Supporting Information

**Regiospecific N-Arylation of Aliphatic Amines under Mild and Metal-Free Reaction Conditions**

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Supporting Information

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1 General Experimental Procedure

All reactions were carried out in oven-dried glassware unless otherwise noted. Toluene was dried using a VAC-purification system, and degassed for 15 minutes by bubbling argon through a long needle prior to all reactions. Diaryliodonium salts and bases were dried under vacuum and stored in a desiccator. The amine substrates were either newly purchased, freshly distilled or purified through a silica plug prior to use. 

mCPBA (Aldrich, 77% active oxidant) was dried at RT on high vacuum for several hours, and titrated by iodometric titration[1] prior to use. TLC analysis was performed on pre-coated Merck silica gel 60 F254 plates using UV light. Column chromatography was conducted by flash column chromatography using 40 - 60 µm, 60 Å silica gel as stationary phase. Flash column chromatography was done on SiO2 purchased from Aldrich (technical grade, 60 Å pore size, 230-400 mesh, 40-63 µm). Melting points were measured using a STUART SMP3 and are reported uncorrected. The melting point measurements refer to the solidified materials as the result of the given experimental procedures, no additional recrystallization was done. All NMR spectra were recorded using a 400 MHz Bruker AVANCE II with a BBO probe at 298 K using CDCl3 as solvent. Chemical shifts are given in ppm relative to the residual solvent peak (1H NMR: CDCl3 δ 7.26 DMSO δ 2.50, CD3OD δ 3.31; 13C NMR: CDCl3 δ 77.16, DMSO δ 39.52, CD3OD δ 49.00) with multiplicity (b = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, app.= apparent), coupling constants (in Hz) and integration. High-resolution mass analyses were obtained using a Bruker microTOF ESI. High performance liquid chromatography was performed on or Waters Alliance 2695 equipped with a Waters 2489 UV/VIS detector.

Full analytical data is given if the compound is novel or not fully characterized in the literature; for literature reported compounds only 1H NMR and 13C NMR are given.

2 Synthesis of Diaryliodonium Salts

2.1 Our One-Pot Methods

The majority of the diaryliodonium salts used in this investigation were synthesized according to the one-pot procedures developed in the Olofsson group using Methods I-V in Table S1. The reactions were run without precautions to avoid air or moisture, and sometimes combined with an anion exchange. Anion exchanges can either be performed in situ, by addition of the appropriate acid,[2] or by treatment with the a solution of the appropriate sodium salt[3] (Scheme S1). Reaction details are given in Table S2.

Table S1. Our methods for one-pot synthesis of diaryliodonium salts.

| Method | Reaction | Conditions |
|--------|----------|------------|
| I[4]   | R1+I2   | mCPBA (1.1 equiv)  \\
|        |         | TIOH (2-3 equiv)  \\
|        |         | CH2Cl2, temp., time |
| II[4]  | R1+I2   | mCPBA (3-4 equiv)  \\
|        |         | TIOH (4-5 equiv)  \\
|        |         | CH2Cl2, temp., time |
| III[5] | R1+I2   | mCPBA (1.1 equiv)  \\
|        |         | BF3·OEt (2-3 equiv)  \\
|        |         | CH2Cl2, temp., time |
| IV[2]  | R1+I2   | mCPBA (1.1 equiv)  \\
|        |         | TsOH·H2O (1.1 equiv)  \\
|        |         | CH2Cl2, temp., time |
| V[2]   | R1+I2   | mCPBA (3 equiv)  \\
|        |         | TsOH (3-4 equiv)  \\
|        |         | CH2Cl2, temp., time |
Scheme S1. Anion exchanges[3]

NaX (85 mmol) was dissolved in H₂O (100 mL). The diaryliodonium salt (3.4 mmol) was dissolved in CH₂Cl₂ (20 mL) and washed 5 x 20 mL with the aqueous solution of NaX. The organic layer was concentrated without drying. Et₂O was added and the mixture was stirred at RT for 30 min. The solid was filtered, washed with Et₂O and dried under vacuum. The method was used to exchange BF₄ to OTs using NaOTs, and to exchange OTs to OTf using NaOTf.

Table S2. Synthesis of diaryliodonium salts and references to analytical data.

| Diaryliodonium salt | Method | Acid (equiv) | T (°C) | Time | Yield (%) | Ref. |
|---------------------|--------|--------------|--------|------|-----------|------|
| 2a                  | I      | 2.0          | rt     | 15 h | 85        | [4, 6]|
| 2c                  | III    | 2.5          | rt     | 90 min | 50       | [7]  |
| 2g                  | IV[a]  | 1.1          | 1) 60  | 1) 2 h 2) 18 h | 96 | [8] |
| 2h                  | I      | 3.0          | rt     | 1 h  | 93        | [4, 6]|
| 2i                  | I      | 2.0          | rt     | 18 h | 79        | [4, 9]|
| 2j                  | I      | 2.0          | rt     | 15 h | 89        | [6]  |
| 2k                  | I      | 2.0          | 80     | 15 h | 63        | [4, 6]|
| 2l                  | IV     | 1.1          | 40     | 4 h  | 74        | [2, 9]|

[a] Method IV used for 2g.
2m

|       | I   | 3.0 | 0   | 1 h  | 91  | [4, 6] |

2n

|       | I   | 2.0 | rt  | 10 min | 52  | [4, 6] |

2o

|       | II  | 5.0 | rt  | 20 min | 78  | [4, 6] |

2p

|       | V   | 1.0 | rt  | 14 h   | 71  | [10]   |

2q

|       | IV  | 1.0 | rt  | 18 h   | 58  | [2, 11]|

2r

|       | II  | 4.0 | 0 to rt | 6 h   | 92  | [12]   |

2u

|       | II  | 4.0 | rt  | 1 h    | 52  | [6]    |

2v

|       | I[c] | 4.0 | 1) 60 | 1) 30 min | 81  | [13]   |

[a] Synthesized by stepwise addition.  
[b] *In situ* anion exchange by treatment with TfOH.  
[c] Stepwise addition of H₂O (2 equiv) at 0 °C.
2.2 Synthesis of Novel Diaryliodonium Salts

Synthesis of (2-fluoro-4-nitropheno)(phenyl)iodonium trifluoromethanesulfonate (2s):

\[
\begin{align*}
\text{mCPBA (1.1 equiv) & TfOH (2.0 equiv) } \text{CH}_2\text{Cl}_2, \text{rt, 30 min} \quad \text{O}_2\text{N} \quad + \quad \text{I} \quad \text{F} \quad \text{O} \quad \text{OTf} \\
\text{rt., 17 h} \quad \text{72 %}
\end{align*}
\]

mCPBA (2.06 mmol, 1.1 equiv) was dissolved in DCM followed by the addition of 1-iodo-2-methyl-4-nitrobenzene (0.5 g, 1.87 mmol, 1 equiv). The solution was cooled down to 0 °C and TfOH (0.33 mL, 3.75 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to reach rt over a 30 min time period. Benzene (0.185 mL, 2.06 mmol, 1.1 equiv) was then added to the solution, which continued to react for 17 h at rt. The solvent was removed under reduced pressure and excess of Et₂O (50 mL) was added which caused precipitation to occur. The crude was stored in the freezer >16 h, for further precipitation. The solid was filtered off and washed with Et₂O, obtaining the product (2s) as off-white solid (0.663 g, 1.34 mmol, 72%); mp: 157.3 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 8.68 (dd, J = 8.7 Hz, 5.9 Hz, 1H), 8.44 (dd, J = 8.1 Hz, 2.4 Hz, 1H), 8.31–8.29 (m, 2H), 8.21 (dd, J = 8.7 Hz, 2.4 Hz, 1H), 7.72–7.68 (m, 1H), 7.58–7.54 (m, 2H).

¹³C NMR (101 MHz, DMSO) δ 159.1 (d, ³J_F-C = 252.0 Hz), 151.3 (d, ³J_F-C = 8.5 Hz), 138.0, 135.4, 132.5, 132.1, 122.1 (d, ³J_F-C = 3.5 Hz), 120.7 (q, J = 320 Hz, CF₃SO₃⁻), 117.2, 112.5 (d, ³J_F-C = 28.7 Hz), 110.8 (d, ³J_F-C = 24.1 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -77.7 (s, 3F), -94.0 (s, 1F). HRMS (ESI): calcd for C₁₂H₈INO₂ ([M–TfO⁻]): 343.9578; found: 343.9595.

Synthesis of (2-methyl-4-nitrophenyl)(phenyl)iodonium trifluoromethanesulfonate (2t):

\[
\begin{align*}
\text{mCPBA (1.1 equiv) & TfOH (2.0 equiv) } \text{CH}_2\text{Cl}_2, \text{rt, 18 h} \quad \text{O}_2\text{N} \quad + \quad \text{I} \quad \text{O}_2\text{N} \quad \text{I} \\
\end{align*}
\]

mCPBA (1.33 mmol, 1.1 equiv) was dissolved in DCM followed by the addition of 1-iodo-2-methyl-4-nitrobenzene (0.35 g, 1.31 mmol, 1 equiv) and benzene (0.13 mL, 1.46 mmol, 1.1 equiv). The solution was cooled down to 0 °C and TfOH (0.24 mL, 2.66 mmol, 2.0 equiv) was added dropwise. The mixture was allowed to reach rt and continued to react for 18 h at rt. The solvent was removed under reduced pressure and excess of Et₂O (50 mL) was added which caused precipitation to occur. The crude was stored in the freezer >16 h, for further precipitation. The solid was filtered off and washed with Et₂O, obtaining the product (2t) as brown solid (0.400 g, 0.81 mmol, 61%); mp: 132.2 °C; ¹H NMR (400 MHz, DMSO-d₆) δ 8.66 (d, J = 8.7 Hz, 1H), 8.38 (d, J = 2.6, 1H), 8.29–8.27 (m, 2H), 8.11, (dd, J = 8.7 Hz, 2.6 Hz, 1H), 7.70–7.66 (m, 1H), 7.56–7.52 (m, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 159.1 (d, ³J_F-C = 252.0 Hz), 151.3 (d, ³J_F-C = 8.5 Hz), 138.0, 135.4, 132.5, 132.1, 122.1 (d, ³J_F-C = 3.5 Hz), 120.7 (q, J = 320 Hz, CF₃SO₃⁻), 117.2, 112.5 (d, ³J_F-C = 28.7 Hz), 110.8 (d, ³J_F-C = 24.1 Hz). ¹⁹F NMR (377 MHz, CDCl₃) δ -77.74; HRMS (ESI): calcd for C₁₃H₁₁INO₂ ([M–TfO⁻]): 339.9829; found: 339.9828.
### 2.3 Other Methods used for Synthesis of Diaryliodonium Salts

Table S3. Diaryliodonium salts synthesized by other methods.

| Compound | Formula | Preparation Details |
|----------|---------|---------------------|
| 2b       | ![2b Formula](image) | 4-Nitrophenyl(phenyl)iodonium bromide (2b)\(^{[14]}\) was prepared in 85% via an anion exchange from 2a according to literature reports.\(^{[15]}\) |
| 2d       | ![2d Formula](image) | 4-Nitrophenyl(phenyl)iodonium tosylate (2d) was prepared in 86% in a stepwise fashion, via isolation of the Koser reagent, following literature reports.\(^{[16]}\) |
| 2e       | ![2e Formula](image) | 4-Nitrophenyl(2,4,6-trimethoxyphenyl)iodonium tosylate (2e) was prepared in 90% according to literature reports.\(^{[15]}\) |
| 2f       | ![2f Formula](image) | 4-Nitrophenyl(2,4,6-trimethoxyphenyl)iodonium trifluoroacetate (2f) was prepared in 85% according to literature reports.\(^{[17]}\) |
3 Investigation of the N-Arylation of Amines

3.1 Optimization of Nitrophenylation

The arylation was initially optimized with amine 1a and nitro salt 2a in a 1:1 ratio in refluxing toluene, delivering alkyl aryl amine 3a (Table S4). The reaction showed poor conversion in the absence of an external base, also upon increased loading of salt 2a (entries 1-4). To the contrary, excess amine proved efficient, with the second equivalent of amine likely acting as base (entry 5). To avoid the need for excess amine, we investigated the addition of organic and inorganic bases with varying reaction time, and both triethylamine and sodium carbonate proved good (entries 6-14). Variation of times and temperature did not improve the yield further, neither did excess base (entries 14-19). The counterion of the diaryliodonium salts 2 proved important (entries 20-22).

