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Letters in Organic Chemistry, **2013,** *10,* **541-548**

Halogen Exchange via a Halogenation of Diaryliodonium Salts with Cuprous Halide

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Received February 18, 2013: Revised June 08, 2013: Accepted June 10, 2013

Abstract: An efficient halogenation reaction has been developed with diaryliodonium salts and cuprous halides. Various diaryliodonium salts **1** could perform the reaction with readily available CuBr or CuCl in CH_3CN at 80°C, assembling bromoarenes or chloroarenes in up to 92% yields. This provides us a method for the transformation from iodoarenes to other haloarenes.

Keywords: Diaryliodonium salts, Halogenation, Cuprous halide, Aromatic halides, Iodoarenes.

INTRODUCTION

Hypervalent iodine compounds are of great interest as mild, nontoxic, and selective reagents in organic synthesis [1]. Diaryliodonium salts are the best known compounds in this class. Several studies in the literature have reported the application of diaryliodonium salts because of their highly electron-deficient nature and excellent leaving-groupability, usually they serve as versatile arylating agents with variety of nucleophiles, such as indoles, pyrroles, phenols, carboxylic acids, aniline and carbonyls [2]. In particular, the groups of Gaunt and Olofsson have conducted lots of work with the synthesis and applications of diaryliodonium salts. Recently, they developed efficient one-pot routes to diaryliodonium salts, and these compounds are now inexpensive and easily available [3].

For many decades, aromatic halides have been an important class of compounds, due to their role as precursors for the synthesis of organo metallic reagents [4] and for nucleophilic substitution reactions [5] In addition, with the advent of cross-coupling chemistry [6], the importance of bromo- and chloro- arenes has tremendously increased, and hence they can be classified as the core building blocks of organic synthesis. Consequently, efficient and selective methods to access this class of compounds are highly valuable. As a result, considerable efforts have been directed toward the development of efficient and selective methods for preparation of aromatic halides.

The traditional synthetic method of aromatic halogenations includes electrophilic aromatic substitution, conversion of an amine to a halide via the diazonium salt (the Sandmeyer reaction) [7]. For example, aryl bromides are synthesized from arenediazonium salt and HBr, the reaction requires an excess of CuBr and concentrated acid at high temperatures (up to 100-120°C) [8]. In addition, to a lesser extent, the synthetic pathway of aromatic halides is the halogenations of an arylmetallic species.

Recent year, Carroll and Widdowson reported the fluorination of diaryliodonium salts with CsF and many fluorine-18 labeled arenes and heterocycles were synthesized through this way (Scheme **1**) [9]. This provides us with a simple method for the synthesis of fluoro aromatics. As part of our ongoing interest in developing application of diaryliodonium salts [10], we herein wish to report a simple, efficient method for preparation of aromatic halides with copper halide (Scheme **1**). This provides us a method for the halogen exchange of aryl halides.

RESULTS AND DISCUSSION

Our initial study was focused on the reaction of diphenyliodonium salt **1a** and several halogen sources, but KBr or KCl gave the negative results, therefore no product was detected (entry **1, 2,** Table **1**). It was pleased that 25% yield of bromobenzene **2a** was collected by employing CuBr in DMF at room temperature for 24 hours (entry **3,** Table **1**). So we carried on our investigations using diphenyliodonium salt **1a** and CuBr as model substrates, after testing various reaction conditions for the bromination of diphenyliodonium salt **1a**, the results was summed up in (Table **1**). The reaction proceeds in various solvents, such as DMSO, DMAC, THF, CH_3CN, DCM and H_2O. CH_3CN was found to be the solvent of choice regarding both the yield and the reaction rate to give product bromobenzene in 45% yield (entry **7**). When 2 equiv of K_2CO_3 was used, 38% yield was obtained (entry **10**). Gratifyingly, when the temperature was increased from 25°C to 80°C, the yield was promoted to 91% after 2 hours. Encouraged by these results, $CuBr_2$ was employed for this bromination under the same condition, but desired result was not obtained, the yield was decreased to 73% (entry **12**).

