Synthesis L. Liu et al. Special Topic

Hypervalent Iodine Mediated C–C Double Bond Activation: A Cascade Access to α-Keto Diacetates from Readily Available Cinnamic Acids

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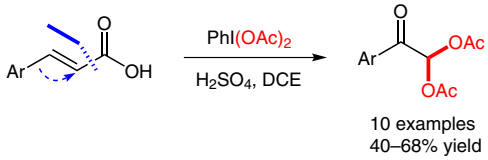

10 examples
40–68% yield

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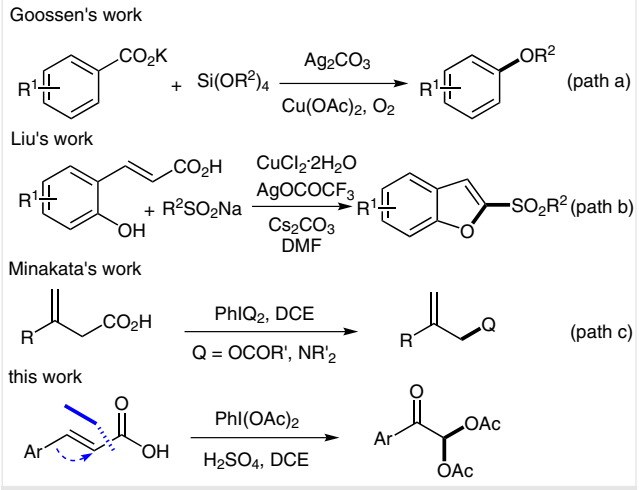
Abstract The reaction of cinnamic acids with (diacetoxyiodo)benzene in 1,2-dichloroethane in the presence of sulfuric acid provides an easy and direct access to the α-keto diacetate framework. This hypervalent iodine mediated oxidative reaction involves a tandem sequence of aryl migration, insertion of an oxygen atom, decarboxylation and diacetoxylation. A reaction mechanism is proposed and discussed in light of control experiments.

Key words hypervalent iodine reagents, C–C double bond activation, decarboxylation, aryl migration, α-keto diacetates

Decarboxylative functionalization of carboxylic acids has attracted an appreciable amount of attention in recent decades since such transformations employ commercially available carboxylic acids as the starting materials and show ostensible advantages in generating a great diversity of products during functionalization.[1] Consequently, many efficient methods have been developed in this area, even though most cases involve a C–C bond formation.[2] Methods promoting a carbon–heteroatom bond formation,[3] especially C–O bond formation, have been, relatively speaking, much less exploited.[4] The standard, classic strategy usually requires a heavy metal reagent, such as lead(IV) acetate or copper(II) acetate, as well as harsh reaction conditions.[5] For example, by using silver carbonate and copper(II) acetate under aerobic conditions, Goossen and co-workers realized a decarboxylative Chan–Evans–Lam type of coupling reaction for the construction of diaryl and alkyl aryl ethers starting from aromatic acids (Scheme 1, path a).[4a] In 2014, Li and Liu demonstrated a cascade reaction involving protodecarboxylation and C–S/C–O bond formation in realizing the assemblage of 2-sulfonylbenzo[*b*]furans from *trans*-2-hydroxycinnamic acids and sodium sulfinates by using a copper(II)/silver(I) oxidative system (Scheme 1, path b).[4b] In addition, a metal-free approach employing a hypervalent iodine reagent was developed by Minakata and co-workers; their method enabled a decarboxylative C–O or C–N bond formation starting from β,γ-unsaturated acids (Scheme 1, path c).[4c] In this article, we disclose another methodology for decarboxylative functionalization in realizing the conversion of cinnamic acids into α-keto diacetates. Mediated by a hypervalent iodine reagent under mild conditions, this metal-free process involves C–C double bond activation of the cinnamic acid, two C–C bond cleavages and three C–O bond formations.



