An Efficient Method for the Selective Iodination of α,β-Unsaturated Ketones

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Abstract: An efficient approach to α,β-unsaturated α′-iodo ketones directly from α,β-unsaturated ketones by selective iodination at the α′-position, without effect on the double bond and the activated benzene ring, in the presence of copper(II) oxide/iodine is described. The present method has the advantages of high yields, short reaction times, inexpensive reagents, mild reaction conditions, ease of manipulation, and the formation of cleaner products.

Key words: iodination, α,β-unsaturated ketones, α,β-unsaturated α′-iodo ketones, self-sorting

α,β-Unsaturated α′-halo ketones have attracted a great deal of interest due to their applications as important reaction intermediates in the synthesis of drugs[1] and heterocyclic compounds,[2] or as important structural fragments found in numerous natural products[3] (e.g., compounds **1** and **2**, Figure 1). Probably because *N*-bromosuccinimide (NBS), an excellent and efficient brominating reagent, could react with α,β-unsaturated ketones not only by substitution at the α′-position, but also by addition at the double bond,[4] α,β-unsaturated α′-bromo ketones are usually synthesized from the corresponding silyl enol ether[1a] or by using pyrrolidone hydrotribromide (PTH)[1c] as the bromonium source. It is well known that iodo-substituted compounds have higher reactivity than the corresponding bromo-substituted compounds. To date, although many excellent methods have been reported for the α-iodination of carbonyl compounds,[5–9] few of them are suitable for α,β-unsaturated ketone substrates due to harsh reaction conditions or the use of strong oxidants. In addition, it was found that the double bond of α,β-unsaturated ketones (α-position) was easily iodinated by I_2/Et_3N,[10] $I_2/py/CCl_4$,[11] $I_2/DMAP/K_2CO_3$,[12] or $I_2/Py/PhI(OCOCF_3)_2$[13] systems. Only Stavber[14] and Kim[15] reported one example for the synthesis of (*E*)-1-iodo-4-phenylbut-3-en-2-one and (*E*)-4-(4-hydroxy-3-methoxyphenyl)-1-iodobut-3-en-2-one with elemental iodine mediated by 1-(chloromethyl)-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate) (N-F reagent) and bis(tetrabutylammonium) peroxydisulfate (iodination at the double bond for α,β-unsaturated cyclic ketone substrates), respectively. The use of complex reagents limited substrates scope among these reported methods.[14,15] Accordingly, it is necessary to establish a simple and efficient method for the selective iodination of α,β-unsaturated ketones at the α′-position.

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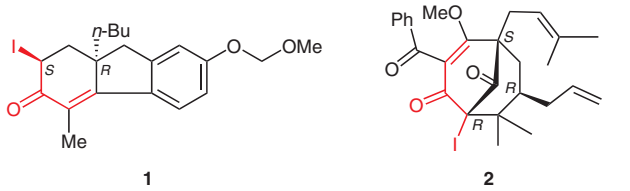
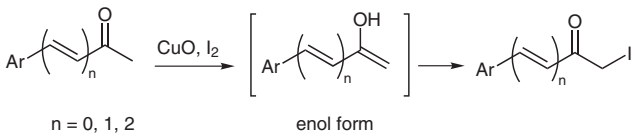
Our recent experimental results indicated that α-iodination of carbonyl compounds was excellently achieved by a copper(II) oxide/iodine system.[16] The reaction mechanism showed that copper(II) oxide promoted the formation of a highly reactive enol-form intermediate that could be stabilized by the aromatic ring via π-π conjugated interactions (Scheme 1, n = 0). α,β-Unsaturated α′-iodo ketones have potential applications as important intermediates in organic synthesis, hence we considered the insertion of a C=C bond (or C≡C bond) between the aromatic ring and carbonyl group in the aromatic ketone (Scheme 1, n = 1, 2) as most probably the α,β-unsaturated ketone could be selectively iodinated at the α′-position without an effect on the double bond and the activated benzene ring. The detailed research results are reported in this paper.



