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First palladium-catalyzed denitrated coupling of nitroarenes with sulfinates

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ABSTRACT

The first example of palladium-catalyzed protocol for the denitrated coupling of nitroarenes with sulfinates was developed, achieving aryl and heterocyclic sulfones in moderate to excellent yields. The cyclopalladated ferrocenylimine (I) exhibited highly catalytic activity for this transformation with low catalyst loading (0.75 mol %). The efficiency of this reaction was demonstrated by compatibility with a wide range of groups. Thus, the method represents a simple and facile procedure to access aryl and heterocyclic sulfones.

1. Introduction

Aryl sulfones and derivatives thereof, are ubiquitous structural motifs that frequently occur in synthetic intermediates and pharmacologically active compounds.[1–3] For example, they have been shown to possess antifungal, antibacterial, antitumor activities or to inhibit HIV-1 reverse transcriptase (Fig. 1).[4]

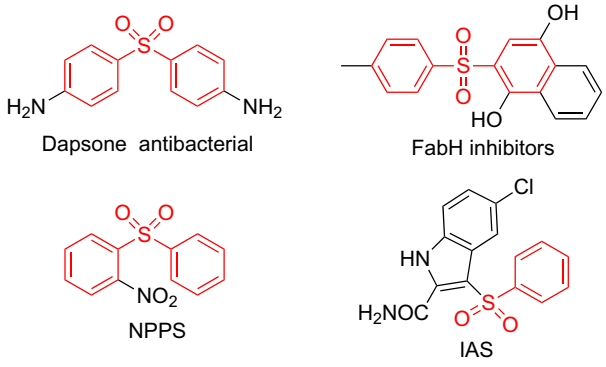

Fig. 1. Examples of important biologically active sulfones.

Traditional methods for the preparation of these compounds involve the oxidation of the corresponding sulfides, the sulfonylation of arenes,[5] the reaction of organomagnesium halides or organolithium compounds with sulfonate esters,[6] and the copper-mediated displacement reaction of nonactivated aryl iodides with arenesulfinates.[7] However, these methods suffer from drawbacks (e.g., limited substrates scope, often low yields, inferior tolerance of functional groups and use of stoichiometric amounts copper) as a result of limited application. Thus, the development of new methods for the preparation of aryl sulfones and derivatives under relatively mild reaction conditions has received much attention. Recently, some improved methods have been reported for constructing aryl sulfones and derivatives in the presence of copper, palladium and nickel catalytic systems (Scheme 1).[8] Also metal-free protocols have attracted considerable attention.[9] Generally, aryl halides or arylboronic acids are employed as coupling partners. However, some shortcomings appear with them. For example, aryl halides are not always easily available, which often involves tedious steps, harsh reaction conditions, and waste production.[10] Electron-withdrawing arylboronic acids, which are less nucleophilic, and hence transmetalate slowly, are prone to homocoupling and protodeboronation side reactions.[11] Thus, an alternative coupling partner to aryl halide or arylboronic acid is still an extremely attractive yet challenging goal.

Very recently, we have developed palladacycle-catalyzed (Fig. 2) denitrated coupling reactions of nitroarenes with arylboronic acids and phenols.[12] As a continuation of our interest in the development

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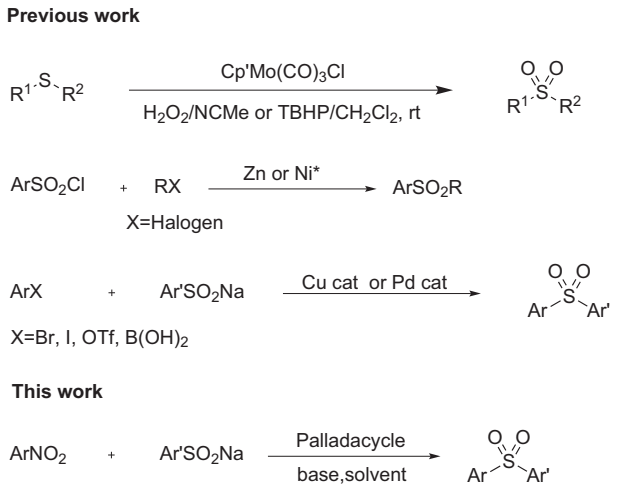
0040-4020/



Scheme 1. Synthesis of sulfones.

