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Iodine Triggered Aerobic Oxysulfonylation of Styrenes

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Abstract. An iodine triggered dioxygen activation in oxysulfonylation reaction of unactivated olefins using sulfonyl hydrazides and iodine catalyst is reported here. In one pot, near quantitative synthesis of *β*-hydroxysulfones were achieved at 70 ºC, within 7 h, in acetonitrile and under aerobic condition. A plausible mechanism is established by radical trapping and ^{18}O labelling experiments for the operationally simple, efficient and economically viable transformation. The direct activation of aerial oxygen under metal free and mild condition is anticipated for the oxysulfonylation of olefins.

Keywords: Dioxygen Activation; Iodine Triggered; Metal Free; Oxysulfonylation; Sulfonyl Hydrazides

Introduction

Activation of aerial dioxygen is a popular research topic in the areas of bioinorganic chemistry,[1] synthetic chemistry,[2] enzymology,[3] etc.[4] The terminal oxidant dioxygen is also considered to be an ideal oxygen source for the functionalization of organic molecules towards development of green and sustainable protocols in organic synthesis. The dioxygen activation process is mainly explored using transition metals Pd,[5] Ni,[6] Fe,[7] Cu,[8] etc.[9] Moreover, transition metal peroxide mediated radical reactions generally lead to undesired products and have limited scopes in pharmaceuticals and material industry.[10] Therefore, under metal-free condition the use of dioxygen is undoubtedly an encouraging route to widen the potential applicability in pharmaceuticals and synthetic laboratories, however, very few reports are available till date with regard to such potentiality.[3b]

Sulfonyl group is one of the important precursors in natural and non-natural products.[11] In particular, *β*-hydroxysulfones are present as a basic scaffold in numerous biologically active molecules, and provide useful building blocks in organic synthesis.[10a, 12] *β*-Hydroxysulfones are prepared *via* chemical or bio-reduction of *β*-keto-sulfones, nucleophilic ring opening of epoxides with sulfinate, or *via* hydroxylation of *α,β*-unsaturated sulfones.[13] These efficient and flexible transformations have significant limitations such as involvement of multistep synthetic procedure for synthesis of starting materials, production of unwanted byproducts, harsh reaction conditions, among others.[14] In this regard, developments of efficient, direct and environmentally benign synthetic methods are highly desirable.[15] Towards synthesis of organosulfur compounds oxidative cross-coupling reactions between different nucleophiles in the presence of appropriate oxidant have gained popularity.[10a, 16]

Results and Discussion

In continuation of our research interest in iodine reagent mediated reactions,[17] herein we report a metal-free approach *via* iodine triggered[18] and an expedient dioxygen activation method for an oxysulfonylation reaction[18a] towards synthesis of *β*-hydroxysulfones from styrenes (Figure 1a).[19] The aerial oxygen was activated for the introduction of -OH group at benzylic position and near quantitative synthesis of *β*-hydroxysulfones was achieved from styrenes and sulfonyl hydrazides using pyridine additive (10 mol %) and iodine (10 mol %) as catalyst.[20] Sulfonyl hydrazides are well known aryl source through the cleavage of C–S bonds[15c, 18a, 21] but limited for direct sulfonylation.[7a, 22] Eco-friendly molecular iodine triggered reactions are popular but inadequate examples are known towards functionalization aromatic olefins.[18, 23] The iodine catalyzed example of oxysulfonylation from sulfonyl hydrazide and olefins is depicted in Figure 1b.[21b] In Figure 1c, pyridine catalyzed dioxygen activation from sulfinic acid is presented.[13c]

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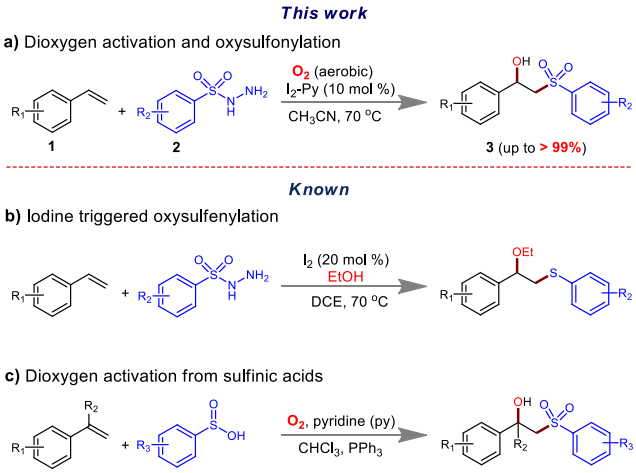
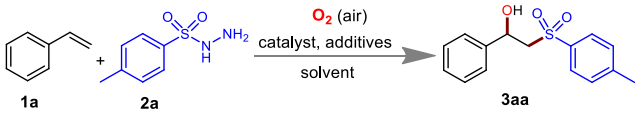


Figure 1. *β*-Hydroxysulfone synthesis by dioxygen activation. a) Our approach based on iodine as catalyst. b) Yang *et al.*, described the oxysulfonylation using iodine catalyst.[21b] c) Lei's oxysulfonylation method from sulfinic acid *via* pyridine catalyzed.[13c]

Table 1. Optimization Method[a]



Entry	Catalyst (equiv)	Additive (equiv)	Solvent	**3aa** (%)[b]
1	I_2 (0.2)	---	MeCN	65[c]
2	I_2 (0.1)	Pyridine (0.1)	EtOH	85
3	I_2 (0.1)	Pyridine (0.1)	DCE	82
4	I_2 (0.1)	Pyridine (0.1)	DMSO	38
5	I_2 (0.1)	Pyridine (0.1)	H_2O	--[d]
6	I_2 (0.1)	Pyridine (0.1)	MeCN-H_2O	96
7	I_2 (0.1)	Pyridine (0.1)	MeCN	99
8	I_2 (0.05)	Pyridine (0.05)	MeCN	40
9	--	Pyridine (0.1)	MeCN	--[d]
10	I_2 (0.1)	Pyridine (0.05)	MeCN	83
11	I_2 (0.1)	Pyridine (0.15)	MeCN	74
12	I_2 (0.1)	2,6-Lutidine	MeCN	30
13	I_2 (0.1)	2,4,6-Collidine	MeCN	49
14	I_2 (0.1)	Pyrrole (0.1)	MeCN	10
15	I_2 (0.1)	Et_3N (0.1)	MeCN	19
16	I_2 (0.1)	DMAP (0.1)	MeCN	39
17	I_2 (0.1)	Na_2CO_3 (1)	MeCN	--[d]
18	I_2 (0.1)	K_2CO_3 (1)	MeCN	--[d]
19	I_2 (0.1)	$KHPO_4$ (1)	MeCN	--[d]
20	TBAI	Pyridine (0.1)	MeCN	--[d]
21	TBAB	Pyridine (0.1)	MeCN	--[d]
22	I_2 (0.1)	Pyridine (0.1)	MeCN	59[e]
23	I_2 (0.1)	Pyridine (0.1)	MeCN	63[f]

[a]Condition: **1a** (0.26 mmol), **2a** (0.39 mmol), solvent (1.5 mL), 70 °C, 7 h. [b]After column chromatography. [c]24 h. [d]No oxysulfonylation product. [e]25 °C, 24 h. [f]50 °C.

