JOC The Journal of Organic Chemistry

Article

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

Duo Zhang, Xiuling Cui, Qianqian Zhang, and Yangjie Wu

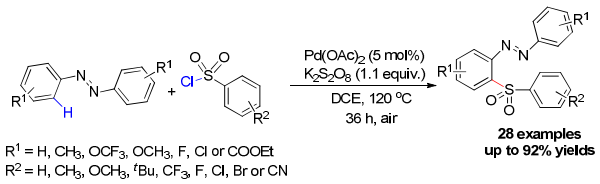
J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo502451k • Publication Date (Web): 05 Jan 2015

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

Duo Zhang,[a] Xiuling Cui,[*a,b] Qianqian Zhang[a] and Yangjie Wu[*a]

[a] Department of Chemistry, Henan Key Laboratory of Chemical Biology and Organic Chemistry, Key Laboratory of Applied Chemistry of Henan Universities, Zhengzhou University, Zhengzhou 450052, P. R. China, Email address: cuixl@zzu.edu.cn; wyj@zzu.edu.cn

[b] Xiamen Key Laboratory of Ocean and Gene Drugs, School of Biomedical Sciences, Institute of Molecular Medicine of Huaqiao University & Engineering Research Centre of Molecular Medicine of Chinese Education Ministry, Fujian, Xiamen 361021, P. R. China



ABSTACT:

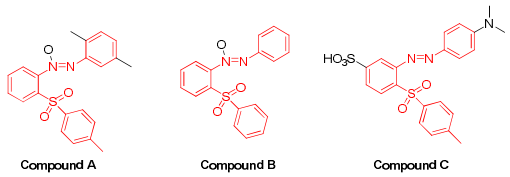
Pd (II) catalyzed C-H sulfonylation of azobenzenes with arylsulfonyl chlorides has been developed. The sulfonylazobenzenes were obtained in moderate to excellent yields for 28 examples. This protocol features with high efficiency, wide functional group tolerance and atomic economy.

INTRUDUCTION:

The sulfonylazobenzenes are essential components in photosensitive composition,[1a] color filter,[1a] chemical indicator,[1b,1c] Raman spectroscopy[1d] and dye.[1a-1h] They also exist widely in pharmaceuticals[1i-1m] and natural

products[1n]. Two examples are exemplified in Figure 1. Compound **A**[1o] and Compound **B**[1p] exhibit in oxidants,[1q] polymer inhibitors and stabilizers.[1r] Compound **C** is used as dye in the textile industry due to its excellent color stability, high reactivity and ecofriend.[1s]

Figure 1. Examples Illustrating the Importance of *ortho*-Sulfonylation Azobenzenes



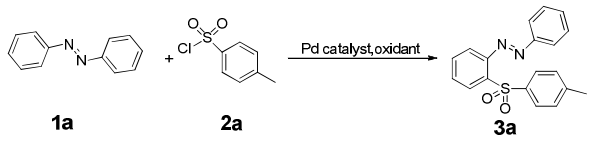
However, building such a structure remains largely unexploited. To the best of our knowledge, only two procedures were reported. In 1964, Bauer[2] obtained the sulfonylazobenzene from diazosulphone, which was synthesized *via* the diazotization of 2-aminoazobenzene and sequential sulfonation with benzenesulphinic acid. Moreover, only sulfonylazobenzene was synthesized. Alexander[1h] achieved sulfonylazobenzene derivatives through multi-step reactions, involving diazotization of anilines, *ortho*-sulfonylation and coupling reaction. These procedures suffered from tedious reaction steps and harsh reaction conditions. During the past few years, transition metal-catalyzed sulfonylation reactions were proved to 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 a sulfonylation reagent.[3] Arylsulfuryl chlorides were outstanding due to its being easily availability and safety to be handled. Considering the importance of sulfonylazobenzenes and the drawbacks of the existing methods, the exploration and development of an efficient and highly regioselective protocol from easily available starting materials to construct such a desirable frame work is highly desired. Recently, azo as a directing group to synthesize azobenzene derivatives have attracted a great attention. The 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 various *ortho*-sulfonylation azobenzenes via palladium-catalyzed direct cross-coupling of azobenzenes with aryl sulfonyl chlorides.

