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Note

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Surfactant-Type Catalyst for Aerobic Oxidative Coupling of Hydrazine with Thiol in Water

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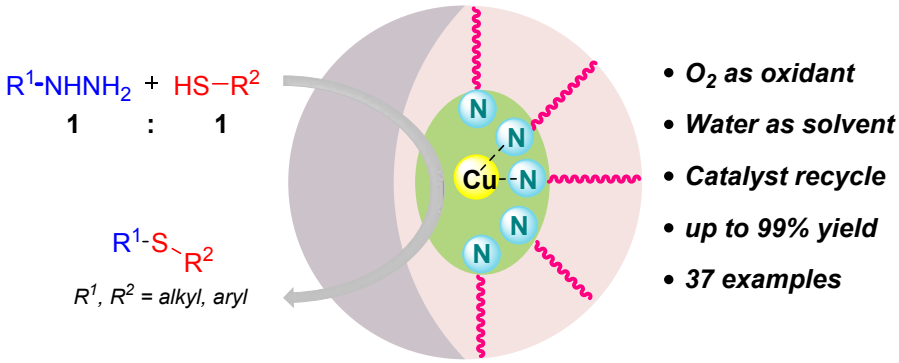
Keywords: Surfactant-type Catalyst • Aerobic Oxidative Coupling • Alkylhydrazine • Water as Solvent • Catalyst Recycle



Abstract: A series of PEG-functionalized nitrogen ligands were developed to conduct the aerobic oxidative cross-coupling between alkyl- or aryl-hydrazines with thiols in water. This surfactant-type catalyst enables high efficiency and selectivity while tolerates a large variety of functional groups. The mother liquor is still catalytically active after five runs.

Organosulfides have triggered considerable interest in synthetic chemistry, material chemistry, food science and pharmaceutical field (Figure 1).[1] For instance, saccharin is an artificial sweetener used in food and drinks with no food energy.[2] Penicillin, dapsone and ceftizoxime are commercialized antibiotics.[1h, 1i] Butoconazole is a typical antifungal used in gynecology.[1i] Omeprazole is used in the treatment of petic ulcer and gastroesophageal reflux.[1j] Organosulfur compounds are widely found in nature due to their involvement in DNA cleavage, DNA binding and protein folding.[3]

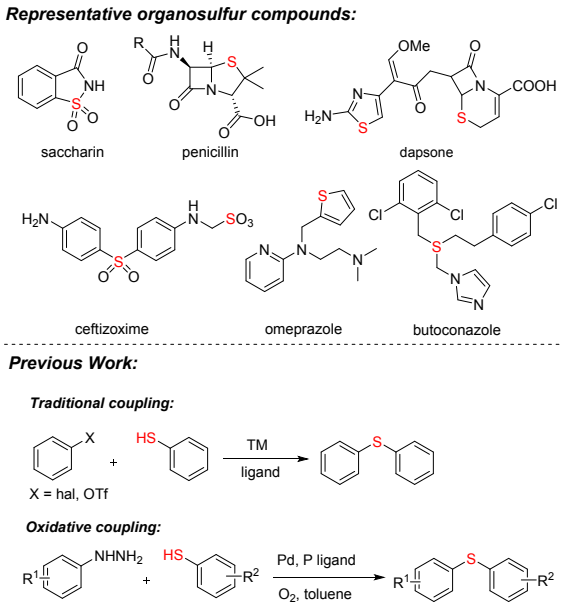


Figure 1. Representative structures and synthesis of organosulfur compounds.

While many efforts have been directed towards the synthesis of organic sulfides,[4] transition metal (mostly palladium) catalyzed cross-coupling reaction of prefunctionalized arenes with thiols is a powerful tool to construct unsymmetrical C-S bond (Figure 1).[5] However, those methods are limited to narrow substrate scopes, harsh reaction conditions, and inert reaction atmosphere. Arylhydrazines are known to generate radical species during oxidative degradation,[6] thus they have emerged as an environmentally benign arylation agents for cross-coupling

reactions since the only byproducts are water and nitrogen gas. Recently, Zhao and coworkers disclosed a Pd(II)-catalyzed oxidative coupling of arylhydrazines with arylthiols in toluene, affording the unsymmetrical diaryl sulfides in 71-84% yields (Figure 1).[7] Later, Hajra *et al* made great progress by developing a rose bengal catalyzed aerobic oxidation to synthesize diarylsulfides in water under 34 W blue LED.[8] However, both Zhao's and Hajra's protocols are limited to aryl substrates, consuming 2 equivalents of arylhydrazines against thiols. Therefore, the development of more efficient and versatile method with higher chemoselectivity and wider scope is desired.

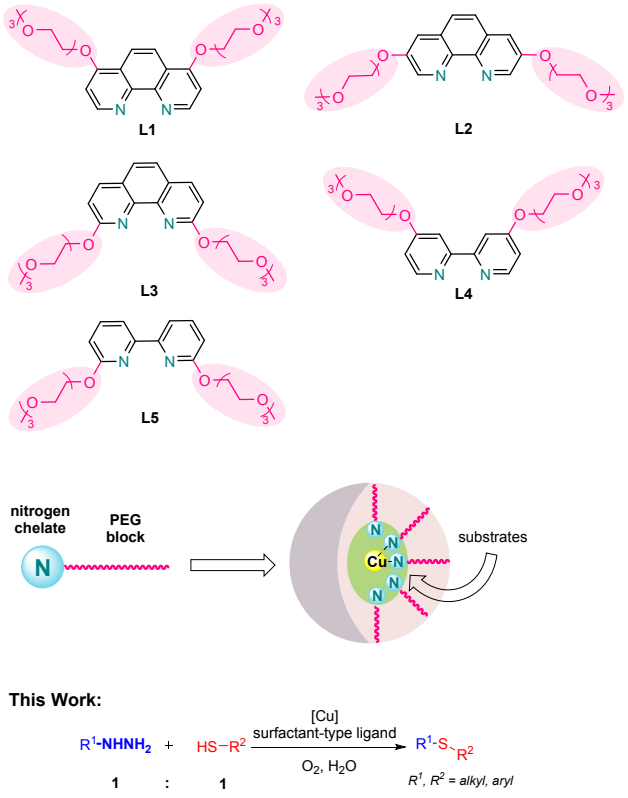
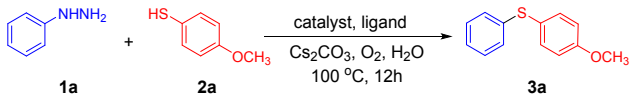


Figure 2. Designed surfactant-type ligands, and proposed process of the aerobic oxidative coupling reaction in water.