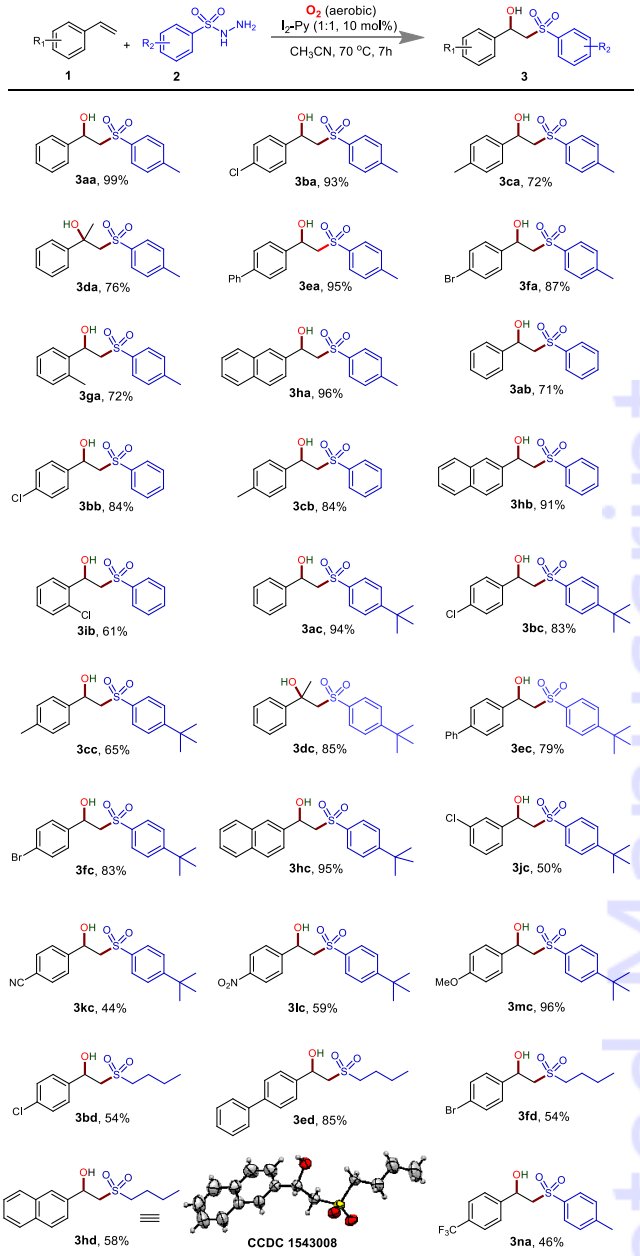


Figure 2. Scope of Oxysulfonylation of Olefins.

The reaction condition was optimized (Table 1) with the substrates styrene (**1a**) and 4-methylbenzenesulfonyl hydrazide (**2a**). *β*-Hydroxysulfone **3aa** was obtained in excellent yield (> 99%) using iodine catalyst (10 mol %) and pyridine-additive (10 mol %) in acetonitrile at 70 °C under aerobic condition (Table 1, entry 7). No additional source of oxygen was supplied for this reaction and sulfonyl radicals were possibly generated from sulfonyl hydrazides. Besides, when the reaction was performed under N_2 atmosphere no desired product was detected which indicated that the source of hydroxyl group possibly from aerial oxygen. A wide range of solvents were screened and it was found that acetonitrile works best for this reaction (Table 1, entries 2-7). The solvent acetonitrile is known to dissolve ~8.1 mM oxygen at 25 °C which is

significantly higher than commonly used solvents.[24] The best results were obtained at 70 ºC and at lower temperature the yield of the product **3aa** was sufficiently lowered (Table 1, entries 22-23). Compared to pyridine, other bases like 2,6-lutidine, 2,4,6-collidine, pyrrole, Et_3N, DMAP, Na_2CO_3, K_2CO_3, $KHPO_4$ were found to be less efficient (Table 1, entries 12-19). Similarly, I_2 was the superior as catalyst (Table 1, entries 20-21) compared to TBAI, TBAB, etc. Interestingly, when pyridine was solely used as a catalyst no product formation was detected (Table 1, entry 9).

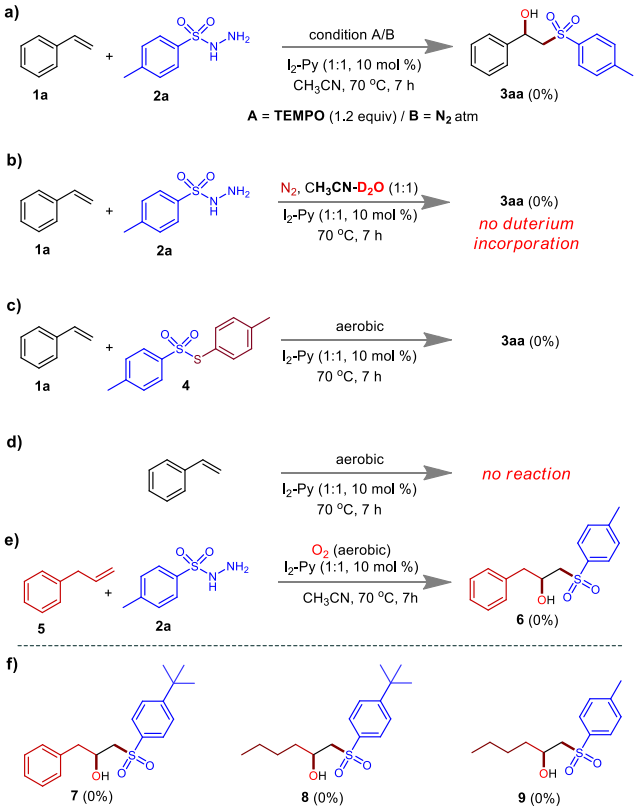


Figure 3. Control Experiments.

