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Oxidant and Transition-Metal-Free Photoinduced Direct Oxidative Annulation of 1-Aryl-2-(furan/thiophe-2-yl)butane-1,3-diones

Jin Zhang,[‡] Xi Zhang,[‡] Tao Wang, Xinbo Yao, Pei Wang, Ping Wang, Sisi Jing, Yong Liang,[†] Zunting Zhang*

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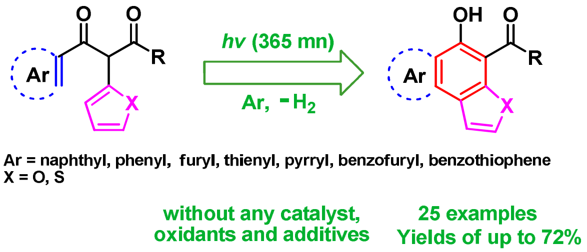
ABSTRACT: A photoinduced direct oxidative annulation of 1-aryl-2-(furan/thiophe-2-yl)butane-1,3-diones and ethyl-2-(furan-2-yl)-3-oxo-3-(aryl-2-yl)propanoates in EtOH without the needs of any transition-metals and oxidants provided access to highly functionalized polyheterocyclic 1-(5-hydroxynaphtho[2,1-*b*]furan-4-yl)ethanones and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-*e*]benzofuran-4-yl)ethanones. The phenomenon of excited-state intramolecular proton transfer (ESIPT) was observed for both 1-(5-hydroxynaphtho[2,1-*b*]furan-4-yl)ethanone and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-*e*]benzofuran-4-yl)ethanone analogues.

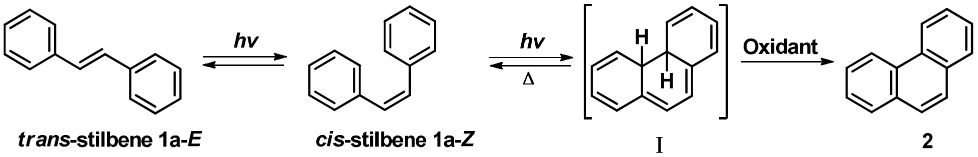
TOC graphic



INTRODUCTION:

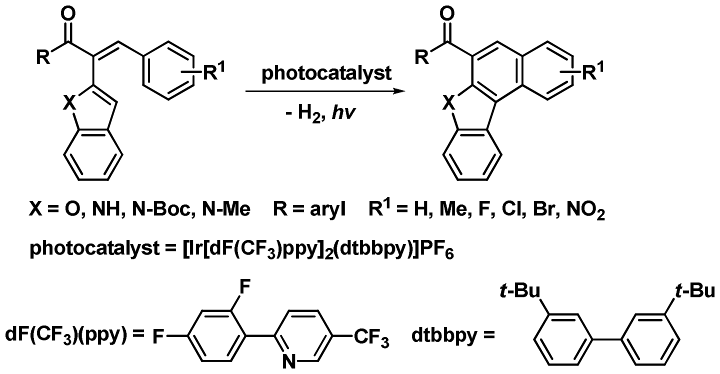
UV irradiation of stilbenes *via* an initial equilibration to a photostationary mixture of *trans*-stilbene (**1a**-*E*) and *cis*-stilbene (**1a**-*Z*) isomers generates an unstable intermediate dihydrophenanthrene **I** by ring closure of *Z*-isomer (Scheme 1). In the presence of an oxidant such as O_2, I_2, $I_2/CuCl_2$ or TCNE,[1-4] the intermediate **I** is converted into phenanthrene **2** by the elimination of two hydrogen atoms. It is the most commonly used method for the synthesis of phenanthrene analogues and related heterocyclic compounds.[5-10]

Scheme 1. Photocyclization of Stilbenes



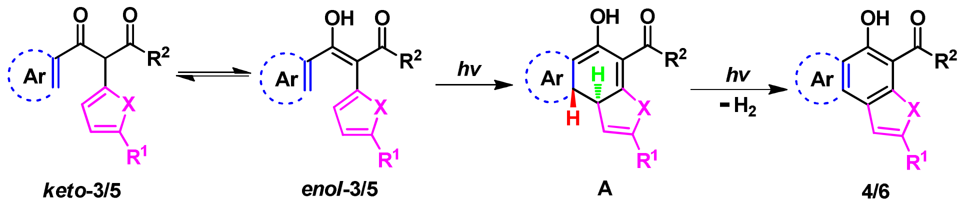
At present, literature reports on the intermolecular photocyclization *via* elimination of hydrogen is very seldom. In 2014, Reiser et al. reported an Ir-catalyzed light-induced dehydrogenation reaction for the synthesis of naphtho[2,1-*b*]furans from vinyl radicals, which were generated from *α*-bromochalcones and heteroarenes (Scheme 2).[11] Most of the photoinduced dehydrogenative reactions need oxidants or transition metals. Our group previously demonstrated, the photoinduced intramolecular dehydrogenative annulation of 2,3-di(hetero)arylchromen-4-one for the synthesis of *13H*-benzo[*c*]furo[2,3-*a*]xanthen-13-ones without any requirements for transition-metals and oxidants.[12]

Scheme 2. Intramolecular Dehydrogenation under Photocatalysis



Following our interest in the synthesis of various heteroaromatics *via* photochemical reactions,[13-16] Herein, we report the photocyclization of 1-aryl-2-(furan/thiophe-2-yl)butane-1,3-diones (**3**) and ethyl-2-(furan-2-yl)-3-oxo-3-(aryl-2-yl)propanoates (**5**) to highly functionalized heteroaromatics **4** or **6** by elimination of a hydrogen molecule from a cyclic intermediate **A**, formed by keto-enol tautomerism of **3** or **5** (Scheme 3). Our mild and bench friendly protocols which do not require any catalysts and oxidants gave access to fluorescent heteroaromatic of type **4** and **6**.

Scheme 3. Photochemical Syntheses of 4 and 6

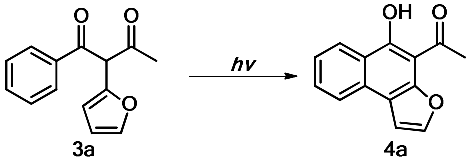


3, 4: Ar = phenyl, naphthyl X = O, S R^1 = H, Me R^2 = Me, OEt
5, 6: Ar = furan, thiophene, pyrrole

RESULTS and DISCUSSION

Irradiation of 2-(furan-2-yl)-1-phenylbutane-1,3-dione [17] (**3a**, 1 mmol) with a high-pressure mercury lamp (500 W) at ambient temperature in MeCN (100 mL) for 8 h gave **4a** in 25% yield (Table 1, entry 1). The yields of **4a** were higher (38%-56%, entries 2-5) in polar protic solvents, e.g. ethanol, methanol or butanol comparing to benzene and hexane (14%-24%, entries 6-7). Interestingly, no significant difference was observed for the yields of **4a** (44%-52%) in either dry EtOH (calcium hydride) or "wet" EtOH (6.7 mL and 5.0 mL of water) (entries 9-11). Irradiation of **3a** in EtOH in the presence of acid (3 M HCl, pH = 4) or base (3 M NaOH, pH = 8) also gave **4a** in comparable yields (56-59%, entries 12-13). Similar yield (55%) was observed with a reduced concentration of **3a** (5×10^{-3} mol/L, entry 8). Finally, the addition of an oxidant (1eq. H_2O_2) drops the yield of **4a** to 35 % (entries 14). Since no improved result from latter part of the optimization, ethanol was finally chosen as the solvent for all further reactions (56%, Table 1, entry 2).

Table 1. Optimization of the Intramolecular Oxidative Annulation of 3a[a]



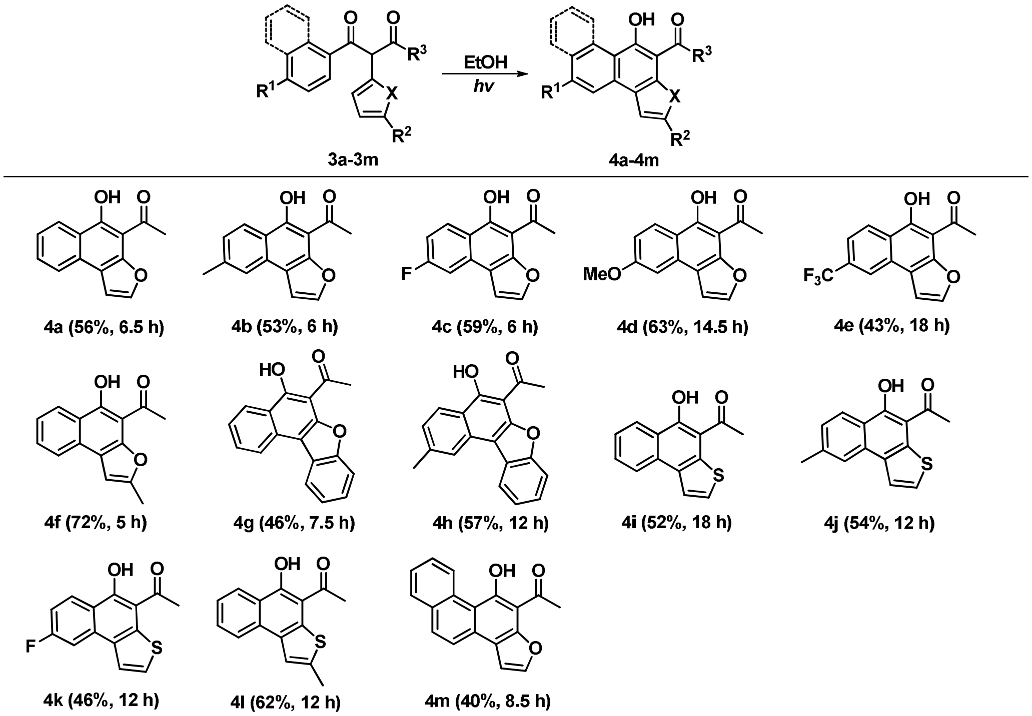
Entry	Solvent	Time(h)	Yield[b]
1	CH_3CN	8	25
2	EtOH	6.5	56
3	MeOH	7.5	40
4	*n*-BuOH	6	38
5	*t*-BuOH	12.5	52
6	PhH	11.5	18
7	Hexane	11.5	14

8[c]	EtOH	6	55
9[d]	EtOH	8.5	52
10	EtOH:H_2O = 2:1	6	44
11	EtOH:H_2O = 3:1	6.5	47
12	EtOH (pH = 4)	7.5	59
13	EtOH (pH = 8)	6.5	56
14	EtOH+1equiv H_2O_2	7.5	35

[a] Compound **3a** (0.2 mmol) was dissolved in various solvents (20 mL) and irradiated with a high-pressure mercury lamp (500 W) under an argon atmosphere at ambient temperature until **3a** was completely consumed as indicated by thin-layer chromatography (TLC). [b] Yields of the isolated product were based on **3a**. [c] c (**3a**) = 5 x10^{-3} mol/L, 40 mL EtOH. [d] EtOH was dried by CaH_2.