Scheme 1 Oxidative decarboxylation reactions involving C–O bond formation

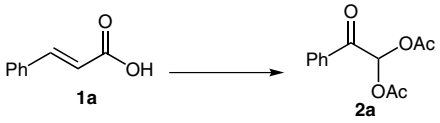
Hypervalent iodine reagents have been widely used in organic chemistry in recent decades due to their unique properties such as nontoxicity, environmentally benign nature and availability through commercial sources.[6] Chemi-

cally, they are not only effective oxidants, but also electrophiles for activating double bonds, which almost always leads to further oxidative rearrangement of some sort.[7] Much of our work has demonstrated the versatile applications of hypervalent iodine reagents in inducing tandem reactions which yield a large variety of rearranged, cleaved and functionalized products.[8]

Based on the results of our recent study of a novel, metal-free, oxidative protocol featuring a tandem oxidative aryl migration and C–C double bond-cleavage process,[8b] we envisaged a similar role for the hypervalent iodine reagent in inducing a reaction by initial interaction with the double bond in cinnamic acid. However, much to our disappointment, after subjecting the commercially available cinnamic acid (**1a**) to the conditions applied to the acrylic compounds in our previous study, no reaction occurred (Table 1, entry 1). Interestingly, simply by switching the solvent from ethyl acetate to 1,2-dichloroethane (DCE), a reaction took place and the diacetoxylated phenyl ketone **2a** was generated in 68% yield (Table 1, entry 2). Further solvent screening did not identify a more suitable solvent, as dioxane, toluene and acetonitrile all gave much lower yields, while the use of 2,2,2-trifluoroethanol and *N*,*N*-dimethylformamide resulted in no reaction (Table 1, entries 3–7). Reducing the amount of the oxidant from 3.0 to 2.0 equivalents of (diacetoxyiodo)benzene [PhI(OAc)$_2$, PIDA] resulted in a decreased yield (Table 1, entry 8). Other additives (CSA, TfOH, AcOH, TMSOTf and Ac_2O) were also examined; unfortunately, no yield improvement was observed (Table 1, entries 9–13). Combined additives were also evaluated; however, the yield was not improved when boron trifluoride–diethyl ether complex, acetic acid or acetic anhydride was coapplied with sulfuric acid, although the reaction time could be shortened (Table 1, entries 14–16).

The scope and generality of this oxidative decarboxylative functionalization reaction were investigated, and the results are listed in Table 2. For substrates bearing a strong electron-donating group (OMe), the reaction proceeded smoothly at –30 °C to room temperature, and the corresponding product was generated in moderate yield (Table 2, entries 2 and 3). For substrates bearing a weak electron-donating substituent (Me and Ph), the corresponding product was obtained in similar moderate yield (Table 2, entries 4–6). The reaction also worked well with 3-(naphthalen-2-yl)acrylic acid (**1g**) and afforded the desired product **2g** in 60% yield under the standard conditions (Table 2, entry 7). However, for substrates bearing a halogen substituent, satisfactory yields in the range of 57–68% were only achieved after extensive optimization studies of the reaction conditions which concluded that the combined additives of sulfuric acid and $BF_3{\cdot}OEt_2$ were required (Table 2, entries 8–10).

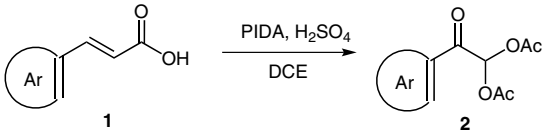
Table 1 Optimization of the Reaction Conditions[a]



Entry	Solvent	Additive	Time (h)	Yield[b] (%)
1	EtOAc	H_2SO_4	24	NR
2	DCE	H_2SO_4	15	68
3	dioxane	H_2SO_4	24	18
4	toluene	H_2SO_4	20	15
5	MeCN	H_2SO_4	20	25
6	DMF	H_2SO_4	24	NR
7	TFE	H_2SO_4	24	NR
8[c]	DCE	H_2SO_4	24	43
9	DCE	CSA	24	ND
10	DCE	TfOH	24	ND
11	DCE	AcOH	24	ND
12	DCE	TMSOTf	24	ND
13	DCE	Ac_2O	24	ND
14[d]	DCE	H_2SO_4	8	58
15[e]	DCE	H_2SO_4	12	61
16[f]	DCE	H_2SO_4	15	45

