Benzylic C(sp³)-H Bond Sulfonylation of 4-Methylphenols with the Insertion of Sulfur Dioxide under Photocatalysis

Xinxing Gong, Jiahao Chen, Lifang Lai, Jiang Cheng, Jiangtao Sun, and Jie Wu*

Supporting Information

1. General experimental methods (S2-S3).
2. Optimization of reaction conditions, general experimental procedure, details for control experiments, and characterization data (S2-S12).
3. $^1$H and $^{13}$C NMR spectra of compounds 3 (S13-S56).
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. $^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

Optimization of Reaction Conditions:

Table 1. Initial studies for the reaction of 2,4,6-trimethylphenol 1a, sulfur dioxide, and p-tolyldiazonium tetrafluoroborate 2a.

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<th>Yield (%)$^b$</th>
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$^{b}$Based on GC analysis.

$^{c}$Photocatalyst: 36 W CFL.
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*a* Reaction conditions: 2,4,6-trimethylphenol 1a (0.2 mmol), metabisulfite (0.4 mmol), p-tolyldiazonium tetrafluoroborate 2a (0.4 mmol), photocatalyst (10 mol %), solvent (2.0 mL), N₂, 36 W CFL, rt, 12 h. *b* Isolated yield. *c* Blue LED was used instead of CFL. *d* The ratio was changed to 1a (0.4 mmol), Na₂S₂O₅ (0.2 mmol), 2a (0.4 mmol). *e* In the presence of NaHCO₃ (2.0 equiv).

**General experimental procedure for the photoinduced reaction of 4-methylphenols 1, sodium metabisulfite, and aryldiazonium tetrafluoroborates 2**

4-Methylphenol 1 (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of aryldiazonium tetrafluoroborate 2 (0.40 mmol), Ir(ppy)₃ (2 mol %), NaHCO₃ (0.40 mmol) and Na₂S₂O₅ (0.20 mmol) at N₂ atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (n-hexane/EtOAc= 4:1 to 2:1) to give the corresponding pale yellow product 3.
Experimental procedure for the control experiments.

**Eq (1):** 2,4,6-Trimethylphenol 1a (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of p-tolyl diazonium tetrafluoroborate 2a (0.40 mmol), Ir(ppy)₃ (2 mol %), NaHCO₃ (0.40 mmol), TEMPO (0.6 mmol), and Na₂S₂O₅ (0.20 mmol) at N₂ atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. As indicated by TLC, no desired product was detected.

**Eq (2):** 2,4,6-Trimethylphenol 1a (0.40 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of p-tolyl diazonium tetrafluoroborate 2a (0.40 mmol), ethene-1,1-diyl dibenzene (0.8 mmol), Ir(ppy)₃ (2 mol %), NaHCO₃ (0.40 mmol) and Na₂S₂O₅ (0.20 mmol) at N₂ atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After consumption of 2,4,6-trimethylphenol 1a, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (n-hexane/EtOAc= 4:1 to 2:1) to give (2-tosylethene-1,1-diyl) dibenzene in 46% yield.

**Eq (3):** 2,4,6-trimethylphenol 1a (0.4 mmol) and 2,6-di-tert-butyl-4-methylphenol 1b (0.4 mmol) in 1,2-dichloroethane (2.0 mL) were added to a mixture of
p-tolyldiazonium tetrafluoroborate 2a (0.40 mmol), Ir(ppy)3 (2 mol %), NaHCO3 (0.40 mmol) and Na2S2O5 (0.20 mmol) at N2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. After completion of reaction as indicated by TLC, the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatography (n-hexane/EtOAc= 4:1 to 2:1) to give the corresponding pale yellow product 3q in 77% yield.

**General experimental procedure for the reactions employing other substituted toluenes.**

![Chemical structures](image)

Substituted toluene (0.40 mmol) and 2,4,6-trimethylphenol or 2,6-di-tert-butylphenol (0.4 mmol) in 1,2-dichloroethane (2.0 mL) was added to a mixture of phenyldiazonium tetrafluoroborate 2a (0.40 mmol), Ir(ppy)3 (2 mol %), NaHCO3 (0.40 mmol) and Na2S2O5 (0.20 mmol) at N2 atmosphere. The mixture was stirred under 36 W compact fluorescent lamp at room temperature overnight. As indicated by TLC, no desired product was formed.
2, 6-Dimethyl-4-(tosylmethyl)phenol (3a)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.55 (d, \(J = 8.2\) Hz, 2H), 7.38 – 7.16 (m, 2H), 6.70 (s, 2H), 4.83 (m, 1H), 4.15 (s, 2H), 2.43 (s, 3H), 2.15 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.8, 144.5, 135.4, 131.1, 129.4, 128.7, 123.3, 119.3, 62.4, 21.6, 15.7. HRMS (ESI) calcd for C\(_{16}\)H\(_{22}\)NO\(_3\)S\(^{+}\): 308.1315 (M+NH\(_4^+\)), found: 308.1333.

