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Shimomoto, Yuya
Matsubara, Ryosuke
Hayashi, Masahiko

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Synthesis of Arylamines via *Non-aerobic* Dehydrogenation Using a Palladium/Carbon–Ethylene System

Yuya Shimomoto,[a] Ryosuke Matsubara,[a] and Masahiko Hayashi[a]*

[a] Department of Chemistry, Graduate School of Science, Kobe University, Nada, Kobe 657-8501, Japan
Fax: (+81)-78-803-5688
E-mail: mhayashi@kobe-u.ac.jp

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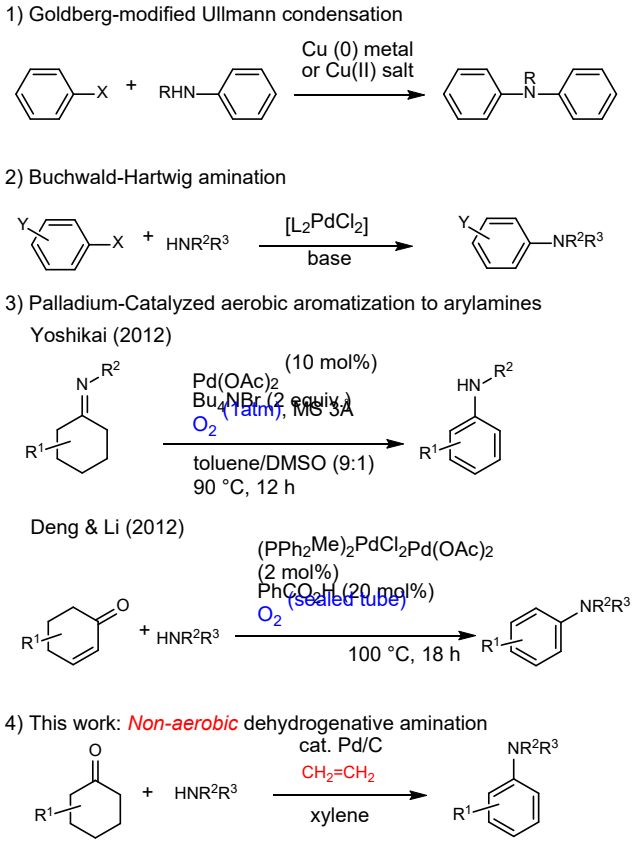
Abstract. The reaction of cyclohexanones with amines proceeded under an ethylene atmosphere in the presence of a catalytic amount of Pd/C to afford a variety of arylamines in good to high yields. The present reaction was carried out under completely non-aerobic conditions, and which is in contrast with the previously reported aerobic system. has wide applicability affording a variety of aromatic amines, and co-product of the reaction is only gaseous ethane. Thus, this method is environmentally friendly. This protocol was applied intramolecularly to provide a novel method for the construction of quinoline and isoquinoline compounds.

Keywords: Arylamines; Palladium/Carbon; Ethylene; Dehydrogenation; Amination

Introduction

Arylamines often constitute common and useful moieties found in biologically active compounds, such as pharmaceuticals and agrochemicals, and electronic materials.[1] A conventional method for the synthesis of biaryl amines is the so-called Goldberg-modified Ullmann condensation reaction, which has been developed and improved since its first discovery in 1906 by Goldberg. [2,3] After the pioneering work by Migita and Kosugi in the palladium-catalyzed amination reaction, [4] Buchwald and Hartwig have expanded the reaction scope of arylamines in the synthesis of arylamines (Scheme 1). [5-13]

Recently, Yoshikai and co-workers reported a palladium-catalyzed *aerobic* amination of cyclohexanone imines to arylamines using 10 mol% $Pd(OAc)_2$, 2 equiv of Bu_4NBr, and MS 3Å under O_2 atmosphere (1 atm) in DMSO at 90 ºC. [14] In their report, they also demonstrated the direct reaction of cyclohexanones with amines to give arylamines in low to moderate yields (18–67% yield) under the same reaction conditions. However, some ketones such as 1-tetralone and 2-substituted cyclohexanones with amines such as morpholine and anilines bearing electron-withdrawing *para*-substituents gave the corresponding arylamines only in < 5% yield. Deng and Li also reported a palladium-catalyzed *aerobic* dehydrogenative aromatization for the synthesis of arylamines in the presence of 2 mol% $(PPh_2Me)_2PdCl_2$ and 20 mol% $PhCO_2H$ in in toluene



Scheme 1. Synthetic Methods for Arylamines

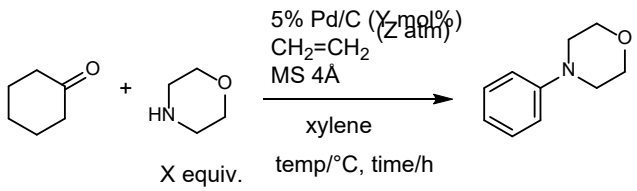
at 100 °C under O_2 atmosphere in a sealed vessel. [15] In their report, 2-cyclohexen-1-ones and a variety of secondary amines were employed as substrates. However, in the reaction of cyclohexanones, suitable amines were limited to only substituted anilines under slightly modified catalytic conditions (5 mol% $Pd(OAc)_2$ and 10 mol% 1,10-phenanthroline). [15] More recently, Lemaire and co-workers also reported a similar type of dehydrogenative amination under aerobic and non-aerobic conditions.[16] Li and co-workers reported the use of phenols as coupling partners instead of aryl halides in palladium-catalyzed reaction. [17] Mizuno and co-workers also described the synthesis of *N*-substituted anilines via dehydrogenative aromatization using supported gold-palladium alloy nanoparticles catalyst (Au-Pd/Al_2O_3) [18] It should be mentioned that Stahl and co-workers reported several important dehydrogenative oxidation, which led to substituted aromatic compounds.[19]

