

Synthesis of α -iodoketals from methyl ketones *via* sustainable and orthogonal tandem catalysis†

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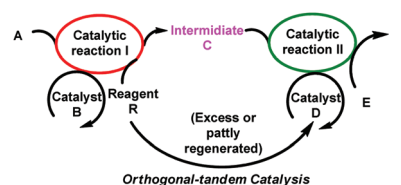
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A highly efficient method for the direct synthesis of α -iodoketals from methyl ketones has been developed *via* sustainable integration of orthogonal tandem catalytic reactions: copper(II) oxide catalyzed iodination reaction and the subsequent excess or regenerated iodine catalyzed regioselective ketalization reaction.

Introduction

In order to maximize synthetic efficiency, great attention has been paid to the sustainable integration of diverse reactions in one process *via* domino or tandem strategies.¹ Considering stoichiometric reagents are still needed for many organic reactions, it is particularly attractive for their stoichiometric byproducts to be internally recycled to catalyze the subsequent reaction in one process. Recently, this strategy has been successfully implemented in a domino nitroarene reduction/imine formation/aza Diels–Alder reaction,^{2a} domino nitrogen protection/imine formation/imine addition reaction,^{2b} domino Wittig–conjugate–reduction reaction.^{2c} Inspired by these excellent studies, we have recently developed a new synthetic strategy for the synthesis of hydantoins and α -formyloxy by sustainable integration of coupled domino processes.^{2d–e} Based on our interests in developing sustainable synthetic strategies, we would like to report herein a novel sustainable orthogonal-tandem catalysis strategy,³ in which the excess or partly regenerated reagent in the upstream reaction could be internally recycled to catalyze the downstream reaction (Scheme 1).

α -Iodoketals have been used as versatile intermediates in synthesis of multifunctional organic compounds⁴ and natural products.⁵ Correspondingly, several methods have been developed for their synthesis, including iodocyclization of alkenes,⁶ ring-opening of aziridines or oxirines,⁷ substitution of stannic or halogenated ketals,⁸ acetalization of α -iodoketones,^{5b,9} and

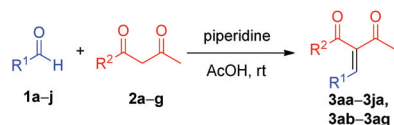
Scheme 1 Sustainable integration of coupled catalytic processes.^aScheme 2 Our hypothesis for the direct synthesis of α -iodoketals.

iodination of ketals.^{9,10} Surprisingly, only limited methods are available for the direct transformation of ketones into α -iodoketals,^{9,11} and their substrates were most limited to saturated aliphatic ketones, probably due to the easy iodination of carbon–carbon double bonds and lower reactivity of aryl ketones.⁶ To complement the previous synthetic methods, it is highly desirable to develop a simple and direct method for the synthesis of α -iodoketals from aryl/vinyl ketones.

In our previous studies, we have developed a highly efficient method for the α -iodination of methyl ketones in methanol or 2-propanol.¹² Encouraged by this result, we wondered whether it would be possible for the direct synthesis of α -iodoketals *via* sustainable integration of α -iodination and ketalization in one process *via* an orthogonal tandem strategy (Scheme 2). To verify this hypothesis, we would like to report herein a highly efficient and regioselective method for the direct synthesis of α -iodoketals from aryl/vinyl methyl ketones, which have potentially broad applications in organic synthesis.¹³

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Scheme 3 Synthesis of (Z)-2-arylidene-1-arylbutane-1,3-diones.

Table 1 Optimization of the reaction conditions^a

Entry	CuO (equiv.)	I ₂ (equiv.)	Temp (°C)	Yield ^b (%)
1	1.0	1.0	60	75
2	1.5	1.2	60	85
3	1.5	1.0	60	72
4	1.5	0.8	60	63
5	2.0	1.2	60	80
6	3.0	1.2	60	75
7	1.2	2.0	60	83
8	1.2	3.0	60	78
9	2.0	2.0	60	75
10	3.0	2.0	60	76
11	3.0	3.0	60	74
12	1.5	1.2	rt	— ^c
13	1.5	1.2	40	65
14	1.5	1.2	80	80
15 ^d	1.5	1.2	100	31
16 ^e	1.5	1.2	100	57
17	1.5	1.2	100	63
18	1.5	1.2	120	42

^a Reaction conditions: (Z)-2-benzylidene-1-phenylbutane-1,3-dione **3aa** (1.0 mmol), CuO (*x* mmol) and iodine (*x* mmol) in 5 mL of ethylene glycol for 5 h. ^b Isolated yields. ^c No desired product was obtained.

^d The reaction time was 1 h. ^e The reaction time was 3 h.

Results and discussion

(Z)-2-Arylidene-1-arylbutane-1,3-diones **3** were first prepared from aldehyde **1** and 1-arylbutane-1,3-dione **2** in excellent yields according to a modified procedure (Scheme 3).¹⁴ Considering ethylene glycol could both serve as the reaction solvent and reagent for acetal protection,¹⁵ we wondered whether it would be possible for the direct synthesis of α-iodo-ketals with ethylene glycol as solvent. On the basis of our previous studies on iodination of methyl ketones,¹² we first tried the experiment using (Z)-2-benzylidene-1-phenylbutane-1,3-dione **3aa** as the model substrate in the presence of iodine and copper(II) oxide with ethylene glycol as the solvent (Table 1). Fortunately, when the reaction was conducted with 1.0 equiv. of copper(II) oxide and 1.0 equiv. of iodine at 60 °C, the desired product **4aa** was obtained in 75% yield (entry 1) and its structure was also clearly confirmed by X-ray diffraction.¹⁶ Further exploration showed that the yield was increased to 85% when the equivalent of copper(II) oxide was 1.5 and iodine was 1.2 (entry 2). A series of screening experiments were

