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Palladium-catalyzed direct *ortho*-sulfonylation of azobenzenes with arylsulfonyl chlorides *via* C-H activation

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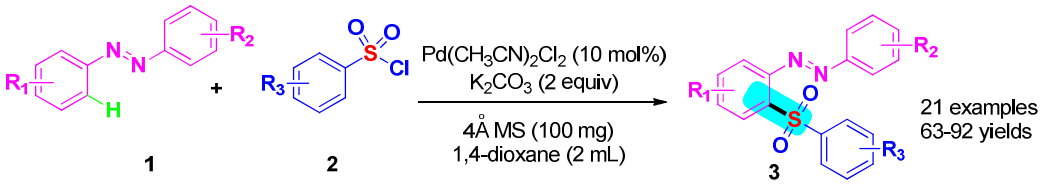
Ortho-sulfonylated azobenzenes were obtained in moderate to high yields by direct ortho-sulfonylation of azobenzenes C-H bond with arylsulfonyl chlorides.



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ARTICLE TYPE

Palladium-catalyzed direct *ortho*-sulfonylation of azobenzenes with arylsulfonyl chlorides *via* C–H activation

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A highly efficient and practical procedure to direct *ortho*-sulfonylation of azobenzenes C-H bond with arylsulfonyl chlorides has been developed. The method was available for both electron-rich and electron-deficient substrates which have good yields for 21 examples. This reaction provides a convenient access to *ortho*-sulfonylated azobenzenes under mild conditions.

Introduction

Transition-metal-catalyzed C-C and C–heteroatom bonds formation *via* C-H bond activation have been broadly explored because it is an efficient method to construct heterocyclic compounds.[1] Recently, more and more effort has been made to develop many techniques to control the reaction selectivity assistance of a directing group. Among them, such as 2-aryloxypyridines[2], quinoline *N*-Oxide[3], arylpyrazoles[4], triazene azoxybenzenes[5], quinoline[6], and 2-aryl-1,2,3-triazoles group[7], etc. were proved to be a versatile directing group to obtain the high regioselectivity on the *ortho*-C(sp^2)-H bond. In recent years, the azobenzenes work as directing group to accelerate the C-H activation/functionalization process have attracted more attentions. For example, many groups have developed a palladium-catalyzed regioselective C-H bond activation of azoarenes and related compounds with a alcohols[8], toluene[9], aldehydes[10], and a-oxocarboxylic acids[11] to synthesis *ortho*-acylazoarenes. But, Sun and co-workers find they get *ortho*-alkoxyazoarenes when $PhI(OAc)_2$ has been added as the oxidant in this reaction.[12] Also, Hao and Li's group have developed a highly efficient method to synthesis of diverse cinnolines and isoquinolines through the rhodium-catalyzed oxidative C-H activation of azobenzenes and ketazines with alkynes. [13] Similarly, azobenzenes derivatives such as *ortho*-acyloxyazoarenes[14], *ortho*-Sulfonamideazoarenes[15], and *ortho*-arylazoarenes[16] have been synthesized by this method.

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† Electronic Supplementary Information (ESI) available: ^1H NMR spectra, ^{13}C NMR spectrum, GC/MS profile, HRMS profile. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Aryl sulfones have attracted considerable interests for their are essential components in medicinal chemistry[17], synthetic intermediate [18] and advanced organic materials.[19] The increasing applications of sulfones have stimulated investigations on development of efficient processes for the synthesis of these compounds. For example, Xu reported a method of palladium-catalyzed direct sulfonylation of 2-aryloxypyridines on the *ortho*-position of the benzene ring using 2-pyridyloxyl as the directing group and sulfonyl chlorides as sulfonylation reagents.[20] Saidi has developed an efficient *meta* sulfonation of 2-phenylpyridines in the presence of ruthenium(II) complexes.[21] Zhao disclosed a method of palladium-catalyzed direct sulfonylation of 2-arylpyridines on the *ortho*-position of the benzene ring using 2-arylpyridine as the directing group.[22] Wu's group reported Pd(II)-catalyzed C-H sulfonylation of azobenzenes with arylsulfonyl chlorides using $K_2S_2O_8$ as oxidant.[23]

As a part of our continuing efforts in C-H bond activation reaction, we have recently developed many methods to formation C-S, C-C bonds.[24] Based on these findings, we develop 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

