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Graphical Abstract

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A Practical Synthesis of Aryl Sulfones *via* Cross-coupling of Sulfonyl Hydrazides with Aryltriazenes using Copper/Ionic Liquid Combination

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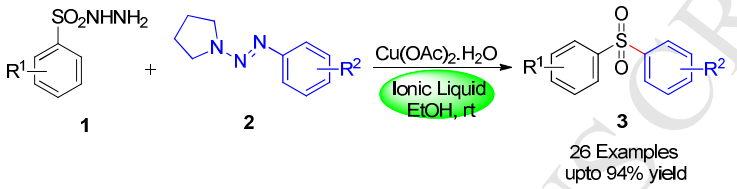

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A Practical Synthesis of Aryl Sulfones *via* Cross-coupling of Sulfonyl Hydrazides with Aryltriazenes using Copper/Ionic Liquid Combination

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ABSTRACT

A new and efficient approach adopting copper-catalyzed cross-coupling of sulfonyl hydrazides with aryltriazenes has been developed to synthesize aryl sulfones using Brønsted acidic ionic liquid as promoter under ambient conditions. The process employs stable and easy to handle reacting partners, and is endowed with broad substrate scope.

1. Introduction

The construction of carbon-sulfur (C−S) bond has always been at the core of organic synthesis owing to its occurrence in a large variety of molecules of biological and material interest.[1] Amongst various organosulfur compounds, aryl sulfones are particularly important due to their distinct medicinal activities such as anti-tumour, anti-inflammatory, antifungal, antibacterial, etc. (Figure 1).[2-5] They have also been explored as potent inhibitors of cyclooxygenase-2 (COX-2),[6] and HIV-1 strains.[7]

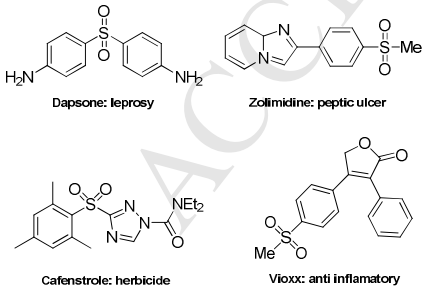
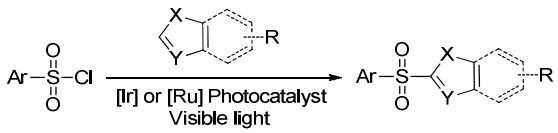


Figure 1. Bio-active molecules with sulfone motifs.

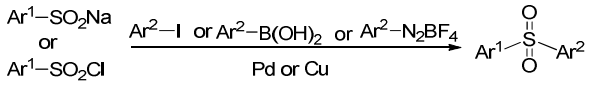
The transition-metal catalyzed coupling strategies have been well established for carbon-nitrogen (C−N) and carbon-oxygen (C−O) bond formation, but are much less explored for carbon-sulfur (C−S) bond creation, as the presence of sulfur causes

Recent strategies:

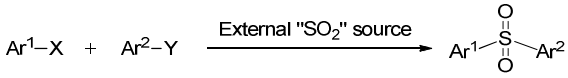
1. Solfonylation of arenes (ref. 10)



2. Coupling of sulfonyl chloride/ sulfinate salts (ref. 11)

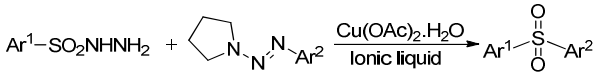


3. Sulfonylative cross- coupling (ref. 12)



X= SiR_3, I, H
Y= I, Br, Cl, $B(OH)_2$, H
"SO_2" Sources= DABSO, $K_2S_2O_8$

Our approach :



Scheme 1. Synthesis of aryl sulfones.

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metal-catalyst deactivation even at low concentrations.[8] Besides oxidation of corresponding sulfides,[9] recent reports for the synthesis of aryl sulfones include sulfonylation of arenes,[10] metal/metal-free cross-coupling between arylsulfonyl chlorides/sodium sulfinates with aryl halides/arylboronic acids/ aryldiazonium salts,[11] and the sulfonylative cross-coupling employing SO_2 surrogate/external SO_2 source[12] (Scheme 1).

Despite their usefulness in creating sulfone moiety, these methods, however, suffer from one or another drawback such as use of expensive materials, harsh conditions and low product yields. Thus, there is enough scope and necessity to develop new and convenient protocols to simplify the sulfone-formation.

Ionic liquids (ILs) have recently emerged as an environmentally benign reaction media in organic synthesis. Ionic nature, non-volatility, high thermal stability and recyclability of ILs have endowed them with enormous advantages.[13] Acidic ionic liquids (AILs) are especially important due to their dual role as catalyst as well as reaction medium.[14] Accordingly some acidic ILs (Figure 2) have been subjected to the envisaged reactions.

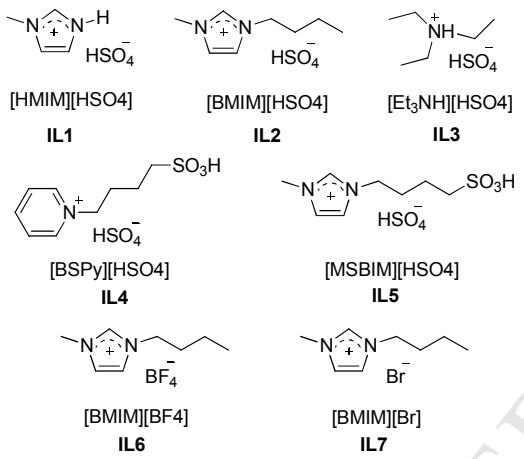


Figure 2. Acidic ionic liquids (AILs) examined.

