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GRAPHICAL ABSTRACT

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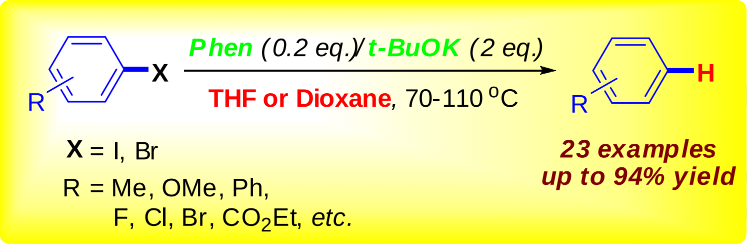


Transition-metal-free dehalogenation of aryl halides promoted by phenanthroline/potassium *tert*-butoxide

Wei Liu* and Fanyi Hou

Lipid Chemistry, College of Food Science and Technology, Henan University of Technology, 100 Lianhua Street, Zhengzhou 450001, P. R. China

*Corresponding author.

E-mail address: liuwei307@hotmail.com (Wei Liu)

ABSTRACT: Transition-metal-free dehalogenation of various aryl halides (iodides and bromides) can take place efficiently at 70-110 °C in the presence of a catalytic amount of 1, 10-phenanthroline and *t*-BuOK using THF or Dioxane as solvent. Control experiments indicated that radical transfer occurred between aryl radical and alkyl C-H bond to generate alkyl radical.

Keywords:

Dehalogenation; aryl halides; transition-metal-free; radical; alkoxy bases

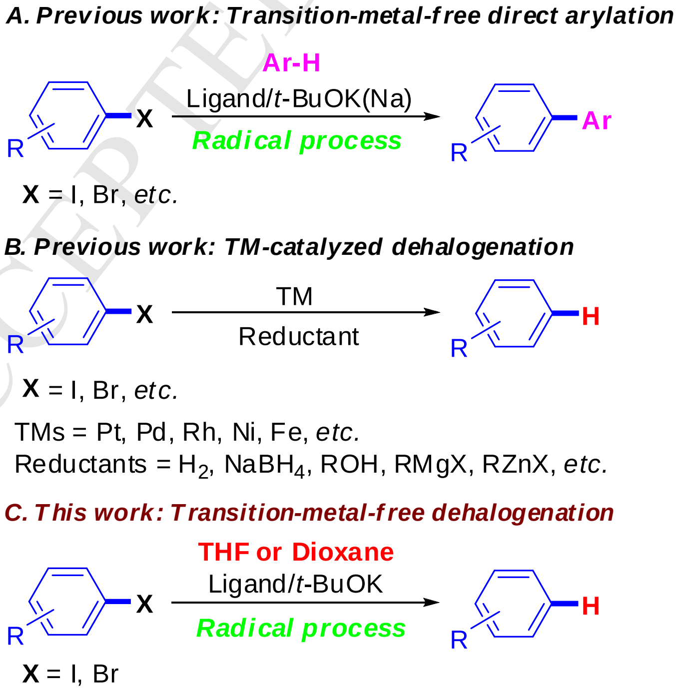
1. Introduction

Cross-coupling reactions catalyzed by various transition metals (*eg.* Pd, Rh, Ni, Cu, Fe, Co, *etc.*) have become one of the most important topics in synthetic organic chemistry during the past several decades.[1] In recent years, the demand for green and sustainable chemistry inspired organic chemists to develop transition-metal-free version of reaction process in recent years.[2]

In 2008, a *t*-BuOK promoted transition-metal-free cross-coupling between nitrogen heterocycles and haloarenes under microwave irradiation has been firstly revealed.[3] In 2010, three research groups independently developed transition-metal-free cross-coupling between unactivated arenes and aryl halides involving base-promoted homolytic aromatic substitution (HAS).[4,5] In these processes, a catalytic amount of nitrogen-containing bidentate ligands (*eg.* phenanthroline,[4a,c] DMEDA[4b]) could efficiently promote the cross-coupling between aryl iodides/bromides with unactivated arenes (*eg.* benzene) under *t*-butoxides (*eg.* *t*-BuOK) mediated conditions. Since then, considerate attentions has been focused on developing new ligands or catalysts[6] toward this novel methodology. Meanwhile, this transition-metal-free strategy has been successfully extended to other type of coupling reactions, such as intramolecular cyclization[7], Heck-type coupling[8], carbonylation[9] and so on.