RESULTS AND DISCUSSION:

Initially, the cross-coupling of azobenzene (**1a**) with *p*-tolysulfonylchloride (**2a**) was chosen as a model reaction to optimize 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 hours (entry 1, Table 1). Inspired by this result, various catalysts, such as $Pd(TFA)_2$, $Pd(CH_3CN)_2Cl_2$ and $PdCl_2$ were screened (entries 1-4, Table 1). $Pd(OAc)_2$ was proved to be best palladium reagent (entry 1,Table 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, Table 1). The yield of **3a** could reach 70% and 79% when the temperature of oil bath increased to 110 ˚C and 120 ˚C, respectively (entries 9-10, Table 1). Higher temperature disfavored this transformation (entry 11, Table 1). No desired product was observed in the absence of the catalyst (entry 12, Table 1). The solvents, such as 1, 4-dioxane, toluene, THF, DMF, DMSO and DCE were screened. DCE was found to be superior to others (entries 10, 13-17, Table 1). Prolonging the reaction time to 36 hours, the 85% yield of **3a** was achieved (entry 18, Table 1). 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, Table 1). When increasing the loading of *p*-tolylsulfonyl chloride (**2a**) to 4 equiv, the yield was not improved significantly (entry 20, Table 1). However, reducing its loading resulted in decreasing 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), ratio of **1a** and **2a** is 1: 3 in DCE at 120 ˚C oil bath under air for 36 hours (entry 19, Table 1). The structure of **3a** was confirmed by single crystal X-ray diffraction[11], and was shown in Figure 1 in the Supporting Information.

Table 1. Optimizing Reaction Conditions for Pd-Catalyzed *ortho*-Sulfonylation of Azobenzene with *p*-Tolylsulfonyl Chlorides.[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

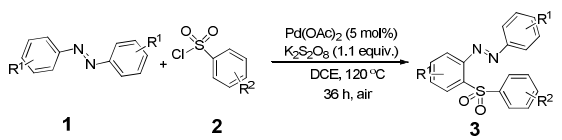
15[d]	$Pd(OAc)_2$	$K_2S_2O_8$	THF	Nr
16[d]	$Pd(OAc)_2$	$K_2S_2O_8$	DMF	trace
17[d]	$Pd(OAc)_2$	$K_2S_2O_8$	DMSO	N.R
18[d,f]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	85
19[d,f,g]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	90
20[d,f,g,h]	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	91

[a]Reaction conditions: azobenzene (**1a**) (0.2 mmol), *p*-tolylsulfonyl chloride (**2a**) (3.0 equiv), catalyst (10 mol%), oxidant (1.1 equiv), solvent (2.0 mL), under air, 100 °C, 24 h. [b]Isolated yield 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)