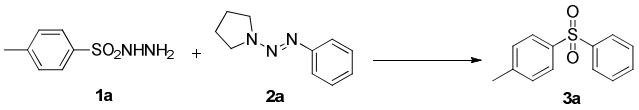
Aryltriazenes have currently gained huge synthetic interest,[15] due to their easy preparation from arylamines, and identical reactivity to that of the corresponding arenediazonium salts. They are markedly stable under ambient conditions, which make them more useful for practical purposes in comparison to the diazonium salts. Further, sulfonyl hydrazides have evolved as an excellent synthon,[16] owing to their adoptability to act as sulfonyl,[17] sulphide,[18] or aryl source,[19] *via* cleavage of the sulfur-nitrogen and carbon-sulfur bonds under varying conditions. An easy access and stability of sulfonyl hydrazides under air and moisture also makes it operationally simple.

In view of the above, and as a part of our ongoing research endeavour,[20] it was envisioned to develop a new and useful protocol involving cross-coupling of sulfonyl hydrazides with aryltriazenes to afford aryl sulfones at room temperature under open air atmosphere (*cf.* Scheme 1).

2. Results and discussion

In order to optimize the reaction conditions, a model reaction employing *p*-toluenesulfonyl hydrazide (**1a**) and 1-(phenyldiazenyl)pyrrolidine (**2a**) was thoroughly investigated by varying different parameters such as catalyst, promoter and solvent (Table 1). The initial reaction conditions made use of **1a** (1.0 mmol), **2a** (1.0 mmol), CuI (20 mol%) and 1-methylimidazolium hydrogen sulfate (**IL1**, 1.0 mmol) in acetonitrile at room temperature for 12 h, which gave rise to the product 1-methyl-4-(phenylsulfonyl) benzene (**3a**) in 46% yield (Table 1, entry 1).

Table 1. Optimization of the reaction conditions[a,b]



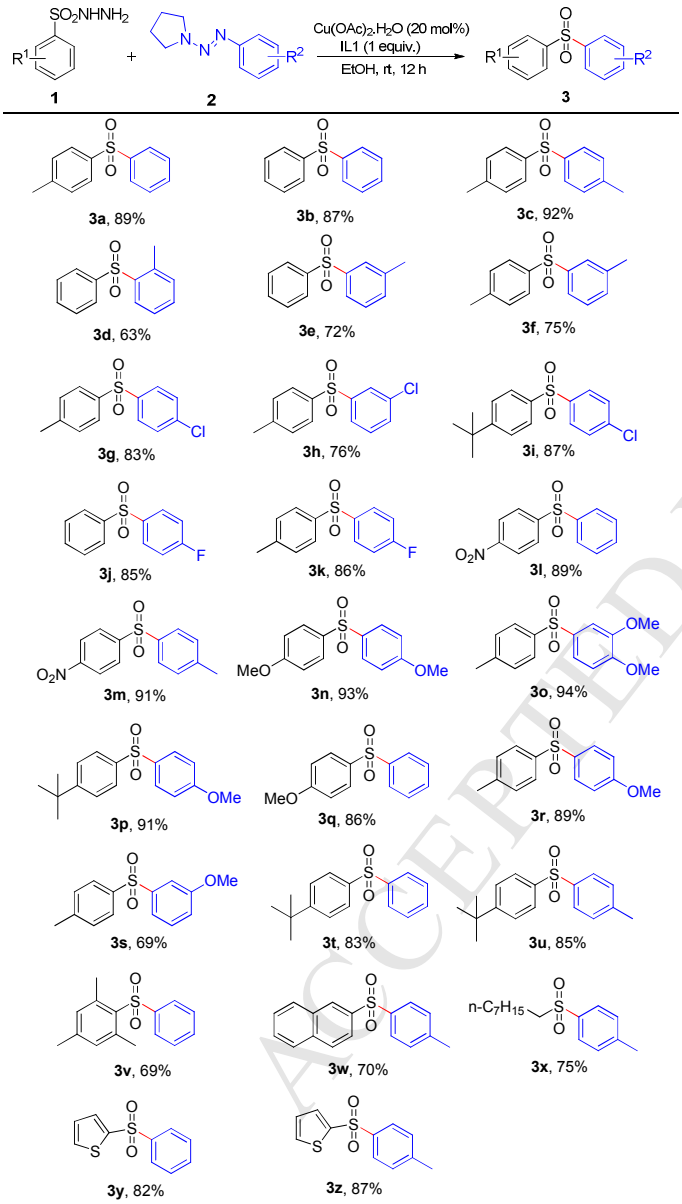
Entry	Catalyst	Promoter	Solvent	Yield (%)[b]
1	CuI	IL1	CH_3CN	46
2	CuCl	IL1	CH_3CN	37
3	CuBr	IL1	CH_3CN	33
4	$CuBr_2$	IL1	CH_3CN	43
5	Cu_2O	IL1	CH_3CN	25
6	$CuCl_2.2H_2O$	IL1	CH_3CN	55
7	$Cu(OAc)_2$	IL1	CH_3CN	74
8	$Cu(OAc)_2.H_2O$	IL1	CH_3CN	76
9	$Cu(OAc)_2.H_2O$	IL1	Toluene	Trace
10	$Cu(OAc)_2.H_2O$	IL1	Benzene	63
11	$Cu(OAc)_2.H_2O$	IL1	DCE	20
12	$Cu(OAc)_2.H_2O$	IL1	DMSO	62
13	$Cu(OAc)_2.H_2O$	IL1	DMF	72
14	$Cu(OAc)_2.H_2O$	IL1	DCM	58
15	$Cu(OAc)_2.H_2O$	IL1	1,4-Dioxane	65
16	$Cu(OAc)_2.H_2O$	IL1	THF	0
17	$Cu(OAc)_2.H_2O$	IL1	MeOH	78
18	$Cu(OAc)_2.H_2O$	IL1	EtOH	89
19	$Cu(OAc)_2.H_2O$	IL1	H_2O	35
20	$Cu(OAc)_2.H_2O$	---	EtOH	0
21	$Cu(OAc)_2.H_2O$	IL2	EtOH	47
22	$Cu(OAc)_2.H_2O$	IL3	EtOH	56
23	$Cu(OAc)_2.H_2O$	IL4	EtOH	68
24	$Cu(OAc)_2.H_2O$	IL5	EtOH	65
25	$Cu(OAc)_2.H_2O$	IL6	EtOH	42
26	$Cu(OAc)_2.H_2O$	IL7	EtOH	18
27	$NiCl_2.6H_2O$	IL1	EtOH	0
28	$FeCl_3$	IL1	EtOH	0
29	$CoCl_2.6H_2O$	IL1	EtOH	Trace

