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Direct *para*-Selective C−H Amination of Iodobenzenes: Highly Efficient Approach for the Synthesis of Diarylamines

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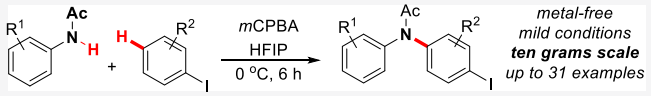
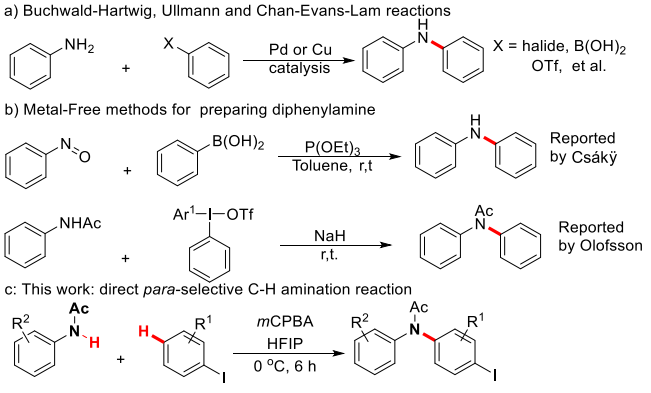
ABSTRACT: Iodine(III)-mediated synthesis of 4-iodo-*N*-phenylaniline from iodobenzene has been achieved, and the reaction can proceed under mild conditions. A variety of functional groups were well tolerated, providing the corresponding products in moderate to good yields. The remaining iodine group provides an effective platform for converting the products into several valuable asymmetric diphenylamines. Most importantly, this reaction can be easily scaled up to the ten-gram scale, highlighting its synthetic utility. The mechanistic study revealed that the in situ generated aryl hypervalent iodine intermediate is the key factor to realize this *para*-selective C−H amination reaction.



1. INTRODUCTION

Diarylamines are important chemicals that are often found in natural products, agrochemicals, pharmaceuticals, organic functional materials, and dyestuffs.[1] The most widely used diphenylamine synthetic methods are based on the metal-catalyzed coupling of anilines and boronic acids or aryl halides under Cu-catalysis (e.g., the Ullmann−Goldberg reaction[2] and Chan−Evans−Lam reaction[3]) or Pd-catalysis (e.g., the Buchwald−Hartwig reaction[4]) (Scheme 1a). These methods have been constantly improved by the development of new ligands, precatalysts, and extensive investigations of the reaction mechanisms.[5] In addition, with the development of C−H activation, the use of metal-catalyzed C−N bond formation to prepare diphenylamines has been extensively explored;[6] however, most of these methods require the use of toxic and expensive metal catalysts, which makes it necessary to remove metal residues in many applications, such as in the pharmaceutical industry. Hence, increasing attention has been devoted to the development of metal-free synthetic strategies.[7]

Scheme 1. Syntheses of Diarylamines and our Work



For example, the Csákÿ group[8] recently reported the direct synthesis of diphenylamines from nitrosoarenes and boronic acids (Scheme 1b). *N*-Arylation of amides with readily available diaryliodonium salts also has been proposed by the Olofsson group,[9] and the metal-free direct amination of 2-cyclohexenones to *N*-arylanilines promoted by iodine was disclosed by Maycock[10] in 2012.

Recently, the *para*-benzylation of iodobenzene diacetate with $BnSiMe_3$ was disclosed by Hyatt[11] and Shafir,[12] respectively. Subsequently, Hyatt[13] demonstrated that iodobenzenes can undergo *para*-selective benzylation via the in situ formation of hypervalent iodine intermediates using Selectfluor as the oxidant. In addition, Lei[14] has reported a two-electron-transfer oxidation-induced strategy for *para*-selective C−H etherification of iodosobenzenes. The iodine group can be easily transformed into other functional groups by various coupling reactions; thus, it would be useful to construct diarylamine skeletons with an iodine group. However, *N*-nucleophiles are easily oxidized and quench the entire reaction path, which is a general challenge. Herein, we report a general protocol for the synthesis of diarylamines by treating aryl iodides and anilides with *m*CPBA as the oxidant in hexafluoroisopropanol (HFIP) under mild conditions. Achieving hypervalent iodide intermediates while keeping *N*-reactivity is the key to achieve this transformation.

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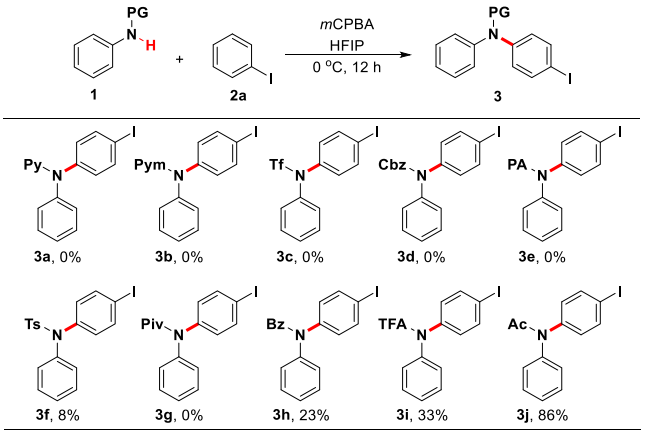
2. RESULTS AND DISCUSSION

*m*CPBA is a readily available and cheap oxidant that can oxidize aryl iodides to hypervalent iodides, as disclosed by the Chun group.[15] Based on these results, we speculated that a diarylamine could be directly prepared from iodobenzenes by using *m*CPBA as the oxidant and anilides as the aminating reagent. With these conditions in mind, Py, Pym, Tf, Cbz, PA, and Ts-protected anilines were directly treated with iodobenzene in the presence of *m*CPBA as the oxidant in the HFIP solvent at 0 °C for 12 h (Table 1). *p*-

Table 1. Screening of Protecting Groups[a]

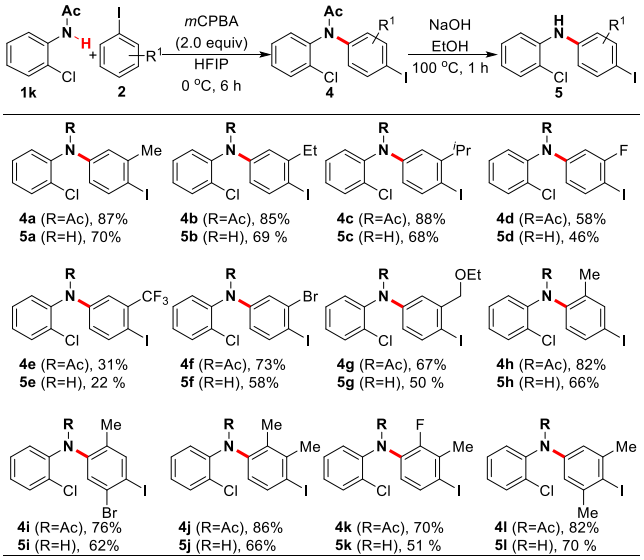


[a]Reactions were carried out on a 0.2 mmol scale, **1** (0.2 mmol), **2a** (0.4 mmol), *m*CPBA (0.4 mmol) in HFIP (1.0 mL) at 0 °C for 12 h in a sealed tube. Isolated yields were given.