We initiated our investigation on the model reaction of azobenzene (**1a**) with *p*-tolylsulfonyl chloride (**2a**) to optimize the reaction parameters (Table1). To our delight, the C_2-sulfonylation took place in the presence of $Pd(OAc)_2$(10 mol%) and K_2CO_3 (2 equiv) in DMSO under air for 12 h, affording compound **3a** in 41% yield (entry 1, Table1). Without catalyst, the reaction could not take place at all. Thus, $PdCl_2$, $[PdCl(allyl)]_2$, $Pd(COD)Cl_2$, $Pd(CH_3CN)_2Cl_2$, CuI and CuCl were tested to catalyze this reaction, in which $Pd(CH_3CN)_2Cl_2$ gave the

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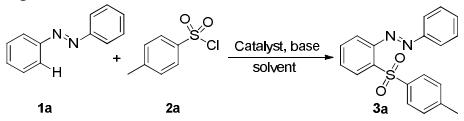
best result (entries 1-7, Table1). K_2CO_3 was superior to other bases, such as Na_2CO_3, KOAc, NaOAc, $CsCO_3$, $NaHCO_3$ and KF (entries 8-13, Table1). The solvent also played an important role in the reaction. Solvents such as DMF, NMP, CH_3CN, 1,4-dioxane, toluene, and DMSO were screened, and 1,4-dioxane was found to be superior to the others (entries 5 and 14-18), affording **3a** in 92% yield (entry 17, Table1). The yield decreased to 73% when the catalyst loading was reduced to 5mol % from 10 mol % (entry 19, Table1). After surveying a variety of catalysts, bases, solvents, and catalyst loadings, we found that the combination of 10 mol % of $Pd(CH_3CN)_2Cl_2$ and 2 equiv of K_2CO_3 in 1,4-dioxane at 130 °C for 12 h served as the optimal conditions for this transformation. These results indicated that this transformationwas facile and practical, as it did not require the use of strong bases, and the oxidants exclusion of air.

Table 1. Optimization of Reaction Conditions.[a]



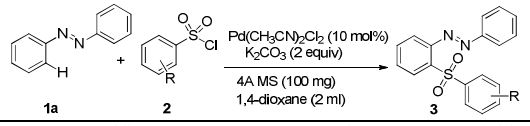
1a 2a 3a

Entry	Catalyst	Base	Solvent	Yield(%)[b]
1	$Pd(OAc)_2$	K_2CO_3	DMSO	41
2	$PdCl_2$	K_2CO_3	DMSO	33
3	$[PdCl(allyl)]_2$	K_2CO_3	DMSO	39
4	$Pd(COD)Cl_2$	K_2CO_3	DMSO	15
5	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	DMSO	77
6	CuI	K_2CO_3	DMSO	N.R.
7	CuCl	K_2CO_3	DMSO	N.R.
8	$Pd(CH_3CN)_2Cl_2$	Na_2CO_3	DMSO	40
9	$Pd(CH_3CN)_2Cl_2$	KOAc	DMSO	31
10	$Pd(CH_3CN)_2Cl_2$	NaOAc	DMSO	35
11	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	DMSO	44
12	$Pd(CH_3CN)_2Cl_2$	$NaHCO_3$	DMSO	23
13	$Pd(CH_3CN)_2Cl_2$	KF	DMSO	31
14	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	DMF	45
15	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	NMP	67
16	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	CH_3CN	73
17	**$Pd(CH_3CN)_2Cl_2$**	**K_2CO_3**	**dioxane**	**92**
18	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	toluene	21
19	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	dioxan	73[c]

