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ARTICLE

Copper (I)-mediated synthesis of β-hydroxysulfones from styrenes and sulfonylhydrazides. Electrochemical mechanistic study

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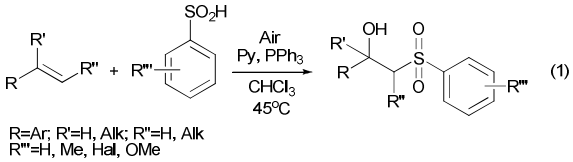
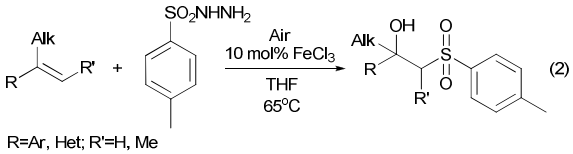
Alexander O. Terent'ev,*[ab] Olga M. Mulina,[a] Dmitry A. Pirgach,[ab] Dmitry V. Demchuk,[a] Mikhail A. Syroeshkin [a] and Gennady I. Nikishin[a]

Copper (I) halides were used as mediators in the β-hydroxysulfones synthesis through oxysulfonylation of styrenes with the use of sulfonylhydrazides. The feature of the developed process lies in the combination of copper (I) salt with oxygen — stoichiometric oxidant. Copper (II) species are responsible for the oxidation of sulfonylhydrazides, they are generated in a small amount in the O_2/Cu(I)/Cu(II) redox system, which is formed during the reaction. The combination of these three components enables to obtain in the case of α-methylstyrenes only β-hydroxysulfones and in the case of α-unsubstituted styrenes β-hydroxysulfones as the main products and β-ketosulfones as the byproducts. With good yields β-hydroxysulfones were prepared by reduction of the reaction mixture containing both products β-hydroxysulfones and β-ketosulfones with $NaBH_4$. Electrochemical study revealed that the Cu (I)/Cu(II) pair can serve as effective mediator of β-hydroxysulfones formation *via* redox processes.

Introduction

β-Hydroxysulfones are of great interest as structural units of antifungal[1] and antitumor[2] compounds, they are known as intermediates in the synthesis of lactones[3] and unsymmetrical alkenes[4]. Traditionally β-hydroxysulfones are obtained through nucleophilic addition of sulfinates to epoxides[5-8], reduction of β-ketosulfones[9,10] and hydroxylation of α, β-unsaturated sulfones[11]. For the last years several oxidative strategies for β-hydroxysulfones preparation from olefins were established. In these reports air and thermally low stable[12,13,14] sulfinic acids in combination with O_2 and PPh_3 (Scheme 1, eq. 1)[15] or sulfonylhydrazides with O_2 and Fe (III) salts were required.





Scheme 1 Recent works for oxysulfonylation of styrenes.

The latter method is applied for the synthesis of structures containing β-hydroxysulfone moiety predominantly at tertiary carbon atom, which cannot be further oxidized (Scheme 1, eq. 2) [16]. For sulfonylation of unsaturated compounds without additional inserting oxygen into the molecule a number of oxidants are exploited: $Cu(OAc)_2$[17,18], CAN[19], NBS[20], $K_2S_2O_8$[21], peroxides[22], I_2/TBHP[23] and TBAI/TBHP[24,25] systems. It is well-known that oxygen is an ideal environment-friendly oxidant, which offers fascinating industrial and academic prospects. In oxidative transformations in most cases it is used in cooperation with transition metals salts and complexes[26-29].

In this context, we disclosed the process of styrenes oxysulfonylation by utilizing sulfonylhydrazides in the presence of O_2/Cu(I) system, leading to β-hydroxysulfones. During the reaction the O_2/Cu(I)/Cu(II) system is formed with a small amount of Cu(II) that is confirmed by the near absence of specific for Cu(II) species colour. As a result, β-hydroxysulfones **3** as main products and β-ketosulfones **4** as byproducts are formed (Scheme 2).

Results and discussion

The synthesis of β-hydroxysulfones **3aa-3fe** and β-ketosulfones **4aa-4ab** from styrenes **1a-1j** with the use of sulfonylhydrazides **2a-2e** was conducted in CH_3CN, CH_3CN–H_2O, THF, THF–H_2O with O_2/Cu(I)/Cu(II) redox system. This system resulted from transformations of CuCl, CuBr, CuI in aerobic conditions (Scheme 2). Our preliminary studies were focused on the reaction of styrene **1a** with sulfonylhydrazide **2a**, leading to 1-phenyl-2-tosylethanol **3aa** and 1-phenyl-2-tosylethanone **4aa** formation. We examined the influence of Cu (I) salt counteranion, oxygen source (air oxygen or 98% oxygen) and solvent type (Table 1) on **3aa** yield.

[a] N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow, 119991, Russian Federation. E-mail: terentev@ioc.ac.ru; Fax: (+7)499-1355328
[b] D.I. Mendeleev University of Chemical Technology of Russia, 9 Miusskaya square, Moscow, 125047, Russian Federation
†Electronic Supplementary Information (ESI) available: [NMR spectra of all synthesized compounds]. See DOI: 10.1039/x0xx00000x

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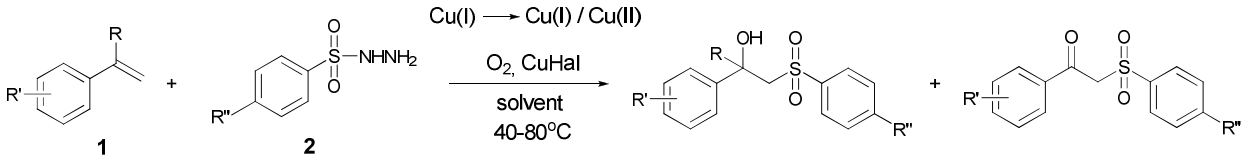
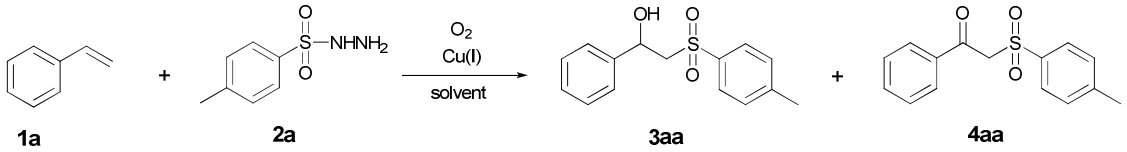


1a: R = H, R' = H; **1b**: R = H, R' = *o*-Me;
1c: R = H, R' = *p*-^{i}Pr; **1d**: R = H, R' = *p*-^{t}Bu;
1e: R = H, R' = *p*-Cl; **1f**: R = Me, R' = H;
1g: R = Me, R' = *p*-Cl; **1h**: R = Me, R' = *p*-Br;
1i: R =Me, R' = *p*-NO_2; **1j**: R = Me, R = *p*-OMe

R'' = **2a** (Me), **2b** (I), **2c** (Br), **2d** (OMe), **2e** (NO_2)

Scheme 2 Oxysulfonylation of styrenes **1a-1j** with the use of sulfonylhydrazides **2a-2e** (in the codification of **3** and **4** the first letter index refers to the styrene **1** moiety, the second letter index to the hydrazide **2** moiety).

Table 1 Screening of the reaction conditions.



