CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201003711

General Copper-Catalyzed Transformations of Functional Groups from Arylboronic Acids in Water

Haijun Yang, Yong Li, Min Jiang, Junmei Wang, and Hua Fu*[a]

Abstract: A simple and general copper-catalyzed method has been developed for transformations of various functional groups (−I, $-N_3$, $-SO_2R$, −OH, $-NH_2$, and $-NO_2$) on aromatic rings from arylboronic acids in water under air. The protocol uses cheap and readily available inorganic salts (KI, NaN_3, $NaSO_2R$, NaOH, $NaNO_2$) and aqueous ammonia as the functional-group sources, simple Cu_2O/NH_3 as the catalyst system, environmentally friendly water as the solvent, and oxygen in air as the oxidant. Importantly, the copper catalyst system in water was recyclable. This study should provide a useful strategy for interconversions of the functional groups on aromatic rings.

Keywords: boron · catalysis · copper · functional-group transformations · water chemistry

Introduction

Aromatic compounds are ubiquitous in the world[1] and their properties are highly dependent on the functional groups of their aromatic rings. For example, aryl halides,[2] azides,[3] sulfones,[4] phenols,[5] arylamines,[6] and nitroarenes[7] are widely used as chemicals, synthetic intermediates, pharmaceuticals, natural products, and materials. Therefore, the functional-group transformation is an important and long-term direction in chemistry. In the past several decades, transition-metal-catalyzed transformations of aromatic halides and tosylates have been powerful methods in the synthesis of, for example, palladium or copper-catalyzed aryl iodides,[8] azides,[9] sulfones,[10] phenols,[11] arylamines,[12] and nitroarenes.[13] However, some shortcomings appear with them, such as the use of expensive, toxic catalysts and ligands for palladium catalysis or harsh reaction conditions, and limited substrate scope for copper catalysis. Aryl boron compounds are common chemicals and they are easily prepared from readily available aryl halides (such as aryl bromides and chlorides) and tosylates[14] or by iridium-catalyzed direct borylations of arenes through C−H bond activation.[15] The aryl boron compounds have been used as the starting materials to make aromatic compounds containing various functional groups (including aryl halides,[16] aryl azides,[17] aryl sulfones,[18] phenols,[19] arylamines developed by us[20] and nitroarenes[21]) through an aerobic oxidative strategy.[22] Unfortunately, the methods need the special ligands of catalysts, organic solvents, and specific temperatures, and the limited substrate scope and unrecyclable catalyst systems greatly limit use of these methods. In modern organic synthesis, the ideal reaction conditions include the use of cheap, highly efficient and recyclable catalyst systems, environment friendly water as the solvent, room temperature reactions under air (without extrusion of air) and easy workup procedures after reactions. Herein, we report general transformations of functional groups (−I, $-N_3$, $-SO_2R$, −OH, $-NH_2$, and $-NO_2$) on aromatic rings from arylboronic acids under the ideal conditions above.

[a] H. Yang, Prof. Dr. Y. Li, M. Jiang, J. Wang, Prof. Dr. H. Fu
Key Laboratory of Bioorganic Phosphorus Chemistry
and Chemical Biology (Ministry of Education)
Department of Chemistry, Tsinghua University
Beijing 100084 (P.R. China)
Fax: (+86) 10-62781695
E-mail: fuhua@mail.tsinghua.edu.cn

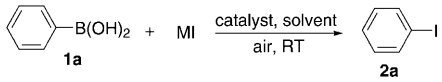
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201003711.

Results and Discussion

It is well known that aryl iodides usually show much higher reactivity than the corresponding aryl bromides and chlorides in the coupling reactions, and some aryl iodides, such as ^{125}I-radiolabeled arenes, show many important applications in pharmacology, medicine, and biochemistry.[23] Unfortunately, direct iodination of arenes with iodine is difficult because of the low reactivity of iodine towards the electrophilic substitution.[24] Therefore, it is very desirable to develop a highly efficient approach to aryl iodides. Considering the ready availability and low toxicity of copper catalysts, we first investigated copper-catalyzed iodination of arylboronic acids in water.

As shown in Table 1, phenylboronic acid (**1a**) was chosen as the model substrate at room temperature to optimize the reaction conditions including catalysts, ligands/additives, solvents, and temperature. CuI and Cu_2O (0.1 equiv relative to the amount of **1a**) were used as the catalysts in water in the presence of five equivalents of KI (Table 1, entries 1 and 2), and only a trace amount of iodobenzene was detected. Various copper/ammonia catalyst systems (0.1 equiv) were screened (preparation of copper/ammonia catalyst systems: a mixture of copper salt (0.1 equiv) and aqueous ammonia

Table 1. Copper-catalyzed iodination of phenylboronic acid to iodobenzene: optimization of conditions.[a]



1a 2a

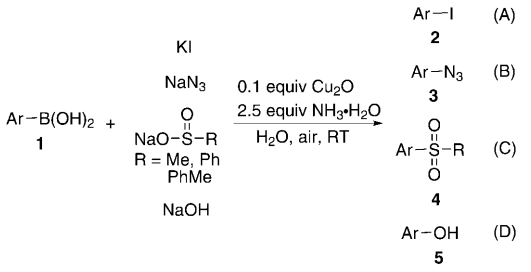
Entry	Cat.	$NH_3{\cdot}H_2O$ [mmol]	Solvent	MI [mmol]	Yield [%][b]
1	CuI	–	H_2O	KI (5)	trace[c]
2	Cu_2O	–	H_2O	KI (5)	trace[c]
3	CuI	2.5	H_2O	KI (5)	80
4	Cu_2O	2.5	H_2O	KI (5)	92
5	CuO	2.5	H_2O	KI (5)	76
6	$Cu(OAc)_2$	2.5	H_2O	KI (5)	70
7	$CuSO_4$	2.5	H_2O	KI (5)	12
8	Cu_2O	1	H_2O	KI (5)	70
9	Cu_2O	2	H_2O	KI (5)	81
10	Cu_2O	2.5	MeOH	KI (5)	72
11	Cu_2O	2.5	CH_3CN	KI (5)	66
12	Cu_2O	2.5	DMF	KI (5)	trace
13	Cu_2O	2.5	H_2O	NaI (5)	89
14	Cu_2O	2.5	H_2O	KI (2)	58
15	Cu_2O	2.5	H_2O	KI (5)	57[d]
16	Cu_2O	2.5	H_2O	KI (5)	trace[e]

[a] Reaction conditions: phenylboronic acid (1 mmol), catalyst (0.1 mmol), solvent (2 mL) under air; reaction time: 24 h; reaction temperature: ~25 °C. [b] Yield determined by ^{1}H NMR spectroscopy. [c] No addition of $NH_3{\cdot}H_2O$. [d] Reaction temperature: 40 °C. [e] Under a nitrogen atmosphere.

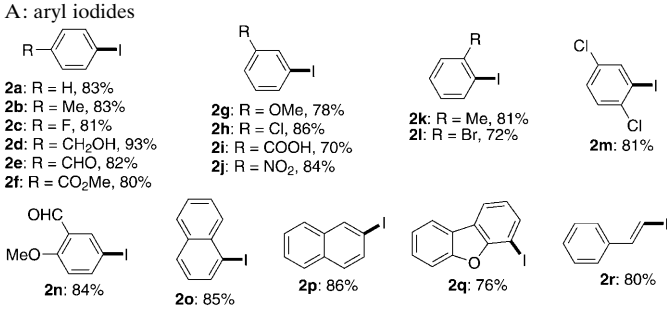
(2.5 equiv) was stirred for 30 min under air; entries 3–7) and the Cu_2O/NH_3 catalyst system showed the best activity (92% conversion yield; entry 4). To our satisfaction, only trace amounts of aniline were observed in the resulting solution, and a possible reason for this is that more of the I^- ion and the higher nucleophilic power of the I^- ion relative to ammonia led to the formation of the major product (iodobenzene). Here, ammonia could act as the ligand of the copper catalyst and additive. Reaction yields decreased when the amount of aqueous ammonia was reduced (entries 8 and 9). The effect of solvents was investigated (compare entries 4, 10–12) and water was the best solvent (entry 4). The result can be attributed to the good dissolving power of the substrates (phenylboronic acid and KI) and copper catalyst system (Cu_2O/NH_3) in water. A slightly lower yield (89%) was provided when NaI replaced KI as the iodic source (entry 13). The yield decreased when the amount of KI was reduced (entry 14). The reaction provided only a 57% yield with more phenol appearing when the temperature was raised to 40 °C (entry 15). Only a trace amount of iodobenzene was found in the absence of air (under nitrogen atmosphere; entry 16) and the result indicated that an oxidative process was involved in the formation of iodobenzene.[22] Therefore, the optimal reaction conditions for the synthesis of aryl iodides are as follows: KI as the iodic source (5 equiv), Cu_2O/NH_3 complex as the catalyst system (0.1 equiv), water as the solvent, and the reaction was carried out under air at room temperature (~25 °C).

