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Pd-Catalyzed Direct C−H Bond Sulfonylation of Azobenzenes with Arylsulfonyl Chlorides

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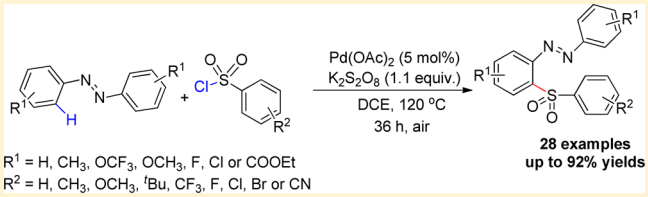
Supporting Information

ABSTRACT: Pd(II)-catalyzed C−H sulfonylation of azobenzenes with arylsulfonyl chlorides has been developed. The sulfonylazobenzenes were obtained in moderate to excellent yields for 28 examples. This protocol features high efficiency, wide functional group tolerance, and atom economy.



INTRODUCTION

Sulfonylazobenzenes are essential components in photosensitive composition,[1a] color filters,[1a] chemical indicators,[1b,c] Raman spectroscopy,[1d] and dyes.[1a−h] They also exist widely in pharmaceuticals[1i−m] and natural products.[1n] Two examples are exemplified in Figure 1. Compounds **A**[1o] and **B**[1p] are found in

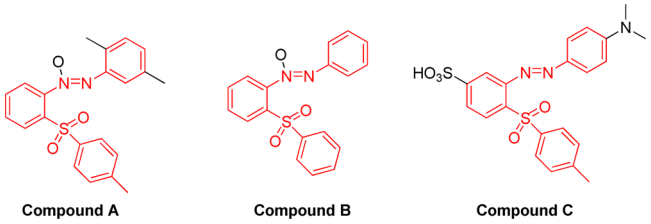


Figure 1. Examples illustrating the importance of *ortho*-sulfonylation of azobenzenes.

oxidants,[1q] polymer inhibitors, and stabilizers.[1r] Compound **C** is used as dye in the textile industry because of its excellent color stability, high reactivity, and ecofriendly nature.[1s]

However, the construction of such a structure remains largely unexploited. To the best of our knowledge, only two procedures have been reported. In 1964, Bauer[2] obtained sulfonylazobenzene from diazosulfone, which was synthesized via the diazotization of 2-aminoazobenzene and sequential sulfonation with benzenesulfinic acid. Moreover, only sulfonylazobenzene was synthesized. Alexander[1h] achieved sulfonylazobenzene derivatives through multistep reactions involving diazotization of anilines, *ortho*-sulfonylation, and coupling reactions. These procedures suffered from tedious reaction steps and harsh reaction conditions. During the past few years, transition-metal-catalyzed sulfonylation reactions have proved to be a powerful strategy in organic synthesis for sulfonylated products. These highly efficient catalyst systems have been developed using sodium benzenesulfinate, thiol, sulfonylhydrazide, sulfuryl chloride, etc., as sulfonylation reagents.[3] Arylsulfuryl chlorides are outstanding because they are readily availabile and safe to handle. In view of the importance of sulfonylazobenzenes and the drawbacks of the existing methods, the exploration and development of an efficient and highly regioselective protocol to construct such a desirable framework from readily available starting materials is highly desired. Recently, the azo group has attracted great attention as a directing group to synthesize azobenzene derivatives. Transition-metal-catalyzed *ortho*-halogenation,[4] *ortho*-acylation,[5] *ortho*-arylation,[6] *ortho*-alkoxylation,[7] *ortho*-acyloxyation,[8] *ortho*-amidation,[9] and cyclization[10] of azobenzenes have been developed recently. Herein we disclose a simple and efficient procedure for the synthesis of various *ortho*-sulfonylated azobenzenes via palladium-catalyzed direct cross-coupling of azobenzenes with arylsulfonyl chlorides.

RESULTS AND DISCUSSION

Initially, the cross-coupling of azobenzene (**1a**) with *p*-tolysulfonyl chloride (**2a**) was chosen as a model reaction for optimization of the reaction parameters. The reaction gave the desired cross-coupling product **3a** in 48% yield using $Pd(OAc)_2$ (10 mol %) as a catalyst in the presence of $K_2S_2O_8$ (1.1 equiv) under air for 24 h (Table 1, entry 1). Inspired by this result, we screened various catalysts, such as $Pd(TFA)_2$, $Pd(CH_3CN)_2Cl_2$, and $PdCl_2$ (entries 2−4). $Pd(OAc)_2$ proved to be best palladium reagent (entry 1). Among the oxidants examined, including Ag_2O, AgCl, AgOTf, $K_2S_2O_8$, and Ag_2CO_3, $K_2S_2O_8$ was the best choice (entry 1 vs entries 5−8). The yield of **3a**

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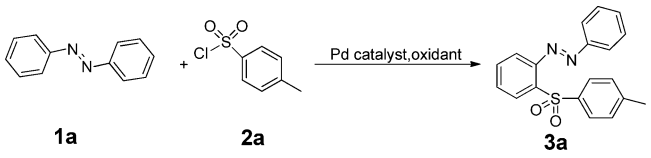
Table 1. Optimization of the Reaction Conditions for Pd-Catalyzed *ortho*-Sulfonylation of Azobenzene with *p*-Tolylsulfonyl Chloride[a]