Based on our preliminary findings, the substrate scope for oxysulfonylation between various olefins and sulfonyl hydrazides was explored (Figure 2). Using 10 mol % of iodine as catalyst under aerobic condition, a range of olefins reacted with sulfonyl hydrazides to afford a variety of *β*-hydroxysulfones in good to excellent yields (> 99%). This method was compatible with aromatic ring having electron-donating and electron-withdrawing groups. Similarly, -Cl and -Br substituents on styrene have also worked well. Bulky substrates, 2-methylstyrene and 2-chlorostyrene efficiently reacted with sulfonyl hydrazides and yielded **3ga** (72%) and **3ib** (61%), respectively. Notably, *α*-methylstyrene has also afforded sterically congested *β*-hydroxysulfone in very good yield (**3da**, **3dc**). The reaction was found to be efficient with both aromatic as well as aliphatic sulfonyl hydrazides. Relatively poor yields of *β*-hydroxysulfones were obtained for the styrenes with electron withdrawing groups like cyano (**3kc**), nitro (**3lc**) and methoxy (**3na**). However, methoxy substituted styrene (**1m**) led to the corresponding *β*-hydroxysulfone (**3mc**) in excellent yield (96%) and no oxysulfonylation product could be isolated from the reaction with 4-amino styrene. In gram scale (9.58 mmol) the product **3aa** was obtained in 84 % yield (2.22 g).

Control experiments were performed to understand the mechanism of the iodine catalyzed[20b, 25] oxysulfonylation reaction (Figures 3-4). Under aerobic condition and at 1 atm, near quantitative **3aa** was obtained from styrene **1a** and tosyl hydrazide **2a**. In an oxidative environment, formation of sulfonyl radical from sulfonyl hydrazides *via* diazene intermediate is known.[26] Involvement of radical pathway was confirmed by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical trapping experiment (Figure 3a). Under optimized condition, also in dry acetonitrile and in absence of olefins, sulfonyl hydrazides led to sulfonothioic acid in low yield (14%) (Supporting Information). As shown in Figure 3c, when **1a** was treated with sulfonothioic acid derivative **4**, no **3aa** could be obtained which ruled out the possibility for the formation of sulfonyl radical *via* sulfonothioic acid. Furthermore, there was no deuterium incorporation and a failure of the reaction under nitrogen atmosphere (Figure 3b) also supports the hypothesis of aerial dioxygen activation. The reaction was completely failed in presence of any aliphatic olefins like allyl benzenes and 1-hexene (Figures 3e,f). Moreover, under standard condition and in absence of sulfonyl hydrazide no reaction was observed with styrene (Figure 3d).

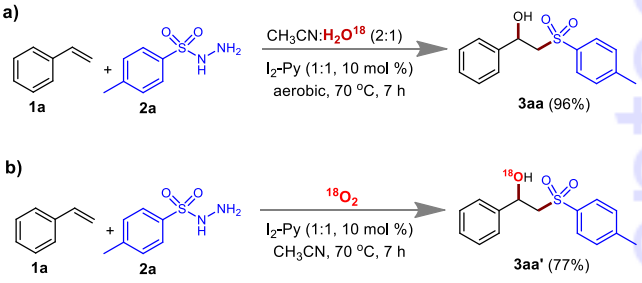


Figure 4. ^{18}O Isotope Labelling Experiments.

Shown in Figure 4, ^{18}O labelling experiments[13c] also helped to understand the origin of the hydroxyl oxygen of *β*-hydroxysulfone. When **1a** and **2a** were treated in the presence of aerobic condition in MeCN:H_2O^{18} (2:1), the reaction failed to produce any ^{18}O incorporated *β*-hydroxysulfone, instead ^{16}O incorporated **3aa** was isolated in 96% yield. Nevertheless, in presence of $^{18}O_2$, reaction of **1a** and **2a** afforded 77% of ^{18}O incorporated **3aa** (Supporting Information). So, the role of aerial oxygen was confirmed for the oxysulfonylation reaction.

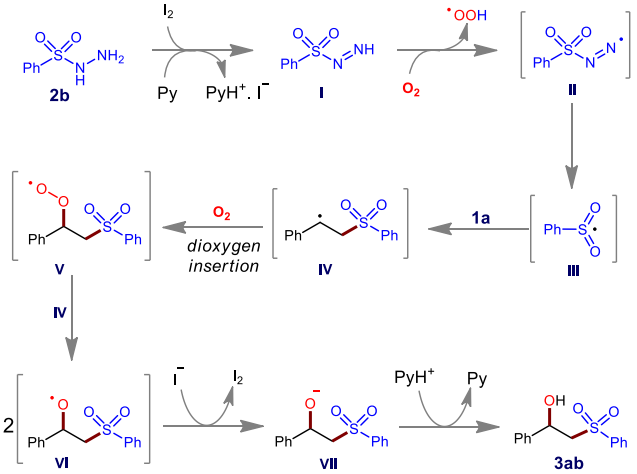


Figure 5. Plausible Mechanism.

A plausible mechanism for oxysulfonylation of olefins (Figure 5) *via* radical pathway was rationalized[27] from control experiments. Sulfonyl hydrazides reacted with iodine to give diazene **I**, which could further be oxidized to sulfonyl radical **III** by triplet dioxygen. Following, sulfonyl radical (**III**) might reacted with the olefins **1a** to produce stable benzylic radical **IV**. The stability of radical **IV** was important and essential requirement for the reaction. It has been found that allyl benzene which generally produce less stable radical could not led to the formation of any oxysulfonylated product (Figure 3d). Further, the benzylic radical **IV** possibly trapped the dioxygen dissolved in acetonitrile to produce alkylhydroperoxy radical intermediate **V**.[28] And then, the intermediate **V** led to **VI** by homolytic cleavage of peroxy linkage by influence of **IV**.[28a] The intermediate **VI** afforded anionic intermediate **VII** by single-electron transfer (SET) from iodide and concomitant proton transfer (PT) from PyH^+ and further produced desired *β*-hydroxysulfone **3ab**. In this reaction amphoteric pyridine[2a, 29] could play another important role by stopping the formation of sulfonothioic acid from sulfonyl hydrazide. This is because pyridine might have accepted the proton from hydroiodic acid (HI) and generated iodide anion which stopped to generate -SPh radical from diazene (**I**). It was also confirmed that sulfonothioic acid derivative **4** with styrene did not results in **3aa**. In parallel, formation of 65% of **3aa** (entry 1, Table 1) in absence of pyridine indicated that the generated sulfonyl radical might have rapidly reacted with olefins and led the stable benzyl radical for follow up reactions. The stability of the benzyl radical was possibly essential for the reaction because no product could be detected with aliphatic olefins (Figure 3f). These aliphatic olefins were expected to create unstable radicals after reaction with sulfonyl radicals. Also, no reaction in absence of sulfonyl hydrazide (Figure 3d) indicated for the involvement of the sulfonyl radical during the reaction.[7a, 30]

