Supporting Information

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**General Information.**

The starting materials and reagents, purchased from commercial suppliers, were used without further purification. Literature procedures were used for the preparation of substrates 2e, 2f, 2h, 2i, 2j, 2k and 2l (TL, 2015, 56, 2512). Solvents were purified by standard methods. DCE was stored in Amber laboratory bottles for 3 to 5 weeks before use. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Flash chromatography was carried out using silica gel 200–300. $^1$HNMR (600 MHz) and $^{13}$CNMR (150 MHz) spectra were measured with CDCl$_3$ as solvent. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HR-MS) were recorded under electrospray ionization (ESI) conditions.

**General procedure for auto-oxidative hydroxysulfenylation**

Thiophenols (1, 1.0 mmol) and alkenes (2, 0.5 mmol) were dissolved in a mixed solvent (MeCN/DCE, 5:1, 10 mL) at room temperature. The reactions were performed open to air (open flask) for the desired reaction time (see Table S1). Thereafter Ph$_3$P (0.5 mmol) was added to the reaction mixture, which was stirred for another two hours. The products were isolated by silica gel column chromatography using petroleum ether/ethyl acetate (v/v 10:1 to 1:1).

**Table S1. Reaction time**

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Characterization of the products

**Methyl 2-hydroxy-2-methyl-3-(p-tolylthio)propanoate (3aa).** The desired pure product was obtained in 96% yield (115.4 mg) as a white solid, mp 44-46 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J$ = 8.1 Hz, 2H), 7.08 (d, $J$ = 7.9 Hz, 2H), 3.51 (s, 1H), 3.50 (s, 3H), 3.36 (d, $J$ = 13.9 Hz, 1H), 3.13 (d, $J$ = 13.9 Hz, 1H), 2.30 (s, 3H), 1.46 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.3, 136.9, 131.8, 131.3, 129.6, 74.6, 52.5, 45.7, 25.4, 21.0. HRMS (ESI) exact mass calcd for C$_{12}$H$_{16}$NaO$_3$S [M+Na] m/z 263.0718, found 263.0713.

**Methyl 2-hydroxy-2-methyl-3-(m-tolylthio)propanoate (3ba).** The desired pure product was obtained in 94% yield (112.8 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.23 – 7.18 (m, 2H), 7.18 – 7.13 (m, 1H), 7.00 (d, $J$ = 7.4 Hz, 1H), 3.51 (s, 3H), 3.50 (s, 1H), 3.40 (d, $J$ = 13.8 Hz, 1H), 3.16 (d, $J$ = 13.8 Hz, 1H), 2.31 (s, 3H), 1.49 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.3, 138.6, 135.2, 131.3, 128.7, 127.7, 127.6, 74.5, 52.5, 45.1, 25.4, 21.3. HRMS (ESI) exact mass calcd for C$_{12}$H$_{16}$NaO$_3$S [M+Na] m/z 263.0718, found 263.0715.

**Methyl 2-hydroxy-2-methyl-3-(o-tolylthio)propanoate (3ca).** The desired pure product was obtained in 87% yield (104.6 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J$ = 7.3 Hz, 1H), 7.18 – 7.09 (m, 3H), 3.50 (s, 4H), 3.37 (d, $J$ = 13.6 Hz, 1H), 3.15 (d, $J$ = 13.6 Hz, 1H), 2.41 (s, 3H), 1.49 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.4, 139.0, 134.5, 130.8, 130.2, 126.8, 126.4, 74.5, 52.6, 44.5, 25.5, 20.7. HRMS (ESI) exact mass calcd for C$_{12}$H$_{16}$NaO$_3$S [M+Na] m/z 263.0718, found 263.0709.
Methyl 2-hydroxy-3-((4-isopropylphenyl)thio)-2-methylpropanoate (3da). The desired pure product was obtained in 90% yield (120.4 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.34 (d, $J$ = 8.2 Hz, 2H), 7.13 (d, $J$ = 8.1 Hz, 2H), 3.52 (s, 1H), 3.45 (s, 3H), 3.38 (d, $J$ = 13.9 Hz, 1H), 3.13 (d, $J$ = 13.9 Hz, 1H), 2.89 – 2.82 (m, 1H), 1.47 (s, 3H), 1.21 (d, $J$ = 6.9 Hz, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.3, 147.9, 132.0, 131.5, 127.0, 74.4, 52.4, 45.7, 33.7, 25.4, 23.9, 23.9. HRMS (ESI) exact mass calcd for C$_{14}$H$_{20}$NaO$_3$S [M+Na] m/z 291.1031, found 291.1029.

