JOC The Journal of Organic Chemistry

UNIVERSITY OF EXETER

Subscriber access provided by the University of Exeter

Note

Elemental Sulfur-Promoted Aerobic Dehydrogenative Aromatization of Cyclohexanones with Amines

Zhen Wang, Cheng Li, Huawen Huang, and Guo-Jun Deng

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.0c01122 • Publication Date (Web): 24 Jun 2020

Downloaded from pubs.acs.org on June 25, 2020

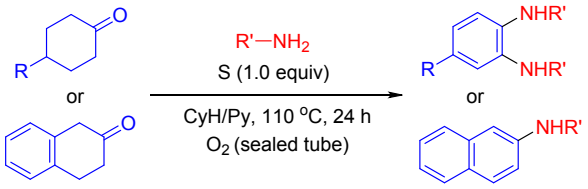
is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Elemental Sulfur-Promoted Aerobic Dehydrogenative Aromatization of Cyclohexanones with Amines

Zhen Wang‡, Cheng Li‡, Huawen Huang*, Guo-Jun Deng*

Key Laboratory for Green Organic Synthesis and Application of Hunan Province, Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, College of Chemistry, Xiangtan University, Xiangtan 411105, China. E-mail: hwhuang@xtu.edu.cn; gjdeng@xtu.edu.cn

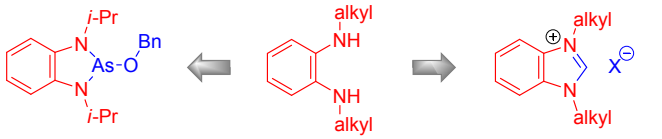
‡ These authors contributed equally to this work.



Abstract: *An elemental sulfur-promoted aerobic dehydrogenation system for the access to N,N'-dialkyl-o-phenylenediamines and N-substituted 2-naphthylamines is reported herein. Readily available cyclohexanones and amines (especially alkylamines) are transformed smoothly into target products. Aromatic amines can be achieved from all aliphatic reagents under aerobic metal-free reaction conditions. Control reactions show that the combinational use of elemental sulfur and molecular oxygen is exceptionally essential for this dehydrogenative aromatizaiton.*

Arylamines are core structural motifs widely used in pharmaceutical development and materials synthesis.[1] Thus great efforts have been made to pursue efficient access to arylamines for decades.[2] Notablely, *N,N'*-dialkyl-*o*-phenylenediamines, as a subclass of arylamines, have emerged as varied building blocks in the synthesis of catalysts

and ligands. For example, the diamine-coordinated arsenic(III) complex **A**, formed from *N,N'*-diisopropylbenzene diamine, showed good catalytic activity for the hydroboration of aldehydes in a recent report (Figure 1, **A**).[3] Moreover, a series of *N*-heterocyclic carbene (NHC), which are derivatives of *N,N'*-dialkyl-*o*-phenylenediamines, have been developed and applied as ligands or catalysts in molecular synthesis (Figure 1, **B**).[4-8] Owing to the significant application values of these arylamines, their synthesis has grabbed considerable interest.



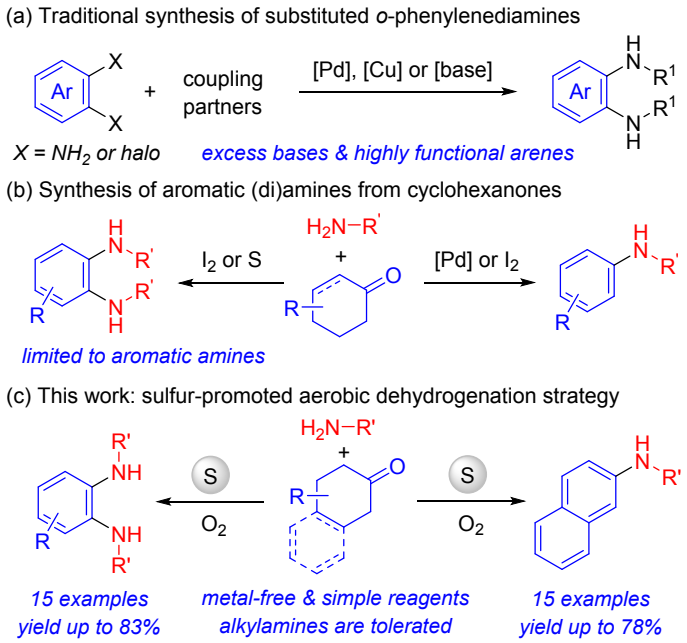
(A) *catalyst for hydroboration* **(B)** *precursors of N-heterocyclic carbenes*

Figure 1. Valuable derivatives from *N,N'*-dialkyl-*o*-phenylenediamines.

Traditional Buchwald-Hartwig amination[9] and Ullmann-type amination[10] remain the most common tools to synthesize *N,N'*-dsubstituted-*o*-phenylenediamines (Scheme 1a). However, these methods have obvious limitations. First, such reactions usually require the use of highly functionalized aromatic substrates (such as benzene-1,2-diamines), thus greatly limiting the substrate scope. Second, excessive additives such as bases and transition-metal catalysts are usually required. Moreover, in order to achieve the alkylation or arylation of both amino groups, it is usually necessary to use excessive reactant, which may lead to overalkylation or arylation. Therefore, selectivity control is crucial for this kind of reaction. As proven superior aryl sources to traditional highly functionalized arenes, cyclohexanones provide a viable access to diverse aromatic products with high value added through

dehydro-aromatization, such as aromatic amines and diamines.[11] In most cases, transition-metal catalysts such as palladium were employed for this kind of trnasformation.[12] In 2018, Pan's group reported an iodine-catalysis for the synthsis of *N,N'*-diaryl-*o*-phenylenediamines from cyclohexanones and anilines, in which alkylamines proved unreactive.[13] In the same year, our group also developed elemental sulfur-promoted aerobic C-N bond construction[14] to access a series of *o*-arylenediamines through aromatization of cyclohexanones (Scheme 1b).[14a] In that system, however, aliphatic amines featured low but promising reactivity. Since the use of cyclohexanones as aryl source could provide efficient approaches for the preparation of arylamines, it is highly desirable to find a proper reaction system that is capable for amination with broader substrate scope including aliphatic amines. Within our ongoing research program on sustainable chemistry,[15] herein, we report a new elemental sulfur-promoted aerobic dehydrogenation coupling/aromatization of cyclohexanones with aliphatic/aromatic amines under metal-free conditions (Scheme 1c). Hence, a range of *N,N'*-dialkyl-*o*-phenylenediamines have been achieved from all non-aromatic reagents. Besides, the coupling of *β*-tetralone instead of cyclohexanones afforded the major 2-naphthylamine products.

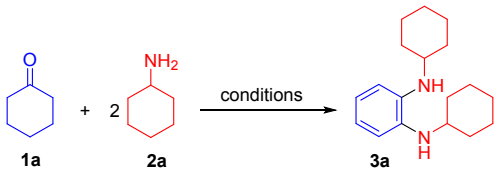
Scheme 1. Synthetic Strategies for Substituted Aromatic (Di)Amines



To investigate the optimal reaction conditions, we selected cyclohexanone (**1a**) and cyclohexylamine (**2a**) as the model substrates (Table 1). When the mixture in the absence of sulfur powder was heated in cyclohexane for 24 hours under oxygen atmosphere, only trace amounts of target product **3a** could be detected by GC-MS (entry 1). Then sulfur powder was added to obtain desired product **3a** in 31% yield (entry 2). Subsequently, various solvents including toluene, chlorobenzene, pyridine and 1,4-dioxane have been screened, and the separation yields were all enhance to moderate (entries 3-6). Of them, pyridine gave the best result (entry 5). Then we examined mixed solvent (entries 7-9). To our delight, the yield of the reaction was significantly increased to 82% when cyclohexane and pyridine (1:1) were used as co-solvent (entry 7). While the yield dramatically declined when the reaction was conducted at 100 °C (entry 10), elevating the reaction temperature to 120 °C furnished almost the same yield (entry 11). Decreasing the amount of sulfur powder to 50 mol%

reduced the yield to 44% (entry 12). In contrast, the reaction yield was not improved when the amount of sulfur powder was increased to 1.5 equiv. (entry 13). Notably, molecular oxygen is critical in this kind of reaction since only trace amounts of product were obtained when the reaction was carried out under air atmosphere (entry 14).