We investigated the scope of the copper-catalyzed iodination of arylboronic acids. As shown in Table 2A, the substrates examined provided good to excellent yields. Elec-

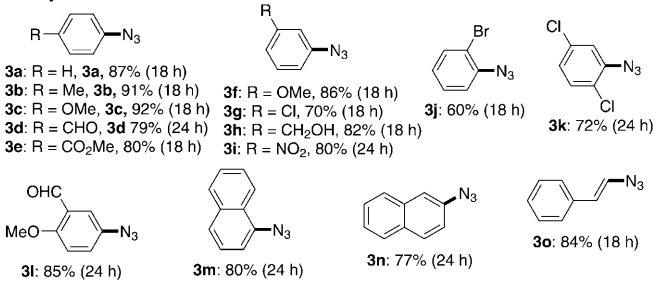
Table 2. Copper-catalyzed synthesis of aryl iodides, azides, sulfones, and phenols.[a]



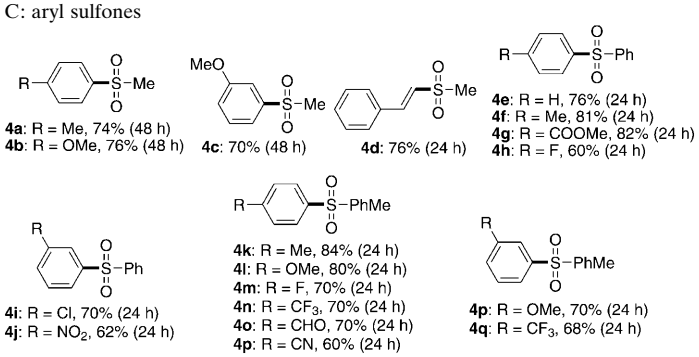
A: aryl iodides



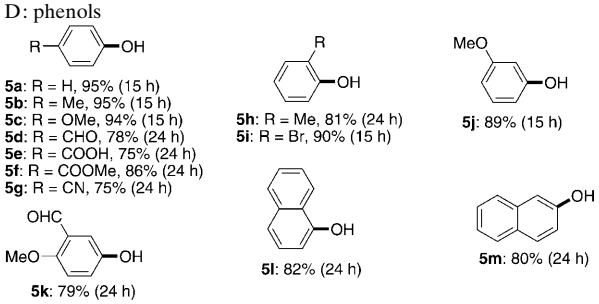
B: aryl azides



C: aryl sulfones



D: phenols



[a] Reaction conditions: reaction temperature: ~25 °C; reaction time: 24 h (for the synthesis of aryl iodides), $ArB(OH)_2$ (1 mmol), KI (5 mmol), NaN_3 (5 mmol), RSO_2Na (5 mmol), NaOH (3 mmol), Cu_2O (0.1 mmol), $NH_3{\cdot}H_2O$ (2.5 mmol), water (2 mL) under air. Yields shown are the yields of the isolated product.

tronic variation in the arylboronic acids, including electron-withdrawing, neutral, and electron-donating effects, did not obviously affect the efficiency of the reactions. Iodination of (*E*)-styrylboronic acid was also investigated and the corresponding target product, (*E*)-1-(2-iodovinyl)benzene (**2r**), was obtained in 80% yield under the standard conditions. Therefore, the present method is suitable for the synthesis of alkenyl iodides.

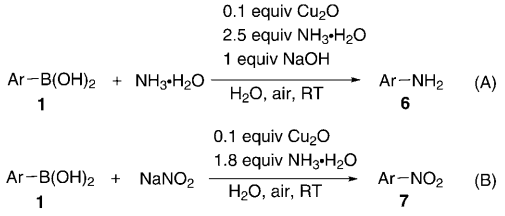
Inspired by the excellent results from iodination of arylboronic acids above, we used the same copper catalyst system (Cu_2O/NH_3) to make aryl azides, sulfones, and phenols (see Table 2B–D). Fortunately, the copper-catalyst system worked well when using NaN_3, $NaSO_2R$ (R = Me, Ph, PhMe), and NaOH as the functional-group sources. The tested substrates also provided good to excellent yields and the arylboronic acids containing electron-donating groups showed higher reactivity than the ones containing electron-withdrawing groups. Similarly, the copper catalyst system (Cu_2O/NH_3) was also suitable for azidonation and sulfonylation of (*E*)-styrylboronic acid (see **3o** and **4d** in Table 2B,C).

We further performed amination and *ipso*-nitration of arylboronic acids under similar copper catalytic conditions as shown in Table 3. For the amination of arylboronic acids, nine equivalents of $NH_3{\cdot}H_2O$ were added to the solution, in which ammonia acted as ligand/additive and substrate. The experiment showed that addition of an extra strong base (such as 1 equiv of NaOH) was necessary because nucleophilic attack of ammonia was helpful in base medium during the coupling reactions. Compared with the synthesis of phenols, more $NH_3{\cdot}H_2O$ and less NaOH were required for the amination of arylboronic acids. The tested substrates provided the corresponding arylamines in good to excellent yields (see Table 3A). We used the catalyst system (0.1 equiv Cu_2O/2.5 equiv $NH_3{\cdot}H_2O$) to perform *ipso*-nitration of phenylboronic acid with $NaNO_2$, and the reaction provided nitrobenzene in only 36% yield. We made a slight change for the copper catalyst system, the experiments showed that Cu_2O (0.1 equiv)/$NH_3{\cdot}H_2O$ (1.8 equiv; relative to the amount of arylboronic acids) was a better ratio, and the catalyst system did not need a previous 30 min stirring. As shown in Table 3B, the aerobic oxidative couplings of arylboronic acids with $NaNO_2$ provided the corresponding nitroarenes in moderate to good yields. Arylboronic acids containing electron-donating groups were of higher reactivity than ones containing electron-withdrawing groups during the amination and *ipso*-nitration of arylboronic acids above.

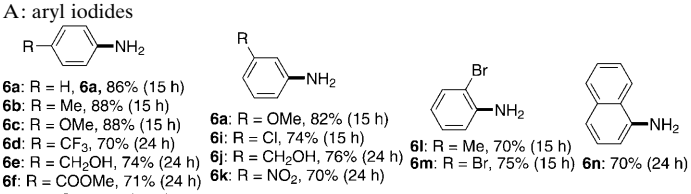
The transformations of functional groups above all showed excellent tolerance of functional groups including carbon–halo bonds, ether, nitro, hydroxyl, amino, aldehyde, nitrile, amine, and carboxyl. In addition, the workup procedure was very simple, most of the target products were purified by extraction from the aqueous solutions with ethyl acetate and the others were obtained by column chromatography on silica gel. Therefore, the general and easy workup method showed many advantages over the previous methods.

Importantly, the copper catalyst system in water is recyclable for the transforms of functional groups from arylboronic acids. As shown in Table 4, phenylboronic acid was chosen as the model substrate to investigate reuse of the copper catalyst system. For example, the resulting solution was extracted with ethyl acetate (3×2 mL) after the first iodination of phenylboronic acid completed and the remaining catalyst system in water could be reused in the following iodination of phenylboronic acid. The yields from the second to fourth cycle were 74, 72, and 72%, respectively. The other functionalizations of arylboronic acids also provided good recyclable results as shown in Table 4.

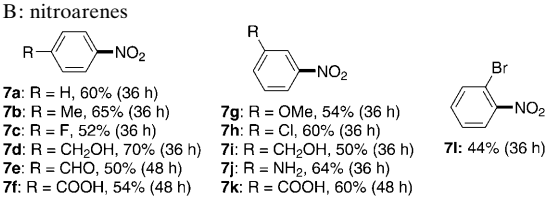
Table 3. Copper-catalyzed synthesis of arylamines and nitroarenes.[a]



A: aryl iodides

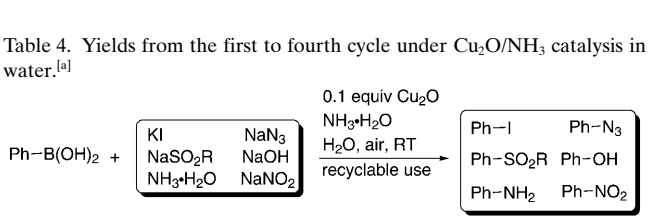


B: nitroarenes



[a] Reaction conditions: reaction temperature: ~25 °C, $ArB(OH)_2$ (1 mmol), $NaNO_2$ (7 mmol), Cu_2O (0.1 mmol), $NH_3{\cdot}H_2O$ (9.0 mmol for the synthesis of arylamines, 1.8 mmol for the synthesis of nitroarenes), and water (2 mL) under air.

Table 4. Yields from the first to fourth cycle under Cu_2O/NH_3 catalysis in water.[a]



Functional group	First [%]	Secondary [%]	Third [%]	Fourth [%]
–I	82	74	72	72
$-N_3$	87	78	76	74
$-SO_2R$	84	76	72	70
–OH	92	85	82	82
$-NH_2$	90	82	78	76
$-NO_2$	68	55	54	51

[a] Isolated product yield.

Conclusion

We have developed a simple, general and efficient copper-catalyzed method for the synthesis of aryl iodides, aryl azides, aryl sulfones, phenols, arylamines, and nitroarenes from arylboronic acids. The protocol uses very cheap Cu_2O/NH_3 as the catalyst system, environmentally friendly water as the solvent, oxygen in air as the oxidant, and the readily available and cheap reagents (KI, NaN_3, $NaSO_2R$, NaOH, $NH_3{\cdot}H_2O$, and $NaNO_2$) as the sources of the functional groups, and the functionalizations of arylboronic acids were performed well at room temperature. The target products were easily extracted with ethyl acetate from aqueous solution and the remaining catalyst system in water could be recovered and reused. The method is of excellent tolerance towards various functional groups in the substrates. To the best of our knowledge, no general method exists for the assembly of functional groups on aromatic rings thus far, so the simple, general, environmentally friendly, and easy workup approach will attract much attention in academic and industrial fields.

Experimental Section

General methods: All reagents and solvents were obtained from commercial suppliers and used without further purification. Cu_2O was commercially available from the Shanghai Qingong Wujiyan Company, and other chemicals were purchased from Beijing Ouhe Technology Company and Alfa Aesar Company. All reagents were weighed and handled in air at room temperature. ^1H and ^{13}C NMR spectra were recorded by using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard (^1H NMR: TMS at $\delta = 0.00$ ppm, $CDCl_3$ at $\delta = 7.26$ ppm; ^{13}C NMR: $CDCl_3$ at $\delta = 77.0$ ppm) or were recorded by using tetramethylsilane (TMS) in the solvent of [D_6]DMSO as the internal standard (^1H NMR: TMS at $\delta = 0.00$ ppm, DMSO at $\delta = 2.50$ ppm; ^{13}C NMR: DMSO at $\delta =$ 39.0 ppm).

General procedure for the synthesis of aryl iodides (2): A round-bottom flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3), and water (0.5 mL), and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), KI (5 mmol, 830 mg), and water (1.5 mL) were added to the flask. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for about 24 h under air at room temperature. Aqueous NaOH (2 N, 1.5 mL) was added to the resulting solution (no addition of NaOH for compound **2i**) and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the pure desired product (**2**; except for compounds **2b** and **2i**). An extra purification by column chromatography on silica gel was required for compounds **2b** and **2i**.

