Visible-light promoted aerobic difunctionalization of alkenes with sulfonyl hydrazides for the synthesis of β-keto/hydroxyl sulfones

Jie Wu, a Yulan Zhang, a Xinchi Gong, a Yunge Meng, a and Chunyin Zhu* a,b

a School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, PR China. E-mail:zhucycn@gmail.com
b State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, P.R. China.

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1. General Information

Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The $^1$H (400 MHz) and $^{13}$C NMR (100 MHz) data were recorded on Bruker AVANCE II 400MHz spectrometer using CDCl$_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. $^1$H NMR spectra was recorded with tetramethylsilane (δ=0.00 ppm) as internal reference; $^{13}$C NMR spectra was recorded with CDCl$_3$ (δ=77.00 ppm) as internal reference.

2. General procedures for synthesis of 3aa-3as and 3ba-33be

To a solution of sulfonhydrazide 2 (0.5 mmol) and alkene 1 (1.5 mmol) in EtOH (1.5 mL) was added Methylene Blue (0.01 mmol) and DABCO (1 mmol). The reaction mixture was stirred at 25°C under air atmosphere (open vial) and irradiated by blue LED (7 W). The reaction was monitored by thin layer chromatography (TLC). Removal of solvent followed by column chromatography afforded desired products.

**Reaction Apparatus:**

Photochemical reactions were carried out under visible light irradiation by blue led bulbs at room temperature.
3. Compound characterizations

1-phenyl-2-tosylethan-1-one (3aa)[1].
Petroleum ether/ethyl acetate = 10:1, white solid, 78\% yield (106 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (d, $J = 7.7$ Hz, 2H), 7.78 (d, $J = 8.1$ Hz, 2H), 7.64 (t, $J = 7.3$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 4.74 (s, 2H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.15, 145.36, 135.82, 134.31, 129.84, 129.34, 128.84, 128.62, 63.61, 21.70.

1-(4-bromophenyl)-2-tosylethan-1-one (3ba)[1].
Petroleum ether/ethyl acetate = 10:1, white solid, 89\% yield (155 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (t, $J = 1.8$ Hz, 1H), 7.91 (ddd, $J = 7.8$, 1.6, 1.0 Hz, 1H), 7.80 – 7.71 (m, 3H), 7.38 (dd, $J = 15.3$, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.69, 144.92, 137.41, 132.04, 130.34, 128.55, 127.98, 123.18, 63.98.

1-(3-bromophenyl)-2-tosylethan-1-one (3ca)[1].
Petroleum ether/ethyl acetate = 10:1, white solid, 67\% yield (118 mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.02 (t, $J = 1.6$ Hz, 1H), 7.91 (d, $J = 7.8$ Hz, 1H), 7.76 (t, $J = 6.9$ Hz, 3H), 7.38 (dd, $J = 15.3$, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 186.98, 145.64, 137.41, 137.12, 135.54, 132.09, 130.40, 129.95, 128.60, 128.03, 123.18, 63.68, 21.75.
1-(4-chlorophenyl)-2-tosylethan-1-one (3da)\textsuperscript{[1]}.

Petroleum ether/ethyl acetate =10:1, white solid, 83% yield (130 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.91 (d, J = 6.8 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 4.70 (s, 2H), 2.46 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 186.90, 145.56, 141.08, 135.62, 134.11, 130.79, 129.91, 129.21, 128.58, 63.74, 21.72.

1-(4-fluorophenyl)-2-tosylethan-1-one (3ea)\textsuperscript{[1]}.

Petroleum ether/ethyl acetate =10:1, white solid, 72% yield (106 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 8.15 – 7.94 (m, 2H), 7.77 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.26 – 7.08 (m, 2H), 4.71 (s, 2H), 2.47 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 186.58, 167.76, 165.20, 145.52, 135.66, 132.51 – 132.12 (m), 129.90, 128.56, 116.21, 115.99, 63.75, 21.71.

1-(p-tolyl)-2-tosylethan-1-one (3fa)\textsuperscript{[1]}.

Petroleum ether/ethyl acetate =20:1, white solid, 68% yield (98 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 7.87 (d, J = 8.3 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.71 (s, 2H), 2.46 (s, 3H), 2.44 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta 187.67, 145.57, 145.30, 135.82, 133.39, 129.82, 129.54 (d, J = 3.7 Hz), 128.61, 63.58, 21.76 (d, J = 7.4 Hz).
1-(m-tolyl)-2-tosylethan-1-one (3ga)\textsuperscript{[1]}.  

