Supporting information

Dual roles of sulfonyl hydrazides in the catalyst-free sulfonylation of unsaturated benzylic alcohols in water

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Part I Experimental Section

1. General information

$^1$H NMR and $^{13}$C NMR were recorded on a Bruker-400MHz Spectrometer ($^1$H NMR: 400 MHz, $^{13}$C NMR: 100 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Commercially available compounds were used without further purification. All solvents were purified according to the standard procedures unless otherwise noted. Substrate 1a-1f, 1g-1l, 4, 5, 7, TsNDND$_2$ (11) was prepared according to the literature procedures.

1.2 Preparation of substrates 1a-1f (1b as an example)

a) Preparation of 2-hydroxybenzaldehyde

\[
\begin{align*}
\text{Ph} & \quad (\text{HCHO}),_n \quad \text{MgCl}_2 \quad \text{Et}_3\text{N}, \text{THF} \\
& \rightarrow \quad \text{Ph} \quad (\text{HO})_2
\end{align*}
\]

*p*-Methyl phenol (2.1 g, 20 mmol), paraformaldehyde (4.2 g), Et$_3$N (10.6 mL, 76 mmol) and MgCl$_2$ (2.8 g, 30 mmol) were mixed in THF (60 mL). After being refluxed for 24 h, the reaction mixture was cooled to room temperature, and its pH was adjusted to 3 with concentrated hydrochloric acid. The resulting aqueous solution was extracted with ethyl acetate (50 mL × 3). The organic layers were separated, combined and dried with Na$_2$SO$_4$. Removal of the solvent gave a crude product which was purified using flash chromatography on a silica gel column with ethyl acetate/petroleum ether = 1/10 as eluent to give a pale yellow solid.

b) Preparation of homoallylic alcohols

To a mixture of 2-hydroxy-5-methylbenzaldehyde (4 mmol) in 8 mL of THF and 16 mL of saturated NH$_4$Cl solution was added zinc powder (0.520 g, 8 mmol) and allyl bromide (700 μL, 8 mmol) at room temperature. After the mixture was stirred for 4 h it was extracted with ethyl acetate for three times. The combined organic extracts were dried using anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The residue was then purified by column chromatography over silica gel to afford the product 1b as a light yellow oil.

1.3 General working procedure for the sulfonylation and control experiments

a) General working procedure for the sulfonylation (3aa as example)

To the mixture of 1a (82 mg, 0.5 mmol) in 2.5 mL water was added tosylhydrazide (186 mg, 1mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 °C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product 3aa as a colorless oil (125 mg, 82% yield).
b) The procedure of control experiments

To the mixture of 1a (82 mg, 0.5 mmol) in 2.5 mL water was added benzene sulfinic acid (142 mg, 1 mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 °C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product 10 as a colorless oil (102 mg, 71% yield).

To the mixture of 1a (82 mg, 0.5 mmol) in 2.5 mL deuterated water was added tosylhydrazide (186 mg, 1 mmol) in a sealed tube. After the mixture was stirred for 12 h at 120 °C, it was extracted with ethyl acetate for three times. The combined organic phase was dried with anhydrous Na₂SO₄ and evaporated under reduced pressure. The resulting residue was purified by column chromatography (PE/EA = 10/1 - 6/1) to afford the product d²-3aa as a colorless oil (123 mg, 81% yield).

**d²-3aa HRMS**

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Figure S1. HRMS spectra of d²-3aa
1.4 Experimental date of the products

2-(1-tosylbutyl)phenol (3aa): Colorless oil in 82% yield (63% yield, with 4 as substrate). $^1$H NMR (400 MHz, CDCl$_3$): δ 7.50-7.48 (d, J = 8.0 Hz, 2H), 7.21-7.14 (m, 3H), 6.86-6.81 (m, 3H), 4.58 (s, 1H), 2.39 (s, 3H), 2.30-2.21 (m, 2H), 1.24-1.14 (m, 2H), 0.88-0.84 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.4, 144.6, 133.9, 129.8, 129.2, 128.9, 120.7, 118.8, 116.9, 62.6, 28.7, 21.5, 19.9, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{29}$O$_2$S [M+H]$^+$ 305.1211, found 305.1206. Spectral data correspond to those described in the literature.$^6$

