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Copper(I)-mediated synthesis of β-hydroxysulfones from styrenes and sulfonylhydrazides: an electrochemical mechanistic study†

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Copper(I) halides were used as mediators in the synthesis of β-hydroxysulfones *via* the oxysulfonylation of styrenes using sulfonylhydrazides. The feature of the developed process lies in the combination of a copper(I) salt with oxygen—the stoichiometric oxidant. Copper(II) species are responsible for the oxidation of sulfonylhydrazides, they are generated in small amounts in the O_2/Cu(I)/Cu(II) redox system, which is formed during the reaction. The combination of these three components enables one 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 by-products. With good yields β-hydroxysulfones were prepared by reduction of the reaction mixture containing both products β-hydroxysulfones and β-ketosulfones with $NaBH_4$. An electrochemical study revealed that the Cu(I)/Cu(II) pair can serve as an 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 the nucleophilic addition of sulfinates to epoxides,[5–8] reduction of β-ketosulfones[9,10] and hydroxylation of α,β-unsaturated sulfones.[11] Over the last few years, several oxidative strategies to prepare β-hydroxysulfones from olefins have been established. In these reports air and low thermally stable sulfinic acids[12–14] in combination with O_2 and PPh_3 (Scheme 1, eqn (1))[15] or sulfonylhydrazides with O_2 and Fe(III) salts are required.

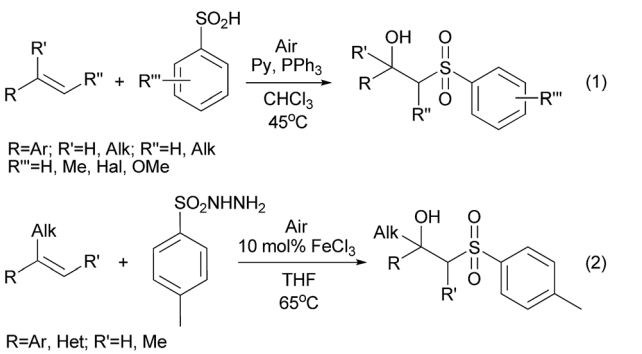
The latter method was applied for the synthesis of structures containing the β-hydroxysulfone moiety predominantly at a tertiary carbon atom, which cannot be further oxidized (Scheme 1, eqn (2)).[16]

For the sulfonylation of unsaturated compounds without additional insertion of oxygen into the molecule, a number of oxidants have been 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 environmentally friendly oxidant, which offers fascinating industrial and academic prospects. In oxidative transformations, in most cases, it is used in combination with transition metals salts and complexes.[26–29]

In this context, we have disclosed a process for the oxysulfonylation of styrenes utilizing sulfonylhydrazides in the presence of a 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) as confirmed by the near absence of the specific colour of Cu(II) species. As a result, β-hydroxysulfones **3** as main products and β-ketosulfones **4** as by-products 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



Scheme 1 Recent works for the oxysulfonylation of styrenes.

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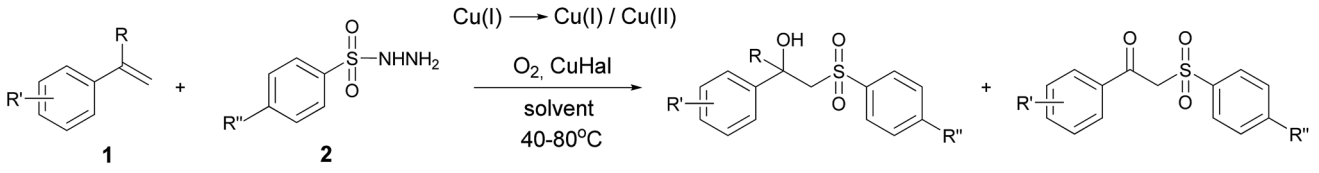


