Supporting Information
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Unexpected Rearrangement of 2-Bromoaniline
Under Biphasic Alkylation Conditions

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SUPPORTING INFORMATION

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General Experimental

Reaction Setup: All reactions were performed in base-washed, oven-dried glassware (130 °C) unless otherwise noted. Reactions were generally run under an inert atmosphere of either dry nitrogen or dry argon, with some exceptions run under air; this information is recorded in each procedure. All reaction temperatures are noted as the oil bath temperature, the internal temperature (monitored by a Teflon-coated thermocouple), or as the room temperature (approximately 23 °C.) Vacuum pressures averaged as follows: rotary evaporator (15 mm Hg), high vacuum (0.1 mm Hg), and diffusion pump high vacuum (1.2 x 10^{-5} mm Hg).

NMR Spectroscopy: $^1$HNMR and $^{13}$CNMR spectra were recorded on a Varian Unity Inova 600 spectrometer (600 MHz, $^1$H; 150 MHz, $^{13}$C; 119 MHz, $^{29}$Si) equipped with a 5mm Varian AutoTuneX $^1$H/X PFG Z probe or a Bruker B500 spectrometer (500 MHz, $^1$H; 125 MHz, $^{13}$C) equipped with a 5mm Bruker Cryoprobe. Spectra are referenced to the residual solvent signal: chloroform-$d_3$ (δ 7.26 ppm, $^1$H; δ 77.16 ppm, $^{13}$C), DMSO-$d_6$ (δ 2.50 ppm, $^1$H; δ 39.52 ppm, $^{13}$C), and 1,4-dioxane-$d_8$ (3.53 ppm, $^1$H; 66.66 ppm, $^{13}$C). Chemical shifts are reported in ppm (δ); multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad singlet), and bm (broad multiplet). Coupling constants, $J$, are reported in Hz. $^1$H and $^{13}$C assignments are supported by COSY, APT, HSQC, HMBC, 2D NOESY, and $^{29}$Si correlation experiments where necessary. Spectra were acquired at temperatures from -40 °C to +120 °C to resolve rotamers by isolation or convergence (respectively) if possible, and all temperatures are reported. High temperature resolution of rotamers often resulted in accumulation of decomposition products (especially in oxygen-containing solvents, e.g. DMSO-$d_6$ and DMF-$d_7$) or failed to resolve rotamers at the maximum probe temperature (120 °C), necessitating low temperature analysis.

Mass Spectrometry: Mass spectrometry was performed by the University of Illinois Mass Spectrometry Laboratory. Mass spectrometric data was collected on a Waters Q-TOF Ultima (ESI) spectrometer, a Waters Synapt G2-Si spectrometer (ESI), a Waters Quattro Ultima spectrometer (ESI), a Micromass 70-VSE spectrometer (EI/CI), and a Waters GCT Premier spectrometer (EI/CI). Low resolution spectral data are reported as (mass, intensity), and high resolution data are reported as calculated and measured masses to 10^{-4} mass accuracy. Fragments are noted where known.
**Infrared Spectroscopy:** Infrared spectra were recorded on a Perkin-Elmer UATR-2 FT-IR spectrophotometer. Peaks are reported in cm$^{-1}$ with relative intensities indicated: s (strong, 67-100%); m (medium, 34-66%), w (weak, 0-33%).

**Elemental Analysis:** Elemental analyses were performed by the University of Illinois Microanalytical Laboratory on an Exeter Model CE 440 CHN Analyzer, or Robertson Microlit (1705 U.S. Highway 46, Suite 1D, Ledgewood, New Jersey 07852, USA). Reported data is the average of at least 2 runs.

**Melting Points:** Melting points (m.p.) were determined on a Thomas-Hoover capillary tube melting point apparatus in vacuum-sealed capillary tubes and are corrected.

**Boiling Points:** Boiling points (b.p.) are the reported as the air bath temperature (ABT) at which material was distilled.

**Chromatography:** Analytical thin-layer chromatography was performed on Merck silica or aluminum oxide, basic gel plates with QF-254 indicator. Visualization was accomplished with UV light, iodine, or aqueous KMnO$_4$. Column chromatography was performed using EM Science 230-400-mesh silica gel or Aldrich 150-mesh aluminum oxide, activated, basic, Brockmann Activity III. Chromatography solvents were of reagent grade unless otherwise noted as HPLC grade and used as received, unless otherwise noted.

**Distillation:** Distillations were performed by a variety of methods (e.g. short path, Kugelrohr) and are specifically noted in each relevant procedure. Diffusion pump high vacuum Kugelrohr distillations were performed on a Buchi GKR-50 Kugelrohr and high vacuum Kugelrohr distillations were performed on a Buchi B-580 Kugelrohr.

**Reagents:** All commercial reagents were purified by chromatography, distillation, sublimation, or recrystallization prior to use. All solvents were passed through solvent delivery system (SDS) columns or distilled over the recommended drying agent. 2-Bromoaniline was purchased from Oakwood Chemical (730 Columbia Hwy. N, Estill, SC 29918).
Experimental Procedures

General Procedure I: Rearrangement Study
The relevant aniline (0.5 mmol) was weighed into an oven-dried, threaded dram vial, followed by the sequential addition of anhydrous DMF (1 mL), an additional reagent (if required), and an alkyl halide (if required) last. The vial was tightly capped and placed in a pre-heated aluminum block (120 °C). After 24 h, the vial was removed from the block and allowed to cool to 23 °C, at which point it was cautiously opened (may be pressurized). The most common reaction colors are: colorless, black, amber, green, and blue. The reaction mixture was diluted with hexanes/EtOAc, 1:1 (20 mL) and was transferred to a 60-mL separatory funnel. The organic phase was washed with 10% aq. NaHCO₃ solution (30 mL), 10% aq. LiCl solution (30 mL), and brine (30 mL), dried over anhydrous Na₂SO₄ (1 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg). The crude product was then dried further under high vacuum (0.1 mm Hg) for 1 h before being diluted with a solution of a known quantity of tetramethylurea (TMU) in CDCl₃ (1 mL). The targeted quantity was 0.05 mmol TMU/1 mL CDCl₃, prepared as stock solutions in 10 mL volumetric flasks at 23 °C. TMU was measured by mass, and the actual quantity per mL CDCl₃ is reported. The solution was then transferred to a 5mm NMR tube and analyzed by ¹H NMR and ¹³C NMR in a 600 MHz spectrometer.

Calculation of NMR Yield
The tetramethylurea (TMU) peak area was set to 12.00 (number of TMU hydrogens). Target peaks of interest were integrated, and the value obtained was submitted to the equation:

\[
\text{mmol}_{\text{TMU}} \times \text{Area}_{\text{target}} \times \frac{100}{\text{Theoretical yield in mmol}} = \% \text{ Yield}
\]

Due to the close proximity of some peaks, each target peak was integrated with varying integral widths, from which the mean was extracted and the standard error of the mean (SEM) calculated. Benzylic CH₂ peaks were usually targeted, but if these were too crowded by overlapping peaks, alternative signals were measured.
General Preparation of Hydrohalide Salts

Hydrochloride and hydrobromide salts were prepared by dissolving N-benzyl-2-bromoaniline (0.5 mmol) or N,N-dibenzyl-2-bromoaniline (0.5 mmol) in 0.5 mL THF in tared dram vials. Conc. HCl or conc. HBr (1.1 equiv) was added, and the material was concentrated on a rotavap (30 °C, 15 mm Hg). The solid residue was suspended in Et₂O (0.5 mL) and sonicated, then again concentrated on a rotavap. The vial and resulting white powders were then placed under high vacuum (0.1 mm Hg) for 6 h to remove residual solvent and acid. The final mass was documented and the hydrohalide salt was subjected to the method described in General Procedure I.

Time Course Study

Following General Procedure I, five (5) reactions were set up in the manner described, each corresponding to a different time point. The t = 0 h time point was worked up after benzyl bromide addition, but was not placed in the aluminum block and was instead worked up as described. The remaining time points were pulled from the aluminum block at the time specified (1 h, 7 h, 12 h, and 30 h) and worked up as described in General Procedure I.
Original Rearrangement

Preparation of N,N-Dibenzyl-4-bromoaniline (2a)

2-Bromoaniline (6.10 g, 35.46 mmol) was weighed into a 50-mL, round-bottomed flask, followed by the addition of anhydrous DMF (35 mL) and granular K$_2$CO$_3$ (14.70 g, 106.38 mmol, 3.0 equiv). Benzyl bromide (9.27 mL, 78.01 mmol, 2.2 equiv) was added last. The flask was fitted with a drying tube (CaCl$_2$) and placed in a pre-heated oil bath (120 °C) and was stirred, over which time the reaction displayed a vibrant blue-green color. After 30 h, the reaction was allowed to cool to 23 °C and was then diluted with hexanes/EtOAc, 1:1 (100 mL). The mixture was transferred to a 250-mL separatory funnel and was washed with 10% aq. LiCl solution (2 x 100 mL portions), water (6 x 100 mL portions), and brine (100 mL), dried over anhydrous Na$_2$SO$_4$ (5 g), filtered, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a green oil (10.22 g). The crude product was then crystallized from boiling anhydrous EtOH (150 mL), and allowed to cool slowly to ambient temperature, then -20 °C in a freezer. The resulting crystals were collected over a sintered glass filter, washed with cold EtOH (20 mL), and dried under high vacuum (0.1 mm Hg) to afford 8.30 g (23.56 mmol, 66%) of the 4-bromoaniline 2a as sharp, white crystals.

Data for 2a:

- m.p.: 114 – 116 °C
- $^1$H NMR: (600 MHz, CDCl$_3$, 23 °C)
  - $\delta$ 7.36 (t, $J = 7.4$ Hz, 4H, HC(4’)), 7.29 (t, $J = 7.3$ Hz, 2H, HC(5’)), 7.27 – 7.22 (m, 6H, HC(3 then 3’)), 6.62 (d, $J = 9.1$ Hz, 2H, HC(2)), 4.65 (s, 4H, H$_2$C(1’))
- $^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)
  - $\delta$ 148.17 (C(1)), 138.10 (C(2’)), 131.99 (C(3)), 128.86 (C(4’)), 127.19 (C(5’)), 126.63 (C(3’)), 114.25 (C(2)), 108.72 (C(4)), 54.54 (C(1’))
- IR: (neat)
  - 3085 (w), 3062 (w), 3028 (w), 3003 (w), 2906 (w), 2865 (w), 2627 (w), 2270 (w), 1949 (w), 1863 (w), 1808 (w), 1740 (w), 1592 (m), 1494 (s), 1452 (m),
1393 (w), 1360 (m), 1328 (w), 1296 (w), 1274 (w), 1252 (w), 1232 (m), 1201 (w), 1175 (w), 1163 (w), 1124 (w), 1107 (w), 1082 (w), 1028 (w), 996 (w), 955 (w), 899 (w), 844 (w), 806 (m), 770 (w), 729 (s), 695 (s), 645 (w), 626 (w), 617 (w), 565 (w), 532 (w), 503 (w), 458 (w),

**MS:** (EI+, TOF)
180.1 (64), 181.1 (48), 260.0 ([M – CH₂(C₆H₅)]⁺, 32), 262.0 ([M – CH₂(C₆H₅)]⁺, 38), 273 (96), 274.0 ([M - Br]⁺, 16), 276.0 ([M - Br]⁺, 2), 294.9 (48), 296.9 (48), 307.1 (24), 351.0 ([M]⁺, 96), 352.0 ([M]⁺, 24), 353.0 ([M]⁺, 96), 354.0 ([M]⁺, 24)

**HRMS:** (EI+, TOF) [M]⁺ Calcd for C₂₀H₁₈BrN
Calcd: 351.06225
Found: 351.06199

**TLC:** Rₜ= 0.51 (hexanes/EtOAc, 3:1) [UV]

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**Preparation of Authentic Samples**

**A**

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**B**

| ![Diagram](s2c-d) | ![Diagram](s3c-d) |
| ![Diagram](s2c-d) | ![Diagram](s3c-d) |
General Procedure II: Benzoylation

The relevant aniline was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of anhydrous CH₂Cl₂ (25 mL) and distilled Et₃N (1.1 – 2.0 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (1.05 – 1.1 equiv) was added dropwise. After complete addition, the cooling bath was removed and the reaction mixture was stirred for a given time. Reaction progress was monitored by TLC. The reaction typically became cloudy with precipitate over the course of the reaction. The reaction mixture was concentrated on a rotavap (30 °C, 15 mm Hg) and the resulting residue was diluted with EtOAc (60 mL). The mixture was transferred to a 125-mL separatory funnel and washed with 1M HCl (2 x 50 mL portions), water (50 mL), 10% aq. Na₂CO₃ solution (2 x 50 mL portions), and brine (50 mL). The organic phase was dried over anhydrous Na₂SO₄ (~2 g), filtered, and concentrated by rotavap (30 °C, 15 mm Hg) followed by high vacuum (23 °C, 0.1 mm Hg).

Preparation of N-(4-Bromophenyl)benzamide (S1)

Following General Procedure II, 4-bromoaniline (0.70 g, 4.07 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of CH₂Cl₂ (25 mL) and distilled Et₃N (0.62 mL, 4.48 mmol, 1.1 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (0.47 mL, 4.27 mmol, 1.05 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 3 h, the reaction mixture was concentrated and worked up as described in General Procedure II, to give a light pink solid (1.16 g) that was purified by recrystallization from boiling EtOAc (10 mL) and cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOAc (5 mL). The filtrate was similarly recrystallized from boiling EtOH (1 mL) and collected over a filter. The
combined crops were dried under high vacuum (0.1 mm Hg) to afford 1.01 g (3.66 mmol, 90%) of the anilide S1 as subtly pink, sharp, square crystals.

Data for S1:

**m.p.:** 200 – 202 °C

**$^1$H NMR:** (600 MHz, DMSO-$d_6$, 25 °C)

δ 10.38 (s, 1H, HN), 7.95 (d, $J = 7.1$ Hz, 2H, HC(3’)), 7.78 (d, $J = 8.8$ Hz, 2H, HC(3)), 7.60 (t, $J = 7.3$ Hz, 1H, HC(5’)), 7.57 – 7.50 (m, 4H, HC(4” and 2))

**$^{13}$C NMR:** (151 MHz, DMSO-$d_6$, 25 °C)

δ 165.66 (C(1’)), 138.58 (C(1)), 134.71 (C(2’)), 131.71 (C(5’)), 131.43 (C(3)), 128.41 (C(4’)), 127.68 (C(3’)), 122.20 (C(2)), 115.33 (C(4))

**IR:** (neat)

3900 (w), 3746 (w), 3647 (w), 3332 (m), 3178 (w), 3085 (w), 3060 (w), 3037 (w), 2876 (w), 2847 (w), 2760 (w), 2628 (w), 2553 (w), 2496 (w), 2418 (w), 2323 (w), 2187 (w), 2082 (w), 1991 (w), 1970 (w), 1924 (w), 1901 (w), 1868 (w), 1818 (w), 1792 (w), 1689 (w), 1645 (s), 1590 (m), 1579 (m), 1515 (m), 1487 (m), 1449 (m), 1392 (m), 1355 (m), 1328 (w), 1301 (m), 1288 (m), 1258 (m), 1241 (m), 1179 (m), 1160 (w), 1119 (w), 1101 (w), 1073 (m), 1026 (w), 1008 (m), 980 (w), 964 (w), 939 (w), 929 (w), 900 (m), 864 (w), 818 (s), 794 (m), 716 (s), 691 (s), 684 (m), 651 (s)

**MS:** (E+, TOF)

197.1 ([M – Br]$^+$, 30), 216.1 (41), 274.0 ([M]$^+$, 32), 275.0 ([M]$^+$, 100), 276.0 ([M]$^+$, 40), 277.0 ([M]$^+$, 99), 278.0 ([M]$^+$, 15)

**HRMS:** (EI+, TOF) [M]$^+$ Calcd for C$_{13}$H$_{10}$BrO

Calcd: 274.99457

Found: 274.99338

**TLC:** R$_f$ = 0.44 (hexanes/EtOAc, 3:1) [UV]
Preparation of N-Phenylbenzamide (S2)

Following General Procedure II, aniline (0.50 g, 5.37 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of CH$_2$Cl$_2$ (25 mL) and distilled Et$_3$N (0.82 mL, 5.91 mmol, 1.1 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (0.65 mL, 5.64 mmol, 1.05 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 3 h, the reaction mixture was concentrated and worked up as described in General Procedure II, to give an off-white solid (1.21 g) that was purified by recrystallization from boiling EtOH (8 mL) and cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL). The filtrate was similarly recrystallized, from boiling EtOH (1 mL) and collected over a filer. The combined crops were dried under high vacuum (0.1 mm Hg) to afford 0.98 g (4.95 mmol, 92%) of the anilide S2 as sharp, white crystals.

