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Synthesis of *N*-Sulfonylamidated and Amidated Azobenzenes under Rhodium Catalysis

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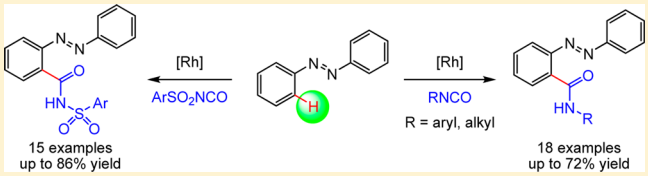
Supporting Information

ABSTRACT: The rhodium(III)-catalyzed *ortho*-C−H amidation of azobenzenes with arylsulfonyl and aryl and alkyl isocyanates is described. The *N*-sulfonyl amidation reaction using arylsulfonyl isocyanates is first reported in the C−H activation strategy. These transformations provide the facile and efficient construction of a range of amide moieties into azobenzenes.



INTRODUCTION

Due to the prevalence in dye industries and material science,[1] azobenzenes have become important synthetic targets, leading to the development of many useful methods for their preparation.[2] Recently, direct C−H functionalization of azobenzenes finds significant attention for the synthesis of unsymmetrical azobenzenes using azo group as a directing group. For example, the oxidative and decarboxylative *ortho*-acylations of azobenzenes and azoxybenzenes with aldehydes[3a] and α-oxocarboxylic acids[4a,b] were demonstrated by Wang et al. using a Pd(II) catalyst (Figure 1). Sun and co-workers described the Pd(II)-catalyzed alkoxylation[5a] and nitration[6a] of azobenzenes. In addition, the highly efficient syntheses of indazoles with azobenzenes and aldehydes using Rh(III),[3e] Co(III),[3f] and Re(I)[3g] catalysts were reported. Lee and co-workers demonstrated the synthesis of 2-aryl-2*H*-benzotriazoles from the C2-selective amidation of azobenzenes followed by oxidative cyclization.[7] Furthermore, halogenation,[8] phosphorylation,[9] amination,[10] olefination,[11] tandem cyclization,[12] cyanation,[13] alkylation,[14] and arylation[15] have been reported.

In last few decades, a great effort has been made toward the transition-metal-catalyzed direct functionalization of inactive C−H bonds with various coupling partners.[16] In particular, the direct addition of C−H bonds to unsaturated C−N multiple bonds represents a valuable pursuit with profound synthetic potentials for the establishment of nitrogen-based functional groups into molecules.[17] Thus, the direct insertion of C−H bonds into the polar C−N π-bond of isocyanates is highly enviable for providing synthetically valuable amide moieties. For example, Kuninobu and Takai reported the Re(I)-catalyzed intermolecular reaction of aromatic aldimines with isocyanates to afford phthalimidine derivatives.[18] Bergman and Ellman reported the Rh(III)-catalyzed amidation of aryl and vinyl C−H bonds with isocyanates for the synthesis of *N*-acyl anthranilamides and β-enamine amides.[19] In addition, various directing groups such as phenylpyridines,[20a] *N*-aryl-pyrazoles,[20b,c] oximes,[21] and benzoic acid derivatives[22] were efficiently coupled with isocyanates to afford the corresponding *ortho*-amidated products under Rh, Ru, Re, and Co catalysis.

Amide moieties not only represent a key structural motif found in many natural products, pharmaceuticals, polymers, and biological systems,[23] but they also find application as crucial intermediates for the preparation of various useful compounds.[24] Particularly, *N*-acylsulfonamides have established significant attention due to their various biological activities as precursors of therapeutic agents for Alzheimer's disease,[25a] as antiproliferative agents,[25b] as tRNA synthetases inhibitors,[25c] as angiotensin II antagonists,[25d] and as antagonists of leukotriene D_4-receptors.[25e] In contrast to the synthesis of amides using isocyanates, and to the best of our knowledge, the synthesis of *N*-acylsulfonamides with arylsulfonyl isocyanates has never been reported in the C−H bond activation area. Inspired by our previous works with the Rh(III)-catalyzed addition of C(sp^2)−H bonds to polarized π-bonds,[26] we herein present the first examples of *N*-sulfonyl amidation via the Rh(III)-catalyzed direct reaction of C−H bonds of azobenzenes with arylsulfonyl isocyanates along with amidation of azobenzenes with aryl and alkyl isocyanates.

RESULTS AND DISCUSSION

Our investigation was initiated by examining the coupling of azobenzene (**1a**) and *p*-tolylsulfonyl isocyanate (**2a**) under rhodium catalysis (Table 1). To our delight, the cationic rhodium catalyst, generated from $[Cp^*RhCl_2]_2$ and $AgSbF_6$ in the presence of NaOAc, was found to promote the coupling of **1a** and **2a** in dichloroethane (DCE) at 110 °C for 24 h to give the *N*-acylsulfonamide product compound **3a** in 64% yield (entry 1). Screening of other catalysts under otherwise identical conditions showed that cationic rhodium complex was found to

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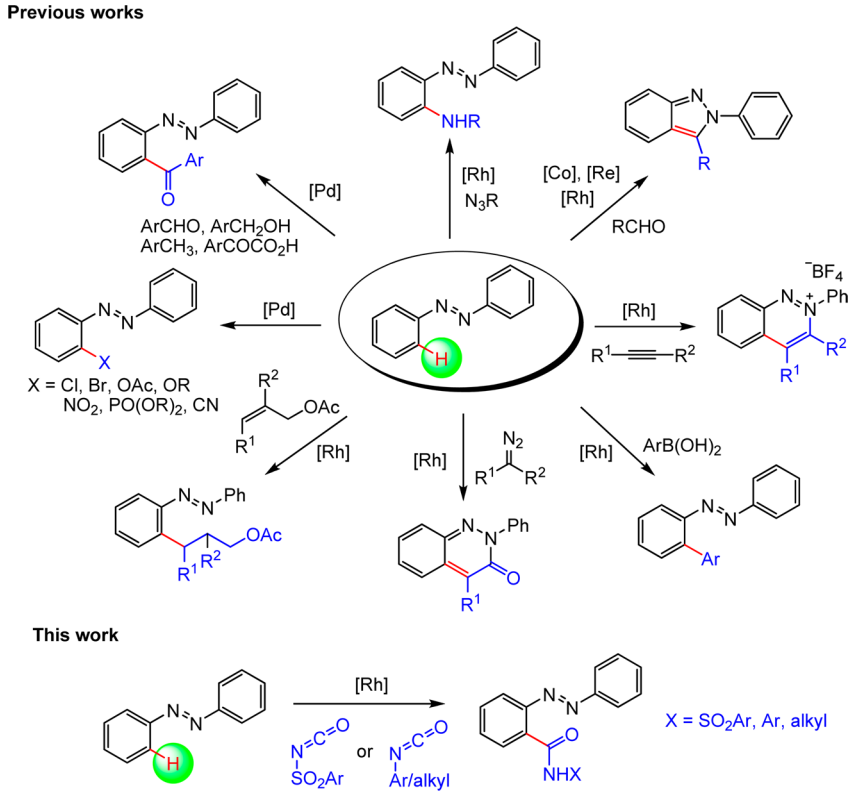
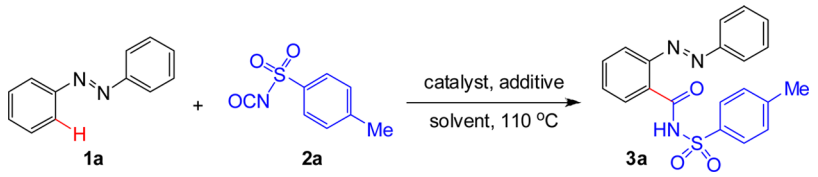


Figure 1. C−H functionalization of azobenzenes.