2, 6-Dimethyl-4-((phenylsulfonyl)methyl)phenol (3b)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 – 7.65 (m, 2H), 7.61 (dd, \(J = 11.8, 4.3\) Hz, 1H), 7.47 (t, \(J = 7.8\) Hz, 2H), 6.68 (s, 2H), 4.91 (m, 1H), 4.17 (s, 2H), 2.14 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 152.8, 138.2, 133.6, 131.1, 128.8, 128.7, 123.4, 119.1, 62.4, 15.7. HRMS (ESI) calcd for C\(_{15}\)H\(_{20}\)NO\(_3\)S\(^{+}\): 294.1158 (M+NH\(_4^+\)), found: 294.1175.

4-(((4-Methoxyphenyl)sulfonyl)methyl)-2,6-dimethylphenol (3c)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.58 (d, \(J = 8.8\) Hz, 2H), 6.92 (d, \(J = 8.8\) Hz, 2H), 6.70 (s, 2H), 4.14 (s, 2H), 3.86 (s, 3H), 2.15 (s, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 163.7, 152.8, 131.1, 130.9, 129.9, 123.4, 119.5, 114.0, 62.6, 55.7, 15.8. HRMS (ESI) calcd for C\(_{16}\)H\(_{22}\)NO\(_4\)S\(^{+}\): 324.1264 (M+NH\(_4^+\)), found: 324.1278.

4-(((4-(tert-Butyl)phenyl)sulfonyl)methyl)-2,6-dimethylphenol (3d)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J$ = 8.6 Hz, 2H), 7.47 (d, $J$ = 8.6 Hz, 2H), 6.65 (s, 2H), 4.80 (m, 1H), 4.14 (s, 2H), 2.13 (s, 6H), 1.34 (s, 9H).  $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.5, 152.6, 134.9, 131.0, 128.5, 125.6, 123.1, 119.2, 62.3, 35.1, 30.95, 15.6. HRMS (ESI) calcd for C$_{19}$H$_{28}$NO$_3$S$: 350.1784 (M+NH$_4^+$), found: 350.1786.

4-(((4-Fluorophenyl)sulfonyl)methyl)-2,6-dimethylphenol (3e)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.52 (m, 2H), 7.13 (t, $J$ = 8.6 Hz, 2H), 6.68 (s, 2H), 4.94 (s, 1H), 4.17 (s, 2H), 2.15 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.7 (d, $^1$JC$_F$ = 256.1 Hz), 152.8, 134.0, 131.5 (d, $^3$JC$_F$ = 9.5 Hz), 130.9, 123.3, 118.9, 115.9 (d, $^2$JC$_F$ = 22.5 Hz), 62.4, 15.7. HRMS (ESI) calcd for C$_{15}$H$_{19}$NFO$_3$S$: 312.1064 (M+NH$_4^+$), found: 312.1062.

4-(((4-Chlorophenyl)sulfonyl)methyl)-2,6-dimethylphenol (3f)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.58 (d, $J$ = 8.7 Hz, 2H), 7.44 (d, $J$ = 8.6 Hz, 2H), 6.70 (s, 2H), 4.78 (m, 1H), 4.17 (s, 2H), 2.16 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.9, 140.4, 136.7, 131.1, 130.2, 129.1, 123.4, 118.9, 62.5, 15.7. HRMS (ESI) calcd for C$_{15}$H$_{19}$NClO$_3$S$: 328.0769 (M+NH$_4^+$), found: 328.0774.

4-(((4-Bromophenyl)sulfonyl)methyl)-2,6-dimethylphenol (3g)
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.67 – 7.56 (m, 2H), 7.55 – 7.43 (m, 2H), 6.69 (s, 2H), 4.82 (s, 1H), 4.16 (s, 2H), 2.16 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.8, 137.0, 132.0, 131.0, 130.2, 128.8, 123.3, 118.7, 62.3, 15.6. HRMS (ESI) calcd for C$_{15}$H$_{19}$NBrO$_3$S$: 372.0264 (M+NH$_4^+$), found: 372.0246.
2, 6-Dimethyl-4-(((4-(trifluoromethyl)phenyl)sulfonyl)methyl)phenol (3h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (dd, $J = 21.4, 8.4$ Hz, 4H), 6.67 (s, 2H), 4.83 (m, 1H), 4.20 (s, 2H), 2.14 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.9, 141.4, 130.9, 129.3, 125.8, 125.7, 123.4, 118.4, 62.3, 15.6. HRMS (ESI) calcd for C$_{16}$H$_{19}$NF$_3$O$_3$S$: 362.1032 (M+NH$_4^+$), found: 362.1031.

