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Magnetically Separable Copper Ferrite Nanoparticles-Catalyzed Synthesis of Diaryl, Alkyl/Aryl Sulfones from Arylsulfinic Acid Salts and Organohalides/Boronic Acids

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Abstract: A recyclable, inexpensive, non-toxic and environmentally benign catalytic system comprised of magnetically separable copper ferrite ($CuFe_2O_4$) nanoparticles has been developed for the synthesis of diaryl, alkyl/aryl sulfones. Arylsulfinic acid salts are coupled with various alkyl/aryl halides/boronic acids to afford the corresponding diaryl, alkyl/aryl sulfones in good to excellent yields under the identical catalytic system. A wide range of functional group tolerance, with facile recovery of the catalyst by application of an external magnetic field, and consistently high catalytic efficiency for five consecutive cycles render the protocol operationally attractive.

Keywords: boron; copper; nanoparticles; sulfones; sulfur

Introduction

Aryl sulfones are valuable moieties found in various pharmaceuticals, agrochemicals, and polymeric compounds.[1] In particular, their unique bioactivities have attracted considerable interest in medicinal chemistry.[1a,2–24] (please see the Supporting Information) Apart from these, they also form an important class of intermediates in organic synthesis,[25] that exhibit interesting chemical properties[26] and have many industrial applications.[27]

Over the years various methods have been developed for the synthesis of sulfones. However, the majority of them are associated with one or more limitations. The sulfonylation approach is limited to electron-rich substrates and also suffers from formation of a mixture of isomeric products.[28] Oxidation processes, on the other hand, depend on the availability of sulfides or sulfoxides.[29] Harsh reaction conditions and lower yields in the case of sulfinate-sulfone rearrangements[30] and low compability of various functional groups on using organometallic reagents[31] are further limitations.

Recently, a significant improvement in this arena has been made by using copper or palladium complexes as catalysts, under neutral or weakly basic reaction conditions and hence compatible with various functional groups like olefin, amine and other acid- or oxidation-sensitive moieties. Some recent methods are the coupling of sulfinic acid salts with aryl halide and/or aryltriflates,[32] the coupling of arylboronic acids with sulfonyl chlorides,[33] and coupling of arylboronic acids with sulfinic acid salts.[34] More recently the Pd-catalyzed and also metal-free arylation of sulfinic acid sodium salts with diaryliodonium salts has also been developed.[35] However, these methods have limited application due to the use of toxic/or expensive transition metals, low functional group tolerance, limited availability of substrate, low yields, particularly with aryl bromides/or other halides and heterocyclic substrates, longer reaction times, and dry reaction conditions. Moreover, non-recyclability of catalysts limited their scope in large or industrial scale productions. In the context of environmental benign, efficient and clean manufacturing processes, the development of new protocols for the synthesis of aryl sulfones is therefore highly desirable.

Magnetic nanoparticles have emerged as a useful group of heterogeneous catalysts that are robust with high surface area and readily availability. Separation of magnetic nanoparticles is simple and is an attractive alternative to filtration or centrifugation and enhances reusability, making the catalyst environmentally benign, cost-effective and promising for industrial applications. With our experience in sulfone chemistry[36a–c] and as a part of our ongoing research program

in the field of magnetic nanoparticles as catalysts,[36d–g] the application of "magnetic $CuFe_2O_4$ nanoparticles" in the synthesis of aryl sulfones has been explored.[37] $CuFe_2O_4$ nanoparticles are of spinel-type structure having catalytically active copper centers, that have been used in several applications including the recently reported azide-alkyne cycloadditions,[38] epoxide-openings,[39] and Ullmann-type couplings.[40] To the best of our knowledge, $CuFe_2O_4$-catalyzed C–S coupling has not been studied so far.

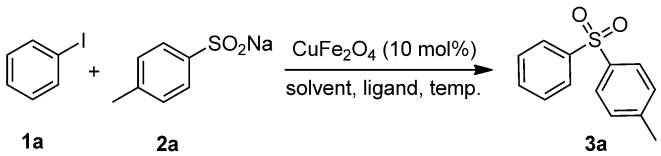
Results and Discussion

To begin with we investigated the traditional cross-coupling reaction of iodobenzene (**1a**) and sodium *para*-toluenesulfinate (**2a**) as a model substrates using $CuFe_2O_4$ catalyst in DMF at 110 °C for synthesis of 1-methyl-4-(phenylsulfonyl)benzene (**3a**).

The initial reaction resulted in a 32% yield of **3a**. To further optimize the reaction conditions, the following reaction variables were examined: the presence or absence of ligands, solvents, and reaction temperature and the results are presented in Table 1. As compared to the initial run (Table 1, entry 1), the addition of 1,10-phenanthroline as ligand significantly improved the yield to 78% of **3a** in DMF (Table 1, entry 8). Furthermore, the bidentate N-ligands like 2,2′-bipyridine, TMEDA, or 1,10-phenanthroline (Table 1, entries 3, 8 and 9) gave good results compared to other ligands used in our model reaction and hence it is interpreted that these ligands can stabilize the generated intermediate copper species in this transformation. Among various solvents used in optimization studies (Table 1, entries 7–15), the best results were obtained by using polar aprotic solvents such as *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (Table 1, entries 1–10) and this can be attributed to the good solubility of sodium arylsulfinic acid salts in these solvents over others. The reaction in solvents like toluene, 1,4-dioxane, THF, water and PEG 400 resulted in significantly lower yields (Table 1, entries 11–15) of **3a**.

Carrying out the reaction without exclusion of air or moisture or under an Ar or N_2 atmosphere resulted in almost the same yield of **3a**; which makes this process advantageous and operationally simple. Use of excess amounts of ligand or catalyst and longer reaction times did not afford any better results. Moreover, to understand the role of iron in the present catalytic system, we carried out two independent reactions with 10 mol% of nano Fe_3O_4 and nano CuO catalysts under the optimized reaction conditions. No yield was observed with nano Fe_3O_4 (Table 1, entry 16) whereas nano CuO (Table 1, entry 17) afforded 40% of the desired product; clearly showing that Cu is the active catalytic center in this reaction. It is worth mentioning

Table 1. Optimization of reaction conditions for the reaction of iodobenzene **1a** with sodium *para*-toluenesulfinate **2a**.[a]



1a **2a** **3a**

Entry	Ligand	Solvent	Yield [%][b]
1	–	DMF	32
2	L-proline	DMF	43
3	2,2′-bipyridine	DMF	46
4	(*S*)-(−)-1,1′-bi(2-naphthol)	DMF	33
5	acetylacetone	DMF	40
6	picolinic acid	DMF	58
7	8-hydroxyquinoline	DMF	31
8	**1,10-phenanthroline**	**DMF**	**78**
9	TMEDA	DMF	43
10	1,10-phenanthroline	DMSO	71
11	1,10-phenanthroline	toluene	32
12	1,10-phenanthroline	1,4-dioxane	34
13	1,10-phenanthroline	THF	0
14	1,10-phenanthroline	water	0
15	1,10-phenanthroline	PEG 400	0
16	1,10-phenanthroline	DMF	0[c]
17	1,10-phenanthroline	DMF	40[d]
18	1,10-phenanthroline	DMF	0[e]
19	1,10-phenanthroline	DMF	10[f]
20	1,10-phenanthroline	DMF	32[g]
21	1,10-phenanthroline	DMF	48[h]

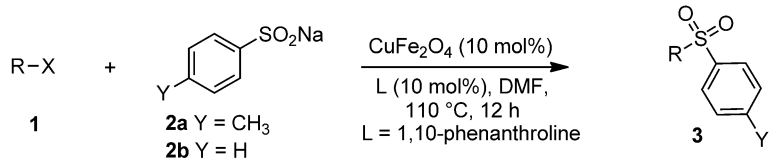
[a] *Reaction conditions:* iodobenzene (1 mmol), sodium *para*-toluenesulfinate (1.2 mmol), ligand (10 mol%) and $CuFe_2O_4$ catalyst (10 mol%) in solvent (2 mL) at 110 °C for 12 h. TMEDA = tetramethylethylenediamine.
[b] Isolated yield.
[c] Reaction with Fe_3O_4 (10 mol%) nanoparticles as catalyst.
[d] Reaction with CuO (10 mol%) nanoparticles as catalyst.
[e] Without catalyst.
[f] Temp. = 25 °C.
[g] Temp. = 60 °C.
[h] Temp. = 80 °C.

that no reaction took place without the catalyst (Table 1, entry 18). Lowering the temperature to 25, 60, and 80 °C resulted in substantially lower yields of 10, 32, and 48%, respectively of **3a** (Table 1, entries 19–21).