**Data for S2:**

- **b.p.:** 161 – 163 °C
- **$^1$H NMR:** (600 MHz, CDCl$_3$, 20 °C) 
  δ 7.92 (bs, 1H, HN), 7.87 (d, $J = 7.4$ Hz, 2H, HC(3')), 7.65 (d, $J = 7.8$ Hz, 2H, HC(2)), 7.54 (t, $J = 7.4$ Hz, 1H, HC(5')), 7.47 (t, $J = 7.6$ Hz, 2H, HC(4')), 7.37 (t, $J = 7.9$ Hz, 2H, HC(3)), 7.16 (t, $J = 7.4$ Hz, 1H, HC(4))
- **$^{13}$C NMR:** (151 MHz, CDCl$_3$, 20 °C) 
  δ 165.92 (C(1')), 138.05 (C(1)), 135.12 (C(2')), 131.96 (C(5')), 129.22 (C(4')), 128.90 (C(3)), 127.15 (C(3')), 124.70 (C(2)), 120.35 (C(4))
- **IR:** (neat) 
  3343 (m), 3054 (w), 1654 (s), 1599 (m), 1579 (w), 1528 (s), 1491 (m), 1448 (m), 1438 (s), 1322 (m), 1300 (w), 1261 (m), 1178 (w), 1165 (w), 1115 (w),
Following General Procedure II, 4-chloroaniline (1.00 g, 7.84 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of CH₂Cl₂ (25 mL) and distilled Et₃N (2.19 mL, 15.68 mmol, 2.0 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (1.00 mL, 8.62 mmol, 1.1 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 2 h, the reaction mixture was concentrated and worked up as described in General Procedure II, to give a brown solid (1.34 g) that was purified by recrystallization from boiling EtOH (20 mL) and cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 0.96 g (4.12 mmol, 53%) of the anilide S₃ as sharp, white crystals.

Data for S₃:

b.p.: 188 – 190 °C

¹H NMR: (600 MHz, DMSO-d₆, 25 °C)

δ 10.39 (bs, 1H, HN), 7.97 (d, J = 7.4 Hz, 2H, HC(3’)), 7.85 (d, J = 8.8 Hz, 2H, HC(3)), 7.59 (t, J = 7.3 Hz, 1H, HC(5’)), 7.53 (t, J = 7.5 Hz, 2H, HC(4’)), 7.41 (d, J = 8.8 Hz, 2H, HC(2))
$^{13}$C NMR: (151 MHz, DMSO-$d_6$, 25 °C)
$\delta$ 165.66 (C(1’)), 138.18 (C(1)), 134.74 (C(2’)), 131.67 (C(5’)), 128.51 (C(3)), 128.40 (C(4’)), 127.70 (C(3’)), 127.29 (C(4)), 121.84 (C(2))

IR: (neat)
3746 (w), 3349 (w), 3186 (w), 3105 (w), 3061 (w), 3036 (w), 2996 (w), 2760 (w), 2629 (w), 2325 (w), 2080 (w), 1972 (w), 1924 (w), 1901 (w), 1825 (w), 1770 (w), 1759 (w), 1653 (m), 1595 (m), 1578 (w), 1515 (m), 1489 (s), 1447 (m), 1397 (m), 1358 (w), 1332 (w), 1312 (m), 1288 (m), 1240 (s), 1178 (m), 1161 (w), 1120 (w), 1091 (m), 1074 (m), 1028 (w), 1013 (m), 1000 (m), 982 (w), 966 (w), 929 (w), 897 (w), 864 (w), 822 (s), 793 (m), 716 (s), 706 (s), 689 (s), 651 (s), 641 (s), 615 (m), 510 (s), 501 (s)

MS: (EI$^+$, TOF)

HRMS: (EI$^+$, TOF) [M]$^+$ Calcd for C$_{13}$H$_{10}$NClO
Calcd: 231.04509
Found: 231.04511

TLC: $R_f=0.35$ (hexanes/EtOAc, 3:1) [UV]

Preparation of N-(2-Bromophenyl)benzamide (S4)

$\begin{align*}
\text{PhCOCl (1.05 equiv),} \\
\text{Et$_3$N (1.1 equiv),} \\
\text{CH$_2$Cl$_2$, 23 °C, 1 h}
\end{align*}$

2-Bromoaniline (10.70 g, 62.20 mmol) was weighed into an oven-dried, 250-mL, round-bottomed flask, followed by the addition of CH$_2$Cl$_2$ (100 mL) and distilled Et$_3$N (9.54 mL, 68.42 mmol, 1.1 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (7.59 mL, 65.31 mmol, 1.05 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 1 h, the reaction mixture was concentrated by rotavap (30 °C, 15 mm
Hg) and the residue was diluted with EtOAc (100 mL). The mixture was transferred to a 250-mL separatory funnel and the organic phase was then washed with 1M aq. HCl (2 x 100 mL portions), water (2 x 100 mL portions), 10% aq. Na₂CO₃ solution (2 x 100 mL portions), and brine (100 mL), dried over anhydrous Na₂SO₄ (8 g), filtered, and concentrated by rotavap (30 °C, 15 mm Hg) to give a clumpy, off-white solid (18.06 g). The crude product was purified by recrystallization from boiling EtOH (40 mL), cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOH (20 mL). The filtrate was similarly recrystallized from boiling EtOH (1 mL) and collected over a filter. The combined crops were dried under high vacuum (0.1 mm Hg) to afford 15.89 g (57.54 mmol, 93%) of the anilide S₄ as fluffy, white crystals.

**Data for S₄:**

- **m.p.:** 111 – 112 °C
- **¹H NMR:** (600 MHz, CDCl₃, 20 °C)
  \[ \delta \text{ 8.54 (d, } J = 8.2 \text{ Hz, 1H, } HC(6)), 8.48 (bs, 1H, } HN) , 7.93 (d, } J = 7.6 \text{ Hz, 2H, } HC(3')) , 7.59 – 7.53 (m, 2H, } HC(5' then 3)), 7.50 (t, } J = 7.5 \text{ Hz, 2H, } HC(4')) , 7.35 (t, } J = 7.8 \text{ Hz, 1H, } HC(5)), 7.00 (t, } J = 7.7 \text{ Hz, 1H, } HC(4))
- **¹³C NMR:** (151 MHz, CDCl₃, 20 °C)
  \[ \delta 165.18 (C(1')), 135.79 (C(1)), 134.50 (C(2')), 132.24 (C(3)), 132.18 (C(5')), 128.92 (C(4')), 128.49 (C(5)), 127.10 (C(3')), 125.30 (C(4)), 121.86 (C(6)), 113.90 (C(2))
- **IR:** (neat)
  3936 (w), 3647 (w), 3277 (m), 3158 (w), 3106 (w), 3081 (w), 3059 (w), 3029 (w), 2995 (w), 2839 (w), 2774 (w), 2641 (w), 2422 (w), 2343 (w), 2101 (w), 2019 (w), 1974 (w), 1954 (w), 1912 (w), 1891 (w), 1830 (w), 1809 (w), 1794 (w), 1764 (w), 1718 (w), 1651 (s), 1603 (m), 1587 (m), 1578 (s), 1530 (s), 1492 (m), 1468 (w), 1446 (m), 1437 (s), 1309 (s), 1278 (m), 1264 (m), 1248 (w), 1180 (w), 1165 (w), 1156 (w), 1133 (w), 1111 (w), 1102 (w), 1073 (w), 1042 (w), 1028 (m), 1001 (w), 989 (w), 940 (w), 924 (w), 905 (w), 856 (w), 838 (w), 795 (w), 749 (s), 717 (m), 706 (s), 690 (m), 683 (m), 659 (m), 641 (s), 616 (m), 584 (w), 534 (w), 493 (w)
**Preparation of N-(2-Chlorophenyl)benzamide (S5)**

Following General Procedure II, 4-chloroaniline (1.00 g, 7.84 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of CH$_2$Cl$_2$ (25 mL) and distilled Et$_3$N (2.19 mL, 15.68 mmol, 2.0 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (1.00 mL, 8.62 mmol, 1.1 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 2 h, the reaction mixture was concentrated on a rotovap and worked up as described in General Procedure II, to give a tan solid (1.90 g) that was purified by recrystallization from boiling EtOH (15 mL) and cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 1.01 g (4.37 mmol, 56%) of the anilide S5 as fluffy, white crystals.

**Data for S5:**

- **m.p.:** 101 – 102 °C
- **$^1$H NMR:** (600 MHz, CDCl$_3$, 23 °C)
  
  δ 8.57 (dd, $J = 8.3$, 1.2 Hz, 1H, HC(6)), 8.46 (s, 1H, HN), 7.93 (d, $J = 7.2$ Hz, 2H, HC(3')), 7.58 (t, $J = 7.4$ Hz, 1H, HC(5')), 7.52 (t, $J = 7.5$ Hz, 2H, HC(4')), 7.42 (dd, $J = 8.0$, 1.3 Hz, 1H, HC(3)), 7.34 (t, $J = 7.8$ Hz, 1H, HC(5)), 7.09 (td, $J = 7.9$, 1.4 Hz, 1H, HC(4))
$^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)

δ 165.38 (C(1’)), 134.84 (C(1)), 134.72 (C(2’)), 132.31 (C(3)), 129.14 (C(5’)), 129.06 (C(4’)), 128.00 (C(5)), 127.20 (C(3’)), 124.86 (C(4)), 123.15 (C(2)), 121.61 (C(6))

IR: (neat)

3279 (m), 3167 (w), 3114 (w), 3081 (w), 3062 (w), 3029 (w), 2843 (w), 2780 (w), 2648 (w), 2429 (w), 2324 (w), 2163 (w), 2113 (w), 2080 (w), 2010 (w), 1980 (w), 1953 (w), 1912 (w), 1891 (w), 1829 (w), 1808 (w), 1795 (w), 1766 (w), 1719 (w), 1651 (s), 1601 (w), 1591 (m), 1584 (m), 1529 (s), 1490 (m), 1472 (m), 1446 (m), 1439 (s), 1311 (s), 1278 (m), 1266 (m), 1181 (w), 1166 (w), 1136 (w), 1117 (w), 1102 (w), 1072 (w), 1051 (m), 1036 (w), 1027 (w), 1001 (w), 990 (w), 940 (w), 923 (w), 905 (m), 858 (w), 839 (w), 795 (w), 750 (s), 720 (w), 710 (s), 690 (s), 670 (m),

MS: (EI$^+$, TOF)

196.1 ([M – Cl]$^+$, 100), 197.1 ([M – Cl]$^+$, 15), 231.1 ([M]$^+$, 26), 232.1 ([M]$^+$, 4), 233.1 ([M]$^+$, 9)

HRMS: (EI$^+$, TOF) [M]$^+$ Calcd for C$_{13}$H$_{10}$NClO

Calcd: 231.04509

Found: 231.04497

TLC: R$_f$ = 0.52 (silica gel, 3:1 hexanes/EtOAc, UV)

Preparation of N-(2,4-Dibromophenyl)benzamide (S6)

![Chemical structure](image)

Following General Procedure II, 2,4-dibromoaniline (1.00 g, 3.99 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask, followed by the addition of CH$_2$Cl$_2$ (25 mL) and
distilled Et₃N (0.61 mL, 4.38 mmol, 1.1 equiv). The solution was cooled to 0 °C and neat benzoyl chloride (0.49 mL, 4.18 mmol, 1.05 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 3 h, the reaction mixture was concentrated and worked up as described in General Procedure II, to give an off-white solid (1.21 g) that was purified by recrystallization from boiling EtOH (10 mL) and cooling to 23 °C then -20 °C in a freezer. The crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL). The filtrate was similarly recrystallized, from boiling EtOH (2 mL) and collected over a filter. The combined crops were dried under high vacuum (0.1 mm Hg) to afford 1.28 g (3.61 mmol, 90%) of the anilide S6 as fluffy, white crystals.

_data for S6:

**b.p.:** 132 – 133 °C  
**1H NMR:** (600 MHz, CDCl₃, 23 °C)  
δ 8.49 (d, J = 8.8 Hz, 1H, HC(6)), 8.42 (bs, 1H, HN), 7.92 (d, J = 7.3 Hz, 2H, HC(3’)), 7.73 (d, J = 2.2 Hz, 1H, HC(3)), 7.60 (t, J = 7.4 Hz, 1H, HC(5’)), 7.53 (t, J = 7.6 Hz, 2H, HC(4’)), 7.49 (dd, J = 8.8, 2.1 Hz, 1H, HC(5))  
**13C NMR:** (151 MHz, CDCl₃, 23 °C)  
δ 165.31 (C(1’)), 135.19 (C(1)), 134.53 (C(3)), 134.37 (C(2’)), 132.55 (C(5’)), 131.70 (C(5)), 129.16 (C(4’)), 127.22 (C(3’)), 122.73 (C(6)), 116.90 (C(4)), 114.16 (C(2))  
**IR:** (neat)  
3286 (w), 3061 (w), 3029 (w), 1980 (w), 1912 (w), 1808 (w), 1651 (s), 1602 (w), 1579 (w), 1572 (w), 1522 (s), 1490 (m), 1462 (w), 1411 (w), 1376 (m), 1304 (m), 1256 (w), 1182 (w), 1145 (w), 1114 (w), 1099 (w), 1077 (w), 1039 (w), 1027 (w), 1000 (w), 927 (w), 906 (w), 862 (w), 840 (w), 821 (w), 795 (w), 714 (w), 692 (w), 670 (w), 632 (w), 614 (w), 547 (w), 505 (w), 465 (w)  
**MS:** (CI⁺, TOF)  
171.0 (13), 195.1 (6), 222.9 (7), 249.9 (6), 274.0 ([M – Br]⁺, 100), 275.0 ([M – Br]⁺, 18), 276.0 ([M – Br]⁺, 99), 277.0 ([M – Br]⁺, 14), 352.9 ([M]⁺, 28), 354.9 ([M]⁺, 54), 355.9 ([M]⁺, 9), 356.9 ([M]⁺, 27)
HRMS: (EI⁺, TOF) [M]⁺ Calcd for C₁₃H₉Br₂O
Calcd: 352.90512
Found: 352.90473

TLC: Rf = 0.59 (hexanes/EtOAc, 3:1) [UV]

General Procedure III: N-Benzyla

The relevant anilide was weighed into an oven-dried, 25-mL Schlenk flask under a blanket of argon, followed by the addition of anhydrous DMF (10 mL). Hexanes-washed NaH (1.3 equiv) was added portion-wise, followed by benzyl bromide (1.1 equiv) once gas evolution had ceased. The reaction typically changed from light yellow or even green to colorless upon addition of benzyl bromide. The reaction mixture was allowed to stir for a given amount of time, after which it was quenched by the careful and dropwise addition of sat. aq. NaHCO₃ solution (2 mL). The reaction mixture was then diluted with hexanes/Et₂O, 1:1 (60 mL). The mixture was transferred to a 125-mL separatory funnel and washed with water (60 mL x 3 portions) and brine (60 mL), dried over anhydrous Na₂SO₄ (~3 g), filtered, and concentrated on a rotavap (30 °C, 15 mm Hg). The crude residue was then purified either by recrystallization or chromatography followed by recrystallization.

Preparation of N-Benzyl-N-phenylbenzamide (S7)

Following General Procedure III, the anilide S2 (0.57 g, 2.91 mmol) was weighed into an oven-dried, 25-mL Schlenk flask under a blanket of argon, followed by the addition of anhydrous
DMF (10 mL). Hexanes-washed NaH (0.08 g, 3.20 mmol, 1.3 equiv) was added portion-wise, followed by benzyl bromide (0.45 mL, 3.78 mmol, 1.1 equiv) once gas evolution had ceased. The reaction changed from light yellow to colorless upon addition of benzyl bromide. After 6 h, the reaction mixture was quenched by the careful and dropwise addition of sat. aq. NaHCO₃ solution (2 mL) and worked up as described by General Procedure III to give a tan solid (1.02 g). The crude product S7 was used in the next step without further purification or characterization.

**Preparation of N-Benzyl-N-(4-chlorophenyl)benzamide (S8)**

Following General Procedure III, the anilide S3 (0.54 g, 2.33 mmol) was weighed into an oven-dried, 25-mL Schlenk flask under a blanket of argon, followed by the addition of anhydrous DMF (10 mL). Hexanes-washed NaH (0.07 g, 3.03 mmol, 1.3 equiv) was added portion-wise, followed by benzyl bromide (0.30 mL, 2.56 mmol, 1.1 equiv) once gas evolution had ceased. The reaction mixture changed from light yellow to colorless upon addition of benzyl bromide. After 2 h, the reaction mixture was quenched by the careful and dropwise addition of sat. aq. NaHCO₃ solution (2 mL) and worked up as described by General Procedure III to give an off-white solid (0.77 g). The crude product was recrystallized from boiling anhydrous EtOH (4 mL), with cooling to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 0.64 g (1.98 mmol, 85%) of benzyl anilide S8 as white crystals.