1a 2a 3a

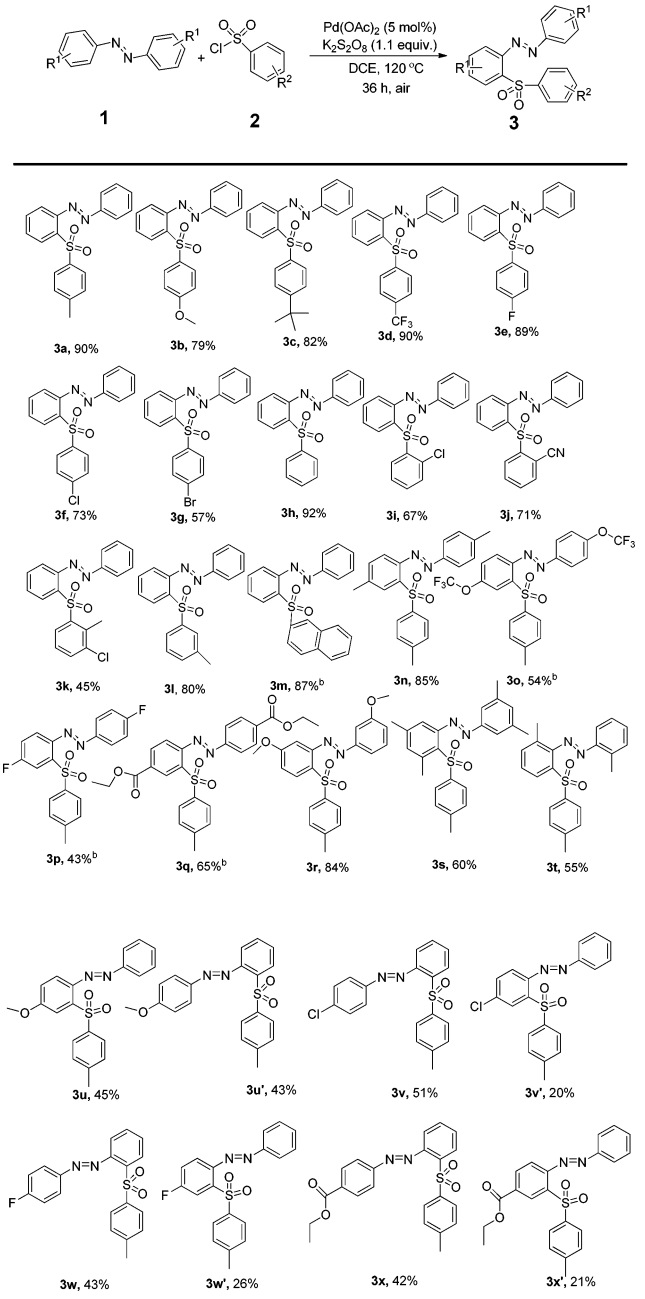
entry	PdX_2	oxidant	solvent	yield (%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	48
2	$Pd(TFA)_2$	$K_2S_2O_8$	DCE	35
3	$Pd(CH_3CN)_2Cl_2$	$K_2S_2O_8$	DCE	15
4	$PdCl_2$	$K_2S_2O_8$	DCE	trace
5	$Pd(OAc)_2$	Ag_2O	DCE	47
6	$Pd(OAc)_2$	AgCl	DCE	21
7	$Pd(OAc)_2$	AgOTf	DCE	5
8	$Pd(OAc)_2$	Ag_2CO_3	DCE	trace
9[c]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	70
10[d]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	79
11[e]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	65
12[d]	–	$K_2S_2O_8$	DCE	n.r.
13[d]	$Pd(OAc)_2$	$K_2S_2O_8$	dioxane	25
14[d]	$Pd(OAc)_2$	$K_2S_2O_8$	toluene	72
15[d]	$Pd(OAc)_2$	$K_2S_2O_8$	THF	n.r.
16[d]	$Pd(OAc)_2$	$K_2S_2O_8$	DMF	trace
17[d]	$Pd(OAc)_2$	$K_2S_2O_8$	DMSO	n.r.
18[d,f]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	85
19[d,f,g]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	90
20[d,f,g,h]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	91

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 equiv), catalyst (10 mol %), oxidant (1.1 equiv), and solvent (2.0 mL) under air at 100 °C for 24 h, unless otherwise noted. [b]Isolated yields based on **1a**. [c]110 °C. [d]120 °C. [e]130 °C. [f]36 h. [g]$Pd(OAc)_2$ (5 mol %). [h]**2a** (4.0 equiv).

reached 70% and 79% when the temperature of the oil bath was increased to 110 and 120 °C, respectively (entries 9 and 10). Higher temperature disfavored this transformation (entry 11). No desired product was observed in the absence of the catalyst (entry 12). Solvents such as 1,4-dioxane, toluene, THF, DMF, DMSO, and DCE were screened, and DCE was found to be superior to the others (entries 10 and 13–17). Prolonging the reaction time to 36 h increased the yield of **3a** to 85% (entry 18). When the catalyst loading was reduced to 5 mol % and the reaction time was 36 h, the product **3a** was obtained in 90% yield (entry 19). Increasing the loading of **2a** to 4 equiv did not significantly improve the yield (entry 20). However, reducing its loading resulted in a decrease in the yield of the desired product. The optimized reaction conditions were identified as follows: $Pd(OAc)_2$ (5 mol %), $K_2S_2O_8$ (1.1 equiv), and a **1a**:**2a** ratio of 1:3 in DCE at 120 °C in an oil bath under air for 36 h (Table 1, entry 19). The structure of **3a** was confirmed by single-crystal X-ray diffraction[11] and is shown in Figure 1 in the Supporting Information.