On the other hand, we developed a non-aerobic oxidation of cyclohexanones and 1,3-cyclohexanediones to phenols and resorcinols, respectively using a Pd/C–ethylene system. [20,21] In this paper, we would like to report a new strategy for the synthesis of arylamines under *non-aerobic* conditions using simple Pd/C–ethylene system. The present method has a wider applicability compared to the methods of Yoshikai, and Deng and Li. In addition, this is the first report to convert cyclohexanones to arylamines by the use of a palladium catalyst under completely *non-aerobic* conditions.

Results and Discussion

To optimize the reaction conditions, we first examined the reaction of cyclohexanone with morpholine, which led to the formation of *N*-phenylmorpholine. [22] The reaction of cyclohexanone with morpholine in the presence of 1 mol% Pd/C under argon atmosphere (in the absence of ethylene) gave the mixture of *N*-phenylmorpholine and *N*-cyclohexylmorpholine in 53% and 44% yield, respectively (entry 1). When the reaction was carried out under ethylene atmosphere, *N*-cyclohexylmorpholine was not obtained (entries 2–12). These results mean that ethylene works as an efficient hydrogen acceptor. Subsequently, we examined the reaction of 5-methyl-1,3-cyclohexanedione with a variety of alcohols. The results obtained are summarized in Table 1.

Table 1. Optimization of the reaction of cyclohexanone with morpholine[a]

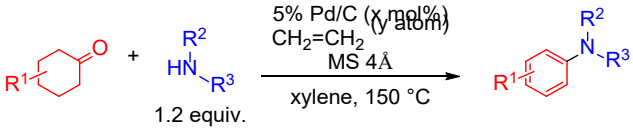


entry	X	Y	Z	temp (°C)	time (h)	yield (%)[b]
1	1.2	1	0[c]	150	4	53[d,e]
2	1.2	1	3	150	24	78
3	1.2	1	1	150	8	84
4	1.2	1	1	150	4	82
5	1.2	1	1	150	2	73
6	1.2	1	1	150	1	46
7	1.2	1	1	100	4	33
8	1.2	1	1	70	4	trace
9	1.2	5	1	150	4	76
10	1.2	10	1	150	4	73
11	2	1	1	150	4	74
12	5	1	1	150	4	77

[a] All reactions were carried out using autoclave.
[b] Isolated yields unless otherwise noted.
[c] Reaction was carried out under argon atmosphere.
[d] Yield was determined by GC analysis.
[e] *N*-cyclohexylmorpholine was obtained in 44% yield.

The results of this screening are shown in Table 1, from which the standard conditions were chosen as follows: ratio of ketone:amine = 1:1.2, Pd/C (1 mol%), CH_2=CH_2 (1 atm), in the presence of MS 4Å, in xylene at 150 °C for 24 h. Under the standard conditions, the reaction of various cyclohexanones and amines was next investigated (Table 2).

Table 2. Reaction of substituted ketones with amines[a]



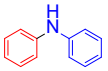
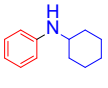
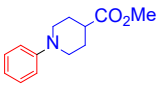
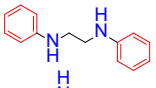
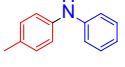
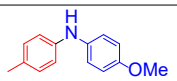
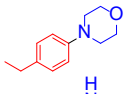
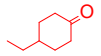
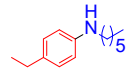
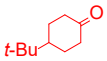
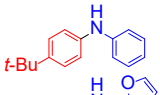
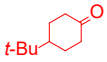
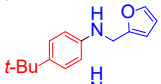
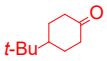
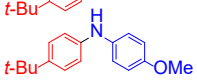
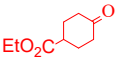
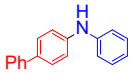
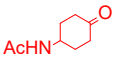
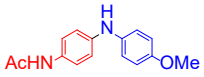
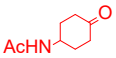
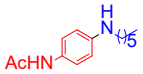
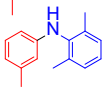
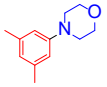
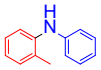
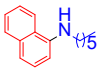
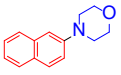
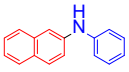
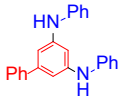
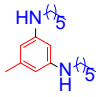
entry	substrate	x (mol%)	y (atm)	time (h)	product	yield (%)[b]
1[c,d]		2	3	24		82[e]
2[c]		1	1	4		84
3		1	1	24		85
4[f]		10	1	24		48[g]
5[h]		1	1	24		32
6		3	1	24		90