Table S4. Optimization with nitrophenyl(phenyl)iodonium salts 2a-g.

| Entry | 1a (equiv) | 2 (equiv) | Salt 2 (X) | Ar | Base (equiv) | Temp (°C) | Time (h) | Isolated yield (%) |
|-------|------------|-----------|------------|----|-------------|-----------|----------|-------------------|
| 1     | 1.0        | 1.0       | 2a (OTf)   | Ph | -           | rt        | 24       | no rxn            |
| 2[a]  | 1.0        | 1.0       | 2a (OTf)   | Ph | -           | 110       | 1        | 35                |
| 3[a]  | 1.1        | 1.0       | 2a (OTf)   | Ph | -           | 110       | 1        | 49                |
| 4[a]  | 1.0        | 2.0       | 2a (OTf)   | Ph | -           | 110       | 2        | 25                |
| 5     | 2.0        | 1.0       | 2a (OTf)   | Ph | -           | 110       | 2        | 86                |
| 6     | 1.0        | 1.0       | 2a (OTf)   | Ph | K2PO4 (1.0) | 110       | 1        | 63                |
| 7     | 1.0        | 1.0       | 2a (OTf)   | Ph | K2PO4 (1.5) | 110       | 1        | 51                |
| 8     | 1.0        | 1.0       | 2a (OTf)   | Ph | K2CO3 (1.0) | 110       | 1        | 56                |
| 9     | 1.0        | 1.0       | 2a (OTf)   | Ph | Cs2CO3 (1.0) | 110     | 1        | 17                |
| 10    | 1.0        | 1.0       | 2a (OTf)   | Ph | Et3N (1.0)  | 110       | 1        | 59                |
| 11    | 1.0        | 1.0       | 2a (OTf)   | Ph | Et3N (1.0)  | 110       | 2        | 74                |
| 12    | 1.0        | 1.0       | 2a (OTf)   | Ph | Et3N (1.0)  | 90        | 4        | 70                |
| 13    | 1.1        | 1.0       | 2a (OTf)   | Ph | KF (1.5)    | 110       | 2        | 44                |
| 14    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (1.0) | 110     | 1        | 68                |
| 15    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (0.0) | **110** | 4        | **81**           |
| 16    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (1.0) | 110     | 6        | 80                |
| 17    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (1.0) | 90      | 1        | 28                |
| 18    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (1.0) | 90      | 22       | 70                |
| 19    | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (2.0) | 110     | 1        | 63                |
| 20    | 1.0        | 1.0       | 2b (Br)    | Ph | Na2CO3 (1.0) | 110     | 4        | 4                 |
| 21    | 1.0        | 1.0       | 2c (BF4)   | Ph | Na2CO3 (1.0) | 110     | 4        | 54                |
| 22    | 1.0        | 1.0       | 2d (OTs)   | Ph | Na2CO3 (1.0) | 110     | 4        | 77                |
| 23    | 1.0        | 1.0       | 2e (OTs)   | TMP | Na2CO3 (1.0) | 110     | 4        | 62                |
| 24    | 1.0        | 1.0       | 2f (TFA)   | TMP | Na2CO3 (1.0) | 110     | 4        | 43                |
| 25    | 1.0        | 1.0       | 2g (OTs)   | Anisy | Na2CO3 (1.0) | 110    | 4        | 36                |
| 26[b] | 1.0        | 1.0       | 2a (OTf)   | Ph | Na2CO3 (1.0) | 110    | 4        | 5% conv.         |
| 27[c] | 2.0        | 1.0       | 2a (OTf)   | Ph | -           | 110      | 15       | 77                |

Reaction conditions: Diaryliodonium salt 2 (0.1 mmol), base and amine 1a were added to a vial under argon. Anhydrous and degassed toluene (0.5 mL) was added and the mixture was stirred at the specified temperature. [a] Toluene not degassed, [b] In presence of air. [c] 1, 1-diphenylethelene (DPE, 2.0 equiv) added.
Unsymmetric salts 2e and 2f, with a trimethoxyphenyl (TMP) as “dummy” delivered the product in moderate yield (entries 23-24). A salt with an anisyl dummy (2g) could also be chemoselectively employed in moderate yield (entry 25). The reaction was severely retarded in the presence of air (entry 25), whereas addition of the radical trap 1, 1-diphenylethelene (DPE) did not influence the reaction much (compare entries 5 and 27).

3.2 Comparison to literature

Only decomposition was observed when 1a was reacted with 2f using Stuart’s recently reported procedure for cyclic amines (Scheme S3).[18]

Scheme S3. Literature comparison.

Only decomposition was observed when 1a was reacted with 2f using Stuart’s recently reported procedure for cyclic amines (Scheme S3).[18]

3.3 Optimization of Phenylation

The phenylation of 1a with Ph₂IOTf (2h) was briefly investigated with different bases, delivering the product 3p in moderate yields together with some diphenylated product 3p’ (Table S5). Triethylamine was found to give a poor ratio of 3p and 3p’, and sodium carbonate was again the best choice. Longer reaction time was needed to reach good conversion, and 22 h was used as standard. The separation of 3p and 3p’ resulted in a yield drop, and 3p was isolated in 52% with equimolar amounts of 1a and 2h (entry 5). The product ratio was improved by employing slight excess of 1a and 3p was isolated in 66% using 1.5 equiv 1a (entry 7). Further increase to 2 equiv 1a completely suppressed the formation of 3p’, and 3p was obtained in 74% yield (entry 8).

Table S5. Optimization with diaryliodonium triflate (2h).

| Entry | 1a (equiv) | 2h (equiv) | Base (equiv) | Temp (°C) | Time (h) | 3p (%) | 3p’ (%) |
|-------|------------|------------|--------------|-----------|----------|--------|--------|
| 1     | 1.0        | 1.0        | K₂PO₄ (1.0)  | 110       | 19       | 33     | 5      |
| 2     | 2.0        | 1.0        | K₂PO₄ (1.0)  | 110       | 21       | 45     | 5      |
| 3     | 2.0        | 1.0        | K₂PO₄ (1.0)  | 80        | 21       | Only 5% conversion |        |
| 4[a]  | 1.0        | 1.0        | NEt₃ (1.0)   | 110       | 22       | 43     | 20     |
| 5[b]  | 1.0        | 1.0        | Na₂CO₃ (1.0) | 110       | 22       | 52     | 8      |
| 6[a]  | 1.0        | 1.0        | Na₂CO₃ (1.0) | 90        | 22       | 29     | traces |
| 7[a]  | 1.5        | 1.0        | Na₂CO₃ (1.0) | 110       | 22       | 66     | 7      |
| 8[a]  | 2.0        | 1.0        | Na₂CO₃ (1.0) | 110       | 22       | 74     | traces |

Reaction conditions: Diaryliodonium salt 2h (0.1 mmol), base and amine 1a were added to a vial under argon, anhydrous toluene (0.5 mL) was added and the mixture was stirred at the specified temperature. a The toluene was degassed.
While use of excess amine resulted in improved yield of product 3p, this is not ideal from an atom efficiency point of view. We hence continued the scope investigation with 1 equiv amine as the standard conditions, and only investigated the use of 1.5 equiv amine when the obtained yield was modest (footnote b in Scheme 2).

Formation of minor amounts of diphenylated product was often observed, this could in all cases be separated from the desired product. Surprisingly, diarylation was the only product in phenylation of 2-(2-pyridyl)ethylamine under standard conditions (Scheme S4). No monoarylated product was observed, despite the use of equimolar amounts of amine and 2h. This illustrates the different reactivity of salts 2a and 2h, as the former reagent selectively yielded the monoarylated product 3l.

Scheme S4. Diarylation (the yield of 4 is calculated based on 2h, which is the limiting reagent).

Attempts to synthesize other diarylamines as the major product with other substrates, by employing 2 equiv of salt 2h, mainly resulted in decomposition.

3.4 General Procedure for N-arylation of Amines
Diaryliodonium salt 2 (0.1 mmol) and Na₂CO₃ (0.1 mmol, 1.0 equiv) were added to an oven-dried microwave vial, which was sealed with a microwave vial cap. The vial was kept in vacuum for 15 minutes through a needle and then flushed with argon. This procedure was repeated for 3 to 4 times. Amine 1 (0.1 mmol, 1.0 equiv) was added via syringe. Finally anhydrous and degassed toluene (0.5 mL) was added, and the mixture was stirred at 110 °C in a preheated oil bath. After the completion of the reaction, it was brought down to RT. The whole mixture was subjected to purification by silica gel column chromatography, without prior concentration, using a pentane/ethyl acetate or pentane/diethyl ether gradient to obtain arylamine 3-5.

3.5 Competition experiment
A clear preference for arylation of the secondary, cyclic amine morpholine over the primary amine was observed (Scheme S3).

Scheme S5. Competition between a cyclic, secondary amine and a primary amine.
3.6 Scope (in color)

Scheme S6. Arylation of primary amines

\[
\begin{align*}
R-\text{NH}_2 &+ \text{Ar}^1\text{OTf} & \text{Na}_2\text{CO}_3 (1 \text{ equiv}) & \text{toluene} & R-\text{Ar}^1
\end{align*}
\]

- a) Nitrophenylations of primary amines (with 2a, \(\text{Ar}^2 = \text{Ph}\), 4 h):
  - 3a 81%
  - 3b 88%
  - 3c 91%
  - 3d 79%
  - 3e 84%
  - 3f 50%
  - 3g 54%
  - 3h 68%

- b) Phenylations of primary amines (with 2h, \(\text{Ar}^2 = \text{Ph}\), 22 h):
  - 3i 52%
  - 3j 64%

- c) Other arylations of primary amines (4 h):
  - 3k 55%

[a] Reaction time 22-24 h. [b] Amine 1 (1.5 equiv). [c] Amine 1 (2 equiv). [d] Yield based on 2h. [e] OTs anion.