With the optimized reaction conditions in hand, we first examined the scope of the arylsulfonyl chlorides (Scheme 1). The results demonstrated that the reactions of arylsulfonyl chlorides bearing electron-donating or electron-withdrawing groups with azobenzene proceeded smoothly, affording the *ortho*-sulfonylated azobenzenes in moderate to excellent yields (**3a**–**m**). When arylsulfonyl chlorides were substituted at the *para* position with electron-donating groups such as -Me, -OMe, and -*t*Bu, the desired products were obtained in 90%,

Scheme 1. Palladium-Catalyzed C–H Sulfonylation of Azobenzenes[a]



[a]Reaction conditions: **1** (0.2 mmol), **2** (3.0 equiv), $Pd(TFA)_2$ (5 mol %), and $K_2S_2O_8$ (1.1 equiv) in DCE (2.0 mL) under air at 120 °C for 36 h. Isolated yields based on **1** are shown. [b]48 h.

79%, and 82% yield, respectively (**3a**–**c**). Arylsulfonyl chlorides with electron-withdrawing substituents were also suitable substrates. For example, 4-trifluoromethyl-, 4-fluoro-, 4-chloro-, and 4-bromophenylsulfonyl chloride gave the corresponding products in 90%, 89%, 73%, and 57% yield, respectively (**3d**–**g**). Phenylsulfonyl chloride provided the product in 92% yield (**3h**). Benzenesulfonyl chlorides substituted with Cl, CN, and CH_3 at the 2-position also reacted with azobenzene smoothly and provided the desired products in 67%, 71%, and 45% yield, respectively (**3i**–**k**). In addition, 3-methylbenzenesulfonyl chloride and 2-naphthylsulfonyl chloride were also tolerated in this reaction system, affording the desired products in 80%

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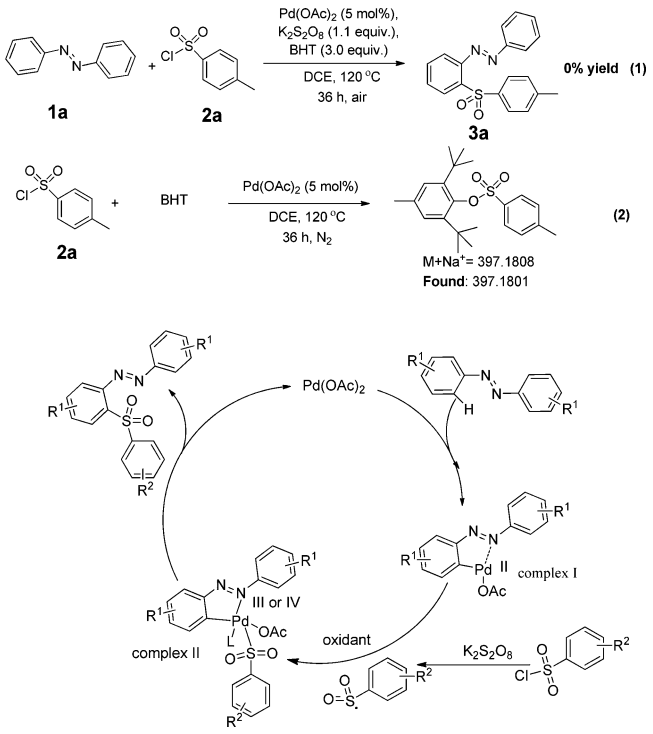
and 87% yield, respectively (**3l** and **3m**). The results obtained above indicated that the electron density in the arylsulfonyl chloride does not affect this transformation significantly. However, a slight influence of the steric hindrance was observed.

Next, the scope and generality of azobenzenes were explored under the standard reaction conditions (**3n**–**t**, Scheme 1). In general, electron-rich azobenzenes were more suitable substrates and gave higher yields than electron-deficient azobenzenes. 4-Methylazobenzene and 3-methoxyazobenzene provided the products in 85% and 84% yield, respectively (**3n** and **3r**), while 4-trifluoromethoxy-, 4-fluoro-, and 4-(ethoxycarbonyl)azobenzene provided the corresponding products in 54%, 43%, and 65% yield, respectively (**3o**–**q**). The steric effects of substituents of the azobenzene were well-tolerated. 2,5-Dimethyl- and 2-methylazobenzene delivered the desired products in 60% and 55% yield, respectively (**3s** and **3t**). The reactions of unsymmetrical azobenzenes also proceeded smoothly and gave the products in good to excellent yields. However, the regioselectivity was poor. Two isolable isomers were obtained (**3u**–**x** and **3u′**–**x′**).