Table 2 Scope of substrates with different R¹ groups^a

Entry	R ¹	4	Yield ^b (%)
1	3aa (C ₆ H ₅)	4aa	85
2	3ba (4-MeC ₆ H ₄)	4ba	83
3	3ca (4-MeOC ₆ H ₄)	4ca	82
4	3da (4-NO ₂ C ₆ H ₄)	4da	84
5	3ea (1-Naphthyl)	4ea	60
6	3fa (2-Naphthyl)	4fa	72
7	3ga (4-ClC ₆ H ₄)	4ga	85
8	3ha (4-BrC ₆ H ₄)	4ha	78
9	3ia (4-FC ₆ H ₄)	4ia	73
10	3ja (2-Thienyl)	4ja	89

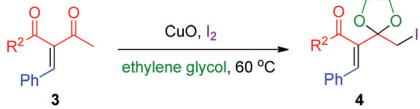
^a Reaction was performed with (Z)-2-arylidene-1-phenylbutane-1,3-dione **3** (1.0 mmol), CuO (1.5 mmol), and I₂ (1.2 mmol) in ethylene glycol (5 mL) at 60 °C for 5 h. ^b Isolated yield.

also conducted with different doses of copper(II) oxide and iodine, but no better results were obtained (entries 3–11). The temperature also has a significant influence on the reaction efficiency. No conversion of **3aa** was observed at room temperature (Table 1, entry 12). When the reaction was conducted at 40 or 80 °C, **4aa** was obtained in 65% and 80% yield, respectively (entries 13, 14). Further increasing the reaction temperature resulted in a significant decrease in the yields (entries 15–18).

Under the optimized reaction conditions (Table 1, entry 2), the reactivity of substrates **3** with various R¹ groups was initially investigated (Table 2). Pleasingly, the electronic nature of arylidenes has little influence on the reaction efficiency. With electron neutral (–H, –Me), electron donating (–OMe) and electron withdrawing groups (–NO₂), the reactions proceeded smoothly and their corresponding products were obtained in good yields (entries 1–4, 82–85%). In addition, moderate yields were obtained for sterically hindered substrates (60–72%; entries 5 and 6). Notably, the halogenated substrates (73–85%; entries 7–9) were also compatible under this reaction, which could be used for further functionalization.¹⁷ Much to our satisfaction, substrate with heteroarylidene group could also give the corresponding product in excellent yield (89%; entry 10).

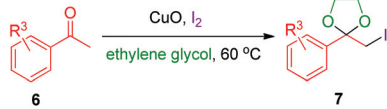
Next, the generality of this reaction was expanded to substrates **3** with different R² groups, which could also proceed efficiently to afford their corresponding products in moderate to excellent yields (Table 3). Although a moderate yield was obtained with the sterically hindered 2-naphthyl group (43%, entry 2), the halogenated aryl groups were compatible under the reaction conditions and good yields were obtained (73–78%; entries 3–4). To our satisfaction, substrates with heteroaryl groups could also give their corresponding products in good to excellent yields (85–88%; entries 5–6).

Considering 1,3-propanediol is also a popular reagent for ketone protection,¹⁴ the reaction was then conducted with

Table 3 Scope of substrates with different R² groups^a


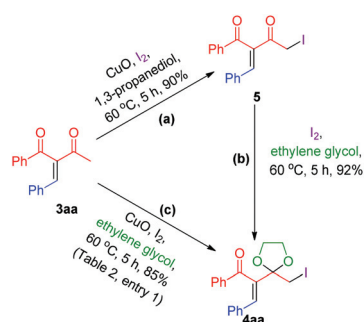
Entry	R ²	2	Yield ^b (%)
1	3ab (4-MeC ₆ H ₄)	4ab	82
2	3ac (2-Naphthyl)	4ac	43
3	3ad (4-ClC ₆ H ₄)	4ad	78
4	3ae (4-BrC ₆ H ₄)	4ae	73
5	3af (2-Furyl)	4af	85
6	3ag (2-Thienyl)	4ag	88

^a Reaction was performed with (Z)-2-benzylidene-1-arylbutane-1,3-dione **3** (1.0 mmol), CuO (1.5 mmol), and I₂ (1.2 mmol) in ethylene glycol (5 mL) at 60 °C for 5 h. ^b Isolated yield.

Table 4 Scope of substrates with aryl methyl ketones^a


Entry	R ³	7	Yield ^b (%)
1	6a (C ₆ H ₅)	7a	36
2	6b (4-ClC ₆ H ₄)	7b	43
3	6c (3,4-Cl ₂ C ₆ H ₃)	7c	46
4	6d (4-BrC ₆ H ₄)	7d	52
5	6e (4-FC ₆ H ₄)	7e	44
6	6f (4-NO ₂ C ₆ H ₄)	7f	98
7	6g (3-NO ₂ C ₆ H ₄)	7g	84
8	6h (2-NO ₂ C ₆ H ₄)	7h	72
9	6i (4-MeOC ₆ H ₄)	7i	— ^c

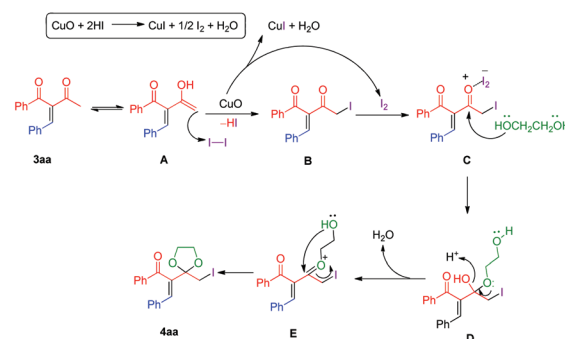
^a Reaction was performed with aryl methyl ketone **6** (1.0 mmol), CuO (1.5 mmol), and I₂ (1.2 mmol) in ethylene glycol (5 mL) at 60 °C for 5 h. ^b Isolated yield. ^c Only the α-iodoketone product was obtained in 92% yield.

