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Oxyhalogenation of thiols and disulfides into sulfonyl chlorides/bromides using oxone-KX (X = Cl or Br) in water†

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A simple and rapid method for efficient synthesis of sulfonyl chlorides/bromides by oxyhalogenation of thiols and disulfides with oxone-KX (X = Cl or Br) using water as the solvent is described.

Introduction

Organic sulfonyl chlorides are highly important as protecting agents in organic synthesis[1] and they are also useful precursors for preparation of sulfonic acids, sulfonamides and sulfonates. In addition, they are industrially important building blocks for manufacture of elastomers, pharmaceuticals, dyes, detergents, ion exchange resins, herbicides, *etc.*[2] Sulfonyl chlorides are generally prepared by oxychlorination of thiols and disulphides using aqueous chlorine.[3] Many methods are available in the literature to accomplish this reaction using a variety of reagents such as $SOCl_2$–H_2O_2,[4] $POCl_3$–H_2O_2,[5] $TiCl_4$–H_2O_2,[6] and Me_3SiCl–KNO_3.[7] The other important approaches for preparation of sulfonyl chlorides include chlorination of sulfonic acid using reagents such as 2,4,6-trichloro-1,3,5-triazine,[8] thionylchloride, and trichloroacetonitrile-triphenylphosphene[9] and reactions of Grignard reagents with sulfur dioxide and thionyl chloride.[10] In most of these methods, toxic and highly corrosive reagents were used and reaction was carried out using organic solvents. These methods also suffer from one or more disadvantages such as vigorous reaction conditions, formation of side products, long reaction times and tedious workup procedures for isolation of the pure products. Therefore, development of a milder and practical method for the synthesis of sulfonyl chlorides is highly desirable.

The growing usage of volatile organic solvents in industry has become a major environmental concern, and in recent years, studies on development of 'green' processes by replacing toxic-organic solvents with alternative non-toxic media have gained high importance.[11] Water is a non-flammable, non-toxic, inexpensive, and abundantly available solvent. In the literature, many organic transformations were known to proceed very efficiently in water medium. Application of water as a reaction medium also has several other advantages. For example, it enables more control on exothermic reactions due to its high specific heat capacity. In a biphasic reaction system, organic products can be easily isolated by phase separation or by simple filtration. Water, with its dense network of hydrogen bonds, can highly influence the reactivity of a substrate. Water has a high dielectric constant and low molecular size and hence, it can dissolve polar and ionic compounds such as salts, surfactants, cyclodextrins, *etc.* very efficiently. For this reason, water is often used as a co-solvent for carrying out reactions between an organic substrate and a reactive inorganic salt such as peroxysulfates, permanganates, perhalates, nitrates, *etc*.

Results and discussion

Oxone or potassium peroxymonosulfate [$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$] is an inexpensive, environmentally benign and widely used stable oxidant. It has been extensively studied in the literature for a variety of oxidative transformations and some other important reactions such as oxidation of alkenes to epoxides,[12] thioethers to sulfones,[13] aldehydes to carboxylic acids,[14] tertiary amines to amine oxides,[15] *etc.* It is also shown to be useful for promoting aromatic bromination,[16] hydroxybromination,[17] and benzylic oxidation[18] reactions in the presence of salts such as NH_4Br, KBr, *etc.* Recently we found that alkynes undergo efficient oxyhalogenation with oxone-KX (X = Cl, Br or I) and convert into α,α-dihaloketones.[19] In continuation of our research interest on oxone mediated oxyhalogenation reactions, we herein report a new application of oxone-KX (X = Cl or Br) for efficient preparation of sulfonyl chlorides (68–98%) and sulfonyl bromides (89–96%) from thiols and disulfides by oxyhalogenation reaction under mild conditions using water as a reaction medium as shown in Scheme 1.

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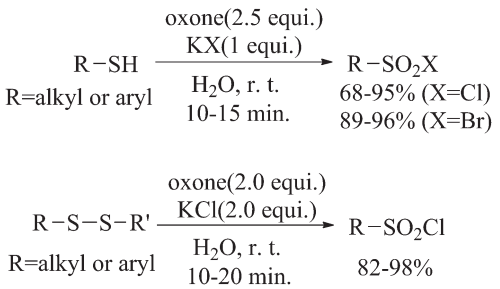
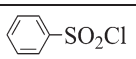
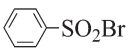
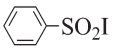
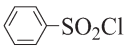
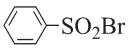
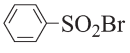
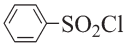
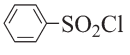
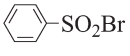


Scheme 1 Synthesis of sulfonyl halides from thiols and disulfides with oxone-KX in water.