Entry	Time (h)	Ratio (mole Cu(I) / mole **1a**)	Oxygen source	Solvent	Yield **3aa** (%)[a]	Yield **4aa** (%)[a]	Total yield **3aa** and **4aa** (%)[a]
1	7	CuBr (2)	air	$CH_3CN–H_2O$	28	14	42
2	7	CuCl (2)	air	$CH_3CN–H_2O$	25	15	40
3	7	CuI (2)	air	$CH_3CN–H_2O$	17	10	27
4[b]	7 + 12	CuBr (2)	air	$CH_3CN–H_2O$	38 (61)	27	65
5[c]	7 + 12	CuBr (2)	air	$CH_3CN–H_2O$	30	16	46
6	7 + 12	CuBr (0.2)	air	$CH_3CN–H_2O$	10	5	15
7	7 + 12	CuBr (5)	air	$CH_3CN–H_2O$	36	17	53
8	7 + 12	CuBr (2)	air	CH_3CN	20	12	32
9	7 + 12	CuBr (2)	air	THF	28	13	41
10	7 + 12	CuBr (2)	air	$THF–H_2O$	18	10	28
11	7 + 12	CuBr (2)	O_2	$CH_3CN–H_2O$	55 (85)	36	91
12	7 + 12	CuBr (0.2)	O_2	$CH_3CN–H_2O$	15	8	23
13	7	CuBr (2)	O_2	$CH_3CN–H_2O$	43 (71)	35	78
14[c]	7 + 12	CuBr (2)	O_2	$CH_3CN–H_2O$	50(77)	30	80

General procedure: to the solution of styrene **1a** (300 mg, 2.88 mmol) in 25 ml ($CH_3CN–H_2O$ (5:1), CH_3CN, THF, $THF–H_2O$ (5:1)) Cu (I) salt (0.58-14.4 mmol, molar ratio 0.2-5 mol of salt / mol **1a**) and sulfonylhydrazide **2a** (537 mg, 2.88 mmol, molar ratio 1 mol **2a** / mol **1a**) were added. The mixture was stirred for 7 h at 40°C. [a] The yield was determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard, isolated yield after reduction with $NaBH_4$ is in parentheses. [b] 7 h at 40°C, then 12 h at 20-25°C.[c] 7 h at 80 °C, then 12 h at 20-25°C.

Entries 1-3 indicated that among copper (I) halides, CuBr, CuCl and CuI, usage of CuBr afforded the highest total yield of oxysulfonylation products and the yield of desired product **3aa** for 7 hours. When the reaction was performed for more prolonged time (entry 4) yield of **3aa** reached 38%. Heating the reaction mixture for the first 7 hours to 80°C (entry 5) didn't increase yield of **3aa**. Decreasing (entry 6) or increasing (entry 7) of molar ratio of CuBr per mol **1a** in comparison with previous entries resulted in reduced yield of the desired product. Employing CH_3CN, THF, THF-H_2O (5:1) in place of $CH_3CN–H_2O$ (5:1) negatively influenced reaction efficiency (entries 8-10). In entry 11 air oxygen was replaced for 98% oxygen, as a result **3aa** yield was improved to 55%, total yield

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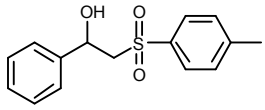
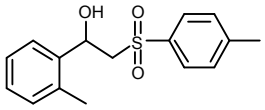
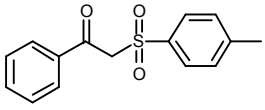
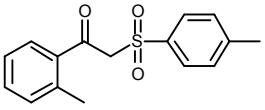
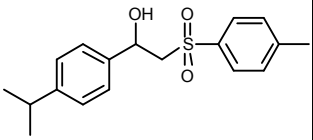
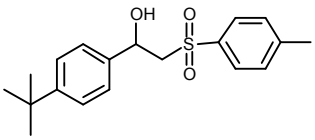
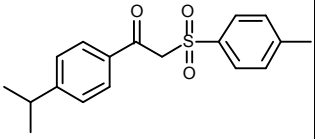
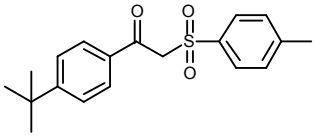
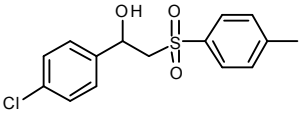
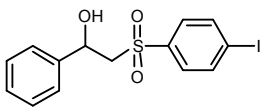
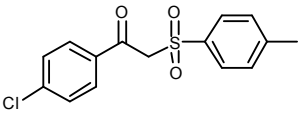
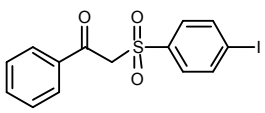
of oxysulfonylation products in this case reached 91%. Attempts failed (entries 12-14) of increasing desired product yield through modification of molar ratio of CuBr per mol **1a**, temperature and reaction time, compared to entry 11 conditions, in which the best result was obtained; total yield **of 3aa** and **4aa** in these experiments didn't exceed 80%.

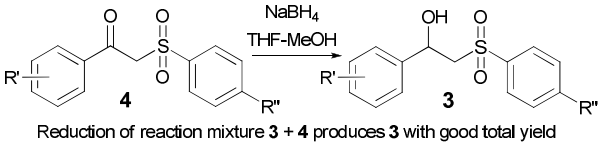
With the optimized reaction conditions in hand (entry 11, Table 1), scope of this copper-mediated oxysulfonylation reaction was investigated. A number of β-hydroxysulfones **3aa-3ab** were formed in 32-65% yield, β-ketosulfones **4aa-4ab** were observed as byproducts in 18-33% yield (Table 2).

Table 2 Structure and yield of β-hydroxysulfones **3** and β-ketosulfones **4** [a].

 **3aa**, 55% (85%)	 **3ba**, 37% (54%)
 **4aa**, 36%	 **4ba**, 18%
 **3ca**, 53% (72%)	 **3da**, 65% (89%)
 **4ca**, 23%	 **4da**, 31%
 **3ea**, 32% (52%)	 **3ab**, 40% (62%)
 **4ea**, 24%	 **4ab**, 25%

[a] The yield was determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard; isolated yield after reduction with $NaBH_4$ is in parentheses.

In all examples hydroxysulfone is predominantly formed independently from the properties of a substituent on the benzene ring. In most cases molar ratio of hydroxysulfone **3** / ketosulfone **4** is 2:1. It is well-known that ketones can be easily reduced into corresponding alcohols[30-32]. That's why in order to transform β-ketosulfones **4**, byproducts, into desired β-hydroxysulfones **3** we filtered the reaction mixture from CuBr after the reaction completed and then carried out reduction of ketosulfones using $NaBH_4$ (Scheme 3). As a result, β-hydroxysulfones **3** were obtained in 52-89% overall yield in two steps (Entries 4, 11, 13, 14 in Table 1 and Table 2).

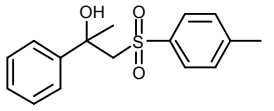
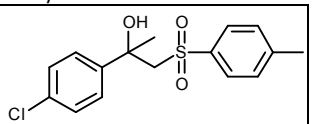
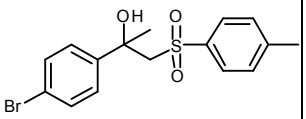
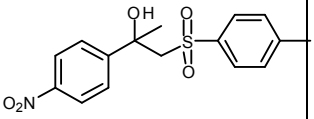
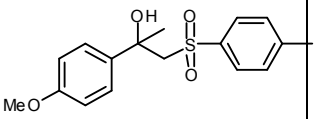
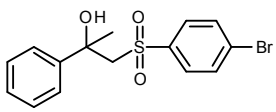
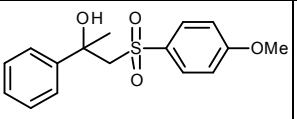
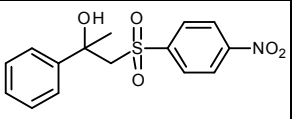


Scheme 3 Reduction of β-ketosulfones with $NaBH_4$.

This oxysulfonylation reaction was also examined by applying of α-methylstyrenes (Table 3). A variety of α-methylstyrenes bearing either electron withdrawing or electron donating substituents on the aryl ring worked well under conditions of entry 11 (Table 1) and target β-hydroxysulfones were formed in most cases in good yields. It is important to note that in the reactions of methylsulfonylhydrazide with styrene **1a**, and octene-1 or cyclohexene with sulfonylhydrazide **2a** oxysulfonylation products were not observed in measurable yields.

The structures of all synthesized hydroxysulfones **3** and ketosulfones **4** were confirmed with ^{1}H, ^{13}C NMR spectroscopy, elemental analysis, HRMS and IR spectroscopy.

Table 3 Structure and yield of β-hydroxysulfones **3** [a].