4-methyl-2-(1-tosylbutyl)phenol (3ba): White solid in 78% yield, m.p. 68-70 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.51-7.50(d, J = 6.8 Hz, 2H), 7.22-7.21(d, J = 7.7 Hz, 2H), 6.97-6.95(d, J = 7.8 Hz, 1H), 6.74(m, 2H), 4.70(s, 1H), 2.40(s, 3H), 2.17(m, 4H), 2.04-2.02(m, 1H), 1.21-1.12(m, 2H), 0.87-0.84(t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.1, 144.6, 133.7, 130.5, 130.2, 129.2, 129.0, 118.7, 117.2, 62.5, 29.3, 21.6, 20.5, 20.0, 13.5; HRMS (ESI) m/z calcd for C$_{19}$H$_{22}$O$_2$S [M+Na]$^+$ 341.1187, found 341.1193.

4-methoxy-2-(1-tosylbutyl)phenol (3ca): Colorless oil in 93% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52-7.50(d, J = 7.6 Hz, 2H), 7.22-7.20(d, J = 7.7 Hz, 2H), 6.71(m, 3H), 6.63(s, 1H), 4.81(s, 1H), 3.66(s, 3H), 2.38(s, 3H), 2.21-2.19(m, 2H), 1.26-1.13(m, 2H), 0.87-0.83(t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.4, 149.3, 144.6, 133.7, 129.2, 128.9, 119.8, 117.8, 115.4, 113.6, 62.5, 55.6, 29.2, 21.5, 19.8, 13.5; HRMS (ESI) m/z calcd for C$_{18}$H$_{23}$O$_3$S [M+Na]$^+$ 357.1136, found 357.1128.

3-(1-tosylbutyl)-1,1'-biphenyl-4-ol (3da): White solid in 70% yield, m.p. 137-139 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.55-7.53(d, J = 7.0 Hz, 2H), 7.37-7.29(m, 6H), 7.25-7.22(m, 3H), 6.92(s, 1H), 6.59(s, 1H), 4.89(s, 1H), 2.39(s, 3H), 2.82-2.62(m, 1H), 2.07-1.85(m, 1H), 1.30-1.16(m, 2H), 0.88-0.84(t, J = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.1, 144.8, 140.3, 133.9, 133.4, 129.3, 129.2, 128.7, 126.8, 126.6, 119.3, 117.6, 62.8, 29.3, 21.6, 19.9, 13.5; HRMS (ESI) m/z calcd for C$_{23}$H$_{23}$O$_2$S [M+Na]$^+$ 403.1344, found 403.1333.

4-bromo-2-(1-tosylbutyl)phenol (3ea): Colorless oil in 75% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.55-7.53(d, J = 7.9 Hz, 2H), 7.27-7.25(d, J = 8.0 Hz, 2H), 7.21-7.19(d, J = 8.3 Hz, 1H), 7.14(s, 1H), 6.66(s, 1H), 4.81(s, 1H), 2.41(s, 3H), 2.14-2.13(m, 1H), 1.97(m, 1H), 1.28-1.08(m, 2H), 0.85-0.82(t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 154.8, 145.0, 133.3, 132.6, 131.3, 129.4, 129.0, 120.9, 118.2, 112.4, 62.1, 29.2, 21.6, 19.7, 13.4; HRMS (ESI) m/z calcd for C$_{19}$H$_{19}$BrO$_2$S [M+H]$^+$ 383.0317, found 383.0326.
2-methyl-6-(1-tosylbutyl)phenol (3fa): Colorless oil in 81% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.46 (s, 2H), 7.21-7.19 (d, J = 7.8 Hz, 2H), 7.08-7.06 (d, J = 7.2 Hz, 1H), 6.71 (s, 2H), 6.11 (s, 1H), 4.76 (s, 1H), 2.40 (s, 3H), 2.23 (m, 4H), 2.07-2.01 (m, 1H), 1.26-1.12 (m, 2H), 0.87-0.84 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 153.8, 144.8, 133.1, 131.4, 129.2, 126.2, 120.7, 118.9, 63.4, 29.2, 21.6, 19.9, 16.3, 13.5; HRMS (ESI) m/z calcd for C$_{18}$H$_{22}$O$_3$S [M+Na]$^+$ 341.1187, found 341.1178.