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), Catalyst (20 mol%), Promoter (1.0 mmol), Solvent (2 mL), rt, 12 h.
[b]Isolated yield after column chromatography.

Thereafter, some other copper salts such as CuBr, CuCl, $CuBr_2$, Cu_2O, $CuCl_2.2H_2O$, $Cu(OAc)_2$ and $Cu(OAc)_2.H_2O$ were screened under identical conditions (entries 2-8), which revealed $Cu(OAc)_2.H_2O$ as the best choice. Maintaining other parameters of the entry 8 as such, the effect of different solvents was then

examined (entries 9-18), which disclosed ethanol as the top option (entry 18) out of all the organic solvents tested. The use of H_2O as solvent could not make any marked effect (entry 19). Notably, no product formation was observed in the absence of the ionic liquid (entry 20). Other Brønsted acidic ionic liquids like **IL2**, **IL3**, **IL4** and **IL5**, when tried, could not provide the product in appreciable yields (entries 21-24). The use of Lewis acidic ionic liquids **IL6** and **IL7** rather provided inferior yields (entries 25 & 26). Attempt to utilize other metal salts namely $NiCl_2.6H_2O$, $FeCl_3$ and $CoCl_2.6H_2O$ also remained futile (entries 27-29). The molar ratio of the reactants and reaction time were also studied in detail, which revealed equivalent quantities of **1a** and **2a** in ethanol at room temperature under open atmosphere for 12 h as the best fit.

Table 2. Scope and versatility of the reaction[a,b]

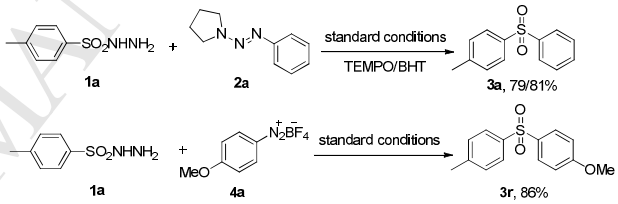


[a]Reaction conditions: **1** (1.0 mmol), **2** (1.0 mmol), $Cu(OAc)_2.H_2O$ (20 mol%), IL1 (1.0 mmol), EtOH (2 mL), rt, 12 h.

[b]Isolated yield after column chromatography.

With the established reaction conditions in hand (entry 18), the scope and versatility of the reaction was examined using a variety of sulfonyl hydrazides (**1**) and aryltriazenes (**2**) with different substitution patterns (ortho/meta/para) and the results are given in Table 2. Both the reacting partners containing different electron-donating as well as electron-withdrawing substituent participated nicely in the reaction and offered the desired products **3a**-**3z** in reasonably good yields. Marked steric influence was observed in the formation of the product **3d** (63%), as its yield was appreciably diminished involving the reaction of 1-(*o*-tolyldiazenyl)pyrrolidine with benzenesulfonyl hydrazide. A bicyclic sulfonyl hydrazide *viz.* naphthalene-2-sulfonohydrazide also underwent the reaction affording reasonably high yield of the product **3w**. An aliphatic sulfonyl hydrazide, i.e. octylsulfonyl hydrazide, when subjected to the established conditions, also delivered the product **3x** in fairly high yield. Thiophene-2-sulfonohydrazide also participated nicely in the reaction to provide the products **3y** (82%) and **3z** (87%) in excellent yields. However, the reaction of 4-(pyrrolidin-1-yldiazenyl)benzonitrile and methyl 4-(pyrrolidin-1-yldiazenyl)benzoate with *p*-tolylsulfonyl hydrazide under standard conditions failed to deliver the desired products.

