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Structural tuning enables piezochromic and photochemical properties in *N*-aryl-β-enaminones†

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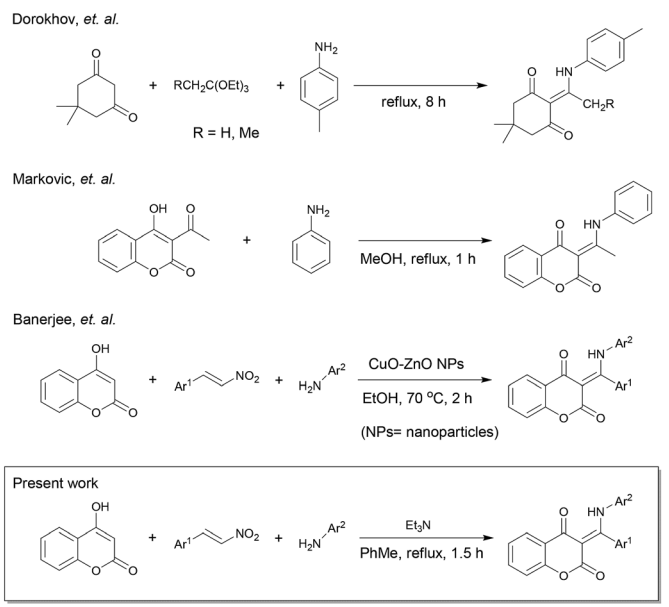
An efficient synthesis of *N*-aryl-β-enaminones *via* Et_3N-mediated, one-pot three-component reaction of 4-hydroxycoumarin/dimedone, β-nitrostyrene/2-(2-nitrovinyl)thiophene, and arylamine in toluene under refluxed conditions is herein presented. Some prepared compounds were found to exhibit piezochromic properties. The XRD and SEM measurements of the piezochromic compound showed substantial crystal packing and morphology changes before and after grinding. Further, one prepared compound was found to be light-sensitive and can be converted to a furo[3,2-*b*]pyridin-2(4*H*)-one derivative upon UV irradiation. A plausible mechanism for this photochemical reaction was proposed.

1 Introduction

The β-enaminones represent a crucial molecular skeleton that is present in various natural products.[1] They were found to be associated with a wide range of pharmacological activities, including antimicrobial,[2] antibacterial,[3] anti-inflammatory,[4] and anti-leukemia[5] properties. Owing to their diverse biological activities, quite a few methodologies for the synthesis of β-enaminones have been reported in the literature.[6] Most of them focused on the preparation of *N*-alkyl-β-enaminones; the synthesis of *N*-aryl-β-enaminones is much less explored. As a result, the photochemical and functional properties of *N*-aryl-β-enaminones have never been reported. Scheme 1 lists the previous syntheses of *N*-aryl-β-enaminones. While they can be readily prepared by either condensation[7] of dimedone, orthoester, and aniline or dehydration[8] of 3-acetyl-4-hydroxycoumarin and arylamine, the scope of these reactions is rather limited. Recently, Banerjee[9] and coworkers reported a highly atom-economical and efficient method for the preparation of *N*-aryl-β-enaminones *via* CuO–ZnO NPs-catalyzed, one-pot three-component reaction of 4-hydroxycoumarin/dimedone, β-nitrostyrene, and arylamine. Nevertheless, the CuO-doped ZnO nanoparticles are currently not commercially available, and the self-prepared nanomaterials need to be analyzed by sophisticated spectroscopic and analytical techniques. Thus, the development of the simple methodology for the preparation of *N*-aryl-β-enaminones with readily available reagents remains desirable. Here, we report the modified preparation of *N*-aryl-β-enaminones *via* base-mediated, one-pot three-component reaction of 4-hydroxycoumarin/dimedone, β-nitrostyrene/2-(2-nitrovinyl)thiophene, and arylamine in toluene under refluxed conditions. The functional and photochemical properties of the prepared compounds such as piezochromism[10] are also investigated.

2 Results and discussion

Our initial efforts toward the preparation of *N*-aryl-β-enaminones called for the base-mediated, one-pot three-component



Scheme 1 Previous and modified synthesis of *N*-aryl-β-enaminones.

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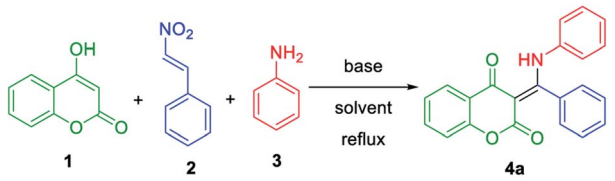
Table 1 Optimization of reaction parameters for **4a**



Entry	Base (equiv.)	Solvent	Time (h)	Yield[a] (%)
1	K_2CO_3 (1.0)	Toluene	1.5	31
2	DABCO (1.0)	Toluene	1.5	68
3	DMAP (1.0)	Toluene	1.5	20
4	Et_3N (1.0)	Toluene	1.5	76
5	Et_3N (0.5)	Toluene	1.5	53
6	Et_3N (1.0)	EtOH	1.5	21
7	Et_3N (1.0)	CH_3CN	1.5	30
8	Et_3N (1.0)	DCE	1.5	44
9	Et_3N (1.0)	Toluene	3.0	76

