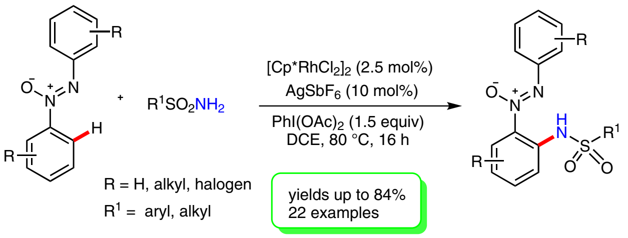
A Highly Selective Amidation of Azoxybenzenes with Sulfonamides via Rhodium(III)-Catalyzed C–H Activation

Hongji Li*
Hong Deng

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



Received: 10.01.2017
Accepted after revision: 07.03.2017

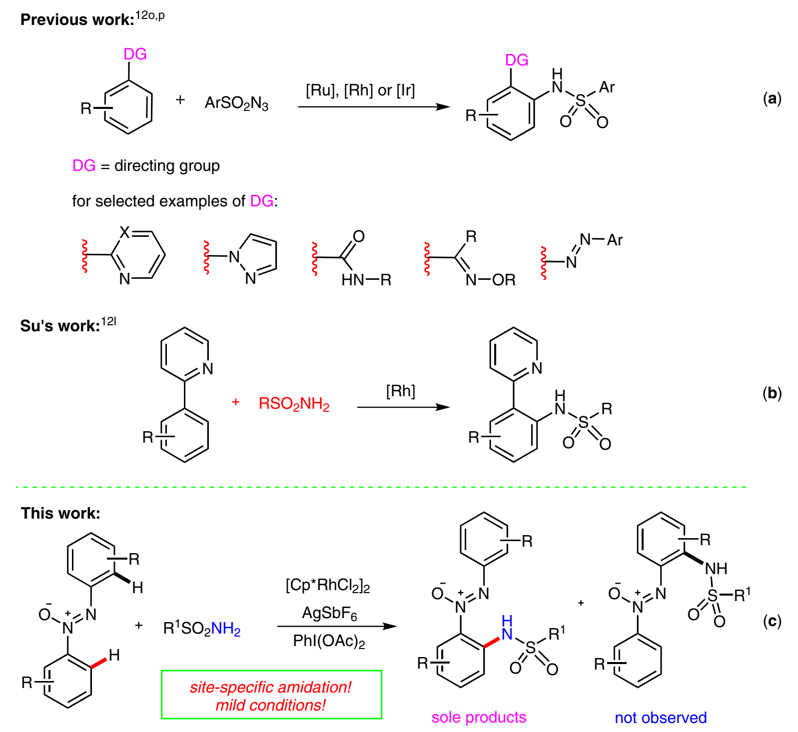
DOI: 10.1055/s-0036-1588165; Art ID: ss-2017-h0019-op

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.[1] As a result, the development of new methods for the formation of C–N bonds has received much attention in organic syntheses.[2] In particular, transition-metal-catalyzed protocols play an important role on the C–N formation.[3–6] For example, both Buchwald–Hartwig amination[3] and Ullmann–Goldberg coupling reactions[4] 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[5] among the previously reported methods.[3–6] 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),[6] *p*-toluenesulfonamide,[7] benzoyl hydroxylamines,[8] and azides,[9] and others[10] have been explored in the direct intermolecular C–H aminations. After the pioneering work contributed by Che et al.,[11] Pd,[12a,b] Ru,[12c–h] Rh,[12i–p] Ir,[12q,r] and other metals,[12s,t] have been used as efficient catalysts in group-directing C–H amination (Scheme 1, a and b).[12] Among them, Rh(III) catalysts exhibited high activity.[12i–p] 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.[12m] 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,[13a] industrial dyes,[13b] molecular machines,[13c] and other fields.[13d] In past years, several strategies have been adopted toward the synthesis of azoxybenzenes and derivatives due to their unique properties.[14] In general, the reported methods, such as oxidation of amines, reduction of nitrobenzenes, and oxidation of azobenzenes, had been used for the generation of corresponding azoxybenzenes, but in narrow scope and poor selectivity. We then found that there was a rare report on the synthesis of steric 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.[12u,v] Based on the early work referring to C–H functionalization and our recent findings,[15] 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.[12o,p] 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.[12l] Interestingly, we observed that the amidation of azoxybenzene with sulfonamide did not proceed under Xu's or Jia's reaction conditions,[12o,p] even though we could not provide a reasonable explanation for the findings. Herein, we wish to report an efficient Rh(III)-catalyzed direct



Scheme 1 The transition-metal-catalyzed amidation reactions

amidation of azoxybenzenes with sulfonamides, which provides a direct and efficient approach to a series of 2-sulfonamidoazoxybenzenes.

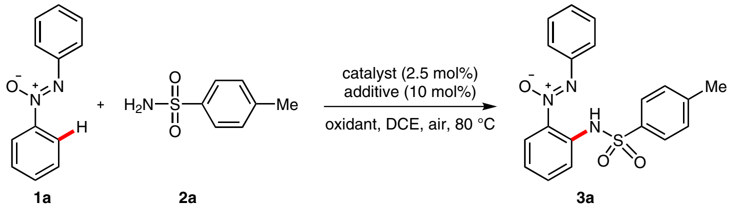
Our investigation started from the model reaction of 1,2-diphenyldiazene oxide (**1a**) with 4-methylbenzenesulfonamide (**2a**) under various reaction conditions, as shown in Table 1. First, the model reaction was carried out in the presence of $[Cp^*RhCl_2]_2$ (2.5 mol%) as catalyst, $PhI(OAc)_2$ (1.5 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 $AgSbF_6$ (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 $[Cp^*RhCl_2]_2$ with $[Cp^*RuCl_2]_2$ in the model amidation reaction (entry 3). Further, the yield of **3a** was improved by increasing the amount of $AgSbF_6$ (entry 4). Other additives, including $NaBF_4$ and K_3PF_6, 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, Ag_2CO_3, $Cu(OAc)_2$, Ag_2O, and BQ (benzoquinone) instead of $PhI(OAc)_2$ shut down the reaction completely (entries 8–12). The further optimization of reaction temperature and the amount of $PhI(OAc)_2$ did not improve the efficiency of the transformation (entries 13–16). The solvent screening showed that DCE was the optimal reaction medium (see Supporting Information for details). Finally, the best reaction conditions were determined to be the following: 2.5 mol% of $[Cp^*RhCl_2]_2$, 10 mol% of $AgSbF_6$, 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 NO_2 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 coupling 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 (Scheme 3). 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 $TsNH_2$ under the above conditions (**3r**/**3s** = 1.4:1) (Scheme 3).