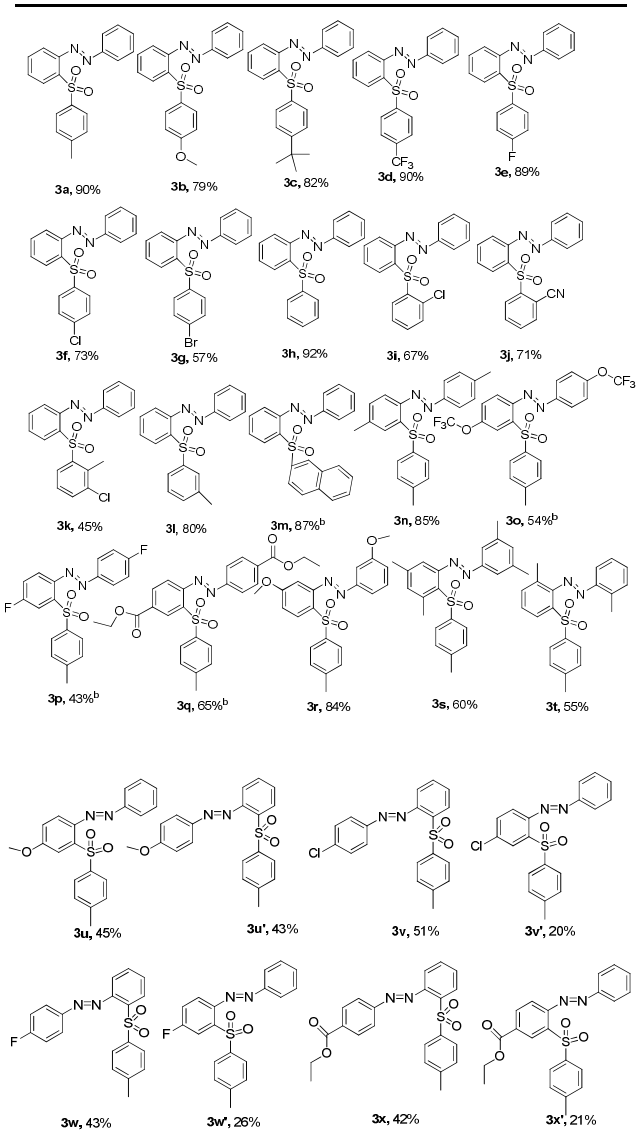
With the optimized reaction conditions in the hand, the scope of the arylsulfonyl chlorides was firstly examined (Scheme 1). These results demonstrated that the reactions of arylsulfonyl chlorides bearing electron-donating or electron-withdrawing groups with azobenzene(**1a**) could proceed smoothly, affording the *ortho*-sulfonylation azobenzenes in moderate to excellent yields (**3a**-**3m** Scheme 1). When arylsulfonyl chlorides were substituted by electron-donating groups, such as -Me, -OMe, -*t*Bu at the *para*-position, the desired products were afforded in 90%, 79% and 82% yields, respectively (**3a**-**3c** Scheme 1). Arylsulfonyl chlorides with electron-withdrawing substituents were also suitable substrates. For example, 4-CF_3, 4-F, 4-Cl and 4-Br phenyl sulfonyl chlorides gave the corresponding products in 90%, 89%, 73% and 57% yields, respectively (**3d**-**3g** Scheme 1). Phenylsulfonyl chloride provided the product in 92% yield (**3h** Scheme 1).

Benzene sulfonyl chloride substituted with Cl, CN and CH_3 at 2-position could also react with azobenzene smoothly and provided the desired product in 67%, 71% and 45% yields, respectively (**3i-3k** Scheme 1). In addition, 3-methyl benzene sulfonyl chloride and 2-naphthol sulfonyl chloride were also tolerated in this reaction system and afforded the desired products in 80% and 87% yields, respectively (**3l** and **3m,** Scheme 1). The results obtained above indicated that the electron density in the arylsulfonyl chlorides did not affect this transformation significantly. However, the slight influence of the steric hindrance was observed. Then, the scope and generality of azobenzene was explored under the standard reaction conditions (**3n-3t** Scheme 1). In general, electron-rich azobenzenes were more suitable substrates and gave higher yields than electron-deficient azobenzenes. 4-Methyl azobenzene and 3-methoxyl azobenzene provided the products in 85% and 84% yields, respectively (**3n, 3r** Scheme 1). While, 4-trifluoromethoxyl, 4-fluoro and 4-ethyl carbonyl azobenzene provided 54%, 43% and 65% yields of the corresponding products, respectively (**3o-3q** Scheme 1). The steric effect substituents of the azobenzene were well-tolerated. 2, 5-Dimethyl and 2-methyl azobenzene could deliver the desired products in 60% and 55% yields, respectively (**3s-3t** Scheme 1). The reactions of unsymmetrical azobenzenes could also proceed smoothly and gave the products in good to excellent yields. However, the regioselectivity was poor. Two isolable isomers were obtained (**3u-3x** and **3u'-3x'** Scheme 1).