After establishing the optimized reaction conditions, i.e., 1.0 equiv. of organohalide, 1.2 equiv. of arylsulfinic acid salt, 10 mol% of $CuFe_2O_4$ and 10 mol% of 1,10-phenanthroline in DMF at 110 °C, we further explored the generality and functional group compatibility of this reaction on various structurally diverse organohalides, and the results are shown in Table 2.

As can be seen from the Table 2, the reaction proceeds smoothly with various aryl or alkyl halides with sodium *para*-toluenesulfinate (**2a**) and/or sodium benzenesulfinate (**2b**) to afford aryl sulfones **3a–3t** in

Table 2. Scope of synthesis of arylsulfones **3** from various organohalides **1**.[a]

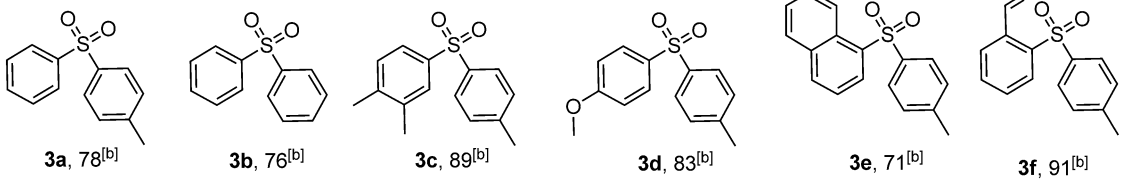


1

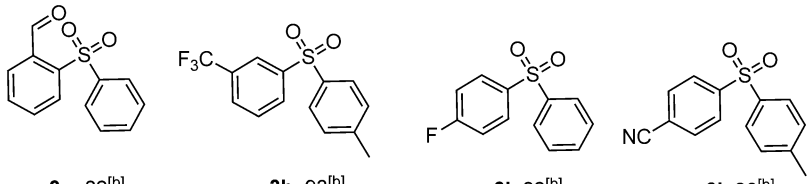
2a Y = CH_3
2b Y = H

3

By using iodo derivatives:

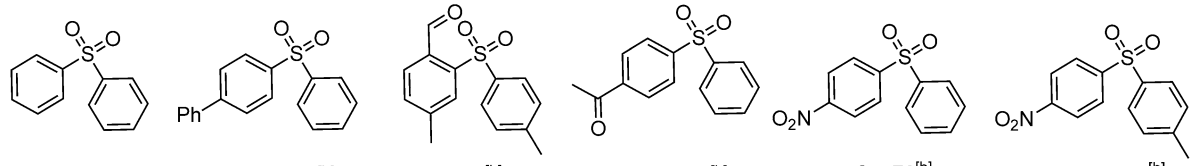


3a, 78[b] **3b**, 76[b] **3c**, 89[b] **3d**, 83[b] **3e**, 71[b] **3f**, 91[b]

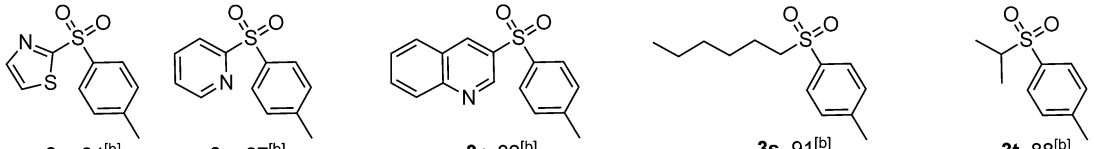


3g, 82[b] **3h**, 93[b] **3i**, 82[b] **3j**, 86[b]

By using bromo derivatives:



3b, 85[b] **3k**, 90[b] **3l**, 67[b] **3m**, 68[b] **3n**, 76[b] **3o**, 88[b]



3p, 84[b] **3q**, 87[b] **3r**, 82[b] **3s**, 91[b] **3t**, 88[b]

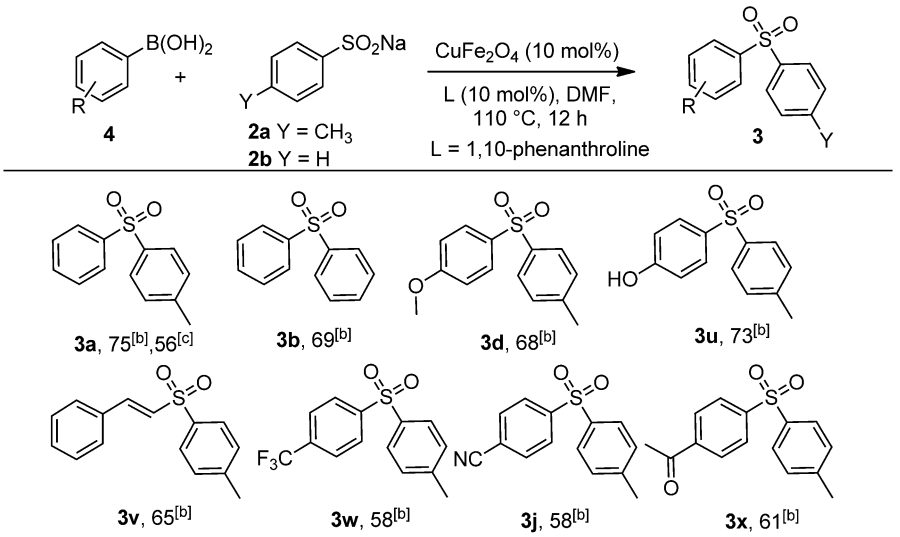
[a] *Reaction conditions:* organohalide (1 mmol), arylsulfinic acid salt (1.2 mmol), 1,10-phenanthroline (10 mol%) and $CuFe_2O_4$ catalyst (10 mol%) in DMF (2 mL) at 110 °C for 12 h.
[b] Isolated yield.

good to excellent yields. The reaction also showed excellent tolerance for various functional groups like ether, nitro, aldehyde, nitrile, and carboxyl.

Notably, regardless of their electronic or steric properties, there is no appreciable difference in the yield with either of the two arylsulfinic acid sodium salts. Moreover, the aromatic substituents have only a minor effect on the outcome of the reaction, for instance, aryl halides having a strong electron-donating substituent such as OMe in 1-iodo-4-methoxybenzene and a strong electron-withdrawing substituent such as F in 1-bromo-4-fluorobenzene provide the desired diaryl sulfones **3d** and **3l** in high yields of 83% and 82%, respectively. However, the outcome of the reaction is favoured for aryl halides having electron-withdrawing substituents. Steric hindrance also does not cause any problem in the reaction, as seen from **3e**, **3f**, **3g**, and **3l** that are obtained in good yields of 71%, 91%, 82%, and 67%, respectively. It was seen that the reactions with organobromine compounds were slightly more sluggish resulting in lower yields of the corresponding aryl sulfones and this can be attributed to the low leaving group property of bromine.