The isotope labeling experiment was carried out by the addition of CD_3OD 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 H_2SO_4 at room temperature over 2 hours, which delivered **5** in 92% isolated yield. Furthermore, the treatment of **5** with

Table 1 Optimization of the Reaction Conditions[a]



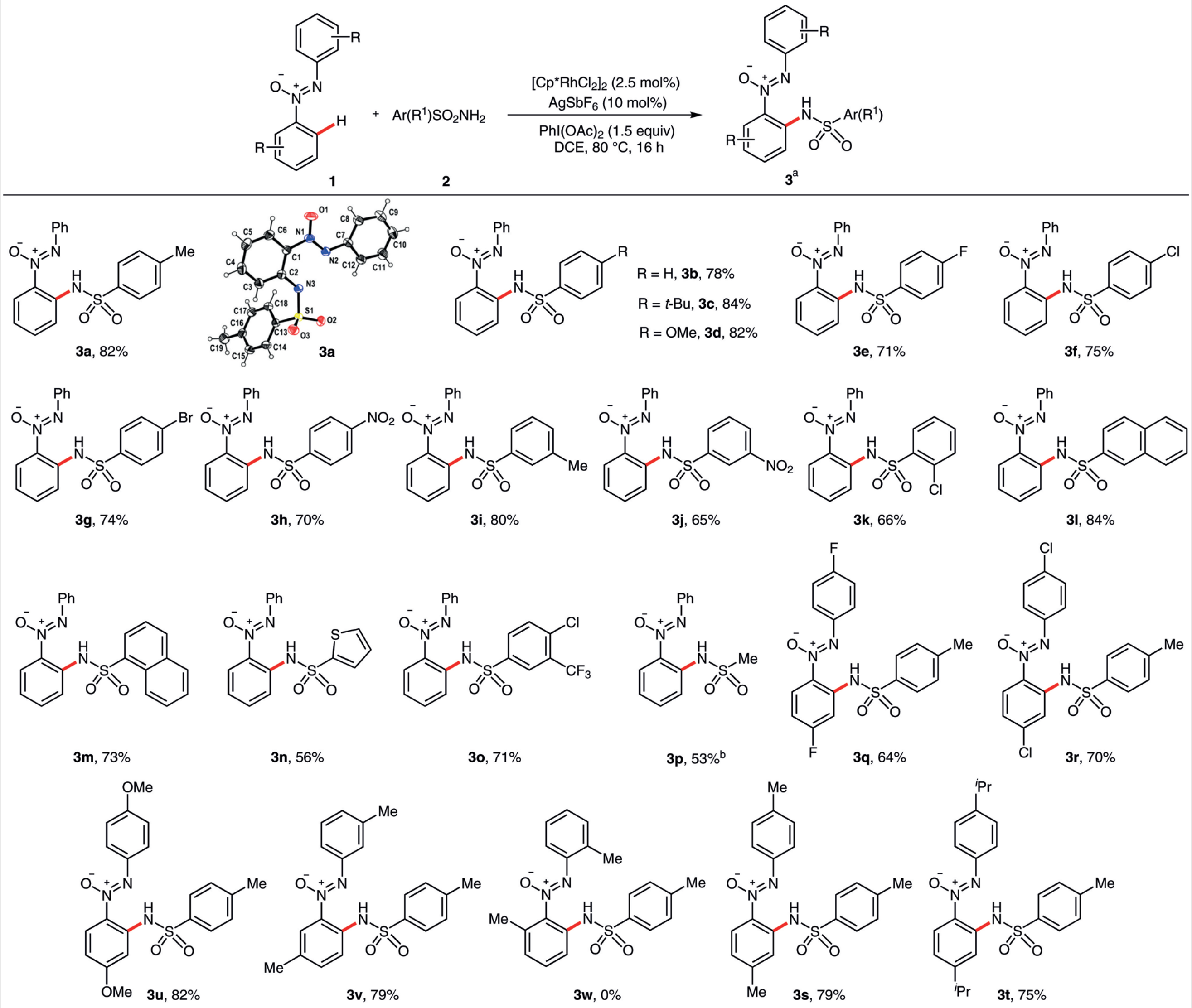
Entry	Catalyst	Oxidant	Additive	Yield of **3a** (%)[b]
1	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	–	trace
2	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	59[c]
3	$[Cp^*RuCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	n.r.
4	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	82
5	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$NaBF_4$	n.r.
6	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	K_3PF_6	trace
7	$[Cp^*RhCl_2]_2$	–	$AgSbF_6$	n.r.
8	$[Cp^*RhCl_2]_2$	AgOAc	$AgSbF_6$	n.r.
9	$[Cp^*RhCl_2]_2$	Ag_2CO_3	$AgSbF_6$	n.r.
10	$[Cp^*RhCl_2]_2$	$Cu(OAc)_2$	$AgSbF_6$	n.r.
11	$[Cp^*RhCl_2]_2$	Ag_2O	$AgSbF_6$	n.r.
12	$[Cp^*RhCl_2]_2$	BQ	$AgSbF_6$	n.r.
13	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	63[d]
14	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	75[e]
15	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	67[f]
16	$[Cp^*RhCl_2]_2$	$PhI(OAc)_2$	$AgSbF_6$	80[g]