Table 2 *(continued)*

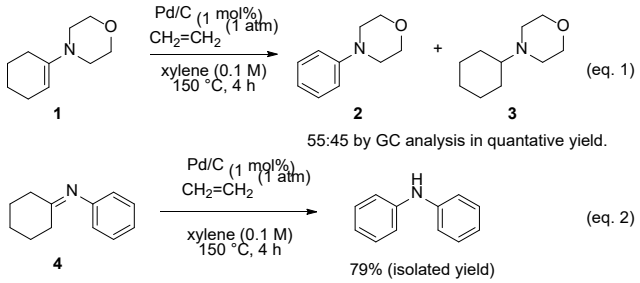
7		1	1	24		83
8		3	1	6.5		76
9		3	1	24		85
10[f]		1	1	24		87
11		1	1	24		65
12[c]		1	1	24		79
13		10	1	24		90
14		1	1	30		95
15		10	1	24		91
16		1	1	24		51
17		1	1	24		47
18		1	1	5		88
19[i]		10	1	48		78
20		1	1	5		69
21		5	1	96		60
22		1	1	24		81
23[e]		1	1	24		86
24		5	1	24		94
25[d]		5	1	72		23
26[d]		10	3	24		25

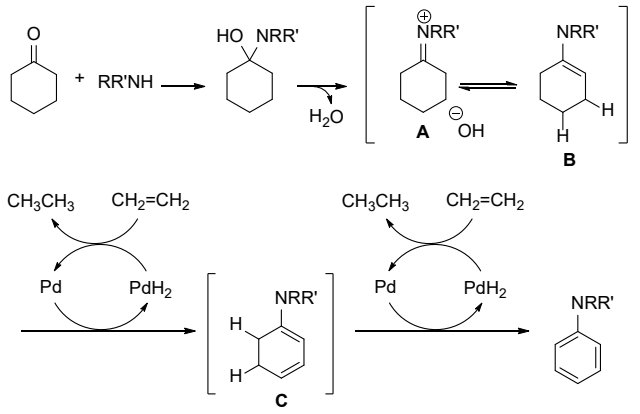
[a] All reactions were carried out using autoclave.
[b] Isolated yield unless otherwise noted.
[c] Without MS 4A.
[d] ketone:amine = 1:5
[e] ketone:amine = 1:2..
[f] Determined by ^{1}H NMR analysis.
[g] ketone:diamine = 2:1.
[h] ketone:amine = 1:3.
[i] Ref. 23 and see Supporting Information.

Cyclohexanone reacted with primary and secondary amines such as aniline, morpholine, and cyclohexylamine under an ethylene atmosphere (1–3 atm) in the presence of Pd/C (1–2 mol%) to afford the corresponding phenylamines in 82–85% yields (entries 1–3). Instead, the reaction with methyl 4-piperidinecarboxylate gave methyl *N*-phenylpiperidine-4-carboxylate in much lower yield (48% yield, entry 4) despite the higher loadings of Pd/C (10 mol%). The reaction of two equiv. of cyclohexanone with ethylenediamine gave diphenylethylenediamine in also a low yield (32% yield, entry 5). 4-Substituted (methyl, *t*-butyl, CO_2Et, phenyl) cyclohexanones reacted with primary and secondary amines to afford the corresponding amines in good to high yields (entries 6–15) except 4-acetoamidocyclohexanone, which afforded the corresponding products in moderate yields (entries 16 and 17). 2- and 3-Methyl and 3,5-dimethyl cyclohexanone reacted with morpholine and anilines to give the corresponding substituted phenyl amines in 60–80% yields (entries 18–21). The reactions of 1- and 2-tetralone also proceeded to give the corresponding amines in high yields (81–94%, entries 22–24). Instead, the reactions of 5-phenyl and 3-methylcyclohexane-1,3-diones with primary amines gave the corresponding diamines in only low yields (23–25%) despite the prolonged reaction times and increased catalyst loadings (entries 25 and 26). Furthermore, it should be noted the reaction of 4-methylcyclohexanone with diphenylamine in the presence of 5 mol% of Pd/C under ethylene atmosphere (1 atm) at 150 ºC for 72 h in xylene gave only 9% of 4-methyl-*N,N*-diphenylaniline and most of the starting material was remained.

We propose the mechanism shown in Scheme 2, based on some supporting experiments. The formation of the hemiaminal of cyclohexanone begins via the reaction of cyclohexanone with the amine, followed by the loss of water to give imine **A**, which readily transformed to the corresponding enamine **B**. Both, imine **A** and enamine **B** may react with Pd/C to lose one molecule of hydrogen and, thus afford intermediate **C** as well as the Pd(H_2)/C species. We performed two independent experiments to identify the tautomer (**A** or **B**) involved in the reaction mechanism. The reaction of enamine 4-(1-cyclohexene-1-yl)-morpholine **1**, derived from cyclohexanone and secondary amine morpholine, under standard conditions gave not only 4-phenylmorpholine **2** but also 4-cyclohexylmorpholine **3** in a ratio of 55:45 in quantitative yield even in the presence of ethylene (eq. 1). This indicates that the double bond in the enamine acts as a hydrogen acceptor, however, actually, excess amount of ethylene as a hydrogen acceptor exists, therefore, the formation of 4-cyclohexylmorpholine **3** was not observed. The reaction of cyclohexanone with a primary amine such as aniline, also proceed via imine **A** and enamine **B**, because treatment of *N*-cyclohexylidene benzeneamine **2** with Pd/C (1 mol%) gave diphenylamine in 79% yield without the