Conclusion

In conclusion, we have developed an operationally simple and efficient method of aerial dioxygen activation for oxysulfonylation reaction towards synthesis of regioselective *β*-hydroxysulfones from non-prefunctionalized olefins and sulfonyl hydrazides. Using a simple and readily available metal-free reagents like 10 mol % iodine catalyst and pyridine additive (10 mol %), successful construction of new C–O and C–S bond in one-pot were achieved *via* an intermolecular reaction. We anticipate that this oxysulfonylation approach *via* organic pathway and direct aerial dioxygen activation might offer an access to several organosulfur compounds in the synthesis of functionalized materials, complex molecules and pharmaceuticals.

Experimental Section

Instrumentation and Chemicals

Styrene were purchased from commercial source used without further purification. Tosyl hydrazines were prepared according to the standard procedure.[31] All the reactions were done under open atmosphere. Column chromatographic purification of the compounds were done using silica gel (mess 230-400) and hexane/ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz and/or 700 MHz instruments at 25 °C. The chemical shift (δ, ppm) values were reported with respect to residual chloroform (7.26 for ^{1}H and 77.16 ppm for ^{13}C). High resolution mass spectroscopy (HR-ESIMS) was recorded on ESI-TOF (Time-of-flight) mass spectroscopy. Infrared spectra were recorded in wave number (cm^{-1}). Melting points of the compound were determined using digital melting point apparatus and uncorrected.

Preparation of arylsulfonyl hydrazides.[31] In a round bottom flask (250 mL) charged with *p*-tolylsulfonyl chloride (26.2 mmol) in THF (15 mL). Then hydrazine mono hydrates (3.37 mL as 80% in water, 55 mmol) were added drop wise to the solution. Following, the reaction mixture were stirred at 0 ºC for 30 min. After that the mixture was concentrated under vacuum and diluted with ethyl acetate. The solution was washed with water and dried over anhyd sodium sulphate. Solvents were removed under reduced pressure and followed by recrystallization from ethanol to obtain pure sulfonyl hydrazide.

4-Methylbenzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.74 (br s, 1H), 3.38 (br s, 2H), 2.45 (s, 3H).

4-(tButyl)benzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.57-7.54 (m, 2H), 5.99 (br s, 1H), 3.63 (br s, 2H), 1.34 (s, 9H).

Benzenesulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 2H), 5.76 (br s, 1H), 3.62 (br s, 2H).

Butane-1-sulfonohydrazide. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (br s, 1H), 3.71 (br s, 2H), 3.12-3.08 (m, 2H), 1.82-1.74 (m, 2H), 1.46 (dd, *J* = 14.8, 7.6 Hz, 2H), 0.94 (t, *J* = 7.2 Hz, 3H).

General procedure for the preparation of Sulfone. Styrene (60 mg, 0.52 mmol), *p*-toluenesulfonyl hydrazide (146 mg, 0.78 mmol) and pyridine (4.5 µL, 0.052 mmol) were placed in an oven-dried seal tube. Then acetonitrile

(3.0 mL) and iodine (13.2 mg, 0.052 mmol) were added. Then the mixture was allowed to stir for 7 h at 70 ºC. After that the mixture was concentrated under vacuum and diluted with ethyl acetate. The solution was washed with water and dried over anhyd sodium sulphate. Resulting mixtures were purified through column chromatography using silica gel and *n*-hexane, ethyl acetate (9:1) solvent mixture as an eluent to afford the product.

Gram scale synthesis. Styrene (1.1 mL, 9.58 mmol), *p*-toluenesulfonyl hydrazide (2.68 g, 14.37 mmol) and pyridine (0.077 mL, 0.96 mmol) were placed in two necked round bottom flask (500 mL). Then acetonitrile (80 mL) and iodine (0.243 mg, 0.96 mmol) were added. Then the mixture was allowed to stir for 7 h at 70 ºC. After that the mixture was concentrated under vacuum and diluted with ethyl acetate. The solution was washed with water and dried over anhyd sodium sulphate. Resulting mixtures were purified through column chromatography using silica gel and *n*-hexane, ethyl acetate (9:1) solvent mixture as an eluent to afford **3aa** in 84% (2.22 g).

1-Phenyl-2-tosylethanol (3aa).[32] R_f = 0.28 (20% ethyl acetate in hexane); off white solid; yield 99% (142 mg); mp 72-74 ºC (lit.[33] 130 - 131 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.34-7.23 (m, 5H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.78 (br s, 1H), 3.47 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 140.8, 136.2, 130.1, 128.8, 128.3, 128.1, 125.7, 68.5, 64.0, 21.7; IR (KBr) ῡ 3484, 3063, 2924, 1640, 1598, 1494, 1453, 1401, 1300, 1288, 1137, 1087, 994, 816; HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_3S$ (M + Na)$^+$ 299.0712, found 299.0713.

1-(4-Chlorophenyl)-2-tosylethanol (3ba).[32] R_f = 0.30 (20% ethyl acetate in hexane); White solid; yield 93% (144 mg); mp 94-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.31-7.21 (m, 4H), 5.23 (d, *J* = 10.0 Hz, 1H), 3.82 (d, *J* = 1.6 Hz, 1H), 3.44 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.28 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.3, 136.1, 134.2, 130.3, 129.0, 128.1, 127.2, 68.0, 64.0, 21.8; IR (KBr) ῡ 3419, 3055, 2987, 2305, 2125, 1641, 1549, 1493, 1264, 1145, 1088, 896; HRMS (ESI-TOF) calcd for $C_{15}H_{15}ClO_3S$ (M + Na)$^+$ 333.0323, found 333.0332.