With the optimized condition in hand, a large array of naphtho[2,1-*b*]furans (**4a**-**4h**, **4m**) and naphtho[2,1-*b*]thiophenes (**4i**-**4l**) have been synthesized and listed in Table 2. Generally, starting substrates **3** bearing an electron-donating substituent (–Me) on furan or thiophene ring gave the corresponding products **4f** or **4l** in higher yields compared to those without a substituent (**4a**-**4e**, **4i**-**4k,** and **4m**). For example, product **4f** was obtained in 72%, while **4a** was obtained only in 56% yield. On the other hand, the presence of electron-withdrawing substituents (–F or –CF_3) on the benzene ring of **3** gave corresponding products **4** in lower yields. Introduction of the benzofuran or thiophene ring to substrates **3** led to the formation of rearrangement products **4** in a longer time than the substrates with a furan ring (**4g**-**4h** and **4i**-**4l** *vs* **4a**-**4c**).

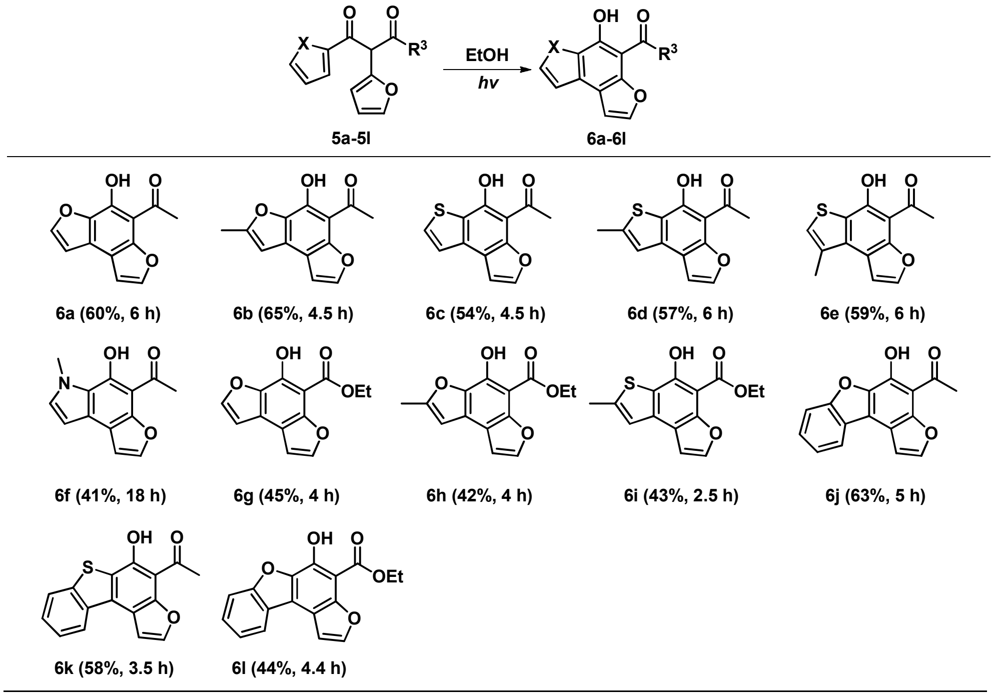
Table 2. Synthesis of Naphtho[2,1-*b*]furans/thiophenes (4a-4m) [a]



[a] All reactions were carried out on 1 mmol of **3** in 100 mL of EtOH and irradiated with a high-pressure mercury lamp (500 W) under an argon atmosphere at ambient temperature until **3** was completely consumed. Isolated yield was calculated based on **3**.

The synthesis of furan/thieno/pyrrolo[3,2-*e*]benzofurans were also explored under similar conditions as depicted in Table 3. Generally, substrates **5** bearing furan (Y = O, **5a**-**5c**, **5g**-**5h** and **5l**) and thiophene (Y = S, **5c**-**5e**, **5i** and **5k**) gave the corresponding cyclization products **6** in higher yields (**6a**-**6e**, **6g**-**6l**) than the pyrrole derivative (**6f**, Y = NMe). For example, ring closure product **6a**, which contains two furan moieties, was obtained in 60% yield, while the pyrrole-containing product **6f** was obtained in only 41% yield. The presence of methyl group on the heterocyclic ring of **5** led to the formation of ring closure products in higher yields (**6b**, **6d**, **6h**-**6i**). In addition, the difference of substituents R^3 also affected the yields of compounds **6a**-**6l**. Ring closure product **6b** (R^3 = Me, 65 %) was obtained in higher yield than **6h** (R^3 = OEt, 49%). It is worth noting that when the furan/thiophene ring on the 2-position of **3a**/**3l** was instead by benzene ring (1,2-diphenylbutane-1,3-dione), the corresponding intramolecular dehydrogenative target product was not obtained.

Table 3. Synthesis of Furan/Thieno/Pyrrolo[3,2-*e*]benzofurans (6a-6l) [a]



5a-5l
6a-6l

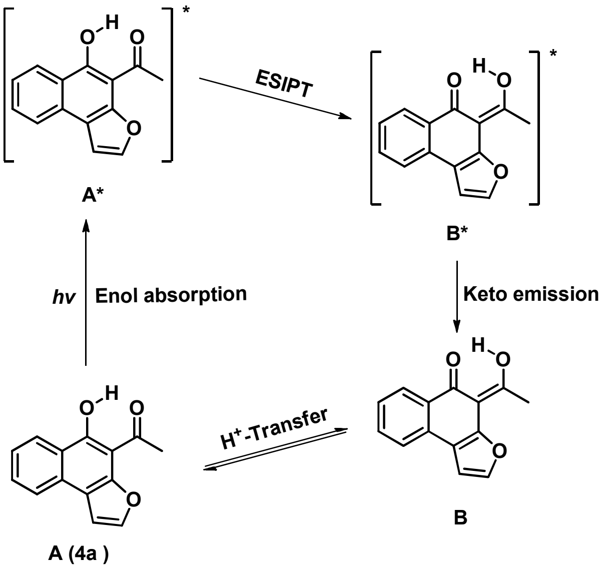
6a (60%, 6 h)
6b (65%, 4.5 h)
6c (54%, 4.5 h)
6d (57%, 6 h)
6e (59%, 6 h)
6f (41%, 18 h)
6g (45%, 4 h)
6h (42%, 4 h)
6i (43%, 2.5 h)
6j (63%, 5 h)
6k (58%, 3.5 h)
6l (44%, 4.4 h)

[a] All reactions were carried out on 1 mmol of **5** in 100 mL of EtOH and irradiated with a high-pressure mercury lamp (500 W) under an argon atmosphere at ambient temperature until **5** was completely. Isolated yield was calculated based on **5**.

The fluorescence spectrum of **4** and **6** were performed in EtOH. The excitation and emission spectra of selected compounds showed yellow-green fluorescence (**4a**-**4h**, **4m**, **6a**-**6f** and **6j**-**6k**, $\lambda_{\text{Ex max}}$ = 365-411 nm; $\lambda_{\text{Em max}}$ = 502-541 nm, see SI-Table 1), and blue-purple fluorescence (**6g**-**6h**, **6i** and **6l**, $\lambda_{\text{Ex max}}$ = 323-371 nm; $\lambda_{\text{Em max}}$ = 396-429 nm, see SI-Table 1). Notably, 1-(5-hydroxynaphtho[2,1-*b*]furan-4-yl)ethanones (**4a**-**4h**, **4m**) and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-*e*]benzofuran-4-yl)ethanones (**6a**-**6f** and **6j**-**6k**) showed the phenomenon of excited-state intramolecular proton transfer (ESIPT), and the Stokes' shift of them were in the range of 112-147 nm.