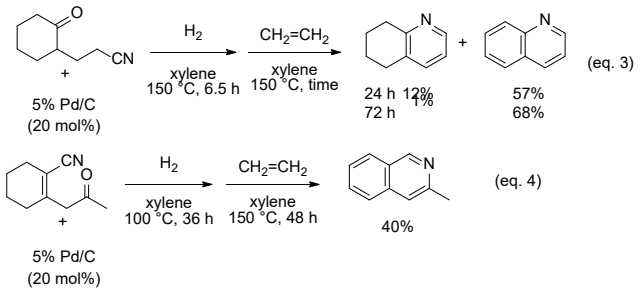
formation of cyclohexylphenylamine (eq. 2). This result indicates both of imine **A** and enamine **B**, may work as a hydrogen acceptor, however both of them work only as an intermediate.[24] The obtained $Pd(H_2)/C$ catalyst then undergoes hydrogen transfer to ethylene to regenerate the free Pd/C species and ethane. Finally, intermediate **C** undergoes Pd/C-catalyzed dehydrogenation to give the aromatic amine product. It should be noted that phenol and enones were ineffective as amination reaction substrates (see Supporting Information eq. S3, eq. S4 and eq. S5, eq. S6, Table S3, respectively).[25]





Scheme 2. Possible mechanism for the formation of arylamines.

Finally, we attempted our amination strategy in an intramolecular reaction that would generate quinoline and isoquinoline derivatives. [26,27] Thus, the treatment of the cyclohexanone possessing a cyano group at an appropriate position (3-(2-oxocyclohexyl)propionitrile), with 5% Pd/C (20 mol%) under a H_2 atmosphere in xylene at 150 ºC for 6.5 h, followed by the replacement of H_2 with ethylene, afforded 5,6,7,8-tetrahydroquinoline and quinoline in 12% and 57% (24 h) and in 1% and in 68% yield (72 h), respectively (eq. 3) (For optimization, see Supporting Information Table S4). This indicates that oxidative aromatization of 1,2,3,4-tetrahydroquinoline proceeds faster than that of 5,6,7,8-tetrahydroquinoline. This hypothesis was corroborated with experimentally; it only took 1 h to obtain quinolone in 92% yield from 1,2,3,4-tetrahydroquinoline, whereas, it took 8 h to obtain quinolone in 92% yield from 5,6,7,8-tetrahydroquinoline (see Supporting Information Figure S1-1 and S1-2). Furthermore, 2-methylisoquinoline was obtained in 40% yield using the same protocol for the reaction of 2-(propyl-2-on)-cyclohex-1-encarbonitrile (eq. 4) (For optimization, see Supporting Information Table S5).[28]



Conclusion

In conclusion, we have developed a non-aerobic dehydrogenative amination of ketones with amines in the presence of a catalytic amount of Pd/C under an ethylene atmosphere. This strategy is simple and has wide applicability affording a variety of aromatic amines. It should be mentioned that ethylene is widely used in the chemical industry, and its worldwide production exceeds that of any other organic compound. [29] Furthermore, the advantage of Pd/C–ethylene system is that co-product of the reaction is only gaseous ethane.[22] Further studies on the reaction mechanism and synthetic applications are currently ongoing in our laboratory.

Experimental Section

General. All reactions were carried out in oven-dried glassware under magnetic stirring. All starting materials were obtained from commercial sources or were synthesized using standard procedures. Melting points were measured on a Yanaco MP-500D instrument and were not corrected. ^1H and ^{13}C NMR spectra (400 and 100 MHz, respectively) were recorded on a Bruker Avance III HD 400 spectrometer; TMS (0 ppm) and $CDCl_3$ (77.0 ppm) were used as internal standards, respectively. The following abbreviations are used to describe NMR peak multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. GC mass spectra were measured on a Thermo Auest LCQ DECA Plus instrument with GL Sciences Inc. Inert Cap5 as a column (70–310 °C). GC analyses were performed using a Shimadzu GC-2025 gas chromatograph equipped with GL Science Inert Cap5 (70–310 °C). HRMS was measured using JEOL JMS-T100LP. Preparative column chromatography was performed with Fuji Silysia BW-4:10MH silica-gel or YMC–GEL Silica (6 nm I-40-63 μm). Thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminum sheets.

Typical procedure for the reaction of cyclohexanone with morpholine in the presence of Pd/C under ethylene atmosphere. In the autoclave were added 4A molecular sieves (45 mg), 5% Pd/C (10.6 mg, 1 mol%), cyclohexanone (49 mg, 0.5 mmol), morpholine (52 mg, 0.6 mmol) and xylene (5 mL). The reaction mixture was capped under 1 atm pressure of ethylene gas. After stirring for 24 h at 150 ℃, the reaction mixture was cooled to ambient temperature and then filtered through celite. The solvent was removed in vacuo. The obtained residue was purified by silica-gel column chromatographed using hexane and ethyl acetate (10:1) as an eluent.

***N*-Phenylaniline:**[30] pale brown solid; mp 45.0–45.1 °C (lit. [30] mp 53 °C); IR (neat) 568, 615, 642, 688, 701, 742, 875, 993, 1023, 1073, 1084, 1158, 1172, 1220, 1243, 1307, 1417, 1458, 1493, 1513, 1588, 3048, 3382; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.60 (br s, 1H), 6.82 (t, 2H), 6.97 (d, 4H), 7.16 (t, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ =117.7, 120.9, 129.3, 143.0.