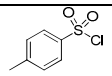
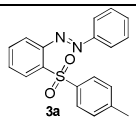
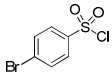
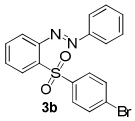
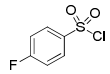
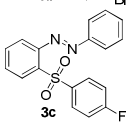
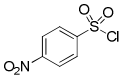
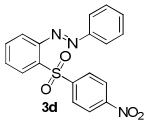
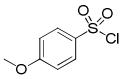
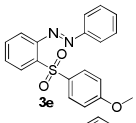
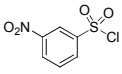
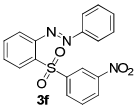
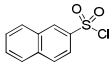
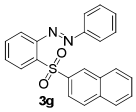
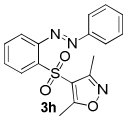
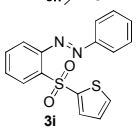
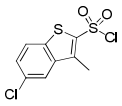
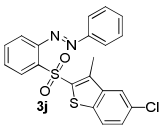
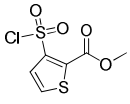
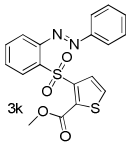
[a] Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 equiv), catalyst (10 mol %), base (2.0 equiv), 4A MS (100 mg) and solvent (2.0 mL) under air at 130 °C for 12 h, unless otherwise noted. [b]Isolated yields. [c] $Pd(CH_3CN)_2Cl_2$ (5 mol %).

With the optimized reaction conditions in hand, the reactivities of different arylsulfonyl chlorides as the sulfonylation reagents were investigated. The results are revealed in Table 2, the C-H sulfonylation of azobenzene (**1a**) with arylsulfonyl chlorides could proceed smoothly and furnish the corresponding ortho-substituted products **3a-n** in 63-92% yields (Table2, entries 1-14). The substrates with a *para*-electron-donating group afforded the products **3a , 3g , 3n** in excellent yields (92% , 84% and 91%). When arylsulfonyl chlorides were substituted at the *para* position with a electron-withdrawing group (such as 4-F, 4-Br, 4-methoxy, 4-Cl groups) there also afforded the products **3b**, **3c**, **3d** and **3m** in good yields (75-86%). But the substrates with a strong electron-withdrawing group (-NO_2) on *para* and *meta* position provided the corresponding product **3d** , **3f** in low yields(67%, 63%). Heteroarysulfonyl chlorides, such as 3,5-dimethyl-isoxazole-4-sulfonyl chloride, thiophene-2-sulfonyl chloride, 5-chloro-3-methylbenzo[b]thiophene-2-sulfonyl chloride, and methyl 2-(chlorosulfonyl)thiophene-3-carboxylate were tested as the substrates. The corresponding *ortho*-sulfonylation products **3h**, **3i**, **3j**, and **3k** were obtained in good yields (73-90%).

Table 2. Preparation of Sulfones from Various Sulfinates[a]



1a 2 3

Entry	Sulfinates	Product	Yield(%)[b]
1		 3a	92
2		 3b	76
3		 3c	86
4		 3d	67
5		 3e	75
6		 3f	63
7		 3g	84
8		 3h	90
9		 3i	87
10		 3j	89
11		 3k	73

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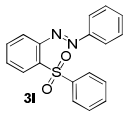
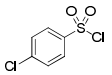
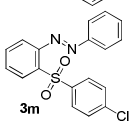
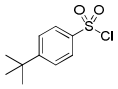
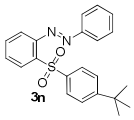
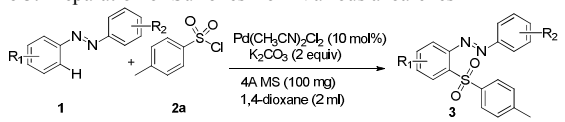
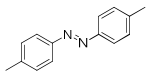
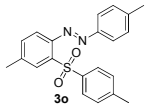
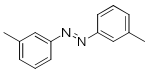
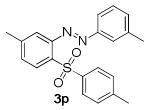
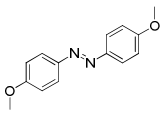
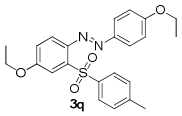
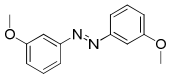
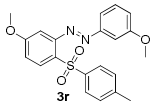
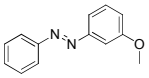
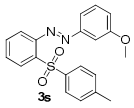
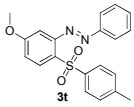
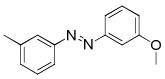
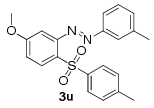
12		 3l	90
13		 3m	82
14		 3n	91

[a] Reaction conditions:**1a** (0.5 mmol), **2** (0.6 equiv), catalyst (10 mol %), base (2.0 equiv), 4A MS (100 mg) and solvent (2.0 mL) under air at 130 °C for 12 h, unless otherwise noted. [b] Isolated yields.