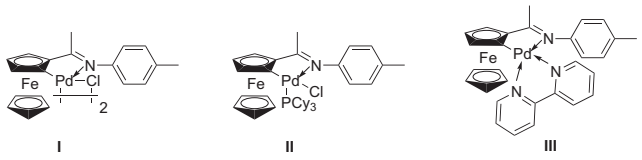


Fig. 2. Cyclopalladated ferrocenylimines.

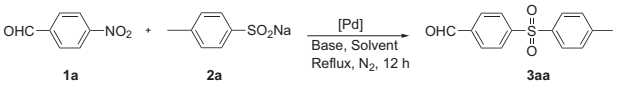
of coupling of nitroarene with various coupling partners, herein we describe a novel cyclopalladated ferrocenylimine-catalyzed denitrated coupling reaction of nitroarenes with sodium sulfinates, affording aryl sulfones and derivatives in moderate to excellent yields (Scheme 1).

2. Results and discussion

The coupling of *p*-nitrobenzaldehyde and sodium *p*-toluenesulfinate to give 4-(toluene-4-sulfonyl)-benzaldehyde **3aa** was chosen as a model reaction for initial reaction evaluation and subsequent optimization studies. To realize the selective generation of **3aa**, we initially ran a series of trial experiments in the presence of copper salts as catalysts by adjust reaction parameters. However, little or no product **3aa** was detected. We next investigated the model reaction using palladium catalysts. To our delight, when **1a** and **2a** were reacted in the presence of 10 mol % $Pd(OAc)_2$ as well as 10 mol % $PdCl_2$, employing K_2CO_3 as base and DMSO as solvent at 110 °C under nitrogen, the denitrated product **3aa** was isolated in 38% and 26% yields, respectively (Table 1, entries 1–2). We were pleased to discover that only when the model reaction was performed in the presence of the cyclopalladated ferrocenylimine (**I**) did the yield dramatically increase to 88% yield (Table 1, entries 3–5). No denitration of *p*-nitrobenzaldehyde to aryl sulfone **3aa** was observed under the reaction conditions in the absence of catalyst (Table 1, entry 6). Encouraged by this promising result, we further adjusted reaction parameters including bases and solvents.

The various reaction conditions were examined by fixing 1 mol % loading of palladacycle **I**. Screening revealed that the use of K_2CO_3 as base achieved the best result. Other bases, including Cs_2CO_3, Et_3N, NaOH, Quinoline, *t*-BuONa, Na_2CO_3 and K_3PO_4 were less efficient (Table 1, entries 7–13). With these partially optimized denitrated conditions, the effects of the solvents were investigated (Table 1, entries 14–20). The solvent also played an important role for this kind of reaction. The results revealed that the use of DMSO

Table 1
Optimization of reaction conditions[a]



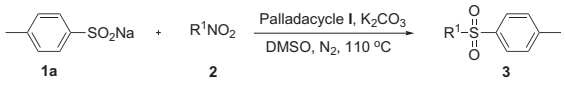
Entry	Catalyst	Base	Solvent	Yield (%)[b]
1[c]	$Pd(OAc)_2$	K_2CO_3	DMSO	38
2[d]	$PdCl_2$	K_2CO_3	DMSO	26
3	Palladacycle (**I**)	K_2CO_3	DMSO	88
4[e]	Palladacycle (**II**)	K_2CO_3	DMSO	84
5[f]	Palladacycle (**III**)	K_2CO_3	DMSO	73
6	—	K_2CO_3	DMSO	0
7	Palladacycle (**I**)	Na_2CO_3	DMSO	79
8	Palladacycle (**I**)	K_3PO_4	DMSO	73
9	Palladacycle (**I**)	Cs_2CO_3	DMSO	63
10	Palladacycle (**I**)	Et_3N	DMSO	40
11	Palladacycle (**I**)	NaOH	DMSO	0
12	Palladacycle (**I**)	Quinoline	DMSO	16
13	Palladacycle (**I**)	*t*-BuONa	DMSO	0
14	Palladacycle (**I**)	K_2CO_3	Toluene	0
15	Palladacycle (**I**)	K_2CO_3	Dioxane	0
16	Palladacycle (**I**)	K_2CO_3	DMF	75
17	Palladacycle (**I**)	K_2CO_3	DMAC	51
18	Palladacycle (**I**)	K_2CO_3	NMP	0
19	Palladacycle (**I**)	K_2CO_3	H_2O	0
20[g]	Palladacycle (**I**)	K_2CO_3	DMSO/H_2O	0
21[h]	Palladacycle (**I**)	K_2CO_3	DMSO	88