In our preliminary experiments, reaction of thiophenol with 0.5 equivalent of oxone and 0.5 equivalent of KCl in water at room temperature was found to produce diphenyl disulfide in a quantitative yield. However, when 1.0 equivalent of oxone and 1.0 equivalent of KCl were used in this reaction, we obtained a mixture of diphenyl disulfide and sulfonyl chloride and with 2.5 equivalents of oxone and 1.0 equivalent of KCl, we obtained phenylsulfonyl chloride in 98% yield. In our study, oxone was found to promote this reaction effectively also with other halogen sources such as aq. HCl, NaCl, KBr, KI, aq. HBr, $AlCl_3$, $FeCl_3$, $ZnCl_2$ and NH_4Br, which gave benzenesulfonyl halide in 88–98% yields in 10–20 minutes. These results are shown in Table 1.

Here, though we could prepare phenyl sulfonyl iodide in high yield (90%) by this method using oxone-KI, it was found to be highly unstable and decomposed rapidly at room temperature. We also studied the scope of oxyhalogenation of a thiol with other oxidants such as 2-iodoxybenzoic acid (IBX), sodium periodate, 30% hydrogen peroxide, *m*-chloroperbenzoic acid (mCPBA) and *t*-butyl hydrogen peroxide (TBHP). For example, results observed in the reaction of thiophenol with these oxidants in the presence of KCl at room temperature using water as the solvent are shown in Table 2. In this study, IBX was found to produce a mixture of disulphenyl disulfide and phenyl sulfonyl chloride in a 2 : 1 ratio and with sodium periodate, we obtained only diphenyl disulfide in a quantitative yield and no reaction was observed with the other oxidants, *i.e.* H_2O_2, mCPBA and TBHP, under the reaction conditions.

Table 1 Screening of various halogen sources

S. no.	Halogen source	Product	Reaction time (min)	%Yield[a]
1	KCl		10	98
2	KBr		10	97
3	KI		15	90
4	NaCl		10	95
5	NaBr		15	90
6	NH_4Br		12	90
7	$AlCl_3$		10	98
8	50% aq. HCl		12	89
9	48% aq. HBr		10	88
10		N.R.	—	—

[a] Isolated yields.

Table 2 Reaction of thiophenol and KCl with various oxidants

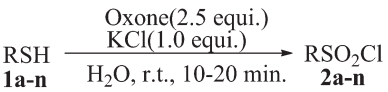
S. no.	Oxidant	Reaction time (h)	%Yield[a] PhSSPh	%Yield[a] $PhSO_2Cl$
1	IBX	10	68	22
2	$NaIO_4$	10	98	0
3	H_2O_2	10	No reaction	
4	*m*-CPBA	10	No reaction	
5	TBHP	10	No reaction	

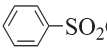
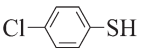
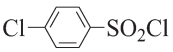
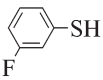
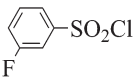
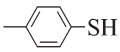
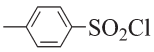
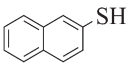
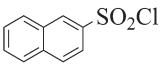
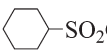
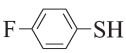
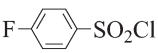
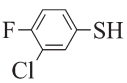
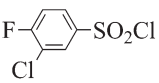
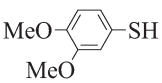
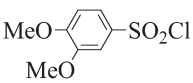
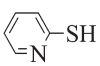
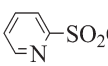
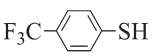
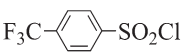
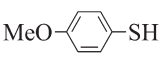
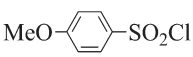
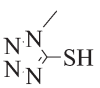
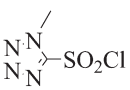
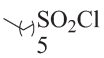
[a] Isolated yields. Reactions were studied at room temperature using 2.5 equiv. of oxidant and 1 equiv. of KCl in water.