**Data for S8:**

\[
\text{m.p.: } 129 - 132 ^\circ C
\]

\[
^1H\text{ NMR: } (600\text{ MHz, CDCl}_3, 23 ^\circ C) \\
\delta 7.34 (d, J = 7.3 Hz, 2H, HC(3')), 7.32 - 7.28 (m, 4H, HC(3'' and 4'')), 7.27 - 7.23 (m, 2H, HC(5' and 5'')), 7.19 (t, J = 7.6 Hz, 2H, HC(4')), 7.10 (d, J = 8.6 Hz, 2H, HC(3)), 6.84 (d, J = 8.5 Hz, 2H, HC(2)), 5.12 (s, 2H, H₂C(1''))
\]
\[ ^{13}C \text{NMR:} \ (151 \ \text{MHz}, \ \text{CDCl}_3, \ 23 \ ^\circ \text{C}) \]
\[ \delta \ 170.49 \ (C(1')), \ 142.07 \ (C(1)), \ 137.24 \ (C(2'')), \ 135.67 \ (C(2')), \ 132.33 \ (C(4)), \ 129.95 \ (C(5')), \ 129.24 \ (C(2)), \ 128.98 \ (C(3)), \ 128.76 \ (C(3'')), \ 128.64 \ (C(4'')), \ 128.44 \ (C(3'')), \ 127.98 \ (C(4'')), \ 127.60 \ (C(5')), \ 53.80 \ (C(1'')) \]

\[ \text{IR:} \ (\text{neat}) \]
\[ 3654 \ (\text{w}), \ 3282 \ (\text{w}), \ 3087 \ (\text{w}), \ 3062 \ (\text{w}), \ 2933 \ (\text{w}), \ 2319 \ (\text{w}), \ 2247 \ (\text{w}), \ 2109 \ (\text{w}), \ 1952 \ (\text{w}), \ 1894 \ (\text{w}), \ 1812 \ (\text{w}), \ 1767 \ (\text{w}), \ 1642 \ (s), \ 1601 \ (w), \ 1592 \ (w), \ 1575 \ (w), \ 1491 \ (s), \ 1454 \ (w), \ 1446 \ (m), \ 1433 \ (w), \ 1409 \ (m), \ 1377 \ (m), \ 1317 \ (m), \ 1287 \ (m), \ 1269 \ (m), \ 1217 \ (w), \ 1179 \ (w), \ 1148 \ (w), \ 1094 \ (m), \ 1079 \ (m), \ 1028 \ (w), \ 1013 \ (m), \ 1002 \ (w), \ 970 \ (w), \ 920 \ (w), \ 835 \ (m), \ 790 \ (m), \ 717 \ (s), \ 696 \ (s), \ 674 \ (w), \ 642 \ (w), \ 618 \ (m), \ 568 \ (w), \ 543 \ (m), \ 516 \ (w), \ 476 \ (w), \ 455 \ (w) \]

\[ \text{MS:} \ (\text{EI}^+, \ \text{TOF}) \]
\[ 182.1 \ (30), \ 196.1 \ ([M – \text{Bn} – \text{Cl}]^+, \ 33), \ 216.1 \ ([M – (C_6H_5)CO]^+, \ 42), \ 217.1 \ ([M – (C_6H_5)CO]^+, \ 100), \ 218.1 \ ([M – (C_6H_5)CO]^+, \ 24), \ 219.1 \ ([M – (C_6H_5)CO]^+, \ 33), \ 231.1 \ (9), \ 273.2 \ (99), \ 274.2 \ (22), \ 321.1 \ ([M]^+, \ 46), \ 322.1 \ ([M]^+, \ 12), \ 323.1 \ ([M]^+, \ 17) \]

\[ \text{HRMS:} \ (\text{EI}^+, \ \text{TOF}) \ [M]^+ \ \text{Calcd for} \ C_{20}H_{16}NClO \]
\[ \text{Calcd:} \ 321.09204 \]
\[ \text{Found:} \ 321.09221 \]

\[ \text{TLC:} \ R_f = 0.39 \ (\text{hexanes/EtOAc, 3:1}) \ [\text{UV}] \]

**Preparation of N-Benzyl-N-(2-bromophenyl)benzamide (S9)**

![Chemical structure diagram]

The anilide **S4** (15.00 g, 54.32 mmol) was weighed into an oven-dried, 250-mL Schlenk flask under a blanket of argon, followed by anhydrous DMF (150 mL). The flask was placed in an
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ice bath and cooled to 0 °C, and washed NaH (1.43 g, 59.75 mmol, 1.1 equiv) was added portionwise. Once gas evolution had ceased, benzyl bromide (6.77 mL, 57.04 mmol, 1.05 equiv) was added dropwise, and the reaction mixture color changed from yellow to colorless. The ice bath was removed and the reaction mixture was stirred at 23 °C. After 1 h, the reaction mixture was quenched by the slow and careful dropwise addition of sat. aq. NaHCO₃ solution (10 mL), then diluted with hexanes/Et₂O, 1:1 (400 mL). The mixture was transferred to a 1.0-L separatory funnel and the organic phase was washed with water (400 mL x 6 portions) and brine (400 mL), dried over anhydrous Na₂SO₄ (12 g), filtered, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a clumpy, white powder (23.44 g). The crude product was recrystallized from boiling anhydrous EtOH (100 mL), and allowed to cool to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a sintered glass filter, washed with cold EtOH (20 mL), and dried under high vacuum (23 °C, 0.1 mm Hg) to afford 17.49 g (47.75 mmol, 88%) of benzylanilide S9 as white crystals.

**Data for S9:**

**m.p.:** 99 – 101 °C

**¹H NMR:** (600 MHz, CDCl₃, 23 °C)

- δ 7.49 (d, J = 7.4 Hz, 1H, HC(3)), 7.38 (d, J = 7.5 Hz, 2H, HC(3’)), 7.33 – 7.28 (m, 2H, HC(3’’)), 7.28 – 7.23 (m, 3H, HC(4’’ then 5’’)), 7.19 (t, J = 7.2 Hz, 1H, HC(5’’)), 7.13 (t, J = 7.5 Hz, 2H, HC(4’’)), 6.97 (t, J = 7.3 Hz 1H, HC(4)), 6.95 (t, J = 7.2 Hz, 1H, HC(5)), 6.68 (d, J = 7.1 Hz, 1H, HC(6)), 5.80, 4.37 (ABq, J = 856.2, 14.3 Hz, 2H, H₂C(1’’))

**¹³C NMR:** (151 MHz, CDCl₃, 23 °C)

- δ 170.64 (C(1’’)), 141.33 (C(1)), 136.80 (C(2’’)), 135.88 (C(2’)), 133.60 (C(3)), 132.32 (C(6)), 129.73 (C(5’’)), 129.41 (C(3’’)), 129.09 (C(5)), 128.39 (C(4’’)), 127.99 (C(3’)), 127.79 (C(4)), 127.60 (C(4’ and 5’’)), 123.25 (C(2)), 52.05 (C(1’’))

**IR:** (neat)

- 3286 (w), 3085 (w), 3061 (w), 3029 (w), 2939 (w), 2340 (w), 2108 (w), 1955 (w), 1891 (w), 1809 (w), 1646 (s), 1602 (w), 1583 (w), 1495 (w), 1474 (s), 1455 (w), 1446 (m), 1434 (m), 1381 (s), 1319 (m), 1296 (m), 1259 (w), 1217
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(w), 1179 (w), 1147 (w), 1122 (w), 1079 (w), 1060 (w), 1029 (m), 1001 (w), 967 (w), 919 (w), 846 (w), 821 (w), 789 (w), 768 (m), 754 (w), 724 (s), 713 (s), 697 (s), 664 (s), 641 (w), 623 (m), 571 (w), 533 (w), 500 (w), 481 (w), 456 (w)

**MS:** (EI\(^+\), TOF)

180.1 (19), 260.0 (15), 286.1 ([M – Br]\(^+\), 100), 287.1 ([M – Br]\(^+\), 22), 365.0 ([M]\(^+\), 21), 366.0 ([M]\(^+\), 10), 367.0 ([M]\(^+\), 22)

**HRMS:** (EI\(^+\), TOF) [M]\(^+\) Calcd for C\(_{20}\)H\(_{16}\)BrNO

Calcd: 365.04152

Found: 365.04095

**TLC:** \(R_f = 0.45\) (hexanes/EtOAc, 3:1) [UV]

### Preparation of N-Benzyl-N-(2-chlorophenyl)benzamide (S10)

![diagram]

Following General Procedure III, the anilide S5 (0.52 g, 2.24 mmol) was weighed into an oven-dried, 25-mL Schlenk flask under a blanket of argon, followed by the addition of anhydrous DMF (10 mL). Hexanes-washed NaH (0.07 g, 2.92 mmol, 1.3 equiv) was added portion-wise, followed by benzyl bromide (0.29 mL, 2.47 mmol, 1.1 equiv) once gas evolution had ceased. The reaction mixture changed from light yellow to colorless upon addition of benzyl bromide. After 2 h, the reaction mixture was quenched by the careful and dropwise addition of sat. aq. NaHCO\(_3\) solution (2 mL) and worked up as described by General Procedure III to give an off-white solid (0.76 g). The crude product was recrystallized from boiling anhydrous EtOH (4 mL), with cooling to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 0.63 g (1.94 mmol, 86%) of benzyl anilide S10 as white crystals.
Data for S10:

**m.p.:** 108 – 110 °C

**1H NMR:** (600 MHz, CDCl$_3$, 20 °C)

\[ \delta 7.35 \text{ (d, } J = 7.5 \text{ Hz, } 2H, HC(3')), 7.32 – 7.23 \text{ (m, } 6H, HC(3", 4", 5", \text{ and } 3')), \\
7.20 \text{ (t, } J = 7.3 \text{ Hz, } 1H, HC(5')), 7.14 \text{ (t, } J = 7.4 \text{ Hz, } 2H, HC(4')), 7.07 \text{ (t, } J = \\
7.6 \text{ Hz, } 1H, HC(4)), 6.93 \text{ (t, } J = 7.6 \text{ Hz, } 1H, HC(5)), 6.69 \text{ (d, } J = 7.8 \text{ Hz, } 1H, \\
HC(6)), 5.72, 4.42 \text{ (ABq, } J = 785.5, 14.4 \text{ Hz, } 2H, HC_2(1'')) \\
\]

**13C NMR:** (151 MHz, CDCl$_3$, 20 °C)

\[ \delta 170.88 \text{ (C(1'))}, 140.03 \text{ (C(1))}, 136.88 \text{ (C(2''))}, 135.92 \text{ (C(2'))}, 132.60 \text{ (C(2))}, \\
131.98 \text{ (C(6))}, 130.40 \text{ (C(3))}, 129.80 \text{ (C(5'))}, 129.38 \text{ (C(3''))}, 128.91 \text{ (C(4))}, \\
128.42 \text{ (C(4''))}, 127.96 \text{ (C(3'))}, 127.68 \text{ (C(4'))}, 127.62 \text{ (C(5'))}, 127.23 \text{ (C(5))}, \\
52.05 \text{ (C(1''))} \\
\]

**IR:** (neat)

3288 (w), 3063 (w), 3030 (w), 2938 (w), 2324 (w), 1961 (w), 1888 (w), 1809 (w), 1650 (s), 1602 (w), 1587 (w), 1578 (w), 1494 (w), 1479 (m), 1454 (w), 1446 (w), 1438 (w), 1383 (m), 1320 (m), 1297 (m), 1259 (w), 1217 (w), 1180 (w), 1147 (w), 1130 (w), 1110 (w), 1080 (w), 1069 (w), 1029 (w), 1002 (w), 967 (w), 920 (w), 846 (w), 821 (w), 790 (w), 768 (w), 755 (w), 727 (m), 718 (m), 698 (s), 678 (w), 646 (w), 624 (w), 571 (w), 496 (w), 465 (w), 453 (w)

**MS:** (EI$^+$, TOF)

149.0 (17), 180.1 (15), 196.1 ([M – Bn – Cl]$^+$, 13), 216.1 (36), 217.1 ([M – (C$_6$H$_5$)CO]$^+$, 10), 218.1 ([M – (C$_6$H$_5$)CO]$^+$, 12), 231.1 ([M – Bn]$^+$, 18), 273.2 (6), 286.1 ([M – Cl]$^+$, 100), 287.2 ([M – Cl]$^+$, 24), 320.1 (12), 321.1 ([M]$^+$, 43), 322.1 ([M]$^+$, 13), 323.1 ([M]$^+$, 15)

**HRMS:** (EI$^+$, TOF) [M]$^+$ Calcd for C$_{20}$H$_{16}$NCIO

Calcd: 321.09204

Found: 321.09183

**TLC:** R$_f$ = 0.41 (hexanes/EtOAc, 3:1) [UV]
Preparation of $N$-Benzyl-$N$-(2,4-dibromophenyl)benzamide (S11)

Following General Procedure III, the anilide S6 (0.35 g, 0.99 mmol) was weighed into an oven-dried, 25-mL Schlenk flask under a blanket of argon, followed by the addition of anhydrous DMF (10 mL). Hexanes-washed NaH (0.03 g, 1.28 mmol, 1.3 equiv) was added portion-wise, followed by benzyl bromide (0.13 mL, 1.08 mmol, 1.1 equiv) once gas evolution had ceased. The reaction mixture changed from light blue to colorless upon addition of benzyl bromide. After 2 h, the reaction mixture was quenched by the careful and dropwise addition of sat. aq. NaHCO$_3$ solution (2 mL) and worked up as described by General Procedure III to give a yellow oil (0.48 g). The crude product was purified by silica gel flash chromatography (~30 g silica gel (45 x 30 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.40 g (0.91 mmol, 92%) of benzyl anilide S11 as a clear, colorless oil.

Data for S11:

$^1$H NMR: (600 MHz, CDCl$_3$, 23 °C)

δ 7.65 (s, 1H, HC(3)), 7.35 (d, $J = 7.3$ Hz, 2H, HC(3’)), 7.27 (s, 5H, HC(3”, 4”, and 5”)), 7.26 – 7.21 (m, 1H, HC(5’)), 7.17 (t, $J = 7.2$ Hz, 2H, HC(4’)), 7.08 (d, $J = 8.0$ Hz, 1H, HC(5)), 6.50 (d, $J = 8.3$ Hz, 1H, HC(6)), 5.77, 4.31 (ABq, $J = 873.5$, 14.3 Hz, 2H, $H_2$C(1”))

$^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)

δ 170.53 (C(1’)), 140.63 (C(1)), 136.52 (C(2”)), 136.07 (C(3)), 135.62 (C(2’)), 133.29 (C(6)), 131.08 (C(5)), 130.04 (C(5’)), 129.47 (C(3”)), 128.56 (C(4’)), 127.99 (C(3’)), 127.86 (C(4’)), 127.83 (C(5’)), 124.15 (C(2)), 121.89 (C(4)), 51.95 (C(1”))

IR: (neat)

3661 (w), 3514 (w), 3287 (w), 3084 (w), 3061 (w), 3028 (w), 2936 (w), 2630 (w), 2323 (w), 2246 (w), 2124 (w), 1955 (w), 1889 (w), 1811 (w), 1648 (s),
1601 (w), 1576 (w), 1552 (w), 1494 (w), 1470 (s), 1455 (m), 1446 (m), 1377 (m), 1355 (m), 1297 (m), 1250 (m), 1216 (w), 1180 (w), 1145 (w), 1108 (w), 1079 (m), 1055 (m), 1028 (w), 1013 (w), 1001 (w), 965 (m), 916 (w), 868 (w), 824 (w), 788 (w), 750 (m), 696 (s), 676 (m), 654 (w), 618 (m), 572 (m), 548 (w), 524 (w), 492 (w), 470 (m), 446.1 ([M⁺], 59), 447.0 ([M⁺], 30)

**HRMS:** (EI⁺, TOF) [M⁺] Calcd for C₂₀H₁₅NOBr₂

Calcd: 442.95207

Found: 442.95125

**TLC:** Rᵣ = 0.56 (silica gel, 3:1 hexanes/EtOAc UV)

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**General Procedure IV: Reduction of the Anilide**

The appropriate anilide S₁–₆ or benzylanilide S₇–₁₁ was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with argon or N₂ and the flask was capped with a septum. The anilide was dissolved in a small volume of anhydrous THF (2 – 4 mL), and a 1.0M BH₃·THF solution (2.0 equiv) was added, resulting in modest warming. The reaction mixture was stirred at a given temperature for a specified time, after which it was diluted with Et₂O (10 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (2 mL). This mixture was stirred for 1 h, after which it was further diluted with Et₂O (30 mL). The mixture was transferred to a 60-mL separatory funnel and washed with sat. aq. sodium potassium tartrate solution (30 mL), 10% aq. Na₂CO₃ solution (30 mL), and brine (30 mL). The organic phase was dried over anhydrous...
Na₂SO₄ (~2 g), filtered, and concentrated on a rotavap (30 °C, 15 mm Hg). The resulting crude product was purified by recrystallization, silica gel chromatography, or both, as reported.