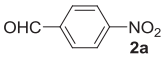
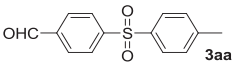
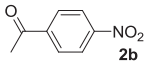
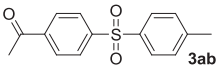
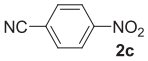
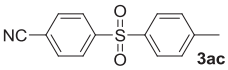
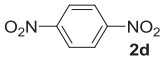
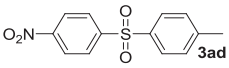
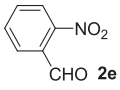
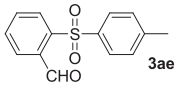
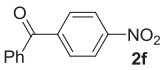
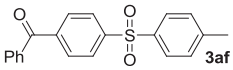
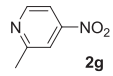
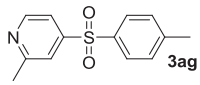
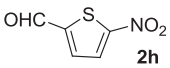
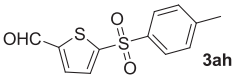
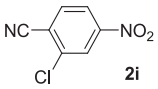
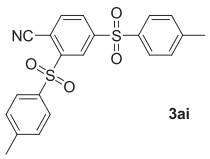
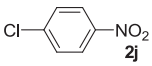
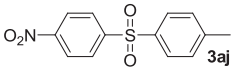
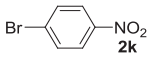
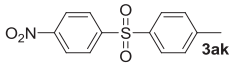
[a] Unless otherwise noted, the reaction conditions were as follows: 4-nitrobenzaldehyde (0.3 mmol), sodium *p*-toluenesulfinate (2 equiv), palladacycle (**I**) (1 mol %), base (1 equiv) and solvent (2 mL), 12 h, 110 °C, under N_2.
[b] Isolated yields.
[c] $Pd(OAc)_2$ (10 mol %).
[d] $PdCl_2$ (10 mol %).
[e] Palladacycle (**II**) (1 mol %).
[f] Palladacycle (**III**) (1 mol %).
[g] DMSO (1 mL), H_2O (1 mL).
[h] Palladacycle (**I**) (0.75 mol %).

as solvent achieved the best result (Table 1, entry 3 vs 14–19). Other solvents, including DMF, DMAC, toluene, dioxane, NMP and H_2O, did not favor this reaction. Unfortunately, no desired product was obtained when the reaction was carried out by employing H_2O as a cosolvent in addition to DMSO (1:1) (Table 1, entry 20). Furthermore, we were pleased to discover that the loading of palladacycle **I** could be reduced to 0.75 mol % with no significant change in yield (Table 1, entry 21).

Having the optimized reaction conditions in hand, we next investigated the scope and generality of the coupling reaction using sodium *p*-toluenesulfinate (**1a**) with various nitroarenes and the results were summarized in Table 2. Generally, nitroarenes containing electron-withdrawing groups (e.g., formacyl, acetyl, benzoyl and cyano) on the phenyl ring afforded the corresponding products in moderated to excellent yields under the standard reaction conditions (Table 2, entries 1, 2, 3, 5, 6 and 9). Also the results demonstrated that the reaction was not significantly affected by the steric effect of the nitroarenes (Table 2, entry 1 vs 5). For example, the coupling of **1a** with *ortho*- and *para*-nitroarenes proceeded smoothly, affording the corresponding products **3aa**, **3ae** in 88% and 87% yields, respectively. Intriguingly, the mono-coupling product **3ad** was selectively produced in 85% yield when 1,4-dinitrobenzene was employed as a coupling partner (Table 2, entry 4). It would be specially mentioned that heterocyclic nitroarene, such as 2-methyl-4-nitropyridine and 5-nitro-thiophene-2-carbaldehyde are good partners for this coupling reaction, and afforded the desired product in 90% and 68% yields (Table 2, entries 7–8). However, nucleophilic displacement of the chloro and bromo groups with sodium *p*-toluenesulfinate was observed when **2j** and **2k** were used under the standard conditions, affording 1-methyl-4-[(4-nitrophenyl)sulfonyl]-benzene in 83% and 88% yields, respectively (Table 2, entries 10–11).