 **3fa**, 92%	 **3ga**, 90%
 **3ha**, 93%	 **3ia**, 89%
 **3ja**, 90%	 **3fc**, 52%
 **3fd**, 85%	 **3fe**, 36%

[a] Isolated yield.

Proposed reaction mechanism

To study plausible reaction mechanism the investigation of redox properties of oxygen, styrene **1a**, *p*-toluenesulfonylhydrazide **2a** and CuBr in CH_3CN–H_2O (5:1) solution with the use of cyclic voltammetry (CV) was carried out. Tetrabutylammonium perchlorate was chosen as a supporting electrolyte. Obtained CV curves are shown in Fig. 1.

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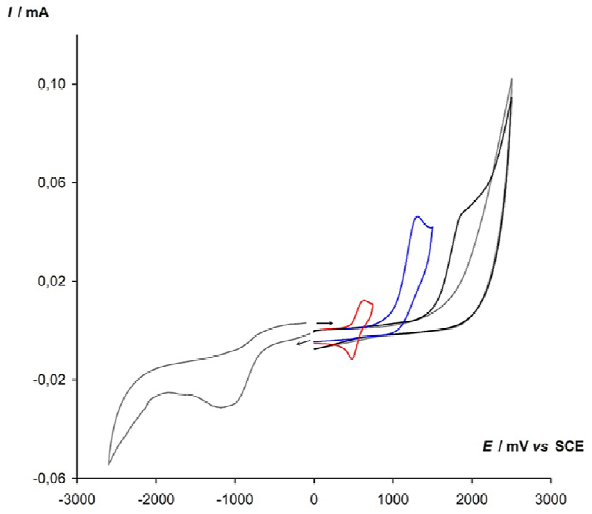
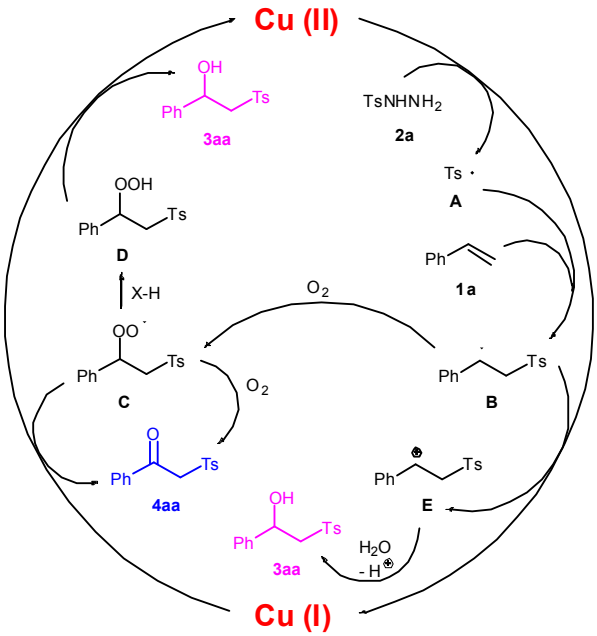


Figure 1 CV curves for 2.0 mmol/L solutions of CuBr (red), *p*-toluenesulfonylhydrazide **2a** (blue), styrene **1a** (black) and aerated supporting solution (grey) in 0.1M Bu_4NClO_4 in $CH_3CN–H_2O$ (5:1) on a working glassy-carbon electrode (d = 1.7 mm) under scan rate 100 mV/s.

Oxidizing properties of oxygen are evidenced in reducing in relatively early potentials, the peak on CV curve with potential -1.10 V is responsible for its reduction. Chemically irreversible styrene **1a** oxidation takes place in far region with maximum at 1.90 V and runs into discharge of the background. Chemically irreversible peak at 1.35 V is responsible for oxidation of *p*-toluenesulfonylhydrazide **2a**, therefore we can conclude that its oxidation goes rather more easily than oxidation of styrene.

Chemically and electrochemically reversible peak with $E_{1/2}$ = 0.55 V corresponds to oxidation of Cu (I) into Cu (II). It takes place in the potential range between oxygen reduction and *p*-toluenesulfonylhydrazide **2a** oxidation. It means that in experimental conditions Cu (I)/Cu (II) pair can serve as effective mediator of *p*-toluenesulfonylhydrazide **2a** oxidation by oxygen.

On the basis of obtained experimental data and previous studies of reactions proceeding through generation of S-centered radicals from sulfonylhydrazides[33-35], we proposed the pathway of oxysulfonylation process (Scheme 4). Cu(I) ions are oxidized to Cu(II) [36-40] in the presence of oxygen, it is confirmed by numerous kinetic studies of this process[41-44]. Almost colourless solution during the reaction evidences for a small amount of Cu(II). Afterwards, as a result of a successive oxidation of hydrazide **2a** under the action of Cu(II) [20, 33, 34], oxygen or peroxyradical **C**, S-centered tosyl radical **A** (Ts) is generated, which reacts with styrene **1a** forming C-centered benzyl radical **B** [20]. On the next step radical **B** is trapped with oxygen forming peroxyradical **C**. Then, after abstraction of hydrogen atom from a hydrogen donor X-H (NH and CH) peroxyradical **C** transforms into hydroperoxide **D**[45], which gives the main product **3aa** after the reduction[46-51]. Alcohol **3aa** can be also formed due to the C-centered benzyl radical **B** oxidation by Cu(II) species to the intermediate cation **E** followed by its hydroxylation[52-54]. Ketone **4aa** is formed after the fragmentation of species generated from the reaction of peroxyradical **C** with Cu(I) ions[55] or oxygen[56-58].



Scheme 4 Plausible oxysulfonylation mechanism on the example of the reaction of styrene **1a** and *p*-toluenesulfonylhydrazide **2a**.

The fact that using of octene-1 and cyclohexene as starting reagents didn't lead to the formation of oxysulfonylation products can be explained with low stability of C-centered alkyl radical generated after addition of tosyl radical **A** to double bond.

Conclusions

In summary, we have demonstrated a novel copper-mediated oxysulfonylation of styrenes using sulfonylhydrazides for synthesis of corresponding β-hydroxysulfones in 32-93% yield. In the case of α-unsubstituted styrenes β-ketosulfones are formed as the byproducts. Applying of α-methylstyrenes in this methodology gives β-hydroxysulfones as single products in high yield. Moreover, using voltammetry, experimental data and previous reports, plausible reaction pathway was proposed. Coupling of two starting reagents proceeds under the action of O_2/Cu(I)/Cu(II) redox system. The distinguishing feature of the work lies in the combination of oxygen and a copper (I) salt, which is oxidized to copper (II) on a limited scale, that makes it possible to obtain β-hydroxysulfones as the main products.

Experimental

NMR spectra were registered on Bruker Avance II 300 MHz instrumental. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 7.25 and δ 77.0 ($CDCl_3$), δ 2.50 and δ 39.51 (DMSO-d_6). IR spectra were recorded on a FT-IR spectrometer. High resolution mass spectra (HRMS) were

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measured using electrospray ionization (ESI).[59] The measurements were done in a positive ionmode (interface capillary voltage 4500 V); the mass ratio was from m/z 50 to 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in CH_3CN (flow rate 3 μL/min). Nitrogen was applied as a dry gas; interface temperature was set at 180 °C. The TLC analyses were carried out on standard silica-gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Chromatography was performed on silica gel (63-200 mesh).