**Preparation of N,N-Dibenzyl-4-chloroaniline (2b)**

Following General Procedure IV, the anilide S₈ (0.55 g, 1.71 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with N₂ and the flask was capped with a septum. The anilide was dissolved in a small volume of anhydrous THF (3 mL), and a 1.0 M BH₃·THF solution (3.42 mL, 3.42 mmol, 2.0 equiv) was added, resulting in modest warming. The reaction mixture was stirred at 23 °C. After 12 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (5 mL). The reaction mixture was then worked up as described in General Procedure IV to give a white crystalline solid (0.49 g). The crude product was purified by recrystallization from boiling anhydrous EtOH (4 mL), with cooling to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 0.322 g (1.05 mmol, 61%) of N,N-dibenzyl-2-chloroaniline 2b as long, needle-like, white crystals.

**Data for 2b:**

- **m.p.:** 100 – 101 °C
- **¹H NMR:** (600 MHz, CDCl₃, 23 °C)
  - δ 7.35 (t, J = 7.5 Hz, 4H, HC(4’)), 7.28 (t, J = 7.3 Hz, 2H, HC(5’)), 7.24 (d, J = 7.3 Hz, 4H, HC(3’)), 7.11 (d, J = 9.1 Hz, 2H, HC(3)), 6.66 (d, J = 9.1 Hz, 2H, HC(2)), 4.65 (s, 4H, H₂C(1’))
- **¹³C NMR:** (151 MHz, CDCl₃, 23 °C)
  - δ 147.78 (C(1)), 138.20 (C(2’)), 129.11 (C(3)), 128.86 (C(4’)), 127.18 (C(5’)), 126.66 (C(3’)), 121.64 (C(4)), 113.77 (C(2)), 54.62 (C(1’))
IR: (neat)
3085 (w), 3062 (w), 3029 (w), 2907 (w), 2865 (w), 1953 (w), 1861 (w), 1808 (w), 1598 (m), 1499 (s), 1452 (m), 1393 (w), 1361 (m), 1328 (w), 1297 (w), 1274 (w), 1252 (w), 1232 (m), 1202 (w), 1191 (w), 1164 (w), 1100 (w), 1075 (w), 1028 (w), 1001 (w), 956 (w), 897 (w), 809 (m), 731 (m), 696 (m), 648 (w), 617 (w), 569 (w), 533 (w), 505 (w), 458 (w)

MS: (EI+, TOF)
181.1 (5), 215.1 (19), 216.1 ([M – (C₆H₅)CH₂]⁺, 12), 218.1 ([M – (C₆H₅)CH₂]⁺, 8), 230.1 (18), 231.1 (4), 232.1 (6), 307.1 ([M]⁺, 100), 308.1 ([M]⁺, 23), 309.1 ([M]⁺, 34), 354.1 (5)

HRMS: (EI+, TOF) [M]⁺ Calcd for C₂₀H₁₈NCl
Calcd: 307.11277
Found: 307.11303

TLC: Rf = 0.60 (hexanes/EtOAc, 3:1) [UV]

**Preparation of N,N-Dibenzyl-4-iodoaniline (2c)**

[Diagram]

4-Iodoaniline (0.34 g, 1.55 mmol) was weighed into a dram vial, followed by the addition of anhydrous DMF (1 mL), distilled i-PrEt₂N (0.81 mL, 4.66 mmol, 3.0 equiv), and benzyl bromide (0.46 mL, 3.88 mL, 2.5 equiv). The vial was tightly capped and placed in a pre-heated aluminum heating block (120 °C). After 18 h, the vial was removed and allowed to cool to the ambient temperature (23 °C). The reaction mixture was quenched by the addition of Et₃N (0.5 mL), and after 10 h was diluted with hexanes/EtOAc, 1:1 (30 mL). The mixture was transferred to a 60-mL separatory funnel and washed with water (3 x 30 mL portions), 10% aq. Na₂CO₃ solution (30 mL), and brine (30 mL), dried over anhydrous Na₂SO₄ (3 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a dark brown solid (0.65 g). The crude product was purified by recrystallization from boiling anhydrous EtOH (5 ml), with cooling to 23 °C then -20 °C in a
freezer. The resulting crystals were collected over a sintered glass filter, washed with cold EtOH (2 mL), and dried under high vacuum (0.1 mm Hg) to afford 0.41 g (1.03 mmol, 66%) of \(N,N\)-dibenzy-4-iodoaniline \(2c\) as a white microcrystals that became slightly green over time.

Data for \(2c\):

\[
\begin{align*}
\text{m.p.:} & \quad 119 - 121 \, ^\circ C \\
\text{\^{1}H NMR:} & \quad (600 \text{ MHz, CDCl}_3, 23 \, ^\circ C) \\
& \quad \delta \ 7.40 \ (d, \ J = 8.8 \text{ Hz}, 2 \text{H}, HC(3)), \ 7.34 \ (t, \ J = 7.5 \text{ Hz}, 4 \text{H}, HC(4')), \ 7.27 \ (t, \ J = 7.3 \text{ Hz}, 2 \text{H}, HC(5')), \ 7.22 \ (d, \ J = 7.5 \text{ Hz}, 4 \text{H}, HC(3')), \ 6.51 \ (d, \ J = 8.9 \text{ Hz}, 2 \text{H}, HC(2)), \ 4.64 \ (s, 4 \text{H}, H_2C(1')) \\
\text{\^{13}C NMR:} & \quad (151 \text{ MHz, CDCl}_3, 23 \, ^\circ C) \\
& \quad \delta \ 148.75 \ (C(1)), \ 138.04 \ (C(2')), \ 137.88 \ (C(3)), \ 128.88 \ (C(3')), \ 127.21 \ (C(5')), \ 126.62 \ (C(4')), \ 114.91 \ (C(2)), \ 77.75 \ (C(4)), \ 54.41 \ (C(1')) \\
\text{IR:} & \quad (\text{neat}) \\
& \quad 3080 \ (w), \ 3059 \ (w), \ 3024 \ (w), \ 3001 \ (w), \ 2899 \ (w), \ 2861 \ (w), \ 2621 \ (w), \ 2324 \ (w), \ 2149 \ (w), \ 2064 \ (w), \ 1955 \ (w), \ 1864 \ (w), \ 1805 \ (w), \ 1753 \ (w), \ 1589 \ (m), \ 1582 \ (m), \ 1558 \ (w), \ 1493 \ (s), \ 1449 \ (w), \ 1434 \ (w), \ 1412 \ (w), \ 1380 \ (m), \ 1348 \ (s), \ 1324 \ (w), \ 1294 \ (w), \ 1270 \ (w), \ 1242 \ (m), \ 1197 \ (m), \ 1174 \ (w), \ 1164 \ (m), \ 1155 \ (w), \ 1128 \ (w), \ 1071 \ (w), \ 1026 \ (w), \ 1001 \ (w), \ 990 \ (w), \ 962 \ (m), \ 921 \ (w), \ 896 \ (w), \ 855 \ (w), \ 798 \ (s), \ 727 \ (s), \ 692 \ (m), \ 653 \ (w), \ 626 \ (w), \ 617 \ (w), \ 578 \ (w), \ 520 \ (m), \ 499 \ (m), \ 454 \ (m) \\
\text{MS:} & \quad (\text{EI}^+, \text{TOF}) \\
& \quad 180.1 \ (40), \ 181 \ (22), \ 184.0 \ (47), \ 186.0 \ (44), \ 198.0 \ (14), \ 227.1 \ (10), \ 229.2 \ (9), \ 240.1 \ (38), \ 242.1 \ (36), \ 272.2 \ ([M – I]^+, \ 18), \ 285.1 \ (10), \ 307.0 \ ([M – (C_6H_5)CH_2]^+, \ 16), \ 308.0 \ ([M – (C_6H_5)CH_2]^+, \ 16), \ 322.0 \ (13), \ 399.1 \ ([M]^+, \ 100), \ 400.1 \ ([M]^+, \ 23) \\
\text{HRMS:} & \quad (\text{EI}^+, \text{TOF}) \ [M]^+ \text{ Calcd for } C_{20}H_{18}N \\
& \quad \text{Calcd:} \quad 399.04842 \\
& \quad \text{Found:} \quad 399.04770 \\
\text{TLC:} & \quad R_f = 0.63 \text{ (hexanes/EtOAc, 3:1) [UV]}
\end{align*}
\]
Preparation of \(N,N\)-Di(\(n\)-butyl)-4-bromoaniline (2d)

4-Bromoaniline (0.33 g, 1.92 mmol) was weighed into a dram vial, followed by the addition of anhydrous DMF (1 mL), distilled \(i\)-PrEt\(_2\)N (1.0 mL, 4.52 mmol, 3.0 equiv), and \(n\)-butyl bromide (0.51 mL, 4.80 mL, 2.5 equiv). The vial was tightly capped and placed in a pre-heated aluminum heating block (120 °C). After 18 h, the vial was removed and allowed to cool to the ambient temperature (23 °C). The reaction mixture was quenched with the addition of Et\(_3\)N (0.5 mL), and after 10 h was diluted with hexanes/EtOAc, 1:1 (30 mL). The mixture was transferred to a 60-mL separatory funnel and washed with water (3 x 30 mL portions), 10% aq. Na\(_2\)CO\(_3\) solution (30 mL), and brine (30 mL), dried over anhydrous Na\(_2\)SO\(_4\) (3 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a dark green/brown oil (0.64 g). The crude product was purified by silica gel flash chromatography (~50 g silica gel (70 x 30 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.43 g (1.52 mmol, 79%) of \(N,N\)-di(\(n\)-butyl)-2-bromoaniline 2d as a clear, yellow liquid. (Some 7:1 contamination by \(N\)-(\(n\)-butyl)-4-bromoaniline.)

Data for 2d:

\(^1\)H NMR: (600 MHz, CDCl\(_3\), 23 °C)
\(\delta\) 7.27 (d, \(J = 9.0\) Hz, 2H, \(HC(3)\)), 6.52 (d, \(J = 9.0\) Hz, 2H, \(HC(2)\)), 3.28 – 3.21 (m, 4H, \(H_2C(1')\)), 1.56 (p, \(J = 7.6\) Hz, 4H, \(H_2C(2')\)), 1.36 (h, \(J = 7.4\) Hz, 4H, \(H_2C(3')\)), 0.97 (t, \(J = 7.4\) Hz, 6H, \(H_3C(4')\))

\(^{13}\)C NMR: (151 MHz, CDCl\(_3\), 23 °C)
\(\delta\) 147.22 (C(1)), 131.86 (C(3)), 113.42 (C(2)), 106.81 (C(4)), 50.96 (C(1’)), 29.35 (C(2’)), 20.44 (C(3’)), 14.12 (C(4’))

IR: (neat)
3414 (w), 3090 (w), 3043 (w), 2956 (m), 2930 (w), 2872 (w), 2076 (w), 1857 (w), 1699 (w), 1637 (w), 1591 (m), 1561 (w), 1496 (s), 1464 (w), 1396 (w), 1367 (m), 1316 (w), 1287 (w), 1255 (w), 1219 (m), 1186 (m), 1148 (w), 1110
Preparation of \( \text{N, N-Dibenzyl-2-bromoaniline (3a)} \)

\[
\begin{align*}
\text{BH}_3\text{THF (2.0 eq),} & \quad \text{THF, 23 °C, 5 h} \\
\text{2-Bromoanilide S9 (17.00 g, 46.42 mmol)} & \quad \text{92%} \\
\rightarrow & \quad \text{3a}
\end{align*}
\]

2-Bromoanilide S9 (17.00 g, 46.42 mmol) was weighed into an oven-dried, 200-mL, round-bottomed flask under \( \text{N}_2 \), followed by anhydrous THF (30 mL). The colorless solution was cooled to 0 °C and a 1.0 M solution of \( \text{BH}_3 \) in THF (92.83 mL, 92.83 mmol, 2.0 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 5 h, the reaction mixture was diluted with \( \text{Et}_2\text{O} \) (100 mL) and quenched by the careful and dropwise addition of sat. aq. \( \text{NaHCO}_3 \) solution (30 mL) and was stirred for 1 h. The mixture was transferred to a 250-mL separatory funnel whereupon the aqueous phase was discarded and the organic phase was washed with sat. aq. sodium potassium tartrate solution (2 x 100 mL portions), 10% aq, \( \text{Na}_2\text{CO}_3 \) solution (2 x 100 mL portions), and brine (100 mL), dried over anhydrous \( \text{Na}_2\text{SO}_4 \) (6 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a cloudy, thick, yellow oil (16.08 g) after further drying under high vacuum (0.1 mm Hg). The crude product was purified by silica gel flash chromatography (~120 g silica gel (85 x 60 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 125 mL fractions) to afford 15.11 g (42.89 mmol, 92%) of the title product 3a as a clear, viscous, colorless oil after warm drying under high vacuum (80 °C, 0.1 mm Hg).
Data for 3a:

$^1$H NMR: (600 MHz, CDCl$_3$, 23 °C)
\[\delta 7.69 \text{ (d, } J = 7.8 \text{ Hz, } 1\text{H}, \text{HC(3))}, \delta 7.44 \text{ (d, } J = 7.4 \text{ Hz, } 4\text{H}, \text{HC(3'))}, \delta 7.37 \text{ (t, } J = 7.5 \text{ Hz, } 4\text{H}, \text{HC(4'))}, \delta 7.31 \text{ (t, } J = 7.2 \text{ Hz, } 1\text{H}, \text{HC(5))}, \delta 7.02 \text{ (d, } J = 7.9 \text{ Hz, } 1\text{H}, \text{HC(6))}, \delta 6.95 \text{ (t, } J = 7.2 \text{ Hz, } 1\text{H}, \text{HC(4))}, 4.29 \text{ (s, } 4\text{H}, H_2\text{C(1'))}

$^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)
\[\delta 148.89 \text{ (C(1))}, 138.05 \text{ (C(2'))}, 133.90 \text{ (C(3))}, 128.69 \text{ (C(3'))}, 128.30 \text{ (C(4'))}, 127.70 \text{ (C(5))}, 127.11 \text{ (C(5'))}, 124.83 \text{ (C(4))}, 124.56 \text{ (C(6))}, 121.55 \text{ (C(2))}, 56.52 \text{ (C(1'))}

IR: (neat)
3084 (w), 3061 (w), 3026 (w), 2931 (w), 2886 (w), 2838 (w), 2805 (w), 2736 (w), 2323 (w), 2256 (w), 2086 (w), 1948 (w), 1870 (w), 1809 (w), 1749 (w), 1696 (w), 1602 (w), 1584 (w), 1494 (m), 1473 (m), 1452 (m), 1437 (m), 1364 (w), 1324 (w), 1288 (w), 1267 (w), 1241 (w), 1207 (w), 1175 (w), 1156 (w), 1135 (w), 1111 (w), 1073 (w), 1054 (w), 1028 (m), 1003 (w), 951 (w), 934 (w), 904 (w), 849 (w), 822 (w), 812 (w), 783 (w), 757 (m), 746 (m), 730 (s), 720 (s), 695 (s), 659 (m), 640 (w), 621 (w), 608 (w), 585 (w), 557 (w), 535 (w), 502 (w), 460 (w)

MS: (EI$^+$, TOF)
180.1 (58), 181.1 (24), 260.0 ([M - CH$_2$(C$_6$H$_5$)]$^+$, 44), 262.0 ([M - \text{CH}_2\text{(C}_6\text{H}_5)]^+$, 38), 274.0 ([M - Br]$^+$, 20), 276.0 ([M - Br]$^+$, 16), 351.0 ([M]$^+$, 76), 352.0 ([M]$^+$, 24), 353.0 ([M]$^+$, 76), 354.0 ([M]$^+$, 16)

HRMS: (EI$^+$, TOF) [M]$^+$ Calcd for C$_{20}$H$_{18}$BrN
Calcd: 351.06225
Found: 351.06260

TLC: R$_f$ = 0.66 (hexanes/EtOAc, 3:1) [UV]
Preparation of \(N_2 \text{,} N\text{-Dibenzyl-2-chloroaniline (3b)}\)

2-Chloroanilide **S10** (0.55 g, 1.71 mmol) was weighed into an oven-dried, 10-mL, round-bottomed flask under \(\text{N}_2\), followed by a small amount of anhydrous THF (1 mL). The concentrated solution was cooled to 0 °C and a 1.0 M solution of BH\(_3\) in THF (3.42 mL, 3.42 mmol, 2.0 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 12 h, the reaction mixture was diluted with Et\(_2\)O (20 mL) and quenched by the careful and dropwise addition of sat. aq. NaHCO\(_3\) solution (5 mL) and was stirred for 1 h. The mixture was transferred to a 60-mL separatory funnel whereupon the aqueous phase was discarded and the organic phase was washed with sat. aq. sodium potassium tartrate solution (2 x 30 mL portions), 10% aq. Na\(_2\)CO\(_3\) solution (2 x 20 mL portions), and brine (20 mL), dried over anhydrous Na\(_2\)SO\(_4\) (1 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a thick, translucent oil (0.50 g) after further drying under high vacuum (0.1 mm Hg). The crude product was purified by silica gel flash chromatography (~25 g silica gel (70 x 30 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.49 g (1.60 mmol, 94%) of the title product **3b** as a clear, viscous, colorless oil after warm drying under high vacuum (80 °C, 0.1 mm Hg).