Recently, great efforts have been devoted to develop new methods achieving the dehalogenation of aromatic halides from the synthetic[10] and environmental[11] points of view. Although numerous dehalogenation methods based on transition-metal-catalysis (Pd[12], Rh[13], Ni[14] and Fe[15]) have been reported, example on transition-metal-free version of dehalogenation of aryl halides is still rare up to now.

Owing to the synthetic importance of dehalogenation process and our continuous interests on transition-metal-free radical cross-coupling reactions,[6g, q] herein, we report our results on this transition-metal-free dehalogenation of aryl halides promoted by phenanthroline/potassium *tert*-butoxide (**Scheme 1**).

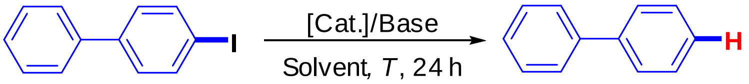


Scheme 1. Previous TM-catalyzed dehalogenation and our work.

2. Results and discussion

We embarked on our research by testing the feasibility of the reaction of 4-iodobiphenyl (**1a**) using dioxane as solvent (**Table 1**). In the presence of *t*-BuOK, trace amount of dehalogenation product was observed at 100 ^oC after 24 h (Table 1, entry 1). Considering the role of ligands, two typical nitrogen-containing bidentate ligands (DMEDA, phenanthroline) were tested for this transition-metal-free dehalogenation reactions, and 0.2 equiv of phenanthroline (Phen) showed 100% conversion of dehalogenation at 100 ^oC (Table 1, entries 2-3). Decreasing the reaction temperature from 100 ^oC to 70 ^oC led to lower yields (5-41%) (Table 1, entries 4-5). Then other common alkyl C-H containing solvents were tested. To our surprise, the combination of *t*-BuOK (4 equiv) and phen (0.2 equiv) could also produce 100% conversion of dehalogenation using THF as solvent at a much lower temperature (70 ^oC) (Table 1, entry 6). And further results showed that decreasing the amount of *t*-BuOK from 4.0 equiv to 2.0 equiv would increase the yield slightly (Table 1, entries 6-8). We next examined other common alkyl C-H solvents, such as diglyme, cyclohexane, hexane, and dioxane under the same conditions (70 ^oC), all of the candicates exhibited less effciency than THF at 70 ^oC (Table 1, entries 10-13). Furthermore, other nitrogen-containing ligands were compared and phen was found to be the most suitable ligand than 2,9-dimethyl-1,10-phenanthroline (Neo) and 2,2'-bipyridine (Bipy) (Table 1, entries 14-15). It was worth noting that other weaker bases, such as *t*-BuONa[4c] and KOH showed no effect on this transition-metal-free dehalogenation reaction at 70 ^oC (Table 1, entries 16-17). And control experiment showed that reaction conducting for 12 h could afford only 81% conversion of **1a**.

Table 1. Optimization of reaction conditions of dehalogenation.[a]