***N*-Phenylmorpholine:**[31] colorless solid; mp 42.1–42.3 °C (lit. [31] 49–51 °C); IR (neat) 534.9, 617.3, 637.1, 698.7, 770.0, 858.6, 923.9, 990.6, 1025.0, 1034.0, 1048.8, 1064.6, 1116.8, 1175.6, 1223.6, 1258.4, 1298.5, 1334.3, 1375.6, 1447.6, 1493.5, 1596.6, 2823.5, 2854.6, 2887.9, 2960.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.16 (t, 4H), 3.87 (t, 4H), 6.87-6.94 (m, 3H), 7.27-7.31(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.3, 66.9, 115.6, 120.0, 129.1, 151.2.

***N*-Cyclohexylaniline:**[32] pale brown liquid; IR (eat) 690, 744, 851, 865, 887, 976, 993, 1027, 1070, 1116, 1146, 1177, 1255, 1319, 1366, 1430, 1449, 1502, 1599, 2851, 2925, 3012, 3050, 3397; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.28-1.30 (m, 3H), 1.40 (q, 2H), 1.68 (d, 1H), 1.79 (d, 2H), 2.09 (d, 2H), 3.27 (tt, 1H), 3.53 (br s, 1H), 6.61 (d, 2H), 6.69 (t, 1H), 7.18 (t, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 25.0, 25.9, 33.4, 51.6, 113.1, 116.7, 129.2, 147.3.

Methyl-*N*-phenylpiperidine-4-carboxylate: pale red liquid. IR (neat) 614, 648, 666, 692, 731, 751, 920, 993, 1032, 1043, 1104, 1168, 1194, 1250, 1312, 1387, 1434, 1448, 1495, 1597, 1731, 2810, 2951; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.87 (qd, 2H), 1.95 (dd, 2H), 2.44 (tt, 1H), 2.78 (dt, 2H), 3.63 (dt, 2H), 3.70 (s, 3H), 6.84 (t, 1H), 6.93 (d, 2H), 7.24 (dt, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 28.0, 40.9, 49.2, 51.7, 116.6, 119.7, 129.0, 151.5, 175.2; HRMS [DART$^+$]. m/z calcd for $C_{13}H_{18}NO_2$: 220.1338 $[M+H]^+$, Found: 220.1351 $[M + H]^+$.

***N,N*-Diphenylethylenediamine:**[33] red liquid; IR (neat) 691, 741, 863, 909, 989, 1027, 1068, 1096, 1148, 1178, 1212, 1263, 1295, 1319, 1341, 1433, 1495, 1511, 1596, 2868, 2921, 2945, 3050, 3415; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 3.41 (s, 4H), 6.67 (d, 4H), 6.77 (t, 2H), 7.22 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =43.2, 113.0, 117.8, 129.3, 148.0.

***N*-Pheny-4-methylaniline:**[30] pale brown solid; mp 83.2–83.5 °C (lit. [30] 90 °C); IR (neat) 616, 692, 706, 744, 770, 806, 845, 874, 995, 1027, 1077, 1109, 1151, 1175, 1241, 1306, 1397, 1498, 1510, 1593, 3394; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.32 (s, 3H), 6.90 (t, 1H), 7.01 (dd, 4H), 7.10 (d, 2H), 7.25 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.7, 116.8, 118.9, 120.3, 129.3, 129.8, 130.9, 140.3, 144.0

***N*-(4-Methylphenyl)-4-methoxyaniline:** [30] gray solid; mp 83.9–84.1 °C (lit. [29] 82 °C); IR (neat) 528, 581, 640, 704, 767, 812, 879, 1033, 1106, 1125, 1179, 1241, 1295, 1315, 1377, 1439, 1466, 1513, 1611, 2835, 2910, 3013, 3414; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.28 (s, 3H), 3.79 (s, 3H), 5.39 (s, 1H), 6.83-6.87 (m, 4H), 7.02-7.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 20.5, 55.6, 114.6, 121.1, 129.3, 129.8, 136.6, 142.3, 154.7.

***N*-(4-Ethylphenyl)morpholine:** pale brown liquid; IR (neat) 608, 700, 732, 754, 822, 859, 929, 1068, 1120, 1232, 1262, 1230, 1329, 1377, 1449, 1515, 1612, 2818, 2853, 2959, 3009; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.23 (t, 3H), 2.59 (q, 2H), 3.13 (t, 4H), 3.87 (t, 4H), 6.87 (dt, 2H), 7.13 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 15.7, 27.9, 49.8, 67.0, 116.0, 128.5, 136.0, 149.3. HRMS [DART$^+$]. m/z calcd for $C_{12}H_{18}N_1O_1$: 192.1389 $[M+H]^+$, Found: 192.1395 $[M+H]^+$.

4-Ethyl-*N*-hexylaniline:[34] orange liquid; IR (neat) 725, 767, 817, 1033, 1181, 1257, 1315, 1376, 1409, 1464, 1479, 1518, 1615, 2855, 2925, 2957; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 0.89 (t, 3H), 1.19 (t, 3H), 1.30-1.43 (m, 6H), 1.61 (quin, 2H), 2.54 (q, 2H), 3.09 (t, 2H), 3.50 (br s, 1H), 6.56 (d, 2H), 7.01 (d, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 14.0, 16.0, 22.6, 26.9, 28.0, 29.6, 31.6, 44.3, 112.8, 128.5, 132.9, 146.5.