In the study of screening of halogen sources (Table 1), we found formation of sulfonyl chlorides and bromides in maximum yields with KCl and KBr respectively. Next, we studied oxychlorination of a variety of aliphatic, aromatic and heteroaromatic thiols **1a–n** with oxone-KCl in water and obtained the corresponding sulfonyl chlorides **2a–n** in 68–95% yields as shown in Table 3. Using a similar procedure, we studied oxybromination of thiols **1a–f** with oxone-KBr and observed formation of the corresponding sulfonyl bromines **3a–f** in 89–96% yields as shown in Table 4. Chloride and, at the end of reaction, no disulfide was observed and only sulfonyl chloride formed. In a control experiment, reaction of thiophenol with 0.5 equivalent of oxone and 0.5 equivalent of KCl gave diphenyl disulfide in 96% yield in 10 min. It shows that oxone-KCl initially oxidizes thiol into disulfide, which undergoes further reaction and converts into sulfonyl chloride. We prepared a variety of symmetrical disulfides, which were found to undergo efficient oxyhalogenation with 2 equivalents of oxone and 2 equivalents of KCl in water at room temperature producing sulfonyl chlorides in 82–98% yields as shown in Table 5.

The plausible mechanism for transformation of thiols into sulfonyl halides *via* disulfides by reaction with oxone-KX is shown in Scheme 2. In this mechanism, oxone initially reacts with KX in water and produces hypohalous acid (HOX).[20] Next, hypohalous acid reacts with thiol to produce sulfinyl halide, which converts into a disulfide by reaction with another molecule of thiophenol. In the subsequent steps, disulfide reacts with HOX and converts into RS(O)-S(O)R. It is amply reported in the literature that RS(O)-S(O)R rapidly rearranges into RSO_2-

Table 3 Synthesis of sulfonyl chloride from thiols with oxone-KCl



Entry	RSH **1**	RSO_2Cl **2**	Reaction time (min)	%Yield[a]
a			10	98
b			15	97
c			12	95
d			12	96
e			15	92
f			10	89
g			15	95
h			15	92
i			12	90
j			10	88
k			10	90
1			20	93
m			15	88
n			12	68

[a] Isolated yields. All products gave satisfactory spectral data.

SR,[21] which upon reaction with HCl cleaves into RSO_2X and RSH. RSH undergoes a few more similar reaction cycles and converts into RSO_2X. In our study, we found that the present oxyhalogenation of a thiol into sulfonyl halide requires 2.5 equivalents of oxone and 1.0 equivalent of KX and it is in accordance with the proposed mechanism.

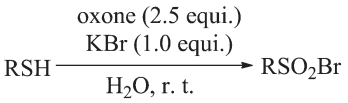
Conclusions

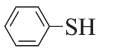
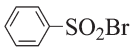
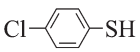
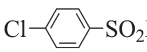
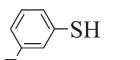
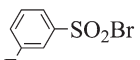
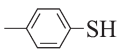
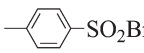
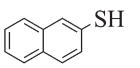
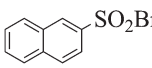
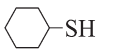
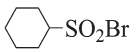
In conclusion, we showed an efficient and rapid method for preparation of sulfonyl chlorides and bromides in high yields by oxyhalogenation of thiols and disulfides with oxone-KX (X = Cl or Br) under mild conditions using water as a solvent.

General information

Oxone, *N*-chlorosuccinimide, NH_4Br, and KBr were purchased from Sigma-Aldrich Ltd, India. HCl, HBr, NaCl, KCl, KI, $AlCl_3$, and solvents used in this study were procured from SD Fine Chem. Ltd, India. Melting points of the compounds were recorded on Veego programmable melting point apparatus in open capillaries and are uncorrected. IR spectra were recorded on a PerkinElmer FT-IR 240-C spectrophotometer using KBr and neat optics. ^1H NMR spectra were recorded on a Bruker AV 300 MHz in $CDCl_3$ using TMS as the internal standard. All the

Table 4 Oxybromination of thiols with oxone-KBr

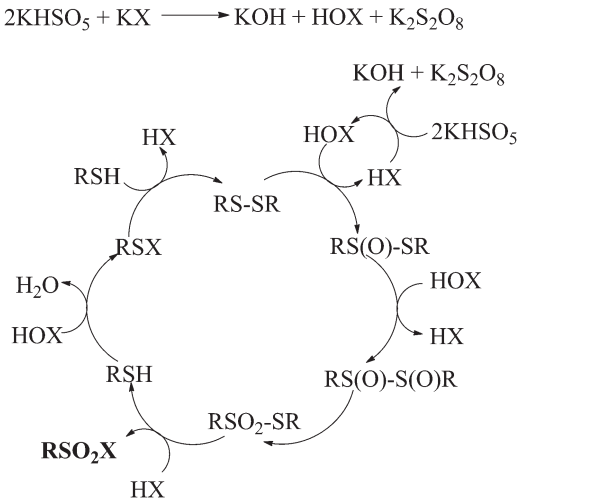


Entry	RSH **1**	RSO_2Br **3**	Reaction time (min)	%Yield[a]
a			10	96
b			10	95
c			12	92
d			10	89
e			15	90
f			10	95

[a] Isolated yields. All products gave satisfactory spectral data.

