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Copper-Catalyzed Direct Synthesis of Di- and Triphenylamines: A Dramatic Accelerating Effect of 2-Aminophenols

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Keywords: Copper / Amines / Amino alcohols / N,O ligands / Reaction mechanisms

Utilizing the dramatic accelerating effect of 2-aminophenols, we developed a copper-catalyzed system for the selective synthesis of di- and triphenylamines. In addition, *N*- and *O*-arylation could be achieved in coupling reactions between 2-aminophenol and nitroaryl halides.

Introduction

Di- and triphenylamines are important building blocks in pharmaceuticals, natural products, and functional photoelectric materials.[1] Copper-mediated arylation of amines (Ullmann condensation) provides some of the most useful practical methods for the synthesis of these compounds. However, the synthetic scope of these transformations was historically restricted because of the often harsh reaction conditions, range of substrates, and the moderate yields obtained.[2] The discovery of efficient Pd/phosphane-ligand-catalyzed amination reactions (Buchwald–Hartwig reaction)[3,4] has been a major breakthrough in this field. Despite these significant improvements, limitations still exist, such as air- and moisture-sensitivity, functional group tolerance, and the high cost of palladium. Recently, the introduction of chelating ligands has led to dramatic improvements in copper/ligand systems (post-Ullmann reactions)[5,6] for the formation of C–N bonds, enabling the use only of catalytic amounts of copper under much milder conditions. There was still a challenge, however, in the synthesis of triphenylamines containing active hydroxy and amine groups, which have often been problematic,[7] and protecting group strategies have always needed to be employed.[8,9]

In our previous work the use of 2-aminophenol derivatives as ligands to promote the Cu-catalyzed formation of C–N bonds was reported.[10] Recently, Buchwald reported Pd- and Cu-catalyzed systems for the selective *O*- and *N*-arylation of aminophenols.[11] As in our own previous study,[10] by using 2-aminophenol itself as the ligand, Buchwald obtained mainly *N*-arylation products, together with 3–7% *N*,*N*-diarylated products in most cases.

2-Aminophenol derivatives should serve as substrates for the synthesis of di- and triphenylamines bearing hydroxy groups, and so a set of reaction conditions to enable the controlled formation of *N*-monoarylated and *N*,*N*-diarylated products from chelating 2-aminophenols was developed. In addition, the wide substrate scope of these reactions was extended and a preliminary mechanism study was also performed.

Results and Discussion

The reaction conditions for the selective synthesis of the di- and triphenylamines were optimized with iodobenzene and 2-aminophenol as a model system and with CuI as catalyst. In the case of the diphenylamine compound, the polar solvents DMSO, DMF, and CH_3CN were more efficient than the less polar toluene (Table 1, Entries 1–4). After screening of a variety of bases, K_3PO_4 was found to give the best result (Table 1, Entry 8). It should be pointed out that an excess of 2-aminophenol was necessary (Table 1, Entries 8–10), because the 2-aminophenol presumably served as not only raw material but also as ligand to promote the conversion; in addition, the excess of 2-aminophenol could restrain the formation of the triphenylamine compound. In the case of the triphenylamine compound, increasing the amount of iodobenzene to 3 equiv. and brief screening of the conditions (the optimization of conditions is detailed in the Supporting Information) allowed us to obtain the triphenylamine compound in 87% isolated yield (Table 1, Entry 11).

The scope of the *N*-arylation for the selective synthesis of diphenylamines was explored with a variety of aryl iodides or bromides, containing either electron-donating or electron-withdrawing groups on their aromatic rings. Generally, the diphenylamines were obtained in good to excel-

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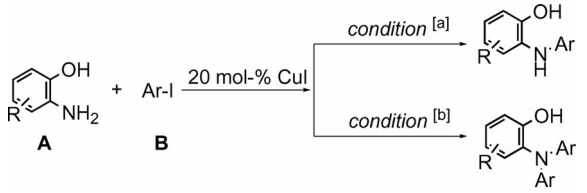
Table 1. Optimized reaction conditions for the selective synthesis of the di- and triphenylamines.[a]



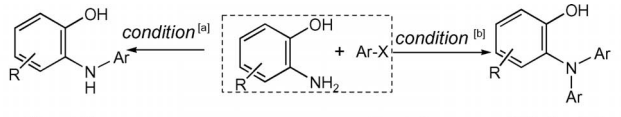
Entry	Base	Solvent	A/B	Yield [%]
1	Cs_2CO_3	DMSO	1.5:1	33
2	Cs_2CO_3	DMF	1.5:1	46
3	Cs_2CO_3	CH_3CN	1.5:1	44
4	Cs_2CO_3	$C_6H_5CH_3$	1.5:1	trace
5	KOH	DMF	1.5:1	40
6	Et_3N	DMF	1.5:1	25
7	K_2CO_3	DMF	1.5:1	46
8	K_3PO_4	DMF	1.5:1	62
9	K_3PO_4	DMF	1.2:1	40
10	K_3PO_4	DMF	2.0:1	95
11	Cs_2CO_3	DMF	1.0:3	87[b]

[a] Reaction conditions: 2-aminophenol, iodobenzene (1 mmol), CuI (0.2 mmol), the base (2 mmol), and the solvent (2 mL) were allowed to react under argon at 80 °C for 16 h. The yield (HPLC) was calibrated with diphenylamine as an internal standard. [b] Reaction conditions: 2-aminophenol (1 mmol), iodobenzene (3 mmol), CuI (0.2 mmol), and Cs_2CO_3 (3 mmol) in DMF (2 mL) were allowed to react at 110 °C for 24 h (isolated yield).