Methyl 2-hydroxy-3-((4-methoxyphenyl)thio)-2-methylpropanoate (3ea). The desired pure product was obtained in 69% yield (87.8 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.37 (d, $J$ = 8.7 Hz, 2H), 6.81 (d, $J$ = 8.7 Hz, 2H), 3.77 (s, 3H), 3.50 (s, 4H), 3.31 (d, $J$ = 13.9 Hz, 1H), 3.07 (d, $J$ = 13.9 Hz, 1H), 1.45 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.4, 159.2, 134.0, 125.7, 114.5, 74.5, 55.3, 52.5, 46.8, 25.4. HRMS (ESI) exact mass calcd for C$_{12}$H$_{16}$NaO$_4$S [M+Na] m/z 279.0667, found 279.0672.

Methyl 2-hydroxy-2-methyl-3-(phenylthio)propanoate (3fa). The desired pure product was obtained in 94% yield (106.0 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.43 – 7.40 (m, 2H), 7.29 – 7.24 (m, 2H), 7.21 – 7.17 (m, 1H), 3.52 (s, 1H), 3.50 (s, 3H), 3.41 (d, $J$ = 13.9 Hz, 1H), 3.18 (d, $J$ = 13.9 Hz, 1H), 1.48 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.3, 135.5, 130.7, 128.9, 126.7, 74.5, 52.6, 45.1, 25.4. HRMS (ESI) exact mass calcd for C$_{11}$H$_{14}$NaO$_3$S [M+Na] m/z 249.0561, found 249.0566.
Methyl 3-((4-fluorophenyl)thio)-2-hydroxy-2-methylpropanoate (3ga). The desired pure product was obtained in 89% yield (108.8 mg) as a white solid, mp 58–60 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.43 – 7.38 (m, 2H), 7.01 – 6.94 (m, 2H), 3.54 (s, 3H), 3.49 (s, 1H), 3.34 (d, $J$ = 13.9 Hz, 1H), 3.13 (d, $J$ = 13.9 Hz, 1H), 1.47 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.3, 162.9, 161.2, 133.5, 133.5, 130.6, 130.6, 116.0, 115.9, 74.6, 52.6, 46.1, 25.5. HRMS (ESI) exact mass calcd for C$_{11}$H$_{13}$FNaO$_3$S [M+Na] m/z 267.0467, found 267.0476.

Methyl 3-((4-chlorophenyl)thio)-2-hydroxy-2-methylpropanoate (3ha). The desired pure product was obtained in 96% yield (126.2 mg) as a white solid, mp 64–66 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H), 3.56 (s, 3H), 3.49 (s, 1H), 3.35 (d, $J$ = 13.9 Hz, 1H), 3.16 (d, $J$ = 13.9 Hz, 1H), 1.48 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.3, 134.2, 132.7, 132.0, 128.9, 74.7, 52.7, 45.1, 25.5. HRMS (ESI) exact mass calcd for C$_{11}$H$_{13}$ClNaO$_3$S [M+Na] m/z 283.0172, found 283.0178.

Methyl 3-((4-bromophenyl)thio)-2-hydroxy-2-methylpropanoate (3ia). The desired pure product was obtained in 81% yield (123.5 mg) as a white solid, mp 54–56 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.41 – 7.36 (m, 2H), 7.30 – 7.26 (m, 2H), 3.57 (s, 3H), 3.48 (s, 1H), 3.35 (d, $J$ = 13.9 Hz, 1H), 3.16 (d, $J$ = 13.9 Hz, 1H), 1.48 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 175.3, 134.9, 132.1, 131.9, 120.6, 74.7, 52.7, 45.0, 25.5. HRMS (ESI) exact mass calcd for C$_{11}$H$_{13}$BrNaO$_3$S [M+Na] m/z 326.9666, found 326.9660.
Methyl 3-((2,4-dimethylphenyl)thio)-2-hydroxy-2-methylpropanoate (3ja). The desired pure product was obtained in 93% yield (117.7 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 7.9$ Hz, 1H), 6.99 (s, 1H), 6.94 (d, $J = 7.9$ Hz, 1H), 3.51 (s, 3H), 3.49 (s, 1H), 3.32 (d, $J = 13.6$ Hz, 1H), 3.10 (d, $J = 13.6$ Hz, 1H), 2.38 (s, 3H), 2.27 (s, 3H), 1.47 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.4, 139.3, 137.0, 131.8, 131.1, 130.8, 127.2, 74.5, 52.5, 45.1, 25.5, 20.9, 20.7. HRMS (ESI) exact mass calcd for C$_{13}$H$_{18}$NaO$_3$S [M+Na] m/z 277.0874, found 277.0882.

