RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2014, **4**, 44621

Received 2nd August 2014
Accepted 5th September 2014

DOI: 10.1039/c4ra08014a

www.rsc.org/advances

Iodine-promoted 2-arylsulfanylphenol formation using cyclohexanones as phenol source†

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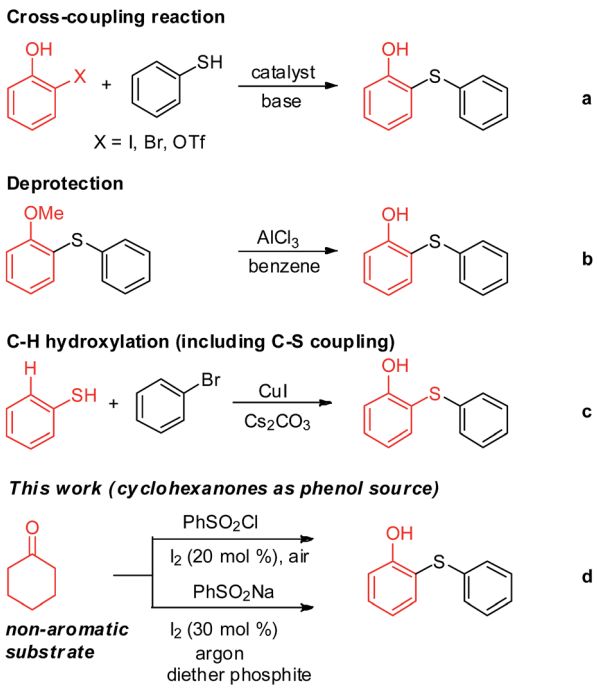
A novel method for the formation of 2-arylsulfanylphenols using cyclohexanones as phenol source *via* dehydrogenation is described. Various aromatic sodium sulfinates and sulfonyl chlorides acted as efficient coupling partners to construct new C–S bonds in the presence of an iodine promoter.

Introduction

Aryl thioethers are important structural motifs which are widely present in agrochemicals, functional materials, naturally occurring compounds and pharmaceutical products.[1] Therefore, the development of efficient methods for the preparation of aryl thioethers has stimulated considerable interest.[2] Over the past several decades, the transition-metal catalyzed cross-coupling reaction of aryl halides with various sulfenylating agents has proved to be powerful method for the construction of new C–S bond. With the tremendous developments in the C–S bond formation, thiols have been the most-popular sulfenylating reagents in the preparation of aryl thioethers.[3] In recent years, the direct sulfenylation of C–H bonds has attracted great interest since this method can potentially lead to more efficient synthesis with a reduced number of synthetic operations. Various sulfenylating agents such as thiols,[4] disulfides,[5] sulfonyl chlorides,[6] sulfenyl halides,[7] sodium sulfinates[8] and sulfonyl hydrazides[9] were successfully employed to couple with electron-rich (hetero)-arenes.

Among various thioether derivatives, 2-arylsulfanylphenols play an important role in biologically and pharmaceutically active molecules due to they also contain a phenol structural motif.[10] However, procedures for preparation of aryl thioethers with a hydroxyl group at the *ortho* position are still rare, and the majors are based on the metal-catalyzed cross-coupling of thiols with 2-halophenols (Scheme 1a).[11] Deprotection of the corresponding methoxy aryl thioethers provided an alternative procedure for 2-arylsulfanylphenols (Scheme 1b).[12] Oxidation of the C–H or C–halogen bond *ortho* to aryl thioethers afforded another efficient procedure for substituted 2-arylsulfanylphenols.[13] In 2010, Pan and co-workers reported an efficient protocol for the preparation of 2-arylsulfanylphenols from thiophenols and aromatic halides *via* a copper-catalyzed tandem transformation of C–S coupling/C–H hydroxylation (Scheme 1c).[14] Although there are other few methods available for 2-arylsulfanylphenol preparation,[15] all of the above-mentioned approaches require two aromatic coupling partners. Aryl thioether preparation from non-aromatic coupling partners is still rare.[16]

Recently, the Stahl group reported a palladium-catalyzed procedure to convert non-aromatic cyclohexanones into phenols or cyclohexenones *via* dehydrogenation strategy under mild reaction conditions using oxygen as the sole oxidant.[17] We



Scheme 1 Various procedures for 2-arylsulfanylphenol preparation.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra08014a

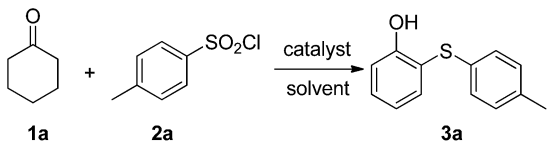
and others successfully used cyclohexanones as aryl sources for C–C,[18] C–N[19] and C–O[20] bond formation. We and Wei's group also found that 2-arylsulfanylphenols could be generated from cyclohexanones using thiophenols or disulfides as the sulfur sources in the presence of iodine catalyst.[21] Nevertheless, these sulfenylating agents possess unpleasant odors or are expensive. Moreover, they suffer from a narrow substrate scope. Cyclohexanones are cheap, readily available, and able to convert into other important organic materials.[22] Thus, cyclohexanones can be used as an ideal aryl source for coupling reaction *via* dehydrogenation strategy. Due to the importance of 2-arylsulfanylphenols in pharmaceutical drugs and other biologically active compounds, it's highly desirable to develop reliable and general procedures for preparation of them using readily available starting materials. As our continuing efforts using cyclohexanones as aryl source for coupling reactions, herein, we describe the iodine-promoted 2-arylsulfanylphenol formation from cyclohexanones using aryl sulfonyl chlorides and sodium sulfinates as the sulfur sources (Scheme 1d).

