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A Retrosynthetic Analysis of α-Alkenyl-β-Diketones: Regio- and Stereoselective Two-step Synthesis of Highly Arylated Representatives from Acetylenes, Ketones and Acyl Chlorides

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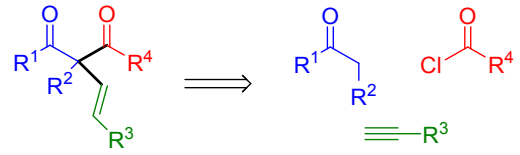


- two-step procedure
- transition-metal free catalytic systems
- 18 examples, up to 80% yields
- (*E*)-stereoselectivity
- valuable tool for the synthesis of polyarylated heterocycles

ABSTRACT: Highly arylated α-alkenyl-β-diketones are synthesized *via* a two-step sequence consisting of (*i*) potassium *tert*-butoxide/DMSO-catalyzed (*E*)-stereoselective C-H functionalization of ketones with acetylenes followed by (*ii*) magnesium bromide etherate/DIPEA-soft enolization of the formed β,γ-unsaturated ketones and regioselective acylation with acyl chlorides. The method is compatible with a broad range of substrates and shown to be applicable as an intermediate stage in the construction of polyarylated heterocycles.

INTRODUCTION

β-Diketone motif is widespread in natural products, biologically active compounds and pharmaceuticals and extensively used as building block in organic synthesis and coordination chemistry.[1] In recent years, β-diketones having an additional alkenyl functionality at the α-position have opened up a new field of opportunity for the synthesis of five-membered heteroaromatics, e.g. pyrazoles,[2] furans,[3] thiophenes,[4] and pyrroles.[5]

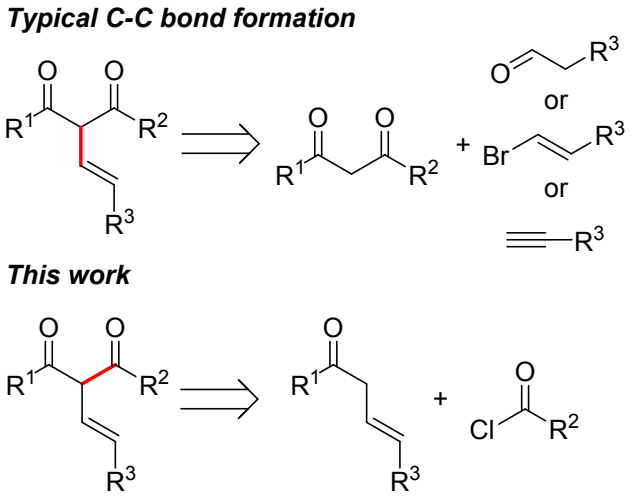
To date, there are three main approaches to construct this prospective structural unit, which all based on the diverse C-C bond forming reactions between β-diketones and alkenyl synthons, namely Knoevenagel condensation with acetaldehyde derivatives,[6] copper iodide/*L*-proline-catalyzed Ulmann-type condensation with vinyl bromides[7] and transition-metal-catalyzed addition to acetylenes[8] (Scheme 1). Although the latter approach attracts significant attention of the synthetic community as the most straightforward route to α-alkenyl-β-diketones, until now there is only one example of *anti*-Markovnikov addition of β-dicarbonyl compounds to acetylenes.[9] The reaction represents an amine-promoted rhenium-catalyzed process and provides

an access to α-styryl-β-diketones, the proposed intermediates of the abovementioned heterocyclizations.[2-5]

Furthermore, a common limitation of the present approaches in the construction of α-alkenyl-β-diketones is a relatively narrow scope of used β-diketones, mainly aliphatic and cycloaliphatic ones. Therefore, no wonder that the synthesis of highly arylated α-alkenyl-β-diketones (R^1, R^2, R^3 = aryl or hetaryl) still remains a challenge especially in relation to their outlooks for the design of polyconjugated heterocyclic scaffolds for organic electronics.[10] It is worthy of note that so far the only report was published when 1,3-diphenyl-2-styrylpropane-1,3-dione (R^1 = R^2 = R^3 = Ph) was occasionally observed under thermolysis of the corresponding pyrazoline.[11]

In order to overcome the limitation of β-diketones scope, in the present work we propose a novel retrosynthetic disconnection of α-alkenyl-β-diketones that consist in the C-C bond formation through acylation of readily available β,γ-unsaturated ketones (Scheme 1).

Scheme 1. Synthetic Approaches to α-Alkenyl-β-Diketones

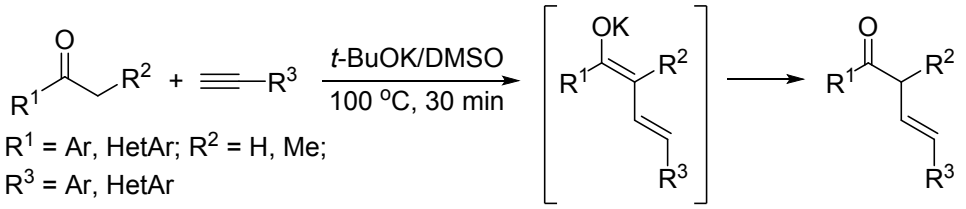


An additional incentive to realize the planned reaction protocol has been provided by the well-documented use of β,γ-unsaturated ketones as carbon nucleophiles in diverse C-C bond forming reactions.[12] Thus, the trapping of the dienolates of β,γ-unsaturated ketones was performed by diverse carbon electrophiles, namely alkyl halides,[12j] aldehydes,[12h,i] allenamides,[12c] di-*tert*-butyl azodicarboxylate[12b] as well as alkenes and alkynes activated by nitro-,[12d,e,i] sulphonyl-[12a,i] or keto-groups.[12f,g] However, an early attempt to couple β,γ-unsaturated ketone with benzoyl chloride[13] in C-regioselective mode failed and since then, as far as we know, no more reports have been presented.

RESULTS AND DISCUSSION

The previously discovered by us[14] and nowadays systematically applied to the assembly of valuable carbo- and heterocyclic compounds[15] C-H functionalization of ketones with acetylenes in the presence of inexpensive and easy-to-handle potassium *tert*-butoxide/DMSO-catalytic system (Scheme 2) was chosen as the first step toward highly arylated α-alkenyl-β-diketones. It is the exclusive (*E*)-stereoselectivity of this reaction that has allowed the construction of highly arylated α-alkenyl-β-diketones to be easily achieved in a stereoselective mode.