[a] Isolated yield.

reaction of 4-hydroxycoumarin, aldehyde, and arylamine in the presence of DABCO as a base in nitromethane under refluxed conditions.[11] Although the desired product was indeed isolated, this reaction suffered from moderate to low yields. Further, the reaction scope for the substrates was somewhat limited. Alternatively, we pursued the target compound synthesis by modifying the three-component reaction conditions reported by Wang.[6c] Table 1 lists the optimization for condensation of 4-hydroxycoumarin (**1**), β-nitrostyrene (**2**), and aniline (**3**) under the influence of different organic bases and solvents. To our delight, we found that the reaction can proceed smoothly in the presence of one equiv. of triethylamine as a base in toluene under refluxed conditions for 1.5 h (Entry 4, Table 1). These optimization reaction conditions were then subsequently employed to the preparation of other *N*-aryl-β-enaminones with different substituents.

Fig. 1 lists the structures of the prepared *N*-aryl-β-enaminones and their yields. The molecular structures of **4a–s** were elucidated by ^1H and ^{13}C NMR spectroscopy. Compounds **4g** and **4j** were further verified by X-ray crystallography, as depicted in Fig. 2.[12] An intramolecular hydrogen bonding between the amine hydrogen and carbonyl oxygen atom is clearly observed for both of the compounds. Generally, the *N*-aryl-β-enaminones with electron-donating group substituted at benzene or coumarin moiety gave better yields compared to their unsubstituted counterparts. The opposite was true for *N*-aryl-β-enaminones with electron-withdrawing group substituted at benzene or coumarin moiety. Further, when the substrate 4-hydroxycoumarin (**1**) was replaced by dimedone, the yield of the corresponding product (**4q**, 56%) was less than that of unsubstituted coumarin counterpart (**4a**, 76%), indicating that 4-hydroxycoumarin is a better substrate than that of dimedone for this multicomponent reaction.

With the availability of *N*-aryl-β-enaminones **4a–s**, their functional properties were then investigated. Interestingly, compounds **4g–j** were found to be sensitive to pressure, especially for **4g**. Upon grinding, compound **4g** changes from yellow to red. It can be swiftly reverted to the original color after exposed to methylene chloride vapor, as shown in Fig. 3.

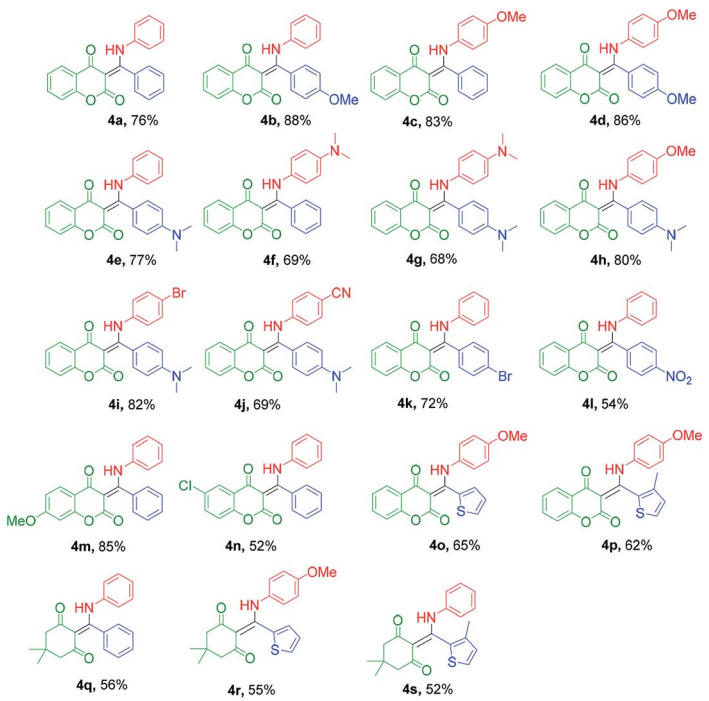


Fig. 1 Structures and yields of the prepared *N*-aryl-β-enaminones **4a–s**.

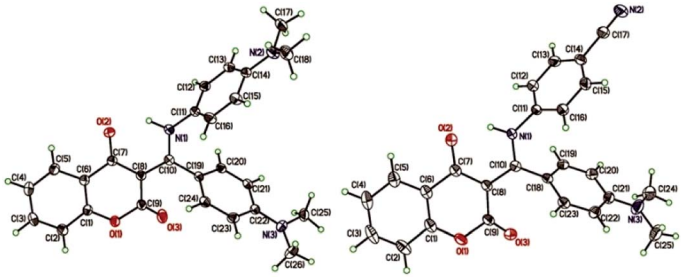


Fig. 2 ORTEP crystal structure of **4g** (left) and **4j** (right).