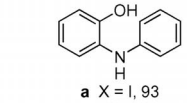
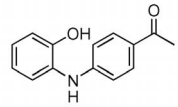
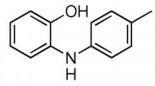
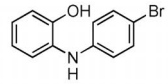
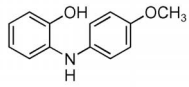
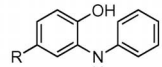
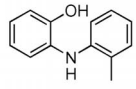
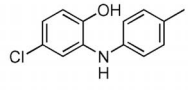
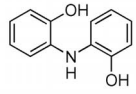
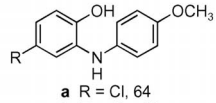
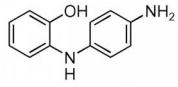
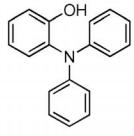
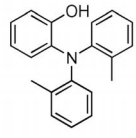
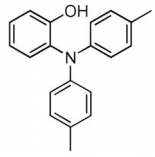
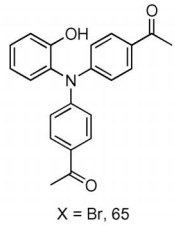
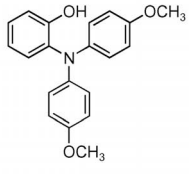
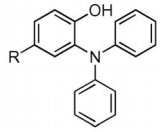
lent yields (Table 2, Entries 1–11). The CuI catalytic system also displayed great tolerance towards a range of functional groups such as methyl, methoxy, and acetyl, and in particular towards free hydroxy and amine groups. In addition, aryl iodides with *ortho*-substituents, which usually need rigorous conditions, coupled with 2-aminophenol in good yields (Table 2, Entries 4, 5), showing that steric hindrance does not have a huge influence on the *N*-arylation process. The aryl bromides were able to couple with 2-aminophenol at 110 °C in the presence of Cs_2CO_3 as base (Table 2, Entries 1b and 2b). We also observed that iodobenzene was more reactive. Consequently, the coupling reaction showed an interesting chemoselectivity, proceeding exclusively at the iodo group, which allowed us to obtain 2-[(4-bromophenyl)amino]phenol selectively with a yield of 84% (Table 2, Entry 8).

The triphenylamines were next synthesized selectively and in satisfactory yields by use of the optimal conditions for *N*,*N*-diarylation (Table 2, Entries 12–17). Iodobenzene gave a higher yield than 1-iodo-4-methylbenzene and 1-iodo-4-methoxybenzene (Table 2, Entries 12–15), whereas bromobenzene and 1-(4-bromophenyl)ethanone gave their corresponding products in 46% and 65% yields, respectively (Table 2, Entries 12b and 16). Steric effects for *N*,*N*-diarylation were significant in relation to those in the case of *N*-arylation, probably because of the weak nucleophilicities of the diphenylamine intermediates for the formation of the triphenylamine systems. Moreover, electronic effects on the 2-aminophenols also showed some influence. The presence of electron-withdrawing groups, as in 2-amino-4-chlorophenol, resulted in slightly lower yields than seen in

Table 2. Scope of *N*-arylation and *N*,*N*-diarylation of 2-aminophenols.



N-arylation X = I, Br *N*,*N*-diarylation

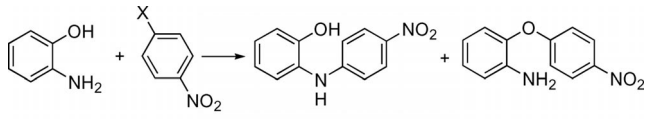
Entry	Yield [%]	Entry	Yield [%]
1	 **a** X = I, 93 **b** X = Br, 72 (Cs_2CO_3, 110 °C)	7	 X = Br, 77
2	 **a** X = I, 85 (70 °C) **b** X = Br, 70 (Cs_2CO_3, 110 °C)	8	 84 (60 °C, 24 h)
3	 74 (70 °C)	9	 **a** R = Cl, 66 **b** R = Me, 85 **c** R = *t*Bu, 81
4	 92	10	 63
5	 82	11	 **a** R = Cl, 64 **b** R = *t*Bu, 68
6	 65		
12	 **a** X = I, 87 **b** X = Br, 46	15	 78
13	 74	16	 X = Br, 65
14	 74	17	 **a** R = Cl, 61 **b** R = Me, 70 **c** R = *t*Bu, 87

[a] Reaction conditions: the 2-aminophenol (2 mmol), the aryl halide (1 mmol), CuI (0.2 mmol), K_3PO_4 (2 mmol), and DMF (2 mL) were allowed to react under argon at 80 °C for 16 h. [b] Reaction conditions: the 2-aminophenol (1 mmol), the aryl halide (3 mmol), CuI (0.2 mmol), Cs_2CO_3 (3 mmol), and DMF (2 mL) were allowed to react under argon at 110 °C for 24 h. Isolated yield.

the case of electron-donating groups (Table 2, Entries 17a, 17b, and 17c).