[a] Reaction conditions: **1a** (0.4 mmol), PIDA (1.2 mmol), additive (0.4 mmol), solvent (8 mL), reflux.
[b] Isolated yield. NR = no reaction; ND = not detected.
[c] PIDA (2.0 equiv) was employed and 30% of **1a** was recovered.
[d] $BF_3{\cdot}OEt_2$ (1.0 equiv) was added to the reaction mixture.
[e] AcOH (2 equiv) was added to the reaction mixture.
[f] Ac_2O (2 equiv) was added to the reaction mixture.

Table 2 Scope of the Reaction[a]



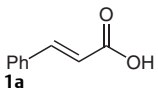
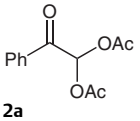
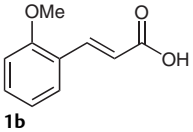
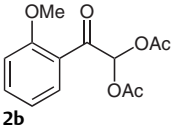
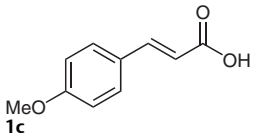
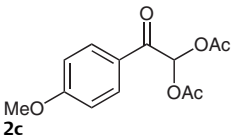
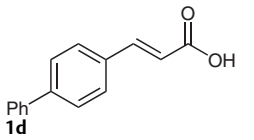
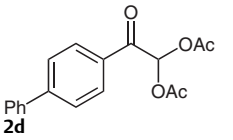
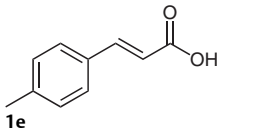
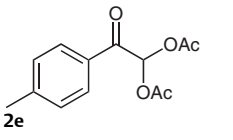
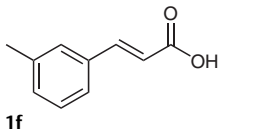
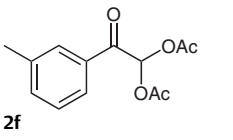
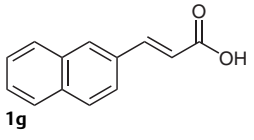
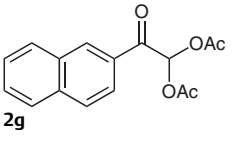
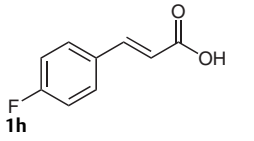
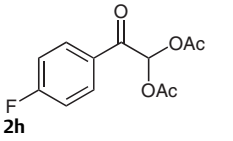
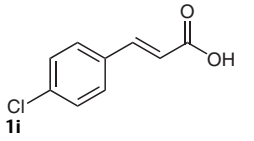
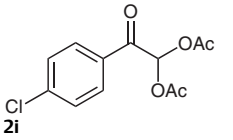
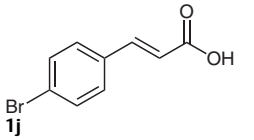
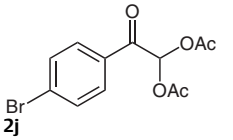
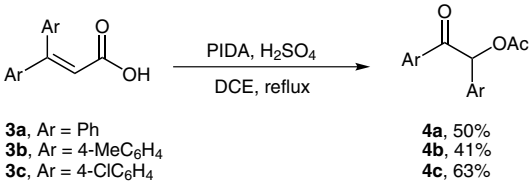
Entry	Substrate	Product	Yield[b] (%)
1	 **1a**	 **2a**	68
2[c]	 **1b**	 **2b**	61

Table 2 (continued)

Entry	Substrate	Product	Yield[b] (%)
3[c]	 **1c**	 **2c**	40
4	 **1d**	 **2d**	54
5	 **1e**	 **2e**	60
6	 **1f**	 **2f**	61
7	 **1g**	 **2g**	60
8[d]	 **1h**	 **2h**	57
9[d]	 **1i**	 **2i**	68
10[d]	 **1j**	 **2j**	65

[a] Reaction conditions: **1** (0.4 mmol), PIDA (1.2 mmol), concd H_2SO_4 (0.4 mmol), DCE (8 mL), reflux.
[b] Isolated yield.
[c] The reaction was carried out at –30 °C to r.t.
[d] $BF_3{\cdot}OEt_2$ (1.0 equiv) was added to the reaction mixture.

