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Copper-Mediated 1,2-Difunctionalization of Styrenes with Sodium Arylsulfinates and *tert*-Butyl Nitrite: Facile Access to α-Sulfonylethanone Oximes

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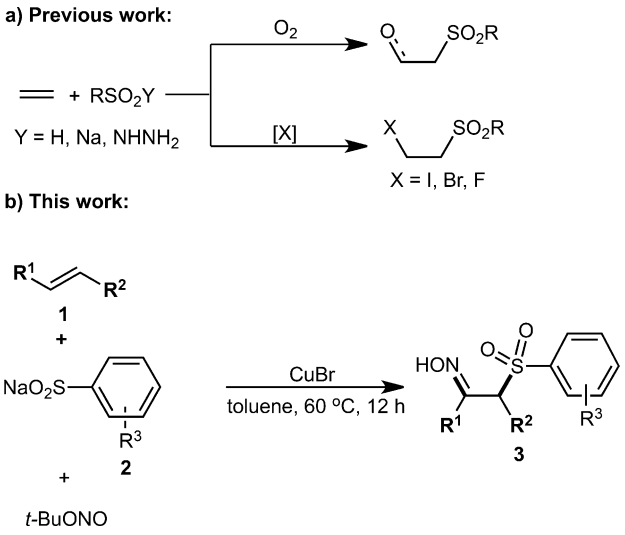
Abstract: A new copper-mediated synthesis of α-sulfonylethanone oximes from styrenes, sodium arylsulfinates and *tert*-butyl nitrite (*t*-BuONO; TBN) is presented. This intermolecular three-component method enables the one-step formation of C–N and C–S bonds under mild conditions, and represents a new, straightforward approach to α-sulfonylethanone oximes.

Keywords: *tert*-butyl nitrite; copper; sodium arylsulfinates; styrenes; α-sulfonylethanone oximes

The difunctionalization of alkenes that simultaneously adds two functional groups across a C=C double bond is one of the most important and straightforward methods for rapidly increasing molecular complexity, and it continues to inspire considerable efforts to develop new transformations.[1,2] In this field, attractive transformations include the difunctionalization reactions of alkenes with sulfonylation reagents and other functional reagents,[3] which provide an efficient tool for assembling useful sulfonyl-functionalized molecules.[4] However, transformations of alkenes using the three-component intermolecular strategy for the incorporation of sulfonyl groups turned out to be challenging. Indeed, the success of such three-component intermolecular difunctionalization transformations is rare and restricted to oxysulfonylation[5] and halosulfonylation (Scheme 1a).[6] Thus, the development of new, mild three-component intermolecular methods for incorporating a sulfonyl group into simple alkenes, which extends beyond oxysulfonylation and halosulfonylation, is highly interesting.

The α-sulfonylethanone oximes are a class of important compounds that are found in some natural products, pharmaceuticals, and materials, and are also valuable intermediates in synthesis.[7] Traditionally, approaches for the synthesis of α-sulfonylethanone oximes often require multiple synthetic steps that have low total yields and limited functional group choice. In 2012, He and co-workers reported the two-component cascade oxidation–addition reactions of olefins with *N*-hydroxysulfonamides for the synthesis of α-sulfonylethanone oximes in which the addition of NO free radicals proceeded through the oxidation of hydroxylamine to form the corresponding oximes.[4h] Inspired by these results, we envisioned that, by using an oxidative–radical strategy, the three-component intermolecular process might be used for introducing the sulfonyl group into the alkenes. Herein, we report a new, three-component intermolecular method to produce α-sulfonylethanone oximes by copper-cata-



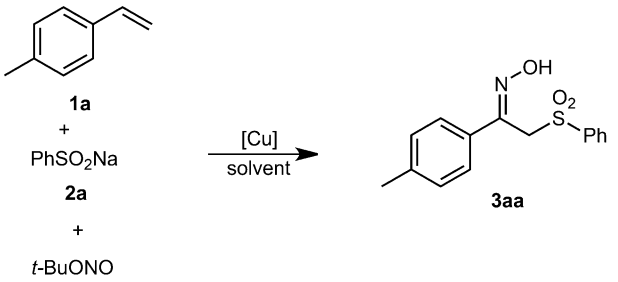
Scheme 1. Difunctionalization reaction of alkenes *via* the incorporation of the sulfonyl group.

lyzed difunctionalization of styrenes with sodium arylsulfinates and *t*-BuONO (Scheme 1b). This method allows the construction of a C–S bond and a C=N double bond through cascade radical addition across the C=C double bond in styrenes. This is accomplished by using sodium arylsulfinates, nitrosation and hydroamination and represents a mild and practical access to α-sulfonylethanone oximes.