Results and discussion

Firstly, we started our study by using cyclohexanone (**1a**) and *p*-toluenesulfonyl chloride (**2a**) as the model substrates to get the optimized reaction conditions. The desired product **3aa** was detected only in trace amount when the reaction was carried out in 1,4-dioxane at 150 °C under air atmosphere in the absence of catalyst (Table 1, entry 1). Subsequently, several iodide-containing catalysts were investigated under similar reaction conditions, and among them iodine showed the best efficiency (entries 2–4). When 20 mol% of iodine was used, the desired product was obtained in 88% yield (entry 4). Other organic solvents were also tested and all of them were less efficient for this kind of transformation (entries 5–10). It's necessary to use 20 mol% of iodine to get satisfactory yield, and the reaction yield decreased to 53% when the catalyst loading was decreased to 10 mol% (Table 1, entry 11). The reaction temperature also affected the reaction yield significantly, and only 68% yield was observed when the reaction was carried out at 130 °C (entry 12). Interestingly, slight lower yields were detected when the reaction were run under oxygen or argon atmosphere (Table 1, entry 13–14).

With the optimized reaction conditions in hand, we first investigated the substrate scope with respect to cyclohexanones as shown in Table 2. Cyclohexanones bearing an alkyl group at the *para* position were able to smoothly react with **2a** to give the desired products (**3aa–3fa**) in good yields. Besides alkyl substituted cyclohexanones, aryl substituted cyclohexanones such as 4-phenylcyclohexanone (**1g**) and 4-(4-hydroxyphenyl)-

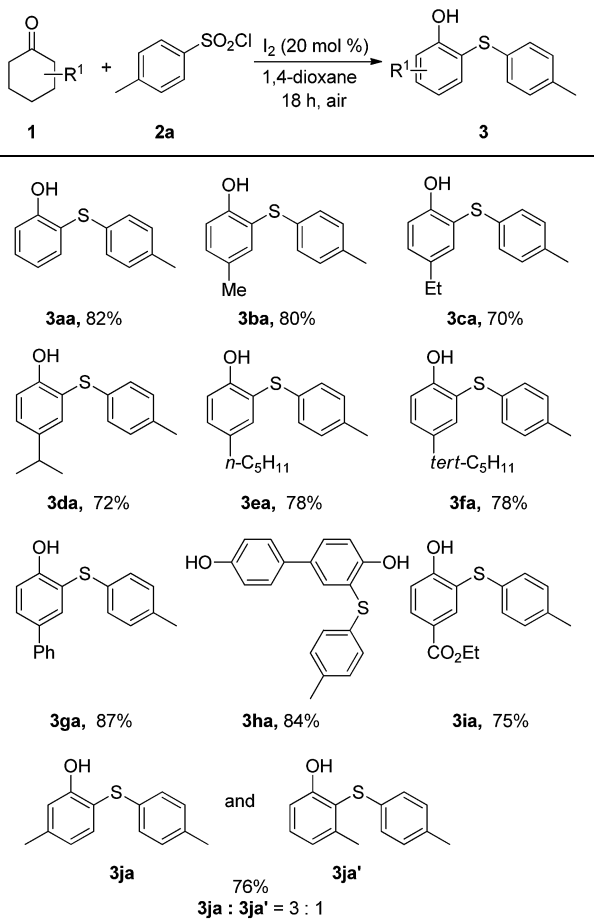
Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Yield[b] (%)
1		1,4-Dioxane	Trace
2	KI	1,4-Dioxane	18
3	NIS	1,4-Dioxane	37
4	I_2	1,4-Dioxane	88
5	I_2	NMP	50
6	I_2	DMA	26
7	I_2	Diglyme	14
8	I_2	Toluene	6
9	I_2	Dibutyl ether	20
10	I_2	Anisole	8
11[c]	I_2	1,4-Dioxane	53
12[d]	I_2	1,4-Dioxane	68
13[e]	I_2	1,4-Dioxane	76
14[f]	I_2	1,4-Dioxane	70

[a] Conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), catalyst (20 mol%), solvent (0.5 mL), 150 °C, 18 h, under air. [b] GC yield. [c] Catalyst (10 mol%). [d] 130 °C. [e] Under argon. [f] Under oxygen.

