Supporting Information
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Supporting Information

A Highly Selective Amidation of Azoxybenzenes with Sulfonamides via Rh(III)-Catalyzed C-H Activation

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Table of Contents for Supporting Information

1. General considerations

2. Effect of solvent on the amidation reaction

3. Typical procedure for the intermolecular competing experiment

4. Typical procedure for mechanistic studies

5. \(^1\)H and \(^{13}\)C NMR spectra of the products
1. General considerations

All $^1$H NMR and $^{13}$C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as $\delta$ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, $J$, are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on a Waters Micromass GCT instrument. Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumber (cm$^{-1}$). Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus.

Azoxynitrobenzenes were prepared from the oxidation of arylamines in SeO$_2$/H$_2$O$_2$/MeOH system according to the reported literature (G. Christin, P. Beate, I. Elisabeth and R.-B. Karola, Synthesis, 2008, 1889). All the synthesized azoxynitrobenzenes should be recrystallized from ethanol or dicholomethane prior to use. The yide 4 was synthesized from PhI(OAc)$_2$ and TsNH$_2$ and which was recrystallized from methol at room temperature prior to use (See: Yamada, Y.; Yamamoto, T.; Okawara, M. Chem. Lett. 1975, 4, 361). The chemicals and solvents were purchased from commercial suppliers either Shanghai Chemical Company, China, or from TCI, Japan. All the solvents were dried by CaH$_2$ or Na and freshly distilled in N$_2$. Products were purified by flash chromatography on 200–300 mesh silica gels, SiO$_2$. 
2. Effect of solvent on the amidation reaction (Table S1)

**Table S1** Effect of the solvent on the amidation of azoxybenzene with TsNH₂

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield (%)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>DCM</td>
<td>57</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>trace</td>
</tr>
<tr>
<td>5</td>
<td>1,4-Dioxane</td>
<td>trace</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>n.r.</td>
</tr>
<tr>
<td>8</td>
<td>DMA</td>
<td>n.r.</td>
</tr>
<tr>
<td>9</td>
<td>HOAc</td>
<td>trace</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: 1,2-diphenyldiazene oxide (1a, 0.40 mmol), 4-methylbenzenesulfonamide (2a, 0.60 mmol), [Cp*RhCl₂]₂ (2.5 mol%), Phl(OAc)₂ (0.60 mmol), AgSbF₆ (10 mol%), solvent (1.0 mL) at 80 °C in air for 16 h.<sup>b</sup> Isolated yield. n.r.= no reaction

3. Typical procedure for intermolecular competing experiment
(a) A Schlenk tube (10 mL) was charged with TsNH$_2$ (68.4 mg, 0.40 mmol), 4-MeC$_6$H$_4$SO$_2$NH$_2$ (80.8 mg, 0.40 mmol), azoxybenzene (1a, 79.2 mg, 0.40 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (13.7 mg, 0.04 mmol), and PhI(OAc)$_2$ (193.2 mg, 0.60 mmol). Then freshly distilled 1, 2-dichloroethane (DCE, 1.0 mL) was injected into the Schlenk tube. The reaction tube was placed in an oil bath and stirred at 80 °C for 16 h; then it was cooled to room temperature and detected by TLC. H$_2$O (10.0 mL) was subsequently added into the reaction mixture and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over MgSO$_4$, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1→5:1, v/v), affording the products 3a (57.3 mg, 39%) and 3h (36.6 mg, 23%). The calculated value for the molar ratio of products 3a:3h is 1.7:1.

(b) A Schlenk tube (10 mL) was charged with (Z)-1,2-bis(4-chlorophenyl)diazene oxide (106.4 mg, 0.40 mmol), (Z)-1,2-di-p-tolyldiazene oxide (90.4 mg, 0.40 mmol), TsNH$_2$ (68.4 mg, 0.40 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (13.7 mg, 0.04 mmol), and PhI(OAc)$_2$ (193.2 mg, 0.60 mmol). Then freshly distilled 1, 2-dichloroethane (DCE, 1.0 mL) was injected into the Schlenk tube. The reaction tube was placed in an oil bath and stirred at 80 °C for 16 h; then it was cooled to room temperature and detected by TLC. H$_2$O (10.0 mL) was subsequently added into the reaction mixture and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over MgSO$_4$, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1→5:1, v/v), affording the products 3r (46.98 mg, 27%) and 3s (31.6 mg, 20%). The calculated value for the molar ratio of products 3r:3s is 1.4:1.

4. Typical procedure for mechanistic studies

(1) Typical procedure for deuterium-labelling experiment

A Schlenk tube (10 mL) was charged with azoxybenzene (1a, 79.2 mg, 0.40 mmol), [Cp*RhCl$_2$]$_2$ (3.1 mg, 0.005 mmol), AgSbF$_6$ (13.7 mg, 0.04 mmol), and PhI(OAc)$_2$ (193.2 mg, 0.60 mmol). Then freshly distilled 1, 2-dichloroethane (DCE, 1.0 mL) and CD$_3$OD (0.2 mL) were injected into the Schlenk tube.
The reaction tube was placed in an oil bath and stirred at 80 °C for 8 h; then it was cooled to room temperature and detected by TLC. H₂O (10.0 mL) was subsequently added into the reaction mixture and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1→5:1, v/v). Obviously, 34.5% D-1a in the mixture was determined by ¹H-NMR method.
(2) Typical procedure for the amidation of azoxybenzene 1a with ylide 4

A Schlenk tube (10 mL) was charged with ylide 4 (149.2, 0.40 mmol), azoxybenzene (1a, 79.2 mg, 0.40 mmol), [Cp*RhCl₂]₂ (3.1 mg, 0.005 mmol), AgSbF₆ (13.7 mg, 0.04 mmol). Then freshly distilled 1, 2-dichloroethane (DCE, 1.0 mL) was injected into the Schlenk tube. The reaction tube was placed in an oil bath and stirred at 80 °C for 8 h; then it was cooled to room temperature and detected by TLC. H₂O (10.0 mL) was subsequently added into the reaction mixture and extracted with dichloromethane (DCM, 3×5.0 mL). The organic layers were combined, dried over MgSO₄, and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate 9:1→5:1, v/v), affording the products 3a (77.8 mg) in 53% yield.
5. $^1$H and $^{13}$C NMR spectra of the products