Vinylbenzene (**1a**), 1-methyl-2-vinylbenzene (**1b**), 1-*tert*-butyl-4-vinylbenzene (**1d**), 1-chloro-4-vinylbenzene (**1e**), isopropenylbenzene (**1f**), *p*-toluenesulfonohydrazide (**2a**), 4-*iso*-propylbenzaldehyde, 4-chloroacetophenone, 4-bromoacetophenone, 4-nitroacetophenone, 4-methoxyacetophenone, 4-iodobenzenesulfonylchloride, 4-bromobenzenesulfonylchloride, 4-methoxybenzenesulfonylchloride, 4-nitrobenzenesulfonylchloride, methyltriphenylphosphonium bromide, t-BuOK, Na_2SO_4, tetra-butylammonium perchlorate, CuBr, CH_3CN, THF, $CHCl_3$, CH_2Cl_2, MeOH, petroleum ether (PE, 40/70), ethyl acetate (EA), hydrazine hydrate (64% w/w water solution of hydrazine) were purchased from commercial sources and were used as is. 1-*iso*-Propyl-4-vinylbenzene (**1c**), 1-chloro-4-isopropenylbenzene (**1g**), 1-bromo-4-isopropenylbenzene (**1h**), 1-nitro-4-isopropenylbenzene (**1i**), 1-methoxy-4-isopropenylbenzene (**1j**) were synthesized via Wittig reaction according to the literature[60]. 4-Iodobenzenesulfonohydrazide (**2b**), 4-bromobenzenesulfonohydrazide (**2c**), 4-methoxybenzenesulfonohydrazide (**2d**), 4-nitrobenzenesulfonohydrazide (**2e**) were synthesized according to the literature[61].

Cyclic voltammetry (CV) were implemented on an IPC-Pro computer-assisted potentiostat manufactured by Econix (scan rate error 1.0%, potential setting 0.25 mV). The experiments were performed in a 10-ml five-neck glass conic electrochemical cell with a water jacket for thermostatting. CV curves were recorded using a three-electrode scheme. The working electrode was a disc glassy-carbon electrode (d = 1.7 mm). A platinum wire served as an auxiliary electrode. A saturated calomel electrode was used as the reference electrode and was linked to the solution by a bridge with a porous ceramic diaphragm filled with background electrolyte. The tested solutions were thermostatted at 25±0.5 °C. In a typical case, 5 ml solution was utilized and the depolarizer concentration was 2 $mmol \cdot L^{-1}$. The working electrode was polished before recording each CV curve.

Synthesis of styrenes 1c, 1g-1j.

Following the literature procedure [60] to the solution of methyltriphenylphosphonium bromide (14.3-19.1 g, 39.9-53.4 mmol) in THF (50 ml) t-BuOK (4.8-6.5 g, 43.1-57.7 mmol) was added while vigorous stirring in Ar atmosphere for 10 minutes. The mixture was stirred for 1 hour at room temperature. Then, the corresponding carbonyl compound (4-*iso*-propylbenzaldehyde, 4-chloroacetophenone, 4-bromoacetophenone, 4-nitroacetophenone or 4-methoxyacetophenone, 3.0 g, 15.1-20.2 mmol) was added. The mixture was stirred for 24 hours at room temperature. After that it was diluted with CH_2Cl_2 (180 ml), washed with water (3×15 ml), and dried over Na_2SO_4. The solvent was removed under reduced pressure (10-20 torr). Styrenes **1c, 1g-1j** were isolated by chromatography on SiO_2 with elution using PE-EA in a linear gradient of the latter from 0 to 10 vol %.

1-Isopropyl-4-vinylbenzene (1c) [62]. 4-*iso*-Propylbenzaldehyde (3.0 g, 20.2 mmol) gave the title compound as a colourless oil (2.2 g, 15.2 mmol, 75%). ^{1}H NMR ($CDCl_3$), δ: 1.24 (d, *J* = 6.9 Hz, 6 H), 2.80-2.96 (m, 1 H), 5.17 (dd, *J* = 10.9, 1.1 Hz, 1 H), 5.69 (dd, *J* = 17.6, 1.1 Hz, 1 H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 23.9, 33.9, 112.8, 126.2, 126.6, 135.2, 136.7, 148.6.

1-Chloro-4-isopropenylbenzene (1g) [63]. 4-Chloroacetophenone (3.0 g, 19.4 mmol) gave the title compound as a colourless oil (2.3 g, 15.1 mmol, 78%). ^{1}H NMR ($CDCl_3$), δ: 2.13 (s, 3 H), 5.10 (s, 1 H), 5.36 (s, 1 H), 7.29 (d, *J* = 8.6 Hz, 2 H), 7.39 (d, *J* = 8.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.7, 112.9, 126.8, 128.3, 133.1, 139.6, 142.1.

1-Bromo-4-isopropenylbenzene (1h) [64]. 4-Bromoacetophenone (3.0 g, 15.1 mmol) gave the title compound as a colourless oil (2.1 g, 10.6 mmol, 70%). ^{1}H NMR ($CDCl_3$), δ: 2.13 (s, 3 H), 5.11 (s, 1 H), 5.36 (s, 1 H), 7.33 (d, *J* = 8.6 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.6, 113.0, 121.3, 127.1, 131.2, 140.1, 142.2.

1-Isopropenyl-4-nitrobenzene (1i) [65]. 4-Nitroacetophenone (3.0 g, 18.2 mmol) gave the title compound as a yellow oil (1.9 g, 11.8 mmol, 65%). ^{1}H NMR ($CDCl_3$), δ: 2.17 (s, 3 H), 5.28 (s, 1 H), 5.51 (s, 1 H), 7.57 (d, *J* = 8.9 Hz, 2 H), 8.15 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.5, 116.3, 123.5, 126.2, 141.5, 146.9, 147.6.

1-Isopropenyl-4-methoxybenzene (1j) [66]. 4-Methoxyacetophenone (3.0 g, 20.0 mmol) gave the title compound as white solid (2.4 g, 16.0 mmol, 80%). White solid, m.p. = 30.5-31.0°C (lit. [66] m.p. = 32.0-32.5°C). ^{1}H NMR ($CDCl_3$), δ: 2.15 (s, 3 H), 3.82 (s, 3 H), 5.01 (s, 1 H), 5.30 (s, 1 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.9, 55.2, 110.6, 113.5, 126.6, 133.7, 142.5, 159.1.

Synthesis of sulfonylhydrazides 2b-2e.

Following the literature procedure [61] the THF (20 ml) solution containing corresponding arylsulfonyl chloride (4-iodobenzenesulfonylchloride, 4-bromobenzenesulfonylchloride, 4-methoxybenzenesulfonylchloride, 4-nitrobenzenesulfonylchloride, 5.0 g, 16.5-24.2 mmol) was cooled in an ice-water bath to 5 °C. Hydrazine hydrate (64% w/w water solution of hydrazine, 2.1-3.0 g; 41.2-60.5 mmol) was slowly added while stirring. Then, the reaction mixture was stirred at 5 °C for 30 min, diluted with THF (20 ml), washed with water (3×5 ml), and dried over Na_2SO_4. The solvent was removed under reduced pressure (10-20 torr) to give pure products **2b-2e.**

4-Iodobenzenesulfonohydrazide (2b) [67]. 4-Iodobenzenesulfonylchloride (5.0 g, 16.5 mmol) gave the title compound as white solid (4.3 g, 14.5 mmol, 88%). White solid, m.p. = 173.0-175.0°C (lit.[67] m.p. = 162.0°C). ^{1}H NMR (DMSO-d_6), δ: 4.16 (br s, 2 H), 7.56 (d, *J* = 8.4 Hz, 2 H), 7.98 (d, *J* = 8.9 Hz, 2 H), 8.46 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 100.7, 129.4, 137.8, 137.9. Calculated for $C_6H_7IN_2O_2S$ C: 24.17 %, H: 2.37 %, I: 42.57 %, N: 9.40 %, S: 10.76 %. Found C: 24.23 %, H: 2.45 %, I: 42.18 %, N: 9.21 %, S: 10.57 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_6H_7IN_2NaO_2S]^+$: 320.9171. Found: 320.9167. IR (KBr), ν, cm^{-1}: 3366, 3291, 1571, 1321, 1158, 1085, 1007, 933, 814, 737, 642, 556.

4-Bromobenzenesulfonohydrazide (2c) [68]. 4-Bromobenzenesulfonylchloride (5.0 g, 19.6 mmol) gave the title compound as white solid (4.5 g, 18.0 mmol, 92%). White solid, m.p. = 114.0-116.0°C (lit.[68] m.p. = 113.0-114.0°C).^{1}H NMR (DMSO-d_6), δ: 4.20 (br

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s, 2 H), 7.73 (d, *J* = 8.6 Hz, 2 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 8.50 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 126.5, 129.7, 132.0, 137.5.

