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Full Paper

A Mild and Convenient Synthesis of 1,2,3-Triiodoarenes via Consecutive Iodination/Diazotization/Iodination Strategy

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A mild and convenient synthesis of 1,2,3-triiodoarenes has been developed. This method consists of two steps which can be performed on multigram scale with moderate to excellent yields. This report discloses a practical synthesis of 1,2,3-triiodoarenes and 1,2,3-trihaloarenes that is general in scope, operationally simple, scalable, and is easy to workup and to purify. We also report the first regioselective transmetalation reaction of 1,2,3-triiodoarenes to provide *ortho*-diiodoaryl derivatives, which are useful building blocks and indeed are hard to make by other means.

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Introduction

Aryl iodides are versatile and useful compounds in organic chemistry. They are used for the synthesis of remarkable intermediates in agricultural chemicals, pharmaceuticals, and also used as contrast agents in medical applications.[1] Due to the relatively weak nature of the C–I bond, it can be transformed into a plethora of other important organic products, particularly by using transition metal catalyzed reactions or by organolithium or organomagnesium intermediates.[2] Although a broad palette of synthetic protocols for iodination of aromatic compounds is available,[3] only a few of them are devoted at the *ortho*-position.[4] One approach relies on the use of relatively expensive 1,2-diiodobenzene as *ortho*-iodophenyl surrogate to provide *ortho*-iodoarenes.[5] While the halogenation of aromatic compounds is one of the most widely studied reactions in the literature,[6] a practical iodination approach to access *ortho*-diiodoaryl derivatives has not been reported.

Ortho-diiodoaryl compounds are found in a number of biologically active compounds. For instance, thyroxine **1** (T_4, pharmaceutically levothyroxine, Fig. 1), is a tyrosine-based hormone produced by the thyroid gland and is responsible for regulation of metabolism.[7] Additionally, 2-(2-chloro-6-iodoanilino) phenylacetic acid (**2**) is a diclofenac derivative

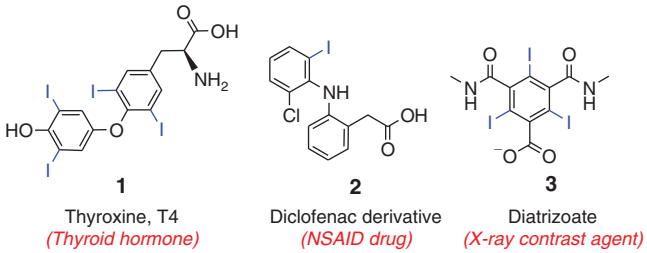


Fig. 1. Some biologically important iodoarenes in nature and in medicine.

comprising an iodo substituent at the *ortho*-position instead of a chloro substituent. Compound **2** was found to inhibit cyclooxygenase slightly more than diclofenac (it inhibits cyclooxygenase at the enzyme level and also rat adjuvant arthritis in vivo). Interestingly, the *ortho*-difluoro derivative was found to be significantly less active than diclofenac. It was concluded that the twist between the two rings is crucial for high activity. The *ortho*-diiodo derivative, which is expected to have a larger twist of the two rings, has not been reported. Moreover, diatrizoate (**3**) is a water-soluble iodinated first generation X-ray contrast agent, developed for general intravascular use.[8]

The most commonly used methods for the synthesis of 1,2,3-triiodoarenes employ direct polyiodination of benzene sulfonic acid and nitroarenes, developed by Mattern and Darby respectively.[9] Each route has different limitations, which hamper their use in routine laboratory applications.[9,10]

Due to our interest in the chemistry of 1,2,3-triiodoarene compounds, a concise and efficient method to access these compounds was needed. Although there exists a large number of established iodination protocols, a practical one for accessing these compounds is still unavailable. We report herein a convenient and effective method for the synthesis of 1,2,3-triiodoarenes and 1,2,3-trihaloarenes that is rather general in scope and gives good yields (45–88 %). The method is operationally simple, scalable, and is easy to workup and to purify. We also show for the first time that these compounds can easily undergo highly regioselective transmetalation reactions to provide *ortho*-diiodoaryl derivatives, which are useful building blocks and indeed are hard to make by other means.