Scheme S7. Arylation of secondary amines

\[
\begin{align*}
R-\text{NH}_2 &+ \text{Ar}^1\text{OTf} & \text{Na}_2\text{CO}_3 (1 \text{ equiv}) & \text{toluene} & R-\text{Ar}^1
\end{align*}
\]

- a) Cyclic secondary amines
  - 5a 98%
  - 5b 97%
  - 5c 87%
  - 5d 76%
  - 5e 25%
  - 5f 99%
  - 5g 95%
  - 5h 90% (\(\text{Ar}^2 = \text{Ph}\))
  - 5i 83% (\(\text{Ar}^2 = \text{Ph}\))
  - 5j 86% (\(\text{Ar}^2 = \text{Ph}\))
  - 5k 83% (\(\text{Ar}^2 = \text{Ph}\))
  - 5l 64% (\(\text{Ar}^2 = \text{Ph}\))
  - 5m 84% (\(\text{Ar}^2 = \text{Ph}\))
  - 5n 49% (\(\text{Ar}^2 = \text{Ph}\))

- b) Acyclic secondary amines
  - 5o 70% (\(\text{Ar}^2 = \text{amiyl}\))
  - 5p 55% (\(\text{Ar}^1 = \text{A}^2\))

[a] Reaction time 22 h. [b] Inseparable from \(\text{Ar}^2\). [c] OTs anion.
4 Preliminary Mechanistic investigation

We have recently performed a thorough mechanistic study of O-arylations with diaryliodonium salts, using both experimental techniques and calculations. In this study, it was shown that arynes readily formed under basic conditions already at room temperature.[19] Arynes were identified using two approaches:
1) the use of an iodonium salt with EDG substituents gives regioisomers if arynes are involved.
2) addition of furan as an aryne trap results in significant formation of the cycloaddition product expected from benzyne.

With this knowledge at hand, we decided to check for arynes in the early stages of the N-arylation project, when t-BuOK was used as the base in reactions with Ph2IOTf (Scheme S6a). While good yields could be obtained with excess base in DCM, the conditions were similar to those where arynes were formed in the O-arylation. Indeed, the reaction shown in Scheme S6b gave a regiosomeric mixture, confirming that the product is formed through arynes rather than through ligand coupling, which is regiospecific. Furthermore, the addition of furan as an aryne trap resulted in significant formation of the cycloaddition product expected from benzyne (Scheme S6c).

Scheme S6. Aryne formation under the initially employed conditions.

Milder conditions were thus investigated, and the reaction proceeded well with the weak base sodium carbonate in refluxing toluene (see Sections 3.3 and 3.5). Under those conditions, only one product was formed in arylations with EDG-substituted salts (e.g. products 3ae-3ah, 5p, 5q, 5w, 5x). This is a strong indication that arynes are not formed under the optimized reaction conditions.

Another standard control experiment is the addition of the radical scavenger 1,1-diphenylethylene (DPE), which can drastically influence arylations where radicals are formed. We have previously reported that addition of DPE in arylation of phenols with Ph2IOTs allows the reaction to proceed well, as a nonproductive radical pathway was inhibited.[3a] To the contrary, product formation that proceeds via a radical pathway can be hampered upon addition of DPE. The addition of DPE to the N-arylation reactions had no significant effect (see Table S4 entry 27), and we hence believe that radicals are not involved in the product formation.
Based on the absence of arynes and radicals, we suggest that the arylation proceeds via ligand coupling mechanism (Scheme S7). This type of mechanism has strong support from several theoretical studies of diaryliodonium salts with a variety of nucleophiles under metal-free conditions.\textsuperscript{[3b, 19-20]} Many nucleophiles are deprotonated prior to the reaction with the diaryliodonium salt. However, our conditions use a weak base, and the amine reacts with the diaryliodonium salt to give the charged T-shaped intermediate A prior to deprotonation by the base or excess amine, yielding intermediate B. This intermediate might be in fast equilibrium with the corresponding four-coordinated intermediate C, and either of them could undergo ligand coupling to form the product and ArI. We recently reported similar four-coordinated intermediates in our mechanistic study on O-arylation with aliphatic alcohols, with support from both experimental and theoretical results.\textsuperscript{[19]} The experimental support for intermediate C in N-arylations is only preliminary, and includes that the reaction proceeds better with 2 equiv amine (see Table S4 and product 3p), and that reactions with equimolar amounts of amine and iodonium salts rarely reach completion despite extended reaction times. This can be compared to the competition experiment shown in Scheme S5, which gave quantitative combined yield of 5c and 3a.

**Scheme S7.** Suggested mechanism.

Nucleophilic aromatic substitution can rarely compete with ligand coupling in reactions with diaryliodonium salts, despite the very good leaving group ability of ArI. We found this to be a possibility only in the arylation of hydroxide with salt 2a, whereas the arylation of aliphatic alcohols proceeded by ligand coupling with all investigated iodonium salts.\textsuperscript{[19]} In analogy with that, we do not believe that the N-arylation proceeds via nucleophile aromatic substitution, but have not performed such studies yet. We plan to perform a thorough mechanistic investigation of the N-arylation to investigate kinetics and observe any intermediates. The latter is generally difficult, as the reactions are heterogeneous and difficult to follow by NMR.
5 Analytical Data of Arylamines 3-5

![Chemical structure of 4-Nitro-N-(3-phenylpropyl)aniline (3a)](image)

4-Nitro-N-(3-phenylpropyl)aniline (3a): 3-Phenylpropyl-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3a (0.0207 g, 0.081 mmol, 81%) as a yellow solid. Rf = 0.1 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.11 – 8.03 (m, 2H), 7.35 – 7.28 (m, 2H), 7.26 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 6.51 – 6.42 (m, 2H), 4.40 (br. s, 1H), 3.24 (td, J = 7.4, 5.5 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.00 (app. p, J = 7.4 Hz, 2H).

13C NMR (101 MHz, CDCl3) δ 153.4, 141.0, 138.1, 128.8, 128.5, 126.6, 126.4, 111.1, 42.9, 33.3, 30.6. The analytical data are consistent with previous reports.[21]

![Chemical structure of 4-Nitro-N-(2-phenethyl)aniline (3b)](image)

4-Nitro-N-(2-phenethyl)aniline (3b): 2-Phenylethan-1-amine (1b, 0.013 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3b (0.0212 g, 0.088 mmol, 88%) as a yellow oil. Rf = 0.2 in 10% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.10 – 8.06 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 6.54 – 6.50 (m, 2H), 4.51 (br. s, 1H), 3.51(q, J = 6.8 Hz, 2H), 2.96 (t, J = 7.0 Hz, 2H). 13C NMR (101 MHz, CDCl3) δ 153.2, 138.3, 138.3, 129.0, 128.8, 127.0, 126.6, 111.3, 44.5, 35.2. HRMS (ESI): calcd for C14H14NaN2O2 [M+Na]+: 265.0947; found: 265.0957.

![Chemical structure of 4-Nitro-N-pentylaniline (3c)](image)

4-Nitro-N-pentylaniline (3c): Pentan-1-amine (1c, 0.012 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3c (0.019 g, 0.091 mmol, 91%) as a yellow solid. Rf = 0.2 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.10 – 8.06 (m, 2H), 7.37 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 6.51 – 6.42 (m, 2H), 4.40 (br. s, 1H), 3.24 (td, J = 7.4, 5.5 Hz, 2H), 2.75 (t, J = 7.4 Hz, 2H), 2.00 (app. p, J = 7.4 Hz, 2H).

13C NMR (101 MHz, CDCl3) δ 153.5, 138.0, 126.6, 111.0, 43.6, 29.3, 29.0, 22.5, 14.1. The analytical data are consistent with previous reports.[22]

![Chemical structure of 4-Nitro-N-hexylaniline (3d)](image)

4-Nitro-N-hexylaniline (3d): Hexan-1-amine (1d, 0.013 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3d (0.0175 g, 0.079 mmol, 79%) as a yellow solid. Rf = 0.6 in 10% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.10 – 8.06 (m, 2H), 6.53 – 6.49 (m, 2H), 4.47 (br. s, 1H), 3.20 (td, J = 7.2, 5.4 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.44-1.33 (m, 4H), 0.98 – 0.90 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 153.6, 138.0, 126.6, 111.0, 43.6, 29.3, 29.0, 22.5, 14.1. The analytical data are consistent with previous reports.[23]
4-Nitro-N-nonylaniline (3e): Nonan-1-amine (1e, 0.018 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 19:1), to give 3e (0.0221 g, 0.084 mmol, 84%) as a yellow solid, Rf = 0.2 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.10 – 8.06 (m, 2H), 6.53 – 6.49 (m, 2H), 4.45 (br. s, 1H), 3.20 (td, J = 7.1, 4.7 Hz, 2H), 1.65 (app. p, J = 7.0 Hz, 2H), 1.42 – 1.21 (m, 12H), 0.91 – 0.87 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 153.6, 138.1, 126.6, 111.1, 43.6, 32.0, 29.6, 29.5, 29.4, 29.3, 27.2, 22.8, 14.2. Mp = 50.7 – 51.2 °C. HRMS (ESI): calcd for C15H24NaN2O2 [M+Na]+: 287.1730; found: 287.1731.

4-Nitro-N-cyclobutylaniline (3f): Cyclobutylamine (1f, 0.009 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3f (0.0096 g, 0.05 mmol, 50%) as a yellow solid. Rf = 0.2 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.09 – 8.05 (m, 2H), 6.48 – 6.44 (m, 2H), 4.65 (br. s, 1H), 4.04 – 3.94 (m, 1H), 2.53 – 2.43 (m, 2H), 1.97 – 1.80 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 152.3, 138.3, 126.6, 111.4, 48.5, 31.0, 15.4. Mp = 53.6 – 53.9 °C. HRMS (ESI): calcd for C10H12NaN2O2 [M+Na]+: 215.0796; found: 215.0793.

4-Nitro-N-cyclohexylaniline (3g): Cyclohexylamine (1g, 0.011 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 19:1), to give 3g (0.0118 g, 0.054 mmol, 54%) as a yellow oil. Rf = 0.5 in 10% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.08 – 8.04 (m, 2H), 6.51 – 6.47 (m, 2H), 4.41 (br. s, 1H), 3.41 – 3.32 (m, 1H), 2.08 – 2.02 (m, 2H), 1.83 – 1.76 (m, 2H), 1.72 – 1.65 (m, 1H), 1.46 – 1.35 (m, 2H), 1.30 – 1.17 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 152.6, 137.8, 126.7, 111.3, 51.7, 33.1, 25.7, 24.9. The analytical data are consistent with previous reports.21

4-Nitro-N-cycloheptylaniline (3h): Cycloheptylamine (1h, 0.013 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3h (0.016 g, 0.068 mmol, 68%) as a yellow oil. Rf = 0.3 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.09 – 8.05 (m, 2H), 6.47 – 6.43 (m, 2H), 4.46 (br. s, 1H), 3.59 – 3.51 (m, 1H), 2.04 – 1.99 (m, 2H), 1.75 – 1.47 (m, 10H). 13C NMR (101 MHz, CDCl3) δ 152.4, 137.7, 126.7, 111.4, 53.8, 34.8, 28.3, 24.4. The analytical data are consistent with previous reports.24

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4-Nitro-N-adamantylaniline (3i): Adamantan-1-amine (1i, 0.015 g, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 24 h. Purified by column chromatography (pentane/EtOAc 100:0 to 19:1), to give 3i (0.0162 g, 0.0595 mmol, 60%) as a yellow solid. 