**Scheme 4** Control experiment.

1,3-propanediol as solvent. Unexpectedly, only the unprotected iodinated product **5** was obtained in excellent yield (90%; Scheme 4a).

To provide insight into the proposed mechanism, a control experiment was then performed (Scheme 4). When α-iodoketone **3aa** was used as substrate in ethylene glycol, the desired product **4aa** was obtained in 92% yield in the presence of iodine (Scheme 4b). However, no desired product **4aa** was obtained without iodine. This result clearly confirmed our suspicion that I₂ could efficiently catalyze the ketalization reaction.¹⁸

To further extend the scope of this reaction, simple aryl methyl ketones **6** were also used as substrates (Table 4). For substrates with electron-neutral substituents (–H), a moderate yield was obtained (36%; entry 1). To our delight, the halogenated substrates were also compatible under this reaction condition, and moderate yields were obtained (43–52%; entries 2–5). Gratifyingly, substrates with electron withdrawing groups afforded good to excellent yields (72–98%; entries 6–8). However, for substrates with electron donating groups (–OMe), only the α-iodoketone product was obtained in high yield (92%). This is because the electron donating substituents on the aromatic rings would decrease the positive charge on the carbonyl carbon, which would make the carbonyl group less electrophilic and retard its acetal formation, whereas electron withdrawing substituents would facilitate it.¹⁵

**Scheme 5** Proposed reaction mechanism.

Based on the previous studies, a possible reaction mechanism was shown in Scheme 5 using **3aa** as an example: substrate **3aa** first undergoes copper(II) oxide-catalyzed iodination to give intermediate **B**, which could be further activated by excess or *in situ* regenerated iodine (from oxidation of HI byproduct by CuO) to form hemiketal **D**. The hydroxyl group in **D** is protonated leading to the oxonium ion intermediate **E**, which accepts the second hydroxyl group of ethylene glycol to afford the desired product **4aa**. The regioselective ketalization of (Z)-2-arylidene-1-arylbutane-1,3-diones **3** is probably due to the conjugation effect of aromatic rings deactivates the adjacent carbonyl group towards acetalisation.¹⁵

Conclusions

In summary, we have developed a sustainable integration strategy for the direct and efficient synthesis of α-iodoketals from (Z)-2-arylidene-1-arylbutane-1,3-diones and aryl methyl ketones *via* successive tandem catalysis of copper(II) oxide and iodine in ethylene glycol. Noteworthy features of this method

are mild reaction condition, ease of manipulation, short reaction time and good yields.

Experimental section

1 General methods

All reagents were purchased from commercial suppliers and used without further purification. IR spectra were recorded on an infrared spectrometer as KBr pellets with absorption in cm^{-1} . ^1H spectra were recorded in CDCl_3 on 400/600 MHz NMR spectrometers and resonances (δ) are given in ppm relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, brs = broad singlet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in CDCl_3 on 100/150 MHz spectrometers and resonances (δ) are given in ppm relative to the center line of a triplet at 77.0 ppm of chloroform- d . HRMS were obtained on an Apex-Ultra MS equipped with APCI or ESI source. Melting points were determined using XT-4 apparatus and not corrected. The X-ray crystal-structure determination of **3ba**, **3ia** and **4aa** was obtained on a Bruker SMART APEX CCD system. Column chromatography was performed on silica gel (200–300 mesh).

2 General procedures

Preparation of (Z)-2-aryliden-1-arylbutane-1,3-dione (3aa as an example). Piperidine (20 mL) was added dropwise to the stirred solution of acetic acid (25 mL) in ice bath. Benzaldehyde **1a** (1.06 g, 10.0 mmol) and 1-phenylbutane-1,3-dione **2a** (1.62 g, 10.0 mmol) were then added into the mixture solution and stirred at room temperature for overnight. After the reaction completed, the mixture was diluted with water and extracted with CH_2Cl_2 (3 \times 200 mL), the combined organic extracts were washed with NaOH (5% w/w, aq.) and brine successively, then dried with Na_2SO_4 , and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether-EtOAc = 10 : 1) to afford a white solid **3aa** (2.15 g, 86%).

Preparation of α -iodoketals of (Z)-2-aryliden-1-arylbutane-1,3-dione (4aa as an example). (Z)-2-Benzyliden-1-phenylbutane-1,3-dione **3aa** (250 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous ethylene glycol (5 mL), the mixture was stirred at 60 $^\circ\text{C}$ for 5 h. After the reaction completed, the mixture was diluted with water and treated with $\text{Na}_2\text{S}_2\text{O}_3$ (5% w/w, aq.). The mixture was then extracted with CH_2Cl_2 (3 \times 20 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether-EtOAc = 20 : 1) to afford a white solid **4aa** (357 mg, 85%).

Preparation of 5. (Z)-2-Benzyliden-1-phenylbutane-1,3-dione **3aa** (250 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous 1,3-propanediol (5 mL), the mixture was

stirred at 60 $^\circ\text{C}$ for 5 h. After the reaction completed, the mixture was diluted with water and treated with $\text{Na}_2\text{S}_2\text{O}_3$ (5% w/w, aq.). The mixture was then extracted with CH_2Cl_2 (3 \times 20 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether-EtOAc = 15 : 1) to afford a yellow solid **5** (339 mg, 90%).