At the same time, we set out to investigate whether or not the phenyl ring of the starting cinnamic acid migrated. Disclosure of the issue was finally achieved by the following control experiments (Scheme 2). Three 3,3-disubstituted acrylic acids **3** were synthesized and examined under the described conditions. When 3,3-diphenylacrylic acid (**3a**) was treated with PIDA in the presence of sulfuric acid in 1,2-dichloroethane, the phenyl group migrated and acetoxylated product **4a** was isolated in moderate 50% yield. Additionally, a weak electron-donating or an electron-withdrawing substituent on the phenyl ring was tolerated, although electron-deficient substrate **3c** gave a better yield of the product. The successful transformation of these disubstituted substrates **3** unambiguously demonstrated that this newly discovered cascade oxidative decarboxylative functionalization reaction also involves an aryl migration process which is consistent with our previous observation on the transformation of acrylic amides and esters.[8b]

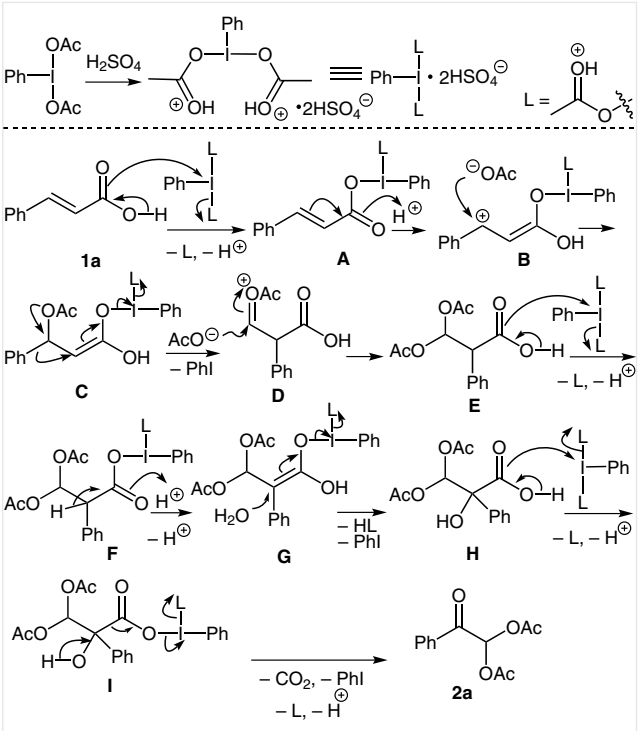


Scheme 2 Control experiments showing aryl migration

Attempts to expand the efficiency and generality of this method by employing an externally added nucleophile, including sodium azide, halogen salts, saccharin, benzoic acid and *p*-toluenesulfonic acid, to participate in the reaction proved to be unsuccessful.

On the basis of the experimental results, as well as our previous work,[8b] a plausible mechanism is proposed (Scheme 3). It is well known that hypervalent iodine reagents can be activated by Lewis acids or Brønsted acids;[9] thus, PIDA is first activated by protonation with sulfuric acid, which increases the electrophilicity of the iodine center. Then, nucleophilic attack of the iodine center by the carbonyl oxygen of cinnamic acid (**1a**) affords the ligand-exchanged iodine(III) species **A**, the protonated structure of which, namely, the benzyl cation **B**, is subsequently trapped by acetate to give intermediate **C**. Assisted by the oxygen lone-pair conjugation, the phenyl group migrates with the release of iodobenzene to generate oxonium **D**,[7c] which is attacked by another acetate to give intermediate **E**. Oxidation of **E** by activated PIDA in a similar fashion generates iodine(III) species **F** which subsequently looses one proton to afford **G**. Nucleophilic attack of the alkene by a water molecule, along with the elimination of iodobenzene, gives the oxidized alcohol **H**, which is further oxidized by a third equivalent of PIDA to furnish intermediate **I**. Finally, deprotonation leads to cleavage of the C–C bond and O–I bond, resulting in decarboxylation and ultimately the formation of **2a**.

