CHEMISTRY
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## Accepted Article

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**To be cited as:** *Chem. Eur. J.* 10.1002/chem.201700630

**Link to VoR:** http://dx.doi.org/10.1002/chem.201700630

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# Polyaniline-induced Arylation with Arenediazonium Salts Derived from Anilines

Dai Hata,[a] Toshiyuki Moriuchi,[a] Toshikazu Hirao,[+][a] and Toru Amaya*[a]

**Abstract:** A catalytic amount of a reduced form of polyaniline, redox-active π-conjugated polymer, induced C-H direct arylation of (hetero)arenes with arenediazonium salts prepared from anilines with methanesulfonic acid ($MeSO_3H$) and *tert*-butyl nitrite (*t*-BuONO). The difficult point is the coexistence of an oxidant and a reductant in this sequential diazotization and arylation system; the diazotization reagents such as alkyl nitrites are weak oxidants and the arylation is induced by a reductant. It was achieved by the careful control of the amount of *t*-BuONO (1.0 equivalent) for the diazotization step and the sequential arylation using 5 mol% of the polyaniline. The reaction took place under mild conditions without any metals and strong bases at room temperature, where the amino group is a formal leaving group. The scope of the substrates demonstrated the versatility in the combination of anilines with a variety of functional groups and several (hetero)arenes. Exploiting mono-Boc-protected 1,4-phenylenediamine, two-directional arylation for the synthesis of the unsymmetrically 1,4-diarylated (furyl and pyrrolyl groups) benzene was achieved, which shows a potential for the synthesis of more complicated oligoarene compounds.

## Introduction

Biaryls are commonly found in natural compounds, medicines, and other functional organic materials. Transition-metal-catalyzed cross-coupling reactions made it possible to get the biaryls directly (Scheme 1a).[1] In terms of environmental aspects, however, the alternative method to access biaryl moieties under transition-metal-free conditions is required. One of such strategies is homolytic aromatic substitution (HAS), [2] which is consisted of the addition of an aryl radical to an arene and the subsequent aromatization (Scheme 1b). Recently, significant improvements of HAS have been achieved with arylhalides as radical precursors and alkali metal *t*-butoxide as a base, where radical chain mechanism is suggested.[3]

Arenediazonium salts **1** have a diazonio group as a desirable leaving group for this reaction, and readily accept one electron to yield aryl radicals. The cross-coupling reaction of **1** with an arene **2** to give a biaryl **3** is known as the Gomberg-Bachmann reaction (Scheme 1c).[4] Due to the low reduction potential ($E_{1/2}$ = +0.14~0.45 V vs SCE[5]) of arenediazonium salts **1**, the radical initiation and propagation steps can be performed under mild conditions. Recently, various reductants such as organic reductants, low-valent metals, and photocatalyst under light, have been reported for this type of reaction.[6-8] As an example for the reactions under metal-free conditions, a photocatalyst eosin Y was demonstrated for the C-H arylation of arenes with arenediazonium salts by König et al.[7b]

For all that, arenediazonium salts **1** are hard to be preserved and the commercial source is limited due to their unhandy character. Alternatively, the arylation with anilines **4** via *in-situ* preparation of arenediazonium salts **1** is attractive, which can not only overcome the preservation problem but become complementary method of arylation with arylhalides because an amino group is a formal leaving group here. It is also advantage that various anilines **4** can be available from commercial sources. However, there is difficulty due to the coexistence of an oxidant and a reductant in this sequential diazotization and arylation system; the diazotization reagents such as alkyl nitrites are weak oxidants and the arylation is induced by a reductant (Scheme 1e). Therefore, the examples have been limited.[8] Recently, transition-metal-free conditions have been reported.[8e,i-k] For examples, ascorbic acid and gallic acid-initiated C-H arylation of arenes were demonstrated by Carrillo and coworkers.[8e,k] Light-induced and catalyst-free method was also described by de Frutos, Kappe et al, where diazo anhydride intermediate was suggested.[8j]

