Synthesis of (*E*)-1,4-diaryl-2-butene-1,4-diones

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Abstract

We report a facile route for the preparation of symmetric and unsymmetric (*E*)-1,4-diaryl-2-butene-1,4-diones **3** by a two-step route, including (1) nucleophilic substitution of **1** with sulfinic acid sodium salts, and (2) K_2CO_3 mediated alkylation of β-ketosulfones **4** with **1** followed by sequential desulfonylation of the resulting 1,4-diketones **5** in acetone. These products were obtained in high yields.

Keywords: Enedione, ketosulfone, quinoxaline, condensation

Introduction

β-Ketosulfones are key synthetic intermediates that can easily be prepared through direct nucleophilic substitution of α-haloacetophenones, aerobic oxysulfonylation of functionalized alkenes and terminal alkynes and oxidation of α-mercapto ketones in organic and medicinal fields.[1-6] Notably, a number of examples have been reported for versatile functional group transformations.[7-29] The diversified skeletons include (1) acyclic diketones,[7] α-methenyl ketones,[8-9] and styrylsulfones,[15] (2) monocyclic sulfones,[10] cyclopropanes,[16] triazoles,[11] pyrazoles,[12-13] dihydrofurans,[14,19] tetrahydrofurans,[17] tetrahydropyrans,[18] pyrroles,[20] furans,[21-22] benzenes,[23] and pyridazines,[24] (3) bicyclic benzosuberans,[25] tetralins,[26] and naphthalenes,[27] (4) tricyclic phenanthrenes,[28] and (5) tetracyclic phenanthrofurans.[29]

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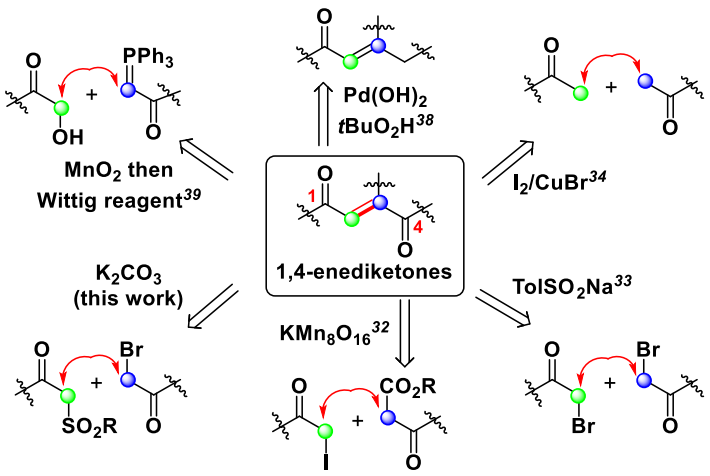

Scheme 1. Synthetic routes toward (*E*)-ene-1,4-diones

Results and Discussion

In continuation of the investigation on synthetic applications of β-ketosulfone, this study develops a facile synthesis of (*E*)-1,4-diaryl-2-butene-1,4-diones via K_2CO_3 mediated alkylative desulfonylation of β-ketosulfone with α-haloacetophenone. As shown in Scheme 1, ene-1,4-diketone is a versatile building block in the synthesis of bioactive molecules.[30-31] A number of articles have highlighted the fascinating development of core 1,4-enedione,[32-39] including KMn_8O_{16} catalyzed reaction of β-ketoesters and α-iodoacetophenones,[32] the direct nucleophilic substitution of α-haloacetophenones and $TolSO_2Na$,[33] iodine/copper complex or hypervalent iodine mediated oxidative self- or cross-coupling of methyl ketones,[35-37] $Pd(OH)_2$/*t*BuO_2H promoted allylic oxidation of enones,[38] and the tandem reaction of α-hydroxyacetophenones with MnO_2 and Wittig reagent.[39] Kong et al. recently reported a one-pot facile method for the synthesis of symmetric and unsymmetric ene-1,4-diones with *E*-form selectivity from the diversified α-bromoacetophenones though a sodium sulfinate (0.5 eq) mediated reaction in the presence of K_2CO_3 (1.5 eq) at rt for 12 h, and in situ the generated β-ketosulfone played a key intermediate in the transformation (Scheme 2 and eq 1).[33]

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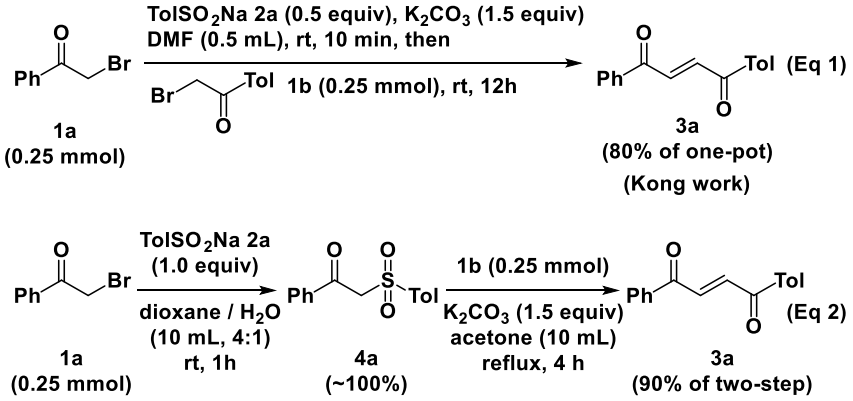

Scheme 2. Synthetic sequence of unsymmetrical ene-1,4-diones.