Water as solvent is not only a strategy to achieve green synthesis, but also promising to enable catalyst recycle and simple work-up procedure.[9] However, most organic catalysts and reaction substrates exhibit poor solubility in water. To overcome this obstacle, the traditional solution is to perform the reaction in the presence of surfactants.[10] Novel surfactant systems for catalyst recovery have been investigated by covalently attaching surfactant scaffolds to the ligands, addressing the solubility problem of catalysts as well as organic reaction partners.[11] We designed and synthesized a series of PEG-functionalized amphiphilic nitrogen ligands **L1-5** (Figure 2). Such ligands bestow aqueous solubility and surfactant characteristic to their corresponding transition metal complexes. The probable micellar structures formed in water by self-aggregation of such surfactant-type ligands are proposed in Figure 2. The hydrophilic PEG tails align to form the hydrophilic surface of the micelle, while the transition metal coordinates to the N-ligands in the micellar core. The hydrophobicity of organic substrates forces them to enter and self-enrich in the micellar core. Hypothetically, the metallomicelles could behave as nanoreactors[12] and facilitate the aerobic oxidative coupling reaction. Herein, we developed surfactant-type catalyst for environmentally friendly and highly chemoselective aerobic oxidative coupling of alkyl- and arylhydrazines with thiols in water, avoiding the employment of excess hydrazines.

Table 1. Optimization of the Reaction Conditions. [a]



1a 2a 3a

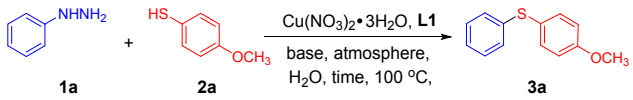
Entry	Catalyst	Ligand	Yield (%) [b]
1	CuCl	**L1**	84
2	$CoCl_2$	**L1**	70
3	$Mn(CH_3COO)_2•2H_2O$	**L1**	75

4	$FeCl_3$	**L1**	60
5	CuBr	**L1**	65
6	CuI	**L1**	85
7	$CuCl_2•2H_2O$	**L1**	85
8	**$Cu(NO_3)_2•3H_2O$**	**L1**	**99** (73 [c])
9	$Cu(CH_3COO)_2•H_2O$	**L1**	70
10	$Cu(OTf)_2$	**L1**	70
11	$Cu(NO_3)_2•3H_2O$	**L2**	57
12	$Cu(NO_3)_2•3H_2O$	**L3**	40
13	$Cu(NO_3)_2•3H_2O$	**L4**	56
14	$Cu(NO_3)_2•3H_2O$	**L5**	60
15	$Cu(NO_3)_2•3H_2O$	--	50
16	--	--	37

[a] **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst (5 mol%), ligand (5 mol%), Cs_2CO_3 (1.0 equiv.), 1 atm O_2, H_2O (2 mL), 100 °C, 12 h. [b] Isolated yields. [c] $Cu(NO_3)_2•3H_2O$ (3 mol%), **L1** (3 mol%).

To test our hypothesis, a model reaction was performed between phenylhydrazine **1a** (1 equiv.) and 4-methoxybenzenethiol **2a** (1 equiv.) with CuCl as catalyst, **L1** as ligand, and Cs_2CO_3 as base under 1 atm O_2 in water (Table 1). Various transition metal salts (Cu, Co, Mn, Fe) were screened (Entry 1-4), and CuCl turned out to be the most active. Subsequently, a series of Cu(I) and Cu(II) species were tested (Entry 5-10). $Cu(NO_3)_2•3H_2O$ was found to be the optimal catalyst and give the desired diarylsulfide **3a** in quantitative yield (Entry 8). Comparing to the result of **L1**, other PEG-modified amphiphilic nitrogen ligands **L2-5** resulted in much lower yields (Entry 11-14). The control experiments were conducted in the absence of $Cu(NO_3)_2•3H_2O$ or **L1**. The target product was formed in much lower yields (Entry 15, 16), indicating the necessity of catalyst and ligand. Furthermore, we tried to bring down the catalyst loading to 3 mol%, however, the product yield decreased to 73% (Entry 8).

Table 2. Screening other reaction parameters. [a]



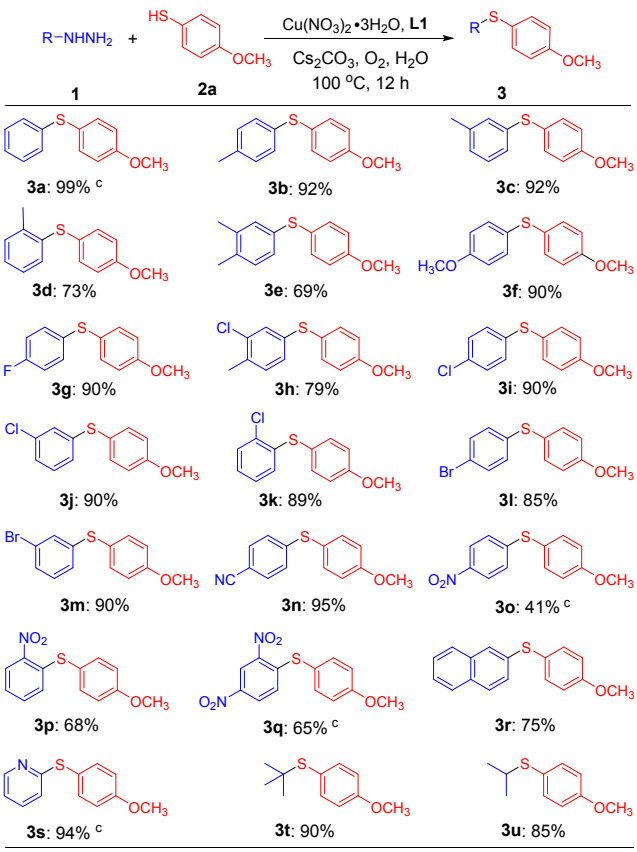
1a 2a 3a

Entry	Base	Time (h)	H_2O (mL)	Atmosphere	Yield (%) [b]
1	Na_2CO_3	12	2	O_2	70
2	K_2CO_3	12	2	O_2	61
3	NaOH	12	2	O_2	52
4	--	12	2	O_2	53
5	Cs_2CO_3	12	2	O_2	72 [c]
6	Cs_2CO_3	10	2	O_2	86
7	Cs_2CO_3	8	2	O_2	82
8	Cs_2CO_3	12	1	O_2	50
9	Cs_2CO_3	12	0.5	O_2	48
10	Cs_2CO_3	12	2	N_2	20
11	Cs_2CO_3	12	2	Air	74

[a] **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(NO_3)_2$•$3H_2O$ (5 mol%), **L1** (5 mol%), base (1.0 equiv.), 1 atm atmosphere, H_2O (x mL), 100 °C, y h. [b] Isolated yields. [c] 80 °C.