Table 1. Optimization of Reaction Conditions[a]

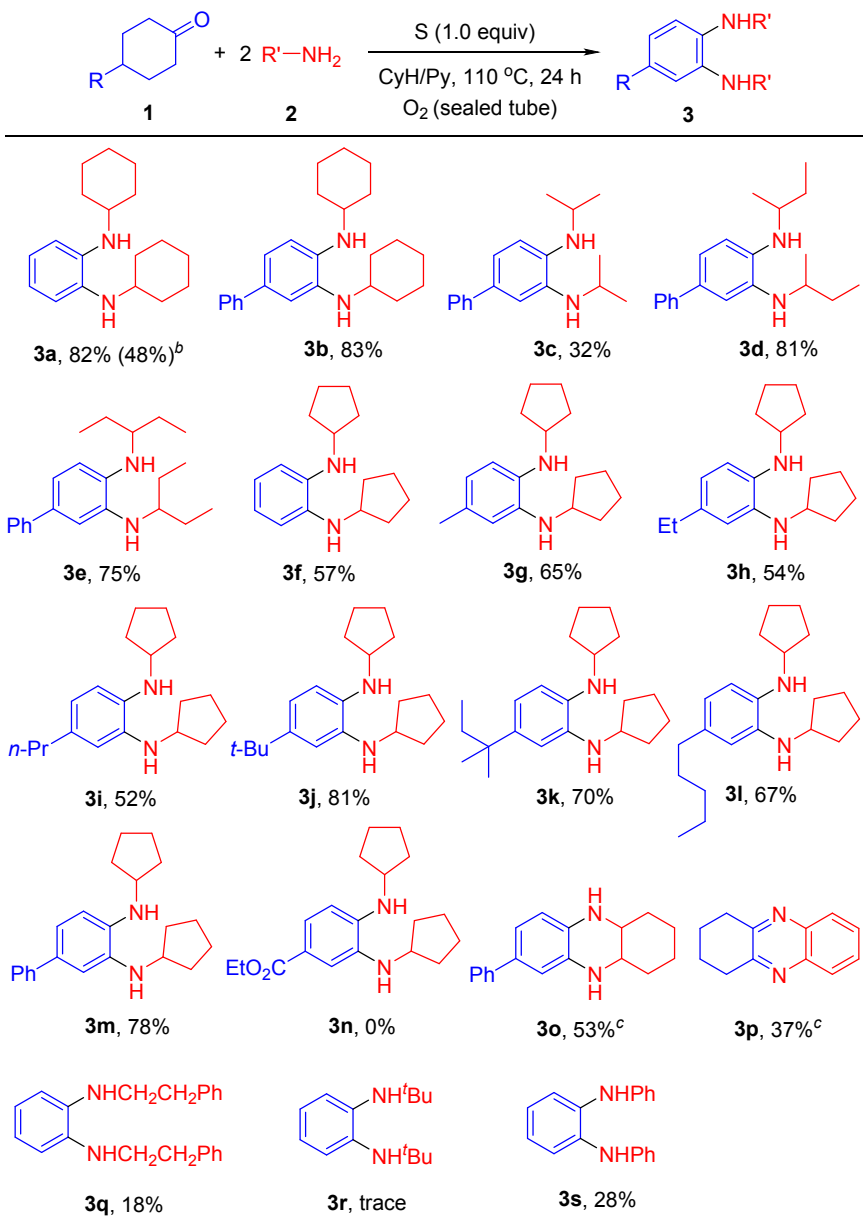


entry	S (equiv.)	solvent	yield (%)[b]
1	0	cyclohexane (CyH)	trace
2	1.0	CyH	31
3	1.0	toluene	54
4	1.0	chlorobenzene	60
5	1.0	pyridine (Py)	68
6	1.0	1,4-dioxane	59
7	1.0	CyH/Py (1:1)	82
8	1.0	CyH/Py (1:2)	72
9	1.0	CyH/Py (2:1)	66
10[c]	1.0	CyH/Py (1:1)	49
11[d]	1.0	CyH/Py (1:1)	80
12	0.5	CyH/Py (1:1)	44
13	1.5	CyH/Py (1:1)	82
14[e]	1.0	CyH/Py (1:1)	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.7 mmol), S (1 equiv.), solvent (0.6 mL), stirred at 110 °C under O_2 for 24 h. [b] Isolated yield. [c] 100 °C. [d] 120 °C. [e] Under air.

With the optimized reaction conditions in hand, we then investigated the scope of substrates in this reaction system (Table 2). When the reaction was conducted on a 10 mmol scale, the yield of **3a** was 48%. The reaction of 4-phenylcyclohexan-1-one and cyclohexanamine generated **3b** in 83% yield. When isopropylamine reacted with 4-phenylcyclohexan-1-one, **3c** was obtained in 32% yield. The target products were obtained in good yields when other α-branched aliphatic amines were used (**3d** and **3e**). Next, the scope of cyclohexanones was explored under similar reaction conditions. When cyclohexanone and *para*-alkyl cyclohexanones were employed in this reaction, the corresponding products were afforded in moderate to good yields (**3f-3m**). Unfortunately, the existences of an electron withdrawing group (such as ester group, **3n**) in cyclohexanone prohibited the transformation and resulted in the corresponding product in very low yield, which may be attributed to the low stability of imine intermediate with an electron-withdrawing group. When 1,2-diaminocyclohexane was treated under standard conditions, the target product (**3o**) was obtained in 53% yield. Interestingly, the reaction of cyclohexanone with benzene-1,2-diamine generated the cyclized product **3p** as major product without dehydro-aromatization of cyclohexanone moiety.

Table 2. Synthesis of *N,N′*-dialkyl-*o*-phenylenediamines[a]



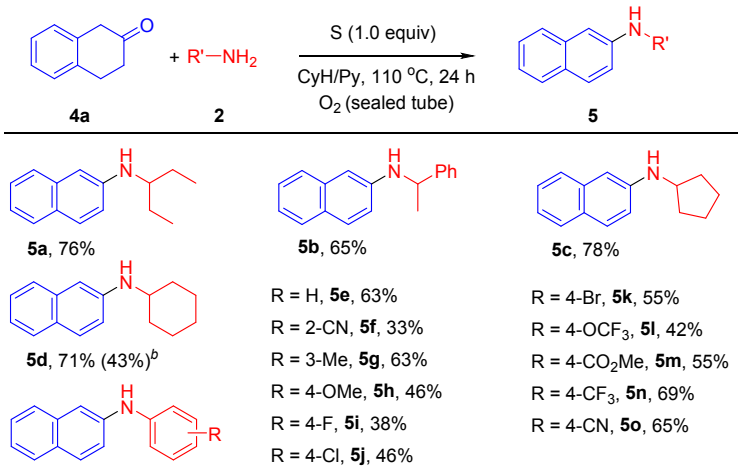
[a] Conditions: **1** (0.2 mmol), **2** (0.7 mmol), S (1.0 equiv.), pyridine/cyclohexane (1:1, 0.6 mL), 110 °C, 24 h, O_2. Isolated yields based on **1**. [b] 10 mmol scale. [c] **2** (0.35 mmol).

Unfortunately, primary aliphatic amines featured very low reactivity in the present system (**3q**, 18% yield), therein the major side product was determined to be tetrahydrobenzo[*d*]imidazole.[14c] As with tertiary aliphatic amines such as *t*-BuNH_2, the possible influence of strong steric hindrance prohibited the *ortho*

difunctionalization (**3r**). Compared with our previous sulfur/BzOH-promoted aerobic reaction with aromatic amines,[14a] the present acid-free system was also not approvingly effective for the aromatized diamination of cyclohexanones with anilines (**3s**, 28% yield), thus revealing the uniqueness of both diamination systems.