Table 2
Scope of the coupling reaction of sodium *p*-toluenesulfinate with nitroarenes[a]



Entry	R^1NO_2 (**2**)	Product (**3**)	Yield (%)[b]
1	 **2a**	 **3aa**	88
2	 **2b**	 **3ab**	65[c]
3	 **2c**	 **3ac**	81
4	 **2d**	 **3ad**	85
5	 **2e**	 **3ae**	87
6	 **2f**	 **3af**	57
7	 **2g**	 **3ag**	90
8	 **2h**	 **3ah**	68
9	 **2i**	 **3ai**	76
10	 **2j**	 **3aj**	83
11	 **2k**	 **3ak**	88

[a] Unless otherwise noted, the reaction conditions were as follows:**1a** (0.6 mmol), **2** (0.3 mmol), palladacycle **I** (0.75 mol %), K_2CO_3 (1 equiv) and DMSO (2 mL), 12 h, 110 °C, under N_2.
[b] Isolated yields.
[c] Gram scale.

In support of the application of this method, we conducted the reaction on a gram scale, and it also showed good performance (Table 2, entry 2). The structure of **3ab** was characterized by X-ray diffraction (Fig. 3), which confirms that the coupling occurs via C–S bond formation.[8c]

Next, we explored the effects of the coupling of *p*-nitrobenzaldehyde (**2a**) with various sodium sulfinates (**1**) (Table 3). As expected, the reactions proceeded smoothly and tolerated a wide range of functional groups, including aryl and alkyl sodium sulfinates.

First, the mono-substituent positions at the aryl moiety of sodium sulfinates such as methyl, fluoro, bromo, chloro, *tert*-butyl, methoxy and trifluoromethyl were evaluated. The electronic properties of the groups on the phenyl ring of sodium sulfinates had some effect on the reaction. In general, sodium sulfinate bearing an electron-donating substituent afforded better yield of aryl sulfone than that with an electron-withdrawing group (Table 3, entries 1, 2, 4, 10 vs 3, 6, 7, 9). It was noteworthy that the fluoro, chloro and bromo moieties

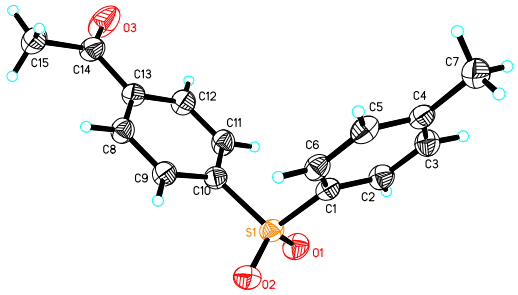
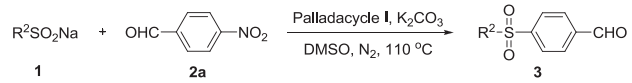
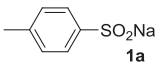
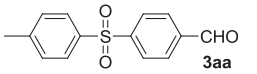
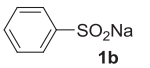
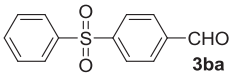
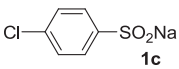
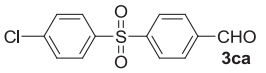
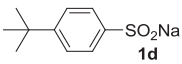
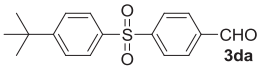
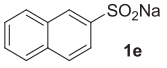
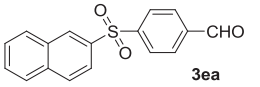
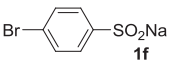
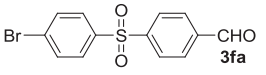
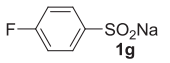
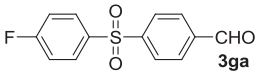
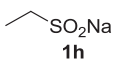


Fig. 3. X-ray crystal structure of **3ab**. CCDC 1008677 contains the supplementary Crystallographic data for this paper.

