Note

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Copper-Catalyzed Diaryl Ether Formation from (Hetero)aryl Halides at Low Catalytic Loadings

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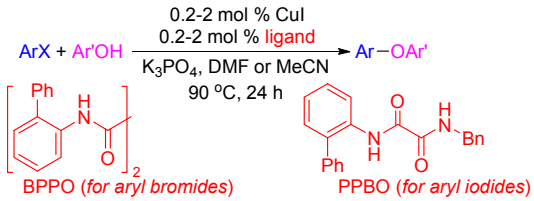
Abstract



Diaryl formation is achieved by coupling phenols and (hetero)aryl halides under the catalysis of CuI/*N*,*N'*-bis(2-phenylphenyl) oxalamide (BPPO) or CuI/ *N*-(2-phenylphenyl)-*N'*-benzyl oxalamide (PPBO) at 90 °C using DMF or MeCN as the solvent. Only 0.2-2 mol % CuI and ligand are required for complete conversion,

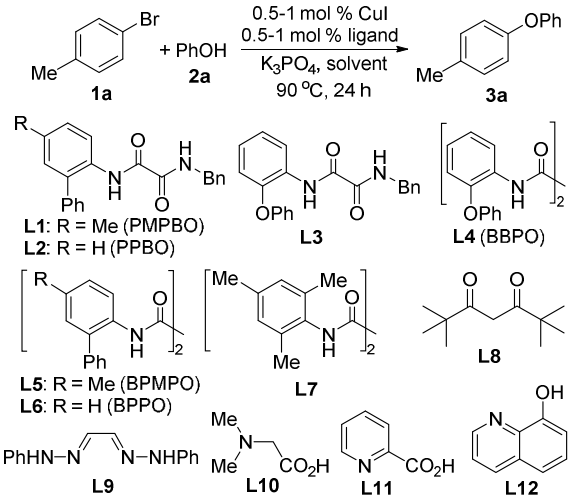
which represents the lowest catalytic loadings for a general Cu/ligand-catalyzed diaryl ether formation.

During the past two decades great attention has been directed to the development of ligand-promoted copper-catalyzed coupling reactions between phenols and aryl halides.[1] To date more than dozens of N,O-,[2] N,N-[3] or O,O-bidentate ligands[4] have been discovered to have such promoting ability. These newly developed catalytic systems make diaryl ether formation proceed under relatively mind conditions, and have been intensively applied in the synthesis of bioactive compounds and material molecules with scale from miligrams[1,5] to hundreds of kilograms.[6] Although the progress in this area is significant, further improvements are still desirable. For examples, in most cases, catalytic loadings are still considerably high (5-20 mol % copper salts and ligands),[7] which is unfavorable from economical and environmental viewpoint.[2-4] Recently, we found that some N,N'-disubstituted oxalamides are powerful ligands for Cu-catalyzed coupling reactions of aryl chlorides with phenols, leading to the formation of diaryl ethers at 120 ^{o}C.[8] Further investigations demonstrated that when more reactive aryl bromides and iodides were used as the coupling partners, our new catalytic systems worked well at much lower catalytic loadings in comparison with the previous Cu/ligand catalytic systems. Herein, we wish to disclose our results.

As indicated in Table 1, using CuI-catalyzed coupling of 4-methylbromo-benzene and phenol as a model reaction, we screened a series of ligands at 0.5 mol % loading. It was found that at 90 ^{o}C after 24 h, almost complete conversion was achieved by using *N*-(2-phenyl-4-methylphenyl)-*N'*-benzyl oxalamide (PMPBO, **L1**) as a ligand (entry 1).[8] Similar results were seen when other N,N'-disubstituted

oxalamides were employed (entries 2-7).[9] Under the same conditions, other known ligands like diketone **L8**, glyoxal bis(phenylhydrazone) **L9**, *N*,*N*-dimethylglycine **L10**, picolinic acid **L11** and 8-hydroxyquinline **L12** gave poor to moderate conversions. These results illustrated that *N*,*N*'-disubstituted oxalamides are superior to the previous ligands for CuI-catalyzed coupling of aryl bromides and phenols. Considered the availability, we chose *N*,*N'*-bis(2-phenylphenyl) oxalamide (BPPO, **L6**) for further studies. CuI/BPPO catalyzed reaction could also proceed smoothly in DMA and MeCN, although reaction yields were slightly decreased (entries 13 and 14). However, a poor conversion was observed when dioxane was used as the solvent (entry 15). Using K_3PO_4 as the base is essential for the reaction, as evident from that KOH and K_2CO_3 gave only 14-18% conversions. To achieve complete conversion, we increased the catalytic loading for both CuI and BPPO to 1 mol %, and were pleased that **3a** was obtained in 92% yield.