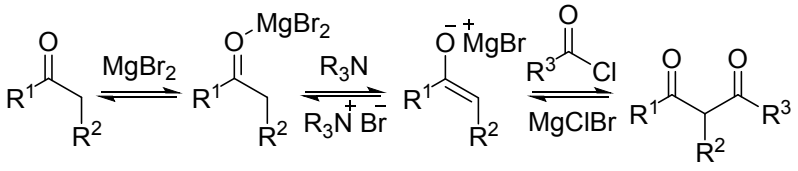
Scheme 2. Synthesis of β,γ-Unsaturated Ketones from Ketones and Acetylenes



Next, the potassium dienolate, formed as a primary adduct of C-H functionalization (Scheme 2), was subjected to the Claisen condensation with ethyl acetate in a one-pot manner. Due to the inefficiency of this protocol under a variety of reaction conditions, we began looking for a better approach for the introduction of acyl moiety, and finally realized that in terms of mild reaction conditions, acylating agent availability and functional group tolerance the best route would be a soft enolization[16] of β,γ-unsaturated ketones **1** followed by acylation with acyl chlorides **2**.

A soft enolization approach includes initial formation of a coordination complex between Lewis acid, *e.g.* magnesium bromide, and ketone providing stronger polarization of the carbonyl function. As a result, the acidity of α-protons increases to ensure the enolization with mild organic bases (Scheme 3). Additionally, a Lewis acid blocks the oxygen-nucleophilic center thus securing C-regioselective acylation of enolate intermediate.

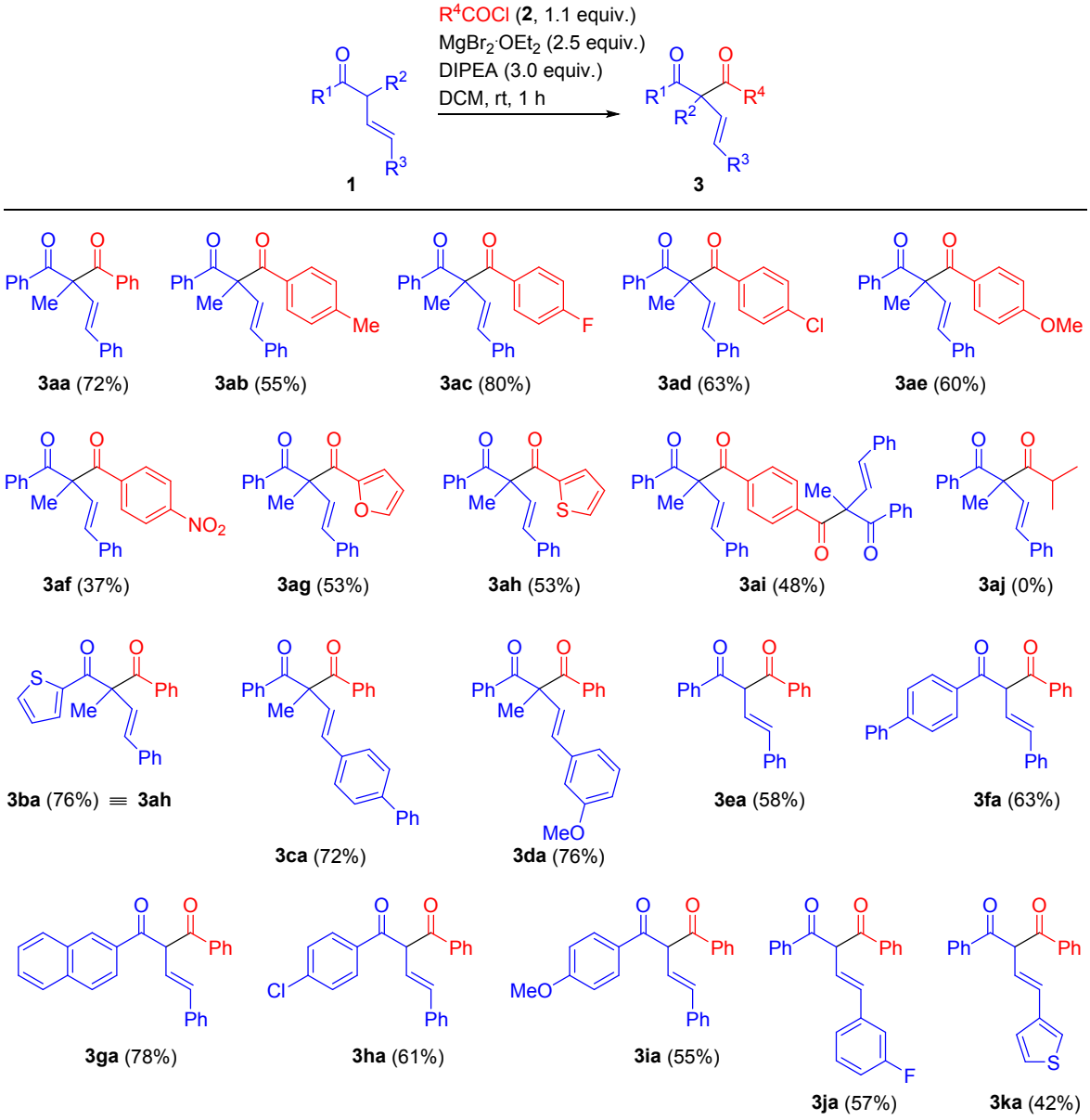
Scheme 3. Soft enolization concept



Given that only acetophenone, benzoyl chloride and isonicotinoyl chloride as aromatic substrates were previously tested in the synthesis of β-diketones[16d] we have decided to check this

stage in details with emphasis on structure both of β,γ-unsaturated ketones **1** and acyl chlorides **2** (Scheme 4).