2-(1-tosylbutyl)aniline (3ga): Colorless oil in 87% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.50-7.48 (d, J = 6.6 Hz, 2H), 7.24-7.22 (d, J = 7.2 Hz, 2H), 7.09 (s, 1H), 6.74-6.69 (m, 3H), 4.54-4.52 (d, J = 9.6 Hz, 1H), 3.98 (br, 2H), 2.41 (s, 3H), 2.22-2.14 (m, 1H), 1.93-1.91 (m, 1H), 1.23-1.10 (m, 2H), 0.84-0.82 (t, J = 6.4 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 147.3, 144.6, 133.3, 129.5, 129.2, 128.6, 119.3, 118.1, 64.7, 30.2, 21.6, 19.6, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{21}$NO$_2$S [M+Na]$^+$ 326.1191, found 326.1192.

4-(1-tosylbutyl)phenol (3ha): White solid in 73% yield, m.p. 134-136 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.45-7.43 (d, J = 7.9 Hz, 2H), 7.22-7.20 (d, J = 7.8 Hz, 2H), 6.96-6.94 (d, J = 8.0 Hz, 2H), 6.71-6.69 (d, J = 8.0 Hz, 2H), 6.45 (s, 1H), 4.01-3.98 (m, 1H), 2.40 (s, 3H), 2.28-2.22 (m, 1H), 2.11-2.02 (m, 1H), 1.25-1.12 (m, 2H), 0.86-0.83 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 156.5, 144.5, 134.0, 131.1, 129.3, 129.0, 123.1, 115.5, 70.7, 29.3, 21.6, 19.9, 13.5; HRMS (ESI) m/z calcd for C$_{17}$H$_{21}$O$_2$S [M+Na]$^+$ 327.1031, found 327.1021.

$\text{N,N-dimethyl-4-(1-tosylbutyl)aniline (3ia)}$: White solid in 75% yield, m.p. 150-152 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.42-7.40 (d, J = 8.0 Hz, 2H), 7.19-7.17 (d, J = 7.9 Hz, 2H), 6.95-6.93 (d, J = 8.4 Hz, 2H), 6.58-6.56 (d, J = 8.4 Hz, 2H), 3.96-3.93 (dd, J = 3.2 Hz, 11.8 Hz, 1H), 2.93 (s, 6H), 2.39 (s, 3H), 2.29-2.26 (m, 1H), 2.07-2.04 (m, 1H), 1.28-1.16 (m, 2H), 0.88-0.84 (t, J = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.4, 143.9, 134.7, 130.5, 129.1, 118.8, 111.9, 70.7, 40.3, 29.2, 21.5, 20.0, 13.6; HRMS (ESI) m/z calcd for C$_{19}$H$_{35}$NO$_2$S [M+Na]$^+$ 354.1504, found 354.1513.

2-(1-(phenylsulfonyl)butyl)phenol (3ab): Colorless oil in 78% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.62-7.54 (m, 3H), 7.41-7.38 (t, J = 7.3 Hz, 2H), 7.17-7.13 (t, J = 7.6 Hz, 1H), 6.99-6.81 (m, 3H), 4.68 (s, 1H), 2.29-2.10 (m, 2H), 1.30-1.13 (m, 2H), 0.88-0.85 (t, J = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.3, 136.9, 133.5, 129.8, 128.8, 128.4, 120.6, 118.5, 116.5, 62.4, 28.7, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{16}$H$_{18}$O$_3$S [M+Na]$^+$ 313.0874, found 313.0864.
2-(1-((4-methoxyphenyl)sulfonyl)butyl)phenol (3ac): Colorless oil in 72% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-7.50 (d, $J = 8.2$ Hz, 2H), 7.17-7.13 (t, $J = 7.5$ Hz, 1H), 6.86-6.84 (m, 5H), 4.59 (s, 1H), 3.83 (s, 3H), 2.27-2.14 (m, 2H), 1.26-1.14 (m, 2H), 0.88-0.84 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.6, 155.4, 131.0, 129.8, 128.2, 120.6, 119.0, 116.6, 113.7, 62.8, 55.5, 28.8, 19.9, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{20}$O$_2$S [M+H]$^+$ 321.1161, found 321.1163.