[a] Reaction conditions: 1,2-Diphenyldiazene oxide (**1a**; 0.40 mmol), $TsNH_2$ (**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.
[b] Isolated yield; n.r. = no reaction.
[c] $AgSbF_6$ used: 5 mol%.
[d] Reaction temperature: 70 °C.
[e] Reaction temperature: 90 °C.
[f] $PhI(OAc)_2$ used: 1.0 equiv.
[g] $PhI(OAc)_2$ used: 2.0 equiv.

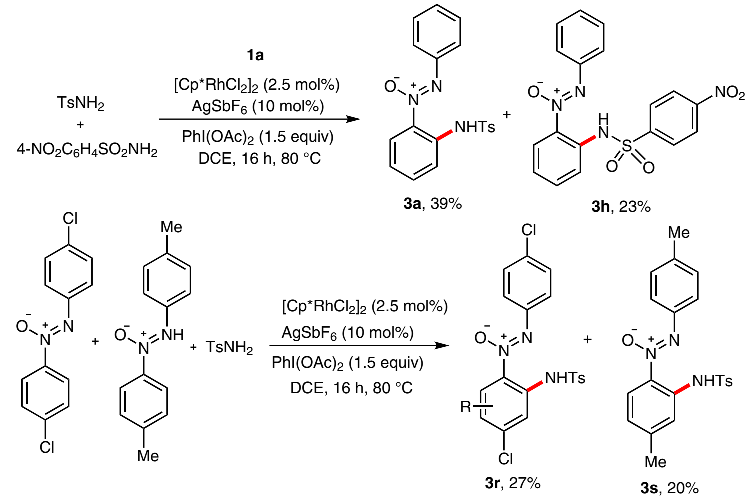
PhI(OAc)$_2$ in toluene generated 1,2,3-triazole **6** in satisfactory yield, although the exact mechanism is not clear at the current stage (Scheme 5).

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**,[12l] 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**,[12l] which next oxidizes the formed intermediate **B** into Rh(V)-species **C**,[17] 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.[12l]

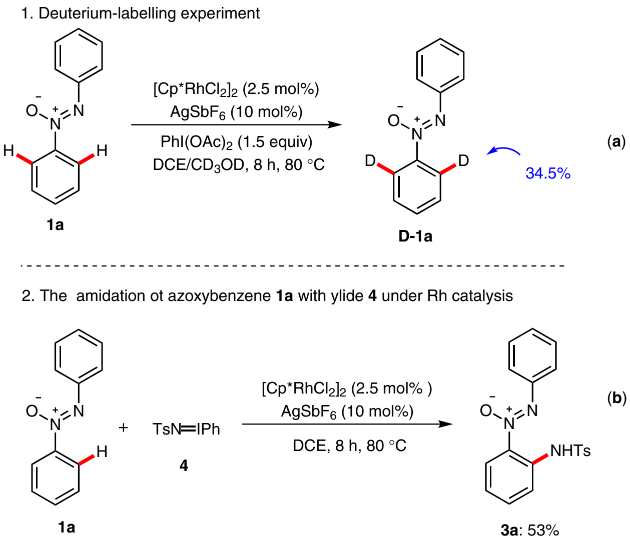
In summary, a Rh(III)-catalyzed direct amidation of azoxybenzenes with sulfonamides was developed under mild conditions, which produced the asymmetric azoxybenzenes in moderate to good yields and excellent selectivity. The efficient amidation reactions not only offer an attractive approach to azoxybenzenes, 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.



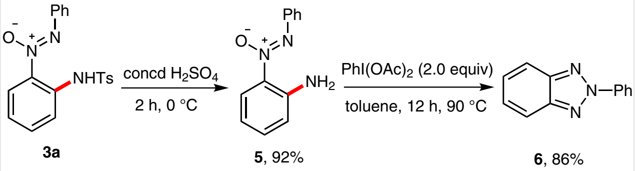
Scheme 2 The scope of azoxybenzenes and sulfonamides. *Reagents and conditions*: 1,2-Diphenyldiazene oxide (**1**, 0.40 mmol), sulfonamide (**2**, 0.60 mmol), [Cp*RhCl$_2$]$_2$ (2.5 mol%), PhI(OAc)$_2$ (1.5 equiv), AgSbF$_6$ (10 mol%), DCE (1.0 mL) at 80 °C in air atmosphere for 16 h. ^{a} Isolated yield. ^{b} 36 h.



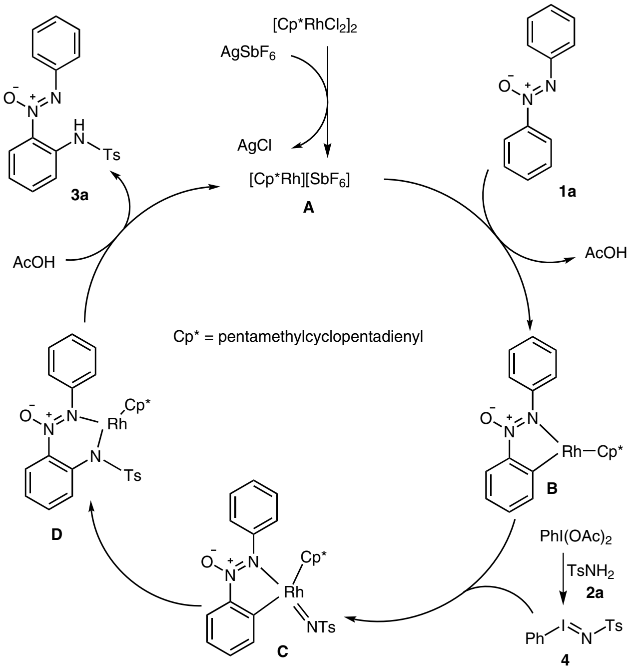
Scheme 3 Intermolecular competition experiments