R_f = 0.2 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.04 – 8.00 (m, 2H), 6.65 – 6.61 (m, 2H), 4.36 (br. s, 1H), 2.17 (s, 3H), 2.00 (d, J = 2.9 Hz, 6H), 1.78 – 1.69 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 137.6, 126.2, 113.6, 52.7, 42.6, 34.8, 29.7. The analytical data are consistent with previous reports.²⁵

4-Nitro-N-(3,4-dimethoxyphenethyl)aniline (3j): 2-(3,4-Dimethoxyphenyl)ethan-1-amine (1j, 0.017 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 7:3), to give 3j (0.0192 g, 0.064 mmol, 64%) as a yellow oil. R_f = 0.5 in 30% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.07 (m, 2H), 6.84 (d, J = 8.1 Hz, 1H), 6.75 (dd, J = 8.1, 2.0 Hz, 1H), 6.71 (d, J = 2.0 Hz, 1H), 6.54 – 6.50 (m, 2H), 4.48 (br. s, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.48 (app. p, J = 6.8, 2H), 2.90 (t, J = 6.9 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.2, 149.4, 148.2, 138.3, 130.7, 126.6, 120.8, 112.0, 111.7, 111.3, 56.1, 56.1, 44.6, 34.8. HRMS (ESI): calcd for C₁₆H₁₈NaN₂O₄ [M+Na]⁺: 325.1159; found: 325.1153.

4-Nitro-N-(4-bromophenethyl)aniline (3k): 2-(4-Bromophenyl)ethan-1-amine (1k, 0.016 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 8:2), to give 3k (0.0178 g, 0.055 mmol, 55%) as a yellow solid. R_f = 0.04 in 10% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.10 – 8.07 (m, 2H), 7.47 – 7.44 (m, 2H), 7.10 – 7.08 (m, 2H), 6.54 – 6.41 (m, 2H), 4.48 (br. s, 1H), 3.49 (q, J = 6.5 Hz, 2H), 2.91 (t, J = 6.9 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 153.0, 138.5, 137.3, 132.1, 130.6, 126.6, 120.9, 111.3, 44.3, 34.7. Mp = 97.2 – 98.4 °C. HRMS (ESI): calcd for C₁₄H₁₀BrNaN₂O₂ [M+Na]⁺: 343.0058; found: 343.0049.

4-Nitro-N-(2-(pyridin-2-yl)ethyl)aniline (3l): 2-(Pyridin-2-yl)ethan-1-amine (1l, 0.012 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 2:3), to give 3l (0.0176 g, 0.072 mmol, 72%) as a yellow solid. R_f = 0.1 in 50% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 8.58 – 8.56 (m, 1H), 8.09 – 8.05 (m, 2H), 7.65 (td, J = 7.7, 1.8 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.56 – 6.52 (m, 2H), 5.48 (br. s, 1H), 3.62 (t, J = 6.4 Hz, 2H), 3.12 (t, J = 6.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 153.4, 149.5, 138.0, 136.0, 126.8, 114.3, 56.3, 56.3.
4-Nitro-N-(3-(triethoxysilyl)propyl)aniline (3m): 3-(Triethoxysilyl)propan-1-amine (1m, 0.023 mL, 0.1 mmol) was arylated with salt 2a (0.048 mg, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 3m (0.0139 g, 0.041 mmol, 41%) as a yellow oil. Rf = 0.2 in 10% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.09 – 8.06 (m, 2H), 6.53 – 6.49 (m, 2H), 4.00 (br. s, 1H), 3.84 (q, J = 7.0 Hz, 6H), 3.21 (app. q, J = 7.2 Hz, 2H), 1.80 (app. p, J = 7.2 Hz, 2H), 1.23 (t, J = 7.0 Hz, 9H), 0.73 – 0.69 (m, 2H). 13C NMR (101 MHz, CDCl3) δ 153.6, 137.9, 126.6, 111.0, 58.7, 45.7, 22.5, 18.5, 7.9. HRMS (ESI): calcd for C15H15N3O4Si [M+Na]+: 365.1503; found: 365.1498. The analytical data are consistent with previous reports.[26]

(R)-4-Nitro-N-(1-phenylethyl)aniline (3n): (R)-1-phenylanethan-1-amine (1n, 0.05 mL, 0.4 mmol) was arylated with salt 2a (0.19 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:5 to 10:4), to give 3n (0.0482 g, 0.02 mmol, 51%) as a yellow oil. Rf = 0.12 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 9.2 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.46 (d, J = 9.2 Hz, 2H), 4.91 (br. s, 1H), 4.60 (p, J = 6.6 Hz, 1H), 1.59 (d, J = 6.7 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 152.4, 143.4, 138.4, 129.1, 127.7, 126.4, 125.8, 112.0, 53.5, 24.7. The analytical data are consistent with previous reports.[27] HPLC-analysis of ee: Chiralpak IA, n-hexane/i-PrOH 95/5, 1 mL/min, 28.7°C, 245 nm, tR = (R): 20.6 min, (S): 23.2 min showed that the ee remained >99%, i.e. no erosion of the ee was observed.

4-Nitro-N-phenylaniline (3o): Aniline (1o, 0.09 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (toluene/EtOAc 100:5 to 10:4), to give 3o (0.019 g, 0.092 mmol, 91%) as a yellow oil. Rf = 0.74 in 10% toluene/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.14 – 8.10 (m, 2H), 7.41 – 7.37 (m, 2H), 7.24 – 7.14 (m, 3H), 6.96 – 6.92 (m, 2H), 6.33 (br. s, 1H). 13C NMR (101 MHz, CDCl3) δ 150.3, 139.9, 139.6, 129.9, 126.4, 124.8, 122.1, 113.8. Mp = 131.2–134.3 °C. HRMS (ESI): calcd for C12H12NNa2O2 [M+Na]+: 237.0634; found: 237.0639. The analytical data are consistent with previous reports.[28]

N-(3-Phenylpropyl)aniline (3p): 3-Phenylpropyl-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1, to give 3p (0.0109 g, 0.052 mmol, 52%) as a colorless oil. Rf = 0.3 in 2% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 7.33 – 7.29 (m, 2H), 7.23 – 7.14 (m, 5H), 6.72 (tt, J = 7.3, 1.1 Hz, 1H), 6.60 – 6.57 (m, 2H), 3.65 (br. s, 1H), 3.18 (t, J = 7.0 Hz, 2H), 2.74 (app. t,
When the reaction was performed with 1a (1.5 equiv) or (2.0 equiv), the isolated yield of 3p was 66% and 74%, respectively. This can be rationalized by diminished formation of diarylated product 3p* (see Section 3.3.), also leading to an easier purification.

$J = 7.6 \text{ Hz}, 2\text{H}$, 2.00 – 1.92 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.4, 141.8, 129.4, 128.6, 128.5, 126.1, 117.4, 112.9, 43.6, 33.5, 31.2. The analytical data are consistent with previous reports.[29]

**N-Phenyl-N-(3-phenylpropyl)aniline (3p’):** The diarylated product 3p’ was isolated as a colorless oil (0.0023 g, 0.008 mmol, 8%) as a byproduct in the synthesis of 3p (see above). $R_t = 0.4$ in 2% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.29 – 7.22 (m, 6H), 7.20 – 7.14 (m, 3H), 6.97 – 6.90 (m, 6H), 3.73 (app. t, $J = 7.6$, 2H), 2.66 (t, $J = 7.8$, 2H), 2.04 – 1.96 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.1, 141.8, 129.4, 128.5, 128.5, 126.0, 121.3, 121.1, 51.8, 33.4, 29.2. HRMS (ESI): calcd for C$_{21}$H$_{22}$N [M+H]+: 288.1747; found: 288.1749.

$N$-(2-Phenethyl)aniline (3q): 2-Phenylethan-1-amine (1b, 0.019 mL, 0.15 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3q (0.0161 g, 0.082 mmol, 82%) as a colorless oil. $R_t = 0.8$ in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 – 7.31 (m, 2H), 7.27 – 7.23 (m, 3H), 7.21 – 7.17 (m, 2H), 6.74 – 6.70 (m, 1H), 6.64 – 6.62 (m, 2H), 3.68 (br. s, 1H), 3.42 (t, $J = 7.0$, 2H), 2.93 (t, $J = 7.0$, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.2, 139.5, 129.4, 128.9, 128.7, 126.6, 117.6, 113.2, 45.2, 35.7. The analytical data are consistent with previous reports.[30]

$N$-Pentylaniline (3r): Pentan-1-amine (1c, 0.012 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3r (0.0061 g, 0.037 mmol, 37%) as a colorless oil. $R_t = 0.5$ in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19 – 7.15 (m, 2H), 6.69 (app. t, $J = 7.3$, 1H), 6.61 (app. d, $J = 7.3$, 2H), 3.59 (br. s, 1H), 3.11 (t, $J = 7.1$, 2H), 1.63 (app. p, $J = 7.3$, 2H), 1.41 – 1.36 (m, 4H), 0.97 – 0.90 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.7, 129.4, 117.2, 112.8, 44.1, 29.5, 29.4, 22.7, 14.2. The analytical data are consistent with previous reports.[31]

$N$-Hexylaniline (3s): Hexan-1-amine (1d, 0.020 mL, 0.15 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3s (0.0076 g, 0.043 mmol, 43%) as a colorless oil. $R_t = 0.5$ in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.20 – 7.15 (m, 2H), 6.71 – 6.67 (m, 1H), 6.63 – 6.59 (m, 2H), 3.59 (br. s, 1H), 3.11 (t, $J = 7.1$, 2H), 1.62 (app. p, $J = 7.1$, 2H), 1.44 – 1.29 (m, 6H), 0.92 – 0.89 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.7, 129.4, 117.2, 112.8, 44.2, 31.8, 29.7, 27.0, 22.8, 14.2. The analytical data are consistent with previous reports.[32]
**N-Nonylaniline (3t):** Nonan-1-amine (1e, 0.027 mL, 0.015 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3t (0.0134 g, 0.061 mmol, 61%) as a colorless oil. R<sub>f</sub> = 0.8 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.21 – 7.15 (m, 2H), 6.69 (tt, <i>J</i> = 7.3, 1.1 Hz, 1H), 6.63 – 6.58 (m, 2H), 3.59 (br. s, 1H), 3.10 (t, <i>J</i> = 7.1 Hz, 2H), 1.62 (app. p, <i>J</i> = 7.0 Hz, 2H), 1.40 – 1.25 (m, 12H), 0.91 – 0.87 (m, 3H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 148.7, 129.4, 117.2, 112.9, 44.2, 32.0, 29.8, 29.7, 29.6, 29.4, 27.4, 22.8, 14.2. The analytical data are consistent with previous reports.[33]

**N-Cyclobutylamidine (3u):** Cyclobutylamine (1f, 0.013 mL, 0.15 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3u (0.006 g, 0.041 mmol, 41%) as a colorless oil. R<sub>f</sub> = 0.2 in 1% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 – 7.12 (m, 2H), 6.69 (tt, <i>J</i> = 7.3, 1.1 Hz, 1H), 6.57 – 6.54 (m, 2H), 3.96 – 3.88 (m, 1H), 3.81 (br. s, 1H), 2.46 – 2.36 (m, 2H), 1.90 – 1.73 (m, 4H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.2, 129.4, 117.6, 113.2, 49.3, 31.4, 15.4. The analytical data are consistent with previous reports.[34]

**N-Cyclohexylaniline (3v):** Cyclohexylamine (1g, 0.011 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3v (0.0104 g, 0.059 mmol, 59%) as a colorless oil. R<sub>f</sub> = 0.6 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 – 7.11 (m, 2H), 6.67 – 6.63 (m, 1H), 6.60 – 6.56 (m, 2H), 3.52 (br. s, 1H) 3.29 – 3.22 (m, 1H), 2.09 – 2.03 (m, 2H), 1.79 – 1.73 (m, 2H), 1.68 – 1.63 (m, 1H), 1.43 – 1.32 (m, 2H), 1.29 – 1.08 (m, 3H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.6, 129.4, 117.0, 113.3, 51.9, 33.7, 26.1, 25.2. The analytical data are consistent with previous reports.[35]