General procedure for the synthesis of azides (3): A round-bottomed flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3), and water (0.5 mL) and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), NaN_3 (5 mmol, 325 mg), and water (1.5 mL) were added to the flask. The flask was not sealed in order that air could enter the flask and the mixture was allowed to stir for the shown time in Table 2B under air at room temperature. After completion of the reaction (the reaction progress was monitored by ^1H NMR spectroscopy), aqueous NaOH (2 N, 1.5 mL) was added to the resulting solution and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the pure desired product (**3**).

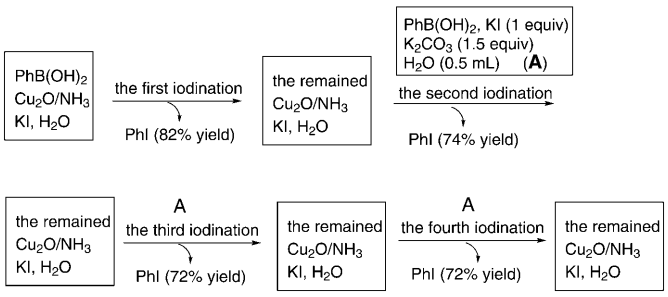
General procedure for the synthesis of sulfones (4): A round-bottomed flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3), and water (0.5 mL) and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), RSO_2Na (5 mmol, 510 mg for R = CH_3; 820 mg for R = Ph; 890 mg for R = $PhCH_3$) and water (1.5 mL) were added to the flask. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for the shown time in Table 2C under air at room temperature. After completion of the reaction (the reaction progress was monitored by ^1H NMR spectrsocopy), aqueous NaOH (2 N, 1.5 mL) was added to the resulting solution, and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the pure desired product (**4**; except for compounds **4a–c**, **4g**, and **4m–r**). An extra purification by column chromatography on silica gel was required for compounds **4a–c**, **4g**, and **4m–r**.

General procedure for the synthesis of phenols (5): A round-bottomed flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3), and water (0.5 mL), and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), NaOH (3 mmol, 120 mg), and water (1.5 mL) were added to the flask. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for the shown time in Table 2D under air at room temperature. After completion of the reaction (the reaction progress was monitored by ^1H NMR spectroscopy), HCl (1 N, 2 mL) was added to acidify the solution (pH 2–3), and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered, and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the pure desired product (**5**).

General procedure for the synthesis of arylamines (6): A round-bottom flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.19 mL, 2.5 mmol of NH_3), and water (0.5 mL), and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), aqueous ammonia (6.5 mmol, 0.5 mL), and water (1.0 mL) were added to the flask. The flask was not sealed in order that air could enter the flask and the mixture was allowed to stir for the shown time in Table 3A under air at room temperature. After completion of the reaction (the reaction progress was monitored by ^1H NMR spectroscopy), aqueous NaOH (2 N, 1.5 mL) was added to the resulting solution, and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the pure desired product (**6**).

General procedure for the synthesis of nitroarenes (7): A round-bottomed flask was charged with a magnetic stirrer, Cu_2O (0.1 mmol, 14.3 mg), 25% aqueous ammonia (0.14 mL, 1.8 mmol of NH_3), and water (0.5 mL), and the mixed solution was stirred for 30 min under air at room temperature (~25 °C). Arylboronic acid (1 mmol), $NaNO_2$ (7 mmol, 483 mg), and water (1.5 mL) were added to the flask. The flask was not sealed in order that air could enter the flask, and the mixture was allowed to stir for the shown time in Table 3B under air at room temperature. After completion of the reaction (the reaction progress was monitored by ^1H NMR spectroscopy) the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered, the solvent of the filtrate was removed with the aid of a rotary evaporator, and the residue was purified by column chromatography on silica gel to provide the desired product (**7**).

Reuse of the copper/ammonia catalyst system (Cu_2O/NH_3): Here, iodination of phenylboronic acid was chosen as a model example (see Scheme 1). The resulting solution was extracted with ethyl acetate (3× 2 mL) after the first iodination of phenylboronic acid under the standard conditions and the copper/ammonia catalyst system in the remaining

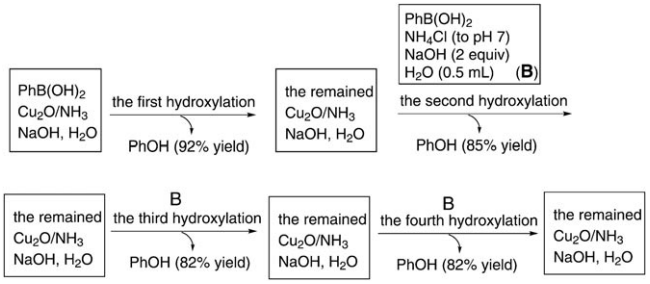


Scheme 1. Reuse of the copper/ammonia catalyst system for the iodination of phenylboronic acid.

aqueous phase was reused in the following iodination of phenylboronic acid. The organic phase was washed with aqueous NaOH (2 N, 3× 1.5 mL), dried over anhydrous $MgSO_4$, and concentrated to give iodobenzene in 82% yield (the first time). Then, phenylboronic acid (1 mmol), KI (1 mmol), K_2CO_3 (1.5 mmol), and water (0.5 mL) were added to the remaining aqueous phase with the copper/ammonia catalyst system above (the addition of K_2CO_3 aimed at neutralizing the released boronic acid from the first time). The second iodination was performed under the same conditions and the target product was provided in 74% yield after a similar workup procedure to the first cycle. Further, the third and fourth cycles afforded 1-iodobenzene in the same yield (72%).

The recyclable experimental procedures for the azidonation, sulfonylation, amination, and *ipso*-nitration of phenylboronic acid were similar to ones for iodination of phenylboronic acid.

For hydroxylation of phenylboronic acid, the experimental details were slightly different to the procedures above (see Scheme 2). After completion of the first coupling reaction, HCl (1 N, 2 mL) was added to acidify



Scheme 2. Reuse of the copper/ammonia catalyst system for the hydroxylation of phenylboronic acid.

the solution (pH 2–3), and the target product was extracted with ethyl acetate (3×2 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and filtered and the solvent of the filtrate was removed with the aid of a rotary evaporator to provide the phenol in 92% yield (the first time). NH_4Cl was added to the remaining aqueous solution till pH 7 and then phenylboronic acid (1 mmol), NaOH (2 mmol), and water (0.5 mL) were added to the solution. The second hydroxylation was performed under the same conditions and the target product was provided in 85% yield after a similar workup procedure to the first cycle. Further, the third and fourth cycles provided the phenol in the same yield (82%).

Iodobenzene (2a):[25] Colorless oil; yield: 83% (169 mg); ^{1}H NMR ($CDCl_3$, 600 MHz) δ=7.69 (d, 2H, J=7.6 Hz), 7.32 (t, 1H, J=7.6 Hz), 7.09 ppm (t, 2H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.4, 130.2, 127.4, 94.4 ppm; EIMS: m/z: 204.0 $[M]^+$.

4-Iodotoluene (2b):[26] Eluent: ethyl acetate/*n*-pentane (1:7); yellow solid; yield: 83% (181 mg); m.p. 34–35 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.55 (d, 2H, J=4.1 Hz), 6.91 (d, 2H, J=4.1 Hz), 2.27 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.5, 137.2, 131.2, 90.2 ppm; EIMS: m/z: 218.0 $[M]^+$.

4-Fluoroiodobenzene (2c):[25] Colorless oil; yield: 81% (180 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.63 (m, 2H), 6.83 ppm (t, 2H, J=8.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=162.7 (d, J=247.1 Hz), 138.9 (d, J=7.2 Hz), 117.8 (d, J=21.7 Hz), 86.9 ppm (d, J=2.9 Hz); EIMS: m/z: 222.0 $[M]^+$.

4-Iodobenzyl alcohol (2d):[27] White solid; yield: 93% (218 mg); m.p. 71–73 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.68 (d, 2H, J=8.3 Hz), 7.11 (d, 2H, J=8.3 Hz), 4.69 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=140.5, 137.7, 129.0, 128.9, 93.1, 64.8 ppm; EIMS: m/z: 234.0 $[M]^+$.

4-Iodobenzaldehyde (2e):[27] Yellow solid; yield: 82% (190 mg); m.p. 77–78 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=9.96 (s, 1H), 7.92 (d, 2H, J=8.1 Hz), 7.59 ppm (d, 2H, 8.1 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=191.5, 138.5, 138.5, 135.6, 130.9, 130.9, 102.9 ppm; EIMS: m/z: 232.0 $[M]^+$.

Methyl 4-iodobenzoate (2f):[28] White solid; yield: 80% (210 mg); m.p. 119–120 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.80 (d, 2H, J=8.2 Hz), 7.74 (d, 2H, J=8.2 Hz), 3.91 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=166.7, 137.8, 131.1, 129.7, 100.8, 52.4 ppm; EIMS: m/z: 262.0 $[M]^+$.

4-Iodophenyl methyl ether (2g):[26] Yellow liquid; yield: 78% (183 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.27 (d, 1H, J=7.6 Hz), 7.24 (s, 1H), 6.98 (dd, 1H, J=7.6, 8.2 Hz), 6.85 (d, 1H, J=7.6, 8.2 Hz), 3.77 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=160.2, 130.9, 129.9, 123.1, 113.9, 94.5, 55.5 ppm; EIMS: m/z: 234.0 $[M]^+$.

1-Chloro-3-iodo-benzene (2h):[29] Colorless oil; yield: 86% (205 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.72 (s, 1H), 7.59 (d, 1H, J=8.3 Hz), 7.32 (d, 1H, J=8.3 Hz), 7.03 ppm (t, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.2, 135.76, 135.1, 131.1, 128.1, 94.2 ppm; EIMS: m/z: 237.9 $[M]^+$.