1a: R = H, R' = H; **1b**: R = H, R' = *o*-Me;
1c: R = H, R' = *p*-^{i}Pr; **1d**: R = H, R' = *p*-^{t}Bu;
1e: R = H, R' = *p*-Cl; **1f**: R = Me, R' = H;
1g: R = Me, R' = *p*-Cl; **1h**: R = Me, R' = *p*-Br;
1i: R =Me, R' = *p*-NO_2; **1j**: R = Me, R = *p*-OMe

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

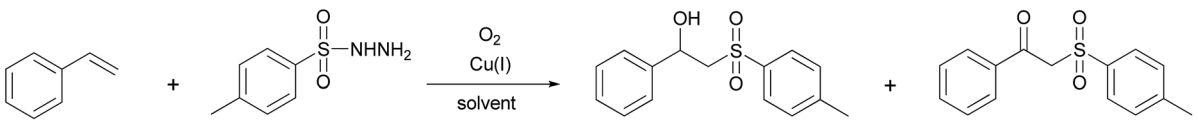
Scheme 2 The oxysulfonylation of styrenes **1a–1j** using sulfonylhydrazides **2a–2e** (in the codification of **3** and **4** the first letter index refers to the styrene 1 moiety, the second letter index to the hydrazide 2 moiety).

2a–2e was conducted in CH_3CN, CH_3CN–H_2O, THF and THF–H_2O using a O_2/Cu(I)/Cu(II) redox system. This system was a result of the transformation of CuCl, CuBr and CuI under aerobic conditions (Scheme 2).

Our preliminary studies were focused on the reaction of styrene **1a** with sulfonylhydrazide **2a**, leading to the formation of 1-phenyl-2-tosylethanol **3aa** and 1-phenyl-2-tosylethanone **4aa**. We examined the influence of the Cu(I) salt counter-ion, oxygen source (air oxygen or 98% oxygen) and solvent type (Table 1) on the yield of **3aa**.

Entries 1–3 indicated that among the copper(I) halides (CuBr, CuCl and CuI), the use of CuBr afforded the highest total yield of oxysulfonylation products and the yield of the desired product **3aa** after 7 h. When the reaction was performed for a more prolonged time (entry 4) the yield of **3aa** reached 38%. Heating the reaction mixture for the first 7 h to 80 °C (entry 5) didn't increase the yield of **3aa**. Decreasing (entry 6) or increasing (entry 7) the molar ratio of CuBr per mol of **1a** in comparison with the previous entries resulted in a reduced yield of the desired product. Employing CH_3CN, THF or THF–H_2O (5 : 1) in place of CH_3CN–H_2O (5 : 1) negatively influenced the reaction efficiency (entries 8–10). In entry 11, air oxygen was replaced with 98% oxygen and as a result the yield of **3aa** was improved to 55%, the total yield of oxysulfonylation products in this case reached 91%. Attempts failed (entries 12–14) to increase the yield of desired product through modification of

Table 1 Screening of the reaction conditions[a]



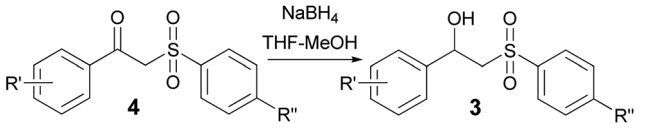
Entry	Time (h)	Ratio (mole Cu(I)/mole **1a**)	Oxygen source	Solvent	Yield **3aa**[b] (%)	Yield **4aa**[b] (%)	Total yield **3aa** and **4aa**[b] (%)
1	7	CuBr (2)	Air	CH_3CN–H_2O	28	14	42
2	7	CuCl (2)	Air	CH_3CN–H_2O	25	15	40
3	7	CuI (2)	Air	CH_3CN–H_2O	17	10	27
4[c]	7 + 12	CuBr (2)	Air	CH_3CN–H_2O	38 (61)	27	65
5[d]	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[d]	7 + 12	CuBr (2)	O_2	CH_3CN–H_2O	50 (77)	30	80

[a] General procedure: to a solution of styrene **1a** (300 mg, 2.88 mmol) in 25 mL of (CH_3CN–H_2O (5 : 1), CH_3CN, THF, THF–H_2O (5 : 1)), the 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. [b] The yield was determined by ^{1}H NMR using 1,4-dinitrobenzene as an internal standard, the isolated yield after reduction with $NaBH_4$ is reported in the parentheses. [c] 7 h at 40 °C, then 12 h at 20–25 °C. [d] 7 h at 80 °C, then 12 h at 20–25 °C.

the molar ratio of CuBr per mol of **1a**, temperature and reaction time when compared to the conditions of entry 11, in which the best result was obtained; the total yield of **3aa** and **4aa** in these experiments didn't exceed 80%.