In order to further extend the application of this reaction system, a range of amines were tested to react with *β*-tetralone, which exclusively afforded monoaminative naphthalen-2-amine products (Table 3). Aliphatic amines afforded the target products (**5a**-**5d**) in moderate to good yields with high selectivity. What's more, the 5 mmol scale reaction afforded **5d** in 43% yield. Besides aliphatic amines, aniline was also reactive in this transformation and afforded desired product (**5e**) in 63% yield. When a cyano group was located at the *ortho*-position of aniline, **5f** was obtained in low yield whereas a moderate yield could be achieved when *para*-cyano aniline was used (**5o**). Furthermore, moderate yields were given by *meta*-methyl aniline (**5g**) and *para*-trifluoromethyl aniline (**5n**). Generally, methoxy, halogens, trifluoromethoxy and ester group were all tolerated under the standard conditions to give the desired diarylamine products in moderate yields (**5h**-**5m**). In the present system, *α*-tetralone (3,4-dihydronaphthalen-1(2H)-one) was not a suitable substrate for either diamination or monoamination.

Table 3. Synthesis of *N*-substituted 2-Naphthylamines[a]

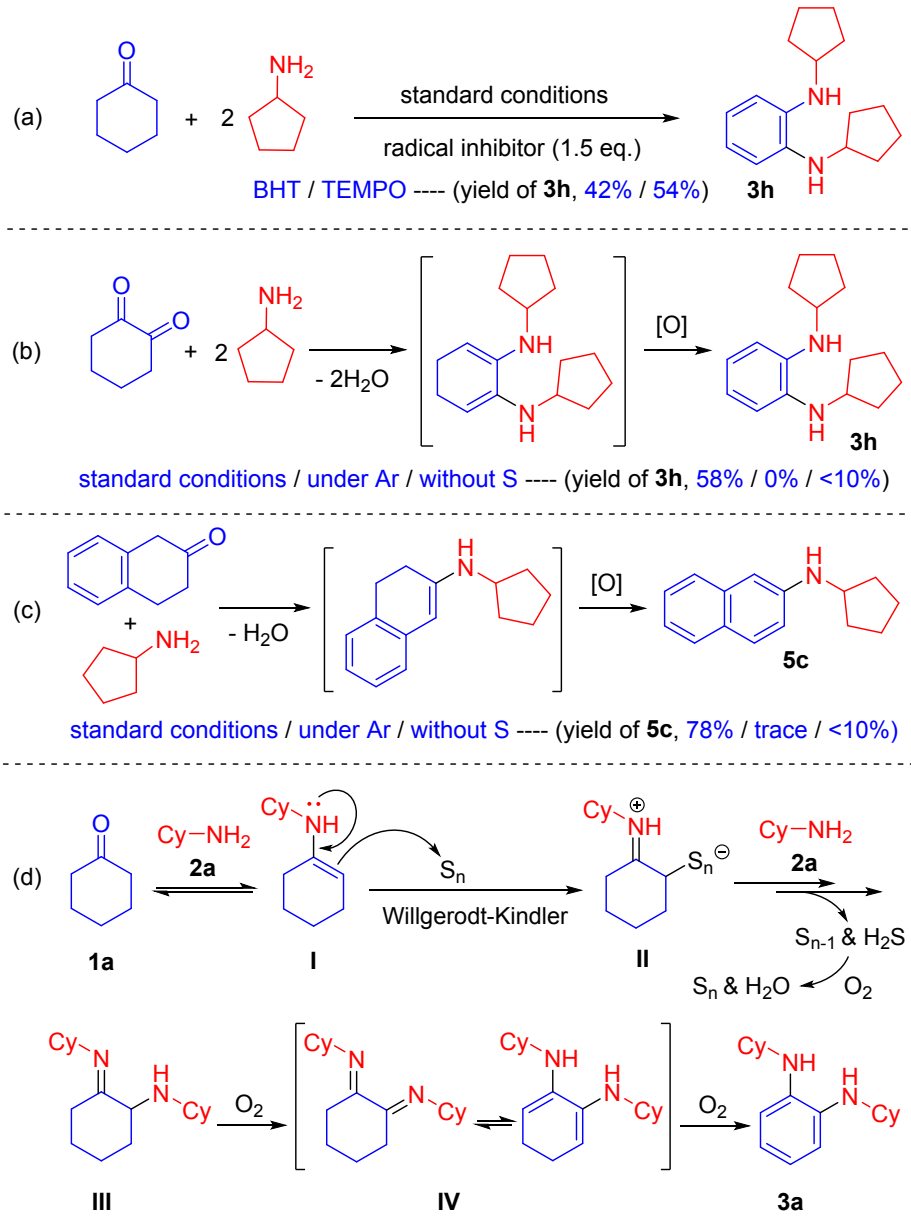


[a] Conditions: **4a** (0.4 mmol), **2** (0.2 mmol), S (1 equiv.), pyridine/cyclohexane (1:1, 0.6 mL), 110 °C, 24 h, O_2. [b] 5 mmol scale.

To get mechanistic insight upon the current sulfur-mediated aerobic diamination, some control experiments were carried out. When radical inhibitor such as BHT or TEMPO was added into the reaction system, the reaction yield of **3h** was not significantly affected (Scheme 2a). As a possible intermediate alternative, cyclohexane-1,2-dione was treated under the standard conditions and the yield of **3h** was obtained in 58%.[14] The reaction was completely prohibited in argon atmosphere and much lower yield was achieved in the absence of elemental sulfur. These results revealed that both oxygen and elemental sulfur are indispensable in the terminal dehydroaromatization process (Scheme 2b). Furthermore, the condensation intermediate, which was formed in situ, of *β*-tetralone and cyclopentamine smoothly generated mono-amination product **5c** in 78% yield under this dehydrogenation system (Scheme 2c). This means the reaction selectivity control is closely related with the type of cyclohexanone substrate. On the basis of experimental results and our previous observations,[14a] a possible reaction mechanism was proposed (Scheme 2d).

The transformation is initiated through the condensation of cyclohexanone **1a** and cyclohexanamine **2a** to afford enamine intermediate **I**. Subsequently, Willgerodt-Kindler-type sulfuration of **I** with elemental sulfur occurs to give α-sulfurated ketimine **II**, with nucleophilic substitution with the second cyclohexanamine followed by dehydrogenative aromatization via aerobic oxidation to furnish the final product **3a**. We suspect that the increased alkalinity of aliphatic amines that led to low reactivity of them in our previous acidic system with anilines. In present system, we used a enhanced alkaline system with pyridine that may promote the condensation. Comparably, the enamine intermediate was formed from 2-tetralone and amines that favor direct aromatization to afford the mono-amination products.

Scheme 2. Control Experiments and Mechanistic Proposal



In summary, we have developed an elemental sulfur-promoted aerobic dehydrogenative access to *N,N′*-dialkyl-*o*-phenylenediamines and *N*-substituted 2-naphthylamines from readily available cyclohexanone analogues and amines. The combination use of elemental sulfur and oxygen could efficiently promote this kind of transformation. When aliphatic amines were used as the amination reagents, the corresponding bis-amination products *N,N′*-dialkyl-*o*-phenylenediamines were

selectively generated from all non-aromatic substrates under metal-free conditions. This reaction system complements well to our previous aromatized bis-amination of cyclohexanones with aromatic amines, and also provides an effective metal-free alternative for the preparation of *N*-substituted 2-naphthylamines through dehydrogenative aromatization.

EXPERIMENTAL SECTION

General information. All reactions were carried out under an atmosphere of oxygen unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using Chloroform-d or acetone-d6 as solvent and TMS as an internal standard. Mass spectra were measured on Agilent 5975 GC-MS instrument (EI). High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. The structures of known compounds were further corroborated by comparing their ^{1}H NMR, ^{13}C NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

General procedure for the synthesis of diamines (3). A 10 mL reaction vessel was charged with cyclohexanone (**1a**, 21 μL, 0.2 mmol), cyclohexanamine (**2a**, 80 μL, 0.7 mmol), S_8 (6.4 mg, 12.5 mol %), pyridine/cyclohexane (1:1, 0.6 mL) under O_2. The mixture was heated in an oil bath at 110 ^{o}C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was

purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the desired product **3a** as red oil, 44.6 mg, yield 82%.