2-(1-((4-propylphenyl)sulfonyl)butyl)phenol (3ad): White solid in 80% yield, m.p. 121-123 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-7.50 (d, $J = 7.9$ Hz, 2H), 7.20-7.13 (m, 3H), 6.84-6.82 (m, 3H), 4.62 (s, 1H), 2.63-2.59 (t, $J = 7.5$ Hz, 2H), 2.26-2.09 (m, 2H), 1.67-1.57 (m, 2H), 1.31-1.14 (m, 2H), 0.91-0.73 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.4, 149.2, 133.9, 132.8, 129.9, 129.0, 128.6, 120.8, 119.0, 117.4, 63.3, 37.8, 28.5, 24.0, 19.9, 13.48, 13.45; HRMS (ESI) m/z calcd for C$_{19}$H$_{22}$O$_2$S [M+Na]$^+$ 355.1344, found 355.1334.

2-(1-((4-butyrylphenyl)sulfonyl)butyl)phenol (3ae): White solid in 71% yield, m.p. 138-140 ºC. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-7.50 (d, $J = 7.5$ Hz, 2H), 7.21-7.12 (m, 3H), 7.00-6.81 (m, 3H), 4.68 (s, 1H), 2.65-2.62 (t, $J = 7.2$ Hz, 2H), 2.25-2.14 (m, 2H), 1.61-1.53 (m, 2H), 1.35-1.12 (m, 4H), 0.93-0.84 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.5, 149.5, 133.8, 132.8, 129.9, 129.0, 128.6, 120.9, 119.1, 117.6, 63.1, 35.5, 33.0, 28.6, 22.1, 20.0, 13.8, 13.5; HRMS (ESI) m/z calcd for C$_{20}$H$_{26}$O$_2$S [M+H]$^+$ 347.1681, found 347.1673.

2-(1-((4-(tert-butylyl)phenyl)sulfonyl)butyl)phenol (3af): Colorless oil in 78% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.56-7.54 (d, $J = 8.2$ Hz, 2H), 7.42-7.40 (d, $J = 8.4$ Hz, 2H), 7.14-7.10 (t, $J = 7.6$ Hz, 1H), 6.97 (s, 1H), 6.80 (s, 2H), 4.73 (s, 1H), 2.22-2.04 (m, 2H), 1.30 (s, 9H), 1.22-1.14 (m, 2H), 0.86-0.83 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 157.6, 155.5, 133.7, 129.9, 128.8, 125.6, 120.7, 118.9, 117.3, 62.8, 35.1, 30.9, 28.8, 19.9, 13.4; HRMS (ESI) m/z calcd for C$_{20}$H$_{26}$O$_2$S [M+H]$^+$ 347.1681, found 347.1675.

2-(1-((4-(trifluoromethoxy)phenyl)sulfonyl)butyl)phenol (3ag): Colorless oil in 65% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63-7.61 (d, $J = 8.4$ Hz, 2H), 7.19-7.17 (d, $J = 8.2$ Hz, 2H), 7.15-7.11 (t, $J = 7.6$ Hz, 1H), 6.86 (s, 1H), 6.69 (s, 1H), 6.23 (s, 1H), 4.82 (s, 1H), 2.35-2.15 (m, 2H), 1.39-1.14 (m, 2H), 0.90-0.86 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.1, 152.8, 135.4, 131.2, 130.1, 129.2, 124.0-116.2 (q, $J_{C-F} = 258.1$ Hz), 120.9, 120.1, 118.5, 116.2, 62.6, 28.5, 19.9, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$F$_3$O$_2$S [M+H]$^+$ 375.0878, found 375.0888.
2-(1-((4-bromophenyl)sulfonyl)butyl)phenol (3ah): Colorless oil in 65% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.51-7.49 (d, $J = 8.4$ Hz, 2H), 7.44-7.42 (d, $J = 8.4$ Hz, 2H), 7.17-7.10 (m, 2H), 6.86 (s, 1H), 6.70 (s, 1H), 4.83 (s, 1H), 2.29-2.14 (m, 2H), 1.35-1.14 (m, 2H), 0.88-0.85 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.1, 136.2, 131.7, 130.4, 130.0, 128.8, 120.8, 118.3, 116.1, 62.2, 28.6, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{16}$H$_17$BrO$_3$S [M+H]$^+$ 369.0160, found 369.0153.

