2J(C,F) = 28.4 Hz, CH], 118.0 [*C*C(O)O], 118.1 [^3J(H,F) = 11.2 Hz, C$_{quat}$], 118.1 [^2J(H,F) = 25.1 Hz, CH], 121.3 [^3J(C,F) = 8.3 Hz, CH], 130.1 (*C*=*C*H$_2$), 139.5 (C=CH$_2$), 145.2 (C$_{quat}$), 148.5 (C$_{quat}$), 157.1 [^1J(C,F) = 251.8 Hz, C$_{quat}$], 160.4 [*C*(O)O]. MS (70 eV, EI): *m*/*z* (%) = 219/218 (15/100) [M]$^{\cdot+}$, 203 (28) [M – CH$_3$]$^{\cdot+}$, 189 (10) [M – CO]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for $C_{13}H_{11}FO_2$: 217.0670, found 217.0664; elemental analysis calcd. (%) for $C_{13}H_{11}O_2F$ (218.1): C 71.55, H 5.08; found C 71.43, H 4.85.

4-Ethyl-3-vinylcoumarin (3j): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as yellowish oil in 316 mg (79%) yield. R_f = 0.35 (cyclohexane/EtOAc, 9:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 [t, 3 H, ^3J(H,H) = 7.8 Hz, CH_3], 2.89 [q, 2 H, ^3J(H,H) = 7.8 Hz, CH_2CH$_3$], 5.58 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*cis* H,H) = 11.7 Hz, CH=CH_2], 6.15 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*trans* H,H) = 17.4 Hz, CH=CH_2], 6.66 [dd, 1 H, ^3J(*cis* H,H) = 11.7 Hz, ^3J(*trans* H,H) = 17.4 Hz, C*H* = CH$_2$], 7.24 [td, 1 H, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.5 Hz, Ar-H], 7.26 [d, 1 H, ^3J(H,H) = 8.1 Hz, Ar-H], 7.43 [td, 1 H, ^3J(H,H) = 8.1 Hz, Ar-H], 7.61 [dd, 1 H, ^4J(H,H) = 1.5 Hz, ^3J(H,H) = 8.1 Hz, Ar-H] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5 (CH$_3$), 21.6 (*C*H$_2$CH$_3$), 116.9 (CH = *C*H$_2$), 119.2 (C$_{quat}$), 121.3 (CH), 122.6 [*C*C(O)O], 124.2 (CH), 124.7 (CH), 128.3 (*C*H = CH$_2$), 131.0 (C$_{quat}$), 152.0 (C$_{quat}$), 152.5 (CH), 160.0 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 200 (100) [M]$^{\cdot+}$, 185 (70) [M – CH$_3$]$^{\cdot+}$, 157 (38) [M – C$_2$H$_3$O]$^{\cdot+}$. HRMS (EI): *m*/*z* [M]$^+$ calcd. for $C_{13}H_{12}O_2$: 200.0837, found 200.0838.

4-Phenyl-3-vinylcoumarin (3k): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 95:5) as yellow crystals in 368 mg (50%) yield. R_f = 0.39 (cyclohexane/EtOAc, 9:1); m.p. 146–148 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.13 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*cis* H,H) = 11.4 Hz, HC=CH_2], 6.00 [dd, 1 H, ^3J(*cis* H,H) = 11.4 Hz, ^3J(*trans* H,H) = 18.0 Hz, *H*C=CH$_2$], 6.17 [dd, 1 H, ^2J(H,H) = 2.1 Hz, ^3J(*trans* H,H) = 18.0 Hz, HC=CH_2], 6.76 [dd, 1 H, ^3J(H,H) = 8.1, Ar-H], 6.87 [td, 1 H, ^3J(H,H) = 8.1, Ar-H], 6.99 [dd, 2 H, ^3J(H,H) = 7.8 Hz, Ar-H], 7.10 [dd, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H], 7.22 [td, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H], 7.27 [m, 3 H, ^3J(H,H) = 7.8 Hz, Ar-H] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.4 (HC=CH$_2$), 120.7 (C$_{quat}$), 121.3 (C$_{quat}$), 122.4 (CH), 124.0 (CH), 128.8 (CH), 128.8 (CH), 129.4 (CH), 131.3 (CH), 134.4 [*C*C(O)O], 150.9 (C$_{quat}$), 152.4 (C$_{quat}$), 159.7 [*C*(O)O]. MS (70 eV, EI): *m*/*z* (%) = 248 (100) [M]$^{\cdot+}$, 219 (36) [M – CHO]$^{\cdot+}$, 203 (40) [M – CHO$_2$]$^{\cdot+}$, 189 (20) [M – C$_2$H$_3$O$_2$]$^{\cdot+}$. HRMS (EI): *m*/*z* [M – H]$^+$ calcd. for $C_{17}H_{12}O_2$: 247.0765, found 247.0762; elemental analysis calcd. (%) for $C_{17}H_{12}O_2$ (248.1): C 82.24; H 4.87, found C 81.83, H 4.91.

