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N,N-Dimethylformamide (DMF) as a Source of Oxygen To Access α-Hydroxy Arones via the α-Hydroxylation of Arones

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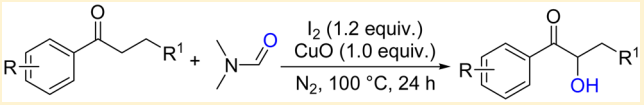
Supporting Information

ABSTRACT: An unprecedented α-hydroxylation strategy was developed for the synthesis of α-hydroxy arones using *N,N*-dimethylformamide (DMF) as an oxygen source. Control experiments demonstrated that the oxygen atom of the hydroxy group in the α-hydroxy arones produced in this reaction was derived from DMF. This new reaction therefore not only provides an alternative strategy for the α-hydroxylation of arones but also highlights the possibility of using the inexpensive common solvent DMF as a source of oxygen in organic synthesis.



In recent years, α-hydroxyketones[1] have attracted considerable interest because of their potential application to the synthesis of biologically active compounds and natural products.[2] For this reason, a large number of methods have been developed for the synthesis of α-hydroxyketones.[3] One of the most commonly used approaches for the synthesis of compounds belonging to this structural class involves the oxidation of silylenol ethers or enolates with a suitable oxidant such as a metal oxidant, hypervalent iodine reagent, or peroxide.[4] However, α-hydroxyketones can also be prepared by the reduction of diketones.[5]

N,N-Dimethylformamide (DMF) is a popular, inexpensive, aprotic polar solvent, which is widely used as a solvent in various organic reactions.[6] DMF is also used as a reagent[7] and a multipurpose precursor for the introduction of various functional groups such as −CHO,[8] −CO,[9] −CON$(CH_3)_2$,[10] −N$(CH_3)_2$,[11] −CN,[12] =CH,[13] and −H[14] moieties in organic chemistry. Li and co-workers recently reported a transition-metal-free approach for the synthesis of 2-aryliminochromenes from arynes, N,S-keteneacetals, and DMF, where DMF was used as a source of oxygen to form the chromeneskeleton.[15] Despite the success of this procedure, there have been very few reports in the literature pertaining to the use of DMF as an oxygen source in organic transformations (Scheme 1).[16] Herein, we report an efficient process for the synthesis of α-hydroxy arones from arones using DMF as a source of oxygen for the hydroxyl group (Scheme 1).

We initially investigated the reaction of propiophenone (**1a**) with DMF under a variety of different conditions to determine the optimum conditions for this transformation (Table 1). When the reaction was conducted in the presence of CuO (1.0 equiv) and I_2 (1.2 equiv) in DMF at 100 °C, we observed a moderate yield of the desired α-hydroxylated product **2a** after 16 h (63%). Increasing the reaction time to 24 or 32 h led to a minor increase in the yield to 75% (Table 1, entries 1−3). A variety of different copper species were investigated in the reaction, including $CuCl_2$, $CuBr_2$, $Cu(OAc)_2$, Cu_2O, CuCl, CuBr, and CuI, but CuO was found to be the most efficient oxidant in terms of the yield of 2-hydroxy-1-phenylpropan-1-one (**2a**) (Table 1, entries 4−10). It is noteworthy that $CuCl_2$, Cu_2O, and CuCl were found to be totally ineffective for this α-hydroxylation process, affording none of the desired product (Table 1, entries 4, 7−8). However, the use of CuI as a surrogate for CuO afforded the desired product **2a** in 69% yield by GC (Table 1, entry 10). The reaction did not afford any of the desired product when it was conducted in the absence of CuO or iodine (I_2), which indicated that these two species play a cooperative role in this reaction. We also investigated the effects of adding different amounts of CuO and I_2 to the reaction and found that the optimal amounts of these two materials were 1.0 and 1.2 equiv, respectively (Table 1, entries 12−14). Interestingly, we obtained different yields for the desired α-hydroxylated product **2a** when the reaction was conducted under oxygen (75%) and nitrogen (84%) atmospheres, indicating that O_2 is less effective for this transformation (Table 1, entries 15−16). Finally, we investigated the effect of the temperature on the reaction, and the results showed that