Methyl 3-((2,6-dimethylphenyl)thio)-2-hydroxy-2-methylpropanoate (3ka). The desired pure product was obtained in 96% yield (123.3 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.11 – 7.05 (m, 3H), 3.54 (s, 1H), 3.48 (s, 3H), 3.16 (d, $J = 13.1$ Hz, 1H), 2.97 (d, $J = 13.1$ Hz, 1H), 2.52 (s, 6H), 1.45 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.6, 142.6, 133.0, 128.2, 128.2, 74.5, 52.6, 45.2, 25.7, 22.0. HRMS (ESI) exact mass calcd for C$_{13}$H$_{18}$NaO$_3$S [M+Na] m/z 277.0874, found 277.0878.

Methyl 2-hydroxy-2-methyl-3-(naphthalen-2-ylthio)propanoate (3la). The desired pure product was obtained in 46% yield (63.2 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.86 (s, 1H), 7.50 – 7.40 (m, 3H), 3.55 (s, 1H), 3.50 (d, $J = 13.9$ Hz, 1H), 3.42 (s, 3H), 3.27 (d, $J = 13.9$ Hz, 1H), 1.52 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 175.4, 133.5, 132.8, 132.0, 129.0, 128.4, 128.3, 127.6, 127.2, 126.6, 126.0, 74.6, 52.6, 44.9, 25.5. HRMS (ESI) exact mass calcd for C$_{15}$H$_{16}$NaO$_3$S [M+Na] m/z 299.0718, found 299.0708.
Butyl 2-hydroxy-2-methyl-3-(p-tolylthio)propanoate (3ab). The desired pure product was obtained in 49% yield (66.0 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 2H), 4.36 (dd, $J = 10.2$, 5.6 Hz, 1H), 4.11 – 4.05 (m, 1H), 4.00 – 3.94 (m, 1H), 3.34 (dd, $J = 14.0$, 4.1 Hz, 1H), 3.21 (dd, $J = 14.0$, 5.7 Hz, 1H), 3.13 (d, $J = 6.2$ Hz, 1H), 2.31 (s, 3H), 1.59 – 1.51 (m, 2H), 1.36 – 1.29 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 172.9, 137.0, 131.3, 129.7, 69.5, 65.8, 39.8, 30.4, 21.0, 19.0, 13.6. HRMS (ESI) exact mass calcd for C$_{14}$H$_{20}$NaO$_3$S [M+Na] m/z 291.1031, found 291.1039.

Allyl 2-hydroxy-2-methyl-3-(p-tolylthio)propanoate (3ac). The desired pure product was obtained in 93% yield (124.3 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.32 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 5.84 – 5.72 (m, 1H), 5.25 (dd, $J = 17.2$, 1.3 Hz, 1H), 5.22 (dd, $J = 10.5$, 0.9 Hz, 1H), 4.50 (dd, $J = 13.0$, 5.9 Hz, 1H), 4.27 (dd, $J = 13.0$, 5.8 Hz, 1H), 3.48 (s, 1H), 3.38 (d, $J = 13.8$ Hz, 1H), 3.16 (d, $J = 13.8$ Hz, 1H), 2.30 (s, 3H), 1.49 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 174.6, 136.9, 131.9, 131.4, 129.6, 118.8, 74.6, 66.3, 45.7, 25.4, 21.0. HRMS (ESI) exact mass calcd for C$_{14}$H$_{18}$NaO$_3$S [M+Na] m/z 289.0874, found 289.0877.