1 2

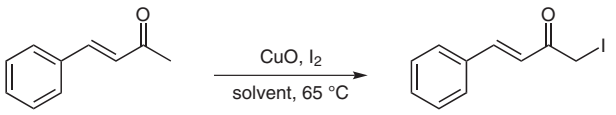
Figure 1



Scheme 1

We first synthesized benzalacetone (**4a**) in 89% yield via the aldol condensation of benzaldehyde with acetone catalyzed by sodium hydroxide according to a modified method[17] (Table 2, entry 1). In the published papers, it was found that the solvent played an important role in the direct α-iodination of carbonyl compounds.[8,16b] Therefore, herein benzalacetone (**4a**) was used as a model substrate to investigate the effect of solvents on the synthesis of (*E*)-1-iodo-4-phenylbut-3-en-2-one (**10a**). The mixture of benzalacetone (0.5 mmol), copper(II) oxide (0.5 mmol), and iodine (0.5 mmol) in various solvents (6 mL) was heated at 65 °C for 4–6 hours; the results are summarized in Table 1. The reaction afforded the expected methyl iodinated product **10a** instead of iodination at the C=C bond or on the benzene ring in good yields (68–85%) regardless of the solvent, e.g. methanol, ethanol, propanol,

Table 1 Effect of Solvents on the Synthesis of (*E*)-I-iodo-4-phenylbut-3-en-2-one (**10a**)



4a **10a**

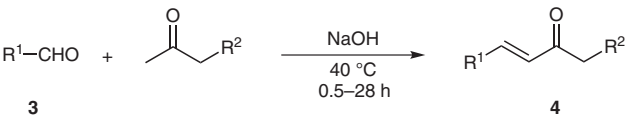
Entry	Solvent	Time (h)	Yield[a] (%)
1	MeOH	4	72
2	EtOH	4	80
3	PrOH	4	78
4	*i*-PrOH	4	85
5	BuOH	4	68
6	*t*-BuOH	4	50
7	THF	6	0
8	MeCN	6	0
9	benzene	6	0

[a] Isolated yield.

propan-2-ol, or butanol (Table 1, entries 1–5). Product **10a** was obtained in moderate yield (50%) using *tert*-butyl alcohol as a solvent (Table 1, entry 6). However, it was interesting to find that almost no reaction was observed in aprotic solvents such as tetrahydrofuran, benzene, and acetonitrile (Table 1, entries 7–9). It was obvious that propan-2-ol was the optimal solvent in this reaction (Table 1, entry 4).

To assess the generality of this iodination method and to evaluate the electronic influence of the aromatic ring substituents, a series of other α,β-unsaturated ketones **4b–l** were prepared in 65–96% yields by the above-mentioned aldol condensation of aldehydes with acetone or butanone (Table 2, entries 2–12). It should be noted that vanillin (**3j**) was condensed with acetone at 40 °C in the presence of sodium hydroxide (1.2 equiv), followed by acidification of the reaction solution using dilute hydrochloric acid also to afford the desired product (*E*)-4-(4-hydroxy-3-methoxyphenyl)but-3-en-2-one (**4j**) in 95% yield[18] (Table 2, entry 10). The structures of all compounds **4** in Table 2 were confirmed by ^{1}H NMR, which were agreement with data given in the literature.[19] Furthermore, the structure of new compound (*E*)-4-(9-anthryl)but-3-en-2-one (**4i**) was characterized by ^{13}C NMR, MS, and IR. Subsequently, **4j** was reacted with benzyl bromide in *N*,*N*-dimethylformamide at 70 °C for eight hours in the presence of potassium hydroxide to give (*E*)-4-[4-(benzyloxy)-3-methoxyphenyl]but-3-en-2-one (**5**) in 90% yield;[20] (*E*)-4-(4-acetoxy-3-methoxyphenyl)but-3-en-2-one (**6**) was obtained in 92% yield by the reaction of **4j** with acetyl chloride for 30 minutes using triethylamine as an acid-binding agent at room temperature[21] (Scheme 2).

Table 2 Synthesis of α,β-Unsaturated Ketones **4** via Aldol Condensation Reactions[a]