Results and Discussion

We initiated this project by looking for an efficient iodination method. Despite the large number of reports on regioselective[11] and direct aromatic iodination,[6] the iodination of

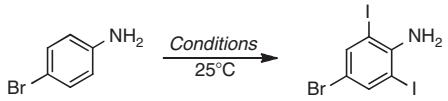
activated aromatic derivatives like aniline and phenol remains a challenging task providing mixtures of *ortho* and *para* iodinated products.[6] However, the low electrophilicity of iodine compared to other halogens such as chlorine and bromine, and the formation of HI which may cause decomposition of sensitive intermediates, make direct iodination the least reactive aromatic halogenation reaction. To overcome these limitations, direct iodinations are often performed either under oxidative conditions or under Lewis acidic conditions to remove the iodide ions by oxidation or by precipitation respectively.[6] Oxidative conditions are harsh and indeed not compatible with many functionalized and sensitive substrates. While the iodination of aromatic compounds is one of the most studied reactions, only a few reports using Lewis acids have been evaluated.[6] The most common Lewis acids are silver and mercuric salts in combination with I_2 or with ICl. This is understandable by the fact that silver and mercury can remove iodide efficiently as AgI and HgI_2.[12]

We decided to revisit these latter conditions with different solvents using 4-bromoaniline as a model substrate (Table 1). First, a combination of silver sulfate and iodine was utilized at room temperature. A quick optimization of solvent revealed that ethanol and 1,2-ethanediol were the best solvents for the desired transformation (entries 4 and 5). All other solvents were found to be unsuitable for this reaction (entries 1–3). Using ethanol with $Hg(OAc)_2/I_2$ instead of Ag_2SO_4/I_2 provided less than 10 % of the desired product (entry 6).

Using $Hg(OAc)_2/I_2$ in DCM instead of EtOH provided a mixture of iodinated products in 35 % yield (entry 7). Using ethanol as a solvent, we then examined the influence of other silver reagents on iodination of 4-bromoaniline to further establish the reaction conditions. $AgNO_3/I_2$ led to a similar result as Ag_2SO_4/I_2 (entry 8), while both $AgCl/I_2$ and $AgOAc/I_2$ provided the desired product in 25 and 37 % respectively (entries 9 and 10). No iodination was observed with *N*-iodosuccinimide (NIS) in EtOH (entry 11), while NIS in acetonitrile provided product in 29 % yield (entry 12). Using the more reactive reagent ICl provided the desired product in only 21 % (entry 13). Thus the best yields for iodination were obtained by using 1.1 equivalent of Ag_2SO_4 (entry 14) or 2.2 equivalents of $AgNO_3$ (entry 8) with 2.0 equivalents of I_2. The reaction under the former conditions also worked well on multigram scale (entry 16).

We next evaluated the substrate scope for direct iodination of anilines using the optimized reaction conditions (Scheme 1). Different aniline derivatives were subjected to the optimized reaction conditions to provide the desired iodinated products. For instance, anilines bearing chloro or bromo substituents provided the desired iodinated products (**4**, **5**, **10**, and **11**) in the best yields (Scheme 1), whereas those bearing electron-withdrawing deactivating substituents, such as fluoro and nitro, gave products **6** and **9** in only low yields. Electron-rich groups containing lone pairs of electrons for conjugation enhance the reactivity of *ortho* and *para* positions towards electrophilic substitution reactions. However, the iodination of highly activated aromatic compounds, such as 4-anisidine, provided an inseparable mixture of iodinated products (**14**). Neutral substrates were also subjected to the same reaction conditions to