When 2-aminophenol was coupled with 1-iodo-4-nitrobenzene (lower temperatures were employed to prevent dehalogenation), the *N*-arylation product was obtained in a yield of 70%, but at the same time the *O*-arylation byproduct was detected by HPLC (Table 3, Entry 1). A similar result was observed with 1-bromo-4-nitrobenzene (Table 3, Entry 2). Particularly interestingly, with 1-chloro-4-nitrobenzene, the *N*-arylation and the *O*-arylation products were obtained in a ratio of 5:4 (Table 3, Entry 3). These results prompted us to investigate selective *N*- and *O*-arylation further. With use of a mixed solvent system of DMF and H_2O, 2-aminophenol was transformed into the *O*-arylation product in 74% yield (Table 3, Entry 4). With use of DMF as solvent and an increase in the temperature to 110 °C, the *N*-arylation product could be obtained in 86% yield (Table 3, Entry 5).

Table 3. Selective *N*- and *O*-arylation of 2-aminophenol.[a]



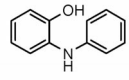
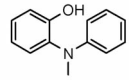
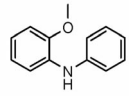
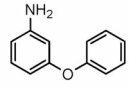
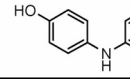
Entry	X	*T* (°C)	Solvent	Product[b]	N/O[c]
1	I	60	DMF	70 (N–Ar)	12:1
2	Br	80	DMF	69 (N–Ar)	11:1
3	Cl	80	DMF	53 (N–Ar) 42 (O–Ar)	5:4
4	Cl	80	DMF/H_2O (5:1)	74 (O–Ar)	1:15
5	Cl	110	DMF	86 (N–Ar)	29:1

[a] Reaction conditions: 2-aminophenol (2 mmol), the aryl halide (1 mmol), CuI (0.2 mmol), the solvent (2 mL), and K_3PO_4 (2 mmol) were allowed to react under argon for 16 h. [b] Isolated yield. [c] Calculated by HPLC at 267.5 nm.

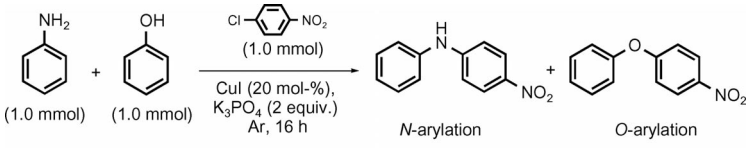
Competition experiments were carried out with 1-chloro-4-nitrobenzene and an aniline and phenol mixture (1:1) under different conditions (Scheme 1). The *O*-arylation product was obtained as the main product either at 80 °C in DMF/H_2O (5:1) or at 110 °C in DMF. We reasoned that *N*-arylation was directed by chelation with 2-aminophenol, whereas *O*-arylation was an S_NAr process. When nitroaryl halides were used as substrates, *N*- and *O*-arylation of 2-aminophenol occurred simultaneously. Because the oxidative addition of 1-iodo-4-nitrobenzene was fast, primarily *N*-arylation was observed. In the case of 1-chloro-4-nitrobenzene, because the C–Cl bond is less active, *N*- and *O*-arylation took place equally. Raising the reaction temperature to 110 °C made the C–Cl bond active enough for yields of the *O*-arylation product to approach those of the *N*-arylation product. The addition of H_2O increased the phenoxide concentration, so the *O*-arylation product was obtained almost exclusively. In the competition experiments, large amounts of the diaryl ether were obtained at 110 °C in DMF because the aniline could not form the chelate.

The *N*-arylation of aminophenol derivatives was investigated (Table 4). Steric hindrance at the nitrogen atom depressed the chelation of 2-(*N*-methylamino)phenol with copper, leading to a decline in the yield (Table 4, Entry 2). No *N*-arylation of 2-methoxybenzenamine took place (Table 4, Entry 3). 3-Aminophenol only afforded a 32% yield of the diaryl ether, quite consistently with the result of the competition experiments (Table 4, Entry 4). *N*-Arylation of 4-aminophenol was also in low yield (Table 4, Entry 5). All these results indicated that the *ortho*-hydroxy group in 2-aminophenol plays an important role through the formation of the five-membered chelate.

Table 4. *N*-Arylation of aminophenol derivatives.[a]

Entry	Substrates	Products	Yield [%]
1			93
2			52
3			trace
4			32
5			64

[a] Reaction conditions: the aniline derivatives (2 mmol), iodobenzene (1 mmol), CuI (0.2 mmol) and K_3PO_4 (2 mmol) in DMF (2 mL) were allowed to react under argon at 80 °C for 16 h. Isolated yield.

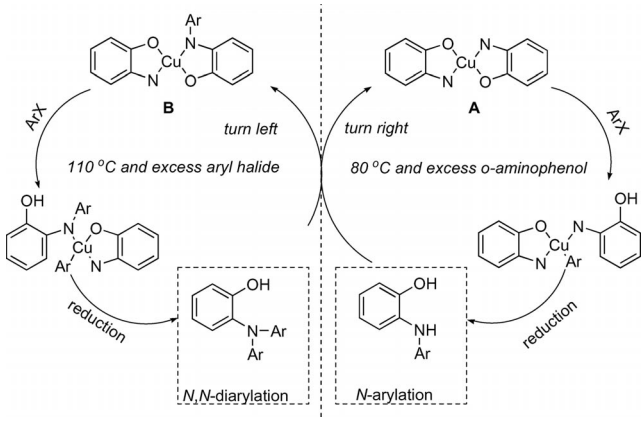


T (°C)	solvent	*N*-Ar [%][a]	*O*-Ar [%][a]	*N*/*O*-Ar
80	DMF/H_2O (5:1)	3.0	38.4	1:13
110	DMF	3.1	62.4	1:20

[a] Calculated by HPLC at 254 nm.