Table 3. Preparation of Sulfones from Various azoarenes [a]



1 2a 3

Entry	Azoarenes	Product	Yield(%)[b]
1		 3o	86
2		 3p	75
3		 3q	83
4		 3r	85
5		 3s	15
6		 3t	71
7		 3u	81

[a] Reaction conditions:**1a** (0.5 mmol), **2** (0.6 equiv), catalyst (10 mol %), base (2.0 equiv), 4A MS (100 mg) and solvent (2.0 mL) under air at 130 °C for 12 h, unless otherwise noted. [b] Isolated yields.

After screening of different arylsulfonyl chlorides, we explored the scope of differently substituted azobenzenes. Representative azoxybenzenes were firstly synthesized and examined. The results are shown in table 3. It was found that these electron-rich azobenzenes gave higher yields than those electron-deficient azobenzenes. For instance, the reactions of 4,4'-dimethyl-azoxybenzene, 3,3'-dimethylazoxybenzene, 4,4'-di methoxy azoxybenzene, 3,3'-di methoxy azoxybenzene, provided the corresponding products in 75-86% yields **(3o-3r)**. The reactions of unsymmetrical azobenzenes also proceeded smoothly and gave the products which could be determined by ^{1}H NMR, were obtained in good yields (71% for **3t**; 78% for **3u**, respectively).

A single crystal of **3b** was obtained from trichloromethane. Its crystal structure (Fig. 1) exhibited that such palladium-catalyzed direct sulfonylation of azobenzene on the *ortho*-position. The crystal data, refinement parameters, bond lengths and bond angles are given in the **Table S1**.

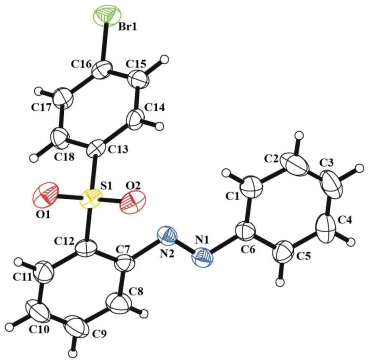
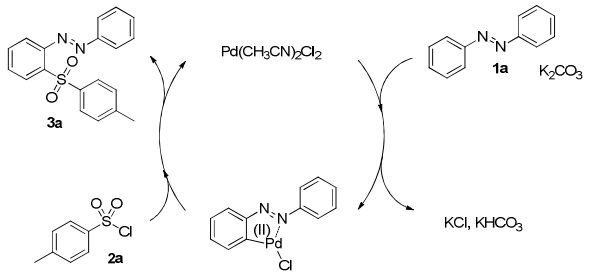


Fig 1 ORTEP diagram of catalyst **3b** showing atomlabelling scheme. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability.



Scheme 1. Plausible Reaction Mechanism

In addition, when some radical scavengers such as TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or HQ (Hydroquinone) were used in this C-S coupling reaction, the reaction can be carried out smoothly. So this experiment can exclude the free radical mechanism. On the basis of thses results and other previous related studies,[19-22] a plausible reaction mechanism of this palladium-catalyzed sulfonylation of an azobenzene compounds is proposed, as shown in Scheme 1. Step (i) , azobenzene **1a** firstly reacts with $Pd(CH_3CN)_2Cl_2$ to form a cyclopalladated (II) intermediate through *ortho*-C-H bond insertion. In step (ii), the sulfonylation could go through a direct displacement-type reaction to give the final product **3a**. Meanwhile, the Pd(II) was regenerated for the next catalytic cycle.

Conclusions

In conclusion, we have developed a palladium-catalyzed direct C(sp^2)-H sulfonylation of azobenzene with arylsulfonyl Chlorides. The reaction exhibits a good tolerance for a broad range of general functional groups. The present work demonstrated the utility of azobenzene as a removable directing group through the

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direct C-H bond activation/functionalization and deprotecting group to form *ortho*-sulfonylated azobenzenes.

Experimental section

General information

All reactions were run under argon in Schlenk tubes using vacuum lines. DMF, NMP, CH_3CN, 1,4-dioxane, toluene, and DMSO, analytical grade were not distilled before use. Commercial arylsulfonyl chlorides and azobenzenes were used without purification. ^{1}H NMR, ^{13}C NMR spectra were recorded using a 500 MHz spectrometer in $CDCl_3$ and DMSO with shifts referenced to $SiMe_4$ ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using LC-MS and HRMS (ESI-TOF analyzer) equipment.

