Supporting Information

Molecular-iodine-catalyzed aerobic oxidative synthesis of β-hydroxy sulfoxides from alkenes

Atsumasa Kariya, Tomoaki Yamaguchi, Tomoya Nobuta, Norihiro Tada, Tsuyoshi Miura and Akichika Itoh*

Gifu Pharmaceutical University, 1-25-4 Daigaku-nishi, Gifu 501-1196, Japan

E-mail: itoha@gifu-pu.ac.jp

1. General Information SI-2
2. General Procedure SI-2
3. References SI-5

Appendix: $^1$H and $^{13}$C spectra SI-6
1. General Information.

All dry solvents were obtained from Kanto Kagaku Co., Ltd. Other chemicals used were of reagent grade and were obtained from Tokyo Kasei Kogyo Co., Ltd., Wako Pure Chemical Industries, Ltd., and Nacalai Tesque. $^1$H NMR and $^{13}$C NMR spectra were obtained on a JEOL ECA 500 and a JEOL AL 400 at room temperature in CDCl$_3$ or CD$_3$OD as a solvent (500 MHz and 400MHz for $^1$H NMR and 125 MHz and 100MHz for $^{13}$C NMR). Chemical shifts (δ) are expressed in parts per million and are internally referenced [0.00 ppm (tetramethylsilane) for $^1$H NMR and 77.0 ppm (CDCl$_3$) or 49.0 (CD$_3$OD) for $^{13}$C NMR]. Flash column chromatography was performed with Silica Gel 60N (Kanto Chemical Co., Inc., 40–50 μm spherical, neutral).

2. General Procedure

**Synthesis of 1-phenyl-2-(phenylsulfonyl)ethanol (3aa) (Table 1, Entry 21):** A solution of styrene (1a, 0.3 mmol), sodium benzenesulfinate dihydrate (2a, 0.6 mmol), I$_2$ (0.03 mmol) in MeCN (1 mL) and AcOH (0.4 mL) was stirred for 20 h. The reaction mixture was washed with aq. Na$_2$S$_2$O$_3$, dried over magnesium sulfate, and concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (hexane : ethyl acetate = 5 : 1) provided 1-phenyl-2-(phenylsulfonyl)ethanol (3aa) (73.2 mg, 93%).

**1H-NMR (500 MHz, CDCl$_3$):** δ = 7.95 (d, J = 7.5 Hz, 2H), 7.68 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.32-7.24 (m, 5H), 5.27 (d, J = 9.7 Hz, 1H), 3.72 (br s, 1H), 3.50 (dd, J = 14.3 Hz, 9.7 Hz, 1H), 3.33 (dd, J = 14.3 Hz, 1.7 Hz, 1H).

**13C-NMR (125 MHz, CDCl$_3$):** δ = 140.5, 139.0, 134.1, 129.4, 128.7, 128.3, 127.9, 125.6, 68.4, 63.8.

**1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanol (3ba) (Table 2)**

1H-NMR (500 MHz, CDCl$_3$): δ = 7.93 (d, J = 7.5 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 2H), 7.27-7.24 (m, 5H), 5.27 (d, J = 9.7 Hz, 1H), 3.72 (br s, 1H), 3.50 (dd, J = 14.3 Hz, 9.7 Hz, 1H), 3.33 (dd, J = 14.3 Hz, 1.7 Hz, 1H).

**13C-NMR (125 MHz, CDCl$_3$):** δ = 140.5, 139.0, 134.1, 129.4, 128.7, 128.3, 127.9, 125.6, 68.4, 63.8.

**1-(4-bromophenyl)-2-(phenylsulfonyl)ethanol (3ca) (Table 2)**

1H-NMR (500 MHz, CDCl$_3$): δ = 7.92 (d, J = 7.7 Hz, 2H), 7.68 (t, J = 7.7 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.6 Hz, 2H), 5.26 (d, J = 10.1 Hz, 1H), 3.87 (br s, 1H), 3.46 (dd, J = 14.4 Hz, 10.1 Hz, 1H), 3.29 (dd, J = 14.4 Hz, 1.7 Hz, 1H).