Table 2 Reaction of *p*-toluenesulfonyl chloride (**2a**) with various cyclohexanones[a]

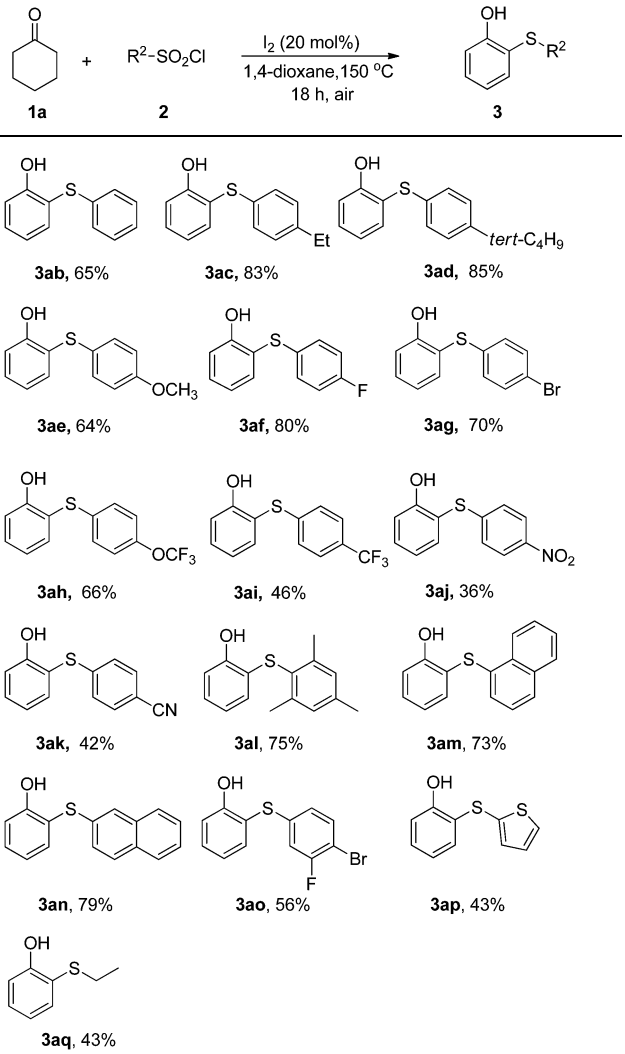


[a] Conditions: **1** (0.5 mmol), **2a** (0.6 mmol), I_2 (0.1 mmol), 1,4-dioxane (1.0 mL), 150 °C, 18 h, air; isolated yield.

cyclohexanone (**1h**) also participated well in this process, and gave the corresponding products **3ga** and **3ha** in 87% and 84% yields, respectively. To our delight, the ester functional group was well tolerated in this reaction, and the corresponding product **3ia** was obtained in 75% yield. When 3-methylcyclohexanone was used, two isomers were obtained in a combination yield of 76% (**3ja** : **3ja'** = 3 : 1). The substituent position in cyclohexanone profoundly affected the reaction yield, and only a trace amount of product could be detected when 2-methylcyclohexanone was used.

To further explore the scope and the limitation of the reaction, various aromatic sulfonyl chlorides (**2**) were treated with cyclohexanone (**1a**) under the optimized conditions (Table 3). The reaction with arylsulfonyl chlorides bearing electron-donating groups at the aromatic ring (**2b–2e**) smoothly proceeded to give the desired products (**3ab–3ae**) in good to excellent yields. In general, introduction of strong electron-withdrawing substituents into the arylsulfonyl chlorides significantly decreased reaction yields, partially due to more side reactions occurred (**3ai–3ak**). It was noteworthy that halogen substituents such as fluoro (**2f**) and bromo (**2g**) were well tolerated in this kind of transformation, and the corresponding functionalized products (**3af** and **3ag**) could be used as substrates for further functionalization. More bulky substrates such as naphthalene-1-sulfonyl chloride (**2m**) and naphthalene-2-sulfonyl chloride (**2n**) gave the corresponding products (**3am** and **3an**) in 73% and 79% yields, respectively. Congested 2,4,6-trimethylbenzene-1-sulfonyl chloride (**2l**) also could smoothly react with **1a** to give the product (**3al**) in 75% yield. To our delight, aliphatic sulfonyl chloride (**2q**) and heterocyclic sulfonyl chloride (**2p**) also could react with cyclohexanone to give the products (**3aq** and **3ap**) in moderate yields.

Table 3 Reaction of cyclohexanone (**1a**) with various sulfonyl chlorides[a]

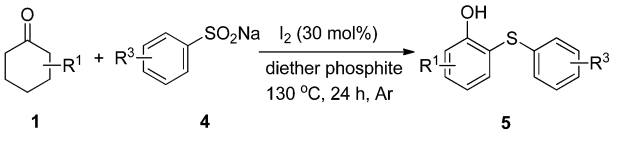


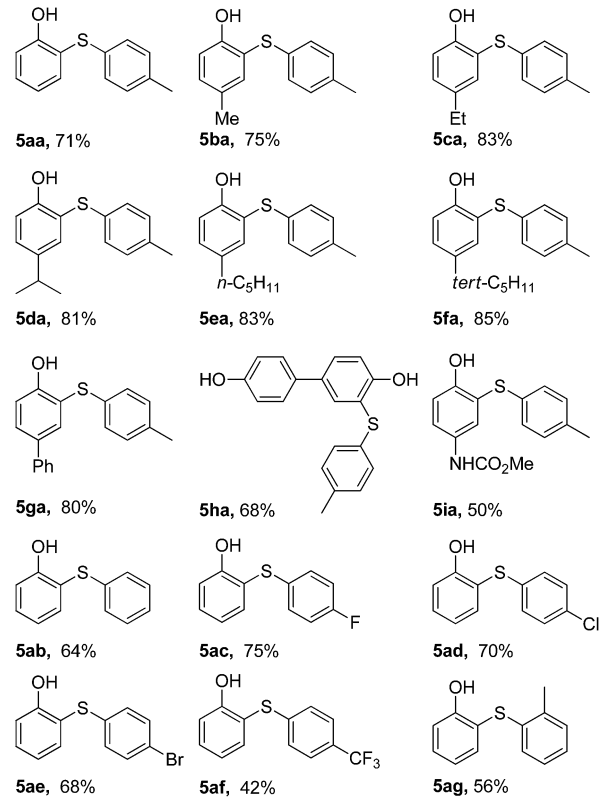
[a] Conditions: **1a** (0.5 mmol), **2** (0.6 mmol), I_2 (0.1 mmol), 1,4-dioxane (1.0 mL), 150 °C, 18 h, air; isolated yield.