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

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

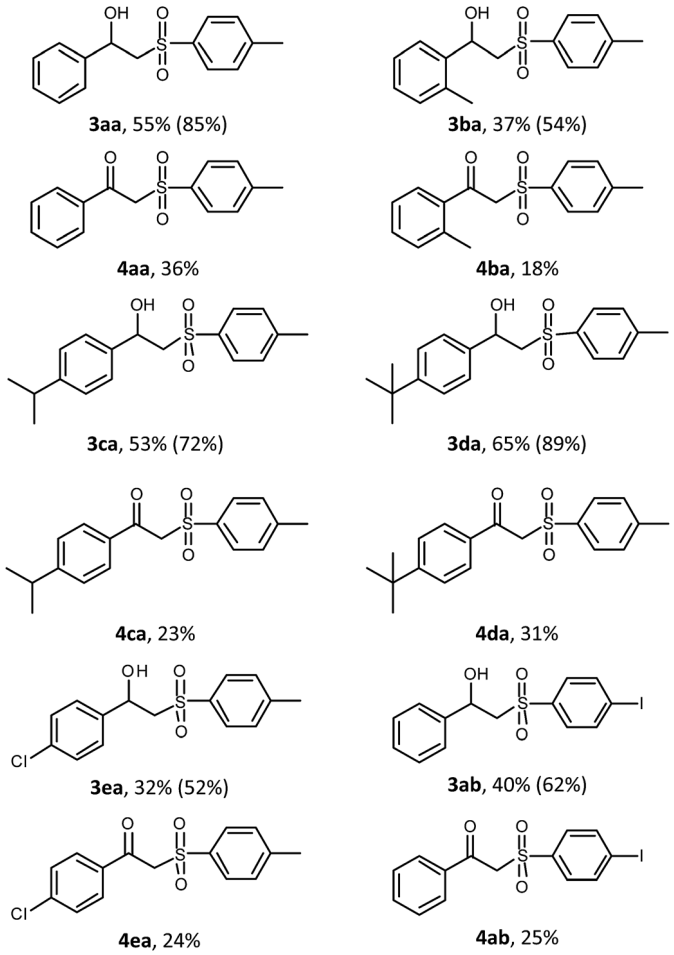


Scheme 3 The reduction of β-ketosulfones using $NaBH_4$.

The 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 the conditions of entry 11 (Table 1) and the target β-hydroxysulfones were formed in most cases in good yield. It is important to note that in the reactions of methylsulfonylhydrazide with styrene **1a** and octene-1 or cyclohexene with sulfonylhydrazide **2a** the oxysulfonylation products were not observed in measurable yield.

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

Table 2 The structure and yield of β-hydroxysulfones **3** and β-ketosulfones **4**[a]