Toluenesulfonanilide provided the product **3f** in 8% yield. We next turned our attention to the acyl protecting group. The benzoyl-protected aniline afforded the aminated product **3h** in 23% yield, while the trifluoroacetyl-protected aniline afforded the aminated product **3i** in 33% yield. When acetanilide was used, the desired product was obtained in 86% yield. Pivaloyl-protected aniline did not give the corresponding product **3g**, and the starting material was recovered, possibly because the steric hindrance of the pivaloyl group reduced the reactivity of substrate **1g**. Subsequently, a variety of solvents such as DCE, EtOH, *t*-Amyl-OH, AcOH, and TFE were investigated, and HFIP was determined to be the best solvent. Other peroxide oxidants, including H_2O_2, K_2SO_8, DTBP, TBHP, and Oxone, were screened, but none provided satisfactory results in this amination reaction (see the Supporting Information). A control reaction revealed that the oxidant is indispensable for this reaction. It is worth noting that the deiodination *N*-arylation reaction was not observed under these reaction conditions.[9]

After optimizing the reaction conditions, we investigated the substrate scope of various iodobenzenes to explore the versatility of this *para*-selective amination protocol. The results are summarized in Table 2. Both the electron-donating group (−Me, −Et, −*i*Pr, and $-CH_2OC_2H_5$) and the electron-withdrawing group ($-CF_3$) in iodobenzene were tolerated in this reaction (**4a**−**4c**, **4e**, and **4g**). Additionally, *ortho*- and *meta*-methyl-substituted iodobenzene (**4a**; **4h**) produced similar results, so the position of the methyl group in iodobenzene did not affect the reaction yield. It should be noted that iodobenzenes with halogen substituents, such as bromine and fluorine, were suitable substrates for the synthesis

Table 2. Substrate Scope of Iodobenzenes[a]



[a]Reaction conditions: **1k** (0.2 mmol), **2** (0.4 mmol), *m*CPBA (0.4 mmol) in HFIP (1.0 mL) at 0 °C for 6 h in a sealed tube, isolated yield after chromatography. Then, **4**, NaOH (1.0 mmol) in EtOH (1.0 mL) at 100 °C in an oil bath for 1 h in a sealed tube, isolated yield after chromatography.

of the corresponding polysubstituted diarylamines (**4d**; **4f**). Next, disubstituted iodobenzenes were used for synthesis and were found to be compatible with this reaction (**4i**−**4l**).

To further demonstrate the applicability of our new method and avoid the effect of a tertiary amine on the ^{13}C NMR spectrum (see the Supporting Information), the deprotection of the acetyl group was examined. After treatment with NaOH or K_2CO_3 in ethanol under reflux conditions, the products were isolated in different yields.

Next, we evaluated the reaction scope using various anilides, and the results are summarized in Table 3. We found that this reaction was tolerant to a variety of functional groups, such as fluoride, chloride, bromide, phenyl, ester, acetoxy, and trifluoromethyl groups. A small increase in temperature (from 0 to 60 °C) was sometimes necessary to obtain better transformation. The substrates containing nonsubstituted or electron-withdrawing groups at the *ortho*, *meta*, and *para*-position all provided the corresponding products in moderate to good yields ranging from 52% to 89% (**3j**−**3l**; **3n**−**3v**). *Meta*-aromatic substitution afforded a biphenyl derivative (**3m**). Interestingly, *ortho* and *meta*-iodoacetanilide also afforded the corresponding products (**3w**; **3x**) in 62% and 51% yields rather than the dimerization products. This might provide a convenient means to install other functional groups through known protocols. Indeed, the electron-donating group (isopropyl) at the *meta* position was tolerated in this reaction, and the desired product (**3y**) was obtained in 72% yield. However, when we attempted the reaction with 3-methoxyacetanilide, the desired product was not detected. These observations indicated that the electronegativity of the acetanilide substituent may greatly impact the reaction. This reaction was not only suitable for monosubstituted substrates but also for substrates bearing several substituents at different positions. Substitutions with aliphatic and halide substituents (**3z**, **3aa**) were both well tolerated. Moreover, both *meta* and *para* positions with a halide (**3ab**) gave very good results.

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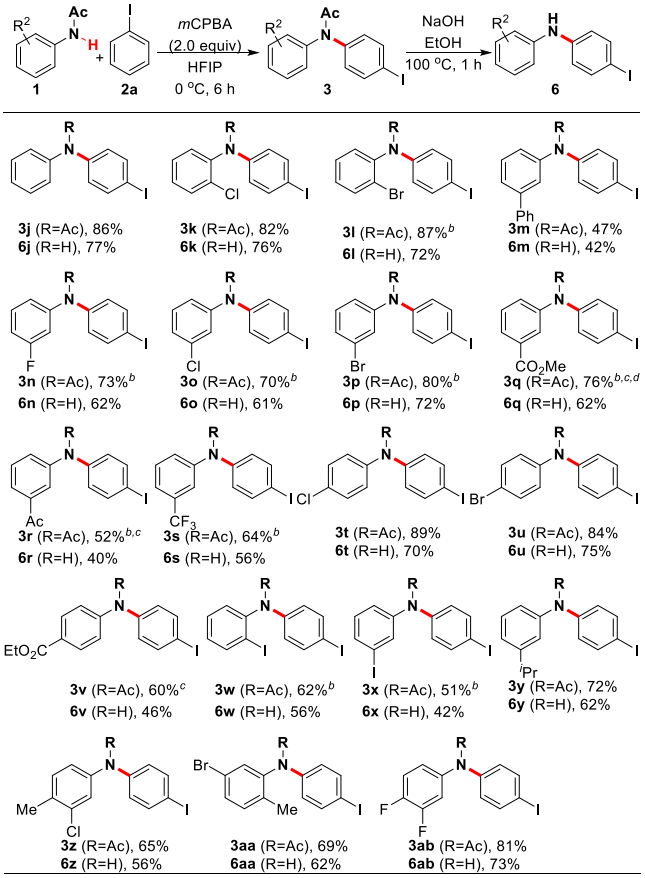
Table 3. Substrate Scope of Anilides[a]

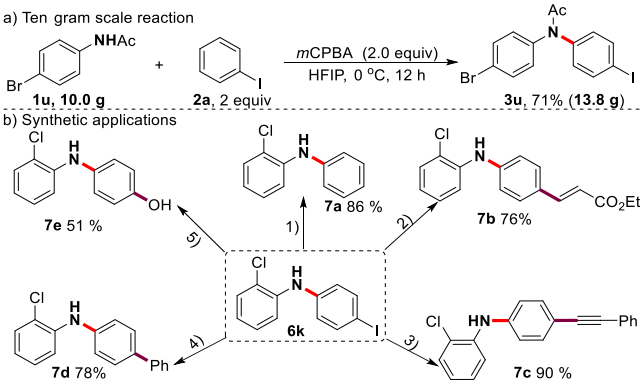


[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), *m*CPBA (0.4 mmol) in HFIP (1.0 mL) at 0 °C for 6 h in a sealed tube, isolated yield after chromatography. Then, **3**, NaOH (1.0 mmol) in EtOH (1.0 mL) at 100 °C in an oil bath for 1 h in a sealed tube, isolated yield after chromatography. [b]60 °C in an oil bath. [c]K_2CO_3 instead of NaOH. [d]MeOH instead of EtOH.