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



1 2 3

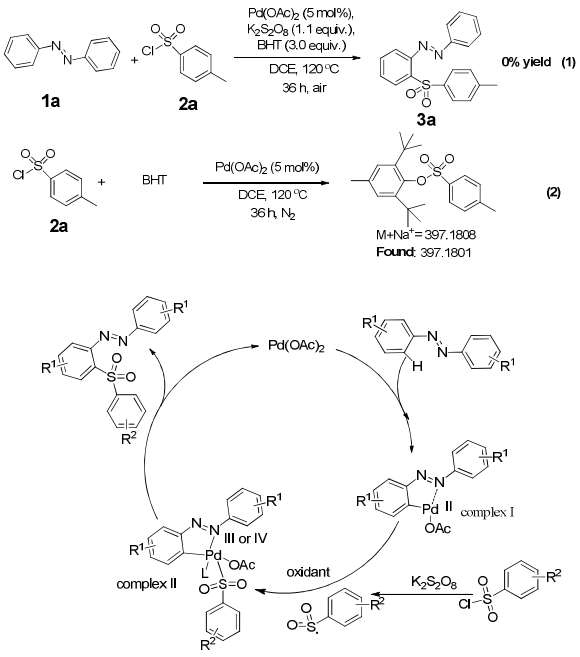


[a]Reaction conditions: azobenzene (**1a**) (0.2 mmol), *p*-tolylsulfonyl chloride (**2a**) (3.0 equiv), $Pd(TFA)_2$ (5 mol%), oxidant(1.1 equiv), solvent (2.0 mL), under air, 120 °C, 36 h, isolated yield based on **1a**. [b]48 h.

To clarify the reaction mechanism, some controlled experiments were carried out under the optimized conditions as follows: (1) Adding a radical scavenger (BHT) to the reaction mixture, this reaction was inhibited. And 3**a** was no detected (eq. 1, Scheme 2); (2) The *p*-tolylsulfonyl radical was captured by BHT in (eq. 2, Scheme 2), perhaps because $K_2S_2O_8$ and high temperature helped to activate the *p*-tolylsulfonyl

radical.[12] Based on the results obtained and literatures,[13] a radical process was suggested to be involved in this catalytic system. The possible reaction pathway was proposed and described in Scheme 2. Azobenzene **1a** firstly reacted with $Pd(OAc)_2$ to form palladacycle I through the *ortho*-C–H bond insertion, which accounted for the high regioselectivity in the reactions. Then, the palladacycle I reacted with the *p*-tolylsulfonyl radical and generated Pd(IV) or Pd(III) species II.[5a,14] Subsequently, the species II underwent reductive elimination to afford the sulfonylation product **3a**. Pd(II) was regenerated for the next catalytic cycle.

Scheme 2. Proposed Reaction Mechanism



CONCLUSION:

In summary, we have developed a Pd(II) catalyzed C-H sulfonylation of azobenzenes with arylsulfonyl chlorides. Sulfonylazobenzene series compounds were obtained smoothly by this process. This method features with a simple system, one step operation, high efficiency, atomic economy, environmental

friendliness and ligand, additives and base free conditions. Further investigations to expand the substrate scope and application such chemistry in organic synthesis are underway.

EXPERIMENT SECTION

General Information

Unless otherwise noted, all 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 ppm relative to tetramethylsilane. The multiplicity of signals was designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants, *J*, were reported in Hertz (Hz). ^{13}C NMR spectra were recorded at 100 MHz spectrometer. The chemical shifts δ were reported relative to residual $CHCl_3$ (δ_c= 77.00 ppm). High resolution mass spectra (HR-MS) were obtained on a Q-TOF spectrometer with micromass MS software using electrospray ionization (ESI). X-ray analysis was obtained with a X-ray single crystal diffractometer.

Typical procedure for the synthesis of azobenzenes

The 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. Then cooling down to room temperature and concentrating *in vacuum*, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether) to afford the desired products.[14]

Typical procedure for the synthesis of sulfonylazobenzenes:

(*E*)-1-Phenyl-2-(2-tosylphenyl)diazene (3a)*:* In the oil bath, to a 50 mL reaction tube were successively added 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). 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 (60.4mg, 90%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{17}N_2O_3S$: 353.0954, found: 353.0958.