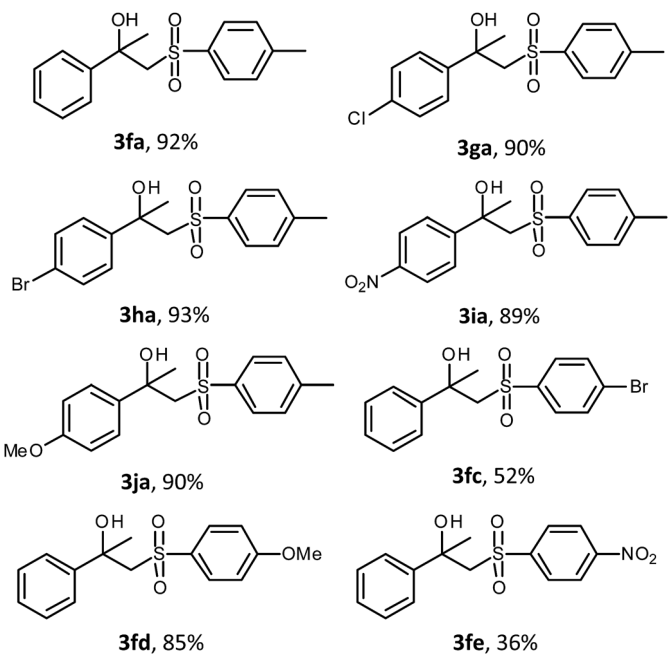


[a] The yield was determined by ^1H NMR using 1,4-dinitrobenzene as an internal standard; the isolated yield after reduction with $NaBH_4$ is reported in the parentheses.

Proposed reaction mechanism

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

Table 3 The structure and yield of β-hydroxysulfones **3**[a]



[a] Isolated yield.

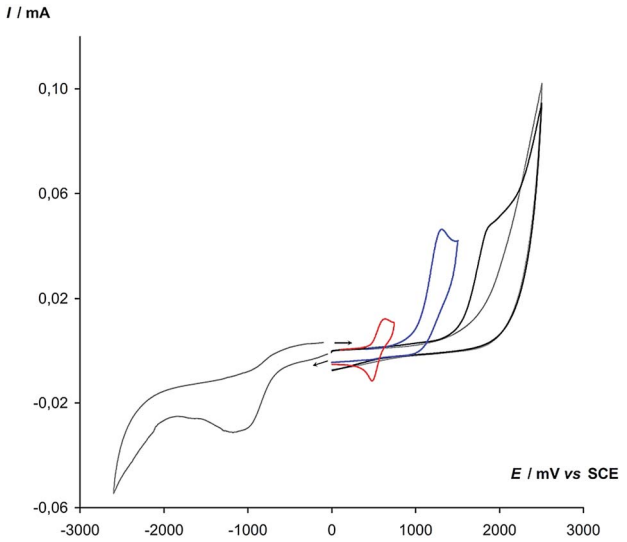
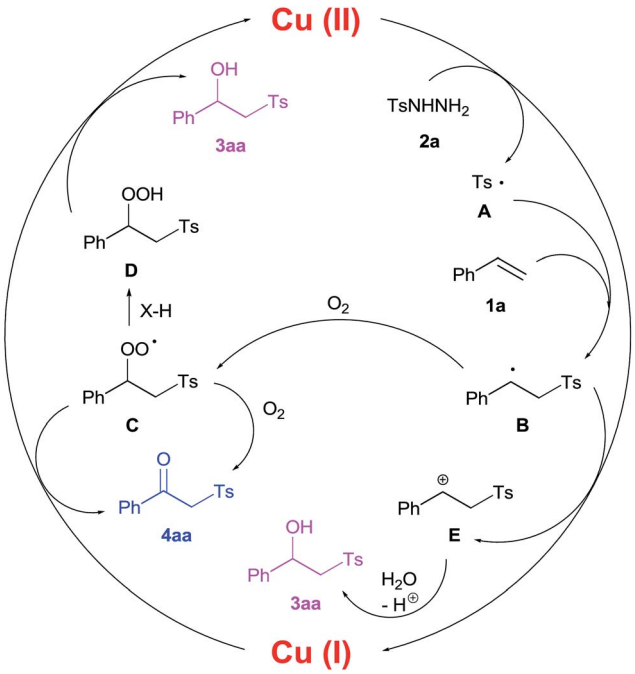


Fig. 1 The CV curves obtained for 2.0 mmol L^{-1} solutions of CuBr (red), *p*-toluenesulfonylhydrazide **2a** (blue), styrene **1a** (black) and aerated supporting solution (grey) in 0.1 M Bu_4NClO_4 in CH_3CN–H_2O (5 : 1) on a working glassy-carbon electrode ($d = 1.7$ mm) at a scan rate of 100 mV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



Scheme 4 A plausible oxysulfonylation mechanism using the example of the reaction of styrene **1a** and *p*-toluenesulfonylhydrazide **2a**.