2-(1-((4-chlorophenyl)sulfonyl)butyl)phenol (3ai): Colorless oil in 70% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.52-7.50 (d, $J = 8.2$ Hz, 2H), 7.36-7.34 (d, $J = 8.4$ Hz, 2H), 7.17-7.13 (m, 2H), 6.86 (s, 1H), 6.74 (s, 1H), 4.76 (s, 1H), 2.34-2.14 (m, 2H), 1.34-1.14 (m, 2H), 0.89-0.86 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.1, 140.3, 135.6, 130.4, 130.1, 128.8, 121.1, 118.6, 116.7, 62.4, 28.4, 19.9, 13.5; HRMS (ESI) m/z calcd for C$_{16}$H$_17$ClO$_3$S [M+Na]$^+$ 347.0485, found 347.0487.

2-(1-((4-fluorophenyl)sulfonyl)butyl)phenol (3aj): Colorless oil in 90% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.58 (m, 2H), 7.28-7.14 (m, 2H), 7.07-7.03 (t, $J = 8.4$ Hz, 2H), 6.87 (s, 1H), 6.71 (s, 1H), 6.40 (s, 1H), 4.86 (s, 1H), 2.31-2.29 (m, 1H), 2.20-2.14 (m, 1H), 1.31-1.17 (m, 2H), 0.90-0.86 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 166.9-164.4 (d, $J_{F,C} = 254.5$ Hz), 155.1, 132.9, 131.8-131.7 (d, $J_{F,C} = 9.5$ Hz), 130.0, 128.8, 120.8, 118.5, 115.8-115.6 (d, $J_{F,C} = 22.8$ Hz), 62.2, 28.5, 19.8, 13.5; HRMS (ESI) m/z calcd for C$_{16}$H$_17$FO$_3$S [M+Na]$^+$ 331.0780, found 331.0778.

2-(1-((4-trifluoromethyl)phenyl)sulfonyl)butyl)phenol (3ak): Colorless oil in 67% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.72-7.62 (m, 4H), 7.17-7.13 (t, $J = 7.6$ Hz, 2H), 6.88 (s, 1H), 6.69 (s, 1H), 4.81 (s, 1H), 2.37-2.17 (m, 2H), 1.35-1.16 (m, 2H), 0.90-0.87 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.1, 141.0 135.5-134.5 (q, $J_{F,C} = 32.4$ Hz), 130.2, 129.5, 129.3, 127.2-119.0 (q, $J_{F,C} = 271.4$ Hz), 125.4, 120.9, 118.1, 116.0, 62.3, 28.5, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{17}$F$_3$O$_3$S [M+H]$^+$ 359.0929, found 359.0938.

2-(1-(m-tolylsulfonyl)butyl)phenol (3ai): Colorless oil in 70% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ 7.43-7.32 (m, 3H), 7.28-7.24 (t, $J = 7.6$ Hz, 1H), 7.13-7.10 (t, $J = 7.4$ Hz, 1H), 6.82 (m, 1H), 6.76 (m, 1H), 4.76 (s, 1H), 2.29 (s, 3H), 2.25-2.13 (m, 2H), 1.31-1.13 (m, 2H), 0.87-0.83 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 155.5, 138.8, 136.7, 134.4, 129.9, 129.4, 128.4, 126.1, 120.7, 118.8, 116.9, 62.7, 28.7, 21.1, 19.9, 14.1, 13.5; HRMS (ESI) m/z calcd for C$_{17}$H$_{20}$O$_3$S [M+H]$^+$ 305.1211, found 305.1206.
2-(1-o-tolylsulfonyl)butylphenol (3am): Colorless oil in 75% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.66-7.64 (d, $J = 7.9$ Hz, 1H), 7.39-7.35 (t, $J = 7.4$ Hz, 1H), 7.20-7.12 (m, 3H), 7.07-7.04 (t, $J = 7.4$ Hz, 1H), 6.83 (m, 1H), 6.65 (s, 1H), 4.91 (s, 1H), 2.60 (s, 3H), 2.19-2.17 (m, 2H), 1.31-1.13 (m, 2H), 0.86-0.82 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.4, 139.0, 135.4, 133.4, 132.3, 131.0, 129.7, 125.8, 120.6, 118.2, 116.2, 61.5, 28.7, 20.3, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{17}$H$_{30}$O$_3$S [M+H]$^+$ 305.1211, found 305.1217.