Although this one-pot route is mild, simple and convenient, the probability for two incomplete conversions should increase, especially for the formation of an unsymmetric skeleton of ene-1,4-dione, including (1) a nucleophilic substitution of α-bromoacetophenone (**1a**) with $TolSO_2Na$ (**2a**, 0.5 equiv) in the presence of K_2CO_3 (1.5 equiv) affording β-ketosulfone and followed by (2) a desulfonylative elimination of the resulting β-ketosulfone with α-bromo 4-methylacetophenone (**1b,** 1.0 equiv) producing ene-1,4-dione **3a**. Under a highly concentrated reaction mixture (1.5 M, based on all substrates/DMF), we assumed that a different solubility of substrates should perform a competitive reaction easily during the overall process. However, this domino route often had other drawbacks, such as the use of a high boiling point solvent, and moderate isolated yields. Inspired by this route and with our interest in exploring practical applications of β-ketosulfones, herein we report the synthesis of symmetric and unsymmetric (*E*)-1,4-Diaryl-2-butene-1,4-diones by the conventional step-by-step route (Scheme 2 and eq 2). Initially, the nucleophilic substitution of **1a** with 1.0 equivalent of **2a** provided **4a** in a quantitative yield after the recrystallization process.

Following a stepwise sequence, the K_2CO_3 (1.5 equiv) mediated reaction of **4a** and **1b** (1.0 equiv) produced **3a** (46%) and **5a** (43%) with a yield ratio of 1:1 at rt for 4 h, as shown in Table 1 and entry 1. By an elongated time (3 → 20 h), the yield of **3a** (52%) increased slightly and 33% yield of **5a** was formed (entry 2). To elevate the reaction temperature (rt → reflux), **3a** was isolated in a 90% yield at 4 h (entry 3). Compared with the reaction temperature and time, the refluxing condition could enhance the yield of **3a**. To combine the reaction condition of the reflux temperature (56 ^oC) and elongating time (20 h), the yield of **3a** was decreased (90% → 72%, entry 4). When the equivalent of K_2CO_3 was doubled, no obvious changes occurred (entry 5). Changing the solvent to THF, only the starting material **4a** was recovered in an 84% yield due to the low solubility of K_2CO_3 in THF (entry 6). Controlling the reflux (56 ^oC) and time (4 h) condition, other inorganic bases have been examined in entries 7-9. Changing K_2CO_3 to Li_2CO_3, Na_2CO_3, or Cs_2CO_3, these yields of **3a** did not exhibit any obvious changes. Further variations of the reaction parameters such as the organic bases were carried out (entries 10-11). However, treatment of **4a** with DBU and DABCO in THF at reflux for 4 h afforded **5a** in low yields (10% and 6%). In entries 10-11, major **4a** was recovered and no isolation of **3a** was observed. On the basis of a higher yield,

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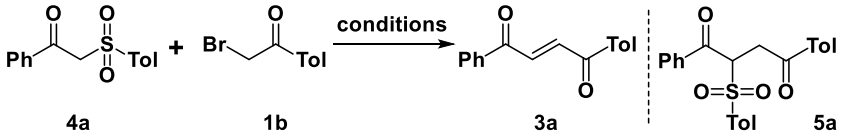
we believe that the combination of K_2CO_3/refluxing acetone/4 h should be an optimal reaction condition for the formation of **3a**. With the facile reaction condition in hand (Table 1, Entry 3), we further explored the conversion of other substrate scopes, and the results are shown in Table 2. K_2CO_3-mediated alkylative desulfonylation of β-ketosulfones **4a-f** (Ar = 4-$MeOC_6H_4$, Tol, 4-PhC_6H_4; and R = Tol, Ph, Me) and α-bromoacetophenones **1a-1i** (Ar^1 = Tol, Ph, 3-$MeOC_6H_4$, 4-FC_6H_4, 4-$MeOC_6H_4$, 4-PhC_6H_4, 2,4-$(MeO)_2C_6H_3$, 2,5-$(MeO)_2C_6H_3$, 2-naphthyl) in acetone at reflux provided **3a-r** in a yield range of 86%~94%. The structures of **3n** and **3r** were determined by single-crystal X-ray crystallography.[41]

Table 1. Optimal conditions[a]



Entry	Base (equiv)	Solvent	Temp (°C)	Time (h)	**3a** (%)[b]
1	K_2CO_3 (1.5)	acetone	25	4	46 (43)[c]
2	K_2CO_3 (1.5)	acetone	25	20	52 (33)[c]
3	K_2CO_3 (1.5)	acetone	56	4	90
4	K_2CO_3 (1.5)	acetone	56	20	72
5	K_2CO_3 (3.0)	acetone	56	4	85
6	K_2CO_3 (1.5)	THF	67	4	—[d]
7	Li_2CO_3 (1.5)	acetone	56	4	80
8	Na_2CO_3 (1.5)	acetone	56	4	86
9	Cs_2CO_3 (1.5)	acetone	56	4	88
10	DBU (1.5)	THF	67	4	—[d]
11	DABCO (1.5)	THF	67	4	—[d]

[a]Reaction was run with **1a** (0.25 mmol), **1b** (1.0 equiv) and solvent (10 mL). [b]Isolated yields. [c]Isolated yield of **5a**. [d]**3a** was recovered (for entry 6, 84%; for entry 10, 86%; for entry 11, 86%).

The yield of **3** did not change much as the function of the structures of **4** and **1** under these conditions. Changing the base to 1.0 equivalent of LDA (from 1.5 equivalent of K_2CO_3) and decreasing the temperature to -78°C (from reflux), the alkylation of **4** (Ar =; **4a**, Ph; **4c**, Tol; **4b**, 4-$MeOC_6H_4$; **4g**, 2,4-$(MeO)_2C_6H_3$) with **1** (Ar^1 =; **1b**, Tol; **1g**, 3,4-$(MeO)_2C_6H_3$; **1e**, 4-$MeOC_6H_4$) provided **5a-e** in a yield range of 73~81% at -78 °C for 4 h, as shown in Table 3. Compared with the K_2CO_3/acetone/reflux condition, we found that the LDA/THF/-78 °C system could perform only the generation of sulfonyl 1,4-diketones **5** and no isolation of ene-1,4-diones **3**.