4-Methoxybenzenesulfonohydrazide (2d) [69]. 4-Methoxybenzenesulfonylchloride (5.0 g, 24.2 mmol) gave the title compound as white solid (4.6 g, 23.0 mmol, 95%). White solid, m.p. = 107.0-109.0°C (lit.[69] m.p. = 105.0-110.0°C). ^{1}H NMR (DMSO-d_6), δ: 3.83 (s, 3 H), 3.92 (br s, 1 H), 7.12 (d, *J* = 8.8 Hz, 2 H), 7.74 (d, *J* = 8.8, 2 H), 8.21 (s, 1 H). ^{13}C NMR (DMSO-d_6), δ: 55.7, 114.2, 129.5, 129.8, 162.4.

4-Nitrobenzenesulfonohydrazide (2e) [69]. 4-Nitrobenzenesulfonylchloride (5.0 g, 22.6 mmol) gave the title compound as yellow solid (3.7 g, 16.9 mmol, 75%). Yellow solid, m.p. = 150.0-152.0°C (lit.[69] m.p. = 152.0-157.0°C). ^{1}H NMR (DMSO-d_6): δ 4.34 (br s, 2 H), 8.05 (d, *J* = 8.9 Hz, 2 H), 8.42 (d, *J* = 8.9 Hz, 2 H), 8.75 (s, 1 H). ^{13}C NMR (DMSO-d_6): δ 124.2, 129.2, 144.2, 149.7.

General procedure 1. Preparation of 3aa and 4aa.Optimization of the reaction conditions for oxysulfonylation of styrene 1a with sulfonylhydrazide 2a (Table 1).

To the solution of styrene **1a** (300 mg, 2.88 mmol) in 25 ml (CH_3CN–H_2O (5:1), CH_3CN, THF, THF–H_2O (5:1)) Cu (I) salt (0.58-14.4 mmol, molar ratio 0.2-5 mol of salt / mol **1a**) and *p*-toluenesulfonylhydrazide **2a** (537 mg, 2.88 mmol, molar ratio 1 mol **2a** / mol **1a**) were added. The mixture was stirred in the air, in oxygen atmosphere for 7 h at 40°C, for 7 h at 80°C, then for 12 hours at room temperature.

Treatment of the reaction mixture containing 3aa and 4aa.

After that the solvent was removed under reduced pressure (10-20 torr). The reaction residue was diluted with a mixture of solvents PE/$CHCl_3$/EA in volume ratio 1/2/2 (50 mL) and then filtered from the precipitate using SiO_2 (d=20 mm, h=80mm). The precipitate was washed with a mixture of solvents PE/$CHCl_3$/EA in volume ratio 1/2/2 (3×30 mL). The combined organic phases were concentrated under reduced pressure (10-20 torr). The yields of **3aa** and **4aa** were determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard.

General procedure 2. Synthesis of β-hydroxysulfones 3aa-3ab and β-ketosulfones 4aa-4ab (Table 2). To the solution of styrene **1a-1e** (300 mg, 1.87-2.88 mmol) in 25 ml CH_3CN–H_2O (5:1) CuBr (3.74-5.76 mmol, molar ratio 2 mol / mol **1a-1e**) and sulfonylhydrazide **2a-2b** (1.87-2.88 mmol, molar ratio 1 mol **2** / mol **1a-1e**) were added. The mixture was stirred in oxygen atmosphere for 7 h at 40°C, then for 12 hours at room temperature. After that the reaction mixture was treated as described above (General procedure 1). The yields of **3aa, 3ba, 3ca, 3da, 3ea, 3ab** and **4aa, 4ba, 4ca, 4da, 4ea, 4ab** were determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard. The products **3aa, 3ba, 3ca, 3da, 3ea, 3ab** and **4aa, 4ba, 4ca, 4da, 4ea, 4ab** were isolated by chromatography on SiO_2 with elution using PE-EA in a linear gradient of the latter from 10 to 40 vol %.

General procedure 3. Synthesis of β-hydroxysulfones 3aa-3ab using $NaBH_4$ (Table 2, yield in parentheses). After the reaction the mixture was treated as described above (General procedure 1). Afterwards the residue was diluted with 10 ml of THF-MeOH (1:1) mixture, and $NaBH_4$ (molar ratio 3 mol / mol **4aa, 4ba, 4ca, 4da, 4ea, 4ab**) was added while vigorous stirring. The mixture was stirred for 3 h at 0-5°C. The solvent was removed under reduced pressure (10-20 torr). The residue was diluted with EA (50 ml) and washed with water (2×5 ml), brine (3×5 ml) and again water (2×5 ml), dried over Na_2SO_4 and concentrated under reduced pressure (10-20 torr). The desired products **3aa, 3ba, 3ca, 3da, 3ea, 3ab** were isolated by chromatography on SiO_2 with elution using PE-EA in a linear gradient of the latter from 10 to 40 vol %.

2-[(4-Methylphenyl)sulfonyl]-1-phenylethanol (3aa) [70]. White solid, m.p. = 68.5-70.0 °C. (lit.[70] m.p. = 68.5−69.5 °C). Yield 85%. R_f= 0.26 (TLC, PE:EA, 5:1). ^{1}H NMR ($CDCl_3$), δ: 2.45 (s, 3 H, CH_3), 3.31 (dd, *J* = 14.3, 1.8 Hz, 1 H), 3.47 (dd, *J* = 10.0, 14.3 Hz, 1 H), 3.76 (d, *J* =2.0 Hz, 1 H), 5.23 (ddd, *J* = 10.3, 2.0, 1.8 Hz, 1H), 7.23-7.32 (m, 5H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.82 (d, *J* = 8.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.6, 63.9, 68.4, 125.6, 127.9, 128.2, 128.6, 130.0, 136.1, 140.7, 145.1. Calculated for $C_{15}H_{16}O_3S$ C: 65.19 %, H: 5.84 %, S: 11.60 %. Found C: 65.12 %, H: 5.78 %, S: 11.66 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{15}H_{16}NaO_3S]^+$: 299.0718. Found: 299.0712. IR (KBr), ν, cm^{-1}: 3496, 1391, 1286, 1167, 1137, 1087, 1064, 1020, 998, 834, 818, 779, 747, 706, 640, 555, 537, 514, 500, 462.

1-(2-Methylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanol (3ba) [70]. White solid, m.p. = 118.0-120.0 °C (lit.[70] m.p. = 116.1−118.0 °C). Yield 54%. R_f= 0.34 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 2.08 (s, 3 H), 2.46 (s, 3 H), 3.22 (dd, *J* = 14.5, 1.3 Hz, 1 H), 3.39 (dd, *J* = 14.5, 9.8 Hz, 1 H), 3.69 (s, 1 H), 5.42 (d, *J* = 9.8 Hz, 1 H), 7.07 (dd, *J* = 7.2, 2.0 Hz, 1 H), 7,11 -7.24 (m, 2 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.48 (dd, *J* = 7.2, 1.7 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 18.5, 21.6, 62.9, 65.0, 125.2, 126.5, 127.9, 128.0, 130.0, 130.5, 133.6, 136.0, 138.7, 145.2. Calculated for $C_{16}H_{18}O_3S$ C: 66.18 %, H: 6.25 %, S: 11.04 %. Found C: 66.15 %, H: 6.21 %, S: 10.89 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{16}H_{18}NaO_3S]^+$: 313.0874. Found: 313.0869. IR (KBr), ν, cm^{-1}: 3517, 1299, 1287, 1247, 1236, 1199, 1189, 1170, 1158, 1142, 1086, 1047, 857, 803, 758, 749, 721, 638, 564, 518, 506, 456.