Further optimizations revealed that this reaction proceeded more efficiently in the presence of Cs_2CO_3 as base (Table 2, Entry 1-4). Interestingly, the ion effect of base plays an important role on the reaction (Entry 1-2). Other reaction parameters including reaction temperature, reaction hour, and solvent volume were tested to get the optimal reaction conditions (Entry 4-9). Control experiments were conducted under nitrogen (Entry 10) and air (Entry 11), stating the necessity of molecular oxygen as the oxidant for this oxidative coupling reaction.

Table 3. Substrate scope of hydrazines. [a, b]

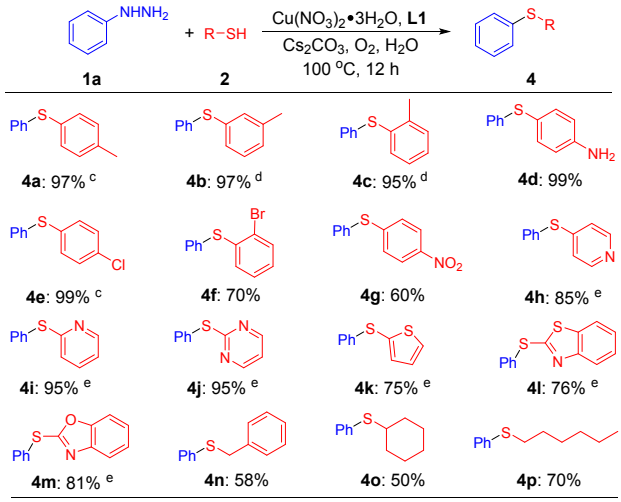


[a] **1** (R-NHNH$_2$•HCl, 0.2 mmol), **2a** (0.2 mmol), Cu(NO$_3$)$_2$•3H$_2$O (5 mol%), **L1** (5 mol%), Cs$_2$CO$_3$ (2 equiv.), 1 atm O$_2$, H$_2$O (2 mL), 100 °C, 12 h. [b] Isolated yields. [c] **1** (R-NHNH$_2$), Cs$_2$CO$_3$ (1 equiv.)

With the optimal condition in hand, we proceed to examine the substrate scopes of hydrazines to react with 4-methoxybenzenethiol **2a** (Table 3). One extra equivalent of base was added to quench the acid when RNHNH$_2$•HCl was adopted as substrate. Fortunately, a large variety of aryl- and alkylhydrazines were well tolerated. Arylhydrazines bearing electron-donating groups, such as methyl (at *para*-, *meta*- or *ortho*-position), dimethyl and methoxy groups, led to the formation of products **3b-f** in good to excellent yields. Compared to **3b** and **3c**, the relatively lower yield of product **3d** might be caused by the steric effect of methyl group at *ortho*-position on the benzene ring. Halogen (F, Cl, Br) substituted arylhydrazines furnished the corresponding diarylsulfides successfully (**3g-m**), providing potential synthetic applications via conventional coupling reaction. Arylhydrazines with strong electron-withdrawing substituents, such as nitrile

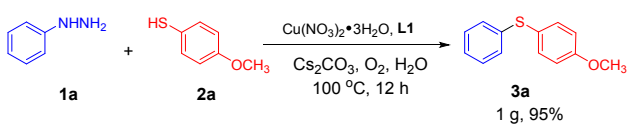
and nitro, furnished products smoothly (**3n-q**). 2-Naphthylhydrazine and 2-pyridinylhydrazine as substrates could also give products (**3r**, **3s**) in excellent yields. To be noticed, alkylhydrazines were well tolerated and gave the corresponding organosulfides (**3t**, **3u**) in excellent yields.

Table 4. Substrate scope of thiols. [a, b]



[a] **1a** (0.2 mmol), **2** (0.2 mmol), $Cu(NO_3)_2•3H_2O$ (5 mol%), **L1** (5 mol%), Cs_2CO_3 (1 equiv.), H_2O (2 mL), 1 atm O_2, 100 °C, 12 h. [b] Isolated yields. [c] 24 h. [d] 36 h. [e] No base.

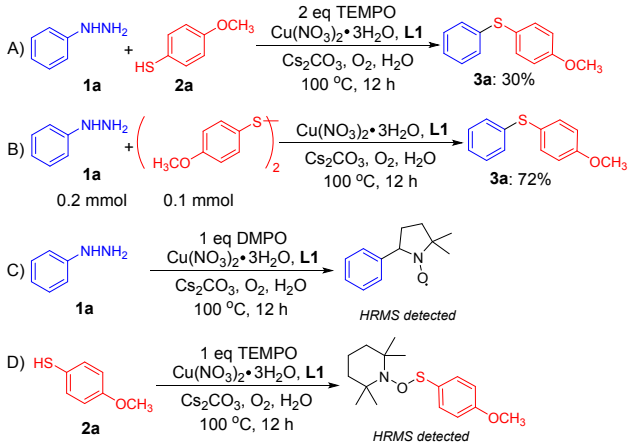
Further insight into the aerobic oxidative coupling reaction of hydrazines with thiols was obtained by examining the substrate scope of thiols (Table 4). Nearly all phenylthiols bearing electron-donating and electron-withdrawing groups, except for nitro-substituted phenylthiol (**2g**), afforded the target products in 70-99% yields. Interestingly, heteroaromatic thiols were successfully converted in good to excellent yields (**4h-m**) in the absence of base. Benzyl thiol and alkyl thiols were also tolerated (**4n-p**).



Scheme 1. Gram-scale synthesis.