2-(1-(2,5-dichlorophenyl)sulfonyl)butylphenol (3an): Colorless oil in 62% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.76 (s, 1H), 7.42-7.33 (m, 3H), 7.13-7.09 (t, $J = 7.5$ Hz, 1H), 6.89 (s, 1H), 6.69 (s, 1H), 5.34 (s, 1H), 2.23-2.11 (m, 2H), 1.35-1.17 (m, 2H), 0.89-0.85 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.3, 136.8, 134.5, 133.2, 132.8, 132.0, 131.5, 130.3, 121.0, 117.3, 116.5, 62.0, 28.6, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{16}$H$_{16}$Cl$_2$O$_3$S [M+H]$^+$ 359.0275, found 359.0269.

2-(1-(3,5-bis(trifluoromethyl)phenyl)sulfonyl)butylphenol (3ao): Colorless oil in 67% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.98 (s, 1H), 7.90 (s, 2H), 7.39 (s, 1H), 7.14-7.10 (t, $J = 7.6$ Hz, 1H), 6.97-6.95 (m, 1H), 6.52 (s, 1H), 5.88 (s, 1H), 4.90 (s, 1H), 2.46-2.38 (m, 1H), 2.21-2.16 (m, 1H), 1.42-1.24 (m, 2H), 0.94-0.90 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 154.4, 140.2, 132.4-131.4 (q, $J_{F,C} = 34.1$ Hz), 130.5, 129.4, 128.8, 126.7, 126.4-118.2 (q, $J_{F,C} = 271.7$ Hz), 121.3, 117.7, 115.2, 62.3, 27.6, 19.8, 13.3; HRMS (ESI) m/z calcd for C$_{18}$H$_{16}$F$_2$O$_3$S [M+Na]$^+$ 449.0622, found 449.0629.

2-(1-naphthalen-2-ylsulfonyl)butylphenol (3ap): Colorless oil in 83% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.20 (s, 1H), 7.85-7.79 (m, 3H), 7.63-7.54 (m, 3H), 7.13-7.09 (m, 2H), 6.80-6.74 (m, 2H), 4.84 (s, 1H), 2.29-2.08 (m, 2H), 1.26-1.12 (m, 2H), 0.86-0.82 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.4, 135.1, 134.0, 131.7, 130.9, 129.9, 129.3, 129.1, 128.5, 127.8, 127.3, 123.5, 120.7, 118.7, 116.9, 62.8, 28.8, 19.8, 13.4; HRMS (ESI) m/z calcd for C$_{20}$H$_{20}$O$_3$S [M+H]$^+$ 341.1211, found 341.1203.

2-(1-butylsulfonyl)butylphenol (3aq): Colorless oil in 63% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.39 (s, 1H), 7.24-7.20 (t, $J = 7.4$ Hz, 1H), 6.97-6.93 (m, 2H), 4.71 (s, 1H), 2.91-2.71 (m, 2H), 2.34-2.32 (m, 1H), 2.16 (m, 1H), 1.84-1.65 (m, 2H), 1.40-1.19 (m, 4H), 0.91-0.83 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.0, 130.0, 121.0, 119.0, 116.4, 60.2, 50.2, 27.6, 23.1, 21.6, 19.7, 13.42, 13.36; HRMS (ESI) m/z calcd for C$_{10}$H$_{12}$O$_3$S [M+Na]$^+$ 293.1187, found 293.1181.
1-methyl-4-((phenyl(4-propoxyphenyl)methyl)sulfonyl)benzene (6): Colorless oil in 71% yield. 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.51 (m, 2H), 7.50-7.48 (d, J = 7.9 Hz, 2H), 7.43-7.41 (d, J = 8.2 Hz, 2H), 7.29 (m, 3H), 7.15-7.14 (d, J = 7.6 Hz, 2H), 6.84-6.82 (d, J = 8.2 Hz, 2H), 5.22 (s, 1H), 3.90-3.86 (t, J = 6.3 Hz, 2H), 2.36 (s, 3H), 1.81-1.75 (m, 2H), 1.03-0.99 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 159.3, 144.2, 135.4, 133.4, 131.1, 129.8, 129.2, 129.0, 128.6, 124.6, 114.5, 75.8, 69.4, 22.4, 21.6, 10.5; HRMS (ESI) m/z calcd for C$_{29}$H$_{26}$O$_5$S [M+Na]$^+$ 403.1344, found 403.1346.