1-(4-Isopropylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanol (3ca). White solid, m.p. = 92.5-95.0 °C. Yield 72%. R_f= 0.39 (TLC, PE:EA, 3:1). ^{1}H NMR (DMSO-d_6), δ: 1.16 (d, *J* = 6.9 Hz, 6 H), 2.39 (s, 3 H), 2.83 (m, *J* = 6.9 Hz, 1 H), 3.50 (dd, *J* = 14.5, 3.7 Hz, 1 H), 3.67 (dd, *J* = 14.5, 8.5 Hz, 1 H), 4.96 (ddd, *J* = 8.5, 4.7, 3.7 Hz, 1 H), 5.52 (d, *J* = 4.7 Hz, 1 H), 7.13 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 21.0, 23.9, 33.1, 63.0, 67.8, 126.0, 126.1, 127.8, 129.4, 137.6, 140.5, 143.7, 147.6. Calculated for $C_{18}H_{22}O_3S$ C: 67.89 %, H: 6.96 %, S: 10.07 %. Found C: 67.87 %, H: 7.01 %, S: 10.14 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{18}H_{22}NaO_3S]^+$: 341.1187. Found: 341.1178. IR (KBr), ν, cm^{-1}: 3500, 2966, 1410, 1302, 1287, 1253, 1170, 1140, 1086, 1052, 1001, 862, 851, 822, 776, 734, 635, 597, 568, 547, 532, 509, 471, 449.

1-(4-*tert*-Butylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanol (3da). White solid, m.p. = 106.0-107.0 °C. Yield 89%. R_f= 0.40 (TLC, PE:EA, 3:1). ^{1}H NMR (DMSO-d_6), δ: 1.24 (s, 9 H), 2.39 (s, 3 H), 3.50 (dd, *J* = 14.6, 3.8 Hz, 1 H), 1H), 3.67 (dd, *J* = 14.6, 8.5 Hz, 1 H), 4.96 (ddd, *J* = 8.5, 4.7, 3.8 Hz, 1 H), 5.52 (d, *J* = 4.7 Hz, 1 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.1 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 21.0, 31.1, 34.1, 62.9, 67.7, 124.8,

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125.8, 127.7, 129.4, 137.6, 140.0, 143.6, 149.8. Calculated for $C_{19}H_{24}O_3S$ C: 68.64 %, H: 7.28 %, S: 9.64 %. Found C: 68.57 %, H: 6.94 %, S: 9.51 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{19}H_{24}NaO_3S]^+$: 313.0874. Found: 313.0869. IR (KBr), ν, cm^{-1}: 3521, 2962, 1303, 1289, 1242, 1174, 1140, 1113, 1087, 1057, 864, 844, 823, 773, 737, 636, 579, 543, 528, 506.

1-(4-Chlorophenyl)-2-[(4-methylphenyl)sulfonyl]ethanol (3ea) [70]. White solid, m.p. = 89.5-92.5 °C (lit. [70] m.p. = 88.0–91.0 °C). Yield 52%. R_f= 0.28 (TLC, PE:EA, 3:1). ^{1}H NMR (DMSO-d_6), δ: 2.40 (s, 3 H), 3.55 (dd, *J* = 14.6, 4.0 Hz, 1 H), 3.67 (dd, *J* = 14.6, 8.2 Hz, 1 H), 4.97 (ddd, *J* = 8.2, 5.0, 4.0 Hz, 1 H), 5.70 (d, *J* = 5.0 Hz, 1 H), 7.32 (s, 4H), 7.39 (d, *J* = 8.1 Hz, 1 H), 7.75 (d, *J* = 8.1 Hz, 1 H). ^{13}C NMR (DMSO-d_6), δ: 21.0, 62.6, 67.3, 127.8, 128.0, 128.1, 129.4, 131.9, 137.5, 141.9, 143.8. Calculated for $C_{15}H_{15}ClO_3S$ C: 57.97 %, H: 4.86 %, Cl: 11.41 %, S: 10.32 %. Found C: 57.95 %, H: 4.93 %, Cl: 11.34 %, S:10.25 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for: $[C_{15}H_{15}ClNaO_3S]^+$: 333.0328. Found: 333.0323. IR (KBr), ν, cm^{-1}: 3485, 1311, 1300, 1287, 1160, 1145, 1138, 1087, 1076, 1064, 1013, 813, 714, 562, 511, 502.

2-[(4-Iodophenyl)sulfonyl]-1-phenylethanol (3ab). White solid, m.p. = 108.0-112.0 °C. Yield 62%. R_f= 0.32 (TLC, PE:EA, 5:1). ^{1}H NMR (DMSO-d_6), δ: 3.55 (dd, *J* = 14.6, 3.3 Hz, 1 H), 3.76 (dd, *J* = 14.6, 9.2 Hz, 1 H), 5.00 (ddd, *J* = 9.2, 4.8, 3.3 Hz, 1 H), 5.62 (d, *J* = 4.8 Hz, 1 H), 7.19-7.34 (m, 5 H), 7.65 (d, *J* = 8.4 Hz, 2 H), 7.99 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 62.6, 67.9, 101.9, 126.1, 127.4, 128.2, 129.5, 137.8, 140.3, 142.9. Calculated for $C_{14}H_{13}IO_3S$ C: 43.31 %, H: 3.38 %, I: 32.69 %, S: 8.26 %. Found C: 43.28 %, H: 3.31 %, I: 32.32 %, S: 8.09 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{14}H_{13}INaO_3S]^+$: 410.9528. Found: 410.9522. IR (KBr), ν, cm^{-1}: 3464, 1384, 1303, 1270, 1135, 1083, 1061, 1003, 993, 817, 745, 701, 566, 549, 531.

2-[(4-Methylphenyl)sulfonyl]-1-phenylethanone (4aa) [71]. White solid, m.p. = 102.5-104.5 °C (lit. [71] m.p. = 102.0–103.0 °C). Yield 36%. R_f= 0.73 (TLC, PE:EA, 2:1). ^{1}H NMR ($CDCl_3$), δ: 2.43 (s, 3 H), 4.73 (s, 2 H), 7.32 (d, *J* = 8.2 Hz, 2 H), 7.46 (dd, *J* = 7.5, 7.3 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.77 (d, *J* = 8.2 Hz, 2 H), 7.94 (d, *J* = 7.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.6, 63.5, 128.5, 128.7, 129.2, 129.7, 134.2, 135.7, 135.8, 145.2, 188.1. Calculated for $C_{15}H_{14}O_3S$ C: 65.67 %, H: 5.14 %, S: 11.69 %. Found C: 65.57 %, H: 5.34 %, S: 11.59 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{15}H_{14}NaO_3S]^+$: 297.0561. Found: 297.0556. IR (KBr), ν, cm^{-1}: 1680, 1596, 1320, 1271, 1150, 1087, 993, 750, 739, 686, 590, 535, 503.

1-(2-Methylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanone (4ba) [72]. White solid, m.p. = 108-110 °C (lit. [72] m.p. = 109-111 °C). Yield 18%. R_f= 0.37 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 2.45 (s, 6 H), 4.70 (s, 2 H), 7.23-7.31 (m, 2 H), 7.31-7.36 (m, 2 H), 7.39-7.46 (m, 1 H), 7.71-7.79 (m, 3 H). ^{13}C NMR ($CDCl_3$), δ: 21.4, 21.6, 65.5, 125.8, 128.4, 129.7, 130.3, 132.2, 132.7, 135.7, 136.0, 139.9, 145.1, 190.5. Calculated for $C_{16}H_{16}O_3S$ C: 66.64 %, H: 5.59 %, S: 11.12 %. Found C: 66.38 %, H: 5.80 %, S: 11.29 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{16}H_{16}NaO_3S]^+$: 311.0718. Found: 311.0714. IR (KBr), ν, cm^{-1}: 2956, 2910, 1685, 1314, 1291, 1142, 1084, 978, 823, 761, 747, 556, 517.

1-(4-Isopropylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanone (4ca). White solid, m.p. = 127.0-129.5 °C. Yield 23%. R_f= 0.43 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 1.26 (d, *J* = 7.0 Hz, 6 H), 2.43 (s, 3 H), 2.97 (m, *J* = 7.0 Hz, 1 H), 4.69 (s, 2 H), 7.32 (2d, *J* = 8.2, 8.4 Hz, 4 H), 7.76 (d, *J* = 8.2 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.6, 23.5, 34.3, 63.5, 126.9, 128.6, 129.6, 129.7, 133.7, 135.8, 145.2, 156.1, 187.6. Calculated for $C_{18}H_{20}O_3S$ C: 68.33 %, H: 6.37 %, S: 10.13 %. Found C: 67.86 %, H: 6.82 %, S: 9.70 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{18}H_{20}NaO_3S]^+$: 339.1031. Found: 339.1025. IR (KBr), ν, cm^{-1}: 2953, 1686, 1311, 1290, 1183, 1142, 1084, 828, 549.