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

A chemically and electrochemically reversible peak at $E_{1/2} =$ 0.55 V corresponds to the oxidation of Cu(I) into Cu(II), which takes place in the potential range between oxygen reduction and *p*-toluenesulfonylhydrazide **2a** oxidation. This means that under experimental conditions the Cu(I)/Cu(II) couple can serve as an effective mediator of *p*-toluenesulfonylhydrazide **2a** oxidation using oxygen.

On the basis of the obtained experimental data and previous studies of reactions proceeding through the generation of S-centered radicals from sulfonylhydrazides,[33–35] we proposed the pathway of the oxysulfonylation process (Scheme 4). Cu(I) ions are oxidized to Cu(II)[36–40] in the presence of oxygen, as confirmed by numerous kinetic studies of this process.[41–44] An almost colourless solution during the reaction is evidence for a small amount of Cu(II). Afterwards, as a result of the successive oxidation of hydrazide **2a** under the action of Cu(II),[16,33,34] oxygen or peroxyradical **C**, an S-centered tosyl radical **A** (Ts) is generated, which reacts with styrene **1a** to form a C-centered benzyl radical **B**.[16] In the next step, radical **B** is trapped with oxygen forming peroxyradical **C**. Then, after abstraction of an hydrogen atom from a hydrogen donor X–H (NH and CH) the peroxyradical **C** transforms into hydroperoxide **D**,[45] which gives the main product **3aa** after reduction.[46–51] Alcohol **3aa** can also be formed due to 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 the species generated from the reaction of peroxyradical **C** with Cu(I) ions[55] or oxygen.[56–58]

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

Conclusions

In summary, we have demonstrated a novel copper-mediated oxysulfonylation of styrenes using sulfonylhydrazides for the synthesis of β-hydroxysulfones in 32–93% yield. In the case of α-unsubstituted styrenes, β-ketosulfones are formed as the by-products. Applying α-methylstyrenes in this methodology gives β-hydroxysulfones as single products in high yield. Moreover, using cyclic voltammetry, experimental data and previous reports, a plausible reaction pathway was proposed. Coupling of two starting reagents proceeds under the action of the 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, which makes it possible to obtain β-hydroxysulfones as the main products.

Experimental

NMR spectra were recorded on a Bruker Avance II 300 MHz instrument. Chemical shifts are measured relative to the residual solvent peaks as an internal standard set to δ 7.25 and

δ 77.0 ($CDCl_3$), and 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 measured using electrospray ionization (ESI).[59] The measurements were carried out in positive ion mode (interface capillary voltage 4500 V); the mass ratio was from m/z 50 to 3000 Da; external/internal calibration was performed using an electrospray calibrant solution. Syringe injection was used for solutions in CH_3CN (flow rate 3 μL min^{-1}). Nitrogen was applied as a dry gas and the interface temperature was set at 180 °C. TLC analyses were carried out on standard silica-gel chromatography plates. 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-iodobenzene-sulfonylchloride, 4-bromobenzenesulfonylchloride, 4-methoxy-benzenesulfonylchloride, 4-nitrobenzenesulfonylchloride, methyltri-phenylphosphonium 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) and hydrazine hydrate (64% w/w water solution of hydrazine) were purchased from commercial sources and were used as received. 1-Iso-propyl-4-vinylbenzene (**1c**), 1-chloro-4-isopropenylbenzene (**1g**), 1-bromo-4-isopropenylbenzene (**1h**), 1-nitro-4-isopropenylbenzene (**1i**) and 1-methoxy-4-isopropenylbenzene (**1j**) were synthesized *via* the Wittig reaction according to the literature.[60] 4-Iodobenzenesulfono-hydrazide (**2b**), 4-bromobenzenesulfonohydrazide (**2c**), 4-methoxy-benzenesulfonohydrazide (**2d**) and 4-nitrobenzenesulfonohydrazide (**2e**) were synthesized according to the literature.[61]

Cyclic voltammetry (CV) was 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 of solution was utilized and the depolarizer concentration was 2 mmol L^{-1}. The working electrode was polished before recording each CV curve.