***N*-Phenyl-4-*tert*-butylaniline:**[35] pale yellow solid; mp 64.6–65.0 °C (lit. [35] 65–66 °C); IR (neat) 609, 689, 741, 804, 839, 851, 993, 1026, 1076, 1110, 1152, 1174, 1264, 1303, 1362, 1393, 1496, 1514, 1593, 1666, 2959, 3048, 3386. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.31 (s, 9H), 6.89 (t, 1H), 7.03 (d, 4H), 7.22-7.30 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.5, 34.2, 117.1, 118.1, 120.4, 126.1, 129.3, 140.3, 143.7, 144.2.

***N*-(2-Furanylmethyl)-4-*tert*-butylaniline:** yellow liquid; IR (neat) = 549, 598, 729, 819, 918, 1011, 1071, 1127, 1145, 1193, 1261, 1303, 1320, 1362, 1392, 1461, 1519, 1614, 1712, 2865, 2958, 3409. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.28 (s, 9H), 3.94 (br s, 1H), 4.30 (s, 2H), 6.24 (dd, 1H), 6.33 (dd, 1H), 6.64 (dt, 2H), 7.22 (dt, 2H), 7.37 (dd, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.5, 33.9, 41.7, 106.9, 110.3, 112.8, 126.0, 140.7, 141.8, 145.3, 152.9; HRMS [DART$^+$]. m/z calcd for $C_{15}H_{20}NO$: 230.1545 $[M+H]^+$, Found: 230.1562 $[M+H]^+$.

***N*-(4-*tert*-Butylphenyl)-4-methoxyaniline:**[36] yellow solid; mp 75.5–75.8 °C (lit.[36] 80–81 °C); IR (neat) 583, 639, 727, 764, 800, 817, 1029, 1066, 1109, 1181, 1192, 1232, 1265, 1292, 1324, 1360, 1392, 1453, 1470, 1508, 1607, 1715, 2832, 2959, 3034, 3380; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.20 (s, 9H), 3.69 (s, 3H), 6.75 (dt, 2H), 6.77 (d, 2H), 6.94 (d, 2H). 7.14 (dt, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 31.5, 34.0, 55.6, 114.6, 115.8, 121.4, 126.0, 128.3, 136.3, 142.4, 142.6, 154.8; HRMS [DART$^+$]. m/z calcd for $C_{17}H_{22}NO$: 256.1701 $[M+H]^+$, Found: 256.1700 $[M+H]^+$.

Ethyl-4-anilinobenzoate:[30] cololess solid; mp 109.1—109.4 °C (lit. [30] 111 °C); IR (neat) 582, 693, 750, 768, 806, 845, 960, 1019, 1109, 1173, 1249, 1271, 1334, 1364, 1407, 1475, 1495, 1528, 1587, 1676, 1687, 2965, 3338, 3365; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.38 (t, 3H), 4.33 (q, 2H), 7.00 (d, 2H), 7.06 (t, 1H), 7.17 (d, 2H), 7.33 (t, 2H), 7.92 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =14.4, 60.4, 114.5, 120.2, 121.3, 123.0, 129.4, 131.3, 140.9, 148.0, 166.5.

***N*-(4-Phenylphenyl)-morpholine:**[37] brown solid; mp 30.3—30.6 °C; IR (neat); 632, 693, 719, 762, 826, 864, 922, 1054, 1073, 1119, 1178, 1233, 1261, 1305, 1325, 1381, 1448, 1487, 1526, 1604, 2845; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 3.20 (t, 4H), 3.88 (t, 4H), 6.97 (d, 2H), 7.30 (t, 1H), 7.42 (t, 2H) 7.56 (t, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.1, 66.9, 115.7, 126.5, 127.8, 128.7, 132.7, 140.7, 150.5.

***N*-Phenyl-4-phenylaniline:**[38,39] colorlesshite solid; mp 113.9—114.2 °C (lit.[38] 113 °C); IR (neat) 630, 649, 692, 737, 759, 846, 879, 993, 1004, 1024, 1079, 1115, 1147, 1183, 1262, 1399, 1434, 1484, 1495, 1522, 1595, 3027, 3369, 3406; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 5.79 (br s, 1H), 6.96 (t, 1H), 7.13 (t, 4H), 7.29 (t, 3H), 7.42 (t, 2H), 7.51 (d, 2H), 7.57 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 117.8, 118.1, 121.2, 126.5, 126.6, 128.0, 128.7, 129.4, 133.7, 140.8, 142.5, 142.8.

***N*-(4-(4-Methoxyphenylamino)phenyl)acetoamide:**[40] pale brown solid; mp 139.5—139.8 °C (lit. [40] 138—142 °C); IR (neat) 567, 607, 638, 655, 768, 818, 829, 1034, 1106, 1172, 1243, 1296, 1314, 1367, 1440, 1465, 1510, 1547, 1592, 1652, 3268, 3419; ^{1}H NMR (400 MHz), δ = 2.12 (s, 3H), 3.78 (s, 3H), 5.50 (s, 3H), 6.84 (t, 4H), 7.00 (d, 2H), 7.30 (d, 2H), 7.52 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ =24.2, 55.5, 114.6, 116.4, 121.3, 122.0, 130.2, 136.1, 141.8, 154.9, 168.4. HRMS [DART$^+$]. m/z calcd for $C_{15}H_{17}N_2O_2$: 257.1290 $[M+H]^+$, Found: 257.1295 $[M+H]^+$.