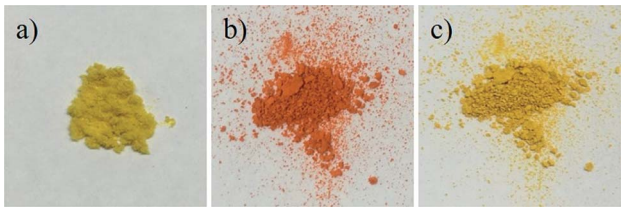


Fig. 3 Color transition of **4g** (a) before grinding; (b) after grinding; (c) after exposed to fuming CH_2Cl_2.

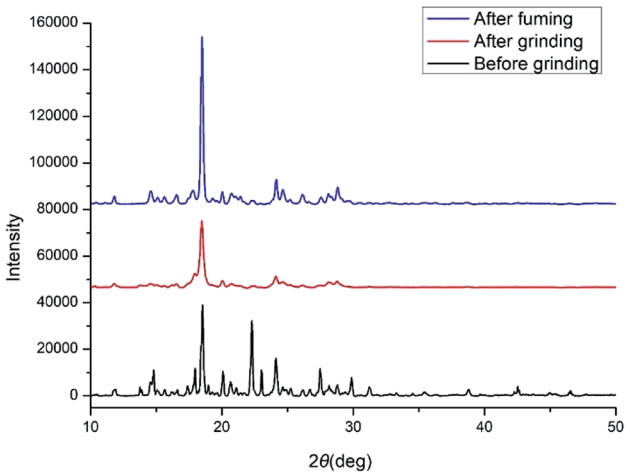


Fig. 4 XRD spectra of **4g** (a) before grinding; (b) after grinding; (c) after fuming with CH_2Cl_2.

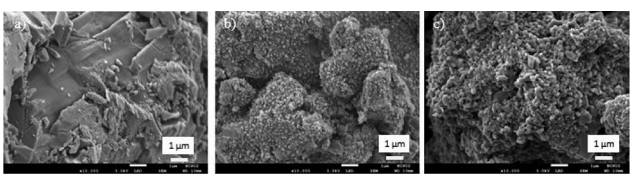
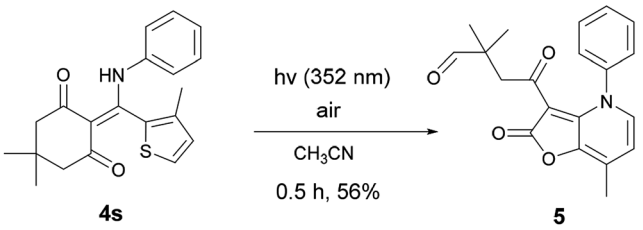


Fig. 5 SEM image of **4g** (a) before grinding; (b) after grinding (c) after fuming with CH_2Cl_2.

To investigate the phase transition during the piezochromic process, the X-ray diffraction (XRD) patterns of **4g** in different solid states were recorded, as depicted in Fig. 4. Several sharp and strong peaks were observed for the crystal sample of **4g**, illustrating the presence of a crystalline structure (Fig. 4a). Nevertheless, the diffraction peaks of **4g** became substantially weaker after grinding (Fig. 4b). The sharp and strong diffraction peaks were recovered when the ground powder of **4g** was exposed to CH_2Cl_2 vapor for 10 s (Fig. 4c).

To obtain more information about the morphology of different aggregated states of **4g** prior to and after grinding, the scanning electron microscopy (SEM) images were also recorded, as illustrated in Fig. 5. Before grinding, the prepared **4g** showed regular plate crystals with a relatively smooth surface (Fig. 5a). However, the smooth surface became rough after grinding (Fig. 5b). This external stimuli-induced damage to the surface topography was swiftly repaired by exposing to CH_2Cl_2 vapor (Fig. 5c). While the detailed piezochromic mechanism of **4g–j** remains to be investigated, the presence of an *N*,*N*-dimethylamino substituent on β-nitrostyrene substrate seems to be required for their color change upon grinding. The discovery of piezochromism from the prepared *N*-aryl-β-enaminones **4g–j** suggests that multicomponent reactions may serve as a useful tool not only to prepare compounds with potential biological and pharmaceutical activities but also to unearth molecules with novel functional properties.

As for their photochemical properties, the prepared *N*-aryl-β-enaminones **4a–r** were all found to be light-insensitive even after prolonged (more than 30 min) irradiation with UV light, except for compound **4s**. Upon UV irradiation in acetonitrile under aerobic conditions for half an hour, compound **4s** was converted to furo[3,2-*b*]pyridin-2(4*H*)-one **5** in 56% yield (Scheme 2). Both of the molecular structures of **4s** and **5** were confirmed by the X-ray crystallography, as shown in Fig. 6.[12] While the detailed photochemical mechanism for this transformation is currently unclear, this photo-oxidation substantially alters the molecular structure of **4s** by opening up two rings, that is, thiophene and dimedone, and forming of a new fused ring, that is, furopyridinone. To gain insights into the mechanism of this photo-oxidation, compound **4s** was subjected to EPR measurement under UV irradiation, and the result turned out to be EPR-silent. Further, the yield of the photoreaction was not affected by the presence of a radical scavenger like TEMPO. These observations suggest the photo-oxidation might not proceed with the radical mechanism. Scheme 3 depicts the plausible intermediates involved in this photo-oxidation. It presumably starts with light-mediated ring-opening of thiophene ring to give the thiol **6**, which



Scheme 2 Photochemical reaction of **4s**.