Scheme 1. Competition experiments with phenol/aniline (1:1).

From these results and previous findings in our group,[10] we postulated that the reaction proceeded through a mechanism as shown in Scheme 2. In this process, 2-aminophenol would not only serve as substrate but would also play the role of ligand. Firstly, with the help of base, two molecules of 2-aminophenol, losing protons, would combine with copper to provide the five-membered chelate **A** as shown. Next, the aryl halides would go through a process of oxidative addition and reductive elimination to effect *N*-arylation. At this point, if the temperature was 80 °C and the 2-aminophenol was in excess, the chelate **A** would be the major complex and the catalyst cycle would be turned to the right in the scheme to provide the *N*-arylated product continuously. If the aryl halide was in excess and at 110 °C, the chelate **B** would become the major complex and the catalyst cycle would turned to the left to provide the *N*,*N*-diarylation product.



Scheme 2. Plausible catalytic mechanism for the selective synthesis of di- and triphenylamines.

Conclusions

In conclusion, by utilizing the dramatic self-accelerating effect of 2-aminophenols, we have developed a copper-catalyzed system capable of selective *N*-arylation and *N*,*N*-diarylation of 2-aminophenols. In addition, both *N*- and *O*-arylation products of 2-aminophenol could be obtained when nitroaryl halides were used as substrates. This catalyst system is likely to find considerable application because it provides a direct and efficient way to synthesize 2-hydroxy-substituted di- and triphenylamines.

Experimental Section

General Procedure for *N*-Arylation of 2-Aminophenol: A flame-dried test tube containing a magnetic stirring bar was charged under argon with 2-aminophenol or a derivative (2.0 mmol), an aryl halide (1.0 mmol), CuI (0.2 mmol, 38 mg), K_3PO_4 or Cs_2CO_3 (2.0 mmol), and DMF (2 mL). The mixture was treated at the indicated temperature for 16 h and allowed to cool to room temperature. The resulting mixture was acidified with HCl (2 M) to adjust the pH to 6. The aqueous fraction was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried with Na_2SO_4 and concentrated in vacuo. The resulting residue was purified by column chromatography on silica gel (petroleum ether/acetone) to provide the desired product. All the physical data for the known compounds were in agreement with the literature.

General Procedure for *N*,*N*-Diarylation of 2-Aminophenols: 2-Aminophenol or a derivative (1.0 mmol), an aryl halide (3.0 mmol), CuI (0.2 mmol, 38 mg), Cs_2CO_3 (3.0 mmol, 978 mg), and DMF (2 mL) were allowed to react under argon at 110 °C for 24 h. The resulting mixture was acidified with HCl (2 M) to adjust the pH to 4.

2-(Phenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) by the General Procedure under the standard conditions (Table 2, Entry 1). When bromobenzene was used as substrate, Cs_2CO_3 was used as the base and the reaction temperature was 110 °C. The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a light yellow solid; yield 172 mg, 93% (Br: 133 mg, 72%). CAS: 644-71-3. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 (br., 1 H, NH), 5.76 (br., 1 H, OH), 6.77 (d, J = 7.6 Hz, 2 H, Ar-H), 6.85–6.90 (m, 2 H, Ar-H), 6.98 (d, J = 8.0 Hz, 1 H, Ar-H), 7.09 (t, J = 8.0 Hz, 1 H, Ar-H), 7.16–7.23 (m, 3 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.6, 116.1, 120.5, 121.2, 124.6, 126.0, 129.4, 129.6, 145.5, 151.0 ppm. MS (API): m/z = 186.1 $[M + H]^+$.

2-(*p*-Tolylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-iodo-4-methylbenzene (218 mg, 1.0 mmol) at 70 °C by the General Procedure (Table 2, Entry 2). When bromobenzene was used as substrate, Cs_2CO_3 was used as the base and the reaction temperature was 110 °C. The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a beige solid; yield 169 mg, 85% (Br: 139 mg, 70%). CAS: 87671-67-8. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, Me), 5.19 (br., 1 H, NH), 5.83 (br., 1 H, OH), 6.71 (d, J = 7.2 Hz, 2 H, Ar-H), 6.87 (m, 1 H, Ar-H), 6.97 (m, 1 H, Ar-H), 7.03 (m, 3 H, Ar-H), 7.14 (d, J = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.5, 115.3, 116.4, 121.0, 123.8, 125.4, 129.9, 142.8, 150.5 ppm. MS (API): m/z = 200.1 $[M + H]^+$, 222.1 $[M + Na]^+$.

2-(4-Methoxyphenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol) at 70 °C by the General Procedure (Table 2, Entry 3). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a white solid; yield 159 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H, OMe), 5.63 (br., 2 H, OH, NH), 6.81–6.88 (m, 5 H, Ar-H), 6.93 (d, J = 7.6 Hz, 1 H, Ar-H), 6.98–7.00 (m, 1 H, Ar-H), 7.09 (d, J = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 114.8, 115.1, 118.8, 121.1, 122.2, 124.4, 131.0, 138.3, 149.5, 154.4 ppm. MS (API): m/z = 216.1 $[M + H]^+$, 250.1 $[M + Cl]^-$.