***N*-4-Hexylamino-acetoamide:**[41] pale brown solid; mp 101.2—101.5 °C (lit. [41]108 °C); IR (neat) 571, 604, 709, 731, 749, 820, 899, 924, 963, 1016, 1035, 1091, 1135, 1156, 1178, 1223, 1247, 1278, 1292, 1310, 1364, 1402, 1466, 1481, 1513, 1550, 1600, 1651, 2854, 2929, 2960, 31137, 3293, 3401 ; ^{1}H NMR (400 MHz), δ = 0.90 (t, 3H), 1.31-1.40 (m, 6H), 1.60 (quin, 3H), 2.13 (s, 3H), 3.08 (t, 3H), 3.6 (br s, 1H), 6.56 (d, 2H) 6.97 (s, 1H), 7.25 (d, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0, 22.6, 24.2, 26.8, 29.4, 31.6, 44.3, 112.9, 122.4, 128..0, 128.1, 145.6, 168.3. HRMS [DART$^+$]. m/z calcd for $C_{14}H_{23}N_2O$: 235.1810 $[M+H]^+$, Found: 235.1804 $[M+H]^+$.

***N*-2-Methylphenylmorpholine:**[31] yellow solid; mp 28.4—28.6 °C (lit. [31] 37—38 °C); IR (neat) 532, 642, 693, 710, 775, 846, 876, 936, 952, 991, 1066, 1122, 1189, 1244, 1264, 1301, 1337, 1364, 1379, 1447, 1494, 1581, 1601, 2827, 2851, 2887, 2966; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.36 (s, 3H), 3.17 (t, 4H), 3.88 (t, 4H), 6.77 (m, 3H), 7.22 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 49.4, 66.9, 112.8, 116.4, 120.9, 128.9, 138.8, 151.3.

***N*-(2-Methylphenyl)-2,6-dimethylaniline:**[42] pale brown liquid; IR (neat) 557, 627, 691, 731, 766, 851, 909, 994, 1034, 1093, 1164, 1216, 1261, 1.09, 1376, 1474, 1502, 1586, 1606; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.21 (s, 6H), 2.25 (s, 3H), 5.1 (br s, 1H), 6.30 (d, 1H), 6.35 (s, 1H), 6.57 (d, 1H), 7.02-7.14 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 18.3, 21.5, 110.6, 114.2, 119.1, 125.6, 128.4, 129.0, 135.8, 138.3, 139.0, 146.2.

***N*-(3,5-Dimethylphenyl)morpholine:**[43] yellow liquid. IR (neat) 556, 666, 693, 826, 872, 930, 959, 1016, 1070, 1120, 1195, 1262, 1303, 1348, 1376, 1449, 1475, 1593, 2818, 2851, 2914, 2955, 3013; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.31 (s, 6H), 3.15 (t, 4H), 3.87 (t, 4H), 6.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 49.5, 67.0, 113.7, 122.0, 138.7, 151.4.

2-methyl-*N*-phenylaniline. pale brown liquid; IR (neat) 692, 761, 878, 1027, 1047, 1077, 1111, 1175, 1250, 1292, 1308, 1418, 1464, 1494, 1593, 3046, 3388; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 2.25 (s, 3H), 5.37 (br s, 1H), 6.87-7.00 (m, 4H), 7.13 (dt, 1H), 7.18-7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 17.8, 117.4, 118.8, 120.4, 122.0, 126.7, 128.3, 129.2, 1330.9, 141.2, 144.0.

***N*-Hexyl-1-naphthalenamine:**[44] black liquid; IR (neat) 569, 765, 783, 941, 1132, 1251, 1282, 1343, 1375, 1408, 1477, 1525, 1582, 2854, 2925, 3051; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 0.93 (t, 3H), 1.36-1.39(m, 4H), 1.50 (quin, 2H), 1.78 (quin, 2H), 3.27 (t, 2H), 4.31 (br s, 1H), 6.61 (d, 1H), 7.30 (d, 1H), 7.40 (t, 1H), 7.41 (m, 2H), 7.79 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.1, 22.6, 27.0, 29.4, 31.7, 44.2, 104.1, 117.0, 119.7, 123.3, 124.5, 125.6, 126.6, 128.6, 134.3, 143.6.

***N*-Naphthalen-2-yl-morpholine:**[31] colorless solid; mp 88.7—89.2 °C (lit. [31] 87—88 °C); IR (neat) 597, 625, 650, 746, 811, 838, 876, 930, 958, 1030, 1046, 1066, 1116, 1148, 1195, 1210, 1254, 1266, 1303, 1354, 1379, 1392, 1446, 1471, 1507, 1595, 1626; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 3.26 (t, 4H), 3.92 (t, 4H), 7.12 (d, 1H), 7.26 (dd, 1H), 7.31 (t, 1H), 7.41 (t, 1H), 7.70-7.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 49.7, 66.8, 110.0, 118.8, 123.5, 126.3, 126.7, 127.4, 128.6, 128.7, 134.4, 149.0.

***N*-Phenyl-2-naphalenamine:**[31] brown solid; mp 105.2—105.5 °C (lit. [31] 107—108 °C); IR (neat) 657, 690, 736, 815, 853, 880, 957, 1017, 1071, 1117, 1172, 1216, 1239, 1303, 1414, 1464, 1494, 1595, 1626, 3053, 3392; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 5.85 (br s, 1H), 7.00 (t, 1H), 7.18 (d, 2H), 7.24 (dd, 1H), 7.31-7.35 (m, 3H), 7.42 (dt, 1H), 7.46 (d, 1H), 7.66 (d, 1H), 7.76 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.6, 118.2, 120.0, 121.4, 123.5, 126.4, 126.5, 127.6, 129.1, 129.4, 134.6, 140.8, 142.9.