Petroleum ether/ethyl acetate =20:1, white solid, 65% yield (93mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.79 (s, 1H), 7.77 (s, 2H), 7.75 (s, 1H), 7.73 (s, 1H), 7.44 (d, \( J = 7.6 \) Hz, 1H), 7.37 (dd, \( J = 15.3, 7.8 \) Hz, 3H), 4.72 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 188.30, 145.33, 138.74, 135.83, 135.15, 129.76 (d, \( J = 10.2 \) Hz), 128.67 (d, \( J = 5.5 \) Hz), 126.66, 63.58, 21.68, 21.31.

\begin{figure}
\centering
\includegraphics[width=0.6\textwidth]{m-tolyl}
\end{figure}

1-(4-methoxyphenyl)-2-tosylethan-1-one (3ha)\textsuperscript{[1]}.  

Petroleum ether/ethyl acetate =5:1, white solid, 77% yield (117mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.95 (d, \( J = 8.9 \) Hz, 2H), 7.76 (d, \( J = 8.2 \) Hz, 2H), 7.34 (d, \( J = 8.1 \) Hz, 2H), 6.95 (d, \( J = 8.9 \) Hz, 2H), 4.68 (s, 2H), 3.96 (s, 3H), 2.45 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 186.36, 164.55, 145.26, 135.85, 131.93, 129.81, 128.92, 128.57, 114.07, 63.55, 55.64, 21.71.

\begin{figure}
\centering
\includegraphics[width=0.6\textwidth]{4-methoxyphenyl}
\end{figure}

1-(3,4-dimethoxyphenyl)-2-tosylethan-1-one (3ia).  

Petroleum ether/ethyl acetate =5:1, white solid, 82% yield (136mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.77 (d, \( J = 8.2 \) Hz, 2H), 7.62 (d, \( J = 10.3 \) Hz, 1H), 7.48 (s, 1H), 7.34 (d, \( J = 8.1 \) Hz, 2H), 6.91 (d, \( J = 8.5 \) Hz, 1H), 4.70 (s, 2H), 3.96 (s, 3H), 3.91 (s, 3H), 2.45 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 186.41, 154.48, 149.23, 145.27, 135.85, 129.81, 129.04, 128.57, 125.15, 110.67, 110.13, 63.48, 56.12 (d, \( J = 19.0 \) Hz), 21.71. MS (ESI, \textit{m/z}) 335.1 (M + H\textsuperscript{+}), 357.1 (M + Na\textsuperscript{+}). Anal. calcd for C\textsubscript{17}H\textsubscript{18}O\textsubscript{5}S: C, 61.06; H, 5.43. Found: C, 60.84; H, 5.56.
2-tosyl-1-(3-vinylphenyl)ethan-1-one (3ja).

Petroleum ether/ethyl acetate = 20:1, white solid, 73% yield (109 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (s, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.8 Hz, 1H), 7.35 (d, J = 8.1 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.38 (d, J = 10.9 Hz, 1H), 4.75 (s, 2H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 188.12, 145.42, 138.36, 137.42, 136.08, 135.54, 131.74, 129.85, 129.04, 128.63, 126.96, 115.88, 63.69, 21.70. MS (ESI, m/z) 301.1 (M + H⁺), 323.1 (M + Na⁺). Anal. calcd for C₁₇H₁₆O₃S: C, 67.98; H, 5.37. Found: C, 67.74; H, 5.26.

2-tosyl-1-(4-vinylphenyl)ethan-1-one (3ka).

Petroleum ether/ethyl acetate = 40:1, white solid, 64% yield (96 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 17.6, 10.9 Hz, 1H), 5.69 (dd, J = 189.7, 19.5 Hz, 2H), 4.72 (s, 2H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 187.46, 145.38, 143.33 (s), 135.77, 135.68, 134.89, 129.83 (d, J = 1.9 Hz), 128.61, 126.53, 117.76, 63.68, 21.71. MS (ESI, m/z) 301.1 (M + H⁺), 323.1 (M + Na⁺). Anal. calcd for C₁₇H₁₆O₃S: C, 67.98; H, 5.37. Found: C, 67.86; H, 5.24.

