Supporting Information
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1. General methods

All the chemicals used in present study were purchased from the commercial suppliers and used as such. HPLC grade solvents were used to conduct the experiments without drying. Analytical thin layer chromatography was done on Merck DC-Alufolien SiO2 60 F254 0.2 mm thick precoated TLC plates. Column chromatography was performed using commercially available silica gel (60 Å, 40-63 μm). 1H NMR and 13C NMR spectra were recorded with 500 MHz Ultrashield Plus 500 spectrometer and 125 MHz on a Bruker instrument. 1H NMR and 13C NMR spectra were recorded with 500 MHz Ultrashield Plus 500 spectrometer and 126 MHz on a Bruker instrument. The chemical shifts (δ) are reported in ppm using the solvent residual peak as reference and all coupling constants (J) are expressed in Hertz (Hz). The following abbreviations are used for multiplicity for NMR resonances: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. HPLC and LC-MS: HPLC analysis was performed on a Dionex UltiMate 3000 system, which incorporates an UltiMate 3000 diode array UV/Vis detector capable of measuring absorbance of light in the 190 – 800 nm range. LC-MS analyses were carried out by connecting the above mentioned HPLC apparatus to a Bruker MicroTOF-QII system equipped with an ESI source with nebulizer gas at 1.2 bar, dry gas at 10 L/min, dry temperature at 200 °C, capillary at 4500 V and end plate offset at -500 V. The ion transfer was conducted with funnel 1 and funnel RF’s at 200.0 Vpp and hexapole RF at 100.0 Vpp while the quadrupole ion energy was set at 5.0 eV with a low mass cut-off at 100.00 m/z. In the collision cell, collision energy was set at 8.0 eV, collision RF at 100.0 Vpp, and a transfer time of 80.0 μs and pre-pulse storage of 1.0 μs were used.
2. Characterization data of products:

(benzylsulfonyl)benzene (2a)

The title compound was synthesized using benzyl bromide as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 94%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66 – 7.56 (m, 3H), 7.47 – 7.42 (m, 2H), 7.35 – 7.29 (m, 1H), 7.28 – 7.23 (m, 2H), 7.13 – 7.04 (m, 2H), 4.31 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.0, 133.8, 131.0, 129.0, 128.9, 128.8, 128.7, 128.3, 63.0. HRMS (EI) m/z calculated for C$_{13}$H$_{13}$O$_2$S [M+H]$^+$ 233.0636, found 233.0636.

(methylsulfonyl)benzene (2b)

The title compound was synthesized using methyl iodide as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 92%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.98 – 7.93 (m, 2H), 7.68 – 7.63 (m, 1H), 7.60 – 7.55 (m, 2H), 3.06 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 140.7, 133.8, 129.5, 127.5, 44.6. HRMS (EI) m/z calculated for C$_7$H$_9$O$_2$S [M+H]$^+$ 157.0323, found 157.0320.

1-Phenylsulfonylbutane (2c)

The title compound was synthesized using both butyl iodide and butyl bromide as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 94%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94 – 7.88 (m, 2H), 7.69 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 3.12 – 3.06 (m, 2H), 1.75 – 1.64 (m, 2H), 1.39 (h, $J$ = 7.4 Hz, 2H), 0.89 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.4, 133.7, 129.4, 128.2, 56.2, 24.8, 21.7, 13.6. HRMS (EI) m/z calculated for C$_{10}$H$_{15}$O$_2$S [M+H]$^+$ 199.0793, found 199.0791.

(2-Propen-1-ylsulfonyl)benzene (2d)

The title compound was synthesized using allyl bromide as an electrophile and isolated as colorless oil after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 92%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.94 – 7.83 (m, 2H), 7.69 – 7.59 (m, 1H), 7.60 – 7.50 (m, 2H), 5.79 (ddt, $J$ = 17.4, 10.1, 7.4 Hz, 1H), 5.33 (d, $J$ = 10.1 Hz, 1H), 5.14 (dd, $J$ = 17.0, 1 Hz, 1H), 3.81 (d, $J$ = 7.4 Hz, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 138.4, 133.9, 129.2, 128.6, 124.9, 124.8, 61.0. HRMS (EI) m/z calculated for C$_9$H$_{11}$O$_2$S [M+H]$^+$ 183.0480, found 183.0477.