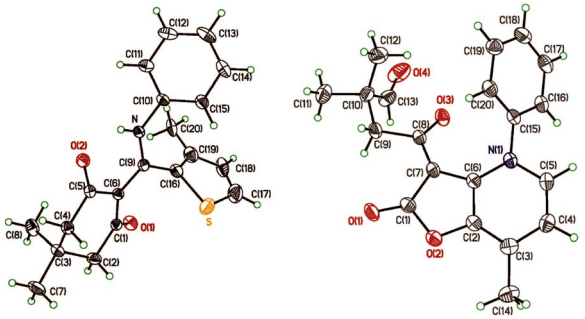
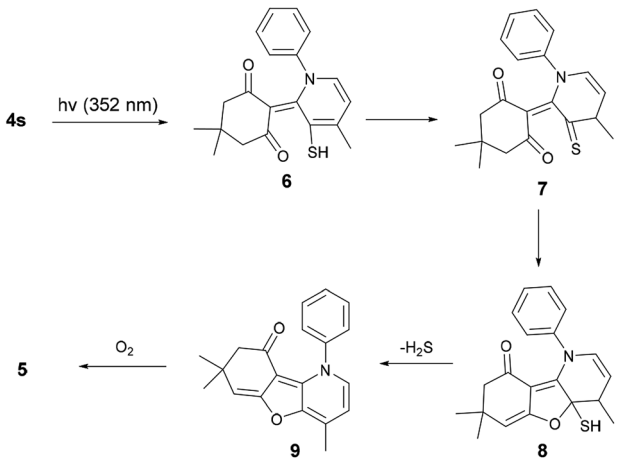


Fig. 6 ORTEP crystal structure of **4s** (left) and **5** (right).



Scheme 3 Proposed intermediates for the formation of **5** from **4s**.

undergoes enol–keto tautomerization to yield the thiolactone **7**. The keto–enol tautomerization of ketone **7** and the subsequent intramolecular cyclization furnish the hemithioketal **8**. The elimination of hydrogen sulfide from **8** yields benzofuropyridinone **9**. Final oxidative cleavage of the double bond of vinyl ether **9** affords the furopyridinone **5**. The fact that compound **4s** is light-sensitive and compound **4r** is not implies that the methyl substituent on the thiophene moiety of **4s** plays a crucial role in its photochemical properties.

3 Conclusions

In summary, we have demonstrated that *N*-aryl-β-enaminones **4a–s** can be efficiently synthesized *via* one-pot three-component reaction of 4-hydroxycoumarin/dimedone, β-nitrostyrene/2-(2-nitrovinyl)thiophene, and arylamine in the presence of trimethylamine as a base in toluene under refluxed conditions. Moreover, compounds **4g–j** were found to exhibit piezochromic properties, whereas compound **4s** was found to be sensitive to light and could be converted to the furo[3,2-*b*]pyridin-2(4*H*)-one upon UV irradiation. Further exploration of other functional properties such as photochromism *via* structural tuning of *N*-aryl-β-enaminones is currently underway and will be reported in due course.

4 Experimental

4.1 General

Melting points were determined on a Mel-Temp melting point apparatus in open capillaries and are uncorrected. Infrared (IR) spectra were recorded using 1725XFT-IR spectrophotometer. High-resolution mass spectra (HRMS) were obtained on a Thermo Fisher Scientific Finnigan MAT95XL spectrometer using magnetic sector analyzer. X-ray diffraction (XRD) spectra were recorded using PHILIPS X'PERT Pro MPD. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6500F. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 or 150 MHz) spectra were recorded on a Bruker 400 or Agilent Technologies DD2 600 spectrometer. Chemical shifts were reported in parts per million on the δ scale relative to an internal standard (tetramethylsilane, or appropriate solvent peaks) with coupling constants given in hertz. ^{1}H NMR multiplicity data are denoted by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60G-254 plates (25 mm) and developed with the solvents mentioned. Visualization was accomplished by using portable UV light, ninhydrin spray, or iodine chamber. Flash chromatography was performed in columns of various diameters with Merck silica gel (230–400 mesh ASTM 9385 kieselgel 60H) by elution with the solvent systems. Solvents, unless otherwise specified, were reagent grade and distilled once prior to use. All new compounds exhibited satisfactory spectroscopic and analytical data.