Scheme 1. DMF as a Source of Oxygen in Organic Transformations

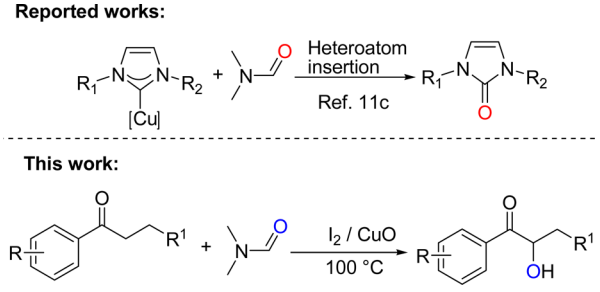


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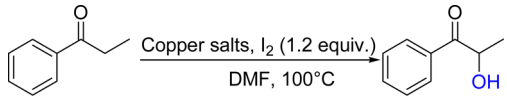
Table 1. Optimization Studies[a]



1a 2a

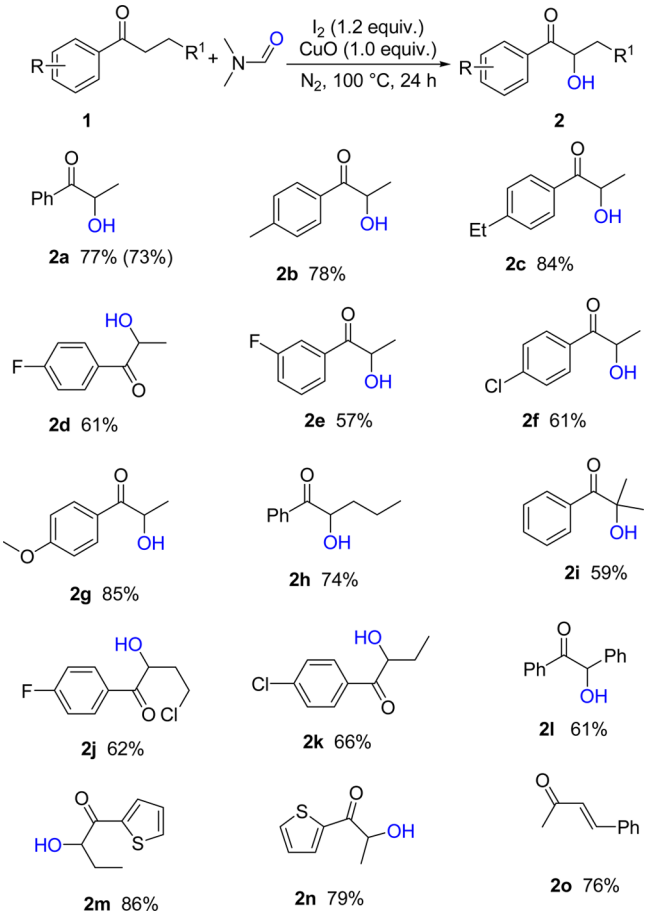
entry	copper salts (1.0 equiv)	time (h)	yield (%)[b]
1	CuO	16	63
2	CuO	24	75
3	CuO	32	75
4	$CuCl_2$	24	–
5	$CuBr_2$	24	trace
6	$Cu(OAc)_2$	24	trace
7	Cu_2O	24	–
8	CuCl	24	–
9	CuBr	24	13
10	CuI	24	69
11	–	24	–
12[c]	CuO	24	63
13[d]	CuO	24	72
14[e]	CuO	24	59
15[f]	CuO	24	66
16[g]	CuO	24	84
17[g,h]	CuO	24	84
18[g,i]	CuO	24	47

[a]Reaction conditions: **1a** (0.25 mmol), DMF (2.0 mL). [b]GC yield. [c]I_2: 0.5 equiv. [d]I_2: 1.0 equiv. [e]CuO: 0.5 equiv. [f]O_2 (balloon) [g]N_2 (balloon) [h]Reaction temperature: 120 °C [i]Reaction temperature: 60 °C.

the optimal temperature was 100 °C. Increasing the reaction temperature to 120 °C did not lead to a further increase in the yield, whereas reducing the reaction temperature to 60 °C led to a pronounced decrease in the yield (Table 1, entries 17−18). It is noteworthy that several other metal salts and metal oxides were evaluated in this reaction, including $FeCl_2$, $FeCl_3$, $NiCl_2$, MgO, and CaO, but all failed to afford any of the desired product.