1-(p-Tolyl)-2-tosylethanol (3ca).[13c] R_f = 0.28 (20% ethyl acetate in hexane); Colourless oil; yield 70% (77 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.21 (d, *J* = 10.0 Hz, 1H), 3.65 (d, *J* = 2.0 Hz, 1H), 3.47 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.47 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 138.2, 137.9, 136.3, 130.2, 129.5, 128.1, 125.7, 68.5, 64.1, 21.8, 21.2; IR (KBr) ῡ 3422, 2963, 2877, 2090, 1640, 1422, 1265, 896; HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_3S$ (M + Na)$^+$ 313.0869, found 313.0883.

2-Phenyl-1-tosylpropan-2-ol (3da).[32] R_f = 0.40 (20% ethyl acetate in hexane); White solid; yield 76% (102 mg); mp 100-102 ºC (lit.[7a] 84-85 ºC) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.36-7.26 (m, 2H), 7.26-7.08 (m, 5H), 4.63 (br s, 1H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.59 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 144.6, 137.5, 129.8, 128.4, 127.7, 127.3, 124.8, 73.3, 66.8, 30.9, 21.7; IR (KBr) ῡ 3500, 3062, 2984, 2930, 2101, 1632, 1598, 1494, 1447, 1381, 1268, 1184, 1122, 1083, 1048, 1028, 945, 850; HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_3S$ (M + Na)$^+$ 313.0869, found 313.0889.

1-([1,1'-Biphenyl]-4-yl)-2-tosylethanol (3ea). R_f = 0.26 (20% ethyl acetate in hexane); White solid; yield 95% (111 mg); mp 105-106 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.60-760 (m, 4H), 7.48-7.30 (m, 7H), 5.31 (d, *J* = 10.0 Hz, 1H), 3.78 (d, *J* = 1.6 Hz, 1H), 3.52 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.37 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 141.4, 140.6, 139.8, 136.3, 130.2, 128.9, 128.2, 127.62, 127.60, 127.2, 126.3, 68.4, 64.1, 21.8; IR (KBr) ῡ 3475, 3031, 2995, 2155, 1639, 1598, 1487, 1402, 1288, 1137, 1087, 844; HRMS (ESI-TOF) calcd for $C_{21}H_{20}O_3S$ (M + Na)$^+$ 375.1025, found 375.1022.

1-(4-Bromophenyl)-2-tosylethanol (3fa).[13c] R_f = 0.35 (20% ethyl acetate in hexane); White solid; yield 87% (141 mg); mp 109-110 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.22 (d, *J* = 10.0 Hz, 1H), 3.82 (d, *J* = 1.6 Hz, 1H), 3.42 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.28 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.6, 139.8, 136.1, 132.0, 130.3, 128.1, 127.5, 122.3, 68.0, 63.9, 21.8; IR (KBr) ν 3484, 3063, 2982, 2924, 2305, 2104, 1916, 1641, 1596, 1487, 1400, 1300, 1288, 1196, 1137, 1102, 1087, 1070, 1010, 913, 863; HRMS (ESI-TOF) calcd for $C_{15}H_{15}BrO_3S$ (M + Na)$^+$ 376.9817, found 376.9827.

1-(o-Tolyl)-2-tosylethanol (3ga).[32] R_f = 0.27 (20% ethyl acetate in hexane); White solid; yield 72% (97 mg); mp 125-126 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.24-7.12 (m, 2H), 7.08 (d, *J* = 7.2 Hz, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 3.67 (d, *J* = 1.6 Hz, 1H), 3.40 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.24 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 138.8, 136.2, 133.8, 130.7, 130.3, 128.21, 128.18, 126.7, 125.4, 65.2, 63.1, 21.8, 18.7; IR (KBr) ῡ 3420, 3105, 2975, 2115, 1643, 1554, 1264, 1140, 896; HRMS (ESI-TOF) calcd for $C_{16}H_{18}O_3S$ (M + Na)$^+$ 313.0869, found 313.0844.

1-(Naphthalen-2-yl)-2-tosylethanol (3ha).[13b] R_f = 0.27 (20% ethyl acetate in hexane); off white solid; yield 96% (142 mg); mp 102-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.79-7.72 (m, 4H), 7.46 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.36-7.28 (m,3H), 5.41 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.96 (br s, 1H), 3.57 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.41 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 138.1, 136.2, 133.2, 133.1, 130.1, 128.7, 128.0 (x 2), 127.7, 126.4, 126.3, 124.8, 123.4, 68.7, 63.9, 21.7; IR (KBr) ῡ 3420, 2965, 2876, 2376, 2307, 2114, 1641, 1550, 1511, 1264, 1136, 1087, 896, 860; HRMS (ESI-TOF) calcd for $C_{19}H_{18}O_3S$ (M + Na)$^+$ 349.0869, found 349.0871.

1-Phenyl-2-(phenylsulfonyl)ethanol (3ab).[34] R_f = 0.38 (20% ethyl acetate in hexane); White solid; yield 71% (97 mg); mp 91-93 ºC (lit.[35] 92-94 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.73-7.65 (m, 1H), 7.64-7.54 (m, 2H), 7.36-7.27 (m, 5H), 5.28 (d, *J* = 10.0 Hz, 1H), 3.68 (br s, 1H), 3.51 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.34 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 139.3, 134.2, 129.6, 128.9, 128.5, 128.1, 125.8, 68.6, 64.1; IR (KBr) ῡ 3483, 2927, 2089, 1641, 1494, 1479, 1394, 1303, 1199, 1138, 1085, 1025, 996; HRMS (ESI-TOF) calcd for $C_{14}H_{14}O_3S$ (M + Na)$^+$ 285.0556, found 285.0572.

1-(4-Chlorophenyl)-2-(phenylsulfonyl)ethanol (3bb).[13d] R_f = 0.32 (20% ethyl acetate in hexane); White solid; yield 84% (124 mg); mp 104-105 ºC (lit.[36] 61 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.77-7.65 (m, 1H), 7.65-7.55 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 5.27 (d, *J* = 10.0 Hz, 1H), 3.75 (br s, 1H), 3.46 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 139.1, 134.4, 134.3, 129.7, 129.1, 128.1, 127.2, 68.0, 63.9; IR (KBr) ῡ 3443, 3055, 2987, 2305, 1641, 1492, 1447, 1421, 1306, 1265, 1146, 1086, 896; HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_3S$ (M + Na)$^+$ 319.0166, found 319.0180.