General procedure for preparation of azoxybenzenes

All of the azo-compounds were prepared from arylamines, according to the literature.[1] Mix CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), arylamines (93 mg, 1 mmol) in toluene (4 ml) under air (1 atm). The reaction mixture was vigorously stirred at 60 °C for 20 h. After 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 azo-compound.

General procedure for Palladium-Catalyzed Direct ortho-Sulfonylation of Azobenzenes with Arylsulfonyl Chlorides via C-H Activation

Mix azoic compound (0.5equiv), benzene sulfonyl chloride (0.6equiv), $Pd(CH_3CN)_2Cl_2$ (10 mol%), K_2CO_3 (2 equiv), 4A MS (100 mg) in 1,4-dioxane (2 ml) under air. The reaction mixture was vigorously stirred at 130 °C for 12 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford corresponding product.

Diazene. (1a)[1]

(*E*)-1,2-di-*p*-tolyldiazene.

Obtained as a yellow solid in 90% yield; M.p. 138-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 4H), 7.30 (d, J = 8.0 Hz, 4H), 2.42 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.85, 141.22, 129.73, 122.75, 21.50. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2$: $[M+H]^+$ 211.123, Found 211.1032.

(*E*)-1,2-di-*m*-tolyldiazene

Obtained as a yellow solid in 87% yield; M.p. 123-124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.40 – 7.34 (m, 2H), 7.25 (d, J = 7.0 Hz, 2H), 2.42 (d, J = 3.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.87, 139.00, 131.75, 128.95, 122.97, 120.54, 21.43. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2$: $[M+H]^+$ 211.123, Found 211.1034.

(*E*)-1,2-bis(4-ethoxyphenyl)diazene.

Obtained as a yellow solid in 92% yield; M.p. 150-151 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 6.98 (d, J = 8.9 Hz, 4H), 4.10 (q, J = 7.0 Hz, 4H), 1.44 (t, J = 7.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.01, 146.93, 124.36, 114.66, 63.79, 14.80.HRMS (ESI+): Calculated for $C_{16}H_{18}N_2O_2$: $[M+H]^+$ 270.1368, Found 271.1373.

(*E*)-1,2-bis(3-methoxyphenyl)diazene.

Obtained as a yellow solid in 85% yield; M.p. 70-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (ddd, J = 7.8, 1.6, 0.9 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.36 (t, J = 8.0 Hz, 2H), 6.98 (ddd, J = 8.2, 2.6, 0.8 Hz, 2H), 3.83 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 159.31, 152.79, 128.76, 116.85, 116.14, 104.69, 54.46. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_2$: $[M+H]^+$ 243.1128, Found 243.0686.

(*E*)-1-(3-methoxyphenyl)-2-phenyldiazene.

Obtained as a yellow solid in 60% yield; M.p.30-31 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.57 – 7.41 (m, 6H), 7.07 – 7.02 (m, 1H), 3.90 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.34, 153.91, 152.61, 131.05, 129.80, 129.11, 122.89, 117.83, 117.14, 105.74, 55.50. HRMS (ESI+): Calculated for $C_{13}H_{12}N_2O_1$: $[M+H]^+$ 213.1022, Found 213.061.

(*E*)-1-(3-methoxyphenyl)-2-(*m*-tolyl)diazene.

Obtained as a yellow liquid in 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 5.8 Hz, 2H), 7.55 (ddd, J = 7.8, 1.5, 1.0 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.41 (dd, J = 16.4, 8.3 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.03 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.45 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.32, 153.94, 152.68, 138.99, 131.83, 129.76, 128.91, 122.93, 120.55, 117.72, 117.04, 105.69, 55.47, 21.37. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_1$: $[M+H]^+$ 227.1179, Found 227.075.

(*E*)-1-phenyl-2-(2-tosylphenyl)diazene. (3a)

Obtained as a white solid in 78% yield; M.p. 157-158 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J = 7.7, 1.5 Hz, 1H), 7.86 – 7.80 (m, 4H), 7.65 (dtd, J = 22.0, 7.5, 1.4 Hz, 2H), 7.58 (dd, J = 7.7, 1.3 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.16 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.72, 149.07, 143.91, 139.43, 138.88, 134.35, 131.97, 130.54, 129.35, 129.29, 129.11, 128.20, 123.77, 116.90, 21.51. HRMS (ESI+): Calculated for $C_{23}H_{18}N_2O_3S$: [M+H]+ 336.0916, Found 337.0989.