Scheme 4. Synthesis of α-Alkenyl-β-Diketones 3 by Acylation of β,γ-Unsaturated Ketones 1

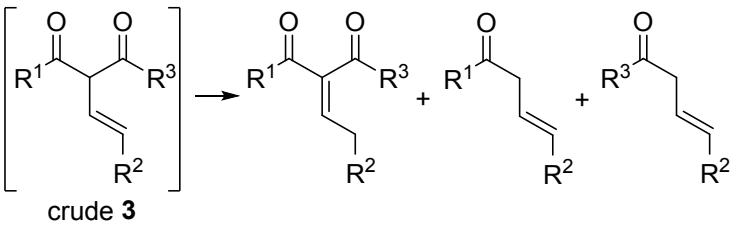


The synthesis of α-alkenyl-β-diketones **3** was implemented as follows: to a solution of acyl chloride **2** in dry DCM were sequentially added magnesium bromide etherate and β,γ-unsaturated ketone **1**, a mixture was stirred at ambient temperature for 5 min, then N,N-diisopropylethylamine was added, and the resulting reaction mixture was stirred at ambient temperature. The model reaction between ketone **1a** and benzoyl chloride **2a** was completed within 1 h to afford α-alkenyl-β-diketone **3aa** in 72% yield, while a similar reaction of acetophenone was conducted for 24 h giving 1,3-diphenylpropane-1,3-dione in 79% yield.[16d] Attempts to decrease the metal salt (to 1.5 equiv.) or the base (to 2.0 equiv.) loadings gave

slightly lower yields of diketone **3aa** (65% and 63%, respectively), whilst in the absence of the magnesium bromide etherate, the formation of only O-acylation product was observed. Acylation of the model ketone **1a** effectively proceeded with substituted aroyl **2b-2e**,**2i** and heteroaroyl **2g,h** chlorides providing the corresponding α-alkenyl-β-diketones **3ab-3ae**,**3ag-3ai** in good yields (48-80%, Scheme 4). Oddly, acylation of ketone **1a** with isobutyryl chloride **2j** did not afford the desired α-alkenyl-β-diketone **3aj** (only product of O-acylation was detected by ^{1}H NMR spectroscopy in a crude reaction mixture), although 4-methyl-1-phenylpentane-1,3-dione was formed from acetophenone in excellent 91% yield.[16d] According to the HSAB principle[17] the presence of alkenyl substituent at the methylene group of β,γ-unsaturated ketones **1** supposed to make softer the α-carbon nucleophilic center due to an extended conjugation system in the intermediate carbanion. As a result even under soft enolization approach β,γ-unsaturated ketones **1** in comparison with acetophenone turn out to be less suitable for the reaction with harder acyl chlorides (*e.g.*, 4-nitrobenzoyl chloride **2f** and isobutyryl chloride **2j**, Scheme 4).

On first glance, the structure of β,γ-unsaturated ketones **1** have no significant effect on the acylation reaction (*cf.* yields of **3aa** and **3ba-3da**, Scheme 4). However, the isolation and purification of α-alkenyl-β-diketones **3ea-3ka** having at the α-position hydrogen substituent instead of methyl group were a challenge because of instability of the synthesized diketones when subjected to active surfaces for column chromatography. In this case partial isomerization[18] and decomposition of α-alkenyl-β-diketones **3** to starting β,γ-unsaturated ketones **1** were observed (Scheme 5). Finally, α-alkenyl-β-diketones **3ea-3ka** were purified by a sequential extraction of crude with pentane/diethyl ether mixture. Because of partial solubility of diketones **3** even in a pure pentane, the yields of diketones **3ea-3ka** varied from 42% to 78% (Scheme 4).

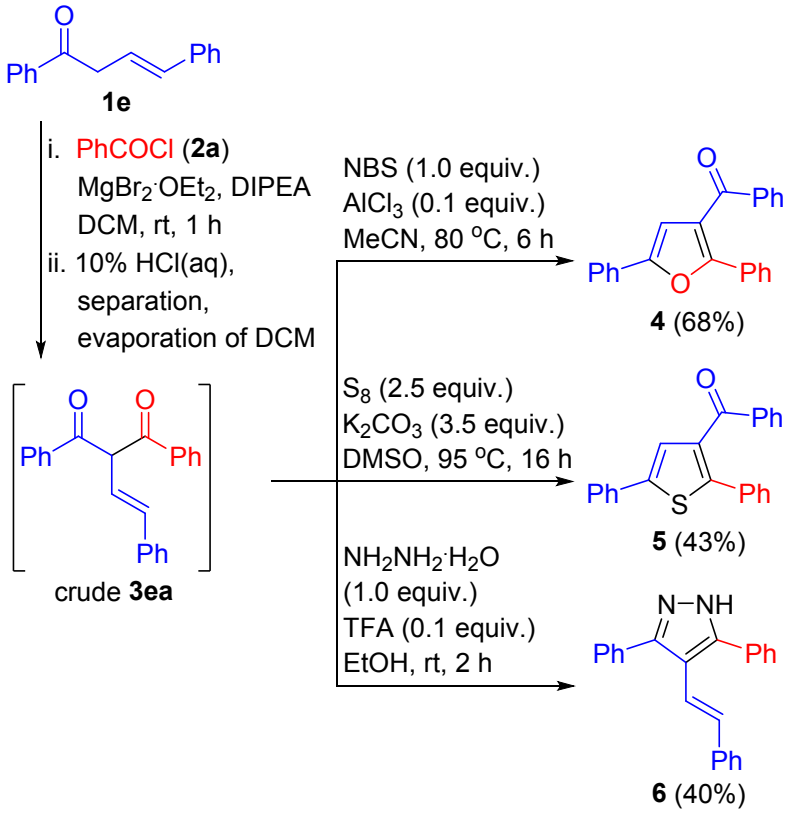
Scheme 5. Transformations of α-Alkenyl-β-Diketones 3 on Active Surfaces



Therefore it was important to demonstrate that α-alkenyl-β-diketones **3** can be used for further synthetic transformation in a crude form without purification. Thus, the treatment of a crude **3ea** with *N*-bromosuccinimide in the presence of a catalytic amount of aluminum chloride[3]

led to the formation of 3-benzoyl-2,5-diphenylfuran **4** in 68% yield. The similar sulfur derivative **5** was obtained in 43% yield from the reaction of a crude **3ea** with elemental sulfur under basic conditions.[4] The implementation of a classic cyclization of β-diketones with hydrazine hydrate on the example of α-alkenyl-β-diketone **3ea** afforded to the isomerically pure *N*-styrylpyrazole **6** in 40% yield (Scheme 6). Obviously, all the above reaction protocols can be optimized if necessary.