1a **2a**

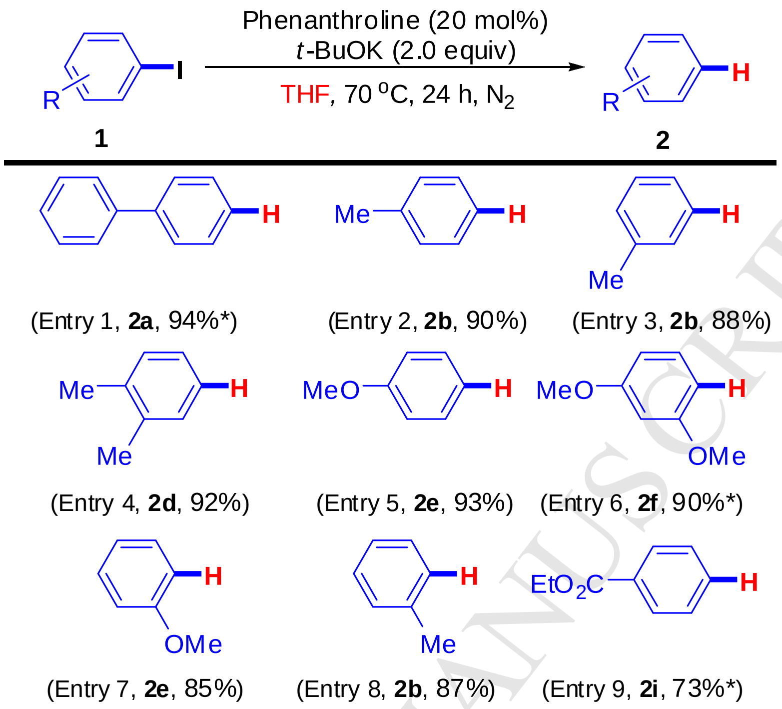
entry	[cat.] (eq.)/base (eq.)	solvent	temp. (^{o}C)	yield (%)[b]
1	None/*t*-BuOK (4.0)	Dioxane	100	<5
2	DMEDA (0.2)/*t*-BuOK (4.0)	Dioxane	100	12
3	Phen (0.2)/*t*-BuOK (4.0)	Dioxane	100	87 (100)
4	DMEDA (0.2)/*t*-BuOK (4.0)	Dioxane	70	<5
5	Phen (0.2)/*t*-BuOK (4.0)	Dioxane	70	41
6	Phen (0.2)/*t*-BuOK (4.0)	THF	70	92 (100)
7	Phen (0.2)/*t*-BuOK (3.0)	THF	70	95 (100)
8	**Phen (0.2)/*t*-BuOK (2.0)**	**THF**	**70**	**96 (100)**
9	Phen (0.2)/*t*-BuOK (1.0)	THF	70	49
10	Phen (0.2)/*t*-BuOK (2.0)	Diglyme	70	<5
11	Phen (0.2)/*t*-BuOK (2.0)	Cyclohexane	70	32
12	Phen (0.2)/*t*-BuOK (2.0)	Hexane	70	0
13	Phen (0.2)/*t*-BuOK (2.0)	Dioxane	70	43
14	Neo(0.2)/*t*-BuOK (2.0)	THF	70	91
15	Bipy (0.2)/*t*-BuOK (2.0)	THF	70	<5
16	Phen (0.2)/*t*-BuONa (2.0)	THF	70	<5
17	Phen (0.2)/KOH (2.0)	THF	70	0

[a] Standard reactions conditions: **1a** (0.5 mmol), solvent (4.0 mL), 24 h, N_2.
[b] Calibrated GC yields were reported using hexadecane as the internal standard; value in parentheses indicates the conversion of **1a**.

With the optimal conditions (0.2 equiv of phen, 2.0 equiv of *t*-BuOK, THF as solvent, 70 ^{o}C) in hand, we investigated the dehalogenation of various aryl iodides (**Table 2**). In general, electron-rich aryl iodides (**1a-e**) took place dehalogenation reaction smoothly and afforded the corresponding dehalogenated products (**2a-e**) in excellent yields (90-94%) (Table 2, entries 1-5). Sterically hindered aryl iodides, such as 1-iodo-2,4-dimethoxybenzene (**1f**), 1-iodo-2-methoxybenzene and 1-iodo-2-methylbenzene were also suitable under the same reaction conditions and afforded the corresponding dehalogenated products in good to excellent yields (85-90%), respectively (Table 2, entries 6-8). Moreover, electron-poor aryl iodides, such as ethyl 4-iodobenzoate (**1i**) could take place dehalogenation smoothly and afforded the corresponding dehalogenated product (**2i**) in 73% yield (Table 2, entry

9).

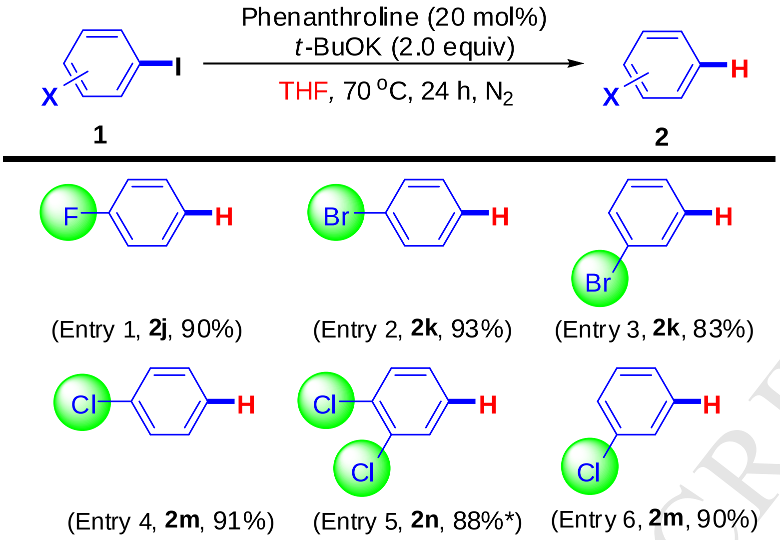
Table 2. Transtion-metal-free dehalogenation of aryl iodides.