In addition, studies about the influence of different diphenyliodonium anions were carried out, satisfactory results could be obtained with diaryliodonium 4-methy-lben-zenesulfonate, chloride, bromide, tetrafluoroborates, hexa-

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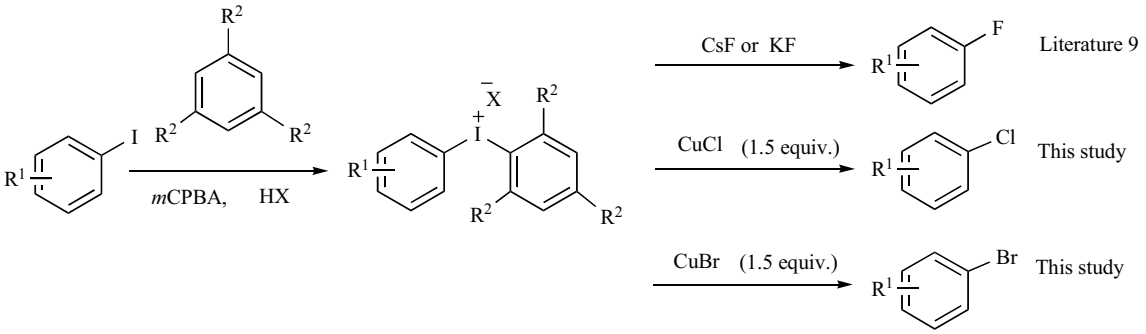
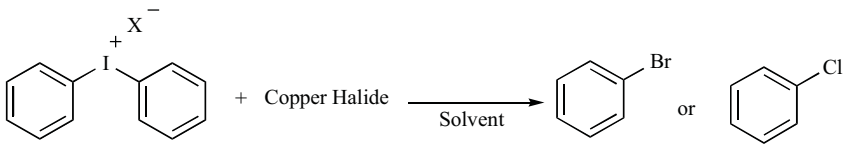


Scheme 1. Halogen exchange from Iodine to the other halogens.

Table 1. Optimization of the Model Reaction [a]



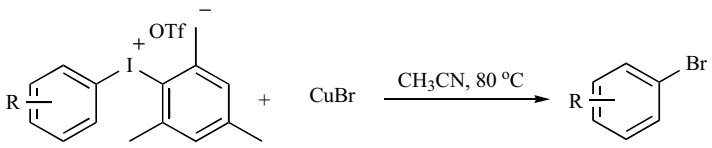
1a **2**

Entry	Halide Resources	X	Solvent	T(℃)	Yield(%) [b]
1	KBr	OTf	CH_3CN	25	-
2	KCl	OTf	CH_3CN	25	-
3	CuBr	OTf	DMF	25	25
4	CuBr	OTf	DMSO	25	13
5	CuBr	OTf	DMAC	25	21
6	CuBr	OTf	THF	25	5
7	CuBr	OTf	CH_3CN	25	45
8	CuBr	OTf	CH_2Cl_2	25	23
9	CuBr	OTf	H_2O	25	11
10 [c]	CuBr	OTf	CH_3CN	25	38
11	CuBr	OTf	CH_3CN	80	91
12	$CuBr_2$	OTf	CH_3CN	80	73
13	CuBr	OTs	CH_3CN	80	71
14	CuBr	Br	CH_3CN	80	40
15	CuBr	Cl	CH_3CN	80	45
16	CuBr	BF_4	CH_3CN	80	63
17	CuBr	PF_6	CH_3CN	80	65
18	CuCl	OTf	CH_3CN	80	88
19	$CuCl_2$	OTf	CH_3CN	80	65

[a] Diphenyliodonium salt (0.5 mmol) and copper halide (0.75 equiv) were mixed in solvent (1 mL) at r. t. , then heating to 80 ºC for 2 hours.
[b] Isolated yield.
[c] K_2CO_3 (1mmol) was added.

fluorophosphates under(entries **12-17,** Table **1**). It's noted that the effect of different anions on the reactivity of diphenyliodonium salts were different, which was due to the different solubilities and nucleophilicities of diaryliodonium salts **1c**. Moreover, the search for chlorination of diphenyliodonium salt **1a** was investigated, CuCl was chosen correspondingly as chlorination reagents, 88% of yield was obtained in CH_3CN at 80 °C in 2 hours (entry **18,** Table **1**).