Scheme 4 Mechanistic studies



Scheme 5 Transformation of **3a** into 1,2,3-triazole **6**



Scheme 6 The proposed reaction mechanism

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 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 SeO_2/H_2O_2/MeOH system,[18] The synthesized azoxybenzenes must be recrystallized from EtOH before use. The chemicals and solvents were purchased from commercial suppliers either from Aldrich, USA or Shanghai Chemical Company, China or Tokyo Chemical Industry, Japan. Products were purified by flash chromatography on 200–300 mesh silica gel.

Rhodium-Catalyzed Amidation of Azoxybenzenes with Sulfonamides; (*Z*)-1-[2-(4-Methylphenylsulfonamido)phenyl]-2-phenyldiazene Oxide (3a); Typical Procedure

In air, a 10 mL of dried Schlenk tube was charged with azoxybenzene (**1a**; 79.2 mg, 0.40 mmol), $TsNH_2$ (**2a**; 102.6 mg, 0.60 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 the freshly distilled 1,2-dichloroethane (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 r.t. and the reaction completion was checked by TLC. H_2O (10.0 mL) was subsequently added to the reaction mixture and extracted with CH_2Cl_2 (3 × 5.0 mL). The organic layers were combined, dried ($MgSO_4$), and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (silica gel, PE/EtOAc 9:1 → 5:1, v/v), affording the product **3a** as a pale yellow solid (120.4 mg, 0.33 mmol, 82%); mp 202–204 °C; $R_f = 0.46$ (20% EtOAc in PE).

IR (KBr): 3143, 2920, 1729, 1597, 1490, 1335, 1166, 900, 852, 738, cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.99, 142.90, 135.93, 132.14, 131.59, 130.72, 129.68, 128.84, 126.82, 125.66, 124.67, 124.62, 123.48, 21.39.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}N_3O_3S$: 368.1069; found: 368.1071.

(*Z*)-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, $R_f = 0.43$); mp 218–220 °C.

IR (KBr): 3054, 1609, 1491, 1372, 1257, 1167, 951, 904, 759, 713 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.31 (s, 1 H), 8.07 (d, *J* = 8.0 Hz, 2 H), 8.00 (d, *J* = 8.4 Hz, 1 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.54–7.47 (m, 4 H), 7.43 (t, *J* = 7.2 Hz, 1 H), 7.31–7.27 (m, 2 H), 7.23–7.20 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.81, 138.87, 133.07, 132.19, 131.45, 130.73, 129.02, 128.86, 126.79, 125.64, 124.73, 124.65, 123.28.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{16}N_3O_3S$: 354.0912; found: 354.0915.

(*Z*)-1-{2-[4-(*tert*-Butyl)phenylsulfonamido]phenyl}-2-phenyldiazene Oxide (3c)

Under the optimal reaction conditions, the desired product **3c** (137.5 mg, 0.34 mmol, 84%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, $R_f = 0.48$); mp 189–191 °C.

IR (KBr): 3056, 2964, 1608, 1596, 1492, 1337, 950, 834, 760, 726 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.27 (s, 1 H), 8.06–8.00 (m, 3 H), 7.80 (dd, *J* = 8.4, 2.1 Hz, 1 H), 7.62–7.59 (m, 2 H), 7.53–7.45 (m, 4 H), 7.30–7.27 (m, 2 H), 7.24–7.19 (m, 1 H), 1.20 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.86, 142.83, 135.93, 132.19, 131.70, 130.67, 128.85, 127.79, 126.64, 126.31, 126.06, 125.68, 124.64, 124.59, 123.40, 34.97, 30.81.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{24}N_3O_3S$: 410.1538; found: 410.1538.

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

Under the optimal reaction conditions, the desired product **3d** (125.7 mg, 0.33 mmol, 82%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, $R_f = 0.43$); mp 209–211 °C.

IR (KBr): 3071, 2917, 1735, 1595, 1489, 1383, 1261, 1093, 863, 764 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.14 (s, 1 H), 8.09 (dd, *J* = 8.4, 1.6 Hz, 2 H), 7.99 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.62–7.59(m, 2 H), 7.54–7.47 (m, 4 H), 7.24–7.20 (m, 1 H), 6.72 (d, *J* = 8.8 Hz, 2 H), 3.71 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.11, 142.98, 132.14, 131.74, 130.70, 129.03, 128.87, 125.70, 124.66, 123.60, 114.24, 55.42.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}N_3O_4S$: 384.1018; found: 384.1019.

(*Z*)-1-[2-(4-Fluorophenylsulfonamido)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, $R_f = 0.42$); mp 172–174 °C.

IR (KBr): 3212, 1605, 1591, 1491, 1386, 1341, 1090, 899, 869, 763 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.19 (d, $J_{C,F} = 254.3$ Hz), 142.86, 134.87 (d, $J_{C,F} = 3.4$ Hz), 132.22, 131.18, 130.94, 129.62 (d, $J_{C,F} = 9.5$ Hz), 128.95, 125.70, 125.15, 124.73, 123.84, 116.34 (d, $J_{C,F} = 22.5$ Hz).

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}FN_3O_3S$: 372.0818; found: 372.0820.

(*Z*)-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, $R_f = 0.41$); mp 180–182 °C.