Table 3
Scope of the coupling reaction of sodium sulfinates with *p*-nitrobenzaldehyde[a]



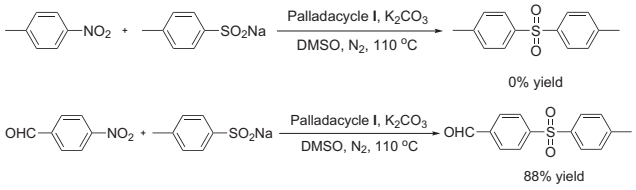
Entry	R^2SO_2Na (**1**)	Product (**3**)	Yield (%)[b]
1	 **1a**	 **3aa**	88
2	 **1b**	 **3ba**	83
3	 **1c**	 **3ca**	82
4	 **1d**	 **3da**	83
5	 **1e**	 **3ea**	76
6	 **1f**	 **3fa**	74
7	 **1g**	 **3ga**	69
8	 **1h**	**3ha**	48
9	**1i**	**3ia**	51
10	**1j**	**3ja**	87
11	**1k**	**3ka**	0
12	**1l**	**3la**	0

[a] Unless otherwise noted, the reaction conditions were as follows: **1** (0.6 mmol), **2a** (0.3 mmol) palladacycle **I** (0.75 mol %), K_2CO_3 (1 equiv) and DMSO (2 mL), 12 h, 110 °C, under N_2.
[b] Isolated yields.

(commonly used for cross-coupling reactions) in sodium sulfinates (**1c**, **1f**, and **1g**) were all tolerated and afforded a novel route to

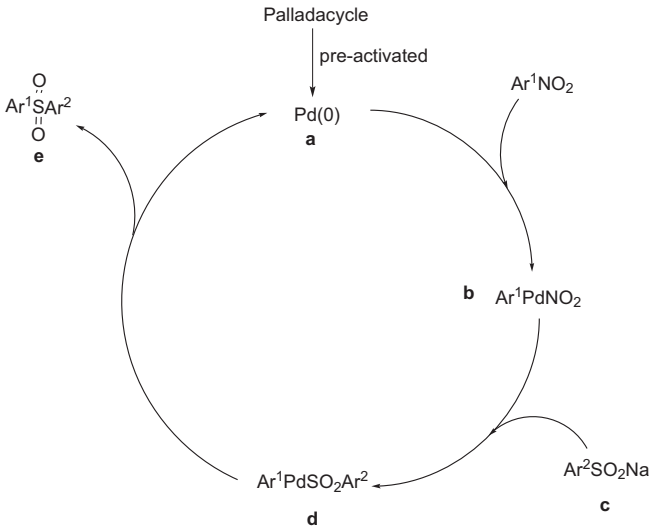
compounds (**3ca**, **3fa**, and **3ga**) in excellent yields, making further elaborations of the corresponding biaryl sulfones (Table 3, entries 3, 6–7). However, the results demonstrated that steric effects of substituents had significant effects on the reaction. For example, the coupling of **2a** with *para*- and *ortho*-chlorobenzenesulfinic acid sodium salt was examined (Table 3, entries 3, 11), 82% of **3ca** was isolated, while no product of **3ka** was detected. The same phenomenon was observed in the reaction of **2a** with **1a** and **1l** (Table 3, entries 1, 12). More substrate such as 2-naphthylsulfinic acid sodium salt also efficiently reacted with *p*-nitrobenzaldehyde and gave the product in 76% yield (Table 3, entry 5). Moreover, ethyl-substituted substrate **1h** possessing the sluggish group, was also tolerated and afforded the product **3ha** in 48% yield (Table 3, entry 8).

In order to understand the reaction more clearly, some control experiments were carried out under the standard conditions as shown in Scheme 2. Reaction of 4-nitrotoluene with sodium *p*-toluenesulfinate failed to deliver the desired product under the same reaction conditions. However, the reaction of *p*-nitrobenzaldehyde with sodium *p*-toluenesulfinate afforded the desired product in 88% yield.



Scheme 2. Control experiments.

Therefore, a possible mechanism for the formation of the aryl sulfone was proposed as shown in Scheme 3. First, the palladacycle was pre-activated to form **a**. Addition of nitroarene formed arylpalladium species **b**. Next, sodium arylsulfinate **c** could be converted to the sulfonylpalladium intermediate **d** by nucleophile displacement of a nitro group. The reductive elimination of **d** gave the aryl sulfone **e** and regenerated the palladium catalyst **a**.