Table 1. Selected Optimization of Reaction Conditions[a]



entry	catalyst (mol %)	additive (mol %)	solvent	yield (%)[b]
1	$[RhCp^*Cl_2]_2$ (5)	$AgSbF_6$ (20), NaOAc (30)	DCE	64
2	$[RuCl_2(p\text{-cymene})]_2$ (5)	$AgSbF_6$ (20), NaOAc (30)	DCE	N.R.
3	$Cp^*Co(CO)I_2$ (5)	$AgSbF_6$ (20), NaOAc (30)	DCE	21
4	$Pd(OAc)_2$ (10)	NaOAc (30)	DCE	N.R.
5	$[RhCp^*Cl_2]_2$ (5)	NaOAc (30)	DCE	10
6	$[RhCp^*Cl_2]_2$ (5)	$AgSbF_6$ (20)	DCE	5
7	$[RhCp^*Cl_2]_2$ (5)	$AgNTf_2$ (20), NaOAc (30)	DCE	68
8	**$[RhCp^*Cl_2]_2$ (2.5)**	**$AgNTf_2$ (10), NaOAc (30)**	**DCE**	**85**
9[c]	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	DCE	56
10[d]	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	DCE	65
11	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), $Cu(OAc)_2$ (30)	DCE	60
12	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	THF	trace
13	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	xylene	20
14	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	PhCl	15
15	$[RhCp^*Cl_2]_2$ (2.5)	$AgNTf_2$ (10), NaOAc (30)	toluene	25
16	$[RhCp^*Cl_2]_2$ (1)	$AgNTf_2$ (4), NaOAc (30)	DCE	80

[a]*Reaction conditions*: **1a** (0.2 mmol), **2a** (0.4 mmol), catalyst (quantity noted), additive (quantity noted), solvent (1 mL) at 110 °C for 24 h under N_2 atmosphere in reaction tubes. [b]Isolated yield by column chromatography. [c]**2a** (0.6 mmol) was used. [d]Under air.

be the most effective in this transformation (entries 2−4). In addition, treatment of either NaOAc or $AgSbF_6$ was found to be less effective in this coupling reaction (entries 5 and 6). Exchange of silver additive to $AgNTf_2$ afforded the slightly increased reactivity (entry 7). Interestingly, low catalyst loading displayed higher reactivity to afford the desired product **3a** in 85% yield (entry 8). However, an increased amount (3 equiv) of **2a** provided a significant decrease in the yield of **3a** (entry 9). We were delighted to observe the formation of **3a** under air conditions, albeit in relatively low yield (entry 10). Addition-

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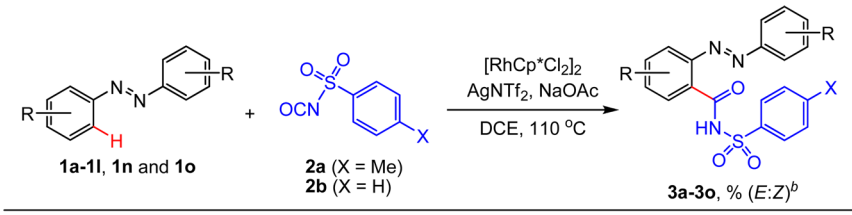
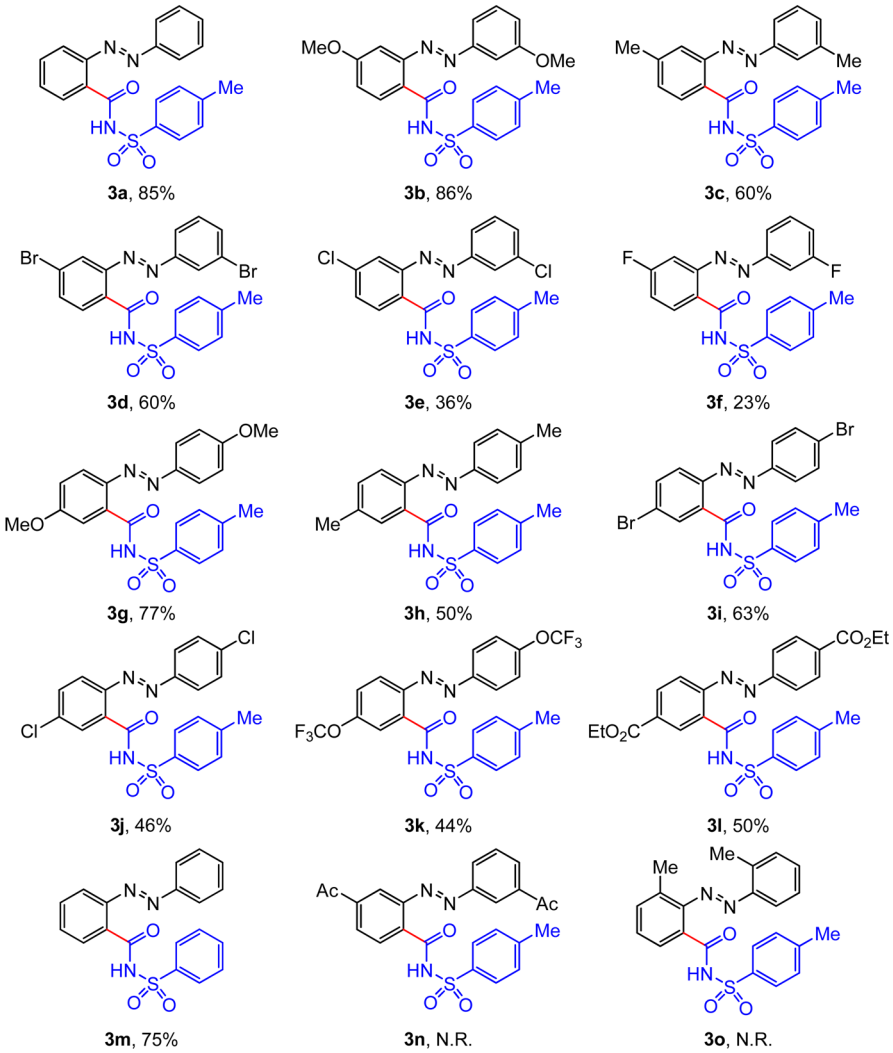
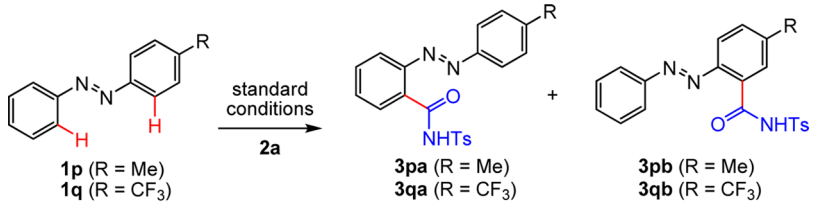
Table 2. Scope of Azobenzenes with Arylsulfonyl Isocyanates[a]





[a]*Reaction conditions*: **1a**−**1l**, **1n** and **1o** (0.2 mmol), **2a** and **2b** (0.4 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgNTf_2$ (10 mol %), NaOAc (30 mol %), DCE (1 mL) at 110 °C for 24 h under N_2 atmosphere in reaction tubes. [b]Isolated yield by flash column chromatography.

Scheme 1. Reaction of Unsymmetrical Azobenzenes with Arylsulfonyl Isocyanate



ally, changing the acetate additive and solvent under otherwise identical conditions resulted in the decreased formation of *N*-acylsulfonamide product **3a** (entries 11−15). Furthermore, this reaction can proceed with 1 mol % loading of rhodium catalyst to give almost comparable yield of the desired product (entry 16).