(*E*)-1-Phenyl-2-(2-((4-(tert-butyl)phenyl)sulfonyl)phenyl)-2-phenyldiazene(3c): red solid (61.8 mg,82%); m.p. 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{22}H_{23}N_2O_2S$: 379.1475, found: 379.1475.

(*E*)-1-Phenyl-2-(2-((4-trifluoromethyl)phenylsulfonyl)phenyl)diazene(3d): red solid (70.3 mg, 90%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 166.5, 164.0, 152.6, 148.9, 138.3 (d, $J_{C\text{-}F}$ = 9.2 Hz), 138.2, 134.7, 132.2, 131.1 (d, $J_{C\text{-}F}$ = 9.5 Hz), 130.7, 129.3, 129.2, 123.6, 117.0, 116.0 (d, $J_{C\text{-}F}$ = 22.5 Hz); HR-MS (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%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{14}N_2O_2S$: 323.0849, found: 323.0855.

(*E*)-1-(2-((2-Chlorophenyl)sulfonyl)phenyl)-2-2pheny)diazene(3i): red solid (47.7 mg, 67%); m.p. 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{18}H_{14}ClN_2O_2S$: 357.0459, found: 357.0462.

(*E*)-2-((2-Phenyldiazenyl)phenyl)sulfonyl)benzonitrile (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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for

$C_{19}H_{17}N_2O_2S$: 337.1011, found: 337.1008.

(*E*)-1-(2-(Naphthalene-1-ylselfonyl)phenyl)-2-phenyldiazene(3m): red solid （64.8 mg, 87%）; m.p. 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 ppm 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; HR-MS (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%); m.p. 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 ppm 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; HR-MS (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-(trifluoromethyl)phenyl)diazene(3o): red solid (53.8 mg, 54%); m.p. 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 ppm 151.8, 150.5, 150.4, 146.6, 144.7, 141.0, 138.4, 129.8 (dd, *J* = 3.6 Hz), 129.5 (dd, *J* = 3.8 Hz), 128.2, 127.9, 126.2, 125.4, 121.7, 121.2, 118.8, 21.6; HR-MS (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%); m.p. 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– .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 ppm 166.2, 164.5, 163.7, 162.0, 149.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 145.9(d, $J_{C\text{-}F}$ = 3.8 Hz), 144.4, 141.2 (d, $J_{C\text{-}F}$ = 6.7 Hz), 138.7, 129.4, 128.2, 125.9 (d, $J_{C\text{-}F}$ = 9.1 Hz), 121.4, 121.1, 119.1(d, $J_{C\text{-}F}$ = 8.1 Hz), 116.7 (d, $J_{C\text{-}F}$ =26.1 Hz), 116.2 (d, $J_{C\text{-}F}$ =22.9 Hz), 21.6; HR-MS (ESI) ($[M+H]^+$) Calcd. for

$C_{19}H_{15}F_2N_2O_2S$: 373.0817, found: 373.0819.

(*E*)-Ethyl 4-((4-ethoxycarbonyl)phenyldiazenyl)3-tosylbenzoate (3q): red solid (62.2 mg, 65%); m.p. 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 ppm 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; HR-MS (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%); m.p. 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– .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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{21}H_{21}N_2O_4S$: 397.1217, found: 397.1218.

(*E*)-1-(3,5-Dimethyl-2-(3,5-dimethylenyl)diazene(s): red solid (47.1 mg, 60%); m.p. 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 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 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; HR-MS (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 ppm 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; HR-MS (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%) m.p. 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 ppm 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; HR-MS (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%) m.p. 138.5-139.5 ˚C; ^1H 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 ppm 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; HR-MS (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%) m.p. 170.6-171.3 ˚C; ^1H 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, 2), 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 ppm 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; HR-MS (ESI) ($[M+H]^+$) Calcd. for $C_{19}H_{16}ClN_2O_2S$: 371.0616, found: 371.0615.