After screening various sulfonyl chlorides, we next sought to expand the scope of sulfenylation of cyclohexanones with sulfonyl chlorides to sodium sulfinates. These compounds are more stable and moisture-insensitive compared to sulfonyl chlorides. Unfortunately, only trace amount of the desired product (**5aa**) was observed when *p*-toluenesulfinic acid sodium reacted with cyclohexanone (**1a**) under the previously optimized reaction conditions for sulfonyl chlorides. To get the best reaction conditions for sodium sulfinate substrates, we reinvestigated the reaction conditions for this kind of transformation. After systematic investigation, we found that diethyl phosphite and iodine both were necessary. When *p*-toluenesulfinic acid sodium (**4a**) reacted with cyclohexanone at 130 °C under an argon atmosphere, the desired product **5aa** was obtained in 71% yield (Table 4). Various substituted cyclohexanones and arylsulfinic acid sodium salts were used under the optimized conditions, and the corresponding 2-arylsulfonylphenols were obtained in good to high yields. Cyclohexanones bearing alkyl or aryl substituents were smoothly transformed into the corresponding products (**5ba–5ha**). To our delight, functional groups such as acetamido, fluoro, chloro, and bromo were well tolerated to give the corresponding products (**5ia**, **5ac–5ae**) in good yields. However, much lower yields were obtained when sodium 4-(trifluoromethyl)benzenesulfinate (**4f**) and sodium 2-methylbenzenesulfinate (**4g**) were employed for this kind of reaction. Unfortunately, aliphatic sodium sulfinates such as sodium methanesulfinate and sodium ethanesulfinate were not suitable for this kind of transformation under the current reaction conditions.

Although the exact mechanism for 2-arylsulfanylphenol formation from cyclohexanones and sulfonyl chlorides was not well understood at this stage, we proposed a plausible mechanism for this transformation on the basis of our previous observations and literature[6] (Fig. 1). Reduction of sulfonyl chloride (**2a**) with iodine generates intermediate **A** and IO^-. Electrophilic attack of **A** on the cyclohexanone ring yields intermediate 2-(phenylthio)cyclohexanone (**B**) with the release of the acidic HCl. Finally, dehydrogenation–tautomerization of **B** affords the final product **3ab** and regenerates the iodine catalyst.

Table 4 Reaction of various sodium sulfinates with cyclohexanones[a]





[a] Conditions: **1** (0.2 mmol), **4** (0.6 mmol), I_2 (0.06 mmol), diether phosphite (2 equiv.), DMSO (0.1 mL), toluene (0.5 mL), 130 °C, 24 h, under argon; isolated yield.

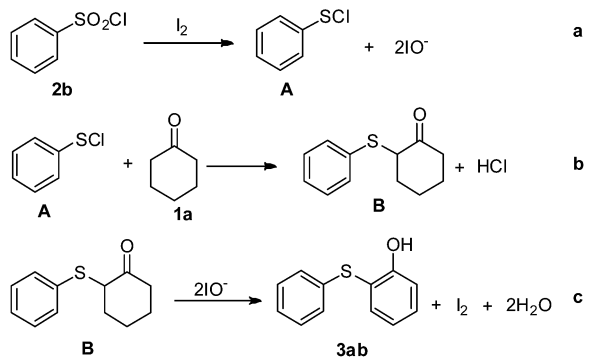


Fig. 1 Plausible mechanism for sulfonyl chloride substrate.

A plausible mechanism for sodium sulfinate substrates was also proposed (Fig. 2). Reaction of **4b** with diethyl phosphite and I_2 generates an electrophilic species PhSI,[8] which can attack **1a** to give an intermediate **1.** Dehydrogenation–tautomerization

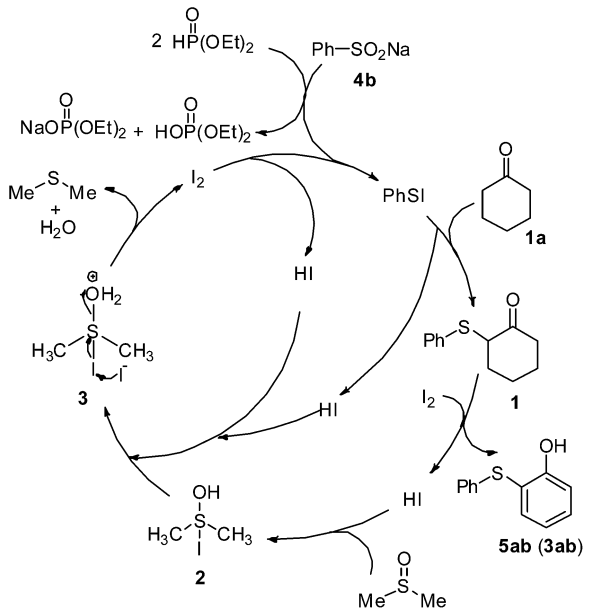


Fig. 2 Plausible mechanism for sodium sulfinate substrate.

of intermediate **1** with the aid of I_2 gives the desired product **5ab** (**3ab**) and HI.[16,21a] Then part of HI reacts with the S=O bond of DMSO to give intermediate **2,** which is followed by protonation of the oxygen atom to give intermediate **3.** Another portion of the HI nucleophilically attacks on the iodide atom of **3** to regenerate I_2 with the formation of dimethylsulfane and water.[5e,27] A control experiment was carried out using phenyl sulfoxide as the oxidant, and diphenylsulfane was observed by GC-MS.[8a] This means DMSO was possibly reduced to dimethylsulfane during the reaction process.