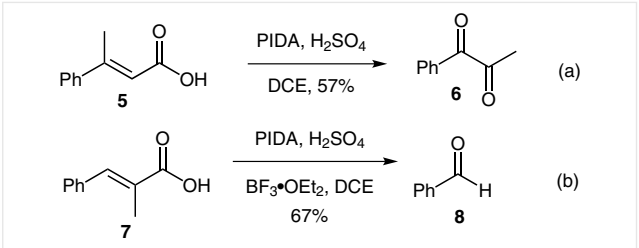
The proposed mechanism is supported by the results regarding those 3,3-disubstituted acrylic acids **3** which were successfully transformed under the optimal conditions into the corresponding decarboxylative functional-



Scheme 3 Proposed mechanism of the cascade reaction for the formation of **2a** from **1a**

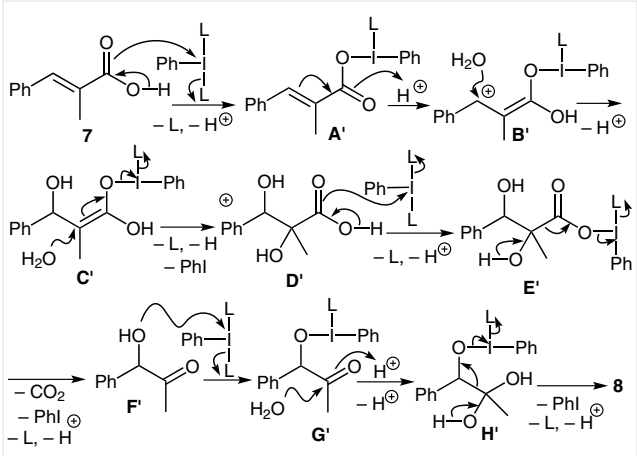
ized products carrying the characteristic of an aryl migration (Scheme 2). Among the acids, the one bearing the most electron-withdrawing substituent, **3c**, gave the highest yield, arguably suggesting that the nucleophilic attack by water of **G** in forming **H** is the rate-determining step in the series of reactions.

Additionally, a set of control experiments involved two methyl-phenyl-disubstituted acrylic acids as reactants (Scheme 4). When (*E*)-3-phenylbut-2-enoic acid (**5**) was treated with PIDA in the presence of sulfuric acid in 1,2-dichloroethane, 1-phenylpropane-1,2-dione (**6**) was isolated in 57% yield (Scheme 4, path a). It is evident that the reaction proceeds via a similar oxidative aryl migration and subsequent decarboxylation process. The formation of 1,2-dione **6** can be understood as water (instead of acetate anion) attacking the intermediate **B** and later **D**, and the resulting geminal diol undergoing the loss of water to form likely the thermodynamically more stable diketone through the extended π-conjugation of the carbonyl groups.



