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Rhodium-Catalyzed Direct *ortho* C−N Bond Formation of Aromatic Azo Compounds with Azides

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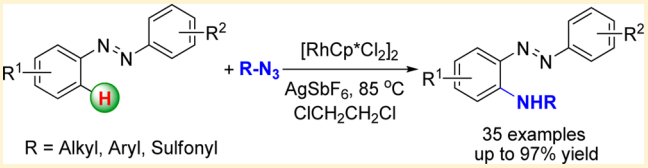
Supporting Information

ABSTRACT: An efficient rhodium-catalyzed regioselective C−N bond formation of azo compounds in good to excellent yields through C−H bond functionalization using azides as the nitrogen source was developed. Alkyl, aryl, and sulfonyl azides could be efficiently assembled in this reaction with excellent functional group tolerance.

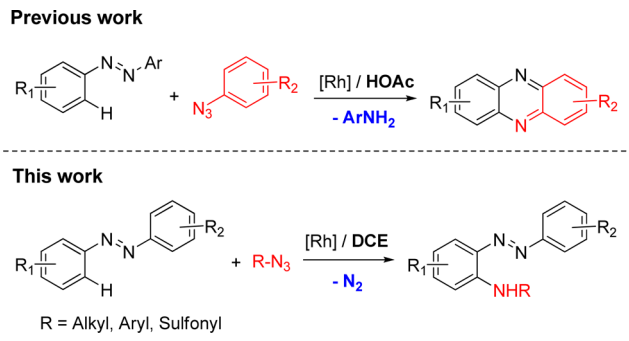


In the past decade, transition-metal-catalyzed direct functionalization of C−H bonds has achieved great success in the formation of C−C, C−N, and C−heteroatom bonds, which provides much more efficient protocols to construct useful molecules.[1−3] Among those strategies developed for C−N bond formation on arenes, the direct C−H amidation protocol appears appealing in terms of its convenient step and atom economy, which avoids prefunctionalization of the substrates.[4−6] Although direct intermolecular amination of arenes with aniline derivatives remains challenging, great success has been achieved by using preactivated amination reagents such as *N*-carboxylates,[7] *N*-fluorobenzenesulfonimide (NFSI),[8] *N*-tosylates,[9] *N*-halides,[10] benzoyl hydroxylamines,[11] and highly active nitrene precursors (e.g., azides).[12−21] In 2012, Chang reported the first rhodium-catalyzed intermolecular C−N bond formation using sulfonyl azide[12] and aryl azide[13,15] derivatives as aminating agents, which was further extended to benzyl and alkyl azides.[14] Recently, Jiao reported the rhodium-catalyzed intermolecular C−H amination of heteroaryl arenes using aryl azides as the amine source.[16] Besides, the use of a ruthenium[17−21] or iridium[22,23] catalytic system was also fully addressed using azides as friendly aminating agents.

As a group of important conjugated molecules, aromatic azo compounds have special properties and are widely applied in many fields as industrial dyes, food additives, materials,[24] molecular machines,[25] and protein probes.[26] As a result of their importance, numerous methods to prepare azobenzene and its derivatives have been developed, including the coupling reaction of anilines with diazonium salts[27] or nitrosobenzene intermediates,[28] gold nanoparticle-[29] or Cu(I)-catalyzed dehydrogenative coupling of anilines,[30] and aerobic oxidative dimerization of aromatic amines in the presence of *t*-BuOI,[31] although the substrate scope may be limited to specific structures.

Metal-catalyzed C−H activation reactions directed by azo groups have recently attracted considerable attention, although the first C(sp^2)−H bond chlorination of azobenzene was reported in 1971 by Fahey.[32] Among them, palladium-catalyzed C−H bond halogenation,[33] acylation,[34−37] and alkoxylation[38] of aromatic azo compounds have been reported. Rhodium-catalyzed C−H bond addition of azobenzenes to aldehydes or azides was also developed by the Ellman group, leading to a facile synthesis of indazoles[39] and phenazines[40] (Scheme 1). The formation of phenazines was

Scheme 1. Rhodium-Catalyzed Amination of Azobenzenes with Azides



proposed through an intramolecular electrophilic aromatic substitution from an *ortho*-aminated azobenzene intermediate under the catalysis of $[RhCp^*Cl_2]_2$ and $AgB(C_6F_5)_4$ using acetic acid as the solvent.[40] However, the oxidative C(sp^2)−H bond amidation or amination of azobenzenes to afford valuable N-functionalized azo products has remained un-

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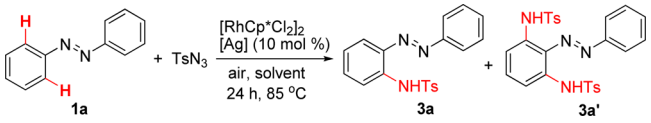
developed. Thus, a direct and selective C−N bond formation would be highly desirable, as it would obviate the need for traditional tedious and costly preactivation steps. Herein we report a rhodium-catalyzed, regioselective C−N bond formation of azo compounds using azides as nitrogen sources to afford amidated or aminated azo derivatives in good yields.

To determine the feasibility of the chelation effect of an azo group in the C−H bond amidation reaction, we initially examined the reaction of azobenzene (**1a**) with *p*-toluenesulfonyl azide (TsN_3) in the presence of $[RhCp^*Cl_2]_2$ (2.5 mol %) in dioxane using $AgSbF_6$ as an additive. Intriguingly, the *ortho* amidation product **3a** was isolated in 32% yield (Table 1, entry 1). The solvents were vital to the catalytic reaction. Among all of the solvents screened, DCE proved to be the most efficient one, while DMF, DMSO, toluene, *t*-AmOH, and MeOH were ineffective (Table 1, entries 2−6). Among various Ag sources screened (entries 7−12), only $AgSbF_6$ and $AgBF_4$ could give corresponding amidated products, and the use of $AgSbF_6$ afforded better regioselectivity (entry 7). No product was observed in the absence of Rh catalyst or Ag salt (entries 13 and 14). Replacement of the Rh catalyst with $[RuCl_2(p\text{-cymene})]_2$ gave no desired product (entry 15).

Table 1. Condition Optimizations for Amidation Reaction[a]



entry	Ag source	solvent	T (°C)	yield (%)[b]	mono/di[c]
1	$AgSbF_6$	dioxane	120	32	1:0
2	$AgSbF_6$	DMF	85	0	
3	$AgSbF_6$	DMSO	85	0	
4	$AgSbF_6$	toluene	85	0	
5	$AgSbF_6$	*t*-AmOH	85	0	
6	$AgSbF_6$	MeOH	90	<5	
7	**$AgSbF_6$**	**DCE**	**85**	**93**	**1.8:1**
8	$AgBF_4$	DCE	85	82	1:1
9	Ag_2CO_3	DCE	85	0	
10	AgOAc	DCE	85	0	
11	Ag_2O	DCE	85	0	
12	$AgPF_6$	DCE	85	<5	
13[d]	$AgSbF_6$	DCE	85	0	
14	–	DCE	85	0	
15[e]	$AgSbF_6$	DCE	85	0	

[a]Reaction conditions: **1a** (0.2 mmol), TsN_3 (0.3 mmol), $[RhCp^*Cl_2]_2$ (2.5 mol %), [Ag] (10 mol %), and solvent (1.0 mL) under air at 85 °C for 24 h. $[RhCp^*Cl_2]_2$ = Dichloro(pentamethylcyclopentadienyl)-rhodium(III) dimer. DCE = 1,2-dichloroethane. [b]Isolated yields. [c]mono/di = **3a**/**3a′**. [d]Without rhodium catalyst. [e]$[RuCl_2(p\text{-cymene})]_2$ (2.5 mol %) was used instead of the rhodium catalyst.

With the optimized reaction conditions in hand, we then examined the substrate scope of this transformation, as summarized in Scheme 2. Substrates bearing *ortho* or *meta* substitutions reacted with *p*-toluenesulfonyl azide smoothly to give monoamidation products in moderate to good yields with high regioselectivity (**3a**−**g**). For *meta*-substituted substrates, the monoamidation reaction selectively occurred at the less sterically hindered position regardless of their electronic properties (**3c**−**g**). However, attempting to achieve *ortho*-monoamidated azo products using a *para*-substituted substrate gave unsatisfactory results, and the selectivity of mono- and diamidation products was poor at a ratio of 1:1.3 (**3ha**). To our delight, when *p*-nitrobenzenesulfonyl azide (NsN_3) was used instead of TsN_3, the monoamidation product was obtained predominantly with higher selectivity (**3hb**). Other *para*-substituted substrates with either electron-rich (**3i** and **3j**) or electron-deficient groups (**3k** and **3l**) gave similar results using NsN_3 as the amidation reagent, affording the corresponding amidated azo products in excellent yields with good selectivity. Substrates with 2,4- or 3,4-disubstitution gave the desired products in moderate to good yields (**3m** and **3n**). We next turned our attention to unsymmetrical azo substrates, and this amidation reaction proceeded selectively at one aryl substituent of the azo compounds (**3o** and **3p**). Interestingly, a substrate with an *o*-methyl substitution at one side gave the monoamidation product on the electron-rich aromatic ring (**3o**), while diamidation occurred on the electron-poor aryl ring for a *meta*-substituted substrate (**3p**). We envisioned that the different selectivity of unsymmetrical azobenzenes may be governed by both steric and electronic effects.[39] It should be noted that the reaction of **1c** with TsN_3 could be carried out without difficulty on a 10 mmol scale to give **3c** in 81% yield with a rhodium catalyst loading of only 1.0 mol %.