2-hydroxyethyl 2-hydroxy-2-methyl-3-(p-tolylthio)propanoate (3ad). The desired pure product was obtained in 72% yield (96.7 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 2H), 4.14 – 4.04 (m, 2H), 3.76 (s, 1H), 3.75 – 3.71 (m, 2H), 3.38 (d, $J = 13.6$ Hz, 1H), 3.18 (d, $J = 13.7$ Hz, 1H), 2.57 (s, 1H), 2.29 (s, 3H), 1.49 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 174.9, 137.1, 131.7, 131.2, 129.7, 75.1, 67.2, 60.6, 45.6, 25.5, 21.0. HRMS (ESI) exact mass calcd for C$_{13}$H$_{18}$NaO$_4$S [M+Na] m/z 293.0823, found 293.0816.
The desired pure product was obtained in 71% yield (220.2 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.35 – 7.30 ppm (m, 2H), 7.07 ppm (d, $J = 7.2$ Hz, 2H), 5.38 – 5.30 ppm (m, 1H), 5.16 ppm (dd, $J = 15.1$, 8.7 Hz, 1H), 5.02 ppm (dd, $J = 15.1$, 8.7 Hz, 1H), 4.54 – 4.45 ppm (m, 1H), 3.51 ppm (d, $J = 8.9$ Hz, 1H), 3.36 – 3.31 ppm (m, 1H), 3.17 ppm (d, $J = 13.6$ Hz, 1H), 2.32 – 2.23 ppm (m, 4H), 2.09 – 2.02 ppm (m, 1H), 2.01 – 1.94 ppm (m, 2H), 1.90 – 1.78 ppm (m, 2H), 1.75 – 1.67 ppm (m, 1H), 1.65 – 1.60 ppm (m, 1H), 1.59 – 1.38 ppm (m, 12H), 1.30 – 1.23 ppm (m, 1H), 1.22 – 1.12 ppm (m, 3H), 1.11 – 0.90 ppm (m, 10H), 0.89 – 0.76 ppm (m, 9H), 0.69 ppm (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.5, 139.2, 139.1, 138.3, 136.7, 132.4, 131.2, 131.1, 129.6, 129.6, 129.3, 123.0, 122.9, 76.0, 74.7, 74.6, 56.7, 55.9, 51.2, 50.0, 45.6, 42.2, 40.5, 39.6, 37.8, 36.8, 36.5, 36.5, 31.9, 31.8, 28.9, 27.3, 25.5, 25.4, 24.3, 21.2, 21.1, 20.1, 21.0, 19.3, 19.00, 12.2, 12.0. HRMS (ESI) exact mass calcd for C$_{40}$H$_{60}$NaO$_3$S [M+Na] m/z 643.4161, found 643.4171.

The desired pure product was obtained in 80% yield (198.2 mg) as a white solid, mp 125–128 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.32 ppm (dd, $J = 7.9$, 4.3 Hz, 2H), 7.07 ppm (dd, $J = 7.8$, 4.0 Hz, 2H), 5.37 ppm (dd, $J = 23.8$, 4.8 Hz, 1H), 4.52 – 4.44 ppm (m, 1H), 3.49 ppm (d, $J = 5.2$ Hz, 1H), 3.33 ppm (dd, $J = 13.7$, 3.6 Hz, 1H), 3.17 ppm (d, $J = 13.7$ Hz, 1H), 2.45 ppm (dd, $J = 19.3$, 8.8 Hz, 1H), 2.35 – 2.23 ppm (m, 4H), 2.13 – 2.08 ppm (m, 2H), 1.98 – 1.91 ppm (m, 1H), 1.88 – 1.80 ppm (m, 3H), 1.70 – 1.60 ppm (m, 4H), 1.58 – 1.49 ppm (m, 2H), 1.48 – 1.42 ppm (m, 4H), 1.32 – 1.25 ppm (m, 1H), 1.15 – 1.04 ppm (m, 1H), 1.03 – 0.97 ppm (m, 4H), 0.88 ppm (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 220.9, 174.5, 139.5, 139.5, 136.8, 136.7, 132.4, 131.2, 129.1, 129.7, 129.6, 122.2, 122.1, 75.7, 75.7, 74.7, 74.7, 51.7, 50.1, 47.5, 45.6, 45.6, 37.8, 37.5, 36.8, 36.7, 36.6, 35.8, 31.4, 31.4, 30.8, 27.5, 27.3, 25.5, 21.9, 21., 21.0, 20.3, 19.3, 19.3, 13.5. HRMS (ESI) exact mass calcd for C$_{30}$H$_{40}$NaO$_4$S [M+Na] m/z 519.2545, found 519.2540.
**Methyl 2-hydroxy-3-(p-tolylthio)propanoate (3ag).** The desired pure product was obtained in 59% yield (67.0 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, $J$ = 8.1 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 4.36 (dd, $J$ = 10.2, 5.8 Hz, 1H), 3.61 (s, 3H), 3.33 (dd, $J$ = 14.0, 4.2 Hz, 1H), 3.21 (dd, $J$ = 14.1, 5.8 Hz, 1H), 3.11 (d, $J$ = 6.3 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 173.2, 137.2, 131.4, 131.0, 129.8, 69.4, 52.5, 39.8, 21.0. HRMS (ESI) exact mass calcd for C$_{11}$H$_{14}$NaO$_3$S [M+Na] m/z 249.0561, found 249.0549.