Scheme 6. Synthesis of Arylated Heterocycles from α-Alkenyl-β-Diketones



CONCLUSIONS

In summary, a novel retrosynthetic disconnection of α-alkenyl-β-diketones was proposed and verified by regio- and stereoselective two-step synthesis of highly arylated representatives. The developed reactions are operationally simple, tolerate to a broad range of commercially available aryl and hetaryl ketones, acetylenes and acyl chlorides and do not require sophisticated catalytic systems. The synthetic potential of the obtained highly arylated α-alkenyl-β-diketones was demonstrated by the assemblies of arylated heterocycles which are demanded for the design of novel pharmaceuticals and advanced materials.

EXPERIMENTAL SECTION

General Remarks. All chemicals and solvents were purchased from commercial sources. Dichloromethane was distilled over phosphorus pentoxide and stored over 4Å MS in order to remove any water. Magnesium bromide ethyl etherate was prepared from magnesium turnings and 1,2-dibromoethane in diethyl ether.[19]

Thin layer chromatography was carried out on Merck silica gel 60 F_{254} pre-coated aluminium foil sheets and were visualized using UV light (254 nm). Column chromatography was carried out using slurry packed Sigma Aldrich silica gel (SiO_2), 70-230 mesh, pore size 60 Å.

NMR spectra were recorded from solutions in $CDCl_3$ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^1H and 100.6 MHz for ^{13}C). Chemical shifts (δ) are quoted in parts per million (ppm). The residual solvent peak, δ_H 7.26 and δ_C 77.10 for $CDCl_3$ and δ_C 39.50 for DMSO-d_6, was used as a reference. Coupling constants (*J*) are reported in Hertz (Hz). The multiplicity abbreviations used are: s singlet, d doublet, dd doublet of doublet, t triplet, m multiplet, br broad signal. High-resolution mass spectra were recorded from acetonitrile solution with 0.1% HFBA on HPLC Agilent 1200/Agilent 6210 TOF instrument equipped with an electrospray ionization (ESI) source. Melting points (uncorrected) were measured on a digital melting point apparatus Electrothermal IA 9200.

General Procedure for the Synthesis of Starting β,γ-Unsaturated Ketones 1. A mixture of ketone (4.0 mmol), acetylene (4.0 mmol), and *t*-BuOK (449 mg, 4.0 mmol) in dry DMSO (10 mL) was stirred at 100 °C (silicon oil bath) for 30 min. The reaction mixture after cooling to room temperature was diluted with water (10 mL), neutralized with NH_4Cl (aq), and extracted with diethyl ether (4×10 mL). The combined organic extracts were washed with water (3×5 mL) and dried ($MgSO_4$). After removal of the solvent, the residue was purified by column chromatography to afford the desired β,γ-unsaturated ketones **1** in good and reproducible yields of 35-80%. Spectroscopic data for ketones **1a**,**b**,**d-k** were identical to that reported previously.[12h,j,14]

*(E)-4-([1,1'-Biphenyl]-4-yl)-2-methyl-1-phenylbut-3-en-1-one (**1c**)*. Following the general procedure, **1c** was prepared from propiophenone (536 mg, 4.0 mmol) and 4-ethynyl-1,1'-biphenyl (712 mg, 4.0 mmol); **1c** was purified by column chromatography using 2:98 ethyl acetate-hexane (v/v) as an eluent and isolated as a white solid (810 mg, 65% yield), mp 98-100 °C, R_f = 0.65 (hexane-diethyl ether, 3:1, v/v). ^1H NMR ($CDCl_3$,400.1 MHz): δ 8.07-8.05 (m, 2H), 7.61-7.54 (m, 5H), 7.51-7.42 (m, 6H), 7.37-7.33 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.44 (dd, *J* = 6.8 Hz, *J* = 16.0 Hz, 1H), 4.40-4.33 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.6 MHz): δ 201.1, 140.7, 140.4, 136.5, 136.0, 133.1, 131.3, 130.0, 128.8, 128.7,

128.6, 127.4, 127.3, 127.0, 126.8, 45.0, 17.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}O$ 313.1592; Found 313.1591.

General Procedure for the Synthesis of α-Alkenyl-β-Diketones 3. A 10-mL round-bottom flask with stir bar was sequentially charged with acyl chloride **2** (0.55 mmol, 1.1 equiv.), DCM (3 mL), $MgBr_2 \cdot OEt_2$ (323 mg, 1.25 mmol, 2.5 equiv.) and β,γ-unsaturated ketone **1** (0.5 mmol, 1.0 equiv.). The resulting suspension was stirred for 5 min, and then DIPEA (260 μL, 1.5 mmol, 3.0 equiv.) was added, the reaction flask was capped with a glass stopper, and the reaction mixture was stirred for 1 h. The reaction mixture was then quenched with 10% HCl(aq) (10 mL), stirred for 10 min, extracted with DCM (2×10 mL), the combined organic extracts were washed with water (1×10 mL), dried (K_2CO_3 or $CaCl_2$), filtered, and evaporated under reduced pressure at room temperature to give a crude diketone **3**. Diketones **3aa-3ai** and **3ca-3ea** were purified by column chromatography over silica gel. Diketones **3fa-3ka** were purified by sequential extraction of crude with diethyl ether-pentane mixture (gradient from 0/1 to 1/0, v/v) and isolated after evaporation of combined organic extracts (TLC control).