During the catalytic synthesis of aryl heteroaryl sulfones, the basic N-atom present in these substrates can deactivate the catalyst *via* binding with the active catalytic sites. Hence, it is worthwhile to mention that the present protocol can also be extended to synthesize aryl heteroaryl sulfones that are of special interest for the development of new drug molecules. $CuFe_2O_4$ has shown excellent catalytic activity with heteroaryl halides and gave the corresponding aryl heteroaryl sulfones in good to excellent yields, for example, 2-bromothiazole, 2-bromopyridine and 3-bro-

Table 3. Scope of synthesis of diaryl sulfones **3** from various boronic acids **4**.[a]



[a] *Reaction conditions:* boronic acid (1 mmol), arylsulfinic acid salt (1.2 mmol), 1,10-phenanthroline (10 mol%) and $CuFe_2O_4$ catalyst (10 mol%) in DMF (2 mL) at 110 °C for 12 h.
[b] Isolated yield.
[c] Reaction of *para*-toluneboronic acid with sodium benzenesulfinate.

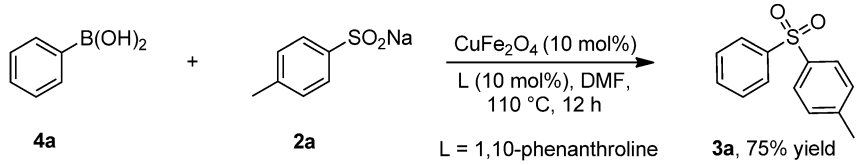
moquinoline afforded the corresponding desired products **3p**, **3q** and **3r** in good yields of 84%, 87%, and 82%, respectively.[41] Notably, alkyl halides like 1-bromohexane and 2-bromopropane also showed excellent conversion to the corresponding alkyl aryl sulfones **3s** and **3t** with yields of 91% and 88%, respectively. The alkylsulfinic acid salts, like methanesulfinic acid sodium salt did not afford the desired product under these reaction conditions. Even the reactions with aryl chlorides were also unfruitful.

Aryl Sulfones *via* Coupling of Boronic Acids with Arylsulfinic Salts

Boronic acids are very common chemicals and are commercially available. Moreover, these can be easily synthesized from aryl halides, triflates and tosylates or by direct borylation of arenes by an iridium-catalyzed C–H bond activation procedure.[42] Furthermore, the boronic acids have been used as a coupling partner with various nucleophiles to synthesize aromatic compounds containing various functional groups *via* an oxidative strategy.[43,44] Based on the previous reports on copper-catalyzed cross-coupling reactions between arylsulfinic salts and boronic acids to synthesize diaryl sulfones,[34] we thought to investigate the feasibility of analogous cross-coupling reactions under our optimized reaction conditions with the present catalytic system. To our delight the cross-coupling between phenylboronic acid (**4a**) and sodium *para*-toluenesulfinate (**2a**) under the optimized reaction conditions resulted in a 75% yield of **3a** (Scheme 1).

Notably this was one of the foremost advantages of the present protocol over existing methods as earlier no single catalytic system was used for two different protocols and also as reported by Batey et al., there is no need to add any oxidant or dehydrating agent in this method.[34b]

We further explored the scope and functional group compatibility of this protocol on various structurally diverse boronic acids, and the results are shown in Table 3.



Scheme 1. The cross-coupling between phenylboronic acid (**4a**) and sodium *para*-toluenesulfinate (**2a**).

A variety of arylboronic acids was subjected to the optimized reaction condition to couple with arylsulfinic acid salts to afford the corresponding diaryl sulfones with moderate to excellent yields. Both electron-rich and electron-deficient substituents on boronic acids have only minor influence on the reaction outcome. A variety of functional groups was also well tolerated under the reaction conditions. It is noteworthy to mention that despite the tendency to get polymerized, the *trans*-2-phenylvinylboronic acid coupled with sodium *para*-toluenesulfinate (**2a**) and resulted in the corresponding (*E*)-1-methyl-4-(styrylsulfonyl)-benzene (**3v**) with 65% yield. It is also worth mentioning that no product was observed by the self-coupling of boronic acids or aryl halides.

Recycling of the Catalyst

Finally, we studied the recyclability of the catalytic system (Table 4). For this, we subjected the $CuFe_2O_4$ nanoparticles to the cross-coupling of iodobenzene (**1a**) with sodium *para*-toluenesulfinate (**2a**) and an analogous, cross-coupling of phenylboronic acid (**4a**) with sodium *para*-toluenesulfinate (**2a**) separately under the optimized reaction conditions for five consecutive cycles.

Table 4. Recovery and reuse of $CuFe_2O_4$ nanoparticles for the sulfonylation of iodobenzene (**1a**)[a] and phenylboronic acid (**4a**)[b].

Run	1st	2nd	3rd	4th	5th	Average
Yield [%][a,c]	78	78	78	76	76	77
Yield [%][b,c]	75	75	74	72	72	73

[a] *Reaction conditions:* iodobenzene (1 mmol), sodium *para*-toluenesulfinate (1.2 mmol), 1,10-phenanthroline (10 mol%) and $CuFe_2O_4$ catalyst (10 mol%) in DMF (2 mL) at 110 °C for 12 h.

[b] *Reaction conditions:* phenylboronic acid (1 mmol), sodium *para*-toluenesulfinate (1.2 mmol), 1,10-phenanthroline (10 mol%) and $CuFe_2O_4$ catalyst (10 mol%) in DMF (2 mL) at 110 °C for 12 h.

[c] Isolated yield.

After completion of the reaction, the reaction mixture was cooled to room temperature, and the catalyst easily separated from the reaction mixture by applying an external magnetic field, then the reaction product was extracted with ethyl acetate. The reaction vial with catalyst was dried in an oven and subjected to a second run of the sulfonylation by charging with the same substrates. The results of five runs showed almost consistent yields. The yields from the second to fifth cycle for sulfonylation of iodobenzene were 78%, 78%, 76%, and 76%, respectively and those of sulfonylation of phenylboronic acid were 75%, 74%, 72%, and 72%, respectively.

Synthesis and Characterization of Catalyst (Nano-$CuFe_2O_4$)

The $CuFe_2O_4$ nanoparticles were prepared according to the literature procedure and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and atomic absorption spectroscopy (AAS).[37] XRD spectra of fresh and used $CuFe_2O_4$ nanoparticles are shown in Figure 1.

The XRD patterns are characteristic of tetragonal $CuFe_2O_4$ (JCPDS card No. 34-0425) with good crystallinity. The XRD analysis shows that the metal oxides present are in the form of the spinel structure of $CuFe_2O_4$ ($d = 2.53$, 2.98, 1.49, 1.61 Å). The particle size was calculated by means of the Debye–Scherrer formula based on the full width at half-maximum of the highest intensity diffraction peak at $2\theta = 35.6°$ and was found to be ~18 nm and is in agreement with

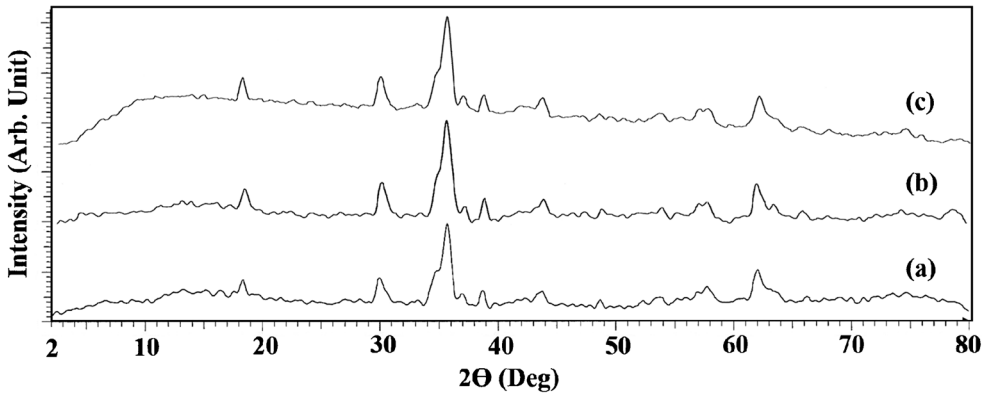


Figure 1. X-ray diffraction patterns of the $CuFe_2O_4$ nanoparticles (a) used in the coupling of sodium *para*-toluenesulfinate with iodobenzene, (b) used in the coupling of sodium *para*-toluenesulfinate with phenylboronic acid after the 5th cycle and (c) fresh catalyst.