To get an insight into the reaction mechanism, a number of control experiments were carried out (Scheme 2). The reaction between **1a** and **2a** under the standard conditions in the presence of radical scavengers like TEMPO and BHT remained almost unaffected, thereby withholding the possibility of a radical pathway. The reaction of a representative diazonium salt, *p*-methoxybenzenediazonium tetrafluoroborate (**4a**) with **1a** under standard conditions, also gave rise to the corresponding product (**3r**, 86%), suggesting an intermediacy of the arenediazonium cation during the course of reaction.



Scheme 2. Control experiments.

Based on existing literature,[18a, 21-26] isolation of products and control experiments, a plausible mechanism is outlined in Figure 3.

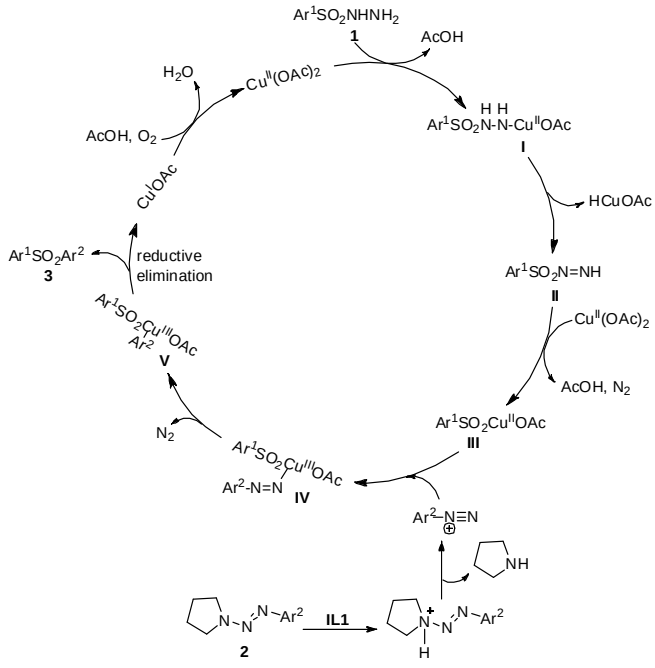


Figure 3. Plausible reaction mechanism.

The reaction is assumed to proceed by the coordination of sulfonyl hydrazide **1** with copper(II) acetate to give the intermediate **I**, which on sequential removal of hydrogen and extrusion of N_2 provides the intermediates **II** and **III** successively. Acidic ionic liquid (**IL1**)-assisted generation of the arenediazonium cation from aryltriazene **2** couples with the intermediate **III** to produce a Cu(III) intermediate **IV**, which further forms intermediate **V** by extrusion of N_2. Intermediate **V** undergoes reductive elimination to afford the desired sulfone product **3** and Cu(I) species which undergoes oxidation to regenerate the copper(II) acetate by aerial oxygen and AcOH to complete the catalytic cycle.

3. Conclusions

In summary, an efficient and new approach to aryl sulfones has been developed using sulfonyl hydrazides and aryltriazenes as coupling partners in the presence of cupric acetate and ionic liquid under open air atmosphere at room temperature. The protocol employs mild and easy to handle reaction conditions and offers broad substrate scope.

4. Experimental Section

General procedure for the synthesis of Aryl sulfones:

A mixture of sulfonyl hydrazide **1** (1.0 mmol), aryltriazene **2** (1.0 mmol), $Cu(OAc)_2.H_2O$ (20 mol%), IL1 (1.0 mmol) and EtOH, placed in a 10-mL borosilicate vial, was stirred under open atmosphere at room temperature for 12 h. After completion of the reaction (monitored through TLC), ethanol was removed under reduced pressure, and the resulting mixture was worked-up using water-ethyl acetate. The organic phase was then dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The resulting crude product was finally purified by silica gel column chromatography using n-hexane and ethyl acetate as eluent.

5. Spectral Data

*5.1. 1-Methyl-4-(phenylsulfonyl)benzene (**3a**)[12c]:*

White Solid; Yield (89%, 207 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 7.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.56–7.47 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.3, 142.1, 138.8, 133.1, 130.0, 129.3, 127.8, 127.6, 21.7.

*5.2. Sulfonyldibenzene (**3b**)[12c]:*

White Solid; Yield (87%, 190 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 8.0 Hz, 4H), 7.57–7.48 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.7, 133.3, 129.4, 127.8.

*5.3. 4,4'-Sulfonylbis(methylbenzene) (**3c**)[12c]:*

White Solid; Yield (92%, 227 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.82 (d, *J* = 8.0 Hz, 4H), 7.29 (d, *J* = 8.5 Hz, 4H), 2.38 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.0, 139.2, 130.0, 127.7, 21.7.

*5.4. 1-Methyl-2-(phenylsulfonyl)benzene (**3d**)[27]:*

Colorless oil; Yield (63%, 146 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.59–7.38 (m, 5H), 7.24 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.4, 138.9, 138.1, 133.8, 133.2, 132.8, 129.5, 129.2, 127.8, 126.6, 20.3.

*5.5. 1-Methyl-3-(phenylsulfonyl)benzene (**3e**):*

White Solid; Yield (72%, 168 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.94 (t, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 7.5 Hz, 2H), 7.53–7.45 (m, 3H), 7.37–7.31 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 141.7, 141.4, 139.6, 134.0, 133.1, 129.3, 129.2, 127.9, 127.6, 124.8, 21.3; HRMS: calcd. For $C_{13}H_{13}O_2S$ $(M+H)^+$: 233.0631; Found: 233.0618.