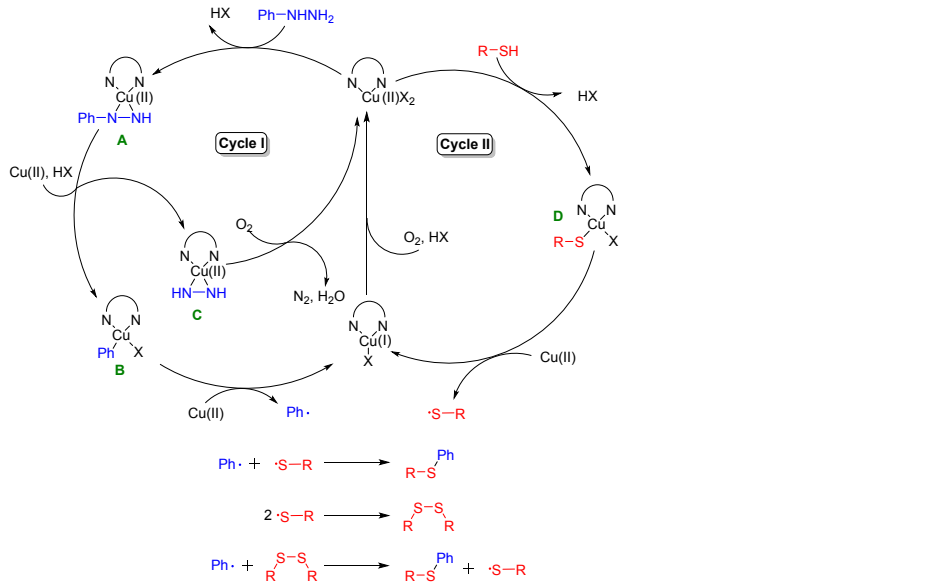
The scalability of our protocol was evaluated by performing the reaction on a 5 mmol scale (Scheme 1). The target product **3a** was formed in 95% yield, showing good potential in practical synthesis. Since the use of water as solvent offers the opportunity to recycle the catalyst, we performed mother liquor circulation experiments on the model reaction of **1a** with **2a** (Figure S1, see supporting information). As product **3a** is a liquid, it was obtained by simple extraction of the aqueous phase with hexane. Fresh batch of substrates was added to the recovered mother liquor for next run. The aqueous phase is still catalytically active after five runs with minor decrease in reactivity or product yield.

To probe the reaction mechanism, we added a typical radical scavenger, 2,2,6,6-(tetramethylpiperidin-1-yl)oxyl (TEMPO), to the oxidative coupling reaction between hydrazine **1a** and thiol **2a** under the standard reaction conditions (Scheme 2, reaction A). The reaction was sufficiently suppressed by TEMPO, indicating radical intermediates might be involved in the catalytic cycle. We utilized 1,2-bis(4-methoxyphenyl)disulfane instead of 4-methoxybenzenethiol **2a** to react with phenylhydrazine **1a** (Scheme 2, reaction B). The desired product was obtained in 72% yield. Furthermore, the reaction of **1a** with DMPO in the absence of **2a** was carried out, and the products were analyzed via HRMS. The corresponding adduct of DMPO with the phenyl radical generated from **1a** was detected (Scheme 2, reaction C). When **2a** was treated with TEMPO in the absence of **1a**, adduct of TEMPO with the thiyl radical from **2a** was observed as well (Scheme 2, reaction D). Conclusively, the reaction possibly proceeds via a radical pathway.



Scheme 2. Mechanistic studies by experiments.

A possible mechanism for this Cu-catalyzed aerobic oxidative cross-coupling reaction between phenylhydrazine and thiol was proposed in Scheme 3. In cycle I, ligand exchange of the $Cu^{(II)}$ precursor by phenylhydrazine leads to the formation of copperdiaziridine intermediate **A**. Protonolysis of **A** releases the organocopper intermediate **B** and a copperdiaziridine complex **C**, which the latter collapses to release nitrogen gas and water in the presence of O_2 while regenerate the $Cu^{(II)}$. On the other hand, phenylcopper specie **B** affords the corresponding phenyl radical and $Cu^{(I)}$ specie with the aid of $Cu^{(II)}$. In cycle II, the reaction of $Cu^{(II)}$ complex with thiol generate thiyl copper intermediate **D**, then transformed into the corresponding thiyl radical and $Cu^{(I)}$. Heterocoupling of thiyl radical and phenyl radical furnishes the desired product, while $Cu^{(II)}$ could be regenerated by the oxidation of $Cu^{(I)}$. Meanwhile, the disulfide is produced by the homocoupling of thiyl radicals, then reacts with phenyl radical to give the desired product and regenerate the thiyl radical.



Scheme 3. Proposed Reaction Mechanism.

In summary, we have established an efficient and benign surfactant-type catalyst for aerobic oxidative coupling of hydrazines with thiols. Organosulfides can be obtained in good to excellent yields by using O_2 as the sole oxidant and water as solvent. This new Cu-surfactant catalysis leads to highly effecient and chemoselective cross-coupling reaction thus no excess amount of one substrate is required. A large range of substituents are bearable, including halogens (Cl, Br). More importantly, alkylhydrazines are able to afford the desired products in excellent yields. Gram-scale reaction were successfully performed, providing an valuable tool for synthetic chemistry as well as industrial manufacturing. The mother liquor could be recycle for five run with minor loss in reactivity and product yield.

EXPERIMENTAL SECTION

General Information. All materials and catalysts were purchased from general merchant and used in the original state unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded

at a Bruker Avance III HD spectrometer (Bremen, Germany) at 600 MHz (400 MHz) for ^{1}H NMR and 150 MHz (100 MHz) for ^{13}C NMR with $CDCl_3$ or d_6-DMSO as the solvent and TMS as the internal standard. High resolution mass spectra (HRMS) were measured with an Agilent 1290-6540 Q-TOF (Santa Clara, USA). (Santa Clara, USA). Low resolution mass spectra (LRMS) were recorded at an electron ionization (EI) conditions by using a Shimadzu GCMS-QP2010 Plus mass spectrometer (Kyoto, Japan). The melting points of the products were determined by an X-4 micro-melting point apparatus (Beijing, China).

