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ARTICLE

Copper-Catalyzed Oxidative Decarboxylative Coupling of α-Keto Acids and Sulfoximines

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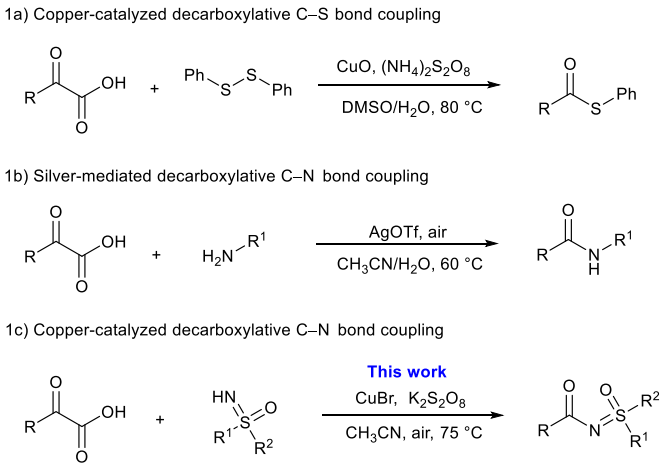
A copper-catalyzed oxidative decarboxylative coupling of α-keto acids with *NH*-sulfoximines has been developed. With CuBr as the catalyst and $K_2S_2O_8$ as the oxidant, this reaction enables the formation of C–N bond and gives *N*-aroylsulfoximine products in moderate to excellent yields. The reaction mechanism is likely to involve a generation of a reactive aroyl radical intermediate.

Introduction

Carboxylic acids are vital class of compounds for synthetic chemistry, pharmaceutical and industrial applications. A significant number of carboxylic acids have been considered as versatile starting materials in many organic transformations due to their remarkable features including the readily availability, low toxicity, high stability, and ease of storage and handling.[1,2] In the past decade, transition metal-catalyzed decarboxylative coupling reactions have emerged as an attractive method for a formation of carbon–carbon (C–C) bonds and carbon–heteroatom (C–X) bonds.[3] Significant contributions to this rapidly evolving field have been made by many research groups such as Gooßen[4], Myers[5], Bilodeau[6], Liu[7] and other groups.[8]

α-keto acids or α-oxocarboxylic acids are important in biological system. Several of them play key roles in metabolism in plants and animals such as in Krebs citric acid cycle and in glycolysis.[9] In organic synthesis, α-keto acids can be used as the source of acylating/aroylating agents to deliver a carbonyl group into molecules *via* the decarboxylative coupling process.[10] In fact, in 1991, Minisci and co-workers reported the silver-catalyzed decarboxylative acylation of pyridines and pyrazines with α-keto acids to form Csp^2– Csp^2 under mild conditions.[11] The mechanism for this transformation is believed to involve a generation of an acyl or an aroyl radical by oxidative decarboxylation. Inspired by Minisci's work, several efficient protocols involving metal[12] (Pd, Fe, Ag, Cu), visible-light photoredox catalysis[13] and other related work[14] have been explored for the decarboxylative C–C bonds coupling of α-keto acid precursors. For example, Wang[15], Ge[16] and other groups[17] developed the palladium-catalyzed decarboxylative acylation and aroylation of arenes with α-keto acids in the construction of C–C bonds. Duan[18] and Li[19] groups showed the efficient silver-catalyzed decarboxylative aroylation of α-keto acids and olefins under mild conditions. In addition, Wang[20] and Guo[21] have independently reported a dual decarboxylative cross-coupling of α-keto acids with cinnamic acids under Ag and Fe catalysis.

In contrast to decarboxylative C–C bond coupling, only a few reports on the metal-catalyzed decarboxylative coupling of α-keto acids in the construction of C–X (X = N, O and S) bonds are found in literature. In 2015, Rong and co-workers presented the direct approach of the construction of C–S bond through a copper-catalyzed decarboxylative coupling of α-keto acids and diphenyl disulfides (Scheme 1a).[22] In 2016, He and Xu reported a silver-promoted decarboxylative amidation of α-keto acids with various aromatic amines giving amide products in good yields (Scheme 1b).[23]



Scheme 1 Metal-catalyzed/promoted decarboxylative carbon–heteroatom bond coupling reactions of α-keto acid substrate.

Sulfoximines represent important structural motifs with potent biological and pharmaceutical activity. Despite of the

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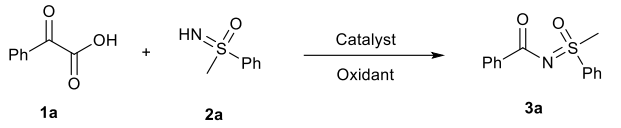
discovery in early 1950s, many sulfoximines and other sulfur-containing compounds with related core structures had limited their investigation and utilization.[24] They have recently received increased attentions in chemical synthesis, medicinal chemistry, material science and agriculture.[25] Several studies demonstated the high chemical stability and potential applications of these sulfoximine building blocks in drug discovery.[26] Thus, exploration into the sulfoximine chemistry, particularly in the development of new and efficient synthetic methodology for their preparation and derivatization will lead to a better understanding and further enhance their utilization in organic, pharmaceutical chemistry and other related areas.