IR (KBr): 2923, 1598, 1569, 1482, 1473, 1341, 1251, 1090, 875, 848 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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* $[M + H]^+$ calcd for $C_{18}H_{15}ClN_3O_3S$: 388.0523; found: 388.0524.

(*Z*)-1-[2-(4-Bromophenylsulfonamido)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, R_f = 0.43); mp 192–194 °C.

IR (KBr): 3096, 2919, 1608, 1584, 1493, 1184, 1069, 911, 750, 736 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.13 (s, 1 H), 8.08–8.06 (m, 2 H), 7.98 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.77 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.54–7.48 (m, 6 H), 7.38–7.36 (m, 2 H), 7.27–7.25 (m, 1 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.85, 137.88, 132.32, 132.18, 131.03, 130.91, 128.91, 128.28, 128.22, 125.71, 125.22, 124.73, 123.90.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}BrN_3O_3S$: 432.0017; found: 432.0020.

(*Z*)-1-[2-(4-Nitrophenylsulfonamido)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, R_f = 0.37); mp 226–228 °C.

IR (KBr): 3250, 2923, 1605, 1529, 1450, 1385, 1177, 897, 872, 765 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): 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).

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

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}N_4O_5S$: 399.0763; found: 399.0765.

(*Z*)-1-[2-(3-Methylphenylsulfonamido)phenyl]-2-phenyldiazene Oxide (3i)

Under the optimal reaction conditions, the desired product **3i** (117.5 mg, 0.32 mmol, 80%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, R_f = 0.45); mp 206–208 °C.

IR (KBr): 3067, 2923, 1608, 1579, 1378, 1343, 1163, 950, 868, 764 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.16 (s, 1 H), 8.06 (d, *J* = 8.4 Hz, 2 H), 7.97 (d, *J* = 8.4 Hz, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.52–7.45 (m, 5 H), 7.41 (d, *J* = 7.6 Hz, 1 H), 7.23–7.12 (m, 3 H), 2.12 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.84, 139.45, 138.66, 133.92, 132.13, 131.44, 130.72, 128.88, 128.76, 126.99, 125.67, 124.87, 124.59, 123.94, 123.83, 20.96.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{18}N_3O_3S$: 368.1069; found: 368.1070.

(*Z*)-1-[2-(3-Nitrophenylsulfonamido)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, R_f = 0.40); mp 230–232 °C.

IR (KBr): 3246, 2923, 1609, 1536, 1438, 1267, 1073, 927, 838, 768 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): 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 (t, *J* = 7.6 Hz, 1 H), 7.51–7.43 (m, 4 H), 7.32–7.27 (m, 1 H).

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

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}N_4O_5$: 399.0763; found: 399.0765.

(*Z*)-1-[2-(2-Chlorophenylsulfonamido)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, R_f = 0.46); mp 194–196 °C.

IR (KBr): 3067, 1654, 1607, 1489, 1381, 1175, 1043, 903, 832, 758 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): 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 (t, *J* = 7.6 Hz, 1 H).

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

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{15}ClN_3O_3S$: 388.0523; found: 388.0523.

(*Z*)-1-[2-(Naphthalene-2-sulfonamido)phenyl]-2-phenyldiazene Oxide (3l)

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

IR (KBr): 3059, 1610, 1583, 1492, 1448, 1376, 1297, 950, 899, 769 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): 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 (td, *J* = 7.6, 0.8 Hz, 1 H), 7.49–7.44 (m, 5 H), 7.18–7.15 (m, 1 H).

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

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}N_3O_3S$: 404.1069; found: 404.1071.

(*Z*)-1-[2-(Naphthalene-1-sulfonamido)phenyl]-2-phenyldiazene Oxide (3m)

Under the optimal reaction conditions, the desired product **3m** (117.7 mg, 0.29 mmol, 73%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, R_f = 0.48); mp 242–244 °C.

IR (KBr): 3171, 3057, 1592, 1583, 1432, 1226, 1199, 1025, 863, 766 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.70 (s, 1 H), 8.54 (d, *J* = 8.8 Hz, 1 H), 8.20 (d, *J* = 7.2 Hz, 1 H), 7.98–7.93 (m, 3 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.77 (t, *J* = 9.2 Hz, 2 H), 7.49–7.48 (m, 3 H), 7.42–7.37 (m, 2 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.26–7.21 (m, 1 H), 7.07 (t, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 142.86, 134.86, 133.99, 133.59, 132.02, 131.60, 130.60, 130.23, 128.92, 128.77, 128.39, 127.68, 126.78, 125.66, 124.62, 124.08, 123.75, 123.66, 121.94.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{18}N_3O_3S$: 404.1069; found: 404.1070.

(*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, R_f = 0.57); mp 180–182 °C.

IR (KBr): 3119, 3091, 1652, 1539, 1434, 1258, 1163, 1021, 857, 769 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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, 123.43.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{14}N_3O_3S_2$: 360.0477; found: 360.0480.

(*Z*)-1-{2-[4-Chloro-3(trifluoromethyl)phenylsulfonamido]phenyl}-2-phenyldiazene Oxide (3o)

Under the optimal reaction conditions, the desired product **3o** (129.2 mg, 0.28 mmol, 71%) was obtained as a pale yellow solid after flash column chromatography (30% EtOAc in PE, R_f = 0.31); mp 162–164 °C.

IR (KBr): 3055, 1607, 1585, 1488, 1394, 1261, 1166, 960, 828, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.08 (s, 1 H), 8.05 (d, *J* = 8.0 Hz, 2 H), 7. 98 (d, *J* = 8.4 Hz, 1 H), 7.88 (s, 1 H), 7.78 (d, *J* = 8.0 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.68, 139.51, 137.88, 137.71 (q, $J_{C,F}$ = 1.6 Hz), 132.43, 132.35, 131.19, 130.83, 130.45, 129.33 (q, $J_{C,F}$ = 32.3 Hz), 128.98, 126.16 (q, $J_{C,F}$ = 5.2 Hz), 125.93, 125.76, 125.71, 124.83, 124.58, 121.57 (q, $J_{C,F}$ = 272.4 Hz).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{14}ClF_3N_3O_3S$: 456.0396; found: 456.0396.