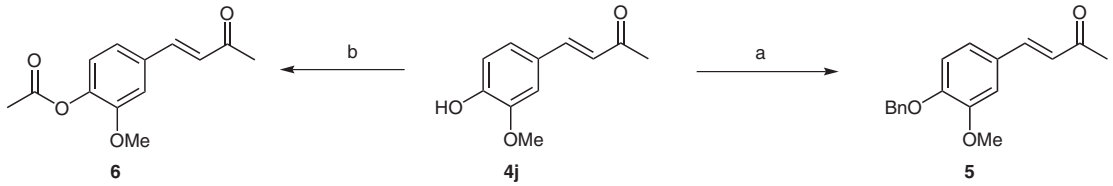


3 **4**

Entry	R^1	R^2	Product[b]	Yield[c] (%)
1	Ph	H	**4a**	89
2	4-MeC_6H_4	H	**4b**	95
3	4-MeOC_6H_4	H	**4c**	90
4	4-EtOC_6H_4	H	**4d**	85
5	4-ClC_6H_4	H	**4e**	93
6	2,4-$Cl_2C_6H_3$	H	**4f**	84
7	4-BrC_6H_4	H	**4g**	87
8	3-O_2N-C_6H_4	H	**4h**	96
9	9-anthryl	H	**4i**	80
10	3-MeO-4-HOC_6H_3	H	**4j**	95[d]
11	(*Z*)-CH=CHPh	H	**4k**	71
12	Ph	Me	**4l**	65[e]

[a] Reagents and conditions: aldehyde (0.1 mol), acetone (20 mL), H_2O (40 mL), 5% NaOH soln (8 mL), 40 °C.
[b] See ref. 19 for the spectral data of known compounds.
[c] Isolated yields.
[d] NaOH (1.2 equiv) was required and diluted HCl was used for treatment of the reaction mixture.
[e] Benzaldehyde (0.05 mol), butanone (0.06 mol), EtOH (30 mL).

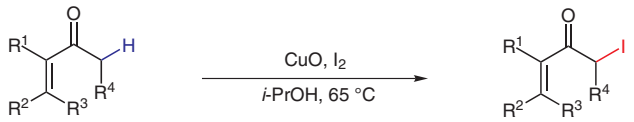
Next, other readily synthesized α,β-unsaturated ketones **4b–l** in Table 2 were examined for the iodination reaction using the copper(II) oxide/iodine system under the above-mentioned optimal reaction conditions, the results are summarized in Table 3. It could be seen from Table 3 that as for the derivatives of benzalacetone, the corresponding α′-iodinated products **10b–g** were obtained in 73–92% yields while the benzene rings bear electron-donating groups (e.g., Me, OMe, OEt) or moderate electron-withdrawing groups (e.g., Cl, Br), and the C=C bonds were not affected (Table 3, entries 2–7).



6 **4j** **5**

Scheme 2 *Reagents and conditions*: (a) BnBr, KOH, DMF, 70 °C, 8 h, 90%; (b) AcCl, Et_3N, CH_2Cl_2, r.t., 0.5 h, 92%.

Table 3 Synthesis of α,β-Unsaturated α′-Iodo Ketones Directly from α,β-Unsaturated Ketones



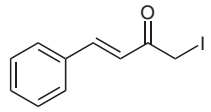
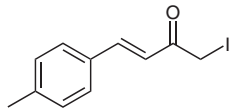
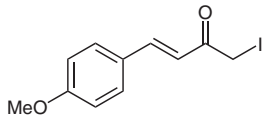
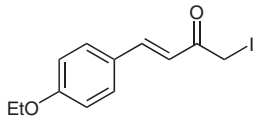
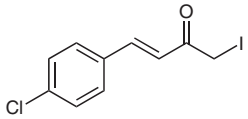
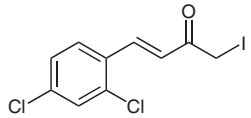
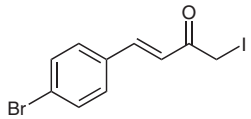
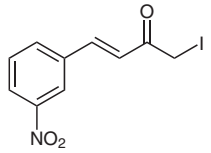
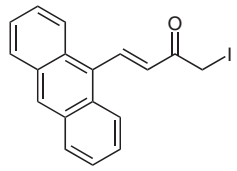
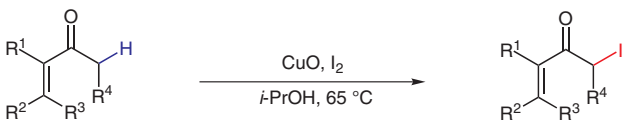
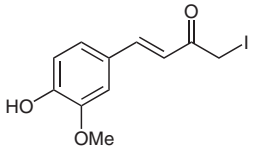
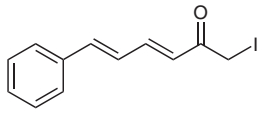
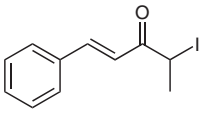
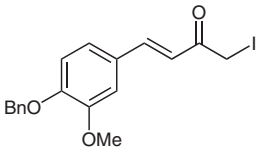
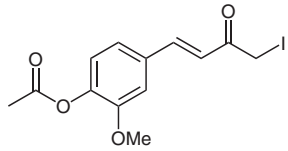
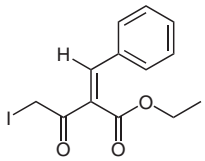
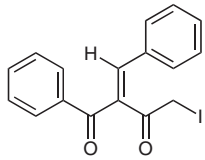
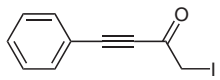
Entry	Substrate	Product	Time (h)	Yield[a] (%)
1	**4a**	 **10a**	4	85
2	**4b**	 **10b**	2	92
3	**4c**	 **10c**	2	83
4	**4d**	 **10d**	2	89
5	**4e**	 **10e**	1	89
6	**4f**	 **10f**	2.5	73
7	**4g**	 **10g**	4.5	82
8	**4h**	 **10h**	1.5	70
9	**4i**	 **10i**	3	70