2-(3-phenylpropyl)phenol (8): Colorless oil in 80% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.29-7.25 (t, J = 7.4 Hz, 2H), 7.20-7.15 (m, 3H), 7.11-7.04 (m, 2H), 6.87-6.84 (t, J = 7.4 Hz, 1H), 6.73-6.71 (d, J = 7.9 Hz, 1H), 4.83 (br, 1H) 2.69-2.62 (m, 4H), 1.99-1.91 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 153.4, 142.3, 130.2, 128.4, 128.3, 128.1, 127.1, 125.7, 120.8, 115.2, 36.6, 31.2, 29.4; $^1$H and $^{13}$C NMR spectral data are in good agreement with the literature data. 

2-(1-(phenylsulfonyl)but-3-en-1-yl)phenol (10): Colorless oil in 71% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62-7.60 (d, J = 7.6 Hz, 2H), 7.57-7.54 (t, J = 7.4 Hz, 1H), 7.41-7.31 (m, 2H), 7.15-7.11 (t, J = 7.5 Hz, 2H), 6.84 (m, 1H), 6.74 (m, 1H), 6.47 (br, 1H), 5.58-5.48 (m, 1H), 5.07-5.02 (d, J = 17.0 Hz, 1H), 5.00-4.93 (d, J = 10.1 Hz, 1H), 4.83 (s, 1H), 3.10-3.07 (m, 1H), 2.91 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 155.2, 136.6, 133.7, 132.6, 130.1, 129.4, 129.0, 128.6, 120.8, 118.3, 116.9, 62.4, 31.0; HRMS (ESI) m/z calcd for C$_{16}$H$_{16}$O$_5$S [M+Na]$^+$ 311.0718, found 311.0727. Spectral data correspond to those described in the literature.

Reference:
Part II NMR Spectra

3aa $^1$H NMR

3aa $^{13}$C NMR
3ba $^1$H NMR

3ba $^{13}$C NMR
3ca $^1$H NMR

3ca $^{13}$C NMR
3da $^1$H NMR

3da $^{13}$C NMR
3fa $^1$H NMR

3fa $^{13}$C NMR
3ga $^1$H NMR

3ga $^{13}$C NMR
3ha $^1$H NMR

![3ha $^1$H NMR spectrum image]

3ha $^{13}$C NMR

![3ha $^{13}$C NMR spectrum image]
3ia $^1$H NMR

3ia $^{13}$C NMR
3ac $^1$H NMR

3ac $^{13}$C NMR
3ad $^1$H NMR

3ad $^{13}$C NMR
3af $^1$H NMR

3af $^{13}$C NMR
3ag $^1$H NMR

3ag $^{13}$C NMR
3ah $^1$H NMR

3ah $^{13}$C NMR
3ai $^1$H NMR

3ai $^{13}$C NMR
3aj $^1$H NMR

3aj $^{13}$C NMR
3ak $^1$H NMR

3ak $^{13}$C NMR
3al $^1$H NMR

3al $^{13}$C NMR
3am $^1$H NMR

3am $^{13}$C NMR
3an $^1$H NMR

3an $^{13}$C NMR
3ao $^1$H NMR

3ao $^{13}$C NMR
3ap $^1$H NMR

3ap $^{13}$C NMR
3aq $^1$H NMR

3aq $^{13}$C NMR
$^6$H NMR

$^6$C NMR
$^1$H NMR

$^{13}$C NMR
d²-3aa ^1H NMR