(*E*)-1-(2-((4-bromophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3b)

Obtained as a orange solid in 66% yield; M.p. 200-201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, J = 7.8 Hz, 1H), 7.84 – 7.78 (m, 4H), 7.71 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.5 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.52 – 7.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.68, 148.96, 141.34, 138.17, 134.82, 132.20, 131.96, 130.71, 129.78, 129.42, 129.23, 128.20, 123.67, 117.06. HRMS (ESI+): Calculated for $C_{18}H_{13}BrN_2O_2S$: $[M+Na]^+$ 422.9773, Found 422.9178.

(*E*)-1-(2-((4-fluorophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3c)

Obtained as a orange solid in 86% yield; M.p. 107-108 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J = 7.8, 1.4 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.83 – 7.79 (m, 2H), 7.70 (dd, J = 7.7, 1.5 Hz, 1H), 7.65 (td, J = 7.6, 1.4 Hz, 1H), 7.60 (dd, J = 7.8, 1.3 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.03 (t, J = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.69, 148.95, 138.43, 134.70, 132.16, 131.12, 131.05, 130.67, 129.35, 129.21, 123.66, 117.04, 116.01, 115.83.

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HRMS (ESI+): Calculated for $C_{18}H_{13}FN_2O_2S$: $[M+Na]^+$ 341.0755, Found 341.0211.

(*E*)-1-(2-((4-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3d)

Obtained as a pale yellow solid in 67% yield; M.p. 134-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.74 (qd, *J* = 15.1, 7.5 Hz, 4H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.57, 150.15, 148.90, 148.06, 137.29, 135.42, 132.50, 130.92, 129.65, 129.36, 123.90, 123.57, 117.21. HRMS (ESI+): Calculated for $C_{18}H_{13}N_3O_4S$: $[M+H]^+$ 368.07, Found 368.0128.

(*E*)-1-(2-((4-methoxyphenyl)sulfonyl)phenyl)-2-phenyldiazene. (3e)

Obtained as a white solid in 75% yield; M.p. 139-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.7 Hz, 1H), 7.87 (dd, *J* = 20.9, 6.6 Hz, 4H), 7.64 (dt, *J* = 21.9, 7.4 Hz, 2H), 7.55 (dd, *J* = 12.8, 6.5 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.21, 152.75, 149.02, 139.16, 134.23, 133.81, 131.95, 130.54, 129.16, 123.75, 116.92, 113.87, 55.57. HRMS (ESI+): Calculated for $C_{19}H_{16}N_2O_3S$: $[M+H]^+$ 353.0954, Found 4353.0419.

(*E*)-1-(2-((3-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3f)

Obtained as a yellow solid in 63% yield; M.p. 162-163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 3.1, 2.1 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.56 (ddd, *J* = 9.7, 5.2, 4.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.48, 148.85, 147.95, 144.55, 137.37, 135.39, 133.71, 132.55, 130.89, 130.09, 129.61, 129.39, 127.50, 123.75, 123.59, 117.29. HRMS (ESI+): Calculated for $C_{18}H_{13}N_3O_4S$: $[M+H]^+$ 368.07, Found 368.0146.

(*E*)-1-(2-(naphthalen-2-ylsulfonyl)phenyl)-2-phenyldiazene. (3g)

Obtained as a pale yellow solid in 84% yield; M.p. 139-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.64 (s, 1H), 8.57 – 8.44 (m, 1H), 8.57 – 8.46 (m, 1H), 7.86 (dd, *J* = 22.7, 8.8 Hz, 3H), 7.78 (d, *J* = 8.1 Hz, 3H), 7.70 (ddd, *J* = 9.2, 6.0, 1.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.47 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.72, 149.00, 138.98, 138.59, 134.97, 134.59, 132.01, 131.95, 130.63, 130.19, 129.46, 129.17, 129.11, 128.96, 127.87, 127.36, 123.76, 123.03, 116.89. HRMS (ESI+): Calculated for $C_{22}H_{16}N_2O_2S$: [M+H]+ 373.1005, Found 373.0445.