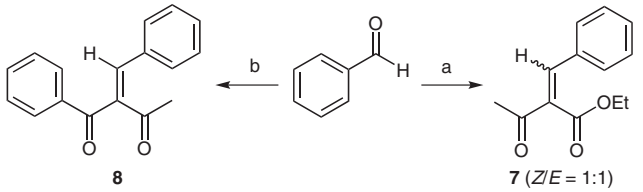
Table 3 Synthesis of α,β-Unsaturated α′-Iodo Ketones Directly from α,β-Unsaturated Ketones (continued)



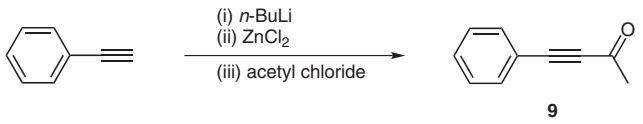
Entry	Substrate	Product	Time (h)	Yield[a] (%)
10	**4j**	 **10j**	4.5	85
11	**4k**	 **10k**	2	79
12	**4l**	 **10l**	6	72
13	**5**	 **10m**	4	87
14	**6**	 **10n**	4	80
15	(*Z*)-**7**	 **10o**	1	65
16	(*E*)-**8**	 **10p**	10	62
17	**9**	 **10q**	4	–[b]

[a] Isolated yield.
[b] Trace product was detected by GC-MS.

The substrate bearing the strongly electron-withdrawing nitro group on the phenyl ring delivered the iodinated product (*E*)-1-iodo-4-(3-nitrophenyl)but-3-en-2-one (**10h**) in slightly lower yield (70%, Table 3, entry 8). In addition, (*E*)-4-(9-anthryl)but-3-en-2-one (**4i**) also produced (*E*)-4-(9-anthryl)-1-iodobut-3-en-2-one (**10i**) in 70% yield (Table 3, entry 9). To our great satisfaction, compounds **4j**, **5**, and **6** gave the expected α′-iodinated products **10j**, **10m**, and **10n** in 85%, 87%, and 80% yields, respectively (Table 3, entries 10, 13, and 14). Such an approach to the synthons **10j**, **10m**, and **10n** could present new possibilities for the synthesis of analogues of this type with biomedicinal importance. It should be noted that sensitive hydroxy group (OH) was not affected under these mild reaction conditions and the hydrogens of the acetyl group of compound **6** were not replaced by iodine, probably due to the difficulty in the formation of the enol form (see the following reaction mechanism). We also found that (3*E*,5*E*)-6-phenylhexa-3,5-dien-2-one (**4k**) and (*E*)-1-phenylpent-1-en-3-one (**4l**) delivered the corresponding iodinated products **10k** and **10l** in 79% and 72% yields, respectively (Table 3, entries 11 and 12).



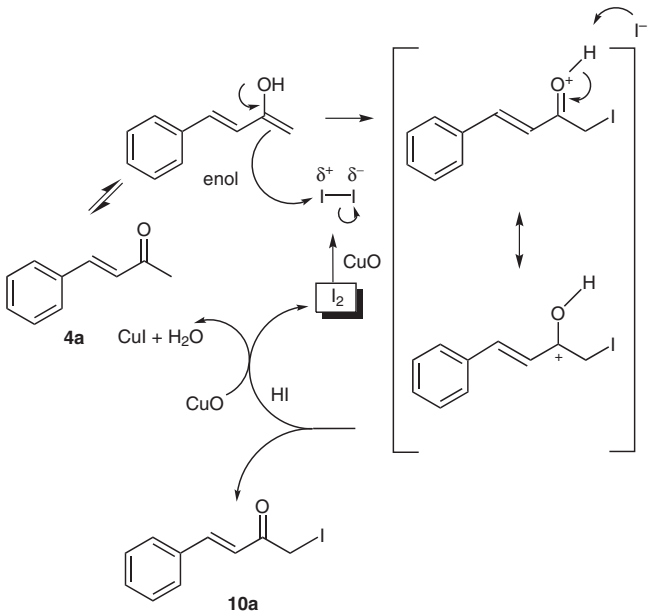
Scheme 3 *Reagents and conditions*: (a) $MeCOCH_2CO_2Et$, piperidine, AcOH, 90%; (b) $PhCOCH_2COMe$, piperidine, AcOH, 78%.