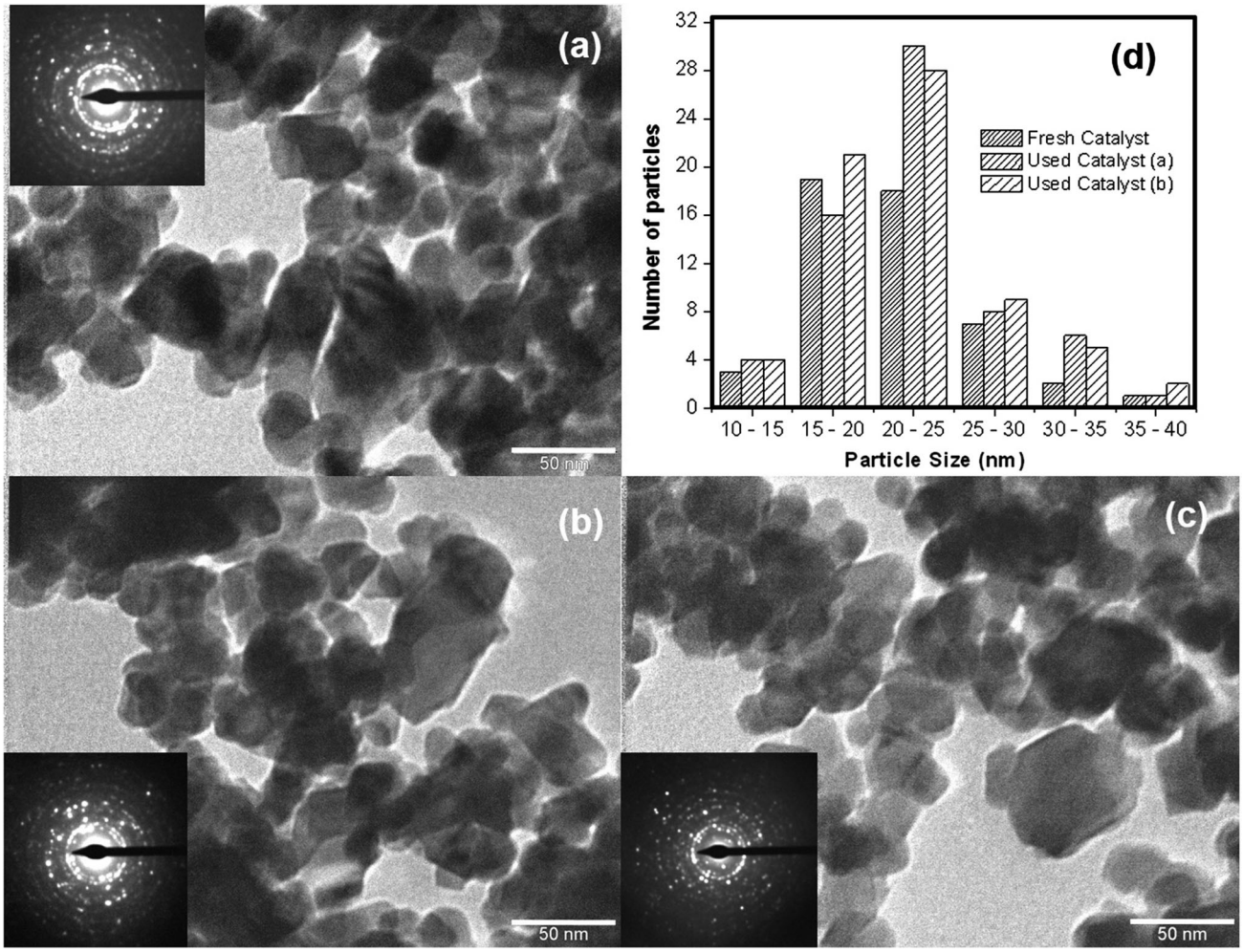


Figure 2. TEM images of $CuFe_2O_4$ nanoparticles (a) used in the coupling of sodium *para*-toluenesulfinate with iodobenzene, (b) used in the coupling of sodium *para*-toluenesulfinate with phenylboronic acid after the 5th cycle, (c) fresh catalyst observed at 120 kV and (d) average size distribution.

TEM analysis (Figure 2), which shows mainly nanoparticles with a particle size in the range of 10–30 nm.

Notably, the morphology and size of the particles were unaltered even after five catalytic cycles, which correlates well with retention of catalytic activity after recycling. The SAED images also confirm the crystalline nature of both the fresh and used magnetic nanoparticles. The oxidation states of the elements in $CuFe_2O_4$ nanoparticles were characterized by XPS, as shown in Figure 3.

The survey scan of $CuFe_2O_4$ nanoparticles shows characteristic peaks for C 1*s* (285 eV), O 1*s* (535 eV), Fe 2*p* (710 eV), and Cu 2*p* (935 eV; Figure 3, A). The high resolution narrow scans for Cu 2*p* in $CuFe_2O_4$ displays binding energy peaks for $2p_{3/2}$ and $2p_{1/2}$, at 934.2 and 953.3 eV (Figure 3, B), clearly showing that copper is in its +2 oxidation state. Likewise the high-resolution narrow scan for Fe 2*p* in $CuFe_2O_4$ reveals Fe $2p_{3/2}$ and Fe $2p_{1/2}$ binding-energy peaks at 710.0 and 723.7 eV (Figure 3, C), respectively. The binding energy peaks for Fe 2*p* of both the fresh and used catalyst could be deconvoluted into two peaks. The peaks centered at 710 eV and 722.6 eV correspond to Fe $2p_{3/2}$ and Fe $2p_{1/2}$ and are due to Fe in +2 oxidation state. The peaks centered around 712.3 and 724.5 eV, corresponding to Fe $2p_{3/2}$ and Fe $2p_{1/2,}$ respectively, and are consistent with typical values for the ferric oxides. The copper content in the catalyst, was determined to be 27.3% by AAS. The leaching of the metal after the five cycles was determined by AAS and was found to be negligible. (0.048%).