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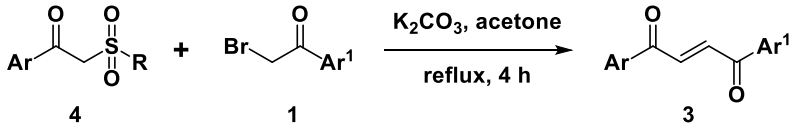
Table 2. Synthesis of **3a-r**[a]



Entry	**4**, Ar =, R =	**1**, Ar^1 =	**3** (%)[b]
1	**4a**, Ph, Tol	**1b**, Tol	**3a**, 90
2	**4a**, Ph, Tol	**1a**, Ph	**3b**, 90
3	**4a**, Ph, Tol	**1c**, 3-$MeOC_6H_4$	**3c**, 93
4	**4a**, Ph, Tol	**1d**, 4-FC_6H_4	**3d**, 87
5	**4a**, Ph, Tol	**1e**, 4-$MeOC_6H_4$	**3e**, 94
6	**4a**, Ph, Tol	**1f**, 4-PhC_6H_4	**3f**, 91
7	**4a**, Ph, Tol	**1g**, 2,4-$(MeO)_2C_6H_3$	**3g**, 92
8	**4a**, Ph, Tol	**1h**, 2,5-$(MeO)_2C_6H_3$	**3h**, 88
9	**4a**, Ph, Tol	**1i**, 2-naphthyl	**3i**, 86
10	**4b**, 4-$MeOC_6H_4$, Tol	**1e**, 4-$MeOC_6H_4$	**3j**, 94
11	**4b**, 4-$MeOC_6H_4$, Tol	**1b**, Tol	**3k**, 90
12	**4b**, 4-$MeOC_6H_4$, Tol	**1c**, 3-$MeOC_6H_4$	**3l**, 89
13	**4b**, 4-$MeOC_6H_4$, Tol	**1f**, 4-PhC_6H_4	**3m**, 91
14	**4b**, 4-$MeOC_6H_4$, Tol	**1i**, 2-naphthyl	**3n**, 87
15	**4c**, Tol, Tol	**1c**, 3-$MeOC_6H_4$	**3o**, 86
16	**4c**, Tol, Tol	**1f**, 4-PhC_6H_4	**3p**, 93
17	**4c**, Tol, Tol	**1i**, 2-naphthyl	**3q**, 91
18	**4d**, 4-PhC_6H_4, Tol	**1h**, 2,5-$(MeO)_2C_6H_3$	**3r**, 88
19	**4e**, Ph, Ph	**1a**, Ph	**3b**, 88
20	**4f**, Ph, Me	**1a**, Ph	**3b**, 91

[a]The synthesis of **3** was run with **4** (0.25 mmol),**1** (0.25 mmol), acetone (10 mL), 4 h, reflux.
[b]Isolated yields.

As an extension of this method, we were able to execute a synthesis of quinoxaline, as shown in Scheme 3. Quinoxaline was a versatile scaffold for useful synthetic intermediates.[41-42] It was also known to exhibit versatile biological activities.[43-44] On the basis of these significant characteristics, many protocols have been developed for the synthesis of quinoxalines. According to reported literature, the most popular procedures are derived from the condensation of 1,2-diaminobenzenes with a number of polar *ortho*-carbon units, such as aldehydes, ketones, 1,2-diketones, epoxides, vicinal diols, diazoketone, alkenes, and alkyne.[45] Among these starting substrates, only one example on the skeleton of 1,4-enediketone has been reported for the formation of quinoxaline.[46] Furthermore, condensation of **3b** with 1,2-diaminobenzenes **6a-d** in dioxane for 4 h at reflux provided quinoxalines **7a-d** (78%-86%) and acetophenone (**8**) via a tandem process

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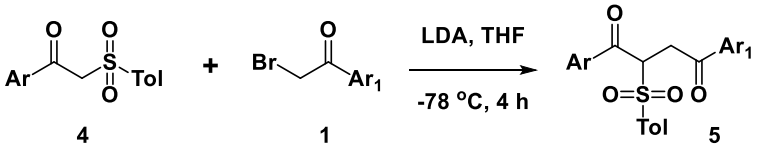
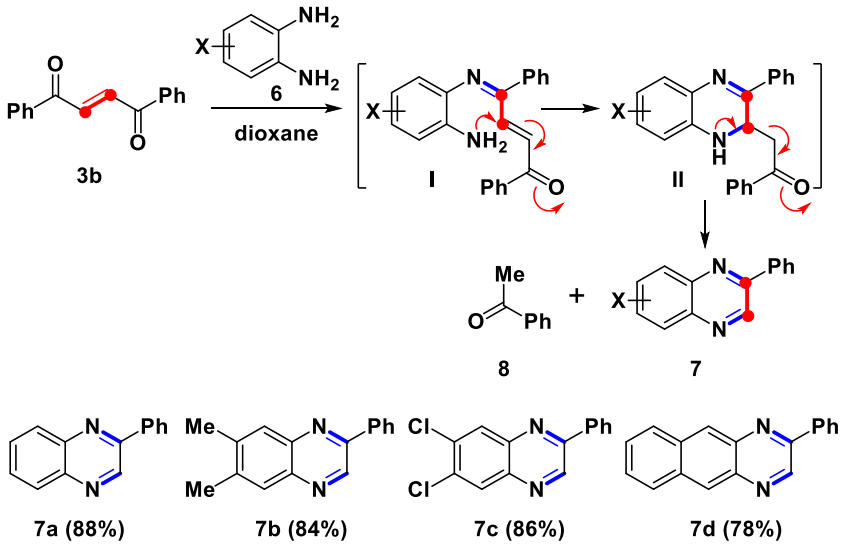
of the condensation of **3b** and **6**, the intramolecular Michael addition of intermediate **I**, and the retro-aldol reaction of intermediate **II**.

