Supporting Information

Palladium-Catalyzed Allylic Amination of Homoallylic Alcohols with Amine via C-C bond Cleavage

Gui-Jun Sun\textsuperscript{a,b}, Yong Wang\textsuperscript{b}, and Qiang Kang\textsuperscript{*b}

\textsuperscript{a} College of Chemistry, Fuzhou University, 350108, P. R. China.
\textsuperscript{b} Key Laboratory of Coal to Ethylene Glycol and Its Related Technology, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, 350002, P. R. China.

Table of Contents

I General Information 2

II Screening Conditions 3

III Experimental Section 7

IV NMR Spectra of Products 24
I General Information

All reactions were performed in Schlenk tubes under an atmosphere of nitrogen using oven-dried glassware and standard Schlenk. 1,2-dichlorobenzene (ODCB) was distilled from CaH$_2$. Tetrahydrofuran (THF) was distilled from sodium and benzophenone. Commercially obtained reagents were used without further purification, unless otherwise noted. Reactions were checked for completion by TLC analysis and plates were visualized with short-wave UV light (254 nm). The $^1$H and $^{13}$C NMR spectra were obtained in CDCl$_3$ or DMSO-d$_6$ using a Bruker Avance III spectrometer at 400 and 100 MHz for $^1$H and $^{13}$C NMR, respectively. Chemical shifts are reported in parts per million (δ value) calibrated against the residual solvent peak. Signal patterns are indicated as follows: s, singlet; br. s, broad singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (J) are given in hertz (Hz). The infrared spectra were recorded on a VERTEX 70 IR spectrometer as KBr pellets, with absorption reported in cm$^{-1}$. HRMS data were obtained on a Thermo Fisher Scientific LTQ FT Ultra system.
II Screening Conditions

Table S1. Screening Base

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)</th>
<th>Entry</th>
<th>Base</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cs$_2$CO$_3$</td>
<td>36</td>
<td>4</td>
<td>NaOH</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>K$_2$CO$_3$</td>
<td>33</td>
<td>5</td>
<td>DBU</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>K$_3$PO$_4$</td>
<td>10</td>
<td>6</td>
<td>CsF</td>
<td>23</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), Pd(OAc)$_2$ (10 mol%), base (1.5 equiv.), ODCB (2 mL), 48 h.

b NMR yield using DCE as internal standard.

c K$_3$PO$_4$ (1.0 equiv) was employed.

d Base (3.0 equiv).

Table S2. Screening Ligand

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (%)</th>
<th>Entry</th>
<th>Ligand</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cy$_3$P</td>
<td>15</td>
<td>5</td>
<td>L2</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_3$P</td>
<td>45</td>
<td>6</td>
<td>L3</td>
<td>58</td>
</tr>
<tr>
<td>3</td>
<td>dppf</td>
<td>trace</td>
<td>7</td>
<td>dppb</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>L1</td>
<td>66</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), Pd(OAc)$_2$ (10 mol%), ligand (10 mol%), anhydrous Cs$_2$CO$_3$ (1.5 equiv.), H$_2$O (1.5 equiv.), ODCB (2 mL), 48 h.

b NMR yield using DCE as internal standard.

c Ligand (24 mol%).

d Ligand (20 mol%).
Table S3. Screening Catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
<th>Entry</th>
<th>Catalyst</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(dppe)Cl₂</td>
<td>43</td>
<td>4</td>
<td>Pd(OAc)₂</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>Pd(CF₃CO₂)₂</td>
<td>25</td>
<td>5</td>
<td>[Ir(cod)Cl]₂</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>PdCl₂</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), cat. (10 mol%), dppb (10 mol%), anhydrous Cs₂CO₃ (1.5 equiv.), H₂O (1.5 equiv.), ODCB (2 mL), 48 h.

<sup>b</sup> NMR yield using DCE as internal standard.

<sup>c</sup> Without ligand.

Table S4. Screening Solvent

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ODCB</td>
<td>90</td>
<td>5</td>
<td>DMF</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>15</td>
<td>6</td>
<td>dioxane</td>
<td>n.d.</td>
</tr>
<tr>
<td>3</td>
<td>DMSO</td>
<td>19</td>
<td>7</td>
<td>PhCF₃</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>PhCl</td>
<td>44</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), Pd(OAc)₂ (10 mol%), dppb (10 mol%), H₂O (1.5 equiv.), solvent (2 mL), 100 °C, 48 h.
anhydrous Cs₂CO₃ (1.5 equiv.), H₂O (1.5 equiv.), solvent (2 mL), 48 h.

b NMR yield using DCE as internal standard.