(*Z*)-1-[2-(Methylsulfonamido)phenyl]-2-phenyldiazene Oxide (3p)

Under the optimal reaction conditions, the desired product **3p** (61.7 mg, 0.21 mmol, 53%) was obtained as a pale yellow solid after flash column chromatography (10% EtOAc in PE, R_f = 0.62); mp 131–133 °C.

IR (KBr): 3063, 2930, 1718, 1582, 1486, 1331, 1161, 971, 877, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.35 (s, 1 H), 8.23 (d, *J* = 8.4 Hz, 1 H), 8.16 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.56–7.45 (m, 4 H), 7.26 (t, *J* = 8.4 Hz, 1 H), 3.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.82, 132.67, 132.17, 130.81, 128.95, 125.72, 125.19, 123.94, 120.49, 40.10.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{14}N_3O_3S$: 292.0756; found: 292.0755.

(*Z*)-1-[4-Fluoro-2-(4-methylphenylsulfonamido)phenyl]-2-(4-fluorophenyl)diazene Oxide (3q)

Under the optimal reaction conditions, the desired product **3q** (103.2 mg, 0.27 mmol, 64%) was obtained as a pale yellow solid after flash column chromatography (20% EtOAc in PE, R_f = 0.49); mp 201–203 °C.

IR (KBr): 3313, 2959, 1731, 1633, 1494, 1397, 1345, 1122, 861, 775 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.67 (s, 1 H), 8.19–8.16 (m, 2 H), 8.10–8.06 (m, 1 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.49 (dd, *J* = 9.6, 1.6 Hz, 1 H), 7.21–7.15 (m, 4 H), 6.87–6.82 (m, 1 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.99 (d, $J_{C,F}$ = 252.3 Hz), 163.06 (d, $J_{C,F}$ = 253.2 Hz), 144.44, 139.22 (d, $J_{C,F}$ = 3.4 Hz), 135.78, 134.08 (d, $J_{C,F}$ = 1.9 Hz), 129.86, 128.21 (d, $J_{C,F}$ = 8.5 Hz), 126.98, 126.91 (d, $J_{C,F}$ = 10.4 Hz), 126.86, 115.96 (d, $J_{C,F}$ = 22.6 Hz), 111.18 (d, $J_{C,F}$ = 23.1 Hz), 108.61 (d, $J_{C,F}$ = 27.5 Hz), 21.44.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}F_2N_3O_3S$: 404.0880; found: 404.0883.

(*Z*)-1-[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 (20% EtOAc in PE, R_f = 0.51); mp 215–217 °C.

IR (KBr): 3100, 2957, 1635, 1480, 1403, 1307, 1089, 829, 714 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.15–7.13 (m, 3 H), 2.31 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 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.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{16}Cl_2N_3O_3S$: 436.0289; found: 436.0288.

(*Z*)-1-[4-Methyl-2-(4-methylphenylsulfonamido)phenyl]-2-(*p*-tolyl)diazene Oxide (3s)

Under the optimal reaction conditions, the desired product **3s** (124.9 mg, 0.32 mmol, 79%) was obtained as a pale yellow solid after flash column chromatography (10% EtOAc in PE, R_f = 0.59); mp 197–199 °C.

IR (KBr): 2922, 2360, 1635, 1586, 1375, 1339, 1169, 1091, 816, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.37 (m, 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), 6.96 (d, *J* = 8.8 Hz, 1 H), 2.43 (s, 3 H), 2.39 (s, 3 H), 2.24 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{21}H_{22}N_3O_3S$: 396.1382; found: 396.1383.

(*Z*)-1-[4-Isopropyl-2-(4-methylphenylsulfonamido)phenyl]-2-(4-isopropylphenyl)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, R_f = 0.43); mp 205–207 °C.

IR (KBr): 2961, 1726, 1600, 1383, 1346, 1284, 1166, 1074, 863, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): 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, 3 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).

^{13}C NMR (100 MHz, $CDCl_3$): 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.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{25}H_{30}N_3O_3S$: 452.2008; found: 452.2012.

(*Z*)-1-[4-Methoxy-2-(4-methylphenylsulfonamido)phenyl]-2-(4-methoxyphenyl)diazene Oxide (3u)

Under the optimal reaction conditions, the desired product **3u** (140.1 mg, 0.33 mmol, 82%) was obtained as a pale yellow solid after flash column chromatography (30% EtOAc in PE, $R_f = 0.35$); mp 212–214 °C.

IR (KBr): 2922, 1591, 1461, 1342, 1268, 1185, 1074, 892, 745, 726 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.93 (s, 1 H), 8.17 (d, *J* = 8.8 Hz, 2 H), 7.97 (d, *J* = 9.2 Hz, 1 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.26–7.24 (m, 1 H), 7.10 (d, *J* = 8.4 Hz, 2 H), 6.98 (d, *J* = 9.2 Hz, 2 H), 6.65 (dd, *J* = 9.6, 2.0 Hz, 1 H), 3.89 (s, 3 H), 3.84 (s, 3 H), 2.28 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.85, 160.90, 143.99, 136.85, 135.99, 133.38, 129.65, 127.93, 126.96, 125.97, 113.91, 110.43, 106.09, 55.75, 55.53, 21.42.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{22}N_3O_5S$: 428.1280; found: 428.1281.