3-Iodobenzoic acid (2i):[30] Eluent: ethyl acetate/*n*-pentane 1:4; white solid; yield: 70% (174 mg); m.p. 186–189 °C; ^{1}H NMR ([D$_6$]DMSO, 600 MHz): δ=13.23 (s, 1H), 8.23 (s, 1H), 7.98 (d, 1H, J=8.3 Hz), 7.94 (d, 1H, J=7.6 Hz), 7.31 ppm (dd, 1H, J=7.6, 8.3 Hz); ^{13}C NMR ([D$_6$]DMSO, 150 MHz): δ=165.4, 140.8, 137.1, 132.3, 130.3, 128.0, 94.1 ppm; ESIMS: m/z: 249.0 $[M+H]^+$.

3-Iodonitrobenzene (2j):[29] Yellow solid; yield: 84% (209 mg); m.p. 35–37 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.56 (s, 1H), 8.21 (d, 1H, J=8.3 Hz), 8.03 (d, 1H, J=8.3 Hz), 7.30 ppm (t, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=148.6, 143.6, 132.51, 130.8, 122.8, 93.6 ppm; EIMS: m/z: 249.0 $[M]^+$.

2-Iodotoluene (2k):[26] Pale-yellow oil; yield: 81% (176 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.81 (d, 1H, J=7.6 Hz), 7.24 (d, 2H, J=4.1 Hz), 6.86 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.3, 138.9, 129.7, 128.1, 127.4, 101.1, 28.1 ppm; EIMS: m/z: 217.9 $[M]^+$.

1-Bromo-2-iodo-benzene (2l):[25] Red oil; yield: 72% (204 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.83 (d, 1H, J=7.6 Hz), 7.61 (d, 1H, J=7.6 Hz), 7.20 (t, 1H, J=7.6 Hz), 6.98 ppm (t, 1H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=140.4, 132.9, 129.8, 129.5, 128.5, 101.3 ppm; EIMS: m/z: 281.9, 283.9 $[M]^+$.

2,5-Dichloroiodobenzene (2m):[31] Brown oil; yield: 81% (220 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.84 (d, 1H, J=2.1 Hz), 7.35 (d, 1H, J=8.3 Hz), 7.26 ppm (dd, 1H, J=2.1, 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=139.5, 137.2, 132.9, 129.8, 129.6, 98.4 ppm; EIMS: m/z: 271.9 $[M]^+$.

5-Iodo-2-methoxybenzaldehyde (2n):[32] Yellow solid; yield: 84% (220 mg); m.p. 142–143 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=10.3 (s, 1H), 8.09 (d, 1H, J=2.0 Hz), 7.82 (dd, 1H, J=2.0, 8.9 Hz), 6.78 (d, 1H, J=8.9 Hz), 3.92 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=188.4, 166.5, 144.2, 137.1, 126.6, 114.2, 83.1, 56.0 ppm; EIMS: m/z: 262.0 $[M]^+$.

1-Iodonaphthalene (2o):[26] Dark-brown oil; yield: 85% (216 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.08 (d, 2H, J=8.3 Hz), 7.84 (d, 1H, 8.3 Hz), 7.77 (d, 1H, J=8.3 Hz), 7.58 (t, 1H, J=8.3 Hz), 7.52 (t, 1H, J=8.3 Hz), 7.18 ppm (t, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.5, 134.5, 134.2, 132.2, 129.1, 128.7, 127.8, 126.9, 126.8, 99.7 ppm; EIMS: m/z: 254.0 $[M]^+$.

2-Iodonaphthalene (2p):[30] White solid; yield: 86% (218 mg); m.p. 53–55°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.23 (s, 1H), 7.77 (dd, 1H, J=3.5, 6.2 Hz), 7.70 (m, 2H), 7.55 (d, 1H, J=8.9 Hz), 7.47 ppm (dd, 2H, J=3.5, 6.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=136.7, 135.1, 134.5, 132.2, 129.6, 127.9, 126.9, 126.6, 125.89, 91.5 ppm; EIMS: m/z: 254.0 $[M]^+$.

4-Iododibenzofuran (2q):[33] Purple solid; yield: 76% (223 mg); m.p. 47–49°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.91 (d, 1H, J=8.2 Hz), 7.89 (d, 1H, J=7.6 Hz), 7.80 (d, 1H, J=8.2 Hz), 7.65 (d, 1H, J=8.2 Hz), 7.48 (dd, 1H, J=8.2, 7.6 Hz), 7.36 (dd, 1H, J=8.2, 7.6 Hz), 7.09 ppm (dd, 1H, J=7.6 Hz, 8.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=156.4, 155.7, 135.9, 127.7, 124.6, 124.5, 124.4, 123.2, 121.1, 120.5, 112.1, 75.4 ppm; EIMS: m/z: 294.0 $[M]^+$.

(*E*)-(2-Iodovinyl)benzene (2r):[34] Colorless oil; yield: 80% (184 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.42 (d, 1H, J=15.1 Hz), 7.30 (m, 5H), 6.81 ppm (d, 1H, J=15.1 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=145.1, 137.8, 128.8, 128.5, 126.1, 76.7 ppm; EIMS: m/z: 229.9 $[M]^+$.

Azidobenzene (3a):[9] Yellow oil; yield: 87% (104 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.35 (t, 2H, J=7.6 Hz), 7.14 (t, 1H, J=7.6 Hz), 7.03 ppm (d, 2H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=140.0, 129.7, 124.9, 119.0 ppm; EIMS: m/z: 119.0 $[M]^+$.

1-Azido-4-methylbenzene (3b):[9] Brown oil; yield: 91% (121 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.14 (d, 2H, J=8.3 Hz), 6.92 (d, 2H, J=8.3 Hz), 2.32 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.1, 134.5, 130.2, 118.8, 20.7 ppm; EIMS: m/z: 133.0 $[M]^+$;

1-Azido-4-methoxybenzene (3c):[9] Black oil; yield: 92% (137 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=6.95 (d, 2H, J=8.9 Hz), 6.88 (d, 2H, J=8.9 Hz), 3.79 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=157.0, 132.4, 120.0, 115.1, 55.6 ppm; EIMS: m/z: 149.1 $[M]^+$.

4-Azidobenzaldehyde (3d):[35] Yellow oil; yield: 79% (116 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=9.95 (s, 1H), 7.89 (d, 2H, J=8.3 Hz), 7.16 ppm (d, 2H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=190.6, 146.3, 133.2, 131.5, 119.5 ppm; EIMS: m/z: 147.0 $[M]^+$.

Methyl 4-azidobenzoate (3e):[9] Yellow oil; yield: 89% (157 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.02 (d, 2H, J=8.3 Hz), 7.05 (d, 2H, J=8.3 Hz), 3.90 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=166.2, 144.7, 131.3, 126.6, 118.7, 52.0 ppm; EIMS: m/z: 177.1 $[M]^+$.

1-Azido-3-methoxybenzene (3f):[9] Black oil; yield: 86% (128 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.25 (t, 1H, J=8.3 Hz), 6.69 (d, 1H, J=8.3 Hz), 6.64 (d, 1H, J=8.3 Hz), 6.55 (s, 1H), 3.80 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=160.8, 141.3, 130.4, 111.3, 110.7, 104.9, 55.4 ppm; EIMS: m/z: 149.0 $[M]^+$.

1-Azido-3-chlorobenzene (3g):[9] Brown oil; yield: 70% (107 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.25 (dd, 1H, J=7.6, 8.3 Hz), 7.10 (d, 1H, J=7.6 Hz), 7.00 (s, 1H), 6.90 ppm (d, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.4, 135.4, 130.6, 125.0, 119.3, 117.2 ppm; EIMS: m/z: 153.0 $[M]^+$.

1-Azido-3-benzyl alcohol (3h):[36] Brown oil; yield: 82% (122 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.33 (dd, 1H, J=8.3, 7.6 Hz), 7.11 (d, 1H, J=7.6 Hz), 7.04 (s, 1H), 6.94 (d, 1H, J=8.3 Hz), 4.67 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=142.9, 140.3, 129.9, 123.2, 118.2, 117.3, 64.7 ppm; EIMS: m/z: 149.1 $[M]^+$.

1-Azido-3-nitrobenzene (3i):[9] Yellow oil; yield: 80% (131 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.00 (d, 1H, J=8.3 Hz), 7.89 (s, 1H), 7.54 (t, 1H, J=8.3 Hz), 7.34 ppm (d, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=149.2, 141.9, 130.5, 124.8, 119.6, 114.0 ppm; EIMS: m/z: 164.0 $[M]^+$.

1-Azido-2-bromobenzene (3j):[37] Brown oil; yield: 60% (118 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.55 (d, 1H, J=8.2 Hz), 7.34 (t, 1H, J=7.6 Hz), 7.17 (d, 1H, J=8.2 Hz), 7.00 ppm (t, 1H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=138.6, 133.8, 128.5, 125.9, 119.4, 113.8 ppm; EIMS: m/z: 196.9, 198.9 $[M]^+$.

2-Azido-1,4-dichlorobenzene (3k):[35] Yellow oil; yield: 72% (135 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.29 (d, 1H, J=8.6 Hz), 7.15 (d, 1H, J=2.4 Hz), 7.05 ppm (dd, 1H, J=8.6, 2.4 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=138.4, 133.4, 131.5, 125.7, 123.4, 119.8 ppm; EIMS: m/z 187.0, 189.0, 191.0 $[M]^+$.

5-Azido-2-methoxybenzaldehyde (3l): Brown solid; yield: 85% (150 mg); m.p. 86–88°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ=10.44 (s, 1H), 7.53 (s, 1H), 7.18 (d, 1H, J=8.9 Hz), 6.99 (d, 1H, J=8.9 Hz), 3.93 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=188.7, 159.1, 133.2, 126.4, 125.5, 118.0, 113.3, 56.1 ppm; EIMS: m/z: 177.1 $[M]^+$.

1-Azidonaphthalene (3m):[17b] Black oil; yield: 80% (135 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.02 (d, 1H, J=7.6 Hz), 7.74 (d, 1H, J=7.6 Hz), 7.55 (d, 1H, J=8.3 Hz), 7.43 (m, 2H), 7.38 (t, 1H, J=7.6 Hz), 7.18 ppm (d, 1H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=136.5, 134.3, 127.7, 126.8, 126.1, 125.6, 124.7, 122.5, 113.9 ppm; EIMS: m/z: 168.9 $[M]^+$.