10 mmol scale reaction of 3a. A 50 mL round bottom flask was charged with cyclohexanone (**1a**, 1.05 mL, 10 mmol), cyclohexanamine (**2a**, 4.00 mL, 35 mmol), S_8 (0.32 g, 6.25 mmol), pyridine/cyclohexane (1:1, 15 mL). The reaction vessel was purged with oxygen for three times and connected with a condenser pipe and an oxygen balloon. The mixture was heated in an oil bath at 110 °C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the desired product **3a** as red oil, 1.31 g, yield 48%.

General procedure for the synthesis of naphthylamines (5). A 10 mL reaction vessel was charged with *β*-tetralone (**4a**, 54 μL, 0.4 mmol), cyclohexanamine (**2a**, 23 μL, 0.2 mmol), S_8 (6.4 mg, 12.5 mol %), pyridine/ cyclohexane (1:1, 0.6 mL) under O_2. The mixture was heated in an oil bath at 110 °C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 100:1) to give the desired product **5d** as yellow oil, 31.9 mg, yield 71%.

5 mmol scale reaction of 5d: A 50 mL round bottom flask was charged with *β*-tetralone (**4a**, 675 μL, 2.5 mmol), cyclohexanamine (**2a**, 2.00 mL, 17.5 mmol), S_8 (0.16 g, 3.125 mmol), pyridine/cyclohexane (1:1, 10 mL). The reaction vessel was purged with oxygen for three times and connected with a condenser pipe and an oxygen balloon. The mixture was heated in an oil bath at 110 °C for 24 h. After cooling to room temperature, the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the desired product **5d** as yellow oil, 453.6 mg, yield 43%.

*N^1,N^2-Dicyclohexylbenzene-1,2-diamine (**3a**, CAS: 24464-62-8).*[16] ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.78−6.66 (m, 4H), 3.20−3.13 (m, 2H), 2.07−2.00 (m, 4H),

1.79−1.72 (m, 4H), 1.67−1.62 (m, 2H), 1.39−1.31 (m, 4H), 1.28−1.16 (m, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 136.5, 118.9, 113.6, 52.1, 33.6, 26.0, 25.0; HRMS calcd. for: $C_{18}H_{29}N_2^+$ $(M+H)^+$ 273.2325, found 273.2329.

N^3,N^4-Dicyclohexyl-[1,1'-biphenyl]-3,4-diamine ***(3b)***. 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and cyclohexanamine (80 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3b** as green oil, 57.8 mg, yield 83%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.58−7.52 (m, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.93 (d, J = 6.7 Hz, 2H), 6.70 (d, J = 8.7 Hz, 1H), 3.83 (s, 2H), 3.36−3.23 (m, 2H), 2.11−2.04 (m, 4H), 1.79−1.72 (m, 4H), 1.67−1.60 (m, 2H), 1.46−1.19 (m, 10H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6) δ 143.3, 137.4, 137.3, 131.6, 129.5, 127.1, 126.6, 117.9, 117.9, 113.6, 112.7, 52.9, 52.8, 34.3, 34.3, 27.0, 26.9, 25.9; HRMS (ESI) m/z calcd for $C_{24}H_{33}N_2^+$ $(M+H)^+$ 349.2638, found 349.2642.

N^3,N^4-Diisopropyl-[1,1'-biphenyl]-3,4-diamine ***(3c)***. 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and isopropylamine (60 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3c** as yellow solid, 17.1 mg, yield 32%. Mp: 62−64 ^{o}C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.60−7.54 (m, 2H), 7.38−7.34 (m, 2H), 7.23−7.18 (m, 1H), 6.99−6.91 (m, 2H), 6.68 (d, J = 8.0 Hz, 1H), 4.01−3.70 (m, 2H), 3.70−3.59 (m, 2H), 1.21 (t, J = 6.0 Hz, 12H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6) δ 143.3, 137.5, 137.4, 131.6, 129.5, 127.1,

126.7, 117.8, 113.3, 112.2, 45.1, 45.0, 23.4; HRMS calcd. for: $C_{18}H_{25}N_2^+$ $(M+H)^+$ 269.2012, found 269.2015.

N^3,N^4-Di-sec-butyl-[1,1'-biphenyl]-3,4-diamine ***(3d)***. 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and *sec*-butylamine (70 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3d** as red oil, 47.9 mg, yield 81%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.59−7.53 (m, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 6.99−6.87 (m, 2H), 6.69 (d, J = 8.0 Hz, 1H), 3.80 (d, J = 32.6 Hz, 2H), 3.49−3.39 (m, 2H), 1.70−1.60 (m, 2H), 1.56−1.46 (m, 2H), 1.22−1.16 (m, 6H), 1.01−0.96 (m, 6H); ^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6) δ 143.2, 137.6, 137.5, 131.4, 129.4, 127.0, 126.8, 117.7, 113.4, 112.4, 50.9, 50.9, 50.9, 50.8, 20.6, 10.9, 10.9; HRMS calcd. for: calcd for $C_{20}H_{29}N_2^+$ $(M+H)^+$ 297.2325, found 297.2329.

N^3,N^4-Di(pentan-3-yl)-[1,1'-biphenyl]-3,4-diamine ***(3e)***. 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and 3-aminopentane (81 μL, 0.7 mmol) were used as the substrate under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3e** as red oil, 45.4 mg, yield 75%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.59−7.54 (m, 2H), 7.38−7.33 (m, 2H), 7.23−7.18 (m, 1H), 6.92−6.94 (m, 2H), 6.70−6.65 (m, 1H), 3.83 (d, J = 25.2 Hz, 2H), 3.35−3.26 (m, 2H), 1.66−1.50 (m, 8H), 0.98−0.93 (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, Acetone-d_6) δ 143.3, 137.8, 131.3, 129.5, 128.4, 127.0, 126.6, 117.7, 113.4, 112.5, 56.7, 56.6, 27.5, 27.4, 10.7; HRMS calcd. for: $C_{22}H_{33}N_2^+$

$(M+H)^+$ 325.2638, found 325.2641.

*N^1,N^2-Dicyclopentylbenzene-1,2-diamine (**3f**).* Cyclohexanone (21 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3f** as brown oil, 27.9 mg, yield 57%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.78−6.75 (m, 2H), 6.71−6.68 (m, 2H), 3.76 (p, J = 6.0 Hz, 2H), 2.07−1.99 (m, 4H), 1.76−1.73 (m, 4H), 1.64−1.59 (m, 4H), 1.55−1.49 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 137.1, 118.7, 112.4, 54.7, 33.7, 24.4; HRMS calcd. for: $C_{16}H_{25}N_2^+$ $(M+H)^+$ 245.2012, found 245.2012.

*N^1,N^2-Dicyclopentyl-4-methylbenzene-1,2-diamine (**3g**).* 4-Methylcyclohexan-1-one (25 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3g** as brown oil, 33.6 mg, yield 65%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.60 (d, J = 7.8 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 6.49 (s, 1H), 3.79−3.69 (m, 2H), 2.79 (s, 2H), 2.27 (s, 3H), 2.07−1.96 (m, 4H), 1.74−1.70 (m, 4H), 1.64−1.58 (m, 4H), 1.54−1.48 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 137.9, 134.3, 128.6, 118.5, 113.4, 113.2, 55.2, 54.8, 33.8, 33.7, 24.4, 21.2; HRMS calcd. for: $C_{17}H_{27}N_2^+$ $(M^+H)^+$ 259.2169, found 259.2169.

*N^1,N^2-Dicyclopentyl-4-ethylbenzene-1,2-diamine (**3h**).* 4-Ethylcyclohexan-1-one (28 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column

chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3h** as red oil, 29.4 mg, yield 54%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.63 (d, J = 7.9 Hz, 1H), 6.60−6.54 (m, 1H), 6.53 (s, 1H), 3.78−3.70 (m, 2H), 2.56 (q, J = 7.6 Hz, 2H), 2.07−1.98 (m, 4H), 1.77−1.70 (m, 4H), 1.64−1.58 (m, 4H), 1.55−1.49 (m, 4H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 137.7, 135.1, 134.6, 117.2, 113.1, 112.1, 55.1, 54.7, 33.7, 28.6, 24.3, 24.3, 16.0; HRMS calcd. for: $C_{18}H_{29}N_2^+$ $(M+H)^+$ 273.2325, found 273.2329.