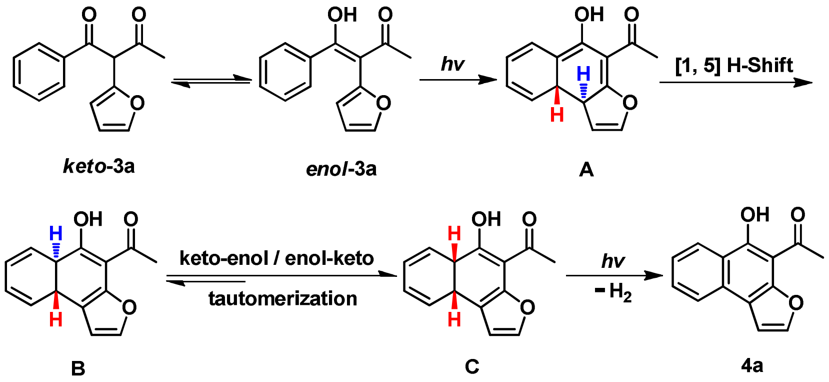
ESIPT molecules always have a six-membered ring structure *via* intramolecular H-bonds between C=O (or =N⁻) and O-H (or N-H) groups on the conjugated system, and the ESIPT phenomenon possesses two remarkable characteristics: relatively large Stokes shifts (>100 nm) and ketone-enol tautomerism.[18-20] The ESIPT phenomenon of **4** and **6** can be attributed to an intramolecular hydrogen bond formed between the acetyl and hydroxyl in 1-(5-hydroxynaphtho[2,1-*b*]furan-4-yl)ethanone (**4a**) (Scheme 4). The enol form of **A** could get to an excited state **A*** upon the UV irradiation, followed by the quick conversation to a more stable keto form **B*** by ESIPT. With the release of energy, transition state **B*** emits fluorescence from the excited state to the ground state B. In this series of processes, **4a** has a good Stokes' shift.

Scheme 4. Intramolecular Dehydrogenation under Photocatalysis



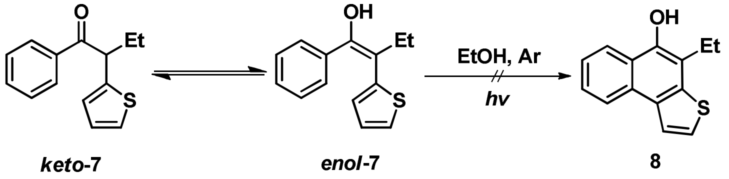
A plausible mechanism for the photocyclization of **4** and **6** has been proposed and presented in Scheme 5. First of all, compound **3** undergoes an initial equilibration to a photostationary mixture of *keto*-**3** and *enol*-**3** isomers, followed by a photochemically allowed ring closure of the *enol*-**3** to give an unstable intermediate **A**. Then, a thermal suprafacial [1,5]-H shift gives the intermediate **B**. The driving force of this [1,5]-sigmatropic shift can be attributed to the reformation of the aromatic furan ring, which stabilizes the system in terms of thermodynamics.[16, 21] The keto-enol/enol-keto tautomerization of **B** give a *syn*-intermediate **C**.[22] This relevant transformation has been reported in a number of publications.[23, 24] Finally, the *syn*-intermediate **C** yields annulation product **4** by the elimination of a hydrogen molecule. To our delight, the formation of by-product hydrogen has been successfully detected by Gas Chromatography and the corresponding experiments were recorded in supporting information (SI-Figure S4). Interestingly, the dehydrogenative annulation product **4** was still obtained in yield 35% with the presence of an oxidant (H_2O_2), and the intramolecular photoinduced dehydrogenative cyclization was believed to proceed through the S1 state.

Scheme 5. Proposed Mechanisms for Photocyclization Reaction



In order to validate the rationality of the proposed mechanism, substrate **7** [25] was subjected to the optimal photocyclization condition (Scheme 6). However, neither dehydrogenation product **8** nor byproduct (H_2) was detected, which could be explained by the lacking of keto-enol tautomerization. It was further indicated that the keto-enol/enol-keto tautomerization of the intermediate is crucial for the formation of heteroaromatics **4/6** *via* the intramolecular dehydrogenative cyclization.

Scheme 6. Attempted Photocyclization of 1-Phenyl-2-(thiophen-2-yl)ethanones (7)



CONCLUSION

We have developed an efficient protocol for the synthesis of naphtha[2,1-*b*]heterozryl and heterozryl[3,2-*e*]benzofuran by an intramolecular dehydrogenative photocyclization in EtOH. This photo-induced direct oxidative annulation of 1-aryl-2-(furan/thiophe-2-yl) butane-1,3-diones and ethyl-2-(furan-2-yl)-3-oxo-3-(aryl-2-yl)propanoates does not require the usage of transition metal-catalysts and oxidants. The phenomenon of ESIPT with a more than 110 nm Stokes' shift for both 1-(5-hydroxynaphtho[2,1-*b*]furan-4-yl)ethanones and 1-(5-hydroxyfuran/thieno/pyrrolo[3,2-*e*]benzofuran-4-yl)ethanones has been observed.

EXPERIMENTAL PROCEDURES AND ANALYTICAL DATA

General Information. All solvents and reagents were obtained from commercial sources and used without further purification. Thin-layer chromatography was performed on precoated silica gel 60 GF254 plates. Silica gel (200−300 mesh) was used for column chromatography. ^{1}H NMR spectra were recorded on 300, 400 or 600 MHz spectrometers. Spectra were referenced internally to the residual proton resonance in $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (2.50 ppm). ^{13}C NMR spectra were recorded on 75, 100 or 150 MHz spectrometers and the spectra were referenced to $CDCl_3$ or DMSO-d_6 (δ 77.16 ppm or 39.52 ppm, the middle peak). Coupling constants (J) were reported in hertz (Hz). High-resolution mass spectrometry (HRMS) was performed using electron-spray ionization quadrupole-time of flight (ESI-Q-TOF) techniques. Melting points were measured with a X-5 micro-melting point apparatus and are uncorrected. IR spectra were recorded with a Nicolet 170SX FT-IR spectrophotometer on KBr pellets.

General Procedures for Syntheses of Naphtho[2,1-*b*]furans/thiophenes (4a-4m) and Furan/Thieno/Pyrrolo[3,2-*e*]benzofuran (6a-6l).

2-(Furan-2-yl)-1-phenylbutane-1,3-diones **3a** (1 mmol) were added to an EtOH solution (100 mL), and the mixture was contained in 100 mL quartz tubes, deaerated by bubbling Ar for 30 min and irradiated with a high-pressure mercury lamp (500 W), which was cooled to about 20 °C with tap water by means of an internal cold finger. The progress of the reaction was monitored by TLC at regular intervals until **3a** had disappeared completely. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (50:1→20:1) or chloroform-methanol (100:0.5→50:1) to give the corresponding product **4a**. Similarly, compounds **4b-4m** and **6a-6l** were prepared with the same method as described above with yields 41~72%.

*1-(5-Hydroxy-naphtho[2,1-b]furan-4-yl)-ethanone (**4a**).* Yield: 56%, 144 mg; Yellow solid; m.p. 134.5-136.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.61 (s, 1H), 8.47 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.69 (m, 2H), 7.49 (m, 1H), 7.14 (d, J = 1.3 Hz, 1H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.7, 162.7, 149.6, 142.6, 130.9, 130.8, 125.8, 124.8, 123.1, 123.0, 114.8, 105.6, 104.7, 31.5. IR (KBr) v (cm^{-1}) 3140, 2920, 1610, 1574, 1372, 1302, 1255, 1139, 1104, 1024, 982, 867, 768, 728, 694, 599, 557. HRMS (ESI): m/z $[M + H]^+$ calculated for $C_{14}H_{11}O_3$: 227.0708; found 227.0715.

*1-(5-Hydroxy-8-methyl-naphtho[2,1-b]furan-4-yl)-ethanone (**4b**).* Yield: 53%, 128 mg; Yellow solid; m.p. 125.4-126.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.62 (s, 1H), 8.33 (d, J = 8.5 Hz, 1H), 7.70 (s, 1H), 7.65 (d, J = 2.1 Hz, 1H), 7.30 (dd, J = 8.5, 2.1 Hz, 1H), 7.09 (d, J = 2.1 Hz, 1H), 2.90 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.4, 162.9, 149.8, 142.4, 141.5, 131.2, 126.7, 125.6, 122.7, 120.9, 114.3, 105.5, 104.2, 31.3, 22.2. IR (KBr) v (cm^{-1}) 3738, 2995, 1608, 1467, 1415, 1364, 1306, 1249, 1129, 1026, 986, 858, 813, 731, 694, 615. HRMS (ESI): m/z $[M + Na]^+$ calculated for $C_{15}H_{12}O_3Na$: 263.0684; found 263.0688.

*1-(8-Fluoro-5-hydroxy-naphtho[2,1-b]furan-4-yl)-ethanone (**4c**).* Yield: 59%, 146 mg; Yellow solid; m.p. 141.2-143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.64 (s, 1H), 8.44 (m, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.50 (m, 1H), 7.19 (m, 1H), 7.04 (d, J = 2.1 Hz, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.5, 164.3(^{1}J = 253 Hz), 162.6, 150.2, 142.7, 132.6(^{3}J = 10 Hz), 128.9(^{3}J = 10 Hz), 119.7, 114.3(^{2}J = 25 Hz), 114.4, 107.8(d, ^{2}J = 23 Hz), 105.6, 104.2, 31.4. IR (KBr) v (cm^{-1}) 3161, 3016, 1928, 1757, 1609, 1516, 1428, 1362, 1296, 1252, 1185, 1138, 1098, 1018, 953, 811, 696, 606. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{14}H_{10}FO_3$: 245.0614; found 245.0619.

1-(5-Hydroxy-8-methoxynaphtho[2,1-b]furan-4-yl)ethanone (***4d***)*.* Yield: 63%, 163 mg; Yellow solid; m.p. 181.8-184.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.73 (s, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 7.69 (s, 1H), 7.27 (s, 1H), 7.11 (m, 2H), 4.00 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.1, 163.2, 162.1, 150.4, 142.4, 133.2, 127.9, 117.4, 115.9, 114.2, 105.6, 103.6, 103.4, 55.7, 31.3. IR (KBr) *v* (cm^{-1}) 3146, 3111, 2928, 2031, 1907, 1739, 1612, 1435, 1384, 1309, 1214, 1149, 1086, 1018, 851, 748, 702, 603, 534. HRMS (ESI): *m/z* [M + H]$^+$ calculated for $C_{15}H_{13}O_4$: 257.0814; found 257.0814.