Table S5. Screening the loading of H₂O

<table>
<thead>
<tr>
<th>Entry</th>
<th>x equiv.</th>
<th>Yield (%)b</th>
<th>Entry</th>
<th>x equiv.</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>63</td>
<td>4</td>
<td>5.0</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>1.5</td>
<td>93(93)c</td>
<td>5</td>
<td>10.0</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>99</td>
<td>6d</td>
<td>5.0</td>
<td>99</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), Pd(OAc)₂ (10 mol%), dppb (12 mol%), anhydrous Cs₂CO₃ (1.5 equiv.), H₂O (x equiv.), ODCB (2 mL), 24 h.

b NMR yield using DCE as internal standard.

c Isolated yield in parenthesis.

d 36 h.

Table S6. Screening Base loading

<table>
<thead>
<tr>
<th>Entry</th>
<th>x equiv.</th>
<th>Yield (%)b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>93(93)c</td>
</tr>
<tr>
<td>2</td>
<td>1.2</td>
<td>99(98)c</td>
</tr>
</tbody>
</table>

a Reaction conditions: 1a (0.6 mmol), 2a (0.2 mmol), Pd(OAc)₂ (10 mol%), dppb (12 mol%), anhydrous Cs₂CO₃ (x equiv.), H₂O (3.0 equiv.), ODCB (2 mL), 24 h.

b NMR yield using DCE as internal standard.

c Isolated yield in parenthesis.
Table S7. Screening the loading of 1a

<table>
<thead>
<tr>
<th>Entry</th>
<th>x equiv.</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.0</td>
<td>93(93)&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>2&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.0</td>
<td>85</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1a (x equiv.), 2a (0.2 mmol), Pd(OAc)<sub>2</sub> (10 mol%), dppb (12 mol%), anhydrous Cs<sub>2</sub>CO<sub>3</sub> (1.2 equiv.), H<sub>2</sub>O (3.0 equiv.), ODCB (2 mL), 100 °C, 24 h.

<sup>b</sup> NMR yield using DCE as internal standard.

<sup>c</sup> Isolated yield in parenthesis.

<sup>d</sup> 34 h.
III Experimental Section

General procedure of preparation of homoallylic alcohols 1: To a solution of the ketone (1 equiv.) dissolved in dry THF (3 mL/mol) stirring at 0°C was added dropwise allylmagnesium chloride (1.0 M in Et₂O, 1.2 equiv.). The resulting suspension was stirred at room temperature overnight and then quenched by addition of saturated ammonium chloride at 0 °C, extracted with EtOAc (x3). The combined organic layer was washed with saturated brine (x1), dried over anhydrous Na₂SO₄, filtered and evaporated. The crude products were purified by silica gel column chromatography (EtOAc/Petroleum ether) to afford homoallylic alcohols 1.

\[
\text{Ph} \quad \text{Me} \quad \text{OH}
\]

2-Phenylpent-4-en-2-ol (1a) \(^1\)

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.43\) (d, \(J = 7.9\) Hz, 2 H), 7.34 (t, \(J = 7.6\) Hz, 2 H), 7.23-7.19 (m, 1 H), 5.66-5.56 (m, 1 H), 5.15-5.10 (m, 2 H), 2.68 (dd, \(J = 6.4\) Hz, \(J = 14.0\) Hz, 1 H), 2.49 (dd, \(J = 8.0\) Hz, \(J = 13.6\) Hz, 1 H), 2.04 (s, 1 H), 1.54 (s, 3 H).

\[
\text{Ph} \quad \text{Ph} \quad \text{OH}
\]

1,1-Diphenyl-3-buten-1-ol (1b) \(^2\)

\(^1\)H NMR (400 MHz, CDCl₃): \(\delta = 7.44-7.42\) (m, 4 H), 7.31-7.27 (m, 4 H), 7.24-7.20 (m, 2 H), 5.70-5.59 (m, 1 H), 5.28-5.15 (m, 1 H), 3.06 (d, \(J = 7.2\) Hz, 2 H), 2.56 (s, 1 H).

\[
\text{MeO} \quad \text{OH} \quad \text{MeO}
\]

1-(2,4-dimethoxyphenyl)but-3-en-1-ol (1c) \(^3\)
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.24$ (d, $J = 8.2$ Hz, 1 H), 6.50-6.46 (m, 2 H), 5.90-5.80 (m, 1 H), 5.15-5.08 (m, 2 H), 4.93-4.88 (m, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 2.60-2.50 (m, 2 H), 2.47 (d, $J = 5.4$ Hz, 1 H).

2-(2,4-dimethoxyphenyl)pent-4-en-2-ol (1d)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.21$ (d, $J = 8.5$ Hz, 2 H), 6.49-6.42 (m, 2 H), 5.68-5.58 (m, 1 H), 5.05-5.00 (m, 2 H), 3.85 (s, 3 H), 3.80 (s, 3 H), 2.80-2.75 (m, 1 H), 2.60-2.51 (m, 1 H), 1.54 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): 159.8, 157.6, 135.0, 127.3, 127.1, 127.3, 117.7, 103.8, 99.3, 55.3, 46.3, 27.1.