1-Phenylsulfonyldecane (2e)

The title compound was synthesized using 1-bromo dodecane as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 92%. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.93 – 7.88 (m, 2H), 7.65 (m, 1H), 7.57 (m, 2H), 3.11 – 3.04 (m, 2H), 1.70 (m, 2H), 1.37 – 1.19 (m, 20H), 0.87 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 139.4, 133.7, 129.4, 128.2, 56.5, 32.0, 29.7, 29.6, 29.5, 29.4, 29.1, 28.4, 22.8, 22.8, 14.2. HRMS (EI) m/z calculated for C$_{18}$H$_{31}$O$_2$S [M+H]$^+$ 311.2045, found 311.2046.
((1-Methylethyl)sulfonyl)benzene (2f)

The title compound was synthesized using 2-bromopropane as an electrophile and isolated as colorless oil after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 68%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.96 – 7.86 (m, 2H), 7.73 – 7.65 (m, 1H), 7.59 (dd, $J = 8.4, 7.2$ Hz, 2H), 3.22 (hept, $J = 6.9$ Hz, 1H), 1.32 (d, $J = 6.9$ Hz, 6H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 137.1, 133.7, 129.5, 129.2, 55.7, 15.8. HRMS (EI) m/z calculated for C$_9$H$_{13}$O$_2$S [M+H]$^+$ 185.0636, found 185.0654.

((methylsulfonyl)methyl)benzene (2i)

The title compound was synthesized using benzyl bromide as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 82%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.41 (s, 5H), 4.25 (s, 2H), 2.75 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 130.6, 129.3, 128.5, 61.5, 39.1. HRMS (EI) m/z calculated for C$_8$H$_{11}$O$_2$S [M+H]$^+$ 171.0480, found 171.0484.

((ethylsulfonyl)methyl)benzene (2j)

The title compound was synthesized using benzyl bromide as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 84%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.49 – 7.31 (m, 5H), 4.22 (s, 2H), 2.85 (q, $J = 7.5$ Hz, 2H), 1.35 (t, $J = 7.5$ Hz, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 130.6, 129.2, 129.2, 128.2, 58.9, 45.5, 6.6. HRMS (EI) m/z calculated for C$_9$H$_{13}$O$_2$S [M+H]$^+$ 185.0636, found 185.0635.

1-phenyl-2-(phenylsulfonyl)ethan-1-one (2k)

The title compound was synthesized using 2-bromoacetophenone as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 92%. $^1$H NMR (500 MHz, CDCl$_3$) δ 7.95 – 7.93 (m, 2H), 7.91 – 7.89 (m, 2H), 7.68 – 7.60 (m, 2H), 7.60 – 7.54 (m, 2H), 7.50 – 7.47 (m, 2H), 4.74 (s, 2H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 188.1, 138.9, 135.9, 134.5, 129.4, 129.4, 129.0, 128.7, 63.6. HRMS (EI) m/z calculated for C$_{14}$H$_{13}$O$_3$S [M+H]$^+$ 261.0585, found 261.0586.

2-(methylsulfonyl)-1-phenylethan-1-one (2l)

The title compound was synthesized using 2-bromoacetophenone as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 82%. $^1$H NMR (500 MHz, CDCl$_3$) δ 8.03 – 7.98 (m, 2H), 7.70 – 7.63 (m, 1H), 7.57 – 7.49 (m, 2H), 4.60 (s, 2H), 3.15 (s, 3H). $^{13}$C NMR (126 MHz, CDCl$_3$) δ 189.3, 135.7, 134.9, 129.4, 129.2, 61.4, 41.9. HRMS (EI) m/z calculated for C$_9$H$_{11}$O$_3$S [M+H]$^+$ 199.0429, found 199.0426.
2-(ethylsulfonyl)-1-phenylethan-1-one (2m)

The title compound was synthesized using 2-bromoacetophenone as an electrophile and isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 85%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.04 – 7.99 (m, 2H), 7.69 – 7.62 (m, 1H), 7.56 – 7.51 (m, 2H), 4.56 (s, 2H), 3.29 (q, \(J = 7.5\) Hz, 2H), 1.47 (t, \(J = 7.5\) Hz, 3H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 189.4, 135.9, 134.8, 129.5, 129.2, 58.9, 48.3, 6.8. HRMS (EI) m/z calculated for C\(_{10}\)H\(_{13}\)O\(_3\)S [M+H]\(^+\) 213.0585, found 213.0587.