With the optimized conditions in hand, we proceeded to investigate the scope of this α-hydroxylation reaction using a wide range of different propiophenones **1a−g** (Scheme 2). Pleasingly, all of the propiophenones tested reacted smoothly under the optimized conditions to give the corresponding α-hydroxylated products **2** in 57−85% yields. A comparison of the results for the different substrates revealed that the electronic effects of the substituents on the benzene ring played an important role in this transformation. For example, propiophenones bearing electron-donating groups (e.g., Me−, Et−, and methoxy groups) reacted much more effectively than those bearing electron-withdrawing groups (e.g., F− and Cl−) to afford the corresponding α-hydroxylated products **2** in higher yields. The scope of this reaction was further extended to a series of α-substituted arones (**1h−n**), which all reacted as anticipated to give the corresponding α-hydroxy arones (**2h−n**) in moderate to good isolated yields (59−86%). It is noteworthy that heterocyclic ketone substrates, including 1-(thiophen-2-yl)butan-1-one (**1m**) and 1-(thiophen-2-yl)propan-1-one (**1n**), reacted as arone surrogates under the optimized conditions to afford the corresponding α-hydroxylated products **2m** and **2n**. To determine whether the reaction could be applied to other ketones, we employed 4-phenylbutan-2-one and acetophenone as the partners of α-substituted arones under the same conditions. Unfortunately, these two reactions failed to undergo

Scheme 2. Synthesis of α-Hydroxy Arones (2a−o) from α-Substituted Arones[a]



[a]All of these reactions were carried out on a 1.0 mmol scale using DMF (2.0 mL) as a solvent. The number in parentheses is the isolated yield of propiophenone **1a** (10.0 mmol scale) after purification by column chromatography.

the desired conversion, with the former providing (*E*)-4-phenylbut-3-en-2-one (**2o**) as the main product. Compound **2o** was most likely formed from 3-hydroxy-4-phenylbutan-2-one, which would be generated *in situ* from 4-phenylbutan-2-one.

To develop a better understanding of the mechanism of this hydroxylation, we conducted several trial experiments in parallel (Scheme 3). Under the optimized conditions, compound **1a** was completely consumed to give the desired α-hydroxylation product **2a**, even when the reaction was conducted in the presence of the radical scavenger TEMPO. This result suggested that this transformation did not proceed via a radical mechanism. However, compound **1a** failed to afford any of the desired product **2a** when the reaction was conducted in dioxane or DMSO instead of DMF. Furthermore, when the reaction of **1a** was carried out in the presence of 2.0 equiv of $H_2{}^{18}O$, **2a** was obtained in 76% yield with no ^{18}O-labeled in the product, thereby excluding the possibility of the hydroxyl group being derived from H_2O in the DMF solvent. We also noticed that this reaction afforded **2a** in 69% yield when cuprous iodide (CuI) was used instead of CuO (Table 1, entry 10). Taken together, the results of these experiments demonstrate that the oxygen atom of the hydroxyl group in the product is derived from DMF. Furthermore, when 2-iodo-1-phenylpropan-1-one was used as a substrate instead of

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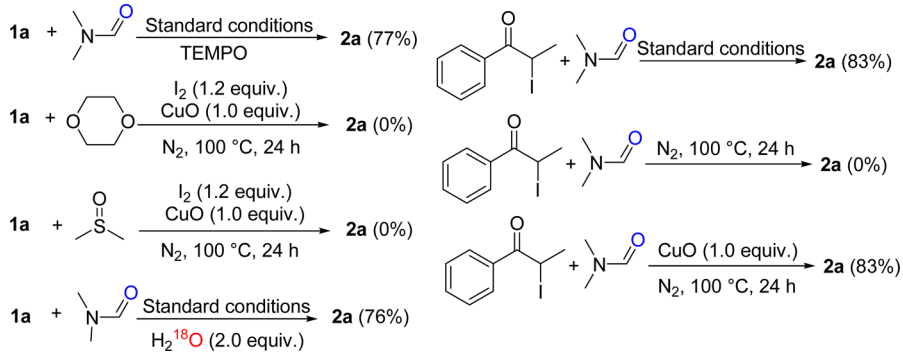
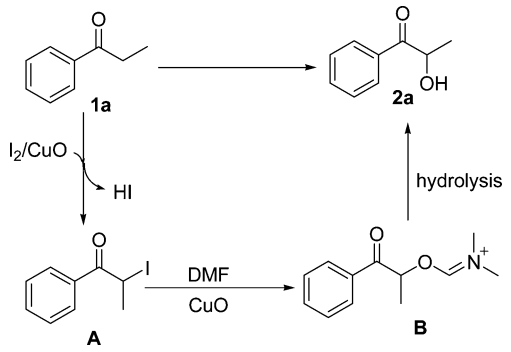
Scheme 3. Investigation of the Reaction Mechanism



propiophenone under the optimized conditions or in the absence of I_2, compound **2a** was isolated in 83% yield. In contrast, these reactions failed to afford any of the desired product when they were conducted in the absence of CuO. These results therefore suggest that 2-iodo-1-phenylpropan-1-one could be generated *in situ* as an intermediate from **1a**.