1-(5-Hydroxy-8-(trifluoromethyl)naphtho[2,1-b]furan-4-yl)ethanone (***4e***)*.* Yield: 43%, 131 mg; Yellow solid; m.p. 125.9-128.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.53 (s, 1H), 8.61 (d, *J* = 8.7 Hz, 1H), 8.24 (s, 1H), 7.76 (d, *J* = 2.1 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.21 (d, J = 2.1 Hz, 1H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.0, 161.8, 150.2, 143.4, 132.2 (J^2 = 32.3 Hz), 127.0, 124.8, 124.5 (J^1 = 270.9 Hz), 120.7 (J^3 = 4.2 Hz), 120.6 (J^3 = 3.4 Hz), 115.3, 105.8, 105.6, 31.7. IR (KBr) ν (cm^{-1}) 3146, 2923, 1951, 1704, 1616, 1519, 1480, 1418, 1289, 1154, 1108, 1061, 1025, 989, 938, 885, 833, 746, 704, 593. HRMS (ESI): m/z [M + H]$^+$ calculated for $C_{15}H_{10}F_3O_3$: 295.0582; found 295.0588.

1-(5-Hydroxy-2-methylnaphtho[2,1-b]furan-4-yl)ethanone (***4f***)*.* Yield: 72%, 75 mg; Yellow solid; m.p. 112.4-114.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.45 (s, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.65 (m, 1H), 7.46 (m, 1H), 6.71 (s, 1H), 2.90 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.8, 161.6, 152.9, 148.7, 130.7, 130.5, 125.7, 124.4, 123.1, 122.7, 116.2, 104.7, 101.5, 31.5, 14.2. IR (KBr) *v* (cm^{-1}) 3103, 2917, 1942, 1825, 1616, 1569, 1433, 1364, 1323, 1244, 1168, 1111, 1025, 986, 934, 810, 795, 684, 615, 544. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{15}H_{12}O_3Na$: 263.0684; found 263.0688.

1-(5-Hydroxynaphtho[2,1-b]benzofuran-6-yl)ethanone (***4g***)*.* Yield: 46%, 83 mg; Yellow solid; m.p. 165.0-167.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.90 (s, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.82 (m, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.56 (m, 1H), 7.45 (m, 2H), 3.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.0, 164.4, 155.1, 152.0, 132.0, 131.4, 126.0, 124.6, 124.6, 124.5, 123.7, 123.0, 122.8, 120.9, 111.7, 109.2, 104.3, 31.8. IR (KBr) *v* (cm^{-1}) 3061, 3005, 2920, 2319, 1942, 1614, 1566, 1513, 1437, 1370, 1317, 1267, 1209, 1064, 1022, 856, 738, 674, 510. HRMS (ESI): m/z [M + H]$^+$ calculated for $C_{18}H_{13}O_3$: 277.0865; found 277.0868.

1-(5-Hydroxy-2-methylnaphtho[2,1-b]benzofuran-6-yl)ethanone (***4h***)*.* Yield: 57%, 124 mg; Yellow solid; m.p. 171.5-173.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.69 (s, 1H), 8.21-8.28 (m, 1H), 7.88-7.86 (m, 1H), 7.72 (m, 1H), 7.47-7.45 (m, 1H), 7.32-7.31 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 1H), 2.81 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.6, 164.2, 154.8, 151.9, 141.9, 131.9, 126.2, 125.5, 124.4, 124.2, 123.3, 122.4, 120.7, 120.4, 111.3, 108.4, 103.5, 31.6, 22.5. IR (KBr) *v* (cm^{-1}) 3067, 3120, 2914, 1928, 1748, 1613, 1516, 1436, 1377, 1272, 1202, 1151, 1102, 1062, 984, 889, 874, 783, 690, 632, 592. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{19}H_{14}O_3Na$: 313.0841; found 313.0842.

1-(5-Hydroxynaphtho[2,1-b]thiophen-4-yl)ethanone (***4i***)*.* Yield: 52%, 48 mg; Yellow solid; m.p. 140.2-142.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 15.43 (s, 1H), 8.56 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 5.5 Hz, 1H), 7.75 (m, 1H), 7.57 (m, 1H), 7.43 (d, *J* = 5.5 Hz, 1H), 2.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.1, 164.5, 135.2, 132.6, 131.3, 129.8, 125.8, 124.2, 123.5, 122.5, 122.2, 110.4, 77.36, 31.6. IR (KBr) *v* (cm^{-1}) 3035, 2920, 1828, 1604, 1551, 1491, 1420, 1365, 1245, 1163, 1084, 1023, 979, 876, 774, 702, 648, 586, 506. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{14}H_{10}O_2SNa$: 265.0299; found 265.0301.

1-(5-Hydroxy-8-methylnaphtho[2,1-b]thiophen-4-yl)ethanone (***4j***)*.* Yield: 54%, 58 mg; Yellow solid; m.p. 143.3-145.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 15.33 (s, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.77 (s, 1H), 7.70 (d, *J* = 5.1 Hz, 1H), 7.27 (m, 2H), 2.79 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.6, 164.5, 141.7, 135.1, 132.6, 129.2, 127.5, 125.5, 123.0, 122.0, 121.9, 109.7, 31.4, 22.3. IR (KBr) *v* (cm^{-1}) 3075, 2987, 1913, 1742, 1589, 1486, 1417, 1365, 1299, 1238, 1092, 1022, 976, 896, 813, 773, 722, 645, 594, 551. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{15}H_{12}O_2SNa$: 279.0456; found 279.0457.

1-(8-Fluoro-5-hydroxynaphtho[2,1-b]thiophen-4-yl)ethanone ***(4k)***. Yield: 46%, 48 mg; Yellow solid; m.p. 153.2-155.7 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 15.46 (s, 1H), 8.53 (dd, *J* = 8.5, 5.7 Hz, 1H), 7.78 (d, *J* = 5.7 Hz, 1H), 7.74 (m, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 7.29 (d, *J* = 5.5 Hz, 1H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 203.0, 164.6 (^1J = 254 Hz), 164.2, 136.4, 134.4 (^3J = 10 Hz), 129.0 (^3J = 10 Hz), 125.8, 122.7, 122.2, 121.0, 115.2 (^2J = 24 Hz), 110.00, 108.3 (^2J = 24 Hz), 31.5. IR (KBr) *v* (cm^{-1}) 3025, 2993, 1904, 1700, 1588, 1446, 1411, 1365, 1219, 1208, 1090, 1021, 971, 888, 811, 703, 641, 574, 533. HRMS (ESI): *m/z* [M + H]$^+$ calculated for $C_{14}H_{10}FO_2S$: 261.0386, found 261.0382.

1-(5-Hydroxy-2-methylnaphtho[2,1-b]thiophen-4-yl)ethanone ***(4l)***. Yield: 62%, 52 mg;Yellow solid; m.p. 123.1-125.0 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 15.23 (s, 1H), 8.51 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.70 (m, 1H), 7.52 (m, 2H), 2.84 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 203.0, 163.4, 136.7, 134.0, 132.2, 130.9, 129.9, 125.6, 125.4, 124.0, 123.4, 119.9, 110.3, 31.4, 15.5. IR (KBr) *v* (cm^{-1}) 3070, 2914, 2852, 2378, 2307, 1936, 1672, 1602, 1567, 1527, 1418, 1366, 1285, 1235, 1084, 1020, 978, 935 , 874, 803, 788, 692, 629, 580, 542. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{15}H_{12}O_2SNa$: 279.0456; found 279.0456.

1-(10-Hydroxyphenanthro[2,1-b]furan-11-yl)ethanone ***(4m)***. Yield: 40%, 110 mg; Yellow solid; m.p. 218.6-220.4 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 15.66 (s, 1H), 9.92 (d, *J* = 8.7 Hz, 1H), 7.98 (m, 3H), 7.74 (m, 2H), 7.62 (m, 1H), 7.25 (d, *J* = 8.7 Hz, 1H), 3.03 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 203.2, 165.4, 150.7, 143.0, 133.0, 132.2, 132.1, 132.0, 129.1, 128.2, 128.1, 126.0, 122.1, 117.0, 116.1, 105.9, 105.3, 31.9. IR (KBr) *v* (cm^{-1}) 3152, 2917, 2357, 1957, 1825, 1686, 1610, 1424, 1374, 1333, 1264, 1207, 1133, 1096, 1023, 974, 869, 810, 754, 693, 664. HRMS (ESI): *m/z* [M + H]$^+$ calculated for $C_{18}H_{13}O_3$: 277.0865; found 277.0868.

1-(5-Hydroxybenzo[1,2-b:4,3-b']difuran-4-yl)ethanone ***(6a)***. Yield: 60%, 113 mg; Yellow solid; m.p. 138.1-138.9 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 13.73 (s, 1H), 7.86 (d, *J* = 2.0 Hz, 1H), 7.70 (d, *J* = 2.1 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 2.1 Hz, 1H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 203.2, 150.1, 149.2, 149.0, 143.5, 140.8, 127.0, 111.4, 106.5, 105.8, 104.1, 31.6. IR (KBr) *v* (cm^{-1}) 3018, 1612, 1527, 1475, 1415, 1363, 1299, 1143, 1012, 972, 875, 827, 756, 611, 480. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{12}H_8O_4Na$: 239.0320; found: 239.0298.

1-(5-Hydroxy-7-methylbenzo[1,2-b:4,3-b']difuran-4-yl)ethanone ***(6b)***. Yield: 67%, 172 mg; Yellow solid; m.p. 153.2-154.4 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 13.74 (s, 1H), 7.67 (d, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 1.8 Hz, 1H), 6.57 (s, 1H), 2.91 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 203.0, 160.8, 150.3, 148.4, 143.3, 140.0, 129.0, 110.9, 105.8, 103.4, 103.1, 31.5, 14.7. IR (KBr) *v* (cm^{-1}) 3116, 2925, 1828, 1608, 1508, 1404, 1363, 1307, 1211, 1147, 1024, 892, 808, 740, 690, 630, 595. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{13}H_{10}O_4Na$: 253.0477; found: 253.0477.