Scheme 4 Control experiments where aryl migration is and is not prevented

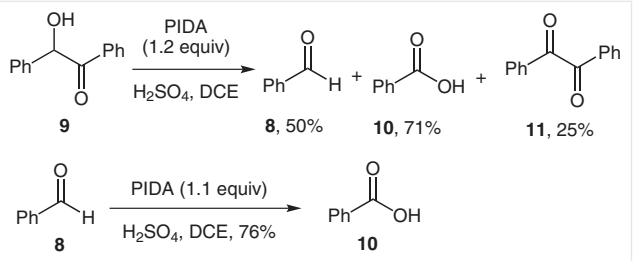
On the other hand, reaction of **7**, in which the α-position is blocked by a methyl group, delivered a complex mixture under the standard conditions. After excess $BF_3{\cdot}OEt_2$ was added along with sulfuric acid as the additive, the double bond was cleaved and benzaldehyde was formed in 67% yield (Scheme 4, path b). The mechanistic pathway for this conversion is illustrated in Scheme 5. The acid moiety nucleophilically attacks the iodine center, followed by protonation, to generate benzyl cation **B′**, which is trapped by water instead of acetate. This could be attributed to the addition of excess $BF_3{\cdot}OEt_2$ to the reaction mixture, resulting in decreased nucleophilicity of the acetate ions. Then, water attacks the double bond of intermediate **C′**, leading to the elimination of iodobenzene while generating the α,β-dihydroxy acid **D′**. Next, oxidation of **D′** gives the iodine(III) species **E′**, which undergoes deprotonation to induce decarboxylation and elimination of iodobenzene leading to the formation of **F′**. Further oxidation of **F′** affords **G′**. Subsequently, **G′** is protonated under acidic conditions followed by the addition of water to generate intermediate **H′**. Finally, deprotonation causes the cleavage of the C–C and O–I bonds, yielding benzaldehyde (**8**).



Scheme 5 Proposed mechanistic pathway for the transformation of **7**

With reference to the proposed mechanistic pathway for the transformation of **7** to benzaldehyde, additional experiments were carried out and the results proved to be supportive. Thus, when benzoin (**9**), which shares the same skeleton as the key intermediate **F′**, was treated with 1.2 equivalents of PIDA in the presence of sulfuric acid, the expected benzaldehyde and benzoic acid were isolated in acceptable yields, along with the formation of benzil (**11**), the oxidized product of benzoin (**9**), in 25% yield (Scheme 6). The unequal yield of benzaldehyde (**8**) and benzoic acid (**10**) is attributed to oxidation of the resulting benzaldehyde

under such conditions, which was further proved by a control experiment. These results provide unambiguous evidence for the existence of **F′**, as suggested in Scheme 5 for the transformation of **7**.



Scheme 6 Additional control experiments

In conclusion, we have developed a novel, metal-free, oxidative protocol for the decarboxylative functionalization of cinnamic acids. The procedure, mediated by a nonmetallic hypervalent iodine reagent under mild conditions, features a tandem process consisting of oxidative aryl migration, C–O bond formation, decarboxylation and diacetoxylation. To our knowledge, this is the first example of a rather complicated, concerted process for the synthesis of α-keto diacetates from readily available cinnamic acids. Further mechanistic studies aiming for a more detailed insight into the transformation are currently being undertaken in our laboratory.

All reactions were carried out at room temperature under air unless otherwise noted. ^{1}H (600 MHz) and ^{13}C (150 MHz) NMR spectra were recorded at 25 °C. Chemical shifts (δ) are reported in ppm with reference to TMS (0 ppm) and coupling constants (*J*) are given in Hz. High-resolution mass spectrometry (HRMS) data were obtained on a Q-TOF micro mass spectrometer. Melting points were determined with a Micro melting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 40 °C under reduced pressure.

α-Keto Diacetates 2; General Procedure

To a solution of a cinnamic acid **1** (0.4 mmol) and PIDA (1.2 mmol) in DCE (8 mL) was added concd H_2SO_4 (0.4 mmol) at r.t. under vigorous stirring. The resulting mixture was then heated to reflux and monitored by TLC. Upon reaction completion, the mixture was cooled to r.t., poured into a sat. aq solution of $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layer was washed with brine (100 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure and purification of the crude residue by flash column chromatography on silica gel (EtOAc–PE) gave the desired product **2**. For substrates **1b** and **1c**, the reactions were carried out at –30 °C for 1 h, and then warmed to r.t. For substrates **1h–j**, $BF_3{\cdot}OEt_2$ (1.0 equiv) was added after the addition of H_2SO_4.