4-(1-Phenyl-1*H*-pyrazolyl)-3-vinylcoumarin (3l): Variation from the general procedure: after the reaction mixture was stirred under reflux conditions for two days, further 1.3 mmol acyl chloride was added. Work up was performed after three days of stirring under reflux conditions, respectively. 4-(2-Hydroxybenzoyl)-1-phenyl-1*H*-pyrazole (264 mg, 1.0 mmol), 15.0 mL acetone, potassium carbonate (0.415 g, 6.0 mmol) and 2-butenoyl chloride (131 mg, 1.3 mmol) were used. **3l** was obtained after column chromatography (cyclohexane/ethyl acetate, 80:20) as colourless crystals in 186 mg (59%) yield. R_f = 0.43 (cyclohexane/EtOAc, 8:2); m.p. 124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.52 [dd, 1 H, ^2J(H,H) = 3.6 Hz, ^3J(*cis* H,H) = 10.4 Hz, HC=CH_2], 6.51 [dd, 1 H, ^2J(H,H) = 3.6 Hz, ^3J(*trans* H,H) = 17.6 Hz, HC=CH_2], 6.55 [dd, 1 H, ^3J(*cis* H,H) = 10.4 Hz, ^3J(*trans* H,H) = 17.6 Hz, *H*C=CH$_2$], 7.20 [td, 1 H, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, Ar-H], 7.37 [t, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H], 7.48 [dd, 1 H, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.6 Hz, Ar-H], 7.52 (m, 4 H, Ar-H), 7.77 [dd, 1 H, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.2 Hz, Ar-H], 7.79 (s, 1 H, *H*CN), 8.08 (s, 1 H, *H*C=N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.9 (C$_{quat}$), 116.6 (HC=CH$_2$), 119.2 (2 × CH), 120.3 [*C*C(O)O], 122.3 (C$_{quat}$), 123.0 (CH), 124.2 (CH), 127.0 (CH), 127.2 (CH), 127.4 (CH), 129.4 (CH), 129.6 (2 × CH), 131.4 (C$_{quat}$), 139.5 (H*C*=*C*H$_2$), 141.5 (CH), 141.6 (C$_{quat}$), 152.4 (C$_{quat}$), 159.4 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 314 (100) [M]$^{\cdot+}$, 286 (60) [M – CO]$^{\cdot+}$, 269 (20) [M – CHO$_2$]$^{\cdot+}$. HRMS (EI): *m*/*z* [M]$^+$ calcd. for $C_{20}H_{14}N_2O_2$: 313.0983, found 313.0977; elemental analysis calcd. (%) for $C_{20}H_{14}N_2O_2$ (314.1): C 76.42, H 4.49; found C 76.20, H 4.50.

7-Methoxy-3-vinylcoumarin[23] (3m): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 75:25) as yellow crystals in 392 mg (97%) yield. R_f = 0.48 (cyclohexane/EtOAc, 75:25); m.p. 118 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.85 (s, 3 H, OCH_3), 5.39 [dd, 1 H, ^2J(H,H) = 1.2 Hz, ^3J(*cis* H,H) = 11.4 Hz, HC=CH_2], 6.08 [dd, 1 H, ^2J(H,H) = 1.2 Hz, ^3J(*trans* H,H) = 17.7 Hz, HC=CH_2], 6.67 [dd, 1 H, ^3J(*cis* H,H) = 11.4 Hz, ^3J(*trans* H,H) = 17.7 Hz, *H*C=CH$_2$], 6.79 (s, 1 H, Ar-H), 6.83 [dd, 1 H, ^3J(H,H) = 8.7 Hz, Ar-H], 7.36 [d, 1 H, ^3J(H,H) = 8.7 Hz, Ar-H], 7.63 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7 (O*C*H$_3$), 100.4 (HC=CH$_2$), 112.8 (CH), 113.0 (C$_{quat}$), 118.1 (CH), 121.6 [*C*C(O)O], 128.7 (CH), 130.6 (CH), 137.8 (H*C*=*C*H$_2$), 154.8 (C$_{quat}$), 160.4 (CH), 162.5 [*C*(O)O]. MS (70 eV, EI): *m*/*z* (%) = 202 (100) [M]$^{\cdot+}$, 174 (20) [M – CO]$^{\cdot+}$, 159 (52) [M – C$_2$H$_3$O]$^{\cdot+}$. HRMS (EI): *m*/*z* [M]$^+$ calcd. for $C_{15}H_{10}O_2$: 202.0630, found 222.0625.