**Data for 3b:**

\(^1\text{H NMR:}\) (600 MHz, CDCl\(_3\), 23 °C)
\[\delta 7.47 (d, J = 8.1 \text{ Hz}, 1\text{H}, \text{HC}(3)), 7.41 (d, J = 7.6 \text{ Hz}, 4\text{H}, \text{HC}(3')), 7.35 (t, J = 7.4 \text{ Hz}, 4\text{H}, \text{HC}(4')), 7.29 (t, J = 7.2 \text{ Hz}, 2\text{H}, \text{HC}(5')), 7.13 (t, J = 7.6 \text{ Hz}, 1\text{H}, \text{HC}(5)), 7.00 (m, 2\text{H}, \text{HC}(\text{6 then 4})), 4.29 (s, 4\text{H}, \text{H}_2\text{C}(1'))\]

\(^{13}\text{C NMR:}\) (151 MHz, CDCl\(_3\), 23 °C)
\[\delta 147.65 (\text{C}(1)), 138.19 (\text{C}(2')), 130.73 (\text{C}(3)), 130.23 (\text{C}(2)), 128.59 (\text{C}(3')), 128.33 (\text{C}(4')), 127.11 (\text{C}(5')), 127.04 (\text{C}(5)), 124.05 (\text{C}(4)), 123.97 (\text{C}(6)), 56.19 (\text{C}(1'))\]
**IR:** (neat)

3085 (w), 3062 (w), 3027 (w), 2934 (w), 2887 (w), 2839 (w), 2806 (w), 2740 (w), 2708 (w), 2328 (w), 2103 (w), 1947 (w), 1870 (w), 1809 (w), 1747 (w), 1602 (w), 1587 (w), 1494 (m), 1478 (m), 1453 (m), 1440 (m), 1363 (w), 1325 (w), 1289 (w), 1269 (w), 1242 (w), 1208 (w), 1177 (w), 1156 (w), 1139 (w), 1117 (m), 1073 (w), 1060 (w), 1040 (m), 1029 (m), 1002 (w), 952 (w), 934 (w), 904 (w), 848 (w), 822 (w), 787 (w), 757 (m), 731 (s), 724 (s), 696 (s), 679 (m), 640 (w), 621 (w), 608 (w), 586 (w), 559 (w), 540 (w), 513 (w), 484 (w), 461 (w)

**MS:** (EI⁺, TOF)

215.0 ([M – CH₂(C₆H₅)]⁺, 22), 216.0 ([M – CH₂(C₆H₅)]⁺, 58), 217.0 ([M – CH₂(C₆H₅)]⁺, 20), 218.0 ([M – CH₂(C₆H₅)]⁺, 22), 230.0 (26), 232.0 (6), 307.1 ([M⁺, 64), 308.1 ([M⁺, 28), 309.1 ([M⁺, 32)

**HRMS:** (EI⁺, TOF) [M⁺] Calcd for C₂₀H₁₈ClN

Calcd: 307.11277

Found: 307.11283

**TLC:** Rᵢ = 0.63 (hexanes/EtOAc, 3:1) [UV]

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**Preparation of N,N-Dibenzyl-2-iodoaniline (3c)**

![Chemical Structure](image)

2-Iodoaniline (0.33 g, 1.51 mmol) was weighed into a dram vial, followed by the addition of anhydrous DMF (1 mL), distilled i-PrEt₂N (0.79 mL, 4.52 mmol, 3.0 equiv), and benzyl bromide (0.45 mL, 3.77 mL, 2.5 equiv). The vial was tightly capped and placed in a pre-heated aluminum heating block (120 °C). After 18 h, the vial was removed and allowed to cool to the ambient temperature (23 °C). The reaction mixture was quenched with the addition of Et₃N (0.5 mL), and after 10 h was diluted with hexanes/EtOAc, 1:1 (30 mL). The mixture was transferred to
a 60-mL separatory funnel and washed with water (3 x 30 mL portions), 10% aq. Na₂CO₃ solution (30 mL), and brine (30 mL), dried over anhydrous Na₂SO₄ (3 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a dark yellow oil (0.64 g). The crude product was purified by silica gel flash chromatography (~40 g silica gel (60 x 30 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to give a yellow oil (0.50 g) that was further purified by Kugelrohr distillation (220 °C (ABT), 0.1 mm Hg) to afford 0.45 g (1.13 mmol, 75%) of N,N-dibenzyl-2-iodoaniline 3c as a clear, viscous, subtly yellow oil.

Data for 3c:

b.p.: 220 °C (ABT), 0.1 mm Hg

¹H NMR: (600 MHz, CDCl₃, 23 °C)
δ 7.92 (dd, J = 7.8, 1.5 Hz, 1H, HC(3)), 7.39 (d, J = 7.4 Hz, 4H, HC(3′)), 7.33 (t, J = 7.5 Hz, 4H, HC(4′)), 7.27 (d, J = 7.3 Hz, 2H, HC(5′)), 7.21 (td, J = 7.6, 1.5 Hz, 1H, HC(5)), 6.92 (dd, J = 8.0, 1.4 Hz, 1H, HC(6)), 6.80 (td, J = 7.6, 1.5 Hz, 1H, HC(4)), 4.18 (s, 4H, H₂C(1′))

¹³C NMR: (151 MHz, CDCl₃, 23 °C)
δ 151.64 (C(1)), 140.20 (C(3)), 137.78 (C(2′)), 129.03 (C(3′)), 128.61 (C(5)), 128.26 (C(4′)), 127.16 (C(5′)), 125.87 (C(4)), 124.67 (C(6)), 99.86 (C(2)), 57.14 (C(1′))

IR: (neat)
3084 (w), 3060 (w), 3027 (w), 2925 (w), 2839 (w), 2052 (w), 1948 (w), 1869 (w), 1810 (w), 1602 (w), 1579 (w), 1494 (m), 1468 (s), 1453 (m), 1434 (m), 1364 (w), 1322 (w), 1265 (w), 1205 (w), 1157 (w), 1131 (w), 1105 (w), 1074 (w), 1053 (w), 1029 (w), 1012 (m), 951 (w), 905 (w), 822 (w), 782 (w), 761 (m), 745 (m), 731 (m), 720 (m), 697 (s), 649 (w), 621 (w), 609 (w), 586 (w), 560 (w), 534 (w), 497 (w), 460 (w)

MS: (EI⁺, TOF)
180.1 (100), 181.1 (38), 182.1 (7), 184.0 (76), 185 (9), 186.0 (75), 200.0 (12), 203.0 (9), 227 (18), 229.0 (19), 240.0 (32), 242.1 (32), 272.2 ([M – (C₆H₅)CH₂]⁺, 42), 283.1 (10), 308.0 ([M – I]⁺, 23), 322.0 (12), 399.1 ([M]⁺, 63), 400.1 ([M]⁺, 14)
HRMS: (EI⁺, TOF) [M]⁺ Calcd for C₂₀H₁₈NI
Calcd: 399.04842
Found: 399.04807

TLC: R₉ = 0.67 (hexanes/EtOAc, 3:1) [UV]

Preparation of N,N-Dibenzyl-2-iodoaniline (3d)

2-Bromoaniline (1.78 g, 10.35 mmol) was weighed into a 25-mL pressure tube, followed by the addition of anhydrous DMF (10 mL), distilled i-PrEt₂N (5.41 mL, 31.04 mmol, 3.0 equiv), and n-butyl bromide (2.79 mL, 25.87 mL, 2.5 equiv). The tube was tightly capped and placed in a pre-heated oil bath (120 °C). After 48 h, the vial was removed and allowed to cool to the ambient temperature (23 °C). The reaction mixture was diluted with hexanes/EtOAc, 1:1 (100 mL). The mixture was transferred to a 250-mL separatory funnel and washed with water (3 x 100 mL portions), 10% aq. Na₂CO₃ solution (100 mL), and brine (100 mL), dried over anhydrous Na₂SO₄ (3 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a dark yellow liquid (3.35 g). The crude product was purified by silica gel flash chromatography (~70 g silica gel (100 x 30 mm silica bed), 99:1 hexanes/CH₂Cl₂ isocratic elution, 50 mL fractions) to give a clear liquid (2.46 g) that was further purified by Kugelrohr distillation (110 °C (ABT), 0.1 mm Hg) to afford 2.45 g (8.62 mmol, 83%) of N,N-di(n-butyl)-2-bromoaniline 3d as a clear, colorless liquid.

Data for 3d:

b.p.: 110 °C (ABT), 0.1 mm Hg

¹H NMR: (600 MHz, CDCl₃, 25 °C)
δ 7.59 (dd, J = 7.9, 1.1 Hz, 1H, H₃C(3)), 7.26 (t, J = 7.6 Hz, 1H, H₃C(5)), 7.14 (dd, J = 8.0, 1.1 Hz, 1H, H₃C(6)), 6.91 (t, J = 7.6 Hz, 1H, H₃C(4)), 3.10 – 3.04 (m, 4H, H₂C(1’)), 1.47 (p, J = 7.5 Hz, 4H, H₂C(2’)), 1.39 – 1.29 (m, 4H, H₂C(3’)), 0.95 – 0.88 (m, 6H, H₃C(4’))
\[ ^{13}C \text{NMR:} \quad (151 \text{ MHz, CDCl}_3, 23 \degree \text{C}) \]
\[ \delta 149.82 \text{ (C(1))}, 133.82 \text{ (C(3))}, 127.58 \text{ (C(5))}, 124.35 \text{ (C(6))}, 124.30 \text{ (C(4))}, 122.45 \text{ (C(2))}, 53.31 \text{ (C(1'))}, 29.29 \text{ (C(2'))}, 20.49 \text{ (C(3'))}, 14.11 \text{ (C(4'))} \]

IR:  
(neat)  
3059 (w), 2956 (m), 2930 (w), 2871 (w), 2862 (w), 2815 (w), 2075 (w), 2036 (w), 1900 (w), 1771 (w), 1584 (w), 1473 (m), 1436 (w), 1377 (w), 1335 (w), 1280 (w), 1251 (w), 1210 (w), 1165 (w), 1118 (w), 1095 (w), 1048 (w), 1027 (m), 974 (w), 927 (w), 900 (w), 853 (w), 755 (m), 726 (m), 653 (w), 597 (w), 570 (w), 517 (w), 485 (w),

MS:  
(EI\(^\pm\), TOF)  
184.0 (79), 186.0 (73), 198.0 (40), 200.0 (38), 240.0 (100), 241.0 (22), 242.0 (99), 243.0 (21), 283.1 ([M]\(^{\pm}\), 16), 285.1 ([M]\(^{\pm}\), 15)

HRMS:  
(EI\(^\pm\), TOF) [M]\(^{+}\) Calcd for C\(_{14}\)H\(_{22}\)NBr  
Calcd: 283.09355  
Found: 283.09416

TLC:  
R\(_f\) = 0.38 (silica gel, 19:1 hexanes/CH\(_2\)Cl\(_2\), UV)

### Preparation of N-Benzyl-4-bromoaniline (4a)

![Reaction Scheme](attachment:image.png)

The 4-bromoanilide S\(_1\) (0.51 g, 1.85 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask, under N\(_2\). Anhydrous THF (5 mL) was added to this, and the solution was cooled to 0 °C. A 1.0 M solution of BH\(_3\) in THF (3.69 mL, 3.69 mmol, 2.0 equiv) was added dropwise. This was stirred for 1 h, until all of the thick anilide oil was fully dissolved, at which point the cooling bath was removed and the reaction mixture was stirred at 23 °C. After 12 h, the reaction mixture was diluted with Et\(_2\)O (50 mL) and quenched by the careful and dropwise addition of sat. aq. NaHCO\(_3\) solution (5 mL). This mixture was stirred for 1 h, after which the aqueous later was discarded and the mixture was transferred to a 125-mL separatory funnel. The organic phase was washed with sat. aq. sodium potassium tartrate solution (2 x 50 mL portions), 10% aq. Na\(_2\)CO\(_3\)
solution (2 x 50 mL portions), and brine (50 mL), dried over anhydrous Na$_2$SO$_4$ (2 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a thick, yellow oil (0.51 g). The crude product was purified by silica gel flash chromatography (~60 g silica gel (165 x 30 mm silica bed), 19:1 hexanes/EtOAc, 25 mL fractions) to afford 0.42 g (1.59 mmol, 86%) of monobenzylated 4-bromoaniline 4a as a thick, clear, colorless oil after drying under high vacuum (0.1 mm Hg).

**Data for 4a:**

**$^1$H NMR:** (600 MHz, CDCl$_3$, 20 °C)

δ 7.41 – 7.35 (m, 4H, HC(4 then 3)), 7.32 (tt, $J = 5.9, 2.7$ Hz, 1H, HC(5)), 7.27 (d, $J = 8.9$ Hz, 2H, HC(3)), 6.52 (d, $J = 8.9$ Hz, 2H, HC(2)), 4.32 (d, $J = 3.7$ Hz, 2H, H$_2$C(1’)), 4.10 (s, 1H, HN)

**$^{13}$C NMR:** (151 MHz, CDCl$_3$, 20 °C)

δ 147.13 (C(1)), 138.95 (C(2’)), 132.01 (C(3)), 128.79 (C(4’)), 127.46 (C(3’ and 5’)), 114.50 (C(2)), 109.16 (C(4)), 48.28 (C(1’))

**IR:** (neat)

3650 (w), 3425 (w), 3085 (w), 3062 (w), 3028 (w), 2922 (w), 2851 (w), 2710 (w), 2577 (w), 2302 (w), 2069 (w), 1953 (w), 1866 (w), 1809 (w), 1743 (w), 1592 (s), 1493 (s), 1470 (m), 1452 (m), 1398 (w), 1359 (w), 1320 (m), 1293 (m), 1265 (m), 1246 (m), 1178 (m), 1156 (w), 1122 (w), 1068 (m), 1028 (w), 999 (w), 945 (w), 913 (w), 811 (s), 731 (s), 696 (s), 642 (w), 596 (w), 564 (w), 502 (m), 458 (m)

**MS:** (EI$^+$, TOF)

261.0 ([M$^+$], 34), 262.1 ([M$^+$], 30)

**HRMS:** (EI$^+$, TOF) [M$^+$] Calcd for C$_{13}$H$_{12}$NBr

Calcd: \[ 261.01530 \]

Found: \[ 261.01415 \]

**TLC:** $R_f = 0.62$ (hexanes/EtOAc, 3:1) [UV]
Preparation of N-Benzyl-4-chloroaniline (4b)

Following General Procedure IV, anilide S3 (0.59 g, 2.55 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with N₂ and the flask was capped with a septum. A small volume of anhydrous THF (5 mL) was added to dissolve the anilide, and a 1.0 M BH₃·THF solution (5.09 mL, 5.09 mmol, 2.0 equiv) was added, which elicited modest warming. The reaction mixture was stirred at 23 °C. After 12 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (3 mL). The reaction mixture was then worked up as described in General Procedure IV to give a yellow liquid (0.59 g). The crude product was purified by silica gel flash chromatography (~35 g silica gel (50 x 30 mm silica bed), 99:1 hexanes/CH₂Cl₂ isocratic elution, 25 mL fractions) to afford 0.49 g (2.24 mmol, 87%) of N-benzyl-4-chloroaniline 4b as clear, colorless liquid.