As shown in Table 1, we optimized reaction conditions for the three-component reaction of 1-methyl-4-vinylbenzene (**1a**) with sodium benzenesulfinate (**2a**) and *t*-BuONO. To our delight, treatment of styrene **1a** with sodium arylsulfinate **2a**, *t*-BuONO and CuBr in toluene afforded the desired 2-(phenylsulfonyl)-1-(*p*-tolyl)ethan-1-one oxime (**3aa**) in 71% yield (entry 1). A series of other Cu catalysts, including CuI, CuOTf, $CuBr_2$ and $Cu(OAc)_2$, was subsequently tested; each of these catalysts was less effective than CuBr (entries 2–5). However, only a trace amount of product **3aa** was observed by GC-MS analysis in the absence of a copper catalyst (entry 6). The results show that the amount of CuBr affected the reaction (entries 7 and 8): a higher amount of CuBr (20 mol%) gave an identical yield to that obtained with 10 mol% of CuBr, but a lower amount of CuBr (5 mol%) sharply decreased the yield to 38%. A screen of various solvents, such as toluene, MeCN, $ClCH_2CH_2Cl$, CH_2Cl_2, DMF and DMSO, revealed toluene as the best choice (entry 1 *versus* entries 9–13). The reaction at a loading of 3 equiv. H_2O in anhydrous toluene also afforded product **3aa** in good yield (entry 14). Among the reaction temperatures examined, the reaction at 60 °C turned out to be preferred in terms of the yield (entries 1, 15 and 16).

With the optimal reaction conditions in hand, a variety of sodium arylsulfinates **2**, was first investigated in the presence of styrene **1a**, *t*-BuONO and CuBr (Table 2). Gratifyingly, sodium arylsulfinates **2**, bearing either electron-donating (Me and MeO) or electron-withdrawing (Cl, Br and NO_2) groups at the 2 or 4 positions of the aromatic ring were compatible with the optimized conditions (products **3ab**–**ag**). While 4-Me- or 4-MeO-substituted sodium arylsulfinates **2b** and **c** afforded products **3ab** and **3ac** in 57% and 48% yields, respectively, 4-NO_2-substituted sodium arylsulfinate was converted into product **3af** in 61% yield.

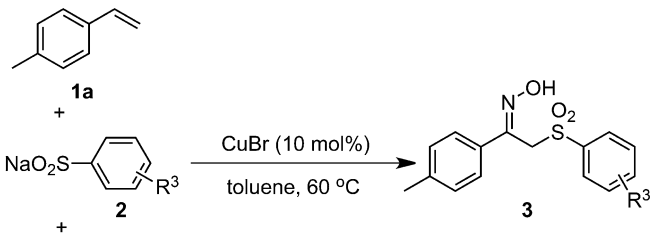
Table 1. Optimization of the reaction conditions.[a]

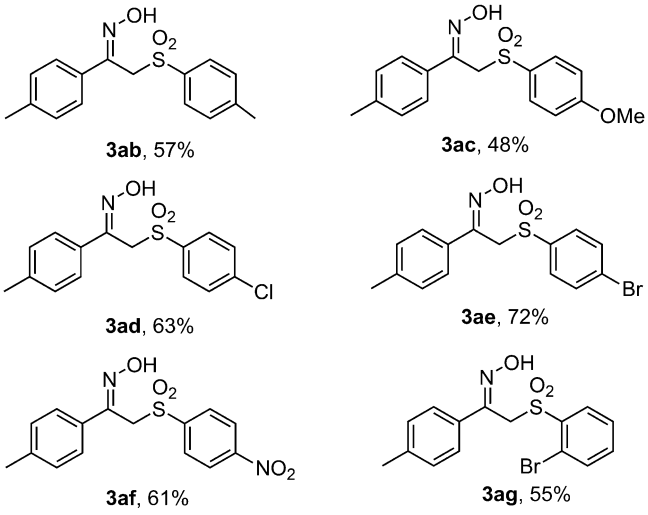


Entry	Cu (mol%)	Solvent	*T* [°C]	Yield [%][b]
1	CuBr (10)	toluene	60	71
2	CuI (10)	toluene	60	63
3	CuOTf (10)	toluene	60	52
4	$CuBr_2$ (10)	toluene	60	28
5	$Cu(OAc)_2$ (10)	toluene	60	56
6	–	toluene	60	trace
7	CuBr (20)	toluene	60	68
8	CuBr (5)	toluene	60	38
9	CuBr (10)	MeCN	60	63
10	CuBr (10)	$ClCH_2CH_2Cl$	60	46
11	CuBr (10)	CH_2Cl_2	60	36
12	CuBr (10)	DMF	60	15
13	CuBr (10)	DMSO	60	25
14[c]	CuBr (10)	toluene	60	70
15	CuBr (10)	toluene	40	44
16	CuBr (10)	toluene	80	55