1-(5-Hydroxythieno[3,2-e]benzofuran-4-yl)ethanone ***(6c)***. Yield: 54%, 115 mg; Yellow solid; m.p. 149.4-150.3 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 13.94 (s, 1H), 7.78 (d, *J* = 5.2 Hz, 1H), 7.67 (s, 1H), 7.49 (d, *J* = 5.2 Hz, 1H), 6.99 (s, 1H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 202.8, 158.1, 151.5, 143.1, 138.0, 133.4, 124.9, 122.3, 114.5, 105.7, 103.4, 31.5. IR (KBr) *v* (cm^{-1}) 2968, 1604, 1527, 1465, 1398, 1357, 1313, 1238, 1134, 1082, 1024, 973, 846, 736, 655, 594, 466. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{12}H_8O_3SNa$: 255.0092; found: 255.0092.

1-(5-Hydroxy-7-methylthieno[3,2-e]benzofuran-4-yl)ethanone ***(6d)***. Yield, 57%, 104 mg; Yellow solid; m.p. 166.1-167.0 °C. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 13.90 (s, 1H), 7.64 (s, 1H), 7.16 (s, 1H), 6.92 (s, 1H), 2.90 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ (ppm) 202.5, 157.7, 151.8, 149.2, 142.9, 138.9, 123.7, 120.7, 113.9, 105.7, 103.0, 31.4, 16.8. IR (KBr) *v* (cm^{-1}) 3001, 1602, 1525, 1471, 1402, 1359, 1290, 1251, 1136, 1018, 973, 852, 729, 659, 594, 484. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{13}H_{11}O_3S$: 247.0429; found: 247.0429.

1-(5-Hydroxy-8-methylthieno[3,2-e]benzofuran-4-yl)ethanone ***(6e)***. Yield: 59%, 117 mg; Yellow solid; m.p. 172.7-173.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.86 (s, 1H), 7.64 (s, 1H), 7.34 (s, 1H), 7.07 (s, 1H), 2.89 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.7, 157.9, 151.6, 142.8, 137.7, 133.3, 128.8, 125.2, 114.2, 105.3, 103.1, 31.5, 16.0. IR (KBr) *v* (cm^{-1}) 2979, 2925, 1639, 1463, 1371, 1319, 1245, 1149, 1010, 894, 844, 759, 578, 530, 474. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{13}H_{10}O_3SNa$: 269.0248; found: 269.0244.

1-(5-Hydroxy-6-methyl-6H-furo[3,2-e]indol-4-yl)ethanone ***(6f)***. Yield: 41%, 68 mg; Yellow solid; m.p. 127.7-128.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 14.64 (s, 1H), 7.62 (d, *J* = 1.4 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 6.92 (d, *J* = 1.4 Hz, 1H), 6.54 (d, *J* = 2.5 Hz, 1H), 4.17 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.5, 154.0, 148.4, 142.1, 134.1, 127.7, 121.9, 111.1, 105.8, 102.2, 100.5, 37.0, 31.2. IR (KBr) *v* (cm^{-1}) 3109, 2923, 2856, 1728, 1612, 1471, 1369, 1271, 1107, 1022, 808, 738, 680, 607, 468. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{13}H_{11}NO_3Na$: 252.0637; found: 252.0635.

Ethyl-5-hydroxybenzo[1,2-b:4,3-b']difuran-4-carboxylate ***(6g)***. Yield: 45%, 137 mg; White solid; m.p. 88.7-89.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.86 (s, 1H), 7.86 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 6.92 (d, *J* = 1.7 Hz, 1H), 4.58 (m, 2H), 1.25 (m, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 170.6, 149.4, 148.5, 147.7, 144.2, 140.9, 126.1, 112.2, 106.5, 105.4, 96.0, 62.0, 14.5. IR (KBr) *v* (cm^{-1}) 3425, 2927, 2852, 2372, 1735, 1633, 1465, 1394, 1288, 1151, 1074, 1024, 740. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{13}H_{10}O_5Na$: 269.0426; found: 269.0420.

Ethyl-5-hydroxy-7-methylbenzo[1,2-b:4,3-b']difuran-4-carboxylate ***(6h)***. Yield: 49%, 138.5 mg; Yellow solid; m.p. 94.5-96.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.83 (s, 1H), 7.68 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H), 6.58 (s, 1H), 4.57 (m, 2H), 2.56 (s, 3H), 1.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.7, 159.9, 149.5, 147.0, 143.9, 140.1, 127.9, 111.7, 105.4, 102.9, 95.0, 61.8, 14.6, 14.5. IR (KBr) *v* (cm^{-1}) 3118, 2925, 2856, 2380, 1730, 1662, 1461, 1407, 1363, 1315, 1263, 1091, 1022, 935, 869, 804, 636, 524. HRMS (ESI): *m/z* $[M + H]^+$ calculated for $C_{14}H_{13}O_5$: 261.0763; found: 261.0761.

Ethyl-5-hydroxy-7-methylthieno[3,2-e]benzofuran-4-carboxylate ***(6i)***. Yield: 43%, 132 mg; White solid; m.p. 108.6-109.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 12.00 (s, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.20 (s, 1H), 6.93 (d, *J* = 2.0 Hz, 1H), 4.57 (m, 2H), 2.68 (s, 3H), 1.52 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.5, 156.2, 151.1, 147.9, 143.5, 138.1, 123.4, 120.6, 114.7, 105.3, 94.9, 61.9, 16.7, 14.6. IR (KBr) *v* (cm^{-1}) 3693, 2923, 2858, 2341, 1722, 1654, 1610, 1452, 1319, 1257, 1107, 1024, 887, 804, 757, 582, 487. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{14}H_{12}O_4SNa$: 299.0354; found: 299.0356.

1-(5-Hydroxybenzo[4,5]furan[3,2-e]benzofuran-4-yl)ethanone ***(6j)***. Yield: 63%, 203 mg; Yellow solid; m.p. 158.5-159.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.53 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.56 (m, 1H), 7.42 (m, 1H), 7.16 (d, *J* = 1.9 Hz, 1H), 2.95 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 203.2, 157.7, 150.3, 148.6, 144.4, 141.4, 128.9, 123.5, 122.8, 122.2, 112.7, 111.9, 105.8, 105.5, 31.8. IR (KBr) *v* (cm^{-1}) 3487, 2923, 2852, 2312, 1533, 1492, 1361, 1296, 1203, 1145, 1095, 1018, 985, 929, 842, 732, 661, 613, 536, 430. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{16}H_{10}O_4Na$: 289.0477; found: 289.0480.

1-(5-Hydroxybenzo[4,5]thieno[3,2-e]benzofuran-4-yl)ethanone ***(6k)***. Yield: 58%, 132 mg; Yellow solid; m.p. 197.1-198.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.73 (s, 1H), 8.34 (m, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.56 (m, 1H), 7.39 (s, 1H), 2.98 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.8, 157.3, 152.3, 143.8, 142.4, 135.2, 133.5, 127.8, 124.8, 124.3, 124.1, 123.5, 114.5, 105.3, 104.7, 31.7. IR (KBr) *v* (cm^{-1}) 3057, 2324, 1722, 1595, 1475, 1357, 1294, 1244, 1137, 1070, 1022, 979, 873, 817, 727, 599, 501. HRMS (ESI):

m/z [M + Na]$^{+}$ calculated for $C_{16}H_{10}O_3SNa$: 305.0248; found: 305.0241.

Ethyl-5-hydroxybenzo[4,5]furan[3,2-e]benzofuran-4-carboxylate ***(6l).*** Yield: 44%, 151.3 mg; Yellow solid; m.p. 159.7-160.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.83 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 2.1 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.56 (m, 1H), 7.44 (m, 1H), 7.20 (d, *J* = 2.1 Hz, 1H), 4.61 (m, 2H), 1.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.3, 157.5, 149.6, 147.5, 145.0, 141.4, 128.6, 123.7, 123.4, 122.1, 112.7, 105.1, 98.0, 62.2, 14.5. IR (KBr) *v* (cm^{-1}) 3057, 2324, 1722, 1595, 1475, 1357, 1294, 1244, 1137, 1070, 1022, 979, 873, 817, 727, 599, 501. HRMS (ESI): *m/z* [M + Na]$^{+}$ calculated for $C_{17}H_{12}O_5Na$: 319.0582; found: 319.0592.

Procedures for Syntheses of 2-(Furan-2-yl)-1-phenylbutane-1,3-diones (3a-3e, 3m).

According to a typical procedure,[26] a mixture of 1-phenylbutane-1,3-dione (1.52 mmol), 2,5-dimethoxy-2,5-dihydrofuran (DHDMF, 2.3 mmol) and K10 montmorillonite clay ($m_{\mathbf{4a}}$: $m_{\text{K10 mont.}}$ = 1:1) was stirred in anhydrous *n*-hexane at 80 °C for 3 h. Then the catalyst was filtered off and the product purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 80:1→40:1) to give **3a** in 75% yield. Similarly, **3b**-**3e** and **3m** were prepared with yields 52~80% (The reaction scheme was in supporting information, SI-Scheme S1).