3-isopropyl-2-methylhex-5-en-3-ol (1e)$^4$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.93$-5.83 (m, 1 H), 5.12-5.06 (m, 2 H), 2.32 (d, $J = 7.4$ Hz, 2 H), 1.98-1.87 (m, 2 H), 0.98-0.93 (m, 12 H).

General procedure of preparation of anilines: Substrates 2a-2l were synthesized by sulfonylation of the corresponding aniline. The aniline (3 mmol) was dissolved in dry CH$_2$Cl$_2$ (6.5 mL), and the solution was treated with sulfony chloride (687 mg, 3.6 mmol) and pyridine (0.73 mL, 9 mmol). The mixture was stirred at room temperature overnight. Then diluted with H$_2$O (x1) and extracted
with CH₂Cl₂ (x3). The combined organic layers were washed with 1M HCl, brine (x1), dried over anhydrous Na₂SO₄, and concentrated in vacuo. The resulting mixture was purified by silica gel column chromatography (EtOAc/Petroleum ether) to afford the sulfonamide 2.

TsHN

4-methyl-N-(p-tolyl)benzenesulfonamide (2a)

¹H NMR (400 MHz, CDCl₃): δ = 7.66 (d, J = 8.1 Hz, 2 H), 7.21 (d, J = 8.1 Hz, 2 H), 7.02 (d, J = 8.0 Hz, 2 H), 6.96 (d, J = 8.2 Hz, 2 H), 6.85 (s, 1 H), 2.37 (s, 3 H), 2.27 (s, 3 H).

TsHN

N-(4-isopropylphenyl)-4-methylbenzenesulfonamide (2b)

Yield: 781 mg (90%); white solid; mp 141-142 °C.

IR (KBr) 3224, 2960, 2923, 2869, 1597, 1511, 1437, 1463, 1400, 1323, 1292, 1223, 1152, 1095, 920, 817, 752, 693 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.67 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 7.6 Hz, 2 H), 7.07 (d, J = 8.0 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 2 H), 6.94 (s, 1 H), 2.87-2.77 (m, 1 H), 2.37 (s, 3 H), 1.18 (d, J = 7.2 Hz, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 146.2, 143.7, 136.3, 134.1, 129.6, 127.3, 127.2, 122.1, 33.5, 31.0, 23.9, 21.6.

4-Methyl-N-(m-tolyl)benzenesulfonamide (2c) 6

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.66\) (d, \(J = 7.6\) Hz, 2 H), \(7.22\) (d, \(J = 8.1\) Hz, 2 H), \(7.10\) (t, \(J = 7.8\) Hz, 1 H), \(6.91\) (d, \(J = 8.0\) Hz, 2 H), \(6.85\) (d, \(J = 8.3\) Hz, 1 H), \(6.72\) (s, 1 H), \(2.38\) (s, 3 H), \(2.27\) (s, 3 H).

4-Methyl-N-phenylbenzenesulfonamide (2d) 6

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.66\) (d, \(J = 8.0\) Hz, 2 H), \(7.26-7.21\) (m, 4 H), \(7.12-7.06\) (m, 3 H), \(6.88\) (br. s, 1 H), \(2.37\) (s, 3 H).

N-mesityl-4-methylbenzenesulfonamide (2e) 7

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.60\) (d, \(J = 8.4\) Hz, 2 H), \(7.24\) (d, \(J = 8.4\) Hz, 2 H), \(6.81\) (s, 2 H), \(5.84\) (s, 1 H), \(2.41\) (s, 3 H), \(2.24\) (s, 3 H), \(1.98\) (s, 6 H).

N-(4-Methoxy-phenyl)-4-methylbenzenesulfonamide (2f) 6

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.58\) (d, \(J = 8.2\) Hz, 2 H), \(7.21\) (d, \(J = 8.1\) Hz, 2 H), \(6.97\) (d, \(J = 8.9\) Hz, 2 H), \(6.76\) (d, \(J = 8.9\) Hz, 2 H), \(6.40\) (br. s, 1 H), \(3.76\) (s, 3 H), \(2.39\) (s, 3 H).
Ethyl 4-(4-methylphenylsulfonamido)benzoate (2g) 8

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.95$ (d, $J = 8.8$ Hz, 2 H), 7.74 (d, $J = 8.4$ Hz, 2 H), 7.30-7.28 (m, 2 H), 7.15 (d, $J = 8.8$ Hz, 2 H), 6.88 (br. s, 1 H), 4.37 (q, $J = 7.2$ Hz, 2 H), 2.41 (s, 3 H), 1.39 (t, $J = 7.2$ Hz, 3 H).

N-(4-Fluorophenyl)-4-methyl-benzenesulfonamide (2h) 6

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.59$ (d, $J = 8.0$ Hz, 2 H), 7.21 (d, $J = 8.0$ Hz, 2 H), 7.03-7.00 (m, 2 H), 6.94-6.88 (m, 2 H), 6.71 (s, 1 H), 2.37 (s, 3 H).