[a] *Reaction conditions:* **1a** (0.2 mmol), **2a** (2 equiv.), *t*-BuONO (2 equiv.), [Cu] and solvent (2 mL) for 12 h. All solvents contain about 0.3% to 0.5% w/w water.
[b] Isolated yields.
[c] H_2O (3 equiv.) in anhydrous toluene.

Table 2. Difunctionalization tandem reaction of 1-methyl-4-vinylbenzene (**1a**) with sodium arylsulfinates (**2**) and *t*-BuONO[a]





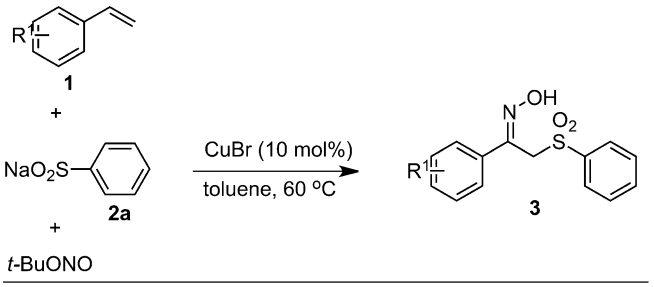
[a] *Reaction conditions:* **1a** (0.2 mmol), **2** (2 equiv.), *t*-BuONO (2 equiv.), CuBr (10 mol%) and toluene (2 mL) at 60 °C for 12 h.

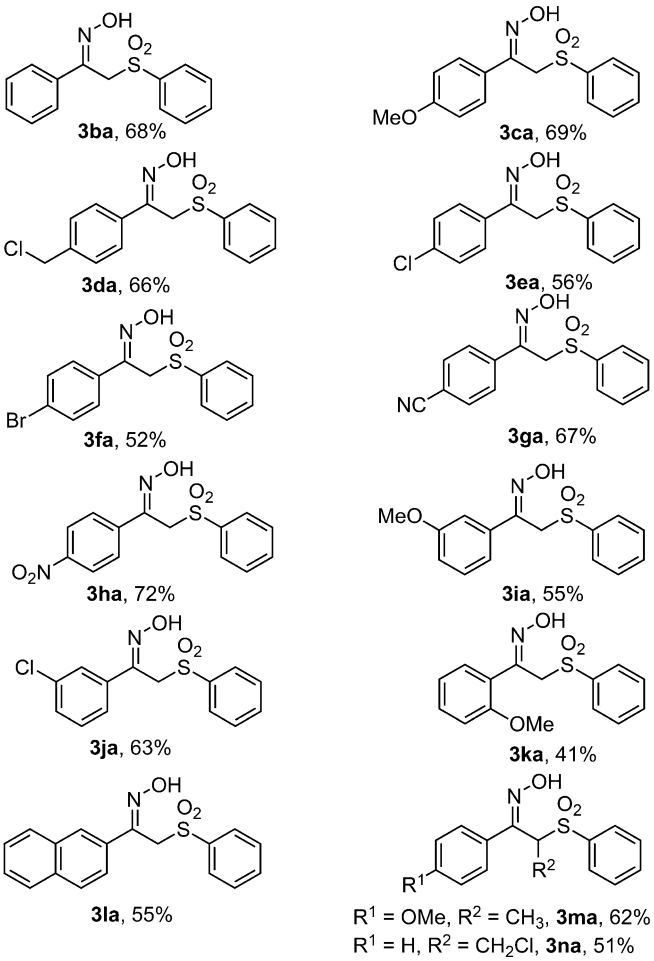
Interestingly, the halogen groups Cl and Br were well-tolerated and, thus, provide additional opportunities for modification of the products (products **3ad**, **3ae** and **3ag**). These results show that the substitution position has a fundamental influence on reactivity. In the case of the bromo-substituted substrates **2e** and **2g**, the reactivity decreased from *para* to *ortho* substitution (products **3ae** and **3ag**).