Our research group are interested in development of a copper-catalyzed coupling strategy to access biologically active nitrogen and sulfur-containing compounds.[27] Realizing that *NH*-sulfoximines can undergo various metal-catalyzed transformations such as arylation, alkylation, vinylation, alkynylation, etc,[28,29] we herein disclose our recent efforts in the development of a copper-catalyzed decarboxylative C–N bond coupling of α-keto acids and sulfoximines under oxidative conditions (Scheme 1c). This catalytic transformation can be used as the alternative approach to access a number of *N*-aroylsulfoxime compounds under mild and air- and moisture-tolerant conditions in a short reaction time.

Results and discussion

N-aroylsulfoximines can be traditionally prepared using pre-activated coupling partners such as aroyl chlorides or by other methods.[29,30] In this work, we are particularly interested in employing α-keto acids as aroylating agent in copper-catalyzed aroylation reaction of *NH*-sulfoximines. To explore the decarboxylative process for the formation of *N*-aroylsulfoximines, screening of reaction conditions were performed with phenylglyoxylic acid (**1a**) and methyl phenyl sulfoximine (**2a**). With potassium persulfate ($K_2S_2O_8$) as the oxidant in the presence of 10 mol% of CuBr as catalyst in CH_3CN solvent at room temperature (Table 1, entry 1), the *N*-aroyl sulfoximine **3a** was obtained in 43% yield. Upon increasing reaction temperature, we observed higher yields of coupling product and the reaction essentially completed in 1 h at 75 °C. Next, we optimized the reaction conditions with respect to catalysts. Different sources of copper (I) and copper (II) species, including CuCl, CuBr, CuI, $CuCl_2$, $CuBr_2$, and $Cu(OAc)_2$ were tested (entries 3– 8). Among them, CuBr showed highest catalytic activity. Other metal catalysts such as Ag, Ni, Pd and Fe resulted in lower yields or no reaction.[31] The subsequent screening revealed that the yield was critically affected by the solvent used, and CH_3CN is found to be the suitable solvent for this transformation. Other solvents gave much lower yields or no reactions (entries 9–16). Furthermore, lower conversions were observed when replacing $K_2S_2O_8$ by other oxidants (entries 17 and 18).[31] While, in the absence of the catalyst or oxidant, trace amount of product was detected by GC. This outcome suggested that both copper catalyst and $K_2S_2O_8$ oxidant are required for this catalytic decarboxylative coupling reaction. Overall, the optimal conditions for the copper-catalyzed decarboxylative C–N bond coupling reaction of α-keto acids and sulfoximines was established (Table 1, entry 3; 1 equiv. of α-oxo carboxylic acid, 2 equiv. of *NH*-sulfoximine substrate, 10 mol% of CuBr, 1.1 equiv. of $K_2S_2O_8$, CH_3CN, 75 °C, 1 h).

Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	Catalyst	Oxidant	Solvent	Temp (°C)	Yield[b] (%)
1	CuBr	$K_2S_2O_8$	CH_3CN	rt	43[c]
2	CuBr	$K_2S_2O_8$	CH_3CN	50	55
3	**CuBr**	**$K_2S_2O_8$**	**CH_3CN**	**75**	**75 (79[d])**
4	CuCl	$K_2S_2O_8$	CH_3CN	75	64
5	CuI	$K_2S_2O_8$	CH_3CN	75	23
6	$CuBr_2$	$K_2S_2O_8$	CH_3CN	75	68
7	$CuCl_2$	$K_2S_2O_8$	CH_3CN	75	68
8	$Cu(OAc)_2$	$K_2S_2O_8$	CH_3CN	75	12
9	CuBr	$K_2S_2O_8$	H_2O	75	trace
10	CuBr	$K_2S_2O_8$	CH_3OH	75	trace
11	CuBr	$K_2S_2O_8$	DMSO	75	trace
12	CuBr	$K_2S_2O_8$	DMF	75	trace
13	CuBr	$K_2S_2O_8$	THF	75	trace
14	CuBr	$K_2S_2O_8$	1,4-dioxane	75	9
15	CuBr	$K_2S_2O_8$	Toluene	75	15
16	CuBr	$K_2S_2O_8$	DCE	75	44
17	CuBr	$(NH_4)_2S_2O_8$	CH_3CN	75	67
18	CuBr	$Na_2S_2O_8$	CH_3CN	75	59
19	-	$K_2S_2O_8$	CH_3CN	75	trace
20	CuBr	-	CH_3CN	75	trace

[a] Conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), $K_2S_2O_8$ (0.55 mmol), catalyst (0.05 mmol, 10 mol%), solvent (3 mL), 1 h. [b] GC yield. [c] 24 h. [d] Isolated yield.