To further demonstrate the practicality of this new reaction, a more meaningful gram-scale reaction between 10 g of **1u** and 2 equivalents of **2a** was carried out at 0 °C. The desired product **3u** was isolated in 71% (13.8 g) (Scheme 2a), highlighting the synthetic utility of this method. Furthermore, the applicability of this method was illustrated by the functionalization of product **6k** (Scheme 2b). The remaining iodide atom could be converted to other functional groups, including alkenyl, alkynyl,[16] phenyl,[17] and hydroxyl[18] groups (**7b**−**7e**) by palladium or copper catalysts. A dehalogenation reaction could also be carried out (**7a**).[19]

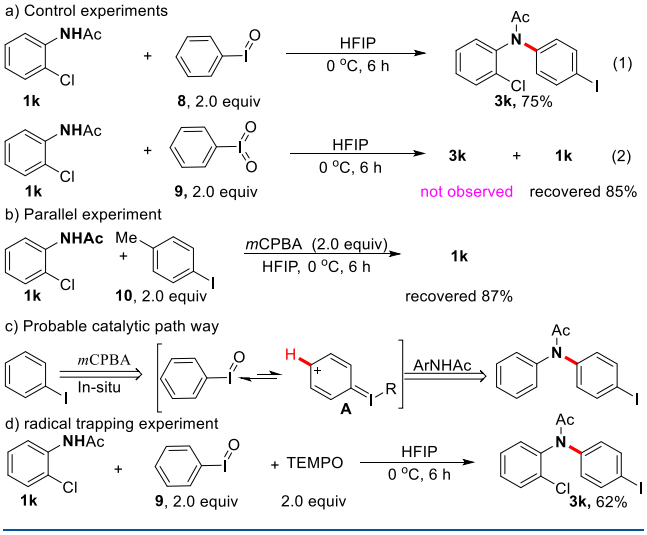
To gain preliminary mechanistic information about this reaction, several control experiments were performed. According to literature reports, aryl iodides can be conveniently oxidized with *m*CPBA to hypervalent iodosobenzene **8** or iodoxybenzene **9**.[15] To explore whether hypervalent iodine(III) or iodine(V) played a role in the reaction process, we individually reacted **8** and **9** with acetanilide **1k** in HFIP for 6 h. Iodosobenzene **8** afforded the desired product **3k** in a relatively low yield (75%), but iodoxybenzene **9** failed. This proved that the iodine atom was oxidized to form iodine(III) intermediates (Scheme 3a). When *p*-iodotoluene **10** was selected to participate in the reaction, as expected, the reaction did not proceed (Scheme 3b), possibly because the key

Scheme 2. Gram-Scale Reaction and Transformation[a]



[a]Reaction conditions: (1) $NaBH_4$ (15.0 eq), CuCl (75 mol %), MeOH, 0 °C, 1 h. (2) Ethyl acrylate (2.0 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3 (5 mol %), Et_3N, 100 °C, 24 h. (3) Phenylacetylrene (2.0 equiv), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), Et_3N, 100 °C, 24 h. (4) $PhB(OH)_2$ (2.0 equiv), $Pd(OAc)_2$ (10 mol %), K_3PO_4 (2.0 equiv), xantphos (20 mol %), Tol, N_2, 120 °C, 16 h. (5) CuI (10 mol %), KOH (5.0 equiv), Phen (20 mol %), DMSO/H_2O = 1:1, 120 °C, 24 h.

Scheme 3. Mechanism Experiment



intermediate **A** was not formed when the *para*-position was blocked (Scheme 3b,c). In addition, a radical inhibition experiment was performed in the presence of the radical scavenger TEMPO, and the desired product **3k** was obtained in only a slightly lower yield, indicating that a radical pathway was most likely not involved in this transformation (Scheme 3d), which was different from Li's work.[20] As we proposed, this *para* C−H amination reaction might proceed via a nucleophilic process rather than a radical process.

Based on our experimental observations, we suspected that the HFIP solvent might play an important role in this reaction. To validate the potential interactions between aniline, iodobenzene, and HFIP, a set of NMR experiments were designed with $CDCl_3$ as the solvent (for details see the Supporting Information). These results support the hydrogen bonding between HFIP and the N atom of the acetanilide; therefore, trivalent iodine may more easily combine with oxygen than nitrogen.

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We also tracked the reaction between **1v** and the same amount of iodosobenzene **8** using NMR spectroscopy (Figure 1). Initially, the reaction was stirred at 0 °C for 1 h (Figure 1e).

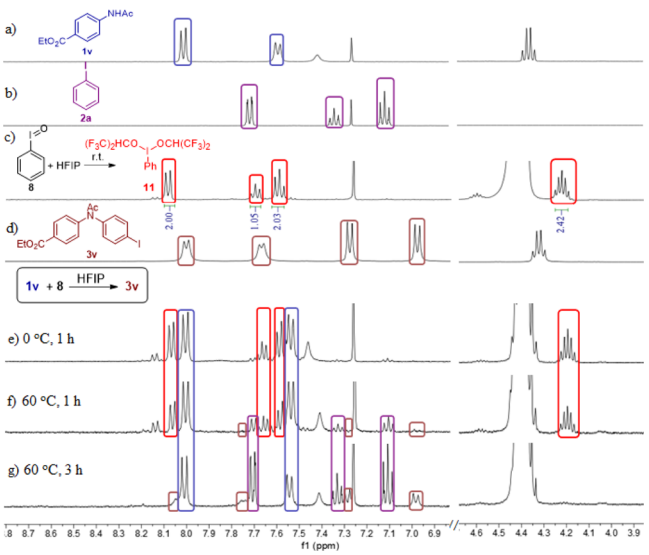
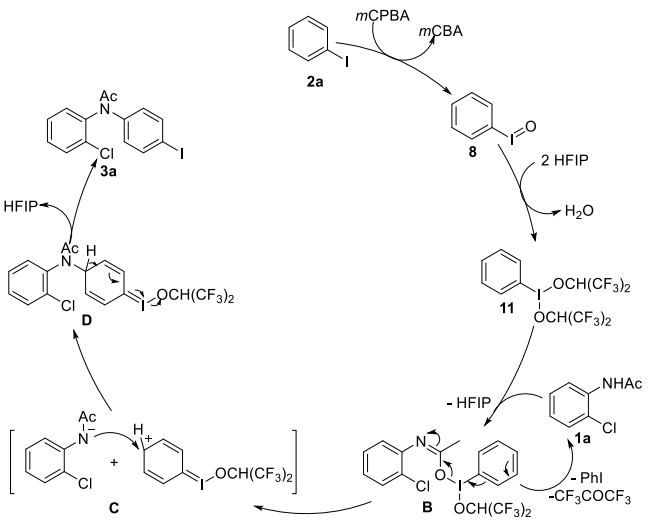


Figure 1. Tracking experiments by NMR spectroscopy.

We found that **8** quickly disappeared, and **11** (PhI(OC(H)-$(CF_3)_2)_2$) formed in HFIP (Figure 1c);[21] thus, the amination reaction failed. Then, we increased the temperature to 60 °C (Figure 1f,g) and recorded the NMR spectrum. We observed the gradual emergence of product **3v**. To our surprise, iodobenzene was also formed. We speculated that trivalent iodine underwent a redox reaction with HFIP. To verify this conjecture, ^{19}F NMR analysis of the reaction mixture was performed. Compared with the ^{19}F NMR spectra of HFIP, a new singlet at −82.6 ppm (s) appeared, which was known as hexafluoroacetone (see the Supporting Information).[22] Therefore, it could be proved that HFIP participated in the redox reaction.

Based on the results of the above experiments and a previous literature survey, a plausible reaction pathway that was different from Li's is proposed in Scheme 4.[20] First, **2a** reacted with *m*CPBA to produce iodosobenzene **8**. Then, iodosobenzene **8** reacted with HFIP to form **11**. Trivalent iodine compound **11** combined with **1a** to form intermediate **B**. Afterward, **B** transformed into **C**, which activated the *para*-position of iodobenzene and formed a carbocation. Subsequently, carbocations were attacked by the nitrogen anions to generate intermediate **D**. Finally, the desired product **3a** was obtained after re-aromatization of **D**.

Scheme 4. Proposed Mechanism



3. CONCLUSIONS

In conclusion, we have developed a practical approach for the synthesis of 4-iodo-*N*-phenylaniline derivatives by an oxidation-induced method. A wide variety of anilines and iodobenzenes were used in this study and were found to be suitable for this reaction, producing the corresponding products in moderate to good yields under mild conditions. The direct conversion to products highlights the potential synthetic applications of this method.

4. EXPERIMENTAL SECTION

4.1. General. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Column chromatography purifications were performed using 200−300 mesh silica gel. NMR spectra were recorded on Varian Inova−400 MHz, Inova−300 MHz, Bruker DRX−400, or Bruker DRX−500 instruments and calibrated using residual solvent peaks as internal reference. Multiplicities are recorded as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, and m = multiplet. HRMS analysis was carried out using a Bruker micrOTOF−Q instrument or a TOF−MS instrument.

*4.1.1. General Procedure for the Compound (**1j−1ab**).*[23] A 100 mL round bottom flask was charged with aniline derivatives (20 mmol), CH_2Cl_2 (40 mL) and Et_3N (4.0 mL, 28 mmol). Then, the reaction solution was cooled to 0 °C. Acetyl chloride (1.7 mL, 24 mmol) was added dropwise. After addition, the solution was stirred at room temperature for 10 h. Then, the reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layer was dried and concentrated, and the resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) on silica gel to provide *N*-phenylacetamide derivatives.

*4.1.2. General Procedure for the Compound (**3j−3z, 3aa,** and **3ab**).* A mixture of **1** (0.2 mmol, 1.0 equiv), **2** (0.4 mmol, 2.0 equiv), *m*CPBA (0.4 mmol, 2.0 equiv), and HFIP (1.0 mL) in a 15 mL glass vial sealed was maintained at 0 or 60 °C in an oil bath for 6 h. The reaction mixture was concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) on silica gel to give the pure product.

*4.1.3. General Procedure for the Compound (**5a−5l, 6j−6z, 6aa,** and **6ab**).* A mixture of **3** or **4** (0.2 mmol, 1.0 equiv), NaOH (1.0 mmol, 5.0 equiv) or K_2CO_3 (1.0 mmol, 5.0 equiv), and EtOH (10.0 mL) in a 50 mL round bottom flask was heated at 100 °C in an oil bath for 1 h. The reaction mixture cooled to room temperature, and it was filtered through a pad of celite and concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100) on silica gel to give the pure product **5** or **6**.

4.1.4. General Procedure for Gram-Scale Reaction. A mixture of **1u** (4.7 mmol, 10.0 g), **2a** (9.4 mmol, 2.0 equiv), *m*CPBA (9.4 mmol, 2.0 equiv), and HFIP (23.5 mL) in a 100 mL round bottomed flask glass was cooled at 0 °C for 12 h. The reaction mixture was filtered through a pad of celite and concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:5) on silica gel to give the pure product **3u** (13.8 g).

*4.1.5. General Procedure for the Synthesis of Compounds **7a**.* A mixture of **6k** (0.2 mmol, 1.0 equiv), $NaBH_4$ (3.0 mmol, 15 equiv), CuCl (75 mol %), and MeOH (2.0 mL) in a 15 mL glass vial sealed was cooled at 0 °C for 1 h. The reaction mixture was filtered through a pad of celite and concentrated in vacuo. The resulting residue was

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purified by column chromatography (ethyl acetate/petroleum ether = 1:100) on silica gel to give the pure product **7a**.

*4.1.6. General Procedure for the Synthesis of Compounds **7b**.* A mixture of **6k** (0.2 mmol, 1.0 equiv), ethyl acrylate (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol %), PPh_3 (5 mol %), and Et_3N (0.5 mL) in a 15 mL glass vial sealed was stirred at 100 °C in an oil bath for 24 h. The reaction mixture was filtered through a pad of celite and concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100) on silica gel to give the pure product **7b**.

*4.1.7. General Procedure for the Synthesis of Compounds **7c**.* A mixture of **6k** (0.2 mmol, 1.0 equiv), phenylacetylene (0.4 mmol, 2.0 equiv), $Pd(PPh_3)_4$ (5 mol %), CuI (10 mol %), and Et_3N (0.5 mL) in a 15 mL glass vial sealed was stirred at 100 °C in an oil bath for 24 h. The reaction mixture was filtered through a pad of celite and concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100) on silica gel to give the pure product **7c**.

*4.1.8. General Procedure for the Synthesis of Compounds **7d**.* A mixture of **6k** (0.2 mmol, 1.0 equiv), phenylboronic acid (0.4 mmol, 2.0 equiv), $Pd(OAc)_2$ (10 mol %), K_3PO_4 (2.0 equiv), xantphos (20 mol %), and Et_3N (0.5 mL) in a 15 mL glass vial sealed was stirred at 100 °C in an oil bath for 16 h under nitrogen. The reaction mixture was filtered through a pad of celite and concentrated in vacuo. The resulting residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100) on silica gel to give the pure product **7d**.

*4.1.9. General Procedure for the Synthesis of Compounds **7e**.* A mixture of **6k** (0.2 mmol, 1.0 equiv), CuI (10 mol %), KOH (5.0 equiv), Phen (20 mol %), and DMSO/H_2O (0.25 mL:0.25 mL) in a 15 mL glass vial sealed was stirred at 120 °C in an oil bath for 24 h under nitrogen. The reaction mixture was filtered through a pad of celite and extracted with ethyl acetate concentrated. The resulting residue was concentrated in vacuo and purified by column chromatography (ethyl acetate/petroleum ether = 1:5) on silica gel to give the pure product **7e**.

*N-(4-Iodophenyl)-4-methyl-N-phenylbenzenesulfonamide (**3f**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as a white solid, m.p. 159−160 °C; yield: 7.2 mg, 8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.60 (m, 2H), 7.58−7.56 (m, 2H), 7.35−7.26 (m, 5H), 7.24−7.20 (m, 2H), 7.04−6.99 (m, 2H), 2.44 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.9, 141.5, 141.1, 138.4, 137.3, 129.8, 129.7, 129.4, 128.4, 127.8, 127.7, 92.4, 21.6. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{16}INO_2SNa$ 471.9844; found: 471.9856.

*N-(4-Iodophenyl)-N-phenylbenzamide (**3h**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as a white solid, m.p. 124−126 °C; yield: 18.3 mg, 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.7 Hz, 2H), 7.48−7.41 (m, 2H), 7.37−7.26 (m, 3H), 7.24−7.17 (m, 3H), 7.13−7.08 (m, 2H), 6.91 (d, J = 8.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.6, 143.8, 143.6, 138.3, 135.8, 130.6, 129.4, 129.3, 129.2, 128.1, 127.7, 126.8, 91.1. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{19}H_{14}INONa$ 422.0018; found: 422.0022.

*2,2,2-Trifluoro-N-(4-iodophenyl)-N-phenylacetamide (**3i**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as a white solid, m.p. 74−75 °C; yield: 25.8 mg, 33%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.44−7.31 (m, 5H), 7.08 (d, J = 8.2 Hz, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −66.8. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.4 (q, J = 36.2 Hz), 138.7, 130.5, 129.7, 129.4, 128.7, 127.9, 126.1, 116.3 (q, J_{C-F} = 288.9 Hz), 92.7. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_9F_3INONa$ 413.9579; found: 413.9588.

*N-(4-Iodophenyl)-N-phenylacetamide (**3j**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as a white solid, m.p. 93−94 °C; yield: 57.96 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 7.31−7.24 (m, 3H), 7.17−7.14 (m, 2H), 6.97−6.91 (m, 2H), 1.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.4, 142.8, 138.2, 129.9, 128.3, 126.7, 90.8, 24.0. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{12}INONa$: 359.9861; found: 359.9871.

*N-(2-Chlorophenyl)-N-(4-iodophenyl)acetamide (**3k**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 60.8 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 2H), 7.51 (s, 1H), 7.35 (s, 3H), 7.08 (d, J = 8.2 Hz, 2H), 2.00 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 141.1, 140.0, 137.9, 133.7, 131.0, 130.1, 128.5, 127.7, 90.8, 23.5. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}ClINONa$: 393.9472; found: 393.9477.

*N-(2-Bromophenyl)-N-(4-iodophenyl)acetamide (**3l**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 72.2 mg, 87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.52 (m, 3H), 7.39 (s, 2H), 7.26 (s, 1H), 7.12 (d, J = 8.3 Hz, 2H), 2.00 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 141.3, 140.8, 137.5, 134.2, 131.0, 130.1, 129.1, 127.3, 124.1, 90.4, 23.7. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}BrINONa$: 437.8966; found: 437.8960.

*N-([1,1′-Biphenyl]-3-yl)-N-(4-iodophenyl)acetamide (**3m**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 38.8 mg, 47%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.63 (m, 2H), 7.62−7.43 (m, 6H), 7.42−7.38 (m, 1H), 7.28−7.25 (m, 1H), 7.10 (d, J = 8.2 Hz, 2H), 2.14 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.3, 143.1, 142.6, 139.7, 138.1, 130.1, 128.9, 127.9, 127.1, 90.8, 24.0. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{16}INONa$: 436.0174; found: 436.0179.

*N-(3-Fluorophenyl)-N-(4-iodophenyl)acetamide (**3n**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 51.7 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2H), 7.30 (s, 1H), 7.05−6.82 (m, 5H), 2.04 (s, 3H). ^{19}F NMR (376 MHz, CDCl3) δ −112.0. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.1, 164.1, 161.6, 143.9, 142.3, 130.5, 124.2, 122.5, 114.5, 92.1, 23.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}FINONa$: 377.9767; found: 377.9770.

*N-(3-Chlorophenyl)-N-(4-iodophenyl)acetamide (**3o**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 51.9 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 2H), 7.39−7.17 (m, 3H), 7.14 (d, J = 7.0 Hz, 1H), 7.04−6.97 (m, 2H), 2.06 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.0, 143.6, 142.3, 138.6, 134.9, 130.3, 128.3, 126.8, 124.7, 23.9. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}ClINONa$: 393.9472; found: 393.9476.

*N-(3-Bromophenyl)-N-(4-iodophenyl)acetamide (**3p**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 66.4 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.41 (s, 2H), 7.19 (s, 2H), 7.00 (d, J = 8.2 Hz, 2H), 2.05 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.9, 143.7, 142.2, 138.6, 130.6, 129.8, 126.9, 125.3, 122.7, 23.8. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{14}H_{11}BrINONa$: 437.8966; found: 437.8967.

*Methyl 3-(N-(4-iodophenyl)acetamido)benzoate (**3q**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 60.0 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 2H), 7.59 (s, 2H), 7.38 (s, 2H), 7.01−6.92 (m, 2H), 3.79 (s, 3H), 1.97 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 169.5, 165.5, 142.4, 142.0, 138.1, 131.1, 129.0, 93.0, 90.8, 51.9, 23.4. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}INO_3Na$: 417.9916; found: 417.9920.

*N-(3-Acetylphenyl)-N-(4-iodophenyl)acetamide (**3r**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 39.4 mg, 52%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 2H), 7.63 (s, 2H), 7.41 (s, 2H), 6.98 (d, J = 8.2 Hz, 2H), 2.52 (s, 3H), 2.00 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 196.9, 169.9, 142.8, 142.2, 138.4, 129.7, 126.3, 93.2, 26.6, 23.6. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{16}H_{14}INO_2Na$: 401.9967; found: 401.9968.

*N-(4-Iodophenyl)-N-(3-(trifluoromethyl)phenyl)acetamide (**3s**)* The compound was purified by flash column chromatography (ethyl

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acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 51.8 mg, 64%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.59−7.37 (m, 4H), 7.01 (d, J = 8.6 Hz, 2H), 2.06 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 143.0, 142.3, 139.0, 130.0, 125.0, 123.6, 122.3, 23.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{11}F_3INONa$: 427.9735; found: 427.9739.

N-(4-Chlorophenyl)-N-(4-iodophenyl)acetamide (**3t**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 66.0 mg, 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.34 (s, 2H), 7.17 (d, J = 8.5 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 2.05 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 142.5, 141.2, 138.7, 129.8, 128.4, 23.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{11}ClINONa$: 393.9472; found: 393.9471.

N-(4-Bromophenyl)-N-(4-iodophenyl)acetamide (**3u**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 69.7 mg, 84%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.47 (s, 2H), 7.10 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.1 Hz, 2H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.0, 142.3, 141.6, 138.6, 132.6, 130.0, 128.2, 23.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{11}BrINONa$: 437.8966; found: 437.8966.

Ethyl 4-(N-(4-iodophenyl)acetamido)benzoate (**3v**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 49.1 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 6.98 (d, J = 8.6 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 2.03 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.8, 165.5, 146.3, 142.1, 138.6, 129.5, 128.6, 126.6, 92.5, 61.0, 24.0, 14.2. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{16}INO_3Na$: 432.0073; found: 432.0077.

N-(2-Iodophenyl)-N-(4-iodophenyl)acetamide (**3w**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 57.4 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.60 (s, 2H), 7.40 (d, J = 17.3 Hz, 4H), 7.11 (d, J = 8.5 Hz, 3H), 1.98 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 144.6, 140.7, 137.5, 130.6, 130.0, 127.3, 100.7, 90.2, 24.4. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{11}I_2NONa$: 485.8828; found: 485.8829.

N-(3-Iodophenyl)-N-(4-iodophenyl)acetamide (**3x**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 47.2 mg, 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 2H), 7.59 (s, 2H), 7.20 (d, J = 8.0 Hz, 1H), 7.07 (s, 1H), 7.02−6.95 (m, 2H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 143.5, 142.1, 138.5, 137.0, 130.8, 130.7, 94.3, 23.8. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{11}I_2NONa$: 485.8828; found: 485.8825.

N-(4-Iodophenyl)-N-(3-isopropylphenyl)acetamide (**3y**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 54.6 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.4 Hz, 2H), 7.31 (t, J = 7.8 Hz, 1H), 7.19 (s, 1H), 7.09 (t, J = 1.9 Hz, 1H), 7.06−7.00 (m, 3H), 2.93−2.86 (m, 1H), 2.04 (s, 3H), 1.23 (d, J = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.3, 151.0, 142.7, 138.0, 129.6, 128.1, 126.0, 125.7, 90.5, 33.9, 24.0, 23.9. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{17}H_{18}INONa$: 402.0331; found: 402.0333.

N-(3-Chloro-4-methylphenyl)-N-(4-iodophenyl)acetamide (**3z**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 50.0 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 2H), 7.26−7.17 (m, 2H), 7.06−7.03 (m, 1H), 7.02−6.96 (m, 2H), 2.33 (s, 3H), 2.03 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.8, 142.2, 141.1, 138.2, 136.0, 134.6, 131.4, 129.8, 128.2, 126.6, 124.8, 92.9, 90.8, 23.6, 19.5. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{13}ClINONa$: 407.9628; found: 407.9629.

N-(5-Bromo-2-methylphenyl)-N-(4-iodophenyl)acetamide (**3aa**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 59.2 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.40 (s, 2H), 7.17 (d, J = 8.2 Hz, 1H), 6.99 (d, J = 8.3 Hz, 2H), 2.16 (s, 3H), 1.98 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 142.4, 137.9, 135.3, 133.2, 132.5, 126.8, 120.1, 23.9, 17.6. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{15}H_{13}BrINONa$: 451.9123; found: 451.9133.

N-(3,4-Difluorophenyl)-N-(4-iodophenyl)acetamide (**3ab**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as yellow oil; yield: 60.4 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.19−7.04 (m, 2H), 7.02−6.92 (m, 3H), 2.03 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −133.4, −135.6, −136.6, −139.9. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 151.2, 148.7, 142.1, 138.7, 130.0, 128.2, 124.7, 122.4, 117.4, 115.9, 93.4, 91.3, 23.6. HRMS (ESI) m/z: [M + Na]$^+$ Calcd for $C_{14}H_{10}F_2INONa$: 395.9673; found: 395.9677.

