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Direct synthesis of *N*-sulfinyl- and *N*-sulfonylimines *via* copper/L-proline-catalyzed aerobic oxidative cascade reaction of alcohols with sulfinamides or sulfonamides†

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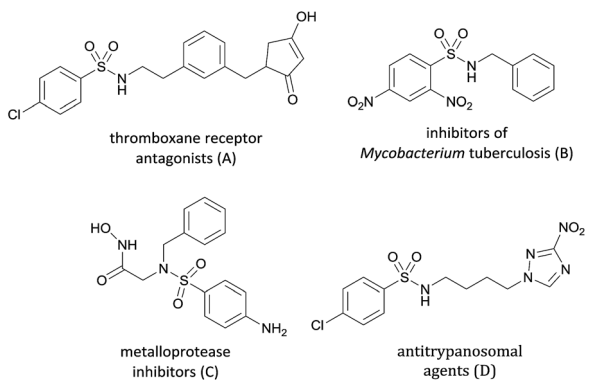
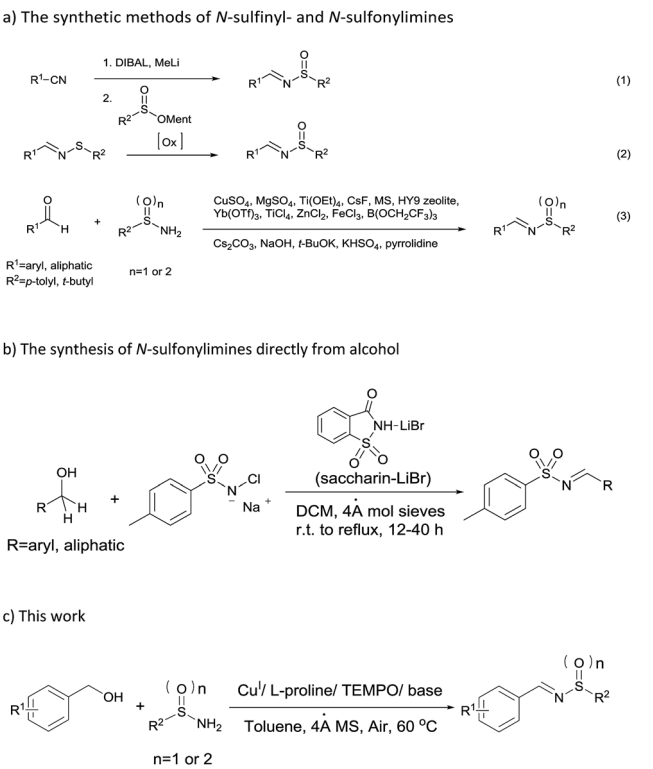
An efficient one-pot synthetic method of *N*-sulfinyl- and *N*-sulfonylimines by the condensation of alcohols with sulfinamides or sulfonamides under mild and green conditions has been developed using a combination of CuI, L-proline and TEMPO. This system shows excellent functional group compatibility for a wide range of substrates and affords the corresponding products in good to excellent yields.

N-Sulfinyl- and *N*-sulfonylimines are versatile intermediates in organic synthesis.[1] As active substrates, they can undergo various nucleophilic addition reactions,[2] radical reactions,[2j] and hetero-Diels–Alder reactions[3] to afford the expected *N*-sulfinyl- and *N*-sulfonylamide derivatives which are a class of important structure motifs prevalent in drugs, such as potent thromboxane receptor antagonists (A),[4a] inhibitors of *Mycobacterium tuberculosis* (B),[4b] metalloprotease inhibitors (C)[4c] and potential antitrypanosomal agents (D)[4d] (Scheme 1).

Due to the wide range of synthetic utility of these *N*-sulfinyl- and *N*-sulfonylaldimines, numerous synthetic methods have been developed. The main methods for the preparation of *N*-sulfinyl- and *N*-sulfonylimines include: (1) reaction of nitriles with an organometallic reagent (DIBAL, MeLi) and menthyl sulfinate;[5] (2) asymmetric oxidation of sulfenimines[6] and (3) condensation of sulfinamides or sulfonamides with aldehydes (Scheme 2a). The last method seems to be the most common and useful because the pure starting materials are now commercially available. Therefore, in the past decades, much attention have been paid to the direct condensation of



Scheme 1 Biologically active sulfonamides scaffold.



Scheme 2 Methods for the preparation of *N*-sulfinyl- and *N*-sulfonylimines.

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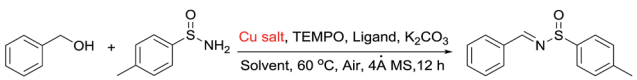
sulfinamides or sulfonamides with aldehydes for the synthesis of *N*-sulfinyl- and *N*-sulfonylimines [Scheme 2a, eqn (3)].[5e,7–18] Even though these reported protocols could be easier to obtain *N*-sulfinyl- or *N*-sulfonylimines, excess Lewis acid or stoichiometric base had to be used, which generated a large amount of environmentally unfriendly metallic waste. On the other hand, aldehydes can be obtained from the oxidation of alcohols.[19] Therefore, the method that utilizing alcohol as one of the staring materials to afford the *N*-sulfinyl- or *N*-sulfonylimine was attractive. To the best of our knowledge, there was only one report on the formation of *N*-sulfonyl-imines starting directly from alcohols, which involved saccharin–lithium bromide-catalyzed oxidation of alcohols to aldehydes/ketones with chloramine-T followed by their condensation to afford *N*-tosylimines (Scheme 2b).[20]

Recently, Stahl[19a,b] reported a copper/TEMPO-catalyzed alcohols oxidation to desired aldehydes efficiently under mild conditions with ambient air as the oxidant. Therefore, we sought to utilize the combination of copper salt, ligand and TEMPO as efficient catalysts for oxidation of alcohols to aldehydes followed by condensation with sulfin- or sulfonamides. Herein, we reported a copper-catalyzed one-pot multi-step reaction system for synthesis of *N*-sulfinyl- and *N*-sulfonylimines from alcohols with sulfin- or sulfonamides under air (Scheme 2c).

Initially, benzalcohol and 4-toluenesulfinamide were selected as the model substrates to determine the optimal conditions. First, the effect of solvent on this oxidative cascade transformation was examined (Table 1, entries 1–6). Good conversion of *N*-sulfinylimine was obtained, when the reaction was performed in CH_2Cl_2 or CH_3OH with 5 mol% CuI and 5 mol% L-proline in the presence of 1.0 equiv. K_2CO_3 under air at 60 °C (Table 1, entries 1 and 4). The employment of THF, DMSO or DMF led to moderate conversions of the substrates (entries 2, 3, 6). To our delight, when switching the solvent to toluene, the conversion reached to 88% (entry 5). After then, the different copper salts were screened. As a result, the catalytic efficiency of Cu(I) salts were better than Cu(II) salts in this catalytic system

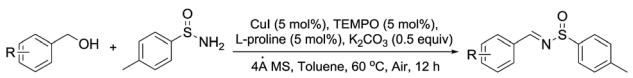
Table 1 The optimization of copper-catalyzed oxidative cascade reaction between alcohol and 4-toluenesulfinamide[a]



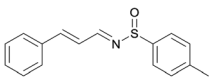
Entry	Solvent	Cu salt	Ligand	Conv.[b] (%)
1	CH_2Cl_2	CuI	L-Proline	81
2	THF	CuI	L-Proline	76
3	DMSO	CuI	L-Proline	51
4	CH_3OH	CuI	L-Proline	83
5	Toluene	CuI	L-Proline	88
6	DMF	CuI	L-Proline	54
7	Toluene	CuCl	L-Proline	82
8	Toluene	CuBr	L-Proline	83
9	Toluene	$CuCl_2$	L-Proline	73
10	Toluene	$CuBr_2$	L-Proline	74
11	Toluene	$CuSO_4$	L-Proline	45
12	Toluene	$Cu(OAc)_2$	L-Proline	68
13[c]	Toluene	CuI	L-Proline	Trace
14[d]	Toluene	CuI	L-Proline	Trace
15[e]	Toluene	CuI	L-Proline	74
16[f]	Toluene	CuI	L-Proline	76
17[g]	Toluene	CuI	L-Proline	8
18	Toluene	CuI	L-Valine	77
19	Toluene	CuI	β-Alanine	40
20	Toluene	CuI	L-Histidine	61
21	Toluene	CuI	Sarcosine	57
22	Toluene	CuI	Glycine	68
23	Toluene	CuI	Phenprobamate	46
24	Toluene	CuI	Pyrrolidine	69
25[h]	**Toluene**	**CuI**	**L-Proline**	**>99 (94[k])**
26[i]	Toluene	CuI	L-Proline	31
27[j,h]	Toluene	CuI	L-Proline	11
28[h]	Toluene	—	L-Proline	10
29[h]	Toluene	CuI	—	20

[a] Reaction conditions: benzalcohol (1.0 mmol), 4-toluenesulfinamide (1.0 mmol), copper salt (5.0 mol%), TEMPO (5.0 mol%), ligand (5.0 mol%), K_2CO_3 (1.0 mmol), solvent (4 mL), 4 Å MS (700 mg), 60 °C, 12 h. [b] Determined by HPLC. [c] 120 °C. [d] 100 °C. [e] 80 °C. [f] 40 °C. [g] 25 °C. [h] K_2CO_3 (0.5 equiv.). [i] K_2CO_3 was omitted. [j] TEMPO was omitted. [k] Isolated yields.

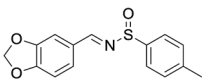
Table 2 Scope of *N*-*p*-tolylsulfinyl aldimines formation[a]



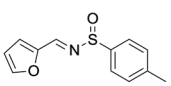
Entry	Product	Yield[b] (%)
1	R = H	94
2	R = 3,4-Me	90
3	R = *p*-OMe	91
4	R = 3,4,5-OMe	91
5	R = *p*-SMe	89
6	R = *p*-Cl	89
7	R = *p*-F	92
8	R = *p*-Br	91
9	R = *p*-NO_2	93
10	R = *p*-CF_3	93
11	R = *o*-Br	88
12	R = *o*-I	85
13	R = *o*-Cl	86
14	R = 2,4-Cl	90
15	R = *o*-Me	88
16	R = *m*-NO_2	93



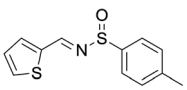
17
93[b]



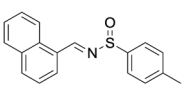
18
90[b]



19
88[b]



20
90[b]



21
90[b]

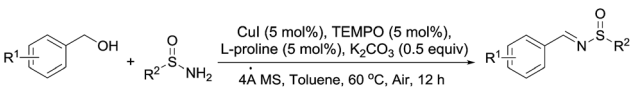
[a] Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K_2CO_3 (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C, 12 h. [b] Isolated yields.

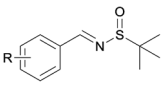
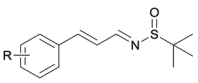
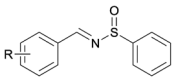
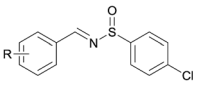
(entries 5, 7–12), and CuI showed the better catalytic efficiency than other Cu(I) salts with the 88% conversion (entries 5, 7 and 8). Furthermore, the temperature also played a decisive role in this system. As shown in Table 1 entries 13 to 17, trace conversion of *N*-sulfinylimine was obtained at 120 °C or 100 °C, and the conversions at 80 °C, 40 °C and 25 °C were only 74%, 76% and 8%, respectively. Further investigation revealed that the ligand played a critical role in this copper-catalyzed transformation. Among the examined ligands such as L-proline, L-valine, β-alanine, L-histidine, sarcosine, glycine, phenprobamate and pyrrolidine, L-proline was the best (Table 1, entries 5, 18–24). Finally, control experiments showed that when CuI, TEMPO, L-proline or K_2CO_3 was omitted most substrates were recovered (entries 26–29), and quantitative conversion was obtained when 0.5 equiv. K_2CO_3 was used under the reaction conditions (Table 1, entry 25). Thus, the optimized reaction conditions (entry 25): substrates (1.0 mmol), TEMPO (5 mol%), K_2CO_3 (0.5 equiv.) at 60 °C with CuI (5 mol%) as catalyst and L-proline (5 mol%) as ligand were found.