Table 3. Alkylation of **4** with **1**[a]



Entry	**4**, Ar =	**1**, Ar^1 =	**5** (%)[b]
1	**4a**, Ph	**1b**, Tol	**5a**, 81
2	**4c**, Tol	**1b**, Tol	**5b**, 75
3	**4c**, Tol	**1g**, 2,4-$(MeO)_2C_6H_3$	**5c**, 77
4	**4b**, 4-$MeOC_6H_4$	**1g**, 2,4-$(MeO)_2C_6H_3$	**5d**, 73
5	**4g**, 2,4-$(MeO)_2C_6H_3$	**1e**, 4-$MeOC_6H_4$	**5e**, 76

[a]The synthesis of **5** was run with **4** (0.25 mmol),**1** (0.25 mmol), LDA (0.5 M in THF, 1.0 equiv), THF (5 mL). [b]Isolated yields.



Scheme 3. Condensation of **3b** with 1,2-diaminobenzenes **6a-d.**

Conclusions

We have developed a mild and facile synthesis of substituted symmetric and unsymmetric ene-1,4-diketones **3** in good yields by a two-step route, including (1) nucleophilic substitution of α-bromoacetophenones **1** with sulfinic acid sodium salts **2** in a co-solvent of dioxane and water at rt

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for 1 h, and (2) K_2CO_3 mediated alkylation of β-ketosulfones **4** with substituted α-bromoacetophenones **1** followed by sequential desulfonylation of the resulting α-sulfonyl 1,4-diketones **5** in acetone at reflux for 4 h. Morever, quinoxalines **7** have been synthesized from a condensation of ene-1,4-diketone **3b** with 1,2-diaminobenzenes **6**. Further investigation regarding the synthetic applications of β-ketosulfones will be conducted and published in due course.

Experimental Section

General. All other reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry nitrogen with magnetic stirring. Products in organic solvents were dried with anhydrous $MgSO_4$ before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 200/400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD). Elemental analyses were carried out with Heraeus Vario III-NCSH, Heraeus CHN-OS-Rapid Analyzer or Elementar Vario EL III.

A representative procedure for compounds 3a-r is as follows. A solution of sodium arenesulfinic acid salts **2** (0.25 mmol) in H_2O (2 mL) was added to a solution of substituted α-bromoacetophenones **1** (0.25 mmol) in dioxane (8 mL) at rt. The reaction mixture was stirred at rt for 1 h and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product **4a-f** in nearly quantitative yields. Without further purification, K_2CO_3 (52 mg, 0.377 mmol) was added to a solution of the resulting **4** (~0.25 mmol) in acetone (8 mL) at rt. The reaction mixture was stirred at rt for 5 min. α-Bromoacetophenones **1a-i** (0.25 mmol) in acetone (2 mL) was added to the resulting reaction mixture at rt. The reaction mixture was refluxed for 4 h, cooled to rt, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc 10/1~3/1) afforded compounds **3a-r**.

1-Phenyl-4-p-tolylbut-2-ene-1,4-dione (3a). R_f 0.3 (hexanes : EtOAc 6:1); Yield 90% (56 mg); Colorless solid; mp 83-84 ^oC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{15}O_2$ 251.1072, found 251.1075; ^1H NMR (400 MHz, $CDCl_3$): δ 8.08-8.04 (m, 2H), 8.00 (s, 2H), 7.97 (d, *J* 8.0 Hz, 2H), 7.65-7.61 (m, 1H), 7.55-7.50 (m, 2H), 7.32 (d, *J* 8.0 Hz, 2H), 2.44

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(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.87, 189.25, 144.93, 136.92, 135.26, 134.73, 134.41, 133.77, 129.58 (2x), 129.12 (2x), 128.84 (4x), 21.74.

1,4-Diphenylbut-2-ene-1,4-dione (3b). In Table 2, for entry 2, R_f 0.3 (hexanes : EtOAc 6:1); Yield 90% (53 mg); For entry 19, Yield 88% (52 mg); For entry 20, Yield 91% (54 mg); Colorless solid; mp 108-109 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{13}O_2$ 237.0916, found 237.0912; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08-8.05 (m, 4H), 8.02 (s, 2H), 7.66-7.62 (m, 2H), 7.55-7.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.81 (2x), 136.85 (2x), 135.09 (2x), 133.86 (2x), 128.89 (4x), 128.87 (4x).

1-(3-Methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (3c). R_f 0.3 (hexanes : EtOAc 4:1); Yield 93% (62 mg); Colorless solid; mp 65-66 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{15}O_3$ 267.1021, found 267.1020; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07-8.03 (m, 2H), 8.00 (s, 1H), 7.99 (s, 1H), 7.65-7.61 (m, 2H), 7.57-7.50 (m, 3H), 7.43 (t, *J* 8.0 Hz, 1H), 7.19-7.16 (m, 1H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.77, 189.54, 160.02, 138.17, 136.82, 135.10, 135.04, 133.83, 129.84, 128.86 (2x), 128.84 (2x), 121.62, 120.63, 112.65, 55.47.

1-(4-Fluorophenyl)-4-phenylbut-2-ene-1,4-dione (3d). R_f 0.3 (hexanes : EtOAc 8:1); Yield 87% (55 mg); Colorless solid; mp 102-103 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{12}FO_2$ 255.0821, found 255.0817; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13-8.05 (m, 4H), 8.01 (s, 1H), 8.00 (s, 1H), 7.66-7.62 (m, 1H), 7.56-7.51 (m, 2H), 7.23-7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.64, 188.13, 166.19 (d, *J* 255.5 Hz), 136.79, 135.26, 134.66, 133.92, 133.31 (d, *J* 3.1 Hz), 131.65, 131.56, 128.91 (2x), 128.87 (2x), 116.13 (d, *J* 22.0 Hz, 2x).