Scheme 4

Encouraged by the success of the above iodination reactions starting from α,β-unsaturated ketones, we turned our attention to other substrates. As shown in Scheme 3, Knoevenagel condensation of benzaldehyde with ethyl acetoacetate catalyzed by piperidine gave compound **7** in 90% yield (*Z*/*E* 1:1); the *Z*-isomer was separated by column chromatography as a white solid.[22] Similarly, the *E*-isomer of compound **8** was obtained as the major product (78%) via condensation of benzaldehyde with benzoylacetone.[23] We were glad to find that the desired iodinated products **10o** and **10p** were also obtained in 65% and 62% yields from compounds (*Z*)-**7** and (*E*)-**8** respectively (Table 3, entries 15 and 16). Finally, we synthesized 4-phenylbut-3-yn-2-one (**9**) in 89% yield by the reaction of phenylacetylene with acetyl chloride in the presence of butyllithium and zinc chloride[24] (Scheme 4). The expected iodinated product 1-iodo-4-phenylbut-3-yn-2-one (**10q**) was confirmed by GC-MS using compound **9** as the starting material, though we did not separate it (Table 3, entry 17). The possible reason for the low yield is that C≡C bond, which can easily react with molecular iodine, has higher reactivity than the C=C bond.[25]

It has been reported by Cort[26] that copper(II) nitrate could reoxidize the iodide ion (I^-) to molecular iodine (I_2) by the treatment of enol silyl ethers or enol acetates with the copper(II) nitrate/iodine system. In addition, on the basis of our previous study,[16b] a hypothetic reaction mechanism is shown in Scheme 5 using benzalacetone (**4a**) as an example. It is thought that copper(II) oxide plays a multiple role through random self-sorting. First, it acts as an oxidizing agent or catalyst to convert molecular iodine into the reacting species iodonium ion (I^+) analogous to the function of other metal salts.[6b,26b] Meanwhile, it can acted as a weak base to neutralize hydrogen iodide and reoxidize the iodide ion to molecular iodine together with insoluble copper(I) iodide and water.



Scheme 5 Possible reaction mechanism

In conclusion, a series of α,β-unsaturated ketones have been synthesized via classical aldol or Knoevenagel condensation reactions. An efficient approach to α,β-unsaturated α′-iodo ketones directly from α,β-unsaturated ketones by selective iodination at the α′-position without effect on the double bond and the activated benzene ring in the presence of copper(II) oxide/iodine is described. The possible reaction mechanism shows copper(II) oxide plays a multiple role in this kind of reaction through random self-sorting. The present method has the advantages of high yields, short reaction times, inexpensive reagents, mild reaction conditions, ease of manipulation, and the formation of cleaner products. Moreover, as far as we know, this is the first systematical investigation of the synthesis of important α,β-unsaturated α′-iodo ketones from α,β-unsaturated ketones.

Finely powdered CuO was purchased from commercial sources (>98%). ^{1}H spectra were recorded on a Varian Mercury 400 or 600 MHz spectrometer. All ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz (^{13}C at 100 MHz) spectrometer. Chemical shifts are reported relative to TMS (internal standard). IR spectra of samples as KBr pellets were recorded on a PE-983 spectrophotometer. MS was carried out on a Finnigan Trace MS spectrometer (EI, 70 eV). Column chromatography was performed on silica gel (200–300 mesh).

(*E*)-α,β-Unsaturated Ketones 4; General Procedure

To the mixture of aldehyde (0.1 mmol), acetone (20 mL, excess), and H_2O (40 mL) was slowly added 5% aq NaOH soln (8 mL) from a dropping funnel at 40 °C. After disappearance of the reactant (TLC), acetone was removed under reduced pressure and the residue was poured into EtOAc (50 mL), the mixture was extracted with EtOAc (3 × 50 mL), and the combined organic layers were dried (anhyd Na_2SO_4). Removal of the solvent and purification of the residue by column chromatography or recrystallization gave the target products.