*5.6. 1-Methyl-3-tosylbenzene (**3f**)[28]:*

White Solid; Yield (75%, 185 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.0 Hz, 2H), 7.38–7.32 (m, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 2.38 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.2, 141.9, 139.6, 138.9, 133.9, 130.0, 129.2, 127.9, 127.8, 124.8, 21.7, 21.4.

*5.7. 1-Chloro-4-tosylbenzene (**3g**)[12c]:*

White Solid; Yield (83%, 221 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.5 Hz, 2H), 7.82, (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.7, 140.6, 139.8, 138.3, 130.2, 129.7, 129.1, 127.8, 21.7.

*5.8. 1-Chloro-3-tosylbenzene (**3h**)[29]:*

White Solid; Yield (76%, 202 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.90–7.80 (m, 4H), 7.51–7.41 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.8, 143.9, 138.0, 135.5, 133.3, 130.7, 130.2, 128.0, 127.7, 125.7, 21.7.

*5.9. 1-(tert-Butyl)-4-((4-chlorophenyl)sulfonyl)benzene (**3i**)[30]:*

White Solid; Yield (87%, 268 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 2H) 7.52 (d, *J* = 9.0 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.6, 140.7, 139.8, 138.3, 129.7, 129.2, 127.7, 126.6, 35.4, 31.2.

*5.10. 1-Fluoro-4-(phenylsulfonyl)benzene (**3j**)[12c]:*

White Solid; Yield (85%, 201 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97–7.91 (m, 4H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.5 (d, *J* =256.4 Hz), 141.5, 137.8 (d, *J* =3.0 Hz), 133.4, 130.6 (d, *J* =9.6 Hz), 129.5, 127.7, 116.8 (d, *J* =22.8 Hz).

*5.11. 1-Fluoro-4-tosylbenzene (**3k**)[12c]:*

White Solid; Yield (86%, 215 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: ^{1}H NMR (500 MHz,) δ 7.96–7.93 (m, 2H), 7.82 (d, *J* =8.0 Hz, 2H), 7.31 (d, *J* =8.0 Hz, 2H), 7.18 (t, *J* = 8.5 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 166.4 (d, *J* =256.3 Hz), 144.49, 138.6 (d, *J* =54.8 Hz), 130.4 (d, *J* =9.6 Hz), 130.13, 127.73, 116.7 (d, *J* =23.0 Hz), 21.67.

*5.12. 1-Nitro-4-(phenylsulfonyl)benzene (**3l**)[27]:*

Light Yellow Solid; Yield (89%, 234 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.34–8.32 (m, 2H), 8.14–8.12 (m, 2H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 7.0 Hz, 1H), 7.57–7.54 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 150.5, 147.5, 140.1, 134.2, 129.8, 129.1, 128.1, 124.6.

*5.13. 1-Methyl-4-((4-nitrophenyl)sulfonyl)benzene (**3m**)[31]:*

Light Yellow Solid; Yield (91%, 252 mg); ^{1}H NMR (500 MHz, $CDCl_3$+DMSO) δ: 8.37 (d, *J* = 7.5 Hz, 2H), 8.16 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 7.5 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$+DMSO) δ: 149.6, 147.0, 144.9, 136.3, 129.8, 128.3, 127.5, 124.0, 21.0.

*5.14. 4,4'-Sulfonylbis(methoxybenzene) (**3n**)[12c] :*

White Solid; Yield (93%, 259 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84 (d, *J* = 8.5 Hz, 4H), 6.94 (d, *J* = 8.5 Hz, 4H), 3.81; ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.2, 134.0, 129.6, 114.5, 55.7.

*5.15. 1,2-Dimethoxy-4-tosylbenzene (**3o**)[12c]:*

White Solid; Yield (94%, 275 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.38 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 6H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 153.0, 149.3, 144.0, 139.4, 133.6, 123.0, 127.4, 121.8, 111.0, 110.0, 56.3, 56.2, 21.6.

*5.16. 1-(tert-Butyl)-4-((4-methoxyphenyl)sulfonyl)benzene (**3p**):*

White Solid; Yield (91%, 277 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.89–7.87 (m, 2H), 7.84–7.81 (m, 2H), 7.49–7.47 (m, 2H), 6.97–6.94 (m, 2H), 3.83 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.4, 156.8, 139.5, 133.7, 129.9, 127.3, 126.3, 114.6, 55.7, 35.3, 31.2. HRMS: calcd. For $C_{17}H_{21}O_3S$ $(M+H)^+$: 305.1206; Found: 305.1181.

*5.17. 1-Methoxy-4-(phenylsulfonyl)benzene (**3q**)[27]:*

White Solid; Yield (86%, 214 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91–7.86 (m, 4H), 7.52–7.45 (m, 3H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.5, 142.4, 133.1, 132.9, 129.9, 129.3, 127.4, 114.6, 55.7.

*5.18. 1-Methoxy-4-tosylbenzene (**3r**)[31]:*

White Solid; Yield (89%, 233 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 163.3, 143.9, 139.6, 133.7, 130.0, 129.8, 127.5, 114.6, 55.7, 21.6.