With the optimized reaction conditions in hand, we screened various azobenzenes with arylsulfonyl isocyanates, as shown in

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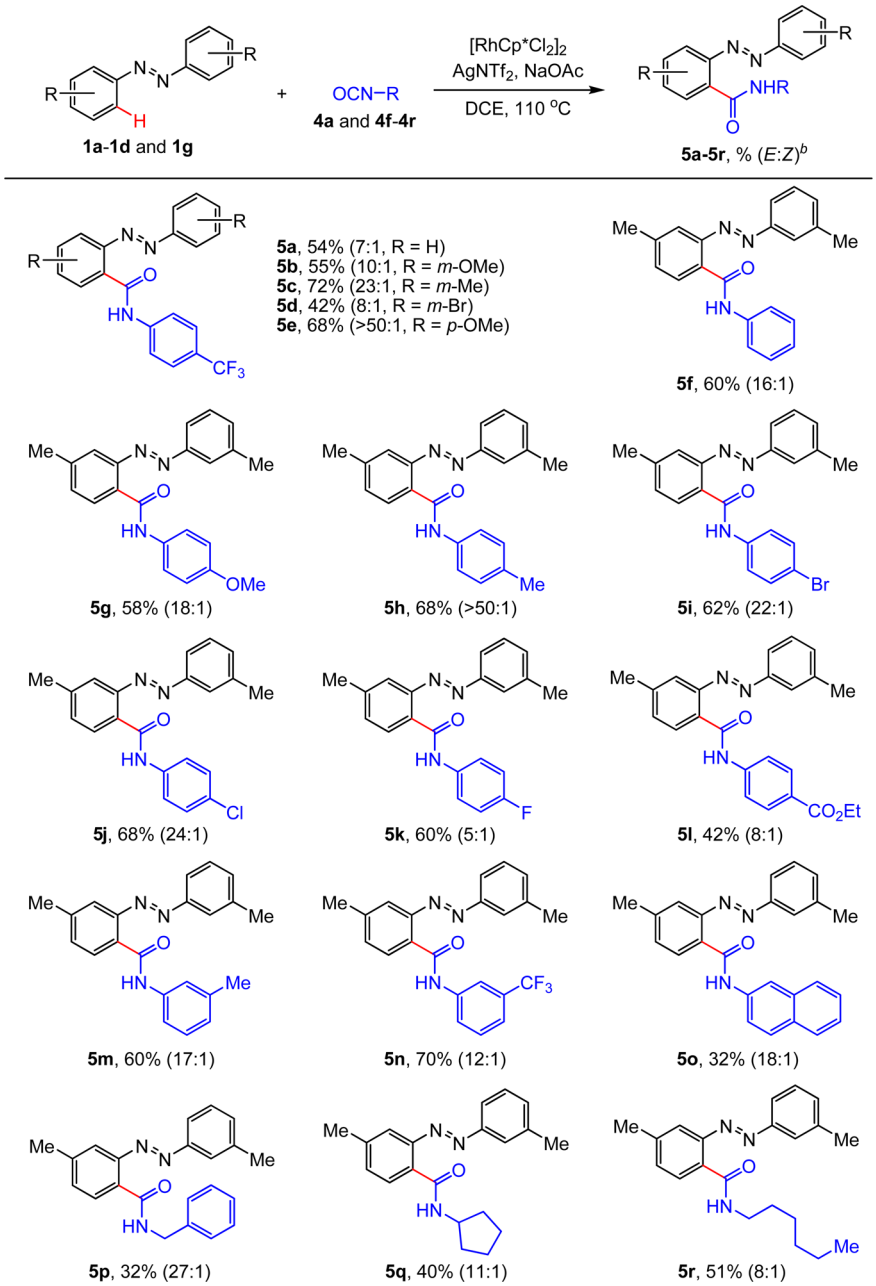
Table 3. Scope of Azobenzenes with Aryl and Alkyl Isocyanates[a]



[a]*Reaction conditions*: **1a−1d** and **1g** (0.2 mmol), **4a** and **4f−4r** (0.6 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgNTf_2$ (20 mol %), NaOAc (30 mol %), DCE (1 mL) at 110 °C for 24 h under N_2 atmosphere in reaction tubes. [b]Isolated yield by flash column chromatography. Parentheses show the ratio of *E* and *Z* isomers determined by ^1H NMR analysis.

Table 2. The *meta*-substituted azobenzenes **1b−1f** were found to couple with *p*-tolylsulfonyl isocyanate (**2a**) to give the corresponding *N*-acylsulfonamide products **3b−3f**. Electron-donating substituents at the *meta*-position provided higher yields compared to electron-withdrawing substituents. Further, a highly electron-withdrawing group (**1n**) at the *meta*-position did not deliver the coupling reaction. However, azobenezenes **1g−1l** containing electron-donating and electron-withdrawing groups at the *para*-position were found to be compatible to furnish the corresponding products **3g−3l** in high to moderate yields. It is quite surprising that *ortho*-substituted azobenezene **1o** did not undergo *N*-sulfonyl amidation. In addition, phenylsulfonyl isocyanate (**2b**) was coupled with **1a** to provide **3m** in 75% yield. It should be noted that all amide products **3a−3m** were exclusively found to be *E* isomers.

Furthermore, the reactions of unsymmetrical *para*-substituted azobenzenes **1p** and **1q** containing electron-rich and electron-deficient groups (Me and CF_3) with **2a** were screened under standard reaction conditions (Scheme 1). In the case of **1p**, no significant distinction of product distribution between **3pa** and **3pb** was observed. However, in the case of unsymmetrical azobenzene **1q** with an electron-deficient substitutent, *N*-sulfonyl amidation predominantly occurred on the electron-rich aromatic ring to provide **3qa** as a major product.

Next we focused on the coupling of azobenzenes with aryl and alkyl isocyanates **4a** and **4f−4r**, as shown in Table 3. To

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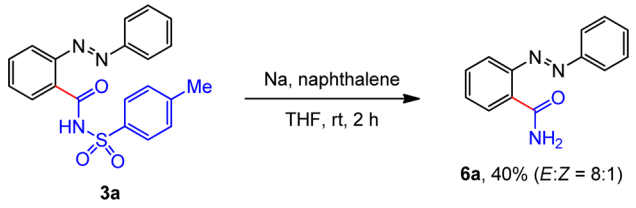
our delight, the coupling of azobenzene (**1a**) with *p*-trifluoromethylphenyl isocyanate (**4a**) under the slightly modified reaction conditions (3 equiv of **4a** and 20 mol % of $AgNTf_2$) provided the amidation product **5a** in 54% yield. Moreover, various *meta*- and *para*-substituted azobenzenes **1b**–**1d** and **1g** were subjected to the optimized conditions with **4a** to afford the corresponding amide products **5b**–**5e** in moderate to good yields. To extend the scope of this transformation, the optimal reaction conditions were applied to a range of aryl and alkyl isocyanates **4f**–**4r**. Electron-rich and electron-deficient groups (OMe, Me, Br, F, Cl, and CO_2Et) at the *para*-position on the aromatic ring of aryl isocyanates were tolerated under the standard reaction conditions to afford the corresponding products **5g**–**5l**. Additionally, both electron-rich and electron-deficient *meta*-substituted aryl isocyanates also underwent the amidation reaction to provide **5m** (60%), **5n** (70%), and **5o** (32%). Moreover, this transformation is not limited to aryl isocyanates. Aliphatic isocyanates such as benzyl isocyanate (**4p**) and cyclopentyl isocyanate (**4q**) and *n*-hexyl isocyanate (**4r**) also participated in redox-neutral amidation reactions to furnish **5p**–**5r**, respectively. At this stage, we are unclear about the formation of a mixture of *E* and *Z* isomers in the case of aryl and alkyl isocyanates. However, in the case of arylsulfonyl isocyanates, only *E* isomer was formed, presumably due to the steric repulsion between the sulfonamide moiety and azobenzenes.