2-Azidonaphthalene (3n):[38] Black oil; yield: 77% (130 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.83 (d, 1H, J=8.3 Hz), 7.81 (d, 1H, J=8.3 Hz), 7.76 (d, 1H, J=8.3 Hz), 7.49 (t, 1H, J=8.3 Hz), 7.45 (s, 1H), 7.43 (t, 1H, J=7.6 Hz), 7.16 ppm (d, 1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=137.5, 134.0, 131.0, 129.9, 127.8, 127.0, 125.4, 118.7, 115.8 ppm; EIMS: m/z: 169.1 $[M]^+$.

(*E*)-(2-Azidovinyl)benzene (3o):[9] Black oil; yield: 84% (122 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.31–7.17 (m, 5H), 6.57 (d, 1H, J=13.8 Hz), 6.25 ppm (d, 1H, J=13.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=135.0, 128.7, 127.3, 126.6, 125.8, 119.7 ppm; EIMS: m/z: 145.0 $[M]^+$.

1-Methyl-4-(methylsulfonyl)benzene (4a):[39] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 84–86°C; yield: 74% (126 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.83 (d, 2H, J=8.3 Hz), 7.37 (d, 2H, J=8.3 Hz), 3.04 (s, 3H), 2.46 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=144.6, 137.7, 129.9, 127.3, 44.6, 21.6 ppm; EIMS: m/z: 170.1 $[M]^+$.

1-Methoxy-4-(methylsulfonyl)benzene (4b):[18] Eluent: ethyl acetate/petroleum ether (1:10); brown solid; m.p. 110–113°C; yield: 76% (139 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.88 (d, 2H, J=8.9 Hz), 7.03 (d, 2H, J=8.9 Hz), 3.89 (s, 3H), 3.03 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=163.7, 132.3, 129.5, 114.5, 55.7, 44.8 ppm; EIMS: m/z: 186.0.

1-Methoxy-3-(methylsulfonyl)benzene (4c):[40] Eluent: ethyl acetate/petroleum ether (1:10); black oil; yield: 70% (130 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.53 (d, 1H, J=7.6 Hz), 7.48 (t, 1H, J=7.6 Hz), 7.44 (s, 1H), 7.17 (d, 1H, J=7.6 Hz), 3.88 (s, 3H), 3.06 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=160.1, 141.7, 130.5, 120.1, 119.4, 111.8, 55.7, 44.4 ppm; EIMS: m/z: 186.1 $[M]^+$.

(*E*)-[2-(Methylsulfonyl)vinyl]benzene (4d):[18] Black solid; m.p. 75–77°C; yield: 76% (176 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.63 (d, 1H, J=15.8 Hz), 7.52 (d, 2H, J=6.2 Hz), 7.44 (m, 3H), 6.92 (d, 1H, J=15.8 Hz), 3.04 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=144.0, 131.4, 129.2, 128.6, 126.2, 43.3 ppm; EIMS: m/z: 182.0 $[M]^+$.

Sulfonyldibenzene (4e):[41] White solid; m.p. 125–126°C; yield: 76% (166 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.95 (d, 4H, J=7.6 Hz), 7.56 (t, 2H, J=7.6 Hz), 7.50 ppm (t, 4H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=141.7, 133.3, 129.4, 127.8 ppm; EIMS: m/z: 218.0 $[M]^+$.

1-Methyl-4-(phenylsulfonyl)benzene (4f):[41] White solid; m.p. 126–127°C; yield: 81% (188 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.93 (d, 2H, J=8.2 Hz), 7.82 (d, 2H, J=8.2 Hz), 7.53 (t, 1H, J=7.6 Hz), 7.49 (t, 2H, J=7.6 Hz), 7.29 (d, 2H, J=8.2 Hz), 2.39 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=144.1, 142.0, 138.6, 132.9, 129.9, 129.2, 127.7, 127.5, 21.5 ppm; EIMS: m/z: 232.0 $[M]^+$.

Methyl 4-(phenylsulfonyl)benzoate (4g):[41] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 142–145°C; yield: 82% (226 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.15 (d, 2H, J=7.6 Hz), 8.01 (d, 2H, J=7.6 Hz), 7.95 (d, 2H, J=7.6 Hz), 7.60 (d, 1H, J=6.9 Hz), 7.53 (m, 2H), 3.94 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=165.5, 145.5, 140.8, 134.3, 133.6, 130.4, 129.4, 127.9, 127.7, 52.7 ppm; EIMS: m/z: 276.0 $[M]^+$.

1-Fluoro-4-(phenylsulfonyl)benzene (4h):[39] White solid; m.p. 105–107°C; yield: 60% (142 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.95 (m, 4H), 7.58 (t, 1H, J=7.6 Hz), 7.51 (t, 2H, J=7.6 Hz), 7.18 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=165.4 (d, J=258.6 Hz), 141.5, 137.7, 133.3, 130.5 (d, J=10.1 Hz), 129.4, 127.6, 116.6 ppm (d, J=23.1 Hz); EIMS: m/z 236.0 $[M]^+$.

1-Chloro-3-(phenylsulfonyl)benzene (4i): Yellow solid; m.p. 100–101°C; yield: 70% (176 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.94 (m, 3H), 7.83 (d, 1H, J=7.6 Hz), 7.60 (t, 1H, J=7.6 Hz), 7.53 (m, 3H), 7.45 ppm (t,

1H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=143.4, 140.9, 135.5, 133.6, 133.3, 130.6, 129.4, 127.4, 127.8, 127.7, 125.8 ppm; EIMS: m/z: 252.0 $[M]^+$.

1-Nitro-3-(phenylsulfonyl)benzene (4j): Yellow solid; m.p. 77–78 °C; yield: 62 % (163 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.77 (s, 1H), 8.42 (d, 1H, J=8.2 Hz), 8.27 (d, 1H, J=7.6 Hz), 7.99 (d, 2H, J=8.2 Hz), 7.74 (t, 1H, J=8.2 Hz), 7.63 (t, 1H, J=7.6 Hz), 7.57 ppm (t, 2H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=148.4, 144.0, 140.1, 134.1, 133.1, 130.7, 129.7, 128.0, 127.7, 122.9 ppm; EIMS: m/z: 263.0 $[M]^+$.

4,4′-Sulfonylbis(methylbenzene) (4k):[41] White solid; m.p. 158–160 °C; yield: 84 % (207 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=7.79 (d, 4H, J=7.9 Hz), 7.25 (d, 4H, J=7.9 Hz), 2.36 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=143.9, 139.0, 129.8, 127.5, 21.4 ppm; EIMS: m/z: 246.1 $[M]^+$.

1-Methoxy-4-tosylbenzene (4l):[41] Yellow solid; m.p. 100–102 °C; yield: 80 % (209 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.85 (d, 2H, J=7.6 Hz), 7.79 (d, 2H, J=8.2 Hz), 7.26 (d, 2H, J=7.6 Hz), 6.94 (d, 2H, J=8.2 Hz), 3.82 (s, 3H), 2.37 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=163.2, 143.7, 139.3, 133.4, 129.8, 129.6, 127.3, 114.4, 55.6, 21.4 ppm; EIMS: m/z: 262.0 $[M]^+$.

1-Fluoro-4-tosylbenzene (4m):[10] Eluent: ethyl acetate/petroleum ether (1:20); brown solid; m.p. 83–85 °C; yield: 70 % (175 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.94 (m, 2H), 7.81 (d, 2H, J=8.3 Hz), 7.30 (d, 2H, J=7.6 Hz), 7.16 (dd, 2H, J=8.3, 8.9 Hz), 2.40 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=165.3 (d, J=249.3 Hz), 144.3, 138.5, 138.1, 130.3 (d, J=9.4 Hz), 130.2, 130.0, 127.6, 116.5 (d, J=22.4 Hz), 21.5 ppm: EIMS: m/z: 250.0 $[M]^+$.

1-Tosyl-4-(trifluoromethyl)benzene (4n):[39] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 105–107 °C; yield: 70 % (210 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.05 (d, 2H, J=8.2 Hz), 7.84 (d, 2H, J=8.2 Hz), 7.75 (d, 2H, J=8.2 Hz), 7.33 (d, 2H, J=8.2 Hz), 2.41 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=145.6, 144.9, 137.6, 134.6 (q, J=30.3 Hz), 130.2, 128.0, 127.9, 126.4 (q, J=2.9 Hz), 123.1 (q, J=273.1 Hz), 21.6 ppm; EIMS: m/z: 300.0 $[M]^+$.

4-Tosylbenzaldehyde (4o):[10] Eluent: ethyl acetate/petroleum ether (1:5); yellow solid; m.p. 142–144 °C; yield: 70 % (182 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=10.1 (s,1H), 8.09 (d, 2H, J=8.6 Hz), 7.98 (d, 2H, J=7.9 Hz), 7.85 (d, 2H, J=8.3 Hz), 7.33 (d, 2H, J=7.9 Hz), 2.41 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=190.7, 147.1, 144.9, 139.0, 137.5, 130.2, 130.1, 128.1, 128.0, 21.6 ppm; EIMS: m/z: 260.1 $[M]^+$.

4-Tosylbenzonitrile (4p):[10] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 129–131 °C; yield: 60 % (154 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ=8.03 (d, 2H, J=8.6 Hz), 7.83 (d, 2H, J=8.6 Hz), 7.78 (d, 2H, J=8.3 Hz), 7.34 (d, 2H, J=8.3 Hz), 2.42 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=146.2, 145.2, 137.1, 133.0, 130.3, 128.1, 128.0, 117.2, 116.7, 21.6 ppm; EIMS: m/z: 257.1 $[M]^+$.

1-Methoxy-3-tosylbenzene (4q):[10] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 65–67 °C; yield: 70 % (183 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.82 (d, 2H, J=8.2 Hz), 7.49 (d, 1H, J=7.6 Hz), 7.44 (s, 1H), 7.38 (t, 1H, J=7.6 Hz), 7.29 (d, 2H, J=8.2 Hz), 7.05 (dd, 1H, J=2.0, 8.2 Hz), 3.83 (s, 3H), 2.39 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ=160.0, 144.1, 143.1, 138.6, 130.3, 129.9, 127.7, 119.7, 119.3, 112.1, 55.6, 21.5 ppm; EIMS: m/z: 262.0 $[M]^+$.