N^1,N^2-Dicyclopentyl-4-propylbenzene-1,2-diamine ***(3i)***. 4-Propylcyclohexan-1-one (31 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3i** as brown oil, 29.8 mg, yield 52%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.61 (d, J = 7.9 Hz, 1H), 6.56 (d, J = 8.1 Hz, 1H), 6.51 (s, 1H), 3.79−3.69 (m, 2H), 2.95 (s, 2H), 2.49 (t, J = 7.7 Hz, 2H), 2.07−1.96 (m, 4H), 1.77−1.70 (m, 4H), 1.66−1.58 (m, 6H), 1.54−1.46 (m, 4H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 137.5, 134.5, 133.6, 118.0, 113.1, 112.7, 55.1, 54.7, 37.9, 33.7, 25.0, 24.3, 14.0; HRMS calcd. for: $C_{19}H_{31}N_2^+$ $(M+H)^+$ 287.2482, found 287.2486.

4-(tert-Butyl)-N^1,N^2-dicyclopentylbenzene-1,2-diamine ***(3j)***. 4-(*tert*-Butyl)cyclohexan-1-one (30.8 mg, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3j** as green oil, 48.6 mg, yield 81%. ^{1}H NMR (400 MHz,

Acetone-d_6) δ 6.68 (d, J = 2.1 Hz, 1H), 6.64 (dd, J = 8.1, 2.1 Hz, 1H), 6.53 (d, J = 8.1 Hz, 1H), 3.84−3.72 (m, 2H), 2.91 (s, 2H), 2.02−1.92 (m, 4H), 1.75−1.67 (m, 4H), 1.62−1.47 (m, 8H), 1.26 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, Acetone-d_6) δ 141.4, 137.7, 135.5, 115.0, 112.7, 110.5, 55.8, 55.6, 34.6, 34.2, 34.2, 32.1, 25.0, 25.0; HRMS calcd. for: $C_{20}H_{33}N_2^+$ $(M+H)^+$ 301.2638, found 301.2640.

N^1,N^2-Dicyclopentyl-4-(tert-pentyl)benzene-1,2-diamine ***(3k)***. 4-(*tert*-Pentyl)cyclohexan-1-one (38 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3k** as green oil, 44.6 mg, yield 70%. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.70 (d, J = 7.9 Hz, 1H), 6.66 (s, 1H), 6.62 (d, J = 8.1 Hz, 1H), 3.79−3.72 (m, 2H), 2.86 (s, 2H), 2.08−1.97 (m, 4H), 1.75−1.73 (m , 4H), 1.64−1.57 (m, 6H), 1.51 (s, 4H), 1.25 (s, 6H), 0.71 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 139.9, 136.7, 134.6, 115.8, 112.1, 110.8, 55.0, 54.8, 37.3, 37.0, 33.8, 33.7, 28.6, 24.4, 24.4, 9.3; HRMS calcd. for: $C_{21}H_{35}N_2^+$ $(M+H)^+$ 315.2795, found 315.2797.

N^1,N^2-Dicyclopentyl-4-pentylbenzene-1,2-diamine ***(3l)***. 4-Pentylcyclohexan-1-one (38 μL, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3l** as brown oil, 42.1 mg, yield 67%. ^1H NMR (400 MHz, Chloroform-*d*) δ 6.61 (d, J = 7.8 Hz, 1H), 6.55 (d, J = 7.9 Hz, 1H), 6.50 (s, 1H), 3.79−3.69 (m, 2H), 3.10 (s, 2H),

2.54−2.48 (m, 2H), 2.07−1.96 (m, 4H), 1.78−1.70 (m, 4H), 1.66−1.56 (m, 6H), 1.51−1.48 (m, 4H), 1.34−1.31 (m, 4H), 0.89 (t, J = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 137.5, 134.6, 133.7, 117.9, 113.0, 112.6, 55.1, 54.7, 35.8, 33.7, 31.7, 24.3, 22.6, 14.1; HRMS calcd. for: $C_{21}H_{35}N_2^+$ $(M+H)^+$ 315.2795, found 315.2800.

*N^3,N^4-Dicyclopentyl-[1,1'-biphenyl]-3,4-diamine (**3m**).* 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and cyclopentanamine (68 μL, 0.7 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **3m** as green oil, 50.1 mg, yield 78%. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.57 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.23−7.19 (m, 1H), 6.92 (s, 2H), 6.69 (d, J = 6.4 Hz, 1H), 3.88 (d, J = 29.1 Hz, 2H), 2.10−1.99 (m, 4H), 1.78−1.53 (m, 14H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Acetone-d_6) δ 143.6, 137.9, 137.6, 129.5, 127.1, 127.0, 126.6, 117.5, 112.6, 111.3, 55.6, 34.2, 25.1, 25.0; HRMS calcd. for: $C_{22}H_{29}N_2^+$ $(M+H)^+$ 321.2325, found 321.2327.

*7-Phenyl-1,2,3,4,4a,5,10,10a-octahydrophenazine (**3o**).*[17] 4-Phenylcyclohexan-1-one (34.8 mg, 0.2 mmol) and 1,2-diaminocyclohexane (43 μL, 0.35 mmol) were used as the substrate under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3n** as yellow solid, 28.1 mg, yield 53%. Mp: 155−158 ^{o}C ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 7.3 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.25−7.21 (m,1H), 6.88−6.80 (m, 1H), 6.75 (dd, J = 13.9, 1.6 Hz, 1H), 6.55 (dd, J = 14.0, 8.0 Hz, 1H), 3.49−3.18 (m,

2H), 3.08−2.82 (m, 2H), 1.85 (dd, J = 40.0, 10.0 Hz, 4H), 1.45−1.25 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 141.8, 133.9, 133.5, 131.8, 128.5, 126.4, 126.0, 117.7, 114.5, 113.0, 55.4, 55.3, 31.5, 31.5, 24.2.

*1,2,3,4-Tetrahydrophenazine (**3p**).*[18] Cyclohexanone (21 μL, 0.2 mmol) and 1,2-diaminobenzene (37.8 mg, 0.35 mmol) was used as the substrate under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **3o** as white solid, 13.7 mg, yield 37%. Mp: 101−103 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.98 (dd, J = 6.3, 3.5 Hz, 2H), 7.67 (dd, J = 6.4, 3.4 Hz, 2H), 3.17 (s, 4H), 2.06−2.03 (m, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, Chloroform-*d*) δ 154.1, 141.1, 128.9, 128.3, 33.1, 22.7.

*N,N'-Diphenethylbenzene-1,2-diamine (**3q**).*[14c] Cyclohexanone (21 μL, 0.2 mmol) and 2-phenylethanamine (88 μL, 0.7 mmol) was used as the substrate under the given reaction conditions. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 95:5) to yield the desired product **3p** as yellow solid (11.5 mg, 18% yield), mp 85-86 °C. ^1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33-7.29 (m, 4H), 7.23-7.21 (m, 6H), 6.79-6.78 (m, 4H), 6.70-6.68 (m, 2H), 3.32 (t, J = 6.8 Hz, 4H), 2.92 (t, J = 6.8 Hz, 4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm) δ 139.4, 137.1, 128.7, 128.5, 126.4, 119.3, 112.0, 45.5, 35.8.

*N^1,N^2-Diphenylbenzene-1,2-diamine (**3s**).*[14a] Cyclohexanone (21 μL, 0.2 mmol), aniline (64 μL, 0.7 mmol) was used as the substrate under the given reaction conditions. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 50:1) to give the desired product **3r** as yellow solid

(14.8 mg, yield 28%). mp 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 - 7.28 (m, 2H), 7.26 - 7.22 (m, 4H), 6.95 - 6.88 (m, 8H), 5.66 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9, 134.8, 129.3, 122.9, 120.5, 120.2, 117.2.

*N-(Pentan-3-yl)naphthalen-2-amine (**5a**).* *β*-Tetralone (54 μL, 0.4 mmol) and cyclohexanamine (23 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5a** as red oil, 32.4 mg, yield 76%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67−7.54 (m, 3H), 7.33 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.85 (dd, J = 8.7, 2.2 Hz, 1H), 6.79−6.72 (m, 1H), 3.37 (p, J = 6.0 Hz, 1H), 1.71−1.60 (m, 2H), 1.59−1.48 (m, 2H), 0.96 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 145.8, 135.3, 128.9, 127.6, 127.1, 126.2, 125.7, 121.5, 118.2, 104.4, 55.4, 26.7, 10.2; HRMS calcd. for: $C_{15}H_{20}N^+$ $(M+H)^+$ 214.1590, found 214.1590.

