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

Hongji Li*
Hong Deng

Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, P. R. of China
hongjili@chnu.edu.cn
hongjiliah@gmail.com

**Abstract**

A new amidation of azoxybenzenes with sulfonamides catalyzed by a rhodium(III) salt has been developed. This sulfonamidation proceeds efficiently under mild reaction conditions to generate new C–N bonds through C–H bond activation and functionalization, affording the corresponding 2-sulfonamidoazoxybenzenes in good yields with high regioselectivity.

**Key words** rhodium catalysis, azoxybenzenes, sulfonamides, C–H activation, amidation

The units of carbon–nitrogen bonds are widely found in pharmaceuticals, natural products, and agrochemicals. As a result, the development of new methods for the formation of C–N bonds has received much attention in organic syntheses. In particular, transition-metal-catalyzed protocols play an important role on the C–N formation. For example, both Buchwald–Hartwig amination and Ullmann–Goldberg coupling reactions have proven to be the powerful tools for the synthesis of amines and their derivatives. It should be noted that atom- and step-economic C–H amination by transition metal catalysis is more attractive among the previously reported methods. However, this strategy also faces problems because of the possible catalyst poisoning caused by amines in the direct C–H amination process. Despite these facts, several alternative nitrogen-containing reagents, such as N-fluorobenzenesulfonimide (NFSI), p-toluenesulfonamide, benzoyl hydroxylamines, and azides, and others have been explored in the direct intermolecular C–H aminations. After the pioneering work contributed by Che et al., Pd, Ru, Rh, Ir, and other metals, have been used as efficient catalysts in group-directing C–H amination (Scheme 1, a and b). Among them, Rh(III) catalysts exhibited high activity. Very recently, Chang and co-workers made deep insight into the mechanism of Rh-catalyzed direct C–H amination by use of azides as nitrogen sources. These achievements inspired us to develop the new C–N bond formation through Rh-catalyzed direct C–H amidation.

Aromatic azoxy compounds, as important organic molecules, prevail in materials, industrial dyes, molecular machines, and other fields. In past years, several strategies have been adopted toward the synthesis of azoxybenzenes and derivatives due to their unique properties. In general, the reported methods, such as oxidation of amines, reduction of nitrobenzenes, and oxidation of azobenzenes, had been used for the generation of azoxybenzenes, but in narrow scope and poor selectivity. We then found that there was a rare report on the synthesis of sterically hindered azoxybenzenes, especially for 2-substituted azoxybenzenes. More recently, transition-metal-catalyzed ortho-selective C–H activations and functionalization of azoxybenzenes to the corresponding ortho-substituted azoxybenzenes were realized in our laboratory. Based on the early work referring to C–H functionalization and our recent findings, we have explored a feasible amidation of azoxybenzene with sulfonamide in the presence of Rh catalyst, which underwent sulfonamidation to deliver the desired products (Scheme 1, c). It is worth noting that Jia’s and Xu’s groups reported Rh-catalyzed amidation of azoxybenzenes with sulfonyl azides independently in 2014. However, from the point of view of actual safety, sulfonamide as a nitrogen source is superior to sulfonyl azide in organic synthesis. Su and co-workers recently reported a Rh(III)-catalyzed intermolecular aromatic C–H amidation with amides. Interestingly, we observed that the amidation of azoxybenzene with sulfonamide did not proceed under Xu’s or Jia’s reaction conditions, even though we could not provide a reasonable explanation for the findings. Herein, we wish to report an efficient Rh(III)-catalyzed direct
amidation of azoxybenzenes with sulfonamides, which provides a direct and efficient approach to a series of 2-sulfonamidoazoxybenzenes.

Our investigation started from the model reaction of 1,2-diphenyldiazene oxide (1a) with 4-methylbenzenesulfonamide (2a) under various reaction conditions, as shown in Table 1. First, the model reaction was carried out in the presence of [Cp*RhCl2]2 (2.5 mol%) as catalyst, PhI(OAc)2 (1.5 equiv) as additive in 1,2-dichloroethane (DCE) at 80 °C, but only trace amount of product 3a was isolated (Table 1, entry 1). To our delight, the addition of AgSbF6 (5 mol%) into the above reaction system led to the formation of 3a in 59% yield (entry 2). It was found that no reaction occurred while replacing [Cp*RhCl2]2 with [Cp*RuCl2]2 in the model amidation reaction (entry 3). Further, the yield of 3a was improved by increasing the amount of AgSbF6 (entry 4). Other additives, including NaBF4 and K3PF6, did not promote this amidation (entries 5 and 6). Product 3a was not detected in the absence of PhI(OAc)2 in the model reaction (entry 7). It was found that other tested oxidants, such as AgOAc, Ag2CO3, Cu(OAc)2, Ag2O, and BQ (benzoquinone) instead of PhI(OAc)2, shut down the reaction completely (entries 8–12). The best reaction conditions were determined to be the following: 2.5 mol% of [Cp*RhCl2]2, 10 mol% of AgSbF6, and 1.5 equiv of PhI(OAc)2 in DCE at 80 °C under air.

