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Copper-Catalyzed Aerobic Oxidative Cleavage of C−C Bonds in Epoxides Leading to Aryl Ketones

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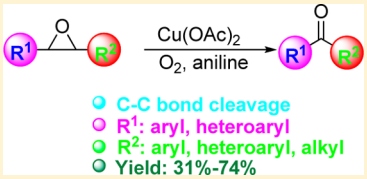
Supporting Information

ABSTRACT: A novel copper-catalyzed aerobic synthesis of ketones from epoxides via cleavage of C−C single bonds has been discovered. This reaction constitutes a new transformation from epoxides into ketones.

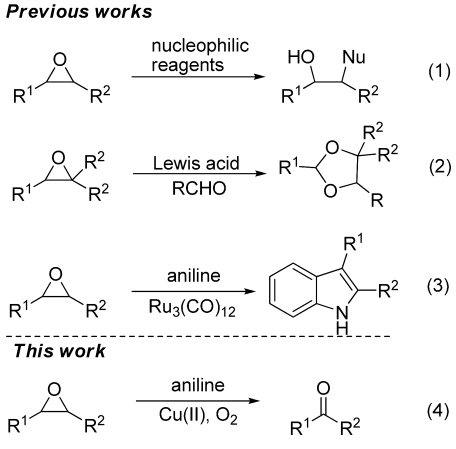


C−C bonds widely exist in natural and synthetic chemicals. Undoubtedly, C−C bond activation/functionalization offers unique opportunities to develop novel transformations, because it allows reorganization of bond connections, leading to novel molecular structures with high complexity.[1] Although significant progress has been achieved in the development of methods to cleave C−C single bonds,[2] the selective oxidative cleavage of C−C single bonds still remains one of the most challenging issues in chemistry and biology because (1) in general, the bond dissociation energy of a C−C single bond is high, and therefore, such bonds are thermodynamically hard to break; and (2) the selectivity between C−C bond and C−H bond cleavage of unstrained substrates should be controlled. Chemists have always been pursuing new methods to solve these challenges. For instance, the ring-opening of strained molecules, such as three- and four-membered rings, has been well-studied.[3] Other than these studies, the cleavage of the carbon−nitrile (C−CN) bond of nitriles and strategies that make use of chelation assistance have been well-investigated.[4,5] To cleave unstrained inert C−C bonds, harsh conditions with stoichiometric oxidants have been required. Therefore, the chemoselective C−C single bond cleavage, which could be used to perform synthetic chemistry in a greener and more atom-economical way, is highly appealing.

Saturated carbonyl compounds, for example, ketones, constitute the essential synthetic elements in organic chemistry, which can be transformed into a large variety of functionalized organic molecules with applications for several fields, such as pharmaceutical chemistry and material science.[6] Their importance in synthetic and medicinal chemistry has attracted considerable attention for the development of new synthetic strategies for these compounds.

An epoxide is a cyclic ether with three ring atoms. Industrially, epoxides are utilized as pharmaceutical drugs polymer precursors, and as biologically and chemically important building blocks.[7] Because of the significance and wide applications of such chemistry in organic synthesis, the exploration for new types of epoxide transformations is very attractive to researchers. The classical elaborations of epoxides are the ring-opening of epoxides with nucleophilic reagents (Scheme 1, eq (1)).[7] Recently, Zhang and co-workers reported a beautiful transformation from a 2,2,3-trisubstituted epoxide into a 1,3-dioxolane via Lewis acid catalyzed C−C bond cleavage (Scheme 1, eq (2)).[8] In 2013, the group of Beller made the remarkable observation that anilines react with 2,3-disubstituted epoxides in the presence of $Ru_3(CO)_{12}$ as catalyst to form indoles (Scheme 1, eq (3)).[9] As part of our ongoing efforts to develop transition-metal-catalyzed organic reactions,[10] we herein report a novel copper-catalyzed aerobic synthesis of ketones from 2,3-disubstituted epoxides (Scheme 1, eq (4)).[11] This reaction constitutes a new transformation from 2,3-

Scheme 1. Direct Transformations of Epoxides



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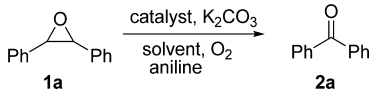
disubstituted epoxides into ketones. This protocol also provides a practical, neutral, and mild synthetic approach to aryl ketones.

In the initial phase of this study, we investigated the reaction of 2,3-diphenyloxirane **1a** with aniline in the presence of K_2CO_3 (1 equiv) and $CuCl_2$ (15 mol %) at 120 °C in dimethyl sulfoxide (DMSO) under an O_2 atmosphere. To our delight, the desired product was isolated with 53% yield after reacting for 15 h (Table 1, entry 1). Screening of solvents indicated that

Table 1. Screening Optimal Conditions[a]



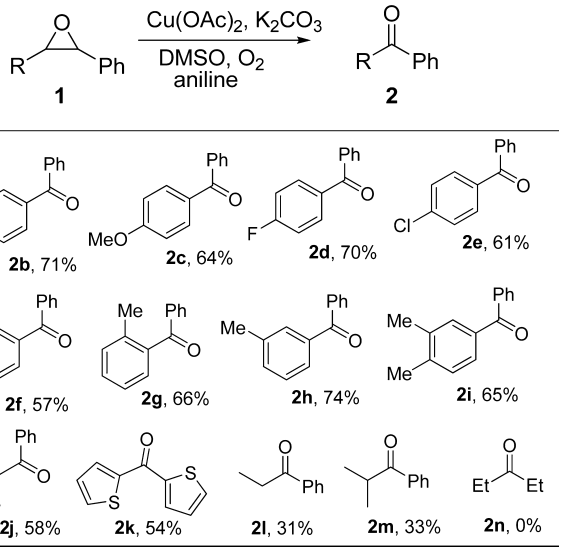
entry	catalyst	solvent	yield (%)[b]
1	$CuCl_2$	DMSO	53
2	$CuCl_2$	DCE	trace
3	$CuCl_2$	$PhCF_3$	trace
4	$CuCl_2$	DMF	22
5	$Cu(OAc)_2$	DMSO	74
6	CuCl	DMSO	13
7	$Cu(OTf)_2$	DMSO	31
8	$CuBr_2$	DMSO	18
9	$Pd(OAc)_2$	DMSO	26
10	$NiCl_2$	DMSO	0
11	none	DMSO	0
12[c]	$Cu(OAc)_2$	DMSO	0
13[d]	$Cu(OAc)_2$	DMSO	74
14[e]	$Cu(OAc)_2$	DMSO	72
15[f]	$Cu(OAc)_2$	DMSO	0
16[g]	$Cu(OAc)_2$	DMSO	0

[a]Reaction conditions: **1a** (0.5 mmol), catalyst (15 mol %), K_2CO_3 (1 equiv), aniline (0.6 mmol), solvent (3 mL), 120 °C in O_2 atmosphere for 16 h. [b]Isolated yield. [c]Ar (1 atm). [d]*p*-Toluidine (0.6 mmol) was used. [e]*p*-Chloroaniline (0.6 mmol) was used. [f]*n*-Butylamine (0.6 mmol) was used. [g]Without aniline.

DMSO was optimal (Table 1, entries 1–4). DMSO is likely to stabilize the copper catalyst and also assist in the aerobic oxidation process. It was found that $Cu(OAc)_2$ was superior to other copper sources (Table 1, entries 5–8). Reactions catalyzed by other transition metals, such as $Pd(OAc)_2$ and $NiCl_2$, did not proceed or gave a poor yield (Table 1, entries 9 and 10). Both $Cu(OAc)_2$ and O_2 are essential for reactivity (Table 1, entries 11 and 12). Replacement of aniline with *p*-toluidine or *p*-chloroaniline did not affect the reaction efficiency (Table 1, entries 13 and 14). However, *n*-butylamine did not afford the desired product (Table 1, entry 15). Notably, the absence of aniline resulted in no detectable amounts of benzophenone **2a** (Table 1, entry 16).

With the standard reaction conditions in hand, we next investigated the substrate scope of the reaction by employing a variety of epoxides **1**. As summarized in Table 2, the standard reaction conditions were found to be compatible with a wide range of epoxides **1**, including aryl and heteroaryl epoxides. Furthermore, several substituents, such as Me, MeO, F, Cl, and Br, on the aryl ring of epoxides were well-tolerated (Table 2, entries **2b**–**2f**). It is noteworthy that substituents at different positions on the aryl ring (*para*, *meta*, and *ortho* positions) did not affect the reaction efficiency (Table 2, entries **2b**, **2g**, **2h**). Importantly, the halogens F, Cl, and Br were tolerated under the reaction conditions, thereby facilitating additional modifications at the halogenated positions. When using a dimethyl-

Table 2. Scope of Epoxides[a,b]

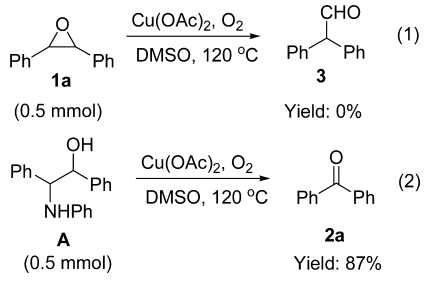


[a]Reaction conditions: **1** (0.5 mmol), catalyst (15 mol %), K_2CO_3 (1 equiv), aniline (0.6 mmol), DMSO (3 mL), 120 °C in O_2 atmosphere for 16–18 h. [b]Isolated yield.

substituted aryl epoxide, a satisfactory yield was still achieved under the same reaction conditions (Table 2, entry **2i**). Interestingly, the introduction of heterocycles into this system made this methodology more useful for the preparation of pharmaceuticals and functional materials (Table 2, entries **2j** and **2k**). Efforts were made to apply this methodology for the synthesis of aryl alkyl ketones. It was found that reactions with **1l** and **1m** proceeded sluggishly to give the aryl alkyl ketones **2l** and **2m** in low yields (Table 2, entries **2l** and **2m**). Unfortunately, 2,3-dialkyl-substituted substrate **1n** did not deliver the desired product (Table 2, entry **2n**).

Some control experiments were carried out in order to probe the mechanism of this transformation. It has been reported that an epoxide can be transformed into an aldehyde. Then, the aldehyde undergoes the C–C cleavage to form a ketone in the presence of aniline.[12] To rule out this possibility, we checked the possibilities of the formation of aldehydes by the reactions of 2,3-diphenyloxirane **1a** (0.5 mmol), in the presence of K_2CO_3 (0.5 mmol) and $Cu(OAc)_2$ (15 mol %) at 120 °C in DMSO under an O_2 atmosphere [eq (1)] (Scheme 2). No 2,2-diphenylacetaldehyde **3** was found, which provided evidence that the reaction does not proceed via an aldehyde intermediate. Furthermore, in the presence of K_2CO_3 (0.5 mmol) and $Cu(OAc)_2$ (15 mol %) at 120 °C in DMSO under an O_2 atmosphere, 1,2-diphenyl-2-(phenylamino)ethanol **A** could give the desired product **2a** in 87% yield after 15 h [eq

Scheme 2. Control Experiment



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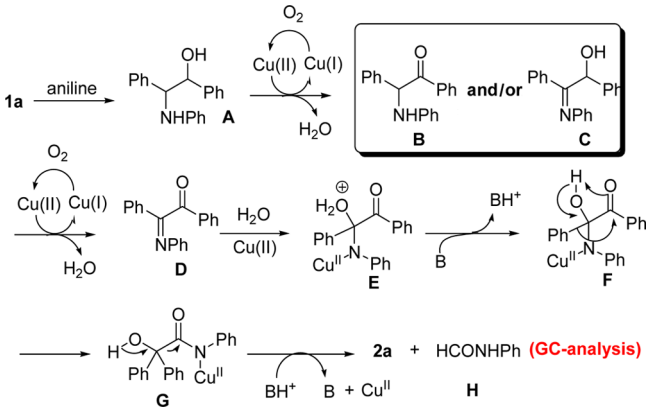
(2)]. The results indicate that compound **A** may be involved in this process.

On the basis of these preliminary results and previous studies,[2k,13] the catalytic cycle of this transformation was hypothesized as shown in Scheme 3. Ring opening of 2,3-

Scheme 3. Possible Mechanism



diphenyloxirane **1a** with aniline gives intermediate **A**. Thereafter, intermediate **A** is oxidized to produce intermediate **B** and/or **C**. With the aid of Cu and O_2, intermediate **B** and/or **C** is readily transformed into α-imine ketone **D**, which quickly converts into hydrated species **E** by picking up one molecule of water. Following a benzylic acid rearrangement, **F** affords intermediate **G**, which decomposes to the desired product benzophenone **2a**.

In summary, the chemoselective oxidative cleavage of the C−C single bond of 2,3-disubstituted epoxides that yields ketones has been described for the first time. The application of selective C−C bond cleavage in organic synthesis presents one of the most attractive and challenging projects. This chemistry provides a new means of C−C bond cleavage. A wide range of 2,3-disubstituted epoxides can be subjected to this copper-catalyzed method under an oxygen atmosphere; the oxidation terminates at the ketone stage. Mechanistic, scope, and limitation studies of the reaction are in progress in our laboratory.

EXPERIMENTAL SECTION

Instrumentation and Chemicals. Reagents were obtained commercially and used as received. Solvents were purified and dried by standard methods. All products were characterized by IR, MS, ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry (HRMS). ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$, and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as an internal standard. Chemical shift values (δ) are given in parts per million (ppm). Coupling constants (J) were measured in Hz. HRMS spectra were recorded on a micrOTOF-Q II analyzer.

Typical Experimental Procedure for Synthesis of Ketones 2. An oven-dried Schlenk tube was charged with a magnetic stir bar, 2,3-disubstituted epoxides **1** (0.5 mmol), aniline (0.6 mmol), K_2CO_3 (0.5 mmol), $Cu(OAc)_2$ (0.075 mmol), and DMSO (3 mL). The tube was sealed, and oxygen was purged through a syringe. The reaction was stirred at 120 °C for 16−18 h. After the reaction was finished, the reaction mixture was diluted in 30 mL of ethyl acetate and filtered on a Celite pad. The organic portion was washed with a saturated solution of brine (8 mL), saturated NH_4Cl (8 mL), and a saturated solution of brine (8 mL), dried (Na_2SO_4), and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to afford the desired products **2**.

*Benzophenone (**2a**):*[14] Yield: 74%, 67 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.83 (dd, J = 8.0 Hz, J = 1.6 Hz, 4H), 7.61−7,56 (m, 2H), 7.51−7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.7, 137.8, 132.5, 130.2, 128.4; IR (neat cm^{-1}): 1660 (C═O); LRMS (EI 70 ev) m/z (%): 182 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{11}O$ $(M + H)^+$ 183.0804, found 183.0801.

*Phenyl(p-tolyl)methanone (**2b**):*[14] Yield: 71%, 70 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.4, 143.2, 137.9, 134.8, 132.1, 130.2, 129.8, 128.9, 128.1, 21.6; IR (neat cm^{-1}): 1658 (C═O); LRMS (EI 70 ev) m/z (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M + H)^+$ 197.0960, found 197.0963.

*(4-Methoxyphenyl)(phenyl)methanone (**2c**):*[14] Yield: 64%, 68 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 2H), 7.51−7.45 (m, 3H), 6.96 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 197.1, 163.2, 138.2, 132.4, 131.7, 130.0, 129.5, 128.2, 113.6, 55.8; IR (neat cm^{-1}): 1652 (C═O); LRMS (EI 70 ev) m/z (%): 212 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O_2$ $(M + H)^+$ 213.0909, found 213.0913.

*(4-Florophenyl)(phenyl)methanone (**2d**):*[14] Yield: 70%, 70 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86−7.83 (m, 2H), 7.78 (d, J = 4.2 Hz, 2H), 7.62 (dd, J = 7.2 Hz, J = 1.2 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.18 (t, J = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.5, 165.5 (J_{C-F} = 252.9 Hz), 137.6, 132.7 (J_{C-F} = 2.5 Hz), 132.6 (J_{C-F} = 14.8 Hz), 132.0, 129.8, 128.3, 115.5 (J_{C-F} = 21.8 Hz); IR (neat cm^{-1}): 1661 (C═O); LRMS (EI 70 ev) m/z (%): 200 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{10}FO$ $(M + H)^+$ 201.0710, found 201.0719.

*(4-Chlorophenyl)(phenyl)methanone (**2e**):*[14] Yield: 61%, 66 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (t, J = 7.2 Hz, 4H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (dd, J = 7.6 Hz, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.4, 138.8, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.3; IR (neat cm^{-1}): 1664 (C═O); LRMS (EI 70 ev) m/z (%): 218 (41), 216 (M^+, 100); HRMS m/z (ESI) calcd for $C_{13}H_{10}ClO$ $(M + H)^+$ 217.0415, found 217.0410.

*(4-Bromophenyl)(phenyl)methanone (**2f**):*[14] Yield: 57%, 74 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (t, J = 4.2 Hz, 2H), 7.69 (dd, J = 2.0 Hz, J = 2.0 Hz, 2H), 7.64−7.58 (m, 3H), 7.51 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 195.6, 137.1, 136.3, 132.6, 131.6, 131.5, 129.9, 128.4, 127.5; IR (neat cm^{-1}): 1659 (C═O); LRMS (EI 70 ev) m/z (%): 260 (M^+, 100), 258 (81); HRMS m/z (ESI) calcd for $C_{13}H_{10}BrO$ $(M + H)^+$ 260.9909, found 260.9913.