Table 1. CuI-catalyzed Coupling of 4-Methylbromobenzene with Phenol under the Assistance of Different Ligands[a]



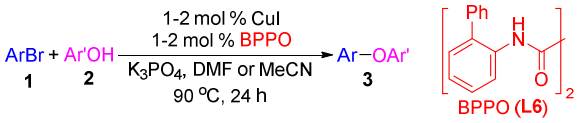
entry	ligand	yield (%)[b]	entry	ligand	yield (%)[b]
1	**L1**	88	10	**L10**	48
2	**L2**	88	11	**L11**	45
3	**L3**	87	12	**L12**	38
4	**L4**	86	13[c]	**L6**	71
5	**L5**	89	14[d]	**L6**	72
6	**L6**	89	15[e]	**L6**	36
7	**L7**	85	16[f]	**L6**	18
8	**L8**	46	17[g]	**L6**	14
9	**L9**	50	18[h]	**L6**	92

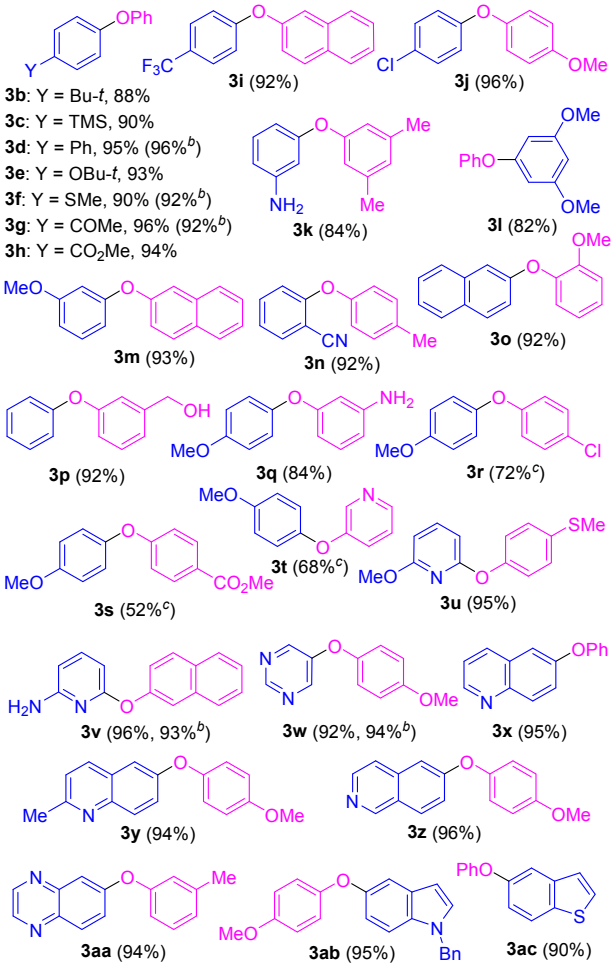
[a]General conditions: **1a** (5 mmol), phenol (7.5 mmol), CuI (0.025 mmol), ligand (0.025 mmol), K_3PO_4 (10 mmol), DMF (2.0 mL). [b]The yield was determined by ^1H NMR analysis of crude products using CH_2Br_2 as the internal standard. [c]DMA as the

solvent. [d]MeCN as the solvent. [e]Dioxane as the solvent.[f]KOH as the base. [g]K_2CO_3 as the base. [h]1 mol % CuI and **L6** were used.

The established optimized conditions were examined by varying (hetero)aryl bromides and phenols and the results are summarized in Table 2. A series of aryl bromides bearing either electron-donating or electron-withdrawing groups at the *para*-position worked well, giving diaryl ethers **3b-3j** in 88-96% yields. Coupling of three *meta*-substituted and one *ortho*-substituted aryl bromides with different phenols proceeded smoothly to afford **3k-3n** in 82-93% yields. For phenols, electron-rich ones gave the better results (**3o-3q**), while less reactive electron-poor ones required increasing catalytic loadings to 2 mol % to obtain the corresponding in reasonable yields (**3r-3t**). Additionally, a number of heteroaryl bromides are also compatible with these conditions, leading to formation of heterocycle-embodied diaryl ethers **3u-3ac** with excellent yields.

Table 2. CuI/BPPO Catalyzed Coupling of (Hetero)aryl Bromides with Phenols[a]



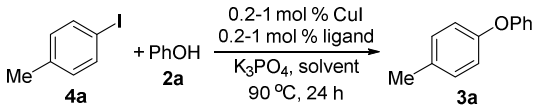


[a]**1** (5 mmol), **2** (7.5 mmol), CuI (0.5 mmol), BBPO (0.5 mmol), K_3PO_4 (10 mmol), DMF (2.0 mL). [b]Reaction was carried out in MeCN. [c]Reaction was carried out with 2 mol % CuI and BBPO.

For coupling with more reactive aryl iodides, we quickly screened some *N*,*N*'-disubstituted oxalamide ligands and found that two *N*-aryl-*N*'-alkyl substituted oxalamides **L1** and **L2** gave the best results when coupling reaction of

4-methyliodobenzene with phenol was conducted in MeCN at 90 °C (Table 3, entries 1-5). Thus, we chose relatively simple *N*-(2-phenylphenyl)-*N'*-benzyl oxalamide (PPBO, **L2**) for further reaction condition optimization. Among the solvents examined, DMF and DMA gave similar results with MeCN (entries 6 and 7), NMP led to a decreased yield (entry 8), while a poor yield was seen in dioxane (entry 9). Accordingly, we decided to use PPBO as the ligand and MeCN as the solvent to explore the reaction scope. Under these conditions the loading for both catalyst and ligand could be reduced to 0.2 mol % without affecting the reaction yield (entry 10).