2, 6-Dimethyl-4-((m-tolylsulfonyl)methyl)phenol (3i)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (m, 2H), 7.43 – 7.32 (m, 2H), 6.70 (s, 2H), 4.98 (s, 1H), 4.15 (s, 2H), 2.37 (s, 3H), 2.14 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.8, 139.0, 137.9, 134.2, 131.1, 128.9, 128.6, 125.7, 123.2, 118.9, 62.3, 21.1, 15.7. HRMS (ESI) calcd for C$_{16}$H$_{22}$NO$_3$S$: 308.1315 (M+NH$_4^+$), found: 308.1331.

4-(((3-Methoxyphenyl)sulfonyl)methyl)-2,6-dimethylphenol (3j)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38 (t, $J = 7.8$ Hz, 1H), 7.30 (m, 1H), 7.13 (m, 2H), 6.71 (s, 2H), 4.81 (s, 1H), 4.16 (s, 2H), 3.76 (s, 3H), 2.16 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.7, 152.8, 131.2, 129.9, 123.3, 120.9, 120.5, 119.2, 112.9, 62.4, 55.6, 15.7. HRMS (ESI) calcd for C$_{16}$H$_{22}$NO$_4$S$: 324.1264 (M+NH$_4^+$), found: 324.1280.
4-(((3-Chlorophenyl)sulfonyl)methyl)-2,6-dimethylphenol (3k)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 – 7.36 (m, 4H), 6.70 (s, 2H), 4.75 (s, 1H), 4.17 (s, 2H), 2.17 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 152.9, 139.8, 135.1, 133.7, 131.1, 130.0, 128.8, 126.8, 123.4, 118.7, 62.4, 15.7. HRMS (ESI) calcd for C$_{15}$H$_{19}$ClO$_3$S$: 328.0769 (M+NH$_4^+$), found: 328.0775.

2-(tert-Butyl)-6-methyl-4-(tosylmethyl)phenol (3l)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 1.8$ Hz, 1H), 6.40 (d, $J = 2.1$ Hz, 1H), 5.15 – 4.88 (m, 1H), 4.17 (s, 2H), 2.41 (s, 3H), 2.20 (s, 3H), 1.21 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.2, 144.5, 135.6, 134.9, 131.0, 129.4, 128.9, 127.8, 123.5, 119.2, 62.9, 34.3, 29.4, 21.6, 15.9. HRMS (ESI) calcd for C$_{19}$H$_{28}$NO$_3$S$: 350.1784 (M+NH$_4^+$), found: 350.1786.

3, 4'-Dimethyl-5-(tosylmethyl)-[1, 1'-biphenyl]-2-ol (3m)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.3$ Hz, 2H), 7.30 – 7.22 (m, 4H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 1.7$ Hz, 1H), 6.60 (d, $J = 2.1$ Hz, 1H), 5.59 – 5.07 (m, 1H), 4.20 (s, 2H), 2.41 (m, 6H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.0, 144.4, 137.9, 135.0, 133.3, 132.5, 130.1, 129.9, 129.4, 128.7, 127.5, 124.9, 119.4, 115.8, 62.3, 21.5, 21.1, 16.0. HRMS (ESI) calcd for C$_{22}$H$_{26}$NO$_3$S$: 384.1628 (M+NH$_4^+$), found: 384.1623.
4′-Chloro-3-methyl-5-(tosylmethyl)-[1, 1′-biphenyl]-2-ol (3n)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 8.2 Hz, 2H), 7.41 (d, $J$ = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 (d, $J$ = 8.4 Hz, 2H), 6.95 (s, 1H), 6.63 (d, $J$ = 1.9 Hz, 1H), 5.15 (s, 1H), 4.19 (s, 2H), 2.43 (s, 3H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.0, 144.6, 135.3, 135.1, 133.2, 130.4, 130.3, 129.5, 129.4, 128.9, 126.6, 125.2, 119.9, 62.3, 21.6, 16.1. HRMS (ESI) calcd for C$_{21}$H$_{23}$NClO$_3$S$: 404.1082 (M+NH$_4^+$), found: 404.1067.