(*Z*)-1-[5-Methyl-2-(4-methylphenylsulfonamido)phenyl]-2-(*m*-tolyl)diazene Oxide (3v)

Under the optimal reaction conditions, the desired product **3v** (124.9 mg, 0.32 mmol, 79%) was obtained as a pale yellow solid after flash column chromatography (10% EtOAc in PE, $R_f = 0.61$); mp 194–196 °C.

IR (KBr): 2920, 1596, 1510, 1456, 1372, 1223,1163, 1091, 830, 781 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.85 (s, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.80 (s, 1 H), 7.72 (s, 1 H), 7.66 (d, *J* = 8.4 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 1 H), 7.38 (t, *J* = 8.0 Hz, 1 H), 7.28–7.26 (m, 2 H), 7.01 (d, *J* = 7.6 Hz, 2 H), 2.44 (s, 3 H), 2.35 (s, 3 H), 2.23 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.76, 142.98, 138.60, 135.92, 135.28, 132.76, 131.43, 129.59, 128.72, 128.56, 126.77, 126.12, 124.63, 124.27, 122.57, 21.39, 21.34, 20.70.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{22}N_3O_3S$: 396.1382; found: 396.1382.

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

(1) In air, a 5 mL of round-bottomed flask charged with concd H_2SO_4 (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 r.t. for 2 h; then the resulting mixture was neutralized with aq $NaHCO_3$. The mixture was subsequently extracted with CH_2Cl_2 (3 × 5.0 mL). The organic layers were combined, dried (Na_2SO_4). and concentrated under reduced pressure to yield the crude product, which was further purified by flash chromatography (20% EtOAc in PE, $R_f = 0.62$), affording the product **5** as an orange yellow solid (196.0 mg, 92%); mp 163–165 °C.

IR (KBr): 3356, 2959, 1611, 1570, 1489, 1469, 1412, 1076, 932, 758 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, *J* = 8.4, 1.6 Hz, 1 H), 8.06–8.04 (m, 2 H), 7.50 (td, *J* = 7.6, 2.0 Hz, 2 H), 7.41–7.37 (m, 1 H), 7.30–7.26 (m, 1 H), 6.82–6.70 (m, 2 H), 5.76 (br s, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.85, 141.95, 132.15, 129.07, 128.68, 125.00, 124.97, 118.18, 116.99.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{12}H_{12}N_3O$: 214.0975; found: 214.0977.

(2) A 5 mL Schlenk tube was charged with **5** (127.9 mg, 0.6 mmol), $PhI(OAc)_2$ (386.5 mg, 1.2 mmol), and toluene (3.0 mL). The reaction vessel was sealed and stirred at 90 °C for 12 h. Afterwards, toluene was removed under vacuum, and the residue was directly purified by flash chromatography (10% EtOAc in PE, $R_f = 0.55$), affording the 1,2,3-triazole **6** as a white solid (100.7 mg, 86%); mp 96–98 °C.[19]

IR (KBr): 3063, 2959, 1594, 1564, 1488, 1459, 1288, 964, 746, 685 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.01, 140.33, 129.38, 128.93, 127.14, 120.60, 118.35.

Acknowledgment

This work was financially supported by the National Science Foundation of China (No. 21402060) and The Department of Education, Anhui Province (No. KJ2016A882).

Supporting Information

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

References

(1) (a) Ricci, A. *Amino Group Chemistry: From Synthesis to the Life Sciences*; Wiley-VCH: Weinheim, **2008**. (b) Hili, R.; Yudin, A. K. *Nat. Chem. Biol.* **2006**, *2*, 284. (c) Boaen, N. K.; Hillmyer, M. A. *Chem. Soc. Rev.* **2005**, *34*, 267.

(2) For selected reviews, see: (a) Monnier, F.; Taillefer, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 6954. (b) Song, G.; Wang, F.; Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651. (c) Louillat, M.-L.; Patureau, F. W. *Chem. Soc. Rev.* **2014**, *43*, 901. (d) Ng, K.-H.; Ng, F.-N.; Yu, W.-Y. *Chem. Commun.* **2012**, *48*, 11680. (e) Grohmann, C.; Wang, H.; Glorius, F. *Org. Lett.* **2012**, *14*, 656. (f) Song, W.; Kozhushkov, S. I.; Ackermann, L. *Angew. Chem. Int. Ed.* **2013**, *52*, 6576.

(3) (a) Paul, F.; Patt, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 5969. (b) Guram, A. S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 7901.

(4) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054.

(5) Wang, H.; Wang, Y.; Peng, C.; Zhang, J.; Zhu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 13217.

(6) Sun, K.; Li, Y.; Xiong, T.; Zhang, J.; Zhang, Q. *J. Am. Chem. Soc.* **2011**, *133*, 1694.

(7) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790.

(8) Yoo, E. J.; Ma, S.; Mei, T.-S.; Chan, K. S. L.; Yu, J.-Q. *J. Am. Chem. Soc.* **2011**, *133*, 7652.

(9) (a) Ryu, J.; Shin, K.; Park, S. H.; Kim, J. Y.; Chang, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 9904. (b) Shin, K.; Baek, Y.; Chang, S. *Angew. Chem. Int. Ed.* **2013**, *52*, 8031. (c) Kim, H. J.; Ajitha, M. J.; Lee, Y.; Ryu, J.; Kim, J.; Lee, Y. J.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 1132. (d) Tang, C.; Yuan, Y.; Cui, Y.; Jiao, N. *Eur. J. Org. Chem.* **2013**, 7480.

(10) (a) Ng, K.-H.; Chan, A. S. C.; Yu, W.-Y. *J. Am. Chem. Soc.* **2010**, *132*, 12862. (b) Kawano, T.; Hirano, K.; Satoh, T.; Miura, M. *J. Am. Chem. Soc.* **2010**, *132*, 6900.

(11) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048.