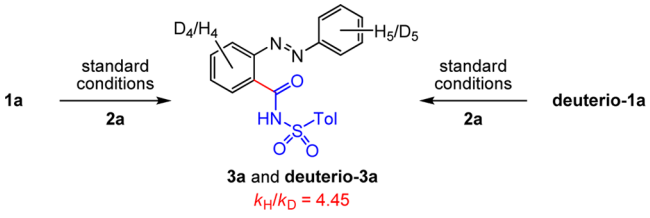
To show the synthetic transformation of azobenzene containing an *N*-acylsulfonamide moiety, treatment of **3a** under reductive conditions provided benzamide **6a** (Scheme 2).[27]

Scheme 2. Transformation of *N*-Acylsulfonamide



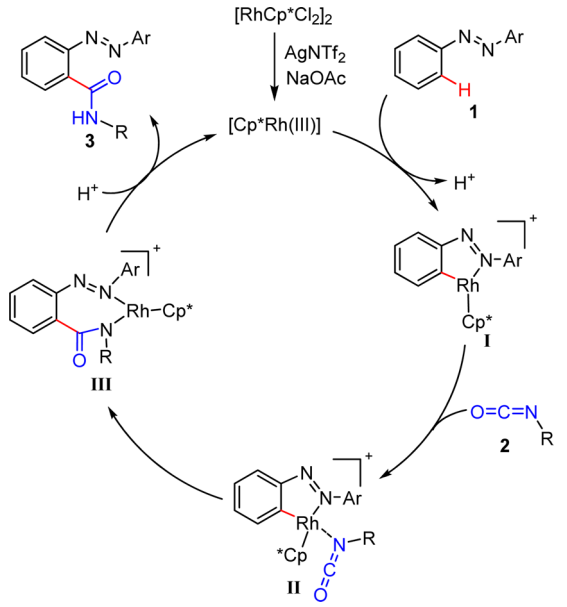
To obtain mechanistic insight, two parallel reactions of **1a** and **deuterio-1a** with **2a** under standard reaction conditions were carried out, which resulted in the kinetic isotope effect (k_H/k_D) of 4.45 (Scheme 3), thus indicating that C–H bond cleavage might be involved in the rate-limiting step.[28]

Scheme 3. Kinetic Isotope Effect Experiment



A plausible reaction mechanism for the Rh(III)-catalyzed amidation reaction of azobenzenes with isocyanates is depicted in Scheme 4. First, treatment of $[RhCp^*Cl_2]_2$ with $AgNTf_2$ and NaOAc generates the cationic Rh(III) catalyst, which undergoes C–H metalation with **1** to yield the cyclorhodated complex **I**.[12a] Subsequent coordination of isocyanate (**2**) with **I**

Scheme 4. Plausible Mechanistic Pathway



provides intermediate **II**,[20c,22] which on migratory insertion into the Rh–C bond delivers complex **III**.[21] Finally, protonation of **III** affords our desired product **3** and the regeneration of active Rh(III) catalyst.

CONCLUSION

In conclusion, we disclosed the rhodium(III)-catalyzed direct C–H *N*-sulfonyl amidation of azobenzenes with arylsulfonyl isocyanates. This protocol allows the generation of *N*-acylsulfonamides, which are known to be crucial synthetic precursors of biologically active compounds. In addition, this protocol was successfully applied to aryl and alkyl isocyanates to deliver *ortho*-amidated azobenzenes. Further applications of our protocol to the synthesis of bioactive molecules and a detailed mechanistic investigation are in progress.

EXPERIMENTAL SECTION

Typical procedure for the amidation of azobenzenes (3a–3m, 3pa+3pb, 3qa, 3qb, and 5a–5r). To an oven-dried sealed tube charged with (*E*)-1,2-diphenyldiazene (**1a**) (36.4 mg, 0.2 mmol, 100 mol %), $[RhCp^*Cl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), $AgNTf_2$ (7.8 mg, 0.02 mmol, 10 mol %), and NaOAc (4.9 mg, 0.06 mmol, 30 mol %) was added 4-methylbenzenesulfonyl isocyanate (**2a**) (60.6 μL, 0.4 mmol, 200 mol %) and DCE (1 mL) under N_2 atmosphere. The reaction mixture was allowed to stir for 24 h at 110 °C. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 5:1) to afford **3a** (64.8 mg) in 85% yield.

*(E)-2-(Phenyldiazenyl)-N-tosylbenzamide (**3a**).* 64.8 mg (85%); Orange solid; mp = 172.4–173.1 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 12.36 (s, 1H), 8.30 (dd, *J* = 7.9, 1.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 2H), 8.02–8.00 (m, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.67–7.61 (m, 4H), 7.58 (td, *J* = 8.4, 1.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 151.9, 149.3, 145.0, 136.2, 134.0, 133.5, 132.2, 132.1, 130.0, 129.7, 128.7, 128.3, 124.0, 116.3, 21.8; IR (KBr) υ 2920, 2851, 1690, 1592, 1448, 1353, 1211, 1164, 1084, 879, 840, 819, 768, 680 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{17}N_3O_3S$ $[M]^+$ 379.0991, found 379.0997.

*(E)-4-Methoxy-2-((3-methoxyphenyl)diazenyl)-N-tosylbenzamide (**3b**).* 75.6 mg (86%); Orange solid; mp = 179.2–179.6 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.24 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.44

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(s, 1H), 7.40 (s, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.19 (dd, J = 8.2, 1.6 Hz, 1H), 7.09 (dd, J = 8.8, 2.5 Hz, 1H), 4.00 (s, 3H), 3.91 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.9, 162.8, 161.1, 153.0, 151.0, 144.9, 136.3, 134.0, 130.6, 129.6, 128.7, 121.5, 121.1, 120.2, 118.6, 104.5, 100.1, 56.1, 56.0, 21.8; IR (KBr) υ 2292, 2851, 1682, 1595, 1423, 1339, 1257, 1158, 1078, 1026, 835, 814, 765 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O_5S$ $[M]^+$ 439.1202, found 439.1199.

*(E)-4-Methyl-2-(m-tolyldiazenyl)-N-tosylbenzamide (**3c**).* 48.9 mg (60%); Orange solid; mp = 191.5−192.4 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.47 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 8.03 (dt, J = 7.6, 1.8 Hz, 2H), 7.84 (d, J = 8.0 Hz, 1H), 7.82 (s, 1H), 7.42 (s, 1H), 7.54 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 7.9 Hz, 2H), 2.54 (s, 3H), 2.45 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 151.9, 148.9, 144.9, 144.7, 140.2, 136.1, 134.1, 132.8, 132.0, 129.6, 129.5, 128.5, 125.5, 122.8, 122.7, 116.1, 21.7, 21.3; IR (KBr) υ 2920, 2851, 1692, 1595, 1445, 1343, 1162, 1078, 835, 812, 768 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O_3S$ $[M]^+$ 407.1304, found 407.1311.

*(E)-4-Bromo-2-((3-bromophenyl)diazenyl)-N-tosylbenzamide (**3d**).* 64.6 mg (60%); Orange solid; mp = 205.2−206.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.19−8.16 (m, 2H), 8.07−8.05 (m, 3H), 7.94 (d, J = 7.0 Hz, 1H), 7.77 (d, J = 7.9 Hz, 1H), 7.73 (dd, J = 8.5, 2.0 Hz, 1H), 7.55 (t, J = 7.9 Hz, 1H), 7.33 (d, J = 7.9 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.0, 152.6, 149.2, 145.3, 136.6, 135.9, 135.4, 133.7, 131.4, 129.8, 129.1, 128.8, 128.5, 127.6, 124.1, 122.3, 119.6, 21.9; IR (KBr) υ 3355, 3260, 2923, 2854, 1736, 1698, 1527, 1386, 1298, 1155, 1096, 902, 814, 701 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{15}Br_2N_3O_3S$ $[M]^+$ 534.9201, found 534.9199.

*(E)-4-Chloro-2-((3-chlorophenyl)diazenyl)-N-tosylbenzamide (**3e**).* 32.3 mg (36%); Orange solid; mp = 191.6−193.6 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.27 (d, J = 8.6 Hz, 1H), 8.06 (dt, J = 7.6, 1.8 Hz, 2H), 8.03−8.02 (m, 1H), 7.92−7.89 (m, 2H), 7.64−7.60 (m, 2H), 7.58 (dd, J = 8.6, 2.1 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.9, 152.5, 149.4, 145.3, 140.7, 136.3, 135.9, 133.8, 133.7, 132.5, 131.2, 129.8, 128.8, 127.1, 124.8, 121.8, 116.5, 21.9; IR (KBr) υ 3356, 3260, 2922, 2853, 1697, 1527, 1443, 1299, 1155, 1096, 902, 813, 702 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{15}Cl_2N_3O_3S$ $[M]^+$ 447.0211, found 447.0208.