Synthesis of styrenes 1c, 1g–1j

Following a literature procedure[60] to a 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 with vigorous stirring under an Ar atmosphere for 10 min. The mixture was stirred for 1 h 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 h at room temperature. Then, the mixture 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 with 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, 6H), 2.80–2.96 (m, 1H), 5.17 (dd, J = 10.9, 1.1 Hz, 1H), 5.69 (dd, J = 17.6, 1.1 Hz, 1H), 6.68 (dd, J = 17.6, 10.9 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H). ^{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, 3H), 5.10 (s, 1H), 5.36 (s, 1H), 7.29 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H). ^{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, 3H), 5.11 (s, 1H), 5.36 (s, 1H), 7.33 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H). ^{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, 3H), 5.28 (s, 1H), 5.51 (s, 1H), 7.57 (d, J = 8.9 Hz, 2H), 8.15 (d, J = 8.9 Hz, 2H). ^{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 a white solid (2.4 g, 16.0 mmol, 80%). Mp = 30.5–31.0 °C (lit.[66] mp = 32.0–32.5 °C). ^{1}H NMR ($CDCl_3$), δ: 2.15 (s, 3H), 3.82 (s, 3H), 5.01 (s, 1H), 5.30 (s, 1H), 6.88 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H). ^{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 a literature procedure[61] a THF (20 mL) solution containing the corresponding arylsulfonyl chloride (4-iodobenzenesulfonylchloride, 4-bromobenzenesulfonylchloride, 4-methoxybenzenesulfonylchloride, 4-nitrobenzenesulfonylchloride, 5.0 g, 16.5–24.2 mmol) was cooled using 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 with 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 the pure products **2b–2e**.

4-Iodobenzenesulfonohydrazide (2b).[67] 4-Iodobenzenesulfonyl-chloride (5.0 g, 16.5 mmol) gave the title compound as a white solid (4.3 g, 14.5 mmol, 88%). Mp = 173.0–175.0 °C (lit.[67] mp = 162.0 °C). ^{1}H NMR (DMSO-d_6), δ: 4.16 (br s, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.98 (d, J = 8.9 Hz, 2H), 8.46 (s, 1H). ^{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 a white solid (4.5 g, 18.0 mmol, 92%). Mp = 114.0–116.0 °C (lit.[68] mp = 113.0–114.0 °C).^{1}H NMR (DMSO-d_6), δ: 4.20 (br s, 2H), 7.73 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 8.50 (s, 1H). ^{13}C NMR (DMSO-d_6), δ: 126.5, 129.7, 132.0, 137.5.

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

4-Nitrobenzenesulfonohydrazide (2e).[69] 4-Nitrobenzene-sulfonyl-chloride (5.0 g, 22.6 mmol) gave the title compound as a yellow solid (3.7 g, 16.9 mmol, 75%). Mp = 150.0–152.0 °C (lit.[69] mp = 152.0–157.0 °C). ^{1}H NMR (DMSO-d_6): δ 4.34 (br s, 2H), 8.05 (d, J = 8.9 Hz, 2H), 8.42 (d, J = 8.9 Hz, 2H), 8.75 (s, 1H). ^{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 a solution of styrene **1a** (300 mg, 2.88 mmol) in 25 mL of (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 or an oxygen atmosphere for 7 h at 40 °C, for 7 h at 80 °C, then for 12 h at room temperature.