Conclusions

In summary, we have developed an iodine-promoted approach for the synthesis of 2-arylsulfanylphenols using cyclohexanones as a reliable phenol source under transition-metal-free conditions. Iodine was used as an effective catalyst in this transformation. Various sulfonyl chlorides and sodium sulfinates were used as the sulfur source to smoothly couple with cyclohexanones. The C–S bond formation, dehydrogenation and tautomerization were realized in one-pot in the absence of transition-metals. Since sulfonyl chlorides and sulfinic acid sodium salts are readily available starting materials, this method affords an efficient approach for 2-arylsulfanylphenols with a broad range of functional groups. The scope, mechanism and synthetic applications of this reaction are under investigation.

Experimental section

General methods

Flash column chromatography was performed over silica gel 48–75 μm. Unless otherwise noted, ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz,

respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by ^{1}H NMR, ^{13}C NMR, MS and HRMS. The structure of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

General procedure (3aa)

The reaction mixture of cyclohexanone (**1a**, 52 μL, 0.5 mmol), *p*-toluenesulfonyl chloride (**2a**, 114 mg, 0.6 mmol), iodine (25.4 mg, 0.1 mmol) and 1,4-dioxane (1 mL) in a 10 mL oven-dried reaction vessel was stirred at 150 °C for 18 h under an air atmosphere. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 95 : 5) to yield the desired product **3aa** as pale yellow liquid (88.6 mg, 82% yield).

General procedure (5aa)

Iodine (15.3 mg, 0.06 mmol) and *p*-toluenesulfinic acid sodium (**4a**, 107 mg, 0.6 mmol) were added to a 10 mL oven-dried reaction vessel. The reaction vessel was purged with argon for three times and was added diether phosphite (50 μL, 0.4 mmol), cyclohexanone (**1a**, 21 μL, 0.2 mmol), DMSO (0.1 mL) and toluene (0.5 mL) by syringe. The reaction mixture was stirred at 130 °C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 98 : 2) to yield the desired product **5aa** as pale yellow liquid (30.6 mg, 71% yield). The product is same as **3aa**.

2-(*p*-Tolylthio)phenol (3aa, CAS: 59010-83-2):.[21a] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.06–7.00 (m, 5H), 6.93 (t, J = 6.0 Hz, 1H), 6.53 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.1, 136.7, 136.3, 132.2, 132.1, 130.0, 127.5, 121.2, 117.2, 115.5, 21.0; MS (EI) *m*/*z* (%) 216 (100), 201, 183, 96, 91.

4-Methyl-2-(*p*-tolylthio)phenol (3ba):.[21a] Pale yellow liquid; yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.06–7.01 (m, 4H), 6.95 (d, J = 8.0 Hz, 1H), 6.36 (s, 1H), 2.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.0, 136.7, 136.2, 132.8, 132.5, 130.5, 130.1, 127.6, 116.8, 115.3, 21.0, 20.4; MS (EI) *m*/*z* (%) 230 (100), 197, 110, 91, 77, 65.

4-Ethyl-2-(*p*-tolylthio)phenol (3ca):.[21a] Pale yellow liquid; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.35 (s, 1H), 7.19 (d, J = 8.0 Hz, 1H), 7.06–6.97 (m, 5H), 6.36 (s, 1H), 2.58 (q, J = 8.0 Hz, 2H), 2.28 (s, 3H), 1.21 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.2, 137.1, 136.2, 135.6, 132.5, 131.6, 130.0, 127.5, 116.8, 115.4, 27.9, 21.0, 15.8; MS (EI) *m*/*z* (%) 244 (100), 229, 211, 124, 91, 77.

4-(Iso-propyl)-2-(*p*-tolylthio)phenol (3da). Pale yellow liquid; yield 72%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.37 (s, 1H), 7.22 (d, J = 8.0 Hz, 1H), 7.06–6.97 (m, 5H), 6.35 (s, 1H), 2.88–2.82 (m, 1H), 2.28 (s, 3H), 1.22 (d, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.2, 141.8, 136.1, 134.4, 132.5, 130.3, 130.1, 127.3, 116.5, 115.3, 33.3, 24.2, 21.0; MS (EI) *m*/*z* (%) 258, 243 (100), 151, 123, 91, 79; HRMS calcd for: $C_{16}H_{17}OS$ $[M - H]^-$: 257.0995, found 257.0999.