N-(2-Chlorophenyl)-4-iodo-3-methylaniline (**5a**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 48.1 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.4 Hz, 1H), 7.41 (dd, J = 8.0, 1.5 Hz, 1H), 7.30 (dd, J = 8.2, 1.6 Hz, 1H), 7.21−7.16 (m, 1H), 7.06 (d, J = 2.8 Hz, 1H), 6.88 (td, J = 7.7, 1.6 Hz, 1H), 6.74 (dd, J = 8.5, 2.8 Hz, 1H), 6.06 (s, 1H), 2.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.4, 141.9, 139.6, 139.5, 129.9, 127.5, 122.1, 121.0, 121.0, 118.7, 116.2, 91.6, 28.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{13}H_{12}ClIN$ 343.9703; found: 343.9691.

N-(2-Chlorophenyl)-3-ethyl-4-iodoaniline (**5b**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 49.2 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.5 Hz, 1H), 7.39 (dd, J = 8.0, 1.5 Hz, 1H), 7.28 (dd, J = 8.2, 1.5 Hz, 1H), 7.19−7.15 (m, 1H), 7.05 (d, J = 2.8 Hz, 1H), 6.88−6.84 (m, 1H), 6.75 (dd, J = 8.4, 2.8 Hz, 1H), 2.72 (q, J = 7.5 Hz, 2H), 1.24 (t, J = 7.5 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.7, 142.2, 140.0, 139.7, 129.9, 127.6, 122.1, 121.0, 120.0, 119.0, 116.1, 90.9, 34.2, 14.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{14}H_{14}ClIN$ 357.9859; found: 357.9861.

N-(2-Chlorophenyl)-4-iodo-3-isopropylaniline (**5c**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 50.4 mg, 68%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, J = 8.4, 1.3 Hz, 1H), 7.38 (dt, J = 8.1, 1.5 Hz, 1H), 7.27−7.23 (m, 1H), 7.15 (tt, J = 8.4, 1.4 Hz, 1H), 7.05 (t, J = 2.6 Hz, 1H), 6.86−6.80 (m, 1H), 6.78−6.75 (m, 1H), 6.09 (s, 1H), 3.22−3.15 (m, 1H), 1.25 (dd, J = 6.8, 2.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.7, 142.3, 140.1, 139.8, 130.0, 127.6, 122.0, 120.9, 119.3, 117.9, 115.9, 91.7, 38.1, 23.2. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{15}H_{16}ClIN$ 372.0016; found: 372.0011.

N-(2-Chlorophenyl)-3-fluoro-4-iodoaniline (**5d**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 31.9 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.56 (m, 1H), 7.39 (dd, J = 8.0, 1.5 Hz, 1H), 7.31 (dd, J = 8.2, 1.5 Hz, 1H), 7.19 (td, J = 8.2, 7.8, 1.5 Hz, 1H), 6.92 (td, J = 7.7, 1.5 Hz, 1H), 6.87 (dd, J = 9.9, 2.5 Hz, 1H), 6.68 (dd, J = 8.5, 2.6 Hz, 1H), 6.11 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −92.73 − −92.78 (m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 244.2 Hz), 144.4 (d, $J_{C\text{-}F}$ = 9.6 Hz), 139.6 (d, $J_{C\text{-}F}$ = 3.3 Hz), 138.6, 130.2, 127.7, 123.4, 122.5, 117.8, 116.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 105.7 (d, $J_{C\text{-}F}$ = 27.4 Hz), 70.2 (d, $J_{C\text{-}F}$ = 25.9 Hz). HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{12}H_9ClFIN$ 347.9452; found: 347.9457.

N-(2-Chlorophenyl)-4-iodo-3-(trifluoromethyl)aniline (**5e**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 17.4 mg, 22%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 1H), 7.41 (dd, J = 8.0, 1.6 Hz, 2H), 7.28 (dd, J = 8.2, 1.6 Hz, 1H), 7.20 (td, J = 8.3, 7.8, 1.5 Hz, 1H), 6.99−6.91 (m, 2H), 6.14 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.00. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.8, 142.6, 138.4, 134.6 (q, $J_{C\text{-}F}$ = 30.9 Hz), 130.3, 127.8, 123.6, 122.8, 122.7 (q, $J_{C\text{-}F}$ = 272.5 Hz), 122.2, 117.8 (q, $J_{C\text{-}F}$ = 5.7

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Hz), 117.7, 79.6 (q, J_{C-F} = 1.9 Hz). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_9ClF_3IN$ 397.9420; found: 397.9420.

3-Bromo-N-(2-chlorophenyl)-4-iodoaniline (**5f**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 47.2 mg, 58%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.6 Hz, 1H), 7.41 (d, J = 2.6 Hz, 1H), 7.38 (dd, J = 8.0, 1.5 Hz, 1H), 7.28 (dd, J = 8.2, 1.6 Hz, 1H), 7.21−7.16 (m, 1H), 6.93−6.89 (m, 1H), 6.78 (dd, J = 8.6, 2.6 Hz, 1H), 6.04 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.4, 140.6, 138.6, 130.4, 130.2, 127.7, 123.2, 122.5, 122.3, 119.1, 117.5, 90.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_9BrClIN$ 407.8652; found: 407.8636.

N-(2-Chlorophenyl)-3-(ethoxymethyl)-4-iodoaniline (**5g**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 38.7 mg, 50%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.4 Hz, 1H), 7.27 (dd, J = 8.0, 1.5 Hz, 1H), 7.21−7.14 (m, 2H), 7.07−7.03 (m, 1H), 6.78−6.71 (m, 2H), 6.01 (s, 1H), 4.35 (s, 2H), 3.55 (q, J = 7.0 Hz, 2H), 1.20 (t, J = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 142.3, 142.0, 139.7, 139.5, 129.9, 127.6, 122.3, 121.2, 119.8, 119.7, 116.4, 87.4, 76.2, 66.5, 15.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{16}ClINO$ 387.9965; found: 387.9964.

N-(2-Chlorophenyl)-4-iodo-2-methylaniline (**5h**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 45.3 mg, 66%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 2.1 Hz, 1H), 7.39 (dd, J = 8.4, 2.1 Hz, 1H), 7.29 (dd, J = 8.0, 1.5 Hz, 1H), 7.04 (ddd, J = 8.6, 7.3, 1.5 Hz, 1H), 6.92 (d, J = 8.4 Hz, 1H), 6.87 (dd, J = 8.2, 1.5 Hz, 1H), 6.73 (td, J = 7.6, 1.5 Hz, 1H), 5.73 (s, 1H), 2.15 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 139.7, 139.7, 135.8, 133.0, 129.8, 127.6, 122.9, 121.6, 120.5, 115.8, 86.6, 17.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{12}ClIN$ 343.9703; found: 343.9691.

5-Bromo-N-(2-chlorophenyl)-4-iodo-2-methylaniline (**5i**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 52.2 mg, 62%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 1.0 Hz, 1H), 7.49 (s, 1H), 7.39 (dd, J = 8.0, 1.5 Hz, 1H), 7.20−7.16 (m, 1H), 7.08 (dd, J = 8.2, 1.6 Hz, 1H), 6.89 (td, J = 7.6, 1.6 Hz, 1H), 5.82 (s, 1H), 2.20 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.61, 141.45, 139.12, 130.11, 129.86, 127.69, 127.09, 122.77, 122.41, 121.57, 116.90, 92.01, 17.10. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{11}BrClIN$ 421.8808; found: 421.8820.

N-(2-Chlorophenyl)-4-iodo-2,3-dimethylaniline (**5j**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 47.1 mg, 66%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.4 Hz, 1H), 7.35 (dd, J = 8.0, 1.5 Hz, 1H), 7.12−7.05 (m, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.80−6.71 (m, 2H), 5.85 (s, 1H), 2.52 (s, 3H), 2.28 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.4, 140.7, 139.8, 137.0, 132.3, 129.6, 127.6, 123.0, 120.6, 119.7, 114.9, 96.9, 26.3, 15.9. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}ClIN$ 357.9859; found: 357.9864.