(*E*)-3,5-dimethyl-4-((2-(phenyldiazenyl)phenyl)sulfonyl)isoxazole. (3h)

Obtained as a white solid in 90% yield; M.p. 101-102 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (dd, *J* = 12.3, 7.0 Hz, 4H), 2.50 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.00, 157.64, 152.98, 149.64, 137.80, 135.01, 132.19, 130.43, 129.24, 129.13, 123.30, 117.89, 117.64, 13.04, 10.81. HRMS (ESI+): Calculated for $C_{17}H_{15}N_3O_3S$: [M+H]+ 342.0907, Found 342.0377.

(*E*)-1-phenyl-2-(2-(thiophen-2-ylsulfonyl)phenyl)diazene. (3i)

Obtained as a white solid in 87% yield; M.p. 100-101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.82 – 7.77 (m, 1H), 7.76 – 7.69 (m, 2H), 7.68 – 7.63 (m, 1H), 7.63 – 7.53 (m, 4H), 7.00 (t, *J* = 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.67, 149.00, 143.44, 139.35, 134.53, 134.38, 134.06, 132.12, 130.82, 129.25, 129.21, 127.23, 124.09, 116.89. HRMS (ESI+): Calculated for $C_{16}H_{12}N_2O_2S_2$: [M+H]+ 329.0413, Found 329.0336.

(*E*)-1-(2-((5-chloro-3-methylbenzo[*b*]thiophen-2-yl)sulfonyl)phenyl)-2-phenyldiazene. (3j)

Obtained as a pale yellow solid in 89% yield; M.p. 156-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.63 (m, 1H), 7.52 (q, *J* = 5.3 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 2.51 (d, *J* = 0.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.46, 149.41, 140.55, 139.83, 138.46, 137.09, 134.91, 132.15, 131.31, 130.53, 129.58, 128.98, 127.89, 124.12, 123.63, 123.21, 117.17, 12.35. HRMS (ESI+): Calculated for $C_{21}H_{15}N_2O_2S_2$: [M+H]+ 427.0336, Found 426.9721.

(*E*)-methyl3-((2-(phenyldiazenyl)phenyl)sulfonyl)thiophene-2-carboxylate. (3k)

Obtained as a pale yellow solid in 73% yield; M.p. 92-93 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.85 (d, *J* = 5.2 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.68 – 7.61 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 3.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.44, 154.45, 152.40, 151.33, 146.00, 145.89, 139.06, 134.18, 132.02, 131.79, 130.11, 130.09, 128.90, 123.69, 116.34, 52.59. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 387.0468, Found 386.9885.

(*E*)-1-phenyl-2-(2-(phenylsulfonyl)phenyl)diazene. (3l)

Obtained as a orange solid in90% yield; M.p. 149-150 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.95 (dt, *J* = 6.3, 2.0 Hz, 2H), 7.83 – 7.75 (m, 2H), 7.68 (dtd, *J* = 22.5, 7.5, 1.5 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 7.37 (dd, *J* = 10.6, 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.56, 143.29, 142.32, 138.53, 134.56, 132.96, 132.04, 130.59, 129.46, 129.11, 128.66, 128.05, 123.77, 116.92. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 356.0395, Found 357.0432.

(*E*)-1-(2-((4-chlorophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3m)

Obtained as a orange solid in 82% yield; M.p. 170-171 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.84 – 7.76 (m, 2H), 7.71 (td, *J* = 7.6, 1.5 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.57 – 7.51 (m, 3H), 7.37 – 7.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.65, 148.94, 140.76, 139.61, 138.19, 134.79, 132.17, 130.68, 129.69, 129.40, 129.20, 128.95, 123.65, 117.03. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 322.0776, Found 323.0832.

(*E*)-1-(2-((4-(*tert*-butyl)phenyl)sulfonyl)phenyl)-2-phenyldiazene. (3n)

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Obtained as a orange solid in 91% yield; M.p. 140-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.70 – 7.60 (m, 2H), 7.57 – 7.54 (m, 1H), 7.53 – 7.49 (m, 3H), 7.38 – 7.32 (m, 2H), 1.22 (d, *J* = 3.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.81, 152.66, 149.13, 139.31, 138.77, 134.40, 131.98, 130.54, 129.28, 129.07, 127.89, 125.71, 123.78, 116.92, 35.08, 31.00. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 378.1402, Found 379.1446.