Treatment of the reaction mixture containing 3aa and 4aa

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 a volume ratio of 1/2/2 (50 mL) and then filtered from the precipitate using SiO_2 (d = 20 mm, h = 80 mm). The precipitate was washed with a mixture of solvents PE/$CHCl_3$/EA in a volume ratio of 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 a solution of styrene **1a–1e** (300 mg, 1.87–2.88 mmol) in 25 mL of CH_3CN–H_2O (5 : 1), CuBr (3.74–5.76 mmol, molar ratio 2 mol mol^{-1} **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 under an oxygen atmosphere for 7 h at 40 °C, then for 12 h at room temperature. Then, 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)

The reaction mixture was treated as described above (General procedure 1). Then, the residue was diluted with 10 mL of THF-MeOH (1 : 1) mixture and $NaBH_4$ (molar ratio 3 mol mol^{-1} **4aa**, **4ba**, **4ca**, **4da**, **4ea**, **4ab**) was added with 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, mp = 68.5–70.0 °C (lit.[70] mp = 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, 3H, CH_3), 3.31 (dd, J = 14.3, 1.8 Hz, 1H), 3.47 (dd, J = 10.0, 14.3 Hz, 1H), 3.76 (d, J = 2.0 Hz, 1H), 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, 2H), 7.82 (d, J = 8.1 Hz, 2H). ^{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, mp = 118.0–120.0 °C (lit.[70] mp = 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, 3H), 2.46 (s, 3H), 3.22 (dd, J = 14.5, 1.3 Hz, 1H), 3.39 (dd, J = 14.5, 9.8 Hz, 1H), 3.69 (s, 1H), 5.42 (d, J = 9.8 Hz, 1H), 7.07 (dd, J = 7.2, 2.0 Hz, 1H), 7, 11–7.24 (m, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.48 (dd, J = 7.2, 1.7 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H). ^{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, mp = 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, 6H), 2.39 (s, 3H), 2.83 (m, J = 6.9 Hz, 1H), 3.50 (dd, J = 14.5, 3.7 Hz, 1H), 3.67 (dd, J = 14.5, 8.5 Hz, 1H), 4.96 (ddd, J = 8.5, 4.7, 3.7 Hz, 1H), 5.52 (d, J = 4.7 Hz, 1H), 7.13 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H). ^{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, mp = 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, 9H), 2.39 (s, 3H), 3.50 (dd, J = 14.6, 3.8 Hz, 1H), 3.67 (dd, J = 14.6, 8.5 Hz, 1H), 4.96 (ddd, J = 8.5, 4.7, 3.8 Hz, 1H), 5.52 (d, J = 4.7 Hz, 1H), 7.20 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 8.2 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H). ^{13}C NMR (DMSO-d$_6$), δ: 21.0, 31.1, 34.1, 62.9, 67.7, 124.8, 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, mp = 89.5–92.5 °C (lit.[70] mp = 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, 3H), 3.55 (dd, J = 14.6, 4.0 Hz, 1H), 3.67 (dd, J = 14.6, 8.2 Hz, 1H), 4.97 (ddd, J = 8.2, 5.0, 4.0 Hz, 1H), 5.70 (d, J = 5.0 Hz, 1H), 7.32 (s, 4H), 7.39 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H). ^{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, mp = 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, 1H), 3.76 (dd, J = 14.6, 9.2 Hz, 1H), 5.00 (ddd, J = 9.2, 4.8, 3.3 Hz, 1H), 5.62 (d, J = 4.8 Hz, 1H), 7.19–7.34 (m, 5H), 7.65 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H). ^{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, mp = 102.5–104.5 °C (lit.[71] mp = 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, 3H), 4.73 (s, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 7.5, 7.3 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 7.3 Hz, 2H). ^{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, mp = 108–110 °C (lit.