The scope and limitation of this reaction was determined under the established conditions. First, we evaluated the reactivity of phenylglyoxylic acid **1a** towards various sulfoximines and the results are summarized in Table 2. Treating α-keto acid **1a** with diphenylsulfoximine resulted in the formation of *N*-aroylsulfoximine **3b** in high yield. The diphenylsulfoximines bearing chloro substitutuents at *para*-position can be converted to the desired products **3c** in moderate yield under the optimal conditions. To our delight, the reaction of **1a** and the 2-bromophenyl methyl sulfoximine substrate proceeded smoothly offering the formation of product **3d** in good yield. In addition, benzyl phenyl *NH*-sulfoximine were successfully transformed into the product **3e** in high quantity. We also examined coupling reactions of dialkyl *NH*-sulfoximine substrates, and the dimethyl and tetramethylene *NH*-sulfoximines are found to be viable coupling partners under oxidative decarboxylative transformation (**3f** and **3g**). Conversely, other dialkyl sulfoximines such as dibenzyl and dibutyl *NH*-sulfoximines gave much lower amounts of corresponding *N*-aroylated sulfoximine products (**3h** and **3i**). Thus, steric hinderance from the alkyl

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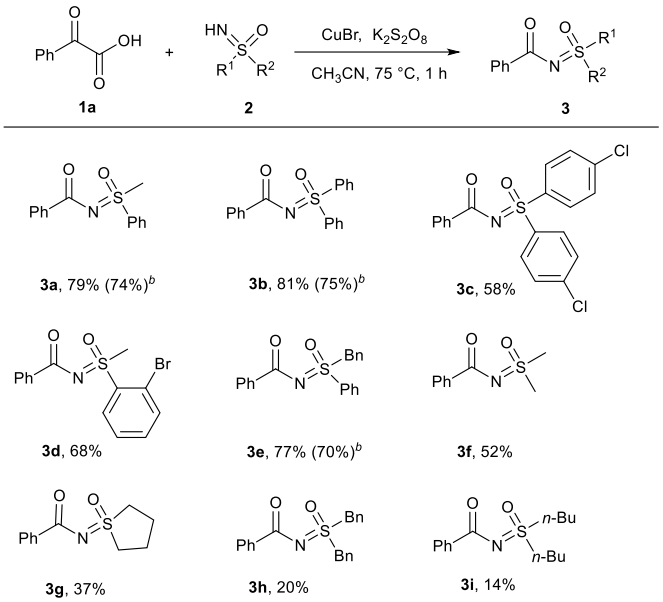
groups on *NH*-sulfoximine substrates has a substantial effect on the efficiency of this reaction.

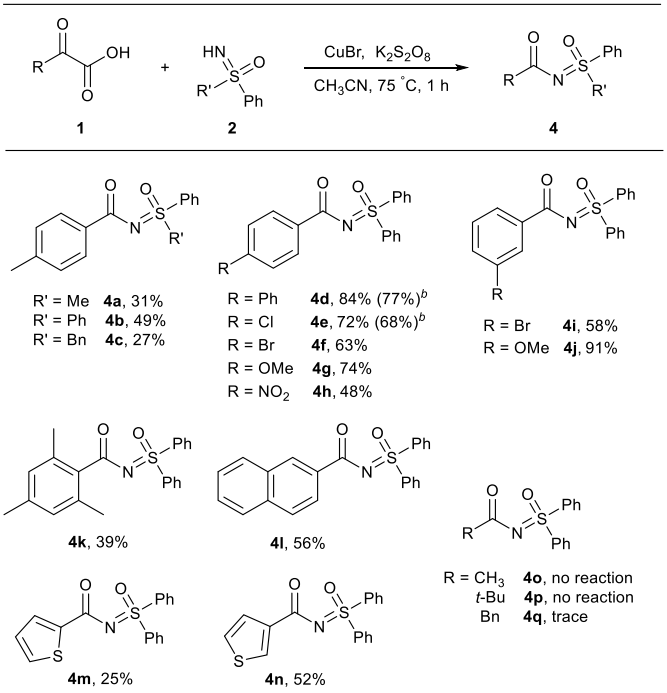
Table 2 Reaction of phenylglyoxylic acid **1a** with sulfoximine[a]



[a] Conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $K_2S_2O_8$ (0.55 mmol), CuBr (0.05 mmol; 10 mol%), CH_3CN (3 mL), 75 ºC, 1 h. Isolated yield.
[b] Isolated yield at 1 mmol scale reaction.

Encouraged by the promising results obtained from the copper-catalyzed decarboxylative C–N bond coupling between phenylglyoxylic acid (**1a**) with different sulfoximines, the scope of α-oxo carboxylic acids was investigated next (Table 3). We tested 4-methylphenylglycoxylic acid with different sulfoximines under the optimal conditions, and the corresponding products (**4a**–**4c**) were formed in low to modest yields. When coupled 4-biphenyl oxo-acetic acid with diphenylsulfoximine, the desired product **4d** could be obtained in decent yield. The phenylglycoxylic acids bearing halogen substituents such as Cl and Br at the *para* position are well-tolerated with this copper-catalyzed reaction, affording the expected products **4e** and **4f** in moderate to good quantities. Dehalogenation or other side reactions were not observed in these cases. It is also worth mentioning that the (4-methoxy)phenyl glycoxylic acid is an effective substrate, and very good yield of product **4g** was realized. However, α-oxo carboxylic acid containg a strong electron withdrawing NO_2 substituent provided slightly lower yield than the case of substrates bearing electron donating groups. In addition, the *meta*-subsitituted phenylglycoxylic acids could successfully participate in the reaction and the corresponding products were isolated in moderate to excellent yields (**4i** and **4j**). Nonetheless, somewhat low yield was obtained in case of the steric hindered mesitylene oxo-acetic acid substrate. This result suggested that the steric hinderance from the methyl group at C-2 position (*o*-substition) could interfere with the product formation. We also found that the naphthalene glyoxylic acid is a suitable substrate for this transformation, furnishing the coupling product **4l** in reasonable quantity (56%). Notably, both 2-thiophene and 3-thiophene glyoxylic acids reacted with sulfoximine, but low to moderated yields of products (**4m** and **4n**) were obtained. On the other hand, aliphatic α-keto acids (such as R = methyl, *tert*-butyl, benzyl) were unsuccessful substrates under the optimized conditions. Only trace amount of acylated products could be detected in this reaction. For reason yet unclear, they also failed to undergo radical oxidative decarboxylative coupling transformations in other previous literature reports.[10e,20,32,33] These could be due to the less stable aliphatic acyl radical intermediates compared with the aromatic acyl (aroyl) radicals.[33]

Table 3 Substrate scope with various α-keto acids[a]



[a] Conditions: **1** (0.5 mmol), **2** (1.0 mmol), $K_2S_2O_8$ (0.55 mmol), CuBr (0.05 mmol; 10 mol%), CH_3CN (3 mL), 75 ºC, 1 h. Isolated yield.
[b] Isolated yield at 1 mmol scale reaction.

To develop a better understanding of the mechanism of this catalytic transformation, control experiments using radical scavenger such as 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) and hydroquinone were conducted, and only a trace amount of the *N*-aroylated sulfoximine product was obtained (Scheme 2a). This outcome indicated that the reaction was inhibited by a radical scavenger; therefore, this reaction is likely to involve a radical process. We speculated that an aroyl radical is a reactive intermediate in this present decarboxylative reaction. To support this hypothesis, a radical-trapping experiment was carried out using stoichiometric amount of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in the presence of sulfoximine (Scheme 2b). The result showed that the yield of **3a** was dramatically decreased to 4%. Additionally, detection of radical coupling adduct **5** (2,2,6,6-tetramethylpiperidin-1-yl benzoate) by LC-MS and NMR indicated the existence of aroyl radical intermediate and suggested that the reactive aroyl

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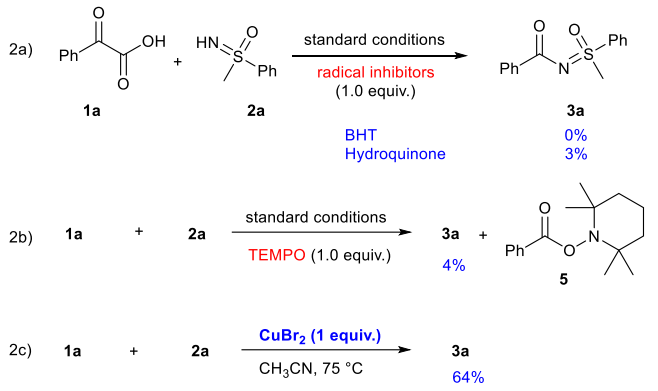
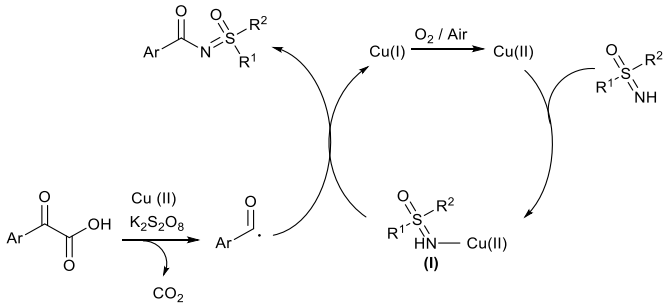
radical is generated from the α-keto acid precursor.[31] Furthermore, as this reaction also proceeded well using $CuBr_2$ and $CuCl_2$ as catalyst (see Table 1), it is likely that Cu(I) catalyst is oxidized to Cu(II) under the established oxidation conditions either by air or by persulfate.[29] Therefore, stoichiometric amount (1 equivalent) of $Cu(II)Br_2$ was subjected to the reaction in the absence of the persulfate oxidant and good yield of product was obtained (Scheme 2c). This result suggested that copper (II) species is important for the decarboxylative coupling process.