2-Oxo-2-phenylethane-1,1-diyl Diacetate (2a)[10]

Pale yellow oil; yield: 64.2 mg (68%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.3 Hz, 2 H), 7.65–7.61 (m, 2 H), 7.50 (t, *J* = 7.8 Hz, 2 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, DMSO-d_6): δ = 189.0, 168.6, 134.5, 132.7, 129.1, 128.6, 86.5, 20.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}O_5$: 237.0757; found: 237.0755.

2-(2-Methoxyphenyl)-2-oxoethane-1,1-diyl Diacetate (2b)

Yellow solid; mp 58–60 °C; yield: 64.9 mg (61%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.5 Hz, 1 H), 7.59 (s, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.96 (d, *J* = 8.0 Hz, 1 H), 3.86 (s, 3 H), 2.15 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 190.1, 168.9, 159.0, 135.3, 131.8, 123.9, 121.2, 111.4, 89.1, 55.7, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}O_6$: 267.0863; found: 267.0867.

2-(4-Methoxyphenyl)-2-oxoethane-1,1-diyl Diacetate (2c)[11]

Colorless oil; yield: 42.6 mg (40%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 8.7 Hz, 2 H), 7.61 (s, 1 H), 6.96 (d, *J* = 8.7 Hz, 2 H), 3.88 (s, 3 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.1, 168.7, 164.5, 131.3, 126.1, 114.2, 86.1, 55.6, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}O_6$: 267.0863; found: 267.0867.

2-(Biphenyl-4-yl)-2-oxoethane-1,1-diyl Diacetate (2d)[10]

Yellow solid; mp 89–91 °C; yield: 67.4 mg (54%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.67 (s, 1 H), 7.63 (d, *J* = 7.4 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.42 (t, *J* = 6.9 Hz, 1 H), 2.20 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.4, 168.8, 147.0, 139.5, 131.8, 129.5, 129.1, 128.6, 127.5, 127.3, 86.3, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{17}O_5$: 313.1071; found: 313.1073.

2-Oxo-2-*p*-tolylethane-1,1-diyl Diacetate (2e)

Yellowish solid; mp 46–48 °C; yield: 60.0 mg (60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.1 Hz, 2 H), 7.61 (s, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 2.42 (s, 3 H), 2.17 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.3, 168.7, 145.5, 130.7, 129.6, 129.0, 86.2, 21.8, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}O_5$: 251.0914; found: 251.0917.

2-Oxo-2-*m*-tolylethane-1,1-diyl Diacetate (2f)

Colorless oil; yield: 61.0 mg (61%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (s, 1 H), 7.71 (d, *J* = 7.7 Hz, 1 H), 7.62 (s, 1 H), 7.44 (d, *J* = 7.7 Hz, 1 H), 7.37 (t, *J* = 7.7 Hz, 1 H), 2.41 (s, 3 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 189.0, 168.7, 138.9, 135.1, 133.3, 129.3, 128.7, 126.0, 86.2, 21.3, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{15}O_5$: 251.0914; found: 251.0917.

2-(Naphthalen-2-yl)-2-oxoethane-1,1-diyl Diacetate (2g)

Pale yellow solid; mp 94–96 °C; yield: 68.7 mg (60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.47 (s, 1 H), 7.98 (d, *J* = 8.5 Hz, 2 H), 7.92 (d, *J* = 8.5 Hz, 1 H), 7.89 (d, *J* = 8.2 Hz, 1 H), 7.79 (s, 1 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.58 (t, *J* = 7.5 Hz, 1 H), 2.20 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.8, 168.8, 136.1, 132.4, 131.1, 130.6, 129.9, 129.3, 128.9, 127.9, 127.1, 124.0, 86.3, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_5$: 287.0914; found: 287.0917.