Next, the substrate scope of azoxybenzenes and sulfonamides was explored under the optimized reaction conditions, as described in Scheme 2. A series of arylsulfonamides bearing different substituents on the aromatic rings were treated with 1,2-diphenyldiazene oxide (1a) to afford the corresponding products in good yields. The reactions showed excellent group tolerance in some cases. For example, the incorporation of electron-donating groups on the benzene rings of 2, such as Me, t-Bu and MeO, is beneficial to the amidation reaction, providing the desired products 3a–d in 78–84% yields. In addition, the structure of product 3a was determined by spectroscopic analysis and confirmed by single-crystal X-ray diffraction,16 which demonstrated the high selectivity in the reaction. Then, introduction of electron-withdrawing groups including F, Cl, Br, and NO2 at the para-positions on the phenyl rings in 2, afforded 70–75% yields of products 3e–h. The substituents at the meta-positions showed little effect toward the reaction in comparison with the substitutes at the para- positions (3a vs 3i, 3h vs 3j). However, an obvious steric hindrance of 2-chlorobenzenesulfonamide was found in the formation of the product 3k. Both 2-naphthalenesulfonamide and 1-naphthalenesulfonamide could react with azoxybenzene 1a to produce 3l and 3m in satisfactory yield of 84% and 73%, respectively. Notably, 2-thiophenesulfonamide as a cou-
pling partner with 1a led to inferior yield of product 3n. When 4-chloro-3-(trifluoromethyl)benzenesulfonamide was examined, 71% yield of 3o was obtained. It was found that prolonging reaction time up to 36 hours is necessary for the reaction of azoxybenzene (1a) with methanesulfonamide, generating 3p in 53% yield.

In addition, several substituted azoxybenzenes were examined. Particularly, azoxybenzenes attached to F behaved with lower activity and afforded 3q in 64% yield. Other azoxybenzenes with Cl, Me, i-Pr, and MeO at the para- and meta-positions on the benzene rings in 1, reacted smoothly with 2a to afford the anticipated products 3r–v in 70–82% yields under the standard reaction conditions. However, the use of more sterically hindered azoxybenzene as substrate failed to generate the product 3w. Moreover, intermolecular competing experiments were carried out under standard conditions. It was found that the introduction of electron-donating group into sulfonamide gave high yields of amidated product (3a/3h = 1.7:1). Similar results were observed for the amidation of azoxybenzenes with TsNH₂ under the above conditions (3r/3s = 1.4:1) (Scheme 3).

The isotope labeling experiment was carried out by the addition of CD₃OD into the amidation reaction under the optimized conditions (Scheme 4, a). We observed that 34.5% ortho-C–H was deuterated in 8 hours, suggesting C–H activation is the key step for the catalytic amidations. The reaction of ylide 4 with azoxybenzene under standard conditions delivered product 3a in 53% yield, indicating that the in situ formed 4 is a plausible intermediate involved in the reaction (Scheme 4, b). In addition, it was found that the tosyl group within product 3, taking 3a as an example, could be easily removed in the presence of concentrated H₂SO₄ at room temperature over 2 hours, which delivered 5 in 92% isolated yield. Furthermore, the treatment of 5 with

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Oxidant</th>
<th>Additive</th>
<th>Yield of 3a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>–</td>
<td>trace</td>
</tr>
<tr>
<td>2</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>59c</td>
</tr>
<tr>
<td>3</td>
<td>[Cp*RuCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>4</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>NaF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>6</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>K₂PO₄</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>[Cp*RhCl₂]₂</td>
<td>–</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>8</td>
<td>[Cp*RhCl₂]₂</td>
<td>–</td>
<td>AgOAc</td>
<td>n.r.</td>
</tr>
<tr>
<td>9</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂CO₃</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>10</td>
<td>[Cp*RhCl₂]₂</td>
<td>Cu(OAc)₂</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>11</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ag₂O</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>12</td>
<td>[Cp*RhCl₂]₂</td>
<td>BQ</td>
<td>AgSbF₆</td>
<td>n.r.</td>
</tr>
<tr>
<td>13</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>63d</td>
</tr>
<tr>
<td>14</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>75e</td>
</tr>
<tr>
<td>15</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>67f</td>
</tr>
<tr>
<td>16</td>
<td>[Cp*RhCl₂]₂</td>
<td>Ph(OAc)₂</td>
<td>AgSbF₆</td>
<td>80g</td>
</tr>
</tbody>
</table>