N-(4-Chlorophenyl)-4-methyl-benzenesulfonamide (2i) 6

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.67$ (d, $J = 8.2$ Hz, 2 H), 7.33 (br. s, 1 H), 7.23 (d, $J = 8.1$ Hz, 2 H), 7.18 (d, $J = 8.7$ Hz, 2 H), 7.03 (d, $J = 8.7$ Hz, 2 H), 2.38 (s, 3 H).

N-(3-Chlorophenyl)-4-methyl-benzenesulfonamide (2j) 6

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.69$ (d, $J = 8.0$ Hz, 2 H), 7.26 (d, $J = 7.2$ Hz, 2 H), 7.17-7.11 (m,
2 H), 7.07 (d, J = 7.2 Hz, 1 H), 6.97 (d, J = 9.2 Hz, 2 H), 2.39 (s, 3 H).

4-Methyl-N-(4-trifluoromethyl-phenyl)-benzenesulfonamide (2k) 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.75 (d, $J$ = 8.4 Hz, 2 H), 7.51 (d, $J$ = 8.4 Hz, 2 H), 7.29 (d, $J$ = 6.8 Hz, 2 H), 7.20 (d, $J$ = 8.4 Hz, 2 H), 2.42 (s, 3 H).

4-Methyl-N-(naphthalen-2-yl)benzenesulfonamide (2l) 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.74-7.68 (m, 5 H), 7.55 (d, $J$ = 2.4 Hz, 1 H), 7.46-7.35 (m, 2 H), 7.26-7.23 (m, 1 H), 7.17 (d, $J$ = 8.0 Hz, 2 H), 2.31 (s, 3 H).

N-Benzyl-4-methylbenzenesulfonamide (2m) 

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.77 (d, $J$ = 8.0 Hz, 2 H), 7.33-7.27 (m, 5 H), 7.21-7.19 (m, 2 H), 4.60 (br. s, 1 H), 4.13 (d, $J$ = 6.0 Hz, 2 H), 2.45 (s, 3 H).

N-[4-(4-methylphenylsulfamido)phenyl]acetamide (2n) 

$^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta$ = 10.01 (s, 1 H), 9.86 (s, 1 H), 7.59 (d, $J$ = 8.2 Hz, 2 H), 7.41 (d, $J$ = 8.8 Hz, 2 H), 7.32 (d, $J$ = 8.0 Hz, 2 H), 6.98 (d, $J$ = 8.2 Hz, 2 H), 2.32 (s, 3 H), 1.98 (s, 1 H).
4-Methyl-N-(pyridin-2-yl)benzenesulfonamide (2o) \(^1\)

\(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta = 8.03\) (d, \(J = 4.8\) Hz, 1 H), 7.77 (d, \(J = 8.4\) Hz, 2 H), 7.74-7.70 (m, 1 H), 7.35 (d, \(J = 8.4\) Hz, 2 H), 7.15 (d, \(J = 8.4\) Hz, 1 H), 6.88 (t, \(J = 6.4\) Hz, 1 H), 2.36 (s, 3 H).

\[\text{NHTs} \quad \text{TsHN} \]

N-Butyl-4-methylbenzenesulfonamide (2p) \(^2\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.79\text{-}7.76\) (m, 2 H), 7.34\text{-}7.32 (m, 2 H), 4.38 (br. s, 1 H), 2.99\text{-}2.93 (m, 2 H), 2.45 (s, 3 H), 1.50\text{-}1.42 (m, 2 H), 1.36\text{-}1.27 (m, 2 H), 0.88 (t, \(J = 7.3\) Hz, 3 H).

\[\text{NHTs} \quad \text{N} \quad \text{H} \]

N-[2-(1H-indol-3-yl)ethyl]-4-methylbenzenesulfonamide (2q) \(^3\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.12\) (br. s, 1 H), 7.62 (d, \(J = 8.4\) Hz, 2 H), 7.39 (d, \(J = 8.0\) Hz, 1 H), 7.32 (d, \(J = 8.0\) Hz, 1 H), 7.20\text{-}7.15 (m, 3 H), 7.04 (t, \(J = 7.6\) Hz, 1 H), 6.93 (s, 1 H), 4.57 (t, \(J = 6.0\) Hz, 1 H), 3.24 (q, \(J = 6.4\) Hz, 2 H), 2.90 (t, \(J = 6.4\) Hz, 2 H), 2.37 (s, 3 H).