Table 2. Bromination of Diaryliodonium Salts with CuBr [a]



1 **2**

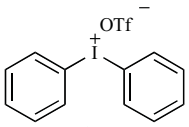
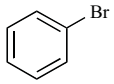
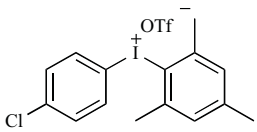
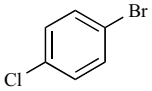
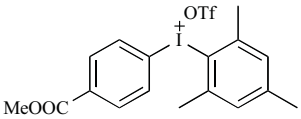
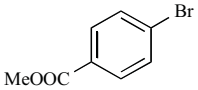
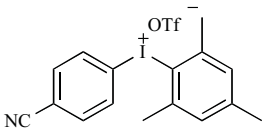
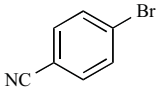
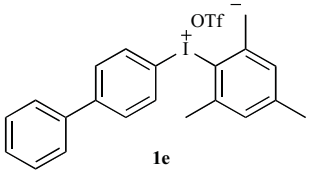
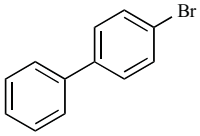
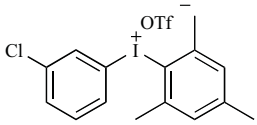
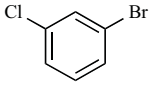
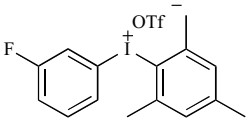
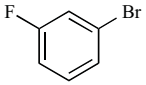
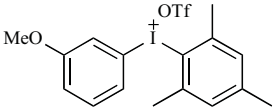
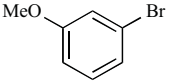
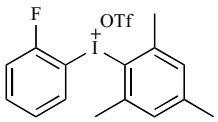
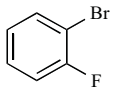
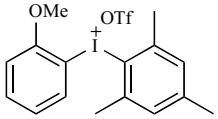
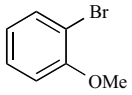
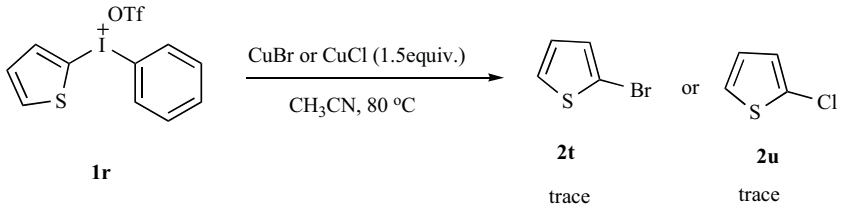
Entry	Substrate	Product	Yield (%) [b]
1	 **1a**	 **2a**	91
2	 **1b**	 **2b**	85
3	 **1c**	 **2c**	83
4	 **1d**	 **2d**	89
5	 **1e**	 **2e**	87
6	 **1f**	 **2f**	92
7	 **1g**	 **2g**	91
8	 **1h**	 **2h**	64

Table 2. Contd….

Entry	Substrate	Product	Yield (%) [b]
9	 **1i**	 **2i**	71
10	 **1j**	 **2j**	47

[a] Diaryliodonium salt (0.5 mmol) and CuBr (0.75 mmol) were mixed in CH_3CN (1 mL) at r. t., then heating to 80 ºC for 2 hours.
[b] Isolated yield.



Scheme 2. Halogenation of Diaryliodonium Salts 1r.