Preparation of α -iodoketals of (Z)-2-aryliden-1-arylbutane-1,3-dione (7a as an example). Acetophenone **6a** (120 mg, 1.0 mmol), CuO (120 mg, 1.5 mmol), and iodine (305 mg, 1.2 mmol) were placed in a sealed tube. After addition of anhydrous 1,3-propanediol (5 mL), the mixture was stirred at 60 $^\circ\text{C}$ for 5 h. After the reaction completed, the mixture was diluted with water and treated with $\text{Na}_2\text{S}_2\text{O}_3$ (5% w/w, aq.). The mixture was then extracted with CH_2Cl_2 (3 \times 20 mL), the combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether-EtOAc = 80 : 1) to afford a yellow solid **7a** (104 mg, 36%).

3 Spectroscopic data

(Z)-2-Benzyliden-1-phenylbutane-1,3-dione (3aa). Yield 86%; white solid; m.p. 92.8–93.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.92 (d, J = 7.6 Hz, 2H), 7.79 (s, 1H), 7.53 (t, J = 7.6 Hz, 1H), 7.41–7.38 (m, 2H), 7.35–7.33 (m, 2H), 7.28–7.20 (m, 3H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.0, 195.8, 141.1, 139.6, 135.9, 134.0, 132.8, 130.4, 130.2, 129.1, 128.9, 128.8, 27.2; IR (KBr): 1678, 1651, 1619, 1233, 1207 cm^{-1} ; HRMS (APCI): m/z [$M + H$] $^+$ calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2$: 251.1067; found: 251.1068.

(Z)-2-(4-Methylbenzyliden)-1-phenylbutane-1,3-dione (3ba). Yield 82%; white solid; m.p. 72.5–74.2 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.94–7.91 (m, 2H), 7.76 (s, 1H), 7.55–7.51 (m, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 2.38 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.3, 195.9, 141.3, 141.1, 138.5, 136.0, 134.0, 130.4, 129.9, 129.5, 129.1, 128.9, 27.0, 21.3; IR (KBr): 1669, 1646, 1601, 1246, 1234, 1210 cm^{-1} ; HRMS (APCI): m/z [$M + H$] $^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2$: 265.1223; found: 265.1224.

(Z)-2-(4-Methoxybenzyliden)-1-phenylbutane-1,3-dione (3ca). Yield 80%; white solid; m.p. 70.6–72.1 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.93 (d, J = 7.2 Hz, 2H), 7.74 (s, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.31–7.27 (m, 2H), 6.73 (d, J = 8.8 Hz, 2H), 3.72 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.5, 195.8, 161.4, 141.0, 137.2, 136.0, 133.9, 132.4, 129.0, 128.8, 125.2, 114.3, 55.2, 26.9; IR (KBr): 1670, 1645, 1601, 1513, 1178 cm^{-1} ; HRMS (APCI): m/z [$M + H$] $^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3$: 281.1172; found: 281.1173.

(Z)-2-(4-Nitrobenzyliden)-1-phenylbutane-1,3-dione (3da). Yield 88%; light yellow solid; m.p. 152.1–153.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.08–8.05 (m, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.82 (s, 1H), 7.60–7.56 (m, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.45–7.41 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.9, 195.1, 148.2, 142.7, 139.2, 137.7, 135.4, 134.7, 130.6, 129.2, 129.1, 123.9, 27.5; IR (KBr): 1678, 1657, 1595, 1519,

1347, 1231 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_4$: 296.0917; found: 296.0917.

(Z)-2-(Naphthalen-1-ylmethylene)-1-phenylbutane-1,3-dione (3ea). Yield 77%; yellow oil; ^1H NMR (CDCl_3 , 400 MHz): δ 8.60 (s, 1H), 8.10 (d, $J = 8.4$ Hz, 1H), 7.80–7.78 (m, 3H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.63–7.59 (m, 1H), 7.54–7.50 (m, 1H), 7.40–7.35 (m, 2H), 7.24–7.19 (m, 3H), 2.48 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.4, 195.5, 141.4, 139.2, 136.1, 133.7, 133.3, 131.4, 130.6, 130.4, 128.9, 128.8, 128.6, 127.9, 127.0, 126.4, 125.2, 123.7, 27.8; IR (KBr): 1679, 1658, 1595, 1231 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2$: 301.1223; found: 301.1224.

(Z)-2-(Naphthalen-2-ylmethylene)-1-phenylbutane-1,3-dione (3fa). Yield 78%; light yellow solid; m.p. 98.7–99.4 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.97–7.95 (m, 3H), 7.89 (s, 1H), 7.73–7.68 (m, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.51–7.35 (m, 6H), 2.43 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.2, 195.8, 141.2, 139.5, 136.1, 134.1, 133.8, 132.8, 131.9, 130.3, 129.1, 128.9, 128.6, 128.5, 127.7, 127.5, 126.7, 125.9, 27.2; IR (KBr): 1675, 1648, 1610, 1362, 1262, 1231, 1174 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2$: 301.1223; found: 301.1224.

(Z)-2-(4-Chlorobenzylidene)-1-phenylbutane-1,3-dione (3ga). Yield 83%; white solid; m.p. 90.2–91.7 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 7.6$ Hz, 2H), 7.74 (s, 1H), 7.58–7.54 (m, 1H), 7.42 (t, $J = 7.2$ Hz, 2H), 7.29–7.27 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.7, 195.5, 139.9, 139.5, 136.5, 135.7, 134.3, 131.4, 131.3, 129.1, 129.0, 27.2; IR (KBr): 1679, 1655, 1618, 1230, 1210, 1089 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_2$: 285.0677; found: 285.0679.