(*E*)-4-(9-Anthryl)but-3-en-2-one (4i)

IR (KBr): 1665, 1621, 1360, 1252, 737 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.50 (d, *J* = 16.4 Hz, 1 H), 8.47 (s, 1 H), 8.21 (d, *J* = 9.2 Hz, 2 H), 8.33 (d, *J* = 8.8 Hz, 2 H), 7.52–7.26 (m, 4 H), 6.72 (d, *J* = 16.4 Hz, 1 H), 2.57 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 140.4, 135.8, 131.1, 129.2, 129.1, 128.9, 128.4, 126.4, 125.3, 125.0, 28.0.

MS (EI, 70 eV): *m*/*z* (%) = 246 (35), 204 (73), 202 (100).

α,β-Unsaturated α′-Iodo Ketones 10; General Procedure

Finely powdered CuO (0.40 g, 5.0 mmol) and I_2 (1.27 g, 5.0 mmol) were added to a well-stirred soln of α,β-unsaturated ketone (5.0 mmol) in *i*-PrOH (20 mL). The mixture was stirred for 5 min and then was heated at 65 °C for 1–10 h. After disappearance of the reactant (TLC), the mixture was filtered and the solvent was removed under reduced pressure (*Note*: the mixture could not be treated with $Na_2S_2O_3$ because it reacted with the iodinated product at r.t.), then direct purification of the residue by column chromatography (petroleum ether–EtOAc) gave the target products in good yield.

(*E*)-1-Iodo-4-phenylbut-3-en-2-one (10a)[15]

IR (KBr): 3445, 1640, 1573, 1436, 1270, 1072, 990, 874, 803, 764, 704 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 16.4 Hz, 1 H), 7.59–7.57 (m, 2 H), 7.43–7.41 (m, 3 H), 6.89 (d, *J* = 16.4 Hz, 1 H), 4.02 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 144.8, 133.8, 130.9, 128.9, 128.4, 122.2, 5.0.

MS (EI, 70 eV): *m*/*z* (%) = 272 (13), 146 (33), 144 (39), 131 (100), 104 (17), 91 (8), 78 (7).

(*E*)-1-Iodo-4-(4-tolyl)but-3-en-2-one (10b)

IR (KBr): 1669, 1607, 1566, 1382, 1276, 1134, 988, 823 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 16.2 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 2 H), 7.23 (d, *J* = 7.8 Hz, 2 H), 6.85 (d, *J* = 16.2 Hz, 1 H), 4.01 (s, 2 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 144.8, 141.4, 130.9, 129.5, 128.4, 120.9, 21.4, 5.3.

MS (EI, 70 eV): *m*/*z* (%) = 286 (99), 159 (3), 145 (22), 141 (59), 127 (53), 115 (100), 91 (43).

(*E*)-1-Iodo-4-(4-methoxyphenyl)but-3-en-2-one (10c)

IR (KBr): 3049, 1634, 1599, 1512, 1256, 1177, 1019, 972, 822, 936, 764 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 16.2 Hz, 1 H), 7.54 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 16.2 Hz, 1 H), 4.00 (s, 2 H), 3.86 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 192.2, 161.8, 144.8, 130.3, 126.4, 119.7, 114.3, 55.3, 5.2.

MS (EI, 70 eV): *m*/*z* (%) = 302 (22), 175 (16), 161 (100), 147 (19), 103 (22), 77 (14).

(*E*)-4-(4-Ethoxyphenyl)-1-iodobut-3-en-2-one (10d)

IR (KBr): 3444, 1641, 1620, 1599, 1509, 1252, 1173, 1035, 973, 825, 807 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 16.0 Hz, 1 H), 7.52 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.76 (d, *J* = 16.0 Hz, 1 H), 4.08 (q, *J* = 7.2 Hz, 2 H), 4.00 (s, 2 H), 1.44 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 161.3, 144.9, 130.4, 126.3, 119.6, 114.8, 63.6, 14.6, 5.1.

MS (EI, 70 eV): *m*/*z* (%) = 316 (100), 189 (30), 176 (78), 175 (96), 147 (61), 133 (65), 91 (32), 77 (19).