With optimized reaction conditions in hand, we probed the scope of diaryliodonium salts with CuBr in CH_3CN at 80 ºC. The results are summarized in (Table **2**). The reaction scope was subsequently explored by using a series of asymmetrical diaryliodonium salts **1**, which were prepared from appropriate iodoarene under simple procedure [10, 11]. Common functional groups, such as fluorine, chlorine, ester, cyano, phenyl and methoxy groups were well tolerated under the standard reaction conditions (entries **2-9,** Table **2**). The diaryliodonium salts bearing an electron-withdrawing group on benzene ring resulted in better yield (entries **3, 4,** Table **2**) than the one bearing an electron-donating group (entry **8,** Table **2**).

It is interesting that substituent groups in the *meta*-position were very well tolerated and gave corresponding products **2f-g** in higher yields (entries **6, 7,** Table **2**). Likewise, *ortho*-substituted salts posed no problem in this reaction, as exemplified by *o*-methyl product (entry **10**).

The results encouraged us to extend our protocol to investigate this halogenation method. In this regard chlorination of diaryliodonium salts **1** with CuCl was surveyed under the optimized reaction conditions. To our delight, the results exceeded our expectations; we found that this methodology was broadly applicable to a variety of asymmetrical diaryliodonium salts **1**, affording halogenation products in synthetically valuable yields (Table **3**). Substituted diphenyliodoniumtriflate with electron-withdrawing substituents worked equally well as those with electron-donating substituents, giving chlorobenzenes **2l-p** in high yields (entries **2-7,** Table **3**). In particular, diaryliodonium salts of 4-tert-butylbenzene **1n** resulted in higher yield of product **2o** (entry **6**). These *ortho*-substituted products **2q** and **2r** were obtained in good yields under optimized reaction conditions (entries **8, 9**). Functional group in the *meta*- position was very well tolerated, as demonstrated by chlorination with salt **1q** to yield product **2s** (entry **10**).

The present reaction was also examined with heterocyclic diaryliodonium salts, such as thiophene (Scheme **2**). But only products **2t** and **2u** were detected by GC-MS .

The plausible mechanism of this halogenation reaction is depicted in (Fig. **1**). At first, oxidative addition of CuX with diaryliodonium salts occurred in the reaction system, which afforded copper-complex **3** by eliminating of 2-iodomesitylene. Elimination of (Trifluoromethylsulfonyloxy) copper from intermediate **3** afforded product **2**.

CONCLUSION

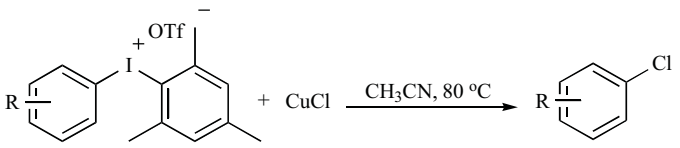
In conclusion, an efficient halogenation reaction has been developed with diaryliodonium salts and cuprous halide. Various diaryliodonium salts **1** could perform the reaction with readily available CuBr or CuCl in CH_3CN at 80°C, assembling bromoarenes or chloroarenes in up to 92% yields. This provides a method for the transformation iodoarenes to other haloarenes. Further investigations on reaction mechanism and other synthetic utility of diaryliodonium salts are currently underway.

EXPERIMENTAL

General Procedure for Halogenation Reaction of Diaryliodonium Salts with Cuprous Halide

A mixture of diaryliodonium salt (0.5 mmol), cuprous halide (0.75 mmol) and CH_3CN (1mL) was taken in a 10mL

Table 3. Chlorination of Diaryliodonium Salts with CuCl [a]