Based on the results of the experiments described above, we have proposed a plausible mechanism for this conversion, which is shown in Scheme 4. Briefly, propiophenone **1a** would undergo an iodination reaction to generate the key intermediate α-iodo propiophenone **A**.[17] The subsequent nucleophilic attack of DMF to **A** would lead to the formation of iminium **B** in the presence of CuO and DMF, which would be hydrolyzed to give the final product **2a**.

Scheme 4. Proposed Mechanism for the α-Hydroxylation



In conclusion, we have developed a simple and efficient strategy for the synthesis of α-hydroxy arones from readily available starting materials including arones, copper oxide, iodine, and DMF. This method could expand the use of DMF as a source of oxygen for the synthesis of α-hydroxy arones.

EXPERIMENTAL SECTION

General Information. All the reactions were carried out at 100 °C for 24 h under a N_2 atmosphere in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard; δ values are given in ppm, and coupling constants (J) in Hz. HR-MS were obtained on a Q-TOF micro spectrometer.

Typical Procedure: 2-Hydroxy-1-phenylpropan-1-one (2a). A mixture of propiophenone (**1a**) (134 mg, 1.0 mmol), CuO (79 mg, 2.0 mmol), iodine (305 mg, 1.2 mmol), and DMF (2.0 mL) was added successively in a round-bottom flask under a N_2 balloon, and the resulting solution was stirred for 24 h at 100 °C. The mixture was purified by column chromatography on silica gel to afford product **2a** with PE/ethyl acetate = 10/1 as the eluent.

*2-Hydroxy-1-phenylpropan-1-one (**2a**).*[18] Yield: 77% (115 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.93 (d, J = 7.2 Hz, 2H), 7.63 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 5.16 (q, J = 7.2 Hz, 1H), 3.67 (s, 1H), 1.46 (d, J = 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 202.3, 133.9, 133.3, 128.8, 128.6, 69.3, 22.2.

*2-Hydroxy-1-p-tolylpropan-1-one (**2b**).*[19] Yield: 77% (128 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.83 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 2H), 5.12 (q, J = 7.2 Hz, 1H), 3.02 (s, 1H), 2.43 (s, 3H), 1.44 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 201.9, 145.0, 130.7, 129.5, 128.7, 69.1, 22.4, 21.7.

*1-(4-Ethylphenyl)-2-hydroxypropan-1-one (**2c**).* Yield: 77% (150 mg); Pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.84 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.2 Hz, 2H), 2.72 (q, J = 7.2 Hz, 2H), 2.21 (s, 1H), 1.44 (d, J = 7.2 Hz, 3H), 1.23 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 201.9, 151.1, 130.9, 128.9, 128.3, 69.1, 29.0, 18.3, 15.0; HRMS (ESI): calcd for $C_{11}H_{15}O_2$: [M + H$^+$] 179.1066, found 179.1082.

*1-(4-Fluorophenyl)-2-hydroxypropan-1-one (**2d**).*[19] Yield: 77% (102 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.96 (dd, J = 7.2 Hz, J = 9.0 Hz, 2H), 7.18 (t, J = 7.2 Hz, 2H), 5.27 (q, J = 7.2 Hz, 1H), 3.16 (s, 1H), 1.43 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 200.7, 166.2 (d, $^1J_{C-F}$ = 254.9 Hz), 131.4, 131.3, 129.7, 129.7, 116.2, 115.9, 69.2, 22.2.

*1-(3-Fluorophenyl)-2-hydroxypropan-1-one (**2e**).*[19] Yield: 77% (96 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.70 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.48 (q, J = 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 5.10 (q, J = 7.2 Hz, 1H), 3.59 (s, 1H), 1.44 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 201.2, 162.8 (d, $^1J_{C-F}$ = 247.3 Hz), 135.4, 135.3, 130.6, 130.5, 124.3, 124.3, 121.1, 120.9, 115.5, 115.3, 69.5, 22.1.