On the other hand, polyaniline is a redox-active π-conjugated polymer. We have constructed redox-reaction systems based on polyanilines.[9] Its reduced form **5** (Scheme 1d) is a suitable single-electron donor for the reduction of arenediazonium salts in terms of the redox potentials (the oxidation potential is reported to be $E_{1/2}$ = +0.13 V vs SCE[10]). Moreover, the formed radical cation of polyaniline is stabilized by its π-conjugated system. Polyaniline is also able to be removed easily from the reaction mixture. In this regard, we have achieved the arylation of (hetero)arenes using arenediazonium salts induced by a catalytic amount of the reduced form of polyaniline **5** (Scheme 1d).[11] In this context, this study was conducted to develop the sequential diazotization and arylation (Scheme 1e). Development of such mehod leads to iterative and polydirectional arylation if some amino-groups can be differentiated using protecting groups.[12] Herein, we report the polyaniline-induced arylation with arenediazonium salts **1** derived from anilines **4** without the use of any metal additives, strong bases, and light (Scheme 1e-I). We also demonstrate the two-directional arylation strategy using Boc-protected 1,4-phenylenediamine **6** to synthesize the arene **7** with furyl and pyrrolyl groups (Scheme 1e-II).

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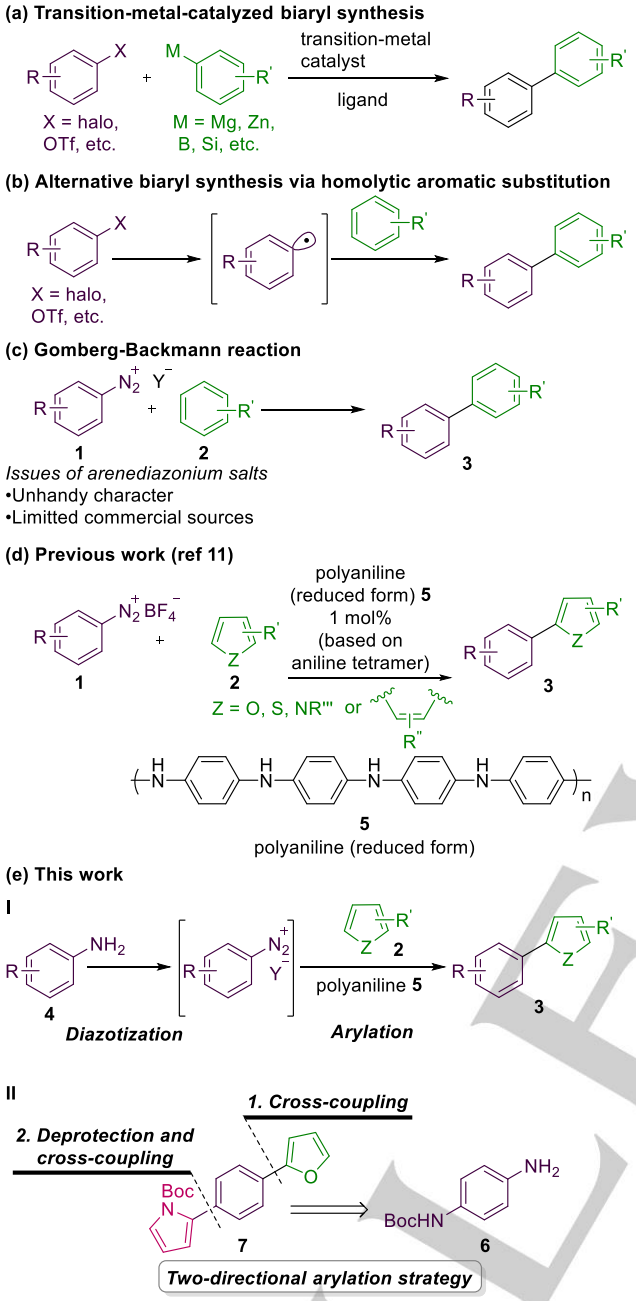
10.1002/chem.201700630



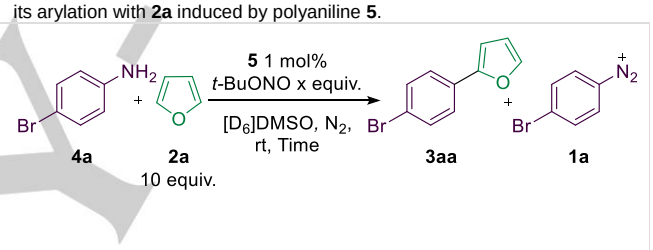




**Scheme 1.** (a) Transition-metal-catalyzed biaryl synthesis, (b) alternative biaryl synthesis via homolytic aromatic substitution, (c) Gomberg-Backmann reaction, (d) previous work, and (e) this work, I: sequential diazotization and arylation, and II: two-directional arylation strategy.