General procedure of preparation of allylic amines 3a-3q: To an oven-dried 25-mL Schlenk tube equipped with a stir bar was added Cs\(_2\)CO\(_3\) (78 mg, 0.24 mmol) in the glove box. Pd(OAc)\(_2\) (4.5 mg, 0.02 mmol) was added along with dppb (11 mg, 0.024 mmol) and aniline 2 (0.2 mmol) under
a nitrogen atmosphere. To this mixture was added purified water (10.8 μL, 0.6 mmol), followed by a homoallylic alcohol 1 (0.6 mmol) dissolved in 1,2-dichlorobenzene. The mixture was stirred at 100 °C until the reaction was completed. The resulting mixture was then cooled to r.t. and directly purified by silica gel column chromatography (EtOAc/Petroleum ether) to afford the allylic amine product 3.

\[ \text{N-Allyl-4-methyl-N-(4-methylphenyl)benzenesulfonamide (3a)} \]

Yield: 59 mg (98%); pale yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ = 7.52 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.2 Hz, 2 H), 7.10 (d, J = 8.2 Hz, 2 H), 6.94 (d, J = 8.2 Hz, 2 H), 5.81-5.71 (m, 1 H), 5.11-5.05 (m, 2 H), 4.17 (d, J = 6.3 Hz, 2 H), 2.45 (s, 3 H), 2.35 (s, 3 H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ = 114.3, 136.7, 135.4, 134.7, 132.0, 128.5, 128.3, 127.7, 126.7, 117.6, 52.6, 20.5, 20.1.

\[ \text{N-Allyl-N-(4-isoproplyphenyl)-4-methylbenzenesulfonamide (3b)} \]

Yield: 49 mg (74%); colorless solid; mp 86-87 °C.

IR (KBr) 3042, 2961, 2923, 2899, 2866, 1597, 1508, 1442, 1352, 1338, 1289, 1166, 1092, 924, 874, 817, 662 cm\(^{-1}\).
\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.50\) (d, \(J = 8.4\) Hz, 2 H), 7.25 (d, \(J = 8.0\) Hz, 2 H), 7.13 (d, \(J = 8.4\) Hz, 2 H), 6.95 (d, \(J = 8.4\) Hz, 2 H), 5.79-5.69 (m, 1 H), 5.11-5.03 (m, 2 H), 4.14 (d, \(J = 6.0\) Hz, 2 H), 2.93-2.83 (m, 1 H), 2.43 (s, 3 H), 1.23 (d, \(J = 6.8\) Hz, 6 H).

\(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 148.3, 143.1, 136.5, 135.5, 132.8, 129.2, 128.4, 127.5, 126.6, 118.3, 53.5, 33.5, 23.6, 21.3\)


\[N\text{-Allyl-4-methyl-N-(3-methylphenyl)benzenesulfonamide (3c)}\]

Yield: 50 mg (83%); colorless solid; mp 51-53 °C.

IR (KBr) 3087, 3067, 3037, 2919, 2864, 1607, 1584, 1486, 1453, 1343, 1308, 1287, 1272, 1165, 1092, 1076, 1024, 990, 931, 907, 827, 813, 693, 662 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.48\) (d, \(J = 8.4\) Hz, 2 H), 7.23 (d, \(J = 8.4\) Hz, 2 H), 7.13 (t, \(J = 7.6\) Hz, 1 H), 7.05 (d, \(J = 7.6\) Hz, 1 H), 6.90 (s, 1 H), 6.74 (d, \(J = 7.6\) Hz, 1 H), 5.76-5.67 (m, 1 H), 5.07-5.00 (m, 2 H), 4.13 (d, \(J = 6.4\) Hz, 2 H), 2.40 (s, 3 H), 2.27 (s, 3 H).

\(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 143.4, 139.1, 138.8, 135.6, 133.0, 129.9, 129.4, 128.6, 128.5, 127.8, 125.4, 118.6, 53.6, 21.5, 21.3\).

**N- Allyl-4-methyl-N-phenylbenzenesulfonamide (3d)**

Yield: 38 mg (66%); yellowish solid; mp 62-64 °C.

IR (KBr) 3058, 3038, 2981, 2959, 2925, 1645, 1596, 1493, 1451, 1427, 1403, 1346, 1307, 1162, 1092, 1038, 860, 812, 770, 728, 696 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.48 (d, J = 8.0 Hz, 2 H), 7.31-7.23 (m, 5 H), 7.06-7.02 (m, 2 H), 5.78-5.68 (m, 1 H), 5.09-5.02 (m, 2 H), 4.17 (d, J = 6.4 Hz, 2 H), 2.43 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.3, 138.0, 134.3, 131.7, 128.3, 127.7, 126.7, 126.6, 117.7, 52.4, 20.4.


\[ \text{Ts} \]

**N- Allyl-N- mesityl-4-methylbenzenesulfonamide (3e)**

Yield: 43 mg (65%); colorless solid; mp 101-102 °C.