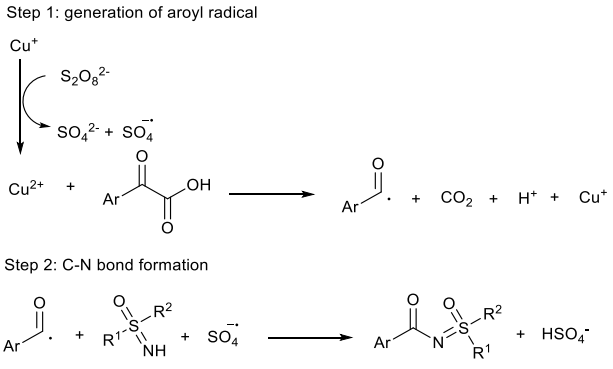


Scheme 2 Control experiments

Pathway A



Pathway B



Scheme 3 Possible mechanism

Although the detailed reaction mechanism is still not clear at this stage, we believed that the aroyl radical intermediate is involved in this transformation. Two plausible mechanism pathways are proposed as shown in Scheme 3 based on our observation and relevant literature.[10f,22,29,34] In pathway A, Cu(I) catalyst is initially oxidized by O_2 in the air to generate Cu(II). This Cu(II) species interacts with sulfoximine leading to a formation of an intermediate (**I**), which can react with an aroyl radical, generated from a decarboxylation of α-keto acid by Cu(II) and potassium persulfate. Subsequent eletron transfer process could result in a formation of the aroylsulfoximine product and the Cu(I) species. This Cu(I) is then re-oxidized to Cu(II) to resume the catalytic cycle. In pathway B, firstly, the Cu(I) catalyst is oxidized by potassium persulfate and generate Cu(II) species. This Cu(II) can facilitate the decarboxylation process of α-keto acid, resulting in a production of Cu (I) ion and the reactive aroyl radical intermediate. Lastly, the aroyl radical further undergoes radical reaction with sulfoximine and a sulfate radical anion to furnish the corresponding aroylsulfoximine product.

Conclusions

In summary, the copper-catalyzed oxidative decarboxylative coupling of α-keto acid and *NH*-free sulfoximines to construct *N*-aroylsulfoximines was developed. In this reaction proceeds under mild and easy to handle conditions within 1 h. Moreover, a variety of aryl α-oxocarboxylic acids and many sulfoximine substrates were well-compatible. The preliminary mechanistic investigation suggested that this transformation is likely to involve the radical process and the reactive aroyl radical is generated under standard conditions. More detailed studies on the mechanism and expansion of the synthetic utility and applications of this methodology are currently under exploration in our laboratory.

Experimental section

General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All experiments were carried out under air atmosphere, and oven-dried glasswares were used in all cases. Column chromatography was performed over silica gel (SiO_2; 60 Å silica gel, Merck Grade, 70–230 Mesh). GC experiments were carried out with an Agilent 6890N GC-FID on chromatograph equipped with an Agilent column ZB-1, dimethyl polysiloxane column (30 m × 0.25 mm ID × 0.25 µm). ^1H and ^{13}C NMR spectra were recorded on Bruker-AV400 spectrometers in $CDCl_3$ solution, at 400 and 100 MHz, respectively. NMR chemical shifts are reported in ppm, and were measured relative to $CHCl_3$ (7.26 ppm for ^1H and 77.00 ppm for ^{13}C). IR spectra were recorded on Bruker FT-IR Spectrometer Model ALPHA by neat method, and only partial data are listed. Melting points were determined on Buchi Melting Point M-565 apparatus. High resolution mass spectroscopy (HRMS) data were analysed by a high-resolution micrOTOF instrument with electrospray ionization (ESI). The structures of known compounds were corroborated by comparing their ^1H NMR, ^{13}C NMR data with those of literature.

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Typical procedure for the copper-catalyzed decarboxylative C–N bond coupling: formation of *N*-aroylsulfoximines 3a–3i and 4a–4n. To a 2 dram vial equipped with a magnetic stir bar, α-keto acid (0.50 mmol, 1.00 equiv.), sulfoximines (1.00 mmol, 2.00 equiv.), copper (I) bromide (CuBr) (7.2 mg, 0.05 mmol, 0.10 equiv.), potassium persulfate ($K_2S_2O_8$) (149 mg, 0.55 mmol, 1.10 equiv.) and acetonitrile (CH_3CN) (3.00 mL) were added, respectively. The reaction mixture was stirred at 75 °C for 1 h. Upon completion, distilled deionized H_2O (5 mL) was added, and the mixture was extracted with ethyl acetate (EtOAc) (2 × 10 mL). The combined organic layer was washed with saturated NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by SiO_2 column chromatography to afford the *N*-aroylsulfoximinine product.

***N*-Benzoyl-*S*-methyl-*S*-phenyl sulfoximine (3a)**.[30e] White solid (102 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 7.2 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 138.9, 135.5, 133.7, 132.1, 129.6, 129.3, 127.9, 127.1, 44.3; HRMS (ESI): calcd for $C_{14}H_{13}NO_2SNa$ $[M+Na]^+$ 282.0565, found 282.0576.

***N*-Benzoyl-*S,S*-diphenyl sulfoximine (3b)**.[30e] White solid (130 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27–8.25 (m, 2H), 8.07 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.61–7.51 (m, 7H), 7.46–7.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 139.8, 135.8, 133.3, 132.2, 129.6, 129.5, 128.1, 127.6; HRMS (ESI): calcd for $C_{19}H_{15}NO_2SNa$ $[M+Na]^+$ 344.0721, found 344.0723.

***N*-Benzoyl-*S,S*-di-4-chlorophenyl sulfoximine (3c)**. White solid (113 mg, 58% yield); m.p. 215.4–216.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 4H), 7.57–7.51 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.8, 140.3, 138.0, 135.2, 132.5, 130.0, 129.5, 129.0, 128.1; IR (neat, cm^{-1}): ν 3084, 1633, 1578, 1475, 1312, 1223, 1170, 1089, 941, 845, 712; HRMS (ESI): calcd for $C_{19}H_{13}Cl_2NO_2SNa$ $[M+Na]^+$ 411.9942, found 411.9936.