1-(4-Methoxyphenyl)-4-phenylbut-2-ene-1,4-dione (3e). R_f 0.3 (hexanes : EtOAc 4:1); Yield 94% (63 mg); Colorless solid; mp 80-81 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{17}H_{15}O_3$ 267.1021, found 267.1018; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.01 (m, 4H), 8.02 (s, 1H), 8.01 (s, 1H), 7.65-7.61 (m, 1H), 7.55-7.51 (m, 2H), 7.01-6.98 (m, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.95, 187.94, 164.22, 136.94, 135.29, 134.39, 133.78, 131.34 (2x), 129.97, 128.86 (4x), 114.12 (2x), 55.56.

1-Biphenyl-4-yl-4-phenylbut-2-ene-1,4-dione (3f). R_f 0.3 (hexanes : EtOAc 6:1); Yield 91% (71 mg); Colorless solid; mp 155-156 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{22}H_{17}O_2$ 313.1229, found 313.1230; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16-8.13 (m, 2H), 8.09-8.07 (m, 2H), 8.06 (s, 1H), 8.05 (s, 1H), 7.76-7.73 (m, 2H), 7.66-7.62 (m, 3H), 7.55-7.40 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.75, 189.15, 146.49, 139.52, 136.84, 135.03, 135.03, 134.92, 133.81, 129.47 (2x), 128.85 (2x), 128.85 (4x), 128.42, 127.45 (2x), 127.25 (2x).

1-(2,4-Dimethoxyphenyl)-4-phenylbut-2-ene-1,4-dione (3g). R_f 0.2 (hexanes : EtOAc 4:1); Yield 92% (68 mg); Colorless solid; mp 105-106 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_4$ 297.1127, found 297.1130; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03-8.01 (m, 2H), 7.93 (dd, *J* 0.8, 15.2 Hz, 1H), 7.81 (dd, *J* 0.8, 8.8 Hz, 1H), 7.79 (dd, *J* 0.8, 15.2 Hz, 1H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 6.54 (ddd, *J* 0.8, 2.0, 8.8 Hz, 1H), 6.45 (d, *J* 2.0 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.69, 189.15, 165.22, 161.22, 140.52, 137.10, 133.37, 133.22, 131.99, 128.73 (2x), 128.62 (2x), 120.77, 105.68, 98.24, 55.62, 55.49.

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1-(2,5-Dimethoxyphenyl)-4-phenylbut-2-ene-1,4-dione (3h). R_f 0.2 (hexanes : EtOAc 4:1); Yield 88% (65 mg); Colorless viscous oil; HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_4$ 297.1127, found 297.1130; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06-8.04 (m, 2H), 7.89 (d, *J* 15.2 Hz, 1H), 7.82 (d, *J* 15.2 Hz, 1H), 7.65-7.60 (m, 1H), 7.54-7.49 (m, 2H), 7.28 (d, *J* 3.6 Hz, 1H), 7.10 (dd, *J* 3.6, 9.2 Hz, 1H), 6.95 (d, *J* 9.2 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.24, 190.71, 153.71, 153.65, 139.87, 137.11, 133.60, 132.72, 128.89 (2x), 128.78 (2x), 127.95, 121.30, 114.19, 113.30, 56.28, 55.87.

1-Naphthalen-2-yl-4-phenylbut-2-ene-1,4-dione (3i). R_f 0.3 (hexanes : EtOAc 6:1); Yield 86% (61 mg); Colorless solid; mp 115-116 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{20}H_{15}O_2$ 287.1072, found 287.1075; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H), 8.21 (d, *J* 15.2 Hz, 1H), 8.14-8.07 (m, 4H), 8.01 (d, *J* 8.4 Hz, 1H), 7.95 (d, *J* 8.4 Hz, 1H), 7.90 (d, *J* 8.0 Hz, 1H), 7.67-7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.86, 189.49, 136.92, 135.89, 135.13, 134.93 (2x), 134.28, 133.88, 132.46, 131.16, 129.77, 129.05, 128.94 (2x), 128.90 (2x), 127.86, 127.06, 124.05.

1,4-Bis-(4-methoxyphenyl)but-2-ene-1,4-dione (3j). R_f 0.2 (hexanes : EtOAc 4:1); Yield 94% (70 mg); Colorless solid; mp 161-162 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_4$ 297.1127, found 297.1130; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* 8.8 Hz, 4H), 8.01 (s, 2H), 6.98 (d, *J* 8.8 Hz, 4H), 3.89 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.07 (2x), 164.14 (2x), 134.56 (2x), 131.31 (4x), 130.06 (2x), 114.08 (4x), 55.53 (2x).

1-(4-Methoxyphenyl)-4-*p*-tolylbut-2-ene-1,4-dione (3k). R_f 0.3 (hexanes : EtOAc 4:1); Yield 90% (63 mg); Colorless solid; mp 105-106 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_3$ 281.1178, found 281.1175; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* 8.8 Hz, 2H), 8.00 (s, 2H), 7.97 (d, *J* 8.0 Hz, 2H), 7.31 (d, *J* 8.4 Hz, 2H), 6.98 (d, *J* 8.8 Hz, 2H), 3.89 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.40, 188.02, 164.17, 144.84, 134.91, 134.56, 131.31 (2x), 130.02, 129.55 (2x), 129.00 (2x), 127.81, 114.09 (2x), 55.54, 21.74.