Conclusions

In conclusion, we have developed an efficient and environmental friendly catalytic system using magnetically separable $CuFe_2O_4$ nanoparticles for the cross-

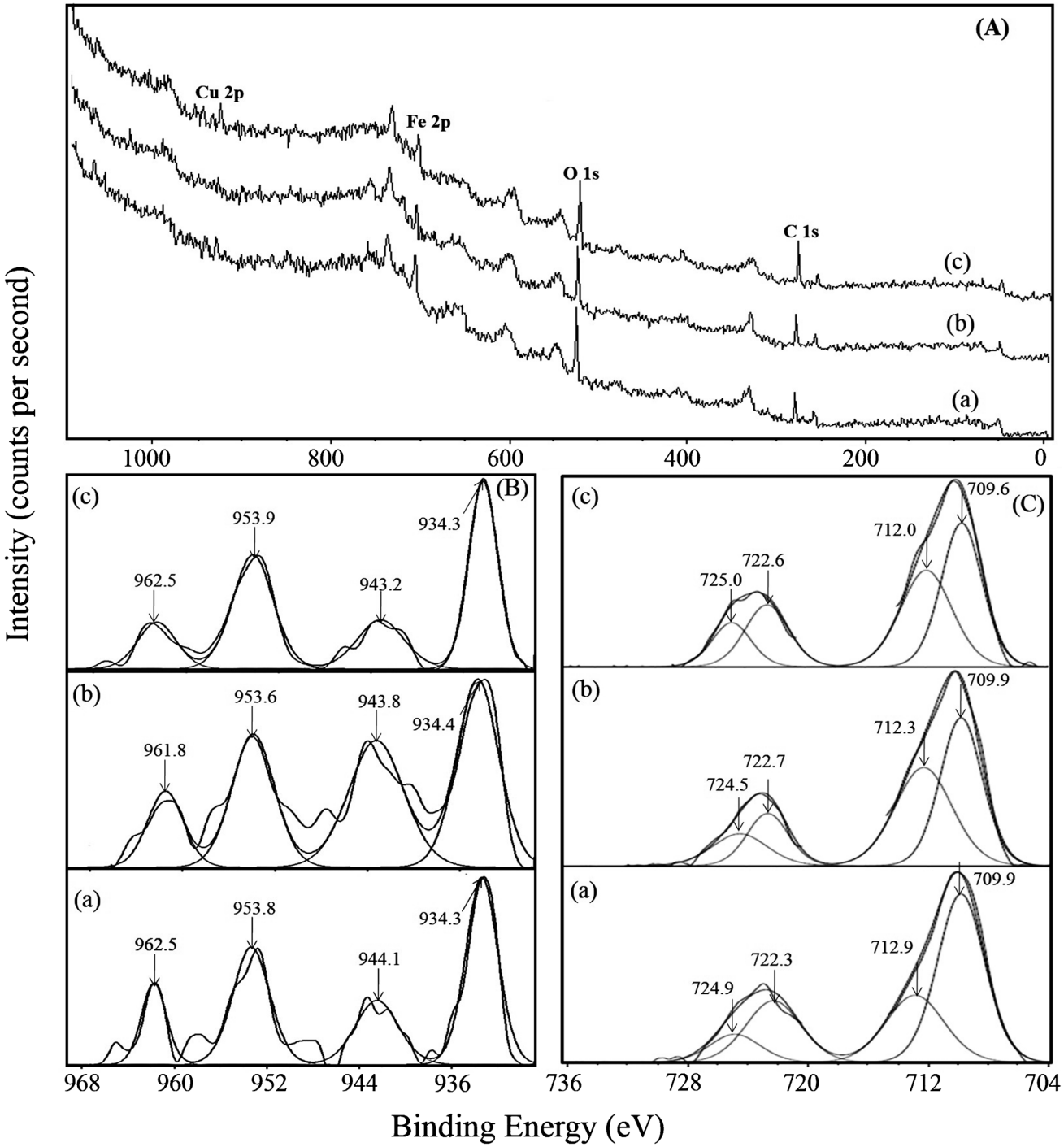


Figure 3. XPS spectra of $CuFe_2O_4$ nanoparticles (a) used in the coupling of sodium *para*-toluenesulfinate with iodobenzene, (b) used in the coupling of sodium *para*-toluenesulfinate with phenylboronic acid after the 5th cycle, and (c) fresh catalyst. (A) XPS survey scans, (B) high-resolution spectra for Cu 2*p* and (C) high-resolution spectra for Fe 2*p*.

coupling between arylsulfinic acid salts with various alkyl or/aryl halide/and boronic acids to generate the corresponding aryl sulfones under similar reaction conditions. The catalyst is magnetically separable and eliminates the requirement of nano catalyst centrifugation after completion of the reaction, which is an additional sustainable attribute of this protocol. The recyclability of the catalytic system makes the reaction economically and potentially viable for commercial applications. To the best of our knowledge it is the first report on the C–S coupling with $CuFe_2O_4$ magnetic nanoparticles. Furthermore, this protocol can be extended for the synthesis of vinyl sulfones.

Experimental Section

General Information

All chemicals were purchased from Sigma–Aldrich and S.D Fine Chemicals, Pvt. Ltd. India and used as received. The particle size and morphology of the samples were studied using a Philips TECNAI F12 FEI transmission electron microscope (TEM). The X-ray powder diffraction (XRD) patterns were recorded on a Rigaku diffractometer with Cu Kα radiation. XPS measurements were obtained on a KRATOS-AXIS 165 instrument equipped with dual aluminium–magnesium anodes using Mg Kα radiation (hν = 1253.6 eV) operated at 5 kV and 15 mA with pass energy 80 eV and an increment of 0.1 eV. The samples were degassed out for several hours in the XPS chamber to minimize air contamination to the sample surface. To overcome the charging problem, a charge neutralizer of 2 eV was applied and the binding energy of C 1*s* core level (BE = 284.6 eV) of adventitious hydrocarbon was used as a standard. The XPS spectra were fitted using a non-linear square method with the convolution of Lorentzian and Gaussian functions after a polynomial background was subtracted from the raw spectra. The IR spectra of all compounds were recorded on a Perkin–Elmer, Spectrum GX FTIR spectrometer. The IR values are reported in reciprocal centimeters (cm^{-1}). ESI mass spectra were recorded on a Finnigan LCQ Advantagemax spectrometer. High-resolution mass spectra (HR-MS) were recorded on a QSTAR XL Hybrid MS/MS mass spectrometer using ESI-QTOF mass spectrometry. All the glassware was dried before use. Ethyl acetate, hexane and acetone were distilled before use. Silica gel (100–200 mesh) was used for column chromatography and reactions were monitored by thin layer chromatography (TLC) carried out on 0.25 mm silica gel coated glass plates $60F_{254}$ using UV light as visualizing agent and iodine or $KMnO_4$ solution followed by heating as developing agent. ^{1}H NMR spectra were recorded at 300 MHz. The chemical shifts are expressed (ppm), referenced to TMS (0.00 ppm) peak. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet. ^{13}C NMR spectra were recorded at 75 MHz. The chemical shifts are expressed (in ppm), reported from the central peak of deuterochloroform (77 ppm). The ^{13}C NMR spectra are proton decoupled. Fe_3O_4 [< 50 nm particle size (TEM), ≥ 98%] and CuO (< 50 nm particle size) were purchased from Sigma–Aldrich.

General Procedure for the Synthesis of Diaryl, Alkyl/Aryl Sulfones

$CuFe_2O_4$ (24 mg, 0.1 mmol) was added to a mixture of organohalide (1 mmol) or boronic acid (1 mmol), arylsulfinic acid salt (1.2 mmol) and 1,10-phenanthroline (0.1 mmol) in 2 mL DMF in a pressure tube, and stirred at 110 °C for 12 h. After completion of the reaction, ethyl acetate (5 mL) was added to the reaction mixture. An external magnetic field applied using a magnet outside the reaction vial to accumulate catalyst then the organic layer decanted, the aforementioned procedure was followed 2 more times with ethyl acetate. The separated catalyst with vial was dried in an oven. For the subsequent run, fresh starting materials were added to the vial and the reaction was conducted as described above. The decanted organic layer was extracted with water twice then the organic layers were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was loaded on a silica gel column and eluted with hexane and ethyl acetate as eluting mixture to afford the pure product.