Table 1. Effect of different iodinating agents in the direct iodination of 4-bromoaniline[A]



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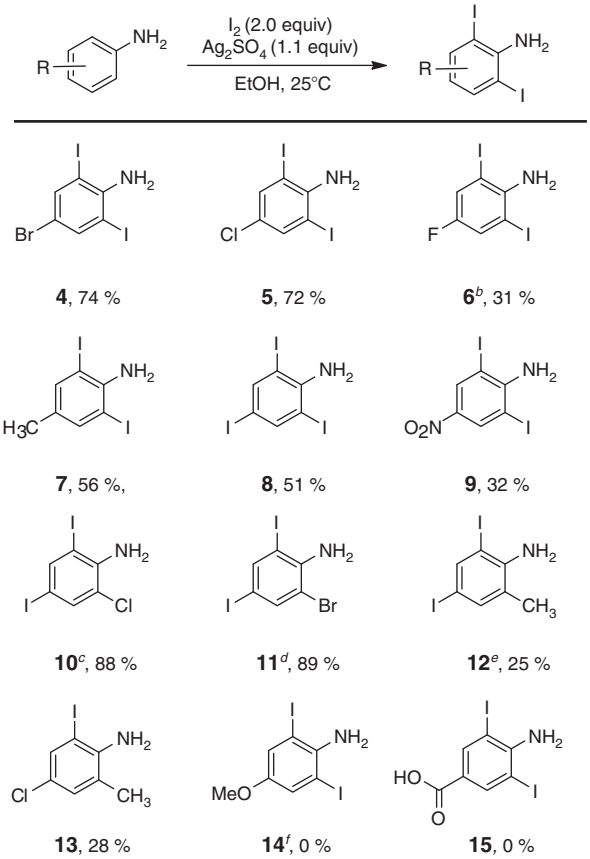
Entry	Solvent	Iodinating agent	*t* [h]	Yield [%][B]
1	THF	Ag_2SO_4/I_2	12	0[C]
2	CH_2Cl_2	Ag_2SO_4/I_2	12	23[D]
3	CH_3CN	Ag_2SO_4/I_2	12	12[D]
4	$HOCH_2CH_2OH$	Ag_2SO_4/I_2	12	69
5	EtOH	Ag_2SO_4/I_2	12	73
6	EtOH	$Hg(OAc)_2/I_2$	14	9
7	CH_2Cl_2	$Hg(OAc)_2/I_2$	12	35[D]
8	EtOH	$AgNO_3/I_2$	12	70
9	CH_3CN	$AgCl/I_2$	15	25
10	EtOH	$AgOAc/I_2$	15	37
11	EtOH	NIS	12	0[C]
12	CH_3CN	NIS	12	29
13	EtOH	ICl	12	21
14	**EtOH**	**Ag_2SO_4/I_2[E]**	**12**	**72**
15	EtOH	Ag_2SO_4/I_2[F]	12	74
16[G]	EtOH	Ag_2SO_4/I_2[E]	12	68

[A]All reactions were carried out using 7.9 mmol (1.0 equiv.) of aniline starting material, 2 equiv. of iodinating agent, and were stirred at 25°C for the time specified.
[B]Isolated yield.
[C]No reaction was observed.
[D]Mixture of mono and diiodinated products were isolated.
[E]Ag_2SO_4 (1.1 equiv. of Ag).
[F] Ag_2SO_4 (1.5 equiv. of Ag).
[G]3 g scale (17.4 mmol).



[a]Yields are given for isolated compounds (reaction scale: 5.81 mmol).
[b]Recovered starting material (32 %). [c]Starting from 2-chloroaniline.
[d]Starting from 2-bromoaniline. [e]Starting from *ortho*-toludine.
[f]A non-separable mixture of iodinated products (71 %).

Scheme 1. Direct iodination of aniline derivatives.[a]

provide the desired iodinated products (**7**, **8**, **12**, and **13**). A substrate with a carboxylic acid group did not provide the desired iodinated product (**15**).