**2-hydroxy-2-methyl-N-phenyl-3-(p-tolylthio)propanamide (3ah).** The desired pure product was obtained in 48% yield (71.9 mg) as a white solid, mp 78−80 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.61 (s, 1H), 7.42 (d, $J$ = 7.6 Hz, 2H), 7.34 − 7.27 (m, 4H), 7.11 − 7.07 (m, 1H), 7.01 (d, $J$ = 8.0 Hz, 2H), 3.74 (d, $J$ = 14.0 Hz, 1H), 3.55 (s, 1H), 3.14 (d, $J$ = 14.0 Hz, 1H), 2.24 (s, 3H), 1.52 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 172.2, 137.5, 137.2, 131.4, 131.0, 130.8, 129.8, 69.4, 52.5, 39.8, 21.0. HRMS (ESI) exact mass calcd for C$_{17}$H$_{19}$NNaO$_2$S [M+Na] m/z 324.1034, found 324.1028.

**2-hydroxy-2-methyl-N-(p-tolyl)-3-(p-tolylthio)propanamide (3ai).** The desired pure product was obtained in 63% yield (93.3 mg) as a white solid, mp 88−90 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.54 (s, 1H), 7.34 − 7.28 (m, 4H), 7.09 (d, $J$ = 8.2 Hz, 2H), 7.02 (d, $J$ = 7.9 Hz, 2H), 3.73 (d, $J$ = 14.0 Hz, 1H), 3.46 (s, 1H), 3.14 (d, $J$ = 14.0 Hz, 1H), 2.31 (s, 3H), 2.25 (s, 3H), 1.51 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 172.0, 137.4, 137.2, 131.4, 130.4, 130.0, 128.8, 124.3, 119.6, 75.2, 45.5, 26.1, 21.0. HRMS (ESI) exact mass calcd for C$_{18}$H$_{21}$NNaO$_2$S [M+Na] m/z 338.1191, found 338.1200.
N-(4-bromophenyl)-2-hydroxy-2-methyl-3-(p-tolylthio)propanamide (3aj). The desired pure product was obtained in 61% yield (115.1 mg) as a white solid, mp 114–116°C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 8.61 (s, 1H), 7.38 (d, \(J = 8.7\) Hz, 2H), 7.33 – 7.28 (m, 4H), 7.00 (d, \(J = 7.9\) Hz, 2H), 3.74 (d, \(J = 14.1\) Hz, 1H), 3.57 (s, 1H), 3.10 (d, \(J = 14.1\) Hz, 1H), 2.23 (s, 3H), 1.50 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 172.3, 137.6, 136.3, 131.7, 131.5, 130.1, 129.9, 121.1, 116.9, 75.2, 45.4, 26.1, 21.0. HRMS (ESI) exact mass calcd for C\(_{17}\)H\(_{18}\)BrNNaO\(_2\)S [M+Na] m/z 402.0139, found 402.0144.

N-(4-cyano-3-(trifluoromethyl)phenyl)-2-hydroxy-2-methyl-3-(p-tolylthio)propanamide (3ak). The desired pure product was obtained in 60% yield (118.2 mg) as a colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 8.95 (s, 1H), 7.89 (s, 1H), 7.73 (d, \(J = 8.5\) Hz, 1H), 7.68 (dd, \(J = 8.5, 1.6\) Hz, 1H), 7.28 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 7.9\) Hz, 2H), 3.80 (d, \(J = 14.3\) Hz, 1H), 3.72 (s, 1H), 3.05 (d, \(J = 14.3\) Hz, 1H), 2.17 (s, 3H), 1.51 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 173.2, 141.3, 138.0, 135.5, 133.9, 133.7, 131.7, 129.9, 129.3, 121.6, 117.1, 117.1, 117.1, 115.5, 104.4, 75.1, 45.2, 26.2, 20.9. HRMS (ESI) exact mass calcd for C\(_{19}\)H\(_{17}\)F\(_3\)N\(_2\)NaO\(_2\)S [M+Na] m/z 417.0861, found 417.0867.

2-hydroxy-N,2-dimethyl-N-phenyl-3-(p-tolylthio)propanamide (3al). The desired pure product was obtained in 73% yield (115.8 mg) as a colorless oil. \(^1\)H NMR (600 MHz, CDCl\(_3\)) δ 7.38 – 7.32 (m, 3H), 7.25 – 7.19 (m, 4H), 7.09 – 7.04 (m, 2H), 4.51 (s, 1H), 3.28 (s, 3H), 2.98 (s, 2H), 2.30 (s, 3H), 1.28 (s, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) δ 174.0, 136.3, 132.9, 130.3, 129.6, 129.5, 128.5, 128.2, 75.7, 45.9, 41.2, 27.2, 21.0. HRMS (ESI) exact mass calcd for C\(_{18}\)H\(_{21}\)NNaO\(_2\)S [M+Na] m/z 338.1191, found 338.1194.
1-phenyl-2-(p-tolylthio)ethanol (5aa). The desired pure product was obtained in 91% yield (110.8 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.41 – 7.32 (m, 6H), 7.31 – 7.27 (m, 1H), 7.14 (d, $J = 7.9$ Hz, 2H), 4.69 (dd, $J = 9.6$, 3.3 Hz, 1H), 3.28 (dd, $J = 13.8$, 3.4 Hz, 1H), 3.04 (dd, $J = 13.8$, 9.6 Hz, 1H), 2.90 (s, 1H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 142.2, 137.1, 131.1, 130.9, 129.9, 128.5, 127.9, 125.8, 71.5, 44.9, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{16}$NaOS [M+Na] m/z 267.0820, found 267.0818.