Characterization Data of Compounds

1-Methyl-4-(phenylsulfonyl)benzene (3a):[35c] Colorless solid; yield: 180 mg (78%); mp 126–128 °C (Lit.[35c] 127–129 °C). IR (KBr): ν = 547, 577, 652, 685, 728, 758, 816, 1019, 1069, 1105, 1155, 1302, 1386, 1446, 1593, 1743, 2924, 3424 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 7.29 (d, 2H, *J* = 8.1 Hz), 7.46–7.57 (m, 3H), 7.83 (d, 2H, *J* = 8.1 Hz), 7.90–7.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 127.4, 127.6, 129.1, 129.8, 132.9, 138.5, 141.8, 144.1; ESI-MS: *m/z* = 233 $(M+H)^+$, 255 $(M+Na)^+$; ESI-HR-MS: *m/z* = 233.0626 $(M+H)^+$, calcd. for $C_{13}H_{13}O_2S$: 233.0630.

Sulfonyldibenzene (3b):[35c] Colorless solid; yield: 166 mg (76%); mp 120–122 °C (Lit.[35c] 122–124 °C). IR (KBr): ν = 426, 559, 587, 686, 727, 761, 995, 1021, 1067, 1103, 1154, 1312, 1446, 1475, 1579, 1743, 1902, 1969, 2852, 2922, 3062, 3422 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.53 (m, 4H), 7.54–7.60 (m, 2H), 7.93–7.98 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.5, 129.2, 133.1, 141.5; ESI-MS: *m/z* = 219 $(M+H)^+$, 241 $(M+Na)^+$; ESI-HR-MS: *m/z* = 219.0466 $(M+H)^+$, calcd. for $C_{12}H_{11}O_2S$: 219.0474.

1,2-Dimethyl-4-tosylbenzene (3c):[45a] White solid; yield: 232 mg (89%); mp 54–56 °C (Lit.[45a] 55 °C). IR (KBr): ν = 441, 546, 576, 650, 685, 727, 757, 816, 995, 1018, 1068, 1104, 1154, 1309, 1399, 1446, 1592, 1656, 1727, 1925, 2852, 2921, 2959, 3061, 3423 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3H), 2.29 (s, 3H), 2.38 (s, 3H), 7.23 (d, 1H, *J* = 7.9 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 7.63–7.69 (m, 2H), 7.81 (d, 2H, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.7, 19.9, 21.5, 125.0, 127.4, 128.2, 129.7, 130.2, 137.9, 139.0, 139.0, 142.6, 143.7; ESI-MS: *m/z* = 261 $(M+H)^+$; ESI-HR-MS: *m/z* = 261.0937 $(M+H)^+$, calcd. for $C_{15}H_{17}O_2S$: 261.0943.

1-Methoxy-4-tosylbenzene (3d):[34a] Yellow solid; yield: 218 mg (83%); mp 101–103 °C (Lit.[34a] 100–102 °C). IR (KBr): ν = 551, 632, 678, 711, 803, 831, 1018, 1071, 1106, 1150, 1180, 1264, 1295, 1317, 1412, 1457, 1494, 1596, 1743, 1916, 2924, 2971, 3095, 3448 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3H), 3.84 (s, 3H), 6.95 (d, 2H, *J* = 8.8 Hz), 7.28 (d, 2H, *J* = 8.1 Hz), 7.80 (d, 2H, *J* = 8.1 Hz), 7.86 (d, 2H, *J* = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 55.5, 114.3, 127.3, 129.6, 129.7, 133.4, 139.3, 143.6, 163.1; ESI MS: *m/z* = 263 $(M+H)^+$, 285 $(M+Na)^+$; ESI-HR-MS: *m/z* = 263.0730 $(M+H)^+$, calcd. for $C_{14}H_{15}O_3S$: 263.0736.

1-Tosylnaphthalene (3e):[28d] White solid; yield: 200 mg (71%); mp 100–102 °C (Lit.[28d] 102–104 °C). IR (KBr): ν = 446, 504, 542, 580, 648, 688, 739, 773, 810, 970, 1016, 1083, 1131, 1153, 1196, 1307, 1400, 1504, 1592, 1654, 1735, 1920, 2853, 2923, 3060, 3421 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.34 (s, 3H), 7.23–7.27 (m, 2H), 7.50–7.64 (m, 3H), 7.85 (d, 2H, *J* = 8.3 Hz), 7.89 (d, 1H, *J* = 8.1 Hz), 8.07 (d, 1H, *J* = 8.1 Hz), 8.48–8.51 (m, 1H), 8.64 (d, 1H, *J* = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, DMSO-d_6): δ = 19.4, 122.0, 122.8, 125.1, 125.4, 125.9, 126.5, 127.4, 127.7, 128.0, 132.1,

133.4, 133.9, 136.6, 142.2; ESI-MS: m/z = 283 $(M+H)^+$, 305 $(M+Na)^+$; ESI-HR-MS: m/z = 283.0773 $(M+H)^+$, calcd. for $C_{17}H_{15}O_2S$: 283.0787.

2-Tosylbenzaldehyde (3f): White solid; yield: 237 mg (91%); mp 72–73 °C (Lit.[32b] 73–74 °C). IR (KBr): ν = 461, 506, 574, 652, 705, 731, 771, 814, 1045, 1088, 1119, 1157, 1184, 1258, 1314, 1396, 1449, 1493, 1589, 1692, 1922, 2923, 3083, 3449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.33 (d, 2H, J = 8.1 Hz), 7.68–7.83 (m, 4H), 7.98–8.05 (m, 1H), 8.14–8.22 (m, 1H), 10.86 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 127.4, 129.3, 129.3, 130.1, 130.2, 133.6, 133.7, 138.3, 142.6, 144.9, 189.4; ESI-MS: m/z = 283 $(M+Na)^+$; ESI-HR-MS: m/z = 283.0384 $(M+Na)^+$, calcd. for $C_{14}H_{12}O_3NaS$: 283.0399.

2-(Phenylsulfonyl)benzaldehyde (3g):[45b] White solid; yield: 202 mg (82%); mp 90–92 °C (Lit.[45b] 92.0–93.5 °C). IR (KBr): ν = 450, 484, 561, 585, 680, 734, 1087, 1119, 1152, 1188, 1313, 1397, 1445, 1473, 1579, 1700, 1963, 2767, 2853, 2889, 2922, 3069, 3448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.57 (m, 2H), 7.59–7.64 (m, 1H), 7.72–7.80 (m, 2H), 7.89–7.92 (m, 2H), 8.01–8.05 (m, 1H), 8.19–8.22 (m, 1H), 10.85 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.3, 129.0, 129.4, 129.4, 129.5, 133.6, 133.7, 133.8, 141.3, 142.1, 189.2; ESI-MS: m/z = 269 $(M+Na)^+$; ESI-HR-MS: m/z = 269.0230 $(M+Na)^+$, calcd. for $C_{13}H_{10}O_3NaS$: 269.0242.

1-Tosyl-3-(trifluoromethyl)benzene (3h):[34a] Yellow solid; yield: 279 mg (93%); mp 80–82 °C (Lit.[34a] 81–83 °C). IR (KBr): ν = 493, 540, 576, 666, 696, 725, 806, 905, 1066, 1107, 1136, 1326, 1402, 1437, 1489, 1598, 1927, 2922, 3449 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.34 (d, 2H, J = 8.2 Hz), 7.65 (t, 1H, J = 7.8 Hz), 7.80 (d, 1H, J = 7.8 Hz), 7.85 (d, 2H, J = 8.2 Hz), 8.11 (d, 1H, J = 7.8 Hz), 8.19 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 124.5, 127.8, 129.6, 130.0, 130.1, 130.7, 131.7, 137.5, 143.2, 144.8; ESI-MS: m/z = 323 $(M+Na)^+$; ESI-HR-MS: m/z = 301.0491 $(M+H)^+$, calcd. for $C_{14}H_{12}O_2F_3S$: 301.0504.