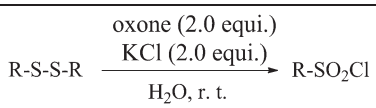
reactions were monitored by thin layer chromatography (TLC) on precoated silica gel 60 F254 (mesh); spots were visualized with UV light or by charring with anisaldehyde solution. Merck silica gel (60–120 mesh) was used for column chromatography.

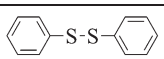
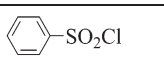
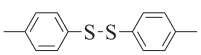
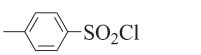
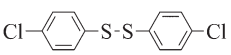
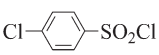
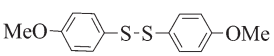
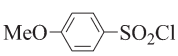
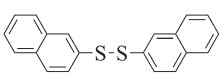
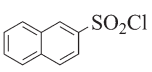
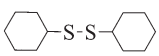
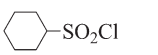
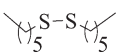
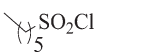
General procedure for the preparation of sulfonyl chlorides with oxone-KX. A mixture of thiol (3.4 mmol), oxone (8.6 mmol), KCl (3.4 mmol), and water (10 mL) was taken in a round bottomed flask and stirred at room temperature. This reaction is slightly exothermic and the temperature of the mixture rose to 45 °C. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (silica gel 60–120 mesh, *n*-hexane) to obtain the corresponding sulfonyl chloride. A similar procedure was used for preparation of sulfonyl bromides with oxone-KBr.



Scheme 2 Plausible mechanism for transformation of thiols and disulfides into sulfonyl halides with oxone-KX.

Table 5 Preparation of sulfonyl chlorides from disulfides with oxone-KCl



S. no.	R–S–S–R	RSO_2Cl	Reaction time (min)	%Yield[a]
1			10	95
2			10	96
3			12	94
4			10	82
5			15	98
6			10	90
7			10	91

[a] Isolated yields. All products gave satisfactory spectral data.

General procedure for the preparation of sulfonyl chlorides from disulfides. A mixture of disulfide (1.7 mmol), oxone (3.5 mmol) KCl (3.5 mmol), and water (10 mL) was taken in a round bottomed flask and stirred at room temperature. After completion of the reaction (TLC), the reaction mixture was extracted with ethyl acetate (4 × 5 mL) and the combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product obtained was purified by normal column chromatography (silica gel 60–120 mesh, *n*-hexane) to obtain the corresponding sulfonyl chloride.

Characterization data of sulfonyl halides 2a–n and 3a–f

Benzenesulfonyl chloride (2a). Colorless oil (0.31 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05–8.04 (m, 2H), 7.76 (t, J = 7.3 Hz, 1H), 7.62 (t, J = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.4, 133.6, 131.3, 129.3, 128.7, 127.4; IR (neat): ν 3065, 2926, 2855, 1444, 1326, 1144, 1077, 750, 593 cm^{-1}. EI-MS 176, 159, 112, 95, 75, 57; EI-HRMS: exact mass observed for $C_6H_5ClO_2S$: 175.9695 (calculated: 175.9698).

4-Chlorobenzene-1-sulfonyl chloride (2b). White solid (0.28 g, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.6 Hz, 2H) 7.60 (d, J = 8.6 Hz, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 140.4, 137.6; IR (neat): ν 3109, 3052, 1573, 1474, 1184, 1088, 825, 755, 559 cm^{-1}. EI-MS 212, 201, 177, 175, 111, 75, 69; EI-HRMS: exact mass observed for $C_6H_4Cl_2O_2S$: 209.9319 (calculated: 209.9309).

3-Fluorobenzene-1-sulfonyl chloride (2c). Pale yellow solid (0.28 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 6.69 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 131.4, 122.7, 122.4, 114.1, 113.7; IR (neat): ν 3108, 3056, 2927, 2757, 1593, 1474, 1368, 1228, 1163, 884, 595 cm^{-1}. EI-HRMS: exact mass observed for $C_6H_4ClFO_2S$: 193.9602 (calculated: 193.9604).