*5.19. 1-(tert-Butyl)-4-(phenylsulfonyl)benzene (**3s**)[32]:*

White Solid; Yield (83%, 228 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96–7.94 (m, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.55–7.48 (m, 5H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.2, 142.1, 138.7, 133.1, 129.3, 127.6, 127.7, 126.4, 35.3, 31.2.

*5.20. 1-Methoxy-3-tosylbenzene (**3t**)[27]:*

White Solid; Yield (69%, 181 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 160.1, 144.3, 143.2, 138.7, 130.4, 130.0, 127.8, 119.9, 119.5, 112.2, 55.8, 21.7.

*5.21. 1-(tert-Butyl)-4-tosylbenzene (**3u**)[30]:*

White Solid; Yield (85%, 245 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.83–7.81 (m, 4H), 7.49–7.46 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 157.0, 144.0, 139.1, 130.0, 127.8, 127.5, 126.4, 35.3, 31.2, 21.7.

*5.22. 1,3,5-Trimethyl-2-(phenylsulfonyl)benzene (**3v**)[27]:*

Yellow oil; Yield (69%, 180 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80–7.78 (m, 2H), 7.56–7.53 (m, 1H), 7.49–7.46 (m, 2H), 6.95 (s, 2H), 2.60 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 143.7, 143.5, 140.3, 133.9, 132.7, 132.3, 129.0, 126.4, 23.0, 21.2.

*5.23. 2-Tosylnaphthalene (**3w**)[29]:*

White Solid; Yield (70%, 198 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.56 (s, 1H), 7.98–7.83 (m, 6H), 7.64–7.58 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.3, 138.9, 138.8, 135.1, 132.4, 130.1, 129.7, 129.5, 129.2, 129.0, 128.0, 127.9, 127.7, 122.8, 21.7.

*5.24. 1-Methyl-4-(octylsulfonyl)benzene (**3x**)[33]:*

Colorless oil; Yield (75%, 201 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 3.08 (t, *J* = 8.5 Hz, 2H), 2.44 (s, 3H), 1.72–1.66 (m, 2H), 1.35–1.22 (m, 10H), 0.87 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.6, 136.2, 129.9, 128.0, 56.4, 31.6, 28.9, 28.9, 28.2, 22.7, 22.6, 21.6, 14.0.

*5.25. 2-(Phenylsulfonyl)thiophene (**3y**)[34]:*

White Solid; Yield (82%, 184 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.00 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 4.0 Hz, 1H), 7.65 (d, *J* = 4.5 Hz, 1H), 7.59–7.50 (m, 3H), 7.09 (t, *J* = 4.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 143.1, 142.1, 134.0, 133.5, 133.4, 129.4, 127.9, 127.7, 127.4.

*5.26. 2-Tosylthiophene (**3z**)[35]:*

White Solid; Yield (87%, 207 mg); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 3.0 Hz, 1H), 7.62 (d, *J* = 4.5 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.07 (t, *J* = 4.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 144.5, 143.6, 139.3, 133.7, 133.2, 130.1, 127.9, 127.5, 21.7.

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Supplementary data

Supplementary data associated with this article can be found in the online version at

References and notes

1. (a) Shen, C.; Zhang, P.; Sun, Q.; Bai, S.; Hor, T. S. A.; Liu, X. *Chem. Soc. Rev.* **2015**, *44*, 291; (b) Chauhan, P.; Mahajan, S.; Enders, D. *Chem. Rev.* **2014**, *114*, 8807; (c) Wang, L.; Hea, W.; Yu, Z. *Chem. Soc. Rev.* **2013**, *42*, 599; (d) Kondo, T.; Mitsudo, T.-a. *Chem. Rev.* **2000**, *100*, 3205.
2. Parent, E. E.; Dence, C. S.; Jenks, C.; Sharp, T. L.; Welch, M. J.; Katzenellenbogen, J. A. *J. Med. Chem.* **2007**, *50*, 1028.
3. Crosignani, S.; Pretre, A.; Lebrun, C. J.; Fraboulet, G.; Seenisamy, J.; Augustine, J. K.; Missotten, M.; Humbert, Y.; Cleva, C.; Abla, N.; Aaff, H.; Schott, O.; Schneider, M.; Charvillon, F. B.; Rivron, D.; Namernig, I.; Arrighi, J. F.; Gaudet, M.; Zimmerli, S. C.; Juillard, P.; Joson, Z. *J. Med. Chem.* **2011**, *54*, 7299.
4. Hussain, I.; Yawer, M. A.; Lalk, M.; Lindequist, U.; Villinger, A.; Fischer, C.; Langer, P. *Bioorg. Med. Chem.* **2008**, *16*, 9898.
5. (a) Xu, W.; He, J.; He, M.; Han, F.; Chen, X.; Pan, Z.; Wang, J.; Tong, M. *Molecules* **2011**, *16*, 9129; (b) Otzen, T.; Wempe, E. G.; Kunz, B.; Bartels, R.; Yvetot, G. L.; Hansel, W.; Schaper, K. J.; Seydel, J. K. *J. Med. Chem.* **2004**, *47*, 240.
6. (a) Prasit, P.; Wang, Z.; Brideau, C.; Chan, C.-C.; Charleson, S.; Cromlish, W.; Ethier, D.; Evans, J. F.; Hutchinson, A. W. F.; Gauthier, J. Y.; Gordon, R.; Guay, J.; Gresser, M.; Kargman, S.; Kennedy, B.; Leblanc, Y.; L´eger, S.; Mancini, J.; O'Neill, G. P.; Ouellet, M.; Percival, M. D.; Perrier, H.; Riendeau, D.; Rodger, I.; Tagari, P.; Th´erien, M.; Vockers, P.; Wong, E.; Xu, L. J.; Young, R. N.; Zamboni, R.; Boyce, S.; Rupniak, N.; Forrest, M.; Visco, D.; Patrick, D. *Bioorg. Med. Chem. Lett.* **1999**, *9*, 1773; (b) Hawkey, C. J. *Lancet* **1999**, *353*, 307.
7. Regina, G. L.; Coluccia, A.; Brancale, A.; Piscitelli, F.; Famiglini, V.; Cosconati, S.; Maga, G.; Samuele, A.; Gonzalez, E.; Clotet,