IR (KBr) 2977, 2921, 1596, 1480, 1338, 1304, 1220, 1155, 1138, 1087, 1074, 1006, 940, 856, 817, 712, 698, 663, 611 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.68 (d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 6.83 (s, 2 H), 5.92-5.82 (m, 1 H), 5.03-4.99 (m, 2 H), 4.09 (d, J = 7.2 Hz, 2 H), 2.43 (s, 3 H), 2.25(s, 3 H), 2.01 (s, 6 H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.2, 138.8, 138.4, 137.9, 134.2, 133.3, 129.7, 129.6, 127.4, 118.2, 53.9, 21.6, 21.0, 19.1.

**N- Allyl-N-(4-methoxyphenyl)-4-methylbenzenesulfonamide (3f)**

Yield: 44 mg (69%); colorless solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.48 (d, $J$ = 8.4 Hz, 2 H), 7.23 (d, $J$ = 8.4 Hz, 2 H), 6.91 (d, $J$ = 8.8 Hz, 2 H), 6.77 (d, $J$ = 8.8 Hz, 2 H), 5.77-5.67 (m, 1 H), 5.06-5.01 (m, 2 H), 4.12 (d, $J$ = 6.4 Hz, 2 H), 3.76 (s, 3 H), 2.41 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 159.0, 143.4, 135.5, 133.0, 131.6, 130.2, 129.4, 127.8, 118.7, 114.1, 55.4, 53.8, 21.6.

---

**Ethyl 4-(N- Allyl-4-methylphenylsulfonamido) benzoate (3g)**

Yield: 61 mg (84%); yellowish solid; mp 74-75 °C.

IR (KBr) 3051, 2090, 1708, 1648, 1604, 1494, 1468, 1399, 1368, 1352, 1275, 1166, 1110, 1060, 935, 876, 814, 707 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.97 (d, $J$ = 8.4 Hz, 2 H), 7.36 (d, $J$ = 8.4 Hz, 2 H), 7.25 (d, $J$ = 8.4 Hz, 2 H), 7.14 (d, $J$ = 8.8 Hz, 2 H), 5.76-5.66 (m, 1 H), 5.10-5.04 (m, 2 H), 4.40-4.31 (m, 2 H), 4.21 (d, $J$ = 6.0 Hz, 2 H), 2.42 (s, 3 H), 1.38 (t, $J$ = 7.2 Hz, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 165.9, 143.8, 143.3, 135.0, 132.4, 130.2, 129.6, 129.4, 128.0, 127.6, 119.2, 61.2, 53.0, 21.6, 14.3.
HRMS (ESI): m/z [M+H]^+ calcd for C_{19}H_{22}O_{4}NS: 360.1264; Found: 360.1259.

\[
\text{N- Allyl-N-}(4\text{-fluorophenyl})\text{-4-methylbenzenesulfonamide (3h) }^{15}
\]

Yield: 55 mg (90%); white solid.

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 7.48\) (d, 2 H, \(J = 8.4\) Hz), 7.26 (d, \(J = 8.0\) Hz, 2 H), 7.01-6.94 (m, 4 H), 5.77-5.67 (m, 1 H), 5.07-5.03 (m, 2 H), 4.14 (d, \(J = 6.0\) Hz, 2 H), 2.43 (s, 3 H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 162.0, 159.6, 142.6, 134.2, 133.9, 131.6, 129.7, 126.7, 118.1, 114.9, 114.7, 52.7, 20.5\).

\[
\text{N- Allyl-N-}(4\text{-chlorophenyl})\text{-4-methylbenzenesulfonamide (3i) }^{15}
\]

Yield: 46 mg (71%); white powder.

\(^1\)H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 7.47\) (d, \(J = 8.4\) Hz, 2 H), 7.27-7.24 (m, 4 H), 7.00 (d, \(J = 8.8\) Hz, 2 H), 5.75-5.67 (m, 1 H), 5.08-5.04 (m, 2 H), 4.13 (d, \(J = 6.0\) Hz, 2 H), 2.43 (s, 3 H).

\(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 143.7, 137.6, 135.1, 133.6, 132.5, 130.1, 129.6, 129.1, 127.7, 119.2, 53.4, 21.6\).
**N-allyl-N-(3-chlorophenyl)-4-methylbenzenesulfonamide (3j).**

Yield: 52 mg (81%); white powder; mp 76-77 °C.