(Z)-2-(4-Bromobenzylidene)-1-phenylbutane-1,3-dione (3ha). Yield 84%; white solid; m.p. 88.0–89.4 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.90 (d, $J = 8.0$ Hz, 2H), 7.71 (s, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.35–7.33 (m, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.6, 195.5, 140.0, 139.5, 135.6, 134.2, 131.9, 131.6, 131.4, 129.0, 128.9, 124.9, 27.1; IR (KBr): 1673, 1653, 1616, 1583, 1238 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{BrO}_2$: 329.0172; found: 329.0173.

(Z)-2-(4-Fluorobenzylidene)-1-phenylbutane-1,3-dione (3ia). Yield 80%; light yellow solid; m.p. 110.6–111.8 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.92–7.90 (m, 2H), 7.76 (s, 1H), 7.56 (t, $J = 7.6$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.36–7.33 (m, 2H), 6.92 (t, $J = 8.4$ Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.0, 195.6, 165.0, 162.5, 139.8, 139.27, 139.25, 135.8, 134.3, 132.4, 132.3, 129.1, 129.0, 116.2, 116.0, 27.3; IR (KBr): 1681, 1650, 1620, 1596, 1508, 1228, 1164 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{FO}_2$: 269.0972; found: 269.0974.

(Z)-1-Phenyl-2-(thiophen-2-ylmethylene)butane-1,3-dione (3ja). Yield 84%; white solid; m.p. 123.6–124.9 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.99–7.97 (m, 2H), 7.90 (s, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.38 (d, $J = 4.8$ Hz, 1H), 7.27–7.26 (m, 1H), 6.98–6.96 (m, 1H), 2.36 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.7, 195.2, 136.5, 136.2, 135.9, 134.2, 133.2, 132.0, 129.2, 128.9, 128.0, 27.0; IR (KBr): 1670, 1647,

1601, 1267, 1238, 1219, 1202 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{S}$: 257.0631; found: 257.0632.

(Z)-2-Benzylidene-1-(*p*-tolyl)butane-1,3-dione (3ab). Yield 83%; white solid; m.p. 106.0–107.2 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.77 (s, 1H), 7.35 (d, $J = 7.6$ Hz, 2H), 7.26–7.19 (m, 5H), 2.37 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.5, 195.8, 145.1, 140.8, 139.7, 133.6, 132.8, 130.3, 130.2, 129.6, 129.2, 128.7, 27.2, 21.6; IR (KBr): 1675, 1649, 1620, 1605, 1237, 1208, 1182 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{O}_2$: 265.1223; found: 265.1224.

(Z)-2-Benzylidene-1-(naphthalen-2-yl)butane-1,3-dione (3ac). Yield 75%; yellow solid; m.p. 86.5–87.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.37 (s, 1H), 8.07 (d, $J = 8.4$ Hz, 1H), 7.88–7.81 (m, 4H), 7.56 (t, $J = 6.8$ Hz, 1H), 7.48 (t, $J = 6.8$ Hz, 1H), 7.40–7.38 (m, 2H), 7.20–7.16 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.9, 195.8, 141.2, 139.6, 136.0, 133.4, 132.8, 132.5, 131.8, 130.5, 130.3, 129.7, 129.0, 128.9, 128.8, 127.7, 126.8, 123.8, 27.3; IR (KBr): 1668, 1653, 1620, 1243, 1182 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{17}\text{O}_2$: 301.1223; found: 301.1224.

(Z)-2-Benzylidene-1-(4-chlorophenyl)butane-1,3-dione (3ad). Yield 83%; white solid; m.p. 108.4–111.0 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.86–7.82 (m, 2H), 7.79 (s, 1H), 7.39–7.35 (m, 2H), 7.33–7.22 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.7, 195.9, 141.6, 140.6, 139.1, 134.3, 132.6, 130.7, 130.4, 130.2, 129.3, 128.9, 27.1; IR (KBr): 1681, 1648, 1621, 1586, 1230, 1208 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{ClO}_2$: 285.0677; found: 285.0679.

(Z)-2-Benzylidene-1-(4-bromophenyl)butane-1,3-dione (3ae). Yield 84%; white solid; m.p. 125.4–126.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.79–7.75 (m, 3H), 7.54 (d, $J = 8.4$ Hz, 2H), 7.33–7.23 (m, 5H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.9, 195.9, 141.6, 139.1, 134.7, 132.5, 132.2, 130.7, 130.5, 130.2, 129.4, 128.9, 27.0; IR (KBr): 1680, 1647, 1622, 1583, 1230, 1209 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{BrO}_2$: 329.0172; found: 329.0173.

(Z)-2-Benzylidene-1-(furan-2-yl)butane-1,3-dione (3af). Yield 60%; white solid; m.p. 118.5–119.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.79 (s, 1H), 7.56 (brs, 1H), 7.39–7.37 (m, 2H), 7.33–7.25 (m, 3H), 7.06 (d, $J = 3.6$ Hz, 1H), 6.45–6.43 (m, 1H), 2.42 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.3, 184.6, 152.2, 147.9, 142.1, 138.5, 132.8, 130.5, 130.1, 128.8, 120.4, 112.6, 27.2; IR (KBr): 1665, 1646, 1617, 1242 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{O}_3$: 241.0859; found: 241.0860.