1-Fluoro-4-(phenylsulfonyl)benzene (3i):[35c] Colorless solid; yield: 194 mg (82%); mp 111–112 °C (Lit.[35c] 112–113 °C). IR (KBr): ν = 405, 454, 546, 575, 653, 686, 730, 757, 841, 1002, 1068, 1102, 1152, 1236, 1291, 1318, 1403, 1447, 1491, 1586, 1916, 2922, 3073, 3100, 3451 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.15–7.21 (m, 2H), 7.49–7.54 (m, 2H), 7.56–7.60 (m, 1H), 7.92–7.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 116.5 (d, J = 22.50 Hz), 127.4, 129.3, 130.4 (d, J = 9.88 Hz), 133.2, 137.5 (d, J = 2.74 Hz), 141.3, 165.4 (d, J = 255.74 Hz); ESI-MS: m/z = 259 $(M+Na)^+$; ESI-HR-MS: m/z = 259.0194 $(M+Na)^+$, calcd. for $C_{12}H_9O_2FNaS$: 259.0199.

4-Tosylbenzonitrile (3j):[34a] Yellow solid; yield: 222 mg (86%); mp 129–131 °C (Lit.[34a] 129–131 °C). IR (KBr): ν = 419, 472, 521, 562, 610, 637, 669, 704, 780, 813, 844, 976, 1015, 1069, 1102, 1154, 1185, 1287, 1320, 1396, 1456, 1489, 1593, 1661, 1741, 1932, 2231, 2852, 2922, 2958, 3093, 3411 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.34 (d, 2H, J = 8.7 Hz), 7.79 (d, 2H, J = 8.7 Hz), 7.83 (d, 2H, J = 8.3 Hz), 8.04 (d, 2H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 116.6, 117.1, 127.9, 128.0, 130.2, 132.9, 136.9, 145.1, 146.1; ESI-MS: m/z = 280 $(M+Na)^+$; ESI-HR-MS; m/z = 280.0406 $(M+Na)^+$, calcd. for $C_{14}H_{11}NO_2NaS$: 280.0408.

4-(Phenylsulfonyl)-1,1′-biphenyl (3k):[45c] Pale yellow solid; yield: 265 mg (90%); mp 150–151 °C (Lit.[45c] 148–149 °C). IR (KBr): ν = 407, 537, 594, 664, 724, 760, 842, 1001, 1072, 1108, 1156, 1182, 1291, 1308, 1394, 1446, 1594, 1726, 2853, 2924, 2956, 3060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.62 (m, 8H), 7.70 (d, 2H, J = 8.4 Hz), 7.92–8.06 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 127.2, 127.6, 127.8, 128.1, 128.5, 129.0, 129.2, 133.1, 139.1, 140.0, 141.6, 146.1; ESI-MS: m/z = 295 $(M+H)^+$; ESI-HR-MS: m/z = 295.0780 $(M+H)^+$, calcd. for $C_{18}H_{15}O_2S$: 295.0787.

4-Methyl-2-tosylbenzaldehyde (3l): Pale yellow solid; yield: 184 mg (67%); mp 120–122 °C. IR (KBr): ν = 456, 508, 574, 632, 654, 708, 789, 819, 884, 1049, 1088, 1150, 1200, 1310, 1405, 1448, 1492, 1594, 1695, 1743, 1940, 2779, 2854, 2922, 3373 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 2.51 (s, 3H), 7.32 (d, 2H, J = 8.1 Hz), 7.50 (d, 1H, J = 7.9 Hz), 7.77 (d, 2H, J = 8.1 Hz), 7.93 (d, 1H, J = 7.9 Hz), 8.01 (s, 1H), 10.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 21.7, 127.3, 129.4, 129.7, 130.1, 131.2, 134.2, 138.5, 142.3, 144.7, 145.2, 189.1; ESI-MS: m/z = 275 $(M+H)^+$, 297 $(M+Na)^+$; ESI-HR-MS: m/z = 297.0543 $(M+Na)^+$, calcd. for $C_{15}H_{14}O_3NaS$: 297.0555.

1-[4-(Phenylsulfonyl)phenyl]ethanone (3m):[45d] Yellow solid; yield: 177 mg (68%); mp 131–133 °C (Lit.[32d] 132–134 °C). IR (KBr): ν = 456, 496, 555, 591, 628, 702, 766, 846, 961, 1070, 1104, 1161, 1254, 1299, 1322, 1359, 1396, 1446, 1581, 1685, 1937, 2855, 2923, 3039, 3089, 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.62 (s, 3H), 7.49–7.64 (m, 3H), 7.96 (d, 2H, J = 7.6 Hz), 8.01–8.10 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.8, 127.7, 127.9, 129.0, 129.4, 133.6, 140.2, 140.6, 145.3, 196.6; ESI-MS: m/z = 283 $(M+Na)^+$; ESI-HR-MS: m/z = 261.0583 $(M+H)^+$, calcd. for $C_{14}H_{13}O_3S$: 261.0579.

1-Nitro-4-(phenylsulfonyl)benzene (3n):[35c] Yellow solid; yield: 200 mg (76%); mp 140–142 °C (Lit.[35c] 143–145 °C). IR (KBr): ν = 475, 560, 604, 680, 733, 854, 922, 1006, 1067, 1103, 1154, 1300, 1354, 1449, 1475, 1529, 1582, 1606, 1745, 1802, 2854, 2925, 3099, 3446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.52–7.68 (m, 3H), 7.98 (d, 2H, J = 7.6 Hz), 8.14 (d, 2H, J = 8.3 Hz), 8.35 (d, 2H, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 124.4, 127.9, 128.9, 129.6, 134.0, 139.9, 147.2, 150.2; ESI-MS: m/z = 286 $(M+Na)^+$; ESI-HR-MS: m/z = 286.0148 $(M+Na)^+$, calcd. for $C_{12}H_9NO_4NaS$: 286.0150.

1-Methyl-4-[(4-nitrophenyl)sulfonyl]benzene (3o):[45e] Yellow solid; yield: 244 mg (88%); mp 163–165 °C (Lit.[45e] 164–165 °C). IR (KBr): ν = 443, 494, 545, 592, 655, 684, 738, 815, 857, 1012, 1035, 1068, 1104, 1157, 1300, 1349, 1403, 1528, 1592, 1693, 2862, 2914, 3036, 3065, 3103, 3448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H), 7.35 (d, 2H, J = 8.1 Hz), 7.85 (d, 2H, J = 8.1 Hz), 8.11 (d, 2H, J = 8.6 Hz), 8.33 (d, 2H, J = 8.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, DMSO-d_6): δ = 20.9, 123.8, 127.3, 128.1, 129.6, 136.2, 144.7, 146.9, 149.5; ESI-MS: m/z = 300 $(M+Na)^+$; ESI-HR-MS: m/z = 278.0487 $(M+H)^+$, calcd. for $C_{13}H_{12}O_4NS$: 278.0481.

2-Tosylthiazole (3p): Yellow solid; yield: 201 mg (84%); mp 124–126 °C. IR (KBr): ν = 470, 540, 583, 672, 705, 733, 813, 965, 1012, 1052, 1090, 1146, 1169, 1295, 1329, 1400, 1468, 1592, 1662, 1740, 1940, 2413, 2853, 2923, 2956, 3049, 3123, 3448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 7.37 (d, 2H, J = 8.1 Hz), 7.65 (d, 1H, J = 2.9 Hz), 7.95 (d, 1H, J = 2.9 Hz), 7.99 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7, 124.6, 125.6, 128.7, 130.1, 135.7, 145.2, 145.6; ESI-MS: m/z = 240 $(M+H)^+$, 262 $(M+Na)^+$;

ESI-HR-MS: m/z = 240.0150 $(M+H)^+$, calcd. for $C_{10}H_{10}O_2NS_2$: 240.0147.