2-(*o*-Tolylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-iodo-2-methylbenzene (218 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 4). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:25), giving a beige solid; yield 183 mg, 92%. CAS: 92028-38-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 3 H, Me), 5.68 (br., 2 H, OH, NH), 6.64 (d, J = 8.0 Hz, 1 H, Ar-H), 6.83–6.91 (m, 2 H, Ar-H), 6.99 (d, J = 7.8 Hz, 1 H, Ar-H), 7.06–7.11 (m, 3 H, Ar-H), 7.17 (d, J = 7.2 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 115.2, 115.5, 120.7, 121.2, 124.7, 125.2, 126.0, 127.3, 129.5, 130.9, 143.5, 150.9 ppm. MS (API): m/z = 200.1 $[M + H]^+$.

2-(2-Hydroxyphenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 2-iodophenol (220 mg, 1.0 mmol) un-

der the standard conditions by the General Procedure (Table 2, Entry 5). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:6), giving a white solid; yield 165 mg, 82%. CAS: 2391-71-1. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.45 (br., 3 H, OH, NH), 6.84–6.85 (m, 4 H, Ar-H), 6.91–6.95 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.1, 120.6, 121.4, 123.5, 131.5, 148.0 ppm. MS (API): *m*/*z* = 202.1 $[M + H]^+$, 224.1 $[M + Na]^+$.

2-(4-Aminophenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 4-iodoaniline (219 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 6). The resulting mixture did not add HCl. The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:6), giving a brown solid; yield 130 mg, 65%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 4.80 (br., 2 H, NH_2), 6.38 (br., 1 H, NH), 6.48–6.53 (m, 3 H, Ar-H), 6.58 (t, *J* = 7.6 Hz, 1 H, Ar-H), 6.74 (d, *J* = 8.0 Hz, 1 H, Ar-H), 6.78 (d, *J* = 8.0 Hz, 1 H, Ar-H), 6.84 (d, *J* = 8.8 Hz, 2 H, Ar-H), 9.31 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 112.4, 114.4, 114.7, 117.6, 119.2, 122.3, 131.9, 134.7, 143.5, 145.0 ppm. MS (API): *m*/*z* = 235.1 $[M + Cl]^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{12}H_{11}N_2O$ $[M - H]^-$: 199.0871; found 199.0868.

1-[4-(2-Hydroxyphenylamino)phenyl]ethanone: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 4-acetylbromobenzene (199 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 7). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:6), giving a yellow solid; yield 175 mg, 77%. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.43 (s, 3 H, Me), 6.78–6.82 (m, 1 H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 2 H, Ar-H), 6.92–6.98 (m, 2 H, Ar-H), 7.21 (d, *J* = 7.6 Hz, 1 H, Ar-H), 7.76 (d, *J* = 8.4 Hz, 2 H, Ar-H), 8.06 (br., 1 H, Ar-H), 9.57 (br., 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 26.0, 113.1, 116.1, 119.2, 123.1, 124.4, 126.6, 128.0, 130.2, 150.0, 150.3, 195.3 ppm. MS (API): *m*/*z* = 226.1 $[M - H]^-$, 262.1 $[M + Cl]^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{14}H_{12}NO_2$ $[M - H]^-$: 226.0868; found 226.0867.

2-(4-Bromophenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-bromo-4-iodobenzene (283 mg, 1.0 mmol) at 60 °C for 16 h by the General Procedure (Table 2, Entry 8). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a white solid; yield 222 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.31 (br., 1 H, NH), 5.63 (br., 1 H, OH), 6.66 (d, *J* = 8.4 Hz, 2 H), 6.87–6.89 (m, 1 H), 6.97 (d, *J* = 7.6 Hz, 1 H), 7.07–7.10 (m, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.4 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.4, 115.7, 117.7, 121.3, 124.4, 126.5, 128.7, 132.4, 144.6, 150.9 ppm. MS (API): *m*/*z* = 262.0, 264.0 $[M - H]^-$, 297.9, 299.9 $[M + Cl]^-$.

4-Chloro-2-(phenylamino)phenol: 2-Amino-4-chlorophenol (287 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 9a). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a brown solid; yield 143 mg, 66%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.72 (dd, *J* = 8.4, *J* = 2.4 Hz, 1 H, Ar-H), 6.81–6.86 (m, 2 H, Ar-H), 7.06–7.08 (m, 3 H, Ar-H), 7.23 (t, *J* = 8.0 Hz, 2 H, Ar-H), 7.35 (br., 1 H, Ar-H), 9.80 (br., 1 H. OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]-DMSO): δ = 115.5, 116.0, 117.6, 119.6, 120.1, 122.5, 128.9, 132.9, 142.9, 146.0 ppm. GC–MS (EI): *m*/*z* = 219 $[M]^+$, 221 $[M + 2]^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{12}H_9ClNO$ $[M - H]^-$: 218.0373; found 218.0379.