2-(Phenylsulfonyl)-1-(p-tolyl)ethanol (3cb).[13d] R_f = 0.33 (20% ethyl acetate/hexane); white solid; yield 84% (105 mg); mp 82-83 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07-

7.85 (m, 2H), 7.75-7.65 (m, 1H), 7.64-7.53 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.59 (d, *J* = 1.6 Hz, 1H), 3.50 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.33 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.3, 137.8, 134.2, 129.6, 129.5, 128.1, 125.7, 68.4, 64.1, 21.2; IR (KBr) ῡ 3483, 3062, 2923, 1994, 1907, 1641, 1585, 1548, 1514, 1478, 1447, 1304, 1199, 1138, 1086, 1022, 998, 913, 864; HRMS (ESI-TOF) calcd for $C_{15}H_{16}O_3S$ $(M + Na)^+$ 299.0712, found 299.0694.

1-(Naphthalen-2-yl)-2-(phenylsulfonyl)ethanol (3hb). R_f = 0.34 (20% ethyl acetate in hexane); White solid; yield 91% (110 mg); mp 94-96 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.92 (m, 2H), 7.82-7.76 (m, 4H), 7.71-7.64 (m, 1H), 7.61-7.54 (m, 2H), 7.50-7.44 (m, 2H), 7.36 (dd, *J* = 8.0, 2.0 Hz, 1H), 5.46 (d, *J* = 10.0 Hz, 1H), 3.81 (br s, 1H), 3.59 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.43 (dd, *J* = 14.4, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 138.0 (x2C), 134.3, 133.31, 133.29, 129.6, 128.8, 128.1, 127.8, 126.6, 126.5, 124.9, 123.4, 68.7, 64.0; IR (KBr) ῡ 3455, 3089, 2096, 1632, 1509, 1476, 1446, 1387, 1367, 1266, 1136, 1085,737; HRMS (ESI-TOF) calcd for $C_{18}H_{16}O_3S$ $(M + Na)^+$ 335.0712, found 335.0691.

1-(2-Chlorophenyl)-2-(phenylsulfonyl)ethanol (3ib).[13d] R_f = 0.34 (20% ethyl acetate in hexane); Colourless liquid; yield 61% (84 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04-7.96 (m, 2H), 7.73-7.57 (m, 4H), 7.33-7.27 (m, 1H), 7.25-7.17 (m, 2H), 5.44 (d, *J* = 10.0 Hz, 1H), 3.99 (br s, 1H), 3.52 (dd, *J* = 14.4, 1.2 Hz, 1H), 3.30 (dd, *J* = 14.4, 10.0 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 138.6, 137.9, 134.3, 131.0, 129.6, 129.5, 129.4, 128.3, 127.5, 127.3, 65.6, 61.9; IR (KBr) ῡ 3421, 3056, 2998, 2305, 2114, 1641, 1447, 1421, 1265, 1143, 909, 896; HRMS (ESI-TOF) calcd for $C_{14}H_{13}ClO_3S$ $(M + Na)^+$ 319.0166, found 319.0174.

2-((4-^{t}Butylphenyl)sulfonyl)-1-phenylethanol (3ac). R_f = 0.32 (20% ethyl acetate in hexane); white solid; yield 94% (120 mg); mp 113-115 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.30-7.19 (m, 5H), 5.25 (d, *J* = 10.0 Hz, 1H), 3.77 (d, *J* = 1.6 Hz, 1H), 3.46 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 140.8, 136.2, 128.8, 128.4, 127.9, 126.6, 125.8, 68.5, 64.0, 35.4, 31.1; IR (KBr) ῡ 3444, 2965, 2865, 2100, 1641, 1550, 1492, 1451, 1396, 1288, 1197, 1140, 1084, 844; HRMS (ESI-TOF) calcd for $C_{18}H_{22}O_3S$ $(M + Na)^+$ 341.1182, found 341.1172.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(4-chlorophenyl)ethanol (3bc). R_f = 0.30 (20% ethyl acetate in hexane); White solid; yield 83% (146 mg); mp 120-122 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.30-7.21 (m, 4H), 5.27 (d, *J* = 10.0 Hz, 1H), 3.84 (d, *J* = 1.6 Hz, 1H), 3.45 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.5, 139.3, 136.1, 134.2, 129.0, 127.9, 127.2, 126.7, 67.9, 63.9, 35.5, 31.2; IR (KBr) ῡ 3422, 3057, 2968, 2377, 2306, 2115, 1785, 1640, 1550, 1493, 1399, 1307, 1263, 1198, 1107, 1085, 1014, 995, 896, 864; HRMS (ESI-TOF) calcd for $C_{18}H_{21}O_3SCl$ $(M + Na)^+$ 375.0792, found 375.0782.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(p-tolyl)ethanol (3cc). R_f = 0.34 (20% ethyl acetate in hexane); White solid; yield 65% (98 mg); mp 97-99 ºC; 1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.70 (d, *J* = 1.6 Hz, 1H), 3.49 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.33 (dd, *J* = 14.4, 2.0 Hz, 1H), 2.31 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 138.2, 137.9, 136.2, 129.5, 127.9, 126.6, 125.7, 68.4, 64.0, 35.4, 31.1, 21.2; IR (KBr) ῡ 3474, 3060, 2967, 2871, 2307, 2099, 1923,1640, 1514, 1476, 1399, 1306, 1267, 1199, 1107, 1085, 1057, 1014, 864, 840; HRMS (ESI-TOF) calcd for $C_{19}H_{24}O_3S$ $(M + Na)^+$ 355.1338, found 355.1325.

1-((4-^{t}Butylphenyl)sulfonyl)-2-phenylpropan-2-ol (3dc). R_f = 0.40 (20% ethyl acetate in hexane); White solid; yield 85% (130 mg); mp 92-93 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.27-7.23 (m, 2H), 7.18-7.08 (m, 3H), 4.69 (br s, 1H), 3.73 (d, *J* = 14.4 Hz, 1H), 3.60 (d, *J* = 14.4 Hz, 1H), 1.68 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 144.4, 137.2, 128.3, 127.5, 127.3, 126.2, 124.8, 73.2, 66.6, 35.3, 31.2 (x2C); IR (KBr) ῡ 3450, 2965, 2076, 1640, 1493, 1397, 1307, 1251, 1158, 1082, 850; HRMS (ESI-TOF) calcd for $C_{19}H_{24}O_3S$ $(M + Na)^+$ 355.1338, found 355.1343.