* Reaction conditions: 1,2-Diphenyldiazene oxide (1a; 0.40 mmol), TsNH₂ (2a; 0.60 mmol), catalyst (2.5 mol%), oxidant (1.5 equiv), additive (10 mol%), DCE (1.0 mL) at 80 °C in air for 16 h. Cp* = pentamethylcyclopentadienyl.
* Isolated yield; n.r. = no reaction.
* AgSbF₆ used: 5 mol%.
* Reaction temperature: 70 °C.
* Reaction temperature: 90 °C.
* Ph(OAc)₂ used: 1.0 equiv.
* Ph(OAc)₂ used: 2.0 equiv.
PhI(OAc)$_2$ in toluene generated 1,2,3-triazole 6 in satisfactory yield, although the exact mechanism is not clear at the current stage (Scheme 5).

A possible reaction mechanism for this Rh(III)-catalyzed direct sulfonamidation is outlined in Scheme 6. At first, the anion exchange between [Cp*RhCl$_2$]$_2$ with AgSbF$_6$ produces a highly active Rh(III)-species A, which next coordinates with azoxybenzene 1a to form a rhodacycle B and AcOH. Meanwhile, PhI(OAc)$_2$ reacts with TsNH$_2$ (2a) to generate 4, which next oxidizes the formed intermediate B into Rh(V)-species C, followed by a reductive elimination to give Rh(III)-species D, along with the formation of C–N bond via intramolecular insertion. Finally, the interaction of AcOH with D releases the corresponding product 3a and the active species A for the next run. Although a Rh(III)/Rh(V)-mechanism is proposed for this amidation reaction, another Rh(I)/Rh(III)-process cannot be absolutely ruled out.

In summary, a Rh(III)-catalyzed direct amidation of azoxybenzenes with sulfonamides was developed under mild conditions, which produced the asymmetric azoxybenzenes in moderate to good yields and excellent selectivity. The efficient amidation reactions not only offer an attractive approach to azoxybenzenes, but also enrich the route for the C–N bond formation. Further application of these obtained azoxybenzenes in fluorescent materials is currently underway in our laboratory.
All 1H NMR and 13C NMR spectra were recorded on a 400 MHz Bruker FT-NMR spectrometers (400 MHz or 100 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to TMS as an internal standard. Standard abbreviations were used to indicate the peak multiplicities. The coupling constants, J, are reported in hertz (Hz). High-resolution mass spectroscopy data of the products were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). IR spectra were recorded on a Nicolet 6700 spectrophotometer and are reported as wavenumbers (cm⁻¹). Melting points were determined in open capillary tube using WRS-1B digital melting point apparatus. Azoxybenzenes were prepared from the direct oxidation of arylamines in SeO₂/H₂O₂/MeOH system. The synthesized azoxybenzenes must be recrystallized from EtOH before use. The chemicals and solvents were purchased from commercial suppliers.
(2)-2-Phenyl-1-[2-(phenylsulfonamido)phenyl]-diazene Oxide (3b)

Under the optimal reaction conditions, the desired product 3b (110.2 mg, 0.31 mmol, 78%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.43); mp 218–220 °C.

IR (KBr): 3064, 1609, 1491, 1372, 1257, 1167, 951, 904, 759, 713 cm⁻¹.

1H NMR (400 MHz, CDCl₃): J = 10.19 (s, 1 H), 8.06 (d, J = 8.0 Hz, 2 H), 7.98 (d, J = 8.4 Hz, 1 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.52–7.46 (m, 4 H), 7.20 (t, J = 8.0 Hz, 1 H), 7.04 (d, J = 7.6 Hz, 2 H). 2.25 (s, 3 H).

13C NMR (100 MHz, CDCl₃): δ = 143.99, 142.90, 135.93, 131.14, 131.59, 130.72, 129.68, 128.84, 126.82, 125.66, 124.67, 124.62, 123.48, 21.39.