4-Methyl-2-(phenylamino)phenol: 2-Amino-4-methylphenol (246 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 9b). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a yellow solid; yield 169 mg, 85%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.16 (s, 3 H, Me), 6.56 (dd, *J* = 8.0, *J* = 1.6 Hz, 1 H, Ar-H), 6.72–6.75 (m, 2 H, Ar-H), 6.97–6.99 (m, 3 H, Ar-H), 7.07 (br., 1 H, Ar-H), 7.14–7.18 (m, 2 H, Ar-H), 9.16 (br., 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 20.4, 115.2, 116.0, 118.6, 119.1, 121.7, 127.6, 128.7, 130.3, 144.4, 145.7 ppm. GC–MS (EI): *m*/*z* = 199 $[M]^+$.

4-*tert*-Butyl-2-(phenylamino)phenol: 2-Amino-4-*tert*-butylphenol (330 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 9c). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a brown solid; yield 195 mg, 81%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.20 (s, 9 H, Me), 6.70 (t, *J* = 7.2 Hz, 1 H, Ar-H), 6.75–6.81 (m, 2 H, Ar-H), 6.93 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.13 (d, *J* = 7.6 Hz, 2 H, Ar-H), 7.17–7.18 (m, 2 H, Ar-H), 9.17 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.5, 33.8, 115.0, 115.4, 116.6, 118.3, 118.4, 128.9, 129.5, 141.3, 144.9, 146.2 ppm. GC–MS (EI): *m*/*z* = 241 $[M]^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{16}H_{18}NO$ $[M - H]^-$: 240.1388; found 240.1382.

4-Chloro-2-(*p*-tolylamino)phenol: 2-Amino-4-chlorophenol (287 mg, 2.0 mmol) was coupled with 1-iodo-4-methylbenzene (218 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 10). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:15), giving a dark purple solid; yield 147 mg, 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, Me), 5.48 (br., 2 H, Ar-H), 6.81–6.84 (m, 3 H, Ar-H), 6.89 (dd, *J* = 8.6, *J* = 2.4 Hz, 2 H, Ar-H), 7.08 (d, *J* = 8.0 Hz, 2 H, Ar-H), 7.12 (d, *J* = 2.4 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.8, 116.3, 118.5, 119.0, 122.2, 125.6, 130.1, 131.3, 132.7, 140.7, 146.4 ppm. GC–MS (EI): *m*/*z* = 233 $[M]^+$, 235 $[M + 2]^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{13}H_{11}ClNO$ $[M - H]^-$: 232.0529; found 232.0538.

4-Chloro-2-(4-methoxyphenylamino)phenol: 2-Amino-4-chlorophenol (286 mg, 2.0 mmol) was coupled with 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 11a). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:15), giving a dark purple solid; yield 160 mg, 64%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.73 (s, 3 H, Me), 6.58 (dd, *J* = 8.4, *J* = 2.4 Hz, 1 H, Ar-H), 6.76 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.80 (d, *J* = 2.4 Hz, 1 H, Ar-H), 6.88 (d, *J* = 9.2 Hz, 2 H, Ar-H), 7.08–7.10 (m, 3 H, Ar-H), 9.72 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 55.2, 112.0, 114.4, 115.4, 117.4, 121.9, 122.7, 135.1, 135.3, 144.4, 154.4 ppm. GC–MS (EI): *m*/*z* = 249 $[M]^+$, 251 $[M + 2]^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{13}H_{11}ClNO_2$ $[M - H]^-$: 248.0478; found 248.0475.

4-*tert*-Butyl-2-(4-methoxyphenylamino)phenol: 2-Amino-4-*tert*-butylphenol (330 mg, 2.0 mmol) was coupled with 1-iodo-4-methoxybenzene (234 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 11b). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a dark purple solid; yield 184 mg, 68%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 1.19 (s, 9 H, Me), 3.69 (s, 3 H, OMe), 6.66 (dd, *J* = 8.2, *J* = 2.4 Hz, 1 H, Ar-H), 6.73 (d, *J* = 8.4 Hz, 1 H, Ar-H), 6.82 (d, *J* = 8.8 Hz, 2 H, Ar-H), 6.98 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.07 (d, *J* = 2.4 Hz, 1 H, Ar-H), 9.13 (br., 1

H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.4, 33.7, 55.2, 113.0, 114.3, 114.4, 116.3, 118.8, 131.5, 137.3, 141.3, 144.4, 153.0 ppm. GC–MS (EI): *m*/*z* = 271 [M]$^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{17}H_{20}NO_2$ [M – H]$^-$: 270.1494; found 270.1483.

2-(Diphenylamino)phenol: 2-Aminophenol (109 mg, 1.0 mmol) was coupled with iodobenzene (612 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 12). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 227 mg, 87% (Br: 120 mg, 46%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.56 (br., 1 H, OH), 6.95 (td, *J* = 7.8, *J* = 1.2 Hz, 1 H, Ar-H), 7.05 (m, 7 H, Ar-H), 7.12 (dd, *J* = 8.0, *J* = 1.2 Hz, 1 H, Ar-H), 7.22 (td, *J* = 7.8, *J* = 1.2 Hz, 1 H, Ar-H), 7.17 (m, 4 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.7, 121.6, 121.9, 122.9, 127.9, 129.6, 133.3, 146.9 152.5 ppm. MS (API): *m*/*z* = 262.1 [M + H]$^+$.