4-Pentyl-2-(*p*-tolylthio)phenol (3ea):.[21a] Pale yellow liquid; yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.06–6.96 (m, 5H), 6.36 (s, 1H), 2.53 (t, J = 8.0 Hz, 2H), 2.28 (s, 3H), 1.61–1.57 (m, 2H), 1.33–1.27 (m, 4H), 0.88 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 155.2, 136.2, 136.1, 135.8, 132.6, 132.1, 130.0, 127.4, 116.6, 115.3, 34.9, 31.4, 31.3, 22.6, 21.0, 14.0; MS (EI) *m*/*z* (%) 286, 229 (100), 137, 91, 77, 65.

4-(*tert*-Pentyl)-2-(*p*-tolylthio)phenol (3fa):.[21a] Pale yellow liquid; yield 78%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.46 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 8.0 Hz, 3H), 6.34 (s, 1H), 2.28 (s, 3H), 1.63–1.59 (m, 2H), 1.25 (s, 6H), 0.67 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.8, 142.4, 136.0, 134.3, 132.6, 130.0, 129.9, 126.9, 115.9, 114.9, 37.5, 37.0, 28.6, 20.9, 9.2; MS (EI) *m*/*z* (%) 286, 257 (100), 134, 91, 77, 65.

3-(*p*-Tolylthio)-[1,1′-biphenyl]-4-ol (3ga):.[21a] Pale yellow solid; yield 87%; mp 56–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.78 (s, 1H), 7.61–7.53 (m, 3H), 7.41 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.14–7.06 (m, 5H), 6.55 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.7, 140.0, 136.5, 135.1, 134.6, 132.2, 130.8, 130.2, 129.0, 127.8, 127.2, 126.8, 118.0, 116.0, 21.1; MS (EI) *m*/*z* (%) 292 (100), 172, 139, 91, 77, 65.

3-(*p*-Tolylthio)-[1,1′-biphenyl]-4,4′-diol (3ha). White solid; yield 84%; mp 119–121 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.71–7.70 (m, 1H), 7.54–7.52 (m, 1H), 7.41 (d, J = 8.0 Hz, 2H), 7.11–7.06 (m, 5H), 6.87 (d, J = 8.0 Hz, 2H), 6.50 (s, 1H), 4.81 (s, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, ppm) δ 157.0, 155.5, 136.8, 132.8, 132.0, 131.0, 130.8, 130.4, 130.2, 127.5, 127.1, 121.5, 116.5, 116.2, 21.1; MS (EI) *m*/*z* (%) 308 (100), 281, 207, 188, 91, 28; HRMS calcd for: $C_{19}H_{15}O_2S$ $[M - H]^-$: 307.0787, found 307.0791.

Ethyl 4-hydroxy-3-(*p*-tolylthio)benzoate (3ia):.[21a] Pale yellow solid; yield 75%; mp 72–74 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.27 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.09–7.03 (m, 5H), 6.95 (s, 1H), 4.34 (q, J = 6.7 Hz, 2H), 2.29 (s, 3H), 1.38 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 165.7, 160.8, 138.4, 136.8, 133.5, 131.3, 130.2, 128.1, 123.7, 118.2, 115.4, 61.0, 21.0, 14.4; MS (EI) *m*/*z* (%) 288 (100), 260, 243, 171, 91, 63.

2-(Phenylthio)phenol (3ab, CAS: 55214-86-3):.[13] Pale yellow liquid; yield 65%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 1H), 7.24–7.22 (m, 2H), 7.17–7.13 (m, 1H), 7.09–7.07 (m, 3H), 6.96 (t, J = 8.0 Hz, 1H), 6.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.3, 136.9, 135.9, 132.3, 129.2, 127.0, 126.2, 121.3, 116.5, 115.6; MS (EI) *m*/*z* (%) 202 (100), 169, 141, 96, 77, 51.

2-((4-Ethylphenyl)thio)phenol (3ac). Pale yellow liquid; yield 83%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 1H), 7.08–7.02 (m, 5H), 6.94 (t, J = 8.0 Hz, 1H), 6.55 (s, 1H), 2.61–2.55 (m, 2H), 1.18 (d, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.2, 142.7, 136.7, 132.4, 132.0, 128.8, 127.6, 121.1, 117.3, 115.5, 28.3, 15.4; MS (EI) *m*/*z* (%) 230 (100), 215, 105, 91, 77, 63; HRMS calcd for: $C_{14}H_{13}OS$ $[M - H]^-$: 229.0682, found 229.0686.

2-((4-(*tert*-Butyl)phenyl)thio)phenol (3ad, CAS: 2976-28-5):.[23] Pale yellow liquid; yield 85%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.28–7.26 (m, 2H), 7.08–7.03 (m, 3H), 6.95 (t, J = 8.0 Hz, 1H), 6.55 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.3, 149.5, 136.9, 132.3, 132.2, 127.0, 126.4, 121.3, 116.9, 115.6, 34.5, 31.3; MS (EI) m/z (%) 258, 243 (100), 125, 108, 97, 77.

2-((4-Methoxyphenyl)thio)phenol (3ae):.[21a] Pale yellow solid; yield 64%; mp 62–64 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.50 (d, J = 8.0 Hz, 1H), 7.32 (t, J = 8.0 Hz, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 2H), 6.57 (s, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.0, 156.8, 136.1, 131.6, 130.3, 126.2, 121.2, 118.8, 115.5, 115.1, 55.4; MS (EI) m/z (%) 232 (100), 217, 171, 108, 96.