Scheme 3. Plausible reaction mechanism.

3. Conclusions

We have developed a new protocol for the synthesis of aryl sulfones in moderate to excellent yields from the palladacycle-catalyzed denitrated coupling of nitroarenes with sodium sulfinates. The reaction proceeds without the use of a large number of metal catalysts and other additives, which make it significantly greener than current alternatives. Ongoing work seeks to gain further mechanistic studies on cross-coupling processes mediated by palladacycle **I** and extend the applications of the transformation in organic synthesis in our laboratory.

4. Experimental

4.1. General experimental details

^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer with $CDCl_3$ as the solvent and TMS as an internal standard. Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. High-resolution mass spectra were ensured on a MALDI-FTMS. GC analysis was performed on Agilent 4890D gas chromatograph. Ethyl acetate and petroleum ether (analytical grade) were used for column chromatography without further purification. Other solvents were purified according to the standard methods.

4.2. General procedure for the preparation of sodium sulfinates

4-Methoxybenzenesulfinic acid sodium salt (**1j**) was prepared by heating 2.5 g of sodium sulfite, 2.06 g of 4-methoxybenzenesulphonyl chloride, and 1.68 g of sodium bicarbonate in 9.6 mL of water at 70–80 °C for 4 h. After cooling to room temperature, water was removed under vacuum and the residue was extracted by ethanol, recrystallization as a white solid, the yield was 67% (1.34 g). Similarly, other sodium arenesulfinates were prepared from their corresponding sulphonyl chlorides.

4.3. General procedure for the first palladium-catalyzed denitrated coupling of nitroarenes with aryl sulfinates

Under N_2 atmosphere, a reaction vessel was charged with a mixture of sodium sulfinates **1** (0.6 mmol), nitroarenes **2** (0.3 mmol), palladacycle **I** (0.75 mol %) and K_2CO_3 (1.0 equiv) in DMSO (2 ml) at room temperature. After that, the mixture was heated to 110 °C and incubated in an oil bath for 12 h under N_2 atmosphere. After the completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with brine three times. The combined organic solution was dried with Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by thin-layer chromatography on silica gel GF 254 (ethyl acetate/petroleum ether) to give the pure product.

*4.3.1. 4-(Toluene-4-sulfonyl)-benzaldehyde (**CAS**: **113823-55-5**, **3aa**).*[8c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.83 (d, J=8.1 Hz, 2H), 7.97 (d, J=8.1 Hz, 2H), 8.07 (d, J=8.1 Hz, 2H), 10.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 128.0, 128.2, 130.2, 130.3, 137.6, 139.0, 144.9, 147.1, 190.8.

*4.3.2. 1-[4-(Toluene-4-sulfonyl)-phenyl]-ethanone (**CAS**: **129644-41-3**, **3ab**).*[8c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 2.61 (s, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.83 (d, J=8.2 Hz, 2H), 8.00–8.05 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 27.0, 127.9, 128.0, 129.1, 130.2, 137.9, 140.2, 144.9, 145.9, 196.8.

*4.3.3. 4-(Toluene-4-sulfonyl)-benzonitrile (**CAS**: **38111-56-7**, **3ac**).*[8c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.41 (s, 3H), 7.33 (d, J=7.9 Hz, 2H), 7.77 (d, J=8.2 Hz, 2H), 7.83 (d, J=8.0 Hz, 2H), 8.03 (d, J=8.2 Hz, 2H);

^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 116.7, 117.3, 128.1, 128.2, 130.3, 133.1, 137.1, 145.3, 146.3.

*4.3.4. 1-Methyl-4-[(4-nitrophenyl)sulfonyl]-benzene (**CAS: 4094-37-5**, **3ad**).*[8c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 7.34 (d, J=8.1 Hz, 2H), 7.84 (d, J=8.3 Hz, 2H), 8.10 (d, J=8.8 Hz, 2H), 8.31 (d, J=8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 124.5, 128.1, 128.8, 130.4, 137.0, 145.4, 147.8, 150.2.