2-[Bis(4-methylphenyl)amino]phenol: 2-Aminophenol (109 mg, 1.0 mmol) was coupled with 1-iodo-2-methylbenzene (654 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 13). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 214 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 (s, 6 H, Me), 5.46 (br., 1 H, OH), 6.76–6.82 (m, 5 H, Ar-H), 6.89–6.97 (m, 6 H, Ar-H), 7.04 (t, *J* = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.9, 116.5, 117.0, 121.5, 121.9, 129.1, 130.1, 132.3, 133.8, 144.7, 152.3 ppm. MS (API): *m*/*z* = 290.3 [M + H]$^+$, 312.1 [M + Na]$^+$.

2-[Bis(4-methoxyphenyl)amino]phenol: 2-Aminophenol (109 mg, 1.0 mmol) was coupled with 1-iodo-4-methoxybenzene (702 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 14). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 238 mg, 74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 6 H, OMe), 5.58 (br., 1 H, OH), 6.83 (t, *J* = 7.8 Hz, 1 H, Ar-H), 6.88 (d, *J* = 8.4 Hz, 4 H, Ar-H), 6.96–7.03 (m, 6 H, Ar-H), 7.09 (t, *J* = 7.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.5, 115.1, 124.4, 125.9, 128.3, 129.1, 135.6, 138.8, 160.0 ppm. MS (API): *m*/*z* = 322.1 [M + H]$^+$, 344.0 [M + Na]$^+$.

2-(Di-*o*-tolylamino)phenol: 2-Aminophenol (109 mg, 1.0 mmol) was coupled with 1-iodo-2-methylbenzene (654 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 15). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 225 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94 (s, 6 H, Me), 5.16 (br., 1 H, OH), 6.76 (dd, *J* = 7.6, *J* = 1.2 Hz, 2 H, Ar-H), 6.81 (td, *J* = 7.6, *J* = 1.2 Hz, 2 H, Ar-H), 6.94 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.05–7.10 (m, 5 H, Ar-H), 7.17 (d, *J* = 7.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7, 116.4, 121.0, 124.8, 126.1, 126.3, 126.9, 127.1, 127.3, 132.1, 133.0, 135.0, 150.5 ppm. MS (API): *m*/*z* = 290.1 [M + H]$^+$, 312.1 [M + Na]$^+$. HR-ESI-MS: *m*/*z* calcd. for $C_{20}H_{18}NO$ [M – H]$^-$: 288.1388; found 288.1385.

2-[Bis(4-acetylphenyl)amino]phenol: 2-Aminophenol (109 mg, 1.0 mmol) was coupled with 4-acetylbromobenzene (594 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 16). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 224 mg, 65%. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.50 (s, 6 H, Me), 6.90 (t, *J* = 8.0 Hz, 1 H, Ar-H), 7.02 (m, 5 H, Ar-H), 7.12 (d, *J* = 8.0 Hz, 1 H, Ar-H), 7.23 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.87 (d, *J* = 8.4 Hz, 4 H, Ar-H), 9.73 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 26.7, 117.4, 120.2, 120.4, 128.8, 129.8, 130.5, 131.1, 150.1, 154.1, 196.0 ppm. MS (API): *m*/*z* = 344.1 [M – H]$^-$, 380.1 [M + Cl]$^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{22}H_{18}NO_3$ [M – H]$^-$: 344.1287; found 344.1282.

4-Chloro-2-(diphenylamino)phenol: 2-Amino-4-chlorophenol (143 mg, 1.0 mmol) was coupled with iodobenzene (612 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 17a). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:30), giving a light brown solid; yield 181 mg, 61%. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 6.88–6.95 (m, 7 H, Ar-H), 7.03 (d, *J* = 2.8 Hz, 1 H, Ar-H), 7.14 (dd, *J* = 8.8, *J* = 2.8 Hz, 1 H, Ar-H), 7.23 (t, *J* = 7.2 Hz, 4 H, Ar-H), 9.75 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 118.4, 121.1, 121.6, 122.5, 126.7, 128.9, 129.4, 134.1, 146.7, 153.0 ppm. MS (API): *m*/*z* = 294.0, 296.0 [M – H]$^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{18}H_{13}ClNO$ [M – H]$^-$: 294.0686; found 294.0688.

2-(Diphenylamino)-4-methylphenol: 2-Amino-4-methylphenol (123 mg, 1.0 mmol) was coupled with iodobenzene (612 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 17b). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light yellow solid; yield 193 mg, 70%. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 2.15 (s, 3 H, Me), 6.82–6.92 (m, 9 H, Ar-H), 7.19 (t, *J* = 7.8 Hz, 4 H, Ar-H), 9.13 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 20.2, 116.9, 120.7, 120.9, 127.9, 128.7, 128.9, 130.6, 132.3, 147.1, 151.8 ppm. MS (API): *m*/*z* = 274.1 [M – H]$^-$, 549.2 [2M – H]$^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{19}H_{16}NO$ [M – H]$^-$: 274.1232; found 274.1233.

4-*tert*-Butyl-2-(diphenylamino)phenol: 2-Amino-4-*tert*-butylphenol (165 mg, 1.0 mmol) was coupled with iodobenzene (612 mg, 3.0 mmol) under the standard conditions by the General Procedure (Table 2, Entry 17c). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:40), giving a light brown solid; yield 278 mg, 87%. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 1.19 (s, 9 H, Me), 6.85–6.90 (m, 7 H, Ar-H), 7.06 (d, *J* = 2.4 Hz, 1 H, Ar-H), 7.14 (dd, *J* = 8.4, *J* = 2.4 Hz, 1 H, Ar-H), 7.18–7.22 (m, 4 H, Ar-H), 9.19 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 31.3, 33.7, 116.6, 120.7, 120.9, 124.1, 127.0, 128.9, 131.8, 142.4, 147.1, 151.8 ppm. MS (API): *m*/*z* = 316.1 [M – H]$^-$. HR-ESI-MS: *m*/*z* calcd. for $C_{22}H_{22}NO$ [M – H]$^-$: 316.1701; found 316.1716.