To explore the generality of this method further, various azides were investigated under the optimized conditions. As illustrated in Scheme 3, reactions involving aliphatic (**4a** and **4b**) and aromatic sulfonyl azides (**4c**−**k**) led to the desired products in moderate to excellent yields. The electronic properties of the sulfonyl azide have little influence on the output, as azides containing both electron-donating (**4e**−**g**) and electron-withdrawing groups (**4d** and **4h**−**l**) afforded monoamidated azo products predominantly. The identity of **4l** was determined by spectral analysis and further unambiguously confirmed by X-ray crystallographic analysis.[41] To extend the scope of this reaction further, several aryl azides were used, and to our delight, the desired products were obtained in moderate yields in all cases (**4m**−**o**) without any further cyclization to give corresponding phenazines as reported by Ellman.[40] The previous formation of phenazines may due to the use of a completely noncoordinating counterion $[B(C_6F_5)_4^-]$ as well as a relatively strong acid (acetic acid), which could facilitate the subsequent cyclization step and sequester the released aniline by hydrogen bonding or salt formation.[40] It should be noted that aliphatic azides with benzyl or *n*-hexyl substitution could also undergo this reaction and generally gave the corresponding aminated products smoothly (**4p**−**r**).

To gain insight into the reaction mechanism, several control reactions were carried out, as shown in Scheme 4. First, in a competitive reaction of azo **1c** with TsN_3 and NsN_3 under the optimized conditions, product **3c** was slightly favored over **4k**, which indicated that the relatively electron-rich azide shows higher reactivity (eq 1). To investigate the electronic effect of the substrate on the reaction, a scrambling test of **1c** and **1f** with TsN_3 under the optimized conditions afforded **3c** predominantly, which strongly suggested an electrophilic-type activation manifold (eq 2). Furthermore, H/D exchange at the *ortho* position of **1a** was observed when deuterium oxide was added to the reaction mixture (eq 3), which proposed that the *ortho* C−H bond activation occurs by a reversible electrophilic-type metalation.

A plausible mechanism for this reaction can be proposed on the basis of the above results (Scheme 5). Initially, treatment

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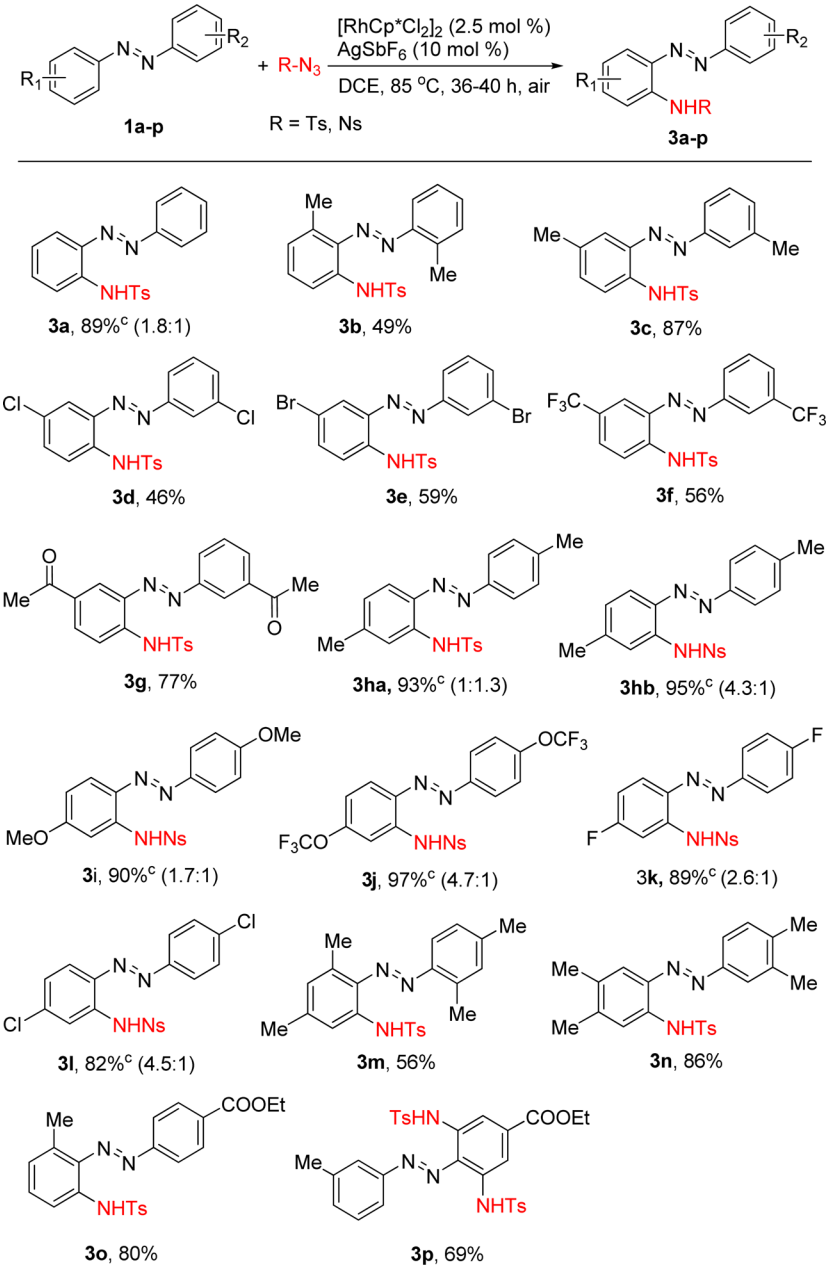
Scheme 2. Substrate Scope of Azo Compounds[a,b]



[a]Reaction conditions: **1a–p** (0.5 mmol), RN_3 (1.5 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), and DCE (2.5 mL) under air at 85 °C for 36–40 h. Ns = *p*-nitrobenzenesulfonyl. [b]Isolated yields are shown. [c]Combined yield of isolated mono- and diamidation products (the mono/di ratio is indicated in the parentheses).

of $[RhCp^*Cl_2]_2$ with the $AgSbF_6$ additive generates a cationic Rh(III) active species that triggers the C–H bond activation with **1a** to afford five-membered rhodacycle intermediate **I**.[12,39,40] Coordination of azide to **I** followed by release of molecular nitrogen and migratory insertion gives intermediate **III**,[40] protonolysis of which delivers the desired product **3a** and regenerates the Rh(III) catalyst.

In summary, we have developed an efficient rhodium-catalyzed regioselective C–N bond formation reaction of aromatic azo compounds that uses azides as the nitrogen source. The characteristics of excellent functional group tolerance and synthesis modularity will provide the described reaction with a broad utility in organic synthesis.

EXPERIMENTAL SECTION

General Information. All of the solvents were purified before use according to standard procedures. All melting points were taken on a digital melting point apparatus without correction. Infrared spectra were obtained using an FT-IR spectrometer. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded at 500, 125, and 470 MHz, respectively, with chemical shift (δ) values being reported in parts per million relative to chloroform (δ = 7.26 ppm), dimethyl sulfoxide (δ = 2.50 ppm), or TMS (δ = 0.00 ppm) for ^1H NMR, chloroform (δ = 77.16 ppm) or dimethyl sulfoxide (δ = 39.52 ppm) for ^{13}C NMR, and C_6F_6 (δ = −164.9 ppm) for ^{19}F NMR. Mass spectrometry and high-resolution mass spectrometry (HRMS) were performed using electron impact (EI) or electrospray ionization (ESI) techniques. Elemental analyses were carried out on an elemental analyzer. X-ray structure analysis was performed on an X-ray diffractometer. GF254