1-(3-Methoxyphenyl)-4-(4-methoxyphenyl)but-2-ene-1,4-dione (3l). R_f 0.3 (hexanes : EtOAc 4:1); Yield 89% (66 mg); Colorless solid; mp 93-94 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_4$ 297.1127, found 297.1123; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* 8.8 Hz, 2H), 7.98 (br s, 1H), 7.97 (br s, 1H), 7.63 (ddd, *J* 0.8, 1.6, 8.0 Hz, 1H), 7.50 (dd, *J* 1.6, 2.4 Hz, 1H), 7.41 (d, *J* 8.0 Hz, 1H), 7.17-7.14 (m, 1H), 6.98 (d, *J* 8.8 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.62, 187.86, 164.16, 159.97, 138.24, 135.20, 134.36, 131.28 (2x), 129.92, 129.78, 121.57, 120.50, 114.07 (2x), 112.62, 55.50, 55.43.

1-Biphenyl-4-yl-4-(4-methoxyphenyl)but-2-ene-1,4-dione (3m). R_f 0.3 (hexanes : EtOAc 6:1); Yield 91% (78 mg); Colorless solid; mp 168-169 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O_3$ 343.1334, found 343.1330; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* 8.8 Hz, 2H), 8.09 (d, *J* 9.2 Hz, 2H), 8.05 (s, 2H), 7.74 (d, *J* 8.8 Hz, 2H), 7.67-7.63 (m, 2H), 7.50-7.45 (m, 2H), 7.43-7.39 (m, 1H), 6.99 (d, *J* 9.2 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.32, 187.90, 164.19, 146.42, 139.57, 135.63, 135.13, 134.35, 131.33 (2x), 129.98, 129.47 (2x), 128.96 (2x), 128.40, 127.43 (2x), 127.27 (2x), 114.11 (2x), 55.54.

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1-(4-Methoxyphenyl)-4-naphthalen-2-ylbut-2-ene-1,4-dione (3n). R_f 0.3 (hexanes : EtOAc 6:1); Yield 87% (69 mg); Colorless solid; mp 137-138 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{17}O_3$ 317.1178, found 317.1173; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, *J* 1.2 Hz, 1H), 8.19 (d, *J* 15.2 Hz, 1H), 8.14-8.07 (m, 2H), 8.09 (d, *J* 8.8 Hz, 2H), 8.00 (d, *J* 8.4 Hz, 1H), 7.94 (d, *J* 8.8 Hz, 1H), 7.90 (d, *J* 8.0 Hz, 1H), 7.65-7.56 (m, 2H), 7.00 (d, *J* 8.8 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.61, 187.96, 164.23, 135.85, 135.10, 134.44, 134.35, 132.46, 131.36 (2x), 131.12, 130.03, 129.75, 128.98, 128.87, 127.83, 127.01, 124.07, 114.13 (2x), 55.55. Single-crystal X-Ray diagram: crystal of compound **3n** was grown by slow diffusion of EtOAc into a solution of compound **3n** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P21/n, *a* =15.9940(17) Å, *b* = 5.7255(6) Å, *c* = 18.2554(18) Å, *V* = 1567.5(3) Å^3, *Z* = 4, d_{calcd} = 1.340 g/cm^3, *F*(000) = 644, 2*θ* range 1.469~26.403º, R indices (all data) R1 = 0.1443, wR2 = 0.1617.

1-(3-Methoxyphenyl)-4-*p*-tolylbut-2-ene-1,4-dione (3o). R_f 0.3 (hexanes : EtOAc 4:1); Yield 86% (60 mg); Colorless solid; mp 76-77 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{17}O_3$ 281.1178, found 281.1174; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (br s, 1H), 7.98 (br s, 1H), 7.96 (d, *J* 8.0 Hz, 2H), 7.64 (dt, *J* 0.8, 8.0 Hz, 1H), 7.56 (dd, *J* 1.6, 2.4 Hz, 1H), 7.43 (d, *J* 8.0 Hz, 1H), 7.32 (d, *J* 8.4 Hz, 2H), 7.19-7.16 (m, 1H), 3.88 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.63, 189.25, 160.01, 144.94, 138.23, 135.24, 134.75, 134.38, 129.82, 129.58 (2x), 129.01 (2x), 121.62, 120.59, 112.64, 55.47, 21.75.

1-Biphenyl-4-yl-4-*p*-tolylbut-2-ene-1,4-dione (3p). R_f 0.3 (hexanes : EtOAc 6:1); Yield 93% (76 mg); Colorless solid; mp 154-155 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{23}H_{19}O_2$ 327.1385, found 327.1380; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* 8.8 Hz, 2H), 8.06 (s, 2H), 7.99 (d, *J* 8.4 Hz, 2H), 7.76 (d, *J* 8.4 Hz, 2H), 7.68-7.65 (m, 2H), 7.51-7.40 (m, 3H), 7.34 (d, *J* 8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.35, 189.32, 146.53, 144.99, 139.62, 135.63, 135.19, 134.75, 134.45, 129.62 (2x), 129.51 (2x), 129.05 (2x), 129.00 (2x), 128.44, 127.50 (2x), 127.31 (2x), 21.79.

1-Naphthalen-2-yl-4-*p*-tolylbut-2-ene-1,4-dione (3q). R_f 0.3 (hexanes : EtOAc 6:1); Yield 91% (68 mg); Colorless solid; mp 126-127 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{21}H_{17}O_2$ 301.1229, found 301.1225; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61 (d, *J* 0.8 Hz, 1H), 8.20 (d, *J* 15.2 Hz, 1H), 8.13 (dd, *J* 2.0, 8.8 Hz, 1H), 8.09 (d, *J* 15.2 Hz, 1H), 8.02-7.99 (m, 1H), 8.01 (d, *J* 8.4 Hz, 2H), 7.95 (d, *J* 8.8 Hz, 1H), 7.90 (d, *J* 8.0 Hz, 1H), 7.66-7.57 (m, 2H), 7.34 (d, *J* 8.4 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.59, 189.33, 145.01, 135.88, 135.12, 134.79, 134.33, 132.47, 131.16, 131.12, 129.77, 129.62 (2x), 129.07 (2x), 129.02, 128.92, 127.86, 127.05, 124.08, 21.79.