2-(Furan-2-yl)-1-phenylbutane-1,3-dione ***(3a).*** Yield: 75%, 260 mg; Yellow solid; m.p. 51.2-53.6 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.40 (s, 1H, enol), 7.46 (s, 1H, enol), 7.31 (m, 5H, enol), 6.34 (s, 1H, enol), 6.04 (d, *J* = 2.6 Hz, 1H, enol), 2.11 (s, 3H, enol) ppm. **3a** is known.[26]

2-(Furan-2-yl)-1-(p-tolyl)butane-1,3-dione ***(3b).*** Yield: 63%, 243 mg; Yellow solid; m.p. 50.1-52.3 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.49 (s, 1H, enol), 7.47 (s, 1H, enol), 7.21 (d, *J* = 8.1 Hz, 2H, enol), 7.06 (d, *J* = 8.1 Hz, 2H, enol), 6.36 (d, *J* = 3.1 Hz, 1H, enol), 6.06 (d, *J* = 3.1 Hz, 1H, enol), 2.32 (s, 3H, enol), 2.10 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 185.5, 149.9, 142.2, 141.9, 133.0, 128.8, 128.5, 111.5, 111.5, 104.1, 25.1, 21.6 ppm. HRMS (ESI): m/z [M + Na]$^{+}$ calculated for $C_{15}H_{14}O_3Na$: 265.0841; found: 265.0843.

1-(4-Fluorophenyl)-2-(furan-2-yl)butane-1,3-dione ***(3c).*** Yield: 75%, 250 mg; Yellow solid; m.p. 51.7-52.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.32 (s, 1H, enol), 7.47 (d, *J* = 1.9 Hz, 1H, enol), 7.21 (m, 1H, enol), 6.04 (m, 3H, enol), 6.36 (dd, *J* = 3.1, 1.9 Hz, 1H, enol), 6.07 (d, *J* = 3.1 Hz, 1H, enol), 2.12 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.5, 184.1, 162.2 (^{1}J = 245 Hz), 149.0, 142.4, 137.9 (^{3}J = 7 Hz), 129.6 (^{3}J = 8 Hz), 124.1 (^{4}J = 3 Hz), 118.2 (^{2}J = 21 Hz), 115.4 (^{2}J = 23 Hz), 111.9, 111.56, 104.6, 25.1. HRMS (ESI): m/z [M + H]$^{+}$ calculated for $C_{14}H_{12}FO_3$: 247.0770; found: 247.0792.

2-(Furan-2-yl)-1-(4-methoxyphenyl)butane-1,3-dione ***(3d).*** Yield: 60%, 262 mg; Yellow solid; m.p. 52.1-53.8 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.62 (s, 1H, enol), 7.48 (d, *J* = 1.9 Hz, 1H, enol), 7.27 (m, 2H, enol), 6.74 (m, 2H, enol), 6.38 (dd, *J* = 3.2, 1.9 Hz, 1H, enol), 6.08 (d, *J* = 3.2 Hz, 1H, enol), 3.78 (s, 3H, enol), 2.08 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 185.1, 162.2, 150.0, 142.2, 130.6, 128.0, 113.4, 111.5, 111.4, 103.5, 55.4, 24.9. HRMS (ESI): m/z [M + Na]$^{+}$ calculated for $C_{15}H_{14}O_4Na$: 281.0790; found 281.0791.

2-(Furan-2-yl)-1-(4-(trifluoromethyl)phenyl)butane-1,3-dione ***(3e).*** Yield: 80%, 307 mg; Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.25 (s, 1H, enol), 7.51 (d, *J* = 8.3 Hz, 2H, enol), 7.46 (s, 1H, enol), 7.40 (d, *J* = 8.3 Hz, 2H, enol), 6.35 (d, *J* = 3.2 Hz, 1H, enol), 6.06 (d, *J* = 3.2 Hz, 1H, enol), 2.13 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.9, 183.8, 148.8, 142.5, 139.2, 132.6 (^{2}J = 33 Hz), 128.7, 125.0 (^{3}J = 3 Hz), 123.8 (^{1}J = 273 Hz), 112.0, 111.6, 105.0, 25.2. HRMS (ESI): m/z [M + Na]$^{+}$ calculated for $C_{15}H_{11}F_3O_3Na$: 319.0558; found 319.0562.

2-(Furan-2-yl)-1-(naphthalen-1-yl)butane-1,3-dione ***(3m).*** Yield: 72%, 279 mg; Yellow solid; m.p. 65.6-66.7 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.17 (s, 1H, enol), 7.94 (d, *J* = 8.4 Hz, 1H, enol), 7.58 (d, *J* = 7.8 Hz, 1H, enol), 7.56 (d, *J* = 1.9 Hz, 1H, enol), 7.28 (m, 2H, enol), 7.11 (m, 2H, enol), 7.03 (m, 1H, enol), 5.83 (dd, *J* = 3.2, 1.9 Hz, 1H, enol), 5.56 (d, *J* = 3.2 Hz, 1H, enol), 2.01 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 187.8, 148.8, 141.9, 133.7, 133.3, 130.1, 130.0, 128.2, 126.8, 126.1, 125.9, 125.2, 124.4, 111.1, 110.7, 107.3, 25.3. HRMS (ESI): m/z [M + Na]$^+$ calculated for $C_{18}H_{14}O_3Na$ [M+Na]$^+$: 301.0841; found 301.0848.

Syntheses of 2-(Furan-2-yl)-1-phenylbutane-1,3-diones, 3f-3l.

4-Picoline-N-oxide (1.4 mmol) was added with stirring to a suspension of IPrAuCl (0.035 mmol) and $AgNTf_2$ (0.035 mmol) in dichloromethane (8 mL) and the mixture was stirred for 5 min at room temperature. After that, $HNTf_2$ (0.84 mmol) was added and the mixture was stirred for an additional 5 min. To the resulting solution was added propargyl alcohol (0.7 mmol) and the combined solution was then stirred at room temperature until the reaction was complete (monitored by TLC). After evaporation of the solution, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 40:1→15:1) to give **3f** in a yield of 62%. Similarly, **3g-3l** were prepared with yields 55~75% (The reaction scheme was in supporting information, SI-Scheme S2).

*2-(5-Methylfuran-2-yl)-1-phenylbutane-1,3-dione **(3f)**.* Yield: 62%, 98.5 mg; Yellow solid; m.p. 52.0-53.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.42 (s, 1H, enol), 7.29 (m, 2H, enol), 7.23 (d, *J* = 7.3 Hz, 1H, enol), 7.15 (m, 2H, enol), 5.84 (d, *J* = 3.0 Hz, 1H, enol), 5.82 (d, *J* = 3.0 Hz, 1H, enol), 2.20 (s, 3H, enol), 2.05 (s, 3H, enol). **3f** is known.[27]

*2-(Benzofuran-2-yl)-1-phenylbutane-1,3-dione **(3g)**.* Yield: 73%, 182 mg; Yellow solid; m.p. 64.4-66.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.53 (s, 1H, enol), 7.47 (m, 2H, enol), 7.39 (d, *J* = 7.5 Hz, enol), 7.29 (m, 2H, enol), 7.19 (m, 3H, enol), 6.42 (s, 1H, enol), 2.16 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 186.0, 154.8, 152.4, 135.6, 131.4, 128.8, 128.3, 128.1, 124.4, 122.9, 121.1, 111.4, 108.6, 104.4, 25.3. HRMS (ESI): m/z [M + Na]$^+$ calculated for $C_{18}H_{14}O_3Na$: 301.0841; found 301.0841.

*2-(Benzofuran-2-yl)-1-(p-tolyl)butane-1,3-dione **(3h)**.* Yield: 75%, 219 mg; Yellow solid; m.p. 63.2-65.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.52 (s, 1H, enol), 7.32 (d, *J* = 8.2 Hz, 3H, enol), 7.14 (m, 2H, enol), 7.05 (d, *J* = 7.5 Hz, 1H, enol), 6.78 (d, *J* = 8.2 Hz,, 2H, enol), 6.27 (s, 1H, enol), 2.04 (s, 3H, enol), 1.97 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 185.8, 154.7, 152.6, 141.9, 132.6, 130.1, 128.8, 128.4, 124.3, 122.8, 121.0, 111.3, 108.4, 104.0, 25.1, 21.4. HRMS (ESI): m/z [M + H]$^+$ calculated for $C_{19}H_{17}O_3$: 293.1178; found 293.1181.

*1-Phenyl-2-(thiophen-2-yl)butane-1,3-dione **(3i)**.* Yield: 60%, 93 mg; Yellow solid; m.p. 80.0-82.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.62 (s, 1H, enol), 7.43 (s, 1H, enol), 7.41 (s, 1H, enol), 7.33 (d, *J* = 7.2 Hz, 1H, enol), 7.29 (d, *J* = 5.5 Hz, 1H, enol), 7.22 (m, 2H, enol), 6.97 (dd, *J* = 5.5, 3.2 Hz, 1H, enol), 6.82 (d, *J* = 3.2 Hz, 1H, enol), 2.17 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.9, 184.3, 138.3, 136.0, 130.7, 130.0, 128.7, 127.8, 127.3, 127.2, 106.2, 25.6. HRMS (ESI): m/z [M + Na]$^+$ calculated for $C_{14}H_{12}O_2SNa$: 267.0456; found 267.0458.

*2-(Thiophen-2-yl)-1-(p-tolyl)butane-1,3-dione **(3j)**.* Yield: 64%, 109 mg; Yellow solid; m.p. 79.2-81.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.67 (s, 1H, enol), 7.32 (s, 1H, enol), 7.30 (m, 2H, enol), 7.02 (d, *J* = 8.1 Hz, 2H, enol), 6.98 (m, 1H, enol), 6.83 (dd, *J* = 3.4, 1.0 Hz, 1H, enol), 2.30 (s, 3H, enol), 2.15 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.7, 184.3, 141.4, 138.7, 133.2, 129.9, 128.9, 128.6, 127.4, 127.2, 105.9, 25.6, 21.6. HRMS (ESI): m/z [M + Na]$^+$ calculated for $C_{15}H_{14}O_2SNa$: 281.0612; found 281.0614.