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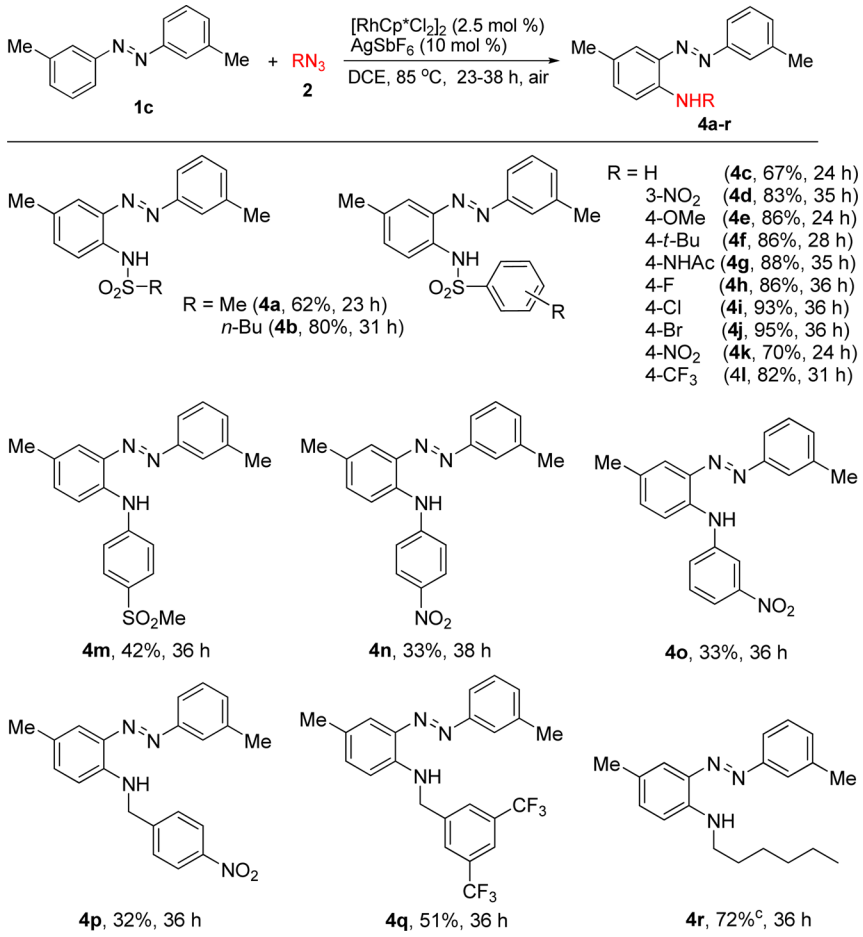
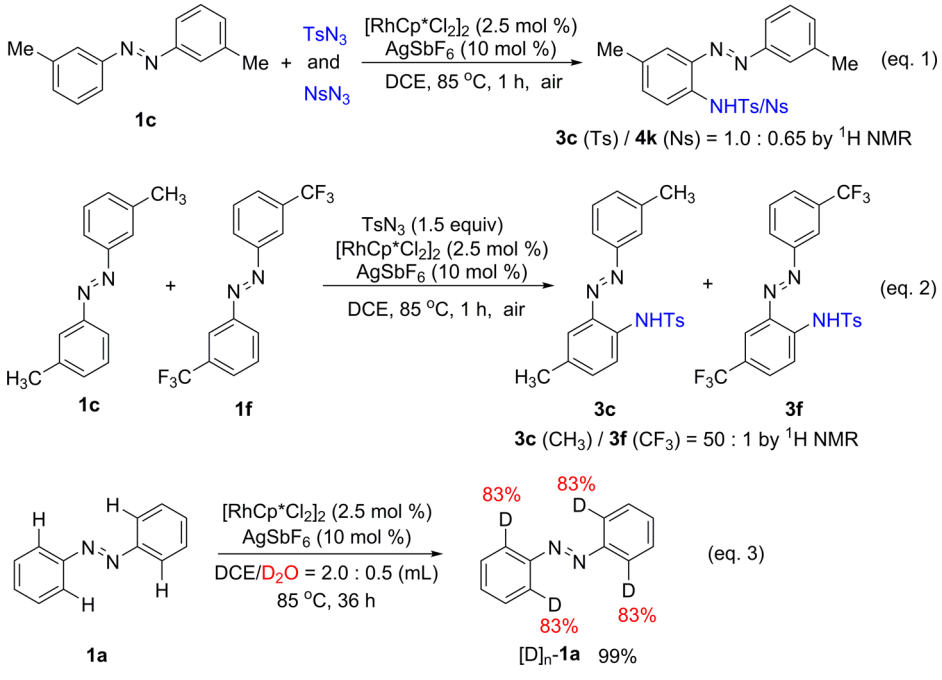
Scheme 3. Substrate Scope of Azides[a,b]



[a]Reaction conditions: **1c** (0.5 mmol), **2a–r** (1.5 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %) and DCE (2.5 mL) under air at 85 °C for 23–38 h. [b]Isolated yields are shown. [c]Yield based on 18% conversion of **1c**.

Scheme 4. Preliminary Mechanistic Studies



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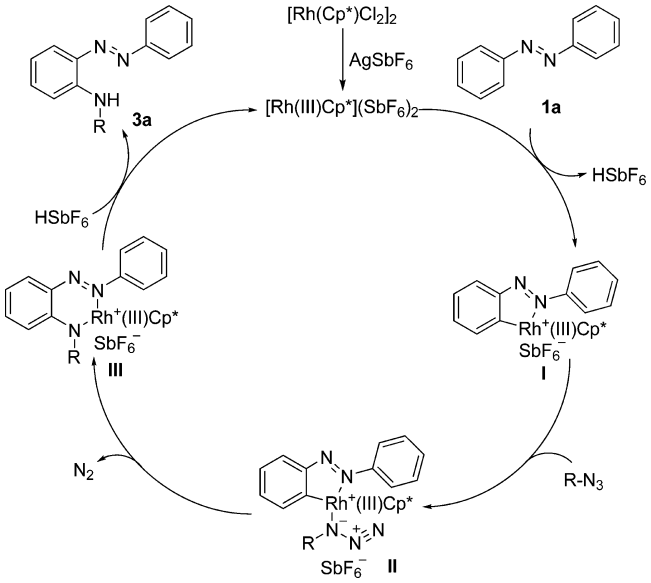
Scheme 5. Proposed Mechanism for the Synthesis of 3a from 1a



silica gel plates were used for thin-layer chromatography (TLC) and silica gel H or 300−400 mesh were used for flash column chromatography. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise indicated.

Synthesis of Starting Materials. Azobenzenes **1a−c**, **1h−m**, and **1o−1p**,[30] **1d** and **1n**,[42] **1e**,[43] **1f**,[44] and **1g**[45] were synthesized as reported in the literature.

General Procedure for Amidation of Azobenzenes. To a tube with a Teflon stirring bar were added azobenzene **1** (0.5 mmol), azide **2** (0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions. The reaction mixture was stirred in a preheated oil bath at 85 °C for 24−40 h, cooled to room temperature, filtered through a plug of Celite, and then washed with EtOAc (3 × 10 mL). The solvents were removed under reduced pressure, and the crude reaction mixture was purified by chromatography on silica gel using a petroleum ether/dichloromethane mixture as the eluent to give the desired product **3** or **4**.

(*E*)-4-Methyl-*N*-(2-(phenyldiazenyl)phenyl)benzenesulfonamide (3a) and (*E*)-*N*,*N*′-(2-(Phenyldiazenyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3a′). Following the general procedure using (*E*)-1,2-diphenyldiazene (**1a**) (91.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3a** (100.0 mg, 57%) as an orange solid and diamidated **3a′** (84.0 mg, 32%) as an orange solid.

Data for **3a**: Mp 162−164 °C; IR (KBr, cm^{-1}) 3232, 3102, 1527, 1342, 1173, 738, 690; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.74 (s, 1H), 7.81 (dd, J = 8.5, 2.0 Hz, 2H), 7.75 (dd, J = 8.0, 1.5 Hz, 1H), 7.72 (dd, J = 8.5, 1.0 Hz, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.54−7.52 (m, 3H), 7.39 (td, J = 7.0, 1.5 Hz, 1H), 7.15 (td, J = 7.0, 1.0 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.9, 144.0, 140.0, 136.1, 134.5, 132.5, 131.7, 129.6, 129.3, 127.1, 124.2, 122.8, 122.7, 120.1, 21.4; ESI-MS ($C_{19}H_{17}N_3O_2S$) 352 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{19}H_{17}N_3O_2S$ $[M + H]^+$ 352.1114, found 352.1126.

Data for **3a′**: Mp 222−224 °C; IR (KBr, cm^{-1}) 3250, 3063, 1596, 1389, 1336, 1167, 1091, 774, 711, 664; ^1H NMR ($CDCl_3$, 500 MHz) δ 10.41 (s, 2H), 7.76−7.74 (m, 2H), 7.67 (d, J = 8.0 Hz, 4H), 7.56−7.55 (m, 3H), 7.29−7.24 (m, 3H), 7.16 (d, J = 8.0 Hz, 4H), 2.33 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.0, 144.3, 136.1, 135.3, 134.3, 132.2, 129.7, 129.6, 127.1, 126.4, 122.5, 113.2, 21.5; ESI-MS ($C_{26}H_{24}N_4O_4S_2$) 521 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{26}H_{24}N_4O_4S_2$ $[M + H]^+$ 521.1311, found 521.1309.

(*E*)-4-Methyl-*N*-(3-methyl-2-(*o*-tolyldiazenyl)phenyl)benzenesulfonamide (3b). Following the general procedure using (*E*)-1,2-di-*o*-tolyldiazene (**1b**) (105.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3b** (93.0 mg, 49%) as an orange solid. Mp 194−196 °C; IR (KBr, cm^{-1}) 3272, 2921, 1592, 1483, 1162, 1091, 764, 662, 556; ^1H NMR ($CDCl_3$, 500 MHz) δ 12.55 (s, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.41−7.39 (m, 2H), 7.31−7.28 (m, 1H), 7.22−7.18 (m, 3H), 7.00 (d, J = 8.0 Hz, 1H), 2.82 (s, 3H), 2.67 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.1, 143.8, 142.5, 137.7, 136.8, 136.1, 132.4, 131.6, 131.4, 130.4, 129.6, 127.2, 126.7, 125.4, 115.9, 115.4, 21.5, 19.2, 18.6; ESI-MS ($C_{21}H_{21}N_3O_2S$) 380 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{21}H_{21}N_3O_2S$ $[M + H]^+$ 380.1427, found 380.1440.