*Phenyl(o-tolyl)methanone (**2g**):*[14] Yield: 66%, 65 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, J = 7.2 Hz, 2H), 7.54−7.50 (m, 1H), 7.43−7.36 (m, 2H), 7.33−7.26 (m, 1H), 7.25−7.20 (m, 3H); 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.5, 138.8, 138.1, 137.0, 133.5, 131.7, 130.6, 130.3, 129.0, 128.8, 125.4, 20.4; IR (neat cm^{-1}): 1647 (C═O); LRMS (EI 70 ev) m/z (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M + H)^+$ 197.0960, found 197.0961.

*Phenyl(m-tolyl)methanone (**2h**):*[15] Yield: 74%, 72 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (dd, J = 1.2 Hz, J = 8.4 Hz, 2H), 7.62−7.57 (m, 3H), 7.46−7.40 (m, 2H), 7.38 (dd, J = 4.4 Hz, J = 4.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 196.8, 138.1, 137.4, 137.1, 133.0, 132.1, 130.6, 130.1, 128.4, 128.0, 127.2, 21.3; IR (neat cm^{-1}): 1663 (C═O); LRMS (EI 70 ev) m/z (%): 196 (M^+, 100); HRMS m/z (ESI) calcd for $C_{14}H_{13}O$ $(M + H)^+$ 197.0960, found 197.0954.

*(3,4-Dimethylphenyl)(phenyl)methanone (**2i**):*[16] Yield: 65%, 68 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (t, J = 4.2 Hz, 2H), 7.61 (s, 1H), 7.59−7.52 (m, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.3, 141.9, 138.0, 136.7, 135.3, 132.0, 131.1, 129.9, 129.4, 128.1, 128.0, 20.0, 19.7; IR (neat cm^{-1}): 1661 (C═O); LRMS (EI 70 ev) m/z (%): 210 (M^+, 100); HRMS m/z (ESI) calcd for $C_{15}H_{15}O$ $(M + H)^+$ 211.1116, found 211.1111.

*Phenyl(thiophen-2-yl)methanone (**2j**):*[17] Yield: 58%, 54 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 4.8 Hz, 1H), 7.65 (d, J = 3.6 Hz, 1H), 7.61 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.17 (t, J = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:

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188.2, 143.6, 138.1, 134.8, 134.1, 132.2, 129.1, 128.3, 127.9; IR (neat cm^{-1}): 1638 (C═O); LRMS (EI 70 ev) m/z (%): 188 (M^+, 100); HRMS m/z (ESI) calcd for $C_{11}H_9OS$ $(M + H)^+$ 189.0368, found 189.0361.

*Dithiophen-2-ylmethanone (**2k**):*[2k] Yield: 54%, 52 mg; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.08 (dd, J = 4.0 Hz, J = 1.2 Hz, 2H), 7.86 (dd, J = 4.8 Hz, J = 1.2 Hz, 2H), 7.22−7.17 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 182.8, 138.5, 137.3, 137.0, 128.6; IR (neat cm^{-1}): 1631 (C═O); LRMS (EI 70 ev) m/z (%): 194 (M^+, 100); HRMS m/z (ESI) calcd for $C_9H_7OS_2$ $(M + H)^+$ 194.9932, found 194.9936.

*Propiophenone (**2l**):*[14] Yield: 31%, 21 mg; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.81 (dd, J = 1.6 Hz, J = 0.8 Hz, 2H), 7.50 (dd, J = 6.4 Hz, J = 1.6 Hz, 1H), 7.40−7.35 (m, 2H); 2.92−2.89 (m, 2H), 1.19−1.14 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.0, 136.4, 132.3, 128.0, 127.4, 31.2, 7.6; IR (neat cm^{-1}): 1681 (C═O); LRMS (EI 70 ev) m/z (%): 134 (M^+, 100); HRMS m/z (ESI) calcd for $C_9H_{11}O$ $(M + H)^+$ 135.0805, found 135.0813.

*2-Methyl-1-phenylpropan-1-one (**2m**):*[14] Yield: 33%, 24 mg; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.96−7.92 (m, 2H), 7.58−7.52 (m, 1H), 7.48−7.42 (m, 2H); 3.69−3.54 (m, 1H), 1.26 (d, J = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.1, 136.0, 132.4, 128.6, 128.1, 35.0, 18.9; IR (neat cm^{-1}): 1677 (C═O); LRMS (EI 70 ev) m/z (%): 148 (M^+, 100); HRMS m/z (ESI) calcd for $C_{10}H_{13}O$ $(M + H)^+$ 149.0961, found 149.0967.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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