2-(4-Nitrophenoxy)benzenamine: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-chloro-4-nitrobenzene (157 mg, 1.0 mmol) in DMF/H_2O (5:1) at 80 °C for 24 h by the General Procedure (Table 3, Entry 4). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:8), giving a yellow solid; yield 170 mg, 74%. CAS: 18226-25-0. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 5.05 (br., 2 H, NH_2), 6.61 (td, *J* = 7.4, *J* = 1.6 Hz, 1 H, Ar-H), 6.85 (dd, *J* = 8.0, *J* = 1.6 Hz, 1 H, Ar-H), 6.93 (dd, *J* = 8.0, *J* = 1.2 Hz, 1 H, Ar-H), 7.00–7.04 (m, 3 H, Ar-H), 8.23 (d, *J* = 8.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 116.2, 116.3, 116.5, 121.5, 125.9, 126.5, 139.4, 140.8, 141.7, 163.1 ppm. MS (API): *m*/*z* = 231.3 [M + H]$^+$, 253.3 [M + Na]$^+$.

2-(4-Nitrophenylamino)phenol: 2-Aminophenol (218 mg, 2.0 mmol) was coupled with 1-iodo-4-nitrobenzene (249 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 3, Entry 5). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:6), giving an orange solid; yield 198 mg, 86%. CAS: 119707-16-3. ^{1}H NMR (400 MHz, [D$_6$]-DMSO): δ = 6.80–6.86 (m, 3 H, Ar-H), 6.96 (d, *J* = 6.8 Hz, 1 H, Ar-H), 7.05 (t, *J* = 7.6 Hz, 1 H, Ar-H), 7.20 (d, *J* = 6.8 Hz, 1 H,

Ar-H), 8.03 (d, J = 9.2 Hz, 2 H, Ar-H), 8.74 (br., 1 H, NH), 9.73 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 112.7, 116.3, 119.3, 124.8, 125.7, 125.9, 126.6, 137.0, 151.2, 152.3 ppm. MS (API): m/z = 231.1 [M + H]$^+$, 253.1 [M + Na]$^+$.

2-[Methyl(phenyl)amino]phenol: 2-(Methylamino)phenol (246 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 4, Entry 2). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a white solid; yield 103 mg, 52%. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.13 (s, 3 H, Me), 6.55 (d, J = 8.0 Hz, 2 H, Ar-H), 6.63 (t, J = 7.2 Hz, 1 H, Ar-H), 6.84 (td, J = 8.0, J = 1.2 Hz, 1 H, Ar-H), 6.98 (dd, J = 8.0, J = 1.2 Hz, 1 H, Ar-H), 7.06–7.13 (m, 4 H, Ar-H), 9.35 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 38.8, 112.9, 116.5, 117.0, 119.9, 127.3, 128.7, 129.0, 134.5, 149.2, 154.0 ppm. MS (API): m/z = 200.1 [M + H]$^+$, 222.1 [M + Na]$^+$.

3-Phenoxyaniline: 3-Aminophenol (218 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 4, Entry 4). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a white solid; yield 59 mg, 32%. CAS: 3586-12-7. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 5.23 (br., 2 H, NH$_2$), 6.14 (dd, J = 6.8, J = 2.4 Hz, 1 H, Ar-H), 6.19 (d, J = 2.4 Hz, 1 H, Ar-H), 6.33 (d, J = 8.0 Hz, 1 H, Ar-H), 6.97–7.01 (m, 3 H, Ar-H), 7.09 (t, J = 7.2 Hz, 1 H, Ar-H), 7.36 (t, J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 103.8, 105.9, 109.3, 118.6, 123.0, 129.9, 130.1, 150.5, 157.0, 157.6 ppm. GC–MS (EI): m/z = 185 [M]$^+$.

4-(Phenylamino)phenol: 4-Aminophenol (218 mg, 2.0 mmol) was coupled with iodobenzene (204 mg, 1.0 mmol) under the standard conditions by the General Procedure (Table 4, Entry 5). The crude product was purified over a silica gel column with use of acetone/petroleum ether (1:20), giving a white solid; yield 118 mg, 64%. CAS: 112-37-2. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 6.65 (t, J = 7.2 Hz, 1 H, Ar-H), 6.71 (d, J = 8.8 Hz, 2 H, Ar-H), 6.86 (d, J = 7.6 Hz, 2 H, Ar-H), 6.94 (d, J = 8.8 Hz, 2 H, Ar-H), 7.12 (t, J = 7.6 Hz, 2 H, Ar-H), 7.64 (br., 1 H, NH), 9.01 (br., 1 H, OH) ppm. ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 114.2, 115.7, 117.6, 121.4, 129.1, 134.3, 145.8, 152.1 ppm. GC–MS (EI): m/z = 185 [M]$^+$.

Supporting Information (see also the footnote on the first page of this article): Experimental procedures, characterization data, and copies of the original ^{1}H NMR and ^{13}C NMR spectra for all compounds.

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