To clarify the reaction mechanism, some control experiments were carried out under the optimized conditions as follows. (1) When a radical scavenger (BHT) was added to the reaction mixture, this reaction was inhibited, and no **3a** was detected (eq 1 in Scheme 2). (2) The *p*-tolylsulfonyl radical was captured by

Scheme 2. Proposed Reaction Mechanism



BHT (eq 2 in Scheme 2), perhaps because $K_2S_2O_8$ and high temperature helped to activate the *p*-tolylsulfonyl radical.[12] On the basis of the results obtained and the literature,[13] a radical process is suggested to be involved in this catalytic system. A possible reaction pathway is proposed and described in Scheme 2. Azobenzene **1a** first reacts with $Pd(OAc)_2$ to form palladacycle I through *ortho*-C–H bond insertion, which accounts for the high regioselectivity in the reactions. Then palladacycle I reacts with the *p*-tolylsulfonyl radical to generate Pd(IV) or Pd(III) species II.[5a,14] Subsequently, intermediate II undergoes reductive elimination to afford the sulfonylation product **3a** and Pd(II) is regenerated for the next catalytic cycle.

CONCLUSION

In summary, we have developed a Pd(II)-catalyzed C–H sulfonylation of azobenzenes with arylsulfonyl chlorides. Sulfonylazobenzene compounds were obtained smoothly by this process. This method features a simple system, one-step operation, high efficiency, atom economy, environmental friendliness, and ligand-, additive-, and base-free conditions. Further investigations to expand the substrate scope and the applications of such chemistry in organic synthesis are underway.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all of the reagents were purchased from commercial suppliers and used without purification. Dichloroethane was distilled from calcium hydride. Melting points were measured on a microscopic apparatus and were uncorrected. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer in deuterated chloroform. The chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. The multiplicities of signals are designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J) are reported in hertz. ^{13}C NMR spectra were recorded using a 100 MHz spectrometer. The chemical shifts are reported relative to residual $CHCl_3$ (δ_c = 77.00 ppm). High-resolution mass spectrometry (HRMS) was performed on a Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI). X-ray analysis was performed with a single-crystal X-ray diffractometer.

Typical Procedure for the Synthesis of Azobenzenes. A mixture of CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), and arylamine (1 mmol) in toluene (4 mL) was stirred at 60 °C under air (1 atm) for 20 h and then cooled to room temperature and concentrated under vacuum. The residue was purified by flash chromatography on a short silica gel column, eluting with petroleum ether, to afford the desired products.[14]

Typical Procedure for the Synthesis of Sulfonylazobenzenes: Synthesis of (*E*)-1-Phenyl-2-(2-tosylphenyl)diazene (3a). In an oil bath, azobenzene (**1a**) (36.4 mg, 0.2 mmol), *p*-tolylsulfonyl chloride (**2a**) (114.3 mg, 0.6 mmol), $Pd(OAc)_2$ (2.25 mg, 0.01 mmol), $K_2S_2O_8$ (59.5 mg, 0.22 mmol), and DCE (2 mL) were successively added to a 50 mL reaction tube. The mixture was stirred on a heating block at 120 °C for 36 h. (Note: the reaction was sluggish at temperatures below 120 °C.) After cooling to ambient temperature, the resulting mixture was filtered through a pad of tripolite and washed with 50 mL of ethyl acetate. The filtrate was concentrated in vacuum, and the resulting residue was purified by preparative thin-layer chromatography (silica gel, ethyl acetate/petroleum ether = 1:7 v/v) to afford the target product **3a** as a red solid (60.4 mg, 90%).

*(E)-1-Phenyl-2-(2-tosylphenyl)diazene (**3a**).* Red solid (60.4 mg, 90%); mp 162.8–163.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.4 Hz, 1H), 7.86–7.82 (m, 4H), 7.68–7.60 (m, 2H), 7.52–7.59 (m, 4H), 7.16 (d, J = 8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.6, 149.0, 143.9, 139.3, 138.8, 134.4, 132.0, 130.6, 129.30 129.1, 128.2, 123.8, 116.9, 21.54; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{17}N_2O_2S$ 337.1005, found 337.1006.

*(E)-1-(2-((4-Methoxyphenyl)sulfonyl)phenyl)-2-phenyldiazene (**3b**).* Red solid (55.6 mg, 79%); mp 158.6–159.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, J = 1.7 Hz, J = 3.2 Hz, 1H), 7.90 (d, J = 8.8 Hz, 2H), 7.86–7.84 (m, 2H), 7.65–7.60 (m, 2H), 7.59–7.57 (m, 1H), 7.54–7.52 (m, 3H), 6.82 (d, J = 9.0 Hz, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 152.7, 148.9, 139.1, 134.3, 132.0, 130.6, 130.5, 129.2, 123.7, 116.9, 113.9, 55.6; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{17}N_2O_3S$ 353.0954, found 353.0958.