*(E)-2-Methyl-1,3-diphenyl-2-styrylpropane-1,3-dione (**3aa**)*. Following the general procedure, **3aa** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3aa** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a colorless oil (123 mg, 72% yield), which slowly crystallized on standing to a white solid, mp 87-89 °C, R_f = 0.53 (hexane-diethyl ether, 3:1, v/v). Additionally, a larger scale synthesis was performed starting from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (895 mg, 3.79 mmol) and benzoyl chloride **2a** (584 mg, 4.17 mmol); **3aa** was isolated as a white solid (815 mg, 63%). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.85-7.83 (m, 4H), 7.53 (d, *J* = 16.7 Hz, 1H), 7.40-7.35 (m, 4H), 7.29-7.25 (m, 6H), 7.24-7.19 (m, 1H), 6.41 (d, *J* = 16.7 Hz, 1H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.8, 136.8, 135.6, 133.0, 131.6, 129.7, 129.4, 128.6, 128.6, 127.9, 126.5, 64.4, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}O_2$ 341.1542; Found 341.1542.

*(E)-2-Methyl-1-phenyl-2-styryl-3-(p-tolyl)propane-1,3-dione (**3ab**)*. Following the general procedure, **3ab** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 4-methylbenzoyl chloride **2b** (85 mg, 0.55 mmol); **3ab** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a white solid (98 mg, 55% yield), mp 110-112 °C, R_f = 0.50 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.84-7.82 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 16.7 Hz, 1H), 7.40-7.38 (m, 3H), 7.31-7.27 (m, 4H), 7.23-7.20 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.38 (d, *J* = 16.7 Hz, 1H), 2.28 (s, 3H), 1.90 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 198.0, 197.4, 143.9, 136.9, 135.6, 133.0, 133.0, 131.5, 129.9, 129.6, 129.4, 129.3, 128.6, 128.6, 127.9, 126.5,

64.3, 25.3, 21.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O_2$ 355.1698; Found 355.1698.

*(E)-1-(4-Fluorophenyl)-2-methyl-3-phenyl-2-styrylpropane-1,3-dione (**3ac**)*. Following the general procedure, **3ac** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 4-fluorobenzoyl chloride **2c** (87 mg, 0.55 mmol); **3ac** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a colorless oil (144 mg, 80% yield), which slowly crystallized on standing to a white solid, mp 80-82 °C, R_f = 0.49 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.89-7.85 (m, 2H), 7.83-7.81 (m, 2H), 7.51 (d, *J* = 16.7 Hz, 1H), 7.43-7.39 (m, 3H), 7.32-7.29 (m, 4H), 7.25-7.21 (m, 1H), 6.98-6.94 (m, 2H), 6.38 (d, *J* = 16.7 Hz, 1H), 1.91 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.9, 196.3, 165.4 (d, *J* = 256.0 Hz), 136.7, 135.5, 133.2, 132.2 (d, *J* = 9.3 Hz), 131.8, 129.5, 129.4, 128.7, 128.7, 128.7, 128.1, 126.6, 115.8 (d, *J* = 21.9 Hz), 64.3, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}FO_2$ 359.1447; Found 359.1446.

*(E)-1-(4-Chlororophenyl)-2-methyl-3-phenyl-2-styrylpropane-1,3-dione (**3ad**)*. Following the general procedure, **3ad** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 4-chlorobenzoyl chloride **2d** (96 mg, 0.55 mmol); **3ad** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a colorless oil (119 mg, 63% yield), which slowly crystallized on standing to a white solid, mp 101-103 °C, R_f = 0.56 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.83-7.81 (m, 2H), 7.77 (d, *J* = 16.7 Hz, 2H), 7.49 (d, *J* = 16.7 Hz, 1H), 7.44-7.38 (m, 3H), 7.33-7.21 (m, 7H), 6.38 (d, *J* = 16.7 Hz, 1H), 1.91 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.7, 196.6, 139.5, 136.7, 135.5, 133.9, 133.2, 131.9, 130.8, 129.4, 129.4, 129.0, 128.7, 128.7, 128.1, 126.6, 64.3, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}ClO_2$ 375.1152; Found 375.1153.

*(E)-1-(4-Methoxyphenyl)-2-methyl-3-phenyl-2-styrylpropane-1,3-dione (**3ae**)*. Following the general procedure, **3ae** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 4-methoxybenzoyl chloride **2e** (94 mg, 0.55 mmol); **3ae** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a colorless oil (111 mg, 60% yield), which slowly crystallized on standing to a white solid, mp 98-100 °C, R_f = 0.30 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.85-7.83 (m, 4H), 7.53 (d, *J* = 16.7 Hz, 1H), 7.40-7.37 (m, 3H), 7.31-7.27 (m, 4H), 7.24-7.20 (m, 1H), 6.77 (d, *J* = 9.0 Hz, 2H), 6.38 (d, *J* = 16.7 Hz, 1H), 3.76 (s, 3H), 1.91 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 198.1, 196.2, 163.3, 136.9, 135.6, 132.9, 131.8, 131.4, 130.1, 129.4, 128.6, 128.6, 128.5, 127.9, 126.5, 113.8, 64.1, 55.4, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O_3$ 371.1647; Found 371.1647.

*(E)-2-Methyl-1-(4-nitrophenyl)-3-phenyl-2-styrylpropane-1,3-dione (**3af**)*. Following the general procedure, **3af** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 4-nitrobenzoyl chloride **2f** (102 mg, 0.55 mmol); **3af** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a pale yellow solid (72 mg, 37% yield), mp 142-144 °C, R_f = 0.43 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.12 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.83-7.81 (m, 2H), 7.47 (d, *J* = 16.7 Hz, 1H), 7.46-7.42 (m, 1H), 7.40-7.38 (m, 2H), 7.35-7.29 (m, 4H), 7.26-7.23 (m, 1H), 6.40 (d, *J* = 16.7 Hz, 1H), 1.95 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.4, 196.3, 149.9, 140.3, 136.3, 135.3, 133.5, 132.5, 130.3, 129.4, 128.9, 128.7, 128.6, 128.3, 126.6, 123.7, 64.6, 25.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_4$ 386.1392; Found 386.1394.

*(E)-1-(Furan-2-yl)-2-methyl-3-phenyl-2-styrylpropane-1,3-dione (**3ag**)*. Following the general procedure, **3ag** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 2-furoyl chloride **2g** (72 mg, 0.55 mmol); **3ag** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as an yellow oil (88 mg, 53% yield), R_f = 0.31 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.85-7.83 (m, 2H), 7.41 (d, *J* = 16.7 Hz, 1H), 7.41-7.39 (m, 4H), 7.33-7.28 (m, 4H), 7.24-7.21 (m, 1H), 7.16 (d, *J* = 3.5 Hz, 1H), 6.44 (d, *J* = 16.7 Hz, 1H), 6.37 (dd, *J* = 1.5 Hz, *J* = 3.5 Hz, 1H), 1.86 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 196.6, 186.6, 151.4, 146.4, 136.7, 135.7, 132.8, 131.8, 129.1, 128.6, 128.5, 128.4, 127.9, 126.5, 119.1, 112.4, 63.2, 23.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}O_3$ 331.1334; Found 331.1333.