Data for 4b:

**¹H NMR:** (600 MHz, CDCl₃, 23 °C)
δ 7.46 – 7.39 (m, 4H, HC(3’ and 4’)), 7.38 – 7.31 (m, 1H, HC(5’)), 7.17 (d, J = 8.6 Hz, 2H, HC(3)), 6.58 (d, J = 8.6 Hz, 2H, HC(2)), 4.34 (s, 2H, H₂C(1’)), 4.09 (s, 1H, HN)

**¹³C NMR:** (151 MHz, CDCl₃, 23 °C)
δ 146.71 (C(1)), 139.01 (C(2’)), 129.12 (C(4’)), 128.76 (C(3)), 127.46 (C(3’)), 127.42 (C(5’)), 122.08 (C(4)), 113.98 (C(2)), 48.35 (C(1’))

**IR:**
(neat)
3661 (w), 3426 (w), 3085 (w), 3063 (w), 3028 (w), 2922 (w), 2852 (w), 2712 (w), 2580 (w), 2299 (w), 2102 (w), 1951 (w), 1865 (w), 1809 (w), 1770 (w), 1759 (w), 1599 (m), 1496 (s), 1470 (m), 1452 (m), 1401 (w), 1360 (w), 1321 (m), 1295 (m), 1264 (m), 1246 (m), 1177 (m), 1157 (w), 1122 (w), 1095 (w), 1087 (w), 1069 (w), 1028 (w), 1003 (w), 991 (w), 944 (w), 914 (w), 813 (s), 732 (s), 697 (s), 676 (w), 632 (w), 616 (w), 578 (w), 505 (m), 459 (m)
**Preparation of N-Benzyl-2-bromoaniline (5a)**

Following General Procedure IV, anilide **S4** (1.00 g, 1.56 mmol) was weighed into an oven-dried, 50-mL, round-bottomed flask. The headspace was purged with argon or N₂ and the flask was capped with a septum. The anilide was dissolved in a small volume of anhydrous THF (4 mL), and a 1.0 M BH₃·THF solution (11.30 mL, 11.30 mmol, 2.0 equiv) was added, resulting in modest warming. The reaction mixture was stirred at 23 °C. After 12 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (8 mL). The reaction mixture was then worked up as described in General Procedure IV with doubled volumes, to give a cloudy, colorless oil (1.15 g). The crude product was purified by silica gel flash chromatography (~180 g silica gel (145 x 40 mm), 19:1 hexanes/EtOAc, 125 mL fractions) to afford 0.72 g (2.74 mmol, 48%) of N-benzyl-2-bromoaniline **5a** as a clear, colorless oil after drying under high vacuum (80 °C, 0.1 mm Hg).
**Data for 5a:**

**$^1$H NMR:** (600 MHz, CDCl$_3$, 23 °C)
$\delta$ 7.49 (dd, $J = 7.8$, 1.2 Hz, 1H, HC(3)), 7.44 – 7.37 (m, 4H, HC(3’ and 4’)),
7.33 (td, $J = 6.0$, 2.5 Hz, 1H, HC(5’)), 7.17 (t, $J = 7.7$ Hz, 1H, HC(5)), 6.65 (d,
$J = 8.1$ Hz, 1H, HC(6)), 6.62 (t, $J = 7.6$ Hz, 1H, HC(4)), 4.81 (bs, 1H, HN),
4.44 (d, $J = 5.4$ Hz, 2H, H$_2$C(1’))

**$^{13}$C NMR:** (151 MHz, CDCl$_3$, 23 °C)
$\delta$ 144.88 (C(1)), 138.78 (C(2’)), 132.48 (C(3)), 128.83 (C(3’)), 128.59 (C(5)),
127.44 (C(5’)), 127.32 (C(4’)), 118.07 (C(4)), 111.72 (C(6)), 109.77 (C(2)),
48.08 (C(1’))

**IR:**
(neat)
3628 (w), 3415 (w), 3062 (w), 3028 (w), 2924 (w), 2855 (w), 2583 (w), 2526 (w), 2323 (w), 2115 (w), 1948 (w), 1921 (w), 1882 (w), 1807 (w), 1753 (w),
1667 (w), 1595 (s), 1507 (s), 1495 (s), 1470 (w), 1451 (m), 1427 (m), 1361 (w), 1321 (m), 1293 (m), 1262 (w), 1234 (w), 1194 (w), 1175 (w), 1161 (w),
1128 (w), 1089 (w), 1067 (m), 1045 (w), 1018 (s), 989 (w), 923 (w), 901 (w),
862 (w), 832 (w), 801 (w), 730 (s), 695 (s), 670 (m), 658 (m), 626 (w), 614 (w), 539 (w), 514 (m), 456 (m),

**MS:**
(EI$^+$, TOF)
180.1 (24), 181.1 (6), 182.1 ([M – Br]$^+$, 11), 183.1 ([M – Br]$^+$, 2), 184.0 (15),
185.0 (2), 186.0 (12), 260.0 ([M]$^+$, 24), 261.0 ([M]$^+$, 100), 262.0 ([M]$^+$, 35),
263.0 ([M]$^+$, 97), 264.0 ([M]$^+$, 14)

**HRMS:**
(EI$^+$, TOF) [M]$^+$ Calcd for C$_{13}$H$_{12}$NBr
Calcd: 261.01530
Found: 261.01488

**TLC:**
$R_f$ = 0.64 (hexanes/EtOAc, 3:1) [UV]
Preparation of N-Benzyl-2-chloroaniline (5b)

Following General Procedure IV, anilide S5 (0.52 g, 2.24 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with argon and the flask was capped with a septum. A small volume of anhydrous THF (2 mL) was added to dissolve the anilide, and a 1.0 M BH$_3$·THF solution (4.49 mL, 4.49 mmol, 2.0 equiv) was added, which elicited modest warming. The reaction mixture was stirred at 23 °C. After 14 h, the reaction mixture was diluted with Et$_2$O (30 mL) and quenched by the careful addition of sat. aq. NaHCO$_3$ solution (3 mL). The reaction mixture was then worked up as described in General Procedure IV to give a cloudy, colorless liquid (0.47 g). The crude product was purified by silica gel flash chromatography (~50 g silica gel (70 x 30 mm silica bed), 39:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.37 g (1.68 mmol, 75%) of N-benzyl-2-chloroaniline 5b as clear, colorless oil.

Data for 5b:

$^1$H NMR: (600 MHz, CDCl$_3$, 23 °C)
$\delta$ 7.51 – 7.44 (m, 4H, HC(3’ and 4’)), 7.43 – 7.37 (m, 2H, HC(3 and 5’)), 7.20 (t, $J = 8.3$ Hz, 1H, HC(5)), 6.79 – 6.72 (m, 2H, HC(4 and 6)), 4.86 (bs, 1H, HN), 4.48 (d, $J = 5.6$ Hz, 2H, H$_2$C(1’))

$^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)
$\delta$ 143.90 (C(1)), 138.80 (C(2’)), 129.16 (C(3)), 128.77 (C(3’)), 127.88 (C(5)), 127.40 (C(5’)), 127.30 (C(4’)), 119.14 (C(2)), 117.48 (C(4)), 111.58 (C(6)), 47.85 (C(1’))

IR: (neat)
3424 (w), 3063 (w), 3030 (w), 2926 (w), 2848 (w), 2619 (w), 2528 (w), 2324 (w), 2115 (w), 1950 (w), 1923 (w), 1882 (w), 1770 (w), 1759 (w), 1668 (w), 1597 (s), 1510 (s), 1502 (s), 1470 (w), 1461 (m), 1452 (m), 1430 (m), 1384 (w), 1361 (w), 1323 (m), 1294 (m), 1278 (w), 1240 (m), 1193 (w), 1177 (w),
1161 (w), 1133 (w), 1093 (w), 1068 (m), 1047 (w), 1033 (s), 1002 (w), 989 (w), 923 (w), 834 (w), 805 (w), 732 (s), 696 (s), 683 (m), 628 (w), 614 (w), 544 (w), 518 (w), 457 (m)

**MS:** (EI⁺, TOF)

111.0 (8), 140.0 (21), 180.1 (12), 216.1 ([M⁺], 37), 217.2 ([M⁺], 100), 218.1 ([M⁺], 31), 219.1 ([M⁺], 48)

**HRMS:** (EI⁺, TOF) [M⁺] Calcd for C₁₃H₁₂NCl

Calcd: 217.06582
Found: 217.06616

**TLC:** Rf = 0.58 (hexanes/EtOAc, 3:1) [UV]

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**Preparation of N,N-Dibenzyl-2,4-dibromoaniline (6a)**

![Diagram](image.png)

2,4-Dibromoanilide S11 (0.65 g, 1.46 mmol) was weighed into an oven-dried, 10 mL, round-bottomed flask under N₂, followed by a small amount of anhydrous THF (3 mL). The solution was cooled to 0 °C and a 1.0 M solution of BH₃ in THF (2.92 mL, 2.92 mmol, 2.0 equiv) was added dropwise. The cooling bath was removed and the reaction mixture was stirred at 23 °C. After 14 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful and dropwise addition of sat. aq. NaHCO₃ solution (5 mL) and was stirred for 1 h. The aqueous phase was discarded and the mixture was transferred to a 60-mL separatory funnel. The organic phase was washed with sat. aq. sodium potassium tartrate solution (2 x 30 mL portions), 10% aq. Na₂CO₃
solution (2 x 20 mL portions), and brine (20 mL), dried over anhydrous Na$_2$SO$_4$ (1 g), decanted, and concentrated on a rotavap (30 °C, 15 mm Hg) to give a thick, translucent oil (0.61 g) after drying under high vacuum (0.1 mm Hg). The crude product was purified by silica gel flash chromatography (~20 g silica gel (60 x 30 mm silica bed), 19:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.58 g (1.35 mmol, 92%) of the title product 6a as a clear, viscous, colorless oil after warm drying under high vacuum (80 °C, 0.1 mm Hg). The product was further purified to analytical purity by Kugelrohr distillation (100 °C (ABT), 1.5 x 10^{-5} mm Hg) to give a clear, colorless, oil.

**Data for 6a:**

- **b.p.:** 100 °C (ABT), 1.5 x 10^{-5} mm Hg
- **$^1$H NMR:** (600 MHz, CDCl$_3$, 23 °C) $\delta$ 7.74 (d, $J = 2.2$ Hz, 1H, HC(3)), 7.34 – 7.27 (m, 8H, HC(3' then 4')), 7.26 – 7.21 (m, 3H, HC(5' then 5)), 6.77 (d, $J = 8.6$ Hz, 1H, HC(6)), 4.17 (s, 4H, H$_2$C(1'))
- **$^{13}$C NMR:** (151 MHz, CDCl$_3$, 23 °C) $\delta$ 148.12 (C(1)), 137.62 (C(2')), 136.16 (C(3)), 130.72 (C(5)), 128.67 (C(3')), 128.43 (C(4')), 127.31 (C(5')), 125.67 (C(6)), 122.19 (C(2)), 116.56 (C(4)), 56.53 (C(1))
- **IR:** (neat) 3418 (w), 3084 (w), 3061 (w), 3026 (w), 2933(w), 2885 (w), 2805 (w), 2708 (w), 2313 (w), 2113 (w), 1948 (w), 1872 (w), 1808 (w), 1744 (w), 1603 (w), 1585 (w), 1574 (w), 1548 (w), 1494 (m), 1469 (s), 1452 (m), 1362 (m), 1324 (w), 1289 (w), 1265 (w), 1257 (w), 1238 (w), 1206 (m), 1196 (m), 1178 (w), 1149 (w), 1119 (w), 1085 (w), 1074 (w), 1045 (m), 1028 (m), 1002 (w), 950 (w), 903 (w), 867 (w), 801 (m), 750 (m), 735 (s), 719 (m), 696 (s), 678 (m), 639 (w), 621 (w), 608 (m), 574 (w), 557 (m), 512 (w), 487 (w), 465 (m)
- **MS:** (EI⁺, TOF) 339.9 ([M – CH$_2$(C$_6$H$_5$)]⁺, 8), 352.0 ([M – Br]⁺, 8), 353.0 ([M – Br]⁺, 8), 428.9 ([M ]⁺, 8), 430.9 ([M]⁺, 16), 431.9 ([M]⁺, 6), 432.9 ([M]⁺, 8)
HRMS: (EI⁺, TOF) [M]+ Calcd for C₂₀H₁₇NBr₂
  
Calcd: 428.97280  
Found: 428.97287

TLC: Rₚ = 0.64 (hexanes/EtOAc, 3:1) [UV]

Analysis: C₂₀H₁₇Br₂N (431.17)  
  
Calcd: C, 55.71%; H, 3.97%; N, 3.25%  
Found: C, 55.93%; H, 4.07%; N, 3.25%

Preparation of N,N-Dibenzylaniline (6e)

Following General Procedure IV, anilide S7 (0.67 g, 2.30 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with N₂ and the flask was capped with a septum. The anilide was dissolved in a small volume of anhydrous THF (3 mL), and a 1.0 M BH₃·THF solution (4.59 mL, 4.59 mmol, 2.0 equiv) was added, resulting in modest warming. The reaction mixture was stirred at 23 °C. After 14 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (2 mL). The reaction mixture was then worked up as described in General Procedure IV to give an off-white solid (0.64 g). The crude product was purified by recrystallization from boiling anhydrous EtOH (3 mL), with cooling to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a filter without washing and dried under high vacuum to afford 0.51 g (1.87 mmol, 82%) of N,N-dibenzylaniline 6e as white crystals.

Data for 6e:

  m.p.: 62 – 64 °C  
  
¹H NMR: (600 MHz, CDCl₃, 20 °C)  
δ 7.37 (t, J = 7.5 Hz, 4H, HC(4’)), 7.31 (d, J = 6.6 Hz, 6H, HC(3 and 3’)), 7.22 (t, J = 8.0 Hz, 2H, HC(5’)), 6.80 (d, J = 8.0 Hz, 2H, HC(2)), 6.76 (t, J = 7.3 Hz, 1H, HC(4)), 4.71 (s, 4H, H₂C(1’))
$^{13}$C NMR: (151 MHz, CDCl$_3$, 20 °C)
\[ \delta 149.28 \text{(C(1))}, 138.71 \text{(C(2')), 129.34 \text{(C(3))}, 128.76 \text{(C(4'))}, 126.99 \text{(C(5'))}, 126.76 \text{(C(3'))}, 116.82 \text{(C(4))}, 112.54 \text{(C(2))}, 54.29 \text{(C(1'))} \]

IR: (neat)
3085 (w), 3061 (w), 3027 (w), 2906 (w), 2863 (w), 2620 (w), 2517 (w), 1987 (w), 1949 (w), 1862 (w), 1811 (w), 1752 (w), 1597 (s), 1575 (w), 1505 (s), 1494 (s), 1451 (m), 1436 (w), 1394 (m), 1358 (m), 1328 (w), 1296 (w), 1275 (w), 1257 (w), 1229 (m), 1201 (m), 1163 (w), 1108 (w), 1074 (w), 1028 (w), 1002 (w), 989 (w), 956 (m), 898 (w), 864 (w), 847 (w), 791 (w), 747 (s), 728 (s), 693 (s), 641 (w), 616 (w), 527 (w), 510 (w), 458 (w)

MS: (EI$^+$, TOF)
180.1 (17), 181.1 (22), 182.1 ([M − Bn]$^+$, 43), 183.1 ([M − Bn]$^+$, 49), 196.1 ([M − (C$_6$H$_5$)]$^+$, 33), 217.1 (8), 273.2 ([M]$^+$, 100), 274.2 ([M]$^+$, 22)

HRMS: (EI$^+$, TOF) [M]$^+$ Calcd for C$_{20}$H$_{19}$N
Calcd: 273.15175
Found: 273.15118

TLC: $R_f = 0.66$ (hexanes/EtOAc, 3:1) [UV]

**Preparation of N-Benzyl-2,4-dibromoaniline (7a)**

Following General Procedure IV, anilide S6 (0.59 g, 1.65 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with N$_2$ and the flask was capped with a septum. A small volume of anhydrous THF (4 mL) was added to dissolve the anilide, and a 1.0 M BH$_3$·THF solution (3.30 mL, 3.30 mmol, 2.0 equiv) was added, which elicited modest warming. The reaction mixture was stirred at 23 °C. After 14 h, the reaction mixture was diluted with Et$_2$O (30 mL) and quenched by the careful addition of sat. aq. NaHCO$_3$ solution (3 mL). The reaction mixture was then worked up as described in General Procedure IV to give a cloudy, colorless oil (0.57 g). The crude product was purified by silica gel flash chromatography (~105 g
silica gel (150 x 30 mm silica bed), 39:1 hexanes/EtOAc isocratic elution, 25 mL fractions) to afford 0.45 g (1.33 mmol, 81%) of N-benzyl-2,4-dibromoaniline 7a as a clear, colorless oil.