(*E*)-4-(4-Chlorophenyl)-1-iodobut-3-en-2-one (10e)

IR (KBr): 3423, 1669, 1641, 1623, 1591, 1490, 1385, 1148, 1088, 980, 835, 881, 791 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 16.0 Hz, 1 H), 7.52 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 16.0 Hz, 1 H), 4.01 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 143.5, 136.9, 132.3, 129.7, 129.2, 122.4, 5.0.

MS (EI, 70 eV): *m*/*z* (%) = 308 (M + 2), 306 (9), 179 (12), 167 (34), 165 (100), 137 (22), 115 (33), 101 (20), 75 (9).

(*E*)-4-(2,4-Dichlorophenyl)-1-iodobut-3-en-2-one (10f)

IR (KBr): 3455, 1672, 1649, 1583, 1130, 1101, 984, 866, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 16.4 Hz, 1 H), 7.61 (d, *J* = 8.8 Hz, 1 H), 7.47 (s, 1 H), 7.30 (d, *J* = 8.8 Hz, 1 H), 6.84 (d, *J* = 16.4 Hz, 1 H), 4.04 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 139.2, 136.9, 136.0, 130.7, 130.0, 128.4, 127.5, 124.7, 4.7.

MS (EI, 70 eV): *m*/*z* (%) = 344 (M + 4, 1), 342 (M+2, 8), 340 (M, 11), 307 (39), 305 (100), 201 (54), 199 (79), 99 (27), 74 (22).

(*E*)-4-(4-Bromophenyl)-1-iodobut-3-en-2-one (10g)

IR (KBr): 3425, 1670, 1643, 1619, 1583, 1143, 1068, 1007, 981, 879, 832 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 16.0 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 6.88 (d, *J* = 16.0 Hz, 1 H), 4.00 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 143.5, 132.8, 132.2, 129.8, 125.3, 122.5, 5.0.

MS (EI, 70 eV): *m*/*z* (%) = 352 (M + 2, 8), 352 (M, 8), 212 (57), 211 (60), 209 (100), 208 (63), 115 (52), 102 (31), 101 (22).

(*E*)-1-Iodo-4-(3-nitrophenyl)but-3-en-2-one (10h)

IR (KBr): 1695, 1613, 1522, 1348, 1052, 976, 866, 816 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 7.88 (d, *J* = 8.4 Hz, 1 H), 7.73 (d, *J* = 16.0 Hz, 1 H), 7.64 (d, *J* = 8.4 Hz, 1 H), 7.02 (d, *J* = 16.0 Hz, 1 H), 4.03 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.4, 148.5, 141.7, 135.6, 134.2, 130.0, 124.9, 124.6, 122.6, 5.1.

MS (EI, 70 eV): *m*/*z* (%) = 317 (100), 190 (8), 176 (99), 115 (79), 102 (51).

(*E*)-4-(9-Anthryl)-1-iodobut-3-en-2-one (10i)
IR (KBr): 1674, 1600, 1405, 1263, 1194, 1040, 994, 889, 841, 782, 737 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.65 (d, *J* = 16.0 Hz, 1 H), 8.44 (s, 1 H), 8.22 (d, *J* = 8.4 Hz, 2 H), 8.01 (d, *J* = 8.4 Hz, 2 H), 7.54–7.47 (m, 4 H), 6.85 (d, *J* = 16.0 Hz, 1 H), 4.11 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 142.1, 131.0, 130.9, 129.4, 128.8, 128.6, 126.5, 125.3, 124.8, 5.2.

MS (EI, 70 eV): *m*/*z* (%) = 372 (14), 245 (41), 202 (100).

(*E*)-4-(4-Hydroxy-3-methoxyphenyl)-1-iodobut-3-en-2-one (10j)[14]
IR (KBr): 3393, 1674, 1583, 1510, 1426, 1271, 1159, 1044, 1028, 978, 845, 810 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 15.6 Hz, 1 H), 7.15 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1 H), 7.07 (d, *J* = 1.8 Hz, 1 H), 6.95 (d, *J* = 8.4 Hz, 1 H), 6.73 (d, *J* = 15.6 Hz, 1 H), 6.01 (s, 1 H, OH), 4.01 (s, 2 H), 3.95 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 148.7, 146.7, 145.4, 126.2, 123.9, 119.6, 114.8, 109.7, 55.9, 4.9.

MS (EI, 70 eV): *m*/*z* (%) = 318 (100), 191 (2), 141 (23), 103 (33), 91 (16), 77 (11).