General procedure for PEG-functionalized ligands: A 25 mL Schlenk tube was charged with triethylene glycol monomethyl ether (3 mmol, 5.0 equiv), NaH (3.6 mmol, 6.0 equiv) and DMF (3 mL). The resulting mixture was stirred at room temperature for 10 minutes until no bubbles appeared. Then, 2,9-dibromo-1,10-phenanthroline (0.6 mmol, 1.0 equiv) was added. The reaction mixture was heated at 110 ^{o}C for 4 h. Once finished, the reaction mixture was cooled to room temperature then extracted with dichloromethane (3 × 50 mL). The organic phase was collected and dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated by rotovap, and the residue was purified via column chromatography to afford products **L1-L5.**

General procedure for synthesis of organosulfide: A 25 mL Schlenk tube was charged with hydrazine (21.7 mg, 0.2 mmol), thiol (28.0 mg, 0.2 mmol), $Cu(NO_3)_2$•$3H_2O$ (2.4 mg, 0.01 mmol), **L1** (4.8 mg, 0.01 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol), H_2O (2 mL), 1 atm O_2, and then the resulting mixture was stirred at 100 ^{o}C. After 12 h, the reaction mixture was extracted with dichloromethane (3 × 50 mL), and then dried over anhydrous sodium sulfate and filtered. After evaporation of the solvent under vacuum, the residue was purified via column chromatography to afford products **3a**-**3u**, **4a**-**4p**.

Procedure for mother liquor circulation: To a reactor (50 mL) was added phenylhydrazine (65.1 mg, 0.6 mmol), 4-methoxythiophenol (84.1 mg, 0.6 mmol), $Cu(NO_3)_2•3H_2O$ (7.2 mg, 0.03 mmol), **L1** (14.4 mg, 0.03 mmol), Cs_2CO_3 (195.5 mg, 0.6 mmol), H_2O (6 mL).The reactor was charged with O_2 1 atm three times. Subsequently, the reactor was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was extracted with hexane. The organic phase was dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated in vacuo. The crude material was purified by column chromatography (hexane : DCM = 2 : 1 as eluent) to afford the desired product. The aqueous phase was reused directly in the next run by adding a fresh batch of 4-methoxythiophenol (84.1 mg, 0.6 mmol) and phenylhydrazine (65.1 mg, 0.6 mmol). The aqueous phase was used for 5 runs, with the yields varying as follow: 99%, 95%, 92%, 90%, 88%.

Procedure for gram scale synthesis: A 250 mL Schlenk flask was charged with phenylhydrazine (540.7 mg, 5 mmol), 4-methoxythiophenol (701.0 mg, 5 mmol), $Cu(NO_3)_2•3H_2O$ (60.0 mg, 0.25 mmol), **L1** (120.0 mg, 0.25 mmol), Cs_2CO_3 (1629.1 mg, 5 mmol), H_2O (50 mL). Subsequently, the reactor was stirred under at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was extracted with hexane. The organic phase was dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated on rotovap. The crude material was purified by column chromatography (hexane : DCM = 2 : 1 as eluent) to afford the desired product in 95% yield.

4,7-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,10-phenanthroline (L1). Orange oil (284.9 mg, 94% yield) (methyl alcohol as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.99 (d, *J* = 5.2 Hz, 2H), 8.20 (s, 2H), 6.99 (d, *J* = 5.3 Hz, 2H), 4.44-4.37 (m, 4H), 4.07-4.01 (m, 4H), 3.85-3.80 (m, 4H), 3.74-3.65 (m, 8H), 3.57-3.52 (m, 4H), 3.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4,

151.1, 146.9, 120.9, 119.1, 103.5, 71.9, 71.1, 70.7, 70.6, 69.4, 68.1, 59.1. HRMS (ESI): m/z calcd for $C_{26}H_{37}N_2O_8$ $[M+H]^+$, 505.2544; found, 505.2548.

3,8-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,10-phenanthroline (L2). Yellow oil (248.5 mg, 82% yield) (ethyl acetate : methyl alcohol = 10 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.90 (d, *J* = 2.9 Hz, 2H), 7.68 (s, 2H), 7.51 (d, *J* = 2.9 Hz, 2H), 4.33-4.28 (m, 4H), 3.99-3.93 (m, 4H), 3.81-3.75 (m, 4H), 3.73-3.64 (m, 8H), 3.57-3.50 (m, 4H), 3.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.6, 142.9, 140.5, 127.9, 126.7, 115.2, 71.9, 70.9, 70.6, 70.6, 69.6, 67.9, 59.0. HRMS (ESI): m/z calcd for $C_{26}H_{37}N_2O_8$ $[M+H]^+$, 505.2544; found, 505.2548.

2,9-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-1,10-phenanthroline (L3). Cololess oil (272.7 mg, 90% yield) (ethyl acetate as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.7 Hz, 2H), 7.56 (s, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 4.89-4.82 (m, 4H), 4.03-3.97 (m, 4H), 3.81-3.74 (m, 4H), 3.71-3.60 (m, 8H), 3.54-3.48 (m, 4H), 3.34 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1, 142.9, 139.0, 125.2, 123.4, 113.6, 71.9, 70.6, 70.6, 70.5, 69.9, 65.1, 59.0. HRMS (ESI): m/z calcd for $C_{26}H_{37}N_2O_8$ $[M+H]^+$, 505.2544; found, 505.2543.

4,4'-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bipyridine (L4). Yellow oil (284.9 mg, 89% yield) (ethyl acetate as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (d, *J* = 5.7 Hz, 2H), 7.98 (d, *J* = 2.4 Hz, 2H), 6.90-6.82 (m, 2H), 4.31-4.25 (m, 4H), 3.92-3.86 (m, 4H), 3.76-3.62 (m, 12H), 3.56-3.49 (m, 4H), 3.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.9, 157.8, 150.1, 111.5, 106.6, 71.9, 70.9, 70.7, 70.6, 69.4, 67.5, 59.1. HRMS (ESI): m/z calcd for $C_{24}H_{37}N_2O_8$ $[M+H]^+$, 481.2544; found, 481.2549.

6,6'-Bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-2,2'-bipyridine (L5). Yellow oil (284.9 mg, 89% yield) (ethyl acetate as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98-7.92 (m, 2H), 7.71-

7.61 (m, 2H), 6.82-6.74 (m, 2H), 4.61 (t, J = 3.8 Hz, 4H), 3.96-3.88 (m, 4H), 3.79-3.63 (m, 12H), 3.57-3.52 (m, 4H), 3.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.9, 153.2, 139.3, 113.7, 111.3, 71.9, 70.7, 70.7, 70.6, 69.8, 64.9, 59.1. HRMS (ESI): m/z calcd for $C_{24}H_{37}N_2O_8$ $[M+H]^+$, 481.2544; found, 481.2549.