Data for 7a:

$^1$H NMR: (600 MHz, CDCl$_3$, 23 °C)
δ 7.59 (d, $J = 2.2$ Hz, 1H, HC(3)), 7.42 – 7.35 (m, 4H, HC(3’ and 4’)), 7.32 (t, $J = 6.9$ Hz, 1H, HC(5’)), 7.23 (dd, $J = 8.7$, 2.2 Hz, 1H, HC(5)), 6.48 (d, $J = 8.7$ Hz, 1H, HC(6)), 4.81 (s, 1H, HN), 4.39 (d, $J = 5.6$ Hz, 2H, $H_2$C(1’))

$^{13}$C NMR: (151 MHz, CDCl$_3$, 23 °C)
δ 143.98 (C(1)), 138.20 (C(2’)), 134.36 (C(4)), 131.30 (C(5)), 128.89 (C(3’)), 127.59 (C(5’)), 127.23 (C(4’)), 112.72 (C(6)), 109.96 (C(2)), 108.37 (C(4)), 48.04 (C(1’))

IR: (neat)
3413 (w), 3170 (w), 3085 (w), 3063 (w), 3029 (w), 2923 (w), 2854 (w), 2706 (w), 2585 (w), 2504 (w), 2317 (w), 2247 (w), 2114 (w), 1947 (w), 1860 (w), 1806 (w), 1732 (w), 1587 (m), 1559 (w), 1494 (s), 1468 (m), 1453 (m), 1441 (m), 1387 (m), 1357 (m), 1319 (m), 1297 (m), 1273 (m), 1266 (m), 1230 (w), 1195 (w), 1177 (w), 1150 (w), 1092 (w), 1067 (m), 1027 (m), 1002 (w), 989 (w), 907 (w), 867 (m), 818 (w), 797 (s), 731 (s), 706 (m), 695 (s), 678 (m), 639 (w), 620 (m), 611 (m), 576 (w), 540 (m), 458 (m)

MS: (EI⁺, TOF)

HRMS: (EI⁺, TOF) [M]⁺ Calcd for C$_{13}$H$_{11}$NBr$_2$
Calcd: 338.92585
Found: 338.92514

TLC: $R_f$ = 0.65 (hexanes/EtOAc, 3:1) [UV]
Preparation of N-Benzylaniline (7e)

Following General Procedure IV, anilide S2 (0.37 g, 1.89 mmol) was weighed into an oven-dried, 25-mL, round-bottomed flask. The headspace was purged with N₂ and the flask was capped with a septum. A small volume of anhydrous THF (3 mL) was added to dissolve the anilide, and a 1.0 M BH₃·THF solution (3.77 mL, 3.77 mmol, 2.0 equiv) was added, which elicited modest warming. The reaction mixture was stirred at 23 °C. After 14 h, the reaction mixture was diluted with Et₂O (30 mL) and quenched by the careful addition of sat. aq. NaHCO₃ solution (3 mL). The reaction mixture was then worked up as described in General Procedure IV to give an off-white solid (0.37 g). The crude product was purified by recrystallization from boiling anhydrous EtOH (2 mL), with cooling to 23 °C then -20 °C in a freezer. The resulting crystals were collected over a filter and dried under high vacuum (0.1 mm Hg) to afford 0.31 g (1.66 mmol, 88%) of N-benzylaniline 7e as white microcrystals.

Data for 7e:

- m.p.: 38 – 39 °C
- ¹H NMR: (600 MHz, CDCl₃, 23 °C)
  δ 7.40 (d, J = 7.4 Hz, 2H, HC(3')), 7.37 (t, J = 7.5 Hz, 2H, HC(4')), 7.30 (t, J = 7.1 Hz, 1H, HC(5')), 7.20 (t, J = 7.9 Hz, 2H, HC(3)), 6.74 (t, J = 7.3 Hz, 1H), 6.66 (d, J = 7.7 Hz, 2H, HC(4)), 4.35 (s, 2H, HC(2)), 4.04 (s, 1H, H₂C(1'))
- ¹³C NMR: (151 MHz, CDCl₃, 23 °C)
  δ 148.26 (C(1)), 139.55 (C(2')), 129.39 (C(3)), 128.76 (C(4')), 127.63 (C(3')), 127.35 (C(5')), 117.68 (C(4)), 112.95 (C(2)), 48.44 (C(1'))
- IR: (neat)
  3419 (w), 3084 (w), 3052 (w), 3026 (w), 2920 (w), 2841 (w), 2575 (w), 1920 (w), 1818 (w), 1767 (w), 1683 (w), 1601 (s), 1505 (s), 1472 (w), 1453 (m), 1430 (w), 1360 (w), 1324 (m), 1298 (w), 1267 (w), 1252 (w), 1180 (w), 1154 (w), 1114 (w), 1099 (w), 1077 (w), 1065 (w), 1028 (w), 990 (w), 913 (w), 869
Preparation of N,N-Dibenzyl-4-bromo-2-chloroaniline (9)

\[
\begin{align*}
\text{NBS (1.0 equiv),} \\
\text{DMF, 23 °C, 12 h} \\
\end{align*}
\]

N,N-Dibenzyl-2-chloroaniline 3b (0.70 g, 2.27 mmol) was weighed into a 25-mL, round-bottomed flask, followed by anhydrous DMF (15 mL) and NBS (0.23 g, 1.27 mmol, 1.2 equiv). The reaction mixture was stirred at 23 °C, over which time the solution became orange in color. After 12 h, the reaction mixture was diluted with EtOAc (60 mL) and the mixture was transferred to a 125-mL separatory funnel. The organic phase was washed with 10% aq. Na₂CO₃ solution (3 x 60 mL portions) and brine (60 mL), dried over anhydrous Na₂SO₄ (2 g), and concentrated on a rotavap (30 °C, 15 mm Hg) to give a red oil (0.93 g). The crude product was purified by silica gel flash chromatography (~70 g silica gel (100 x 30 mm silica bed), 19:1 CH₂Cl₂/hexanes, 25 mL fractions) to afford a clear, colorless oil (0.48 g) that was further purified by Kugelrohr distillation (120 °C (ABT), 1.3 x 10⁻⁵ mm Hg) to provide 0.47 g (1.22 mmol, 53%) of N,N-dibenzyl-4-bromo-2-chloroaniline 9 as a clear, colorless oil.
Data for 9:

b.p.: 120 °C (ABT), 1.3 x 10^{-5} mm Hg

{\textsuperscript{1}H NMR:} (600 MHz, CDCl\textsubscript{3}, 20 °C)
\[ \delta 7.56 \ (d, \ J = 2.3 \ Hz, 1H, HC(3)), \ 7.37 - 7.28 \ (m, 8H, HC(3' \ then \ 4')) \], 7.25 (t, \ J = 6.6 \ Hz, 2H, HC(5'))

{\textsuperscript{13}C NMR:} (151 MHz, CDCl\textsubscript{3}, 20 °C)
\[ \delta 146.84 \ (C(1)), \ 137.72 \ (C(2')), \ 133.20 \ (C(3)), \ 131.14 \ (C(2)), \ 130.09 \ (C(5)), \ 128.54 \ (C(3')), \ 128.44 \ (C(4')) \]

IR: (neat)
3386 (w), 3085 (w), 3062 (w), 3027 (w), 2936 (w), 2887 (w), 2806 (w), 2315 (w), 2072 (w), 1948 (w), 1870 (w), 1808 (w), 1743 (w), 1603 (w), 1578 (w), 1552 (w), 1494 (m), 1474 (s), 1452 (m), 1380 (w), 1362 (m), 1327 (w), 1290 (w), 1268 (w), 1257 (w), 1207 (m), 1197 (m), 1180 (w), 1155 (w), 1122 (w), 1085 (m), 1073 (w), 1059 (m), 1029 (w), 1002 (w), 950 (w), 905 (w), 867 (w), 805 (m), 736 (s), 722 (m), 696 (s), 645 (w), 622 (w), 608 (w), 576 (w), 559 (m), 526 (w), 490 (w), 466 (m), 452 (w).

MS: (EI\textsuperscript{+}, TOF)
293.9 ([M – CH\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsuperscript{+}, 20], 295.9 ([M – CH\textsubscript{2}(C\textsubscript{6}H\textsubscript{5})\textsuperscript{+}, 22], 385.0 ([M]\textsuperscript{+}, 40), 386.0 ([M]\textsuperscript{+}, 18), 387.0 ([M]\textsuperscript{+}, 52), 388.0 ([M]\textsuperscript{+}, 18), 389.0 ([M]\textsuperscript{+}, 18)

HRMS: (EI\textsuperscript{+}, TOF) [M]\textsuperscript{+} Calcd for C\textsubscript{20}H\textsubscript{17}BrClN
Calcd: 385.02280
Found: 385.02267

TLC: R\textsubscript{f} = 0.71 (hexanes/EtOAc, 3:1) [UV]

Analysis: C\textsubscript{20}H\textsubscript{17}BrClN (386.72)
Calcd: C, 62.12; H, 4.43; N, 3.62 %
Found: C, 62.35; H, 4.29; N, 3.50 %
Table 1, Entry 1

HNMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>32%</td>
</tr>
<tr>
<td>4a</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>3a</td>
<td>15%</td>
</tr>
<tr>
<td>5a</td>
<td>21%</td>
</tr>
</tbody>
</table>

0.50 mmol

BnBr (2.2 equiv), K₂CO₃ (3.0 equiv), DMF, 120 °C, 24 h

TMU Internal Standard
6.21 mg/mL CDCl₃
0.0535 mmol
### Table 1, Entry 1

$^{13}$CNMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>32%</td>
</tr>
<tr>
<td>4a</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>3a</td>
<td>15%</td>
</tr>
<tr>
<td>5a</td>
<td>21%</td>
</tr>
</tbody>
</table>

**Reaction Conditions:**
- BnBr (2.2 equiv), K$_2$CO$_3$ (3.0 equiv), DMF, 120 °C, 24 h

**TMU Internal Standard**
- 6.21 mg/mL CDCl$_3$
- 0.0535 mmol

**NMR Chart:**
- 148.10 (2a)
- 138.03 (2a)
- 131.93 (2a)
- 128.81 (2a)
- 126.58 (2a)
- 114.20 (2a)
- 77.37 CDCl$_3$
- 77.16 CDCl$_3$
- 76.95 CDCl$_3$
- 54.48 (2a)
- 38.69 TMU
Table 1, Entry 2

$^1$HNMR
Table 1, Entry 2

$^{13}$C NMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>147.92 (2a)</td>
</tr>
<tr>
<td>4a</td>
<td>137.69 (2a)</td>
</tr>
<tr>
<td>3a</td>
<td>131.80 (2a)</td>
</tr>
<tr>
<td>5a</td>
<td>128.73 (2a)</td>
</tr>
<tr>
<td>2a</td>
<td>127.05 (2a)</td>
</tr>
<tr>
<td>2a</td>
<td>126.45 (2a)</td>
</tr>
<tr>
<td>2a</td>
<td>114.10 (2a)</td>
</tr>
<tr>
<td>2a</td>
<td>77.37 CDCl₃</td>
</tr>
<tr>
<td>2a</td>
<td>77.16 CDCl₃</td>
</tr>
<tr>
<td>2a</td>
<td>76.95 CDCl₃</td>
</tr>
<tr>
<td>2a</td>
<td>54.38 (2a)</td>
</tr>
<tr>
<td>TMU</td>
<td>38.58 TMU</td>
</tr>
</tbody>
</table>

TMU Internal Standard:
6.41 mg/mL CDCl₃
0.0562 mmol
Table 1, Entry 3
\(^1\)HNMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>2e</th>
<th>4e</th>
<th>3e</th>
<th>5e</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50 mmol</td>
<td>9%</td>
<td>52%</td>
<td>22%</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

(6.50 (4e), 6.48 (4e))

2.25 (2e), 2.23 (4e), 3.10 (4e), 3.08 (TMU)

0.90 (2e)
Table 1, Entry 3

\[ ^{13}\text{C} \text{NMR} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
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<td>2e</td>
<td>9%</td>
</tr>
<tr>
<td>4e</td>
<td>52%</td>
</tr>
<tr>
<td>3e</td>
<td>22%</td>
</tr>
<tr>
<td>5e</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

**Reaction Conditions**

\[
\text{ArBrNH}_2 + (n-\text{Bu})\text{Br} (2.2 \text{ equiv}) \rightarrow \text{ArNBr}(n-\text{Bu}) \rightarrow \text{ArNBr}(n-\text{Bu}) \rightarrow \text{ArNBr}(n-\text{Bu}) \rightarrow \text{ArNBr}(n-\text{Bu})
\]

**Yield**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2e</td>
<td>9%</td>
</tr>
<tr>
<td>4e</td>
<td>52%</td>
</tr>
<tr>
<td>3e</td>
<td>22%</td>
</tr>
<tr>
<td>5e</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

**Chemical Shifts**

- 131.87 (4e)
- 113.43 (4e)
- 77.16 CDCl3
- 76.95 CDCl3
- 50.88 (4e)
- 29.34 (4e)
- 20.43 (4e)
- 14.12 (4e)
Table 1, Entry 4
$^1$HNMR

$\text{Br} \quad \text{BnCl (2.2 equiv.),} \quad \text{DMF, 120 °C, 24 h} \quad \text{Br}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0%</td>
</tr>
<tr>
<td>4a</td>
<td>0%</td>
</tr>
<tr>
<td>3a</td>
<td>53%</td>
</tr>
<tr>
<td>5a</td>
<td>32%</td>
</tr>
</tbody>
</table>

TMU Internal Standard

6.21 mg/mL CDCl$_3$

0.0535 mmol
Table 1, Entry 4

$^{13}$CNMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H (ppm)</th>
<th>$^{13}$C (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>77.37 (CDC3)</td>
<td>148.85 (3a)</td>
</tr>
<tr>
<td>4a</td>
<td>77.16 (CDC3)</td>
<td>138.02 (3a)</td>
</tr>
<tr>
<td>3a</td>
<td>76.95 (CDC3)</td>
<td>128.78 (5a)</td>
</tr>
<tr>
<td>5a</td>
<td></td>
<td>122.51 (5a)</td>
</tr>
</tbody>
</table>

BnCl (2.2 equiv.), DMF, 120 °C, 24 h

TMU Internal Standard

6.21 mg/mL CDCl$_3$

0.0535 mmol

0.50 mmol
Table 1, Entry 5

\[ \text{HNMR} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>90%</th>
<th>40%</th>
</tr>
</thead>
</table>

- 2: 0%
- 4: 0%
- 3b: 22%
- 5b: 40%

**Reaction Conditions:**
BnBr (2.2 equiv.), DMF, 120 °C, 24 h

**TMU Internal Standard:**
6.21 mg/mL CDCl₃
0.0535 mmol
Table 1, Entry 5

$^{13}$C NMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>147.55 (3b)</td>
</tr>
<tr>
<td>2</td>
<td>126.50 (3b)</td>
</tr>
<tr>
<td>3b</td>
<td>119.09 (3b)</td>
</tr>
<tr>
<td>4</td>
<td>127.27 (3b)</td>
</tr>
<tr>
<td>5b</td>
<td>111.54 (5b)</td>
</tr>
</tbody>
</table>

Reaction conditions:
BnBr (2.2 equiv), DMF, 120 °C, 24 h

Yields:
- 2: 0%
- 4: 0%
- 3b: 22%
- 5b: 40%

Internal Standard: TMU (38.64 ppm)
Table 1, Entry 6
$^1$HNMR

0.50 mmol of $\text{NH}_2$ reacts with BnBr (2.2 equiv) in DMF at 120 °C for 24 h, resulting in the formation of compounds 2a,c, 4a,c, 3a,c, and 5a,c.

The NMR spectrum shows peaks corresponding to these compounds. The TMU internal standard is used for comparison, with a concentration of 6.21 mg/mL in CDCl$_3$, 0.0535 mmol.
Table 1, Entry 6

$\text{C}^1\text{NMR}$

\begin{align*}
\text{ArNH}_2 & \xrightarrow{\text{BnBr (2.2 equiv),}} \xrightarrow{\text{DMF, 120 °C, 24 h}} \text{ArN}^\text{Bn} \\
& 0.50 \text{ mmol} \\
2\text{a,c} & 0\% \\
4\text{a,c} & 0\% \\
3\text{a,c} & 0\% \\
5\text{a,c} & 0\%
\end{align*}

- $77.37$ CDCl$_3$
- $77.16$ CDCl$_3$
- $76.95$ CDCl$_3$

- 38.65 TMU
Table 2, Entry 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ratio</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>1:9</td>
<td>0%</td>
</tr>
<tr>
<td>4a</td>
<td></td>
<td>0%</td>
</tr>
<tr>
<td>3a</td>
<td></td>
<td>83%</td>
</tr>
<tr>
<td>5a</td>
<td></td>
<td>12%</td>
</tr>
</tbody>
</table>

**HNMR**

- 4.41 (5a)
- 3.14 (3a)
- 2.83 TMU

**Conditions:** DMF, 120 °C, 24 h

**NMR Data:**
- 7.46 mg/mL CDCl₃, 0.0642 mmol
Table 2, Entry 1

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Product</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>DMF, 120 °C, 24 h</td>
<td>2a</td>
<td>0%</td>
</tr>
<tr>
<td>4a</td>
<td>DMF, 120 °C, 24 h</td>
<td>4a</td>
<td>0%</td>
</tr>
<tr>
<td>3a</td>
<td>DMF, 120 °C, 24 h</td>
<td>3a</td>
<td>83%</td>
</tr>
<tr>
<td>5a</td>
<td>DMF, 120 °C, 24 h</td>
<td>5a</td>
<td>12%</td>
</tr>
</tbody>
</table>

**CNMR**

- **77.37 ppm (3a)**
- **77.16 ppm (3a)**
- **76.95 ppm (3a)**
- **56.51 ppm (5a)**
- **48.05 ppm (5a)**
- **38.70 ppm (TMU)**

**Chemical Shifts**

- 148.87 (3a)
- 144.85 (5a)
- 138.74 (5a)
- 133.88 (3a)
- 132.45 (3a)
- 128.80 (3a)
- 128.68 (3a)
- 128.57 (3a)
- 127.41 (5a)
- 127.28 (5a)
- 127.09 (3a)
- 124.82 (3a)
- 124.55 (3a)
- 118.04 (5a)
- 111.70 (5a)
- 109.74 (5a)
Table 2, Entry 2

\[ \text{HNMR} \]

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>33%</td>
<td>4a</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>3a</td>
<td>21%</td>
<td>5a</td>
<td>43%</td>
</tr>
</tbody>
</table>

- **Overview**: Reactant (BF₃·Et₂O) reacts with benzylamine (0.51 mmol) in DMF at 120°C for 24 h to produce the following products:
  - **2a**: 33%
  - **4a**: <1%
  - **3a**: 21%
  - **5a**: 43%

- **Maximum Yield**: 7.46 mg/mL CDCl₃, 0.0642 mmol

- **Key Units**:
  - 4.68 (6e)
  - 4.64 (2a)
  - 4.41 (5a)
  - 4.37 (7a)
  - 4.30 (4a)
  - 4.22 (3a)
  - 4.19 (6a)

- **1H NMR Spectrum**:
  - **Integration**:
    - 2.83 (TMU)
    - 3.40 (7e)
    - 1.75 (3a)
    - 10.37 (7a)
    - 3.36 (3a)
    - 1.70 (7a)
    - 0.21 (2a)
    - 6.53 (2a)
    - 1.12 (7e)
    - 12.00 (TMU)

- **Spectrogram**:
  - The spectrogram shows various peaks at different ppm values, indicating the presence of various functional groups and their relative intensities.

- **Chemical Shifts**:
  - 3.40 ppm (7e)
  - 1.75 ppm (3a)
  - 10.37 ppm (7a)
  - 3.36 ppm (3a)
  - 1.70 ppm (7a)
  - 0.21 ppm (2a)
  - 6.53 ppm (2a)
  - 1.12 ppm (7e)
  - 12.00 ppm (TMU)
Table 2, Entry 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0.51 mmol</td>
<td>33%</td>
</tr>
<tr>
<td>4a</td>
<td>0.51 mmol</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>3a</td>
<td>0.51 mmol</td>
<td>21%</td>
</tr>
<tr>
<td>5a</td>
<td>0.51 mmol</td>
<td>43%</td>
</tr>
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</table>

TMS Internal Standard

{\text{H}^1}^3\text{C}NMR

\text{DMF, 120 °C, 24 h}

\begin{align*}
\text{148.86 (3a)} & \quad 148.11 (2a) \\
\text{144.94 (5a)} & \quad 138.74 (3a) \\
\text{138.03 (2a)} & \quad 132.44 (5a) \\
\text{131.94 (2a)} & \quad 128.81 (5a) \\
\text{128.56 (5a)} & \quad 128.67 (3a) \\
\text{128.28 (5a)} & \quad 127.40 (5a) \\
\text{127.14 (2a)} & \quad 127.08 (3a) \\
\text{126.59 (3a)} & \quad 127.40 (5a) \\
\text{124.54 (3a)} & \quad 121.52 (3a) \\
\text{118.03 (5a)} & \quad 114.21 (2a) \\
\text{111.70 (5a)} & \quad 109.73 (5a) \\
\text{108.67 (2a)} & \quad {77.37 \text{ CDC}13} \\
\text{77.16 \text{ CDC}13} & \quad 76.95 \text{ CDC}13 \\
\text{56.50 (3a)} & \quad 54.49 (2a) \\
\text{48.03 (5a)} & \quad 47.99 (7a) \\
\text{38.70 TMU} & \quad  \end{align*}
Table 2, Entry 3
$^1$HNMR

DMF, 120 °C, 24 h

0.51 mmol

2a  <1%
4a  0%
3a  0%
5a  26%

4.65 unknown (not 2a)
4.42 (5a)
4.39 (7a)
4.37 unknown (not 4a)
4.19 (6a)

2.83 TMU

7.46 mg/mL CDCl$_3$
0.0642 mmol
Table 2, Entry 3

\[
\begin{align*}
\text{\textsuperscript{13}C NMR} \\
\text{(7a)}
\end{align*}
\]

\[
\begin{align*}
\text{DMF, 120 °C, 24 h} \\
0.51 \text{ mmol} \\
\end{align*}
\]

\[
\begin{align*}
2a & \quad <1\% \\
3a & \quad 0\% \\
4a & \quad 0\% \\
5a & \quad 26\% \\
\end{align*}
\]
Table 2, Entry 4

\[ \text{HNMR} \]

\[ \begin{array}{c}
\text{DMF, } 120^\circ \text{C, } 24 \text{ h}
\end{array} \]

\[ \begin{array}{cccc}
\text{2a} & \text{4a} & \text{3a} & \text{5a} \\
0\% & 0\% & 56\% & 34\%
\end{array} \]

\[ \text{TMU Internal Standard} \]

\begin{align*}
6.21 \text{ mg/mL CDCl}_3 \\
0.0535 \text{ mmol}
\end{align*}
Table 2, Entry 4

$^1$H NMR

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>148.87 (5a)</td>
</tr>
<tr>
<td>4a</td>
<td>143.94 (5a)</td>
</tr>
<tr>
<td>3a</td>
<td>138.04 (5a)</td>
</tr>
<tr>
<td>5a</td>
<td>128.68 (5a)</td>
</tr>
<tr>
<td>77.37 CDCl3</td>
<td>77.16 CDCl3</td>
</tr>
</tbody>
</table>

TMU Internal Standard

6.21 mg/mL CDCl3
0.0535 mmol

f1 (ppm)
Table 3, Entry 1
$^1$HNMR, 600 MHz, CDCl$_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>0%</td>
</tr>
<tr>
<td>3a</td>
<td>82%</td>
</tr>
<tr>
<td>4a</td>
<td>0%</td>
</tr>
<tr>
<td>5a</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

$^{1}$HNMR: 600 MHz, CDCl$_3$

0.50 mmol

BnBr (2.2 equiv), DIPEA (3.0 equiv), DMF, 120 °C, 24 h

TMU Internal Standard
6.21 mg/mL CDCl$_3$
0.0535 mmol

---

NMR spectrum showing peaks at 1.23, 3.34, 5.03, and 12.00 ppm.
Table 3, Entry 1
\(^1\)HNMR, 600 MHz, CDCl\(_3\)

BnBr (2.2 equiv.), DIPEA (3.0 equiv.), DMF, 120 °C, 24 h

<table>
<thead>
<tr>
<th>Compound</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
<th>5a</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>0%</td>
<td>82%</td>
<td>0%</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

0.50 mmol

6.21 mg/mL CDCl\(_3\) 0.0535 mmol

TMU internal Standard
Time Course Study, $t = 0 \text{ h}$

$^1$H NMR, 600 MHz, CDCl$_3$

0.50 mmol

BnBr (2.2 equiv), DMF, 120 °C, 24 h
Time Course Study, $t = 1\ h$

$^1$HNMR, 600 MHz, CDCl$_3$
Time Course Study, $t = 7$ h
$^1$HNMR, 600 MHz, CDCl$_3$
Barraza and Denmark

Time Course Study, $t = 12\,$h

$^1$HNMR, 600 MHz, CDCl$_3$
Time Course Study, \( t = 30 \) h

\(^1\)HNMR, 600 MHz, CDCl\(_3\)

0.50 mmol

BnBr (2.2 equiv), DMF, 120 °C, 24 h

[Chemical structures and spectra are shown here, but not transcribed into text.]
Scheme 3 Crossover Experiment
$^1$HNMR, 600 MHz, CDCl$_3$

0.5 mmol 0.5 mmol

0.05 0.60 2.68 0.81 3.13 0.59 0.66 0.33 0.35 0.37 2.92 0.46 12.00

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5

$^1$HNMR, 600 MHz, CDCl$_3$
Scheme 3 Crossover Experiment

$^{13}$C-NMR, 151 MHz, CDCl₃

![Chemical reaction scheme](image)

- **2a**: 34%
- **6e**: 21%
- **7a**: 17%
- **9**: 15%

**TMU Internal Standard**
- 14.50 mg/mL CDCl₃
- 0.125 mmol
- 77.37 ppm CDCl₃
- 77.95 ppm CDCl₃
- 54.54 ppm (2a)
- 54.29 ppm (6e)
- 38.71 ppm
Scheme 4 Crossover Experiment
$^1$HNMR, 600 MHz, CDCl$_3$

Barraza and Denmark

S78
Scheme 4 Crossover Experiment

$^{13}$CNMR, 151 MHz, CDCl$_3$

![Scheme 4 Crossover Experiment Diagram](image-url)
Scheme 5 Crossover Experiment
$^1$HNMR, 600 MHz, CDCl$_3$

0.25 mmol 0.25 mmol

HNMR 600 MHz, CDCl$_3$
Scheme 5 Crossover Experiment

$^{15}$CNMR, 151 MHz, CDCl$_3$

0.25 mmol BnBr (2.2 equiv), DMF, 120 °C, 24 h

2a: 45%  
7a: 11%  
6a: 4%

$\text{Br}_2\begin{array}{c} \text{NH}_2 \\ 0.25 \text{ mmol} \end{array} + \begin{array}{c} \text{Br}_2 \\ \text{NH}_2 \\ 0.25 \text{ mmol} \end{array}$

NMR spectrum showing multiplicities and chemical shifts
N,N-Dibenzyl-4-bromoaniline (2a)
$^1$HNMR, 600 MHz, CDCl$_3$
$N,N$-Dibenzyl-4-bromoaniline (2a)

$^{13}$C NMR, 151 MHz, CDCl$_3$
N,N-Dibenzyl-4-chloroaniline (2b)

$^1$H NMR, 600 MHz, CDCl$_3$
$N,N$-Dibenzyl-4-chloroaniline (2b)

$^{13}$C NMR, 151 MHz, CDCl$_3$
**N,N-Dibenzyl-4-iodoaniline (2c)**

$^1$H NMR, 600 MHz, CDCl$_3$
$N,N$-Dibenzyl-4-iodoaniline (2c)

$^{13}$C NMR, 151 MHz, CDCl$_3$
N,N-Di-(n-butyl)-4-bromoaniline (2d)

\(^1\)H NMR, 600 MHz, CDCl\(_3\)
$N,N$-Di-(\(n\)-butyl)-4-bromoaniline (2d)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N,N-Dibenzyl-2-bromoaniline (3a)
$^1$H NMR, 600 MHz, CDCl$_3$
N,N-Dibenzyl-2-bromoaniline (3a)

$^{13}$C NMR, 151 MHz, CDCl$_3$
$N,N$-Dibenzyl-2-chloroaniline (3b)
$\textsuperscript{1}H$NMR, 600 MHz, CDCl$_3$
N,N-Dibenzyl-2-chloroaniline (3b)

$^{13}$CNMR, 151 MHz, CDCl$_3$
$N,N$-Dibenzy1-2-iodoaniline (3c)
$^1$HNMR, 600 MHz, CDCl$_3$
$\text{N,N-Dibenzyl-2-iodoaniline (3c)}$

$\text{^{13}C NMR, 151 MHz, CDCl}_3$

![Chemical structure](image)

**151.64**

- 140.20
- 137.78
- 129.03
- 128.61
- 128.26
- 127.16
- 125.87
- 124.67
- 99.86
- 77.37 CDCl₃
- 77.16 CDCl₃
- 76.95 CDCl₃
- 57.14
**N,N-Di-(n-butyl)-2-bromoaniline (3d)**

$^1$HNMR, 600 MHz, CDCl$_3$
$N,N$-Di-(n-butyl)-2-bromoaniline (3d)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N-Benzyl-4-bromoaniline (4a)

$^1$H NMR, 600 MHz, CDCl$_3$
N-Benzyl-4-bromoaniline (4a)
$^{13}$C NMR, 151 MHz, CDCl$_3$
N-Benzyl-4-chloroaniline (4b)

$^1$H NMR, 600 MHz, CDCl$_3$
$N$-Benzy1-4-chloroaniline (4b)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N-Benzyl-2-bromoaniline (5a)

$^1$H NMR, 600 MHz, CDCl$_3$
N-Benzyl-2-bromoaniline (5a)

$^{13}$C NMR, 151 MHz, CDCl$_3$

5a
N-Benzyl-2-chloroaniline (5b)
$^1$H NMR, 600 MHz, CDCl$_3$
$N$-Benzyl-2-chloroaniline (5b)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N,N-Dibenzyl-2,4-dibromoaniline (6a)

$^1$H NMR, 600 MHz, CDCl$_3$
N,N-Dibenzyl-2,4-dibromoaniline (6a)

$^{13}$C NMR, 151 MHz, CDCl$_3$
N,N-Dibenzylaniline (6e)

$^1$H NMR, 600 MHz, CDCl$_3$
$N,N$-Dibenzylaniline (6e)

$^{13}$C NMR, 151 MHz, CDCl$_3$
N-Benzyl-2,4-dibromoaniline (7a)
$^1$H NMR, 600 MHz, CDCl$_3$
$N$-Benzyl-2,4-dibromoaniline (7a)

$^{13}$C NMR, 151 MHz, CDCl$_3$
N-Benzylaniline (7e)
$^1$HNMR, 600 MHz, CDCl$_3$
N-Benzylaniline (7e)
$^{13}$C NMR, 151 MHz, CDCl$_3$
N,N-Dibenzyl-4-bromo-2-chloroaniline (9)
$^1$HNMR, 600 MHz, CDCl$_3$
\( \text{N,N-Dibenzyl-4-bromo-2-chloroaniline (9)} \)

\(^{13}\text{CNMR, 151 MHz, CDCl}_3\)
N-(4-Bromophenyl)benzamide (S1)
$^{1}$H NMR, 600 MHz, DMSO-$d_6$
N-(4-Bromophenyl)benzamide (S1)

$^{13}$C NMR, 151 MHz, DMSO-$d_6$
N-Phenylbenzamide (S2)
\(^1\)HNMR, 600 MHz, CDCl\(_3\)
$N$-Phenylbenzamide (S2)

$^{13}$C NMR, 151 MHz, CDCl$_3$

![N-Phenylbenzamide (S2) NMR spectrum](image)
N-(4-Chlorophenyl)benzamide (S3)

$^1$H NMR, 600 MHz, DMSO-$d_6$
$N$-(4-Chlorophenyl)benzamide (S3)

$^{13}$CNMR, 151 MHz, DMSO-$d_6$
N-(2-Bromophenyl)benzamide (S4)

$^1$HNMR, 600 MHz, CDCl$_3$
N-(2-Bromophenyl)benzamide (S4)

$^{13}$CNMR, 151 MHz, CDCl₃
N-(2-Chlorophenyl)benzamide (S5)

$^1$HNMR, 600 MHz, CDCl$_3$
$N$-(2-Chlorophenyl)benzamide (S5)

$^{13}$CNMR, 151 MHz, CDCl$_3$
$N$-(2,4-Dibromophenyl)benzamide (S6)

$^1$HNMR, 600 MHz, CDCl$_3$
N-(2,4-Dibromophenyl)benzamide (S6)
$^{13}$CNMR, 151 MHz, CDCl$_3$
N-Benzyl-N-(4-chlorophenyl)benzamide (S8)

$^1$H NMR, 600 MHz, CDCl$_3$
N-Benzy1-N-(4-chlorophenyl)benzamide (S8)

$^{13}$CNMR, 151 MHz, CDCl₃

![Chemical Structure](image)

**S8**

- 170.49
- 142.07
- 137.24
- 135.67
- 132.33
- 129.95
- 129.24
- 128.98
- 128.76
- 128.64
- 128.44
- 127.98
- 127.60

77.37 ppm (CDC₃)
77.16 ppm (CDC₃)
76.95 ppm (CDC₃)
53.80 ppm

**f1 (ppm)**

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
**N-Benzyl-N-(2-Bromophenyl)benzamide (S9)**

$^1$HNMR, 600 MHz, CDCl$_3$
N-Benzyl-N-(2-bromophenyl)benzamide (S9)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N-Benzyl-N-(2-chlorophenyl)benzamide (S10)

\(^1\)HNMR, 600 MHz, CDCl\(_3\)
N-Benzyl-N-(2-chlorophenyl)benzamide (S10)

$^{13}$CNMR, 151 MHz, CDCl$_3$
N-Benzyl-N-(2,4-dibromophenyl)benzamide (S11)

$^1$HNMR, 600 MHz, CDCl$_3$
$N$-Benzyl-$N$-(2,4-dibromophenyl)benzamide (S11)

$^1$H NMR, 151 MHz, CDCl$_3$

![Chemical structure diagram]