7-Methoxy-3-(propen-2-yl)coumarin (3n): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 80:20) and recrystallization from ethanol as colourless crystals in 406 mg (94%) yield. R_f = 0.37 (cyclohexane/EtOAc, 8:2); m.p. 99–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (s, 3 H, CH_3), 3.86 (s, 3 H, OCH_3), 5.30 (s, 1 H, C=CH_2), 5.86 (s, 1 H, C=CH_2), 6.79 [d, ^4J(H,H) = 2.4 Hz, 1 H, Ar-H], 6.83 [dd, 1 H, ^4J(H,H) = 2.4 Hz, ^3J(H,H) = 8.0 Hz, Ar-H], 6.37 [d, 1 H, ^3J(H,H) = 8.0 Hz, Ar-H], 7.59 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.2

(CH_3), 55.7 (OCH_3), 100.2 ($C{=}CH_2$), 112.6 (CH), 112.9 (C_{quat}), 118.3 (CH), 125.1 [*C*C(O)O], 128.7 (CH), 138.2 (CH), 138.3 (*C*=*C*H$_2$), 154.9 (C_{quat}), 160.0 (C_{quat}), 162.4 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 216 (100) $[M]^{+\cdot}$, 201 (20) $[M - CH_3]^{+}$, 188 (24) $[M - CO]^{+\cdot}$, 173 (56) $[M - C_2H_3O]^{+}$. HRMS (EI): *m*/*z* $[M]^+$ calcd. for $C_{13}H_{12}O_3$: 216.0786, found 216.0785; elemental analysis calcd. (%) for $C_{13}H_{12}O_3$ (216.1): C 72.21, H 5.59; found C 71.80, H 5.75.

7-Methoxy-3-(2-methylpropen-2-yl)coumarin (3o): This compound was prepared according to the general procedure using 2-hydroxy-4-methoxybenzaldehyde (304 mg, 2.0 mmol), 10.0 mL acetone, potassium carbonate (0.83 g, 6.0 mmol) and 4-methyl-2-pentenoyl chloride (296 mg, 2.5 mmol).[24] **3o** was obtained after column chromatography (cyclohexane/ethyl acetate, 80:20) and recrystallization from ethanol as colourless crystals in 408 mg (89%) yield. R_f = 0.46 (cyclohexane/EtOAc, 8:2); m.p. 91–93 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (s, 3 H, HC=CC*H*$_3$), 1.93 (s, 3 H, HC=CC*H*$_3$), 3.85 (s, 3 H, OC*H*$_3$), 6.17 (s, 1 H, *H*C=C), 6.79 [d, 1 H, ^4J(H,H) = 2.4 Hz, Ar-H], 6.83 [dd, 1 H, ^4J(H,H) = 2.4 Hz, ^3J(H,H) = 8.8 Hz, Ar-H], 6.34 [d, 1 H, ^3J(H,H) = 8.8 Hz, Ar-H], 7.44 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.9 (HC=C*C*H$_3$), 26.9 (HC=C*C*H$_3$), 55.7 (O*C*H$_3$), 100.2 (HC=C), 112.6 (CH), 112.9 (C_{quat}), 118.3 (CH), 125.1 [*C*C(O)O], 128.7 (CH), 138.2 (CH), 138.3 (H*C*=*C*), 154.9 (C_{quat}), 160.0 (*C*OCH$_3$), 162.4 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 230 (100) $[M]^{+\cdot}$, 215 (20) $[M - CH_3]^{+}$, 202 (16) $[M - CO]^{+\cdot}$, 187 (28) $[M - C_2H_3O]^{+}$. HRMS (EI): *m*/*z* $[M]^+$ calcd. for $C_{14}H_{14}O_3$: 230.0943, found 230.0941; elemental analysis calcd. (%) for $C_{13}H_{12}O_3$ (230.1): C 73.03, H 6.13; found C 72.74, H 6.06.