**13C-NMR (125 MHz, CDCl$_3$):** δ = 139.1, 138.9, 134.2, 134.0, 129.5, 128.8, 127.9, 127.0, 67.7, 63.7.

**1-(4-chlorophenyl)-2-(phenylsulfonyl)ethanol (3ba) (Table 2)**

1H-NMR (500 MHz, CDCl$_3$): δ = 7.92 (d, J = 7.7 Hz, 2H), 7.69 (t, J = 7.7 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 5.23 (d, J = 9.8 Hz, 1H), 3.87 (br s, 1H), 3.46 (dd, J = 14.3 Hz, 9.8 Hz, 1H), 3.29
J = 14.3 Hz, 1.7 Hz, 1H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 139.6, 138.9, 134.2, 131.8, 129.5, 127.9, 127.3, 122.2, 67.8, 63.6.

1-(4-carboxylic acid phenyl)-2-(phenylsulfonyl)ethanol (3da) (Table 2)

\[
\text{HO}_2\text{C} \quad \begin{array}{c} \text{O} \\
\text{SO}_2\text{Ph} \end{array} 
\]

$^1$H-NMR (400 MHz, CD$_2$OD): $\delta$ = 7.95-7.91 (m, 4H), 7.70-7.60 (m, 1H), 7.59-7.56 (m, 2H), 7.40 (d, $J$ = 8.4 Hz, 2H), 5.21 (dd, $J$ = 8.8 Hz, 3.7 Hz 1H), 4.93 (br s, 1H), 3.68 (dd, $J$ = 14.8 Hz, 8.8 Hz, 1H), 3.55 (dd, $J$ = 14.8 Hz, 3.7 Hz 1H).

$^{13}$C-NMR (100 MHz, CD$_2$OD): $\delta$ = 169.4, 148.8, 141.5, 134.8, 131.0, 130.2, 129.3, 127.2, 69.6, 64.3. Anal. Calcd for C$_{15}$H$_{14}$O$_5$S: C, 58.81; H, 4.61. Found: C, 58.67; H, 4.58.

2-(phenylsulfonyl)-1-$p$-tolylethanol (3ea)$^1$ (Table 2)

\[
\text{Me} \quad \begin{array}{c} \text{O} \\
\text{SO}_2\text{Ph} \end{array} 
\]

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 7.94 (d, $J$ = 8.0 Hz, 2H), 7.67 (t, $J$ = 8.0 Hz, 1H), 7.58 (t, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.1 Hz, 2H), 7.15 (d, $J$ = 8.1 Hz, 2H), 5.23 (d, $J$ = 10.3 Hz, 1 H), 3.62 (br s, 1H), 3.49 (dd, $J$ = 14.3 Hz, 10.3 Hz, 1H), 3.32 (dd, $J$ = 14.3 Hz, 1.7 Hz, 1H), 2.31 (s, 3H).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 139.1, 138.2, 137.6, 134.1, 129.4, 127.9, 125.5, 68.3, 63.8, 21.1.

1-(4-$t$-Butylphenyl)-2-(phenylsulfonyl)ethanol (3fa) (Table 2)

\[
\text{t-Bu} \quad \begin{array}{c} \text{O} \\
\text{SO}_2\text{Ph} \end{array} 
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.94 (d, $J$ = 8.3 Hz, 2H), 7.66 (t, $J$ = 8.3 Hz, 1H), 7.56 (t, $J$ = 8.3 Hz, 2H), 7.33 (d, $J$ = 8.6 Hz, 2H), 7.21 (d, $J$ = 8.6 Hz, 2H), 5.25 (d, $J$ = 10.0 Hz, 1 H), 3.63 (br s, 1H), 3.52 (dd, $J$ = 14.2 Hz, 10.0 Hz, 1H), 3.35 (dd, $J$ = 14.2 Hz, 1.5 Hz, 1H), 1.27 (s, 9H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 151.4, 139.2, 137.6, 134.0, 129.4, 127.9, 125.6, 68.2, 63.8, 34.5, 31.2. Anal. Calcd for C$_{18}$H$_{22}$O$_3$S: C, 67.89; H, 6.96. Found: C, 67.63; H, 6.99.