IR (KBr) 3075, 2979, 2921, 1586, 1492, 1472, 1420, 1163, 1092, 1071, 1013, 930, 889, 804, 702, 682, 668 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.49 (d, J = 8.4 Hz, 2 H), 7.28-7.20 (m, 4 H), 7.05-7.04 (m, 1 H), 7.00-6.94 (m, 1 H), 5.76-5.66 (m, 1 H), 5.14-5.06 (m, 2 H), 4.14 (d, J = 6.3 Hz, 2 H), 2.43 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.9, 140.4, 135.1, 134.3, 132.5, 129.8, 129.6, 129.0, 128.1, 127.8, 127.0, 119.3, 53.5, 21.6.


\[
\text{N-allyl-N-(3-chlorophenyl)-4-methylbenzenesulfonamide (3j).}
\]

**N-allyl-4-methyl-N-[4-(trifluoromethyl)phenyl]benzenesulfonamide (3k).**

Yield: 36 mg (50%); yellowish solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.56 (d, J = 8.4 Hz, 2 H), 7.48 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.4 Hz, 2 H), 5.76-5.66 (m, 1 H), 5.11-5.06 (m, 2 H), 4.20 (d, J = 6.4 Hz, 2 H), 2.43 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.9, 141.3, 134.9, 131.2, 128.6, 127.6, 126.5, 124.9, 118.3, 52.1, 20.5.
**N- Allyl-4-methyl-N-2-naphthylbenzenesulfonamide (3l)**

Yield: 47 mg (70%); yellowish solid; mp 86-87 °C.

IR (KBr) 3060, 2986, 2920, 2361, 2341, 1596, 1505, 1431, 1342, 1163, 1130, 1110, 1089, 923, 822, 762, 708, 668 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.82-7.80 (m, 1 H), 7.76-7.72 (m, 2 H), 7.53-7.45 (m, 5 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.16-7.13 (m, 1 H), 5.82-5.72 (m, 1 H), 5.11-5.00 (m, 2 H), 4.27 (d, J = 6.2 Hz, 2 H), 2.42 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 143.5, 136.5, 135.5, 133.3, 132.8, 132.5, 129.5, 128.7, 128.0, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 118.9, 53.6, 21.6.


![N- Allyl-4-methyl-N-2-naphthylbenzenesulfonamide (3l)](image)

**N- Allyl-N-benzyl-4-methylbenzenesulfonamide (3m)**

Yield: 43 mg (71%); colorless solid.

¹H NMR (400 MHz, CDCl₃): δ = 7.69 (d, J = 8.4 Hz, 2 H), 7.28-7.19 (m, 7 H), 5.47-5.37 (m, 1 H), 5.02-4.92 (m, 2 H), 4.29 (s, 2 H), 3.70 (d, J = 6.4 Hz, 2 H), 2.39 (s, 3 H).

¹³C NMR (100 MHz, CDCl₃): δ = 142.3, 136.5, 135.0, 131.2, 128.7, 127.5, 127.4, 126.7, 126.2, 118.3, 49.1, 48.4, 20.5.

![N- Allyl-N-benzyl-4-methylbenzenesulfonamide (3m)](image)

**N- [4-[Allyl(tosyl)amino]phenyl]acetamide (3n)**

Yield: 28 mg (41%); yellowish solid; mp 54-55 °C.
IR (KBr) 3311, 3061, 2922, 1671, 1600, 1536, 1510, 1469, 1408, 1344, 1311, 1161, 1090, 869, 813, 716, 662 cm$^{-1}$.

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 10.02$ (s, 1 H), 7.50-7.38 (m, 6 H), 6.94 (d, $J = 8.8$ Hz, 2 H), 5.71-5.61 (m, 1 H), 5.14-5.02 (m, 2 H), 4.14 (d, $J = 5.6$ Hz, 2 H), 2.40 (s, 3 H), 2.03 (s, 3 H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$): $\delta = 168.9, 143.9, 139.0, 135.3, 133.6, 133.5, 130.2, 129.3, 127.8, 119.4, 119.2, 53.1, 24.4, 21.5.$

HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{18}$H$_{21}$O$_3$N$_2$S: 345.1267; Found: 345.1262.

\[
\begin{array}{c}
\text{N- Allyl-4-methyl-N-(2-pyridyl)benzenesulfonamide (3o)} \\
\end{array}
\]

Yield: 22 mg (39%); yellowish solid; mp 75-77 °C.

IR (KBr) 3092, 3056, 2920, 2853, 1633, 1599, 1555, 1503, 1456, 1370, 1353, 1283, 1266, 1167, 1137, 1084, 972, 914, 827, 766, 660 cm$^{-1}$.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.83$ (d, $J = 8.0$ Hz, 2 H), 7.71-7.68 (m, 1 H), 7.50-7.47 (m, 2 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 6.54-6.51 (m, 1 H), 6.01-5.92 (m, 1 H), 5.31-5.28 (m, 2 H), 4.77 (d, $J = 6.0$ Hz, 2 H), 2.38 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 155.5, 141.7, 140.8, 140.1, 138.2, 131.1, 129.1, 126.4, 120.0, 118.3, 110.8, 54.9, 21.5.$

HRMS (ESI): m/z [M+H]$^+$ calcd for C$_{15}$H$_{17}$O$_2$N$_2$S: 289.1005; Found: 289.1000.
N-Allyl-N-[2-(1H-indol-3-yl)ethyl]-4-methylbenzenesulfonamide (3q).  