A wide range of terminal styrenes **1b–l** and internal alkenes **1m–n** were subjected to the optimized conditions to produce products **3ba–na** (Table 3). We were pleased to find that styrene **1b** was able to furnish the desired product, 1-phenyl-2-(phenylsulfonyl)ethan-1-one oxime (**3ba**), in 68% yield. Styrenes **1** with a substituent, such as MeO, CH_2Cl, Cl, Br, CN and NO_2, on the aromatic ring were compatible with the optimized reaction conditions, providing the corresponding products **3ca–ka** in moderate to good yields. Notably, the steric hindrance effects of substituents impacted on the reactivity. For example, the MeO-substituted styrenes **1c**, **1i** and **1k** smoothly underwent the difunctionalization reaction (products **3ca**, **3ia** and **3ka**, respectively), but the reactivity, as measured by yield, decreased from *para* to *meta* to *ortho* substitution. Gratifyingly, the 2-vinylnaphthalene **1l** was a suitable substrate for the reaction (product **3la**). It was noted that the internal alkenes 1-methoxy-4-(prop-1-en-1-yl)benzene (**1m**) and (3-chloroprop-1-en-1-yl)benzene (**1n**) successfully reacted with sodium arylsulfinate **2a** and *t*-BuONO in 62% and 51% yields, respectively (products **3ma** and **3na**). Unfortunately, the aliphatic alkene **1o** failed to react under the optimized reaction conditions.

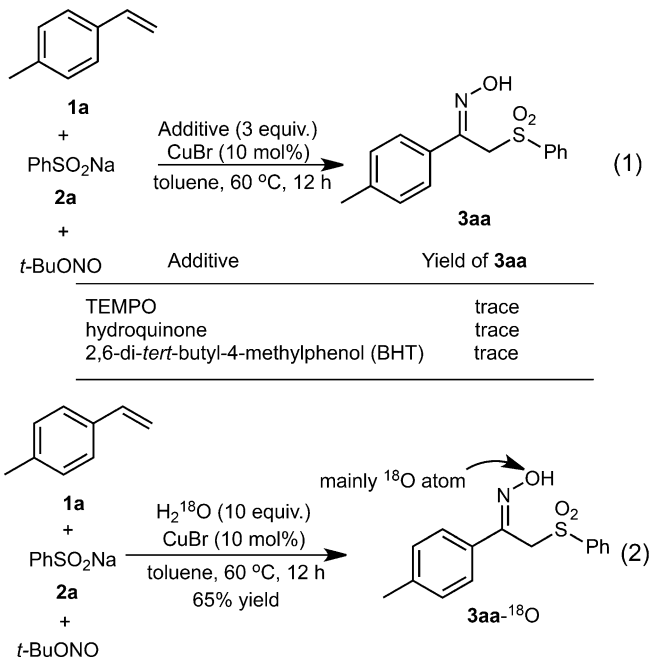
To understand the mechanism of the three-component intermolecular reaction, control experiments were performed (Scheme 2). This reaction was substantially inhibited by radical scavengers, including 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,4-di-*tert*-butyl-4-methylphenol (BHT) [Eq. (1)], suggesting that the reaction involves a radical pathway. An ^{18}O-labelling experiment was also performed by using $H_2{}^{18}O$; the ^{18}O-labelled product **3aa**-^{18}O was observed, which indicates that the hydroxy group's oxygen atom is from H_2O [Eq. (2)].

Table 3. Variation of the styrenes.[a]



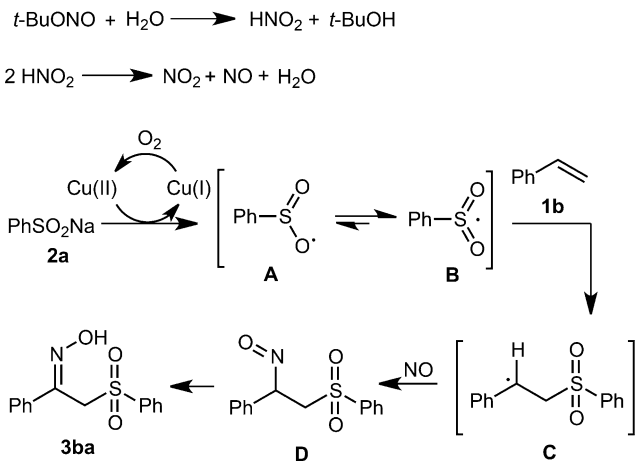


[a] *Reaction conditions:* **1** (0.2 mmol), **2a** (2 equiv.), *t*-BuONO (2 equiv.), CuBr (10 mol%) and toluene (2 mL) at 60 °C for 12 h.