(*E*)-1-(4-Chloro-2-tosylphenyl)-2phenyldiazene (3v'): red solid (14.8 mg, 20%) m.p. 182.0-183.1 ˚C; ^1H 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, 2), 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 ppm 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; HR-MS (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 liquid (30.4 mg, 43%) m.p. 169.3-170.7 ˚C; ^1H 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 ppm 166.6, 164.1, 149.5 (d, $J_{C\text{-}F}$ = 2.8), 149.3,

144.4, 139.5 (d, J_{C-F} = 62.7), 134.8, 131.0, 129.8, 129.7, 128.4, 126.3 (d, J_{C-F} = 9.1), 117.2, 116.6 (d, J_{C-F} = 22.4), 21.9; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{19}H_{16}FN_2O_2S$: 355.0911, found: 355.0914.

(*E*)-1-(4-Fluoro-2tosylphenyl)-2-phenyldiazene (3w'): red liquid (18.2 mg, 26%) m.p. 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 ppm 164.9, 162.4, 145.7, 144.7, 141.7 (d, J_{C-F} = 6.6), 139.1, 132.4, 129.8, 129.5, 128.8, 124.1, 121.6 (d, J_{C-F} = 22.5), 119.5 (d, J_{C-F} = 80.7), 117.1(d, J_{C-F} = 26.0), 21.9; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{19}H_{16}FN_2O_2S$: 355.0911, found: 355.0912.

(*E*)-Ethyl-4-((2-tosylphenyl)diazenly)benzoate (3x): red solid (34.2 mg, 42%) m.p. 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 ppm 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; HR-MS (ESI) ([M+H]$^+$) Calcd. for $C_{22}H_{21}N_2O_4S$: 409.1217, found: 409.1220.

(*E*)-Ethyl-4-((2-tosylphenyl)diazenly)benzoate (3x'): red solid (17.4 mg, 21%) m.p. 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 ppm 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; HR-MS (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** are available free of charge *via* the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cuixl@zzu.edu.cn.

*E-mail: wyj@zzu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge NSF of China (21102133, 21172200) for financial support.

REFERENCES

(1) For the application of sulfonylazobenzenes, see: (a) Takakuwa, H.; Araki, K.; Mizukawa, Y. U.S. Patent 20060251976 A1 20061109, **2006**. (b) Anderson, R. G.; Nickless, G. *Analyst* **1968**, *93*, 13. (c) Anderson, R. G.; Nickless, G. *Analyst* **1967**, *92*, 207. (d) Salpin, F.; Trivier, F.; Lecomte, S.; Coupry, C. *J. Raman. Spectrosc.* **2006**, *37*, 1403. (e) Hua, W. G. Patent CN. 101397426 A 20090401, **2009**. (f) Uhlir-Tsang, L. C.; McGorrin, M. A.; Moffatt, J. R. U.S. Patent 20060233976 A1 20061019, **2006**. (g) Yang, Z. A.; Ai, J. L.; Shang, L. J.; Cui, A. G.; Li, M. Y.; Li, H. L.; Jiang, M. L. Patent CN 101665629 A 20100310, **2010**. (h) Alexander, M.; Rainer, H.; Siro, D. N. Patent WO 2013/087400 A2 20130620, **2013**. (i) Jenkins, J. L.; Shapiro, R. *Biochemistry* **2003**, *42,* 6674. (j) Latham, G. J.; Winkler, M. M.; Pasloske, B. L.; Kudlicki, W. A. U.S. Patent 20050014169 A1 20050120, **2005**. (k) Hopkins, S. C.; Vale, R. D.; Kuntz, I. D. *Biochemistry* **2000**, *39,* 2805. (l) Shapiro, R.; Jenkins, J. L.; Latham, G. J. Patent WO 2004/076640 A2 20040910, **2004**. (m) Kao, R. Y. T.; Jenkins, J. L.; Olson, K. A.; Key, M. E.; Fett, J. W.; Shapiro, R. *PANS.* **2002**, *99*, 10666. (n) Ciullini, I.; Gullotto, A.; Tilli, S.; Sannia, G.; Basosi, R.; Scozzafava, A.; Briganti, F. *Appl. Microbiol. Biotechnol.* **2012**, *96*, 395. (o) Dziomko, V. M.; Dunaevskaya, K. A. *Zhurnal Obshchei Khimii* **1961**, *31*, 3385. (p) Giuseppe, L.; Amerigo, R. *Annali*