(3*E*,5*E*)-1-Iodo-6-phenylhexa-3,5-dien-2-one (10k)
IR (KBr): 3424, 1671, 1583, 1413, 1006, 753, 688, 642 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.50–7.33 (m, 6 H), 7.03–6.88 (m, 2 H), 6.43 (d, *J* = 15.6 Hz, 1 H), 3.95 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.3, 145.0, 142.7, 135.7, 129.5, 128.8, 127.4, 126.1, 125.4, 4.8.

MS (EI, 70 eV): *m*/*z* (%) = 298 (17), 171 (100), 157 (32), 128 (88), 102 (7), 77 (5).

(*E*)-4-Iodo-1-phenylpent-1-en-3-one (10l)
IR (KBr): 3421 (s), 1680 (s), 1610 (s), 1572 (s), 1444 (s), 1092 (s), 1040 (s), 975 (s), 761 (s), 709 (s), 683 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 16.0 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.42–7.40 (m, 3 H), 6.93 (d, *J* = 16.0 Hz, 1 H), 4.87 (q, *J* = 6.8 Hz, 1 H), 2.00 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.7, 144.1, 134.0, 130.7, 128.8, 128.5, 121.8, 24.5, 21.5.

MS (EI, 70 eV): *m*/*z* (%) = 286 (12), 159 (10), 131 (76), 127 (39), 103 (47), 91 (30), 77 (89), 51 (100).

(*E*)-4-[4-(Benzyloxy)-3-methoxyphenyl]-1-iodobut-3-en-2-one (10m)
IR (KBr): 1667, 1616, 1591, 1512, 1276, 1256, 1138, 993, 917, 867 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 16.0 Hz, 1 H), 7.44–7.32 (m, 5 H), 7.11–7.09 (m, 2 H), 6.89 (d, *J* = 8.8 Hz, 1 H), 6.73 (d, *J* = 16.0 Hz, 1 H), 5.22 (s, 2 H), 4.01 (s, 2 H), 3.95 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 150.7, 149.5, 145.0, 136.2, 128.5, 128.0, 127.1, 127.0, 123.3, 120.0, 113.0, 110.2, 70.6, 55.9, 5.0.

MS (EI, 70 eV): *m*/*z* (%) = 408 (3), 365 (2), 281 (20), 91 (100).

(*E*)-4-(4-Acetoxy-3-methoxyphenyl)-1-iodobut-3-en-2-one (10n)
IR (KBr): 1748, 1668, 1645, 1509, 1226, 1201, 1160, 1121, 1033, 985, 914, 864 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 16.0 Hz, 1 H), 7.19 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1 H), 7.65 (d, *J* = 1.6 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 6.82 (d, *J* = 16.0 Hz, 1 H), 4.02 (s, 2 H), 3.89 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 168.7, 151.3, 144.3, 141.8, 132.8, 123.3, 122.2, 121.7, 111.5, 55.9, 20.6, 4.9.

MS (EI, 70 eV): *m*/*z* (%) = 360 (5), 318 (100), 191 (88), 177 (95), 159 (84), 145 (37), 131 (47), 103 (20), 91 (8).

Ethyl (*E*)-2-Benzylidene-4-iodo-3-oxobutanoate (10o)
IR (KBr): 3444, 1717, 1697, 1618, 1257, 1198, 1025, 692 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (s, 1 H), 7.42–7.40 (m, 5 H), 4.33 (q, *J* = 7.2 Hz, 2 H), 4.10 (s, 2 H), 1.36 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.8, 163.9, 144.0, 132.5, 130.9, 130.1, 129.7, 129.0, 128.7, 61.8, 14.1, 8.7.

MS (EI, 70 eV): *m*/*z* (%) = 344 (11), 299 (100), 217 (99), 115 (41), 102 (42), 76 (19).

(*Z*)-2-Benzylidene-4-iodo-1-phenylbutane-1,3-dione (10p)
IR (KBr): 3444, 1668, 1637, 1617, 1594, 1573, 1233, 1258, 1211, 915, 782, 769 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H), 7.95 (d, *J* = 8.0 Hz, 2 H), 7.54–7.51 (m, 1 H), 7.41–7.21 (m, 7 H), 4.20 (s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 190.7, 143.5, 135.7, 135.6, 134.1, 132.4, 130.8, 130.4, 129.2, 128.7, 128.6, 2.3.

MS (EI, 70 eV): *m*/*z* (%) = 376 (5), 249 (89), 105 (100), 77 (48).

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