Table 3. CuI-Catalyzed Coupling of 4-Methyliodobenzene with Phenol under the Assistance of Different Ligands[a]



entry	ligand	yield (%)[b]	entry	ligand	yield (%)[b]
1	**L1**	93	6[c]	**L2**	91
2	**L2**	92	7[d]	**L2**	88
3	**L4**	80	8[e]	**L2**	76
4	**L5**	84	9[f]	**L2**	34
5	**L6**	82	10[g]	**L2**	90

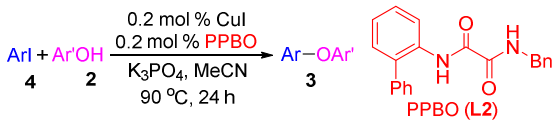
[a]General conditions: **4a** (10 mmol), phenol (15 mmol), CuI (0.1 mmol), ligand (0.1 mmol), K_3PO_4 (20 mmol), MeCN (4.0 mL). [b]The yield was determined by ^{1}H NMR analysis of crude products using CH_2Br_2 as the internal standard. [c]DMF as the solvent.

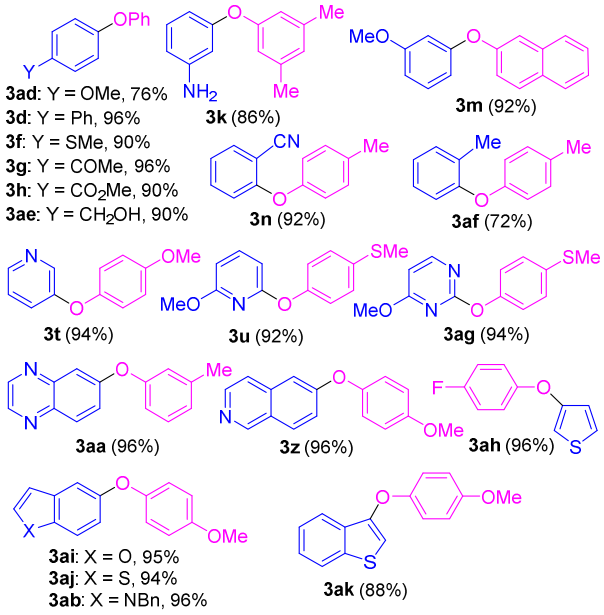
[d]DMA as the solvent. [e]NMP as the solvent. [f]Dioxane as the solvent. [g]0.2 mol % CuI and **L2** were used.

The reaction scope and limitations were explored with a range of (hetero)aryl iodides and phenols (Table 4). Generally, they all gave the corresponding diaryl ethers with excellent yields. When sterically hindered 2-methyliodobenzene was used, coupling reaction still proceeded smoothly under these conditions to give **3af**, although a decreased yield was observed.

Another notable feature for present coupling reactions is that a wide range of functional groups such as ester, ketone, alcohol, amino, cyanide and chloro moieties, are tolerated under these conditions. Additionally, a series of heterocycles that include thiophene, pyridine, pyrimidine, quinoline, isoquinoline, quinoxaline, benzothiaphene, indole and benzofuran could be introduced into the coupling products by choosing suitable heteroaryl halides or hydroxylated heteroarenes as the starting materials. These advantages allow diverse synthesis of functionalized diaryl ethers.

Table 4. CuI/PPBO Catalyzed Coupling of (Hetero)aryl Iodides with Phenols[a]





[a]General conditions: **4** (10 mmol), **2** (15 mmol), CuI (0.02 mmol), ligand (0.02 mmol), K_3PO_4 (20 mmol), MeCN (4.0 mL).

In conclusion, we have identified that two easily available N,N'-disubstituted oxalamides are efficient ligands for Cu-catalyzed coupling of phenols with (hetero)aryl bromides and iodides. The reactions worked well even with 0.2-2 mol % catalyst loadings to give a broad range of diaryl ethers in good to excellent yields. The present results represent the lowest catalytic loadings for a general Cu/ligand-catalyzed diaryl ether formation, and further demonstrated the power of N,N'-disubstituted oxalamide ligands to promote Cu-catalyzed arylation of nucleophiles.

Experimental

General procedure for coupling of (hetero)aryl bromides with phenols. A Schlenk tube was charged with CuI (9.5 mg, 0.05 mmol), BPPO (19.6 mg, 0.05 mmol), (hetero)aryl bromide (if solid, 5.0 mmol), phenol (if solid, 7.5 mmol) and K_3PO_4 (2.12 g, 10 mmol). The tube was evacuated and backfilled with argon before anhydrous DMF (2.0 mL) or MeCN (2.0 mL) was added via syringe (NOTE: for liquid substrates, they were added into the tube via syringe after the tube was backfilled with argon). The mixture was sealed and stirred at 90 °C for 24 h before diluted with about 50 mL of EtOAc and filtrated. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the corresponding diaryl ethers.

General procedure for coupling of (hetero)aryl iodides with phenols. A Schlenk tube was charged with CuI (3.8 mg, 0.02 mmol), PPBO (6.6 mg, 0.02 mmol), (hetero)aryl iodide (if solid, 10.0 mmol), phenol (if solid, 15.0 mmol) and K_3PO_4 (4.24 g, 20 mmol). The tube was evacuated and backfilled with argon before anhydrous MeCN (4.0 mL) was added via syringe (Note: for liquid substrates, they were added into the tube via syringe after the tube was backfilled with argon). The mixture was sealed and stirred at 90 °C for 24 h before diluted with EtOAc and filtrated. The filtrate was concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the corresponding diaryl ethers.