*(E)-4-Fluoro-2-((3-fluorophenyl)diazenyl)-N-tosylbenzamide (**3f**).* 19.1 mg (23%); Orange solid; mp = 151.8−155.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.37−8.35 (m, 1H), 8.05 (dt, J = 7.6, 1.9 Hz, 2H), 7.83 (d, J = 7.9 Hz, 1H), 7.71 (dt, J = 7.9, 2.1 Hz, 1H), 7.67−7.63 (m, 2H), 7.39−7.36 (m, 1H), 7.34−7.30 (m, 3H), 2.42 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.8 (d, J_{C-F} = 255.9 Hz), 163.7 (d, J_{C-F} = 248.5 Hz), 161.8, 153.0 (d, J_{C-F} = 7.0 Hz), 150.8 (d, J_{C-F} = 7.2 Hz), 145.2, 136.0, 134.9 (d, J_{C-F} = 9.0 Hz), 131.4 (d, J_{C-F} = 7.9 Hz), 129.7, 128.8, 125.2 (d, J_{C-F} = 2.3 Hz), 120.8 (d, J_{C-F} = 20.3 Hz), 120.0, 119.7 (d, J_{C-F} = 22.1 Hz), 111.2 (d, J_{C-F} = 22.6 Hz), 103.3 (d, J_{C-F} = 24.2 Hz), 21.9; IR (KBr) υ 3078, 2923, 2854, 1695, 1594, 1442, 1348, 1247, 1159, 1085, 883, 840, 815, 787, 768 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{15}F_2N_3O_3S$ $[M]^+$ 415.0802, found 415.0796.

*(E)-5-Methoxy-2-((4-methoxyphenyl)diazenyl)-N-tosylbenzamide (**3g**).* 67.7 mg (77%); Yellow solid; mp = 182.9−184.6 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.97 (s, 1H), 8.04 (d, J = 7.9 Hz, 2H), 7.96 (d, J = 8.4 Hz, 3H), 7.76 (s, 1H), 7.32 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 8.7 Hz, 3H), 3.93 (s, 3H), 3.87 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 163.2, 162.1, 146.4, 144.9, 144.1, 136.3, 129.7, 129.3, 128.7, 126.o, 121.4, 118.3, 115.2, 114.1, 56.1, 56.0, 21.8; IR (KBr) υ 3355, 3259, 2922, 2838, 2357, 1695, 1592, 1437, 1328, 1256, 1158, 1029, 835, 816 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O_5S$ $[M]^+$ 439.1202, found 439.1205.

*(E)-5-Methyl-2-(p-tolyldiazenyl)-N-tosylbenzamide (**3h**).* 40.7 mg (50%); Light orange solid; mp = 204.5−207.3 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.58 (s, 1H), 8.10 (s, 1H), 8.03 (dt, J = 7.6, 1.9 Hz, 2H), 7.89 (dt, J = 7.7, 2.1 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.41 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 2.49 (s, 3H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 150.2, 147.6, 144.9, 144.4, 142.7, 136.3, 134.7, 132.3, 130.7, 129.6, 128.8, 127.8, 124.0, 116.3, 21.9, 21.8, 21.6; IR (KBr) υ 3260, 2920, 2852, 1686, 1599, 1447, 1349, 1226, 1155, 1084, 836, 815, 704 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O_3S$ $[M]^+$ 407.1304, found 407.1311.

*(E)-5-Bromo-2-((4-bromophenyl)diazenyl)-N-tosylbenzamide (**3i**).* 67.7 mg (63%); Orange solid; mp = 231.2−233.4 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.13 (s, 1H), 8.45 (s, 1H), 8.03 (d, J = 8.0 Hz, 2H), 7.86 (d, J = 8.4 Hz, 2H), 7.83−7.79 (m, 3H), 7.74 (d, J = 8.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.5, 150.6, 147.9, 145.4, 137.0, 135.8, 135.1, 133.5, 129.8, 129.7, 128.9, 128.8, 127.5, 125.4, 118.0, 21.9; IR (KBr) υ 3259, 2921, 2853, 1689, 1580, 1449, 1349, 1297, 1159, 1082, 849, 837, 700 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{15}Br_2N_3O_3S$ $[M]^+$ 534.9201, found 534.9208.

*(E)-5-Chloro-2-((4-chlorophenyl)diazenyl)-N-tosylbenzamide (**3j**).* 41.2 mg (46%); Yellow solid; mp = 223.3−224.8 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.18 (s, 1H), 8.29 (s, 1H), 8.03 (dt, J = 7.6, 1.8 Hz, 2H), 7.94 (dt, J = 8.1, 2.7 Hz, 2H), 7.91 (d, J = 8.6 Hz, 1H), 7.64 (dt, J = 8.1, 2.7 Hz, 2H), 7.58 (dd, J = 8.7, 2.5 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.6, 150.3, 147.6, 145.4, 140.2, 139.1, 135.8, 134.0, 132.1, 130.5, 129.8, 129.7, 128.9, 125.3, 118.0, 21.9; IR (KBr) υ 3093, 2923, 2853, 1697, 1586, 1450, 1352, 1253, 1165, 1068, 841, 814 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{15}Cl_2N_3O_3S$ $[M]^+$ 447.0211, found 447.0216.

*(E)-N-Tosyl-5-(trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)-diazenyl)benzamide (**3k**).* 48.2 mg (44%); Light brown solid; mp = 148.3−150.4 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.17 (s, 1H), 8.16 (s, 1H), 8.08−8.02 (m, 5H), 7.50 (d, J = 8.2 Hz, 2H), 7.47−7.45 (m, 1H), 7.34 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.4, 153.0, 152.0, 149.7, 147.2, 145.5, 135.7, 130.5, 129.8, 128.9, 125.9, 125.8, 123.5, 121.9, 120.5 (q, J_{C-F} = 258.4 Hz), 120.4 (q, J_{C-F} = 258.5 Hz), 118.7, 21.9; IR (KBr) υ 2922, 2852, 2362, 1702, 1595, 1455, 1355, 1251, 1158, 1084, 923, 853, 822, 757 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{15}F_6N_3O_5S$ $[M]^+$ 547.0637, found 547.0640.

*(E)-Ethyl 4-((4-(ethoxycarbonyl)phenyl)diazenyl)-3-(tosylcarbamoyl)benzoate (**3l**).* 52.2 mg (50%); Orange solid; mp = 155.9−157.4 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.96 (s, 1H), 8.33 (dt, J = 7.7, 1.9 Hz, 2H), 8.29 (dd, J = 8.4, 1.9 Hz, 1H), 8.07−8.05 (m, 4H), 7.98 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 4.39 (q, J = 7.0 Hz, 2H), 2.42 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.6, 164.9, 162.0, 154.2, 151.2, 145.4, 135.9, 134.9, 134.8, 134.1, 133.7, 131.5, 129.8, 128.9, 124.0, 116.7, 62.0, 61.9, 21.9, 14.5, 14.4; IR (KBr) υ 2920, 2850, 1726, 1693, 1595, 1455, 1352, 1276, 1164, 1087, 865, 826, 757 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{26}H_{25}N_3O_7S$ $[M]^+$ 523.1413, found 523.1417.

*(E)-2-(Phenyldiazenyl)-N-(phenylsulfonyl)benzamide (**3m**).* 54.8 mg (75%); Light orange solid; mp = 188.1−189.4 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.42 (s, 1H), 8.31 (d, J = 7.9 Hz, 1H), 8.16 (d, J = 7.4 Hz, 2H), 8.02 (d, J = 7.2 Hz, 2H), 7.95 (d, J = 8.1 Hz, 1H), 7.68−7.59 (m, 6H), 7.53 (t, J = 7.9 Hz, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.8, 151.8, 149.2, 139.0, 133.9, 133.8, 133.4, 132.1, 132.0, 129.9, 128.9, 128.5, 128.0, 123.8, 116.2; IR (KBr) υ 2921, 2852, 1685, 1592, 1447, 1341, 1172, 1087, 997, 879, 846, 762, 718 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{19}H_{15}N_3O_3S$ $[M]^+$ 365.0834, found 365.0833.