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*(E)-1-Phenyl-2-(2-((4-(tert-butyl)phenyl)sulfonyl)phenyl)-2-phenyldiazene (**3c**).* Red solid (61.8 mg, 82%); mp 147.6−148.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (dd, J = 3.3 Hz, J = 5.0 Hz, 1H), 7.87 (d, J = 8.5 Hz, 2H), 7.79−7.77 (m, 2H), 7.69−7.60 (m, 2H), 7.57−7.51 (m, 4H), 7.36 (d, J = 8.6 Hz, 2H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 152.6, 149.1, 139.3, 138.7, 134.4, 132.0, 130.5, 129.2, 129.1, 127.9, 125.7, 123.8, 116.9, 35.1, 31.0; HRMS (ESI) ([M + H]$^+$) calcd for $C_{22}H_{23}N_2O_2S$ 379.1475, found 379.1475.

*(E)-1-Phenyl-2-(2-((4-trifluoromethylphenyl)sulfonyl)phenyl)-diazene (**3d**).* Red solid (70.3 mg, 90%); mp 131.8−132.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, J = 3.4 Hz, J = 4.4 Hz, 1H), 8.09 (d, J = 8.2 Hz, 2H), 7.75−7.71 (m, 3H), 7.70−7.68 (m, 1H), 7.64−7.62 (m, 3H), 7.54−7.53 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.9, 145.8, 137.6, 135.1, 132.3, 130.8, 129.5, 129.2, 128.6, 125.8 (dd, J_1 = 7.3 Hz, J_2 = 3.7 Hz), 123.6, 117.1, 26.8; HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{14}F_3N_2O_2S$ 391.0723, found 391.0725.

*(E)-1-(2-((4-Fluorophenyl)sulfonyl)phenyl)-2-phenyldiazene (**3e**).* Red solid (60.3 mg, 89%); mp 191.3−192.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (dd, J = 1.9 Hz, J = 3.1 Hz, 1H), 8.28 (dd, J = 0.3 Hz, J = 4.8 Hz, 2H), 7.89−7.87 (m, 2H), 7.74−7.69 (m, 2H), 7.66 (dd, J = 3.1 Hz, J = 4.4 Hz, 1H), 7.61−7.60 (m, 3H), 7.10 (t, J = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 164.0, 152.6, 148.9, 138.3 (d, J_{C-F} = 9.2 Hz), 138.2, 134.7, 132.2, 131.1 (d, J_{C-F} = 9.5 Hz), 130.7, 129.3, 129.2, 123.6, 117.0, 116.0 (d, J_{C-F} = 22.5 Hz); HRMS (ESI) ([M + H]$^+$) calcd for $C_{18}H_{14}FN_2O_2S$ 341.0755, found 341.0757.

*(E)-1-(2-((4-Chlorophenyl)sulfonyl)phenyl)-2-phenyldiazene (**3f**).* Red solid (51.9 mg, 73%); mp 171.0−172.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 7.6 Hz, 1H), 7.91 (d, J = 9.6 Hz, 2H), 7.82−7.79 (m, 2H), 7.72−7.65 (m, 2H), 7.63−7.54 (m, 4H), 7.35 (d, J = 8.6 Hz, J = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.9, 140.7, 139.6, 138.2, 134.8, 132.2, 130.7, 129.7, 129.4, 129.2, 129.0, 123.7, 117.0; HRMS (ESI) ([M + H]$^+$) calcd for $C_{18}H_{14}ClN_2O_2S$ 357.0459, found 357.0462.

*(E)-1-(2-((4-Bromophenyl)sulfonyl)phenyl)-2-phenyldiazene (**3g**).* Red solid (45.5 mg, 57%); mp 190.7−191.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 7.7 Hz, 1H), 7.90−7.85 (m, 4H), 7.80−7.70 (m, 2H), 7.68−7.60 (m, 4H), 7.57 (d, J = 8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.9, 141.3, 138.1, 134.8, 132.2, 132.0, 130.7, 129.8, 129.4, 129.2, 128.2, 123.7, 117.0; HRMS (ESI) ([M + H]$^+$) calcd for $C_{18}H_{14}BrN_2O_2S$ 400.9954, found 400.9955.

*(E)-1-Phenyl-2-(2-(phenylsulfonyl)phenyl)diazene (**3h**).*[2] Red solid (59.3 mg, 92%); mp 160−161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 7.5 Hz, 1H), 7.96 (d, J = 8 Hz, 2H), 7.80−7.78 (m, 2H), 7.71−7.63 (m, 2H), 7.61−7.51 (m, 4H), 7.46 (d, J = 5.1 Hz, 1H), 7.38 (t, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 149.0, 142.3, 138.5, 134.58, 133.0, 132.1, 130.6, 129.4 129.3, 128.7, 128.0, 127.6, 123.7, 116.9; HRMS (ESI) ([M + H]$^+$) calcd for $C_{18}H_{14}N_2O_2S$ 323.0849, found 323.0855.

*(E)-1-(2-((2-Chlorophenyl)sulfonyl)phenyl)-2-phenyldiazene (**3i**).* Red solid (47.7 mg, 67%); mp 146.7−148.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, J = 1.7 Hz, J = 3.9 Hz, 1H), 8.38 (dd, J = 1.0 Hz, J = 6.3 Hz, 1H), 7.74−7.66 (m, 2H), 7.62−7.56 (m, 3H), 7.48−7.42 (m, 3H), 7.40 (t, J = 5.5 Hz, 1H), 7.35−7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 148.7, 139.9, 138.0, 134.7, 134.2, 132.1, 132.1, 131.5, 131.4, 130.7, 130.5, 128.9, 126.7, 123.7, 116.5; HRMS (ESI) ([M + H]$^+$) calcd for $C_{18}H_{14}ClN_2O_2S$ 357.0459, found 357.0462.