***N*^{1}, *N*^{3}-Diphenyl-5-phenylbenzenediamine:** black solid; mp 109.1—109.4 °C; IR (neat) 548, 560, 571, 600, 618, 633, 691, 757, 818, 851, 1028, 1074, 1154, 1172, 1229, 1263, 1293 ,1326, 1415, 1467, 1491, 1575, 1590, 3038, 3358; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 5.8 (br s, 2H), 6.76 (t, 1H), 6.86 (d, 2H), 6.95 (t, 2H), 7.13 (dd, 4H), 7.26-7.35 (m, 5H), 7.41 (t, 2H), 7.56 (dd, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 105.0, 109.1, 118.4, 121.3, 127.0, 127.4, 128.6, 129.3,

141.2, 142.8, 143.5, 144.7; HRMS [DART$^+$]. m/z calcd for $C_{24}H_{21}N_2$: 337.1704 $[M+H]^+$, Found: 337.1739 $[M+H]^+$.

***N*^{1}, *N*^{3}-Dihexyl-5-methylbenzenediamine:** dark brown liquid; IR (neat) 548, 640, 684, 726, 796, 830, 847, 908, 990, 1038, 1101, 1150, 1199, 1232, 1264, 1319, 1380, 1465, 1521, 1599, 2856, 2925, 2951, 3326; ^{1}H NMR (400 MHz, $CDCl_3$), δ = 0.90 (t, 6H), 1.26-1.42 (m, 12H), 1.59 (quin, 4H), 2.19 (s, 3H), 3.07 (t, 4H), 3.44 (br s, 2H), 5.70 (s, 1H), 5.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 14.0, 21.8, 22.6, 26.9, 29.7, 31.6, 44.0, 94.3, 103.6, 139.7, 149.7; HRMS [DART$^+$]. m/z calcd for $C_{19}H_{35}N_2$: 291.2800 $[M+H]^+$ Found: 291.2848 $[M+H]^+$.

3-(2-Oxocyclohexyl)propanenitrile:[45]. yellow liquid. Synthesized according to reference. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.33-1.43 (dq, 1H), 1.46-1.54 (sext, 1H), 1.56-1.77 (m, 2H), 1.88 (d, 1H), 2.02-2.11 (m, 3H), 2.28-2.37 (m, 2H), 2.43-2.49 (m, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 15.2, 25.1, 25.5, 27.9, 34.2, 42.2, 48.8, 119.7, 211.7.

2-(Propyl-2-on)cyclohex-1-ene-carbonitrile: In the Schlenk tube was placed NaH (871 mg, 36 mmol, 1.5 eq.) and cooled to –0 °C. THF (48 mL) was added then the solution, diethyl (2-oxopropyl)phosphonate (6.99g, 36mmol, 1.5 eq.)[46] in THF (24 mL) was added. After stirring at 0 °C for 10 min, ice bath was removed then the solution of 2-oxo-cyclohexanecarbonitrile (2.97 g, 24 mmol)[47] in THF (48 mL) was added by dropwise. The mixture was stirred at 85 °C for 10 h then organic solvent was evaporated *in vacuo*. The obtained residue was purified by silica-gel column chromatography using hexane and ethyl acetate (1:1) as an eluent to give 2-(propyl-2-on)-1-cyclohexene-carbonitrile (2.79g, 71%). Yellow liquid. IR (neat) 540, 569, 755, 954, 954, 977, 1016, 1088, 1135, 1160, 1203, 1273, 1314, 1357, 1419, 1638, 1718, 2208, 2863, 2936. ^{1}H NMR (400 MHz, $CDCl_3$), δ = 1.65 (quin, 4H), 2.13 (d, 2H), 2.22 (s, 3H), 2.28 (s, 2H), 3.46 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.1, 21.3, 27.2, 30.0, 30.1, 51.0, 110.3, 118.6, 150.1, 203.7. HRMS [DART$^+$]. m/z calcd for $C_{10}H_{14}N_1O_1$: 164.1075 $[M+H]^+$, Found: 164.1090 $[M+H]^+$.

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[24] The reaction of cyclohexanone with halogenated aniline afforded the corresponding *N*-phenylaniline with a loss of halogen atom (see Supporting Information, eq. S1 and eq. S2).When the reaction was carried out using more amount of Pd/C (5 mol%) and/or for longer time (48 h), *N*-phenylaniline was obtained in 22–35% yield (see, Supporting Information, Table S1).
[25] Treatment of dicyclohexylamine with 5% Pd/C (5 mol%) under ethylene atmosphere (1 atm) in xylene at 150 ºC for 72 h gave *N*-phenylaniline in 95% yield, whereas, the reaction for 24 h afford the mixture of *N*-cyclohexylaniline and *N*-phenylaniline in a ratio of 65:21 (see Supporting Information Table S2).
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Synthesis of Arylamines via *Non-aerobic* Dehydrogenation Using a Palladium/Carbon–Ethylene System

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Yuya Shimomoto, Ryosuke Matsubara, and Masahiko Hayashi*