(*E*)-4-Methyl-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (3c). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3c** (165.0 mg, 87%) as an orange solid. Mp 120−122 °C; IR (KBr, cm^{-1}) 3263, 3082, 2920, 1501, 1381, 1328, 1164, 1093, 800, 693; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.48 (s, 1H), 7.64−7.61 (m, 3H), 7.59 (d, J = 9.0 Hz, 2H), 7.52 (d, J = 2.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.21 (dd, J = 8.5, 1.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H), 2.33 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 143.8, 140.3, 139.2, 136.1, 134.4, 133.2, 132.4, 132.0, 129.5, 129.0, 127.1, 123.1, 122.4, 120.7, 120.0, 21.4, 21.3, 20.7; ESI-MS ($C_{21}H_{21}N_3O_2S$) 380 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{21}H_{21}N_3O_2S$ $[M + H]^+$ 380.1427, found 380.1438.

(*E*)-*N*-(4-Chloro-2-((3-chlorophenyl)diazenyl)phenyl)-4-methylbenzenesulfonamide (3d). Following the general procedure using (*E*)-1,2-bis(3-chlorophenyl)diazene (**1d**) (125.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 40 h gave **3d** (97.0 mg, 46%) as a yellow solid. Mp 139−142 °C; IR (KBr, cm^{-1}) 3257, 3059, 2921, 1594, 1478, 1332, 1268, 1166, 1091, 901, 790, 688; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.46 (s, 1H), 7.90 (t, J = 1.5 Hz, 1H), 7.89−7.87 (m, 1H), 7.65−7.59 (m, 4H), 7.49 (d, J = 2.5 Hz, 1H), 7.47 (d, J = 8.5 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 2.10 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 153.0, 145.3, 143.6, 136.7, 135.7, 134.4, 132.6, 132.0, 131.5, 131.3, 129.8, 129.0, 126.9, 125.6, 121.0, 115.8, 21.2; ESI-MS ($C_{19}H_{15}Cl_2N_3O_2S$) 420 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{19}H_{15}Cl_2N_3O_2S$ $[M + H]^+$ 420.0334, found 420.0346.

(*E*)-*N*-(4-Bromo-2-((3-bromophenyl)diazenyl)phenyl)-4-methylbenzenesulfonamide (3e). Following the general procedure using (*E*)-1,2-bis(3-bromophenyl)diazene (**1e**) (170.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 40 h gave **3e** (150.0 mg, 59%) as an orange solid. Mp 193−195 °C; IR (KBr, cm^{-1}) 3318, 3077, 2922, 1474, 1337, 1164, 1089, 914, 778, 661; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.03 (s, 1H), 7.82 (t, J = 2.0 Hz, 2H), 7.75 (dt, J = 8.0, 1.5 Hz, 1H), 7.66−7.62 (m, 4H), 7.52 (dd, J = 8.5, 2.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.15 (d, J = 8.5 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.6, 144.4, 141.0, 135.7, 135.5, 134.7, 134.4, 130.7, 129.8, 127.0, 124.8, 123.6, 123.3, 122.9, 122.5, 117.9, 21.5; ESI-MS ($C_{19}H_{15}Br_2N_3O_2S$) 507 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{19}H_{15}Br_2N_3O_2S$ $[M + H]^+$ 507.9324, found 507.9323.

(*E*)-4-Methyl-*N*-(4-(trifluoromethyl)-2-((3-(trifluoromethyl)phenyl)diazenyl)phenyl)benzenesulfonamide (3f). Following the general procedure using (*E*)-1,2-bis(3-(trifluoromethyl)phenyl)-diazene (**1f**) (159 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide

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(147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3f** (135.0 mg, 56%) as a yellow solid. Mp 182−184 °C; IR (KBr, cm^{-1}) 3440, 3335, 3080, 2960, 1616, 1332, 1165, 1124, 891, 812, 665; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.84 (s, 1H), 8.29 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 7.5 Hz, 2H), 7.81 (t, J = 9.0 Hz, 3H), 7.58 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 2.07 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 152.1, 143.8, 143.6, 140.1, 136.7, 130.8, 130.6, 130.4, 129.8, 129.3, 129.2, 128.5, 126.9, 126.6, 126.5, 126.4, 126.1, 125.4, 125.1, 123.2, 122.9, 119.5, 119.4, 113.4, 21.0. ^{19}F NMR (DMSO-d_6, 470 MHz) −61.2 (s, Ar−CF_3), −61.3 (s, Ar−CF_3); ESI-MS ($C_{21}H_{15}F_6N_3O_2S$) 488 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{21}H_{15}F_6N_3O_2S$ $[M + H]^+$ 488.0861, found 488.0872.

(*E*)-*N*-(4-Acetyl-2-((3-acetylphenyl)diazenyl)phenyl)-4-methylbenzenesulfonamide (3g). Following the general procedure using (*E*)-1,1′-(diazene-1,2-diylbis(1,3-phenylene))bis(ethan-1-one) (**1g**) (133.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3g** (168.0 mg, 77%) as a yellow solid. Mp 151−153 °C; IR (KBr, cm^{-1}) 3291, 3062, 2917, 1686, 1598, 1337, 1277, 1164, 1087, 897, 816, 666; ^1H NMR ($CDCl_3$, 500 MHz) δ 10.21 (s, 1H), 8.39 (s, 1H), 8.36 (s, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.97 (dd, J = 8.5, 1.5 Hz, 1H), 7.76 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 8.5 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 8.0 Hz, 2H), 2.68 (s, 3H), 2.58 (s, 3H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.1, 196.2, 151.8, 144.6, 138.3, 138.27, 138.20, 136.0, 132.4, 132.3, 131.3, 129.9, 129.7, 127.2, 126.4, 124.5, 123.1, 118.4, 26.8, 26.4, 21.5; ESI-MS ($C_{23}H_{21}N_3O_4S$) 436 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{23}H_{21}N_3O_4S$ $[M + H]^+$ 436.1325, found 436.1334.

(*E*)-*N*-(5-Methyl-2-(*p*-tolyldiazenyl)phenyl)-4-methylbenzenesulfonamide (3ha) and (*E*)-*N*,*N*′-(5-Methyl-2-(*p*-tolyldiazenyl)-1,3-phenylene)bis(4-methylbenzenesulfonamide) (3ha′). Following the general procedure using (*E*)-1,2-di-*p*-tolyldiazene (**1h**) (105.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3ha** (78.0 mg, 41%) as an orange solid and diamidated **3ha′** (142 mg, 52%) as a yellow solid.

Data for **3ha**: Mp 183−184 °C; IR (KBr, cm^{-1}) 2918, 1606, 1555, 1499, 1332, 1157, 1093, 906, 660; ^1H NMR ($CDCl_3$, 125 MHz) δ 9.97 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.51 (s, 1H), 7.31 (d, J = 8.5 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.5 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.0, 143.8, 143.2, 142.1, 138.1, 136.3, 133.9, 129.9, 129.6, 127.1, 125.2, 123.3, 122.6, 120.3, 21.9, 21.5, 21.4; ESI-MS ($C_{21}H_{21}N_3O_2S$) 402 $[M^+Na]$; HRMS m/z (ESI-TOF) calcd for $C_{21}H_{21}N_3O_2S$ $[M + Na]^+$ 402.1247, found 402.1240.

Data for **3ha′**: Mp 244−245 °C; IR (KBr, cm^{-1}) 2918, 1604, 1555, 1498, 1332, 1157, 1093, 907, 660; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.13 (s, 2H), 7.66 (d, J = 8.0 Hz, 2H), 7.55 (d, J = 8.5 Hz, 4H), 7.40 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 4H), 7.10 (s, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 2.22 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 149.3, 144.2, 144.1, 142.8, 136.6, 134.5, 130.2, 130.0, 128.7, 127.0, 123.2, 118.3, 22.2, 21.6, 21.3; ESI-MS ($C_{28}H_{28}N_4O_4S_2$) 571 $[M^+Na]$; HRMS m/z (ESI-TOF) calcd for $C_{28}H_{28}N_4O_4S_2$ $[M + Na]^+$ 571.1444, found 571.1434.

(*E*)-*N*-(5-Methyl-2-(*p*-tolyldiazenyl)phenyl)-4-nitrobenzenesulfonamide (3hb) and (*E*)-*N*,*N*′-(5-Methyl-2-(*p*-tolyldiazenyl)-1,3-phenylene)bis(4-nitrobenzenesulfonamide) (3hb′). Following the general procedure using (*E*)-1,2-di-*p*-tolyldiazene (**1h**) (105.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3hb** (158.0 mg, 77%) as an orange solid and diamidated **3hb′** (55.0 mg, 18%) as a yellow solid.

Data for **3hb**: Mp 186−188 °C; IR (KBr, cm^{-1}) 3250, 3101, 3035, 2916, 1525, 1346, 1181, 740, 688; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.60 (s, 1H), 8.02 (dt, J = 8.5, 2.0 Hz, 2H), 7.81 (dt, J = 8.5, 2.0 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 8.0, 1.0 Hz, 1H), 2.38 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.5, 149.5, 145.4, 143.8, 142.9, 142.1, 135.1, 129.9, 128.7, 128.6, 124.5, 123.4, 116.1, 21.55, 21.52; ESI-MS ($C_{20}H_{18}N_4O_4S$) 411 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{18}N_4O_4S$ $[M + H]^+$ 411.1121, found 411.1126.