***N*-Benzoyl-*S*-(2-bromophenyl)-*S*-methyl sulfoximine (3d)**. White solid (115 mg, 68% yield); m.p. 125.6–126.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 1.6 Hz, 1H), 8.14 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.76 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.64–7.60 (m, 1H), 7.52–7.47 (m, 2H), 7.42–7.37 (m, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 138.0, 135.7, 135.1, 134.6, 132.2, 131.9, 129.6, 128.5, 128.0, 119.4, 41.9; IR (neat, cm^{-1}): ν 3025, 2926, 1626, 1578, 1450, 1311, 1284, 1172, 1098, 973, 831, 717; HRMS (ESI): calcd for $C_{14}H_{12}BrNO_2SNa$ $[M+Na]^+$ 359.9664, found 359.9670.

***N*-Benzoyl-*S*-benzyl-*S*-phenyl sulfoximine (3e)**. White solid (129 mg, 77% yield); m.p. 110.1–110.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.2 Hz, 2H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64–7.60 Hz (m, 1H), 7.54–7.40 (m, 5H), 7.31–7.26 (m, 1H), 7.22–7.18 (m, 2H), 7.00 (d, *J* = 7.2 Hz, 2H), 4.95 (d, *J* = 14.0 Hz, 1H), 4.87(d, *J* = 14.0 Hz Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.6, 135.5, 134.2, 133.8, 132.1, 131.2, 130.2, 129.4, 129.3, 129.1, 128.6, 128.5, 128.0, 62.2; IR (neat, cm^{-1}): ν = 3063, 2993, 2923, 1684, 1627, 1577, 1447, 1311, 1279, 1171, 1090, 939, 925, 712; HRMS (ESI): calcd for $C_{20}H_{17}NO_2SNa$ $[M+Na]^+$ 358.0878, found 358.0877.

***N*-Benzoyl-*S,S*-dimethyl sulfoximine (3f)**.[30e] White solid (51 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13–8.07 (m, 2H), 7.52–7.45 (m, 1H), 7.41–7.37 (m, 2H), 3.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 135.4, 132.2, 129.2, 128.0, 41.8; HRMS (ESI): calcd for $C_9H_{11}NO_2SNa$ $[M+Na]^+$ 220.0408, found 220.0399.

***N*-Benzoyl-*S,S*-tetramethylene sulfoximine (3g)**.[30e] White solid (41 mg, 37% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (t, *J* = 7.6 Hz, 2H), 7.52–7.44 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 3.75–3.67 (m, 2H), 3.38–3.30 (m, 2H), 2.39–2.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.0, 135.1, 132.1, 129.2, 127.9, 52.6, 23.7; HRMS (ESI): calcd for calcd for $C_{11}H_{13}NO_2SNa$ $[M+Na]^+$ 246.0565, found 246.0559.

***N*-Benzoyl-*S,S*-dibenzyl sulfoximine (3h)**. White solid (35 mg, 20% yield); m.p. 106.7– 107.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.52–7.48 (m, 1H), 7.41–7.37 (m, 12H), 4.81 (d, *J* = 13.6 Hz, 2H), 4.64 (d, *J* = 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 135.6, 132.1, 131.3, 129.4, 129.3, 129.0, 128.0, 126.2, 56.6; IR (neat, cm^{-1}): ν = 3033, 2927, 1626, 1577, 1455, 1314, 1287, 1217, 1143, 1124, 951, 702; HRMS (ESI): calcd for calcd for $C_{21}H_{19}NO_2SNa$ $[M+Na]^+$ 372.1034, found 372.1029.

***N*-Benzoyl-*S,S*-di-*n*-butyl sulfoximine (3i)**. Colorless oil (20 mg, 14% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14–8.11 (m, 2H), 7.51–7.47 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 3.63–3.55 (m, 2H), 3.42–3.34 (m, 2H), 1.89–1.79 (m, 4H), 1.54–1.44 (m, 4H), 0.96 (t, *J* = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 135.6, 131.9, 129.2, 127.9, 51.2, 23.4, 21.6, 13.5; IR (neat, cm^{-1}): ν = 3012, 2965, 1625, 1575, 1449, 1319, 1294, 1174, 1069, 943, 841; HRMS (ESI): calcd for $C_{15}H_{24}NO_2S$ $[M+H]^+$ 282.1528, found 282.1532.

***N*-(4-Methylbenzoyl)-*S*-methyl-*S*-phenyl sulfoximine (4a)**.[30e] White solid (42 mg, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07–8.03 (m, 4H), 7.69–7.65 (m, 1H), 7.60 (dd, *J* = 8.0, 6.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.2, 142.6, 139.0, 133.7, 132.8, 129.6, 129.4, 128.7, 127.1, 44.3, 21.6; HRMS (ESI): calcd for $C_{15}H_{15}NO_2SNa$ $[M+Na]^+$ 296.0721, found 296.0725.