1-Methyl-4-phenoxybenzene (***3a***). **3a** was prepared from 4-bromotoluene and phenol or from 4-iodotoluene and phenol, and purified by flash chromatography (petroleum

ether, R_f = 0.6) as colorless liquid (846 mg, 92% from 4-bromotoluene; 1.66 g, 90% from 4-iodotoluene). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.29 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.07 (td, J = 7.5, 1.0 Hz, 1H), 6.98 (d, J = 7.5 Hz, 2H), 6.92 (dd, J = 8.0, 1.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.8, 133.0, 130.3, 129.8, 122.9, 119.2, 118.5, 20.8; HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{12}O$ (M^+) 184.0888, found 184.0881.

1-(tert-Butyl)-4-phenoxybenzene (***3b***). **3b** was prepared from 1-bromo-4-(*tert*-butyl)-benzene and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.5) as colorless liquid (994 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 4H), 7.11-7.07 (m, 1H), 7.03-7.01 (m, 2H), 6.95 (td, J = 8.5, 2.0 Hz, 2H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 154.8, 146.1, 129.7, 126.6, 123.0, 118.7, 118.6, 34.4, 31.6; HRMS (EI-TOF) *m/z* calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1366.

1-Trimethylsilyl-4-phenoxybenzene (***3c***). **3c** was prepared from (4-bromophenyl)-trimethylsilane and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.5) as colorless liquid (1.09 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 8.5, 1.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 2H), 7.13 (td, J = 7.5, 1.0 Hz, 1H), 7.05 (dd, J = 7.5, 1.0 Hz, 2H), 7.01 (dd, J = 8.5, 1.0 Hz, 2H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 157.0, 135.0, 134.6, 129.9, 123.5, 119.3, 118.1, -0.8; HRMS (EI-TOF) *m/z* calcd for $C_{15}H_{18}OSi$ (M^+) 242.1127, found 242.1124.

4-Phenoxy-1,1'-biphenyl (***3d***). **3d** was prepared from 4-bromobiphenyl and phenol or from 4-iodobiphenyl and phenol, and purified by flash chromatography (eluting with

petroleum ether, R_f = 0.4) as white solid (from 4-bromobiphenyl, 1.17 g, 95% in DMF; 1.18 g, 96% in MeCN; from 4-iodobiphenyl, 2.36 g, 96%); mp 62-64 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.55 (m, 4H), 7.44 (t, J = 7.6 Hz, 2H), 7.38-7.32 (m, 3H), 7.13 (t, J = 7.2 Hz, 1H), 7.09-7.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 157.0, 140.7, 136.4, 129.9, 128.9, 128.6, 127.2, 127.0, 123.5, 119.2, 119.2; HRMS (EI-TOF) *m/z* calcd for $C_{18}H_{14}O$ (M^+) 246.1045, found 246.1039.

1-(tert-Butoxy)-4-phenoxybenzene (***3e***). **3e** was prepared from 1-(*tert*-butoxy)-4-bromobenzene and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.6) as colorless liquid (1.13 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.09 (t, J = 7.5 Hz, 1H), 7.03-6.95 (m, 6H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 152.7, 151.0, 129.6, 125.4, 122.8, 119.4, 118.2, 78.1, 28.7; HRMS (EI-TOF) *m/z* calcd for $C_{16}H_{18}O_2$ (M^+) 242.1307, found 242.1303.

Methyl(4-phenoxyphenyl)sulfane (***3f***). **3f** was prepared from 4-bromothioanisole and phenol or from 4-iodothioanisole and phenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.5) as colorless liquid (from 4-bromothioanisole, 972 mg, 90% in DMF; 994 mg, 92% in MeCN; from 4-iodothioanisole, 1.94 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.31 (m, 2H), 7.27 (dt, J = 8.5, 2.5 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.5 Hz, 2H), 6.96 (dt, J = 9.0, 2.5 Hz, 2H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 155.4, 132.4, 129.9, 129.3, 123.4, 119.7, 118.8, 17.3; HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{12}OS$ (M^+) 216.0609, found 216.0605.

1-(4-Phenoxyphenyl)ethanone (***3g***). **3g** was prepared from 4-bromoacetophenone and

phenol or from 4-iodoacetophenone and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.4) as yellow solid (from 4-bromoacetophenone, 1.02 g, 96% in DMF; 975 mg, 92% in MeCN; from 4-iodoacetophenone, 2.04 g, 96%). mp 45-47 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.8 Hz, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.8 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 161.6, 155.2, 131.6, 130.3, 129.8, 124.3, 119.8, 116.9, 26.1; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{13}O_2$ $(M + H)^+$ 213.0910, found 213.0912.

Methyl 4-phenoxybenzoate (***3h***). **3h** was prepared from methyl 4-bromobenzoate and phenol or from methyl 4-iodobenzoate and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.5) as white solid (from 4-bromobenzoate, 1.07 g, 94%; from 4-iodobenzoate, 2.05 g, 90%), mp 57-59 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.40 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.5 Hz, 1H), 7.08 (d, J = 8.5 Hz, 2H), 7.03-6.98 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 161.9, 155.7, 131.8, 130.1, 124.6, 124.5, 120.2, 117.3, 52.1; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{13}O_3$ $(M + H)^+$ 229.0859, found 229.0859.