Data for **3hb′**: Mp 270−272 °C; IR (KBr, cm^{-1}) 3275, 3106, 1530, 1350, 1166, 852, 737, 606; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.01 (s, 2H), 8.06 (dt, J = 8.5, 2.0 Hz, 4H), 7.80 (dt, J = 8.5, 2.0 Hz, 4H), 7.39 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.21 (s, 2H), 2.39 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 149.9, 149.4, 145.0, 143.5, 143.0, 132.8, 132.4, 129.9, 128.5, 124.8, 123.2, 123.1, 21.9, 21.5; ESI-MS ($C_{26}H_{22}N_6O_8S_2$) 611 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{26}H_{22}N_6O_8S_2$ $[M + H]^+$ 611.1013, found 611.1023.

(*E*)-*N*-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)phenyl)-4-nitrobenzenesulfonamide (3i) and (*E*)-*N*,*N*′-(5-Methoxy-2-((4-methoxyphenyl)diazenyl)-1,3-phenylene)bis(4-nitrobenzenesulfonamide) (3i′). Following the general procedure using (*E*)-1,2-bis(4-methoxyphenyl)diazene (**1i**) (121.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3i** (126.0 mg, 57%) as a yellow solid and diamidated **3i′** (106 mg, 33%) as a yellow solid.

Data for **3i**: Mp 173−174 °C; IR (KBr, cm^{-1}) 3262, 3094, 2946, 1598, 1252, 1172, 1089, 835, 739, 615; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.61 (s, 1H), 8.01 (dt, J = 8.5, 2.0 Hz, 2H), 7.81 (dt, J = 8.5, 2.5 Hz, 2H), 7.57 (d, J = 8.5 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.39 (s, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 8.0, 1.0 Hz, 1H), 2.38 (s, 6H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 162.15, 162.12, 149.7, 146.7, 145.3, 139.5, 136.6, 128.6, 125.3, 124.6, 117.9, 114.6, 113.5, 111.8, 56.2, 56.0; ESI-MS ($C_{20}H_{18}N_4O_6S$) 443 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{18}N_4O_6S$ $[M + H]^+$ 443.1019, found 443.1029.

Data for **3i′**: Mp 257−258 °C; IR (KBr, cm^{-1}) 3436, 3110, 2923, 1613, 1532, 1349, 1163, 851, 740, 602; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.53 (s, 2H), 8.15 (d, J = 8.5 Hz, 4H), 7.91 (d, J = 8.5 Hz, 4H), 7.59 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.5 Hz, 2H), 6.85 (s, 2H), 3.88 (s, 3H), 3.84 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 162.6, 161.8, 150.2, 145.2, 144.7, 135.3, 128.7, 126.8, 125.1, 125.0, 124.9, 114.9, 105.5, 56.4, 56.2; ESI-MS ($C_{26}H_{22}N_6O_{10}S_2$) 643 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{26}H_{22}N_6O_{10}S_2$ $[M + H]^+$ 643.0911, found 643.0919.

(*E*)-4-Nitro-*N*-(5-(trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)diazenyl)phenyl)benzenesulfonamide (3j) and (*E*)-*N*,*N*′-(5-(Trifluoromethoxy)-2-((4-(trifluoromethoxy)phenyl)diazenyl)-1,3-phenylene)bis-(4-nitrobenzenesulfonamide) (3j′). Following the general procedure using (*E*)-1,2-bis(4-(trifluoromethoxy)phenyl)diazene (**1j**) (121.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3j** (220.0 mg, 80%) as a yellow solid and diamidated **3j′** (64.0 mg, 17%) as a yellow solid.

Data for **3j**: Mp 122−124 °C; IR (KBr, cm^{-1}) 3259, 3109, 1532, 1350, 1251, 1089, 854, 739; ^1H NMR ($CDCl_3$, 500 MHz) δ 10.06 (s, 1H), 8.23 (dt, J = 9.0, 2.5 Hz, 2H), 8.02 (dt, J = 9.0, 2.5 Hz, 2H), 7.88 (dt, J = 9.0, 2.5 Hz, 2H), 7.83 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 1.5 Hz, 1H), 7.39 (dd, J = 8.5, 1.0 Hz, 2H), 7.07−7.04 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.93, 151.91, 151.90, 151.89, 151.83, 151.82, 151.81, 151.7, 151.2, 150.4, 149.6, 144.2, 143.7, 137.9, 134.8, 128.9, 128.4, 125.0, 124.9, 124.54, 124.51, 124.4, 123.4, 123.3, 121.5, 121.3, 121.2, 119.3, 119.2, 117.2, 117.1, 116.7, 111.7; ^{19}F NMR ($CDCl_3$, 470 MHz) −57.6 (s, Ar−OCF_3), −57.7 (s, Ar−OCF_3); ESI-MS ($C_{20}H_{12}F_6N_4O_6S$) 551 $[M^+H]$; HRMS m/z

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(ESI-TOF) calcd for $C_{20}H_{12}F_6N_4O_6S$ $[M + H]^+$ 551.0454, found 551.0464.

Data for **3j′**: Mp 232−233 °C; IR (KBr, cm^{-1}) 3292, 3114, 1590, 1532, 1286, 1167, 1086, 850, 736, 683; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.08 (s, 2H), 8.10 (dt, J = 9.0, 2.5 Hz, 4H), 7.83 (dt, J = 9.0, 2.5 Hz, 4H), 7.66 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.29 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 151.2, 150.1, 149.8, 149.5, 144.9, 134.7, 133.81, 133.80, 133.7, 128.6, 125.5, 124.9, 124.8, 123.5, 123.3, 121.69, 121.63, 121.61, 121.4, 121.3, 119.4, 119.2, 117.1, 114.49, 114.42; ^{19}F NMR ($CDCl_3$, 470 MHz) −56.70 (s, Ar−OCF_3), −56.75 (s, Ar−OCF_3); ESI-MS ($C_{26}H_{16}F_6N_6O_{10}S_2$) 751 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{26}H_{16}F_6N_6O_{10}S_2$ $[M + H]^+$ 751.0346, found 751.0360.

(*E*)-*N*-(5-Fluoro-2-((4-fluorophenyl)diazenyl)phenyl)-4-nitrobenzenesulfonamide (3k) and (*E*)-*N*,*N*′-(5-Fluoro-2-((4-fluorophenyl)diazenyl)-1,3-phenylene)bis(4-nitrobenzenesulfonamide) (3k′). Following the general procedure using (*E*)-1,2-bis(4-fluorophenyl)diazene (**1k**) (109.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3k** (134.0 mg, 64%) as an orange solid and diamidated **3k′** (77.0 mg, 25%) as a yellow solid.

Data for **3k**: Mp 174−176 °C; IR (KBr, cm^{-1}) 3240, 3110, 1606, 1528, 1175, 1089, 852, 738, 685; ^1H NMR ($CDCl_3$, 500 MHz) δ 10.94 (s, 1H), 8.08 (d, J = 9.0 Hz, 2H), 7.88−7.82 (m, 4H), 7.60−7.57 (m, 1H), 7.41−7.36 (m, 3H), 7.25−7.20 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.4, 165.2, 163.4, 163.2, 149.8, 149.06, 149.04, 144.9, 142.15, 142.13, 137.4, 137.3, 128.6, 126.1, 126.0, 124.7, 118.49, 118.41, 116.6, 116.4, 115.0, 114.8, 114.3, 114.1; ^{19}F NMR ($CDCl_3$, 470 MHz) −106.8 (m, Ar−F), −108.4 (m, Ar−F); ESI-MS ($C_{18}H_{12}F_2N_4O_4S$) 419 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{18}H_{12}F_2N_4O_4S$ $[M + H]^+$ 419.0620, found 419.0627.

Data for **3k′**: Mp 256−258 °C; IR (KBr, cm^{-1}) 3322, 3109, 1609, 1532, 1165, 1090, 838, 739, 602; ^1H NMR (DMSO-d_6, 500 MHz) δ 11.0 (s, 2H), 8.11 (dt, J = 8.5, 2.0 Hz, 4H), 7.87 (dt, J = 8.5, 2.0 Hz, 4H), 7.67−7.64 (m, 2H), 7.35 (t, J = 8.5 Hz, 2H), 7.22 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 165.7, 163.9, 163.7, 161.9, 150.1, 148.05, 144.6, 134.6, 134.5, 131.5, 128.6, 125.97, 125.90, 124.9, 116.6, 116.4, 109.2, 109.0; ^{19}F NMR (DMSO-d_6, 470 MHz) −113.7 (m, Ar−F), −107.4 (m, Ar−F); ESI-MS ($C_{24}H_{16}F_2N_6O_8S_2$) 619 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{24}H_{16}F_2N_6O_8S_2$ $[M + H]^+$ 619.0511, found 619.0526.

(*E*)-*N*-(5-Chloro-2-((4-chlorophenyl)diazenyl)phenyl)-4-nitrobenzenesulfonamide (3l) and (*E*)-*N*,*N*′-(5-Chloro-2-((4-chlorophenyl)diazenyl)-1,3-phenylene)bis(4-nitrobenzenesulfonamide) (3l′). Following the general procedure using (*E*)-1,2-bis(4-chlorophenyl)diazene (**1l**) (109.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave monoamidated **3l** (151.0 mg, 67%) as an orange solid and diamidated **3l′** (49.0 mg, 15%) as a yellow solid.