*(E)-2-(p-Tolyldiazenyl)-N-tosylbenzamide (**3pa**) and (E)-5-methyl-2-(phenyldiazenyl)-N-tosylbenzamide (**3pb**).* **3pa**+**3pb** = 1:1; 34.6 mg (44%); Light orange solid; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.50 (s, 1H), 12.44 (s, 1H), 8.29 (dd, J = 7.7, 1.4 Hz, 1H), 8.10 (br s, 1H), 8.05−8.04 (m, 4H), 7.65−7.62 (m, 3H), 7.61−7.59 (m, 1H), 7.56 (dt, J = 7.7, 1.4 Hz, 1H), 7.99−7.98 (m, 2H), 7.93−7.91 (m, 3H), 7.86 (d, J = 8.4 Hz, 1H), 7.45−7.41 (m, 3H), 7.32−7.31 (m, 4H), 2.49 (s, 3H), 2.42 (s, 3H), 2.41 (s, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.0, 162.9, 151.8, 150.0, 149.2, 147.3, 144.7, 144.6, 142.9, 136.1, 136.0, 134.5, 133.7, 132.9, 132.1, 131.8, 131.5, 130.5, 129.8, 129.5, 129.4, 128.6, 128.5, 127.8, 123.9, 123.7, 116.1, 116.0, 21.7, 21.6, 21.4; IR

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(KBr) υ 2920, 2851, 1687, 1593, 1451, 1352, 1160, 1083, 843, 820, 759, 704 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{19}N_3O_3S$ $[M]^+$ 393.1147, found 393.1154.

(E)-N-Tosyl-2-((4-(trifluoromethyl)phenyl)diazenyl)benzamide (**3qa**). 54.4 mg (61%); Orange solid; mp = 198.2−200.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.01 (s, 1H), 8.33 (dd, J = 7.0, 1.4 Hz, 1H), 8.09 (d, J = 7.7 Hz, 2H), 8.04 (d, J = 8.4 Hz, 2H), 7.96−7.92 (m, 3H), 7.68−7.64 (m, 2H), 7.33 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.5, 153.5, 148.9, 145.0, 135.8, 134.1 (q, J_{C-F} = 32.9 Hz), 133.8, 132.9, 132.1, 129.5, 128.7, 128.6, 127.1 (q, J_{C-F} = 3.8 Hz), 123.9, 123.5 (q, J_{C-F} = 271.0 Hz), 116.1, 21.6; IR (KBr) 2922, 2853, 1701, 1613, 1596, 1450, 1326, 1164, 1087, 854, 813, 781 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{16}F_3N_3O_3S$ $[M]^+$ 447.0864, found 447.0870.

(E)-2-(Phenyldiazenyl)-N-tosyl-5-(trifluoromethyl)benzamide (**3qb**). 13.6 mg (15%); Orange solid; mp = 179.6−182.2 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 12.19 (s, 1H), 8.61 (s, 1H), 8.06−8.04 (m, 5H), 7.87 (dd, J = 8.4, 1.4 Hz, 1H), 7.70−7.68 (m, 3H), 7.34 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 161.5, 151.7, 150.8, 145.2, 135.6, 134.3, 133.3 (q, J_{C-F} = 32.9 Hz), 130.3 (q, J_{C-F} = 3.6 Hz), 130.0, 129.6, 129.5 (q, J_{C-F} = 4.2 Hz), 128.7, 128.6, 124.2, 123.1 (q, J_{C-F} = 270.9 Hz), 117.2, 21.7; IR (KBr) υ 2922, 2853, 1701, 1613, 1596, 1450, 1326, 1164, 1087, 854, 813, 781 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{16}F_3N_3O_3S$ $[M]^+$ 447.0864, found 447.0870.

(E)-2-(Phenyldiazenyl)-N-(4-(trifluoromethyl)phenyl)benzamide (**5a**). 39.9 mg (54%); *E*:*Z* = 7:1; Light orange solid; mp = 149.9−152.1 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.49 (dd, J = 7.7, 1.4 Hz, 1H), 7.90−7.89 (m, 2H), 7.87 (dd, J = 8.4, 1.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.66 (ddd, J = 14.7, 7.0, 1.4 Hz, 1H), 7.64−7.59 (m, 6H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.8, 152.7, 149.2, 141.5, 132.6, 132.5, 132.1, 132.0, 130.8, 129.6, 126.3 (q, J_{C-F} = 2.6 Hz), 125.9 (q, J_{C-F} = 32.7 Hz), 124.1 (q, J_{C-F} = 270.3 Hz), 123.0, 119.7, 116.0; IR (KBr) υ 3294, 2919, 2850, 1645, 1514, 1408, 1317, 1257, 1115, 1065, 908, 831, 772, 705 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{14}F_3N_3O$ $[M]^+$ 369.1089, found 369.1090.

(E)-4-Methoxy-2-((3-methoxyphenyl)diazenyl)-N-(4-(trifluoromethyl)phenyl)benzamide (**5b**). 47.2 mg (55%); *E*:*Z* = 10:1; Orange solid; mp = 131.9−134.7 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.96 (s, 1H), 8.42 (dd, J = 9.1, 4.2 Hz, 1H), 7.78 (d, J = 7.7 Hz, 2H), 7.57 (d, J = 7.7 Hz, 2H), 7.52−7.51 (m, 2H), 7.39 (s, 1H), 7.34 (s, 1H), 7.18−7.15 (m, 2H), 3.92 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 162.7, 160.7, 153.8, 150.4, 141.7, 133.7, 130.4, 126.2 (q, J_{C-F} = 4.0 Hz), 125.5 (q, J_{C-F} = 32.2 Hz), 124.1 (q, J_{C-F} = 269.8 Hz), 123.8, 119.6, 118.7, 118.5, 116.3, 107.3, 99.6, 55.7, 55.6; IR (KBr) υ 3244, 2920, 2850, 1660, 1596, 1482, 1316, 1256, 1105, 1030, 933, 886, 838, 781, 755 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{18}F_3N_3O_3$ $[M]^+$ 429.1300, found 429.1295.

(E)-4-Methyl-2-(m-tolyldiazenyl)-N-(4-(trifluoromethyl)phenyl)-benzamide (**5c**). 57.2 mg (72%); *E*:*Z* = 23:1; Orange solid; mp = 139.7−140.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.16 (s, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.7 Hz, 1H), 7.68 (s, 1H), 7.64 (s, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.7 Hz, 1H), 7.43 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.8, 152.7, 148.9, 143.3, 141.7, 139.6, 133.2, 132.7, 132.0, 129.4, 128.1, 126.2 (q, J_{C-F} = 3.3 Hz), 125.6 (q, J_{C-F} = 32.5 Hz), 124.1 (q, J_{C-F} = 269.6 Hz), 122.7, 121.0, 119.5, 116.0, 21.4, 21.3; IR (KBr) υ 3239, 2923, 2855, 2360, 1673, 1537, 1410, 1317, 1258, 1109, 1063, 838, 786 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{18}F_3N_3O$ $[M]^+$ 397.1402, found 397.1406.

(E)-4-Bromo-2-((3-bromophenyl)diazenyl)-N-(4-(trifluoromethyl)-phenyl)benzamide (**5d**). 44.3 mg (42%); *E*:*Z* = 8:1; Light orange solid; mp = 197.3−201.5 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.78 (s, 1H), 8.38 (d, J = 8.4 Hz, 1H), 8.04−8.02 (m, 2H), 7.94 (d, J = 7.7 Hz, 1H), 7.84−7.81 (m, 4H), 7.66−7.63 (m, 2H), 7.54 (t, J = 7.7 Hz, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 162.7, 153.1, 149.0, 141.1, 135.6, 135.3, 133.7, 131.2, 130.1, 127.4, 126.4 (q, J_{C-F} = 3.8 Hz), 126.2 (q, J_{C-F} = 32.7 Hz), 124.5, 124.0 (q, J_{C-F} = 269.6 Hz), 123.8, 123.6, 119.7, 119.2, 29.7; IR (KBr) υ 3295, 2920, 2851, 2362, 1644, 1529, 1406, 1320, 1272, 1157, 1112, 1065, 907, 832, 790 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{12}Br_2F_3N_3O$ $[M]^+$ 524.9299, found 524.9299.