## Results and Discussion

One-pot reaction was examined as an initial investigation, where *tert*-butyl nitrite (*t*-BuONO) as a diazotization reagent was added to the [$D_6$]DMSO solution of 4-bromoaniline **4a**, 10 equivalents of furan **2a**, and 1 mol% of a reduced form of polyaniline **5** (mole of **5** was calculated based on aniline tetramer). Table 1 summarizes the yields of 2-(4-bromophenyl)furan (**3aa**) and the corresponding arenediazonium salt **1a** to the equivalents of *t*-BuONO and reaction time (supplementary investigation is also shown in Table S1-S4). In the following optimization, the reactions were performed with an internal standard (1,3,5-tribromobenzene), and the yield was determined by the integral ratio in the $^1$H NMR spectrum after sampling and dilution with [$D_6$]DMSO. Under the conditions with 1.5 equivalents of *t*-BuONO and 0.5 h reaction time, the desired product **3aa** was obtained in 12% (Table 1, entry 1). The reaction required 8.5 h until the yield of **3aa** reached a maximum yield of 36% with the trace amounts of **1a** (Table 1, entry 2). In the reaction, the diazotization step seems to be incomplete judging from the $^1$H NMR spectra of the reaction mixture. Methanesulfonic acid ($MeSO_3H$) dramatically promoted the formation of the corresponding arenediazonium salts **1a** (87%), but the yield of **3aa** remains low (10%; Table 1, entry 3). The foremost concern is the deactivation of **5** by *t*-BuONO under the acidic conditions, which was demonstrated using *N,N'*-diphenylphenylenediamine as a model compound of **5** (Scheme S1).

**Table 1.** One-pot synthesis of **3aa** based on *in-situ* diazotization of **4a** and its arylation with **2a** induced by polyaniline **5**.




| Entry | *t*-BuONO x [equiv.] | Time [h] | Yield [%][a] Arylated furan **3aa** | Yield [%][a] Arenediazonium salt **1a** |
|---|---|---|---|---|
| 1 | 1.5 | 0.5 | 12 | trace |
| 2 | 1.5 | 8.5 | 36 | 17 |
| 3 | 1.5 (with $MeSO_3H$)[b] | 0.5 | 10 | 87 |

[a] Yield was determined by $^1$H NMR analysis of the reaction mixture based on 1,3,5-tribromobenzene as an internal standard. [b] Reaction was performed with 1.0 equivalent of $MeSO_3H$.

With these results in hand, increasing of the amount of polyaniline **5** and the careful investigation on the amount of *t*-BuONO were conducted as shown in Table 2 (Supplementary investigation of nitrites and solvents is also shown in Table S4), where the dropwise procedure was employed. As expected, use of 5 mol% of **5** and 1.0 equivalent of *t*-BuONO gave **3aa** in 73% yield (Table 3, optimized conditions, entry 1) with 11% of diarylated furan **8aa**. Slight increase of the amount of *t*-BuONO (1.1 equivalents) significantly lowered the conversion of the arenediazonium salt **1a** (Table 2, entry 2), which supports the hypothesis of the deactivation of polyaniline **5** by *t*-BuONO. However, further increasing of **5** to 10 mol% gave rise to lower the yield of **3aa** (66% and 64%, Table 3, entries 3 and 4, respectively).

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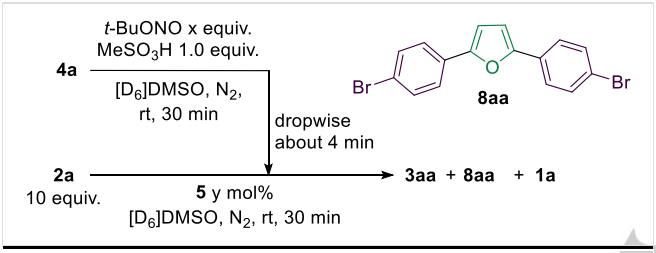
These results indicate that the arylation of polyaniline **5** took place competitively (IR spectroscopy revealed the competitive reaction, see Supporting Information, Figure S1). Without polyaniline **5**, the arylation did not proceed and the arenediazonium salt **1a** remained in 92% yield (Table 3, entry 5). Using the optimized amounts of the substrates and reagents, they are jumbled and mixed together to get **3aa** in a less yield of 57% (Table 3, entry 6, one-pot procedure). As described in our previous study, [11] the arylation induced by **5** was found to be affected by the order and speed for the addition of the substrate. The steady low-kept concentration of the aryl radical by dropwise addition is considered to be a key point in the arylation, which can lead to the situation that an aryl radical is surrounded by large excess of arenes.