2-Tosylpyridine (3q):[45d] Yellow solid; yield: 203 mg (87%); mp 101–102 °C (Lit.[45e] 102–103 °C). IR (KBr): ν = 436, 542, 580, 655, 736, 769, 815, 899, 989, 1040, 1070, 1121, 1168, 1294, 1317, 1427, 1451, 1492, 1593, 1667, 1740, 1935, 2854, 2924, 3055, 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.33 (d, 2H, J = 8.1 Hz), 7.40–7.50 (m, 1H), 7.86–8.02 (m, 3H), 8.19 (d, 1H, J = 7.7 Hz), 8.62–8.73 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 121.8, 126.7, 128.7, 129.6, 135.7, 137.9, 144.7, 150.2, 158.8; ESI MS: m/z = 234 $(M+H)^+$, 256 $(M+Na)^+$; ESI-HR-MS: m/z = 234.0578 $(M+H)^+$, calcd. for $C_{12}H_{12}O_2NS$: 234.0583.

3-Tosylquinoline (3r):[45f] Yellow solid; yield: 234 mg (82%); mp 166–167 °C (Lit.[45f] 165–170 °C); IR (KBr): ν = 406, 473, 550, 679, 755, 787, 815, 918, 1017, 1091, 1149, 1310, 1363, 1452, 1492, 1590, 1742, 2854, 2925, 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.68 (t, 1H, J = 7.8 Hz), 7.87 (t, 1H, J = 7.8 Hz), 7.91 (d, 2H, J = 8.2 Hz), 7.96 (d, 1H, J = 8.3 Hz), 8.16 (d, 1H, J = 8.3 Hz), 8.79–8.83 (m, 1H), 8.26 (d, 1H, J = 1.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 126.3, 127.7, 128.2, 129.0, 129.5, 130.1, 132.5, 135.0, 136.5, 137.9, 144.8, 147.0, 149.1; ESI-MS: m/z = 284 $(M+H)^+$; ESI-HR-MS: m/z = 284.0734 $(M+H)^+$, calcd. for $C_{16}H_{14}O_2NS$: 284.0739.

1-(Hexylsulfonyl)-4-methylbenzene (3s):[45g] Liquid; yield: 219 mg (91%). IR (KBr): ν = 522, 565, 629, 721, 816, 1088, 1145, 1215, 1316, 1460, 1493, 1598, 1741, 2862, 2928, 3426 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.87 (m, 3H), 1.22–1.28 (m, 4H), 1.32–1.38 (m, 2H), 1.65–1.72 (m, 2H), 2.45 (s, 3H), 3.03–3.08 (m, 2H), 7.36 (d, 2H, J = 8.0 Hz), 7.78 (d, 2H, J = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 21.6, 22.2, 22.6, 27.9, 31.1, 56.4, 128.0, 129.8, 136.2, 144.5; ESI-MS: m/z = 241 $(M+H)^+$, 263 $(M+Na)^+$; ESI-HR-MS: m/z = 241.1251 $(M+H)^+$, calcd. for $C_{13}H_{21}O_2S$: 241.1256.

1-(Isopropylsulfonyl)-4-methylbenzene (3t):[45h] White solid; yield: 175 mg (88%); mp 76–77 (Lit.[45 h] 78 °C). IR (KBr): ν = 454, 557, 641, 717, 817, 1019, 1087, 1141, 1262, 1307, 1464, 1596, 2932, 2980, 3424 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 1.29 (d, 6H, J = 6.8 Hz), 2.45 (s, 3H), 3.14–3.20 (m, 1H), 7.36 (d, 2H, J = 8.0 Hz), 7.76 (d, 2H, J = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.6, 21.4, 55.4, 128.9, 129.5, 133.8, 144.4; ESI-MS: m/z = 199 $(M+H)^+$, 221 $(M+Na)^+$; ESI-HR-MS: m/z = 199.0785 $(M+H)^+$, calcd. for $C_{10}H_{15}O_2S$: 199.0787.

4-Tosylphenol (3u):[45i] Colorless solid; yield: 182 mg (73%); mp 140–141 °C (Lit.[45i] 140–142 °C). IR (KBr): ν = 554, 637, 683, 707, 811, 840, 1015, 1069, 1104, 1149, 1240, 1286, 1377, 1445, 1583, 1647, 1742, 1914, 2853, 2924, 3160, 3458 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3H), 6.90 (d, 2H, J = 8.2 Hz), 7.28 (d, 2H, J = 8.0 Hz), 7.71–7.85 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 116.1, 127.1, 129.7, 129.8, 132.1, 138.8, 143.9, 160.7; ESI-MS: m/z = 249 $(M+H)^+$, 271 $(M+Na)^+$; ESI-HR-MS: m/z = 249.0570 $(M+H)^+$, calcd. for $C_{13}H_{13}O_3S$: 249.0579.

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (3v):[45j] White solid; yield: 168 mg (65%); mp 118–120 °C (Lit.[45j] 118–120 °C). IR (KBr): ν = 479, 536, 660, 745, 815, 969, 1081, 1141, 1307, 1388, 1451, 1601, 2856, 2924, 3041, 3448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H), 6.85 (d, 1H, J = 15.4 Hz), 7.34 (d, 2H, J = 8.1 Hz), 7.37–7.42 (m, 3H), 7.46–7.50 (m, 2H), 7.66 (d, 1H, J = 15.4 Hz), 7.83 (d, 2H, J = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 127.5, 127.6, 128.4, 129.0, 129.9, 131.0, 132.4, 137.6, 141.9, 144.3;: ESI-MS: m/z = 259 $(M+H)^+$; ESI-HR-MS: m/z = 259.0788 $(M+H)^+$, calcd. for $C_{15}H_{15}O_2S$: 259.0787.

1-Methyl-4-{[4-(trifluoromethyl)phenyl]sulfonyl}benzene (3w):[34a] Yellow solid; yield: 174 mg (58%); mp 106–107 °C (Lit.[34a] 105–107 °C). IR (KBr): ν = 588, 659, 716, 815, 843, 1058, 1156, 1293, 1323, 1405, 1451, 1495, 1597, 1741, 1934, 2854, 2925, 3060, 3107, 3455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.41 (s, 3H), 7.33 (d, 2H, J = 8.0 Hz), 7.75 (d, 2H, J = 8.0 Hz), 7.84 (d, 2H, J = 8.0 Hz), 8.06 (d, 2H, J = 8.0 Hz);. ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.5, 123.0 (q, J = 273.07 Hz), 126.3 (q, J = 3.63 Hz), 127.8, 127.9, 130.1, 134.5 (q, J = 32.96 Hz), 137.4, 144.8, 145.5; ESI-MS: m/z = 301 $(M+H)^+$, 323 $(M+Na)^+$; ESI-HR-MS: m/z = 323.03161 $(M+Na)^+$, calcd. for $C_{14}H_{11}O_2F_3NaS$: 323.0324.

1-(4-Tosylphenyl)ethanone (3x):[45d] Yellow solid; yield: 168 mg (61%); mp 146–148 °C. IR (KBr): ν = 540, 581, 664, 767, 820, 959, 1011, 1073, 1156, 1182, 1257, 1317, 1462, 1594, 1687, 2854, 2924, 3093, 3447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 3H), 2.61 (s, 3H), 7.32 (d, 2H, J = 8.1 Hz), 7.84 (d, 2H, J = 8.1 Hz), 8.00–8.06 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 26.8, 127.7, 127.8, 128.9, 130.0, 137.6, 140.0, 144.7, 145.7, 196.7; ESI-MS: m/z = 297 $(M+Na)^+$; ESI-HR-MS: m/z = 275.0734 $(M+H)^+$, calcd. for $C_{15}H_{15}O_3S$: 275.0736.

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