(*E*)-1-(4-methyl-2-tosylphenyl)-2-(*p*-tolyl)diazene. (3o)

Obtained as a orange solid in 86% yield; M.p. 174-175 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, J = 8.1, 1.1 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.54 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.91, 147.03, 143.72, 142.46, 141.26, 139.60, 138.53, 134.88, 129.73, 129.62, 129.23, 128.14, 123.73, 116.73, 21.61, 21.53, 21.45. HRMS (ESI+): Calculated for $C_{21}H_{20}N_2O_2S$: [M+H]+ 365.1318, Found 365.076.

(*E*)-1-(5-methyl-2-tosylphenyl)-2-(*m*-tolyl)diazene. (3p)

Obtained as a white solid in 75% yield; M.p. 96-97 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.48 (d, *J* = 10.1 Hz, 6H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.80, 149.06, 145.57, 143.66, 139.72, 138.95, 135.91, 132.69, 130.96, 129.45, 129.24, 128.92, 128.04, 123.82, 121.45, 117.18, 21.62, 21.54, 21.38. HRMS (ESI+): Calculated for $C_{21}H_{20}N_2O_2S$: [M+H]+ 365.1318, Found 365.0756.

(*E*)-1-(4-ethoxy-2-tosylphenyl)-2-(4-ethoxyphenyl)diazene. (3q)

Obtained as a white solid in 83% yield; M.p. 95-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.02 – 6.99 (m, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.16 (d, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.77, 160.33, 147.13, 143.71, 142.76, 140.11, 139.61, 129.22, 128.07, 125.53, 120.75, 118.35, 114.60, 113.75, 64.55, 63.90, 21.53, 14.77, 14.65. HRMS (ESI+): Calculated for $C_{23}H_{24}N_2O_4S$: $[M+H]^+$ 425.153, Found 425.0923.

(*E*)-1-(5-methoxy-2-tosylphenyl)-2-(3-methoxyphenyl)diazene. (3r)

Obtained as a orange solid in 85% yield; M.p. 139−140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.08 (m, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.15, 160.33, 153.79, 150.71, 143.56, 140.06, 131.45, 130.97, 129.82, 129.31, 127.80, 118.86, 118.10, 116.19, 106.73, 101.29, 55.98, 55.56, 21.51. HRMS (ESI+): Calculated for $C_{21}H_{20}N_2O_4S$: [M+H]+ 397.1217, Found 397.0627.

(*E*)-1-(3-methoxyphenyl)-2-(2-tosylphenyl)diazene. (3s)

Obtained as a orange solid in 15% yield; M.p. 73−74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.37 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.07 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.42, 149.01, 143.93, 139.37, 138.70, 137.02, 134.38, 130.58, 129.80, 129.46, 129.35, 128.12, 118.76, 117.98, 116.93, 106.76, 55.56, 21.55. HRMS (ESI+): Calculated for $C_{20}H_{18}N_2O_3S$: [M+H]+ 367.1111, Found 367.0548.

(*E*)-1-(5-methoxy-2-tosylphenyl)-2-phenyldiazene.(3t)

Obtained as a orange solid in 71 % yield; M.p. 70-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.84 – 7.79 (m, 4H), 7.55 – 7.50 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.07 (m, 2H), 3.89 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.13, 152.57, 150.71, 143.54, 140.00, 132.05, 131.36, 131.11, 129.23, 129.12, 127.94, 123.84, 116.15, 101.22, 55.97, 21.51. HRMS (ESI+): Calculated for $C_{20}H_{18}N_2O_3S$: [M+H]+ 367.1111, Found 367.0548.

(*E*)-1-(5-methoxy-2-tosylphenyl)-2-(m-tolyl)diazene.(3u)

Obtained as a orange solid in 81% yield; M.p. 70-71 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.58 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.14, 152.67, 150.79, 143.48, 140.06, 138.98, 132.84, 131.35, 130.95, 129.22, 128.92, 127.89, 123.93, 121.57, 116.04, 101.19, 55.95, 21.53, 21.37. HRMS (ESI+): Calculated for $C_{21}H_{20}N_2O_3S$: [M+H]+ 381.1267, Found 381.0685.

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