*(E)-2-((2-Phenyldiazenyl)phenyl)sulfonylbenzonitrile (**3j**).* Red liquid (49.3 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, J = 0.6 Hz, J = 2.1 Hz, 1H), 8.40−8.37 (m, 1H), 7.79−7.73 (m, 3H), 7.69 (dd, J = 2.3 Hz, J = 3.9 Hz, 1H), 7.64 (dd, J = 3.2 Hz, J = 4.7 Hz, 2H), 7.62−7.56 (m, 3H), 7.49 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 147.7, 143.2, 137.8, 135.3, 134.4, 132.7, 132.1, 131.4, 131.3, 129.7, 129.5, 129.1, 128.1, 122.6, 115.8, 114.2; HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{14}N_3O_2S$ 348.0801, found 348.0804.

*(E)-1-(2-((3-Chloro-2-methylphenyl)sulfonyl)phenyl)-2-phenyldiazene (**3k**).* Red solid (33.2 mg, 45%); mp 142.5−143.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 7.3 Hz, 1H), 8.28 (d, J = 7.2 Hz, 1H), 7.82−7.74 (m, 2H), 7.69−7.67 (m, 3H), 7.54 (d, J = 7.84 Hz, 4H), 7.22 (t, J = 10.5 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 148.8, 142.6, 138.3, 136.4, 135.0, 134.7, 134.0, 132.1, 130.6, 129.5, 128.9, 128.7, 126.3, 123.8, 116.9, 16.6; HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{16}ClN_2O_2S$ 371.0616, found 371.0617.

*(E)-1-Phenyl-2-(2-(m-tolylsulfonyl)phenyl)diazene (**3l**).* Red solid (53.8 mg, 80%); mp 133.5−134.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (dd, J = 1.8 Hz, J = 3.3 Hz, 1H), 7.88 (d, J = 1.9 Hz, 3H), 7.76−7.68 (m, 3H), 7.65−7.58 (m, 4H), 7.31 (d, J = 8.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 148.9, 142.0, 138.8, 138.7, 134.5, 133.8, 130.1, 129.29, 129.26, 129.1, 128.6, 128.6, 125.2, 123.8, 116.8, 21.1; HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{17}N_2O_2S$ 337.1011, found 337.1008.

*(E)-1-(2-(Naphthalene-2-ylsulfonyl)phenyl)-2-phenyldiazene (**3m**).* Red solid (64.8 mg, 87%); mp 151.2−151.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.49 (d, J = 7.2 Hz, 1H), 7.82 (t, J = 9.6 Hz, 3H), 7.75 (d, J = 7.5 Hz, 3H), 7.31 (t, J = 5.3 Hz, 2H), 7.57−7.48 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 148.9, 138.9, 138.5, 134.9, 134.6, 132.0, 131.9, 130.6, 130.2, 129.4, 129.1, 129.1, 128.9, 127.8, 127.4, 123.7, 123.0, 116.9; HRMS (ESI) ([M + H]$^+$) calcd for $C_{22}H_{17}N_2O_2S$ 373.1005, found 373.1005.

*(E)-1-(4-Methyl-2-tosylphenyl)-2-(p-tolyl)diazene (**3n**).* Red solid (62.0 mg, 85%); mp 178.2−179.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.85 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.1 Hz, 1H), 7.45 (d, J = 6.7 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 2.51 (s, 3H), 2.45 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.0, 143.7, 142.5, 141.3, 139.5, 138.5, 134.9, 129.7, 129.6, 129.2, 128.1, 123.7, 116.7, 21.6, 21.5, 21.5; HRMS (ESI) ([M + H]$^+$) calcd for $C_{21}H_{21}N_2O_2S$ 365.1318, found 365.1321.

*(E)-1-(2-Tosyl-4-(trifluoromethoxy)phenyl)-2-(4-(trifluoromethoxy)phenyl)diazene (**3o**).* Red solid (53.8 mg, 54%); mp 129.7−130.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 2.2 Hz, 1H), 7.88 (d, J = 8.8 Hz, 2H), 7.83 (d, J = 8.2 Hz, 2H), 7.69 (d, J = 8.8 Hz, 1H), 7.52−7.49 (m, 1H), 7.39 (d, J = 8.6 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8 (dd, J_1 = 3.7, J_2 = 1.9), 150.5 (dd, J_1 = 3.0, J_2 = 1.7), 150.4, 146.6, 144.7, 141.0, 138.4, 129.8, 129.5, 128.2, 127.9, 126.2, 125.4, 121.7, 121.2, 118.8, 21.6; HRMS (ESI) ([M + H]$^+$) calcd for $C_{21}H_{15}F_6N_2O_4S$ 505.0651, found 505.0655.