Reaction conditions: **1** (0.5 mmol), THF(4.0 mL), 70 °C, 24 h, N_2. Yields are determined by GC. *The yields reported are for products isolated and purified by flash chromatography.

Encouraged by the above results, we focused on the reactivity and chemoselectivity of various aryl iodides bearing halosubstituents (Br, Cl, F) under our optimal conditions (**Table** 3). 1-fluoro-4-iodobenzene, 4-bromoiodobenzene and 3-bromoiodobenzene could efficiently afford the corresponding *mono*-dehalogenated products in 83-93% yields, respectively (Table 3, entries 1-3). Moving to other multi haloarenes, 4-chloroiodobenzene, 3,4-dichloroiodobenzene and 3-chloroiodobenzene could also undergo chemoselective dehalogenation and produced the desired products in 88-91% yields, respectively (Table 3, entries 4-6).

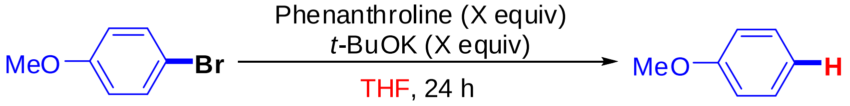
Table 3. Dehalogenation of aryl iodides bearing halosubstituents.



Reaction conditions: **1** (0.5 mmol), THF (4.0 mL), 70 °C, 24 h, N_2. Yields are determined by GC. *The yields reported are for products isolated and purified by flash chromatography.

Next, other unactive aryl halides, such as aryl bromides were examined as well. 4-bromoanisole (**3e**) was less reactive at 70 °C (**Table 4**). Considering the more unactive aromatic C-Br bond in aryl halides, increasing the reaction temperature from 70 °C to 100 °C was conducted to promote the cleavage of aromatic C-Br bond, and moderate conversion of 4-bromoanisole was observed (Table 4, entry 3). And increased the amount of phen (40 mol%) and *t*-BuOK (3.0 equiv) led to 100% conversion of 4-bromoanisole and produced the dehalogenation product in 86% yield at 110 °C (Table 4, entry 5). Moreover, the yield of dehalogenation product could be up to 89% when decreasing the amount of *t*-BuOK (2.5 equiv) (Table 4, entry 6).

Table 4. Optimization of reaction conditions of dehalogenation of ArBr.[a]



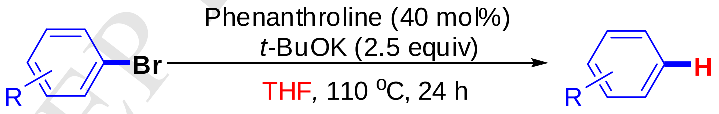
3e **2e**

Entry	Phen (equiv)	*t*-BuOK (equiv)	T (^oC)	Conv. (%)	Yield (%)
1	0.2	2.0	70	<5	0
2	0.2	2.0	100	12	<5
3	0.3	3.0	100	46	34
4	0.3	3.0	120	100	76
5	0.4	3.0	110	100	86
6	**0.4**	**2.5**	**110**	**100**	**89**

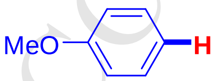
Reaction conditions: **3e** (0.5 mmol), THF (4.0 mL), 24 h, N_2. Yields are determined by GC.

Encouraged by the above results, other aryl bromides were examined and the results were listed in **Table 5**. In general, electron-rich aryl bromides took place dehalogenation smoothly and afforded the corresponding dehalogenated products in good to excellent yields (84-90%) (Table 5, entries 1-5). Dihalide substrates, such as 1-bromo-4-fluorobenzene, 1-bromo-4-chlorobenzene and 1-bromo-2-chlorobenzene could both undergo chemoselective dehalogenation and produced the corresponding products in 84-87% yields, respectively (Table 5, entries 6-8).