2-(4-(Trifluoromethyl)phenoxy)naphthalene (***3i***). **3i** was prepared from 1-bromo-4-(trifluoromethyl)benzene and 2-naphthol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.5) as white solid (1.32 g, 92%), mp 66-68 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (t, J = 9.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 2H), 7.55-7.46 (m, 3H), 7.29 (dt, J = 8.5, 2.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 2H); ^{13}C $\{^{19}F\}$NMR (100 MHz, $CDCl_3$) δ 160.5 (q, J = 1.3 Hz), 153.5, 134.3, 130.8,

130.3, 127.9, 127.3, 127.2 (q, J = 3.8 Hz), 126.8, 125.4, 125.1 (q, J = 32.6 Hz), 124.3 (q, J = 270.1 Hz), 120.2, 118.1, 115.9; HRMS (EI-TOF) *m/z* calcd for $C_{17}H_{11}OF_3$ (M^+) 288.0762, found 288.0764.

1-Chloro-4-(4-methoxyphenoxy)benzene (***3j***). **3j** was prepared from 1-chloro-4-bromobenzene and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.3) as white solid (1.12 g, 96%), mp 49-51 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.90-6.86 (m, 4H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.3, 149.9, 129.7, 127.5, 121.0, 118.9, 115.1, 55.8; HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{11}O_2Cl$ (M^+) 234.0448, found 234.0442.

3-(3,5-Dimethylphenoxy)aniline (***3k***). **3k** was prepared from 3-bromoaniline and 3,5-dimethylphenol or from 3-iodoaniline and 3,5-dimethylphenol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f = 0.4) as white solid (from 3-bromoaniline, 895 mg, 84%; from 3-iodoaniline, 1.83 g, 86%), mp 77-78 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (t, J = 8.0 Hz, 1H), 6.74 (s, 1H), 6.65 (s, 2H), 6.40 (t, J = 7.6 Hz, 2H), 6.32 (s, 1H), 3.67 (s, 2H), 2.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 157.1, 148.0, 139.6, 130.4, 125.1, 116.9, 110.0, 109.1, 105.6, 21.4; HRMS (ESI-TOF) calcd for $C_{14}H_{16}NO$ $(M + H)^+$ 214.1226, found 214.1226.

1,3-Dimethoxy-5-phenoxybenzene (***3l***). **3l** was prepared from 5-bromo-1,3-dimethoxy-benzene and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.4) as colorless liquid (943 mg, 82%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 7.05 (dt, J = 7.5, 1.0 Hz, 2H), 6.22 (t,

J = 2.0 Hz, 1H), 6.18 (d, *J* = 2.0 Hz, 2H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 159.4, 156.8, 129.9, 123.6, 119.4, 97.4, 95.6, 55.5; HRMS (EI-TOF) *m/z* calcd for $C_{14}H_{14}O_3$ (M^+) 230.0943, found 230.0937.

2-(3-Methoxyphenoxy)naphthalene (***3m***). **3m** was prepared from 3-bromoanisole (or 3-iodoanisole) and 2-naphthol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.4) as white solid (from 3-bromoanisole, 1.16 g, 93%; from 3-iodoanisole, 2.30 g, 92%), mp 50-52 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2H), 7.72 (d, *J* = 8.0, 1H), 7.48-7.34 (m, 2H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.28-7.23 (m, 2H), 6.71-6.68 (m, 1H), 6.66-6.64 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.1, 158.5, 154.9, 134.4, 130.3 (2C), 130.0, 127.9, 127.3, 126.6, 124.9, 120.2, 114.5, 111.3, 109.3, 105.1, 55.5; HRMS (ESI-TOF) calcd for $C_{17}H_{15}O_2$ $(M + H)^+$ 251.1067, found 251.1066.

2-(p-Tolyloxy)benzonitrile (***3n***). **3n** was prepared from 2-bromobenzonitrile (or 2-iodobenzonitrile) and *p*-cresol, and purified by flash chromatography (eluting with 1:50 EtOAc/petroleum ether, R_f = 0.3) as white solid (from 2-bromobenzonitrile, 961 mg, 92%; from 2-iodobenzonitrile , 1.92 g, 92%), mp 55-56 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.44 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.98-6.95 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 152.6, 134.8, 134.2, 133.8, 130.6, 122.5, 120.0, 116.4, 116.1, 103.2, 20.8; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{12}NO$ $(M + H)^+$ 210.0913, found 210.0913.

2-(2-Methoxyphenoxy)naphthalene (***3o***). **3o** was prepared from 2-bromonaphthalene

and guaiacol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.3) as white solid (1.15 g, 92%), mp 79-81 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.66 (d, J = 8.0 Hz, 1H), 7.44-7.34 (m, 2H), 7.30-7.26 (m, 1H), 7.20-7.16 (m, 2H), 7.06-7.04 (m, 2H), 6.96 (td, J = 7.6, 1.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 151.6, 145.0, 134.4, 129.9, 129.7, 127.8, 127.1, 126.5, 125.1, 124.4, 121.5, 121.3, 119.1, 113.0, 111.9, 56.1; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{15}O_2$ $(M + H)^+$ 251.1067, found 251.1067.