2-((4-Fluorophenyl)thio)phenol (3af):.[21a] Pale yellow liquid; yield 80%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 8.0 Hz, 1H), 7.11–7.06 (m, 3H), 6.97–6.93 (m, 3H), 6.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.7 (d, J = 243.0 Hz), 157.1, 136.6, 132.3, 130.9 (d, J = 3.0 Hz), 129.3 (d, J = 8.0 Hz), 121.4, 117.1, 116.4 (d, J = 22.0 Hz), 115.7; MS (EI) m/z (%) 220, 128, 96 (100), 75, 61.

2-((4-Bromophenyl)thio)phenol (3ag, CAS: 1254831-59-8):.[21a] Pale yellow liquid; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.42–7.34 (m, 3H), 7.08 (d, J = 8.0 Hz, 1H), 6.99–6.92 (m, 3H), 6.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.3, 136.9, 135.2, 132.7, 132.3, 128.4, 121.6, 120.0, 115.8, 115.8; MS (EI) m/z (%) 282, 280, 201, 168, 96 (100).

2-((4-(Trifluoromethoxy)phenyl)thio)phenol (3ah). Pale yellow liquid; yield 66%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.10–7.08 (m, 5H), 6.98 (d, J = 8.0 Hz, 1H), 6.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 157.3, 147.6, 136.9, 134.7, 132.7, 128.0, 121.9, 121.6, 120.4 (q, J = 256.0 Hz), 115.8, 115.7; MS (EI) m/z (%) 286 (100), 201, 171, 128, 96; HRMS calcd for: $C_{13}H_8O_2F_3S$ $[M - H]^-$: 285.0192, found 285.0195.

2-((4-(Trifluoromethyl)phenyl)thio)phenol (3ai). Pale yellow liquid; yield 46%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.53 (d, J = 8.0 Hz, 1H), 7.48–7.43 (m, 3H), 7.12 (d, J = 8.0 Hz, 3H), 7.01 (t, J = 8.0 Hz, 1H), 6.37 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 157.4, 141.2, 137.1, 133.0, 128.1 (q, J = 32.0 Hz), 126.1, 126.0 (q, J = 3.7 Hz), 124.0 (q, J = 270.0 Hz), 121.7, 116.0, 114.5; MS (EI) m/z (%) 270 (100), 251, 171, 96, 69; HRMS calcd for: $C_{13}H_8OF_3S$ $[M - H]^-$: 269.0243, found 269.0247.

2-((4-Nitrophenyl)thio)phenol (3aj):.[24] Yellow solid; yield 36%; mp 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (d, J = 8.0 Hz, 2H), 7.54–7.46 (m, 2H), 7.15–7.11 (m, 3H), 7.04 (t, J = 8.0 Hz, 1H), 6.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.5, 145.9, 137.1, 133.4, 126.5, 126.0, 124.4, 124.2, 121.9, 116.3; MS (EI) m/z (%) 247 (100), 230, 200, 171, 97.

4-((2-Hydroxyphenyl)thio)benzonitrile (3ak):.[25] Pale yellow solid; yield 42%; mp 82–84 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52–7.44 (m, 4H), 7.13–7.07 (m, 3H), 7.02 (t, J = 8.0 Hz, 1H), 6.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.5, 143.5, 137.1, 133.3, 132.8, 132.6, 126.7, 126.3, 121.8, 118.5, 116.2; MS (EI) m/z (%) 227 (100), 198, 166, 96, 63.

2-(Mesitylthio)phenol (3al). Pale yellow solid; yield 75%; mp 61–63 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.08 (t, J = 8.0 Hz, 1H), 6.96 (s, 2H), 6.90 (d, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.74 (t, J = 6.0 Hz, 1H), 5.84 (s, 1H), 2.39 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 154.1, 142.9, 139.1, 129.9, 129.7, 127.9, 122.2, 121.4, 115.4, 110.0, 21.9, 21.1; MS (EI) m/z (%) 244, 150, 120 (100), 105, 91, 77; HRMS calcd for: $C_{15}H_{15}OS$ $[M - H]^-$: 243.0838, found 243.0842.

2-(Naphthalen-1-ylthio)phenol (3am). Pale yellow solid; yield 73%; mp 87–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.35 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.63–7.54 (m, 3H), 7.41 (t, J = 6.0 Hz, 1H), 7.30–7.28 (m, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.4, 136.9, 134.1, 133.0, 132.2, 131.4, 128.8, 126.9, 126.7, 126.5, 126.0, 124.6, 124.0, 121.6, 116.3, 115.9; MS (EI) m/z (%) 252, 189, 128 (100), 115, 77; HRMS calcd for: $C_{16}H_{11}OS$ $[M - H]^-$: 251.0525, found 251.0530.

2-(Naphthalen-2-ylthio)phenol (3an):.[21a] Pale yellow liquid; yield 79%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.77–7.58 (m, 4H), 7.48–7.40 (m, 4H), 7.24–7.21 (m, 1H), 7.11 (d, J = 8.0 Hz, 1H), 6.99 (t, J = 8.0 Hz, 1H), 6.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.4, 136.9, 133.8, 133.2, 132.3, 131.9, 129.0, 127.8, 127.2, 126.8, 125.9, 125.4, 125.3, 121.4, 116.6, 115.8; MS (EI) m/z (%) 252, 219, 128 (100), 115, 77.