*4.3.5. 2-(Toluene-4-sulfonyl)-benzaldehyde (**CAS: 171503-27-8**, **3ae**).*[7a] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 7.31 (d, J=8.2 Hz, 2H), 7.68–7.77 (m, 4H), 7.99 (dd, J_1=3.4 Hz, J_2=4.8 Hz, 1H), 8.15 (dd, J_1=3.2 Hz, J_2=4.3 Hz, 1H), 10.84 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 127.5, 129.3, 129.4, 130.3, 133.7, 133.8, 134.1, 138.4, 142.7, 145.0, 189.5.

*4.3.6. Phenyl-[4-(toluene-4-sulfonyl)-phenyl]-methanone (**CAS: 97807-46-0**, **3af**).*[13] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 7.35 (d, J=8.0 Hz, 2H), 7.49 (t, J=6.0 Hz, 2H), 7.62 (t, J=7.5 Hz, 1H), 7.76 (d, J=7.4 Hz, 2H), 7.88 (d, J=7.6 Hz, 4H), 8.05 (d, J=8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 127.5, 128.0, 128.6, 130.2, 130.5, 133.3, 136.4, 137.9, 141.6, 144.8, 145.1, 145.8, 195.3.

*4.3.7. 2-Methyl-4-(toluene-4-sulfonyl)-pyridine (**3ag**).* Mp: 83.7–84.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.36 (s, 3H), 2.59 (s, 3H), 7.31 (d, J=8.0 Hz, 2H), 7.51 (d, J=4.8 Hz, 1H), 7.60 (s, 1H),7.81 (d, J=8.1 Hz, 2H),8.64 (d, J=5.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 24.6, 117.6, 119.9, 128.1, 130.2, 136.8, 145.3, 150.3, 150.5, 160.6; HRMS-ESI (positive ESI): m/z calcd for $C_{13}H_{13}NO_2S$ $(M+H)^+$: 248.0740, found: 248.0741.

*4.3.8. 5-(Toluene-4-sulfonyl)-thiophene-2-carbaldehyde (**CAS: 1498230-90-2**, **3ah**).*[9b] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.42 (s, 3H), 7.34 (d, J=8.0 Hz, 2H), 7.66 (s, 1H), 7.70 (s, 1H), 7.88 (d, J=8.2 Hz, 2H), 9.92 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.8, 127.9, 130.3, 132.6, 134.8, 137.7, 145.5, 148.9, 151.8, 182.9.

*4.3.9. 2,4-Bis-(toluene-4-sulfonyl)-benzonitrile (**3ai**).* Mp: 154.6–155.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.44 (s, 6H), 7.38 (dd, J_1=1.9 Hz, J_2=4.0 Hz, 4H), 7.87 (d, J=8.3 Hz, 2H), 7.96 (t, J=0.7 Hz, 3H), 8.21 (dd, J_1=2.0 Hz, J_2=3.8 Hz, 1H), 8.81 (d, J=1.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.6, 21.7, 114.5, 114.9, 128.1, 128.2, 128.9, 130.3, 130.6, 131.7, 135.4, 136.1, 136.6, 145.7, 146.0, 146.2, 147.1; HRMS-ESI (positive ESI): m/z calcd for $C_{21}H_{17}NO_4S_2$ $[M+H]^+$: 412.0672, found: 412.0673.

*4.3.10. 1-Methyl-4-[(4-nitrophenyl)sulfonyl]-benzene (**CAS: 4094-37-5**, **3aj**, **3ak**).*[8c] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 7.34 (d, J=8.1 Hz, 2H), 7.84 (d, J=8.2 Hz, 2H), 8.10 (d, J=8.7 Hz, 2H), 8.32 (d, J=8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 124.5, 128.1, 128.8, 130.4, 137.0, 145.4, 147.8, 150.3.

*4.3.11. 4-Benzenesulfonyl-benzaldehyde (**CAS: 66-39-7**, **3ba**).*[14] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (t, J=7.6 Hz, 2H), 7.45 (t, J=8.6 Hz, 1H), 7.79 (d, J=7.6 Hz, 2H), 7.86 (d, J=8.4 Hz, 2H), 7.94 (d, J=8.3 Hz, 2H), 9.90 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 127.5, 127.9, 129.3, 130.0, 133.6, 138.8, 140.1, 146.1, 190.6.