1-Tosyl-3-(trifluoromethyl)benzene (4r):[10] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 81–83 °C; yield: 68 % (204 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.20 (s, 1H), 8.11 (d, 1H, J=7.6 Hz), 7.84 (d, 2H, J=8.2 Hz), 7.80 (d, 1H, J=8.2 Hz), 7.64 (t, 1H, J=7.6 Hz), 7.33 (d, 2H, J=7.6 Hz), 2.41 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=144.9, 143.4, 130.8, 130.2, 130.0, 129.8, 129.7, 127.9, 127.5, 124.5, 21.6 ppm; EIMS: m/z: 300.1 $[M]^+$.

Phenol (5a):[19,42] Colorless solid; m.p. 38–40 °C; yield: 95 % (89 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.24 (t, 2H, J=7.6 Hz), 6.93 (t, 1H, J=7.6 Hz), 6.83 ppm (d, 2H, J=7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=155.4, 129.7, 120.8, 115.3 ppm; EIMS: m/z: 94.1 $[M]^+$.

***p*-Cresol (5b)**:[43] Colorless solid; m.p. 33–34 °C; yield: 95 % (103 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.03 (d, 2H, J=8.3 Hz), 6.72 (d, 2H, J=8.3 Hz), 4.60 (s, 1H), 2.27 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=153.2, 130.1, 130.0, 115.0, 20.4 ppm; EIMS: m/z: 108.1 $[M]^+$.

4-Methoxyphenol (5c):[19] Colorless solid; m.p. 54–56 °C; yield: 94 % (117 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=6.77 (m, 4H), 4.82 (s, 1H), 3.75 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=153.7, 149.4, 116.0, 114.8, 55.8 ppm; EIMS: m/z: 124.1 $[M]^+$.

4-Hydroxybenzaldehyde (5d):[19] Red solid; m.p. 113–115 °C; yield: 78 % (95 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=9.88 (s, 1H), 7.81 (d, 2H, J=8.3 Hz), 6.95 (d, 2H, J=8.3 Hz), 5.41 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=191.4, 161.9, 132.6, 129.6, 116.0 ppm; ESIMS: m/z: 121.5 $[M-H]^-$.

4-Hydroxybenzoic acid (5e): White solid; m.p. 213–215 °C; yield: 75 % (104 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=10.2 (s, 1H), 7.78 (d, 2H, J=8.3 Hz), 6.82 ppm (d, 2H, J=8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=167.7, 162.1, 132.0, 121.9, 115.6 ppm; ESIMS: m/z: 137.3 $[M-H]^+$.

Methyl 4-hydroxybenzoate (5f): White solid; m.p. 123–125 °C; yield: 86 % (131 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.96 (d, 2H, J=8.3 Hz), 6.86 (d, 2H, J=8.3 Hz), 5.43 (s, 1H), 3.89 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=167.5, 160.3, 131.9, 122.2, 115.3, 52.1 ppm; ESIMS: m/z: 151.6 $[M-H]^+$.

4-Hydroxybenzonitrile (5g):[43] Yellow solid; m.p. 94–95 °C; yield: 75 % (79 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.55 (d, 2H, J=8.3 Hz), 6.94 (d, 2H, J=8.3 Hz), 6.72 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=160.2, 134.3, 119.2, 116.4, 102.9 ppm; EIMS: m/z: 119.1 $[M]^+$.

***o*-Cresol (5h)**:[42] Pink solid; m.p. 30–31 °C; yield: 81 % (88 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.11 (d, 1H, J=6.9 Hz), 7.07 (dd, 1H, J=8.3, 7.6 Hz), 6.84 (dd, 1H, J=7.6, 6.9 Hz), 6.75 (d, 1H, J=8.3 Hz), 4.97 (s, 1H), 2.24 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=153.7, 131.0, 127.1, 123.8, 120.7, 114.9, 15.7 ppm; EIMS: m/z: 108.1 $[M]^+$.

2-Bromophenol (5i): Colorless oil; yield: 90 % (156 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.45 (d, 1H, J=8.3 Hz), 7.21 (dd, 1H, J=7.6 Hz, 8.3 Hz), 7.02 (d, 1H, J=8.3 Hz), 6.80 (d, 1H, J=7.6 Hz), 5.52 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=152.2, 132.0, 129.1, 121.8, 116.1, 110.2 ppm; EIMS: m/z: 172.0, 174.0 $[M]^+$.

3-Methoxyphenol (5j):[19] Yellow oil; yield: 89 % (110 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.13 (t, 1H, J=8.3 Hz), 6.50 (dd, 1H, J=2.1, 8.3 Hz), 6.43 (m, 2H), 4.80 (s, 1H), 3.78 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=161.0, 156.7, 130.1, 107.7, 106.4, 101.5, 55.3 ppm; EIMS: m/z:124.0 $[M]^+$.

5-Hydroxy-2-methoxybenzaldehyde (5k): Yellow solid; m.p. 111–113 °C; yield: 79 % (120 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=10.4 (s, 1H), 7.36 (d, 1H, J=2.8 Hz), 7.12 (dd, 1H, J=2.8, 8.9 Hz), 6.91 (d, 1H, J=8.9 Hz), 5.73 (s, 1H), 3.88 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=190.1, 156.6, 149.8, 125.0, 123.6, 113.7, 113.4, 56.1 ppm; ESIMS: m/z: 151.5 $[M-H]^-$.

Naphthalen-1-ol (5l):[42] Colorless solid; m.p. 109–112 °C; yield: 82 % (118 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=8.17 (m, 1H), 7.81 (m, 1H), 7.48 (m, 2H), 7.44 (d, 1H, J=8.3 Hz), 7.29 (dd, 1H, J=7.6, 8.3 Hz), 6.80 (d, 1H, J=7.6 Hz), 5.26 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=151.3, 134.7, 127.6, 126.4, 125.8, 125.2, 124.3, 121.5, 120.7, 108.6 ppm; EIMS: m/z 144.1 $[M]^+$.

Naphthalen-2-ol (5m):[19] Pink solid; m.p. 123–125 °C; yield: 80 % (115 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.75 (dd, 2H, J=7.6, 8.9 Hz), 7.67 (d, 1H, J=8.3 Hz), 7.42 (dd, 1H, J=6.9, 8.3 Hz), 7.32 (dd, 1H, J=6.9, 7.6 Hz), 7.14 (d, 1H, J=2.8 Hz), 7.09 (dd, 1H, J=2.8, 8.9 Hz), 4.99 ppm (s, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=153.2, 134.5, 129.8, 128.9, 127.7, 126.5, 126.3, 123.6, 117.7, 109.5 ppm; EIMS: m/z: 144.1 $[M]^+$.

Aniline (6a):[20] Colorless oil; yield: 86 % (80 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=7.15 (t, 2H, J=7.6 Hz), 6.76 (t, 1H, J=7.6 Hz), 6.68 (d, 2H, J=7.6 Hz), 3.63 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ=146.5, 129.2, 118.5, 115.1 ppm; EIMS: m/z: 93.1 $[M]^+$.

***p*-Toluidine (6b)**:[20] Red solid; m.p. 44–45 °C; yield: 88 % (93 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ=6.97 (d, 2H, J=8.3 Hz), 6.61 (d, 2H, J=8.3 Hz), 3.51 (s, 2H), 2.24 ppm (s, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ=143.6, 129.7,127.8, 115.3, 20.4 ppm; EIMS: m/z: 106.1 $[M]^+$.

4-Methoxyaniline (6c):[12b] Red solid; m.p. 56–58 °C; yield: 88% (108 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 6.75 (d, 2H, J = 8.9 Hz), 6.65 (d, 2H, J = 8.9 Hz), 3.75 (s, 3H), 3.42 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 152.7, 139.9, 116.4, 114.7, 55.7 ppm; EIMS: m/z: 123.1 $[M]^+$.

4-(Trifluoromethyl)aniline (6d): Yellow oil; yield: 70% (113 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.38 (d, 2H, J = 8.3 Hz), 6.67 (d, 2H, J = 8.3 Hz), 3.90 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 149.3, 126.7 (d, J = 2.9 Hz), 124.8 (d, J = 271.7 Hz), 120.2 (d, J = 33.2 Hz), 114.2 ppm; EIMS: m/z: 161.1 $[M]^+$.

(4-Aminophenyl)methanol (6e):[20] Colorless solid; m.p. 60–63 °C; yield: 82% (102 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.16 (d, 2H, J = 8.3 Hz), 6.67 (d, 2H, J = 8.3 Hz), 4.55 (s, 2H), 3.68 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 146.0, 131.0, 128.8, 115.1, 65.3 ppm; ESIMS: m/z: 124.2 $[M+H]^+$.

Methyl 4-aminobenzoate (6f):[20] White solid; m.p. 112–113 °C; yield: 71% (107 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.84 (d, 2H, J = 8.9 Hz), 6.63 (d, 2H, J = 8.9 Hz), 4.10 (s, 2H), 3.85 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 167.1, 150.8, 131.5, 119.6, 113.7, 51.5 ppm; EIMS: m/z: 151.1 $[M]^+$.

4-Aminobenzonitrile (6g):[20] Yellow solid; m.p. 82–84 °C, yield: 70% (84 mg). ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.34 (d, 2H, J = 8.3 Hz), 6.61 (d, 2H, J = 8.3 Hz), 4.32 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 150.6, 133.6, 133.4, 120.2, 114.2, 114.1, 99.2 ppm; EIMS: m/z 120.2 $[M]^+$.

3-Methoxyaniline (6h):[20] Red oil; yield: 82% (101 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.05 (dd, 1H, J = 8.3, 7.6 Hz), 6.32 (dd, 1H, J = 2.1, 8.3 Hz), 6.29 (dd, 1H, J = 2.1, 7.6 Hz), 6.24 (t, 1H, J = 2.1 Hz), 3.75 (s, 3H), 3.64 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 160.7, 147.7, 130.0, 107.8, 103.9, 101.0, 55.0 ppm; EIMS: m/z 123.1 $[M]^+$.