4.2 General procedure for the synthesis of β-nitrostyrene derivatives

To a solution of NH_4OAc (10.4 g, 135 mmol, 2.4 equiv.) and acetic acid (100 mL) was added nitromethane (23.8 g, 389 mmol, 6.9 equiv.) and appropriate aldehyde (56.4 mmol, 1 equiv.) at room temperature. The resulting mixture was then heated at 100 °C for 6 h. After cooled down to room temperature, the reaction mixture was poured into water (300 mL). The pH of the solution was adjusted to 7 with 2 M $NaOH_{(aq)}$ and the product was then extracted with EtOAc (5 × 150 mL). The organic layers were combined, washed with brine (1 × 150 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (EtOAc/hexanes) to obtain the title compound.

4.3 General procedure for the synthesis of 4

To a mixture of 4-hydroxycoumarin (1.00 mmol, 1 equiv.) in toluene (10 mL) was added β-nitrostyrene (1 equiv.), amine (1 equiv.), and Et_3N (1 equiv.) at room temperature. The resulting mixture was then refluxed for 1.5 h. The progress of the reaction was monitored by TLC. After cooled down to room temperature, the filtrate was concentrated *in vacuo*. The crude product was purified by column chromatography (EtOAc/hexanes) to give the desired compound **4**.

4.3.1 (*E*)-3-(Phenyl(phenylamino)methylene)chromane-2,4-dione (4a). R_f = 0.5 (15% EtOAc/hexanes); light yellow solid; yield 76%; mp 152–153 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.65 (s, 1H), 8.13 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 1H), 7.42–7.34 (m, 3H), 7.30–7.12 (m, 7H), 6.85 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.6, 173.2, 161.1, 154.4, 136.9, 134.4, 133.0, 129.8, 128.9, 128.4, 127.6, 127.1, 126.0, 125.0, 123.6, 120.2, 116.8, 97.8; IR ν (ATR) 3060, 1719, 1548, 1339, 1060, 759 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{15}NO_3$ [M^+] 341.1052 found 341.1050.

4.3.2 (*E*)-3-((4-Methoxyphenyl)(phenylamino)methylene) chromane-2,4-dione (4b). R_f = 0.5 (15% EtOAc/hexanes); yellow solid; yield 88%; mp 200–201 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.49 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.28–7.13 (m, 7H), 6.86 (d, J = 7.2 Hz, 4H), 3.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.4, 172.9, 161.3, 160.8, 154.3, 137.1, 134.3, 129.7, 129.0, 126.9, 126.0, 125.0, 124.8, 123.6, 120.3, 116.8, 114.0, 97.8, 55.2; IR ν (ATR) 3398, 2922, 1715, 1466, 1341, 1021, 754 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{17}NO_4$ [M^+] 371.1158 found 371.1153.

4.3.3 (*E*)-3-(((4-Methoxyphenyl)amino)(phenyl)methylene) chromane-2,4-dione (4c). R_f = 0.5 (15% EtOAc/hexanes); yellow solid; yield 83%; mp 184–185 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.59 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.40–7.34 (m, 3H), 7.29–7.20 (m, 4H), 6.77 (d, J = 8.8 Hz, 2H), 6.68 (d, J = 8.8 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.4, 172.9, 161.1, 158.2 (2C), 154.3, 134.3, 133.1, 129.6, 128.5, 127.5, 126.1, 126.0, 123.6, 120.3, 116.8, 114.1, 97.6, 55.3; IR ν (ATR) 3417, 2922, 1716, 1557, 1241, 831, 766 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{17}NO_4$ [M^+] 371.1158 found 371.1156.

4.3.4 (*E*)-3-((4-Methoxyphenyl)((4-methoxyphenyl)amino) methyl ene)chromane-2,4-dione (4d). R_f = 0.3 (15% EtOAc/hexanes); light orange solid; yield 86%; mp 159–160 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.43 (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 7.56 (td, J = 8.8, 1.6 Hz, 1H), 7.28–7.20 (m, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.71 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.2, 172.5, 161.4, 160.7, 158.1, 154.3, 134.1, 129.9, 129.6, 126.2, 126.0, 125.0, 123.6, 120.4, 116.7, 114.2, 114.0, 97.6, 55.3, 55.2; IR ν (ATR) 3419, 2970, 1715, 1462, 1235, 1029, 760 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{19}NO_5$ [M^+] 401.1263 found 401.1269.

4.3.5 (*E*)-3-((4-(Dimethylamino)phenyl)(phenylamino)methylene) chromane-2,4-dione (4e). R_f = 0.6 (25% EtOAc/hexanes); yellow solid; yield 77%; mp 222–223 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 14.84 (bs, 1H), 8.08 (dd, J = 7.6, 1.6 Hz, 1H), 7.56 (td, J = 7.6, 1.6 Hz, 1H), 7.27–7.20 (m, 4H), 7.15–7.11 (m, 1H), 7.12 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.58 (d, J = 8.0 Hz, 2H), 2.99 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 172.8, 154.1, 151.7 (2C), 137.1 (2C), 134.1, 132.1, 130.4, 126.4, 126.0, 123.6, 120.7, 119.9, 118.3, 116.7, 111.2, 97.8, 39.9; IR ν (ATR) 3401, 2897, 1715, 1604, 1340, 750 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{20}N_2O_3$ [M^+] 384.1474 found 384.1471.