(Z)-2-Benzylidene-1-(thiophen-2-yl)butane-1,3-dione (3ag). Yield 70%; white solid; m.p. 96.3–97.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.79 (s, 1H), 7.66 (d, $J = 4.0$ Hz, 1H), 7.51 (d, $J = 2.8$ Hz, 1H), 7.43–7.41 (m, 2H), 7.32–7.24 (m, 3H), 7.01 (t, $J = 4.4$ Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 195.1, 189.8, 143.6, 141.2, 139.2, 135.7, 134.7, 132.8, 130.6, 130.3, 128.8, 128.5, 27.3; IR (KBr): 1660, 1638, 1615, 1413, 1246 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{13}\text{O}_2\text{S}$: 257.0631; found: 257.0633.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1,3-diphenylprop-2-en-1-one (4aa). Yield 85%; white solid; m.p. 135.5–136.4 $^\circ\text{C}$;

^1H NMR (CDCl_3 , 400 MHz): δ 7.84–7.82 (m, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.21 (s, 1H), 7.19–7.12 (m, 5H), 4.19–4.16 (m, 2H), 4.04–4.01 (m, 2H), 3.88 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.7, 137.6, 135.9, 134.1, 133.4, 131.4, 129.2, 129.1, 128.6, 128.5, 128.4, 107.2, 66.1, 13.3; IR (KBr): 1650, 1238, 1036 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{18}\text{IO}_3$: 421.0295; found: 421.0295.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1-phenyl-3-(*p*-tolyl)-prop-2-en-1-one (4ba). Yield 83%; white solid; m.p. 145.1–146.9 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.86–7.83 (m, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.30 (t, J = 7.2 Hz, 2H), 7.16 (s, 1H), 7.07 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 4.17–4.14 (m, 2H), 4.02–3.99 (m, 2H), 3.87 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.9, 138.7, 136.4, 136.0, 133.3, 131.3, 131.1, 129.1, 128.5, 107.2, 66.0, 21.1, 13.4; IR (KBr): 1648, 1237, 1038 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{IO}_3$: 435.0452; found: 435.0452.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4ca). Yield 82%; white solid; m.p. 127.2–128.7 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.86–7.84 (m, 2H), 7.45 (t, J = 7.2 Hz, 1H), 7.31 (d, J = 7.2 Hz, 2H), 7.14–7.10 (m, 3H), 6.65 (d, J = 8.8 Hz, 2H), 4.17–4.14 (m, 2H), 4.02–3.99 (m, 2H), 3.87 (s, 2H), 3.69 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 198.1, 159.8, 136.0, 135.2, 133.4, 131.0, 130.7, 129.2, 128.5, 126.6, 113.8, 107.2, 66.0, 55.1, 13.5; IR (KBr): 1643, 1608, 1511, 1261, 1178, 1032 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{IO}_4$: 451.0401; found: 451.0401.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (4da). Yield 84%; white solid; m.p. 163.7–164.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.99 (d, J = 8.8 Hz, 2H), 7.81–7.79 (m, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.35–7.31 (m, 4H), 7.25 (s, 1H), 4.23–4.19 (m, 2H), 4.07–4.03 (m, 2H), 3.85 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.8, 147.3, 142.0, 140.6, 135.5, 134.0, 129.6, 129.1, 128.82, 128.76, 123.7, 107.2, 66.3, 12.4; IR (KBr): 1656, 1594, 1515, 1342, 1234, 1034 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{INO}_5$: 466.0146; found: 466.0146.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one (4ea). Yield 60%; white solid; m.p. 131.3–132.4 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.05 (d, J = 8.4 Hz, 1H), 7.95 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.67–7.65 (m, 2H), 7.60–7.56 (m, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.25–7.16 (m, 2H), 7.11 (t, J = 7.2 Hz, 1H), 7.01 (t, J = 7.6 Hz, 2H), 4.29–4.23 (m, 2H), 4.22–4.16 (m, 2H), 4.01 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.2, 139.5, 136.3, 133.2, 132.9, 131.6, 131.2, 130.6, 129.0, 128.63, 128.58, 128.0, 127.6, 126.5, 126.0, 125.1, 123.8, 107.5, 66.2, 13.1; IR (KBr): 1658, 1230, 1176, 1036 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{IO}_3$: 471.0452; found: 471.0452.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (4fa). Yield 72%; white solid; m.p. 120.1–122.0 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.88–7.86 (m, 2H), 7.69–7.65 (m, 3H), 7.55 (d, J = 8.4 Hz, 1H), 7.41–7.35 (m, 4H), 7.27–7.23 (m, 3H), 4.21–4.18 (m, 2H), 4.07–4.03 (m, 2H), 3.93 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.8, 137.7, 136.0, 133.4, 132.91, 132.87, 131.6, 131.4, 129.4, 129.0, 128.5, 128.1,

128.0, 127.4, 126.6, 126.3, 126.0, 107.3, 66.1, 13.3; IR (KBr): 1645, 1233, 1038 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{IO}_3$: 471.0452; found: 471.0453.

(E)-3-(4-Chlorophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ga). Yield 85%; white solid; m.p. 123.7–124.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.83–7.81 (m, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.32 (t, J = 7.2 Hz, 2H), 7.15 (s, 1H), 7.10 (brs, 4H), 4.19–4.16 (m, 2H), 4.03–4.00 (m, 2H), 3.85 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.5, 138.3, 135.7, 134.5, 133.7, 132.6, 130.3, 130.0, 129.1, 128.64, 128.60, 107.2, 66.1, 13.0; IR (KBr): 1649, 1237, 1038 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{ClIO}_3$: 454.9905; found: 454.9906.

(E)-3-(4-Bromophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ha). Yield 78%; white solid; m.p. 126.0–127.0 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.83–7.81 (m, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.12 (s, 1H), 7.04 (d, J = 8.4 Hz, 2H), 4.19–4.15 (m, 2H), 4.03–4.00 (m, 2H), 3.85 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.4, 138.4, 135.7, 133.7, 133.0, 131.6, 130.5, 129.9, 129.1, 128.6, 122.8, 107.1, 66.1, 13.0; IR (KBr): 1648, 1236, 1038 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{BrIO}_3$: 498.9400; found: 498.9402.