1-Biphenyl-4-yl-4-(2,5-dimethoxyphenyl)but-2-ene-1,4-dione (3r). R_f 0.2 (hexanes : EtOAc 4:1); Yield 88% (82 mg); Colorless solid; mp 112-113 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{21}O_4$ 373.1440, found 373.1436; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* 8.8 Hz, 2H), 7.93 (d, *J* 15.6 Hz, 1H), 7.87 (d, *J* 15.6 Hz, 1H), 7.74 (d, *J* 8.4 Hz, 2H), 7.66-7.64 (m, 2H), 7.50-7.46 (m, 2H), 7.44-7.39 (m, 1H), 7.30 (d, *J* 3.2 Hz, 1H), 7.10 (dd, *J* 2.8, 8.8 Hz, 1H), 6.95 (d, *J* 8.8 Hz, 1H), 3.90 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

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191.23, 190.07, 153.69, 153.63, 146.28, 139.74, 139.67, 135.80, 132.68, 129.49 (2x), 128.97 (2x), 128.37, 127.95, 127.39 (2x), 127.27 (2x), 121.26, 114.19, 113.29, 56.27, 55.84. Single-crystal X-Ray diagram: crystal of compound **3r** was grown by slow diffusion of EtOAc into a solution of compound **3r** in CH_2Cl_2 to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P - 1, a =7.1811(18) Å, b = 8.2835(19) Å, c = 31.513(8) Å, V = 1829.5(8) Å^3, Z = 2, d_{calcd} = 1.352 g/cm^3, F(000) = 784, 2θ range 1.945~26.551°, R indices (all data) R1 = 0.0578, wR2 = 0.1045.

A representative procedure of compounds 5a-e is as follows. LDA (0.5 M in THF, 0.5 mL, 0.25 mmol, commercially available) was added to a solution of **4a-c** and **4g** (0.25 mmol) in anhydrous THF (5 mL) at -78 °C. The reaction mixture was stirred at rt for 5 min. α-Bromoacetophenones **1b**, **1e** and **1g** (0.25 mmol) in THF (2 mL) were added to the resulting reaction mixture at -78 °C. The reaction mixture was -78 °C for 4 h, warmed to rt, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 10/1~3/1) afforded compounds **5a-e**.

1-Phenyl-2-(toluene-4-sulfonyl)-4-*p*-tolyl-butane-1,4-dione (5a). R_f 0.2 (hexanes : EtOAc 4:1); Yield 81% (82 mg); Colorless solid; mp 170-171 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{24}H_{23}O_4S$ 407.1317, found 407.1311; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98-7.95 (m, 2H), 7.81-7.78 (m, 2H), 7.64 (d, *J* 8.4 Hz, 2H), 7.57-7.52 (m, 1H), 7.44-7.40 (m, 2H), 7.25-7.23 (m, 4H), 5.69 (dd, *J* 2.8, 11.2 Hz, 1H), 4.09 (dd, *J* 11.2, 18.0 Hz, 1H), 3.84 (dd, *J* 2.8, 18.0 Hz, 1H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.03, 191.61, 145.52, 144.86, 136.67, 133.76, 133.50, 132.91, 129.67 (2x), 129.37 (2x), 129.30 (2x), 129.11 (2x), 128.46 (2x), 128.28 (2x), 65.74, 37.61, 21.66, 21.59.

2-(Toluene-4-sulfonyl)-1,4-di-*p*-tolyl-butane-1,4-dione (5b). R_f 0.2 (hexanes : EtOAc 4:1); Yield 75% (79 mg); Colorless solid; mp 173-174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{25}H_{25}O_4S$ 421.1474, found 421.1470; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* 8.0 Hz, 2H), 7.81 (d, *J* 8.0 Hz, 2H), 7.66 (d, *J* 8.4 Hz, 2H), 7.28-7.23 (m, 6H), 5.70 (dd, *J* 2.8, 11.2 Hz, 1H), 4.08 (dd, *J* 11.2, 18.0 Hz, 1H), 3.83 (dd, *J* 2.8, 18.0 Hz, 1H), 2.42 (s, 3H), 2.40 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.95, 190.97, 145.43, 144.74, 144.62, 134.18, 133.70, 132.92, 129.62 (2x), 129.30 (2x), 129.27 (4x), 129.16 (2x), 128.23 (2x), 65.58, 37.55, 21.63, 21.55 (2x).

4-(2,4-Dimethoxyphenyl)-2-(toluene-4-sulfonyl)-1-*p*-tolyl-butane-1,4-dione (5c). R_f 0.3 (hexanes : EtOAc 2:1); Yield 77% (90 mg); Colorless solid; mp 172-173 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{27}O_6S$ 467.1528, found 467.1523; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* 8.0 Hz, 2H), 7.71 (d, *J* 8.8 Hz, 1H), 7.63 (d, *J* 8.0 Hz, 2H), 7.24 (d, *J* 8.4 Hz, 2H), 7.21 (d, *J* 8.4 Hz, 2H), 6.42-6.37 (m, 2H), 5.63 (dd, *J* 2.8, 11.2 Hz, 1H), 3.91 (dd, *J* 11.2, 18.0 Hz, 1H), 3.84 (s, 3H), 3.80 (dd, *J* 2.8, 18.0 Hz, 1H), 3.75 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.59, 191.28, 165.17, 161.43, 145.16, 144.26,

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134.38, 133.72, 132.78, 129.37 (2x), 129.30 (2x), 129.15 (2x), 129.05 (2x), 118.41, 105.40, 97.89, 65.70, 55.37 (2x), 43.32, 21.51, 21.44.