4-Methylbenzene-1-sulfonyl chloride (2d). White solid (0.29 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 2.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.8, 130.2, 126.9, 21.7; IR (KBr): ν 3009, 1690, 1598, 1481, 1231, 993, 796 cm^{-1}. EI-MS 191, 175, 128, 111, 75, 55; EI-HRMS: exact mass observed for $C_7H_7ClO_2S$: 189.9854 (calculated: 189.9855).

Naphthalene-1-sulfonyl chloride (2e). White solid (0.25 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 8.08–7.96 (m, 4H), 7.78–7.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.3, 130.2, 129.8, 128.9, 128.3, 128.1, 121.2; IR (neat): ν 3108, 3073, 2928, 1589, 1492, 1380, 1182, 1081, 840 cm^{-1}. EI-MS: 226, 210, 208, 146, 127, 115, 77, 57; EI-HRMS: exact mass observed for $C_{10}H_7ClO_2S$: 225.9854 (calculated: 225.9855).

Cyclohexanesulfonyl chloride (2f). Colorless oil (0.27 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56–3.46 (m, 1H), 2.42–2.37 (m, 2H), 2.01–1.95 (m, 2H), 1.75–1.62 (m, 3H), 1.48–1.18 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 74.7, 27.0, 24.8, 24.5; IR (neat): ν 2938, 2859, 1451, 1369, 1219, 1160, 751, 589 cm^{-1}; EI-MS: *m*/*z*. 182, 118, 99, 83, 67, 55; EI-HRMS: exact mass observed for $C_6H_{11}ClO_2S$: 182.0164 (calculated:182.0168).

4-Fluorobenzene-1-sulfonyl chloride (2g). Colorless oil (0.28 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.10–8.07 (m, 2H), 7.33–7.28 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.1, 130.1, 130.0, 117.2, 116.9; IR (neat): ν 3108, 3073, 2928, 1589, 1492, 1380, 1182, 840, 569 cm^{-1}. EI-HRMS: exact mass observed for $C_6H_4ClFO_2S$: 193.9601 (calculated: 193.9604).

3-Chloro-4-fluorobenzene-1-sulfonyl chloride (2h). Colorless oil (0.25 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.14 (dd, J = 2.4 Hz, 1H), 8.01–7.92 (m, 1H), 7.43–7.39 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.7, 130.1, 127.8, 127.6, 118.2, 117.8; IR (neat): ν 2927, 2757, 1593, 1474, 1228, 1163, 1101, 884 cm^{-1}. EI-MS: 227, 224, 195, 193, 129. 129, 109, 94, 79; EI-HRMS: exact mass observed for $C_6H_3Cl_2FO_2S$: 227.9211 (calculated: 227.9214).

3,4-Dimethoxybenzene-1-sulfonyl chloride (2i). White solid (0.24 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.68 (dd, J = 2.2 Hz, 1H), 7.44 (d, J = 2.2 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.6, 149.2, 135.8, 121.6, 110.4, 108.9, 56.4, 56.3; IR (neat): ν 2929, 2862, 1461, 1406, 1229, 1183, 1119, 1034, 819 cm^{-1}. EI-MS: 236, 201, 153, 137, 94, 79; EI-HRMS: exact mass observed for $C_8H_{10}ClO_4S$: 235.9916 (calculated: 235.9910).

Pyridine-2-sulfonyl chloride (2j). Colorless oil (0.28 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.64–8.55 (m, 1H), 7.98–7.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-D_6): δ = 155.2, 146.0, 140, 126.1, 123.3; IR (neat): ν 3029, 1453, 1028, 638 cm^{-1}. EI-MS 177, 175, 159, 111, 69, 57; EI-HRMS: exact mass observed for $C_5H_4ClO_2S$: 176.96526 (calculated: 176.96513).

4-(Trifluoromethyl)benzene-1-sulfonyl chloride (2k). Colourless oil (0.24 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, J = 8.3 Hz, 2H), 7.92 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 147.0, 136.9, 136.4, 136.1, 127.6, 127.0, 126.9; IR (neat): ν 3026, 1454, 1242, 1145, 1014, 940, 780 cm^{-1}; EI-HRMS: exact mass observed for $C_7H_4ClF_3O_2S$: 243.9569 (calculated: 243.9572).