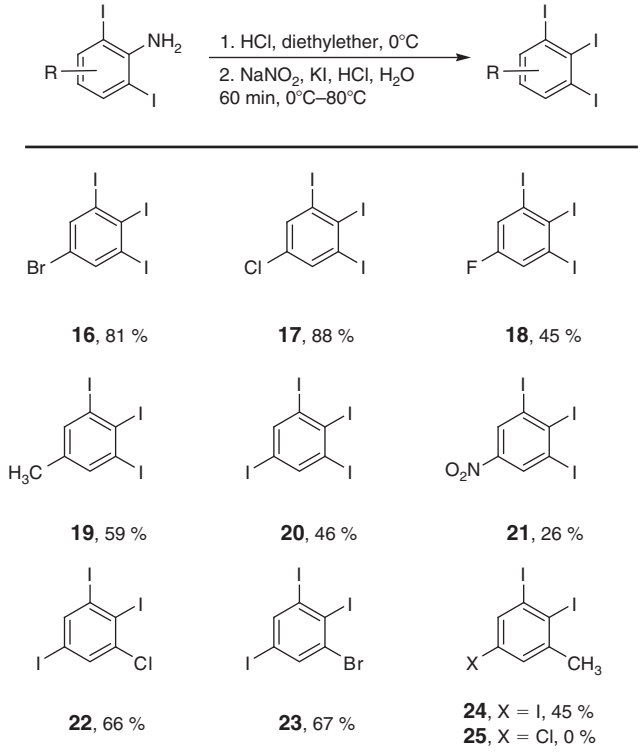
With the desired iodinated aniline derivatives in hand, we then subjected them to the most commonly used method for preparing aromatic iodides, the Sandmeyer reaction,[13] to provide the desired triiodo and trihaloarenes (Scheme 2).

The advantage of the Sandmeyer reaction over other methods for direct electrophilic iodination of aromatic compounds is the selective addition of an iodo substituent into a specified position on the aromatic ring, whereas direct iodination usually provides mixtures of regioisomers. The process of diazotization-iodination in the 'Sandmeyer reaction' is usually carried out with sodium nitrite in hydrochloric or sulfuric acid at low temperatures, followed by a subsequent reaction with iodine and KI, sometimes in the presence of copper salts.[13] Other modified methods such as the use of different alkyl nitrites, different iodinating agents, and different solvents have also been reported.[14]

Using 4-bromo-2,6-diiodoaniline as a model substrate, a sequential diazotization-iodination in one-pot provided the triiodoarene product in low yield. Trying to overcome the solubility issue of this reaction in water, the ammonium chloride salt was prepared and isolated from a reaction between 4-bromo-2,6-diiodoaniline and hydrochloric acid in diethyl ether at 0°C. The salt was then subjected to the same diazotization-iodination reaction conditions. Surprisingly, the desired triiodoarene **16** was isolated as the sole product in 81 % yield. Different diiodoaniline derivatives were subjected to these optimal reaction conditions, giving the desired triiodoarene and trihaloarene products in good to excellent yields (Scheme 2).

The geometry of the triiodoarene products was supported by X-ray crystallographic analysis of one of the products, 5-fluoro-1,2,3-triiodobenzene (Fig. 2, **18**),[15] which clearly indicates the positions of the iodo substituents. The molecular geometry shows an intramolecular steric repulsion between the vicinal iodines. This steric repulsion results in the reduction of the endocyclic angle (C−C−C = 117.9°) instead of elongation of the C−I bonds.[15]

To demonstrate the utility of 1,2,3-triiodoarenes as useful intermediates in organic synthesis, different synthetic transformations were performed. 1,2,3-Triiodoarenes **16–19** were converted into *ortho*-diiodoarene derivatives by highly regioselective metal-halogen exchange reaction in good yields (Scheme 3: **25**–**30**).