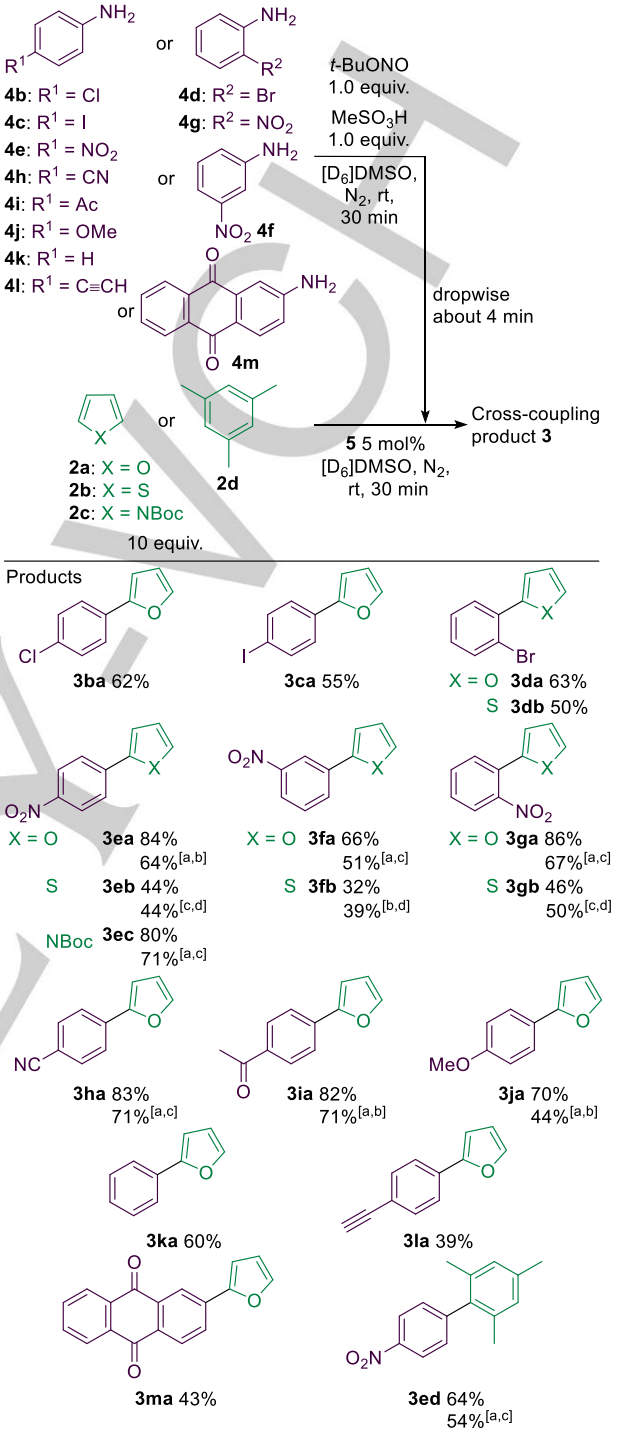
**Table 2.** Investigation of the amounts of *t*-BuONO and polyaniline **5** in the cross-coupling reaction under the conditions with a dropwise addition of the solution of the prepared arenediazonium salt **1a** from **4a** to the mixture of **5** and **2a**




| Entry | *t*-BuONO x [equiv.] | Polyaniline **5** y [mol%] | Yield [%][a] Mono-arylated furan **3aa** | di-arylated furan **8aa** | Arene diazonium salt **1a** |
|---|---|---|---|---|---|
| 1 | 1.0 | 5 | 73 | 11 | - |
| 2 | 1.1 | 5 | 22 | 1 | 63 |
| 3 | 1.0 | 10 | 66 | 12 | - |
| 4 | 1.1 | 10 | 64 | 9 | - |
| 5 | 1.0 | 0 | - | - | 92 |
| 6[b] | 1.0 | 5 | 57 | 7 | - |

[a] Yield was determined by $^1$H NMR analysis of the reaction mixture based on 1,3,5-tribromobenzene as an internal standard. [b] One-pot procedure was employed instead of the dropwise one.