4-Methoxybenzene-1-sulfonyl chloride (2l). Colorless oil (0.27 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 132.6, 128.3, 114.5, 55.3; IR (neat): ν 3052, 3007, 2926, 2854, 1574, 1463, 1367, 1281, 1171, 1088, 944 cm^{-1}. EI-MS 206, 190, 175, 142, 75, 55; EI-HRMS: exact mass observed for $C_7H_7ClO_3S$: 205.9803 (calculated: 205.9804).

1-Methyl-1*H*-tetrazole-5-sulfonyl chloride (2m). Colorless oil (0.27 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 40.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.08; IR (neat): ν 2928, 2858, 1633, 1343, 1056, 771 cm^{-1}. Mass: ESI-MS: 181 (M + H), 203 (M + Na).

Hexane-1-sulfonyl chloride (2n). Colorless oil (0.21 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.38 (t, J = 7.3, 7.4 Hz, 2H), 1.69–1.62 (m, 2H), 1.41–1.30 (m, 6H), 0.89 (t, J = 6.6, 6.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.5, 36.1, 31.0, 23.3, 22.3, 13.8; IR (neat): ν 2929, 2857, 1463, 1378, 1256, 988, 725 cm^{-1}. EI-MS: 184, 141, 125, 109, 77, 69, 57; EI-HRMS: exact mass observed for $C_6H_{13}ClO_2S$: 184.0322 (calculated: 184.0324).

Benzenesulfonyl bromide (3a). Colorless oil (0.38 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02–7.99 (m, 2H), 7.76 (t, J = 7.3 Hz, 1H), 7.63 (t, J = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.4, 133.6, 131.3, 129.3, 128.7, 127.4; IR (neat): ν 3022, 2919, 1489, 1329, 1143, 806, 653 cm^{-1}. EI-MS 220, 171, 158, 137, 97, 69; EI-HRMS: exact mass observed for $C_6H_5ClO_2S$: 219.91920 (calculated: 219.91936).

4-Chlorobenzene-1-sulfonyl bromide (3b). White solid (0.35 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.6 Hz, 2H), 7.60 (d, J = 8.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.4, 140.4, 130.0; IR (neat): ν 3109, 3052, 1573, 1474, 1184, 1088, 825, 755, 559 cm^{-1}. EI-MS 256, 254, 177, 175, 113, 111, 75, 76; EI-HRMS: exact mass observed for $C_6H_4Cl_2O_2S$: 253.87998 (calculated: 253.88039).

3-Fluorobenzene-1-sulfonyl bromide (3c). Colorless oil (0.34 g, 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84–7.80 (m, 2H), 7.72–7.60 (m, 2H), 7.49–7.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.5, 131.4, 122.7, 122.4, 114.1, 113.7; IR (neat): ν 3073, 2938, 1564, 1485, 1378, 1192, 846 cm^{-1}. EI-HRMS: exact mass observed for $C_6H_4BrFO_2S$: 237.9096 (calculated: 237.9099).

4-Methylbenzene-1-sulfonyl chloride (3d). White solid (0.33 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.20, 136.81, 130.06, 126.40, 21.80; IR (KBr): ν 3010, 2923, 1584, 1457, 1027, 696 cm^{-1}. EI-MS 234, 202, 186, 171, 139, 123, 107, 92, 77; EI-HRMS: exact mass observed for $C_7H_7BrO_2S$: 233.9348 (calculated: 233.9350).

Naphthalene-2-sulfonyl bromide (3e). Pale yellow solid (0.30 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 8.10–7.99 (m, 4H), 7.80–7.70 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.6, 132.1, 130.3, 130.1, 129.9, 128.3, 128.1, 121.0; IR (neat): ν 3063, 2946, 1589, 1455, 1237, 1025, 840 cm^{-1}. EI-MS: 270, 185, 149, 139, 123, 69, 57; EI-HRMS: exact mass observed for $C_{10}H_7ClO_2S$: 269.93500 (calculated: 269.93501).

Cyclohexanesulfonyl bromide (3f). Colorless oil (0.37 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54–3.44 (m, 1H), 2.40–2.36 (m, 2H), 1.97–1.94 (m, 2H), 1.73–1.60 (m, 3H), 1.45–1.12 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 74.7, 27.0, 24.8, 24.5; IR (neat): ν 2938, 2859, 1451, 1369, 1219, 1160, 751, 589 cm^{-1}; EI-MS: m/z. 227, 225, 191, 163, 148, 111, 97, 83, 69, 55; EI-HRMS: exact mass observed for $C_6H_{11}BrO_2S$: 225.9661 (calculated: 225.9663).

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