Scheme 2. Control experiments.

Therefore, we propose a possible mechanism, which is outlined in Scheme 3, for this tandem protocol.[8–10] Initially, *t*-BuONO readily decomposes into HNO_2 and *t*-BuOH in the presence of H_2O, and HNO_2 is quickly converted into NO_2, NO and H_2O.[9,10] Sodium benzenesulfinate releases the oxygen-centered radical **A**, which is in resonance with the sulfonyl radical **B**, with the aid of CuBr.[8] Addition of sulfonyl radical **B** across styrene **1b** forms intermediate **C**, which then reacts with *t*-BuONO[9,10] to afford intermediate **D**. Finally, intermediate **D** is converted to the desired oxime, **3ba**, *via* a tautomerization process.[9i]



Scheme 3. Possible mechanisms.

In summary, we have developed a new, copper-mediated difunctionalization reaction of styrenes with sodium arylsulfinates and *t*-BuONO for the selective synthesis of diverse α-sulfonylethanone oximes. This method proceeds through a sequence of radical addition, nitrosation and hydroamination and is a simple and highly generalizable route for the production of α-sulfonylethanone oximes with excellent functional group tolerance. Further studies on the development of conceptually novel, three-component intermolecular reactions are currently underway in our laboratory.

Experimental Section

General Considerations

The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or acetone-d_6 solvents on an NMR spectrometer using TMS as the internal standard. LR-MS was performed on a GC-MS instrument, and HR-MS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. Melting points are uncorrected.

Typical Procedure for the Synthesis of Sodium Arylsulfinates (3)

4-Methylbenzenesulfinic acid sodium salt **2b** was prepared by heating 5.0 g of sodium sulfite, 3.80 g of 4-methylbenzenesulfonyl chloride, and 3.36 g of sodium bicarbonate in 20 mL of water at 80 °C for 8 h. After cooling to room temperature, water was removed under vacuum. Recrystallization of the residue in ethanol produced a white solid; yield: 1.78 g (55%).

Similarly, other sodium arylsulfinates **2c**–**2g** were prepared from their corresponding sulfonyl chlorides.

Typical Procedure for Copper-Mediated Synthesis of Oximes from Styrenes

A mixture of styrene **1** (0.2 mmol), sodium arylsulfinate **2** (0.4 mmol), *t*-BuONO (0.4 mmol), and CuBr (10 mol%) was stirred in toluene (2 mL) at 60 °C (oil-bath temperature) for the indicated time (about 12 h) until the complete consumption of the starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, and washed with brine. The aqueous phase was re-extracted with EtOAc (3×10 mL) and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate) to isolate the desired products **3**.

Analytical Data for 3aa–3ag and 3ba–3na

2-(Phenylsulfonyl)-1-(*p*-tolyl)ethan-1-one oxime (3aa): yield: 41.0 mg (71%); white solid; mp 153.9–154.3 °C (uncorrected); ^1H NMR (400 MHz, acetone-d_6): δ = 10.78 (s, 1H), 7.82 (d, *J* = 7.6 Hz, 2H), 7.70–7.66 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.57–7.53 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.87 (s, 2H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 146.4, 140.5, 139.0, 133.6, 132.0, 128.8, 128.3, 126.5, 51.7, 20.4; LR-MS (EI, 70 eV): *m/z* (%) = 273 (48), 208 (100), 209 (87), 193 (43); HR-MS (ESI): *m/z* = 290.0833, calcd. for $C_{15}H_{16}NO_3S$ $(M+H)^+$: 290.0845.

3aa-^{18}O: yield: 37.8 mg (65%); HR-MS (ESI): *m/z* = 292.0873, calcd. for $C_{15}H_{16}N^{18}O^{16}O_2S$ $(M+H)^+$: 292.0888.

1-(*p*-Tolyl)-2-tosylethan-1-one oxime (3ab): yield: 34.5 mg (57%); white solid; mp 160.9–161.3 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.70 (s, 2H), 2.37(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8, 144.8, 140.1, 136.5, 130.8, 129.4, 129.3, 128.4, 126.5, 52.7, 21.6, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 288 (1), 119 (100), 91 (37), 108 (23); HR-MS (ESI): *m/z* = 304.0990, calcd. for $C_{16}H_{18}NO_3S$ $(M+H)^+$: 304.1002.