*N-(1-Phenylethyl)naphthalen-2-amine (**5b**).*[19] *β*-Tetralone (54 μL, 0.4 mmol) and DL-alpha-methylbenzylamin (26 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5b** as red oil, 32.1 mg, yield 65%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63−7.57 (m, 2H), 7.47 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 7.4 Hz, 2H), 7.33−7.20 (m, 4H), 7.15 (t, J = 7.5 Hz, 1H), 6.89 (dd, J = 8.8, 2.2 Hz, 1H), 6.65 (s, 1H), 4.62 (q, J = 6.7 Hz, 1H), 1.58 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 144.6, 144.4, 134.9, 128.8, 128.7, 127.5, 127.5, 127.0, 126.1, 126.0, 125.9, 122.0, 118.0, 106.1, 53.8, 24.7.

*N-Cyclopentylnaphthalen-2-amine (**5c**).* *β*-Tetralone (54 μL, 0.4 mmol) and cyclopentylamine (20 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5c** as brown oil, 32.9 mg, yield 78%. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.67−7.57 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.90−6.73 (m, 2H), 3.90 (p, *J* = 6.2 Hz, 1H), 2.12−2.04 (m, 2H), 1.79−1.62 (m, 4H), 1.56−1.48 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) *δ* 145.6, 135.2, 128.8, 127.6, 127.2, 126.2, 125.82 121.7, 118.3, 104.8, 54.6, 33.5, 24.1; HRMS calcd. for: $C_{15}H_{18}N^{+}$ $(M+H)^{+}$ 212.1434, found 212.1432.

*N-Cyclohexylnaphthalen-2-amine (**5d**, CAS: 23761-52-6).*[20] *β*-Tetralone (54 μL, 0.4 mmol) and cyclohexylamine (23 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5d** as yellow oil, 31.9 mg, yield 71%. ^{1}H NMR (400 MHz, Chloroform-*d*) *δ* 7.65−7.57 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 6.86−6.77 (m, 2H), 3.43−3.35 (m, 1H), 2.17−2.09 (m, 2H), 1.79 (dt, *J* = 13.0, 3.5 Hz, 2H), 1.68 (dt, *J* = 12.5, 3.5 Hz, 1H), 1.47−1.38 (m, 2H), 1.28−1.17 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) *δ* 144.9, 135.3, 128.9, 127.6, 127.2, 126.2, 125.7, 121.7, 118.2, 104.7, 51.7, 33.3, 25.9, 25.0.

*N-Phenylnaphthalen-2-amine (**5e**, CAS: 135-88-6).*[13] *β*-Tetralone (54 μL, 0.4 mmol) and aniline (18 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5e** as yellow solid, 27.6 mg, yield 63%. Mp:

104−106 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.48 (s, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.34−7.29 (m, 3H), 7.25−7.23 (m, 1H), 7.19 (d, J = 7.8 Hz, 2H), 7.00 (t, J = 7.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 142.7, 140.7, 134.6, 129.4, 129.2, 127.6, 126.5, 126.5, 123.6, 121.7, 120.0, 118.4, 112.0.

*2-(Naphthalen-2-ylamino)benzonitrile (**5f**).* β-Tetralone (54 μL, 0.4 mmol) and 2-aminobenzonitrile (23.6 mg, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5f** as white solid, 16.1 mg, yield 33%. Mp:119−121 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (t, J = 9.2 Hz, 2H), 7.73 (d, J = 8.1 Hz, 1H), 7.58 (s, 1H), 7.55−7.51 (m, 1H), 7.49−7.36 (m, 3H), 7.34−7.27 (m, 2H), 6.87 (t, J = 7.5 Hz, 1H), 6.52 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 147.1, 137.4, 134.1, 133.9, 133.1, 130.6, 129.5, 127.7, 127.0, 126.7, 125.0, 121.8, 119.5, 117.6, 117.5, 114.5, 98.7; HRMS calcd. for: $C_{17}H_{13}N_2^+$ $(M+H)^+$ 245.1073, found 245.1074.

*N-(m-Tolyl)naphthalen-2-amine (**5g**, CAS: 76783-57-8).*[21] β-Tetralone (54 μL, 0.4 mmol) and *m*-toluidine (21 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 100:1) to give **5g** as red oil, 29.4 mg, yield 63%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.43−7.37 (m, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.23−7.16 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 7.4 Hz, 1H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz,

Chloroform-*d*) δ 142.8, 140.9, 139.3, 134.6, 129.2, 129.1, 129.1, 127.6, 126.5, 126.4, 123.5, 122.4, 120.1, 119.0, 115.4, 111.7, 21.5.

*N-(4-Methoxyphenyl)naphthalen-2-amine (**5h**, CAS: 6949-67-3).*[22] β-Tetralone (54 μL, 0.4 mmol) and *p*-anisidine (24.6 mg, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5h** as yellow solid, 22.9 mg, yield 46%. Mp: 104−106 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72−7.68 (m, 2H), 7.58 (d, J = 8.2 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.26 (s, 1H), 7.22 (s, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.11 (dd, J = 8.8, 2.2 Hz, 1H), 6.94−6.88 (m, 2H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 155.6, 142.9, 135.5, 134.8, 129.1, 128.6, 127.6, 126.4, 126.2, 122.9, 122.6, 118.9, 114.7, 108.8, 55.5.

*N-(4-Fluorophenyl)naphthalen-2-amine (**5i**, CAS: 582-05-8).*[22] β-Tetralone (54 μL, 0.4 mmol) and 4-fluoroaniline (19 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5i** as yellow solid, 18.1 mg, yield 38%. Mp: 84−86 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72−7.76 (m, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.41−7.36 (m, 1H), 7.30−7.25 (m, 2H), 7.13−7.08 (m, 3H), 7.00 (t, J = 8.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.2 (d, $J_{C\text{-}F}$ = 240.6 Hz), 141.6, 138.7 (d, J = 2.5 Hz), 134.6, 129.3, 128.9, 127.6, 126.5, 126.3, 123.3, 121.0 (d, J = 7.8 Hz), 119.3, 116.0 (d, J = 22.4 Hz), 110.3.

*N-(4-chlorophenyl)naphthalen-2-amine (**5j**, CAS: 55566-60-4).*[23] β-Tetralone (54 μL, 0.4 mmol) and 4-chloroaniline (25.5 mg, 0.2 mmol) were used as the substrates under

the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5j** as red solid, 23.3 mg, yield 46%. Mp: 102−104 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.44−7.38 (m, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.26−7.22 (m, 2H), 7.18 (dd, J = 8.8, 2.3 Hz, 1H), 7.09−7.04 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 141.6, 140.3, 134.5, 129.3, 129.3, 127.7, 126.6, 126.5, 125.9, 123.8, 120.0, 119.3, 112.1.

*N-(4-Bromophenyl)naphthalen-2-amine (**5k**, 70539-21-8).*[23] β-Tetralone (54 μL, 0.4 mmol) and 4-bromoaniline (34.4 mg, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5k** as white solid, 32.7 mg, yield 55%. Mp: 113−115 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, J = 8.6 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.44−7.35 (m, 4H), 7.32 (t, J = 7.5 Hz, 1H), 7.18 (dd, J = 8.8, 2.3 Hz, 1H), 7.04−6.98 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 142.2, 140.1, 134.5, 132.3, 129.4, 129.3, 127.7, 126.6, 126.5, 123.8, 120.1, 119.5, 113.0, 112.4.