1-(p-tolyl)-2-(p-tolylthio)ethanol (5ab). The desired pure product was obtained in 79% yield (101.8 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.34 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.18 – 7.12 (m, 4H), 4.66 (dd, $J = 9.5$, 3.4 Hz, 1H), 3.26 (dd, $J = 13.8$, 3.5 Hz, 1H), 3.05 (dd, $J = 13.8$, 9.5 Hz, 1H), 2.86 (s, 1H), 2.35 (s, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 139.2, 137.6, 137.0, 131.1, 131.0, 129.9, 129.2, 125.8, 71.4, 44.7, 21.1, 21.1. HRMS (ESI) exact mass calcd for C$_{16}$H$_{18}$NaOS [M+Na] m/z 281.0976, found 281.0982.

1-(4-(tert-butyl)phenyl)-2-(p-tolylthio)ethanol (5ac). The desired pure product was obtained in 65% yield (98.2mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.29 – 7.25 (m, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 4.68 (dd, $J = 9.4$, 2.9 Hz, 1H), 3.28 (dd, $J = 13.8$, 3.4 Hz, 1H), 3.07 (dd, $J = 13.8$, 9.5 Hz, 1H), 2.82 (s, 1H), 2.34 (s, 3H), 1.31 (s, 9H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 150.9, 139.2, 136.9, 131.2, 130.9, 129.9, 125.6, 71.4, 44.6, 34.5, 31.3, 21.0. HRMS (ESI) exact mass calcd for C$_{19}$H$_{24}$NaOS [M+Na] m/z 323.1446, found 323.1442.
1-(4-methoxyphenyl)-2-(p-tolylthio)ethanol (5ad). The desired pure product was obtained in 91% yield (125.1 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.33 (d, $J = 8.1$ Hz, 2H), 7.28 – 7.24 (m, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.89 – 6.86 (m, 2H), 4.64 (d, $J = 7.7$ Hz, 1H), 3.80 (s, 3H), 3.24 (dd, $J = 13.8$, 3.6 Hz, 1H), 3.04 (dd, $J = 13.8$, 9.5 Hz, 1H), 2.84 (d, $J = 1.7$ Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 159.3, 137.0, 134.3, 131.1, 131.0, 129.9, 127.1, 113.9, 71.2, 55.3, 44.7, 21.0. HRMS (ESI) exact mass calcd for C$_{16}$H$_{18}$NaO$_2$S [M+Na] m/z 297.0925, found 297.0920.

1-(4-fluorophenyl)-2-(p-tolylthio)ethanol (5ae). The desired pure product was obtained in 86% yield (112.7 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.34 (d, $J = 8.1$ Hz, 2H), 7.32 – 7.28 (m, 2H), 7.16 – 7.13 (m, 2H), 7.01– 6.99 (m, 2H), 4.65 (d, $J = 9.4$ Hz, 1H), 3.24 (dd, $J = 13.9$, 3.5 Hz, 1H), 2.99 (dd, $J = 13.8$, 9.5 Hz, 1H), 2.96 (dd, $J = 5.7$, 2.4 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 163.2, 161.5, 137.9, 137.9, 137.3, 131.2, 130.7, 130.0, 127.6, 127.5, 115.4, 115.3, 70.9, 44.9, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$FNaOS [M+Na] m/z 285.0725, found 285.0729.

1-(4-bromophenyl)-2-(p-tolylthio)ethanol (5af). The desired pure product was obtained in 86% yield (139.3 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.45 (d, $J = 8.2$ Hz, 2H), 7.33 (d, $J = 7.8$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 2H), 4.62 (d, $J = 9.4$ Hz, 1H), 3.23 (dd, $J = 13.9$, 3.4 Hz, 1H), 3.00 – 2.94 (m, 2H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 141.1, 137.4, 131.6, 131.3, 130.5, 130.0, 127.6, 121.7, 70.8, 44.8, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$BrNaOS [M+Na] m/z 344.9925, found 344.9931.
1-(4-chlorophenyl)-2-(p-tolylthio)ethanol (5ag). The desired pure product was obtained in 75% yield (104.8 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.33 (d, $J = 8.1$ Hz, 2H), 7.31 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 4.64 (dd, $J = 9.5$, 3.4 Hz, 1H), 3.25 (dd, $J = 13.9$, 3.5 Hz, 1H), 3.01 – 2.95 (m, 2H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 140.6, 137.4, 133.5, 131.3, 130.6, 130.0, 128.6, 127.2, 70.8, 44.9, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$ClNaOS [M+Na] m/z 301.0430, found 301.0433.