[a]Yields are given for isolated compounds.

Scheme 2. Diazotization-iodination of iodinated aniline derivatives.[a]

Conclusion

We have developed a mild and practical method for the synthesis of different 1,2,3-triiodoarenes and 1,2,3-trihaloarenes from aniline derivatives. This method is general in scope, operationally simple, scalable, and is easy to workup and to purify. The constitution of these compounds was confirmed on the basis of X-ray crystallographic analysis. We also report the first regioselective transmetalation reaction of 1,2,3-triiodoarenes to provide *ortho*-diiodoaryl derivatives, which are useful building blocks and indeed are hard to make by other

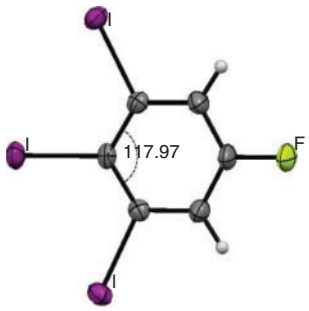
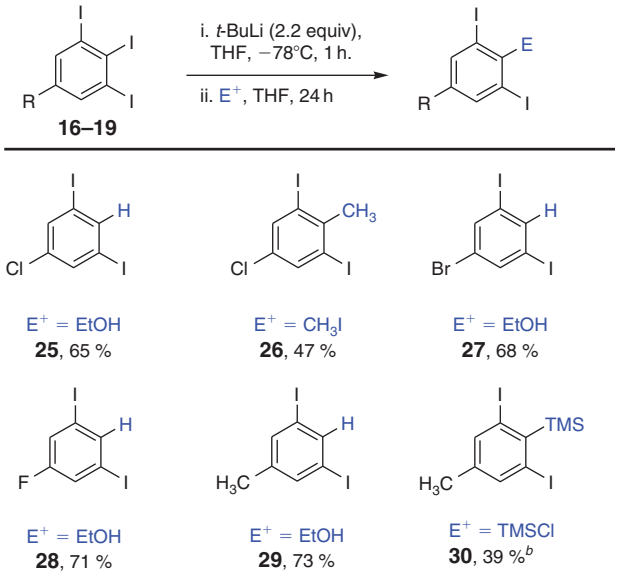


Fig. 2. *ORTEP* view of 5-fluoro-1,2,3-triiodobenzene (**18**). Thermal Gaussian ellipsoids at 20 % probability level.



[a]Yields are given for isolated compounds. [b]Recovered starting material (55 %).

Scheme 3. Regioselective metal-halogen exchange reactions of 1,2,3-triiodoarenes **16**–**19.**

means. With other iodo substituents, further elaboration can easily be achieved.

Experimental

General

All commercial reagents and chromatography solvents were used as obtained unless otherwise stated. Anhydrous solvents were distilled over appropriate drying agents before use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. Merck silica gel 60 (0.063–0.2 mm) was used for column chromatography. Visualization of TLC was accomplished with ultraviolet light (254 nm). NMR spectra were recorded on a Bruker-Avance 400 MHz spectrometer. The residual solvent protons (^{1}H) or the solvent carbon peaks (^{13}C) were used as internal standards. ^{1}H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, integration, coupling constant). The following abbreviations are used in reporting NMR data: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; dq, doublet of quartets; dd, doublet of doublets; m, mutiplet. High resolution mass spectra were recorded by Jordan University of Science & Technology.

General Procedure for Iodination of Aniline Derivatives

Aniline derivative (7.9 mmol, 1.0 equiv.), iodine (17.3 mmol, 2.2 equiv), and silver(I) sulfate (3.2 mmol, 1.1 equiv) were dissolved in ethanol (40 mL) and stirred for 24 h at room temperature. The mixture was filtered over Celite 545 to remove AgI precipitate. Water (200 mL) was added to the filtrate and then the mixture was then extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with aqueous sodium sulfite to remove excess iodine, brine, and then dried over Na_2SO_4, filtered, and concentrated. The residue was chromatographed on silica gel (hexane/ethyl acetate 7 : 1) to yield the pure desired product.