(12) (a) Zhao, G.; Chen, C.; Yue, Y.; Yu, Y.; Peng, J. *J. Org. Chem.* **2015**, *80*, 2827. (b) Li, Z.; Sun, S.; Qiao, H.; Yang, F.; Zhu, Y.; Kang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2016**, *18*, 4594. (c) Yadav, M. R.; Rit, R.

K.; Sahoo, A. K. *Org. Lett.* **2013**, *15*, 1638. (d) Zhen, Q.-Z.; Liang, Y.-F.; Qin, C.; Jiao, N. *Chem. Commun.* **2013**, *49*, 5654. (e) Thirunavukkarasu, V. S.; Raghuvanshi, K.; Ackermann, L. *Org. Lett.* **2013**, *15*, 3286. (f) Kim, J. Y.; Kim, J. W.; Chang, S. *Chem. Eur. J.* **2013**, *19*, 7328. (g) Bhanuchandra, M.; Yadav, M. R.; Rit, R. K.; Kuram, M. R.; Sahoo, A. K. *Chem. Commun.* **2013**, *49*, 5225. (h) Pan, C.-D.; Abdukader, A.; Han, J.; Cheng, Y.-X.; Zhu, C.-J. *Chem. Eur. J.* **2014**, *20*, 3606. (i) Zhou, B.; Yang, Y.-X.; Shi, J.-J.; Feng, H.-J.; Li, Y.-C. *Chem. Eur. J.* **2013**, *19*, 10511. (j) Kim, J. K.; Park, S. H.; Ryu, J.; Cho, S. H.; Kim, S. H.; Chang, S. *J. Am. Chem. Soc.* **2012**, *134*, 9110. (k) Yu, D.-G.; Suri, M.; Glorius, F. *J. Am. Chem. Soc.* **2013**, *135*, 8802. (l) Zhao, H.; Shang, Y.; Su, W. *Org. Lett.* **2013**, *15*, 5106. (m) Park, S. H.; Kwak, J.; Shin, K.; Ryu, J.; Park, Y.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 2492. (n) Park, Y.; Heo, J.; Baik, M.-H.; Chang, S. *J. Am. Chem. Soc.* **2016**, *138*, 14020. (o) Wang, H.; Yu, Y.; Hong, X.; Tan, Q.; Xu, B. *J. Org. Chem.* **2014**, *79*, 3279. (p) Jia, X.; Han, J. *J. Org. Chem.* **2014**, *79*, 4180. (q) Kim, J. W.; Chang, S. *Angew. Chem. Int. Ed.* **2014**, *53*, 2203. (r) Kim, H.; Shin, K.; Chang, S. *J. Am. Chem. Soc.* **2014**, *136*, 5904. (s) Xiao, B.; Gong, T.-J.; Xu, J.; Liu, Z.-J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 1466. (t) Tran, L. D.; Roane, J.; Daugulis, O. *Angew. Chem. Int. Ed.* **2013**, *52*, 6043. (u) Li, H.; Li, P.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 9170. (v) Li, H.; Xie, X.; Wang, L. *Chem. Commun.* **2014**, *50*, 4218.

(13) (a) *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S. Wiley: Chichester, **1997**, 729–730. (b) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Vogtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714. (c) Ferri, V.; Elbing, M.; Pace, G.; Dickey, M. D.; Zharnikov, M.; Samorì, P.; Mayor, M.; Rampi, M. A. *Angew. Chem. Int. Ed.* **2008**, *47*, 3290. (d) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512.

(14) (a) Hou, Z.; Fujiware, Y.; Taniguchi, H. *J. Org. Chem.* **1988**, *53*, 3118. (b) Sakai, N.; Fuji, K.; Nabeshima, S.; Ikeda, R.; Konakahara, T. *Chem. Commun.* **2010**, *46*, 3173. (c) Wada, S.; Urano, M.; Suzuki, H. *J. Org. Chem.* **2002**, *67*, 8254.

(15) (a) Li, C.; Wang, L.; Li, P.; Zhou, W. *Chem. Eur. J.* **2011**, *17*, 10208. (b) Zhou, W.; Li, H.; Wang, L. *Org. Lett.* **2012**, *14*, 4594. (c) Li, H.; Li, P.; Wang, L. *Org. Lett.* **2013**, *15*, 620. (d) Li, H.; Li, P.; Tan, H.; Wang, L. *Chem. Eur. J.* **2013**, *19*, 14432. (e) Zhou, W.; Li, P.; Zhang, Y.; Wang, L. *Adv. Synth. Catal.* **2013**, *355*, 2343. (f) Li, D.; Xu, N.; Zhang, Y.; Wang, L. *Chem. Commun.* **2014**, *50*, 14862. (g) Tan, H.; Li, H.; Ji, W.; Wang, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 8374.

(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.

(17) For Rh(V) species, see: (a) Duckett, S. B.; Perutz, R. N. *Organometallics* **1992**, *11*, 90. (b) Vyboishchikov, S. F.; Nikonov, G. I. *Organometallics* **2007**, *26*, 4160. (c) Brayshaw, S. K.; Sceats, E. L.; Green, J. C.; Weller, A. S. *Proc. Natl. Acad. Sci., U.S.A.* **2007**, *104*, 6921. (d) Wencel-Delord, J.; Nimphius, C.; Patureau, F. W.; Glorius, F. *Angew. Chem. Int. Ed.* **2012**, *51*, 2247. (e) Schröder, N.; Wencel-Delord, J.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 8298.

(18) Gebhardt, C.; Priewisch, B.; Irran, E.; Rück-Braun, K. *Synthesis* **2008**, 1889.

(19) Ryu, T.; Min, J.; Choi, W.; Jeon, W. H.; Lee, P. H. *Org. Lett.* **2014**, *16*, 2810.