**N-Phenylcycloheptanamine (3w):** Cycloheptylamine (1h, 0.019 mL, 0.015 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3w (0.0110 g, 0.058 mmol, 58%) as a colorless oil. R<sub>f</sub> = 0.2 in 1% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.19 – 7.14 (m, 2H), 6.68 – 6.64 (m, 1H), 6.58 – 6.53 (m, 2H), 3.57 (br. s, 1H), 3.49 – 3.43 (m, 1H), 2.06 – 1.98 (m, 2H), 1.71 – 1.44 (m, 11H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 147.5, 129.4, 116.9, 113.4, 53.8, 35.1, 28.5, 24.6. The analytical data are consistent with previous reports.[36]

**N-(3,4-Dimethoxyphenethyl)aniline (3x):** 2-(3,4-Dimethoxyphenyl)ethan-1-amine (1j, 0.019 mL, 0.011 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 3x (0.0219 g, 0.085
mmol, 85%) as a colorless oil. $R_f = 0.05$ in 2% pentane/ethyl acetate. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.21 – 7.16 (m, 2H), 6.83 (d, $J = 8.1$ Hz, 1H), 6.77 (dd, $J = 8.1$, 2.0 Hz, 1H), 6.74 – 6.68 (m, 2H), 6.65 – 6.60 (m, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.39 (t, $J = 6.9$ Hz, 2H), 2.87 (t, $J = 6.9$ Hz, 2H). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 149.2, 148.2, 147.9, 132.0, 129.4, 120.9, 117.7, 113.2, 112.3, 111.7, 56.1, 56.0, 45.3, 35.2. The analytical data are consistent with previous reports.$^{[37]}$

N-(4-Bromophenethyl)aniline (3y): 2-(4-Bromophenyl)ethan-1-amine (1k, 0.023 mL, 0.15 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:4), to give 3y (0.0138 g, 0.050 mmol, 50%) as a yellow solid. $R_f = 0.4$ in 5% pentane/ethyl acetate. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 – 7.42 (m, 2H), 7.22 – 7.17 (m, 2H), 7.12 – 7.09 (m, 2H), 6.75 – 6.70 (m, 1H), 6.63 – 6.60 (m, 2H), 3.65 (br, s, 1H), 3.39 (t, $J = 7.0$ Hz, 2H), 2.88 (t, $J = 7.0$ Hz, 2H). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 147.9, 138.4, 131.8, 130.7, 129.5, 120.4, 117.8, 113.1, 45.0, 35.1. The analytical data are consistent with previous reports.$^{[38]}

4-Cyano- N-(3-phenylpropyl)aniline (3z): 3-Phenylpropan-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2i (0.046 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (toluene/EtOAc 100:0 to 100:2), to give 3z (0.019 g, 0.080 mmol, 80%) as a beige solid. $R_f = 0.17$ in toluene. $^1H$ NMR (400 MHz, CD$_2$OD) $\delta$ 7.38 – 7.31 (m, 2H), 7.27 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 6.59 – 6.51 (m, 2H), 3.08 (app. t, $J = 7.2$ Hz, 2H), 2.68 (app. t, $J = 7.5$ Hz, 2H), 1.88 (app. p, $J = 7.5$ Hz, 2H). $^{13}C$ NMR (101 MHz, CD$_2$OD) $\delta$ 154.0, 143.0, 134.6, 129.5, 129.4, 126.9, 121.8, 112.8, 97.26, 43.0, 34.2, 31.8. Mp = 76.5 – 80.8 °C. HRMS (ESI): calcd for C$_{16}$H$_{16}$N$_2$Na [M+Na]$^+$: 259.1206; found: 259.1206.

4-(trifluoromethyl)-N-(3-phenylpropyl)aniline (3aa): 3-Phenylpropan-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2j (0.053 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 3aa (0.0228 g, 0.081 mmol, 81%) as a pale yellow oil. $R_f = 0.5$ in 5% pentane/ethyl acetate. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.17 (m, 3H), 6.55 (d, $J = 8.4$ Hz, 2H), 3.94 (br, s, 1H), 3.18 (t, $J = 7.0$ Hz, 2H), 2.75 (t, $J = 7.5$ Hz, 2H), 1.97 (app. p, 2H, $J = 7.2$ Hz). $^{13}C$ NMR (101 MHz, CDCl$_3$) $\delta$ 150.8, 141.4, 128.7, 126.8, 126.7 (q, $J_{C,F} = 3.8$ Hz), 125.2 (q, $J_{C,F} = 270.1$ Hz), 118.7 (q, $J_{C,F} = 32.6$ Hz), 111.9, 77.4, 77.2, 76.8, 43.0, 33.4, 30.9. $^{19}F$ NMR (377 MHz, CDCl$_3$) $\delta$ -61.0. HRMS (ESI): calcd for C$_{16}$H$_{17}$F$_3$N [M+H]$^+$: 280.1308; found: 280.1309.

3-(trifluoromethyl)-N-(3-phenylpropyl)aniline (3ab): 3-Phenylpropan-1-amine (1a, 0.06 mL, 0.4 mmol) was arylated with salt 2k (0.20 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3ab (0.0498 g, 0.18 mmol, 45%) as a pale yellow oil. $R_f = 0.48$ in 5% pentane/ethyl acetate. $^1H$ NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 – 7.30

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3-Azido-N-(3-phenylpropyl)aniline (3ac): 3-Phenylpropan-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2I (0.052 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 3ac (0.0101 g, 0.040 mmol, 40%) as a yellow oil. Rf = 0.75 in 5% pentane/ethyl acetate. ^1H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.24 – 7.19 (m, 2H), 7.11 (t, J = 8.0 Hz, 1H), 6.39 – 6.33 (m, 2H), 6.18 (app. t, J = 2.2 Hz, 1H), 3.71 (br. s, 1H), 3.14 (t, J = 7.0 Hz, 2H), 2.74 (t, J = 7.1 Hz, 2H), (app. p, 2H J = 7.1 Hz). ^13C NMR (101 MHz, CDCl₃) δ 149.8, 141.6, 141.2, 130.5, 128.6, 128.5, 126.2, 109.9, 107.7, 102.9, 43.4, 33.5, 31.0. HRMS (ESI): calcd for C₁₁H₁₇N₃ [M+H]^+: 253.1448; found: 253.1448.

4-Bromo-N-phenethylaniline (3ad): 2-Phenylethan-1-amine (1b, 0.013 mL, 0.1 mmol) was arylated with salt 2m (0.059 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:2), to give 3ad (0.0202 g, 0.073 mmol, 73%) as a colorless oil. Rf = 0.3 in 5% pentane/diethyl ether. ^1H NMR (400 MHz, CDCl₃) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.18 (m, 5H), 6.50 – 6.46 (m, 2H), 3.69 (br. s, 1H), 3.37 (t, J = 7.0 Hz, 2H), 2.91 (t, J = 7.0 Hz, 2H). ^13C NMR (101 MHz, CDCl₃) δ 147.1, 139.1, 132.1, 128.9, 128.8, 126.7, 114.7, 109.1, 45.1, 35.5. HRMS (ESI): calcd for C₁₁H₁₅BrN [M+H]^+: 276.0378; found: 276.0379.

4-Methyl-N-phenethylaniline (3ae): 2-Phenylethan-1-amine (1b, 0.013 mL, 0.1 mmol) was arylated with salt 2n (0.046 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:2), to give 3ae (0.0194 g, 0.092 mmol, 92%) as a colorless oil. Rf = 0.3 in 5% pentane/diethyl ether. ^1H NMR (400 MHz, CDCl₃) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.24 (m, 3H), 7.01 (d, J = 8.1 Hz, 2H), 6.59 – 6.53 (m, 2H), 3.55 (br. s, 1H), 3.40 (t, J = 7.0 Hz, 2H), 2.92 (t, J = 7.0 Hz, 2H), 2.75 (s, 3H). ^13C NMR (101 MHz, CDCl₃) δ 145.9, 139.6, 129.9, 128.9, 128.7, 126.9, 126.5, 113.4, 45.6, 35.7, 20.5. The analytical data are consistent with previous reports.[39]

4-(tert-Butyl)-N-(3-phenylpropyl)aniline (3af): 3-Phenylpropyl-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2o (0.034 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 24 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 3af (0.0111 g, 0.042 mmol, 42%) as a colorless oil, Rf = 0.3 in 2% pentane/ethyl acetate. ^1H NMR (400 MHz, CDCl₃) δ 7.32 – 7.28 (m, 2H), 7.24 – 7.17 (m, 5H), 6.58 – 6.53 (m, 2H), 3.58 (br. s, 1H), 3.14 (t, J = 7.0 Hz, 2H), 2.74 (app. t, J = 7.6 Hz, 2H), 1.95 (app. p, J = 7.6 Hz, 2H), 1.28 (s, 9H). ^13C NMR (101 MHz, CDCl₃) δ 146.1, 141.9, 140.2,
4-Methoxy-N-phenethylaniline (3ag): 2-Phenylethan-1-amine (1b, 0.013 mL, 0.1 mmol) was arylated with salt 2p (0.049 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 9:1), to give 3ag (0.0103 g, 0.045 mmol, 45%) as a colorless oil. R<sub>t</sub> = 0.3 in 10% pentane/diethyl ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35 – 7.33 (m, 2H), 7.26 – 7.20 (m, 3H), 6.82 – 6.77 (m, 2H), 6.62 – 6.58 (m, 2H), 3.76 (s, 3H), 3.45 (br. s, 1H), 3.37 (t, J = 7.0 Hz, 2H), 2.91 (t, J = 7.0 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 152.4, 142.4, 139.5, 128.9, 128.7, 126.5, 115.1, 114.5, 56.0, 46.2, 35.8. The analytical data are consistent with previous reports.\(^{[40]}\)

3-Methoxy-N-(3-phenylpropyl)aniline (3ah): 3-Phenylpropan-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2q (0.052 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:3), to give 3ah (0.0160 g, 0.066 mmol, 66%) as a yellow oil. R<sub>t</sub> = 0.46 in 5% pentane/ethyl acetate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.28 (m, 2H), 7.24-7.20 (m, 3H), 7.08 (t, J = 8.1 Hz, 1H), 6.27 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.21 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.14 (app. t, J = 2.3 Hz, 1H), 3.77 (s, 3H), 3.65 (br. s, 1H), 3.15 (t, J = 7.2 Hz, 2H), 2.74 (t, J = 7.2 Hz, 2H), 1.97 (app. p, 2H J = 7.2 Hz). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.0, 149.9, 141.8, 130.1, 128.6, 128.5, 126.1, 106.1, 102.4, 98.8, 55.2, 43.5, 33.5, 31.2. HRMS (ESI): calcd for C<sub>19</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>: 242.1539; found: 242.1539. The analytical data are consistent with previous reports.\(^{[41]}\)

Methyl-2-methoxy-5-(phenethylamino)benzoate (3ai): 2-Phenylethan-1-amine (1b, 0.013 mL, 0.1 mmol) was arylated with salt 2r (0.061 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 7:3), to give 3ai (0.0177 g, 0.062 mmol, 62%) as a colorless oil. R<sub>t</sub> = 0.4 in 5% pentane/diethyl ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.31 (m, 2H), 7.25 – 7.20 (m, 3H), 7.07 (d, J = 3.0 Hz, 1H), 6.86 (d, J = 8.8 Hz, 1H), 6.74 (dd, J = 8.9, 3.0 Hz, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.49 (br. s, 1H), 3.38 (t, J = 6.9 Hz, 2H), 2.91 (t, J = 6.9 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.1, 151.8, 141.9, 139.3, 128.9, 128.8, 126.0, 120.9, 118.4, 116.0, 114.6, 57.1, 52.2, 45.9, 35.6. HRMS (ESI): calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub> [M+Na]<sup>+</sup>: 308.1257; found: 308.1255.