*1-(4-Fluorophenyl)-2-(thiophen-2-yl)butane-1,3-dione **(3k)**.* Yield: 68%, 106 mg; Yellow solid; m.p. 78.3-80.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.60 (s, 1H, enol), 7.41 (m, 2H, enol), 7.31 (dd, *J* = 5.3, 1.1 Hz, 1H, enol), 6.98 (dd, *J* = 5.3, 3.5 Hz, 1H, enol), 6.89 (m, 2H, enol), 6.82 (dd, *J* = 3.4, 1.1 Hz, 1H, enol), 2.15 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 183.3, 164.1 (^1J = 253.5 Hz), 138.3, 132.2, 131.3 (^3J = 9.1

Hz), 130.0, 127.5, 124.3, 115.0 (^2J = 21.2 Hz), 106.0, 25.5. HRMS (ESI): m/z [M + Na]$^+$ calculated for $C_{14}H_{11}FO_2SNa$: 285.0361; found 285.0365.

2-(5-Methylthiophen-2-yl)-1-phenylbutane-1,3-dione ***(3l)***. Yield: 55%, 85 mg; Yellow solid; m.p. 76.4-78.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) ^{1}H NMR (400 MHz, $CDCl_3$) δ 17.57 (s, 1H, enol), 7.43 (s, 1H, enol), 7.4 (d, J = 1.5 Hz, 1H, enol), 7.23 (d, J = 7.5 Hz, 1H, enol), 7.15 (m, 2H, enol), 6.54 (dd, J = 3.3, 1.5 Hz, 1H, enol), 6.51 (d, J = 3.3 Hz, 1H, enol), 2.35 (m, 3H, enol), 2.11 (s, 3H, enol). **3l** is known.[28]

Syntheses of 1-(Furan/Thiophen/Pyrrol-2-yl)-2-(furan-2-yl)butane-1,3-diones (5a-5l).

According to a typical procedure,[24] a mixture of 1-(furan-2-yl)butane-1,3-dione (**11a**, 1.4 mmol), 2,5-dimethoxy-2,5-dihydrofuran (DHDMF, 5.6 mmol) and K10 montmorillonite clay ($m_{\mathbf{4a}}$: $m_{\text{K10 mont.}}$ = 1:2) was stirred in anhydrous *n*-hexane at 80 °C for 3 h. Then the catalyst was filtered off and the product purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 80:1→40:1) to give **5a** in 74% yield. Similarly, **5b-5l** were prepared with yields of 53~90% (The reaction scheme was in supporting information, SI-Scheme S3).

1,2-Di(furan-2-yl)butane-1,3-dione ***(5a)***. Yield: 74%, 225 mg; Yellow solid; m.p. 67.4-69.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.31 (s, 1H, enol), 7.53 (m, 2H, enol), 6.50 (d, J = 1.4 Hz, 1H, enol), 6.34 (d, J = 1.4 Hz, 1H, enol), 6.31 (d, J = 3.3 Hz, 1H, enol), 5.79 (d, J = 3.3 Hz, 1H, enol), 2.02 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 193.3, 176.6, 158.0, 148.7, 148.6, 146.6, 142.6, 118.54, 112.5, 111.9, 111.6, 102.0, 23.5. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{12}H_{10}O_4Na$: 241.0477; found: 241.0476.

2-(Furan-2-yl)-1-(5-methylfuran-2-yl)butane-1,3-dione ***(5b)***. Yield: 77%, 260 mg; Yellow oil. A mixture of keto/enol tautomers as 0.9:1 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.37 (s, 1H, enol), 7.52 (d, J = 1.4 Hz, 1H, enol), 7.05 (d, J = 3.4 Hz, 2H, keto), 6.48 (m, 1H, enol), 6.28 (d, J = 3.2 Hz, 1H, enol), 6.14 (d, J = 3.3 Hz, 2H, keto), 5.98 (s, 1H, enol), 5.97 (d, J = 3.2 Hz, 1H, enol), 5.70 (m, 1H, keto), 3.87 (s, 1H, keto), 2.37 (s, 3H, enol), 2.30 (s, 3H, keto), 2.10 (s, 3H, enol), 2.00 (s, 3H, keto). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 191.9 (keto), 188.0 (enol), 177.0 (keto), 176.8 (enol), 157. 9 (keto), 157.3 (enol), 149.2 (enol), 148.9 (keto), 147.4 (keto), 142.4 (enol), 120.6 (keto), 117.5 (enol), 111.7 (enol), 111.5 (keto), 109.7 (keto), 109.4 (enol), 109.3 (enol), 101.5 (keto), 95.8 (enol), 54.3 (keto), 24.2 (enol), 23.1 (keto), 14.1 (enol), 14.0 (keto). HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{13}H_{12}O_4Na$: 255.0633; found: 255.0642.

2-(Furan-2-yl)-1-(thiophen-2-yl)butane-1,3-dione ***(5c)***. Yield: 72%, 215 mg; Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.51 (s, 1H, enol), 7.57 (d, J = 1.5 Hz, 1H, enol), 7.51 (d, J = 1.5 Hz, 1H, enol), 6.95 (m, 1H, enol), 6.87 (d, J = 3.2 Hz, 1H, enol), 6.52 (d, J = 3.2 Hz, 1H, enol), 6.37 (d, J = 3.2 Hz, 1H, enol), 2.04 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.9, 179.9, 148.8, 142.9, 139.4, 133.5, 132.7, 127.9, 112.9, 111.7, 102.2, 24.0. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{12}H_{10}O_3SNa$: 257.0248; found: 257.0256.

2-(Furan-2-yl)-1-(5-methylthiophen-2-yl)butane-1,3-dione ***(5d)***. Yield: 68%, 185 mg; Yellow solid; m.p. 52.7-54.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.55 (s, 1H, enol), 7.56 (s, 1H, enol), 6.69 (d, J = 3.7 Hz, 1H, enol), 6.62 (d, J = 3.3 Hz, 1H, enol), 6.51 (s, 1H, enol), 6.35 (d, J = 3.3 Hz, 1H, enol), 2.43 (s, 3H, enol), 2.01 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.1, 178.0, 149.6, 148.9, 142.8, 136.9, 133.5, 126.8, 112.8, 111.7, 101.8, 23.8, 15.7. HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{13}H_{12}O_3SNa$: 271.0405; found: 271.0406.

2-(Furan-2-yl)-1-(4-methylthiophen-2-yl)butane-1,3-dione ***(5e)***. Yield: 70%, 201 mg; Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.52 (s, 1H, enol), 7.56 (s, 1H, enol), 7.10 (s, 1H, enol), 6.70 (s, 1H, enol), 6.52 (s, 1H, enol), 6.36 (d, J = 3.2 Hz, 1H, enol), 2.15 (s, 3H, enol), 2.03 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.9, 179.7, 148.7, 142.8, 138.6, 138.5, 134.9, 129.7, 112.9, 111.7, 102.1, 24.0, 15.5. HRMS (ESI): *m/z* [M

+ Na]$^+$ calculated for $C_{13}H_{12}O_3SNa$: 271.0405; found: 271.0401.

*2-(Furan-2-yl)-1-(1-methyl-1H-pyrrol-2-yl)butane-1,3-dione (**5f**).* Yield: 53%, 168 mg; Yellow oil. A mixture of keto/enol tautomers as 2:5 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.78 (s, 1H, enol), 7.51 (s, 1H, enol), 7.41 (s, 0.4H, keto), 7.00 (d, *J* = 3.2 Hz, 0.4H, keto), 6.87 (s, 0.4H, keto), 6.74 (s, 1H, enol), 6.47 (d, *J* = 3.0 Hz, 1H, enol), 6.44 (d, *J* = 3.3 Hz, 0.4H, keto), 6.39 (d, *J* = 3.9 Hz, 0.4H, keto), 6.24 (d, *J* = 2.8 Hz, 1H, enol), 6.14 (m, 0.4H, keto), 5.93 (m, 1H, enol), 5.53 (d, *J* = 5.3 Hz, 1H, enol), 5.50 (s, 0.4H, keto), 3.95 (m, 1.2H, keto), 3.94 (m, 3H, enol), 2.26 (s, 1.2H, keto), 1.99 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.6 (keto), 189.1 (enol), 182.5 (enol), 182.4 (keto), 150.3 (enol), 148.1 (keto), 142.7 (keto), 142.0 (enol), 132.8 (keto), 131.1 (enol), 129.9 (keto), 127.9 (enol), 121.3 (keto), 119.2 (enol), 111.5 (enol), 111.4 (enol),111.1 (keto), 109.3 (keto), 108.9 (keto), 108.6 (enol), 102.3 (enol), 62.9 (keto), 38.6 (enol), 38.0 (keto), 28.9 (keto), 22.7 (enol). HRMS (ESI): *m/z* [M + H]$^+$ calculated for $C_{13}H_{14}NO_3$: 232.0974; found: 232.0975.

*Ethyl 2,3-di(furan-2-yl)-3-oxopropanoate (**5g**).* Yield: 85%, 307 mg; Yellow oil. A mixture of keto/enol tautomers as 25:7 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.79 (s, 0.28H, enol), 7.61 (s, 1H, keto), 7.51 (s, 0.28H, enol), 7.46 (s, 0.28H, enol), 7.40 (s, 0.28H, keto), 7.28 (d, *J* = 3.6 Hz, 1H, keto), 6.55 (d, *J* = 3.6 Hz, 1H, keto), 6.46 (d, *J* = 3.4 Hz, 1H, keto), 6.38 (d, *J* = 2.4 Hz, 1H, keto), 6.36 (d, *J* = 3.6 Hz, 0.28H, enol), 6.27 (d, *J* = 3.3 Hz, 0.28H, enol), 5.94 (d, *J* = 3.6 Hz, 0.28H, enol), 5.52 (s, 1H, keto), 4.27 (m, 0.56H, enol), 4.24 (m, 2H, keto), 1.26 (m, 0.84H, enol), 1.24 (m, 3H, keto) ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 179.7 (keto), 173.2 (enol), 166.7 (keto), 163.9 (enol), 151.3 (keto), 150.4 (enol), 147.3 (keto), 147.0 (enol), 146.1 (keto), 145.3 (enol), 142.9 (keto), 142.2 (enol), 119.2 (keto), 116.5 (enol), 112.9 (keto), 112.2 (enol), 111.4 (enol), 111.1 (enol), 111.0 (keto), 110.0 (keto), 92.3 (enol), 62.2 (keto), 61.5 (enol), 54.6 (keto), 14.3 (enol), 14.1 (keto). HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{13}H_{12}O_5Na$: 271.0582; found: 271.0580.