4-(2,4-Dimethoxyphenyl)-1-(4-methoxyphenyl)-2-(toluene-4-sulfonyl)butane-1,4-dione (5d). R_f 0.3 (hexanes : EtOAc 2:1); Yield 73% (88 mg); Colorless viscous gum; HRMS (ESI, M^++1) calcd for $C_{26}H_{27}O_7S$ 483.1478, found 483.1475; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* 8.8 Hz, 2H), 7.72 (d, *J* 8.8 Hz, 1H), 7.63 (d, *J* 8.4 Hz, 2H), 7.25 (d, *J* 8.0 Hz, 2H), 6.90 (d, *J* 8.8 Hz, 2H), 6.41 (dd, *J* 2.4, 8.8 Hz, 1H), 6.38 (d, *J* 2.4 Hz, 1H), 5.62 (dd, *J* 2.8, 11.2 Hz, 1H), 3.91 (dd, *J* 11.2, 18.0 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.81 (dd, *J* 2.8, 18.0 Hz, 1H), 3.76 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.71, 189.94, 165.18, 163.81, 161.45, 145.15, 133.79, 132.83, 131.50 (2x), 129.91, 129.43 (2x), 129.33 (2x), 118.54, 113.64 (2x), 105.40, 97.96, 65.58, 55.41 (3x), 43.23, 21.51.

1-(2,5-Dimethoxyphenyl)-4-(4-methoxyphenyl)-2-(toluene-4-sulfonyl)-butane-1,4-dione (5e). R_f 0.3 (hexanes : EtOAc 2:1); Yield 76% (92 mg); Colorless solid; mp 147-148 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{26}H_{27}O_7S$ 483.1478, found 483.1480; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* 8.8 Hz, 2H), 7.59 (d, *J* 8.4 Hz, 2H), 7.27 (d, *J* 3.2 Hz, 1H), 7.16 (d, *J* 8.0 Hz, 2H), 6.98 (dd, *J* 3.6, 9.2 Hz, 1H), 6.89 (d, *J* 8.8 Hz, 2H), 6.71 (d, *J* 8.8 Hz, 1H), 6.42 (dd, *J* 3.6, 10.4 Hz, 1H), 4.04 (dd, *J* 10.4, 17.2 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H), 3.74 (dd, *J* 2.8, 17.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.90, 190.65, 163.76, 153.56, 153.27, 144.90, 134.72, 130.41 (2x), 129.06 (2x), 128.94 (2x), 128.79, 126.36, 121.63, 114.49, 113.70 (2x), 113.46, 69.10, 56.13, 55.65, 55.37, 36.24, 20.91.

A representative procedure of compounds 7a-d is as follows: 1,2-Diaminobenzenes **6a-d** (0.25 mmol) were added to a solution of **3b** (60 mg, 0.25 mmol) in dioxane (5 mL) at rt. The reaction mixture was stirred at reflux for 4 h, cooled to rt, and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc 10/1~3/1) afforded skeleton **7a-d**.

2-Phenylquinoxaline (7a). R_f 0.2 (hexanes : EtOAc 4:1); Yield 88% (45 mg); Colorless solid; mp 75-76 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{14}H_{11}N_2$ 207.0922, found 207.0916; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.31 (s, 1H), 8.19-8.10 (m, 4H), 7.78-7.70 (m, 2H), 7.57-7.48 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.70, 143.21, 142.18, 141.42, 136.63, 130.19, 130.09, 129.51, 129.45, 129.05 (2x), 128.99, 127.45 (2x).

6,7-Dimethyl-2-phenylquinoxaline (7b). R_f 0.2 (hexanes : EtOAc 4:1); Yield 84% (49 mg); Colorless solid; mp 130-131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{16}H_{15}N_2$ 235.1235, found 235.1232; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.17-8.14 (m, 2H), 7.90 (s, 1H), 7.85 (s, 1H), 7.57-7.47 (m, 3H), 2.50 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.96, 142.22, 141.19, 140.86, 140.35, 140.19, 137.01, 129.83, 129.04 (2x), 128.58, 127.99, 127.34 (2x), 20.36, 20.33.

6,7-Dichloro-2-phenylquinoxaline (7c). R_f 0.2 (hexanes : EtOAc 4:1); Yield 86% (59 mg); Colorless solid; mp 155-156 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1)

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calcd for $C_{14}H_9Cl_2N_2$ 275.0143, found 275.0135; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H), 8.28 (s, 1H), 8.24 (s, 1H), 8.20-8.17 (m, 2H), 7.61-7.54 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.64, 144.27, 141.09, 140.24, 135.97, 134.93, 134.01, 130.77, 130.18, 129.77, 129.27 (2x), 127.57 (2x). **2-Phenylbenzo[*g*]quinoxaline (7d).** R_f 0.2 (hexanes : EtOAc 4:1); Yield 78% (50 mg); Colorless solid; mp 158-159 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI, M^++1) calcd for $C_{18}H_{13}N_2$ 257.1079, found 257.1072; ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40 (s, 1H), 8.79 (s, 1H), 8.75 (s, 1H), 8.29-8.26 (m, 2H), 8.15-8.11 (m, 2H), 7.63-7.56 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.68, 143.62, 138.48, 136.89, 136.20, 134.43, 133.84, 130.79, 129.29 (2x), 128.56, 128.52, 127.86, 127.75 (2x), 127.27, 127.14, 126.99.

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Supplementary Material

^{1}H and ^{13}C NMR ($CDCl_3$) spectral data for **3a-3r**, **5a-5e** and **7a-7d** are available as supplementary inormation.

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