4.3.6 (*E*)-3-(((4-(Dimethylamino)phenyl)amino)(phenyl) methylene) chromane-2,4-dione (4f). R_f = 0.6 (25% EtOAc/hexanes); orange solid; yield 69%; mp 190–191 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.64 (s, 1H), 8.11 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.41–7.36 (m, 3H), 7.27–7.19 (m, 4H), 6.67 (d, J = 9.2 Hz, 2H), 6.44 (d, J = 9.2 Hz, 2H), 2.89 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.0, 171.2, 161.3, 154.3, 149.0, 133.9, 133.6, 129.5, 128.5, 127.5, 125.9, 125.6, 125.4, 123.5, 120.4, 116.8, 111.8, 97.3, 40.2; IR ν (ATR) 3412, 2921, 1719, 1605, 1346, 958, 756 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{20}N_2O_3$ [M^+] 384.1474 found 384.1475.

4.3.7 (*E*)-3-((4-(Dimethylamino)phenyl)((4-(dimethyl amino) phenyl) amino)-methylene)chromane-2,4-dione (4g). R_f = 0.3 (25% EtOAc/hexanes); yellow solid; yield 68%; mp 251–252 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 14.84 (bs, 1H), 8.08 (dd, J = 7.6, 1.6 Hz, 1H), 7.53 (td, J = 7.6, 1.6 Hz, 1H), 7.25–7.20 (m, 2H), 7.14 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 9.2 Hz, 2H), 6.62 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 9.2 Hz, 2H), 3.00 (s, 6H), 2.91 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 181.1, 171.2, 162.5, 154.1, 151.3, 148.6, 133.5, 130.1, 126.7, 125.9, 125.4, 123.3, 121.0, 119.6, 116.6, 112.0, 111.3, 97.2, 40.3, 40.0; IR ν (ATR) 3420, 2888, 2810, 1608, 1337, 816 cm^{-1}; HRMS (EI) m/z calcd for $C_{26}H_{25}N_3O_3$ [M^+] 427.1896 found 427.1892.

4.3.8 (*E*)-3-((4-(Dimethylamino)phenyl)((4-methoxyphenyl) amino)-methylene)chromane-2,4-dione (4h). R_f = 0.4 (25% EtOAc/hexanes); yellow solid; yield 80%; mp 229–230 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 14.81 (bs, 1H), 8.08 (d, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 1H), 7.26–7.20 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 3.76 (s, 3H), 3.00 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 181.1, 172.5, 162.5, 157.8, 154.1, 151.4, 133.8, 130.7, 130.3, 126.0, 126.0, 123.4, 120.8, 119.0, 116.6, 114.1, 111.1, 97.3, 55.3, 39.9; IR ν (ATR) 3417, 2970, 1737, 1530, 1353, 1217, 829, 774 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{22}N_2O_4$ [M^+] 414.1580 found 414.1583.

4.3.9 (*E*)-3-(((4-Bromophenyl)amino)(4-(dimethylamino) phenyl)-methylene)chromane-2,4-dione (4i). R_f = 0.5 (25% EtOAc/hexanes); yellow solid; yield 82%; mp 258–259 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.19 (bs, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.56 (td, J = 7.6, 1.2 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.27–7.25 (m, 2H), 7.10 (d, J = 8.4 Hz, 2H), 6.75 (d, J = 8.4 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.01 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.4, 172.8, 161.3, 154.1, 151.6, 137.9, 133.9, 130.4, 128.9, 126.4, 126.0, 124.9, 123.4, 120.8, 118.8, 116.7, 111.1, 97.5, 39.9; IR ν (ATR) 3422, 2970, 1727, 1530, 1338, 1065, 812, 753 cm^{-1}; HRMS (EI) m/z calcd for $C_{24}H_{19}BrN_2O_3$ [M^+] 462.0579 found 462.0580.

4.3.10 (*E*)-4-(((4-(Dimethylamino)phenyl)(2,4-dioxochroman-3-ylid ene)-methyl)amino)benzonitrile (4j). R_f = 0.5 (25% EtOAc/hexanes); orange solid; yield 69%; mp 252–253 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 14.92 (bs, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.58 (td, J = 7.6, 1.6 Hz, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.28–7.22 (m, 2H), 7.11

(d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.8 Hz, 2H), 3.03 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.4, 172.5, 161.3, 154.1, 152.0, 142.3, 134.4, 132.9, 130.6, 126.1, 125.1, 123.7, 120.4, 118.1, 117.8, 116.7, 111.1, 109.4, 98.3, 39.9; IR ν (ATR) 3390, 2970, 1717, 1426, 1366, 1197, 770 cm^{-1}; HRMS (EI) m/z calcd for $C_{25}H_{19}N_3O_3$ [M$^+$] 409.1426 found 409.1423.