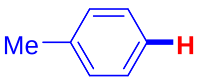
Table 5. Transtion-metal-free dehalogenation of aryl bromides.



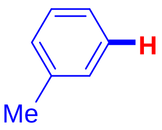
3 **2**



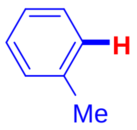
(Entry 1, **2e**, 89%)



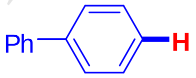
(Entry 2, **2b**, 90%)



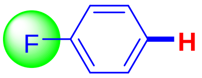
(Entry 3, **2b**, 88%)



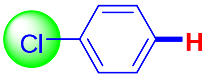
(Entry 4, **2b**, 84%)



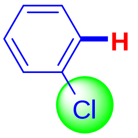
(Entry 5, **2a**, 85%*)



(Entry 6, **2j**, 84%)



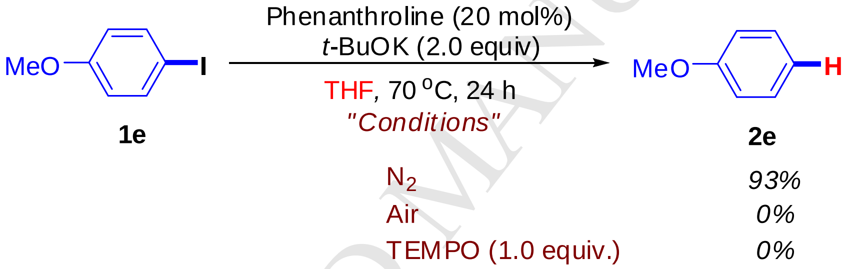
(Entry 7, **2m**, 87%)



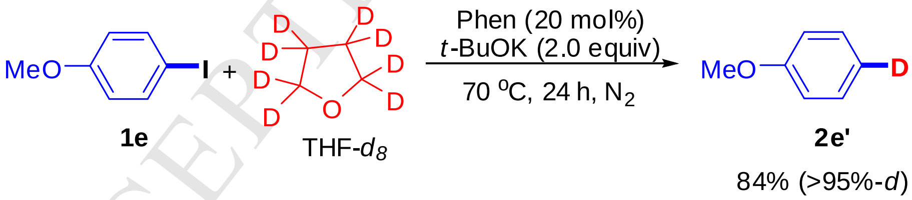
(Entry 8, **2m**, 85%)

Reaction conditions: **3** (0.5 mmol), THF (4.0 mL), 110 ^oC, 24 h, N_2. Yields are determined by GC. *The yields reported are for products isolated.

To gain some preliminary insights into the mechanism of such transition-metal-free dehalogenation, we conducted a set of control experiments (**Scheme 2**). When the reaction was conducted under air atmosphere, nearly no conversion of 1-iodo-4-methoxybenzene (**1e**) was observed, which indicated that this reaction was oxygen sensitive. On the other hand, the dehalogenation reaction was almost shut down when 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) was added as radical inhibitors. These results suggested that this transition-metal-free dehalogenation transformation involved a radical reaction mechanism.[5,16] Moreover, the dehalogenation of 1-iodo-4-methoxybenzene (**1e**) in THF-*d8* gave a 84% yield of 4-deuterioanisole (**Scheme 3**) (**Figure S1**), implying that aryl radical generated by reaction of ArI with Phen/*t*-BuOK abstracts a deuterium from THF-*d8*.