2-((4-Bromo-3-fluorophenyl)thio)phenol (3ao). Pale yellow liquid; yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.45–7.38 (m, 2H), 7.10 (d, J = 8.0 Hz, 1H), 7.00 (t, J = 8.0 Hz, 1H), 6.77–6.74 (m, 2H), 6.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.4 (d, J = 248.0 Hz), 157.3, 138.0 (d, J = 6.0 Hz), 136.9, 133.9, 133.0, 123.4 (d, J = 4.0 Hz), 121.7, 116.1, 115.0, 114.7 (d, J = 25.0 Hz), 106.4 (d, J = 21.0 Hz); MS (EI) m/z (%) 300 (100), 218, 186, 109, 96, 63; HRMS calcd for: $C_{12}H_7$-BrFOS $[M - H]^-$: 296.9380, found 296.9382.

2-(Thiophen-2-ylthio)phenol (3ap). Pale yellow solid; yield 43%; mp 39–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 (d, J = 8.0 Hz, 1H), 7.30–7.29 (m, 2H), 7.15 (s, 1H), 7.00–6.87 (m, 3H), 6.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 156.0, 134.9, 133.6, 132.1, 131.5, 129.1, 127.6, 121.2, 120.4, 115.7; MS (EI) m/z (%) 208 (100), 175, 147, 96, 84, 71; HRMS calcd for: $C_{10}H_7OS_2$ $[M - H]^-$: 206.9933, found 206.9935.

2-(Ethylthio)phenol (3aq, CAS: 29549-60-8):.[26] Pale yellow liquid; yield 43%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.47 (d, J = 8.0 Hz, 1H), 7.32–7.26 (m, 1H), 6.99 (d, J = 8.0 Hz, 1H), 6.88 (t, J = 6.0 Hz, 1H), 6.77 (s, 1H), 2.72 (q, J = 8.0 Hz, 2H), 1.22 (t, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.1, 136.1, 131.1, 120.7, 118.8, 114.7, 30.8, 14.9; MS (EI) m/z (%) 154 (100), 139, 126, 97, 53.

4-Methyl-2-(*p*-tolylthio)phenol (5ba):.[21a] Pale yellow liquid; yield 75%. The product is same as **3ba**.

4-Ethyl-2-(*p*-tolylthio)phenol (5ca):.[21a] Pale yellow liquid; yield 83%. The product is same as **3ca**.

4-(Iso-propyl)-2-(*p*-tolylthio)phenol (5da). Pale yellow liquid; yield 81%. The product is same as **3da**.

4-Pentyl-2-(*p*-tolylthio)phenol (5ea):.[21a] Pale yellow liquid; yield 83%. The product is same as **3ea**.

4-(*tert*-Pentyl)-2-(*p*-tolylthio)phenol (5fa):.[21a] Pale yellow liquid; yield 85%. The product is same as **3fa**.

3-(*p*-Tolylthio)-[1,1′-biphenyl]-4-ol (5ga):.[21a] Pale yellow solid; yield 80%. The product is same as **3ga**.

3-(*p*-Tolylthio)-[1,1′-biphenyl]-4,4′-diol (5ha). White solid; yield 68%. The product is same as **3ha**.

***N*-(4-Hydroxy-3-(*p*-tolylthio)phenyl)acetamide (5ia):**.[21a] Pale yellow liquid; yield 50%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.62 (s, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.05–6.99 (m, 6H), 6.38 (s, 1H), 2.28 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.5, 153.8, 136.6, 131.7, 131.2, 130.1, 128.1, 128.0, 124.5, 117.9, 115.6, 24.2, 21.0; MS (EI) m/z (%) 273 (100), 231, 207, 139, 111, 91.

2-(Phenylthio)phenol (5ab, CAS: 55214-86-3):.[13] Pale yellow liquid; yield 64%. The product is same as **3ab**.

2-((4-Fluorophenyl)thio)phenol (5ac):.[21a] Pale yellow liquid; yield 75%. The product is same as **3af**.

2-((4-Chlorophenyl)thio)phenol (5ad, CAS: 59010-71-8):.[21a] Pale yellow liquid; yield 70%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.19 (t, J = 8.0 Hz, 2H), 7.09–6.95 (m, 4H), 6.43 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.2, 136.8, 134.5, 132.5, 132.3, 129.3, 128.3, 121.4, 116.2, 115.8; MS (EI) m/z (%) 236 (100), 220, 200, 168, 96.

2-((4-Bromophenyl)thio)phenol (5ae, CAS: 1254831-59-8):.[21a] Pale yellow liquid; yield 68%. The product is same as **3ag**.

2-((4-(Trifluoromethyl)phenyl)thio)phenol (5af). Pale yellow liquid; yield 42%. The product is same as **3ai**.

2-(*o*-Tolylthio)phenol (5ag):.[21a] Pale yellow liquid; yield 56%; ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.48 (d, J = 8.0 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.09–6.95 (m, 4H), 6.66 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.4, 136.8, 135.7, 134.9, 134.9, 132.0, 130.4, 126.8, 126.2, 126.0, 121.4, 115.6, 20.0; MS (EI) m/z (%) 216 (100), 201, 122, 96, 91.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (21172185, 21372187), the Hunan Provincial Innovative Foundation for Postgraduate (CX2013B269), the New Century Excellent Talents in University from Ministry of Education of China (NCET-11-0974) and the Research Fund for the Doctoral Program of Higher Education of China, Ministry of Education of China (20124301110005).

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