4.3.11 (*E*)-3-((4-Bromophenyl)(phenylamino)methylene) chromane 2,4-dione (4k). R_f = 0.4 (15% EtOAc/hexanes); yellow solid; yield 72%; mp 192–193 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.65 (s, 1H), 8.12 (d, J = 7.6 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.28 (t, J = 7.6 Hz, 1H), 7.24–7.18 (m, 4H), 7.12 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.6, 172.1, 161.1, 154.3, 136.5, 134.6, 131.8, 129.3, 129.1, 127.4, 126.0, 125.4, 125.1, 124.2, 123.7, 120.1, 116.9, 97.7; IR ν (ATR) 3407, 3102, 1709, 1538, 1339, 758 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{14}BrNO_3$ [M$^+$] 419.0157 found 419.0159.

4.3.12 (*E*)-3-((4-Nitrophenyl)(phenylamino)methylene) chromane-2,4-dione (4l). R_f = 0.4 (15% EtOAc/hexanes); orange solid; yield 54%; mp 227–228 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.75 (s, 1H), 8.21 (d, J = 8.4 Hz, 2H), 8.14 (d, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.43–7.38 (m, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.24–7.21 (m, 4H), 6.88 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 182.9, 171.2, 161.2, 154.4, 148.1, 139.6, 136.1, 135.0, 129.4, 128.8, 127.9, 126.2, 125.4, 124.0, 123.7, 120.0, 117.0, 97.7; IR ν (ATR) 3084, 1703, 1464, 1340, 767, 718 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{14}N_2O_5$ [M$^+$] 386.0903 found 386.0899.

4.3.13 (*E*)-7-Methoxy-3-(phenyl(phenylamino)methylene) chromane-2,4-dione (4m). R_f = 0.5 (15% EtOAc/hexanes); light yellow solid; yield 85%; mp 205–206 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.65 (s, 1H), 8.03 (d, J = 8.8 Hz, 1H), 7.39–7.33 (m, 3H), 7.26–7.23 (m, 2H), 7.16–7.12 (m, 3H), 6.83 (d, J = 8.0 Hz, 3H), 6.66 (d, J = 1.6 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 182.1, 172.9, 164.8, 161.3, 156.1, 137.0, 133.1, 129.6, 128.8, 128.4, 127.6, 127.5, 126.9, 125.0, 113.6, 112.0, 100.1, 96.9, 55.7; IR ν (ATR) 3065, 1719, 1532, 1333, 1104, 763, 704 cm^{-1}; HRMS (EI) m/z calcd for $C_{23}H_{17}NO_4$ [M$^+$] 371.1158 found 371.1159.

4.3.14 (*E*)-6-Chloro-3-(phenyl(phenylamino)methylene) chromane-2,4-dione (4n). R_f = 0.5 (15% EtOAc/hexanes); light yellow solid; yield 52%; mp 188–189 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 15.55 (s, 1H), 8.08 (s, 1H), 7.51 (d, J = 8.4 Hz, 1H), 7.40–7.34 (m, 3H), 7.26–7.15 (m, 6H), 6.85 (d, J = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 181.3, 173.5, 160.6, 152.7, 136.6, 134.3, 132.7, 129.9, 129.2, 129.0, 128.5, 127.5, 127.3, 125.6, 125.1, 121.3, 118.5, 97.6; IR ν (ATR) 3418, 3072, 1959, 1719, 1543, 1334, 988 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{14}ClNO_3$ [M$^+$] 375.0662 found 375.0667.

4.3.15 (*E*)-3-(((4-methoxyphenyl)amino)(thiophen-2-yl) methylene)chromane-2,4-dio-ne (4o). R_f = 0.50 (30% EtOAc/hexanes); yellow solid; yield 65%; mp 166–168 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.08 (bs, 1H), 8.08 (dd, J = 7.6, 1.6 Hz, 1H), 7.57 (td, J = 7.2, 1.6 Hz, 1H), 7.50 (dd, J = 4.0, 2.0 Hz, 1H), 7.28–7.24 (m, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.00–6.99 (m, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 166.1, 161.8, 158.6, 154.2, 134.4, 132.8, 129.97, 129.89, 129.5, 127.3, 126.2, 126.1, 123.8, 120.5, 116.8, 114.3, 98.7, 55.4; IR ν_{max} (KBr) 3454, 2929, 1714, 1608, 1546, 1365, 1228, 1032, 1653, 727 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{15}NO_4S$ [M$^+$] 377.0722, found 377.0725.

4.3.16 ((*E*)-3-(((4-methoxyphenyl)amino)(3-methylthiophen-2-yl) methylene)chromane-2,4-dione (4p). R_f = 0.40 (30% EtOAc/hexanes); yellow solid; yield 62%; mp 170–172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.60 (bs, 1H), 8.10 (bd, J = 8.4 Hz, 1H), 7.57 (td, J = 8.4, 1.6 Hz, 1H), 7.39 (d, J = 4.8 Hz, 1H), 7.28–7.20 (m, 2H), 6.88 (d, J = 9.2 Hz, 2H), 6.80 (d, J = 4.8 Hz, 1H), 6.75 (d, J = 9.2 Hz, 2H), 3.77 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 166.0, 160.4, 158.5, 154.2, 137.6, 134.4, 130.0, 127.95, 127.79, 126.2, 125.6, 125.3, 120.3, 116.8, 114.3, 114.0, 99.0, 55.4, 14.6; IR ν_{max} (KBr) 3067, 2968, 1711, 1608, 1558, 1463, 1339, 1247, 1028, 882 cm^{-1}; HRMS (EI) m/z calcd for $C_{22}H_{17}NO_4S$ [M$^+$] 391.0878, found 391.0874.