*N-(4-(Trifluoromethoxy)phenyl)naphthalen-2-amine (**5l**).* β-Tetralone (54 μL, 0.4 mmol) and 4-trifluoromethoxyaniline (27 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5l** as yellow solid, 25.5 mg, yield 42%. Mp: 59−61 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.2 Hz, 1H), 7.44−7.39 (m, 2H), 7.32 (t, J = 7.4 Hz,

1H), 7.19 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.15−7.08 (m, 4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 143.0, 141.9, 140.2, 134.5, 129.4, 129.3, 127.7, 126.6, 126.5, 123.8, 122.4, 120.6 (q, $J_{C\text{-}F}$ = 256.3 Hz), 120.1, 118.6, 112.4; HRMS calcd. for: $C_{17}H_{13}F_3NO^+$ $(M+H)^+$ 304.0944, found 304.0947.

*Methyl 4-(Naphthalen-2-ylamino)benzoate (**5m**).*[24] *β*-Tetralone (54 μL, 0.4 mmol) and methyl 4-aminobenzoate (30.2 mg, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5m** as yellow solid, 30.5 mg, yield 55%. Mp: 177−179 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98−7.93 (m, 2H), 7.79 (t, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 2.3 Hz, 1H), 7.48−7.42 (m, 1H), 7.40−7.35 (m, 1H), 7.29 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.09−7.04 (m, 2H), 3.88 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 167.0, 147.9, 138.4, 134.3, 131.5, 130.1, 129.4, 127.7, 126.8, 126.6, 124.5, 121.4, 121.2, 115.5, 114.9, 51.7.

*N-(4-(Trifluoromethyl)phenyl)naphthalen-2-amine (**5n**).* *β*-Tetralone (54 μL, 0.4 mmol) and 4-aminobenzotrifluoride (25 μL, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5n** as yellow solid, 39.6 mg, yield 69%. Mp: 96−98 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80−7.76 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.54−7.47 (m, 3H), 7.44 (t, *J* = 7.1 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, Chloroform-*d*) δ 146.6, 138.8, 134.3, 130.0, 129.4, 127.7,

126.8, 126.7 (q, J = 4.0 Hz), 126.7, 124.6 (q, $J_{C\text{-}F}$ = 270.5 Hz), 124.4, 122.0 (q, J = 32.4 Hz), 120.9, 115.7, 114.9; HRMS calcd. for: $C_{17}H_{13}F_3N^+$ $(M+H)^+$ 288.0994, found 288.0998.

*4-(Naphthalen-2-ylamino)benzonitrile (**5o**, CAS: 1292486-76-0).*[25] β-Tetralone (54 μL, 0.4 mmol) and 4-aminobenzonitrile (23.6 mg, 0.2 mmol) were used as the substrates under the given reaction conditions. The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give **5o** as yellow solid, 31.8 mg, yield 65%. Mp: 142−144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (t, J = 8.4 Hz, 2H), 7.72 (d, J = 8.1 Hz, 1H), 7.57 (s, 1H), 7.51−7.37 (m, 4H), 7.28 (dd, J = 8.8, 2.1 Hz, 1H), 7.04 (d, J = 8.8 Hz, 2H), 6.30 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 147.8, 137.6, 134.1, 133.8, 130.4, 129.5, 127.7, 126.9, 126.7, 124.9, 121.5, 119.9, 116.7, 115.2, 101.7.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc

Copies of ^{1}H NMR and ^{13}C NMR spectra for all products

AUTHOR INFORMATION

Corresponding Author

*E-mail: hwhuang@xtu.edu.cn.

*E-mail: gjdeng@xtu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We are grateful for financial support from the National Natural Science Foundation of China (21871226, 21372187), the Science and Technology Planning Project of Hunan Province (2019RS2039), and the Collaborative Innovation Center of New Chemical Technologies for Environmental Benignity and Efficient Resource Utilization.

References:

(1) (a) Law, K.-Y. Organic photoconductive materials: recent trends and developments. *Chem. Rev.* **1993**, *93*, 449. (b) D'Aproano, G.; Lecleric, M.; Zotti, G.; Schiavon, G. Synthesis and Characterization of Polyaniline Derivatives: Poly(2-alkoxyanilines) and Poly(2,5-dialkoxyanilines). *Chem. Mater.* **1995**, *7*, 33. (c) Horton, D.-A.; Bourne, G.-T.; Smythe, M. L. The Combinatorial Synthesis of Bicyclic Privileged Structures or Privileged Substructures. *Chem. Rev.* **2003**, *103*, 893. (d) Ohta, K.; Chiba, Y.; Ogawa, T.; Endo, Y. Bioorg. Promising core structure for nuclear receptor ligands: Design and synthesis of novel estrogen receptor ligands based on diphenylamine skeleton. *Med. Chem. Lett.* **2008**, *18*, 5050. (e) Ricci, A. *Amino Group Chemistry: From Synthesis to the Life Sciences*, Wiley-VCH, Weinheim, 2008.

(2) (a) Aubin, Y.; Fischmeister, C.; Thomas, C.; Renaud, J.-L.; Direct amination of aryl halides with ammonia. *Chem. Soc. Rev.* **2010**, *39*, 4130. (b) Bariwal, J.;

Eycken, E. C–N bond forming cross-coupling reactions: an overview. *Chem. Soc. Rev.* **2013**, *42*, 9283. (c) Zhao, Y.; Xia, W. Recent advances in radical-based C–N bond formation via photo-/electrochemistry. *Chem. Soc. Rev.* **2018**, *47*, 2591.

(3) Ould, D.-M.-C.; Melen, R.-L. Arsenic Catalysis: Hydroboration of Aldehydes Using a Benzo-Fused Diaza-benzyloxy-arsole. *Chem. Eur. J.* **2018**, *24*, 15201.

(4) Rivas, F.-M.; Riaz, U.; Giessert, A.; Smulik, J.-A.; Diver, S.-T. A Versatile Synthesis of Substituted Benzimidazolium Salts by an Amination/Ring Closure Sequence. *Org. Lett.* **2001**, *3*, 2673.

(5) Page, P.; Buckley, B.; Christie, S.; Edgar, M.; Poulton, A.; Elsegood, M.; McKee, V. A new paradigm in *N*-heterocyclic carbenoid ligands *J. Organomet. Chem.* **2005**, *690*, 6210.

(6) Huang, W.; Guo, J.; Xiao, Y.; Zhu, M.; Zou, G.; Tang, J. Palladium–benzimidazolium salt catalyst systems for Suzuki coupling: development of a practical and highly active palladium catalyst system for coupling of aromatic halides with arylboronic acids. *Tetrahedron* **2005**, *61*, 9783.

(7) Jia, Y.-X.; Katayev, D.; Bernardinelli, G.; Seidel, T.-M.; Kündig, E.-P. New Chiral *N*-Heterocyclic Carbene Ligands in Palladium-Catalyzed α-Arylations of Amides: Conformational Locking through Allylic Strain as a Device for Stereocontrol. *Chem. Eur. J.* **2010**, *16*, 6300.

(8) He, W.; Zhao, W.; Zhou B.; Liu, H.; Li, X.; Li, L.; Li, J.; Shi, J. Synthesis of C_2-Symmetric Benzimidazolium Salts and Their Application in Palladium-Catalyzed Enantioselective Intramolecular α-Arylation of Amides.

Molecules **2016**, *21*, 742.

(9) (a) Surry, D.-S.; Buchwald S.-L. Biaryl Phosphane Ligands in Palladium-Catalyzed Amination. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338. (b) Surrya, D.-S.; Buchwald, S.-L. Dialkylbiaryl phosphines in Pd-catalyzed amination: a user's guide. *Chem. Sci.* **2011**, *2*, 27.

(10) (a) Ley, S.; Thomas A. Modern Synthetic Methods for Copper-Mediated C(aryl)-O, C(aryl)-N, and C(aryl)-S Bond Formation. *Angew. Chem. Int. Ed.* **2003**, *42*, 5400. (b) Beletskaya, I.-P.; Cheprakov A.-V. Copper in cross-coupling reactions: The post-Ullmann chemistry. *Coord. Chem. Rev.* **2004**, *248*, 2337.