2-[(4-Methoxyphenyl)sulfonyl]-1-(*p*-tolyl)ethan-1-one oxime (3ac): yield: 30.6 mg (48%); white solid; mp 143.9–144.7 °C (uncorrected); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 4.70 (s, 2H), 3.84 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.8, 148.3, 140.1, 131.0, 130.8, 130.7, 129.3, 126.5, 113.9, 55.6, 52.7, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 223.9 (100), 303 (95), 238 (93), 207 (90); HR-MS (ESI): *m/z* = 320.0940, calcd. for $C_{16}H_{18}NO_4S$ $(M+H)^+$: 320.0951.

2-[(4-Chlorophenyl)sulfonyl]-1-(*p*-tolyl)ethan-1-one oxime (3ad): yield: 40.7 mg (63%); white solid; mp 165.9–167.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.46 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 140.6, 140.4, 137.7, 130.5, 130.0, 129.4, 129.0, 126.5, 52.7, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 307 (1), 119 (100), 91 (24), 117 (13); HR-MS (ESI): *m/z* = 324.0447, calcd. for $C_{15}H_{15}{}^{35}ClNO_3S$ $(M+H)^+$: 324.0456.

2-[(4-Bromophenyl)sulfonyl]-1-(*p*-tolyl)ethan-1-one oxime (3ae): yield: 52.7 mg (72%); white solid; mp 174.9–175.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.6, 140.4, 138.2, 132.0, 130.4, 130.1, 129.4, 129.2, 126.5, 52.6, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 318 (71), 254 (12), 207 (77), 253 (59); HR-MS (ESI): *m/z* = 367.9943, calcd. for $C_{15}H_{15}{}^{79}BrNO_3S$ $(M+H)^+$: 367.9951.

2-[(4-Nitrophenyl)sulfonyl]-1-(*p*-tolyl)ethan-1-one oxime (3af): yield: 40.7 mg (61%); white solid; mp 181.9–183.3 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.9, 147.4, 144.6, 140.8, 130.2, 130.1, 129.5, 126.5, 123.8, 52.6, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 352 (41), 206 (100), 286 (57), 289 (55); HR-MS (ESI): *m/z* = 335.0688, calcd. for $C_{15}H_{15}N_2O_5S$ $(M+H)^+$: 335.0696.

2-[(2-Bromophenyl)sulfonyl]-1-(*p*-tolyl)ethan-1-one oxime (3ag): yield: 40.3 mg (55%); white solid; mp 179.9–180.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (s, 1H), 7.96–7.93 (m, 1H), 7.71–7.69 (m, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.40–7.34 (m, 2H), 7.12 (d, *J* = 8.0 Hz,2H), 5.03 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 140.0, 139.4, 135.2, 134.5, 132.2, 130.9, 129.2, 127.7, 126.6, 121.3, 50.4, 21.3; LR-MS (EI, 70 eV): *m/z* (%) = 317 (100), 301 (99), 260 (27), 318 (25); HR-MS (ESI): *m/z* = 367.9956, calcd. for $C_{15}H_{15}{}^{79}BrNO_3S$ $(M+H)^+$: 367.9951.

1-Phenyl-2-(phenylsulfonyl)ethan-1-one oxime (3ba): yield: 37.4 mg (68%); white solid; mp 165.9–166.6 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ = 10.9 (s, 1H), 7.83 (m, *J* = 8.0 Hz, 2H), 7.72–7.71 (m, 2H), 7.70–7.66 (m, 1H), 7.57–7.53 (m, 2H), 7.36–7.32 (m, 3H), 4.90 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 146.5, 140.5, 134.8, 133.7, 129.1, 128.9, 128.2 (2C), 126.6, 51.7; LR-MS (EI, 70 eV): *m/z* (%) = 259 (66), 194 (100), 195 (79), 91 (57); HR-MS (ESI): *m/z* = 276.0680, calcd. for $C_{22}H_{19}N_2O_4$ $(M+H)^+$: 276.0689.

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3ca): yield: 42.1 mg (69%); white solid; mp 167.9–168.5 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 7.6 Hz, 2H), 7.61–7.57 (m, 3H), 7.48–7.44 (m, 2H), 6.88 (d, *J* = 9.2 Hz, 2H), 4.72 (s, 2H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.0, 147.4, 139.4, 133.8, 128.8, 128.5, 128.1, 126.0, 114.0, 55.3, 52.5; LR-MS (EI, 70 eV): *m/z* (%) = 289 (4), 135 (100), 77 (23), 133 (22); HR-MS (ESI): *m/z* = 306.0787, calcd. for $C_{15}H_{16}NO_4S$ $(M+H)^+$: 306.0795.