Under the optimized reaction conditions, the scope and limitation of the arylation of heteroarenes (furan **2a**, thiophene **2b**, and *N*-Boc-pyrrole **2c**) and an arene **2d** were investigated (Scheme 2). In the case of the reaction using **4b**-**4k** with furan **2a**, mono-arylated furans **3ba**-**3ka** were obtained in moderate to good yields (51 to 86%) regardless of the electronic state of the aniline derivatives **4b**-**4k**. Large family of functional groups were tolerated in the arylation, such as chloro, bromo, iodo, nitro, cyano, acetyl, and methoxy groups. Moreover, the aniline **4l** with ethynyl group can be used for the reaction to give the biaryl **3la** in 39%.




**Scheme 2.** Scope and limitation of the sequential diazotization of anilines **4** and the arylation with arenes **2** induced by polyaniline **5**. Yield was determined by $^1$H NMR analysis based on 1,2,4,5-tetrabromobenzene as an internal standard. The reaction was conducted using 0.2 mmol of **4**. In some cases, the reaction was conducted in DMSO instead of [D$_6$]DMSO (see experimental section). [a] Isolated yield. [b] 1.0 mmol of **4** was used. [c] 2.0 mmol of **4** was used. [d] Isolated yield of the coupling products at the C2 and C3 positions (91:9 for **3eb**, 90:10 for **3fb**, 95:5 for **3gb**).

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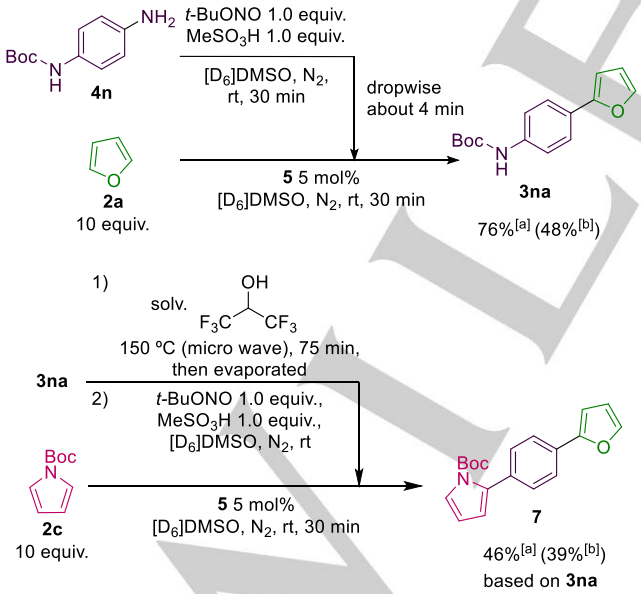
The reaction employing the substrate **4m** bearing quinone moiety also took place to afford **3ma** in 43% yield. The arylation of thiophene **2b** was conducted with **4d**-**4g** to give the corresponding products **3db-3gb** in moderate yields (32 to 50%). In the case of thiophene, the coupling product at the C-3 position of thiophene was also observed as a minor product (ca. 5-10%) in $^1$H NMR and GC-MS. Boc-protected pyrrole **2c** was also available with this arylation, where Boc-protecting group remained intact (80% NMR yield in 0.2 mmol scale and 71% isolated yield in 2.0 mmol scale for **3ec**). *m*-Nitroaniline **4f** is less reactive to give the products **3fa** and **3fb** to result in 15 to 20% less than those of *p*- and *o*-nitroanilines **4e** and **4g**. Mesitylene **2d** was demonstrated as a six-membered arene to provide **3ed** in moderate yields.

As *N*-Boc amino group was tolerated through the reaction as demonstrated in the synthesis of **3ec** in Scheme 3, it motivated us further investigation of the potential of our methodology. That is, the synthesis of arene **7** with furyl and pyrrolyl groups using *N*-Boc-phenylenediamine **4n** was carried out. This two-directional arylation strategy is attractive because it is able to prepare a variety of hetero-substituted benzene. First, **4n** was diazotized and the resulting arenediazonium salt cross-coupled with **2a** in the presense of 5 mol% of **5** to give the corresponding heterobiaryl **3na** in 76% yield, where Boc group was intact. Deprotection of Boc group was performed in hexafluoroisopropanol at 150 °C under microwave irradiation for 75 min to give the corresponding aniline.[13] After the evaporation of hexafluoroisopropanol, the reaction mixture was used for the next reaction without purification. Finally, the second sequential diazotization and arylation with **2c** induced by polyaniline **5** was demonstrated to afford the desired oligoarene **7** in 46% yield based on **3na**.