![Chemical structure of 3n](image)

2-(tert-Butyl)-6-methyl-4-((phenylsulfonyl)methyl)phenol (3o)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.66 – 7.54 (m, 3H), 7.50 – 7.38 (m, 2H), 6.93 (d, $J$ = 1.8 Hz, 1H), 6.44 (d, $J$ = 2.1 Hz, 1H), 4.91 (s, 1H), 4.20 (s, 2H), 2.20 (s, 3H), 1.21 (s, 9H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 153.1, 137.7, 135.4, 133.4, 130.9, 128.8, 128.6, 127.7, 123.4, 118.9, 62.6, 34.1, 29.3, 15.8. HRMS (ESI) calcd for C$_{18}$H$_{26}$NO$_3$S$: 336.1628 (M+NH$_4^+$), found: 336.1625.

![Chemical structure of 3o](image)

2, 6-Di-tert-butyl-4-(tosylmethyl)phenol (3q)$^1$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44 (d, $J$ = 8.2 Hz, 2H), 7.21 (d, $J$ = 8.0 Hz, 2H), 6.73 (s, 2H), 5.25 (s, 1H), 4.19 (s, 2H), 2.40 (s, 3H), 1.32 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.2, 144.3, 136.0, 135.0, 129.3, 128.9, 127.7, 119.0, 63.3, 34.1, 30.1, 21.5.

![Chemical structure of 3q](image)

2, 6-Di-tert-butyl-4-((phenylsulfonyl)methyl)phenol (3t)$^1$

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J$ = 8.1 Hz, 3H), 7.43 (t, $J$ = 7.7 Hz, 2H), 6.75 (s, 2H), 5.26 (s, 1H), 4.22 (s, 2H), 1.32 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.1, 137.7, 135.9, 133.3, 128.8, 128.6, 127.6, 118.6, 63.0, 34.0, 30.0.
2, 6-Di-tert-butyl-4-(((4-methoxyphenyl)sulfonyl)methyl)phenol (3u)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 8.6$ Hz, 2H), 6.88 (d, $J = 8.6$ Hz, 2H), 6.75 (s, 2H), 5.26 (s, 1H), 4.19 (s, 2H), 3.84 (s, 3H), 1.33 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 163.4, 154.1, 135.8, 130.9, 129.3, 127.5, 119.0, 113.7, 63.3, 55.5, 34.0, 30.0. HRMS (ESI) calcd for C$_{22}$H$_{34}$NO$_4$S$^+$: 408.2203 (M+NH$_4^+$), found: 408.2209.

2, 6-Di-tert-butyl-4-(((4-(tert-butyl)phenyl)sulfonyl)methyl)phenol (3v)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, $J = 7.1$ Hz, 4H), 6.73 (s, 2H), 5.26 (s, 1H), 4.21 (s, 2H), 1.32 (d, $J = 4.7$ Hz, 27H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.2, 154.1, 135.8, 134.6, 128.7, 127.6, 125.6, 118.8, 63.0, 34.0, 31.0, 30.0. HRMS (ESI) calcd for C$_{25}$H$_{40}$NO$_3$S$^+$: 434.2723 (M+NH$_4^+$), found: 434.2722.

2, 6-Di-tert-butyl-4-(((4-fluorophenyl)sulfonyl)methyl)phenol (3w)

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (dd, $J = 8.5$, 5.2 Hz, 2H), 7.10 (t, $J = 8.5$ Hz, 2H), 6.76 (s, 2H), 5.29 (s, 1H), 4.22 (s, 2H), 1.33 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 165.6 (d, $J = 256.1$ Hz), 154.2, 136.1, 133.7, 131.6 (d, $J = 9.5$ Hz), 127.5, 118.5, 115.8 (d, $J = 22.5$ Hz), 34.0, 30.0. HRMS (ESI) calcd for C$_{21}$H$_{31}$NO$_3$S$^+$: 396.2003 (M+NH$_4^+$), found: 396.2026.
4-(((4-Bromophenyl)sulfonyl)methyl)-2,6-di-tert-butylphenol (3x)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.56 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 6.74 (s, 2H), 5.29 (s, 1H), 4.21 (s, 2H), 1.33 (s, 18H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.3, 136.6, 136.1, 131.8, 130.3, 128.7, 127.5, 118.3, 63.2, 34.0, 30.0. HRMS (ESI) calcd for C$_{21}$H$_{31}$NBrO$_3$S$: 456.1203$ (M+NH$_4^+$), found: 456.1201.

(2-Tosylethene-1,1-diyl)dibenzene

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.2$ Hz, 2H), 7.36 (m, 2H), 7.30 (t, $J = 7.4$ Hz, 4H), 7.20 (d, $J = 7.4$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 7.1$ Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.9, 144.0, 139.4, 138.8, 135.8, 130.5, 123.0, 129.6, 129.2, 128.8, 128.4, 128.0, 21.8.

Reference: