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Full Paper

A Simple and Efficient Two-Step Synthesis of 1,2,3-Triiodoarenes via Consecutive *C–H* Iodination/*ipso*-Iododecarboxylation Strategy: A Potential Application towards *ortho*-Diiodoarenes by Regioselective Metal–Iodine Exchange Reaction

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A general, robust, and efficient method for the conversion of benzoic acids to 1,2,3-triiodoarenes and 1,2,3-trihaloarenes via a two-step synthesis is reported. Commercially available benzoic acids were used that can allow the reactions to be performed on multi-gram scales with good-to-excellent yields. This report discloses a practical method for the synthesis of 1,2,3-triiodoarenes and 1,2,3-trihaloarenes that is general in scope, scalable, and easy to workup and purify. A potential application of the target compounds as precursors for novel regioselective metal–iodine exchange reaction of 1,2,3-triiodoarenes was also demonstrated. It provided *ortho*-diiodoaryl derivatives in a high regioselective fashion that are useful intermediates in synthesis and indeed are hard to synthesize by any other means.

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Introduction

Aryl halides, especially iodides, are versatile compounds in organic synthesis. They are used in the synthesis of many biologically active targets and remarkable intermediates.[1] Due to the relatively weak nature of the C–I bond,[2] it has found particular use in transition metal-catalyzed homo- or hetero-coupling processes or in nucleophilic displacement reactions using organolithium or organomagnesium intermediates.[2,3] A broad palette of synthetic methods for iodination of aromatic compounds are reported in literature.[4] For instance, the classical Friedel–Crafts reactions of aromatic and polycyclic aromatic compounds readily undergo halogenation with chloride or bromide to yield haloarene derivatives with moderate regioselectivity, whereas the corresponding reaction with iodine fails. Alternatively, *ipso*-substitution reaction of amines, bromides, or other functional groups on the aromatic ring, such as the diazotization of corresponding amines, followed by treatment with alkali metal iodide or the conversion of aromatic bromides to aryl lithium or aryl magnesium reagents and subsequent treatment with iodine molecule respectively exclusively provide one regioisomer.[5]

Ipso-iododecarboxylation of carboxylic acids has recently emerged as an alternative method for *C–H* transformations in which the regioselectivity is easily controlled by the position of the carboxylic acid group, whereas in common *C–H* activation methodology, regioselectivity is still a problem. Therefore, the preparation of iodoarenes by directed *C–H* iodination or *ipso*-iododecarboxylation of carboxylic acids is a particularly alternative method due to the following considerations: aromatic carboxylic acids are inexpensive substrates, broadly available, easily removed from the product by a simple basic workup, and most importantly, are highly regioselective-controlled substrates.[6]

1,2,3-Triiodoarenes are found in several biologically active compounds. For instance, 6,7-dihydroxy-1-(3,4,5-triiodobenzyl)-1,2,3,4-tetrahydroisoquinoline (**1**, Fig. 1) is a trimetoquinol derivative comprising triiodo substituents at 3,4,5-positions, instead of trimethoxy substituents, and is found to have β_1-, β_2-, and β_3-subtypes adrenoceptor activities.[7] Interestingly, the iodo derivatives resulted in a 65-fold increase in potency along with an increased activity at the β_3-adrenoceptor.[7b,7c] Additionally, morphinan derivative **2** is an amido-functionalized morphine derivative which has recently been reported to have a useful analgesical activity especially for constipation and respiratory depression.[8] Furthermore, pregnenolone derivative **3** is a steroidal compound reported as an X-ray contrast agent for diseases with macrophage localization due to tumour, inflammation, and infection such as in the liver, spleen, alveolus, lymph node, lymphatic vessel, or kidney epithelium.[9] Lastly, 2,6,7-trioxabicyclo[2,2,2]octane **4** and *N*-acetonylbenzamide **5** are reported to have a potential pesticidal and fungicidal activity, respectively.[10]

Although there are several published methods for iodination of aromatic carboxylic acids in literature, each method has its own limitations, and a practical approach to access 1,2,3-triiodoarenes from benzoic acids has not been reported yet. Recently, we disclosed a two-step synthesis of 1,2,3-triiodoarenes from aromatic amines via an iodination–diazotization–iodination strategy.[5a] Although this method provides the desired 1,2,3-triiodoarenes in good yields, the aromatic amines need to be *para*-substituted to enhance their iodination towards *ortho*-positions and to minimize the total number of products. Herein, we report a practical, efficient, and operationally simple protocol for a formal two-step *C–H* iodination/*ipso*-iododecarboxylation of aromatic carboxylic acids, providing 1,2,3-triiodoarenes and 1,2,3-trihaloarenes, and is rather general in scope, easy to workup and purify, and gives good yields. We also examine the activity of these compounds towards metal–halogen exchange reactions that undergo high regioselective mono- and double transmetalation reactions to provide new aryl iodide derivatives. The latter are useful building blocks and indeed are hard to synthesize by any other means.

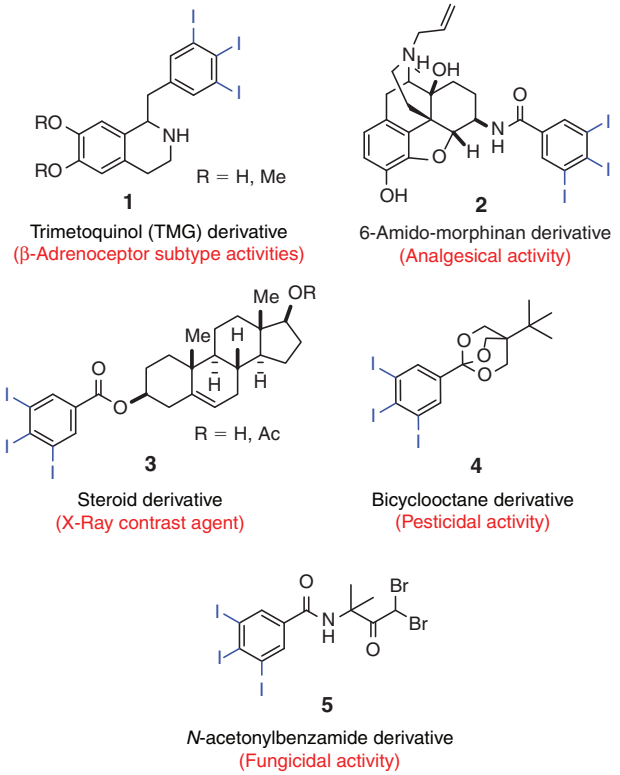
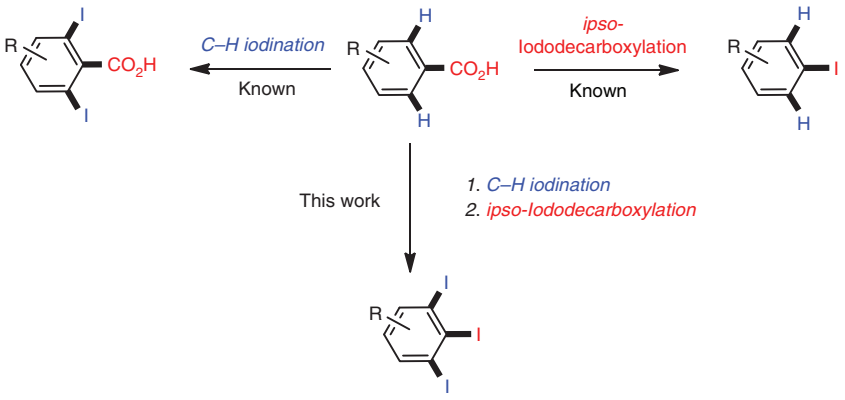


Fig. 1. Examples of some biologically important triiodoarenes in medicine.

Results and Discussion

Due to our interest in the chemistry of 1,2,3-triiodoarenes with the aim of expanding their applications in synthesis and medicine, we felt intrigued in pursuing an alternative method to increase the scope of these substrates. Accordingly, we envisioned that sequential C–H iodination/*ipso*-iododecarboxylation could be a potential methodology (Scheme 1). Our approach originated by screening the literature for an efficient regioselective *ortho*-iodination approach. In spite of the large number of reports on regioselective[11] and direct aromatic iodination,[5c] activated aromatic derivatives remain a challenging task.[5c] On the other hand, the low electrophilicity of iodine when compared with that of chlorine and bromine makes iodination the least reactive aromatic halogenation reaction. Aromatic carboxylic acid proved to be an excellent *C–H* directing group for aromatic *ortho*-functionalization. Multiple examples of Pd and Ag-catalyzed carboxylate-directed transformations have been reported.[12] For instance, pioneering work from the group of Yu established Pd^{II}-catalyzed *ortho*-iodination and bromination of *C–H* bonds at 100°C as the current state-of-the-art method, having a good substrate scope for benzoic acids, but limited for *meta*-substituent benzoic acids providing a mixture of mono and diiodinated products.[12f] A variety of functionalized aromatic carboxylic acids were subjected to the optimized reaction conditions to provide the desired iodinated benzoic acids in good-to-excellent yields. For instance, benzoic acids bearing fluoro or chloro substituents provided the desired iodinated products in higher yields (Scheme 2: **6**, **7**, **12**, **15**, and **20**), whereas those bearing bromo or iodo substituents can undergo further couplings and subsequently decomposed (Scheme 2: **8** and **9**).

Ortho-bromobenzoic acid (Scheme 2: **13**) was an exception, providing the desired iodinated product in 86 % yield, whereas *meta*-bromobenzoic acid (Scheme 2: **16**) only furnished the monoiodinated product by favouring the less hindered *ortho*-position. Neutral substrates were also subjected to the same reaction conditions, providing the desired iodinated products (Scheme 2: **10**, **14**, and **17**). Electron-rich substituted benzoic

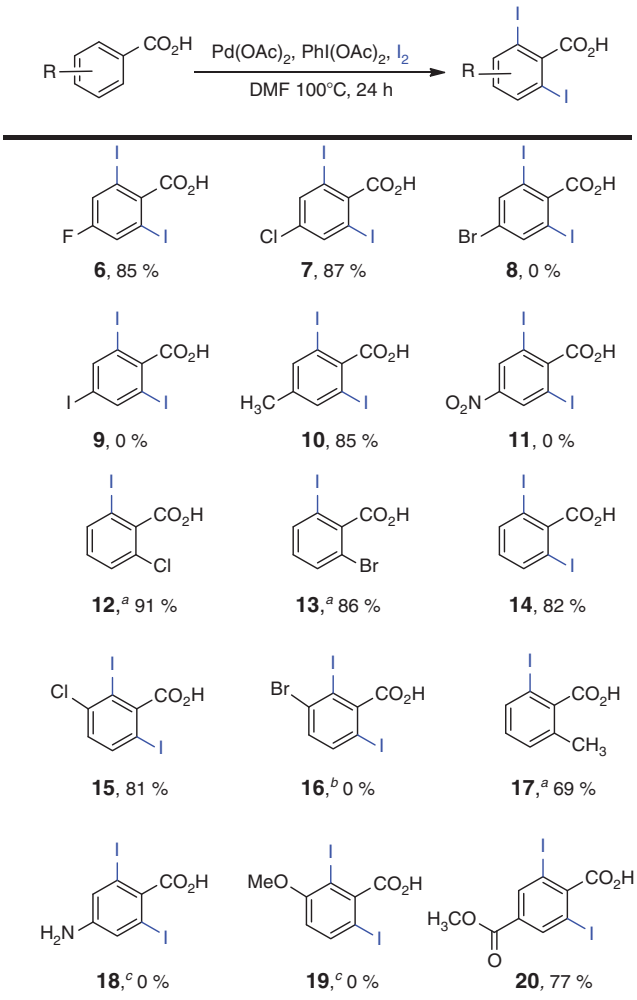


Scheme 1. Synthetic approach to preparing 1,2,3-triiodoarene derivatives.

acids were found to be less effective substrates. For instance, 4-aminobenzoic acid and 3-anisic acid (Scheme 2: **18** and **19**) provided a non-separable mixture of products. On the other hand, electron-poor substituted benzoic acids were found to be more effective and high yielding. The *para*-nitrobenzoic acid did not work under these conditions (Scheme 2: **11**).

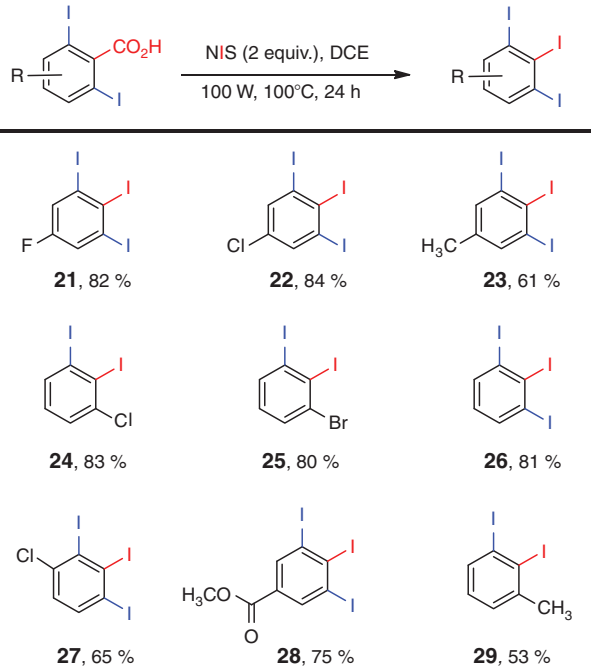
With the desired *ortho*-diiodinated benzoic acids in hand, we then subjected these compounds to one of the common methods for preparing aromatic iodides, the *ipso*-iododecarboxylative method, to obtain the desired triiodoarenes (Scheme 3). This latter transformation has received considerable attention in recent years as the heart of numerous C–H, C–X, and C–C bonds formations not only for using the carboxylate group to direct aromatic *ipso*-functionalization providing one regioisomer, but also due to the versatility of aromatic carboxylic acids as readily available starting materials.[6a–c,6e,12g,12h,12j,12l,13]

Ipso-halodecarboxylation of carboxylic acids, the Hunsdiecker reaction, is one of the fundamental organic reactions carried out for functional group transformations.[14] It is believed that the extrusion of CO_2 is the rate-determining step in these transformations. Several stoichiometric and catalytic methods were developed. For instance, Borodine[15] and Hunsdiecker[16] reported the use of anhydrous silver(I) carboxylates for the conversion of aliphatic carboxylic acids into alkyl bromides with one-carbon shorter. Modifications to the Borodine–Hunsdiecker reaction conditions were also reported.[17] Due to the difficulty of working with anhydrous silver(I) salts, other protocols were developed subsequently such as the use of more stable thallium(I) or mercury(II) salts.[16,18] The mixture of HgO and halogen (Cristol–Firth–Hunsdiecker modification) tolerates the direct transformation of carboxylic acids.[19] The use of mercury-mediated process is limited due to the need for stoichiometric mercury salts and the toxicity of organomercury(II) species. The use of (diacetoxy)iodobenzene and iodine under UV photolysis (Suarez modification) were reported thereafter for the *ipso*-iododecarboxylation of aliphatic carboxylic acids.[6c,6d] A combination of $Pb(OAc)_4$ and lithium halides (Kochi modification) were used for the transformations of aliphatic carboxylic acids into alkyl halides.[20] Another approach for *ipso*-halodecarboxylation was developed involving the use of thiohydroxamate esters in solvents such as $BrCCl_3$ or CHI_3 (Barton modification).[21] The remarkable use of cationic gold(I) complexes for *ipso*-halodecarboxylation of aromatic and heteroaromatic carboxylic acids was recently reported (Larrosa modification).[6e] The above methods suffer from harsh conditions, limited scope, the use of toxic reagents, and stoichiometric reagents. To avoid these limitations, which hamper their use in industrial applications, several catalytic *ipso*-fluoro, *ipso*-chloro, and *ipso*-bromodecarboxylative methods for either aromatic or aliphatic carboxylic acids were reported.[12g,12h,12j] It is worth mentioning that no catalytic *ipso*-iododecarboxylative method of aromatic acids has been reported to date. Pioneering work from the group of Gandelman established a protocol for *ipso*-iododecarboxylation of aromatic and aliphatic carboxylic acids without the use of heavy metals or strong oxidizing agents.[6b] Even though this method is not



Yields are given for isolated compounds (reaction scale: 16.4 mmol). Reaction conditions: $Pd(OAc)_2$ (5 mol-%), $PhI(OAc)_2$ (1.5 equiv.), I_2 (1.5 equiv.). [a]$PhI(OAc)_2$ (0.75 equiv.) and I_2 (0.75 equiv.) were used with **12**, **13**, and **17**.[b] Less hindered monoiodo benzoic acid derivative was isolated. [c]Non-separable mixture of products.

Scheme 2. *Ortho*-Iodination and diiodination of benzoic acid derivatives.



Yields are given for isolated compounds (reaction scale: 2.67 mmol).

Scheme 3. *Ipso*-Iododecarboxylation of *ortho*-diiodobenzoic acids.

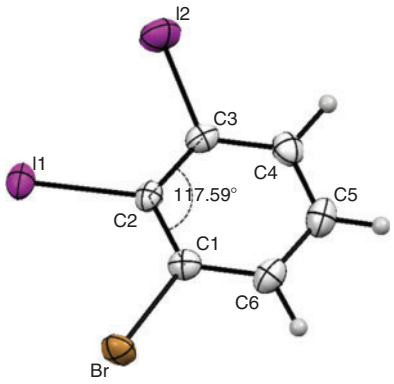


Fig. 2. *ORTEP* view of 1-bromo-2,3-diiodobenzene (**25**). Thermal Gaussian ellipsoids at 20 % probability level.

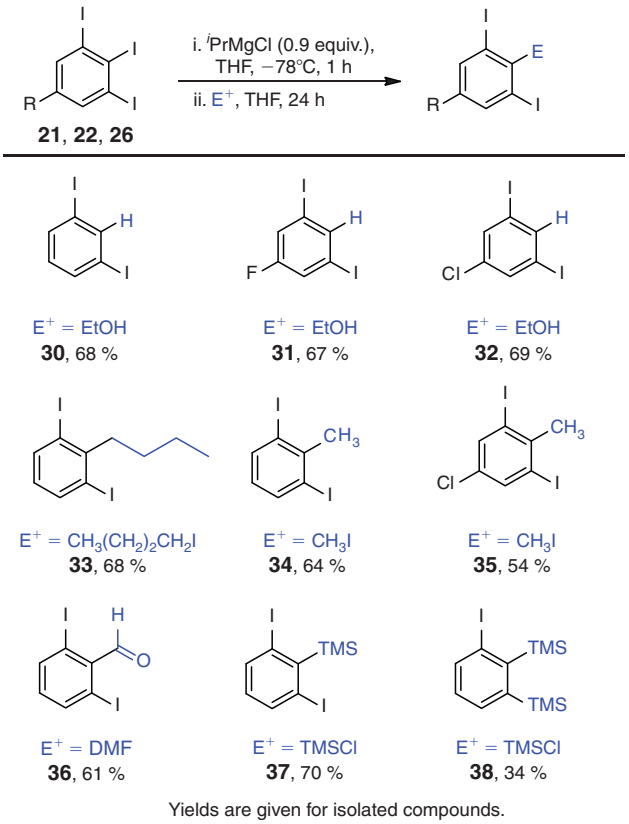
catalytic, it provides as the current state of the art, a good substrate scope, biodegradable by-products and good yields.

Our interest in the synthesis and application of 1,2,3-triiodoarenes encouraged us to test this efficient and metal-free *ipso*-iododecarboxylation protocol on our *ortho*-diiodobenzoic acids in order to increase the scope of 1,2,3-triiodoarene compounds for future applications.

We quickly subjected the isolated *ortho*-diiodinated benzoic acid derivatives to the optimized reaction conditions for *ipso*-iododecarboxylation developed by Gandelman and coworkers.[6b] We were pleased to see that the desired 1,2,3-triiodoarene and 1,2,3-trihaloarene products were easily isolated in good-to-excellent yields (Scheme 3). It is known in the literature that an *ortho*-halo for benzoic acid is a requirement for enhancing the *ipso*-decarboxylation. Our substrates are *ortho*-dihalobenzoic acids, which may explain the high obtained yields under these conditions. On the other hand, the rate of *ipso*-iododecarboxylation is slightly influenced by the nature of the substituent on the aromatic ring. For instance, electron-poor substituted benzoic acids at *para*- and *meta*-positions to the carboxyl group were found to be more effective substrates for *ipso*-iododecarboxylation providing slightly higher yields (Scheme 3: **21**, **22**, **27**, and **28**). *Ipso*-decarboxylation of *ortho*-dihalobenzoic acids proceeded smoothly, indicating that an electron-withdrawing group at *para*-position is not a requirement for this type of substrates (Scheme 3: **24**–**26**). Neutral substrates were also subjected to the optimized reaction conditions to provide the desired products in good yields (Scheme 3: **23** and **29**).

The geometry of 1,2,3-triiodoarenes is supported by X-ray crystallographic analysis as shown for one of the products, 1-bromo-2,3-diiodobenzene (Fig. 2, **25**), and clearly shows the positions of the three halo substituents. The molecular geometry indicates an intermolecular steric repulsion between the vicinal halogens. The extent of this intermolecular repulsion decreased by reducing the endocyclic angle (C–C–C = 117.59°) rather than elongation of the C–X bonds. CCDC-992711 contains the supplementary crystallographic data for compound **25**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or via www.ccdc.cam.ac.uk/data_request/cif.