4-Fluoro-2,6-diiodoaniline (**6**)

The title compound was prepared using the general procedure for halogenation of aniline derivatives and isolated in 31 % yield as a white solid. Mp 67–69°C. δ_H (400 MHz, $CDCl_3$): 7.44 (d, 2H, *J* 7.4, CH), 4.46 (s, 2H, NH_2). δ_C (100 MHz, $CDCl_3$): 154.8, 152.3, 142.7, 125.6, 125.3, 78.9, 78.8. ν_{max}(neat)/cm^{-1} 3377, 3258, 3037, 2957, 1616, 1584, 1419, 1004, 900. *m*/*z* (HR-MS EI) 362.8434; $[M-H]^-$ requires 362.8417.

2-Chloro-4,6-diiodoaniline (**10**)

The title compound was prepared using the general procedure for halogenation of aniline derivatives and isolated in 88 % yield as a white solid. Mp 71–73°C. δ_H (400 MHz, $CDCl_3$): 7.79 (s, 1H, CH), 7.50 (s, 1H, CH), 4.56 (s, 2H, NH_2). δ_C (100 MHz, $CDCl_3$): 144.4, 143.2, 137.2, 118.3, 83.8, 77.5. ν_{max}(neat)/cm^{-1} 3416, 3387, 3055, 1652, 1167, 1121, 950. *m*/*z* (HR-MS EI) 377.8179; $[M-H]^-$ requires 377.8122.

2-Bromo-4,6-diiodoaniline (**11**)

The title compound was prepared using the general procedure for halogenation of aniline derivatives and isolated in 89 % yield as a white solid. Mp 65–67°C. δ_H (400 MHz, $CDCl_3$): 7.84 (s, 1H, CH), 7.67 (s, 1H, CH), 4.64 (s, 2H, NH_2). δ_C (100 MHz, $CDCl_3$): 145.1, 143.9, 140.1, 107.6, 83.4, 77.9. ν_{max}(neat)/cm^{-1} 3412, 3314, 2954, 1622, 1095, 930. *m*/*z* (HR-MS EI) 423.7640; $[M+H]^-$ requires 423.7616.

4-Chloro-2-iodo-6-methylaniline (**13**)

The title compound was prepared using the general procedure for halogenation of aniline derivatives and isolated in 28 % yield as a white solid. Mp 58–60°C. δ_H (400 MHz, $CDCl_3$) δ: 7.50 (d, 1H, *J* 1.9, CH), 7.02 (d, 1H, *J* 1.9, CH), 4.06 (s, 2H, NH_2), 2.20 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$) δ: 143.6, 135.5, 130.1, 123.3, 122.8, 83.6, 18.8. ν_{max}(neat)/cm^{-1} 3511, 3395, 3120, 2915, 1682, 1154, 1321, 892. *m*/*z* (HR-MS EI) 265.9378; $[M-H]^-$ requires 265.9312.

General Procedure for Diazotization of Aniline Derivatives

Concentrated HCl was added dropwise to a solution of iodinated aniline derivative (1.4 mmol, 1.0 equiv.) in 15 mL diethyl ether at 0°C until no more precipitate formed. The aniline salt was then filtered, washed with cold diethyl ether, and collected. A solution of $NaNO_2$ (1.53 mmol, 1.1 equiv.) in water (1.0 mL) was added dropwise to a mixture of aniline salt in water (3.5 mL) and concentrated hydrochloric acid (1.5 mL) below 5°C, and the mixture was stirred for 10 min. A solution of potassium iodide (2.1 mmol, 1.5 equiv.) in water (1.0 mL) was then added dropwise to the reaction mixture. The mixture was stirred for 15 min without cooling, at 50°C for 30 min and then followed by 45 min at 80°C. The mixture was then cooled to 0°C, and a solution of 5 % aqueous sodium sulfite (30 mL) was added. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was chromatographed on silica gel (hexane) to yield the pure desired product.