(E)-5-Methoxy-2-((4-methoxyphenyl)diazenyl)-N-(4-(trifluoromethyl)phenyl)benzamide (**5e**). 58.4 mg (68%); *E*:*Z* = >50:1; Orange solid; mp = 141.2−146.5 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.98 (d, J = 2.8 Hz, 1H), 7.90 (d, J = 9.1 Hz, 1H), 7.84 (dt, J = 8.4, 2.8 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.10 (dd, J = 9.1, 2.8 Hz, 1H), 7.07 (dt, J = 8.4, 2.8 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.8, 162.8, 162.1, 146.9, 143.9, 141.6, 132.0, 126.3 (q, J_{C-F} = 3.8 Hz), 125.7 (q, J_{C-F} = 32.7 Hz), 124.8, 124.1 (q, J_{C-F} = 270.2 Hz), 119.8, 119.7, 118.0, 114.7, 114.5, 55.8, 55.7; IR (KBr) υ 2921, 2849, 1721, 1671, 1593, 1411, 1317, 1250, 1109, 1064, 835, 808, 743 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{18}F_3N_3O_3$ $[M]^+$ 429.1300, found 429.1307.

(E)-4-Methyl-N-phenyl-2-(m-tolyldiazenyl)benzamide (**5f**). 39.5 mg (60%); *E*:*Z* = 16:1; Orange solid; mp = 110.1−112.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.7 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.65 (s, 1H), 7.49 (t, J = 7.7 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 7.0 Hz, 1H), 7.35 (t, J = 7.0 Hz, 2H), 7.12 (t, J = 8.4 Hz, 1H), 2.49 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.5, 152.8, 149.0, 142.8, 139.6, 138.6, 133.1, 132.7, 132.0, 129.4, 129.0, 128.7, 124.0, 122.6, 121.3, 120.0, 115.9, 21.4, 21.3; IR (KBr) υ 3247, 2921, 2854, 1720, 1666, 1539, 1498, 1313, 1249, 1148, 1071, 998, 838, 785, 750 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{19}N_3O$ $[M]^+$ 329.1528, found 329.1525.

(E)-N-(4-Methoxyphenyl)-4-methyl-2-(m-tolyldiazenyl)-benzamide (**5g**). 41.7 mg (58%); *E*:*Z* = 18:1; Brown solid; mp = 124.0−128.7 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.81 (s, 1H), 8.40 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.71 (s, 1H), 7.65 (s, 1H), 7.63 (dt, J = 8.4, 3.5 Hz, 2H), 7.48 (t, J = 7.0 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 6.89 (dt, J = 8.4, 3.5 Hz, 2H), 3.81 (s, 3H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.3, 156.2, 152.8, 149.0, 142.7, 139.6, 133.0, 132.7, 131.9, 129.4, 128.8, 122.7, 121.5, 121.1, 115.9, 114.1, 55.5, 21.4, 21.3; IR (KBr) 3257, 2924, 2854, 1721, 1659, 1508, 1462, 1377, 1219, 1173, 1031, 826, 787, 768 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O_2$ $[M]^+$ 359.1634, found 359.1635.

(E)-4-Methyl-N-(p-tolyl)-2-(m-tolyldiazenyl)benzamide (**5h**). 46.7 mg (68%); *E*:*Z* = > 50:1; Orange solid; mp = 132.8−134.8 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.40 (d, J = 7.7 Hz, 1H), 7.74 (d, J = 8.4 Hz, 1H), 7.72 (s, 1H), 7.65 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.15 (d, J = 8.4 Hz, 2H), 2.49 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.4, 152.7, 149.0, 142.7, 139.5, 136.1, 133.6, 133.1, 132.7, 132.0, 129.5, 129.4, 128.7, 122.5, 121.4, 119.9, 115.8, 21.4, 21.3, 20.9; IR (KBr) υ 3245, 2919, 2856, 1665, 1511, 1404, 1313, 1248, 1147, 1085, 889, 809, 785 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O$ $[M]^+$ 343.1685, found 343.1683.

(E)-N-(4-Bromophenyl)-4-methyl-2-(m-tolyldiazenyl)benzamide (**5i**). 50.6 mg (62%); *E*:*Z* = 22:1; Light orange solid; mp = 135.3−136.9 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.00 (s, 1H), 8.37 (d, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.68 (s, 1H), 7.64 (s, 1H), 7.60 (dt, J = 8.0, 3.5 Hz, 2H), 7.48 (t, J = 7.7 Hz, 1H), 7.46 (br s, 1H), 7.44 (dt, J = 8.4, 2.8 Hz, 2H), 7.40 (d, J = 7.7 Hz, 1H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.6, 152.8, 148.9, 143.1, 139.6, 137.7, 133.2, 132.7, 132.0, 131.9, 129.4, 128.3, 122.6, 121.5, 121.2, 116.4, 115.9, 21.4, 21.3; IR (KBr) υ 3235, 2921, 2854, 1722, 1669, 1536, 1487, 1307, 1247, 1149, 1072, 825, 786 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{18}BrN_3O$ $[M]^+$ 407.0633, found 407.0631.

(E)-N-(4-Chlorophenyl)-4-methyl-2-(m-tolyldiazenyl)benzamide (**5j**). 49.5 mg (68%); *E*:*Z* = 24:1; Orange solid; mp = 128.4−131.5 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 11.00 (s, 1H), 8.37 (d, J = 8.4 Hz, 1H), 7.71 (d, J = 7.7 Hz, 1H), 7.68 (s, 1H), 7.66−7.65 (m, 3H), 7.49 (t, J = 7.7 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 7.0 Hz, 1H), 7.29 (dt, J = 8.4, 2.8 Hz, 2H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR

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(175 MHz, $CDCl_3$) δ 163.6, 152.8, 148.9, 143.1, 139.6, 137.2, 133.2, 132.7, 132.0, 129.4, 129.0, 128.8, 128.3, 122.6, 121.2, 121.1, 115.9, 21.4, 21.3; IR (KBr) υ 3226, 2917, 2852, 1668, 1536, 1487, 1305, 1243, 1122, 1083, 801, 783, 747 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{18}ClN_3O$ $[M]^+$ 363.1138, found 363.1137.

*(E)-N-(4-Fluorophenyl)-4-methyl-2-(m-tolyldiazenyl)benzamide (**5k**).* 41.7 mg (60%); *E*:*Z* = 5:1; Orange solid; mp = 112.6−113.4 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.69 (s, 1H), 7.67−7.65 (m, 3H), 7.50−7.45 (m, 2H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.05−7.02 (m, 2H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.5, 158.5 (d, J_{C-F} = 242.3 Hz), 152.8, 149.0, 143.0, 139.6, 134.7 (d, J_{C-F} = 2.4 Hz), 133.1, 132.7, 131.9, 129.4, 128.4, 122.7, 121.5 (d, J_{C-F} = 7.5 Hz), 121.0, 115.9, 115.5 (d, J_{C-F} = 22.4 Hz), 21.4, 21.3; IR (KBr) υ 3242, 2919, 2851, 1661, 1507, 1409, 1309, 1208, 1145, 1012, 916, 829, 794, 767 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{18}FN_3O$ $[M]^+$ 347.1434, found 347.1441.

*(E)-Ethyl 4-(4-methyl-2-(m-tolyldiazenyl)benzamido)benzoate (**5l**).* 33.7 mg (42%); *E*:*Z* = 8:1; Orange solid; mp = 117.4−118.9 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 11.20 (s, 1H), 8.39 (d, *J* = 8.4 Hz, 1H), 8.02 (dt, *J* = 7.7, 1.4 Hz, 2H), 7.77 (dt, *J* = 7.7, 1.4 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.70 (s, 1H), 7.66 (s, 1H), 7.50 (t, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 4.36 (q, *J* = 7.0 Hz, 2H), 2.50 (s, 3H), 2.48 (s, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 166.2, 163.8, 152.8, 149.0, 143.3, 142.7, 139.7, 133.3, 132.8, 132.1, 130.8, 129.5, 128.2, 125.7, 122.4, 121.4, 119.1, 116.0, 60.8, 21.4, 21.3, 14.3; IR (KBr) υ 3237, 2923, 2853, 1711, 1673, 1532, 1408, 1308, 1270, 1104, 1020, 854, 769 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{24}H_{23}N_3O_3$ $[M]^+$ 401.1739, found 401.1740.