HRMS (ESI): m/z [M + H]⁺ calc for C₁₈H₁₅ClN₃O₃S: 368.0869; found: 368.0171.

(Z)-1-[2-(4-Methoxyphenylsulfonamido)phenyl]-2-phenyldiazene Oxide (3e)

Under the optimal reaction conditions, the desired product 3e (105.4 mg, 0.28 mmol, 71%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.43); mp 172–174 °C.

IR (KBr): 3212, 1605, 1591, 1491, 1386, 1341, 1090, 889, 869, 763 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.15 (s, 1 H), 8.08 (d, J = 7.6 Hz, 2 H), 7.98 (d, J = 8.4 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.67 (dd, J = 7.6, 5.2 Hz, 2 H), 7.55–7.49 (m, 4 H), 7.25 (t, J = 8.0 Hz, 1 H), 6.93 (t, J = 8.0 Hz, 2 H).

13C NMR (100 MHz, CDCl₃): δ = 165.19 (d, J = 254.3 Hz), 142.86, 134.87 (d, J = 3.4 Hz), 132.22, 131.18, 130.94, 129.62 (d, J = 9.5 Hz), 128.95, 125.70, 125.15, 124.73, 123.84, 116.34 (d, J = 22.5 Hz).


(2)-1-[2-(4-Chlorophenylsulfonamido)phenyl]-2-phenyldiazene Oxide (3f)

Under the optimal reaction conditions, the desired product 3f (116.1 mg, 0.30 mmol, 75%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.41); mp 180–182 °C.

IR (KBr): 2923, 1598, 1569, 1482, 1473, 1341, 1251, 1090, 875, 848 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.13 (s, 1 H), 8.07 (d, J = 7.6 Hz, 2 H), 7.98 (d, J = 8.4 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 1 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.55–7.49 (m, 4 H), 7.27–7.23 (m, 1 H), 7.20 (d, J = 8.4 Hz, 2 H).

13C NMR (100 MHz, CDCl₃): δ = 142.85, 139.67, 137.31, 132.21, 131.04, 130.95, 129.36, 128.93, 128.24, 125.72, 125.25, 124.73, 123.95.

HRMS (ESI): m/z [M + H]⁺ calc for C₁₈H₁₄ClN₂O₃S: 388.0523; found: 388.0524.
(Z)-1-[2-(4-Bromophenylsulfonylamido)phenyl]-2-phenyldiazene Oxide (3g)

Under the optimal reaction conditions, the desired product 3g (127.6 mg, 0.30 mmol, 74%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.43); mp 192–194 °C.

IR (KBr): 3096, 2919, 1608, 1584, 1493, 1315, 1069, 911, 750, 736 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.13 (s, 1 H), 7.68–7.65 (m, 2 H), 7.58 (td, J = 7.2 Hz, 1 H), 7.51–7.43 (m, 4 H), 7.32–7.27 (m, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 142.85, 137.88, 132.32, 132.18, 131.03, 128.91, 128.28, 125.71, 125.22, 124.73, 123.90.


(2)-1-[2-(4-Nitrophenoxyphenylsulfonylamido)phenyl]-2-phenyldiazene Oxide (3h)

Under the optimal reaction conditions, the desired product 3h (111.5 mg, 0.28 mmol, 70%) was obtained as a pale yellow solid after flash column chromatography (30% EtOAc in PE, Rf = 0.37); mp 226–228 °C.

IR (KBr): 3250, 2923, 1605, 1529, 1450, 1385, 1177, 897, 872, 765 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.05 (s, 1 H), 8.03–8.01 (m, 4 H), 7.93 (d, J = 8.0 Hz, 1 H), 7.80–7.77 (m, 3 H), 7.56–7.48 (m, 4 H), 7.32–7.28 (m, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 149.98, 144.44, 142.67, 139.53, 132.28, 131.30, 130.20, 129.01, 128.06, 125.96, 125.63, 124.76, 124.64, 124.62, 124.16.


(2)-1-[2-(3-Methylphenylsulfonylamido)phenyl]-2-phenyldiazene Oxide (3i)

Under the optimal reaction conditions, the desired product 3i (135.4 mg, 0.34 mmol, 84%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.45); mp 236–238 °C.