*Ethyl 2-(furan-2-yl)-3-(5-methylfuran-2-yl)-3-oxopropanoate (**5h**).* Yield: 80%, 284 mg; Yellow oil. A mixture of keto/enol tautomers as 50:9 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.79 (s, 0.18H, enol), 7.44 (s, 0.18H, enol), 7.34 (s, 1H, keto), 7.15 (s, 1H, keto), 6.41 (s, 1H keto and 0.18H enol), 6.32 (s, 1H, keto), 6.20 (s, 0.18H, enol), 6.13 (s, 1H, keto), 5.93 (s, 0.18H, enol), 5.83 (d, *J* = 3.2 Hz, 0.18H, enol), 5.43 (s, 1H, keto), 4.21 (m, 0.36H, enol), 4.18 (m, 2H, keto), 2.33 (s, 3H, keto), 2.21 (s, 0.54H, enol), 1.20 (m, 3H keto and 0.54H enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 178.65 (keto), 173.10 (enol), 166.73 (keto), 163.89 (enol), 159.00 (keto), 155.95 (enol), 149.76 (keto), 147.04 (enol), 146.31 (keto), 145.31 (enol), 142.61 (keto), 141.78 (enol), 121.39 (keto), 118.07 (enol), 111.24 (enol), 110.84 (keto), 109.66 (keto), 108.82 (enol), 90.78 (enol), 61.92 (enol), 61.12 (keto), 54.10 (keto), 14.10 (enol), 14.01 (keto), 13.93 (keto), 13.62 (enol). HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{14}H_{14}O_5Na$: 285.0739; found: 285.0732.

*Ethyl 2-(furan-2-yl)-3-(5-methylthiophen-2-yl)-3-oxopropanoate (**5i**).* Yield: 69%, 310 mg; Yellow solid; m.p. 38.2-40.0 ^{o}C. A mixture of keto/enol tautomers as 10:3 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.88 (s, 0.3H, enol), 7.57 (d, *J* = 3.8 Hz, 1H, keto), 7.53 (m, 0.3H, enol), 7.39 (d, *J* = 1.9 Hz, 1H, keto), 6.85 (d, *J* = 3.8 Hz, 0.3H, enol), 6.78 (d, *J* = 3.2 Hz, 1H, keto), 6.62 (d, *J* = 3.2 Hz, 0.3H, enol), 6.48 (m, 1H, keto and enol), 6.37 (dd, *J* = 3.2, 1.9 Hz, 1H, keto), 6.31 (d, *J* = 3.2 Hz, 0.3H, enol), 5.49 (s, 1H, keto), 4.24 (m, 2H, keto and enol), 2.52 (s, 3H, keto), 2.42 (s, 0.9H, enol), 1.23 (m, 3H keto and 0.9H enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 183.2 (keto), 173.3 (enol), 168.3 (enol), 166.9 (keto), 151.7 (keto), 147.4 (enol), 147.1 (enol), 146.6 (keto), 142.8 (keto), 142.5 (enol), 140.2 (keto), 134.4 (keto), 133.7 (enol), 132.1 (enol), 127.2 (keto), 126.1 (enol), 112.4 (enol), 111.6 (enol), 111.1 (keto), 109.9 (keto), 91.3 (enol), 62.2 (keto), 61.3 (enol), 55.4 (keto), 16.2 (keto), 15.5 (enol), 14.3 (enol), 14.1 (keto). HRMS (ESI): *m/z* [M + Na]$^+$ calculated for $C_{14}H_{14}O_4SNa$: 301.0510; found: 301.0512.

*1-(Benzofuran-2-yl)-2-(furan-2-yl)butane-1,3-dione (**5j**).* Yield: 76%, 325 mg; Yellow solid; m.p. 80.1-82.4 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.30 (s, 1H, enol), 7.61 (s, 1H, enol), 7.51 (d, *J* = 7.8 Hz, 1H, enol), 7.48 (d, *J* = 7.8 Hz, 1H, enol), 7.38 (m, 1H, enol), 7.21 (m, 1H, enol), 6.56 (s, 1H, enol), 6.37 (d, *J* = 3.0 Hz, 1H, enol), 6.23 (s, 1H, enol), 2.09 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 194.9, 176.5, 155.4, 149.4, 148.4, 142.8, 127.8, 127.5, 123.7, 122.9, 114.1, 112.1, 111.7, 103.3, 24.0. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{16}H_{12}O_4Na$: 291.0633; found: 291.0633.

1-(Benzo[b]thiophen-2-yl)-2-(furan-2-yl)butane-1,3-dione (**5k**). Yield: 58%, 230 mg; Yellow solid; m.p. 83.9-85.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 17.46 (s, 1H, enol), 7.77 (d, *J* = 8.0 Hz, enol), 7.70 (d, *J* = 7.9 Hz, 1H, enol), 7.63 (d, *J* = 1.3 Hz, 1H, enol), 7.34 (m, 2H, enol), 7.09 (s, 1H, enol), 6.58 (dd, J = 3.1, 1.3 Hz, 1H, enol), 6.43 (d, *J* = 3.1 Hz, 1H, enol), 2.09 (s, 3H, enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 195.8, 179.8, 148.4, 143.0, 142.6, 139.0, 138.9, 129.9, 126.9, 125.7, 124.8, 122.4, 113.1, 111.8, 103.2, 24.3. HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{16}H_{12}O_3SNa$: 307.0405; found: 307.0417.

Ethyl 3-(benzofuran-2-yl)-2-(furan-2-yl)-3-oxopropanoate (**5l**). Yield: 90%, 348 mg; Yellow solid; m.p. 89.2-91.9 °C. A mixture of keto/enol tautomers as 10:7 by ^{1}H NMR. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 13.81 (s, 0.7H, enol), 7.70 (d, *J* = 7.8 Hz, 1H, keto), 7.61 (s, 1H, keto), 7.58 (s, 0.7H, enol), 7.55 (s, 1H, keto), 7.52 (d, *J* = 6.8 Hz, 1H, keto), 7.48 (d, *J* = 8.1 Hz, 0.7H, enol), 7.43 (s, 1H, keto), 7.41 (s, 0.7H, enol), 7.34 (d, *J* = 7.4 Hz, 1H, keto), 7.31 (d, *J* = 7.4 Hz, 0.7H, enol), 7.21 (m, 0.7H, enol), 6.52 (m, 1H keto and 0.7H enol), 6.39 (s, 1H keto and 0.7H enol), 6.32 (s, 0.7H, enol), 5.66 (s, 1H, keto), 4.24-431 (m, 2H keto and 1.4H enol), 1.26 (m, 3H keto and 2.1H enol). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 181.7 (enol), 173.0 (keto), 166.6 (enol), 163.9 (keto), 156.0 (keto), 155.2 (enol), 151.2 (keto), 148.6 (enol), 146.6 (enol), 145.8 (keto), 143.1 (keto), 142.3 (enol), 129.0 (keto), 127.6 (enol), 127.1 (enol), 126.9 (keto), 124.3 (keto), 123.7 (keto), 123.5 (enol), 122.3 (enol), 115.0 (keto), 112.7 (keto), 112.2 (enol), 112.0 (enol), 111.5 (enol), 111.4 (enol), 111.1 (keto), 110.2 (keto), 94.7 (enol), 62.4 (keto), 61.7 (enol), 55.0 (keto), 14.2 (enol), 14.1 (keto). HRMS (ESI): *m/z* $[M + Na]^+$ calculated for $C_{17}H_{14}O_5Na$: 321.0739; found: 321.0750.

Syntheses of 1-Phenyl-2-thiophen-2-yl-butan-1-one (7).[29]

An oven-dried round bottom flask was charged with 65% dispersion of NaH in mineral oil (7.5 mmol), anhydrous THF (10 ml), 1-phenyl-2-(thiophen-2-yl)ethanone (1.5 mmol), and iodoethane (2.25 mmol). The reaction mixture was heat at reflux overnight, and the reation was quenched at 0 °C by adding 1 M HCl and saturated $NaHCO_3$ sequentially, then the mixture extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. Purification by silica gel chromatography provided the desired **7** as a yellow oil in 28% yield.

1-Phenyl-2-thiophen-2-yl-butan-1-one (7). Yield: 28%, 97 mg; Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (m, 2H), 7.50 (m, 1H), 7.36-7.32 (m, 3H), 7.04-6.99 (m, 2H), 4.98 (s, 1H), 2.54-2.38 (m, 2H), 0.86 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 201.1, 147.2, 134.1, 133.3, 129.8, 128.5, 127.3, 126.1, 125.5, 32.6, 7.7. HRMS (ESI): m/z $[M + Na]^+$ calculated for $C_{14}H_{14}OSNa$: 253.0663; found 253.0657.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

H_2 detection for the photochemical dehydrocyclization of **3a** by GC.

Determination of fluorescence quantum yield for **4a-4m** and **6a-6l**.

NMR spectra of compounds **3-6**. Fluorescence spectra of **4** and **6**.

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Notes

The authors declare no competing financial interest.

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