5-Bromo-1,2,3-triiodobenzene (**16**)

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 81 % yield as a white solid. Mp 138–140°C. δ_H (400 MHz, $CDCl_3$) δ: 7.97 (s, 2H, CH). δ_C (100 MHz, $CDCl_3$): 141.7, 140.2, 122.6, 106.7. ν_{max}(neat)/cm^{-1} 2987, 1642, 1546, 1051, 860. *m*/*z* (HR-MS EI) 533.6499; $[M]^+$ requires 533.6474.

5-Chloro-1,2,3-triiodobenzene (**17**)

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 88 % yield as a white solid. Mp 118–120°C. δ_H (400 MHz, $CDCl_3$): 7.86 (s, 2H, CH). δ_C (100 MHz, $CDCl_3$): 138.3, 135.3, 119.2, 106.8. ν_{max}(neat)/cm^{-1} 3025, 1633, 1492, 894. *m*/*z* (HR-MS EI) 489.6939; $[M]^+$ requires 489.6979.

5-Fluoro-1,2,3-triiodobenzene (**18**)

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 45 % yield as a white solid. Mp 127–129°C. δ_H (400 MHz, $CDCl_3$) δ: 7.62 (d, 2H, $J = 4.0$ Hz). δ_C (100 MHz, $CDCl_3$) δ: 161.8, 159.3, 126.2, 125.9, 115.1, 105.5, 105.4. ν_{max}(neat)/cm^{-1} 3065, 2941, 1596, 1435, 1187, 852. *m*/*z* (HR-MS EI) 473.7213; $[M]^+$ requires 473.7275.

1,2,3-Triiodo-5-methylbenzene (**19**)

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 59 % yield as a white solid. Mp 113–115°C. δ_H (400 MHz, $CDCl_3$): 7.69 (s, 2H, CH), 2.17 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$): 140.9, 139.1, 116.3, 106.3, 19.4. ν_{max}(neat)/cm^{-1} 3149, 2985,

1614, 1587, 1215, 1146, 840. *m/z* (HR-MS EI) 469.7594; $[M]^+$ requires 469.7525.

*1,2,3,5-Tetraiodobenzene (**20**)*

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 46 % yield as a white solid. Mp 133–135°C. δ_H (400 MHz, $CDCl_3$): 8.13 (s, 2H, CH). δ_C (100 MHz, $CDCl_3$): 146.1, 121.0, 108.1, 94.9. ν_{max}(neat)/cm^{-1} 2987, 1534, 1145, 1009, 873. *m/z* (HR-MS EI) 581.6358; $[M]^+$ requires 581.6335.

*1-Chloro-2,3,5-triiodobenzene (**22**)*

The title compound was prepared using the general procedure for diazotization aniline derivatives and isolated in 66 % yield as a white solid. Mp 112–114°C. δ_H (400 MHz, $CDCl_3$): 8.07 (s, 1H, CH), 7.71 (s, 1H, CH). δ_C (100 MHz, $CDCl_3$): 145.1, 139.6, 136.6, 112.6, 110.8, 94.2. ν_{max}(neat)/cm^{-1} 3012, 2983, 1642, 1548, 1124, 863. *m/z* (HR-MS EI) 489.6935; $[M]^+$ requires 489.6979.

*1-Bromo-2,3,5-triiodobenzene (**23**)*

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 67 % yield as a white solid. Mp 113–115°C. δ_H (400 MHz, $CDCl_3$): 8.10 (s, 1H, CH), 7.88 (s, 1H, CH). δ_C (100 MHz, $CDCl_3$): 145.5, 139.7, 130.2, 115.3, 110.3, 94.5. ν_{max}(neat)/cm^{-1} 3042, 2968, 1604, 1523, 1154, 760. *m/z* (HR-MS EI) 533.6423; $[M]^+$ requires 533.6474.