1-(4-*tert*-Butylphenyl)-2-[(4-methylphenyl)sulfonyl]ethanone (4da). White solid, m.p. = 98.5-101.0 °C. Yield 31%. R_f= 0.49 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 1.34 (s, 9 H), 2.44 (s, 3 H), 4.69 (s, 2 H), 7.32 (d, *J* = 7.9 Hz, 2 H), 7.48 (d, *J* = 8.2 Hz, 2 H), 7.76 (d, *J* = 7.9 Hz, 2 H), 7.88 (d, *J* = 8.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.7, 31.0, 35.2, 63.6, 125.8, 128.6, 129.3, 129.8, 133.3, 135.9, 145.2, 158.3, 187.6. Calculated for $C_{19}H_{22}O_3S$ C: 69.06 %, H: 6.71 %, S: 9.70 %. Found C: 69.01 %, H: 6.65 %, S: 9.59 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{19}H_{22}NaO_3S]^+$: 353.1187. Found: 353.1182. IR (KBr), ν, cm^{-1}: 1681, 1314, 1290, 1141, 1083, 828, 768, 590, 549, 516.

1-(4-Chlorophenyl)-2-[(4-methylphenyl)sulfonyl]ethanone (4ea) [71]. White solid, m.p. = 128.0-130.5 °C (lit. [71] m.p. = 137.0–138.0 °C). Yield 24%. R_f= 0.46 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 2.45 (s, 3 H), 4.68 (s, 2 H), 7.34 (d, *J* = 8.2 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.90 (d, *J* = 8.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.7, 63.7, 128.5, 129.2, 129.9, 130.7, 134.1, 135.6, 141.0, 145.5, 187.0. Calculated for $C_{15}H_{13}ClO_3S$ C: 58.35 %, H: 4.24 %, Cl: 11.48 %, S: 10.38 %. Found C: 58.37 %, H: 4.31 %, Cl: 10.98 %, S: 9.93 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{15}H_{13}ClNaO_3S]^+$: 331.0172. Found: 331.0166. IR (KBr), ν, cm^{-1}: 1679, 1589, 1315, 1290, 1277, 1148, 1091, 1083, 1004, 784, 759, 724, 537, 507.

2-[(4-Iodophenyl)sulfonyl]-1-phenylethanone (4ab). White solid, m.p. = 125.0-127.0 °C. Yield 25%. R_f= 0.38 (TLC, PE:EA, 5:1). ^{1}H NMR ($CDCl_3$), δ: 4.73 (s, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.56-7.68 (m, 3H), 7.87-7.95 (m, 4H). ^{13}C NMR ($CDCl_3$), δ: 63.2, 102.5, 128.9, 129.2, 129.9, 134.5, 135.5, 138.3, 138.4, 187.8. Calculated for $C_{14}H_{11}IO_3S$ C: 43.54 %, H: 2.87 %, I: 32.86 %, S: 8.30 %. Found C: 43.58 %, H: 3.01 %, I: 32.65 %, S: 8.25 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for $[C_{14}H_{11}INaO_3S]^+$: 408.9371. Found: 408.9366. IR (KBr), ν, cm^{-1}: 1677, 1563, 1379, 1314, 1273, 1151, 1002, 756, 741, 727, 565, 516.

General procedure 4. Synthesis of β-hydroxysulfones 3fa-3fe (Table 3). To the solution of styrene **1f-1j** (300 mg, 1.52-2.54 mmol) in 25 ml CH_3CN–H_2O (5:1) CuBr (3.04-5.08 mmol, molar ratio 2 mol / mol **1f**-**1j**) and sulfonylhydrazide **2a-2e** (1.52-2.54 mmol, molar ratio 1 mol **2** / mol **1f-1j**) were added. The mixture was stirred in oxygen atmosphere for 7 h at 40°C, then for 12 hours at room temperature. After that the reaction mixture was treated as described above (General procedure 1). The desired products **3fa, 3ga, 3ha, 3ia, 3ja, 3fc, 3fd, 3fe** were isolated by chromatography on SiO_2 with elution using PE-EA in a linear gradient of the latter from 10 to 40 vol %.

1-[(4-Methylphenyl)sulfonyl]-2-phenylpropan-2-ol (3fa) [73] . White solid, m.p. = 99.5-100.5 °C (lit.[73] m.p. = 103–104 °C). Yield 92%. R_f= 0.64 (TLC, PE:EA, 2:1). ^{1}H NMR ($CDCl_3$), δ: 1.71 (d, *J* = 1.1 Hz, 3 H), 2.39 (s, 3 H), 3.61 (dd, *J* = 14.6, 1.1 Hz, 1 H), 3.72 (d, *J* = 14.6, 1.1 Hz, 1 H), 4.66 (br s, 1 H), 7.14-7.24 (m, 5 H), 7.26-7.34 (m, 2 H), 7.49 (dd, *J* = 8.2, 1.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.5, 30.7, 66.6, 73.0, 124.5, 127.0, 127.4, 128.1, 129.6, 137.3, 144.4. Calculated for $C_{16}H_{18}O_3S$ C: 66.18 %, H: 6.25 %, S: 11.04 %. Found C: 66.23 %, H: 6.06 %, S: 11.12 %. HRMS (ESI) m/z $[M+Na]^+$: Calculated for

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$[C_{16}H_{18}NaO_3S]^+$: 313.0874. Found: 313.0879. IR (KBr), ν, cm^{-1}: 3500, 2973, 1451, 1355, 1300, 1268, 1247, 1182, 1155, 1119, 1081, 1036, 1024, 1017, 947, 858, 813, 767, 707, 637, 570, 555, 532, 509, 477.

2-(4-Chlorophenyl)-1-[(4-methylphenyl)sulfonyl]propan-2-ol (3ga). White solid, m.p. = 142-144 °C. Yield 90%. R_f= 0.68 (TLC, PE:EA, 2:1). ^{1}H NMR ($CDCl_3$), δ: 1.62 (s, 3 H), 2.39 (s, 3 H), 3.55 (d, *J* = 14.8 Hz, 1 H), 3.69 (d, *J* = 14.8 Hz, 1H,), 7.07 (d, *J* = 8.7 Hz, 2 H) 7.15 (d, *J* = 8.7 Hz, 2 H) 7.15 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.5, 30.9, 66.3, 72.7, 126.2, 127.5, 128.2, 129.7, 133.1, 137.0, 142.8, 144.7. Calculated for $C_{16}H_{17}ClO_3S$ C: 59.16 %, H: 5.28 %, Cl: 10.91 %, S: 9.87 %. Found C: 58.99 %, H: 5.29 %, Cl: 11.04 %, S: 9.98 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{16}H_{17}ClNaO_3S]^+$: 347.0485. Found: 347.0479.IR (KBr), ν, cm^{-1}: 3496, 1308, 1302, 1252, 1158, 1128, 1082, 1044, 849, 771, 645, 543, 522, 460.

2-(4-Bromophenyl)-1-[(4-methylphenyl)sulfonyl]propan-2-ol (3ha) [16]. Light-brown solid, m.p. = 160.5-163 °C (lit. [16] m.p. = 164.0-166.0 °C). Yield 93%. R_f= 0.29 (TLC, PE:EA, 3:1).^{1}H NMR (DMSO-d_6), δ: 1.55 (s, 3 H), 2.37 (s, 3 H), 3.77 (d, *J* = 14.8 Hz, 1 H), 3.84 (d, *J* = 14.8 Hz, 1 H), 7.24-7.35 (m, 6 H), 7.52 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 21.0, 30.0, 66.0, 71.5, 119.8, 127.5, 127.6, 129.2, 130.3, 138.2, 143.4, 145.4. Calculated for $C_{16}H_{17}BrO_3S$ C: 52.04 %, H: 4.64 %, Br: 21.64 %, S: 8.68 %. Found C: 52.14 %, H: 4.73 %, Br: 21.12 %, S: 8.47 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{16}H_{17}BrNaO_3S]^+$: 390.9979. Found: 390.9974. IR (KBr), ν, cm^{-1}: 3489, 1251, 1158, 1127, 1081, 771, 639, 585, 540, 522, 486.