With the optimized conditions in hand, various aromatic alcohols were subjected to the standard reaction conditions. As shown in Table 2, various aromatic alcohols and 4-toluenesulfinamide were efficiently oxidative condensed into the corresponding *N*-sulfinylimines. The reaction was not only highly efficient but also showed excellent functional groups compatibility. A wide range of aromatic alcohols bearing electron-donating groups such as methyl and methoxy, or electron-withdrawing groups including halogen, nitro and trifluoromethyl substituents were converted into their corresponding *N*-sulfinylimines with good to excellent isolated yields (entries 1–16, 18, 21). Surprisingly, the efficient transformation of *p*-methylthiobenzyl alcohol and 4-toluenesulfinamide into the desired product was observed without transformation to sulfoxide or sulfone (entry 5). In addition, it was worth noting that the sterically hindered alcohols also provided the corresponding *N*-sulfinylimines in 85–90% yields (entries 11–15). Gratifyingly, heteroaryl alcohols such as 2-thienyl and 2-furyl methanol were also well tolerated to give the desire products in 88–90% yields (entries 19–20). Unsaturated alcohol (entries 17) also reacted to form the imine in 93% isolated yield. Unfortunately, less active aliphatic alcohols and secondary alcohols were not suitable in the reaction.

Next, the compatibility of a variety of other sulfinamides on this oxidative cascade reaction was examined, including *tert*-butanesulfinamide, bezenesulfinamide and 4-chloro-bezenesulfinamide, shown in Table 3. Good to excellent isolated yields were obtained for aromatic alcohols with electron-withdrawing (products 2, 4–6, 8, 10, 12, 15) and electron-donating (products 1, 3, 11, 13, 14) substituents. For aromatic alcohols bearing either *ortho*- (products 2, 3, 12) or *meta*- (product 14) substituents, the reactions proceeded smoothly and afforded *N*-sulfinylimines in good yields. In addition, allyl alcohols could also well tolerated under the optimal conditions in good isolated yields (entries 7, 8). However less active aliphatic alcohols and secondary alcohols could not afford the target products. In general, aromatic alcohols bearing electron-withdrawing substituents condensed more effectively with sulfinamides than those bearing electron-donating substituents (product 6 *vs.* 1, product 12 *vs.* 11, product 15 *vs.* 13).

Table 3 Scope of *N*-sulfinyl aldimines formation[a]

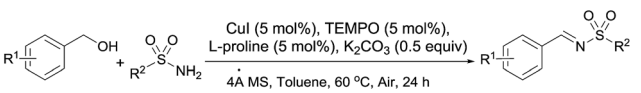


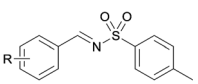
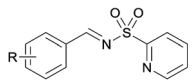
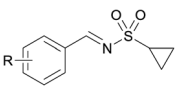
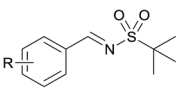
	Product	Yield[b] (%)
	(1) R = 3,4,5-OMe	86
	(2) R = *o*-I	80
	(3) R = *o*-OMe	78
	(4) R = *p*-Br	96
	(5) R = *p*-Cl	95
	(6) R = *p*-NO_2	97
	(7) R = H	92
	(8) R = *p*-NO2	95
	(9) R = H	91
	(10) R = *p*-Cl	92
	(11) R = 3,4,5-OMe	89
	(12) R = *o*-NO_2	95
	(13) R = 3,4-Me	89[c]
	(14) R = *m*-OMe	90[d]
	(15) R = *p*-F	91[e]

[a] Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K_2CO_3 (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C. [b] Isolated yields. [c] Reaction time 15 h. [d] Reaction time 14 h. [e] Reaction time 13 h.

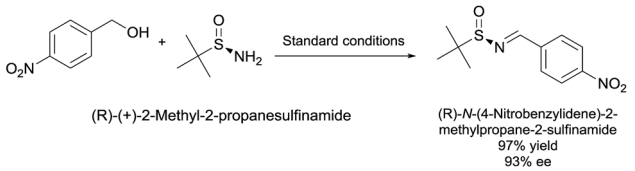
Finally, we turned our efforts to expand the scope of sulfonamides (Table 4). Although the strong electron-withdrawing character of the sulfonyl group leads to very low nucleophilicity of the RSO_2NH_2 nitrogen (much lower than of

Table 4 Scope of *N*-sulfonyl aldimines formation[a]