1-Methoxy-4-(phenylthio)-Benzene (3a)[7] Yellow oil. (42.7 mg, 99% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43-7.40 (m, 2H), 7.24-7.11 (m, 5H), 6.91-6.87 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.9, 138.6, 135.4, 129.0, 128.2, 125.8, 124.3, 115.0, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{12}OS$ $[M]^+$, 216; found, 216.

Methoxy-4-[(4-methylphenyl) thio]-benzene (3b)[7] Yellow solid. (44.3 mg, 92% yield) (hexane : DCM = 2 : 1 as eluent) 45-46 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, J = 8.9 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 3.73 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.5, 136.1, 134.4, 134.4, 129.8, 129.4, 125.6, 114.9, 55.4, 21.0. LRMS (EI) m/z calcd for $C_{14}H_{14}OS$ $[M]^+$, 230; found, 230.

1-[(4-Methoxyphenyl) thio]-3-methyl-Benzene (3c)[7] Yellow oil. (42.3 mg, 92% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36-7.30 (m, 2H), 7.05 (t, J = 7.7 Hz, 1H), 6.94 (s, 1H), 6.88 (d, J = 7.6 Hz, 2H), 6.85-6.78 (m, 2H), 3.75 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 138.8, 138.2, 135.2, 128.9, 128.8, 126.8, 125.4, 124.5, 114.9, 55.4, 21.4. LRMS (EI) m/z calcd for $C_{14}H_{14}OS$ $[M]^+$, 230; found, 230.

1-[(4-Methoxyphenyl) thio]-2-methyl-Benzene (3d)[7] Yellow oil. (33.5 mg, 73% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.24 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 7.4 Hz, 1H), 7.03-6.95 (m, 2H), 6.90 (d, J = 7.6 Hz, 1H), 6.80 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.6, 137.1, 137.1, 134.1, 130.2, 129.1,

126.5, 126.2, 124.5, 115.1, 55.4, 20.3. LRMS (EI) m/z calcd for $C_{14}H_{14}OS$ $[M]^+$, 230; found, 230.

4-[(4-Methoxyphenyl) thio]-1,2-dimethyl-Benzene (3e)[7] Yellow oil. (33.2 mg, 69% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31-7.25 (m, 2H), 6.99-6.87 (m, 3H), 6.81-6.76 (m, 2H), 3.73 (s, 3H), 2.13 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.4, 137.5, 135.0, 134.4, 134.2, 130.7, 130.3, 127.1, 125.8, 114.8, 55.4, 19.8, 19.4. LRMS (EI) m/z calcd for $C_{15}H_{16}OS$ $[M]^+$, 244; found, 244.

1,1'-Thiobis[4-methoxybenzene] (3f)[13] Yellow oil. (44.3 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.21 (d, *J* = 7.6 Hz, 4H), 6.76 (d, *J* = 7.6 Hz, 4H), 3.82 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 159.0, 132.7, 127.5, 114.8, 55.4. LRMS (EI) m/z calcd for $C_{14}H_{14}O_2S$ $[M]^+$, 246; found, 246.

1-Fluoro-4-[(4-methoxyphenyl) thio]-Benzene (3g)[13] Yellow oil. (42.1 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.8 Hz, 2H), 7.15-7.09 (m, 2H), 6.88 (t, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 160.4, 159.7, 134.6, 133.2, 133.1, 131.1, 131.0, 125.2, 116.2, 116.0, 115.0, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}FOS$ $[M]^+$, 234; found, 234.

4-[(4-Methoxyphenyl) thio]-1-methyl-2-chloro-Benzene (3h).Yellow oil. (41.7 mg, 79% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.30 (m, 2H), 7.07-6.97 (m, 2H), 6.92-6.97 (m, 1H), 6.85-6.80 (m, 2H), 3.75 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.0, 137.3, 135.4, 134.9, 133.7, 131.2, 128.5, 126.7, 123.9, 115.1, 55.4, 19.6. HRMS (ESI) m/z calcd for $C_{14}H_{14}ClOS$ $[M+H]^+$, 265.0448; found, 265.0437.

1-Chloro-4-[(4-methoxyphenyl) thio]-Benzene (3i)[7] Yellow solid. (45.0 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.31 (m, 2H), 7.14-7.09 (m, 2H), 7.03-6.96 (m, 2H), 6.85-6.80 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1, 137.4, 135.5, 131.6, 129.3, 129.0, 123.8, 115.2, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}ClOS$ $[M]^+$, 250; found, 250.

1-Chloro-3-[(4-methoxyphenyl) thio]-Benzene (3j)[14] Yellow solid. (45.0 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). 50-53 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39-7.33 (m, 2H), 7.06 (t, *J* = 7.7 Hz, 1H), 7.02-6.97 (m, 2H), 6.94-6.90 (m, 1H), 6.87-6.82 (m, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.3, 141.4, 136.2, 134.8, 129.9, 127.0, 125.6, 125.4, 122.6, 115.3, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}ClOS$ $[M]^+$, 250; found, 250.

1-Chloro-2-[(4-methoxyphenyl) thio]-Benzene (3k)[13] Yellow oil. (44.5 mg, 89% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.37 (m, 2H), 7.28-7.24 (m, 1H), 6.99-6.95 (m, 2H), 6.92-6.86 (m, 2H), 6.66-6.61 (m, 1H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 138.8, 137.0, 131.0, 129.5, 127.5, 127.1, 126.0, 121.6, 115.4, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}ClOS$ $[M]^+$, 250; found, 250.

1-Bromo-4-[(4-methoxyphenyl) thio]-Benzene (3l)[7] Yellow solid. (49.9 mg, 85% yield) (hexane : DCM = 2 : 1 as eluent). 54-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1, 138.2, 135.7, 131.9, 129.4, 123.5, 119.4, 115.2, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}BrOS$ $[M]^+$, 294; found, 294.

1-Bromo-3-[(4-methoxyphenyl) thio]-Benzene (3m)[15] Yellow solid. (52.7 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). 48-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39-7.32 (m, 2H),

7.18-7.12 (m, 2H), 7.02-6.93 (m, 2H), 6.87-6.81 (m, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.3, 141.6, 136.2, 130.2, 129.9, 128.5, 126.0, 123.0, 122.7, 115.3, 55.4. LRMS (EI) m/z calcd for $C_{13}H_{11}BrOS$ $[M]^+$, 294; found, 294.