Data for **3l**: Mp 207−210 °C; IR (KBr, cm^{-1}) 3281, 3098, 1528, 1348, 1176, 1084, 835, 741, 660; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.96 (s, 1H), 8.06 (dt, J = 8.5, 2.5 Hz, 2H), 7.84 (dt, J = 8.5, 2.0 Hz, 2H), 7.75 (dt, J = 8.5, 2.5 Hz, 2H), 7.63−7.60 (m, 2H), 7.59 (t, J = 2.0 Hz, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.44 (dd, J = 8.5, 2.5 Hz, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 150.8, 149.8, 144.8, 144.2, 137.1, 136.7, 129.7, 128.6, 128.0, 127.7, 125.4, 124.7, 117.9; ESI-MS ($C_{18}H_{12}Cl_2N_4O_4S$) 451 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{18}H_{12}Cl_2N_4O_4S$ $[M + H]^+$ 451.0029, found 451.0042.

Data for **3l′**: Mp 267−269 °C; IR (KBr, cm^{-1}) 3281, 3101, 1531, 1167, 1090, 837, 738, 605; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.97 (s, 2H), 8.07 (dt, J = 8.5, 2.5 Hz, 4H), 7.80 (dt, J = 8.5, 2.5 Hz, 4H), 7.54−7.49 (m, 4H), 7.44 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz) 150.05, 150.01, 144.8, 137.6, 136.1, 135.1, 133.0, 129.4, 128.5, 125.1, 124.8, 123.4; ESI-MS ($C_{24}H_{16}Cl_2N_6O_8S_2$) 651 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{24}H_{16}Cl_2N_6O_8S_2$ $[M + H]^+$ 650.9920, found 650.9933.

(*E*)-*N*-(2-((2,4-dimethylphenyl)diazenyl)-3,5-dimethylphenyl)-4-methylbenzenesulfonamide (3m). Following the general procedure using (*E*)-1,2-bis-(2,4-dimethylphenyl)diazene (**1m**) (119.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3m** (114.0 mg, 56%) as a yellow solid. Mp 183−185 °C; IR (KBr, cm^{-1}) 2916, 1604, 1555, 1497, 1331, 1159, 1093, 907, 818, 660; ^1H NMR ($CDCl_3$, 500 MHz) δ 12.72 (s, 1H), 7.70 (d, J = 8.5 Hz, 2H), 7.57 (s, J = 8.0 Hz, 1H), 7.33 (s, 1H), 7.18 (d, J = 8.0 Hz, 3H), 7.08 (dt, J = 8.0, 1.0 Hz, 1H), 6.80 (t, J = 1.0 Hz, 1H), 2.76 (s, 3H), 2.61 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.2, 143.6, 142.1, 141.6, 137.4, 136.9, 134.4, 132.1, 130.4, 129.6, 127.5, 127.1, 126.4, 126.2, 116.2, 115.2, 21.9, 21.5, 21.4, 19.0, 18.5; ESI-MS ($C_{23}H_{25}N_3O_2S$) 408 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{23}H_{25}N_3O_2S$ $[M + H]^+$ 408.1740, found 408.1753.

(*E*)-*N*-(2-((3,4-Dimethylphenyl)diazenyl)-4,5-dimethylphenyl)-4-methylbenzenesulfonamide (3n). Following the general procedure using (*E*)-1,2-bis-(3,4-dimethylphenyl)diazene (**1n**) (119.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3n** (175.0 mg, 86%) as a yellow solid. Mp 172−174 °C; IR (KBr, cm^{-1}) 3426, 2918, 1608, 1497, 1334, 1161, 1095, 908, 662; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.77 (s, 1H), 7.64 (dt, J = 8.5, 2.0 Hz, 2H), 7.54 (s, 1H), 7.52 (dd, J = 8.0, 2.0 Hz, 1H), 7.50 (d, J = 7.0 Hz, 2H), 7.26 (d, J = 7.5 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.4, 143.6, 141.8, 140.7, 138.6, 137.6, 136.3, 133.1, 131.7, 130.4, 129.5, 127.0, 123.8, 123.6, 121.6, 120.2, 21.4, 20.3, 19.9, 19.8, 19.1; ESI-MS ($C_{23}H_{25}N_3O_2S$) 408 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{23}H_{25}N_3O_2S$ $[M + H]^+$ 408.1740, found 408.1742.

Ethyl (*E*)-4-((2-Methyl-6-((4-methylphenyl)sulfonamido)-phenyl)diazenyl)benzoate (3o). Following the general procedure using ethyl (*E*)-4-(*o*-tolyldiazenyl)benzoate (**1o**) (134.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3o** (175.0 mg, 80%) as a red solid. Mp 152−154 °C; IR (KBr, cm^{-1}) 3412, 2097, 2929, 1714, 1272, 1164, 1089, 773, 658; ^1H NMR ($CDCl_3$, 500 MHz) δ 12.32 (s, 1H), 8.20 (dt, J = 8.5, 2.0 Hz, 2H), 7.88 (dt, J = 8.5, 2.0 Hz, 2H), 7.68 (t, J = 8.5, 2.0 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.0 Hz, 1H), 4.43 (q, J = 7.0 Hz, 2H), 2.64 (s, 3H), 2.32 (s, 3H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) 165.8, 154.0, 143.9, 143.0, 136.7, 136.2, 133.3, 132.5, 130.8, 130.5, 129.6, 127.1, 125.8, 122.3, 116.7, 61.4, 21.5, 19.1, 14.3; ESI-MS ($C_{23}H_{23}N_3O_4S$) 438 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{23}H_{23}N_3O_4S$ $[M + H]^+$ 438.1482, found 438.1479.

Ethyl (*E*)-3,5-Bis((4-methylphenyl)sulfonamido)-4-(*m*-tolyldiazenyl)benzoate (3p). Following the general procedure using ethyl (*E*)-4-(*m*-tolyldiazenyl)benzoate (**1p**) (134.0 mg, 0.5 mmol), 4-methylbenzenesulfonyl azide (147.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **3p** (209.0 mg, 69%) as a yellow solid. Mp 221−222 °C; IR (KBr, cm^{-1}) 3312, 2923, 1720, 1576, 1164, 1091, 1023, 852, 706, 664; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.91 (s, 2H), 7.80 (s, 2H), 7.60−7.46 (m, 8H), 7.17 (d, J = 8.5 Hz, 4H), 4.34 (q, J = 7.0 Hz, 2H), 2.46 (s, 3H), 2.24 (s, 6H), 1.34 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 164.5, 151.1, 144.5, 139.9, 135.9, 135.0, 134.6, 133.8, 129.8, 129.5, 127.8, 127.4, 124.0, 119.4, 113.6, 61.7, 21.5, 21.3, 14.2; ESI-MS ($C_{30}H_{30}N_4O_6S_2$) 607 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{30}H_{30}N_4O_6S_2$ $[M + H]^+$ 607.1679, found 607.1688.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)methanesulfonamide (4a). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), methanesulfonyl azide (**2a**) (91.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$

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(17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 23 h gave **4a** (94.0 mg, 62%) as a yellow solid. Mp 137−139 °C; IR (KBr, cm^{-1}) 3332, 3041, 2919, 1505, 1322, 1149, 973, 783; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.37 (s, 1H), 7.70 (s, 1H), 7.68 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.29 (dd, J = 8.5, 1.0 Hz, 1H), 3.02 (s, 3H), 2.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 139.8, 139.3, 134.3, 133.5, 132.6, 132.3, 129.1, 123.2, 122.8, 120.1, 119.3, 39.6, 21.3, 20.7; ESI-MS ($C_{15}H_{17}N_3O_2S$) 304 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{15}H_{17}N_3O_2S$ [M + H]$^+$ 304.1114, found 304.1127.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)butane-1-sulfonamide (4b). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), butane-1-sulfonyl azide (**2b**) (122.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 31 h gave **4b** (138.0 mg, 80%) as an orange solid. Mp 95−96 °C; IR (KBr, cm^{-1}) 3269, 2950, 2870, 1498, 1381, 1334, 1152, 921, 785; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.37 (s, 1H), 7.70−7.66 (m, 4H), 7.42 (t, J = 8.0 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.28 (dd, J = 8.5, 1.0 Hz, 1H), 3.13−3.09 (m, 2H), 2.47 (s, 3H), 2.39 (s, 3H), 1.78−1.71 (m, 2H), 1.33 (m, 2H), 0.79 (t, J = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.1, 139.5, 139.3, 134.0, 133.5, 132.5, 132.4, 129.1, 123.1, 122.9, 120.1, 119.1, 51.4, 25.3, 21.38, 21.33, 20.7, 13.4; ESI-MS ($C_{18}H_{23}N_3O_2S$) 346 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{18}H_{23}N_3O_2S$ [M + H]$^+$ 346.1583, found 346.1595.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (4c). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), benzene- sulfonyl azide (**2c**, 137.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 24 h gave **4c** (123.0 mg, 67%) as a yellow solid. Mp 142−144 °C; IR (KBr, cm^{-1}) 3268, 2916, 1504, 1329, 1173, 1151, 1091, 904, 788, 759, 690; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.56 (s, 1H), 7.76 (d, J = 7.5 Hz, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 9.0 Hz, 2H), 7.53 (s, 1H), 7.44−7.39 (m, 2H), 7.31 (t, J = 7.5 Hz, 3H), 7.21 (d, J = 7.0 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.0, 140.3, 139.2, 139.1, 134.5, 133.2, 132.9, 132.4, 131.8, 129.0, 128.9, 127.0, 123.1, 122.6, 120.8, 120.0, 21.4, 20.7; ESI-MS ($C_{20}H_{19}N_3O_2S$) 366 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{19}N_3O_2S$ [M + H]$^+$ 366.1270, found 366.1281.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)-3-nitrobenzenesulfonamide (4d). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105 mg, 0.5 mmol), 3-nitrobenzenesulfonyl azide (**2d**) (171 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 35 h gave **4d** (171.0 mg, 83%) as an orange solid. Mp 175−177 °C; IR (KBr, cm^{-1}) 3234, 3071, 2919, 1533, 1347, 1174, 803, 675; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.41 (s, 1H), 8.57 (t, J = 2.0 Hz, 1H), 8.23−8.20 (m, 1H), 7.91 (dt, J = 8.0, 1.0 Hz, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.53−7.50 (m, 3H), 7.47 (t, J = 8.0 Hz, 1H), 7.40 (t, J = 8.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.28 (dd, J = 8.5, 2.0 Hz, 1H), 2.47 (s, 3H), 2,36 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.8, 148.0, 141.2, 140.9, 139.4, 136.0, 133.3, 132.8, 132.4, 130.5, 130.1, 129.2, 127.3, 123.1, 122.5, 122.34, 122.31, 120.0, 21.3, 20.8; ESI-MS ($C_{20}H_{18}N_4O_4S$) 411 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{18}N_4O_4S$ [M + H]$^+$ 411.1121, found 411.1128.