*(E)-4-Methyl-N-(m-tolyl)-2-(m-tolyldiazenyl)benzamide (**5m**).* 41.2 mg (60%); *E*:*Z* = 17:1; Red solid; mp = 74.7−80.3 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 10.89 (s, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.72 (s, 1H), 7.65 (s, 1H), 7.55 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.93 (d, *J* = 7.7 Hz, 1H), 2.49 (s, 3H), 2.48 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.5, 152.7, 149.0, 142.8, 139.5, 138.8, 138.6, 133.1, 132.7, 132.0, 129.4, 128.8, 128.7, 124.8, 122.2, 121.7, 120.6, 117.1, 115.9, 21.5, 21.4, 21.3; IR (KBr) υ 3250, 2919, 2856, 1713, 1666, 1547, 1487, 1306, 1241, 1148, 1085, 998, 837, 777 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O$ $[M]^+$ 343.1685, found 343.1682.

*(E)-4-Methyl-2-(m-tolyldiazenyl)-N-(3-(trifluoromethyl)phenyl)-benzamide (**5n**).* 55.6 mg (70%); *E*:*Z* = 12:1; Orange solid; mp = 107.4−108.6 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 11.18 (s, 1H), 8.38 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.68 (s, 1H), 7.65 (s, 1H), 7.49 (t, *J* = 7.7 Hz, 1H), 7.46−7.45 (m, 2H), 7.41 (d, *J* = 7.0 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 2.48 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 163.8, 152.7, 149.0, 143.3, 139.8, 139.2, 133.3, 132.7, 132.0, 131.2 (q, J_{C-F} = 31.6 Hz), 129.5, 129.4, 128.0, 123.9 (q, J_{C-F} = 270.7 Hz), 123.0, 122.6, 121.1, 120.4 (q, J_{C-F} = 3.6 Hz), 116.5 (q, J_{C-F} = 4.0 Hz), 116.0, 21.4, 21.2; IR (KBr) υ 3247, 2924, 2855, 1714, 1671, 1555, 1445, 1332, 1223, 1123, 1069, 893, 789 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{18}F_3N_3O$ $[M]^+$ 397.1402, found 397.1398.

*(E)-4-Methyl-N-(naphthalen-2-yl)-2-(m-tolyldiazenyl)benzamide (**5o**).* 24.3 mg (32%); *E*:*Z* = 18:1; Brown solid; mp = 158.5−160.8 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 11.14 (s, 1H), 8.50 (d, *J* = 7.7 Hz, 1H), 8.30 (d, *J* = 7.7 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.69 (t, *J* = 7.7 Hz, 3H), 7.57 (s, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.0 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 7.12 (t, *J* = 7.7 Hz, 1H), 2.52 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 164.1, 152.5, 149.7, 143.0, 139.5, 134.1, 133.3, 133.0, 132.6, 132.2, 129.2, 128.6, 128.5, 126.9, 125.9, 125.7, 125.1, 122.8, 121.8, 121.4, 120.3, 116.4, 21.5, 21.1; IR (KBr) υ 3361, 3046, 2922, 1621, 1513, 1404, 1375, 1286, 1142, 1013, 854, 787, 767 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{25}H_{21}N_3O$ $[M]^+$ 379.1685, found 379.1683.

*(E)-N-Benzyl-4-methyl-2-(m-tolyldiazenyl)benzamide (**5p**).* 30.0 mg (32%); *E*:*Z* = 27:1; Orange solid; mp = 124.4−126.9 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 9.00 (s, 1H), 8.35 (d, *J* = 8.4 Hz, 1H), 7.57 (s, 1H), 7.47 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 1H), 7.31−7.29 (m, 2H), 7.27−7.26 (m, 1H), 7.24−7.23 (m, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 4.71 (d, *J* = 5.6 Hz, 2H), 2.45 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.6, 152.3, 149.5, 142.3, 139.3, 138.3, 132.7, 132.3, 131.8, 129.1, 128.7, 128.3, 128.1, 127.4, 124.5, 119.4, 115.9, 44.4, 21.4, 21.2; IR (KBr) υ 3280, 2921, 2853, 1702, 1642, 1536, 1454, 1377, 1249, 1145, 1077, 971, 839, 790, 734 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{22}H_{21}N_3O$ $[M]^+$ 343.1685, found 343.1684.

*(E)-N-Cyclopentyl-4-methyl-2-(m-tolyldiazenyl)benzamide (**5q**).* 25.7 mg (40%); *E*:*Z* = 11:1; Orange solid; mp = 73.6−75.8 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 1H), 7.63 (s, 1H), 7.55 (s, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 4.46 (q, *J* = 6.3 Hz, 1H), 2.10−2.07 (m, 2H), 2.00−1.64 (m, 4H), 1.54−1.51 (m, 2H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.2, 152.7, 149.4, 142.0, 139.4, 132.8, 132.3, 131.6, 129.2, 128.8, 122.5, 121.2, 115.7, 51.6, 33.3, 23.9, 21.4, 21.3; IR (KBr) υ 3298, 2921, 2858, 1715, 1650, 1527, 1452, 1376, 1250, 1186, 1085, 838, 786 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{20}H_{23}N_3O$ $[M]^+$ 321.1841, found 321.1845.

*(E)-N-Hexyl-4-methyl-2-(m-tolyldiazenyl)benzamide (**5r**).* 34.4 mg (51%); *E*:*Z* = 8:1; Orange solid; mp = 44.5−48.8 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.54 (s, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 1H), 3.51−3.48 (m, 2H), 2.47 (s, 3H), 2.43 (s, 3H), 1.64−1.60 (m, 2H), 1.35−1.32 (m, 2H), 1.27−1.22 (m, 4H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 165.6, 152.6, 149.4, 142.0, 139.3, 132.7, 132.2, 131.1, 129.2, 128.7, 123.1, 120.6, 115.8, 40.1, 31.5, 29.5, 26.8, 22.4, 21.3, 13.9; IR (KBr) υ 3310, 2924, 2855, 1651, 1535, 1464, 1376, 1283, 1250, 1147, 1039, 838, 786, 725 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{21}H_{27}N_3O$ $[M]^+$ 337.2154, found 337.2156.

*Transformation of N-acylsulfonamide (**6a**).* To an oven-dried sealed tube charged with naphthalene (210 mg, 1.66 mmol, 800 mol %) in THF (5 mL) was added sodium (23.0 mg, 1.0 mmol, 500 mol %). The reaction mixture was allowed to stir at room temperature for 30 min under N_2 atmosphere. The resulting solution was then added dropwise using a syring to sealed tube containing a solution of (*E*)-2-(phenyldiazenyl)-*N*-tosylbenzamide (**3a**) (98.6 mg, 0.26 mmol, 100 mol %) in THF (3 mL) at 0 °C. The reaction mixture was allowed to stir for 2 h at room temperature under N_2 atmosphere. The reaction mixture was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried on $MgSO_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 4:1) to afford **6a**.

*(E)-2-(Phenyldiazenyl)benzamide (**6a**).* 23.4 mg (40%); *E*:*Z* = 8:1; Orange solid; mp = 160.9−165.2 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 8.42 (br s, 1H), 8.40 (dd, *J* = 7.7, 2.1 Hz, 1H), 7.84 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.80 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.61−7.59 (m, 2H), 7.57−7.55 (m, 3H), 6.15 (s, 1H); ^{13}C NMR (175 MHz, $CDCl_3$) δ 167.6, 152.5, 149.7, 132.2, 132.1, 131.8, 131.5, 130.5, 129.5, 123.1, 115.9; IR (KBr) υ 3378, 3162, 2924, 2775, 1638, 1594, 1433, 1397, 1302, 1256, 1150, 1020, 927, 817, 779 cm^{-1}; HRMS (quadrupole, EI) calcd for $C_{13}H_{11}N_3O$ $[M]^+$ 225.0902, found 225.0902.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01149.

Kinetic Isotope Effect experiment and ^1H and ^{13}C NMR copy for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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