***N*-(4-Methylbenzoyl)-*S,S*-diphenyl sulfoximine (4b)**. Pale yellow oil (82 mg, 49% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 7.2 Hz, 4H), 7.59–7.51 (m, 6H), 7.26–7.23 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.9, 142.7, 139.9, 133.2, 129.5, 129.4, 129.3, 128.7, 127.6, 21.6; IR (neat, cm^{-1}): ν = 3027, 2925, 1633, 1448, 1310, 1279, 1232, 1174, 1094, 937, 843, 685; HRMS (ESI): calcd for calcd for $C_{20}H_{17}NO_2SNa$ $[M+Na]^+$ 358.0878, found 358.0872.

***N*-(4-Methylbenzoyl)-*S*-benzyl-*S*-phenyl sulfoximine (4c)**. White solid (47 mg, 27% yield); m.p. 153.0–154.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.30–7.27(m, 1H), 7.23–7.17(m, 4H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.95 (d, *J* = 13.6 Hz, 1H), 4.86 (d, *J* = 13.6 Hz, 1H), 2.41(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.5, 142.6, 135.6, 133.7, 133.1, 131.2, 129.5, 129.0, 128.7, 128.5, 128.4, 128.0, 127.4, 62.1, 21.6; IR (neat, cm^{-1}): ν = 3030, 2923, 1631, 1577, 1445, 1308,

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1287, 1174, 1130, 1088, 938, 853, 700; HRMS (ESI): calcd for $C_{21}H_{19}NO_2SNa$ $[M+Na]^+$ 372.1034, found 372.1036.

***N*-(4-Phenylbenzoyl)-*S,S*-diphenyl sulfoximine (4d)**. Pale yellow solid (167 mg, 84% yield); m.p. 73.7−74.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.09 (dd, *J* = 8.4, 1.2 Hz, 4H), 7.68−7.64 (m, 4H), 7.60 – 7.53 (m, 6H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 144.9, 140.4, 139.9, 133.9, 133.3, 130.1, 129.6, 128.9, 127.9, 127.7, 127.3, 126.8; IR (neat, cm^{-1}): ν = 3029, 1630, 1580, 1447, 1310, 1278, 1224, 1174, 1134, 1007, 934, 720; HRMS (ESI): calcd for calcd for $C_{25}H_{19}NO_2SNa$ $[M+Na]^+$ 420.1034, found 420.1045.

***N*-(4-Chlorobenzoyl)-*S,S*-diphenyl sulfoximine (4e)**. Pale yellow oil (128 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.4 Hz, 2H), 8.06–8.03 (m, 4H), 7.59–7.53 (m, 6H), 7.39 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 139.5, 138.4, 133.3, 130.8, 129.7, 129.5, 128.2, 127.5; IR (neat, cm^{-1}): ν = 3071, 3027, 1635, 1592, 1477, 1448, 1399, 1276, 1233, 1207, 1136, 1092, 1014, 934, 842, 685; HRMS (ESI): calcd for calcd for $C_{19}H_{14}ClNO_2SNa$ $[M+Na]^+$ 378.0331, found 378.0336.

***N*-(4-Bromobenzoyl)-*S,S*-diphenyl sulfoximine (4f)**. Yellow oil (126 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$): 8.11−8.03 (m, 6H), 7.62−7.52 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.0, 139.6, 133.9, 133.4, 131.3, 131.1, 129.7, 129.5, 127.5; IR (neat, cm^{-1}): ν = 3070, 3012, 1635, 1587, 1448, 1396, 1281, 1233, 1170, 1134, 1094, 1011, 998, 841, 684; HRMS (ESI): calcd for calcd for $C_{19}H_{14}BrNO_2SNa$ $[M+Na]^+$ 421.9821, found 421.9824.

***N*-(4-Methoxybenzoyl)-*S,S*-diphenyl sulfoximine (4g)**. Light yellow oil (130 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.8 Hz, 2H), 8.05 (dd, *J* = 6.8, 1.6 Hz, 4H), 7.56–7.48 (m, 6H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 162.8, 139.9, 133.1, 131.4, 129.6, 129.4, 127.4, 113.1, 55.3; IR (neat, cm^{-1}): ν = 3012, 1630, 1603, 1448, 1280, 1255, 1231, 1165, 1094, 1033, 998, 938, 847, 696; HRMS (ESI): calcd for calcd for $C_{20}H_{18}NO_3S$ $[M+H]^+$ 352.1002, found 352.1004.

***N*-(4-Nitrobenzoyl)-*S,S*-diphenyl sulfoximine (4h)**. Yellow oil (88 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.8 Hz, 2H), 8.26 (d, *J* = 8.8 Hz, 2H), 8.07–8.05 (m, 4H), 7.63–7.55 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 150.0, 141.1, 139.1, 133.6, 130.4, 129.6, 127.5, 123.2; IR (neat, cm^{-1}): ν = 3069, 3011, 1639, 1603, 1527, 1448, 1477, 1351, 1300, 1283, 1234, 1135, 1095, 1034, 933, 727, 668; HRMS (ESI): calcd for calcd for $C_{19}H_{14}N_2O_4SNa$ $[M+Na]^+$ 389.0572, found 389.0575.