IR (KBr): 3059, 1610, 1583, 1492, 1448, 1376, 1297, 950, 899, 769 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.38 (s, 1 H), 8.30 (s, 1 H), 7.96–7.91 (m, 3 H), 7.86 (dd, J = 8.4, 1.2 Hz, 1 H), 7.73 (dd, J = 8.4, 2.4 Hz, 2 H), 7.69–7.63 (m, 2 H), 7.55 (dd, J = 7.6, 0.8 Hz, 1 H), 7.49–7.44 (m, 5 H), 7.18–7.15 (m, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 142.74, 138.54, 135.78, 134.76, 132.09, 131.82, 131.45, 131.44, 130.57, 129.41, 129.03, 128.82, 128.73, 128.45, 127.70, 127.38, 125.51, 124.68, 124.59, 123.31, 121.58.


(2)-1-[2-(3-Nitrophenylsulfonylamido)phenyl]-2-phenyldiazene Oxide (3j)

Under the optimal reaction conditions, the desired product 3j (103.5 mg, 0.26 mmol, 65%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.40); mp 230–232 °C.

IR (KBr): 3246, 2923, 1609, 1536, 1438, 1267, 1073, 927, 838, 768 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.13 (s, 1 H), 8.47 (s, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 8.03–8.01 (m, 2 H), 7.94 (d, J = 8.0 Hz, 1 H), 7.90 (d, J = 7.6 Hz, 1 H), 7.80 (d, J = 7.6 Hz, 1 H), 7.56 (s, J = 7.6 Hz, 1 H), 7.51–7.43 (m, 4 H), 7.32–7.27 (m, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 147.95, 142.60, 140.83, 139.41, 132.42, 132.12, 131.28, 130.38, 130.29, 129.01, 127.49, 125.98, 125.66, 124.80, 124.59, 122.11.


(2)-1-[2-(2-Chlorophenylsulfonylamido)phenyl]-2-phenyldiazene Oxide (3k)

Under the optimal reaction conditions, the desired product 3k (102.2 mg, 0.26 mmol, 66%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.46); mp 194–196 °C.

IR (KBr): 3067, 1654, 1607, 1489, 1381, 1175, 1043, 903, 832, 758 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 11.10 (s, 1 H), 8.18–8.14 (m, 3 H), 8.08 (d, J = 8.0 Hz, 1 H), 7.69 (d, J = 8.4 Hz, 1 H), 7.56–7.45 (m, 3 H), 7.43–7.33 (m, 4 H), 7.11 (d, J = 7.6 Hz, 1 H).

13C NMR (100 MHz, CDCl₃): δ = 142.78, 135.97, 134.27, 132.17, 131.85, 131.83, 131.81, 131.11, 130.64, 128.86, 126.94, 125.61, 124.94, 123.60, 119.56.

(Z)-2-Phenyl-1-[2-(thiophene-2-sulfonamido)phenyl]diazene Oxide (3n)
Under the optimal reaction conditions, the desired product 3n (80.4 mg, 0.22 mmol, 56%) was obtained as a pale yellow solid after flash column chromatography (10% EtOAc in PE, Rf = 0.57); mp 180–182 °C.
IR (KBr): 3119, 3091, 1652, 1539, 1434, 1258, 1163, 1021, 857, 769 cm⁻¹.

1H NMR (400 MHz, CDCl₃): δ = 10.45 (s, 1 H), 8.09–8.06 (m, 3 H), 7.87 (d, J = 8.4 Hz, 1 H), 7.56–7.47 (m, 4 H), 7.44–7.43 (m, 2 H), 7.27 (t, J = 7.6 Hz, 1 H), 6.90–6.88 (m, 1 H).
13C NMR (100 MHz, CDCl₃): δ = 142.86, 139.46, 132.75, 132.67, 132.28, 131.34, 130.76, 128.92, 127.36, 125.70, 125.05, 124.75, 124.33.

(Z)-1-[2-(4-Chloro-2-(4-methylphenylsulfonamido)phenyl)(trifluoromethyl)phenylsulfonamido)phenyl]-2-(p-tolyl)diazene Oxide (3s)
Under the optimal reaction conditions, the desired product 3s (121.8 mg, 0.28 mmol, 70%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.51); mp 215–217 °C.
IR (KBr): 3100, 2957, 1635, 1403, 1307, 1089, 829, 714 cm⁻¹.
1H NMR (400 MHz, CDCl₃): δ = 10.43 (s, 1 H), 8.06 (d, J = 8.8 Hz, 2 H), 7.98 (d, J = 8.8 Hz, 1 H), 7.78 (s, 1 H), 7.72 (d, J = 8.4 Hz, 1 H), 7.70 (d, J = 8.4 Hz, 1 H), 7.57–7.47 (m, 4 H), 7.35–7.29 (m, 2 H).
13C NMR (100 MHz, CDCl₃): δ = 144.46, 141.19, 138.58, 136.48, 135.78, 133.06, 129.90, 129.23, 127.14, 127.00, 125.90, 124.42, 122.12, 21.50.