2-phenyl-1-tosylpropan-2-ol (3la)².

Petroleum ether/ethyl acetate = 10:1, white solid, 72% yield (103 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, J = 8.3 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.14 (m, 5H), 4.66 (s, 1H), 3.67 (dd, J = 45.6, 14.6 Hz, 2H), 2.40 (s, 3H), 1.72 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.53, 137.39, 133.62, 129.71, 128.25, 127.56, 127.13, 124.65, 73.17, 66.69, 30.76, 21.57.
2-(4-bromophenyl)-1-tosylpropan-2-ol (3ma)\textsuperscript{[2]}.

Petroleum ether/ethyl acetate = 10:1, white solid, 81\% yield (183 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 7.45 (dd, \textit{J} = 13.3, 5.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.19 (d, \textit{J} = 8.1 Hz, 2H), 7.15 – 7.08 (m, 2H), 4.72 (s, 1H), 3.66 (dd, \textit{J} = 53.1, 14.7 Hz, 2H), 2.45 (d, \textit{J} = 7.6 Hz, 3H), 1.64 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 144.81, 143.28, 136.84, 131.17, 129.75, 127.51, 126.61, 121.32, 72.80, 66.25, 31.02, 21.62.

2-(3-chlorophenyl)-1-tosylpropan-2-ol (3na)\textsuperscript{[2]}.

Petroleum ether/ethyl acetate = 10:1, white solid, 76\% yield (161 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 8.02 (t, \textit{J} = 1.6 Hz, 1H), 7.91 (d, \textit{J} = 7.8 Hz, 1H), 7.76 (t, \textit{J} = 6.9 Hz, 3H), 7.38 (dd, \textit{J} = 15.3, 7.8 Hz, 3H), 4.70 (s, 2H), 2.47 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 186.98, 145.64, 137.41, 137.12, 135.54, 132.09, 130.40, 129.95, 128.60, 128.03, 123.18, 63.68, 21.75.

1,1-diphenyl-2-tosylethan-1-ol (3oa)\textsuperscript{[2]}.

Petroleum ether/ethyl acetate = 10:1, white solid, 75\% yield (132 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 7.44 (d, \textit{J} = 8.3 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.26 – 7.19 (m, 6H), 7.15 (d, \textit{J} = 8.1 Hz, 2H), 5.41 (s, 1H), 4.21 (s, 2H), 2.41 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \textsuperscript{\delta} 144.51, 143.73, 137.42, 129.70, 128.28, 127.57 (d, \textit{J} = 18.7 Hz), 125.87, 65.51, 21.61.
2-(naphthalen-2-yl)-1-tosylpropan-2-ol (3pa)[2].

Petroleum ether/ethyl acetate =10:1, white solid, 70% yield (119mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 – 7.93 (m, 1H), 7.87 (d, J = 7.3 Hz, 1H), 7.67 (dd, J = 8.7, 4.1 Hz, 2H), 7.49 – 7.40 (m, 1H), 7.39 – 7.32 (m, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.78 (d, J = 8.1 Hz, 2H), 4.87 (s, 1H), 4.13 (dd, J = 220.5, 15.0 Hz, 2H), 2.21 (s, 3H), 2.00 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.70, 139.04, 134.54, 129.37, 129.20, 128.82, 126.94, 125.72, 125.09, 124.77, 124.55, 124.38, 73.52, 65.00, 30.14, 21.35.

2-(4-methoxyphenyl)-1-tosylpropan-2-ol (3qa)[2].

Petroleum ether/ethyl acetate =5:1, white solid, 77% yield (123mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, J = 7.1 Hz, 2H), 7.19 (dd, J = 8.6, 3.3 Hz, 4H), 6.71 (d, J = 8.8 Hz, 2H), 4.61 (s, 1H), 3.77 (s, 3H), 3.64 (dd, J = 49.7, 14.6 Hz, 2H), 2.40 (s, 3H), 1.69 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 158.70, 144.41, 136.64, 129.65, 127.57, 125.87, 113.50, 72.89, 66.85, 55.24, 30.70, 21.57.

2-(pyridin-3-yl)-1-tosylpropan-2-ol (3ra)[3].