4-[(4-Methoxyphenyl) thio]-Benzonitrile (3n)[16] White solid. (45.8 mg, 95% yield) (hexane : DCM = 2 : 1 as eluent). 94-95 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42-7.33 (m, 4H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 147.4, 137.2, 132.3, 126.0, 120.3, 119.0, 115.6, 108.0, 55.5. LRMS (EI) m/z calcd for $C_{14}H_{11}NOS$ $[M]^+$, 241; found, 241.

1-Methoxy-4-[(4-nitrophenyl) thio]-Benzene (3o)[7] Yellow solid. (19.7 mg, 41% yield) (hexane : DCM = 2 : 1 as eluent). 59-60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.9 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.1, 150.1, 145.0, 137.2, 125.6, 124.0, 120.2, 115.7, 55.5. LRMS (EI) m/z calcd for $C_{13}H_{11}NO_3S$ $[M]^+$, 261; found, 261.

1-[(4-Methoxyphenyl) thio]-2-nitro-Benzene (3p)[17] Yellow solid. (35.5 mg, 68% yield) (hexane : DCM = 2 : 1 as eluent). 91-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, *J* = 8.2 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.30-7.22 (m, 1H), 7.15-7.06 (m, 1H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.2, 144.6, 140.8, 137.8, 133.4, 127.9, 125.8, 124.7, 121.2, 115.7, 55.5. LRMS (EI) m/z calcd for $C_{13}H_{11}NO_3S$ $[M]^+$, 261; found, 261.

1-[(4-Methoxyphenyl) thio]-2, 4-dinitro-Benzene (3q)[18] Yellow solid. (39.8 mg, 65% yield) (hexane : DCM = 2 : 1 as eluent). 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.03 (d, *J* = 2.3 Hz, 1H), 8.09-8.00 (m, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.92 (d, *J* = 9.1

Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.9, 149.6, 144.1, 143.6, 137.6, 128.7, 126.8, 121.5, 119.2, 116.3, 55.6. LRMS (EI) m/z calcd for $C_{13}H_{10}N_2O_5S$ $[M]^+$, 306; found, 306.

2-[(4-Methoxyphenyl) thio]-Naphthalene (3r)[7] White solid. (39.6 mg, 75% yield) (hexane : DCM = 2 : 1 as eluent). 65-66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70-7.55 (m, 3H), 7.52 (d, *J* = 1.3 Hz, 1H), 7.41-7.28 (m, 4H), 7.24-7.18 (m , 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.9, 135.9, 135.3, 133.8, 131.7, 128.6, 127.7, 127.2, 126.7, 126.5, 126.4, 125.7, 124.4, 115.1, 55.4. LRMS (EI) m/z calcd for $C_{17}H_{14}OS$ $[M]^+$, 266; found, 266.

2-[(4-methoxyphenyl) thio]-Pyridine (3s)[13] Colorless solid. (40.8 mg, 94% yield) (hexane : DCM = 2 : 1 as eluent). 45-46 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36-8.29 (m, 1H), 7.49-7.43 (m, 2H), 7.39-7.30 (m, 1H), 6.94-6.83 (m, 3H), 6.71 (d, *J* = 8.1 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.8, 160.7, 149.3, 137.3, 136.7, 121.0, 120.4, 119.5, 115.3, 55.4. LRMS (EI) m/z calcd for $C_{12}H_{11}NOS$ $[M]^+$, 217; found, 217.

1-[(1, 1-Dimethylethyl) thio]-4-methoxy-Benzene (3t)[16] Colorless oil. (35.3 mg, 90% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40-7.34 (m, 2H), 6.81-6.76 (m, 2H), 3.75 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.3, 138.9, 123.6, 114.0, 55.3, 45.5, 30.8. LRMS (EI) m/z calcd for $C_{11}H_{16}OS$ $[M]^+$, 196; found, 196.

1-Methoxy-4-[(1-methylethyl) thio]-Benzene (3u)[19] Colorless oil. (30.9 mg, 85% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 3H), 3.18-3.03 (m, 1H), 1.17 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 158.4, 134.6, 124.4, 113.3, 54.3, 38.5, 22.1. LRMS (EI) m/z calcd for $C_{10}H_{14}OS$ $[M]^+$, 182; found, 182.

1-Methyl-4-(phenylthio)-Benzene (4a)[20] Colorless oil. (38.8 mg, 97% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37 (d, *J* = 8.1 Hz, 2H), 7.34-7.30 (m, 4H), 7.27-7.22 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 137.7, 137.2, 132.4, 131.3, 130.2, 129.8, 129.1, 126.5, 21.2. LRMS (EI) m/z calcd for $C_{13}H_{12}S$ $[M]^+$, 200; found, 200.

1-Methyl-3-(phenylthio)-Benzene (4b)[21] Colorless oil. (38.8 mg, 97% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.26 (m, 4H), 7.25 -7.12 (m, 4H), 7.06 (d, *J* = 7.4 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 136.1, 135.2, 131.9, 130.8, 129.2, 129.1, 128.4, 128.1, 126.9, 21.3. LRMS (EI) m/z calcd for $C_{13}H_{12}S$ $[M]^+$, 200; found, 200.

1-Methyl-2-(phenylthio)-Benzene (4c)[22] Colorless oil. (38.0 mg, 95% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23-7.05 (m, 9H), 2.30 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 140.0, 136.2, 133.8, 133.0, 130.6, 129.7, 129.2, 127.9, 126.8, 126.4, 20.6. LRMS (EI) m/z calcd for $C_{13}H_{12}S$ $[M]^+$, 200; found, 200.

4-(Phenylthio)-Benzenamine (4d)[23] Colorless oil. (39.6 mg, 99% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, DMSO) δ = 7.27-7.20 (m, 2H), 7.20-7.14 (m, 2H), 7.13-7.05 (m, 1H), 7.02-6.97 (m, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.53 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ = 150.1, 140.2, 136.5, 129.0, 125.9, 125.0, 114.8, 114.5. LRMS (EI) m/z calcd for $C_{11}H_9NS$ $[M]^+$, 201; found, 201.