1-[4-(Chloromethyl)phenyl]-2-(phenylsulfonyl)ethan-1-one oxime (3da): yield: 42.6 mg (66%); white solid; mp 156.9–158.1 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ = 10.99 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.70–7.76 (m, 1H), 7.57–7.53 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 4.90 (s, 2H), 4.73 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 146.1, 140.4, 138.9, 134.8, 133.7, 128.9, 128.6, 128.3, 126.9, 51.7, 45.5; LR-MS (EI, 70 eV): *m/z* (%) = 223 (100), 286 (86), 194 (75), 77 (70); HR-MS (ESI): *m/z* = 324.0468, calcd. for $C_{15}H_{15}{}^{35}ClNO_3S$ $(M+H)^+$ 324.0456.

1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3ea): yield: 34.6 mg (56%); white solid; mp 166.9–167.8 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.61–7.57 (m, 3H), 7.50–7.46 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 4.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9, 139.3, 136.1, 134.0, 132.0, 128.9, 128.8, 128.4, 127.9, 52.5; LR-MS (EI, 70 eV): *m/z* (%) = 293 (1), 139 (100), 141 (13), 77 (39); HR-MS (ESI): *m/z* = 310.0375, calcd. for $C_{14}H_{13}{}^{35}ClNO_3S$ $(M+H)^+$: 310.0299.

1-(4-Bromophenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3fa): yield: 36.6 mg (52%); white solid; mp 188.9–189.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.07 (s, 1H), 7.84–7.82 (m, 2H), 7.72–7.66 (m, 3H), 7.59–7.53 (m, 4H), 4.90 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.7, 140.3, 134.1, 133.8, 131.3, 128.9, 128.5, 128.3, 122.9, 51.5; LR-MS (EI, 70 eV): *m/z* (%) = 338 (37), 193 (100), 117 (61), 273 (51); HR-MS (ESI): *m/z* = 353.9786, calcd. for $C_{14}H_{13}{}^{79}BrNO_3S$ $(M+H)^+$: 353.9794.

4-[1-(Hydroxyimino)-2-(phenylsulfonyl)ethyl]benzonitrile (3ga): yield: 40.2 mg (67%); white solid; mp 173.9–174.7 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ = 11.41 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.73–6.69 (m, 1H), 7.60–7.56 (m, 2H), 4.96 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 145.5, 140.1, 139.0, 133.9, 132.0, 129.0, 128.2, 127.3, 118.2, 112.4, 51.3; LR-MS (EI, 70 eV): *m/z* (%) = 284 (1), 130 (100), 77 (70), 221 (48); HR-MS (ESI): *m/z* = 301.0633, calcd. for $C_{15}H_{13}N_2O_3S$ $(M+H)^+$: 301.0641.

1-(4-Nitrophenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3ha): yield: 46.1 mg (72%); white solid; mp 155.9–157.3 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ = 11.52 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 8.8 Hz, 2H), 7.85 (d, *J* = 7.6 Hz, 2H), 7.73–7.70 (m, 1H), 7.60–7.56 (m, 2H), 5.00 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ = 148.1, 145.4, 140.9, 140.1, 133.9, 129.0, 128.3, 127.7, 123.3, 51.4; LR-MS (EI, 70 eV): *m/z* (%) = 304 (81), 240 (100), 193 (73), 77 (55); HR-MS (ESI): *m/z* = 321.0541, calcd. for $C_{14}H_{13}N_2O_5S$ $(M+H)^+$: 321.0540.

1-(3-Methoxyphenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3ia): yield: 33.6 mg (55%); white solid; mp 157.9–158.6 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.58 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 7.58–7.55 (m, 1H), 7.46–7.42 (m, 2H), 7.28–7.24 (m, 1H), 7.17 (d, *J* = 7.2 Hz, 2H), 6.94–6.92 (m, 1H), 4.73(s, 2H), 3.80(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 147.6, 139.4, 134.9, 133.8, 129.6, 128.8, 128.4, 119.2, 115.9, 111.8, 55.3, 52.8; LR-MS (EI, 70 eV): *m/z* (%) = 289 (29), 135 (100), 77 (36), 107 (25); HR-MS (ESI): *m/z* = 306.0782, calcd. for $C_{15}H_{16}NO_4S$ $(M+H)^+$: 306.0795.