*4.3.12. 4-(4-Chloro-benzenesulfonyl)-benzaldehyde (**CAS: 77422-24-3**, **3ca**).*[15] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.50 (d, J=8.6 Hz, 2H), 7.89 (d, J=8.6 Hz, 2H), 8.00 (d, J=8.4 Hz, 2H), 8.08 (d, J=8.3 Hz, 2H), 10.07 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 128.4, 129.4, 129.9, 130.5, 139.1, 139.3, 140.7, 146.2, 190.7.

*4.3.13. 4-(4-tert-Butyl-benzenesulfonyl)-benzaldehyde (**3da**).* Mp: 125.5–125.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.29 (s, 9H), 7.53 (d, J=8.5 Hz, 2H), 7.87 (d, J=8.5 Hz, 2H), 7.99 (d, J=8.3 Hz, 2H), 8.10 (d, J=8.3 Hz, 2H), 10.06 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.0, 35.3, 126.6, 127.8, 128.3, 130.3, 137.5, 139.0, 147.0, 157.9, 190.9; HRMS-ESI (positive ESI): m/z calcd for $C_{17}H_{18}O_3S$ $[M+H]^+$: 303.1049, found: 303.1050.

*4.3.14. 4-(Naphthalene-2-sulfonyl)-benzaldehyde (**CAS: 194668-82-1**, **3ea**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60–7.68 (m, 2H), 7.84–7.89 (m, 2H), 7.94–8.00 (m, 4H), 8.16 (d, J=8.3 Hz, 2H), 8.60 (s, 1H), 10.05 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.6, 127.9, 128.0, 128.4, 129.5, 129.6, 129.7, 130.0, 130.4, 132.2, 135.3, 137.3, 139.1, 146.7, 190.8.

*4.3.15. 4-(4-Bromo-benzenesulfonyl)-benzaldehyde (**CAS: 96462-90-7**, **3fa**).* ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, J=8.5 Hz, 2H), 7.82 (d, J=8.5 Hz, 2H), 8.01 (d, J=8.3 Hz, 2H), 8.09 (d, J=8.3 Hz, 2H), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 128.4, 129.3, 129.5, 130.5, 132.9, 139.3, 139.6, 146.2, 190.7.

*4.3.16. 4-(4-Fluoro-benzenesulfonyl)-benzaldehyde (**CAS: 81326-26-3**, **3ga**).*[16] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.22 (t, J=9.3 Hz, 2H), 7.98–8.03 (m, 4H), 8.10 (d, J=8.1 Hz, 2H), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 117.0 (d, J=22.7 Hz), 128.3, 130.5, 130.8 (d, J=9.8 Hz), 136.7 (d, J=2.6 Hz), 139.3, 146.5, 165.8 (d, J=225.5 Hz), 190.7.

*4.3.17. 4-Ethanesulfonyl-benzaldehyde (**CAS: 50899-03-1**, **3ha**).*[17] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.28 (t, J=7.4 Hz, 3H), 3.15 (q, J=7.5 Hz, 2H), 8.07 (s, 4H), 10.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.3, 50.5, 129.1, 130.3, 139.7, 143.5, 190.8.

*4.3.18. 4-(4-Trifluoromethyl-benzenesulfonyl)-benzaldehyde (**3ia**).* Mp: 126.3–127.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, J=8.0 Hz, 2H), 8.05 (d, J=8.0 Hz, 2H), 8.14 (t, J=7.6 Hz, 4H), 10.10 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 123.0 (q, J=273.1 Hz), 126.7 (q, J=3.6 Hz), 128.6, 128.7, 130.6, 135.6 (q, J=33.0 Hz), 139.6, 144.2, 145.6, 190.6; HRMS-ESI (positive ESI): m/z calcd for $C_{14}H_9F_3O_3S$ $[M+H]^+$: 315.0297, found: 315.0299.

*4.3.19. 4-(4-Methoxy-benzenesulfonyl)-benzaldehyde (**CAS: 477256-37-4**, **3ja**).*[18] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3H), 7.01 (d, J=8.9 Hz, 2H), 7.90 (d, J=8.9 Hz, 2H), 8.00 (d, J=8.3 Hz, 2H), 8.11 (d, J=8.3 Hz, 2H), 10.08 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.8, 114.8, 128.0, 130.2, 130.3, 131.9, 138.9, 147.5, 163.9, 190.9.

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.09.087.

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