1 **2**

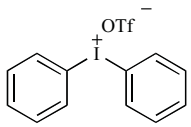
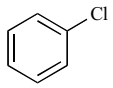
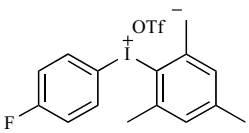
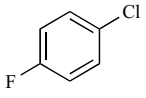
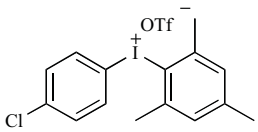
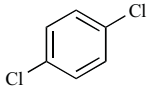
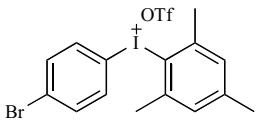
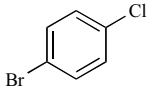
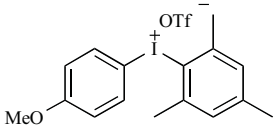
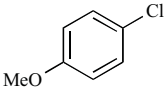
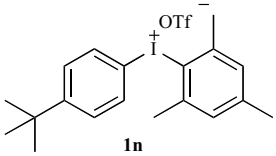
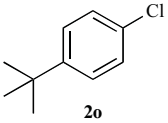
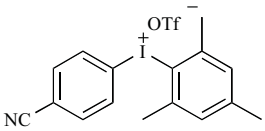
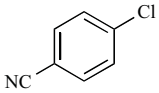
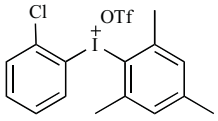
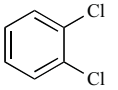
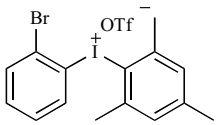
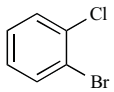
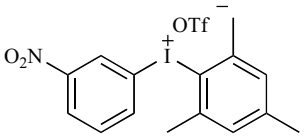
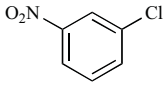
Entry	Substrate	Product	Yield (%) [b]
1	 **1a**	 **2k**	88
2	 **1k**	 **2l**	85
3	 **1b**	 **2m**	83
4	 **1l**	 **2b**	89
5	 **1m**	 **2n**	87
6	 **1n**	 **2o**	92
7	 **1d**	 **2p**	91
8	 **1o**	 **2q**	64

Table 3. Contd.....

Entry	Substrate	Product	Yield (%) [b]
9	 **1p**	 **2r**	80
10	 **1q**	 **2s**	85

[a] Diaryliodonium salt (0.5 mmol) and CuCl (0.75 mmol) were mixed in CH_3CN (1 mL) at r. t., then heating to 80 ºC for 2 hours.
[b] Isolated yield.

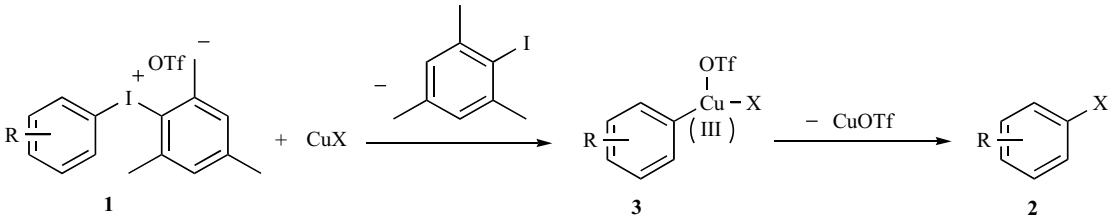


Fig. (1). Possible mechanism of the halogenations.

reaction tube and heated at 80°C temperature for 2 hours under vigorous stirring. After completion of the reaction (observed on TLC or GC) the reaction mass was cooled to room temperature, and 5 ml of water was added. The mixture was stirred for 10 mins, the product was extracted with ethyl acetate (3 * 10mL). The organic layer was washed with water and dried over anhydrous sodium sulphate. Solvent was evaporated under reduced pressure to obtain the product. The crude product was purified on silica gel column by using petroleum ether and ethyl acetate as solvents to obtain the pure product. The obtained product was analyzed by ^{1}H NMR, ^{13}C NMR.

Bromobenzene (2a) [12]

Yield: 71mg (91%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.2 Hz, 2H), 7.29 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.57, 131.54, 131.51, 130.07, 130.04, 130.01, 126.88, 122.52.

1-Bromo-4-chlorobenzene (2b) [13]

Yield: 81mg (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.22, 132.82, 132.80, 132.77, 132.74, 130.23, 130.20, 130.17, 120.27.

Methyl 4-bromobenzoate (2c) [14]

Yield: 89mg (83%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 3.91(s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.37, 131.72, 131.12, 129.06, 128.05, 52.30.