To show the role of 1,2,3-triiodoarenes as useful intermediates in synthesis, different synthetic transformations were performed. Selected 1,2,3-triiodoarenes **21, 22**, and **26** were converted into *ortho*-diiodoarene derivatives via highly



Scheme 4. Regioselective metal–iodine exchange reactions of 1,2,3-triiodoarenes **21**, **22**, and **26**.

regioselective metal–iodine exchange reactions in moderate-to-good yields (Scheme 4: **30**–**38**). A sequential double metal–iodine exchange reaction is performed to isolate the disubstituted product **38** in 34 % yield.

Conclusion

In conclusion, we have developed a mild, efficient, and practical method for the synthesis of different 1,2,3-triiodoarenes and 1,2,3-trihaloarenes from benzoic acids. This method is general, operationally simple, scalable, and is easy to workup and purify. The isolated triiodoarenes are crystalline solids and remarkably bench-stable compounds. The molecular geometry was determined by X-ray crystallographic analysis. We also report the regioselective metal–iodine reaction of 1,2,3-triiodoarenes and the one-pot double metal–iodine reaction to provide *ortho*-diiodoarenes and disubstituted iodoarene, respectively, which are valuable building blocks and indeed are hard to synthesize by any other methods. With other iodo groups on the aryl structure, further elaboration can easily be achieved.

Experimental

General

All commercial reagents and chromatography solvents were used as obtained unless otherwise stated, i.e. ethanol (EtOH), diethyl ether (Et_2O), hydrochloric acid, chlorobenzene (C_6H_5Cl), chloroform, ethyl acetate (EtOAc), palladium(II) diacetate [$Pd(OAc)_2$], iodobenzene diacetate $PhI(OAc)_2$, *N*-iodosuccinimide (NIS), anhydrous sodium sulfate, *iso*-propylmagnesium chloride (^{i}PrMgCl; 2 M), and iodine (I_2).

Anhydrous solvents were distilled over appropriate drying agents before use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F254. Merck silica gel 60 (0.063–0.2 mm) was used for column chromatography. Visualization of TLC was accomplished with UV light (254 nm). NMR spectra were recorded on Bruker Avance 300 and 400 MHz spectrometers. The residual solvent protons (^{1}H) or the solvent carbon (^{13}C) were used as internal standards. ^{1}H NMR data are presented as follows: chemical shift in ppm (δ) downfield from trimethylsilane (TMS) (multiplicity, integration, coupling constant). The following abbreviations are used in reporting the NMR data: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dq, doublet of quartets; dd, doublet of doublets; and m, multiplet. High-resolution mass spectra were recorded using chemical ionization (CI) and electrospray ionization (ESI) techniques.

General Procedure for ortho*-Diiodination of Benzoic Acid Derivatives*

In a flame-dried 100 mL round-bottom flask, benzoic acid starting material (16.4 mmol, 1.0 equiv.), palladium acetate (0.05 equiv.), iodobenzene diacetate (1.5 equiv.), and iodine (1.5 equiv.) were dissolved in anhydrous DMF (40 mL) under atmospheric air. The flask was then sealed with a septum and the reaction mixture was stirred at 100°C for 24 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate, and then washed with 0.5 N HCl (4 × 20 mL). The organic phase was washed with brine, dried over Na_2SO_4, and concentrated in a rotary evaporator. The residue was purified by column chromatography on silica gel (3 : 1 hexane/EtOAc) to give the desired iodinated product.

*Synthesis of 3-Chloro-2,6-Diiodobenzoic Acid (**15**)*

The title compound was prepared using the general procedure for iodination of arene carboxylic acids and isolated in 81 % yield as a white solid, mp 148–150°C. ν_{max} (KBr)/cm^{-1} 1790, 1652, 1548, 1152, 965. δ_H (*d*-$CDCl_3$, 400 MHz) 7.74 (d, 1H, *J* 8.0), 7.20 (d, 1H, *J* 8.0). δ_C (*d*-$CDCl_3$, 100 MHz) 172.2, 146.8, 142.6, 139.3, 130.3, 95.7, 86.9. *m*/*z* 406.7824. High-resolution mass spectrometry (HRMS; ESI) Anal. Calc. for $C_7H_2ClI_2O_2$ [M–H]$^-$ 406.7833.