**Scheme 4.** Synthesis of the 1,4-disubstituted benzene **7** with furyl and pyrrolyl groups based on two-directional arylation strategy using *N*-Boc-phenylenediamine **4n**. [a] Yield was determined by $^1$H NMR analysis of the reaction mixture based on 1,3,5-tribromobenzene as an internal standard. [b] Isolated yield.

## Conclusions

In summary, a catalytic amount of polyaniline **5**-induced C-H arylation of arenes **2** with arenediazonium salts **1** prepared by the preceding diazotization of anilines **4** has been developed, where the amino group in anilines **4** is a formal leaving group. This sequential reaction proceeds under mild conditions without any metals and strong bases at room temperature to yield biaryls. Although there is difficulty in the coexistence of diazotization of amino group and the arylation induced by one-electron reduction, it can be achieved by the careful control of the amount of *t*-BuONO (1.0 equivalent) for the diazotization step and the sequential arylation using 5 mol% of polyaniline **5**. Employing the developed arylation, the two-directional arylation strategy using *N*-Boc-phenylenediamine **4n** was demonstrated by the synthesis of 1,4-disubstituted benzene **7** with furyl and pyrrolyl groups**.** This strategy may be applied to the synthesis of more complicated oligoarenes. Further investigation and application are now in progress.

## Experimental Section

**General.** NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer. Chemical shifts in $CDCl_3$ were reported in ppm on the $\delta$ scale relative to a residual solvent ($\delta$ 7.26 for $^1$H NMR and 77.16 ppm for $^{13}$C NMR) as an internal standard. Infrared spectra were recorded as KBr pellets on a JASCO FT/IR-480plus. Mass spectra were measured on a JEOL JMS-DX-303 spectrometer using fast atom bombardment (FAB) mode, a BRUKER AUTOFLEX III (MALDI−TOF) mass spectrometer, or SHIMADZU GC-2010 PARVUM2 100V (GC-MS, EI). Reaction under microwave irradiation was performed on a Biotage initiator 2.5. Silica gel column chromatography was performed on a Yamazen EPCLC-W-Prep 2XY A-Type with an ULTRA PACK™ cartridge.

**Materials.** A reduced form of polyaniline **5** was prepared according to the reported method.[11] Anilines **4a-n,** arenes **2a-d**, *t*-BuONO, $MeSO_3H$, DMSO, $[D_6]$DMSO, and hexafluoroisopropanol were purchased from the commercial sources, and used without further purification unless otherwise mentioned.

**Polyaniline-induced arylation with arenediazonium salts via *in-situ* diazotization: synthesis of 3ia.** In an oven-dried 30 mL two-necked flask with a stirring tip, aniline **4i** (169 mg, 1.25 mmol) was dissolved in 9.5 mL of DMSO under a nitrogen atmosphere. To the solution were added $MeSO_3H$ (81 µL, 1.25 mmol) and *t*-BuONO (165 µL, 1.25 mmol). Then, the reaction mixture was stirred at room temperature for 30 min, 80 volume % of which was dropwise added by using a syringe pump (60 mL/h) to the 2 mL DMSO solution of polyaniline **5** (18 mg, 50 µmol, based on aniline tetramer) and arene **2a** (730 µL, 10 mmol) in another oven-dried 30 mL two-necked flask with a stirring tip. After the reaction for 30 minutes, the reaction mixture was poured into the mixture of $Et_2O$ and water. The resulting black solid of the polyaniline **5** was filtered through silica gel before the liquid-liquid separating operation. The aqueous layer was extracted with $Et_2O$ three times. The combined organic layer was washed with water and brine, then dried with $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane/ethyl acetate = 9/1) to give the product **4fa** (132 mg, 0.71 mmol, 71%). The reactions for 2 mmol scale synthesis were also carried out with the same procedure. In the synthesis of **3ha**, aniline **4h** (295 mg, 2.5 mmol), $MeSO_3H$ (81 µL, 1.25 mmol) and *t*-BuONO (165 µL, 1.25 mmol),

polyaniline **5** (36 mg, 100 µmol, based on aniline tetramer), and arene **2a** (1.45 mL, 20 mmol) were used. The speed of dropwise addition of diazotization reaction mixture was 120 mL/h. After purification by silica gel column chromatography (hexane/ethyl acetate = 9/1), the product **3ha** (240 mg, 1.42 mmol, 71%) was obtained.