(E)-3-(4-Fluorophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-1-phenylprop-2-en-1-one (4ia). Yield 73%; white solid; m.p. 113.7–115.1 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.83–7.81 (m, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.17–7.14 (m, 3H), 6.81 (t, J = 8.8 Hz, 2H), 4.20–4.16 (m, 2H), 4.04–4.00 (m, 2H), 3.87 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.6, 163.8, 161.3, 137.5, 135.8, 133.6, 130.9, 130.8, 130.3, 130.25, 130.2, 129.1, 128.5, 115.6, 115.4, 107.2, 66.1, 13.1; IR (KBr): 1657, 1597, 1505, 1234, 1035 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{FIO}_3$: 439.0201; found: 439.0201.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (4ja). Yield 89%; white solid; m.p. 144.4–146.0 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.95–7.93 (m, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.23 (s, 1H), 7.15 (d, J = 5.2 Hz, 1H), 6.94 (d, J = 3.6 Hz, 1H), 6.84–6.82 (m, 1H), 4.18–4.14 (m, 2H), 4.04–4.01 (m, 2H), 3.81 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.2, 137.0, 136.0, 135.7, 133.7, 129.9, 129.2, 128.7, 128.1, 127.3, 123.3, 106.9, 66.1, 13.1; IR (KBr): 1653, 1232, 1209, 1170, 1035 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{IO}_3\text{S}$: 426.9859; found: 426.9860.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-phenyl-1-(*p*-tolyl)-prop-2-en-1-one (4ab). Yield 82%; white solid; m.p. 92.6–94.2 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.74 (d, J = 8.0 Hz, 2H), 7.20–7.17 (m, 3H), 7.13–7.08 (m, 5H), 4.18–4.14 (m, 2H), 4.03–3.99 (m, 2H), 3.87 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.3, 144.3, 137.7, 134.1, 133.5, 131.0, 129.3, 129.2, 129.1, 128.5, 128.4, 107.2, 66.0, 21.6, 13.4; IR (KBr): 1651, 1604, 1240, 1211, 1179, 1039 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{IO}_3$: 435.0452; found: 435.0452.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-1-(naphthalen-2-yl)-3-phenylprop-2-en-1-one (4ac). Yield 43%; white solid; m.p. 112.1–113.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.34 (s, 1H), 7.95–7.93 (m, 1H), 7.82–7.76 (m, 3H), 7.56–7.52 (m, 1H), 7.49–7.45 (m, 1H), 7.27–7.23 (m, 3H), 7.12–7.06 (m, 3H),

4.20–4.16 (m, 2H), 4.07–4.04 (m, 2H), 3.91 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 197.7, 137.8, 135.7, 134.1, 133.4, 132.4, 131.53, 131.49, 129.7, 129.1, 128.64, 128.60, 128.5, 127.7, 126.6, 124.3, 107.3, 66.2, 13.3; IR (KBr): 1653, 1626, 1218, 1184, 1033 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{20}\text{IO}_3$: 471.0452; found: 471.0452.

(E)-1-(4-Chlorophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-phenylprop-2-en-1-one (4ad). Yield 78%; white solid; m.p. 98.7–100.1 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.77–7.75 (m, 2H), 7.27–7.25 (m, 2H), 7.23 (s, 1H), 7.15 (brs, 5H), 4.20–4.17 (m, 2H), 4.02–3.99 (m, 2H), 3.86 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.5, 139.8, 137.1, 134.3, 133.9, 131.7, 130.5, 129.1, 128.84, 128.80, 128.5, 107.3, 66.1, 13.0; IR (KBr): 1658, 1228, 1040 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{ClIO}_3$: 454.9905; found: 454.9906.

(E)-1-(4-Bromophenyl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-phenylprop-2-en-1-one (4ae). Yield 73%; white solid; m.p. 111.5–112.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.68 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.22 (s, 1H), 7.15 (brs, 5H), 4.20–4.17 (m, 2H), 4.02–3.99 (m, 2H), 3.86 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.7, 137.1, 134.7, 133.8, 131.8, 131.7, 130.5, 129.0, 128.8, 128.7, 128.5, 107.2, 66.1, 13.0; IR (KBr): 1658, 1221, 1040 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{17}\text{BrIO}_3$: 498.9400; found: 498.9402.

(E)-1-(Furan-2-yl)-2-(2-(iodomethyl)-1,3-dioxolan-2-yl)-3-phenylprop-2-en-1-one (4af). Yield 85%; white solid; m.p. 137.6–139.2 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.434–7.428 (m, 1H), 7.21–7.17 (m, 6H), 6.93 (d, J = 3.6 Hz, 1H), 6.34–6.33 (m, 1H), 4.21–4.17 (m, 2H), 4.07–4.04 (m, 2H), 3.88 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 184.6, 152.4, 147.1, 137.0, 134.2, 132.7, 128.8, 128.6, 128.4, 119.7, 112.3, 106.8, 66.0, 12.8; IR (KBr): 1641, 1624, 1040 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{IO}_4$: 411.0088; found: 411.0087.

(E)-2-(2-(Iodomethyl)-1,3-dioxolan-2-yl)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one (4ag). Yield 88%; white solid; m.p. 136.4–137.3 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.53–7.51 (m, 1H), 7.45–7.44 (m, 1H), 7.26–7.23 (m, 2H), 7.19–7.16 (m, 4H), 6.91–6.89 (m, 1H), 4.20–4.19 (m, 2H), 4.07–4.04 (m, 2H), 3.89 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 189.5, 143.8, 138.0, 134.7, 134.2, 133.9, 131.8, 129.1, 128.7, 128.4, 128.1, 107.0, 66.1, 13.0; IR (KBr): 1642, 1625, 1411, 1245, 1054 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{16}\text{IO}_3\text{S}$: 426.9859; found: 426.9860.