1-([1,1'-Biphenyl]-4-yl)-2-((4-(tert-butyl)phenyl)sulfonyl)ethanol (3ec). R_f = 0.35 (20% ethyl acetate in hexane); White solid; yield 79% (103 mg); mp 115-116 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.57-7.52 (m, 4H), 7.47-7.29 (m, 5H), 5.35 (d, *J* = 10.0 Hz, 1H), 3.81 (d, *J* = 1.6 Hz, 1H), 3.53 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.39 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 141.4, 140.6, 139.8, 136.2, 128.9, 128.0, 127.62, 127.59, 127.2, 126.7, 126.3, 68.3, 64.0 35.5, 31.2; IR (KBr) ῡ 3443, 2928, 2850, 2358, 2096, 1642, 1275, 1261, 764; HRMS (ESI-TOF) calcd for $C_{24}H_{26}O_3S$ $(M + Na)^+$ 417.1495, found 417.1467.

1-(4-Bromophenyl)-2-((4-(tert-butyl)phenyl)sulfonyl)ethanol (3fc). R_f = 0.33 (20% ethyl acetate in hexane); White solid; yield 83% (150 mg); mp 134-136 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.76 (m, 2H), 7.62-7.54 (m, 2H), 7.47-7.38 (m, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 5.26 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.84 (br s, 1H), 3.44 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 139.8, 136.0, 131.9, 127.9, 127.6, 126.7 122.3, 68.0, 63.8, 35.5, 31.2; IR (KBr) ῡ 3508, 3055, 2969, 2305, 2099, 1643, 1594, 1421, 1398, 1306, 1291, 1198, 1107, 1085, 1011, 895; HRMS (ESI-TOF) calcd for $C_{18}H_{21}BrO_3S$ $(M + Na)^+$ 419.0287, found 419.0269.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(naphthalen-2-yl)ethanol (3hc). R_f = 0.34 (20% ethyl acetate in hexane); White solid; yield 95% (136 mg); mp 132-134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.83-7.74 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.52-7.43 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 5.47 (d, *J* = 10.0 Hz, 1H), 3.89 (br s, 1H), 3.58 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.44 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 138.1, 136.2, 133.3, 133.2, 128.8, 128.1, 128.0, 127.8, 126.6, 126.5, 126.4, 125.0, 123.4, 68.7, 63.9, 35.4, 31.1; IR (KBr) ῡ 3507, 3085, 2970, 2340, 2098, 1642, 1510, 1476, 1399, 1365, 1291, 1265, 1152, 1085, 896, 860; HRMS (ESI-TOF) calcd for $C_{22}H_{24}O_3S$ $(M + Na)^+$ 391.1338, found 391.1357.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(3-chlorophenyl)ethanol (3jc). R_f = 0.38 (20% ethyl acetate in hexane); White solid; yield 50% (83 mg); mp 77-79 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.81 (m, 2H), 7.64-7.56 (m, 2H), 7.32 (s, 1H), 7.25-7.15 (m, 3H), 5.27 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.85 (br s, 1H), 3.45 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.0, 2.0 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 142.8, 136.0, 134.8, 130.2, 128.6, 128.0, 126.7, 126.1, 124.0, 68.0, 63.9, 35.5, 31.2; IR (KBr) ῡ 3421, 2956, 2356, 2090, 1640, 1275, 1260, 1055; HRMS (ESI-TOF) calcd for $C_{18}H_{21}ClO_3S$ $(M + Na)^+$ 375.0792, found 375.0776.

4-(2-((4-^{t}Butylphenyl)sulfonyl)-1-hydroxyethyl)benzonitrile (3kc): R_f = 0.25 (20% ethyl acetate in hexane); White solid; yield 44% (69 mg); mp 120-124 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.57 - 7.63 (m, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 5.37 (d, *J* = 10.0 Hz, 1H), 4.03 (s, 1H), 3.43 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.32 (d, *J* = 14.4 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.7, 145.9, 135.8, 132.6, 127.9, 126.8, 126.6, 118.5, 112.2, 67.9, 63.6, 35.5, 31.1; IR (KBr) ῡ 3484, 3059, 2966, 2871, 2304, 2229, 2098, 1636, 1463,

1397, 1291, 1266, 1198, 1143, 1107; HRMS (ESI-TOF) calcd for $C_{19}H_{21}NO_3S$ (M + Na)$^+$ 366.1146, found 366.1134.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(4-nitrophenyl)ethanol (3lc): R_f = 0.22 (20% ethyl acetate in hexane); White solid; yield 59% (100 mg); mp 130-132 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 5.43 (d, *J* = 10.0 Hz, 1H), 4.08 (brs, 1H), 3.45 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.34 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 158.8, 147.82, 147.81, 135.8, 128.0, 126.8, 126.7, 124.1, 67.8, 63.6, 35.5, 31.1; IR (KBr) ῡ 3487, 2964, 2870, 1594, 1521, 1346, 1305, 1198, 1144, 1107, 1084; HRMS (ESI-TOF) calcd for $C_{18}H_{21}NO_5S$ (M + Na)$^+$ 386.1007, found 386.1033.

2-((4-^{t}Butylphenyl)sulfonyl)-1-(4-methoxyphenyl)ethanol (3mc): R_f = 0.32 (20% ethyl acetate in hexane); white solid ; yield 96% (125 mg); mp 115-119 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.23 (d, *J* = 10.0 Hz, 1H), 3.77 (s, 3H), 3.69 (d, *J* = 1.2 Hz, 1H), 3.49 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.31 (dd, *J* = 14.4, 2.0 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 159.7, 158.3, 136.3, 133.0, 128.0, 127.2, 126.6, 114.2, 68.2, 64.0, 55.4, 35.5, 31.2; IR (KBr) ῡ 3466, 2966, 2084, 1632, 1514, 1397, 1304, 1249, 1141, 1032; HRMS (ESI-TOF) calcd for (M + Na)$^+$ 371.1290, found 371.1288.