1-(4-methoxyphenyl)-2-(phenylsulfonyl)ethanol (3ga)$^1$ (Table 2)

\[
\text{MeO} \quad \begin{array}{c} \text{O} \\
\text{SO}_2\text{Ph} \end{array} 
\]

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta$ = 7.95 (d, $J$ = 8.0 Hz, 2H), 7.68 (t, $J$ = 8.0 Hz, 1H), 7.59 (t, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 8.6 Hz, 2H), 6.84 (d, $J$ = 8.6 Hz, 2H), 5.23 (d, $J$ = 9.3 Hz, 1 H), 3.78 (s, 3H), 3.60 (br s, 1H), 3.50 (dd, $J$ = 14.4 Hz, 9.3 Hz, 1H), 3.32 (dd, $J$ = 14.4 Hz, 1.2 Hz, 1H).

$^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta$ = 159.5, 139.1, 134.1, 132.7, 129.5, 128.0,
2-(phenylsulfonyl)-1-o-tolylethanol (3ha) (Table 2)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, dashed] (0,0) -- (0,1);
\draw[thick, dashed] (1,0) -- (1,1);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) -- (0.5,0.7);
\draw[thick] (0.5,0.5) -- (0.3,0.7);
\draw[thick] (0.5,0.5) -- (0.7,0.7);
\draw[thick] (0.5,0.5) -- (0.6,0.3);
\draw[thick] (0.5,0.5) -- (0.4,0.3);
\draw[thick] (0.5,0.5) -- (0.6,0.7);
\draw[thick] (0.5,0.5) -- (0.4,0.7);
\end{tikzpicture}}
\]

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 7.97$ (d, $J = 8.1$ Hz, 2H), 7.68 (t, $J = 8.1$ Hz, 1H), 7.59 (t, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 7.8$ Hz, 1H), 7.19-7.14 (m, 2H), 7.07 (d, $J = 7.8$ Hz, 1H), 5.43 (d, $J = 10.0$ Hz, 1 H), 3.68 (br s, 1H), 3.43 (dd, $J = 14.3$ Hz, 10.0 Hz, 1H), 3.24 (d, $J = 14.3$ Hz, 1H), 2.07 (s, 3H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 138.9, 138.6, 134.1, 133.6, 130.5, 129.5, 128.0, 126.0, 125.2, 64.9, 62.8, 18.5.$

2-Hydroxy-2-phenylpropyl 4-methylphenyl sulfone (3ia) (Table 2)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, dashed] (0,0) -- (0,1);
\draw[thick, dashed] (1,0) -- (1,1);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) -- (0.5,0.7);
\draw[thick] (0.5,0.5) -- (0.3,0.7);
\draw[thick] (0.5,0.5) -- (0.7,0.7);
\draw[thick] (0.5,0.5) -- (0.6,0.3);
\draw[thick] (0.5,0.5) -- (0.4,0.3);
\draw[thick] (0.5,0.5) -- (0.6,0.7);
\draw[thick] (0.5,0.5) -- (0.4,0.7);
\end{tikzpicture}}
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.59-7.51$ (m, 3H), 7.38 (t, $J = 7.8$ Hz, 2H), 7.27 (d, $J = 7.1$ Hz, 2H), 7.17 (d, $J = 7.1$ Hz, 3H), 4.64 (br s, 1H), 3.75 (d, $J = 14.8$ Hz, 1H), 3.62 (d, $J = 14.8$ Hz, 1H), 1.70 (s, 3H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 144.2, 140.1, 133.4, 129.0, 128.2, 127.4, 127.2, 124.6, 73.1, 66.5, 30.8.$

1-Benzene sulphonyl-2-iodocyclohexane (4ja) (Table 2)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, dashed] (0,0) -- (0,1);
\draw[thick, dashed] (1,0) -- (1,1);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) -- (0.5,0.7);
\draw[thick] (0.5,0.5) -- (0.3,0.7);
\draw[thick] (0.5,0.5) -- (0.7,0.7);
\draw[thick] (0.5,0.5) -- (0.6,0.3);
\draw[thick] (0.5,0.5) -- (0.4,0.3);
\draw[thick] (0.5,0.5) -- (0.6,0.7);
\draw[thick] (0.5,0.5) -- (0.4,0.7);
\end{tikzpicture}}
\]