3-Chloroaniline (6i):[20] Colorless oil; yield: 70% (89 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.05 (dd, 1H, J = 7.6, 8.3 Hz), 6.71 (d, 1H, J = 7.6 Hz), 6.66 (s, 1H), 6.53 (d, 1H, J = 8.3 Hz), 3.71 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 147.6, 134.8, 130.3, 118.4, 114.9, 113.1 ppm. EIMS: m/z: 127.0 $[M]^+$.

(3-Aminophenyl)methanol (6j):[20] Colorless soild; m.p. 91–93 °C; yield: 76% (94 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.14 (t, 1H, J = 7.6 Hz), 6.74 (d, 1H, J = 7.6 Hz), 6.70 (s, 1H), 6.61 (m, 1H), 4.60 (s, 2H), 3.69 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 146.6, 142.2, 129.5, 117.1, 114.4, 113.5, 65.4 ppm; ESIMS: m/z: 124.2 $[M+H]^+$.

3-Nitroaniline (6k):[20] Yellow solid; m.p. 113–115 °C; yield: 70% (97 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.57 (dd, 1H, J = 2.1, 8.3 Hz), 7.49 (t, 1H, J = 2.1 Hz), 7.26 (d, 1H, J = 8.3 Hz), 6.95 (dd, 1H, J = 2.1, 8.3 Hz), 4.00 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 149.2, 147.3, 129.9, 120.6, 113.2, 109.0 ppm; EIMS: m/z 138.1 $[M]^+$.

***o*-Toluidine (6l)**:[12c] Red oil; yield: 70% (75 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.04 (m, 2H), 6.71 (t, 1H, J = 7.6 Hz), 6.67 (d, 1H, J = 7.6 Hz), 3.58 (s, 2H), 2.17 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 144.5, 130.4, 126.9, 122.3, 118.6, 114.9, 17.3 ppm; EIMS: m/z: 107.1 $[M]^+$.

2-Bromoaniline (6m):[20] White solid; m.p. 30–31 °C; yield: 78% (134 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.40 (dd, 1H, J = 1.4, 8.3 Hz), 7.60 (m, 1H), 6.76 (dd, 1H, J = 1.4, 8.3 Hz), 6.61 (m, 1H), 4.06 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 144.0, 132.5, 128.3, 119.4, 115.8, 109.4 ppm; EIMS: m/z: 171.0, 173.0 $[M]^+$.

Naphthalen-1-amine (6n):[20] Red solid; m.p. 48–50 °C; yield: 70% (100 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.80 (m, 2H), 7.45 (m, 2H), 7.29 (m, 2H), 6.77 (d, 1H, J = 6.9 Hz), 4.14 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 142.0, 134.4, 128.5, 126.3, 125.8, 124.8, 123.6, 120.7, 118.9, 109.6 ppm; EIMS: m/z: 143.1 $[M]^+$.

Nitrobenzene (7a):[21a] Eluent: ethyl acetate/petroleum ether (1:20); yellow oil, yield: 60% (74 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.16 (d, 2H, J = 7.6), 7.68 (t, 1H, J = 7.6 Hz), 7.52 ppm (t, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 147.7, 134.3, 128.9, 122.9 ppm; EIMS: m/z: 123.0 $[M]^+$.

4-Nitrotoluene (7b):[44] Eluent: ethyl acetate/petroleum ether (1:20); yellow solid; m.p. 52–53 °C; yield: 65% (89 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.11 (d, 2H, J = 8.9 Hz), 7.32 (d, 2H, J = 8.3 Hz), 2.47 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 146.1, 145.9, 129.8, 123.5, 21.6 ppm; EIMS: m/z: 137.0 $[M]^+$.

4-Fluoronitrobenzene (7c):[21a] Eluent: ethyl acetate/petroleum ether (1:20); yellow oil, yield: 52% (73 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.28 (m, 2H), 7.22 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 167.1, 165.4, 144.4, 126.3, 126.2, 116.5, 116.3 ppm; EIMS: m/z 141.0 $[M]^+$.

4-Nitrobenzenemethanol (7d):[45] Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 89–90 °C; yield: 70% (107 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.21 (d, 2H, J = 8.3 Hz), 7.53 (d, 2H, J = 8.3 Hz), 4.84 (d, 2H, J = 4.8 Hz), 2.20 ppm (t, 1H, J = 4.8 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 148.2, 147.2, 127.0, 123.7, 63.9 ppm; EIMS: m/z: 153.0 $[M]^+$.

4-Nitrobenzaldehyde (7e):[45] Eluent: ethyl acetate/petroleum ether (1:10); white solid; m.p. 103–105 °C; yield: 50% (76 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 10.17 (s, 1H), 8.40 (d, 2H, J = 8.3 Hz), 8.08 ppm (d, 2H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 190.3, 151.1, 140.0, 130.5, 124.3 ppm; EIMS: m/z: 151.0 $[M]^+$.

4-Nitrobenzoic acid (7f):[45] Eluent: ethyl acetate/petroleum ether (1:5); yellow solid; m.p. 229–231 °C; yield: 54% (90 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 13.7 (s, 1H), 8.33 (d, 2H, J = 8.2 Hz), 8.18 ppm (d, 2H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.3, 150.6, 136.9, 131.2, 124.3 ppm; ESIMS: m/z: 166.1 $[M-H]^-$.

3-Nitroanisole (7g):[46] Eluent: ethyl acetate/petroleum ether (1:20); yellow oil; yield: 54% (83 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.83 (dd, 1H, J = 2.1, 8.3 Hz), 7.74 (dd, 1H, J = 2.1, 2.8 Hz), 7.43 (t, 1H, J = 8.3 Hz), 7.23 (dd, 1H, J = 2.8, 8.3 Hz), 3.90 ppm (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 160.1, 149.2, 129.9, 121.3, 115.8, 108.1, 55.8 ppm; EIMS: m/z: 153.0 $[M]^+$.

3-Nitrochlorobenzene (7h):[21a] Eluent: ethyl acetate/petroleum ether (1:20); yellow solid; m.p. 46–47 °C; yield: 60% (94 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 8.24 (s, 1H), 8.14 (d, 1H, J = 8.3 Hz), 7.69 (d, 1H, J = 8.3 Hz), 7.51 ppm (t, 1H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 148.8, 135.4, 134.7, 130.3, 123.8, 121.6 ppm; EIMS: m/z: 157.0 $[M]^+$.

3-Nitrobenzyl alcohol (7i):[47] Eluent: ethyl acetate/petroleum ether (1:20); yellow oil; yield: 50% (77 mg); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.25 (s, 1H), 8.15 (d, 1H, J = 8.3 Hz), 7.70 (d, 1H, J = 8.3 Hz), 7.54 (t, 1H, J = 8.3 Hz), 4.83 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 148.3, 142.8, 132.6, 129.4, 122.5, 121.5, 64.0 ppm; EIMS: m/z: 153.0 $[M]^+$.

3-Nitroaniline (7j): Eluent: ethyl acetate/petroleum ether (1:10); yellow solid; m.p. 94–96 °C; yield: 64% (88 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.57 (d, 1H, J = 8.2 Hz), 7.49 (s, 1H), 7.27 (t, 1H, J = 8.2 Hz), 6.95 (d, 2H, J = 8.2 Hz), 4.00 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 149.3, 147.4, 129.9, 120.6, 113.1, 109.0 ppm; EIMS: m/z: 138.1 $[M]^+$.

3-Nitrobenzoic acid (7k):[47] Eluent: ethyl acetate/petroleum ether (1:5); white solid; m.p. 142–143 °C; yield: 60% (100 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 13.71 (s, 1H), 8.62 (d, 1H, J = 1.4 Hz), 8.47 (dd, 1H, J = 1.4, 8.3 Hz), 8.35 (d, 1H, J = 7.6 Hz), 7.82 ppm (dd, 1H, J = 8.3, 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 166.0, 148.4, 135.9, 133.0, 131.1, 127.9, 124.2 ppm; ESIMS: m/z: 166.3 $[M-H]^-$.

1-Bromo-2-nitrobenzene (7l):[44] Eluent: ethyl acetate/petroleum ether (1:10); yellow oil; yield: 44% (89 mg); ^{1}H NMR ($CDCl_3$, 600 MHz): δ = 7.84 (d, 1H, J = 7.6 Hz), 7.75 (d, 1H, J = 8.3 Hz), 7.46 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ = 149.9, 135.0, 133.2, 128.2, 125.5, 114.4 ppm; EIMS: m/z: 201.0, 203.0 $[M]^+$.

Acknowledgements

The authors wish to thank the National Natural Science Foundation of China (grant no. 20972083) and the Ministry of Science and Technology of China (2009ZX09501-004) for financial support.

[1] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* **2002**, *102*, 1359.