B.; Schols, D.; Este, J. A.; Novellinoand, E.; Silvestri, R. *J. Med. Chem.* **2012**, *55*, 6634.
8. (a) Liu, Y.-J.; Xu, H.; Kong, W.-J.; Shang, M.; Dai, H.-X.; Yu, J.-Q. *Nature* **2014**, *515*, 389; (b) Beletskaya, I. P.; Ananikov, V. P. *Chem. Rev.* **2011**, *111*, 1596.
9. (a) Ahammeda, S.; Kundu, D.; Siddiqui, M. N.; Ranu, B. C. *Tetrahedron Lett.* **2015**, *56*, 335; (b) Bahrami, K.; Khodaei, M. M.; Sheikh, A. M. *J. Org. Chem.* **2010**, *75*, 6208.
10. (a) Pagire, S. K.; Hossain, A.; Reiser, O. *Org. Lett.* **2018**, *20*, 648; (b) Liu, N.-W.; Liang, S.; Manolikakes, G. *Synthesis* **2016**, *48*, 1939.
11. (a) Liu, N.-W.; Hofman, K.; Herbert, A.; Manolikakes, G. *Org. Lett.* **2018**, *20*, 760; (b) Liang, S.; Bolte, M.; Manolikakes, G. *Chem. Eur. J.* **2017**, *23*, 96; (c) Day, J. J.; Neill, D. L.; Xu, S.; Xian, M. *Org. Lett.* **2017**, *19*, 3819; (d) Liu, S.-L.; Li, X.-H.; Zhang, S.-S.; Hou, S.-K.; Yang, G.-C.; Gong, J.; Song, M.-P. *Adv. Synth. Catal.* **2017**, *359*, 2241; (e) Hu, F.; Lei, X. *ChemCatChem* **2015**, *7*, 1539.
12. (a) Wolff, N. v.; Char, J.; Frogneux, X.; Cantat, T. *Angew. Chem. Int. Ed.* **2017**, *56*, 5616; (b) Chen, Y.; Willis, M. C. *Chem. Sci.* **2017**, *8*, 3249; (c) Yang, Y.; Chen, Z.; Rao, Y. *Chem. Commun.* **2014**, *50*, 15037.
13. (a) Muhammad, N.; Man, Z.; Elsheikh, Y. A.; Bustam, M. A.; Mutalib, M. I. A. *J. Chem. Eng. Data* **2014**, *59*, 579; (b) Xin, B.; Hao, J. *Chem. Soc. Rev*. **2014**, *43*, 7171.
14. (a) Hajipour, A. R.; Rafiee, F. *Org Prep Proced Int*. **2010**, *42*, 285; (b) Martins, M. A. P.; Frizzo, C. P.; Tier, A. Z.; Moreira, D. N.; Zanatta, N.; Bonacorso, H. G. *Chem. Rev*. **2008**, *108*, 2015; (c) Pârvulescu, V. I.; Hardacre, C. *Chem. Rev*. **2007**, *107*, 2615; (d) Welton, T. *Coord. Chem. Rev*. **2004**, 248, 2459; (e) Earle, M. J.; Seddon, K. R. *Pure Appl. Chem.* **2000**, *72*, 1391.
15. (a) Suleymanov, A. A.; Scopelliti, R.; Tirani, F. F.; Severin, K. *Org. Lett.* **2018**, *20*, 3323; (b) Daia, W.-C.; Wang, Z.-X. *Org. Chem. Front.* **2017**, *4*, 1281; (c) Zhang, Y.; Hu, H.C.; Liu, J.; Cao, D.; Wang, B.; Sun, Y.; Abdukader, A. *Asian J. Org. Chem.* **2017**, *6*, 102; (d) Zhang, Y.; Li, Y.; Zhang, X.; Jiang, X. *Chem. Commun.* **2015**, *51*, 941; (e) Wang, R.; Falck, J. R. *Org. Chem. Front.* **2014**, *1*, 1029; (f) Liu, C.; Lv, J.; Luo, S.; Cheng, J.-P. *Org. Lett.* **2014**, *16*, 5458; (g) Wang, C.; Sun, H.; Fang, Y.; Huang, Y. *Angew. Chem. Int. Ed.* **2013**, *52*, 5795; (h) Wang, C.; Chen, H.; Wang, Z.; Chen, J.; Huang, Y. *Angew. Chem. Int. Ed.* **2012**, *51*, 7242.
16. (a) Xu, K.; Li, L.; Yan, W.; Wu, Y.; Wang, Z.; Zhang, S. *Green Chem.* **2017**, *19*, 4494; (b) Qiu, J.-K.; Hao, W.-J.; Wang, D.-C.; Wei, P.; Sun, J.; Jiang, B.; Tu, S.-J. *Chem. Commun.* **2014**, *50*, 14782; (c) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496; (d) Kang, X.; Yan, R.; Yu, G.; Pang, X.; Liu, X.; Li, X.; Xiang, L.; Huang, G. J. *J. Org. Chem.* **2014**, *79*, 10605; (e) Guo, S.-r.; He, W.-m.; Xiang, J.-n.; Yuan, Y.-q. *Chem. Commun.* **2014**, *50*, 8578; (f) Zhao, X.; Zhang, L.; Li, T.; Liu, G.; Wang, H.; Lu, K. *Chem. Commun.* **2014**, *50*, 13121.