(Z)-1-[2-(4-Chloro-2-(4-methylphenylsulfonamido)phenyl)-2-(4-chlorophenyl)diazene Oxide (3r)
Under the optimal reaction conditions, the desired product 3r (121.8 mg, 0.28 mmol, 70%) was obtained as a pale yellow solid after flash column chromatography (10% EtOAc in PE, Rf = 0.59); mp 197–199 °C.
IR (KBr): 2922, 2360, 1635, 1586, 1375, 1339, 1169, 1091, 816, 736 cm⁻¹.
1H NMR (400 MHz, CDCl₃): δ = 10.37 (s, 1 H), 7.99 (d, J = 8.4 Hz, 2 H), 7.85 (d, J = 8.4 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 3 H), 7.28 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.0 Hz, 2 H), 7.00 (d, J = 8.0 Hz, 2 H), 6.96 (d, J = 8.8 Hz, 1 H), 2.43 (s, 3 H), 2.39 (s, 3 H), 2.24 (s, 3 H).
13C NMR (100 MHz, CDCl₃): δ = 143.83, 142.93, 141.31, 140.75, 135.96, 131.29, 129.59, 129.40, 126.79, 125.71, 125.42, 124.34, 123.52, 21.58, 21.44, 21.36.
HRMS (ESI): m/z [M + H]+ calcd for C₁₉H₁₄Cl₂N₃O₃S: 396.1382; found: 396.1383.

(Z)-1-[4-Isopropyl-2-(4-methylphenylsulfonamido)phenyl)-2-(4-isopropenyl)phenyl]diazene Oxide (3t)
Under the optimal reaction conditions, the desired product 3t (143.8 mg, 0.30 mmol, 75%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, Rf = 0.43); mp 205–207 °C.
IR (KBr): 2961, 1726, 1600, 1383, 1346, 1284, 1166, 1074, 863, 705 cm⁻¹.
1H NMR (400 MHz, CDCl₃): δ = 10.45 (s, 1 H), 8.05 (d, J = 8.0 Hz, 2 H), 7.92 (d, J = 8.4 Hz, 1 H), 7.64 (s, 1 H), 7.59 (d, J = 7.6 Hz, 2 H), 7.37 (d, J = 8.8 Hz, 2 H), 7.08–7.02 (m, 2 H), 3.01–2.96 (m, 2 H), 2.26 (s, 3 H), 1.33–1.29 (m, 6 H), 1.27–1.24 (m, 6 H).
13C NMR (100 MHz, CDCl₃): δ = 153.66, 152.07, 143.88, 141.04, 136.00, 131.53, 129.56, 126.99, 126.81, 125.86, 124.49, 122.99, 122.63, 122.62, 120.76, 34.17, 33.99, 23.69, 23.45, 21.39.
(2)-1-[4-Methoxy-2-(4-methylphenylsulfonamido)phenyl]-2-(4-methoxyphenyl)diazene Oxide (3u)

Under the optimal reaction conditions, the desired product 3u (124.9 mg, 0.33 mmol, 82%) was obtained as a pale yellow solid after flash chromatography (10% EtOAc in PE, Rf = 0.62); affording the product 3u as a white solid (100.7 mg, 86%); mp 96–98 °C.\(^{19}\)

H NMR (400 MHz, CDCl3): δ = 8.38–8.36 (m, 2 H), 7.94 (dd, J = 6.8, 3.2 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.48–7.41 (m, 3 H).

13C NMR (100 MHz, CDCl3): δ = 145.01, 140.33, 129.38, 128.93, 127.14, 120.60, 118.35.

Transformation of 3a into 1,2,3-Triazole 6

(1) In air, a 5 mL of round-bottomed flask charged with concd H 2SO4 (1.0 mL) was cooled to 0 °C in an ice bath, followed by the batchwise addition of 3a (367.1 mg, 1.0 mmol) into the cooled vessel. The reaction vessel was stirred at rt for 2 h, then the resulting mixture was neutralized with aq NaHCO3. The mixture was subsequently extracted with CH2Cl2 (3 × 5.0 mL). The organic layers were combined, dried (135.99, 133.38, 129.65, 127.93, 127.14, 120.60, 118.35.


Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588165.

References


(16) X-ray single crystal structure of product 3a. CCDC 1062443 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