**General procedure for the optimization and the substrate scope investigation of the sequential diazotization and arylation.** In an oven-dried 10 mL two-necked flask with stirring tip, aniline **4** (0.2 mmol) were reacted with arene **2** (2.0 mmol) as described above (synthesis of **3ia**) in the presence of an internal standard (ca. 0.10 mmol). The speed of dropwise addition of diazotization reaction mixture was 25.4 mL/h. A sample was taken from the reaction mixture after a certain time and diluted ten times with [$D_6$]DMSO to be measured by NMR spectroscopy. The yield of products **3** was calculated based on the integral ratio in the $^1$H NMR spectrum. The reactions conducted with DMSO as a solvent were carried out similarly (**3ea**, **3eb**, **3ec**, **3fa**, **3fb**, **3ga**, **3gb**, **3la**, **3ma**). The yield was determined by $^1$H NMR analysis of the crude mixture based on 1,3,5-tribromobenzene as an internal standard after the similar work-up as described in the synthesis of **3ia**.

Identification of the products **3** was conducted by comparison with the data reported previously except for new compounds after isolation of the product by preparative TLC or silica gel chromatography, see supporting information: 2-(4-bromophenyl)furan (**3aa**)[7b], 2-(4-chlorophenyl)furan (**3ba**)[7b], 2-(4-iodophenyl)furan (**3ca**)[14], 2-(2-bromophenyl)furan (**3da**)[15], 2-(2-bromophenyl)thiophene (**3db**)[16], 2-(4-nitrophenyl)furan (**3ea**)[7b], 2-(4-nitrophenyl)thiophene (**3eb**)[7b], *tert*-butyl 2-(4-nitrophenyl)-1H-pyrrole-1-carboxylate (**3ec**)[7b], 2-(3-nitrophenyl)furan (**3fa**)[8j], 2-(3-nitrophenyl)thiophene (**3fb**)[8j], 2-(2-nitrophenyl)furan (**3ga**)[8j], 2-(2-nitrophenyl)thiophene (**3gb**)[8j], 4-(furan-2-yl)benzonitrile (**3ha**)[7b], 1-(4-(furan-2-yl)phenyl)ethanone (**3ia**)[17], 2-(4-methoxyphenyl)furan (**3ja**)[7b], 2-phenylfuran (**3ka**)[7b], 2-(furan-2-yl)-dihydroanthracene-9,10-dione (**3ma**)[8d], 2,4,6-trimethyl-4'-nitro-1,1'-biphenyl (**3ed**)[18], 2,5-bis(4-bromophenyl)furan (**8aa**)[19].

**Two-directional arylation: synthesis of 7.** The mono-arylated furan **3na** was synthesized following the procedure mentioned above. The yield was determined by $^1$H NMR analysis of the crude mixture based on 1,3,5-tribromobenzene as an internal standard (76%). The crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate = 10/0→9/1) to give the product **3na** (124 mg, 0.48 mmol, 48%), where the isolated yield decreased from the $^1$H NMR yield because the separation of the product **3na** from the by-product *N*-Boc aniline was difficult. Microwave vial for 2-5 mL was charged with **3na** (130 mg, 0.5 mmol) and hexafluoroisopropanol (5.0 mL) under the flow of nitrogen, and sealed with the special cap. Then the suspension of **3na** was treated under the irradiation of microwave at 150 °C for 75 min, then evaporated. In an oven-dried 10 mL two-necked flask with a stirring tip, the resulting solid was dissolved in 3.8 mL of DMSO under a nitrogen atmosphere. When $MeSO_3H$ (32 µL, 0.5 mmol) and *t*-BuONO (66 µL, 0.5 mmol) were added to the solution, 80 volume % of the reaction mixture dropwise added immediately by syringe to the DMSO solution of polyaniline **5** (7.0 mg, 20 µmol, based on aniline tetramer) and arene **2c** (670 µL, 4 mmol) in another oven-dried 10 mL two-necked flask with a stirring tip. After the reaction for 30 minutes, the reaction mixture was poured into the mixture of $Et_2O$ and water. The aqueous layer was extracted with $Et_2O$ three times. The combined organic layer was washed with water and brine, then dried with $Na_2SO_4$, and concentrated *in vacuo*. The black solid of polyaniline was filtered during the liquid-liquid separating operation. The yield was determined by $^1$H NMR analysis of the crude mixture based on 1,3,5-tribromobenzene as an internal standard (46%).The crude mixture was purified by preparative thin layer chromatography (hexane/ethyl acetate = 85/15) to give the product **7** (48 mg, 0.16 mmol, 39%).