(E)-2-Benzylidene-4-iodo-1-phenylbutane-1,3-dione (5). Yield 90%; yellow solid; m.p. 112.5–113.6 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 600 MHz): δ 7.98 (s, 1H), 7.95 (d, J = 7.2 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 2H), 7.33 (d, J = 7.2 Hz, 2H), 7.29–7.26 (m, 1H), 7.22 (t, J = 7.2 Hz, 2H), 4.20 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 196.8, 190.6, 143.6, 135.9, 135.8, 134.1, 132.6, 130.8, 130.5, 129.4, 128.8, 128.7, 2.3; IR (KBr): 1668, 1639, 1616, 1258, 1233, 1211 cm^{-1} ; HRMS (APCI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{17}\text{H}_{14}\text{IO}_2$: 377.0033; found: 377.0034.

2-(Iodomethyl)-2-phenyl-1,3-dioxolane (7a). Yield 36%; yellow solid; m.p. 65.5–67.0 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.51–7.49 (m, 2H), 7.38–7.33 (m, 3H), 4.20–4.17 (m, 2H), 3.88–3.84 (m, 2H), 3.58 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz):

δ 139.1, 128.6, 128.3, 125.8, 106.7, 65.6, 14.0; IR (KBr): 1208, 1159, 1035, 960, 703 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{IO}_2$: 290.9876; found: 290.9877.

2-(4-Chlorophenyl)-2-(iodomethyl)-1,3-dioxolane (7b). Yield 43%; yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.44 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.20–4.18 (m, 2H), 3.87–3.84 (m, 2H), 3.54 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 137.7, 134.6, 128.5, 127.4, 106.4, 65.7, 13.5; IR (KBr): 1487, 1208, 1091, 1040, 978, 832 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{ClIO}_2$: 324.9487; found: 424.9488.

2-(3,4-Dichlorophenyl)-2-(iodomethyl)-1,3-dioxolane (7c). Yield 46%; yellow oil; ^1H NMR (CDCl_3 , 400 MHz): δ 7.60 (d, J = 2.4 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.35–7.32 (m, 1H), 4.21–4.18 (m, 2H), 3.89–3.85 (m, 2H), 3.51 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 139.7, 132.6, 130.4, 128.1, 125.4, 106.0, 65.9, 12.8; IR (KBr): 1467, 1378, 1208, 1167, 1033, 977 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{IO}_2$: 358.9097; found: 358.9099.

2-(4-Bromophenyl)-2-(iodomethyl)-1,3-dioxolane (7d). Yield 52%; yellow solid; m.p. 56.2–58.3 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.49 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.4 Hz, 2H), 4.20–4.17 (m, 2H), 3.87–3.84 (m, 2H), 3.53 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 138.3, 131.5, 127.7, 122.9, 106.5, 65.7, 13.3; IR (KBr): 1584, 1479, 1405, 1208, 1039, 976, 956, 940, 830 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{BrIO}_2$: 368.8982; found: 368.8982.

2-(4-Fluorophenyl)-2-(iodomethyl)-1,3-dioxolane (7e). Yield 44%; yellow oil; ^1H NMR (CDCl_3 , 600 MHz): δ 7.49–7.47 (m, 2H), 7.05–7.02 (m, 2H), 4.20–4.19 (m, 2H), 3.87–3.85 (m, 2H), 3.55 (s, 2H); ^{13}C NMR (CDCl_3 , 150 MHz): δ 163.6, 162.0, 135.0, 127.8, 127.7, 115.2, 115.1, 106.4, 65.7, 13.8; IR (KBr): 1602, 1504, 1225, 1158, 1040, 978, 840, 566 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{FIO}_2$: 308.9782; found: 308.9784.

2-(Iodomethyl)-2-(4-nitrophenyl)-1,3-dioxolane (7f). Yield 98%; white solid; m.p. 108.1–111.4 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.22 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.8 Hz, 2H), 4.26–4.23 (m, 2H), 3.91–3.88 (m, 2H), 3.55 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.1, 146.4, 127.1, 123.5, 106.3, 66.0, 12.3; IR (KBr): 1518, 1345, 1214, 1037, 855, 700 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{INO}_4$: 335.9727; found: 335.9723.

2-(Iodomethyl)-2-(3-nitrophenyl)-1,3-dioxolane (7g). Yield 84%; white solid; m.p. 83.0–84.1 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 8.39–8.38 (m, 1H), 8.22–8.20 (m, 1H), 7.87–7.85 (m, 1H), 7.57 (t, J = 8.0 Hz, 1H), 4.27–4.23 (m, 2H), 3.92–3.89 (m, 2H), 3.56 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 148.2, 141.8, 132.1, 129.4, 123.7, 121.2, 106.2, 66.0, 12.5; IR (KBr): 1524, 1347, 1213, 1045, 979, 690 cm^{-1} ; HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{INO}_4$: 335.9727; found: 335.9726.

2-(Iodomethyl)-2-(2-nitrophenyl)-1,3-dioxolane (7h). Yield 72%; white solid; m.p. 108.3–110.5 $^\circ\text{C}$; ^1H NMR (CDCl_3 , 400 MHz): δ 7.72 (d, J = 7.6 Hz, 1H), 7.57–7.47 (m, 3H), 4.18–4.15 (m, 2H), 3.92 (s, 2H), 3.79–3.76 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): δ 149.6, 132.0, 131.2, 129.9, 129.0, 123.5, 105.7, 65.9, 12.5; IR (KBr): 1539, 1361, 1205, 1030, 976,

786 cm⁻¹; HRMS (ESI): m/z [M + H]⁺ calcd for C₁₀H₁₁INO₄: 335.9727; found: 335.9727.

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