6-Iodo-3-(2-methylpropen-2-yl)coumarin (3p): This compound was prepared according to the general procedure, using 2-hydroxy-5-iodobenzaldehyde (248 mg, 1.0 mmol), 10.0 mL acetone, potassium carbonate (0.42 g, 3.0 mmol) and 4-methyl-2-pentenoyl chloride (165 mg, 1.25 mmol).[24] **3p** was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as colourless crystals in 124 mg (38%) yield. R_f = 0.60 (cyclohexane/EtOAc, 9:1); m.p.117–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.90 (s, 3 H, HC=CC*H*$_3$), 1.96 (s, 3 H, HC=CC*H*$_3$), 6.22 (s, 1 H, *H*C=CCH$_3$), 7.06 [d, 1 H, ^3J(H,H) = 8.8 Hz, Ar-H], 7.39 (s, 1 H, Ar-H), 7.71 [dd, 1 H, ^4J(H,H) = 2.0 Hz, ^3J(H,H) = 8.8 Hz, Ar-H], 7.79 [d, 1 H, ^4J(H,H) = 2.0 Hz, Ar-H] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.0 (HC=C*C*H$_3$), 27.1 (HC=C*C*H$_3$), 87.1 (HC=*C*CH$_3$), 118.2 [^2J(C,I) = 23.4 Hz, *C*I], 121.7 (C_{quat}), 126.8 [*C*C(O)O], 135.7 (CH), 136.8 (CH), 139.0 (CH), 141.7 (H*C*=*C*), 152.3 (C_{quat}), 160.8 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 326 (100) $[M]^{+\cdot}$, 298 (16) $[M - CO]^{+\cdot}$, 283 (12) $[M - C_2H_3O]^{+\cdot}$. HRMS (EI): *m*/*z* $[M]^+$ calcd. for $C_{13}H_{11}IO_2$: 325.9804, found 325.9798, elemental analysis calcd. (%) for $C_{13}H_{11}IO_2$ (326.0): C 47.88, H 3.40; found C 47.29, H 3.34.

3-Vinylbenzo[*f*]coumarin (3q): This compound was obtained after column chromatography (cyclohexane/ethyl acetate, 90:10) as yellow crystals in 320 mg (72%) yield. R_f = 0.24 (cyclohexane/EtOAc, 9:1); m.p. 132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.54 [dd, 1 H, ^2J(H,H) = 1.2 Hz, ^3J(*cis* H,H) = 11.6 Hz, HC=C*H*$_2$], 6.30 [dd, 1 H, ^2J(H,H) = 1.2 Hz, ^3J(*trans* H,H) = 17.6 Hz, HC=C*H*$_2$], 6.82 [dd, 1 H, ^3J(*cis* H,H) = 11.6 Hz, ^3J(*trans* H,H) = 17.6 Hz, *H*C=CH$_2$], 7.42 [d, 1 H, ^3J(H,H) = 8.8 Hz, Ar-H], 7.56 [td, 1 H, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, Ar-H], 7.68 [t, 1 H, ^3J(H,H) = 7.2 Hz, Ar-H], 7.88 [d, 1 H, ^3J(H,H) = 8.0 Hz, Ar-H], 7.92 [d, 1 H, ^3J(H,H) = 8.0 Hz, Ar-H], 8.24 [d, 1 H, ^4J(H,H) = 1.6 Hz, Ar-H], 8.42 (s, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 113.4 (HC=CH$_2$), 116.6 (C_{quat}), 119.6 (CH), 121.4 (CH), 123.9 (CH), 126.0 (CH), 128.1 (C-H), 128.9 (C_{quat}), 129.0 (CH), 130.3 [*C*C(O)O], 131.0 (CH), 132.6 (C_{quat}), 133.6 (H*C*=*C*H$_2$), 152.6 (C_{quat}), 160.1 [*C*(O)O] ppm. MS (70 eV, EI): *m*/*z* (%) = 222 (100) $[M]^{+\cdot}$, 194 (52) $[M - CO]^{+\cdot}$, 165 (32) $[C_{13}H_9]^+$. HRMS (EI): *m*/*z* $[M - -H]^+$ calcd. for $C_{15}H_{10}O_2$: 222.0681, found 222.0679.

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