1-(3-chlorophenyl)-2-(p-tolylthio)ethanol (5ah). The desired pure product was obtained in 29% yield (40.5 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.37 – 7.32 (m, 3H), 7.28 – 7.23 (m, 2H), 7.22 – 7.18 (m, 1H), 7.14 (d, $J = 7.9$ Hz, 2H), 4.63 (d, $J = 9.4$ Hz, 1H), 3.25 (dd, $J = 13.9$, 3.3 Hz, 1H), 3.01 (d, $J = 2.0$ Hz, 1H), 2.98 (dd, $J = 13.9$, 9.6 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.2, 137.4, 134.4, 131.3, 130.5, 130.0, 129.8, 128.0, 126.1, 124.0, 70.8, 44.9, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$ClNaOS [M+Na] m/z 301.0437, found 301.0433.

1-(2-chlorophenyl)-2-(p-tolylthio)ethanol (5ai). The desired pure product was obtained in 87% yield (121.5 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.65 (d, $J = 7.7$ Hz, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 7.32 – 7.27 (m, 2H), 7.24 – 7.19 (m, 1H), 7.13 (d, $J = 7.9$ Hz, 2H), 5.07 (d, $J = 9.7$ Hz, 1H), 3.48 (dd, $J = 14.0$, 2.7 Hz, 1H), 3.05-3.03 (m, 1H), 2.83 (dd, $J = 14.0$, 9.8 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 139.5, 137.1, 131.6, 131.0, 130.4, 129.8, 129.4, 128.8, 127.2, 127.1, 68.1, 42.7, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$ClNaOS [M+Na] m/z 301.0430, found 301.0424.
4-(1-hydroxy-2-(p-tolylthio)ethyl)benzonitrile (5aj). The desired pure product was obtained in 96% yield (129.3 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.60 (d, $J = 8.2$ Hz, 2H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 4.71 – 4.67 (m, 1H), 3.24 (dd, $J = 14.0$, 3.5 Hz, 1H), 3.15 (d, $J = 2.3$ Hz, 1H), 2.95 (dd, $J = 14.0$, 9.4 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.4, 137.7, 132.3, 131.5, 130.1, 130.1, 126.6, 118.7, 111.5, 70.7, 44.9, 21.1. HRMS (ESI) exact mass calcd for C$_{16}$H$_{15}$NNaOS [M+Na] m/z 292.0772, found 292.0765.

1-(4-nitrophenyl)-2-(p-tolylthio)ethanol (5ak). The desired pure product was obtained in 97% yield (140.9 mg) as a yellow solid, mp 83–85°C. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.16 (d, $J = 8.6$ Hz, 2H), 7.49 (d, $J = 8.6$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 7.9$ Hz, 2H), 4.74 (d, $J = 9.3$ Hz, 1H), 3.27 (dd, $J = 14.0$, 3.5 Hz, 1H), 3.18 (d, $J = 1.7$ Hz, 1H), 2.97 (dd, $J = 13.9$, 9.4 Hz, 1H), 2.34 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 149.4, 147.4, 137.8, 131.6, 130.1, 130.0, 126.7, 123.7, 70.5, 45.0, 21.1. HRMS (ESI) exact mass calcd for C$_{15}$H$_{15}$NNaO$_3$S [M+Na] m/z 312.0670, found 312.0677.

1-phenyl-2-(p-tolylthio)propan-1-ol (5al). The desired pure product was obtained in 57% yield (74.3 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.42 (d, $J = 8.0$ Hz, 2H), 7.35 – 7.31 (m, 2H), 7.30 – 7.23 (m, 3H), 7.17 (d, $J = 7.9$ Hz, 2H), 4.75 (s, 1H), 3.49 (qd, $J = 7.0$, 2.9 Hz, 1H), 2.83 – 2.79 (m, 1H), 2.37 (s, 3H), 1.13 (d, $J = 7.0$ Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 140.9, 137.9, 133.0, 130.2, 130.0, 128.2, 127.3, 125.9, 73.0, 51.9, 21.2, 13.0. HRMS (ESI) exact mass calcd for C$_{16}$H$_{18}$NaOS [M+Na] m/z 281.0976, found 281.0983.
2-phenyl-1-(p-tolylthio)propan-2-ol (5am). The desired pure product was obtained in 83% yield (107.5 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.48 – 7.43 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 7.06 (d, $J = 8.0$ Hz, 2H), 3.51 (d, $J = 13.3$ Hz, 1H), 3.32 (d, $J = 13.3$ Hz, 1H), 2.91 (s, 1H), 2.31 (s, 3H), 1.61 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 146.3, 136.6, 132.8, 130.6, 129.7, 128.2, 127.0, 124.8, 74.0, 50.3, 29.4, 21.0. HRMS (ESI) exact mass calcd for C$_{16}$H$_{18}$NaOS [M+Na] m/z 281.0976, found 281.0981.