(3-Phenoxyphenyl)methanol (***3p***). **3p** was prepared from bromobenzene and 3-hydroxybenzyl alcohol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f = 0.3) as colorless liquid (920 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 3H), 7.13-7.09 (m, 2H), 7.03-7.00 (m, 3H), 6.94 (d, J = 8.0 Hz, 1H), 4.68 (d, J = 5.6 Hz, 2H), 1.66 (t, J = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 157.2, 143.1, 130.0, 129.9, 123.5, 121.7, 119.2, 118.1, 117.2, 65.1; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{13}O_2$ $(M + H)^+$ 201.0910, found 201.0911.

3-(4-Methoxyphenoxy)aniline (***3q***). **3q** was prepared from 4-bromoanisole and 3-aminophenol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f = 0.3) as yellow liquid (903 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (t, J = 8.0 Hz, 1H), 6.98 (dt, J = 9.0, 3.0 Hz, 2H), 6.87 (dt, J = 9.0, 3.0 Hz, 2H), 6.36 (dd, J = 7.5, 2.5 Hz, 1H), 6.33 (dd, J = 7.5, 2.5 Hz, 1H), 6.26 (t, J = 2.5 Hz, 1H), 3.80 (s, 3H), 3.66 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 156.0, 150.1, 148.0, 130.4, 121.2, 114.9, 109.5, 107.9, 104.4, 55.8; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NO_2$ $(M + H)^+$ 216.1019, found 216.1019.

1-Chloro-4-(4-methoxyphenoxy)benzene (***3r***). **3r** was prepared from 4-methoxybromobenzene and 4-chlorophenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.3) as white solid (842 mg, 72%), mp 49-51 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 9.2 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.90-6.86 (m, 4H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.3, 149.9, 129.7, 127.5, 121.0, 118.9, 115.1, 55.8; HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{11}O_2Cl$ (M^+) 234.0448, found 234.0442.

Methyl 4-(4-Methoxyphenoxy)benzoate (***3s***). **3s** was prepared from 1-bromo-4-methoxybenzene and methyl 4-hydroxybenzoate, and purified by flash chromatography (eluting with 1:20 EtOAc/petroleum ether, R_f = 0.4) as light yellow solid (671 mg, 52%), mp 93-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 4H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 162.9, 156.8, 148.8, 131.8, 124.0, 121.8, 116.5, 115.2, 55.8, 52.1; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{15}O_4$ $(M + H)^+$ 259.0965, found 259.0967.

3-(4-Methoxyphenoxy)pyridine (***3t***). **3t** was prepared from 3-hydroxypyridine and 1-bromo-4-methoxybenzene or from 3-iodopyridine and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f= 0.3) as white solid (from 1-bromo-4-methoxybenzene, 683 mg, 68%; from 3-iodopyridine, 1.89 g, 94% yield), mp 36-37 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.31 (m, 1H), 7.23-7.20 (m, 2H), 7.00 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.2, 149.3, 143.8, 140.6, 124.2, 124.1,

121.0, 115.2, 55.8; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{12}NO_2$ $(M + H)^+$ 202.0863, found 202.0863.

2-Methoxy-6-(4-methylthiophenoxy)pyridine (***3u***). **3u** was prepared from 2-bromo-6-methoxypyridine (or 2-iodo-6-methoxypyridine) and 4-methylthiophenol, and purified by flash chromatography (eluting with 1:50 EtOAc/petroleum ether 1:50, R_f= 0.3) as light yellow liquid (from 2-bromo-6-methoxypyridine, 1.17 g, 95%; from 2-iodo-6-methoxypyridine, 2.27 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.10-7.08 (m, 2H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.3, 152.0, 141.4, 133.8, 128.3, 121.7, 104.2, 101.3, 53.5, 16.7; HRMS (ESI-TOF) *m/z* calcd for $C_{13}H_{14}NO_2S$ $(M + H)^+$ 248.0740, found 248.0740.

6-(Naphthalen-2-yloxy)pyridin-2-amine (***3v***). **3v** was prepared from 2-bromo-6-aminopyridine and 2-naphthol, and purified by flash chromatography (eluting with 1:3 EtOAc/petroleum ether, R_f= 0.4) as light yellow solid (1.13 g, 96% in DMF; 1.10 g, 93% in MeCN), mp 92-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8, 2.0 Hz, 2H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 2.0 Hz, 1H), 7.49-7.39 (m, 3H), 7.30 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.21 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.6 Hz, 1H), 4.39 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 157.9, 152.4, 141.0, 134.3, 130.8, 129.6, 127.9, 127.5, 126.5, 125.2, 121.4, 117.1, 102.6, 99.6; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{13}N_2O$ $(M + H)^+$ 237.1022, found 237.1021.

5-(4-Methoxyphenoxy)pyrimidine (***3w***). **3w** was prepared from 5-bromopyrimidine and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:3

EtOAc/petroleum ether, R_f = 0.4) as light yellow solid (929 mg, 92% in DMF; 949 mg, 94% in MeCN), mp 54-56 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (s, 1H), 8.41 (s, 2H), 7.02 (dt, *J* = 9.2, 2.8 Hz, 2H), 6.93 (dt, *J* = 9.2, 2.8 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 153.4, 152.7, 148.2, 146.0, 121.0, 115.5, 55.8; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{11}N_2O_2$ $(M + H)^+$ 203.0815, found 203.0815.