4-(phenylsulfonyl)morpholine (4a)

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 95%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.78 – 7.74 (m, 2H), 7.66 – 7.61 (m, 1H), 7.59 – 7.54 (m, 2H), 3.77 – 3.72 (m, 4H), 3.03 – 2.98 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 135.3, 133.2, 129.3, 128.0, 66.2, 46.1. HRMS (EI) m/z calculated for C\(_{10}\)H\(_{14}\)NO\(_3\)S [M+H]\(^+\) 228.0694, found 228.0693.

1-(phenylsulfonyl)piperidine (4b)

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 90%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.76 (m, 2H), 7.62 – 7.55 (m, 1H), 7.55 – 7.49 (m, 2H), 2.99 (t, \(J = 5.5\) Hz, 4H), 1.64 (p, \(J = 5.8\) Hz, 4H), 1.47 – 1.38 (m, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 136.5, 132.7, 129.1, 127.8, 47.1, 25.3, 23.6. HRMS (EI) m/z calculated for C\(_{11}\)H\(_{16}\)NO\(_2\)S [M+H]\(^+\) 226.0905, found 226.0905.

1-(phenylsulfonyl)pyrrolidine (4c)

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 90%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.83 (dd, \(J = 8.4, 1.4\) Hz, 2H), 7.62 – 7.56 (m, 1H), 7.53 (dd, \(J = 8.4, 6.9\) Hz, 2H), 3.29 – 3.21 (m, 4H), 1.79 – 1.73 (m, 4H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 137.1, 132.7, 129.1, 127.6, 48.1, 25.4. HRMS (EI) m/z calculated for C\(_{10}\)H\(_{14}\)NO\(_2\)S [M+H]\(^+\) 212.0760.

N-benzylbenzenesulfonamide (4d)

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 72%. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.92 – 7.84 (m, 2H), 7.62 – 7.55 (m, 1H), 7.51 (m, 2H), 7.31 – 7.24 (m, 3H), 7.23 – 7.16 (m, 2H), 4.75 (t, \(J = 6.3\) Hz, 1H), 4.15 (d, \(J = 6.2\) Hz, 2H). \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.1, 136.3, 132.9, 129.3, 128.9, 128.1, 128.0, 127.3, 47.5. HRMS (EI) m/z calculated for C\(_{13}\)H\(_{14}\)NO\(_2\)S [M+H]\(^+\) 248.0748, found 248.0748.
**N-butylbenzenesulfonamide (4e)**

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 72%. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.90 – 7.85 (m, 2H), 7.61 – 7.56 (m, 1H), 7.54 – 7.49 (m, 2H), 4.47 (t, J = 6.4 \text{ Hz, } 1H), 2.96 (td, J = 7.1, 6.1 \text{ Hz, } 2H), 1.48 – 1.40 (m, 2H), 1.33 – 1.24 (m, 2H), 0.85 (t, J = 7.4 \text{ Hz, } 3H). \]

\[ ^{13}C \text{NMR} (126 \text{ MHz, CDCl}_3) \delta 140.1, 132.7, 129.2, 127.2, 43.1, 31.7, 19.8, 13.6. \]

**HRMS (EI) m/z** calculated for C\textsubscript{10}H\textsubscript{16}NO\textsubscript{2}S [M+H\textsuperscript{+}] 214.0902, found 214.0902.

**N,N-dibenzylbenzenesulfonamide (4f)**

The title compound was isolated as white solid after column chromatography using 10-20% ethyl acetate in petroleum ether. Yield 61%. 

\[ ^1H \text{NMR} (500 \text{ MHz, CDCl}_3) \delta 7.87 – 7.83 (m, 2H), 7.62 – 7.57 (m, 1H), 7.54 – 7.49 (m, 2H), 7.23 – 7.19 (m, 6H), 7.07 – 7.02 (m, 4H), 4.34 (s, 4H). \]

\[ ^{13}C \text{NMR} (126 \text{ MHz, CDCl}_3) \delta 141.0, 135.7, 132.6, 129.3, 128.7, 128.7, 128.6, 127.8, 127.3, 50.6. \]

**HRMS (EI) m/z** calculated for C\textsubscript{20}H\textsubscript{20}NO\textsubscript{2}S [M+H\textsuperscript{+}] 338.1215, found 338.1213.
3. ESI-MS spectra

**Figure S1**: ESI-MS spectra of reaction mixture before addition of electrophile indicating the presence of benzenesulfonic acid (after protonation of sulfinate anion). ESI-MS m/z calculated for C₆H₇O₂S [M+H]⁺ 143.01613, found 143.0162.
4. Copies of NMR spectra