*(E)-2-Methyl-1-phenyl-2-styryl-3-(thiophen-2-yl)propane-1,3-dione (**3ah**)*. Following the general procedure, **3ah** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and 2-thenoyl chloride **2h** (81 mg, 0.55 mmol) and purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent, isolated as an yellow oil (92 mg, 53% yield). Also **3ah** (as **3ba**, Scheme 4) was prepared from (*E*)-2-methyl-4-phenyl-1-(thiophen-2-yl)but-3-en-1-one **1b** (121 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol) and isolated as an yellow oil (132 mg, 76% yield), which slowly crystallized on standing to an yellow solid, mp 84-86 °C, R_f = 0.44 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.88-7.87 (m, 2H), 7.53-7.51 (m, 2H), 7.47 (d, *J* = 16.7 Hz, 1H), 7.42-7.38 (m, 3H), 7.34-7.28 (m, 4H), 7.24-7.21 (m, 1H), 6.96-6.94 (m, 1H), 6.41 (d, *J* = 16.7 Hz, 1H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.2, 190.8, 142.6, 136.7, 135.4, 134.4, 133.2, 133.0, 131.8, 129.4, 129.4, 128.6, 128.6, 128.4, 128.0, 126.5, 64.3, 25.1. HRMS (ESI-TOF) m/z: [M+H]+ Calcd for $C_{22}H_{19}O_2S$ 347.1106; Found 347.1106.

3,3'-(1,4-Phenylene)bis(2-methyl-1-phenyl-2-((E)-styryl)propane-1,3-dione) ***(3ai)***. Following the general procedure, **3ai** was prepared from (*E*)-2-methyl-1,4-diphenylbut-3-en-1-one **1a** (118 mg, 0.5 mmol) and terephthaloyl dichloride **2i** (51 mg, 0.25 mmol); **3ai** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as a pale yellow solid (72 mg, 48% yield), mp 163-165 °C, R_f = 0.28 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.72-7.70 (m, 4H), 7.68 (s, 4H), 7.41-7.33 (m, 7H), 7.30-7.26 (m, 5H), 7.24-7.19 (m, 6H), 6.33 (d, *J* = 16.7 Hz, 2H), 1.85 (s, 3H), 1.84 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.5, 197.2, 138.6, 136.5, 135.4, 133.1, 132.0, 129.3, 129.3, 129.0, 128.7, 128.7, 128.1, 126.6, 64.5, 25.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{42}H_{35}O_4$ 603.2535; Found 603.2537.

(E)-2-(2-([1,1'-Biphenyl]-4-yl)vinyl)-2-methyl-1,3-diphenylpropane-1,3-dione ***(3ca)***. Following the general procedure, **3ca** was prepared from (*E*)-4-([1,1'-biphenyl]-4-yl)-2-methyl-1-phenylbut-3-en-1-one **1c** (156 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ca** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent isolated as a colorless oil (149 mg, 72% yield), which slowly crystallized on standing to a white solid, mp 126-128 °C, R_f = 0.43 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.88-7.86 (m, 4H), 7.61-7.54 (m, 5H), 7.50-7.48 (m, 2H), 7.45-7.38 (m, 4H), 7.36-7.29 (m, 5H), 6.46 (d, *J* = 16.7 Hz, 1H), 1.96 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.8, 140.7, 140.6, 135.8, 135.6, 133.0, 131.2, 129.8, 129.4, 128.8, 128.6, 128.6, 127.4, 127.3, 127.0, 64.4, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{30}H_{25}O_2$ 417.1855; Found 417.1854.

(E)-2-(3-Methoxystyryl)-2-methyl-1,3-diphenylpropane-1,3-dione ***(3da)***. Following the general procedure, **3da** was prepared from (*E*)-4-(3-methoxyphenyl)-2-methyl-1-phenylbut-3-en-1-one **1d** (133 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3da** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent isolated as a colorless oil (140 mg, 76% yield), which slowly crystallized on standing to a white solid, mp 107-109 °C, R_f = 0.35 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.84-7.82 (m, 4H), 7.52 (d, *J* = 16.7 Hz, 1H), 7.41-7.37 (m, 2H), 7.31-7.27 (m, 4H), 7.21 (dd, *J* = 7.7 Hz, *J* = 8.2 Hz, 1H), 6.99 (dd, *J* = 1.8 Hz, *J* = 7.7 Hz, 1H), 6.93 (s, 1H), 6.78 (dd, *J* = 1.8 Hz, *J* = 8.2 Hz, 1H), 6.37 (d, *J* = 16.7 Hz, 1H), 3.80 (s, 3H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 197.8, 159.9, 138.2, 135.6, 133.0, 131.6, 130.0, 129.6, 129.4, 128.6, 119.2, 113.7, 111.7, 64.3, 55.3, 25.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}O_3$ 371.1647; Found 371.1646.

(E)-1,3-Diphenyl-2-styrylpropane-1,3-dione ***(3ea)***. Following the general procedure, **3ea** was prepared from (*E*)-1,4-diphenylbut-3-en-1-one **1e** (111 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ea** was purified by column chromatography using 5:95 diethyl ether-hexane (v/v) as an eluent and isolated as an yellow oil (95 mg, 58% yield, mixture of tautomers),

R_f = 0.36 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.04-8.02 (m, 4H), 7.58-7.55 (m, 2H), 7.48-7.41 (m, 6H), 7.32-7.29 (m, 2H), 7.26-7.24 (m, 1H), 6.79 (dd, *J* = 8.2 Hz, *J* = 16.1 Hz, 1H), 6.68 (d, *J* = 16.1 Hz, 1H), 6.04 (d, *J* = 8.2 Hz, 1H); some characteristic signals of isomeric 1,3-diketone: δ 7.98-7.96 (m, 2H), 7.82-7.80 (m, 2H), 6.90 (t, *J* = 8.0 Hz, 1H), 3.60 (d, *J* = 8.0 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.4, 136. 5, 135.9, 135.5, 133.7, 129.0, 129.0, 128.6, 128.1, 126.7, 122.9, 61.9; some characteristic signals of isomeric 1,3-diketone: δ 195.3, 194.2, 147.1, 141.9, 129.5, 129.4, 128.8, 36.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}O_2$ 327.1385; Found 327.1387.