6-Phenoxyquinoline (***3x***). **3x** was prepared from 6-bromoquinoline and phenol, and purified by flash chromatography (eluting with 1:3 EtOAc/petroleum ether, R_f = 0.4) as yellow liquid (1.05 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 3.2 Hz, 1H), 8.10 (d, *J* = 9.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.50 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.42-7.35 (m, 3H), 7.26-7.17 (m, 2H), 7.10 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.7, 149.1, 145.2, 135.2, 131.4, 130.0, 129.2, 124.1, 123.3, 121.5, 119.6, 112.9; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{12}NO$ $(M + H)^+$ 222.0913, found 222.0913.

6-(4-Methoxyphenoxy)-2-methylquinoline (***3y***). **3y** was prepared from 6-bromo-2-methylquinoline and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:10 EtOAc/petroleum ether, R_f = 0.4) as yellow liquid (1.06 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.43 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.05 (dt, *J* = 9.0, 3.0 Hz, 2H), 6.93 (dt, *J* = 9.0, 3.0 Hz, 2H), 3.83 (s, 3H), 2.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 156.4, 156.3, 149.8, 144.5, 135.4, 130.5, 127.3, 122.5, 122.5, 121.3, 115.1, 111.5, 55.8, 25.3; HRMS (ESI-TOF) *m/z* calcd for $C_{17}H_{16}NO_2$ $(M + H)^+$ 266.1176, found 266.1178.

6-(4-Methoxyphenoxy)isoquinoline (***3z***). **3z** was prepared from 6-bromoiosquinoline (or 6-iodoiosquinoline) and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:1 EtOAc/petroleum ether, R_f = 0.4) as light yellow solid (from 6-bromoiosquinoline, 1.20 g, 96%; from 6-iodoiosquinoline, 2.41 g, 96%), mp 76-79 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.42 (d, J = 6.0 Hz, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.44 (d, J = 5.6 Hz, 1H), 7.35 (dd, J = 9.2, 2.4 Hz, 1H), 7.10-7.06 (m, 2H), 7.01 (d, J = 2.4 Hz, 1H), 6.98-6.94 (m, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 156.7, 151.7, 148.5, 143.4, 137.3, 129.8, 125.0, 121.7, 120.3, 119.8, 115.1, 109.1, 55.6; HRMS (ESI-TOF) *m/z* calcd for $C_{16}H_{14}NO_2$ $(M + H)^+$ 252.1019, found 252.1019.

6-(m-Tolyloxy)quinoxaline (***3aa***). **3aa** was prepared from 6-bromo-quinoxaline (or 6-iodo-quinoxaline) and 3-methylphenol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f = 0.3) as light yellow solid (from 6-bromo-quinoxaline, 1.11 g, 94%; from 6-iodo-quinoxaline, 2.27 g, 96%), mp 44-46 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (d, J = 9.0 Hz, 2H), 8.07 (d, J = 9.5 Hz, 1H), 7.57 (dd, J = 9.5, 2.5 Hz, 1H), 7.41 (d, J = 2.5 Hz, 1H), 7.31 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.98-6.94 (m, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 155.4, 145.3, 144.3, 143.3, 140.6, 139.8, 131.0, 130.0, 125.8, 123.8, 121.2, 117.5, 113.0, 21.5; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{13}N_2O$ $(M + H)^+$ 237.1022, found 237.1024.

1-Benzyl-5-(4-methoxyphenoxy)-1H-indole (***3ab***). **3ab** was prepared from 1-benzyl-5-bromo-indole (or 1-benzyl-5-iodo-indole) and 4-methoxyphenol, and purified by flash

chromatography (eluting with 1:50 EtOAc/petroleum ether, R_f= 0.3) as yellow liquid (from 1-benzyl-5-bromo-indole, 1.57 g, 95%; from 1-benzyl-5-iodo-indole, 3.17 g, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 3H), 7.22-7.20 (m, 2H), 7.14-7.12 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.90 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.85 (d, *J* = 9.2 Hz, 2H), 6.46 (d, *J* = 2.4 Hz, 1H), 5.31 (s, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 152.5, 151.6, 137.5, 133.0, 129.4, 129.3, 128.9, 127.8, 126.9, 119.5, 114.8, 114.7, 110.6, 110.0, 101.6, 55.8, 50.4. HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{20}NO_2$ $(M + H)^+$ 330.1489, found 330.1489.

5-Phenoxybenzo[b]thiophene (***3ac***). **3ac** was prepared from 5-bromobenzo[*b*]-thiophene and phenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f= 0.5) as white solid (1.02 g, 90%), mp 49-51 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 5.5 Hz, 1H), 7.43 (d, *J* = 2.5 Hz, 1H), 7.35 (t, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.11 (td, *J* = 8.0, 1.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.0, 154.6, 140.9, 134.9, 129.9, 128.1, 123.8, 123.6, 123.1, 118.6, 117.6, 113.2; HRMS (EI-TOF) *m/z* calcd for $C_{14}H_{10}OS$ (M^+) 226.0452, found 226.0451.

1-Methoxy-4-phenoxybenzene (***3ad***). **3ad** was prepared from 1-methoxy-4-iodobenzene and phenol, and purified by flash chromatography (eluting with petroleum ether, R_f= 0.4) as colorless liquid (1.52 g, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.28 (m, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 7.00-6.97 (m, 2H), 6.96-6.93 (m, 2H), 6.91-6.87 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 156.0, 150.3, 129.7, 122.6, 121.0, 117.7, 115.0, 55.8; HRMS (EI-TOF) *m/z* calcd for

$C_{13}H_{12}O_2$ (M^+) 200.0837, found 200.0841.