[72] mp = 109–111 °C). Yield 18%. R_f = 0.37 (TLC, PE : EA, 3 : 1). ^{1}H NMR ($CDCl_3$), δ: 2.45 (s, 6H), 4.70 (s, 2H), 7.23–7.31 (m, 2H), 7.31–7.36 (m, 2H), 7.39–7.46 (m, 1H), 7.71–7.79 (m, 3H). ^{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, mp = 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, 6H), 2.43 (s, 3H), 2.97 (m, J = 7.0 Hz, 1H), 4.69 (s, 2H), 7.32 (**2d**, J = 8.2, 8.4 Hz, 4H), 7.76 (d, J = 8.2 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H). ^{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, mp = 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, 9H), 2.44 (s, 3H), 4.69 (s, 2H), 7.32 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 7.9 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H). ^{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, mp = 128.0–130.5 °C (lit.[71] mp = 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, 3H), 4.68 (s, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 7.74 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H). ^{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, mp = 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, 2H), 7.49 (t, J = 7.2 Hz, 2H), 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 a solution of styrene **1f–1j** (300 mg, 1.52–2.54 mmol) in 25 mL of CH_3CN–H_2O (5 : 1), CuBr (3.04–5.08 mmol, molar ratio 2 mol mol^{-1} **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 under an oxygen atmosphere for 7 h at 40 °C, then for 12 h at room temperature. Then, 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, mp = 99.5–100.5 °C (lit.[73] mp = 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, 3H), 2.39 (s, 3H), 3.61 (dd, J = 14.6, 1.1 Hz, 1H), 3.72 (d, J = 14.6, 1.1 Hz, 1H), 4.66 (br s, 1H), 7.14–7.24 (m, 5H), 7.26–7.34 (m, 2H), 7.49 (dd, J = 8.2, 1.0 Hz, 2H). ^{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 $[C_{16}H_{18}NaO_3S]^+$: 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, mp = 142–144 °C. Yield 90%. R_f = 0.68 (TLC, PE : EA, 2 : 1). ^{1}H NMR ($CDCl_3$), δ: 1.62 (s, 3H), 2.39 (s, 3H), 3.55 (d, J = 14.8 Hz, 1H), 3.69 (d, J = 14.8 Hz, 1H), 7.07 (d, J = 8.7 Hz, 2H) 7.15 (d, J = 8.7 Hz, 2H) 7.15 (d, J = 8.3 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H). ^{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, mp = 160.5–163 °C (lit.[16] mp = 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, 3H), 2.37 (s, 3H), 3.77 (d, J = 14.8 Hz, 1H), 3.84 (d, J = 14.8 Hz, 1H), 7.24–7.35 (m, 6H), 7.52 (d, J = 8.0 Hz, 2H). ^{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, mp = 137.5–138.5 °C (lit.[16] mp = 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, 3H), 2.33 (s, 3H), 3.84 (d, J = 14.8 Hz, 1H), 4.01 (d, J = 14.8 Hz, 1H), 5.71 (s, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.9 Hz, 2H), 8.02 (d, J = 8.8 Hz, 2H). ^{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, mp = 90–93 °C (lit.[16] mp = 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, 3H), 2.37 (s, 3H), 3.54 (d, J = 14.5 Hz, 1H), 3.67 (d, J = 14.5 Hz 1H), 3.74 (s, 3H), 6.68 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H). ^{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, mp = 153–156 °C (lit.[16] mp = 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, 3H), 3.86 (s, 2H), 4.75 (br s, 1H), 7.11–7.23 (m, 3H), 7.33–7.39 (m, 2H), 7.62 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H). ^{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, mp = 87.5–89 °C (lit.[16] mp = 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, 3H), 3.58 (d, J = 14.7 Hz, 1H), 3.70 (d, J = 14.7 Hz, 1H), 3.82 (s, 3H), 6.81 (d, J = 8.9 Hz, 2H), 7.11–7.24 (m, 3H), 7.25–7.31 (m, 2H), 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, mp = 177.5–179.5 °C (lit.[16] mp = 187–190 °C). Yield 36%. R_f = 0.25 (TLC, PE : EA, 3 : 1). ^{1}H NMR (DMSO-d_6), δ: 1.61 (s, 3H), 3.93–4.05 (m, 2H), 5.44 (s, 1H), 7.08–7.23 (m, 3H), 7.31–7.39 (m, 2H), 7.96 (d, J = 8.7 Hz, 2H), 8.29 (d, J = 8.7 Hz, 2H). ^{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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