Petroleum ether/ethyl acetate =10:1, white solid, 63% yield (92mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.18 (d, J = 4.7 Hz, 1H), 7.66 (q, J = 8.4 Hz, 2H), 7.49 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 7.07 (dd, J = 6.6, 4.8, 1.7 Hz, 1H), 3.90 (dd, J = 152.0, 14.5 Hz, 2H), 2.38 (s, 3H), 1.62 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 162.51, 147.95, 144.23, 137.45, 136.93, 129.55, 127.70, 122.13, 119.34, 74.04, 65.17, 30.11, 21.56.
1-phenyl-2-(phenylsulfonyl)ethan-1-one (3ab)[4].
Petroleum ether/ethyl acetate =10:1, white solid, 75% yield (98mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.74 (s, 2H), 7.48 (tt, $J = 7.8$, 1.6 Hz, 2H), 7.55 (tt, $J = 7.8$, 1.6 Hz, 2H), 7.62 (tt, $J = 7.4$, 1.2 Hz, 1H), 7.66 (tt, $J = 7.6$, 1.2 Hz, 1H), 7.90 (m, 2H), 7.94 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 188.1, 138.8, 135.8, 134.5, 134.4, 129.4, 129.3, 129.0, 128.7, 63.6.

2-((4-fluorophenyl)sulfonyl)-1-phenylethan-1-one (3ac)[4].
Petroleum ether/ethyl acetate =10:1, white solid, 75% yield (104mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.75 (s, 2H), 7.20-7.26 (m, 2H), 7.50 (t, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.90-7.95 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.1, 166.3 (d, $IJCF = 245.4$ Hz), 135.7, 134.8 (d, $4JCF = 3.1$ Hz), 134.7, 131.8 (d, $3JCF = 9.7$ Hz), 129.4, 129.1, 116.7 (d, $2JCF = 22.6$ Hz), 63.6.

2-((4-chlorophenyl)sulfonyl)-1-phenylethan-1-one (3ad)[4].
Petroleum ether/ethyl acetate =10:1, white solid, 69% yield (101mg). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.75 (s, 2H), 7.48-7.53 (m, 4H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.83 (d, $J = 8.8$ Hz, 2H), 7.93 (d, $J = 8.4$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 188.0, 141.3, 137.2, 135.7, 134.7, 130.3, 129.7, 129.4, 129.1, 63.5.
2-((4-nitrophenyl)sulfonyl)-1-phenylethan-1-one (3ae)\(^4\).

Petroleum ether/ethyl acetate =10:1, white solid, 77\% yield (117mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.45 – 8.35 (m, 1H), 8.14 (ddt, \(J = 11.3, 9.3, 2.4\) Hz, 1H), 7.94 (dt, \(J = 7.1, 1.4\) Hz, 1H), 7.72 – 7.63 (m, 0H), 7.52 (t, \(J = 7.8\) Hz, 1H), 4.82 (s, 1H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 187.60, 144.03, 135.33, 134.86, 130.34, 129.19, 129.09, 124.31, 63.00.

1-phenyl-2-(thiophen-2-ylsulfonyl)ethan-1-one (3af)\(^5\).

Petroleum ether/ethyl acetate =5:1, white solid, 73\% yield(102mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 7.95 (d, \(J = 7.4\) Hz, 2 H), 7.74 (dd, \(J = 4.9, 1.3\) Hz, 1 H), 7.69 (dd, \(J = 3.8, 1.2\) Hz, 1 H), 7.63 (t, \(J = 7.4\) Hz, 1 H), 7.49 (t, \(J = 7.4\) Hz, 2 H), 7.13 (dd, \(J = 4.9, 3.9\) Hz, 1 H), 4.83 (s, 2 H) ppm. \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) = 187.8, 139.4, 135.7, 135.5, 135.0, 134.5, 129.2, 128.9, 127.9, 64.4 ppm.
4. Luminescence quenching by compound 2a

A Varian Cary Eclipse fluorescence spectrometer was used to record the emission intensities. All the solutions were excited at 664 nm and the emission intensity at 685 nm was observed. EtOH was degassed with a stream of N₂ for 30 min. In a typical experiment, the emission spectrum of a 1×10⁻² M solution of Methylene Blue in EtOH was collected. Then, appropriate amount of quencher 2a was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. \( I_0 \) and \( I \) represent the intensities of the emission in the absence and presence of the quencher at 685 nm.
5. Reference


6. Spectroscopic Data for Products

![Spectroscopic Data for Products](image-url)
3ba