4-Bromobenzonitrile (2d) [15]

Yield: 81mg (89%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.01, 132.62, 128.01, 118.05, 111.23.

4-Bromobiphenyl (2e) [14]

Yield: 101mg (87%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (m, 4H), 7.43 (m, 4H), 7.35 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.15, 140.01, 131.86, 128.93, 128.90, 128.87, 128.78, 128.75, 127.64, 126.95, 121.54;

1-Bromo-3-chlorobenzene (2f) [12]

Yield: 87mg (92%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, J = 0.8 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.21 (m, 1H), 7.16 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.18, 131.50, 130.78, 129.79, 127.35, 122.80.

1-Bromo-3-fluorobenzene (2g) [16]

Yield: 79mg (91%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (m, 3H), 7.00 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.70, 161.70, 131.01, 130.94, 127.50, 127.49, 127.47, 127.44, 127.42, 127.38, 127.37, 122.65, 122.57, 119.32, 119.29, 119.12, 114.34, 114.18.

1-Bromo-3-methoxybenzene (2h) [12]

Yield: 60mg (64%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 (m, 3H), 6.83 (d, J = 8.0 Hz, 1H), 3.78(s, 3H). ^{13}C NMR

(125 MHz, $CDCl_3$): δ = 160.37, 130.52, 123.76, 122.82, 117.16, 113.10, 113.07, 55.42.

1-Bromo-2-fluorobenzene (2i) [17]

Yield: 62mg (71%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (m, 1H), 7.28 (m, 1H), 7.13 (m, 1H), 7.04 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.11, 158.15, 133.61, 128.98, 128.92, 125.29, 125.26, 116.64, 116.46, 109.15, 108.98.

1-bromo-2-methoxybenzene (2j) [18]

Yield: 43mg (47%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (m, 1H), 7.33 (m, 1H), 6.84 (m, 1H), 6.73 (m, 1H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.06, 139.49, 129.52, 122.50, 110.99, 85.97, 56.27.

Chlorobenzene (2k) [12]

Yield: 48mg (88%) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (m, 3H), 7.32 (m, 1H), 7.25 m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.25 129.73, 128.62, 126.45.

1-Chloro-4-fluorobenzene (2l) [12]

Yield: 55mg (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 2H), 6.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.31, 160.35, 129.99, 129.97, 129.95, 129.92, 129.18, 129.16, 116.83, 116.79, 116.64.

1,4-Dichlorobenzene (2m) [13]

Yield: 61mg (83%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (m, 2H), 7.24 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.03, 130.47, 128.75, 126.93, 126.90.

1-Chloro-4-methoxybenzene (2n) [13]

Yield: 62mg (87%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 2H), 6.99 (m, 2H), 3.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.20, 129.30, 125.53, 115.21, 115.18, 55.49.

1-tert-Butyl-4-chlorobenzene (2o) [13]

Yield: 77mg (92%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.12, 131.09, 131.08, 131.06, 131.00, 130.99, 130.97, 130.96, 130.94, 127.25, 127.24, 127.22, 127.19, 127.16, 127.14, 119.21, 34.52, 31.33, 31.32, 31.30, 31.29, 31.27, 31.26, 31.24, 31.21, 31.15.

4-Chlorobenzonitrile (2p) [15]

Yield: 62mg (91%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 139.58, 133.40, 129.72, 117.97, 110.82.

1,2-Dichlorobenzene (2q) [19]

Yield: 47mg (64%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (m, 2H), 7.25 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.57, 130.54, 127.75, 127.71, 127.68.

1-Bromo-2-chlorobenzene (2r) [20]

Yield: 76mg (80%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.24 (m, 1H), 7.11 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.55, 133.85, 130.49, 128.47, 127.93, 122.58.

1-Chloro-3-nitrobenzene (2s) [13]

Yield: 67mg (85%) ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.76 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.81, 135.44, 134.72, 134.69, 130.40, 123.91, 121.76, 121.71, 121.66.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

We are grateful to the grants from the Foundation of Chang Zhou Municipal Bureau of Science and Technology (No. KYZ1102100C) and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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