N-(2-Chlorophenyl)-2-fluoro-4-iodo-3-methylaniline (**5k**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 36.8 mg, 51%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 8.6, 1.6 Hz, 1H), 7.39 (dd, J = 7.9, 1.5 Hz, 1H), 7.24 (dd, J = 8.2, 1.6 Hz, 1H), 7.17 (td, J = 8.2, 7.7, 1.5 Hz, 1H), 6.96−6.87 (m, 2H), 6.09 (s, 1H), 2.39 (d, J = 2.8 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −127.1. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3 (d, J_{C-F} = 244.8 Hz), 138.7, 133.7 (d, J_{C-F} = 4.3 Hz), 130.5 (d, J_{C-F} = 12.7 Hz), 130.0, 129.2 (d, J_{C-F} = 16.4 Hz), 127.5, 123.2, 121.9, 117.7 (d, J_{C-F} = 2.2 Hz), 117.1, 90.8 (d, J_{C-F} = 3.0 Hz), 20.1 (d, J_{C-F} = 4.5 Hz). HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{11}ClFIN$ 361.9609; found: 361.9626.

N-(2-Chlorophenyl)-4-iodo-3,5-dimethylaniline (**5L**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 49.9 mg, 70%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, J = 8.0, 1.5 Hz, 1H), 7.28 (dd, J = 8.2, 1.6 Hz, 1H), 7.16 (td, J = 8.2, 7.8, 1.5 Hz, 1H), 6.91 (s, 2H), 6.84 (td, J = 7.6, 1.6 Hz, 1H), 5.99 (s, 1H), 2.46 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.1, 141.3, 139.9, 129.9, 127.6, 122.1, 120.9, 118.4, 116.4, 99.1, 29.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}ClIN$ 357.9859; found: 357.9871.

4-Iodo-N-phenylaniline (**6j**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 102−103 °C; yield: 45.4 mg, 77%. ^1H NMR (400 MHz, CDCl3) δ 7.61−7.53 (m, 2H), 7.39−7.31 (m, 2H), 7.14−7.08 (m, 2H), 7.05 (tt, J = 7.3, 1.1 Hz, 1H), 6.89−6.82 (m, 2H), 5.69 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.1, 142.1, 138.0, 129.5, 121.8, 119.3, 118.5, 82.2. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{11}IN$ 295.9936; found: 295.9951.

2-Chloro-N-(4-iodophenyl)aniline (**6k**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 70−71 °C; yield: 50.0 mg, 76%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56−7.51 (m, 2H), 7.33 (dd, J = 8.0, 1.5 Hz, 1H), 7.21 (dd, J = 8.2, 1.5 Hz, 1H), 7.10 (td, J = 8.2, 7.8, 1.5 Hz, 1H), 6.88−6.83 (m, 2H), 6.81−6.79 (m, 1H), 6.01 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.5, 139.4, 138.3, 129.9, 127.6, 122.3, 121.5, 121.3, 116.3, 84.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}ClIN$ 329.9546; found: 329.9547.

2-Bromo-N-(4-iodophenyl)aniline (**6l**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 62−63 °C; yield: 53.7 mg, 72%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.56 (m, 2H), 7.54 (dd, J = 8.0, 1.5 Hz, 1H), 7.24 (dd, J = 8.2, 1.8 Hz, 1H), 7.21−7.16 (m, 1H), 6.94−6.87 (m, 2H), 6.81−6.77 m, 1H), 6.03 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.7, 140.6, 138.4, 133.2, 128.3, 121.9, 121.6, 116.7, 113.0, 84.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}BrIN$ 373.9041; found: 373.9050.

N-(4-Iodophenyl)-[1,1′-biphenyl]-3-amine (**6m**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 92−93 °C; yield: 31.2 mg, 42%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 4H), 7.47−7.41 (m, 2H), 7.40−7.33 (m, 2H), 7.29 (t, J = 2.0 Hz, 1H), 7.21 (dt, J = 7.7, 1.3 Hz, 1H), 7.05 (m, 1H), 6.92−6.85 (m, 2H), 5.77 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.1, 142.8, 142.8, 141.0, 138.3, 130.0, 128.9, 127.6, 127.2, 120.8, 119.6, 117.4, 117.2, 82.5. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}IN$ 372.0249; found: 372.0264.

3-Fluoro-N-(4-iodophenyl)aniline (**6n**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 98−99 °C; yield: 38.8 mg, 62%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.53 (m, 2H), 7.23−7.17 (m, 1H), 6.88−6.83 (m, 2H), 6.80−6.73 (m, 2H), 6.65−6.60 (m, 1H), 5.75 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −111.81. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.8 (d, J_{C-F} = 244.8 Hz), 144.5 (d, J_{C-F} = 10.4 Hz), 142.1, 138.4, 130.7 (d, J_{C-F} = 9.9 Hz), 120.5, 113.3, 108.0 (d, J_{C-F} = 21.4 Hz), 104.4 (d, J_{C-F} = 24.9 Hz), 83.7. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}FIN$ 313.9842; found: 313.9838.

3-Chloro-N-(4-iodophenyl)aniline (**6o**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 82−83 °C; yield: 40.1 mg, 61%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2H), 7.18 (t, J = 8.0 Hz, 1H), 7.03 (t, J = 2.1 Hz, 1H), 6.93−6.87 (m, 2H), 6.87−6.82 (m, 2H), 5.69 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 142.1, 138.4, 135.2, 130.6, 121.4, 120.5, 117.5, 115.9, 83.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}ClIN$ 329.9546; found: 329.9555.

3-Bromo-N-(4-iodophenyl)aniline (**6p**) The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 85−86 °C; yield: 53.7 mg, 72%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.53 (m, 2H), 7.18 (t, J = 2.0 Hz, 1H), 7.12 (t, J = 7.9 Hz, 1H), 7.08−7.05 (m, 1H), 6.94 (ddd, J = 7.9, 2.2, 1.1 Hz, 1H), 6.86−6.80 (m, 2H), 5.68 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 142.0, 138.3, 130.8, 124.3, 123.2, 120.4, 120.4, 116.3, 83.8. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{10}BrIN$ 373.9041; found: 373.9046.

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*Methyl 3-((4-iodophenyl)amino)benzoate (**6q**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 80−81 °C; yield: 43.8 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.63 (d, J = 7.7 Hz, 1H), 7.57 (d, J = 8.7 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 7.9 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 5.82 (s, 1H), 3.92 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 142.8, 142.5, 138.4, 131.6, 129.6, 122.7, 122.3, 120.0, 118.9, 83.3, 52.3. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{13}INO_2$ 353.9991; found: 353.9997.

*1-(3-((4-Iodophenyl)amino)phenyl)ethan-1-one (**6r**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 122−123 °C; yield: 26.9 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (t, *J* = 2.0 Hz, 1H), 7.60−7.56 (m, 2H), 7.53−7.52 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.28−7.25 (m, 1H), 6.90−6.85 (m, 2H), 5.85 (s, 1H), 2.60 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 198.1, 143.1, 142.4, 138.6, 138.4, 129.8, 122.4, 121.7, 120.1, 117.2, 83.4, 26.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{14}H_{13}INO$ 338.0042; found: 338.0043.

*N-(4-Iodophenyl)-3-(trifluoromethyl)aniline (**6s**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 40.6 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.56 (m, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.23−7.18 (m, 2H), 6.90−6.84 (m, 2H), 5.81 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.68. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 141.87, 138.2, 131.9 (q, $J_{C\text{-}F}$ = 32.2 Hz), 130.1, 124.1 (q, $J_{C\text{-}F}$ = 270.8 Hz), 120.5 (d, $J_{C\text{-}F}$ = 1.4 Hz), 120.4, 117.8 (q, $J_{C\text{-}F}$ = 3.9 Hz), 114.0 (q, $J_{C\text{-}F}$ = 3.9 Hz), 84.0. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{10}F_3IN$ 363.9810; found: 363.9829.