4.3.17 5,5-Dimethyl-2-(phenyl(phenylamino)methylene) cyclohexane-1,3-dione (4q). R_f = 0.55 (30% EtOAc/hexanes); pale yellow solid; yield 56%; mp 146–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.70 (bs, 1H), 7.34–7.27 (m, 3H), 7.14–7.05 (m, 5H), 6.76 (d, J = 7.6 Hz, 2H), 2.57 (s, 2H), 2.33 (s, 2H), 1.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 195.3, 169.2, 137.2, 134.0, 129.0, 128.8, 128.3, 127.7, 126.4, 125.1, 108.5, 53.3, 52.5, 30.3, 28.5; IR ν_{max} (KBr) 2953, 1716, 1661, 1535, 1434, 1335, 1219, 1210, 983, 776 cm^{-1}; HRMS (EI) m/z calcd for $C_{21}H_{21}NO_2$ [M$^+$] 319.1572, found 319.1577.

4.3.18 2-(((4-Methoxyphenyl)amino)(thiophen-2-yl)methylene)-5,5 -dimethylcyclohexane-1,3-dione (4r). R_f = 0.40 (30% EtOAc/hexanes); brown solid; yield 55%; mp 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.40 (bs, 1H), 7.41 (dd, J = 5.2, 1.2 Hz, 1H), 6.93 (dd, J = 3.6, 1.2 Hz, 1H), 6.84–6.82 (m, 1H), 6.82 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 2.47 (s, 4H), 1.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4 (2C), 162.1, 158.1, 134.3, 130.2, 129.2, 128.4, 127.0, 126.1, 114.1, 109.7, 55.4, 52.8, 30.4, 28.5; IR ν_{max} (KBr) 3078, 2836, 1652, 1578, 1547, 1407, 1247, 1031, 895, 825 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{21}NO_3S$ [M$^+$] 355.1242, found 355.1237.

4.3.19 5,5-Dimethyl-2-((3-methylthiophen-2-yl)(phenylamino) methylene)cyclohexane-1,3-dione (4s). R_f = 0.30 (30% EtOAc/hexanes); light yellow solid; yield 52%; mp 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.62 (bs, 1H), 7.31 (d, J = 4.8 Hz, 1H), 7.22 (t, J = 7.2 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.74 (d, J = 4.8 Hz, 1H), 2.61, 2.56 (ABq, J = 17.2 Hz, 1H each), 2.46, 2.35 (ABq, J = 16.4 Hz, 1H each), 1.97 (s, 3H), 1.15 (s, 3H), 1.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 194.9, 161.8, 137.4, 136.9, 129.8, 129.0, 128.9, 127.0, 126.6, 124.2, 110.0, 53.3, 52.4, 30.2, 28.6, 28.3, 14.5; IR ν_{max} (KBr) 2956, 2872, 1735, 1652, 1561, 1333, 1128, 982, 763 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{21}NO_2S$ [M$^+$] 339.1293, found 339.1290.

4.4 Photoirradiation of *N*-aryl-β-enaminone 4s

The solution of compound **4s** (50 mg) in acetonitrile (1000 mL) was irradiated under aerobic conditions using a photochemical reactor (PR-2000, 352 nm × 10 lamps) for 30 min. The solution was then concentrated *in vacuo* and the crude product was purified by column chromatography (40% EtOAc/hexanes) to obtain the brown solid furopyridinone **5**.

4.4.1 2,2-Dimethyl-4-(7-methyl-2-oxo-4-phenyl-2,4-dihydrofuro[3,2-b]pyridin-3-yl)-4-oxobutanal (5). $R_f = 0.20$ (50% EtOAc/hexanes); 28 mg; yield 56%; mp charred @ 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.49–7.47 (m, 3H), 7.36 (d, $J = 7.2$ Hz, 1H), 7.28–7.26 (m, 2H), 6.74 (d, $J = 7.2$ Hz, 1H), 3.20 (s, 2H), 2.46 (s, 3H), 0.98 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.1, 190.8, 167.8, 145.2, 143.9, 143.0, 133.2, 129.5, 129.3, 125.5, 123.8, 116.2, 90.6, 49.5, 44.2, 22.1, 15.0; IR ν_{max} (KBr) 2923, 2853, 1738, 1720, 1365, 1217, 1092, 757 cm^{-1}; HRMS (EI) m/z calcd for $C_{20}H_{19}NO_4$ [M^+] 337.1314, found 337.1309.

Conflicts of interest

There are no conflicts to declare.

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12 Crystallographic data (excluding structure factors) for **4g**, **4j**, **4s**, and **5** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-1913301, 1913302, 1953598, and 1953599 respectively.