2-(Butylsulfonyl)-1-(4-chlorophenyl)ethanol (3bd). R_f = 0.32 (20% ethyl acetate in hexane); White solid; yield 54% (74 mg); mp 97-99 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.28 (m, 4H), 5.39-5.34 (m, 1H), 3.36 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.22 (d, *J* = 2.0 Hz, 1H), 3.18-3.05 (m, 3H), 1.90-1.80 (m, 2H), 1.53-1.43 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.7, 134.5, 129.3, 127.2, 68.4, 60.4, 54.7, 24.0, 21.9, 13.7; IR (KBr) ῡ 3422, 3055, 2987, 2685, 2410, 2305, 2124, 1640, 1551, 1421, 1265, 1127, 895; HRMS (ESI-TOF) calcd for $C_{12}H_{17}ClO_3S$ (M + Na)$^+$ 299.0479, found 299.0501.

1-([1,1'-biphenyl]-4-yl)-2-(butylsulfonyl)ethanol (3ed). R_f = 0.30 (20% ethyl acetate in hexane); White solid; yield 85% (90 mg); mp 115-118 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.54 (m, 4H), 7.53-7.40 (m, 4H), 7.39-7.33 (m, 1H), 5.44 (d, *J* = 10.0 Hz, 1H), 3.45 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.23-3.05 (m, 4H), 1.93-1.82 (m, 2H), 1.52-1.46 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.5, 140.2, 129.0, 127.8, 127.7, 127.2, 126.3, 68.9, 60.5, 54.7, 24.0, 21.9, 13.7; IR (KBr) ῡ 3422, 3056, 2988, 2306, 2115, 1641, 1534, 1421, 1265, 895; HRMS (ESI-TOF) calcd for $C_{18}H_{22}O_3S$ (M + Na)$^+$ 341.1182, found 341.1162.

1-(4-Bromophenyl)-2-(butylsulfonyl)ethanol (3fd). R_f = 0.31 (20% ethyl acetate in hexane); White solid; yield 42% (62 mg); mp 94-95 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.45 (m, 2H), 7.28-7.25 (m, 2H), 5.33 (dd, *J* = 10.0, 2.0 Hz, 1H), 3.35 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.30 (d, *J* = 2.8 Hz, 1H), 3.16-3.04 (m, 3H), 1.90-1.77 (m, 2H), 1.55-1.40 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 132.2, 127.5, 122.6, 68.4, 60.4, 54.7, 24.0, 21.8, 13.7; IR (KBr) ῡ 3442, 2965, 2875, 2115, 1639, 1527, 1489, 1398, 1124, 1069, 1010; HRMS (ESI-TOF) calcd for $C_{12}H_{17}BrO_3S$ (M + Na)$^+$ 342.9974, found 342.9987.

2-(Butylsulfonyl)-1-(naphthalen-2-yl)ethanol (3hd). R_f = 0.33 (20% ethyl acetate in hexane); White solid; yield 58% (66 mg); mp 112-114 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.80 (m, 4H), 7.55-7.44 (m, 3H), 5.56 (d, *J* = 10.0 Hz, 1H), 3.49 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.37-3.08 (m, 4H), 1.92-1.82 (m, 2H), 1.53-1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 133.37, 133.36, 129.1, 128.2, 127.9, 126.8, 126.6, 124.9, 123.3, 69.2, 60.5, 54.7, 24.0, 21.8, 13.7; IR (KBr) ῡ 3422, 2104, 1640, 1264, 1128, 803; HRMS (ESI-TOF) calcd for $C_{16}H_{20}O_3S$ (M + Na)$^+$ 315.1025, found 315.1014.

2-Tosyl-1-(4-(trifluoromethyl)phenyl)ethanol (3na): R_f = 0.30 (20% ethyl acetate in hexane); White solid; yield 46% (55 mg); mp 98-100 ºC; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.34 (d, *J* = 10.0 Hz, 1H), 3.91 (s, 1H), 3.44 (dd, *J* = 14.4, 10.0 Hz, 1H), 3.32 (d, *J* = 14.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 145.7, 144.6, 136.0, 130.4, 128.1, 126.20, 125.84 (q, *J* = 3.7 Hz), 124.8, 123.3, 68.1, 63.9, 21.8; IR (KBr) ῡ 3400, 3034, 2986, 2928, 2306, 2106, 1926, 1633, 1494, 1412, 1324, 1162, 1133, 1066, 1016; HRMS (ESI-TOF) calcd for $C_{16}H_{15}F_3O_3S$ (M + Na)$^+$ 367.0579, found 367.0586.

Preparation of sulfothionic acid (4). *p*-Toluenesulfonyl hydrazide (100 mg, 0.54 mmol) was allowed to stir at standard condition for 8 h. Then the mixture was concentrated under vacuum and purified through silica gel column chromatography to afford the 14% of **4**.

S-p-Tolyl-4-methylbenzenesulfonothioate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.25-7.19 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 142.2, 140.6, 136.6, 130.3, 129.5, 127.8, 124.8, 21.8, 21.62.

H_2O^{18} Labelling experiments. An oven dried schlenk tube was charged with dry CH_3CN (3.0 mL), styrene (60 mg, 0.522 mmol), *p*-toluenesulfonyl hydrazide (146 mg, 0.784 mmol), iodine (13.2 mg, 0.052 mmol), pyridine (4.5 µL, 0.052 mmol). Then 0.5 mL of H_2O^{18} was added to the reaction mixture and stirred at 70 ºC for 7 h. After that the mixture was concentrated under vacuum and diluted with ethyl acetate. The solution was washed with water and dried over anhyd sodium sulphate. Silica gel column chromatographic purification of the crude product afforded 96% of **3aa.**

O^{18} Labelling experiments. An oven dried schlenk tube was charged with dry CH_3CN (3.0 mL), styrene (60 mg, 0.52 mmol), *p*-toluenesulfonyl hydrazide (146 mg, 0.78 mmol), iodine (13.2 mg, 0.052 mmol), pyridine (4.5 µL, 0.052 mmol) in a glove box. After taking out the schlenk tube from glove box $^{18}O_2$ gas purged and stirred at 70 ºC for 7 h. After that the mixture was concentrated under vacuum and diluted with ethyl acetate. The solution was washed with water and dried over anhyd sodium sulphate. Silica gel column chromatographic purification of the crude product afforded **3aa** in 77% yield.

CCDC-1543183 (**3da)** and CCDC-1543008 (**3hd)** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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