(4-Phenoxyphenyl)methanol (***3ae***). **3ae** was prepared from 4-iodobenzyl alcohol and phenol, and purified by flash chromatography (eluting with 1:3 EtOAc/petroleum ether, R_f = 0.4) as light yellow solid (1.80 g, 90%), mp 48-50 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 4H), 7.12-7.09 (m, 1H), 7.02-6.99 (m, 4H), 4.66 (d, J = 5.5 Hz, 2H), 1.77 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 156.9, 135.8, 129.9, 128.8, 123.4, 119.1, 119.0, 65.0; HRMS (EI-TOF) *m/z* calcd for $C_{13}H_{12}O_2$ (M^+) 200.0837, found 200.0840.

1-Methyl-2-(p-tolyloxy)benzene (***3af***). **3af** was prepared from 2-iodotoluene and *p*-cresol, and purified by flash chromatography (eluting with petroleum ether, R_f = 0.6) as colorless liquid (1.43 g, 72%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 7.5 Hz, 1H), 7.14 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 8.5 Hz, 2H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 155.1, 132.0, 131.5, 130.2, 129.8, 127.2, 123.7, 119.3, 117.6, 20.8, 16.4; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{15}O$ $(M + H)^+$ 199.1117, found 199.1117.

4-Methoxy-2-(4-methylthiophenoxy)pyrimidine (***3ag***). **3ag** was prepared from 2-iodo-4-methoxypyrimidine and 4-methylthiophenol, and purified by flash chromatography (eluting with 1:5 EtOAc/petroleum ether, R_f = 0.4) as white solid (2.33 g, 94%), mp 106-108 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 6.0 Hz, 1H), 7.31 (dt, J = 9.0, 2.5 Hz, 2H), 7.14 (dt, J = 9.0, 2.5 Hz, 2H), 6.45 (d, J = 5.5 Hz, 1H), 3.95 (s, 3H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 165.1, 158.6,

150.6, 135.1, 128.2, 122.4, 103.5, 54.2, 16.6; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{13}O_2N_2S$ $(M + H)^+$ 249.0692, found 249.0694.

3-(4-Fluorophenoxy)thiophene (***3ah***). **3ah** was prepared from 3-iodothiophene and 4-fluorophenol, and purified by flash chromatography (eluting with petroleum ether, R_f= 0.5) as yellow liquid (1.86 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.02 (d, *J* = 6.0 Hz, 4H), 6.83 (dd, *J* = 5.0, 1.5 Hz, 1H), 6.53 (dd, *J* = 3.5, 1.5 Hz, 1H); ^{13}C {^{19}F}NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 240.3 Hz), 155.0, 153.9 (d, *J* = 2.4 Hz), 125.5, 120.5, 119.7 (d, *J* = 8.3 Hz), 116.3 (d, *J* = 23.2 Hz), 106.1; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_8OFS$ $(M + H)^+$ 195.0274, found 195.0275.

5-(4-Methoxyphenoxy)benzofuran (***3ai***). **3ai** was prepared from 5-iodobenzofuran and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f= 0.4) as light yellow solid (2.28 g, 95%), mp 39-41 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.00-6.94 (m, 3H), 6.89-6.86 (m, 2H), 6.69 (m, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 154.1, 151.7, 151.2, 146.2, 128.3, 120.0, 116.1, 114.9, 112.1, 110.0, 106.9, 55.7; HRMS (EI-TOF) *m/z* calcd for $C_{15}H_{12}O_3$ (M^+) 240.0786, found 240.0783.

5-(4-Methoxyphenoxy)benzo[b]thiophene (***3aj***). **3aj** was prepared from 5-iodobenzo[*b*]thiophene and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f= 0.4) as light yellow solid (2.41 g, 94%), mp 69-71 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 9.0 Hz,

1H), 7.46 (d, J = 5.5 Hz, 1H), 7.32 (d, J = 2.0 Hz, 1H), 7.22 (d, J = 5.5 Hz, 1H), 7.08 (dd, J = 9.0, 2.5 Hz, 1H), 7.03-6.99 (m, 2H), 6.92-6.88 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.9, 150.9, 140.8, 134.1, 128.0, 123.8, 123.5, 120.6, 116.7, 115.0, 111.6, 55.8; HRMS (EI-TOF) *m/z* calcd for $C_{15}H_{12}O_2S$ (M^+) 256.0558, found 256.0556.

3-(4-Methoxyphenoxy)benzo[b]thiophene (***3ak***). **3ak** was prepared from 3-iodobenzo[*b*]thiophene and 4-methoxyphenol, and purified by flash chromatography (eluting with 1:100 EtOAc/petroleum ether, R_f = 0.5) as light yellow solid (2.25 g, 88%), mp 93-95 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 9.2, 5.6 Hz, 2H), 7.39-7.37 (m, 2H), 7.10 (d, J = 9.2 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.44 (s, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 150.9, 149.7, 138.1, 132.2, 125.3, 124.2, 123.2, 121.2, 120.1, 114.9, 104.3, 55.8; HRMS (EI-TOF) *m/z* calcd for $C_{15}H_{12}O_2S$ (M^+) 256.0558, found 256.0555.

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Supporting Information: The copies of ^{1}H and ^{13}C NMR spectrum of products. This material is available free of charge via the Internet at http://pubs.acs.org

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