2-Fluoro-4-nitro-N-(3-phenylpropyl)aniline (3aj): (R)-1-phenylethan-1-amine (1a, 0.014 mL, 0.1 mmol) was arylated with salt 2s (0.049g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:5), to give 3aj (0.017 mg, 0.062 mol, 62%) as a yellow oil. R<sub>t</sub> = 0.15 in 5% pentane/ethyl acetate. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97 (dd, J = 9.0 Hz, 2.4 Hz, 1H), 7.87 (dd, J = 11.6 Hz, 2.4 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.25 – 7.18 (m, 3H), 6.55 (t, J = 8.6 Hz, 1H), 4.63 (br. s, 1H), 3.27 (q, J = 6.8 Hz, 2H), 2.16 (t, J = 7.4 Hz, 2H), 2.03 (app. p, J = 7.3 Hz, 2H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.1 (d, J<sub>FC</sub> = 240 Hz), 142.8, 142.7, 140.8, 136.7 (d, J<sub>FC</sub> = 8.6 Hz), 128.8, 128.5, 126.5, 122.5 (d, J<sub>FC</sub> = 2.3 Hz) 110.9 (d, J<sub>FC</sub> = 23.1 Hz), 109.2 (d, J<sub>FC</sub> = 4.0 Hz), 42.5, 33.2, 30.5.
19F NMR (377 MHz, CDCl₃) δ – 135.61. HRMS (ESI): calcd for C₁₅H₁₅N₂O₂F ([M +Na⁺]): 297.1010; found: 297.1037

2-methyl-4-nitro-N-(3-phenylpropyl)aniline (3ak): (R)-1-phenylethan-1-amine (1a, 0.05 mL, 0.35 mmol) was arylated with salt 2t (0.172g, 1.0 equiv) according to the general procedure in toluene (1.75 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:10) to give 3ak (0.071 mg, 0.26 mmol, 75%) as a yellow oil. Rf = 0.31 in 10% pentane/ethyl acetate.

1H NMR (400 MHz, CDCl₃) δ 8.05 (dd, J = 9.0 Hz, 2.5 Hz, 1H), 7.95 (d, J = 2.2 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.27 – 7.23 (m, 3H), 6.48 (d, J = 9.0 Hz, 1H), 4.34 (br. s, 1H), 3.32 (q, J = 7.0 Hz), 2.81 (t, J = 7.3 Hz, 2H), 2.11 – 2.04 (m, 5H).

13C NMR (101 MHz, CDCl₃) δ 151.6, 141.1, 137.2, 128.7, 128.4, 126.3, 126.0, 124.7, 121.0, 107.6, 43.1, 33.4, 30.4, 17.1; HRMS (ESI): calcd for C₁₆H₁₈N₂O₂ ([M +Na⁺]): 293.1260; found: 293.1255.

2,4,6-trimethyl-N-(3-phenylpropyl)aniline (3al). (R)-1-phenylethan-1-amine (1a, 0.05 mL, 0.35 mmol) was arylated with salt 2u (0.181 g, 1.0 equiv) according to the general procedure in toluene (1.75 mL) for 22 h. Purified by column chromatography (pentane/EtOAc 100:5), to give 3al (0.078 g, 0.31 mmol, 88%) as a colorless oil. Rf = 0.28 in 5% pentane/ethyl acetate.

1H NMR (400 MHz, CDCl₃) δ 7.34 – 7.30 (m, 2H), 7.24 – 7.20 (m, 3H), 6.84 (s, 2H), 3.00 (t, J = 7.1 Hz, 2H), 2.75 (t, J = 7.5 Hz, 2H), 2.27 (s, 6H), 2.26 (s, 3H), 1.94 (app. p, J = 7.5 Hz), 2H).

13C NMR (101 MHz, CDCl₃) δ 143.7, 142.0, 131.2, 129.6, 129.5, 128.5, 126.0, 48.7, 33.7, 33.0, 21.7, 18.5. The analytical data are consistent with previous reports.[43]

N-Phenyl-N-(2-(pyridin-2-yl)ethyl)aniline (4): 2-(Pyridin-2-yl)ethan-1-amine (1p, 0.012 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 22 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 4:1), to give 4 (0.0103 g, 0.038 mmol, 75%, yield calculated with respect to the consumption of 2h) as a colorless oil. Rf = 0.3 in 20% pentane/diethyl ether. The monoarylated product was not detected. 1H NMR (400 MHz, CDCl₃) δ 8.57 – 8.55 (m, 1H), 7.56 (td, J = 7.6, 1.8 Hz, 1H), 7.28 – 7.23 (m, 5H), 7.14 – 7.08 (m, 2H), 7.00 – 6.98 (m, 3H), 7.06 – 6.92 (m, 2H), 4.13 (app. t, J = 7.6 Hz, 2H), 3.13 (app. t, J = 7.6 Hz, 2H). 15C NMR (101 MHz, CDCl₃) δ 143.7, 142.0, 131.2, 129.6, 129.5, 128.5, 126.0, 48.7, 33.7, 33.0, 21.7, 18.5. HRMS (ESI): calcd for C₁₉H₁₉N₂ ([M+H⁺]: 275.1543; found: 275.1538.

1-(4-Nitrophenyl)piperidine (5a): Piperidine (1q, 0.010 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:3), to give 5a (0.0203 g, 0.098 mmol, 98%) as a yellow oil. Rf = 0.4 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl₃) δ 8.11 – 8.07 (m, 2H), 6.80 – 6.76 (m, 2H),
3.47 – 3.40 (m, 4H), 1.70 – 1.67 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.1, 137.7, 126.3, 112.5, 48.5, 25.4, 24.4. The analytical data are consistent with previous reports.$^{[44]}

1-(4-Nitrophenyl)-4-phenylpiperidine (5b): 4-Phenylpiperidine (1r, 0.016 g, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for xx h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 5b (0.0274 g, 0.097 mmol, 97%) as a yellow solid. $R_f$ = 0.3 in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 – 8.12 (m, 2H), 7.37 – 7.30 (m, 2H), 6.89 – 6.85 (m, 2H), 4.12 – 4.07 (m, 2H), 3.09 (td, $J_i$ = 12.1, 2.7 Hz, 2H), 2.80 (tt, $J_i$ = 12.1, 3.8 Hz, 1H), 2.06 – 1.98 (m, 2H), 1.87 – 1.77 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 154.9, 145.2, 138.1, 128.8, 126.9, 126.8, 126.3, 112.8, 48.4, 42.6, 32.8. Mp = 163.9 – 164.4 °C. HRMS (ESI): calcd for C$_{17}$H$_{18}$NaN$_2$O$_2$ [M+Na]$^+$: 305.1266; found: 305.1267.

4-(4-Nitrophenyl)morpholine (5c): Morpholine (1s, 0.009 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 4:1), to give 5c (0.0181 g, 0.087 mmol, 87%) as a yellow solid, $R_f$ = 0.2 in 4:1 pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.17 – 8.11 (m, 2H), 6.85 – 6.81 (m, 2H), 3.88 – 3.85 (m, 4H), 3.39 – 3.36 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 155.2, 139.3, 126.0, 112.8, 66.5, 47.4. The analytical data are consistent with previous reports.$^{[18]}

4-(4-Nitrophenyl)thiomorpholine (5d): Thiomorpholine (1t, 0.010 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 5d (0.0171 g, 0.076 mmol, 76%) as a yellow solid. $R_f$ = 0.7 in 20% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 – 8.11 (m, 2H), 6.80 – 6.76 (m, 2H), 3.87 – 3.85 (m, 4H), 2.73 – 2.70 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.8, 138.3, 126.4, 113.0, 50.5, 26.0. Mp = 138.4 – 139.8 °C. HRMS (ESI): calcd for C$_{10}$H$_{12}$NaN$_2$O$_2$S [M+Na]$^+$: 247.0517; found: 247.0514.

1-(4-Nitrophenyl)-4-phenylpiperazine (5e): 1-Phenylpiperazine (1u, 0.015 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 9:1), to give 5e (0.0071 g, 0.025 mmol, 25%) as a yellow solid. $R_f$ = 0.2 in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.18 – 8.14 (m, 2H), 7.35 – 7.28 (m, 2H), 6.98 – 6.86 (m, 5H), 3.61 – 3.58 (m, 4H), 3.38 – 3.35 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ
154.9, 150.8, 138.9, 129.5, 126.1, 120.6, 116.5, 112.9, 49.1, 47.2. The analytical data are consistent with previous reports.\[45\]

1-(4-Nitrophenyl)pyrrolidine (5f): 1-Phenylpiperazine (1v, 0.008 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 92:8), to give 5f (0.0191 g, 0.099 mmol, 99%) as a yellow solid. \( R_f = 0.3 \) in 10% pentane/diethyl ether. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.14 – 8.10 (m, 2H), 6.49 – 6.45 (m, 2H), 3.43 – 3.38 (m, 4H), 2.11 – 2.04 (m, 4H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 152.0, 136.8, 126.5, 110.6, 48.1, 25.6. The analytical data are consistent with previous reports.\[46\]

2-(4-Nitrophenyl)-1,2,3,4-tetrahydroisoquinoline (5g): 1,2,3,4-Tetrahydroisoquinoline (1w, 0.013 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 92:8), to give 5g (0.0242 g, 0.095 mmol, 95%) as a yellow solid. \( R_f = 0.2 \) in 10% pentane/diethyl ether. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.20 – 8.15 (m, 2H), 7.25 – 7.16 (m, 4H), 6.85 – 6.80 (m, 2H), 4.58 (s, 2H), 3.70 (t, \( J = 5.9 \) Hz, 2H), 3.03 (t, \( J = 5.9 \) Hz, 2H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 154.0, 137.8, 135.0, 133.3, 128.2, 127.3, 126.8, 126.5, 126.3, 111.4, 49.0, 44.9, 29.1. The analytical data are consistent with previous reports.\[47\]

1-Phenylpiperidine (5h): Piperidine (1q, 0.010 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:2), to give 5h (0.0145 g, 0.090 mmol, 90%) as a colorless oil. \( R_f = 0.5 \) in 5% pentane/diethyl ether. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.30 – 7.21 (m, 2H), 7.00 – 6.93 (m, 2H), 6.84 – 6.80 (m, 1H), 3.20 – 3.10 (m, 4H), 1.76 – 1.67 (m, 4H), 1.61 – 1.55 (m, 2H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 152.4, 129.1, 119.3, 116.7, 50.8, 26.0, 24.5. The analytical data are consistent with previous reports.\[48\]

1,4-Diphenylpiperidine (5i): 4-Phenylpiperidine (1r, 0.016 g, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:2), to give 5i (0.0196 g, 0.083 mmol, 83%) as a white solid. \( R_f = 0.5 \) in 5% pentane/diethyl ether. \( ^1H \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.36 – 7.18 (m, 7H), 7.02 – 6.96 (m, 2H), 6.89 – 6.84 (m, 1H), 3.83 – 3.78 (m, 2H), 2.82 (td, \( J = 12.0, 3.4 \) Hz, 2H), 2.69 – 2.61 (m, 1H), 1.99 – 1.82 (m, 4H). \( ^13C \) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 152.0, 146.2, 129.2, 128.6, 127.0, 126.4, 119.6, 116.8, 50.7, 42.7, 33.5. The analytical data are consistent with previous reports.\[49\]
4-Phenylmorpholine (5j): Morpholine (1s, 0.009 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 5j (0.0141 g, 0.086 mmol, 86%) as a white solid, $R_f = 0.3$ in 100:5 pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31 – 7.27 (m, 2H), 6.94 – 6.86 (m, 3H), 3.88 – 3.86 (m, 4H), 3.18 – 3.15 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.4, 129.3, 120.2, 115.9, 67.1, 49.5. The analytical data are consistent with previous reports.$^{[50]}$

4-Phenylthiomorpholine (5k): Thiomorpholine (1t, 0.010 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:3), to give 5k (0.0148 g, 0.083 mmol, 83%) as a colorless oil. $R_f = 0.3$ in 5% pentane/diethyl ether. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 – 7.24 (m, 2H), 6.95 – 6.84 (m, 3H), 3.53 – 3.51 (m, 4H), 2.77 – 2.74 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.5, 129.4, 120.0, 117.3, 52.3, 27.0. HRMS (ESI): calcd for C$_{10}$H$_{14}$NS [M+H]$^+$: 180.0841; found: 180.0846.