1-[(4-Methylphenyl)sulfonyl]-2-(4-nitrophenyl)propan-2-ol (3ia) [16]. White solid, m.p. = 137.5-138.5 °C (lit. [16] m.p.= 140.0-142.0 °C). Yield 89%. R_f= 0.40 (TLC, PE:EA, 2:1). ^{1}H NMR (DMSO-d_6), δ: 1.57 (s, 3 H), 2.33 (s, 3 H), 3.84 (d, *J* = 14.8 Hz, 1 H), 4.01 (d, *J* = 14.8 Hz, 1 H), 5.71 (s, 1 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 7.51 (d, *J* = 8.0 Hz, 2 H), 7.64 (d, *J* = 8.9 Hz, 2 H), 8.02 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 21.0, 30.5, 65.7, 71.8, 122.6, 126.7, 127.7, 129.2, 138.1, 143.6, 146.1, 153.7. Calculated for $C_{16}H_{17}NO_5S$ C: 57.30 %, H: 5.11 %, N: 4.18%, S: 9.56 %. Found C: 57.28 %, H: 5.08 %, N: 4.16%, S: 9.48 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{16}H_{17}NNaO_5S]^+$: 358.0725. Found: 358.0713. IR (KBr), ν, cm^{-1}: 3480, 1520, 1349, 1310, 1301, 1291, 1268, 1147, 1121, 1084, 855, 815, 757, 537, 518.

1-[(4-Methylphenyl)sulfonyl]-2-(4-methoxyphenyl)propan-2-ol (3ja) [16]. White solid, m.p. = 90-93 °C (lit. [16] m.p. = 94.5-95.5 °C). Yield 90%. R_f= 0.25 (TLC, PE:EA, 3:1). ^{1}H NMR ($CDCl_3$), δ: 1.66 (s, 3 H), 2.37 (s, 3 H), 3.54 (d, *J* = 14.5 Hz, 1 H), 3.67 (d, *J* = 14.5 Hz 1 H), 3.74 (s, 3 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 7.16 (d, *J* = 8.3 Hz, 2 H), 7.17 (d, *J* = 8.8 Hz, 2 H), 7.47 (d, *J* = 8.3 Hz, 2 H). ^{13}C NMR ($CDCl_3$), δ: 21.5, 30.7, 55.2, 66.8, 72.8, 113.5, 125.8, 127.5, 129.6, 136.6, 137.4, 144.3, 158.7. Calculated for $C_{17}H_{20}O_4S$ C: 63.73 %, H: 6.29 %, S: 10.01 %. Found C: 63.88 %, H: 6.29 %, S: 10.01 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{17}H_{20}NaO_4S]^+$: 343.0980. Found: 343.0975. IR (KBr), ν, cm^{-1}: 3472, 1607, 1598, 1514, 1309, 1292, 1251, 1183, 1146, 1120, 1083, 1032, 832, 823, 810, 766, 676, 557, 536, 513.

1-[(4-Bromophenyl)sulfonyl]-2-phenylpropan-2-ol (3fc) [16]. Yellow solid, m.p. = 153-156 °C (lit. [16] m.p. = 153.0-153.5 °C). Yield 52%. R_f= 0.40 (TLC, PE:EA, 3:1). ^{1}H NMR (DMSO-d_6), δ: 1.60 (s, 3 H), 3.86 (s, 2 H), 4.75 (br s, 1 H), 7.11-7.23 (m, 3 H), 7.33-7.39 (m, 2 H), 7.62 (d, *J* = 8.6 Hz, 2 H), 7.70 (d, *J* = 8.6 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 29.9, 66.1, 71.7, 125.0, 126.4, 127.1, 127.6, 129.8, 131.7, 140.6, 146.5. Calculated for $C_{15}H_{15}BrO_3S$ C: 50.71 %, H: 4.26 %, Br: 22.49 %, S: 9.03 %. Found C: 50.78 %, H: 4.31 %, Br: 22.48 %, S: 9.02 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{15}H_{15}BrNaO_3S]^+$: 376.9823. Found: 376.9821. IR (KBr), ν, cm^{-1}: 3507, 1576, 1392, 1312, 1295, 1270, 1149, 1122, 1084, 1067, 1010, 942, 821, 775, 765, 714, 701, 579, 545, 528, 411.

1-[(4-Methoxyphenyl)sulfonyl]-2-phenylpropan-2-ol (3fd) [16]. White solid, m.p. = 87.5-89 °C (lit. [16] m.p. = 90.5-92.5 °C). Yield 85%. R_f= 0.45 (TLC, PE:EA, 2:1). ^{1}H NMR ($CDCl_3$), δ: 1.68 (s, 3 H), 3.58 (d, *J* = 14.7 Hz, 1 H), 3.70 (d, *J* = 14.7 Hz, 1H), 3.82 (s, 3 H), 6.81 (d, *J* = 8.9 Hz, 2 H), 7.11-7.24 (m, 3 H), 7.25-7.31 (m, 2 H), 7.50 (d, *J* = 8.9 Hz, 2H). ^{13}C NMR ($CDCl_3$), δ: 30.8, 55.6, 66.7, 73.0, 114.2, 124.6, 127.1, 128.2, 129.7, 131.8, 144.5, 163.5. Calculated for$C_{16}H_{18}O_4S$ C: 62.72 %, H: 5.92 %, S: 10.47 %. Found C: 62.81 %, H: 5.95 %, S: 10.46 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{16}H_{18}NaO_4S]^+$: 329.0824. Found: 329.0813. IR (KBr), ν, cm^{-1}: 3501, 1594, 1497, 1307, 1295, 1261, 1249, 1151, 1117, 1079, 1026, 830, 758, 697, 570, 529, 480, 468.

1-[(4-Nitrophenyl)sulfonyl]-2-phenylpropan-2-ol (3fe) [16]. White solid, m.p. = 177.5-179.5 °C (lit. [16] m.p. = 187-190 °C). Yield 36%. R_f= 0.25 (TLC, PE:EA, 3:1). ^{1}H NMR (DMSO-d_6), δ: 1.61 (s, 3 H), 3.93-4.05 (m, 2 H), 5.44 (s, 1 H), 7.08-7.23 (m, 3 H), 7.31-7.39 (m, 2 H), 7.96 (d, *J* = 8.7 Hz, 2 H), 8.29 (d, *J* = 8.7 Hz, 2 H). ^{13}C NMR (DMSO-d_6), δ: 29.9, 65.8, 71.6, 123.7, 124.9, 126.4, 127.5, 129.4, 146.3, 146.6, 149.7. Calculated for $C_{15}H_{15}NO_5S$ C: 56.06 %, H: 4.70 %, N: 4.36%, S: 9.98 %. Found C: 56.04 %, H: 4.85 %, N: 4.21%, S: 9.96 %. HRMS (ESI) m/z [M+Na]$^+$: Calculated for $[C_{15}H_{15}NNaO_5S]^+$: 344.0569. Found: 344.0563. IR (KBr), ν, cm^{-1}: 3492, 1525, 1350, 1305, 1148, 1121, 1083, 849, 771, 742, 579, 525.

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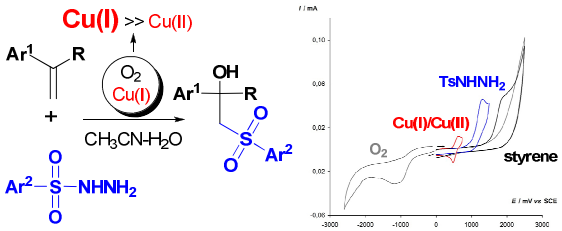

Oxidation potentials: **styrene** > **$TsNHNH_2$** > **Cu(I)**