***N*-(3-Bromobenzoyl)-*S,S*-diphenyl sulfoximine (4i)**. White solid (115 mg, 58% yield); m.p. 136.5−137.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (t, *J* = 1.6 Hz, 1H), 8.15 (d, *J* = 7.6 Hz, 1H), 8.05 (d, *J* = 6.8 Hz, 4H), 7.66–7.63 (m, 1Hz) 7.60–7.53 (m, 6H), 7.31 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 139.5, 137.8, 135.0, 133.4, 132.5, 129.6, 129.6, 128.0, 127.5, 122.2; IR (neat, cm^{-1}): ν = 3045, 1625, 1562, 1447, 1275, 1258, 1229, 1194, 1134, 1083, 941, 839, 743, 679; HRMS (ESI): calcd for calcd for $C_{19}H_{14}BrNO_2SNa$ $[M+Na]^+$ 421.9821, found 421.9825.

***N*-(3-Methoxybenzoyl)-*S,S*-diphenyl sulfoximine (4j)**. White solid (160 mg, 91% yield); m.p. 97.4– 98.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 7.2 Hz, 4H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.75 (s, 1H), 7.59–7.52 (m, 6H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 159.4, 139.8, 137.2, 133.2, 129.5, 129.0, 127.6, 122.1, 118.6, 113.9, 55.4; IR (neat, cm^{-1}): ν = 3060, 1631, 1578, 1447, 1293, 1270, 1218, 1115, 1084, 959, 807, 757, 682; HRMS (ESI): calcd for calcd for $C_{20}H_{17}NO_3SNa$ $[M+Na]^+$ 374.0821, found 374.0829.

***N*-(2,4,6-Trimethylbenzoyl)-*S,S*-diphenyl sulfoximine (4k)**. Yellow oil (71 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.2 Hz, 4H), 7.60–7.49 (m, 6H), 6.83 (s, 2H), 2.37 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 139.6, 137.7, 134.0, 133.2, 129.5, 129.3, 128.2, 127.6, 21.0, 19.7; IR (neat, cm^{-1}): ν = 3027, 3011, 2924, 1632, 1611, 1477, 1448, 1277, 1230, 1170, 1106, 1023, 998, 912, 853, 831 HRMS (ESI): calcd for calcd for $C_{22}H_{21}NO_2SNa$ $[M+Na]^+$ 386.1185, found 386.1191.

***N*-(2-Naphthoyl)-*S,S*-diphenyl sulfoximine (4l)**.[35] White solid (104 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.83 (s, 1H), 8.29 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.0, 1.6 Hz, 4H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.58 –7.54 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0, 139.8, 135.3, 133.6, 133.3, 133.1, 132.6, 130.6, 129.7, 129.5, 129.4, 127.7, 127.6, 126.2, 125.7; HRMS (ESI): calcd for calcd for $C_{23}H_{18}NO_2S$ $[M+H]^+$ 372.1058, found 372.1053.

***N*-(Thiophene-2-carbonyl)-*S,S*-diphenyl sulfoximine (4m)**. Pale yellow solid (40 mg, 25% yield); m.p. 140.6– 141.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (d, *J* = 6.8 Hz, 4H), 7.85 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.60−7.49 (m, 7H), 7.09 (dd, *J* = 5.2, 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 168.4, 139.6, 133.8, 133.3, 132.1, 131.5, 129.5, 127.7, 127.6; IR (neat, cm^{-1}): ν = 3025, 2923, 1600, 1580, 1447, 1351, 1268, 1224, 1115, 1092, 1037, 995, 898, 721; HRMS (ESI): calcd for $C_{17}H_{13}NO_2S_2Na$ $[M+Na]^+$ 350.0285, found 350.0293

***N*-(Thiophene-3-carbonyl)-*S,S*-diphenyl sulfoximine (4n)**. Colorless oil (85 mg, 52% yield); ^{1}H NMR (400 MHz, $CDCl_3$): 8.23 (dd, *J* = 3.2, 1.2 Hz, 1H), 8.06−8.04 (m, 4H), 7.64 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.58−7.53 (m, 6H), 7.28−7.26 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): 169.7, 139.8, 133.8, 133.2, 131.9, 129.5, 128.3, 127.6, 125.3; IR (neat, cm^{-1}): ν = 3013, 2928, 1626, 1585, 1448, 1269, 1223, 1191, 1121, 1094, 1070, 969, 836; HRMS (ESI): calcd for $C_{17}H_{13}NO_2S_2Na$ $[M+Na]^+$ 350.0285, found 350.0287.

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Copper-Catalyzed Oxidative Decarboxylative Coupling of α-Keto Acids and Sulfoximines

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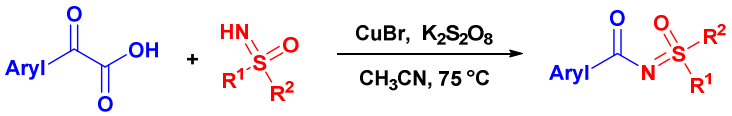

A formation of *N*-aroylsulfoximines *via* a copper-catalyzed oxidative decarboxylative coupling of α-keto acids with *NH*-sulfoximines is reported.

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