*(E)-1-(4-Fluoro-2-tosylphenyl)-2-(4-fluorophenyl)diazene (**3p**).* Red solid (32.0 mg, 43%); mp 191.5−192.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 1.5 Hz, J = 3.6 Hz, 1H), 7.86−0.82 (m, 4H), 7.70−7.67 (m, 1H), 7.38−7.34 (m, 1H), 7.24−7.19 (m, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 164.5, 163.7, 162.0, 149.1 (d, J_{C-F} = 2.8 Hz), 145.9 (d, J_{C-F} = 3.8 Hz), 144.4, 141.2 (d, J_{C-F} = 6.7 Hz), 138.7, 129.4, 128.2, 125.9 (d, J_{C-F} = 9.1 Hz), 121.4, 121.1, 119.1 (d, J_{C-F} = 8.1 Hz), 116.7 (d, J_{C-F} = 26.1 Hz), 116.2 (d, J_{C-F} = 22.9 Hz), 21.6; HRMS (ESI) ([M + H]$^+$) calcd for $C_{19}H_{15}F_2N_2O_2S$ 373.0817, found 373.0819.

*(E)-Ethyl 4-(2-(4-Ethoxycarbonyl)phenyl)diazenyl)-3-tosylbenzoate (**3q**).* Red solid (62.2 mg, 65%); mp 151.6−152.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.35 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 8.2 Hz, 2H), 7.90−7.84 (m, 4H), 7.60 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 4.51−4.43 (m, 4H), 2.34 (s, 3H), 1.49−1.44 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 153.8, 150.0, 143.4, 138.3, 137.6, 134.5, 129.6, 128.4, 127.2, 122.6, 121.8, 60.3, 20.5, 13.8; HRMS (ESI) ([M + H]$^+$) calcd for $C_{25}H_{25}N_2O_6S$ 481.1428, found 481.1431.

*(E)-1-(5-Methoxy-2-tosylphenyl)-2-(3-methoxyphenyl)diazene (**3r**).* Red solid (66.5 mg, 84%); mp 96.6−97.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.6 Hz, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.50−7.49 (m, 1H), 7.43 (t, J = 7.9 Hz, 1H), 7.38 (t, J = 3.6 Hz, 1H), 7.16 (d, J = 8.3 Hz, 2H), 7.11−7.07 (m, 3H), 3.91 (s, 3H), 3.87 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 160.3, 153.7, 150.7, 143.6, 140.0, 131.4, 130.9, 129.8, 129.3, 127.8, 118.9, 118.1, 116.2, 106.7, 101.2, 56.0, 55.5, 21.5; HRMS (ESI) ([M + H]$^+$) calcd for $C_{21}H_{21}N_2O_4S$ 397.1217, found 397.1218.

*(E)-1-(3,5-Dimethyl-2-tosylphenyl)-2-(3,5-dimethylphenyl)-diazene (**3s**).* Red solid (47.1 mg, 60%); mp 141.2−141.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.36 (s, 2H), 7.16 (t, J = 9.8 Hz, 4H), 6.98 (s, 1H), 2.88 (s, 3H), 2.42 (s, 6H), 2.37

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(s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 151.0, 143.4, 142.2, 140.5, 139.1, 137.6, 134.1, 132.2, 131.6, 128.1, 125.8, 120.5, 115.1, 21.3, 20.5, 20.3, 20.2; HRMS (ESI) ($[M + H]^+$) calcd for $C_{23}H_{25}N_2O_2S$ 393.1631, found 393.1631.

*(E)-1-(2-Methyl-6-tosylphenyl)-2-(o-tolyl)diazene (**3t**).* Red liquid (40.0 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.51 (d, J = 7.7 Hz, 2H), 7.45−7.38 (m, 2H), 7.33 (t, J = 9.1 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 2.52 (s, 3H), 2.32 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 150.3, 143.6, 139.3, 138.9, 137.4, 135.8, 132.1, 131.3, 129.2, 128.7, 127.9, 127.4, 127.3, 126.4, 115.8, 21.5, 19.2, 17.5; HRMS (ESI) ($[M + H]^+$) calcd for $C_{21}H_{21}N_2O_2S$ 365.1318, found 365.1325.

*(E)-1-(4-Methoxy-2-tosylphenyl)-2-phenyldiazene (**3u**).* Red solid (32.7 mg, 45%); mp 154.4−155.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 2.6 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.78 (d, J = 7.8 Hz, 2H), 7.71 (d, J = 8.9 Hz, 1H), 7.51−7.49 (m, 3H), 7.16 (d, J = 7.9 Hz, 3H), 3.98 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 148.3, 146.2, 142.8, 138.5, 137.3, 133.4, 128.9, 128.3, 127.1, 125.0, 116.0, 113.3, 54.7, 20.6; HRMS (ESI) ($[M + H]^+$) calcd for $C_{20}H_{19}N_2O_3S$ 367.1111, found 367.1114.

*(E)-1-(4-Methoxyphenyl)-2-(2-tosylphenyl)diazene (**3u′**).* Red solid (31.3 mg, 43%); mp 138.5−139.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 8.5 Hz, 4H), 7.66 (t, J = 7.4 Hz, 1H), 7.59 (t, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.8 Hz, 2H), 3.91 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 150.3, 143.6, 139.3, 138.9, 137.4, 135.8, 132.1, 131.3, 129.2, 128.7, 127.9, 127.4, 127.3, 126.4, 115.8, 21.5, 19.2, 17.5; HRMS (ESI) ($[M + H]^+$) calcd for $C_{20}H_{19}N_2O_3S$ 367.1111, found 367.1118.