[2] *Metal-Catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1997**.
[3] E. F. V. Scriven, K. Turnbull, *Chem. Rev.* **1988**, *88*, 297.
[4] K. Schank in *The Chemistry of Sulfones and Sulfoxides* (Eds.:S. Patai, Z. Rappoport, C. J. M. Stirling), Wiley, New York, **1988**, Chapter 7.
[5] Z. Rappoport, *The Chemistry of Phenols*, Wiley-VCH, Weinheim, **2003**.
[6] S. A. Lawrence, *Amines: Synthesis Properties and Application*. Cambridge University Press, Cambridge, **2004**.
[7] W. E. Muller, *The Benzodiazepine Receptor*, Cambridge University Press, Cambridge, **1988**.
[8] A. Klapars, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 14844.
[9] W. Zhu, D. Ma, *Chem. Commun.* **2004**, 888.
[10] S. Cacchi, G. Fabrizi, A. Goggiamani, L. M. Parisi, R. Bernini, *J. Org. Chem.* **2004**, *69*, 5608.
[11] a) K. W. Anderson, T. Ikawa, R. E. Tundel, S. L. Buchwald, *J. Am. Chem. Soc.* **2006**, *128*, 10694; b) D. Zhao, N. Wu, S. Zhang, P. Xi, X. Su, J. Lan, J. You, *Angew. Chem.* **2009**, *121*, 8885–8888; *Angew. Chem. Int. Ed.* **2009**, *48*, 8729–8732; c) A. Tlili, N. Xia, F. Monnier, M. Taillefer, *Angew. Chem.* **2009**, *121*, 8881; *Angew. Chem. Int. Ed.* **2009**, *48*, 8725.
[12] a) Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 10028; b) N. Xia, M. Taillefer, *Angew. Chem.* **2009**, *121*, 343; *Angew. Chem. Int. Ed.* **2009**, *48*, 337; c) H. Xu, C. Wolf, *Chem. Commun.* **2009**, 3035.
[13] B. P. Fors, S. L. Buchwald, *J. Am. Chem. Soc.* **2009**, *131*, 12898.
[14] a) T. Ishiyama, M. Murata, N. Miyaura, *J. Org. Chem.* **1995**, *60*, 7508; b) M. Murata, S. Watanabe, Y. Masuda, *J. Org. Chem.* **1997**, *62*, 6458; c) M. Murata, T. Oyama, S. Watanabe, Y. Masuda, *J. Org. Chem.* **2000**, *65*, 164; d) C. Kleeberg, L. Dang, Z. Lin, T. B. Marder, *Angew. Chem.* **2009**, *121*, 5454; *Angew. Chem. Int. Ed.* **2009**, *48*, 5350.
[15] a) I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.* **2010**, *110*, 890; b) J. Y. Cho, M. K. Tse, D. Holmes, R. J. Maleczka, M. R. Smith, *Science* **2002**, *295*, 305; c) T. M. Boller, J. M. Murphy, M. Hapke, T. Ishiyama, N. Miyaura, J. F. Hartwig, *J. Am. Chem. Soc.* **2005**, *127*, 14263; d) I. A. I. Mkhalid, D. N. Coventry, D. Albesa-Jove, A. S. Batsanov, J. A. K. Howard, R. N. Perutz, T. B. Marder, *Angew. Chem.* **2006**, *118*, 503; *Angew. Chem. Int. Ed.* **2006**, *45*, 489; e) S. Kawamorita, H. Ohmiya, K. Hara, A. Fukuoka, M. Sawamura, *J. Am. Chem. Soc.* **2009**, *131*, 5058.
[16] For the synthesis of aryl halides, see: a) G. W. Kabalka, E. E. Gooch, *J. Org. Chem.* **1980**, *45*, 3578; b) G. W. Kabalka, E. E. Gooch, *J. Org. Chem.* **1981**, *46*, 2582; c) G. W. Kabalka, V. Namboodiri, M. R. Akula, *J. Labelled Compd. Radiopharm.* **2001**, *44*, 921; d) G. W. Kabalka, A. R. Mereddy, *Organometallics* **2004**, *23*, 4519; e) R. H. Szumigala, P. N. Devine, D. R. Gauthier, R. P. Volante, *J. Org. Chem.* **2004**, *69*, 566; f) A. L. S. Thompson, G. W. Kabalka, M. R. Alkula, J. W. Huffman, *Synthesis* **2005**, 547; g) J. M. Murphy, X. Liao, J. F. Hartwig, *J. Am. Chem. Soc.* **2007**, *129*, 15434; h) T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2008**, *130*, 10060; i) T. Furuya, T. Ritter, *Org. Lett.* **2009**, *11*, 2860; j) H. Wu, J. Hynes, Jr., *Org. Lett.* **2010**, *12*, 1192; k) M.-L. Yao, M. S. Reddy, L. Yong, I. Walfish, D. W. Blevins, G. W. Kabalka, *Org. Lett.* **2010**, *12*, 700; l) G. W. Kabalka, A. R. Mereddy, *Tetrahedron Lett.* **2004**, *45*, 343; m) L. Yong, M.-L. Yao, J. F. Green, H. Kelly, G. W. Kabalka, *Chem. Commun.* **2010**, *46*, 2623; n) G. W. Kabalka, K. A. R. Sastry, H. C. Hsu, M. D. Hylarides, *J. Org. Chem.* **1981**, *46*, 3113; o) G. W. Kabalka, M. R. Akula, J. Zhang, *Nucl. Med. Biol.* **2002**, *29*, 841; p) G. W. Kabalka, M.-L. Yao, *J. Organomet. Chem.* **2009**, *694*, 1638; q) G. W. Kabalka, G. Tang, A. R. Mereddy, *J. Labelled Compd. Radiopharm.* **2007**, *50*, 446; r) G. W. Kabalka, R. S. Varma, Y.-Z. Gai, R. M. Baldwin, *Tetrahedron Lett.* **1986**, *27*, 3843; s) C. Thiebes, G. K. S. Prakash, N. A. Petasis, G. A. Olah, *Synlett* **1998**, 141.
[17] For the synthesis of aryl azides, see: a) Y. Li, L.-X. Gao, F.-S. Han, *Chem. Eur. J.* **2010**, *16*, 7969; b) C. Tao, X. Cui, J. Li, A. Liu, L. Liu, Q. Guo, *Tetrahedron Lett.* **2007**, *48*, 3525.
[18] For the synthesis of aryl sulfones, see: A. Kar, I. A. Sayyed, W. F. Lo, H. M. Kaiser, M. Beller, M. K. Tse, *Org. Lett.* **2007**, *9*, 3405.
[19] For the synthesis of phenols, see: J. Xu, X. Wang, C. Shao, D. Su, G. Cheng, Y. Hu, *Org. Lett.* **2010**, *12*, 1964.
[20] For the synthesis of arylamines, see: H. Rao, H. Fu, Y. Jiang, Y. Zhao, *Angew. Chem.* **2009**, *121*, 1134; *Angew. Chem. Int. Ed.* **2009**, *48*, 1114.
[21] For the synthesis of nitroarenes, see: a) G. K. S. Prakash, C. Panja, T. Mathew, V. Surampudi, N. A. Petasis, G. A. Olah, *Org. Lett.* **2004**, *6*, 2205; b) G. K. S. Prakash, T. Mathew, *Angew. Chem.* **2010**, *122*, 1771; *Angew. Chem. Int. Ed.* **2010**, *49*, 1726.
[22] a) D. M. T. Chan, P. Y. S. Lam in *Boronic Acids* (Ed.: D. G. Hall), Wiley, New York, **2005**; pp. 205–240; b) P. Y. S. Lam, C. G. Clark, S. Saubern, J. Adams, M. P. Winters, D. M. T. Chan, A. Combs, *Tetrahedron Lett.* **1998**, *39*, 2941.
[23] R. H. Seevers, R. E. Counsell, *Chem. Rev.* **1982**, *82*, 575.
[24] J. March, *Advanced Organic Chemistry* 4th ed. Wiley-Interscience, New York, **2000**.
[25] G. Stavber, J. Iskra, M. Zupan, S. Stavber, *Adv. Synth. Catal.* **2008**, *350*, 2921.
[26] O. V. Branytska, R. Neumann, *J. Org. Chem.* **2003**, *68*, 9510.
[27] S. Farhadi, Z. Momeni, *J. Mol. Catal. A* **2007**, *277*, 47.
[28] F. W. Foss, Jr., T. P. Mathews, Y. Kharel, P. C. Kennedy, A. H. Snyder, M. D. Davis, K. R. Lynch, T. L. Macdonald, *Bioorg. Med. Chem.* **2009**, *17*, 6123.
[29] A. R. Hajipour, M. Arbabian, A. E. Ruoho, *J. Org. Chem.* **2002**, *67*, 8622.
[30] V. L. Blair, W. Clegg, R. E. Mulvey, L. Russo, *Inorg. Chem.* **2009**, *48*, 8863.
[31] I. L. Reich, H. J. Reich, *J. Org. Chem.* **1981**, *46*, 3721.
[32] S. Tchilibon, B. V. Joshi, S. K. Kim, H. T. Duong, Z. G. Gao, K. A. Jacobson, *J. Med. Chem.* **2005**, *48*, 1745.
[33] C. Y. Lo, M. P. Kumar, H. K. Chang, S. F. Lush, R. S. Liu, *J. Org. Chem.* **2005**, *70*, 10482.
[34] P. Pawluc', G. Hreczycho, J. Szudkowska, M. Kubicki, B. Marciniec, *Org. Lett.* **2009**, *11*, 3390.
[35] M. A. Fazio, O. P. Lee, D. I. Schuster, *Org. Lett.* **2008**, *10*, 4979.
[36] J. T. Spletstoser, P. T. Flaherty, R. H. Himes, G. I. Georg, *J. Med. Chem.* **2004**, *47*, 6459.
[37] M. Pudlo, D. Csanyi, F. Moreau, G. Hajos, Z. Riedl, J. Sapi, *Tetrahedron* **2007**, *63*, 10320.
[38] S. P. Klump, H. Shechter, *Tetrahedron Lett.* **2002**, *43*, 8421.
[39] M. Peyronneau, M. T. Boisdon, N. Roques, S. Mazieres, C. L. Roux, *Eur. J. Org. Chem.* **2004**, 4636.
[40] P. Hanson, R. A. A. J. Hendrickx, J. R. L. Smith, *Org. Biomol. Chem.* **2008**, *6*, 745.
[41] B. P. Bandgar, S. V. Bettigeri, J. Phopase, *Org. Lett.* **2004**, *6*, 2105.
[42] D. Yang, H. Fu, *Chem. Eur. J.* **2010**, *16*, 2366.
[43] A. G. Sergeev, T. Schulz, C. Torborg, A. Spannenberg, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 7731; *Angew. Chem. Int. Ed.* **2009**, *48*, 7595.
[44] K. B. Saitanya, H. Sahid, K. Manoranjan, K. C. Mihir, *Catal. Commun.* **2008**, *9*, 919.
[45] A. Chacko, B. Mathew, *J. Appl. Polym. Sci.* **2003**, *90*, 3708.
[46] J. Cornella, C. Sanchez, D. Banawa, I. Larrosa, *Chem. Commun.* **2009**, 7176.
[47] A. Chacko, R. Devi, S. Abraham, B. Mathew, *J. Appl. Polym. Sci.* **2005**, *96*, 1897.

Received: December 23, 2010
Published online: April 8, 2011

Please note: Minor changes have been made since the publication in *Chemistry–A European Journal* Early View. The Editor.