General Procedure for ipso*-Iododecarboxylation of* ortho*-Diiodobenzoic Acid Derivatives*

A mixture of *ortho*-diiodobenzoic acid derivative (2.67 mmol, 1.0 equiv.), NIS (2.0 equiv.), and 1,2-dichloroethane (DCE; 10 mL) were added to a flame-dried 100 mL round-bottom flask, and the mixture was irradiated with 100 W (tungsten lamp) under reflux conditions for 24 h. The reaction mixture was then cooled to room temperature. The mixture was then washed with saturated $NaHSO_3$, saturated $NaHCO_3$, and brine. The organic layers were collected and then dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator. The residue was then purified by flash chromatography on silica gel (100 % hexane) to give the desired iodinated product.

*Synthesis of 1-Chloro-2,3-Diiodobenzene (**24**)*

The title compound was prepared using the general procedure for *ipso*-iododecarboxylation of benzoic acid derivatives and isolated in 83 % yield as a white solid, mp 83–84°C. ν_{max} (KBr)/cm^{-1} 2978, 2948, 1642, 1581, 1100, 741. δ_H (*d*-$CDCl_3$, 400 MHz) 7.75 (d, 1H, *J* 8.0), 7.39 (d, 1H, *J* 8.1), 6.98 (dd, 1H, *J* 8.0, 8.1). δ_C (*d*-$CDCl_3$, 100 MHz) 138.5, 137.0, 130.0, 127.8, 112.3, 109.3. *m*/*z* 363.8008. HRMS (CI) Anal. Calc. for $C_6H_3ClI_2$ [M$^+$] 363.8013.

*Synthesis of 1-Bromo-2,3-Diiodobenzene (**25**)*

The title compound was prepared using the general procedure for *ipso*-iododecarboxylation of benzoic acid derivatives and isolated in 80 % yield as a white solid, mp 92–93°C. ν_{max} (KBr)/cm^{-1} 2987, 2962, 1601, 1542, 1118, 624. δ_H (*d*-$CDCl_3$, 400 MHz) 7.81 (d, 1H, *J* 8.0), 7.58 (d, 1H, *J* 8.0), 6.89 (t, 1H, *J* 8.0). δ_C (*d*-$CDCl_3$, 100 MHz) 137.5, 131.3, 130.2, 129.1, 114.9, 108.8. *m*/*z* 407.7497. HRMS (CI) Anal. Calc. for $C_6H_3BrI_2$ [M$^+$] 407.7507.

*Synthesis of 1-Chloro-2,3,4-Triiodobenzene (**27**)*

The title compound was prepared using the general procedure for *ipso*-iododecarboxylation of benzoic acid derivatives and isolated in 65 % yield as a white solid, mp: 85–86°C. ν_{max} (KBr)/cm^{-1} 3088, 2941, 1605, 1544, 1142, 570. δ_H (*d*-$CDCl_3$, 400 MHz) 7.83 (d, 1H, *J* 8.0), 7.13 (d, 1H, *J* 8). δ_C (*d*-$CDCl_3$, 100 MHz) 138.9, 137.7, 128.9, 123.1, 112.6, 103.8. *m*/*z* 489.6970. HRMS (CI) Anal. Calc. for $C_6H_2ClI_3$ [M$^+$] 489.6979.

*Synthesis of Methyl 3,4,5-Triiodobenzoate (**28**)*

The title compound was prepared using the general procedure for *ipso*-iododecarboxylation of benzoic acid derivatives and isolated in 75 % yield as a white solid, mp 145–146°C. ν_{max} (KBr)/cm^{-1} 3058, 2967, 1548, 1520, 1047, 654. δ_H (*d*-$CDCl_3$, 400 MHz) 8.40 (s, 2H). δ_C (*d*-$CDCl_3$, 100 MHz) 163.5, 139.0, 138.6, 129.3, 106.5, 52.3. *m*/*z* 513.7415. HRMS (CI) Anal. Calc. for $C_8H_5I_3O_2$ [M$^+$] 513.7424.

General Procedure for Metal–Iodine Exchange Reaction of 1,2,3-Triiodoarenes

Isopropyl magnesium chloride (2 M in THF, 0.23 mL, 0.70 mmol) was added to a solution of 1,2,3-triiodoarene (0.66 mmol, 1 equiv.) in THF (15 mL) at −78°C. 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.