*(E)-1-([1,1'-Biphenyl]-4-yl)-3-phenyl-2-styrylpropane-1,3-dione (**3fa**)*. Following the general procedure, **3fa** was prepared from (*E*)-1-([1,1'-biphenyl]-4-yl)-4-phenylbut-3-en-1-one **1f** (149 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol) and isolated as an yellow solid (127 mg, 63% yield), mp 64-66 °C, R_f = 0.33 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.09 (d, *J* = 7.9 Hz, 2H), 8.05-8.03 (m, 2H), 7.68-7.66 (m, 2H), 7.63-7.55 (m, 3H), 7.48-7.38 (m, 7H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.81 (dd, *J* = 8.2 Hz, *J* = 16.2 Hz, 1H), 6.69 (d, *J* = 16.2 Hz, 1H), 6.04 (d, *J* = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.4, 193.9, 146.4, 139.7, 136.4, 135.9, 135.5, 134.5, 133.7, 129.6, 129.0, 129.0, 129.0, 128.6, 128.4, 128.1, 127.6, 127.3, 126.7, 122.9, 62.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{29}H_{23}O_2$ 403.1698; Found 403.1697.

*(E)-1-(Naphthalen-2-yl)-3-phenyl-2-styrylpropane-1,3-dione (**3ga**)*. Following the general procedure, **3ga** was prepared from (*E*)-1-(naphthalen-2-yl)-4-phenylbut-3-en-1-one **1g** (136 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ga** was isolated as an orange solid (146 mg, 78% yield), mp 62-64 °C, R_f = 0.34 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.57 (s, 1H), 8.06-8.04 (m, 3H), 7.94-7.85 (m, 2H), 7.62-7.52 (m, 4H), 7.47-7.41 (m, 4H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 6.85 (dd, *J* = 8.2 Hz, *J* = 16.1 Hz, 1H), 6.72 (d, *J* = 16.1 Hz, 1H), 6.15 (d, *J* = 8.2 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.5, 194.3, 136.4, 135.9, 135.8, 135.5, 133.7, 133.2, 132.5, 130.9, 129.8, 128.9, 128.9, 128.9, 128.9, 128.6, 128.1, 127.8, 127.0, 126.7, 124.3, 123.0, 62.04. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{27}H_{21}O_2$ 377.1542; Found 377.1543.

*(E)-1-(4-Chlorophenyl)-3-phenyl-2-styrylpropane-1,3-dione (**3ha**)*. Following the general procedure, **3ha** was prepared from (*E*)-1-(4-chlorophenyl)-4-phenylbut-3-en-1-one **1h** (128 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ha** was isolated as a cream solid (110 mg, 61% yield), mp 121-123 °C, R_f = 0.43 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.01-8.00 (m, 2H), 7.94 (d, *J* = 8.7 Hz, 2H), 7.60-7.56 (m, 1H), 7.48-7.39 (m, 6H), 7.32-7.29 (m, 2H), 7.26-7.22 (m, 1H), 6.76 (dd, *J* = 8.0 Hz, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 16.1 Hz, 1H), 5.94 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.2, 193.3,

140.2, 136.3, 135.7, 134.2, 133.9, 130.3, 129.3, 129.0, 129.0, 128.7, 128.7, 128.3, 126.7, 122.5, 62.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}ClO_2$ 361.0995; Found 361.0996.

*(E)-1-(4-Methoxyphenyl)-3-phenyl-2-styrylpropane-1,3-dione (**3ia**)*. Following the general procedure, **3ia** was prepared from (*E*)-1-(4-methoxyphenyl)-4-phenylbut-3-en-1-one **1i** (126 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ia** was isolated as a cream solid (98 mg, 55% yield), mp 113-115 °C, R_f = 0.20 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.02-8.00 (m, 4H), 7.57-7.53 (m, 1H), 7.46-7.40 (m, 4H), 7.32-7.28 (m, 2H), 7.25-7.21 (m, 1H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.80 (dd, *J* = 8.2 Hz, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 16.2 Hz, 1H), 5.94 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.6, 192.7, 164.0, 136.5, 135.9, 135.1, 133.6, 131.3, 128.9, 128.9, 128.7, 128.6, 128.0, 126.6, 123.3, 114.1, 61.9, 55.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{24}H_{21}O_3$ 357.1491; Found 357.1492.

*(E)-2-(3-Fluorostyryl)-1,3-diphenylpropane-1,3-dione (**3ja**)*. Following the general procedure, **3ja** was prepared from (*E*)-4-(3-fluorophenyl)-1-phenylbut-3-en-1-one **1j** (120 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ja** was isolated as a cream solid (98 mg, 57% yield), mp 85-87 °C, R_f = 0.35 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.01-8.00 (m, 4H), 7.59-7.55 (m, 2H), 7.48-7.44 (m, 4H), 7.29-7.23 (m, 1H), 7.18-7.16 (m, 1H), 7.12-7.09 (m, 1H), 6.96-6.91 (m, 1H), 6.79 (dd, *J* = 8.3 Hz, *J* = 16.1 Hz, 1H), 6.63 (d, *J* = 16.1 Hz, 1H), 6.01 (d, *J* = 8.3 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.1, 163.1 (d, *J* = 245.6 Hz), 138.7 (d, *J* = 7.6 Hz), 135.7, 134.3 (d, *J* = 2.2 Hz), 133.8, 130.1 (d, *J* = 8.3 Hz), 129.0, 128.9, 124.4, 122.5 (d, *J* = 2.5 Hz), 114.9 (d, *J* = 21.4 Hz), 113.2 (d, *J* = 21.9 Hz), 61.66. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}FO_2$ 345.1291; Found 345.1293.