1,1-diphenyl-2-(p-tolylthio)ethanol (5an). The desired pure product was obtained in 85% yield (136.3 mg) as a white solid, mp 68−70 °C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.48 – 7.43 (m, 4H), 7.34 – 7.27 (m, 6H), 7.27 – 7.23 (m, 2H), 7.07 (d, $J = 7.9$ Hz, 2H), 3.84 (s, 2H), 3.60 (s, 1H), 2.31 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 145.2, 136.9, 132.8, 130.9, 129.8, 128.2, 127.3, 126.2, 77.7, 49.8, 21.0. HRMS (ESI) exact mass calcd for C$_{21}$H$_{20}$NaOS [M+Na] m/z 343.1133, found 343.1128.

2-methyl-1-(p-tolylthio)but-3-en-2-ol (5ao). The desired pure product was obtained in 32% yield (33.2 mg) as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.31 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 7.6$ Hz, 2H), 5.89 (dd, $J = 17.2$, 10.7 Hz, 1H), 5.31 (d, $J = 17.3$ Hz, 1H), 5.09 (d, $J = 10.7$ Hz, 1H), 3.20 (d, $J = 13.2$ Hz, 1H), 3.07 (d, $J = 13.2$ Hz, 1H), 2.46 (s, 1H), 2.31 (s, 3H), 1.36 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 143.2, 136.6, 133.0, 131.0, 130.5, 129.9, 129.7, 113.2, 72.7, 48.3, 27.2, 21.0. HRMS (ESI) exact mass calcd for C$_{12}$H$_{16}$NaOS [M+Na] m/z 231.0820, found 231.0827.
**N-(4-cyano-3-(trifluoromethyl)phenyl)-3-((4-fluorophenyl)thio)-2-hydroxy-2-methylpropanamide (3gk).** $^1$H NMR (600 MHz, CDCl$_3$) δ 8.99 (s, 1H), 7.91 (s, 1H), 7.75 (s, 2H), 7.41 – 7.37 (m, 2H), 6.91 – 6.85 (m, 2H), 3.75 (d, $J = 14.2$ Hz, 1H), 3.55 (s, 1H), 3.10 (d, $J = 14.2$ Hz, 1H), 1.53 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 173.0, 163.2, 161.5, 141.2, 135.7, 134.1, 133.8, 133.8, 133.7, 128.5, 123.0, 121.6, 121.1, 117.1, 117.1, 117.1, 116.3, 116.2, 115.4, 104.6, 75.3, 45.7, 26.2. HRMS (ESI) exact mass calcd for C$_{18}$H$_{14}$F$_{4}$N$_{2}$NaO$_{2}$S [M+Na] m/z 421.0610, found 421.0601.

**N-(4-cyano-3-(trifluoromethyl)phenyl)-3-((4-fluorophenyl)sulfonyl)-2-hydroxy-2-methylpropanamide**. $^1$H NMR (600 MHz, DMSO) δ 10.36 (s, 1H), 8.41 (s, 1H), 8.20 (d, $J = 8.6$ Hz, 1H), 8.07 (d, $J = 8.6$ Hz, 1H), 7.93-7.88 (m, 2H), 7.37-7.32 (m,2H), 6.38 (s, 1H), 3.92 (d, $J = 14.9$ Hz, 1H), 3.70 (d, $J = 14.9$ Hz, 1H), 1.39 (s, 3H).

**2,2,6,6-tetramethyl-1-((p-tolylthio)oxy)piperidine (6).** $^1$H NMR (600 MHz, CDCl$_3$) δ 7.58 – 7.50 (m, 2H), 7.29 – 7.19 (m, 2H), 2.38 (s, 3H), 1.88 – 1.24 (m, 15H), 0.92 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 147.3, 139.7, 129.5, 126.2, 61.4, 58.9, 43.7, 41.6, 35.6, 32.8, 29.0, 28.2, 21.4, 17.5.
5ac
bicalutamide