2-(4-Fluorophenyl)-2-oxoethane-1,1-diyl Diacetate (2h)

Pale yellow oil; yield: 57.9 mg (57%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (dd, *J* = 8.5, 5.4 Hz, 2 H), 7.57 (s, 1 H), 7.17 (t, *J* = 8.5 Hz, 2 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.4, 168.7, 166.4 (d, J_{C-F} = 255.7 Hz), 131.7 (d, J_{C-F} = 9.5 Hz), 129.6 (d, J_{C-F} = 3.0 Hz), 116.2 (d, J_{C-F} = 21.9 Hz), 86.3, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{12}FO_5$: 255.0663; found: 255.0667.

2-(4-Chlorophenyl)-2-oxoethane-1,1-diyl Diacetate (2i)[10]

Pale yellow oil; yield: 73.4 mg (68%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, *J* = 8.5 Hz, 2 H), 7.55 (s, 1 H), 7.47 (d, *J* = 8.5 Hz, 2 H), 2.18 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 187.8, 168.6, 140.9, 131.5, 130.3, 129.3, 86.3, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{12}{}^{35}ClO_5$: 271.0368; found: 271.0369.

2-(4-Bromophenyl)-2-oxoethane-1,1-diyl Diacetate (2j)

Yellow solid; mp 70–72 °C; yield: 81.6 mg (65%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 8.4 Hz, 2 H), 7.48 (s, 1 H), 2.11 (s, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 188.1, 168.7, 132.3, 131.9, 130.3, 129.7, 86.2, 20.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{12}{}^{79}BrO_5$: 314.9863; found: 314.9866.

2-Oxo-1,2-diphenylethyl Acetate (4a)[12]

White solid; mp 120–122 °C; yield: 50.8 mg (50%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (d, *J* = 7.9 Hz, 2 H), 7.51 (t, *J* = 7.3 Hz, 1 H), 7.46 (d, *J* = 7.3 Hz, 2 H), 7.42–7.32 (m, 5 H), 6.86 (s, 1 H), 2.20 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.7, 170.5, 134.6, 133.6, 133.5, 129.4, 129.2, 128.8, 128.7, 128.7, 77.7, 20.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{15}O_3$: 255.1016; found: 255.1018.

2-Oxo-1,2-di(*p*-tolyl)ethyl Acetate (4b)[13]

Yellow oil; yield: 46.3 mg (41%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 7.8 Hz, 2 H), 7.34 (d, *J* = 7.6 Hz, 2 H), 7.20–7.13 (m, 4 H), 6.82 (s, 1 H), 2.34 (s, 3 H), 2.31 (s, 3 H), 2.19 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 193.3, 170.6, 144.4, 139.7, 132.0, 130.9, 129.9, 129.3, 128.9, 128.7, 77.5, 21.7, 21.3, 20.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{19}O_3$: 283.1329; found: 283.1324.

1,2-Bis(4-chlorophenyl)-2-oxoethyl Acetate (4c)[14]

Yellow oil; yield: 81.1 mg (63%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.7 Hz, 4 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 6.76 (s, 1 H), 2.20 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 192.4, 170.4, 140.3, 135.7, 132.7, 131.8, 130.1, 129.9, 129.5, 129.2, 76.7, 20.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{13}{}^{35}Cl_2O_3$: 323.0236; found: 323.0231.

1-Phenylpropane-1,2-dione (6)[15]

Yellow oil; yield: 33.8 mg (57%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 7.5 Hz, 2 H), 7.65 (t, *J* = 7.3 Hz, 1 H), 7.50 (t, *J* = 7.5 Hz, 2 H), 2.53 (s, 3 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 200.6, 191.4, 134.6, 131.8, 130.3, 128.9, 26.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_9H_9O_2$: 149.0597; found: 149.0595.

Benzil (11)[16]

Pale yellow solid; mp 93–95 °C; yield: 21 mg (25%).

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 7.5 Hz, 2 H), 7.67 (t, *J* = 7.5 Hz, 1 H), 7.52 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (150 MHz, $CDCl_3$): δ = 194.6, 134.9, 132.9, 129.9, 129.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{11}O_2$: 211.0759; found: 211.0756.

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Supporting Information

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