1-(3-Chlorophenyl)-2-(phenylsulfonyl)ethan-1-one oxime (3ja): yield: 38.9 mg (63%); white solid; mp 161.9–163.4 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1H),

7.84 (m, J=7.6 Hz, 2H), 7.61–7.57 (m, 1H), 7.56 (s, 1H), 7.52–7.48 (m, 1H), 7.45 (d, J=7.6 Hz, 2H), 7.34 (d, J=8.0 Hz, 1H), 7.30–7.26 (m, 1H), 4.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=146.5, 139.2, 135.4, 134.6, 134.0, 129.9, 129.8, 128.3, 126.5, 124.8, 52.5; LR-MS (EI, 70 eV): m/z (%)=293 (88), 229 (100), 193 (89), 228 (66); HR-MS (ESI): m/z=310.0375, calcd. for $C_{22}H_{19}N_2O_4$ $(M+H)^+$: 310.0299.

1-(2-Methoxyphenyl)-2-(phenylsulfonyl)propan-1-one oxime (3ka): yield: 25.0 mg (41%); white solid; mp 166.9–167.8 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ=10.87 (s, 1H), 7.68 (d, J=8.0 Hz, 2H), 7.62–7.59 (m, 1H), 7.49–7.45 (m, 2H), 7.32–7.28 (m, 1H), 7.24 (d, J=7.6 Hz, 1H), 6.94–6.90 (m, 1H), 6.81 (d, J=8.4 Hz, 1H), 4.96 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=157.3, 147.1, 140.4, 133.3, 130.9, 130.6, 128.7, 128.0, 123.8, 120.3, 110.8, 54.8, 52.6; LR-MS (EI, 70 eV): m/z (%)=289 (13), 134 (100), 148 (64), 147 (41); HR-MS (ESI): m/z=306.0781. calcd. for $C_{15}H_{16}NO_4S$ $(M+H)^+$: 306.0795.

1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethan-1-one oxime (3la): yield: 35.8 mg (55%); white solid; mp 177.9–178.9 °C (uncorrected); ^{1}H NMR (400 MHz, acetone-d_6): δ=11.04 (s, 1H), 8.20 (s, 1H), 7.92–7.88 (m, 3H), 7.87–7.84 (m, 3H), 7.65–7.62 (m, 1H), 7.54–7.51 (m, 4H), 5.04 (s, 2H); ^{13}C NMR (100 MHz, acetone-d_6): δ=146.5, 140.5, 133.7 (2C), 133.1, 132.2, 128.9, 128.6, 128.3, 127.8, 127.6, 127.0, 126.7, 126.4, 123.6, 51.6; LR-MS (EI, 70 eV): m/z (%)=309 (89), 244 (100), 245 (84), 141 (52); HR-MS (ESI): m/z=326.0837, calcd. for $C_{18}H_{16}NO_3S$ $(M+H)^+$: 326.0845.

1-(4-Methoxyphenyl)-2-(phenylsulfonyl)propan-1-one oxime (3ma): yield: 39.6 mg (62%); white solid; mp 179.9–180.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.16 (s, 1H), 7.84 (d, J=8.0 Hz, 2H), 7.63–7.59 (m, 1H), 7.52–7.48 (m, 2H), 7.35 (d, J=12 Hz, 2H), 6.88 (d, J=12 Hz, 2H), 4.35–4.30 (m, 1H), 3.82 (s, 3H), 1.62(d, J=8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=160.1, 151.9, 137.4, 133.7, 129.8, 129.3, 128.9, 124.1, 113.6, 66.3, 55.3, 13.9, 52.6; LR-MS (EI, 70 eV): m/z (%)=288 (13), 107 (100), 147 (63), 77 (45); HR-MS (ESI): m/z=320.0943, calcd. for $C_{16}H_{18}NO_4S$ $(M+H)^+$: 320.0951.

3-Chloro-1-phenyl-2-(phenylsulfonyl)propan-1-one oxime (3na): yield: 32.9 mg (51%); white solid; mp 161.9–162.7 °C (uncorrected); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.69 (d, J=8.0 Hz, 2H), 7.64–7.61 (m, 3H), 7.46–7.36 (m, 5H), 5.27–5.24 (m, 1H), 5.15–5.12 (m, 1H), 4.66–4.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=152.5, 135.6, 134.7, 130.8, 129.1, 128.9, 128.7, 127.7, 127.1, 72.8, 72.6; LR-MS (EI, 70 eV): m/z (%)=307 (13), 104 (100), 141 (45), 77 (67); HR-MS (ESI): m/z=324.0470, calcd. for $C_{15}H_{15}{}^{35}ClNO_3S$ $(M+H)^+$: 324.0456.

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