*1,2,5-Triiodo-3-methylbenzene (**24**)*

The title compound was prepared using the general procedure for diazotization of aniline derivatives and isolated in 45 % yield as a white solid. Mp 114–116°C. δ_H (400 MHz, $CDCl_3$): 8.00 (s, 1H, CH), 7.49 (s, 1H, CH), 2.54 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$): 145.8, 143.9, 136.6, 113.7, 110.5, 93.8, 31.8. ν_{max}(neat)/cm^{-1} 3125, 2945, 2913, 1642, 1574, 1351, 1121, 931. *m/z* (HR-MS EI) 469.7618; $[M]^+$ requires 469.7525.

General Procedure for Metal-Halogen Exchange Reactions of 1,2,3-Triiodoarenes

To a solution of triiodoarene (0.42 mmol) in THF (15 mL) at −78°C was added dropwise isopropyl magnesium chloride (2M in THF, 0.23 mL, 0.46 mmol). The mixture was stirred at that temperature for 2 h and then the electrophile was added. The solution was slowly warmed to room temperature and stirred overnight. Saturated NH_4Cl was added and the resulting mixture was stirred for 30 min at room temperature. The aqueous layer was extracted with Et_2O (2 × 50 mL). The organic phase was dried with Na_2SO_4, filtered, and then the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (100 % hexane) to yield the pure desired product.

*1-Chloro-3,5-diiodobenzene (**25**)*

The title compound was prepared using the general procedure for metal-halogen exchange reaction and isolated in 65 % yield as a white solid. Mp 131–133°C. δ_H (400 MHz, $CDCl_3$): 7.94 (s, 1H, CH), 7.68 (s, 2H, CH). δ_C (100 MHz, $CDCl_3$): 143.0, 136.1, 135.1, 93.9. ν_{max}(neat)/cm^{-1} 2945, 2916, 1623, 1586, 1414, 1125, 762. *m/z* (HR-MS EI) 363.7996; $[M]^+$ requires 363.8013.

*5-Chloro-1,3-diiodo-2-methylbenzene (**26**)*

The title compound was prepared using the general procedure for metal-halogen exchange reaction and isolated in 47 % yield as a white solid. Mp 145–147°C. δ_H (400 MHz, $CDCl_3$): 7.82 (s, 2H, CH), 2.72 (s, 3H, CH_3). δ_C (100 MHz, $CDCl_3$): 141.2, 138.3, 131.8, 97.8, 33.7. ν_{max}(neat)/cm^{-1} 3148, 2975, 2846, 1634, 1573, 1243, 1147, 876. *m/z* (HR-MS EI) 377.8144; $[M]^+$ requires 377.8169.

*(2,6-Diiodo-4-methylphenyl)trimethylsilane (**30**)*

The title compound was prepared using the general procedure for Metal-Halogen Exchange reaction and isolated in 39 % yield as a colourless oil. δ_H (400 MHz, $CDCl_3$): 7.81 (s, 2H, CH), 2.18 (s, 3H, CH_3), 0.64 (s, 9H, $Si(CH_3)_3$). δ_C (100 MHz, $CDCl_3$): 141.8, 141.2, 136.9, 102.6, 19.1, 4.53. ν_{max}(neat)/cm^{-1} 3201, 2918, 2894, 1687, 1548, 1423, 1250, 1146, 944. *m/z* (HR-MS EI) 415. 8913; $[M]^+$ requires 415. 8954.

Supplementary Material

^1H and ^{13}C NMR, IR and HRMS data, experimental procedures for new compounds, and X-ray crystallographic data for compound **18** can be found on the Journal's website.

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[15] CCDC-907172 contains the supplementary crystallographic data for compound **18**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.