17. (a) Khakyzadeh, V.; Wang, Y. H.; Breit, B. *Chem. Commun.* **2017**, *53*, 4966; (b) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240; (c) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem.* **2011**, *9*, 3151; (d) Ukrainets, I. V.; Tkach, A. A.; Kravtsova, V. V.; Shishkina, S. V. *Chem. Heterocycl. Comp.* **2008**, *44*, 677.
18. (a) Wang, T. T.; Yang, F. L.; Tian, S. K. *Adv. Synth. Catal.* **2015**, *357*, 928; (b) Yang, F. L.; Tian, S. K. *Angew. Chem. Int. Ed.* **2013**, *125*, 5029.
19. (a) Liu, C.; Ding, L.; Guo, G.; Liub, W.; Yang, F. L. *Org. Biomol. Chem.* **2016**, *14*, 2824; (b) Liu, B.; Li, J.; Song, F.; You, J. *Chem. Eur. J.* **2012**, *18*, 10830; (c) Yu, X.; Li, X.; Wan, B. *Org. Biomol. Chem.* **2012**, *10*, 7479.
20. (a) Kumar, S.; Singh, R.; Singh, K. N. *Asian J. Org. Chem.* **2018**, *7*, 359; (b) Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. *Adv. Synth. Catal.* **2015**, *357*, 1181; (c) Singh, R.; Allam, B. K.; Singh, N.; Kumari, K.; Singh, S. K.; Singh, K. N. *Org. Lett.* **2015**, *17*, 2656; (d) Singh, N.; Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 5874; (e) Singh, R.; Raghuvanshi, D. S.; Singh, K. N. *Org. Lett.* **2013**, *15*, 4202.
21. Du, B.; Li, Z.; Qian, P.; Han, J.; Pan, Y. *Chem. Asian J.* **2016**, *11*, 478.
22. Qian, L. W.; Sun, M.; Dong, J.; Xu, Q.; Zhou, Y.; Yin, S. F. *J. Org. Chem.* **2017**, *82*, 6764.
23. Yang, F.-L.; Ma, X.-T.; Tian, S.-K. *Chem. Eur. J.* **2012**, *18*, 1582.
24. Yu, Y.; Chen, X.; Wu, Q.; Liu, D.; Hu, L.; Yu, L.; Tan, Z.; Gui, Q.; Zhu, G. *J. Org. Chem.* **2018**, *83*, 8556.
25. Cao, D.; Zhang, Y.; Liu, C.; Wang, B.; Sun, Y.; Abdukadera, A.; Hu, H.; Liu, Q. *Org. Lett.* **2016**, *18*, 2000.
26. (a) Roglans, A. Quintana, A. P.; Manas, M. M. *Chem. Rev.* **2006**, *106*, 4622; (b) Masllorens, J.; Manas, M. M.; Quintana, A. P.; Roglans, A. *Org. Lett.* **2003**, *5*, 1559; (c) Quintana A. P.; Roglans, A. *ArkiVoc* **2005**, (ix), 51; (d) Cowdrey, W. A.; Davie, D. S. *J. Chem. Soc.* **1949**, *0*, S48-S59.
27. Liu, X.; Li, W.; Zheng, D.; Fan, X.; Wu, J. *Tetrahedron* **2015**, *71*, 3359.
28. Emmett, E. J.; Hayter, B. R.; Willis, M. C. *Angew. Chem. Int. Ed.* **2013**, *52*, 12679.
29. Wu, X.; Wang, Y. *Synlett* **2014**, *25*, 1163.
30. Yang, X.; Shi, L.; Fu, H. *Synlett* **2014**, *25*, 847.
31. Duc, G. L.; Bernoud, E.; Prestat, G.; Cacchi, S.; Fabrizi, G.; Iazzetti, A.; Madec, D.; Poli, G. *Synlett* **2011**, *20*, 2943.
32. Wu, X.; Wang, Y. *New J. Chem.* **2018**, *42*, 10953.
33. Fu, Y.; Xu, Q. S.; Zhou, Q.; Du, Z.; Wang, K. H.; Huang, D.; Hu, Y. *Org. Biomol. Chem.* **2017**, *15*, 2841.
34. Hu, F.; Lei, X. *ChemCatChem* **2015**, *10*, 1539.
35. Richter, H.; Beckendorf, S.; Mancheno, O. G. *Adv. Synth. Catal.* **2011**, *353*, 295.