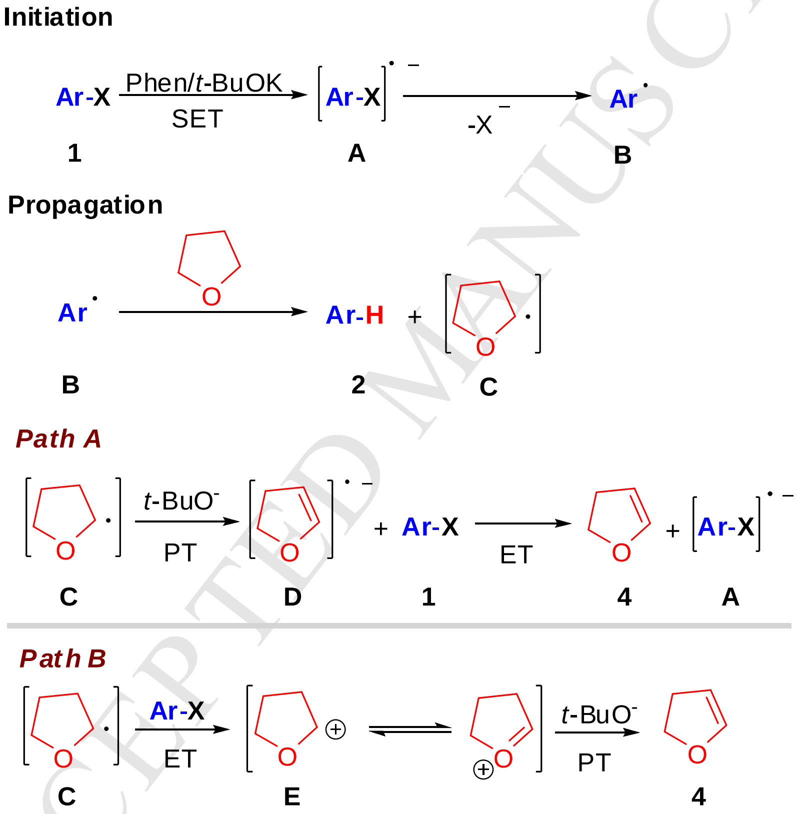
Scheme 2. Control experiments for transition-metal-free dehalogenation.



Scheme 3. Involvement of aryl radical intermediates.

Furthermore, we attempted to monitor the reaction between 4-bromoanisole and THF in the presence of 1, 10-phenanthroline and *t*-BuOK (**Figure S2**). An apparent induction period was observed, which suggested that 1, 10-phenanthroline was not the “true catalyst”.[17] And the reaction mixture showed a dark purple colour after heating at 110°C within half an hour (**Figure S3**), which indicated that π-electron-rich species might be generated as the “true catalyst”.[6l]

On the basis of above results and previous studies[6s,18], a plausible mechanism is proposed as shown in **Scheme 4**. An aryl halide radical anion (**A**) is generated from aryl halides (**1**) by SET process in the presence of Phen/*t*-BuOK and converted to an aryl radical (**B**) upon elimination of X^{-}. Aryl radical **B** reacts with THF to afford product **2** and radical (**C**). From radical **C**, two possible pathways are presented. One pathway is a deprotonation of radical **C** with the assistance of *t*-BuOK, followed by another SET with **1** to form aryl halide radical anion (**A**) and 2,3-dihydrofuran. The other pathway is a SET between radical **C** and **1** to produce cation **E**, followed by a deprotonation by *t*-BuOK to give 2,3-dihydrofuran (**4**).



Scheme 4. Possible mechanism of this transition-metal-free dehalogenation.

3. Conclusion

In conclusion, we have developed a transition-metal-free dehalogenation reaction of various aryl halides in the presence of a catalytic amount of 1, 10-phenanthroline and *t*-BuOK under mild conditions. Both aryl iodides and bromides could be employed as substrate to afford the dehalogenation products in moderate to excellent yields. Control experiments indicated that radical transfer occurred between aryl radical and alkyl C-H bond, and then alkyl radical generated in this process.

4. Experimental section

4.1 General Information

Analytical gas chromatography (GC) was performed using a Gas Chromatography fitted with a flame ionization detector (FID). ^{1}H NMR spectra were obtained at 300 or 500 MHz. The chemical shifts were quoted in parts per million (ppm) and referenced to 0 ppm for internal tetramethylsilane (TMS). ^{13}C NMR spectra were obtained at 75 or 125 MHz and referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet, m = multiplet. Coupling constants *J* were reported in hertz unit (Hz). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash column chromatography was performed employing 200-300 mesh silica gel.

4.2 General procedure for the dehalogenation of aryl iodides

A Schlenk tube was charged with aryl iodides (0.5 mmol), phen (18 mg, 0.1 mmol) and *t*-BuOK (112 mg, 1.0 mmol) under an atmosphere of nitrogen at room temperature, and then THF (4.0 mL) was added. The resulting mixture was stirred at 70^{o}C for 24 h. After cooling to room temperature, the reaction mixture was quenched and extracted with ethyl ether (10 ml×3). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph to yield the desired dehalogenation product.