1-Phenylpyrrolidine (5l): Pyrrolidine (1v, 0.008 mL, 0.1 mmol) was arylated with salt 2h (0.043 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:2), to give 5l (0.0094 g, 0.064 mmol, 64%) as a colorless oil. $R_f = 0.6$ in 5% pentane/diethyl ether. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 – 7.20 (m, 2H), 6.68 – 6.65 (m, 1H), 6.59 – 6.56 (m, 2H), 3.30 – 3.27 (m, 4H), 2.23 – 1.99 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.1, 129.3, 115.5, 111.8, 47.7, 25.6. The analytical data are consistent with previous reports.$^{[51]}$

2-methyl-1-phenylindoline (5m). 2-methylindoline (1x, 0.05 mL, 0.4 mmol) was arylated with salt 2h (0.17 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:1), to give 5m (0.0675 g, 0.032 mmol, 84%) as a colorless oil. $R_f = 0.76$ in 5% pentane/ethyl acetate. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.42 (m, 2H), 7.37 – 7.31 (m, 2H), 7.22 (dd, $J = 7.3, 1.4$ Hz, 1H), 7.17 – 7.08 (m, 2H), 6.96 – 6.91 (m, 1H), 6.82 (td, $J = 7.3, 1.0$ Hz, 1H), 4.46 (ddq, $J = 8.8, 7.5, 6.2$ Hz, 1H), 3.40 (dd, $J = 15.5, 8.8$ Hz, 1H), 2.83 (dd, $J = 15.5, 7.5$ Hz, 1H), 1.41 (d, $J = 6.2$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.6, 143.4, 129.6, 129.3, 127.2, 125.0, 122.7, 121.4, 118.7, 108.3, 59.7, 37.2, 20.1. HRMS (ESI): calcd for C$_{15}$H$_{18}$N [M+H]$^+$: 210.1277; found: 210.1276. The $^{13}$C NMR spectral data were in good agreement with those reported in the literature, whereas the $^1$H NMR data differs slightly.$^{[52]}$
2-methyl-1-(pyridin-3-yl)indoline (5n). 2-methylindoline (1x, 0.05 mL, 0.4 mmol) was arylated with salt 2v (0.18 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 10:1 to 10:3), to give 5n (0.0365 g, 0.018 mmol, 45%) as a yellow oil. Rf = 0.37 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 8.66 (br. s, 1H), 8.34 (br. s, 1H), 7.58 – 7.55 (m, 1H), 7.31 – 7.28 (m, 1H), 7.16 (app. d, J = 7.3 Hz, 1H), 7.06 (app. t, J = 7.7 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.79 (app. t, J = 7.4 Hz, 1H), 4.41 (dp, J = 8.8, 6.2 Hz, 1H), 3.36 (dd, J = 15.5, 8.8 Hz, 1H), 2.77 (dd, J = 15.5, 6.9 Hz, 1H), 1.34 (d, J = 6.2 Hz, 1H). 13C NMR (101 MHz, CDCl3) δ 147.3, 143.2, 143.1, 140.2, 129.7, 127.3, 125.2, 124.0, 119.7, 108.4, 59.6, 37.2, 20.0. HRMS (ESI): calcd for C14H15N2 [M+H]+: 211.1230; found: 211.1229.

1-(4-(Trifluoromethyl)phenyl)piperidine (5o): Piperidine (1q, 0.009 mL, 0.1 mmol) was arylated with salt 2j (0.053 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:5), to give 5o (0.0119 g, 0.055 mmol, 55%) as a pale yellow oil in an inseparable mixture with 4-iodoanisole. Rf = 0.62 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.27 (m, 4H), 1.75 – 1.58 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 153.9, 126.4, (q, J F-C = 3.7 Hz), 125.2, (q, J F-C = 266.9 Hz), 119.7, 49.5, 25.6, 24.4. 19F NMR (377 MHz, CDCl3) δ -61.2. HRMS (ESI): calcd for C12H15F3N [M+H]+: 230.1151; found: 230.1150. The analytical data are consistent with previous reports.[53]

4-Iodoanisole: 1H NMR (400 MHz, CDCl3) δ 7.56 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 159.6, 138.3, 116.5, 82.8, 55.5.

1-(4-(tert-Butyl)phenyl)piperidine (5p): Piperidine (1q, 0.009 mL, 0.1 mmol) was arylated with salt 2o (0.054 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:5), to give 5p (0.0119 g, 0.055 mmol, 55%) as a pale yellow oil. Rf = 0.62 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 7.46 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 3.27 (m, 4H), 1.75 – 1.58 (m, 6H). 13C NMR (101 MHz, CDCl3) δ 150.1, 142.0, 125.9, 116.4, 51.0, 34.1, 31.6, 26.2, 24.5. The analytical data are consistent with previous reports.[54]

1-(3-Methoxyphenyl)piperidine (5q): Piperidine (1q, 0.04 mL, 0.4 mmol) was arylated with salt 2q (0.21 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 5q (0.0348 g, 0.18 mmol, 46%) as a colorless oil. Rf = 0.60 in 5% pentane/ethyl acetate. 1H NMR (400 MHz, CDCl3) δ 7.17 (t, J = 8.4 Hz, 1H), 6.57 (dd, J = 8.4, 2.1 Hz, 1H), 6.50 (t, J = 2.4 Hz, 1H), 6.40 (dd, J = 8.4, 2.1 Hz, 1H), 3.80 (s, 3H), 3.17 (t, J = 5.4, 4H), 1.76 – 1.66 (m,
N,N-Dibutyl-4-nitroaniline (5r): Dibutylamine (1y, 0.017 mL, 0.1 mmol) was arylated with salt 2a (0.048 g, 1.0 equiv) according to the general procedure in toluene (0.5 mL) for 4 h. Purified by column chromatography (pentane/diethyl ether 100:0 to 100:5), to give 5r (0.0193 g, 0.077 mmol, 77%) as a yellow solid. Rf = 0.5 in 10% pentane/diethyl ether. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J$ = 9.4 Hz, 2H), 7.36 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 7.19 – 7.14 (m, 2H), 6.65 (d, $J$ = 9.4 Hz, 2H), 4.67 (s, 2H), 3.19 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.3, 137.3, 136.7, 129.0, 127.6, 126.8 (q, $^2$J$_{F-C}$ = 27.1 Hz), 126.6 (q, $^4$J$_{F-C}$ = 3.7 Hz), 126.5, 125.3 (q, $^1$J$_{F,C}$ = 269.6 Hz), 117.9 (q, $^3$J$_{F,C}$ = 32.6 Hz), 111.3, 56.2, 38.8. $^{19}$F NMR (377 MHz, CDCl$_3$) δ -60.7. HRMS (ESI): calcd for C$_{14}$H$_{13}$ClF$_3$N [M+Na$^+$]: 265.0947; found: 265.0946. The analytical data are consistent with previous reports.\[56\]

N-Benzyl-N-methyl-4-nitroaniline (5s): N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2a (0.19 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:7), to give 5s (0.0780 g, 0.32 mmol, 79%) as a yellow solid. Rf = 0.15 in 5% pentane/ethyl acetate. \[57\]

N-Benzyl-N-methyl-4-(trifluoromethyl)aniline (5t): N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2j (0.20 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 5t (0.0722 g, 0.27 mmol, 68%) as a pale yellow oil. Rf = 0.74 in 5% pentane/ethyl acetate. \[58\]

3-Azido-N-benzyl-N-methylaniline (5u): N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2i (0.21 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:3), to give 5u (0.055 g, 0.23 mmol, 57%) as a yellow oil in an inseparable mixture with 4-iodoanisole. Rf = 0.71 in 5% pentane/ethyl acetate. \[59\]

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 152.7, 136.4, 126.6, 110.1, 51.2, 29.4, 20.4, 14.1. The analytical data are consistent with previous reports. $^{[55]}$
130.4, 128.8, 127.1, 126.7, 109.2, 106.9, 102.8, 56.5, 38.7. HRMS (ESI): calcd for C₁₄H₁₅N₄ [M+H]+: 239.1291; found: 239.1291.

4-Iodoanisole: ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), ¹³C NMR (101 MHz, CDCl₃) δ 159.6, 138.3, 116.5, 82.8, 55.45

**N-Benzyl-N-methylaniline (5v):** N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2h (0.18 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 5v (0.0563 g, 0.29 mmol, 71%) as a pale yellow oil. Rᵣ = 0.82 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.32 (m, 2H), 7.29 – 7.21 (m, 5H), 6.80 – 6.73 (m, 3H), 4.55 (s, 2H), 3.03 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.8, 139.1, 129.3, 128.7, 127.0, 126.8, 116.7, 112.5, 56.7, 38.6. The analytical data are consistent with previous reports.[57]

**N-Benzyl-4-(tert-butyl)-N-methylaniline (5w):** N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2o (0.22 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:5), to give 5w (0.0593 g, 0.23 mmol, 58%) as a colorless oil. Rᵣ = 0.61 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.20 (m, 7H), 6.76 – 6.72 (m, 2H), 4.50 (s, 2H), 2.99 (s, 3H), 1.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 147.8, 139.5, 139.4, 128.6, 127.0, 126.9, 126.1, 112.3, 57.1, 33.9, 31.7. HRMS (ESI): calcd for C₁₈H₂₄N [M+H]+: 254.1903; found: 254.1901. The analytical data are consistent with previous reports.[59]

**N-benzyl-3-methoxy-N-methylanilinil (5x):** N-methyl-1-phenylmethanamine (1z, 0.05 mL, 0.4 mmol) was arylated with salt 2q (0.21 g, 1.0 equiv) according to the general procedure in toluene (2 mL) for 4 h. Purified by column chromatography (pentane/EtOAc 100:0 to 100:3), to give 5x (0.059 g, 0.26 mmol, 65%) in an inseparable mixture with 4-iodoanisole. Rᵣ = 0.54 in 5% pentane/ethyl acetate. ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 7.16 – 7.09 (m, 1H), 6.41 – 6.35 (m, 1H), 6.32 – 6.29 (m, 2H), 4.53 (s, 2H), 3.78 (s, 3H), 3.01 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.9, 151.3, 139.1, 130.0, 128.7, 127.0, 126.9, 105.7, 101.5, 99.1, 56.7, 55.4. 38.7. HRMS (ESI): calcd for C₁₃H₁₃NO [M+H]+: 228.1383; found: 228.1390. The analytical data are consistent with previous reports.[60] 4-Iodoanisole: ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 3.78 (s, 3H), ¹³C NMR (101 MHz, CDCl₃) δ 159.6, 138.3, 116.5, 82.8, 55.4
6 References

[1] A. I. Vogel, B. S. Furniss, A. J. Hannaford, V. Rogers, P. W. G. Smith, A. R. Tatchell, Vogel's Textbook of Practical Organic Chemistry 5th Ed., Prentice Hall: Harlow, 1996.