*1-(4-Chlorophenyl)-2-hydroxypropan-1-one (**2f**).*[19] Yield: 77% (112 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.86 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 7.2 Hz, 2H), 5.11 (q, J = 7.2 Hz, 1H), 2.89 (s, 1H), 1.45 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 201.2, 140.5, 131.6, 130.0, 129.2, 69.3, 22.1.

*2-Hydroxy-1-(4-methoxyphenyl)propan-1-one (**2g**).*[20] Yield: 77% (153 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.93 (d, J = 7.2 Hz, 2H), 6.96 (d, J = 7.2 Hz, 2H), 5.11 (q, J = 7.2 Hz, 1H), 3.83 (s, 3H), 2.98 (s, 1H), 1.44 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 200.6, 164.1, 131.0, 126.0, 114.0, 68.8, 55.5, 22.6.

*2-Hydroxy-1-phenylpentan-1-one (**2h**).*[21] Yield: 77% (132 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.92 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 5.09 (q, J = 7.2 Hz, 1H), 3.69 (s, 1H), 1.48 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 202.2, 133.9, 133.7, 128.8, 128.5, 72.9, 37.9, 18.2, 13.8.

*2-Hydroxy-2-methyl-1-phenylpropan-1-one (**2i**).*[19] Yield: 77% (96 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 8.01 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 3.19 (s, 1H), 1.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 204.7, 133.7, 132.9, 129.6, 128.4, 76.2, 28.4.

*4-Chloro-1-(4-fluorophenyl)-2-hydroxybutan-1-one (**2j**).* Yield: 77% (134 mg); orange oil; ^{1}H NMR ($CDCl_3$, 300 Hz) δ 8.00 (dd, J

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= 7.2 Hz, J = 9.0 Hz, 2H), 7.62 (t, J = 7.2 Hz, 2H), 5.27 (dd, J = 2.4 Hz, J = 9.9 Hz, 1H), 3.88 (m, 1H), 3.73 (m, 1H), 3.39 (s, 1H), 2.25 (m, 1H), 1.86 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 199.6, 166.4 (d, $^1J_{C-F}$ = 255.6 Hz), 131.5, 131.4, 129.4, 129.4, 116.4, 116.2, 69.4, 41.4, 38.9; HRMS (ESI): calcd for $C_{10}H_{11}ClFO_2$: [M + H$^+$] 217.0426, found 217.0441.

1-(4-Chlorophenyl)-2-hydroxybutan-1-one (**2k**).[22] Yield: 77% (130 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.86 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H), 5.02 (q, J = 7.2 Hz, 1H), 3.17 (s, 1H), 1.92 (m, 1H), 1.60 (m, 1H), 0.94 (d, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 200.9, 140.4, 132.0, 129.8, 129.2, 73.9, 28.8, 8.82.

2-Hydroxy-1,2-diphenylethanone (**2l**).[23] Yield: 77% (129 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.93 (d, J = 8.0 Hz, 2H), 7.54 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 2H), 7.30 (m, 5H), 5.97 (s, 1H), 4.56 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 199.1, 138.9, 133.8, 133.4, 129.1, 129.1, 128.6, 128.5, 127.7, 76.2.

2-Hydroxy-1-(thiophen-2-yl)butan-1-one (**2m**).[21] Yield: 77% (146 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.77 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 7.73 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 7.18 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 4.86 (q, J = 6.9 Hz, 1H), 2.88 (s, 1H), 1.98 (m, 1H), 1.71 (m, 1H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 194.5, 139.9, 134.6, 132.8, 128.3, 74.8, 29.8, 8.96.

2-Hydroxy-1-(thiophen-2-yl)propan-1-one (**2n**).[19] Yield: 77% (140 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.77 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 7.74 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 7.19 (dd, J = 1.2 Hz, J = 5.1 Hz, 1H), 4.97 (q, J = 6.9 Hz, 1H), 3.60 (s, 1H), 1.53 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 195.0, 139.4, 134.7, 133.0, 128.3, 70.1, 23.1.

(E)-4-Phenylbut-3-en-2-one (**2o**).[24] Yield: 77% (111 mg); ^{1}H NMR ($CDCl_3$, 300 Hz) δ 7.55 (m, 3H), 7.41 (m, 3H), 6.73 (d, J = 16.2 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 Hz) δ 198.4, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02751.

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

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Notes

The authors declare no competing financial interest.

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