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.90$ (d, $J = 8.1$ Hz, 2H), 7.70 (t, $J = 8.1$ Hz, 1H), 7.59 (d, $J = 8.1$ Hz, 2H), 5.12 (d, $J = 2.7$ Hz, 1 H), 3.36 (dd, $J = 2.7$ Hz, 2.0 Hz, 1H), 2.28-2.19 (m, 2H), 2.05-1.95 (m, 3H), 1.75-1.67 (m, 2H), 1.57-1.53 (m, 1H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 138.0, 134.0, 129.4, 128.5, 67.4, 33.5, 25.1, 22.4, 21.7, 21.0.$

2-Hydroxy-2-phenylethyl 4-methylphenyl sulfone (3ab) (Table 2)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, dashed] (0,0) -- (0,1);
\draw[thick, dashed] (1,0) -- (1,1);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) -- (0.5,0.7);
\draw[thick] (0.5,0.5) -- (0.3,0.7);
\draw[thick] (0.5,0.5) -- (0.7,0.7);
\draw[thick] (0.5,0.5) -- (0.6,0.3);
\draw[thick] (0.5,0.5) -- (0.4,0.3);
\draw[thick] (0.5,0.5) -- (0.6,0.7);
\draw[thick] (0.5,0.5) -- (0.4,0.7);
\end{tikzpicture}}
\]

$^1$H-NMR (500 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.32-7.24 (m, 5H), 5.24 (d, $J = 9.3$ Hz, 1 H), 3.79 (br s, 1H), 3.47 (dd, $J = 14.3$ Hz, 9.3 Hz, 1H), 3.31 (dd, $J = 14.3$ Hz, 1.8 Hz, 1H), 2.45 (s, 3H). $^{13}$C-NMR (125 MHz, CDCl$_3$): $\delta = 145.2, 140.6, 136.0, 130.1, 128.7, 128.2, 128.0, 125.6, 68.4, 63.9, 21.6.$

2-Hydroxy-2-phenylethyl 4-chlorophenyl sulfone (3ac) (Table 2)

\[
\text{\begin{tikzpicture}
\draw[thick] (0,0) -- (1,0) -- (1,1) -- (0,1) -- cycle;
\draw[thick, dashed] (0,0) -- (0,1);
\draw[thick, dashed] (1,0) -- (1,1);
\draw[thick] (0.5,0.5) circle (0.1);
\draw[thick] (0.5,0.5) -- (0.5,0.7);
\draw[thick] (0.5,0.5) -- (0.3,0.7);
\draw[thick] (0.5,0.5) -- (0.7,0.7);
\draw[thick] (0.5,0.5) -- (0.6,0.3);
\draw[thick] (0.5,0.5) -- (0.4,0.3);
\draw[thick] (0.5,0.5) -- (0.6,0.7);
\draw[thick] (0.5,0.5) -- (0.4,0.7);
\end{tikzpicture}}
\]
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 7.87$ (m, 2H), 7.53 (m, 2H), 7.35-7.26 (m, 5H), 5.27 (dd, $J = 10.2$ Hz, 2.0 Hz, 1 H), 3.52 (dd, $J = 14.6$ Hz, 10.2 Hz, 1H), 3.33 (dd, $J = 14.6$ Hz, 2.0 Hz, 1H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 140.8, 140.5, 137.7, 129.7, 129.5, 128.8, 128.4, 125.6, 68.5, 63.9$. Anal. Calcd for C$_{14}$H$_{13}$ClO$_3$S: C, 56.66; H, 4.42. Found: C, 56.46; H, 4.13.

3. References

OH
SO₂Ph
Me
3ea
3ga

\[
\text{MeO} \quad \text{SO}_2\text{Ph}
\]
\[
\text{OH} \quad \text{SO}_2\text{Ph} \\
3\text{ha}
\]
OH

SO₂Ph

3ia