*(E)-1-(4-Chlorophenyl)-2-(2-tosylphenyl)diazene (**3v**).* Red solid (37.8 mg, 51%); mp 170.6−171.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.69−7.63 (m, 2H), 7.60−7.58 (m, 1H), 7.50 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 149.2, 144.4, 139.8, 139.4, 138.5, 134.7, 131.3, 129.9, 129.8, 129.7, 128.4, 125.4, 117.2, 21.9; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{16}ClN_2O_2S$ 371.0616, found 371.0615.

*(E)-1-(4-Chloro-2-tosylphenyl)-2-phenyldiazene (**3v′**).* Red solid (14.8 mg, 20%); mp 182.0−183.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.2 Hz, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.77 (d, J = 8.6 Hz, 2H), 7.69−7.63 (m, 2H), 7.60−7.58 (m, 1H), 7.50 (d, J = 8.6 Hz, 2H), 7.19 (d, J = 8.2 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 149.2, 144.4, 139.8, 139.4, 138.5, 134.7, 131.3, 129.9, 129.8, 129.7, 128.4, 125.4, 117.2, 21.9; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{16}ClN_2O_2S$ 371.0616, found 371.0618.

*(E)-1-(4-Fluorophenyl)-2-(2-tosylphenyl)diazene (**3w**).* Red solid (30.4 mg, 43%); mp 169.3−170.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 7.4 Hz, 1H), 7.86−7.81 (m, 4H), 7.69−7.61 (m, 2H), 7.57 (d, J = 7.6 Hz, 1H), 7.20 (dd, J_1 = 7.6 Hz, J_2 =15.7 Hz, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.1, 149.5 (d, J_{C-F} = 2.8 Hz), 149.3, 144.4, 139.5 (d, J_{C-F} = 62.7 Hz), 134.8, 131.0, 129.8, 129.7, 128.4, 126.3 (d, J_{C-F} = 9.1 Hz), 117.2, 116.6 (d, J_{C-F} = 22.4 Hz), 21.9; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{16}FN_2O_2S$ 355.0911, found 355.0914.

*(E)-1-(4-Fluoro-2-tosylphenyl)-2-phenyldiazene (**3w′**).* Red solid (18.2 mg, 26%); mp 189.7−190.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, J_1 = 2.6 Hz, J_1 = 8.0 Hz, 1H), 7.85−7.81 (m, 4H), 7.69 (q, J = 5.0 Hz, 1H), 7.54 (d, J = 1.6 Hz, 3H), 7.37−7.32 (m, 1H), 7.19 (d, J = 8.1 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 162.4, 145.7, 144.7, 141.7 (d, J_{C-F} = 6.6 Hz), 139.1, 132.4, 129.8, 129.5, 128.8, 124.1, 121.6 (d, J_{C-F} = 22.5 Hz), 119.5 (d, J_{C-F} = 80.7 Hz), 117.1 (d, J_{C-F} = 26.0 Hz), 21.9; HRMS (ESI) ($[M + H]^+$) calcd for $C_{19}H_{16}FN_2O_2S$ 355.0911, found 355.0912.

*(E)-Ethyl 4-(2-(2-Tosylphenyl)diazenyl)benzoate (**3x**).* Red solid (34.2 mg, 42%); mp 114.1−115.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (m, 1H), 8.12 (d, J = 8.6 Hz, 2H), 7.69 (t, J = 6.5 Hz, 4H), 7.62−7.59 (m, 2H), 7.54−7.51 (m, 1H), 7.10 (d, J = 8.2 Hz, 2H), 4.36 (dd, J = 7.0 Hz, J = 14.2 Hz, 2H), 2.25 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 155.3, 149.2, 144.5, 139.74, 139.68, 134.8, 133.4, 131.6, 130.9, 129.9, 129.7, 128.5, 123.8, 120.7, 117.1, 61.8, 21.9, 14.7; HRMS (ESI) ($[M + H]^+$) calcd for $C_{22}H_{21}N_2O_4S$ 409.1217, found 409.1220.

*(E)-Ethyl 4-(2-phenyldiazenyl)-3-tosylbenzoate (**3x′**).* Red solid (17.4 mg, 21%); mp 153.1−153.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 1.4 Hz, 1H), 8.25 (dd, J_1 = 1.6 Hz, J_2 = 8.3 Hz, 1H), 7.79 (d, J = 8.2 Hz, 4H), 7.53−7.48 (m, 4H), 7.11 (d, J = 8.1 Hz, 2H), 4.39 (dd, J = 7.8 Hz, J = 14.2 Hz, 2H), 2.26 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 153.1, 151.9, 144.7, 139.34, 139.26, 135.9, 133.0, 132.6, 131.0, 129.8, 129.6, 128.7, 124.4, 122.7, 117.7, 62.3, 21.9, 14.7; HRMS (ESI) ($[M + H]^+$) calcd for $C_{22}H_{21}N_2O_4S$ 409.1217, found 409.1218.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all products and crystallographic data for **3a** (CIF). 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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