1-Chloro-4-(phenylthio)-Benzene (4e)[20] Colorless oil. (43.6 mg, 99% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.29-7.22 (m, 4H), 7.22-7.15 (m, 5H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 135.1, 134.7, 133.0, 132.0, 131.3, 129.4, 129.4, 127.5. LRMS (EI) m/z calcd for $C_{12}H_9ClS$ $[M]^+$, 220; found, 220.

1-Bromo-2-(phenylthio)-Benzene (4f)[21] Colorless oil. (37.1 mg, 70% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51-7.45 (m, 1H), 7.41-7.28 (m, 5H), 7.10-7.03 (m, 1H), 6.96-6.90 (m, 1H), 6.85-6.81 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 138.8, 133.6, 133.0, 132.7, 129.8, 129.7, 128.5, 127.8, 127.3, 123.0. LRMS (EI) m/z calcd for $C_{12}H_9BrS$ $[M]^+$, 265; found, 265.

1-Nitro-4-(phenylthio)-Benzene (4g)[7] Brown oil. (27.7 mg, 60% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 9.0 Hz, 2H), 7.51-7.44 (m, 2H), 7.41-7.36 (m, 3H), 7.10 (d, *J* = 9.0 Hz, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6, 145.4, 134.8, 130.4, 130.1, 129.7, 126.7, 124.1. LRMS (EI) m/z calcd for $C_{12}H_9NO_2S$ $[M]^+$, 231; found, 231.

4-(Phenylthio)-Pyridine (4h)[20] Brown oil. (31.8 mg, 85% yield) (hexane : EtOAc = 10 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 5.7 Hz, 2H), 7.51-7.43 (m, 2H), 7.43-7.34 (m, 3H), 6.87 (d, *J* = 6.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.7, 149.2, 135.3, 130.0, 129.8, 129.3, 120.8. LRMS (EI) m/z calcd for $C_{11}H_9NS$ $[M]^+$, 187; found, 187.

2-(Phenylthio)-Pyridine (4i)[21] Brown oil. (34.0 mg, 95% yield) (hexane : EtOAc = 10 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.41-8.30 (m, 1H), 7.57-7.47 (m, 2H), 7.42-7.32 (m, 4H), 6.97-6.88 (m, 1H), 6.81 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.6, 149.4, 136.9, 135.0, 130.9, 129.7, 129.2, 121.4, 119.9. LRMS (EI) m/z calcd for $C_{11}H_9NS$ $[M]^+$, 187; found, 187.

2-(Phenylthio)-Pyrimidine (4j)[22] Brown oil. (33.1 mg, 95% yield) (hexane : EtOAc = 2 : 1 as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.42 (d, *J* = 4.1 Hz, 2H), 7.57 (d, *J* = 2.2 Hz, 2H), 7.37 (s, 3H), 6.90 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.9, 157.6, 135.3, 129.4, 129.4, 129.3, 117.1. LRMS (EI) m/z calcd for $C_{10}H_8N_2S$ $[M]^+$, 188; found, 188.

2-(Phenylthio)-Thiophene (4k)[20] Colorless oil. (28.8 mg,75% yield) (hexane as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 5.3 Hz, 1H), 7.24-7.15 (m, 3H), 7.14-7.05 (m, 3H), 7.03-6.98 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 138.7, 136.1, 131.3, 129.0, 127.9, 127.8, 127.2, 126.1. LRMS (EI) m/z calcd for $C_{10}H_8S_2$ $[M]^+$, 192; found, 192.

2-(Phenylthio)-Benzothiazole (4l)[24] Yellow oil. (36.9 mg, 76% yield) (hexane as eluent). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.49-7.36 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.22-7.16 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 169.7, 153.9, 135.6, 135.4, 130.5, 130.0, 130.0, 126.2, 124.4, 122.0, 120.8. LRMS (EI) m/z calcd for $C_{13}H_9NS_2$ $[M]^+$, 243; found, 243.

2-(Phenylthio)-Benzoxazole (4m)[24] Yellow oil. (36.7 mg, 81% yield) (hexane as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67-7.60 (m, 2H), 7.56-7.50 (m, 1H), 7.42-7.32 (m, 4H), 7.20-7.16 (m, 2H). ^{13}C NMR (100MHz, $CDCl_3$) δ = 163.4, 151.9, 142.0, 134.5, 130.3, 130.0, 127.1, 124.4, 124.3, 119.1, 110.1. LRMS (EI) m/z calcd for $C_{13}H_9NOS$ $[M]^+$, 227; found, 227.

[(Phenylmethyl) thio]-Benzene (4n)[20] White solid. (23.2 mg, 58% yield) (hexane : DCM = 2 : 1 as eluent). 35-38 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.30-7.02 (m, 10H), 4.04 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 137.5, 136.4, 129.9, 128.8, 128.5, 127.2, 126.4, 39.1. LRMS (EI) m/z calcd for $C_{13}H_{12}S$ $[M]^+$, 265; found, 265.

(Cyclohexylthio)-Benzene (4o)[20] Colorless oil. (19.0 mg, 50% yield) (hexane : DCM = 2 : 1 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35-7.29 (m, 2H), 7.22-7.19 (m, 2H), 7.16-7.11 (m, 1H), 3.06-2.99 (m, 1H), 1.96-1.86 (m, 2H), 1.74-1.66 (m, 2H), 1.57-1.51 (m, 1H), 1.31-1.16 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.2, 131.9, 128.8, 126.6, 46.6, 33.4, 26.1, 25.8. LRMS (EI) m/z calcd for $C_{12}H_{16}S$ $[M]^+$, 192; found, 192.

(Hexylthio)-Benzene (4p)[25] Colorless oil. (27.2 mg, 70% yield) (hexane as eluent). ^{1}H NMR (600 MHz, CDCl3) δ = 7.27-7.12 (m, 4H), 7.05 (t, *J* = 7.0 Hz, 1H), 2.81 (t, *J* = 7.3 Hz, 2H), 1.63-1.48 (m, 2H), 1.36-1.15 (m, 6H), 0.79 (t, *J* = 6.3 Hz, 3H). ^{13}C NMR (150MHz, $CDCl_3$) δ = 137.2, 128.9, 128.8, 125.6, 33.6, 31.4, 29.2, 28.6, 22.6, 14.1. LRMS (EI) m/z calcd for $C_{12}H_8S$ $[M]^+$, 194; found, 194.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Copies of ^{1}H NMR and ^{13}C NMR spectra for all compounds (PDF).

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Notes

The authors declare no conflict of interest.

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