Yield: 17 mg (24%); white solid.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.00$ (s, 1 H), 7.70 (d, $J = 8.0$ Hz, 2 H), 7.54 (d, $J = 8.0$ Hz, 1 H), 7.35 (d, $J = 8.0$ Hz, 1 H), 7.26 (d, $J = 5.6$ Hz, 2 H), 7.18 (t, $J = 8.0$ Hz, 1 H), 7.10 (t, $J = 8.0$ Hz, 1 H), 7.00 (d, $J = 2.0$ Hz, 1 H), 5.72-5.62 (m, 1 H), 5.20-5.14 (m, 2 H), 3.85 (d, $J = 6.4$ Hz, 2 H), 3.43-3.39 (m, 2 H), 3.04-3.00 (m, 2 H), 2.40 (s, 3 H).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 143.2$, 137.2, 136.2, 133.4, 129.7, 127.3, 127.2, 122.1, 119.4, 119.4, 118.9, 118.7, 112.7, 111.2, 51.1, 47.9, 25.1, 21.5.

References:


\textsuperscript{1}H NMR spectra of compound 1a

\textsuperscript{1}H NMR spectra of compound 1b
$^1$H NMR spectra of compound 1c
(400 MHz, CDCl$_3$)

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)
$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 1e

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^1$H NMR spectra of compound 1e
$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR and $^{13}$C spectra of compound 2b

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^1$H NMR spectra of compound 2c
H NMR spectra of compound \(2d\)

(400 MHz, CDCl\(_3\))

\(^1\)H NMR spectra of compound \(2e\)

(400 MHz, CDCl\(_3\))
$^1$H NMR spectra of compound 2f

(400 MHz, CDCl₃)

$^1$H NMR spectra of compound 2g

(400 MHz, CDCl₃)
H NMR spectra of compound 2h

TsHN

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^1$H NMR spectra of compound 2i

TsHN

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)
H NMR spectra of compound 2j

1H NMR spectrum
(400 MHz, CDCl₃)

H NMR spectra of compound 2k

1H NMR spectrum
(400 MHz, CDCl₃)
\( ^1\text{H} \) NMR spectra of compound 2l
(400 MHz, CDCl\(_3\))

\( ^1\text{H} \) NMR spectra of compound 2m
(400 MHz, CDCl\(_3\))
$^1$H NMR spectra of compound 2n

$^1$H NMR spectra of compound 2o
$^1$H NMR spectra of compound 2p

$^1$H NMR spectra of compound 2q
\[ ^1\text{H NMR spectrum} \]

(400 MHz, CDCl\textsubscript{3})

\[ ^{13}\text{C NMR spectrum} \]

(100 MHz, CDCl\textsubscript{3})

\[ ^1\text{H NMR} ^{13}\text{C} \text{ spectra of compound } 3a \]
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3b
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3c
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3d
$^1$H NMR spectra of compound 3e

(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum

(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3e
$^1$H NMR spectra of compound 3f

(400 MHz, CDCl$_3$)

$^1$H NMR spectrum

$^13$C NMR spectrum

(100 MHz, CDCl$_3$)

$^1$H NMR $^13$C spectra of compound 3f
The image contains two sets of NMR spectra for compound 3g. The first is a 1H NMR spectrum (400 MHz, CDCl₃) and the second is a 13C NMR spectrum (100 MHz, CDCl₃). The spectra show chemical shifts for various protons and carbons, with peak positions indicated on the x-axis in ppm. The molecular structure of the compound is also shown along with a Ts (tosyl) group attached to a benzene ring.
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3h
$^1$H NMR spectra of compound 3i

$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 3i
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^13$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^13$C spectra of compound 3j
H NMR and 13C spectra of compound 3k

(400 MHz, CDCl₃)

13C NMR spectrum
(100 MHz, CDCl₃)

1H NMR 13C spectra of compound 3k
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)

$^1$H NMR $^{13}$C spectra of compound 31
$^1$H NMR spectra of compound 3m

$^1$H NMR (400 MHz, CDCl$_3$)

$^1$C NMR spectrum

$^1$C NMR (100 MHz, CDCl$_3$)

$^1$H NMR $^1$C spectra of compound 3m
$^1$H NMR and $^{13}$C spectra of compound 3n

$^1$H NMR spectrum

(400 MHz, DMSO-$d_6$)

$^{13}$C NMR spectrum

(100 MHz, DMSO-$d_6$)
\[ ^1\text{H NMR spectrum} \]

(400 MHz, CDCl\textsubscript{3})

\[ ^{13}\text{C NMR spectrum} \]

(100 MHz, CDCl\textsubscript{3})

\[ ^1\text{H NMR} \quad ^{13}\text{C} \text{ spectra of compound 3o} \]
$^1$H NMR spectrum
(400 MHz, CDCl$_3$)

$^{13}$C NMR spectrum
(100 MHz, CDCl$_3$)