(*E*)-4-Methoxy-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (4e). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-methoxybenzenesulfonyl azide (**2e**) (160.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 24 h gave **4e** (170.0 mg, 86%) as a yellow solid. Mp 125−127 °C; IR (KBr, cm^{-1}) 3317, 2928, 2837, 1596, 1497, 1333, 1263, 1160, 1147, 1093, 890, 831, 795, 689; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.45 (s, 1H), 7.67 (d, J = 9.0 Hz, 2H), 7.60 (t, J = 8.5 Hz, 3H), 7.52 (d, J = 1.0 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.5 Hz, 1H), 7.21 (dd, J = 8.5, 1.5 Hz, 1H), 6.75 (d, J = 9.0 Hz, 2H), 3.71 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 163.0, 152.1, 140.4, 139.2, 134.4, 133.2, 132.3, 132.0, 130.6, 129.2, 129.0, 123.2, 122.4, 120.8, 120.0, 114.0, 55.4, 21.3, 20.7; ESI-MS ($C_{21}H_{21}N_3O_3S$) 396 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{21}H_{21}N_3O_3S$ [M + H]$^+$ 396.1376, found 396.1388.

(*E*)-4-(*tert*-Butyl)-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)-benzenesulfonamide (4f). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-(*tert*-butyl)benzenesulfonyl azide (**2f**) (179.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 28 h gave **4f** (181.0 mg, 86%) as an orange solid. Mp 165−166 °C; IR (KBr, cm^{-1}) 3252, 2965, 1500, 1336, 1167, 1114, 908, 795, 687; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.48 (s, 1H), 7.67 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 1H), 7.56 (t, J = 7.5 Hz, 3H), 7.40 (td, J = 7.5, 1.0 Hz, 1H), 7.36−7.28 (m, 3H), 7.22 (dd, J = 8.5, 1.5 Hz, 1H), 2.47 (s, 3H), 2.34 (s, 3H), 1.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.7, 152.0, 140.3, 139.1, 136.2, 134.3, 133.2, 132.3, 132.1, 129.0, 126.8, 125.9, 123.2, 122.3, 120.8, 120.1, 35.0, 30.9, 21.8, 20.7; ESI-MS ($C_{24}H_{27}N_3O_2S$) 422 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{24}H_{27}N_3O_2S$ [M + H]$^+$ 422.1896, found 422.1902.

(*E*)-*N*-(4-(*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)sulfamoyl)-phenyl)acetamide (4g). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105 mg, 0.5 mmol), 4-acetamidobenzenesulfonyl azide (**2g**) (180.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 35 h gave **4g** (186.0 mg, 88%) as a yellow solid. Mp 189−190 °C; IR (KBr, cm^{-1}) 3337, 3286, 2921, 1682, 1593, 1322, 1157, 1097, 916, 639; ^1H NMR (DMSO-d_6, 500 MHz) δ 10.11 (s, 1H), 10.09 (s, 1H), 7.65 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.43 (t, J = 8.5 Hz, 2H), 7.36−7.31 (m, 3H), 2.43 (s, 3H), 2.29 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz) δ 169.2, 152.5, 144.5, 143.4, 138.9, 136.1, 133.8, 133.5, 133.2, 132.5, 129.3, 128.2, 126.5, 123.5, 121.3, 118.5, 116.5, 24.5, 21.3, 20.9; ESI-MS ($C_{22}H_{22}N_4O_3S$) 423 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{22}H_{22}N_4O_3S$ [M + H]$^+$ 423.1485, found 423.1495.

(*E*)-4-Fluoro-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (4h). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-fluorobenzenesulfonyl azide (**2h**) (151.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4h** (165.0 mg, 86%) as an orange solid. Mp 113−114 °C; IR (KBr, cm^{-1}) 3258, 3079, 2916, 1591, 1497, 1334, 1170, 838, 693; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.50 (s, 1H), 7.76−7.72 (m, 2H), 7.72 (d, J = 8.5 Hz, 1H), 7.59 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 1.0 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.32 (d, J = 7.0 Hz, 1H), 7.23 (dd, J = 8.0, 2.0 Hz, 1H), 6.95 (t, J = 8.5 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.1, 164.1, 152.0, 140.7, 139.2, 135.1, 135.08, 135.00, 133.2, 132.5, 131.5, 129.89, 129.81, 129.1, 123.2, 122.6, 121.3, 120.0, 116.2, 116.0, 21.3, 20.7; ^{19}F NMR ($CDCl_3$, 470 MHz) −104.4 (m, Ar−F); ESI-MS ($C_{20}H_{18}FN_3O_2S$) 384 [M^+H]; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{18}FN_3O_2S$ [M + H]$^+$ 384.1176, found 384.1177.

(*E*)-4-Chloro-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (4i). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105 mg, 0.5 mmol), 4-chlorobenzenesulfonyl azide (**2i**) (163.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4i** (186.0 mg, 93%) as an orange solid. Mp 143−144 °C; IR (KBr, cm^{-1}) 3265, 3096, 2918, 1501, 1331, 1166, 1092, 798, 756, 691, 653; ^1H NMR ($CDCl_3$, 500 MHz) δ 9.50 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 1H), 7.60 (d, J = 6.5 Hz, 2H), 7.56 (d, J = 1.5 Hz, 1H), 7.43 (td, J = 7.5, 1.0 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 7.29−7.24 (m, 3H), 2.50 (s, 3H), 2.37 (s, 3H); ^{13}C NMR ($CDCl_3$, 125

MHz) δ 152.0, 140.7, 139.5, 139.3, 137.4, 135.1, 133.2, 132.5, 131.2, 129.2, 129.1, 128.5, 123.2, 122.7, 121.2, 119.9, 21.3, 20.8; ESI-MS ($C_{20}H_{18}ClN_3O_2S$) 400 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{20}H_{18}ClN_3O_2S$ [M + H]⁺ 400.0881, found 400.0883.

(*E*)-4-Bromo-*N*-(4-methyl-2-(*m*-tolyldiazenyl)phenyl)benzenesulfonamide (4j). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-bromobenzenesulfonyl azide (**2j**) (197.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4j** (211.0 mg, 95%) as an orange solid. Mp 147−148 °C; IR (KBr, cm⁻¹) 3268, 3094, 2919, 1574, 1501, 1379, 1330, 1166, 1090, 797, 743, 651; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.47 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.60−7.55 (m, 4H), 7.53 (d, *J* = 1.0 Hz, 1H), 7.43−7.39 (m, 3H), 7.33 (d, *J* = 7.0 Hz, 1H), 7.23 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.48 (s, 3H), 2.35 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.0, 140.7, 139.3, 138.0, 135.1, 133.2, 132.5, 132.2, 131.2, 129.1, 128.5, 128.0, 123.3, 122.7, 121.3, 119.9, 21.4, 20.8; ESI-MS ($C_{20}H_{18}BrN_3O_2S$) 444 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{20}H_{18}BrN_3O_2S$ [M + H]⁺ 444.0375, found 444.0381.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)-4-nitrobenzenesulfonamide (4k). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-nitrobenzenesulfonyl azide (**2k**) (171.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 24 h gave **4k** (144.0 mg, 70%) as an orange solid. Mp 155−156 °C; IR (KBr, cm⁻¹) 3232, 3100, 2919, 1527, 1345, 1174, 1089, 800, 738, 689; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.47 (s, 1H), 8.06 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.83 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.53−7.51 (m, 3H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.26 (dd, *J* = 7.0, 1.5 Hz, 1H), 2.47 (s, 3H), 2.36 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 151.9, 150.0, 144.5, 141.1, 139.4, 136.0, 133.2, 132.8, 130.4, 129.2, 128.3, 124.0, 123.3, 122.8, 122.1, 119.7, 21.3, 20.8; ESI-MS ($C_{20}H_{18}N_4O_4S$) 411 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{20}H_{18}N_4O_4S$ [M + H]⁺ 411.1121, found 411.1128.