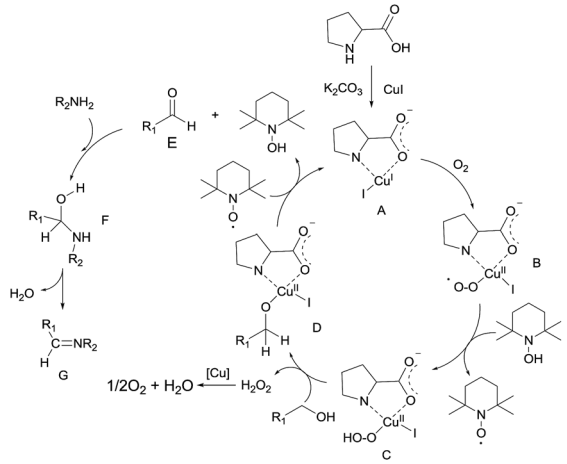


	Product	Yield[b] (%)
	(1) R = H	93
	(2) R = *p*-Br	91
	(3) R = 3,4,5-OMe	89[c]
	(4) R = H	76
	(5) R = *o*-Me	78
	(6) R = *m*-OMe	81
	(7) R = *p*-NO_2	80
	(8) R = H	87
	(9) R = *p*-NO_2	90
	(10) R = *p*-F	89[c]

[a] Reaction conditions: substrates (1.0 mmol), CuI (5 mol%), L-proline (5 mol%), TEMPO (5 mol%), K_2CO_3 (0.5 equiv.), toluene (4.0 mL), 4 Å MS (700 mg), 60 °C. [b] Isolated yields. [c] 1.2 equiv. of alcohol was used.



Scheme 3 Oxidative condensation of 4-nitrobenzyl alcohol and (*R*)-(+)-2-methyl-2-propanesulfinamide.



Scheme 4 A plausible catalytic cycle for the aerobic oxidative cascade condensation.

$RSONH_2$), prolonging the reaction time to 24 h also obtained satisfying results. Here we investigated the oxidative cascade reaction of aryl alcohols with various kinds of sulfonamides. Electron-donating and -withdrawing substituents at the *ortho*-, *para*- and *meta*- positions of the aryl alcohol partners were well tolerated, providing the desired products in good yields. Surprisingly, the 2-pyridinesulfonamide was also toleranted in this system, giving the corresponding products in good isolated yields (Table 4, products 4–7). Beyond that, branched alkyl sulfonamides also underwent oxidative cascade condensation successfully to give the corresponding products in 87–90% isolated yields, such as *tert*-butylsulfonamide and cyclopropylsulfonamide (products 8–10).

Given the synthetic importance of chiral sulfinamides in organic synthesis, we checked whether racemization occurred in the reaction using pure stereochemical *tert*-butylsulfin-amide as one of starting materials (Scheme 3). Satisfyingly, the imine product was obtained in 97% yield with 93% e.e. It was obvious that the chiral sulfinamide was also suitable in our system.

Based on the above promising results and related published research studies,[17,19r,21] a possible mechanism was depicted in Scheme 4. The reaction of L-proline, K_2CO_3 and CuI gave the complex A, which reacted with O_2 to afford a Cu(II)-superoxide species B. Species B abstracted a hydrogen from TEMPOH to form species C. Subsequent reaction of the species C with alcohol released H_2O_2 and afforded species D. β-Hydrogen elimination of the alkoxo moiety in D would occur to give a carbonyl product and TEMPOH, and regenerate A, followed by the insertion of a sulfinamide or sulfonamide to afford species F. Liberation of water from the F gave the product G.

Conclusions

In summary, an efficient and mild copper-catalyzed aerobic oxidative cascade system for the synthesis of *N*-sulfinyl- and *N*-sulfonylimines directly from aryl or allyl alcohols with sulfinamides or sulfonamides in one pot has been successfully developed. Under the optimized conditions, a wide range of arylalcohols and various sulfinamides (including chiral *tert*-sulfinamide) or sulfonamides were smoothly condensed into corresponding *N*-sulfinyl- or *N*-sulfonylimines with good to excellent isolated yields. Less active aliphatic alcohols and secondary alcohols were not suitable in the oxidative condensation system, unfortunately. What's more, this is the first example of copper-catalyzed aerobic oxidative cascade condensation for the formation of *N*-sulfinyl- and *N*-sulfonyl-imines from sulfinamides or sulfonamides with alcohols.

Acknowledgements

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