di Chimica **1956**, *46*, 296-306. (q) Worth, A. F.; Kenneth, L. *Trans. Kansas Acad. Sci.* **1932**, *35*, 146. (r) Huang,J. M.; J. Kuo, F.; Chen, C. Y. *J. Appl. Polym. Sci.*, **1995**, *55*, 1217. (s) Dieter, M.; Rudolf, H.; Hansrudolf, S. Patent EP 42357 A2 19811223. **1981.**

(2) Bauer, H.; Bedford, G. R.; Katritsky, A. R. *J. Chem. Soc.* **1964**, 751.

(3) For the transition metal-catalyzed sulfonylation reactions, see: (a) Cacchi, S.; Fabrizi, G.; Goggiamani, A.; Parisi, L. M.; Bernini, R. *J .Org. Chem.* **2004**, *69*, 5608. (b) Tang, X.; Huang, L.; Xu, Y.; Yang, J.; Wu, W.; Jiang, H. *Angew.Chem., Int. Ed.,* **2014**, *53*, 4205. (c) Zhou, X. Y.; Luo, J. Y.; Liu, J.; Peng, S. M.; Deng, G. J. *Org. Lett.,* **2011**, *13*, 1432. (d) Yuan, Y. Q.; Guo, S. R. *Synlett*. **2011**, *18*, 2750. (e) Gamelas, C. A.; Lourenço, T.; Costa, A. P. D.; Simplício, A. L.; Royo, B.; Romão, C. C. *Tetrahedron Lett*. **2008,** *49*, 4708. (f) Wei, W.; Liu, C. L.; Yang, D. S.; Wen, J. W.; You, J. M.; Suo, Y. R.; Wang, H.; *Chem. Commun*. **2013**, *49*, 10239. (g) Zhao, X. D.; Dimitrijevic, E.; Dong, V. M. *J. Am. Chem. Soc*. **2009**, *131*. 3466. (h) Saidi, O.; Marafie, J.; Ledger, A. E. W.; Liu, P. M.; Mahon, M.F.; Köhn, G. K.; Whittlesey, M. K.; Forst, C. G. *J. Am. Chem. Soc*. **2011**, *133*. 19298. (i) Wu, Z. Y.; Song, H. Y.; Cui, X. L.; Pi, Chao.; Du, W. W.; Wu, Y. J. *Org. Lett.* **2013**, *15*. 1270. (j) Xu, Y. H.; Wang, M.; Lu, P.; Loh, T. P. *Tetrahedron* **2013**, *69*, 4403. (k) Wang, X. B.; Xue, L. J.; Wang, Z. Y. *Org. Lett.* **2014**, *16*. 4056. (l) Johnson, M. W.; Bagley, S. W.; Mankad, N. P.; Bergman, R. G.; Mascitti, V.; Toste, F. D. *Angew. Chem., Int. Ed.* **2014**, *53*, 4404. (m) Richards-Taylor, C. S.; Blakemore, D. C.; Willis, M. C. *Chem. Sci.* **2014**, *52*, 12679.

(4) Ma, X. T.; Tian, S. K. *Adv. Synth. Catal.* **2013**, *355*, 337.

(5) (a) Song, H. Y.; Chen, D.; Pi, C.; Cui, X. L.; Wu, Y. J. *J. Org. Chem.* **2014**, *79*, 2955. (b) Li, H. J.; Li, P. H.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 9170. (c) Li, Z. Y.; Li, D. D.; Wang, G. W. *J. Org. Chem.* **2013**, *78*, 10414. (d) Xiong, F.; Qian, C.; Lin, D. E.; Zeng, W.; Lu, X. X. *Org. Lett*. **2013**, *15*, 5444. (e) Li, H. J.; Li, P. H.; Wang, L. *Org. Lett.* **2013**, *15*, 623. (f) Tang, H.; Qian, C.; Lin, D. E.; Jiang, H. F.; Zeng, W. *Adv. Synth. Catal.* **2014**, *356*, 519.