**Spectral data for the new compounds.**

2-(4-Ethynylphenyl)furan (**3la**): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.61-7.65 (m, 2H), 7.53-7.46 (m, 3H), 6.69 (d, *J* = 3.7 Hz, 1H), 6.49 (dd, *J* = 3.7 Hz, 1.8 Hz, 1H), 3.12 (s, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 153.37, 142.75, 132.64, 131.21, 123.69, 120.87, 112.02, 106.25, 83.80, 77.95 ppm; IR(KBr) 3285, 3126, 2926, 2105, 1921, 1612, 1509, 1475, 1417, 1376, 1281, 1221, 1157, 1112, 1042, 1010, 903, 885, 842, 807, 738, 665, 620, 595, 540 cm$^{-1}$; HRMS (FAB) (*m/z*): $[M]^+$ calcd for $C_{12}H_8O$, 168.0575; found, 168.0576.

*tert*-Butyl (4-(furan-2-yl)phenyl)carbamate (**3na**): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.58-7.62 (m, 2H), 7.43 (d, *J* = 1.8 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 3.5 Hz, 3H), 6.49 (br, 1H), 6.45 (dd, *J* = 3.5 Hz, 1.8 Hz, 1H), 1.53 (s, 9H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 154.00, 152.74, 141.77, 137.71, 126.16, 124.73, 118.71, 111.73, 104.13, 80.84, 28.51 ppm; IR(KBr) 3367, 3006, 2985, 2933, 1700, 1614, 1594, 1577, 1523, 1509, 1484, 1462, 1446, 1415, 1393, 1368, 1315, 1297, 1265, 1236, 1160, 1117, 1079, 1058, 1017, 1008, 903, 884, 838, 805, 770, 733, 663, 648, 628, 594, 518 cm$^{-1}$; HRMS (FAB) (*m/z*): $[M]^+$ calcd for $C_{15}H_{17}NO_3$, 259.1208; found, 259.1208.

*tert*-Butyl 2-(4-(furan-2-yl)phenyl)-1*H*-pyrrole-1-carboxylate (**7**): $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.63-7.67 (m, 2H), 7.48 (dd, *J* = 1.8 Hz, 0.9 Hz, 1H), 7.39-7.34 (m, 3H), 6.60 (dd, *J* = 3.7 Hz, 0.9 Hz, 1H), 6.48 (dd, *J* = 3.7 Hz, 1.8 Hz, 1H), 6.26-6.20 (m, 2H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 154.10, 149.54, 142.21, 134.89, 133.47, 129.82, 129.56, 123.16, 122.94, 114.70, 111.83, 110.81, 105.15, 83.90, 27.84 ppm; IR(KBr) 3147, 3118, 3003, 2981, 2930, 2850, 1733, 1515, 1469, 1455, 1416, 1394, 1370, 1338, 1316, 1257, 1221, 1149, 1075, 1010, 975, 903, 882, 849, 817, 805, 773, 749, 725, 670, 598 cm$^{-1}$; HRMS (FAB) (*m/z*): $[M]^+$ calcd for $C_{19}H_{19}NO_4$, 309.1365; found, 309.1368.

## Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Innovative Areas “Advanced Molecular Transformations by Organocatalysts” from The Ministry of Education, Culture, Sports, Science and Technology, Japan (26105736).

**Keywords:** C-C coupling • Gomberg-Bachmann reaction • Radical reactions • Polyaniline • *In-situ* diazotization

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10.1002/chem.201700630

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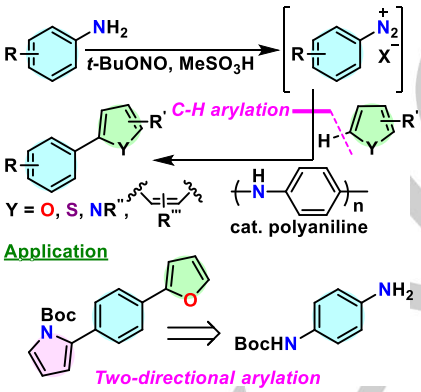
## FULL PAPER

A catalytic amount of a reduced form of polyaniline induced C-H direct arylation of (hetero)arenes with arenediazonium salts prepared from anilines with methanesulfonic acid ($MeSO_3H$) and *tert*-butyl nitrite (*t*-BuONO). Exploiting mono-Boc-protected 1,4-phenylenediamine, two-directional arylation for the synthesis of the unsymmetrically 1,4-diarylated (furyl and pyrrolyl groups) benzene was also achieved.

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