*Synthesis of 2-Butyl-1,3-Diiodobenzene (**33**)*

The title compound was prepared using the general procedure for metal–iodine exchange reaction and isolated in 68 % yield as a colourless oil. ν_{max} (KBr)/cm^{-1} 3050, 2971, 1612, 1594, 1217, 1078, 684. δ_H (*d*-$CDCl_3$, 300 MHz) 7.80 (d, 2H, *J* 7.8), 6.47 (t, 1H, *J* 7.8), 3.04 (t, 2H, *J* 6.9), 1.52 (m, 4H), 1.01 (t, 3H, *J* 6.9). δ_C (*d*-$CDCl_3$, 75 MHz) 146.5, 140.0, 129.1, 98.9, 46.6, 30.4, 22.8, 13.8. *m*/*z* 385.9016. HRMS (CI) Anal. Calc. for $C_{10}H_{12}I_2$ [M$^+$] 385.9028.

*Synthesis of 1,3-Diiodo-2-methylbenzene (**34**)*

The title compound was prepared using the general procedure for metal–iodine exchange reaction and isolated in 64 % yield as a colourless oil. ν_{max} (KBr)/cm^{-1} 3102, 2942, 2810,

1583, 1512, 1389, 1125, 1014, 894. δ_H (*d*-$CDCl_3$, 400 MHz) 7.82 (d, 2H, *J* 8.0), 6.49 (t, 1H, *J* 8.0), 2.75 (s, 3H). δ_C (*d*-$CDCl_3$, 100 MHz) 142.5, 139.2, 128.6, 99.0, 34.6. *m*/*z* 343.8548. HRMS (CI) Anal. Calc. for $C_7H_6I_2$ [M^+] 343.8559.

*Synthesis of 2,6-Diiodobenzaldehyde (**36**)*

The title compound was prepared using the general procedure for metal–iodine exchange reaction and isolated in 61 % yield as a colourless oil. ν_{max} (KBr)/cm^{-1} 3114, 2974, 2711, 1713, 1234, 1019, 787. δ_H (*d*-$CDCl_3$, 400 MHz) 9.79 (s, 1H), 8.02 (d, 2H, *J* 8.0), 6.68 (t, 1H, *J* 8.0). δ_C (*d*-$CDCl_3$, 100 MHz) 195.7, 141.6, 135.6, 134.6, 97.5. *m*/*z* 357.8347. HRMS (CI) Anal. Calc. for $C_7H_4I_2O$ [M^+] 357.8352.

*Synthesis of (2,6-Diiodophenyl)trimethylsilane (**37**)*

The title compound was prepared using the general procedure for metal–iodine exchange reaction and isolated in 70 % yield as a colourless oil. ν_{max} (KBr)/cm^{-1} 2986, 2915, 1589, 1468, 1269, 1146, 849. δ_H (*d*-$CDCl_3$, 500 MHz) 7.94 (d, 2H, *J* 7.5), 6.53 (t, 1H, *J* 7.5), 0.64 (s, 9H). δ_C (*d*-$CDCl_3$, 125 MHz) 141.4, 131.2, 103.3, 4.9. *m*/*z* 401.8788. HRMS (CI) Anal. Calc. for $C_9H_{12}I_2Si$ [M^+] 401.8798.

*Synthesis of (3-Iodo-1,2-phenylene)bis(trimethylsilane) (**38**)*

The title compound was prepared using the general procedure for metal–iodine exchange reaction and isolated in 34 % yield as a colourless oil. ν_{max} (KBr)/cm^{-1} 2984, 2946, 1612, 1578, 1272, 1269, 1146, 844, 789. δ_H (*d*-$CDCl_3$, 400 MHz) 7.88 (dd, 1H, *J* 8.0, 2.0), 7.60 (dd, 1H, *J* 8.0, 2.0), 6.88 (t, 1H, *J* 8.0), 0.55 (s, 9H), 0.36 (s, 9H). δ_C (*d*-$CDCl_3$, 100 MHz) 151.0, 150.8, 140.5, 134.1, 127.9, 107.2, 3.43, 2.54. *m*/*z* 348.0217. HRMS (CI) Anal. Calc. for $C_{12}H_{21}ISi_2$ [M^+] 348.0226.

Supplementary Material

Supplementary material contains the experimental procedures, reaction yields and NMR data of all new compounds. These data are available on the Journal's website.

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