4.3 General procedure for the dehalogenation of aryl bromides

A Schlenk tube was charged with aryl bromides (0.5 mmol), phen (36 mg, 0.2 mmol) and *t*-BuOK (140 mg, 1.25 mmol) under an atmosphere of nitrogen at room temperature, and then THF (4.0 mL) was added. The resulting mixture was stirred at 110^{o}C for 24 h. After cooling to room temperature, the reaction mixture was quenched and extracted with ethyl ether (10 ml×3). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure, and then purified by silica gel chromatograph to yield the desired dehalogenation product.

4.4 Characterization data of product 2

***biphenyl* (2a)**[4b]: Yield 94% (72.4 mg); white solid; ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.63 (d, J = 7.2Hz, 4H), 7.48 (t, J = 7.4Hz, 4H), 7.33 (t, J = 7.4Hz, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 141.2, 128.8, 127.3, 127.2. Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.35; H, 6.32.

***toluene* (2b)**[19]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.26-7.23 (m, 3H), 7.16 (t, J = 7.5Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 137.9, 129.1, 128.3, 125.3, 21.5. Anal. Calcd for C_7H_8: C, 91.25; H, 8.75. Found: C, 91.07; H, 8.57.

***o-xylene* (2d)**[19]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.13-7.07 (m, 4H), 2.25 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 136.5, 129.6, 125.9, 19.8. Anal. Calcd for C_8H_{10}: C, 90.51; H, 9.49. Found: C, 90.35; H, 9.28.

anisole (2e)[12d]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.28 (t, J = 7.5Hz, 2H), 6.94 (t, J = 7.0Hz, 1H), 6.90 (d, J = 9.5Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 159.4, 129.5, 120.7, 114.1, 55.1. Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.27.

1,3-dimethoxybenzene (2f)[12d]: Yield 90% (62.1 mg); yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.18 (t, J = 8.0Hz, 1H), 6.52-6.47 (m, 3H), 3.79 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 160.9, 129.9, 106.2, 100.5, 55.3. Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: 69.42; H, 7.14.

ethyl benzoate (2i)[12d]***:*** Yield 73% (54.8 mg); yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.04 (d, J = 1.5Hz, 2H), 7.54 (t, J = 8.5Hz, 1H), 7.40 (t, J = 7.5Hz, 2H), 3.79 (s, 6H), 4.38 (q, J = 7.0Hz, 2H), 1.39 (t, J = 7.5Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 166.6, 132.8, 130.5, 129.5, 128.3, 60.9, 14.3. Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.81; H, 6.51.

fluorobenzene (2j)[19]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.32 (t, J = 11.0Hz, 2H), 7.13-7.03 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 163.9, 161.9, 129.9, 124.0, 115.3. Anal. Calcd for C_6H_5F: C, 74.99; H, 5.24. Found: C, 74.86; H, 5.01.

bromobenzene (2k)[19]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.48 (t, J = 4.2Hz, 2H), 7.29-7.20 (m, 3H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 131.6, 130.1, 126.9, 122.6. Anal. Calcd for C_6H_5Br: C, 45.90; H, 3.21. Found: C, 45.77; H, 3.11.

chlorobenzene (2m)[19]: colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.34-7.21 (m, 5H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 134.3, 129.7, 128.6, 126.4. Anal. Calcd for C_6H_5Cl: C, 64.02; H, 4.48. Found: C, 63.84; H, 4.25.

1,2-dichlorobenzene (2n)[19]: Yield 88% (64.7 mg); yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.44 (d, J = 5.0Hz, 2H), 7.20 (d, J = 4.8Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$): δ 132.6, 130.5, 127.7. Anal. Calcd for $C_6H_4Cl_2$: C, 49.02; H, 2.74. Found: C, C, 48.83; H, 2.56.

ACKNOWLEDGMENT

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ASSOCIATED CONTENT

Supporting Information. Optimization of reaction conditions and spectra of ^{1}H NMR and ^{13}C NMR for products. This material is available free of charge via the internet at http://pubs.acs.org.).

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