(6) Miyamura, S.; Tsurugi, H.; Satoh, T.; Miura, M. *J. Organomet. Chem*. **2008**, *693*, 2438.

(7) (a) Yin, Z. W.; Jiang, X. Q.; Sun, P. P. *J. Org. Chem.* **2013**, *78*, 10002. (b) Shi, S.; Kuang, C. *J. Org. Chem.* **2014**, *79*, 6105.

(8) (a) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126 ,* 2300. (b) Tato, F.; García-Domínguez, A.; Cárdenas, D. J. *Organometallics* **2013**, *32*, 7487. (c) Kocher, B. C.; Weder, C.; Smith, P. *Adv. Funct. Mater.* **2003**, *13*, 427.

(9) Jia, X. F.; Han, J. *J. Org. Chem.* **2014**, *79*, 4180.

(10) (a) Takagi, K.; Al-Amin, M.; Naoyuki Hoshiya, N.; Wouters, J.; Sugimoto, H.; Shiro, Y.; Fukuda, H.; Shuto, S.; Arisawa, M. *J. Org. Chem.* **2014**, *79*, 6366; (b)Jo, J. Y.; Lee, H. Y.; Liu, W. J.; Olasz, A.; Chen, C. H.; Lee, D. *J. Am. Chem. Soc.* **2012**, *134*, 16000. (c) Zhao, D. B.; Wu, Q.; Huang, X. L.; Song, F. J.; Lv, T. Y.; You, J. *S. Chem. Eur. J.* **2013**, *19*, 6239. (d) Muralirajan, K.; Cheng, C. H. *Chem. Eur. J.* **2013**, *19*, 6198. (e) Alberti, A.; Bedogni, N.; Benaglia, M.; Leardini, R.; Nanni, D.; Pedulli, G. F.; Tundo, A.; Zanardi, G. *J. Org. Chem.* **1992**, *57*, 607. (f) Huang, X. L.; Chen, X. Y.; Ye, S. *J. Org. Chem.* **2009**, *74*, 7585. (g) Mochalov, S. S.; Khasanov, M. I.; Fedotov, A. N.; Trofimova, E. V. *Chem. Heterocycl Compd.* **2008**, *44*, 229. (h) Han, W. J.; Zhang, G. Y.; Li, G. X.; Huang, H. M. *Org. Lett.* **2014**, *16*, 3532.

(11) CCDC-1010067 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www. ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK.; deposit@ccdc.cam.ac.uk).

(12) (a) Siddaraju,Y.; Lamani, M.; Kandikere Ramaiah Prabhu, K. R. *J. Org. Chem.* **2014**, *79*, 3856. (b) Chawla, R.; Singh, A. K.; Yadav, L. D. S. *Eur. J. Org. Chem.* **2014**, 2032. (c) Xie, P.; Liu, X.; Cheng, R.; Wu, Y. P.; Deng, J. P. *Ind. Eng. Chem. Res.* **2014**, *53*, 8069. (d) Minisci, F. *Acc. Chem. Res.* **1975**, *8*, 165.

(13) (a) Chen, X.; Engle, K. M.; Wang, D. H.; Yu, J. Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094; (b) Xu, L. M.; Li, B. J.; Yang, Z.; Shi, Z. J.; *Chem. Soc. Rev.* **2010**, *39*, 712. (c) Engle, K. M.; Mei, T. S.; Wasa, M.; Yu, J. Q.; *Acc. Chem. Rev.*

2012, *45*, 788. (d) Powaers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009,** *131*, 17050. (e) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974.

(14) (a) Qian, C.; Lin, D. E.; Deng, Y. F.; Zhang, X. Q.; Jiang, H. F. Miao, G.; Tang, X. H.; Zeng, W. *Org. Biomol. Chem.* **2014**, 12, 5866. (b) Zhang, M. L.; Zhang, S. H.; Liu, M. C.; Cheng, J. *Chem. Commun.* **2011**, 47, 11522.