[2] M. Zhu, N. Jalalian, B. Olofsson, Synlett 2008, 592-596.

[3] aN. Jalalian, T. B. Petersen, B. Olofsson, Chem. Eur. J. 2012, 18, 14140-14149; bP.-O. Norrby, T. B. Petersen, M. Bielawski, B. Olofsson, Chem. Eur. J. 2010, 16, 8251-8254.

[4] M. Bielawski, B. Olofsson, Chem. Commun. 2007, 2521-2523.

[5] M. Bielawski, D. Alli, B. Olofsson, J. Org. Chem. 2008, 73, 4602-4607.

[6] M. Bielawski, M. Zhu, B. Olofsson, Adv. Synth. Catal. 2007, 349, 2610-2618.

[7] A. Monastyrsky, N. K. Namelikonda, R. Manetsch, J. Org. Chem. 2015, 80, 2513-2520.

[8] T. B. Petersen, R. Khan, B. Olofsson, Org. Lett. 2011, 13, 3462-3465.

[9] G. L. Tolnai, U. J. Nilsson, B. Olofsson, Angew. Chem. Int. Ed. 2016, 55, 11226-11230.

[10] N. Jalalian, E. E. Ishikawa, L. F. Silva, B. Olofsson, Org. Lett. 2011, 13, 1552-1555.

[11] J.-H. Chun, S. Lu, V. W. Pike, Eur. J. Org. Chem. 2011, 4439-4447.

[12] Y. Wang, C. Wang, Y. Wang, L. Dong, J. Sun, RSC Advances 2015, 5, 12354-12357.

[13] M. Bielawski, J. Malmgren, L. M. Pardo, Y. Wikmark, B. Olofsson, ChemistryOpen 2014, 3, 19-22.

[14] P. Kazmierczak, L. Skulski, Synthesis 1995, 1027-1032.

[15] T. L. Seidl, S. K. Sundalam, B. McCullough, D. R. Stuurt, J. Org. Chem. 2016, 81, 1998-2009.

[16] aE. A. Merritt, V. M. T. Carneiro, L. F. Silva, B. Olofsson, J. Org. Chem. 2010, 75, 7416-7419; bT. Dohi, M. Ito, K. Morimoto, Y. Minamisugi, N. Takenaga, Y. Kita, Chem. Commun. 2007, 4152-4154.

[17] V. Carreras, A. H. Sandtorv, D. R. Stuurt, J. Org. Chem. 2017, 82, 1279-1284.

[18] A. H. Sandtorv, D. R. Stuurt, Angew. Chem. Int. Ed. 2016, 55, 15812-15815.

[19] E. Striffeldt, E. Lindstedt, M. Reitti, J. Blid, P.-O. Norrby, B. Olofsson, Chem. Eur. J. 2017, DOI: 10.1002/chem.201703057.

[20] aM. Ochiai, Top. Curr. Chem. 2003, 224, 5-68; bM. Ochiai, Y. Kitagawa, M. Toyonari, ARKIVOC 2003, (iv), 43-48; cH. Pinto de Magalhães, H. P. Lüthi, A. Togni, J. Org. Chem. 2014, 79, 8374-8382; dH. Pinto de Magalhães, H. P. Lüthi, A. Togni, Org. Lett. 2012, 14, 3830-3833.

[21] J. P. Patel, A.-H. Li, H. Dong, V. L. Korlipara, M. J. Mulvihill, Tetrahedron Lett. 2009, 50, 5975-5977.

[22] R. Arundhati, D. C. Kumar, B. Sreedhar, Eur. J. Org. Chem. 2010, 2010, 3621-3630.

[23] K. Yang, Y. Qiu, Z. Li, Z. Wang, S. Jiang, J. Org. Chem. 2011, 76, 3151-3159.

[24] P. L. Reddy, R. Arundhati, D. S. Rawat, RSC Advances 2015, 5, 92121-92127.

[25] Z. Wei, J. Li, N. Wang, Q. Zhang, D. Shi, K. Sun, Tetrahedron 2014, 70, 1395-1400.

[26] K. Ladewig, A. Seifert, H. Hahn, M. Hietschold, N. Moszner, P. Burtscher, S. Spange, J. Mat. Chem. 2012, 22, 3839-3852.

[27] X. Lei, L. Yan-Ping, S. Lin, X. Yan, C. Zhong-Sheng, F. Min, Y. Rong-Xin, D. Hong-Bin, Chem. Eur. J. 2016, 22, 6268-6276.

[28] X. Ding, M. Huang, Z. Yi, D. Du, X. Zhu, Y. Wan, J. Org. Chem. 2017, 82, 5416-5423.

[29] W. Liao, Y. Chen, Y. Liu, H. Duan, J. L. Petersen, X. Shi, Chem. Commun. 2009, 6436-6438.

[30] Z. Shao, S. Fu, M. Wei, S. Zhou, Q. Liu, Angew. Chem. Int. Ed. 2016, 55, 14653-14667.

[31] M.-L. Yuan, J.-H. Xie, Q.-L. Zhou, ChemCatChem 2016, 8, 3036-3040.

[32] P. Liu, R. Liang, L. Lu, Z. Yu, F. Li, J. Org. Chem. 2017, 82, 1943-1950.

[33] L. Wu, I. Fleischer, R. Jackstell, M. Beller, J. Am. Chem. Soc. 2013, 135, 3989-3996.

[34] J. M. Lophchuk, K. Fjelbye, Y. Kawamata, L. R. Malins, C.-M. Pan, R. Gianatassio, J. Wang, L. Prieto, J. Bradow, T. A. Brandt, M. R. Collins, J. Elleraas, J. Ewanicki, W. Farrell, O. O. Fadeyi, G. M. Gallego, J. J. Mousseau, R. Oliver, N. W. Sach, J. K. Smith, J. E. Spangler, H. Zhu, J. Zhu, P. S. Baran, J. Am. Chem. Soc. 2017, 139, 3209-3226.

[35] D. B. Bagal, R. A. Wattle, M. V. Khedkar, K. P. Dhake, B. M. Bhanage, Catal. Sci. Tech. 2012, 2, 354-358.

[36] P. Yin, T.-P. Loh, Org. Lett. 2009, 11, 3791-3793.

[37] M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson, J. M. J. Williams, J. Am. Chem. Soc. 2009, 131, 1766-1774.

[38] M.-C. Fu, R. Shang, W.-M. Cheng, Y. Fu, Angew. Chem. Int. Ed. 2015, 54, 9042-9046.

[39] A. Heutling, F. Pohlki, S. Doye, Chem. Eur. J. 2004, 10, 3059-3071.

[40] S.-L. Shi, S. L. Buchwald, Angew. Chem. Int. Ed. 2015, 54, 1646-1650.

[41] S. Neogi, D. Naskar, Synth. Commun. 2011, 41, 1901-1915.

[42] M. Bollenbach, P. Wagner, P. G. V. Aquino, J.-J. Bourguignon, F. Bihel, C. Salomé, M. Schmitt, ChemSusChem 2016, 9, 3244-3249.

[43] H. Li, M. Achard, C. Bruneau, J.-B. Sortais, C. Darcel, RSC Advances 2014, 4, 25892-25897.

[44] N. Iranpoor, F. Panahi, Adv. Synth. Catal. 2014, 356, 3067-3073.
[45] M. Khatri, S. K. Rai, S. Alam, A. Vij, M. Tiwari, Bioorg. Med. Chem 2009, 17, 1890-1897.
[46] Z. Zhang, C. Miao, C. Xia, W. Sun, Org. Lett. 2016, 18, 1522-1525.
[47] G. Toma, R. Yamaguchi, Eur. J. Org. Chem. 2010, 2010, 6404-6408.
[48] T. J. Barker, E. R. Jarvo, J. Am. Chem. Soc. 2009, 131, 15598-15599.
[49] T. Shimasaki, M. Tobisu, N. Chatani, Angew. Chem. Int. Ed. 2010, 49, 2929-2932.
[50] K. Swapna, A. Vijay Kumar, V. Prakash Reddy, K. Rama Rao, J. Org. Chem. 2009, 74, 7514-7517.
[51] D. Hollmann, S. Bähn, A. Tillack, R. Parton, R. Altink, M. Beller, Tetrahedron Lett. 2008, 49, 5742-5745.
[52] S. Riedmüller, B. J. Nachtsheim, Synlett 2015, 26, 651-655.
[53] Y. Lin, M. Li, J. Ji, J. Wu, S. Cao, Tetrahedron 2017, 73, 1466-1472.
[54] S. A. Girard, X. Hu, T. Knauber, F. Zhou, G.-O. Simon, G.-J. Deng, C.-J. Li, Org. Lett. 2012, 14, 5606-5609.
[55] Y. Fang, Y. Zheng, Z. Wang, Eur. J. Org. Chem. 2012, 2012, 1495-1498.
[56] R. Kuwano, M. Utsunomiya, J. F. Hartwig, J. Org. Chem. 2002, 67, 6479-6486.
[57] S. Roy, M. J. Sarma, B. Kashyap, P. Phukan, Chem. Commun. 2016, 52, 1170-1173.
[58] X.-Q. Zhang, Z.-X. Wang, Org. Biomol. Chem. 2014, 12, 1448-1453.
[59] X. Bei, T. Uno, J. Norris, H. W. Turner, W. H. Weinberg, A. S. Guram, J. L. Petersen, Organometallics 1999, 18, 1840-1853.
[60] C. Borch Jacobsen, M. Meldal, F. Diness, Chem. Eur. J. 2017, 23, 846-851.

7 NMR Spectra

NMR spectrometer:
$^1$H 400 MHz; $^{13}$C 101 MHz, $^{19}$F 377 MHz

NMR solvents:
Diaryliodonium salts $2s$, $2t$ DMSO-$d_6$
All products except $3z$ CDCl$_3$
$3z$ CD$_3$OD
O₂N

2t
3d

\[
\text{H} \quad \text{\( \text{C}_{18} \text{H}_{13} \text{N} \) \( \text{NO}_2 \)}
\]
3e
3h
3p

**Chemical Shifts**

- **7.32 ppm**: 2.00
- **7.33 ppm**: 1.01
- **6.63 ppm**: 3.66
- **6.60 ppm**: 4.00
- **3.17 ppm**: 3.16
- **2.04 ppm**: 2.16
- **1.98 ppm**: 1.95
- **1.92 ppm**: 1.95

**1H NMR Spectrum**

- **f1 (ppm)**: 7.00 - 7.32
3v

- 7.26 CDCl3
- 2.07
- 7.20 7.16 f1 (ppm)
- 6.68 6.63 6.60 f1 (ppm)
- 3.29 3.22 f1 (ppm)
- 2.05 2.17 3.40 3.84 f1 (ppm)
3aa

\[ \text{Chemical Structure} \]

\[ \text{NMR Spectra} \]
3aa
3ab
3ab
3ad
3ag

![Chemical Structure](image-url)
3ah
5n
5u

\[
\text{Bn} \quad \text{N}_3
\]