*(E)-1,3-Diphenyl-2-(2-(thiophen-3-yl)vinyl)propane-1,3-dione (**3ka**)*. Following the general procedure, **3ka** was prepared from (*E*)-1-phenyl-4-(thiophen-3-yl)but-3-en-1-one **1k** (114 mg, 0.5 mmol) and benzoyl chloride **2a** (77 mg, 0.55 mmol); **3ka** was isolated as a cream solid (70 mg, 42% yield), mp 112-114 °C, R_f = 0.31 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 8.02-8.00 (m, 4H), 7.59-7.55 (m, 2H), 7.48-7.44 (m, 4H), 7.27-7.26 (m, 2H), 7.18 (s, 1H), 6.69 (d, *J* = 16.1 Hz, 1H), 6.60 (dd, *J* = 8.0 Hz, *J* = 16.1 Hz, 1H), 5.99 (d, *J* = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 194.4, 139.1, 135.8, 133.7, 129.6, 129.0, 128.9, 126.2, 125.1, 123.1, 122.6, 61.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}O_2S$ 333.0949; Found 333.0949.

Procedures for the Synthesis of Heterocycles 4, 5 and 6. A crude diketone **3ea** was prepared as follows. A 10-mL round-bottom flask with stir bar was sequentially charged with benzoyl chloride **2a** (77 mg, 0.55 mmol, 1.1 equiv.), DCM (3 mL), $MgBr_2{\cdot}OEt_2$ (323 mg, 1.25 mmol, 2.5 equiv.) and (*E*)-1,4-diphenylbut-3-en-1-one **1e** (111 mg, 0.5 mmol, 1.0 equiv.). The

resulting suspension was stirred for 5 min, and then DIPEA (260 μL, 1.5 mmol, 3.0 equiv.) was added, the reaction flask was capped with a glass stopper, and the reaction mixture was stirred for 1 h. The reaction mixture was then quenched with 10% HCl(aq) (10 mL), stirred for 10 min, extracted with DCM (2×10 mL), the combined organic extracts were washed with water (1×10 mL), dried ($CaCl_2$), filtered, and evaporated under reduced pressure at room temperature to give a crude diketone **3ea**, which was used for the synthesis of heterocycles **4**, **5** and **6**.

*(2,5-Diphenylfuran-3-yl)(phenyl)methanone (**4**)*.[20] To a crude diketone **3ea** (0.5 mmol) were sequentially added MeCN (1 mL), *N*-bromosuccinimide (89 mg, 0.5 mmol, 1.0 equiv.) and anhydrous $AlCl_3$ (7 mg, 0.05 mmol, 0.1 equiv.). The mixture was then stirred at 80 °C (silicone oil bath) for 6 h. After reaction, the solvent was evaporated; the furan **4** was purified by column chromatography over silica gel using 5:95 diethyl ether-hexane (v/v) and isolated as an yellow oil (110 mg, 68% yield), which slowly crystallized on standing to an yellow solid, mp 68-70 °C, R_f = 0.48 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.91-7.89 (m, 2H), 7.80-7.76 (m, 4H), 7.56-7.52 (m, 1H), 7.46-7.39 (m, 4H), 7.36-7.31 (m, 4H), 6.94 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 191.8, 155.0, 152.5, 138.1, 133.0, 129.8, 129.8, 129.1, 128.9, 128.9, 128.4, 128.4, 128.2, 127.5, 124.1, 122.9, 108.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}O_2$ 325.1229; Found 325.1229.

*(2,5-Diphenylthiophen-3-yl)(phenyl)methanone (**5**)*.[21] To a crude diketone **3ea** (0.5 mmol) were sequentially added DMSO (2.5 mL), S_8 (40 mg, 1.25 mmol, 2.5 equiv.) and K_2CO_3 (242 mg, 1.75 mmol, 3.5 equiv.). The mixture was then stirred at 95 °C (silicone oil bath) for 16 h. After cooling to room temperature the reaction mixture was poured into water (10 mL), extracted with diethyl ether (3×10 mL) and dried over K_2CO_3. The residue after solvent evaporation was purified by column chromatography over silica gel using 5:95 diethyl ether-hexane (v/v) and the thiophene **5** was isolated as an yellow oil (73 mg, 43% yield), R_f = 0.50 (hexane-diethyl ether, 3:1, v/v). ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 7.80-7.79 (m, 2H), 7.65-7.63 (m, 2H), 7.49 (s, 1H), 7.46-7.40 (m, 3H), 7.38-7.35 (m, 2H), 7.33-7.29 (m, 3H), 7.23-7.21 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz): δ 192.9, 146.6, 143.2, 137.6, 137.5, 133.4, 133.1, 132.9, 130.0, 129.1, 129.1, 128.5, 128.4, 128.2, 128.2, 125.9, 125.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{17}OS$ 341.1000; Found 341.1000.

*(E)-3,5-Diphenyl-4-styryl-1H-pyrazole (**6**)*. To a crude diketone **3ea** (0.5 mmol) were sequentially added EtOH (2 mL), trifluoroacetic acid (4 μL, 0.05 mmol, 0.1 equiv.) and hydrazine [40 mg of 40%(aq) solution, 0.5 mmol, 1.0 equiv.]. After stirring at room temperature for 2 h, the volatiles were evaporated. The residue was recrystallized from EtOH to afford the pyrazole **6** as a white solid (64 mg, 40% yield), mp 203-205 °C. ^{1}H NMR ($CDCl_3$, 400.1 MHz): δ 11.18 (br s, 1H), 7.61-7.59 (m, 4H), 7.44-7.37 (m, 6H), 7.30-7.26 (m, 4H), 7.22-7.18 (m, 1H),

7.05 (d, J = 16.6 Hz, 1H), 6.59 (d, J = 16.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 100.6 MHz): δ 149.5 (br s), 141.0 (br s), 137.3, 133.8 (br s), 130.1, 128.6, 128.1, 128.0 (br s), 127.1, 125.7, 119.4, 113.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}N_2$ 323.1548; Found 323.1548.

ASSOCIATED CONTENT

Supporting Information

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

Copies of ^1H and ^{13}C NMR spectra of all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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