(*E*)-*N*-(4-Methyl-2-(*m*-tolyldiazenyl)phenyl)-4-(trifluoromethyl)benzenesulfonamide (4l). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 4-(trifluoromethyl)benzenesulfonyl azide (**2l**) (188.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 31 h gave **4l** (178.0 mg, 82%) as an orange solid. Mp 100−101 °C; IR (KBr, cm⁻¹) 3237, 2921, 1322, 1175, 1062, 716, 688; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.56 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 6.5 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 3H), 7.40 (td, *J* = 7.5, 2.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.46 (s, 3H), 2.34 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 151.9, 142.5, 140.9, 139.3, 135.4, 134.8, 134.5, 134.3, 134.0, 133.2, 132.6, 130.9, 129.1, 127.6, 126.3, 126.07, 126.05, 126.02, 125.9, 124.1, 123.3, 122.7, 121.9, 121.6, 119.9, 119.8, 21.3, 20.7; ¹⁹F NMR ($CDCl_3$, 470 MHz) −63.2 (s, Ar−CF_3); ESI-MS ($C_{21}H_{18}F_3N_3O_2S$) 434 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{21}H_{18}F_3N_3O_2S$ [M + H]⁺ 434.1144, found 434.1148.

(*E*)-4-Methyl-*N*-(4-(methylsulfonyl)phenyl)-2-(*m*-tolyldiazenyl)aniline (4m). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-azido-4-(methylsulfonyl)benzene (**2m**) (148.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4m** (80.0 mg, 42%) as an orange solid. Mp 194−195 °C; IR (KBr, cm⁻¹) 3340, 3013, 2917, 1589, 1511, 1138, 777, 681; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.38 (s, 1H), 7.85 (m, 1H), 7.83 (m, 1H), 7.72 (d, *J* = 1.0 Hz, 1H), 7.66−7.65 (m, 2H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.32 (m, 1H), 7.31 (m, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 8.0, 1.5 Hz, 1H), 3.04 (s, 3H), 2.46 (s, 3H), 2.39 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.5, 147.1, 139.6, 139.1, 135.2, 133.0, 131.83, 131.80, 131.1, 129.3, 129.0, 125.4, 122.8, 119.8, 117.6, 117.1, 44.8, 21.4, 20.6; ESI-MS ($C_{21}H_{21}N_3O_2S$) 380 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{21}H_{21}N_3O_2S$ [M + H]⁺ 380.1427, found 380.1425.

(*E*)-4-Methyl-*N*-(4-nitrophenyl)-2-(*m*-tolyldiazenyl)aniline (4n). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-azido-4-nitrobenzene (**2n**) (123.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 38 h gave **4n** (57.0 mg, 33%) as an orange solid. Mp 144−146 °C; IR (KBr, cm⁻¹) 3382, 1589, 1290, 1111, 834, 750, 688; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.41 (s, 1H), 8.18 (dt, *J* = 9.0, 2.0 Hz, 2H), 7.73 (d, *J* = 1.0 Hz, 1H), 7.65 (m, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.26−7.22 (m, 3H), 2.48 (s, 3H), 2.41 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.5, 148.3, 140.8, 140.0, 139.2, 134.6, 132.9, 131.9, 129.0, 126.0, 125.1, 122.9, 119.8, 117.8, 116.5, 113.0, 21.4, 20.6; ESI-MS ($C_{20}H_{18}N_4O_2$) 347 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{20}H_{18}N_4O_2$ [M + H]⁺ 347.1502, found 347.1501.

(*E*)-4-Methyl-*N*-(3-nitrophenyl)-2-(*m*-tolyldiazenyl)aniline (4o). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-azido-3-nitrobenzene (**2o**) (123.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4o** (57.0 mg, 33%) as an orange solid. Mp 99−100 °C; IR (KBr, cm⁻¹) 3387, 2916, 1531, 1350, 733, 685; ¹H NMR ($CDCl_3$, 500 MHz) δ 9.53 (s, 1H), 8.10 (t, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.74 (s, 1H), 7.66 (t, *J* = 2.0 Hz, 2H), 7.53 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 1.5 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.5, 149.3, 143.1, 139.1, 138.8, 136.1, 133.2, 131.6, 130.1, 130.0, 129.0, 126.3, 125.3, 122.7, 119.7, 116.5, 115.6, 113.7, 21.4, 20.5; ESI-MS ($C_{20}H_{18}N_4O_2$) 347 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{20}H_{18}N_4O_2$ [M + H]⁺ 347.1502, found 347.1498.

(*E*)-4-Methyl-*N*-(4-nitrobenzyl)-2-(*m*-tolyldiazenyl)aniline (4p). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-(azidomethyl)-4-nitrobenzene (**2p**) (133.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4p** (58.0 mg, 32%) as a red solid. Mp 126−128 °C; IR (KBr, cm⁻¹) 3441, 2916, 1517, 1342, 1217, 789, 737, 687; ¹H NMR ($CDCl_3$, 500 MHz) δ 8.98 (s, 1H), 8.19 (d, *J* = 8.5 Hz, 2H), 7.71 (d, *J* = 1.0 Hz, 1H), 7.64−7.60 (m, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.05 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.54 (d, *J* = 8.5 Hz, 1H), 4.64 (s, 2H), 2.45 (s, 3H), 2.32 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.8, 147.2, 146.9, 140.7, 139.0, 136.7, 133.7, 130.8, 129.4, 128.9, 127.5, 126.2, 123.9, 122.3, 119.5, 112.1, 46.6, 21.4, 20.1; ESI-MS ($C_{21}H_{20}N_4O_2$) 361 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{21}H_{20}N_4O_2$ [M + H]⁺ 361.1659, found 361.1663.

(*E*)-*N*-(3,5-Bis(trifluoromethyl)benzyl)-4-methyl-2-(*m*-tolyldiazenyl)aniline (4q). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-(azidomethyl)-3,5-bis(trifluoromethyl)benzene (**2q**) (202.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4q** (118.0 mg, 51%) as a red solid. Mp 62−63 °C; IR (KBr, cm⁻¹) 3429, 2925, 2866, 1571, 1379, 1277, 1128, 878, 788, 682; ¹H NMR ($CDCl_3$, 500 MHz) δ 8.79 (s, 1H), 7.87 (s, 2H), 7.83 (s, 1H), 7.73 (d, *J* = 1.5 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.64 (s, 2H), 2.45 (s, 3H), 2.34 (s, 3H); ¹³C NMR ($CDCl_3$, 125 MHz) δ 152.8, 142.0, 140.7, 139.0, 136.7, 133.8, 132.4, 132.1, 131.9, 131.6, 130.8, 129.5, 128.9, 127.1, 127.0, 126.5, 126.4, 124.4, 122.5, 122.2, 121.37, 121.34, 121.31, 121.2, 120.0, 119.3, 111.9, 46.7, 21.3, 20.1; ¹⁹F NMR ($CDCl_3$, 470 MHz) −62.7 (s, Ar−CF_3); ESI-MS ($C_{23}H_{19}F_6N_3$) 452 [M⁺H]; HRMS *m*/*z* (ESI-TOF) calcd for $C_{23}H_{19}F_6N_3$ [M + H]⁺ 452.1555, found 452.1554.

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(*E*)-*N*-Hexyl-4-methyl-2-(*m*-tolyldiazenyl)aniline (4r). Following the general procedure using (*E*)-1,2-di-*m*-tolyldiazene (**1c**) (105.0 mg, 0.5 mmol), 1-azidohexane (**2r**) (95.0 mg, 0.75 mmol), $[RhCp^*Cl_2]_2$ (7.9 mg, 0.013 mmol), $AgSbF_6$ (17.1 mg, 0.05 mmol), and 1,2-dichloroethane (2.5 mL) under atmospheric conditions for 36 h gave **4r** (20.0 mg, 13%, with 18% conversion) as a red solid. Mp 54−55 °C; IR (KBr, cm^{-1}) 3244, 2925, 2854, 1571, 1522, 1157, 785, 688; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.08 (s, 1H), 7.67 (d, J = 1.0 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.37 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.12 (dd, J = 8.5, 2.0 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 3.28 (t, J = 6.5 Hz, 2H), 2.45 (s, 3H), 2.33 (s, 3H), 1.77−7.70 (m, 2H), 1.52−1.45 (m, 2H), 1.38−1.35 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.0, 141.3, 138.9, 136.1, 133.7, 130.6, 130.2, 128.8, 122.1, 119.3, 112.0, 43.0, 29.7, 29.1, 26.9, 22.6, 21.4, 20.1, 14.0; ESI-MS ($C_{20}H_{27}N_3$) 310 $[M^+H]$; HRMS m/z (ESI-TOF) calcd for $C_{20}H_{27}N_3$ $[M + H]^+$ 310.2277, found 310.2271.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^1H, ^{13}C, and ^{19}F NMR spectra for all compounds; X-ray structure of compound **4l**; and details of mechanistic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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