(11) For synthetic methods via dehydrogenative aromatization of cyclohexanones, see: (a) Girard, S.; Huang, H.; Zhou, F.; Deng, G.-J.; Li C.-J. Catalytic dehydrogenative aromatization: an alternative route to functionalized arenes. *Org. Chem. Front.* **2015**, *2*, 279. (b) Liu, X.; Chen, J.; Ma, T. Catalytic dehydrogenative aromatization of cyclohexanones and cyclohexenones. *Org. Biomol. Chem.* **2018**, *16*, 8662. (c) Xu, Z.; Huang, H.; Chen, H.; Deng, G.-J. Catalyst- and additive-free annulation/aromatization leading to benzothiazoles and naphthothiazoles. *Org. Chem. Front.* **2019**, *6*, 3060. (d) Lu, C.; Huang, H.; Tuo, X.; Jiang, P.; Zhang, F.; Deng, G.-J. Chemoselective metal-free indole arylation with cyclohexanones. *Org. Chem. Front.* **2019**, *6*, 2738.

(12) For representative examples, see: (a) Xie, Y.; Liu, S.; Liu, Y.; Wen, Y.; Deng, G.-J. Palladium-Catalyzed One-Pot Diarylamine Formation from Nitroarenes and Cyclohexanones. *Org. Lett.* **2012**, *14*, 1692. (b) Hong, W.; Iosub, A.; Stahl, S.

Pd-Catalyzed Semmler–Wolff Reactions for the Conversion of Substituted Cyclohexenone Oximes to Primary Anilines. *J. Am. Chem. Soc.* **2013**, *135*, 13664. (c) Koizumi,Y.; Jin, X.; Yatabe, T.; Miyazaki, R.; Hasegawa, J.-y.; Nozaki, K.; Mizuno, N.; Yamaguchi, K. Selective Synthesis of Primary Anilines from NH_3 and Cyclohexanones by Utilizing Preferential Adsorption of Styrene on the Pd Nanoparticle Surface. *Angew. Chem. Int. Ed.* **2019**, *58*, 10893, and references cited therein.

(13) Xiong, M.; Gao, Z.; Liang, X.; Cai, P.; Zhu, H.; Pan, Y. Iodine-catalyzed synthesis of *N,N′*-diaryl-*o*-phenylenediamines from cyclohexanones and anilines using DMSO and O_2 as oxidants. *Chem. Commun.* **2018**, *54*, 9679.

(14) For elemental sulfur-mediated C-N bond formation, see: (a) Wang, Z.; Chen, X.; Xie, H.; Wang, D.; Huang, H.; Deng, G.-J. Synthesis of *o*-Arylenediamines through Elemental Sulfur-Promoted Aerobic Dehydrogenative Aromatization of Cyclohexanones with Arylamines. *Org. Lett.* **2018**, *20*, 5470. (b) Xie, Y.; Chen, X.; Wang, Z.; Huang, H.; Yi, B.; Deng, G.-J. Metal-free oxidative cyclization of 2-aminobenzothiazoles and cyclic ketones enabled by the combination of elemental sulfur and oxygen. *Green Chem.* **2017**, *19*, 4294. (c) Chen, X.; Wang, Z.; Huang, H.; Deng, G.-J. Elemental Sulfur-Promoted Aerobic Cyclization of Ketones and Aliphatic Amines for Synthesis of Tetrasubstituted Imidazoles. *Adv. Synth. Catal.* **2018**, *360*, 4017. (d) Tan, J.; Ni P.; Huang, H.; Deng, G.-J. Metal- and base-free synthesis of imidazo[1,2-*a*]pyridines through elemental sulfur-initiated oxidative annulation of 2-aminopyridines and aldehydes. *Org.*

Biomol. Chem. **2018**, *16*, 4227. (e) Xu, Z.; Deng, G.-J.; Zhang, F.; Chen, H.; Huang, H. Three-Component Cascade Bis-heteroannulation of Aryl or Vinyl Methylketoxime Acetates toward Thieno[3,2-*c*]isoquinolines. *Org. Lett.* **2019**, *21*, 8630. (f) Shibahara, F.; Sugiura, R.; Yamaguchi, E.; Kitagawa, A.; Murai, T. Synthesis of Fluorescent 1,3-Diarylated Imidazo[1,5-*a*]pyridines: Oxidative Condensation−Cyclization of Aryl-2-Pyridylmethylamines and Aldehydes with Elemental Sulfur as an Oxidant. *J. Org. Chem.* **2009**, *74*, 3566.

(15) (a) Huang, H.; Cai, J.; Ji, X.; Xiao, F.; Chen, Y.; Deng, G.-J. Internal Oxidant-Triggered Aerobic Oxygenation and Cyclization of Indoles under Copper Catalysis. *Angew. Chem., Int. Ed.* **2016**, *55*, 307. (b) Wang, Z.; Liu, Q.; Ji, X.; Deng, G.-J.; Huang, H. Bromide-Promoted Visible-Light-Induced Reductive Minisci Reaction with Aldehydes. *ACS Catal.* **2020**, *10*, 154. (c) Wang, Z.; Ji, X.; Zhao, J.; Huang, H. Visible-light-mediated photoredox decarbonylative Minisci-type alkylation with aldehydes under ambient air conditions. *Green Chem.* **2019**, *21*, 5512. (d) Jiang, J.; Huang, H.; Deng, G.-J. Four-component thiazole formation from simple chemicals under metal-free conditions. *Green Chem.* **2019**, *21*, 986.

(16) Chen, Z.; Zeng, H.; Girard, S. A.; Wang, F.; Chen, N.; Li, C. J. Formal Direct Cross-Coupling of Phenols with Amines. *Angew. Chem. Int. Ed*. **2015**, *54*, 14487.

(17) Li, Y. J.; Zhang, L.; Yan, N.; Meng, X. H.; Zhao, Y. L. Acid/Base-Co-catalyzed Direct Oxidative *α*-Amination of Cyclic Ketones: Using Molecular Oxygen as the Oxidant. *Adv. Synth. Catal.* **2018**, *360*, 455.

(18) Nguyen, T. B.; Retailleau, P. Elemental Sulfur as Reaction Medium for the Synthesis of Fused Nitrogen Heterocycles by Oxidative Coupling between Cycloalkanones and Nitrogen Nucleophiles. *Adv. Synth. Catal.* **2017**, *359*, 3843.

(19) (a) Forkosh, H.; Vershinin, V.; Reiss, H.; Pappo, D. Stereoselective Synthesis of Optically Pure 2-Amino-2′-hydroxy-1,1′-binaphthyls. *Org. Lett.* **2018**, *20*, 2459. (b) Meadows, R. E.; Woodward, S. Steric effects in palladium-catalysed amination of aryl triflates and nonaflates with the primary amines $PhCH(R)NH_2$ (R=H, Me). *Tetrahedron* **2008**, *64*, 1218.

(20) Li, X.; Yang, D.; Jiang, Y.; Fu, H. Efficient copper-catalyzed *N*-arylations of nitrogen-containing heterocycles and aliphatic amines in water. *Green Chem.* **2010**, *12*, 1097.

(21) Novaled, G.; Koehller, M.; Koehler, M.; Wallikewitz, B. Phosphorescent OLED and Hole Transporting Materials for Phosphorescent OLEDs. US2017/47519 A1, 2017-02-16, 2017.

(22) Mishra, A. K.; Verma, A.; Biswas, S. Nucleophilic *ipso*-Substitution of Aryl Methyl Ethers through Aryl C–OMe Bond Cleavage; Access to Functionalized Bisthiophenes. *J. Org. Chem.* **2017**, *82*, 3403.

(23) Li, X.; Wu, W.; Fan, X.; Yang, L. A facile, regioselective and controllable bromination of aromatic amines using a $CuBr_2$/Oxone® system. *RSC Adv.* **2013**, *3*, 12091.

(24) Cui, H.; Kamal, Z.; Ai, T.; Xu, Y.; More, S.; Wilson, D. J.; Chen, L. Discovery of Potent and Selective Sirtuin 2 (SIRT2) Inhibitors Using a Fragment-Based

Approach. *J. Med. Chem.* **2014**, *57*, 8340.

(25) Samsung Mobile Display Co., Ltd.; Jung, H.-J.; Hwang, S.-H.; Kim, Y.-K.; Lim, J.-O.; Han, S.-H.; Kim, S.-Y.; Yun, J.-Y.; Lee, J.-H. Heterocyclic compound and organic light-emitting diode including the same. US2013/112948 A1, 2013-05-09, 2013.