*4-Chloro-N-(4-iodophenyl)aniline (**6t**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 75−76 °C; yield: 46.0 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.49 (m, 2H), 7.25−7.20 (m, 2H), 7.02−6.93 (m, 2H), 6.82−6.77 (m, 2H), 5.65 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.8, 141.0, 138.3, 129.5, 126.5, 119.7, 119.7, 82.9. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{10}ClIN$ 329.9546; found: 329.9554.

*4-Bromo-N-(4-iodophenyl)aniline (**6u**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 98−99 °C; yield: 55.9 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.51 (m, 2H), 7.39−7.33 (m, 2H), 6.95−6.90 (m, 2H), 6.83−6.78 (m, 2H), 5.65 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.5, 141.6, 138.3, 132.4, 119.8, 119.8, 113.7, 83.1. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{10}BrIN$ 373.9041; found: 373.9050.

*Ethyl 4-((4-iodophenyl)amino)benzoate (**6v**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 157−158 °C; yield: 33.7 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.17 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.6, 147.2, 141.0, 138.4, 131.5, 122.2, 121.8, 115.3, 85.0, 60.7, 14.5. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{15}INO_2$ 368.0147; found: 368.0144.

*2-Iodo-N-(4-iodophenyl)aniline (**6w**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 100−101 °C; yield: 47.1 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.60−7.54 (m, 2H), 7.25−7.17 (m, 2H), 6.91−6.84 (m, 2H), 6.69−6.65 (m, 1H), 5.85 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.2, 142.2, 139.8, 138.4, 129.3, 123.0, 121.3, 116.9, 89.9, 84.3. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{10}I_2N$ 421.8903; found: 421.8916.

*3-Iodo-N-(4-iodophenyl)aniline (**6x**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 96−97 °C; yield: 35.3 mg, 42%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.53 (m, 2H), 7.40 (s, 1H), 7.30−7.28 (m, 1H), 7.00 (d, *J* = 4.0 Hz, 2H), 6.89−6.81 (m, 2H), 5.68 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.9, 142.0, 138.3, 131.0, 130.4, 126.4, 120.3, 117.1, 95.0, 83.7. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{10}I_2N$ 421.8903; found: 421.8916.

*N-(4-Iodophenyl)-3-isopropylaniline (**6y**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 41. 8 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.51 (m, 2H), 7.26 (t, *J* = 7.8 Hz, 1H), 6.98 (t, *J* = 2.0 Hz, 1H), 6.97−6.90 (m, 2H), 6.88−6.83 (m, 2H), 5.70 (s, 1H), 2.92 (m, 1H), 1.32 (s, 3H), 1.30 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 150.5, 143.4, 142.1, 138.1, 129.4, 120.2, 119.2, 117.0, 116.1, 81.9, 34.2, 24.1. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{17}IN$ 338.0406; found: 338.0406.

*3-Chloro-N-(4-iodophenyl)-4-methylaniline (**6z**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 95−96 °C; yield: 38.4 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.48 (m, 2H), 7.12 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.81−6.76 (m, 2H), 5.59 (s, 1H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.9, 141.3, 138.3, 135.0, 131.6, 129.2, 119.4, 119.1, 117.2, 82.6, 19.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{12}ClIN$ 343.9703; found: 343.9687.

*5-Bromo-N-(4-iodophenyl)-2-methylaniline (**6aa**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 82−83 °C; yield: 48.0 mg, 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.52 (m, 2H), 7.30 (s, 1H), 7.05 (d, *J* = 1.2 Hz, 2H), 6.77−6.72 (m, 2H), 5.35 (s, 1H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.8, 142.2, 138.4, 132.4, 127.0, 125.1, 121.1, 120.2, 120.1, 83.2, 17.6. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{13}H_{12}BrIN$ 387.9198; found: 387.9209.

*3,4-Difluoro-N-(4-iodophenyl)aniline (**6ab**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 85−86 °C; yield: 48.3 mg, 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56−7.51 (m, 2H),7.09−7.03 m, 1H), 690−6.85 (m, 1H), 6.80−6.76 (m, 2H), 6.75−6.71 (m, 1H), 5.62 (s, 1H). ^{19}F NMR (376 MHz, $CDCl_3$) δ −135.68 − −135.83 (m), −146.16 − −146.27 (m). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.9 (d, $J_{C\text{-}F}$ = 13.4 Hz), 149.5 (d, $J_{C\text{-}F}$ = 13.5 Hz), 146.8 (d, $J_{C\text{-}F}$ = 12.9 Hz), 144.4 (d, $J_{C\text{-}F}$ = 12.8 Hz), 142.7139.2 (dd, $J_{C\text{-}F}$ = 8.2, 2.7 Hz), 138.3, 119.6, 117.8 (dd, $J_{C\text{-}F}$ = 18.1, 1.7 Hz), 114.4 (dd, $J_{C\text{-}F}$ = 5.7, 3.3 Hz), 107.7 (d, $J_{C\text{-}F}$ = 19.9 Hz), 83.1. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_9F_2IN$ 331.9748; found: 331.9758.

*2-Chloro-N-phenylaniline (**7a**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 34.9 mg, 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.27 (m, 4H), 7.21−7.11 (m, 3H), 7.06 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.85−6.80 (m, 1H), 6.13 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.5, 140.3, 129.8, 129.5, 127.5, 122.7, 121.5, 120.4, 120.2, 115.6. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{12}H_{11}ClN$ 204.0580; found: 204.0592.

*Ethyl (E)-3-(4-((2-chlorophenyl)amino)phenyl)acrylate (**7b**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 45.7 mg, 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.9 Hz, 1H), 7.48−7.41 (m, 2H), 7.40−7.36 (m, 2H), 7.20−7.16 (m, 1H), 7.11−7.07 (m, 2H), 6.92−6.8 (m, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 6.26 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.4, 144.2, 144.0, 138.6, 130.0, 129.6, 127.8, 127.5, 123.2, 122.0, 118.0, 117.8, 115.5, 60.4, 14.4. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{17}H_{17}ClNO_2$ 302.0948; found: 302.0938.

*2-Chloro-N-(4-(phenylethynyl)phenyl)aniline (**7c**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as colorless oil; yield: 54.5 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.52 (m, 2H), 7.51−7.46 (m, 2H), 7.42−7.30 (m, 5H), 7.23−7.14 (m, 1H), 7.14−7.08 (m, 2H), 6.88 (td, *J* = 7.7, 1.5 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.9, 139.1, 132.9, 131.5, 130.0, 128.4, 128.0, 127.5,

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123.6, 122.6, 121.5, 118.5, 116.9, 116.4, 89.6, 88.6. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{15}ClN$ 304.0893; found: 304.0885.

*N-(2-Chlorophenyl)-[1,1′-biphenyl]-4-amine (**7d**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:100) to give the product as a white solid, m.p. 67−68 °C; yield: 43.5 mg, 78%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.3 Hz, 2H), 7.49 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.32 (dd, J = 8.0, 1.5 Hz, 1H), 7.30−7.23 (m, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.11−7.04 (m, 1H), 6.76 (td, J = 7.7, 1.5 Hz, 1H), 6.10 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.0, 140.7, 140.1, 135.4, 129.9, 128.9, 128.1, 127.6, 126.9, 126.7, 121.8, 120.7, 120.2, 116.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{15}ClN$ 280.0893; found: 280.0891.

*4-((2-Chlorophenyl)amino)phenol (**7e**)* The compound was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:5) to give the product as colorless oil; yield: 22.3 mg, 51%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 7.9, 1.5 Hz, 1H), 7.11−7.05 (m, 3H), 6.97 (dd, J = 8.2, 1.5 Hz, 1H), 6.87−6.81 (m, 2H), 6.73 (td, J = 7.6, 1.5 Hz, 1H), 5.95 (s, 1H), 5.10 (s, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 152.2, 142.2, 134.3, 129.6, 127.6, 124.9, 120.1, 119.2, 116.4, 114.0. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{12}H_{11}ClNO$ 220.0529; found: 220.0531.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00681.

^1H, ^{13}C, and ^{19}F NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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